Supplementary Information:

A remarkably simple α-oximation of aldehydes via organo-SOMO catalysis

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General Procedures and Materials.

$^1$H-NMR and $^{13}$C-NMR spectra were recorded on a Bruker AC 300 spectrometer (300 MHz) using CDCl$_3$ and DMSO-d$_6$ as solvents. Chemical shifts are referred to the solvent signal and expressed in parts per million (δ scale); coupling constants are expressed in Hertz (Hz). Infrared (IR) spectra were obtained by using a Perkin–Elmer 1600 (FTIR) spectrometer; data are presented as wavenumbers $\nu$ (cm$^{-1}$). GC analyses were run on a Varian CP 3800 instrument, equipped with 5% phenyl silicone 30m×0.25mm×25μm capillary column. GC–MS analyses have been run on a HP 5892 series II GC, equipped with a 5% phenyl silicone 30m×0.25mm×25μm capillary column and coupled to a HP 5972 MSD instrument operating at 70 eV. High-resolution mass spectra (HRMS) were performed with an Electrospray Ionisation Time of Flight Micromass spectrometer. All chemicals were of highest commercially available quality and were used as received. Tetrahydrofuran (THF) was distilled over sodium benzophenone ketyl radical under an atmosphere of argon. Dimethylformamide (DMF) was distilled under reduced pressure and stored over 4Å molecular sieves under argon atmosphere. Dichloromethane (CH$_2$Cl$_2$), acetonitrile (CH$_3$CN) and dimethylsulfoxide (DMSO) were purchased from Aldrich, stored over 4Å molecular sieves and handled under an atmosphere of argon.

Experimental Procedures.

Preparation of the aldehydes 1e, 1f and 1h: aldehydes were prepared by TEMPO/BAIB oxidation of the corresponding alcohols in 50-78 % yield$^1$. The following are the $^1$H NMR data of 1e-h.

2-Cyclohexylethanal 1e$^2$ $^1$H NMR (300 MHz; CDCl$_3$): δ 9.75 (1H, t, J=2.3 Hz, CHO); 2.28 (2H, dd, J=6.8 Hz, 2.3 Hz, CH$_2$CHO); 1.96-1.73 (1H, m, CH); 1.70-1.59 (5H, m, 5 HCH); 1.36-0.91 (5H, m, 5 HCH).

3,7-dimethyl-6-octenal 1f$^3$ $^1$H NMR (300 MHz; CDCl$_3$): δ 9.75 (1H, t, J=2.2 Hz, CHO); 5.12-5.03 (1H, m, CH=); 2.47-1.94 (5H, m); 1.64 (3H, d, J=15.8 Hz, CHC$_3$); 1.39-1.23 (2H, m, CH$_2$); 0.98 (3H, s, CCH$_3$); 0.95 (3H, s, CCH$_3$).

(2Z)-3,7-dimethyl-2,6-octadienal 1h$^4$ $^1$H NMR (300 MHz; CDCl$_3$): δ 9.88 (1H, d, J=8.2 Hz, CHO); 5.85 (1H, d, J=8.0 Hz, C=CHCHO); 5.11-5.05 (1H, m, CH=CH(CH$_3$)$_2$); 2.57 (2H, t, J=7.5 Hz CH$_2$C(CH$_3$)$_3$); 2.25-2.15 (2H, m, CH$_2$CH=C); 1.96 (3H, d, J=1.3 Hz, CH$_3$); 1.66 (3H, s, CH$_3$); 1.58 (3H, s, CH$_3$).
**General procedure for α-oximation of aldehydes.**

Reactants were introduced in reaction vessel in the following order: pyrrolidine (0.4 mmol, 33 μL) was added to a solution of monohydrate p-TsOH (0.4 mmol, 76 mg) in 3 mL of anhydrous DMF, followed by addition of distilled water (4.0 mmol) and aldehyde (2.0 mmol). After mixing solution for 5 minutes, NaNO₂ (2.0 mmol, 138 mg) was added and then anhydrous FeCl₃ (2.0 mmol, 324 mg) was introduced in aliquotes (careful: reaction is exothermic). The reaction was monitored by thin layer chromatography. At the end of experiment (3 - 4.5 h), the internal standard was added, followed by addition of a saturated NaCl solution (5 mL). The mixture was extracted with ethyl acetate (30 mL); the organic phases were washed with a saturated solution of NaCl and dried over Na₂SO₄. The quantitative yields of α-oximation reaction were determined by GC analysis (error ± 3%).

**Characterization of α-oximation reaction products.**

All 2-hydroxyimino-aldehydes were synthesized by following the general procedure. After evaporation of the solvent under reduced pressure, all products were isolated by chromatographic purification on silica gel using several mixtures of hexane/ethyl acetate as eluent and characterized by spectroscopic analysis. When injected to GC and GC-MS, all 2-hydroxyimino-aldehydes lose slightly HCOOH, giving the corresponding nitrile derivatives as confirmed by comparing with authentic samples.

**2-hydroxyimino-3-phenylpropanal 2a**: after column chromatography (eluent hexane/ethyl acetate 50/3) 276 mg (85%) of a yellow oil was obtained. ¹H-NMR (300 MHz; CDCl₃): δ 9.52 (1H, s, CHO), 8.38 (1H, broad s, OH), 7.28-7.19 (5H, m, ArH), 3.86 (2H, s, CH₂). ¹³C-NMR (300 MHz; CDCl₃): δ 190.7, 159.8, 135.6, 129.4, 128.8, 126.9, 28.1. GC-MS: m/z 163 (M⁺, 48%), 117 (98), 91 (100). IR (CHCl₃): / cm⁻¹ 3552 (OH), 1706 (conj. CO), 1602 (CN) and 1006 (NO). HRMS (ESI-TOF) calcd for [C₉H₉NO₂ - H⁺] 162.0550, found 162.05496.

**2-hydroxyimino-2-phenylethanal 2b**: after column chromatography (eluent hexane/ethyl acetate 10/1) 192 mg (64%) of a yellow oil was obtained, from which the dimer crystallizes on standing as white solid. ¹H-NMR (300 MHz; DMSO-d₆): δ 9.61 (1H, s, CHO), 7.43-7.42 (5H, m, ArH). ¹³C-NMR (300 MHz; CDCl₃): δ 190.7, 157.2, 132.5, 130.5, 129.6, 128.4. GC-MS: m/z 149 (M⁺, 40%),
2-hydroxyiminodecanal 2c: after column chromatography (eluent hexane/ethyl acetate 40/1) 253 mg (70%) of a white solid (mp 60-62°C from hexane/ethyl acetate) was obtained. $^1$H-NMR (300 MHz; CDCl$_3$): δ 9.45 (1H, s, CHO), 8.64 (1H, broad s, NOH), 2.49 (2H, t, J=7.7 Hz, CH$_2$C=NOH), 1.49-1.44 (2H, m, CH$_2$CH$_2$C=NOH), 1.27-1.26 (10H, m), 0.87 (3H, t, J=6.7 Hz, CH$_3$). $^{13}$C-NMR: (300 MHz; CDCl$_3$) δ 191.3, 162.2, 32.2, 30.0, 29.5, 29.4, 25.8, 23.0, 22.2, 14.4. GC-MS: m/z 185 (M$^+$, 2%), 168 (7), 156 (30), 138 (21), 124 (15), 110 (20), 96 (25), 87 (46), 81 (25), 71 (37), 69 (37), 55 (100). IR (CHCl$_3$): $\tilde{\nu}$/cm$^{-1}$ 3557 (OH), 1705 (conj. CO), 1603 (CN) and 1012 (NO). HRMS (ESI-TOF) calcd for [C$_{10}$H$_{19}$NO$_2$ - H$^+$] 184.1338, found 184.1340.

2-hydroxyimino-3,5,5-trimethylhexanal 2d: after column chromatography (eluent hexane/ethyl acetate 50/3) 275 mg (80%) of a yellow oil was obtained. $^1$H-NMR (300 MHz; CDCl$_3$): δ 9.397 and 9.392 (1H, s, CHO, E and Z isomers), 3.36-3.34 (1H, m, CH), 2.01 (1H, dd, J=14.3 Hz and 8.9 Hz, H$_3$CH$_2$), 1.35 (1H, dd, J=14.3 Hz and 3.9 Hz, H$_3$CH), 1.18 (3H, d, J=7.1 Hz, CHCH$_3$), 0.84 (9H, s, C(CH$_3$)$_3$). $^{13}$C-NMR (300 MHz; CDCl$_3$): δ 191.6, 165.5, 46.9, 31.5, 29.8, 26.0, 19.2. GC-MS: m/z 171 (M$^+$, 1%), 154 (2), 115 (10), 110 (10), 98 (30), 83 (20), 69 (25), 57 (100). IR (CHCl$_3$): $\tilde{\nu}$/cm$^{-1}$ 3556 (OH), 1706 (conj. CO), 1610 (CN) and 1000 (NO). HRMS (ESI-TOF) calcd for [C$_9$H$_{17}$NO$_2$ - H$^+$] 170.1181, found 170.1185.

2-cyclohexyl-2-hydroxyiminoethanal 2e: after column chromatography (eluent hexane/ethyl acetate 25/2) 251 mg (81%) of a yellow oil was obtained. $^1$H-NMR (300 MHz, CDCl$_3$): δ 9.365 and 9.361 (1H, s, CHO, E and Z isomers), 3.09-3.01 (1H, m, CH), 1.91-1.27 (10H, m, 5CH$_2$). $^{13}$C-NMR (300 MHz; CDCl$_3$): δ 191.7, 163.6, 35.0, 27.6, 26.6, 26.1. GC-MS: m/z 155 (M$^+$, 5%), 138 (53), 126 (14), 108 (67), 81 (76), 67 (78), 55 (100). IR (CHCl$_3$): $\tilde{\nu}$/cm$^{-1}$ 3556 (OH), 1706 (conj. CO), 1607 (CN) and 1037 (NO). HRMS (ESI-TOF) calcd for [C$_8$H$_{13}$NO$_2$ - H$^+$] 154.0868, found 154.0862.

2-hydroxyimino-3,7-dimethyl-oct-6-enal 2f: after column chromatography (eluent hexane/ethyl acetate 20/1) 190 mg (49%) of a yellow oil was obtained. $^1$H-NMR (300 MHz; CDCl$_3$): δ 9.386 and 9.381 (1H, s, CHO, E and Z isomers), 5.08-4.91 (1H, m, CH=CH), 3.28-3.18 (1H, m, CH$_2$CH), 1.95-1.75 4H, m, CH$_2$CH$_2$), 1.65 (3H, s, CCH$_3$), 1.55 (3H, s, CCH$_3$), 1.19 (3H, d, J=7.0 Hz, CHCH$_3$). $^{13}$C-NMR (300 MHz; CDCl$_3$): δ 190.7, 163.1, 131.6, 123.5, 32.2, 28.9, 26.0, 25.2, 17.2, 15.8. GC-
MS: \( m/z \) 183 (M\(^+\), 2\%), 166 (30), 101 (50), 83 (60), 69 (80), 55 (100). IR (CHCl\(_3\)): \( \tilde{\nu} \)/cm\(^{-1}\) 3559 (OH), 1703 (conj. CO), 1614 (CN) and 1015 (NO). HRMS (ESI-TOF) calcd for [C\(_{10}\)H\(_{17}\)NO\(_2\) - H\(^+\)] 182.1181, found 182.1184.

2-hydroxyimino-3,3-dimethyl-butanal 2g: after column chromatography (eluent hexane/ethyl acetate 40/1) 196 mg (76%) of a white solid (mp 102-104°C from hexane) was obtained, as a mixture of Z and E isomers (ratio 3/1). The diastereomeric ratio was determined by \(^1\)H-NMR spectroscopy via integration of the aldehyde signals.

\(^1\)H-NMR (300 MHz; CDCl\(_3\)): isomer Z \( \delta \) 10.29 (1H, s, CHO), 1.23 (9H, s, C(CH\(_3\)_3)); isomer E \( \delta \) 9.35 (1H, s, CHO), 1.37 (9H, s, C(CH\(_3\)_3)). \(^{13}\)C-NMR (300 MHz; DMSO-d\(_6\)): isomer Z \( \delta \) 192.0, 141.1, 37.2, 28.8, 28.5, 27.9; isomer E \( \delta \) 193.3, 142.3, 35.9, 29.6, 29.0, 27.6. GC-MS: \( m/z \) 129 (M\(^+\), 32\%), 112 (23), 100 (50), 84 (25), 68 (24), 57 (100). IR (CHCl\(_3\)): \( \tilde{\nu} \)/cm\(^{-1}\) 3572 (OH), 1708 (conj. CO), 1614 (CN) and 1012 (NO). HRMS (ESI-TOF) calcd for [C\(_6\)H\(_{11}\)NO\(_2\)-H\(^+\)] 128.0706, found 128.0712.

(E)-2-benzyl-5-phenylpent-2-enal 3\(^e\): was synthesized following the general procedure, but in absence of FeCl\(_3\) and extending reaction time to 48 h. After column chromatography (eluent hexane/ethyl acetate 100/1) 100 mg (40%) of a colourless oil was obtained. \(^1\)H-NMR (300 MHz; CDCl\(_3\)): \( \delta \) 9.45 (1H, s, CHO), 7.29-7.10 (10H, m, 2 ArH), 6.63 (1H, apparent t, J=6.33 Hz, C=CH), 3.59 (2H, s, CH\(_2\)), 2.76 (4H, m, CH\(_2\)CH\(_2\)). GC-MS: \( m/z \) 250 (M\(^+\), 6\%), 232 (5), 159 (31), 145 (41), 131 (16), 115 (10), 91 (100).

2-methyl-5-(1-hydroxy-1-methylethyl)cyclopentanecarbaldehyde 4: after column chromatography (eluent hexane/ethyl acetate 50/1) 75 mg (20%) of a colourless oil was obtained, as a mixture of 4a and 4b diastereomers (dr 2/1). The diastereomeric ratio was determined by \(^1\)H-NMR spectroscopy via integration of the aldehyde signals.

HRMS (ESI-TOF) calcd for [C\(_{10}\)H\(_{18}\)O\(_2\)-H\(^+\)] 169.1229, found 169.1228.

diastereomer 4a \(^1\)H-NMR (300 MHz; CDCl\(_3\)): \( \delta \) 9.66 (1H, d, J=3.5 Hz, CHO), 2.69-2.60 (1H, m, CHC(CH\(_3\))\(_2\)OH); 2.46-2.40 (1H, dt, J=8.4 Hz and 3.5 Hz, CHCHO), 2.21-2.11 (1H, m, CHCH\(_3\)), 2.00-1.86 (2H, m, CH\(_2\)H\(_5\)-CH\(_2\)H\(_5\)),1.56 (3H, s, CH\(_3\)), 1.50 (3H, s, CH\(_3\)), 1.45-1.30 (2H, m, CH\(_3\)H\(_5\)-CH\(_3\)H\(_5\)), 1.10 (3H, d, J=6.7 Hz, CH\(_3\)). \(^{13}\)C-NMR (300 MHz; CDCl\(_3\)): \( \delta \) 203.8, 73.8, 62.2, 53.0, 37.5, 34.3, 32.0, 31.0, 28.0, 19.0. GC-MS: \( m/z \) 152 (M\(^+\), 10\%), 137 (11), 123 (84), 111 (27), 109 (39), 95 (24), 93 (27), 91 (15), 82 (24), 81 (100), 79 (20), 77 (20), 70 (49), 67 (32), 55 (24), 53 (14).

diastereomer 4b \(^1\)H-NMR (300 MHz; CDCl\(_3\)): \( \delta \) 9.83 (1H, d, J=2.6 Hz, CHO), 2.92-2.98 (1H, m,
3-phenyl-propionic acid \(^{12}\): yield 67% (eluent hexane/ethyl acetate 10:1). white solid (mp 40-50°C from hexane). \(^1\)H NMR (300 MHz; CDCl\(_3\)): \(\delta\) 9.5 (1H, broad s, OH); 7.36-7.21 (5H, m, ArH); 2.97 (2H, t, \(J=7.8\) Hz, \(\text{CH}_2\text{CO}_2\text{H}\)); 2.70 (2H, t, \(J=7.7\) Hz, \(\text{CH}_2\text{Ph}\)). \(^13\)C NMR (300 MHz; CDCl\(_3\)): \(\delta\) 179.5, 140.5, 128.9, 128.6, 126.7, 35.9, 30.9.

**General procedure for oxidative cyclization of citronellal 1f.**

Reactants were introduced in reaction vessel in the following order: pyrrolidine (0.065 mmol, 5.4 μL) was added to a solution of monohydrate \(p\)-TsOH (0.065 mmol, 12 mg) in 0.5 mL of anhydrous DMF, followed by addition of 1f (0.33 mmol). After mixing solution for 5 minutes, the oxidant (0.65 mmol) was added. The mixture was stirred for 24 h at 80°C or room temperature. At the end of experiment, the internal standard was added, followed by addition of a saturated NaCl solution (1 mL). The mixture was extracted with ethyl acetate (5 mL); organic phases were washed with a saturated solution of NaCl and dried over Na\(_2\)SO\(_4\). Quantitative yields of cyclization products were determined by GC analysis (error ± 3%).

**Characterization of 2-methyl-5-(prop-1-en-2-yl)cyclopentanecarbaldehyde 8.**

It was synthesized by following the general procedure. A crude product was obtained which, upon concentration and column chromatography on silica gel (hexane/ethyl acetate 80/1), produced 217 mg (44 %) of a yellow oil as a mixture of \(8a\), \(8b\), \(8c\) and \(8d\) diastereomers. The diastereomeric ratio \(8a:8b:8c:8d = 29:5:1:1\) was determined by \(^1\)H-NMR spectroscopy via integration of the aldehyde signals.

**Diastereomer 8a:** \(^1\)H-NMR (300 MHz; CDCl\(_3\)): \(\delta\) 9.56 (1H, d, \(J=3.6\) Hz, \(\text{CHO}\)), 4.72 (1H, br s, C=CH\(_2\)H\(_5\)), 4.75 (1H, br s, C=CH\(_2\)H\(_5\)), 2.83 (1H, apparent q, \(J=8.7\) Hz, \(\text{CH}=\text{CH}_2\)), 2.30 – 2.20 (2H, m, \(\text{CH}_3\text{CH}=\text{CHCHO}\)), 2.00–1.86 (2H, m, \(\text{CH}=\text{CH}_2\text{CH}=\text{CHCHO}\)), 1.71 (3H, s, \(\text{CH}_3\)), 1.45–1.30 (2H, m, \(\text{CH}_2\text{CH}=\text{CH}_2\text{CH}=\text{CHCHO}\)), 1.06 (3H, d, \(J=6.4\) Hz, \(\text{CH}_3\)). \(^13\)C-NMR (300 MHz; CDCl\(_3\)): \(\delta\) 204.4, 146.2,
110.4, 63.7, 49.1, 36.2, 33.5, 30.3, 20.4, 19.5. GC-MS: m/z 152 (M+, 2%), 137 (9), 123 (100), 109 (20), 95 (33), 81 (54), 67 (27), 55 (14).

diastereomer 8b, 7, 8, 9, 10: 1H-NMR (300 MHz; CDCl3): δ 9.75 (1H, d, J=3.4 Hz, CHO), 4.84 (1H, br s, C=CHbHb), 4.81 (1H, br s, C=CHbHb), 3.04 (1H, apparent q, J=8.5 Hz, CHCH3), 2.69 (1H, ddd, J=8.8 Hz, 8.7 Hz and 3.4 Hz, CHCHO), 2.60–2.45 (1H, m, CH2Hb-CHbHb), 1.59 (3H, s, CH3), 1.45–1.27 (2H, m, CH2Hb-CHbHb), 1.05 (3H, d, J=7.0 Hz, CH3). 13C-NMR (300 MHz; CDCl3): δ 205.7, 146.8, 110.0, 58.5, 46.0, 37.3, 34.7, 30.6, 20.7, 16.7. GC-MS: m/z 152 (M+, 2%), 137 (9), 123 (100), 109 (20), 95 (33), 81 (54), 67 (27), 55 (14).

diastereomer 8c, 11: partial data 1H-NMR (300 MHz; CDCl3): δ 9.50 (1H, d, J=3.7Hz, CHO). 13C-NMR (300 MHz; CDCl3): δ 201.2, 61.5, 52.0. GC-MS. m/z 152 (M+., 1%), 137 (7), 123 (8), 109 (47), 95 (25), 82 (42), 81 (100), 70 (93), 69 (49), 67 (58), 55 (30).

diastereomer 8d, 9: partial data 1H-NMR (300 MHz; CDCl3): δ 9.30 (1H, d, J=4.5 Hz, CHO). 13C-NMR (300 MHz, CDCl3): δ 202.9, 111.5, 60.4, 48.9, 36.3, 34.2, 30.7, 23.0, 21.2.

References

NMR Spectra Data

$^1$H-NMR (300 MHz; CDCl$_3$) 2-hydroxyimino-3-phenylpropanal 2a
$^{13}$C-NMR (300 MHz; CDCl$_3$) 2-hydroxyimino-3-phenylpropanal 2a
$^1$H-NMR (300 MHz; DMSO-$d_6$) 2-hydroxyimino-2-phenylethanal 2b
$^{13}$C-NMR (300 MHz; CDCl$_3$) 2-hydroxyimino-2-phenylethanal 2b
$^1$H-NMR (300 MHz; CDCl$_3$) 2-hydroxyiminodecanal 2c
$^{13}$C-NMR (300 MHz; CDCl$_3$) 2-hydroxyiminodecanal 2c
$^1$H-NMR (300 MHz; CDCl$_3$) 2-hydroxyimino-3,5,5-trimethylhexanal 2d
$^{13}$C-NMR (300 MHz; CDCl$_3$) 2-hydroxyimino-3,5,5-trimethylhexanal 2d
$^1$H-NMR (300 MHz; CDCl$_3$) 2-cyclohexyl-2-hydroxyiminoethanal 2e
$^{13}$C-NMR (300 MHz; CDCl$_3$) 2-cyclohexyl-2-hydroxyiminoethanal $2e$
$^1$H-NMR (300 MHz; CDCl$_3$) 2-hydroxyimino-3,7-dimethyl-oct-6-enal 2f
$^{13}$C-NMR (300 MHz; CDCl$_3$) 2-hydroxyimino-3,7-dimethyl-oct-6-enal 2f
$^{1}$H-NMR (300 MHz; CDCl$_3$) 2-hydroxyimino-3,3-dimethyl-butanal 2g
$^{13}$C-NMR (300 MHz; CDCl$_3$) 2-hydroxyimino-3,3-dimethyl-butanal 2g
$^{1}$H-NMR (300 MHz; CDCl$_3$) (E)-2-benzyl-5-phenylpent-2-enal 3
$^{1}$H-NMR (300 MHz; CDCl$_3$) 2-methyl-5-(1-hydroxy-1-methylethyl)cyclopentanecarbaldehyde 4
$^{13}$C-NMR (300 MHz; CDCl$_3$) 2-methyl-5-(1-hydroxy-1-methylethyl)cyclopentanecarbaldehyde 4
DEPT-NMR (300 MHz; CDCl$_3$) 2-methyl-5-(1-hydroxy-1-methylethyl)cyclopentanecarbaldehyde
COSY-NMR (300 MHz; CDCl₃) 2-methyl-5-(1-hydroxy-1-methylethyl)cyclopentanecarbaldehyde
$^{1}\text{H-NMR (300 MHz; CDCl}_3\text{)}$ 3-phenyl-propionic acid
$^1$H-NMR (300 MHz; CDCl$_3$) 2-methyl-5-(prop-1-en-2-yl)cyclopentanecarbaldehyde 8
$^{13}$C-NMR (300 MHz; CDCl$_3$) 2-methyl-5-(prop-1-en-2-yl)cyclopentanecarbaldehyde 8
DEPT-NMR (300 MHz; CDCl₃) 2-methyl-5-(prop-1-en-2-yl)cyclopentanecarbaldehyde 8