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

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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  $(R^3-N(-O)=C(R^1)R^2)$  starting with N,N-disubstituted hydroxylamines [6] and is well investigated for the generation of nitroso compounds from hydroxylamines which lack an  $\alpha$ -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  $\mathbf{3}$  are achieved if tautomerization of  $\mathbf{2}$  is slow as compared to condensation with 1 to give 4. An oxidation process that involves formation of 2 as an intermediate or

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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*-benzylhydroxyl-amine 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<sub>3</sub>N in THF at room temperature. The reaction worked equally well in  $\alpha, \alpha, \alpha$ -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** – **11**, with TEMPO, 4-OH-TEMPO, or 4-acetamido-TEMPO (4-AcNH-TEMPO; 2.2 equiv.) in BTF<sup>1</sup>).

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).  $\alpha,\alpha$ -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-

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<sup>a</sup>)

Entry	Substrate 1	Х	Product 3		Time [h]	Yield [%] <sup>b</sup> )
1°) <sup>d</sup> )	<b>1a</b> · HCl	Н	Ph N OH	<b>3a</b>	0.5	99
2	1b	Н	Ph	3b	4	74
3	1c	Н	∕∕∕∕N∕ <sup>OH</sup>	3c	6	42
4°)	1d	Н	Ph Ph N-OH	3d	2	95
5	1e	Н	Et Ph N OH	3e	0.5	98
6°)	1f	Н	O N OH	3f	0.5	76
7	1g	Н	ОН	3g	1	99
8	1h	Н	∕∕∕∕ <sup>OBn</sup>	3h	12	94
9	1i	AcNH	Ph <sup>OMe</sup>	3i	12	86
10	1j	AcNH	Ph N OBn	3j	12	99
11	1k	Н	OBn	3k	12	94
12	11	Н	Et Ph N OBn	31	12	96

<sup>a</sup>) According to *Scheme 2* on a 0.5 mmol scale under Ar. <sup>b</sup>) Yield of isolated **3**. <sup>c</sup>) Run at r.t. <sup>d</sup>) With 1.1 equiv. of Et<sub>3</sub>N. <sup>e</sup>) 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<sub>2</sub> 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.

	A: 4-X-TEMPO (5 mol-%), $O_2$ ; or B: $O_2$	
R <sup>2</sup>	BTF, 24 h, r.t. or 80°	$R^2$
1a – 1I		3a – 3l

Entry	Temp. [°]	Х	Product <b>3</b>	Yield [%] <sup>b</sup> )	
				Method A	Method B
1°)	r.t.	ОН	<b>3</b> a	94	88
2	80	Н	3b	15 <sup>d</sup> )	13 <sup>d</sup> )
3	80	Н	3c	$< 1^{d}$ )	<1 <sup>d</sup> )
4	r.t.	Н	3d	58	<1
5	r.t.	Н	3e	43 <sup>d</sup> )	<1
6	r.t.	Н	3f	94	9
7	80	Н	3h	92	<1
8	80	Н	3i	90	<1
9	80	AcNH	3i	88	<1
10	80	Н	3j	98	<1
11	80	AcNH	3j	94	<1
12	80	Н	3k	91	<1
13	80	Н	31	85°)	<1

Table 2. Nitroxide-Catalyzed Aerobic Oxidation of Hydroxylamines and Alkoxyamines<sup>a</sup>)

<sup>a</sup>) According to *Scheme 3* on a 0.5 mmol scale. <sup>b</sup>) Yield of isolated **3**. <sup>c</sup>) With **1a**  $\cdot$  HCl and 1.1 equiv. of Et<sub>3</sub>N. <sup>d</sup>) The corresponding diazene-*N*-oxide of type **4** was formed (see *Scheme 1*). <sup>e</sup>) 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 Obenzyl 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 31 (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 Obenzylhydroxylamine (5.5 equiv.) and Et<sub>3</sub>N 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<sup>1</sup> and R<sup>2</sup>, see Table 3.

R <sup>1</sup> 	NH <sub>2</sub> OBn (5.5 equiv.) TEMPO (2.2 equiv.)	
R <sup>2</sup> Br	Et <sub>3</sub> N (1.1 equiv.)	R <sup>2</sup> N OBn
	EtOH, 6 h, 80°	3j, 3m – 3y

Entry	$\mathbb{R}^1$	$\mathbb{R}^2$	Product	Yield [%] <sup>b</sup> )
1	Н	Ph	3j	79
2	Н	$4-'Bu-C_6H_4$	3m	84
3	Н	$4-Me-C_6H_4$	3n	63
4	Н	$4-MeO-C_6H_4$	30	57
5	Н	$4-Br-C_6H_4$	3р	60
6	Н	$3-Me-C_6H_4$	3q	91
7	Н	$3-NO_2-C_6H_4$	3r	78
8	Н	$3-I-C_6H_4$	3s	74
9	Н	$2-Me-C_6H_4$	3t	82
10	Н	$2,4-Me_2C_6H_3$	3u	84
11	Н	$2\text{-Br-C}_6\text{H}_4$	3v	73
12	Н	(E)-PhCH = CH	3w	48
13	Me	Ph	3x	44
14°)	COOMe	Ph	3у	84

Table 3. TEMPO-Mediated Oxidation of in situ Generated Alkoxyamines<sup>a</sup>)

<sup>a</sup>) According to *Scheme 4* from the corresponding activated bromide on a 1 mmol scale. <sup>b</sup>) Yield of isolated **3**. <sup>c</sup>) 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<sub>2</sub>OH, 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  $\alpha$ -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

$$R \xrightarrow{H} \stackrel{\text{TEMPO}}{\longrightarrow} \stackrel{\text{TEMPO}}{\longrightarrow} R \xrightarrow{H} \stackrel{\text{TEMPO}}{\longrightarrow} \frac{\text{TEMPO}}{-\text{TEMPOH}} R \xrightarrow{N_{O}} \stackrel{\text{taut.}}{\longrightarrow} R \xrightarrow{N_{OH}} (1)$$

$$R^{1} \xrightarrow{N_{OR^{2}}} \stackrel{\text{TEMPO}}{\longrightarrow} \stackrel{\text{TEMPO}}{\longrightarrow} \stackrel{\text{TEMPO}}{\xrightarrow{N_{OR^{2}}}} \xrightarrow{\text{TEMPO}} R^{1} \xrightarrow{N_{OR^{2}}} (2)$$

**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.

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#### **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<sub>3</sub>N 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<sub>3</sub> soln. and extracting with CH<sub>2</sub>Cl<sub>2</sub> (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<sub>2</sub>; *Merck*). Flash chromatography (FC): silica gel 60 (SiO<sub>2</sub>, 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<sup>-1</sup>. <sup>1</sup>H- and <sup>13</sup>C-NMR Spectra: *Bruker-DPX-300* spectrometer; in CDCl<sub>3</sub> at 25°;  $\delta$  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<sub>3</sub>CN [23] or BH<sub>3</sub> · pyridine complex [24].

N-(3-Phenylpropyl)hydroxylamine (= N-Hydroxybenzenepropanamine; **1b**) [25a]: According to [21][24a] in 84% yield over two steps. Colorless solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.34–7.14 (*m*, 5 arom. H); 5.19 (br. *s*, NH, OH); 2.97 (*t*, *J* = 7.2, CH<sub>2</sub>N); 2.68 (*t*, *J* = 7.7, CCH<sub>2</sub>); 1.88 (*m*, CH<sub>2</sub>CH<sub>2</sub>N). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 141.8 (C); 128.5 (2 CH); 127.6 (CH); 125.9 (2 CH); 53.3 (CH<sub>2</sub>); 33.4 (CH<sub>2</sub>); 28.7 (CH<sub>2</sub>). HR-ESI-MS: 152.1072 ([M + H]<sup>+</sup>, C<sub>9</sub>H<sub>14</sub>NO<sup>+</sup>; calc. 152.1070).

N-*Hexylhydroxylamine* (= N-*Hydroxyhexan-1-amine*; **1c**) [25b]: According to [21][23] in 84% yield over two steps. Colorless solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 2.94 (t, J = 7.1, CH<sub>2</sub>N); 1.49–1.43 (m, CH<sub>2</sub>CH<sub>2</sub>N); 1.41–1.21 (m, CH<sub>2</sub>); 0.97–0.77 (m, Me). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 54.0 (CH<sub>2</sub>); 31.7 (CH<sub>2</sub>); 27.0 (CH<sub>2</sub>); 26.8 (CH<sub>2</sub>); 22.6 (CH<sub>2</sub>); 14.0 (Me). HR-ESI-MS: 118.1230 ([M + H]<sup>+</sup>, C<sub>6</sub>H<sub>16</sub>NO<sup>+</sup>; calc. 118.1226).

N-Benzhydrylhydroxylamine (= N-Hydroxy- $\alpha$ -phenylbenzenemethanamine; 1d) [25c]: According to [21][23] in 85% yield over two steps. Colorless solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.47–7.16 (*m*, 10 arom. H); 5.58 (br. *s*, OH); 5.23 (*s*, CHN); 4.99 (br. *s*, NH). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 140.7 (2 C);

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128.7 (4 CH); 127.7 (4 CH); 127.6 (2 CH); 70.8 (CH). HR-ESI-MS: 222.0884 ( $[M + Na]^+$ , C<sub>13</sub>H<sub>13</sub>NNaO<sup>+</sup>; calc. 222.0889).

N-(*1-Phenylpropyl*)*hydroxylamine* (= $\alpha$ -*Ethyl*-N-*hydroxybenzenemethanamine*; **1e**) [25d]: According to [21][23] in 54% yield over two steps. Colorless solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 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<sub>2</sub>); 0.83 (*t*, *J* = 7.5, Me). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 141.2 (C); 128.5 (2 CH); 127.8 (2 CH); 127.6 (CH); 68.7 (CH); 26.4 (CH<sub>2</sub>); 10.6 (Me). HR-ESI-MS: 152.1068 ([*M* + H]<sup>+</sup>, C<sub>9</sub>H<sub>14</sub>NO<sup>+</sup>; calc. 152.1070).

N-(*Chroman-4-yl*)*hydroxylamine* (= 3,4-*Dihydro*-N-*hydroxy*-2H-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*. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.30–7.15 (*m*, 2 arom. H); 6.96–6.81 (*m*, 2 arom. H); 4.33–4.18 (*m*, CH<sub>2</sub>O); 4.15–4.06 (*m*, CHN); 2.27–2.19 (*m*, 1 H, *CH*<sub>2</sub>CH); 2.13–1.94 (*m*, 1 H, *CH*<sub>2</sub>CH). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 155.7 (C); 130.3 (CH); 129.5 (CH); 120.3 (CH); 119.8 (C); 117.2 (CH); 62.0 (CH<sub>2</sub>); 54.9 (CH); 25.2 (CH<sub>2</sub>). HR-ESI-MS: 166.0864 ([*M*+H]<sup>+</sup>, C<sub>9</sub>H<sub>12</sub>NO<sup>+</sup><sub>2</sub>; calc. 166.0863).

N-*Cyclopentylhydroxylamine* (= N-*Hydroxycyclopentanamine*; **1g**) [25e]: According to [21][23] in 67% yield over two steps. Colorless solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 4.69 (br. *s*, NH, OH); 3.39-3.26 (*m*, CHN); 1.64-1.12 (*m*, 4 CH<sub>2</sub>). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 63.3 (CH); 30.4 (2 CH<sub>2</sub>); 24.7 (2 CH<sub>2</sub>). HR-ESI-MS: 102.0902 ([*M*+H]<sup>+</sup>, C<sub>5</sub>H<sub>12</sub>NO<sup>+</sup>; 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): 3090w, 3065w, 3032w, 2929s (br.), 2857s (br.), 2363w, 2338w, 1496w, 1454m, 1363m, 1207w, 1059w, 1009m (br.), 961m (br.), 910w, 743m, 698s, 612w. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.38–7.27 (m, 5 arom. H); 5.54 (br. s, NH); 4.71 (s, CH<sub>2</sub>O); 2.94 (t, J = 7.0, CH<sub>2</sub>N); 1.56–1.46 (m, CH<sub>2</sub>); 1.37–1.23 (m, 3 CH<sub>2</sub>); 0.96–0.83 (m, Me). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 138.1 (C); 128.4 (2 CH); 128.4 (2 CH); 127.8 (CH); 76.2 (CH<sub>2</sub>); 52.3 (CH<sub>2</sub>); 31.7 (CH<sub>2</sub>); 27.3 (CH<sub>2</sub>); 26.9 (CH<sub>2</sub>); 22.6 (CH<sub>2</sub>); 14.0 (Me). HR-ESI-MS: 208.1686 ( $[M + H]^+$ , Cl<sub>3</sub>H<sub>22</sub>NO<sup>+</sup>; calc. 208.1696).

N-Benzyl-O-methylhydroxylamine (= N-Methoxybenzenemethanamine; **1i**) [25f]: According to [24b] in 91% yield. Colorless oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.40–7.27 (*m*, 5 arom. H); 5.06 (br. *s*, NH); 4.07 (*s*, CH<sub>2</sub>); 3.54 (*s*, Me). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 137.6 (C); 128.8 (2 CH); 128.5 (CH); 127.5 (2 CH); 61.8 (CH<sub>2</sub>); 56.2 (Me). HR-ESI-MS: 138.0919 ( $[M + H]^+$ , C<sub>8</sub>H<sub>12</sub>NO<sup>+</sup>; calc. 138.0913).

N,O-Dibenzylhydroxylamine (= N-(Phenylmethoxy)benzenemethanamine; **1j**) [8]: According to [22] [23] in 95% yield over two steps. Colorless oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.41 – 7.25 (*m*, 10 arom. H); 5.73 (br. *s*, NH); 4.67 (*s*, CH<sub>2</sub>O); 4.06 (*s*, CH<sub>2</sub>N). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 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<sub>2</sub>); 56.6 (CH<sub>2</sub>). HR-ESI-MS: 214.1220 ( $[M + H]^+$ , C<sub>14</sub>H<sub>16</sub>NO<sup>+</sup>; 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): 3088w, 3064w, 3031w, 2956s (br.), 2910m (br.), 2868m (br.), 1496w, 1453m, 1356m, 1207w, 1053m, 1027m, 986s, 910m, 737s, 697s. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.41–7.27 (m, 5 arom. H); 5.37 (br. s, NH); 4.73 (s, CH<sub>2</sub>O); 3.62–3.51 (m, CH); 1.82–1.41 (m, 4 CH<sub>2</sub>). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 138.1 (C); 128.4 (2 CH); 128.3 (CH); 127.7 (2 CH); 76.5 (CH<sub>2</sub>); 61.9 (CH); 30.5 (2 CH<sub>2</sub>); 24.4 (2 CH<sub>2</sub>). HR-ESI-MS: 192.1388 ( $[M + H]^+$ , C<sub>12</sub>H<sub>18</sub>NO<sup>+</sup>; calc. 192.1383).

O-Benzyl-N-(1-phenylpropyl)hydroxylamine (= $\alpha$ -Ethyl-N-(phenylmethoxy)benzenemethamine; **11**) [25g]: According to [21][23] in 92% yield over two steps. Colorless oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.39–7.19 (*m*, 10 arom. H); 5.69 (br. *s*, NH); 4.62 (*d*, *J* = 11.4, 1 H, CH<sub>2</sub>O); 4.55 (*d*, *J* = 11.4, 1 H, CH<sub>2</sub>O); 3.90 (*dd*, *J* = 8.5, 5.6, CHN); 1.93–1.54 (*m*, MeCH<sub>2</sub>); 0.81 (*t*, *J* = 7.5, Me). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 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<sub>2</sub>); 67.5 (CH); 26.7 (CH<sub>2</sub>); 10.6 (Me). HR-ESI-MS: 242.1537 ([*M* + H]<sup>+</sup>, C<sub>16</sub>H<sub>20</sub>NO<sup>+</sup>; 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.; 0.2 $\mu$ ) 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<sub>3</sub>N (157  $\mu$ l, 1.10 mmol, 1.1 equiv.) and the activated bromide (1.00 mmol, 1.0 equiv.; 0.25 $\mu$ ) were added to a soln. of TEMPO (344 mg, 2.20 mmol, 2.2 equiv.) and NH<sub>2</sub>OBn (570  $\mu$ l, 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<sub>3</sub>N (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/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<sub>3</sub>N (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/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). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 8.15 (*s*, CH); 8.08 (*s*, OH); 7.53–7.63 (*m*, 2 arom. H); 7.44–7.33 (*m*, 3 arom. H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 148.5 (CH); 130.1 (C); 128.1 (CH); 126.9 (2 CH); 125.1 (2 CH). HR-ESI-MS: 144.0417 ([*M* + Na]<sup>+</sup>, C<sub>7</sub>H<sub>7</sub>NNaO<sup>+</sup>; 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<sub>2</sub> 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. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>; (*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<sub>2</sub>); 2.77 – 2.64 (*m*, CH<sub>2</sub>, (*Z*)-isomer); 2.59 – 2.46 (*m*, CH<sub>2</sub>, (*E*)-isomer). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>; 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<sub>2</sub>); 31.9 (CH<sub>2</sub>); 31.2 (CH<sub>2</sub>); 26.4 (CH<sub>2</sub>). HR-ESI-MS: 172.0736 ([*M* + Na]<sup>+</sup>, C<sub>9</sub>H<sub>11</sub>NNaO<sup>+</sup>; 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*. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>; both stereoisomers): 7.89 (br. *s*, OH, 1<sup>st</sup> isomer); 7.53 (br. *s*, OH, 2<sup>nd</sup> isomer); 7.43 (*t*, *J* = 6.1, CH, 2<sup>nd</sup> isomer); 6.72 (*t*, *J* = 5.5, CH, 1<sup>st</sup> isomer); 2.44–2.32 (*m*, CH<sub>2</sub>CH, 1<sup>st</sup> isomer); 2.26–2.13 (*m*, CH<sub>2</sub>CH, 2<sup>nd</sup> isomer); 1.58–1.43 (*m*, 4 H, CH<sub>2</sub>CH<sub>2</sub>CH); 1.42–1.23 (*m*, 8 H, MeCH<sub>2</sub>CH<sub>2</sub>); 1.01–0.91 (*m*, 6 H, Me). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>; both stereoisomers): 153.1 (CH); 152.4 (CH); 31.5 (CH<sub>2</sub>); 31.2 (CH<sub>2</sub>); 29.4 (CH<sub>2</sub>); 26.2 (CH<sub>2</sub>); 25.7 (CH<sub>2</sub>); 24.9 (CH<sub>2</sub>); 22.3 (2 CH<sub>2</sub>); 13.9 (2 Me). HR-ESI-MS: 138.0886 ([*M*+Na]<sup>+</sup>, C<sub>6</sub>H<sub>13</sub>NNaO<sup>+</sup>; 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/'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<sub>2</sub> for 24 h at r.t. FC (pentane/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**: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.73 (*s*, OH); 7.52–7.28 (*m*, 10 arom. H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 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]<sup>+</sup>, C<sub>13</sub>H<sub>11</sub>NNaO<sup>+</sup>; 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<sub>2</sub> 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**: <sup>1</sup>H-NMR (300, CDCl<sub>3</sub>): 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<sub>2</sub>); 1.18 (*t*, *J* = 7.6, Me). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 160.8 (C); 135.6 (C); 129.2 (CH); 128.7 (CH); 128.5 (CH); 127.8 (CH); 126.5 (CH); 19.8 (CH<sub>2</sub>); 10.9 (Me). HR-ESI-MS: 172.0726 ([M + Na]<sup>+</sup>, C<sub>9</sub>H<sub>11</sub>NNaO<sup>+</sup>; calc. 172.0733).

2,3-Dihydro-4H-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  $80^{\circ}$ . 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<sub>2</sub> 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**: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 8.01 (br. *s*, OH); 7.83 (*dd*, J = 7.9, 1.7, CH<sub>arom</sub>CO); 7.31 – 7.22 (*m*, CHCCN); 7.03 – 6.84 (*m*, 2 arom. H); 4.25 (*t*, J = 6.2, CH<sub>2</sub>O); 2.99 (*t*, J = 6.2, CH<sub>2</sub>CN). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 156.8 (C); 150.0 (C); 131.3 (CH); 124.0 (CH); 121.5 (CH); 118.2 (C); 117.9 (CH); 65.0 (CH<sub>2</sub>); 23.6 (CH<sub>2</sub>). HR-ESI-MS: 186.0527 ([M + Na]<sup>+</sup>, C<sub>9</sub>H<sub>9</sub>NNaO<sup>+</sup><sub>2</sub>; 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. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.92 (br. *s*, OH); 2.52–2.29 (*m*, 4 H, CH<sub>2</sub>CN); 1.84–1.66 (*m*, 2 CH<sub>2</sub>). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 167.4 (C); 30.9 (CH<sub>2</sub>); 27.1 (CH<sub>2</sub>); 25.0 (CH<sub>2</sub>); 24.6 (CH<sub>2</sub>). HR-ESI-MS: 122.0566 ( $[M + Na]^+$ , C<sub>5</sub>H<sub>9</sub>NNaO<sup>+</sup>; calc. 122.0576).

*Hexanal* O-(*Phenylmethyl*)*oxime* (**3h**): According to *GP1*, with **1h** (104 mg, 507  $\mu$ mol, 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 *GP*2, with **1h** (207 mg, 1.00 mmol, 1 equiv.) and TEMPO (78 mg, 50 µmol, 5 mol-%) in the presence of O<sub>2</sub> 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*. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>; 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<sub>2</sub>O, minor isomer); 5.06 (*s*, CH<sub>2</sub>O, major isomer); 2.43 – 2.32 (*m*, CH<sub>2</sub>CH, minor isomer); 2.25 – 2.13 (*m*, CH<sub>2</sub>CH, major isomer); 1.54 – 1.41 (*m*, 4 H, CH<sub>2</sub>); 1.39 – 1.22 (*m*, 8 H, CH<sub>2</sub>); 0.97 – 0.82 (*m*, 6 H, Me). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>; 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<sub>2</sub>); 75.5 (CH<sub>2</sub>); 31.5 (CH<sub>2</sub>); 31.3 (CH<sub>2</sub>); 29.5 (CH<sub>2</sub>); 26.4 (CH<sub>2</sub>); 25.9 (CH<sub>2</sub>); 25.8 (CH<sub>2</sub>); 22.3 (2 CH<sub>2</sub>); 13.9 (2 Me). HR-ESI-MS: 228.1359 ([*M* + Na]<sup>+</sup>, C<sub>13</sub>H<sub>19</sub>NNaO<sup>+</sup>; 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**: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 8.06 (*s*, CHN); 7.62–7.54 (*m*, 2 arom. H); 7.40–7.38 (*m*, 3 arom. H); 3.98 (*s*, Me). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 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<sub>8</sub>H<sub>10</sub>NO<sup>+</sup>; calc. 136.0757).

Benzaldehyde O-(Phenylmethyl)oxime (**3**j) [22]: According to GP1, with **1**j (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 **3**j (with 4-OH-TEMPO: 97 mg, 92%; with 4-AcNH-TEMPO: 104 mg, 99%). Colorless oil.

According to *GP2*, with **1j** (107 mg, 501  $\mu$ mol, 1 equiv.) and TEMPO (3.9 mg, 26  $\mu$ mol, 5 mol-%) or 4-AcNH-TEMPO (4.9 mg, 25  $\mu$ mol, 5 mol-%) in the presence of O<sub>2</sub> 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/'BuOMe 100:1) afforded **3j** (167 mg, 79%). Colorless oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 8.15 (*s*, CHN); 7.64–7.52 (*m*, 2 arom. H); 7.48–7.28 (*m*, 8 arom. H); 5.22 (*s*, CH<sub>2</sub>). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 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<sub>2</sub>). HR-ESI-MS: 234.0887 ([M + Na]<sup>+</sup>, C<sub>14</sub>H<sub>13</sub>NNaO<sup>+</sup>; 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 *GP*2, with **1k** (191 mg, 1.00 mmol, 1 equiv.) and TEMPO (78 mg, 50 µmol, 5 mol-%) in the presence of O<sub>2</sub> 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**: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.40–7.27 (*m*, 5 arom. H); 5.09 (*s*, CH<sub>2</sub>O); 2.52–2.32 (*m*, 2 CH<sub>2</sub>); 1.81–1.67 (*m*, 2 CH<sub>2</sub>). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 167.1 (C); 138.4 (C); 128.3 (2 CH); 127.9 (2 CH); 127.6 (CH); 75.5 (CH<sub>2</sub>); 31.0 (CH<sub>2</sub>); 30.0 (CH<sub>2</sub>); 25.2 (CH<sub>2</sub>); 24.7 (CH<sub>2</sub>). HR-ESI-MS: 212.1052 ([*M* + Na]<sup>+</sup>, C<sub>12</sub>H<sub>15</sub>NONa<sup>+</sup>; calc. 212.1046).

*1-Phenylpropan-1-one* O-(*Phenylmethyl*)oxime (**3**I) [26f]: According to *GP1*, with **1**I (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 **3**I (114 mg, 481 µmol, 96%). Colorless oil.

According to *GP2*, with **11** (121 mg, 501 µmol, 1 equiv.) and TEMPO (7.8 mg, 50 µmol, 10 mol-%) in the presence of O<sub>2</sub> for 48 h at 80°. FC (pentane/AcOEt 50 : 1) afforded **31** (102 mg, 85%). Colorless oil. In the control experiment under identical conditions without addition of nitroxide catalyst, 99% of **11** was recovered. **31**: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.69–7.58 (*m*, 2 arom. H); 7.46–7.27 (*m*, 8 arom. H); 5.24 (*s*, CH<sub>2</sub>O); 2.80 (*q*, J = 7.6, CH<sub>2</sub>CN); 1.15 (*t*, J = 7.6, Me). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 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<sub>2</sub>); 20.3 (CH<sub>2</sub>); 11.1 (Me). HR-ESI-MS: 262.1197 ([M + Na]<sup>+</sup>, C<sub>16</sub>H<sub>17</sub>NNaO<sup>+</sup>; calc. 262.1202).

4-(1,1-Dimethylethyl)benzaldehyde O-(Phenylmethyl)oxime (**3m**): According to *GP3*, with 4-tertbutylbenzyl bromide (184  $\mu$ l, 1.00 mmol, 1 equiv.). FC (pentane/BuOMe 100:1) afforded **3m** (254 mg, 84%). Colorless solid. M.p. 27°. IR (neat): 3069w, 3032w, 2969m (br.), 2904m, 2868m, 1611m, 1496m, 1454m, 1395w, 1364m, 1340m, 1269m, 1219m, 1107m, 1082m, 1038s, 1014s, 985s, 936s, 914s, 860m, 830s, 733s, 695s, 642m, 615m. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 8.17 (s, CHN); 7.61–7.43 (m, 2 arom. H); 7.42–7.31 (m, 7 arom. H); 5.25 (s, CH<sub>2</sub>O); 1.36 (s, 3 Me). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 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<sub>2</sub>); 33.7 (C); 30.1 (3 Me). HR-ESI-MS: 290.1511 ( $[M + Na]^+$ , C<sub>18</sub>H<sub>21</sub>NNaO<sup>+</sup>; calc. 290.1515). Anal. calc. for C<sub>18</sub>H<sub>21</sub>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/BuOMe 100:1) afforded **3n** (142 mg, 63%). Colorless oil. IR (neat): 3067w, 3031w, 2922m (br.), 2871w (br.), 1612m (br.), 1513m, 1497m, 1454m,

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*. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 8.13 (*s*, CHN); 7.55 – 7.29 (*m*, 7 arom. H); 7.23 – 7.14 (*m*, 2 arom. H); 5.22 (*s*, CH<sub>2</sub>O); 2.37 (*s*, Me). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 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<sub>2</sub>); 21.4 (Me). HR-ESI-MS: 248.1046 ([M + Na]<sup>+</sup>, C<sub>15</sub>H<sub>15</sub>NNaO<sup>+</sup>; calc. 248.1046).

4-Methoxybenzaldehyde O-(Phenylmethyl)oxime (**30**) [26g]: According to *GP3*, with 4-methoxybenzyl bromide (201 mg, 1.00 mmol, 1 equiv.). FC (pentane/BuOMe 100:1) afforded **30** (138 mg, 57%). Colorless oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 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<sub>2</sub>); 3.83 (*s*, Me). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 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<sub>2</sub>); 55.3 (Me). HR-ESI-MS: 264.0991 ([*M*+Na]<sup>+</sup>, C<sub>15</sub>H<sub>15</sub>NNaO<sup>+</sup><sub>2</sub>; 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/'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*. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 8.08 (*s*, CH); 7.58 – 7.29 (*m*, 9 arom. H); 5.22 (*s*, CH<sub>2</sub>). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 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<sub>2</sub>). HR-ESI-MS: 290.0177 ([*M*+H]<sup>+</sup>, C<sub>14</sub>H<sub>13</sub>BrNO<sup>+</sup>; 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/BuOMe 100:1) afforded **3q** (205 mg, 91%). Colorless oil. IR (neat): 3063w, 3032w, 2921w, 2870w, 1950w, 1880w, 1605w, 1580w, 1496w, 1454m, 1366m, 1339m, 1249w, 1249w, 1209w, 1159m, 1082m, 1038m, 1025m, 985m, 945s, 913m, 782s, 733s, 692s, 650m, 606m. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 8.13 (*s*, CHN); 7.51–7.14 (*m*, 9 arom. H); 5.23 (*s*, CH<sub>2</sub>O); 2.37 (*s*, Me). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 149.3 (CH); 138.4 (C); 137.6 (C); 132.2 (C); 130.7 (2 CH); 128.6 (2 CH); 128.4 (CH); 127.9 (CH); 127.5 (CH); 124.5 (CH); 76.4 (CH<sub>2</sub>); 21.3 (Me). HR-ESI-MS: 226.1227 ([M + H]<sup>+</sup>, C<sub>15</sub>H<sub>16</sub>NO<sup>+</sup>; 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/'BuOMe 100:1) afforded **3r** (200 mg, 78%). Colorless solid. M.p. 36°. IR (neat): 3092w, 3033w, 2928w (br.), 2875w (br.), 1737w, 1611w, 1528s, 1454m, 1352s, 1212m, 1081m, 1018m, 950m, 920m, 829w, 807w, 735s, 697m, 677m, 642w. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 8.46–8.40 (*m*, CCHCNO<sub>2</sub>); 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, CHCHCNO<sub>2</sub>); 7.47–7.30 (*m*, 5 arom. H); 5.26 (*s*, CH<sub>2</sub>). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 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<sub>2</sub>). HR-ESI-MS: 279.0745 ([*M* + Na]<sup>+</sup>, C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>NaO<sup>+</sup><sub>3</sub>; 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/BuOMe 100:1) afforded **3s** (248 mg, 74%). Colorless oil. IR (neat): 4050w, 3061w, 3031w, 2926w (br.), 2875w, 1875w, 1588w, 1556m, 1496w, 1467w, 1454m, 1418w, 1366w, 1336w, 1249w, 1206m, 1016s, 994s, 941s, 918s, 872m, 782m, 733m, 684s, 641w, 609m. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 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, CHCHCI); 5.22 (s, CH<sub>2</sub>). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 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<sub>2</sub>). HR-ESI-MS: 338.0039 ([M + H]<sup>+</sup>, C<sub>14</sub>H<sub>13</sub>INO<sup>+</sup>; 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/'BuOMe 100:1) afforded **3t** (92 mg, 82%). Colorless oil. IR (neat): 3067s, 3031s, 2924s, 2871s, 2362s, 2336s, 1610s, 1496s, 1454m, 1366m, 1292s, 1226s, 1209s, 1082s, 1016s, 984s, 936s, 915s, 858m, 783m, 752s, 696s, 640m, 612m. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 8.32 (*s*, CHN); 7.65–7.57 (*m*, 1 arom. H); 7.38–7.04 (*m*, 8 arom. H); 5.14 (*s*, CH<sub>2</sub>); 2.31 (*s*, Me). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 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<sub>2</sub>); 19.9 (Me). HR-ESI-MS: 248.1037 ([*M* + Na]<sup>+</sup>, C<sub>15</sub>H<sub>15</sub>NNaO<sup>+</sup>; 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/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*. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 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<sub>2</sub>); 2.38 (*s*, 1 Me); 2.33 (*s*, 1 Me). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 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<sub>2</sub>); 21.3 (Me); 19.8 (Me). HR-ESI-MS: 262.1198 ([*M* + Na]<sup>+</sup>, C<sub>16</sub>H<sub>17</sub>NNaO<sup>+</sup>; 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/BuOMe 100:1) afforded **3v** (206 mg, 73%). Colorless oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 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<sub>2</sub>). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 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<sub>2</sub>). HR-ESI-MS: 312.0005 ([*M* + Na]<sup>+</sup>, C<sub>14</sub>H<sub>12</sub>BrNNaO<sup>+</sup>; 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/BuOMe 100:1) afforded **3w** (114 mg, 48%; *ca.* 2.5:1 (*E*)/(*Z*)-mixture). Colorless solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>; 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, CHCH); 5.22 (*s*, CH<sub>2</sub>, (*Z*)-isomer); 5.17 (*s*, CH<sub>2</sub>, (*E*)-isomer). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>; 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<sub>2</sub>); 76.3 (CH<sub>2</sub>). HR-ESI-MS: 260.1042d ([*M*+Na]<sup>+</sup>, C<sub>16</sub>H<sub>15</sub>NNaO<sup>+</sup>; calc. 260.1046).

*1-Phenylethanone* O-(*Phenylmethyl*)*oxime* (**3x**) [26j]: According to *GP3*, with (1-bromoethyl)benzene (137  $\mu$ l, 1.00 mmol, 1 equiv.). FC (pentane/BuOMe 100 : 1) afforded **3x** (99 mg, 44%). Colorless oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.69–7.64 (*m*, 2 arom. H); 7.47–7.30 (*m*, 8 arom. H); 5.27 (*s*, CH<sub>2</sub>); 2.28 (*s*, Me). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): 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<sub>2</sub>); 12.9 (Me). HR-ESI-MS: 248.1040 ([*M* + Na]<sup>+</sup>, C<sub>15</sub>H<sub>15</sub>NNaO<sup>+</sup>; calc. 248.1046).

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

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