SUPPLEMENTARY INFORMATION

Structure-reactivity correlations of the abnormal Beckmann reaction of dihydrolevoglucosenone oxime

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Table S1. Bond distances and angles for oximes 1-8 derived from single crystal X-ray structures.

Distances are in Ångstroms, angles are in degrees. pK_a values are from Ref.{Dean, 1999 #7949} Except for 4-bromobenzyl alcohol, for which the pK_a value was predicted using the Advanced Chemistry Development (ACD/Labs) Software V11.02.

pK_a value	N-O	C1-C2	C2-C3	C1-O1	C1-O5	N-C2	C1-C2-N	C2-N-O	O1-C1-O5	C3-C2-N	O1-C1-C2	O5-C1-C2
16	1.405(1)	1.503(2)	1.500(1)	1.416(2)	1.425(1)	1.278(1)	116.4(4)	112.69(9)	105.39(9)	127.9(1)	108.31(9)	109.98(9)
	1.408(1)	1.505(2)	1.500(2)	1.409(1)	1.428(1)	1.280(1)	115.8(1)	112.27(9)	105.45(9)	127.1(1)	109.33(9)	109.11(9)
14.2	1.417(5)	1.505(5)	1.504(6)	1.405(5)	1.420(5)	1.278(5)	115.5(3)	111.5(3)	105.8(3)	128.7(4)	110.1(3)	109.3(3)
	1.410(5)	1.502(5)	1.499(6)	1.415(5)	1.425(5)	1.276(5)	115.5(3)	112.1(3)	105.9(3)	130.0(4)	107.7(3)	110.3(3)
9.9	1.426(2)	1.505(2)	1.449(2)	1.403(2)	1.425(2)	1.276(2)	114.3(1)	110.5(1)	106.0(1)	129.1(1)	109.2(1)	109.0(1)
7.15	1.437(2)	1.513(3)	1.500(3)	1.405(2)	1.425(2)	1.273(2)	115.5(2)	109.7(1)	106.2(1)	129.0(2)	109.0(2)	108.1(2)
4.75	1.441(1)	1.515(2)	1.499(2)	1.403(2)	1.423(2)	1.276(2)	114.4(1)	109.4(1)	106.1(1)	129.9(1)	110.0(1)	107.6(1)
3.46	1.442(1)	1.515(1)	1.501(1)	1.406(1)	1.421(1)	1.275(2)	114.61(9)	109.30(8)	105.94(8)	130,4(1)	107.38(8)	110.03

3.44	1.445(3)	1.516(5)	1.499(5)	1.405(4)	1.411(4)	1.275(4)	114.0(3)	109.1(2)	106.2(3)	129.4(3)	109.3(3)	108.4(3)
	1.444(5)	1.509(5)	1.505((5)	1.413(4)	1.425(4)	1.271(4)	114.7(3)	108.8(3)	105.6(3)	130.7(3)	107.2(3)	110.1(3)
	1.448(4)	1.512(5)	1.498(5)	1.406(5)	1.420(4)	1.276(4)	115.9(3)	108.1(2)	105.8(3)	129.1(3)	108.7(3)	108.7(3)
	1.447(4)	1.510(5)	1.498(5)	1.412(4)	1.419(4)	1.272(5)	115.0(3)	108.0(3)	105.9(3)	130.6(3)	107.7(3)	109.9(3)
2.85	1.445(3)	1.516(5)	1.499(5)	1.405(4)	1.411(4)	1.278(3)	115.1(2)	108.3(2)	106.2(2)	128.9(2)	109.0(2)	108.1(2)

Table S2. Natural atomic charges for oximes at PW6B95/def2-TZVP level of theory.

		Cyrene oximes				Cyclohexanone oximes	
R	pK_a	C1	O5	O6	C2	C1	C-anti
H	16	0.30583	-0.48453	-0.49869	0.17671	0.22821	-0.43697
C_6H_5	9.9	0.30544	-0.48230	-0.49703	0.20595	0.25918	-0.43845
CH_3CO	4.75	0.30460	-0.48048	-0.49566	0.21098	0.27141	-0.44008
3-$NO_2C_6H_4CO$	3.46	0.30443	-0.47820	-0.49448	0.21763	0.27124	-0.43989
3,5-$(NO_2)_2C_6H_3CO$	2.85	0.30461	-0.47741	-0.49314	0.22550	0.28207	-0.44088
CF_3CO	0.50	0.30450	-0.47660	-0.49214	0.23163	0.28227	-0.44089

Table S3. Donor-acceptor stabilization energies ($E(2)$) for $\sigma_{C1\text{-}C2} \rightarrow \sigma^*_{N\text{-}O}$ interactions in Cyrene and cyclohexanone oximes at the revPBE/def2-TZVP level of theory.

Calculations at this level of theory were only performed on a subset of structurally simple oximes.

		Cyrene oximes		
R	pK_a	$E(2)$ (kcal mol^{-1})	ΔE_{ij} (au)	q_i
H	16	4.81	0.46	1.96979
CH_3CO	4.75	5.42	0.44	1.96598
CF_3CO	0.50	5.96	0.42	1.96096

Table S4. Donor-acceptor stabilization energies ($E(2)$) for $n_{O5} \rightarrow \sigma^*_{C1\text{-}C2}$ and $n_{O6} \rightarrow \sigma^*_{C1\text{-}C2}$ interactions for Cyrene oximes at the revPBE/def2-TZVP level of theory.

Calculations at this level of theory were only performed on a subset of structurally simple oximes.

		LP O5			LP O6		
R	pK_a	$E(2)$ (kcal mol^{-1})	ΔE_{ij} (au)	q_i	$E(2)$ (kcal mol^{-1})	ΔE_{ij} (au)	q_i
H	16	1.76	0.66	1.88928	1.79	0.65	1.89863
CH_3CO	4.75	1.85	0.65	1.88648	1.85	0.64	1.89639
CF_3CO	0.50	1.95	0.64	1.88361	1.95	0.64	1.89368

Table S5. Donor-acceptor stabilization energies ($E(2)$) for $\sigma_{C1\text{-}C2} \rightarrow \sigma^*_{N\text{-}O}$ interactions in Cyrene and cyclohexanone oximes at the TPSS/def2-TZVP level of theory.

		Cyrene oximes			Cyclohexanone oximes		
R	pK_a	$E(2)$ (kcal mol^{-1})	ΔE_{ij} (au)	q_i	$E(2)$ (kcal mol^{-1})	ΔE_{ij} (au)	q_i
H	16	4.84	0.49	1.97051	4.80	0.47	1.96761
C_6H_5	9.9	5.13	0.49	1.96884	5.12	0.46	1.96591
CH_3CO	4.75	5.46	0.47	1.96671	5.36	0.45	1.96436
3-$NO_2C_6H_4CO$	3.46	5.51	0.47	1.96350	5.42	0.45	1.96400
3,5-$(NO_2)_2C_6H_3CO$	2.85	5.69	0.46	1.96364	5.58	0.44	1.96252
CF_3CO	0.50	6.01	0.44	1.96171	5.90	0.42	1.95950

Table S6. Donor-acceptor stabilization energies ($E(2)$) for $n_{O5} \rightarrow \sigma^*_{C1\text{-}C2}$ and $n_{O6} \rightarrow \sigma^*_{C1\text{-}C2}$ interactions for Cyrene oximes at the TPSS/def2-TZVP level of theory.

		LP O5			LP O6		
R	pK_a	$E(2)$ (kcal mol^{-1})	ΔE_{ij} (au)	q_i	$E(2)$ (kcal mol^{-1})	ΔE_{ij} (au)	q_i
H	16	1.81	0.70	1.89305	1.85	0.69	1.90177
C_6H_5	9.9	1.86	0.70	1.89160	1.85	0.69	1.90050
CH_3CO	4.75	1.91	0.69	1.89036	1.92	0.69	1.89964
3-$NO_2C_6H_4CO$	3.46	1.97	0.69	1.88918	1.94	0.68	1.89829
3,5-$(NO_2)_2C_6H_3CO$	2.85	2.02	0.69	1.8820	1.98	0.68	1.89721
CF_3CO	0.50	2.02	0.69	1.88752	2.02	0.68	1.89698

Table S7. Donor-acceptor stabilization energies ($E(2)$) for $\sigma_{C1\text{-}C2} \rightarrow \sigma^*_{N\text{-}O}$ interactions in Cyrene and cyclohexanone oximes at the B3LYP/def2-TZVP level of theory.

Calculations at this level of theory were only performed on a subset of structurally simple oximes.

		Cyrene oximes		
R	pK_a	$E(2)$ (kcal mol^{-1})	ΔE_{ij} (au)	q_i
H	16	5.23	0.60	1.97314
CH_3CO	4.75	5.94	0.58	1.96958
CF_3CO	0.50	6.62	0.55	1.96512

Table S8. Donor-acceptor stabilization energies ($E(2)$) for $n_{O5} \rightarrow \sigma^*_{C1\text{-}C2}$ and $n_{O6} \rightarrow \sigma^*_{C1\text{-}C2}$ interactions for Cyrene oximes at the B3LYP/def2-TZVP level of theory.

Calculations at this level of theory were only performed on a subset of structurally simple oximes.

		LP O5			LP O6		
R	pK_a	$E(2)$ (kcal mol^{-1})	ΔE_{ij} (au)	q_i	$E(2)$ (kcal mol^{-1})	ΔE_{ij} (au)	q_i
H	16	2.77	0.73	1.90473	2.91	0.73	1.91281
CH_3CO	4.75	2.90	0.73	1.90272	2.90	0.72	1.91135
CF_3CO	0.50	3.06	0.72	1.90046	3.15	0.71	1.90928

Table S9. Donor-acceptor stabilization energies ($E(2)$) for $\sigma_{C1\text{-}C2} \rightarrow \sigma^*_{N\text{-}O}$ interactions in Cyrene and cyclohexanone oximes at the PBE0/def2-TZVP level of theory.

Calculations at this level of theory were only performed on a subset of structurally simple oximes.

		Cyrene oximes		
R	pK_a	$E(2)$ (kcal mol^{-1})	ΔE_{ij} (au)	q_i
H	16	5.79	0.65	1.97346
CH_3CO	4.75	6.58	0.63	1.96981
CF_3CO	0.50	7.34	0.60	1.96540

Table S10. Donor-acceptor stabilization energies ($E(2)$) for $n_{O5} \rightarrow \sigma^*_{C1\text{-}C2}$ and $n_{O6} \rightarrow \sigma^*_{C1\text{-}C2}$ interactions for Cyrene oximes at the PBE0/def2-TZVP level of theory.

Calculations at this level of theory were only performed on a subset of structurally simple oximes.

		LP O5			LP O6		
R	pK_a	$E(2)$ (kcal mol^{-1})	ΔE_{ij} (au)	q_i	$E(2)$ (kcal mol^{-1})	ΔE_{ij} (au)	q_i
H	16	3.40	0.75	1.90483	3.59	0.75	1.91286
CH_3CO	4.75	3.55	0.75	1.90287	3.70	0.74	1.91140
CF_3CO	0.50	3.72	0.74	1.90068	3.87	0.73	1.90939

Table S11. NBO hybrid orbitals for the $\sigma_{C1\text{-}C2}$ bond.

R	pK_a	bond	atom	h_A	C_A	%s	%p	%d
H	16	σC1-C2	C1	$sp^{2.49}d^{0.01}$	0.7043	28.64	71.20	0.15
			C2	$sp^{2.38}$	0.7099	29.54	70.32	0.10
C_6H_5	9.9	σC1-C2	C1	$sp^{2.51}d^{0.01}$	0.7037	28.46	71.38	0.15
			C2	$sp^{2.41}$	0.7105	29.27	70.59	0.10
CH_3CO	4.75	σC1-C2	C1	$sp^{2.54}d^{0.01}$	0.7029	28.20	71.63	0.15
			C2	$sp^{2.44}$	0.7113	29.06	70.80	0.10
3-$NO_2C_6H_4CO$	3.46	σC1-C2	C1	$sp^{2.57}d^{0.01}$	0.7018	27.97	71.87	0.15
			C2	$sp^{2.43}$	0.7123	29.09	70.77	0.10
3,5-$(NO_2)_2C_6H_3CO$	2.85	σC1-C2	C1	$sp^{2.60}d^{0.01}$	0.7010	27.77	72.06	0.15
			C2	$sp^{2.44}$	0.7131	29.02	70.84	0.10
CF_3CO	0.50	σC1-C2	C1	$sp^{2.61}d^{0.01}$	0.7007	27.64	72.19	0.15
			C2	$sp^{2.46}$	0.7134	28.85	71.02	0.10

h_A: natural atomic hybrids; C_A: polarization coefficient.

Table S12. NBO hybrid orbitals for the $\sigma_{C2\text{-}N}$ and $\pi_{C2\text{-}N}$ bonds.

R	pK_a	bond	atom	h_A	C_A	%s	%p	%d
H	16	σC2-N	C2	$sp^{1.84}$	0.6486	35.23	64.65	0.07
			N	$sp^{1.47}d^{0.01}$	0.7611	40.36	59.13	0.49
		πC2-N	C2					
			N	$sp^{1.00}$	0.6561	0.00	99.85	0.10
				$sp^{1.00}$	0.7547	0.00	99.69	0.29
C_6H_5	9.9	σC2-N	C2	$sp^{1.82}$	0.6467	35.45	64.43	0.07
			N	$sp^{1.48}d^{0.01}$	0.7627	40.19	59.30	0.50
		πC2-N	C2	$sp^{1.00}$	0.6478	0.00	99.85	0.11
			N	$sp^{1.00}$	0.7618	0.00	99.68	0.30
CH_3CO	4.75	σC2-N	C2	$sp^{1.81}$	0.6490	35.51	64.37	0.08
			N	$sp^{1.52}d^{0.01}$	0.7608	39.45	60.01	0.52
		πC2-N	C2	$sp^{1.00}$	0.6466	0.00	99.84	0.11
			N	$sp^{1.00}$	0.7628	0.00	99.65	0.33
3-$NO_2C_6H_4CO$	3.46	σC2-N	C2	$sp^{1.82}$	0.6487	35.44	64.44	0.08
			N	$sp^{1.52}d^{0.01}$	0.7611	39.44	60.01	0.53
		πC2-N	C2	$sp^{1.00}$	0.6433	0.00	99.84	0.12
			N	$sp^{1.00}$	0.7656	0.00	99.64	0.34
3,5-$(NO_2)_2C_6H_3CO$	2.85	σC2-N	C2	$sp^{1.83}$	0.6482	35.35	64.52	0.08
			N	$sp^{1.52}d^{0.01}$	0.7615	39.52	59.94	0.53
		πC2-N	C2	$sp^{1.00}$	0.6389	0.00	99.83	0.12
			N	$sp^{1.00}$	0.7693	0.00	99.64	0.34
CF_3CO	0.5	σC2-N	C2	$sp^{1.83}$	0.6481	35.31	64.57	0.08
			N	$sp^{1.50}d^{0.01}$	0.7616	39.71	59.75	0.53
		πC2-N	C2	$sp^{1.00}$	0.6351	0.00	99.83	0.13
			N	$sp^{1.00}$	0.7724	0.00	99.64	0.34

h_A: natural atomic hybrids; C_A: polarization coefficient.

Table S13. NBO hybrid orbitals for the $\sigma_{C1\text{-}O5}$ bond.

R	pK_a	bond	atom	h_A	C_A	%s	%p	%d
H	16	σ C1-O5	C1	$sp^{3.52}d^{0.01}$	0.5918	22.10	77.77	0.12
			O5	$sp^{3.24}d^{0.01}$	0.8061	23.52	76.13	0.34
C_6H_5	9.9	σ C1-O5	C1	$sp^{3.51}d^{0.01}$	0.5924	22.17	77.70	0.12
			O5	$sp^{3.23}d^{0.01}$	0.8056	23.56	76.09	0.35
CH_3CO	4.75	σ C1-O5	C1	$sp^{3.50}d^{0.01}$	0.5924	22.21	77.65	0.12
			O5	$sp^{3.21}d^{0.01}$	0.8056	23.65	76.00	0.35
3-$NO_2C_6H_4CO$	3.46	σ C1-O5	C1	$sp^{3.47}d^{0.01}$	0.5931	22.32	77.55	0.12
			O5	$sp^{3.21}d^{0.01}$	0.8051	23.67	75.97	0.35
3,5-$(NO_2)_2C_6H_3CO$	2.85	σ C1-O5	C1	$sp^{3.46}d^{0.01}$	0.5936	22.39	77.48	0.12
			O5	$sp^{3.20}d^{0.01}$	0.8048	23.71	75.93	0.35
CF_3CO	0.5	σ C1-O5	C1	$sp^{3.46}d^{0.01}$	0.5938	22.40	77.47	0.12
			O5	$sp^{3.21}d^{0.01}$	0.8046	23.68	75.97	0.35

h_A: natural atomic hybrids; C_A: polarization coefficient.

Table S14. NBO hybrid orbitals for the $\sigma_{C1\text{-}O6}$ bond.

R	pK_a	bond	atom	h_A	C_A	%s	%p	%d
H	16	σ C1-O6	C1	$sp^{3.54}d^{0.01}$	0.5905	22.00	77.88	0.11
			O6	$sp^{3.11}d^{0.01}$	0.8071	24.26	75.42	0.30
C_6H_5	9.9	σ C1-O6	C1	$sp^{3.53}d^{0.01}$	0.5911	22.07	77.81	0.11
			O6	$sp^{3.10}d^{0.01}$	0.8066	24.30	75.39	0.31
CH_3CO	4.75	σ C1-O6	C1	$sp^{3.52}d^{0.01}$	0.5911	22.10	77.78	0.11
			O6	$sp^{3.10}d^{0.01}$	0.8066	24.32	75.36	0.31
3-$NO_2C_6H_4CO$	3.46	σ C1-O6	C1	$sp^{3.51}d^{0.01}$	0.5917	22.16	77.72	0.11
			O6	$sp^{3.10}d^{0.01}$	0.8062	24.32	75.36	0.31
3,5-$(NO_2)_2C_6H_3CO$	2.85	σ C1-O6	C1	$sp^{3.49}d^{0.01}$	0.5924	22.27	77.61	0.11
			O6	$sp^{3.09}d^{0.01}$	0.8057	24.39	75.30	0.31
CF_3CO	0.5	σ C1-O6	C1	$sp^{3.47}d^{0.01}$	0.5927	22.36	77.52	0.11
			O6	$sp^{3.08}d^{0.01}$	0.8055	24.44	75.24	0.31

h_A: natural atomic hybrids; C_A: polarization coefficient.

Table S15. NBO hybrid orbitals for the $\sigma_{N\text{-}O}$ bonds.

R	pK_a	bond	atom	h_A	C_A	%s	%p	%d
H	16	σ N-O	N	$sp^{5.75}d^{0.01}$	0.6392	14.77	84.99	0.22
			O	$sp^{4.38}d^{0.01}$	0.7690	18.54	81.20	0.25
C_6H_5	9.9	σ N-O	N	$sp^{5.85}d^{0.01}$	0.6310	14.58	85.21	0.20
			O	$sp^{4.28}d^{0.01}$	0.7758	18.90	80.92	0.16
CH_3CO	4.75	σ N-O	N	$sp^{6.48}d^{0.02}$	0.6226	13.35	86.43	0.21
			O	$sp^{4.33}d^{0.01}$	0.7826	18.72	81.11	0.16
3-$NO_2C_6H_4CO$	3.46	σ N-O	N	$sp^{6.72}d^{0.02}$	0.6167	12.92	86.85	0.21
			O	$sp^{4.25}d^{0.01}$	0.7872	19.02	80.82	0.14
3,5-$(NO_2)_2C_6H_3CO$	2.85	σ N-O	N	$sp^{7.04}d^{0.02}$	0.6122	12.41	87.37	0.21
			O	$sp^{4.26}d^{0.01}$	0.7907	18.97	80.88	0.14
CF_3CO	0.5	σ N-O	N	$sp^{7.56}d^{0.02}$	0.6093	11.65	88.12	0.22
			O	$sp^{4.35}d^{0.01}$	0.7930	18.66	81.18	0.14

h_A: natural atomic hybrids; C_A: polarization coefficient.

Table S16. NBO hybrid orbitals for the $\sigma_{C2\text{-}C3}$ bond.

R	pK_a	bond	atom	h_A	C_A	%s	%p	%d
H	16	σC2-C3	C2	$sp^{1.83}$	0.7050	35.25	64.64	0.05
			C3	$sp^{2.84}d^{0.01}$	0.7092	25.99	73.84	0.15
C_6H_5	9.9	σC2-C3	C2	$sp^{1.83}$	0.7059	35.30	64.60	0.05
			C3	$sp^{2.84}d^{0.01}$	0.7083	26.00	73.84	0.14
CH_3CO	4.75	σC2-C3	C2	$sp^{1.82}$	0.7059	35.44	64.46	0.05
			C3	$sp^{2.85}d^{0.01}$	0.7083	25.96	73.87	0.14
3-$NO_2C_6H_4CO$	3.46	σC2-C3	C2	$sp^{1.81}$	0.7062	35.49	64.41	0.05
			C3	$sp^{2.85}d^{0.01}$	0.7080	25.93	73.91	0.14
3,5-$(NO_2)_2C_6H_3CO$	2.85	σC2-C3	C2	$Sp^{1.80}$	0.7074	35.65	64.25	0.05
			C3	$Sp^{2.86}d^{0.01}$	0.7068	25.86	73.97	0.14
CF_3CO	0.5	σC2-C3	C2	$Sp^{1.78}$	0.7088	35.88	64.01	0.05
			C3	$sp^{2.88}d^{0.01}$	0.7054	25.75	74.08	0.15

h_A: natural atomic hybrids; C_A: polarization coefficient.

Table S17. NBO hybrid orbitals for the N lone pair.

R	pK_a	bond	atom	h_A	%s	%p	%d
H	16	nN	LPN	$sp^{1.22}$	45.03	54.84	0.13
C_6H_5	9.9	nN	LPN	$sp^{1.20}$	45.33	54.55	0.12
CH_3CO	4.75	nN	LPN	$sp^{1.11}$	47.30	52.55	0.15
3-$NO_2C_6H_4CO$	3.46	nN	LPN	$sp^{1.09}$	47.71	2.14	0.15
3,5-$(NO_2)_2C_6H_3CO$	2.85	nN	LPN	$sp^{1.07}$	48.16	51.70	0.14
CF_3CO	0.5	nN	LPN	$sp^{1.05}$	48.72	51.13	0.14

h_A: natural atomic hybrids; C_A: polarization coefficient.

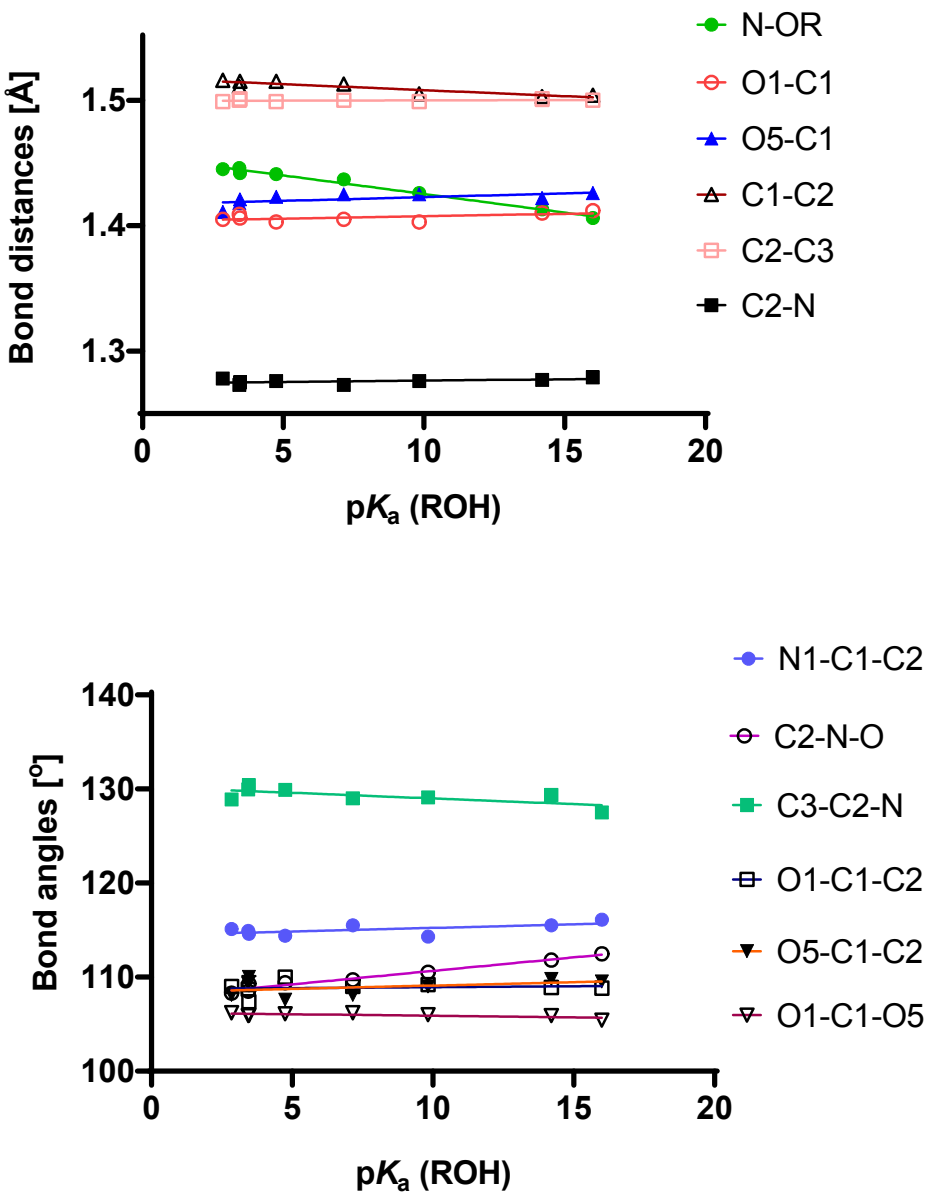


Figure S1. Plots showing variations in a range of geometric parameters for the series of oximes 1-8. (a) Bond distances and (b) angles, as a function of leaving group ability.

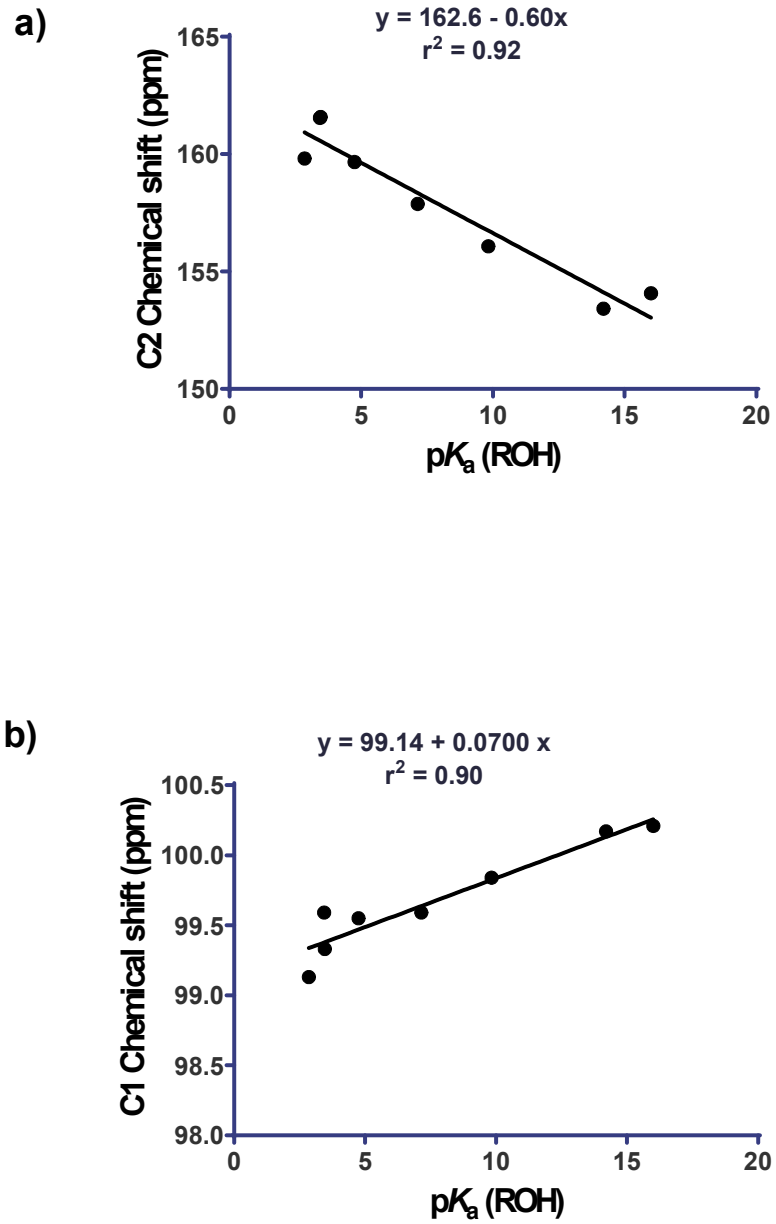


Figure S2. Plots showing variations in (a) C2 chemical shift and (b) C1 chemical shift, as a function of leaving group ability.

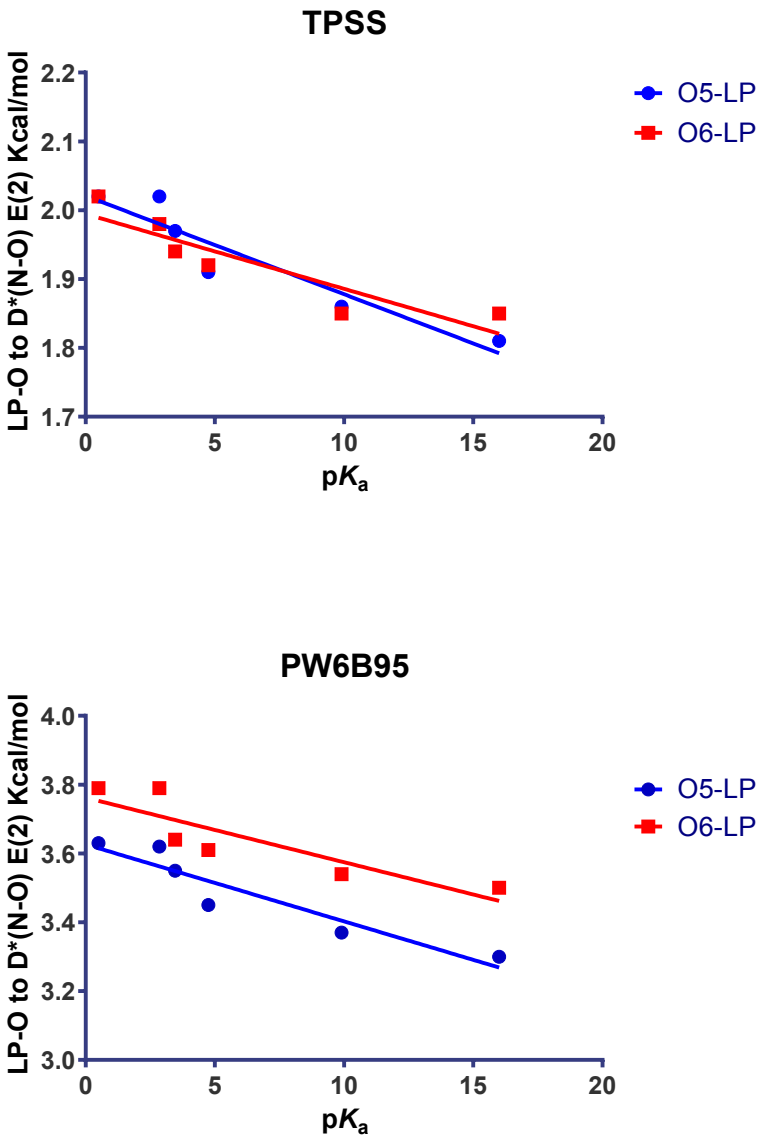


Figure S3. Plots showing comparison of $n_{O5} \rightarrow \sigma^*_{C1\text{-}C2}$ and $n_{O6} \rightarrow \sigma^*_{C1\text{-}C2}$ interactions at the TPSS and PW6B95 levels of theory, as a function of leaving group ability.

Optimized Geometries of Cyrene Oximes

All geometries were optimized at the TPSS-D3(BJ)/def2-TZVP level of theory and are presented in Cartesian coordinates (Å).

(Z)-Dihydrolevoglucosenone oxime

C	1.530162	5.679199	3.446329
H	2.235403	5.784281	2.744992
C	1.836637	6.527974	4.648167
C	0.856054	6.432445	5.779331
H	0.099521	7.050040	5.614362
H	1.296330	6.704544	6.622884
C	0.325699	4.993938	5.915761
H	0.956936	4.462796	6.461867
H	-0.546092	5.008904	6.384734
C	0.155917	4.334469	4.560138
H	-0.202445	3.405609	4.655977
C	-0.703454	5.155700	3.602139
H	-1.172141	4.569470	2.956145
H	-1.373735	5.690344	4.096758
N	2.899049	7.236322	4.587907
O	1.429960	4.331126	3.867768
O	0.244040	6.011003	2.931270
O	3.095625	8.016953	5.738836
H	3.887288	8.298286	5.640394

Total Energy : -514.60360283 Eh

(*Z*)-Dihydrolevoglucosenone *O*-(phenyl)oxime

C	1.004174	3.706666	14.868272
H	0.368505	4.381750	14.493376
C	2.425367	4.054490	14.514096
C	3.471778	3.037281	14.857789
H	3.855530	3.253708	15.744479
H	4.202416	3.085884	14.191233
C	2.910797	1.603347	14.887453
H	3.004171	1.197331	13.989343
H	3.437893	1.059206	15.524524
C	1.447962	1.580407	15.298503
H	1.090987	0.646446	15.287953
C	1.159441	2.256683	16.638262
H	0.377767	1.842544	17.082789
H	1.941929	2.196383	17.241455
C	4.084515	6.589935	12.904912
C	5.307014	7.232976	13.013529
H	5.956544	6.933690	13.638736
C	5.566386	8.323138	12.191653
H	6.398482	8.777044	12.257559
C	4.617536	8.753561	11.275879
H	4.799709	9.498704	10.715888
C	3.402771	8.093174	11.179529
H	2.755346	8.389517	10.550911
C	3.121983	6.998958	11.995607
H	2.290148	6.544371	11.930057
N	2.565166	5.202205	13.974802

O	0.709228	2.422691	14.386521
O	0.884007	3.630389	16.286093
O	3.941979	5.463539	13.708723

Total Energy : -745.71680526 Eh

(*Z*)-Dihydrolevoglucosenone *O*-(acetyl)oxime

C	3.097172	8.963653	4.490746
H	3.514514	8.831023	3.591853
C	3.402240	7.796792	5.407153
C	2.752979	7.846332	6.757889
H	3.337597	8.340324	7.386244
H	2.642406	6.924663	7.103474
C	1.377340	8.535506	6.690671
H	0.690088	7.870005	6.437157
H	1.144287	8.889029	7.585845
C	1.368268	9.672267	5.685715
H	0.478582	10.129104	5.666146
C	2.496677	10.676868	5.898623
H	2.235839	11.576118	5.576130
H	2.741638	10.737383	6.855929
C	5.520701	5.103902	5.527599
C	5.865462	4.178471	6.648598
H	5.757724	3.251472	6.351054
H	5.270637	4.348883	7.407769
H	6.794840	4.328503	6.921485
N	4.225582	6.948806	4.926054
O	1.709626	9.137514	4.380476
O	3.593559	10.142900	5.114697
O	4.519819	5.949065	5.921617
O	6.033306	5.127418	4.448086

Total Energy : -667.33248082 Eh

(*Z*)-Dihydrolevoglucosenone *O*-(3-nitrobenzoyl)oxime

C	5.182307	13.247564	8.859416
H	5.530629	13.568219	9.841088
C	5.100345	11.740544	8.724775
C	4.651111	11.246734	7.373377
H	3.553126	11.276868	7.368104
H	4.946325	10.206349	7.229857
C	5.203332	12.146394	6.242254
H	6.232712	11.855822	6.008126
H	4.604165	12.013359	5.333939
C	5.215285	13.616120	6.661638
H	5.653718	14.257507	5.894455
C	3.861140	14.123450	7.177771
H	3.758869	15.208085	7.070775
H	3.008299	13.622867	6.706227
C	5.736848	8.855314	10.505592
C	5.410060	7.428824	10.191640
C	5.965128	6.448232	11.018760
H	6.601514	6.725177	11.850779
C	5.683175	5.116905	10.747578
C	4.867972	4.721115	9.690188
H	4.682920	3.666264	9.526101
C	4.314881	5.706864	8.877199
H	3.672369	5.424160	8.049173
C	4.583229	7.052711	9.122741
H	4.147582	7.817438	8.490436
N	5.399559	11.076851	9.777176

N	6.275072	4.068915	11.618004
O	6.041279	13.748981	7.848291
O	3.885064	13.798631	8.587664
O	5.224093	9.662941	9.512795
O	6.362944	9.229877	11.464546
O	6.988011	4.439394	12.551897
O	6.013416	2.893409	11.347164

Total Energy : -1064.99930653 Eh

(*Z*)-Dihydrolevoglucosenone *O*-(3,5-dinitrobenzoyl)oxime

C	5.297132	2.813160	7.687402
H	5.868419	2.365627	8.500629
C	3.963867	3.376720	8.141265
C	3.121459	3.977912	7.045847
H	3.471029	5.009397	6.904054
H	2.075640	4.032874	7.350133
C	3.276407	3.186657	5.725522
H	2.620569	2.309977	5.740626
H	2.974420	3.814329	4.879341
C	4.711606	2.696053	5.539757
H	4.822425	2.084157	4.642464
C	5.765959	3.805697	5.654526
H	6.690839	3.552319	5.127023
H	5.401123	4.781294	5.315971
C	2.032857	3.736253	10.976759
C	0.726612	4.451756	11.164990
C	0.159438	5.254189	10.169243
H	0.645254	5.400927	9.214155
C	-1.055155	5.880283	10.421738
C	-1.736051	5.743772	11.624022
H	-2.682489	6.238291	11.801341
C	-1.142516	4.939547	12.589094
C	0.071196	4.293560	12.390341
H	0.504641	3.675638	13.168158
N	3.734388	3.293386	9.397431
N	-1.653540	6.729868	9.356981

N	-1.846298	4.764927	13.889827
O	5.059489	1.853938	6.671695
O	6.046884	3.869385	7.073469
O	2.443985	3.905539	9.680555
O	2.600416	3.111424	11.836305
O	-1.037736	6.815671	8.292129
O	-2.721774	7.285860	9.611423
O	-2.919691	5.352383	14.031061
O	-1.305681	4.045691	14.729602

Total Energy : -1269.81293791 Eh

(*Z*)-Dihydrolevoglucosenone *O*-(trifluoroacetyl)oxime

C	3.137552	9.007999	4.501389
H	3.578735	8.948622	3.506633
C	3.516250	7.832886	5.384364
C	2.912945	7.849123	6.764219
H	3.553058	8.495013	7.380109
H	2.938009	6.854199	7.209804
C	1.475146	8.419911	6.730432
H	0.772072	7.634614	6.434336
H	1.188946	8.764311	7.730791
C	1.357353	9.561979	5.721447
H	0.334749	9.935787	5.642474
C	2.398158	10.673448	5.918266
H	2.064623	11.629860	5.503759
H	2.693265	10.805004	6.964709
C	5.444853	4.995340	5.316115
C	5.647896	3.891018	6.395859
N	4.313913	6.993553	4.843021
O	1.724528	9.057200	4.409015
O	3.540821	10.215935	5.155669
O	4.587615	5.920261	5.805258
O	5.988301	4.948471	4.249738
F	5.073978	4.175465	7.585195
F	6.964125	3.699725	6.607047
F	5.119651	2.730046	5.950779

Total Energy : -966.27892763 Eh

Cyclohexanone oxime

O	5.664252	5.562310	2.337721
H	4.805896	5.147920	2.157509
N	5.339667	6.948099	2.158414
C	6.359034	7.705499	2.339808
C	6.136555	9.183298	2.156674
H	6.300241	9.685881	3.121878
H	5.100555	9.361985	1.856013
C	7.134761	9.752825	1.128244
H	6.900422	9.340375	0.137995
H	7.015381	10.840412	1.062168
C	8.577833	9.390046	1.503201
H	8.835332	9.868096	2.459437
H	9.273646	9.784794	0.753386
C	8.751108	7.871083	1.632923
H	9.777621	7.624863	1.928141
H	8.575208	7.400178	0.657039
C	7.765230	7.272403	2.660013
H	7.834998	6.184483	2.689958
H	8.020909	7.653946	3.659599

Total Energy : -365.77780667 Eh

Cyclohexanone *O*-(phenyl)oxime

O	5.123221	5.675012	2.915194
N	4.953359	7.079924	2.693643
C	6.088238	7.681306	2.676855
C	6.045331	9.165771	2.427935
H	6.425279	9.679774	3.323513
H	5.010524	9.481677	2.271643
C	6.941793	9.535222	1.227794
H	6.502133	9.118099	0.312409
H	6.962696	10.624558	1.109501
C	8.361705	8.983930	1.409960
H	8.829844	9.465671	2.280433
H	8.978551	9.234127	0.538834
C	8.342297	7.464687	1.620399
H	9.357484	7.084454	1.781121
H	7.954479	6.975564	0.717450
C	7.455621	7.068762	2.822059
H	7.387777	5.985961	2.925618
H	7.908113	7.468638	3.741382
C	3.925667	4.984638	2.945707
C	2.668678	5.572032	2.796562
C	4.054432	3.606625	3.145541
C	1.536749	4.757209	2.850371
C	2.913301	2.811945	3.195855
H	5.046076	3.178807	3.258418
H	2.590591	6.640281	2.643413
C	1.646743	3.381518	3.048846

H	0.556257	5.211414	2.735145
H	0.757805	2.759381	3.089051
H	3.016957	1.741514	3.350970

Total Energy : -597.21265974 Eh

Cyclohexanone *O*-(acetyl)oxime

O	5.323610	5.660763	2.793778
N	5.097212	7.078514	2.583283
C	6.208007	7.721085	2.612559
C	6.114154	9.207173	2.380294
H	6.443845	9.719992	3.295918
H	5.073978	9.486451	2.193064
C	7.036310	9.628756	1.216761
H	6.644879	9.208772	0.281053
H	7.016200	10.719589	1.114473
C	8.470341	9.131974	1.439946
H	8.891006	9.621960	2.329700
H	9.103706	9.416633	0.591719
C	8.504403	7.610843	1.633421
H	9.526989	7.268824	1.827203
H	8.169304	7.116505	0.712516
C	7.593698	7.164513	2.799455
H	7.568332	6.079209	2.893500
H	7.994075	7.577930	3.736698
C	4.164948	4.906766	2.809017
C	2.855956	5.632626	2.634225
H	2.729295	6.386004	3.416491
H	2.054796	4.894930	2.677354
H	2.838693	6.166091	1.680071
O	4.295903	3.716145	2.965882

Total Energy : -518.67816269 Eh

Cyclohexanone *O*-(3-nitrobenzoyl)oxime

O	5.227503	5.727545	2.986038
N	5.043523	7.138930	2.750105
C	6.175764	7.741499	2.698788
C	6.116500	9.221879	2.429619
H	6.518625	9.748225	3.307716
H	5.076317	9.530490	2.297877
C	6.978194	9.576239	1.199592
H	6.515164	9.143513	0.303354
H	6.988546	10.663509	1.065133
C	8.405591	9.035576	1.351141
H	8.895780	9.534166	2.199477
H	8.995748	9.273704	0.458716
C	8.401003	7.520024	1.586619
H	9.421626	7.147491	1.728000
H	7.992645	7.013260	0.702763
C	7.549119	7.138706	2.818354
H	7.492575	6.057480	2.942929
H	8.021358	7.558789	3.718212
C	4.036556	5.047192	3.054318
C	2.782313	5.643820	2.934574
C	4.155023	3.666440	3.261861
C	1.668522	4.815060	3.028844
C	3.013198	2.875871	3.349743
H	5.145722	3.231836	3.351379
H	2.671309	6.706031	2.775167
C	1.744335	3.441777	3.233626

N	0.327512	5.439643	2.903210
H	0.837228	2.854729	3.297336
O	0.275995	6.659735	2.724448
O	-0.657563	4.699271	2.984635
H	3.114758	1.806950	3.510115

Total Energy : -802.03376042 Eh

Cyclohexanone *O*-(3,5-dinitrobenzoyl)oxime

O	5.228202	5.731803	2.995125
N	5.040137	7.149431	2.751042
C	6.174089	7.748644	2.699881
C	6.114651	9.227795	2.423553
H	6.516622	9.755932	3.300308
H	5.075035	9.537256	2.289699
C	6.978200	9.574824	1.192455
H	6.515459	9.138578	0.297867
H	6.988181	10.661372	1.053886
C	8.405021	9.034486	1.348191
H	8.895473	9.537980	2.193271
H	8.995003	9.266677	0.454315
C	8.399675	7.520557	1.592070
H	9.419237	7.147980	1.738662
H	7.993069	7.007983	0.710881
C	7.546376	7.146299	2.825417
H	7.491810	6.066027	2.957727
H	8.015710	7.573989	3.722942
C	4.043156	5.056631	3.064593
C	2.784600	5.652261	2.940182
C	4.159489	3.678323	3.277895
C	1.665094	4.831985	3.034450
C	2.999863	2.920853	3.361384
H	5.128877	3.205265	3.376070
H	2.677865	6.714487	2.776176
C	1.724714	3.461271	3.244027

N	0.323619	5.464611	2.902505
H	0.834796	2.851276	3.312065
N	3.132668	1.456919	3.586240
O	0.286027	6.683165	2.720061
O	-0.660093	4.727223	2.984678
O	4.273530	0.999583	3.688744
O	2.093947	0.798635	3.655257

Total Energy : -1006.84930733 Eh

Cyclohexanone *O*-(trifluoroacetyl)oxime

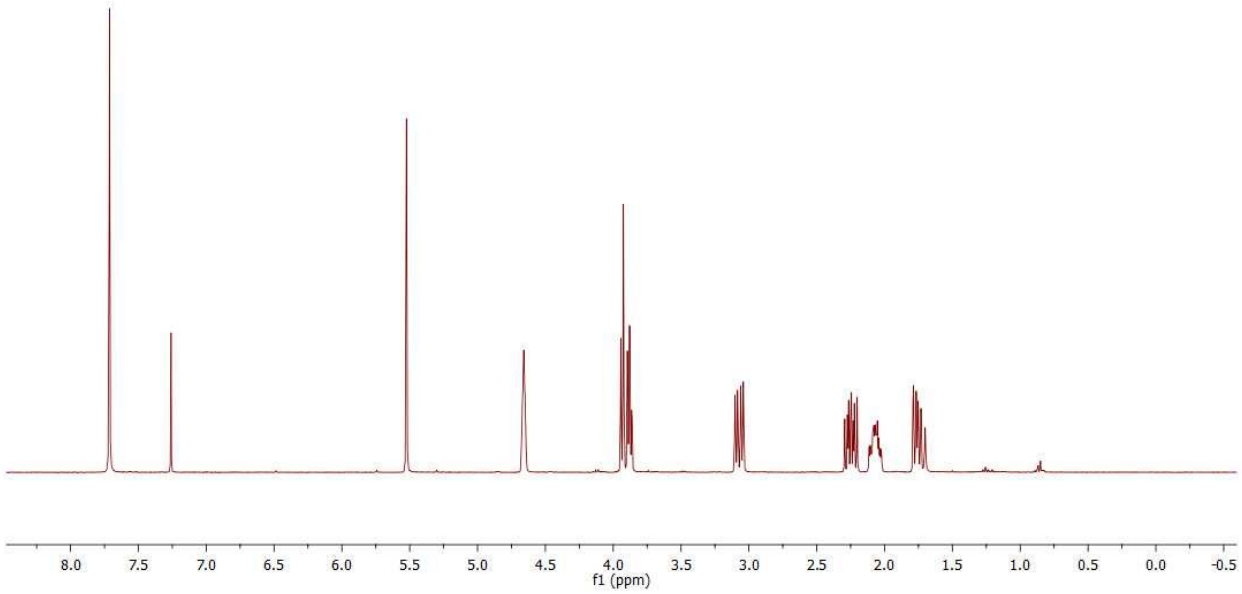
O	5.258111	5.763511	2.877651
N	5.053545	7.207864	2.641476
C	6.187814	7.803329	2.655613
C	6.140033	9.287736	2.395846
H	6.502811	9.800227	3.298451
H	5.108060	9.601156	2.219868
C	7.058598	9.650279	1.209011
H	6.629669	9.236188	0.287627
H	7.082078	10.739367	1.093028
C	8.474896	9.096509	1.410357
H	8.938233	9.584961	2.279256
H	9.098424	9.335594	0.541429
C	8.449476	7.580014	1.635586
H	9.459832	7.195731	1.811407
H	8.066229	7.079764	0.737032
C	7.553826	7.202508	2.836949
H	7.494770	6.122709	2.967698
H	7.985920	7.634223	3.750859
C	4.125287	5.031971	2.941565
C	2.755229	5.768083	2.800367
O	4.180014	3.841914	3.108446
F	1.768039	4.865474	2.931982
F	2.615072	6.349372	1.589264
F	2.578182	6.704014	3.757601

Total Energy : -816.83490193 Eh

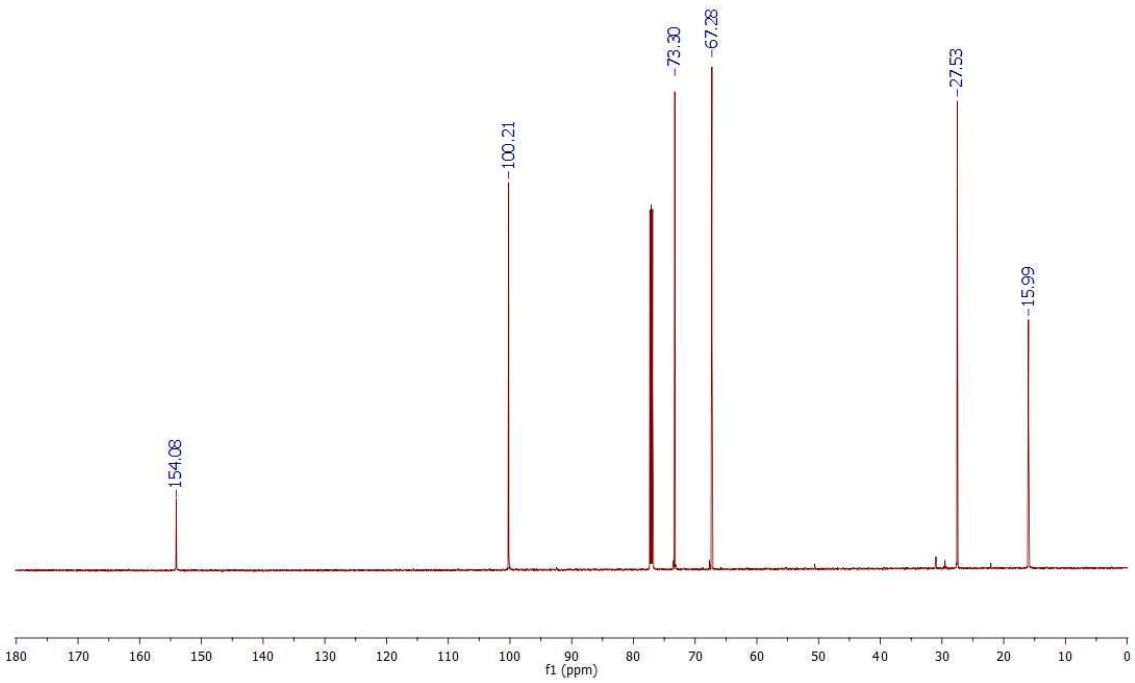
^{1}H-NMR and ^{13}C-NMR spectra for Oximes (1-8):

(*Z*)-Dihydrolevoglucosenone oxime (1).

^{1}H-NMR



^{13}C-NMR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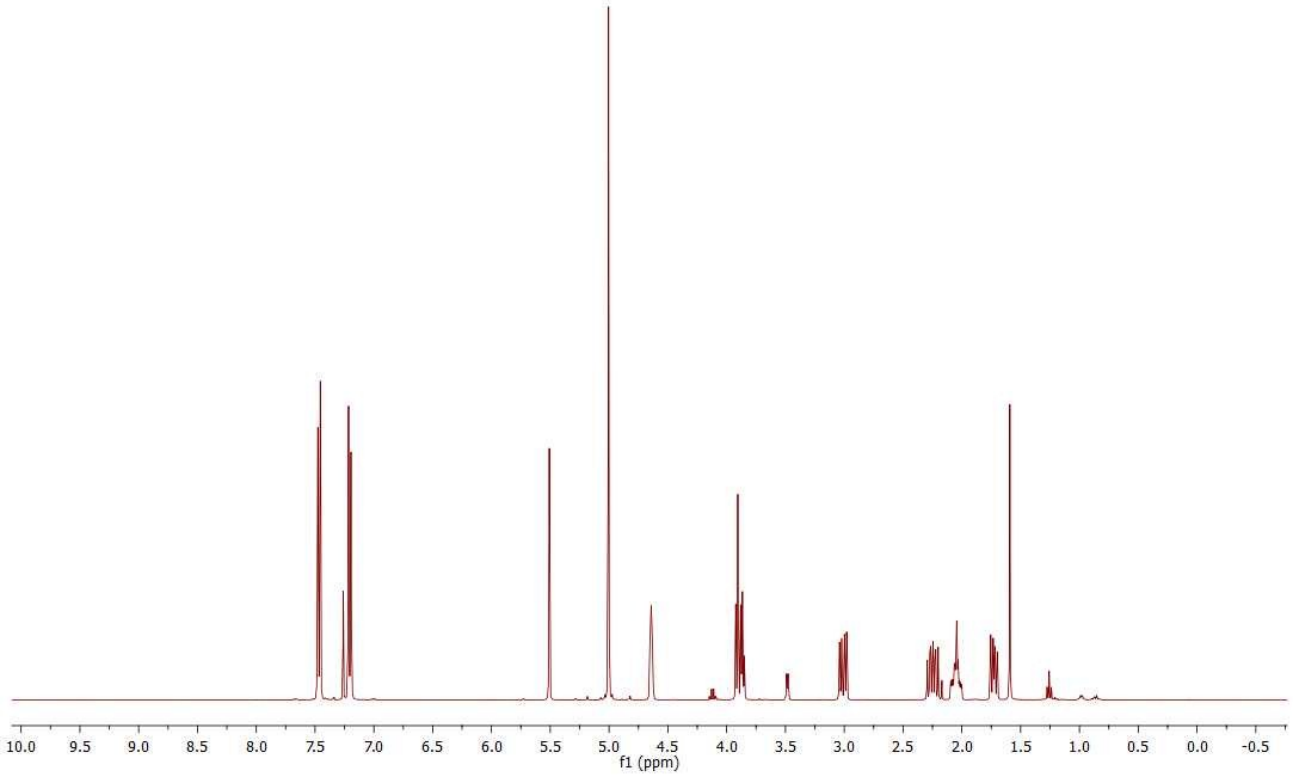
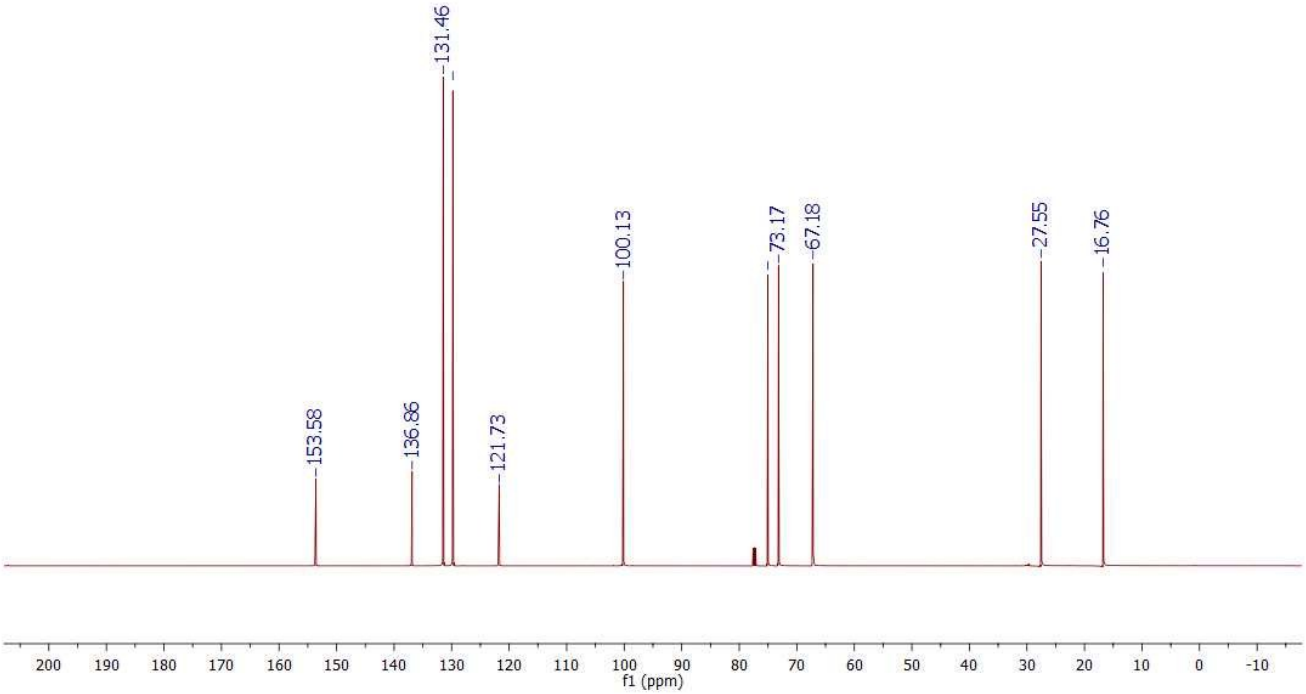
73.30
67.28
27.53
15.99
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

(*Z*)-Dihydrolevoglucosenone *O*-(4-bromobenzyl)oxime (2).

^{1}H-NMR

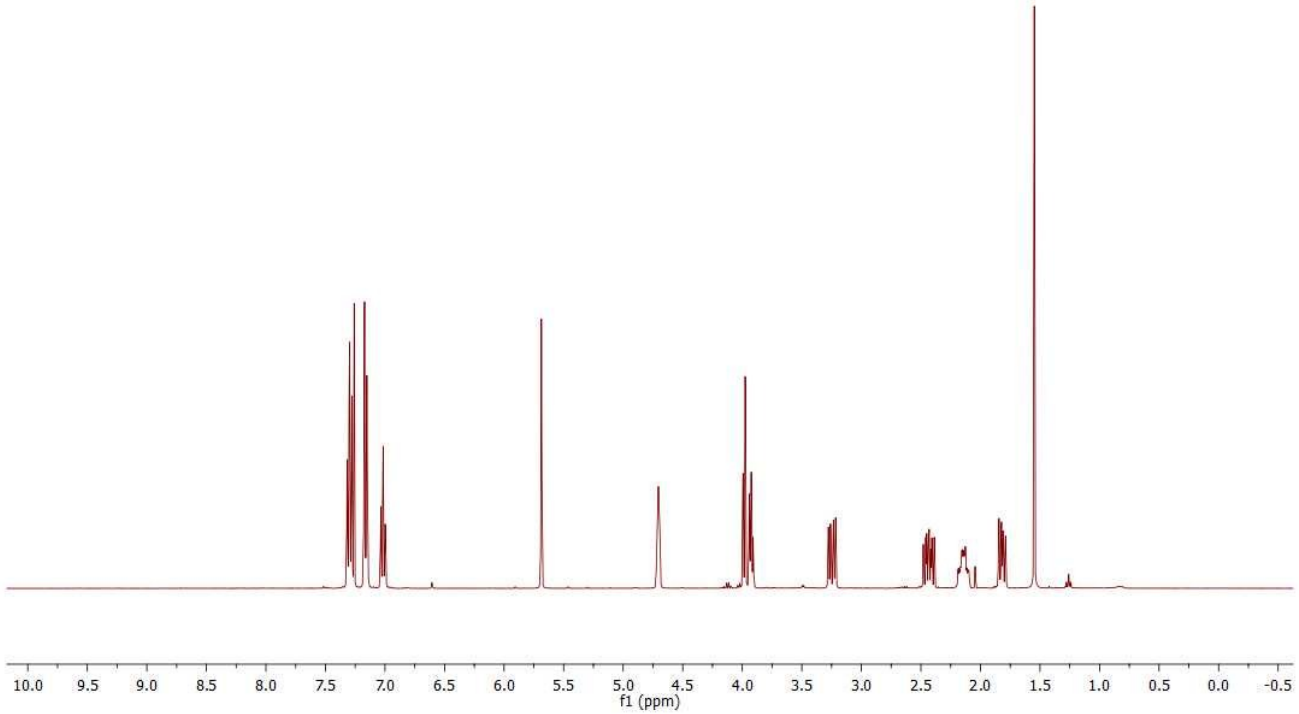


^{13}C-NMR

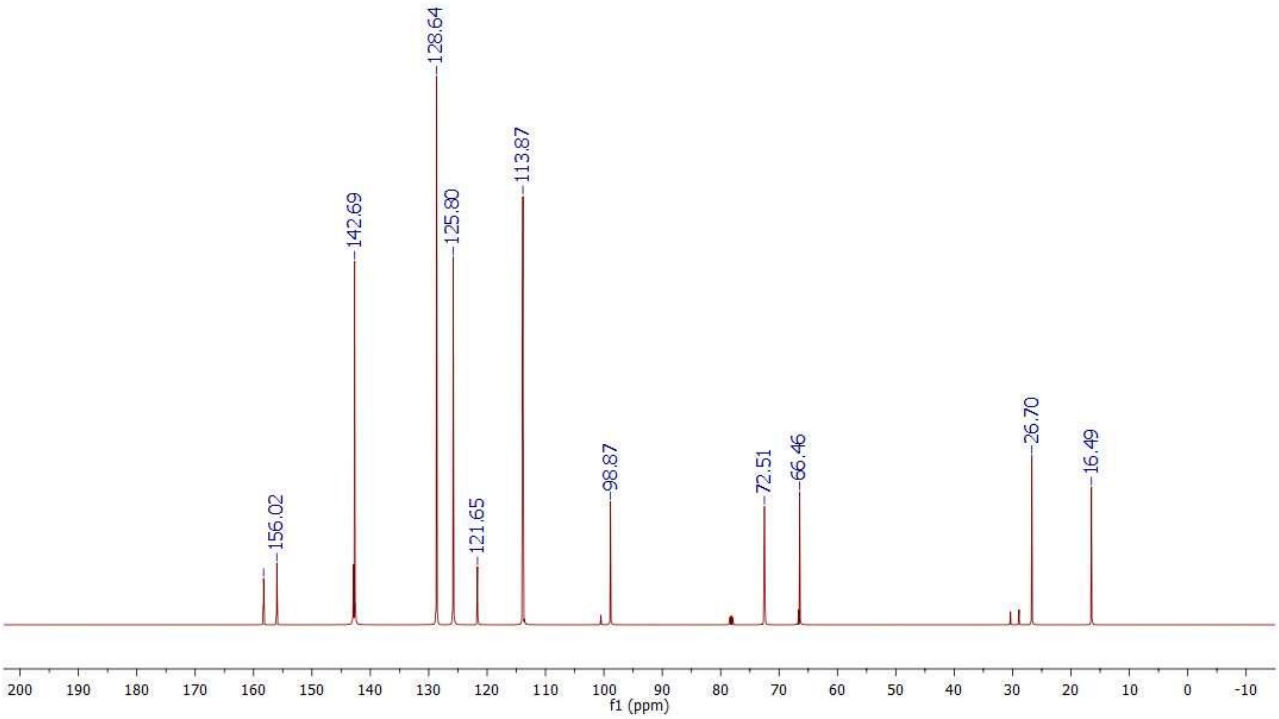

153.58
136.86
131.46
121.73
100.13
73.17
67.18
27.55
16.76
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

(*Z*)-Dihydrolevoglucosenone *O*-(phenyl)oxime (3).

^{1}H-NMR

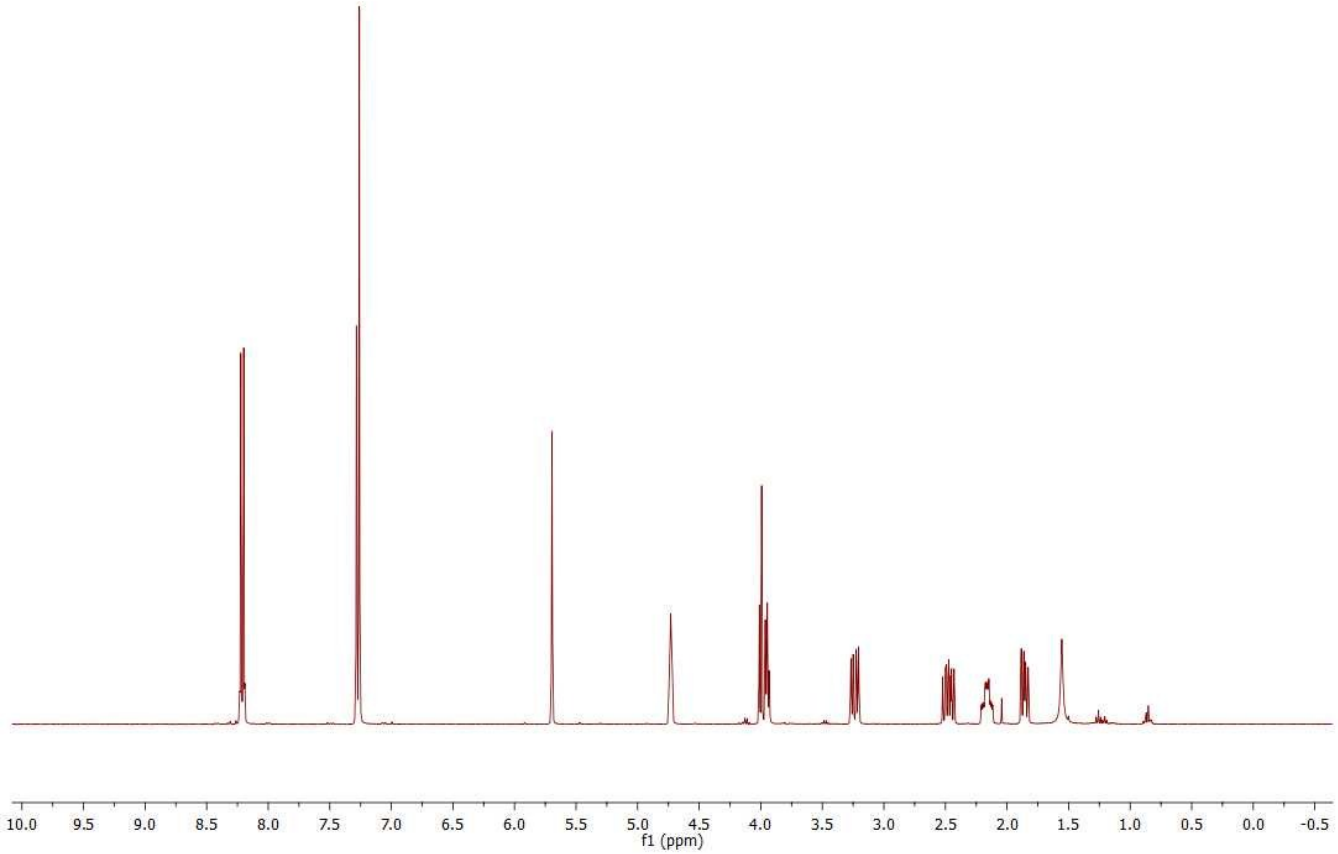


^{13}C-NMR


128.64
113.87
142.69
125.80
156.02
121.65
98.87
72.51
66.46
26.70
16.49
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

(*Z*)-Dihydrolevoglucosenone *O*-(4-nitrophenyl)oxime (4).

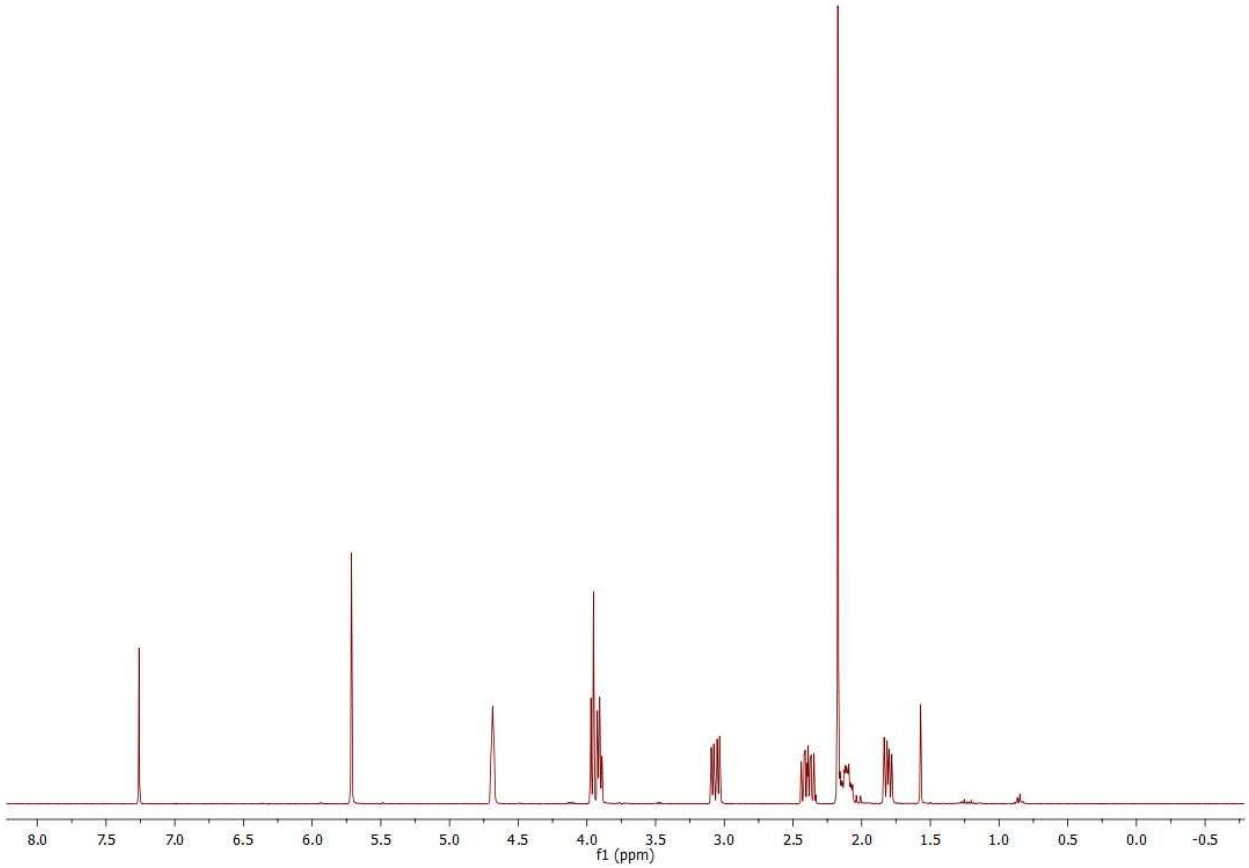
^{1}H-NMR



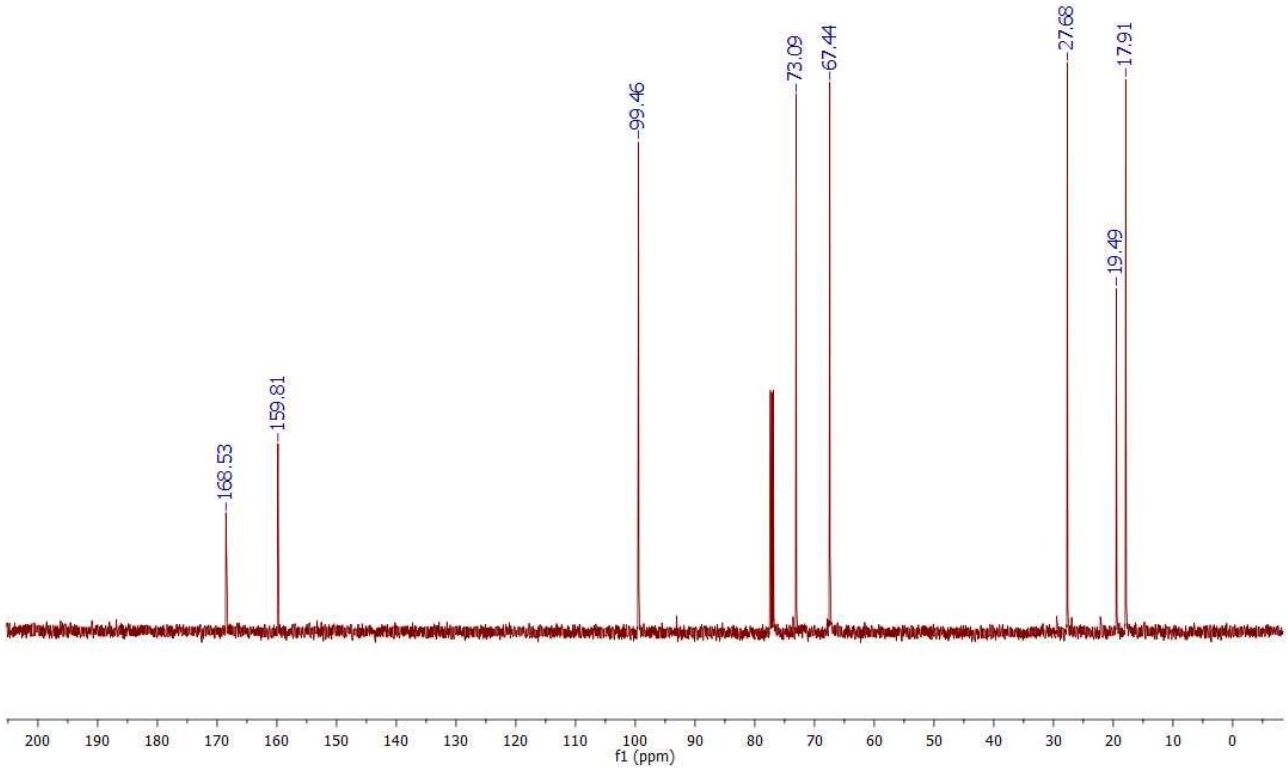
^{13}C-NMR

(*Z*)-Dihydrolevoglucosenone *O*-(acetyl)oxime (5).

^{1}H-NMR

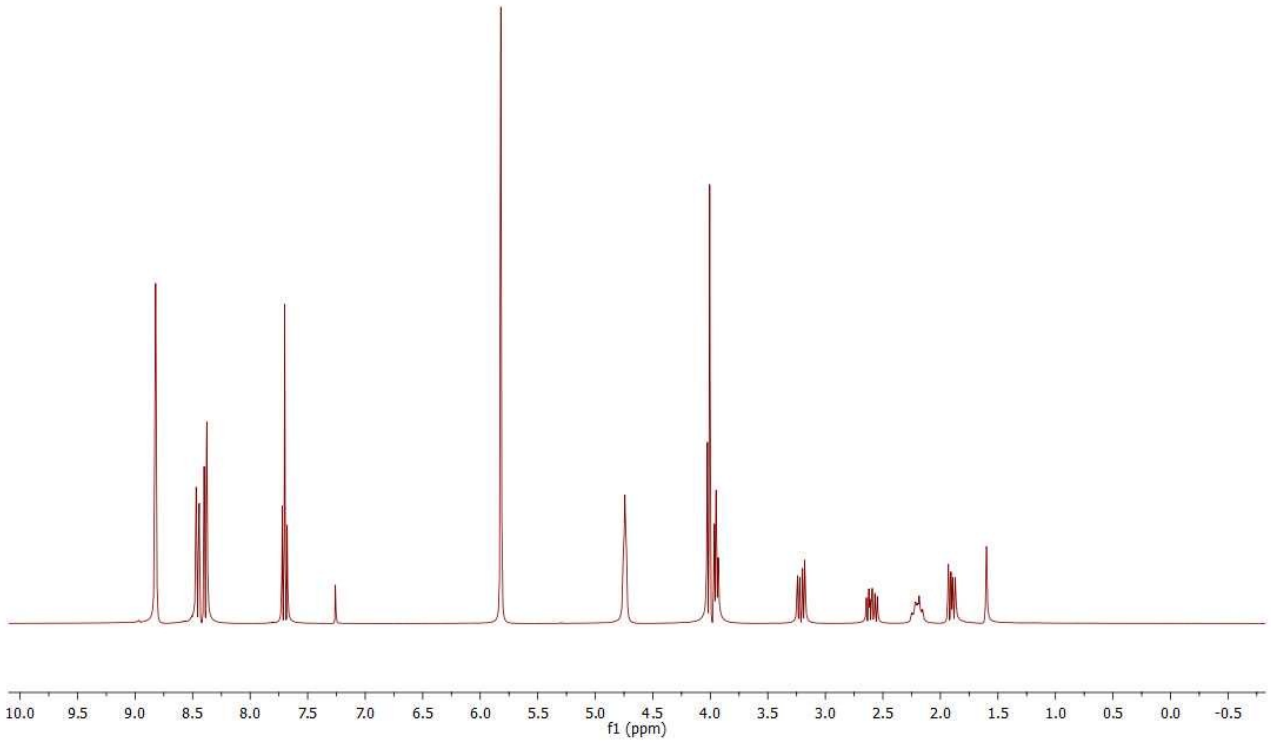


^{13}C-NMR

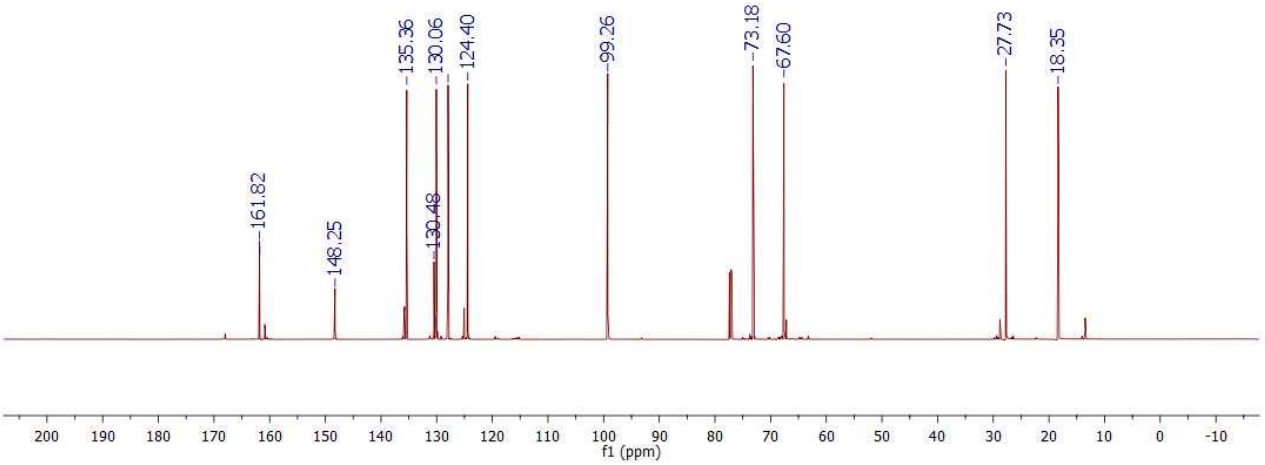

168.53
159.81
99.46
73.09
67.44
27.68
19.49
17.91
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

(*Z*)-Dihydrolevoglucosenone *O*-(3-nitrobenzoyl)oxime (6).

^{1}H-NMR

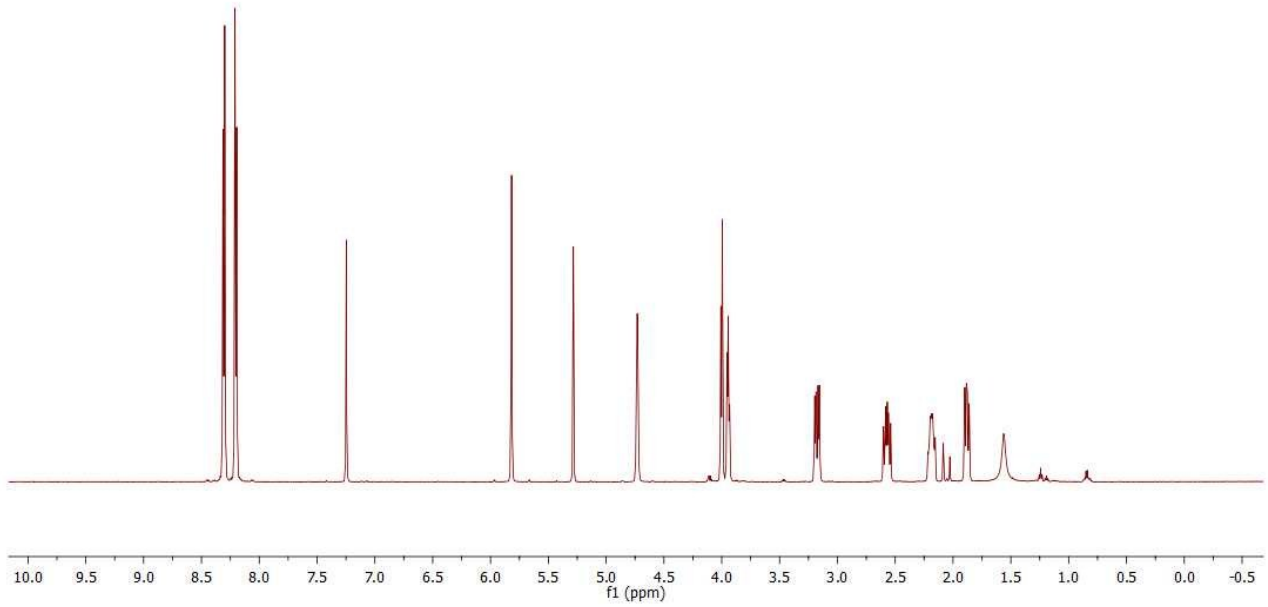


^{13}C-NMR

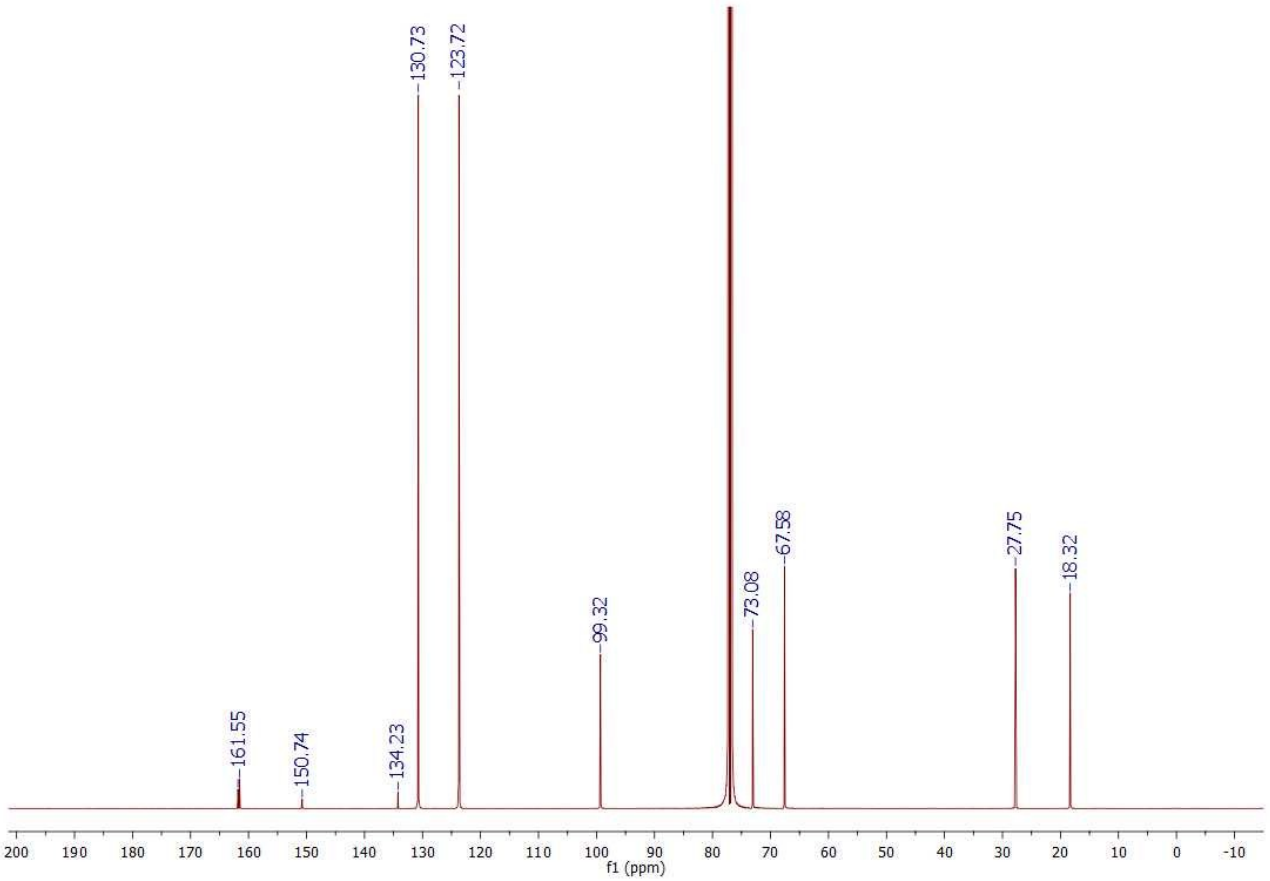

161.82
148.25
135.36
130.48
130.06
124.40
99.26
73.18
67.60
27.73
18.35
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

(*Z*)-Dihydrolevoglucosenone *O*-(4-nitrobenzoyl)oxime (7).

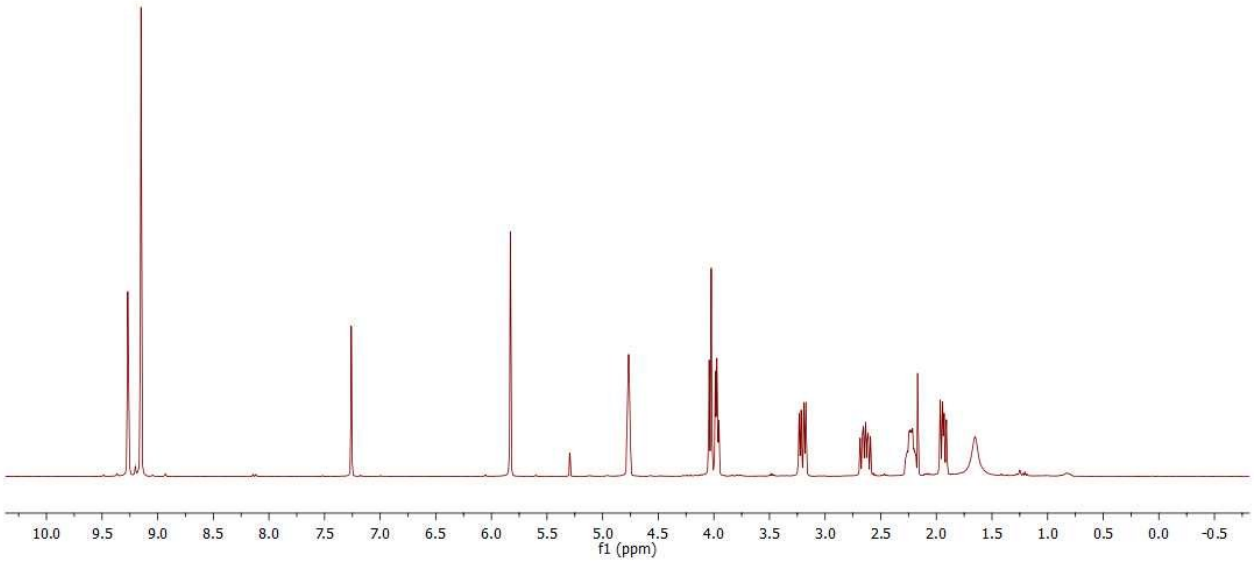
^{1}H-NMR



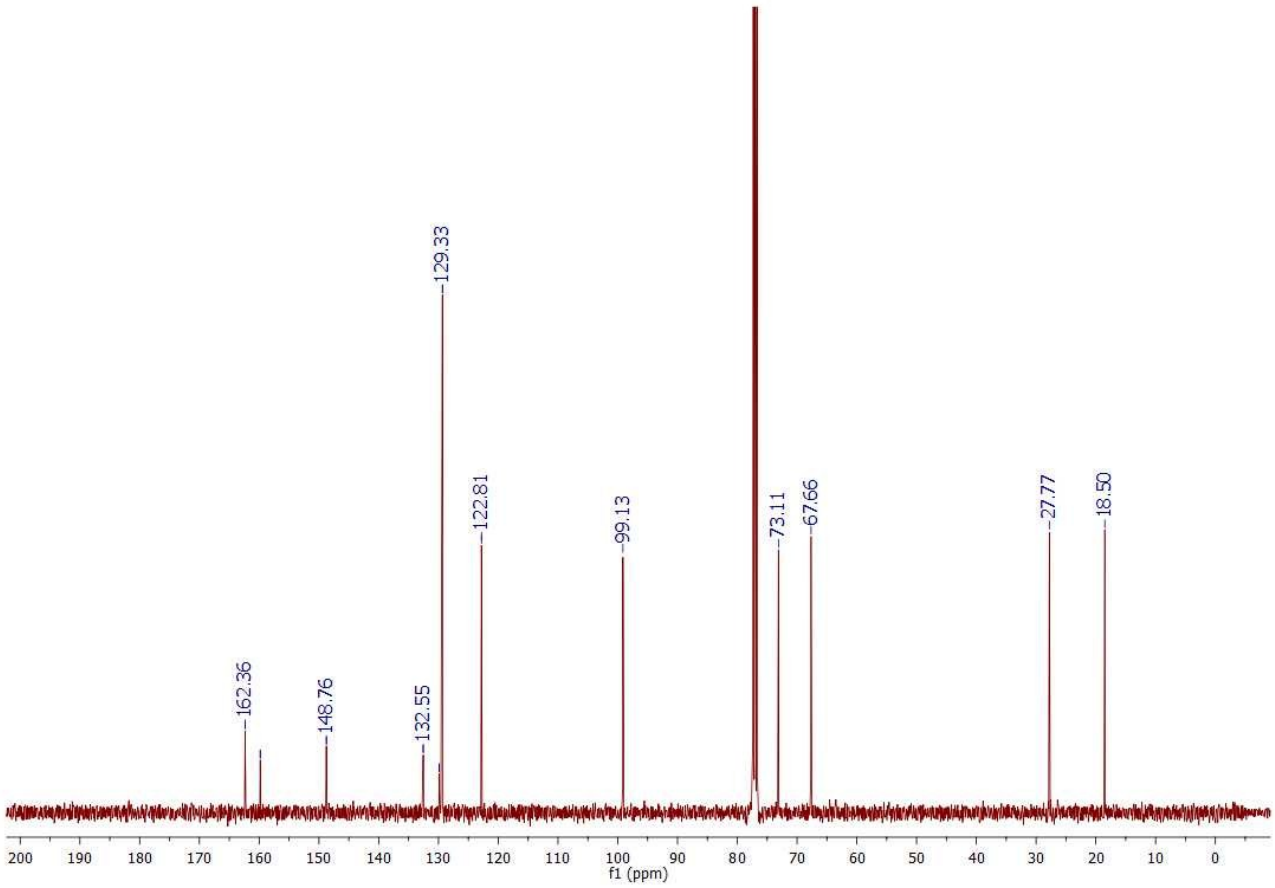
^{13}C-NMR


161.55
150.74
134.23
130.73
123.72
99.32
73.08
67.58
27.75
18.32
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

(*Z*)-Dihydrolevoglucosenone *O*-(3,5-dinitrobenzoyl)oxime (8).
^{1}H-NMR

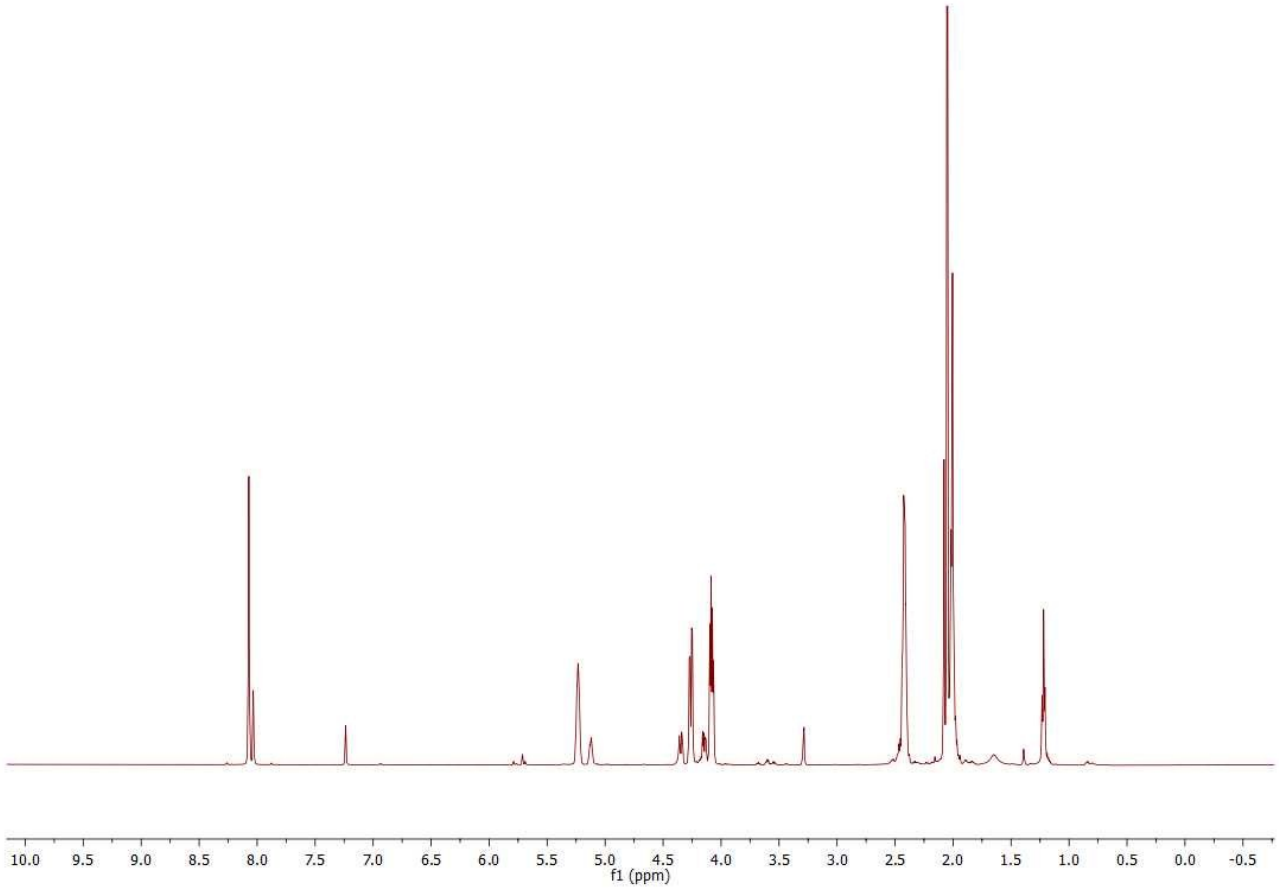


^{13}C-NMR

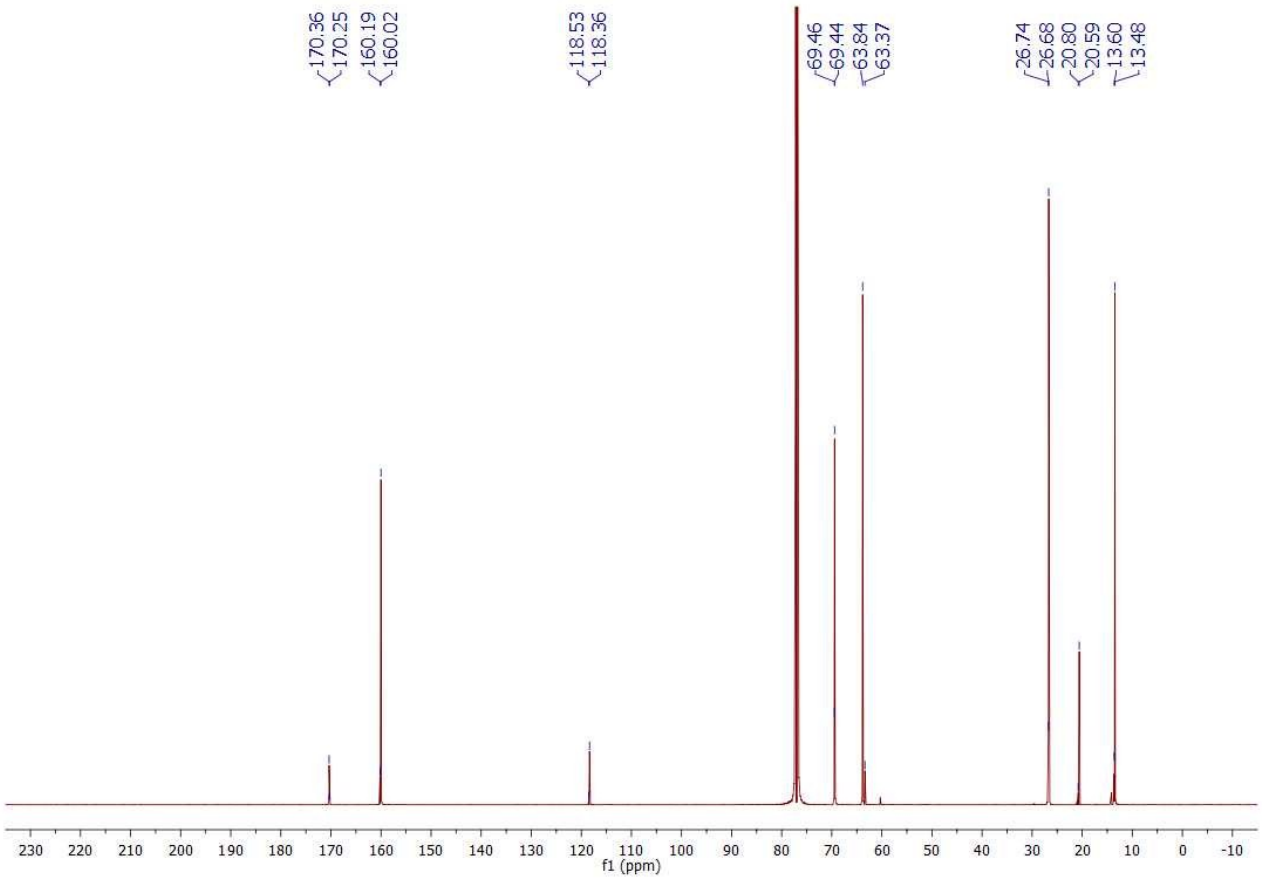

129.33
122.81
99.13
73.11
67.66
27.77
18.50
162.36
148.76
132.55
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Nitriles 9 and 10.

^{1}H-NMR

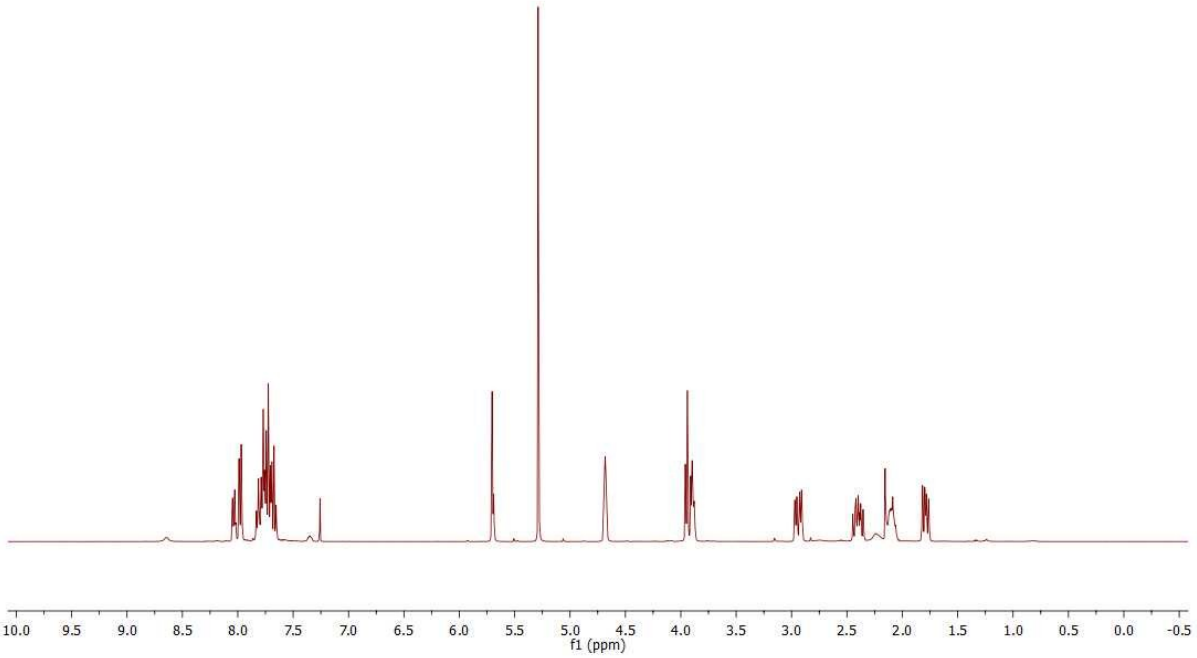


^{13}C-NMR

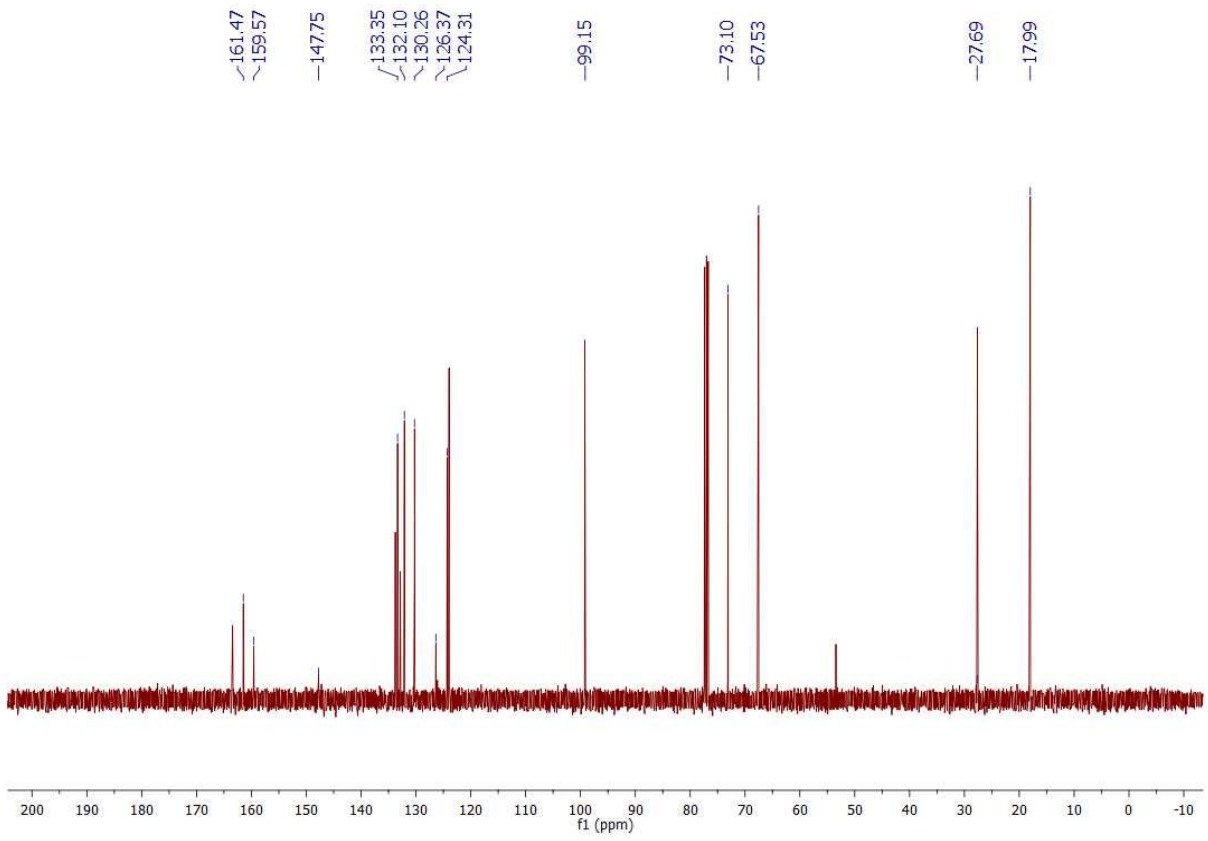

170.36
170.25
160.19
160.02
118.53
118.36
69.46
69.44
63.84
63.37
26.74
26.68
20.80
20.59
13.60
13.48
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Dihydrolevoglucosenone *O*-(2-nitrobenzoyl)oxime (11).

^{1}H-NMR

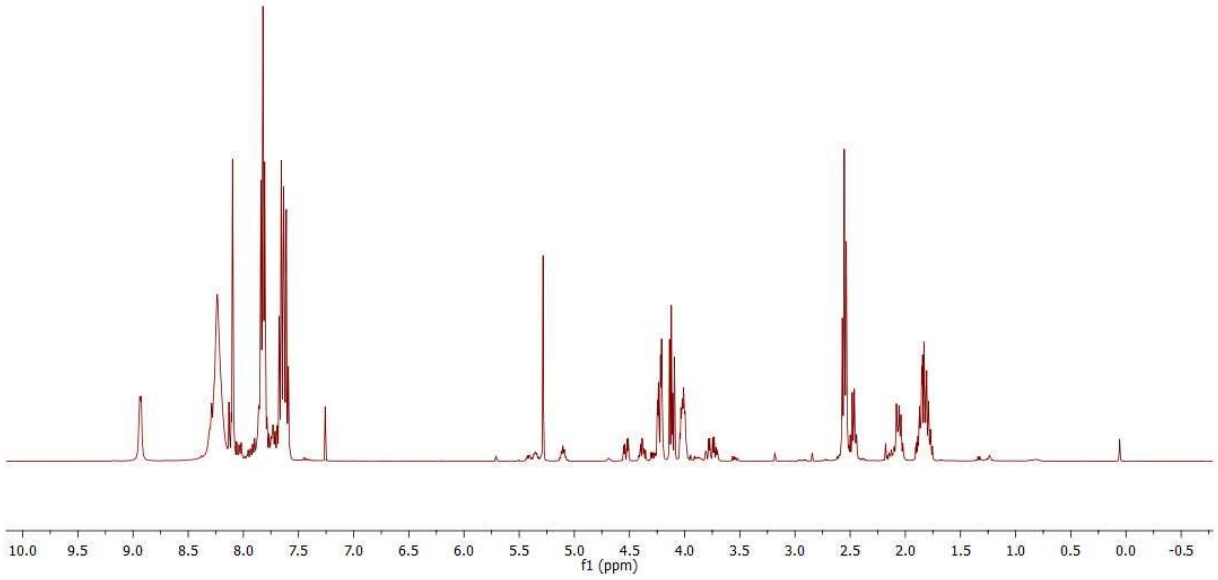


^{13}C-NMR



Nitriles 12 and 13

^{1}H-NMR



^{13}C-NMR