Metal-Free 2,2,6,6-Tetramethylpiperidin-1-yloxy Radical (TEMPO) Catalyzed Aerobic Oxidation of Hydroxylamines and Alkoxyamines to Oximes and Oxime Ethers

by **Sebastian Wertz** and **Armido Studer***

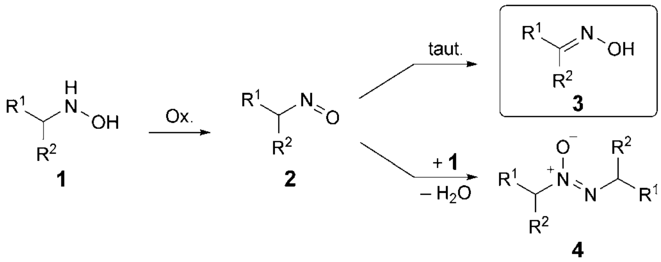
Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstr. 40,
DE-48149 Münster (phone: +49-251-8333291; fax: +49-251-8336523;
e-mail: studer@uni-muenster.de)

Dedicated to Prof. *Dieter Seebach* on the occasion of his 75th birthday

TEMPO-Mediated oxidation of hydroxylamines (=hydroxyamines) and alkoxyamines to the corresponding oxime derivatives is reported (TEMPO=2,2,6,6-tetramethylpiperidin-1-yloxy radical; *Scheme 2*). These environmentally benign oxidations proceed in good to excellent yields (*Table 1*). For alkoxyamines, oxidation to the corresponding oxime ethers can be performed by using dioxygen as a terminal oxidant in the presence of 5–10 mol-% of TEMPO or 4-substituted derivatives thereof as a catalyst (*Scheme 3* and *Table 2*). Importantly, benzyl bromides can directly be transformed to oxime ethers *via in situ* alkoxyamine formation by a nucleophilic substitution followed by TEMPO-mediated oxidation (*Scheme 4* and *Table 3*).

Introduction. – As valuable intermediates in organic synthesis [1] as well as in biosynthesis [2] and therapeutics [2][3], oximes and derivatives thereof have been intensively investigated. Condensation of aldehydes and ketones with hydroxylamines is the most commonly used synthetic route to oximes. Other methods for oxime formation not discussed in detail herein are also known [4]. In biological systems, formation of oximes as final metabolites in the degradation of biogenic amines is reported to presumably occur *via* an alternative pathway, namely *via* the oxidation of intermediately formed hydroxylamines (=hydroxyamines) [5]. This oxidative approach has found application mainly for the synthesis of nitrones ($\mathrm{R}^3\text{–}\overset{\oplus}{\mathrm{N}}(\text{–}\overset{\ominus}{\mathrm{O}})=\mathrm{C}(\mathrm{R}^1)\mathrm{R}^2$) starting with *N*,*N*-disubstituted hydroxylamines [6] and is well investigated for the generation of nitroso compounds from hydroxylamines which lack an α-H-atom (for reviews, see [7]). Moreover, 2-iodoxybenzoic acid (IBX) as a stoichiometric oxidant was successfully used for the oxidation of hydroxylamines and alkoxyamines to their corresponding oxime derivatives [8]. Transformation of hydroxylamines to oximes by reaction with dioxygen is known; however, only few substrates seem to be oxidized under aerobic conditions in the absence of any catalyst [9]. Problematic in this aerobic oxidation is the formation of diazene *N*-oxides of the type **4** as by-products, which result from condensation of an intermediately formed nitroso compound **2** with unreacted hydroxylamine **1** (*Scheme 1*) [10]. Low yields of oximes **3** are achieved if tautomerization of **2** is slow as compared to condensation with **1** to give **4**. An oxidation process that involves formation of **2** as an intermediate or which adheres to conditions accelerating tautomerization of **2** or suppressing condensation of **1** with **2** might offer an answer to that problem. Along this line, a successful transition-metal-catalyzed aerobic oxidation of alkoxyamines to oxime ethers was published in 2006 [11]. Herein we report our results on 2,2,6,6-tetramethylpiperidin-1-yloxy (=2,2,6,6-tetramethylpiperidine 1-oxyl; TEMPO) radical mediated oxidation of hydroxylamines and alkoxyamines to oximes and oxime ethers.

Scheme 1. *Oxidation of Hydroxylamines*



Results and Discussion. – TEMPO and derivatives thereof have widely been used as mild commercially available oxidants in organic synthesis (for recent reviews, see [12]). In most of the cases, the *N*-oxoammonium salt, readily generated *in situ* from TEMPO by the use of a co-oxidant, is the active reagent. Due to the low redox potential of TEMPO as compared to its *N*-oxoammonium salt (E(TEMPO$^+$/TEMPO) = 0.64 V *vs.* SCE, see [13]), reports on TEMPO acting as a direct oxidizing reagent without the aid of any transition metal are rare [14][15].

In line with our own investigation towards transition-metal-free TEMPO-mediated oxidation processes [15], we found that commercially available *N*-benzylhydroxylamine hydrochloride (**1a** · HCl) was cleanly and quantitatively transformed to the corresponding oxime **3a** within 30 min in the presence of 2.2 equiv. of 4-hydroxy-TEMPO (4-OH-TEMPO) and 1.1 equiv. of Et_3N in THF at room temperature. The reaction worked equally well in α,α,α-trifluorotoluene (= benzotrifluoride, BTF) and TEMPO as oxidant (*Scheme 2* and *Table 1*, *Entry 1*). The fluorinated solvent better dissolves dioxygen [16]; this fact will become an important issue for the aerobic nitroxide-catalyzed oxidations which will be discussed below. To study the substrate scope, we treated various hydroxylamines and alkoxyamines, *i.e.*, **1b** – **1l**, with TEMPO, 4-OH-TEMPO, or 4-acetamido-TEMPO (4-AcNH-TEMPO; 2.2 equiv.) in BTF[1]).

Aliphatic hydroxylamines turned out to be less reactive. A longer reaction time at higher temperature was necessary to reach full conversion. Oximes **3b** and **3c** were isolated in moderate to good yields (*Entries 2* and *3*). α,α-Disubstituted hydroxylamines **1d**, **1e**, the cyclic congener **1f**, and the aliphatic *N*-cyclopentylhydroxylamine (**1g**) were cleanly oxidized to the corresponding ketoximes in excellent yields (*Entries 4–7*). Oxidation of the aliphatic *N*-(benzyloxy)hexanamine (**1h**) with TEMPO gave oxime ether **3h** in 94% yield (*Entry 8*). As compared to the hydroxyl-

---

[1]) The cheaper 4-AcNH-TEMPO could be used. As by-products, TEMPOH or 4-AcNH-TEMPOH were formed in these reactions. In cases where TEMPOH is difficult to separate from the product by column chromatography, we recommend to switch to 4-AcNH-TEMPO or 4-OH-TEMPO.

Scheme 2. *Nitroxide-Mediated Oxidation of Hydroxylamines and Alkoxyamines.* For X and **3**, see *Table 1.*

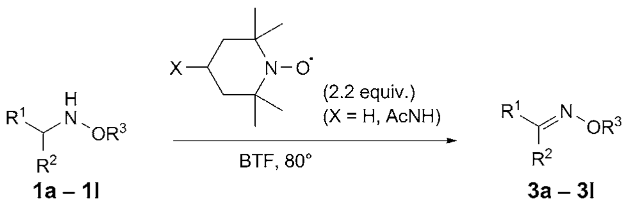
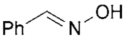
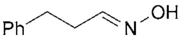
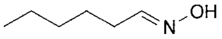
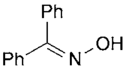
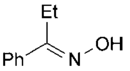
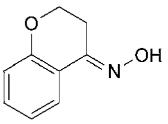
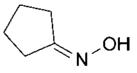
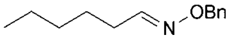
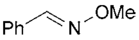
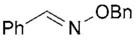
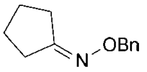
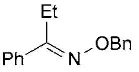


Table 1. *Nitroxide-Mediated Oxidation of Hydroxylamines and Alkoxyamines to Oximes and Oxime Ethers*a)

Entry	Substrate **1**	X	Product **3**		Time [h]	Yield [%]b)
*1*c)d)	**1a** · HCl	H		**3a**	0.5	99
2	**1b**	H		**3b**	4	74
3	**1c**	H		**3c**	6	42
*4*c)	**1d**	H		**3d**	2	95
5	**1e**	H		**3e**	0.5	98
*6*e)	**1f**	H		**3f**	0.5	76
7	**1g**	H		**3g**	1	99
8	**1h**	H		**3h**	12	94
9	**1i**	AcNH		**3i**	12	86
10	**1j**	AcNH		**3j**	12	99
11	**1k**	H		**3k**	12	94
12	**1l**	H		**3l**	12	96

a) According to *Scheme 2* on a 0.5 mmol scale under Ar. b) Yield of isolated **3**. c) Run at r.t. d) With 1.1 equiv. of Et_3N. e) Product obtained as a single stereoisomer.

amine oxidations, a longer reaction time was required in this case. However, in contrast to the results obtained for the oxidation of aliphatic hydroxylamines (see *Entries 2* and *3*), the reaction with alkoxyamine **1h** was high yielding. Encouraged by the clean conversion of alkoxyamines **1h**, we tested other substrates of this compound class. Thus oxime ethers **3i**–**3l** were isolated in excellent yields from **1i**–**1l** (*Entries 9–12*). We did not find any difference on the reaction outcome by switching from TEMPO to the less expensive 4-AcNH-TEMPO or 4-OH-TEMPO.

Encouraged by the work of *Han* and co-workers on nitroxide-catalyzed aerobic oxidation of cyclic acetals [14] and by our own results on aerobic TEMPO-catalyzed homocouplings of arylboronic acids [17], we decided to develop a protocol that uses catalytic amounts of a nitroxide in combination with dioxygen as the terminal oxidant. For the catalytic protocol (*Scheme 3*, *Method A*), we used 5 mol-% of TEMPO under an O_2 atmosphere in BTF (24 h). To establish the catalytic activity of TEMPO, each reaction was repeated in the absence of nitroxide under otherwise identical conditions (*Method B*). Results are summarized in *Table 2*.

Scheme 3. *Nitroxide-Catalyzed Aerobic Oxidation of Hydroxylamines and Alkoxyamines.* For X and **3**, see *Tables 2* and *1*, resp.

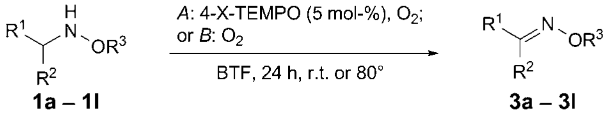


Table 2. *Nitroxide-Catalyzed Aerobic Oxidation of Hydroxylamines and Alkoxyamines*[a])

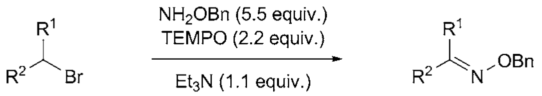
Entry	Temp. [°]	X	Product **3**	Yield [%][b])	
				Method A	*Method B*
1[c])	r.t.	OH	**3a**	94	88
2	80	H	**3b**	15[d])	13[d])
3	80	H	**3c**	< 1[d])	< 1[d])
4	r.t.	H	**3d**	58	< 1
5	r.t.	H	**3e**	43[d])	< 1
6	r.t.	H	**3f**	94	9
7	80	H	**3h**	92	< 1
8	80	H	**3i**	90	< 1
9	80	AcNH	**3i**	88	< 1
10	80	H	**3j**	98	< 1
11	80	AcNH	**3j**	94	< 1
12	80	H	**3k**	91	< 1
13	80	H	**3l**	85[e])	< 1

[a]) According to *Scheme 3* on a 0.5 mmol scale. [b]) Yield of isolated **3**. [c]) With **1a**·HCl and 1.1 equiv. of Et_3N. [d]) The corresponding diazene-*N*-oxide of type **4** was formed (see *Scheme 1*). [e]) 10 mol-% of catalyst for 48 h.

For the reactive hydroxylamine **1a**, we found that oxidation also occurred efficiently with dioxygen at room temperature (*Entry 1*, *Method B*). Only little acceleration was noted upon adding the nitroxide as a catalyst (*Entry 1*, *Method A*). The less reactive aliphatic hydroxylamine **1b** was oxidized to **3b** in a low yield, and TEMPO did not affect the reaction outcome (*Entry 2*). Hydroxylamine **1c** did not react to **3c** under aerobic conditions neither in the absence nor in the presence of TEMPO (*Entry 3*). Obviously, for less reactive substrates, a stoichiometric amount of TEMPO is required for successful oxidation. Pleasingly, a catalytic effect of TEMPO was observed in the formation of ketoxime **3d** (58%; *Entry 4*); the oxidation was clean, and **3d** was the only detectable product in the oxidation of hydroxylamine **1d**, the remaining starting material (34%) being recovered. In the absence of TEMPO, **3d** was not formed, clearly documenting the catalytic activity of TEMPO for this reaction. A slightly lower yield was achieved for the catalytic oxidation of **1e** (*Entry 5*). The cyclic hydroxylamine **1f** was cleanly oxidized under aerobic conditions with TEMPO as a catalyst (94%; *Entry 6*). In the absence of nitroxide, only low conversion towards the desired oxime **3f** (9%) was achieved. As for the nitroxide mediated oxidations discussed above, alkoxyamines turned out to be excellent substrates for the catalytic process (*Entries 7–13*). The corresponding oxime ethers were isolated in good to excellent yields in the presence of nitroxide catalyst. It should be noted that in the absence of the organocatalyst, these alkoxyamines remained unreacted upon exposure to dioxygen (*Method B*); full recovery of the starting materials was possible in all these cases. The aliphatic alkoxyamine **1h** was converted to the corresponding oxime ether **3h** in very good yield (92%; *Entry 7*). Alkoxyamines **1i** and **1j** were cleanly transformed to oxime ethers **3i** and **3j** under TEMPO catalysis (*Entries 8* and *10*), and switching to 4-AcNH-TEMPO gave similar results in both cases (*Entries 9* and *11*). The slightly enhanced reactivity of the (benzyloxy)amine **1j** as compared to the methoxyamine **1i** was also observed in the oxidation to oxime ethers with stoichiometric amounts of TEMPO (see *Table 1*, *Entries 9* and *10*). While the cyclic alkoxyamine **1k** gave cyclopentanone *O*-benzyl oxime (**3k**) in a very good yield (91%) by TEMPO catalysis (*Entry 12*), a higher nitroxide loading and prolonged reaction time were necessary to oxidize the sterically more crowded alkoxyamine **3l** (85% yield with 10 mol-% of TEMPO for 48 h, *Entry 13*).

Finally, we decided to develop an oxime ether synthesis *via* a two-step one-pot process starting with halides in which the alkoxyamine to be oxidized is generated *in situ* by a nucleophilic substitution reaction with *O*-benzylhydroxylamine. A problem to be solved was the competing overalkylation of the intermediately formed alkoxyamine. As a test substrate we chose benzyl bromide. After intensive experimentation, we found that the highest yield (79%) of oxime ether **3j** was achieved with an excess of *O*-benzylhydroxylamine (5.5 equiv.) and Et_3N in the presence of 2.2 equiv. of TEMPO in EtOH (*Scheme 4* and *Table 3*, *Entry 1*). Transformation of benzyl chloride under the same conditions provided **3j** in significantly lower yield (43%), but aliphatic halides were not converted to the targeted oxime ethers under these conditions. Therefore, all further experiments were conducted with activated bromides. Benzyl bromides bearing an electron-withdrawing or electron-donating substituent at the *para*-position were readily oxidized to oxime ethers **3m**–**3p** in 57–84% yield (*Entries 2–5*). *ortho*- and *meta*-Substituents were tolerated in that two-step process, and products **3q**–**3v** were isolated in good to excellent yields (73–91%, *Entries 6–11*). Electronic effects at the arene moiety did not influence the reaction outcome to a large extent. Allyl and secondary benzyl bromides gave the desired oxime ethers **3w** and **3x** in moderate yields (*Entries 12* and *13*). In these cases, formation of unidentified by-products was

Scheme 4. *TEMPO-Mediated Oxidation of* in situ *Generated Alkoxyamines.* For R^1 and R^2, see *Table 3.*



3j, **3m** – **3y**

Table 3. *TEMPO-Mediated Oxidation of* in situ *Generated Alkoxyamines*[a])

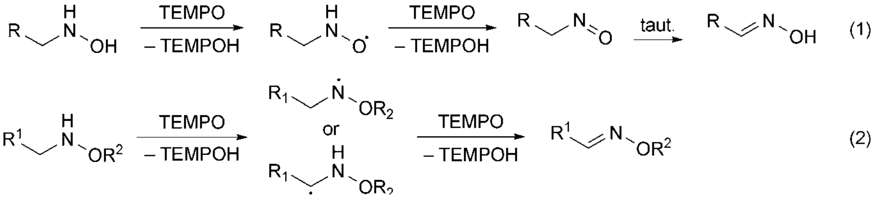
Entry	R^1	R^2	Product	Yield [%][b])
1	H	Ph	**3j**	79
2	H	4-^{t}Bu–C_6H_4	**3m**	84
3	H	4-Me–C_6H_4	**3n**	63
4	H	4-MeO–C_6H_4	**3o**	57
5	H	4-Br–C_6H_4	**3p**	60
6	H	3-Me–C_6H_4	**3q**	91
7	H	3-NO_2–C_6H_4	**3r**	78
8	H	3-I–C_6H_4	**3s**	74
9	H	2-Me–C_6H_4	**3t**	82
10	H	2,4-$Me_2C_6H_3$	**3u**	84
11	H	2-Br–C_6H_4	**3v**	73
12	H	(*E*)-PhCH = CH	**3w**	48
13	Me	Ph	**3x**	44
14[c])	COOMe	Ph	**3y**	84

[a]) According to *Scheme 4* from the corresponding activated bromide on a 1 mmol scale. [b]) Yield of isolated **3**. [c]) MeOH as solvent.

observed. However, preparation of ketoxime ether **3y** was achieved in 84% yield from the corresponding doubly activated bromide in a good yield (*Entry 14*).

The exact mechanism for the TEMPO-mediated oxidation of hydroxylamines and alkoxyamines to the corresponding oxime derivatives is not known. Due to the fact that for some hydroxylamine oxidations, diazene-*N*-oxides **4** were isolated as by-products, we currently assume that the oxidation of hydroxylamines occurs *via* nitroso compounds. Nitroso compounds are probably generated *via* H-abstraction from OH by TEMPO. This process should be thermodynamically feasible as the bond dissociation energy (BDE) difference between hydroxylamine (NH_2OH, *ca.* 81–82 kcal/mol for NH and 75–77 kcal/mol for OH) [18] which should be further lowered by the introduction of substituents and TEMPOH (69 kcal/mol) [19] is rather small. Renewed H-transfer to a second equivalent of TEMPO leads to the nitroso derivative that eventually isomerizes to the oxime (*Scheme 5*, *Eqn. 1*). As nitroso compounds are likely intermediates, we currently disregard disproportionation of two aminoxyl radicals to give the oxime and the starting hydroxylamine [20], see also [15f]. Note that this pathway can not be followed for the oxidation of alkoxyamines. For these substrates, the reaction might proceed *via* H-transfer from either the α-CH next to the N-atom or from NH to TEMPO (*Eqn. 2*). A second H-transfer from these intermediately formed C- or N-centered radicals to TEMPO would directly lead to oxime ethers.

Scheme 5. *Possible Mechanisms for TEMPO-Mediated Oxidation of Hydroxylamines and Alkoxyamines*



Conclusions. – We presented a high-yielding TEMPO-mediated oxidation of various hydroxylamines and alkoxyamines to the corresponding oximes and oxime ethers. For alkoxyamines, reactions could be run with catalytic amounts of a nitroxide with dioxygen as a terminal oxidant. In addition, a method for direct conversion of benzyl bromides to oxime ethers *via in situ* formation of alkoxyamines was developed.

The project has been funded within the research cluster 'SusChemSys' by the *Ministerium für Innovation, Wissenschaft und Forschung*, NRW.

Experimental Part

1. *General.* All reactions involving moisture- and/or air-sensitive reagents and/or intermediates were carried out in heat-gun-dried glassware under Ar and were performed by using standard *Schlenk* techniques. A dioxygen atmosphere was provided by the balloon technique. Solvents and Et_3N were freshly distilled from appropriate drying reagents or stored over molecular sieve under Ar. *O*-Benzylhydroxylamine was liberated from its hydrochloride salt by dissolving in sat. aq. $NaHCO_3$ soln. and extracting with CH_2Cl_2 (3 ×). All other chemicals were purchased from *Sigma Aldrich*, *Fluka*, *Acros Organics*, *ABCR*, or *Alfa Aesar* and were used as received. TLC: silica gel *60 F_{254}* plates (SiO_2; *Merck*). Flash chromatography (FC): silica gel *60* (SiO_2, 40–63 µm; *Merck*) with Ar excess pressure of *ca.* 0.4 bar. M.p.: *SMP-10* apparatus (*Stuart Scientific*); uncorrected. IR Spectra: *Digilab-FTS-4000* instrument equipped with a *Specac-MKII-Golden-Gate* single reflection ATR system; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker-DPX-300* spectrometer; in $CDCl_3$ at 25°; δ in ppm rel. to solvent residual peak as internal standard, *J* in Hz. HR-ESI-MS: *Bruker MicroTof* spectrometer; in *m/z*.

2. *Hydroxylamines (= Hydroxyamines) or Alkoxyamines from the Corresponding Carbonyl Compounds.* Starting materials were prepared according to literature procedures starting from the corresponding carbonyl compounds. Condensation with hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) or *O*-benzylhydroxylamine hydrochloride ($NH_2OBn \cdot HCl$) at r.t. [21] or under reflux conditions [22] afforded the desired oxime or oxime ether which was subsequently reduced to the desired hydroxylamine or alkoxyamine upon treatment with $NaBH_3CN$ [23] or $BH_3 \cdot$ pyridine complex [24].

N-*(3-Phenylpropyl)hydroxylamine* (= N-*Hydroxybenzenepropanamine*; **1b**) [25a]: According to [21][24a] in 84% yield over two steps. Colorless solid. ^1H-NMR (300 MHz, $CDCl_3$): 7.34–7.14 (*m*, 5 arom. H); 5.19 (br. *s*, NH, OH); 2.97 (*t*, *J* = 7.2, CH_2N); 2.68 (*t*, *J* = 7.7, CCH_2); 1.88 (*m*, CH_2CH_2N). ^{13}C-NMR (75 MHz, $CDCl_3$): 141.8 (C); 128.5 (2 CH); 127.6 (CH); 125.9 (2 CH); 53.3 (CH_2); 33.4 (CH_2); 28.7 (CH_2). HR-ESI-MS: 152.1072 ($[M+H]^+$, $C_9H_{14}NO^+$; calc. 152.1070).

N-*Hexylhydroxylamine* (= N-*Hydroxyhexan-1-amine*; **1c**) [25b]: According to [21][23] in 84% yield over two steps. Colorless solid. ^1H-NMR (300 MHz, $CDCl_3$): 2.94 (*t*, *J* = 7.1, CH_2N); 1.49–1.43 (*m*, CH_2CH_2N); 1.41–1.21 (*m*, CH_2); 0.97–0.77 (*m*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 54.0 (CH_2); 31.7 (CH_2); 27.0 (CH_2); 26.8 (CH_2); 22.6 (CH_2); 14.0 (Me). HR-ESI-MS: 118.1230 ($[M+H]^+$, $C_6H_{16}NO^+$; calc. 118.1226).

N-*Benzhydrylhydroxylamine* (= N-*Hydroxy-α-phenylbenzenemethanamine*; **1d**) [25c]: According to [21][23] in 85% yield over two steps. Colorless solid. ^1H-NMR (300 MHz, $CDCl_3$): 7.47–7.16 (*m*, 10 arom. H); 5.58 (br. *s*, OH); 5.23 (*s*, CHN); 4.99 (br. *s*, NH). ^{13}C-NMR (75 MHz, $CDCl_3$): 140.7 (2 C);

128.7 (4 CH); 127.7 (4 CH); 127.6 (2 CH); 70.8 (CH). HR-ESI-MS: 222.0884 ($[M+Na]^+$, $C_{13}H_{13}NNaO^+$; calc. 222.0889).

N-*(1-Phenylpropyl)hydroxylamine* (= *α-Ethyl*-N-*hydroxybenzenemethanamine*; **1e**) [25d]: According to [21] [23] in 54% yield over two steps. Colorless solid. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.39 – 7.23 (*m*, 5 arom. H); 4.71 (br. *s*, NH, OH); 3.87 (*dd*, *J* = 8.5, 5.6, CHN); 1.96 – 1.51 (*m*, CH_2); 0.83 (*t*, *J* = 7.5, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 141.2 (C); 128.5 (2 CH); 127.8 (2 CH); 127.6 (CH); 68.7 (CH); 26.4 (CH_2); 10.6 (Me). HR-ESI-MS: 152.1068 ($[M+H]^+$, $C_9H_{14}NO^+$; calc. 152.1070).

N-*(Chroman-4-yl)hydroxylamine* (= *3,4-Dihydro*-N-*hydroxy-2*H-*1-benzopyran-4-amine*; **1f**): According to [21] [23] in 88% yield over two steps. Colorless solid. M.p. 128°. IR (neat): 3258*m*, 3163*m* (br.), 2934*m*, 2888*m*, 1607*m*, 1581*m*, 1489*s*, 1452*m*, 1414*m*, 1314*m*, 1272*m*, 1250*m*, 1221*s*, 1179*m*, 1138*m*, 1118*m*, 1096*m*, 1055*s*, 1007*s*, 974*m*, 910*s*, 767*s*, 752*s*, 667*m*, 605*m*, 561*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.30 – 7.15 (*m*, 2 arom. H); 6.96 – 6.81 (*m*, 2 arom. H); 4.33 – 4.18 (*m*, CH_2O); 4.15 – 4.06 (*m*, CHN); 2.27 – 2.19 (*m*, 1 H, CH_2CH); 2.13 – 1.94 (*m*, 1 H, CH_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 155.7 (C); 130.3 (CH); 129.5 (CH); 120.3 (CH); 119.8 (C); 117.2 (CH); 62.0 (CH_2); 54.9 (CH); 25.2 (CH_2). HR-ESI-MS: 166.0864 ($[M+H]^+$, $C_9H_{12}NO_2^+$; calc. 166.0863).

N-*Cyclopentylhydroxylamine* (= N-*Hydroxycyclopentanamine*; **1g**) [25e]: According to [21] [23] in 67% yield over two steps. Colorless solid. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.69 (br. *s*, NH, OH); 3.39 – 3.26 (*m*, CHN); 1.64 – 1.12 (*m*, 4 CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 63.3 (CH); 30.4 (2 CH_2); 24.7 (2 CH_2). HR-ESI-MS: 102.0902 ($[M+H]^+$, $C_5H_{12}NO^+$; calc. 102.0913).

O-*Benzyl*-N-*hexylhydroxylamine* (= N-*(Phenylmethoxy)hexan-1-amine*; **1h**): According to [22] [23] in 85% yield over two steps. Colorless oil. IR (neat): 3090*w*, 3065*w*, 3032*w*, 2929*s* (br.), 2857*s* (br.), 2363*w*, 2338*w*, 1496*w*, 1454*m*, 1363*m*, 1207*w*, 1059*w*, 1009*m* (br.), 961*m* (br.), 910*w*, 743*m*, 698*s*, 612*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.38 – 7.27 (*m*, 5 arom. H); 5.54 (br. *s*, NH); 4.71 (*s*, CH_2O); 2.94 (*t*, *J* = 7.0, CH_2N); 1.56 – 1.46 (*m*, CH_2); 1.37 – 1.23 (*m*, 3 CH_2); 0.96 – 0.83 (*m*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.1 (C); 128.4 (2 CH); 128.4 (2 CH); 127.8 (CH); 76.2 (CH_2); 52.3 (CH_2); 31.7 (CH_2); 27.3 (CH_2); 26.9 (CH_2); 22.6 (CH_2); 14.0 (Me). HR-ESI-MS: 208.1686 ($[M+H]^+$, $C_{13}H_{22}NO^+$; calc. 208.1696).

N-*Benzyl*-O-*methylhydroxylamine* (= N-*Methoxybenzenemethanamine*; **1i**) [25f]: According to [24b] in 91% yield. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.40 – 7.27 (*m*, 5 arom. H); 5.06 (br. *s*, NH); 4.07 (*s*, CH_2); 3.54 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 137.6 (C); 128.8 (2 CH); 128.5 (CH); 127.5 (2 CH); 61.8 (CH_2); 56.2 (Me). HR-ESI-MS: 138.0919 ($[M+H]^+$, $C_8H_{12}NO^+$; calc. 138.0913).

N,O-*Dibenzylhydroxylamine* (= N-*(Phenylmethoxy)benzenemethanamine*; **1j**) [8]: According to [22] [23] in 95% yield over two steps. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.41 – 7.25 (*m*, 10 arom. H); 5.73 (br. *s*, NH); 4.67 (*s*, CH_2O); 4.06 (*s*, CH_2N). ^{13}C-NMR (75 MHz, $CDCl_3$): 137.9 (C); 137.7 (C); 129.0 (2 CH); 128.5 (2 CH); 128.4 (2 CH); 128.4 (CH); 127.8 (2 CH); 127.5 (CH); 76.3 (CH_2); 56.6 (CH_2). HR-ESI-MS: 214.1220 ($[M+H]^+$, $C_{14}H_{16}NO^+$; calc. 214.1226).

O-*Benzyl*-N-*cyclopentylhydroxylamine* (= N-*(Phenylmethoxy)cyclopentanamine*; **1k**): According to [22] [23] in 89% yield over two steps. Colorless oil. IR (neat): 3088*w*, 3064*w*, 3031*w*, 2956*s* (br.), 2910*m* (br.), 2868*m* (br.), 1496*w*, 1453*m*, 1356*m*, 1207*w*, 1053*m*, 1027*m*, 986*s*, 910*m*, 737*s*, 697*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.41 – 7.27 (*m*, 5 arom. H); 5.37 (br. *s*, NH); 4.73 (*s*, CH_2O); 3.62 – 3.51 (*m*, CH); 1.82 – 1.41 (*m*, 4 CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.1 (C); 128.4 (2 CH); 128.3 (CH); 127.7 (2 CH); 76.5 (CH_2); 61.9 (CH); 30.5 (2 CH_2); 24.4 (2 CH_2). HR-ESI-MS: 192.1388 ($[M+H]^+$, $C_{12}H_{18}NO^+$; calc. 192.1383).

O-*Benzyl*-N-*(1-phenylpropyl)hydroxylamine* (= *α-Ethyl*-N-*(phenylmethoxy)benzenemethamine*; **1l**) [25g]: According to [21] [23] in 92% yield over two steps. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.39 – 7.19 (*m*, 10 arom. H); 5.69 (br. *s*, NH); 4.62 (*d*, *J* = 11.4, 1 H, CH_2O); 4.55 (*d*, *J* = 11.4, 1 H, CH_2O); 3.90 (*dd*, *J* = 8.5, 5.6, CHN); 1.93 – 1.54 (*m*, $MeCH_2$); 0.81 (*t*, *J* = 7.5, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 141.7 (C); 137.9 (C); 128.5 (2 CH); 128.3 (2 CH); 127.9 (2 CH); 127.7 (2 CH); 127.4 (2 CH); 76.8 (CH_2); 67.5 (CH); 26.7 (CH_2); 10.6 (Me). HR-ESI-MS: 242.1537 ($[M+H]^+$, $C_{16}H_{20}NO^+$; calc. 242.1539).

3. *Nitroxide-Mediated Oxidation of Hydroxylamines or Alkoxyamines: General Procedure 1* (*GP1*). TEMPO, 4-OH-TEMPO, or 4-AcNH-TEMPO (1.1 mmol, 2.2 equiv.) was added to a soln. of the hydroxylamine or alkoxyamine (0.50 mmol, 1.0 equiv.; 0.2M) in BTF (2.5 ml). The mixture was stirred at r.t. or 80° until complete conversion of starting material (TLC monitoring). After evaporation of the solvent, the crude mixture was purified by FC to afford the desired oxime or oxime ether.

Nitroxide-Catalyzed Aerobic Oxidation of Hydroxylamines or Alkoxyamines: General Procedure 2 (*GP2*). TEMPO, 4-OH-TEMPO, or 4-AcNH-TEMPO (5–10 mol-%) was added to a soln. of the hydroxylamine or alkoxyamine (0.50 mmol, 1 equiv.; 0.2M) in BTF (2.5 ml). The mixture was vigorously stirred under dioxygen (balloon technique) at r.t. or 80° for 24–48 h. Evaporation of the solvent followed by FC afforded the desired oxime or oxime ether. Each experiment was repeated in the absence of any nitroxide catalyst under otherwise identical conditions.

TEMPO-Mediated Oxidation of in situ *Generated Alkoxyamines: General Procedure 3* (*GP3*). Et_3N (157 µl, 1.10 mmol, 1.1 equiv.) and the activated bromide (1.00 mmol, 1.0 equiv.; 0.25M) were added to a soln. of TEMPO (344 mg, 2.20 mmol, 2.2 equiv.) and NH_2OBn (570 µl, 5.50 mmol, 5.5 equiv.) in EtOH (4 ml). The mixture was then heated to 80° over 30 min, and stirring was continued at 80° for an additional 6 h. After evaporation of the solvent, the crude mixture was purified by FC to afford the desired oxime ether.

Benzaldehyde Oxime (**3a**) [26a]: *Preparation with a Stoichiometric Amount of 4-OH-TEMPO:* Et_3N (0.70 ml, 1.1 mmol, 1.1 equiv.) was added to a soln. of **1a** · HCl (160 mg, 1.00 mmol, 1.0 equiv.) in THF (2.5 ml). After 5 min stirring at r.t., 4-OH-TEMPO (378 mg, 2.20 mmol, 2.2 equiv.) was added, and the mixture was stirred for another 0.5 h at r.t. The precipitate was filtered off and the solvent evaporated. FC (petroleum ether/^{t}BuOMe 20:1) afforded **3a** (120 mg, 99%). Colorless solid. The experiment was repeated under analogous conditions in BTF on a 0.5 mmol scale with TEMPO as the oxidant to give **3a** in 99% isolated yield.

Preparation with a Catalytic Amount of 4-OH-TEMPO in the Presence of O_2. Et_3N (0.35 ml, 0.55 mmol, 1.1 equiv.) was added to a soln. of **1a** · HCl (80 mg, 0.50 mmol, 1.0 equiv.) in BTF (2.5 ml). 4-OH-TEMPO (3.9 mg, 25 µmol, 5 mol-%) was added after 5 min stirring at r.t., and the mixture was exposed to dioxygen (balloon technique). After 24 h stirring at r.t., the solvent was removed under reduced pressure. FC (pentane/^{t}BuOMe 20:1) afforded **3a** (57 mg, 94%). Colorless solid. The control experiment under identical conditions without addition of nitroxide catalyst afforded **3a** in 88% yield (53 mg). ^{1}H-NMR (300 MHz, $CDCl_3$): 8.15 (*s*, CH); 8.08 (*s*, OH); 7.53–7.63 (*m*, 2 arom. H); 7.44–7.33 (*m*, 3 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 148.5 (CH); 130.1 (C); 128.1 (CH); 126.9 (2 CH); 125.1 (2 CH). HR-ESI-MS: 144.0417 ($[M + Na]^+$, $C_7H_7NNaO^+$; calc. 144.0420).

Benzenepropanal Oxime (**3b**) ([25a] for (*E*)-isomer): According to *GP1*, with **1b** (75 mg, 0.50 mmol, 1.0 equiv.) and TEMPO (173 mg, 1.10 mmol, 2.2 equiv.) for 4 h at 80°. FC (petroleum ether/AcOEt 20:1) afforded **3b** (55 mg, 0.37 mmol, 74%). Colorless solid.

According to *GP2*, with **1b** (75 mg, 0.50 mmol, 1 equiv.) and TEMPO (3.9 mg, 25 µmol, 5 mol-%) in the presence of O_2 for 24 h at 80°. FC (pentane/AcOEt 20:1) afforded **3b** (11 mg, 15%). Colorless solid. In the control experiment under identical conditions without addition of nitroxide catalyst, 13% (10 mg) of **3b** were isolated. ^{1}H-NMR (300 MHz, $CDCl_3$; (*E*)/(*Z*) mixtures were obtained; both stereoisomers): 7.47 (*t*, $J = 5.8$, CHN, (*E*)-isomer); 7.37–7.15 (*m*, 10 arom. H); 6.76 (*t*, $J = 5.3$, CHN, (*Z*)-isomer); 2.89–2.77 (*m*, 4 H, CH_2); 2.77–2.64 (*m*, CH_2, (*Z*)-isomer); 2.59–2.46 (*m*, CH_2, (*E*)-isomer). ^{13}C-NMR (75 MHz, $CDCl_3$; both stereoisomers): 151.6 (CH); 151.3 (CH); 140.6 (C); 140.6 (C); 128.5 (4 CH); 128.3 (2 CH); 128.2 (2 CH); 126.2 (2 CH); 32.8 (CH_2); 31.9 (CH_2); 31.2 (CH_2); 26.4 (CH_2). HR-ESI-MS: 172.0736 ($[M + Na]^+$, $C_9H_{11}NNaO^+$; calc. 172.0733).

Hexanal Oxime (**3c**): According to *GP1*, with **1c** (59 mg, 0.50 mmol, 1 equiv.) and TEMPO (173 mg, 1.10 mmol, 2.2 equiv.) for 6 h at 80°. FC (pentane/AcOEt 20:1) afforded **3c** (24 mg, 42%, *ca.* 1:1 (*E*)/(*Z*)-mixture). Colorless solid. M.p. 53°. IR (neat): 3255*m* (br.), 3110*m* (br.), 2956*s*, 2928*s*, 2863*m*, 1661*w*, 1359*m*, 1380*w*, 1302*w*, 1047*w*, 981*m*, 924*s*, 727*m*, 600*m*. ^{1}H-NMR (300 MHz, $CDCl_3$; both stereoisomers): 7.89 (br. *s*, OH, 1st isomer); 7.53 (br. *s*, OH, 2nd isomer); 7.43 (*t*, $J = 6.1$, CH, 2nd isomer); 6.72 (*t*, $J = 5.5$, CH, 1st isomer); 2.44–2.32 (*m*, CH_2CH, 1st isomer); 2.26–2.13 (*m*, CH_2CH, 2nd isomer); 1.58–1.43 (*m*, 4 H, CH_2CH_2CH); 1.42–1.23 (*m*, 8 H, $MeCH_2CH_2$); 1.01–0.91 (*m*, 6 H, Me). ^{13}C-NMR (75 MHz, $CDCl_3$; both stereoisomers): 153.1 (CH); 152.4 (CH); 31.5 (CH_2); 31.2 (CH_2); 29.4 (CH_2); 26.2 (CH_2); 25.7 (CH_2); 24.9 (CH_2); 22.3 (2 CH_2); 13.9 (2 Me). HR-ESI-MS: 138.0886 ($[M + Na]^+$, $C_6H_{13}NNaO^+$; calc. 138.0889).

Diphenylmethanone Oxime (**3d**) [21]: According to *GP1*, with **1d** (100 mg, 501 µmol, 1.0 equiv.) and TEMPO (172 mg, 1.10 mmol, 2.2 equiv.) for 2 h at r.t. FC (pentane/^{t}BuOMe 20:1) afforded **3d** (94 mg, 95%). Colorless solid.

According to *GP2*, with **1d** (100 mg, 501 µmol, 1.0 equiv.) and TEMPO (3.9 mg, 25 µmol, 5 mol-%) in the presence of O_2 for 24 h at r.t. FC (pentane/^{t}BuOMe 20 : 1) afforded **3d** (57 mg, 58%). Colorless solid, beside 34% of recovered **1d**. In the control experiment under identical conditions without addition of nitroxide catalyst, 99% **1d** was recovered. **3d**: ^{1}H-NMR (300 MHz, $CDCl_3$): 7.73 (*s*, OH); 7.52 – 7.28 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 158.1 (C); 136.2 (C); 132.7 (C); 129.5 (CH); 129.2 (2 CH); 129.1 (CH); 128.3 (2 CH); 128.2 (2 CH); 127.9 (2 CH). HR-ESI-MS: 220.0732 ($[M+Na]^+$, $C_{13}H_{11}NNaO^+$; calc. 220.0733).

1-Phenylpropan-1-one Oxime (**3e**) [26b]: According to *GP1*, with **1e** (76 mg, 0.50 mmol, 1.0 equiv.) and TEMPO (172 mg, 1.10 mmol, 2.2 equiv.) for 0.5 h at 80°. FC (pentane/AcOEt 20 : 1) afforded **3e** (73 mg, 0.49 mmol, 98%). Colorless solid.

According to *GP2*, with **1e** (119 mg, 788 µmol, 1 equiv.) and TEMPO (5.9 mg, 38 µmol, 5 mol-%) in the presence of O_2 for 24 at r.t. FC (pentane/AcOEt 20 : 1) afforded **3e** (50 g, 43%). Colorless solid. In the control experiment under identical conditions without addition of nitroxide catalyst, 99% of **1e** was recovered. **3e**: ^{1}H-NMR (300, $CDCl_3$): 8.07 (br. *s*, OH); 7.68 – 7.56 (*m*, 2 arom. H); 7.44 – 7.33 (*m*, 3 arom. H); 2.82 (*q*, $J = 7.6$, CH_2); 1.18 (*t*, $J = 7.6$, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 160.8 (C); 135.6 (C); 129.2 (CH); 128.7 (CH); 128.5 (CH); 127.8 (CH); 126.5 (CH); 19.8 (CH_2); 10.9 (Me). HR-ESI-MS: 172.0726 ($[M+Na]^+$, $C_9H_{11}NNaO^+$; calc. 172.0733).

*2,3-Dihydro-4*H*-1-benzopyran-4-one Oxime* (**3f**) [26c]: According to *GP1* with **1f** (83 mg, 0.50 mmol, 1.0 equiv.) and TEMPO (172 mg, 1.10 mmol, 2.2 equiv.) for 0.5 h at 80°. FC (petroleum ether/AcOEt 20 : 1) afforded **3f** (62 mg, 76%). Colorless solid.

According to *GP2*, with **1f** (83 mg, 0.50 mmol, 1 equiv.) and TEMPO (3.9 mg, 25 µmol, 5 mol-%) in the presence of O_2 for 24 h at r.t. FC (pentane/AcOEt 20 : 1) afforded **3f** (76 mg, 94%). Colorless solid. The control experiment under identical conditions without addition of nitroxide catalyst yielded 9% (7 mg, 43 µmol) of **3f**, beside 77% of recovered **1f**. **3f**: ^{1}H-NMR (300 MHz, $CDCl_3$): 8.01 (br. *s*, OH); 7.83 (*dd*, $J = 7.9, 1.7$, $CH_{arom}CO$); 7.31 – 7.22 (*m*, CHCCN); 7.03 – 6.84 (*m*, 2 arom. H); 4.25 (*t*, $J = 6.2$, CH_2O); 2.99 (*t*, $J = 6.2$, CH_2CN). ^{13}C-NMR (75 MHz, $CDCl_3$): 156.8 (C); 150.0 (C); 131.3 (CH); 124.0 (CH); 121.5 (CH); 118.2 (C); 117.9 (CH); 65.0 (CH_2); 23.6 (CH_2). HR-ESI-MS: 186.0527 ($[M+Na]^+$, $C_9H_9NNaO_2^+$; calc. 186.0525).

Cyclopentanone Oxime (**3g**) [26d]. According to *GP1*, with **1g** (51 mg, 0.50 mmol, 1.0 equiv.) and TEMPO (172 mg, 1.10 mmol, 2.2 equiv.) for 1 h at 80°. FC (pentane/AcOEt 10 : 1) afforded **3g** (49 mg, 99%). Colorless solid. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.92 (br. *s*, OH); 2.52 – 2.29 (*m*, 4 H, CH_2CN); 1.84 – 1.66 (*m*, 2 CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.4 (C); 30.9 (CH_2); 27.1 (CH_2); 25.0 (CH_2); 24.6 (CH_2). HR-ESI-MS: 122.0566 ($[M+Na]^+$, $C_5H_9NNaO^+$; calc. 122.0576).

Hexanal O-*(Phenylmethyl)oxime* (**3h**): According to *GP1*, with **1h** (104 mg, 507 µmol, 1.0 equiv.) and TEMPO (172 mg, 1.10 mmol, 2.2 equiv.) for 12 h at 80°. FC (pentane/AcOEt 100 : 1) afforded **3h** (97 mg, 94%; *ca.* 2 : 3 (*E*)/(*Z*)-mixture). Colorless oil.

According to *GP2*, with **1h** (207 mg, 1.00 mmol, 1 equiv.) and TEMPO (7.8 mg, 50 µmol, 5 mol-%) in the presence of O_2 for 24 h at 80°. FC (petroleum ether/AcOEt 100 : 1) afforded **3h** (189 mg, 92%; *ca.* 2 : 3 (*E*)/(*Z*)-mixture). Colorless oil. In the control experiment under identical conditions without addition of nitroxide catalyst, 99% of **1h** was recovered. **3h**: IR (neat): 3065*w*, 3033*m*, 2957*s* (br.), 2929*s* (br.), 2861*s* (br.), 2360*w*, 2335*w*, 1497*m*, 1455*m*, 1367*m*, 1309*w*, 1209*w*, 1055*s*, 1014*s*, 916*m*, 879*m*, 837*w*, 736*m*, 697*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; both stereoisomers): 7.45 (*t*, $J = 6.2$, CH, major isomer); 7.40 – 7.26 (*m*, 10 arom. H); 6.68 (*t*, $J = 5.5$, CH, minor isomer); 5.11 (*s*, CH_2O, minor isomer); 5.06 (*s*, CH_2O, major isomer); 2.43 – 2.32 (*m*, $\mathit{CH_2}CH$, minor isomer); 2.25 – 2.13 (*m*, $\mathit{CH_2}CH$, major isomer); 1.54 – 1.41 (*m*, 4 H, CH_2); 1.39 – 1.22 (*m*, 8 H, CH_2); 0.97 – 0.82 (*m*, 6 H, Me). ^{13}C-NMR (75 MHz, $CDCl_3$; both stereoisomers): 152.6 (CH); 151.7 (CH); 138.2 (C); 137.8 (C); 128.3 (2 CH); 128.2 (2 CH); 127.9 (2 CH); 127.8 (2 CH); 127.7 (2 CH); 75.7 (CH_2); 75.5 (CH_2); 31.5 (CH_2); 31.3 (CH_2); 29.5 (CH_2); 26.4 (CH_2); 25.9 (CH_2); 25.8 (CH_2); 22.3 (2 CH_2); 13.9 (2 Me). HR-ESI-MS: 228.1359 ($[M+Na]^+$, $C_{13}H_{19}NNaO^+$; calc. 228.1359).

Benzaldehyde O-*Methyloxime* (**3i**) [11]: According to *GP1*, with **1i** (69 mg, 0.50 mmol, 1.0 equiv.) and 4-OH-TEMPO (189 mg, 1.10 mmol, 2.2 equiv.) or 4-AcNH-TEMPO (234 mg, 1.10 mmol, 2.2 equiv.) for 12 h at 80°. FC (pentane/AcOEt 10 : 1) afforded **3i** (with 4-OH-TEMPO: 58 mg, 85%; with 4-AcNH-TEMPO: 60 mg, 86%). Yellow oil.

According to *GP2*, with **1i** (69 mg, 0.50 mmol, 1 equiv.) and TEMPO (3.9 mg, 26 μmol, 5 mol-%) or 4-AcNH-TEMPO (4.9 mg, 23 μmol, 5 mol-%) in the presence of O_2 for 24 h at 80°. FC (pentane/AcOEt 20 : 1) afforded **3i** (with TEMPO: 61 mg, 90%; with 4-AcNH-TEMPO: 59 mg, 88%). Yellow oil. In the control experiment under identical conditions without addition of nitroxide catalyst, 99% of **1i** was recovered. **3i**: ^{1}H-NMR (300 MHz, $CDCl_3$): 8.06 (*s*, CHN); 7.62 – 7.54 (*m*, 2 arom. H); 7.40 – 7.38 (*m*, 3 arom. H); 3.98 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 148.6 (C); 132.1 (CH); 129.8 (CH); 128.7 (2 CH); 127.0 (2 CH); 62.0 (Me). HR-ESI-MS: 136.0765 ($[M+H]^+$, $C_8H_{10}NO^+$; calc. 136.0757).

Benzaldehyde O-*(Phenylmethyl)oxime* (**3j**) [22]: According to *GP1*, with **1j** (107 mg, 501 μmol, 1.0 equiv.) and 4-OH-TEMPO (189 mg, 1.10 mmol, 2.2 equiv.) or 4-AcNH-TEMPO (234 mg, 1.10 mmol, 2.2 equiv.) for 12 h at 80°. FC (pentane/AcOEt 20 : 1) afforded **3j** (with 4-OH-TEMPO: 97 mg, 92%; with 4-AcNH-TEMPO: 104 mg, 99%). Colorless oil.

According to *GP2*, with **1j** (107 mg, 501 μmol, 1 equiv.) and TEMPO (3.9 mg, 26 μmol, 5 mol-%) or 4-AcNH-TEMPO (4.9 mg, 25 μmol, 5 mol-%) in the presence of O_2 for 24 h at 80°. FC (pentane/AcOEt 20 : 1) afforded **3j** (with TEMPO: 103 mg, 98%; with 4-AcNH-TEMPO: 99 mg, 94%). Colorless oil. In the control experiment under identical conditions without addition of nitroxide catalyst, 99% of **1j** was recovered.

According to *GP3*, with benzyl bromide (120 μl, 1.00 mmol, 1 equiv.). FC (pentane/^{t}BuOMe 100 : 1) afforded **3j** (167 mg, 79%). Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.15 (*s*, CHN); 7.64 – 7.52 (*m*, 2 arom. H); 7.48 – 7.28 (*m*, 8 arom. H); 5.22 (*s*, CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 149.0 (CH); 137.6 (C); 132.3 (C); 129.8 (2 CH); 128.7 (2 CH); 128.4 (2 CH); 128.0 (2 CH); 127.1 (2 CH); 76.4 (CH_2). HR-ESI-MS: 234.0887 ($[M+Na]^+$, $C_{14}H_{13}NNaO^+$; calc. 234.0889).

Cyclopentanone O-*(Phenylmethyl)oxime* (**3k**) [26e]: According to *GP1*, with **1k** (96 mg, 0.50 mmol, 1.0 equiv.) and TEMPO (172 mg, 1.10 mmol, 2.2 equiv.) for 12 h at 80°. FC (pentane/AcOEt 100 : 1) afforded **3k** (89 mg, 94%). Colorless oil.

According to *GP2*, with **1k** (191 mg, 1.00 mmol, 1 equiv.) and TEMPO (7.8 mg, 50 μmol, 5 mol-%) in the presence of O_2 for 24 h at 80°. FC (pentane/AcOEt 100 : 1) afforded **3k** (172 mg, 91%). Colorless oil. In the control experiment under identical conditions without addition of nitroxide catalyst, 99% of **1k** was recovered. **3k**: ^{1}H-NMR (300 MHz, $CDCl_3$): 7.40 – 7.27 (*m*, 5 arom. H); 5.09 (*s*, CH_2O); 2.52 – 2.32 (*m*, 2 CH_2); 1.81 – 1.67 (*m*, 2 CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.1 (C); 138.4 (C); 128.3 (2 CH); 127.9 (2 CH); 127.6 (CH); 75.5 (CH_2); 31.0 (CH_2); 30.0 (CH_2); 25.2 (CH_2); 24.7 (CH_2). HR-ESI-MS: 212.1052 ($[M+Na]^+$, $C_{12}H_{15}NONa^+$; calc. 212.1046).

1-Phenylpropan-1-one O-*(Phenylmethyl)oxime* (**3l**) [26f]: According to *GP1*, with **1l** (121 mg, 501 μmol, 1.0 equiv.) and TEMPO (172 mg, 1.10 mmol, 2.2 equiv.) for 12 h at 80°. FC (pentane/AcOEt 20 : 1) afforded **3l** (114 mg, 481 μmol, 96%). Colorless oil.

According to *GP2*, with **1l** (121 mg, 501 μmol, 1 equiv.) and TEMPO (7.8 mg, 50 μmol, 10 mol-%) in the presence of O_2 for 48 h at 80°. FC (pentane/AcOEt 50 : 1) afforded **3l** (102 mg, 85%). Colorless oil. In the control experiment under identical conditions without addition of nitroxide catalyst, 99% of **1l** was recovered. **3l**: ^{1}H-NMR (300 MHz, $CDCl_3$): 7.69 – 7.58 (*m*, 2 arom. H); 7.46 – 7.27 (*m*, 8 arom. H); 5.24 (*s*, CH_2O); 2.80 (*q*, $J = 7.6$, CH_2CN); 1.15 (*t*, $J = 7.6$, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 160.0 (C); 138.3 (C); 135.7 (C); 129.0 (2 CH); 128.4 (2 CH); 128.3 (CH); 128.1 (2 CH); 127.7 (CH); 126.3 (2 CH); 76.2 (CH_2); 20.3 (CH_2); 11.1 (Me). HR-ESI-MS: 262.1197 ($[M+Na]^+$, $C_{16}H_{17}NNaO^+$; calc. 262.1202).

4-(1,1-Dimethylethyl)benzaldehyde O-*(Phenylmethyl)oxime* (**3m**): According to *GP3*, with 4-*tert*-butylbenzyl bromide (184 μl, 1.00 mmol, 1 equiv.). FC (pentane/^{t}BuOMe 100 : 1) afforded **3m** (254 mg, 84%). Colorless solid. M.p. 27°. IR (neat): 3069*w*, 3032*w*, 2969*m* (br.), 2904*m*, 2868*m*, 1611*m*, 1496*m*, 1454*m*, 1395*w*, 1364*m*, 1340*m*, 1269*m*, 1219*m*, 1107*m*, 1082*m*, 1038*s*, 1014*s*, 985*s*, 936*s*, 914*s*, 860*m*, 830*s*, 733*s*, 695*s*, 642*m*, 615*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.17 (*s*, CHN); 7.61 – 7.43 (*m*, 2 arom. H); 7.42 – 7.31 (*m*, 7 arom. H); 5.25 (*s*, CH_2O); 1.36 (*s*, 3 Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 152.0 (CH); 147.8 (C); 136.6 (C); 128.4 (C); 127.3 (2 CH); 127.2 (2 CH); 126.8 (CH); 125.8 (2 CH); 124.5 (2 CH); 75.2 (CH_2); 33.7 (C); 30.1 (3 Me). HR-ESI-MS: 290.1511 ($[M+Na]^+$, $C_{18}H_{21}NNaO^+$; calc. 290.1515). Anal. calc. for $C_{18}H_{21}NO$: C 80.86, H 7.92, N 5.24, found: C 80.89, H 8.03, N 5.51.

4-Methylbenzaldehyde O-*(Phenylmethyl)oxime* (**3n**): According to *GP3*, with 4-methylbenzyl bromide (185 mg, 1.00 mmol, 1 equiv.). FC (pentane/^{t}BuOMe 100 : 1) afforded **3n** (142 mg, 63%). Colorless oil. IR (neat): 3067*w*, 3031*w*, 2922*m* (br.), 2871*w* (br.), 1612*m* (br.), 1513*m*, 1497*m*, 1454*m*, 1366*m*, 1341*w*, 1311*w*, 1249*w*, 1210*m*, 1178*w*, 1109*w*, 1082*w*, 1038*s*, 1017*s*, 958*m*, 938*s*, 914*m*, 856*m*, 814*s*, 776*m*, 734*m*, 697*s*, 623*m*. ^{1}H-NMR (300 MHz, CDCl$_3$): 8.13 (*s*, CHN); 7.55 – 7.29 (*m*, 7 arom. H); 7.23 – 7.14 (*m*, 2 arom. H); 5.22 (*s*, CH$_2$O); 2.37 (*s*, Me). ^{13}C-NMR (75 MHz, CDCl$_3$): 149.1 (CH); 140.0 (C); 137.7 (C); 129.5 (2 CH); 129.4 (2 CH); 128.4 (C); 128.4 (CH); 127.9 (2 CH); 127.1 (2 CH); 76.3 (CH$_2$); 21.4 (Me). HR-ESI-MS: 248.1046 ([M + Na]$^+$, C$_{15}$H$_{15}$NNaO$^+$; calc. 248.1046).

4-Methoxybenzaldehyde O*-(Phenylmethyl)oxime* (**3o**) [26g]: According to *GP3*, with 4-methoxybenzyl bromide (201 mg, 1.00 mmol, 1 equiv.). FC (pentane/^{t}BuOMe 100 : 1) afforded **3o** (138 mg, 57%). Colorless oil. ^{1}H-NMR (300 MHz, CDCl$_3$): 8.10 (*s*, CHN); 7.55 – 7.50 (*m*, 2 arom. H); 7.45 – 7.29 (*m*, 5 arom. H); 6.92 – 6.87 (*m*, 2 arom. H); 5.19 (*s*, CH$_2$); 3.83 (*s*, Me). ^{13}C-NMR (75 MHz, CDCl$_3$): 161.0 (CH); 148.7 (C); 137.7 (C); 133.0 (2 CH); 128.6 (2 CH); 128.5 (2 CH); 128.4 (CH); 124.9 (C); 114.2 (2 CH); 76.2 (CH$_2$); 55.3 (Me). HR-ESI-MS: 264.0991 ([M + Na]$^+$, C$_{15}$H$_{15}$NNaO$_2^+$; calc. 264.0995).

4-Bromobenzaldehyde O*-(Phenylmethyl)oxime* (**3p**): According to *GP3*, with 4-bromobenzyl bromide (249 mg, 1.00 mmol, 1 equiv.). FC (pentane/^{t}BuOMe 100 : 1) afforded **3p** (172 mg, 601 μmol, 60%). Colorless solid. M.p. 58°. IR (neat): 3064*w*, 3032*w*, 2930*w* (br.), 2875*w* (br.), 1606*w*, 1590*m*, 1487*s*, 1454*m*, 1398*m*, 1366*w*, 1342*w*, 1301*w*, 1210*m*, 1070*m*, 1036*m*, 1009*s*, 986*m*, 948*s*, 918*m*, 849*m*, 819*s*, 734*m*, 698*s*, 632*w*, 609*m*. ^{1}H-NMR (300 MHz, CDCl$_3$): 8.08 (*s*, CH); 7.58 – 7.29 (*m*, 9 arom. H); 5.22 (*s*, CH$_2$). ^{13}C-NMR (75 MHz, CDCl$_3$): 147.9 (CH); 137.4 (C); 131.9 (2 CH); 131.2 (C); 128.5 (2 CH); 128.5 (2 CH); 128.4 (2 CH); 128.1 (CH); 124.0 (CH); 76.6 (CH$_2$). HR-ESI-MS: 290.0177 ([M + H]$^+$, C$_{14}$H$_{13}$BrNO$^+$; calc. 290.0175).

3-Methylbenzaldehyde O*-(Phenylmethyl)oxime* (**3q**): According to *GP3*, with 3-methylbenzyl bromide (137 μl, 1.00 mmol, 1 equiv.). FC (pentane/^{t}BuOMe 100 : 1) afforded **3q** (205 mg, 91%). Colorless oil. IR (neat): 3063*w*, 3032*w*, 2921*w*, 2870*w*, 1950*w*, 1880*w*, 1605*w*, 1580*w*, 1496*w*, 1454*m*, 1366*m*, 1339*m*, 1249*m*, 1249*w*, 1209*w*, 1159*m*, 1082*m*, 1038*m*, 1025*m*, 985*m*, 945*s*, 913*m*, 782*s*, 733*s*, 692*s*, 650*m*, 606*m*. ^{1}H-NMR (300 MHz, CDCl$_3$): 8.13 (*s*, CHN); 7.51 – 7.14 (*m*, 9 arom. H); 5.23 (*s*, CH$_2$O); 2.37 (*s*, Me). ^{13}C-NMR (75 MHz, CDCl$_3$): 149.3 (CH); 138.4 (C); 137.6 (C); 132.2 (C); 130.7 (2 CH); 128.6 (2 CH); 128.4 (CH); 128.4 (CH); 127.9 (CH); 127.5 (CH); 124.5 (CH); 76.4 (CH$_2$); 21.3 (Me). HR-ESI-MS: 226.1227 ([M + H]$^+$, C$_{15}$H$_{16}$NO$^+$; calc. 226.1226).

3-Nitrobenzaldehyde O*-(Phenylmethyl)oxime* (**3r**): According to *GP3*, with 3-nitrobenzyl bromide (216 mg, 1.00 mmol, 1 equiv.). FC (pentane/^{t}BuOMe 100 : 1) afforded **3r** (200 mg, 78%). Colorless solid. M.p. 36°. IR (neat): 3092*w*, 3033*w*, 2928*w* (br.), 2875*w* (br.), 1737*w*, 1611*w*, 1528*s*, 1454*m*, 1352*s*, 1212*m*, 1081*m*, 1018*m*, 950*m*, 920*m*, 829*w*, 807*w*, 735*s*, 697*m*, 677*m*, 642*w*. ^{1}H-NMR (300 MHz, CDCl$_3$): 8.46 – 8.40 (*m*, CCHCNO$_2$); 8.26 – 8.15 (*m*, 1 arom. H); 8.18 (*s*, CH); 7.92 – 7.87 (*m*, 1 arom. H); 7.54 (*t*, *J* = 8.0, C*H*CHCNO$_2$); 7.47 – 7.30 (*m*, 5 arom. H); 5.26 (*s*, CH$_2$). ^{13}C-NMR (75 MHz, CDCl$_3$): 148.6 (CH); 146.6 (C); 137.0 (C); 134.2 (C); 132.5 (CH); 129.7 (CH); 128.5 (2 CH); 128.5 (2 CH); 128.2 (CH); 124.2 (CH); 121.8 (CH); 77.0 (CH$_2$). HR-ESI-MS: 279.0745 ([M + Na]$^+$, C$_{14}$H$_{12}$N$_2$NaO$_3^+$; calc. 279.0740).

3-Iodobenzaldehyde O*-(Phenylmethyl)oxime* (**3s**): According to *GP3*, with 3-iodobenzyl bromide (297 mg, 1.00 mmol, 1 equiv.). FC (pentane/^{t}BuOMe 100 : 1) afforded **3s** (248 mg, 74%). Colorless oil. IR (neat): 4050*w*, 3061*w*, 3031*w*, 2926*w* (br.), 2875*w*, 1875*w*, 1588*w*, 1556*m*, 1496*w*, 1467*w*, 1454*m*, 1418*w*, 1366*w*, 1336*w*, 1249*w*, 1206*m*, 1016*s*, 994*s*, 941*s*, 941*s*, 918*s*, 872*m*, 782*m*, 733*m*, 684*s*, 641*w*, 609*m*. ^{1}H-NMR (300 MHz, CDCl$_3$): 8.03 (*s*, CH); 7.96 (*m*, CCHCI); 7.72 – 7.66 (*m*, 1 arom. H); 7.54 – 7.49 (*m*, 1 arom. H); 7.45 – 7.29 (*m*, 5 arom. H); 7.10 (*t*, *J* = 7.8, C*H*CHCI); 5.22 (*s*, CH$_2$). ^{13}C-NMR (75 MHz, CDCl$_3$): 147.4 (CH); 138.6 (CH); 137.3 (C); 135.6 (CH); 134.4 (C); 130.3 (CH); 128.5 (2 CH); 128.4 (2 CH); 128.1 (CH); 126.4 (CH); 94.5 (C); 76.7 (CH$_2$). HR-ESI-MS: 338.0039 ([M + H]$^+$, C$_{14}$H$_{13}$INO$^+$; calc. 338.0036).

2-Methylbenzaldehyde O*-(Phenylmethyl)oxime* (**3t**): According to *GP3*, with 2-methylbenzyl bromide (134 μl, 1.00 mmol, 1 equiv.). FC (pentane/^{t}BuOMe 100 : 1) afforded **3t** (92 mg, 82%). Colorless oil. IR (neat): 3067*s*, 3031*s*, 2924*s*, 2871*s*, 2362*s*, 2336*s*, 1610*s*, 1496*s*, 1454*m*, 1366*m*, 1292*s*, 1226*s*, 1209*s*, 1082*s*, 1016*s*, 984*s*, 936*s*, 915*s*, 858*m*, 783*m*, 752*s*, 696*s*, 640*m*, 612*m*. ^{1}H-NMR (300 MHz, CDCl$_3$): 8.32 (*s*, CHN); 7.65 – 7.57 (*m*, 1 arom. H); 7.38 – 7.04 (*m*, 8 arom. H); 5.14 (*s*, CH$_2$); 2.31 (*s*, Me). ^{13}C-NMR (75 MHz, CDCl$_3$): 148.1 (CH); 137.6 (C); 136.8 (C); 130.8 (2 CH); 130.5 (C); 129.6 (2 CH); 128.5 (CH); 128.5 (CH); 128.0 (CH); 127.0 (CH); 126.1 (CH); 76.4 (CH$_2$); 19.9 (Me). HR-ESI-MS: 248.1037 ([M + Na]$^+$, C$_{15}$H$_{15}$NNaO$^+$; calc. 248.1046).

2,4-Dimethylbenzaldehyde O-*(Phenylmethyl)oxime* (**3u**): According to *GP3*, with 2,4-dimethylbenzyl bromide (199 mg, 1.00 mmol, 1 equiv.). FC (pentane/^{t}BuOMe 100 : 1) afforded **3u** (202 mg, 84%). Colorless oil. IR (neat): 3031*w*, 2921*m*, 2869*w*, 1616*m*, 1497*m*, 1454*m*, 1366*m*, 1342*w*, 1248*w*, 1209*w*, 1082*w*, 1035*s*, 1017*s*, 984*s*, 941*s*, 818*s*, 734*m*, 697*s*, 626*m*. ^{1}H-NMR (300 MHz, CDCl$_3$): 8.40 (*s*, CHN); 7.61 (*d*, $J = 7.7$, 1 arom. H); 7.52 – 7.28 (*m*, 5 arom. H); 7.08 – 6.97 (*m*, 2 arom. H); 5.23 (*s*, CH$_2$); 2.38 (*s*, 1 Me); 2.33 (*s*, 1 Me). ^{13}C-NMR (75 MHz, CDCl$_3$): 148.1 (CH); 139.7 (C); 137.7 (C); 136.7 (C); 131.6 (C); 128.5 (2 CH); 128.5 (CH); 127.9 (CH); 127.6 (CH); 127.0 (CH); 126.9 (2 CH); 76.3 (CH$_2$); 21.3 (Me); 19.8 (Me). HR-ESI-MS: 262.1198 ([*M* + Na]$^+$, $C_{16}H_{17}NNaO^+$; calc. 262.1202).

2-Bromobenzaldehyde O-*(Phenylmethyl)oxime* (**3v**) [26h]: According to *GP3*, with 2-bromobenzyl bromide (249 mg, 1.00 mmol, 1 equiv.). FC (pentane/^{t}BuOMe 100 : 1) afforded **3v** (206 mg, 73%). Colorless oil. ^{1}H-NMR (300 MHz, CDCl$_3$): 8.54 (*s*, CHN); 7.91 – 7.85 (*m*, 1 arom. H); 7.58 – 7.53 (*m*, 1 arom. H); 7.47 – 7.17 (*m*, 7 arom. H); 5.24 (*s*, CH$_2$). ^{13}C-NMR (75 MHz, CDCl$_3$): 148.4 (CH); 137.3 (C); 133.1 (C); 131.6 (CH); 131.0 (CH); 128.5 (CH); 128.4 (2 CH); 128.1 (CH); 127.6 (2 CH); 127.5 (CH); 123.9 (C); 76.7 (CH$_2$). HR-ESI-MS: 312.0005 ([*M* + Na]$^+$, $C_{14}H_{12}BrNNaO^+$; calc. 311.9994).

3-Phenylprop-2-enal O-*(Phenylmethyl)oxime* (**3w**) [26i]: According to *GP3*, with cinnamyl bromide (197 mg, 1.00 mmol, 1 equiv.). FC (pentane/^{t}BuOMe 100 : 1) afforded **3w** (114 mg, 48%; *ca.* 2.5 : 1 (*E*)/(*Z*)-mixture). Colorless solid. ^{1}H-NMR (300 MHz, CDCl$_3$; both stereoisomers): 7.95 (*dd*, $J = 8.0$, 1.1, CHN, (*E*)-isomer); 7.52 – 7.28 (*m*, CHN, (*Z*)-isomer, and 20 arom. H); 6.91 – 6.74 (*m*, 4 H, C*HCH*); 5.22 (*s*, CH$_2$, (*Z*)-isomer); 5.17 (*s*, CH$_2$, (*E*)-isomer). ^{13}C-NMR (75 MHz, CDCl$_3$; both stereoisomers): 151.1 (CH); 148.5 (CH); 140.1 (C); 138.6 (C); 137.9 (C); 137.5 (C); 136.1 (CH); 135.9 (CH); 129.3 (2 CH); 128.8 (2 CH); 128.5 (2 CH); 128.3 (2 CH); 128.1 (2 CH); 128.0 (2 CH); 127.9 (4 CH); 127.5 (2 CH); 126.9 (2 CH); 122.0 (CH); 116.5 (CH); 76.3 (CH$_2$); 76.3 (CH$_2$). HR-ESI-MS: 260.1042d ([*M* + Na]$^+$, $C_{16}H_{15}NNaO^+$; calc. 260.1046).

1-Phenylethanone O-*(Phenylmethyl)oxime* (**3x**) [26j]: According to *GP3*, with (1-bromoethyl)benzene (137 μl, 1.00 mmol, 1 equiv.). FC (pentane/^{t}BuOMe 100 : 1) afforded **3x** (99 mg, 44%). Colorless oil. ^{1}H-NMR (300 MHz, CDCl$_3$): 7.69 – 7.64 (*m*, 2 arom. H); 7.47 – 7.30 (*m*, 8 arom. H); 5.27 (*s*, CH$_2$); 2.28 (*s*, Me). ^{13}C-NMR (75 MHz, CDCl$_3$): 155.0 (C); 138.1 (C); 136.7 (C); 129.0 (CH); 128.4 (CH); 128.1 (2 CH); 128.0 (2 CH); 127.8 (2 CH); 126.1 (2 CH); 76.2 (CH$_2$); 12.9 (Me). HR-ESI-MS: 248.1040 ([*M* + Na]$^+$, $C_{15}H_{15}NNaO^+$; calc. 248.1046).

Methyl 2-[(Benzyloxy)imino]-2-phenylacetate (= *Methyl α-[(Phenylmethoxy)imino]benzeneacetate*; **3y**): According to *GP3*, with methyl α-bromophenylacetate (158 μl, 1.00 mmol, 1 equiv.) in MeOH (4 ml). FC (pentane/^{t}BuOMe 20 : 1) afforded **3y** (226 mg, 84%). Colorless oil. IR (neat): 3065*w*, 3032*w*, 2953*w*, 1739*s*, 1604*w*, 1497*m*, 1454*m*, 1446*m*, 1434*m*, 1366*m*, 1333*m*, 1311*m*, 1220*s*, 1183*m*, 1038*w*, 1057*m*, 1006*s*, 999*s*, 951*m*, 919*m*, 878*m*, 840*m*, 769*m*, 751*m*, 734*m*, 689*s*, 654*m*. ^{1}H-NMR (300 MHz, CDCl$_3$): 7.63 – 7.52 (*m*, 2 arom. H); 7.45 – 7.29 (*m*, 8 arom. H); 5.29 (*s*, CH$_2$); 3.95 (*s*, Me). ^{13}C-NMR (75 MHz, CDCl$_3$): 164.0 (C); 151.0 (C); 137.3 (C); 130.3 (CH); 130.1 (C); 128.7 (2 CH); 128.3 (2 CH); 127.8 (CH); 127.8 (2 CH); 126.3 (2 CH); 77.0 (CH$_2$); 52.3 (Me). HR-ESI-MS: 292.0946 ([*M* + Na]$^+$, $C_{16}H_{15}NNaO_3^+$; calc. 292.0944).

REFERENCES

[1] A. I. Mikhaleva, A. B. Zaitsev, B. A. Trofimov, *Russ. Chem. Rev.* **2006**, *75*, 797; J. P. Adams, *J. Chem. Soc., Perkin Trans. 1* **2000**, 125; E. Abele, E. Lukevics, *Heterocycles* **2000**, *53*, 2285; K. Narasaka, M. Kitamura, *Eur. J. Org. Chem.* **2005**, 4505; M. Yamane, K. Narasaka, in 'Science of Synthesis', Ed. A. Padwa, Thieme, Stuttgart, 2004, Vol. 27, Chapt. 15.

[2] Y. Ashani, I. Silman, in 'The Chemistry of Hydroxylamines, Oximes and Hydroxamic Acids', Part 2, Eds. S. Patai, Z. Rappoport, John Wiley & Sons, London, 2009, p. 628 ff.

[3] J. Kassa, *Clin. Toxicol.* **2002**, *40*, 803.

[4] A. Porcheddu, G. Giacomelli, in 'The Chemistry of Hydroxylamines, Oximes and Hydroxamic Acids', Part 1, Eds. S. Patai, Z. Rappoport, John Wiley & Sons, London, 2009, p. 170 ff; S. Dayagi, Y. Degani, in 'The Chemistry of the Carbon-Nitrogen Double Bond', Ed. S. Patai, Wiley Interscience, London, 1970, p. 69 ff.

[5] J. Lin, J. R. Cashman, *J. Pharmacol. Exp. Ther.* **1997**, *282*, 1269; J. R. Cashman, Y. N. Xiong, L. Xu, A. Janowsky, *J. Pharmacol. Exp. Ther.* **1999**, *288*, 1251.

[6] J. Hamer, A. Macaluso, *Chem. Rev.* **1964**, *64*, 473; S. Cicchi, M. Marradi, A. Goti, A. Brandi, *Tetrahedron Lett.* **2001**, *42*, 6503; A. K. Qureshi, B. Sklarz, *J. Chem. Soc. C* **1966**, 412; S. Cicchi, M. Corsi, A. Goti, *J. Org. Chem.* **1999**, *64*, 7243; F. Cardona, L. Gorini, A. Goti, *Lett. Org. Chem.* **2006**, *3*, 118.

[7] B. G. Gowenlock, G. B. Richter-Addo, *Chem. Rev.* **2004**, *104*, 3315; H. Yamamoto, N. Momiyama, *Chem. Commun.* **2005**, 3514.

[8] K. C. Nicolaou, C. J. N. Mathison, T. Montagon, *J. Am. Chem. Soc.* **2004**, *126*, 5192.

[9] A. H. Beckett, A. R. Purkaystha, P. H. Morgan, *J. Pharm. Pharmacol.* **1977**, *29*, 15; F. J. Alvarez, R. T. Slade, *Pharm. Res.* **1992**, *9*, 1465; M. A. Mortellaro, S. Hong, D. T. Winn, A. W. Czarnik, *Bioorg. Med. Chem. Lett.* **1994**, *4*, 2041.

[10] T. Hino, A. Hasegawa, J.-J. Liu, M. Nakagawa, *Chem. Pharm. Bull.* **1990**, *38*, 59; H. Meister, *Liebigs Ann. Chem.* **1964**, *679*, 83; H. Stetter, E. Smulder, *Chem. Ber.* **1971**, *104*, 917; J. G. Aston, D. E. Ailman, *J. Am. Chem. Soc.* **1938**, *60*, 1930; E. Bamberger, A. Rising, *Liebigs Ann. Chem.* **1901**, *316*, 257; D. Zhao, M. Johansson, J.-E. Bäckvall, *Eur. J. Org. Chem.* **2007**, 4431; M. Anvar, V. Lee, *Tetrahedron* **2009**, *65*, 5834.

[11] J.-R. Wang, Y. Fu, B.-B. Zhang, X. Cui, L. Liu, Q.-X. Guo, *Tetrahedron Lett.* **2006**, *47*, 8293.

[12] T. Vogler, A. Studer, in 'Science of Synthesis (Nitroxyl Radicals (Nitroxides))', Eds. D. Enders, E. Schaumann, Thieme, Stuttgart–New York, 2008, p. 845; T. Vogler, A. Studer, *Synthesis* **2008**, 1979; L. Tebben, A. Studer, *Angew. Chem.* **2011**, *123*, 5138; *Angew. Chem., Int. Ed.* **2011**, *50*, 5034.

[13] T. Suga, Y.-J. Pu, K. Oyaizu, H. Nishide, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 2203.

[14] J. E. Barbiaz, G. T. Cunkle, A. D. DeBellis, D. Eveland, S. D. Pastor, S. P. Shum, *J. Org. Chem.* **2002**, *67*, 6831; Y.-X. Chen, L.-F. Qian, W. Zhang, B. Han, *Angew. Chem.* **2008**, *120*, 9470; *Angew. Chem., Int. Ed.* **2008**, *47*, 9330; B. Han, C. Wang, R.-F. Han, W. Yu, X.-Y. Duan, R. Fang, X.-L. Yang, *Chem. Commun.* **2011**, *47*, 7818.

[15] a) J. Guin, S. De Sarkar, S. Grimme, A. Studer, *Angew. Chem.* **2008**, *120*, 8855; *Angew. Chem., Int. Ed.* **2008**, *47*, 8727; b) M. S. Maji, T. Pfeifer, A. Studer, *Angew. Chem.* **2008**, *120*, 9690; *Angew. Chem., Int. Ed.* **2008**, *47*, 9547; c) M. S. Maji, A. Studer, *Synthesis* **2009**, 2467; d) M. S. Maji, T. Pfeifer, A. Studer, *Chem. – Eur. J.* **2010**, *16*, 5872; e) M. S. Maji, S. Murarka, A. Studer, *Org. Lett.* **2010**, *12*, 3878; f) S. Murarka, A. Studer, *Adv. Synth. Catal.* **2011**, *353*, 2708.

[16] A. Endres, G. Maas, *Chem. Unserer Zeit* **2000**, *34*, 382; A. Ogawa, D. P. Curran, *J. Org. Chem.* **1997**, *62*, 450; J. Deschamps, F. M. Costa Gomes, A. H. H. Pádua, *J. Fluorine Chem.* **2004**, *125*, 409.

[17] T. Vogler, A. Studer, *Org. Lett.* **2008**, *10*, 129.

[18] J. Lind, G. Merényi, *J. Phys. Chem. A* **2006**, *110*, 192.

[19] P. Astolfi, P. Brandi, C. Galli, P. Gentili, M. F. Gerini, L. Greci, O. Lanzalunga, *New J. Chem.* **2005**, *29*, 1308.

[20] A. Nilsen, R. Braslau, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 697.

[21] S. Liu, Y. Yu, L. S. Liebeskind, *Org. Lett.* **2007**, *9*, 1947.

[22] T. J. Donohoe, L. P. Fishlock, P. A. Procopiou, *Org. Lett.* **2008**, *10*, 285.

[23] R. Grigg, Z. Rankovic, M. Thoroughgood, *Tetrahedron* **2000**, *56*, 8025.

[24] a) M. Kawase, Y. Kikugawa, *Chem. Pharm. Bull.* **1981**, *29*, 1615; b) P. Beak, G. W. Selling, *J. Org. Chem.* **1989**, *54*, 5574.

[25] a) Y. Nakano, Y. Kato, K. Imai, E. Ochiai, J. Namekawa, S. Ishizuka, K. Takenouchi, A. Tanatani, Y. Hashimoto, K. Nagasawa, *J. Med. Chem.* **2006**, *49*, 2398; b) A. C. Biraboneye, S. Madonna, P. Maher, J.-L. Kraus, *ChemMedChem* **2010**, *5*, 79; c) R. Sivappa, N. M. Hernandez, Y. He, C. J. Lovely, *Org. Lett.* **2007**, *9*, 3861; d) I. Patel, N. A. Smith, S. N. G. Tyler, *Org. Process Res. Dev.* **2009**, *13*, 49; e) J. Moran, J. Y. Pfeiffer, S. I. Gorelsky, A. M. Beauchemin, *Org. Lett.* **2009**, *11*, 1895; f) R. W. Gantt, P. Peltier-Pain, W. J. Cournoyer, J. S. Thorson, *Nat. Chem. Biol.* **2011**, *7*, 685; g) H. Miyabe, R. Shibata, M. Sangawa, C. Ushiro, T. Naito, *Tetrahedron* **1998**, *54*, 11431.

[26] a) M. Mori, T. Sugiyama, M. Nojima, S. Kusabayashi, K. J. McCullough, *J. Org. Chem.* **1992**, *57*, 2285; b) H. Zhao, C. P. Vandenbossche, S. G. Koenig, S. P. Singh, R. P. Bakale, *Org. Lett.* **2008**, *10*, 505; c) K. Huang, F. G. Merced, M. Ortiz-Marciales, H. J. Mélendez, W. Correa, M. De Jesús, *J. Org. Chem.* **2008**, *73*, 4017; d) J. R. Hwu, W. N. Tseng, H. V. Patel, F. F. Wong, D.-N. Horng, B. R. Liaw,

L. C. Lin, *J. Org. Chem.* **1999**, *64*, 2211; e) S. Kim, J.-J. Yoon, *J. Am. Chem. Soc.* **1997**, *119*, 5982; f) Y. Chu, Z. Shan, D. Liu, N. Sun, *J. Org. Chem.* **2006**, *71*, 3998; g) M. L. Di Gioia, A. Leggio, A. Le Pera, A. Liguori, C. Siciliano, *J. Org. Chem.* **2005**, *70*, 10494; h) A. Shirai, O. Miyata, N. Tohnai, M. Miyata, D. J. Procter, D. Sucunza, T. Naito, *J. Org. Chem.* **2008**, *73*, 4464; i) M. Ueda, H. Miyabe, H. Shimizu, H. Sugino, O. Miyata, T. Naito, *Angew. Chem.* **2008**, *120*, 5682; *Angew. Chem., Int. Ed.* **2008**, *47*, 5600; j) J. A. Blake, K. U. Ingold, S. Lin, P. Mulder, D. A. Pratt, B. Sheeller, J. C. Walton, *Org. Biomol. Chem.* **2004**, *2*, 415.

Received April 5, 2012