Supporting Information
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New Rearrangement of Conjugated Cyclic Ene Nitroso O-Trimethylsilyl Acetals: Convenient Synthesis of Dihydro-2H-pyrane- and Furane-3-one Oximes

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All reactions were performed in oven-dried (150 °C) glassware. Melting points were determined on a Koffler melting point apparatus and are uncorrected. Chromatographic separations were performed on silica gel (Acros, 40 – 60 μm, 60 Å) with analytical-grade solvents, driven by air pressure. Analytical thin-layer chromatography was performed on Fluka silica gel plates with fluorescent indicator (254 nm). Visualization was accomplished with UV light and/or anisaldehyde and/or ninhydrine. 1D and 2D NMR spectra were recorded on the NMR-spectrometer Bruker AV-300 (1H: 300.13 MHz, 13C: 75.47 MHz, 29Si: 59.63 MHz) for CDCl3 solutions at 298 K (unless otherwise mentioned) with residual solvent peak as an internal standard. The INEPT pulse sequence was used for observation of the 29Si signals. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Coupling constants, J, are reported in Hertz. Determination of C=N bond configuration (E or Z) was made basing on the chemical shifts in 13C NMR spectra: the carbon atom in syn-arrangement towards OX-group (X = H, SiMe3) is shifted to upper fields in comparison to signal from the same carbon in the opposite isomer.

Elemental analyses were performed by the analytical centre of N.D. Zelinsky Institute of Organic Chemistry. HRMS were recorded on Bruker MicroTOF spectrometer.

Solvents: hexane, EtOAc, Et₂O, MeOH, EtOH, dioxane - were analytical grade and used without additional purification. The following reaction solvents and reagents were distilled from the CaH₂: toluene, triethylamine, TMSBr and 2,3-dihydrofurane. Methylene chloride and THF were distilled from CaH₂ and stored over MS 4Å. Glacial acetic acid was recrystallized twice. The following chemicals were purchased from the indicated sources and used as received: NH₄F (Acros), LiF (Acros), ZnF₂ (Acros), HMPA (Aldrich), NMP (Aldrich), t-BuOK (Acros), Me₃SiONa (Aldrich), NaOH (Acros), DMAP (Acros), NaHSO₄ (Acros), tin tetrachloride (Aldrich), AlMe₃ (2M in heptane) (Aldrich), ethylvinyl ether (Acros), isobutylene (Aldrich), 1-pentene (Fluka), 4-methoxy-benzaldehyde (Acros), nitroethane (Acros), butylamine (Acros), AcONH₄ (Acros), TiCl₃ (10% solution in 20-30% HCl) (Aldrich), HCl (4M in dioxane) (Fluka), Raney Nickel (50% slurry in water) (Acros), MS 3Å (powder) (Fluka), MS 4Å (beads 4-8 mesh) (Aldrich). BuLi (solution in hexane) was purchased from Acros and titrated according to Watson and Eastham prior to use. TBAF was purchased as 1M in THF (Aldrich) and TBAF·3H₂O (Fluka). Brine refers to a saturated aqueous solution of NaCl.
1-Methoxy-4-((E)-2-nitro-1-propenyl)benzene

The solution of 4-methoxybenzaldehyde (136 g, 121 mL, 1 mol), nitroethane (75 g, 72 mL, 1 mol) and butylamine (15 g, 20 mL, 0.2 mol) in toluene (200 mL) was refluxed for 8 h with a Dean-Stark trap. The solvent was evaporated in vacuum and the residue was recrystallized from EtOH to give 43 g of yellow solid. Three additional recrystallizations of mother liquor residue gave another 84 g. Total yield 66%.
Mp = 39-42 °C (Lit. Mp = 43-44 °C (EtOH)).
Methyl (3E)-4-(4-methoxyphenyl)-3-nitrobut-3-enoate

\[
\begin{align*}
\text{OMe} & & \text{H} & & \text{NO}_2 \\
\text{H} & & \text{CO}_2\text{Me} & & \text{BuNH}_2, \text{toluene}
\end{align*}
\]

The solution of 4-methoxybenzaldehyde (2.24 g, 2.0 mL, 16.5 mmol), methyl-3-nitropropionate\textsuperscript{5} (2.0 g, 15 mmol) and butylamine (0.15 g, 0.2 mL, 2 mmol) in toluene (25 mL) was refluxed for 4 h with a Dean-Stark trap. Then the Dean-Stark trap was replaced with the dropping funnel with MS 4Å (5.5 g). Additional butylamine (0.30 g, 0.4 mL, 4 mmol) was added and the mixture was refluxed for 20 h. The solvent was evaporated in vacuum, then dissolved in Et\textsubscript{2}O, filtered through Celite\textsuperscript{®} and evaporated. The residue was subjected to column chromatography (eluent: CHCl\textsubscript{3}-MeOH, 50:1). The remaining 4-methoxybenzaldehyde was evaporated at 120 °C (external temperature) / 0.25 mbar to give 0.97 g (26 %) of target nitroalkene as brown oil (pure according to NMR). Crystallization from EtOH afforded 0.50 g (13%) of nitroalkene as yellow needles.

M\textsubscript{p} = 59-61 °C; R\textsubscript{f} = 0.57 (Hexane-EtOAc, 1:1) (UV).

\textsuperscript{1}H NMR: \( \delta = 3.79 \) and 3.87 (both s, both 3 H, 2×OCH\textsubscript{3}), 3.90 (s, 2 H, CH\textsubscript{2}), 6.99 (d, \( J = 8.8 \) 2 H, CH\textsubscript{o}-OMe), 7.41 (d, \( J = 8.8 \) 2 H, CH\textsubscript{m}-OMe), 8.29 (s, 1 H, =CH).

\textsuperscript{13}C NMR: \( \delta = 33.6 \) (CH\textsubscript{2}), 52.6 (CO\textsubscript{2}Me), 55.4 (Ar−OMe), 114.8 (CH\textsubscript{o}-OMe), 123.9 (C\textsubscript{p}-OMe), 131.7 (CH\textsubscript{m}-OMe), 136.9 (=CH), 142.8 (C−NO\textsubscript{2}), 161.7 (C=OMe), 169.3 (CO\textsubscript{2}Me).

Anal. Calcd for C\textsubscript{12}H\textsubscript{13}NO\textsubscript{5}: C, 57.37; H, 5.22; N, 5.58. Found: C, 57.35; H, 5.32; N, 5.41.

\textsuperscript{1}H NMR
$^{13}$C NMR
rel-(4S,4aS,7aR)-4-(4-methoxyphenyl)-3-methyl-4a,5,6,7a-tetrahydro-4H-furo[3,2-e][1,2]oxazine 2-oxide (2h) and rel-(4R,4aS,7aR)-4-(4-methoxyphenyl)-3-methyl-4a,5,6,7a-tetrahydro-4H-furo[3,2-e][1,2]oxazine 2-oxide (2h’)

To a stirring solution of 1-methoxy-4-((E)-2-nitro-1-propenyl)benzene (1.93 g, 10 mmol) in CH2Cl2 (50 mL) at –94 °C under argon atmosphere SnCl4 (2.87 g, 1.30 mL, 11 mmol, 1.1 equiv) was added. The resulted mixture was stirred for 5 min and 2,3-dihydrofuran (1.20 g, 1.30 mL, 17 mmol, 1.7 equiv) was added at –78 °C. The reaction mixture was stirred for 5 min at –78 °C and poured into a mixture of EtOAc (200 mL) and saturated aqueous solution of Na2CO3 (100 mL). The water layer was extracted with EtOAc (100 mL). The combined organic layer was washed with a H2O (150 mL), brine (2×100 mL) and dried over Na2SO4. The solvents were removed in vacuum. Crude product was recrystallized from hexane-EtOAc, 4:1 (100 mL) to give 2.24 g (85%) of target oxazine N-oxide as white solid. dr = 2:1. Recrystallization from EtOAc (30 mL) afforded 1.35 g of target oxazine N-oxide as white solid. dr = 4.6:1.

Mp = 138-141 °C; Rf = 0.10 (Hexane-EtOAc, 1:1) (anisaldehyde).

Anal. Calcd for C14H17NO4: C, 63.87 H, 6.51; N, 5.32. Found: C, 63.51; H, 6.71; N, 5.33.

Major isomer (2h)

1H NMR (COSY, NOESY): δ = 1.68-1.79 (m, 1 H, H13), 1.81-1.89 (m, 1 H, H13), 1.94 (s, 3 H, 7-CH3), 2.90-3.00 (m, 1 H, H5), 3.81 (s, 3 H, 12-CH3), 3.87 (ddd, J = 8.1, 7.3, 6.6, 1 H, H14), 4.08-4.13 (m, 2 H, H4 and H3-t14), 5.84 (d, J = 4.4, 1 H, H6), 6.89 (d, J = 8.5, 2 H, H10), 7.08 (d, J = 8.5, 2 H, H9).

13C NMR (HSQC): δ = 17.0 (C7), 26.5 (C13), 43.8 (C5), 44.5 (C4), 55.3 (C12), 69.2 (C14), 106.4 (C6), 114.4 (C10), 128.5 (C3), 129.7 (C9), 130.1 (C8), 159.1 (C11).

Minor isomer (2h’)

1H NMR (COSY, NOESY): δ = 1.82-1.91 (m, 1 H, H13), 2.01 (s, 3 H, 7-CH3), 2.27 (dddd, J = 12.5, 9.5, 8.1, 7.3, 1 H, H13), 2.90-3.00 (m, 1 H, H5), 3.65 (d, J = 3.7, 1 H, H4), 3.81 (s, 3 H, 12-CH3), 3.99 (ddd, J = 8.8, 8.1, 5.1, H14), 4.19 (dt, J = 8.8, 7.3, H14), 5.85-5.87 (m, 1 H, H6), 6.89 (d, J = 8.5, 2 H, H10), 7.15 (d, J = 8.5, 2 H, H9).

13C NMR (HSQC): δ = 17.8 (C7), 30.7 (C13), 46.2 (C5), 47.4 (C4), 55.3 (C12), 68.4 (C14), 106.9 (C6), 114.5 (C10), 124.7 (C3), 128.9 (C9), 130.1 (C8), 159.1 (C11).
$^1$H NMR

$^{13}$C NMR
rel-(4S,6R)-3-ethyl-4-(4-methoxyphenyl)-6-propyl-5,6-dihydro-4H-1,2-oxazine 2-oxide (2p)

To a stirring solution of 1-methoxy-4-((E)-2-nitro-1-butenyl)benzene\(^6\) (1.30 g, 6.3 mmol) in CH\(_2\)Cl\(_2\) (35 mL) at –94 °C under argon atmosphere SnCl\(_4\) (1.80 g, 0.81 mL, 6.9 mmol, 1.1 equiv) was added. The resulted mixture was stirred for 5 min and 1-pentene (0.88 g, 1.4 mL, 12.6 mmol, 2 equiv) was added at –78 °C. The reaction mixture was maintained at –20 °C for 1 day and poured into a mixture of EtOAc (200 mL) and saturated aqueous solution of Na\(_2\)CO\(_3\) (100 mL). The water layer was extracted with EtOAc (100 mL). The combined organic layer was washed with H\(_2\)O (150 mL), brine (2×100 mL) and dried over Na\(_2\)SO\(_4\). The solvents were removed in vacuum. Crude product was subjected to column chromatography (eluent: hexane-EtOAc, 1:1) to give 1.30 g (74%) of target oxazine N-oxide 2p as colorless oil.

R\(_f\) = 0.39 (Hexane-EtOAc, 1:1) (anisaldehyde).

\(^1\)H NMR: \(\delta = 0.86\) (t, \(J = 6.9\), 3 H, 16-CH\(_3\)), 1.04 (t, \(J = 7.7\), 3 H, 13-CH\(_3\)), 1.32-1.55 (m, 3 H), 1.60-1.72 (m, 1 H), 1.81-1.85 (d, \(J = 13.2\), 1 H), and 2.00-2.17 (m, 2 H) – 5-CH\(_2\) and H\(_b7\), 14-CH\(_2\) and 15-CH\(_2\), 2.55 (dq, \(J = 13.9\), 7.7, 1 H, H\(_b7\)), 3.74-3.80 (m, 1 H, H\(_4\)), 3.80 (s, 3 H, 12-CH\(_3\)), 4.34-4.42 (m, 1 H, H\(_6\)), 6.87 (d, \(J = 8.8\), 2 H, H\(_{10}\)), 7.09 (d, \(J = 8.4\), 2 H, H\(_9\)).

\(^{13}\)C NMR (DEPT): \(\delta = 8.9\) and 13.8 (C13 and C16), 18.0 and 25.4 (C14 and C15), 33.9 and 35.4 (C7 and C5), 40.3 (C4), 55.3 (C12), 76.8 (C6), 114.4 (C10), 125.0 (C3), 129.0 (C9), 133.8 (C8), 158.9 (C11).

HRMS: \(m/z [M+H]^+\) calcd for C\(_{16}\)H\(_{23}\)NO\(_3\): 278.1751, found: 278.1762.
$^{13}$C NMR (DEPT)
3-benzyl-4-(4-methoxyphenyl)-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazine 2-oxide (2q)

To a stirring solution of 1-methoxy-4-(2-nitro-3-phenyl-1-propenyl)benzene (2.69 g, 10 mmol) in CH$_2$Cl$_2$ (50 mL) at $-94 \, ^\circ\text{C}$ under argon atmosphere SnCl$_4$ (2.87 g, 1.30 mL, 11 mmol, 1.1 equiv) was added. The resulted mixture was stirred for 5 min and isobutylene (3.5 g, 63 mmol, 6.3 equiv) was added at $-78 \, ^\circ\text{C}$. The reaction mixture was stirred at $-78 \, ^\circ\text{C}$ for 0.5 h and poured into a mixture of EtOAc (200 mL) and saturated aqueous solution of Na$_2$CO$_3$ (100 mL). The water layer was extracted with EtOAc (100 mL). The combined organic layer was washed with H$_2$O (150 mL), brine (2×100 mL) and dried over Na$_2$SO$_4$. The solvents were removed in vacuum. Crude product was recrystallized from hexane-EtOAc, 5:1 to give 2.13 g (66%) of target oxazine N-oxide as colorless powder.

Mp = 98-100 °C. R$_f$ = 0.35 (Hexane-EtOAc, 1:1) (anisaldehyde).

$^1$H NMR: $\delta = 1.29$ and 1.36 (both s, both 3 H, 13-CH$_3$ and 14-CH$_3$), 1.93 (dd, $J = 13.7, 11.0, 1 \, \text{H}$, H$_{5}$), 2.03 (dd, $J = 13.7, 8.5, 1 \, \text{H},$ H$_{5}$), 3.03 (d, $J = 14.7, 1 \, \text{H},$ H$_{7}$), 3.63 (dd, $J = 11.0, 8.5, 1 \, \text{H},$ H$_{4}$), 3.80 (s, 3 H, 12-CH$_3$), 4.19 (d, $J = 14.7, 1 \, \text{H},$ H$_{7}$), 6.85 (d, $J = 8.4, 2 \, \text{H},$ H$_{10}$), 7.01 (d, $J = 8.4, 2 \, \text{H},$ H$_{9}$), 7.07-7.11 (m, 2 H) and 7.17-7.26 (m, 3 H) – H$_{16}$, H$_{17}$ and H$_{18}$.

$^{13}$C NMR (DEPT): $\delta = 22.0$ and 27.8 (C13 and C14), 35.5 and 41.8 (C5 and C7), 40.1 (C4), 55.3 (C12), 81.5 (C6), 114.5 (C10), 125.0 (C3), 126.9 (C18), 128.5, 129.1 and 129.2 (C9, C16 and C17), 132.0 (C8), 136.4 (C15), 159.0 (C11).

Anal. Calcd for C$_{20}$H$_{23}$NO$_3$: C, 73.82; H, 7.12; N, 4.30. C, 73.73; H, 7.17; N, 4.33.
$^1$H NMR

$^{13}$C NMR
$^{13}$C NMR (DEPT)
To a stirring solution of methyl (3E)-4-(4-methoxyphenyl)-3-nitrobut-3-enoate (0.40 g, 1.6 mmol) in CH₂Cl₂ (8 mL) at –94 °C under argon atmosphere SnCl₄ (0.46 g, 0.21 mL, 1.76 mmol, 1.1 equiv) was added. The resulted mixture was stirred for 5 min and isobutylene (2 g, 36 mmol) was added at –78 °C. The reaction mixture was stirred at –78 °C for 15 min and poured into a mixture of EtOAc (200 mL) and saturated aqueous solution of Na₂CO₃ (100 mL). The water layer was extracted with EtOAc (100 mL). The combined organic layer was washed with a H₂O (150 mL), brine (2×100 mL) and dried over Na₂SO₄. The solvents were removed in vacuum. Crude product was recrystallized from hexane-EtOAc, 3:1 to give 0.32 g (65%) of target oxazine N-oxide **2r** as slightly brown powder.

Mp = 105-107 °C. Rf = 0.13 (Hexane-EtOAc, 1:1) (anisaldehyde).

**¹H NMR:** δ = 1.43 and 1.57 (both s, both 3 H, 13-CH₃ and 14-CH₃), 1.99 (dd, J = 13.9, 11.1, 1 H, H₅), 2.14 (dd, J = 13.9, 8.1, 1 H, H₅), 2.87 (d, J = 16.9, 1 H, H₇), 3.55 (d, J = 16.9, 1 H, H₇), 3.67 (s, 3 H, 16-CH₃), 3.80 (s, 3 H, 12-CH₃), 3.87 (dd, J = 11.1, 8.1, 1 H, H₄), 6.87 (d, J = 8.1, 2 H, H₁₀), 7.10 (d, J = 8.1, 2 H, H₉).

**¹³C NMR:** δ = 22.0 and 27.8 (C₁₃ and C₁₄), 35.4 and 41.5 (C₅ and C₇), 41.7 (C₄), 52.1 (C₁₆), 55.3 (C₁₂), 82.3 (C₆), 114.7 (C₁₀), 120.0 (C₃), 129.1 (C₉), 131.3 (C₈), 159.2 (C₁₁), 168.8 (C₁₅).

$^{13}$C NMR (DEPT)
To the stirring solution of ethyl vinyl ether (1.5 g, 2 mL, 21 mmol, 3 equiv) in toluene (70 mL) AlMe₃ (7 mL, 14 mmol, 2 M solution in heptane, 2 equiv) was added under argon atmosphere at –75 °C (internal). The resulted mixture was stirred for 5 min and solution of 1-methoxy-4-((E)-2-nitro-1-propenyl)benzene (1.35 g, 7 mmol) in toluene (30 mL) was added during 10 min, maintaining temperature at –72 to –65 °C. The reaction mixture was maintained for 2 d, ethyl vinyl ether (0.38 g, 0.5 mL, 5 mmol) was added, the temperature was slowly increased to –30 °C, stirred for 3 h, cooled to –78 °C and MeOH (10 mL) was slowly added. After addition of water (20 mL) the mixture was poured into EtOAc (150 mL) / water (200 mL). To the water layer NaOH (1.68 g in 30 mL of water) was added and was extracted with EtOAc (3×100 mL). Combined organic layer was washed with water (100 mL), brine (2×100 mL) and dried over Na₂SO₄. The solvents were evaporated in vacuum and the residue was recrystallized from hexane-EtOAc, 5:1 (48 mL) to give 1.36 g (73%) of target oxazine N-oxide 2k as white solid.

Spectra data are consistent with previously reported.⁸
4,6,6-trimethyl-3-methylene-2-((trimethylsilyl)oxy)-1,2-oxazinane 1d

\[ \text{TMSBr, NEt}_3, \text{CH}_2\text{Cl}_2 \]

\[ ^1\text{H NMR} \]
rel-(4S,6R)-4-(4-methoxyphenyl)-6-propyl-2-((trimethylsilyl)oxy)-1,2-oxazinane (1e)
\(^{13}\)C NMR (335 K, DEPT)

\[ \text{Diagram of } ^{13}\text{C NMR spectrum} \]
$rel$-$(4S,4aS,7aR)-4-(4$-methoxyphenyl)-3$-methylene-2$-((trimethylsilyl)$oxy$)hexahydro-2$H$-furo[3,2-e][1,2]oxazine (1h) and $rel$-$(4R,4aS,7aR)-4-(4$-methoxyphenyl)-3$-methylene-2$-((trimethylsilyl)$oxy$)hexahydro-2$H$-furo[3,2-e][1,2]oxazine (1h')

$\text{CH}_2\text{Cl}_2$, NEt$_3$ (0.24 g, 0.33 mL, 2.4 mmol, 1.2 equiv) and TMSBr (0.34 g, 0.29 mL, 2.2 mmol, 1.1 equiv) were successively added to the stirring solution of nitronates 2h-2h' (dr = 4.6 : 1) (0.53 g, 2 mmol) in $\text{CH}_2\text{Cl}_2$ (5 mL) at $-78 \degree \text{C}$ under argon atmosphere. The mixture was maintained for 1 day at the same temperature, diluted with hexane (10 mL) and transferred into hexane (40 mL) / H$_2$O (20 mL). Organic layer was washed with solution of NaHSO$_4$ (60 mg/mmol of 2) in H$_2$O (20 mL), Brine (2 × 20 mL), treated with activated charcoal, filtered and dried over Na$_2$SO$_4$. The solvent was evaporated in vacuum to give 0.64 g (95 %) of target enamines 1h-1h' as colorless oil, that was sufficiently pure (NMR analysis) and used without additional purification. dr = 4 : 1.

**HRMS:** $m/z$ [M+H]$^+$ calcd for C$_{17}$H$_{25}$NO$_4$Si: 336.1626, found: 336.1626.

**Major isomer (1h)**

$^1$H NMR (COSY, NOESY): $\delta = 0.29$ (s, 9 H, 15-CH$_3$), 1.74-1.84 (m, 1 H, Ha13), 2.22 (dq, $J = 11.7$, 8.8, 1 H, Hb13), 2.51-2.61 (m, 1 H, H5), 3.77-3.86 (m, 1 H, H4a14), 3.82 (s, 3 H, 12-CH$_3$), 4.05 (br s, 1 H, H4), 4.24-4.30 (m, 2 H, Hb14 and Ha7), 5.05 (d, $J = 2.2$, 1 H, H_b7), 5.57 (d, $J = 5.9$, 1 H, H6), 6.89 (d, $J = 8.8$, 2 H, H10), 7.23 (d, $J = 8.8$, 2 H, H9).

$^{13}$C NMR (DEPT): $\delta = -1.0$ (C15), 26.6 (C13), 43.8 and 46.1 (C4 and C5), 55.2 (C12), 68.8 (C14), 99.3 (C7), 103.3 (C6), 113.9 (C10), 130.3 (C9), 132.4 (C8), 156.3 (C3), 158.7 (C11).

Characteristic NOE-contacts: H5-H6, H5-H9;

**Minor isomer (1h')**

$^1$H NMR (COSY, NOESY): $\delta = 0.27$ (s, 9 H, 15-CH$_3$), 1.74-1.84 (m, 1 H, H_a13), 2.02-2.10 (m, 1 H, H_b13), 2.71-2.81 (m, 1 H, H5), 3.61 (d, $J = 8.8$, 1 H, H4), 3.82 (s, 3 H, 12-CH$_3$), 3.95 (td, $J = 8.1$, 5.9, 1 H, H_b14), 4.05 (br s, 1 H, H_a7), 4.15 (dt, $J = 8.1$, 7.3, 1 H, H_b14), 4.73 (br s, 1 H, H_b7), 5.73 (d, $J = 5.1$, 1 H, H6), 6.90 (d, $J = 8.5$, 2 H, H10), 7.25 (d, $J = 8.5$, 2 H, H9).

$^{13}$C NMR (DEPT): $\delta = -0.7$ (C15), 30.0 (C13), 44.2 and 46.1 (C4 and C5), 55.2 (C12), 68.7 (C14), 97.0 (C7), 101.2 (C6), 113.9 (C10), 129.9 (C9), 132.4 (C8), 156.3 (C3), 158.7 (C11).

Characteristic NOE-contacts: H5-H6, H5-H9;
Methyl \((2E)-(4-(4-methoxyphenyl)-6,6-dimethyl-2-(trimethylsilyloxy)-1,2-oxazinan-3-ylidene)acetate\) (1r)

\[
\text{OMe} \quad \text{CO}_2\text{Me} \\
\text{CH}_2\text{Cl}_2 \quad \text{TMSBr, NEt}_3 \\
\text{1r} \quad \text{2r}
\]

NEt\(_3\) (61 mg, 84 \(\mu\)L, 0.60 mmol, 1.2 equiv) and TMSBr (84 mg, 73 \(\mu\)L, 0.55 mmol, 1.1 equiv) were successively added to the stirring solution of nitronate \(2r\) (148 mg, 0.5 mmol) in CH\(_2\)Cl\(_2\) (1 mL) at \(-78\) °C under argon atmosphere. The mixture was maintained for 1 day at the same temperature, diluted with hexane (10 mL) and transferred into hexane (40 mL) / H\(_2\)O (20 mL). Organic layer was washed with solution of NaHSO\(_4\) (60 mg/mmol of \(2\)) in H\(_2\)O (20 mL), Brine (2 \(\times\) 20 mL), treated with activated charcoal, filtered and dried over Na\(_2\)SO\(_4\). The solvent was evaporated in vacuum to give 187 mg (100%) of target enamine \(1r\) as colorless oil, that was sufficiently pure (NMR analysis) and used without additional purification.

\(^1\)H NMR (NOESY): \(\delta = 0.29\) (s, 9 H, 13-CH\(_3\)), 1.02 and 1.33 (both s, both 3 H, 14-CH\(_3\) and 15-CH\(_3\)), 2.07 (d, \(J = 4.4\), 2 H, 5-CH\(_2\)), 3.57 (s, 3 H, 17-CH\(_3\)), 3.77 (s, 3 H, 12-CH\(_3\)), 5.15 (t, \(J = 4.4\), 1 H, H4), 5.88 (s, 1 H, H7), 6.81 (d, \(J = 8.8\), 2 H, H10), 7.25 (d, \(J = 8.8\), 2 H, H9);

\(^{13}\)C NMR: \(\delta = -0.6\) (C13), 27.2 and 28.7 (C14 and C15), 38.9 and 41.0 (C4 and C5), 50.9 (C17), 55.1 (C12), 79.6 (C6), 100.8 (C7), 113.5 (C10), 128.7 (C9), 135.3 (C8), 157.8 (C11), 166.4 and 166.8 (C3 and C16).

\(^{29}\)Si NMR: \(\delta = 28.8\).

Characteristic NOE-contacts: H7 – H13, H9 - 17-CH\(_3\). Contacts H7 – H9 and 17-CH\(_3\) – H13 were not observed.

HRMS: \(m/z \ [\text{M+H}]^+\) calcd for C\(_{19}\)H\(_{29}\)NO\(_5\)Si: 380.1888, found: 380.1884.
$^1$H NMR

$^{13}$C NMR
2-(tert-Butyldimethylsilyloxy)-5,6-dimethyl-3-methylene-4-phenyl-1,2-oxazinane (1n)

\[
\begin{align*}
\text{OMe} & \quad \text{TBSOTf, NEt}_3, \\
\text{CH}_2\text{Cl}_2 & \\
\end{align*}
\]

NEt\textsubscript{3} (0.30 g, 0.42 mL, 3 mmol, 1.2 equiv) and TBSOTf\textsuperscript{8} (0.63 g, 0.55 mL, 2.4 mmol, 1.2 equiv) were successively added to the stirring solution of nitronate 2a (0.50 g, 2 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (4 mL) at -78 °C under argon atmosphere. The mixture was stirred for 2 h at the same temperature, diluted with hexane (10 mL) and transferred into hexane (40 mL) / H\textsubscript{2}O (20 mL). Organic layer was washed with solution of NaHSO\textsubscript{4} (120 mg) in H\textsubscript{2}O (20 mL), Brine (2 × 20 mL) and dried over Na\textsubscript{2}SO\textsubscript{4}. The solvent was evaporated in vacuum to give 0.77 g (c.a. 100%) of target enamine 1n as colorless oil. Crude product was sufficiently pure (NMR analysis) and used without additional purification.

\textsuperscript{1}H NMR: \(\delta = 0.22 \text{ (s, 3 H, 15-CH}_3\text{)}, 0.24 \text{ (s, 3 H, 16-CH}_3\text{)}, 0.97 \text{ (s, 9 H, 18-CH}_3\text{)}, 1.31 \text{ (s, 3 H, 13-CH}_3\text{)}, 1.52 \text{ (s, 3 H, 14-CH}_3\text{)}, 1.73 \text{ (dd, } J = 12.5, 5.1, 1 \text{ H, Hax}_5\text{)}, 2.01 \text{ (dd, } J = 13.2, 12.5, 1 \text{ H, Heq}_5\text{)}, 3.72-3.81 \text{ (m, 1 H, H}_4\text{)}, 3.82 \text{ (s, 3 H, 12-CH}_3\text{)}, 3.95 \text{ (s, 1 H, H}_a7\text{)}, 5.04 \text{ (s, 1 H, H}_b7\text{)}, 6.89 \text{ (d, } J = 8.8, 2 \text{ H, H}_10\text{)}, 7.19 \text{ (d, } J = 8.8, 2 \text{ H, H}_9\text{)};

\textsuperscript{13}C NMR (INEPT): \(\delta = -5.1 \text{ (C15)}, -5.0 \text{ (C16)}, 25.7 \text{ (C13)}, 25.9 \text{ (C18)}, 29.0 \text{ (C14)}, 42.0 \text{ (C4)}, 43.8 \text{ (C5)}, 55.2 \text{ (C12)}, 76.8 \text{ (C6)}, 97.2 \text{ (C7)}, 113.8 \text{ (C10)}, 129.7 \text{ (C9)}, 158.5 \text{ (C11)}. \text{Signals of C3, C8 and C17 could not be unambiguously identified due to low intensity and broadening because of dynamic processes.}\textsuperscript{3}
$^1$H NMR

$^{13}$C NMR
$^{13}$C NMR (INEPT)
Optimization of reaction conditions 1a → 3a or 4a (see table 1)

If molecular sieves were used they had been dried at ca. 200 °C in vacuum (0.7 mbar) for 10 min prior to use. The reagent was stirred with molecular sieves for 20 minutes before subsequent operations. Reactions were performed on 0.25 – 1 mmol of enamine 1a.

For entries 1-2. To the solution of TBAF (1M THF solution or TBAF·3H2O was taken) (0.1 equiv) in CH2Cl2 (2 mL / mmol of enamine 1a) at –78 °C, enamine 1a solution (1 equiv, 0.5M in CH2Cl2) was added under stirring in Ar atmosphere. The reaction mixture was stirred for 1.5 h, allowed to warm to room temperature and mixture of NH4F (1.5 equiv) / AcOH (2 equiv) / MeOH (2 mL/ 1 mmol of enamine) was added. The reaction mixture was stirred for an additional 0.5 h and poured into Et2O (40 mL) /H2O (30 mL) mixture. Water layer was extracted with Et2O (20 mL). Combined organic layer was washed with brine (2 × 30 mL), dried over Na2SO4 and evaporated in vacuum. Residue was subjected to column chromatography (eluent: hexane-EtOAc, 5:1, then 3:1).

For entries 3-4. To the solution of TBAF (1M THF solution was taken) (0.1 equiv) in CH2Cl2 (2 mL / mmol of enamine 1a) with MS 3 Å (0.1 g / mmol of enamine 1a) at –78 °C, enamine 1a solution (1 equiv, 0.5M in CH2Cl2) was added under stirring in Ar atmosphere. The reaction mixture was stirred for 0.5 h and poured into Et2O (40 mL) /H2O (30 mL) mixture (for entry 3 - cooling bath was removed, the reaction mixture was stirred for an additional 1 h and then poured into Et2O / H2O). Organic layer was washed with brine (2 × 30 mL), dried over Na2SO4 and evaporated in vacuum.

For entries 5-6. To the solution of TBAF (dried on heating in vacuum10) (0.1 equiv) in CH2Cl2 (2 mL / mmol of enamine 1a) at –78 °C enamine 1a solution (1 equiv, 0.5M in CH2Cl2) was added under stirring in Ar atmosphere. The reaction mixture was stirred for 1.5 h, cooling bath was removed and the reaction mixture was stirred for an additional 0.5 h (for entry 5). For entry 6 addition was performed at r.t. followed by stirring for 1 h. Mixture of NH4F (1.5 equiv) / AcOH (2 equiv) / MeOH (2 mL/ 1 mmol of enamine 1a) was added. The reaction mixture was stirred for an additional 1 h and poured into Et2O (40 mL) /H2O (30 mL) mixture. Water layer was extracted with Et2O (20 mL). Combined organic layer was washed with brine (2 × 30 mL), dried over Na2SO4 and evaporated in vacuum. For entry 5 the residue was subjected to column chromatography (eluent: hexane-EtOAc, 5:1, then 3:1).

For entry 7. To the solution of TBAF (1M THF solution) (0.1 equiv) in CH2Cl2 (2 mL / mmol of enamine 1a) with MS 3 Å at –78 °C enamine 1a solution (1 equiv, 0.5M in CH2Cl2) was added under stirring in Ar atmosphere. The reaction mixture was stirred for 1.5 h, cooling bath was removed, the reaction mixture was stirred for an additional 1 h, mixture of NH4F (1.5 equiv) / AcOH (2 equiv) / MeOH (2 mL/ 1 mmol of enamine 1a) was added. The reaction mixture was stirred for an additional 1 h and mixture of NH4F (1.5 equiv) / AcOH (2 equiv) / MeOH (2 mL/ 1 mmol of enamine 1a) was added. The reaction mixture was stirred for an additional 1 h and poured into Et2O (40 mL) /H2O (30 mL) mixture. Water layer was extracted with Et2O (20 mL). Combined organic layer was washed with brine (2 × 30 mL), dried over Na2SO4 and evaporated in vacuum. For entry 5 the residue was subjected to column chromatography (eluent: hexane-EtOAc, 5:1, then 3:1).

For entry 8. To the solution of TBAF (0.1 equiv, TBAF·3H2O was taken) in CH2Cl2 (1 mL / 1 mmol of enamine 1a) with MS 3 Å MeOH (1 mL / 1 mmol of enamine 1a) was added. The temperature was decreased to –78 °C and enamine 1a solution (1 equiv, 0.5M in CH2Cl2) was added under stirring in Ar atmosphere. The reaction mixture was stirred for 1.5 h, cooling bath was removed, the reaction mixture was stirred for an additional 1 h and mixture of NH4F (1.5 equiv) / AcOH (2 equiv) / MeOH (2 mL/ 1 mmol of enamine 1a) was added. The reaction mixture was stirred for an additional 1 h and poured into Et2O (40 mL) /H2O (30 mL) mixture. Organic layer was washed with brine (2 × 30 mL), dried over Na2SO4 and evaporated in vacuum.

For entry 9. To the mixture of NH4F (2 equiv) / Et2O (3 mL / 1 mmol of enamine 1a) / MeOH (2 mL / 1 mmol of enamine 1a) at –78 °C enamine 1a solution (1 equiv, 0.5M in CH2Cl2) was added under stirring in Ar atmosphere. The reaction mixture was stirred for 1.5 h, temperature was increased to –30 °C, the reaction mixture was stirred for an additional 10 min and poured into
EtOAc (40 mL) / H2O (30 mL) mixture. Organic layer was washed with brine (2 × 30 mL), dried over Na2SO4 and evaporated in vacuum.

For entries 10-11. To the MFn (0.5 equiv) in HMPA / CH2Cl2 (each 2 mL / 1 mmol of enamine 1a, for entry 10) or NMP (2 mL/ 1 mmol of enamine 1a, for entry 11) enamine 1a solution (1 equiv, 0.5 M in CH2Cl2) was added under stirring in Ar atmosphere. The reaction mixture was stirred for 3 d and poured into hexane (40 mL) / H2O (30 mL) mixture (for entry 10) or Et2O (40 mL) / H2O (30 mL) mixture (for entry 11). Organic layer was washed with brine (2 × 30 mL), dried over Na2SO4 and evaporated in vacuum.

For entries 12-13. To the mixture of t-BuOK (0.1 equiv) / THF (0.1 mL / mmol of enamine 1a) / CH2Cl2 (2 mL / mmol of enamine 1a) (for entry 12) or Me3SiONa (3 equiv) / THF (4 mL / mmol of enamine 1a) (for entry 13) at –78 °C enamine 1a solution (1 equiv, 0.5 M in CH2Cl2) was added under stirring in Ar atmosphere. The reaction mixture was stirred for 0.5 h, cooling bath was removed, the reaction mixture was stirred for an additional 1 h and mixture of NH4F (1.5 equiv) / AcOH (2 equiv) / MeOH (2 mL/ 1 mmol of enamine 1a) (for entry 12) or AcOH (4 equiv) / MeOH (2 mL/ 1 mmol of enamine 1a) (for entry 13) was added. The reaction mixture was stirred for an additional 1 h (for entry 12) or 15 min (for entry 13) and poured into Et2O (40 mL) / H2O (30 mL) mixture. Water layer was extracted with Et2O (20 mL). Combined organic layer was washed with brine (2 × 30 mL), dried over Na2SO4 and evaporated in vacuum.

For entry 14. To the solution of enamine 1a in THF (3 mL / mmol of enamine 1a) BuLi (0.87 equiv, 2.4 M in hexane) was added at –78 °C under stirring in Ar atmosphere. The mixture was stirred for 0.5 h and AcOH (2 equiv) / MeOH (1.5 mL / 1 mmol of enamine 1a) was added. Cooling bath was removed, the reaction mixture was stirred for 1.5 h and poured into Et2O (40 mL) / H2O (30 mL) mixture. Water layer was extracted with Et2O (20 mL). Combined organic layer was washed with brine (2 × 30 mL), dried over Na2SO4 and evaporated in vacuum.

For entry 15. To the solution of NaOH (0.2 equiv) in MeOH (2 mL / mmol of enamine 1a) with MS 3Å enamine 1a solution (1 equiv, 0.5 M in CH2Cl2) was added under stirring in Ar atmosphere. The reaction mixture was stirred for 1 h and mixture of NH4F (1.5 equiv) / AcOH (2 equiv) / MeOH (2 mL / 1 mmol of enamine 1a) was added. The reaction mixture was stirred for an additional 1 h and poured into Et2O (40 mL) / H2O (30 mL) mixture. Water layer was extracted with Et2O (20 mL). Combined organic layer was washed with brine (2 × 30 mL), dried over Na2SO4 and evaporated in vacuum.

For entry 16. To the solution of enamine 1a in CH2Cl2 (2 mL / mmol of enamine) NEt3 (0.1 equiv) was added under stirring in Ar atmosphere. The mixture was maintained for 2 d and poured into Et2O (40 mL) / NaHSO4 (60 mg/mmol of enamine 1a) in H2O (20 mL) mixture. Organic layer was washed with brine (2 × 30 mL), dried over Na2SO4 and evaporated in vacuum.

For entry 17 see 4-(4-methoxyphenyl)-6,6-dimethylidihydro-2H-pyran-3(4H)-one O-(trimethylsilyl)oxime (3a)
4-(4-methoxyphenyl)-6,6-dimethyldihydro-2H-pyran-3(4H)-one O-(trimethylsilyl)oxime (3a)

1H NMR
4-(4-methoxyphenyl)-6,6-dimethylidihydro-2H-pyran-3(4H)-one oxime 4a

$1^H$ NMR
$^{13}$C NMR

$^{13}$C NMR (DEPT)
6,6-dimethyl-4-phenyldihydro-2H-pyran-3(4H)-one oxime (4b)

Obtained from enamine 1b (1 mmol, 2 mL of 0.5M solution in CH₂Cl₂) according to GP-1 as colorless oil. Yield: 200 mg (91 %). $E : Z = 4.7:1$.

Mp = 182-184 °C (MeOH). $R_f = 0.75$ and 0.61 (Hexane-EtOAc, 1:1) (anisaldehyde).

Anal. Calcd for C₁₃H₁₇NO₂: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.05; H, 8.07; N, 6.41.

**E-isomer**

$^1$H NMR: $\delta = 1.09$ (s, 3 H, 12-CH₃), 1.27 (s, 3 H, 13-CH₃), 2.03 (dd, $J = 14.7$, 6.6, 1 H, H₅), 2.15 (dd, $J = 14.7$, 7.3, 1 H, H₆), 4.21 (d, $J = 13.9$, 1 H, H₂), 4.40 (t, $J = 7.3$, 1 H, H₄), 4.44 (d, $J = 13.9$, 1 H, H₂), 7.16-7.36 (m, 5 H, H₉, H₁₀, H₁₁), 8.98 (br s, 1 H, H₇).

$^{13}$C NMR (DEPT): $\delta = 27.4$ (C₁₃), 28.4 (C₁₄), 36.9 (C₄), 41.5 (C₅), 62.2 (C₂), 72.7 (C₆), 126.4, 127.1 and 128.6 (C₉, C₁₀, C₁₁), 140.7 (C₈), 156.9 (C₃).

**Z-isomer**

$^1$H NMR: $\delta = 1.32$ (s, 3 H, 12-CH₃), 1.38 (s, 3 H, 13-CH₃), 1.97 (dd, $J = 13.2$, 5.1, 1 H, H₅), 1.99-2.10 (m, 1 H, H₆), 3.79 (dd, $J = 13.2$, 4.7, 1 H, H₄), 4.47 (d, $J = 16.9$, 1 H, H₂), 4.71 (d, $J = 16.9$, 1 H, H₂), 7.16-7.36 (m, 5 H, H₉, H₁₀, H₁₁), 8.80 (br s, 1 H, H₇).

$^{13}$C NMR (DEPT): $\delta = 25.9$ (C₁₃), 28.1 (C₁₄), 41.4 (C₄), 42.4 (C₅), 58.4 (C₂), 72.4 (C₆), 126.4, 127.0 and 128.4 (C₉, C₁₀, C₁₁), 139.5 (C₈), 160.6 (C₃).

$^1$H NMR
5-(Hydroxyimino)-2,2-dimethyltetrahydro-2H-pyran-4-y1 benzoate (4c)

Obtained from enamine 1c (0.75 mmol, 1.5 mL of 0.5M solution in CH₂Cl₂) according to GP-1 as colorless oil. Yield: 139 mg (71%). E : Z = 6:1. 

Rf = 0.68 and 0.60 (Hexane-EtOAc, 1:1) (anisaldehyde).


E-isomer

1H NMR: δ = 1.35 (s, 3 H, 13-CH₃), 1.39 (s, 3 H, 14-CH₃), 2.05 (dd, J = 13.5, 8.0, 1 H, H₅), 2.15 (dd, J = 13.5, 5.1, 1 H, H₅), 4.53 (d, J = 16.1, 1 H, H₂), 4.71 (d, J = 16.1, 1 H, H₂), 5.89 (dd, J = 8.0, 5.1, 1 H, H₄), 7.44 (t, J = 7.5, 2 H, H₁₁), 7.57 (t, J = 7.3, 1 H, H₁₂), 8.06 (d, J = 7.5, 2 H, H₁₀), 8.98 (br s, 1 H, H₇).

13C NMR (DEPT): δ = 26.8 (C₁₃), 27.6 (C₁₄), 41.1 (C₅), 56.8 (C₂), 67.4 (C₄), 72.2 (C₆), 128.4, 129.8 and 133.2 (C₁₀, C₁₁, C₁₂), 130.2 (C₉), 153.6 (C₃), 165.2 (C₈).

Z-isomer

1H NMR: δ = 1.27 (s, 3 H, 13-CH₃), 1.47 (s, 3 H, 14-CH₃), 1.95 (dd, J = 15.1, 4.5, 1 H, H₅), 2.09-2.14 (m, 1 H, H₅), 4.19 (d, J = 13.6, 1 H, H₂), 4.62 (d, J = 13.6, 1 H, H₂), 6.45 (dd, J = 4.5, 3.7, 1 H, H₄), 7.46 (t, J = 7.5, 2 H, H₁₁), 7.56 (t, J = 7.3, 1 H, H₁₂), 7.87 (d, J = 7.5, 2 H, H₁₀), 8.98 (br s, 1 H, H₇).

13C NMR (DEPT): δ = 24.8 (C₁₃), 30.1 (C₁₄), 40.1 (C₅), 60.7 (C₂), 61.1 (C₄), 71.8 (C₆), 128.5, 129.7 and 133.2 (C₁₀, C₁₁, C₁₂), 133.5 (C₉), 151.4 (C₃), 170.6 (C₈).
$^{13}$C NMR (DEPT)
4,6,6-trimethyldihydro-2H-pyran-3(4H)-one oxime (4d)

Obtained from enamine 1d (1 mmol, 2 mL of 0.5M solution in CH₂Cl₂) according to GP-1 as colorless oil. Yield: 126 mg (80 %). Z : E = 1.4:1.

Rₜ = 0.62 and 0.55 (Hexane-EtOAc, 1:1) (anisaldehyde).

HRMS: m/z [M+H]+ calcd for C₈H₁₅NO₂: 158.1176, found: 158.1169.

**Z-isomer**

1H NMR: δ = 1.13 (d, J = 6.6, 3 H, 8-CH₃), 1.23 (s, 3 H, 9-CH₃), 1.30 (s, 3 H, 10-CH₃), 1.42 (t, J = 13.5, 1 H, H₅), 1.78 (dd, J = 13.5, 4.7, 1 H, H₅), 2.61-2.73 (m, 1 H, H₄), 4.31 (d, J = 16.9, 1 H, H₂), 4.65 (d, J = 16.9, 1 H, H₂), 9.19 (s, 1 H, H7).

13C NMR (DEPT): 15.9, 25.9, 28.1 and 29.8 (C₄, C₈, C₉, C₁₀), 44.0 (C₅), 58.0 (C₂), 72.0 (C₆), 161.6 (C₃).

**E-isomer**

1H NMR: δ = 1.18 (s, 3 H, 9-CH₃), 1.28 (d, J = 6.6, 3 H, 8-CH₃), 1.29 (s, 3 H, 10-CH₃), 1.64 (dd, J = 14.2, 7.7, 1 H, H₅), 1.77 (dd, J = 14.2, 6.6, 1 H, H₅), 3.14-3.25 (m, 1 H, H₄), 4.01 (d, J = 13.5, 1 H, H₂), 4.28 (d, J = 13.5, 1 H, H₂), 9.17 (s, 1 H, H7).

13C NMR (DEPT): 17.3, 26.5, 28.2 and 28.5 (C₄, C₈, C₉, C₁₀), 41.1 (C₅), 61.2 (C₂), 72.6 (C₆), 159.8 (C₃).

**Z-isomer**

1H NMR
$^{13}$C NMR
$^{13}$C NMR (DEPT)

$E$-isomer (with some $Z$-isomer)

$^1$H NMR
$^{13}$C NMR
rel-(4S,6R)-4-(4-methoxyphenyl)-6-propyldihydro-2H-pyran-3(4H)-one oxime (4e)

![Chemical structure of 4e](image)

Obtained from enamine 1e (0.64 mmol, 1.4 mL of 0.46M solution in CH₂Cl₂) according to GP-1 as colorless oil. Yield: 160 mg (95 %). E : Z = 10:1. 
Rᶠ = 0.81 and 0.72 (Hexane-EtOAc, 1:1) (anisaldehyde).

**E-isomer**

¹H NMR: δ = 0.93 (t, J = 6.9, 3 H, 15-CH₃), 1.32-1.62 (m, 4 H, 13-CH₂ and 14-CH₂), 1.92 (ddd, J = 14.7, 11.3, 5.9, 1 H, H₅), 2.27 (d, J = 13.9, 1 H, H₆), 3.61-3.69 (m, 1 H, H₄), 3.81 (s, 3 H, 12-CH₃), 4.12 (d, J = 13.5, 1 H, H₂), 4.29 (d, J = 13.5, 1 H, H₂), 4.78 (d, J = 5.9, 1 H, H₆), 6.91 (d, J = 8.4, 2 H, H₁₀), 7.19 (d, J = 8.4, 2 H, H₉), 9.27 (br s, 1 H, H₇).

¹³C NMR (DEPT): δ = 14.1 (C₁₅), 18.8 (C₁₄), 34.6 (C₄), 35.7 and 37.9 (C₅ and C₁₃), 55.2 (C₁₂), 66.8 (C₂), 73.3 (C₆), 114.2 (C₁₀), 128.5 (C₉), 130.7 (C₈), 157.0 (C₃), 158.3 (C₁₁).

Signals of minor isomer are too low intensive to be unambiguously identified. For determination of E/Z ratio was used signal: 4.97 (d, J = 16.1, 1 H, H₂).

$^1$H NMR

$^{13}$C NMR
\( ^{13}C \text{ NMR (DEPT)} \)
**rel-(4S,6S)-4-(4-methoxyphenyl)-6-phenyldihydro-2H-pyran-3(4H)-one oxime (4f)**

![Chemical Structure](image)

Obtained from enamine 1f (0.7 mmol, 1.4 mL of 0.5M solution in CH₂Cl₂) according to GP-1 as colorless oil, that solidifies upon storage. Yield: 159 mg (76%). *E : Z* = 3.6:1.

Mp = 115-117 °C. Rₓ = 0.66 and 0.60 (Hexane-EtOAc, 1:1) (anisaldehyde).

Analytically pure sample was obtained after drying in drying pistol over P₂O₅ in vacuum at 78 °C. Anal. Calcd for C₁₈H₁₉NO₃: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.42; H, 6.63; N, 4.73.

**E-isomer**

¹H NMR: δ = 2.21-2.34 (m, 1 H, H₅), 2.41 (ddd, *J = 14.7, 8.3, 2.9*, 1 H, H₅), 3.82 (s, 3 H, 12-CH₃), 4.43 (t, *J = 8.3*, 1 H, H₄), 4.49 (d, *J = 13.9*, 1 H, H₂), 4.77 (dd, *J = 11.7*, 2.9, 1 H, H₆), 4.82 (d, *J = 13.9*, 1 H, H₂), 6.91 (d, *J = 8.8*, 2 H, H₁₀), 7.25 (d, *J = 8.8*, 2 H, H₉), 7.20-7.46 (m, 5 H, H₁₄, H₁₅ and H₁₆), 8.97 (br s, 1 H, H₇).

¹³C NMR (DEPT): δ = 39.3 (C₄), 39.8 (C₅), 55.3 (C₁₂), 65.7 (C₂), 76.1 (C₆), 114.1 (C₁₀), 125.8, 127.7, 128.4 and 128.5 (C₉, C₁₄, C₁₅ ad C₁₆), 133.2 (C₁₃), 142.2 (C₈), 157.1 and 158.3 (C₃ and C₁₁).

**Z-isomer**

¹H NMR: δ = 2.19-2.48 (m, 2 H, 5-CH₂), 3.79 (s, 3 H, 12-CH₃), 3.79-3.88 (m, 1 H, H₄), 4.13 (d, *J = 15.1*, 1 H, H₂), 4.72-4.77 (m, 1 H, H₆), 5.47 (d, *J = 15.1*, 1 H, H₂), 6.91 (d, *J = 8.8*, 2 H, H₁₀), 7.20-7.46 (m, 7 H, H₉, H₁₄, H₁₅ and H₁₆), 8.86 (br s, 1 H, H₇).

¹³C NMR (DEPT): δ = 41.3 (C₅), 45.6 (C₄), 55.3 (C₁₂), 62.7 (C₂), 78.8 (C₆), 114.1 (C₁₀), 125.8, 127.7 and 128.4 (C₁₄, C₁₅ ad C₁₆), 129.5 (C₉), 131.4 (C₁₃), 141.5 (C₈), 157.5 and 158.7 (C₃ and C₁₁).
$^1$H NMR

$^{13}$C NMR
*rel*-(4S,4aR,8aR)-4-(4-Methoxyphenyl)-hexahydro-2H-chromen-3(4H)-one oxime (4g)

1. Obtained from enamine 1g (1.27 mmol, 2.4 mL of 0.53 M solution in CH$_2$Cl$_2$) according to GP-1 as colorless oil. Yield: 185 mg (53%). $E : Z = 1.2:1$.

2. Obtained according to GP-1 with changes: by addition of solution of enamine 1g (0.5 mmol, 5 mL of 0.1 M solution in CH$_2$Cl$_2$) to solution of TBAF (0.05 mmol) in CH$_2$Cl$_2$ (5 mL) (addition time – 14 min). Crude product was purified by column chromatography (eluent: hexane-EtOAc, 5:1) to give 84 mg (61%) of title oxime as colorless oil. $E : Z = 1:1$.

Spectra data are consistent with previously reported.$^{6}$
rel-(3aS,4S,7aR)-4-(4-methoxyphenyl)tetrahydro-4H-furo[2,3-b]pyran-5(6H)-one oxime (4h) and rel-(3aS,4R,7aR)-4-(4-methoxyphenyl)tetrahydro-4H-furo[2,3-b]pyran-5(6H)-one oxime (4h’)

![Chemical structures of 4h and 4h']

Obtained from enamines 1h-1h’ (0.75 mmol, 1.5 mL of 0.5M solution in CH2Cl2) according to GP-1 as colorless oil. Yield: 105 mg (53 %). dr = 2.5:1. E/Z-ratio was not determined.

Rf = 0.35 (Hexane-EtOAc, 1:1) (anisaldehyde).


**Major isomer (4h)**

1H NMR (COSY): δ = 1.49-1.59 (m, 1 H, H₃13), 1.63-1.77 (m, 1 H, H₅), 3.61 (td, J = 8.8, 7.3, 1 H, H₄14), 3.80 (s, 3 H, 12-CH₃), 3.93 (ddd, J = 8.8, 8.1, 3.7, 1 H, H₆14), 4.17 (d, J = 14.5, 1 H, H₂14), 4.29 (d, J = 7.3, 1 H, H₄), 4.47 (d, J = 14.5, 1 H, H₂6), 5.42 (d, J = 6.6, 1 H, H₆), 6.85 (d, J = 8.5, 2 H, H₁₀), 7.13 (d, J = 8.5, 2 H, H₉), 8.36 (br s, 1 H, H₇).

13C NMR (DEPT, HSQC): δ = 29.3 (C13), 39.2 (C4), 42.0 (C5), 55.2 (C12), 61.9 (C2), 67.1 (C14), 101.1 (C6), 113.8 (C10), 129.1 (C9), 130.9 (C8), 155.2 (C3), 158.2 (C11).

**Minor isomer (4h’)**

1H NMR (COSY): δ = 1.81-1.96 (m, 1 H, H₃13), 2.13-2.23 (m, 1 H, H₁₃), 2.65-2.76 (m, 1 H, H₉), 3.76-3.85 (m, 1 H, H₄14), 3.80 (s, 3 H, 12-CH₃), 4.10-4.21 (m, 3 H, 2-CH₂ and H₂14), 4.65 (s, 1 H, CH(4)), 5.45 (d, J = 5.1, 1 H, H₆), 6.86 (d, J = 8.8, 2 H, H₁₀), 7.31 (d, J = 8.8, 2 H, H₉), 8.57 (br s, 1 H, H₇).

13C NMR (DEPT, HSQC): δ = 29.8 (C13), 38.8 (C4), 43.4 (C5), 55.2 (C12), 60.9 (C2), 67.3 (C14), 99.7 (C6), 114.2 (C10), 128.9 (C9), 132.0 (C8), 155.4 (C3), 158.5 (C11).
$^1$H NMR
$^{13}$C NMR

$^{13}$C NMR (DEPT)
COSY

HSQC
rel-(4S,6S)-6-methoxy-4-(4-methoxyphenyl)-6-methyldihydro-2H-pyran-3(4H)-one oxime (4i)

![Chemical structure of 4i](image)

Obtained from enamine 1i (2.2 mmol, 4.4 mL of 0.5M solution in CH2Cl2) according to GP-2 as colorless oil, that solidifies upon storage. Yield: 482 mg (83 %). Z : E = 5:1.

Mp = 81-87 °C. Rf = 0.41 (Hexane-EtOAc, 1:1) (anisaldehyde).

HRMS: m/z [M+H]+ calcd for C14H19NO4: 266.1387, found: 266.1385.

**Z-isomer**

1H NMR (COSY, NOESY): δ = 1.38 (s, 3 H, 13-CH3), 2.04-2.12 (m, 2 H, 5-CH2), 3.33 (s, 3 H, 14-OCH3), 3.79 (s, 3 H, 12-CH3), 3.95-4.01 (m, 2 H, H2 and H4), 4.96 (d, J = 15.4, 1 H, Hb2), 6.85 (d, J = 8.1, 2 H, H10), 7.13 (d, J = 8.1, 2 H, H9), 8.02 (br s, 1 H, H7);

13C NMR (DEPT): δ = 22.9 (C13), 40.1 (C4), 43.0 (C5), 48.5 (C14), 55.2 (C12), 56.4 (C2), 97.9 (C6), 114.0 (C10), 129.5 (C9), 131.6 (C8), 157.4 (C3), 158.5 (C11).

Characteristic NOE-contacts: 14-CH3 - H2, 14-CH3 - H4. Contact 14-CH3 - Hb2 was not observed.

**E-isomer**

1H NMR (COSY, NOESY): δ = 1.16 (s, 3 H, 13-CH3), 2.14 (dd, J = 13.9, 6.6, 1 H, Ha5), 2.26 (dd, J = 13.9, 6.9, 1 H, Ha5), 3.23 (s, 3 H, 14-CH3), 3.79 (s, 3 H, 12-CH3), 4.29-4.41 (m, 3 H, 2-CH2 and H4), 6.85 (d, J = 8.5, 2 H, H10), 7.16 (d, J = 8.5, 2 H, H9), 8.33 (br s, 1 H, H7);

13C NMR (DEPT), characteristic signals: δ = 36.0 (C4), 46.1 (C5), 61.8 or 64.0 (C2). Other signals are too low intensive to be unambiguously identified.
rel-(4S,6S)-6-ethoxy-4-(4-methoxyphenyl)dihydro-2H-pyran-3(4H)-one oxime (4j)

\[ \text{1H NMR} \]
$^{13}$C NMR

$^{13}$C NMR (DEPT)
rel-(4S,6R)-6-ethoxy-4-(4-methoxyphenyl)dihydro-2H-pyran-3(4H)-one oxime (4k)

![Chemical Structure](image)

**4k**

Obtained from enamine 1k (0.94 mmol, 1.9 mL of 0.5 M solution in CH₂Cl₂) according to GP-2 as colorless oil, that solidifies upon storage. Yield: 224 mg (90 %). dr = 10:1.

Mp = 90-93 °C (MeOH). R₇ = 0.46 (Hexane-EtOAc, 1:1) (anisaldehyde).

Anal. Calcd for C₁₄H₁₉NO₄: C, 63.38; H, 7.22; N, 5.28. Found: C, 63.47; H, 7.31; N, 5.23.

**Major isomer**

\(^1\)H NMR: δ = 1.25 (t, J = 7.3, 3 H, 14-CH₃), 2.00 (ddd, J = 13.9, 13.5, 6.6, 1 H, H₅), 2.38 (ddd, J = 13.9, 5.9, 4.2, 1 H, H₄), 3.53 (dq, J = 8.8, 7.3, 1 H, H₁₃), 3.63 (dd, J = 13.5, 4.2, 1 H, H₄), 3.80 (s, 3 H, 12-CH₃), 3.79-3.89 (m, 1 H, H₄), 4.49 (d, J = 17.6, 1 H, H₂), 4.59 (d, J = 17.6, 1 H, H₂), 5.05 (dd, J = 6.6, 5.9, 1 H, H₆), 6.87 (d, J = 8.5, 2 H, H₁₀), 7.11 (d, J = 8.5, 2 H, H₉), 8.01 (br s, 1 H, H₇).

\(^{13}\)C NMR: δ = 15.1 (C₁₄), 35.9 (C₅), 40.0 (C₄), 55.2 (C₁₂), 57.7 (C₂), 63.3 (C₁₃), 97.9 (C₆), 114.0 (C₁₀), 129.6 (C₉), 130.4 (C₈), 158.6 (C₁₁), 161.3 (C₃).

Characteristic NOE-contacts: MeCH₂ - H₆, H₅, H₉, H₅ - H₆, H₅ - H₄, H₆ - H₄; Contact MeCH₂ - 2-CH₂ was not observed.

**Minor isomer**

\(^1\)H NMR, characteristic signals: δ = 2.19-2.25 (m, 1 H, H₄), 4.84 (d, J = 15.4, 1 H, H₂), 4.91-4.95 (m, 1 H, H₆).

\(^{13}\)C NMR: Signals are too low intensive to be unambiguously identified.
$^1$H NMR

$^{13}$C NMR
NOESY

HSQC
5-Phenyldihydrofuran-3(2H)-one oxime (4I)

\[ \text{4I} \]

$^1\text{H NMR}$
Methyl 4-(hydroxyimino)-2-methyltetrahydro-furan-2-carboxylate (4m)

Obtained from enamine 1m (1 mmol, 2 mL of 0.5M solution in CH₂Cl₂) according to GP-1 as colorless oil, that solidifies upon storage. Yield: 104 mg (60 %). E : Z = 2.5:1. Mp = 93-95 °C (MeOH). Rₜ = 0.44 (Hexane-EtOAc, 1:1) (anisaldehyde).


**E-isomer**

$^1$H NMR: $\delta = 1.56$ (s, 3 H, 7-CH₃), 2.59 (d, $J = 18.3$, 1 H, H₄a), 3.21 (dt, $J = 18.3$, 1.5, 1 H, H₄b), 3.74 (9-CH₃), 4.47 (s, 2 H, 2-CH₂), 9.01 (br s, 1 H, H₆).

$^{13}$C NMR (DEPT): $\delta = 24.1$ (C₇), 37.5 (C₄), 52.6 (C₉), 67.9 (C₂), 83.7 (C₅), 160.7 (C₃), 173.8 (C₈).

**Z-isomer**

$^1$H NMR: $\delta = 1.56$ (s, 3 H, 7-CH₃), 2.59 (d, $J = 18.3$, 1 H, H₄a), 3.06 (d, $J = 16.1$, 1 H, H₄b), 3.74 (9-CH₃), 4.55-4.67 (m, 2 H, 2-CH₂), 9.01 (br s, 1 H, H₆).

$^{13}$C NMR (DEPT): $\delta = 23.7$ (C₇), 39.6 (C₄), 52.6 (C₉), 66.7 (C₂), 83.4 (C₅), 161.8 (C₃), 174.5 (C₈).

$^1$H NMR
rel-1-((4S,6R)-4-(4-methoxyphenyl)-6-propyl-5,6-dihydro-4H-1,2-oxazin-3-yl)ethanol (8p)

\[
\begin{align*}
\text{OMe} & \\
\text{N} & \\
\text{O} & \\
\text{OSiMe}_3 & \\
\end{align*}
\]

*i*: TMSBr, NEt₃, CH₂Cl₂; *ii*: 1. TBAF, MS 3A, CH₂Cl₂ 2. NH₄F/AcOH/MeOH

NEt₃ (0.11 g, 0.15 mL, 1.1 mmol, 1.2 equiv) and TMSBr (0.15 g, 0.13 mL, 1.0 mmol, 1.1 equiv) were successively added to the stirring solution of nitronate 2p (0.25 g, 0.9 mmol) in CH₂Cl₂ (1.4 mL) at −78 °C under argon atmosphere. The mixture was maintained for 1 day at the same temperature, diluted with hexane (10 mL) and transferred into hexane (40 mL) / H₂O (20 mL). Organic layer was washed with solution of NaHSO₄ (60 mg/mmol of 2) in H₂O (20 mL), Brine (2 × 20 mL), treated with activated charcoal, filtered and dried over Na₂SO₄. The solvent was evaporated in vacuum. Crude product thus obtained was subjected to GP-1. Crude product was purified by column chromatography (eluent: hexane-EtOAc, 5:1, then 1:1) to give 0.10 g (40%) of title oxazine as colorless oil. dr = 2.7:1. Relative configuration of CH*(OH) in diastereomers was not determined.

Rₛ = 0.45 (Hexane-EtOAc, 1:1) (anisaldehyde).

HRMS: \( m/z \ [\text{M}+\text{H}]^+ \) calcd for C₁₆H₂₃NO₃: 278.1751, found: 278.1756.

**Major diastereomer**

\(^1\)H NMR: δ = 0.89 (t, \( J = 7.3 \), 3 H, 17-CH₃), 1.28 (d, \( J = 6.6 \), 3 H, 14-CH₃), 1.34-1.55 (m, 3 H, 16-CH₂ and H₁₅), 1.58-1.70 (m, 1 H, H₁₅), 1.76-1.83 (m, 1 H, H₇), 1.86-1.98 (m, 1 H, H₅), 3.04 (br s, 1 H, H₁₃), 3.55 (br d, \( J = 4.4 \), 1 H, H₄), 3.77-3.84 (m, 1 H, H₆), 3.81 (s, 3 H, 12-CH₃), 4.29 (q, \( J = 6.6 \), 1 H, H₇), 6.89 (d, \( J = 8.8 \), 2 H, H₁₀), 7.09 (d, \( J = 8.4 \), 2 H, H₉).

\(^{13}\)C NMR: δ = 14.0 (C₁₇), 18.2 (C₁₆), 22.1 (C₁₄), 33.3 (C₅), 35.3 (C₄), 36.1 (C₁₅), 55.2 (C₁₂), 67.8 (C₇), 70.8 (C₆), 114.3 (C₁₀), 129.2 (C₉), 133.6 (C₈), 158.7 and 158.9 (C₃ and C₁₁).

**Minor diastereomer**

\(^1\)H NMR: δ = 0.89 (t, \( J = 7.3 \), 3 H, 17-CH₃), 1.29 (d, \( J = 6.6 \), 3 H, 14-CH₃), 1.21-2.00 (m, 5-CH₂, 15-CH₂, 16-CH₂, overlapped with the signals of major diastereomer), 3.04 (br s, 1 H, H₁₃), 3.70 (br d, \( J = 3.7 \), 1 H, H₄), 3.77-3.84 (m, 4 H, 12-CH₃ and H₆), 4.03-4.10 (m, 1 H, H₇), 6.89 (d, \( J = 8.8 \), 2 H, H₁₀), 7.08 (d, \( J = 8.4 \), 2 H, H₉).

\(^{13}\)C NMR: δ = 14.0 (C₁₇), 18.2 (C₁₆), 20.9 (C₁₄), 32.9 (C₅), 35.8 (C₄), 36.3 (C₁₅), 55.2 (C₁₂), 68.5 (C₇), 70.4 (C₆), 114.2 (C₁₀), 129.4 (C₉), 134.0 (C₈), 158.3 and 158.7 (C₃ and C₁₁).
HSQC
(4-(4-methoxyphenyl)-6,6-dimethyl-5,6-dihydro-4H-1,2-oxazin-3-yl)(phenyl)methanol (8q)

\[ \begin{align*}
\text{OMe} & \quad \text{OMe} \\
\text{2q} & \quad \text{7q} & \quad \text{8q}
\end{align*} \]

\( i: \text{TMSBr, NEt}_3, \text{CH}_2\text{Cl}_2; \quad ii: \text{1. TBAF, MS 3A, CH}_2\text{Cl}_2 \text{ 2. NH}_4\text{F/AcOH/MeOH} \)

NEt\(_3\) (0.12 g, 0.17 mL, 1.2 mmol, 1.2 equiv) and TMSBr (0.17 g, 0.15 mL, 1.1 mmol, 1.1 equiv) were successively added to the stirring solution of nitronate 2q (0.33 g, 1 mmol) in CH\(_2\)Cl\(_2\) (2 mL) at –78 °C under argon atmosphere. The mixture was maintained for 1 day at the same temperature, diluted with hexane (10 mL) and transferred into hexane (40 mL) / H\(_2\)O (20 mL). Organic layer was washed with solution of NaHSO\(_4\) (60 mg/mmol of 2) in H\(_2\)O (20 mL), Brine (2 x 20 mL), treated with activated charcoal, filtered and dried over Na\(_2\)SO\(_4\). The solvent was evaporated in vacuum. Crude product thus obtained was subjected to GP-1. Crude product was purified by column chromatography (eluent: hexane-EtOAc, 5:1, then 3:1) to give 0.22 g (66%) of title oxazine as colorless oil. dr = 3.7:1. Relative configuration of CH*(OH) in diastereomers was not determined.

R\(_f\) = 0.59 (Hexane-EtOAc, 1:1) (anisaldehyde)

HRMS: \( m/z \) [M+Na]\(^+\) calcd for C\(_{20}\)H\(_{23}\)NO\(_3\): 348.1570, found: 348.1579.

**Major diastereomer**

\(^1\)H NMR: \( \delta = 1.13 \) (s, 3 H, 14-CH\(_3\)), 1.37 (s, 3 H, 15-CH\(_3\)), 1.87 (dd, \( J = 13.9, 11.7, 1 \) H, H\(_5\)), 1.96 (dd, \( J = 13.9, 8.1, 1 \) H, H\(_6\)), 2.93 (dd, \( J = 11.7, 8.1, 1 \) H, H\(_4\)), 3.84 (s, 3 H, 12-CH\(_3\)), 4.63 (br s, 1 H, H13), 4.93 (s, 1 H, H7), 6.89 (d, \( J = 8.8, 2 \) H, H10), 6.94 (d, \( J = 8.8, 2 \) H, H9), 7.07-7.10 (m, 2 H) and 7.29-7.33 (m, 3 H) – H17, H18, H19.

\(^{13}\)C NMR: \( \delta = 22.8 \) (C14), 28.3 (C15), 36.6 (C4), 41.3 (C5), 55.3 (C12), 73.0 (C7), 75.5 (C6), 114.5 (C10), 127.4, 128.5 and 129.6 (C9, C17, C18), 128.3 (C19), 131.4 (C8), 140.5 (C16) 157.7 and 158.9 (C3 and C11).

**Minor diastereomer**

\(^1\)H NMR: \( \delta = 1.28 \) (s, 3 H, 14-CH\(_3\)), 1.37 (s, 3 H, 15-CH\(_3\)), 1.87-2.05 (m, 2 H, 5-CH\(_2\)), 3.48 (dd, \( J = 11.0, 8.8, 1 \) H, H4), 3.78 (s, 3 H, 12-CH\(_3\)), 5.12 (s, 1 H, H7), 6.71 (d, \( J = 8.5, 2 \) H, H10), 6.90 (d, \( J = 8.5, 2 \) H, H9), 7.07-7.10 (m, 2 H) and 7.19-7.32 (m, 3 H) – H17, H18, H19.
Major diastereomer

$^1$H NMR

$^{13}$C NMR
4-(4-methoxyphenyl)-6,6-dimethyldihydro-2H-pyran-3(4H)-one 9 (cf.\textsuperscript{23})

\[\text{TiCl}_3, \text{NH}_4\text{OAc, AcOH, dioxane, H}_2\text{O}\]

\(^1\text{H} \text{NMR}\]
$^{13}$C NMR

$^{13}$C NMR (DEPT)
4-(4-methoxyphenyl)-6,6-dimethyltetrahydro-2H-pyran-3-amine (10) and 4-(4-methoxyphenyl)-6,6-dimethyltetrahydro-2H-pyran-3-aminium chloride (10·HCl)

Spectra with dominant *trans*-isomer

$^1$H NMR (DMSO-d$_6$)
$^{13}$C NMR (DMSO-d$_6$)

COSY (DMSO-d$_6$)
NOESY (D$_2$O)
Spectra with dominant *cis*-isomer

$^1$H NMR (DMSO-d$_6$)

$^{13}$C NMR
COSY (DMSO-d$_6$)

HSQC (DMSO-d$_6$)
References