Supporting Information

Analysis of Seven-Membered Lactones by Computational NMR Methods: Proton NMR Chemical Shift Data are More Discriminating than Carbon

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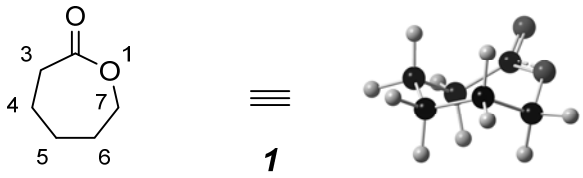
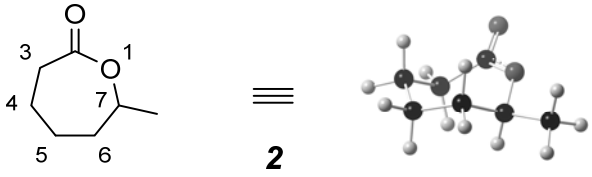
Table S1. Experimental and computed ^{13}C and ^{1}H NMR chemical shifts ($CDCl_3$, 125 and 500 MHz, respectively) for caprolactone (**1**).



1

Atom number	Carbon		Proton				COSY
	δ_{Cexp}	δ_{Ccomp}	δ_{Hexp}	δ_{Hcomp}	Mult	*J*[Hz]	(to ^{1}H-#)
2	176.2	187.37	-	-	-	-	-
3	34.4	38.81	2.64	2.64	t	Virtual coupling	4
4	29.2/22.8	28.31	1.73-1.81	1.71	m		3
5	29.2/22.8	34.51	1.73-1.81	1.75	m		-
6	28.8	34.06	1.84-1.89	1.79	m		7
7	69.2	73.79	4.22	4.28	t	Virtual coupling	6

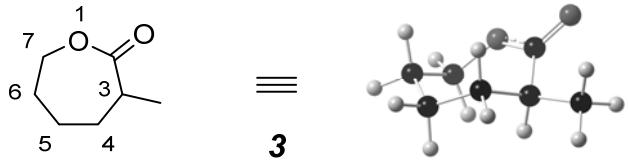
Table S2. Experimental and computed ^{13}C and ^{1}H NMR chemical shifts ($CDCl_3$, 125 and 500 MHz, respectively) for 7-methylcaprolactone (**2**).



2

Atom number	Carbon		Proton				COSY
	δ_{Cexp}	δ_{Ccomp}	δ_{Hexp}	δ_{Hcomp}	Mult	*J*[Hz]	(to ^{1}H-#)
2	175.7	186.39	-	-	-	-	-
3	35.1	39.22	2.62	2.53	ddd	2.0, 11.4, 13.5	
			2.66	2.74	dddd	2.0, 2.0, 7.7, 14.0	4
4	23.0	28.21	1.57, 1.93	1.55, 1.87	m		3, 5
5	28.3	33.68	1.60, 1.93	1.60, 1.89	m		-
6	36.3	40.55	1.64, 1.88	1.56, 1.83	m		5, 7
7	76.9	82.13	4.46	4.54	ddq	0.6, 8.6, 6.4	8, 6
8	22.6	24.28	1.36	1.26	d	6.4	7

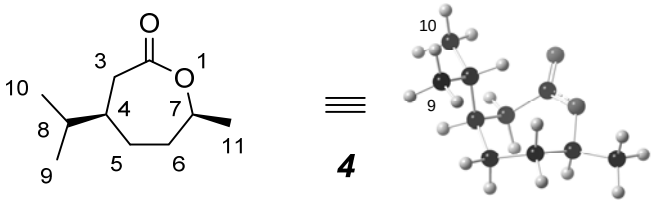
Table S3. Experimental and computed ^{13}C and ^{1}H NMR chemical shifts ($CDCl_3$, 125 and 500 MHz, respectively) for 3-methylcaprolactone (**3**).



3

Atom number	Carbon		Proton				COSY
	δ_{Cexp}	δ_{Ccomp}	δ_{Hexp}	δ_{Hcomp}	Mult	*J*[Hz]	(to ^{1}H-#)
2	178.3	189.28	-	-	-	-	-
3	37.6	43.13	2.72	2.81	ddq	2.0, 10.9, 6.7	8, 4
4α	32.1	37.01	1.73 br	1.65	d	14	-
4β			1.53	1.46	dddd	3.0, 10.9, 12.5, 14.0	3, 4α
5	29.1	34.00	1.95, 1.60-1.76	1.93, 1.64	m	-	5
6	28.6	33.71	1.95, 1.60-1.76	1.83, 1.69	m	-	7
7α	68.6	72.88	4.21	4.35	dddd	0.8, 0.8, 10.6, 12.8	6
7β			4.29	4.26	dddd	1.5, 2.2, 4.9, 12.7	6
8	18.7	20.37	1.21	1.08	d	6.7	3

Table S4. Experimental and computed ^{13}C and ^{1}H NMR chemical shifts ($CDCl_3$, 125 and 500 MHz, respectively) for normal *cis*-carvomenthide (**4**).



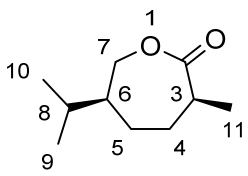
Atom Number[a]	Carbon		Proton				COSY
	δ_{Cexp}	δ_{Ccomp}	δ_{Hexp}	δ_{Hcomp}	Mult	*J*[Hz]	(to ^{1}H-#)
2	174.5	185.05					
3α	38.7	42.81	2.76	2.88	dd	14.1, 3.7	3β, 4
3β			2.80	2.79	ddd	14.2, 5.6, 1.5[c]	3α, 4, 5β[c]
4	39.1	45.12	1.51-1.57	1.41	nfom		3α, 3β
5α	30.4	35.63	1.58-1.65	1.56	m		
5β			1.98	2.04	ddddd	14.1, 5.0, 5.0, 3.5, 1.5[c]	3β[c]
6α	32.4	35.84	1.71	1.59	dddd	15.0, 7.5, 4.2, 2.0	7, 5β
6β			1.76	1.76	dddd	15.0, 15.0, 9.2, 3.4	7, 5β
7	76.6	82.14	4.44	4.54	ddq	15.0, 2.0, 6.4	Me11, 6α, 6β
8	29.3	35.15	1.58-1.65	1.57	m		
Me9	20.9[b]	22.56	1.02[b]	1.00	d	6.4	8
Me10	20.6[b]	22.05	0.90[b]	0.87	d	6.5	8
Me11	22.5	24.07	1.35	1.26	d	6.3	7

[a] α (=*trans*) and β (= *cis*) are designated relative to the C4 ^{i}Pr group

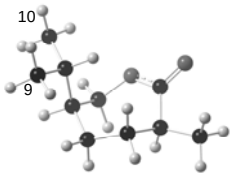
[b] the proton and carbon chemical shifts for each of the isopropyl Me groups have been correlated by HMQC; however, the assignment to the pro-*S* and pro-*R* C9 and C10 is arbitrary.

[c] protons 5β and 3β experience $^{4}J_{HH}$ (4 bond W-coupling)

Table S5. Experimental and computed ^{13}C and ^{1}H NMR chemical shifts ($CDCl_3$, 125 and 500 MHz, respectively) for abnormal *cis*-carvomenthide (**5**).



5



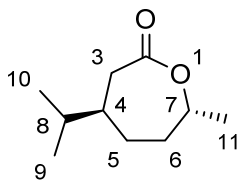
Atom	Carbon		Proton				COSY
number[a]	δ_{Cexp}	δ_{Ccomp}	δ_{Hexp}	δ_{Hcomp}	Mult	*J*[Hz]	(to ^{1}H-#)
2	178.1	189.23					
3	37.6	43.30	2.75	2.81	ddq	9.1, 4.4, 6.7	4α, 4β, Me11
4α	28.1	31.93	1.52-1.62	1.47	m		3, 5β, 6
4β			1.52-1.62	1.57	m		3, 5β, 6
5α	30.5	35.44	1.61-1.69	1.60	m		
5β			2.01	2.11	nfom[c]		4α, 4β, 5α, 6
6	43.6	49.87	1.42	1.27	ddddd	10.2, 4.3, 4.3, 4.3, 1.8	7α, 7β, 8, 5α, 5β
7α	69.6	73.36	4.30	4.42	dd	12.9, 1.8	7β, 6
7β			4.36	4.45	ddd	12.9, 4.2, 1.8	7α, 6
8	25.6	30.64	1.73	1.71	dsept	9.9, 6.6	6, Me9, Me10
Me9	20.83[b]	22.39	0.91[b]	1.01	d	6.5	8
Me10	20.75[b]	22.15	1.01[b]	0.89	d	6.7	8
Me11	18.6	20.57	1.20	1.09	d	6.7	3

[a] α (=*trans*) and β (= *cis*) are designated relative to the C4 ^{i}Pr group.

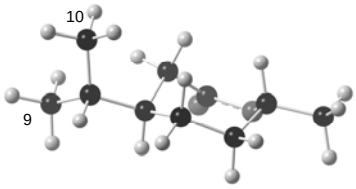
[b] the proton and carbon chemical shifts for each of the isopropyl Me groups have been correlated by HMQC; however, the assignment to the pro-*S* and pro-*R* C9 and C10 is arbitrary.

[c] non first-order multiplet.

Table S6. Experimental and computed ^{13}C and ^{1}H NMR chemical shifts ($CDCl_3$, 125 and 500 MHz, respectively) for normal *trans*-carvomenthide (**6**).



6

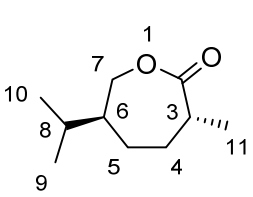


Atom	Carbon		Proton				COSY
number[a]	δ_{Cexp}	δ_{Ccomp}	δ_{Hexp}	δ_{Hcomp}	Mult	*J*[Hz]	(to ^{1}H-#)
2	175.7	186.60					
3α	38.2	42.44	2.42-2.51	2.35	m		4
3β			2.42-2.51	2.59	m		4
4	40.4	46.33	1.57	1.53	nfom	sum of Js = 31.1	3α, 3β, 5β, 8
5α	31.3	36.02	1.82	1.73	br dddd	13.3, 3.5, 3.5, 3.5	5β, 6α
5β			1.48	1.53	dddd	12.7, 12.7, 12.7, 3.6	4, 5α, 6β, 6α
6α	35.9	40.46	1.65	1.55	dddd	15.3, 12.5, 9.4, 3.0	5α, 5β, 6β, 7
6β			1.93	1.87	ddd	15.2, 3.9, 3.9	5β, 5α, 7
7	76.7	81.92	4.43	4.51	ddq	9.3, 0.5, 6.4	6α, 6β, Me11
8	33.6	40.36	1.69	1.64	dqq	3.8, 6.9, 6.9	4, Me9, Me10
Me9	18.9[b]	19.85	0.90[b]	0.85	d	6.9	8
Me10	18.6[b]	19.72	0.87[b]	0.86	d	6.8	8
Me11	22.7	24.41	1.35	1.25	d	6.4	7

[a] α (=*trans*) and β (= *cis*) are given relative to C4 ^{i}Pr group

[b] the proton and carbon chemical shifts for each of the isopropyl Me groups have been correlated by HMQC; however, the assignment to the pro-*S* and pro-*R* C9 and C10 is arbitrary.

Table S7. Experimental and computed ^{13}C and ^{1}H NMR chemical shifts ($CDCl_3$, 125 and 500 MHz, respectively) for abnormal *trans*-carvomenthide (**7**).



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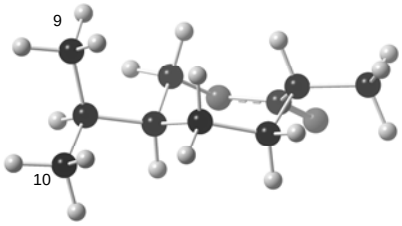


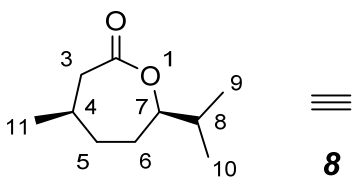
Atom	Carbon		Proton				COSY
number[a]	δ_{Cexp}	δ_{Ccomp}	δ_{Hexp}	δ_{Hcomp}	Mult	*J*[Hz]	(to ^{1}H-#)
2	178.3	189.17					
3	37.2	42.59	2.72	2.80	nfom	Sum of Js = 35.3	4α, Me11
4α	32.1	37.04	1.52-1.60	1.47	m		
4β			1.78	1.72	nfom	Sum of Js = 20.1	3
5α	31.27	35.79	1.86	1.79	nfom	Sum of Js = 19.7	7α[c]
5β			1.52	1.59	dddd	12, 12, 12, 3.0	
6	44.8	49.72	1.52-1.60	1.51	m		7α, 7β, 8
7α	71.8	76.14	4.16	4.14	ddd	12.4, 1.9, 1.9[c]	5α[c], 6, 7β
7β			4.09	4.23	dd	12.4, 8.4	6, 7α
8	31.31	37.76	1.68	1.62	dqq	4.0, 6.9, 6.9	6, Me9, Me10
Me9	19.6[b]	20.14	0.91[b]	0.88	d	6.9	8
Me10	19.4[b]	20.88	0.90[b]	0.87	d	6.9	8
Me11	18.6	20.25	1.20	1.07	d	6.7	3

[a] α (= *trans*) and β (= *cis*) relative to C6 ^{i}Pr group.

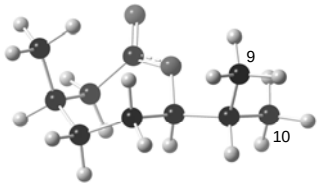
[b] the proton and carbon chemical shifts for each of the isopropyl Me groups have been correlated by HMQC; however, the assignment to the pro-*S* and pro-*R* C9 and C10 is arbitrary.

[c] protons 5α and 7α experience $^{4}J_{HH}$ (4 bond W-coupling)

Table S8. Experimental and computed ^{13}C and ^{1}H NMR chemical shifts ($CDCl_3$, 125 and 500 MHz, respectively) for normal *cis*-menthide (**8**).



8

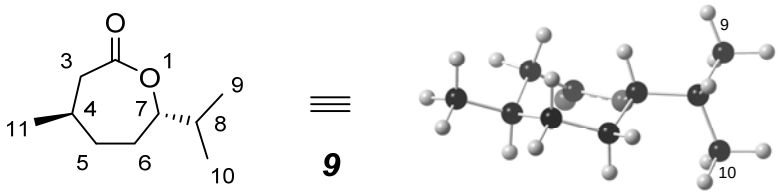


Atom	Carbon		Proton				COSY
number[a]	δ_{Cexp}	δ_{Ccomp}	δ_{Hexp}	δ_{Hcomp}	Mult	*J*[Hz]	(to ^{1}H-#)
2	174.5	185.23	-		-	-	-
3α	40.8	44.71	2.91	3.05	dd	13.6, 3.2	3β, 4
3β			2.54	2.48	ddd	13.6, 5.9, 1.1	3α, 4
4	26.70	33.49	2.18	2.04	nfom		3α, 3β, 5, Me11
5α	34.3/26.74	39.53	1.70-1.80	1.78	m		
5β			1.70-1.80	1.78	m		
6α	34.3/26.74	30.95	1.70-1.80	1.64	m		
6β			1.70-1.80	1.82	m		
7	84.9	90.01	4.02	4.16	ddd	7, 5, 2	6, 8
8	33.3	39.74	1.87	1.86	dqq	6.8, 6.8, 4.6	7, Me9, Me10
Me9	18.5[b]	18.13	0.982[b]	0.94	d	6.9	8
Me10	17.7[b]	20.34	0.977[b]	0.96	d	6.9	8
Me11	17.3	19.05	1.04	1.00	d	7.2	4

[a] α (= *trans*) and β (= *cis*) are relative to the C7 iPr.

[b] the proton and carbon chemical shifts for each of the isopropyl Me groups have been correlated by HMQC; however, the assignment to the pro-*S* and pro-*R* C9 and C10 is arbitrary.

Table S9. Experimental and computed ^{13}C and ^{1}H NMR chemical shifts ($CDCl_3$, 125 and 500 MHz, respectively) for normal *trans*-menthide (**9**).



9

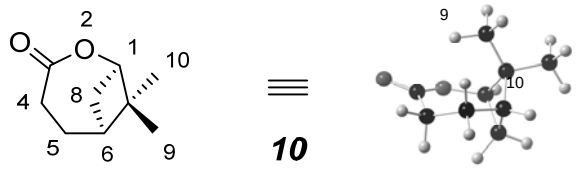
Atom number[a]	Carbon		Proton				COSY
	δ_{Cexp}	δ_{Ccomp}	δ_{Hexp}	δ_{Hcomp}	Mult	*J*[Hz]	(to ^{1}H-#)
2	175.3	185.51					
3α	42.6	46.42	2.57	2.61	dd	13.4, 11.6	3β, 4
3β			2.46	2.34	ddd	13.4, 1.9, 1.9[c]	3α, 4, 5β[c]
4	30.4/33.3	37.12	1.84	1.75	m		3α, 3β, 5α, 5β, Me11
5β	37.5	42.82	1.95	1.90	ddddd	13.7, 3.4, 3.4, 3.4, 1.8[c]	3β, 4, 5α, 6β[c]
5α			1.31	1.24	dddd	13.5, 13.5, 11.5, 3.5	5β, 4, 6β
6β	31.0	35.42	1.60	1.52	dddd	3.0, 9.3, 13.3, 15.3	5α, 6α
6α			1.85-1.90	1.91	m		6β
7	84.8	89.91	4.05	4.13	dd	9.2, 4.1	6β
8	30.4/33.3	39.56	1.84	1.78	dqq	3.4, 6.7, 6.7	Me9, Me10
Me9	18.4[b]	19.85	0.98[b]	0.94	d	7.0	8
Me10	17.1[b]	18.94	0.97[b]	0.94	d	7.0	8
Me11	24.0	26.32	1.04	0.99	d	6.7	4

[a] α (= *trans*), β (= *cis*) are relative to the C7 iPr.

[b] the proton and carbon chemical shifts for each of the isopropyl Me groups have been correlated by HMQC; however, the assignment to the pro-*S* and pro-*R* C9 and C10 is arbitrary.

[c] protons 3β and 5β experience $^{4}J_{HH}$ (4 bond W-coupling)

Table S10. Experimental and computed ^{13}C and ^{1}H NMR chemical shifts ($CDCl_3$, 125 and 500 MHz, respectively) for the normal nopinone-derived lactone **10**.

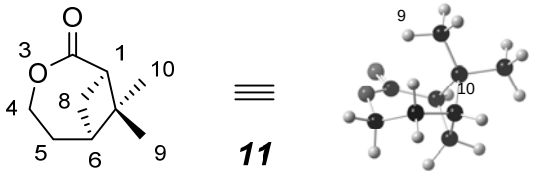


10

Atom	Carbon		Proton				COSY
Number[a]	δ_{Cexp}	δ_{Ccomp}	δ_{Hexp}	δ_{Hcomp}	Mult	*J*[Hz]	(to ^{1}H-#)
1	84.2	88.51	4.33	4.31	dd	5.7, 4.5	6, 8anti
3	175.1	186.15	-	-	-	-	
4α	34.1	39.06	2.91	3.03	ddd	16.7, 11.1, 7.8,	5α, 5β
4β			2.88	2.76	ddd	16.7, 6.4, 2.8	5α, 5β
5α	22.2	27.20	1.87	1.79	dddd	14.4, 7.5, 6.5, 2.6	4α, 4β
5β			1.95	1.98	ddd	14.2, 10.7, 6.2	4α, 4β
6	41.1	45.37	2.28	2.16	br ddd	6, 6, 6	1, 5, 8anti
7	43.2	48.51	-	-	-	-	-
8syn	26.5	28.20	2.11	2.18	d	14.1	8anti
8anti			2.65	2.57	ddd	14.1, 7.1, 6.1	1, 6, 8syn
9(syn)	18.5	20.28	0.89	0.81	s	-	-
10(anti)	27.4	28.89	1.30	1.22	s	-	-

[a] α (=*trans*) and β (= *cis*) are designated relative to the gem-dimethylated bridge

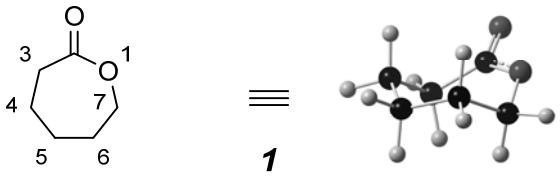
Table S11. Experimental and computed ^{13}C and ^{1}H NMR chemical shifts ($CDCl_3$, 125 and 500 MHz, respectively) for the abnormal nopinone-derived lactone **11**.



Atom	Carbon		Proton				COSY
Number [a]	δ_{Cexp}	δ_{Ccomp}	δ_{Hexp}	δ_{Hcomp}	Mult	*J*[Hz]	(to ^{1}H-#)
1	53.4	57.97	2.94	2.87	dd	7.6, 4.8, 1.0	8anti, 6
2	174.7	185.24					
4α	66.3	70.48	4.69	4.84	ddd	13.1, 13.1, 3.7	4β, 5α, 5β
4β			4.32	4.25	ddd	13.0, 5.8, 1.3	4α, 5β
5α	27.6	31.94	1.86	1.75	dddd	15.2, 7.7, 3.7, 1.4	4α, 5β, 6
5β			2.46	2.52	ddd	15.0, 13.3, 5.8	5α, 4α, 4β
6	41.0	45.42	2.26	2.16	ddd	7.4, 7.4, 4.6	1, 5β, 8an
7	40.6	45.97	-	-	-		
8syn	19.9	21.97	2.30	2.36	d	12.7	8anti
8anti			2.45	2.38	ddd	12.8, 7.5, 7.5	1, 8syn, 6
9(syn)	20.8	22.19	1.04	0.99	s		
10(anti)	28.6	29.99	1.38	1.31	s		

[a] α (=*trans*) and β (= *cis*) are designated relative to the gem-dimethylated bridge.

Table S12-^{1}H. Error analysis and correction of the ^{1}H NMR data for Lactone **1**.



1

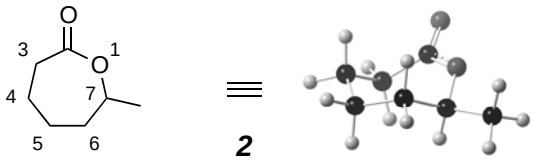
Atom number	Experimental Shift (δH_{exp})	Computed Shift (δH_{comp})	Computed Shift of the CH_2 Pair	Error ($\lvert\delta H_{exp} - \delta H_{comp}\rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
3R	2.64	2.55	2.64	0.00	2.65	0.01
3S		2.73				
4R	1.73–1.81	1.54	1.71	0.06	1.76	0.01
4S		1.88				
5R	1.73–1.81	1.55	1.75	0.02	1.80	0.03
5S		1.96				
6R	1.84–1.89	1.88	1.79	0.07	1.84	0.03
6S		1.71				
7R	4.22	4.30	4.28	0.06	4.22	0.00
7S		4.27				
	Slope 0.955 Intercept 0.126			0.04 Mean Absolute Error (MAE)		0.01 Corrected Mean Absolute Error (CMAE)

Table S12-^{13}C. Error analysis and correction of the ^{13}C NMR data for Lactone **1**.

Atom number	Experimental Shift (δC_{exp})	Computed Shift (δC_{comp})	Error ($\lvert\delta C_{exp} - \delta C_{comp}\rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
2	176.2	187.37	11.17	176.70	0.50
3	34.4	38.81	4.41	33.81	0.59
4	**22.8**/29.2[a]	28.31	5.51	23.71	0.91
5	22.8/**29.2**[a]	34.51	5.31	29.68	0.48
6	28.8	34.06	5.26	29.25	0.45
7	69.2	73.79	4.59	67.46	1.74
	Slope 0.962 Intercept –3.52		6.0 Mean Absolute Error (MAE)		0.8 Corrected Mean Absolute Error (CMAE)

[a] The assignment for these resonances were ambiguous. However, for the purpose of the CMAE calculation, the bold chemical shift value was used to determine the error value.

Table S13-^{1}H. Error analysis and correction of the ^{1}H NMR data for Lactone **2**.



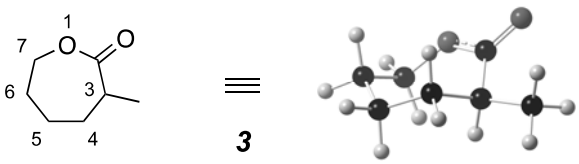
2

Atom number	Experimental Shift (δH_{exp})	Computed Shift (δH_{comp})	Error ($\lvert \delta H_{exp} - \delta H_{comp} \rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
3α	2.66	2.74	0.08	2.74	0.08
3β	2.62	2.53	0.09	2.54	0.08
4α	1.93	1.87	0.06	1.92	0.01
4β	1.57	1.55	0.02	1.62	0.05
5α	1.60	1.60	0.00	1.66	0.11
5β	1.93	1.89	0.04	1.93	0.16
6α	1.88	1.83	0.05	1.88	0.12
6β	1.64	1.56	0.08	1.62	0.14
7	4.46	4.54	0.08	4.43	0.03
8	1.36	1.26	0.10	1.34	0.02
	Slope 0.950 Intercept 0.133		0.06 Mean Absolute Error (MAE)		0.03 Corrected Mean Absolute Error (CMAE)

Table S13-^{13}C. Error analysis and correction of the ^{13}C NMR data for Lactone **2**.

Atom number	Experimental Shift (δC_{exp})	Computed Shift (δC_{comp})	Error ($\lvert \delta C_{exp} - \delta C_{comp} \rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
2	175.7	186.39	10.69	175.91	0.21
3	35.1	39.22	4.12	34.96	0.14
4	23.0	28.21	5.21	24.42	1.42
5	28.3	33.68	5.38	29.66	1.36
6	36.3	40.55	4.25	36.24	0.06
7	76.9	82.13	5.23	76.06	0.84
8	22.6	24.28	1.68	20.66	1.94
	Slope 0.958 Intercept –2.596		5.2 Mean Absolute Error (MAE)		0.9 Corrected Mean Absolute Error (CMAE)

Table S14-^{1}H. Error analysis and correction of the ^{1}H NMR data for Lactone **3**.



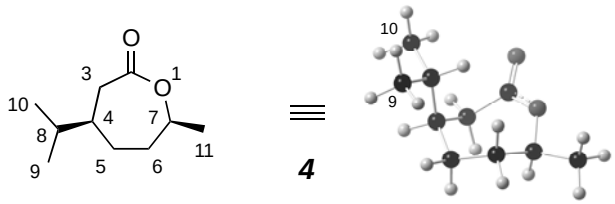
3

Atom number	Experimental Shift (δH_{exp})	Computed Shift (δH_{comp})	Error ($\lvert \delta H_{exp} - \delta H_{comp} \rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
3	2.72	2.81	0.09	2.81	0.09
4α	1.73	1.65	0.08	1.71	0.02
4β	1.53	1.46	0.07	1.52	0.01
5α	1.60–1.76	1.64	0.04	1.70	0.02
5β	1.95	1.93	0.02	1.97	0.02
6α	1.95	1.83	0.12	1.88	0.07
6β	1.60–1.76	1.69	0.01	1.74	0.06
7α	4.21	4.35	0.14	4.27	0.06
7β	4.29	4.26	0.03	4.18	0.11
8	1.21	1.08	0.13	1.17	0.04
	Slope 0.947 Intercept 0.145		0.07 Mean Absolute Error (MAE)		0.05 Corrected Mean Absolute Error (CMAE)

Table S14-^{13}C. Error analysis and correction of the ^{13}C NMR data for Lactone **3**.

Atom number	Experimental Shift (δC_{exp})	Computed Shift (δC_{comp})	Error ($\lvert \delta C_{exp} - \delta C_{comp} \rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
2	178.3	189.28	10.98	178.45	0.15
3	37.6	43.13	5.53	38.58	0.98
4	32.1	37.01	4.91	32.72	0.62
5	29.1	34.00	4.90	29.84	0.74
6	28.6	33.71	5.11	29.57	0.97
7	68.6	72.88	4.28	67.05	1.55
8	18.7	20.37	1.67	16.79	1.91
	Slope 0.957 Intercept –2.697		5.3 Mean Absolute Error (MAE)		1.0 Corrected Mean Absolute Error (CMAE)

Table S15-^{1}H. Error analysis and correction of the ^{1}H NMR data for Lactone **4**.



4

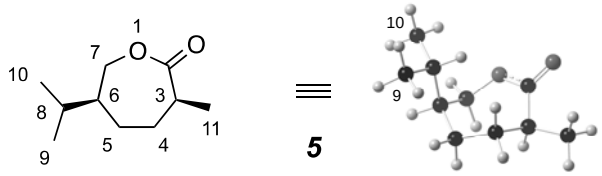
Atom number[a]	Experimental Shift (δH_{exp})	Computed Shift (δH_{comp})	Error ($\lvert \delta H_{exp} - \delta H_{comp} \rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
3α	2.76	2.88	0.12	2.85	0.09
3β	2.80	2.79	0.01	2.76	0.04
4	1.51–1.57	1.41	0.13	1.46	0.08
5α	1.58–1.65	1.56	0.06	1.60	0.02
5β	1.98	2.04	0.06	2.06	0.08
6α	1.71	1.59	0.12	1.63	0.08
6β	1.76	1.76	0.00	1.79	0.03
7	4.44	4.54	0.10	4.42	0.02
8	1.58–1.65	1.57	0.05	1.61	0.01
Me9	1.02[b]	1.00	0.02	1.07	0.05
Me10	0.90[b]	0.87	0.03	0.95	0.05
Me11	1.35	1.26	0.09	1.32	0.03
	Slope 0.946 Intercept 0.124		0.07 Mean Absolute Error (MAE)		0.05 Corrected Mean Absolute Error (CMAE)

Table S15-^{13}C. Error analysis and correction of the ^{13}C NMR data for Lactone **4**.

Atom number	Experimental Shift (δC_{exp})	Computed Shift (δC_{comp})	Error ($\lvert \delta C_{exp} - \delta C_{comp} \rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
2	174.5	185.05	10.55	174.12	0.38
3	38.7	42.81	4.11	38.76	0.06
4	39.1	45.12	6.02	40.96	1.86
5	30.4	35.63	5.23	31.93	1.53
6	32.4	35.84	3.44	32.13	0.27
7	76.6	82.14	5.54	76.19	0.41
8	29.3	35.15	5.85	31.48	2.18
9	20.9[b]	22.56	1.66	19.50	1.40
10	20.6[b]	22.05	1.45	19.00	1.60
11	22.5	24.07	1.57	20.93	1.57
	Slope 0.952 Intercept –1.977		4.5 Mean Absolute Error (MAE)		1.1 Corrected Mean Absolute Error (CMAE)

[a] α (=*trans*) and β (= *cis*) are designated relative to the C4 ^{i}Pr group. [b] the proton and carbon chemical shifts for each of the isopropyl Me groups have been correlated by HMQC; however, the assignment to the pro-*S* and pro-*R* C9 and C10 is arbitrary.

Table S16-^{1}H. Error analysis and correction of the ^{1}H NMR data for Lactone **5**.



5

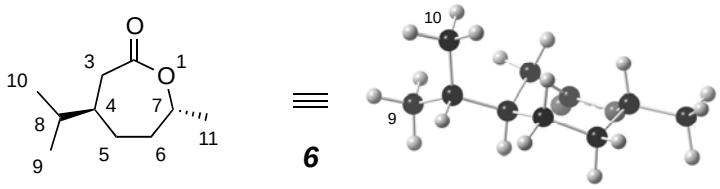
Atom number[a]	Experimental Shift (δH_{exp})	Computed Shift (δH_{comp})	Error ($\lvert\delta H_{exp} - \delta H_{comp}\rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
3	2.75	2.81	0.06	2.77	-0.02
4α	1.62-1.52	1.47	0.10	1.51	0.06
4β	1.62-1.52	1.57	0.00	1.61	-0.04
5α	1.61-1.69	1.60	0.05	1.63	0.02
5β	2.01	2.11	0.10	2.11	-0.10
6	1.42	1.27	0.15	1.32	0.10
7α	4.30	4.42	0.12	4.30	0.00
7β	4.36	4.45	0.09	4.33	0.03
8	1.73	1.71	0.02	1.73	0.00
Me9	0.91[b]	1.01	0.10	1.07	-0.16
Me10	1.01[b]	0.89	0.12	0.96	0.05
Me11	1.20	1.09	0.11	1.15	0.05
	Slope 0.946 Intercept 0.118		0.09 Mean Absolute Error (MAE)		0.05 Corrected Mean Absolute Error (CMAE)

Table S16-^{13}C. Error analysis and correction of the ^{13}C NMR data for Lactone **5**.

Atom number	Experimental Shift (δC_{exp})	Computed Shift (δC_{comp})	Error ($\lvert\delta C_{exp} - \delta C_{comp}\rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
2	178.1	189.23	11.13	177.98	0.12
3	37.6	43.30	5.70	39.16	-1.56
4	28.1	31.93	3.83	28.34	-0.24
5	30.5	35.44	4.94	31.68	-1.18
6	43.6	49.87	6.27	45.41	-1.81
7	69.6	73.36	3.76	67.75	1.85
8	25.6	30.64	5.04	27.12	-1.52
9	20.83[b]	22.39	1.56	19.27	1.56
10	20.75[b]	22.15	1.40	19.04	1.71
11	18.6	20.57	1.97	17.53	1.07
	Slope 0.951 Intercept –2.030		4.6 Mean Absolute Error (MAE)		1.3 Corrected Mean Absolute Error (CMAE)

[a] α (=*trans*) and β (= *cis*) are designated relative to the C4 ^{i}Pr group. [b] the proton and carbon chemical shifts for each of the isopropyl Me groups have been correlated by HMQC; however, the assignment to the pro-*S* and pro-*R* C9 and C10 is arbitrary.

Table S17-^{1}H. Error analysis and correction of the ^{1}H NMR data for Lactone **6**.



6

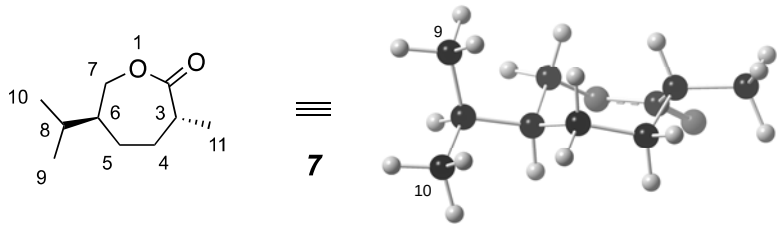
Atom number[a]	Experimental Shift (δH_{exp})	Computed Shift (δH_{comp})	Error ($\lvert \delta H_{exp} - \delta H_{comp} \rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
3α	2.42-2.51	2.35	0.12	2.36	0.10
3β	2.42-2.51	2.59	0.13	2.59	0.13
4	1.57	1.53	0.04	1.57	0.00
5α	1.82	1.73	0.09	1.77	0.05
5β	1.48	1.53	0.05	1.57	0.09
6α	1.65	1.55	0.10	1.59	0.06
6β	1.93	1.87	0.06	1.90	0.03
7	4.43	4.51	0.08	4.43	0.00
8	1.69	1.64	0.05	1.68	0.01
Me9	0.90[b]	0.85	0.05	0.92	0.02
Me10	0.87[b]	0.86	0.01	0.93	0.06
Me11	1.35	1.25	0.10	1.30	0.05
	Slope 0.960 Intercept 0.105		0.07 Mean Absolute Error (MAE)		0.05 Corrected Mean Absolute Error (CMAE)

Table S17-^{13}C. Error analysis and correction of the ^{13}C NMR data for Lactone **6**.

Atom number	Experimental Shift (δC_{exp})	Computed Shift (δC_{comp})	Error ($\lvert \delta C_{exp} - \delta C_{comp} \rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
2	175.7	186.60	10.90	175.22	0.48
3	38.2	42.44	4.24	38.41	0.21
4	40.4	46.33	5.93	42.10	1.70
5	31.3	36.02	4.72	32.32	1.02
6	35.9	40.46	4.56	36.53	0.63
7	76.7	81.92	5.22	75.88	0.82
8	33.6	40.36	6.76	36.43	2.83
9	18.9[b]	19.85	0.95	16.97	1.93
10	18.6[b]	19.72	1.12	16.85	1.75
11	22.7	24.41	1.71	21.30	1.40
	Slope 0.949 Intercept –1.869		4.6 Mean Absolute Error (MAE)		1.3 Corrected Mean Absolute Error (CMAE)

[a] α (=*trans*) and β (= *cis*) are given relative to C4 ^{i}Pr group. [b] the proton and carbon chemical shifts for each of the isopropyl Me groups have been correlated by HMQC; however, the assignment to the pro-*S* and pro-*R* C9 and C10 is arbitrary.

Table S18-^{1}H. Error analysis and correction of the ^{1}H NMR data for Lactone **7**.



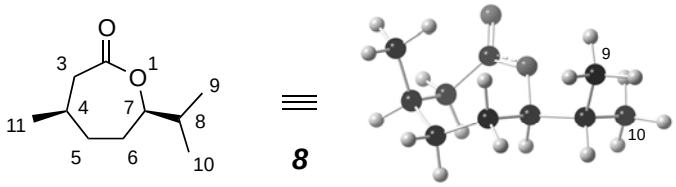
Atom number[a]	Experimental Shift (δH_{exp})	Computed Shift (δH_{comp})	Error ($\lvert\delta H_{exp} - \delta H_{comp}\rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
3	2.72	2.80	0.08	2.79	0.07
4α	1.56	1.47	0.09	1.51	0.05
4β	1.78	1.72	0.06	1.75	0.03
5α	1.86	1.79	0.07	1.82	0.04
5β	1.52	1.59	0.07	1.63	0.11
6	1.56	1.51	0.05	1.55	0.01
7α	4.16	4.14	0.02	4.07	0.09
7β	4.09	4.23	0.14	4.16	0.07
8	1.68	1.62	0.06	1.66	0.02
Me9	0.91[b]	0.88	0.04	0.94	0.03
Me10	0.90[b]	0.87	0.02	0.94	0.04
Me11	1.20	1.07	0.13	1.13	0.07
	Slope 0.957 Intercept 0.104		0.07 Mean Absolute Error (MAE)		0.05 Corrected Mean Absolute Error (CMAE)

Table S18-^{13}C. Error analysis and correction of the ^{13}C NMR data for Lactone **7**.

Atom number	Experimental Shift (δC_{exp})	Computed Shift (δC_{comp})	Error ($\lvert\delta C_{exp} - \delta C_{comp}\rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
2	178.3	189.17	10.87	177.98	0.32
3	37.2	42.59	5.39	38.59	1.39
4	32.1	37.04	4.94	33.31	1.21
5	31.27	35.79	4.52	32.12	0.85
6	44.8	49.72	4.92	45.37	0.57
7	71.8	76.14	4.34	70.49	1.31
8	31.31	37.76	6.45	34.00	2.69
9	19.6[b]	20.14	1.28	17.95	1.65
10	19.4[b]	20.88	0.74	17.24	2.16
11	18.6	20.25	1.65	17.35	1.25
	Slope 0.951 Intercept -1.913		4.5 Mean Absolute Error (MAE)		1.3 Corrected Mean Absolute Error (CMAE)

[a] α (= *trans*) and β (= *cis*) relative to C6 ^{i}Pr group. [b] the proton and carbon chemical shifts for each of the isopropyl Me groups have been correlated by HMQC; however, the assignment to the pro-*S* and pro-*R* C9 and C10 is arbitrary.

Table S19-^{1}H. Error analysis and correction of the ^{1}H NMR data for Lactone **8**.



8

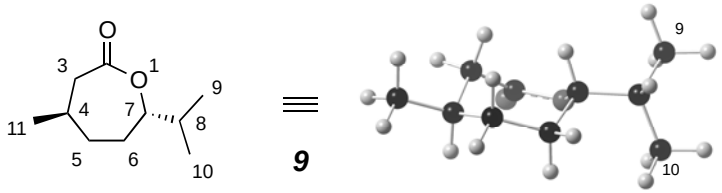
Atom number[a]	Experimental Shift (δH_{exp})	Computed Shift (δH_{comp})	Error ($\lvert \delta H_{exp} - \delta H_{comp} \rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
3α	2.91	3.05	0.14	3.00	0.09
3β	2.54	2.47	0.07	2.45	0.09
4	2.18	2.04	0.14	2.04	0.14
5α	1.70-1.80	1.78	0.03	1.80	0.05
5β	1.70-1.80	1.77	0.02	1.79	0.04
6α	1.70-1.80	1.64	0.11	1.67	0.08
6β	1.70-1.80	1.83	0.08	1.84	0.09
7	4.02	4.16	0.14	4.04	0.02
8	1.87	1.76	0.11	1.78	0.09
Me9	0.982[b]	0.94	0.04	1.01	0.03
Me10	0.977[b]	0.96	0.02	1.03	0.05
Me11	1.04	1.00	0.04	1.06	0.02
	Slope 0.942 Intercept 0.123		0.08 Mean Absolute Error (MAE)		0.07 Corrected Mean Absolute Error (CMAE)

Table S19-^{13}C. Error analysis and correction of the ^{13}C NMR data for Lactone **8**.

Atom number	Experimental Shift (δC_{exp})	Computed Shift (δC_{comp})	Error ($\lvert \delta C_{exp} - \delta C_{comp} \rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
2	174.5	185.23	10.73	174.36	0.16
3	40.8	44.71	3.91	40.42	0.39
4	26.7	33.49	6.79	29.72	3.03
5	26.74/**34.3**[c]	39.53	5.23	35.47	1.22
6	**26.74**/34.3[c]	30.95	4.21	27.30	0.52
7	84.9	90.01	5.11	83.59	1.26
8	33.3	39.74	6.44	35.67	2.41
9	18.5[b]	18.13	0.37	15.08	1.34
10	17.7[b]	20.34	2.64	17.18	2.58
11	17.3	19.05	1.75	15.95	1.45
	Slope 0.953 Intercept –2.205		4.7 Mean Absolute Error (MAE)		1.4 Corrected Mean Absolute Error (CMAE)

[a] α (= *trans*) and β (= *cis*) are relative to the C7 iPr. [b] the proton and carbon chemical shifts for each of the isopropyl Me groups have been correlated by HMQC; however, the assignment to the pro-*S* and pro-*R* C9 and C10 is arbitrary. [c] The assignment for these resonances were ambiguous. However, for the purpose of the CMAE calculation, the bold chemical shift value was used to determine the error value.

Table S20-^{1}H. Error analysis and correction of the ^{1}H NMR data for Lactone **9**.



9

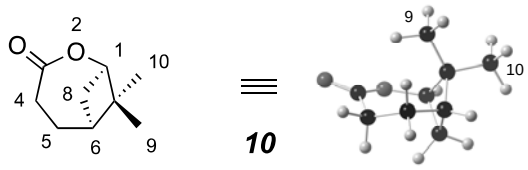
Atom number[a]	Experimental Shift (δH_{exp})	Computed Shift (δH_{comp})	Error ($\lvert\delta H_{exp} - \delta H_{comp}\rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
3α	2.57	2.61	0.04	2.62	0.05
3β	2.46	2.34	0.12	2.35	0.11
4	1.84	1.75	0.09	1.79	0.05
5α	1.95	1.24	0.07	1.30	0.01
5β	1.31	1.90	0.05	1.93	0.02
6α	1.60	1.91	0.03	1.94	0.06
6β	1.85-1.90	1.52	0.08	1.57	0.03
7	4.05	4.13	0.08	4.08	0.03
8	1.84	1.78	0.06	1.82	0.02
Me9	0.98[b]	0.94	0.04	1.01	0.03
Me10	0.97[b]	0.94	0.03	1.01	0.04
Me11	1.04	0.99	0.05	1.06	0.02
	Slope 0.963 Intercept 0.106		0.07 Mean Absolute Error (MAE)		0.04 Corrected Mean Absolute Error (CMAE)

Table S20-^{13}C. Error analysis and correction of the ^{13}C NMR data for Lactone **9**.

Atom number	Experimental Shift (δC_{exp})	Computed Shift (δC_{comp})	Error ($\lvert\delta C_{exp} - \delta C_{comp}\rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
2	175.3	185.51	10.21	175.19	0.11
3	42.6	46.42	3.82	42.00	0.60
4	**30.4**/33.3[c]	37.12	6.72	33.10	2.70
5	37.5	42.82	5.32	38.55	1.05
6	31.0	35.42	4.42	31.47	0.47
7	84.8	89.91	5.11	83.65	1.15
8	30.4/**33.3**[c]	39.56	6.26	35.44	2.14
9	18.4[b]	18.94	0.54	15.69	2.71
10	17.1[b]	19.85	2.75	16.56	0.54
11	24.0	26.32	2.32	22.76	1.24
	Slope 0.958 Intercept –2.447		4.7 Mean Absolute Error (MAE)		1.3 Corrected Mean Absolute Error (CMAE)

[a] α (= *trans*), β (= *cis*) are relative to the C7 iPr. [b] the proton and carbon chemical shifts for each of the isopropyl Me groups have been correlated by HMQC; however, the assignment to the pro-*S* and pro-*R* C9 and C10 is arbitrary. [c] The assignment for these resonances were ambiguous. However, for the purpose of the CMAE calculation, the bold chemical shift value was used to determine the error value.

Table S21-^{1}H. Error analysis and correction of the ^{1}H NMR data for Lactone **10**.



10

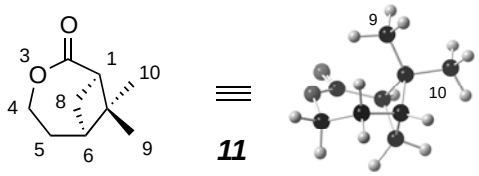
Atom number[a]	Experimental Shift (δH_{exp})	Computed Shift (δH_{comp})	Error ($\lvert\delta H_{exp} - \delta H_{comp}\rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
1	4.33	4.31	0.02	4.30	0.03
4α	2.91	3.03	0.12	3.05	0.14
4β	2.88	2.76	0.12	2.78	0.10
5α	1.87	1.79	0.08	1.84	0.03
5β	1.95	1.98	0.03	2.02	0.07
6	2.28	2.16	0.12	2.20	0.08
8syn	2.11	2.18	0.07	2.22	0.11
8anti	2.65	2.57	0.08	2.60	0.05
9(syn)	0.89	0.81	0.08	0.88	0.01
10(anti)	1.30	1.22	0.08	1.28	0.02
	Slope 0.977 Intercept 0.088		0.08 Mean Absolute Error (MAE)		0.06 Corrected Mean Absolute Error (CMAE)

Table S21-^{13}C. Error analysis and correction of the ^{13}C NMR data for Lactone **10**.

Atom number	Experimental Shift (δC_{exp})	Computed Shift (δC_{comp})	Error ($\lvert\delta C_{exp} - \delta C_{comp}\rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
1	84.2	88.51	4.31	82.54	1.66
3	175.1	186.15	11.05	175.40	0.30
4	34.1	39.06	4.96	35.51	1.41
5	22.2	27.20	5.00	24.22	2.02
6	41.1	45.37	4.27	41.51	0.41
7	43.2	48.51	5.31	44.49	1.29
8	26.5	28.20	1.70	25.17	1.33
9	18.5	20.28	1.78	17.64	0.86
10	27.4	28.89	1.49	25.83	1.57
	Slope 0.951 Intercept –1.652		4.4 Mean Absolute Error (MAE)		1.2 Corrected Mean Absolute Error (CMAE)

[a] α (=*trans*) and β (= *cis*) are designated relative to the gem-dimethylated bridge

Table S22-^{1}H. Error analysis and correction of the ^{1}H NMR data for Lactone **11**.

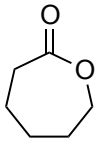


Atom number[a]	Experimental Shift (δH_{exp})	Computed Shift (δH_{comp})	Error ($\lvert \delta H_{exp} - \delta H_{comp} \rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
1	2.94	2.87	0.07	2.88	0.06
4α	4.69	4.84	0.15	4.78	0.09
4β	4.32	4.25	0.07	4.21	0.11
5α	1.86	1.75	0.11	1.80	0.06
5β	2.46	2.52	0.06	2.55	0.09
6	2.26	2.16	0.10	2.20	0.06
8syn	2.30	2.36	0.06	2.39	0.09
8anti	2.45	2.38	0.07	2.42	0.03
9(syn)	1.04	0.99	0.05	1.08	0.04
10(anti)	1.38	1.31	0.07	1.39	0.01
	Slope 0.963 Intercept 0.121		0.08 Mean Absolute Error (MAE)		0.06 Corrected Mean Absolute Error (CMAE)

Table S22-^{13}C. Error analysis and correction of the ^{13}C NMR data for Lactone **11**.

Atom number	Experimental Shift (δC_{exp})	Computed Shift (δC_{comp})	Error ($\lvert \delta C_{exp} - \delta C_{comp} \rvert$)	Scaled (Linearly Corrected) Shift	Corrected Error
1	53.4	57.97	4.57	53.66	0.26
2	174.7	185.24	10.54	174.51	0.19
4	66.3	70.48	4.18	65.53	0.77
5	27.6	31.94	4.34	28.94	1.34
6	41.0	45.42	4.42	41.74	0.74
7	40.6	45.97	5.37	42.26	1.66
8	19.9	21.97	2.07	19.48	0.42
9	20.8	22.19	1.39	19.68	1.12
10	28.6	29.99	1.39	27.09	1.51
	Slope 0.950 Intercept –1.391		4.3 Mean Absolute Error (MAE)		0.9 Corrected Mean Absolute Error (CMAE)

[a] α (=*trans*) and β (= *cis*) are designated relative to the gem-dimethylated bridge



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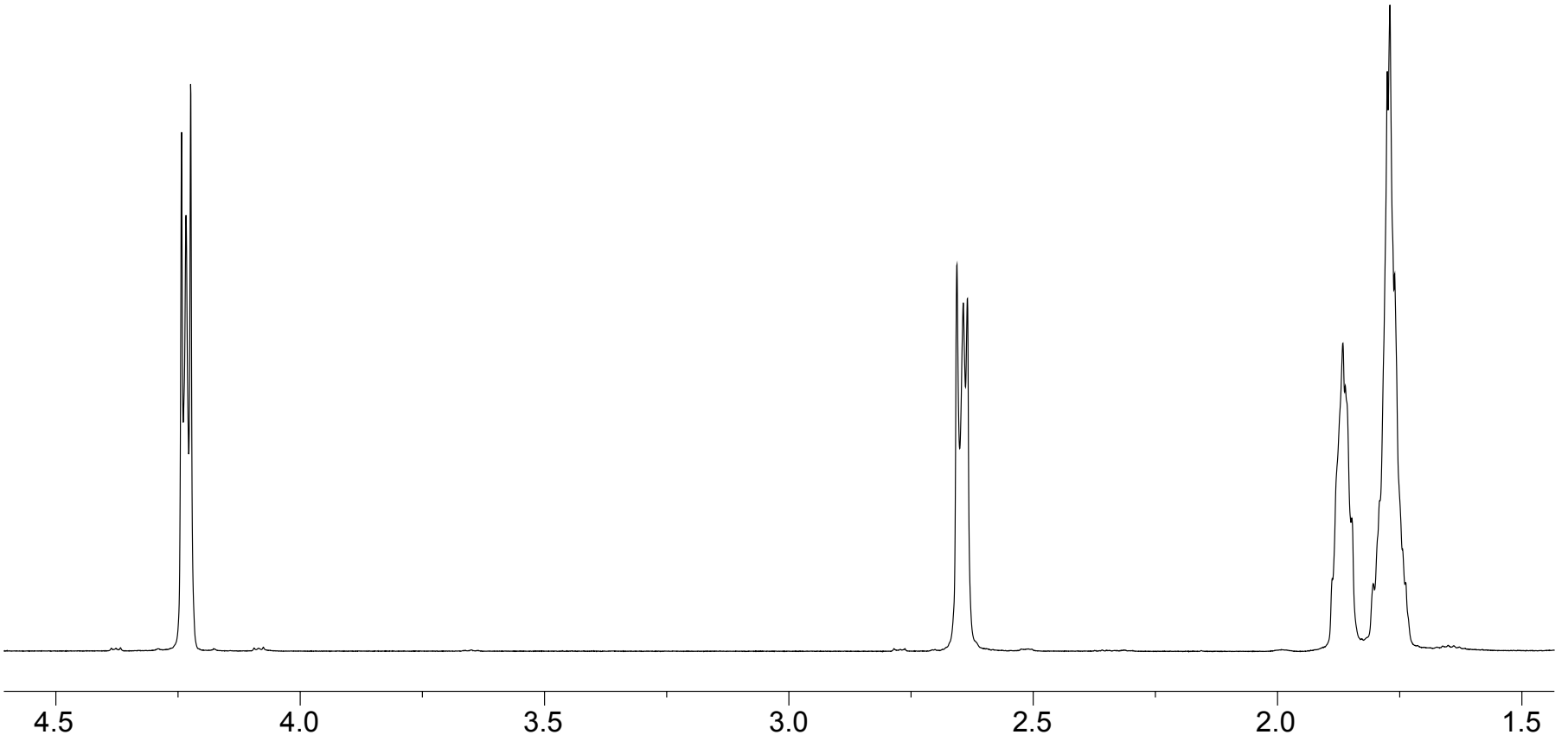

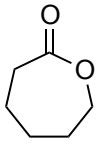

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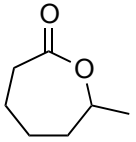

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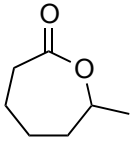

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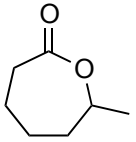

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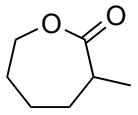

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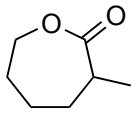

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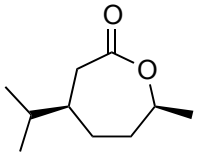

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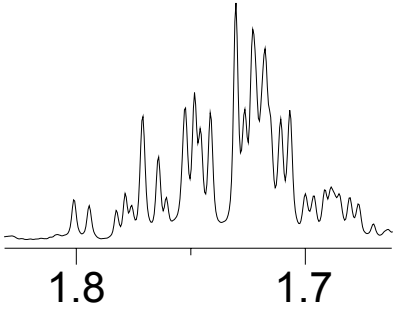

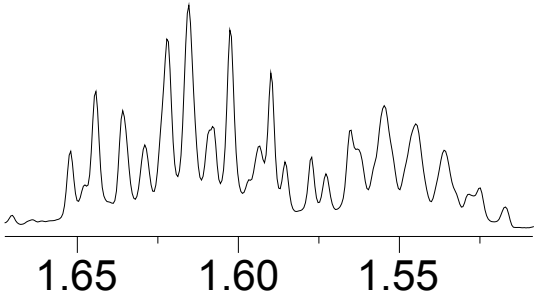

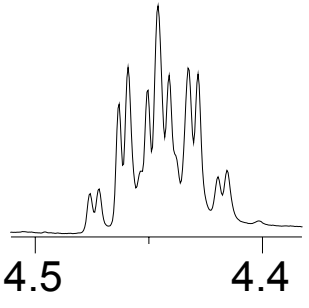

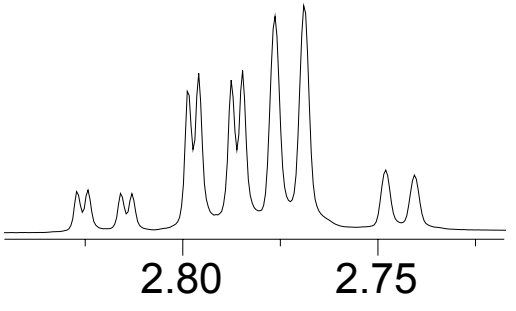

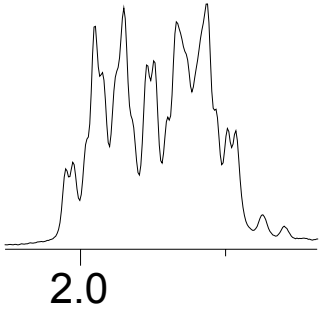

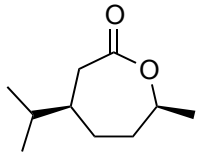

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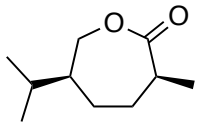

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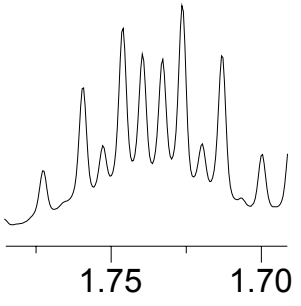
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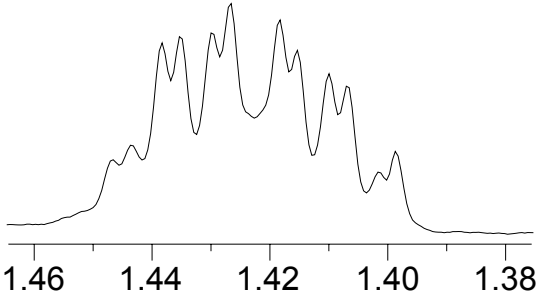
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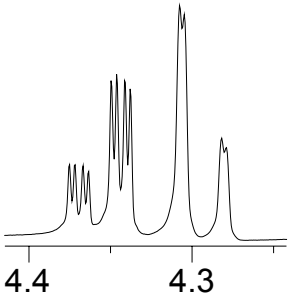
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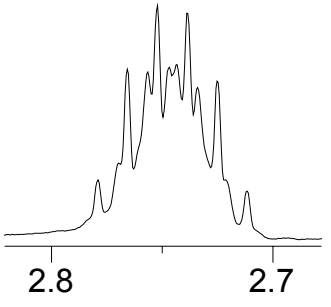
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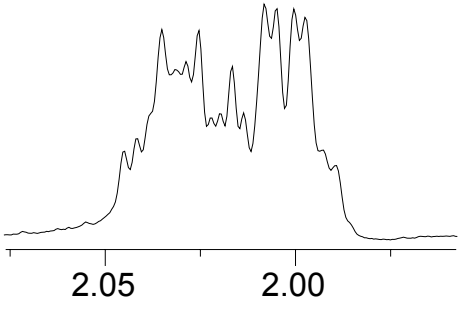
2.7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3.0
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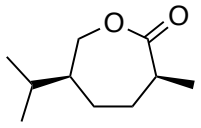

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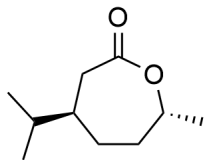

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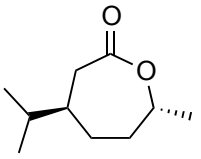

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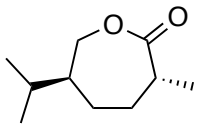

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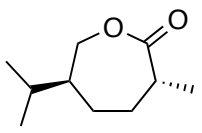

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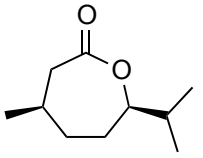

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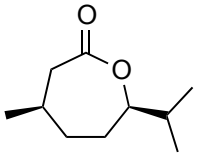

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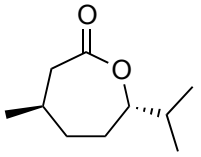

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2.60 2.55 2.50 2.45
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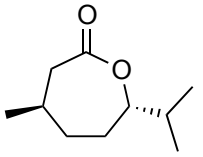
1.65 1.60 1.55
ppm 4.0 3.5 3.0 2.5 2.0 1.5 1.0



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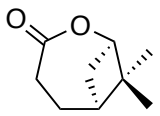

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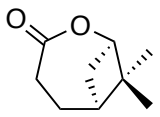

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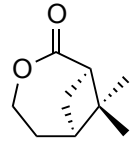
O
O

11

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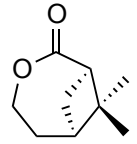


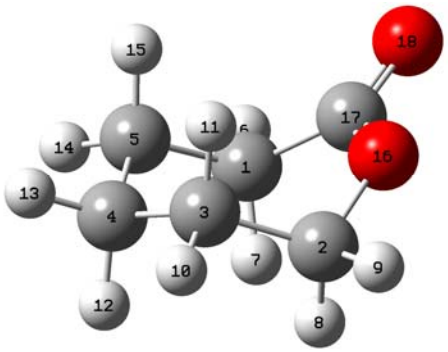
11

Cartesian and Computed Chemical Shift Data of Each Conformer for Each of 1–11

All geometries extracted are in the standard (x,y,z) coordinate system. All geometries were optimized to minimum stationary points and were confirmed to have no imaginary frequencies. Energies reported (in Hartrees) indicate the level of theory they are obtained at. Energies reported include: 1) energies from optimizations (SCF Energy), 2) energies from nuclear magnetic resonance (NMR) calculations (SCF Energy from NMR), 3) Gibb's free energy (Sum of Electronic and Thermal Free Energies)

Caprolactone (1)

Conformer 1a

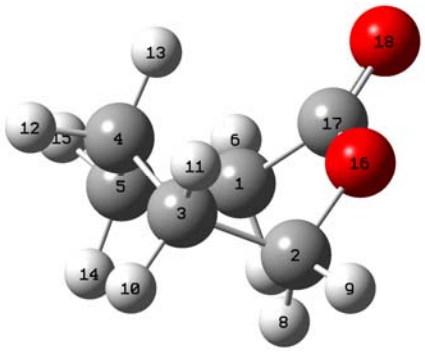


SCF Energy – E(RM062X)	−384.978 62 E_h
SCF Energy from NMR – E(RB3LYP)	−384.249 63 E_h
Sum of Electronic and Thermal Free Energies	−384.852 23 E_h

Table S1a – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 1a

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-0.587127	1.127622	0.616016	144.7737	38.8339
2	C	0.553851	-1.478011	0.429370	109.7811	73.8265
3	C	1.641126	-0.796107	-0.388786	149.5118	34.0958
4	C	1.855967	0.676514	-0.041854	149.0043	34.6033
5	C	0.620447	1.553175	-0.240517	155.2368	28.3708
6	H	-1.302623	1.946241	0.697754	29.3132	2.5517
7	H	-0.255243	0.867873	1.628135	29.1415	2.7234
8	H	0.602742	-1.194273	1.486639	27.5662	4.2987
9	H	0.646946	-2.562012	0.362486	27.5955	4.2694
10	H	2.573083	-1.344833	-0.214149	29.9803	1.8846
11	H	1.396763	-0.913922	-1.451777	30.1615	1.7034
12	H	2.174021	0.748639	1.007211	30.3200	1.5449
13	H	2.677527	1.072551	-0.647921	29.9013	1.9636
14	H	0.869550	2.584163	0.027512	29.9792	1.8857
15	H	0.329225	1.564816	-1.298019	30.3260	1.5389
16	O	-0.774096	-1.230645	-0.073218	---	---
17	C	-1.357433	-0.025265	0.015645	-3.7793	187.3869
18	O	-2.485026	0.091044	-0.418921	---	---

Conformer 1b



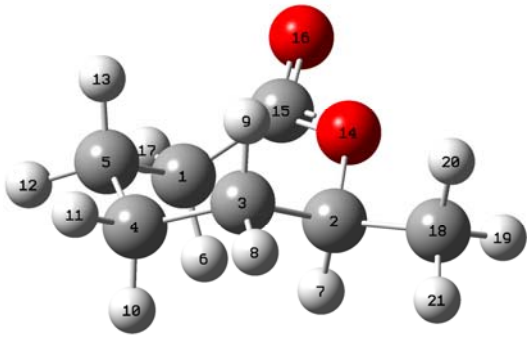
SCF Energy – E(RM062X)	−384.974 52 E_h
SCF Energy from NMR – E(RB3LYP)	−385.244 17 E_h
Sum of Electronic and Thermal Free Energies	−384.848 03 E_h

Table S1b – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 1b

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-0.759060	1.068577	0.712586	146.8645	36.7431
2	C	0.722332	-1.293240	0.636868	112.8353	70.7723
3	C	1.782781	-0.647630	-0.244190	152.2341	31.3735
4	C	1.320919	0.702626	-0.802190	157.0948	26.5128
5	C	0.633248	1.581803	0.247804	160.9334	22.6742
6	H	-1.518390	1.839826	0.586196	29.2402	2.6247
7	H	-0.743220	0.806377	1.775840	28.8232	3.0417
8	H	0.650202	-0.793400	1.607022	27.4271	4.4378
9	H	0.931748	-2.348320	0.813762	27.5949	4.27
10	H	2.681718	-0.515170	0.369377	30.3782	1.4867
11	H	2.043155	-1.321850	-1.065880	29.7931	2.0718
12	H	2.183382	1.235949	-1.212790	30.1565	1.7084
13	H	0.635122	0.539221	-1.643020	30.3224	1.5425
14	H	1.290509	1.683823	1.118489	30.3064	1.5585
15	H	0.502616	2.584021	-0.167280	30.0103	1.8546
16	O	-0.564740	-1.276610	-0.007230	---	---
17	C	-1.282310	-0.138850	-0.039310	-2.0405	185.6481
18	O	-2.330790	-0.142160	-0.649170	---	---

7-Methylcaprolactone (2)

Conformer 2a

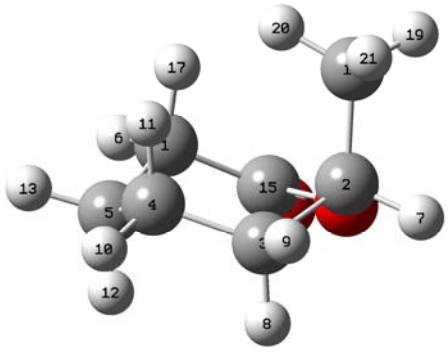


SCF Energy – E(RM062X)	−424.279 54 E_h
SCF Energy from NMR – E(RB3LYP)	−424.579 14 E_h
Sum of Electronic and Thermal Free Energies	−424.126 81 E_h

Table S2a – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 2a

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-1.58411	0.191698	0.682478	144.3459	39.2617
2	C	1.234798	-0.191095	0.315528	101.3804	82.2272
3	C	1.152947	1.112193	-0.475890	143.0021	40.6055
4	C	0.031321	2.053800	-0.038950	149.6909	33.9167
5	C	-1.372789	1.464372	-0.158900	155.2480	28.3596
6	H	-1.119835	0.312168	1.668281	29.1282	2.7367
7	H	1.021381	-0.011020	1.376477	27.3241	4.5408
8	H	2.112100	1.629025	-0.360380	30.0279	1.8370
9	H	1.056185	0.853763	-1.538530	30.3163	1.5486
10	H	0.203287	2.344625	1.006383	30.2696	1.5953
11	H	0.085252	2.972513	-0.632450	29.9651	1.8998
12	H	-2.100501	2.209600	0.175661	29.9796	1.8853
13	H	-1.604795	1.247563	-1.208920	30.3232	1.5417
14	O	0.280906	-1.167213	-0.176280	---	---
15	C	-1.041935	-1.044173	0.004509	-2.8293	186.4369
16	O	-1.757405	-1.930788	-0.416730	---	---
17	H	-2.647896	0.004350	0.830965	29.3338	2.5311
18	C	2.586231	-0.867336	0.173830	159.2247	24.3829
19	H	2.589387	-1.831376	0.687253	30.4917	1.3732
20	H	2.815225	-1.030541	-0.883670	30.5148	1.3501
21	H	3.363419	-0.233415	0.607361	30.8214	1.0435

Conformer 2b

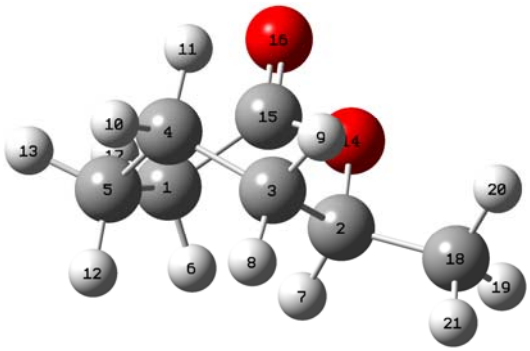


SCF Energy – E(RM062X)	−424.274 70 E_h
SCF Energy from NMR – E(RB3LYP)	−424.573 77 E_h
Sum of Electronic and Thermal Free Energies	−424.122 18 E_h

Table S2b – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 2b

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	0.994939	0.934330	0.774595	141.1043	42.5033
2	C	-0.875452	-1.124061	-0.351531	102.6317	80.9759
3	C	-1.554687	0.140533	-0.872283	145.3226	38.2850
4	C	-1.398821	1.405177	-0.031123	155.5444	28.0632
5	C	0.041226	1.901920	0.059378	154.8413	28.7663
6	H	1.917116	1.450148	1.045254	29.1814	2.6835
7	H	-1.173508	-1.938199	-1.016807	27.2516	4.6133
8	H	-1.184552	0.325001	-1.888520	29.8914	1.9735
9	H	-2.619646	-0.102589	-0.964687	29.9467	1.9182
10	H	-2.018115	2.191682	-0.475242	30.1211	1.7438
11	H	-1.791075	1.237534	0.980267	29.9608	1.9041
12	H	0.425980	2.117108	-0.945423	30.3825	1.4824
13	H	0.061132	2.846111	0.612194	30.0401	1.8248
14	O	0.562648	-1.126323	-0.556866	---	---
15	C	1.444627	-0.251244	-0.053010	-2.5227	186.1303
16	O	2.619001	-0.444653	-0.300819	---	---
17	H	0.539830	0.575055	1.703260	29.1564	2.7085
18	C	-1.244145	-1.535826	1.066897	165.2397	18.3679
19	H	-0.726129	-2.460812	1.331140	30.4150	1.4499
20	H	-1.008714	-0.777404	1.814750	29.9567	1.9082
21	H	-2.321633	-1.720803	1.107764	30.8899	0.9750

Conformer 2c



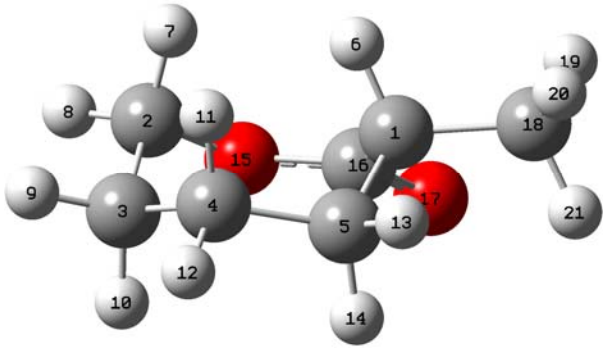
SCF Energy – E(RM062X)	−424.276 21 E_h
SCF Energy from NMR – E(RB3LYP)	−424.574 62 E_h
Sum of Electronic and Thermal Free Energies	−424.123 51 E_h

Table S2c – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 2c

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-1.532099	0.069674	0.880229	146.5673	37.0403
2	C	1.217093	-0.126592	0.334738	104.4537	79.1539
3	C	1.167002	1.182699	-0.447573	144.2611	39.3465
4	C	-0.261935	1.640848	-0.752217	156.4750	27.1326
5	C	-1.203089	1.527599	0.451916	160.6010	23.0066
6	H	-1.127969	-0.145901	1.874788	28.8645	3.0004
7	H	0.902952	0.043059	1.370125	27.2221	4.6428
8	H	1.685141	1.939682	0.153510	30.2383	1.6266
9	H	1.729221	1.065935	-1.381317	30.1615	1.7034
10	H	-0.239381	2.679425	-1.095672	30.2010	1.6639
11	H	-0.667949	1.053164	-1.585104	30.3526	1.5123
12	H	-0.768780	2.065753	1.301716	30.3051	1.5598
13	H	-2.142697	2.029185	0.208085	30.0163	1.8486
14	O	0.314075	-1.089702	-0.259278	---	---
15	C	-1.012509	-0.997313	-0.061636	-1.2786	184.8862
16	O	-1.731961	-1.790099	-0.633387	---	---
17	H	-2.609544	-0.085035	0.932848	29.2545	2.6104
18	C	2.589357	-0.769648	0.326686	161.2670	22.3406
19	H	2.592351	-1.688271	0.917714	30.3841	1.4808
20	H	2.886597	-1.006505	-0.698798	30.6792	1.1857
21	H	3.320230	-0.075696	0.750561	30.7159	1.1490

3-Methylcaprolactone (3)

Conformer 3a

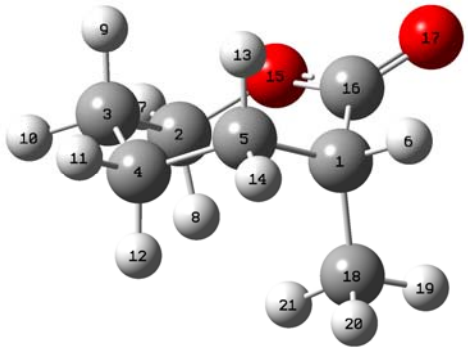


SCF Energy – E(RM062X)	−424.275 59 E_h
SCF Energy from NMR – E(RB3LYP)	−424.574 07 E_h
Sum of Electronic and Thermal Free Energies	−424.122 62 E_h

Table S3a – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 3a

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-0.864898	0.537588	0.399265	140.4800	43.1276
2	C	1.537092	-1.026424	0.602671	110.6713	72.9363
3	C	2.174642	0.063287	-0.245501	149.8431	33.7645
4	C	1.506950	1.430449	-0.110162	149.4258	34.1818
5	C	0.024470	1.447318	-0.479118	146.5194	37.0882
6	H	-0.475527	0.559035	1.425774	29.0646	2.8003
7	H	1.312800	-0.675612	1.616146	27.5135	4.3514
8	H	2.200349	-1.888179	0.680432	27.6033	4.2616
9	H	3.223966	0.143875	0.059005	30.0284	1.8365
10	H	2.170384	-0.269042	-1.290925	30.1848	1.6801
11	H	1.613050	1.774521	0.927827	30.2276	1.6373
12	H	2.039100	2.153774	-0.736801	29.9308	1.9341
13	H	-0.352550	2.469742	-0.370042	30.2174	1.6475
14	H	-0.112145	1.175233	-1.534076	30.4081	1.4568
15	O	0.348361	-1.580651	0.006473	---	---
16	C	-0.803378	-0.896877	-0.096847	-5.7084	189.3160
17	O	-1.744681	-1.461593	-0.613603	---	---
18	C	-2.313004	1.020381	0.406746	163.2133	20.3943
19	H	-2.954083	0.352990	0.986718	30.6718	1.1931
20	H	-2.359832	2.021364	0.843301	31.0479	0.8170
21	H	-2.706196	1.065914	-0.612641	30.6365	1.2284

Conformer 3b

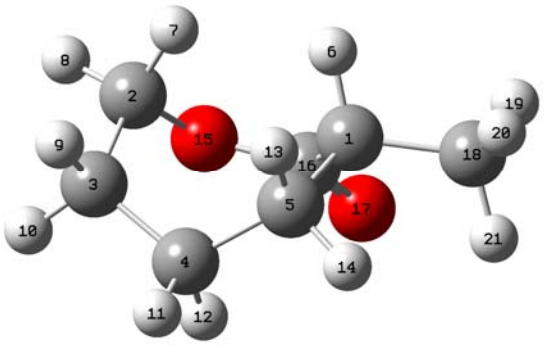


SCF Energy – E(RM062X)	−424.270 59 E_h
SCF Energy from NMR – E(RB3LYP)	−424.569 48 E_h
Sum of Electronic and Thermal Free Energies	−424.117 80 E_h

Table S3b – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 3b

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	0.752845	0.986651	-0.161657	134.1631	49.4445
2	C	-0.828881	-1.381755	0.736044	110.2239	73.3837
3	C	-1.893863	-0.785365	-0.167877	148.6318	34.9758
4	C	-1.841083	0.735846	-0.278911	155.7679	27.8397
5	C	-0.557951	1.255798	-0.922600	149.7308	33.8768
6	H	1.538361	1.526024	-0.697428	28.8027	3.0622
7	H	-1.070364	-2.419627	0.967745	27.6633	4.2016
8	H	-0.747912	-0.836205	1.680577	27.3203	4.5446
9	H	-1.810342	-1.247817	-1.159524	30.1409	1.7240
10	H	-2.863808	-1.086803	0.243457	29.9715	1.8934
11	H	-2.691670	1.080282	-0.876519	30.1463	1.7186
12	H	-1.965754	1.176141	0.718814	29.9866	1.8783
13	H	-0.467335	0.843005	-1.935501	30.0458	1.8191
14	H	-0.632267	2.343512	-1.034388	30.1779	1.6870
15	O	0.474171	-1.488752	0.129528	---	---
16	C	1.241672	-0.453047	-0.244913	-5.0637	188.6713
17	O	2.352145	-0.716470	-0.662957	---	---
18	C	0.759991	1.517578	1.280429	167.8668	15.7408
19	H	1.746630	1.383663	1.731507	30.4904	1.3745
20	H	0.535342	2.588260	1.260820	30.8957	0.9692
21	H	0.022211	1.037101	1.924784	30.1442	1.7207

Conformer 3c



SCF Energy – E(RM062X)	−424.271 63 E_h
SCF Energy from NMR – E(RB3LYP)	−424.569 28 E_h
Sum of Electronic and Thermal Free Energies	−424.118 92 E_h

Table S3c – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 3c

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-0.956530	0.418093	0.520579	142.3742	41.2334
2	C	1.572776	-0.754685	0.804990	113.9277	69.6799
3	C	2.201977	0.341423	-0.048408	152.8739	30.7337
4	C	1.159309	1.122041	-0.852951	157.0263	26.5813
5	C	-0.061444	1.563723	-0.039618	149.7839	33.8237
6	H	-0.737022	.284479	1.585647	28.6974	3.1675
7	H	1.143489	-0.350858	1.725174	27.3814	4.4835
8	H	2.302285	-1.516486	1.080673	27.6136	4.2513
9	H	2.745708	1.014474	0.624647	30.3612	1.5037
10	H	2.934348	-0.097613	-0.732834	29.8213	2.0436
11	H	1.633654	2.005962	-1.290081	30.2209	1.6440
12	H	0.822248	0.510001	-1.698972	30.3620	1.5029
13	H	0.257502	2.199622	0.794177	29.9694	1.8955
14	H	-0.691541	2.183667	-0.686136	30.5572	1.3077
15	O	0.560746	-1.470080	0.073292	---	---
16	C	-0.648372	-0.915342	-0.143804	-4.2493	187.8569
17	O	-1.430306	-1.519484	-0.845879	---	---
18	C	-2.439124	0.751076	0.382126	163.2375	20.3701
19	H	-3.066478	-0.022288	0.831570	30.7421	1.1228
20	H	-2.644786	1.702373	0.881088	30.9151	0.9498
21	H	-2.714471	0.845200	-0.671747	30.6840	1.1809

Normal *cis*-Carvomenthide (4)

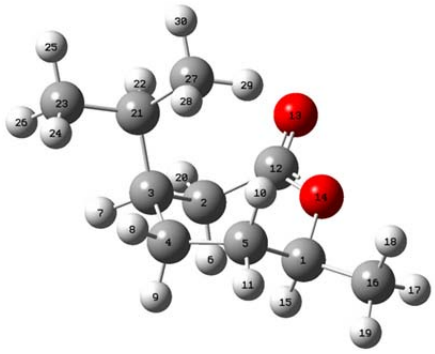
Conformer 4a

SCF Energy – E(RM062X)	−542.169 26 E_h
SCF Energy from NMR – E(RB3LYP)	−542.548 84 E_h
Sum of Electronic and Thermal Free Energies	−541.935 53 E_h

Table S4a – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 4a

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	−2.055131	−0.327730	0.109051	100.9720	82.6356
2	C	0.274970	0.914930	1.266550	140.5636	43.0440
3	C	0.999288	−0.399149	0.885769	138.1549	45.4527
4	C	0.028421	−1.586084	0.926571	147.1657	36.4419
5	C	−1.119496	−1.518524	−0.080958	148.3533	35.2543
6	H	−0.425689	0.722447	2.087010	28.9935	2.8714
7	H	1.742705	−0.571535	1.677420	30.5060	1.3589
8	H	0.581600	−2.518929	0.782370	29.7326	2.1323
9	H	−0.401237	−1.638689	1.935873	30.2907	1.5742
10	H	−0.748484	−1.500506	−1.114152	30.1042	1.7607
11	H	−1.724899	−2.426303	0.019996	30.2878	1.5771
12	C	−0.462949	1.541626	0.105097	−1.3645	184.9721
13	O	−0.140604	2.606945	−0.381136	---	---
14	O	−1.497656	0.890467	−0.447697	---	---
15	H	−2.241423	−0.157444	1.176915	27.3433	4.5216
16	C	−3.376194	−0.511273	−0.615990	159.1524	24.4552
17	H	−3.996541	0.382031	−0.515055	30.4933	1.3716
18	H	−3.198050	−0.697917	−1.679397	30.5235	1.3414
19	H	−3.914132	−1.364067	−0.195075	30.8182	1.0467
20	H	0.985283	1.667899	1.608816	29.0190	2.8459
21	C	1.782507	−0.266740	−0.438210	149.4261	34.1815
22	H	1.078730	0.013209	−1.236606	30.3061	1.5588
23	C	2.843946	0.834080	−0.339291	160.4138	23.1938
24	H	3.545914	0.611062	0.474020	31.4098	0.4551
25	H	3.416469	0.896542	−1.269553	30.9610	0.9039
26	H	2.403477	1.817255	−0.155002	30.1582	1.7067
27	C	2.441843	−1.588626	−0.840795	161.2666	22.3410
28	H	3.071316	−1.968142	−0.025952	31.3759	0.4890
29	H	1.707934	−2.359965	−1.090401	30.5995	1.2654
30	H	3.079881	−1.441302	−1.717324	31.0051	0.8598

Conformer 4b

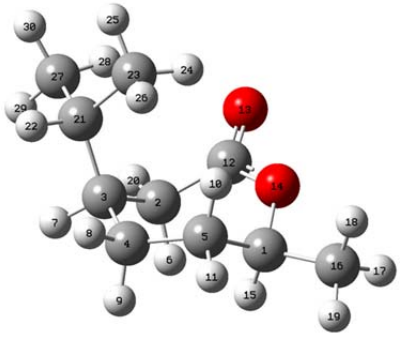


SCF Energy – E(RM062X)	−542.164 39 E_h
SCF Energy from NMR – E(RB3LYP)	−542.544 84 E_h
Sum of Electronic and Thermal Free Energies	−541.930 68 E_h

Table S4b – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 4b

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	1.982353	−0.542589	−0.188145	102.0054	81.6022
2	C	−0.174012	0.930545	−1.333792	139.6398	43.9678
3	C	−1.105414	−0.230149	−0.920861	140.4514	43.1562
4	C	−0.344999	−1.551893	−0.708200	152.6906	30.9170
5	C	0.898408	−1.545676	0.191589	144.3578	39.2498
6	H	0.489669	0.597069	−2.139331	28.7803	3.0846
7	H	−1.726249	−0.393582	−1.811362	30.0766	1.7883
8	H	−1.043553	−2.309211	−0.332673	29.8129	2.0520
9	H	−0.024045	−1.902271	−1.698104	30.1893	1.6756
10	H	0.650742	−1.377116	1.244140	29.9035	1.9614
11	H	1.348197	−2.543741	0.135067	30.2169	1.6480
12	C	0.652507	1.509875	−0.212054	−2.8714	186.4790
13	O	0.446095	2.610506	0.258970	---	---
14	O	1.657213	0.784306	0.300854	---	---
15	H	2.101461	−0.488433	−1.277171	27.2050	4.6599
16	C	3.318341	−0.872959	0.452254	159.3255	24.2821
17	H	4.053109	−0.096152	0.229263	30.4674	1.3975
18	H	3.205938	−0.950210	1.537960	30.5375	1.3274
19	H	3.686460	−1.827354	0.068278	30.8330	1.0319
20	H	−0.776010	1.757238	−1.715083	29.4151	2.4498
21	C	−2.096838	0.170373	0.199231	145.7069	37.9007
22	H	−2.345479	1.227802	0.031323	29.8498	2.0151
23	C	−3.394980	−0.633799	0.073836	158.3263	25.2813
24	H	−3.204696	−1.706131	0.200211	30.8003	1.0646
25	H	−4.112128	−0.333080	0.844018	30.9180	0.9469
26	H	−3.863074	−0.485246	−0.904419	31.0493	0.8156
27	C	−1.560150	0.042047	1.629202	161.4196	22.1880
28	H	−1.421963	−1.011724	1.896712	31.2378	0.6271
29	H	−0.610919	0.562359	1.783792	30.5920	1.2729
30	H	−2.285213	0.466635	2.330423	30.9932	0.8717

Conformer 4c

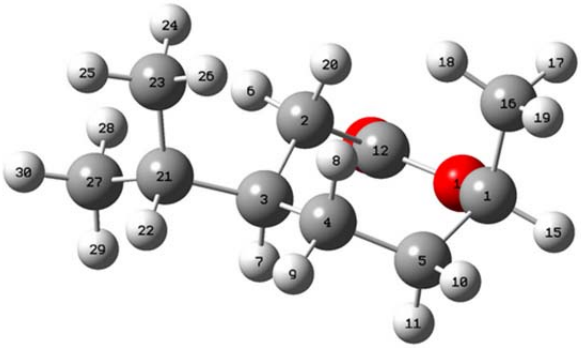


SCF Energy – E(RM062X)	−542.164 22 E_h
SCF Energy from NMR – E(RB3LYP)	−542.544 09 E_h
Sum of Electronic and Thermal Free Energies	−541.930 08 E_h

Table S4c – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 4c

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	2.065495	−0.121331	−0.202303	102.2069	81.4007
2	C	−0.467219	0.620451	−1.298259	146.5638	37.0438
3	C	−0.988637	−0.771408	−0.873821	140.2793	43.3283
4	C	0.146897	−1.790310	−0.673764	145.9931	37.6145
5	C	1.338912	−1.396715	0.208185	144.5956	39.0120
6	H	0.246294	0.488103	−2.119980	29.0608	2.8041
7	H	−1.535932	−1.119023	−1.760469	29.9164	1.9485
8	H	−0.286270	−2.721010	−0.286340	29.9812	1.8837
9	H	0.550018	−2.029882	−1.666773	29.8931	1.9718
10	H	1.063309	−1.287999	1.261658	29.7847	2.0802
11	H	2.067040	−2.214618	0.160045	30.1471	1.7178
12	C	0.186492	1.445595	−0.215483	−3.5721	187.1797
13	O	−0.307042	2.463898	0.227175	---	---
14	O	1.367578	1.053747	0.283483	---	---
15	H	2.142257	−0.048443	−1.294019	27.2424	4.6225
16	C	3.450963	−0.028524	0.411328	159.3275	24.2801
17	H	3.915539	0.929439	0.167459	30.4690	1.3959
18	H	3.386746	−0.122113	1.499681	30.5238	1.3411
19	H	4.080345	−0.834452	0.026267	30.8186	1.0463
20	H	−1.290249	1.227953	−1.676417	29.1566	2.7083
21	C	−2.049203	−0.756598	0.252496	143.0121	40.5955
22	H	−2.513896	−1.752290	0.212781	30.0133	1.8516
23	C	−1.510636	−0.581375	1.677034	163.3878	20.2198
24	H	−0.922228	0.334764	1.792934	30.8878	0.9771
25	H	−2.350073	−0.517299	2.377101	31.1389	0.7260
26	H	−0.893093	−1.429316	1.983828	30.6868	1.1781
27	C	−3.148255	0.272253	−0.030568	159.8772	23.7304
28	H	−2.780503	1.293300	0.117615	30.3791	1.4858
29	H	−3.519701	0.188457	−1.058228	30.9461	0.9188
30	H	−3.992741	0.121041	0.648514	30.8754	0.9895

Conformer 4d

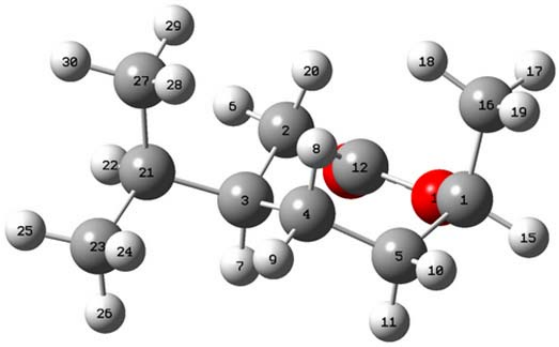


SCF Energy – E(RM062X)	−542.163 49 E_h
SCF Energy from NMR – E(RB3LYP)	−542.546 00 E_h
Sum of Electronic and Thermal Free Energies	−541.931 40 E_h

Table S4d – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 4d

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	2.304665	−0.569330	−0.218367	102.7965	80.8111
2	C	−0.257854	0.743061	0.571561	142.3522	41.2554
3	C	−0.876035	−0.174422	−0.502740	136.9666	46.6410
4	C	−0.100464	−1.487454	−0.636863	149.0473	34.5603
5	C	1.334701	−1.315590	−1.131097	145.8154	37.7922
6	H	−0.967133	1.517757	0.867365	29.3512	2.5137
7	H	−0.818127	0.347861	−1.469802	30.3811	1.4838
8	H	−0.102196	−2.019655	0.323244	29.7538	2.1111
9	H	−0.628351	−2.132656	−1.348991	30.4171	1.4478
10	H	1.774942	−2.305891	−1.296124	29.9429	1.9220
11	H	1.332613	−0.807271	−2.103339	29.8063	2.0586
12	C	0.967485	1.504579	0.117892	−2.6991	186.3067
13	O	0.970483	2.717931	0.039768	---	---
14	O	2.095533	0.867830	−0.225609	---	---
15	H	3.289554	−0.631067	−0.687861	27.2731	4.5918
16	C	2.440424	−1.117993	1.195287	165.1893	18.4183
17	H	3.161514	−0.519756	1.757433	30.4186	1.4463
18	H	1.499641	−1.141968	1.746721	29.9445	1.9204
19	H	2.816891	−2.143456	1.135384	30.8712	0.9937
20	H	−0.019302	0.162302	1.467967	29.4581	2.4068
21	C	−2.375834	−0.427716	−0.225926	143.2827	40.3249
22	H	−2.683950	−1.204181	−0.940001	30.2027	1.6622
23	C	−2.646994	−0.955235	1.186238	167.2360	16.3716
24	H	−2.424851	−0.191469	1.940175	31.4317	0.4332
25	H	−3.702909	−1.222110	1.292358	31.0930	0.7719
26	H	−2.053420	−1.845117	1.417133	30.7917	1.0732
27	C	−3.229939	0.811477	−0.504833	160.4172	23.1904
28	H	−3.007016	1.622546	0.197051	30.8619	1.0030
29	H	−3.064066	1.187301	−1.519443	30.9776	0.8873
30	H	−4.292889	0.572471	−0.399448	30.8954	0.9695

Conformer 4e

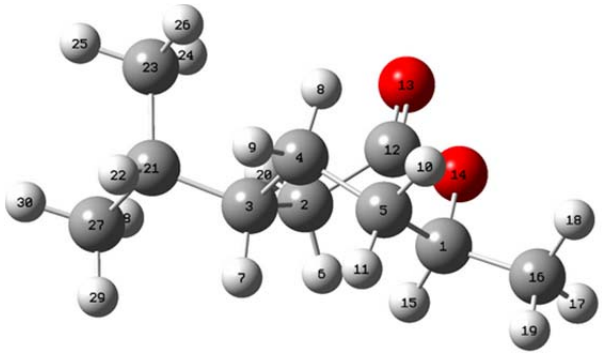


SCF Energy – E(RM062X)	−542.163 42 E_h
SCF Energy from NMR – E(RB3LYP)	−542.545 84 E_h
Sum of Electronic and Thermal Free Energies	−541.931 19 E_h

Table S4e – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 4e

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	2.097508	−0.984012	−0.215801	102.6984	80.9092
2	C	0.037371	1.040575	0.537683	133.7876	49.8200
3	C	−0.889425	0.199083	−0.362946	137.1544	46.4532
4	C	−0.492663	−1.279081	−0.350343	158.4283	25.1793
5	C	0.885650	−1.549602	−0.952112	145.9129	37.6947
6	H	−0.432700	2.001874	0.757659	29.4802	2.3847
7	H	−0.781744	0.568586	−1.394203	30.3071	1.5578
8	H	−0.533103	−1.663539	0.677099	30.2321	1.6328
9	H	−1.223345	−1.855995	−0.926674	30.2157	1.6492
10	H	1.044105	−2.633025	−1.005002	29.9352	1.9297
11	H	0.917043	−1.177033	−1.983538	29.9266	1.9383
12	C	1.371394	1.394628	−0.080404	−2.4276	186.0352
13	O	1.680037	2.547455	−0.313063	---	---
14	O	2.261154	0.446622	−0.405469	---	---
15	H	2.983203	−1.358104	−0.735385	27.2675	4.5974
16	C	2.227941	−1.381588	1.248057	165.1819	18.4257
17	H	3.134174	−0.942757	1.672302	30.4170	1.4479
18	H	1.375289	−1.081249	1.858555	29.9568	1.9081
19	H	2.312510	−2.470756	1.306753	30.8919	0.9730
20	H	0.202277	0.532513	1.492815	28.9616	2.9033
21	C	−2.363603	0.441482	0.033956	142.8225	40.7851
22	H	−2.514111	1.528656	−0.018825	30.1584	1.7065
23	C	−3.337559	−0.200875	−0.957114	160.2623	23.3453
24	H	−3.340293	−1.292365	−0.868315	30.9244	0.9405
25	H	−4.357504	0.145137	−0.762904	30.7830	1.0819
26	H	−3.082597	0.057240	−1.990554	30.9724	0.8925
27	C	−2.685739	−0.005297	1.462926	167.6379	15.9697
28	H	−2.590750	−1.091754	1.567020	31.2474	0.6175
29	H	−2.030531	0.467769	2.201290	30.9162	0.9487
30	H	−3.716690	0.260301	1.716756	31.0947	0.7702

Conformer 4f

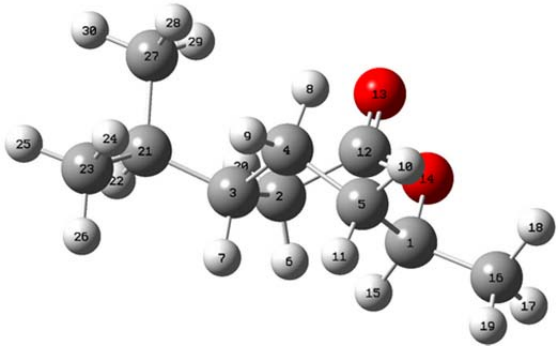


SCF Energy – E(RM062X)	−542.165 75 E_h
SCF Energy from NMR – E(RB3LYP)	−542.546 98 E_h
Sum of Electronic and Thermal Free Energies	−541.933 15 E_h

Table S4f – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 4f

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	−2.076727	−0.484595	0.349955	104.8322	78.7754
2	C	0.414186	0.713125	0.856392	146.0696	37.5380
3	C	0.856309	−0.657455	0.255316	141.1340	42.4736
4	C	0.025982	−1.053576	−0.974369	149.2078	34.3998
5	C	−1.410196	−1.453078	−0.622844	144.0410	39.5666
6	H	0.045036	0.584389	1.879461	29.0562	2.8087
7	H	0.683855	−1.426080	1.021939	30.0904	1.7745
8	H	0.010122	−0.227174	−1.695985	30.2841	1.5808
9	H	0.514873	−1.891861	−1.483423	30.4706	1.3943
10	H	−2.014278	−1.516304	−1.535314	30.1433	1.7216
11	H	−1.420261	−2.444351	−0.153737	30.2020	1.6629
12	C	−0.651302	1.453884	0.074538	−1.9229	185.5305
13	O	−0.481268	2.561097	−0.393432	---	---
14	O	−1.853939	0.876228	−0.088783	---	---
15	H	−1.643812	−0.597625	1.349990	27.2339	4.6310
16	C	−3.579255	−0.665136	0.430696	161.3390	22.2686
17	H	−4.016174	0.028395	1.152792	30.3899	1.4750
18	H	−4.031674	−0.488545	−0.549228	30.6809	1.1840
19	H	−3.808428	−1.687869	0.741961	30.7178	1.1471
20	H	1.253191	1.407187	0.912357	29.4091	2.4558
21	C	2.369194	−0.681702	−0.051964	142.6631	40.9445
22	H	2.579414	−1.693468	−0.426423	30.2030	1.6619
23	C	2.773125	0.312626	−1.143807	168.1073	15.5003
24	H	2.537210	1.343263	−0.854277	31.0951	0.7698
25	H	3.851564	0.259431	−1.322697	31.2341	0.6308
26	H	2.266704	0.105906	−2.090996	30.8868	0.9781
27	C	3.209281	−0.479394	1.211326	160.8121	22.7955
28	H	3.100985	0.535145	1.610475	30.9600	0.9049
29	H	2.919063	−1.185598	1.996762	31.0789	0.7860
30	H	4.270688	−0.631636	0.992629	30.9205	0.9444

Conformer 4g

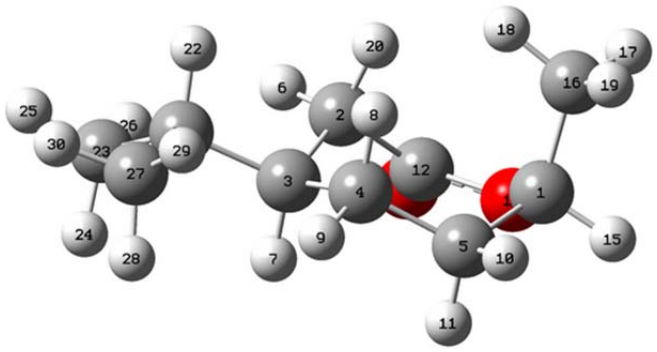


SCF Energy – E(RM062X)	−542.165 70 E_h
SCF Energy from NMR – E(RB3LYP)	−542.546 82 E_h
Sum of Electronic and Thermal Free Energies	−541.932 84 E_h

Table S4g – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 4g

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	−2.004242	−0.675639	0.257835	104.7445	78.8631
2	C	0.169525	0.929209	1.017768	138.3358	45.2718
3	C	0.905585	−0.348918	0.506771	140.9627	42.6449
4	C	0.305845	−0.881024	−0.803472	157.8956	25.7120
5	C	−1.073835	−1.517340	−0.610268	144.1054	39.5022
6	H	−0.287657	0.742112	1.995425	28.5826	3.2823
7	H	0.776696	−1.131719	1.267268	30.1568	1.7081
8	H	0.235291	−0.065231	−1.534204	30.6877	1.1772
9	H	0.975202	−1.625486	−1.245574	30.2602	1.6047
10	H	−1.546986	−1.684349	−1.584896	30.1350	1.7299
11	H	−0.970869	−2.494985	−0.123896	30.3256	1.5393
12	C	−0.909160	1.478673	0.106912	−1.4856	185.0932
13	O	−0.878612	2.600136	−0.357050	---	---
14	O	−1.967516	0.702502	−0.182550	---	---
15	H	−1.677010	−0.710096	1.302604	27.2441	4.6208
16	C	−3.452943	−1.111894	0.171597	161.3388	22.2688
17	H	−4.082382	−0.501670	0.823313	30.3986	1.4663
18	H	−3.812671	−1.019301	−0.857053	30.6848	1.1801
19	H	−3.538322	−2.157893	0.478386	30.7193	1.1456
20	H	0.876259	1.750069	1.151868	29.5222	2.3427
21	C	2.422119	−0.072283	0.402958	142.4021	41.2055
22	H	2.708726	0.426064	1.339842	30.2754	1.5895
23	C	3.236549	−1.364436	0.310256	161.0799	22.5277
24	H	3.039825	−1.897763	−0.625891	30.9176	0.9473
25	H	4.307701	−1.141361	0.340039	30.8613	1.0036
26	H	3.007341	−2.039141	1.141759	31.0334	0.8315
27	C	2.764357	0.866706	−0.757023	167.0320	16.5756
28	H	2.603092	0.369802	−1.719924	31.3165	0.5484
29	H	2.155654	1.777468	−0.742790	30.6446	1.2203
30	H	3.816337	1.164045	−0.709490	31.1165	0.7484

Conformer 4h



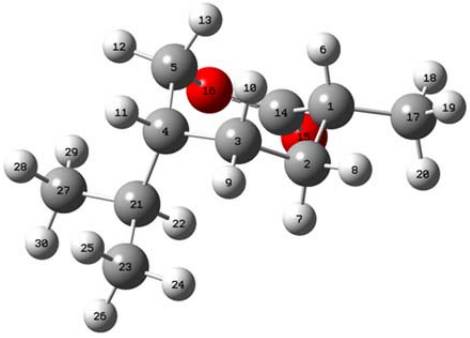
SCF Energy – E(RM062X)	−542.161 92 E_h
SCF Energy from NMR – E(RB3LYP)	−542.544 68 E_h
Sum of Electronic and Thermal Free Energies	−541.929 26 E_h

Table S4h – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 4h

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	2.262643	−0.769533	−0.237074	103.0430	80.5646
2	C	−0.034810	0.897345	0.636696	136.8196	46.7880
3	C	−0.908528	−0.066762	−0.194215	135.6202	47.9874
4	C	−0.269343	−1.456473	−0.254281	151.1870	32.4206
5	C	1.105158	−1.490097	−0.923057	145.7829	37.8247
6	H	−0.608151	1.776676	0.929153	29.0907	2.7742
7	H	−0.983219	0.320127	−1.223416	30.8443	1.0206
8	H	−0.212744	−1.872302	0.762333	30.3216	1.5433
9	H	−0.915364	−2.127195	−0.827217	29.9557	1.9092
10	H	1.418778	−2.535905	−1.021707	29.9107	1.9542
11	H	1.023912	−1.092333	−1.942555	29.8988	1.9661
12	C	1.176570	1.457249	−0.074764	−1.5131	185.1207
13	O	1.259030	2.635920	−0.361533	---	---
14	O	2.208890	0.671250	−0.407881	---	---
15	H	3.161967	−1.006816	−0.810957	27.2734	4.5915
16	C	2.531328	−1.166669	1.208094	165.3263	18.2813
17	H	3.380507	−0.599314	1.596439	30.4101	1.4548
18	H	1.677394	−1.015430	1.869550	29.9268	1.9381
19	H	2.787663	−2.229959	1.233455	30.8808	0.9841
20	H	0.276352	0.393113	1.557078	29.4249	2.4400
21	C	−2.338957	−0.080454	0.398811	144.4375	39.1701
22	H	−2.239223	−0.167917	1.491809	30.7329	1.1320
23	C	−3.081850	1.221548	0.077076	159.9284	23.6792
24	H	−3.258701	1.290453	−1.002865	31.3435	0.5214
25	H	−4.054628	1.241627	0.577572	30.9108	0.9541
26	H	−2.533254	2.116235	0.382373	30.4032	1.4617
27	C	−3.182250	−1.260403	−0.094585	161.3709	22.2367
28	H	−3.207569	−1.284067	−1.191222	31.3235	0.5414
29	H	−2.804552	−2.222713	0.259293	30.5854	1.2795
30	H	−4.212283	−1.156157	0.260005	30.9741	0.8908

Abnormal *cis*-Carvomenthide (5)

Conformer 5a

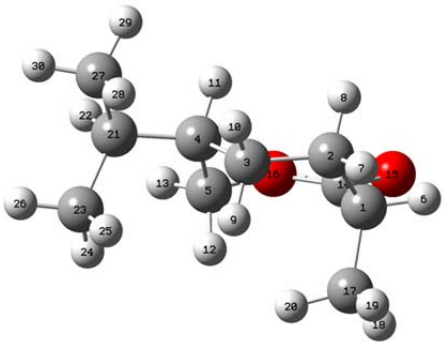


SCF Energy – E(RM062X)	−542.164 62 E_h
SCF Energy from NMR – E(RB3LYP)	−542.544 02 E_h
Sum of Electronic and Thermal Free Energies	−541.931 28 E_h

Table S5a – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 5a

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-1.905425	0.417034	0.236772	140.1980	43.4096
2	C	-0.890383	1.506432	-0.177001	151.8476	31.7600
3	C	0.321235	1.629499	0.747149	147.6298	35.9778
4	C	1.194004	0.370113	0.838145	133.6748	49.9328
5	C	0.404488	-0.797930	1.434280	110.2317	73.3759
6	H	-1.993616	0.426040	1.331499	29.0793	2.7856
7	H	-0.580174	1.333593	-1.215862	30.2808	1.5841
8	H	-1.427824	2.460731	-0.172089	30.4274	1.4375
9	H	0.929717	2.482300	0.431896	29.7080	2.1569
10	H	-0.038809	1.867716	1.757006	30.2667	1.5982
11	H	1.990609	0.582628	1.567864	30.6219	1.2430
12	H	1.074294	-1.561679	1.829852	27.3954	4.4695
13	H	-0.243814	-0.461462	2.250346	27.4509	4.4140
14	C	-1.424755	-0.965415	-0.174454	-5.7268	189.3344
15	O	-1.946793	-1.613170	-1.057677	---	---
16	O	-0.373442	-1.513700	0.457366	---	---
17	C	-3.277696	0.687231	-0.375648	162.9619	20.6457
18	H	-3.992487	-0.097297	-0.117966	30.6775	1.1874
19	H	-3.657605	1.643853	-0.007652	31.0531	0.8118
20	H	-3.207234	0.736379	-1.465744	30.6055	1.2594
21	C	1.886624	-0.017271	-0.485751	153.5849	30.0227
22	H	1.114266	-0.261880	-1.227566	30.1582	1.7067
23	C	2.720634	1.141663	-1.038411	161.3452	22.2624
24	H	2.103499	1.996734	-1.327610	30.5953	1.2696
25	H	3.447958	1.483580	-0.291313	31.3681	0.4968
26	H	3.275526	0.819590	-1.924701	30.9699	0.8950
27	C	2.766695	-1.258342	-0.307666	161.1646	22.4430
28	H	3.508802	-1.092817	0.483602	31.3011	0.5638
29	H	2.179284	-2.143769	-0.050104	30.3313	1.5336
30	H	3.306957	-1.477359	-1.233455	30.9122	0.9527

Conformer 5b

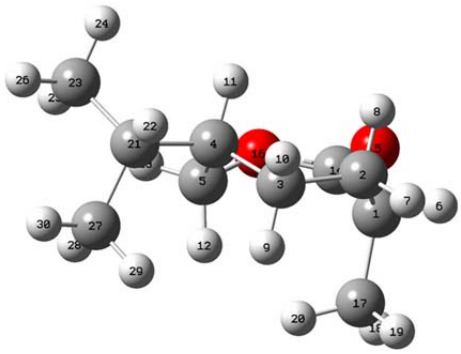


SCF Energy – E(RM062X)	−542.158 67 E_h
SCF Energy from NMR – E(RB3LYP)	−542.540 92 E_h
Sum of Electronic and Thermal Free Energies	−541.926 30 E_h

Table S5b – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 5b

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	2.007276	0.832462	-0.109601	134.3871	49.2205
2	C	0.833531	1.421723	-0.911356	149.6918	33.9158
3	C	-0.574726	1.179021	-0.369364	158.7669	24.8407
4	C	-0.991588	-0.293534	-0.377466	132.6224	50.9852
5	C	-0.122159	-1.129858	0.558146	104.0576	79.5500
6	H	2.921158	1.201870	-0.582661	28.8329	3.0320
7	H	1.008333	2.502648	-0.960171	30.1060	1.7589
8	H	0.891661	1.050174	-1.942425	30.0651	1.7998
9	H	-0.654692	1.578982	0.649874	30.2057	1.6592
10	H	-1.270151	1.758620	-0.985263	30.2066	1.6583
11	H	-0.837635	-0.692102	-1.391845	30.2510	1.6139
12	H	0.038398	-0.633310	1.519052	27.2697	4.5952
13	H	-0.602522	-2.091202	0.754590	27.8750	3.9899
14	C	2.163873	-0.675201	-0.246891	-4.7326	188.3402
15	O	3.215176	-1.170763	-0.602140	---	---
16	O	1.149035	-1.516990	0.003060	---	---
17	C	2.058627	1.291359	1.356402	167.5349	16.0727
18	H	2.963600	0.917468	1.842258	30.4906	1.3743
19	H	2.085201	2.384898	1.379761	30.8884	0.9765
20	H	1.197916	0.969079	1.944575	30.1811	1.6838
21	C	-2.482533	-0.516515	-0.032119	145.3002	38.3074
22	H	-2.650298	-1.600243	-0.104299	30.0352	1.8297
23	C	-2.844352	-0.083680	1.392878	166.5511	17.0565
24	H	-2.238098	-0.594586	2.147844	31.1062	0.7587
25	H	-2.712627	0.996052	1.522514	31.1589	0.7060
26	H	-3.893842	-0.314485	1.600666	31.1043	0.7606
27	C	-3.412697	0.155816	-1.044372	160.1220	23.4856
28	H	-3.402686	1.245425	-0.936366	30.8976	0.9673
29	H	-3.125695	-0.088076	-2.072785	30.9724	0.8925
30	H	-4.443210	-0.178746	-0.890219	30.8078	1.0571

Conformer 5c

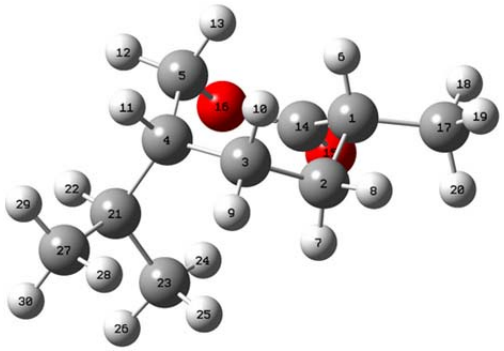


SCF Energy – E(RM062X)	−542.158 49 E_h
SCF Energy from NMR – E(RB3LYP)	−542.540 99 E_h
Sum of Electronic and Thermal Free Energies	−541.926 20 E_h

Table S5c – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 5c

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	2.136246	0.603034	-0.192058	134.4397	49.1679
2	C	1.143321	1.204678	-1.201740	149.4707	34.1369
3	C	-0.311870	1.332213	-0.754916	149.2368	34.3708
4	C	-1.005716	-0.007720	-0.498085	132.5612	51.0464
5	C	-0.365318	-0.760700	0.665076	110.1393	73.4683
6	H	3.128089	0.692559	-0.643180	28.8437	3.0212
7	H	1.523495	2.202576	-1.448649	30.1301	1.7348
8	H	1.186764	0.616884	-2.127523	29.9523	1.9126
9	H	-0.371078	1.958190	0.145275	29.7587	2.1062
10	H	-0.861566	1.866774	-1.538743	30.4212	1.4437
11	H	-0.882218	-0.636274	-1.392985	30.3138	1.5511
12	H	-0.162336	-0.098616	1.511257	27.5405	4.3244
13	H	-1.021482	-1.558006	1.017362	27.7181	4.1468
14	C	2.003653	-0.902390	-0.010179	-4.9593	188.5669
15	O	2.954491	-1.642696	-0.168348	---	---
16	O	0.835749	-1.476209	0.317734	---	---
17	C	2.198420	1.350515	1.149402	167.5304	16.0772
18	H	2.987258	0.934987	1.781800	30.4868	1.3781
19	H	2.435590	2.400469	0.953180	30.8753	0.9896
20	H	1.262468	1.322484	1.709649	30.1818	1.6831
21	C	-2.525711	0.171575	-0.271525	144.0643	39.5433
22	H	-2.865312	0.863491	-1.054067	30.2265	1.6384
23	C	-3.296955	-1.138062	-0.456399	160.4714	23.1362
24	H	-3.088008	-1.586718	-1.432632	30.8514	1.0135
25	H	-3.041803	-1.872438	0.315549	30.7919	1.0730
26	H	-4.374278	-0.956830	-0.388645	30.8558	1.0091
27	C	-2.860587	0.801284	1.085647	166.3115	17.2961
28	H	-2.612189	0.121447	1.908947	31.5108	0.3541
29	H	-2.325738	1.742039	1.247608	30.6856	1.1793
30	H	-3.932485	1.011661	1.149377	31.0708	0.7941

Conformer 5d

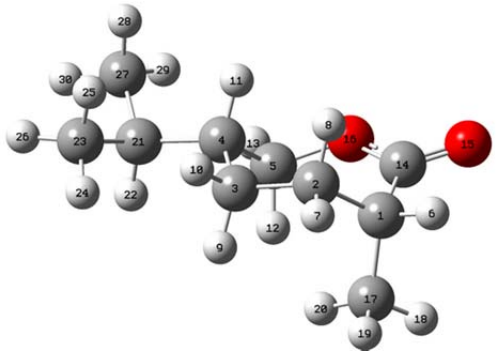


SCF Energy – E(RM062X)	−542.160 15 E_h
SCF Energy from NMR – E(RB3LYP)	−542.540 17 E_h
Sum of Electronic and Thermal Free Energies	−541.926 34 E_h

Table S5d – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 5d

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-1.838755	0.594849	0.237352	141.6817	41.9259
2	C	-0.716745	1.424264	-0.425186	148.1818	35.4258
3	C	0.574349	1.561566	0.392079	152.6104	30.9972
4	C	1.278150	0.276983	0.867935	137.0764	46.5312
5	C	0.328881	-0.695029	1.559402	105.7452	77.8624
6	H	-1.841737	0.801869	1.314814	28.9269	2.9380
7	H	-0.527501	1.017602	-1.423910	30.1757	1.6892
8	H	-1.115348	2.433408	-0.577991	30.3544	1.5105
9	H	1.285701	2.169555	-0.179464	29.7708	2.0941
10	H	0.326606	2.146790	1.287505	30.1590	1.7059
11	H	1.942344	0.592695	1.686102	30.3298	1.5351
12	H	0.903432	-1.471657	2.067537	27.6466	4.2183
13	H	-0.288885	-0.184505	2.305929	27.1633	4.7016
14	C	-1.558047	-0.882346	0.030169	-5.5380	189.1456
15	O	-2.205985	-1.586467	-0.716012	---	---
16	O	-0.513265	-1.441310	0.661842	---	---
17	C	-3.204221	0.952162	-0.343452	163.5024	20.1052
18	H	-3.992832	0.322451	0.074549	30.6798	1.1851
19	H	-3.433184	1.997336	-0.119801	31.0708	0.7941
20	H	-3.205126	0.819733	-1.428965	30.6682	1.1967
21	C	2.199428	-0.417366	-0.165472	145.0504	38.5572
22	H	2.405884	-1.422710	0.228718	29.8416	2.0233
23	C	1.606770	-0.583023	-1.568875	160.6382	22.9694
24	H	0.643259	-1.099334	-1.563200	30.6157	1.2492
25	H	1.479352	0.391489	-2.053794	31.1155	0.7494
26	H	2.294245	-1.167267	-2.188795	30.9474	0.9175
27	C	3.537149	0.323341	-0.267148	157.9734	25.6342
28	H	3.389428	1.348046	-0.628108	30.7753	1.0896
29	H	4.040769	0.375118	0.703351	31.0013	0.8636
30	H	4.205825	-0.180821	-0.971949	30.9211	0.9438

Conformer 5e

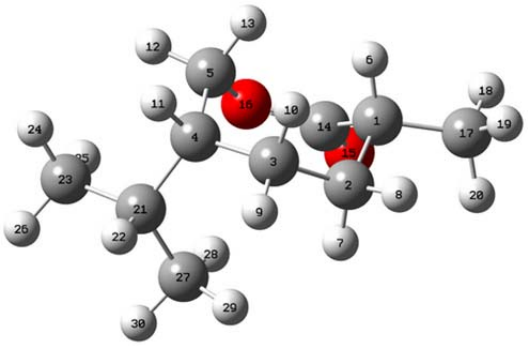


SCF Energy – E(RM062X)	−542.157 35 E_h
SCF Energy from NMR – E(RB3LYP)	−542.539 92 E_h
Sum of Electronic and Thermal Free Energies	−541.924 67 E_h

Table S5e – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 5e

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	2.117892	0.726086	-0.150466	134.7655	48.8421
2	C	0.965842	1.408661	-0.906978	149.8664	33.7412
3	C	-0.431846	1.348122	-0.290271	151.4980	32.1096
4	C	-1.026639	-0.059883	-0.209530	131.7684	51.8392
5	C	-0.166347	-0.962016	0.673727	107.0765	76.5311
6	H	3.035398	0.984277	-0.686287	28.8467	3.0182
7	H	1.250062	2.462138	-1.011050	30.1094	1.7555
8	H	0.924667	0.997808	-1.924013	30.0217	1.8432
9	H	-0.425687	1.794495	0.715110	30.3757	1.4892
10	H	-1.078379	1.980975	-0.904697	29.9963	1.8686
11	H	-1.043213	-0.493887	-1.221928	30.6613	1.2036
12	H	0.120357	-0.440625	1.591945	27.6167	4.2482
13	H	-0.715647	-1.857812	0.962614	27.7094	4.1555
14	C	2.105445	-0.791458	-0.252700	-5.0930	188.7006
15	O	3.082060	-1.409746	-0.627342	---	---
16	O	1.005732	-1.503406	0.037733	---	---
17	C	2.305513	1.220578	1.292628	167.4136	16.1940
18	H	3.182128	0.751185	1.746788	30.4686	1.3963
19	H	2.469999	2.302046	1.271702	30.8657	0.9992
20	H	1.444279	1.030591	1.934937	30.1812	1.6837
21	C	-2.474442	-0.086040	0.343919	149.2472	34.3604
22	H	-2.410773	-0.010969	1.441058	30.7956	1.0693
23	C	-3.333222	1.080571	-0.152502	161.7564	21.8512
24	H	-2.978140	2.047134	0.212925	30.6307	1.2342
25	H	-3.344378	1.111455	-1.248988	31.2964	0.5685
26	H	-4.365320	0.953393	0.188292	30.9871	0.8778
27	C	-3.174967	-1.402138	-0.015046	159.9687	23.6389
28	H	-3.333354	-1.453703	-1.098614	31.2739	0.5910
29	H	-2.603951	-2.286569	0.280068	30.4918	1.3731
30	H	-4.153757	-1.461619	0.470325	30.8856	0.9793

Conformer 5f

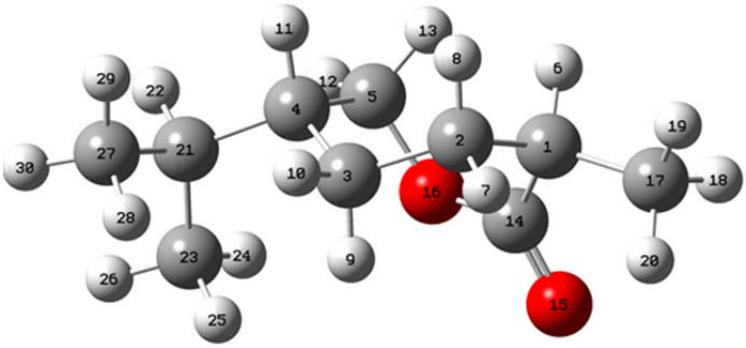


SCF Energy – E(RM062X)	−542.160 10 E_h
SCF Energy from NMR – E(RB3LYP)	−542.539 57 E_h
Sum of Electronic and Thermal Free Energies	−541.925 87 E_h

Table S5f – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 5f

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	1.900491	0.340272	-0.295821	141.7129	41.8947
2	C	1.053930	1.396176	0.448510	148.0961	35.5115
3	C	-0.218808	1.857168	-0.274344	146.3933	37.2143
4	C	-1.243104	0.792515	-0.707941	138.0291	45.5785
5	C	-0.598545	-0.360232	-1.470559	111.8138	71.7938
6	H	1.887197	0.565783	-1.369523	28.8870	2.9779
7	H	0.841477	1.018490	1.453779	30.0411	1.8238
8	H	1.690597	2.277708	0.583168	30.2986	1.5663
9	H	-0.728637	2.599194	0.352841	29.9539	1.9110
10	H	0.103095	2.389155	-1.179441	29.8678	1.9971
11	H	-1.862584	1.276923	-1.477802	30.2170	1.6479
12	H	-1.360193	-0.966653	-1.961525	27.3492	4.5157
13	H	0.075925	0.017679	-2.245847	27.3294	4.5355
14	C	1.286883	-1.031489	-0.081194	-5.3216	188.9292
15	O	1.795455	-1.889549	0.609908	---	---
16	O	0.097772	-1.307226	-0.640005	---	---
17	C	3.345420	0.348238	0.195913	163.4816	20.1260
18	H	3.931660	-0.443607	-0.275680	30.6731	1.1918
19	H	3.804075	1.312589	-0.037715	31.0653	0.7996
20	H	3.382743	0.198036	1.278455	30.6765	1.1884
21	C	-2.245434	0.364327	0.392175	144.5890	39.0186
22	H	-2.849342	1.261852	0.588033	30.0042	1.8607
23	C	-3.194806	-0.726728	-0.110967	160.3968	23.2108
24	H	-3.621571	-0.472141	-1.087735	30.8990	0.9659
25	H	-2.674297	-1.686650	-0.203794	30.6469	1.2180
26	H	-4.020229	-0.865182	0.593642	30.7920	1.0729
27	C	-1.631625	-0.051583	1.733908	161.9697	21.6379
28	H	-0.943860	-0.896105	1.624233	30.9017	0.9632
29	H	-1.098616	0.775448	2.210279	30.5531	1.3118
30	H	-2.429678	-0.360303	2.417317	31.0465	0.8184

Conformer 5g

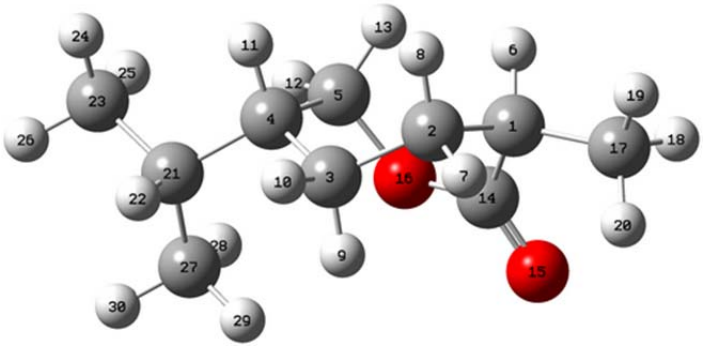


SCF Energy – E(RM062X)	−542.160 41 E_h
SCF Energy from NMR – E(RB3LYP)	−542.540 98 E_h
Sum of Electronic and Thermal Free Energies	−541.927 95 E_h

Table S5g – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 5g

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-2.042015	0.503283	0.336448	143.0289	40.5787
2	C	-1.030875	1.586086	-0.137160	149.6777	33.9299
3	C	0.370966	1.091689	-0.510465	159.9780	23.6296
4	C	1.153847	0.461222	0.647229	134.9334	48.6742
5	C	0.315220	-0.605646	1.363920	108.3262	75.2814
6	H	-2.066106	0.492907	1.431389	28.7579	3.1070
7	H	-1.461118	2.067990	-1.021766	30.5200	1.3449
8	H	-0.958327	2.356915	0.638559	30.0018	1.8631
9	H	0.289023	0.374202	-1.337158	30.5828	1.2821
10	H	0.936941	1.942825	-0.900562	30.3287	1.5362
11	H	1.335222	1.250489	1.391862	30.1598	1.7051
12	H	0.956993	-1.337703	1.859456	27.8188	4.0461
13	H	-0.332114	-0.162808	2.124065	27.1659	4.6990
14	C	-1.600445	-0.884333	-0.094982	-3.9626	187.5702
15	O	-2.195561	-1.567854	-0.900623	---	---
16	O	-0.480149	-1.389834	0.455112	---	---
17	C	-3.450955	0.801070	-0.166335	163.6585	19.9491
18	H	-4.174707	0.080028	0.220979	30.7556	1.1093
19	H	-3.747987	1.802679	0.157491	30.9206	0.9443
20	H	-3.483254	0.765339	-1.258474	30.7045	1.1604
21	C	2.537263	-0.086483	0.231861	143.9978	39.6098
22	H	3.018766	-0.417982	1.163289	30.1116	1.7533
23	C	2.458628	-1.298455	-0.701303	165.7822	17.8254
24	H	1.872716	-2.113635	-0.267234	30.5944	1.2705
25	H	2.002837	-1.033080	-1.661159	31.0978	0.7671
26	H	3.465101	-1.676585	-0.907244	31.0899	0.7750
27	C	3.421204	1.003725	-0.378540	160.7841	22.8235
28	H	3.065868	1.290842	-1.374026	31.0252	0.8397
29	H	3.439850	1.902104	0.248504	31.0277	0.8372
30	H	4.448950	0.644036	-0.487916	30.8579	1.0070

Conformer 5h

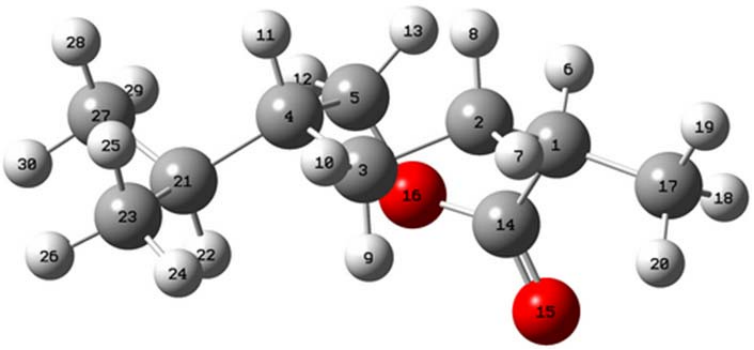


SCF Energy – E(RM062X)	−542.160 58 E_h
SCF Energy from NMR – E(RB3LYP)	−542.541 31 E_h
Sum of Electronic and Thermal Free Energies	−541.927 59 E_h

Table S5h – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 5h

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	2.064214	-0.452806	0.392273	142.9824	40.6252
2	C	1.262458	-1.541598	-0.377261	149.4797	34.1279
3	C	-0.119500	-1.125899	-0.890694	151.3412	32.2664
4	C	-1.133270	-0.763363	0.200616	134.7055	48.9021
5	C	-0.531916	0.232515	1.200016	115.1821	68.4255
6	H	1.945568	-0.618244	1.468523	28.7425	3.1224
7	H	1.864870	-1.839909	-1.242053	30.5327	1.3322
8	H	1.170762	-2.425816	0.263754	29.9010	1.9639
9	H	-0.004968	-0.280778	-1.581882	30.2593	1.6056
10	H	-0.532936	-1.948334	-1.484124	30.4517	1.4132
11	H	-1.341812	-1.677753	0.775208	30.2751	1.5898
12	H	-1.306057	0.807172	1.711958	27.6317	4.2332
13	H	0.057264	-0.278000	1.964850	27.4432	4.4217
14	C	1.516660	0.936222	0.110576	-4.1323	187.7399
15	O	2.126904	1.798767	-0.484509	---	---
16	O	0.280142	1.231546	0.554575	---	---
17	C	3.551971	-0.520436	0.062971	163.6116	19.9960
18	H	4.125630	0.196832	0.654712	30.7636	1.1013
19	H	3.925587	-1.526402	0.274587	30.9211	0.9438
20	H	3.719543	-0.302588	-0.995131	30.6906	1.1743
21	C	-2.472931	-0.285057	-0.401675	145.9759	37.6317
22	H	-2.703429	-0.975536	-1.225335	30.3384	1.5265
23	C	-3.611484	-0.385996	0.616709	159.8148	23.7928
24	H	-3.715026	-1.407022	0.998158	31.0576	0.8073
25	H	-3.440801	0.279417	1.471154	30.9294	0.9355
26	H	-4.563096	-0.093940	0.161726	30.8786	0.9863
27	C	-2.404550	1.131827	-0.980319	164.8734	18.7342
28	H	-2.238389	1.871356	-0.188986	31.1805	0.6844
29	H	-1.600039	1.244183	-1.712586	30.6662	1.1987
30	H	-3.348951	1.380404	-1.474330	31.0891	0.7758

Conformer 5i



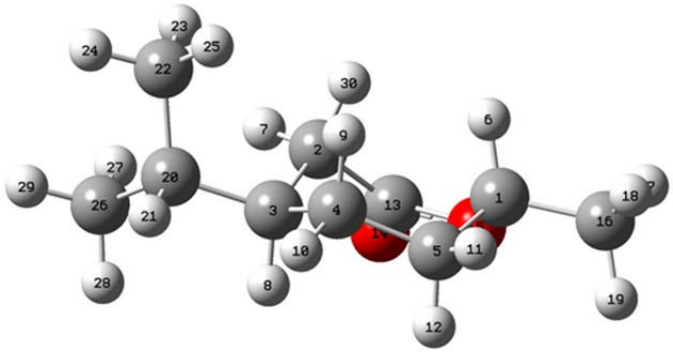
SCF Energy – E(RM062X)	−542.160 22 E_h
SCF Energy from NMR – E(RB3LYP)	−542.541 04 E_h
Sum of Electronic and Thermal Free Energies	−541.927 13 E_h

Table S5i – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 5i

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	2.128294	0.256322	-0.507482	142.6059	41.0017
2	C	1.152568	1.471649	-0.517757	150.5802	33.0274
3	C	-0.194850	1.266256	0.183877	151.7950	31.8126
4	C	-1.146074	0.297407	-0.536315	132.7391	50.8685
5	C	-0.358694	-0.919297	-1.023929	112.8632	70.7444
6	H	2.193161	-0.159504	-1.520204	28.7397	3.1252
7	H	1.664815	2.302295	-0.021820	30.5386	1.3263
8	H	0.980508	1.784252	-1.554267	29.9378	1.9271
9	H	-0.021398	0.908831	1.209304	30.7199	1.1450
10	H	-0.682055	2.240174	0.282456	30.0584	1.8065
11	H	-1.531027	0.799704	-1.438177	30.8003	1.0646
12	H	-1.009262	-1.743133	-1.315952	27.4732	4.3917
13	H	0.267276	-0.669018	-1.883914	27.3822	4.4827
14	C	1.620601	-0.879009	0.367716	-4.2805	187.8881
15	O	2.213759	-1.307432	1.334297	---	---
16	O	0.454228	-1.462704	0.033045	---	---
17	C	3.531593	0.668856	-0.073753	163.0175	20.5901
18	H	4.228123	-0.171330	-0.118388	30.7117	1.1532
19	H	3.896041	1.462500	-0.731954	30.9278	0.9371
20	H	3.518433	1.047796	0.951942	30.7134	1.1515
21	C	-2.354037	-0.105331	0.336133	148.0367	35.5709
22	H	-1.981707	-0.783931	1.117615	30.2267	1.6382
23	C	-2.996421	1.106136	1.019457	161.7042	21.9034
24	H	-2.325446	1.585660	1.736284	30.6104	1.2545
25	H	-3.290402	1.854770	0.272559	31.4391	0.4258
26	H	-3.898007	0.801109	1.559341	31.0196	0.8453
27	C	-3.421959	-0.837489	-0.483166	160.4196	23.1880
28	H	-3.820195	-0.174509	-1.261110	31.4341	0.4308
29	H	-3.043268	-1.739988	-0.969982	30.4262	1.4387
30	H	-4.255618	-1.137581	0.158851	30.8920	0.9729

Normal *trans*-Carvomenthide (6)

Conformer 6a

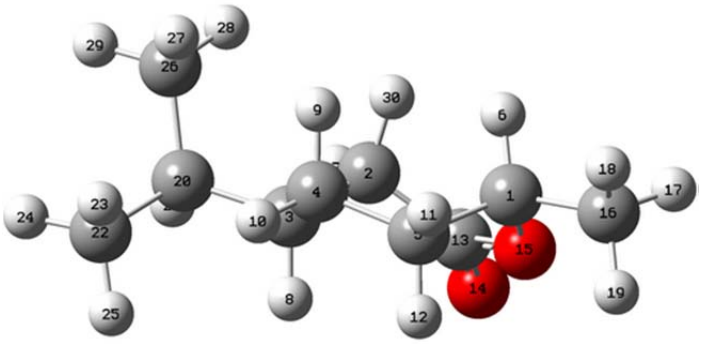


SCF Energy – E(RM062X)	−542.168 50 E_h
SCF Energy from NMR – E(RB3LYP)	−542.551 63 E_h
Sum of Electronic and Thermal Free Energies	−541.936 20 E_h

Table S6a – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 6a

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	2.122385	-0.523656	0.292566	101.7056	81.9020
2	C	-0.425554	0.745873	0.633425	145.2387	38.3689
3	C	-0.943615	-0.258234	-0.422757	137.1790	46.4286
4	C	-0.138409	-1.560578	-0.394293	143.4141	40.1935
5	C	1.353278	-1.402395	-0.690473	142.9742	40.6334
6	H	1.776910	-0.697302	1.319277	27.3507	4.5142
7	H	-1.181238	1.499912	0.858411	29.4730	2.3919
8	H	-0.812019	0.197746	-1.415613	30.3403	1.5246
9	H	-0.250092	-2.031528	0.591928	30.1035	1.7614
10	H	-0.568719	-2.254968	-1.125348	30.2510	1.6139
11	H	1.817720	-2.394598	-0.675621	30.0032	1.8617
12	H	1.509702	-0.993560	-1.697368	30.2589	1.6060
13	C	0.775824	1.517104	0.145834	-3.1892	186.7968
14	O	0.726076	2.696780	-0.140374	---	---
15	O	1.946429	0.883315	-0.012145	---	---
16	C	3.621340	-0.749593	0.213851	159.1872	24.4204
17	H	4.149303	-0.056668	0.872750	30.4775	1.3874
18	H	3.857157	-1.772977	0.515305	30.8251	1.0398
19	H	3.970709	-0.595802	-0.811680	30.5357	1.3292
20	C	-2.456972	-0.522955	-0.255163	143.6497	39.9579
21	H	-2.693970	-1.352553	-0.936017	30.2383	1.6266
22	C	-2.839234	-0.955721	1.163350	167.4817	16.1259
23	H	-2.675671	-0.142490	1.879701	31.4642	0.4007
24	H	-3.900810	-1.218255	1.203598	31.1362	0.7287
25	H	-2.268048	-1.826222	1.499531	30.8266	1.0383
26	C	-3.297378	0.679814	-0.690433	160.6420	22.9656
27	H	-3.133358	1.543491	-0.036671	30.8250	1.0399
28	H	-3.056646	0.981686	-1.714645	30.9807	0.8842
29	H	-4.363451	0.435604	-0.647972	30.9113	0.9536
30	H	-0.187503	0.219767	1.565142	29.4934	2.3715

Conformer 6b

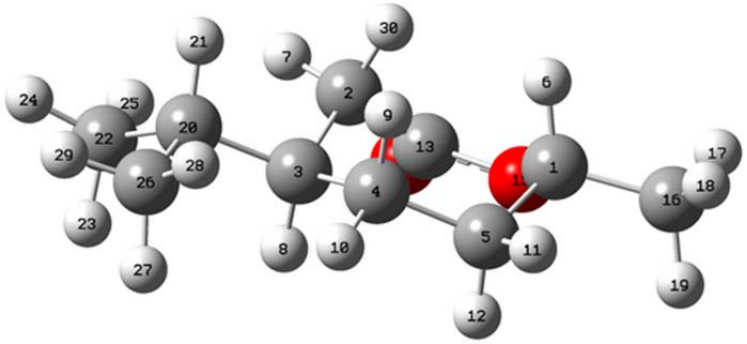


SCF Energy – E(RM062X)	−542.168 39 E_h
SCF Energy from NMR – E(RB3LYP)	−542.551 37 E_h
Sum of Electronic and Thermal Free Energies	−541.936 13 E_h

Table S9b – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 9b

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	1.998079	-0.722052	0.357293	101.5874	82.0202
2	C	-0.195151	1.110832	0.549906	137.0237	46.5839
3	C	-0.976258	0.098184	-0.319902	137.6292	45.9784
4	C	-0.469111	-1.330665	-0.104202	152.4833	31.1243
5	C	1.003606	-1.544146	-0.458021	143.3184	40.2892
6	H	1.683140	-0.662854	1.406484	27.3668	4.4981
7	H	-0.769640	2.032988	0.661422	29.6138	2.2511
8	H	-0.807403	0.363141	-1.374770	30.2423	1.6226
9	H	-0.620172	-1.610825	0.947442	30.5332	1.3317
10	H	-1.067697	-2.023411	-0.704596	30.0668	1.7981
11	H	1.247941	-2.600806	-0.302652	30.0001	1.8648
12	H	1.183775	-1.329682	-1.519645	30.3680	1.4969
13	C	1.114875	1.520402	-0.076082	-2.9691	186.5767
14	O	1.304079	2.627901	-0.538345	---	---
15	O	2.112153	0.628334	-0.159060	---	---
16	C	3.406409	-1.283495	0.281151	159.1620	24.4456
17	H	4.108158	-0.631920	0.806605	30.4905	1.3744
18	H	3.433958	-2.274829	0.739885	30.8289	1.0360
19	H	3.720618	-1.370204	-0.763450	30.5354	1.3295
20	C	-2.494101	0.252142	-0.072167	142.6093	40.9983
21	H	-2.726526	1.304180	-0.288286	30.1224	1.7425
22	C	-3.321262	-0.604972	-1.033551	160.4254	23.1822
23	H	-3.242068	-1.669801	-0.790363	30.9554	0.9095
24	H	-4.379108	-0.332134	-0.968907	30.7994	1.0655
25	H	-2.997214	-0.466528	-2.070628	30.9799	0.8850
26	C	-2.903383	-0.026048	1.377018	167.7908	15.8168
27	H	-2.736217	-1.075884	1.641412	31.2656	0.5993
28	H	-2.352922	0.597765	2.088335	30.9611	0.9038
29	H	-3.969764	0.180233	1.511503	31.1100	0.7549
30	H	-0.020939	0.699603	1.550799	29.0086	2.8563

Conformer 6c

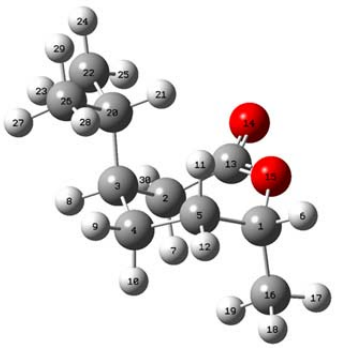


SCF Energy – E(RM062X) −542.167 14 E_h
SCF Energy from NMR – E(RB3LYP) −542.550 37 E_h
Sum of Electronic and Thermal Free Energies −541.934 52 E_h

Table S6c – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 6c

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	2.142659	-0.593717	0.306707	102.0999	81.5077
2	C	-0.233064	0.934500	0.723419	139.9874	43.6202
3	C	-0.980613	-0.131631	-0.113250	135.8838	47.7238
4	C	-0.273106	-1.486530	-0.007856	145.1380	38.4696
5	C	1.187150	-1.498698	-0.465275	142.9449	40.6627
6	H	1.909499	-0.605721	1.378225	27.3167	4.5482
7	H	-0.882124	1.781284	0.944934	29.2391	2.6258
8	H	-0.973480	0.181015	-1.169819	30.8168	1.0481
9	H	-0.327117	-1.829254	1.036847	30.6413	1.2236
10	H	-0.810690	-2.224839	-0.609141	29.8122	2.0527
11	H	1.564238	-2.523517	-0.374550	29.9891	1.8758
12	H	1.259718	-1.228915	-1.527276	30.3423	1.5226
13	C	0.957915	1.522265	0.007463	-1.9837	185.5913
14	O	0.959281	2.649377	-0.446034	---	---
15	O	2.057761	0.775703	-0.162081	---	---
16	C	3.595022	-0.982815	0.098514	159.2483	24.3593
17	H	4.257943	-0.270173	0.594255	30.4899	1.3750
18	H	3.773796	-1.978063	0.512381	30.8293	1.0356
19	H	3.830610	-0.998744	-0.969954	30.5446	1.3203
20	C	-2.459420	-0.185276	0.340108	144.1613	39.4463
21	H	-2.463596	-0.198704	1.441045	30.7460	1.1189
22	C	-3.225535	1.052929	-0.139235	160.1732	23.4344
23	H	-3.305758	1.038801	-1.232672	31.3456	0.5193
24	H	-4.239741	1.059680	0.271307	30.9135	0.9514
25	H	-2.744795	1.992165	0.146292	30.3754	1.4895
26	C	-3.192414	-1.437179	-0.151863	161.6617	21.9459
27	H	-3.107496	-1.529217	-1.241865	31.3640	0.5009
28	H	-2.805946	-2.354097	0.299641	30.6177	1.2472
29	H	-4.256330	-1.366990	0.094556	30.9847	0.8802
30	H	0.073374	0.491564	1.678327	29.4210	2.4439

Conformer 6d



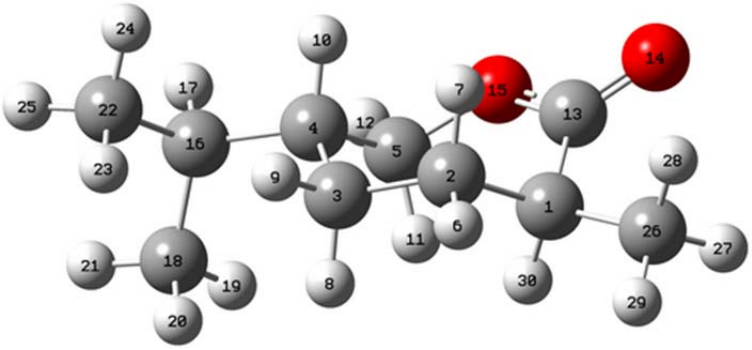
SCF Energy – E(RM062X)	−542.164 34 E_h
SCF Energy from NMR – E(RB3LYP)	−542.543 50 E_h
Sum of Electronic and Thermal Free Energies	−541.931 30 E_h

Table S6d – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 6d

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-2.009190	-0.507958	-0.635952	102.5076	81.1000
2	C	-0.024602	0.843067	1.158642	137.7345	45.8731
3	C	0.829936	-0.407395	0.864811	137.9671	45.6405
4	C	-0.057485	-1.641904	0.659809	153.7936	29.8140
5	C	-0.935129	-1.592801	-0.589961	151.7196	31.8880
6	H	-2.570417	-0.661064	-1.561172	27.2750	4.5899
7	H	-0.820817	0.588516	1.863814	29.0455	2.8194
8	H	1.417032	-0.586423	1.777380	30.5580	1.3069
9	H	0.569927	-2.537120	0.609228	29.8975	1.9674
10	H	-0.688251	-1.768924	1.548677	29.9325	1.9324
11	H	-0.314924	-1.491848	-1.488541	29.6320	2.2329
12	H	-1.467458	-2.546205	-0.688292	30.2696	1.5953
13	C	-0.628615	1.493703	-0.068829	-1.3381	184.9457
14	O	-0.352444	2.633497	-0.388685	---	---
15	O	-1.474311	0.823443	-0.865926	---	---
16	C	-3.012019	-0.522735	0.509967	165.1863	18.4213
17	H	-3.750945	0.269078	0.365539	30.4303	1.4346
18	H	-3.532484	-1.484877	0.504438	30.9047	0.9602
19	H	-2.555061	-0.397994	1.492613	29.8777	1.9872
20	C	1.843874	-0.157825	-0.272653	150.3335	33.2741
21	H	1.291186	0.123705	-1.181789	30.2457	1.6192
22	C	2.786667	0.999291	0.075400	160.4932	23.1144
23	H	3.317873	0.788565	1.012111	31.4008	0.4641
24	H	3.534234	1.130746	-0.712585	30.9769	0.8880
25	H	2.254329	1.947425	0.187416	30.2175	1.6474
26	C	2.659654	-1.414557	-0.587710	161.2276	22.3800
27	H	3.150092	-1.789952	0.319331	31.3554	0.5095
28	H	2.043446	-2.219941	-0.997298	30.5684	1.2965
29	H	3.438963	-1.186495	-1.320968	30.9845	0.8804
30	H	0.578766	1.621978	1.625840	28.9064	2.9585

Abnormal *trans*-Carvomenthide (7)

Conformer 7a

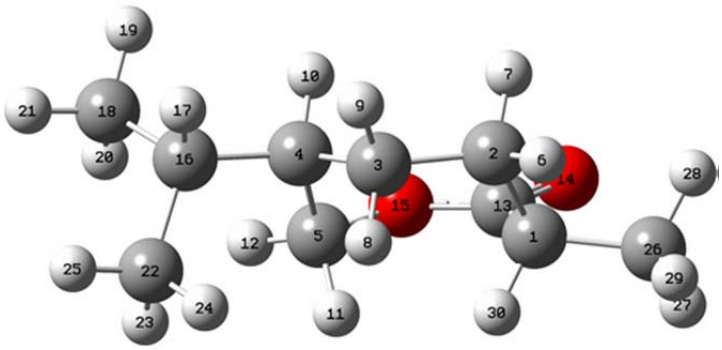


SCF Energy – E(RM062X)	−542.163 73 E_h
SCF Energy from NMR – E(RB3LYP)	−542.545 62 E_h
Sum of Electronic and Thermal Free Energies	−541.930 88 E_h

Table S7a – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 7a

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	1.870093	0.581393	0.447566	140.8188	42.7888
2	C	0.891314	1.447605	-0.377237	146.6269	36.9807
3	C	-0.590631	1.225840	-0.071370	152.5309	31.0767
4	C	-1.098159	-0.188717	-0.365630	134.0328	49.5748
5	C	-0.334062	-1.243723	0.434604	104.6113	78.9963
6	H	1.133998	2.494660	-0.166617	30.1422	1.7227
7	H	1.088310	1.292226	-1.446303	30.4352	1.4297
8	H	-0.764601	1.458772	0.988272	30.4120	1.4529
9	H	-1.170204	1.949539	-0.653621	30.0205	1.8444
10	H	-0.911470	-0.410300	-1.427195	30.2542	1.6107
11	H	-0.164904	-0.932839	1.471351	27.4679	4.3970
12	H	-0.890394	-2.183635	0.450009	27.8288	4.0361
13	C	1.990360	-0.801103	-0.168664	-5.4704	189.0780
14	O	3.004039	-1.210825	-0.694578	---	---
15	O	0.919757	-1.612177	-0.168718	---	---
16	C	-2.617692	-0.358004	-0.135336	145.4479	38.1597
17	H	-2.853712	-1.388569	-0.435923	30.0203	1.8446
18	C	-3.030938	-0.197930	1.331871	166.7126	16.8950
19	H	-2.500347	-0.893589	1.989963	31.1263	0.7386
20	H	-2.841803	0.820389	1.688081	31.1665	0.6984
21	H	-4.102588	-0.390739	1.442476	31.1076	0.7573
22	C	-3.440450	0.576533	-1.024833	160.2474	23.3602
23	H	-3.358321	1.617520	-0.694932	30.9418	0.9231
24	H	-3.114143	0.522721	-2.068990	30.9874	0.8775
25	H	-4.499064	0.302102	-0.984218	30.8259	1.0390
26	C	3.247561	1.233337	0.534225	163.2771	20.3305
27	H	3.956339	0.599538	1.071331	30.6658	1.1991
28	H	3.648455	1.416942	-0.466635	30.6675	1.1974
29	H	3.164689	2.189968	1.056477	31.0500	0.8149
30	H	1.465012	0.467928	1.461665	29.0759	2.7890

Conformer 7b

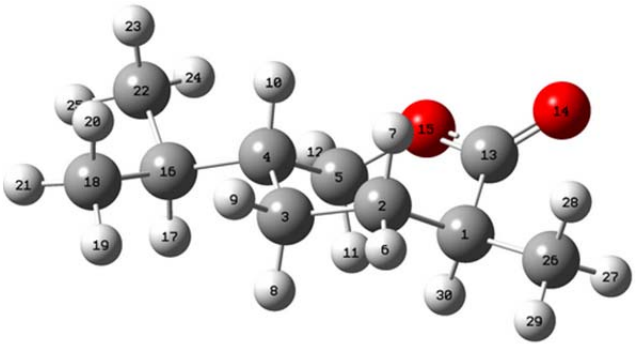


SCF Energy – E(RM062X)	−542.163 58 E_h
SCF Energy from NMR – E(RB3LYP)	−542.545 71 E_h
Sum of Electronic and Thermal Free Energies	−541.930 80 E_h

Table S7b – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 7b

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-1.952121	-0.545803	0.327558	141.0895	42.5181
2	C	-1.154167	-1.341606	-0.730250	146.3249	37.2827
3	C	0.347411	-1.446257	-0.464149	143.4994	40.1082
4	C	1.095638	-0.110421	-0.437402	133.9752	49.6324
5	C	0.541045	0.830569	0.631619	110.5671	73.0405
6	H	-1.572856	-2.353409	-0.755311	30.1590	1.7059
7	H	-1.337414	-0.904657	-1.720849	30.3356	1.5293
8	H	0.495106	-1.961065	0.495304	30.0025	1.8624
9	H	0.795505	-2.083546	-1.235384	30.2230	1.6419
10	H	0.943683	0.389828	-1.405342	30.3370	1.5279
11	H	0.332787	0.302444	1.568864	27.7421	4.1228
12	H	1.246053	1.634557	0.848315	27.6678	4.1971
13	C	-1.831024	0.943802	0.058987	-5.6819	189.2895
14	O	-2.760200	1.632446	-0.307862	---	---
15	O	-0.635596	1.539167	0.200817	---	---
16	C	2.618179	-0.318906	-0.260515	144.9722	38.6354
17	H	2.890141	-1.149323	-0.926125	30.2761	1.5888
18	C	3.418985	0.906857	-0.707357	160.6349	22.9727
19	H	3.186973	1.175531	-1.742601	30.8613	1.0036
20	H	3.208781	1.777767	-0.076616	30.7630	1.1019
21	H	4.492857	0.706470	-0.639308	30.8723	0.9926
22	C	3.008048	-0.717675	1.167871	166.4409	17.1667
23	H	2.837228	0.107650	1.868989	31.5241	0.3408
24	H	2.447365	-1.587386	1.523541	30.7125	1.1524
25	H	4.072634	-0.966571	1.211972	31.0985	0.7664
26	C	-3.422624	-0.954693	0.334624	163.3525	20.2551
27	H	-4.000107	-0.357322	1.043509	30.6765	1.1884
28	H	-3.862488	-0.821126	-0.657740	30.6629	1.2020
29	H	-3.505610	-2.008431	0.612959	31.0461	0.8188
30	H	-1.520494	-0.749512	1.316272	29.0682	2.7967

Conformer 7c

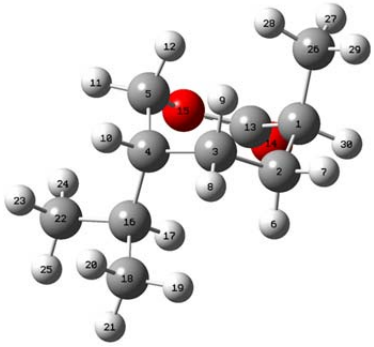


SCF Energy – E(RM062X)	−542.162 59 E_h
SCF Energy from NMR – E(RB3LYP)	−542.544 76 E_h
Sum of Electronic and Thermal Free Energies	−541.929 88 E_h

Table S7c – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 7c

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	1.985793	0.557603	0.375962	141.3243	42.2833
2	C	1.018010	1.419012	-0.465273	146.4985	37.1091
3	C	-0.452193	1.372112	-0.046332	144.9448	38.6628
4	C	-1.117943	-0.004020	-0.145563	133.0241	50.5835
5	C	-0.362102	-1.037516	0.691438	107.4091	76.1985
6	H	1.361237	2.456151	-0.386595	30.1504	1.7145
7	H	1.119083	1.140133	-1.522695	30.4042	1.4607
8	H	-0.540337	1.730761	0.990884	30.6028	1.2621
9	H	-0.996337	2.085182	-0.672138	29.7922	2.0727
10	H	-1.085150	-0.338488	-1.194376	30.7116	1.1533
11	H	-0.082886	-0.620127	1.666113	27.7905	4.0744
12	H	-0.974952	-1.920161	0.872302	27.6207	4.2442
13	C	1.940367	-0.881310	-0.103038	-5.6122	189.2198
14	O	2.874126	-1.436035	-0.643278	---	---
15	O	0.799976	-1.576827	0.037347	---	---
16	C	-2.600091	0.005227	0.305723	149.0898	34.5178
17	H	-2.610140	-0.015176	1.407036	30.8063	1.0586
18	C	-3.360023	1.256310	-0.144237	161.8707	21.7369
19	H	-2.981736	2.167756	0.324768	30.6568	1.2081
20	H	-3.291947	1.376910	-1.232428	31.3266	0.5383
21	H	-4.418841	1.161680	0.115535	31.0002	0.8647
22	C	-3.339825	-1.233958	-0.212277	160.1452	23.4624
23	H	-3.421313	-1.187290	-1.304549	31.2808	0.5841
24	H	-2.838902	-2.171219	0.044150	30.4493	1.4156
25	H	-4.353133	-1.275886	0.198353	30.8966	0.9683
26	C	3.414273	1.088501	0.294330	163.3999	20.2077
27	H	4.108996	0.450871	0.845173	30.6630	1.2019
28	H	3.747777	1.132519	-0.746297	30.6788	1.1861
29	H	3.452114	2.096597	0.715166	31.0569	0.8080
30	H	1.656054	0.580923	1.422640	29.0244	2.8405

Conformer 7d

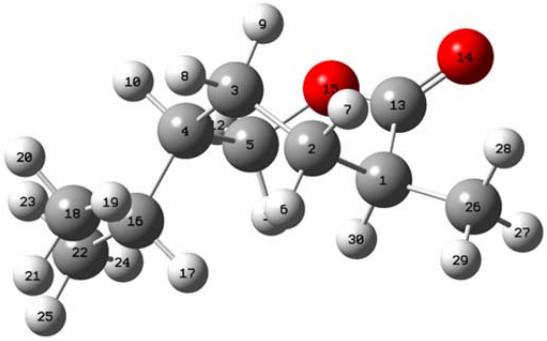


SCF Energy – E(RM062X)	−542.159 72 E_h
SCF Energy from NMR – E(RB3LYP)	−542.539 31 E_h
Sum of Electronic and Thermal Free Energies	−541.925 79 E_h

Table S7d – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 7d

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-1.888046	0.463261	-0.511212	133.8130	49.7946
2	C	-0.757967	1.481899	-0.749386	155.5131	28.0945
3	C	0.214277	1.704729	0.407860	153.7684	29.8392
4	C	1.014910	0.458344	0.809598	132.9585	50.6491
5	C	0.105177	-0.600259	1.431443	109.9798	73.6278
6	H	-0.206353	1.191046	-1.651556	29.8354	2.0295
7	H	-1.248428	2.433484	-0.984472	30.4831	1.3818
8	H	0.900718	2.513084	0.137347	29.9133	1.9516
9	H	-0.336048	2.060846	1.287896	29.9852	1.8797
10	H	1.692930	0.758971	1.623616	30.5793	1.2856
11	H	0.688089	-1.318718	2.008508	27.4733	4.3916
12	H	-0.624096	-0.146119	2.107030	27.2643	4.6006
13	C	-1.441033	-0.992536	-0.450729	-5.1760	188.7836
14	O	-1.881855	-1.817229	-1.227216	---	---
15	O	-0.573695	-1.434732	0.474034	---	---
16	C	1.895302	-0.122137	-0.317004	154.2387	29.3689
17	H	1.243572	-0.473353	-1.128602	30.0807	1.7842
18	C	2.833726	0.942106	-0.892009	161.4703	22.1373
19	H	2.289692	1.751312	-1.387255	30.5520	1.3129
20	H	3.447953	1.382678	-0.096611	31.3355	0.5294
21	H	3.507736	0.495712	-1.629248	30.9435	0.9214
22	C	2.703879	-1.325949	0.176062	161.3073	22.3003
23	H	3.314579	-1.049615	1.044811	31.3139	0.5510
24	H	2.060248	-2.163227	0.459398	30.3926	1.4723
25	H	3.378281	-1.678645	-0.609877	30.9119	0.9530
26	C	-2.811272	0.824248	0.663651	167.7184	15.8892
27	H	-3.635399	0.109658	0.736921	30.5199	1.3450
28	H	-2.300030	0.854381	1.627005	30.0764	1.7885
29	H	-3.235207	1.816420	0.482666	30.9199	0.9450
30	H	-2.507554	0.475525	-1.411758	28.8305	3.0344

Conformer 7e



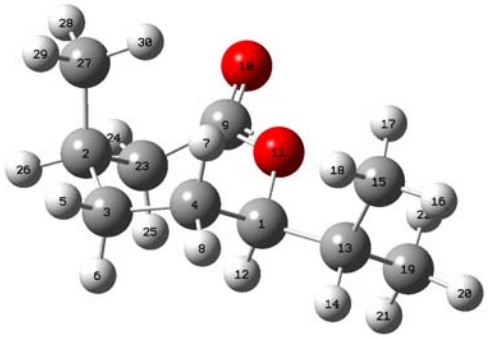
SCF Energy – E(RM062X)	−542.161 62 E_h
SCF Energy from NMR – E(RB3LYP)	−542.541 05 E_h
Sum of Electronic and Thermal Free Energies	−541.927 50 E_h

Table S7e – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 7e

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	1.502087	0.611453	0.581018	142.7210	40.8866
2	C	0.640311	1.414413	-0.423796	152.1622	31.4454
3	C	-0.254505	0.555170	-1.320885	156.4561	27.1515
4	C	-1.150224	-0.444753	-0.576611	136.7659	46.8417
5	C	-0.322374	-1.487084	0.210596	108.0889	75.5187
6	H	0.041708	2.133775	0.146783	29.9730	1.8919
7	H	1.317437	1.996023	-1.059952	30.7309	1.1340
8	H	-0.881217	1.207532	-1.935474	30.0931	1.7718
9	H	0.373582	-0.001120	-2.026112	30.3121	1.5528
10	H	-1.721472	-0.984162	-1.345471	30.2502	1.6147
11	H	-0.293775	-1.246981	1.278386	27.7940	4.0709
12	H	-0.751655	-2.484106	0.109536	27.4436	4.4213
13	C	1.948176	-0.683618	-0.072910	-4.5023	188.1099
14	O	3.075700	-0.889774	-0.468327	---	---
15	O	1.026403	-1.648148	-0.264033	---	---
16	C	-2.177252	0.214106	0.366985	147.3377	36.2699
17	H	-1.624517	0.683089	1.196191	30.2352	1.6297
18	C	-2.996358	1.298238	-0.336598	160.9672	22.6404
19	H	-2.384163	2.153831	-0.634565	30.5141	1.3508
20	H	-3.475378	0.892627	-1.236310	31.3057	0.5592
21	H	-3.785441	1.667253	0.325793	30.9707	0.8942
22	C	-3.119351	-0.840493	0.959362	161.1783	22.4293
23	H	-3.681172	-1.335428	0.157828	31.3871	0.4778
24	H	-2.585007	-1.612418	1.521492	30.8091	1.0558
25	H	-3.840607	-0.375721	1.638296	30.9065	0.9584
26	C	2.698005	1.422774	1.066107	164.8698	18.7378
27	H	3.274857	0.874575	1.815057	30.7622	1.1027
28	H	3.361522	1.662479	0.231510	30.7043	1.1606
29	H	2.347590	2.357872	1.512244	30.9646	0.9003
30	H	0.879796	0.353011	1.444041	28.8748	2.9901

Normal *cis*-Menthide (8)

Conformer 8a

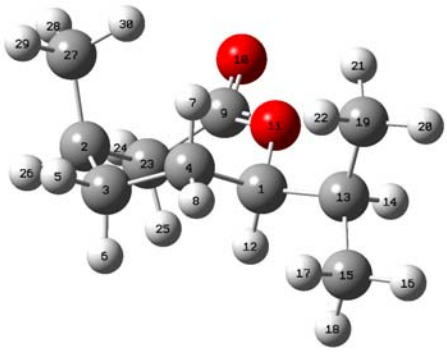


SCF Energy – E(RM062X)	−542.169 63 E_h
SCF Energy from NMR – E(RB3LYP)	−542.550 87 E_h
Sum of Electronic and Thermal Free Energies	−541.936 73 E_h

Table S8a – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 8a

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	0.847119	-0.361778	-0.442073	94.3375	89.2701
2	C	-2.286231	-0.597809	-0.391897	150.1722	33.4354
3	C	-1.296846	-1.750864	-0.602705	143.8569	39.7507
4	C	0.070084	-1.574735	0.061941	150.4846	33.1230
5	H	-1.757084	-2.674885	-0.233568	30.0724	1.7925
6	H	-1.142611	-1.884724	-1.681857	30.0426	1.8223
7	H	-0.026015	-1.500967	1.151385	29.8754	1.9895
8	H	0.674396	-2.466825	-0.140232	30.3724	1.4925
9	C	-0.775900	1.420619	-0.003996	-1.8645	185.4721
10	O	-1.029057	2.456997	0.577354	---	---
11	O	0.412518	0.847420	0.227149	---	---
12	H	0.683209	-0.231335	-1.520434	27.5816	4.2833
13	C	2.357837	-0.450651	-0.203373	143.0585	40.5491
14	H	2.684547	-1.339615	-0.759633	30.2172	1.6477
15	C	2.707429	-0.642555	1.274131	168.6012	15.0064
16	H	3.793405	-0.688848	1.398111	31.1822	0.6827
17	H	2.334753	0.198157	1.867851	30.8796	0.9853
18	H	2.284155	-1.566016	1.679578	30.7280	1.1369
19	C	3.075379	0.769857	-0.781967	161.4491	22.1585
20	H	4.159598	0.642384	-0.712574	30.9197	0.9452
21	H	2.816088	0.921039	-1.835295	30.9821	0.8828
22	H	2.803157	1.674397	-0.229745	30.6668	1.1981
23	C	-1.757091	0.746969	-0.936855	138.8830	44.7246
24	H	-2.583384	1.451011	-1.048933	29.3792	2.4857
25	H	-1.298553	0.602290	-1.921633	28.8088	3.0561
26	H	-3.171858	-0.830225	-0.995101	29.8161	2.0488
27	C	-2.735749	-0.466108	1.065123	164.9719	18.6357
28	H	-3.475448	0.333001	1.174330	30.7428	1.1221
29	H	-3.185188	-1.401441	1.412085	31.0338	0.8311
30	H	-1.897033	-0.230404	1.729673	30.8245	1.0404

Conformer 8b

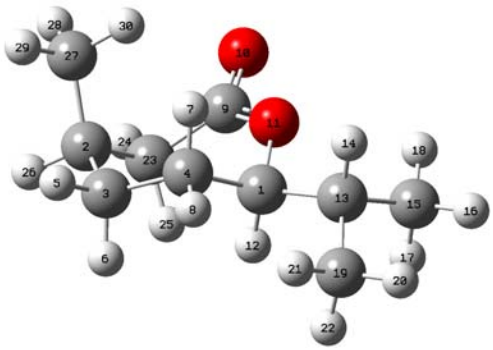


SCF Energy – E(RM062X)	−542.169 20 E_h
SCF Energy from NMR – E(RB3LYP)	−542.550 56 E_h
Sum of Electronic and Thermal Free Energies	−541.936 15 E_h

Table S8b – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 8b

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	0.882167	0.003898	-0.383373	93.6995	89.9081
2	C	-2.081746	-1.050596	-0.233948	150.0271	33.5805
3	C	-0.811505	-1.908736	-0.188179	143.9992	39.6084
4	C	0.425516	-1.224834	0.398335	157.3354	26.2722
5	H	-1.025503	-2.815404	0.389773	30.0611	1.8038
6	H	-0.573732	-2.234993	-1.209602	30.1446	1.7203
7	H	0.259865	-0.928993	1.440936	30.2136	1.6513
8	H	1.246188	-1.950386	0.407895	30.2409	1.6240
9	C	-1.175704	1.332730	-0.319479	-1.4759	185.0835
10	O	-1.725304	2.358257	0.030248	---	---
11	O	0.115084	1.172607	0.003589	---	---
12	H	0.738447	-0.155265	-1.460456	27.6115	4.2534
13	C	2.345455	0.399144	-0.152577	144.4083	39.1993
14	H	2.463764	1.376526	-0.637318	29.8786	1.9863
15	C	3.296510	-0.584756	-0.836414	162.7920	20.8156
16	H	4.325667	-0.222649	-0.758710	30.7840	1.0809
17	H	3.260156	-1.572749	-0.365143	31.1656	0.6993
18	H	3.058591	-0.703004	-1.898586	30.9401	0.9248
19	C	2.681169	0.552846	1.331673	167.5453	16.0623
20	H	3.687910	0.964670	1.448098	31.0860	0.7789
21	H	1.977193	1.223703	1.832021	30.5257	1.3392
22	H	2.657481	-0.416860	1.840909	31.2396	0.6253
23	C	-1.897692	0.235557	-1.068747	138.9282	44.6794
24	H	-2.873215	0.651780	-1.325733	29.3747	2.4902
25	H	-1.368705	0.008379	-2.001039	28.8038	3.0611
26	H	-2.839645	-1.638672	-0.764975	29.8069	2.0580
27	C	-2.630073	-0.733862	1.159444	164.9278	18.6798
28	H	-3.555574	-0.153712	1.091383	30.7449	1.1200
29	H	-2.842308	-1.658237	1.705045	31.0351	0.8298
30	H	-1.919396	-0.149390	1.754401	30.8190	1.0459

Conformer 8c

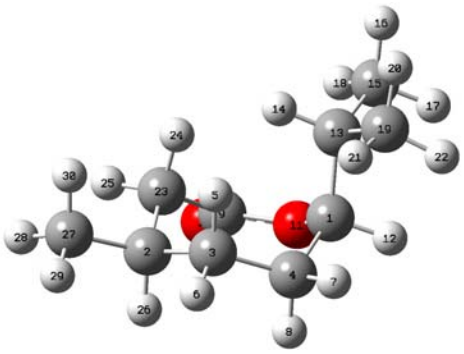


SCF Energy – E(RM062X)	−542.168 34 E_h
SCF Energy from NMR – E(RB3LYP)	−542.550 20 E_h
Sum of Electronic and Thermal Free Energies	−541.935 87 E_h

Table S8c – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 8c

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-0.886997	-0.195932	0.094329	91.2212	92.3864
2	C	2.178598	-0.851092	0.435831	150.2852	33.3224
3	C	1.039723	-1.872977	0.336589	143.8061	39.8015
4	C	-0.187554	-1.432176	-0.465379	152.8728	30.7348
5	H	1.438141	-2.794682	-0.103546	30.0663	1.7986
6	H	0.711099	-2.126879	1.353393	30.0740	1.7909
7	H	0.067141	-1.227619	-1.512716	30.2334	1.6315
8	H	-0.897192	-2.263511	-0.474059	29.8670	1.9979
9	C	0.994259	1.378769	0.135750	-1.4114	185.0190
10	O	1.457074	2.431086	-0.257256	---	---
11	O	-0.198652	1.002312	-0.344152	---	---
12	H	-0.883600	-0.212374	1.194245	28.1007	3.7642
13	C	-2.337294	-0.026411	-0.373279	144.7240	38.8836
14	H	-2.333603	-0.053494	-1.472078	30.1753	1.6896
15	C	-2.906623	1.317562	0.088870	161.8556	21.7520
16	H	-3.946424	1.417167	-0.235809	31.0009	0.8640
17	H	-2.889597	1.378597	1.184294	31.3851	0.4798
18	H	-2.337487	2.158851	-0.309726	30.1692	1.6957
19	C	-3.217867	-1.163799	0.153763	162.1725	21.4351
20	H	-4.260672	-0.980801	-0.120099	30.8576	1.0073
21	H	-2.939783	-2.141739	-0.245198	30.6929	1.1720
22	H	-3.164914	-1.211946	1.248275	31.3129	0.5520
23	C	1.729154	0.471102	1.095008	139.1380	44.4696
24	H	2.601453	1.037510	1.425168	29.3895	2.4754
25	H	1.105896	0.263846	1.971946	28.8083	3.0566
26	H	2.925496	-1.279215	1.114835	29.8070	2.0579
27	C	2.863497	-0.597101	-0.909155	164.9887	18.6189
28	H	3.698592	0.101022	-0.795505	30.7430	1.1219
29	H	3.251083	-1.533077	-1.322464	31.0349	0.8300
30	H	2.173615	-0.166496	-1.643653	30.8168	1.0481

Conformer 8d

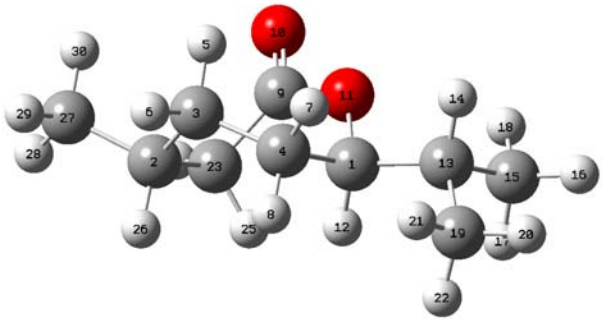


SCF Energy – E(RM062X)	−542.165 80 E_h
SCF Energy from NMR – E(RB3LYP)	−542.547 68 E_h
Sum of Electronic and Thermal Free Energies	−541.933 50 E_h

Table S8d – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 8d

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-1.080305	-0.005969	0.805051	92.7783	90.8293
2	C	1.994189	-0.582627	0.036188	146.6206	36.9870
3	C	0.927782	-1.611027	0.416671	147.2039	36.4037
4	C	-0.150832	-1.083475	1.359917	149.4640	34.1436
5	H	0.471147	-2.006340	-0.502274	30.2882	1.5767
6	H	1.424375	-2.459012	0.902329	30.2423	1.6226
7	H	-0.783514	-1.915120	1.687118	29.7269	2.1380
8	H	0.316644	-0.678396	2.266028	29.9818	1.8831
9	C	0.664245	1.633345	0.122275	-1.2473	184.8549
10	O	1.050486	2.781660	0.227178	---	---
11	O	-0.447871	1.300693	0.791124	---	---
12	H	-1.867024	0.156069	1.551052	28.0462	3.8187
13	C	-1.793487	-0.323060	-0.516231	149.3244	34.2832
14	H	-1.057229	-0.510363	-1.304918	29.4030	2.4619
15	C	-2.675677	0.850584	-0.946394	162.3502	21.2574
16	H	-3.206681	0.605355	-1.870692	30.9792	0.8857
17	H	-3.421878	1.070191	-0.173668	31.1942	0.6707
18	H	-2.090875	1.758090	-1.117021	30.4568	1.4081
19	C	-2.629715	-1.595635	-0.350435	162.5042	21.1034
20	H	-3.219329	-1.775786	-1.253696	30.8916	0.9733
21	H	-2.007903	-2.477862	-0.173441	30.7508	1.1141
22	H	-3.325600	-1.492436	0.490862	31.3577	0.5072
23	C	1.412587	0.624193	-0.722643	133.5052	50.1024
24	H	0.767948	0.272578	-1.535791	29.2853	2.5796
25	H	2.225338	1.194000	-1.177473	29.3578	2.5071
26	H	2.463268	-0.212727	0.958978	30.1343	1.7306
27	C	3.074110	-1.235363	-0.828233	157.5974	26.0102
28	H	3.880877	-0.532257	-1.054156	30.7720	1.0929
29	H	3.506297	-2.102013	-0.319177	30.8017	1.0632
30	H	2.645834	-1.578593	-1.777475	31.0748	0.7901

Conformer 8e

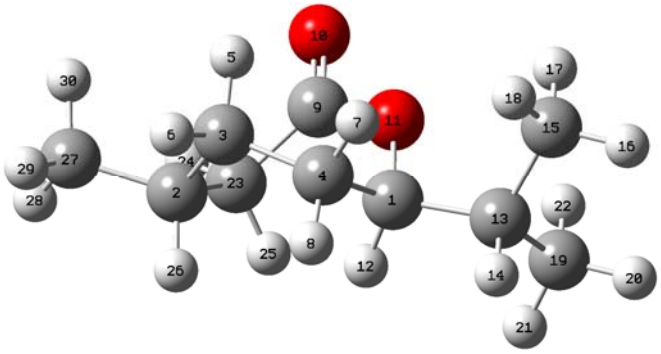


SCF Energy – E(RM062X)	−542.166 50 E_h
SCF Energy from NMR – E(RB3LYP)	−542.548 78 E_h
Sum of Electronic and Thermal Free Energies	−541.933 89 E_h

Table S8e – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 8e

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-0.953566	-0.191988	0.085063	95.2895	88.3181
2	C	2.036043	-0.822875	0.506671	150.4348	33.1728
3	C	1.222162	-1.321532	-0.694800	147.8898	35.7178
4	C	-0.284519	-1.456783	-0.465147	147.3019	36.3057
5	H	1.402023	-0.647375	-1.543311	30.6343	1.2306
6	H	1.615942	-2.297711	-0.997371	30.2652	1.5997
7	H	-0.761111	-1.725808	-1.415839	30.2168	1.6481
8	H	-0.481950	-2.275273	0.236354	30.0263	1.8386
9	C	0.891230	1.379890	-0.069748	-0.6063	184.2139
10	O	1.387900	2.350037	-0.604714	---	---
11	O	-0.329517	0.987403	-0.474193	---	---
12	H	-0.850924	-0.150174	1.176322	27.9413	3.9236
13	C	-2.441163	-0.089732	-0.249173	142.5556	41.0520
14	H	-2.523606	-0.061736	-1.344569	30.2358	1.6291
15	C	-3.048478	1.188840	0.329308	161.7108	21.8968
16	H	-4.108192	1.258549	0.066836	30.9655	0.8994
17	H	-2.972866	1.184034	1.423665	31.3637	0.5012
18	H	-2.541716	2.080314	-0.046821	30.2298	1.6351
19	C	-3.185915	-1.320819	0.273423	163.7499	19.8577
20	H	-4.258028	-1.217828	0.083895	30.9145	0.9504
21	H	-2.847519	-2.244662	-0.202824	30.7326	1.1323
22	H	-3.045941	-1.421997	1.356712	31.3522	0.5127
23	C	1.575401	0.576361	1.011928	140.4662	43.1414
24	H	2.435300	1.163065	1.338738	29.7216	2.1433
25	H	0.900375	0.480275	1.865704	28.6733	3.1916
26	H	1.900333	-1.532211	1.332464	30.0263	1.8386
27	C	3.519870	-0.776066	0.136683	157.6605	25.9471
28	H	4.132315	-0.492444	0.997484	30.7746	1.0903
29	H	3.862613	-1.750754	-0.223961	30.9675	0.8974
30	H	3.689503	-0.039564	-0.657468	30.7766	1.0883

Conformer 8f



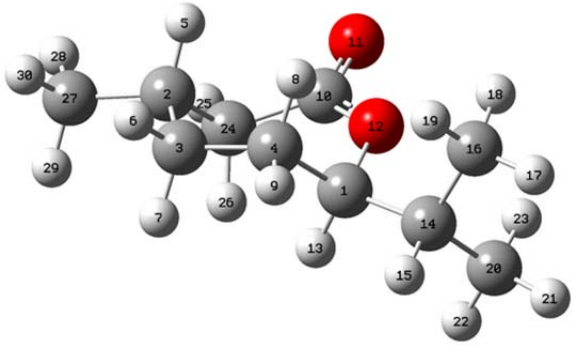
SCF Energy – E(RM062X)	−542.165 13 E_h
SCF Energy from NMR – E(RB3LYP)	−542.547 74 E_h
Sum of Electronic and Thermal Free Energies	−541.933 31 E_h

Table S8f – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 8f

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-0.854194	-0.412653	0.324694	97.6492	85.9584
2	C	2.094645	-0.601518	0.526434	151.1528	32.4548
3	C	1.338975	-1.311191	-0.605792	147.5641	36.0435
4	C	-0.131400	-1.605433	-0.293944	149.4341	34.1735
5	H	1.412687	-0.703068	-1.517802	30.5633	1.3016
6	H	1.847198	-2.254882	-0.830478	30.2925	1.5724
7	H	-0.638988	-1.921914	-1.210243	29.7960	2.0689
8	H	-0.203711	-2.432848	0.422345	30.4462	1.4187
9	C	0.645297	1.392935	-0.275195	-1.1406	184.7482
10	O	0.888992	2.352485	-0.978125	---	---
11	O	-0.545173	0.788128	-0.419208	---	---
12	H	-0.502730	-0.275480	1.354172	27.4108	4.4541
13	C	-2.379678	-0.532491	0.369765	146.2863	37.3213
14	H	-2.581758	-1.493570	0.862553	30.1865	1.6784
15	C	-3.023037	-0.546935	-1.019182	168.2751	15.3325
16	H	-4.107321	-0.654715	-0.922089	31.1512	0.7137
17	H	-2.821493	0.392351	-1.542777	30.9156	0.9493
18	H	-2.661407	-1.370685	-1.640017	30.6767	1.1882
19	C	-2.978198	0.587840	1.223514	160.8037	22.8039
20	H	-4.061869	0.467673	1.311042	30.8622	1.0027
21	H	-2.553074	0.592114	2.232617	30.9299	0.9350
22	H	-2.782529	1.562372	0.764136	30.6963	1.1686
23	C	1.605537	0.860744	0.767441	138.6691	44.9385
24	H	2.452303	1.548999	0.762917	29.6734	2.1915
25	H	1.121820	0.954563	1.745225	28.6018	3.2631
26	H	1.925031	-1.169633	1.450160	30.0114	1.8535
27	C	3.595538	-0.596165	0.230043	156.5252	27.0824
28	H	4.156537	-0.117713	1.038296	30.7345	1.1304
29	H	3.971930	-1.616112	0.106898	30.9492	0.9157
30	H	3.795905	-0.043155	-0.694958	30.8204	1.0445

Normal *trans*-Menthide (9)

Conformer 9a

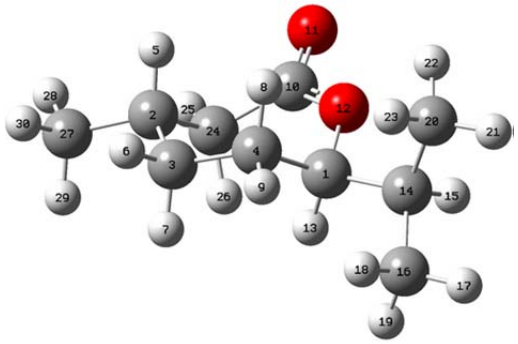


SCF Energy – E(RM062X)	−542.169 99 E_h
SCF Energy from NMR – E(RB3LYP)	−542.553 14 E_h
Sum of Electronic and Thermal Free Energies	−541.937 50 E_h

Table S9a – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 9a

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-0.857662	-0.409469	0.349807	94.9056	88.7020
2	C	2.245895	-0.377236	-0.204793	146.4929	37.1147
3	C	1.381435	-1.619213	0.027254	140.7721	42.8355
4	C	-0.079989	-1.487457	-0.401047	145.1562	38.4514
5	H	2.257574	-0.153014	-1.280775	30.1207	1.7442
6	H	1.833479	-2.462325	-0.507661	29.9770	1.8879
7	H	1.419337	-1.870212	1.097757	30.5819	1.2830
8	H	-0.146784	-1.278651	-1.475889	30.1355	1.7294
9	H	-0.584640	-2.445722	-0.231107	30.1413	1.7236
10	C	0.543647	1.525568	-0.169542	-2.2084	185.8160
11	O	0.638831	2.613479	-0.702544	---	---
12	O	-0.634142	0.892917	-0.242703	---	---
13	H	-0.530494	-0.367329	1.397622	27.5596	4.3053
14	C	-2.374984	-0.619072	0.337307	143.0604	40.5472
15	H	-2.536059	-1.582316	0.839873	30.2113	1.6536
16	C	-2.941794	-0.706420	-1.081500	168.5560	15.0516
17	H	-4.026128	-0.846035	-1.042713	31.1850	0.6799
18	H	-2.738992	0.217624	-1.632136	30.8946	0.9703
19	H	-2.515762	-1.543014	-1.642677	30.7411	1.1238
20	C	-3.083543	0.469715	1.144366	161.5150	22.0926
21	H	-4.151756	0.248719	1.225914	30.9190	0.9459
22	H	-2.672226	0.545929	2.156598	30.9769	0.8880
23	H	-2.973471	1.442792	0.656367	30.6763	1.1886
24	C	1.702198	0.862802	0.537509	137.1302	46.4774
25	H	2.479379	1.626342	0.603021	29.5338	2.3311
26	H	1.416391	0.583570	1.559011	29.2478	2.6171
27	C	3.681586	-0.643546	0.249331	157.2322	26.3754
28	H	4.331558	0.207277	0.026063	30.7399	1.1250
29	H	3.711896	-0.821004	1.330900	31.0827	0.7822
30	H	4.088461	-1.527840	-0.250343	30.8001	1.0648

Conformer 9b

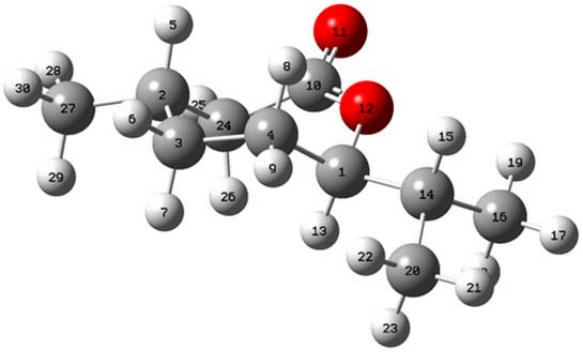


SCF Energy – E(RM062X)	−542.169 54 E_h
SCF Energy from NMR – E(RB3LYP)	−542.552 80 E_h
Sum of Electronic and Thermal Free Energies	−541.937 46 E_h

Table S9b – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 9b

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	0.912188	-0.061797	-0.327385	94.1342	89.4734
2	C	-2.131115	-0.600844	0.318150	146.4012	37.2064
3	C	-1.005620	-1.638471	0.322171	140.7964	42.8112
4	C	0.383146	-1.097326	0.661880	152.0900	31.5176
5	H	-2.208921	-0.163231	1.323355	30.1210	1.7439
6	H	-1.263758	-2.427953	1.037274	29.9534	1.9115
7	H	-0.970553	-2.112397	-0.670166	30.6839	1.1810
8	H	0.387609	-0.649688	1.663526	30.4668	1.3981
9	H	1.085307	-1.937640	0.688250	30.0265	1.8384
10	C	-0.896596	1.578934	-0.168467	-1.7396	185.3472
11	O	-1.239999	2.704436	0.134805	---	---
12	O	0.393953	1.255228	-0.013802	---	---
13	H	0.599998	-0.317206	-1.348802	27.6042	4.2607
14	C	2.436134	0.103970	-0.324505	144.4800	39.1276
15	H	2.634885	0.984455	-0.948679	29.8770	1.9879
16	C	3.120669	-1.099328	-0.974840	162.9034	20.7042
17	H	4.194553	-0.913015	-1.065693	30.7923	1.0726
18	H	2.994604	-2.006518	-0.374247	31.1739	0.6910
19	H	2.724585	-1.294227	-1.976839	30.9414	0.9235
20	C	2.992732	0.370088	1.075088	167.5501	16.0575
21	H	4.056979	0.616006	1.014613	31.0858	0.7791
22	H	2.475673	1.204588	1.557071	30.5366	1.3283
23	H	2.891890	-0.515124	1.712769	31.2633	0.6016
24	C	-1.869538	0.544627	-0.683086	137.1137	46.4939
25	H	-2.796532	1.087884	-0.875273	29.5191	2.3458
26	H	-1.518416	0.129611	-1.635900	29.2486	2.6163
27	C	-3.462795	-1.271282	-0.021568	157.2482	26.3594
28	H	-4.291335	-0.559975	0.039408	30.7420	1.1229
29	H	-3.436064	-1.677141	-1.039735	31.0846	0.7803
30	H	-3.667366	-2.097161	0.666424	30.7994	1.0655

Conformer 9c

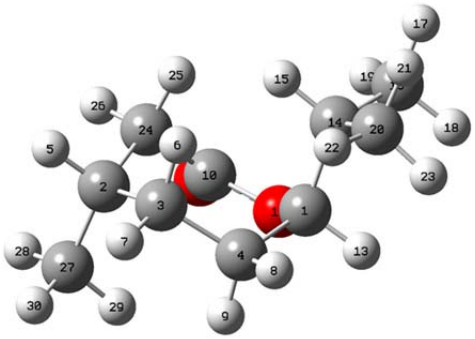


SCF Energy – E(RM062X)	−542.168 63 E_h
SCF Energy from NMR – E(RB3LYP)	−542.552 44 E_h
Sum of Electronic and Thermal Free Energies	−541.937 34 E_h

Table S9c – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 9c

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-0.919386	-0.224788	0.017890	91.8084	91.7992
2	C	2.227146	-0.493680	-0.160400	146.5522	37.0554
3	C	1.213257	-1.638636	-0.223456	140.7742	42.8334
4	C	-0.160514	-1.276542	-0.788993	147.3639	36.2437
5	H	2.408496	-0.127801	-1.180893	30.1030	1.7619
6	H	1.641222	-2.448502	-0.825322	29.9760	1.8889
7	H	1.083126	-2.038757	0.793167	30.6243	1.2406
8	H	-0.072922	-0.905656	-1.818372	30.4555	1.4094
9	H	-0.761728	-2.188517	-0.832854	29.6701	2.1948
10	C	0.743543	1.571859	-0.051946	-1.7224	185.3300
11	O	1.023186	2.697939	-0.413321	---	---
12	O	-0.470841	1.099578	-0.360664	---	---
13	H	-0.741064	-0.355337	1.095608	28.0945	3.7704
14	C	-2.434500	-0.229269	-0.216889	144.6951	38.9125
15	H	-2.599242	-0.181926	-1.302631	30.1780	1.6869
16	C	-3.098073	0.984122	0.439856	162.0719	21.5357
17	H	-4.181971	0.940724	0.298557	31.0121	0.8528
18	H	-2.900019	0.985800	1.519044	31.3781	0.4868
19	H	-2.732381	1.924006	0.023525	30.1759	1.6890
20	C	-3.064276	-1.513895	0.330511	162.1505	21.4571
21	H	-4.148616	-1.481806	0.192682	30.8441	1.0208
22	H	-2.696234	-2.416858	-0.161839	30.7016	1.1633
23	H	-2.868027	-1.605871	1.405569	31.3125	0.5524
24	C	1.719895	0.690796	0.689521	137.3621	46.2455
25	H	2.554339	1.340706	0.958774	29.5363	2.3286
26	H	1.271456	0.314742	1.617048	29.2578	2.6071
27	C	3.551378	-0.995882	0.416001	157.3501	26.2575
28	H	4.312639	-0.210707	0.402047	30.7383	1.1266
29	H	3.415485	-1.320798	1.454319	31.0892	0.7757
30	H	3.925853	-1.848088	-0.159117	30.8033	1.0616

Conformer 9d



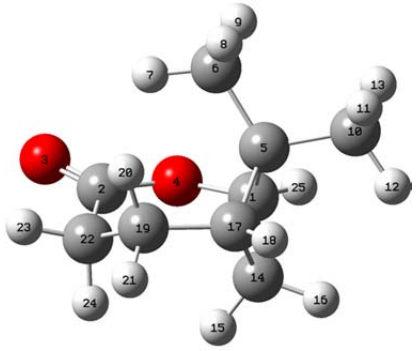
SCF Energy – E(RM062X)	−542.165 25 E_h
SCF Energy from NMR – E(RB3LYP)	−542.545 41 E_h
Sum of Electronic and Thermal Free Energies	−541.932 25 E_h

Table S9d – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 9d

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	0.914812	-0.107380	-0.807131	92.4804	91.1272
2	C	-1.790772	-0.906698	0.726880	150.2969	33.3107
3	C	-0.657947	-1.849009	0.303046	150.2422	33.3654
4	C	0.120140	-1.405495	-0.935389	155.7061	27.9015
5	H	-2.228730	-1.331565	1.638190	29.8767	1.9882
6	H	0.033459	-1.977971	1.146135	29.7748	2.0901
7	H	-1.089295	-2.837122	0.103890	30.2842	1.5807
8	H	0.831546	-2.191170	-1.210409	29.9755	1.8894
9	H	-0.553263	-1.296555	-1.792985	29.7094	2.1555
10	C	-0.916408	1.395728	-0.027461	-1.6231	185.2307
11	O	-1.498475	2.443718	-0.229524	---	---
12	O	0.059675	1.064481	-0.884947	---	---
13	H	1.497840	0.006078	-1.728375	28.0662	3.7987
14	C	1.916637	-0.023462	0.352758	149.9747	33.6329
15	H	1.399149	-0.162025	1.307604	29.3594	2.5055
16	C	2.607986	1.341342	0.369413	162.4368	21.1708
17	H	3.348511	1.379827	1.173502	30.9903	0.8746
18	H	3.127064	1.517541	-0.580189	31.1966	0.6683
19	H	1.896591	2.157566	0.519540	30.4991	1.3658
20	C	2.946422	-1.149547	0.219027	162.2537	21.3539
21	H	3.720923	-1.040074	0.983316	30.8883	0.9766
22	H	2.493774	-2.137853	0.339033	30.7528	1.1121
23	H	3.434568	-1.112360	-0.762339	31.3458	0.5191
24	C	-1.288917	0.491994	1.130641	135.4092	48.1984
25	H	-0.440489	0.410019	1.816587	28.8990	2.9659
26	H	-2.083654	1.025636	1.655533	29.2401	2.6248
27	C	-2.902925	-0.808473	-0.320327	164.9915	18.6161
28	H	-3.731821	-0.199204	0.052846	30.7889	1.0760
29	H	-2.550275	-0.347797	-1.249714	30.7105	1.1544
30	H	-3.289654	-1.802560	-0.565148	31.0496	0.8153

Normal Nopinone derived Lactone (10)

Conformer 10a

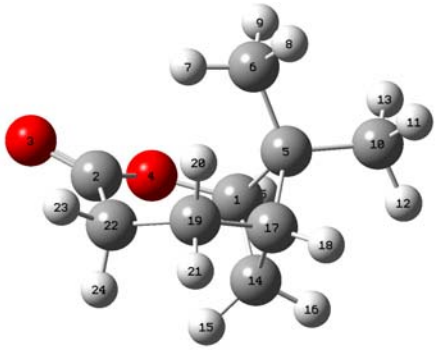


SCF Energy – E(RM062X)	−501.635 90 E_h
SCF Energy from NMR – E(RB3LYP)	−501.975 41 E_h
Sum of Electronic and Thermal Free Energies	−501.450 49 E_h

Table S10a – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 10a

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-0.496124	-0.504913	-1.081236	95.0974	88.5102
2	C	1.788127	-0.396856	-0.136537	-2.5374	186.1450
3	O	2.790865	-1.042224	0.093129	---	---
4	O	0.849500	-0.978317	-0.905720	---	---
5	C	-1.272166	-0.314349	0.246733	135.0936	48.5140
6	C	-0.819271	-1.116860	1.458847	163.3260	20.2816
7	H	0.244906	-1.012551	1.686374	30.8750	0.9899
8	H	-1.377132	-0.795292	2.345238	31.1767	0.6882
9	H	-1.018803	-2.181480	1.298483	31.1015	0.7634
10	C	-2.766945	-0.538718	0.013080	154.7181	28.8895
11	H	-3.334684	-0.202034	0.886681	30.7964	1.0685
12	H	-3.135027	0.010159	-0.858991	30.3526	1.5123
13	H	-2.974386	-1.602830	-0.141956	30.7759	1.0890
14	C	-0.657250	1.000486	-1.360635	155.4110	28.1966
15	H	0.184164	1.517625	-1.826136	29.6821	2.1828
16	H	-1.548068	1.179417	-1.964973	29.2984	2.5665
17	C	-0.911611	1.204279	0.155756	138.2349	45.3727
18	H	-1.727461	1.882399	0.427964	29.7029	2.1620
19	C	0.358244	1.584108	0.914107	156.4086	27.1990
20	H	0.272429	1.262211	1.957403	29.8890	1.9759
21	H	0.451605	2.674739	0.933372	30.0725	1.7924
22	C	1.667878	1.050420	0.311001	144.5429	39.0647
23	H	2.486187	1.197637	1.017279	29.1063	2.7586
24	H	1.922250	1.634877	-0.580960	28.8373	3.0276
25	H	-0.914188	-1.206124	-1.805746	27.5547	4.3102

Conformer 10b



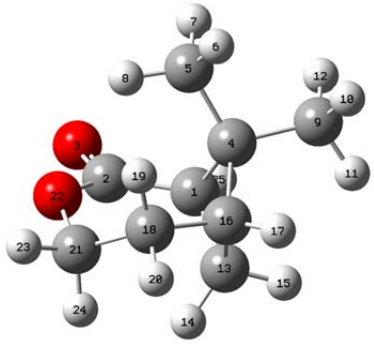
SCF Energy – E(RM062X)	−501.635 90 E_h
SCF Energy from NMR – E(RB3LYP)	−501.975 41 E_h
Sum of Electronic and Thermal Free Energies	−501.450 49 E_h

Table S10b – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 10b

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-0.496124	-0.504913	-1.081236	95.0973	88.5103
2	C	1.788127	-0.396856	-0.136537	-2.5374	186.1450
3	O	2.790866	-1.042224	0.093129	---	---
4	O	0.849500	-0.978318	-0.905720	---	---
5	C	-1.272166	-0.314349	0.246733	135.0936	48.5140
6	C	-0.819272	-1.116860	1.458847	163.3261	20.2815
7	H	0.244904	-1.012551	1.686375	30.8750	0.9899
8	H	-1.377135	-0.795294	2.345238	31.1767	0.6882
9	H	-1.018803	-2.181481	1.298481	31.1015	0.7634
10	C	-2.766945	-0.538717	0.013079	154.7181	28.8895
11	H	-3.334684	-0.202031	0.886680	30.7964	1.0685
12	H	-3.135027	0.010160	-0.858992	30.3526	1.5123
13	H	-2.974387	-1.602829	-0.141956	30.7759	1.0890
14	C	-0.657250	1.000485	-1.360635	155.4110	28.1966
15	H	0.184164	1.517624	-1.826137	29.6821	2.1828
16	H	-1.548068	1.179416	-1.964973	29.2983	2.5666
17	C	-0.911611	1.204279	0.155756	138.2349	45.3727
18	H	-1.727460	1.882399	0.427963	29.7029	2.1620
19	C	0.358245	1.584108	0.914107	156.4086	27.1990
20	H	0.272429	1.262212	1.957403	29.8890	1.9759
21	H	0.451605	2.674739	0.933372	30.0725	1.7924
22	C	1.667878	1.050420	0.311001	144.5429	39.0647
23	H	2.486187	1.197636	1.017280	29.1063	2.7586
24	H	1.922250	1.634878	-0.580960	28.8373	3.0276
25	H	-0.914188	-1.206124	-1.805745	27.5547	4.3102

Abnormal Nopinone derived Lactone (11)

Conformer 11a

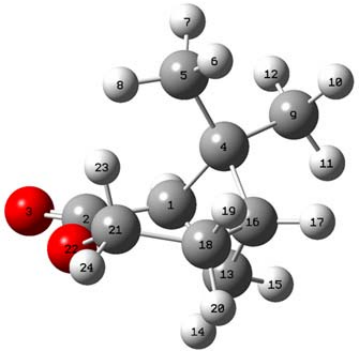


SCF Energy – E(RM062X)	−501.634 25 E_h
SCF Energy from NMR – E(RB3LYP)	−501.973 76 E_h
Sum of Electronic and Thermal Free Energies	−501.448 04 E_h

Table S11a – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 11a

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-0.221474	-0.743948	-0.832199	125.6433	57.9643
2	C	1.121626	-1.077428	-0.229616	-1.6233	185.2309
3	O	1.515809	-2.224881	-0.161389	---	---
4	C	-1.197509	-0.151801	0.248351	137.6390	45.9686
5	C	-0.963053	-0.501796	1.712993	161.4246	22.1830
6	H	-1.616750	0.105944	2.349030	31.1786	0.6863
7	H	-1.207787	-1.555048	1.887448	31.0260	0.8389
8	H	0.067568	-0.338892	2.036879	30.4130	1.4519
9	C	-2.644295	-0.483637	-0.119002	153.6197	29.9879
10	H	-3.327339	0.096546	0.511075	30.8395	1.0254
11	H	-2.871865	-0.253614	-1.163694	30.0830	1.7819
12	H	-2.844953	-1.547002	0.047417	30.7275	1.1374
13	C	-0.367332	0.593557	-1.600395	161.6493	21.9583
14	H	0.500771	0.989021	-2.129518	29.5067	2.3582
15	H	-1.190187	0.516776	-2.311695	29.4810	2.3839
16	C	-0.799969	1.263711	-0.274050	138.1865	45.4211
17	H	-1.629536	1.977010	-0.328554	29.7054	2.1595
18	C	0.381900	1.896242	0.465169	151.6682	31.9394
19	H	0.201319	1.889868	1.545296	29.3414	2.5235
20	H	0.468628	2.948382	0.168461	30.1174	1.7475
21	C	1.743199	1.286406	0.153913	113.1358	70.4718
22	O	1.877878	-0.135170	0.365187	---	---
23	H	2.496457	1.710084	0.818854	27.6139	4.2510
24	H	2.047227	1.502159	-0.872941	27.0235	4.8414
25	H	-0.561607	-1.648655	-1.339428	28.9960	2.8689

Conformer 11b



SCF Energy – E(RM062X)	−501.626 89 E_h
SCF Energy from NMR – E(RB3LYP)	−501.967 20 E_h
Sum of Electronic and Thermal Free Energies	−501.441 87 E_h

Table S11b – Cartesian Coordinates, Isotropic Shielding Tensors and Scaled NMR Shifts for Conformer 11b

Center #	Atom Type	Cartesian Coordinates X	Y	Z	NMR Shielding Tensor	Scaled NMR Shifts
1	C	-0.147254	-0.997579	-0.550244	123.6353	59.9723
2	C	1.282459	-0.982149	-0.067140	-6.1618	189.7694
3	O	1.919221	-2.003805	0.088049	---	---
4	C	-1.187994	-0.194094	0.294482	138.8110	44.7966
5	C	-1.007619	-0.106376	1.812176	157.2783	26.3293
6	H	-1.385801	0.850762	2.189376	30.5464	1.3185
7	H	-1.573544	-0.903654	2.304005	30.7893	1.0756
8	H	0.030363	-0.214237	2.133601	30.6301	1.2348
9	C	-2.596533	-0.722257	0.003887	150.8277	32.7799
10	H	-3.336518	-0.063513	0.472054	30.6540	1.2109
11	H	-2.813317	-0.765092	-1.067203	30.2082	1.6567
12	H	-2.720547	-1.726937	0.420586	30.8059	1.0590
13	C	-0.357440	0.034355	-1.688248	150.3092	33.2984
14	H	0.534214	0.343615	-2.239772	30.2567	1.6082
15	H	-1.117065	-0.302667	-2.394184	29.3695	2.4954
16	C	-0.898746	1.029290	-0.633852	136.6651	46.9425
17	H	-1.791219	1.593936	-0.925981	29.6819	2.1830
18	C	0.184456	2.010738	-0.194041	148.2542	35.3534
19	H	-0.238031	2.764441	0.481178	29.7772	2.0877
20	H	0.526502	2.544730	-1.088003	29.5372	2.3277
21	C	1.388243	1.431579	0.546541	110.5938	73.0138
22	O	1.946635	0.187883	0.067953	---	---
23	H	1.169954	1.302992	1.607088	27.0351	4.8298
24	H	2.227562	2.123308	0.468558	27.4667	4.3982
25	H	-0.396838	-2.041356	-0.750681	28.8261	3.0388