Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Characteristic nuclear spin-induced optical rotation in oxygen-containing organic molecules

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Supporting Information

Contents

1 List of molecules

Table S 1: The molecules used in implicit solvent calculations. (*) The molecule was also used in conformation search; (**) The molecule was also used in vacuum and explicit solvent calculations; (***) The molecule was also used in NMR calculations

Alcohols	4-(1-ethyl-2-methylpropyl)-3,4,5-trimethyl-3-octanol (*)(**)(***)
	3-ethyl-6,6-dimethyl-4-(1,1-dimethylpropyl)-2-octanol
	6-(1-ethylpropyl)-2,3,7,7-tetramethyl-2-nonanol
	2,3,3-trimethyl-2-hexanol
	4,4,5,5,6,6-hexamethyl-2-octanol
	2,4,4,5,5-pentamethyl-2-heptanol
	4,5,5,8-tetramethyl-4-nonanol
	3-ethyl-6-methyl-4-(1,1-dimethylethyl)-4-propyl-2-heptanol (**)(***)
	3-ethyl-4,4-dimethyl-1-hexanol (**)
	3,4-dimethyl-1-hexanol
	4-methyl-1-pentanol (***)
Ethers	4,4-dimethyl-2-isopropoxypentane (*)(**)(***)
	4-(1-methylpropyl)-3-methoxyoctane
	5-ethyl-2,3,3-trimethyl-2-methoxyheptane
	2,4,4,5-tetramethyl-5-propyl-2-methoxyoctane
	2,3,3,5-tetramethyl-4-propyl-2-methoxyheptane
	3-ethyl-2-methoxy-2,3,4,4-tetramethylheptane (**)(***)
	2,2,4,4,5,5-hexamethyl-3-(1-methylethyl)-1-ethoxyhexane
	4,4-dimethyl-1-ethoxyhexane
	3,4,4-trimethyl-1-ethoxyhexane
	3,3,4,4-tetramethyl-1-ethoxyhexane
	3,3,4,4,5-pentamethyl-1-ethoxyhexane
	3,3,4,4,5,5-hexamethyl-1-ethoxyhexane
	3,4,4-trimethyl-3-(1-methylethyl)-2-(1-methylpropyl)-1-(2-methylpropoxy)pentane (**)(***)
Ketones	3-ethyl-4-(1-methylpropyl)-2-octanone (*)(**)(***)
	4,4,5,5,6-pentamethyl-2-nonanone
	4,4,5,5,7-pentamethyl-3-octanone (**)(***)
	6-ethyl-5,5,6-trimethyl-3-octanone
	4,4,5,8-tetramethyl-6-propyl-3-nonanone
	3,3,7,7,8,9,9-heptamethyl-4-decanone (**)
	6-ethyl-3,7-dimethyl-4,5-bis(1-methylethyl)-2-octanone
	4-methyl-5-(1-methylethyl)-6-(1,1-dimethylethyl)-3-decanone
	6,6-diethyl-3-methyl-4-(2,2-dimethylpropyl)-2-nonanone
Aldehydes	2,4,6,6-tetramethylheptanal (*)(**)(***)
	2,5-diethyl-2,4,5-trimethylheptanal
	3,6-diethyl-2-methyl-5-(1-methylethyl)octanal
	2,3-diethyl-2,5-dimethylhexanal (**)
	3-ethyl-5,5,6,6-tetramethyloctanal
	3,3,6,6-tetramethylheptanal
	2,2,3,3,4,6-hexamethyl-4-propylheptanal (***)
	4-ethyl-3,3,4-trimethylhexanal (**)
	2,3,3,4,5,5,6,6-octamethyloctanal
	4-ethyl-4,5-dimethylhexanal (***)

2 Investigation of energies

Table S 2: Ordering of energies in conformation search. Conformer number 1 has the lowest energy, conformer number 15 has the highest energy. The conformers are numbered according to the order by XTB.

Alcohol			Ketone			Ether			Aldehyde		
XTB	PBE0	B3LYP	XTB	PBE0	B3LYP	XTB	PBE0	B3LYP	XTB	PBE0	B3LYP
1	5	5	1	1	1	1	8	1	1	2	2
2	1	1	2	2	3	2	6	2	2	1	1
3	6	6	3	4	4	3	7	3	3	4	15
4	9	7	4	9	10	4	10	13	4	3	3
5	2	4	5	6	7	5	14	15	5	15	14
6	3	3	6	5	5	6	11	14	6	7	6
7	14	14	7	8	8	7	1	4	7	8	7
8	4	2	8	7	6	8	9	11	8	13	11
9	10	10	9	13	14	9	5	6	9	11	8
10	11	11	10	10	9	10	2	5	10	12	12
11	13	13	11	3	2	11	13	10	11	10	10
12	12	12	12	11	13	12	12	12	12	9	9
13	7	8	13	12	11	13	3	9	13	14	13
14	8	9	14	14	15	14	15	8	14	5	4
15	15	15	15	15	12	15	4	7	15	6	5

3 Details of the PCM calculations

The radii for atoms in the PCM model were defined for heavy atoms only. The radii are given in Table S3 in Ångtröms.

Table S 3: The radii of the PCM spheres (Å).

Atom type	radius
C (quartenary carbon)	1.70
CH, CH_2	1.90
CH_3	2.00
O	1.52
OH group	1.72
O in water	1.72

4 Effect of conformation

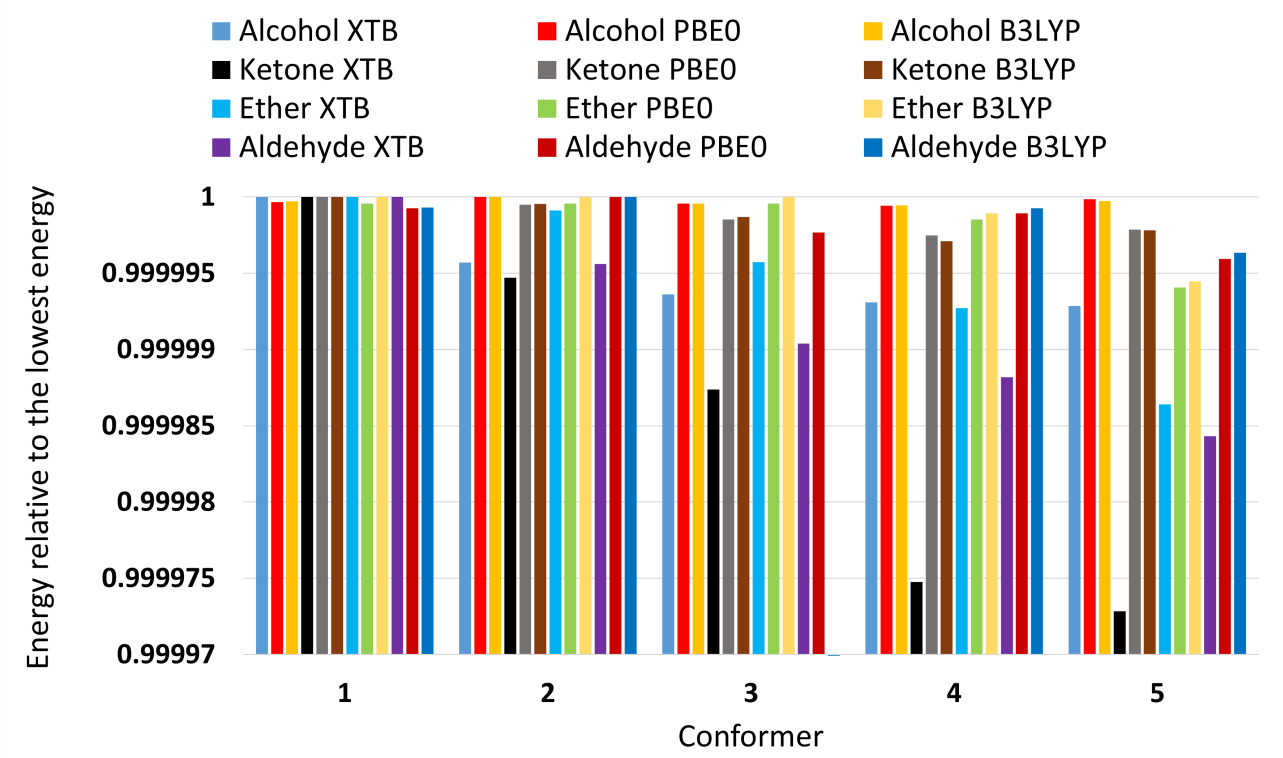

Figure S 1: Energies relative to the lowest energy for the first five conformers in different quantum-chemical methods. All of the energies are negative, meaning that the bar for the lowest energy is the tallest. For example, if the lowest energy was -100 arbitrary units and the next energy was -98, then the bars would have values -100/-100=1 and -98/-100=0.98, respectively. This facilitates easy interpretation of the figure: The higher the bar, the lower the energy. The bar for conformer 3 in the aldehyde with method B3LYP is much shorter than all the other bars, so that's why it is not clearly visible.

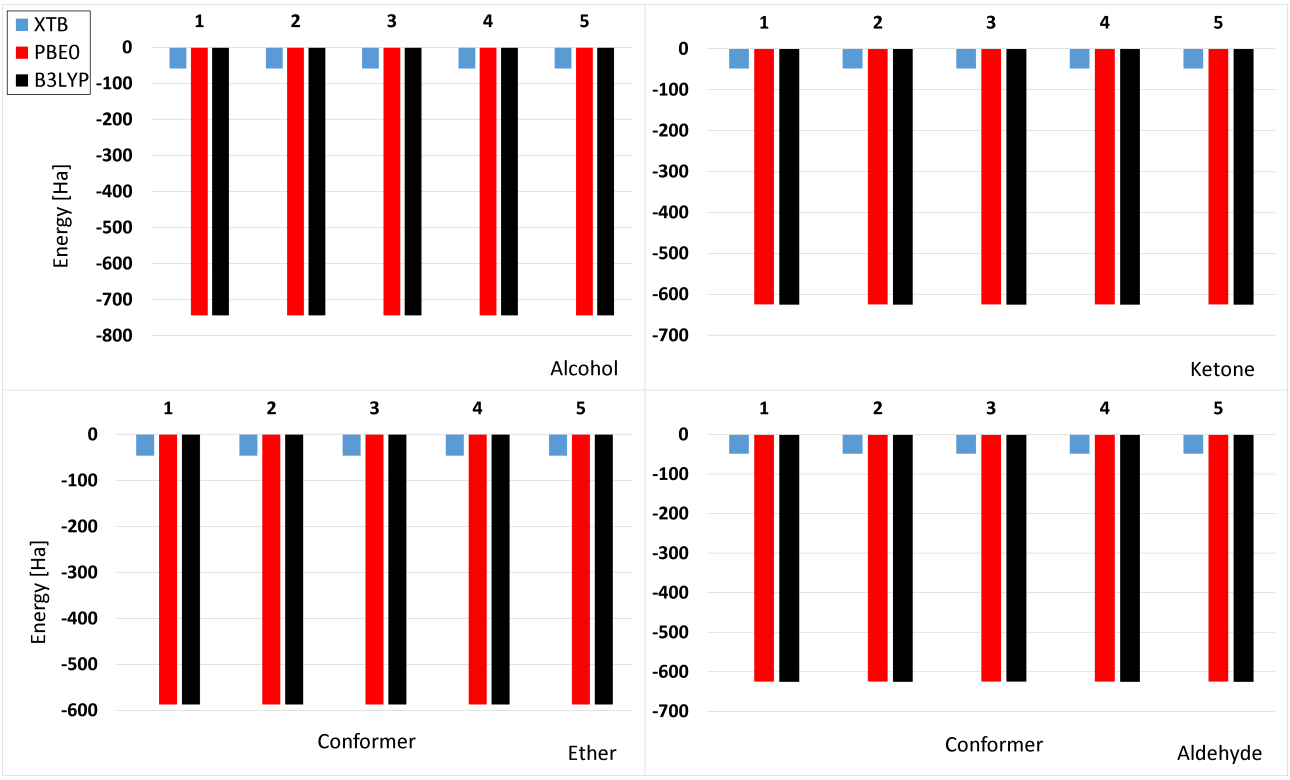

Figure S 2: Absolute energies for the five first conformers in different quantum-chemical methods. The x-axis shows the conformer and the y-axis shows the energy in Hartrees.

5 Dihedral scan

To further investigate the effect of conformation, NSOR of four short-chain model molecules was calculated (2-methylbutanol, 2-methylbutanal, 3-methylpentan-2-one, 1-methoxy-2-methylbutane) with geometries where the dihedral angle defined by oxygen and three carbons along the carbon chain was fixed at a certain angle. We scanned from 30 to 345 degrees with 30 degree steps. Reference structure was freely optimized. Also energies were observed.

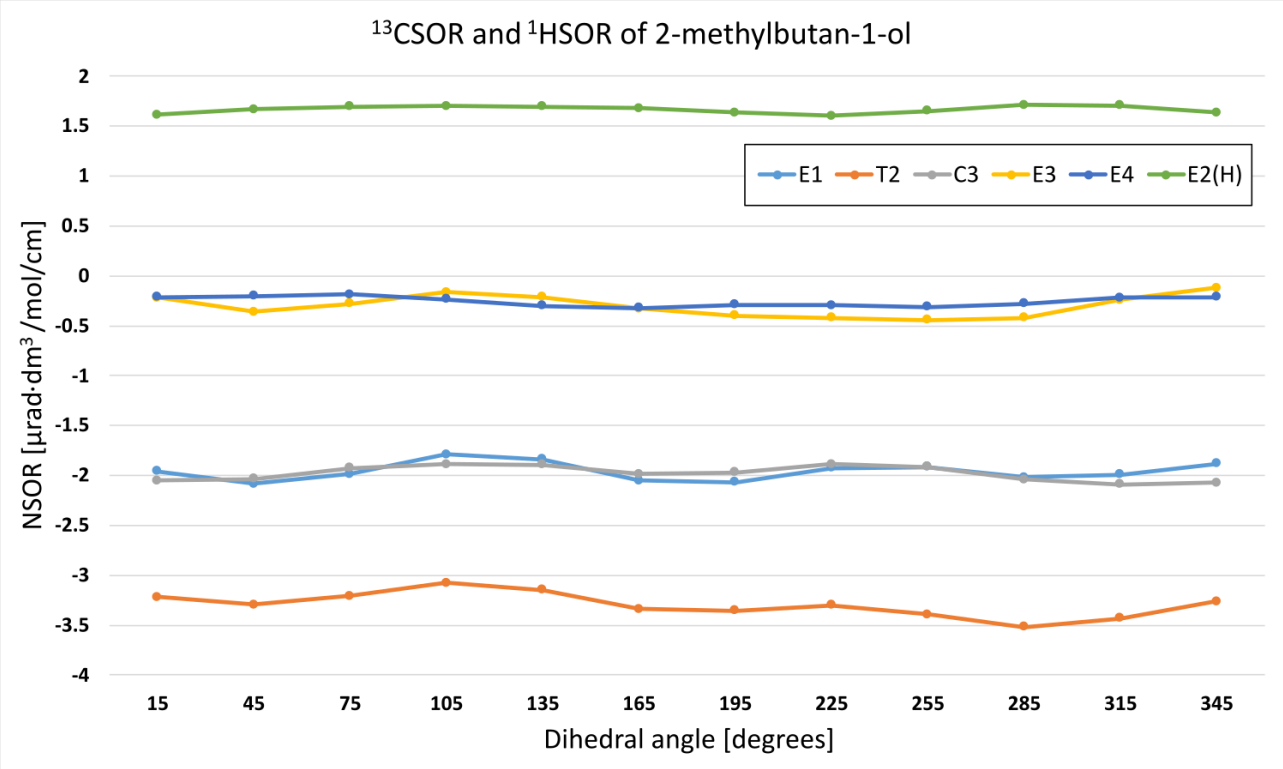

Figure S 3: NSORs of different atom types in the alcohol structure at different dihedral angles.

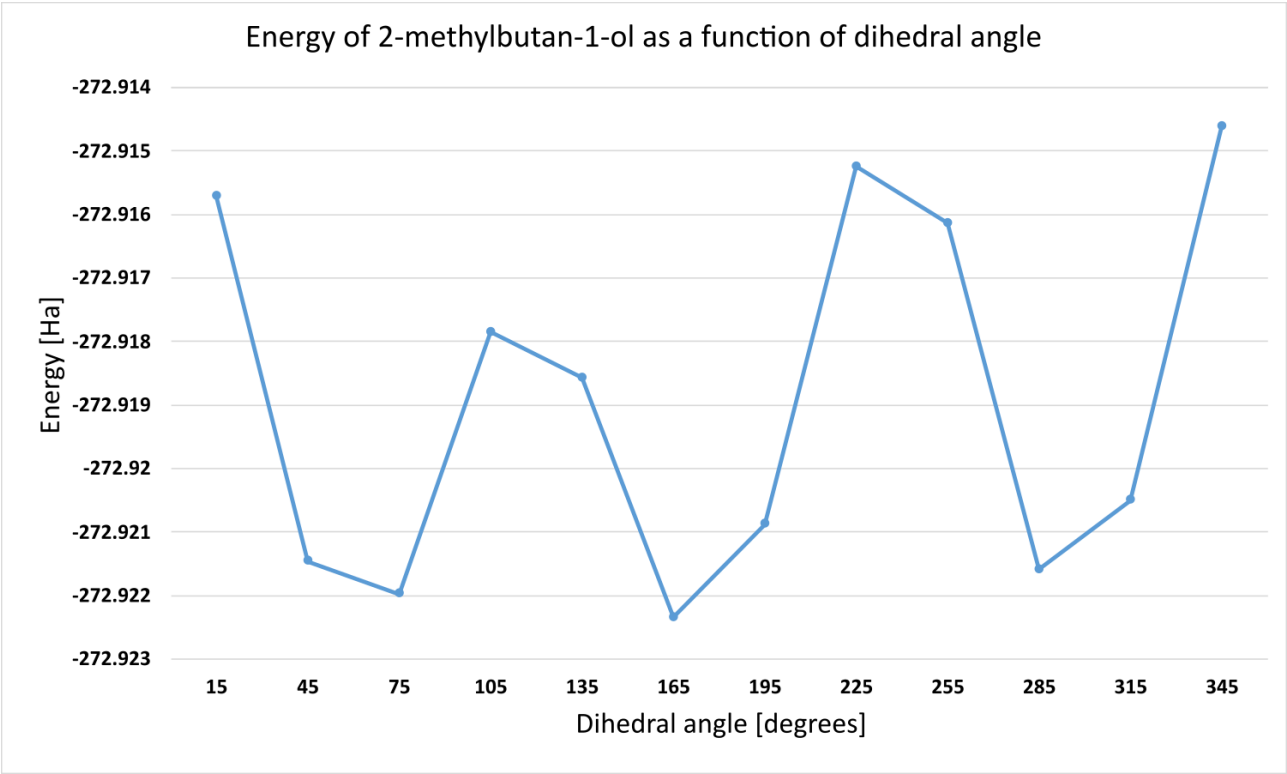

Figure S 4: Molecular energies of the alcohol at different diheral angles.

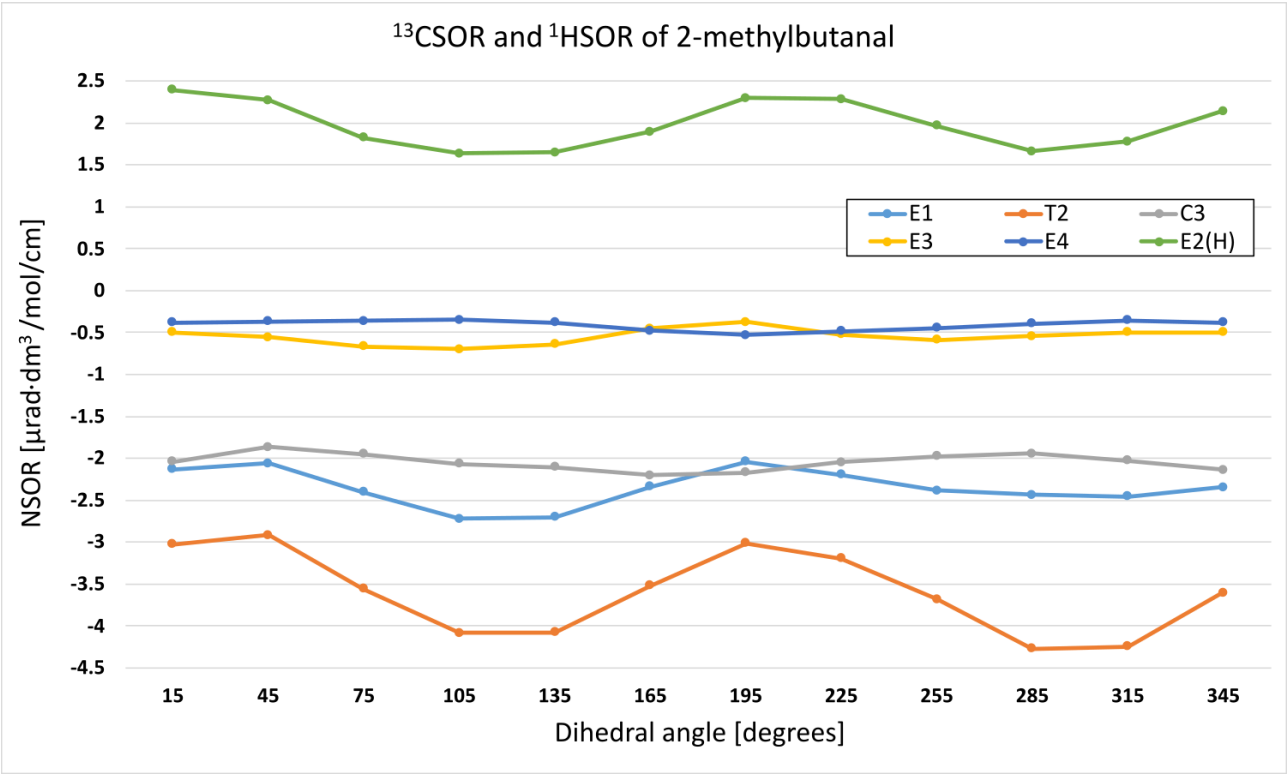

Figure S 5: NSORs of different atom types in the aldehyde structure at different dihedral angles.

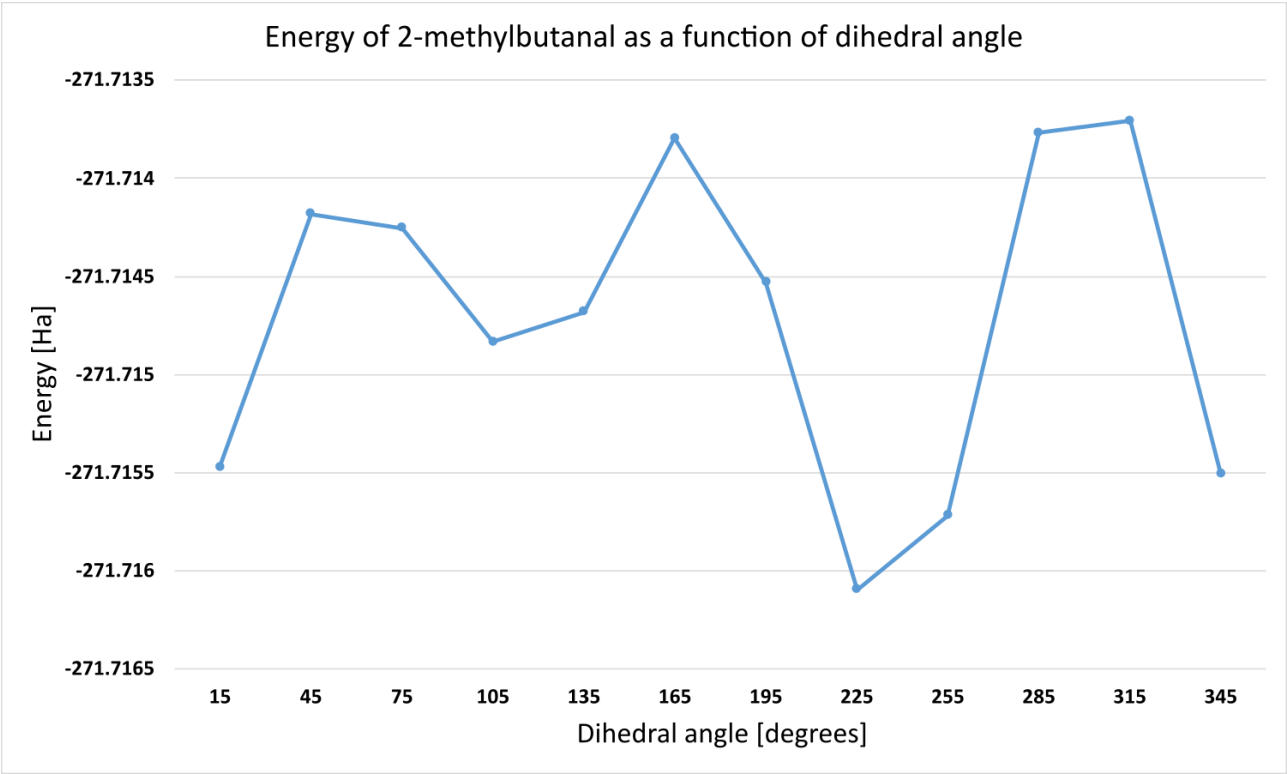

Figure S 6: Molecular energies of the aldehyde at different diheral angles.

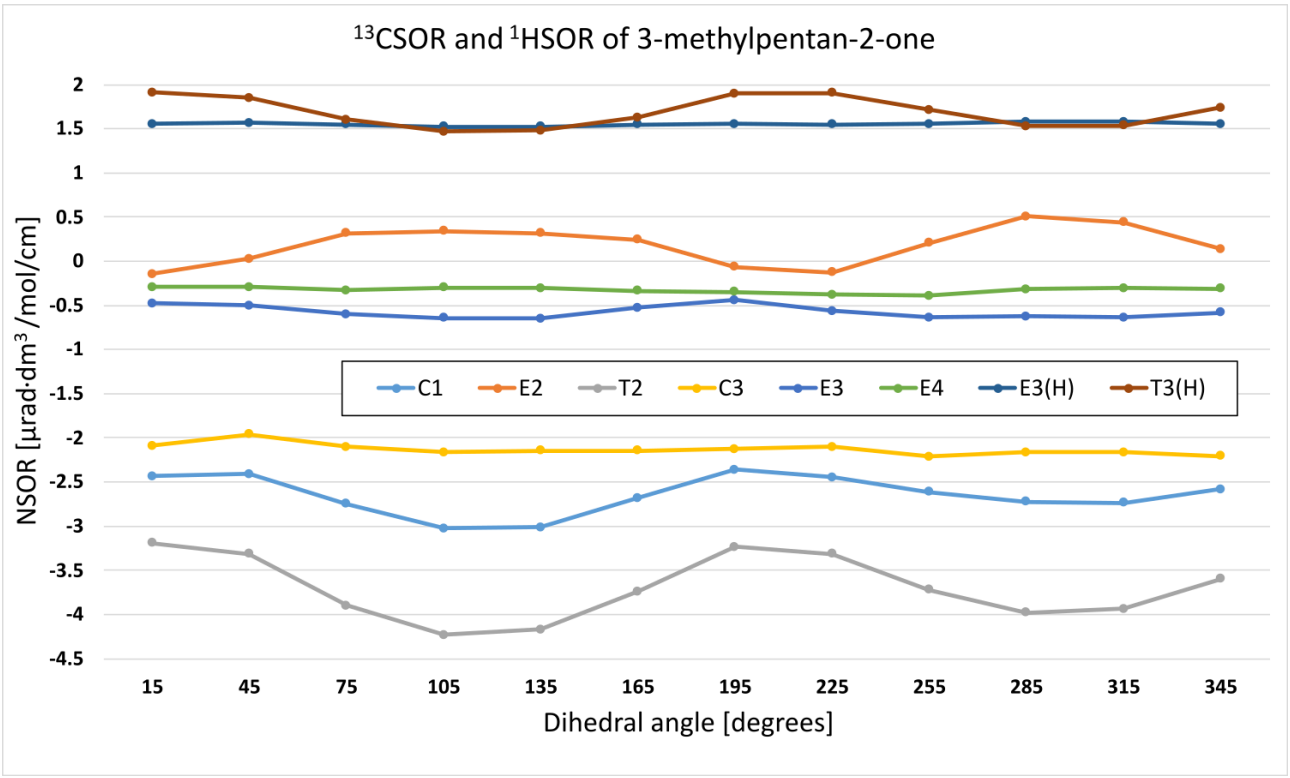

Figure S 7: NSORs of different atom types in the ketone structure at different dihedral angles.

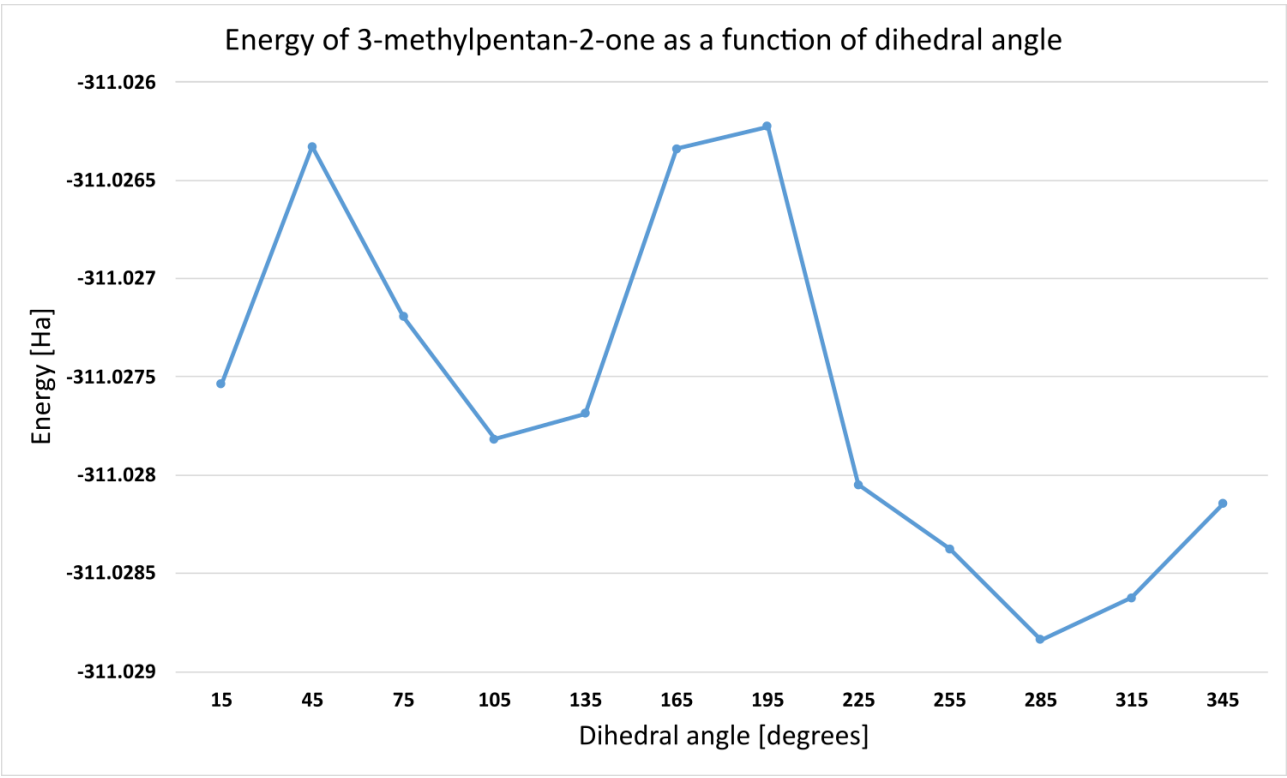

Figure S 8: Molecular energies of the ketone at different dihedral angles.

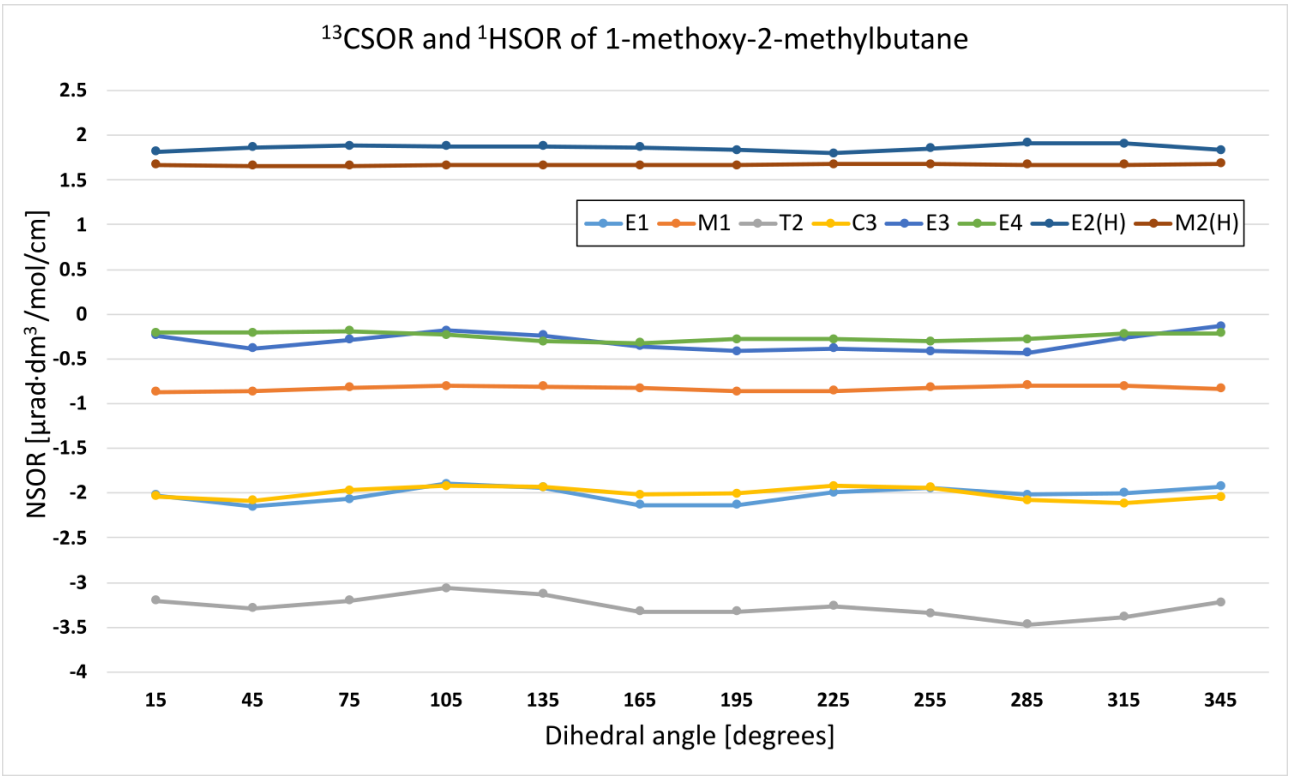

Figure S 9: NSORs of different atom types in the ether structure at different dihedral angles.

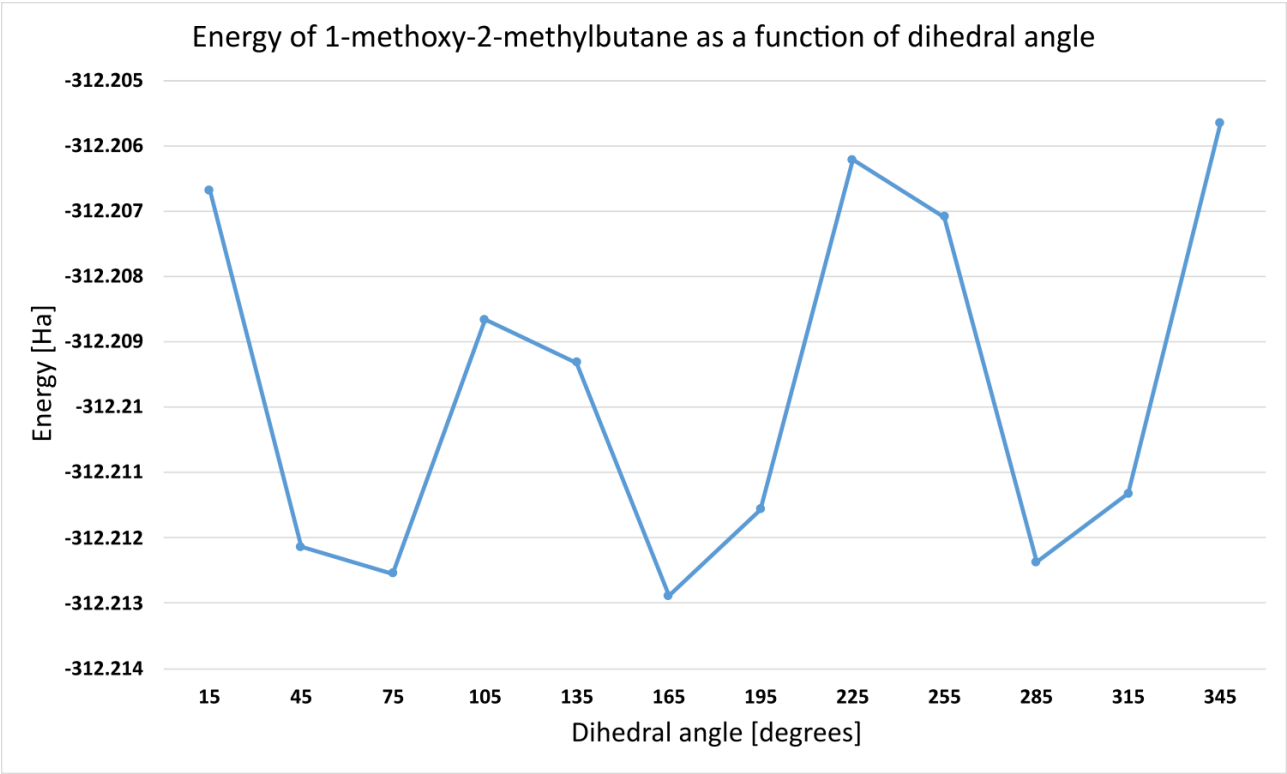

Figure S 10: Molecular energies of the ether at different diheral angles.

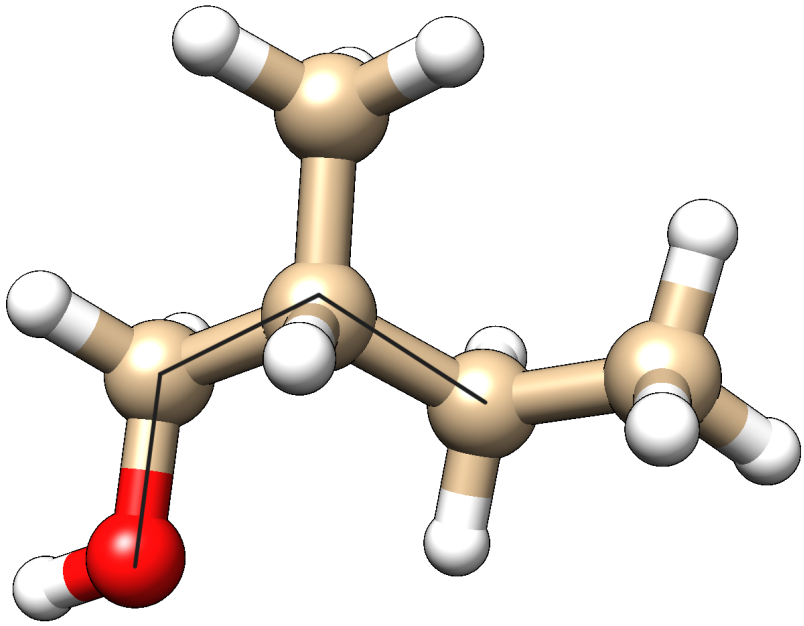

Figure S 11: Structure of 2-methylbutan-1-ol. Black line indicates the fixed dihedral angle.

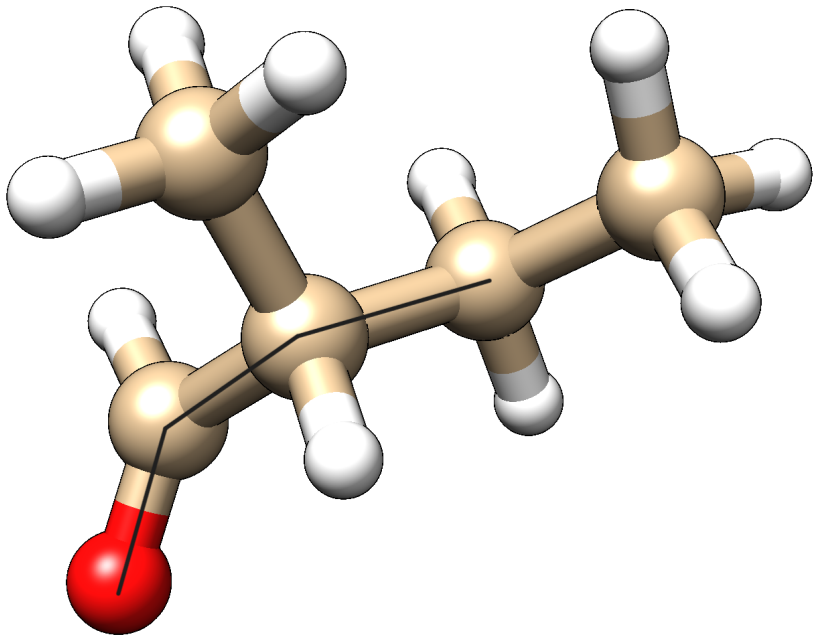

Figure S 12: Structure of 2-methylbutanal. Black line indicates the fixed dihedral angle.

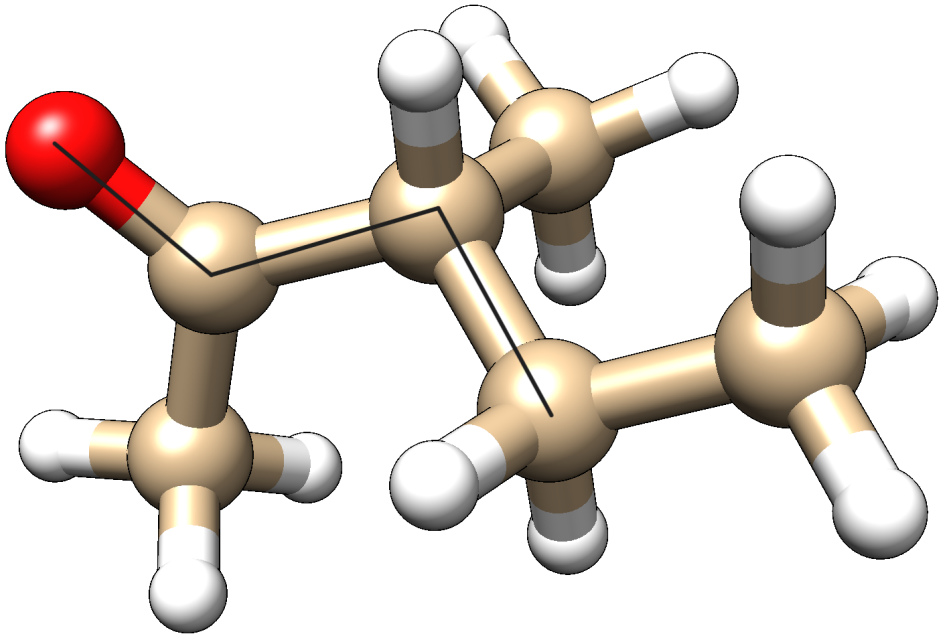

Figure S 13: Structure of 3-methylpentan-2-one. Black line indicates the fixed dihedral angle.

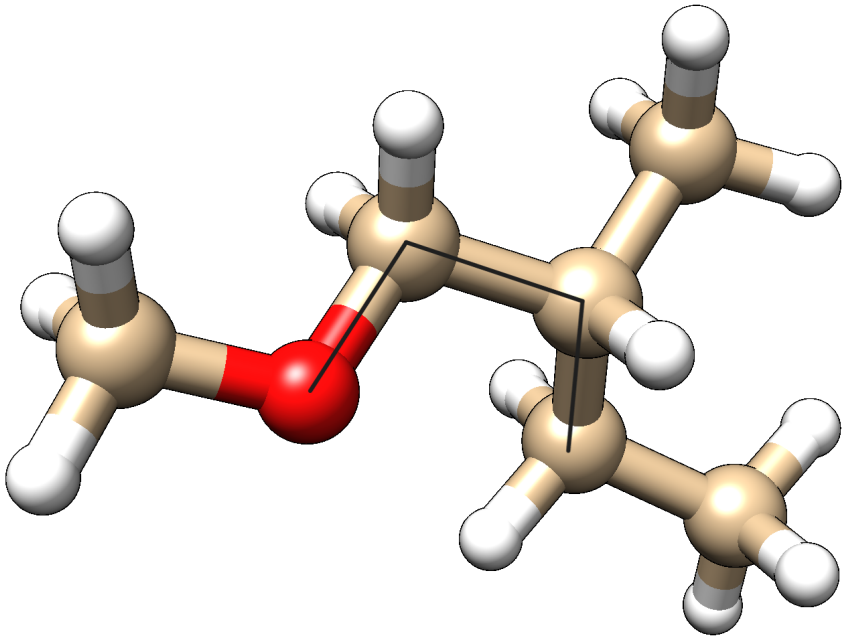

Figure S 14: Structure of 1-methoxy-2-methylbutane. Black line indicates the fixed dihedral angle.

6 Effect of solvent model

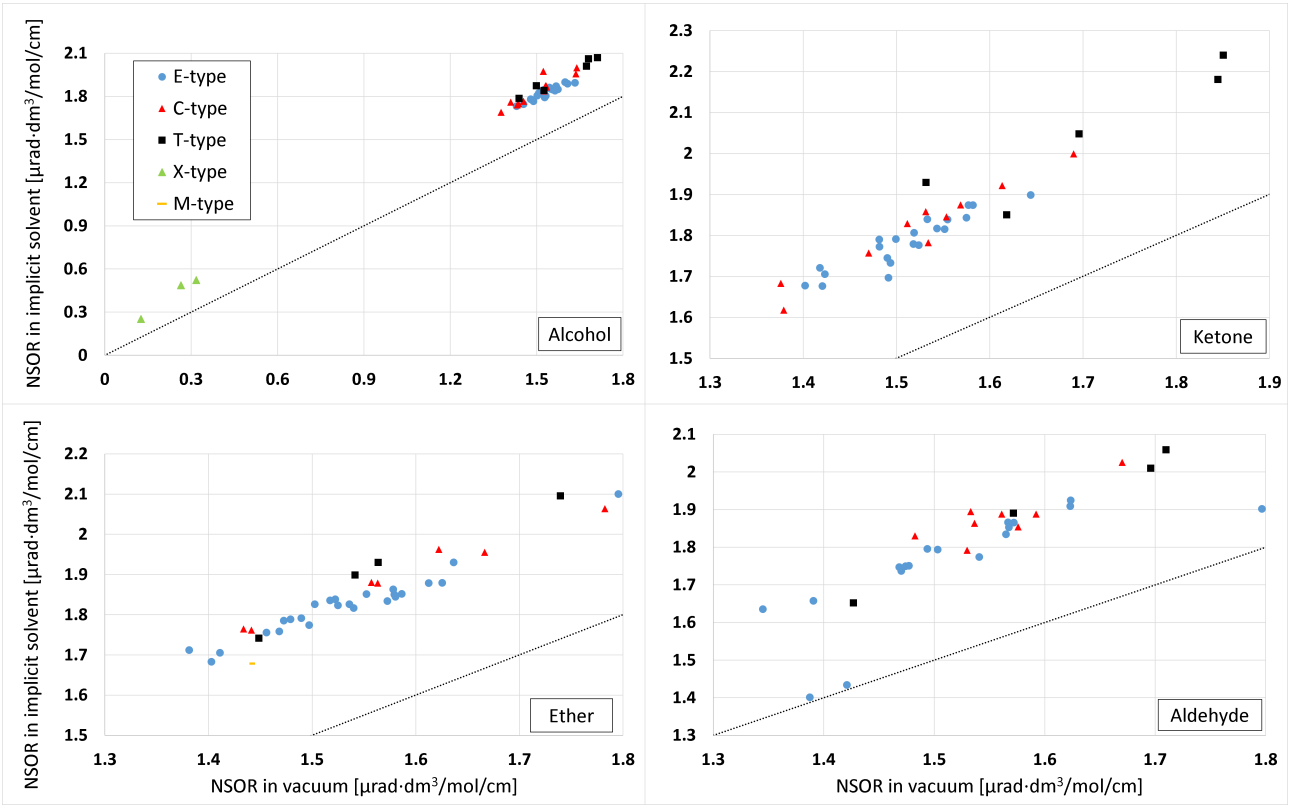

Figure S 15: Correlation between NSOR signals in vacuum and NSOR signals in implicit solvent for ^{1}H nuclei. In each subfigure the x-axis shows the NSOR values in vacuum and on the y-axis are the NSOR values in implicit solvent. The unit of the angles is μrad·dm^3/mol/cm.

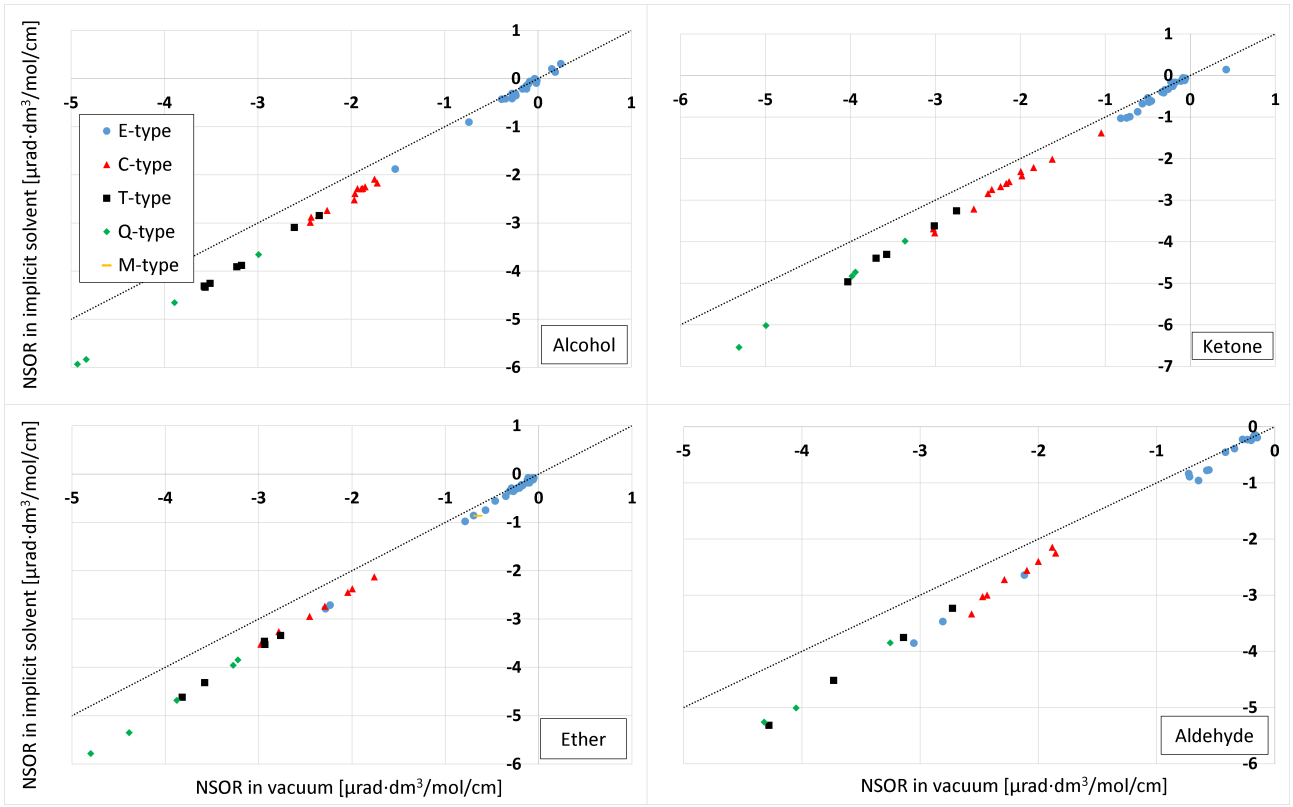

Figure S 16: Correlation between NSOR signals in vacuum and NSOR signals in implicit solvent for ^{13}C nuclei. In each subfigure the x-axis shows the NSOR values in vacuum and on the y-axis are the NSOR values in implicit solvent. The unit of the angles is μrad·dm^3/mol/cm.

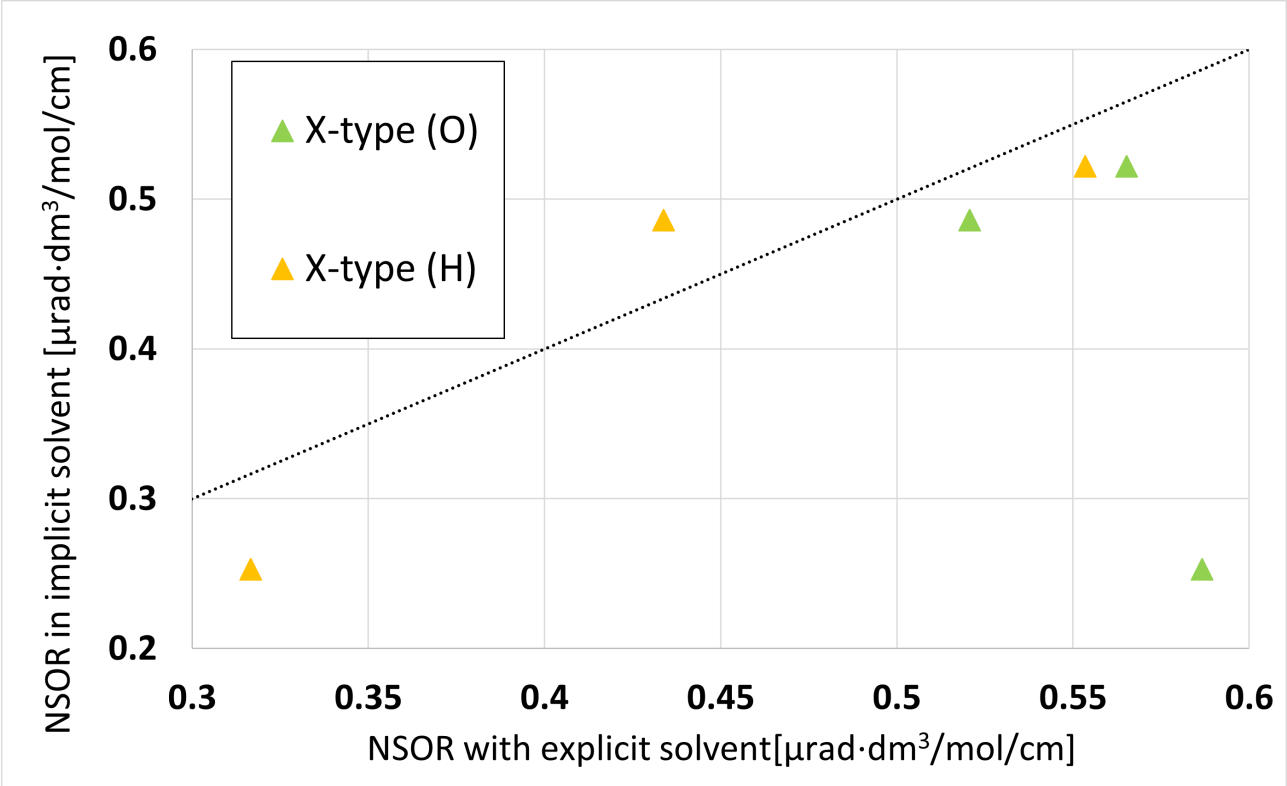

Figure S 17: NSOR signals with explicit solvent plotted against NSOR in implicit solvent for ^{1}H X-type in alcohols.

7 Carboxylic acid calculations

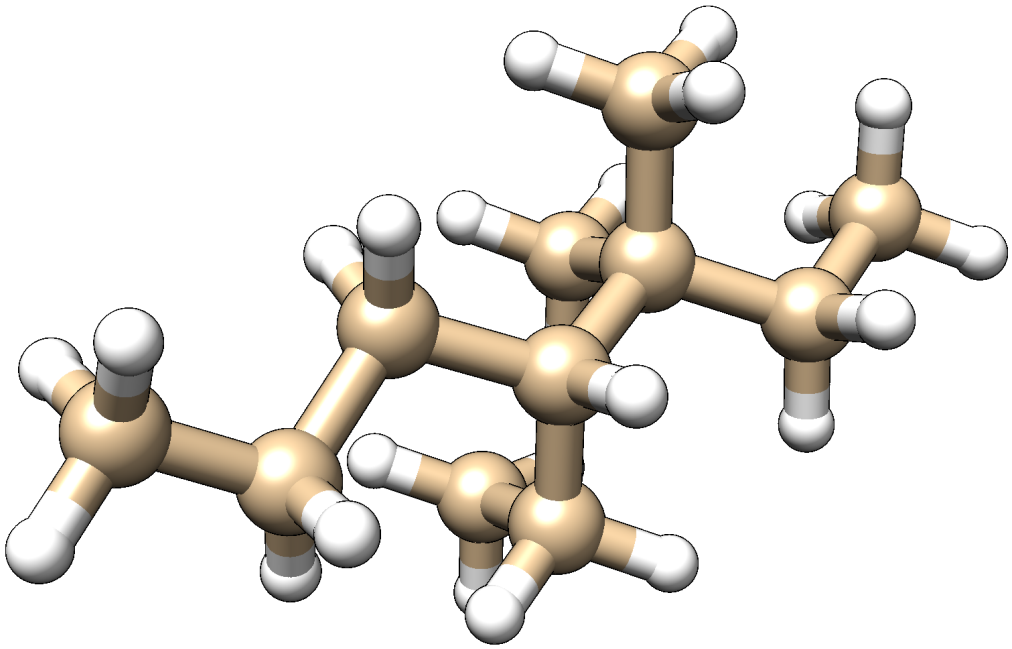

Figure S 18: 4-ethyl-5,5-dimethylheptane.

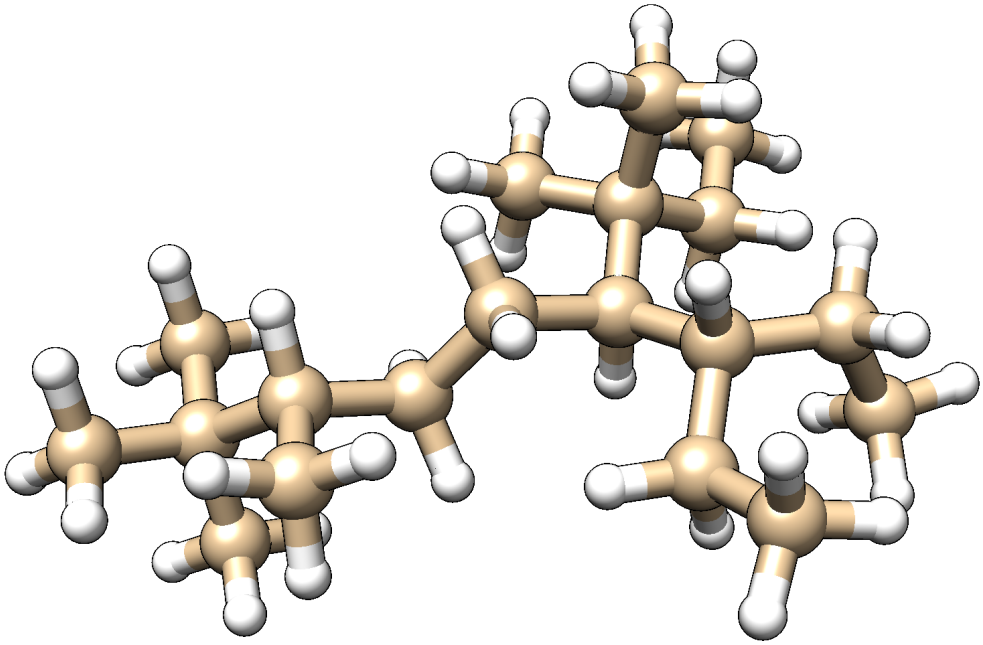

Figure S 19: 7-ethyl-2,2,3-trimethyl-6-(2-methyl-2-butyl)nonane.

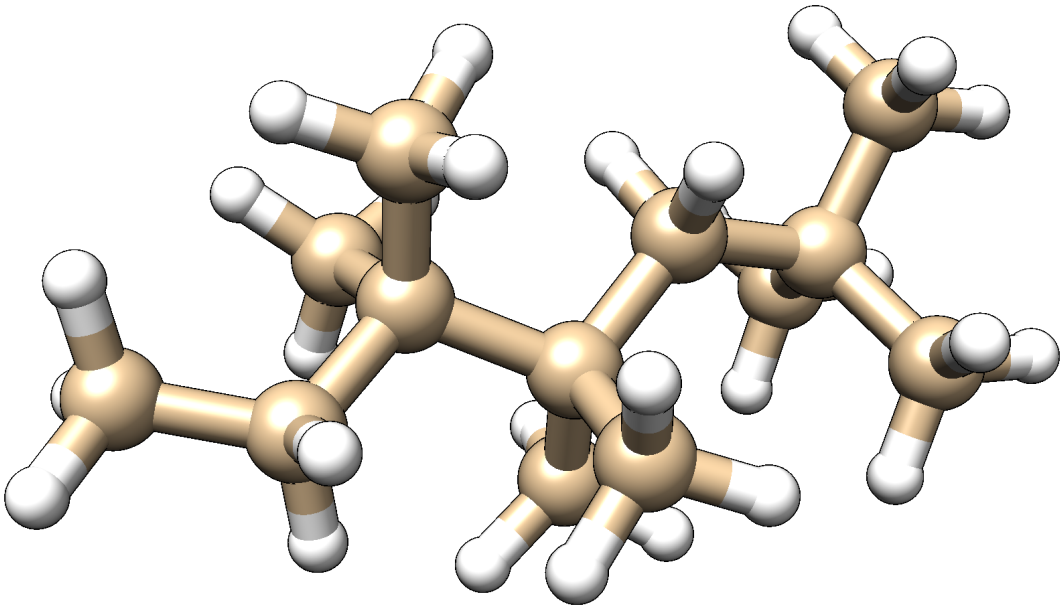

Figure S 20: 2,2,4,4,5,5-hexamethylheptane.

Figure S21 shows how the NSOR signals from three different carbon skeletons progress as the molecule is oxidized.

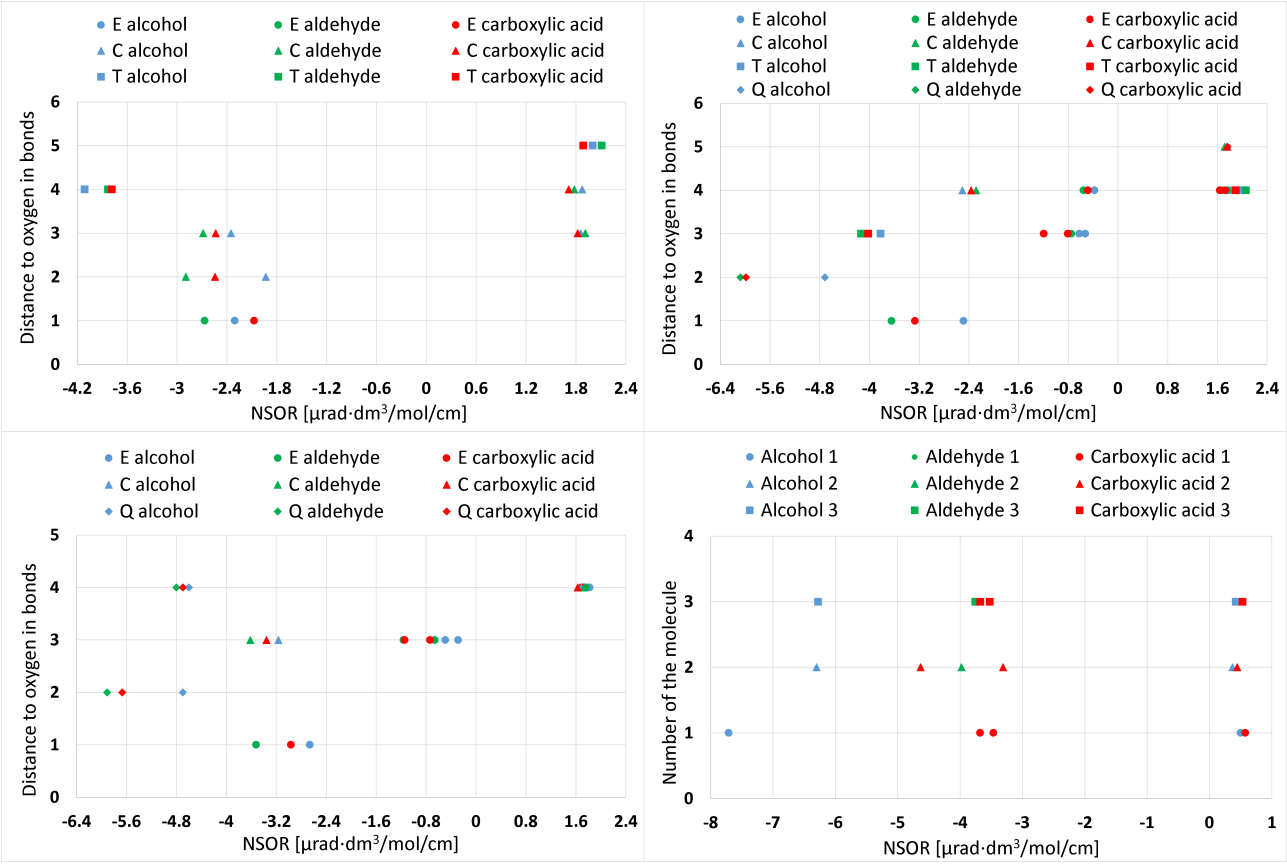

Figure S 21: The first three figures show NSOR of ^{1}H and ^{13}C nuclei from three different carbon skeletons in different state of oxidation. In each figure the NSOR angle is on the x-axis in μrad and distance to the oxygen is on the y-axis in bonds. In carboxylic acids the oxygen atom in the hydroxyl group is the reference atom with distance 0. Alcohol, aldehyde and carboxylic acid are denoted by blue, green and red colors, respectively. E-, C-, T- and Q-type nuclei are denoted by a sphere, triangle, square and diamond, respectively. Carbons have negative NSOR and they are on the left side of zero in each figure. Protons have positive NSOR, located on the right sides of the figures. The bottom right figure shows NSOR of ^{17}O and ^{1}H from -OH groups in alcohols, aldehydes and carboxylic acids. The numberings of the molecules refer to the molecules in top left, top right and bottom left figures, respectively. In the last figure positive signals are from protons and negative signals are from oxygens.

Table S 4: Molecules used in carboxylic acid calculations. The geometries that did not converge perfectly are marked with an asterisk in parentheses (*).

Alcohols	4-ethyl-5,5-dimethyl-1-heptanol (*)
	7-ethyl-2,2,3-trimethyl-6-(2-methyl-2-butyl)-1-nonanol (*)
	2,2,4,4,5,5-hexamethyl-1-heptanol
Aldehydes	4-ethyl-5,5-dimethylheptanal
	7-ethyl-2,2,3-trimethyl-6-(2-methyl-2-butyl)nonanal
	2,2,4,4,5,5-hexamethylheptanal
Carboxylic acids	4-ethyl-5,5-dimethylheptanoic acid
	7-ethyl-2,2,3-trimethyl-6-(2-methyl-2-butyl)nonanoic acid
	2,2,4,4,5,5-hexamethylheptanoic acid