Supplementary material

NIR Excitation-Driven Conformational Isomerizations of Thymol and Carvacrol Isolated in a Nitrogen Cryomatrix

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1. Figures

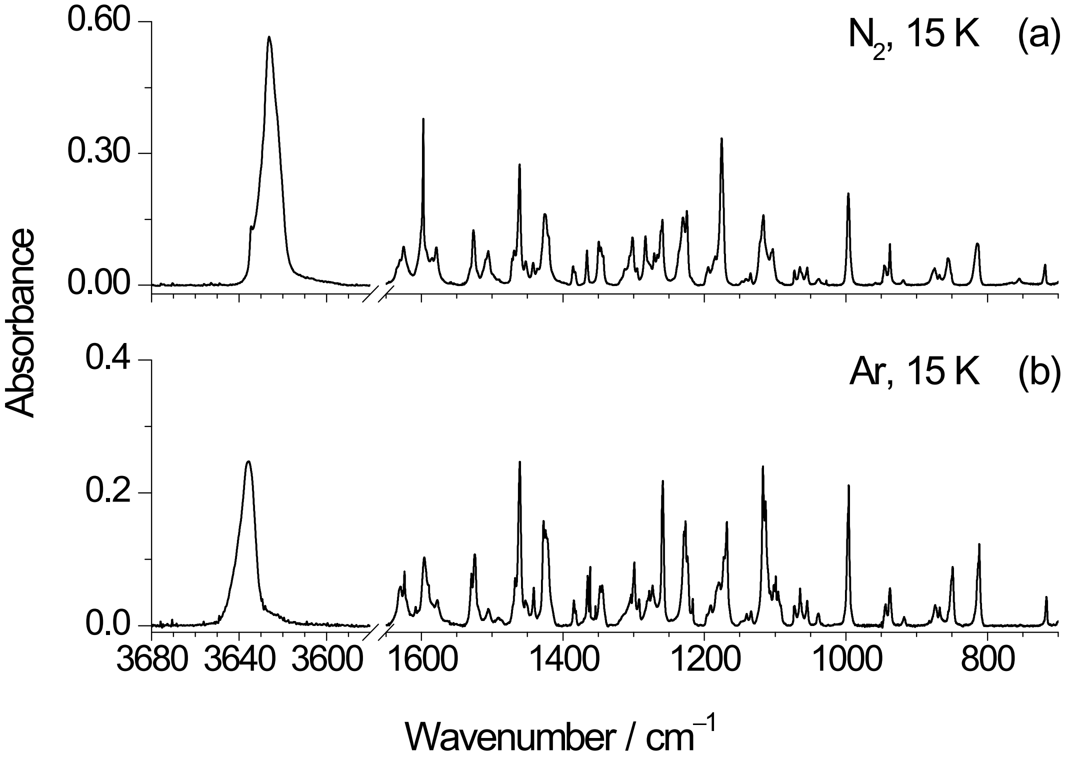


Figure S1. Mid-IR spectrum of carvacrol isolated in a **(a)** N_2 matrix at 15 K compared with spectra recorded in Ar **(b)** at the same temperature, illustrating the influence of the matrix environment on the band's positions and profiles.

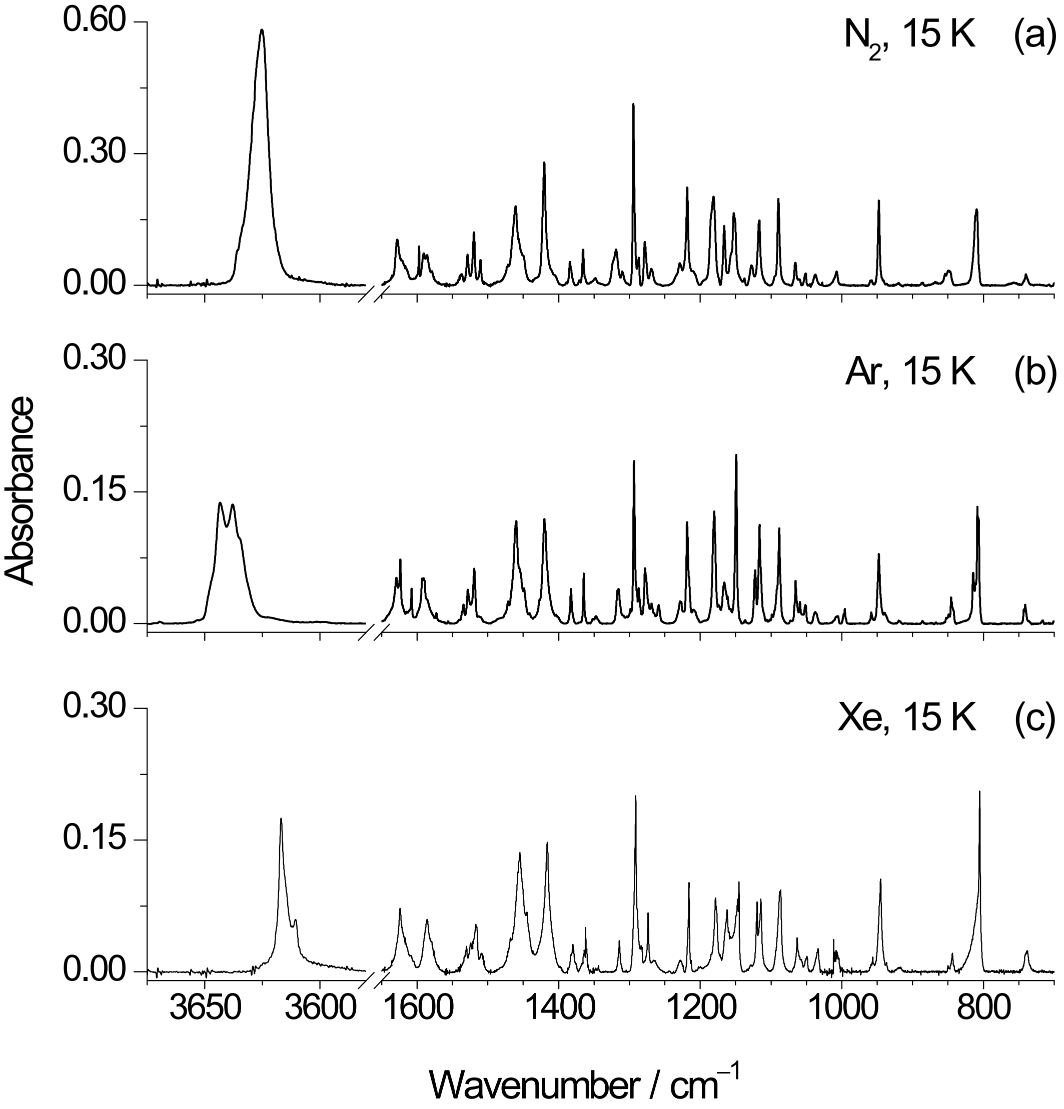


Figure S2. Mid-IR spectrum of thymol isolated in a **(a)** N_2 matrix at 15 K compared with spectra recorded in Ar **(b)** and Xe **(c)** matrixes at the same temperature, illustrating the influence of the matrix environment on the band's positions and profiles.

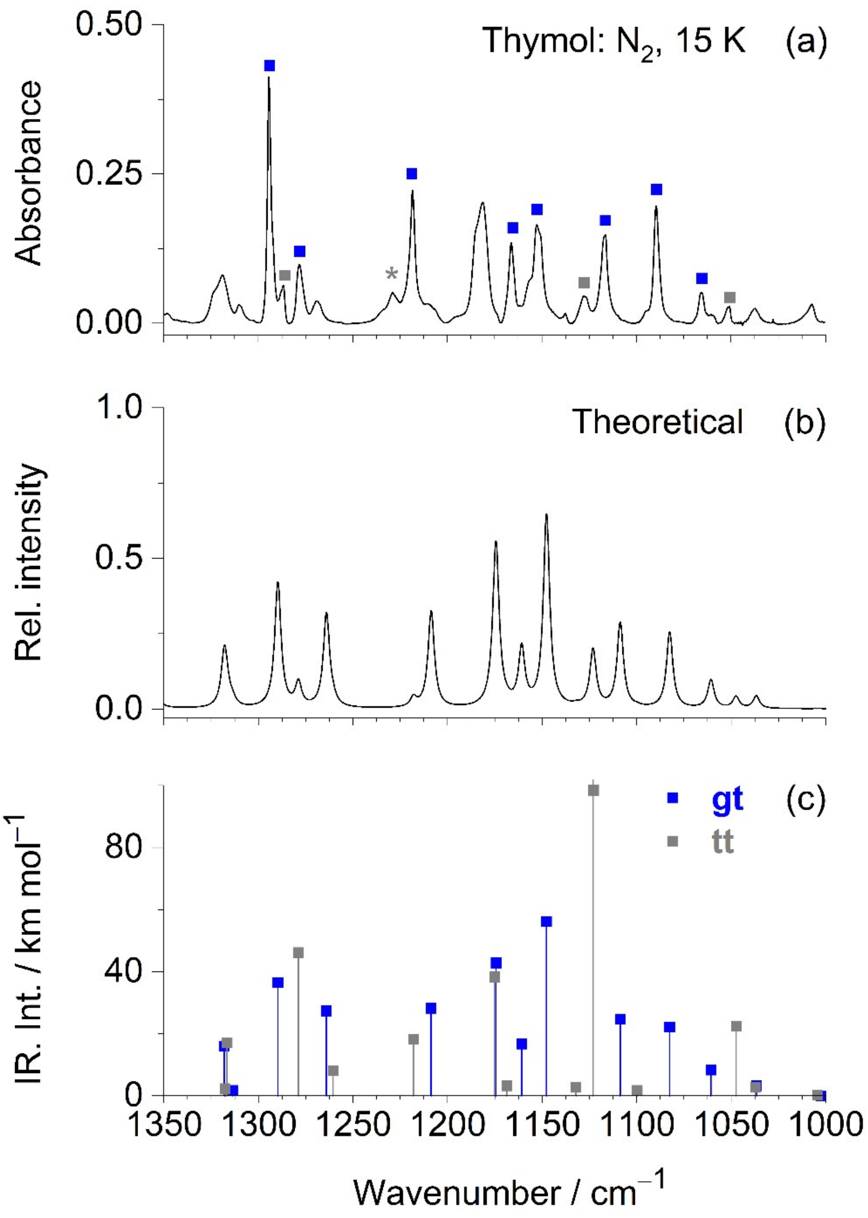


Figure S3. (a) Fragment of the experimental mid-IR spectrum of thymol isolated in a N_2 matrix at 15 K. Bands highlighted in the experimental spectrum with blue and grey squares and are assigned to the **gt** and **tt** conformers, respectively, by comparison with the computed vibrational data. The band at 1229 cm^{-1}, marked with an asterisk, is tentatively attributed to the **tt** conformer, but it may also originate from the high-energy **cc** conformer, as demonstrated by the results of the NIR irradiation experiments discussed in section 3.2 of the manuscript. (b) Theoretical spectrum of a mixture of the **gt** and **tt** conformers, which was simulated from the B3LYP/6-311++G(d,p) vibrational calculations carried out for both conformers. Lorentzian functions (FWHM = 4 cm^{-1}) centred at the calculated wavenumbers were used and the intensities were scaled by 1.0 (**gt**) and 0.15 (**tt**) to best match the experimental spectrum. (c) Scaled wavenumbers and unscaled IR intensities extracted from the harmonic vibrational calculations performed for the **gt** (blue) and **tt** (purple) conformers.

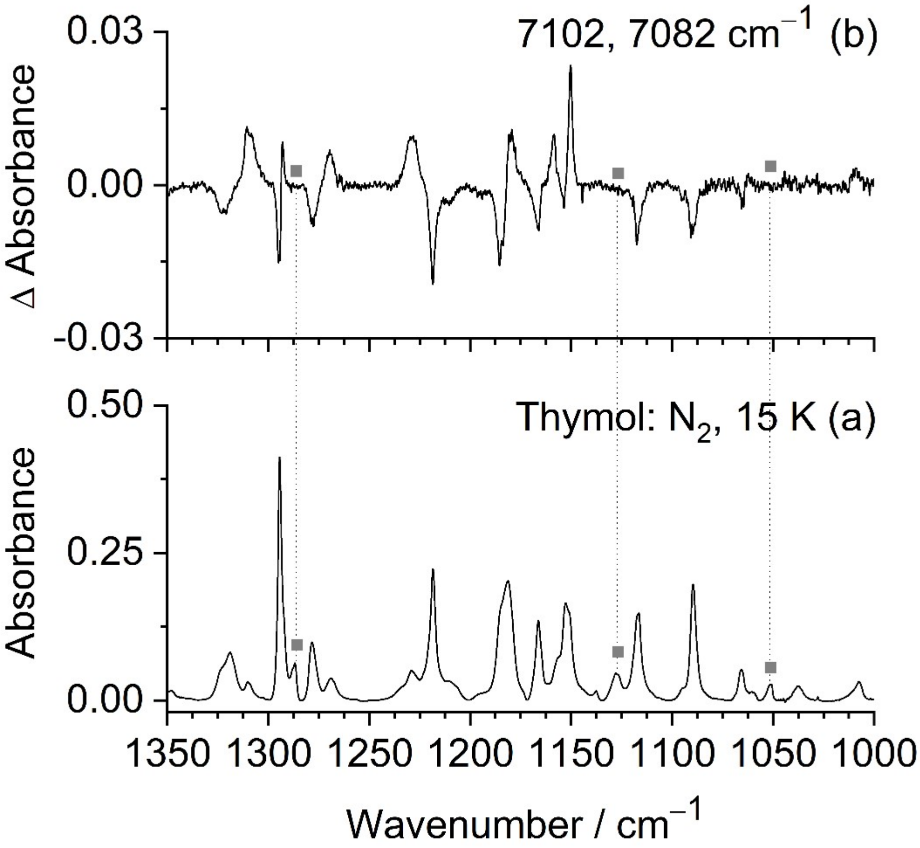
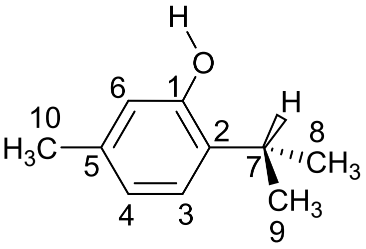


Figure S4. Spectral indication of the absence of changes in the population of the **tt** conformer of thymol following NIR irradiations at 7102 or 7082 cm^{-1}. (a) Fragment of the experimental mid-IR spectrum of thymol isolated in a N$_2$ matrix at 15 K. Bands marked with purple circles are tentatively assigned to the **tt** conformer (see Figure S3). (b) Difference spectrum obtained after 40 min of NIR irradiation at 7102 or 7082 cm^{-1} (positive bands correspond to conformer formation), showing that the bands assigned to the **tt** conformer are not affected.

2. Tables

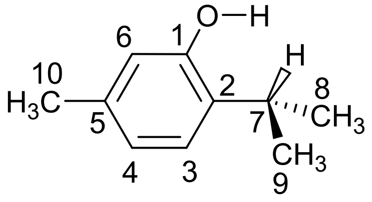
Table S1. Experimental (N_2, 15 K) and calculated [B3LYP/6-311++G(d,p)] infrared absorptions for the **gt** conformer of thymol (2-isopropyl-5-methylphenol).



Exp. [a]	Calc. (**gt**) [b]		Approximate description [c]
	ν [b]	A^{th}	
3625	3626.3	56.5	$\nu(\mathrm{OH})$
1628	1623.8	34.9	$\nu(\mathrm{CC})_{\mathrm{ph}}$
1588	1584.8	20.6	$\nu(\mathrm{CC})_{\mathrm{ph}}$
1520	1518.2	24.7	$\nu(\mathrm{CC})_{\mathrm{ph}}$; $\delta(\mathrm{CH})_{\mathrm{ph}}$
1461	1467.7	24.8	$\delta(\mathrm{CH_3})_{\mathrm{as}}$
1421	1417.0	54.5	$\delta(\mathrm{CH})_{\mathrm{ph}}$; $\nu(\mathrm{CC})_{\mathrm{R}}$; $\nu(\mathrm{CO})$
1384	1387.4	3.8	$\delta(\mathrm{CH_3})_{\mathrm{iso,s}}\,(+)$
1366	1367.4	6.8	$\delta(\mathrm{CH_3})_{\mathrm{iso,s}}\,(-)$
1349	1355.1	6.8	$\delta(\mathrm{C_7H})$
1323	1318.0	16.0	$\nu(\mathrm{CC})_{\mathrm{ph}}$; $\delta(\mathrm{OH})$
1295	1289.8	36.5	$\nu(\mathrm{CC})_{\mathrm{ph}}$; $\delta(\mathrm{CH})_{\mathrm{ph}}$
1278	1264.0	27.4	$\nu(\mathrm{CO}) + \nu(\mathrm{C_2C_7}) + \nu(\mathrm{C_5C_{10}})$; $\nu(\mathrm{CC})_{\mathrm{ph}}$
1217	1208.7	28.2	$\nu(\mathrm{C_2C_7})$
1185	1174.4	42.8	$\delta(\mathrm{OH})$; $\delta(\mathrm{CH})_{\mathrm{ph}}$
1166	1160.8	16.7	$\nu(\mathrm{CO}) - \nu(\mathrm{C_5C_{10}})$; $\delta(\mathrm{CH})_{\mathrm{ph}}$
1154	1147.7	56.1	$\delta(\mathrm{OH})$; $\delta(\mathrm{CH})_{\mathrm{ph}}$; $\nu(\mathrm{CC})_{\mathrm{ph}}$
1117	1108.7	24.8	$\nu(\mathrm{C_7C_8}) - \nu(\mathrm{C_7C_9})$
1090	1082.6	22.1	$\delta(\mathrm{CCC})_{\mathrm{ph}}$
1065	1060.7	8.3	$\rho(\mathrm{CH_3})_{\mathrm{iso}}\,(+)$
948	939.6	16.0	$\delta(\mathrm{CCC})_{\mathrm{ph}}$; $\nu(\mathrm{CO}) - \nu(\mathrm{C_5C_{10}})$
853	831.6	7.0	$\gamma(\mathrm{CH})_{\mathrm{ph}}$
811	805.0	34.5	$\gamma(\mathrm{CH})_{\mathrm{ph}}$

[a] Experimental wavenumbers correspond to the positions of the minima (for decreasing bands) or maxima (for increasing bands) observed upon NIR irradiations at 7102/7082 or 7072/7062 cm^{-1}, respectively. [b] Calculated harmonic wavenumbers were multiplied by 0.945 or 0.980, for the regions above or below 2000 cm^{-1}, respectively. Calculated vibrations with very low intensity or without a corresponding feature in the experimental difference spectra are not shown. [c] Abbreviations: ν, stretching; δ, in-plane bending; γ, out-of-plane bending; iso, isopropyl group; ph, phenyl ring; as, antisymmetric; s, symmetric. Signs "+" and "–" designate combination of vibrations occurring in the same phase and in the opposite phase, respectively.

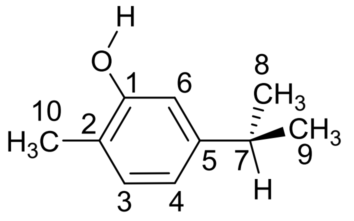
Table S2. Experimental (N_2, 15 K) and calculated [B3LYP/6-311++G(d,p)] infrared absorptions for the **gc** conformer of thymol (2-isopropyl-5-methylphenol).

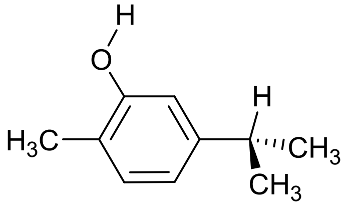


Exp. [a]	Calc. (**gc**) [b]		Approximate description [c]
	ν [b]	A^{th}	
3631	3626.0	62.4	$\nu(\mathrm{OH})$
1634	1630.8	32.1	$\nu(\mathrm{CC})_{\mathrm{ph}}$
1579	1577.5	37.1	$\nu(\mathrm{CC})_{\mathrm{ph}}$
1511	1507.1	54.9	$\nu(\mathrm{CC})_{\mathrm{ph}}$; $\delta(\mathrm{CH})_{\mathrm{R}}$
1468	1468.9	19.7	$\delta(\mathrm{CH_3})_{\mathrm{as}}$
1454	1463.3	18.2	$\delta(\mathrm{CH_3})_{\mathrm{iso,as}}$ (−)
	1458.3	7.8	$\delta(\mathrm{CH_3})_{\mathrm{as'}}$
1432	1427.7	15.8	$\delta(\mathrm{CH})_{\mathrm{R}}$; $\nu(\mathrm{CC})_{\mathrm{R}}$; $\nu(\mathrm{CO})$
1389	1392.8	5.3	$\delta(\mathrm{CH_3})_{\mathrm{iso,s}}$ (+)
1371	1372.1	6.9	$\delta(\mathrm{CH_3})_{\mathrm{iso,s}}$ (−)
1310	1310.4	40.1	$\nu(\mathrm{CC})_{\mathrm{ph}}$; $\delta(\mathrm{OH})$
1294	1288.3	29.8	$\nu(\mathrm{CC})_{\mathrm{ph}}$; $\nu(\mathrm{CO})$; $\delta(\mathrm{CH})_{\mathrm{ph}}$
1269	1256.7	42.2	$\nu(\mathrm{CO}) + \nu(\mathrm{C_2C_7}) + \nu(\mathrm{C_5C_{10}})$; $\nu(\mathrm{CC})_{\mathrm{ph}}$
1228	1220.7	38.0	$\delta(\mathrm{OH})$; $\nu(\mathrm{C_2C_7}) - \nu(\mathrm{C_5C_{10}})$
1180	1174.7	42.3	$\delta(\mathrm{CH})_{\mathrm{ph}}$; $\delta(\mathrm{OH})$
1159	1153.5	15.5	$\delta(\mathrm{CH})_{\mathrm{ph}}$; $\nu(\mathrm{CO})$; $\delta(\mathrm{C_8C_7C_9})$
1150	1148.2	47.7	$\delta(\mathrm{CH})_{\mathrm{ph}}$; $\delta(\mathrm{OH})$
1062	1057.4	3.0	$\rho(\mathrm{CH_3})_{\mathrm{iso}}$ (+)
1044	1037.4	5.0	$\rho(\mathrm{CH_3})$
1009	1002.5	8.2	$\rho(\mathrm{CH_3})'$
949	940.4	28.0	$\delta(\mathrm{CCC})_{\mathrm{ph}}$
870	867.6	9.4	$\gamma(\mathrm{CH})_{\mathrm{ph}}$
807	801.6	27.7	$\gamma(\mathrm{CH})_{\mathrm{ph}}$

[a] Experimental wavenumbers correspond to the positions of the minima (for decreasing bands) or maxima (for increasing bands) observed upon NIR irradiations at 7072/7062 or 7102/7082 cm^{-1}, respectively. [b] Calculated harmonic wavenumbers were multiplied by 0.945 or 0.980, for the regions above or below 2000 cm^{-1}, respectively. Calculated vibrations with very low intensity or without a corresponding feature in the experimental difference spectra are not shown. [c] Abbreviations: ν, stretching; δ, in-plane bending; γ, out-of-plane bending; iso, isopropyl group; ph, phenyl ring; as, antisymmetric; s, symmetric. Signs "+" and "−" designate combination of vibrations occurring in the same phase and in the opposite phase, respectively. The prime symbol (') is used to distinguish between different types of antisymmetric in-plane bending and rocking vibrations of the CH_3 group.

Table S3. Experimental (N_2, 15 K) and calculated [B3LYP/6-311++G(d,p)] infrared absorptions for the **tt** and **ct** conformers of carvacrol (5-isopropyl-2-methylphenol).

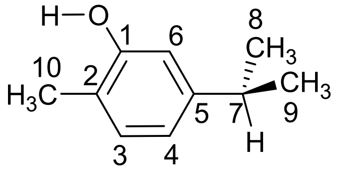


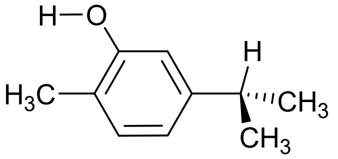


Exp. [a]	Calc. (**tt**) [b]		Calc. (**ct**) [b]		Approximate description [c]
	ν [b]	A^{th}	ν [b]	A^{th}	
3628	3625.5	52.1	3625.1	55.4	ν(OH)
1625	1623.6	27.9	1623.6	28.9	ν(CC)$_{\mathrm{ph}}$
1598*	1587.4	36.7	1588.4	39.8	ν(CC)$_{\mathrm{ph}}$
1527	1516.9	29.0	1517.5	28.5	ν(CC)$_{\mathrm{ph}}$; δ(CH)$_{\mathrm{ph}}$
1470	1477.8	3.3	1478.1	8.5	δ(CH$_3$)$_{\mathrm{iso,as}}$ (+)
1462	1467.7	25.8	1467.9	24.7	δ(CH$_3$)$_{\mathrm{as}}$
1443	1449.3	7.1	1449.9	7.1	δ(CH$_3$)$_{\mathrm{as'}}$
1426/1420	1421.8	58.1	1421.1	56.7	δ(CH)$_{\mathrm{ph}}$; ν(CC)$_{\mathrm{R}}$; ν(CO)
1384	1390.2	2.2	1390.5	2.5	δ(CH$_3$)$_{\mathrm{iso,s}}$ (+)
1365	1370.6	6.8	1369.3	6.5	δ(CH$_3$)$_{\mathrm{iso,s}}$ (−)
1350	1351.7	28.6	1346.9	9.2	δ(C$_7$H)
1302/1296	1304.8	10.2	1301.0	7.6	ν(CC)$_{\mathrm{ph}}$; δ(CH)$_{\mathrm{R}}$
	1291.8	3.2	1288.4	24.7	δ(CH)$_{\mathrm{ph}}$; δ(OH)
1279/1260	1255.7	71.4	1266.7	56.5	ν(CO) + ν(C$_5$C$_7$); δ(CH)$_{\mathrm{ph}}$; δ(C$_7$H)
1230	1211.8	36.4	1217.4	51.6	δ(OH); ν(C$_2$C$_{10}$)
1195/1187	1178.8	10.5	1176.4	4.8	δ(OH); δ(CH)$_{\mathrm{ph}}$; ν(C$_5$C$_7$)
1175**	1168.9	26.6	1169.6	34.3	δ(CH)$_{\mathrm{ph}}$; δ(OH)
1117/1104	1115.3	89.6	1104.4	89.1	δ(CH)$_{\mathrm{ph}}$; δ(OH); ν(CC)$_{\mathrm{ph}}$
1067/1058	1060.8	19.5	1051.9	12.4	ρ(CH$_3$)$_{\mathrm{iso}}$ (+)
998	994.8	22.8	993.5	29.1	ρ(CH$_3$)
857	838.5	20.7	837.4	20.4	γ(CH)$_{\mathrm{R}}$; γ(C)$_{\mathrm{ph}}$
818	810.4	17.0	807.9	16.1	γ(CH)$_{\mathrm{ph}}$
719	705.3	4.2	705.0	4.6	γ(C)$_{\mathrm{ph}}$
698	688.4	3.8	688.0	2.2	δ(CCC)$_{\mathrm{ph}}$
646	641.7	11.0	640.4	10.9	γ(C)$_{\mathrm{ph}}$

[a] Experimental wavenumbers correspond to the positions of the minima (for decreasing bands) or maxima (for increasing bands) observed upon NIR irradiations at 7090/7083 or 7072 cm^{-1}, respectively. Band at 1598 cm^{-1} is partially due to monomeric water. The band at 1175 cm^{-1} has a major contribution from the **tc** and **cc** conformers, as evidenced by the NIR irradiation results (see Figure 8 of the manuscript), but it is also expected to include partial contributions from the **tt** and **ct** conformers (see Figure 4 of the manuscript). [b] Calculated harmonic wavenumbers were multiplied by 0.945 or 0.980, for the regions above or below 2000 cm^{-1}, respectively. Calculated vibrations with very low intensity or without a corresponding feature in the experimental difference spectra are not shown. [c] Abbreviations: ν, stretching; δ, in-plane bending; γ, out-of-plane bending; iso, isopropyl group; ph, phenyl ring; as, antisymmetric; s, symmetric. Signs "+" and "–" designate combination of vibrations occurring in the same phase and in the opposite phase, respectively. The prime symbol (') is used to distinguish between different types of antisymmetric in-plane bending and rocking vibrations of the CH$_3$ group.

Table S4. Experimental (N_2, 15 K) and calculated [B3LYP/6-311++G(d,p)] infrared absorptions for the **tc** and **cc** conformers of carvacrol.





Exp.[a]	Calc. (**tc**)[b]		Calc. (**cc**)[b]		Approximate description[c]
	ν[b]	A^{th}	ν[b]	A^{th}	
3631	3632.9	66.3	3629.6	65.8	$\nu(\mathrm{OH})$
1635	1631.0	24.6	1630.8	25.5	$\nu(\mathrm{CC})_{\mathrm{ph}}$
1578	1579.2	58.1	1580.0	62.4	$\nu(\mathrm{CC})_{\mathrm{ph}}$
1507 (split)	1506.1	60.6	1507.3	55.6	$\nu(\mathrm{CC})_{\mathrm{ph}}$; $\delta(\mathrm{CH})_{\mathrm{ph}}$
1472	1477.8	6.7	1478.4	16.2	$\delta(\mathrm{CH_3})_{\mathrm{as}}$; $\delta(\mathrm{CH_3})_{\mathrm{iso,as}}$ (+)
1468	1472.4	13.7	1471.5	13.8	$\delta(\mathrm{CH_3})_{\mathrm{iso,as'}}$ (+)
1457	1460.9	2.8	1460.2	5.2	$\delta(\mathrm{CH_3})_{\mathrm{iso,as}}$ (−)
	1459.3	7.7	1459.8	5.3	$\delta(\mathrm{CH_3})_{\mathrm{as'}}$
1436	1433.6	28.0	1433.2	25.6	$\delta(\mathrm{CH})_{\mathrm{ph}}$; $\nu(\mathrm{CO})$; $\delta(\mathrm{C_7H})$
1346	1354.3	6.6	1348.9	29.9	$\delta(\mathrm{C_7H})$; $\delta(\mathrm{OH})$
1314/1305	1306.4	39.9	1298.3	5.6	$\nu(\mathrm{CC})_{\mathrm{ph}}$; $\delta(\mathrm{CH})_{\mathrm{ph}}$
1286	1278.2	57.7	1285.4	5.7	$\delta(\mathrm{CH})_{\mathrm{ph}}$; $\delta(\mathrm{OH})$
1271	1257.6	17.1	1262.8	64.9	$\nu(\mathrm{CO}) + \nu(\mathrm{C_5C_7}) + \nu(\mathrm{C_2C_{10}})$; $\delta(\mathrm{CH})_{\mathrm{ph}}$
1237	1217.3	53.5	1223.1	64.5	$\nu(\mathrm{C_5C_7}) - \nu(\mathrm{C_2C_{10}})$; $\delta(\mathrm{OH})$
1175* (split)	1167.6	90.6	1167.4	73.8	$\delta(\mathrm{CH})_{\mathrm{ph}}$; $\delta(\mathrm{OH})$
1147	–	–	1143.7	17.6	$\delta(\mathrm{CH})_{\mathrm{ph}}$; $\delta(\mathrm{OH})$
993	987.2	26.8	986.4	34.0	$\rho(\mathrm{CH_3})$
878	873.7	14.3	870.8	14.1	$\gamma(\mathrm{CH})_{\mathrm{ph}}$; $\gamma(\mathrm{C})_{\mathrm{R}}$
813	806.8	21.9	803.9	21.2	$\gamma(\mathrm{CH})_{\mathrm{ph}}$

[a] Experimental wavenumbers correspond to the positions of the minima (for decreasing bands) or maxima (for increasing bands) observed upon NIR irradiations at 7072 or 7090/7083 cm^{-1}, respectively. The band at 1175 cm^{-1} has a major contribution from the **tc** and **cc** conformers, as evidenced by the NIR irradiation results (see Figure 8 of the manuscript), but it is also expected to include partial contributions from the **tt** and **ct** conformers (see Figure 4 of the manuscript). [b] Calculated harmonic wavenumbers were multiplied by 0.945 or 0.980, for the regions above or below 2000 cm^{-1}, respectively. Calculated vibrations with very low intensity or without a corresponding feature in the experimental difference spectra are not shown. [c] Abbreviations: ν, stretching; δ, in-plane bending; γ, out-of-plane bending; iso, isopropyl group; R, phenyl ring; as, antisymmetric; s, symmetric. Signs "+" and "–" designate combination of vibrations occurring in the same phase and in the opposite phase, respectively. The prime symbol (') is used to distinguish between different types of antisymmetric in-plane bending and rocking vibrations of the CH_3 group.

3. Computational data

The optimized structures of each conformer of Thymol and Carvacrol are found below. The data was obtained at the B3LYP/6-311++g(2d,2p).

3.1 – Thymol

Optimized Structures:

GC = -464.8778758 Hartree

C	0.09305	-1.33237	0.04382
C	-0.58072	-0.12201	-0.12296
C	0.21248	1.03387	-0.20518
C	1.59982	0.96880	-0.12676
C	2.25412	-0.24715	0.04771
H	-0.47543	-2.24957	0.10336
H	2.15754	1.89254	-0.20656
C	3.75672	-0.30143	0.16477
H	4.23426	0.42254	-0.49552
H	4.07867	-0.07362	1.18372
H	4.13722	-1.29103	-0.08538
C	-2.09956	-0.02913	-0.17929
H	-2.36102	0.76205	-0.89445
C	-2.68388	0.36893	1.19115
H	-3.76347	0.51580	1.12706
H	-2.49150	-0.41652	1.92322
H	-2.23742	1.28736	1.57313
C	-2.78159	-1.29805	-0.70541
H	-3.85054	-1.12271	-0.83023
H	-2.37232	-1.60300	-1.66820
H	-2.67011	-2.13096	-0.01042
O	-0.32030	2.28922	-0.36682
H	-1.27388	2.23008	-0.46937
C	1.47846	-1.40332	0.13020
H	1.95693	-2.36564	0.25582

TC = -464.8763597 Hartree

C	1.72964	-1.34802	0.01109
C	0.34910	-1.49725	0.01908
C	-0.52710	-0.40926	0.00453
C	0.05985	0.86566	-0.02075
C	1.44332	1.02273	-0.02881
C	2.29849	-0.07435	-0.01026
H	2.36430	-2.22426	0.01889
H	-0.07128	-2.49530	0.03385
H	1.83648	2.03056	-0.05255
C	3.79440	0.11581	0.01240
H	4.09295	0.99561	-0.55725
H	4.15623	0.25136	1.03446
H	4.30929	-0.74917	-0.40433
C	-2.03047	-0.66047	0.01166
H	-2.14050	-1.74645	0.03271
C	-2.73734	-0.18739	-1.27331
H	-3.78397	-0.49538	-1.26469
H	-2.72370	0.89758	-1.39797
H	-2.26346	-0.61589	-2.15585
C	-2.73273	-0.13805	1.27989
H	-3.77972	-0.44487	1.28629
H	-2.25652	-0.53343	2.17653
H	-2.71699	0.95079	1.36300
O	-0.66439	2.03291	-0.04230
H	-1.60383	1.83891	-0.04231

GT = -464.8790281 Hartree

C	1.47172	-1.41170	0.14666
C	0.08305	-1.33959	0.05676
C	-0.59014	-0.13353	-0.11666
C	0.20412	1.02077	-0.19869
C	1.59001	0.95747	-0.11547
C	2.24842	-0.26069	0.05990
H	1.94917	-2.37324	0.28110
H	-0.48637	-2.25599	0.12059
H	2.16571	1.87468	-0.18797
C	3.75325	-0.31271	0.14452
H	4.21520	0.03805	-0.78057

TT = -464.8783827 Hartree

C	-1.72774	-1.35483	-0.01100
C	-0.34427	-1.51125	-0.01234
C	0.53719	-0.43215	-0.00112
C	-0.04422	0.84568	0.01167
C	-1.42520	1.01110	0.01314
C	-2.29122	-0.08280	0.00217
H	-2.36664	-2.22782	-0.02046
H	0.07035	-2.51153	-0.02286
H	-1.83228	2.01733	0.02282
C	-3.78525	0.12237	0.00736
H	-4.11099	0.64474	0.90906

H	4.12823	0.31817	0.95252
H	4.10137	-1.32836	0.32534
C	-2.10510	-0.02187	-0.18829
H	-2.32731	0.78598	-0.88800
C	-2.68883	0.38805	1.17739
H	-3.76816	0.53455	1.10587
H	-2.50176	-0.38654	1.92355
H	-2.24444	1.31633	1.53319
C	-2.79273	-1.28745	-0.71298
H	-3.85875	-1.10124	-0.84844
H	-2.38094	-1.60074	-1.67275
H	-2.69858	-2.12217	-0.01640
O	-0.44302	2.22265	-0.36681
H	0.20821	2.92678	-0.43234

H	-4.10746	0.72043	-0.84707
H	-4.31224	-0.82943	-0.03417
C	2.03920	-0.67251	-0.00363
H	2.16085	-1.75861	-0.01438
C	2.72765	-0.15873	1.27307
H	3.78173	-0.44197	1.27149
H	2.66872	0.92568	1.34582
H	2.26636	-0.58476	2.16467
C	2.72744	-0.13358	-1.27004
H	3.78154	-0.41673	-1.27421
H	2.26604	-0.54196	-2.16981
H	2.66843	0.95205	-1.32136
O	0.79053	1.93900	0.02240
H	0.25989	2.74082	0.03052

Transition States:

GC-TC = -464.8682288 Hartree			
C	1.60339	-1.36849	-0.11048
C	0.22177	-1.37282	-0.20394
C	-0.56314	-0.20879	-0.16843
C	0.15647	0.99503	-0.05268
C	1.54998	1.00141	0.05497
C	2.29682	-0.16516	0.03131
H	2.14289	-2.30589	-0.14855
H	-0.26637	-2.32826	-0.31861
H	2.03191	1.96540	0.14909
C	3.79744	-0.13683	0.17074
H	4.27169	-0.83838	-0.51630
H	4.19717	0.85631	-0.02935
H	4.10205	-0.41789	1.18157
C	-2.09021	-0.34622	-0.33716
H	-2.28000	-0.45078	-1.41126
C	-2.95246	0.83887	0.14541
H	-4.00183	0.54522	0.15038
H	-2.70095	1.14370	1.16287
H	-2.90672	1.70570	-0.51950
C	-2.63828	-1.61785	0.34008
H	-3.71676	-1.67855	0.19143
H	-2.20987	-2.53202	-0.06209
H	-2.44461	-1.60027	1.41392
O	-0.39623	2.25126	-0.05178
H	-1.35288	2.19644	-0.06251

GT-GC = -464.8733043 Hartree			
C	-1.42630	-1.40551	0.15393
C	-0.04384	-1.29041	0.11780
C	0.59541	-0.05503	-0.02518
C	-0.22934	1.07023	-0.11927
C	-1.61685	0.95946	-0.09554
C	-2.24114	-0.27725	0.04066
H	-1.87726	-2.38310	0.26821
H	0.55558	-2.18739	0.20343
H	-2.20193	1.86484	-0.19117
C	-3.74463	-0.39593	0.03562
H	-4.11693	-0.62062	-0.96678
H	-4.08133	-1.19692	0.69375
H	-4.21827	0.53009	0.35967
C	2.11082	0.05616	-0.06309
H	2.34533	1.09503	-0.29163
C	2.72623	-0.80639	-1.17661
H	3.80568	-0.65356	-1.22266
H	2.55146	-1.86988	-1.00617
H	2.30629	-0.55051	-2.14927
C	2.73625	-0.27722	1.30261
H	3.81852	-0.13963	1.27389
H	2.33550	0.36155	2.09069
H	2.53918	-1.31264	1.58582
O	0.32077	2.33819	-0.30869
H	0.49944	2.74691	0.54270

TC-TT = -464.8724456 Hartree			
C	1.73367	-1.34394	-0.03978
C	0.35279	-1.50792	-0.04329

TT -GT = -464.8693153 Hartree			
C	1.59811	-1.37595	-0.13998
C	0.21390	-1.37992	-0.23438

C	-0.52946	-0.42565	-0.02128	C	-0.57374	-0.22215	-0.17636
C	0.05084	0.85027	-0.00581	C	0.14272	0.97936	-0.04256
C	1.42947	1.02012	0.00738	C	1.53531	0.98797	0.06592
C	2.29828	-0.07099	-0.00893	C	2.28918	-0.17768	0.02554
H	2.37446	-2.21607	-0.05767	H	2.13982	-2.31104	-0.19578
H	-0.05737	-2.50996	-0.06091	H	-0.27525	-2.33293	-0.36788
H	1.81461	2.03131	0.03651	H	2.03690	1.94442	0.17536
C	3.79241	0.13056	0.02847	C	3.78853	-0.14369	0.17622
H	4.10567	0.91834	-0.65748	H	4.20425	0.80293	-0.16839
H	4.12513	0.42063	1.02768	H	4.08018	-0.26823	1.22184
H	4.32098	-0.78234	-0.24253	H	4.26010	-0.94632	-0.39024
C	-2.03000	-0.67728	0.00070	C	-2.09895	-0.35366	-0.33452
H	-2.14430	-1.76353	-0.03552	H	-2.28126	-0.51270	-1.40371
C	-2.76296	-0.12111	-1.23228	C	-2.94462	0.86105	0.08272
H	-3.79489	-0.47563	-1.24761	H	-4.00032	0.60565	-0.01878
H	-2.79783	0.96820	-1.22329	H	-2.76575	1.13188	1.12386
H	-2.28446	-0.44324	-2.15773	H	-2.74761	1.73667	-0.52596
C	-2.68715	-0.19905	1.30701	C	-2.64681	-1.59121	0.40413
H	-3.74386	-0.47250	1.32092	H	-3.72532	-1.65673	0.25818
H	-2.20988	-0.65740	2.17345	H	-2.21890	-2.52794	0.05411
H	-2.61161	0.88176	1.41162	H	-2.45687	-1.51527	1.47629
O	-0.74257	1.99555	0.06733	O	-0.52392	2.18202	-0.03364
H	-0.99496	2.27115	-0.81808	H	0.11961	2.88874	0.06981

3.2 – Carvacrol

Optimized Structures:

CC = -464.8800487 Hartree				CT = -464.8805402 Hartree			
C	0.35224	-1.95355	0.00000	C	0.35895	-1.96465	0.00000
C	-0.92437	-1.38226	0.00000	C	-0.91603	-1.39136	0.00000
C	-1.09631	-0.00088	0.00000	C	-1.08736	-0.00982	0.00000
C	-0.00302	0.86021	0.00000	C	0.00598	0.85560	0.00000
C	1.27707	0.29828	0.00000	C	1.28215	0.29136	0.00000
C	1.44032	-1.08042	0.00000	C	1.44335	-1.09010	0.00000
C	-0.21505	2.36587	0.00000	C	-0.20761	2.36109	0.00000
C	0.35224	3.02585	1.26742	C	0.35895	3.02192	1.26731
C	0.35224	3.02585	-1.26742	C	0.35895	3.02192	-1.26731
C	0.53381	-3.44991	0.00000	C	0.52829	-3.45966	0.00000
O	-2.06531	-2.14558	0.00000	O	-1.98705	-2.25218	0.00000
H	-2.10585	0.38829	0.00000	H	-2.09301	0.39775	0.00000
H	2.15250	0.93306	0.00000	H	2.15863	0.92480	0.00000
H	2.43995	-1.49690	0.00000	H	2.44294	-1.50647	0.00000
H	-1.29490	2.53273	0.00000	H	-1.28787	2.52833	0.00000
H	0.13132	4.09453	1.27502	H	0.13757	4.09052	1.27484
H	-0.07560	2.58375	2.16728	H	-0.06786	2.57949	2.16751

H	1.43579	2.91058	1.32245
H	-0.07560	2.58375	-2.16728
H	0.13132	4.09453	-1.27502
H	1.43579	2.91058	-1.32245
H	0.08805	-3.91861	-0.88271
H	1.59074	-3.70886	0.00000
H	0.08805	-3.91861	0.88271
H	-1.83405	-3.07838	0.00000

H	1.44242	2.90686	1.32183
H	-0.06786	2.57949	-2.16751
H	0.13757	4.09052	-1.27484
H	1.44242	2.90686	-1.32183
H	0.05922	-3.91280	-0.87500
H	1.58360	-3.72728	0.00000
H	0.05922	-3.91280	0.87500
H	-2.80420	-1.74558	0.00000

TC = -464.880176 Hartree

C	1.22603	-1.60196	0.00000
C	1.47734	-0.22335	0.00000
C	0.43968	0.70057	0.00000
C	-0.89118	0.28464	0.00000
C	-1.15073	-1.08615	0.00000
C	-0.10693	-2.00512	0.00000
C	-2.03074	1.29093	0.00000
C	-2.03074	2.16134	1.26733
C	-2.03074	2.16134	-1.26733
C	2.35840	-2.59670	0.00000
O	2.75404	0.28198	0.00000
H	0.69969	1.75028	0.00000
H	-2.17369	-1.43882	0.00000
H	-0.33095	-3.06454	0.00000
H	-2.95815	0.71293	0.00000
H	-2.89482	2.82783	1.27500
H	-2.06670	1.54739	2.16736
H	-1.13390	2.78029	1.32214
H	-2.06670	1.54739	-2.16736
H	-2.89482	2.82783	-1.27500
H	-1.13390	2.78029	-1.32214
H	2.99689	-2.49341	0.88273
H	1.97508	-3.61512	0.00000
H	2.99689	-2.49341	-0.88273
H	3.39044	-0.43809	0.00000

TT = -464.8806328 Hartree

C	1.22644	-1.61758	0.00000
C	1.47998	-0.24001	0.00000
C	0.44527	0.68751	0.00000
C	-0.89062	0.27835	0.00000
C	-1.15086	-1.08971	0.00000
C	-0.10698	-2.01230	0.00000
C	-2.02644	1.28874	0.00000
C	-2.02640	2.15915	1.26739
C	-2.02640	2.15915	-1.26739
C	2.36144	-2.60504	0.00000
O	2.79859	0.14684	0.00000
H	0.69147	1.74367	0.00000
H	-2.17460	-1.44032	0.00000
H	-0.33474	-3.07084	0.00000
H	-2.95472	0.71244	0.00000
H	-2.89055	2.82550	1.27573
H	-2.06135	1.54508	2.16725
H	-1.13031	2.77969	1.32243
H	-2.06135	1.54508	-2.16725
H	-2.89055	2.82550	-1.27573
H	-1.13031	2.77969	-1.32243
H	3.00073	-2.47563	0.87494
H	1.98292	-3.62583	0.00000
H	3.00073	-2.47563	-0.87494
H	2.85013	1.10690	0.00000

Transition States:

CC-TC = -464.8764373 Hartree

C	1.95711	-0.50220	0.02868
C	1.38967	0.77458	-0.03138
C	0.01445	0.95373	-0.13299
C	-0.85966	-0.13294	-0.17974
C	-0.29617	-1.41227	-0.12023
C	1.07915	-1.58227	-0.01903
C	-2.36758	0.07305	-0.34589
C	-3.20426	-1.07741	0.23449

CT-CC = -464.8747712 Hartree

C	1.91215	-0.55671	-0.00068
C	1.47284	0.76880	-0.00746
C	0.11875	1.08396	-0.01280
C	-0.85654	0.08790	0.00327
C	-0.42442	-1.24008	0.01755
C	0.93013	-1.54892	0.01327
C	-2.33268	0.45228	-0.00392
C	-3.04254	-0.05237	-1.27099

C	-2.86653	1.40911	0.22531	C	-3.05269	-0.03643	1.26355
C	3.44808	-0.68916	0.14219	C	3.38005	-0.89035	-0.01167
O	2.15520	1.91429	0.00884	O	2.40659	1.79999	-0.08529
H	-0.34628	1.96996	-0.17332	H	-0.16365	2.12859	-0.03934
H	-0.92255	-2.29014	-0.15163	H	-1.14600	-2.04613	0.02638
H	1.48496	-2.58524	0.02669	H	1.23740	-2.58719	0.01744
H	-2.55986	0.09509	-1.42498	H	-2.38807	1.54364	-0.01114
H	-4.26600	-0.86938	0.09929	H	-4.08324	0.27573	-1.28453
H	-2.99866	-2.02965	-0.25130	H	-2.55586	0.32258	-2.17137
H	-3.01869	-1.19714	1.30341	H	-3.03771	-1.14241	-1.31916
H	-2.41567	2.26868	-0.26749	H	-2.57413	0.35037	2.16342
H	-3.94555	1.49066	0.09150	H	-4.09363	0.29113	1.26416
H	-2.65366	1.48307	1.29331	H	-3.04808	-1.12572	1.32611
H	3.85183	-0.23386	1.05168	H	3.87516	-0.55946	0.90409
H	3.70137	-1.74698	0.17430	H	3.53041	-1.96494	-0.10140
H	3.98290	-0.25603	-0.70859	H	3.89048	-0.39792	-0.83941
H	3.08468	1.68062	0.07927	H	2.64398	2.09595	0.79808

TC-TT = -464.8749094 Hartree				TT-CT =-464.8769209 Hartree			
C	-1.98064	-0.41881	0.00005	C	1.96738	-0.51006	0.02918
C	-1.27010	0.78647	0.01246	C	1.39916	0.76579	-0.02958
C	0.11732	0.81253	0.01430	C	0.02384	0.94591	-0.13109
C	0.86144	-0.36942	-0.01138	C	-0.85542	-0.14023	-0.17904
C	0.15985	-1.57353	-0.03140	C	-0.29080	-1.41622	-0.12039
C	-1.23167	-1.59375	-0.02340	C	1.08706	-1.58565	-0.01946
C	2.38143	-0.35051	-0.00838	C	-2.36296	0.06746	-0.34657
C	2.95269	0.34362	-1.25558	C	-3.20019	-1.08087	0.23708
C	2.94634	0.27405	1.27800	C	-2.86266	1.40482	0.22131
C	-3.48573	-0.43321	0.01528	C	3.45686	-0.68604	0.14250
O	-1.96871	1.98916	0.09911	O	2.26295	1.83379	0.02051
H	0.60403	1.77820	0.04595	H	-0.35511	1.95872	-0.17152
H	0.70512	-2.50862	-0.04785	H	-0.91668	-2.29450	-0.15257
H	-1.74907	-2.54482	-0.03231	H	1.49183	-2.58899	0.02545
H	2.70733	-1.39323	-0.03645	H	-2.55615	0.08702	-1.42552
H	4.04237	0.28587	-1.26205	H	-4.26187	-0.87423	0.09910
H	2.58233	-0.12038	-2.16988	H	-2.99262	-2.03450	-0.24479
H	2.67726	1.39918	-1.28183	H	-3.01585	-1.19648	1.30659
H	2.57257	-0.24056	2.16320	H	-2.41628	2.26421	-0.27690
H	4.03612	0.21763	1.28583	H	-3.94200	1.48461	0.08975
H	2.66814	1.32574	1.36236	H	-2.64782	1.48328	1.28864
H	-3.90197	0.01168	-0.89132	H	3.84602	-0.20831	1.04323
H	-3.86041	-1.45286	0.08828	H	3.71803	-1.74248	0.17477
H	-3.87756	0.14167	0.85451	H	3.97618	-0.22934	-0.70168
H	-2.13967	2.33398	-0.78188	H	1.76128	2.65280	-0.02358