Supporting Information

Mechanistic Twist of the [8+2] Cycloadditions of Dienylisobenzofurans and Dimethyl Acetylenedicarboxylate: Stepwise [8+2] versus [4+2]/[1,5]-Vinyl Shift Mechanisms Revealed Through a Theoretical and Experimental Study

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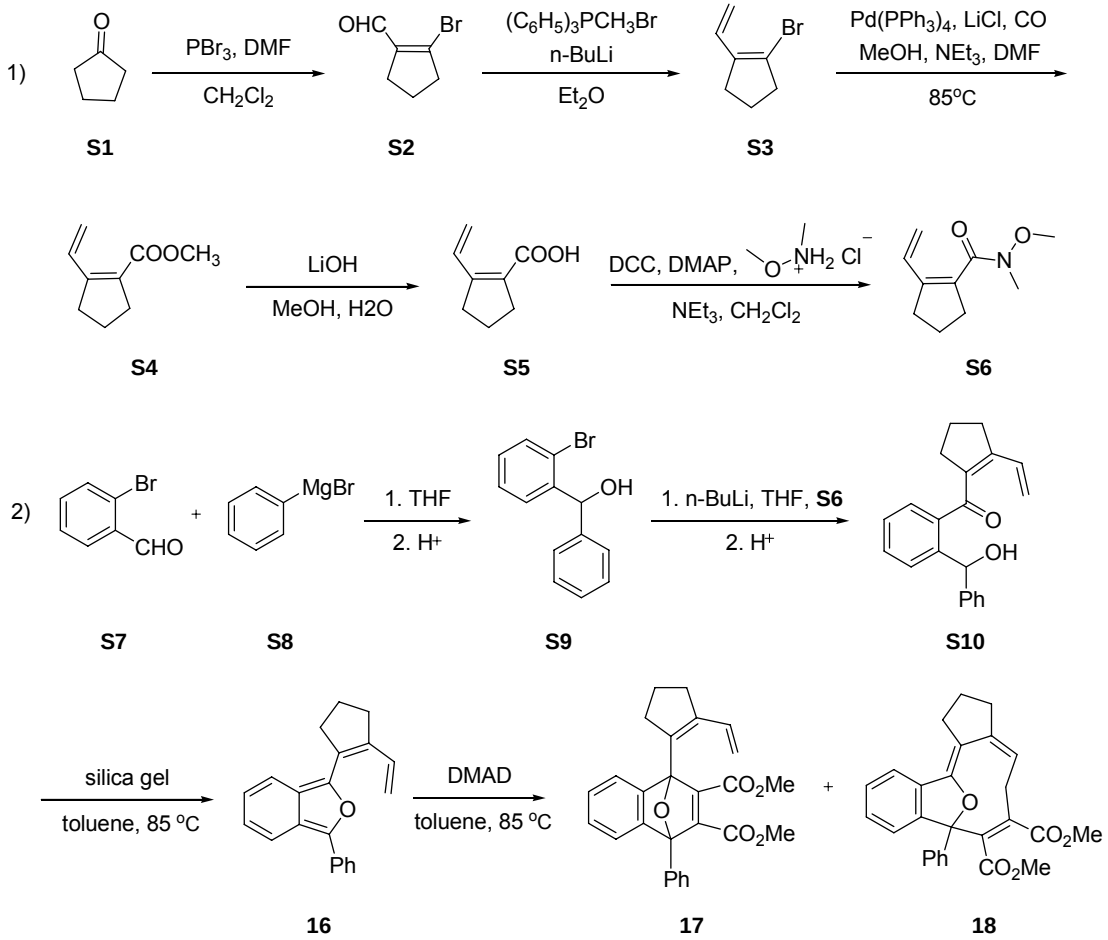
Contents

1. Experimental Procedures and Spectroscopic and Analytical Data of the Products

Note: ^{1}H and ^{13}C NMR spectra were recorded on Bruker ARX 400 spectromer (400 MHz). The MS data were obtained with EI (70 eV), and the relative intensity (%) is given in brackets. High-resolution mass spectral analysis (HRMS) data were measured on a VG-ZAB-HS mass spectromer (EI).

1.1—— Synthesis of compounds 17 and 18

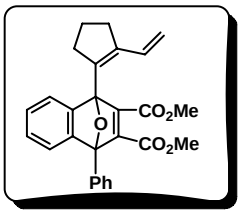


Compounds **S1-S10, 16** and **18** were prepared according to the literature procedures [Luo, Y. M.; Herndon, J. W.; Cervantes-Lee, F. *J. Am. Chem. Soc.* **2003**, *125*, 12720. In the Supporting Information of this paper, the formation of **18** was reported to require 1 h. This should be 3.5 h or longer].

Synthesis of **17** and **18**

To a solution of keto alcohol **S10** (0.550 g, 1.8 mmol) in toluene (150 mL) was added flash silica gel (0.250 g) and the mixture was heated to 85°C. After 1 h, DMAD (1.000 g, 7.00 mmol) was added and heating was continued for 50 min. After the solution cooled to room temperature, excess diethylamine was added. The mixture was concentrated *in vacuo* and purified via flash chromatography using benzene: triethylamine (10:0.1). Compounds **17** (0.345g, 45% yield) and **18** (0.108g, 14%) were obtained.

The Spectroscopic Data for **17**



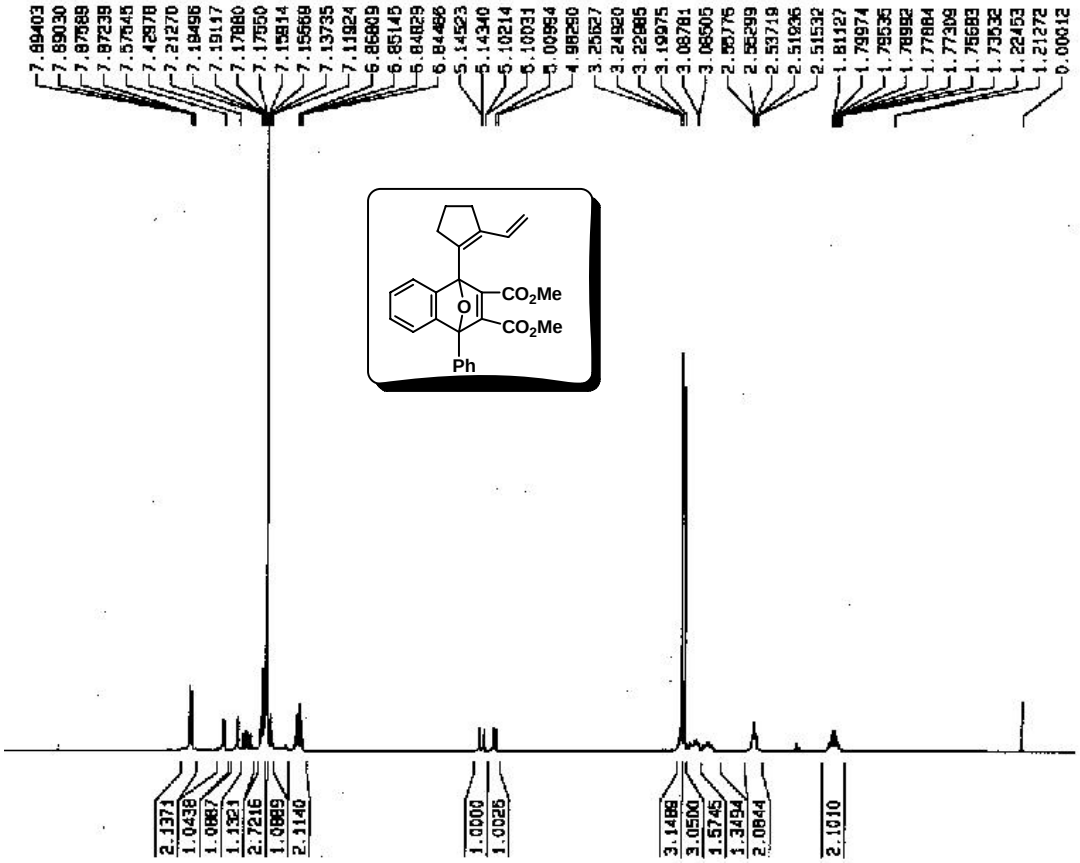
Colorless oil. **^{1}H NMR** (400 MHz, C_6D_6): δ 7.88 (m, 2H), 7.58 (m, 1H), 7.43 (m, 1H), 7.34 (dd, J = 11, 17 Hz, 1H), 7.21-7.10 (m, 4H), 6.85 (m, 1H), 5.12 (d, J = 17 Hz, 1H), 5.00 (d, J = 11 Hz, 1H), 3.23 (s, 3H), 3.20 (s, 3H), 3.16-2.95 (m, 2H), 2.54 (m, 2H), 1.79 (m, 2H);

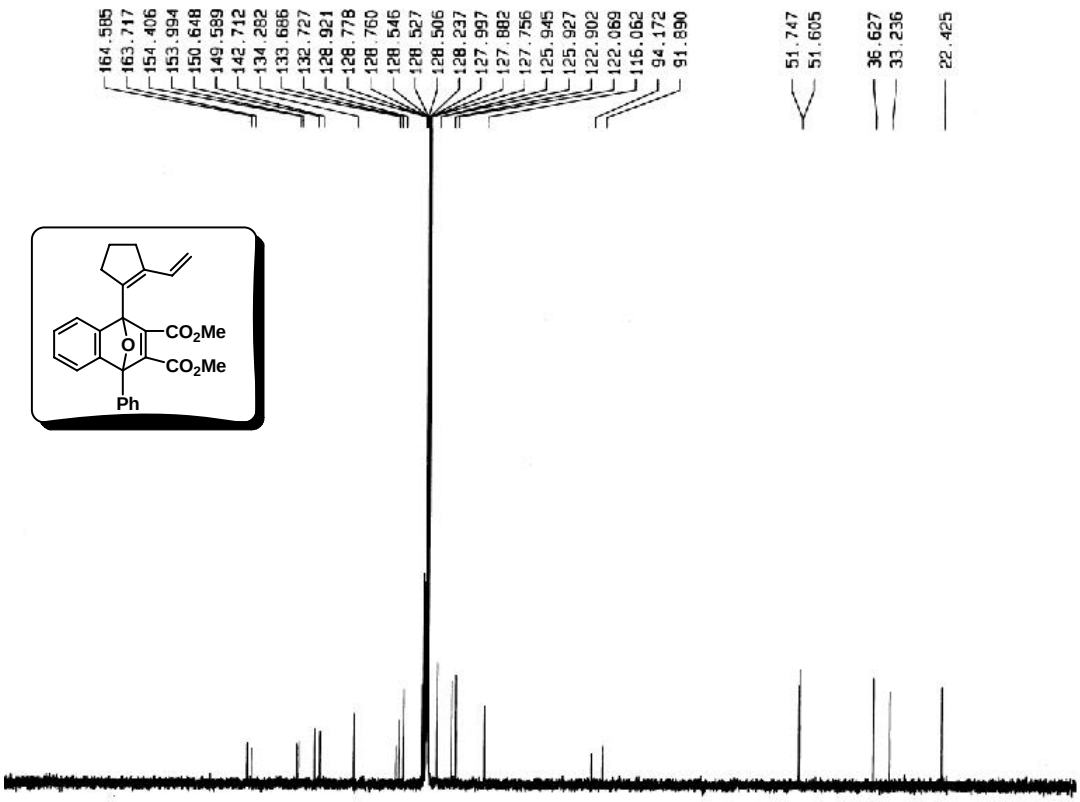
^{13}C NMR (100 MHz, C_6D_6): δ 164.6, 163.7, 154.4, 154.0, 150.6, 149.6, 142.7, 134.3, 133.7, 132.7, 128.9, 128.8, 128.5, 125.94, 125.93, 122.9, 122.1, 116.1, 94.2, 91.9, 51.7, 51.6, 36.6, 33.2, 22.4; **IR** v (cm^{-1}): 2952, 1722, 1451, 1434, 1302, 1258;

MS (EI) m/z: 428 (M^+, 5), 396 (14), 369 (24), 337 (32), 309 (35), 286 (38), 210 (42), 105 (100), 77 (48);

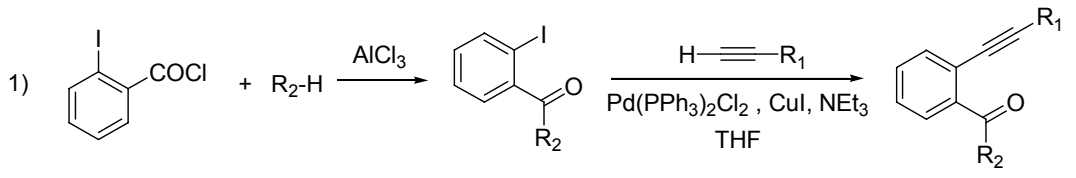
HRMS: Calcd for $C_{27}H_{24}O_5$: 428.1624. Found: 428.1633.

1.2—— Copies of ^{1}H and ^{13}C NMR Spectra for 17

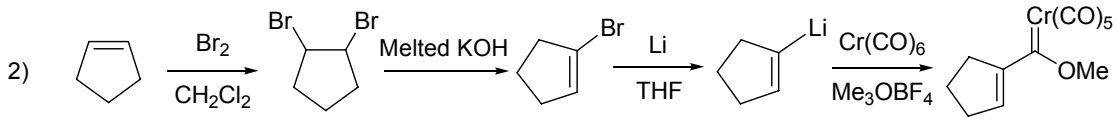




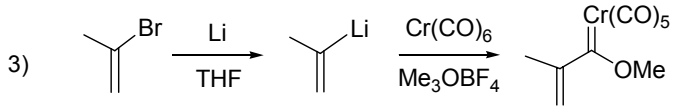
1.3—— Synthesis of compounds 23a-d and 24a-d according to literature procedures [Luo, Y. M.; Herndon, J. W.; Cervantes-Lee, F. *J. Am. Chem. Soc.* **2003**, *125*, 12720]



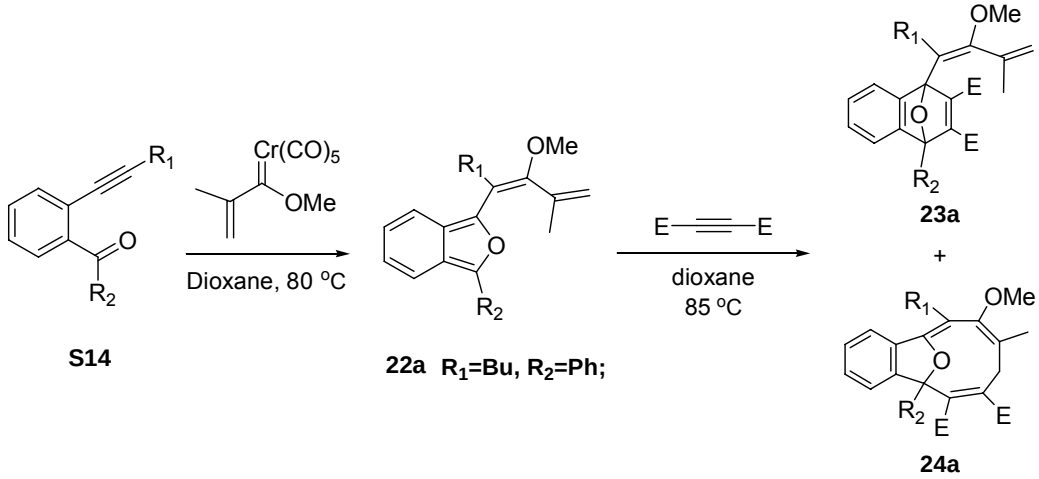
S11 **S12** **S13** **S14**



S15 **S16** **S17** **S18** **S19**



S20 **S21** **S22**



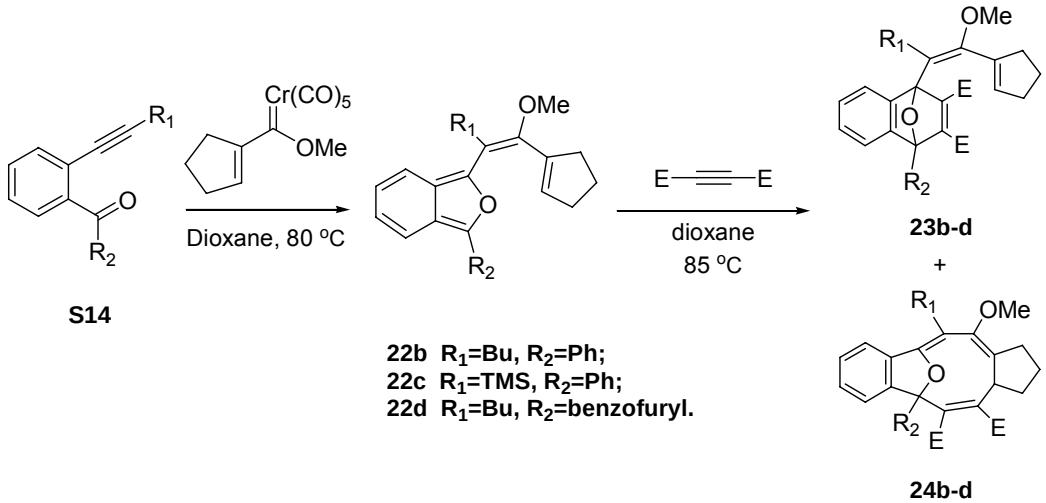
S14

22a R_1=Bu, R_2=Ph;

23a

24a

E=-CO_2Me



S14

22b R_1=Bu, R_2=Ph;
22c R_1=TMS, R_2=Ph;
22d R_1=Bu, R_2=benzofuryl.

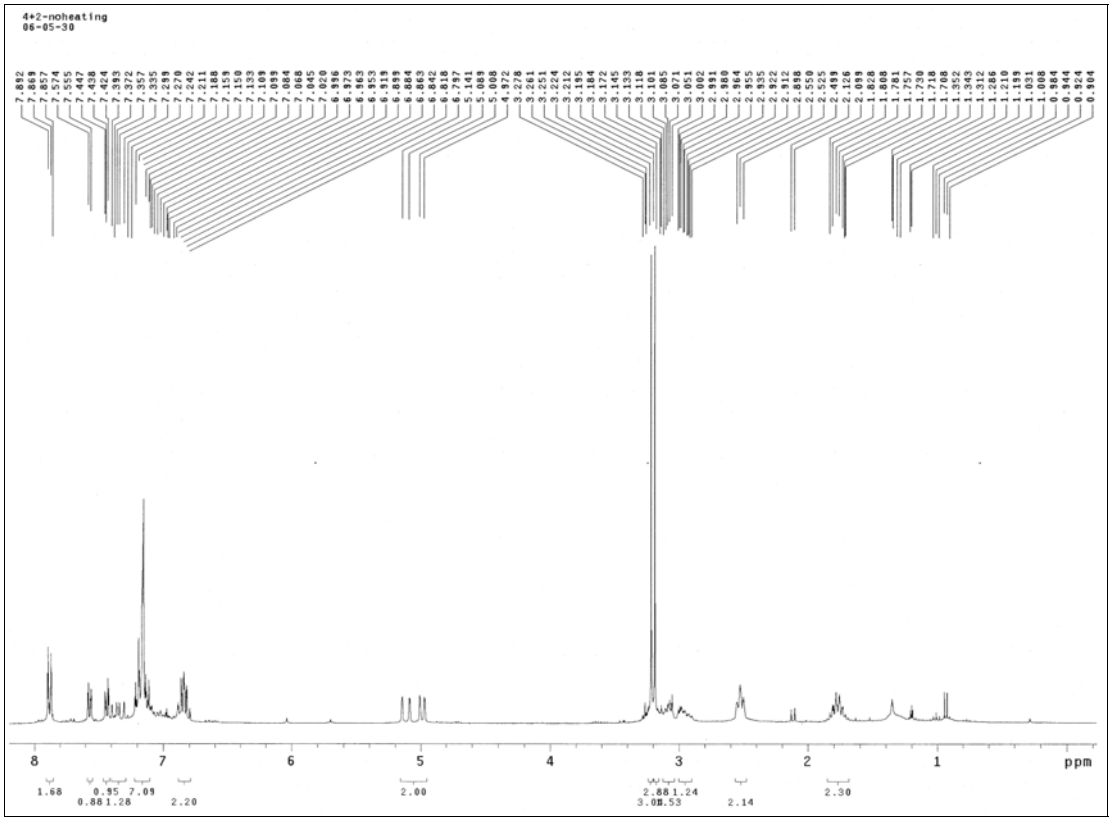
23b-d

24b-d

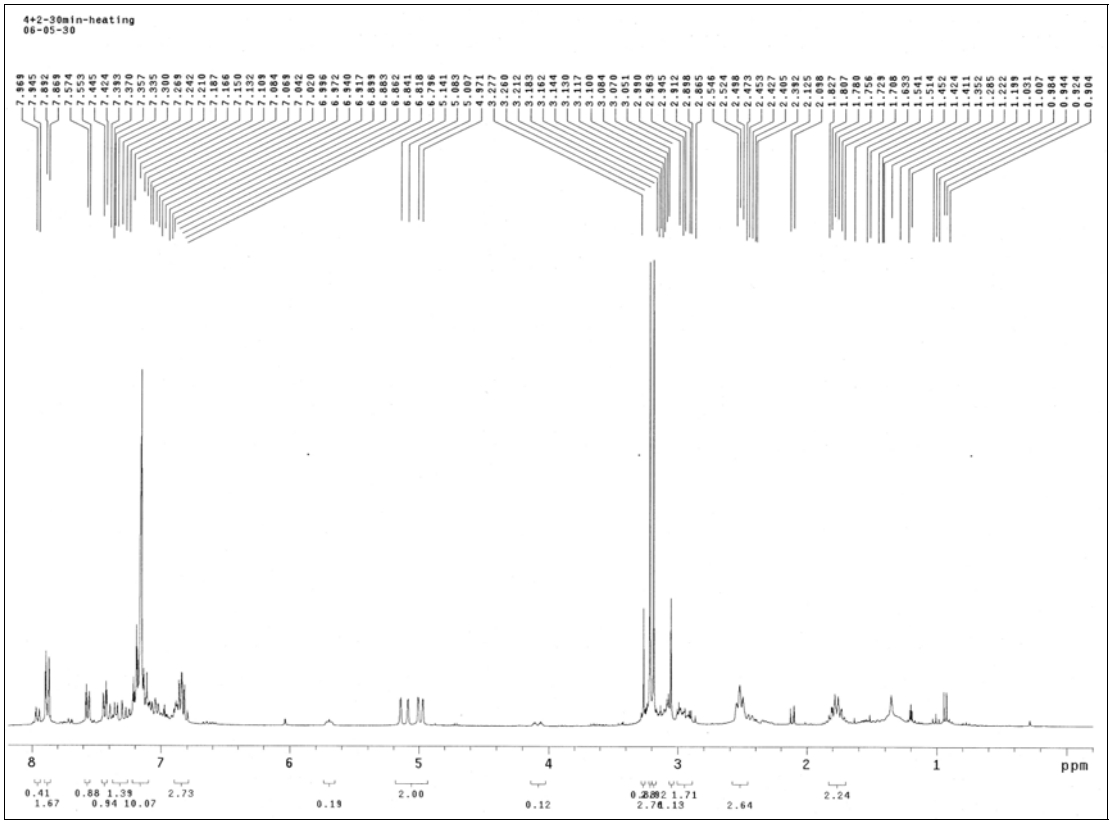
2. Kinetic Experiments for [1,5]-Vinyl Shift of 17 to 18

2.1—— The original spectra of isomerization of 17 to 18 in benzene at 80 °C (300 MHz ^{1}H NMR)

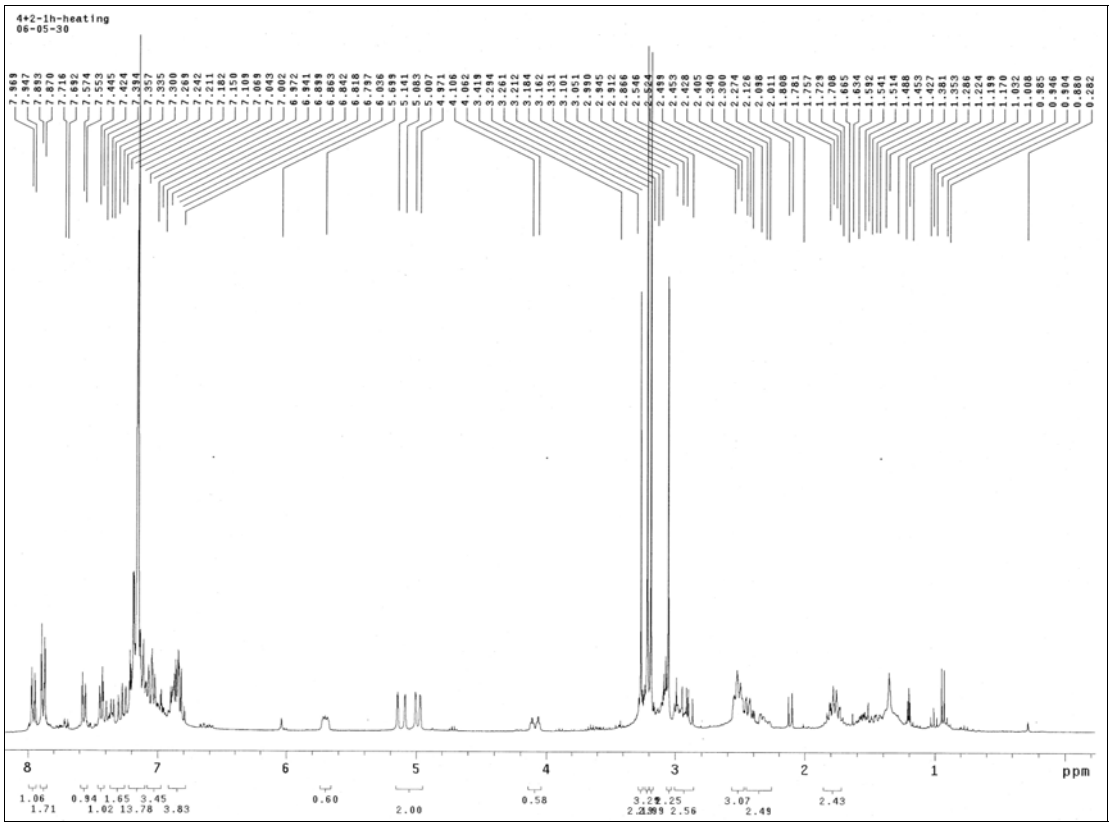
Copy of ^{1}H NMR Spectrum (300 MHz) for 17



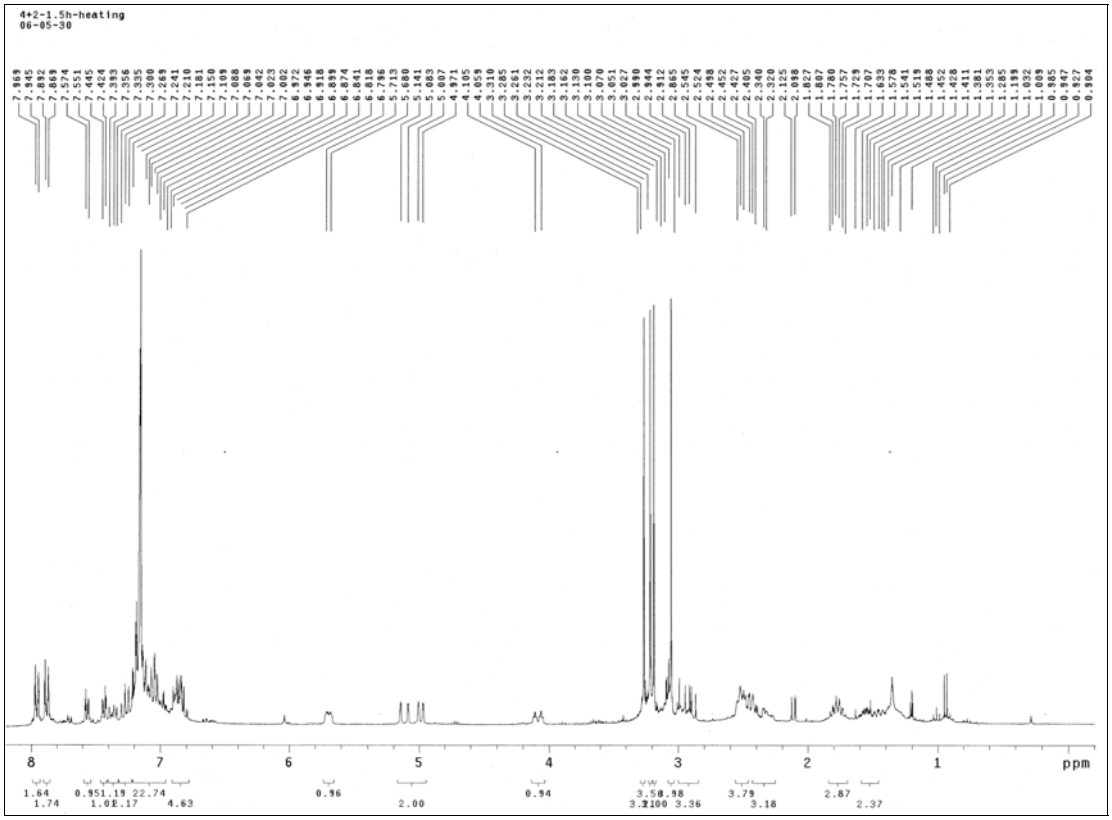
Copy of ^{1}H NMR Spectrum (300 MHz) for 17 after heating for 0.5 h



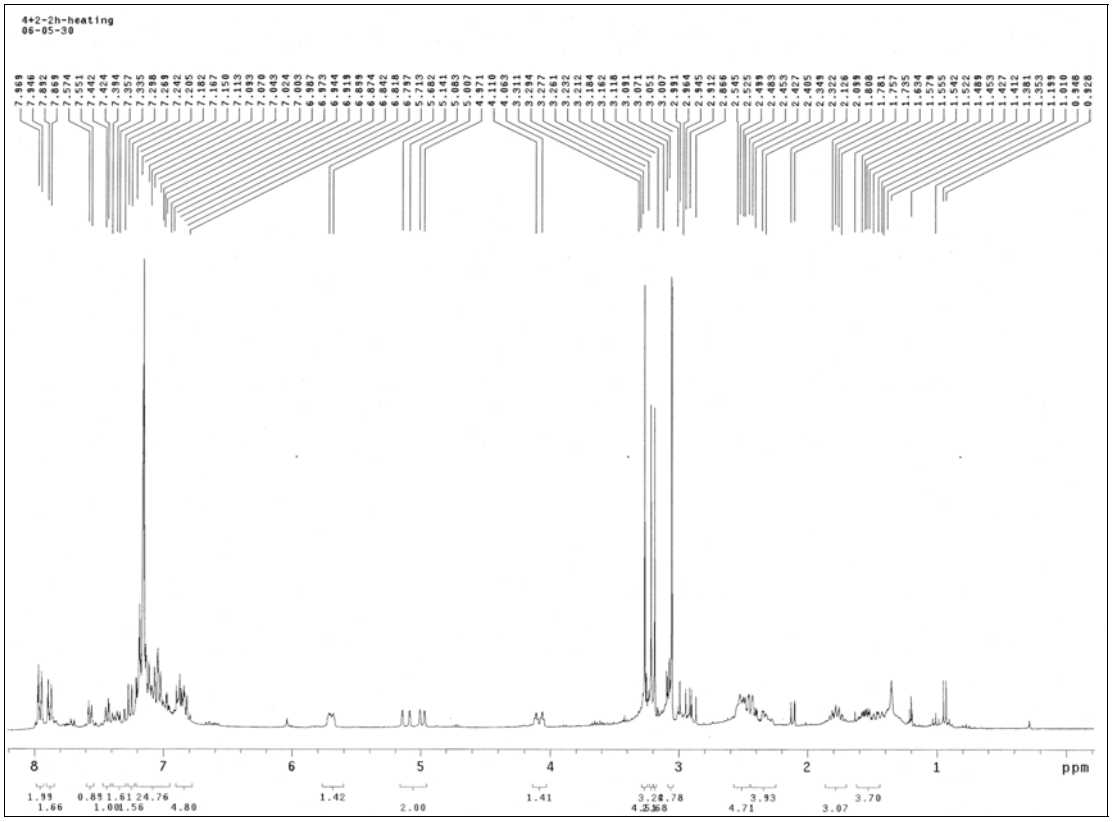
Copy of ^{1}H NMR Spectrum (300 MHz) for 17 after heating for 1 h



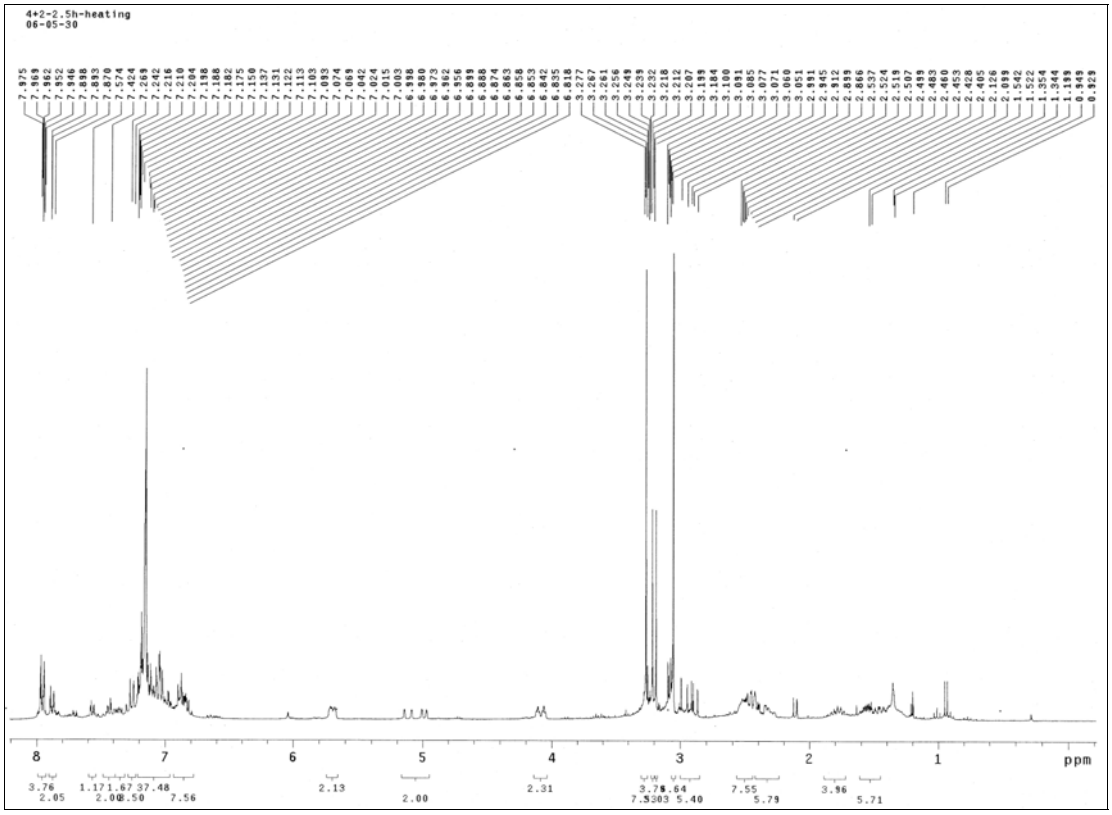
Copy of ^{1}H NMR Spectrum (300 MHz) for 17 after heating for 1.5 h



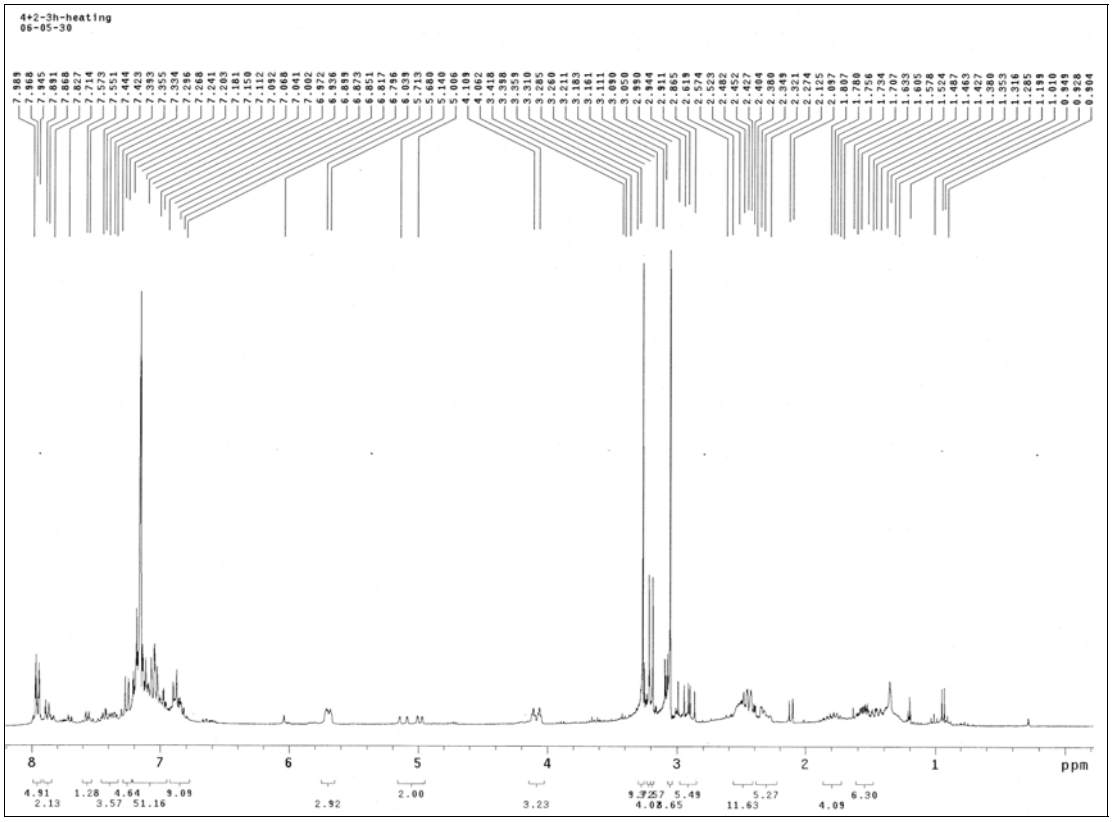
Copy of ^{1}H NMR Spectrum (300 MHz) for 17 after heating for 2 h



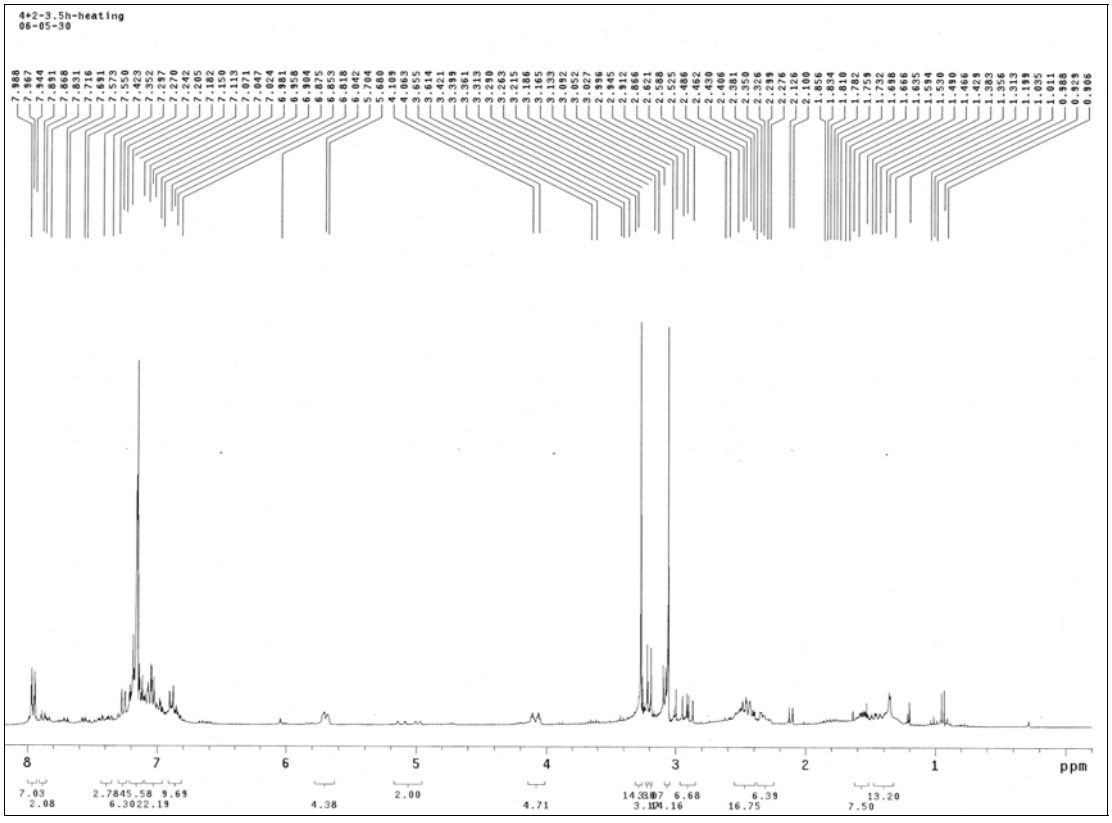
Copy of ^{1}H NMR Spectrum (300 MHz) for 17 after heating for 2.5 h



Copy of ^{1}H NMR Spectrum (300 MHz) for 17 after heating for 3 h



Copy of ^{1}H NMR Spectrum (300 MHz) for 17 after heating for 3.5 h



2.2—— Rate Constant *k* at Four Different Temperatures, 75.0, 85.0, 95.0, 105.0 ˚C

For kinetic measurements, the [1,5]-vinyl shift of **17** was carried out in toluene-d_8 in NMR tube at four different temperatures, 75.0, 85.0, 95.0, 105.0 ˚C , respectively. The ^{1}H NMR spectrum of each run showed reducing characteristic peak of **17** and increasing of **18** due to the conversion from **17** to **18**. The plots of -ln([A]/[A_o]) vs. time gave straight lines (Figures S1-S4), where [A] and [A_o] denote the concentration of **17** remained and the initial concentration of **17**, respectively. The [1,5]-vinyl shift was observed to follow first-order kinetics: 10^3 *k*/min = 2.47 (75.0 ˚C), 8.45 (85.0 ˚C), 18.1 (95.0 ˚C), 32.2 (105.0 ˚C), where *k* is the rate constant.

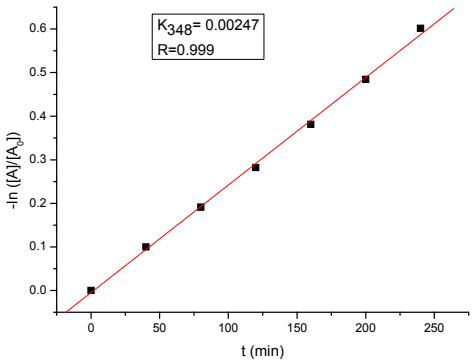


Figure S1. First-order plots for the [1,5]-vinyl shift of **17** at 75.0 ˚C.

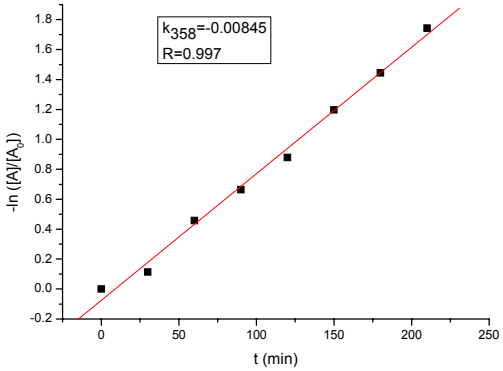


Figure S2. First-order plots for the [1,5]-vinyl shift of **17** at 85.0 ˚C.

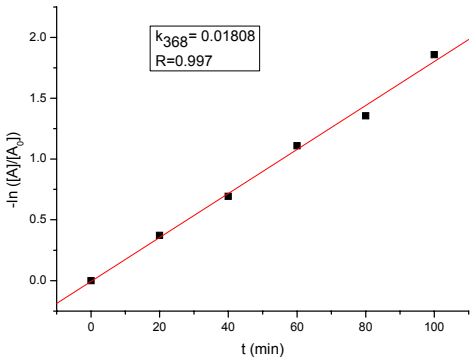


Figure S3. First-order plots for the [1,5]-vinyl shift of **17** at 95.0 ˚C.

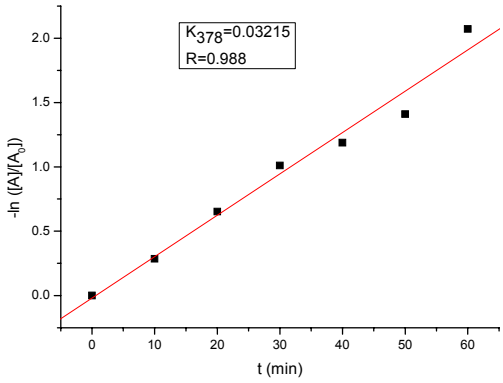


Figure S4. First-order plots for the [1,5]-vinyl shift of **17** at 105.0 ˚C.

2.3—— Arrhenius Plot and Eyring Plot for The [1,5]-Vinyl Shift of 17

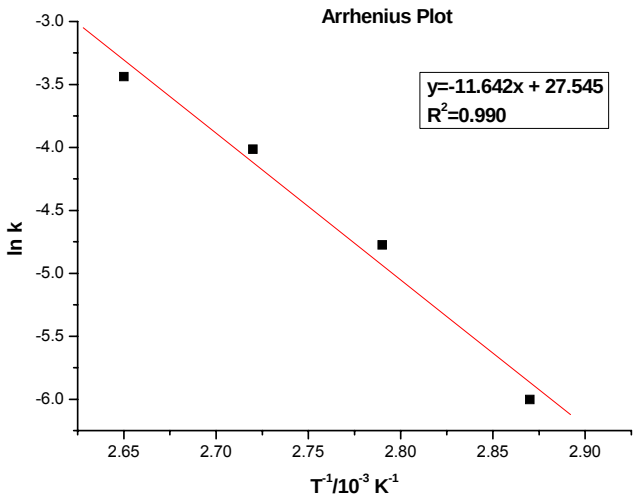


Figure S5. Arrhenius plot for the [1,5]-vinyl shift of **17**.

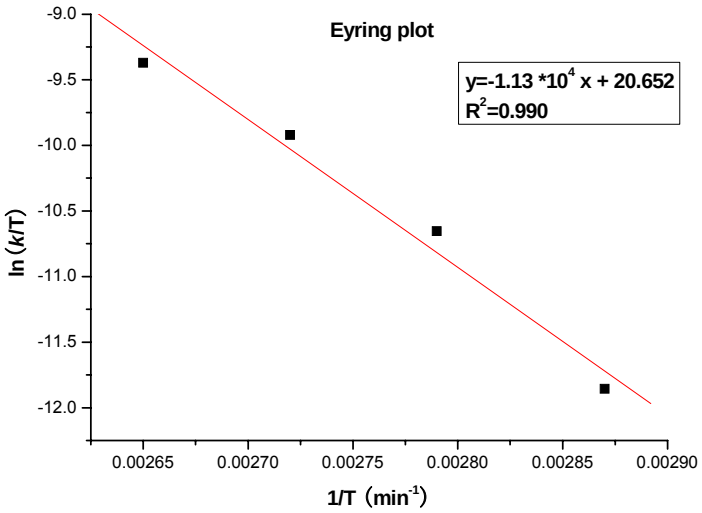


Figure S6. Eyring plot for the [1,5]-vinyl shift of **17**.

Figure S5 shows the plot of ln *k* vs. the reciprocal of the temperature (Arrhenius plot), which gives a straight line. From Arrhenius plots, the activation energy of the [1,5]-vinyl shift is estimated to be 23.04 ± 2.33 kcal·mol^{-1}. Figure S6 shows the plot of ln(*k*/T) vs. the reciprocal of the temperature (Eyring plot), which gives a straight line.

$\ln [A] = -kt + C$

$[A] = [A] / [A_0]$

$k = A \cdot e^{-Ea/RT}$

$\ln k = -E_a/R \cdot 1/T + \ln A$

$- E_a/R = K_a$

$E_a = -R \cdot K_a = -8.314 \times (-1.16 \times 10^4) = 9.68 \times 10^4$ J·mol^{-1} = 23.04 kcal·mol^{-1}

(Error = 1.18×10^3 E_a = 23.04 ± 2.33 kcal·mol^{-1})

$\ln A = 27.54$; $A = 9.17 \times 10^{11}$ min^{-1}

$E_a = 23.04$ kcal/mol

$k = 9.17 \times 10^{11} \exp(-23.04/RT)$ min^{-1}

$\ln(k/T) = (-\Delta H^{\neq}/R)T + \ln(k_B/h) + \Delta S^{\neq}/R$

$-\Delta H^{\neq}/R = K_e$

$\Delta H^{\neq} = -R \cdot K_e = -8.314 \times (-1.13 \times 10^4) = 9.38 \times 10^4$ $J \cdot mol^{-1} = 22.33$ $kcal \cdot mol^{-1}$

(Error $= 1.18 \times 10^3$ $\Delta H^{\neq} = 22.33 \pm 2.34$ $kcal \cdot mol^{-1}$)

$\ln(k_B/h) + \Delta S^{\neq}/R = 20.65$

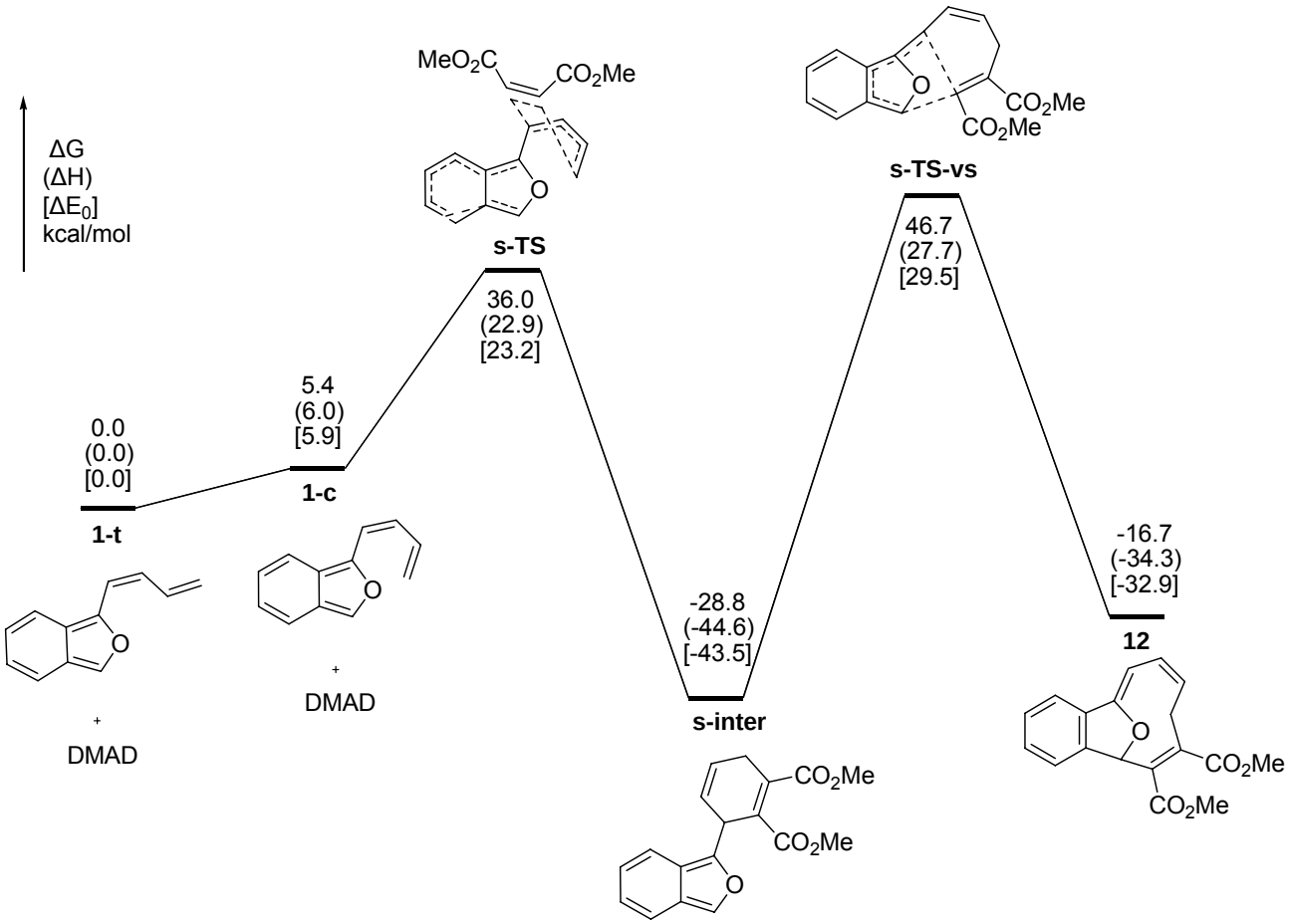
$\Delta S^{\neq} = -6.15$ cal/(mol·K)

$\Delta G = \Delta H - T\Delta S = 24.16$ kcal/mol (T = 298K)

75.0 ˚C		85.0 ˚C		95.0 ˚C		105.0 ˚C	
time/min	ln[A]	time/min	ln[A]	time/min	ln[A]	time/min	ln[A]
0	0	0	0	0	0	0	0
40	-0.09982	30	-0.11317	20	-0.37106	10	-0.28502
80	-0.19116	60	-0.45728	40	-0.69315	20	-0.65201
120	-0.28236	90	-0.66359	60	-1.10866	30	-1.01060
160	-0.38126	120	-0.87948	80	-1.35480	40	-1.18744
200	-0.48451	150	-1.19733	100	-1.85790	50	-1.41059
240	-0.60148	180	-1.44392			60	-2.07147
		210	-1.74297				

T(˚C)	k (min^{-1})	1/T(K^{-1})	ln k
75.0	0.00247	0.00287	-6.00354
85.0	0.00845	0.00279	-4.77359
95.0	0.01808	0.00272	-4.01295
105.0	0.03215	0.00265	-3.43734

3. Pathway D of Model Reaction II



	E_{ele}	G	H	E_0
s-TS	-1071.547803	-1071.302901	-1071.224592	-1071.247659
s-inter	-1071.659445	-1071.406091	-1071.332177	-1071.353933
s-TS-vs	-1071.540349	-1071.285804	-1071.217093	-1071.237743

4. Table of Energies and Other Thermodynamic Parameters

4.1—— Model Reaction I

	E_{ele}	G	H	E_0
1-t	-538.483428	-538.336671	-538.288170	-538.299745
1-c	-538.474200	-538.328021	-538.278679	-538.290328
TS2	-615.779500	-615.609605	-615.554246	-615.568766
3	-615.798462	-615.626291	-615.571375	-615.585709
TS4	-615.782541	-615.607291	-615.556230	-615.569274
5	-615.884225	-615.699954	-615.651491	-615.663452
TS6	-615.781807	-615.609381	-615.555759	-615.569773
7-t	-615.852269	-615.671111	-615.622699	-615.634595
7-c	-615.844343	-615.664296	-615.613743	-615.626452
TS8	-615.804124	-615.622475	-615.575639	-615.586965

4.2—— Model Reaction II

	E_{ele}	G	H	E_0
TS9	-1071.556159	-1071.306902	-1071.227046	-1071.250546
10	-1071.563944	-1071.317310	-1071.239595	-1071.262879
TS11	-1071.564082	-1071.312704	-1071.240267	-1071.262086
12	-1071.643493	-1071.386824	-1071.315895	-1071.337135
TS13	-1071.562007	-1071.317312	-1071.239237	-1071.262652
14-t	-1071.623071	-1071.372162	-1071.297050	-1071.319367
14-c	-1071.614077	-1071.362591	-1071.288122	-1071.310458
TS15	-1071.578779	-1071.323810	-1071.255296	-1071.275937

4.3—— Model Reaction III

	E_{ele}	G	H	E_0
1-OMe	-653.004207	-652.829088	-652.773887	-652.788186
TS25	-1185.727627	-1185.812647	-1185.726682	-1185.752768
26	-1185.731565	-1185.820254	-1185.736393	-1185.762215
TS27	-1185.737811	-1185.815176	-1185.736867	-1185.761277
28	-1186.168084	-1185.883006	-1185.805515	-1185.829551
TS29	-1186.090682	-1185.816296	-1185.732335	-1185.758271
30-t	-1186.142230	-1185.862931	-1185.781274	-1185.806427
30-c	-1186.139228	-1185.859773	-1185.778424	-1185.803606
TS31	-1186.102522	-1185.819261	-1185.743968	-1185.767434

4.4—— Model Reaction IV

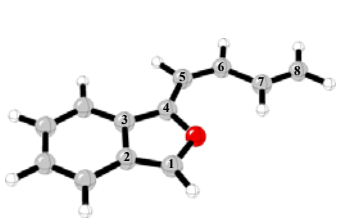
	E_{ele}	G	H	E_0
1-OMe-C	-769.739504	-769.504098	-769.442279	-769.459120
TS32	-1302.819819	-1302.485999	-1302.394604	-1302.423123
33	-1302.841215	-1302.503437	-1302.413926	-1302.442135
TS34	-1302.840076	-1302.496610	-1302.413650	-1302.440346
35	-1302.903680	-1302.556680	-1302.474386	-1302.500930
TS36	-1302.826346	-1302.490713	-1302.401068	-1302.429477
37	-1302.882109	-1302.539924	-1302.453986	-1302.481384
TS38	-1302.839472	-1302.493950	-1302.413814	-1302.439797

4.5—— Isomerization from 19 to 21

	E_{ele}	G	H	E_0
19-t	-1188.358803	-1188.045725	-1187.965910	-1187.990782
19-c	-1188.352312	-1188.039611	-1187.959743	-1187.984637
TS20	-1188.321681	-1188.005421	-1187.931245	-1187.954545
21	-1188.382977	-1188.065069	-1187.988519	-1188.012357

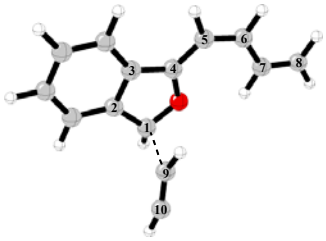
5. The computed geometries of stationary points involved in four model reactions and the isomerization of 19 to 21 (distances in Å).

5.1 —— The Computed Geometries of Stationary Points of Model Reaction I



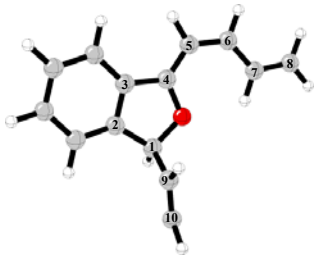
C1-C8 = 5.642

1-t



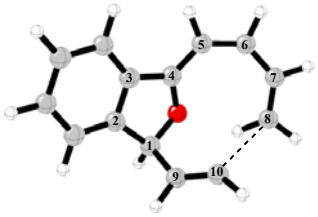
C1-C9 = 1.940

TS2



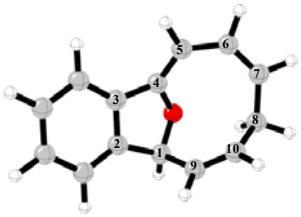
C1-C9 = 1.516

3



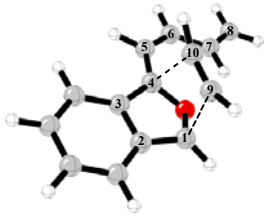
C1-C9 = 1.538
C8-C10 = 3.017

TS4



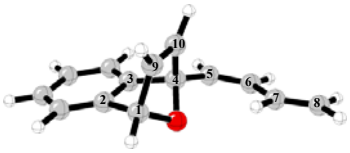
C1-C9 = 1.523
C8-C10 = 1.526

5



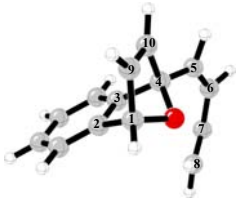
C1-C9 = 2.085
C4-C10 = 2.422

TS6



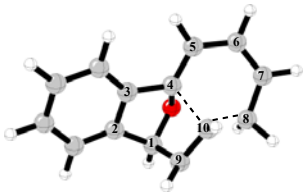
C1-C9 = 1.541
C4-C10 = 1.551

7-t



C1-C9 = 1.540
C4-C10 = 1.549

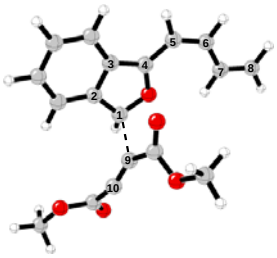
7-c



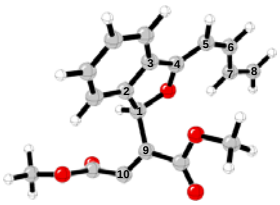
C4-C10 = 1.914
C8-C10 = 1.567

TS8

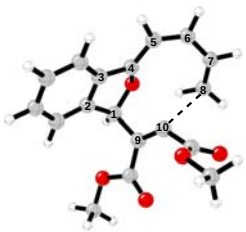
5.2 —— The Computed Geometries of Stationary Points of Model Reaction II



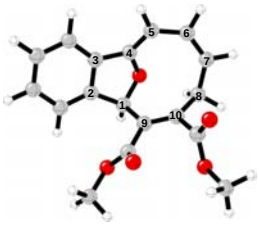
C1-C9 = 2.058
C9-C10 = 1.257
TS9



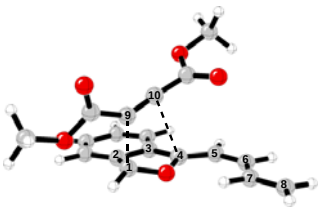
C1-C9 = 1.579
10



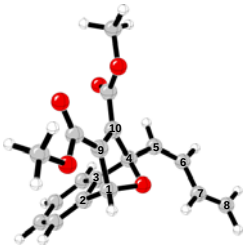
C1-C9 = 1.575
C8-C10 = 2.787
TS11



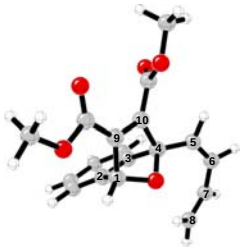
C1-C9 = 1.542
C8-C10 = 1.534
12



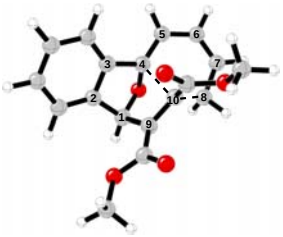
C1-C9 = 2.060
C4-C10 = 2.936
TS13



C1-C9 = 1.544
C4-C10 = 1.568
14-t

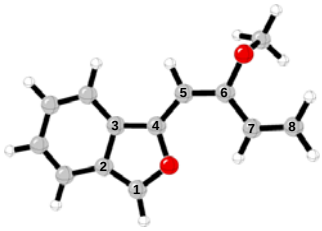


C1-C9 = 1.545
C4-C10 = 1.564
14-c

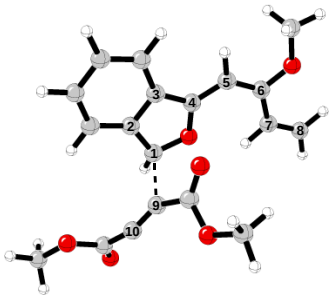


C4-C10 = 1.993
C8-C10 = 1.569
TS15

5.3 —— The Computed Geometries of Stationary Points of Model Reaction III

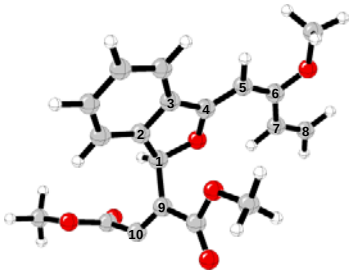


1-OMe



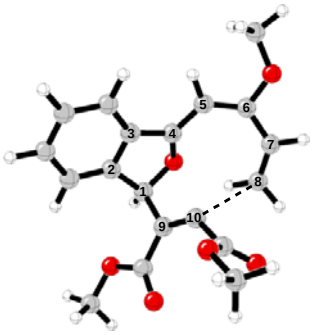
C1-C9 = 2.109
C10-C9-C1-C4 = 176.634°

TS25



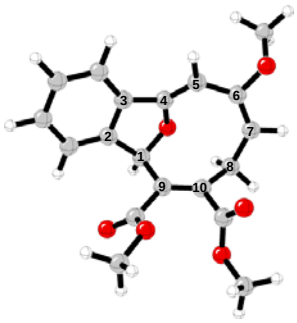
C1-C9 = 1.544

26



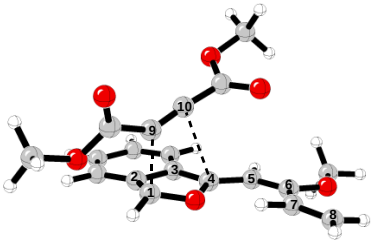
C1-C9 = 1.572
C8-C10 = 2.817

TS27



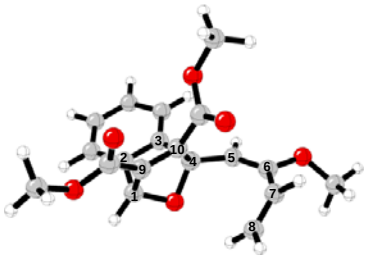
C1-C9 = 1.543
C8-C10 = 1.539

28



C1-C9 = 2.117
C4-C10 = 3.000
C10-C9-C1-C4=0.550

TS29

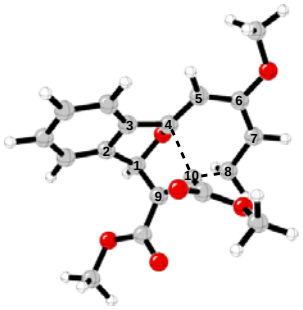


C1-C9 = 1.545
C4-C10 = 1.569

30-c

C1-C9 = 1.545
C4-C10 = 1.571

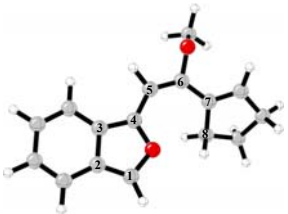
30-t



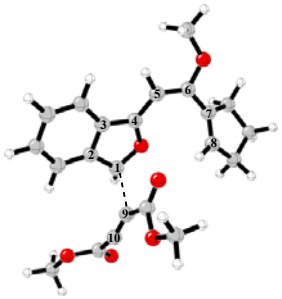
C4-C10 = 2.001
C8-C10 = 1.574

TS31

5.4 —— The Computed Geometries of Stationary Points of Model Reaction IV

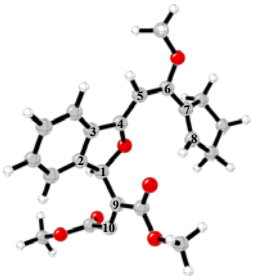


1-OMe-C



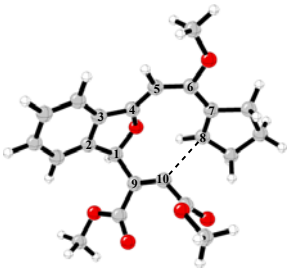
C1-C9 = 2.150
C10-C9-C1-C4 = 178.777

TS32



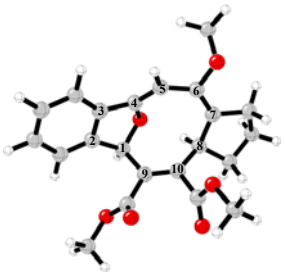
C1-C9 = 1.548

33



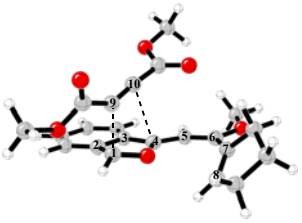
C1-C9 = 1.563
C8-C10 = 2.662

TS34



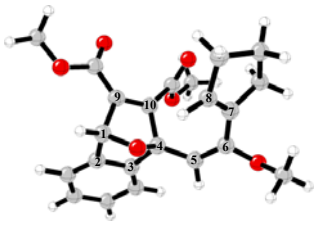
C1-C9 = 1.543
C8-C10 = 1.537

35



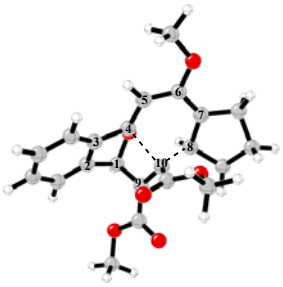
C1-C9 = 2.142
C4-C10 = 3.037
C10-C9-C1-C4=1.420

TS36



C1-C9 = 1.544
C4-C10 = 1.569

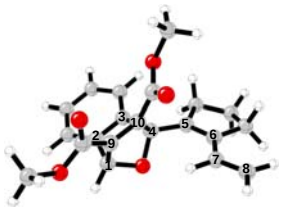
37



C4-C10 = 2.042
C8-C10 = 1.580

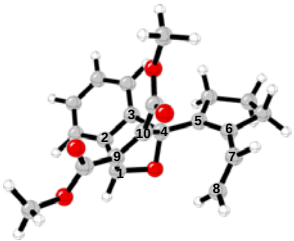
TS38

5.5 —— The Computed Geometries of Stationary Points of isomerization from 19 to 21



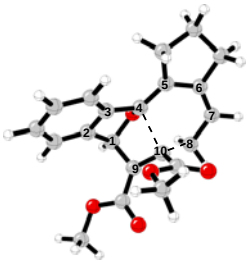
C1-C9 = 1.546
C4-C10 = 1.573

19-t



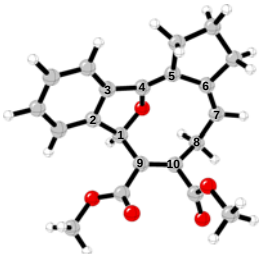
C1-C9 = 1.546
C4-C10 = 1.571

19-c



C4-C10 = 2.042
C8-C10 = 1.580

TS20



C1-C9 = 1.542
C8-C10 = 1.537

21

6. Solvation Energies

6.1—— Solvation energies of model reaction I in dioxane

	(Polarized solute)-Solvent (kcal/mol)	Total non electrostatic (kcal/mol)	Total solvation energy (kcal/mol)
1-t	-2.75	4.01	1.26
TS2	-5.24	7.21	1.97
3	-4.78	6.63	1.85
TS4	-5.18	5.42	0.24
5	-5.23	2.96	-2.27
TS6	-4.09	6.30	2.21
7-t	-5.23	5.29	0.06
7-c	-5.47	5.48	0.01
TS8	-6.03	2.69	-3.34
DMAD	-4.14	3.69	-0.45

6.2—— Solvation energies of model reaction I in benzene

	(Polarized solute)-Solvent (kcal/mol)	Total non electrostatic (kcal/mol)	Total solvation energy (kcal/mol)
1-t	-1.28	1.72	0.44
TS2	-2.09	4.29	2.2
3	-1.74	3.79	2.05
TS4	-2.08	2.95	0.87
5	-1.96	1.26	-0.70
TS6	-1.78	3.52	1.74
7-t	-2.10	3.00	0.90
7-c	-2.26	3.08	0.82
TS8	-2.28	1.25	-1.03
DMAD	-2.33	1.93	-0.40

6.3—— Solvation energies of model reaction II in dioxane

	(Polarized solute)-Solvent (kcal/mol)	Total non electrostatic (kcal/mol)	Total solvation energy (kcal/mol)
1-t	-2.75	4.01	1.26
TS9	-7.75	11.38	3.63
10	-14.00	12.14	-1.86
TS11	-9.49	10.40	0.91
12	-8.94	9.08	0.14
TS13	-7.85	11.90	4.05
14-t	-7.54	10.80	3.26
14-c	-7.78	11.21	3.43
TS15	-8.52	9.40	0.88
DMAD	-4.14	3.69	-0.45

6.4—— Solvation energies of model reaction II in benzene

	(Polarized solute)-Solvent (kcal/mol)	Total non electrostatic (kcal/mol)	Total solvation energy (kcal/mol)
1-t	-1.28	1.72	0.44
TS9	-3.92	7.09	3.17
10	-8.47	7.76	-0.71
TS11	-4.45	6.51	2.06
12	-4.01	5.68	1.67
TS13	-4.13	7.57	3.44
14-t	-3.17	6.81	3.64
14-c	-3.31	7.24	3.93
TS15	-3.71	5.93	2.22
DMAD	-2.33	1.93	-0.40

6.5—— Solvation energies of isomerization from 19 to 21 in dioxane

	(Polarized solute)-Solvent (kcal/mol)	Total non electrostatic (kcal/mol)	Total solvation energy (kcal/mol)
19-t	-8.73	12.62	3.89
19-c	-8.45	12.56	4.11
TS20	-8.92	10.39	1.47
21	-8.74	9.38	0.64

6.6—— Solvation energies of isomerization from 19 to 21 in benzene

	(Polarized solute)-Solvent (kcal/mol)	Total non electrostatic (kcal/mol)	Total solvation energy (kcal/mol)
19-t	-3.95	8.35	4.40
19-c	-3.73	8.38	4.65
TS20	-3.73	6.85	3.12
21	-3.47	5.90	2.43

6.7—— Solvation energies of model reaction III in dioxane

	(Polarized solute)-Solvent (kcal/mol)	Total non electrostatic (kcal/mol)	Total solvation energy (kcal/mol)
1-OMe	-3.38	4.87	1.49
TS25	-8.23	12.39	4.16
26	-16.01	13.21	-2.80
TS27	-10.99	11.11	0.12
28	-9.51	10.46	0.95
TS29	-8.32	13.73	5.41
30-t	-8.84	13.19	4.35
30-c	-8.46	12.89	4.43
TS31	-9.34	10.60	1.26
DMAD	-4.14	3.69	-0.45

6.8—— Solvation energies of model reaction III in benzene

	(Polarized solute)-Solvent (kcal/mol)	Total non electrostatic energy (kcal/mol)	Total solvation energy (kcal/mol)
1-OMe	-1.61	2.21	0.60
TS25	-4.23	7.70	3.47
26	-10.03	8.43	-1.60
TS27	-5.44	6.83	1.39
28	-4.17	6.59	2.42
TS29	-4.45	8.87	4.42
30-t	-4.04	8.62	4.58
30-c	-3.73	8.41	4.68
TS31	-3.97	6.76	2.79
DMAD	-2.33	1.93	-0.40

6.9—— Solvation energies of model reaction IV in dioxane

	(Polarized solute)-Solvent (kcal/mol)	Total non electrostatic energy (kcal/mol)	Total solvation energy (kcal/mol)
1-OMe-C	-3.88	4.72	0.84
TS32	-8.39	12.34	3.95
33	-15.38	12.43	-2.95
TS34	-10.77	11.14	0.37
35	-9.36	11.78	2.42
TS36	-8.23	13.90	5.67
37	-8.60	13.66	5.06
TS38	-9.25	12.84	3.59

6.10—— Solvent effect of model reaction IV in benzene

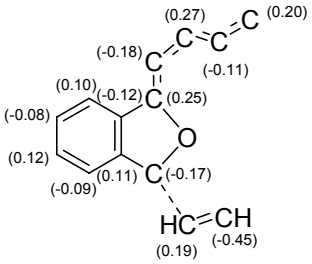
	(Polarized solute)-Solvent (kcal/mol)	Total non electrostatic energy (kcal/mol)	Total solvation energy (kcal/mol)
1-OMe-C	-1.62	2.25	0.63
TS32	-4.03	7.84	3.81
33	-8.65	7.92	-0.73
TS34	-5.07	6.94	1.87
35	-3.86	7.44	3.58
TS36	-4.02	9.17	5.15
37	-3.56	9.11	5.55
TS38	-3.92	8.37	4.45

6.11—— Solvent effect of TS9, TS13, TS25, TS29, TS32 and TS36 in different solvents

	TS9	**TS13**	**TS25**	**TS29**	**TS32**	**TS36**
Dioxane[a]	*-7.75*	*-7.85*	*-8.23*	*-8.32*	*-8.39*	*-8.23*
	11.38	11.90	12.39	13.73	12.34	13.90
Ether	*-7.82*	*-8.15*	*-8.38*	*-8.67*	*-8.13*	*-7.93*
	7.71	8.13	8.44	9.51	8.26	9.50
THF	*-6.88*	*-7.26*	*-7.49*	*-7.76*	*-7.09*	*-7.04*
	7.85	8.33	8.61	9.83	8.28	9.70
Toluene	*-4.10*	*-4.30*	*-4.42*	*-4.61*	*-4.23*	*-4.18*
	5.87	6.39	6.38	7.58	6.38	7.76
CH_3OH	*-16.46*	*-16.58*	*-17.27*	*-17.24*	*-17.08*	*-16.98*
	3.97	4.48	4.37	5.53	3.79	5.14
Benzene	*-3.92*	*-4.13*	*-4.23*	*-4.45*	*-4.03*	*-4.02*
	7.09	7.57	7.70	8.87	7.84	9.17

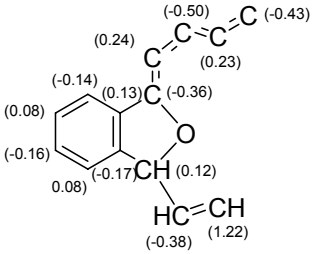
[a]The italic values are the energy of (Polarized solute)-Solvent, the plainic values are the energy of Total non electrostatic (kcal/mol).

7. The Computed Spin Distribution of the Diradical Species



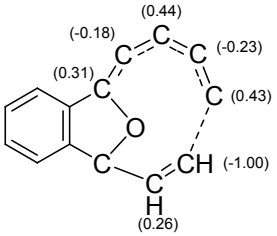
<S2> 0.3335

TS2



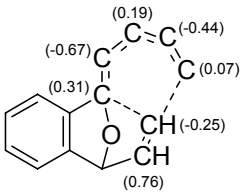
<S^2> 1.0471

3



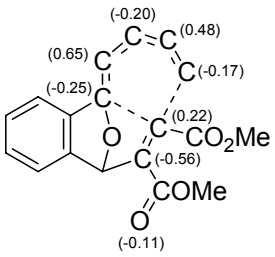
<S^2> 0.8121

TS4



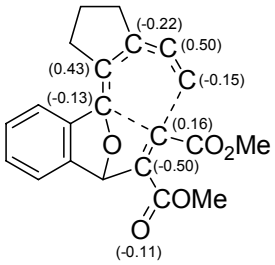
<S^2> 0.5139

TS8



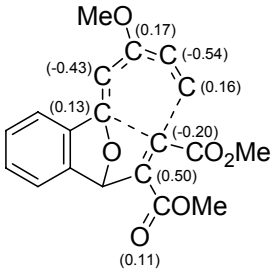
<S^2> 0.5309

TS15



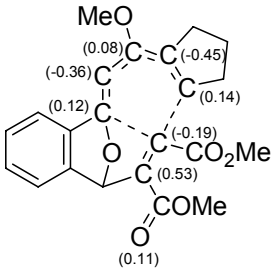
<S^2> 0.5755

TS20



<S^2> 0.5471

TS31



<S^2> 0.5476

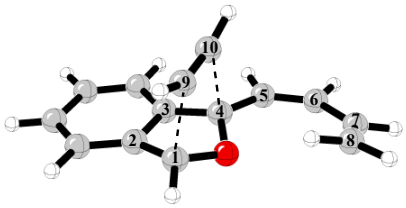
TS38

Singlet and Triplet Diradical Energies and the Spin Correction Energies Using Yamaguchi-Houk Method

	TS2	3	TS4	TS8	TS15	TS20	TS31	TS38
E_{ele} (singlet)	-615.779500	-615.798462	-615.782541	-615.804124	-1071.578779	-1188.321681	-1186.102522	-1302.839472
E_{ele} (triplet)	-615.756609	-615.798254	-615.773322	-615.783483	-1071.563637	-1188.307049	-1186.086453	-1302.824329
Spin-Correction Energy (kcal/mol)	-2.87	-0.14	-3.95	-4.48	-3.37	-3.71	-3.80	-3.58

8. TS6′ (This transition state is higher in energy than TS6 by 5.75 kcal/mol in terms of electronic energy) and TS-8+2 (concerted [8+2] transition structure located using B3LYP/6-31G(d) method)

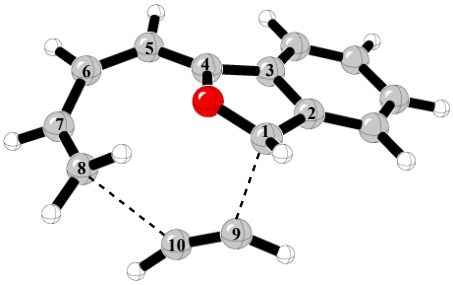
TS6′



C1-C9 = 2.085
C4-C10 = 2.422

	E_{ele}	G	H	E_0
TS6′	-615.772778	-615.600447	-615.546558	-615.560610

TS-8+2



C1-C9 = 2.092
C8-C10 = 2.541

	E_{ele}	G	H	E_0
TS-8+2	-615.741232	-615.567061	-615.514685	-615.528332

9. Full Citation of Gaussian 03

Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

10. Cartesian Coordinates of All Computed Structures

a) Model Reaction I.

Acetylene

C	-0.000135	0.000000	-0.001312
C	-0.000135	0.000000	1.206256
H	0.013185	0.000000	2.273715
H	0.013185	0.000000	-1.068771

1-t

C	0.000000	0.000000	0.000000
C	0.000000	1.397400	0.000076
C	0.160761	1.814477	1.378377
C	0.246786	0.652783	2.115851
O	0.150943	-0.424234	1.294280
C	0.199102	3.204341	1.707006
C	0.080584	4.117276	0.690824
C	-0.078807	3.704438	-0.675717
C	-0.119664	2.376971	-1.026123
H	0.369267	0.436541	3.166201
H	0.319430	3.524182	2.738643
H	0.106699	5.180558	0.914656
H	-0.168451	4.467540	-1.444338
H	-0.240783	2.081128	-2.064857
C	-0.125372	-0.937488	-1.074967
C	-0.125123	-2.300252	-1.074486
C	0.006888	-3.200570	0.054939
C	-0.007429	-4.543236	-0.068783
H	0.093460	-5.194955	0.794274
H	-0.120542	-5.027011	-1.037472

H	0.122136	-2.761635	1.041865
H	-0.238479	-2.781043	-2.045838
H	-0.238204	-0.449079	-2.040944

1-c

C	0.000000	0.000000	0.000000
C	0.008432	1.446833	-0.020159
C	-1.133735	2.166293	-0.486260
C	-2.224801	1.451042	-0.909622
C	-2.234093	0.015741	-0.891294
C	-1.151250	-0.705550	-0.448784
C	1.243782	-0.405789	0.500928
O	1.973235	0.721148	0.774223
C	1.243984	1.822007	0.465556
H	1.724365	2.772348	0.642375
H	-1.132691	3.252894	-0.502935
H	-3.107096	1.974179	-1.269058
H	-3.122932	-0.505142	-1.237332
H	-1.175483	-1.792004	-0.441699
C	1.752555	-1.723760	0.710870
C	2.933530	-2.246202	1.158182
C	4.190340	-1.683773	1.639265
C	4.549561	-0.414438	1.919945
H	1.009239	-2.468010	0.428884
H	2.945571	-3.335205	1.148653
H	4.948127	-2.449783	1.809293
H	5.552026	-0.208693	2.286335
H	3.882745	0.429118	1.803604

TS2

C	0.483233	1.286620	-0.705873
C	0.480210	2.431387	0.860011
C	0.813523	3.643661	0.829762
H	1.171093	4.495929	0.282848
H	0.123712	1.714140	1.590596
C	1.519422	0.314585	-0.484346
C	0.878076	-0.861536	0.004779
C	-0.520811	-0.626486	-0.051767
O	-0.728009	0.611677	-0.595007
C	2.922231	0.384482	-0.569805
C	3.661336	-0.723581	-0.189076
C	3.025898	-1.896638	0.301780
C	1.650238	-1.976924	0.409356
C	-1.602410	-1.461964	0.324209
C	-2.957275	-1.242926	0.269239
C	-3.656190	-0.062990	-0.182140

C	-5.004532	0.036108	-0.188672
H	0.473276	2.021916	-1.499184
H	3.413132	1.286669	-0.924598
H	4.745408	-0.699266	-0.259600
H	3.638343	-2.743800	0.599093
H	1.175798	-2.876708	0.791568
H	-1.279143	-2.426917	0.709165
H	-3.587957	-2.061493	0.615112
H	-3.061999	0.778061	-0.527344
H	-5.505908	0.936806	-0.530386
H	-5.639385	-0.781541	0.148033

3

C	0.510272	1.396359	-0.456539
C	1.546272	0.314319	-0.260761
C	0.878011	-0.897327	-0.005822
C	-0.542885	-0.639293	-0.031636
O	-0.755516	0.694319	-0.300273
C	2.932788	0.383540	-0.298080
C	3.666536	-0.791166	-0.082440
C	3.007076	-2.005233	0.170876
C	1.614950	-2.073420	0.213581
C	-1.595245	-1.524207	0.166616
C	-2.975422	-1.299451	0.146008
C	-3.668948	-0.071499	-0.091538
C	-5.026295	0.035083	-0.086639
H	3.440171	1.326582	-0.486196
H	4.752331	-0.762558	-0.109288
H	3.591394	-2.906595	0.337167
H	1.116213	-3.018179	0.411774
H	-1.276540	-2.545189	0.366086
H	-3.599815	-2.172558	0.334698
H	-3.073233	0.816072	-0.285438
H	-5.521388	0.983735	-0.271579
H	-5.665655	-0.825362	0.102329
H	0.525733	1.813413	-1.469585
C	0.585253	2.522861	0.554709
C	0.797671	3.781833	0.247434
H	0.910203	4.729599	0.757638
H	0.464514	2.212093	1.599968

TS4

C	-3.562585	0.553709	-0.150227
C	-1.362424	2.191923	1.105419
C	-0.254802	2.326935	0.412108
C	0.215819	1.399028	-0.720904

O	-0.762381	0.375525	-0.960340
C	-0.365719	-0.795482	-0.374981
C	1.065472	-0.720587	-0.144569
C	1.456731	0.613637	-0.365367
C	2.775211	1.016052	-0.184815
C	3.717096	0.057951	0.210975
C	3.331047	-1.273543	0.437424
C	2.005514	-1.674234	0.271939
C	-1.249596	-1.803499	-0.034356
C	-2.645667	-1.807144	0.149574
C	-3.620098	-0.767995	0.213909
H	-1.811454	2.748504	1.918472
H	0.450958	3.142161	0.615356
H	0.313185	1.975676	-1.648266
H	3.078013	2.047683	-0.348564
H	4.755907	0.347049	0.345483
H	4.076594	-2.001723	0.745861
H	1.714818	-2.705224	0.454664
H	-0.754864	-2.739250	0.221276
H	-3.032595	-2.783012	0.439186
H	-4.559761	-1.098186	0.660312
H	-4.415257	1.196713	0.051583
H	-2.752491	0.964901	-0.729420

5

C	0.002777	0.000707	-0.001588
O	0.005323	0.002205	1.443473
C	1.332240	0.001210	1.829539
C	2.064986	-0.783854	0.827537
C	1.257461	-0.797509	-0.323584
C	1.689136	-1.406346	-1.495174
C	2.946099	-2.029082	-1.499205
C	3.752418	-2.016610	-0.353322
C	3.324059	-1.385568	0.819935
H	3.954630	-1.379479	1.705203
H	4.721934	-2.507562	-0.374583
H	3.296940	-2.527987	-2.398754
H	1.071291	-1.410710	-2.390412
H	-0.924910	-0.481592	-0.330329
C	0.116564	1.447516	-0.461933
C	-0.148364	2.519541	0.300074
C	-0.822454	2.571926	1.667634
C	0.020225	2.683636	2.930702
C	1.041803	1.930770	3.407764
C	1.771457	0.818488	2.808244
H	2.804094	0.690696	3.127458

H	1.454717	2.264714	4.360297
H	-0.285647	3.500856	3.583661
H	-1.476257	3.453739	1.648318
H	-1.479564	1.702631	1.773828
H	0.077896	3.493965	-0.133606
H	0.521699	1.594358	-1.462404

TS6

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	2.084539
C	2.183154	0.000000	1.847690
C	1.191335	-0.032674	-0.361988
H	2.067727	-0.037240	-0.976054
H	-1.042961	0.021448	-0.263556
O	1.117202	0.788973	2.184607
C	1.809836	-1.360790	2.110366
C	0.403089	-1.353639	2.318594
C	-0.296424	-2.550694	2.556199
C	0.427448	-3.732182	2.612839
C	1.830493	-3.741310	2.408844
C	2.528121	-2.571880	2.148013
H	3.602766	-2.594813	1.986297
H	2.366523	-4.685352	2.463080
H	-0.083786	-4.668758	2.819578
H	-1.373875	-2.550571	2.701720
H	-0.915355	0.482761	2.404615
C	3.512364	0.551210	1.751582
C	3.931640	1.844585	1.761557
C	3.127822	3.048132	1.876245
C	3.660799	4.285852	1.883529
H	4.278245	-0.214570	1.642284
H	5.005951	2.005001	1.670119
H	2.051083	2.930193	1.954062
H	3.038544	5.172517	1.963906
H	4.735132	4.446446	1.810048

7-t

C	0.001029	0.001077	-0.012129
O	-0.004625	-0.002437	1.436456
C	1.447660	-0.004484	1.609977
C	1.813652	1.199108	0.705739
C	0.919414	1.207269	-0.285166
C	1.776493	-1.270340	0.771528
C	0.835310	-1.261434	-0.271206
C	0.824437	-2.251349	-1.235454
C	1.787899	-3.278098	-1.138298

C	2.720551	-3.286264	-0.102206
C	2.725243	-2.268546	0.875666
C	1.912819	0.057871	3.030235
C	1.390312	-0.578779	4.097632
C	0.237884	-1.471766	4.122084
C	-0.183712	-2.082129	5.243696
H	-1.041964	-2.748097	5.240750
H	0.316144	-1.932232	6.199407
H	-0.289129	-1.632143	3.185768
H	1.876619	-0.413350	5.060033
H	2.785815	0.688087	3.192117
H	2.679905	1.834425	0.852605
H	0.870439	1.849065	-1.157033
H	-1.014368	0.030616	-0.406507
H	3.445465	-2.286188	1.689969
H	3.449952	-4.090007	-0.040957
H	1.797625	-4.074884	-1.877725
H	0.095771	-2.254866	-2.043204

7-c

C	0.004296	-0.004086	0.001560
C	0.003802	-0.005048	1.406036
C	1.184746	-0.007064	2.124594
C	2.396894	-0.005728	1.402657
C	2.396083	-0.012646	0.008252
C	1.184946	-0.015416	-0.714737
C	-1.494833	-0.034382	-0.393799
O	-2.032611	0.765020	0.715604
C	-1.484018	-0.044064	1.783902
C	-2.005776	-1.435420	1.377737
C	-2.002884	-1.432577	0.043348
H	1.188049	-0.008179	-1.801763
H	3.340436	-0.009037	-0.530348
H	3.341327	0.002312	1.940973
H	1.191694	-0.004867	3.212466
H	-1.773549	0.346732	2.759220
H	-2.229676	-2.246794	2.060376
H	-2.225740	-2.241173	-0.644005
H	-2.546708	-0.310486	-2.282429
H	-2.061239	1.612018	-3.427412
C	-0.901227	2.754980	-2.024549
C	-0.748294	3.266143	-0.792208
C	-1.659681	1.560484	-2.413924
H	-0.462650	3.295584	-2.864937
H	-0.168470	4.173713	-0.642854
H	-1.198795	2.805537	0.080781

C	-1.929591	0.414513	-1.754120

TS8

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.914223
C	1.546651	0.000000	-0.250057
C	2.308518	-1.076170	0.452950
C	1.941705	-1.555505	1.680875
C	0.768864	-1.117526	2.343747
O	0.551524	1.331284	1.886263
C	-0.526346	2.015470	1.212408
C	-1.730605	1.551506	2.022312
C	-1.393900	0.243091	2.412523
C	-2.305642	-0.547066	3.100566
C	-3.557624	0.005171	3.418362
C	-3.887595	1.307931	3.029625
C	-2.975512	2.095031	2.306719
C	-0.708789	1.227901	-0.088571
H	-3.242570	3.101673	1.993222
H	-4.860437	1.716561	3.290927
H	-4.278582	-0.587588	3.975479
H	-2.065947	-1.565344	3.397164
H	0.319200	-1.773064	3.087107
H	2.494560	-2.386113	2.115730
H	3.149238	-1.530706	-0.066651
H	1.701440	-0.074694	-1.335337
H	1.921734	0.980878	0.056151
H	-0.481138	-0.865365	-0.463764
H	-1.655909	1.319023	-0.614020
H	-0.312820	3.084405	1.170883

****

b) Model Reaction II.

DMAD

C	4.123324	-0.622871	-0.389670
O	2.685359	-0.605522	-0.528222
C	2.034459	0.248741	0.279016
O	2.558372	0.981873	1.092537
C	0.602683	0.190708	0.060816
C	-0.602684	0.190710	-0.060815
C	-2.034460	0.248747	-0.279012
O	-2.558375	0.981897	-1.092515
O	-2.685357	-0.605536	0.528207
C	-4.123323	-0.622880	0.389660

H	-4.534756	0.363596	0.617220
H	-4.467193	-1.363812	1.110721
H	-4.399752	-0.910110	-0.627806
H	4.399750	-0.910076	0.627804
H	4.534763	0.363596	-0.617255
H	4.467192	-1.363824	-1.110711

TS9

C	-0.102040	0.331129	-0.914973
C	-1.078303	-0.944161	0.371801
C	-2.277254	-1.186058	0.081126
C	-3.435249	-1.112935	-0.743967
O	-3.619652	-1.796604	-1.744093
O	-4.339324	-0.202701	-0.281467
C	-5.566522	-0.121108	-1.027031
H	-5.373430	0.187791	-2.058449
H	-6.167373	0.626781	-0.507963
H	-6.076282	-1.088698	-1.032057
C	-0.103899	-1.275827	1.424974
O	0.814846	-0.561411	1.780981
O	-0.359485	-2.485843	1.962190
C	0.520994	-2.889441	3.028163
H	1.552585	-2.946384	2.670177
H	0.162966	-3.872888	3.333805
H	0.463890	-2.180843	3.858858
C	-0.099872	1.635680	-0.332735
C	1.259081	1.963802	-0.043707
C	2.042687	0.883884	-0.507851
O	1.233195	-0.033335	-1.077131
C	-1.137479	2.529559	0.008372
C	-0.795494	3.721123	0.618916
C	0.559193	4.045337	0.918137
C	1.585943	3.180201	0.601505
C	3.452170	0.685369	-0.429618
C	4.209494	-0.375650	-0.838721
C	3.774605	-1.609163	-1.457995
C	4.638480	-2.581534	-1.817142
H	-0.702750	0.007441	-1.753409
H	-2.175040	2.278874	-0.192611
H	-1.575435	4.429235	0.886343
H	0.779623	4.988464	1.410503
H	2.615852	3.426597	0.844457
H	3.976956	1.520188	0.028417
H	5.283200	-0.288599	-0.673667
H	2.712653	-1.746463	-1.635893
H	4.296189	-3.502136	-2.280512

H	5.710541	-2.481449	-1.657342

10

C	-0.671748	0.103084	0.122318
C	0.146519	0.732855	1.316455
C	1.591598	0.395673	1.457355
O	2.111069	-0.119232	0.298384
C	3.511579	-0.437717	0.342241
H	4.099797	0.456119	0.567142
H	3.756510	-0.817922	-0.650932
H	3.708905	-1.196096	1.105163
O	2.269313	0.553087	2.449172
C	-0.452474	1.591785	2.123062
C	-1.805134	2.032668	2.183525
O	-2.728913	1.415905	2.717057
O	-1.985428	3.275571	1.622476
C	-3.292869	3.843058	1.791054
H	-4.056596	3.225638	1.307788
H	-3.243925	4.826898	1.320624
H	-3.535975	3.940447	2.853371
H	-1.719200	0.141810	0.427069
C	-0.401708	0.666774	-1.227509
C	0.063117	-0.365894	-2.068268
C	0.429829	-0.107199	-3.403711
C	0.303301	1.192703	-3.869795
C	-0.165084	2.223866	-3.023670
C	0.082349	-1.561754	-1.281107
O	-0.394923	-1.326151	-0.066369
C	0.533652	-2.853576	-1.665812
C	0.609579	-3.992583	-0.904637
C	0.268532	-4.174625	0.485409
C	0.409125	-5.370397	1.098463
H	-0.852053	2.773612	-1.041985
H	-0.250271	3.232815	-3.418191
H	0.571365	1.426603	-4.896191
H	0.800853	-0.896053	-4.052077
H	0.851795	-2.923117	-2.702395
H	0.783647	-6.244493	0.569117
H	0.153752	-5.502939	2.145451
H	-0.107972	-3.323967	1.043288
C	-0.512530	1.975840	-1.696839
H	0.984620	-4.880159	-1.414221

TS11

C	-2.780436	-0.677315	-1.794697
C	-0.996140	0.487215	0.001585

C	0.111391	0.855232	-0.620094
C	0.973150	-0.257849	-1.326688
O	0.065047	-1.330024	-1.643029
C	-0.086252	-2.062275	-0.519640
C	1.136454	-1.950573	0.259310
C	1.865011	-0.878608	-0.289631
C	3.094936	-0.503715	0.241359
C	3.596154	-1.240884	1.319382
C	2.865760	-2.305529	1.876710
C	1.621180	-2.664172	1.362042
C	-1.137215	-2.984125	-0.324870
C	-2.467362	-2.915859	-0.694528
C	-3.229918	-1.822511	-1.205577
H	1.437917	0.082783	-2.249293
H	3.647787	0.336758	-0.166449
H	4.564995	-0.983322	1.739162
H	3.277344	-2.853086	2.720033
H	1.053731	-3.478487	1.803733
H	-0.868688	-3.817300	0.322425
H	-3.062293	-3.767098	-0.365946
H	-4.298414	-1.894582	-1.001778
H	-3.465436	0.147740	-1.963106
H	-1.790584	-0.596225	-2.212804
C	-1.957784	1.250792	0.769304
O	-2.991624	1.733090	0.328708
O	-1.619358	1.294889	2.086555
C	-2.517585	2.032964	2.930481
H	-2.107375	1.940609	3.937400
H	-2.551886	3.082589	2.625133
H	-3.525831	1.610698	2.884552
C	0.679544	2.227443	-0.603966
O	0.171822	3.204635	-0.092579
O	1.882108	2.283072	-1.254541
C	2.501984	3.580790	-1.300234
H	1.852617	4.294254	-1.814476
H	2.702716	3.943392	-0.288408
H	3.432217	3.439854	-1.852566

12

C	0.008228	0.003946	-0.000164
O	0.009577	0.007195	1.437551
C	1.333973	0.001430	1.842455
C	2.073506	-0.771325	0.842667
C	1.273423	-0.793697	-0.313829
C	1.700323	-1.457925	-1.458354
C	2.947480	-2.097715	-1.434916

C	3.754012	-2.054679	-0.290179
C	3.326336	-1.386005	0.860564
C	1.749823	0.786035	2.856150
C	1.000612	1.871946	3.473220
C	-0.032667	2.610320	3.003113
C	-0.869660	2.488146	1.739683
C	-0.198949	2.522171	0.358072
C	0.076701	1.477274	-0.452517
H	-0.912076	-0.481383	-0.338420
H	1.083023	-1.487698	-2.350079
H	3.291291	-2.634782	-2.315012
H	4.718307	-2.556051	-0.292856
H	3.947515	-1.365238	1.751991
H	2.778242	0.657314	3.186861
H	1.410006	2.206657	4.426213
H	-0.345644	3.429466	3.647898
H	-1.567932	3.335065	1.742240
H	-1.478669	1.584133	1.802702
C	0.043845	3.939782	-0.097700
O	0.902366	4.649595	0.379498
O	-0.875460	4.351885	-0.993895
C	-0.699786	5.692286	-1.495307
H	0.254068	5.766057	-2.023938
H	-1.534805	5.855877	-2.177120
H	-0.721665	6.413618	-0.674209
C	0.472268	1.736938	-1.869309
O	1.145880	2.663349	-2.272210
O	-0.055199	0.794306	-2.690172
H	1.321738	0.908879	-4.257477
C	0.241875	0.948727	-4.091407
H	-0.258837	0.115916	-4.586411
H	-0.145486	1.903097	-4.456948

TS13

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	2.936373
C	1.250972	0.000000	0.028314
C	1.991800	-0.025749	1.950631
O	1.012534	-0.802820	2.531577
C	0.453548	1.346732	2.912316
C	1.765717	1.323710	2.355248
C	2.502271	2.516361	2.207274
C	1.923123	3.697072	2.636313
C	0.611514	3.723496	3.186356
C	-0.131695	2.567044	3.321463
H	2.937174	-0.532933	1.826569

H	3.494593	2.502980	1.767212
H	2.475918	4.628864	2.550186
H	0.191296	4.674085	3.503348
H	-1.135902	2.597155	3.735001
C	-1.414978	-0.106565	-0.013751
O	-2.029036	-1.163987	0.053861
O	-2.018755	1.110483	-0.121668
C	-3.452897	1.077402	-0.209956
H	-3.770668	0.510698	-1.089940
H	-3.757443	2.121312	-0.296761
H	-3.886503	0.622087	0.685028
C	2.374433	0.044211	-0.922572
O	2.271303	-0.185730	-2.109621
O	3.550976	0.381535	-0.334488
C	4.680687	0.466359	-1.224181
H	4.856001	-0.497567	-1.708892
H	4.505163	1.227949	-1.988458
H	5.525959	0.740479	-0.591946
C	-1.225080	-0.535888	3.440294
C	-1.650314	-1.830597	3.501318
C	-0.963924	-3.029010	3.066618
C	-1.484142	-4.259557	3.244310
H	-1.904391	0.227882	3.811488
H	-2.636441	-1.989598	3.936803
H	-0.003113	-2.918884	2.574699
H	-0.964256	-5.150410	2.904504
H	-2.447999	-4.408456	3.727583

14-t

O	-0.141077	-0.179932	0.039514
C	-0.104260	-0.161750	1.485555
C	1.452262	-0.087201	1.682690
C	1.978372	-0.792008	0.665867
C	0.766502	-1.289429	-0.151596
C	0.073337	-2.358349	0.698359
C	-0.474283	-1.640555	1.771835
C	-1.170582	-2.274000	2.783566
C	-1.323869	-3.672135	2.695029
C	-0.781837	-4.387534	1.626814
C	-0.063814	-3.731287	0.606566
H	0.930526	-1.490613	-1.207428
H	0.357680	-4.293539	-0.223261
H	-0.915595	-5.465116	1.578452
H	-1.874013	-4.198828	3.470409
H	-1.592468	-1.722178	3.618883
C	2.082851	0.509352	2.884358

O	1.719439	0.232589	4.013779
C	3.739205	1.974279	3.703620
H	4.450215	2.672982	3.263361
H	3.040483	2.493122	4.364994
H	4.260092	1.190410	4.259156
C	3.383995	-1.187659	0.451151
O	4.304785	-0.996503	1.221250
O	3.523029	-1.826252	-0.737414
C	4.854024	-2.276502	-1.052976
H	5.538441	-1.425782	-1.106945
H	5.207185	-2.977437	-0.291989
C	-0.916152	0.892536	2.159238
H	4.769903	-2.766910	-2.023037
H	-0.774604	0.895707	3.238301
C	-1.771516	1.791506	1.633307
C	-2.145918	2.001314	0.238718
C	-3.027413	2.946244	-0.133138
H	-2.259312	2.459741	2.344670
H	-1.687953	1.361976	-0.508723
H	-3.299802	3.091530	-1.174729
H	-3.503737	3.603092	0.593089
O	3.036417	1.397770	2.584127

14-c

C	0.272118	0.027024	0.474914
C	0.192693	-0.213620	2.001900
O	1.613117	-0.395922	2.291899
C	1.862507	-1.433999	1.318263
C	1.359303	-0.747221	0.044448
C	1.723928	-0.796950	-1.289019
C	0.968122	-0.036574	-2.203762
C	-0.120031	0.724680	-1.774437
C	-0.488449	0.760160	-0.415339
H	-1.337208	1.350665	-0.082266
H	-0.691857	1.300101	-2.497844
H	1.235322	-0.046572	-3.257362
H	2.564686	-1.396946	-1.629135
H	2.894753	-1.774561	1.353125
C	0.773376	-2.450196	1.723102
C	-0.260528	-1.704741	2.149935
C	-1.645465	-2.105336	2.502197
O	-2.619236	-1.686890	1.904381
O	-1.690343	-2.924388	3.561217
C	-2.993673	-3.432135	3.912804
H	-3.678448	-2.608665	4.131566
H	-2.830042	-4.047867	4.796986

H	-3.390575	-4.033219	3.090840
C	0.815573	-3.906805	1.496728
O	-0.120252	-4.673898	1.618121
O	2.056357	-4.295849	1.111669
C	2.217231	-5.702428	0.848879
H	1.542909	-6.018141	0.048398
H	3.258445	-5.822234	0.548577
H	2.004885	-6.282530	1.750824
C	-0.498348	0.771932	2.891160
C	-0.315574	2.104475	2.989664
C	0.612955	3.018195	2.313511
C	1.862608	2.762372	1.894653
H	-1.267900	0.344184	3.529118
H	-0.993030	2.607628	3.681494
H	0.229754	4.033563	2.199764
H	2.453025	3.542916	1.421197
H	2.324576	1.789116	2.021549

TS15

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.993417
C	1.553392	0.000000	-0.217942
O	0.579759	1.298039	1.935858
C	-0.481326	2.020112	1.279727
C	-1.698229	1.570484	2.075550
C	-1.388136	0.257724	2.467601
C	-2.314310	-0.520573	3.152580
C	-3.551727	0.055334	3.468897
C	-3.856105	1.366395	3.080461
C	-2.934299	2.136805	2.356900
H	-3.182444	3.142514	2.030792
H	-4.822791	1.790785	3.339288
H	-4.287734	-0.525360	4.018624
H	-2.097198	-1.546993	3.435657
H	-0.246418	3.082735	1.246454
C	0.765691	-1.133371	2.390494
C	1.942350	-1.553064	1.730711
C	2.307540	-1.070679	0.500896
H	0.316335	-1.798756	3.124878
H	2.493483	-2.389468	2.155539
H	3.143621	-1.533336	-0.018254
H	1.917271	0.978925	0.104136
H	1.729714	-0.074788	-1.296979
C	-0.657613	1.271096	-0.049780
C	-1.615671	1.670110	-1.066802
O	-2.208265	2.863127	-0.765163

O	-1.830706	1.071367	-2.112660
C	-3.130021	3.362438	-1.747481
H	-3.492561	4.311303	-1.349566
H	-3.957254	2.660765	-1.886035
C	-0.750278	-1.169090	-0.585305
O	-1.878132	-1.476324	-0.253462
H	-2.624048	3.514531	-2.705185
O	-0.015967	-1.880946	-1.468346
C	-0.685548	-3.005274	-2.066927
H	-0.974933	-3.728918	-1.299935
H	0.039866	-3.440487	-2.755245
H	-1.576383	-2.668355	-2.603306

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c) Model Reaction III.

1-OMe

C	0.000112	0.018250	0.004341
O	0.002384	0.029065	1.373661
C	1.285433	0.025402	1.825490
C	2.156660	0.012023	0.757848
C	1.328065	0.007172	-0.431060
C	1.935449	-0.009385	-1.718316
C	3.306653	-0.020218	-1.798177
C	4.128046	-0.014862	-0.619650
C	3.580562	0.000809	0.637340
H	1.407667	0.030834	2.897749
H	4.209236	0.003917	1.523803
H	5.208565	-0.024434	-0.737237
H	3.789874	-0.034456	-2.771511
H	1.327136	-0.015995	-2.618994
C	-1.220292	0.024145	-0.741301
C	-2.522717	0.002737	-0.336039
C	-3.012676	-0.042210	1.034655
C	-4.303665	-0.220610	1.373709
H	-1.068557	0.025368	-1.818153
O	-3.483235	-0.046476	-1.337380
C	-4.024543	1.222687	-1.715819
H	-4.805624	1.015525	-2.451385
H	-4.458702	1.745148	-0.854168
H	-3.250473	1.855199	-2.170973
H	-2.264039	0.062885	1.813151
H	-4.605408	-0.253107	2.416455
H	-5.078890	-0.357496	0.625750

TS25

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	2.108508
C	1.138495	0.000000	2.634993
C	2.559840	0.063709	2.646273
O	3.211681	1.098357	2.566438
O	3.128225	-1.169919	2.779913
C	4.563417	-1.178870	2.865602
H	5.008747	-0.767932	1.954880
H	4.836342	-2.228032	2.987112
H	4.899845	-0.591852	3.724969
C	-1.419878	-0.043424	2.486380
O	-2.314563	-0.521816	1.813570
O	-1.618056	0.516952	3.698133
C	-2.975339	0.494232	4.177465
H	-3.330151	-0.535861	4.270751
H	-2.939399	0.979916	5.153057
H	-3.630825	1.042980	3.495567
O	-1.075215	0.718865	-0.526598
C	-1.955037	-0.114990	-1.115557
C	-1.420871	-1.425018	-1.103401
C	-0.164411	-1.347732	-0.429619
C	0.623670	-2.508145	-0.259892
C	0.145209	-3.701621	-0.764642
C	-1.113759	-3.781995	-1.426958
C	-1.901543	-2.661652	-1.594094
H	0.911792	0.579627	-0.019099
H	1.572526	-2.461717	0.266654
H	0.736150	-4.606703	-0.650253
H	-1.455878	-4.744525	-1.797176
H	-2.866902	-2.732213	-2.088446
C	-3.207696	0.325633	-1.625268
C	-3.769000	1.580707	-1.610777
C	-3.161272	2.775890	-1.033641
C	-3.732736	3.993105	-1.042653
O	-4.991466	1.830210	-2.148726
C	-5.742585	0.781941	-2.751063
H	-5.208209	0.354668	-3.608764
H	-6.668864	1.246196	-3.092773
H	-5.972993	-0.006490	-2.023955
H	-3.774736	-0.479831	-2.076750
H	-2.189178	2.636197	-0.578004
H	-3.224962	4.841416	-0.593353
H	-4.704898	4.171899	-1.490301

26

C	0.082562	0.177255	-0.120425
C	0.077557	0.118865	1.441890
C	2.530298	-0.256439	1.574820
C	1.211773	-0.118875	2.092491
O	3.295653	0.673173	1.308049
O	2.919253	-1.574217	1.449729
C	4.294548	-1.778213	1.099473
H	4.954735	-1.328637	1.847564
H	4.430255	-2.861443	1.076182
H	4.522644	-1.344131	0.120663
C	-1.216712	0.256613	2.164161
O	-1.364836	0.457723	3.350045
O	-2.292942	0.113841	1.319865
C	-3.579371	0.196738	1.950822
H	-4.308457	0.051049	1.151356
H	-3.715116	1.174347	2.422598
H	-3.684866	-0.581855	2.711538
O	-0.700326	1.311370	-0.659054
C	-1.659239	0.890852	-1.467498
C	-1.566477	-0.532682	-1.656095
C	-0.508980	-0.983047	-0.843652
C	-0.177585	-2.336446	-0.785883
C	-0.916598	-3.223669	-1.567447
C	-1.980083	-2.776937	-2.382290
C	-2.320943	-1.432151	-2.431112
H	1.109436	0.401720	-0.415701
H	0.628096	-2.681481	-0.143682
H	-0.674690	-4.282924	-1.547263
H	-2.539006	-3.497343	-2.972864
H	-3.146789	-1.093998	-3.051374
C	-2.616062	1.758238	-2.040501
C	-2.760555	3.123939	-1.852051
C	-1.937660	3.949392	-0.975226
C	-2.110814	5.274709	-0.821276
H	-3.307322	1.258112	-2.707285
H	-1.155468	3.434088	-0.433541
H	-1.466823	5.835082	-0.150452
H	-2.884271	5.824489	-1.347694
O	-3.719405	3.825562	-2.484572
C	-4.617850	3.195300	-3.399713
H	-4.071506	2.748914	-4.238222
H	-5.263343	3.994544	-3.764725
H	-5.222850	2.435026	-2.892692

TS27

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	2.816972
C	1.233548	0.000000	3.301439
C	2.233616	-1.133887	2.872745
C	2.046761	-2.336952	3.750571
C	1.168757	-3.202816	3.074781
C	0.929629	-2.616980	1.765990
O	1.809537	-1.620714	1.578554
C	0.078358	-3.106776	0.771559
C	-0.549866	-2.444044	-0.287151
C	-0.718726	-1.034102	-0.506599
H	0.971528	-0.125137	0.444792
H	-0.357562	1.015127	-0.139206
H	-1.601394	-0.812897	-1.104154
O	-1.319261	-3.146429	-1.159129
C	-1.364285	-4.571192	-1.129768
H	-1.889357	-4.932919	-0.237278
H	-0.355706	-4.998435	-1.171370
H	-1.926346	-4.859106	-2.019215
H	-0.240811	-4.127424	0.953811
H	3.252121	-0.764860	2.767015
C	2.467629	-2.619662	5.047495
C	2.009704	-3.796812	5.646152
C	1.122556	-4.658734	4.975854
C	0.682929	-4.365098	3.687411
H	-0.012671	-5.026179	3.177553
H	0.775357	-5.561100	5.471401
H	2.338272	-4.048786	6.651023
H	3.128325	-1.942164	5.578835
C	1.744320	0.964880	4.309575
O	1.135315	1.907682	4.772692
O	3.031681	0.675436	4.686195
C	3.610201	1.572442	5.649819
H	4.624462	1.206400	5.817459
H	3.034509	1.557509	6.579529
H	3.629005	2.592852	5.257769
C	-1.090464	0.917792	3.035625
O	-1.356135	1.879335	2.323034
O	-1.880813	0.531186	4.078343
C	-3.003458	1.382826	4.349046
H	-3.524977	0.915095	5.186140
H	-3.660261	1.449509	3.476243
H	-2.665863	2.386911	4.621914

28

C	0.009260	0.005385	0.002735
C	0.014220	0.025434	1.393226
C	1.251842	0.025790	2.051884
C	2.452001	-0.014630	1.329245
C	2.445022	-0.044717	-0.068631
C	1.212709	-0.019666	-0.722783
C	0.839678	-0.048312	-2.139869
O	-0.464259	0.405266	-2.217215
C	-1.127232	-0.024716	-1.015246
C	-1.668043	-1.446530	-1.272770
C	-1.817358	-1.981581	-2.503339
C	-1.736254	-1.246653	-3.852986
C	-0.486566	-1.314829	-4.711963
C	0.803274	-0.993572	-4.458665
C	1.447790	-0.593648	-3.209944
O	1.697611	-1.241988	-5.498865
C	2.414288	-0.101398	-5.966619
H	1.727324	0.638454	-6.400898
H	3.097705	-0.464501	-6.737813
H	2.992512	0.376408	-5.164120
H	-0.656838	-1.664416	-5.727393
H	-2.545756	-1.670376	-4.460806
H	-2.000023	-0.200934	-3.681103
H	-1.935059	0.679482	-0.797641
H	-0.914684	0.033661	1.954107
H	1.279833	0.057380	3.137921
H	3.399791	-0.014351	1.861251
H	3.377028	-0.067532	-0.627161
H	2.491851	-0.878750	-3.106104
C	-2.239091	-3.415188	-2.695651
O	-1.514357	-4.273108	-3.150536
O	-3.549060	-3.599284	-2.418135
C	-4.053720	-4.930039	-2.646747
H	-3.521371	-5.649391	-2.018734
H	-5.109671	-4.887410	-2.378621
H	-3.930972	-5.208359	-3.696840
C	-2.086826	-2.151991	-0.027003
O	-2.615690	-1.568433	0.904245
O	-1.816835	-3.469204	-0.020544
C	-2.256647	-4.201109	1.139920
H	-1.939104	-5.229346	0.966161
H	-3.343845	-4.138412	1.237295
H	-1.786840	-3.798238	2.040655

TS29

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	2.999577
C	1.248196	0.000000	0.027407
C	1.996423	0.013930	2.007414
O	1.022417	-0.780370	2.579852
C	0.422439	1.356548	2.951215
C	1.734821	1.356443	2.390389
C	2.442125	2.567670	2.229191
C	1.835507	3.738638	2.642601
C	0.523448	3.741504	3.194769
C	-0.189604	2.568837	3.345956
C	2.389695	0.003079	-0.898770
O	2.314217	-0.302537	-2.071353
O	3.548871	0.395318	-0.311197
C	4.692681	0.447052	-1.184753
H	4.895204	-0.541287	-1.605657
H	5.520925	0.776658	-0.556434
H	4.517530	1.156174	-1.998083
C	-1.414715	-0.081898	0.038566
O	-2.048555	-1.118739	0.197851
O	-2.001080	1.137334	-0.137148
C	-3.435838	1.125621	-0.194643
H	-3.782902	0.505062	-1.026032
H	-3.724228	2.166560	-0.348163
H	-3.860158	0.742354	0.737948
C	-1.208304	-0.536569	3.530145
C	-1.639780	-1.840554	3.572340
C	-0.923472	-2.991036	3.028019
C	-1.311826	-4.265994	3.194553
O	-2.813496	-2.191364	4.156561
C	-3.652001	-1.202385	4.741043
H	-3.990050	-0.478112	3.989725
H	-4.512050	-1.745202	5.136201
H	-3.138635	-0.680390	5.558516
H	-1.856894	0.229392	3.939079
H	-0.036703	-2.762414	2.451288
H	-0.742802	-5.076202	2.748423
H	-2.196881	-4.531280	3.763559
H	-1.193998	2.581559	3.760921
H	0.080228	4.685812	3.499017
H	2.365731	4.682229	2.543002
H	3.435068	2.573699	1.790006
H	2.947787	-0.480220	1.882509

30-t

O	0.891703	0.368780	0.099498
C	0.611272	0.251471	1.512253
C	2.007111	-0.100736	2.036204
C	2.563788	-0.895401	1.021808
C	1.479904	-0.954091	-0.077191
C	3.827727	-1.440067	1.149291
C	4.551093	-1.155630	2.325482
C	4.000127	-0.361296	3.330694
C	2.703390	0.176067	3.197836
H	2.276222	0.791395	3.986005
H	4.576701	-0.152544	4.228132
H	5.551969	-1.561225	2.448063
H	4.263460	-2.067640	0.376103
C	1.938064	-1.245290	-1.467097
C	1.233736	-1.076991	-2.606310
C	-0.140989	-0.577058	-2.703083
C	-0.876454	-0.620972	-3.824911
O	1.840092	-1.462629	-3.790425
C	2.438972	-0.397495	-4.536980
H	1.708348	0.384789	-4.775676
H	3.273621	0.043232	-3.976219
H	2.813106	-0.845993	-5.460089
H	-0.561360	-0.167629	-1.789823
H	-1.899105	-0.255649	-3.834370
H	-0.488778	-1.040203	-4.748924
H	2.942814	-1.645698	-1.566826
C	0.319571	-1.812469	0.544210
C	-0.206603	-1.059000	1.522913
C	-1.223323	-1.444115	2.520006
O	-1.693066	-2.555695	2.660566
O	-1.567221	-0.380994	3.290153
C	-2.554120	-0.641478	4.306084
H	-2.697622	0.309669	4.819361
H	-2.192777	-1.406492	4.998493
H	-3.487456	-0.980103	3.848653
C	-0.029113	-3.185989	0.095172
O	-1.093125	-3.502188	-0.388944
O	1.023920	-4.015423	0.242265
C	0.819033	-5.371665	-0.206230
H	1.758480	-5.885557	-0.002196
H	0.592548	-5.383769	-1.275483
H	-0.003381	-5.830392	0.348222
H	0.123109	1.143408	1.897567

30-c

C	0.104457	-0.182401	0.169859
C	0.073638	0.001009	1.706224
C	1.418960	0.106233	2.091901
C	2.192849	0.013799	0.772226
O	1.363217	-0.923716	0.055604
C	-0.946787	0.073891	2.635493
C	-0.592719	0.238066	3.990389
C	0.744424	0.336651	4.374029
C	1.777296	0.277186	3.415794
C	1.880226	1.312163	-0.003834
C	0.595726	1.203640	-0.377490
H	3.230218	-0.311414	0.803116
H	2.818422	0.358344	3.718873
H	0.995107	0.459762	5.424529
H	-1.374068	0.287441	4.744368
H	-1.991990	0.006937	2.344566
C	2.745820	2.496710	-0.121615
O	2.423955	3.562022	-0.613093
O	3.973437	2.255117	0.404273
C	4.901233	3.354741	0.353561
H	4.505704	4.210926	0.906590
H	5.815120	2.982907	0.817712
H	5.084821	3.648309	-0.683388
C	-0.285395	2.208880	-1.036499
O	-0.298646	2.450437	-2.223570
O	-1.105374	2.777384	-0.131445
C	-2.022780	3.763988	-0.648095
H	-2.580577	4.116970	0.219408
H	-2.693088	3.309556	-1.382462
H	-1.468532	4.582555	-1.113796
C	-1.077538	-0.856428	-0.434080
H	-1.829913	-1.212699	0.264103
C	-1.349657	-1.047053	-1.742984
O	-2.612834	-1.520795	-2.028702
C	-2.734894	-2.505623	-3.059634
H	-2.166339	-3.408203	-2.802620
H	-3.798957	-2.744216	-3.112006
H	-2.397215	-2.128086	-4.031121
C	-0.504217	-0.716738	-2.905549
C	0.785679	-1.046325	-3.045668
H	-1.009841	-0.168950	-3.700701
H	1.338244	-0.743158	-3.931419
H	1.322605	-1.599521	-2.282322

TS31

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	2.000927
C	1.563391	0.000000	-0.185717
C	2.305480	-1.071677	0.535207
C	1.946574	-1.543873	1.780063
C	0.757995	-1.128129	2.417731
H	0.279872	-1.792749	3.130521
O	2.724883	-2.560200	2.278330
C	2.413213	-3.109499	3.552354
H	1.490679	-3.704448	3.522675
H	3.249949	-3.764179	3.803328
H	2.319510	-2.324033	4.313664
H	3.123791	-1.575262	0.028088
H	1.760074	-0.073908	-1.260974
H	1.910341	0.981804	0.143886
O	0.573638	1.299497	1.942632
C	-0.485776	2.016527	1.278325
C	-0.658962	1.263770	-0.051140
C	-1.631563	1.653144	-1.059135
O	-1.860262	1.046039	-2.097056
O	-2.224675	2.846218	-0.757775
C	-3.164048	3.333260	-1.729482
H	-3.990232	2.626830	-1.848992
H	-3.524433	4.284040	-1.334087
H	-2.674155	3.479402	-2.696414
C	-0.731786	-1.173445	-0.600554
O	-1.840428	-1.523584	-0.246653
O	-0.002347	-1.834947	-1.524311
C	-0.656218	-2.956002	-2.145954
H	-0.905490	-3.714200	-1.398520
H	0.062995	-3.346046	-2.866991
H	-1.569332	-2.625413	-2.647740
H	-0.253488	3.079713	1.244599
C	-1.704595	1.564381	2.070193
C	-1.392140	0.253633	2.466745
C	-2.319168	-0.525173	3.149761
C	-3.559485	0.047810	3.460178
C	-3.865904	1.357204	3.068094
C	-2.943099	2.128025	2.346345
H	-3.192161	3.132255	2.016570
H	-4.834817	1.779501	3.321910
H	-4.296138	-0.534210	4.007669
H	-2.101967	-1.550871	3.435880

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d) Model Reaction IV.

1-OMe-C

C	3.390009	-0.381109	1.079070
C	2.336747	-0.084798	0.015559
C	2.307456	-1.057141	-0.912077
C	3.301837	-2.156063	-0.626468
C	4.224440	-1.522981	0.448306
C	1.476309	1.105547	0.086810
O	2.126833	2.309594	0.323799
C	3.166494	2.658672	-0.591912
C	0.120404	1.182325	0.050219
C	-0.897324	0.171429	0.032207
C	-2.287771	0.304884	0.020057
C	-2.835425	-1.037663	0.030875
C	-1.750079	-1.885959	0.048708
O	-0.597826	-1.160766	0.048803
C	-3.163668	1.427688	0.005642
C	-4.518907	1.205550	-0.000243
C	-5.061522	-0.125043	0.007945
C	-4.251656	-1.231299	0.023480
H	-5.204046	2.049184	-0.011351
H	-6.141676	-0.247459	0.002499
H	-4.671148	-2.233969	0.030690
H	-2.767677	2.439907	-0.001102
H	-1.631624	-2.958548	0.062509
H	-0.280166	2.192494	0.097910
H	1.617183	-1.086637	-1.750224
H	3.851379	-2.480595	-1.519552
H	2.781859	-3.048865	-0.242725
H	4.575736	-2.249160	1.188785
H	5.111488	-1.100825	-0.040127
H	3.994937	0.493208	1.345319
H	2.889802	-0.703153	2.005290
H	3.582865	3.600939	-0.228732
H	3.955923	1.898233	-0.627017
H	2.759054	2.800381	-1.602060

1-OMe-C'

C	1.818196	-1.892593	-0.440607
O	0.649083	-1.198065	-0.484546
C	0.892416	0.124339	-0.239725
C	2.267331	0.282246	-0.042243
C	2.861361	-1.033066	-0.170387
C	4.272467	-1.197595	-0.015952

C	5.032986	-0.088224	0.251919
C	4.443807	1.215522	0.380046
C	3.090757	1.408222	0.240488
H	2.657488	2.399552	0.345096
H	5.090345	2.062531	0.593916
H	6.108693	-0.188368	0.372273
H	4.726984	-2.180295	-0.110593
H	1.744315	-2.953046	-0.626959
C	-0.149345	1.106332	-0.269670
H	0.234547	2.121984	-0.339138
C	-1.510295	1.025746	-0.293990
O	-2.149130	2.234607	-0.567617
C	-2.828838	2.843637	0.532970
H	-2.112886	3.128824	1.316208
H	-3.588351	2.177380	0.958732
H	-3.309684	3.740572	0.135082
C	-2.404036	-0.119821	-0.120024
C	-3.672201	-0.156545	-0.588200
H	-4.118029	0.621682	-1.200508
C	-4.389914	-1.427443	-0.210518
H	-4.441994	-2.113853	-1.071858
H	-5.426604	-1.256172	0.108134
C	-3.496467	-1.995537	0.919334
H	-3.491754	-3.090452	0.954549
H	-3.868411	-1.636838	1.887516
C	-2.093482	-1.400444	0.648678
H	-1.489746	-2.077769	0.035155
H	-1.523007	-1.216725	1.566985

TS32

C	-0.839298	0.290044	-0.886955
C	-1.974817	-0.794708	0.581305
C	-1.080039	1.658811	-0.580343
C	-2.257930	2.439549	-0.529752
C	-2.151770	3.757134	-0.128442
C	-0.900320	4.327044	0.244825
C	0.258681	3.578647	0.209940
C	0.176207	2.232550	-0.217798
C	1.150098	1.217450	-0.392704
O	0.544411	0.109909	-0.847517
C	2.556264	1.312839	-0.186318
C	3.546469	0.367098	-0.294943
C	3.414531	-1.083873	-0.448504
C	4.354258	-1.905426	-1.322873
C	4.044887	-3.365043	-0.901523
C	2.649905	-3.312991	-0.225242

C	2.500588	-1.863542	0.157771
H	1.722673	-1.500239	0.820917
H	2.567194	-3.989873	0.634613
H	1.843268	-3.599684	-0.919007
H	4.790386	-3.697182	-0.169026
H	4.082139	-4.063594	-1.743720
H	5.406429	-1.639842	-1.181036
H	4.123942	-1.729816	-2.385127
O	4.865271	0.712411	-0.252215
C	5.254966	2.079144	-0.165262
H	4.944132	2.519344	0.790413
H	6.344399	2.076066	-0.225764
H	4.837467	2.660860	-0.996413
H	2.859728	2.325931	0.052587
H	-1.291410	-0.294277	-1.674489
H	-3.220121	2.007536	-0.789709
H	-3.043365	4.377766	-0.088500
H	-0.866159	5.364193	0.567052
H	1.208209	4.014577	0.509613
C	-1.194432	-0.738289	1.822759
O	-0.072253	-0.277395	1.941334
O	-1.883857	-1.273542	2.853283
C	-1.204514	-1.274808	4.121977
H	-0.962450	-0.253280	4.427845
H	-0.284093	-1.862563	4.063656
H	-1.908413	-1.730382	4.819178
C	-3.069956	-1.224396	0.145985
C	-4.038238	-1.513274	-0.855235
O	-4.006762	-2.487287	-1.598058
O	-5.036949	-0.582555	-0.882122
C	-6.089902	-0.838845	-1.827040
H	-5.698536	-0.855141	-2.848357
H	-6.795486	-0.016749	-1.699239
H	-6.572617	-1.796681	-1.612903

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C	-1.756340	-0.789798	0.466406
C	-1.136668	0.241826	-0.507409
C	-1.311009	1.683621	-0.160301
C	-2.477994	2.415095	0.054828
C	-2.351442	3.763519	0.390576
C	-1.086262	4.372606	0.522399
C	0.077573	3.641431	0.316583
C	-0.049715	2.287865	-0.034626
C	0.933973	1.260734	-0.294976
C	2.332608	1.434314	-0.275928

C	3.338677	0.492492	-0.457730
C	3.242455	-0.957342	-0.381557
C	2.404044	-1.638573	0.428070
C	2.558121	-3.124731	0.274205
C	3.876816	-3.278644	-0.528194
C	4.126880	-1.897734	-1.190668
H	3.813429	-1.888119	-2.245142
H	5.182258	-1.609054	-1.172773
H	4.698048	-3.507327	0.161113
H	3.831467	-4.090351	-1.260498
H	2.575699	-3.648314	1.238043
H	1.686533	-3.520910	-0.270689
H	1.682820	-1.184902	1.100609
O	4.604372	0.876944	-0.716549
C	4.940697	2.254272	-0.910282
H	4.830040	2.817110	0.023250
H	5.987969	2.253106	-1.213698
H	4.321261	2.698284	-1.697028
H	2.631593	2.468361	-0.153913
H	1.051254	4.109095	0.434981
H	-1.023861	5.422295	0.795139
H	-3.245300	4.357883	0.560798
H	-3.451942	1.941064	-0.029917
H	-1.492036	-0.003258	-1.510387
O	0.341905	0.128633	-0.612501
C	-1.163014	-0.791246	1.820314
O	-0.211412	-0.083300	2.154747
O	-1.746981	-1.647945	2.680146
C	-1.203913	-1.675180	4.005712
H	-1.278627	-0.690295	4.476616
H	-0.153846	-1.984015	3.992035
H	-1.808072	-2.405126	4.546634
C	-2.793782	-1.554922	0.106506
C	-3.390391	-1.633451	-1.183906
O	-3.040097	-2.383290	-2.098717
O	-4.500535	-0.816794	-1.305711
C	-5.274309	-1.005905	-2.496643
H	-4.686678	-0.780446	-3.392505
H	-6.115047	-0.314007	-2.410340
H	-5.636995	-2.036545	-2.563919

TS34

C	0.326089	1.837587	-0.486137
C	-0.215709	-1.213155	0.100843
C	2.064041	-0.875967	-1.231328
O	-0.020253	1.010893	-1.492707

C	1.621662	2.090371	-0.087446
H	1.697284	2.952663	0.565490
C	2.803741	1.316349	-0.211570
C	2.967517	-0.034385	-0.596581
C	4.234056	-0.806925	-0.232941
C	4.122255	-2.115084	-1.050497
C	2.616390	-2.264058	-1.377293
H	2.426411	-2.669036	-2.379690
H	2.099529	-2.941445	-0.681082
H	4.522755	-2.980360	-0.512632
H	4.695172	-2.015666	-1.980986
H	4.250869	-1.004079	0.849489
H	5.145259	-0.244867	-0.458873
H	1.220947	-0.531094	-1.798115
H	-1.828370	0.426775	-2.272793
C	-1.378642	0.558387	-1.288225
C	-1.966203	1.675533	-0.461036
C	-3.278303	1.984579	-0.109786
C	-0.893668	2.418007	0.061307
C	-1.109484	3.473072	0.955439
H	-0.280945	4.040603	1.370880
C	-2.423583	3.792305	1.291813
H	-2.621381	4.617463	1.970443
C	-3.496810	3.057251	0.760251
H	-4.513986	3.325305	1.033639
H	-4.108647	1.407529	-0.502020
C	-1.328466	-0.781891	-0.485401
C	-2.620083	-1.520376	-0.394570
O	-2.853083	-2.478887	0.312871
O	-3.559849	-1.006374	-1.250845
C	-4.824050	-1.691867	-1.265119
H	-5.434340	-1.163399	-1.999407
H	-5.289734	-1.656982	-0.276144
H	-4.687325	-2.736092	-1.558605
C	-0.010562	-2.384160	0.910030
O	0.363254	-3.478448	0.490812
O	-0.143493	-2.116966	2.242148
C	0.058236	-3.234592	3.118196
H	-0.660389	-4.029581	2.898481
H	-0.101127	-2.843840	4.124935
H	1.073567	-3.631025	3.018535
O	3.965613	1.838223	0.278079
C	4.067632	3.201661	0.678706
H	3.529091	3.384911	1.616617
H	5.133137	3.373551	0.840379
H	3.698373	3.875291	-0.103330

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C	-3.769698	2.872581	1.015399
C	-4.443084	1.909111	0.253713
C	-3.735347	1.029745	-0.578752
C	-2.352770	1.151363	-0.644560
C	-1.678831	2.133217	0.102572
C	-2.377481	2.992473	0.950479
C	-1.283217	0.360425	-1.395463
O	-0.190725	1.299254	-1.418944
C	-0.254360	1.988766	-0.217192
C	0.848777	2.214902	0.519203
C	2.185781	1.672248	0.288829
C	2.564297	0.514549	-0.304850
C	1.715603	-0.549432	-1.028546
C	2.756529	-1.633555	-1.442238
C	4.060446	-0.848131	-1.618898
C	4.029952	0.133543	-0.435909
C	-0.810718	-0.870956	-0.595080
C	0.483692	-1.168269	-0.349513
C	-1.893411	-1.722111	-0.005256
O	-1.945546	-2.128682	1.136537
O	-2.841687	-1.989415	-0.935593
C	-3.933709	-2.819037	-0.491641
C	0.786507	-2.344143	0.552762
O	0.602643	-3.507966	0.260081
O	1.357820	-1.931790	1.697198
C	1.680351	-2.966221	2.648397
O	3.198953	2.399997	0.919112
C	3.365318	3.739758	0.458635
H	-4.336591	3.542880	1.656164
H	-5.526464	1.841814	0.307865
H	-4.259449	0.275893	-1.158018
H	-1.859867	3.750395	1.532531
H	-1.545653	0.115136	-2.428305
H	0.729917	2.804507	1.425790
H	1.356775	-0.086306	-1.949859
H	2.435349	-2.176676	-2.337480
H	2.894740	-2.377201	-0.648867
H	4.946115	-1.493418	-1.620286
H	4.049993	-0.295392	-2.568329
H	4.676658	1.005282	-0.567751
H	4.372273	-0.373198	0.480354
H	-4.466706	-2.335884	0.331824
H	-3.556970	-3.789832	-0.160374
H	-4.581591	-2.932989	-1.361375

H	2.128045	-2.446150	3.495423
H	2.385547	-3.679342	2.212824
H	0.769978	-3.490028	2.950550
H	4.154297	4.179638	1.073558
H	3.668723	3.756144	-0.597772
H	2.445460	4.328584	0.571863

TS36

C	0.869414	0.350580	1.492046
C	-0.252259	-0.821868	-1.075724
C	1.682137	0.996599	0.800881
C	1.458887	0.589775	-1.289746
H	1.820453	1.512167	-1.718058
O	0.084675	0.465543	-1.300886
C	0.923979	-1.615671	-1.172239
C	2.010286	-0.713940	-1.383682
C	3.325382	-1.205565	-1.538875
H	4.156680	-0.522623	-1.684946
C	3.521795	-2.572537	-1.495044
H	4.522684	-2.975717	-1.626376
C	2.440815	-3.472840	-1.275498
H	2.640737	-4.540350	-1.240179
C	1.151143	-3.010157	-1.105936
H	0.333121	-3.704471	-0.932575
C	2.775331	1.965559	0.953191
O	2.921157	2.678462	1.925508
O	3.622913	1.979707	-0.106638
C	4.735412	2.886681	0.008931
H	4.379507	3.914627	0.117341
H	5.350508	2.625267	0.874044
H	5.300718	2.768941	-0.916276
C	-0.128434	-0.361417	2.200768
O	0.354659	-1.520986	2.733636
O	-1.289050	0.011085	2.342703
C	-0.567153	-2.253842	3.554030
H	-0.015106	-3.133211	3.889093
H	-0.884158	-1.651386	4.410595
H	-1.450185	-2.550667	2.980681
C	-1.593724	-1.260889	-0.872190
H	-1.653829	-2.340735	-0.794900
C	-2.747550	-0.550152	-0.658308
O	-3.910836	-1.167909	-0.311092
C	-3.940896	-2.567056	-0.054775
H	-3.715777	-3.142716	-0.961647
H	-4.960813	-2.782763	0.267632
H	-3.235803	-2.833548	0.742005

C	-2.962488	0.899075	-0.740694
C	-3.752334	1.657511	0.317675
H	-3.151279	1.719348	1.234961
H	-4.688964	1.156783	0.582621
C	-3.982191	3.044218	-0.336121
H	-3.919092	3.864072	0.386706
H	-4.983562	3.078262	-0.782354
C	-2.917519	3.155990	-1.459456
H	-2.036864	3.732765	-1.133942
H	-3.298131	3.656507	-2.359262
C	-2.525275	1.721450	-1.709317
H	-1.927544	1.413198	-2.560528

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C	1.356493	0.965454	-0.377896
C	1.678603	0.022905	-1.557947
C	0.400161	0.340357	0.328172
C	0.128039	-1.011290	-0.421449
O	0.378478	-0.554915	-1.792223
C	2.407466	-1.183043	-0.955606
C	1.418573	-1.838535	-0.206120
C	1.707409	-2.977673	0.521565
H	0.950971	-3.484679	1.115074
C	3.026512	-3.473093	0.472341
H	3.279869	-4.373206	1.026500
C	4.007675	-2.824560	-0.277104
H	5.017548	-3.225829	-0.303293
C	3.706087	-1.654051	-1.003436
H	4.474947	-1.149763	-1.583911
C	2.100582	2.180539	-0.003875
O	1.956701	2.812644	1.025067
O	2.997421	2.512898	-0.967138
C	3.794349	3.681879	-0.700663
H	3.153362	4.560575	-0.590327
H	4.377398	3.543292	0.213762
H	4.449788	3.787535	-1.565586
C	-0.198482	0.718679	1.637491
O	-0.988515	1.622164	1.807715
O	0.225883	-0.116240	2.605402
C	-0.296593	0.134118	3.926829
H	-0.029495	1.142947	4.250976
H	-1.384046	0.022599	3.930581
H	0.171091	-0.615493	4.565234
C	-1.155165	-1.745697	-0.243636
H	-1.063881	-2.813571	-0.065060
C	-2.416014	-1.263026	-0.280425

C	-4.460946	-2.336026	-0.894068
O	-3.408555	-2.167795	0.059483
H	-4.069322	-2.773041	-1.822015
H	-5.173615	-3.025171	-0.435947
H	-4.961791	-1.388811	-1.125241
C	-2.864993	0.112466	-0.551108
C	-3.892178	0.819688	0.327553
H	-3.425822	1.074923	1.288660
H	-4.770983	0.205072	0.553438
C	-4.240692	2.090643	-0.486693
H	-4.428433	2.959264	0.152458
H	-5.149439	1.913642	-1.076103
C	-3.039819	2.299791	-1.444999
H	-3.338209	2.689671	-2.426768
H	-2.312016	3.014557	-1.030295
C	-2.415154	0.929478	-1.521179
H	-1.655241	0.656091	-2.245191
H	2.084532	0.475324	-2.459866

TS38

C	0.145584	-0.661652	-0.114292
C	0.132049	1.318141	-0.612601
C	1.384149	-1.039878	-1.018992
C	2.630874	-0.243929	-0.790464
C	2.624814	1.116592	-0.531346
C	1.428682	1.826944	-0.317796
C	3.844047	-1.128982	-0.794619
C	3.293613	-2.530669	-0.443327
C	1.829965	-2.537182	-0.941473
H	1.176344	-3.128641	-0.294764
H	1.766155	-2.974812	-1.945704
H	3.318232	-2.670055	0.641202
H	3.889147	-3.332396	-0.893643
H	4.626288	-0.777611	-0.113143
H	4.292520	-1.129570	-1.802985
O	3.860100	1.688667	-0.332556
C	3.939832	3.075871	-0.032707
H	3.558729	3.295702	0.973499
H	3.391704	3.675073	-0.771460
H	5.001820	3.325782	-0.073444
H	1.026149	-0.831463	-2.028204
H	1.458842	2.739051	0.270666
O	-0.235432	0.920059	-1.922986
C	-1.499230	0.277407	-1.661291
C	-2.175678	1.292429	-0.752681
C	-1.115956	1.898574	-0.055971

C	-1.362021	2.831557	0.946312
C	-2.692858	3.176433	1.213164
C	-3.746380	2.574730	0.512259
C	-3.498693	1.604722	-0.469105
H	-1.985500	0.018591	-2.600501
H	-0.553135	3.286005	1.512534
H	-2.911704	3.916329	1.978568
H	-4.770885	2.859789	0.737495
H	-4.316888	1.115403	-0.988763
C	-1.147255	-0.860611	-0.686199
C	-2.125747	-1.823709	-0.214389
O	-3.352851	-1.628376	-0.786802
O	-1.893560	-2.761629	0.537627
C	-4.363872	-2.579899	-0.420707
H	-4.544789	-2.549412	0.657412
H	-4.060223	-3.591767	-0.704475
H	-5.258147	-2.279803	-0.969185
C	0.250655	-0.817460	1.372447
O	-0.599160	-0.429991	2.152054
O	1.432037	-1.340253	1.780415
C	1.598895	-1.452414	3.204506
H	1.547932	-0.466279	3.674317
H	2.585073	-1.896611	3.347165
H	0.820460	-2.093219	3.627027

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e) Vinyl Shift reaction of 19 to 21.

19-t

C	-0.019207	0.041556	0.010444
O	0.007308	0.140881	1.464848
C	1.438143	0.152843	1.626460
C	1.805902	1.327750	0.719902
C	0.890768	1.251015	-0.344747
C	0.996688	2.115170	-1.422248
C	2.007406	3.097058	-1.392723
C	2.894077	3.185043	-0.320736
C	2.808197	2.279255	0.754515
C	0.929021	-1.201969	-0.160221
C	0.835613	-2.180061	-1.274474
O	0.703131	-3.376105	-1.142064
O	0.869374	-1.542482	-2.465764
C	0.774903	-2.390559	-3.628575
H	0.837078	-1.715263	-4.482186
H	-0.175966	-2.929980	-3.626840

H	1.600100	-3.106972	-3.639744
C	1.818477	-1.124576	0.843522
C	3.027188	-1.943761	1.062481
O	3.483362	-2.760114	0.287424
O	3.592207	-1.650311	2.261121
C	4.786507	-2.387499	2.583418
H	4.570765	-3.458473	2.622539
H	5.097313	-2.019647	3.561588
H	5.560493	-2.201969	1.833918
H	1.724013	0.195681	2.674856
H	3.512800	2.331337	1.581088
H	3.663760	3.952498	-0.317688
H	2.094606	3.794116	-2.222188
H	0.332294	2.052585	-2.277060
C	-1.428467	-0.054958	-0.503913
C	-2.029994	0.945286	-1.473889
C	-3.544278	0.641993	-1.413294
C	-3.642369	-0.805969	-0.887629
C	-2.321643	-1.020929	-0.166536
C	-2.105216	-2.151337	0.729828
C	-3.009610	-3.116870	0.970865
H	-1.805524	1.983170	-1.203286
H	-1.630979	0.791606	-2.489431
H	-4.043828	0.782016	-2.377726
H	-4.019508	1.322125	-0.696429
H	-3.744885	-1.534688	-1.706520
H	-4.506572	-0.953121	-0.229292
H	-1.143516	-2.203336	1.231553
H	-2.781471	-3.939511	1.642497
H	-3.993057	-3.126730	0.508040

19-c

C	0.040784	-0.000885	0.025560
C	-0.014845	0.060772	1.580896
C	1.331975	0.069473	1.984524
C	2.121945	0.059533	0.675493
O	1.270230	-0.774000	-0.131278
C	-1.026430	0.161382	2.521702
C	-0.667987	0.223526	3.883394
C	0.668909	0.206896	4.277499
C	1.696264	0.141432	3.315999
C	0.590505	1.413373	-0.381632
C	1.871165	1.438542	0.023628
C	2.799922	2.585018	0.062275
O	2.511842	3.745531	-0.150803
O	4.051131	2.173530	0.394160

C	5.047375	3.210171	0.468396
H	5.149141	3.707386	-0.499850
H	5.972709	2.702203	0.741561
H	4.771173	3.948647	1.225899
C	-0.237403	2.507307	-0.954516
O	-1.335549	2.705755	-0.188633
C	-2.219548	3.756048	-0.627798
O	0.004558	3.121011	-1.969058
H	-2.624826	3.522496	-1.616114
H	-3.014397	3.793242	0.117570
H	-1.682922	4.707176	-0.670682
H	3.146204	-0.305753	0.689564
H	2.740620	0.148977	3.618895
H	0.921788	0.252625	5.333602
H	-1.450202	0.286930	4.635542
H	-2.072816	0.194500	2.239276
C	-1.092922	-0.601897	-0.755854
C	-2.274306	-1.285403	-0.081903
C	-2.965393	-2.037168	-1.238792
C	-2.549262	-1.261234	-2.503895
C	-1.229508	-0.612702	-2.103794
C	-0.368120	-0.075828	-3.165629
C	0.958515	-0.230128	-3.283280
H	-1.970671	-1.952344	0.733114
H	-2.953059	-0.538755	0.359047
H	-2.570902	-3.058975	-1.295031
H	-4.051131	-2.108779	-1.113205
H	-2.445051	-1.904511	-3.385899
H	-3.282877	-0.482077	-2.768171
H	1.538397	-0.772359	-2.543938
H	1.489734	0.194674	-4.131138
H	-0.901997	0.445022	-3.963524

TS20

C	0.925239	0.624992	-0.647887
C	0.085994	-1.182653	-0.317961
C	1.000250	-2.030658	-1.267382
C	2.468803	-1.888705	-1.040088
C	3.059196	-0.701076	-0.698579
C	2.324470	0.474309	-0.393660
C	3.209466	1.446323	0.361121
C	4.632099	1.016240	-0.069507
C	4.521629	-0.503826	-0.322487
H	5.392168	1.272534	0.675589
H	4.895711	1.529442	-1.002471
H	2.991988	2.494639	0.129770

H	3.089689	1.324285	1.450246
H	5.207385	-0.853211	-1.102429
H	4.753965	-1.073215	0.588628
H	3.074324	-2.792410	-1.065948
H	0.704132	-3.077770	-1.135056
H	0.750799	-1.743063	-2.291224
O	0.444445	0.518638	-1.985737
C	-0.974479	0.474241	-1.754564
H	-1.508014	0.509259	-2.703126
C	-1.169254	-0.757336	-0.855045
C	-2.472851	-1.212558	-0.413214
O	-2.686711	-2.145623	0.351182
C	-4.813887	-0.950652	-0.698601
H	-4.953702	-2.000828	-0.970543
O	-3.483845	-0.518658	-1.023018
H	-5.006295	-0.829886	0.371365
H	-5.478009	-0.311400	-1.282415
C	0.151856	-1.661063	1.103779
O	0.794705	-2.624942	1.479838
O	-0.522124	-0.845441	1.940596
C	-0.586538	-1.270384	3.311661
H	-1.104062	-2.231286	3.379504
H	0.417966	-1.366442	3.733381
H	-1.150449	-0.492938	3.828378
C	0.039436	1.660537	-0.043312
C	-1.161684	1.621783	-0.776438
C	-2.231545	2.452028	-0.469990
H	-3.162195	2.397401	-1.026935
C	-2.074658	3.364025	0.582983
H	-2.883776	4.047259	0.828137
C	-0.889653	3.398122	1.327934
H	-0.791987	4.103936	2.148834
C	0.174850	2.535770	1.032591
H	1.076173	2.565146	1.635298

21

C	0.004734	-0.002856	-0.010340
O	0.001112	-0.009276	1.376644
C	1.367062	-0.001713	1.819044
C	2.053412	0.774529	0.696353
C	1.190008	0.756113	-0.417864
C	1.573376	1.359349	-1.619472
C	2.806899	2.015731	-1.675915
C	3.649172	2.057360	-0.558846
C	3.279889	1.425434	0.637053
H	3.938840	1.449406	1.498310

H	4.598256	2.583679	-0.617704
H	3.109669	2.506640	-2.597229
H	0.925277	1.342925	-2.489332
H	1.406236	0.509122	2.785993
C	-0.869330	-0.779902	-0.687133
C	-1.653416	-1.894070	-0.130518
C	-2.640829	-2.344182	-1.216522
C	-2.592100	-1.235373	-2.283676
C	-1.157221	-0.676208	-2.175696
H	-0.460190	-1.304018	-2.753273
H	-1.079762	0.343673	-2.563962
H	-3.309015	-0.442652	-2.034043
H	-2.832264	-1.596564	-3.289493
H	-3.648719	-2.506927	-0.818400
H	-2.306134	-3.299184	-1.645671
C	-1.509432	-2.606935	1.011909
C	-0.579695	-2.436397	2.201904
C	0.938990	-2.506335	1.977122
C	1.809734	-1.474122	1.931780
H	-2.180134	-3.461129	1.108615
H	-0.800653	-3.251896	2.901552
H	-0.813127	-1.506880	2.722730
C	1.441745	-3.930555	2.013113
O	1.663769	-4.539651	3.040671
O	1.485070	-4.466902	0.784014
C	1.950182	-5.829198	0.710321
H	1.890355	-6.095347	-0.345215
H	1.315000	-6.483280	1.313585
H	2.981942	-5.885951	1.066614
C	3.269494	-1.760676	2.045141
O	3.841346	-2.758056	1.651249
O	3.904208	-0.762770	2.708848
C	5.315277	-0.956241	2.926420
H	5.643366	-0.080310	3.487220
H	5.840606	-1.025419	1.970026
H	5.486186	-1.869528	3.501707

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f) Pathway D of Model Reaction II (see page S13 for species labeling)

s-TS

C	-0.837951	-2.241579	-0.518888
C	1.948469	1.089849	-0.215873
C	2.628217	0.109558	0.183614
C	1.711909	-1.218451	1.337643

C	1.534627	-2.332807	0.516703
C	0.449005	-2.710919	-0.324579
H	0.690175	-3.549740	-0.975631
H	2.410734	-2.969585	0.411733
H	2.525166	-1.275122	2.056823
H	0.861300	-0.625768	1.639730
H	-1.376557	-2.745959	-1.319607
C	-1.657990	-1.265564	0.091713
C	0.812730	1.890232	-0.511381
O	0.101193	1.755413	-1.499866
C	4.031048	-0.346450	0.075358
O	4.481887	-1.375933	0.543813
O	4.773793	0.538022	-0.620194
C	6.161310	0.189950	-0.784012
H	6.256700	-0.757965	-1.320502
H	6.651700	0.106147	0.189681
H	6.590870	1.007168	-1.364062
O	0.620711	2.865681	0.423701
C	-0.495334	3.735408	0.178409
H	-0.389607	4.235732	-0.788269
H	-1.433198	3.170283	0.186989
H	-0.476634	4.462472	0.991623
H	-2.060982	0.891875	2.442833
C	-2.263392	0.275803	1.579395
O	-1.261452	-0.543321	1.189344
C	-2.974293	-0.877310	-0.221212
C	-3.357643	0.120177	0.749179
C	-3.892345	-1.271064	-1.228700
H	-3.619202	-2.014815	-1.972014
C	-5.136271	-0.682479	-1.249030
H	-5.852686	-0.967807	-2.014587
C	-5.516460	0.307402	-0.285169
H	-6.510740	0.741565	-0.346178
C	-4.654021	0.712991	0.702735
H	-4.945779	1.464151	1.431626

s-inter

C	0.012926	0.006752	-0.020536
C	0.001834	0.001569	1.356532
C	1.397977	0.003755	1.763992
O	1.294599	0.007488	-0.467401
C	2.142388	0.009577	0.599431
C	1.731034	-0.002024	3.154442
C	0.712489	-0.010051	4.071596
C	-0.668672	-0.010629	3.667292
C	-1.030113	-0.004351	2.345621

H	-2.076057	-0.003038	2.050088
H	-1.436128	-0.015066	4.436987
H	0.943928	-0.014976	5.133659
H	2.769626	0.000914	3.475898
H	-0.753101	0.015442	-0.780667
C	3.619622	0.005574	0.317846
C	4.048672	-1.263471	-0.386375
C	4.642422	-1.280408	-1.580639
C	4.984392	-0.042969	-2.359068
C	4.695078	1.238477	-1.610465
C	4.068087	1.264404	-0.419881
C	3.705574	2.548440	0.285762
O	2.732743	3.220916	0.023808
O	4.536911	2.777912	1.321760
C	4.282607	3.985446	2.068081
H	5.042643	4.005603	2.849671
H	3.279113	3.961505	2.500843
H	4.379156	4.853072	1.410561
C	5.150354	2.522910	-2.222071
O	5.233725	3.590389	-1.643358
O	5.488391	2.364983	-3.522981
C	5.943152	3.551314	-4.200063
H	6.163820	3.233797	-5.219608
H	6.839219	3.946218	-3.713802
H	5.161327	4.315215	-4.192113
H	4.096773	0.035075	1.310383
H	3.820332	-2.191818	0.133592
H	4.905920	-2.232478	-2.038581
H	6.045505	-0.066496	-2.646681
H	4.440937	-0.038113	-3.316084

s-TS-vs

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.609017
C	2.066865	0.000000	1.715525
O	2.123533	-0.684510	0.508557
C	1.468897	0.244844	-0.337553
C	2.004563	1.552719	0.049855
C	2.397545	1.388661	1.402440
C	2.880328	2.469859	2.146414
C	2.985828	3.705161	1.506906
C	2.577473	3.871891	0.168502
C	2.064838	2.803054	-0.568273
H	1.741767	2.937384	-1.596952
H	2.663730	4.851141	-0.294820
H	3.388584	4.556894	2.049005

H	3.174462	2.352629	3.185772
H	2.430026	-0.550485	2.578574
C	-0.497415	-1.293005	-0.595536
C	-0.558087	-2.439428	0.082079
C	-0.207925	-2.516336	1.551936
C	-0.473955	-1.189725	2.223085
H	-0.618206	0.843028	-0.322054
H	-0.762553	-1.254090	-1.650153
H	-0.877629	-3.357009	-0.408294
H	-0.781279	-3.305917	2.041364
H	0.853522	-2.797001	1.657869
C	-1.319804	-1.162148	3.431019
O	-1.992676	-0.216183	3.814478
O	-1.309302	-2.353514	4.091077
C	-2.150525	-2.428016	5.253606
H	-1.836385	-1.694151	6.001185
H	-3.193764	-2.240753	4.984164
H	-2.026257	-3.442411	5.634835
C	-0.435197	1.321884	2.200966
O	-1.128753	2.133510	1.620728
O	0.099491	1.529130	3.420334
C	-0.384610	2.688668	4.120297
H	-0.174560	3.596432	3.548755
H	0.150671	2.696846	5.070763
H	-1.460873	2.593894	4.285567

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g) TS6' and TS-8+2 (concerted [8+2] transition structure)

TS6'

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	2.428661
C	1.236772	0.000000	-0.152125
C	2.086407	0.032987	1.745405
O	1.124793	-0.766232	2.306170
C	0.424920	1.371877	2.499084
C	-0.235658	2.574049	2.817253
C	0.485988	3.756808	2.755825
C	1.847651	3.768962	2.362758
C	2.505141	2.595500	2.024347
C	1.791457	1.386800	2.109140
H	3.061537	-0.432492	1.668043
H	3.546566	2.610972	1.712482
H	2.381357	4.715206	2.330223
H	0.002278	4.694695	3.016302

H	-1.282198	2.581777	3.110849
H	2.080301	0.010207	-0.820389
H	-1.049069	-0.024732	-0.210457
C	-1.243375	-0.541297	2.915511
C	-1.713084	-1.807910	3.089359
C	-1.179889	-3.135504	2.793686
C	-0.151675	-3.499045	2.003132
H	-1.935197	0.249818	3.201519
H	-2.704749	-1.844773	3.539634
H	-1.756395	-3.937888	3.255913
H	0.074142	-4.552797	1.859725
H	0.472466	-2.782822	1.484073

TS-8+2

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	2.092198
C	1.078261	0.000000	-0.621713
H	-0.366153	1.010602	2.227808
H	-1.070482	-0.033169	-0.112239
C	3.255709	0.610595	0.537843
C	4.071839	-0.454274	0.839045
C	3.978519	-1.471592	1.830231
C	2.909596	-1.944768	2.578349
C	1.598077	-1.461712	2.658964
C	0.356806	-2.139325	2.822205
C	-0.665009	-1.202736	2.488814
C	-2.020326	-1.585243	2.510776
C	-2.331314	-2.883086	2.874168
C	-1.315052	-3.818791	3.197337
C	0.020517	-3.466144	3.163895
O	1.321599	-0.150020	2.402748
H	0.792527	-4.192809	3.400948
H	-1.597405	-4.831427	3.471702
H	-3.370742	-3.197011	2.914551
H	-2.804921	-0.875594	2.261094
H	3.060200	-2.902511	3.073249
H	4.868354	-2.095518	1.900753
H	4.929781	-0.592043	0.178457
H	3.527138	1.245191	-0.301550
H	2.551749	1.019781	1.240472
H	1.714385	-0.039067	-1.477776