Supplementary Materials

A computational study of site-selective hydrogen abstraction reaction with sulfate radical anion

Masahiro Ueda, Atsuki Kitano and Hiroshi Matsubara*

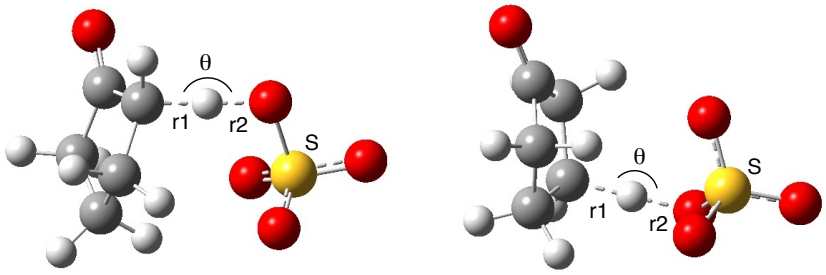
Department of Chemistry, Graduate School of Sciences, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

---

Complexation energies, energy barriers and important geometries for transition states involving cyclohexanone, energy barriers involving 2-propylpyridine, 3-methylbutanol, hydroxyl (•OH), methoxyl (•OMe), hydroperoxyl (•OOH), methylperoxyl (•OOMe), carbonate ($•OCO_2^-$) and potassium sulfate radical ($KOSO_3•$), full lists of references 9 and 10, and energies, imaginary frequencies and Cartesian coordinates for optimised geometries of all structures in this study.

Table of contents

Table S1 Optimised geometries of transition states **10a** and **10b** involved in the abstraction of α- and β-hydrogen in cyclopentanone (**1**) with SO_4 radical anion **5**



10a **10b**

Method	**10a**			**10b**		
	r1/Å	r2/Å	θ/°	r1/Å	r2/Å	θ/°
BHLYP/6-311+G(d,p)	1.260	1.262	174.6	1.245	1.267	177.5
B3LYP/6-311+G(d,p)	1.287	1.271	172.5	1.276	1.264	178.1
B3LYP-D3/6-311+G(d,p)	1.276	1.279	174.1	1.270	1.268	174.6
M06-2X/6-311+G(d,p)	1.220	1.335	174.2	1.208	1.340	173.7
ωB97XD/6-311+G(d,p)	1.252	1.287	174.6	1.238	1.294	175.2

Table S2 Energy barriers (in kJ mol^{-1}) and imaginary (ν) frequencies for abstraction of α- and β-hydrogen in cyclopentanone (**1**) with SO_4 radical anion **5**

Method	**10a**					**10b**				
	$\Delta E_{1a}^{\ddagger}$	$\Delta E_{1a}^{\ddagger}$ +ZPE	$\Delta E_{2a}^{\ddagger}$	$\Delta E_{2a}^{\ddagger}$ +ZPE	ν /cm^{-1}	$\Delta E_{1b}^{\ddagger}$	$\Delta E_{1b}^{\ddagger}$ +ZPE	$\Delta E_{2b}^{\ddagger}$	$\Delta E_{2b}^{\ddagger}$ +ZPE	ν /cm^{-1}
BHLYP/6-311+G(d,p)	67.5	53.9	123.0	111.4	2137i	63.2	49.8	86.8	78.8	1977i
B3LYP/6-311+G(d,p)	52.3	38.9	88.5	75.9	1626i	56.0	42.3	60.6	53.3	1544i
B3LYP-D3/6-311+G(d,p)	45.5	32.3	91.1	77.5	1545i	46.3	32.9	54.6	46.9	1510i
M06-2X/6-311+G(d,p)	45.1	33.6	122.0	108.4	1446i	40.3	28.3	79.8	71.1	1211i
ωB97XD/6-311+G(d,p)	54.6 (53.6)[a]	42.1	105.6 (95.8)[a]	92.0	1713i	50.9 (50.9)[a]	38.4	68.4 (70.8)[a]	60.7	1548i
QCISD/6-311+G(d,p)// ωB97XD/6-311+G(d,p)	63.1	–	117.8	–	–	60.2	–	85.8	–	–
CCSD(T)/6-311+G(d,p)// M06-2X/6-311+G(d,p)	55.9	–	106.3	–	–	54.1	–	73.1	–	–
CCSD(T)/6-311+G(d,p)// ωB97XD/6-311+G(d,p)	58.7	–	109.8	–	–	56.6	–	77.4	–	–

[a]Gibbs free energies ($\Delta G^{\ddagger}$, in kJ mol^{-1}).

Results of benchmark test are summarised in Table S2. At the BHLYP/6-311+G(d,p) level of theory, the $\Delta E_1^{\ddagger}$ values are calculated to be 67.5 and 63.2 kJ mol^{-1} for the reactions involving **10a** and **10b**, respectively. The inclusion of the zero-point vibrational energy (ZPE) correction serves to decrease these barriers by ~13 kJ mol^{-1}. B3LYP calculations yield 7–15 kJ mol^{-1} lower $\Delta E_1^{\ddagger}$ energy barriers than the BHLYP method. The addition of Grimme's

dispersion to the B3LYP functional (B3LYP-D3) decreases $\Delta E_1^{\ddagger}$ energy barriers by 7–10 kJ mol^{-1} while the M06-2X functional produces energy barriers similar to those from the B3LYP-D3 calculations. At the highest level of theory examined herein, i.e. (CCSD(T)/6-311+G(d,p)//ωB97XD/6-311+G(d,p)), the $\Delta E_1^{\ddagger}$ energy barriers are predicted to be 58.7 and 56.6 kJ mol^{-1} for the pathways involving **10a** and **10b**, respectively. In addition, the ωB97XD/6-311+G(d,p) method provides energy barriers of 54.6 and 50.9 kJ mol^{-1} for the processes involving **10a** and **10b**, respectively. Interestingly, CCSD(T) single-point calculations on the geometries which were optimised on the M06-2X level provide very similar energy barriers (~3 kJ mol^{-1}) to those on the structures optimised at the ωB97XD level.

Table S3 Complexation energies (in kJ mol^{-1}) for α- and β-hydrogen abstraction in cyclopentanone (**1**) with SO_4 radical anion **5**

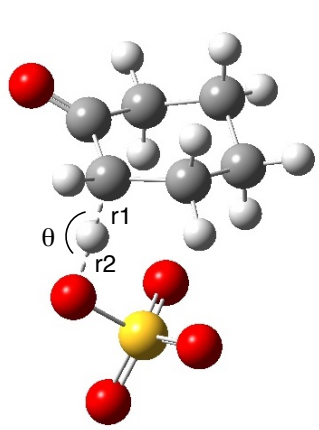
Method	ΔEcomp1	ΔEcomp1 +ZPE	ΔEcomp2a	ΔEcomp2a +ZPE	ΔEcomp2b	ΔEcomp2b +ZPE
BHLYP/6-311+G(d,p)	-40.7	-38.2	-43.7	-41.5	-44.1	-40.8
B3LYP/6-311+G(d,p)	-36.4	-33.9	-38.4	-34.4	-41.0	-37.7
B3LYP-D3/6-311+G(d,p)	-53.6	-50.7	-65.9	-60.1	-63.2	-58.6
M06-2X/6-311+G(d,p)	-50.3	-49.5	-70.4	-64.9	-65.0	-60.5
ωB97XD/6-311+G(d,p)	-49.6 (-11.1)[a]	-47.9	-60.2 (-10.4)[a]	-55.8	-59.2 (-13.5)[a]	-55.9
QCISD/6-311+G(d,p)//ωB97XD/ 6-311+G(d,p)	-48.2	--	-57.0	--	-57.6	--
CCSD(T)/6-311+G(d,p)//M06-2X/ 6-311+G(d,p)	-50.4	--	-60.0	--	-57.9	--
CCSD(T)/6-311+G(d,p)//ωB97XD/ 6-311+G(d,p)	-51.4	--	-61.9	--	-61.1	--

[a]Gibbs free energies (ΔG, in kJ mol^{-1}).

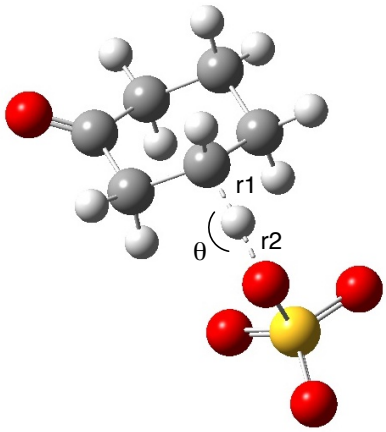
Table S4 Complexation energies (in kJ mol^{-1}) for α- and β-hydrogen abstraction in cyclopentanone (**1**) with SO_4 radical anion **5** in acetonitrile calculated by PCM method.

Method	ΔEcomp1	ΔEcomp2a	ΔEcomp2b
M06-2X/6-311+G(d,p)	-11.3	-27.0	-17.1
ωB97XD/6-311+G(d,p)	-9.2	-19.4	-11.9

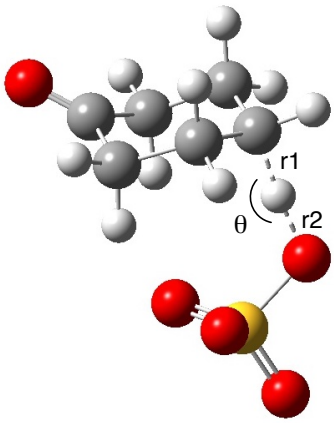
Table S5 Optimised geometries of transition states **14a**, **14b** and **14c** involved in the abstraction of α- β- and γ-hydrogen in cyclohexanone (**12**) with SO_4 radical anion **5**



14a



14b



14c

Method	**14a**			**14b**		
	r1/Å	r2/Å	θ/°	r1/Å	r2/Å	θ/°
M06-2X/6-311+G(d,p)	1.221	1.335	176.0	1.223	1.318	168.0
ωB97XD/6-311+G(d,p)	1.249	1.291	176.3	1.252	1.279	170.4

Method	**14c**		
	r1/Å	r2/Å	θ/°
M06-2X/6-311+G(d,p)	1.216	1.328	175.0
ωB97XD/6-311+G(d,p)	1.244	1.287	175.1

Table S6 Complexation energies (in kJ mol^{-1}) for α- β- and γ-hydrogen abstraction in cyclohexanone (**12**) with SO_4 radical anion **5**

Method	ΔEcomp1	ΔEcomp1 +ZPE	ΔEcomp2a	ΔEcomp2a +ZPE	ΔEcomp2b	ΔEcomp2b +ZPE
M06-2X/6-311+G(d,p)	-59.1	-56.3	-55.3	-53.1	-43.2	-40.5
In CH_3CN	-13.6	--	-10.3	--	-4.5	
ωB97XD/6-311+G(d,p)	-57.1	-53.9	-51.3	-48.9	-41.6	-39.6
In CH_3CN	-12.4	--	-7.6	--	-4.8	

Method	ΔEcomp2c	ΔEcomp2c +ZPE
M06-2X/6-311+G(d,p)	-55.0	-49.9
In CH_3CN	-7.6	--
ωB97XD/6-311+G(d,p)	-63.6	-59.3
In CH_3CN	-12.6	--

Table S7 Energy barriers (in kJ mol^{-1}) and imaginary (ν) frequencies for abstraction of α- β- and γ-hydrogen in cyclohexanone (**12**) with SO_4 radical anion **5**

Method	**14a**					**14b**				
	$\Delta E_{1a}^{\ddagger}$	$\Delta E_{1a}^{\ddagger}$ +ZPE	$\Delta E_{2a}^{\ddagger}$	$\Delta E_{2a}^{\ddagger}$ +ZPE	ν /cm^{-1}	$\Delta E_{1b}^{\ddagger}$	$\Delta E_{1b}^{\ddagger}$ +ZPE	$\Delta E_{2b}^{\ddagger}$	$\Delta E_{2b}^{\ddagger}$ +ZPE	ν /cm^{-1}
M06-2X/6-311+G(d,p)	45.3	32.5	103.1	92.3	1427i	50.7	37.8	61.8	53.6	1383i
In CH_3CN	24.6	--	107.0	--	--	19.1	--	57.3	--	--
ωB97XD/6-311+G(d,p)	54.0	40.7	90.8	80.5	1698i	62.0	48.5	53.0	46.9	1649i
In CH_3CN	30.7	--	91.9	--	--	27.9	--	46.5	--	--

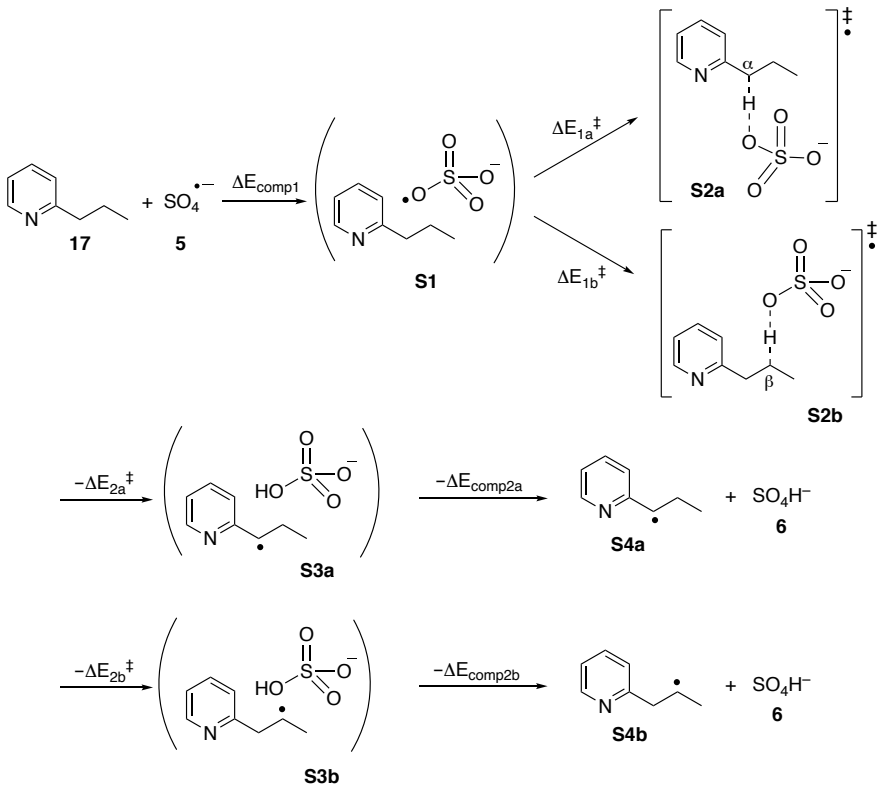
Method	**14c**				
	$\Delta E_{1a}^{\ddagger}$	$\Delta E_{1a}^{\ddagger}$ +ZPE	$\Delta E_{2a}^{\ddagger}$	$\Delta E_{2a}^{\ddagger}$ +ZPE	ν /cm^{-1}
M06-2X/6-311+G(d,p)	43.7	30.9	64.5	54.5	1254i
In CH_3CN	17.9	--	57.0	--	--
ωB97XD/6-311+G(d,p)	53.9	40.4	64.0	54.7	1598i
In CH_3CN	25.1	--	49.0	--	--

Table S8 Complexation energies (in kJ mol^{-1}) for α- and β-hydrogen abstraction in 2-propylpyridine (**17**) with SO_4 radical anion **5** (Scheme S1)

Method	ΔEcomp1	ΔEcomp1 +ZPE	ΔEcomp2a	ΔEcomp2a +ZPE	ΔE comp2b	ΔEcomp2b +ZPE
M06-2X/6-311+G(d,p)	-52.7	-49.8	-64.0	-60.3	-53.8	-51.7
In CH_3CN	-9.9	--	-14.6	--	-11.1	--
ωB97XD/6-311+G(d,p)	-51.5	-48.3	-58.8	-54.8	-54.2	-51.3
In CH_3CN	-12.6	--	-11.3	--	-9.7	--

Table S9 Energy barriers (in kJ mol^{-1}) and imaginary (ν) frequencies for abstraction of α- and β-hydrogen in 2-propylpyridine (**17**) with SO_4 radical anion **5** (Scheme S1)

Method	**S2a**					**S2b**				
	$\Delta E_{1a}^{\ddagger}$	$\Delta E_{1a}^{\ddagger}$ +ZPE	$\Delta E_{2a}^{\ddagger}$	$\Delta E_{2a}^{\ddagger}$ +ZPE	ν /cm^{-1}	$\Delta E_{1b}^{\ddagger}$	$\Delta E_{1b}^{\ddagger}$ +ZPE	$\Delta E_{2b}^{\ddagger}$	$\Delta E_{2b}^{\ddagger}$ +ZPE	ν /cm^{-1}
M06-2X/6-311+G(d,p)	47.1	35.3	123.4	112.7	1111i	42.9	30.9	69.4	62.8	1217i
In CH_3CN	16.4	--	108.5	--	--	14.2	--	62.4	--	--
ωB97XD/6-311+G(d,p)	55.9	43.0	110.6	100.0	1655i	53.2	40.2	60.9	54.5	1556i
In CH_3CN	26.0	--	94.3	--	--	24.7	--	48.1	--	--



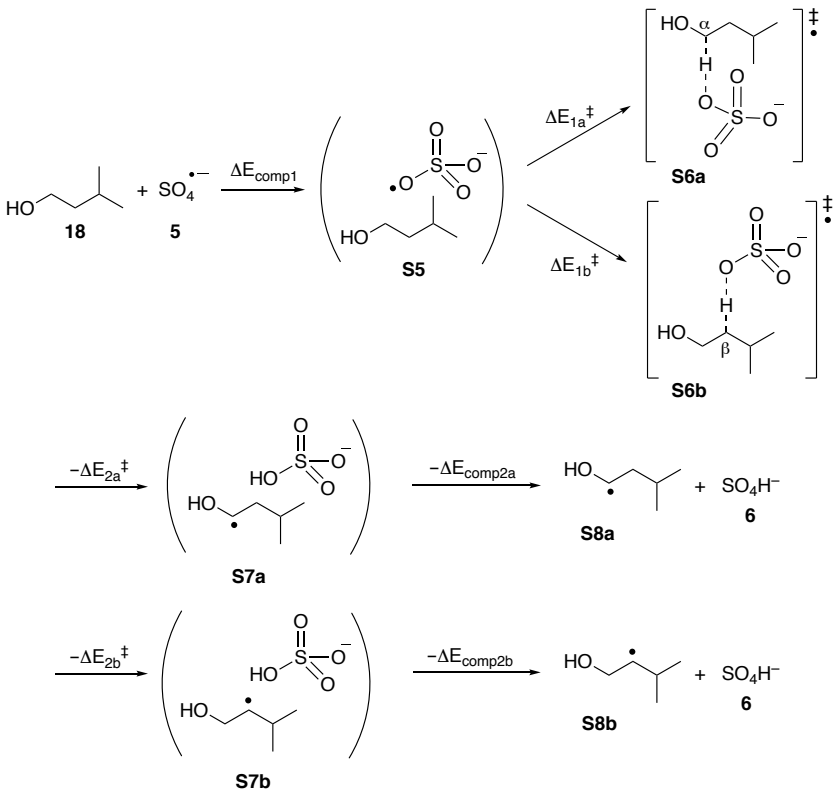
Scheme S1 Reaction pathway for the abstraction of α- and β- hydrogen in 2-propylpyridine (**17**) with SO_4 radical anion **5**.

Table S10 Complexation energies (in kJ mol^{-1}) for α- and β-hydrogen abstraction in 3-methylbutanol (**18**) with SO_4 radical anion **5** (Scheme S2)

Method	ΔEcomp1	ΔEcomp1 +ZPE	ΔEcomp2a	ΔEcomp2a +ZPE	ΔEcomp2b	ΔEcomp2b +ZPE
M06-2X/6-311+G(d,p)	-76.2	-69.5	-97.2	-90.3	-93.7	-86.7
In CH_3CN	-32.2	--	-45.5	--	-46.3	--
ωB97XD/6-311+G(d,p)	-69.9	-64.6	-89.2	-81.5	-81.9	-73.6
In CH_3CN	-27.0	--	-39.1	--	-33.0	--

Table S11 Energy barriers (in kJ mol^{-1}) and imaginary (ν) frequencies for abstraction of α- and β-hydrogen in 3-methylbutanol (**18**) with SO_4 radical anion **5** (Scheme S2)

Method	**S6a**					**S6b**				
	$\Delta E_{1a}^{\ddagger}$	$\Delta E_{1a}^{\ddagger}$ +ZPE	$\Delta E_{2a}^{\ddagger}$	$\Delta E_{2a}^{\ddagger}$ +ZPE	ν /cm^{-1}	$\Delta E_{1b}^{\ddagger}$	$\Delta E_{1b}^{\ddagger}$ +ZPE	$\Delta E_{2b}^{\ddagger}$	$\Delta E_{2b}^{\ddagger}$ +ZPE	ν /cm^{-1}
M06-2X/6-311+G(d,p)	27.7	19.0	93.6	85.7	750i	40.3	28.6	80.3	71.4	1048i
In CH_3CN	10.1	--	88.1	--	--	17.1	--	75.6	--	--
ωB97XD/6-311+G(d,p)	33.2	23.5	79.0	69.8	877i	48.9	36.5	62.6	53.1	1427i
In CH_3CN	11.5	--	69.5	--	--	22.8	--	52.0	--	--



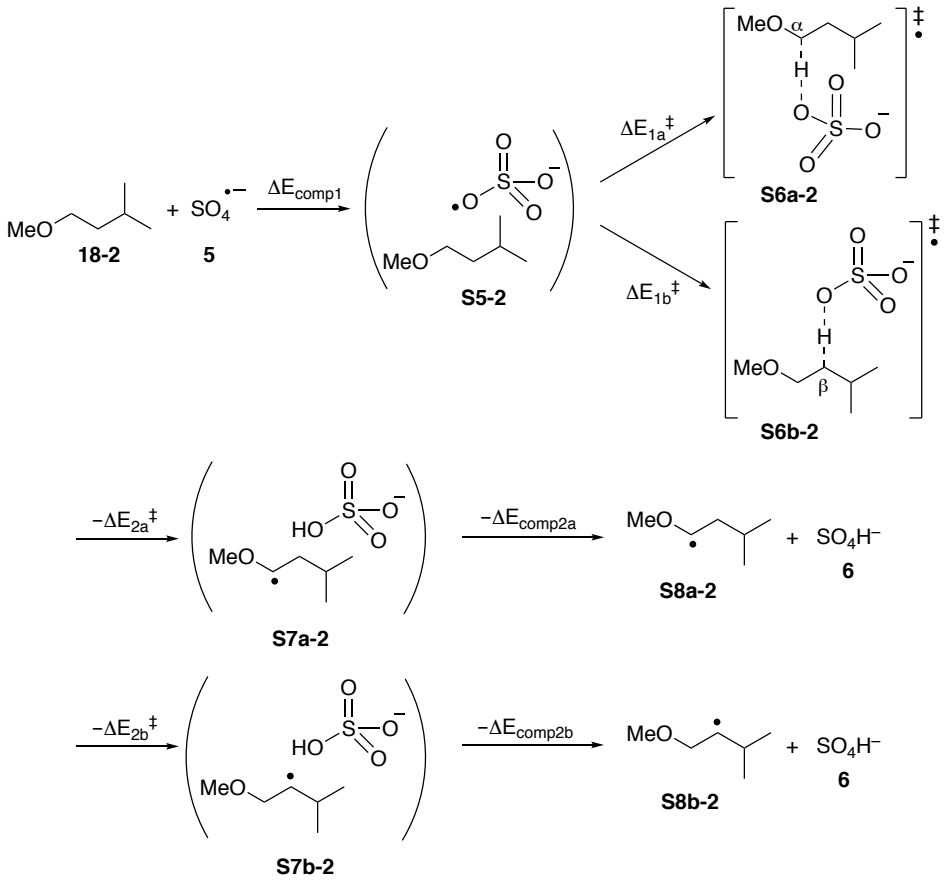
Scheme S2 Reaction pathway for the abstraction of α- and β- hydrogen in 3-methylbutanol (**18**) with SO_4 radical anion **5**.

Table S10-2 Complexation energies (in kJ mol^{-1}) for α- and β-hydrogen abstraction in 3-methyl-1-methoxybutane (**18-2**) with SO_4 radical anion **5** (Scheme S2-2)

Method	ΔEcomp1	ΔEcomp1 +ZPE	ΔEcomp2a	ΔEcomp2a +ZPE	ΔEcomp2b	ΔEcomp2b +ZPE
M06-2X/6-311+G(d,p)	-47.0	-44.0	-46.9	-43.7	-55.2	-49.8
In CH_3CN	-10.6		-8.6		-14.9	
ωB97XD/6-311+G(d,p)	-41.7	-38.4	-47.2	-43.3	-50.5	-45.2
In CH_3CN	-7.6		-8.9		-11.2	

Table S11-2 Energy barriers (in kJ mol^{-1}) and imaginary (ν) frequencies for abstraction of α- and β-hydrogen in 3-methyl-1-methoxybutane (**18-2**) with SO_4 radical anion **5** (Scheme S2-2)

Method	S6a-2					S6b-2				
	$\Delta E_{1a}^{\ddagger}$	$\Delta E_{1a}^{\ddagger}$ +ZPE	$\Delta E_{2a}^{\ddagger}$	$\Delta E_{2a}^{\ddagger}$ +ZPE	ν /cm^{-1}	$\Delta E_{1b}^{\ddagger}$	$\Delta E_{1b}^{\ddagger}$ +ZPE	$\Delta E_{2b}^{\ddagger}$	$\Delta E_{2b}^{\ddagger}$ +ZPE	ν /cm^{-1}
M06-2X/6-311+G(d,p)	39.7	29.5	83.6	74.7	906i	49.4	37.7	79.5	69.4	1266i
In CH_3CN	7.6		69.3		--	19.1		67.0		--
ωB97XD/6-311+G(d,p)	45.3	32.9	75.8	66.1	1196i	51.4	40.1	61.6	54.2	1612i
In CH_3CN	6.8		52.6		--	26.9		53.2		--



Scheme S2-2 Reaction pathway for the abstraction of α- and β- hydrogen in 3-methyl-1-methoxybutane (**18-2**) with SO_4 radical anion **5**.

Table S12 Calculated energy barriers in Gibbs energies (ΔG) at the ωB97XD/6-311+G(d,p) level including solvent effect (acetonitrile) and predicted product ratio for abstraction of α- and β-hydrogen in cyclopentanone (**1**) with sulfate radical anion (SO_4^{-}•, **5**) using the Eyring equation

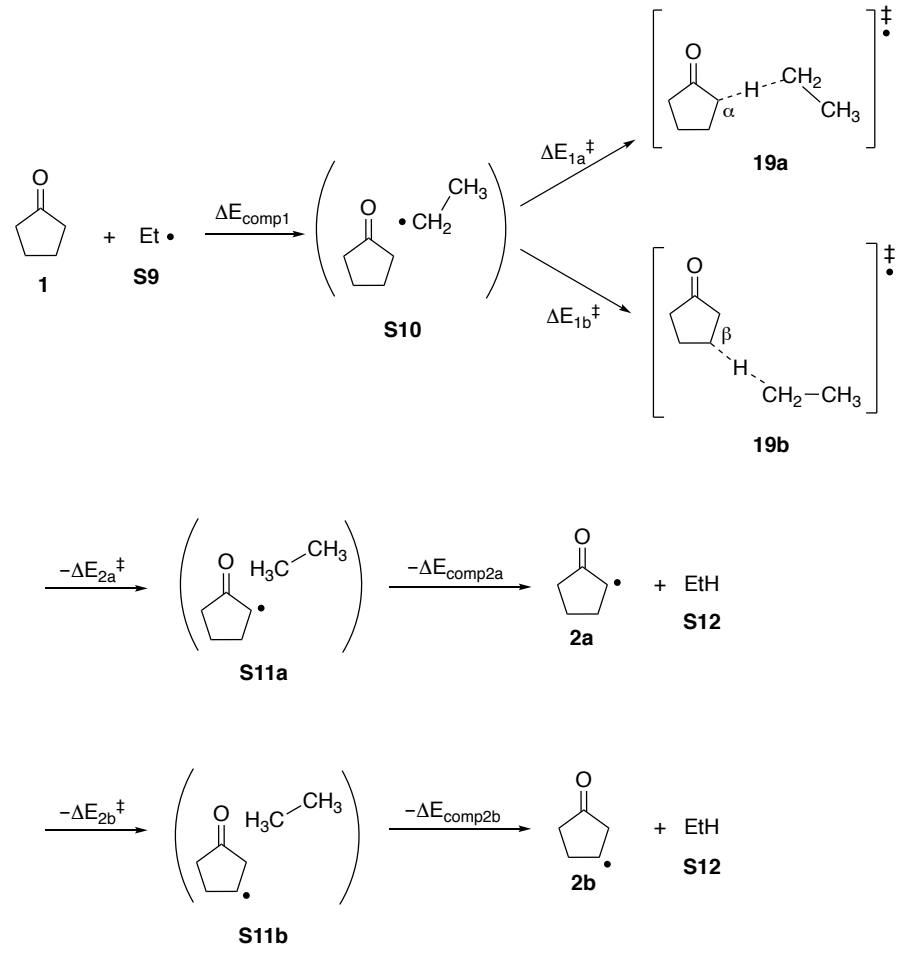
Method		**10a**	**10b**
PCM	ΔG /kJ mol^{-1}	23.8	17.3
	Product ratio	11	89
SMD	ΔG /kJ mol^{-1}	35.4	25.8
	Product ratio	4	96

Table S13 Complexation energies (in kJ mol^{-1}) for α- and β-hydrogen abstraction in cyclopentanone (**1**) with ethyl radical (**S9**) (Scheme S3)

Method	ΔEcomp1	ΔEcomp1 +ZPE	ΔEcomp2a	ΔEcomp2a +ZPE	ΔEcomp2b	ΔEcomp2b +ZPE
ωB97XD/6-311+G(d,p)	-17.0	-12.9	-14.6	-10.9	-16.4	-11.8
In CH_3CN	-14.2		-13.9		-15.5	

Table S14 Energy barriers (in kJ mol^{-1}) and imaginary (ν) frequencies for abstraction of α- and β-hydrogen in cyclopentanone (**1**) with ethyl radical (**S9**) (Scheme S3)

Method	**19a**					**19b**				
	$\Delta E_{1a}^{\ddagger}$	$\Delta E_{1a}^{\ddagger}$ +ZPE	$\Delta E_{2a}^{\ddagger}$	$\Delta E_{2a}^{\ddagger}$ +ZPE	ν /cm^{-1}	$\Delta E_{1b}^{\ddagger}$	$\Delta E_{1b}^{\ddagger}$ +ZPE	$\Delta E_{2b}^{\ddagger}$	$\Delta E_{2b}^{\ddagger}$ +ZPE	ν /cm^{-1}
ωB97XD/6-311+G(d,p)	44.2	36.2	87.5	75.1	1527i	64.2	54.3	76.8	66.3	1704i
In CH_3CN	41.1		88.5		--	63.2		75.6		--



Scheme S3 Reaction pathway for the abstraction of α- and β- hydrogen in cyclopentanone (**1**) with ethyl radical (**S9**).

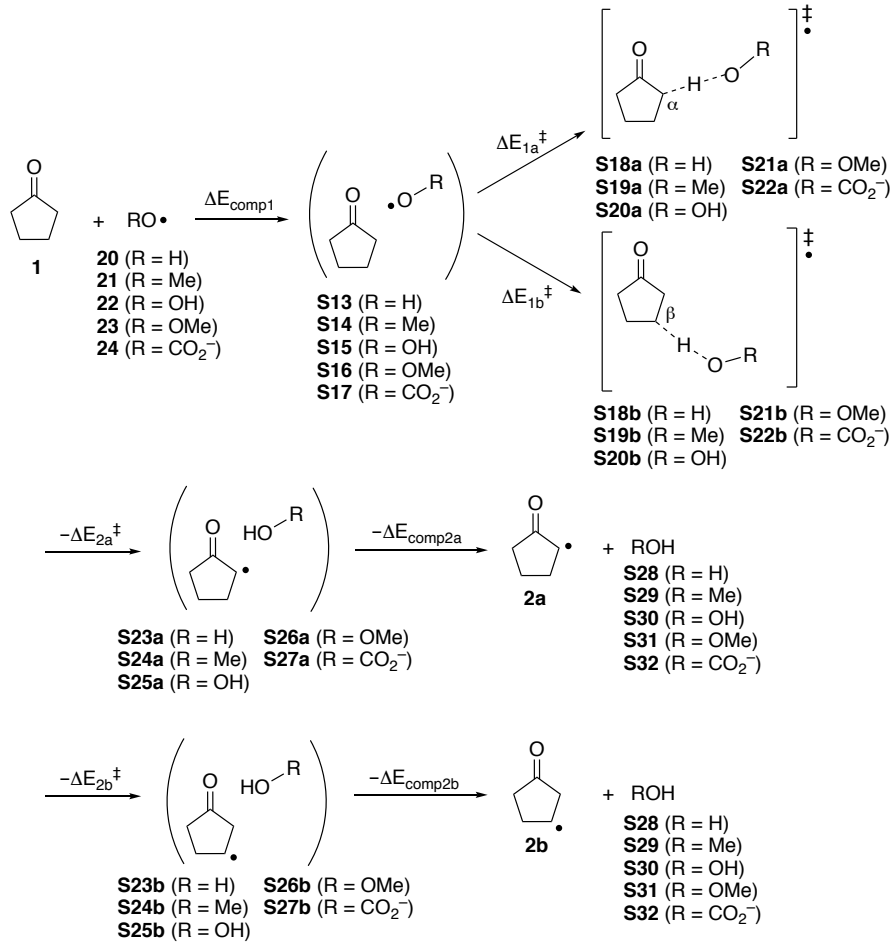
Table S15 Complexation energies (in kJ mol^{-1}) for α- and β-hydrogen abstraction in cyclopentanone (**1**) with hydroxyl (•OH, **20**), methoxyl (•OMe, **21**), hydroperoxyl (•OOH, **22**), and methylperoxyl (•OOMe, **23**) radicals, and carbonate (•OCO_2^-, **24**) radical anion (Scheme S4)

Radical	Method	ΔEcomp1	ΔEcomp1 +ZPE	ΔEcomp2a	ΔEcomp2a +ZPE	ΔEcomp2b	ΔEcomp2b +ZPE
•OH (**20**)	M06-2X/6-311+G(d,p)	-34.9	-27.5	-37.3	-29.0	-32.9	-24.1
	In CH_3CN	-24.2	--	-20.9	--	-18.4	--
	ωB97XD/6-311+G(d,p)	-33.2	-26.1	-35.3	-26.8	-31.3	-23.8
	In CH_3CN	-24.3	--	-20.0	--	-18.3	--
•OMe (**21**)	M06-2X/6-311+G(d,p)	-12.4	-9.3	-33.6	-28.4	-31.6	-25.0
	In CH_3CN	-4.4	--	-20.4	--	-18.4	--
	ωB97XD/6-311+G(d,p)	-11.8	-9.3	-33.2	-27.9	-31.5	-25.8
	In CH_3CN	-4.2	--	-21.2	--	-19.5	--
•OOH (**22**)	M06-2X/6-311+G(d,p)	-51.3	-44.4	-44.4	-37.0	-34.1	-27.2
	In CH_3CN	-38.3	--	-32.0	--	-24.7	--
	ωB97XD/6-311+G(d,p)	-52.0	-44.8	-42.7	-36.3	-27.1	-21.0
	In CH_3CN	-38.8	--	-31.4	--	-18.9	--
•OOMe (**23**)	M06-2X/6-311+G(d,p)	-15.5	-12.6	-43.7	-37.3	-40.9	-34.2
	In CH_3CN	-5.9	--	-32.5	--	-29.9	--
	ωB97XD/6-311+G(d,p)	-14.1	-11.0	-42.4	-35.7	-40.2	-34.3
	In CH_3CN	-4.6	--	-32.0	--	-29.7	--
•OCO_2^- (**24**)	M06-2X/6-311+G(d,p)	-55.2	-51.7	-70.5	-66.9	-72.6	-66.9
	In CH_3CN	-6.5	--	-7.8	--	-12.5	--
	ωB97XD/6-311+G(d,p)	-51.7	-49.0	-68.8	-65.6	-65.8	-62.7
	In CH_3CN	-4.4	--	-5.8	--	-4.7	--

Table S16 Energy barriers (in kJ mol^{-1}) and imaginary (ν) frequencies for abstraction of α- and β-hydrogen in cyclopentanone (**1**) with hydroxyl (·OH, **20**), methoxyl (·OMe, **21**), hydroperoxyl (·OOH, **22**), and methylperoxyl (·OOMe, **23**) radicals, and carbonate (·OCO_2^-, **24**) radical anion (Scheme S4)

Method	$\Delta E_{1a}^{\ddagger}$	$\Delta E_{1a}^{\ddagger}$ +ZPE	$\Delta E_{2a}^{\ddagger}$	$\Delta E_{2a}^{\ddagger}$ +ZPE	ν /cm^{-1}	$\Delta E_{1b}^{\ddagger}$	$\Delta E_{1b}^{\ddagger}$ +ZPE	$\Delta E_{2b}^{\ddagger}$	$\Delta E_{2b}^{\ddagger}$ +ZPE	ν /cm^{-1}
•OH (**20**)			**S18a**					**S18b**		
M06-2X/6-311+G(d,p)	38.9	27.1	149.5	137.4	1043i	41.8	30.5	115.7	108.3	799i
In CH_3CN	36.7	--	152.3	--	--	34.1	--	110.3	--	--
ωB97XD/6-311+G(d,p)	27.1	16.5	138.3	127.5	505i	30.3	20.3	105.0	100.5	236i
In CH_3CN	25.5	--	140.8	--	--	22.7	--	99.6	--	--
•OMe (**21**)			**S19a**					**S19b**		
M06-2X/6-311+G(d,p)	35.3	25.4	111.0	96.0	1473i	39.5	30.1	80.9	69.7	1430i
In CH_3CN	35.8	--	113.7	--	--	35.9	--	75.0	--	--
ωB97XD/6-311+G(d,p)	31.5	22.3	102.8	87.3	1530i	35.8	27.0	73.0	62.0	1551i

In CH_3CN	32.1	--	105.8	--	--	32.0	--	67.3	--	--
•OOH (**22**)			**S20a**					**S20b**		
M06-2X/6-311+G(d,p)	113.5	99.1	84.5	71.1	1917i	122.3	106.0	58.4	48.2	1799i
In CH_3CN	110.9	--	89.6	--	--	113.5	--	52.7	--	--
ωB97XD/6-311+G(d,p)	119.2	103.1	78.9	65.8	2034i	126.8	108.8	51.8	41.9	1893i
In CH_3CN	116.1	--	84.2	--	--	116.1	--	45.2	--	--
•OOMe (**23**)			**S21a**					**S21b**		
M06-2X/6-311+G(d,p)	86.9	73.1	84.8	70.7	86.9	92.8	77.5	55.6	44.5	92.8
In CH_3CN	85.6	--	87.4	--	85.6	87.8	--	50.2	--	87.8
ωB97XD/6-311+G(d,p)	86.1	71.3	74.7	60.6	86.1	95.5	78.6	49.5	38.6	95.5
In CH_3CN	84.8	--	77.8	--	84.8	88.4	--	42.5	--	88.4
•OCO_2^- (**24**)			**S22a**					**S22b**		
M06-2X/6-311+G(d,p)	70.0	57.9	111.6	96.7	1823i	78.2	65.6	89.6	77.0	1866i
In CH_3CN	57.2	--	106.0	--	--	57.8	--	74.5	--	--
ωB97XD/6-311+G(d,p)	84.4	73.5	100.7	85.2	2017i	95.8	84.8	76.7	65.8	2118i
In CH_3CN	68.3	--	90.5	--	--	70.0	--	54.5	--	--



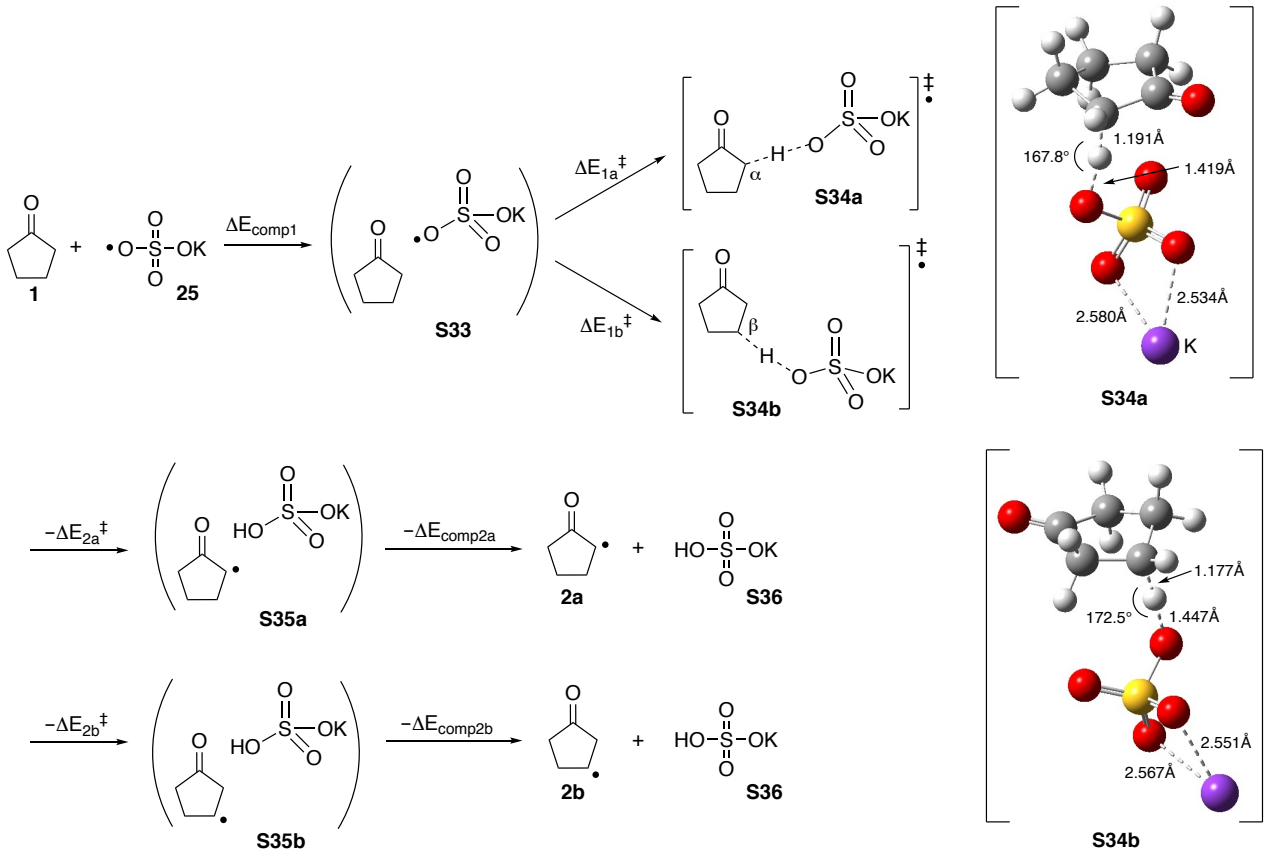
Scheme S4 Reaction pathway for the abstraction of α- and β- hydrogen in cyclopentanone (**1**) with hydroxyl (•OH, **20**), methoxyl (•OMe, **21**), hydroperoxyl (•OOH, **22**), and methylperoxyl (•OOMe, **23**) radicals, and carbonate (•OCO_2^-, **24**) radical anion.

Table S17 Complexation energies (in kJ mol^{-1}) for α- and β-hydrogen abstraction in cyclopentanone (**1**) with SO_4K radical **25** (Scheme S5)

Method	ΔEcomp1	ΔEcomp1 +ZPE	ΔEcomp2a	ΔEcomp2a +ZPE	ΔEcomp2b	ΔEcomp2b +ZPE
ωB97XD/6-311+G(d,p)	-83.7	-80.4	-85.4	-80.3	-81.4	-76.9
In CH_3CN	-29.8	--	-30.6	--	-30.3	--

Table S18 Energy barriers (in kJ mol^{-1}) and imaginary (ν) frequencies for abstraction of α- and β-hydrogen in cyclopentanone (**1**) with SO_4K radical **25** (Scheme S5)

Method	S34a					S34b				
	$\Delta E_{1a}^{\ddagger}$	$\Delta E_{1a}^{\ddagger}$ +ZPE	$\Delta E_{2a}^{\ddagger}$	$\Delta E_{2a}^{\ddagger}$ +ZPE	ν /cm^{-1}	$\Delta E_{1b}^{\ddagger}$	$\Delta E_{1b}^{\ddagger}$ +ZPE	$\Delta E_{2b}^{\ddagger}$	$\Delta E_{2b}^{\ddagger}$ +ZPE	ν /cm^{-1}
ωB97XD/6-311+G(d,p)	95.1	83.1	158.8	146.4	799i	94.2	82.5	121.5	114.7	539i
In CH_3CN	49.5	--	120.1	--	--	44.5	--	78.1	--	--



Scheme S5 Reaction pathway for the abstraction of α- and β- hydrogen in cyclopentanone (**1**) with SO_4K radical **25**.

Full list of Reference 9

Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

Full list of Reference 10

Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

Energies (in hartrees), imaginary frequencies (in cm^{-1}) and Cartesian coordinates for optimised geometries of all structures in this study

Structures in Scheme 4

Cyclopentanone (**1**)

BHLYP/6-311+G(d,p)

E=-270.4836691 E+ZPE=-270.358547

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.526847
3	6	0	1.489865	0.000000	1.896699
4	6	0	2.127696	-0.911621	0.851008
5	6	0	1.265017	-0.745217	-0.387602
6	8	0	1.536561	-1.133909	-1.483118
7	1	0	-0.869803	-0.446217	-0.467575
8	1	0	0.094149	1.012070	-0.392151
9	1	0	-0.537873	0.838823	1.953472
10	1	0	-0.469718	-0.908419	1.897591
11	1	0	1.669155	-0.327435	2.914314
12	1	0	1.890658	1.007044	1.804660
13	1	0	3.168104	-0.707749	0.626580
14	1	0	2.060196	-1.957700	1.147715

B3LYP/6-311+G(d,p)

E=-270.652687 E+ZPE=-270.531965

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.536617
3	6	0	1.499965	0.000000	1.913533
4	6	0	2.151208	-0.901813	0.853689
5	6	0	1.283430	-0.734200	-0.395980
6	8	0	1.564422	-1.115874	-1.505791
7	1	0	-0.870552	-0.460631	-0.470232
8	1	0	0.078032	1.019715	-0.397670
9	1	0	-0.541037	0.844941	1.966492
10	1	0	-0.474942	-0.913688	1.909660
11	1	0	1.676416	-0.340486	2.935451
12	1	0	1.900394	1.016472	1.835732
13	1	0	3.197516	-0.686166	0.630560
14	1	0	2.095323	-1.958788	1.143494

B3LYP-D3/6-311+G(d,p)

E= -270.6614288 E+ZPE=-270.540625

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.536459
3	6	0	1.501052	0.000000	1.906534
4	6	0	2.138824	-0.922425	0.856325
5	6	0	1.272384	-0.753199	-0.393131
6	8	0	1.546007	-1.147105	-1.500277
7	1	0	-0.876224	-0.446505	-0.472771
8	1	0	0.098497	1.018572	-0.395989
9	1	0	-0.541341	0.843874	1.967754
10	1	0	-0.471337	-0.916031	1.908656
11	1	0	1.683036	-0.323935	2.932764
12	1	0	1.905216	1.013154	1.806545
13	1	0	3.188198	-0.727342	0.629698
14	1	0	2.061988	-1.975247	1.155936

M06-2X/6-311+G(d,p)

E=-270.5245122 E+ZPE=-270.402668 In CH_3CN E= -270.5314272

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.531288
3	6	0	1.496938	0.000000	1.895617
4	6	0	2.119627	-0.947957	0.866455
5	6	0	1.259315	-0.773656	-0.382110
6	8	0	1.528052	-1.176815	-1.480512
7	1	0	-0.879484	-0.435821	-0.473707
8	1	0	0.119060	1.015895	-0.393667
9	1	0	-0.538712	0.843903	1.962258
10	1	0	-0.466517	-0.917236	1.903279
11	1	0	1.680293	-0.303201	2.926421
12	1	0	1.905110	1.007114	1.767578
13	1	0	3.171318	-0.775825	0.638129
14	1	0	2.015319	-1.992483	1.181870

ωB97XD/6-311+G(d,p)

E= -270.5637966 E+ZPE= -270.441605 G=-270.470565 In CH_3CN E=-270.5707981

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.530914
3	6	0	1.495315	0.000000	1.897290
4	6	0	2.123559	-0.934403	0.859858
5	6	0	1.261110	-0.765506	-0.386362
6	8	0	1.529639	-1.169182	-1.486860
7	1	0	-0.880602	-0.438974	-0.470717
8	1	0	0.110100	1.016749	-0.396391
9	1	0	-0.538660	0.845931	1.960675
10	1	0	-0.471710	-0.914761	1.905019

11	1	0	1.678017	-0.313517	2.926215
12	1	0	1.903116	1.010115	1.783972
13	1	0	3.174919	-0.751164	0.634685
14	1	0	2.033579	-1.983114	1.168686

QCISD/6-311+G(d,p)//ωB97XD/6-311+G(d,p)
QCISD= -269.9072074

CCSD(T)/6-311+G(d,p)//M06-2X/6-311+G(d,p)
CCSD(T)= -269.9420468

CCSD(T)/6-311+G(d,p)//ωB97XD/6-311+G(d,p)
CCSD(T)= -269.9421024

Cyclopentanon-2-yl radical (**2a**)
BHLYP/6-311+G(d,p)
E=-269.8348501 E+ZPE=-269.723527
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.531047
3	6	0	1.489947	0.000000	1.932104
4	6	0	2.169972	0.632111	0.774672
5	6	0	1.320598	0.650863	-0.379817
6	8	0	1.608879	1.088106	-1.476134
7	1	0	0.000122	-1.012438	-0.400677
8	1	0	-0.836029	0.524553	-0.446878
9	1	0	-0.466634	0.910193	1.896145
10	1	0	-0.542562	-0.835463	1.957250
11	1	0	1.859488	-1.020169	2.066908
12	1	0	1.679525	0.514959	2.870020
13	1	0	3.183530	0.991073	0.758690

B3LYP/6-311+G(d,p)
E=-270.000099 E+ZPE=-269.892705
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.540903
3	6	0	1.501586	0.000000	1.946201
4	6	0	2.194570	0.602566	0.776410
5	6	0	1.347178	0.622141	-0.389018
6	8	0	1.652496	1.036845	-1.504880
7	1	0	-0.030350	-1.018175	-0.405896
8	1	0	-0.827812	0.550586	-0.449603
9	1	0	-0.470523	0.914940	1.910873
10	1	0	-0.544273	-0.842248	1.970585
11	1	0	1.866092	-1.027467	2.109252

12	1	0	1.697181	0.533333	2.882498
13	1	0	3.222105	0.945114	0.759291

B3LYP-D3/6-311+G(d,p)

E= -270.0075118 E+ZPE= -269.900095

No imaginary frequencies

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.540387
3	6	0	1.502834	0.000000	1.938570
4	6	0	2.182843	0.636015	0.778643
5	6	0	1.331695	0.656104	-0.384403
6	8	0	1.623691	1.093862	-1.494720
7	1	0	0.000816	-1.019454	-0.403960
8	1	0	-0.840227	0.528110	-0.452990
9	1	0	-0.466916	0.917530	1.908973
10	1	0	-0.544357	-0.841022	1.972308
11	1	0	1.873628	-1.029988	2.068736
12	1	0	1.701617	0.509338	2.887194
13	1	0	3.203420	0.998209	0.764188

M06-2X/6-311+G(d,p)

E=-269.8714075 E+ZPE=-269.762819 In CH_3CN E=-269.8796768

No imaginary frequencies

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.534420
3	6	0	1.497410	0.000000	1.928981
4	6	0	2.161309	0.686055	0.787421
5	6	0	1.301830	0.709805	-0.373955
6	8	0	1.571137	1.185537	-1.463884
7	1	0	0.053298	-1.018674	-0.399433
8	1	0	-0.858096	0.492025	-0.456583
9	1	0	-0.462504	0.919689	1.900264
10	1	0	-0.542699	-0.840159	1.966682
11	1	0	1.877309	-1.028814	2.014613
12	1	0	1.690317	0.480418	2.891212
13	1	0	3.169841	1.077468	0.777933

ωB97XD/6-311+G(d,p)

E= -269.9073666 E+ZPE= -269.798669 G=-269.828026 In CH_3CN E= -269.9156266

No imaginary frequencies

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.534494
3	6	0	1.495743	0.000000	1.932089
4	6	0	2.170349	0.653957	0.781972

5	6	0	1.317401	0.675254	-0.379375
6	8	0	1.601421	1.127317	-1.478690
7	1	0	0.019670	-1.019067	-0.403390
8	1	0	-0.848892	0.513992	-0.452045
9	1	0	-0.468511	0.916255	1.903785
10	1	0	-0.542772	-0.842713	1.964449
11	1	0	1.872176	-1.028539	2.046835
12	1	0	1.690139	0.500543	2.885201
13	1	0	3.185827	1.030401	0.772834

QCISD/6-311+G(d,p)//ωB97XD/6-311+G(d,p)
QCISD= -269.2547317

CCSD(T)/6-311+G(d,p)//M06-2X/6-311+G(d,p)
CCSD(T)= -269.2883588

CCSD(T)/6-311+G(d,p)//ωB97XD/6-311+G(d,p)
CCSD(T)= -269.2882955

Cyclopentanon-3-yl radical (**2b**)
BHLYP/6-311+G(d,p)
E=-269.8225527 E+ZPE=-269.712912
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.531515
3	6	0	1.448123	0.000000	1.908014
4	6	0	2.315716	0.417467	0.776949
5	6	0	1.374778	0.490905	-0.416566
6	8	0	1.672853	0.871638	-1.507026
7	1	0	-0.105238	-1.009609	-0.392857
8	1	0	-0.772470	0.605216	-0.458949
9	1	0	-0.499381	0.894598	1.912840
10	1	0	-0.538138	-0.845341	1.951911
11	1	0	1.798506	-0.134205	2.914808
12	1	0	2.789955	1.391551	0.914384
13	1	0	3.126863	-0.277284	0.556272

B3LYP/6-311+G(d,p)
E=-269.9871035 E+ZPE=-269.881523
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.541680
3	6	0	1.452013	0.000000	1.926533
4	6	0	2.337349	0.377180	0.789057
5	6	0	1.400853	0.446554	-0.424383
6	8	0	1.719844	0.794050	-1.534057

7	1	0	-0.146855	-1.010259	-0.398904
8	1	0	-0.756052	0.637611	-0.461065
9	1	0	-0.509278	0.898467	1.925770
10	1	0	-0.544219	-0.850761	1.965565
11	1	0	1.798158	-0.137729	2.942488
12	1	0	2.839426	1.349976	0.908080
13	1	0	3.145237	-0.340429	0.585551

B3LYP-D3/6-311+G(d,p)
E= -269.9943441 E+ZPE= -269.888828
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.541714
3	6	0	1.453074	0.000000	1.921764
4	6	0	2.328444	0.412156	0.788679
5	6	0	1.385641	0.492869	-0.418581
6	8	0	1.690857	0.879871	-1.518792
7	1	0	-0.105042	-1.016775	-0.395833
8	1	0	-0.776481	0.608954	-0.465132
9	1	0	-0.504806	0.902425	1.923013
10	1	0	-0.545416	-0.848274	1.968171
11	1	0	1.804272	-0.150844	2.933885
12	1	0	2.816542	1.389676	0.923929
13	1	0	3.143957	-0.290556	0.565803

M06-2X/6-311+G(d,p)
E=-269.8591192 E+ZPE=-269.752332 In CH_3CN E= -269.865653
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.535678
3	6	0	1.455290	0.000000	1.906624
4	6	0	2.311097	0.485997	0.787653
5	6	0	1.359038	0.559597	-0.407859
6	8	0	1.640596	0.987837	-1.492407
7	1	0	-0.046360	-1.022396	-0.389751
8	1	0	-0.802633	0.568790	-0.468396
9	1	0	-0.499028	0.903573	1.914996
10	1	0	-0.538931	-0.849790	1.961262
11	1	0	1.812397	-0.156632	2.914323
12	1	0	2.747223	1.481127	0.951601
13	1	0	3.152090	-0.173853	0.542230

ωB97XD/6-311+G(d,p)
E=-269.8950079 E+ZPE= -269.788092 G=-269.818316 In CH_3CN E= -269.9016699
No imaginary frequencies

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.535676
3	6	0	1.449486	0.000000	1.917557
4	6	0	2.328231	0.390112	0.783156
5	6	0	1.391244	0.458548	-0.421809
6	8	0	1.704043	0.811765	-1.527047
7	1	0	-0.133409	-1.011323	-0.399504
8	1	0	-0.761442	0.630602	-0.460670
9	1	0	-0.504074	0.899622	1.920634
10	1	0	-0.541115	-0.851624	1.959513
11	1	0	1.798648	-0.141330	2.931821
12	1	0	2.819916	1.365793	0.909068
13	1	0	3.137015	-0.322843	0.573821

QCISD/6-311+G(d,p)//ωB97XD/6-311+G(d,p)
QCISD= -269.2434549

CCSD(T)/6-311+G(d,p)//M06-2X/6-311+G(d,p)
CCSD(T)= -269.2772012

CCSD(T)/6-311+G(d,p)//ωB97XD/6-311+G(d,p)
CCSD(T)= -269.2770566

SO_4 radical anion (**5**)
BHLYP/6-311+G(d,p)
E= -698.9884017 E+ZPE= -698.973487
No imaginary frequencies

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	8	0	0.000000	0.000000	0.000000
2	16	0	0.000000	0.000000	1.450013
3	8	0	1.322288	0.000000	2.044993
4	8	0	-0.951273	0.932301	2.065120
5	8	0	-0.737092	-1.330902	1.926754

B3LYP/6-311+G(d,p)
E= -699.1710787 E+ZPE= -699.157404
No imaginary frequencies

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	8	0	0.000000	0.000000	0.000000
2	16	0	0.000000	0.000000	1.475463
3	8	0	1.432455	0.000000	2.040493
4	8	0	-0.819229	1.068439	2.079065
5	8	0	-0.372934	-1.383959	2.039782

B3LYP-D3/6-311+G(d,p)
E=-699.172662 E+ZPE= -699.159022
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.000000
2	16	0	0.000000	0.000000	1.476199
3	8	0	1.433846	0.000000	2.041209
4	8	0	-0.819574	1.069127	2.079878
5	8	0	-0.372378	-1.384640	2.041209

M06-2X/6-311+G(d,p)
E= -699.016326 E+ZPE= -699.001982 In CH_3CN E= -699.1040789
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.000000
2	16	0	0.000000	0.000000	1.459732
3	8	0	1.417104	0.000000	2.029581
4	8	0	-0.829326	1.040225	2.060430
5	8	0	-0.314606	-1.381236	2.030611

ωB97XD/6-311+G(d,p)
E= -699.0471543 E+ZPE= -699.032809 G=-699.061139 In CH_3CN E= -699.1348081
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.000000
2	16	0	0.000000	0.000000	1.461824
3	8	0	1.417133	0.000000	2.025967
4	8	0	-0.820189	1.051844	2.059944
5	8	0	-0.345581	-1.374345	2.025975

QCISD/6-311+G(d,p)//ωB97XD/6-311+G(d,p)
QCISD= -697.9289131

CCSD(T)/6-311+G(d,p)//M06-2X/6-311+G(d,p)
CCSD(T)= -697.9615829

CCSD(T)/6-311+G(d,p)//ωB97XD/6-311+G(d,p)
CCSD(T)= -697.9616852

SO_4H anion (**6**)
BHLYP/6-311+G(d,p)
E= -699.6572015 E+ZPE= -699.629195
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.000000
2	16	0	0.000000	0.000000	1.658613
3	8	0	1.413289	0.000000	2.011902
4	8	0	-0.716919	1.220680	1.959182
5	8	0	-0.688666	-1.234376	2.011336

6	1	0	0.458284	-0.790374	-0.270988

B3LYP/6-311+G(d,p)
E= -699.8366837 E+ZPE= -699.810554
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.000000
2	16	0	0.000000	0.000000	1.714306
3	8	0	1.436288	0.000000	2.069705
4	8	0	-0.728111	1.242696	2.006161
5	8	0	-0.702657	-1.252934	2.069014
6	1	0	0.466106	-0.807105	-0.250677

B3LYP-D3/6-311+G(d,p)
E= -699.8392968 E+ZPE= -699.813163
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.000000
2	16	0	0.000000	0.000000	1.715877
3	8	0	1.437438	0.000000	2.069306
4	8	0	-0.728622	1.242693	2.009558
5	8	0	-0.701943	-1.254364	2.069393
6	1	0	0.472343	-0.805038	-0.245291

M06-2X/6-311+G(d,p)
E= -699.692102 E+ZPE= -699.664474 In CH_3CN E= -699.787642
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.000000
2	16	0	0.000000	0.000000	1.675251
3	8	0	1.422147	0.000000	2.029394
4	8	0	-0.722323	1.229555	1.973403
5	8	0	-0.692793	-1.244699	2.024322
6	1	0	0.436018	-0.818008	-0.259565

ωB97XD/6-311+G(d,p)
E=-699.7189612 E+ZPE= -699.691744 G=-699.720031 In CH_3CN E= -699.814306
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.000000
2	16	0	0.000000	0.000000	1.683572
3	8	0	1.423956	0.000000	2.037214
4	8	0	-0.721978	1.231025	1.979105
5	8	0	-0.695129	-1.242863	2.037145
6	1	0	0.466691	-0.799431	-0.256417

QCISD/6-311+G(d,p)//ωB97XD/6-311+G(d,p)
QCISD= -698.5988431

CCSD(T)/6-311+G(d,p)//M06-2X/6-311+G(d,p)
CCSD(T)= -698.6307885

CCSD(T)/6-311+G(d,p)//ωB97XD/6-311+G(d,p)
CCSD(T)= -698.6309265

Complex (**9**)
BHLYP/6-311+G(d,p)
E= -969.4875531 E+ZPE= -969.346569
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.163752	0.350959	-0.130078
2	6	0	-0.124805	0.795140	1.323623
3	6	0	1.177270	0.219560	1.879775
4	6	0	2.092573	0.104875	0.653248
5	6	0	1.136559	-0.340270	-0.451647
6	8	0	-1.074163	0.552486	-0.885225
7	1	0	-0.119090	1.885299	1.319030
8	1	0	1.606506	0.827609	2.669643
9	1	0	1.008631	-0.775901	2.275738
10	1	0	2.898755	-0.599481	0.813542
11	1	0	2.522003	1.078232	0.411580
12	1	0	0.964867	-1.412157	-0.348569
13	1	0	1.451792	-0.135485	-1.468750
14	8	0	2.442043	-3.404353	3.370348
15	16	0	2.503705	-3.680314	1.800441
16	8	0	3.695844	-2.865645	1.542926
17	8	0	2.673589	-5.103502	1.612397
18	8	0	1.282809	-3.138722	1.225867
19	1	0	-1.026258	0.480978	1.839325

B3LYP/6-311+G(d,p)
E= -969.8376309 E+ZPE= -969.702260
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.186511	0.234378	-0.100506
2	6	0	-0.182716	0.716708	1.355258
3	6	0	1.182392	0.290310	1.921922
4	6	0	2.103169	0.202569	0.681616
5	6	0	1.176850	-0.351826	-0.413684
6	8	0	-1.123452	0.342109	-0.863552
7	1	0	-0.296757	1.808320	1.328013
8	1	0	1.563885	0.981751	2.677843
9	1	0	1.117169	-0.697646	2.383810
10	1	0	2.965475	-0.439878	0.860999

11	1	0	2.464929	1.201870	0.404801
12	1	0	1.105671	-1.443736	-0.298845
13	1	0	1.472413	-0.140988	-1.443688
14	8	0	1.908553	-3.012247	3.000734
15	16	0	2.498288	-3.714844	1.762612
16	8	0	3.758047	-2.828644	1.697502
17	8	0	2.830304	-5.121323	2.033409
18	8	0	1.641020	-3.506359	0.576707
19	1	0	-1.049853	0.318782	1.888266

B3LYP-D3/6-311+G(d,p)
E= -969.8545188 E+ZPE= -969.718946
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.144580	0.246760	-0.156806
2	6	0	-0.202592	0.629667	1.325383
3	6	0	1.126975	0.139319	1.922240
4	6	0	2.104466	0.142756	0.724572
5	6	0	1.227599	-0.329604	-0.446313
6	8	0	-1.044514	0.412511	-0.953546
7	1	0	-0.294636	1.723247	1.362759
8	1	0	1.478436	0.756365	2.752827
9	1	0	1.027127	-0.883749	2.286551
10	1	0	2.958830	-0.512186	0.891823
11	1	0	2.472187	1.160620	0.536246
12	1	0	1.130368	-1.421957	-0.388485
13	1	0	1.569706	-0.060939	-1.447787
14	8	0	2.574683	-2.799341	3.163414
15	16	0	2.470467	-3.548013	1.819421
16	8	0	3.691210	-2.852827	1.187262
17	8	0	2.679541	-4.995250	1.976647
18	8	0	1.225125	-3.182689	1.109509
19	1	0	-1.101519	0.214618	1.787497

M06-2X/6-311+G(d,p)
E= -969.5610251 E+ZPE= -969.423509 In CH_3CN E= -969.6398074
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.116264	0.351125	-0.174416
2	6	0	-0.193555	0.720452	1.306604
3	6	0	1.034917	0.055239	1.937439
4	6	0	2.062097	0.019620	0.791947
5	6	0	1.205678	-0.344072	-0.425532
6	8	0	-0.964723	0.604186	-0.995059
7	1	0	-0.133707	1.814733	1.357649
8	1	0	1.405493	0.578765	2.819742
9	1	0	0.808916	-0.973871	2.222309
10	1	0	2.857001	-0.701857	0.975216

11	1	0	2.510549	1.011810	0.657002
12	1	0	1.014149	-1.424771	-0.396745
13	1	0	1.611284	-0.081882	-1.403100
14	8	0	2.853254	-2.569173	2.948482
15	16	0	2.527315	-3.519070	1.797640
16	8	0	3.736297	-3.061627	0.982355
17	8	0	2.616265	-4.917753	2.185992
18	8	0	1.271791	-3.146446	1.143350
19	1	0	-1.157882	0.423898	1.722336

ωB97XD/6-311+G(d,p)
E=-969.6298492 E+ZPE= -969.492660 G=-969.535947 In CH_3CN E= -969.7091193 G=-969.612444
Using SMD in CH_3CN G=-969.61492
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.150323	0.261800	-0.154946
2	6	0	-0.205451	0.663569	1.317149
3	6	0	1.107416	0.152475	1.919698
4	6	0	2.085132	0.131596	0.730690
5	6	0	1.208623	-0.339425	-0.433477
6	8	0	-1.043385	0.430630	-0.952405
7	1	0	-0.269761	1.759054	1.341952
8	1	0	1.466528	0.766641	2.748465
9	1	0	0.987109	-0.868143	2.288108
10	1	0	2.929687	-0.534295	0.907682
11	1	0	2.468300	1.142101	0.535108
12	1	0	1.095851	-1.429996	-0.359391
13	1	0	1.559849	-0.089353	-1.436014
14	8	0	2.584098	-2.835133	3.144497
15	16	0	2.506391	-3.569765	1.808523
16	8	0	3.730155	-2.867971	1.230284
17	8	0	2.712079	-5.004215	1.956977
18	8	0	1.290008	-3.204851	1.077270
19	1	0	-1.113432	0.274587	1.783045

QCISD/6-311+G(d,p)//ωB97XD/6-311+G(d,p)
QCISD= -967.8544665

CCSD(T)/6-311+G(d,p)//M06-2X/6-311+G(d,p)
CCSD(T)= -967.9228035

CCSD(T)/6-311+G(d,p)//ωB97XD/6-311+G(d,p)
CCSD(T)= -967.9233464

Transition state (**10a**)
BHLYP/6-311+G(d,p)
E= -969.4618445 E+ZPE= -969.326051
Imaginary frequency: -2136.9924

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.490590
3	6	0	1.443911	0.000000	1.928346
4	6	0	2.202283	0.698392	0.780815
5	6	0	1.347942	0.503090	-0.477759
6	8	0	-0.893523	-0.384643	-0.704296
7	1	0	-0.528746	1.101497	1.796405
8	1	0	1.589562	0.515705	2.870315
9	1	0	1.779173	-1.032421	2.048135
10	1	0	3.204421	0.297079	0.664611
11	1	0	2.284264	1.752791	1.005829
12	1	0	1.751327	-0.229410	-1.173234
13	1	0	1.194041	1.431338	-1.018203
14	8	0	-1.047920	2.172595	2.216022
15	16	0	0.054674	3.381582	2.189777
16	8	0	1.112594	2.963677	3.099170
17	8	0	0.493181	3.473182	0.804201
18	8	0	-0.771140	4.477398	2.659576
19	1	0	-0.693712	-0.689601	1.953381

B3LYP/6-311+G(d,p)
E= -969.817705 E+ZPE= -969.687429
Imaginary frequency: -1625.8616

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.489985
3	6	0	1.445811	0.000000	1.944425
4	6	0	2.188219	0.744514	0.805220
5	6	0	1.404392	0.394311	-0.473208
6	8	0	-0.925113	-0.305235	-0.729490
7	1	0	-0.499291	1.145112	1.801067
8	1	0	1.572342	0.488082	2.914544
9	1	0	1.805879	-1.035910	2.039748
10	1	0	3.242774	0.463294	0.745366
11	1	0	2.133171	1.817280	1.000787
12	1	0	1.819850	-0.478029	-0.993771
13	1	0	1.341982	1.205074	-1.203107
14	8	0	-1.000404	2.218296	2.262927
15	16	0	0.061843	3.175421	3.065967
16	8	0	0.646839	2.350103	4.146377
17	8	0	1.055555	3.645495	2.078346
18	8	0	-0.893158	4.214382	3.530797
19	1	0	-0.718789	-0.663596	1.969356

B3LYP-D3/6-311+G(d,p)
E= -969.837198 E+ZPE= -969.706630
Imaginary frequency: -1544.6649

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.491181
3	6	0	1.443992	0.000000	1.944604
4	6	0	2.238384	0.653704	0.774392
5	6	0	1.319634	0.601966	-0.467125
6	8	0	-0.883341	-0.430555	-0.717778
7	1	0	-0.489935	1.145759	1.764198
8	1	0	1.582010	0.561169	2.872120
9	1	0	1.772869	-1.034036	2.120876
10	1	0	3.185180	0.134178	0.604082
11	1	0	2.458420	1.688608	1.029737
12	1	0	1.708439	0.012260	-1.301790
13	1	0	1.098773	1.611399	-0.828086
14	8	0	-0.920606	2.285966	2.153440
15	16	0	0.261365	3.422591	2.127229
16	8	0	1.316782	2.957888	3.057232
17	8	0	0.721767	3.522470	0.724535
18	8	0	-0.524262	4.583584	2.614216
19	1	0	-0.716632	-0.665024	1.972146

M06-2X/6-311+G(d,p)

E= -969.5438332 E+ZPE= -969.410720 In CH_3CN E=-969.6302132

Imaginary frequency: -1445.9233

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.502094
3	6	0	1.452398	0.000000	1.936234
4	6	0	2.223737	0.673076	0.771427
5	6	0	1.350432	0.509796	-0.483987
6	8	0	-0.900114	-0.387786	-0.705325
7	1	0	-0.516262	1.064097	1.801208
8	1	0	1.603389	0.543886	2.870345
9	1	0	1.784691	-1.036088	2.079010
10	1	0	3.212696	0.227513	0.645834
11	1	0	2.349534	1.730090	0.999174
12	1	0	1.741804	-0.206919	-1.211446
13	1	0	1.181310	1.464046	-0.987624
14	8	0	-0.996400	2.231440	2.234537
15	16	0	0.152073	3.370577	1.999879
16	8	0	1.274825	3.000242	2.867360
17	8	0	0.479835	3.308797	0.571998
18	8	0	-0.601214	4.550096	2.426822
19	1	0	-0.682379	-0.721203	1.951169

ωB97XD/6-311+G(d,p)

E= -969.6090465 E+ZPE= -969.476622 G=-969.515534 In CH_3CN E=-969.6964582 G=-969.60339

Using SMD in CH_3CN G= -969.601452

Imaginary frequency: -1712.7365

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.495215
3	6	0	1.446129	0.000000	1.934797
4	6	0	2.222272	0.673967	0.774340
5	6	0	1.321738	0.583062	-0.470498
6	8	0	-0.882965	-0.424447	-0.711054
7	1	0	-0.507905	1.107580	1.784036
8	1	0	1.589019	0.545365	2.870365
9	1	0	1.778340	-1.036046	2.086393
10	1	0	3.190677	0.192708	0.615887
11	1	0	2.398405	1.718633	1.027858
12	1	0	1.719325	-0.041289	-1.275335
13	1	0	1.108636	1.576853	-0.875282
14	8	0	-0.984286	2.231666	2.191167
15	16	0	0.151993	3.406963	2.130841
16	8	0	1.227652	2.979576	3.033349
17	8	0	0.572653	3.492153	0.728038
18	8	0	-0.653461	4.530943	2.613278
19	1	0	-0.698006	-0.692401	1.964926

QCISD/6-311+G(d,p)//ωB97XD/6-311+G(d,p)
QCISD= -967.8304149

CCSD(T)/6-311+G(d,p)//M06-2X/6-311+G(d,p)
CCSD(T)= -967.9014997

CCSD(T)/6-311+G(d,p)//ωB97XD/6-311+G(d,p)
CCSD(T)= -967.9009868

Transition state (**10b**)
BHLYP/6-311+G(d,p)
E= -969.4634852 E+ZPE= -969.327611
Imaginary frequency: -1977.0294

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.517223
3	6	0	1.464004	0.000000	1.915317
4	6	0	2.307556	0.079324	0.644939
5	6	0	1.376640	-0.388321	-0.472775
6	8	0	-0.933240	0.301518	-0.688775
7	1	0	-0.563124	0.849593	1.893249
8	1	0	1.742080	0.696449	2.697988
9	1	0	1.713885	-1.080065	2.482826
10	1	0	3.196973	-0.535398	0.713026
11	1	0	2.616827	1.112664	0.479813
12	1	0	1.401430	-1.474996	-0.527869
13	1	0	1.589140	0.021708	-1.453156

14	8	0	1.935933	-2.204632	3.023198
15	16	0	1.777547	-3.347366	1.866876
16	8	0	2.842157	-3.082647	0.906698
17	8	0	1.935977	-4.554701	2.652749
18	8	0	0.446729	-3.129440	1.307887
19	1	0	-0.500208	-0.912289	1.836123

B3LYP/6-311+G(d,p)
E= -969.8163054 E+ZPE= -969.686125
Imaginary frequency: -1543.8913

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.526886
3	6	0	1.469032	0.000000	1.924631
4	6	0	2.320392	0.011982	0.646489
5	6	0	1.368602	-0.465786	-0.463745
6	8	0	-0.922684	0.346024	-0.705001
7	1	0	-0.581128	0.838954	1.920451
8	1	0	1.762675	0.718764	2.691848
9	1	0	1.724188	-1.095170	2.527650
10	1	0	3.202889	-0.624692	0.738537
11	1	0	2.670795	1.034045	0.443621
12	1	0	1.351783	-1.564127	-0.464377
13	1	0	1.598422	-0.105317	-1.467691
14	8	0	1.982621	-2.198621	3.087002
15	16	0	1.204758	-3.419443	2.293746
16	8	0	1.741893	-3.417587	0.912054
17	8	0	1.609931	-4.573607	3.122648
18	8	0	-0.239680	-3.083729	2.353185
19	1	0	-0.495832	-0.931409	1.848034

B3LYP-D3/6-311+G(d,p)
E= -969.8368901 E+ZPE= -969.706406
Imaginary frequency: -1509.7214

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.527984
3	6	0	1.468539	0.000000	1.925415
4	6	0	2.324160	-0.021374	0.651015
5	6	0	1.364332	-0.466452	-0.465100
6	8	0	-0.926330	0.347922	-0.699053
7	1	0	-0.583859	0.836807	1.921247
8	1	0	1.767150	0.728337	2.681447
9	1	0	1.691376	-1.087459	2.542309
10	1	0	3.169688	-0.705993	0.743561
11	1	0	2.715085	0.986087	0.452049
12	1	0	1.333888	-1.561954	-0.492602
13	1	0	1.599044	-0.089779	-1.461878

14	8	0	1.870062	-2.230168	3.062523
15	16	0	1.663972	-3.367786	1.883445
16	8	0	2.755100	-3.149700	0.903308
17	8	0	1.774856	-4.607096	2.679486
18	8	0	0.320107	-3.099480	1.310386
19	1	0	-0.489893	-0.936643	1.826298

M06-2X/6-311+G(d,p)

E= -969.5456693 E+ZPE= -969.412745 In CH_3CN E= -969.6331493

Imaginary frequency: -1210.9979

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.524990
3	6	0	1.469187	0.000000	1.926002
4	6	0	2.317076	0.113991	0.650138
5	6	0	1.393236	-0.337886	-0.486119
6	8	0	-0.951192	0.274229	-0.688284
7	1	0	-0.565460	0.858849	1.895650
8	1	0	1.739185	0.706558	2.712493
9	1	0	1.714478	-1.059255	2.452976
10	1	0	3.213970	-0.504543	0.708016
11	1	0	2.620580	1.158461	0.508499
12	1	0	1.442344	-1.427926	-0.582816
13	1	0	1.590078	0.120269	-1.455628
14	8	0	1.913293	-2.296714	2.925646
15	16	0	1.747023	-3.306770	1.650229
16	8	0	2.853940	-2.994828	0.738473
17	8	0	1.839120	-4.597476	2.328735
18	8	0	0.432257	-2.983196	1.078030
19	1	0	-0.506205	-0.918337	1.841452

ωB97XD/6-311+G(d,p)

E= -969.6104689 E+ZPE= -969.478018 G=-969.516548 In CH_3CN E= -969.6991784 G= -969.605859

Using SMD in CH_3CN G=-969.605105

Imaginary frequency: -1548.1311

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.522319
3	6	0	1.466629	0.000000	1.920761
4	6	0	2.316957	0.016826	0.646213
5	6	0	1.369093	-0.437878	-0.467923
6	8	0	-0.930118	0.327669	-0.696889
7	1	0	-0.578643	0.841323	1.911972
8	1	0	1.753892	0.732533	2.677332
9	1	0	1.699431	-1.060229	2.516269
10	1	0	3.180470	-0.645503	0.732123
11	1	0	2.678507	1.036342	0.458322
12	1	0	1.357521	-1.534066	-0.502261

13	1	0	1.597127	-0.051048	-1.461927
14	8	0	1.894785	-2.220109	3.055379
15	16	0	1.693912	-3.361691	1.898373
16	8	0	2.766312	-3.139671	0.919177
17	8	0	1.824732	-4.576132	2.701363
18	8	0	0.354675	-3.114825	1.341097
19	1	0	-0.490381	-0.933383	1.827789

QCISD/6-311+G(d,p)//ωB97XD/6-311+G(d,p)
QCISD= -967.83153

CCSD(T)/6-311+G(d,p)//M06-2X/6-311+G(d,p)
CCSD(T)= -967.9021901

CCSD(T)/6-311+G(d,p)//ωB97XD/6-311+G(d,p)
CCSD(T)= -967.9017804

Complex (**11a**)
BHLYP/6-311+G(d,p)
E= -969.5087038 E+ZPE= -969.368507
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.670208	-1.271163	-0.342484
2	6	0	0.445193	-1.112328	1.060930
3	6	0	1.391846	-0.150365	1.666880
4	6	0	2.006627	0.582181	0.455271
5	6	0	1.827228	-0.367383	-0.734629
6	8	0	0.066410	-2.020966	-1.093301
7	1	0	-2.081481	3.527318	2.244379
8	1	0	0.913124	0.535547	2.362576
9	1	0	2.151912	-0.695645	2.237391
10	1	0	3.043770	0.850162	0.624449
11	1	0	1.455999	1.503779	0.303421
12	1	0	2.700441	-1.001282	-0.891617
13	1	0	1.620168	0.132134	-1.674881
14	8	0	-1.505862	4.148558	2.681928
15	16	0	0.021247	3.533214	2.602141
16	8	0	-0.056029	2.273413	3.337187
17	8	0	0.256202	3.336737	1.175566
18	8	0	0.805795	4.570410	3.229541
19	1	0	-0.312882	-1.663192	1.589944

B3LYP/6-311+G(d,p)
E= -969.8514149 E+ZPE= -969.716352
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.149409	-0.112047	0.290222
2	6	0	0.543201	-0.382264	1.644999

3	6	0	1.993030	-0.132059	1.840930
4	6	0	2.577637	-0.118240	0.402199
5	6	0	1.395719	0.296719	-0.495682
6	8	0	-1.002486	-0.142414	-0.159882
7	1	0	-1.632522	1.954925	0.890384
8	1	0	2.093434	0.858255	2.308633
9	1	0	2.478281	-0.855749	2.505990
10	1	0	2.920182	-1.124306	0.134093
11	1	0	3.431249	0.556740	0.314516
12	1	0	1.402258	-0.150617	-1.492803
13	1	0	1.348406	1.385573	-0.596757
14	8	0	-1.694189	2.840041	1.281144
15	16	0	-0.323622	3.076406	2.235735
16	8	0	-0.368632	1.985073	3.241413
17	8	0	0.818149	2.930348	1.295754
18	8	0	-0.543611	4.428575	2.758218
19	1	0	-0.165976	-0.583829	2.435586

B3LYP-D3/6-311+G(d,p)
E= -969.8719127 E+ZPE= -969.736161
No imaginary frequencies

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.127776	-0.063539	0.298794
2	6	0	0.514184	-0.344920	1.651280
3	6	0	1.961079	-0.092900	1.855661
4	6	0	2.555567	-0.079144	0.420803
5	6	0	1.377837	0.320640	-0.490094
6	8	0	-1.026771	-0.062886	-0.149556
7	1	0	-1.594697	1.880668	0.873879
8	1	0	2.047737	0.900053	2.318568
9	1	0	2.444028	-0.812695	2.526355
10	1	0	2.910120	-1.082866	0.159676
11	1	0	3.402020	0.605184	0.337823
12	1	0	1.383421	-0.153250	-1.475084
13	1	0	1.332268	1.405505	-0.617352
14	8	0	-1.647240	2.763032	1.274090
15	16	0	-0.265643	2.992359	2.207786
16	8	0	-0.301356	1.903605	3.218744
17	8	0	0.865157	2.832887	1.255724
18	8	0	-0.466188	4.347281	2.731246
19	1	0	-0.199385	-0.547886	2.436349

M06-2X/6-311+G(d,p)
E= -969.5903244 E+ZPE= -969.452020 In CH_3CN E=-969.6775961
No imaginary frequencies

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.074178	-0.023768	0.282824
2	6	0	0.430354	-0.344513	1.636097

3	6	0	1.881751	-0.182159	1.880536
4	6	0	2.497885	0.207554	0.505842
5	6	0	1.341348	0.251184	-0.511798
6	8	0	-1.069910	0.046533	-0.164700
7	1	0	-1.548790	1.843427	0.925824
8	1	0	2.009386	0.617810	2.618420
9	1	0	2.328031	-1.091022	2.302882
10	1	0	3.267163	-0.507741	0.206205
11	1	0	2.953461	1.192570	0.586984
12	1	0	1.432586	-0.500724	-1.302077
13	1	0	1.233733	1.232131	-0.974388
14	8	0	-1.560988	2.705444	1.369450
15	16	0	-0.124514	2.928333	2.146633
16	8	0	-0.129474	1.964640	3.258141
17	8	0	0.894623	2.593505	1.132645
18	8	0	-0.185352	4.327659	2.534444
19	1	0	-0.305558	-0.549734	2.400728

ωB97XD/6-311+G(d,p)
E= -969.6492671 E+ZPE= -969.511659 G=-969.552011 In CH_3CN E= -969.7373269 G= -969.642224
Using SMD in CH_3CN G= -969.639669
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.134247	-0.063647	0.296891
2	6	0	0.519148	-0.353696	1.648029
3	6	0	1.966020	-0.110326	1.849026
4	6	0	2.552115	-0.091590	0.418046
5	6	0	1.381039	0.328786	-0.482222
6	8	0	-1.013948	-0.065900	-0.149152
7	1	0	-1.573342	1.866094	0.892215
8	1	0	2.058600	0.878912	2.318839
9	1	0	2.445515	-0.838681	2.511337
10	1	0	2.894318	-1.096784	0.146805
11	1	0	3.405107	0.584293	0.337246
12	1	0	1.386676	-0.122744	-1.476958
13	1	0	1.338905	1.417452	-0.581723
14	8	0	-1.639207	2.744489	1.289646
15	16	0	-0.283002	3.013459	2.202372
16	8	0	-0.296905	1.957447	3.228277
17	8	0	0.839924	2.856643	1.259412
18	8	0	-0.500885	4.364944	2.692820
19	1	0	-0.194409	-0.558021	2.433786

QCISD/6-311+G(d,p)//ωB97XD/6-311+G(d,p)
QCISD= -967.8752665

CCSD(T)/6-311+G(d,p)//M06-2X/6-311+G(d,p)
CCSD(T)= -967.9419826

CCSD(T)/6-311+G(d,p)//ωB97XD/6-311+G(d,p)
CCSD(T)= -967.9428094

Complex (**11b**)
BHLYP/6-311+G(d,p)
E= -969.4965456 E+ZPE= -969.357628
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.158651	0.315548	-0.198283
2	6	0	-0.083645	0.504423	1.302635
3	6	0	1.357353	0.783214	1.538979
4	6	0	2.203935	0.390999	0.366228
5	6	0	1.205066	-0.110261	-0.686786
6	8	0	-1.129279	0.497656	-0.878210
7	1	0	-0.778822	1.269631	1.639420
8	1	0	1.768930	0.980782	2.513015
9	1	0	1.978394	-2.438547	3.823070
10	1	0	2.913924	-0.385454	0.641192
11	1	0	2.779217	1.241793	-0.006768
12	1	0	1.193461	-1.197436	-0.689176
13	1	0	1.379654	0.243507	-1.696599
14	8	0	1.932968	-3.332287	3.495030
15	16	0	2.119070	-3.258527	1.857751
16	8	0	3.359685	-2.513574	1.672558
17	8	0	2.159734	-4.652583	1.487476
18	8	0	0.947601	-2.520203	1.392064
19	1	0	-0.376351	-0.449823	1.752527

B3LYP/6-311+G(d,p)
E= -969.8393885 E+ZPE= -969.706419
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.143757	0.103268	-0.155459
2	6	0	0.167455	0.716699	1.205034
3	6	0	1.592204	1.139325	1.074771
4	6	0	2.274212	0.465610	-0.085576
5	6	0	1.168026	-0.374672	-0.762189
6	8	0	-1.237591	0.031398	-0.673274
7	1	0	-0.547786	1.504278	1.466213
8	1	0	2.137341	1.641733	1.864440
9	1	0	1.083581	-4.575944	3.322331
10	1	0	3.093307	-0.179158	0.253077
11	1	0	2.708650	1.199498	-0.782035
12	1	0	1.292103	-1.424813	-0.471764
13	1	0	1.135871	-0.315194	-1.851932
14	8	0	1.541586	-4.388081	2.493331
15	16	0	2.040486	-2.766433	2.606689
16	8	0	3.001235	-2.746806	3.725562

17	8	0	2.613946	-2.541820	1.268620
18	8	0	0.784626	-2.025089	2.876853
19	1	0	0.066749	-0.094941	1.951429

B3LYP-D3/6-311+G(d,p)
E= -969.8577034 E+ZPE= -969.724289
No imaginary frequencies

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-0.224493	0.259278	0.007346
2	6	0	0.310931	0.622128	1.386558
3	6	0	1.784150	0.731940	1.184705
4	6	0	2.218653	0.150338	-0.132925
5	6	0	0.916082	-0.327825	-0.811366
6	8	0	-1.361547	0.427491	-0.380992
7	1	0	-0.188844	1.516592	1.777546
8	1	0	2.474331	0.880798	2.004228
9	1	0	1.262426	-4.326744	3.262858
10	1	0	2.921140	-0.674284	0.030372
11	1	0	2.740782	0.896723	-0.752141
12	1	0	0.825823	-1.413643	-0.708786
13	1	0	0.808218	-0.058993	-1.864553
14	8	0	2.158726	-4.085681	2.996778
15	16	0	2.037960	-2.496418	2.406452
16	8	0	1.549395	-1.706953	3.558128
17	8	0	3.418669	-2.225699	1.982471
18	8	0	1.047384	-2.592294	1.306183
19	1	0	0.072459	-0.207894	2.073262

M06-2X/6-311+G(d,p)
E= -969.5759866 E+ZPE= -969.439832 In CH_3CN E=-969.6598105
No imaginary frequencies

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-0.134657	0.226811	-0.156062
2	6	0	0.121167	0.721260	1.262039
3	6	0	1.609922	0.746470	1.372859
4	6	0	2.276830	0.212361	0.132874
5	6	0	1.134001	-0.415881	-0.682862
6	8	0	-1.169958	0.354155	-0.763674
7	1	0	-0.385122	1.680485	1.421060
8	1	0	2.127146	0.811367	2.319233
9	1	0	1.426618	-3.954999	3.725046
10	1	0	3.049890	-0.521465	0.373295
11	1	0	2.759487	1.021329	-0.436171
12	1	0	1.070293	-1.483131	-0.442426
13	1	0	1.206359	-0.300174	-1.764791
14	8	0	1.886616	-4.111923	2.893475
15	16	0	2.013076	-2.631794	2.147885
16	8	0	2.800602	-1.817020	3.075807

17	8	0	2.673155	-2.973567	0.892893
18	8	0	0.621563	-2.178740	2.006296
19	1	0	-0.314747	-0.016685	1.949347

ωB97XD/6-311+G(d,p)
E= -969.6365138 E+ZPE= -969.501140 G=-969.543505 In CH_3CN E=-969.7205209 G= -969.627746
Using SMD in CH_3CN G= -969.625405
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.222813	0.285717	-0.000395
2	6	0	0.308044	0.646052	1.376336
3	6	0	1.782258	0.724330	1.183370
4	6	0	2.207094	0.161596	-0.142380
5	6	0	0.907385	-0.331570	-0.800800
6	8	0	-1.349696	0.474147	-0.396447
7	1	0	-0.173230	1.554104	1.757177
8	1	0	2.472310	0.838016	2.009024
9	1	0	1.282844	-4.344066	3.252609
10	1	0	2.926924	-0.650951	0.001920
11	1	0	2.702496	0.924788	-0.762295
12	1	0	0.816480	-1.412830	-0.649867
13	1	0	0.800496	-0.105199	-1.863383
14	8	0	2.173686	-4.082008	3.004981
15	16	0	2.047436	-2.524618	2.416335
16	8	0	1.518377	-1.745515	3.540842
17	8	0	3.422487	-2.231426	2.033889
18	8	0	1.098763	-2.637811	1.297582
19	1	0	0.050902	-0.173898	2.067624

QCISD/6-311+G(d,p)//ωB97XD/6-311+G(d,p)
QCISD= -967.8642214

CCSD(T)/6-311+G(d,p)//M06-2X/6-311+G(d,p)
CCSD(T)= -967.9300387

CCSD(T)/6-311+G(d,p)//ωB97XD/6-311+G(d,p)
CCSD(T)= -967.9312692

Structures in Scheme 5

Cyclohexanone (**12**)

M06-2X/6-311+G(d,p)

E=-309.8341358 E+ZPE=-309.682129

In CH_3CN E=-309.8410252

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.995096	-1.258816	-0.295089
2	6	0	0.384861	-1.279787	0.381573
3	6	0	1.148052	-0.000003	0.097897
4	6	0	0.384867	1.279785	0.381571
5	6	0	-0.995091	1.258818	-0.295092
6	6	0	-1.776470	0.000003	0.082322
7	1	0	0.247687	-1.347909	1.468234
8	1	0	0.992458	-2.126079	0.060139
9	1	0	-0.861370	-1.288498	-1.382095
10	1	0	-1.552529	-2.157044	-0.019620
11	1	0	0.247692	1.347910	1.468231
12	1	0	0.992467	2.126074	0.060134
13	1	0	-1.552521	2.157049	-0.019624
14	1	0	-0.861365	1.288498	-1.382097
15	1	0	-1.968447	0.000004	1.162206
16	1	0	-2.750159	0.000004	-0.413943
17	8	0	2.274356	-0.000006	-0.333548

ωB97XD/6-311+G(d,p)

E= -309.8817622 E+ZPE= -309.729760

In CH_3CN E=-309.8888858

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.998133	-1.259711	-0.292143
2	6	0	0.386545	-1.280044	0.373403
3	6	0	1.154405	-0.000003	0.105541
4	6	0	0.386550	1.280041	0.373401
5	6	0	-0.998128	1.259713	-0.292146
6	6	0	-1.780434	0.000003	0.079074
7	1	0	0.259274	-1.361511	1.461145
8	1	0	0.990377	-2.126050	0.041982
9	1	0	-0.872562	-1.300983	-1.380541
10	1	0	-1.553560	-2.157213	-0.006774
11	1	0	0.259279	1.361511	1.461142
12	1	0	0.990386	2.126045	0.041978
13	1	0	-1.553552	2.157217	-0.006778
14	1	0	-0.872557	1.300982	-1.380543
15	1	0	-1.981494	0.000004	1.158150
16	1	0	-2.751879	0.000004	-0.423134
17	8	0	2.294876	-0.000006	-0.292556

Complex (**13**)

M06-2X/6-311+G(d,p)

E=-1008.872962 E+ZPE= -1008.705558 In CH_3CN E= -1008.9502769

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.048879	0.250505	0.632691
2	6	0	0.561644	-0.494402	1.797323
3	6	0	2.087969	-0.574932	1.612830
4	6	0	2.685957	0.824284	1.461661
5	6	0	2.053391	1.578387	0.291133
6	6	0	0.518867	1.630910	0.408470
7	8	0	-0.901729	-0.236503	-0.079168
8	1	0	0.100251	-1.480968	1.868192
9	1	0	0.356549	0.084579	2.705804
10	1	0	2.315935	-1.179280	0.724836
11	1	0	2.529976	-1.086453	2.472303
12	1	0	3.768754	0.756916	1.314546
13	1	0	2.508756	1.387882	2.380249
14	1	0	2.324193	1.086939	-0.652807
15	1	0	2.437289	2.600045	0.260242
16	1	0	0.057816	2.062362	-0.481388
17	1	0	0.253777	2.246701	1.275045
18	8	0	-0.231747	4.108120	2.905310
19	16	0	0.895891	3.516946	3.755667
20	8	0	0.725279	2.072595	3.925973
21	8	0	1.104359	4.253539	4.991549
22	8	0	1.949920	3.827309	2.698110

ωB97XD/6-311+G(d,p)

E=-1008.9506818 E+ZPE= -1008.783176 In CH_3CN E= -1009.0284014

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.084143	0.314644	0.623889
2	6	0	0.530515	-0.321285	1.847364
3	6	0	2.054725	-0.456243	1.690873
4	6	0	2.697381	0.884897	1.338262
5	6	0	2.075746	1.483924	0.076730
6	6	0	0.549029	1.620867	0.205801
7	8	0	-1.008574	-0.188802	0.017389
8	1	0	0.049661	-1.285843	2.024553
9	1	0	0.340284	0.341386	2.701712
10	1	0	2.278206	-1.194169	0.907404
11	1	0	2.475188	-0.840551	2.624497
12	1	0	3.776073	0.756412	1.194648
13	1	0	2.561310	1.578462	2.172136
14	1	0	2.309410	0.847788	-0.788587
15	1	0	2.507299	2.468858	-0.122462
16	1	0	0.089621	1.952748	-0.727908

17	1	0	0.322622	2.355707	0.989153
18	8	0	-0.095683	3.641693	2.871035
19	16	0	0.893444	3.350586	3.994805
20	8	0	0.999155	1.910923	4.244255
21	8	0	0.637256	4.153230	5.181941
22	8	0	2.095691	3.860249	3.201085

Transition state (**14a**)

M06-2X/6-311+G(d,p)

E= -1008.8557214 E+ZPE= -1008.693198 In CH_3CN E= -1008.9409154

Imaginary frequency: -1427.3007

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.508044
3	6	0	1.443679	0.000000	2.036899
4	6	0	2.197567	1.228397	1.528762
5	6	0	2.220218	1.287612	-0.001008
6	6	0	0.857575	1.051183	-0.640422
7	8	0	-0.641035	-0.789539	-0.662177
8	1	0	-0.575654	-0.860116	1.854116
9	1	0	-0.485499	0.929173	1.836499
10	1	0	1.952042	-0.919347	1.716143
11	1	0	1.427554	-0.007125	3.129909
12	1	0	3.227539	1.221046	1.898351
13	1	0	1.718692	2.129307	1.916014
14	1	0	2.903793	0.517039	-0.387129
15	1	0	2.601882	2.259612	-0.323933
16	1	0	0.887920	0.919646	-1.723088
17	1	0	0.182509	2.062488	-0.528741
18	8	0	-0.516333	3.199504	-0.485634
19	16	0	-0.067713	4.066460	0.823938
20	8	0	-0.908275	5.246507	0.618038
21	8	0	1.374437	4.286604	0.685895
22	8	0	-0.418483	3.244560	1.988726

ωB97XD/6-311+G(d,p)

E= -1008.9301119 E+ZPE= -1008.767681 In CH_3CN E= -1009.0167162

Imaginary frequency: -1697.9801

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.507308
3	6	0	1.436609	0.000000	2.052116
4	6	0	2.209904	1.210606	1.532706
5	6	0	2.238902	1.259082	0.003417
6	6	0	0.882196	1.024350	-0.640955
7	8	0	-0.668083	-0.768597	-0.664522
8	1	0	-0.580987	-0.855641	1.857923
9	1	0	-0.488779	0.930797	1.827773

10	1	0	1.941784	-0.931526	1.759307
11	1	0	1.406598	0.014918	3.145708
12	1	0	3.238395	1.194385	1.908716
13	1	0	1.741473	2.122117	1.908711
14	1	0	2.923853	0.486433	-0.379068
15	1	0	2.626170	2.228047	-0.323877
16	1	0	0.913456	0.899239	-1.724688
17	1	0	0.199253	2.065526	-0.539680
18	8	0	-0.479495	3.163132	-0.511857
19	16	0	-0.084934	4.068887	0.791220
20	8	0	-0.963471	5.215934	0.554897
21	8	0	1.351166	4.342495	0.675870
22	8	0	-0.425947	3.253497	1.965543

Transition state (**14b**)

M06-2X/6-311+G(d,p)

E= -1008.8536624 E+ZPE=-1008.691175 In CH_3CN E= -1008.9429943

Imaginary frequency: -1383.4323

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.516709
3	6	0	1.437712	0.000000	2.058927
4	6	0	2.229860	1.183560	1.488282
5	6	0	2.236261	1.118944	-0.025182
6	6	0	0.843152	1.083390	-0.637834
7	8	0	-0.619875	-0.817440	-0.641879
8	1	0	-0.579496	-0.857629	1.862464
9	1	0	-0.496563	0.921193	1.844730
10	1	0	1.924873	-0.944952	1.789611
11	1	0	1.417811	0.051633	3.151025
12	1	0	3.251829	1.193288	1.872007
13	1	0	1.765016	2.123006	1.802367
14	1	0	2.892985	0.334874	-0.417396
15	1	0	2.744525	2.145034	-0.455303
16	1	0	0.866632	0.928040	-1.716398
17	1	0	0.373234	2.054540	-0.423717
18	8	0	3.039595	3.356421	-0.883548
19	16	0	2.441063	4.426526	0.205372
20	8	0	3.215668	4.234193	1.433339
21	8	0	1.022626	4.062862	0.357369
22	8	0	2.689985	5.678685	-0.506656

ωB97XD/6-311+G(d,p)

E= -1008.9270782 E+ZPE= -1008.764713 In CH_3CN E= -1009.0177812

Imaginary frequency: -1648.8107

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.516212

3	6	0	1.433613	0.000000	2.065537
4	6	0	2.235268	1.178645	1.501043
5	6	0	2.234550	1.147558	-0.011781
6	6	0	0.851953	1.074633	-0.637522
7	8	0	-0.638072	-0.804409	-0.643932
8	1	0	-0.579881	-0.856658	1.865980
9	1	0	-0.501155	0.920272	1.841596
10	1	0	1.920304	-0.948517	1.803922
11	1	0	1.407964	0.053508	3.158337
12	1	0	3.261011	1.165086	1.876808
13	1	0	1.792996	2.120513	1.840435
14	1	0	2.936553	0.419847	-0.433188
15	1	0	2.706206	2.237264	-0.407561
16	1	0	0.893663	0.910106	-1.714681
17	1	0	0.363039	2.043742	-0.448285
18	8	0	2.990478	3.426098	-0.783136
19	16	0	2.227557	4.507136	0.187259
20	8	0	2.864128	4.400913	1.503570
21	8	0	0.815078	4.086075	0.198187
22	8	0	2.498986	5.745538	-0.541064

Transition state (**14c**)

M06-2X/6-311+G(d,p)

E= -1008.8563156 E+ZPE= -1008.693780

In CH_3CN E= -1008.9434555 Imaginary frequency: -1254.3274

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.511341
3	6	0	1.446658	0.000000	2.032641
4	6	0	2.246439	1.150581	1.452362
5	6	0	2.176334	1.282393	-0.057715
6	6	0	0.749815	1.150512	-0.623180
7	8	0	-0.549343	-0.862961	-0.651480
8	1	0	-0.558099	-0.867725	1.866100
9	1	0	-0.493892	0.924472	1.836954
10	1	0	1.932610	-0.947844	1.757016
11	1	0	1.448762	0.054461	3.124237
12	1	0	3.277569	1.169073	1.815537
13	1	0	1.811663	2.158649	1.974311
14	1	0	2.809091	0.494357	-0.492634
15	1	0	2.586534	2.247453	-0.362703
16	1	0	0.766281	1.018348	-1.705900
17	1	0	0.195729	2.064736	-0.382483
18	8	0	1.391394	3.227117	2.642401
19	16	0	0.391001	4.057079	1.644167
20	8	0	-0.783062	3.193635	1.455463
21	8	0	1.154180	4.259711	0.407801
22	8	0	0.162199	5.252691	2.452520

ωB97XD/6-311+G(d,p)

E= -1008.9301751 E+ZPE= -1008.767808 In CH_3CN E= -1009.0188357

Imaginary frequency: -1598.0474

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.510422
3	6	0	1.441521	0.000000	2.044075
4	6	0	2.263306	1.127263	1.453979
5	6	0	2.191748	1.265613	-0.053137
6	6	0	0.766725	1.140089	-0.619977
7	8	0	-0.571379	-0.848135	-0.655312
8	1	0	-0.561875	-0.864167	1.870236
9	1	0	-0.494825	0.926209	1.830716
10	1	0	1.923053	-0.958563	1.795008
11	1	0	1.433084	0.074124	3.135144
12	1	0	3.293665	1.136043	1.820745
13	1	0	1.846524	2.172479	1.984576
14	1	0	2.826477	0.481412	-0.494293
15	1	0	2.605520	2.231428	-0.352950
16	1	0	0.784468	1.014301	-1.704126
17	1	0	0.218717	2.058564	-0.379878
18	8	0	1.475707	3.227620	2.621791
19	16	0	0.420728	4.069443	1.689182
20	8	0	-0.749050	3.191727	1.527071
21	8	0	1.122830	4.321987	0.424884
22	8	0	0.206119	5.240631	2.537494

Complex (**15a**)

M06-2X/6-311+G(d,p)

E= -1008.894995 E+ZPE= -1008.728338 In CH_3CN E= -1008.98167

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.087649	-0.045292	-0.055129
2	6	0	0.055179	-0.054880	1.470891
3	6	0	1.424693	0.190535	2.105021
4	6	0	2.060202	1.440844	1.499134
5	6	0	2.321095	1.237374	0.006507
6	6	0	1.200059	0.576494	-0.707181
7	8	0	-0.841178	-0.562714	-0.686152
8	1	0	-0.382375	-1.007219	1.779552
9	1	0	-0.644098	0.730524	1.783818
10	1	0	2.077387	-0.669108	1.913159
11	1	0	1.324866	0.283406	3.190706
12	1	0	2.997529	1.687018	2.003535
13	1	0	1.381173	2.289721	1.648151
14	1	0	3.224271	0.626013	-0.149962
15	1	0	2.570175	2.174711	-0.502088
16	1	0	1.252389	0.528491	-1.789282

17	1	0	5.386565	3.340448	-1.629764
18	8	0	4.504599	3.026772	-1.855945
19	16	0	4.704685	1.507869	-2.533406
20	8	0	3.327183	1.167969	-2.875366
21	8	0	5.281028	0.711952	-1.443434
22	8	0	5.610228	1.729541	-3.657849

ωB97XD/6-311+G(d,p)
E= -1008.9646746 E+ZPE= -1008.798353 In CH_3CN E=-1009.0517192
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.094045	-0.058443	-0.049835
2	6	0	0.054125	-0.073949	1.475707
3	6	0	1.412186	0.192207	2.126227
4	6	0	2.048367	1.444246	1.525988
5	6	0	2.301779	1.257448	0.030230
6	6	0	1.195636	0.585032	-0.691252
7	8	0	-0.824404	-0.588085	-0.689593
8	1	0	-0.368710	-1.034303	1.782798
9	1	0	-0.663323	0.697216	1.786095
10	1	0	2.076086	-0.663966	1.954603
11	1	0	1.294802	0.291550	3.210633
12	1	0	2.989520	1.682838	2.029111
13	1	0	1.375477	2.296716	1.688375
14	1	0	3.215353	0.665018	-0.141200
15	1	0	2.536932	2.204008	-0.468781
16	1	0	1.257858	0.544066	-1.774082
17	1	0	5.414146	3.307910	-1.625308
18	8	0	4.536207	3.035548	-1.905013
19	16	0	4.720171	1.509805	-2.592227
20	8	0	3.353223	1.225251	-3.016152
21	8	0	5.206513	0.681514	-1.480416
22	8	0	5.697315	1.708843	-3.660990

Complex (**15b**)
M06-2X/6-311+G(d,p)
E=-1008.8771912 E+ZPE= -1008.711578 In CH_3CN E= -1008.9648257
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.008004	-0.217677	0.149869
2	6	0	0.116011	-0.129755	1.658811
3	6	0	1.558569	0.155158	2.104863
4	6	0	2.102216	1.419886	1.430544
5	6	0	1.958226	1.337713	-0.049928
6	6	0	0.630467	0.937034	-0.615738
7	8	0	-0.547202	-1.137676	-0.405340
8	1	0	-0.287928	-1.049696	2.085059
9	1	0	-0.519708	0.707850	1.977170

10	1	0	2.192867	-0.695966	1.836786
11	1	0	1.593240	0.253691	3.193098
12	1	0	3.144287	1.604093	1.699758
13	1	0	1.532154	2.288106	1.810449
14	1	0	2.691953	1.834787	-0.670886
15	1	0	4.824542	5.138566	1.839449
16	1	0	0.676467	0.669578	-1.672447
17	1	0	-0.090641	1.773547	-0.524562
18	8	0	5.653001	4.888963	1.417079
19	16	0	5.456887	3.314878	0.907509
20	8	0	4.276776	3.369534	0.032672
21	8	0	5.211364	2.562809	2.144860
22	8	0	6.722226	3.047114	0.244952

ωB97XD/6-311+G(d,p)
E= -1008.9472762 E+ZPE= -1008.782558 In CH_3CN E= -1009.0354879
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.134127	-0.259264	0.063374
2	6	0	0.161032	-0.327392	1.577422
3	6	0	1.504189	0.134396	2.160185
4	6	0	1.880749	1.530485	1.648392
5	6	0	1.841732	1.581333	0.161854
6	6	0	0.642751	1.037830	-0.545297
7	8	0	-0.290022	-1.168403	-0.614854
8	1	0	-0.104091	-1.342806	1.880142
9	1	0	-0.629145	0.348853	1.935282
10	1	0	2.287622	-0.575481	1.874275
11	1	0	1.449913	0.126406	3.253392
12	1	0	2.869578	1.833082	2.001817
13	1	0	1.156253	2.254664	2.069593
14	1	0	2.609034	2.128609	-0.374943
15	1	0	5.182809	5.284210	1.410593
16	1	0	0.810157	0.881433	-1.612581
17	1	0	-0.208391	1.744999	-0.458784
18	8	0	5.979016	4.808429	1.160068
19	16	0	5.489465	3.248317	0.803105
20	8	0	4.482657	3.423823	-0.253537
21	8	0	4.917295	2.753089	2.063580
22	8	0	6.737049	2.625924	0.390947

Complex (**15c**)
M06-2X/6-311+G(d,p)
E=-1008.8808947 E+ZPE= -1008.714538 In CH_3CN E= -1008.9651539
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.119557	0.548041	0.941854
2	6	0	0.833141	-0.730501	1.294048

3	6	0	1.910879	-1.076532	0.230908
4	6	0	2.761842	0.108594	-0.078685
5	6	0	2.049853	1.372678	-0.427326
6	6	0	1.024301	1.735309	0.680079
7	8	0	-1.086806	0.630966	0.842333
8	1	0	0.096522	-1.527949	1.404912
9	1	0	1.369857	-0.585767	2.237416
10	1	0	1.395666	-1.424276	-0.678305
11	1	0	2.522640	-1.892984	0.613932
12	1	0	3.805237	0.118102	0.211772
13	1	0	4.563870	1.636840	3.387689
14	1	0	1.491527	1.256813	-1.369002
15	1	0	2.749044	2.199462	-0.567270
16	1	0	0.409714	2.596703	0.411137
17	1	0	1.575265	1.951643	1.601570
18	8	0	4.967949	0.939534	3.914726
19	16	0	4.934571	-0.435248	2.975428
20	8	0	5.522470	-0.004325	1.700092
21	8	0	3.505760	-0.762941	2.860356
22	8	0	5.726863	-1.366106	3.759707

ωB97XD/6-311+G(d,p)
E= -1008.9545533 E+ZPE= -1008.788654 In CH_3CN E= -1009.0375019
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.236955	0.281920	1.069997
2	6	0	1.071779	-0.957306	1.276479
3	6	0	2.037019	-1.193813	0.084960
4	6	0	2.767792	0.053121	-0.277569
5	6	0	1.964310	1.295545	-0.455888
6	6	0	1.025695	1.530109	0.757500
7	8	0	-0.977141	0.276450	1.143211
8	1	0	0.411268	-1.812842	1.434749
9	1	0	1.685883	-0.801289	2.170302
10	1	0	1.439667	-1.547752	-0.772106
11	1	0	2.739011	-1.983559	0.355811
12	1	0	3.838279	0.118017	-0.126532
13	1	0	5.421479	1.175197	4.489989
14	1	0	1.338372	1.220381	-1.360827
15	1	0	2.612868	2.165150	-0.583883
16	1	0	0.334191	2.357533	0.581111
17	1	0	1.655701	1.740126	1.630063
18	8	0	5.263956	0.254924	4.262203
19	16	0	4.473482	0.273386	2.792447
20	8	0	5.419779	0.902884	1.867729
21	8	0	3.271189	1.084412	3.042046
22	8	0	4.218191	-1.144538	2.565578

Cyclohexanon-2-yl radical (**16a**)

M06-2X/6-311+G(d,p)

E=-309.1818312 E+ZPE=-309.043635 In CH_3CN E= -309.1901208

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.092821	-1.230444	-0.162962
2	6	0	0.360035	-1.174131	0.165440
3	6	0	1.086981	0.044541	0.410385
4	6	0	0.329847	1.362639	0.361167
5	6	0	-0.994840	1.267588	-0.397150
6	6	0	-1.816622	0.088487	0.120804
7	1	0	0.945822	-2.086676	0.193138
8	1	0	-1.191968	-1.478749	-1.231091
9	1	0	-1.561628	-2.063921	0.370899
10	1	0	0.143805	1.661323	1.399615
11	1	0	1.001855	2.109907	-0.064744
12	1	0	-1.550795	2.201885	-0.293795
13	1	0	-0.799858	1.129838	-1.467058
14	1	0	-1.964110	0.199898	1.200711
15	1	0	-2.807555	0.069786	-0.337700
16	8	0	2.288467	0.017296	0.665560

ωB97XD/6-311+G(d,p)

E= -309.226177 E+ZPE= -309.088003 In CH_3CN E= -309.2345326

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.088691	-1.230488	-0.157154
2	6	0	0.362251	-1.174476	0.171798
3	6	0	1.089621	0.040808	0.406104
4	6	0	0.333780	1.359280	0.357636
5	6	0	-0.997705	1.272646	-0.390253
6	6	0	-1.819893	0.087434	0.112224
7	1	0	0.943083	-2.091316	0.203286
8	1	0	-1.182578	-1.491550	-1.223851
9	1	0	-1.558655	-2.062215	0.380383
10	1	0	0.157994	1.661707	1.397565
11	1	0	1.000797	2.108476	-0.074331
12	1	0	-1.553889	2.205669	-0.267992
13	1	0	-0.811545	1.155862	-1.464934
14	1	0	-1.989245	0.197760	1.189686
15	1	0	-2.803995	0.066283	-0.362725
16	8	0	2.295284	0.013389	0.655778

Cyclohexanon-3-yl radical (**16b**)

M06-2X/6-311+G(d,p)

E=-309.1686294 E+ZPE=-309.031700 In CH_3CN E= -309.1754573

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-0.937264	-1.157802	-0.330952
2	6	0	0.437687	-1.250330	0.247883
3	6	0	1.188408	0.070757	0.113831
4	6	0	0.382763	1.310735	0.450448
5	6	0	-0.954490	1.331894	-0.302510
6	6	0	-1.757312	0.051022	-0.029651
7	1	0	0.385498	-1.457250	1.332568
8	1	0	1.037798	-2.039915	-0.204136
9	1	0	-1.374919	-2.024633	-0.807050
10	1	0	0.185341	1.290710	1.530220
11	1	0	0.994073	2.186461	0.231041
12	1	0	-1.529856	2.212516	-0.007307
13	1	0	-0.762096	1.413533	-1.376717
14	1	0	-2.055533	0.052393	1.032599
15	1	0	-2.680170	0.047744	-0.612796
16	8	0	2.341162	0.116868	-0.230545

ωB97XD/6-311+G(d,p)
E= -309.2124555 E+ZPE= -309.075720 In CH_3CN E= -309.2193413
No imaginary frequencies

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-0.946747	-1.164509	-0.310269
2	6	0	0.440648	-1.248543	0.232973
3	6	0	1.193708	0.072720	0.120364
4	6	0	0.383999	1.311805	0.446174
5	6	0	-0.954659	1.332204	-0.302971
6	6	0	-1.761019	0.052657	-0.035723
7	1	0	0.415587	-1.478130	1.315699
8	1	0	1.034093	-2.032370	-0.239905
9	1	0	-1.393048	-2.041435	-0.762760
10	1	0	0.190447	1.296437	1.527625
11	1	0	0.992129	2.190391	0.226494
12	1	0	-1.529589	2.212488	-0.003033
13	1	0	-0.765358	1.423332	-1.377664
14	1	0	-2.080335	0.062284	1.021872
15	1	0	-2.676796	0.048015	-0.631808
16	8	0	2.358030	0.117359	-0.190144

Cyclohexanon-4-yl radical (**16c**)
M06-2X/6-311+G(d,p)
E=-309.1678501 E+ZPE=-309.031066 In CH_3CN E= -309.1746322
No imaginary frequencies

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-0.969740	-1.279376	-0.156258
2	6	0	0.471322	-1.278620	0.400412
3	6	0	1.187933	-0.000003	0.014087
4	6	0	0.471327	1.278618	0.400405
5	6	0	-0.969735	1.279376	-0.156265

6	6	0	-1.673470	0.000002	0.153548
7	1	0	0.426458	-1.321719	1.494252
8	1	0	1.048727	-2.129184	0.038033
9	1	0	-0.911142	-1.418697	-1.247752
10	1	0	-1.519256	-2.137576	0.235062
11	1	0	0.426463	1.321724	1.494245
12	1	0	1.048735	2.129179	0.038022
13	1	0	-1.519248	2.137581	0.235051
14	1	0	-0.911137	1.418691	-1.247760
15	1	0	-2.741128	0.000005	0.331463
16	8	0	2.239067	-0.000007	-0.577640

ωB97XD/6-311+G(d,p)

E= -309.2113794 E+ZPE= -309.074317 In CH_3CN E= -309.2183875

No imaginary frequencies

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-0.974345	-1.281317	-0.148749
2	6	0	0.472346	-1.278426	0.389168
3	6	0	1.198032	-0.000003	0.020016
4	6	0	0.472350	1.278424	0.389161
5	6	0	-0.974341	1.281318	-0.148756
6	6	0	-1.681386	0.000002	0.135172
7	1	0	0.443971	-1.334152	1.483980
8	1	0	1.044017	-2.129505	0.016960
9	1	0	-0.930292	-1.444929	-1.239141
10	1	0	-1.521733	-2.133039	0.262322
11	1	0	0.443976	1.334157	1.483973
12	1	0	1.044025	2.129499	0.016949
13	1	0	-1.521726	2.133043	0.262310
14	1	0	-0.930287	1.444923	-1.239148
15	1	0	-2.753721	0.000005	0.293333
16	8	0	2.274291	-0.000007	-0.528644

Structures in Table 3 and Schemes S1, S2

2-Propylpyridine (**17**)

M06-2X/6-311+G(d,p)

E= -366.1553685 E+ZPE= -365.980953 In CH_3CN E= -366.1605667

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.492594	-1.542227	0.020107
2	6	0	-2.167542	-1.433389	0.447395
3	6	0	-1.543450	-0.194220	0.409655
4	6	0	-2.260114	0.900187	-0.055205
5	6	0	-3.574904	0.695558	-0.459995
6	7	0	-4.182925	-0.487962	-0.428214
7	1	0	-0.516551	-0.084866	0.739135
8	1	0	-1.642497	-2.311470	0.804741
9	1	0	-1.819753	1.887884	-0.103775
10	1	0	-4.170776	1.526606	-0.826210
11	6	0	-4.208957	-2.865721	0.000255
12	1	0	-3.669117	-3.592246	0.615083
13	1	0	-5.201833	-2.728842	0.438807
14	6	0	-4.360606	-3.403152	-1.427691
15	1	0	-3.366523	-3.529402	-1.869366
16	1	0	-4.878784	-2.647820	-2.024570
17	6	0	-5.122326	-4.724446	-1.464348
18	1	0	-5.229055	-5.094610	-2.485718
19	1	0	-4.605359	-5.492206	-0.882364
20	1	0	-6.124197	-4.605949	-1.043420

ωB97XD/6-311+G(d,p)

E= -366.2006958 E+ZPE= -366.026330 In CH_3CN E= -366.2059112

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.504378	-1.531598	0.021008
2	6	0	-2.170697	-1.435864	0.419900
3	6	0	-1.539270	-0.201485	0.384264
4	6	0	-2.258133	0.903491	-0.049736
5	6	0	-3.581326	0.712958	-0.427493
6	7	0	-4.196472	-0.466848	-0.397395
7	1	0	-0.503855	-0.103606	0.691682
8	1	0	-1.641789	-2.321246	0.754380
9	1	0	-1.811047	1.889104	-0.093995
10	1	0	-4.180304	1.552351	-0.770487
11	6	0	-4.227333	-2.851387	-0.000543
12	1	0	-3.707660	-3.571892	0.640021
13	1	0	-5.229487	-2.703918	0.413536
14	6	0	-4.346616	-3.416049	-1.421165
15	1	0	-3.342115	-3.555963	-1.836779
16	1	0	-4.844347	-2.670509	-2.048630
17	6	0	-5.113739	-4.733724	-1.461931

18	1	0	-5.187337	-5.118145	-2.482314
19	1	0	-4.621435	-5.497542	-0.851756
20	1	0	-6.130524	-4.606418	-1.078264

3-Methylbutanol (**18**)

M06-2X/6-311+G(d,p)

E= -272.9241614 E+ZPE= -272.758156 In CH_3CN E= -272.9298558

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.088832	2.897626	0.031740
2	1	0	-3.615138	3.456046	0.846306
3	1	0	-3.883992	3.425547	-0.902246
4	1	0	-5.169162	2.921239	0.193884
5	6	0	-3.573552	1.456720	0.007868
6	1	0	-3.990566	0.958114	-0.876563
7	6	0	-4.049209	0.702114	1.248881
8	1	0	-3.692117	-0.330567	1.246504
9	1	0	-3.671926	1.185602	2.155524
10	1	0	-5.140123	0.685255	1.307484
11	6	0	-2.046855	1.393898	-0.089905
12	1	0	-1.723909	0.348439	-0.124376
13	1	0	-1.601291	1.834189	0.809965
14	6	0	-1.477898	2.093259	-1.310075
15	1	0	-1.630931	3.176544	-1.237737
16	1	0	-1.992092	1.736481	-2.213631
17	8	0	-0.091166	1.792743	-1.370472
18	1	0	0.297243	2.258616	-2.113505

ωB97XD/6-311+G(d,p)

E=-272.9790748 E+ZPE=-272.812978 In CH_3CN E= -272.9847671

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.099201	2.911681	0.056951
2	1	0	-3.648807	3.458871	0.892794
3	1	0	-3.878924	3.461071	-0.862066
4	1	0	-5.184074	2.925723	0.195297
5	6	0	-3.573755	1.474545	0.012545
6	1	0	-3.990540	0.988045	-0.879746
7	6	0	-4.047714	0.692243	1.238105
8	1	0	-3.702486	-0.344998	1.205017
9	1	0	-3.659496	1.144803	2.157159
10	1	0	-5.139343	0.683567	1.305609
11	6	0	-2.045307	1.414539	-0.088014
12	1	0	-1.722545	0.367829	-0.084350
13	1	0	-1.599544	1.883882	0.797554
14	6	0	-1.470433	2.069105	-1.330207
15	1	0	-1.651597	3.151654	-1.313478
16	1	0	-1.961455	1.658190	-2.224814

17	8	0	-0.076263	1.802441	-1.357634
18	1	0	0.309967	2.248676	-2.111074

Complex (**S1**)

M06-2X/6-311+G(d,p)

E=-1065.1917603 E+ZPE=-1065.001887 In CH_3CN E= -1065.2684345

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.205586	0.449829	-0.072951
2	6	0	0.277162	0.520513	1.258531
3	6	0	1.371997	0.097176	1.998936
4	6	0	2.460468	-0.434346	1.310049
5	6	0	2.404047	-0.516142	-0.070481
6	6	0	1.254684	-0.059137	-0.729822
7	1	0	-0.591990	0.941647	1.758038
8	1	0	1.368643	0.183497	3.079009
9	1	0	3.344143	-0.781103	1.834207
10	1	0	3.231201	-0.926883	-0.640125
11	6	0	1.159394	-0.183676	-2.224769
12	6	0	0.779234	-1.610683	-2.641269
13	6	0	0.809983	-1.776447	-4.157260
14	1	0	2.131150	0.043151	-2.670886
15	1	0	0.413365	0.527179	-2.590436
16	1	0	1.501231	-2.299675	-2.196178
17	1	0	-0.211586	-1.850416	-2.238808
18	1	0	1.827353	-1.607393	-4.516533
19	1	0	0.508656	-2.784342	-4.453792
20	1	0	0.137753	-1.063929	-4.646559
21	8	0	5.445480	-3.525589	-2.879755
22	16	0	5.145627	-2.102176	-2.432737
23	8	0	6.326737	-1.514631	-3.190272
24	8	0	5.276106	-1.936307	-0.986265
25	8	0	3.863099	-1.622514	-2.953086

ωB97XD/6-311+G(d,p)

E=-1065.267446 E+ZPE=-1065.077521 In CH_3CN E= -1065.3455259

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.194816	0.459775	-0.088573
2	6	0	0.150937	0.592257	1.238638
3	6	0	1.173982	0.201918	2.088177
4	6	0	2.312902	-0.362115	1.519179
5	6	0	2.377727	-0.506852	0.144909
6	6	0	1.292584	-0.079647	-0.632022
7	1	0	-0.756955	1.037409	1.640865
8	1	0	1.079985	0.336664	3.160071
9	1	0	3.143061	-0.684657	2.139146
10	1	0	3.247006	-0.945146	-0.340126

11	6	0	1.319912	-0.259386	-2.124227
12	6	0	1.062197	-1.716158	-2.533176
13	6	0	1.063360	-1.891131	-4.048495
14	1	0	2.298897	0.031187	-2.518817
15	1	0	0.556502	0.390152	-2.562808
16	1	0	1.841393	-2.348908	-2.095442
17	1	0	0.105452	-2.046352	-2.109331
18	1	0	2.026149	-1.578628	-4.459789
19	1	0	0.902598	-2.937158	-4.324707
20	1	0	0.272782	-1.289820	-4.512681
21	8	0	4.362613	-3.294007	-3.403985
22	16	0	4.917692	-1.976216	-2.885522
23	8	0	6.341914	-2.252524	-3.338952
24	8	0	4.819482	-1.884413	-1.426502
25	8	0	4.332535	-0.828644	-3.579045

Transition state (**S2a**)

M06-2X/6-311+G(d,p)

E=-1065.1738345 E+ZPE=-1064.988441 In CH_3CN E= -1065.2621731

Imaginary frequency: -1111.0863

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.334410
3	6	0	1.151936	0.000000	2.107791
4	6	0	2.381975	0.003423	1.450227
5	6	0	2.404770	-0.001048	0.068005
6	6	0	1.182213	-0.008444	-0.626199
7	1	0	-0.978266	0.002405	1.808573
8	1	0	1.085412	0.003335	3.189117
9	1	0	3.309518	0.015364	2.011951
10	1	0	3.327521	0.024412	-0.506106
11	6	0	1.203413	0.000067	-2.115547
12	6	0	-0.118010	-0.038747	-2.848718
13	6	0	0.087220	0.073335	-4.358514
14	1	0	1.744630	1.025418	-2.418617
15	1	0	1.933615	-0.712843	-2.510379
16	1	0	-0.759933	0.765906	-2.480238
17	1	0	-0.635002	-0.972685	-2.594678
18	1	0	0.605106	1.002182	-4.606230
19	1	0	-0.868213	0.044570	-4.889003
20	1	0	0.721229	-0.735797	-4.727448
21	8	0	2.610948	1.987550	-2.899895
22	16	0	3.920004	1.183323	-3.470031
23	8	0	4.459644	0.448825	-2.317028
24	8	0	4.725147	2.322689	-3.912610
25	8	0	3.420964	0.308047	-4.532149

ωB97XD/6-311+G(d,p)

E=-1065.2461682 E+ZPE=-1065.061165 In CH_3CN E= -1065.3356431

Imaginary frequency: -1654.5085

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.332774
3	6	0	1.152854	0.000000	2.104254
4	6	0	2.379352	-0.008733	1.446248
5	6	0	2.402331	-0.002930	0.063299
6	6	0	1.183338	0.010470	-0.628233
7	1	0	-0.978861	-0.005894	1.807446
8	1	0	1.088372	-0.005963	3.186618
9	1	0	3.308704	-0.032294	2.005639
10	1	0	3.330327	-0.054750	-0.500482
11	6	0	1.158968	0.042464	-2.115302
12	6	0	1.826554	1.237035	-2.774606
13	6	0	1.586469	1.288053	-4.280253
14	1	0	1.794955	-0.970668	-2.472374
15	1	0	0.150143	-0.149716	-2.488237
16	1	0	2.901986	1.206894	-2.570890
17	1	0	1.435301	2.146887	-2.296346
18	1	0	2.034517	0.415751	-4.760334
19	1	0	2.049235	2.179441	-4.713731
20	1	0	0.514209	1.317944	-4.505835
21	8	0	2.536823	-2.008088	-2.718840
22	16	0	4.058171	-1.593032	-3.158620
23	8	0	3.952329	-0.933323	-4.462216
24	8	0	4.677889	-2.919024	-3.176890
25	8	0	4.548220	-0.696088	-2.097770

Transition state (**S2b**)

M06-2X/6-311+G(d,p)

E=-1065.1754095 E+ZPE=-1064.990111 In CH_3CN E= -1065.263034

Imaginary frequency: -1216.8599

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.333529
3	6	0	1.154230	0.000000	2.105256
4	6	0	2.379851	-0.002740	1.445099
5	6	0	2.401659	-0.002700	0.059210
6	6	0	1.182160	0.001343	-0.629000
7	1	0	-0.977807	0.001647	1.808792
8	1	0	1.089951	0.000387	3.186814
9	1	0	3.309522	-0.006548	2.003513
10	1	0	3.326484	-0.007934	-0.511181
11	6	0	1.151193	-0.051031	-2.133387
12	6	0	1.164200	-1.485028	-2.645698
13	6	0	0.843170	-1.634655	-4.115840
14	1	0	2.006573	0.485245	-2.556551
15	1	0	0.228881	0.434227	-2.472389

16	1	0	2.297948	-1.903525	-2.504219
17	1	0	0.583384	-2.155000	-2.003829
18	1	0	1.537682	-1.039024	-4.711061
19	1	0	0.934949	-2.675893	-4.431481
20	1	0	-0.183727	-1.302403	-4.312454
21	8	0	3.581436	-2.292579	-2.540960
22	16	0	4.492004	-1.103990	-3.201268
23	8	0	5.765769	-1.808668	-3.336827
24	8	0	4.496569	-0.007537	-2.220130
25	8	0	3.829272	-0.739615	-4.456830

ωB97XD/6-311+(d,p)
E=-1065.247182 E+ZPE=-1065.062212 In CH_3CN E=-1065.336124
Imaginary frequency: -1556.0085

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.333535
3	6	0	1.153075	0.000000	2.103922
4	6	0	2.378271	-0.000462	1.444406
5	6	0	2.399308	0.000290	0.060130
6	6	0	1.181751	0.001265	-0.628261
7	1	0	-0.978769	0.000801	1.808745
8	1	0	1.089647	-0.000929	3.186438
9	1	0	3.308866	-0.004332	2.002365
10	1	0	3.324859	-0.005803	-0.510199
11	6	0	1.156249	-0.043097	-2.132899
12	6	0	1.186571	-1.464692	-2.669240
13	6	0	0.962922	-1.598640	-4.156094
14	1	0	2.010877	0.506211	-2.540575
15	1	0	0.233495	0.441615	-2.474560
16	1	0	2.334144	-1.902267	-2.461821
17	1	0	0.579094	-2.149643	-2.068652
18	1	0	1.737508	-1.056243	-4.704156
19	1	0	1.009446	-2.645401	-4.465566
20	1	0	-0.023035	-1.199798	-4.430913
21	8	0	3.562129	-2.306874	-2.357650
22	16	0	4.582454	-1.237465	-3.064452
23	8	0	5.848618	-1.954573	-2.915137
24	8	0	4.478055	-0.002559	-2.267309
25	8	0	4.110859	-1.067693	-4.442438

Complex (**S3a**)
M06-2X/6-311+G(d,p)
E=-1065.2208162 E+ZPE=-1065.031376 In CH_3CN E= -1065.3035
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.587427	1.549764	0.579964
2	6	0	0.679279	0.881599	1.718625

3	6	0	1.275720	-0.374950	1.853365
4	6	0	1.815166	-0.972774	0.714966
5	6	0	1.737964	-0.299524	-0.489318
6	6	0	1.114861	0.970634	-0.536071
7	1	0	0.250044	1.371595	2.590431
8	1	0	1.310194	-0.859187	2.821828
9	1	0	2.292215	-1.946436	0.730253
10	1	0	2.150576	-0.751339	-1.384412
11	6	0	1.009124	1.697919	-1.752409
12	6	0	1.480215	1.178461	-3.070893
13	6	0	0.482458	0.183957	-3.692698
14	1	0	1.567050	-3.961771	-3.181018
15	1	0	0.494213	2.650845	-1.693927
16	1	0	2.435743	0.656253	-2.969776
17	1	0	1.631408	2.016429	-3.757267
18	1	0	0.346060	-0.668438	-3.025637
19	1	0	0.875889	-0.203559	-4.633825
20	1	0	-0.487546	0.658436	-3.867453
21	8	0	2.488022	-4.142912	-3.397872
22	16	0	3.385658	-2.961494	-2.649344
23	8	0	2.881718	-1.706492	-3.232890
24	8	0	4.742870	-3.324448	-3.014472
25	8	0	3.044674	-3.093568	-1.226152

ωB97XD/6-311+G(d,p)

E=-1065.2883039 E+ZPE=-1065.099258 In CH_3CN E=-1065.3715471

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.616709	1.566586	0.587087
2	6	0	0.714175	0.896287	1.722919
3	6	0	1.290987	-0.369778	1.847178
4	6	0	1.801467	-0.975989	0.701156
5	6	0	1.716946	-0.302013	-0.500942
6	6	0	1.117122	0.980054	-0.540486
7	1	0	0.306640	1.393406	2.602229
8	1	0	1.333781	-0.856201	2.815292
9	1	0	2.263178	-1.957641	0.709811
10	1	0	2.107464	-0.764080	-1.401891
11	6	0	1.004147	1.714018	-1.745752
12	6	0	1.441642	1.216699	-3.084566
13	6	0	0.391662	0.307962	-3.747907
14	1	0	1.704504	-4.165977	-3.179468
15	1	0	0.500865	2.673898	-1.670477
16	1	0	2.369871	0.642674	-3.009741
17	1	0	1.638778	2.074089	-3.737137
18	1	0	0.234958	-0.585988	-3.141243
19	1	0	0.743195	-0.021782	-4.728493
20	1	0	-0.565495	0.826658	-3.867186
21	8	0	2.635893	-4.277222	-3.388381

22	16	0	3.441455	-3.059457	-2.578252
23	8	0	2.873474	-1.820700	-3.137586
24	8	0	4.827037	-3.324933	-2.923918
25	8	0	3.080545	-3.261569	-1.168245

Complex (**S3b**)

M06-2X/6-11+G(d,p)

E=-1065.2018528 E+ZPE=-1065.014035 In CH_3CN E= -1065.286787

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.469037	0.416386	-0.174912
2	6	0	0.404454	0.469112	1.155367
3	6	0	1.381787	-0.045311	1.997839
4	6	0	2.492791	-0.647893	1.414902
5	6	0	2.577889	-0.714823	0.032500
6	6	0	1.538271	-0.168662	-0.729433
7	1	0	-0.476975	0.952166	1.570302
8	1	0	1.272361	0.029127	3.073220
9	1	0	3.285326	-1.061483	2.029031
10	1	0	3.426154	-1.164131	-0.476212
11	6	0	1.570376	-0.253029	-2.233886
12	6	0	0.566120	-1.232235	-2.754190
13	6	0	0.693050	-1.749729	-4.145097
14	1	0	2.570509	-0.537754	-2.576579
15	1	0	1.359550	0.753169	-2.633178
16	1	0	6.293338	-0.682450	-3.920219
17	1	0	-0.371951	-1.323997	-2.216700
18	1	0	1.732185	-2.019348	-4.357294
19	1	0	0.052004	-2.618876	-4.311620
20	1	0	0.404020	-0.986346	-4.886330
21	8	0	6.435231	-1.632603	-3.849884
22	16	0	5.038880	-2.261904	-3.203314
23	8	0	5.344944	-3.679111	-3.125056
24	8	0	3.992192	-1.880734	-4.160779
25	8	0	4.898560	-1.567275	-1.913312

ωB97XD/6-311+G(d,p)

E=-1065.2703582 E+ZPE=-1065.082972 In CH_3CN E=-1065.3544377

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.497094	0.582136	-0.150478
2	6	0	0.575708	0.567713	1.181139
3	6	0	1.582335	-0.072693	1.887775
4	6	0	2.565911	-0.738307	1.161943
5	6	0	2.499061	-0.739321	-0.220917
6	6	0	1.443370	-0.063183	-0.842312
7	1	0	-0.211062	1.103045	1.709032
8	1	0	1.594357	-0.046140	2.971843

9	1	0	3.379705	-1.252517	1.662413
10	1	0	3.256869	-1.247911	-0.812394
11	6	0	1.316355	-0.078336	-2.345599
12	6	0	0.430404	-1.190739	-2.808497
13	6	0	0.700440	-1.900018	-4.087441
14	1	0	2.304441	-0.202452	-2.799866
15	1	0	0.910680	0.897177	-2.658364
16	1	0	6.385174	-0.584408	-3.185209
17	1	0	-0.498409	-1.359475	-2.269819
18	1	0	1.773594	-2.090151	-4.199267
19	1	0	0.156761	-2.847462	-4.148662
20	1	0	0.396436	-1.295964	-4.960407
21	8	0	6.478390	-1.486860	-3.502090
22	16	0	5.073865	-2.277927	-3.065366
23	8	0	5.293146	-3.610776	-3.600101
24	8	0	4.005511	-1.500092	-3.713021
25	8	0	5.039968	-2.173073	-1.599167

2-Propylpyridine α-radical (**S4a**)

M06-2X/6-311+G(d,p)

E=-365.5043523 E+ZPE=-365.343938 In CH_3CN E= -365.5103094

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.711977	-1.324545	-0.327690
2	6	0	-2.309102	-1.326376	-0.509630
3	6	0	-1.587873	-0.183154	-0.218566
4	6	0	-2.262855	0.940943	0.247359
5	6	0	-3.649967	0.856437	0.399395
6	7	0	-4.363703	-0.222311	0.128879
7	1	0	-0.512324	-0.165562	-0.352395
8	1	0	-1.811729	-2.216605	-0.874119
9	1	0	-1.740413	1.857670	0.487558
10	1	0	-4.207993	1.716303	0.760547
11	6	0	-4.510544	-2.463824	-0.611661
12	1	0	-5.575958	-2.356983	-0.438828
13	6	0	-3.972853	-3.759312	-1.121460
14	1	0	-3.228104	-4.153174	-0.416232
15	1	0	-3.424650	-3.587880	-2.057956
16	6	0	-5.067763	-4.799585	-1.348593
17	1	0	-4.652693	-5.735722	-1.724856
18	1	0	-5.596256	-5.012854	-0.416954
19	1	0	-5.798936	-4.436650	-2.074322

ωB97XD/6-311+G(d,p)

E=-365.5469627 E+ZPE=-365.386649 In CH_3CN E= -365.5529475

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.706624	-1.325350	-0.336143

2	6	0	-2.301380	-1.320929	-0.510793
3	6	0	-1.584369	-0.178680	-0.211848
4	6	0	-2.263754	0.942118	0.254723
5	6	0	-3.650728	0.855677	0.398916
6	7	0	-4.361446	-0.222344	0.121086
7	1	0	-0.507637	-0.158354	-0.339851
8	1	0	-1.796775	-2.207366	-0.875799
9	1	0	-1.743241	1.859110	0.501670
10	1	0	-4.212057	1.713667	0.761060
11	6	0	-4.503555	-2.458766	-0.621742
12	1	0	-5.569653	-2.346336	-0.450329
13	6	0	-3.979030	-3.760330	-1.130195
14	1	0	-3.225819	-4.153661	-0.432466
15	1	0	-3.439534	-3.598147	-2.074457
16	6	0	-5.073630	-4.803814	-1.340812
17	1	0	-4.657047	-5.742494	-1.712896
18	1	0	-5.596473	-5.014826	-0.404078
19	1	0	-5.812939	-4.452359	-2.065570

2-Propylpyridine β-radical (**S4b**)

M06-2X/6-311+G(d,p)

E=-365.4892497 E+ZPE=-365.329887 In CH_3CN E= -365.4949274

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.562951	-1.501847	0.024955
2	6	0	-2.210538	-1.450927	0.365894
3	6	0	-1.547887	-0.232491	0.315349
4	6	0	-2.254226	0.896591	-0.077795
5	6	0	-3.598059	0.746222	-0.402298
6	7	0	-4.244138	-0.417037	-0.354856
7	1	0	-0.498205	-0.166121	0.577767
8	1	0	-1.693804	-2.355538	0.663502
9	1	0	-1.782980	1.869573	-0.133418
10	1	0	-4.186408	1.604635	-0.713146
11	6	0	-4.329173	-2.800547	0.029348
12	1	0	-3.780634	-3.562181	0.594687
13	1	0	-5.276328	-2.630217	0.564873
14	6	0	-4.603452	-3.290833	-1.356809
15	1	0	-4.757772	-2.543566	-2.126369
16	6	0	-5.084592	-4.684022	-1.570441
17	1	0	-5.075679	-4.957211	-2.626674
18	1	0	-4.467483	-5.405264	-1.024383
19	1	0	-6.114971	-4.816851	-1.207347

ωB97XD/6-311+G(d,p)

E=-365.5307753 E+ZPE=-365.371683 In CH_3CN E= -365.536424

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-3.572652	-1.491428	0.020502
2	6	0	-2.216514	-1.451773	0.343673
3	6	0	-1.546880	-0.238131	0.299690
4	6	0	-2.250802	0.899910	-0.069277
5	6	0	-3.598213	0.762248	-0.376518
6	7	0	-4.251163	-0.397253	-0.334567
7	1	0	-0.492877	-0.181810	0.548657
8	1	0	-1.699652	-2.362757	0.622816
9	1	0	-1.773131	1.870851	-0.118027
10	1	0	-4.186165	1.628075	-0.668887
11	6	0	-4.343659	-2.787636	0.022082
12	1	0	-3.807901	-3.544461	0.608264
13	1	0	-5.297848	-2.610314	0.544772
14	6	0	-4.605322	-3.300801	-1.356347
15	1	0	-4.717098	-2.571788	-2.152067
16	6	0	-5.076465	-4.696151	-1.562345
17	1	0	-5.050483	-4.981324	-2.616297
18	1	0	-4.468362	-5.413421	-0.998082
19	1	0	-6.114091	-4.829668	-1.215205

Complex (**S5**)

M06-2X/6-311+G(d,p)

E=-971.9695011 E+ZPE=-971.786613 In CH_3CN E= -972.0461945

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.110084	-0.059222	-0.125118
2	6	0	-0.120462	0.011304	1.286815
3	6	0	1.282155	-0.110602	1.881592
4	6	0	1.289236	-0.421588	3.379826
5	6	0	0.651166	0.704906	4.195798
6	6	0	2.713674	-0.704379	3.852375
7	1	0	0.114952	-0.981085	-0.328078
8	1	0	-0.573622	0.972705	1.547246
9	1	0	-0.756607	-0.782208	1.704575
10	1	0	1.844970	0.813021	1.688959
11	1	0	1.801217	-0.918514	1.358152
12	1	0	0.702289	-1.336283	3.527387
13	1	0	1.187369	1.646686	4.028719
14	1	0	-0.395309	0.861068	3.921687
15	1	0	0.686521	0.483571	5.266764
16	1	0	2.737219	-0.939782	4.920994
17	1	0	3.354946	0.169175	3.684531
18	1	0	3.122098	-1.554650	3.302204
19	8	0	-0.508811	-3.291455	2.276805
20	16	0	0.630759	-3.570912	1.303267
21	8	0	0.469673	-2.813025	0.057461
22	8	0	1.938617	-3.400121	1.925930
23	8	0	0.253721	-5.031835	1.125611

ωB97XD/6-311+G8d,p)
E=-972.052865 E+ZPE=-971.870377 In CH_3CN E= -972.1298515
No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.122851	-0.068160	-0.097265
2	6	0	-0.153576	0.011658	1.311844
3	6	0	1.240068	-0.075955	1.934961
4	6	0	1.233874	-0.389291	3.433754
5	6	0	0.590195	0.730418	4.254799
6	6	0	2.651372	-0.687441	3.920043
7	1	0	0.116818	-0.986490	-0.299673
8	1	0	-0.633933	0.964584	1.559331
9	1	0	-0.779075	-0.792478	1.726845
10	1	0	1.788783	0.858100	1.748122
11	1	0	1.786706	-0.872152	1.421808
12	1	0	0.641147	-1.302479	3.570254
13	1	0	1.135542	1.672486	4.114992
14	1	0	-0.450462	0.900592	3.963431
15	1	0	0.601419	0.492419	5.323979
16	1	0	2.661464	-0.931395	4.988256
17	1	0	3.305742	0.180457	3.767172
18	1	0	3.064179	-1.536512	3.369520
19	8	0	-0.264296	-3.431029	2.195787
20	16	0	0.791208	-3.630945	1.119801
21	8	0	0.494795	-2.831353	-0.076012
22	8	0	2.142431	-3.428682	1.635082
23	8	0	0.474134	-5.099579	0.896674

Transition state (**S6a**)
M06-2X/6-311+G(d,p)
E=-971.9589581 E+ZPE=-971.779380 In CH_3CN E= -972.0423408
Imaginary frequency: -749.9608

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.383170
3	6	0	1.383579	0.000000	2.015687
4	6	0	1.371115	-0.259243	3.524353
5	6	0	0.774596	0.917107	4.300357
6	6	0	2.784730	-0.576101	4.006659
7	1	0	0.367294	-0.871158	-0.262241
8	1	0	-0.643782	0.812592	1.733334
9	1	0	-0.522383	-0.988821	1.753004
10	1	0	1.867448	0.964022	1.800223
11	1	0	1.972030	-0.781250	1.526677
12	1	0	0.759829	-1.151256	3.695619
13	1	0	1.360956	1.827115	4.127016
14	1	0	-0.257712	1.120824	4.004743
15	1	0	0.777200	0.716986	5.375860

16	1	0	2.803672	-0.753392	5.086305
17	1	0	3.464745	0.256193	3.788571
18	1	0	3.147350	-1.473896	3.501962
19	8	0	-0.832439	-2.438060	1.886596
20	16	0	0.429071	-3.258906	1.294721
21	8	0	0.751125	-2.595502	0.010263
22	8	0	1.517236	-3.144710	2.269525
23	8	0	-0.149602	-4.593694	1.157898

ωB97XD/6-311+G(d,p)
E=-972.0402154 E+ZPE=-971.861423 In CH_3CN E= -972.1254674
Imaginary frequency: -876.8604

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.374678
3	6	0	1.376402	0.000000	2.022741
4	6	0	1.364798	-0.274323	3.529097
5	6	0	0.669723	0.837974	4.317436
6	6	0	2.791333	-0.493939	4.029148
7	1	0	0.342352	-0.884888	-0.268303
8	1	0	-0.662347	0.794796	1.733067
9	1	0	-0.517955	-1.025592	1.734250
10	1	0	1.856827	0.968892	1.816318
11	1	0	1.973894	-0.773769	1.532309
12	1	0	0.818530	-1.211158	3.679302
13	1	0	1.168901	1.801579	4.153320
14	1	0	-0.379161	0.949797	4.028573
15	1	0	0.693279	0.628212	5.391968
16	1	0	2.805432	-0.703115	5.104201
17	1	0	3.411791	0.393959	3.850869
18	1	0	3.241012	-1.344370	3.511117
19	8	0	-0.854949	-2.408814	1.850009
20	16	0	0.325839	-3.277944	1.173226
21	8	0	0.621802	-2.589971	-0.110714
22	8	0	1.469529	-3.249754	2.090592
23	8	0	-0.315082	-4.581319	1.014976

Transition state (**S6b**)
M06-2X/6-311+G(d,p)
E=-971.9541626 E+ZPE=-971.775728 In CH_3CN E= -972.039693
Imaginary frequency: -1047.9841

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.408571
3	6	0	1.399355	0.000000	1.995491
4	6	0	1.496721	-0.184697	3.499766
5	6	0	0.793776	0.956416	4.247495
6	6	0	2.959083	-0.292543	3.930896

7	1	0	0.149719	-0.928301	-0.256737
8	1	0	-0.520337	0.911755	1.728946
9	1	0	-0.549951	-0.863286	1.804830
10	1	0	1.998132	0.840287	1.621078
11	1	0	1.976195	-0.950753	1.524838
12	1	0	0.995492	-1.130288	3.734907
13	1	0	1.222339	1.924170	3.963313
14	1	0	-0.276723	0.983200	4.033262
15	1	0	0.917628	0.837384	5.327896
16	1	0	3.037550	-0.471467	5.007072
17	1	0	3.496594	0.634917	3.701665
18	1	0	3.447212	-1.114956	3.404415
19	8	0	2.515122	-2.159227	1.197609
20	16	0	1.271643	-3.213943	1.115640
21	8	0	0.416390	-2.722477	0.018249
22	8	0	0.607186	-3.156160	2.420771
23	8	0	1.988566	-4.451371	0.822240

ωB97XD/6-311+G(d,p)
E=-972.0342294 E+ZPE=-971.856485 In CH_3CN E= -972.1211872
Imaginary frequency: -1426.7138

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.405745
3	6	0	1.393279	0.000000	2.005049
4	6	0	1.490531	-0.218014	3.504327
5	6	0	0.759578	0.884495	4.283402
6	6	0	2.950851	-0.318549	3.945186
7	1	0	0.173652	-0.923852	-0.261858
8	1	0	-0.522897	0.911689	1.726479
9	1	0	-0.554433	-0.861265	1.802433
10	1	0	2.002643	0.836163	1.638601
11	1	0	1.987395	-0.965052	1.511600
12	1	0	1.004412	-1.178463	3.712354
13	1	0	1.173693	1.871309	4.043354
14	1	0	-0.309579	0.902299	4.056826
15	1	0	0.870241	0.727108	5.361399
16	1	0	3.021541	-0.525376	5.018107
17	1	0	3.482796	0.620386	3.746702
18	1	0	3.455323	-1.121878	3.404190
19	8	0	2.548199	-2.093648	1.139076
20	16	0	1.366710	-3.210273	0.974107
21	8	0	0.507711	-2.707072	-0.117733
22	8	0	0.671723	-3.259418	2.264854
23	8	0	2.150877	-4.393502	0.631934

Complex (**S7a**)
M06-2X/6-311+G(d,p)
E=-971.9946206 E+ZPE=-971.812027 In CH_3CN E= -972.075888

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.797780	-0.697659	0.495744
2	6	0	-0.394442	-0.145782	1.663327
3	6	0	1.032890	-0.294874	2.102557
4	6	0	1.227897	-0.319479	3.624387
5	6	0	0.774538	0.989391	4.272079
6	6	0	2.687270	-0.624353	3.952261
7	1	0	-0.405106	-1.601768	0.422607
8	1	0	-0.932205	0.771258	1.887470
9	1	0	-1.140962	-2.128756	2.720630
10	1	0	1.639869	0.532071	1.690121
11	1	0	1.434676	-1.222265	1.686008
12	1	0	0.625655	-1.143997	4.019481
13	1	0	1.338038	1.835326	3.860565
14	1	0	-0.289069	1.176102	4.102736
15	1	0	0.941624	0.969574	5.353037
16	1	0	2.850340	-0.649857	5.033840
17	1	0	3.347617	0.141732	3.528483
18	1	0	2.957444	-1.598369	3.539599
19	8	0	-1.219116	-3.092281	2.816277
20	16	0	0.095178	-3.793328	2.106568
21	8	0	0.140370	-3.175946	0.757305
22	8	0	1.239669	-3.397503	2.931270
23	8	0	-0.242710	-5.203058	2.115460

ωB97XD/6-311+G(d,p)

E=-972.0703063 E+ZPE=-971.888013 In CH_3CN E= -972.1519389

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.774317	-0.714738	0.487293
2	6	0	-0.394299	-0.166342	1.664247
3	6	0	1.030558	-0.290854	2.117041
4	6	0	1.226390	-0.285433	3.639789
5	6	0	0.772864	1.030252	4.274228
6	6	0	2.684399	-0.590901	3.977000
7	1	0	-0.387120	-1.621031	0.420101
8	1	0	-0.951745	0.741181	1.887511
9	1	0	-1.095279	-2.150895	2.704711
10	1	0	1.632578	0.531329	1.684544
11	1	0	1.444381	-1.222384	1.721726
12	1	0	0.622433	-1.102408	4.049253
13	1	0	1.338228	1.874435	3.859092
14	1	0	-0.290424	1.219369	4.100676
15	1	0	0.935457	1.019623	5.357192
16	1	0	2.845068	-0.599476	5.060426
17	1	0	3.352621	0.164348	3.543306
18	1	0	2.956347	-1.572731	3.582867

19	8	0	-1.195596	-3.109336	2.815045
20	16	0	0.084099	-3.850690	2.068115
21	8	0	0.123471	-3.219994	0.724237
22	8	0	1.258151	-3.509481	2.875101
23	8	0	-0.306580	-5.247668	2.068312

Complex (**S7b**)

M06-2X/6-311+G(d,p)

E=-971.9847258 E+ZPE=-971.802900 In CH_3CN E= -972.0684918

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.094125	-0.647566	-0.074743
2	6	0	0.014896	-0.422224	1.315913
3	6	0	1.354147	-0.300321	1.967401
4	6	0	1.497326	-0.391509	3.454138
5	6	0	1.269397	0.983886	4.109158
6	6	0	2.863546	-0.956906	3.850032
7	1	0	0.234278	-1.608454	-0.166581
8	1	0	-0.560765	0.507580	1.454785
9	1	0	-0.538262	-1.230273	1.813364
10	1	0	2.141788	0.188560	1.393632
11	1	0	2.646359	-2.255040	1.146396
12	1	0	0.733539	-1.089110	3.812510
13	1	0	2.035120	1.694132	3.779834
14	1	0	0.291904	1.394440	3.843281
15	1	0	1.323490	0.908290	5.199851
16	1	0	2.984578	-0.954245	4.937628
17	1	0	3.668915	-0.350068	3.419750
18	1	0	2.961590	-1.984079	3.495252
19	8	0	2.760909	-3.216002	1.155403
20	16	0	1.259457	-3.866779	1.414961
21	8	0	0.445858	-3.334521	0.302775
22	8	0	0.845713	-3.336711	2.718989
23	8	0	1.515926	-5.293659	1.358302

ωB97XD/6-311+G(d,p)

E=-972.0580631 E+ZPE=-971.876718 In CH_3CN E= -972.1409885

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.811396	-0.460273	-0.078358
2	6	0	-0.007125	-0.124366	1.040563
3	6	0	0.778556	0.489015	2.153304
4	6	0	1.424384	-0.319642	3.233432
5	6	0	1.360453	0.405518	4.583461
6	6	0	2.887842	-0.644721	2.874065
7	1	0	1.172495	-1.349275	0.091845
8	1	0	-0.752144	0.589679	0.670874
9	1	0	-0.528907	-1.017423	1.404006

10	1	0	1.133671	1.512639	2.018686
11	1	0	2.652137	-3.310933	2.973120
12	1	0	0.880574	-1.267821	3.312275
13	1	0	1.884557	1.367800	4.530998
14	1	0	0.325539	0.600940	4.877661
15	1	0	1.832405	-0.191408	5.371427
16	1	0	3.363347	-1.223721	3.677455
17	1	0	3.468570	0.276060	2.746556
18	1	0	2.940909	-1.213142	1.942560
19	8	0	2.362804	-4.180976	2.681730
20	16	0	1.144830	-3.928586	1.574864
21	8	0	1.745754	-2.972798	0.619457
22	8	0	0.049325	-3.334571	2.347262
23	8	0	0.912462	-5.262576	1.054786

3-Methylbutanol α-radical (**S8a**)

M06-2X/6-311+G(d,p)

E=-272.2655065 E+ZPE=-272.113171 In CH_3CN E= -272.2709309

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.067851	2.894666	0.032268
2	1	0	-3.656805	3.439596	0.888926
3	1	0	-3.806129	3.441952	-0.875632
4	1	0	-5.156925	2.905281	0.120907
5	6	0	-3.538120	1.460012	0.012429
6	1	0	-3.899187	0.970500	-0.899564
7	6	0	-4.059017	0.684553	1.221684
8	1	0	-3.695274	-0.345847	1.219909
9	1	0	-3.725657	1.157226	2.151188
10	1	0	-5.151171	0.659541	1.232619
11	6	0	-2.005066	1.421264	-0.014578
12	1	0	-1.661800	0.381097	-0.007267
13	1	0	-1.626935	1.874575	0.918329
14	6	0	-1.402522	2.086980	-1.199958
15	1	0	-1.660126	3.109394	-1.462070
16	8	0	-0.114215	1.701462	-1.458629
17	1	0	0.237825	2.212077	-2.190962

ωB97XD/6-311+G(d,p)

E=-272.3173238 E+ZPE=-272.165381 In CH_3CN E= -272.3227428

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.065639	2.912883	0.068056
2	1	0	-3.677003	3.431779	0.951540
3	1	0	-3.780706	3.492609	-0.813618
4	1	0	-5.157664	2.923354	0.128451
5	6	0	-3.536705	1.477729	0.015911
6	1	0	-3.907047	1.007901	-0.903521

7	6	0	-4.059542	0.673408	1.206727
8	1	0	-3.724816	-0.366840	1.161851
9	1	0	-3.700315	1.101287	2.149300
10	1	0	-5.152849	0.675344	1.235120
11	6	0	-2.002602	1.430160	-0.018187
12	1	0	-1.665864	0.389191	0.060541
13	1	0	-1.614456	1.936896	0.884060
14	6	0	-1.396850	2.017536	-1.240626
15	1	0	-1.767532	2.945183	-1.671473
16	8	0	-0.055798	1.777774	-1.373765
17	1	0	0.276413	2.228135	-2.150767

3-Methylbutanol β-radical (**S8b**)

M06-2X/6-311+G(d,p)

E=-272.2569451 E+ZPE=-272.105414 In CH_3CN E= -272.2632043

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.133839	2.883697	0.063564
2	1	0	-3.715462	3.376149	0.946178
3	1	0	-3.864598	3.475709	-0.814752
4	1	0	-5.223391	2.887721	0.152094
5	6	0	-3.600841	1.442532	-0.040339
6	1	0	-4.046772	0.998134	-0.943147
7	6	0	-4.038000	0.619941	1.170901
8	1	0	-3.682320	-0.409680	1.094738
9	1	0	-3.629642	1.052885	2.089060
10	1	0	-5.126345	0.602797	1.262034
11	6	0	-2.116352	1.422465	-0.203720
12	1	0	-1.473284	1.074163	0.597489
13	6	0	-1.464486	2.076781	-1.365460
14	1	0	-1.304783	3.150815	-1.166636
15	1	0	-2.123339	2.009418	-2.244868
16	8	0	-0.217838	1.441421	-1.610846
17	1	0	0.274304	1.961808	-2.249312

ωB97XD/6-311+G(d,p)

E=-272.3079442 E+ZPE=-272.156903 In CH_3CN E= -272.3141054

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.140304	2.891622	0.070177
2	1	0	-3.722838	3.392603	0.949219
3	1	0	-3.881386	3.484011	-0.811934
4	1	0	-5.230394	2.889212	0.164246
5	6	0	-3.600916	1.451407	-0.035671
6	1	0	-4.053906	1.009231	-0.937477
7	6	0	-4.034323	0.620280	1.172334
8	1	0	-3.684307	-0.411437	1.085521
9	1	0	-3.621039	1.041359	2.094859

10	1	0	-5.123336	0.604530	1.269666
11	6	0	-2.118055	1.426169	-0.210002
12	1	0	-1.473146	1.054839	0.580730
13	6	0	-1.461862	2.063307	-1.376072
14	1	0	-1.326238	3.146061	-1.195732
15	1	0	-2.108396	1.972174	-2.264546
16	8	0	-0.200834	1.449841	-1.597490
17	1	0	0.294290	1.981546	-2.220852

Structures in Scheme S2-2

3-Methyl-1-methoxybutane (**18-2**)

M06-2X/6-311+G(d,p)

E=-312.2145211 E+ZPE=-312.020122 In CH_3CN E=-312.2182577

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.100186	2.894334	0.041557
2	1	0	-3.631058	3.451728	0.859448
3	1	0	-3.896010	3.427237	-0.889718
4	1	0	-5.180932	2.911401	0.201754
5	6	0	-3.577194	1.456397	0.012487
6	1	0	-3.991842	0.958501	-0.873397
7	6	0	-4.047445	0.695002	1.251432
8	1	0	-3.685946	-0.336128	1.244614
9	1	0	-3.670788	1.176726	2.159289
10	1	0	-5.138166	0.673216	1.311861
11	6	0	-2.050066	1.402601	-0.086602
12	1	0	-1.721342	0.359273	-0.122982
13	1	0	-1.607621	1.844194	0.813965
14	6	0	-1.488541	2.108254	-1.306594
15	1	0	-1.636278	3.195797	-1.237786
16	1	0	-2.002023	1.761040	-2.218124
17	8	0	-0.110432	1.822958	-1.393539
18	6	0	0.500269	2.457181	-2.488064
19	1	0	0.412748	3.549227	-2.415140
20	1	0	1.554617	2.183124	-2.480714
21	1	0	0.051995	2.132503	-3.436450

ωB97XD/6-311+G(d,p)

E=-312.2768240 E+ZPE=-312.082538 In CH_3CN E=-312.2804604

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.111005	2.915249	0.088242
2	1	0	-3.662295	3.448142	0.934143
3	1	0	-3.891892	3.482203	-0.820222
4	1	0	-5.195900	2.923355	0.226785
5	6	0	-3.581109	1.480856	0.017793
6	1	0	-3.999734	1.007367	-0.880559
7	6	0	-4.047153	0.677196	1.232623
8	1	0	-3.702691	-0.359417	1.178937
9	1	0	-3.652657	1.113593	2.156839
10	1	0	-5.138284	0.667718	1.307326
11	6	0	-2.052686	1.428326	-0.089220
12	1	0	-1.724692	0.383495	-0.091314
13	1	0	-1.606610	1.896548	0.796555
14	6	0	-1.488829	2.092336	-1.331131
15	1	0	-1.681755	3.176069	-1.323678
16	1	0	-1.969196	1.679209	-2.234116

17	8	0	-0.100003	1.859598	-1.374590
18	6	0	0.515158	2.447554	-2.489485
19	1	0	0.375414	3.538480	-2.498329
20	1	0	1.581504	2.228064	-2.429143
21	1	0	0.118171	2.038622	-3.430162

Complex (**S5-2**) BuOMe

M06-2X/6-311+G(d,p)

E=-1011.2487578 E+ZPE=-1011.038864 In CH_3CN E=-1011.3263706

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.091594	0.608335	0.080359
2	6	0	0.330742	-0.234971	1.141427
3	6	0	1.231197	0.564047	2.062967
4	6	0	1.754433	-0.250712	3.251425
5	6	0	0.631001	-0.630352	4.217377
6	6	0	2.844856	0.531751	3.984738
7	1	0	-0.546382	-0.625341	1.672776
8	1	0	0.864722	-1.104359	0.739375
9	1	0	0.684077	1.441597	2.432250
10	1	0	2.074297	0.941045	1.472060
11	1	0	2.183685	-1.180843	2.861787
12	1	0	0.127599	0.273038	4.583395
13	1	0	-0.106927	-1.280425	3.745701
14	1	0	1.033918	-1.166364	5.081804
15	1	0	3.239813	-0.039912	4.829473
16	1	0	2.439965	1.471782	4.377331
17	1	0	3.677770	0.777912	3.319800
18	8	0	0.709542	-3.289383	2.196643
19	16	0	-0.569811	-3.725226	1.476345
20	8	0	-0.628383	-3.188529	0.118869
21	8	0	-0.800014	-5.158420	1.576881
22	8	0	-1.448724	-2.923943	2.438120
23	6	0	-0.932020	-0.086934	-0.812057
24	1	0	-1.205495	0.607234	-1.609180
25	1	0	-0.430213	-0.966762	-1.229162
26	1	0	-1.837482	-0.443941	-0.305197

ωB97XD/6-311+G(d,p)

E=-1011.3398654 E+ZPE=-1011.129963 In CH_3CN E=-1011.4181510

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.049938	0.619353	0.045466
2	6	0	0.284333	-0.185893	1.164850
3	6	0	1.239402	0.583522	2.055572
4	6	0	1.743126	-0.231281	3.253877
5	6	0	0.613580	-0.597873	4.218188
6	6	0	2.850308	0.531549	3.983636

7	1	0	-0.629443	-0.466754	1.704393
8	1	0	0.746203	-1.121769	0.827917
9	1	0	0.749583	1.499935	2.412916
10	1	0	2.093561	0.899781	1.444281
11	1	0	2.161572	-1.168377	2.868401
12	1	0	0.100702	0.307244	4.569422
13	1	0	-0.118798	-1.258029	3.750673
14	1	0	1.010817	-1.121040	5.094087
15	1	0	3.251081	-0.055553	4.816274
16	1	0	2.464551	1.472924	4.394698
17	1	0	3.678800	0.775477	3.310462
18	8	0	0.817867	-3.462958	2.139609
19	16	0	-0.494635	-3.847845	1.456090
20	8	0	-0.534752	-3.366653	0.075903
21	8	0	-0.796841	-5.264627	1.611570
22	8	0	-1.339179	-2.975000	2.379835
23	6	0	-0.966263	-0.035712	-0.798511
24	1	0	-1.097111	0.588741	-1.685847
25	1	0	-0.608631	-1.031675	-1.085747
26	1	0	-1.939321	-0.167166	-0.302712

TS (**S6a-2**) BuOMe

M06-2X/6-311+G(d,p)

E=-1011.2336517 E+ZPE=-1011.027612 In CH_3CN E=-1011.3234586

Imaginary frequency: -906.4701

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.107594	0.416075	0.136427
2	6	0	-0.118614	0.091573	1.483299
3	6	0	1.272342	0.140489	2.062738
4	6	0	1.320479	-0.254146	3.542766
5	6	0	0.785649	0.859508	4.446014
6	6	0	2.747956	-0.633947	3.928301
7	1	0	-0.874722	0.678539	2.032240
8	1	0	-0.515409	-1.020804	1.628000
9	1	0	1.690117	1.148443	1.923741
10	1	0	1.879647	-0.558405	1.480761
11	1	0	0.700831	-1.148876	3.662352
12	1	0	1.410374	1.756232	4.358318
13	1	0	-0.240118	1.138968	4.190887
14	1	0	0.793236	0.548286	5.494826
15	1	0	2.815433	-0.889084	4.990331
16	1	0	3.434912	0.199208	3.735679
17	1	0	3.060459	-1.499856	3.341645
18	8	0	-0.894055	-2.365392	1.810332
19	16	0	0.327492	-3.271148	1.213540
20	8	0	0.512195	-2.808562	-0.165265
21	8	0	1.485402	-3.013173	2.078176
22	8	0	-0.261869	-4.604766	1.356693
23	6	0	-1.258182	-0.035208	-0.549580

24	1	0	-1.194108	0.350569	-1.566957
25	1	0	-1.273876	-1.128675	-0.564307
26	1	0	-2.171297	0.346153	-0.071690

ωB97XD/6-311+G(d,p)
E=-1011.3226040 E+ZPE=-1011.117416 In CH_3CN E=-1011.4155507
Imaginary frequency: -1195.9967

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.065173	0.318506	0.088064
2	6	0	0.014087	0.097091	1.447711
3	6	0	1.393194	0.139839	2.053905
4	6	0	1.446889	-0.303442	3.519877
5	6	0	0.606330	0.590703	4.433675
6	6	0	2.899956	-0.350976	3.988995
7	1	0	-0.734844	0.744388	1.935833
8	1	0	-0.441910	-1.006485	1.677981
9	1	0	1.801601	1.157600	1.952246
10	1	0	2.016619	-0.536316	1.462534
11	1	0	1.048029	-1.321312	3.557514
12	1	0	0.911599	1.641401	4.342864
13	1	0	-0.459046	0.524722	4.197593
14	1	0	0.726285	0.297161	5.481695
15	1	0	2.969361	-0.705278	5.022689
16	1	0	3.362583	0.643603	3.941987
17	1	0	3.481474	-1.030054	3.360208
18	8	0	-0.902356	-2.241849	2.005172
19	16	0	0.011199	-3.346748	1.217175
20	8	0	-0.251452	-3.138031	-0.211519
21	8	0	1.398543	-3.062443	1.606595
22	8	0	-0.546276	-4.582621	1.774533
23	6	0	-1.146239	0.029314	-0.581934
24	1	0	-1.021013	0.357098	-1.614825
25	1	0	-1.337485	-1.048131	-0.556205
26	1	0	-1.985623	0.574258	-0.125095

TS (**S6b-2**)
M06-2X/6-311+G(d,p)
E=-1011.2299407 E+ZPE=-1011.024505 In CH_3CN E=-1011.3191043
Imaginary frequency: -1266.0671

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.221214	0.516121	0.212667
2	6	0	-0.177026	0.014855	1.532327
3	6	0	1.234533	0.097410	2.052561
4	6	0	1.398957	-0.187522	3.536472
5	6	0	0.985048	1.035418	4.367402
6	6	0	2.836964	-0.591883	3.859921
7	1	0	-0.857011	0.604351	2.172810
8	1	0	-0.507375	-1.030653	1.559803

9	1	0	1.736251	1.018723	1.732481
10	1	0	1.850045	-0.756658	1.436516
11	1	0	0.752677	-1.036138	3.781953
12	1	0	1.645660	1.882441	4.152201
13	1	0	-0.041145	1.347146	4.157805
14	1	0	1.059500	0.814550	5.436288
15	1	0	2.960914	-0.748582	4.935655
16	1	0	3.535669	0.192772	3.546704
17	1	0	3.090820	-1.514801	3.337861
18	8	0	2.423632	-1.826924	0.874411
19	16	0	1.408898	-3.095268	1.062275
20	8	0	0.256397	-2.842617	0.187941
21	8	0	1.055314	-3.090653	2.488544
22	8	0	2.280345	-4.188230	0.632148
23	6	0	-1.251057	-0.072202	-0.549639
24	1	0	-1.192020	0.355052	-1.551850
25	1	0	-1.114260	-1.156754	-0.597547
26	1	0	-2.239325	0.160047	-0.124320

ωB97XD/6-311+G(d,p)
E=-1011.3202954 E+ZPE=-1011.11469 In CH_3CN E=-1011.4078972
Imaginary frequency: -1611.5694

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.773049	0.801350	0.465832
2	6	0	-0.487726	0.229009	1.725750
3	6	0	0.991799	0.121245	2.031297
4	6	0	1.371753	-0.206242	3.467097
5	6	0	0.976045	0.927285	4.425230
6	6	0	2.869152	-0.497074	3.576149
7	1	0	-0.960645	0.898119	2.454346
8	1	0	-0.948221	-0.764472	1.814955
9	1	0	1.556488	0.969449	1.623062
10	1	0	1.428876	-0.830767	1.348253
11	1	0	0.839273	-1.120263	3.752116
12	1	0	1.460811	1.867346	4.135619
13	1	0	-0.103433	1.097379	4.447920
14	1	0	1.294303	0.687142	5.444797
15	1	0	3.140242	-0.726993	4.611428
16	1	0	3.456508	0.372825	3.255027
17	1	0	3.133949	-1.354897	2.957020
18	8	0	1.836528	-1.873221	0.705305
19	16	0	1.069186	-3.215209	1.259641
20	8	0	-0.367128	-2.945887	1.099465
21	8	0	1.476347	-3.361387	2.661241
22	8	0	1.616301	-4.214457	0.341849
23	6	0	-0.535357	-0.072852	-0.623556
24	1	0	-0.978098	0.399171	-1.503716
25	1	0	0.535239	-0.231353	-0.792926
26	1	0	-0.987952	-1.055246	-0.449810

Complex (**S7a-2**)

M06-2X/6-311+G(d,p)

E=-1011.2654801 E+ZPE=-1011.056042 In CH_3CN E=-1011.3498358

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.181087	-0.254208	0.240565
2	6	0	0.408617	-0.557174	1.430004
3	6	0	1.067684	0.601920	2.091183
4	6	0	1.836821	0.213770	3.359109
5	6	0	0.891040	-0.271486	4.459037
6	6	0	2.673941	1.394779	3.851718
7	1	0	-0.013825	-1.387936	1.993507
8	1	0	-0.807617	-5.379657	2.449219
9	1	0	0.320993	1.372152	2.358247
10	1	0	1.746573	1.079447	1.371609
11	1	0	2.513966	-0.608509	3.097260
12	1	0	0.179563	0.523544	4.711276
13	1	0	0.322702	-1.156115	4.163959
14	1	0	1.450737	-0.518005	5.366574
15	1	0	3.240925	1.129087	4.748472
16	1	0	2.023801	2.238922	4.106992
17	1	0	3.380299	1.734256	3.088336
18	8	0	-1.555429	-5.296828	3.050493
19	16	0	-1.943743	-3.678640	3.084257
20	8	0	-0.667479	-3.019454	3.405174
21	8	0	-2.404707	-3.382565	1.722348
22	8	0	-2.959684	-3.626599	4.121048
23	6	0	-0.874223	-1.346543	-0.346994
24	1	0	-1.407281	-0.951753	-1.212090
25	1	0	-0.159335	-2.109333	-0.675584
26	1	0	-1.572183	-1.802322	0.360420

ωB97XD/6-311+G(d,p)

E=-1011.3514550 E+ZPE=-1011.142577 In CH_3CN E= -1011.4355788

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.185149	-0.264048	0.246829
2	6	0	0.474473	-0.569622	1.397810
3	6	0	1.066916	0.604650	2.092189
4	6	0	1.842468	0.234156	3.363908
5	6	0	0.914904	-0.301237	4.456853
6	6	0	2.639335	1.438827	3.868385
7	1	0	0.128734	-1.448126	1.941676
8	1	0	-1.009941	-5.460096	2.412911
9	1	0	0.276389	1.329049	2.364630
10	1	0	1.728992	1.139984	1.395969
11	1	0	2.553443	-0.558939	3.099214

12	1	0	0.172366	0.460185	4.725764
13	1	0	0.378072	-1.200997	4.146944
14	1	0	1.483412	-0.544584	5.361225
15	1	0	3.204251	1.188021	4.772225
16	1	0	1.964576	2.266439	4.118261
17	1	0	3.346839	1.799041	3.113957
18	8	0	-1.679866	-5.299674	3.082885
19	16	0	-1.937062	-3.648361	3.088451
20	8	0	-0.592145	-3.083032	3.283264
21	8	0	-2.486624	-3.358182	1.757751
22	8	0	-2.855723	-3.485594	4.201675
23	6	0	-0.852217	-1.366647	-0.348884
24	1	0	-1.443356	-0.966699	-1.174514
25	1	0	-0.120374	-2.084031	-0.741365
26	1	0	-1.501642	-1.879736	0.368124

Complex (**S7b-2**)

M06-2X/6-311+G(d,p)

E=-1011.2601967 E+ZPE=-1011.05092 In CH_3CN E=-1011.3446361

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.679689	0.124181	0.000289
2	6	0	-0.098097	-0.273168	1.131570
3	6	0	0.394270	0.437096	2.341815
4	6	0	1.262377	-0.275145	3.328079
5	6	0	1.572736	0.595838	4.543788
6	6	0	2.557857	-0.754328	2.646884
7	1	0	-1.154432	-0.027623	0.930642
8	1	0	-0.017767	-1.357282	1.274490
9	1	0	0.322503	1.521790	2.369934
10	1	0	2.902503	-3.442156	2.556502
11	1	0	0.734383	-1.183519	3.645075
12	1	0	2.126937	1.491930	4.242308
13	1	0	0.654394	0.917484	5.042538
14	1	0	2.182439	0.051642	5.270062
15	1	0	3.159465	-1.335226	3.356225
16	1	0	3.153852	0.100008	2.309361
17	1	0	2.327521	-1.370897	1.773025
18	8	0	2.525299	-4.324663	2.462896
19	16	0	1.018251	-4.117926	1.793142
20	8	0	1.278320	-3.364143	0.555781
21	8	0	0.283192	-3.324744	2.787939
22	8	0	0.566341	-5.486885	1.614364
23	6	0	0.399742	-0.691993	-1.117084
24	1	0	1.043908	-0.356830	-1.931690
25	1	0	0.600183	-1.743878	-0.889437
26	1	0	-0.650288	-0.580363	-1.428273

ωB97XD/6-311+G(d,p)

E=-1011.3437434 E+ZPE=-1011.135341 In CH_3CN E=-1011.4281517

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.641557	0.145939	-0.037839
2	6	0	-0.101651	-0.257384	1.115832
3	6	0	0.426148	0.436122	2.318350
4	6	0	1.314350	-0.280449	3.281951
5	6	0	1.561583	0.535456	4.550114
6	6	0	2.644386	-0.668771	2.604123
7	1	0	-1.165029	-0.008531	0.951742
8	1	0	-0.023308	-1.342259	1.247647
9	1	0	0.342465	1.520897	2.369445
10	1	0	2.791755	-3.434432	2.720940
11	1	0	0.820702	-1.225661	3.544689
12	1	0	2.071180	1.478003	4.314575
13	1	0	0.620370	0.776968	5.053239
14	1	0	2.189795	-0.018286	5.254893
15	1	0	3.276298	-1.225939	3.307808
16	1	0	3.196674	0.222357	2.286403
17	1	0	2.462645	-1.286825	1.720648
18	8	0	2.422085	-4.318293	2.634462
19	16	0	0.970837	-4.137348	1.828104
20	8	0	1.331973	-3.387359	0.614413
21	8	0	0.134955	-3.354120	2.748179
22	8	0	0.559372	-5.515124	1.620606
23	6	0	0.381690	-0.697898	-1.136016
24	1	0	1.012726	-0.357764	-1.960557
25	1	0	0.615591	-1.741449	-0.894815
26	1	0	-0.673566	-0.628650	-1.448712

3-Methyl-1-methoxybutane α-radical (**S8a-2**)

M06-2X/6-311+G(d,p)

E=-311.5555312 E+ZPE=-311.374945 In CH_3CN E=-311.5589352

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.093471	2.883705	0.034382
2	1	0	-3.698868	3.434609	0.894991
3	1	0	-3.831253	3.434802	-0.871078
4	1	0	-5.183370	2.877365	0.113174
5	6	0	-3.541283	1.457652	0.018753
6	1	0	-3.890718	0.961343	-0.894098
7	6	0	-4.054001	0.675701	1.227293
8	1	0	-3.674841	-0.349141	1.227858
9	1	0	-3.730768	1.154462	2.157273
10	1	0	-5.145735	0.634212	1.234982
11	6	0	-2.007377	1.444212	-0.003342
12	1	0	-1.646537	0.410552	0.004332
13	1	0	-1.641527	1.904751	0.930621

14	6	0	-1.414214	2.121730	-1.188436
15	1	0	-1.665082	3.151406	-1.439267
16	8	0	-0.145510	1.737541	-1.482519
17	6	0	0.436989	2.421065	-2.573762
18	1	0	0.477557	3.498130	-2.378191
19	1	0	1.447721	2.035353	-2.691060
20	1	0	-0.134919	2.240290	-3.488972

ωB97XD/6-311+G(d,p)

E=-311.6145370 E+ZPE=-311.434329 In CH_3CN E=-311.6178783

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.078552	2.921146	0.110036
2	1	0	-3.678351	3.421390	0.999093
3	1	0	-3.801510	3.517529	-0.762938
4	1	0	-5.169793	2.933118	0.183293
5	6	0	-3.553738	1.486206	0.023657
6	1	0	-3.940077	1.033324	-0.897733
7	6	0	-4.058565	0.661984	1.208741
8	1	0	-3.732458	-0.379434	1.136576
9	1	0	-3.677079	1.068832	2.151927
10	1	0	-5.151021	0.670983	1.259797
11	6	0	-2.020586	1.436519	-0.035487
12	1	0	-1.684657	0.394492	0.028413
13	1	0	-1.617735	1.934550	0.864694
14	6	0	-1.434899	2.036328	-1.263193
15	1	0	-1.822851	2.959277	-1.694451
16	8	0	-0.103016	1.824165	-1.415313
17	6	0	0.475215	2.435700	-2.548579
18	1	0	0.322267	3.521852	-2.527354
19	1	0	1.543041	2.222653	-2.516905
20	1	0	0.047159	2.029124	-3.471341

3-Methyl-1-methoxybutane β-radical (**S8b-2**)

M06-2X/6-311+G(d,p)

E=-311.5470887 E+ZPE=-311.367488 In CH_3CN E=-311.5513094

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.094721	2.986143	0.379445
2	1	0	-3.686312	3.242763	1.360868
3	1	0	-3.769842	3.748652	-0.331916
4	1	0	-5.185737	3.021200	0.443784
5	6	0	-3.616290	1.583340	-0.040480
6	1	0	-4.065830	1.357629	-1.016746
7	6	0	-4.095159	0.536562	0.968909
8	1	0	-3.802107	-0.469392	0.662484
9	1	0	-3.652786	0.732169	1.950449
10	1	0	-5.182138	0.564356	1.077985

11	6	0	-2.129787	1.544244	-0.186898
12	1	0	-1.501332	1.489221	0.696232
13	6	0	-1.484552	1.947035	-1.461258
14	1	0	-1.753412	2.988054	-1.729851
15	1	0	-1.847963	1.315499	-2.292074
16	8	0	-0.086212	1.837270	-1.344264
17	6	0	0.579599	2.230840	-2.516923
18	1	0	0.367962	3.280205	-2.761140
19	1	0	1.648124	2.113877	-2.341533
20	1	0	0.285698	1.606187	-3.370591

ωB97XD/6-311+G(d,p)

E=-311.6055387 E+ZPE=-311.426374 In CH_3CN E=-311.6095991

No imaginary frequencies:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-4.093782	2.976266	0.326542
2	1	0	-3.668228	3.288695	1.285132
3	1	0	-3.793143	3.706051	-0.429681
4	1	0	-5.184471	3.007640	0.412136
5	6	0	-3.615697	1.555372	-0.036857
6	1	0	-4.078041	1.295341	-0.999891
7	6	0	-4.092588	0.546926	1.011601
8	1	0	-3.809706	-0.472737	0.739100
9	1	0	-3.645790	0.770401	1.986191
10	1	0	-5.179745	0.583447	1.125713
11	6	0	-2.131992	1.507357	-0.200048
12	1	0	-1.494595	1.348285	0.664807
13	6	0	-1.485349	1.970074	-1.450367
14	1	0	-1.710855	3.040546	-1.638311
15	1	0	-1.893585	1.421733	-2.320860
16	8	0	-0.092944	1.790427	-1.368086
17	6	0	0.580254	2.241388	-2.513054
18	1	0	0.412669	3.315247	-2.681881
19	1	0	1.644944	2.069609	-2.354353
20	1	0	0.259848	1.693786	-3.411352

Structures in Scheme S3

Transition state (**19a**)

ωB97XD/6-311+G(d,p)

E= -349.7047303 E+ZPE= -349.524353 In CH_3CN E= -349.7125582

Imaginary frequency: -1526.5415

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.532554
3	6	0	1.493962	0.000000	1.913697
4	6	0	2.128915	-0.851284	0.831690
5	6	0	1.300400	-0.698419	-0.392487
6	8	0	1.587060	-1.074964	-1.506973
7	1	0	-0.859979	-0.486342	-0.463333
8	1	0	0.051059	1.020018	-0.398806
9	1	0	-0.542838	0.843029	1.962669
10	1	0	-0.468993	-0.915824	1.906459
11	1	0	1.669488	-0.385914	2.920956
12	1	0	1.897143	1.019464	1.881857
13	1	0	3.206073	-0.818115	0.681119
14	1	0	1.926378	-2.076112	1.167069
15	6	0	1.636424	-3.409021	1.532911
16	6	0	0.446639	-3.781962	0.693176
17	1	0	2.571076	-3.911626	1.290393
18	1	0	1.465912	-3.320418	2.605313
19	1	0	-0.425465	-3.169816	0.940143
20	1	0	0.658461	-3.654755	-0.371330
21	1	0	0.165035	-4.829664	0.852875

Transition state (**19b**)

ωB97XD/6-311+G(d,p)

E= -349.6971395 E+ZPE= -349.517457 In CH_3CN E= -349.7041124

Imaginary frequency: -1703.6332

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.531913
3	6	0	1.479018	0.000000	1.894527
4	6	0	2.190212	0.811330	0.832793
5	6	0	1.290366	0.708743	-0.396170
6	8	0	1.557357	1.117426	-1.495161
7	1	0	0.069749	-1.021948	-0.391465
8	1	0	-0.863129	0.471759	-0.470892
9	1	0	-0.486313	0.907758	1.911430
10	1	0	-0.533646	-0.852424	1.958925
11	1	0	1.889341	-1.247530	1.715448
12	1	0	1.727031	0.214836	2.933090
13	1	0	2.271948	1.873874	1.098008
14	1	0	3.200602	0.468558	0.592325
15	6	0	2.392583	-2.493046	1.490492

16	6	0	3.689827	-2.559912	2.257134
17	1	0	2.496190	-2.539922	0.405512
18	1	0	1.606928	-3.158463	1.849777
19	1	0	4.395548	-1.799063	1.911472
20	1	0	4.178780	-3.533929	2.139576
21	1	0	3.526953	-2.403445	3.327101

Ethyl radical (**S9**)

ωB97XD/6-311+G(d,p)

E=-79.1512985 E+ZPE=-79.091636 In CH_3CN E=-79.151994

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.141386	-3.793705	1.457200
2	6	0	-0.052659	-4.036045	0.607190
3	1	0	-0.953009	-3.586412	1.033301
4	1	0	0.083815	-3.638756	-0.403735
5	1	0	-0.256969	-5.111893	0.491455
6	1	0	2.139652	-3.903876	1.050588
7	1	0	1.044583	-3.629815	2.523418

Complex (**S10**) involving Et radical

ωB97XD/6-311+G(d,p)

E=-349.7215766 E+ZPE=-349.538149 In CH_3CN E=-349.7281954

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.122762	-0.520140	0.161568
2	6	0	0.184524	-0.218676	1.659928
3	6	0	1.602791	0.347336	1.860576
4	6	0	2.474875	-0.495339	0.924684
5	6	0	1.545078	-0.921673	-0.205845
6	8	0	1.879624	-1.483932	-1.216353
7	1	0	-0.592607	-1.286028	-0.137906
8	1	0	-0.107760	0.387897	-0.410289
9	1	0	-0.594430	0.468444	1.994166
10	1	0	0.076057	-1.150363	2.224910
11	1	0	1.928511	0.304292	2.901090
12	1	0	1.627454	1.398004	1.552527
13	1	0	3.358353	0.008160	0.528793
14	1	0	2.812984	-1.413320	1.417476
15	6	0	1.138323	-3.780746	1.456235
16	6	0	-0.053058	-4.032200	0.606438
17	1	0	-0.952760	-3.563708	1.016946
18	1	0	0.102232	-3.665850	-0.412531
19	1	0	-0.269021	-5.108796	0.524180
20	1	0	2.133744	-3.861569	1.035615
21	1	0	1.047340	-3.687633	2.532535

Complex (**S11a**) involving EtH

ωB97XD/6-311+G(d,p)

E=-349.7380412 E+ZPE=-349.552941 In CH_3CN E=-349.7462419

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.091155	-0.259469	-0.051421
2	6	0	0.028380	-0.197616	1.480595
3	6	0	1.491697	0.025400	1.934040
4	6	0	2.303411	-0.540234	0.827026
5	6	0	1.508659	-0.741541	-0.356882
6	8	0	1.897418	-1.198627	-1.421828
7	1	0	-0.653307	-0.913481	-0.507353
8	1	0	-0.027870	0.732931	-0.501570
9	1	0	-0.643717	0.577217	1.851208
10	1	0	-0.326055	-1.154736	1.872765
11	1	0	1.716284	-0.432476	2.902374
12	1	0	1.710853	1.098185	2.047995
13	6	0	1.476199	-3.784138	1.571335
14	6	0	0.124725	-3.980461	0.891537
15	1	0	-0.169057	-3.092126	0.327080
16	1	0	0.155980	-4.813873	0.185665
17	1	0	-0.662114	-4.190502	1.621349
18	1	0	3.364442	-0.752951	0.867159
19	1	0	2.251763	-3.543458	0.840090
20	1	0	1.441116	-2.968748	2.300325
21	1	0	1.786439	-4.686600	2.104742

Complex (**S11b**) involving EtH

ωB97XD/6-311+G(d,p)

E=-349.7263756 E+ZPE=-349.542707 In CH_3CN E=-349.7328857

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.136544	-0.223667	0.173129
2	6	0	0.066883	-0.333114	1.691733
3	6	0	1.551856	-0.292858	1.887990
4	6	0	2.295142	-0.521504	0.621966
5	6	0	1.221453	-0.496487	-0.463689
6	8	0	1.418037	-0.660871	-1.638201
7	1	0	-0.880078	-0.908925	-0.236811
8	1	0	-0.432519	0.787675	-0.124337
9	1	0	-0.443816	0.463095	2.242884
10	1	0	-0.350807	-1.277419	2.072574
11	6	0	1.324318	-3.920812	1.831435
12	6	0	0.507389	-3.818859	0.546684
13	1	0	1.034221	-3.249987	-0.223943
14	1	0	0.298806	-4.807779	0.130774
15	1	0	-0.454667	-3.329348	0.723524
16	1	0	3.060359	0.233534	0.400805
17	1	0	2.289106	-4.401712	1.649505

18	1	0	1.521647	-2.934127	2.260396
19	1	0	0.799654	-4.509886	2.588325
20	1	0	2.813863	-1.491536	0.579354
21	1	0	2.021954	-0.215098	2.859444

Ethane (**S12**)

ωB97XD/6-311+G(d,p)

E=-79.8251086 E+ZPE=-79.750133 In CH_3CN E=-79.8253251

No imaginary frequencies:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	1.141241	-3.781926	1.458619
2	6	0	-0.081457	-4.046162	0.584452
3	1	0	-0.970095	-3.551650	0.985553
4	1	0	0.071521	-3.676792	-0.433068
5	1	0	-0.298843	-5.115495	0.518654
6	1	0	2.029981	-4.276151	1.057351
7	1	0	0.988416	-4.151599	2.476066
8	1	0	1.358445	-2.712563	1.524721

Structures in Table 6 and Scheme S4

Hydroxyl radical (**20**)

M06-2X/6-311+G(d,p)

E=-75.7265085 E+ZPE=-75.717920 In CH_3CN E=-75.7316729

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	-0.035993
2	1	0	0.000000	0.000000	0.935993

ωB97XD/6-311+G(d,p)

E=-75.7342809 E+ZPE=-75.725643 In CH_3CN E=-75.7394313

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	-0.035411
2	1	0	0.000000	0.000000	0.935411

Methoxyl radical (**21**)

M06-2X/6-311+G(d,p)

E=-115.0304059 E+ZPE=-114.993043 In CH_3CN E=-115.0347634

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.037629	-0.000007	0.023690
2	6	0	-0.037044	0.000017	1.390073
3	1	0	1.011553	-0.000020	1.737285
4	1	0	-0.506084	0.907489	1.788813
5	1	0	-0.506054	-0.907479	1.788805

ωB97XD/6-311+G(d,p)

E=-115.0480053 E+ZPE=-115.011174 In CH_3CN E=-115.0525151

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.039549	-0.000019	0.027122
2	6	0	-0.039934	0.000049	1.383902
3	1	0	1.010144	-0.000060	1.736590
4	1	0	-0.504924	0.909604	1.790536
5	1	0	-0.504835	-0.909574	1.790517

Hydroperoxyl radical (**22**)

M06-2X/6-311+G(d,p)

E=-150.890510 E+ZPE=-150.875901 In CH_3CN E=-150.8971388

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.032266	0.000000	0.048237
2	8	0	0.003426	0.000000	1.354764
3	1	0	0.893976	0.000000	-0.251075

ωB97XD/6-311+G(d,p)
E=-150.9048625 E+ZPE=-150.890308 In CH_3CN E=-150.9114912
No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.032600	0.000000	0.045491
2	8	0	0.004265	0.000000	1.356188
3	1	0	0.893470	0.000000	-0.249753

Methylperoxyl radical (**23**)
M06-2X/6-311+G(d,p)
E=-190.1880445 E+ZPE=-190.144482 In CH_3CN E=-190.1935556
No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.019342	-0.000004	0.054885
2	8	0	-0.066137	0.000003	1.349135
3	6	0	1.388074	0.000000	-0.380646
4	1	0	1.877713	-0.896735	-0.002272
5	1	0	1.877710	0.896734	-0.002268
6	1	0	1.351580	0.000001	-1.467850

ωB97XD/6-311+G(d,p)
E=-190.2095563 E+ZPE=-190.166154 In CH_3CN E=-190.2150569
No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.018505	-0.000002	0.054869
2	8	0	-0.073465	0.000001	1.352973
3	6	0	1.389160	0.000000	-0.379777
4	1	0	1.882167	-0.897463	-0.004482
5	1	0	1.882165	0.897463	-0.004480
6	1	0	1.349751	0.000001	-1.468117

Carbonate radical anion (**24**)
M06-2X/6-311+G(d,p)
E=-263.7861624 E+ZPE=-263.773457 In CH_3CN E=-263.8814942
No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.584443	5.058817	2.734128
2	6	0	0.131523	4.085145	2.291243
3	8	0	1.363391	4.021005	2.326475
4	8	0	-0.656359	3.190956	1.806134

ωB97XD/6-311+G(d,p)
E=-263.8033066 E+ZPE=-263.791692 In CH_3CN E=-263.8982952
No imaginary frequencies:

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	8	0	-0.532117	5.102325	2.758476
2	6	0	0.063071	4.089297	2.289573
3	8	0	1.326432	4.024304	2.326178
4	8	0	-0.603275	3.139997	1.783752

Complex (**S13**) involving OH radical

M06-2X/6-311+G(d,p)

E=-346.2643235 E+ZPE=-346.131046 In CH_3CN E=-346.2723331

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.220331	1.036287	0.341835
2	6	0	0.379787	0.734964	1.825303
3	6	0	1.591730	-0.200039	1.896960
4	6	0	2.461910	0.234847	0.702485
5	6	0	1.439674	0.520702	-0.402221
6	8	0	-0.718990	1.601165	-0.164542
7	1	0	0.580087	1.690502	2.324989
8	1	0	2.119960	-0.140759	2.848025
9	1	0	1.270000	-1.236306	1.758434
10	1	0	3.197997	-0.517354	0.419824
11	1	0	3.001988	1.152158	0.954577
12	1	0	1.134529	-0.407023	-0.901025
13	1	0	1.751420	1.223677	-1.174362
14	8	0	-2.163128	2.284221	2.147560
15	1	0	-0.546426	0.341301	2.248368
16	1	0	-1.922633	2.197852	1.200456

ωB97XD/6-311+G(d,p)

E=-346.3107062 E+ZPE=-346.177203 In CH_3CN E=-346.3194698

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.269280	1.107658	0.428981
2	6	0	0.500622	0.789543	1.894917
3	6	0	1.648031	-0.224265	1.891015
4	6	0	2.481577	0.167571	0.657200
5	6	0	1.430329	0.564699	-0.383976
6	8	0	-0.685016	1.695482	-0.026434
7	1	0	0.806718	1.727609	2.375319
8	1	0	2.228657	-0.214901	2.814171
9	1	0	1.248904	-1.235789	1.763196
10	1	0	3.137596	-0.634849	0.317616
11	1	0	3.113186	1.029311	0.896580
12	1	0	1.053487	-0.314346	-0.921203
13	1	0	1.754111	1.287373	-1.134033
14	8	0	-2.694849	2.197108	1.913206
15	1	0	-0.421530	0.470252	2.382301
16	1	0	-2.072869	2.103740	1.157811

Complex (**S14**) involving OMe radical

M06-2X/6-311+G(d,p)

E=-385.559623 E+ZPE=-385.39926 In CH_3CN E=-385.5678747

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.980806	0.391105	0.120295
2	6	0	1.112242	0.204369	1.627460
3	6	0	2.417054	-0.577962	1.803003
4	6	0	3.291249	-0.091120	0.631806
5	6	0	2.304576	0.015456	-0.534793
6	8	0	-0.004003	0.771796	-0.455535
7	1	0	1.196103	1.206597	2.064008
8	1	0	2.885508	-0.420240	2.774332
9	1	0	2.225370	-1.649864	1.696162
10	1	0	4.129506	-0.756337	0.425575
11	1	0	3.699739	0.896854	0.864674
12	1	0	2.155858	-0.960256	-1.011974
13	1	0	2.566839	0.727685	-1.316970
14	1	0	0.217912	-0.261164	2.041320
15	8	0	-3.632292	2.326302	-2.096333
16	6	0	-2.399802	1.816811	-1.794818
17	1	0	-1.581583	2.516712	-1.999729
18	1	0	-2.397039	1.653811	-0.702498
19	1	0	-2.213611	0.837408	-2.250419

ωB97XD/6-311+G(d,p)

E=-385.6163033 E+ZPE=-385.456312 In CH_3CN E=-385.6249292

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.973671	0.437312	0.288888
2	6	0	1.199314	0.175674	1.771367
3	6	0	2.499613	-0.630723	1.830736
4	6	0	3.303388	-0.126658	0.617918
5	6	0	2.242306	0.069943	-0.468848
6	8	0	-0.039007	0.863524	-0.204753
7	1	0	1.319776	1.154384	2.251909
8	1	0	3.035561	-0.509136	2.772990
9	1	0	2.282943	-1.697376	1.711115
10	1	0	4.095945	-0.815382	0.322328
11	1	0	3.773659	0.832619	0.857732
12	1	0	2.037500	-0.870826	-0.994375
13	1	0	2.475669	0.820106	-1.225527
14	1	0	0.327048	-0.300636	2.220891
15	8	0	-3.765407	2.278523	-1.994224
16	6	0	-2.480984	1.840802	-2.011902
17	1	0	-1.767982	2.592581	-2.380090
18	1	0	-2.203474	1.656706	-0.955341

19	1	0	-2.355108	0.876522	-2.525248

Complex (**S15**) involving OOH radcial

M06-2X/6-311+G(d,p)

E=-421.4345566 E+ZPE=-421.29547 In CH_3CN E=-421.4431458

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.393425	1.205405	0.571165
2	6	0	0.986772	0.989454	1.948571
3	6	0	1.954981	-0.183570	1.762008
4	6	0	2.445369	-0.025814	0.310883
5	6	0	1.186917	0.409762	-0.447375
6	8	0	-0.562565	1.901012	0.308245
7	1	0	1.529510	1.908957	2.202121
8	1	0	2.769171	-0.183262	2.485913
9	1	0	1.415949	-1.129478	1.867806
10	1	0	2.889843	-0.937064	-0.088309
11	1	0	3.200468	0.764110	0.260307
12	1	0	0.570700	-0.457007	-0.715279
13	1	0	1.349254	0.989501	-1.356003
14	8	0	-1.762894	2.311842	3.197626
15	1	0	0.201869	0.864164	2.694685
16	8	0	-2.007957	3.137090	2.215456
17	1	0	-1.517774	2.766334	1.438088

ωB97XD/6-311+G(d,p)

E=-421.4884510 E+ZPE=-421.348961 In CH_3CN E=-421.4970768

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.403562	1.225413	0.554827
2	6	0	0.990537	1.015435	1.933332
3	6	0	1.950688	-0.166167	1.766744
4	6	0	2.437506	-0.043932	0.311519
5	6	0	1.190919	0.413607	-0.453008
6	8	0	-0.547183	1.929213	0.285598
7	1	0	1.536839	1.934574	2.182966
8	1	0	2.767712	-0.154850	2.488775
9	1	0	1.408442	-1.107818	1.899424
10	1	0	2.857190	-0.973306	-0.075247
11	1	0	3.216533	0.722321	0.244509
12	1	0	0.559666	-0.440855	-0.727986
13	1	0	1.372823	0.985394	-1.363919
14	8	0	-1.840385	2.240415	3.210787
15	1	0	0.202451	0.902894	2.679795
16	8	0	-1.986816	3.110524	2.242150
17	1	0	-1.477448	2.738573	1.475643

Complex (**S16**) involving OOMe radical

M06-2X/6-311+G(d,p)

E=-460.7184779 E+ZPE=-460.551939 In CH_3CN E=-460.7272136

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.837054	0.429460	0.327360
2	6	0	1.172079	0.154370	1.788171
3	6	0	2.495347	-0.615544	1.737774
4	6	0	3.198744	-0.045918	0.491687
5	6	0	2.061635	0.112406	-0.522124
6	8	0	-0.218932	0.831611	-0.086309
7	1	0	1.305158	1.129830	2.270601
8	1	0	3.088931	-0.508480	2.645388
9	1	0	2.299477	-1.682041	1.591972
10	1	0	4.006699	-0.683746	0.134064
11	1	0	3.626621	0.933296	0.726635
12	1	0	1.857310	-0.836858	-1.031159
13	1	0	2.209881	0.871738	-1.290014
14	8	0	-3.184423	2.153664	-3.830035
15	1	0	0.345716	-0.350438	2.288453
16	8	0	-3.407679	2.261690	-2.557001
17	6	0	-2.301089	1.767922	-1.780171
18	1	0	-1.409308	2.341805	-2.024624
19	1	0	-2.578602	1.905112	-0.738749
20	1	0	-2.147306	0.714397	-2.005694

ωB97XD/6-311+G(d,p)

E=-460.7787103 E+ZPE=-460.611948 In CH_3CN E=-460.7876102

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.891705	0.459711	0.332311
2	6	0	1.193188	0.144876	1.790846
3	6	0	2.505402	-0.643632	1.756534
4	6	0	3.240280	-0.081339	0.526154
5	6	0	2.124287	0.133452	-0.500100
6	8	0	-0.148851	0.894485	-0.091500
7	1	0	1.324276	1.106428	2.302128
8	1	0	3.085404	-0.548833	2.675414
9	1	0	2.297822	-1.708262	1.607053
10	1	0	4.029381	-0.743659	0.167746
11	1	0	3.704966	0.877553	0.777989
12	1	0	1.904774	-0.794338	-1.042693
13	1	0	2.309949	0.908299	-1.245129
14	8	0	-3.377208	2.113564	-3.841857
15	1	0	0.349766	-0.360590	2.263055
16	8	0	-3.516200	2.270782	-2.557489
17	6	0	-2.365623	1.795942	-1.832010
18	1	0	-1.484312	2.352590	-2.148035
19	1	0	-2.579670	1.975317	-0.781090

20	1	0	-2.232022	0.731931	-2.023100

Complex (**S17**) involving CO_3 radical anion

M06-2X/6-311+G(d,p)

E=-534.3317130 E+ZPE=-534.195796 In CH_3CN E=-534.4154034

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.242477	-0.378410	-0.194153
2	6	0	0.359183	-0.869832	1.248602
3	6	0	1.039509	0.281863	1.997097
4	6	0	1.886794	0.978373	0.917656
5	6	0	0.966671	0.944515	-0.306703
6	8	0	-0.312964	-0.977345	-1.084023
7	1	0	-0.620231	-1.166061	1.628112
8	1	0	0.298727	1.002685	2.348977
9	1	0	1.631059	-0.047007	2.852843
10	1	0	2.805623	0.410122	0.725199
11	1	0	2.144442	1.992875	1.219501
12	1	0	1.441929	1.055842	-1.281959
13	1	0	0.218355	1.738789	-0.173463
14	8	0	-0.341766	4.903532	2.877563
15	1	0	0.988116	-1.768237	1.222897
16	6	0	0.112560	3.842154	2.307041
17	8	0	1.228712	3.533107	2.855676
18	8	0	-0.444910	3.229103	1.387928

ωB97XD/6-311+G(d,p)

E=-534.3867912 E+ZPE=-534.251955 In CH_3CN E=-534.4707578

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.226311	-0.294099	-0.184513
2	6	0	0.322770	-0.861166	1.230704
3	6	0	1.104864	0.189608	2.026313
4	6	0	1.960614	0.910765	0.970203
5	6	0	1.019327	0.989849	-0.234463
6	8	0	-0.364491	-0.818955	-1.100203
7	1	0	-0.674381	-1.084938	1.616420
8	1	0	0.417356	0.922714	2.455229
9	1	0	1.701018	-0.240566	2.834690
10	1	0	2.853454	0.319365	0.725236
11	1	0	2.264204	1.899018	1.317720
12	1	0	1.486702	1.138735	-1.209334
13	1	0	0.306587	1.807772	-0.046884
14	8	0	-0.516943	4.868279	2.839819
15	1	0	0.865121	-1.812214	1.154432
16	6	0	0.034832	3.890713	2.233406
17	8	0	1.295411	3.818205	2.326228
18	8	0	-0.658470	3.062986	1.593788

TS (**S18a**) involving OH

M06-2X/6-311+G(d,p)

E=-346.2495143 E+ZPE=-346.120733 In CH_3CN E=-346.2583512

Imaginary frequency: -1043.3791

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.036811	0.473393	0.123803
2	6	0	0.108860	0.183599	1.609948
3	6	0	1.563210	-0.150767	1.906244
4	6	0	2.340656	0.587337	0.799008
5	6	0	1.448888	0.435288	-0.438601
6	8	0	-0.969332	0.744901	-0.478389
7	1	0	-0.163137	1.219348	2.095937
8	1	0	1.875704	0.137461	2.909993
9	1	0	1.712883	-1.232305	1.811661
10	1	0	3.344980	0.189763	0.655640
11	1	0	2.429549	1.645351	1.060584
12	1	0	1.587083	-0.551829	-0.896297
13	1	0	1.580312	1.188139	-1.214842
14	8	0	-0.748600	2.496212	2.220992
15	1	0	-0.662028	-0.501060	1.961391
16	1	0	-1.361545	2.416045	1.469200

ωB97XD/6-311+G(d,p)

E=-346.3004052 E+ZPE=-346.170901 In CH_3CN E=-346.3097743

Imaginary frequency: -505.3517

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.031408	0.406724	0.088919
2	6	0	0.094937	0.173667	1.584540
3	6	0	1.547318	-0.140153	1.905066
4	6	0	2.334247	0.587351	0.798823
5	6	0	1.454716	0.435910	-0.446873
6	8	0	-0.977566	0.569832	-0.548415
7	1	0	-0.171899	1.216977	2.041404
8	1	0	1.840533	0.167570	2.909849
9	1	0	1.708642	-1.222522	1.834064
10	1	0	3.337899	0.182055	0.664606
11	1	0	2.433755	1.645944	1.056028
12	1	0	1.630417	-0.529258	-0.938172
13	1	0	1.570821	1.213811	-1.202075
14	8	0	-0.673208	2.543078	2.284862
15	1	0	-0.672139	-0.504384	1.957888
16	1	0	-1.365587	2.534275	1.605757

TS (**S19a**) involving OMe

M06-2X/6-311+G(d,p)

E=-385.5461683 E+ZPE=-385.389579 In CH_3CN E=-385.5542386

Imaginary frequency: -1472.8625

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.049315	0.282847	0.015635
2	6	0	0.066297	0.040444	1.498735
3	6	0	1.516283	-0.189862	1.880903
4	6	0	2.287289	0.661037	0.852080
5	6	0	1.487701	0.489223	-0.444703
6	8	0	-0.934539	0.329359	-0.679507
7	1	0	-0.205063	1.148035	1.929087
8	1	0	1.736411	0.087925	2.912454
9	1	0	1.765961	-1.251155	1.761898
10	1	0	3.330114	0.359992	0.755740
11	1	0	2.262321	1.707898	1.165258
12	1	0	1.783744	-0.424419	-0.973231
13	1	0	1.554578	1.316298	-1.151214
14	8	0	-0.474359	2.410521	2.196194
15	1	0	-0.713349	-0.616898	1.878947
16	6	0	-1.719025	2.687105	1.626940
17	1	0	-1.865412	3.767906	1.755681
18	1	0	-1.738387	2.475441	0.551817
19	1	0	-2.537839	2.162393	2.129521

ωB97XD/6-311+G(d,p)

E=-385.6042979 E+ZPE=-385.447811 In CH_3CN E=-385.6127158

Imaginary frequency: -1529.7329

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.073008	0.285737	-0.007019
2	6	0	0.077441	0.075308	1.478377
3	6	0	1.517061	-0.163386	1.883575
4	6	0	2.320217	0.628730	0.833544
5	6	0	1.516365	0.461896	-0.460940
6	8	0	-0.905815	0.321213	-0.712799
7	1	0	-0.205269	1.201336	1.899283
8	1	0	1.729883	0.148688	2.907650
9	1	0	1.745264	-1.234686	1.813796
10	1	0	3.350067	0.280756	0.744049
11	1	0	2.346990	1.683568	1.120514
12	1	0	1.796401	-0.458428	-0.987696
13	1	0	1.602999	1.283256	-1.173293
14	8	0	-0.520250	2.412142	2.222246
15	1	0	-0.711320	-0.565347	1.869636
16	6	0	-1.769705	2.686264	1.666311
17	1	0	-1.940034	3.758052	1.833473
18	1	0	-1.790695	2.512280	0.583370
19	1	0	-2.580566	2.126711	2.148157

TS (**S20a**) involving OOH

M06-2X/6-311+G(d,p)

E=-421.3913357 E+ZPE=-421.257725 In CH_3CN E=-421.4009285

Imaginary frequency: -1917.2399

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.030908	0.623854	0.478459
2	6	0	0.522426	0.393461	1.864948
3	6	0	1.934749	-0.126574	1.776525
4	6	0	2.431127	0.406267	0.416014
5	6	0	1.185329	0.371028	-0.478811
6	8	0	-1.077350	1.009577	0.174541
7	1	0	0.506000	1.679260	2.244047
8	1	0	2.565035	0.179417	2.612817
9	1	0	1.916855	-1.224390	1.771881
10	1	0	3.260835	-0.176003	0.016782
11	1	0	2.771432	1.438552	0.532920
12	1	0	1.035957	-0.629982	-0.900603
13	1	0	1.176189	1.085247	-1.301332
14	8	0	0.098998	2.789909	2.374783
15	1	0	-0.190048	0.021504	2.598866
16	8	0	-1.253589	2.642942	2.532575
17	1	0	-1.580886	2.490365	1.627956

ωB97XD/6-311+G(d,p)

E=-421.4430652 E+ZPE=-421.309686 In CH_3CN E=-421.4528752

Imaginary frequency: -2034.0065

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.023461	0.587758	0.463980
2	6	0	0.511490	0.368791	1.850632
3	6	0	1.933618	-0.120031	1.778287
4	6	0	2.432953	0.403162	0.415432
5	6	0	1.191624	0.372897	-0.485289
6	8	0	-1.097247	0.934189	0.153467
7	1	0	0.469012	1.659165	2.235275
8	1	0	2.549665	0.213416	2.616102
9	1	0	1.941165	-1.218363	1.796030
10	1	0	3.261315	-0.185909	0.020756
11	1	0	2.783774	1.433156	0.527320
12	1	0	1.056678	-0.616024	-0.940354
13	1	0	1.183557	1.108721	-1.289715
14	8	0	0.115323	2.772654	2.400864
15	1	0	-0.194386	-0.019126	2.582797
16	8	0	-1.245865	2.688681	2.561381
17	1	0	-1.582171	2.591297	1.655405

TS (**S21a**) involving OOMe

M06-2X/6-311+G(d,p)

E=-460.6854002 E+ZPE=-460.524086 In CH_3CN E=-460.6945993

Imaginary frequency: -1916.2181

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-0.291487	0.112874	1.003352
2	6	0	0.764204	-0.313607	1.993357
3	6	0	1.799496	-0.120552	-0.202783
4	1	0	-0.394188	1.205816	1.019653
5	1	0	0.748553	0.019897	3.029440
6	1	0	0.564737	-1.621920	2.174293
7	1	0	2.432973	-0.770563	-0.805869
8	1	0	2.063513	0.916547	-0.439936
9	8	0	0.361227	-2.757425	2.448984
10	1	0	-1.275217	-0.309428	1.215091
11	8	0	0.691974	-2.871191	3.768606
12	6	0	2.093787	-3.093081	3.878571
13	1	0	2.276223	-3.243751	4.942039
14	1	0	2.375270	-3.981630	3.311054
15	1	0	2.641788	-2.218826	3.514552
16	6	0	2.074886	-0.318630	1.283848
17	6	0	0.290058	-0.350897	-0.348121
18	1	0	0.088835	-1.417820	-0.478124
19	1	0	-0.145503	0.176953	-1.195846
20	8	0	3.160218	-0.462522	1.794015

ωB97XD/6-311+G(d,p)

E=-460.7459092 E+ZPE=-460.584807 In CH_3CN E=-460.7553288

Imaginary frequency: -2010.7072

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.303090	0.113533	0.986760
2	6	0	0.748810	-0.307613	1.979452
3	6	0	1.798419	-0.117616	-0.206408
4	1	0	-0.424874	1.204866	1.018735
5	1	0	0.722894	0.033014	3.013193
6	1	0	0.557309	-1.627899	2.194286
7	1	0	2.425438	-0.779431	-0.804873
8	1	0	2.084216	0.913204	-0.447905
9	8	0	0.370291	-2.748178	2.479269
10	1	0	-1.283100	-0.323632	1.189499
11	8	0	0.717702	-2.860658	3.798744
12	6	0	2.114293	-3.118343	3.898328
13	1	0	2.298611	-3.261184	4.963624
14	1	0	2.371461	-4.023233	3.342744
15	1	0	2.686377	-2.264242	3.522694
16	6	0	2.061948	-0.313889	1.281584
17	6	0	0.287889	-0.326226	-0.367795
18	1	0	0.074442	-1.386957	-0.528816
19	1	0	-0.133379	0.226135	-1.208378
20	8	0	3.145687	-0.451405	1.801439

TS (**S22a**) involving CO_3

M06-2X/6-311+G(d,p)

E=-534.305054 E+ZPE=-534.173752 In CH_3CN E=-534.3936125

Imaginary frequency: -1822.604

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.055222	0.016777	0.003703
2	6	0	0.024778	0.002265	1.483052
3	6	0	1.449673	0.119583	1.993368
4	6	0	2.325652	0.420464	0.741596
5	6	0	1.350044	0.695340	-0.411168
6	8	0	-0.791306	-0.418441	-0.750396
7	1	0	-0.527033	1.155585	1.755997
8	1	0	1.537863	0.937383	2.711453
9	1	0	1.770156	-0.802979	2.488495
10	1	0	2.952134	-0.445290	0.504713
11	1	0	2.972313	1.277511	0.924511
12	1	0	1.677228	0.346163	-1.391199
13	1	0	1.136945	1.768648	-0.452323
14	8	0	-0.995441	2.220043	2.162606
15	1	0	-0.662428	-0.704678	1.942831
16	6	0	-0.114778	3.260471	2.032119
17	8	0	-0.647118	4.303732	2.453827
18	8	0	1.009723	3.062104	1.555775

ωB97XD/6-311+G(d,p)

E=-534.3546611 E+ZPE=-534.223958 In CH_3CN E=-534.4447475

Imaginary frequency: -2017.4796

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.076501	0.062953	0.009569
2	6	0	0.077408	0.004272	1.481122
3	6	0	1.500863	0.169499	1.973364
4	6	0	2.365965	0.263748	0.690781
5	6	0	1.389431	0.711860	-0.400856
6	8	0	-0.796178	-0.322818	-0.746355
7	1	0	-0.533707	1.174295	1.780016
8	1	0	1.595013	1.110137	2.527618
9	1	0	1.816070	-0.650726	2.626409
10	1	0	2.779184	-0.720790	0.439499
11	1	0	3.198237	0.959099	0.815457
12	1	0	1.670153	0.448211	-1.421896
13	1	0	1.240086	1.796351	-0.322889
14	8	0	-1.053508	2.179618	2.145017
15	1	0	-0.593054	-0.713052	1.949865
16	6	0	-0.255281	3.278133	2.074874
17	8	0	-0.877025	4.296425	2.428186
18	8	0	0.923471	3.167465	1.699180

TS (**S18b**) involving OH

M06-2X/6-311+G(d,p)

E=-346.2483952 E+ZPE=-346.119427 In CH_3CN E=-346.2593618

Imaginary frequency: -798.6294

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.051645	-0.374676	0.128869
2	6	0	0.073395	0.111511	1.578261
3	6	0	1.532892	-0.013191	1.988013
4	6	0	2.327873	0.224739	0.701592
5	6	0	1.486937	-0.468813	-0.375231
6	8	0	-0.936342	-0.639903	-0.498589
7	1	0	-0.236014	1.164403	1.571828
8	1	0	1.839853	0.579260	2.849727
9	1	0	1.746477	-1.118040	2.273671
10	1	0	3.345213	-0.160678	0.766234
11	1	0	2.388168	1.301477	0.507821
12	1	0	1.732603	-1.534705	-0.423149
13	1	0	1.572064	-0.053312	-1.379061
14	8	0	1.837102	-2.565354	2.164507
15	1	0	-0.647056	-0.434064	2.188629
16	1	0	0.962102	-2.779759	2.526863

ωB97XD/6-311+G(d,p)

E=-346.2991857 E+ZPE=-346.169476 In CH_3CN E=-346.3108427

Imaginary frequency: -236.0345

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.013000	-0.182989	-0.008278
2	6	0	0.016281	0.096924	1.493358
3	6	0	1.456912	-0.132784	1.926118
4	6	0	2.309163	0.146792	0.685457
5	6	0	1.451730	-0.377587	-0.469116
6	8	0	-0.964935	-0.230799	-0.704705
7	1	0	-0.276667	1.144572	1.635742
8	1	0	1.767197	0.396971	2.827370
9	1	0	1.581744	-1.258737	2.148384
10	1	0	3.291825	-0.322733	0.741790
11	1	0	2.463021	1.227840	0.586184
12	1	0	1.599773	-1.455828	-0.600627
13	1	0	1.620379	0.100812	-1.434241
14	8	0	1.741175	-2.714240	2.385903
15	1	0	-0.725540	-0.519773	2.002932
16	1	0	1.731851	-2.679545	3.353712

TS (**S19b**) involving OMe

M06-2X/6-311+G(d,p)

E=-385.5445931 E+ZPE=-385.387804 In CH_3CN E=-385.5542106

Imaginary frequency: -1430.0079

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.047086	-0.618554	0.509558
2	6	0	0.195886	0.163918	1.814859
3	6	0	1.694271	0.288051	1.999998

4	6	0	2.291189	0.292916	0.595579
5	6	0	1.411133	-0.703596	-0.166519
6	8	0	-0.975131	-1.093719	0.097068
7	1	0	-0.263722	1.149689	1.662886
8	1	0	2.049119	1.052732	2.689532
9	1	0	2.100906	-0.770760	2.478377
10	1	0	3.347126	0.021720	0.593594
11	1	0	2.201573	1.296032	0.161629
12	1	0	1.776787	-1.725019	-0.012068
13	1	0	1.323422	-0.534319	-1.239331
14	8	0	2.420919	-1.996914	2.749228
15	1	0	-0.348437	-0.322178	2.626645
16	6	0	1.248189	-2.656749	3.122293
17	1	0	1.553226	-3.670906	3.408646
18	1	0	0.764983	-2.197556	3.992955
19	1	0	0.527373	-2.747459	2.299553

ωB97XD/6-311+G(d,p)
E=-385.6026514 E+ZPE=-385.446047 In CH_3CN E=-385.6127327
Imaginary frequency: -1551.2985

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.028893	-0.561569	0.450862
2	6	0	0.192789	0.158650	1.788193
3	6	0	1.690116	0.261413	1.981124
4	6	0	2.302190	0.272611	0.585667
5	6	0	1.395158	-0.667036	-0.214397
6	8	0	-1.007268	-0.979381	0.007456
7	1	0	-0.263194	1.152974	1.688583
8	1	0	2.049592	1.013120	2.683354
9	1	0	2.088196	-0.810426	2.473078
10	1	0	3.348032	-0.037534	0.588523
11	1	0	2.261044	1.289430	0.174807
12	1	0	1.724296	-1.706036	-0.096996
13	1	0	1.325803	-0.459046	-1.282504
14	8	0	2.420172	-1.994984	2.816078
15	1	0	-0.351536	-0.358319	2.581558
16	6	0	1.264447	-2.671943	3.203015
17	1	0	1.586766	-3.675811	3.506534
18	1	0	0.768493	-2.207184	4.065783
19	1	0	0.541906	-2.791597	2.383762

TS (**S20b**) involving OOH
M06-2X/6-311+G(d,p)
E=-421.388002 E+ZPE=-421.255094 In CH_3CN E=-421.3999125
Imaginary frequency: -1799.3477

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.076865	-0.493156	0.200754
2	6	0	0.115258	-0.022362	1.657451

3	6	0	1.584752	0.029367	1.996052
4	6	0	2.338143	0.242519	0.691163
5	6	0	1.498671	-0.510783	-0.348249
6	8	0	-0.917337	-0.784909	-0.402748
7	1	0	-0.335189	0.979277	1.697687
8	1	0	1.898063	0.598319	2.869521
9	1	0	1.888976	-1.210828	2.321094
10	1	0	3.370843	-0.104099	0.744222
11	1	0	2.364511	1.315667	0.462102
12	1	0	1.796967	-1.562540	-0.402390
13	1	0	1.526691	-0.096598	-1.355553
14	8	0	2.053867	-2.395418	2.418736
15	1	0	-0.495747	-0.667490	2.292368
16	8	0	1.042954	-2.938243	1.638090
17	1	0	0.381631	-3.222120	2.282886

ωB97XD/6-311+G(d,p)
E=-421.440178 E+ZPE=-421.307512 In CH_3CN E=-421.4528523
Imaginary frequency: -1892.9270

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.045759	-0.448277	0.183351
2	6	0	0.099264	0.014172	1.639507
3	6	0	1.566653	0.030690	1.984490
4	6	0	2.342157	0.184350	0.685835
5	6	0	1.461838	-0.488531	-0.374069
6	8	0	-0.956991	-0.731101	-0.414973
7	1	0	-0.333662	1.023379	1.686166
8	1	0	1.888773	0.622295	2.840412
9	1	0	1.835673	-1.202200	2.397558
10	1	0	3.343468	-0.245556	0.748475
11	1	0	2.465719	1.253265	0.467367
12	1	0	1.720076	-1.545231	-0.491103
13	1	0	1.498043	-0.024933	-1.360660
14	8	0	1.990482	-2.349116	2.670308
15	1	0	-0.524346	-0.617660	2.276937
16	8	0	1.284393	-3.038396	1.690299
17	1	0	0.462617	-3.280547	2.133286

TS (**S21b**) involving OOMe
M06-2X/6-311+G(d,p)
E=-460.6831498 E+ZPE=-460.522430 In CH_3CN E=-460.6937688
Imaginary frequency: -1863.8668

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.047086	-0.618554	0.509558
2	6	0	0.195886	0.163918	1.814859
3	6	0	1.694271	0.288051	1.999998
4	6	0	2.291189	0.292916	0.595579
5	6	0	1.411133	-0.703596	-0.166519

6	8	0	-0.975131	-1.093719	0.097068
7	1	0	-0.263722	1.149689	1.662886
8	1	0	2.049119	1.052732	2.689532
9	1	0	2.100906	-0.770760	2.478377
10	1	0	3.347126	0.021720	0.593594
11	1	0	2.201573	1.296032	0.161629
12	1	0	1.776787	-1.725019	-0.012068
13	1	0	1.323422	-0.534319	-1.239331
14	8	0	2.420919	-1.996914	2.749228
15	1	0	-0.348437	-0.322178	2.626645
16	6	0	1.248189	-2.656749	3.122293
17	1	0	1.553226	-3.670906	3.408646
18	1	0	0.764983	-2.197556	3.992955
19	1	0	0.527373	-2.747459	2.299553

ωB97XD/6-311+G(d,p)
E=-460.7423265 E+ZPE=-460.582034 In CH_3CN E=-460.753939
Imaginary frequency: -1876.3108

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.028893	-0.561569	0.450862
2	6	0	0.192789	0.158650	1.788193
3	6	0	1.690116	0.261413	1.981124
4	6	0	2.302190	0.272611	0.585667
5	6	0	1.395158	-0.667036	-0.214397
6	8	0	-1.007268	-0.979381	0.007456
7	1	0	-0.263194	1.152974	1.688583
8	1	0	2.049592	1.013120	2.683354
9	1	0	2.088196	-0.810426	2.473078
10	1	0	3.348032	-0.037534	0.588523
11	1	0	2.261044	1.289430	0.174807
12	1	0	1.724296	-1.706036	-0.096996
13	1	0	1.325803	-0.459046	-1.282504
14	8	0	2.420172	-1.994984	2.816078
15	1	0	-0.351536	-0.358319	2.581558
16	6	0	1.264447	-2.671943	3.203015
17	1	0	1.586766	-3.675811	3.506534
18	1	0	0.768493	-2.207184	4.065783
19	1	0	0.541906	-2.791597	2.383762

TS (**S22b**) involving CO_3
M06-2X/6-311+G(d,p)
E=-534.3019361 E+ZPE=-534.170813 In CH_3CN E=-534.3933797
Imaginary frequency: -1865.8998

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.030935	0.082331	-0.042233
2	6	0	-0.007375	-0.084538	1.468047
3	6	0	1.446875	-0.035102	1.907133
4	6	0	2.337328	-0.048285	0.652790

5	6	0	1.399392	-0.346611	-0.525668
6	8	0	-0.868981	0.505425	-0.726609
7	1	0	-0.663835	0.656541	1.926955
8	1	0	1.692449	0.739226	2.634840
9	1	0	1.697300	-1.117870	2.535501
10	1	0	3.120558	-0.803741	0.741604
11	1	0	2.823067	0.925659	0.522889
12	1	0	1.340001	-1.431636	-0.663474
13	1	0	1.655419	0.143064	-1.465687
14	8	0	1.952950	-2.203398	3.051547
15	1	0	-0.416204	-1.088469	1.643186
16	6	0	1.647012	-3.221673	2.149858
17	8	0	1.942834	-4.327588	2.613838
18	8	0	1.143172	-2.890479	1.061018

ωB97XD/6-311+G(d,p)

E=-534.3503183 E+ZPE=-534.219671 In CH_3CN E=-534.4440905

Imaginary frequency: -2117.6823

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.056862	0.043678	-0.050014
2	6	0	0.011925	-0.049431	1.465582
3	6	0	1.462606	-0.019223	1.906772
4	6	0	2.346893	0.064584	0.660771
5	6	0	1.440079	-0.376616	-0.494012
6	8	0	-0.846982	0.411799	-0.763034
7	1	0	-0.624633	0.730868	1.890541
8	1	0	1.714079	0.673322	2.710938
9	1	0	1.732372	-1.186964	2.453020
10	1	0	3.236258	-0.563120	0.756098
11	1	0	2.690070	1.096945	0.504534
12	1	0	1.412402	-1.473142	-0.527197
13	1	0	1.692597	0.028450	-1.474969
14	8	0	2.032933	-2.241565	2.918390
15	1	0	-0.429832	-1.031997	1.684749
16	6	0	1.558515	-3.282783	2.131655
17	8	0	1.933322	-4.379242	2.565724
18	8	0	0.853432	-2.992707	1.145985

Complex (**S23a**) involving HOH

M06-2X/6-311+G(d,p)

E=-346.3064293 E+ZPE=-346.173059 In CH_3CN E=-346.3163366

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.714538	1.212126	0.303529
2	6	0	0.621675	0.700470	1.647980
3	6	0	1.611253	-0.388514	1.862819
4	6	0	2.620651	-0.211988	0.702407
5	6	0	1.808020	0.440131	-0.425155

6	8	0	0.023058	2.098032	-0.189576
7	1	0	-1.233199	2.690182	1.110840
8	1	0	2.075423	-0.354031	2.851228
9	1	0	1.103871	-1.362174	1.793788
10	1	0	3.086019	-1.152112	0.408225
11	1	0	3.414081	0.467545	1.021295
12	1	0	1.318822	-0.311909	-1.054021
13	1	0	2.381033	1.096937	-1.079149
14	8	0	-1.672772	2.699637	1.975837
15	1	0	-2.370519	3.353487	1.916312
16	1	0	-0.113408	1.054828	2.360421

ωB97XD/6-311+G(d,p)

E=-346.3530752 E+ZPE=-346.219443 In CH_3CN E=-346.3634025

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.701867	1.190846	0.317278
2	6	0	0.619355	0.665986	1.652957
3	6	0	1.630830	-0.399303	1.865016
4	6	0	2.626021	-0.220055	0.693734
5	6	0	1.809537	0.450977	-0.420254
6	8	0	-0.010808	2.068727	-0.165213
7	1	0	-1.247717	2.689691	1.127862
8	1	0	2.104787	-0.344650	2.849267
9	1	0	1.140314	-1.383995	1.819569
10	1	0	3.078907	-1.162350	0.383799
11	1	0	3.434091	0.445465	1.008584
12	1	0	1.335705	-0.288956	-1.075870
13	1	0	2.381514	1.128926	-1.054684
14	8	0	-1.711566	2.760589	1.977455
15	1	0	-2.382298	3.431563	1.857107
16	1	0	-0.121992	0.999185	2.370172

Complex (**S24a**) involving HOMe

M06-2X/6-311+G(d,p)

E=-385.5884322 E+ZPE=-385.426126 In CH_3CN E=-385.5975443

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.555708	-0.522492	1.212893
2	6	0	0.209476	0.877190	1.179732
3	6	0	1.424733	1.718419	1.018031
4	6	0	2.494435	0.723109	0.506461
5	6	0	2.068465	-0.639512	1.070127
6	8	0	-0.232539	-1.450840	1.356236
7	1	0	3.503063	1.011692	0.799682
8	1	0	2.460047	0.694044	-0.584971
9	1	0	2.479891	-0.809034	2.071805
10	1	0	2.345554	-1.502296	0.464599

11	8	0	1.493956	-3.686265	1.219199
12	1	0	0.748307	-3.074125	1.302880
13	1	0	1.270274	2.571696	0.353277
14	1	0	-0.803443	1.234744	1.308863
15	1	0	1.715374	2.134850	1.994016
16	6	0	1.021281	-5.011475	1.314765
17	1	0	1.882514	-5.674775	1.229571
18	1	0	0.533653	-5.204820	2.276939
19	1	0	0.317971	-5.255779	0.510607

ωB97XD/6-311+G(d,p)
E=-385.6434437 E+ZPE=-385.481039 In CH_3CN E=-385.6530095
No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.645643	-0.540853	1.372810
2	6	0	0.195904	0.807089	1.152331
3	6	0	1.338325	1.707569	0.857827
4	6	0	2.497188	0.743147	0.507836
5	6	0	2.161485	-0.564681	1.237778
6	8	0	-0.071666	-1.500814	1.643311
7	1	0	3.470700	1.148939	0.784314
8	1	0	2.507990	0.570142	-0.571444
9	1	0	2.581799	-0.581604	2.250379
10	1	0	2.500443	-1.473533	0.738759
11	8	0	1.584596	-3.780735	1.387271
12	1	0	0.912635	-3.108085	1.569667
13	1	0	1.119167	2.432221	0.068216
14	1	0	-0.841862	1.103661	1.241004
15	1	0	1.577630	2.300492	1.754667
16	6	0	0.945903	-5.020430	1.194678
17	1	0	1.715151	-5.755078	0.949112
18	1	0	0.423799	-5.361945	2.098258
19	1	0	0.223894	-4.991172	0.367937

Complex (**S25a**) involving HOOH
M06-2X/6-311+G(d,p)
E=-421.4235309 E+ZPE=-421.284782 In CH_3CN E=-421.4350632
No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.592599	-0.708039	1.686041
2	6	0	0.226204	0.661099	1.426598
3	6	0	1.359687	1.404691	0.817230
4	6	0	2.304146	0.286767	0.311869
5	6	0	2.030389	-0.913030	1.230675
6	8	0	-0.129318	-1.550749	2.211756
7	1	0	0.651427	-4.768875	0.601931
8	1	0	3.348714	0.595772	0.311502
9	1	0	2.033014	0.028294	-0.714080

10	1	0	2.664478	-0.892031	2.124460
11	1	0	2.157499	-1.887661	0.759605
12	8	0	1.237491	-4.027000	0.787789
13	8	0	1.196041	-3.963516	2.210020
14	1	0	0.648673	-3.163587	2.344820
15	1	0	1.045466	2.097641	0.033076
16	1	0	-0.735989	1.072321	1.701918
17	1	0	1.853618	2.014096	1.588614

ωB97XD/6-311+G(d,p)

E=-421.4731236 E+ZPE=-421.334746 In CH_3CN E=-421.4849446

No imaginary frequencies:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.585881	-0.692538	1.658989
2	6	0	0.239766	0.686208	1.448613
3	6	0	1.366561	1.429001	0.832271
4	6	0	2.304373	0.319479	0.297980
5	6	0	2.007115	-0.910954	1.167212
6	8	0	-0.140514	-1.541216	2.173662
7	1	0	0.749611	-4.836591	0.631473
8	1	0	3.353252	0.615724	0.325179
9	1	0	2.051466	0.105120	-0.743539
10	1	0	2.658664	-0.952604	2.048250
11	1	0	2.100543	-1.869247	0.654867
12	8	0	1.353047	-4.137140	0.899581
13	8	0	1.071472	-4.026916	2.294214
14	1	0	0.579163	-3.180976	2.323322
15	1	0	1.041830	2.135278	0.062556
16	1	0	-0.708123	1.110105	1.756215
17	1	0	1.870032	2.033458	1.602979

Complex (**S26a**) involving HOOMe

M06-2X/6-311+G(d,p)

E=-460.7176746 E+ZPE=-460.55102 In CH_3CN E=-460.7279005

No imaginary frequencies:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.686805	-0.912733	1.772938
2	6	0	0.138267	0.324710	1.277647
3	6	0	1.191653	1.146044	0.625306
4	6	0	2.335010	0.136262	0.363249
5	6	0	2.173643	-0.938498	1.448590
6	8	0	0.059579	-1.778858	2.376044
7	1	0	3.316094	0.609443	0.371932
8	1	0	2.192114	-0.318147	-0.619598
9	1	0	2.714431	-0.670117	2.363417
10	1	0	2.489814	-1.937372	1.149500
11	8	0	1.362567	-3.997406	0.822528
12	8	0	1.479918	-4.136996	2.230941

13	1	0	0.974274	-3.358266	2.538023
14	1	0	0.842539	1.653287	-0.277281
15	1	0	-0.895742	0.607738	1.424172
16	1	0	1.519927	1.936390	1.316679
17	6	0	0.213885	-4.714109	0.423387
18	1	0	0.183406	-4.631068	-0.664301
19	1	0	0.296100	-5.763125	0.717303
20	1	0	-0.688463	-4.271895	0.857428

ωB97XD/6-311+G(d,p)

E=-460.7743622 E+ZPE=-460.607868 In CH_3CN E=-460.7849727

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.585566	-0.744348	1.684018
2	6	0	0.220001	0.621566	1.426468
3	6	0	1.336585	1.358451	0.784849
4	6	0	2.287797	0.243927	0.286094
5	6	0	2.009276	-0.959814	1.197655
6	8	0	-0.128251	-1.584618	2.229097
7	1	0	3.332635	0.555144	0.299652
8	1	0	2.034871	-0.009069	-0.746781
9	1	0	2.662547	-0.962475	2.078400
10	1	0	2.114489	-1.933940	0.718333
11	8	0	1.331512	-4.178219	0.968413
12	8	0	1.134664	-4.053524	2.373114
13	1	0	0.629324	-3.216109	2.422056
14	1	0	1.002294	2.035194	-0.007040
15	1	0	-0.733845	1.042591	1.719304
16	1	0	1.833100	1.994052	1.534730
17	6	0	0.402947	-5.126284	0.493874
18	1	0	0.615412	-5.227525	-0.572947
19	1	0	0.541396	-6.090642	0.992085
20	1	0	-0.626499	-4.779076	0.636534

Complex (**S27a**) involving CO_3

M06-2X/6-311+G(d,p)

E=-534.347549 E+ZPE=-534.210589 In CH_3CN E=-534.4339626

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.435467	-0.731442	-0.009453
2	6	0	0.550221	-0.891369	1.420399
3	6	0	1.377003	0.180885	2.018634
4	6	0	2.110620	0.809031	0.809414
5	6	0	1.180855	0.541634	-0.382655
6	8	0	-0.160204	-1.480220	-0.778885
7	1	0	-1.178931	4.793609	1.487883
8	1	0	0.736890	0.947302	2.492904
9	1	0	2.051797	-0.183585	2.800304

10	1	0	3.075263	0.311785	0.658088
11	1	0	2.267189	1.875334	0.964169
12	1	0	1.678045	0.437024	-1.348509
13	1	0	0.446707	1.353664	-0.433819
14	8	0	-1.062977	4.504846	2.397057
15	6	0	-0.314664	3.314746	2.273592
16	8	0	-0.054039	2.753896	3.340239
17	8	0	-0.026631	3.005343	1.097633
18	1	0	0.032034	-1.675365	1.958618

ωB97XD/6-311+G(d,p)
E=-534.3930148 E+ZPE=-534.256411 In CH_3CN E=-534.4792055
No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.441732	-0.752144	0.009525
2	6	0	0.585765	-0.934217	1.430845
3	6	0	1.400796	0.140784	2.031425
4	6	0	2.110025	0.798125	0.824777
5	6	0	1.166065	0.533782	-0.355639
6	8	0	-0.161771	-1.495469	-0.762701
7	1	0	-1.144275	4.941634	1.586583
8	1	0	0.746404	0.897144	2.514771
9	1	0	2.085870	-0.215268	2.809574
10	1	0	3.083209	0.321486	0.653267
11	1	0	2.253723	1.865802	0.989098
12	1	0	1.650719	0.455287	-1.331381
13	1	0	0.425109	1.342593	-0.385276
14	8	0	-1.055838	4.536404	2.452096
15	6	0	-0.350624	3.344494	2.180434
16	8	0	-0.125556	2.641532	3.171521
17	8	0	-0.057410	3.179994	0.977848
18	1	0	0.090701	-1.734846	1.968846

Complex (**S23b**) involving HOH
M06-2X/6-311+G(d,p)
E=-346.292469 E+ZPE=-346.160677 In CH_3CN E=-346.3013534
No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.358730	-1.174609	0.599593
2	6	0	0.899587	-0.430329	1.847200
3	6	0	1.460792	0.938997	1.675734
4	6	0	2.007126	1.148358	0.293137
5	6	0	2.260477	-0.274125	-0.229566
6	8	0	1.059382	-2.306863	0.308380
7	1	0	-0.197435	-0.475519	1.904668
8	1	0	-0.994389	-3.840704	2.593239
9	1	0	2.906895	1.767878	0.286512
10	1	0	1.273084	1.660964	-0.345329

11	1	0	3.288392	-0.589388	-0.019577
12	1	0	2.079298	-0.425287	-1.293310
13	8	0	-0.559530	-2.989580	2.522349
14	1	0	1.242693	-0.964588	2.741815
15	1	0	-0.065216	-3.013900	1.689748
16	1	0	1.311616	1.740826	2.384136

ωB97XD/6-311+G(d,p)
E=-346.3391789 E+ZPE=-346.207745 In CH_3CN E=-346.3487767
No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.333446	-1.152917	0.619916
2	6	0	0.877315	-0.377850	1.846314
3	6	0	1.437137	0.985313	1.649575
4	6	0	2.049976	1.155246	0.292918
5	6	0	2.234518	-0.276757	-0.232834
6	8	0	1.036683	-2.295678	0.361538
7	1	0	-0.219961	-0.420054	1.911179
8	1	0	-0.931500	-4.002790	2.541226
9	1	0	2.989785	1.714946	0.326261
10	1	0	1.382373	1.725839	-0.370469
11	1	0	3.258245	-0.632012	-0.069924
12	1	0	2.011774	-0.416431	-1.291393
13	8	0	-0.585017	-3.111064	2.543388
14	1	0	1.223711	-0.891566	2.753140
15	1	0	-0.067014	-3.030761	1.728606
16	1	0	1.300031	1.798664	2.349287

Complex (**S24b**) involving HOMe
M06-2X/6-311+G(d,p) E=-385.5753932 E+ZPE=-385.414345
In CH_3CN E=-385.5827656
No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.571447	-0.510348	1.350431
2	6	0	0.162096	0.957050	1.277633
3	6	0	1.427101	1.668678	0.939208
4	6	0	2.519336	0.710987	0.561561
5	6	0	2.073142	-0.634271	1.153836
6	8	0	-0.192095	-1.424805	1.541699
7	1	0	3.498080	1.029990	0.927316
8	1	0	2.609711	0.632277	-0.531463
9	1	0	2.501096	-0.787523	2.151107
10	1	0	2.317444	-1.520965	0.568463
11	8	0	1.496855	-3.689771	1.235880
12	1	0	0.755707	-3.094191	1.412995
13	1	0	-0.288102	1.257469	2.231564
14	1	0	-0.631367	1.062495	0.524310
15	1	0	1.497134	2.738421	0.804397

16	6	0	1.043322	-5.025565	1.266595
17	1	0	0.266099	-5.211867	0.517213
18	1	0	1.896492	-5.665753	1.041384
19	1	0	0.654844	-5.304573	2.252385

ωB97XD/6-311+G(d,p)

E=-385.6304376 E+ZPE=-385.469676 In CH_3CN E=-385.638380

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.663954	-0.530613	1.460238
2	6	0	0.154479	0.892928	1.283171
3	6	0	1.347460	1.656042	0.827516
4	6	0	2.508399	0.757423	0.528230
5	6	0	2.160395	-0.573150	1.211960
6	8	0	-0.027251	-1.476377	1.757482
7	1	0	3.458071	1.174697	0.876455
8	1	0	2.622338	0.612140	-0.556718
9	1	0	2.636033	-0.652882	2.196254
10	1	0	2.432961	-1.475509	0.662006
11	8	0	1.589073	-3.781717	1.366803
12	1	0	0.926018	-3.119261	1.604507
13	1	0	-0.277793	1.247357	2.228486
14	1	0	-0.677483	0.885077	0.563545
15	1	0	1.338031	2.715643	0.609848
16	6	0	0.949441	-5.024319	1.191335
17	1	0	0.179425	-4.987140	0.409702
18	1	0	1.708862	-5.746846	0.887132
19	1	0	0.485927	-5.385762	2.118562

Complex (**S25b**) involving HOOH

M06-2X/6-311+G(d,p)

E=-421.4073272 E+ZPE=-421.270542 In CH_3CN E=-421.4182669

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.085511	-0.788610	0.325496
2	6	0	0.120501	-0.080470	1.680299
3	6	0	1.560393	0.255503	1.875970
4	6	0	2.399154	-0.085291	0.672341
5	6	0	1.396612	-0.532445	-0.403200
6	8	0	-0.835829	-1.437905	-0.088376
7	1	0	-0.523303	0.809599	1.624058
8	1	0	1.905282	-1.723572	2.962648
9	1	0	3.099709	-0.898708	0.898540
10	1	0	3.006629	0.766491	0.352817
11	1	0	1.692720	-1.424490	-0.952983
12	1	0	1.207950	0.264373	-1.130327
13	8	0	1.859884	-2.689905	2.887347
14	1	0	-0.322293	-0.722613	2.450641

15	8	0	1.479055	-2.840616	1.525176
16	1	0	0.609032	-3.254395	1.599420
17	1	0	1.926721	0.855705	2.698465

ωB97XD/6-311+G(d,p)
E=-421.4548067 E+ZPE=-421.318369 In CH_3CN E=-421.4662547
No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.068011	-0.753026	0.321845
2	6	0	0.117428	-0.047004	1.675646
3	6	0	1.564191	0.224034	1.893798
4	6	0	2.387693	-0.048920	0.667199
5	6	0	1.393198	-0.542339	-0.395132
6	8	0	-0.873394	-1.367983	-0.103736
7	1	0	-0.480798	0.875594	1.601187
8	1	0	1.885161	-1.717851	2.878701
9	1	0	3.154256	-0.808026	0.866361
10	1	0	2.929906	0.848539	0.346250
11	1	0	1.692885	-1.467120	-0.887040
12	1	0	1.224032	0.206547	-1.176284
13	8	0	1.837559	-2.687188	2.913393
14	1	0	-0.369306	-0.653486	2.447763
15	8	0	1.538057	-2.990837	1.553282
16	1	0	0.649183	-3.356791	1.620814
17	1	0	1.949666	0.758510	2.754286

Complex (**S26b**) involving HOOMe
M06-2X/6-311+G(d,p)
E=-460.704323 E+ZPE=-460.539362 In CH_3CN E=-460.7128847
No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.702870	-0.866788	1.815365
2	6	0	0.102584	0.447108	1.330539
3	6	0	1.211670	1.093063	0.573294
4	6	0	2.366390	0.156170	0.370401
5	6	0	2.170925	-0.934260	1.435903
6	8	0	0.089484	-1.714913	2.418104
7	1	0	3.332410	0.659482	0.454511
8	1	0	2.336461	-0.289913	-0.633866
9	1	0	2.735247	-0.699825	2.345656
10	1	0	2.438826	-1.944443	1.126662
11	8	0	1.308750	-3.987176	0.821188
12	8	0	1.433150	-4.135791	2.228310
13	1	0	0.944246	-3.351376	2.543387
14	1	0	-0.254357	1.022678	2.193590
15	6	0	0.207296	-4.769560	0.411834
16	1	0	0.174642	-4.676685	-0.674918
17	1	0	0.354107	-5.814517	0.694391

18	1	0	-0.722171	-4.389915	0.847617
19	1	0	-0.789425	0.223549	0.728526
20	1	0	1.123048	2.049239	0.078050

ωB97XD/6-311+G(d,p)

E=-460.7611592 E+ZPE=-460.596730 In CH_3CN E=-460.7701258

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.608453	-0.742308	1.721487
2	6	0	0.181714	0.694686	1.464657
3	6	0	1.320785	1.287924	0.714451
4	6	0	2.338210	0.258835	0.326971
5	6	0	2.009487	-0.968368	1.190434
6	8	0	-0.075616	-1.571982	2.276485
7	1	0	3.363210	0.613502	0.472658
8	1	0	2.254680	0.011106	-0.741861
9	1	0	2.668917	-1.036981	2.063148
10	1	0	2.066939	-1.931784	0.680784
11	8	0	1.309784	-4.171383	0.941551
12	8	0	1.154910	-4.075393	2.353891
13	1	0	0.658262	-3.237110	2.434677
14	1	0	-0.037000	1.185624	2.422411
15	6	0	0.385347	-5.129884	0.479138
16	1	0	0.572376	-5.214026	-0.593795
17	1	0	0.553783	-6.097414	0.961348
18	1	0	-0.646102	-4.803405	0.652717
19	1	0	-0.770426	0.690100	0.913336
20	1	0	1.348444	2.314390	0.374056

Complex (**S27b**) involving HCO_3

M06-2X/6-311+G(d,p)

E=-534.3360686 E+ZPE=-534.200137 In CH_3CN E=-534.4217505

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.044874	-0.282249	0.060998
2	6	0	0.104282	0.420029	1.411632
3	6	0	1.554944	0.702036	1.601796
4	6	0	2.412388	-0.094424	0.658457
5	6	0	1.437253	-0.729769	-0.345652
6	8	0	-0.955413	-0.417823	-0.601398
7	1	0	-0.553530	1.296053	1.413494
8	1	0	0.979673	-3.931462	3.622415
9	1	0	2.947178	-0.890843	1.188094
10	1	0	3.163691	0.535776	0.165315
11	1	0	1.483380	-1.819696	-0.268942
12	1	0	1.609487	-0.441482	-1.385821
13	8	0	1.705137	-4.203404	3.053641
14	1	0	-0.265716	-0.301661	2.153709

15	6	0	1.755750	-3.187520	2.075507
16	8	0	2.627884	-3.332119	1.217963
17	8	0	0.905150	-2.282806	2.226941
18	1	0	1.950920	1.137462	2.510600

ωB97XD/6-311+G(d,p)
E=-534.3795251 E+ZPE=-534.244725 In CH_3CN E=-534.4648481
No imaginary frequencies:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.047006	-0.115973	-0.030186
2	6	0	0.127899	0.380952	1.403058
3	6	0	1.580608	0.645368	1.593187
4	6	0	2.411995	-0.058884	0.561117
5	6	0	1.395986	-0.691389	-0.404681
6	8	0	-0.923176	-0.043856	-0.748960
7	1	0	-0.548284	1.223515	1.580375
8	1	0	0.950793	-4.108112	3.671311
9	1	0	3.025430	-0.847676	1.014047
10	1	0	3.089962	0.637447	0.045484
11	1	0	1.342736	-1.766862	-0.198961
12	1	0	1.600768	-0.539998	-1.466379
13	8	0	1.810522	-4.178997	3.250636
14	1	0	-0.186001	-0.472815	2.029163
15	6	0	1.750166	-3.207333	2.226797
16	8	0	2.764810	-3.120647	1.531730
17	8	0	0.669794	-2.578136	2.179411
18	1	0	1.996315	1.019496	2.521604

H_2O (**S28**)
M06-2X/6-311+G(d,p)
E=-76.4208135 E+ZPE=-76.399183 In CH_3CN E=-76.4286873
No imaginary frequencies:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	8	0	-0.018579	0.000000	-0.014226
2	1	0	-0.019710	0.000000	0.944890
3	1	0	0.907622	0.000000	-0.263601

ωB97XD/6-311+G(d,p)
E=-76.4322645 E+ZPE=-76.410586 In CH_3CN E=-76.4401533
No imaginary frequencies:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	8	0	-0.017822	0.000000	-0.013656
2	1	0	-0.019540	0.000000	0.943897
3	1	0	0.906695	0.000000	-0.263178

MeOH (**S29**)
M06-2X/6-311+G(d,p)

E=-115.7042313 E+ZPE=-115.652483 In CH_3CN E=-115.7101137
No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.015178	0.000000	0.004886
2	6	0	0.012283	0.000000	1.418948
3	1	0	0.885534	0.000000	-0.323483
4	1	0	0.505257	0.891703	1.820309
5	1	0	0.505257	-0.891703	1.820309
6	1	0	-1.023820	0.000000	1.754760

ωB97XD/6-311+G(d,p)
E=-115.723450 E+ZPE=-115.671752 In CH_3CN E=-115.7292988
No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.015013	0.000000	0.003978
2	6	0	0.012523	0.000000	1.416766
3	1	0	0.884342	0.000000	-0.322450
4	1	0	0.505812	0.892456	1.821425
5	1	0	0.505812	-0.892456	1.821425
6	1	0	-1.024143	0.000000	1.754585

HOOH (**S30**)
M06-2X/6-311+G(d,p)
E=-151.5352304 E+ZPE=-151.507861 In CH_3CN E=-151.5432016
No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.042186	-0.003785	-0.010985
2	8	0	0.017745	-0.038433	1.411118
3	1	0	0.894192	0.011411	-0.240539
4	1	0	-0.437184	0.780038	1.640407

ωB97XD/6-311+G(d,p)
E=-151.5494836 E+ZPE=-151.52227 In CH_3CN E=-151.5573729
No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.042213	-0.002134	-0.012641
2	8	0	0.019234	-0.037685	1.412726
3	1	0	0.893180	0.010349	-0.239377
4	1	0	-0.437634	0.778699	1.639292

MeOOH (**S31**)
M06-2X/6-311+G(d,p)
E=-190.8296236 E+ZPE=-190.773989 In CH_3CN E=-190.8358555
No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	8	0	-0.017913	0.024691	-0.033704
2	8	0	0.025118	0.048721	1.391831
3	1	0	0.912656	-0.113016	-0.245253
4	6	0	-0.689200	1.199812	1.783392
5	1	0	-1.715614	1.159925	1.410806
6	1	0	-0.195823	2.107737	1.426059
7	1	0	-0.688093	1.173589	2.873468

ωB97XD/6-311+G(d,p)

E=-190.8508565 E+ZPE=-190.795594 In CH_3CN E=-190.8571553

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.023736	-0.011738	-0.031832
2	8	0	0.015473	0.037213	1.395763
3	1	0	0.914557	-0.069832	-0.239182
4	6	0	-0.687031	1.197487	1.778904
5	1	0	-1.717124	1.170306	1.410955
6	1	0	-0.186398	2.103716	1.421678
7	1	0	-0.684611	1.174308	2.870312

$HOCO_2^-$ (**S32**)

M06-2X/6-311+G(d,p)

E=-264.4492842 E+ZPE=-264.422311 In CH_3CN E=-264.5513308

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.579928	5.158824	2.759501
2	6	0	0.103581	4.008584	2.247918
3	8	0	1.343329	4.082043	2.349169
4	8	0	-0.642226	3.142334	1.794931
5	1	0	0.139374	5.716830	3.066251

ωB97XD/6-311+G(d,p)

E=-264.4594631 E+ZPE=-264.432771 In CH_3CN E=-264.5613881

No imaginary frequencies:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.581148	5.159795	2.761466
2	6	0	0.102349	4.009669	2.248488
3	8	0	1.343586	4.083319	2.350245
4	8	0	-0.641899	3.141433	1.793805
5	1	0	0.141242	5.714399	3.063767

Structures in Scheme S5

SO_4K radical (**25**)

ωB97XD/6-311+G(d,p)

E=-1298.9714875 E+ZPE= -1298.955928 In CH_3CN E= -1299.0180777

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.000000
2	16	0	0.000000	0.000000	1.500259
3	8	0	1.363153	0.000000	2.071712
4	8	0	-0.704964	1.311793	1.683517
5	8	0	-0.751813	-1.136913	2.071927
6	19	0	1.110235	-2.060464	3.575965

Complex (**S33**)

ωB97XD/6-311+G(d,p)

E=-1569.5671604 E+ZPE= -1569.428134 In CH_3CN E= -1569.6002219

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.020047	-0.636855	0.006640
2	6	0	-0.727476	-1.117365	1.407592
3	6	0	0.705110	-1.655297	1.337047
4	6	0	1.373235	-0.771306	0.267802
5	6	0	0.271908	-0.545386	-0.773560
6	8	0	-2.123192	-0.359082	-0.425389
7	1	0	-0.768831	-0.221962	2.041670
8	1	0	1.218720	-1.609973	2.297845
9	1	0	0.696768	-2.701909	1.013123
10	1	0	2.269150	-1.227454	-0.155587
11	1	0	1.652716	0.188237	0.708407
12	1	0	0.248073	-1.347480	-1.522536
13	1	0	0.324022	0.409983	-1.298930
14	8	0	-2.108361	3.006377	1.172545
15	16	0	-0.706112	2.983848	0.726755
16	8	0	0.024301	4.268823	1.056837
17	8	0	0.152680	2.079318	1.556415
18	8	0	-0.641864	2.661219	-0.710353
19	19	0	-3.188148	1.917042	-0.966712
20	1	0	-1.488379	-1.815358	1.759893

Transition state (**S34a**)

ωB97XD/6-311+G(d,p)

E= -1569.5309395 E+ZPE= -1569.396497 In CH_3CN E= -1569.5813851

Imaginary frequency: -798.6207

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.515043
3	6	0	1.455234	0.000000	1.930719

4	6	0	2.160367	0.778138	0.801651
5	6	0	1.388398	0.408258	-0.470611
6	8	0	-0.925793	-0.328985	-0.693326
7	1	0	-0.447375	1.061338	1.818772
8	1	0	1.610923	0.443609	2.916127
9	1	0	1.820115	-1.034554	1.976408
10	1	0	3.223398	0.540894	0.737428
11	1	0	2.058776	1.849701	0.981502
12	1	0	1.823319	-0.455217	-0.986603
13	1	0	1.300267	1.224010	-1.188661
14	8	0	-0.735491	2.341868	2.357940
15	16	0	-0.950042	3.403379	1.174614
16	8	0	-2.298856	3.173418	0.610300
17	8	0	-0.958620	4.659872	1.966514
18	8	0	0.136358	3.248090	0.230525
19	19	0	-3.481849	5.130703	1.702383
20	1	0	-0.684094	-0.713434	1.974697

Transition state (**S34b**)

ωB97XD/6-311+G(d,p)

E= -1569.5312797 E+ZPE= -1569.396715 In CH_3CN E= -1569.5832708

Imaginary frequency: -539.2824

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.524890
3	6	0	1.464790	0.000000	1.920044
4	6	0	2.260297	0.462201	0.699701
5	6	0	1.442813	-0.056022	-0.484665
6	8	0	-0.976433	0.056762	-0.698810
7	1	0	-0.525012	0.892451	1.883302
8	1	0	1.710798	0.484523	2.865277
9	1	0	1.795470	-1.118098	2.079822
10	1	0	3.289613	0.099583	0.709812
11	1	0	2.299103	1.558839	0.687632
12	1	0	1.672294	-1.112413	-0.669615
13	1	0	1.569026	0.488292	-1.420457
14	8	0	2.183167	-2.512084	2.089043
15	16	0	1.177565	-3.317604	3.039158
16	8	0	-0.177721	-2.988123	2.650491
17	8	0	1.615370	-4.708725	2.763937
18	8	0	1.518788	-2.965747	4.439266
19	19	0	2.654576	-5.162250	5.067066
20	1	0	-0.547950	-0.871268	1.897926

Complex (**S35a**)

ωB97XD/6-311+G(d,p)

E= -1569.5914288 E+ZPE= -1569.452252 In CH_3CN E= -1569.6271035

No imaginary frequencies

Center	Atomic	Atomic	Coordinates (Angstroms)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.042161	-0.393996	-0.075713
2	6	0	0.066807	-0.563473	1.347832
3	6	0	1.432836	-0.367385	1.886258
4	6	0	2.194590	0.320137	0.729260
5	6	0	1.454119	-0.105689	-0.545773
6	8	0	-0.958391	-0.471038	-0.796290
7	1	0	-0.371613	2.848790	3.092772
8	1	0	1.428952	0.223957	2.804936
9	1	0	1.876695	-1.343345	2.138565
10	1	0	3.253917	0.061108	0.715156
11	1	0	2.100703	1.400855	0.843008
12	1	0	1.863438	-1.030696	-0.971390
13	1	0	1.452227	0.655779	-1.325247
14	8	0	-0.202785	2.354110	2.284455
15	16	0	-0.688775	3.292662	1.015539
16	8	0	-2.153741	3.117560	0.942460
17	8	0	-0.240377	4.631951	1.326742
18	8	0	-0.035324	2.615646	-0.117942
19	19	0	-2.285537	1.690812	-1.234333
20	1	0	-0.815962	-0.797030	1.929571

Complex (**S35b**)

ωB97XD/6-311+G(d,p)

E= -1569.5775609 E+ZPE= -1569.440391 In CH_3CN E= -1569.6130247

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.240169	-0.673096	1.049915
2	6	0	0.101665	0.270447	2.185410
3	6	0	1.125242	1.182625	1.605482
4	6	0	1.652460	0.645368	0.311411
5	6	0	0.546838	-0.295820	-0.184752
6	8	0	-1.037725	-1.588402	1.120894
7	1	0	-0.808122	0.760748	2.554223
8	1	0	1.622631	1.956077	2.175379
9	1	0	3.114562	-1.529580	4.380181
10	1	0	2.568532	0.064271	0.487831
11	1	0	1.899355	1.431086	-0.408096
12	1	0	0.905522	-1.189311	-0.694738
13	1	0	-0.149747	0.224187	-0.854181
14	8	0	2.504549	-1.456222	3.639313
15	16	0	2.667659	-2.803177	2.705136
16	8	0	4.087236	-3.060073	2.618108
17	8	0	1.874003	-3.846410	3.386457
18	8	0	1.989213	-2.378318	1.465821
19	19	0	-0.163100	-3.940887	1.770537
20	1	0	0.499833	-0.327301	3.019425

HSO_4K (**S36**)

ωB97XD/6-311+G(d,p)

E= -1299.6515434 E+ZPE= -1299.622999 In CH_3CN E= -1299.6998054

No imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.000000
2	16	0	0.000000	0.000000	1.636654
3	8	0	1.389495	0.000000	2.037772
4	8	0	-0.789805	1.205194	1.953672
5	8	0	-0.769256	-1.204638	2.030589
6	19	0	-2.832198	0.010634	2.913326
7	1	0	0.769476	-0.499288	-0.291343