

Transformation of cyclic ketones as impurities in cyclohexanone in the caprolactam production process.

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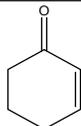
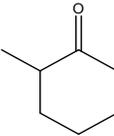
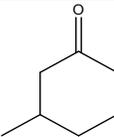
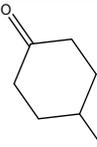
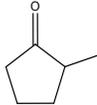
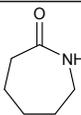
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Table S1. Chemical used.

Compound	Use		Ref.	Purity. (%)	MW (g/mol)	CAS	Scheme
2-Cyclohexen-1-one (CXENONE)	Reactant	Sigma-Aldrich	92509	98	96	930-68-7	
2-methylcyclohexanone (2-MEONE)	Reactant	Sigma-Aldrich	M38400	99	112	583-60-8	
3-methylcyclohexanone (3-MEONE)	Reactant	Sigma-Aldrich	M3860-5	97	112	591-24-2	
4-methylcyclohexanone (4-MEONE)	Reactant	Sigma-Aldrich	W394807	≥ 99	112	589-92-4	
2-methylcyclopentanone (2-MECPONE)	Reactant	Sigma-Aldrich	288438	98	98	1120-72-5	
Sodium Hydroxide	Reactant Titration	Sigma-Aldrich	S5881	≥ 98	40	1310-73-2	NaOH
Nitrocyclohexane	ISTD	Sigma-Aldrich	N16606	97	129	1122-60-7	C ₆ H ₁₁ NO ₂
Ammonium solution	Reactant	Panreac	211129	25	17	1336-21-6	NH ₃
Hydroxylammonium sulfate	Reactant	ACROS	A0388374	99	164	10039-54-0	(HONH ₃) ₂ SO ₄
Sulfuric acid	Reactant	ACROS	30207002 6	96	98	7664-93-9	H ₂ SO ₄
ε-caprolactam	Solvent	Sigma-Aldrich	C2204	99	113	105-60-2	

1. GC/MSD and NMR spectra of pure oximes synthesized from cyclic ketones.

In Figure S1 total ion chromatogram of a mixture of 10000 $mg \cdot kg^{-1}$ of pure oximes of 2-methylcyclopentanone, cyclohexanone, 2-methylcyclohexanone, 3-methylcyclohexanone and 2-cyclohexen-1-one diluted in 1-butanol is shown. In Figure S2 to Figure S6, the experimental mass spectra of the oximes, which were synthesized from pure cyclic ketones, are provided. The assignment was carried out analysing the pure oximes individually. Moreover, some of them were compared with the available spectra on NIST library and Wiley Database in Scifinder.

In Figure S7 to Figure S11, the 1H -NMR spectra of the stereoisomer mixture are provided. These were used to identify the stereoisomers formed in the oximation reaction and mass ratio between them. The identification of stereoisomers was accomplished as follows:

2-methylcyclopentanone oxime (Figure S7): The signal used was the doublet of the methyl group CH_3 (bonded to carbon 2 in cyclic chain). This group is close to the oxime functional group ($C=N-OH$), and the deshielding of the protons of the cis isomers is greater because of oxygen electronegativity. For this reason, the doublet of the cis isomers presents a higher chemical shift (1.20-1.14 ppm) than the trans isomer. The ratio between this isomer was found using the integral of the doublet signals as 9:91% for cis and trans stereoisomers respectively.

2-methylcyclohexanone oxime (Figure S8): Both isomers can be identified using the doublet signals at chemical shift δ 1.09-1.12 ($J=7.2$ Hz) and 1.11-1.13 ($J=6.6$ Hz). These signals are produced by the methyl group at position 2 in the cyclic carbon chain, close to the $C=N-OH$. The doublet signal with the highest chemical shift is due to the cis (*Z*) isomer. The deshielding of the protons is greater due to the oxygen effect. The area integral intensity ratio between the formed stereoisomers was found to be 13 % and 87 % for cis and trans isomers respectively. This ratio was confirmed by the signal from by the hydrogen atom that compounds the group CH (positions 2 in the carbon cyclic chain). The signal is a multiplet with a chemical shift at δ 3.2-3.1 ppm. This corresponds with the isomer cis while the second multiplet at δ 3.6-3.5 ppm is generated by the *Z* isomer.

3-methylcyclohexanone oxime (Figure S9): The ratio between trans/cis isomers was established by studying the integration area of the signals produced by the doublets at 0.99-0.95 ppm and 1.04-

0.99. The highest chemical shift is due to the oxygen effect over the cis isomer. In this group, the oxygen of the oxime functional group of the cis (Z) isomer has a greater effect on the electron density, and the doublet signal of this proton has a higher chemical shift (δ 1.04 ppm) than the same group of the trans (E) isomer (δ 0.95 ppm). The ratio can thus be established as 52% for the trans isomer and 48% for the cis isomer.

4-methylcyclohexanone oxime (Figure S10): Only one isomer is identified because this ketone is symmetric.

2-cyclohexen-1-one oxime (Figure S11): the NMR spectrum presents a doublet generated by the hydrogen atom that conforms the CH group located in position 2 of the carbon cyclic chain. This CH is close to the oxime functional group and the effect of the oxygen is the key to distinguishing the stereoisomers and their mass ratio. As explained above in the other cyclic oximes, the deshielding of the cis isomer is greater than the for the same group in the trans isomer. For this reason, the doublet of CH of the cis isomer has a higher chemical shift (δ 6.82) than the trans isomer (δ 6,14). Moreover, the oxygen atom of the group C=N-OH also affects the hydrogens of the CH₂ in position 6. These signals are triplets, but the oxygen atom affects the CH₂ group of the trans isomer more than the cis isomer. The triplet of the trans isomer thus has a higher chemical shift (δ 2.65) than the cis isomer (δ 2.42). The area integral intensity ratio of isomer production when the 2-cyclohexen-1-one is obtained was found to be 27% and 73 % for cis and trans isomers respectively.

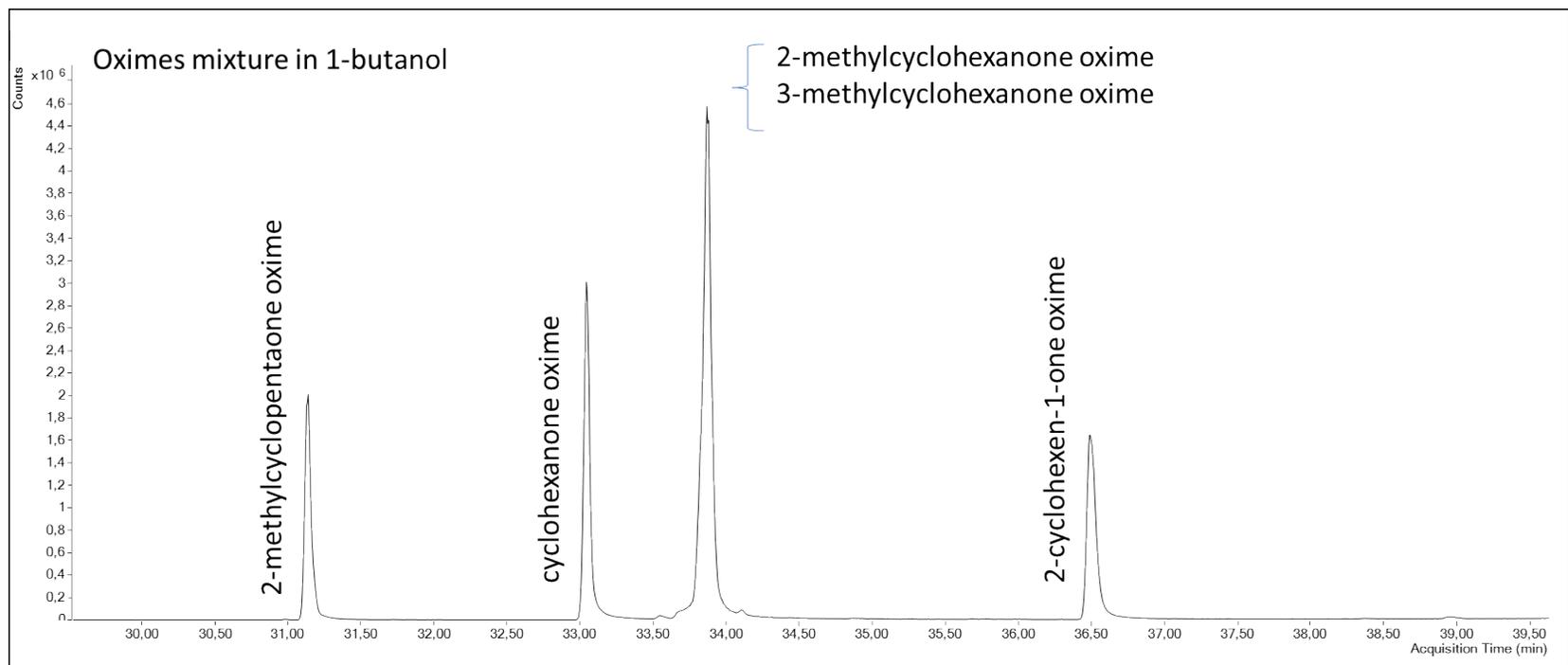


Figure S1. Total ion chromatogram (TIC) of 10000 mg of each pure oxime mixture in 1 kg of 1-butanol using nitro cyclohexane (25.43 min) as ISTD

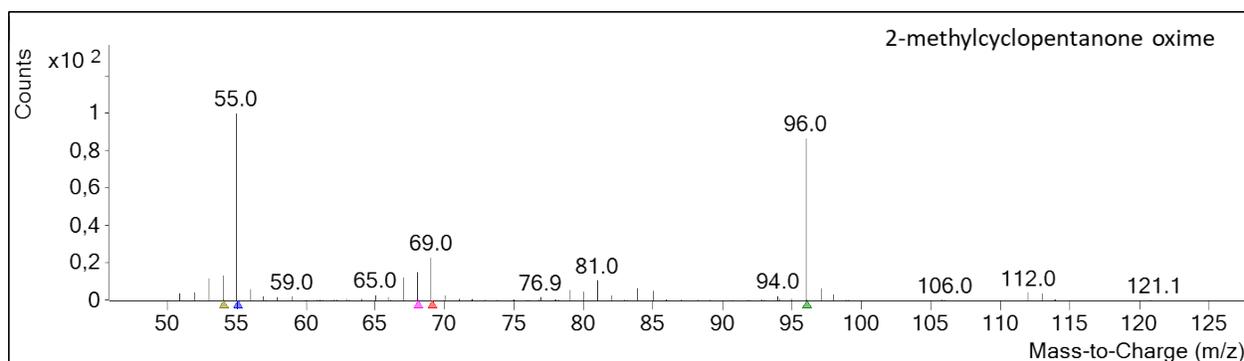


Figure S2. Mass spectra of 2-methylcyclopentanone oxime obtained from the analysis of the pure synthesized compound.

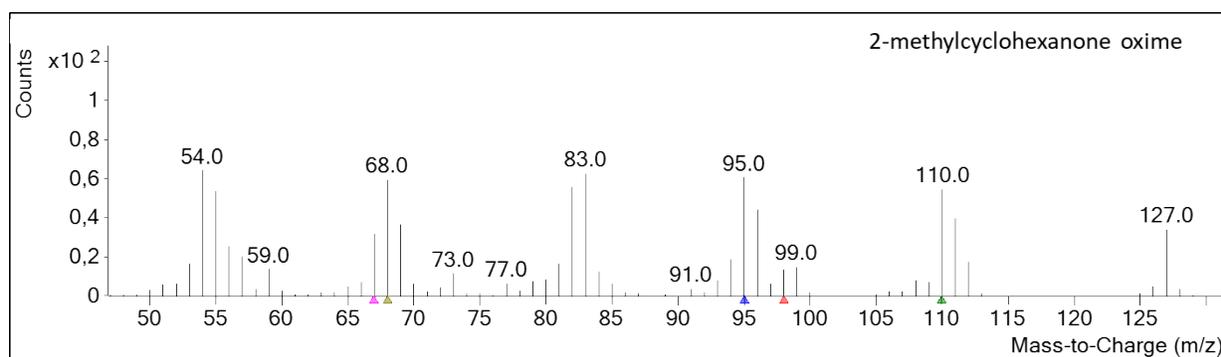


Figure S3. Mass spectra of 2-methylcyclohexanone oxime obtained from the analysis of the pure synthesized compound, identified using NIST database (Version 011) (Babushok et al., 2007).

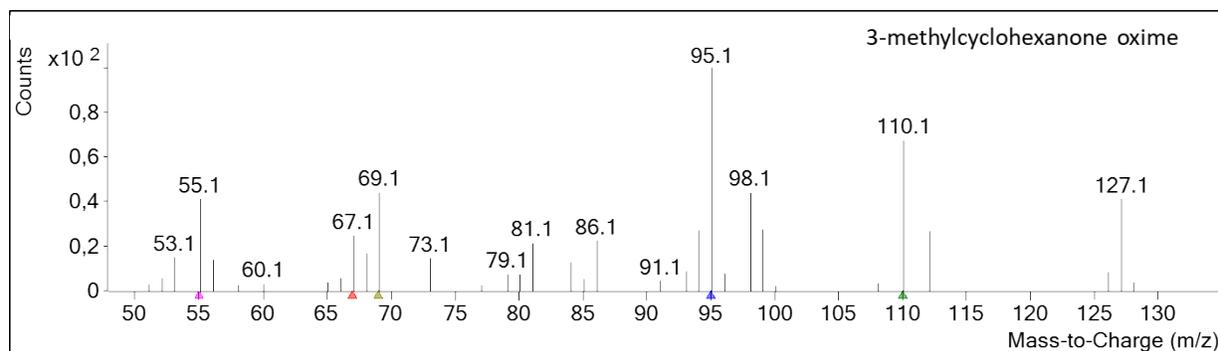


Figure S4. Mass spectra of 3-methylcyclohexanone oxime obtained from the analysis of the pure synthesized compound. It was also identified using SciFinder Database spectra (WSS ID: ID_WID-DLO-005081-7).

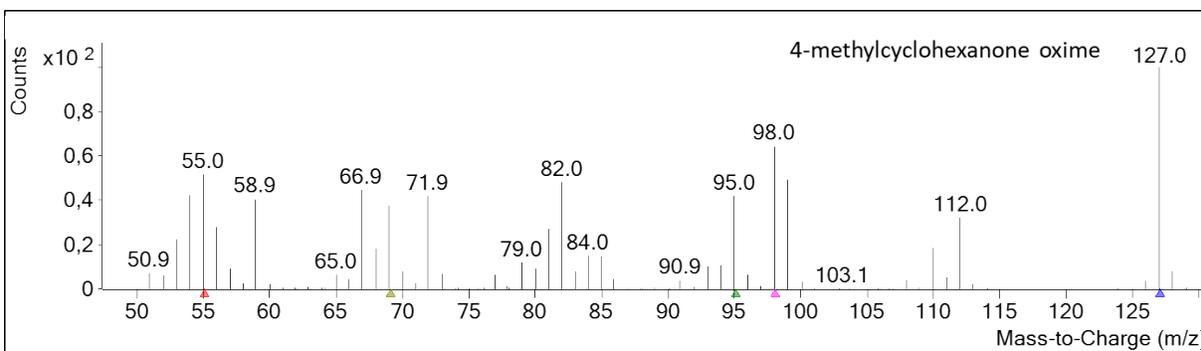


Figure S5. Mass spectra of 4-methylcyclohexanone oxime obtained from the analysis of the pure synthesized compound. It was also identified using SciFinder Database spectra (WSS ID: ID_WID-DLO-005102-5).

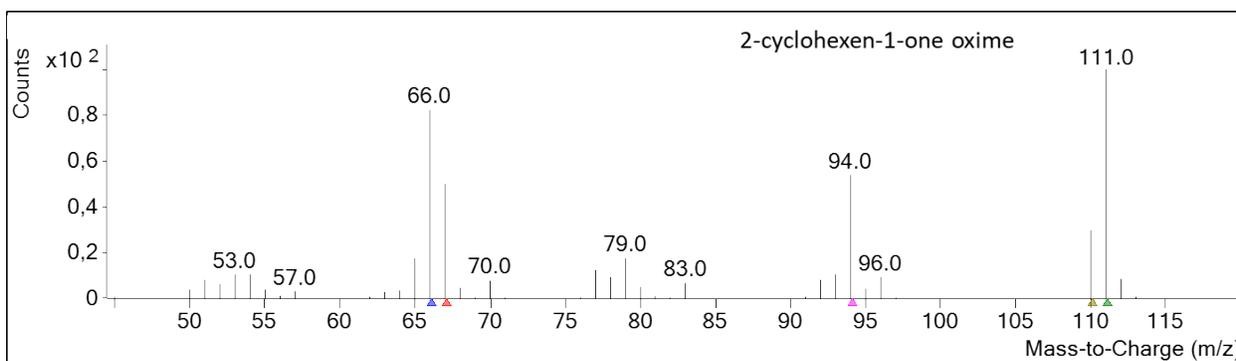


Figure S6. Mass spectra of 2-cyclohexen-1-one oxime obtained from the analysis of the pure synthesized compound, identified using the NIST database (Version 011) (Babushok et al., 2007).

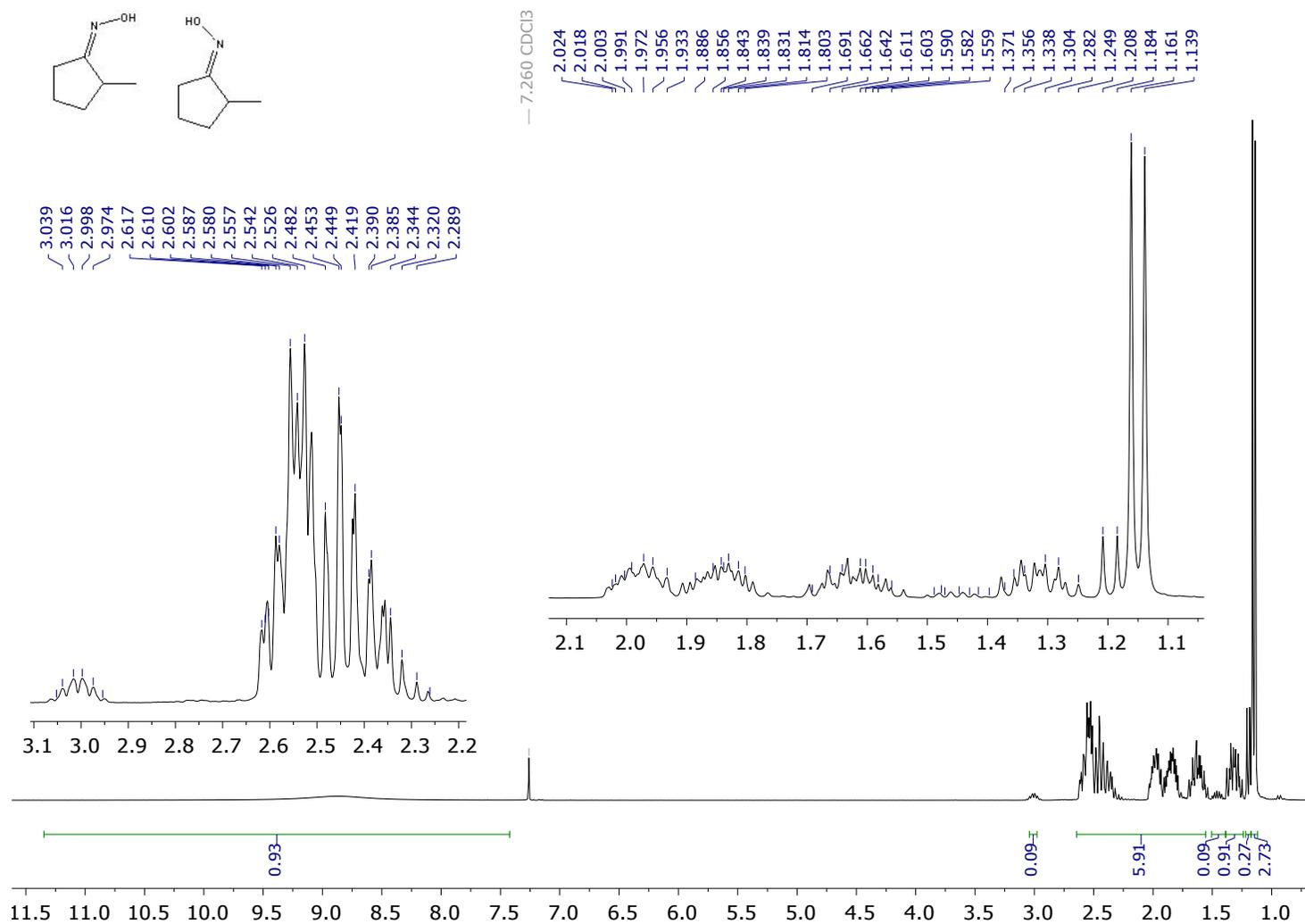


Figure S7. (1E)-2-methylcyclopentanone oxime: $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 2.65-1.55 (m, 6H, CH_2), 1.41-1.26 (m, 1H, CH), 1.20-1.14 (d, $J = 6.7\text{Hz}$, 3H, CH_3). (1Z)-2-methylcyclopentanone oxime: $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 3.1-2.9 (m, 1H, CH), 2.65-1.55 (m, 5H, CH_2), 1.55-1.40 (m, 1H, CH_2), 1.24-1.20 (d, $J = 7.1\text{Hz}$, 3H, CH_3).

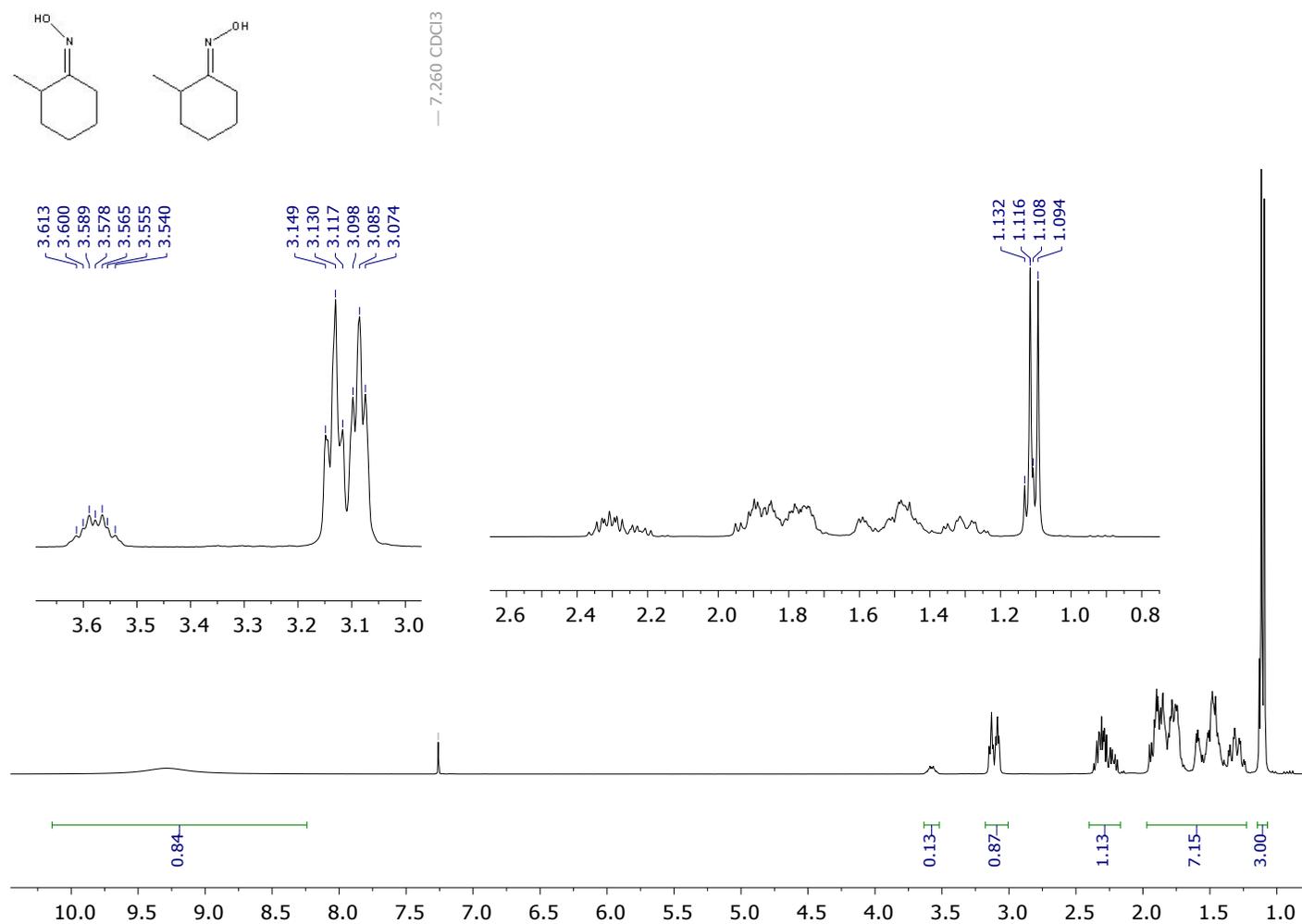


Figure S8. (1Z)-2-methylcyclohexanone oxime: 1H-RMN (300MHz, CDCl₃): δ 3.67-3.54 (dt, 2H CH₂), 2.00-1.2 (m, 6H, 3CH₂), 1.14-1.12 (d, J = 7.2Hz, 3H, CH₃). (1E)-2-methylcyclohexanone oxime: 1H-RMN (300MHz, CDCl₃): δ 3.21-3.07 (dt, 2H, CH₂), 2.00-1.2 (m, 6H, 3CH₂), 1.14-1.12 (d, J = 6.6Hz, 3H, CH₃).

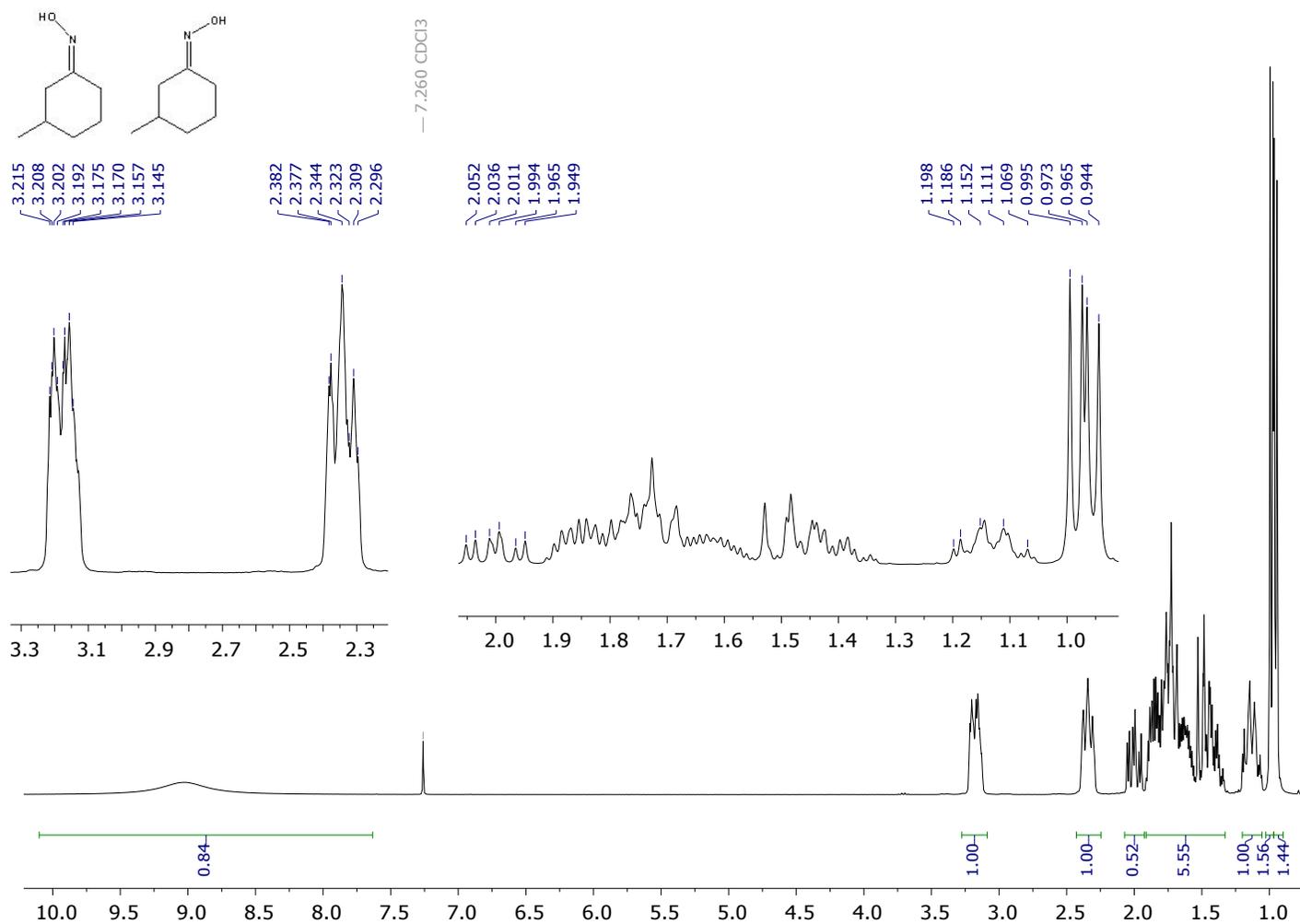


Figure S9. (1E)-3-methylcyclohexanone oxime: ¹H-RMN (300MHz, CDCl₃): δ 3.3-3.1 (m, 1H, CH₂), 2.55-2.3 (m, 1H, CH₂), 1.95-1.1 (m, 7H, 3CH₂, CH) 0.99-0.95 (d, J = 6.24Hz, 3H, CH₃). (1Z)-3-methylcyclohexanone oxime: ¹H-RMN (300MHz, CDCl₃): δ 3.3-3.1 (m, 1H, CH₂), 2.55-2.3 (m, 1H, CH₂), 2.10-1.95 (m, 1H, CH), 1.95-1.1 (m, 6H, 3CH₂), 1.04-0.99 (d, J = 6.39Hz, 3H, CH₃).

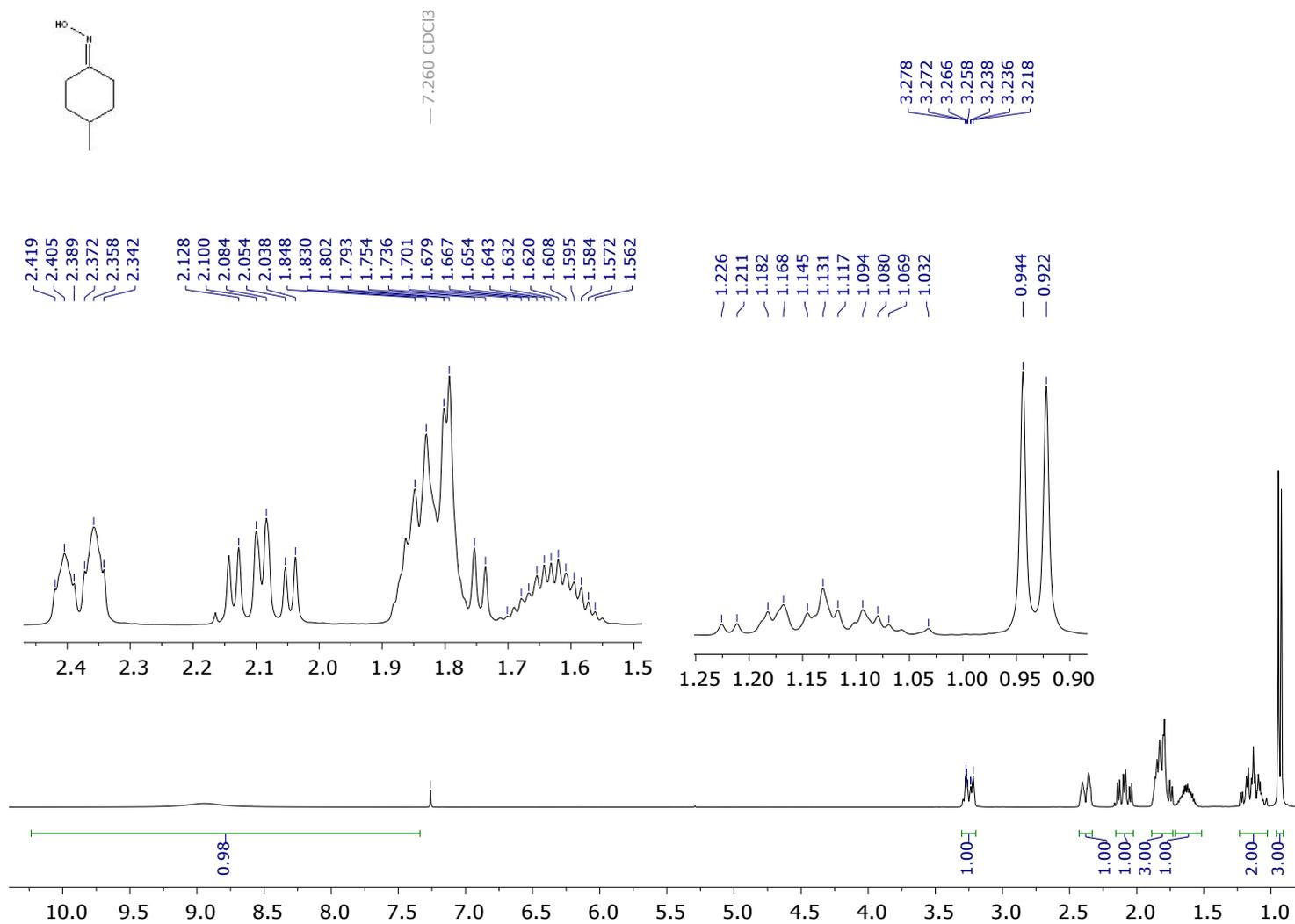


Figure S10. 4-methylcyclohexanone oxime: $^1\text{H-RMN}$ (300MHz, CDCl_3): δ 3.35-3.20 (m, 1H), 2.45-2.35 (dt, $J = 4.4\text{Hz}$, 1H), 2.17-2.05 (m, 1H), 1.90-1.75 (m, 3H), 1.75-1.57 (m, 1H, CH), 1.25-1.05 (m, 2H), 0.98-0.93 (d, $J = 6.57\text{Hz}$, 3H, CH_3).

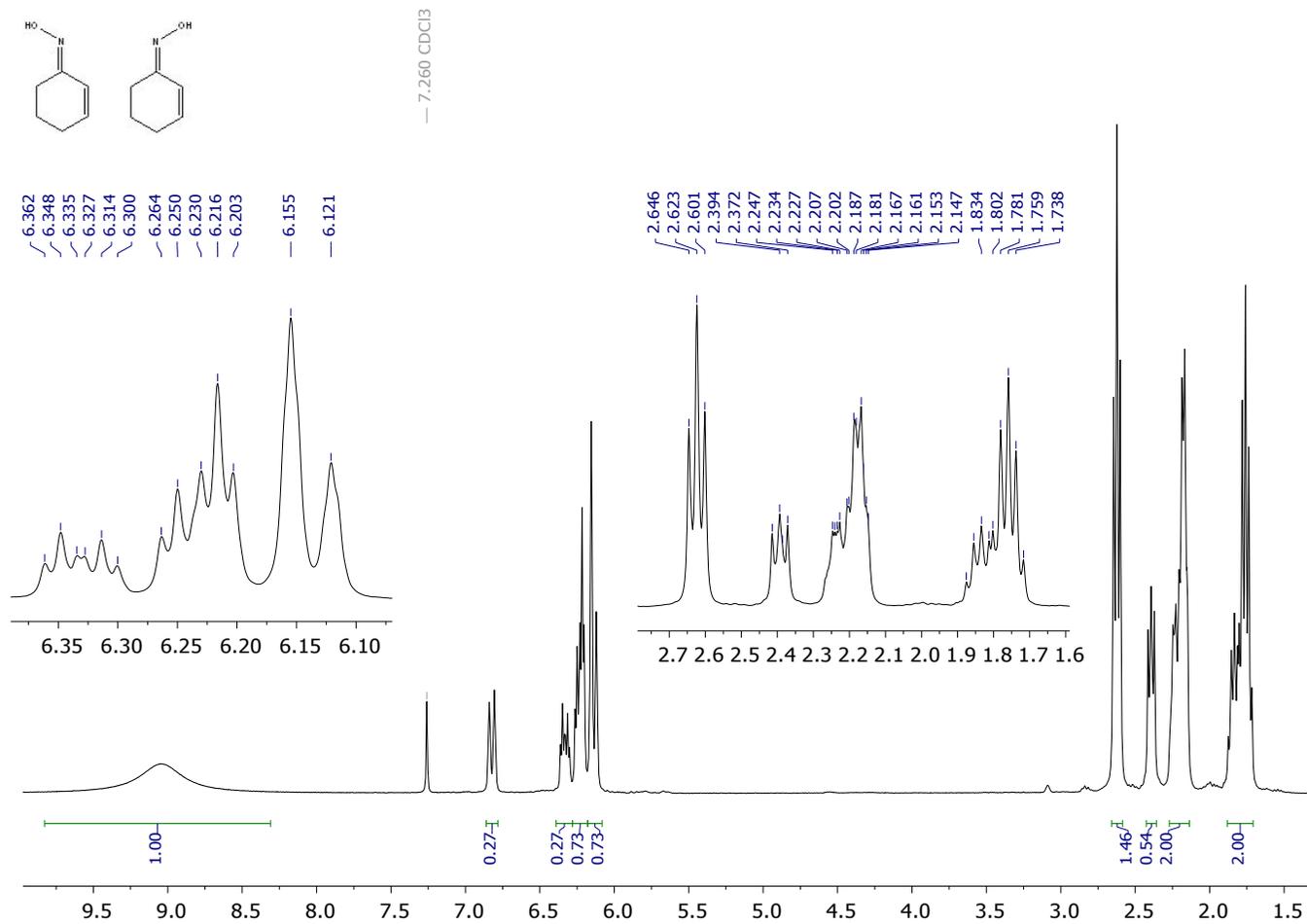


Figure S11. (1E)-2-Cyclohexen-1-ona oxime: ^1H -RMN (300MHz, CDCl_3): δ 1.82 (m, 2H), 2.21 (m, 2H), 2.65 (t, $J = 6.65\text{Hz}$, 2H), 6.16 (d, $J = 10.1\text{Hz}$, 1H), 6.26 (dt, $J_{ab} = 10.24\text{Hz}$, $J_{bc} = 4.07\text{Hz}$, $J_{cd} = 4.07\text{Hz}$). (1Z)- 2-cyclohexen-1-ona oxime: ^1H -RMN (300MHz, CDCl_3): δ 1.82 (m, 2H), 2.21 (m, 2H), 2.42 (t, $J = 6.42\text{Hz}$, 2H), 6.85 (d, $J = 10.27\text{Hz}$, 1H), 6.36 (dt, $J_{ab} = 10.28\text{Hz}$, $J_{bc} = 4.05\text{Hz}$, $J_{cd} = 4.05\text{Hz}$, 1H).

2. GC/MSD spectra of amides from BR of pure cyclic oximes

The detected chromatogram peaks are summarized in Table S2. They were identified by comparing the experimental mass spectra with that provided by the NIST library (Babushok et al., 2007) and/or the Wiley Service.

Table S2. Amides and precursor isomer oxime. Retention time (RT) Target ion and qualifiers (QF1 and QF2) are also summarized

Amide	Precursor	RT, min	Target	QF1	QF2
6-methyl-2-piperidone	(E)2-cyclopentanone oxime	38.37	113	68	98
3-methyl-2-piperidone	(Z)2-cyclopentanone oxime	38.50	98	113	58
7-methylcaprolactam	(E)2-methylcyclohexanone oxime	38.74	127	112	85
3-methylcaprolactam	(Z)2-methylcyclohexanone oxime	38.99	114	87	143
6-methylcaprolactam	(E)3-methylcyclohexanone oxime	41.47	127	98	69
4-methylcaprolactam	(Z)3-methylcyclohexanone oxime	41.59	127	69	56
5-methylcaprolactam	4-methylcyclohexanone oxime	41.89	127	99	69
1,5,6,7-tetrahydro-2H-azepin-2-one	(Z)2-cyclohexen-1-one oxime	43.95	111	83	59

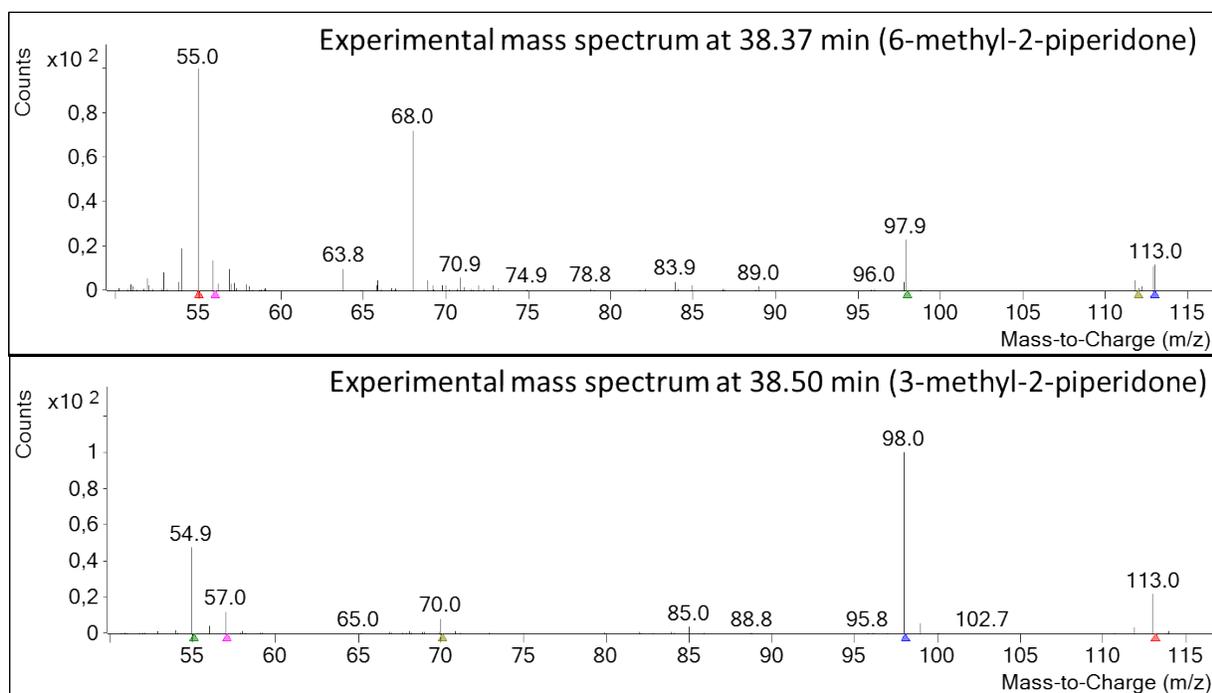


Figure S12. Experimental spectra obtained by GC/MS and SPME of the reaction mixture after Beckmann Rearrangement of the 2-methylcyclopentanone oxime (mixture of stereoisomers). The mass spectrum of 6-methyl-2-piperidone was provided by Wiley Database in Scifinder (ID: ID_WID-DLO-003039-7).

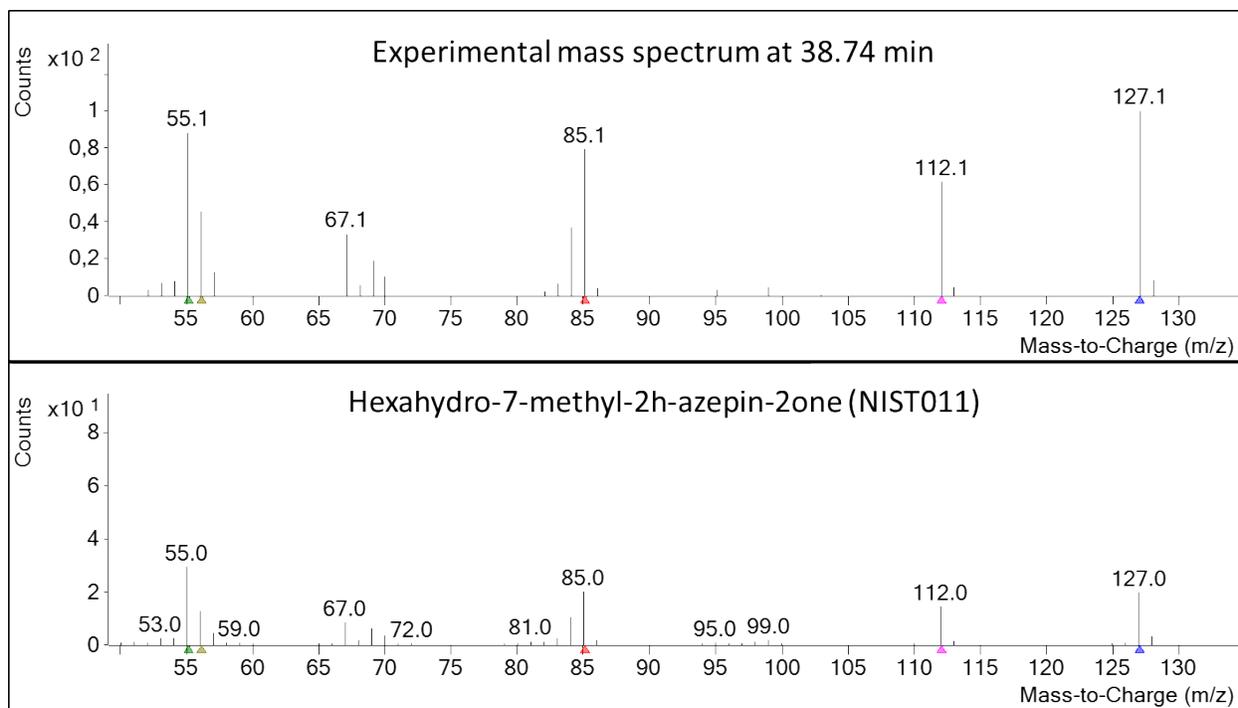


Figure S13. Experimental spectrum obtained by GC/MS and SPME of Beckmann Rearrangement of the (E)-2-methylcyclohexanone oxime. The experimental spectrum was identified using the spectrum provided NIST database (Version 011) (Babushok et al., 2007).

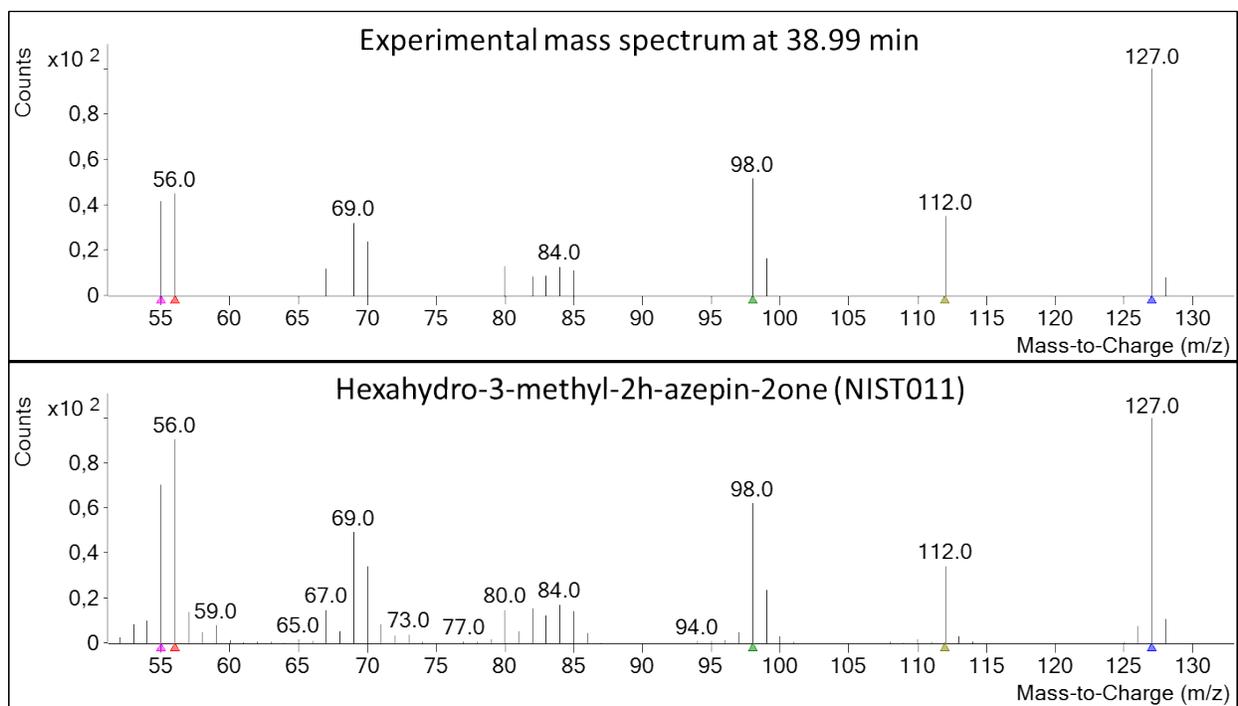


Figure S14. Experimental spectrum obtained by GC/MS and SPME of Beckmann Rearrangement of the (*Z*)-2-methylcyclohexanone oxime. The experimental spectrum was identified using the spectrum provided NIST database (Version 011) (Babushok et al., 2007).

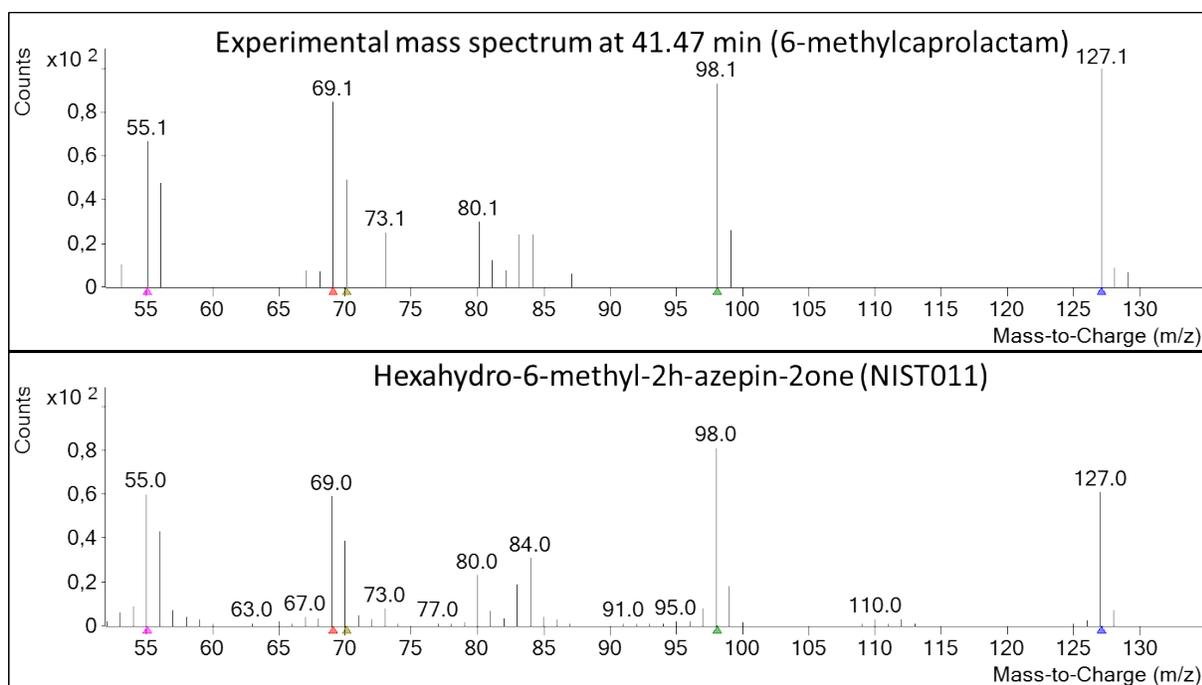


Figure S15. Experimental spectra obtained by GC/MS and SPME of the reaction mixture after Beckmann Rearrangement of the (E)-3-methylcyclohexanone oxime The experimental spectrum was identified using the spectrum provided NIST database (Version 011) (Babushok et al., 2007).

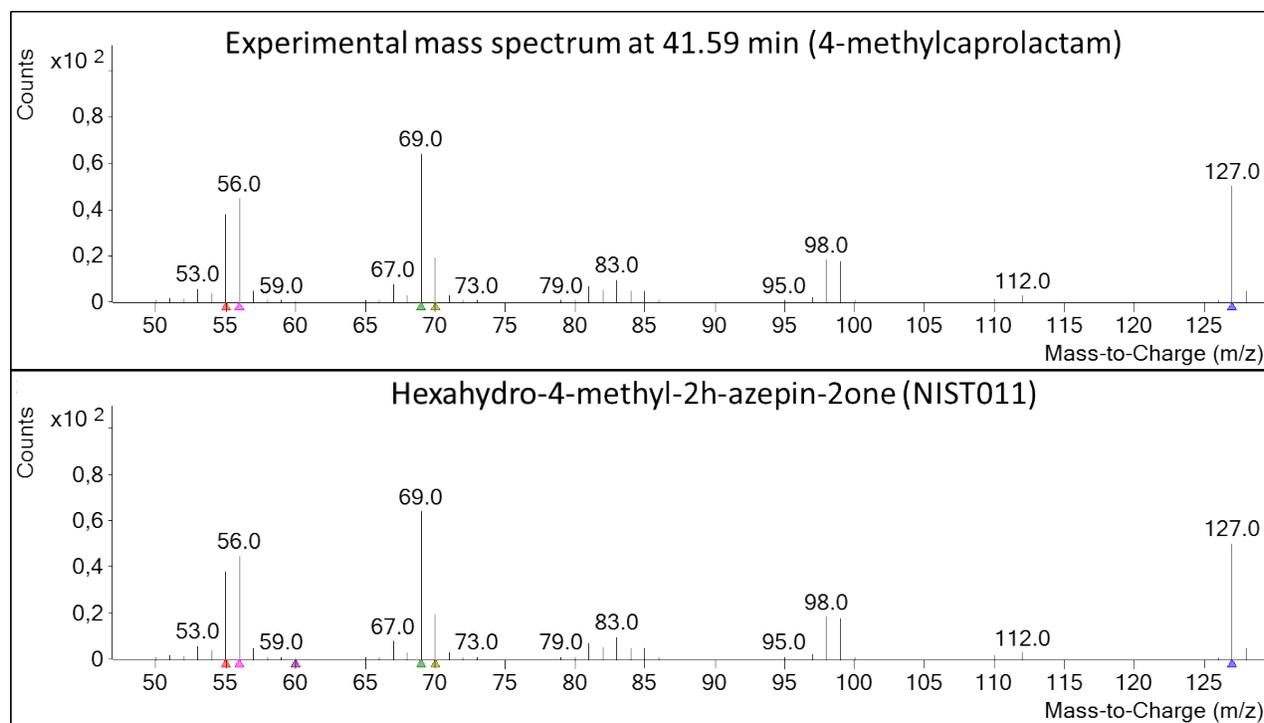


Figure S16. Experimental spectra obtained by GC/MS and SPME of the reaction mixture after Beckmann Rearrangement of the (*Z*)-3-methylcyclohexanone oxime. The experimental spectrum was identified using the spectrum provided NIST database (Version 011) (Babushok et al., 2007).

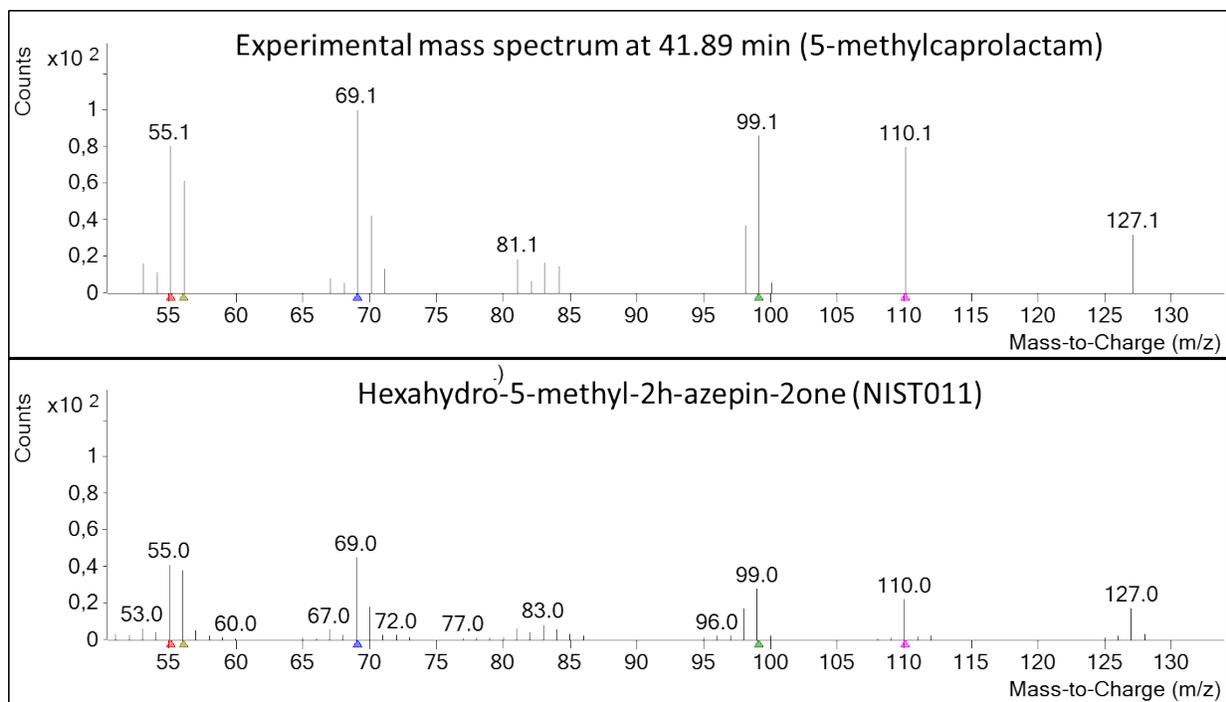


Figure S17. Experimental spectra obtained by GC/MS and SPME of the reaction mixture after Beckmann Rearrangement of the 4-methylcyclohexanone oxime. The experimental spectrum was identified using the spectrum provided NIST database (Version 011) (Babushok et al., 2007).

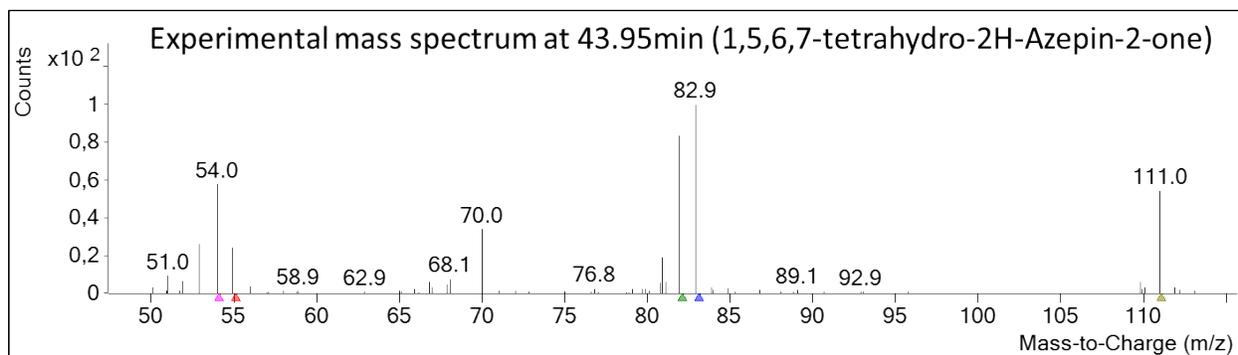


Figure S18. Experimental spectra obtained by GC/MS and SPME of Beckmann Rearrangement of the (Z)-2-cyclohexen-1-one oxime (mixture of stereoisomers). The mass spectrum of 1,5,6,7-tetrahydro-2H-azepin-2-one was provided by Wiley Database (ID: CAS2009_1_011825).

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Babushok, V.I., Linstrom, P.J., Reed, J.J., Zenkevich, I.G., Brown, R.L., Mallard, W.G., Stein, S.E., 2007. Development of a database of gas chromatographic retention properties of organic compounds. *Journal of Chromatography A* 1157, 414-421.