Supporting Information

2-Silyloxy-1,2-Oxazines, New Type of Acetals of Conjugated Nitroso alkenes

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General Experimental

All reactions were performed in oven-dried (150 °C) glassware under an inert atmosphere of dry N₂ or Ar. The following reaction solvents and reagents were distilled from the indicated drying agents: diethyl ether (sodium, benzophenone), methanol (Mg(OMe)₂), triethylamine and pyridine (CaH₂), morpholine and methylene chloride (CaH₂), titanium tetrachloride (CaH₂), titanium tetraisopropoxide and tin tetrachloride (CaH₂), hexane and butyl vinyl ether (Na), ethyl vinyl ether and 2-methyloxypylene (Na), cyclohexene (Na). Brine refers to a saturated aqueous solution of NaCl.

Kugelrohr distillations were performed on a Büchi GKR-50 Kugelrohr, or Edwards E050/60 diffusion pump; boiling points (bp) correspond to uncorrected air-bath temperatures.

NMR Spectra are referenced to residual solvent peak. Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. The INEPT pulse sequence was used for ²⁹Si signals observation.

Data of Mass spectroscopy are reported in the form of *m/z* (intensity relative to base peak = 100).

By analytical thin-layer chromatography visualization was accomplished with UV light and/or anisaldehyde and/or Iodine.

All solvents for chromatography and extractions were technical grade and distilled from the indicated drying agents: hexane and ethyl acetate (K₂CO₃), ether (NaOH).

Literature Preparations

The following compounds were prepared by literature methods: trimethylsilyltriflate,¹ tetrabutyltrimethylsilyltriflate,² benzaldehyde dimethyl acetal,³ anisaldehyde dimethyl acetal,⁴ β -methyl- β -nitrostyrene,⁵ β -methyl- β -nitro-4-methoxystyrene,⁶ β -ethyl- β -nitro-styrene,⁷ β -methyl- β -nitro-4-nitrostyrene.⁸

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¹ Simchen, G., Kober, W. S. *Synthesis* **1976**, 259.

² Corey, E. J., Cho, H., Rucker, C., Hua, D. H. *Tetrahedron Letters* **1981**, 22, 3455.

³ Napolitano, E., Fiashy, R., Mastroilli, E. *Synthesis* **1986**, 122.

⁴ Johansson, R., Samuelsson, B. *J. Chem. Soc. Perkin Trans. 1* **1984**, 2371.

⁵ Ohwada, T., Ohta, T., Shudo, K. *Tetrahedron* **1987**, 297.

⁶ Hoover, F. W., Hass, H. B. *J. Org. Chem.* **1947**, 12, 501.

⁷ Yasushi, K., Yoshikazu, I., Norihiro, T. *Tetrahedron: Asymmetry* **2001**, 12, 309.

⁸ Kerr, K. A., Frandsen, P. D., Silver, R. F., Kelley, S. L., Holmes, H. L. *Can. J. Chem.* **1967**, 45, 1001.

rel (4*R*, 6*R*)-6-Methoxy-6-methyl-5,6-dihydro-3-methyl-4-(4-methoxyphenyl)-1,2-oxazine *N*-oxide (2a)[†]

To a stirred solution of β -nitro- β -methyl-4-methoxystyrene (1.93 g, 10 mmol) in CH_2Cl_2 (50 ml) SnCl_4 (1.4 mL, 12 mmol, 1.2 equiv) was added simultaneously at $-78\text{ }^\circ\text{C}$. After 5 min of stirring the temperature was decreased to $-94\text{ }^\circ\text{C}$ and 2-methoxypropene (1.9 mL, 20 mmol, 2 equiv) was added dropwise. The reaction mixture was stirred for 5 min and poured into a mixture of EtOAc (150 mL) and saturated aqueous solution of NaHCO_3 (50 mL). The aqueous phase was back-extracted with EtOAc ($3 \times 50\text{ mL}$), combined organic layers were washed with a saturated aqueous solution of NaHCO_3 ($3 \times 50\text{ mL}$), brine (20 mL) and dried over Na_2SO_4 . The solvents were removed in vacuum and the residue was recrystallized from Et_2O to give title compound as white crystals (2.44 g, 92 %).

Analytical data for 2a:

mp: 115 – 117 $^\circ\text{C}$ (Et_2O)

^1H NMR: (300.13 MHz, 300K, CDCl_3)

7.09 (d, 2 H, $J = 8.8$), 6.85 (d, $J = 8.8$, 2 H), 3.81 (m, 4 H,), 3.49 (s, 3 H), 2.28 (dd, $J = 13.7$, 7.9, 1 H), 1.92 (dd, $J = 13.7$, 11.8, 1 H), 1.83 (d, $J = 1.5$, 3 H), 1.51 (s, 3 H).

^{13}C NMR: (75.47 MHz, 300K, CDCl_3)

159.0 (C), 131.9 (C), 129.0 (CH), 123.0 (C), 114.6 (CH), 103.8 (C), 55.3 (CH_3), 50.1 (CH_3), 42.1 (CH), 40.3 (CH_2), 20.9 (CH_3), 17.3 (CH_3).

TLC: R_f 0.18 (hexane/EtOAc, 1/1, UV)

Analysis: $\text{C}_{14}\text{H}_{19}\text{NO}_4$ (265.31)

Calculated: C, 63.38; H, 7.22; N, 5.28 %

Found: C, 63.32; H, 7.18; N, 5.42 %

[†]According to data of the X-ray analysis 4-MeOC₆H₄ and Me groups adopt equatorial positions.

rel (4*R*, 6*R*)-6-Ethoxy-5,6-dihydro-3-methyl-4-(4-methoxyphenyl)-1,2-oxazine *N*-oxide (**2b**) and *rel* (4*R*, 6*S*)-6-ethoxy-5,6-dihydro-3-methyl-4-(4-methoxyphenyl)-1,2-oxazine *N*-oxide (**2c**)[†]

To a stirred solution of $\text{Ti}(\text{O}i\text{-Pr})_4$ (1.20 mL, 4 mmol, 2 equiv) in CH_2Cl_2 (5 mL) was added TiCl_4 (0.44 mL, 4 mmol, 2 equiv) at 0 °C and stirred for 30 min. The resulting catalyst was syringed at –78 °C to a solution of β -nitro- β -methyl-4-methoxystyrene (0.39 g, 2 mmol) and ethyl vinyl ether (0.38 mL, 4 mmol, 2 equiv) in CH_2Cl_2 (6 mL). The reaction mixture was stirred at –78 °C for 1 hour, quenched with a 0.5M solution of NaOH in MeOH (16 mL) and poured into a mixture of CH_2Cl_2 (100 mL), 0.1M aqueous solution of NaOH (40 mL) and saturated aqueous solution of Na_2CO_3 (60 mL). The aqueous phase was back-extracted with CH_2Cl_2 (2×100 mL), combined organic layers were washed with 0.1M aqueous solution of NaOH (2×50 mL), brine and dried over Na_2SO_4 . The solvents were removed in vacuum and the residue was subjected to a column chromatography on Silica gel in EtOAc / Hexane 1 : 1 to give **2b** (0.24 g, 45 %) and **2c** (0.20 g, 38 %).

Analytical data for **2b**:

mp: 103 – 105 °C (hexane/EtOAc, 1 : 1)

¹H NMR: (300.13 MHz, 300K, CDCl_3)

7.10 (d, $J = 2.5, 6.6, 2$ H), 6.87 (dd, $J = 2.5, 6.6, 2$ H), 5.35 (dd, $J = 2.1, 2.9, 1$ H), 4.06 (qd, $J = 7.0, 9.9, 1$ H), 3.82 (ddq, $J = 1.7, 7.4, 11.1, 1$ H), 3.80 (s, 3 H), 3.72 (qd, $J = 7.0, 9.9, 1$ H), 2.24 (ddd, $J = 2.1, 7.4, 13.8, 1$ H), 2.09 (ddd, $J = 2.9, 11.1, 13.8, 1$ H), 1.84 (d, $J = 1.7, 3$ H), 1.27 (t, $J = 7.0, 3$ H).

¹³C NMR: (75.47 MHz, 300K, CDCl_3)

159.0 (C), 132.0 (C), 129.0 (CH), 123.4 (CH), 114.6 (CH), 101.0 (CH), 64.9 (CH_2), 55.3 (CH_3), 39.8 (CH), 34.5 (CH), 17.5 (CH_3), 15.1 (CH_3).

TLC: R_f 0.21 (hexane/EtOAc, 1 : 1) [UV]

Analysis: $\text{C}_{14}\text{H}_{19}\text{NO}_4$ (265.31)

Calculated: C, 63.38; H, 7.22; N, 5.28 %

Found: C, 63.44; H, 7.29; N, 5.21 %

Analytical data for **2c**:

mp: 101 – 103 °C (hexane/EtOAc, 1 : 1)

¹H NMR: (300.13 MHz, 300K, CDCl_3)

7.13 (dd, $J = 2.5, 6.6, 2$ H), 6.85 (dd, $J = 2.5, 6.6, 2$ H), 5.35 (dd, $J = 4.1, 5.4, 1$ H), 4.08 (qd, $J = 7.0, 9.5, 1$ H), 3.79 (s, 3 H), 3.68 (m, 2 H), 2.52 (ddd, $J = 4.1, 8.3, 14.0, 1$ H), 2.06 (ddd, $J = 5.4, 7.0, 14.0, 1$ H), 1.85 (d, $J = 1.7, 3$ H), 1.24 (t, $J = 7.0, 3$ H).

¹³C NMR: (75.47 MHz, 300K, CDCl_3)

158.9 (C), 131.9 (C), 129.5 (CH), 124.5 (CH), 114.2 (CH), 102.2 (CH), 65.4 (CH_2), 55.3 (CH_3), 41.5 (CH), 35.4 (CH), 17.1 (CH_3), 15.0 (CH_3).

[†]According to NMR data the EtO group adopts axial position in both **2b** and **2c**, while the 4-MeOC₆H₄ group is equatorial in **2b** and axial in **2c**.

TLC: R_f 0.12 (hexane/EtOAc, 1 : 1) [UV]
Analysis: $C_{14}H_{19}NO_4$ (265.31)
Calculated: C, 63.38; H, 7.22; N, 5.28 %
Found: C, 63.70; H, 7.45; N, 5.54 %

rel (4*R*, 6*R*)-6-Methoxy-6-methyl-5,6-dihydro-3-methyl-4-phenyl-1,2-oxazine *N*-oxide (2d)[†]

To a stirred solution of β -nitro- β -methylstyrene (1.63 g, 10 mmol) in CH_2Cl_2 (50 mL) SnCl_4 (1.4 mL, 12 mmol, 1.2 equiv) was added simultaneously at -78°C . After 5 min of stirring temperature was decreased to -94°C and 2-methoxypropene (1.9 mL, 20 mmol, 2 equiv) was added dropwise. The reaction mixture was stirred for 5 min and poured into a mixture of EtOAc (150 mL) and saturated aqueous solution of NaHCO_3 (50 mL). The aqueous phase was back-extracted with EtOAc (3×50 mL), combined organic layers were washed with a saturated aqueous solution of NaHCO_3 (3×50 mL), brine (20 mL) and dried over Na_2SO_4 . The solvents were removed in vacuum and the residue was recrystallized from Et_2O to give title compound **2d** as white crystals (1.67 g, 71 %).

Analytical data for 2d:

<u>mp</u> :	78 – 79 $^\circ\text{C}$ (Et_2O)		
<u>^1H NMR</u> :	(300.13 MHz, 300K, CDCl_3)		
	7.38 – 7.21 and 7.13 (2 m, 5 H), 3.82 (dd, $J = 7.7, 11.8$, 1 H), 3.47 (s, 3 H), 2.29 (dd, $J = 7.7, 13.6$, 1 H), 1.94 (dd, $J = 11.8, 13.6$, 1 H), 1.83 (s, 3 H), 1.51 (s, 3 H).		
<u>^{13}C NMR</u> :	(75.47 MHz, 300K, CDCl_3)		
	140.1 (C), 129.1, 127.9 and 127.6 (CH), 122.7 (C), 103.9 (C), 50.2 (CH_3), 42.1 (CH), 40.3 (CH_2), 20.9 (CH_3), 17.4 (CH_3)		
<u>TLC</u> :	R_f 0.33 (hexane/EtOAc, 1/1, UV)		
<u>Analysis</u> :	$\text{C}_{13}\text{H}_{17}\text{NO}_3$ (235.28)		
Calculated:	C, 66.36;	H, 7.28;	N, 5.95 %
Found:	C, 66.15;	H, 7.49;	N, 5.79 %

[†]According to NMR data the C_6H_5 group is equatorial in **2d**. The MeO group is postulated to be axial.

rel (4*R*, 6*R*)-6-Butoxy-5,6-dihydro-3-methyl-4-phenyl-1,2-oxazine *N*-oxide (**2e**) and *rel* (4*R*, 6*S*)-6-butoxy-5,6-dihydro-3-methyl-4-phenyl-1,2-oxazine *N*-oxide (**2f**)[†]

To a cold ($-10\text{ }^{\circ}\text{C}$) solution of $\text{Ti}(\text{OPr-}i\text{)}_4$ (2.2 mL, 7.45 mmol, 1.5 equiv) in CH_2Cl_2 (10 mL) was added TiCl_4 (0.82 mL, 7.48 mmol, 1.5 equiv). The bath was removed after 10 min, the colorless solution was stirred for 30 min at ambient temperature and cooled down to $-30\text{ }^{\circ}\text{C}$. Then the solution of β -methyl- β -nitrostyrene (0.82 g, 5 mmol) in CH_2Cl_2 (5 mL) was added, the resulting bright yellow mixture was stirred for 30 min at $-30\text{ }^{\circ}\text{C}$, cooled to $-75\text{ }^{\circ}\text{C}$ and the solution of *n*-butyl vinyl ether (2.6 mL, 20 mmol, 4 equiv) in CH_2Cl_2 (5 mL) was added dropwise. The reaction mixture was stirred for 1 h at $-75\text{ }^{\circ}\text{C}$, quenched with saturated aqueous solution of NaHCO_3 and EtOAc and poured into a mixture of EtOAc (100 mL) and H_2O (100 mL). The aqueous phase was back-extracted with EtOAc ($3 \times 20\text{ mL}$), combined organic layers were washed with H_2O (100 mL), saturated aqueous NH_4Cl (100 mL), H_2O (100 mL), saturated aqueous NaHCO_3 (100 mL), dried over Na_2SO_4 and solvents were evaporated in vacuum. The residue was subjected to column chromatography on silica gel (eluent: hexane $\rightarrow$ EtOAc). The major isomer was purified by recrystallization from Et_2O / hexane to give title compound **2e** as white crystals (0.36 g, 28 %) and minor isomer was distilled in vacuum to give title compound **2f** as colorless crystals (0.23 g, 17 %).

Analytical data for **2e**:

mp: $53 - 54\text{ }^{\circ}\text{C}$ (hexane / Et_2O)

^1H NMR: (500 MHz, 293 K, CDCl_3)

7.38 – 7.26 (m, 3 H), 7.20 (d, $J = 6.8$, 2 H), 5.35 (t, $J = 2.3$, 1 H), 4.01 (dt, $J = 6.8$, 9.5, 1 H), 3.85 (t, $J = 8.5$, 1 H), 3.63 (dt, $J = 6.6$, 9.5, 1 H), 2.27 (ddd, $J = 1.9$, 7.6, 13.7, 1 H), 2.11 (ddd, $J = 2.9$, 11.5, 13.7, 1 H), 1.84 (d, $J = 1.2$, 3 H), 1.63 (m, 2 H), 1.39 (m, 2 H), 0.94 (t, $J = 7.3$, 3 H).

^{13}C NMR: (126 MHz, 293 K, CDCl_3)

140.5 (C), 129.5 (CH), 128.2 (CH), 127.9 (CH), 123.4 (CH), 101.3 (CH), 69.4 (CH_2), 40.9 (CH), 34.7 (CH_2), 31.7 (CH_2), 19.4 (CH_2), 17.8 (CH_3), 14.1 (CH_3).

IR: (KBr)

2958 (s), 2935 (s), 2873 (s), 1614 (s), 1493 (m), 1454 (m), 1350 (m), 1275 (s), 1238 (m), 1209 (m), 1115 (s)

MS: FAB

264 (100, $\text{M}^+ - \text{H}$), 248 (17), 155 (20), 135 (21), 119 (48)

HRMS: calcd for $\text{C}_{15}\text{H}_{22}\text{NO}_3$: 264.159969; found: 264.160100

TLC: R_f 0.33 (silica gel, Et_2O , anisaldehyde)

Analysis: $\text{C}_{15}\text{H}_{21}\text{NO}_3$ (263.16)

Calculated: C, 68.42; H, 8.04; N, 5.32 %

Found: C, 68.39; H, 8.09; N, 5.36 %

[†]According to NMR data the *n*-BuO group adopts axial position in both **2e** and **2f**, while the C_6H_5 group is equatorial in **2e** and axial in **2f**.

Analytical data for 2f:

<u>mp</u> :	34 – 36 °C (hexane / Et ₂ O)		
<u>bp</u> :	110 – 115 °C (9.0×10^{-5})		
<u>¹H NMR</u> :	(500 MHz, 293 K, CDCl ₃)		
	7.35 – 7.21 (m, 5 H), 5.35 (dd, $J = 3.9, 5.4, 1$ H), 4.04 (dt, $J = 6.8, 9.5, 1$ H), 3.74 (ddq, $J = 1.2, 7.1, 8.6, 1$ H), 3.59 (dt, $J = 6.8, 9.5, 1$ H), 2.55 (ddd, $J = 5.4, 7.1, 13.9, 1$ H), 2.10 (ddd, $J = 3.9, 8.8, 13.9, 1$ H), 1.87 (d, $J = 1.5, 3$ H), 1.62 – 1.55 (m, 2 H), 1.39 – 1.30 (m, 2 H), 0.90 (t, $J = 7.3, 3$ H).		
<u>¹³C NMR</u> :	(126 MHz, 293 K, CDCl ₃)		
	140.5 (CH), 129.2 (CH), 128.7 (CH), 127.9 (CH), 124.3 (CH), 102.8 (CH), 70.2 (CH ₂), 42.6 (CH), 35.4 (CH ₂), 31.8 (CH ₂), 19.4 (CH ₂), 17.6 (CH ₃), 14.1 (CH).		
<u>IR</u> :	(KBr)		
	2958 (s), 2935 (s), 2873 (s), 1612 (s), 1494 (m), 1456 (m), 1377 (m), 1242 (s), 1169 (s)		
<u>MS</u> :	FAB		
	264 (77, M ⁺ –H), 248 (43), 155 (50), 135 (48), 119 (100)		
<u>HRMS</u> :	calcd for C ₁₅ H ₂₂ NO ₃ : 264.159969; found: 264.160100		
<u>TLC</u> :	R _f 0.19 (silica gel, Et ₂ O, anisaldehyde)		
<u>Analysis</u> :	C ₁₅ H ₂₁ NO ₃ (263.16)		
	Calculated:	C, 68.42; H, 8.04; N, 5.32 %	
	Found:	C, 68.43; H, 8.20; N, 5.44 %	

6,6-Dimethyl-5,6-dihydro-3-methyl-4-phenyl-1,2-oxazine N-oxide (2g)[†]

To a stirred solution of β -nitro- β -methylstyrene (1.63 g, 10 mmol) in CH_2Cl_2 (50 ml) SnCl_4 (1.4 mL, 12 mmol, 1.2 equiv) was added simultaneously at -78°C . After 5 min of stirring temperature was decreased to -94°C and a solution of isobutylene (2.8 g, 50 mmol, 5 equiv) in CH_2Cl_2 (5 mL) was added dropwise. The reaction mixture was stirred for 5 min and poured into a mixture of EtOAc (150 mL) and saturated aqueous solution of NaHCO_3 (50 mL). The aqueous phase was back-extracted with EtOAc (3×50 mL), combined organic layers were washed with a saturated aqueous solution of NaHCO_3 (3×50 mL), brine (20 mL) and dried over Na_2SO_4 . The solvents were removed in vacuum and the residue was recrystallized from Et_2O to give title compound **2g** as white crystals (1.31 g, 60 %).

Analytical data for **2g**:

<u>mp</u> :	93 – 95 $^\circ\text{C}$ (Et_2O)		
<u>^1H NMR</u> :	(300.13 MHz, 300 K, CDCl_3)		
	7.38 – 7.21 and 7.13 (2 m, 5 H), 3.67 (dd, $J = 7.9, 11.2$, 1 H), 2.12 (dd, $J = 7.9, 13.8$, 1 H), 1.85 (s, 3 H), 1.94 (dd, $J = 11.2, 13.8$, 1 H), 1.45 and 1.39 (2 s, 6 H).		
<u>^{13}C NMR</u> :	(75.47 MHz, 300 K, CDCl_3)		
	140.2 (C), 129.1 (CH), 127.8 (CH), 127.6 (CH), 121.9 (C), 81.2 (C), 43.2 (CH_2), 41.6 (CH), 27.8 (CH_3), 22.1 (CH_3), 17.3 (CH_3).		
<u>TLC</u> :	R_f 0.12 (hexane/EtOAc, 1/1, UV)		
<u>Analysis</u> :	$\text{C}_{13}\text{H}_{17}\text{NO}_2$ (219.28)		
Calculated:	C, 71.21;	H, 7.81;	N, 6.39 %
Found:	C, 71.18;	H, 7.78;	N, 6.20 %

[†]According to NMR data the C_6H_5 group adopts equatorial position in **2g**.

rel (4*R*, 6*R*)-6-Methoxy-6-methyl-5,6-dihydro-3-ethyl-4-phenyl-1,2-oxazine *N*-oxide (2h)[†]

To a stirred solution of β -nitro- β -ethyl-styrene (1.63 g, 10 mmol) in CH_2Cl_2 (50 mL) SnCl_4 (1.4 mL, 12 mmol, 1.2 equiv) was added simultaneously at -78°C . After 5 min of stirring temperature was decreased to -94°C and 2-methoxypropene (1.9 mL, 20 mmol, 2 equiv) was added dropwise. The reaction mixture was stirred for 5 min and poured into a mixture of EtOAc (150 mL) and saturated aqueous solution of NaHCO_3 (50 mL). The aqueous phase was back-extracted with EtOAc (3×50 mL), combined organic layers were washed with a saturated aqueous solution of NaHCO_3 (3×50 mL), brine (20 mL) and dried over Na_2SO_4 . The solvents were removed in vacuum and the residue was recrystallized from Et_2O to give title compound **2h** as white crystals (1.42 g, 57 %).

Analytical data for 2h:

mp:	87 – 88 $^\circ\text{C}$ (Et_2O)		
¹H NMR:	(300.13 MHz, 300 K, CDCl_3)		
	7.38 – 7.10 (m, 5 H), 3.80 (dd, $J = 8.1, 11.0$, 1 H), 3.39 (s, 3 H), 2.25 (m, 2 H), 1.97 (m, 2 H), 1.43 (s, 3 H), 0.89 (t, $J = 7.3$, 3 H).		
¹³C NMR:	(75.47 MHz, 300 K, CDCl_3)		
	140.1 (C), 129.0 (CH), 128.1 (CH), 127.6 (CH), 126.9 (C), 103.9 (C), 50.1 (CH_3), 40.9 (CH), 40.4 (CH_2), 24.2 (CH_2), 20.8 (CH_3), 8.5 (CH_3).		
TLC:	R_f 0.42 (hexane/EtOAc, 1/1, UV)		
Analysis:	$\text{C}_{14}\text{H}_{19}\text{NO}_{13}$ (249.31)		
Calculated:	C, 67.45;	H, 7.68;	N, 5.62 %
Found:	C, 67.52;	H, 7.66;	N, 5.57 %

[†]According to NMR data the C_6H_5 group adopts equatorial position in **2h**. The MeO group is postulated to be axial.

rel (4*R*, 5*S*, 6*S*)-4-(4-Methoxyphenyl)-3-methyl-4a,5,6,7,8,8a-hexahydro-4*H*-benzo[e]-1,2-oxazine *N*-oxide (**2i**)[†]

To a stirred solution of β-nitro-β-ethyl-4-methoxystyrene (1.63 g, 10 mmol) in CH₂Cl₂ (50 mL) SnCl₄ (1.4 mL, 12 mmol, 1.2 equiv) was added simultaneously at -78 °C. After 5 min of stirring temperature was increased to -30 °C and cyclohexene (1.5 mL, 15 mmol, 1.5 equiv) was added dropwise. The reaction mixture was stirred for 5 min and poured into a mixture of EtOAc (150 mL) and saturated aqueous solution of NaHCO₃ (50 mL). The aqueous phase was back-extracted with EtOAc (3 × 50 mL), combined organic layers were washed with a saturated aqueous solution of NaHCO₃ (3 × 50 mL), brine (20 mL) and dried over Na₂SO₄. The solvents were removed in vacuum and the residue was recrystallized from Et₂O to give title compound **2i** as white crystals (2.06 g, 75 %).

Analytical data for **2i**:

<u>mp</u> :	121 – 122 °C (hexane/EtOAc, 1 : 1)		
<u>¹H NMR</u> :	(300.13 MHz, 300 K, CDCl ₃)		
	6.98 (dd, <i>J</i> = 2.5, 6.6, 2 H), 6.79 (dd, <i>J</i> = 2.5, 6.6, 2 H), 4.52 (s, 1 H), 3.70 (s, 3 H), 3.27 (s, 1 H), 2.01 – 1.88 (m, 1 H), 1.86 (s, 3 H), 1.82 – 1.25 (m, 8 H).		
<u>¹³C NMR</u> :	(75.47 MHz, 300 K, CDCl ₃)		
	158.8 (C), 133.4 (C), 128.7 (CH), 114.4 (CH), 120.0 (CH), 75.3 (C), 55.3 (CH ₃), 49.3 (CH), 40.0 (CH), 28.7(CH ₂), 27.4 (CH ₂), 24.6 (CH ₂), 19.9 (CH ₂), 18.8 (CH ₃).		
<u>TLC</u> :	<i>R_f</i> 0.22 (hexane/EtOAc, 1/1, UV)		
<u>Analysis</u> :	C ₁₆ H ₂₁ NO ₃ (275.35)		
Calculated:	C, 69.79;	H, 7.69;	N, 5.09 %
Found:	C, 69.56;	H, 7.95;	N, 5.29 %

[†]1,2-Oxazine *N*-oxide **2i** is described in literature: Denmark, S. E., Kesler, B. S., Moon, Y. C. *J. Org. Chem.* **1992**, 57, 4912.

rel (4*R*, 5*S*, 6*S*)-4-(4-Nitrophenyl)-3-methyl-4a,5,6,7,8,8a-hexahydro-4*H*-benzo[*e*]-1,2-oxazine *N*-oxide (2j)

To a stirred solution of β -nitro- β -ethyl-4-nitrostyrene (1.63 g, 10 mmol) in CH_2Cl_2 (50 mL) SnCl_4 (1.4 mL, 12 mmol, 1.2 equiv) was added simultaneously at -78°C . After 5 min of stirring temperature was increased to -30°C and cyclohexene (5.1 mL, 50 mmol, 5 equiv) was added dropwise. The reaction mixture was stirred for 5 min and poured into a mixture of EtOAc (150 mL) and saturated aqueous solution of NaHCO_3 (50 mL). The aqueous phase was back-extracted with EtOAc (3×50 mL), combined organic layers were washed with a saturated aqueous solution of NaHCO_3 (3×50 mL), brine (20 mL) and dried over Na_2SO_4 . The solvents were removed in vacuum and the residue was recrystallized from Et_2O to give title compound **2j** as white crystals (0.94 g, 45 %).

Analytical data for 2j:

mp: 182 – 184 $^\circ\text{C}$ (hexane/EtOAc, 1 : 1)

^1H NMR: (300.13 MHz, 300 K, CDCl_3)
 8.19 (d, $J = 8.6$, 2 H), 7.33 (d, $J = 8.6$, 2 H), 4.52 (s, 1 H), 3.51 (s, 1 H), 2.10 – 1.95 (m, 1 H),
 1.92 (s, 3 H), 1.85 – 1.25 (m, 8 H).

^{13}C NMR: (75.47 MHz, 300 K, CDCl_3)
 148.7 (C), 147.3 (C), 128.7 (CH), 124.4 (CH), 118.2 (C), 75.4 (CH), 49.9 (CH), 39.8 (CH),
 28.7(CH₂), 27.6 (CH₂), 24.6 (CH₂), 19.8 (CH₂), 18.8 (CH₃).

TLC: R_f 0.12 (hexane/EtOAc, 1/1, UV)

Analysis: $\text{C}_{15}\text{H}_{18}\text{NO}_4$ (290.32)
 Calculated: C, 62.06; H, 6.25; N, 9.65 %
 Found: C, 62.06; H, 6.32; N, 9.73 %

rel (4*R*, 6*R*)-6-Methoxy-6-methyl-2-trimethylsilyloxy-3-methylene-4-(4-methoxyphenyl)-2,3,5,6-tetrahydro-1,2-oxazine (**1a**)[†]

To a stirred solution of nitronate **2a** (0.27 g, 1 mmol) in CH_2Cl_2 (2 mL) was added at -78°C NEt_3 (0.17 mL, 1.2 mmol) and TMSBr (0.15 mL, 1.1 mmol). The reaction mixture was stirred for 24 hours at -78°C , diluted with hexane (5 mL) and poured in a mixture of hexane (15 mL) and H_2O (5 mL). The organic layer was washed with a solution of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ (0.12 g, 0.87 mmol) in H_2O (6 mL), H_2O (6 mL), brine (5 mL), treated with activated charcoal and dried over Na_2SO_4 . Solvents were evaporated in vacuum and the residue was recrystallized from hexane to give title compound **1a** as colourless prisms (0.23 g, 67 %).

Analytical data for **1a**:

<u>mp</u> :	68 – 70 $^\circ\text{C}$ (hexane)		
<u>^1H NMR</u> :	(300.13 MHz, 300 K, CDCl_3)		
	7.15 (d, $J = 8.5$, 2 H), 6.84 (d, $J = 8.5$, 2 H), 4.99 (s, 1 H), 4.02 (br.s, 1 H), 3.95 (s, 1 H), 3.78 (s, 3 H), 3.41 (s, 3 H), 2.09 (dd, $J = 11.8$, 12.5, 1 H), 2.00 (dd, $J = 4.7$, 12.5, 1 H), 1.38 (s, 3 H), 0.26 (s, 9 H).		
<u>^{13}C NMR</u> :	(75.47 MHz, 300 K, CDCl_3)		
	158.5 (C), 158.4 (C), 132.4 (C), 129.7 (CH), 113.9 (CH), 101.9 (C), 97.7 (br, CH_2), 55.2 (CH ₃), 49.5 (CH ₃), 42.5 (CH ₂), 40.3 (br, CH), 22.4 (CH ₃), -0.6 (CH ₃).		
<u>^{29}Si NMR</u> :	(59.63 MHz, 300 K, CDCl_3)		
	26.18		
<u>TLC</u> :	unstable on silica gel		
<u>Analysis</u> :	$\text{C}_{17}\text{H}_{27}\text{NO}_4\text{Si}$ (337.49)		
Calculated:	C, 60.50;	H, 8.06;	N, 4.15 %
Found:	C, 60.26;	H, 7.97;	N, 4.02 %

[†]According to data of the X-ray analysis the 4-MeOC₆H₄ and Me groups adopt equatorial positions in **1a**.

rel (4*R*, 6*R*)-6-Methoxy-6-methyl-2-ethyldimethylsilyloxy-3-methylene-4-(4-methoxy-phenyl)-2,3,5,6-tetrahydro-1,2-oxazine (**1a'**)[†]

To a stirred solution of nitronate **2a** (0.27 g, 1 mmol) in MeCN (2 mL) was added at 20 °C NEt₃ (0.21 mL, 1.5 mmol) and EtMe₂SiCl (0.17 mL, 1.2 mmol). The reaction mixture was stirred for 72 hours at ambient temperature, diluted with hexane (5 mL) and poured in a mixture of hexane (15 mL) and H₂O (5 mL). The organic layer was washed with a solution of NaHSO₄·H₂O (0.12 g, 0.87 mmol) in H₂O (6 mL), H₂O (6 mL), brine (5 mL), treated with an activated charcoal and dried over Na₂SO₄. Solvents were evaporated in vacuum and the residue was crystallized in hexane at – 30 °C to give title compound **1a'** as colorless oil (0.21 g, 60 %).

Analytical data for **1a'**:

<u>mp</u> :	< 0 °C		
<u>¹H NMR</u> :	(300.13 MHz, 297 K, CDCl ₃)		
	7.18 (d, <i>J</i> = 8.8, 2 H), 6.87 (d, <i>J</i> = 8.8, 2 H), 5.01 (s, 1 H), 4.00 (m, 1 H), 3.94 (s, 1 H), 3.80 (s, 3 H), 3.46 (s, 3 H), 2.10 (dd, <i>J</i> = 11.8, 12.5, 1 H), 2.02 (dd, <i>J</i> = 4.4, 12.5, 1 H), 1.38 (s, 3 H), 1.02 (t, <i>J</i> = 8.0, 3 H), 0.73 (q, <i>J</i> = 8.0, 2 H), 0.21 (s, 6 H)		
<u>¹³C NMR</u> :	(75.47 MHz, 297 K, CDCl ₃)		
	158.4 (C), 132.4 (C), 129.6 (CH), 113.8 (CH), 101.8 (C), 97.7 (CH ₂), 55.2 (CH ₃), 49.5 (CH ₃), 42.4 (CH ₂), 40.2 (br, CH), 22.4 (CH ₃), 7.6 (CH ₃), 6.7 (CH ₂), –2.5 (CH ₃), –2.9 (CH ₃).		
<u>²⁹Si NMR</u> :	(59.63 MHz, 297 K, CDCl ₃)		
	27.46		
<u>Analysis</u> :	C ₁₈ H ₂₉ NO ₄ Si (351.52)		
Calculated:	C, 61.50;	H, 8.32;	N, 3.98 %
Found:	C, 61.40;	H, 8.37;	N, 4.12 %

[†]On the basis of the comparison of the NMR data for **1a** with that for **1a'** the equatorial arrangement has been assigned to the 4-MeOC₆H₄ and Me groups of **1a'**.

rel (4*R*, 6*R*)-6-Methoxy-6-methyl-2-(tert-butyldimethylsilyloxy)-3-methylene-4-(4-methoxyphenyl)-2,3,5,6-tetrahydro-1,2-oxazine (**1a''**)[†]

To a stirred solution of nitronate **2a** (0.27 g, 1 mmol) in CH₂Cl₂ (2 mL) was added at -78 °C NEt₃ (0.21 mL, 1.5 mmol) and *t*-BuMe₂SiOTf (0.28 mL, 1.2 mmol). The reaction mixture was stirred for 1 hour at -78 °C, diluted with hexane (5 mL) and poured in a mixture of hexane (15 mL) and H₂O (5 mL). The organic layer was washed with H₂O (2 × 6 mL), brine (5 mL), treated with an activated charcoal and dried over Na₂SO₄. Solvents were evaporated in vacuum and the residue was recrystallized from hexane to give title compound **1a** as colourless prisms (0.27 g, 71 %).

Analytical data for **1a''**:

mp: 62 – 65 °C (hexane)

¹H NMR: (300.13 MHz, 297 K, CDCl₃)

7.18 (d, *J* = 8.5, 2 H), 6.87 (d, *J* = 8.5, 2 H), 5.07 (s, 1 H), 4.00 (m, 2 H), 3.80 (s, 3 H), 3.45 (s, 3 H), 2.14 (dd, *J* = 12.5, 13.1, 1 H), 2.03 (dd, *J* = 5.2, 13.1, 1 H), 1.40 (s, 3 H), 0.99 (s, 9 H), 0.30 and 0.20 (2 s, 6 H).

¹³C NMR: (75.47 MHz, 297 K, CDCl₃)

158.6 (C), 158.5 (C), 132.5 (C), 129.7 (CH), 113.9 (CH), 102.0 (C), 98.0 (br, CH₂), 55.3 (CH₃), 49.7 (CH₃), 42.5 (CH₂), 40.5 (br, CH), 26.1 (CH₃), 22.4 (CH₃), 18.1 (C), -4.5 (CH₃), -5.1 (CH₃).

²⁹Si NMR: (59.63 MHz, 297 K, CDCl₃)

28.04

Analysis: C₂₀H₃₃NO₄Si (379.57)

Calculated: C, 63.29; H, 8.76; N, 3.69 %

Found: C, 63.20; H, 9.00; N, 3.58 %

[†]On the basis of the comparison of the NMR data for **1a** with that for **1a''** the equatorial arrangement has been assigned to the 4-MeOC₆H₄ and Me groups of **1a''**.

rel (4*R*, 6*R*)-6-Ethoxy-2-trimethylsilyloxy-3-methylene-4-(4-methoxyphenyl)-2,3,5,6-tetrahydro-1,2-oxazine (**1b**)[†]

To a stirred solution of nitronate **2b** (0.27 g, 1 mmol) in CH_2Cl_2 (2 mL) was added at -78°C NEt_3 (0.17 mL, 1.2 mmol) and Me_3SiBr (0.15 mL, 1.1 mmol). The reaction mixture was stirred for 24 hours at -78°C , diluted with hexane (5 mL) and poured in a mixture of hexane (15 mL) and H_2O (5 mL). The organic layer was washed with a solution of $\text{NaHSO}_4\cdot\text{H}_2\text{O}$ (0.12 g, 0.87 mmol) in H_2O (6 mL), H_2O (6 mL), brine (5 mL), treated with activated charcoal and dried over Na_2SO_4 . Solvents were evaporated in vacuum and the residue was recrystallized from hexane to give title compound **1a** as colourless prisms (0.33 g, 98 %).

Analytical data for **1b**:

<u>mp</u> :	42 – 43 $^\circ\text{C}$ (hexane)		
<u>^1H NMR</u> :	(300.13 MHz, 300 K, CDCl_3)		
	7.21 (d, $J = 8.4$, 2 H), 6.87 (d, $J = 8.4$, 2 H), 5.09 (dd, $J = 4.6$, 5.3, 1 H), 4.92 (br, 1 H), 4.10 (br.m, 1 H), 4.05 – 3.91 (m, 2 H), 3.80 (s, 3 H), 3.57 (dq, $J = 7.2$, 14.4, 1 H), 2.23 (ddd, $J = 5.3$, 5.9, 13.1, 1 H), 2.10 (ddd, $J = 4.6$, 9.0, 13.1, 1 H), 1.26 (t, $J = 7.2$, 3 H), 0.26 (s, 9 H).		
<u>^{13}C NMR</u> :	(75.47 MHz, 300 K, CDCl_3)		
	158.4 (C), 132.8 (C), 129.5 (CH), 113.8 (CH), 99.3 (C), 97.2 (CH_2), 64.1 (CH_2), 55.2 (CH_3), 40.2 (CH), 36.5 (CH_2), 15.0 (CH_3), -0.8 (CH_3).		
<u>^{29}Si NMR</u> :	(59.63 MHz, 300 K, CDCl_3)		
	26.62		
<u>TLC</u> :	unstable on silica gel		
<u>Analysis</u> :	$\text{C}_{17}\text{H}_{27}\text{NO}_4\text{Si}$ (337.49)		
Calculated:	C, 60.50;	H, 8.06;	N, 4.15 %
Found:	C, 60.77;	H, 8.30;	N, 4.15 %

[†]According to NMR data the 4-MeOC₆H₄ group adopts equatorial position in **1b**. The EtO group is postulated to be axial.

rel (4*R*, 6*S*)-6-Ethoxy-2-trimethylsilyloxy-3-methylene-4-(4-methoxyphenyl)-2,3,5,6-tetrahydro-1,2-oxazine (**1c**)[†]

To a stirred solution of nitronate **2c** (0.27 g, 1 mmol) in CH_2Cl_2 (2 mL) was added at -78°C NEt_3 (0.17 mL, 1.2 mmol) and Me_3SiBr (0.15 mL, 1.1 mmol). The reaction mixture was stirred for 24 hours at -78°C , diluted with hexane (5 mL) and poured in a mixture of hexane (15 mL) and H_2O (5 mL). The organic layer was washed with a solution of $\text{NaHSO}_4\cdot\text{H}_2\text{O}$ (0.12 g, 0.87 mmol) in H_2O (6 mL), H_2O (6 mL), brine (5 mL), treated with activated charcoal and dried over Na_2SO_4 . Solvents were evaporated in vacuum and the residue was recrystallized from hexane to give title compound **1c** as colourless prisms (0.33 g, 98 %).

Analytical data for **1c**:

<u>mp</u> :	27 – 28 °C (hexane)		
<u>^1H NMR</u> :	(300.13 MHz, 320 K, CDCl_3)		
	7.18 (d, $J = 8.5$, 2 H), 6.86 (d, $J = 8.5$, 2 H), 5.23 (dd, $J = 6.4$, 6.5, 1 H), 4.98 (s, 1 H), 4.05 (s, 1 H), 3.96 (dq, $J = 7.2$, 14.2, 1 H), 3.79 (m, 4 H), 3.62 (dq, $J = 7.2$, 14.2, 1 H), 2.10 (m, 2 H), 1.25 (t, $J = 7.2$, 3 H), 0.27 (s, 9 H)		
<u>^{13}C NMR</u> :	(75.47 MHz, 300 K, CDCl_3)		
	158.6 (C), 158.0 (C)(12), 132.8 (C), 129.5 (CH), 113.9 (CH), 99.5 (CH), 98.9 (CH_2), 64.5 (CH_2), 55.2 (CH_3), 40.2 (CH), 36.9 (CH_2), 15.2 (CH_3), $-0.7(\text{CH}_3)$.		
<u>^{29}Si NMR</u> :	(59.63 MHz, 300 K, CDCl_3)		
	26.11		
<u>TLC</u> :	unstable on silica gel		
<u>Analysis</u> :	$\text{C}_{17}\text{H}_{27}\text{NO}_4\text{Si}$ (337.49)		
	Calculated:	C, 60.50;	H, 8.06; N, 4.15 %
	Found:	C, 60.52;	H, 8.12; N, 4.07 %

[†]The configuration of the stereocenters and the arrangement of the substituents in **1c** have been postulated to be the same as in **2c**.

rel (4*R*, 6*R*)-6-Methoxy-6-methyl-2-trimethylsilyloxy-3-methylene-4-phenyl-2,3,5,6-tetrahydro-1,2-oxazine (**1d**)[†]

To a stirred solution of nitronate **2d** (0.24 g, 1 mmol) in CH_2Cl_2 (2 mL) was added at -78°C NEt_3 (0.17 mL, 1.2 mmol) and Me_3SiBr (0.15 mL, 1.1 mmol). The reaction mixture was stirred for 24 hours at -78°C , diluted with hexane (5 mL) and poured in a mixture of hexane (15 mL) and H_2O (5 mL). The organic layer was washed with a solution of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ (0.12 g, 0.87 mmol) in H_2O (6 mL), H_2O (6 mL), brine (5 mL), treated with activated charcoal and dried over Na_2SO_4 . Solvents were evaporated in vacuum and the residue was recrystallized from hexane to give title compound **1d** as colourless prisms (0.30 g, 97 %).

Analytical data for **1d**:

<u>mp</u> :	79 – 80 $^\circ\text{C}$ (hexane)		
<u>^1H NMR</u> :	(300.13 MHz, 275 K, CDCl_3)		
	7.40 – 7.22 (m, 5 H), 5.01 (s, 1 H), 4.02 (dd, $J = 4.4, 12.5$, 1 H), 3.91 (s, 1 H), 3.49 (s, 1 H), 2.12 (dd, $J = 12.5, 13.3$, 1 H), 2.07 (dd, $J = 4.4, 13.3$, 1 H), 1.40 (s, 3 H), 0.26 (s, 9 H)		
<u>^{13}C NMR</u> :	(75.47 MHz, 303 K, CDCl_3)		
	158.0 (C), 140.3 (C), 128.7 (CH), 128.4 (CH), 126.9 (CH), 101.8 (C), 97.6 (CH_2), 49.4 (CH_3), 42.1 (CH_2), 41.0 (CH), 22.3 (CH_3), -0.7 (CH_3) .		
<u>^{29}Si NMR</u> :	(59.63 MHz, 297 K, CDCl_3)		
	26.23		
<u>Analysis</u> :	$\text{C}_{16}\text{H}_{25}\text{NO}_3\text{Si}$	(307.46)	
	Calculated:	C, 62.50;	H, 8.20; N, 4.56 %
	Found:	C, 62.56;	H, 8.14; N, 4.43 %

[†]According to NMR data the C_6H_5 group adopts equatorial position in **1d**. The MeO group is postulated to be axial.

rel (4*R*, 6*R*)-6-Methoxy-6-methyl-2-(*tert*-butyldimethylsilyloxy)-3-methylene-4-phenyl-2,3,5,6-tetrahydro-1,2-oxazine (**1d''**)[†]

To a stirred solution of nitronate **2d** (0.24 g, 1 mmol) in CH₂Cl₂ (2 mL) was added at -78 °C NEt₃ (0.21 mL, 1.5 mmol) and *t*-BuMe₂SiOTf (0.28 mL, 1.2 mmol). The reaction mixture was stirred for 1 hour at -78 °C, diluted with hexane (5 mL) and poured in a mixture of hexane (15 mL) and H₂O (5 mL). The organic layer was washed with H₂O (2 × 6 mL), brine (5 mL), treated with an activated charcoal and dried over Na₂SO₄. Solvents were evaporated in vacuum and the residue was recrystallized from hexane to give title compound **1d''** as colourless prisms (0.33 g, 94 %).

Analytical data for **1d''**:

<u>mp</u> :	38 – 39 °C (hexane)		
<u>¹H NMR</u> :	(300.13 MHz, 320 K, CDCl ₃)		
	7.39 – 7.22 (m, 5 H), 5.08 (s, 1 H), 4.10 (dd, <i>J</i> = 5.3, 12.5, 1 H), 4.03 (s, 1 H), 3.48 (s, 3 H), 2.19 (dd, <i>J</i> = 12.5, 13.3, 1 H), 2.11 (dd, <i>J</i> = 5.3, 13.3, 1 H), 1.40 (s, 3 H), 1.01 (s, 9H), 0.31 and 0.25 (2 s, 6 H)		
<u>¹³C NMR</u> :	(75.47 MHz, 300 K, CDCl ₃)		
	158.2 (C), 140.7 (C), 128.6 (CH), 128.3 (CH), 126.8 (CH), 102.0 (C), 98.5 (CH ₂), 49.5 (CH ₃), 42.2 (CH ₂), 40.7 (CH), 26.0 (C), 22.5 (CH ₃), 18.0 (CH ₃), -4.7 and -5.2 (CH ₃).		
<u>²⁹Si NMR</u> :	(59.63 MHz, 300 K, CDCl ₃)		
	27.99		
<u>Analysis</u> :	C ₁₉ H ₃₁ NO ₃ Si (349.55)		
Calculated:	C, 65.29;	H, 8.94;	N, 4.01 %
Found:	C, 65.34;	H, 8.83;	N, 4.20 %

[†]According to NMR data the C₆H₅ group adopts equatorial position in **1d''**. The MeO group is postulated to be axial.

rel (4*R*, 6*R*)-6-Butoxy-2-(*tert*-butyldimethylsilyloxy)-3-methylene-4-phenyl-2,3,5,6-tetrahydro-1,2-oxazine (1e'')

To a stirred solution of nitronate **2e** (0.26 g, 1 mmol) in CH_2Cl_2 (3 mL) was added at $-78\text{ }^\circ\text{C}$ NEt_3 (0.28 mL, 2.0 mmol, 2 equiv) and $t\text{-BuMe}_2\text{SiOTf}$ (0.30 mL, 1.3 mmol, 1.3 equiv). The reaction mixture was stirred for 1 hour at $-78\text{ }^\circ\text{C}$, diluted with hexane (10 mL) and poured in a mixture of hexane (10 mL) and H_2O (10 mL). The organic layer was washed with H_2O ($2 \times 6\text{ mL}$), brine (5 mL) and dried over Na_2SO_4 . The drying agent was filtered off through 2 cm pad of Celite, solvents were evaporated in vacuum and the residue was distilled in short-path apparatus to give title compound **1e''** as colorless oil (0.35 g, 92 %).

Analytical data for **1e''**:

bp: $120 - 125\text{ }^\circ\text{C}$ ($7.0 \times 10^{-5}\text{ mm Hg}$)

$^1\text{H NMR}$: (500 MHz, 233 K, CDCl_3 , two conformers in the ratio 1 : 5.3)

major: 7.33 – 7.20 (m, 5 H), 5.03 (t, $J = 4.2$, 1 H), 4.90 (s, 1 H), 3.94 – 3.89 (m, 3 H), 3.45 (q, $J = 9.2$, 1 H), 2.28 – 2.23 (m, 1 H), 2.05 – 2.01 (m, 1 H), 1.59 – 1.53 (m, 2 H), 1.36 – 1.28 (m, 2 H), 0.91 (s, 9 H), 0.88 (t, $J = 7.3$, 3 H), 0.23 (s, 3 H), 0.11 (s, 3 H)

minor: 7.33 – 7.20 (m, 5 H), 5.17 (s, 1 H), 4.98 (dd, $J = 1.7, 8.4$, 1 H), 4.55 (s, 1 H), 4.02 (dd, $J = 2.6, 6.0$, 1 H), 3.86 (q, $J = 9.2$, 1 H), 3.39 (q, $J = 9.2$, 1 H), 2.28 – 2.23 (m, 1 H), 2.05 – 2.01 (m, 1 H), 1.53 – 1.46 (m, 2 H), 1.32 – 1.24 (m, 2 H), 0.90 (s, 9 H), 0.83 (t, $J = 7.6$, 3 H), 0.17 (s, 3 H), 0.11 (s, 3 H).

$^{13}\text{C NMR}$: (126 MHz, 233 K, CDCl_3 , two conformers)

major: 158.3 (C), 140.3 (C), 129.0 (CH), 128.7 (CH), 127.3 (CH), 99.9 (CH), 97.9 (CH_2), 68.7 (CH_2), 41.2 (CH), 36.1 (CH_2), 31.6 (CH_2), 26.0 (C), 19.5 (CH_2), 18.1 (CH_3), 14.4 (CH_3), -4.9 (CH_3), -5.3 (CH_3).

minor: 154.0 (C), 142.7 (C), 128.6 (CH), 127.9 (CH), 126.6 (CH), 100.6 (CH_2), 99.1 (CH), 69.7 (CH_2), 41.8 (CH), 37.0 (CH_2), 31.8 (CH_2), 26.0 (C), 19.4 (CH_2), 18.0 (CH_3), 14.3 (CH_3), -4.7 (CH_3), -5.1 (CH_3).

IR: (KBr)

2958 (s), 2931 (s), 2860 (s), 1643 (w), 1603 (w), 1497 (w), 1471 (m), 1462 (m), 1362 (m), 1252 (s), 1159 (m), 1109 (m), 1063 (m), 1020 (m), 839 (s)

MS: FAB

378 (47, $\text{M}^+ - \text{H}$), 320 (100), 154 (42), 136 (50), 115 (18)

HRMS: calcd for $\text{C}_{21}\text{H}_{36}\text{NO}_3\text{Si}$: 378.246448; found: 378.246600

TLC: R_f 0.72 (silica gel, hexane/EtOAc, 3/1, I_2)

Analysis: $\text{C}_{21}\text{H}_{35}\text{NO}_3\text{Si}$ (377.25)

Calculated: C, 66.80; H, 9.34; N, 3.71 %

Found: C, 66.98; H, 9.45; N, 3.91 %

^{††}The configuration of the stereocenters and the arrangement of the substituents in **1e''** have been postulated to be the same as in **2e**.

rel (4*R*, 6*S*)-6-Butoxy-2-(*tert*-butyldimethylsilyloxy)-3-methylene-4-phenyl-2,3,5,6-tetrahydro-1,2-oxazine (1*f*^{''})

To a stirred solution of nitronate **2e** (0.26 g, 1 mmol) in CH₂Cl₂ (3 mL) was added at -78°C NEt₃ (0.28 mL, 2.0 mmol, 2 equiv) and *t*-BuMe₂SiOTf (0.30 mL, 1.3 mmol, 1.3 equiv). The reaction mixture was stirred for 1 hour at -78°C , diluted with hexane (10 mL) and poured in a mixture of hexane (10 mL) and H₂O (10 mL). The organic layer was washed with H₂O (2 $\times$ 6 mL), brine (5 mL) and dried over Na₂SO₄. The drying agent was filtered off through 2 cm pad of Celite, solvents were evaporated in vacuum and the residue was distilled in short-path apparatus to give title compound **1f**^{''} as colorless oil (0.36 g, 95 %).

Analytical data for **1f**^{''}:

bp: 130 – 140 $^{\circ}\text{C}$ (7.0×10^{-5} mm Hg)

¹H NMR: (500 MHz, 233 K, CDCl₃, two conformers in the ratio 1 : 1.6)

major: 7.37 – 7.23 (m, 5 H), 5.24 (dd, $J = 5.2, 8.6$, 1 H), 4.94 (s, 1 H), 4.03 (d, $J = 1.7$, 1 H), 3.99 – 3.91 (m, 2 H), 3.45 (q, $J = 7.1$, 1 H), 2.23 – 2.07 (m, 2 H), 1.62 – 1.54 (m, 2 H), 1.40 – 1.30 (m, 2 H), 0.95 (s, 9 H), 0.91 (t, $J = 7.3$, 3 H), 0.27 (s, 3 H), 0.11 (s, 3 H)
 minor: 7.37 – 7.23 (m, 5 H), 5.12 (s, 1 H), 5.09 (dd, $J = 2.1, 9.4$, 1 H), 3.99 – 3.91 (m, 1 H), 3.87 (d, $J = 1.3$, 1 H), 3.62 – 3.55 (m, 2 H), 2.23 – 2.07 (m, 1 H), 1.99 (dd, $J = 9.4, 12.7$, 1 H), 1.62 – 1.54 (m, 2 H), 1.40 – 1.30 (m, 2 H), 0.93 (s, 9 H), 0.90 (t, $J = 7.3$, 3 H), 0.21 (s, 3 H), 0.17 (s, 3 H)

¹³C NMR: (126 MHz, 233 K, CDCl₃, two conformers)

major: 158.2 (C), 141.5 (C), 128.76 (CH), 128.82 (CH), 127.2 (CH), 102.2 (br, CH₂), 99.0 (CH), 69.2 (CH₂), 40.5 (CH), 35.5 (CH₂), 31.6 (CH₂), 26.1 (C), 19.5 (CH₂), 18.2 (CH₃), 14.4 (CH₃), -5.2 (CH₃), -5.3 (CH₃).
 minor: 156.9 (C), 139.7 (C), 129.2 (CH), 128.83 (CH), 127.5 (CH), 100.4 (CH), 98.5 (CH₂), 69.8 (CH₂), 43.2 (CH), 38.2 (CH₂), 31.8 (CH₂), 26.1 (CH₃), 19.5 (CH₂), 18.3 (CH₃), 14.3 (CH₃), -5.0 (CH₃), -5.3 (CH₃)

IR: (KBr)

2958 (s), 2931 (s), 2860 (s), 1660 (w), 1645 (w), 1497 (w), 1471 (m), 1462 (m), 1375 (w), 1365 (w), 1252 (s), 1163 (m), 1113 (m), 1068 (m), 1051 (m)

MS: FAB

378 (49, M⁺–H), 377 (20), 331 (25), 320 (95), 307 (23), 289 (15), 248 (10), 155 (27), 154 (100), 152 (10), 137 (60), 136 (72), 107 (21)

HRMS: calcd for C₂₁H₃₆NO₃Si: 378.246448; found: 378.246400

TLC: unstable on silica gel

Analysis: C₂₁H₃₅NO₃Si (377.25)

Calculated: C, 66.80; H, 9.34; N, 3.71 %

Found: C, 66.73; H, 9.45; N, 4.00 %

[†]The configuration of the stereocenters and the arrangement of the substituents in **1f**^{''} have been postulated to be the same as in **2f**.

6,6-Dimethyl-2-trimethylsilyloxy-3-methylene-4-phenyl-2,3,5,6-tetrahydro-1,2-oxazine (1g)[†]

To a stirred solution of nitronate **2g** (0.22 g, 1 mmol) in CH_2Cl_2 (2 mL) was added at $-78\text{ }^\circ\text{C}$ NEt_3 (0.17 mL, 1.2 mmol) and Me_3SiBr (0.15 mL, 1.1 mmol). The reaction mixture was stirred for 24 hours at $-78\text{ }^\circ\text{C}$, diluted with hexane (5 mL) and poured in a mixture of hexane (15 mL) and H_2O (5 mL). The organic layer was washed with a solution of $\text{NaHSO}_4\cdot\text{H}_2\text{O}$ (0.12 g, 0.87 mmol) in H_2O (6 mL), H_2O (6 mL), brine (5 mL), treated with activated charcoal and dried over Na_2SO_4 . Solvents were thoroughly evaporated in vacuum to give title compound **1g** as colorless oil (0.28 g, 95 %).

Analytical data for **1g**:

<u>mp</u> :	oil
<u>^1H NMR</u> :	(300.13 MHz, 300 K, CDCl_3)
	7.39 – 7.24 (m, 5 H), 5.00 and 3.97 (2 s, 2 H), 3.83 (dd, $J = 4.9, 12.8$, 1 H), 2.06 (dd, $J = 12.8, 12.9$, 1 H), 1.78 (dd, $J = 4.9, 12.9$, 1 H), 1.53 and 1.32 (2 s, 6 H), 0.27 (s, 9 H)
<u>^{13}C NMR</u> :	(75.47 MHz, 300 K, CDCl_3)
	158.4 (C), 141.0 (C), 128.8 (CH), 128.4 (CH), 126.9 (CH), 97.1 (CH_2), 76.9 (C), 43.5 (CH_2), 42.9 (CH), 29.0 (CH_3), 23.6 (CH_3), -0.7 (CH_3)
<u>^{29}Si NMR</u> :	(59.63 MHz, 300 K, CDCl_3)
	26.17
<u>TLC</u> :	R_f 0.72 (silica gel, hexane/EtOAc, 1/1, UV)
<u>Analysis</u> :	$\text{C}_{16}\text{H}_{25}\text{NO}_2\text{Si}$ (291.47)
Calculated:	C, 65.93; H, 8.65; N, 4.81 %
Found:	C, 66.17; H, 8.90; N, 4.54 %

[†]According to NMR data the C_6H_5 group adopts equatorial position in **1g**.

rel (4*R*, 6*R*)-(*E*)-6-Methoxy-6-methyl-2-trimethylsilyloxy-3-ethylene-4-phenyl-2,3,5,6-tetrahydro-1,2-oxazine (**1h**)[†]

To a stirred solution of nitronate **2h** (0.25 g, 1 mmol) in CH_2Cl_2 (2 mL) was added at -78°C NEt_3 (0.17 mL, 1.2 mmol) and Me_3SiBr (0.15 mL, 1.1 mmol). The reaction mixture was stirred for 24 hours at -78°C , diluted with hexane (5 mL) and poured in a mixture of hexane (15 mL) and H_2O (5 mL). The organic layer was washed with a solution of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ (0.12 g, 0.87 mmol) in H_2O (6 mL), H_2O (6 mL), brine (5 mL), treated with activated charcoal and dried over Na_2SO_4 . Solvents were evaporated in vacuum and the residue was crystallized in hexane at -78°C to give title compound **1h** as colorless oil (0.30 g, 95 %).

Analytical data for **1h**:

<u>mp</u> :	< 0°C		
<u>^1H NMR</u> :	(300.13 MHz, 300 K, CDCl_3)		
	7.45 – 7.15 (m, 5 H), 5.18 (q, $J = 6.6$, 1 H), 4.14 (br.s, 1 H), 3.29 (s, 3 H), 2.50 (dd, $J = 7.3$, 13.2, 1 H), 2.32 (dd, $J = 6.6$, 13.2, 1 H), 1.33 (d, $J = 6.6$, 3 H), 1.12 (s, 3 H), 0.29 (s, 9 H)		
<u>^{13}C NMR</u> :	(75.47 MHz, 300 K, CDCl_3)		
	162.3 (C), 141.1 (C), 126.9 (CH), 126.8 (CH), 126.0 (CH), 115.1 (CH), 97.2 (C), 49.1 (CH_3), 40.5 (CH_2), 39.7 (CH), 37.4 (CH_3), 23.3 (CH_3), -0.6 (CH_3).		
<u>^{29}Si NMR</u> :	(59.63 MHz, 300 K, CDCl_3)		
	24.43		
<u>Analysis</u> :	$\text{C}_{17}\text{H}_{27}\text{NO}_3\text{Si}$	(321.49)	
	Calculated:	C, 63.51;	H, 8.47; N, 4.36 %
	Found:	C, 63.26;	H, 8.40; N, 4.12 %

[†]The configuration of the stereocenters and the arrangement of the substituents in **1f'** have been postulated to be the same as in **2f**.

rel (4*R*, 5*S*, 6*S*)-4-(4-Methoxyphenyl)-3-methylene-2-trimethylsilyloxy-octahydro-benzo[*e*]-1,2-oxazine (1i)

To a stirred solution of nitronate **2i** (0.28 g, 1 mmol) in CH_2Cl_2 (2 mL) was added at -78°C NEt_3 (0.17 mL, 1.2 mmol) and Me_3SiBr (0.15 mL, 1.1 mmol). The reaction mixture was stirred for 24 hours at -78°C , diluted with hexane (5 mL) and poured in a mixture of hexane (15 mL) and H_2O (5 mL). The organic layer was washed with a solution of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ (0.12 g, 0.87 mmol) in H_2O (6 mL), H_2O (6 mL), brine (5 mL), treated with activated charcoal and dried over Na_2SO_4 . Solvents were thoroughly evaporated in vacuum to give title compound **1i** as colorless oil (0.33 g, 95 %).

Analytical data for 1i:

mp: oil

^1H NMR: (300.13 MHz, 300 K, CDCl_3 , two conformers in a ratio 2 : 1)

major: 7.34 (d, $J = 8.5$, 2 H), 6.82 (d, $J = 8.5$, 2 H), 5.21 (s, 1H), 4.53 (s, 1 H), 4.37 (s, 1 H), 3.80 (s, 3 H), 3.46 (s, 1 H), 2.15 – 1.25 (m, 9 H), 0.23 (s, 9 H)

minor: 7.19 (d, $J = 8.5$, 2 H), 6.82 (d, $J = 8.5$, 2 H), 4.86 (s, 1H), 4.34 (s, 1 H), 4.01 (s, 1 H), 3.80 (s, 3 H), 3.40 (d, $J = 8.9$, 1 H), 2.15 – 1.25 (m, 9 H), 0.23 (s, 9 H)

^{13}C NMR: (75.47 MHz, 300 K, CDCl_3 , two conformers)

major: 157.9 (C), 152.9 (C), 135.8 (C), 128.8 (CH), 113.5 (CH), 99.3 (CH_2), 72.1 (CH), 55.2 (CH_3), 51.7 (CH), 42.6 (CH), 30.0 (CH_2), 27.6 (CH_2), 22.5 (CH_2), 20.3 (CH_2), -0.7 (CH_3).

minor: 157.9 (C), 152.9 (C), 135.8 (C), 128.9 (CH), 113.8 (CH), 98.8 (CH_2), 72.9 (CH), 55.2 (CH_3), 47.8 (CH), 42.0 (CH), 27.9 (CH_2), 25.7 (CH_2), 22.4 (CH_2), 20.3 (CH_2), -0.6 (CH_3).

^{29}Si NMR: (59.63 MHz, 300 K, CDCl_3 , two conformers in a ratio 2 : 1)

major: 26.64

minor: 25.42

Analysis: $\text{C}_{19}\text{H}_{29}\text{NO}_3\text{Si}$ (347.53)

Calculated: C, 65.67; H, 8.41; N, 4.03 %

Found: C, 65.90; H, 8.64; N, 3.78 %

[†]The configuration of the stereocenters and the arrangement of the substituents in **1i** have been postulated to be the same as in **2i**.

rel (4*R*, 5*S*, 6*S*)-4-(4-Nitrophenyl)-3-methylene-2-(*tert*-butyldimethylsilyloxy)-octahydro-benzo[e]-1,2-oxazine (**1j''**)[†]

To a stirred solution of nitronate **2j** (0.29 g, 1 mmol) in CH_2Cl_2 (2 mL) was added at -78°C NEt_3 (0.21 mL, 1.5 mmol) and *t*- $\text{BuMe}_2\text{SiOTf}$ (0.28 mL, 1.2 mmol). The reaction mixture was stirred for 1 hour at -78°C , diluted with hexane (5 mL) and poured in a mixture of hexane (15 mL) and H_2O (5 mL). The organic layer was washed with H_2O (2×6 mL), brine (5 mL) and dried over Na_2SO_4 . Solvents were thoroughly evaporated in vacuum to give title compound **1j''** as colorless oil (0.39 g, 98 %).

Analytical data for **1j''**:

<u>mp</u> :	oil
<u>^1H NMR</u> :	(300.13 MHz, 330 K, toluene- D_8)
	8.15 (d, $J = 8.5$, 2 H), 7.54 (d, $J = 8.5$, 2 H), 5.23 (s, 1H), 4.49 (s, 1 H), 4.36 (s, 1 H), 3.52 (s, 1 H), 2.10 – 1.30 (m, 9 H), 1.00 (s, 9 H), 0.20 (s, 6 H)
<u>^{13}C NMR</u> :	(75.47 MHz, 330 K, toluene- D_8)
	157.9 (C), 151.8 (C), 145.8 (C), 137.3 (CH), 123.2 (CH), 101.7 (CH_2), 71.0 (CH), 51.3 (CH), 42.0 (CH), 29.0 (CH_2), 27.9 (CH_2), 24.0 (CH_2), 21.4 (CH_2), 26.2 (C), 18.1 (CH_3), -5.1 (CH_3).
<u>^{29}Si NMR</u> :	(59.63 MHz, 330K, toluene- D_8)
	25.85
<u>Analysis</u> :	$\text{C}_{21}\text{H}_{32}\text{N}_2\text{O}_4\text{Si}$ (404.58)
Calculated:	C, 62.34; H, 7.97; N, 6.92 %
Found:	C, 62.59; H, 8.20; N, 6.62 %

[†]The configuration of the stereocenters and the arrangement of the substituents in **1j''** have been postulated to be the same as in **2i**, **2j** and **1i**.

Trimethylsilyl ether 2-(4-methoxyphenyl)-but-1-en-3-one oxime (3a)

To a stirred solution of nitronate **2a** (0.27 g, 1 mmol) in CH_2Cl_2 (2 mL) was added at $-30\text{ }^\circ\text{C}$ pyridine (0.12 mL, 1.5 mmol) and Me_3SiBr (0.16 mL, 1.2 mmol). The reaction mixture was stirred for 24 hours at $-30\text{ }^\circ\text{C}$, diluted with hexane (5 mL) and poured in a mixture of hexane (15 mL) and H_2O (5 mL). The organic layer was washed with a solution of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ (0.35 g, 2.54 mmol) in H_2O (15 mL), H_2O (10 mL), brine (5 mL), treated with activated charcoal and dried over Na_2SO_4 . Solvents were evaporated in vacuum, the residue was analyzed by NMR with quantitative standard (96 %) and subjected to desilylation (vide infra).

Analytical data for **3a**:

^1H NMR: (300.13 MHz, 300K, CDCl_3)
 7.29 (dd, $J = 2.0, 6.6$, 2 H), 6.85 (dd, $J = 2.0, 6.6$, 2 H), 5.45 (d, $J = 1.4$, 1 H), 5.41 (d, $J = 1.4$, 1 H), 3.80 (s, 3 H), 2.06 (s, 3 H), 0.22 (s, 9 H)

^{13}C NMR: (75.47 MHz, 300K, CDCl_3)
 160.8 (C), 159.2 (C), 146.4 (C), 131.5 (C), 129.3 (CH), 115.8 (CH), 113.2 (CH_2), 55.2 (CH_3), 13.2 (CH_3), -0.6 (CH_3).

Trimethylsilyl ester 2-phenyl-but-1-en-3-one oxime (3d)

To a stirred solution of nitronate **2d** (0.24 g, 1 mmol) in CH_2Cl_2 (2 mL) was added at $-30\text{ }^\circ\text{C}$ pyridine (0.12 mL, 1.5 mmol) and Me_3SiBr (0.16 mL, 1.2 mmol). The reaction mixture was stirred for 24 hours at $-30\text{ }^\circ\text{C}$, diluted with hexane (5 mL) and poured in a mixture of hexane (15 mL) and H_2O (5 mL). The organic layer was washed with a solution of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ (0.35 g, 2.54 mmol) in H_2O (15 mL), H_2O (10 mL), brine (5 mL), treated with activated charcoal and dried over Na_2SO_4 . Solvents were evaporated in vacuum, the residue was analyzed by NMR with quantitative standard (92 %) and subjected to desilylation (vide infra).

NMR data for **3d**:

^1H NMR: (300.13 MHz, 300 K, CDCl_3)

7.30 (m, 5 H), 5.56 (s, 1 H), 5.47 (s, 1 H), 2.09 (s, 3 H), 0.22 (s, 9 H)

^{13}C NMR: (75.47 MHz, 300 K, CDCl_3)

160.5 (C), 147.0 (C), 139.1 (C), 128.4(CH), 127.8 (CH), 127.5 (CH), 117.2 (CH_2), 13.0 (CH_3),
 -0.6 (CH_3).

Trimethylsilyl ester 2-phenyl-pent-1-en-3-one oxime (3h)

To a stirred solution of nitronate **2h** (0.24 g, 1 mmol) in CH_2Cl_2 (2 mL) was added at $-30\text{ }^\circ\text{C}$ pyridine (0.12 mL, 1.5 mmol) and Me_3SiBr (0.16 mL, 1.2 mmol). The reaction mixture was stirred for 24 hours at $-30\text{ }^\circ\text{C}$, diluted with hexane (5 mL) and poured in a mixture of hexane (15 mL) and H_2O (5 mL). The organic layer was washed with a solution of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ (0.35 g, 2.54 mmol) in H_2O (15 mL), H_2O (10 mL), brine (5 mL), treated with activated charcoal and dried over Na_2SO_4 . Solvents were evaporated in vacuum, the residue was analyzed by NMR with quantitative standard (90 %, 2 : 3 mixture of two isomers) and subjected to desilylation (vide infra).

NMR data for major isomer of **3h**:

^1H NMR: (300.13 MHz, 300K, CDCl_3)
 7.3 (m, 5 H), 5.55 (d, $J = 1.5$, 1 H), 5.46 (d, $J = 1.5$, 1 H), 2.58 (q, $J = 7.1$, 2 H), 1.08 (t, $J = 7.1$, 3 H), 0.22 (s, 9 H)

^{13}C NMR: (75.47 MHz, 300K, CDCl_3)
 162.1 (C), 145.5 (C), 140.0 (C), 128.5 (CH), 127.7 (CH), 127.4 (CH), 117.5 (CH_2), 19.3 (CH_2), 10.6 (CH_3), -0.7 (CH_3)

NMR data for minor isomer of **3h**:

^1H NMR: (300.13 MHz, 300 K, CDCl_3)
 7.3 (m, 5 H), 5.49 (s, 1 H), 5.48 (s, 1 H), 2.58 (q, $J = 7.1$, 2 H), 1.03 (t, $J = 7.1$, 3 H), 0.22 (s, 9 H)

^{13}C NMR: (75.47 MHz, 300 K, CDCl_3)
 165.9 (C), 145.6 (C), 139.1 (C), 128.5 (CH), 127.7 (CH), 127.4 (CH), 117.2 (CH_2), 20.1 (CH_2), 10.8 (CH_3), -0.7 (CH_3).

2-(4-Methoxyphenyl-but-1-en-3-one oxime (4a)

To a stirred solution of nitronate **2a** (0.24 g, 1 mmol) in CH_2Cl_2 (2 mL) was added at $-30\text{ }^\circ\text{C}$ pyridine (0.12 mL, 1.5 mmol) and Me_3SiBr (0.16 mL, 1.2 mmol). The reaction mixture was stirred for 24 hours at $-30\text{ }^\circ\text{C}$, diluted with hexane (5 mL) and poured in a mixture of hexane (15 mL) and H_2O (5 mL). The organic layer was washed with a solution of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ (0.35 g, 2.54 mmol) in H_2O (15 mL), H_2O (10 mL), brine (5 mL), treated with activated charcoal and dried over Na_2SO_4 . Solvents were evaporated in vacuum, the residue was dissolved in MeOH (5 mL) and NH_4F (5 mg, 0.14 mmol) was added. After being stirred for 3 hours, the mixture was filtered through a pad of Celite and evaporated. The residue was recrystallized from EtOAc / hexane mixture to give title compound **4a** as a white crystals (0.17 g, 89 %).

Analytical data for **4a**:

mp: $76 - 78\text{ }^\circ\text{C}$ (hexane/ EtOAc , 10/1)

^1H NMR: (300.13 MHz, 300 K, CDCl_3)

9.25 (br, 1 H), 7.23 (dd, $J = 2.2, 6.7$, 2 H), 6.88 (dd, $J = 2.2, 6.7$, 2 H), 5.49 (s, 1 H), 5.38 (s, 1 H), 3.82 (s, 3 H), 2.05 (s, 3 H)

^{13}C NMR: (75.47 MHz, 300K, CDCl_3)

159.3 (C), 157.1 (C), 146.1 (C), 131.4 (C), 129.4 (CH), 116.5 (CH), 113.9 (CH_2), 55.4 (CH_3), 12.3 (CH_3).

TLC: R_f 0.55 (silica gel, hexane/ EtOAc , 1/1, UV)

Analysis: $\text{C}_{11}\text{H}_{13}\text{NO}_2$ (191.23)

Calculated: C, 69.09; H, 6.85; N, 7.32 %

Found: C, 69.31; H, 6.87; N, 7.23 %

2-Phenyl-but-1-en-3-one oxime (4d)

To a stirred solution of nitronate **2d** (0.24 g, 1 mmol) in CH_2Cl_2 (2 mL) was added at -30°C pyridine (0.12 mL, 1.5 mmol) and Me_3SiBr (0.16 mL, 1.2 mmol). The reaction mixture was stirred for 24 hours at -30°C , diluted with hexane (5 mL) and poured in a mixture of hexane (15 mL) and H_2O (5 mL). The organic layer was washed with a solution of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ (0.35 g, 2.54 mmol) in H_2O (15 mL), H_2O (10 mL), brine (5 mL), treated with activated charcoal and dried over Na_2SO_4 . Solvents were evaporated in vacuum, the residue was dissolved in MeOH (5 mL) and NH_4F (5 mg, 0.14 mmol) was added. After being stirred for 3 hours, the mixture was filtered through a pad of Celite and evaporated. The residue was recrystallized from EtOAc / hexane mixture to give title compound **4d** as a white crystals (0.12 g, 81 %).

Analytical data for **4d**:

<u>mp</u> :	100 – 101 $^\circ\text{C}$ (hexane/EtOAc, 10/1)		
<u>^1H NMR</u> :	(300.13 MHz, 300 K, CDCl_3)		
	9.30 (br, 1 H), 7.32 (m, 5 H), 5.61 (s, 1 H), 5.43 (s, 1 H), 2.06 (s, 3 H)		
<u>^{13}C NMR</u> :	(75.47 MHz, 300 K, CDCl_3)		
	156.8 (C), 146.7 (C), 139.1 (C), 128.3 (CH), 128.2 (CH), 127.7 (CH), 117.8 (CH_2), 12.0 (CH_3).		
<u>TLC</u> :	R_f 0.68 (silica gel, hexane/EtOAc, 1/1, UV)		
<u>Analysis</u> :	$\text{C}_{10}\text{H}_{11}\text{NO}$ (161.20)		
Calculated:	C, 74.51;	H, 6.88;	N, 8.69 %
Found:	C, 74.48;	H, 6.80;	N, 8.39 %

2-Phenyl-pent-1-en-3-one oxime (4h)

To a stirred solution of nitronate **2d** (0.24 g, 1 mmol) in CH_2Cl_2 (2 mL) was added at -30°C pyridine (0.12 mL, 1.5 mmol) and Me_3SiBr (0.16 mL, 1.2 mmol). The reaction mixture was stirred for 24 hours at -30°C , diluted with hexane (5 mL) and poured in a mixture of hexane (15 mL) and H_2O (5 mL). The organic layer was washed with a solution of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ (0.35 g, 2.54 mmol) in H_2O (15 mL), H_2O (10 mL), brine (5 mL), treated with activated charcoal and dried over Na_2SO_4 . Solvents were evaporated in vacuum, the residue was dissolved in MeOH (5 mL) and NH_4F (5 mg, 0.14 mmol) was added. After being stirred for 3 hours, the mixture was filtered through a pad of Celite and evaporated. The residue was recrystallized from EtOAc / hexane mixture to give title compound **4h** as a white crystals (0.11 g, 64 %).

Analytical data for **4h**:

<u>mp</u> :	55 – 56 $^\circ\text{C}$ (hexane/EtOAc, 10/1)		
<u>^1H NMR</u> :	(300.13 MHz, 300 K, CDCl_3)		
	9.30 (br, 1 H), 7.32 (m, 5 H), 5.58 (s, 1 H), 5.48 (s, 1 H), 2.55 (q, $J = 7.3$, 2 H), 1.10 (t, $J = 7.3$, 3 H)		
<u>^{13}C NMR</u> :	(75.47 MHz, 300 K, CDCl_3)		
	161.8 (C), 145.5 (C), 139.2 (C), 128.2 (CH), 128.0 (CH), 127.8 (CH), 117.6 (CH_2), 19.3 (CH_2), 10.6 (CH_3)		
<u>TLC</u> :	R_f 0.71 (silica gel, hexane/EtOAc, 1/1, UV)		
<u>Analysis</u> :	$\text{C}_{11}\text{H}_{13}\text{NO}$ (175.23)		
Calculated:	C, 75.40;	H, 7.48;	N, 7.99 %
Found:	C, 75.63;	H, 7.53;	N, 8.02 %

6-Methoxy-6-methyl-4-phenyl-3-(1-trimethylsilyloxyethyl)-5,6-dihydro-4*H*-1,2-oxazine (5**)[†]**

1,2-Oxazine **1h** (0.32 g, 1 mmol) was maintained for 24 hours at room temperature. The resulting title compound **5** was purified by column chromatography on silica gel in hexane / EtOAc 3 : 1 to give (0.30 g, 92 %).

Analytical data for **5**:

<u>mp</u> :	oil
<u>¹H NMR</u> :	(300.13 MHz, 300 K, CDCl ₃)
	7.35 – 7.15 (m, 5 H), 4.29 (q, <i>J</i> = 5.8, 1 H), 3.84 (dd, <i>J</i> = 8.1, 12.5, 1 H), 3.31 (s, 3 H), 2.29 (dd, <i>J</i> = 13.1, 8.1, 1 H), 1.88 (dd, <i>J</i> = 13.1, 12.5, 1 H), 1.44 (s, 3 H), 1.33 (d, <i>J</i> = 5.8, 3 H), 0.12 (s, 9 H)
<u>¹³C NMR</u> :	(75.47 MHz, 300 K, CDCl ₃)
	162.5 (C), 141.3 (C), 128.9 (CH), 128.8 (CH), 126.9 (CH), 96.4 (C), 68.6 (CH), 49.6 (CH ₃), 40.6 (CH ₂), 36.6 (CH), 21.7 (CH ₃), 20.7 (CH ₃), 0.3 (CH ₃)
<u>²⁹Si NMR</u> :	(59.63 MHz, 300 K, CDCl ₃)
	17.09
<u>TLC</u> :	R _f 0.71 [hexane / EtOAc 3/1]
<u>Analysis</u> :	C ₁₇ H ₂₇ NO ₃ Si (321.49)
Calculated:	C, 63.51; H, 8.47; N, 4.36 %
Found:	C, 63.55; H, 8.40; N, 4.15 %

[†]According to NMR data the C₆H₅ group adopts equatorial position in **5**. The arrangement of the other substituents in **5** has been postulated to be the same as in **2h** and **1h**. The configuration of the stereocenter that emerges during the reaction has not been determined.

rel (4*R*, 6*R*)-6-Butoxy-3-(2-methoxy-2-phenyl-ethyl)-4-phenyl-5,6-dihydro-4*H*-1,2-oxazine *N*-oxide (**2k**)[†]

To a cold ($-78\text{ }^{\circ}\text{C}$) solution of pyridine (3 μL , 0.037 mmol, 0.06 equiv) in CH_2Cl_2 (0.7 mL) was added successively Me_3SiOTf (0.15 mL, 0.799 mmol, 1.2 equiv) and a solution of benzaldehyde dimethyl acetal (0.122 g, 0.803 mmol, 1.2 equiv) in CH_2Cl_2 (0.7 mL). Then a solution of nitrosal **1e''** (0.25 g, 0.66 mmol) in CH_2Cl_2 (1.3 mL) was added dropwise. The resultant mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 6 h and a solution of BnEt_3NCl (0.27 g, 1.187 mmol, 1.8 equiv) in CH_2Cl_2 (2 mL) followed by Et_3N (0.26 mL, 1.871 mmol, 2.8 equiv) were added successively. After 5 min of stirring the mixture was poured into a mixture of H_2O (20 mL) and ether, organic layer was separated, aqueous later was diluted with brine (5 mL) and back-extracted with ether ($2 \times 10\text{ mL}$). The combined organic layers were washed with H_2O (15 mL), saturated aqueous NH_4Cl solution (10 mL), H_2O (15 mL), saturated aqueous NaHCO_3 solution (10 mL), H_2O (15 mL), brine (10 mL) and dried over Na_2SO_4 . The solvents were evaporated in vacuum and yellow residue was separated on preparative MPLC (Rexchrom 5/100 Silica, 25 cm $\times$ 21.1 mm, flow rate 15 mL / min, eluent: hexane / *i*-PrOH 1 / 30). The upper product was distilled and recrystallized to give the major isomer of the title compound **2k** (0.08 g, 30 %), the lower product was recrystallized (Et_2O / hexane) to give the minor isomer of the title compound **2k** (0.03 g, 15 %) of white crystals.

Analytical data for the major isomer of **2k**:

bp: 150 – 160 $^{\circ}\text{C}$ (5.0×10^{-5} mm Hg)

mp: 80 – 82 $^{\circ}\text{C}$ (Et_2O / hexane)

^1H NMR: (500 MHz, 300 K, CDCl_3)

7.34 – 7.20 (m, 10 H,), 5.39 (t, $J = 2.8$, 1 H), 4.82 (dd, $J = 2.8$, 10.3, 1 H), 4.20 (dd, $J = 7.7$, 10.9, 1 H), 4.07 (dt, $J = 6.6$, 9.4, 1 H), 3.69 (dt, $J = 6.8$, 9.6, 1 H), 3.24 (s, 3 H), 2.73 (ddd, $J = 1.3$, 2.8, 13.9, 1 H), 2.31 (ddd, $J = 2.1$, 7.7, 13.7, 1 H), 2.15 (ddd, $J = 2.1$, 3.2, 11.2, 13.7, 1 H), 2.12 (dd, $J = 10.3$, 13.9, 1 H), 1.68 (m, 2 H), 1.47 (m, 2 H), 0.97 (t, $J = 7.5$, 3 H).

^{13}C NMR: (126 MHz, 300 K, CDCl_3)

141.8(C), 140.8 (C), 128.9 (CH), 127.8 (CH), 129.5 (CH), 128.7 (CH), 128.6 (CH), 126.5 (CH), 125.9 (C), 101.9 (CH), 79.1 (CH_2), 69.5 (CH_2), 57.3 (CH_3), 41.5 (CH), 40.2 (CH_2), 34.7 (CH_2), 32.0 (CH_2), 19.5 (CH_2), 14.2 (CH_3)

IR: (KBr)

2958 (w), 2933 (w), 1605 (m), 1493 (w), 1454 (w), 1282 (m), 1219 (m), 1103 (s)

MS: FAB

384 (100, $\text{M}^+ - \text{H}$), 368 (20), 353 (12) 309 (6), 205 (13), 195 (10), 155 (16), 135 (13), 121 (66), 119 (40)

HRMS: calcd for $\text{C}_{23}\text{H}_{30}\text{NO}_4$: 384.217484; found: 384.217400

TLC: R_f 0.12 [silica gel, hexane / *i*-PrOH 20 : 1, anisaldehyde]

Analysis: $\text{C}_{23}\text{H}_{29}\text{NO}_4$ (383.22)

Calculated: C, 72.04; H, 7.62; N, 3.65 %

Found: C, 71.93; H, 7.70; N, 3.85 %

[†]According to NMR data the C_6H_5 group adopts equatorial, while *n*-BuO group adopts axial positions in both isomers of **2k**. The configuration of the stereocenter that emerges during the reaction has not been determined.

Analytical data for the minor isomer of **2k**:

<u>mp</u> :	75 – 77 °C (Et ₂ O / hexane)		
<u>¹H NMR</u> :	(500 MHz, 300 K, CDCl ₃)		
	7.37 – 7.21 and 6.90 (2 m, 10 H), 5.26 (t, <i>J</i> = 2.8, 1 H), 4.63 (dd, <i>J</i> = 5.6, 9.0, 1 H), 4.01 (dt, <i>J</i> = 6.6, 9.7, 1 H), 3.61 (dt, <i>J</i> = 6.9, 9.5, 1 H), 3.18 (s, 3 H), 3.16 (ddd, <i>J</i> = 1.7, 5.6, 13.5, 1 H), 3.00 (t, <i>J</i> = 9.2, 1 H), 2.10 (dd, <i>J</i> = 9.0, 13.5, 1 H), 2.00 (d, <i>J</i> = 2.6, 1 H), 1.99 (d, <i>J</i> = 2.8, 1 H), 1.66 (m, 2 H), 1.43 (m, 2 H), 0.99 (t, <i>J</i> = 7.5, 3 H)		
<u>¹³C NMR</u> :	(126 MHz, 300 K, CDCl ₃)		
	141.4 (C), 140.2 (C), 128.5 (CH), 127.9 (CH), 129.4 (CH), 128.8 (CH), 128.5 (CH), 127.2 (CH), 123.5 (C), 101.6 (CH), 78.0 (CH), 69.6 (CH ₂), 56.7 (CH ₃), 40.2 (CH), 39.1 (CH ₂), 34.2 (CH ₂), 31.8 (CH ₂), 19.4 (CH ₂), 14.2 (CH ₃).		
<u>IR</u> :	(KBr)		
	2956 (m), 2933 (m), 2873 (m), 1600 (s), 1492 (w), 1454 (m), 1346 (s), 1269 (s), 1113 (s)		
<u>MS</u> :	FAB		
	384 (100, M ⁺ –H), 369 (20), 368 (21), 353 (18), 205 (25), 133 (12), 121 (89), 105 (12)		
<u>HRMS</u> :	calcd for C ₂₃ H ₃₀ NO ₄ : 384.217484; found: 384.217400		
<u>TLC</u> :	<i>R_f</i> 0.12 [silica gel, hexane / <i>i</i> -PrOH, 20/1, anisaldehyde]		
<u>Analysis</u> :	C ₂₃ H ₂₉ NO ₄ (383.22)		
	Calculated:	C, 72.04;	H, 7.62; N, 3.65 %
	Found:	C, 71.88;	H, 7.69; N, 3.80 %

rel (4*R*, 6*S*)-6-Butoxy-3-(2-methoxy-2-phenyl-ethyl)-4-phenyl-5,6-dihydro-4*H*-1,2-oxazine *N*-oxide (21)[†]

To a cold ($-78\text{ }^\circ\text{C}$) solution of pyridine (4 μL , 0.05 mmol, 0.05 equiv) in CH_2Cl_2 (1 mL) was added successively Me_3SiOTf (0.22 mL, 1.16 mmol, 1.2 equiv) and a solution of benzaldehyde dimethyl acetal (0.18 g, 1.20 mmol, 1.2 equiv) in CH_2Cl_2 (1 mL). Then a solution of nitrosal **1f''** (0.38 g, 1.01 mmol) in CH_2Cl_2 (2 mL) was added dropwise. The resultant mixture was stirred at $-78\text{ }^\circ\text{C}$ for 6 h and a solution of BnEt_3NCl (0.33 g, 1.45 mmol, 1.5 equiv) in CH_2Cl_2 (3 mL) followed by Et_3N (0.40 mL, 2.87 mmol, 2.9 equiv) were added successively. After 5 min of stirring the mixture was poured into a mixture of H_2O (30 mL) and Et_2O (30 mL), organic layer was separated, aqueous later was diluted with brine (10 mL) and back-extracted with ether ($2 \times 15\text{ mL}$). The combined organic layers were washed with H_2O (15 mL), saturated aqueous NH_4Cl solution (10 mL), H_2O (15 mL), saturated aqueous NaHCO_3 solution (10 mL), H_2O (15 mL), brine (10 mL) and dried over Na_2SO_4 . The solvents were evaporated in vacuum and yellow residue was separated on preparative MPLC (Rexchrom 5/100 Silica, 25 cm $\times$ 21.1 mm, flow rate 15 mL / min, eluent: hexane / *i*-PrOH 1 / 40). The upper product was distilled to give the major isomer of the title compound **21** as colorless oil (0.15 g, 39 %), the lower product was recrystallized (Et_2O / hexane) to give the minor isomer of the title compound **21** as white crystals (0.06 g, 16 %).

Analytical data for the major isomer of **21**:

<u>bp</u> :	160 – 170 $^\circ\text{C}$ (1.0×10^{-4} mm Hg)
<u>^1H NMR</u> :	(500 MHz, 300 K, CDCl_3)
	7.38 – 7.20 and 6.98 (m, 10H), 5.10 (dd, $J = 3.6, 5.6, 1\text{ H}$), 4.76 (dd, $J = 6.4, 8.8, 1\text{ H}$), 4.01 (dt, $J = 6.7, 9.4, 1\text{ H}$), 3.54 (dt, $J = 6.7, 9.4, 1\text{ H}$), 3.21 (s, 3 H), 3.10 (ddd, $J = 1.3, 6.4, 13.5, 1\text{ H}$), 2.79 (t, $J = 8.2, 1\text{ H}$), 2.17 (ddd, $J = 3.6, 8.6, 13.7, 1\text{ H}$), 2.12 (dd, $J = 8.6, 13.5, 1\text{ H}$), 1.93 (ddd, $J = 5.6, 7.3, 13.7, 1\text{ H}$), 1.57 (m, 2 H), 1.33 (m, 2 H), 0.90 (t, $J = 7.3, 3\text{ H}$)
<u>^{13}C NMR</u> :	(126 MHz, 300 K, CDCl_3)
	141.6 (C), 140.0 (C), 128.6 (CH), 127.8 (CH), 129.1 (CH), 128.9 (CH), 128.8 (CH), 126.8 (CH), 124.8 (C), 103.8 (CH), 77.6 (CH), 70.2 (CH_2), 56.9 (CH_3), 48.8 (CH_2), 42.1 (CH), 35.3 (CH_2), 31.7 (CH_2), 19.4 (CH_2), 14.1 (CH_3).
<u>IR</u> :	(KBr)
	2958 (m), 2935 (w), 2873 (m), 1601 (s), 1495 (w), 1454 (m), 1255 (m), 1101 (s)
<u>MS</u> :	FAB
	384 (38, $\text{M}^+ - \text{H}$), 368 (13), 353 (14), 195 (37), 155 (29), 154 (10), 153 (18), 135 (39), 118 (100)
<u>HRMS</u> :	calcd for $\text{C}_{23}\text{H}_{30}\text{NO}_4$: 384.217484; found: 384.217400
<u>TLC</u> :	R_f 0.24 [silica gel, hexane / <i>i</i> -PrOH 20/1, anisaldehyde]
<u>Analysis</u> :	$\text{C}_{23}\text{H}_{29}\text{NO}_4$ (383.22)
	Calculated: C, 72.04; H, 7.62; N, 3.65 %
	Found: C, 71.95; H, 7.68; N, 3.88 %

[†]According to NMR data both C_6H_5 and *n*-BuO groups adopt axial positions in both isomers of **21**. The configuration of the stereocenter that emerges during the reaction has not been determined.

Analytical data for the minor isomer of 21:

<u>mp</u> :	66 – 68 °C (Et ₂ O / hexane)		
<u>¹H NMR</u> :	(500 MHz, 300 K, CDCl ₃)		
	7.31 – 7.16 (m, 10 H), 5.36 (dd, <i>J</i> = 3.4, 5.4, 1 H), 4.85 (dd, <i>J</i> = 3.2, 10.1, 1 H), 4.07 (dt, <i>J</i> = 6.7, 9.4, 1 H), 4.03 (dd, <i>J</i> = 6.4, 8.8, 1 H), 3.60 (dt, <i>J</i> = 6.7, 9.4, 1 H), 3.20 (s, 3 H), 2.72 (ddd, <i>J</i> = 0.9, 3.2, 13.9, 1 H), 2.55 (ddd, <i>J</i> = 3.4, 8.8, 13.9, 1 H), 2.21 (dd, <i>J</i> = 10.1, 13.9, 1 H), 2.09 (ddd, <i>J</i> = 5.6, 6.2, 13.9, 1 H), 1.67 – 1.56 (m, 2 H), 1.37 – 1.32 (m, 2 H), 0.91 (t, <i>J</i> = 7.5, 3 H)		
<u>¹³C NMR</u> :	(126 MHz, 300 K, CDCl ₃)		
	141.6 (C), 140.8 (C), 128.0 (CH), 127.6 (CH), 129.1 (CH), 129.0 (CH), 128.8 (CH), 126.7 (CH), 125.8 (C), 103.1 (CH), 78.8 (CH), 70.2 (CH ₂), 57.2 (CH ₃), 42.7 (CH), 40.1 (CH ₂), 35.0 (CH ₂), 31.8 (CH ₂), 19.4 (CH ₂), 14.1 (CH ₃).		
<u>IR</u> :	(KBr)		
	2958 (m), 2935 (m), 2873 (m), 1603 (s), 1495 (w), 1454 (m), 1249 (m), 1219 (m), 1101 (s), 1074 (m)		
<u>MS</u> :	FAB		
	384 (65, M ⁺ –H), 368 (13), 352 (12), 205 (20), 135 (10), 121 (100), 119 (24)		
<u>HRMS</u> :	calcd for C ₂₃ H ₃₀ NO ₄ : 384.217484; found: 384.217400		
<u>TLC</u> :	R _f 0.21 [silica gel, hexane / <i>i</i> -PrOH, 20/1, anisaldehyde]		
<u>Analysis</u> :	C ₂₃ H ₂₉ NO ₄ (383.22)		
	Calculated:	C, 72.04;	H, 7.62; N, 3.65 %
	Found:	C, 71.91;	H, 7.66; N, 3.86 %

rel (4*R*, 6*R*)-6-Butoxy-3-[2-methoxy-2-(4-methoxyphenyl)-ethyl]-4-phenyl-5,6-dihydro-4*H*-1,2-oxazine *N*-oxide (**2m**)[†]

To a cold (-78°C) solution of pyridine (2.6 μL , 0.03 mmol, 0.05 equiv) in CH_2Cl_2 (0.7 mL) was added successively Me_3SiOTf (0.14 mL, 0.77 mmol, 1.2 equiv) and a solution of anisaldehyde dimethyl acetal (0.12 g, 0.68 mmol, 1.1 equiv) in CH_2Cl_2 (0.7 mL). Then a solution of nitrosal **1e''** (0.24 g, 0.64 mmol) in CH_2Cl_2 (1.3 mL) was added dropwise. The resultant mixture was stirred at -78°C for 1.5 h and a solution of BnEt_3NCl (0.28 g, 1.23 mmol, 1.9 equiv) in CH_2Cl_2 (2 mL) followed by Et_3N (0.30 mL, 2.15 mmol, 3.4 equiv) were added successively. After 5 min of stirring the mixture was poured into a mixture of H_2O (20 mL) and Et_2O (20 mL), organic layer was separated, aqueous layer was diluted with brine (5 mL) and back-extracted with ether (2×10 mL). The combined organic layers were washed with H_2O (15 mL), saturated aqueous NH_4Cl solution (10 mL), H_2O (15 mL), saturated aqueous NaHCO_3 solution (10 mL), H_2O (15 mL), brine (10 mL) and dried over Na_2SO_4 . The solvents were evaporated in vacuum and yellow residue was separated on preparative MPLC (Rexchrom 5/100 Silica, 25 cm $\times$ 21.1 mm, flow rate 15 mL / min, eluent: hexane / *i*-PrOH 1 / 30). The upper product was distilled to give the major isomer of the title compound **2m** as yellowish oil (0.11 g, 40 %), the lower product was recrystallized (Et_2O / hexane) to give the minor isomer of the title compound **2m** as white crystals (0.04 g, 15 %).

Analytical data for the major isomer of **2m**:

bp:	160 – 180 $^{\circ}\text{C}$ (8.0×10^{-5} mm Hg)
¹ H NMR:	(500 MHz, 300 K, CDCl_3) 7.34 – 7.19 (m, 7 H), 6.83 (d, $J = 8.6$, 2 H), 5.39 (t, $J = 2.4$, 1 H), 4.76 (dd, $J = 2.8$, 10.3, 1 H), 4.20 (dd, $J = 7.9$, 11.2, 1 H), 4.06 (dt, $J = 6.9$, 9.7, 1 H), 3.78 (s, 3 H), 3.68 (dt, $J = 6.9$, 9.7, 1 H), 3.21 (s, 3 H), 2.72 (dd, $J = 2.8$, 13.9, 1 H), 2.30 (ddd, $J = 2.1$, 7.8, 13.7, 1 H), 2.18 – 2.11 (m, 2 H), 1.71 – 1.65 (m, 2 H), 1.48 – 1.44 (m, 2 H), 0.98 (t, $J = 7.5$, 3 H).
¹³ C NMR:	(126 MHz, 300 K, CDCl_3) 159.4 (C), 140.8 (C), 133.7 (C), 129.5 (CH), 128.6 (CH), 127.8 (CH), 127.8 (CH), 125.9 (C), 114.1 (CH), 101.8 (CH), 78.7 (CH), 69.5 (CH_2), 57.0 (CH_3), 55.5 (CH_3), 41.4 (CH), 40.1 (CH_2), 34.7 (CH_2), 32.0 (CH_2), 19.5 (CH_2), 14.2 (CH_3).
IR:	(KBr) 2956 (m), 2935 (m), 2873 (w), 1610 (s), 1512 (s), 1512 (s), 1248 (s), 1099 (s)
MS:	FAB 414 (9, $\text{M}^+ - \text{H}$), 383 (11), 382 (46), 235 (14), 152 (12), 151 (100), 135 (9)
HRMS:	calcd for $\text{C}_{24}\text{H}_{32}\text{NO}_5$: 414.228048; found: 414.228000
TLC:	R_f 0.23 [silica gel, hexane / <i>i</i> -PrOH 20/1, anisaldehyde]
Analysis:	$\text{C}_{24}\text{H}_{31}\text{NO}_5$ (413.22) Calculated: C, 69.71; H, 7.56; N, 3.39 % Found: C, 69.83; H, 7.52; N, 3.63 %

[†]According to NMR data the C_6H_5 group adopts equatorial position in both isomers of **2m**.

Analytical data for the minor isomer of **2m**:

<u>mp</u> :	86 – 88 °C (Et ₂ O / hexane)
<u>¹H NMR</u> :	(500 MHz, 300 K, CDCl ₃) 7.32 – 7.24 (m, 3 H), 7.15 (dt, <i>J</i> = 2.8, 8.7, 2 H), 6.95 (dt, <i>J</i> = 2.1, 6.9, 2 H), 6.89 (dt, <i>J</i> = 1.9, 8.6, 2 H), 5.27 (t, <i>J</i> = 2.6, 1 H), 4.60 (dd, <i>J</i> = 5.4, 9.2, 1 H), 4.01 (dt, <i>J</i> = 6.7, 9.8, 1 H), 3.85 (s, 3 H), 3.61 (dt, <i>J</i> = 7.1, 9.9, 1 H), 3.18 – 3.13 (m, 4 H), 3.07 (t, <i>J</i> = 9.2, 1 H), 2.11 (dd, <i>J</i> = 9.2, 13.5, 1 H), 2.01 (m, 2 H), 1.66 (m, 2 H), 1.43 (m, 2 H), 0.99 (t, <i>J</i> = 7.3, 3 H)
<u>¹³C NMR</u> :	(126 MHz, 300 K, CDCl ₃) 159.8 (C), 140.3 (C), 133.4 (C), 129.4 (CH), 128.5 (CH), 127.9 (CH), 123.7 (C), 114.1 (CH), 101.6 (CH), 77.5 (CH), 69.6 (CH ₂), 56.4 (CH ₃), 55.6 (CH ₃), 40.2 (CH), 39.0 (CH ₂), 34.2 (CH ₂), 31.8 (CH ₂), 19.5 (CH ₂), 14.2 (CH ₃)
<u>IR</u> :	(KBr) 2956 (m), 2935 (m), 1610 (s), 1512 (s), 1244 (s), 1113 (m), 1095 (m)
<u>MS</u> :	FAB 414 (20, M ⁺ –H), 382 (90), 235 (30), 151 (100)
<u>HRMS</u> :	calcd for C ₂₄ H ₃₂ NO ₅ : 414.228048; found: 414.228000
<u>TLC</u> :	R _f 0.18 [silica gel, hexane / <i>i</i> -PrOH, 20/1, anisaldehyde]

rel (4*R*, 6*R*)-6-Butoxy-3-(2-dimethylamino-ethyl)-4-phenyl-5,6-dihydro-4*H*-1,2-oxazine *N*-oxide (**2n**)[†]

To a cold (0 °C) solution of nitrosal **1e''** (0.38 g, 1.01 mmol) in CH_2Cl_2 (2 mL) was added solid methylenedimethylammonium chloride (0.19 g, 2.03 mmol, 2 equiv). The mixture was allowed to warm to 20 °C in 1 h at stirring and poured into a mixture of Et_2O (20 mL) and H_2O (10 mL). The organic layer was separated and water phase was back-extracted with Et_2O (3×15 mL). The combined organic layers were washed with H_2O (15 mL), saturated aqueous solution of NaHCO_3 (10 mL), H_2O (15 mL), brine (10 mL), dried over Na_2SO_4 and evaporated in vacuum. The residue was recrystallized from hexane to give title compound **2n** as white crystals (0.29 g, 89 %).

Analytical data for **2n**:

<u>mp</u> :	40 – 42 °C (hexane)
<u>¹H NMR</u> :	(500 MHz, 300 K, CDCl_3)
	7.34 (tt, $J = 1.3, 6.9$, 2 H), 7.28 (tt, $J = 1.3, 6.0$, 1 H), 7.21 (dt, $J = 2.1, 7.1$, 2 H), 5.33 (t, $J = 2.6$, 1 H), 4.00 (dt, $J = 6.6, 9.4$, 1 H), 3.96 (dd, $J = 7.7, 11.2$, 1 H), 3.64 (dt, $J = 6.4, 9.4$, 1 H), 2.62 – 2.53 (m, 2 H), 2.29 – 2.21 (m, 2 H), 2.16 – 2.06 (m, 8 H), 1.65 – 1.58 (m, 2 H), 1.43 – 1.38 (m, 2 H), 0.94 (t, $J = 7.5$, 3 H)
<u>¹³C NMR</u> :	(126 MHz, 300 K, CDCl_3)
	140.5 (C), 129.5 (CH), 128.5 (CH), 128.0 (CH), 125.8 (C), 101.5 (CH), 69.3 (CH_2), 53.9 (CH_2), 45.4 (CH_3), 40.4 (CH), 34.8 (CH_2), 31.7 (CH_2), 29.1 (CH_2), 19.5 (CH_2), 14.1 (CH_3)
<u>IR</u> :	(KBr)
	2956 (m), 2941 (m), 2872 (m), 2818 (w), 2771 (w), 1606 (s), 1493 (w), 1456 (m), 1265 (m), 1215 (m), 1115 (s)
<u>MS</u> :	FAB
	321 (100, $\text{M}^+ - \text{H}$), 119 (12)
<u>HRMS</u> :	calcd for $\text{C}_{18}\text{H}_{29}\text{N}_2\text{O}_3$: 321.217818; found: 321.217700
<u>TLC</u> :	R_f 0.28 [silica gel, Et_2O / <i>i</i> -PrOH, 2/1, anisaldehyde]
<u>Analysis</u> :	$\text{C}_{18}\text{H}_{28}\text{N}_2\text{O}_3$ (320.22)
Calculated:	C, 67.47; H, 8.81; N, 8.74 %
Found:	C, 67.42; H, 8.88; N, 8.76 %

[†]According to NMR data the C_6H_5 group adopts equatorial, while *n*-BuO group adopts axial position in **2n**.

6-Methyl-3-morpholin-4-ylmethyl-4-phenyl-5,6-dihydro-4*H*-1,2-oxazin-6-ol (6a)[†] and 1-morpholin-4-yl-3-phenyl-hexane-2,5-dione 2-oxime (7a)

To a solution of nitrosal **1d** (0.31 g, 1 mmol) in CH₂Cl₂ (1 mL) was added simultaneously at ambient temperature morpholine (0.13 mL, 1.5 mmol). The reaction mixture was stirred for 5 min and CH₂Cl₂ was carefully evaporated at 300 mm Hg. The resulting solution was maintained at ambient temperature for 24 hours, diluted with MeOH (3 ml), and after 3 hours of stirring evaporated in vacuum. The residue was recrystallized from a mixture of EtOAc and hexane 1 : 10 to give a mixture of title compounds **6a** and **7a** (0.18 g, 60 %) as white powder.

Analytical data for a mixture **6a** and **7a**:

The ratio of tautomers **6a** and **7a** in DMSO is 1 : 1 at 20 °C and 1 : 3 at 70 °C.

mp: 99 – 103 °C (hexane/EtOAc, 10 : 1)

6a ¹H NMR: (300.13 MHz, 300 K, DMSO-*d*₆)

7.4 – 7.2 (m, 5 H), 6.44 (s, 1 H), 3.79 (dd, *J* = 5.2, 12.5, 1 H), 3.56 (m, 4 H), 2.80 (d, *J* = 12.3, 1 H), 2.56 (d, *J* = 12.3, 1 H), 2.4 – 2.0 (m, 5 H), 1.89 (dd, *J* = 12.4, 12.5, 1 H), 1.49 (s, 3H).

¹³C NMR: (75.47 MHz, 300 K, DMSO-*d*₆)

156.6(C), 140.6 (C), 128.5 (CH), 128.1 (CH), 126.6 (CH), 94.6 (C), 66.2 (CH₂), 59.7 (CH₂), 52.6 (CH₂), 37.9 (CH₂), 37.0 (CH), 26.8 (CH₃)

7a ¹H NMR: (300.13 MHz, 300 K, DMSO-*d*₆)

10.81 (s, 1 H), 7.4 – 7.2 (m, 5 H), 4.79 (dd, *J* = 7.8, 7.3, 1 H), 3.51 (m, 4 H), 3.28 (dd, *J* = 7.8, 17.1, 1 H), 3.05 (dd, *J* = 7.3, 17.1, 1 H), 2.93 (d, *J* = 12.5, 1 H), 2.69 (d, *J* = 12.5, 1 H), 2.4 – 2.0 (m, 4 H), 2.12 (s, 3 H)

¹³C NMR: (75.47 MHz, 300 K, DMSO-*d*₆)

205.8 (C), 154.7 (C), 140.7 (C), 128.4 (CH), 127.9 (CH), 126.1 (CH), 66.0 (CH₂), 59.7 (CH₂), 53.0 (CH₂), 44.6 (CH₂), 37.6 (CH), 29.8 (CH₃) .

TLC: *R_f* 0.11 (silica gel, EtOAc, UV)

Analysis: C₁₆H₂₂N₂O₃ (290.16)

Calculated: C, 66.18; H, 7.64; N, 9.65 %

Found: C, 66.20; H, 7.40; N, 9.76 %

[†]According to NMR data the C₆H₅ group adopts equatorial position in **6a**. The OH group is postulated to be axial.

6-Methyl-3-morpholin-4-ylmethyl-4-phenyl-5,6-dihydro-4*H*-1,2-oxazin-6-ol (6b) and 1-morpholin-4-yl-3-phenyl-hexane-2,5-dione 2-oxime (7b)

To a solution of nitrosal **1a** (0.31 g, 1 mmol) in CH_2Cl_2 (1 mL) was added simultaneously at ambient temperature morpholine (0.13 mL, 1.5 mmol). The reaction mixture was stirred for 5 min and CH_2Cl_2 was carefully evaporated at 300 mm Hg. The resulting solution was maintained at ambient temperature for 24 hours, diluted with MeOH (3 ml), and after 3 hours of stirring evaporated in vacuum. The residue was recrystallized from a mixture of EtOAc and hexane 1 : 10 to give a mixture of title compounds **6b** and **7b** (0.18 g, 60 %) as white powder.

Analytical data for a mixture **6b** and **7b**:

The ratio of tautomers **6b** and **7b** in DMSO is 1 : 1 at 20 °C and 1 : 3 at 70 °C.

mp: 117 – 122 °C (hexane/EtOAc, 10/1)

6b ^1H NMR: (300.13 MHz, 300 K, DMSO- D_6)

7.18 (d, $J = 8.5$, 2 H), 6.88 (d, $J = 8.5$, 2 H), 6.31 (s, 1 H), 3.78 (s, 3 H), 3.65 (dd, $J = 5.2$, 12.7, 1 H), 3.51 (m, 4 H), 2.76 (d, $J = 12.5$, 1 H), 2.58 (d, $J = 12.5$, 1 H), 2.4 – 2.1 (m, 5 H), 1.84 (dd, $J = 12.4$, 12.7, 1 H), 1.44 (s, 3 H)

^{13}C NMR: (75.47 MHz, 300 K, CDCl_3)

158.0 (C), 156.4 (C), 132.1 (C), 129.0 (CH), 113.7 (CH), 94.2 (C), 65.8 (CH_2), 59.1 (CH_2), 54.7 (CH_3), 52.2 (CH_2), 37.9 (CH_2), 35.8 (CH), 26.9 (CH_3).

7b ^1H NMR: (300.13 MHz, 300 K, DMSO- D_6)

10.72 (s, 1 H), 7.30 (d, $J = 8.5$, 2 H), 6.80 (d, $J = 8.5$, 2 H), 4.71 (dd, $J = 7.3$, 7.8, 1 H), 3.78 (s, 3 H), 3.51 (m, 4 H), 3.24 (dd, $J = 7.8$, 17.1, 1 H), 3.05 (dd, $J = 7.3$, 17.1, 1 H), 2.91 (d, $J = 12.5$, 1 H), 2.71 (d, $J = 12.5$, 1 H), 2.4 – 2.1 (m, 4 H), 2.08 (s, 3 H)

^{13}C NMR: (75.47 MHz, 300 K, CDCl_3)

205.3 (C), 157.5 (C), 154.8 (C), 132.3 (C), 128.7 (CH), 113.2 (CH), 65.6 (CH_2), 59.3 (CH_2), 54.7 (CH_3), 52.7 (CH_2), 44.6 (CH_2), 37.1 (CH), 29.0 (CH_3).

TLC: R_f 0.08 (silica gel, EtOAc, UV)

Analysis: $\text{C}_{17}\text{H}_{24}\text{N}_2\text{O}_4$ (320.39)

Calculated: C, 63.73; H, 7.55; N, 8.74 %

Found: C, 63.70; H, 7.55; N, 8.70 %

[†]According to NMR data the 4-MeOC₆H₄ group adopts equatorial position in **6b**. The OH group is postulated to be axial.

Table S1. Crystal data and structure refinement for **1a**

Identification code	1a
Empirical formula	C ₁₆ H ₂₆ NO ₃ Si
Formula weight	308.47
Temperature	163(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	p2(1)/n
Unit cell dimensions	a = 10.786(3) Å α = 90°. b = 12.596(4) Å β = 98.51(3)°. c = 14.031(5) Å γ = 90°.
Volume	1885.3(10) Å ³
Z	4
Density (calculated)	1.087 Mg/m ³
Absorption coefficient	0.133 mm ⁻¹
F(000)	668
Crystal size	0.3 x 0.5 x 0.8 mm ³
Theta range for data collection	2.18 to 25.05°.
Index ranges	0 ≤ h ≤ 12, 0 ≤ k ≤ 15, -16 ≤ l ≤ 16
Reflections collected	3510
Independent reflections	3327 [R(int) = 0.0251]
Completeness to theta = 25.05°	99.6 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3327 / 0 / 216
Goodness-of-fit on F ²	1.025
Final R indices [for 2820 rflns with I > 2σ(I)]	R1 = 0.0435, wR2 = 0.1154
R indices (all data)	R1 = 0.0567, wR2 = 0.1217
Largest diff. peak and hole	0.462 and -0.288 e. Å ⁻³

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1a**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	2279(1)	8498(1)	8038(1)	28(1)
O(1)	1754(1)	7835(1)	10409(1)	27(1)
N(1)	2297(1)	7374(1)	9592(1)	24(1)
C(2A)	2992(2)	7514(2)	7306(2)	47(1)
O(2)	1505(1)	7858(1)	8823(1)	27(1)
C(2B)	993(2)	9245(2)	7318(2)	41(1)
O(3)	3638(1)	7651(1)	11466(1)	35(1)
C(2C)	3508(2)	9375(2)	8660(2)	42(1)
C(3)	2084(2)	6244(1)	9580(1)	24(1)
O(4)	2478(1)	1238(1)	10304(1)	43(1)
C(4)	2739(2)	5736(1)	10498(1)	25(1)
C(5)	2225(2)	6246(2)	11352(1)	30(1)
C(6)	2345(2)	7444(2)	11321(1)	29(1)
C(7)	1500(2)	5746(2)	8816(1)	30(1)
C(8)	2651(2)	4537(2)	10487(1)	26(1)
C(9)	1533(2)	4019(2)	10533(1)	30(1)
C(10)	1430(2)	2919(2)	10478(1)	32(1)
C(11)	2474(2)	2327(2)	10373(1)	30(1)
C(12)	3609(2)	2823(2)	10337(1)	32(1)
C(13)	3693(2)	3916(2)	10398(1)	29(1)
C(17)	1646(2)	8012(2)	12031(2)	41(1)
C(18)	4006(2)	8732(2)	11442(2)	48(1)
C(19)	1303(2)	718(2)	10277(2)	52(1)

Table S3. Bond lengths [Å] and angles [°] for **1a**.

Si(1)-O(2)	1.6825(14)	O(4)-C(11)	1.375(2)
Si(1)-C(2C)	1.844(2)	O(4)-C(19)	1.422(3)
Si(1)-C(2A)	1.847(2)	C(4)-C(8)	1.513(3)
Si(1)-C(2B)	1.848(2)	C(4)-C(5)	1.532(3)
O(1)-C(6)	1.430(2)	C(5)-C(6)	1.516(3)
O(1)-N(1)	1.4806(19)	C(6)-C(17)	1.515(3)
N(1)-O(2)	1.4128(19)	C(8)-C(9)	1.381(3)
N(1)-C(3)	1.442(2)	C(8)-C(13)	1.389(3)
O(3)-C(6)	1.404(2)	C(9)-C(10)	1.390(3)
O(3)-C(18)	1.420(3)	C(10)-C(11)	1.377(3)
C(3)-C(7)	1.318(3)	C(11)-C(12)	1.383(3)
C(3)-C(4)	1.517(2)	C(12)-C(13)	1.382(3)
O(2)-Si(1)-C(2C)	111.64(9)	C(3)-C(4)-C(5)	108.09(15)
O(2)-Si(1)-C(2A)	109.31(10)	C(6)-C(5)-C(4)	110.65(15)
C(2C)-Si(1)-C(2A)	109.61(12)	O(3)-C(6)-O(1)	111.55(15)
O(2)-Si(1)-C(2B)	101.38(9)	O(3)-C(6)-C(17)	113.39(16)
C(2C)-Si(1)-C(2B)	112.47(11)	O(1)-C(6)-C(17)	103.10(15)
C(2A)-Si(1)-C(2B)	112.19(11)	O(3)-C(6)-C(5)	105.51(15)
C(6)-O(1)-N(1)	112.43(13)	O(1)-C(6)-C(5)	109.88(15)
O(2)-N(1)-C(3)	109.85(13)	C(17)-C(6)-C(5)	113.52(17)
O(2)-N(1)-O(1)	99.03(12)	C(9)-C(8)-C(13)	117.49(18)
C(3)-N(1)-O(1)	108.44(13)	C(9)-C(8)-C(4)	121.65(17)
N(1)-O(2)-Si(1)	113.85(10)	C(13)-C(8)-C(4)	120.82(16)
C(6)-O(3)-C(18)	116.71(16)	C(8)-C(9)-C(10)	122.09(18)
C(7)-C(3)-N(1)	122.41(17)	C(11)-C(10)-C(9)	119.09(18)
C(7)-C(3)-C(4)	126.63(17)	O(4)-C(11)-C(10)	124.07(18)
N(1)-C(3)-C(4)	110.62(14)	O(4)-C(11)-C(12)	115.83(17)
C(11)-O(4)-C(19)	116.65(16)	C(10)-C(11)-C(12)	120.10(18)
C(8)-C(4)-C(3)	113.03(15)	C(13)-C(12)-C(11)	119.88(18)
C(8)-C(4)-C(5)	113.39(15)	C(12)-C(13)-C(8)	121.33(17)

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Si(1)	29(1)	30(1)	25(1)	6(1)	3(1)	-3(1)
O(1)	29(1)	29(1)	22(1)	-2(1)	2(1)	4(1)
N(1)	27(1)	26(1)	20(1)	2(1)	4(1)	0(1)
C(2A)	53(1)	50(1)	41(1)	1(1)	20(1)	0(1)
O(2)	27(1)	30(1)	24(1)	6(1)	0(1)	-1(1)
C(2B)	38(1)	45(1)	38(1)	16(1)	0(1)	-2(1)
O(3)	30(1)	33(1)	39(1)	-3(1)	-7(1)	-4(1)
C(2C)	40(1)	43(1)	40(1)	8(1)	0(1)	-13(1)
C(3)	23(1)	25(1)	25(1)	2(1)	9(1)	-2(1)
O(4)	41(1)	25(1)	61(1)	-2(1)	4(1)	-2(1)
C(4)	22(1)	25(1)	27(1)	3(1)	2(1)	-2(1)
C(5)	34(1)	33(1)	23(1)	2(1)	3(1)	-2(1)
C(6)	29(1)	33(1)	22(1)	0(1)	0(1)	-1(1)
C(7)	37(1)	28(1)	27(1)	0(1)	5(1)	-3(1)
C(8)	28(1)	27(1)	23(1)	4(1)	3(1)	-1(1)
C(9)	25(1)	27(1)	37(1)	4(1)	5(1)	0(1)
C(10)	27(1)	31(1)	37(1)	5(1)	2(1)	-5(1)
C(11)	38(1)	24(1)	28(1)	2(1)	1(1)	-1(1)
C(12)	32(1)	31(1)	35(1)	-1(1)	8(1)	5(1)
C(13)	25(1)	32(1)	30(1)	3(1)	6(1)	-2(1)
C(17)	53(1)	44(1)	28(1)	-5(1)	7(1)	5(1)
C(18)	44(1)	41(1)	53(1)	-5(1)	-6(1)	-14(1)
C(19)	48(1)	26(1)	79(2)	1(1)	3(1)	-8(1)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1a**.

	x	y	z	U(eq)
H(1SA)	3668	7139	7715	70
H(1SB)	3333	7879	6785	70
H(1SC)	2352	7004	7030	70
H(2SA)	647	9759	7732	61
H(2SB)	333	8751	7044	61
H(2SC)	1318	9621	6795	61
H(3SA)	4168	8944	9030	63
H(3SB)	3142	9848	9098	63
H(3SC)	3868	9800	8183	63
H(4A)	3647	5925	10558	30
H(5A)	1333	6049	11330	36
H(5B)	2695	5974	11963	36
H(7A)	1436(19)	4997(19)	8806(16)	35(6)
H(7B)	1082(19)	6137(17)	8250(16)	31(5)
H(9A)	811	4426	10604	36
H(10A)	650	2582	10511	38
H(12A)	4331	2413	10270	39
H(13A)	4479	4250	10379	35
H(17A)	1757	8781	11973	62
H(17B)	1978	7787	12688	62
H(17C)	753	7838	11892	62
H(18A)	4923	8779	11554	71
H(18B)	3662	9127	11944	71
H(18C)	3686	9035	10810	71
H(19A)	1419	-50	10225	78
H(19B)	723	970	9719	78
H(19C)	957	876	10869	78

Table S6. Torsion angles [°] for **1a**.

C(6)-O(1)-N(1)-O(2)	177.37(13)	N(1)-O(1)-C(6)-C(17)	-179.87(14)
C(6)-O(1)-N(1)-C(3)	62.82(17)	N(1)-O(1)-C(6)-C(5)	-58.54(18)
C(3)-N(1)-O(2)-Si(1)	-119.31(12)	C(4)-C(5)-C(6)-O(3)	-65.78(18)
O(1)-N(1)-O(2)-Si(1)	127.23(10)	C(4)-C(5)-C(6)-O(1)	54.6(2)
C(2C)-Si(1)-O(2)-N(1)	-48.50(14)	C(4)-C(5)-C(6)-C(17)	169.45(16)
C(2A)-Si(1)-O(2)-N(1)	72.93(14)	C(3)-C(4)-C(8)-C(9)	-70.1(2)
C(2B)-Si(1)-O(2)-N(1)	-168.46(12)	C(5)-C(4)-C(8)-C(9)	53.4(2)
O(2)-N(1)-C(3)-C(7)	16.9(2)	C(3)-C(4)-C(8)-C(13)	107.82(19)
O(1)-N(1)-C(3)-C(7)	124.14(18)	C(5)-C(4)-C(8)-C(13)	-128.71(18)
O(2)-N(1)-C(3)-C(4)	-169.38(13)	C(13)-C(8)-C(9)-C(10)	-1.0(3)
O(1)-N(1)-C(3)-C(4)	-62.14(17)	C(4)-C(8)-C(9)-C(10)	176.94(17)
C(7)-C(3)-C(4)-C(8)	-1.1(3)	C(8)-C(9)-C(10)-C(11)	0.0(3)
N(1)-C(3)-C(4)-C(8)	-174.54(14)	C(19)-O(4)-C(11)-C(10)	4.2(3)
C(7)-C(3)-C(4)-C(5)	-127.5(2)	C(19)-O(4)-C(11)-C(12)	-176.07(19)
N(1)-C(3)-C(4)-C(5)	59.11(18)	C(9)-C(10)-C(11)-O(4)	-179.49(18)
C(8)-C(4)-C(5)-C(6)	179.84(15)	C(9)-C(10)-C(11)-C(12)	0.8(3)
C(3)-C(4)-C(5)-C(6)	-54.02(19)	O(4)-C(11)-C(12)-C(13)	179.80(17)
C(18)-O(3)-C(6)-O(1)	59.0(2)	C(10)-C(11)-C(12)-C(13)	-0.5(3)
C(18)-O(3)-C(6)-C(17)	-56.9(2)	C(11)-C(12)-C(13)-C(8)	-0.6(3)
C(18)-O(3)-C(6)-C(5)	178.30(17)	C(9)-C(8)-C(13)-C(12)	1.4(3)
N(1)-O(1)-C(6)-O(3)	58.11(18)	C(4)-C(8)-C(13)-C(12)	-176.62(17)

Figure S2. Crystal structure of **2a**. Thermal displacement ellipsoids are shown at the 50 % probability level.

Table S2. Crystal data and structure refinement for 1,2-oxazine *N*-oxide **2a**.

Identification code	2a	
Empirical formula	C ₁₄ H ₁₉ NO ₄	
Formula weight	265.30	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.831(4) Å	α = 87.022(10)°.
	b = 8.097(4) Å	β = 71.556(13)°.
	c = 11.193(6) Å	γ = 85.261(12)°.
Volume	670.7(6) Å ³	
Z	2	
Density (calculated)	1.314 Mg/m ³	
Absorption coefficient	0.096 mm ⁻¹	
F(000)	284	
Crystal size	0.3 x 0.4 x 0.7 mm ³	
Theta range for data collection	1.92 to 28.07°.	
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 10, -14 ≤ l ≤ 14	
Reflections collected	6003	
Independent reflections	2840 [R(int) = 0.0511]	
Completeness to theta = 28.07°	86.9 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2840 / 0 / 248	
Goodness-of-fit on F ²	0.881	
Final R indices [for 1453 rflns with I > 2σ(I)]	R1 = 0.0631, wR2 = 0.1461	
R indices (all data)	R1 = 0.1148, wR2 = 0.1723	
Largest diff. peak and hole	0.429 and -0.248 e. Å ⁻³	

Table S8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	4084(2)	6727(2)	5358(2)	27(1)
O(2)	6674(2)	7199(2)	5665(2)	33(1)
N(1)	5147(3)	6629(2)	6192(2)	25(1)
O(3)	1623(2)	8298(2)	6673(2)	29(1)
C(3)	4552(3)	5992(3)	7328(2)	25(1)
O(4)	2780(3)	-1174(2)	10020(2)	36(1)
C(4)	2696(3)	5379(3)	7877(2)	24(1)
C(5)	1696(4)	5387(3)	6901(2)	27(1)
C(6)	2140(3)	6838(3)	5978(2)	25(1)
C(7)	5769(4)	5993(4)	8119(3)	32(1)
C(8)	2768(3)	3656(3)	8502(2)	24(1)
C(9)	3741(3)	2300(3)	7789(2)	29(1)
C(10)	3724(4)	730(3)	8328(2)	29(1)
C(11)	2740(4)	441(3)	9583(2)	28(1)
C(12)	1802(3)	1769(3)	10312(2)	27(1)
C(13)	1849(3)	3350(3)	9760(2)	26(1)
C(14)	1378(4)	6784(4)	4898(3)	30(1)
C(15)	2012(4)	9814(3)	5935(3)	35(1)
C(16)	1714(5)	-1513(4)	11288(3)	39(1)

Table S9. Bond lengths [Å] and angles [°] for **2a**.

O(1)-N(1)	1.429(3)	C(4)-C(5)	1.532(4)
O(1)-C(6)	1.457(3)	C(4)-C(8)	1.533(4)
O(2)-N(1)	1.268(3)	C(5)-C(6)	1.510(4)
N(1)-C(3)	1.302(3)	C(6)-C(14)	1.512(4)
O(3)-C(6)	1.408(3)	C(8)-C(13)	1.383(3)
O(3)-C(15)	1.442(3)	C(8)-C(9)	1.411(3)
C(3)-C(7)	1.492(4)	C(9)-C(10)	1.377(4)
C(3)-C(4)	1.503(3)	C(10)-C(11)	1.391(4)
O(4)-C(11)	1.374(3)	C(11)-C(12)	1.394(4)
O(4)-C(16)	1.426(4)	C(12)-C(13)	1.391(4)
N(1)-O(1)-C(6)	114.86(17)	O(1)-C(6)-C(5)	107.9(2)
O(2)-N(1)-C(3)	127.3(2)	O(3)-C(6)-C(14)	114.2(2)
O(2)-N(1)-O(1)	111.17(18)	O(1)-C(6)-C(14)	103.40(19)
C(3)-N(1)-O(1)	121.5(2)	C(9)-C(10)-C(11)	120.9(2)
C(6)-O(3)-C(15)	114.9(2)	O(4)-C(11)-C(10)	116.3(2)
N(1)-C(3)-C(7)	116.6(2)	O(4)-C(11)-C(12)	124.4(2)
N(1)-C(3)-C(4)	123.2(2)	C(10)-C(11)-C(12)	119.3(2)
C(7)-C(3)-C(4)	120.1(2)	C(13)-C(12)-C(11)	119.1(2)
C(11)-O(4)-C(16)	117.2(2)	C(8)-C(13)-C(12)	122.4(2)
C(3)-C(4)-C(5)	112.3(2)	C(5)-C(6)-C(14)	113.8(2)
C(3)-C(4)-C(8)	111.2(2)	C(13)-C(8)-C(9)	117.4(2)
C(5)-C(4)-C(8)	111.0(2)	C(13)-C(8)-C(4)	122.1(2)
C(6)-C(5)-C(4)	111.7(2)	C(9)-C(8)-C(4)	120.4(2)
O(3)-C(6)-O(1)	109.76(19)	C(10)-C(9)-C(8)	120.7(2)
O(3)-C(6)-C(5)	107.6(2)		

Table S10. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
O(1)	23(1)	33(1)	23(1)	2(1)	-4(1)	0(1)
O(2)	23(1)	34(1)	38(1)	5(1)	-3(1)	-7(1)
N(1)	22(1)	22(1)	30(1)	1(1)	-6(1)	0(1)
O(3)	30(1)	22(1)	29(1)	1(1)	-3(1)	1(1)
C(3)	28(1)	20(1)	26(1)	1(1)	-6(1)	0(1)
O(4)	41(1)	26(1)	35(1)	7(1)	-5(1)	2(1)
C(4)	24(1)	24(1)	22(1)	0(1)	-3(1)	-1(1)
C(5)	27(1)	23(1)	27(1)	3(1)	-5(1)	-3(1)
C(6)	22(1)	24(1)	27(1)	1(1)	-4(1)	-3(1)
C(7)	31(2)	34(2)	32(2)	2(1)	-11(1)	-4(1)
C(8)	26(1)	22(1)	23(1)	3(1)	-5(1)	-3(1)
C(9)	30(1)	29(2)	23(1)	2(1)	-2(1)	-4(1)
C(10)	31(1)	23(1)	31(1)	0(1)	-7(1)	2(1)
C(11)	30(1)	23(1)	30(1)	6(1)	-9(1)	-4(1)
C(12)	27(1)	29(1)	22(1)	4(1)	-5(1)	-4(1)
C(13)	27(1)	26(1)	23(1)	-1(1)	-7(1)	-1(1)
C(14)	27(1)	30(2)	33(2)	3(1)	-8(1)	-3(1)
C(15)	47(2)	22(2)	37(2)	3(1)	-15(2)	-3(1)
C(16)	44(2)	33(2)	38(2)	14(1)	-9(2)	-7(1)

Table S11. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2a**.

	x	y	z	U(eq)
H(4)	2000(30)	6190(30)	8550(20)	17(6)
H(5B)	2020(30)	4340(30)	6400(20)	20(6)
H(5A)	380(40)	5390(30)	7300(20)	19(6)
H(7C)	6970(70)	5390(60)	7760(40)	114(17)
H(7B)	6060(70)	7020(70)	8040(50)	109(17)
H(7A)	5210(70)	5480(60)	8820(50)	96(16)
H(9)	4410(30)	2480(30)	6920(20)	19(6)
H(10)	4480(40)	-210(30)	7840(20)	28(7)
H(12)	1160(40)	1500(30)	11220(20)	28(7)
H(13)	1230(30)	4340(30)	10240(20)	16(6)
H(14C)	1720(40)	5780(40)	4600(30)	46(9)
H(14B)	1950(40)	7640(40)	4250(30)	36(8)
H(14A)	50(50)	6980(40)	5190(30)	47(9)
H(15C)	1350(50)	10030(40)	5320(30)	58(10)
H(15B)	3400(50)	9820(40)	5500(30)	58(10)
H(15A)	1890(40)	10670(40)	6450(30)	38(8)
H(16C)	1870(40)	-2730(40)	11400(30)	40(8)
H(16B)	420(50)	-1200(40)	11420(30)	46(9)
H(16A)	2160(40)	-910(40)	11770(30)	33(8)

Table S12. Torsion angles [°] for **2a**.

C(6)-O(1)-N(1)-O(2)	-153.34(19)	C(4)-C(5)-C(6)-O(1)	58.5(3)
C(6)-O(1)-N(1)-C(3)	27.9(3)	C(4)-C(5)-C(6)-C(14)	172.6(2)
O(2)-N(1)-C(3)-C(7)	2.7(4)	C(3)-C(4)-C(8)-C(13)	121.7(2)
O(1)-N(1)-C(3)-C(7)	-178.7(2)	C(5)-C(4)-C(8)-C(13)	-112.5(3)
O(2)-N(1)-C(3)-C(4)	178.7(2)	C(3)-C(4)-C(8)-C(9)	-60.5(3)
O(1)-N(1)-C(3)-C(4)	-2.7(3)	C(5)-C(4)-C(8)-C(9)	65.2(3)
N(1)-C(3)-C(4)-C(5)	7.2(3)	C(13)-C(8)-C(9)-C(10)	1.7(4)
C(7)-C(3)-C(4)-C(5)	-176.9(2)	C(4)-C(8)-C(9)-C(10)	-176.2(2)
N(1)-C(3)-C(4)-C(8)	132.3(2)	C(8)-C(9)-C(10)-C(11)	0.4(4)
C(7)-C(3)-C(4)-C(8)	-51.8(3)	C(16)-O(4)-C(11)-C(10)	-177.2(3)
C(3)-C(4)-C(5)-C(6)	-35.4(3)	C(16)-O(4)-C(11)-C(12)	3.2(4)
C(8)-C(4)-C(5)-C(6)	-160.5(2)	C(9)-C(10)-C(11)-O(4)	178.5(2)
C(15)-O(3)-C(6)-O(1)	60.9(3)	C(9)-C(10)-C(11)-C(12)	-1.8(4)
C(15)-O(3)-C(6)-C(5)	178.0(2)	O(4)-C(11)-C(12)-C(13)	-179.3(2)
C(15)-O(3)-C(6)-C(14)	-54.7(3)	C(10)-C(11)-C(12)-C(13)	1.0(4)
N(1)-O(1)-C(6)-O(3)	62.1(2)	C(9)-C(8)-C(13)-C(12)	-2.5(4)
N(1)-O(1)-C(6)-C(5)	-54.8(2)	C(4)-C(8)-C(13)-C(12)	175.3(2)
N(1)-O(1)-C(6)-C(14)	-175.64(19)	C(11)-C(12)-C(13)-C(8)	1.1(4)
C(4)-C(5)-C(6)-O(3)	-59.8(3)		

Dynamic NMR section

Typical procedure for the measuring of activation parameters. The ^1H spectra of **1g** have been measured in CDCl_3 at ten different temperatures. In the slow exchange region the temperature dependencies of resonance frequencies of analyzed signals and ratios of isomers were built. Then each spectrum in the region of middle exchange has been subjected to a complete line shape analysis by program DYNMR⁹ based on Bloch equation (variables for iteration: resonance frequencies (found by the extrapolation of temperature dependence from the slow-exchange region, ratios of isomers). The sum of rate constants of direct and reverse exchange has been measured for each spectrum. The results were examined by the estimation in the fast exchange region using known formulas. Coincidence of results was the guarantee of their correctness. The results are followed:

Figure S3. The experimental and calculated split of lines in ^1H NMR spectra of **1g** (the signals of one of protons of terminal $\text{CH}_2=$ group fragment)

⁹ Shastin, A. V.; Godovikova, T. I.; Golova, S. P.; Povorin, M. V.; Dmitriev, D. E.; Dekaprilevich, M.O.; Strelenko, Yu. A.; Struchkov, Yu. T.; Khmelnytsky, L. I.; Korsunsky, B. L. *Khim. Geter. Soed.* **1995**, 5, 679 (Russ.); *Chem. Abstr.* **1996**, 124, 145027c.

T, K	Sum of rate constants	k, sec ⁻¹	k, sec ⁻¹
259	30.4	6.8	23.6
263	45.1	9.2	35.9
267	78.9	17.6	61.3
271	100	22	78
275	145.9	32.1	113.8
280	239.0	53.3	185.7
285	258.7	57.7	201.0
290	620.2	138.3	481.9
295	653.4	145.7	507.7

The obtained rate constants have been plotted in coordinates $\{1/RT, \ln(k/T)\}$ after least squares linear fit for the function $Y = a \times (X) + b$ for each isomer.

Figure S4. The plot of rate constant – temperature dependence after least squares linear fit:

major isomer: $a = -53151.44137 \pm 2664.43896$, $b = 21.08124 \pm 1.16323$, R-factor = -0.9901

minor isomer: $a = -52423.12326 \pm 2698.61544$, $b = 22.03289 \pm 1.17925$, R-factor = -0.99085.

The activation parameters calculated by Eyring equation:

major isomer: $\Delta H^\ddagger = 53.2 \pm 2.7$ kJ/mol, $\Delta S^\ddagger = -22.3 \pm 9.7$ J/mol $\times$ K, $\Delta G^\ddagger_{298} = 59.8 \pm 2.9$ kJ/mol

minor isomer: $\Delta H^\ddagger = 52.4 \pm 2.7$ kJ/mol, $\Delta S^\ddagger = -14.4 \pm 9.8$ J/mol $\times$ K, $\Delta G^\ddagger_{298} = 56.7 \pm 2.9$ kJ/mol

$$T_{\text{coal.}} = 280 \text{ K}$$

$$K_{298} = 0.29, \Delta G^0_{298} = 3.1 \text{ kJ/mol}$$

Nitrosal 1c: nucleus ^1H ; solvent: CDCl_3

major isomer: R-factor = -0.99202, $\Delta H^\ddagger = 49.4 \pm 2.5$ kJ/mol, $\Delta S^\ddagger = -35.7 \pm 8.9$ J/mol $\times$ K, $\Delta G^\ddagger_{298} = 60.1 \pm 2.7$ kJ/mol,

minor isomer: R-factor = -0.99203, $\Delta H^\ddagger = 47.6 \pm 2.4$ kJ/mol, $\Delta S^\ddagger = -37.1 \pm 8.5$ J/mol $\times$ K, $\Delta G^\ddagger_{298} = 58.6 \pm 2.5$ kJ/mol.

$$T_{\text{coal.}} = 286 \text{ K}$$

$$K_{298} = 0.55, \Delta G^0_{298} = 1.5 \text{ kJ/mol}$$

T, K	Sum of rate constants	k, sec ⁻¹	k, sec ⁻¹
268	50.1	15.4	34.7
271	62.8	21.7	41.1
274	87.4	31.5	55.8
277	108.9	41.3	67.6
280	156	52.6	103.4
286	174.1	61.8	112.3
297	474.5	168.5	306.1
303	763.6	271.1	492.5

Nitrosal 1b: Nucleus ^1H ; Solvent: CDCl_3

major isomer: R-factor = -0.99802 , $\Delta H^\ddagger = 108.2 \pm 3.0$ kJ/mol, $\Delta S^\ddagger = 176.4 \pm 11.0$ J/mol $\times$ K, $\Delta G^\ddagger_{298} = 55.7 \pm 3.3$ kJ/mol,

minor isomer: R-factor = -0.99039 , $\Delta H^\ddagger = 107.3 \pm 3.1$ kJ/mol, $\Delta S^\ddagger = 185.7 \pm 11.6$ J/mol $\times$ K, $\Delta G^\ddagger_{298} = 52.0 \pm 3.4$ kJ/mol.

$$T_{\text{coal.}} = 280 \text{ K}$$

$$K_{298} = 0.23, \Delta G^\circ_{298} = 3.7 \text{ kJ/mol}$$

T, K	Sum of rate constants	k, sec $^{-1}$	k, sec $^{-1}$
259	7.4	1.2	6.1
263	15.5	2.8	12.7
267	34.83	6.2	28.6
271	65	11.8	53.2
275	128.9	23.5	105.4
280	423.2	76.2	347.0
289	1326.6	238.8	1087.8

Nitrosal 1a: Nucleus ^1H ; Solvent: CDCl_3

major isomer: R-factor = -0.99184 , $\Delta H^\ddagger = 50.5 \pm 2.9$ kJ/mol, $\Delta S^\ddagger = -29.2 \pm 11.1$ J/mol $\times$ K, $\Delta G^\ddagger_{298} = 59.2 \pm 3.3$ kJ/mol,

minor isomer: R-factor = -0.99039 , $\Delta H^\ddagger = 47.0 \pm 3.3$ kJ/mol, $\Delta S^\ddagger = -27.5 \pm 13.4$ J/mol $\times$ K, $\Delta G^\ddagger_{298} = 55.2 \pm 4.0$ kJ/mol.

$$T_{\text{coal.}} = 278 \text{ K}$$

$$K_{298} = 0.18, \Delta G^\circ_{298} = 4.2 \text{ kJ/mol}$$

T, K	Sum of rate constants	k, sec $^{-1}$	k, sec $^{-1}$
236	8	0.8	7.2
240	12	1.2	10.7
244	19.4	2.8	16.6
248	26.6	4.0	22.6
252	34.7	4.8	29.9
254	55.1	7.3	47.8