SUPPORTING INFORMATION

One-pot synthesis of aldoximes from alkenes via Rh-catalysed hydroformylation in an aqueous solvent system

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Table of contents

1. Experimental procedure

Chemicals:

All substrates used as well as the catalysts, ligands and solvents are commercially available and purchased from ABCR, ACROS ORGANICS, TCI, SIGMA-ALDRICH, VWR or UMICORE. Synthesis gas ($CO:H_2$ = 1:1) was purchased from MESSER INDUSTRIEGASE GMBH.

Condensation Experiments in round flasks:

For condensation experiments, a 25 mL round flask with magnetic stirrer was filled with water, 1-butanol and aqueous hydroxyl amine solution. The mixture was heated to the desired temperature and nonanal was added to the mixture. After addition of the first drop, the reaction was stirred for 20 min. Afterwards the phases were separated, weighed and examined by gas chromatography.

Experiments in 25 mL Autoclaves (Figure S1):

In an argon atmosphere, the rhodium precursor and the ligand were first introduced into the reactors. After that the reactor was closed and put under vacuum. Argon was added and the pressure was withdrawn three times. Then water, 1-butanol, substrate and aqueous hydroxyl amine solution were added to the mixture. The autoclave was pressurized and heated to the required temperature. After the reaction, the autoclaves were cooled down again, the reaction solution was drawn up in syringes and the phases were separated from each other. The respective phases were transferred into separate tubes, weighed and examined by gas chromatography.

Figure S1: 25 mL autoclave

Scale-up experiment in a 350 mL stirred tank reactor (Figure S2):

To an overhead stirred tank reactor (Figure S2) equipped with baffles (Figure S2), a gas-impeller stirrer (Figure S2) and a dropping funnel, rhodium precursor and the ligand were added. The

autoclave was closed and a vacuum was applied and flooded with argon 3 times. In a Schlenk-flask, a mixture of water, 1-butanol, and aqueous hydroxyl amine solution was prepared and transferred to the autoclave via a cannula. The vessel with pressure compensation was filled with 1-octene. The mixture was pressurized with 10 bar synthesis gas and heated to 100 °C. As soon as the reaction temperature was reached, the autoclave was pressurized with 60 bar synthesis gas and 1-octene was added to the reaction mixture by opening the pressure compensation and the valve to the autoclave. The mixture was then stirred at 700 rpm and samples were withdrawn through a built-in cannula. Those samples were analysed by gas chromatography. At the end of the reaction time, the solution was cooled down by an ice bath. Finally, the respective phases were transferred into separate screw-cap glasses, weighed and examined by gas chromatography. During storage a constant argon atmosphere was guaranteed.

Figure S2: 350 mL stirred tank reactor (left), baffles (middle) and gas-impeller stirrer (right)

Recording the gas consumption curves in a 350 mL stirred tank reactor (Figure S2):

To a stirred tank reactor (Figure S2) equipped with baffles, a gas inlet stirrer and dropping funnel, rhodium precursor and the ligand were added. The autoclave was closed and a vacuum was applied and flooded with argon 3 times. In a Schlenk-flask, a mixture of water, 1-butanol, and aqueous hydroxyl amine solution was prepared and transferred to the autoclave via a cannula. The vessel with pressure compensation was filled with substrate. The mixture was pressurized with 10 bar synthesis gas and heated to 100 °C. As soon as the reaction temperature was reached, the autoclave was pressurized with 60 bar synthesis gas. The gas supply was ensured *via* a 1 L reservoir vessel, pressurized with 75 bar synthesis gas, which was equipped with the pressure sensor (Figure S3, left) and a pressure regulator. The reaction pressure was constant at 60 bar and the gas consumption in the storage vessel was recorded. After addition of the substrate the measurement was started and the mixture was stirred at 700 rpm. As soon as no significant pressure drop was observed, the solution was cooled down by an ice bath. Finally, the respective

phases were transferred into separate screw-cap glasses, weighed and examined by gas chromatography. During storage a constant argon atmosphere was guaranteed.

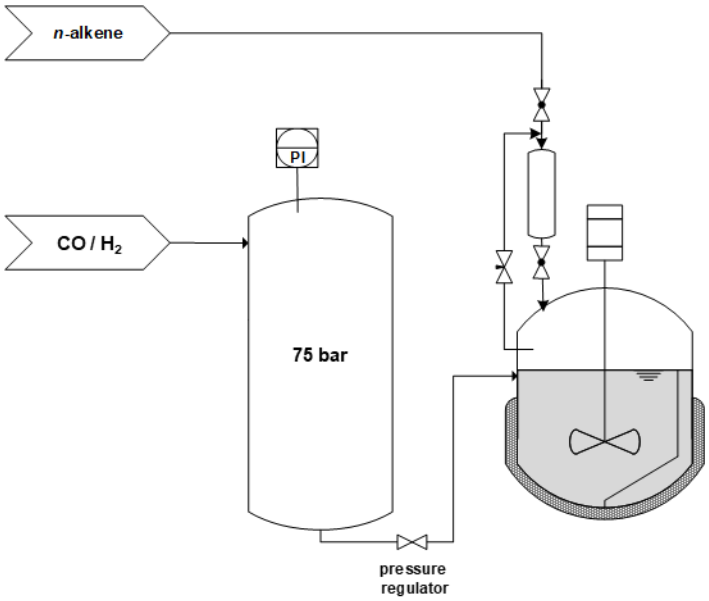


Figure S3: Flow scheme of the used reactor for gas consumption experiments with the gas reservoir for synthesis gas on the left and a dropping funnel for the alkene above the autoclave.

The curves were calculated by relating the percentage drop in pressure to the combined yield of all hydroformylation products. The pressure drop of the build-up (Figure S3) was 0.05 bar h^{-1} and was subtracted from the pressure curves.

2. Analytics

NMR-Spectroscopy: ^{1}H-, ^{13}C-spectra were recorded with spectrometers BRUKER DRX-500, -600 and -700 at ambient temperature with the frequency and solvent noted. Chemical shifts δ are given in ppm relative to tetramethylsilane.

Gaschromatography: Conversion and yield of the reactions were determined via GC on an HEWLETT PACKARD chromatograph of the type HP6890 with a flame ionization detector (FID). A HP-5 column was used (30 m long, 0.32 mm diameter, 0.25 µm thickness of the layer, 3 minutes at 40 °C, heating rate 7.5 °C/min to 150 °C, heating rate 40 °C/min to 320 °C, holding for 8 minutes). The split was set to 1:15. Dodecane was chosen as internal standard and response factors of the substrates and products were obtained experimentally by analysing known quantities of the substances.

Yield of the biotransformations was determined by GC measurements on a Shimadzu GC 2010 with a flame ionization detector (FID).

Method I: Measurements were conducted on a Phenomenex ZB-5MSi column (30 m x 0.25 mm x 0.25 µm). A split injection mode (1:10) was used and a sample amount of 1 µL was injected in this method. As carrier gas a N_2/synthetic air mixture was used in a pressure flow control mode with a total flow of 13.9 mL/min and a column flow of 0.99 mL/min. The following temperature gradient was used in this method: 110 °C start temperature, in 5 °C/min to 140 °C and in 40 °C/min to 240 °C.

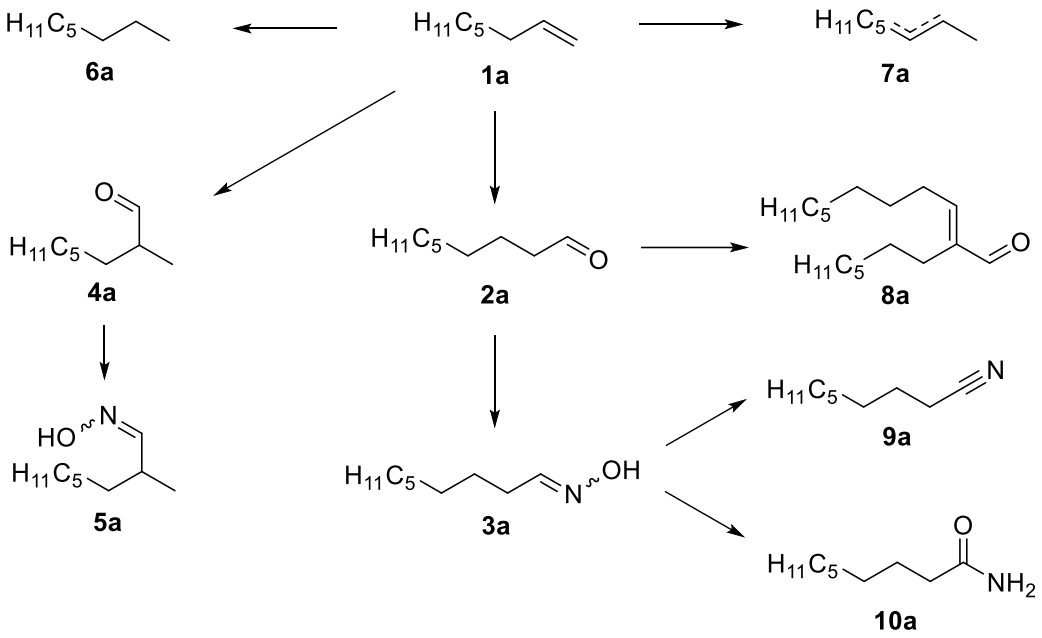
Method II: Measurements were conducted on a BGB-174 column (30 m x 0.25 mm x 0.25 µm). A split injection mode (1:10) was used and a sample amount of 1 µL was injected in this method. As carrier gas a N_2/synthetic air mixture was used in a linear velocity control mode with a total flow of 14.4 mL/min. The following temperature gradient was used in this method: 190 °C start temperature (1 min), in 10 °C/min to 200 °C (0.5 min) and in 50 °C/min to 220 °C (2 min).

Method III: Measurements were conducted on a BGB-174 column (30 m x 0.25 mm x 0.25 µm). A split injection mode (1:10) was used and a sample amount of 1 µL was injected in this method. As carrier gas a N_2/synthetic air mixture was used in a linear velocity control mode with a column flow of 0.96 mL/min. The following temperature gradient was used in this method: 120 °C start temperature (1 min), in 3 °C/min to 150 °C and in 40 °C/min to 200 °C.

Method IV: Measurements were conducted on a BGB-174 column (30 m x 0.25 mm x 0.25 µm). A split injection mode (1:10) was used and a sample amount of 1 µL was injected in this method. As carrier gas a N_2/synthetic air mixture was used in a linear velocity control mode with a column flow of 0.98 mL/min. The following temperature gradient was used in this method: 160 °C start temperature, in 5 °C/min to 210 °C (2 min).

Mass Spectrometry: The qualitative mass analysis was performed via GC as well. A HP-5MS UI 30 m long, 0.25 mm diameter, 0.25 µm thickness of the layer) column was used. The carrier gas was Helium and the detector was of the Type 5977A MSD of AGILENT TECHNOLOGIES INC.

3. Possible products in the hydroformylation/aldoxime formation of 1-octene



Scheme S1: Overview on possible products and by-products of one-pot hydroformylation/aldoxime formation (same declaration as in the manuscript).

4. Investigation on aldoxime formation in an aqueous solvent system

Table S1: Results of condensation of nonanal with hydroxyl amine under aqueous, biphasic conditions

#	temperature [°C]	X_2 [%[a]]	Y_3 [%[a]]
1.1[b]	25	99	91
1.2[c]	25	99	97
1.3[b]	80	99	97
1.4[c]	80	99	97

conditions: 6.7 mmol nonanal (2), 10 mmol hydroxyl amine (as 50 w% aqueous solution), t = 20 min, $m_{1\text{-BuOH}}$ = 1.8 g, $m_{\text{total water}}$ = 1.8 g; [a]conversion and yield determined via GC-FID [b]slow addition of nonanal over 15 min. [c]fast addition of nonanal in 3 s.

5. Hydroformylation of 1-octene in a solvent system consisting of H_2O and 1-BuOH

Table S2: Results of hydroformylation of 1-octene in a solvent system consisting of H_2O and 1-BuOH under literature-known conditions.

#	t [h]	X_{1a} [%[a]]	Y_{2a} [%[a]]	Y_{4a} [%[a]]	Y_{7a} [%[a]]
2.1	0.5	40	35	2	2
2.2	1	67	61	3	3
2.3	1.5	80	72	3	3
2.4	2	86	80	4	3
2.5	3	94	87	4	3

conditions: 134 mmol 1-octene (1a), $Rh(acac)(CO)_2$ (0.1 mol%), $c_{Rh,aq}$ = 0.0037 mol/L Sulfoxantphos (0.5 mol%), $m_{1\text{-}BuOH}$ = 36 g, m_{water} = 36 g, T = 140 °C, p = 40 bar, $CO:H_2$ = 1:1, [a]conversion and yield determined via GC-FID

6. First experiments of one-pot hydroformylation / aldoxime formation in an aqueous biphasic system

Table S3: Results of initial one-pot reaction for hydroformylation / aldoxime formation with 1-octene as substrate.

#	t [h]	X_{1a} [%[a]]	Y_{2a} [%[a]]	Y_{3a} [%[a]]	Y_{4a} [%[a]]	Y_{5a} [%[a]]	Y_{6a} [%[a]]	Y_{7a} [%[a]]	Y_{8a} [%[a]]	Y_{9a} [%[a]]	Y_{10a} [%[a]]
3.1	1	96	2	8	-	1	12	43	1	-	-
3.2	2	97	1	20	-	1	14	32	1	-	-

conditions: 6.7 mmol 1-octene (1a), 8.7 mmol hydroxyl amine (1.3 eq., as 50 w% aqueous solution), $Rh(acac)(CO)_2$ (0.1 mol%), $c_{Rh,aq}$ = 0.0037 mol/L Sulfoxantphos (0.5 mol%), $m_{1\text{-}BuOH}$ = 1.8 g, $m_{water,total}$ = 1.8 g, T = 140 °C, p = 40 bar, $CO:H_2$ = 1:1, [a]conversion and yield determined via GC-FID

7. Optimization of one-pot hydroformylation/aldoxime formation using 1-octene

For clarity, only the conversion of 1-octene, the yield of the linear and iso-oxime and octane isomers are shown with the corresponding variation of the parameters.

Table S4: Results of statistical experiment plan (developed with MODDE 10.1) and corresponding results for yield of linear amine and linear to branched (l/b) ratio.

#	no.	*T* [°C]	*p* [bar]	*CO:H₂*	*Rh:S* [mol%]	*Rh:L*	eq of NH_2OH	X_{1a} [%[a]]	Y_{3a} [%[a]]	Y_{5a} [%[a]]	Y_{7a} [%[a]]
4.1	N9	90	60	1:2	0.5	1:1	1	49	28	1	14
4.2	N52	90	20	2:1	0.05	1:1	1	19	11	0	0
4.3	N15	90	60	2:1	0.5	1:1	3	43	35	1	0
4.4	N125	90	60	2:1	0.05	1:10	3	2	1	0	0
4.5	N103	90	60	1:2	0.5	1:1	1	45	41	1	0
4.6	N27	90	60	1:2	0.5	1:10	3	24	21	1	0
4.7	N33	90	40	1:1	0.275	1:5	2	31	28	1	0
4.8	N123	90	60	2:1	0.5	1:10	1	24	21	0	0
4.9	N56	90	60	1:2	0.5	1:1	1	39	35	1	0
4.10	N50	90	20	1:2	0.05	1:1	3	-	-	-	-
4.11	N113	90	20	1:2	0.5	1:10	3	36	32	2	0
4.12	N70	90	20	2:1	0.05	1:10	3	12	9	0	0
4.13	N99	90	20	2:1	0.05	1:1	1	18	15	0	0
4.14	N64	90	20	1:2	0.05	1:10	1	37	32	1	0
4.15	N101	90	20	2:1	0.5	1:1	3	44	40	1	0
4.16	N109	90	60	2:1	0.5	1:1	3	60	56	1	0
4.17	N97	90	20	1:2	0.05	1:1	3	7	5	0	0
4.18	N74	90	60	1:2	0.5	1:10	3	46	41	1	0
4.19	N3	90	20	1:2	0.05	1:1	3	13	10	0	0
4.20	N115	90	20	2:1	0.5	1:10	1	42	38	1	0
4.21	N1	90	20	1:2	0.5	1:1	1	27	22	2	0
4.22	N31	90	60	2:1	0.05	1:10	3	2	1	0	0
4.23	N60	90	60	2:1	0.05	1:1	1	6	5	0	0
4.24	N21	90	20	2:1	0.5	1:10	1	31	28	1	0
4.25	N105	90	60	1:2	0.05	1:1	3	37	32	1	0
4.26	N107	90	60	2:1	0.05	1:1	1	14	11	0	0
4.27	N111	90	20	1:2	0.05	1:10	1	14	11	0	0
4.28	N76	90	60	2:1	0.5	1:10	1	20	16	0	0
4.29	N119	90	60	1:2	0.05	1:10	1	9	7	0	0
4.30	N17	90	20	1:2	0.05	1:10	1	100	5	0	86
4.31	N58	90	60	1:2	0.05	1:10	3	5	3	0	0
4.32	N48	90	20	1:2	0.5	1:1	1	35	30	1	0
4.33	N121	90	60	1:2	0.5	1:10	3	19	16	0	0
4.34	N11	90	60	1:2	0.05	1:1	3	11	9	0	0

4.35	N29	90	60	2:1	0.5	1:10	1	10	8	0	0
4.36	N25	90	60	1:2	0.05	1:10	1	4	3	0	0
4.37	N62	90	60	2:1	0.5	1:1	3	37	34	1	0
4.38	N19	90	20	1:2	0.5	1:10	3	24	20	1	0
4.39	N13	90	60	2:1	0.05	1:1	1	3	2	0	0
4.40	N23	90	20	2:1	0.05	1:10	3	2	1	0	0
4.41	N54	90	20	2:1	0.5	1:1	3	29	26	1	0
4.42	N95	90	20	1:2	0.5	1:1	1	33	30	1	0
4.43	N127	90	40	1:1	0.5	1:1	2	33	31	1	0
4.44	N72	90	40	1:1	0.275	1:5	2	8	7	0	0
4.45	N78	90	60	2:1	0.05	1:10	3	1	0	0	0
4.46	N117	90	20	2:1	0.05	1:10	3	1	0	0	0
4.47	N80	90	40	1:1	0.275	1:5	2	9	8	0	0
4.48	N66	90	20	1:2	0.5	1:10	3	29	14	1	14
4.49	N5	90	20	2:1	0.05	1:1	1	3	2	0	0
4.50	N68	90	20	2:1	0.5	1:10	1	7	5	0	1
4.51	N7	90	20	2:1	0.5	1:1	3	12	9	0	2
4.52	N38	120	40	2:1	0.275	1:5	2	83	14	3	62
4.53	N41	120	40	1:1	0.275	1:1	2	32	23	1	7
4.54	N39	120	20	1:1	0.275	1:5	2	55	35	2	15
4.55	N43	120	40	1:1	0.5	1:5	2	73	59	3	9
4.56	N89	120	40	1:1	0.275	1:10	2	96	21	13	14
4.57	N129	120	40	1:1	0.275	1:5	1	94	30	2	24
4.58	N42	120	40	1:1	0.275	1:10	2	95	37	1	51
4.59	N36	120	40	1:1	0.275	1:5	3	96	23	1	68
4.60	N85	120	40	2:1	0.275	1:5	2	73	58	2	9
4.61	N45	120	40	1:1	0.275	1:5	2	93	67	2	20
4.62	N94	120	40	1:1	0.275	1:5	2	82	60	2	16
4.63	N139	120	40	1:1	0.275	1:5	2	89	33	3	48
4.64	N46	120	40	1:1	0.275	1:5	2	92	55	3	31
4.65	N50	120	20	1:2	0.05	1:1	1	25	12	0	12
4.66	N137	120	40	1:1	0.05	1:5	2	54	31	1	17
4.67	N131	120	40	1:2	0.275	1:5	2	92	30	2	58
4.68	N84	120	40	1:2	0.275	1:5	2	95	30	3	59
4.69	N87	120	60	1:1	0.275	1:5	2	96	70	5	17
4.70	N82	120	40	1:1	0.275	1:5	1	96	53	5	33
4.71	N44	120	40	1:1	0.5	1:5	2	96	82	2	5
4.72	N40	120	60	1:1	0.275	1:5	2	96	81	2	6
4.73	N136	120	40	1:1	0.275	1:10	2	97	27	2	6
4.74	N132	120	40	2:1	0.275	1:5	2	92	10	1	19
4.75	N141	120	40	1:1	0.275	1:5	2	95	38	2	22
4.76	N83	120	40	1:1	0.275	1:5	3	93	33	2	25
4.77	N88	120	40	1:1	0.275	1:1	2	98	23	2	26

4.78	N138	120	40	1:1	0.5	1:5	2	97	15	0	28
4.79	N92	120	40	1:1	0.275	1:5	2	96	14	1	20
4.80	N91	120	40	1:1	0.5	1:5	2	99	25	2	8
4.81	N130	120	40	1:1	0.275	1:5	3	97	54	2	13
4.82	N93	120	40	1:1	0.275	1:5	2	95	38	2	17
4.83	N133	120	20	1:1	0.275	1:5	2	88	19	2	27
4.84	N135	120	40	1:1	0.275	1:1	2	98	11	1	14
4.85	N134	120	60	1:1	0.275	1:5	2	98	16	2	6
4.86	N47	120	40	1:1	0.275	1:5	2	95	70	2	14
4.87	N37	120	40	1:2	0.275	1:5	2	91	50	2	32
4.88	N35	120	40	1:1	0.275	1:5	1	98	55	5	17
4.89	N86	120	40	1:1	0.275	1:5	2	90	69	2	13
4.90	N90	120	40	1:1	0.05	1:5	2	12	6	0	2
4.91	N18	150	20	1:1	0.5	1:10	1	94	18	3	61
4.92	N26	150	60	1:2	0.5	1:10	1	97	48	8	24
4.93	N106	150	60	1:2	0.5	1:1	3	97	57	6	20
4.94	N120	150	60	1:2	0.5	1:10	1	97	46	8	25
4.95	N71	150	20	2:1	0.5	1:10	3	88	21	2	46
4.96	N102	150	20	2:1	0.05	1:1	3	78	4	2	51
4.97	N53	150	20	2:1	0.5	1:1	1	92	11	2	67
4.98	N51	150	20	1:2	0.5	1:1	3	87	2	0	48
4.99	N96	150	20	1:2	0.05	1:1	1	76	1	1	36
4.100	N16	150	60	2:1	0.05	1:1	3	91	4	3	53
4.101	N75	150	60	1:2	0.05	1:10	3	96	6	2	33
4.102	N12	150	60	1:2	0.5	1:1	3	86	3	6	19
4.103	N118	150	20	2:1	0.5	1:10	3	63	6	1	46
4.104	N6	150	20	2:1	0.5	1:1	1	90	2	0	63
4.105	N59	150	60	1:2	0.5	1:1	3	90	15	3	26
4.106	N4	150	20	1:2	0.5	1:1	3	93	2	0	83
4.107	N32	150	60	2:1	0.5	1:10	3	87	9	3	43
4.108	N61	150	60	2:1	0.5	1:1	1	80	22	7	29
4.109	N126	150	60	2:1	0.5	1:10	3	73	24	5	17
4.110	N116	150	20	2:1	0.05	1:10	1	47	4	1	37
4.111	N55	150	20	2:1	0.05	1:1	3	54	1	0	49
4.112	N20	150	20	1:2	0.05	1:10	3	9	1	0	4
4.113	N49	150	20	1:2	0.05	1:1	1	72	4	1	64
4.113	N14	150	60	2:1	0.5	1:1	1	77	12	6	27
4.115	N81	150	40	1:1	0.275	1:5	2	69	30	4	22
4.116	N110	150	60	2:1	0.05	1:1	3	58	0	1	27
4.117	N34	150	40	1:1	0.275	1:5	2	67	27	3	24
4.118	N28	150	60	1:2	0.05	1:10	3	86	4	2	48
4.119	N10	150	60	1:2	0.05	1:1	1	78	10	3	55
4.120	N122	150	60	1:2	0.5	1:10	3	85	8	3	22

4.121	N24	150	20	2:1	0.5	1:10	3	86	7	1	57
4.122	N22	150	20	2:1	0.05	1:10	1	92	2	0	56
4.123	N98	150	20	1:2	0.5	1:1	3	83	3	1	53
4.124	N8	150	20	2:1	0.05	1:1	3	59	2	1	50
4.125	N63	150	60	2:1	0.05	1:1	3	60	3	3	34
4.126	N114	150	20	1:2	0.05	1:10	3	91	2	0	59
4.127	N79	150	60	2:1	0.5	1:10	3	85	13	5	35
4.128	N104	150	60	1:2	0.05	1:1	1	87	4	2	55
4.129	N65	150	20	1:2	0.5	1:10	1	76	4	1	40
4.130	N2	150	20	1:2	0.05	1:1	1	82	2	0	76
4.131	N69	150	20	2:1	0.05	1:10	1	51	6	1	40
4.132	N112	150	20	1:2	0.5	1:10	1	73	12	2	45
4.133	N57	150	60	1:2	0.05	1:1	1	63	16	8	27
4.134	N108	150	60	2:1	0.5	1:1	1	80	16	7	27
4.135	N124	150	60	2:1	0.05	1:10	1	59	13	6	31
4.136	N73	150	60	1:2	0.5	1:10	1	74	29	8	23
4.137	N30	150	60	2:1	0.05	1:10	1	60	13	7	29
4.138	N100	150	20	2:1	0.5	1:1	1	53	7	2	41
4.139	N67	150	20	1:2	0.05	1:10	3	89	2	0	82
4.140	N77	150	60	2:1	0.05	1:10	1	95	4	3	49
4.141	N128	150	40	1:1	0.275	1:5	2	51	1	2	37

conditions: 6.7 mmol 1-octene (1a), hydroxyl amine (as 50 w% aqueous solution), $Rh(acac)(CO)_2$, Sulfoxantphos, $m_{1\text{-}BuOH}$ = 1.8 g, $m_{water,total}$ = 1.8 g, t = 1.5 h, [a]conversion and yield determined via GC-FID

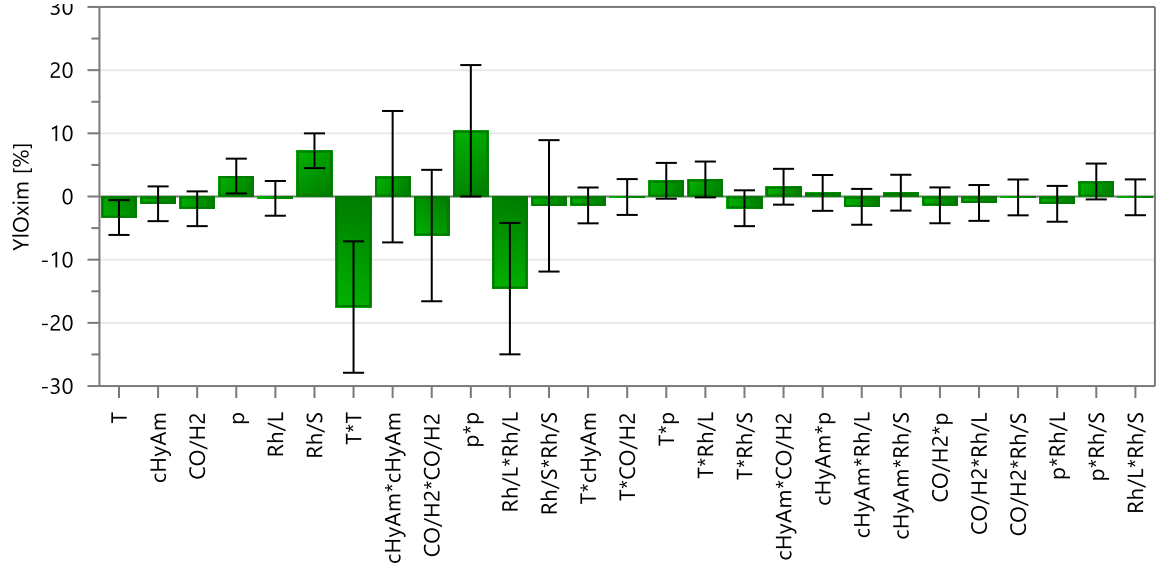


Figure S4: Sensitive plot of the DoE with regard to the yield of the linear oxime (3)

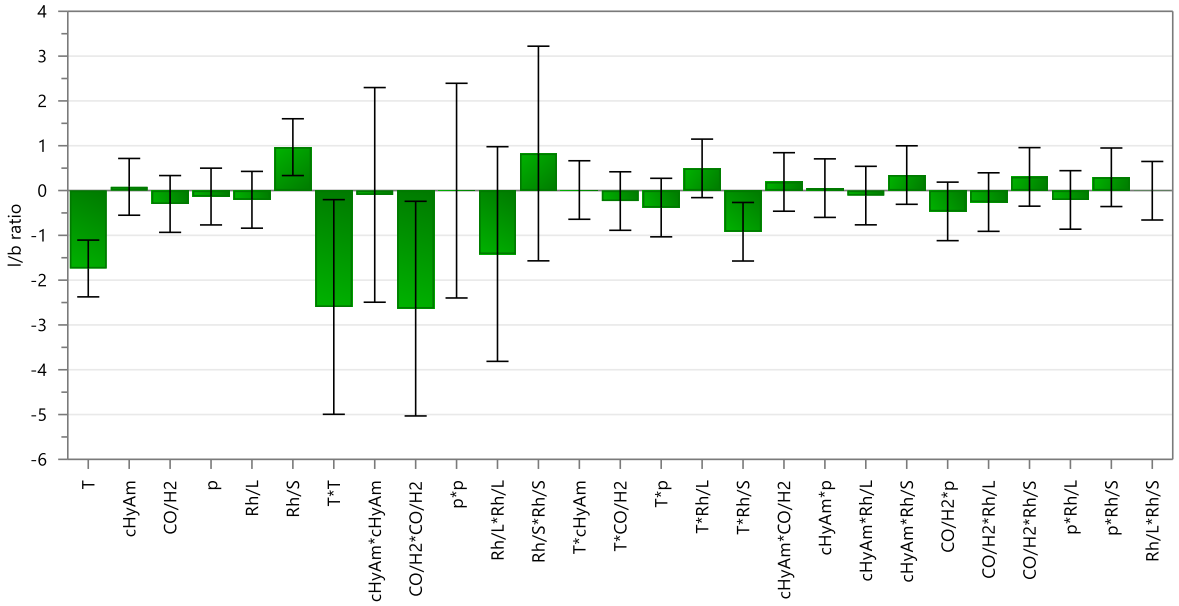


Figure S5: Sensitive plot of the DoE with regard to the ratio of linear and iso-oximes (l/b, linear-to-branched ratio).

8. Small scale one-pot reaction under optimized conditions

Table S5: One-pot hydroformylation / aldoxime formation of 1-octene under optimized conditions.

#	X_{1a} [%[a]]	Y_{2a} [%[a]]	Y_{3a} [%[a]]	Y_{4a} [%[a]]	Y_{5a} [%[a]]	Y_{6a} [%[a]]	Y_{7a} [%[a]]	Y_{8a} [%[a]]	Y_{9a} [%[a]]	Y_{10a} [%[a]]
5.1	95	-	80	-	1	2	7	3	-	-
5.2	97	-	82	-	3	5	4	1	-	<1

conditions: 6.7 mmol 1-octene (1a), 16.75 mmol hydroxyl amine (2.5 eq., as 50 w% aqueous solution), $Rh(acac)(CO)_2$ (0.5 mol%), $c_{Rh,aq}$ = 0.0037 mol/L Sulfoxantphos (2.5 mol%), $m_{1\text{-}BuOH}$ = 1.8 g, $m_{water,total}$ = 1.8 g, T = 100 °C, p = 60 bar, $CO:H_2$ = 1:1, t = 4 h; [a]conversion and yield determined via GC-FID

9. Substrate variation in small scale

Table S6: Application of different substrates in the one-pot hydroformylation / aldoxime formation reaction.

#	ind.	substrate	X_{1x} [%[a]]	Y_{2x} [%[a]]	Y_{3x} [%[a]]	Y_{4x} [%[a]]	Y_{5x} [%[a]]	Y_{6x} [%[a]]	Y_{7x} [%[a]]	Y_{8x} [%[a]]	Y_{9x} [%[a]]	Y_{10x} [%[a]]
6.1	b	1-hexene	>99	-	88	-	4	1	0	-	6	1
6.2	a	1-octene	97	-	82	-	3	5	4	1	-	<1
6.3	c	1-decene	>99	-	74	-	5	7	7	2	6	1
6.4	d	1-dodecene	94	-	41	-	6	9	13	7	13	2
6.5	e	cyclooctene	7	-	-	-	-	6	-	-	-	-
6.6	e	cyclooctene[b]	10	-	1	-	-	5	-	-	-	-
6.7	e	cyclooctene[c]	>99	-	84	-	-	4	-	-	10	-
6.8	f	4-octene	2	-	-	-	-	-	-	-	-	-
6.9	f	4-octene[b]	66	-	-	-	19	34	-	-	2[d]	-
6.10	f	4-octene[c]	99	-	-	-	81	4	-	-	4[d]	-
6.11	g	4-vinyl-cyclohexene	>99	-	82	-	3	6	-	-	8	1
6.12	h	styrene	>99	-	34	-	53	2	-	-	10	1
6.13	i	dihydro-myrcenol	>99	-	68	-	1	6	1	-	21	3
6.14	j	eugenol	>99	-	15	-	2	6	8	-	41	27
6.15	k	methyl 10-undecenoate	>99	-	41	-	4	5	4	-	34	12
6.16	l	1-pentene	46	-	40	-	3	-	-	-	2	1

conditions: 6.7 mmol 1-octene (1a), 16.75 mmol hydroxyl amine (2.5 eq., as 50 w% aqueous solution), $Rh(acac)(CO)_2$ (0.5 mol%), $c_{Rh,aq}$ = 0.0037 mol/L sulfoxantphos (2.5 mol%), $m_{1\text{-}BuOH}$ = 1.8 g, $m_{water,total}$ = 1.8 g, T = 100 °C, p = 60 bar, $CO:H_2$ = 1:1, t = 4 h; [a]conversion and yield determined via GC-FID, [b]use of TPPTS as ligand (Rh:L = 1:10), [c]use of TPP as Ligand (Rh:L = 1:10), [d]yield of branched nitriles

10. Substrate variation in large scale with integrated gas consumption measurements

Table S7: Conversion and yield of large scale experiments of one-pot hydroformylation / aldoxime formation with varying substrates.

#	ind.	substrate	X_{1x} [%[a]]	Y_{2x} [%[a]]	Y_{3x} [%[a]]	Y_{4x} [%[a]]	Y_{5x} [%[a]]	Y_{6x} [%[a]]	Y_{7x} [%[a]]	Y_{8x} [%[a]]	Y_{9x} [%[a]]	Y_{10x} [%[a]]
7.1	b	1-hexene	>99	<1	73	<1	7	4	5	<1	9	2
7.2	a	1-octene	>99	<1	80	<1	6	<1	2	4	5	<1
7.3	c	1-decene	99	<1	75	<1	10	6	2	<1	6	1
7.4	d	1-dodecene	>99	<1	61	<1	11	4	2	2	15	<1
7.5	g	4-vinyl-cyclohexene	>99	<1	85	<1	6	4	1	<1	5	<1
7.6	h	styrene	>99	<1	38	<1	54	3	-	<1	5	1
7.7	i	dihydro-myrcenol	>99	<1	67	<1	4	5	1	<1	20	4
7.8	j	eugenol	>99	<1	22	<1	5	7	6	<1	39	23
7.9	k	methyl 10-undecenoate	>99	<1	35	<1	4	5	3	<1	41	11

conditions: 134 mmol substrate (1x), 335 mmol hydroxyl amine (2.5 eq, as 50 w% aqueous solution), $Rh(acac)(CO)_2$ (0.5 mol%), sulfoxantphos (2.5 mol%), $c_{Rh,aq}$ = 0.015 mol/L, $c_{ligand,aq}$ = 0.074 mol/L, T = 100 °C, p = 60 bar, V_{total} = 105 - 120 mL.

11. Product characterization

E/Z ratios were determined by comparing the areas of the more deep shifted H (E-isomer) and less deep shifted H (Z-isomer) in accordance to the literature[5]:

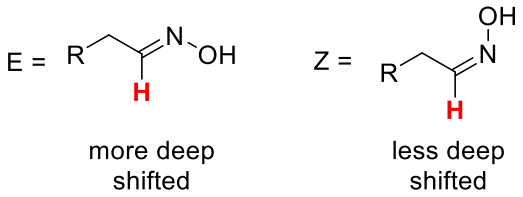


Figure S6: (E) and (Z)-isomer of aldoximes, affecting the chemical shift in NMR-studies.

The chemical shifts of the H from the OH-group could not be identified in all spectra. It usually occurs in regions from 8 to 10 ppm. In the case of heptanal oxime, the remaining shifts are in good accordance with literature values.[6]

Hexanal oxime **3l** (through application of 1-pentene):

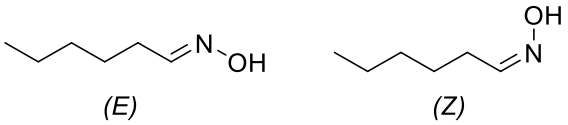


Figure S7: Hexanal oxime in (E)- and (Z)-orientation of the oxime group.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.87-0.92 ppm (m, 3H), 1.30-1.34 ppm (m, 4H), 1.49 ppm (m, 2H), 2.18 ppm (m, 1H), 2.37 ppm (m, 1H), 6.72 ppm (t, J_1 = 5.1 Hz, 0.77H (*Z*)), 7.42 ppm (t, J_1 = 6.1 Hz, 0.23H (*E*)).

E/Z-ratio: 23/77

^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.07 ppm (1C), 22.50 ppm (1C), 25.88 ppm (1C), 26.35 ppm (1C), 29.57 ppm (1C), 31.08 ppm (1C), 31.39 ppm (1C), 31.67 ppm (1C), 152.62 ppm (1C), 153.33 ppm (1C).

HRMS: calculated m/z ($M+H^+$) = 116.10699, found = 116.10651.

EI-MS: m/z (%) = 115 (M^+, 1), 100 (1), 98 (3), 96 (1), 87 (1), 86 (5), 84 (1), 83 (3), 82 (3), 81 (1), 80 (1), 79 (1), 74 (1), 73 (2), 72 (28), 70 (2), 69 (3), 68 (4), 67 (2), 60 (3), 59 (100), 58 (1), 57 (2), 56 (6), 55 (15), 54 (4), 53 (3), 52 (1), 51 (1), 50 (1).

Heptanal oxime **3b** (through application of 1-hexene):

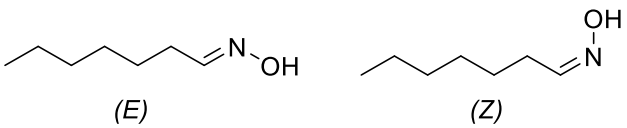


Figure S8: Heptanal oxime in (E)- and (Z)-orientation of the oxime group.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.87-0.91 ppm (m, 3H), 1.25-1.38 ppm (m, 6H), 1.45-1.54 ppm (m, 2H), 2.17-2.40 (m, 2H), 6.71 (t, J_1 = 5.5, 0.79H (*Z*)), 7.43 ppm (t, J_1 = 6.1 Hz, 0.21H (*E*)).

E/Z-ratio: 21/79

^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.19 ppm (1C), 22.68 ppm (1C), 24.97 ppm (1C), 26.21 ppm (1C), 29.19 ppm (1C), 31.65 ppm (1C), 153.60 ppm (1C).

HRMS: calculated: m/z ($M+H^+$) = 130.12264, found: = 130.12225.

EI-MS: m/z (%) = 129 (M^+, 1), 112 (3), 101 (1), 100 (2), 97 (3), 96 (1), 95 (2), 86 (8), 84 (1), 83 (1), 82 (3), 81 (1), 80 (1), 73 (2), 72 (25), 70 (1), 69 (5), 68 (3), 67 (4), 66 (1), 65 (1), 60 (3), 59 (100), 58 (1), 57 (1), 56 (6), 55 (14), 54 (5), 53 (3), 52 (1), 51 (1), 50 (1).

Nonanal oxime **3a** (through application of 1-octene):

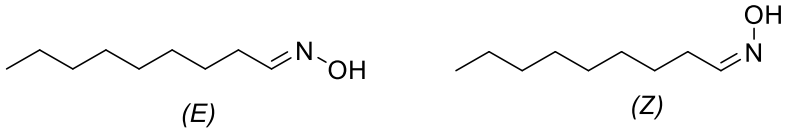


Figure S9: Nonanal oxime in (E)- and (Z)-orientation of the oxime group.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.86 – 0.90 ppm (m, 3H), 1.27-1.36 ppm (m, 10H), 1.45 – 1.52 ppm (m, 2H), 2.16 – 2.22 (m, 1H), 2.33 – 2.40 ppm (m, 1H), 6.71 (t, J_1 = 5.5 Hz, 0.58H (*Z*)), 7.42 ppm (t, J_1 = 6.1 Hz, 0.42H (*E*)).

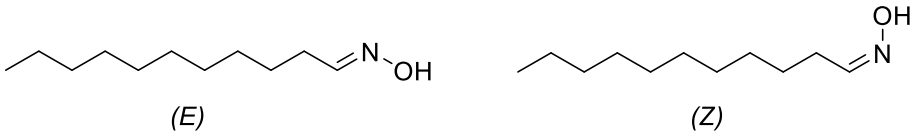
E/Z-ratio: 42/58

^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.24 ppm (1C), 22.79 ppm (1C), 25.04 ppm (1C), 26.22 ppm (1C), 26.67 ppm (1C), 29.25 ppm – 29.60 ppm (5C), 31.97 ppm (1C), 152.66 ppm (1C), 153.36 ppm (1C).

EI-MS: m/z (%) = 157 (M^+, 1), 141 (2), 140 (12), 128 (7), 125 (2), 124 (2), 123 (1), 115 (1), 114 (12), 112 (2), 111 (1), 110 (5), 101 (3), 100 (40), 98 (2), 97 (4), 96 (13), 95 (4), 93 (1), 87 (3), 86 (43), 84 (5), 83 (15), 82 (29), 81 (12), 80 (2), 79 (3), 77 (2), 73 (4), 72 (44), 71 (3), 70 (11), 69 (31), 68 (19), 67 (17), 66 (3), 65 (3), 63 (1), 60 (3), 59 (100), 58 (6), 57 (25), 56 (23), 55 (58), 54 (26), 53 (18), 52 (6), 51 (6), 50 (2).

HRMS: calculated: m/z ($M+H^+$) = 158.1540, found: 158.1539

Undecanal oxime **3c** (through application of 1-decene):



(E) *(Z)*

Figure S10: Undecanal oxime in (E)- and (Z)-orientation of the oxime group.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.81 ppm (t, J_1 = 7.0 Hz, 3H), 1.15-1.3 ppm (m, 14H), 1.42 ppm (m, 2H), 2.12 (m, 1H), 2.30 ppm (m, 1H), 6.65 (t, J_1 = 5.5 Hz, 0.4H (*Z*)), 7.36 ppm (t, J_1 = 6.1 Hz, 0.6H (*E*)).

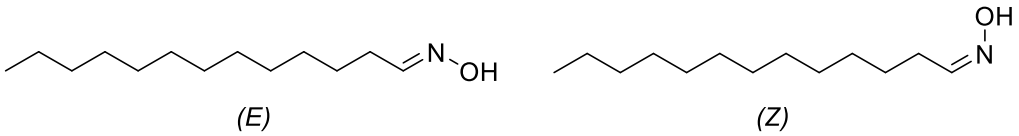
E/Z-ratio: 60/40

^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.04 ppm (1C), 22.62 ppm (1C), 26.02 ppm (1C), 26.47 ppm (1C), 29.04 ppm – 29.50 ppm (7C), 31.83 ppm (1C), 152.56 ppm (1C), 153.29 ppm (1C).

HRMS: calculated: m/z ($M+H^+$) = 186.18524, found = 186.18484.

EI-MS: m/z (%) = 185 (M^+, 1), 169 (3), 168 (27), 156 (2), 152 (3), 143 (1), 142 (6), 140 (1), 138 (3), 129 (1), 128 (12), 124 (4), 123 (1), 116 (1), 115 (1), 114 (15), 112 (2), 111 (5), 110 (9), 109 (4), 108 (1), 101 (4), 100 (56), 98 (4), 97 (16), 96 (18), 95 (11), 94 (2), 93 (3), 91 (2), 87 (3), 86 (59), 85 (4), 84 (6), 83 (22), 82 (30), 81 (14), 80 (4), 79 (7), 78 (1), 77 (4), 73 (5), 72 (51), 71 (8), 70 (12), 69 (34), 68 (21), 67 (26), 66 (3), 65 (5), 63 (1), 60 (4), 59 (100), 57 (28), 56 (29), 55 (77), 54 (25), 53 (19), 52 (4), 51 (4), 50 (1)

Tridecanal oxime **3d** (through application of 1-decene):



(E) *(Z)*

Figure S11: Tridecanal oxime in (E)- and (Z)-orientation of the oxime group.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.88 ppm (t, J_1 = 6.9 Hz, 3H), 1.21-1.35 ppm (m, 18H), 2.17-2.39 ppm (m, 2H), 6.71 ppm (t, J_1 = 5.5 Hz, 0.84H (*Z*)), 7.42 ppm (t, J_1 = 6.1 Hz, 0.16H (*E*)).

E/Z-ratio: 16/84

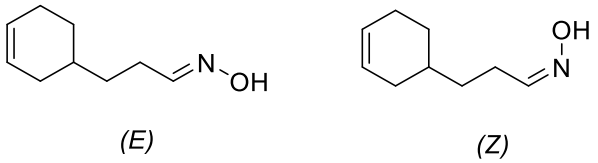
^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.10 ppm (1C), 22.67 ppm (1), 24.78 ppm (1C,), 26.08 ppm (1C), 29.29 ppm-29.63 ppm (8C), 31.89 ppm (1C), 153.46 ppm (1C).

HRMS: calculated: m/z ($M+H^+$) = 214.21654, found = 214.21667.

EI-MS: m/z (%) = 213 (M^+, 1), 197 (7), 196 (38), 184 (2), 180 (2), 170 (5), 156 (3), 152 (4), 142 (3), 140 (1), 139 (1), 138 (5), 137 (2), 129 (1), 128 (12), 126 (1), 125 (5), 124 (7), 123 (3), 115 (1),

114 (15), 112 (3), 111 (9), 110 (11), 109 (4), 107 (1), 101 (4), 100 (51), 98 (4), 97 (21), 96 (22), 95 (11), 94 (3), 93 (3), 91 (2), 87 (2), 86 (47), 85 (5), 84 (7), 83 (25), 82 (29), 81 (16), 80 (4), 79 (8), 77 (3), 73 (5), 72 (57), 71 (9), 70 (15), 69 (38), 68 (16), 67 (24), 66 (3), 65 (4), 60 (4), 59 (100), 57 (40), 56 (33), 55 (83), 54 (23), 53 (16), 52 (4), 51 (3).

3-(cyclohex-3-en-1-yl)propanal oxime **3g** (through application of 4-vinyl cyclohexene):



(E) *(Z)*

Figure S12: 3-(cyclohex-3-en-1-yl)propanal oxime in (E)- and (Z)-orientation of the oxime group.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.19-1.29 (m, 1H), 1.43-1.50 (m, 2H), 1.54-1.79 (m, 4H), 2.04-2.15 (m, 3H), 2.22-2.27 (m, 1H), 2.40-2.46 (m, 1H), 5.62-5.69 ppm (m, 2H), 6.72 ppm (t, J_1 = 5.5 Hz, 0.46H (*Z*)), 7.44 ppm (t, J_1 = 6.1 Hz, 0.54H (*E*)).

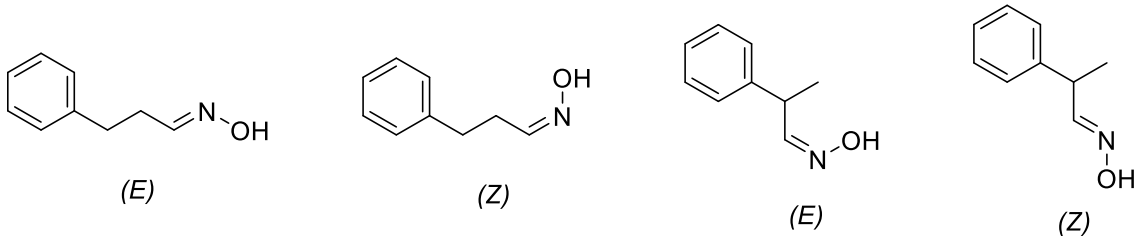
E/Z-ratio: 54/46

^{13}C NMR (151 MHz, $CDCl_3$): δ = 22.62 ppm (1C), 25.25 ppm (1C), 27.14 ppm (1C), 28.76 ppm (1C), 31.70 ppm (1C), 32.89 ppm-33.44 ppm (1C), 126.37 ppm/127.20 ppm (2C), 152.66 ppm/153.36 ppm (1C).

HRMS: calculated: m/z ($M+H^+$) = 154.12264 g/mol, found = 154.12217 g/mol.

EI-MS: m/z (%) = 153 (M^+, 4), 152 (3), 136 (16), 135 (3), 134 (14), 121 (5), 120 (8), 118 (4), 117 (12), 108 (5), 107 (12), 106 (10), 99 (6), 98 (3), 96 (3), 95 (11), 94 (14), 93 (21), 92 (16), 91 (46), 82 (7), 81 (32), 80 (37), 79 (100), 78 (17), 77 (59), 76 (3), 75 (5), 72 (9), 68 (7), 67 (53), 66 (16), 65 (22), 63 (8), 59 (14), 58 (5), 57 (8), 56 (10), 55 (26), 54 (63), 53 (47), 52 (15), 51 (26), 50 (10).

3-Phenylpropanal oxime **3h** and 2-phenylpropanal oxime **5h** (through application of styrene):



(E) *(Z)* *(E)* *(Z)*

Figure S13: 3-Phenylpropanal oxime in (E)- and (Z)-orientation of the oxime group (left two molecules) and 2-phenylpropanal oxime in (E)- and (Z)-orientation of the oxime group (right two molecules).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.43 ppm-1.47 ppm (m, 1.5H), 2.53 ppm (m, 0.5H), 2.71 ppm (m, 0.5H), 2.83 ppm (t, J_1 = 7.8 Hz, 1H), 3.67 ppm (p, J_1 = 7.0 Hz, 0.5H), 4.45 ppm (p, J_1 = 7.3 Hz, 0.5H), 6.76 ppm (t, J_1 = 5.3 Hz, 0.15H (*Z*)), 6.81 ppm (d, J_1 =7.4 Hz, 0.12H (*Z*)), 7.19 ppm-7.36 ppm (m, 5H), 7.47 ppm (t, J_1 = 5.9 Hz, 0.27H (*E*)), 7.52 ppm (d, J_1 = 6.1 Hz, 0.47H (*E*)).

2-phenylpropanal oxime/3-propanal oxime ratio after purification: 58/42

E/Z-ratio: 80/20 (2-phenylpropanal), 64/36 (3-phenylpropanal)

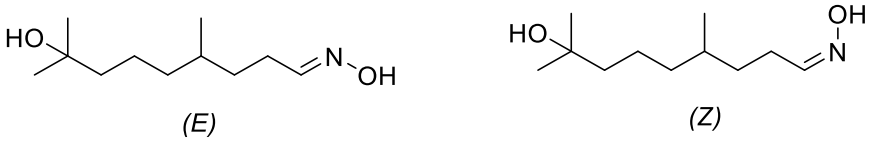
^{13}C NMR (151 MHz, $CDCl_3$): δ = 18.96 ppm (1C), 31.32 ppm (1C), 32.93 ppm (1C), 40.46 ppm (1C), 126.40 ppm-128.89 ppm (5C), 142.13 ppm (1C), 155.13 ppm (1C).

HRMS: calculated: m/z ($M+H^+$) = 150.09134 g/mol, found = 150.09084 g/mol.

EI-MS (3-Phenylpropanal oxime): m/z (%) = 149 (M^+, 1), 132 (8), 131 (1), 130 (4), 118 (3), 117 (33), 115 (5), 106 (2), 105 (17), 104 (16), 103 (14), 102 (4), 92 (7), 91 (100), 89 (9), 87 (2), 86 (1), 79 (8), 78 (16), 77 (25), 76 (5), 75 (4), 74 (6), 73 (1), 72 (1), 66 (2), 65 (29), 64 (3), 63 (13), 62 (6), 61 (2), 58 (3), 54 (1), 53 (2), 52 (6), 51 (19), 50 (11).

EI-MS (2-Phenylpropanal oxime): m/z (%) = 149 (M^+, 15), 132 (49), 131 (15), 130 (43), 117 (46), 116 (16), 115 (11), 106 (11), 105 (97), 104 (47), 103 (61), 102 (16), 91 (57), 90 (13), 89 (26), 79 (50), 78 (55), 77 (100), 76 (15), 75 (13), 74 (16), 65 (14), 63 (29), 62 (12), 52 (16), 51 (53), 50 (30).

<u>8-hydroxy-4,8-dimethylnonanal oxime **3i** (through application of dihydromyrcenol):</u>



(E) *(Z)*

Figure S14: 8-hydroxy-4,8-dimethylnonanal oxime in (E)- and (Z)-orientation of the oxime group.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.90 ppm (t, J_1 = 6.00 Hz, 3H), 1.21 ppm (s, 6H), 1.30 ppm – 1.44 ppm (m, 9H,), 2.15 – 2.25 ppm (m, 1H), 2.35 – 2.45 ppm (m, 1H), 6.70 ppm (t, J_1 = 5.5 Hz, 0.29H (*Z*)), 7.42 ppm (t, J_1 = 6.1 Hz, 0.71H (*E*)).

E/Z-ratio: 71/29

^{13}C NMR (151 MHz, $CDCl_3$): δ =19.48 ppm (1C), 21.78 ppm (1C), 22.75 ppm (1C), 27.30 ppm (1C), 29.35 ppm/29.46 ppm (2C), 33.43 ppm (1C), 33.75 ppm (1C), 33.24 ppm (1C), 33.66 ppm (1C), 37.28 ppm (1C), 37.34 ppm (1C), 44.25 ppm (1C), 71.23 ppm (1C), 152.71 ppm (1C), 153.43 ppm (1C).

HRMS: calculated: m/z ($M+H^+$) = 202.18016, found = 202.17982.

EI-MS: m/z (%) = 186 (2), 168 (2), 166 (6), 140 (1), 127 (1), 126 (9), 114 (3), 112 (1), 111 (3), 110 (5), 109 (7), 108 (4), 107 (2), 100 (4), 99 (3), 98 (5), 97 (2), 96 (5), 95 (5), 94 (2), 93 (2), 91 (1), 86 (3), 84 (2), 83 (5), 82 (7), 81 (8), 80 (2), 79 (3), 77 (1), 73 (3), 72 (38), 71 (10), 70 (4), 69 (16), 68 (5), 67 (10), 65 (2), 60 (4), 59 (100), 58 (16), 57 (8), 56 (9), 55 (31), 54 (8), 53 (8), 52 (1), 51 (2).

4-(4-hydroxy-3-methoxyphenyl)butanal oxime **3j** (through application of eugenol):

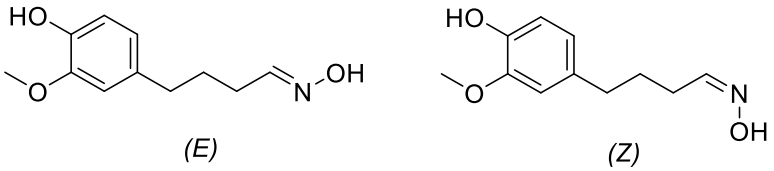


Figure S15: 4-(4-hydroxy-3-methoxyphenyl)butanal oxime in (E)- and (Z)-orientation of the oxime group.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.77-1.82 ppm (m, 2H), 2.22-2.25 ppm (m, 1H), 2.40-2.43 ppm (m, 1H), 2.57-2.61 ppm (m, 2H), 3.87 ppm (s, 3H), 6.66-6.68 ppm (m, 2H), 6.75 ppm (s, 0.42H (*Z*)), 6.82-6.84 ppm (m, 1H), 7.45 ppm (t, J_1 = 6.01 Hz, 0.58H (*E*)).

E/Z-ratio: 58/42

^{13}C NMR (151 MHz, $CDCl_3$): δ = 27.98 ppm (1C), 28.35 (0.5C), 28.85 ppm (0.5C), 34.76 (0.5C), 35.11 ppm (0.5C), 55.82 ppm (1C), 110.99 ppm (1C), 114.24 ppm (1C), 120.95 ppm (1C), 133.40 ppm (1C), 143.72 ppm (1C), 146.34 ppm (1C), 151.89 ppm (0.5C), 152.45 ppm (0.5C).

HRMS: calculated: m/z ($M+H^+$) = 210.11247, found = 210.11273.

EI-MS: m/z (%) = 209 (M^+, 9), 192 (2), 177 (7), 175 (4), 160 (3), 151 (11), 150 (100), 148 (2), 143 (2), 138 (5), 137 (43), 136 (5), 135 (28), 133 (2), 132 (2), 131 (3), 123 (4), 122 (20), 119 (3), 117 (2), 115 (5), 109 (2), 108 (2), 107 (12), 106 (2), 105 (5), 104 (2), 103 (5).

methyl 12-(hydroxyimino)dodecanoate **3k** (through application of methyl 10-undecenoate):

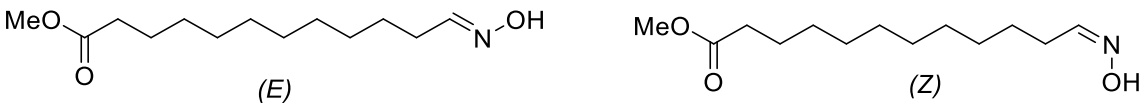


Figure S16: methyl 12-(hydroxyimino)dodecanoate in (E)- and (Z)-orientation of the oxime group.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.28 ppm (m, 12H), 1.45 - 1.52 ppm (m, 2H), 1.58-1.63 ppm (m, 2H), 2.16 – 2.21 ppm (m, 1H), 2.30 ppm (t, J_1 = 7.5 Hz, 2H), 2.34 – 2.39 ppm (m, 1H), 3.66 ppm (s, 3H), 6.71 ppm (t, J_1 = 5.5 Hz, 0.39H (*Z*)), 7.42 ppm (t, J_1 = 6.1 Hz, 0.61H (*E*)).

E/Z-ratio: 61/39

^{13}C NMR (151 MHz, $CDCl_3$): δ = 25.08 ppm (1C), 26.20 ppm (1C), 26.63 ppm (1C), 29.15 ppm-29.54 ppm (8C), 34.25 ppm (1C), 51.61 ppm (1C), 152.67 ppm (1C), 153.40 ppm (1C), 174.54 ppm (1C).

HRMS: calculated: m/z ($M+H^+$) = 244.19072, found = 244.19063.

EI-MS: m/z (%) = 243 (M^+, 1), 227 (1), 226 (5), 210 (1), 196 (1), 195 (2), 194 (13), 193 (5), 186 (5), 185 (42), 183 (3), 182 (2), 179 (1), 178 (1), 177 (1), 176 (2), 171 (2), 170 (16), 168 (3), 167 (4), 166 (13), 164 (2), 161 (2), 159 (2), 156 (1), 155 (3), 154 (13), 153 (100), 151 (3), 150 (4), 149 (7), 143 (2), 140 (2), 139 (3), 138 (14), 137 (4), 136 (11), 135 (67), 133 (3), 131 (1), 129 (4), 128 (5), 129 (4), 128 (5), 127 (2), 126 (4), 125 (9), 124 (16), 123 (7), 122 (8), 121 (5), 120 (2), 115 (5), 114 (8), 113 (5), 112 (14), 111 (31), 110 (28), 109 (17), 108 (7), 107 (19), 106 (2), 105 (4), 102 (1), 101 (8), 100 (18).

12. Aldoxime dehydratase (Oxd) sequences, plasmids and expression

The genes for the aldoxime dehydratases from *Pseudomonas chlororaphis* (OxdA), *Fusarium graminearum* (OxdFG), *Rhodococcus erythropolis* (OxdRE) and *Rhodococcus globerulus* (OxdRG) were purchased by GeneArt (Thermo Scientific) in a for expression in *E. coli* codon optimized form, located in pET28a plasmids with a sixfold N-terminal His-Tag.

The grey-marked areas in the aldoxime dehydratase amino acids sequences are amino acids relating to the terminal His_6-tags.

2.1 Oxd sequences and plasmids

2.1.1 Oxd from *Pseudomonas chlororaphilis* B23 (OxdA) with C-terminal His_6-Tag (Accession number: GenBank: AB093544.1)

Base sequence (codon-optimized for *E. coli*):

ATGGAAAGCGCAATTGATACCCATCTGAAATGTCCGCGTACCCTGAGCCGTCGTGTTCCGG
AAGAATATCAGCCTCCGTTTCCGATGTGGGTTGCACGTGCCGATGAACAGCTGCAGCAGGT
TGTTATGGGTTATCTGGGTGTTCAGTATCGTGGTGAAGCACAGCGTGAAGCAGCACTGCAG
GCAATGCGTCATATTGTTAGCAGCTTTAGCCTGCCGGATGGTCCGCAGACCCATGATCTGA
CCCATCATACCGATAGCAGCGGTTTTGATAATCTGATGGTTGTGGGTTATTGGAAAGATCC
GGCAGCACATTGTCGTTGGCTGCGTAGTGCCGAAGTTAATGATTGGTGGACCAGCCAGGA
TCGTCTGGGTGAAGGTCTGGGTTATTTTCGTGAAATTAGCGCACCGCGTGCAGAACAGTTT
GAAACCCTGTATGCATTTCAGGATAATCTGCCTGGTGTTGGTGCAGTTATGGATAGCACCA
GCGGTGAAATTGAAGAACATGGTTATTGGGGTAGCATGCGTGATCGTTTTCCGATTAGCCA
GACCGATTGGATGAAACCGACCAATGAACTGCAGGTTGTTGCCGGTGATCCGGCAAAAGG
TGGTCGTGTTGTTATTATGGGTCATGATAACATTGCACTGATTCGTAGCGGTCAGGATTGG
GCAGATGCAGAAGCAGAAGAACGTAGCCTGTATCTGGATGAAATTCTGCCGACCCTGCAG
GATGGTATGGATTTTCTGCGTGATAATGGTCAGCCGCTGGGTTGTTATAGCAATCGTTTTGT
TCGTAATATCGATCTGGATGGCAATTTTCTGGATGTGAGCTATAACATTGGTCATTGGCGTA
GCCTGGAAAAACTGGAACGTTGGGCAGAAAGCCATCCGACCCATCTGCGTATTTTTGTTAC
CTTTTTTCGTGTTGCAGCCGGTCTGAAAAAACTGCGTCTGTATCATGAAGTTAGCGTGAGTG
ATGCAAAAAGCCAGGTGTTTGAATATATCAACTGTCATCCGCATACCGGCATGCTGCGTGA
TGCAGTTGTTGCACCGACCAAGCTTGCGGCCGCACTCGAGCACCACCACCACCACCACTG
ACTCGAGCACCACCACCACCACCACTGAGATCCGGCTGCTAACAAAGCCCGAAAGAAGTTT
TTT

Amino acid sequence:

MESAIDTHLKCPRTLSRRVPEEYQPPFPMWVARADEQLQQVVMGYLGVQYRGEAQREAALQA
MRHIVSSFSLPDGPQTHDLTHHTDSSGFDNLMVVGYWKDPAAHCRWLRSAEVNDWWTSQDR
LGEGLGYFREISAPRAEQFETLYAFQDNLPGVGAVMDSTSGEIEEHGYWGSMRDRFPISQTDW

MKPTNELQVVAGDPAKGGRVVIMGHDNIALIRSGQDWADAEAEERSLYLDEILPTLQDGMDFLR
DNGQPLGCYSNRFVRNIDLDGNFLDVSYNIGHWRSLEKLERWAESHPTHLRIFVTFFRVAAGLK
KLRLYHEVSVSDAKSQVFEYINCHPHTGMLRDAVVAPTLEHHHHHH

2.1.2 Oxd from *Bacillus* sp. OxB-1 (OxdB) without Tag
(Accession number: GenBank: AP013294.1)

Base sequence (codon-optimized for *E. coli*):
ATGAAAAATATGCCGGAAAATCACAATCCACAAGCGAATGCCTGGACTGCCGAATTTCCTC
CTGAAATGAGCTATGTAGTATTTGCGCAGATTGGGATTCAAAGCAAGTCTTTGGATCACGCA
GCGGAACATTTGGGAATGATGAAAAAGAGTTTCGATTTGCGGACAGGCCCCAAACATGTGG
ATCGAGCCTTGCATCAAGGAGCCGATGGATACCAAGATTCCATCTTTTTAGCCTACTGGGA
TGAGCCTGAAACATTTAAATCATGGGTTGCGGATCCTGAAGTACAAAAGTGGTGGTCGGGT
AAAAAAATCGATGAAAATAGTCCAATCGGGTATTGGAGTGAGGTAACGACCATTCCGATTGA
TCACTTTGAGACTCTTCATTCCGGAGAAAATTACGATAATGGGGTTTCACACTTTGTACCGA
TCAAGCATACAGAAGTCCATGAATATTGGGGAGCAATGCGCGACCGCATGCCGGTGTCTG
CCAGTAGTGATTTGGAAAGCCCCCTTGGCCTTCAATTACCGGAACCCATTGTCCGGGAGTC
TTTCGGAAAACGGCTAAAAGTCACGGCGCCGGATAATATTTGCTTGATTCGAACCGCTCAA
AATTGGTCTAAATGTGGTAGCGGGGAAAGGGAAACGTATATAGGACTAGTGGAACCGACCC
TCATAAAAGCGAATACGTTTCTTCGTGAAAATGCTAGTGAAACAGGCTGTATTAGTTCAAAA
TTAGTCTATGAACAGACCCATGACGGCGAAATAGTAGATAAATCATGTGTCATCGGATATTA
TCTCTCCATGGGGCATCTTGAACGCTGGACGCATGATCATCCAACACATAAAGCGATCTAC
GGAACCTTTTATGAGATGTTGAAAAGGCATGATTTTAAGACCGAACTTGCTTTATGGCACGA
GGTTTCGGTGCTTCAATCCAAAGATATCGAGCTTATCTATGTCAACTGCCATCCGAGTACTG
GATTTCTTCCATTCTTTGAAGTGACAGAAATTCAAGAGCCTTTACTGAAAAGCCCTAGCGTC
AGGATCCAGTGA

Amino acid sequence:
MKNMPENHNPQANAWTAEFPPEMSYVVFAQIGIQSKSLDHAAEHLGMMKKSFDLRTGPKHVD
RALHQGADGYQDSIFLAYWDEPETFKSWVADPEVQKWWSGKKIDENSPIGYWSEVTTIPIDHF
ETLHSGENYDNGVSHFVPIKHTEVHEYWGAMRDRMPVSASSDLESPLGLQLPEPIVRESFGKR
LKVTAPDNICLIRTAQNWSKCGSGERETYIGLVEPTLIKANTFLRENASETGCISSKLVYEQTHDG
EIVDKSCVIGYYLSMGHLERWTHDHPTHKAIYGTFYEMLKRHDFKTELALWHEVSVLQSKDIELI
YVNCHPSTGFLPFFEVTEIQEPLLKSPSVRIQ

2.1.3 Oxd from *Fusarium graminearum* (OxdFG) with N-terminal His_6-Tag
(Accession number: GenBank: AB214653.1)

Base sequence (codon-optimized for *E. coli*):
ATGGGCAGCAGCCATCATCATCATCATCACAGCAGCGGCCTGGTGCCGCGCGGCAGCCAT
ATGCTGCGTAGCCGTTTTCCGGCAAGCCATCATTTCACCGTTAGCGTTTTTGGTTGTCAGTA
TCATAGCGAAGCACCGAGCGTTGAAAAAACCGAACTGATTGGTCGTTTCGATAAACTGATT
GATAGCGCAGCAATTCATGTGGAACATCTGGAACAGAATGATGTGCCGAGCAAAATTTGGA
TGAGCTATTGGGAAAGTCCGCAGAAATTCAAACAGTGGTGGGAAAAAGATGATACCGCAAG

CTTTTGGGCAAGCCTGCCGGATGATGCAGGTTTTTGGCGTGAAACCTTTAGCCTGCCTGCA
ACCCGTGCAATGTATGAAGGCACCGGTAAAGATGCCTATGGTTTTGGTCATTGTGGTAGCC
TGATTCCGCTGACCACCAAAACCGGCTATTGGGGTGCATATCGTAGCCGTATGACACCGGA
TTTTGAAGGTGATACCTTTTCAAGCCCGATTCCGACCTATGCAGATCAGAGCGTTCCGGCA
GATAAAATTCGTCCGGGTCGTGTTCGTATTACCGATTTTCCGGATAATCTGTGCATGGTTGT
TGAAGGTCAGCATTATGCAGATATGGGTGAACGTGAACGCGAATATTGGAACGAAAATTTT
GATGGTCTGACGAAACAGTGGGTTACCAATGTTGTTACCGCAGGTCATGAACAGGGTATGG
TTATTGCACGTGCCTGTCATGGTTTTGCCGGTGAAAAAAAACTGGGTGCAACCAATGGTCC
GGTGAATGGTATTTTTCCGGGTCTGGATTATGTTCATCAGGCACAGATTCTGATTTGGCAGG
ATATTAGCAAAATGGAACATATCGGTCGTTATGATCAGACCCATGTTAAACTGCGTCGCGAT
TTTATGAAAGCCTATGGTCCGGGTGGTGAAATGGAAGGTGGTGATCTGCTGCTGTGGGTTG
ATCTGGGTATTCTGAAAAAAGACGAAATCGATGCCGAATATGTGGGTTGCTATGAAAGTACC
GGTTTTCTGAAACTGGATAAAGGCCAGTTTTTCAAAGTTGAAAGCACCGCAGGTAGCAAACT
GCCGAGCTTTTTTGATGAACCGATTGAAAGCAAACCGATCGAATGGTAA

Amino acid sequence:

MGSSHHHHHHSSGLVPRGSHMLRSRFPASHHFTVSVFGCQYHSEAPSVEKTELIGRFDKLIDS
AAIHVEHLEQNDVPSKIWMSYWESPQKFKQWWEKDDTASFWASLPDDAGFWRETFSLPATRA
MYEGTGKDAYGFGHCGSLIPLTTKTGYWGAYRSRMTPDFEGDTFSSPIPTYADQSVPADKIRP
GRVRITDFPDNLCMVVEGQHYADMGEREREYYWNENFDGLTKQWVTNVVTAGHEQGMVIARA
CHGFAGEKKLGATNGPVNGIFPGLDYVHQAQILIWQDISKMEHIGRYDQTHVKLRRDFMKAYGP
GGEMEGGDLLLWVDLGILKKDEIDAEYVGCYESTGFLKLDKGQFFKVESTAGSKLPSFFDEPIE
SKPIEW

2.1.4 Oxd from *Rhodococcus erythropolis* (OxdRE) with N-terminal His_6-Tag
(Accession number: GenBank: AB094201.1)

Base sequence (codon-optimized for *E. coli*):

ATGGGCAGCAGCCATCATCATCATCATCACAGCAGCGGCCTGGTGCCGCGCGGCAGCCAT
ATGGAAAGCGCAATTGGTGAACATCTGCAGTGTCCGCGTACCCTGACCCGTCGTGTTCCG
GATACCTATACCCCTCCGTTTCCGATGTGGGTTGGTCGTGCAGATGATGCACTGCAGCAGG
TTGTTATGGGTTATCTGGGTGTTCAGTTTCGTGATGAAGATCAGCGTCCGGCAGCACTGCA
GGCAATGCGTGATATTGTTGCAGGTTTTGATCTGCCGGATGGTCCGGCACATCATGATCTG
ACCCATCATATTGATAATCAGGGCTATGAAAACCTGATTGTGGTGGGTTATTGGAAAGATGT
TAGCAGCCAGCATCGTTGGAGCACCAGCACCCCGATTGCAAGTTGGTGGGAAAGCGAAGA
TCGTCTGAGTGATGGTCTGGGTTTTTTTCGTGAAATTGTGGCACCGCGTGCAGAACAGTTT
GAAACCCTGTATGCATTTCAAGAAGATCTGCCTGGCGTTGGTGCAGTTATGGATGGTATTA
GCGGTGAAATTAACGAACATGGTTATTGGGGTAGCATGCGTGAACGTTTTCCGATTAGCCA
GACCGATTGGATGCAGGCAAGCGGTGAACTGCGTGTTATTGCCGGTGATCCGGCAGTTGG
TGGTCGTGTTGTTGTTCGTGGTCATGATAACATTGCACTGATTCGTAGCGGTCAGGATTGG
GCAGATGCCGAAGCAGATGAACGTAGCCTGTATCTGGATGAAATTCTGCCGACCCTGCAGA
GCGGTATGGATTTTCTGCGTGATAATGGTCCTGCAGTTGGTTGTTATAGCAATCGTTTTGTG
CGCAACATTGATATCGATGGCAATTTTCTGGATCTGAGCTATAACATTGGTCATTGGGCAAG

CCTGGATCAGCTGGAACGTTGGAGCGAAAGCCATCCGACCCATCTGCGTATTTTTACCACC
TTTTTTCGCGTTGCAGCCGGTCTGAGCAAACTGCGTCTGTATCATGAAGTTAGCGTTTTTGA
TGCAGCAGATCAGCTGTATGAATACATTAATTGTCATCCGGGTACAGGTATGCTGCGTGAT
GCAGTTACCATTGCAGAACATTAA

Amino acid sequences:
MGSSHHHHHHSSGLVPRGSHMESAIGEHLQCPRTLTRRVPDTYTPPFPMWVGRADDALQQV
VMGYLGVQFRDEDQRPAALQAMRDIVAGFDLPDGPAHHDLTHHIDNQGYENLIVVGYWKDVS
SQHRWSTSTPIASWWESEDRLSDGLGFFREIVAPRAEQFETLYAFQEDLPGVGAVMDGISGEI
NEHGYWGSMRERFPISQTDWMQASGELRVIAGDPAVGGRVVVRGHDNIALIRSGQDWADAEA
DERSLYLDEILPTLQSGMDFLRDNGPAVGCYSNRFVRNIDIDGNFLDLSYNIGHWASLDQLERW
SESHPTHLRIFTTFFRVAAGLSKLRLYHEVSVFDAADQLYEYINCHPGTGMLRDAVTIAEH

2.1.5 Oxd from *Rhodococcus globerulus* (OxdRG) with N-terminal His_6-Tag
(Accession number: GenBank: AM946017.1)

Base sequence (codon-optimized for *E. coli*):
ATGGGCAGCAGCCATCATCATCATCATCACAGCAGCGGCCTGGTGCCGCGCGGCAGCCAT
ATGGAAAGCGCAATTGGTGAACATCTGCAGTGTCCGCGTACCCTGACCCGTCGTGTTCCG
GATACCTATACCCCTCCGTTTCCGATGTGGGTTGGTCGTGCAGATGATACCCTGCATCAGG
TTGTTATGGGTTATCTGGGTGTTCAGTTTCGTGGTGAAGATCAGCGTCCGGCAGCACTGCG
TGCAATGCGTGATATTGTTGCAGGTTTTGATCTGCCGGATGGTCCGGCACATCATGATCTG
ACCCATCATATTGATAATCAGGGCTATGAAAACCTGATTGTGGTGGGTTATTGGAAAGATGT
TAGCAGCCAGCATCGTTGGAGCACCAGCCCTCCGGTTAGCAGTTGGTGGGAAAGCGAAGA
TCGTCTGAGTGATGGTCTGGGTTTTTTTCGTGAAATTGTGGCACCGCGTGCAGAACAGTTT
GAAACCCTGTATGCATTTCAGGATGATCTGCCTGGTGTTGGTGCAGTTATGGATGGTGTTA
GCGGTGAAATTAATGAACATGGTTATTGGGGTAGCATGCGTGAACGTTTTCCGATTAGCCA
GACCGATTGGATGCAGGCAAGCGGTGAACTGCGTGTTGTTGCCGGTGATCCGGCAGTTGG
CGGTCGTGTTGTGGTTCGTGGTCATGATAACATTGCACTGATTCGTAGCGGTCAGGATTGG
GCAGATGCCGAAGCAGATGAACGTAGCCTGTATCTGGATGAAATTCTGCCGACCCTGCAGA
GCGGTATGGATTTTCTGCGTGATAATGGTCCTGCAGTTGGTTGTTATAGCAATCGTTTTGTG
CGCAACATTGATATCGATGGCAATTTTCTGGATCTGAGCTATAACATTGGTCATTGGGCAAG
CCTGGATCAGCTGGAACGTTGGAGCGAAAGCCATCCGACCCATCTGCGTATTTTTACCACC
TTTTTTCGCGTTGCAGAAGGTCTGAGCAAACTGCGTCTGTATCATGAAGTTAGCGTTTTTGA
TGCAGCAGATCAGCTGTATGAATACATTAATTGTCATCCGGGTACAGGTATGCTGCGTGAT
GCAGTTATTACCGCAGAACATTAA

Amino acid sequence:
MGSSHHHHHHSSGLVPRGSHMESAIGEHLQCPRTLTRRVPDTYTPPFPMWVGRADDTLHQVV
MGYLGVQFRGEDQRPAALRAMRDIVAGFDLPDGPAHHDLTHHIDNQGYENLIVVGYWKDVSS
QHRWSTSPPVSSWWESEDRLSDGLGFFREIVAPRAEQFETLYAFQDDLPGVGAVMDGVSGEI
NEHGYWGSMRERFPISQTDWMQASGELRVVAGDPAVGGRVVVRGHDNIALIRSGQDWADAE
ADERSLYLDEILPTLQSGMDFLRDNGPAVGCYSNRFVRNIDIDGNFLDLSYNIGHWASLDQLER
WSESHPTHLRIFTTFFRVAEGLSKLRLYHEVSVFDAADQLYEYINCHPGTGMLRDAVITAEH

2.2 Oxd expression in *E.coli* BL21-CodonPlus(DE3)-RIL

E.coli BL21-CodonPlus(DE3)-RIL cells harbouring the plasmids with the Oxd-genes were stored as glycerol stocks at -80 °C.

A sample from the glycerol stocks for each Oxd was plated on LB-agar containing 50 µg/mL kanamycin and 34 µg/mL chloramphenicol (OxdA, OxdFG, OxdRE and OxdRG in pET28a) or 100 µg/mL carbenicillin and 34 µg/mL chloramphenicol (OxdB in pUC18) and incubated for 12 to 18 h at 37 °C.

Pre-cultures were prepared in 5 mL LB-medium containing 50 µg/mL kanamycin and 34 µg/mL chloramphenicol (OxdA, OxdFG, OxdRE and OxdRG in pET28a) or 100 µg/mL carbenicillin and 34 µg/mL chloramphenicol (OxdB in pUC18) using a single colony from the LB-agar plate. The cultures were incubated for 12 to 18 h at 37 °C and 180 rpm.

Main cultures for OxdB expression were performed using TB-autoinduction medium. Sterile 20 g/L lactose solution in MilliQ water (50 mL) and sterile 50 g/L D-glucose solution in MilliQ water (5 mL) was added to 445 mL sterile TB-medium (Carl Roth) in a 500 mL Erlenmeyer flask. 100 µg/mL carbenicillin and 34 µg/mL chloramphenicol were added to the medium. Main cultures were inoculated with 1 % (5 mL) of the relating pre-cultures and incubated for 1 h at 37 °C and 120 rpm. After 1 h incubation at 37 °C OxdB-cultures were cultivated at 30 °C for 72 h and 120 rpm.

Main cultures for OxdA, FG, RE and RG expression were performed using TB-medium. 400 mL sterile TB-medium (Carl Roth) in a 500 mL Erlenmeyer flask was mixed with 50 µg/mL kanamycin and 34 µg/mL chloramphenicol. Main cultures were inoculated with 1 % (5 mL) of the relating pre-cultures and incubated for 1 h at 37 °C and 120 rpm. After 1 h incubation at 37 °C the cultures were cultivated at 20 °C for 72 h and 160 rpm.

Cell harvest was performed at 4,000 xg for 15 min at 4 °C. The supernatant was discarded and cells were washed three times with 50 mM potassium phosphate buffer (PPB, KP_i) at pH 7.0. The biomass was determined (bio wet weight (bww)) and cells were resuspended in 50 mM PPB (pH 7.0) to a final concentration of 333 mg/mL cells in buffer. Cell suspensions were stored at 4 °C or on ice before usage in biotransformations.

Table S8: Used vector constructs, origins of the Oxd-genes, provider of the vector constructs and marker-resistance of the constructs.

Entry	Origin of Oxd-gene	Vector construct	Oxd	Provider	Resistance
8.1	*Pseudomonas chlororaphilis* B23	pET28b_OxdA-C-His	OxdA	Asano group	Kanamycin
8.2	*Bacillus* sp. OxB-1	pUC18_OxdB	OxdB	Asano group	Carbenicillin
8.3	*Fusarium graminearum*	pET28a_N-His-OxdFG	OxdFG	Thermo Fisher Scientific	Kanamycin
8.4	*Rhodococcus erythropolis*	pET28a_N-His-OxdRE	OxdRE	Thermo Fisher Scientific	Kanamycin
8.5	*Rhodococcus globerulus*	pET28a_N-His-OxdRG	OxdRG	Thermo Fisher Scientific	Kanamycin

Overexpression of Oxds in *E. coli* Bl21-CodonPlus(DE3)-RIL was analysed by sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) after cell disruption and denaturation of the proteins in the crude extracts.
Crude extracts of 33 w% cell suspensions were obtained by sonication (5x 1 min, 10 – 15% Output, Bandelin Sonopuls®) and subsequent centrifugation at 21,500 xg for 45 min at 4 °C. The pellet including the cell debris was discarded. Protein concentrations in crude extracts were determined by Bradford assay using a bovine serum albumin (BSA)-standard curve (1.4 mg/mL, 0.7 mg/mL, 0.35 mg/mL, 0.175 mg/mL, 0.0875 mg/mL) as reference. Protein dilutions of 1 µg/µL whole cell protein concentration were obtained by dilution of the crude extracts in water and Laemmli-buffer. 10 µL of these samples were transferred to a 12% SDS-PAGE.

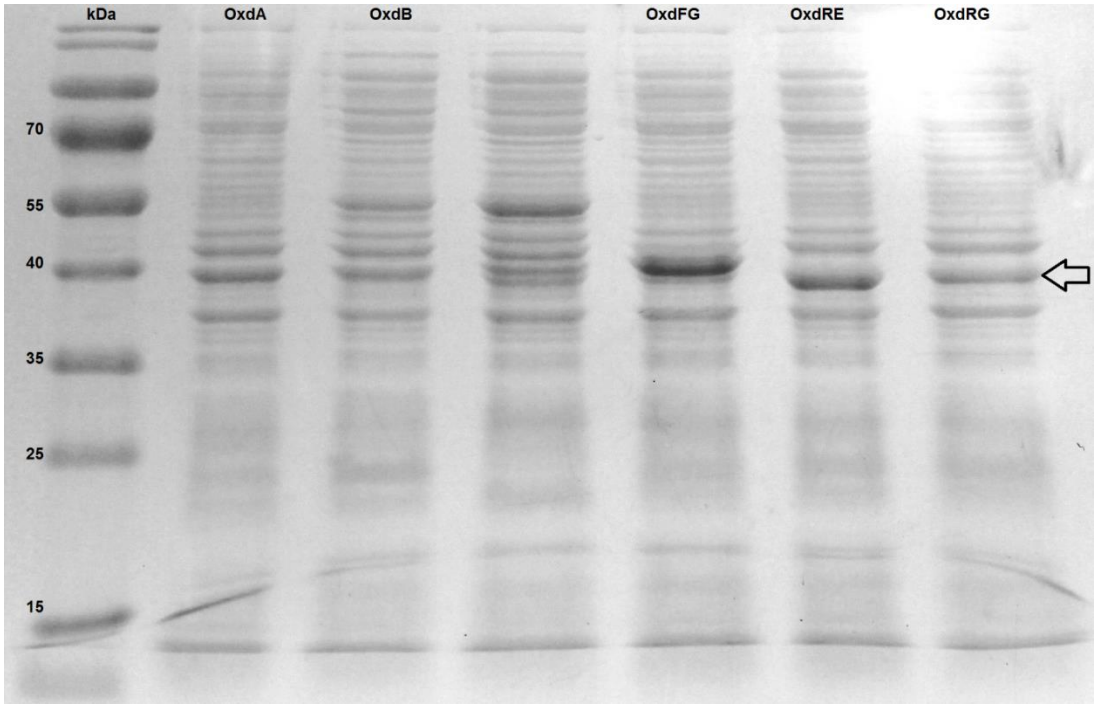


Figure S17: 12% SDS-PAGE of crude extracts of OxdA-, OxdB-, OxdFG-, OxdRE- and OxdRG-overexpressing cells. The molecular weights of the overexpressed Oxds correlates with the molecular weights determined from the amino acid sequences.

13. Standard protocol for activity measurements of the bioconversion of oximes using Oxds in whole cells

Standard activity assays of Oxds in whole cells using oximes (3, 3a, 3b, 3c, 3d, 3e) were performed using 50 mg/mL whole cells (bww) in a total volume of 0.5 mL in 1.5 mL micro reaction tubes. The reaction was conducted in 50 mM PPB (pH 7.0) containing 10%(V/V) isopropanol (iPrOH) as a co-solvent. Total substrate concentration of oxime mixtures of 10 mM was chosen and the activity assay performed at 30 °C for 15 min and 1,000 rpm in an Eppendorf ThermoMixer.

The reaction was stopped by addition of 500 µL ethyl acetate (EtOAc) and extraction of substrates **3** and products **9** into the organic phase. The phase separation was simplified by centrifugation for 5 min at 14,000 xg at room temperature. The organic phase was analysed by GC for conversion determination.

Table S9: Conversion of obtained oximes towards nitriles using Aldoxime dehydrates (Oxds)

#	Ind.	conditions	Enzyme	Y / %	GC-Method
9.1	3b	10 mM	OxdA	90±0	II
9.2			OxdB	92±1	
9.3			OxdFG	95±2	
9.4			OxdRE	96±2	
9.5			OxdRG	97±0	
9.6		100 mM	OxdA	39±1	
9.7			OxdB	61±7	
9.8			OxdFG	32±1	
9.9			OxdRE	56±1	
9.10			OxdRG	64±7	
9.11	3a	10 mM	OxdA	63±2	II
9.12			OxdB	57±3	
9.13			OxdFG	85±6	
9.14			OxdRE	79±3	
9.15			OxdRG	81±3	
9.16		100 mM	OxdA	9±1	
9.17			OxdB	13±3	
9.18			OxdFG	13±0	
9.19			OxdRE	13±1	
9.20			OxdRG	15±2	
9.21	3c	10 mM	OxdA	47±12	III
9.22			OxdB	73±1	

9.23			OxdFG	25±3	
9.24			OxdRE	67±8	
9.25			OxdRG	68±3	
9.26		100 mM	OxdA	3±1	
9.27			OxdB	7±3	
9.28			OxdFG	3±1	
9.29			OxdRE	5±1	
9.30			OxdRG	8±1	
9.31	3g	10 mM	OxdA	63±9[a]	II
9.32			OxdB	71±7[a]	
9.33			OxdFG	94±2[a]	
9.34			OxdRE	95±1[a]	
9.35			OxdRG	96±2[a]	
9.36	3i	10 mM	OxdA	77±3	IV
9.37			OxdB	92±5	
9.38			OxdFG	93±2	
9.39			OxdRE	87±3	
9.40			OxdRG	90±3	
9.41		100 mM	OxdA	75±2	
9.42			OxdB	75±4	
9.43			OxdFG	71	
9.44			OxdRE	76±2	
9.45			OxdRG	79±1	
9.46	5h	10 mM	OxdA	52±2	I
9.47			OxdB	49±3	
9.48			OxdFG	49±1	
9.49			OxdRE	55±2	
9.50			OxdRG	58±1	

9.51	100 mM	OxdA	19±3
9.52		OxdB	13±3
9.53		OxdFG	32±1
9.54		OxdRE	29±3
9.55		OxdRG	39±1

reaction conditions: KPi buffer 50 mM, pH = 7, 33 mg mL^{-1} whole cell suspension (BWW, bio wet weight), iPrOH (10% (*V*/*V*)), substrate concentration 10 or 100 mM, 30 °C, 15 min, extraction with EtOAc, conversion determined via GC, [a] area %.

14. Synthesis of Nitriles as reference compounds

The syntheses were carried out in analogy to *Ma et al*.[1] The oxime was dissolved in acetonitrile (2 ml/$mmol_{oxime}$) at room temperature. Copper(II) acetate (5 mol-%) was added and the solution was heated to reflux for 60 min after reaction control via TLC. The crude product was filtered over a short plug of silica with cyclohexane and purifies by distillation or column chromatography to yield the product as an oil.

Heptanenitrile **9b** (through application of heptanal oxime):

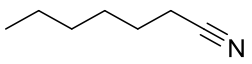


Figure S18: Heptanenitrile.

^{1}H NMR: (500 MHz, $CDCl_3$): δ / ppm = 2.33 (t, J_3 = 7.1 Hz, 2H), 1.65 (p, J_3 = 7.5 Hz, 2H), 1.45 (p, J_3 = 7.1 Hz, 2H), 1.32 (m, 4H), 0.90 (t, J_3 = 6.9 Hz, 3H).

The spectroscopic data is in good accordance with the literature[2].

Nonanenitrile **9a** (through application of nonanal oxime):

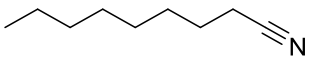


Figure S19: Nonanenitrile.

^{1}H NMR: (500 MHz, $CDCl_3$) δ (ppm) = 2.33 (t, J_3 = 7.5 Hz, 2H), 1.36-1.22 (m, 12H), 0.88 (t, J_3 = 6.5 Hz, 3H).

The spectroscopic data is in good accordance with the literature[3].

3-(cyclohex-3-en-1-yl)propanenitrile **9g** (through application of 3-(cyclohex-3-en-1-yl)propanal oxime):

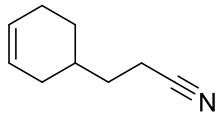


Figure S20: 3-(cyclohex-3-en-1-yl)propanenitrile.

^{1}H NMR (500 MHz, $CDCl_3$): δ / ppm = 5.75–5.66 (m, 1H), 5.67–5.60 (m, 1H), 2.39 (t, J_3 = 7.3 Hz, 2H), 2.17–2.10 (m, 2 H), 2.09–2.04 (m, 2 H), 1.76 (d, J_3 = 15.2 Hz, 0.5 H), 1.70 (m, 2H), 1.67 (p, J_3 = 7.4 Hz, 2 H), 1.31-1.22 (m, 0.5H).

^{13}C NMR (126 MHz, $CDCl_3$): δ / ppm = 127.11, 125.49, 119.90, 77.23, 77.02, 76.81, 32.59, 31.73, 30.98, 29.71, 28.06, 25.37, 24.76, 14.82.

8-hydroxy-4,8-dimethylnonanenitrile **9i** (through application of 8-hydroxy-4,8-dimethylnonanal oxime):

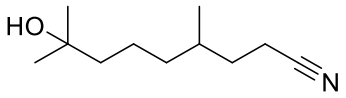


Figure S21: 8-hydroxy-4,8-dimethylnonanenitrile.

^{1}H NMR (500 MHz, $CDCl_3$): / ppm = 2.42–2.27 (m, J_3= 7.6, 7.1 Hz, 2H), 1.69 (dt, J_3 = 13.5, 7.3 Hz, 1H), 1.59 (dt, J_3 = 12.9, 6.5 Hz, 1H), 1.53–1.26 (m, 5H), 1.21 (s, 5H), 0.92 (d, J_3 = 6.6 Hz, 3H).

HRMS: calculated m/z ($M+Na^+$) = 206.1513, found = 206.1516.

Undecanenitrile **9c** (through application of undecanal oxime):

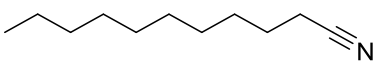


Figure S22: Undecanenitrile.

The synthesis was carried out under inert gas atmosphere. To a solution of *n*-undecanaloxime (258 mg, 1.40 mmol) and triphenylphosphine oxide (4.3 mg, 0.02 mmol) in acetonitrile (dry, 21 mL), trimethylamine (438 mg, 4.33 mmol) was added. Oxalyl chloride (590 mg, 4.7 mmol) was slowly added. The reaction mixture was stirred at room temperature for 2 h, the reaction progress being monitored by thin layer chromatography (solvent: cyclohexane/ethyl acetate 10:1). The reaction solution was filtered over silica and then purified by column chromatography. Removal of the solvent provided *n*-undecanenitrile in the form of a yellow oil (206 mg, 86 %).

^{1}H NMR (500 MHz, DMSO-d_6): δ /_ppm = 2.47 (t, J_3 = 7.1 Hz, 2H), 1.53 (p, J_3 = 7.1 Hz, 2H), 1.25 (s, 14H), 0.86 (t, J_3 = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, DMSO-d_6): δ / ppm = 120.0, 32.0, 29.6, 29.5, 29.4, 28.9, 28.8, 25.5, 22.8, 17.3, 14.2.

EI-MS: m/z = $[2M+ACN+2H]^{2+}$: 105.0, $[2M+NH_4]^+$: 353.3.

The spectroscopic data is in good accordance with the literature.[4]

15. NMR-data for product characterization

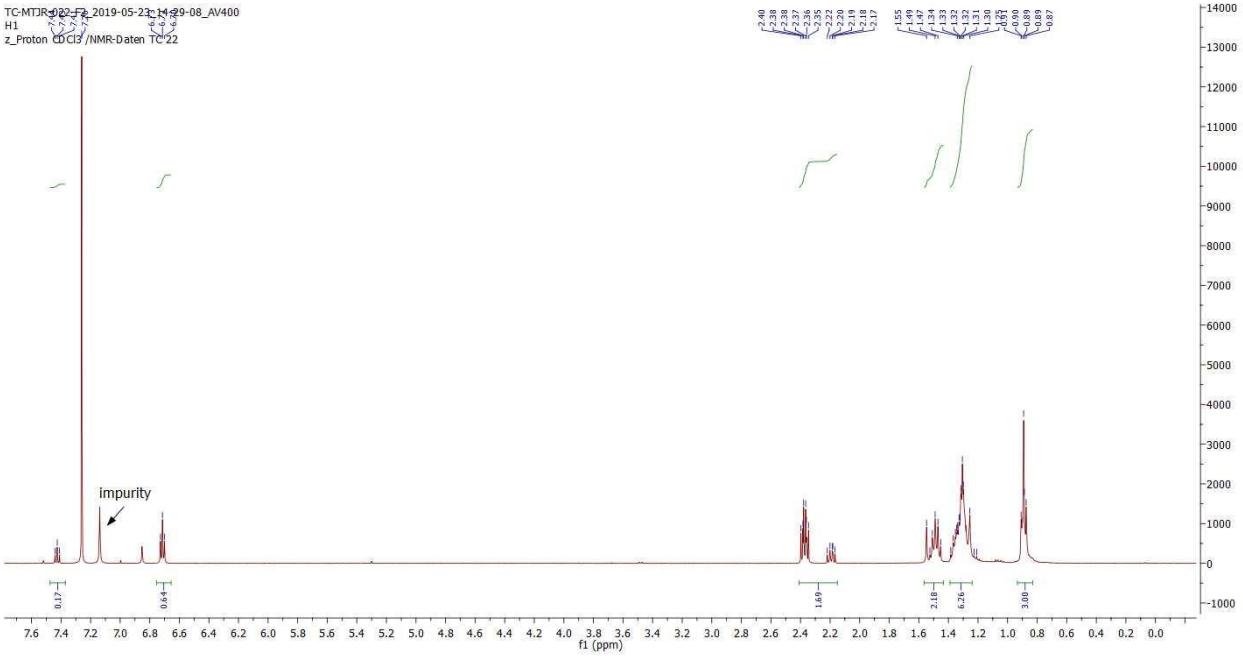


Figure S23: ^{1}H NMR of heptanal oxime **3b** *(mixture of (E)- and (Z) isomers).*

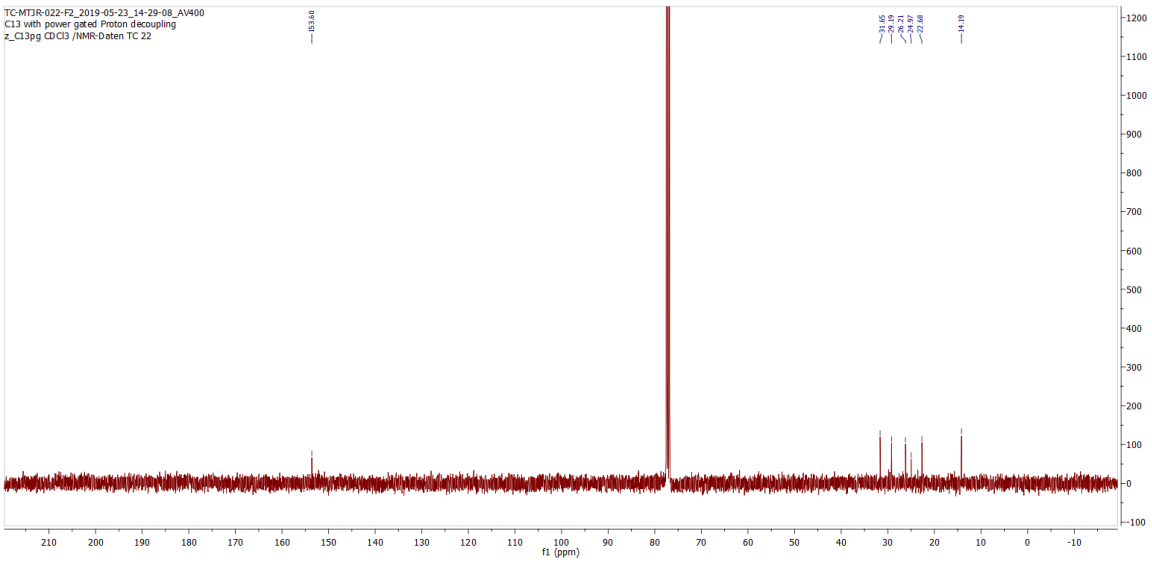


Figure S24: ^{13}C NMR of heptanal oxime **3b** *(mixture of (E)- and (Z) isomers).*

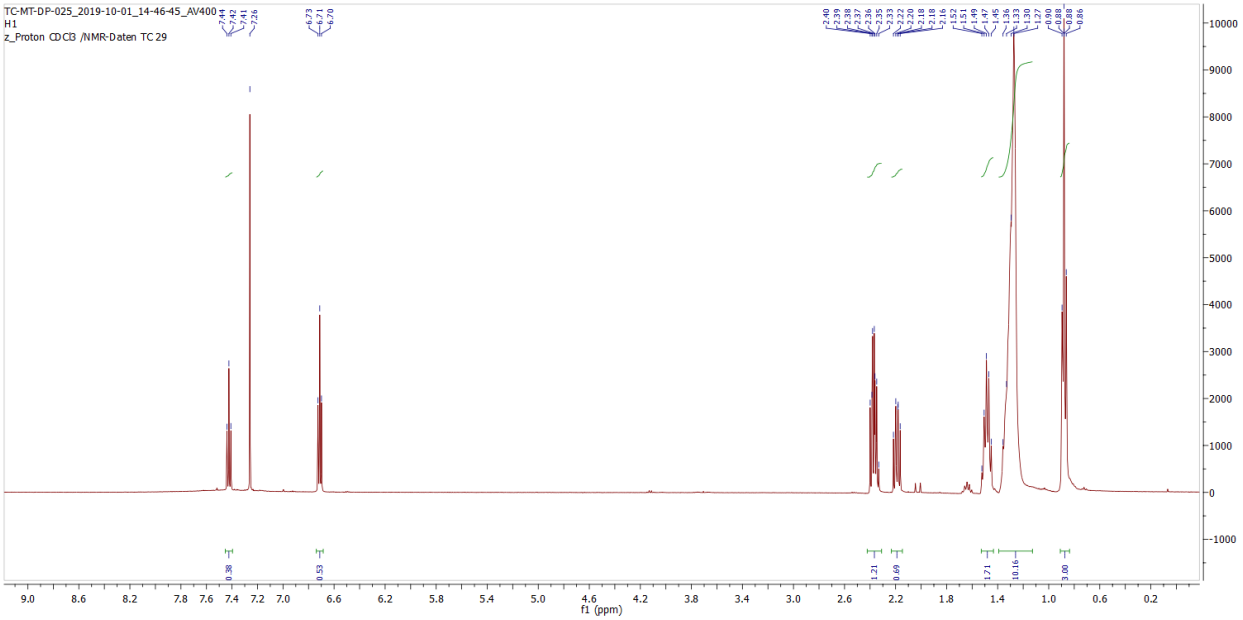


Figure S25: ^{1}H NMR of nonanal oxime **3a** *(mixture of (E)- and (Z) isomers).*

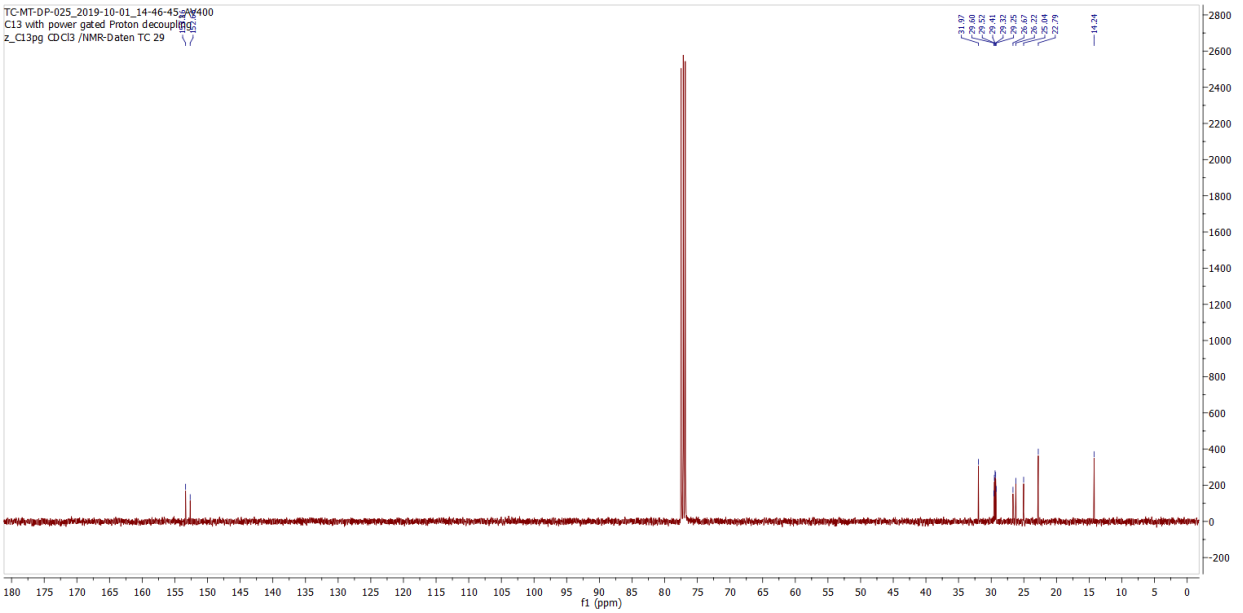


Figure S26: ^{13}C NMR of nonanal oxime **3a** *(mixture of (E)- and (Z) isomers.*

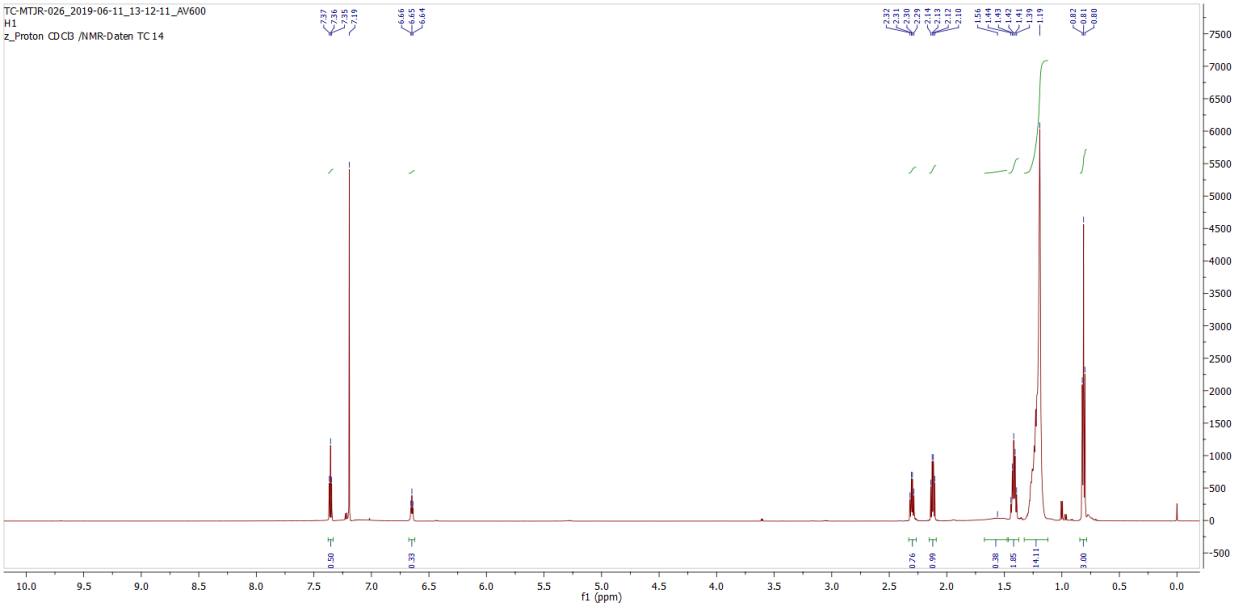


Figure S27: [1]H NMR of undecanal oxime **3c** *(mixture of (E)- and (Z) isomers).*

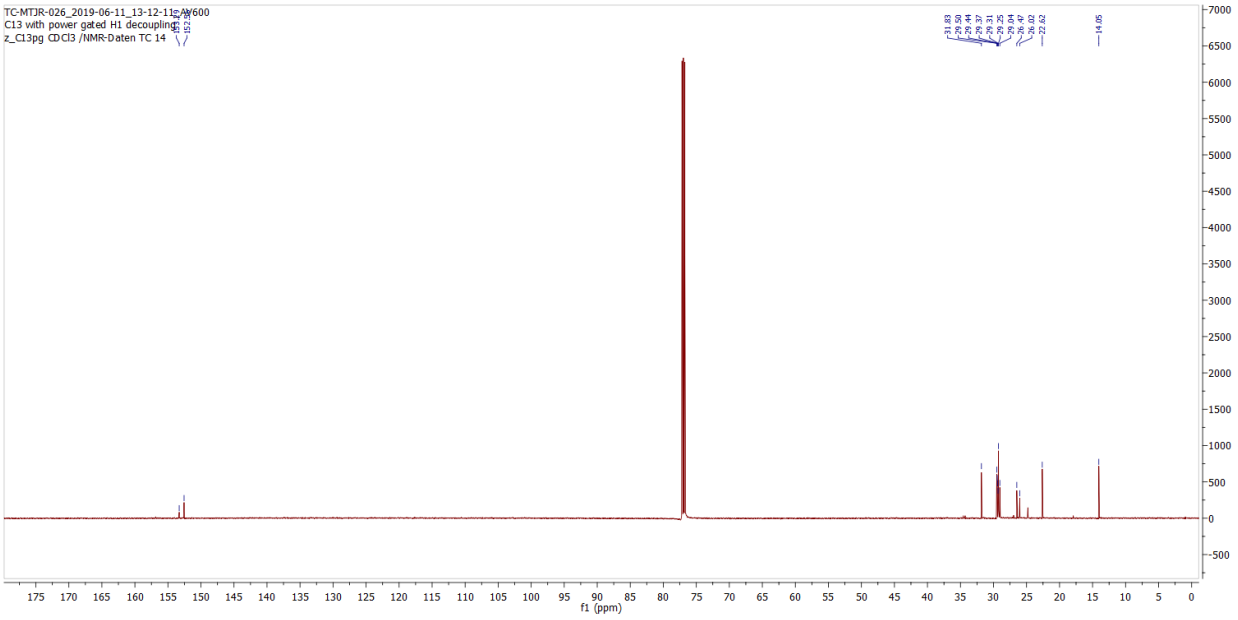


Figure S28: [13]C NMR of undecanal oxime **3c** *(mixture of (E)- and (Z) isomers.*

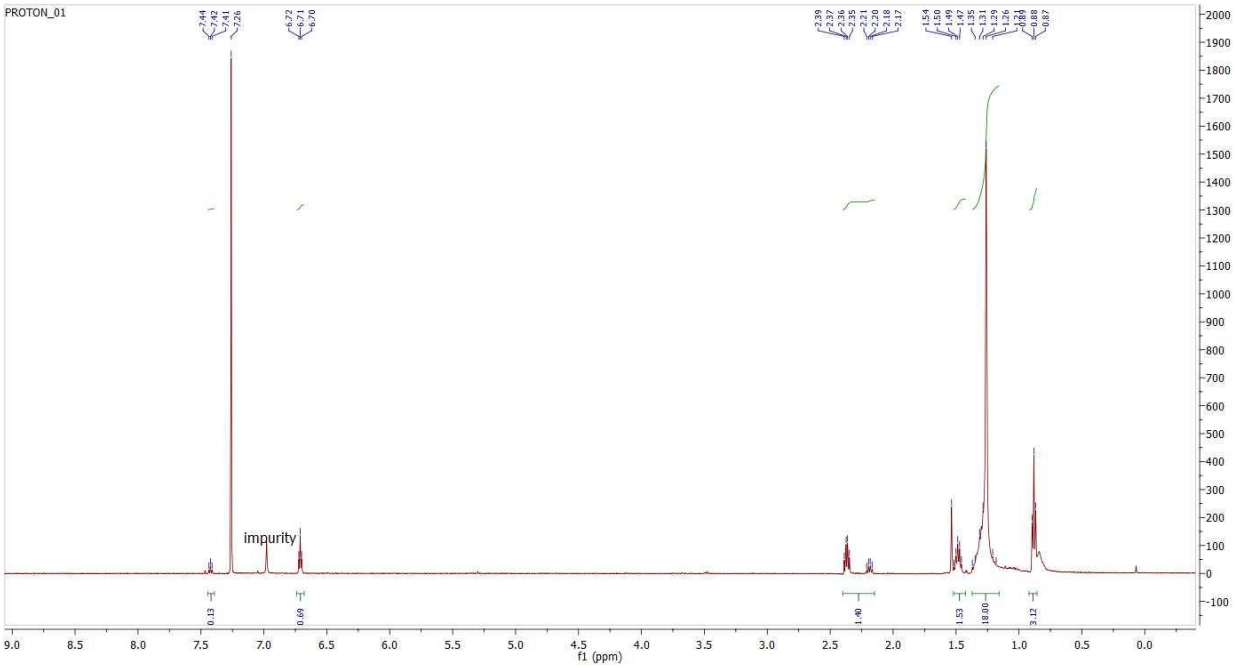


Figure S29: ^{1}H NMR of tridecanal oxime **3d** *(mixture of (E)- and (Z) isomers).*

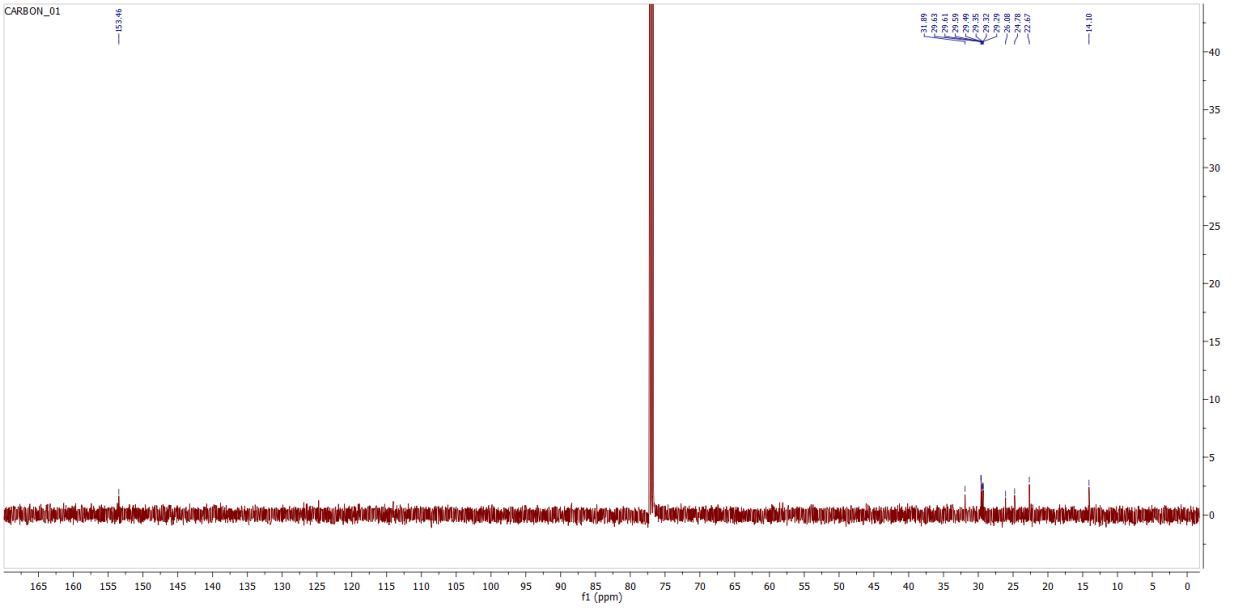


Figure S30: ^{13}C NMR of tridecanal oxime **3d** *(mixture of (E)- and (Z) isomers.*

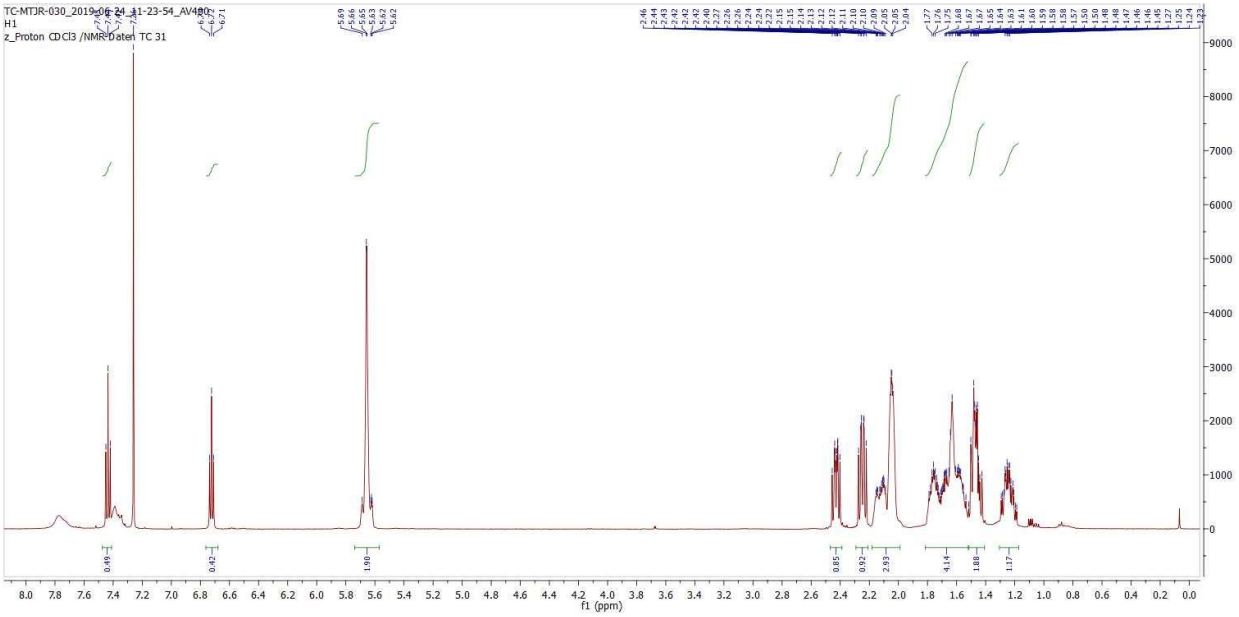


Figure S31: [1]H NMR of 3-(cyclohex-3-en-1-yl)propanal oxime **3g** *(mixture of (E)- and (Z) isomers).*

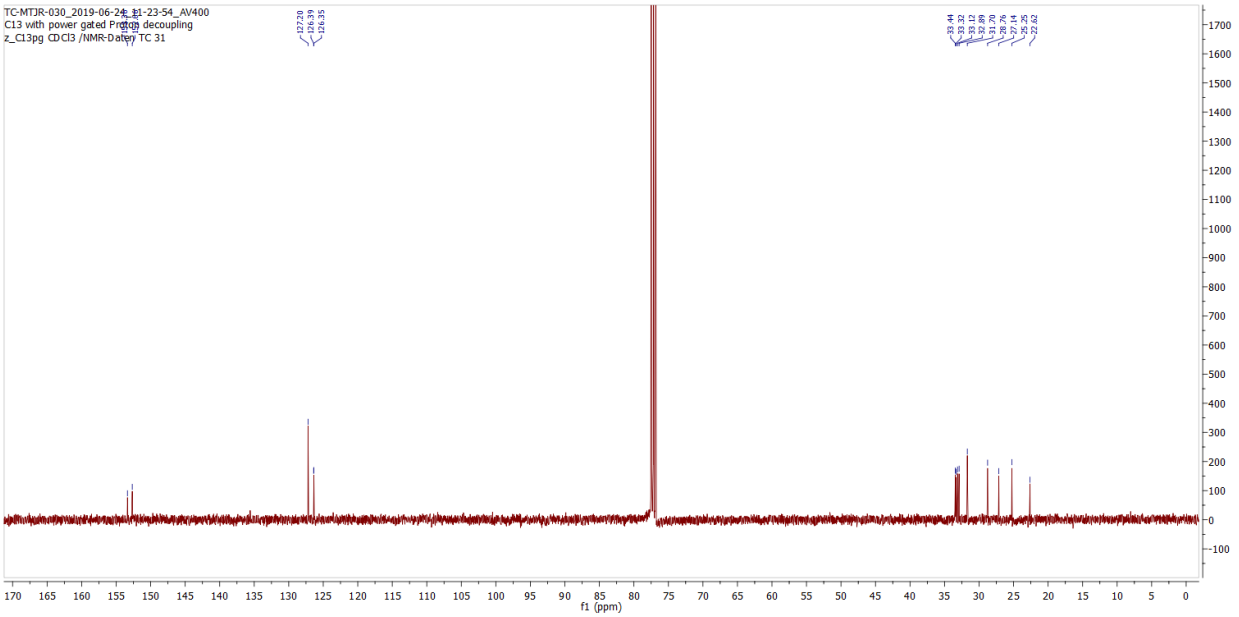


Figure S32: [13]C NMR of 3-(cyclohex-3-en-1-yl)propanal oxime **3g** *(mixture of (E)- and (Z) isomers.*

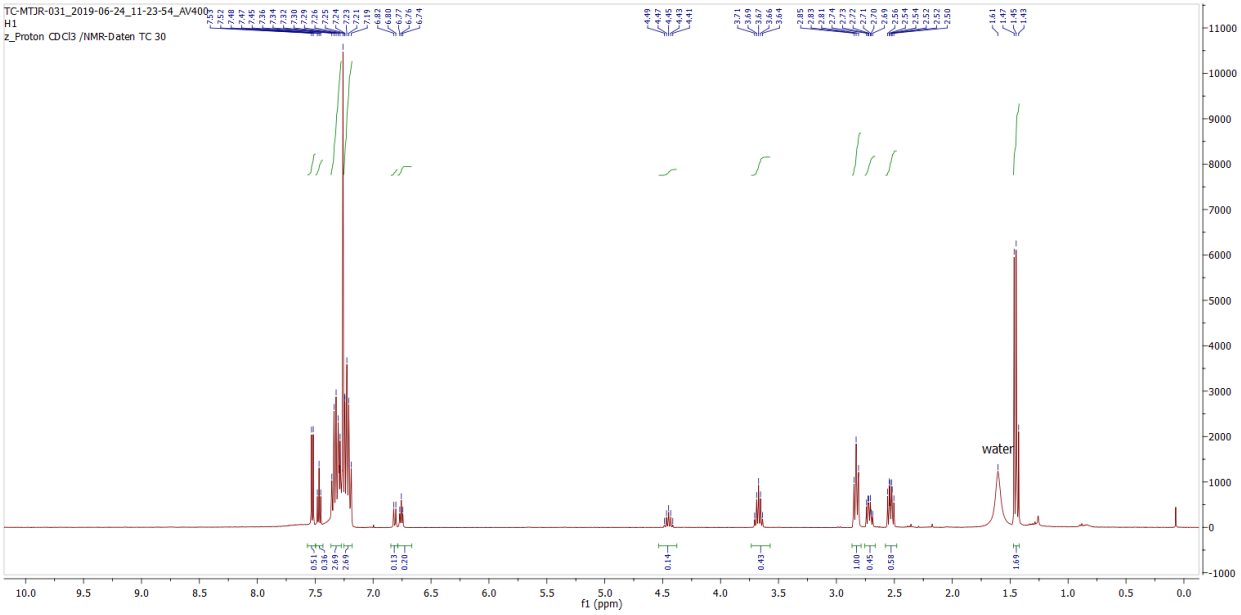


Figure S33: [1]H NMR of 3-Phenylpropanal oxime and 2-phenylpropanal oxime **3h** *(mixture of (E)- and (Z) isomers).*

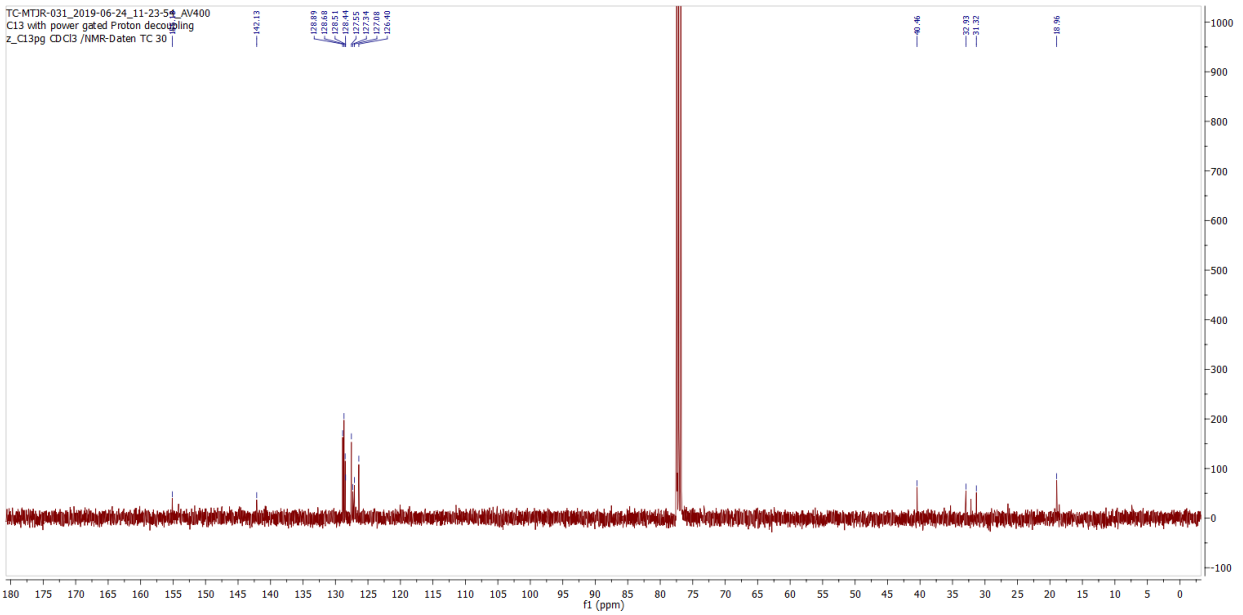


Figure S34: [13]C NMR of 3-Phenylpropanal oxime and 2-phenylpropanal oxime **3h** *(mixture of (E)- and (Z) isomers.*

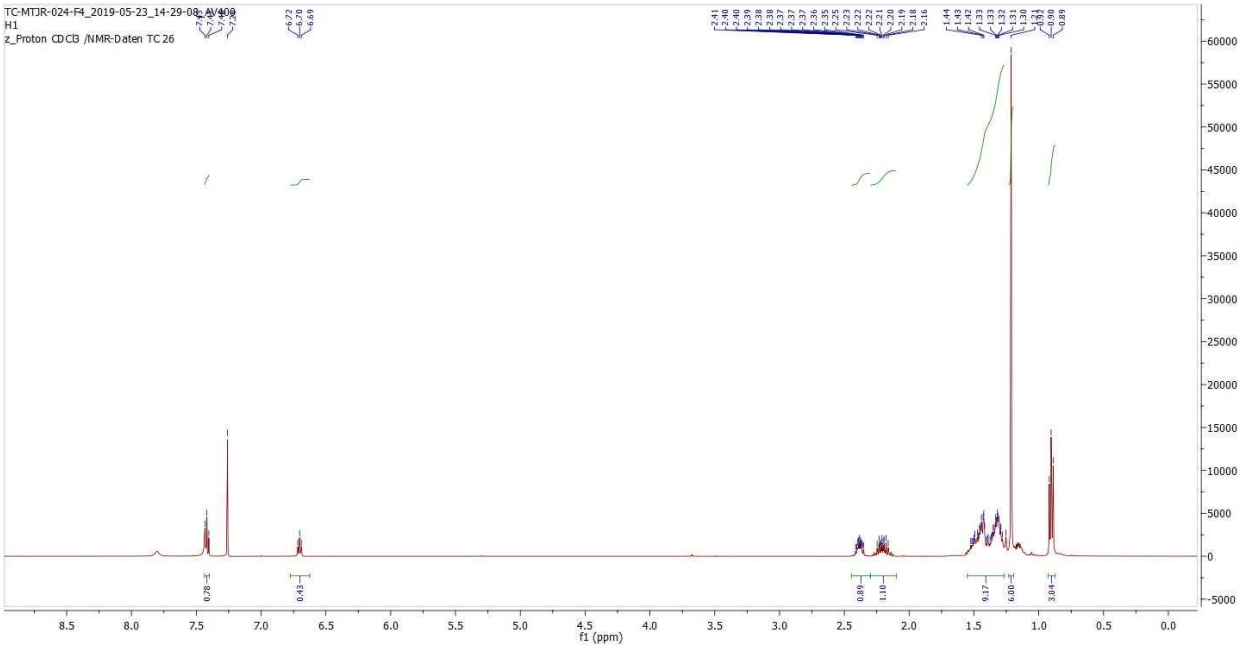


Figure S35: ^{1}H NMR of 8-hydroxy-4,8-dimethylnonanal oxime **3i** *(mixture of (E)- and (Z) isomers).*

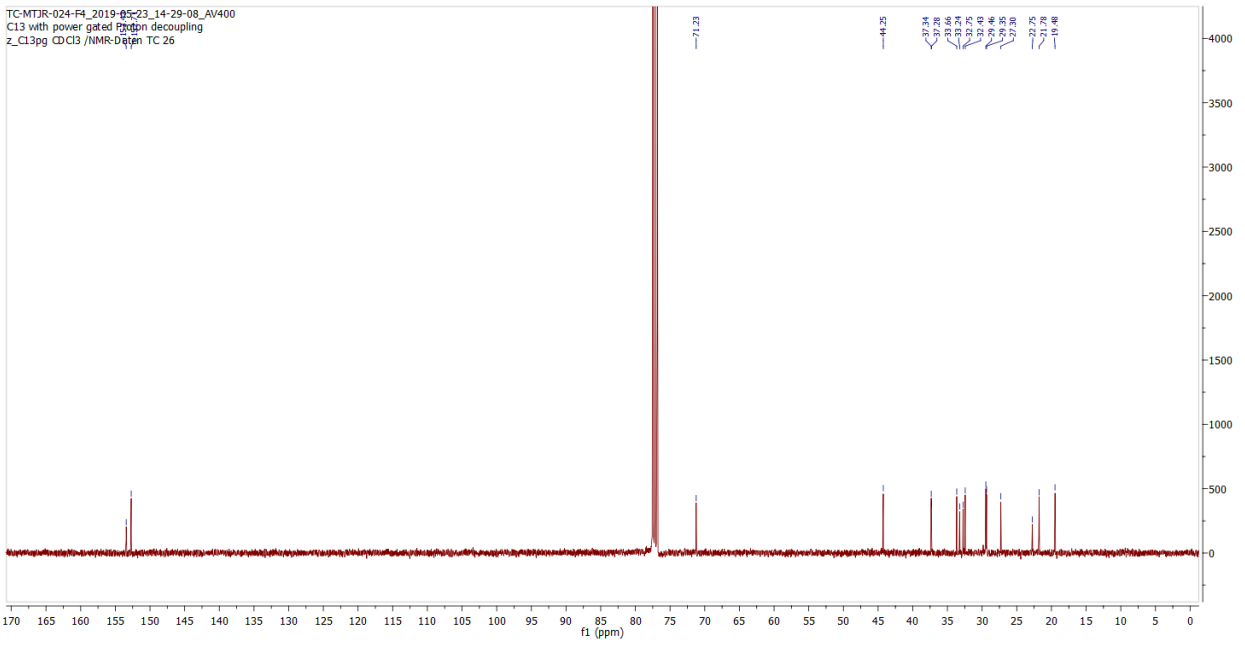


Figure S36: ^{13}C NMR of 8-hydroxy-4,8-dimethylnonanal oxime **3i** *(mixture of (E)- and (Z) isomers.*

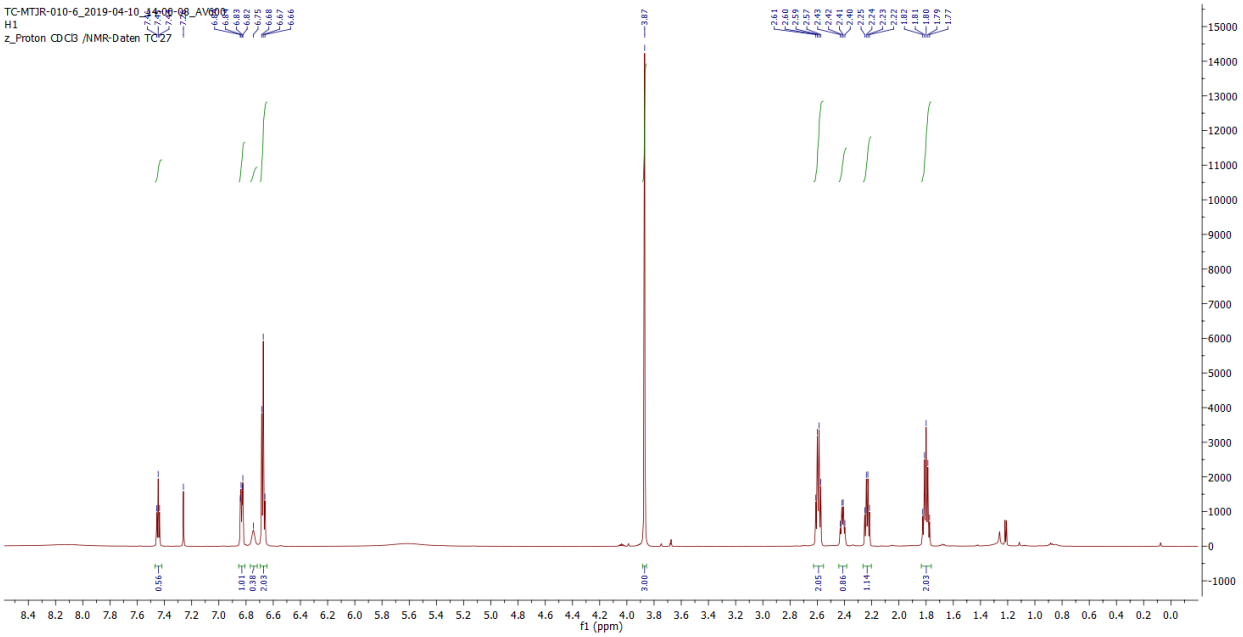


Figure S37: [1]H NMR of 4-(4-hydroxy-3-methoxyphenyl)butanal oxime **3j** *(mixture of (E)- and (Z) isomers).*

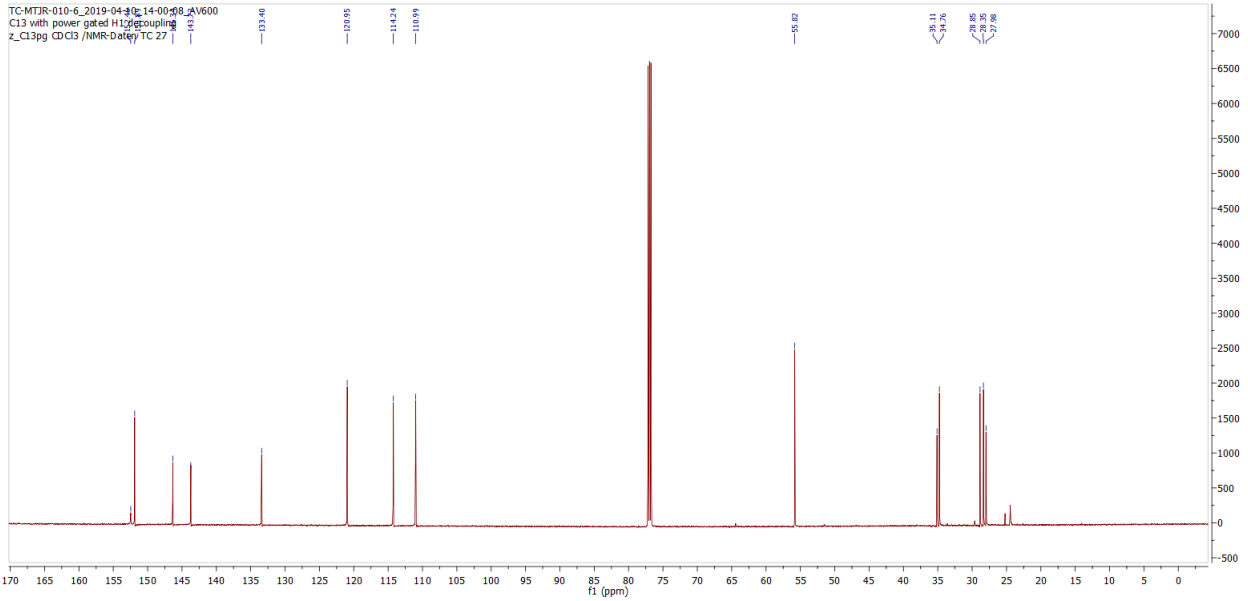


Figure S38: [13]C NMR of 4-(4-hydroxy-3-methoxyphenyl)butanal oxime **3j** *(mixture of (E)- and (Z) isomers.*

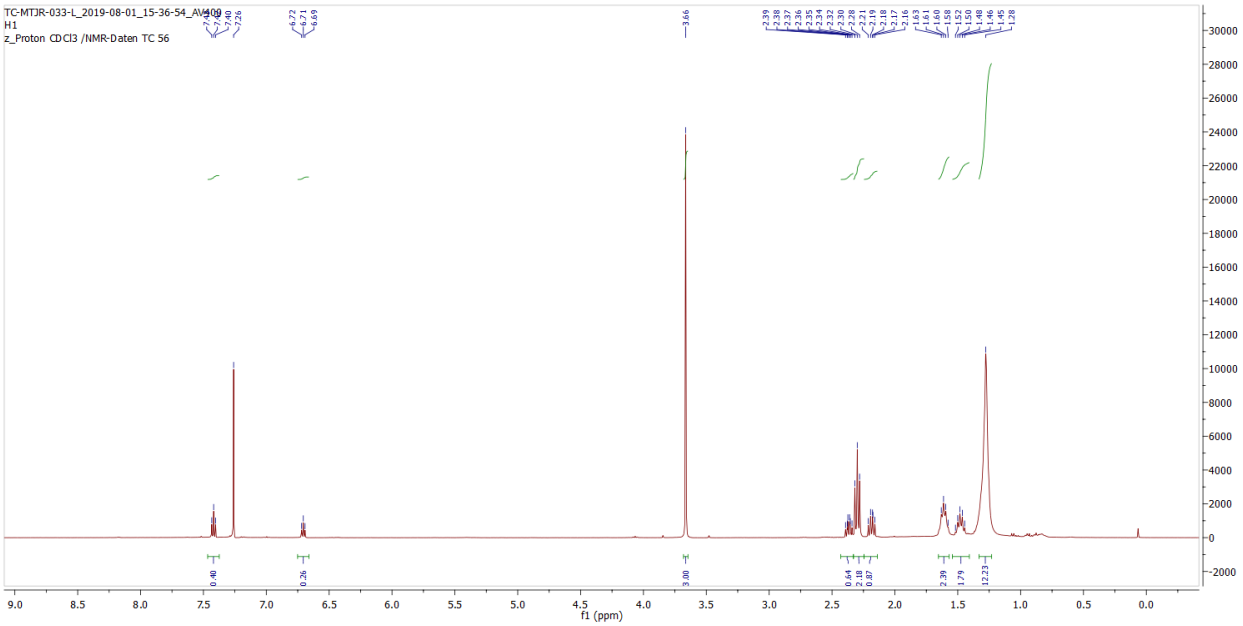


Figure S39: ^{1}H NMR of methyl 12-(hydroxyimino)dodecanoate **3k** *(mixture of (E)- and (Z) isomers).*

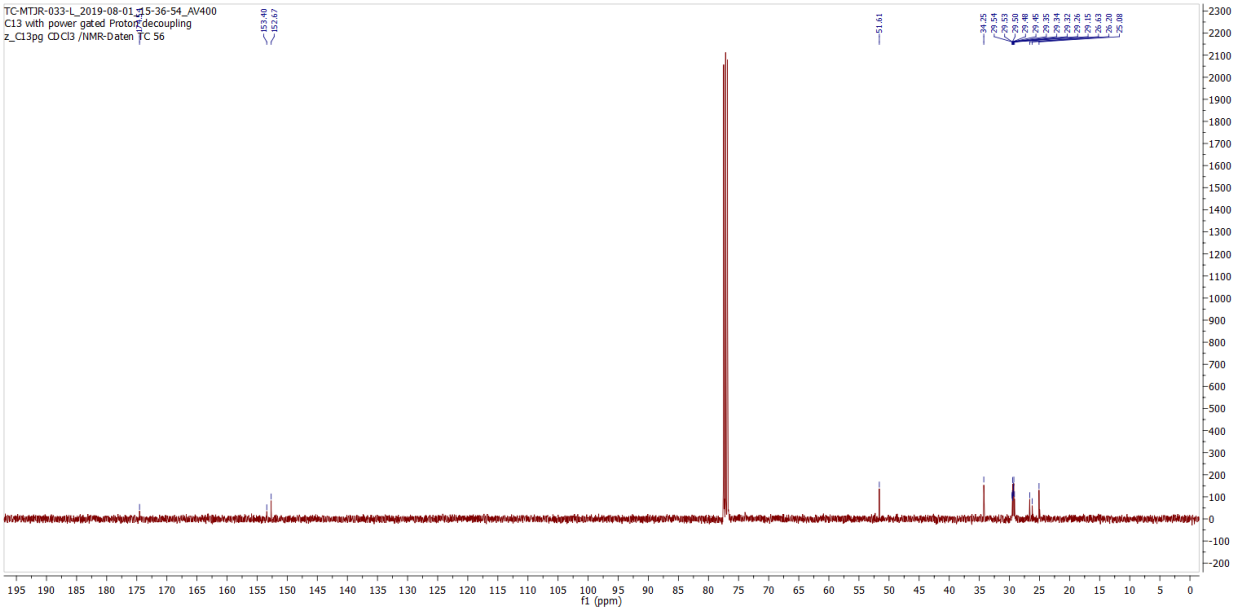


Figure S40: ^{13}C NMR of methyl 12-(hydroxyimino)dodecanoate **3k** *(mixture of (E)- and (Z) isomers.*

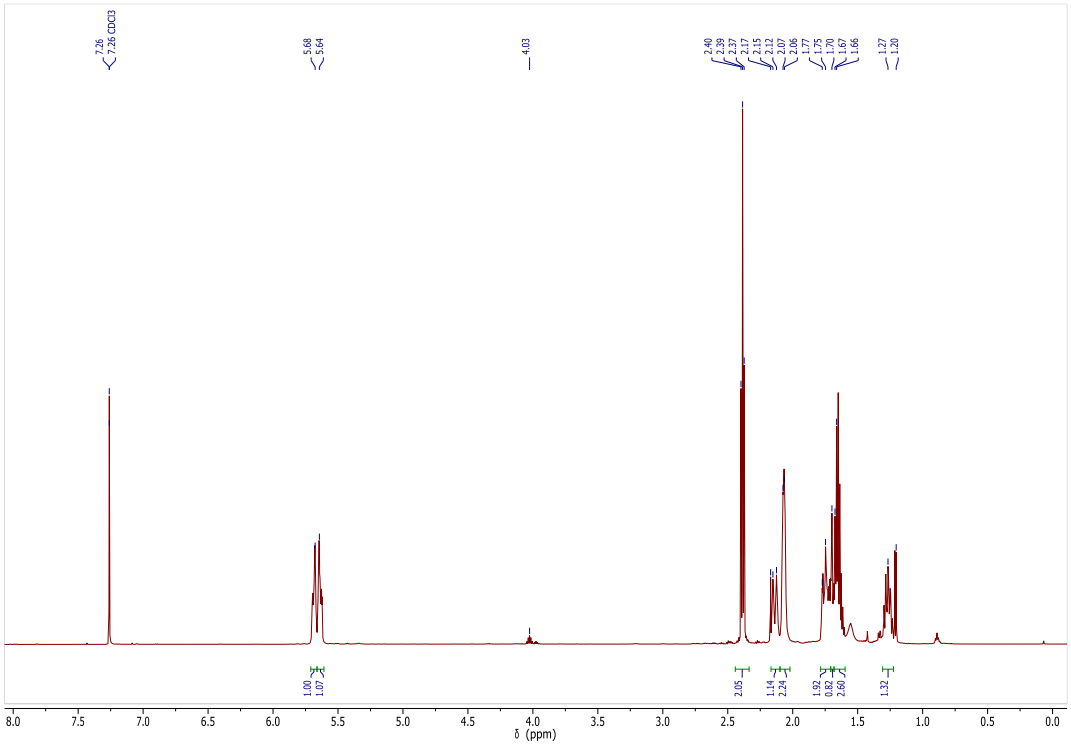


Figure S41: [1]H NMR of 3-(cyclohex-3-en-1-yl)propanenitrile **9g**.

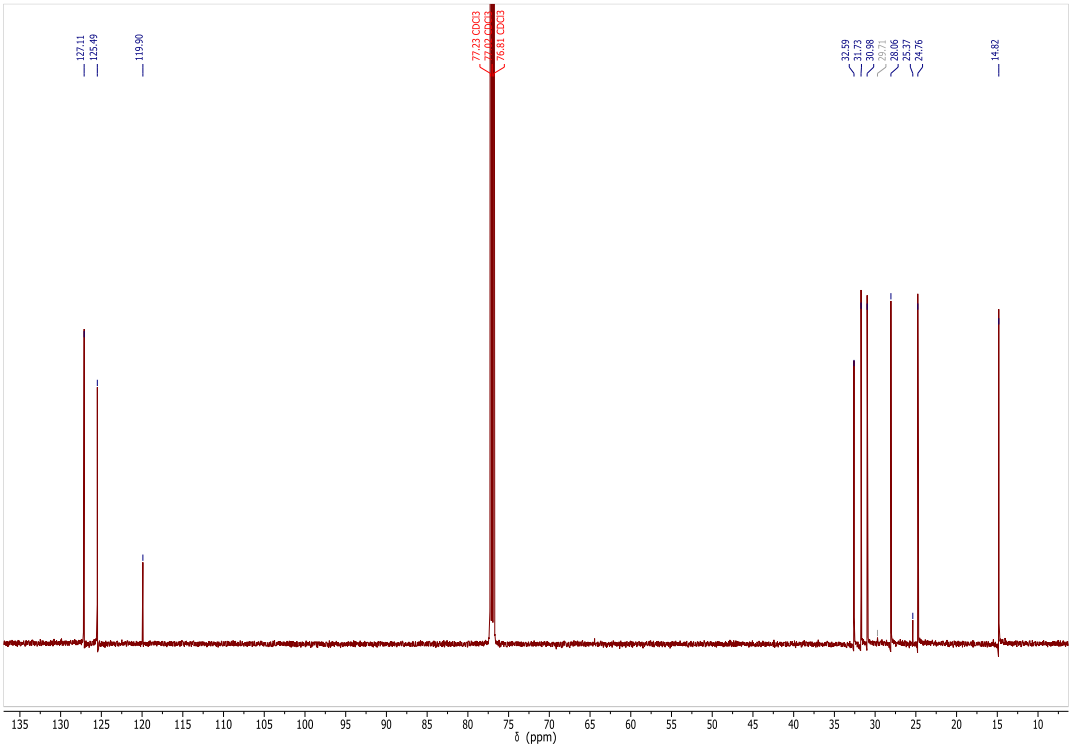


Figure S42: [13]C NMR of 3-(cyclohex-3-en-1-yl)propanenitrile **9g**.

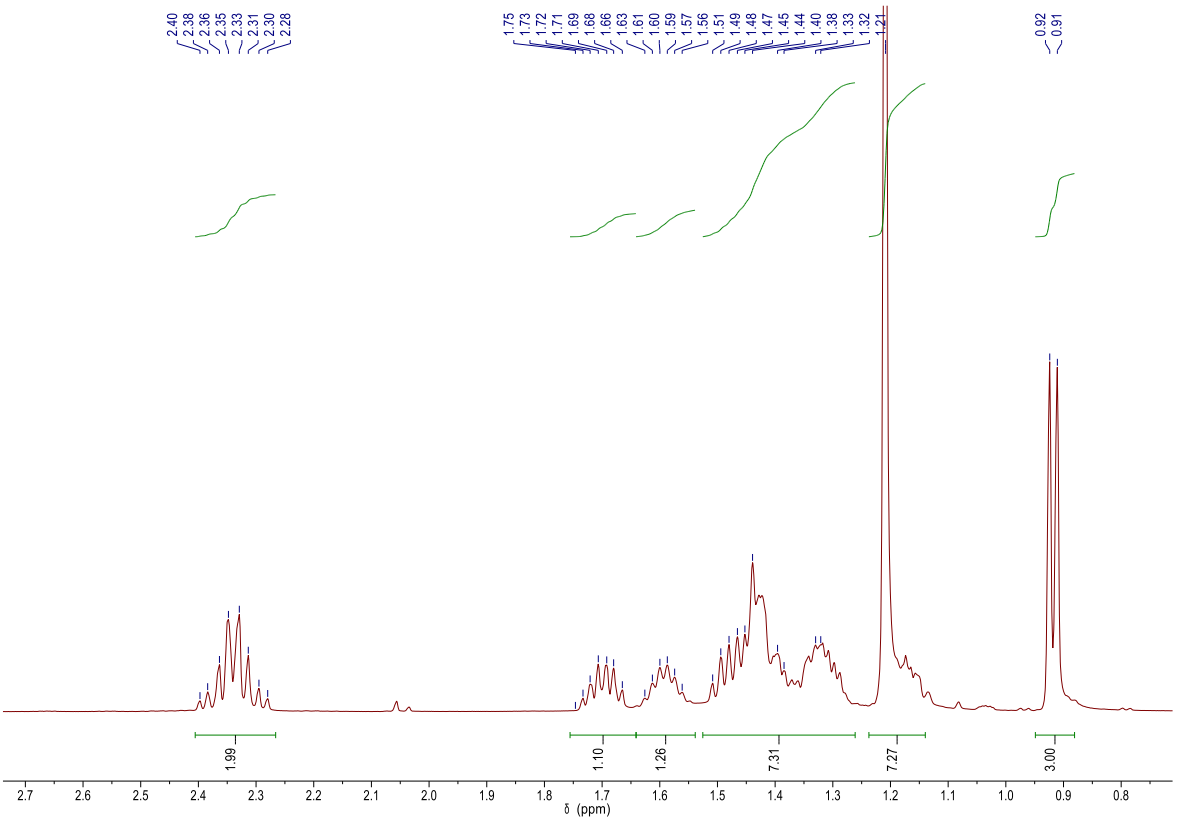


Figure S43: ^{1}H NMR of 8-hydroxy-4,8-dimethylnonanenitrile **9i**.

Additional References:

[1] X.-Y. Ma, Y. He, T.-T. Lu, M. Lu, *Tetrahedron* **2013**, *69*, 2560.
[2] Y. Yamamoto, S. Yamamoto, H. Yatagai, Y. Ishihara, K. Maruyama, *J. Org. Chem.* **1982**, *47*, 119.
[3] J. Campbell, G. McDougald, H. McNab, L. Rees, R. Tyas, *Synthesis* **2007**, *2007*, 3179.
[4] I. Ryu, S. Uehara, H. Hirao, T. Fukuyama, *Org. Lett.* **2008**, *10*, 1005.
[5] C. Plass, A. Hinzmann, M. Terhorst, W. Brauer, K. Oike, H. Yavuzer, Y. Asano, A. J. Vorholt, T. Betke and H. Gröger, *ACS Catal.*, **2019**, 9, 5198–5203.
[6] M. Lomoschitz, H. Peterlik, K. Zorn, S. O. Baumann, U. Schubert, *J. Mater. Chem*. **2010**, *20*, 5527.