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Convenient synthesis of α-nitrooximes mediated by OXONE®†

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A novel OXONE® mediated direct difunctionalization of alkenes with $NaNO_2$ in aqueous acetonitrile for the synthesis of α-nitrooximes was developed. The α-nitrooximes were readily prepared in moderate to high yields at room temperature under mild reaction conditions. The present protocol offers an easy and environmentally benign approach to access various α-nitrooximes derived from styrene derivatives.

Introduction

1,2-Difunctionalizations of the carbon–carbon double bonds in alkenes are among the most powerful transformations in chemical synthesis. They are challenging synthetic transformations in organic chemistry, used for the introduction of functional groups into an unactivated alkene moiety as well as for the enhancement of molecular complexity. In recent years, novel metal-catalyzed and metal-free methods for the difunctionalization of alkenes have been reported, such as dioxygenation,[1] oxyamination,[2] oxythiolation,[3] oxyphosphorylation,[4] and diamination.[5] In particular, the introduction of two vicinal carbon–nitrogen bonds provides powerful access to vicinal diamines which are important scaffolds found in pharmaceutically important compounds, materials and ligands in catalysis (Fig. 1).[6] Therefore, the development of new reactions that allow direct access for the formation of C–N bonds from alkenes has long been a challenge of interest to the synthetic community.

In contrast to the synthesis of oximes from alkenes,[7] the synthesis of α-nitrooximes has been less studied (Scheme 1).[8] Scheinbaum employed the reaction of olefins with nitrous anhydride (N_2O_3) generated by the reaction of nitric oxide and air, followed by the treatment of the initially obtained pseudonitrosites with $ZnCl_2$ (Scheme 1, Path A).[8c] The preformed peroxynitrite-promoted reaction of styrene, leading to a mixture of α-nitrooxime, nitrate, benzaldehyde, α-nitroacetophenone and a nitroalkene was reported by Grossi (Scheme 1, Path B).[8b] Also, a solvent-free synthesis of pseudonitrosites, which can undergo tautomerization to α-nitrooxime, was reported by Shaabani and co-workers (Scheme 1, Path C).[8a] Despite significant developments, available methods toward α-nitrooxime synthesis required gaseous reagents or tedious experimentations for the preparation of the requisite reagent.[8c,9] With continuous research efforts aiming at 1,2-difunctionalizations of alkenes and alkynes,[10] we report herein an alternative, convenient and efficient synthesis of α-nitrooximes from alkenes by employing commercially available reagents ($NaNO_2$ and OXONE®) (Scheme 1). OXONE® is found in many synthetic applications, due to its stability, high efficiency and mild

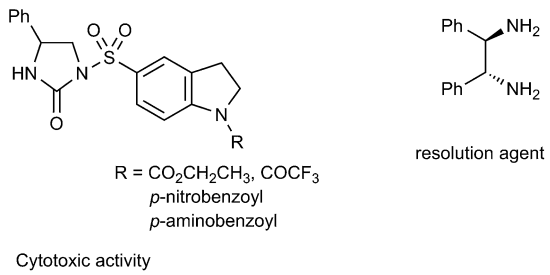
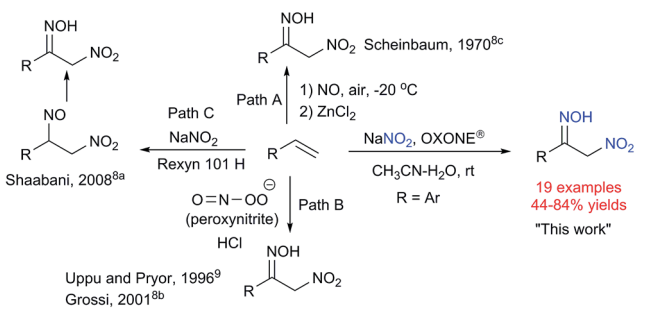


Fig. 1 Representative examples of some important compounds containing the diamine moiety.



Scheme 1 Methods for α-nitrooxime synthesis.

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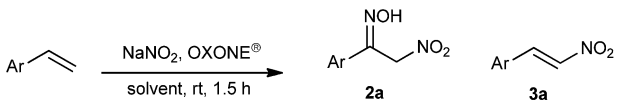
reaction conditions, as well as the minimization of organic chemical waste.[11]

Results and discussion

Initially, the reaction of 4-bromostyrene (**1a**) with $NaNO_2$/OXONE® was chosen as a model reaction in order to find the optimized reaction conditions. The selected results of the optimization experimentation are summarized in Table 1. In a typical reaction procedure, **1a**, $NaNO_2$ (half of the total amount employed) and OXONE® were suspended in an organic solvent, followed by the slow addition of water. After the reaction was stirred at room temperature for 45 min, a second half portion of $NaNO_2$ was added and the reaction was further stirred for an additional 45 min. After chromatographic purification by column chromatography, the corresponding α-nitrooxime **2a** was isolated as a single isomer (^{1}H NMR analysis) along with a nitroalkene **3a** (*E* isomer) as a competing product. The α-nitrooxime **2a** and nitroalkene **3a** could be readily separated by simple column chromatography. In the initial experiment, **1a** was allowed to react with $NaNO_2$ (4 equiv.) and OXONE® (2 equiv.). A screening of the solvents indicated that a combination of acetonitrile and water gave the best results, affording the desired α-nitrooxime **2a** in 84% isolated yield (Table 1, entries 1–8). When the reactions were carried out with a lower ratio of water to CH_3CN, lower yields of **2a** were obtained (Table 1, entry 9). The reaction was less efficient upon a decrease or increase of the amount of either $NaNO_2$ or OXONE® employed (Table 1, entries 10–13). It is worth mentioning that in the reactions shown in Table 1, entry 8 was carried out by employing a single portion of $NaNO_2$ (4 equiv.) in the reaction vessel; a vigorous reaction took place with the observation of heat generation as well as fuming of brownish gaseous species.

Table 1 Reaction optimization[a]



1a; Ar = *p*BrC$_6$H$_4$

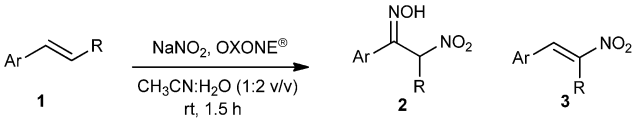
Entry	OXONE® (equiv.)	$NaNO_2$ (equiv.)	Solvent (v/v)	Yield[b] (%) 2a[c]	3a
1	2	4	CH_2Cl_2 : H_2O (1 : 2)	37	8
2	2	4	$ClCH_2CH_2Cl$: H_2O (1 : 2)	40	19
3	2	4	EtOAc : H_2O (1 : 2)	52	7
4	2	4	Acetone : H_2O (1 : 2)	55	10
5	2	4	Toluene : H_2O (1 : 2)	43	13
6	2	4	*i*PrOH : H_2O (1 : 2)	22	—
7	2	4	MeOH : H_2O (1 : 2)	—	—
8	2	4	CH_3CN : H_2O (1 : 2)	84	6
9	2	4	CH_3CN : H_2O (2 : 1)	68	5
10	2	2	CH_3CN : H_2O (1 : 2)	9	10
11	2	3	CH_3CN : H_2O (1 : 2)	44	2
12	1	4	CH_3CN : H_2O (1 : 2)	47	19
13	4	4	CH_3CN : H_2O (1 : 2)	45	13

[a] Reaction conditions: **1a** (0.5 mmol), $NaNO_2$ (half of the total amount employed), and OXONE® were suspended in an organic solvent, followed by the slow addition of water. After the reaction was stirred at room temperature for 45 min, a second half portion of $NaNO_2$ was added and the reaction was further stirred for an additional 45 min. [b] Isolated yield. [c] In all cases, **2a** was obtained as a single isomer after chromatographic purification.

With the above optimal reaction conditions in hand (Table 1, entry 8), the scope and limitations of the reaction were evaluated by employing a range of structurally different styrene derivatives. It should be noted that, except for **2r**, the α-nitrooximes were obtained as a mixture of two isomers (^{1}H NMR analysis of the crude mixtures or after chromatographic purification). Upon column chromatographic purification, in some cases, the α-nitrooximes were isolated as a single isomer. The results are summarized in Table 2. Halogen-substituted styrene derivatives including Br, Cl and F at the *para*-, *meta*-, or *ortho*-positions gave the corresponding products in moderate to good yields (59–84% yields) (Table 2, entries 1–6). Furthermore, 4-nitrostyrene and 3-nitrostyrene also gave moderate yields (62–66% yields) (Table 2, entries 7 and 8). A sensitive formyl group and a chloromethyl group were found to be well accommodated and each of their corresponding products were obtained as a single isomer (Table 2, entries 9 and 10). Electron-releasing substituted styrenes including 4-Me-, 4-MeO-, and 4-*t*Bu-substituted styrenes appeared less efficient, yielding the corresponding α-nitrooximes in moderate yields (45–59% yields) (Table 2, entries 11–13). 4-Acetoxystyrene afforded its corresponding α-nitrooxime in 71% yield (Table 2, entry 14). Moreover, the reactions involving a simple styrene, 1-vinylnaphthalene, and β-substituted styrene derivatives which include β-methylstyrene and 1,2-dihydronaphthalene, were also successful, yielding the respective products in moderate yields (44–63% yields) (Table 2, entries 15–18). Finally, 2-vinylthiophene gave the corresponding α-nitrooxime derivative in 73% yield (Table 2, entry 19) while 2-vinyl- and 4-vinylpyridines led to unidentified complex mixtures. It should be noted that in all cases, the corresponding nitroalkenes (*E* isomers) were also obtained in varying quantities (2–21% yields). Unfortunately, the present protocol was found to be incompatible with aliphatic alkenes including 1-octene and cyclohexene; complex mixtures were observed in the TLC analyses with poor mass recovery.

While no detailed mechanistic studies were carried out, to follow the reaction pathway, some control experiments were conducted. Thus, the reaction with *p*-bromostyrene (**1a**) was carried out in the presence of radical inhibitors, including TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl, 1 equiv.] and BHT (3,5-di-*tert*-butyl-4-hydroxytoluene, 1 equiv.) (Scheme 2). It was found that the α-nitrooxime **2a** was obtained in much lower yields, 19% yield and 32% yield, respectively. Since both the TEMPO and BHT experiments only lower the reaction yields rather than cease the reaction, the control experiments do not fully indicate a radical mechanism. On the basis of previous reports,[8b,c] a mechanistic proposal is predicted as shown in Scheme 3. Primarily, a nitrite anion is oxidized by OXONE®,

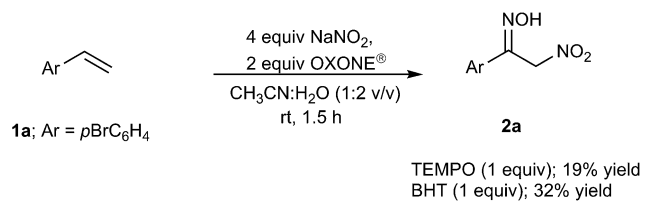
Table 2 Evaluation of scope and limitations of the reaction[a]



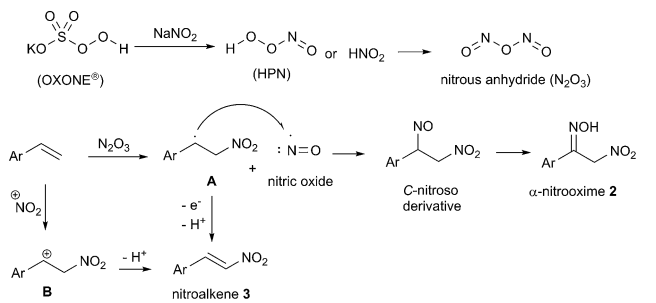
	Substrate		Product; yield[b] (%)	
Entry	Ar =	R =	α-Nitrooxime, **2** (isomer ratio)[c]	Nitroalkene, **3**
1	4-BrC_6H_4	H	**2a**; 84 (single isomer)[d]	**3a**; 6
2	4-ClC_6H_4	H	**2b**; 73 (27.6 : 1)	**3b**; 10
3	3-ClC_6H_4	H	**2c**; 74 (14.4 : 1)	**3c**; 3
4	2-ClC_6H_4	H	**2d**; 59 (1.7 : 1)	**3d**; 6
5	4-FC_6H_4	H	**2e**; 69 (11.5 : 1)	**3e**; 7
6	3-FC_6H_4	H	**2f**; 75 (32.3 : 1)	**3f**; 2
7	4-$O_2NC_6H_4$	H	**2g**; 66 (19.0 : 1)	**3g**; 5
8	3-$O_2NC_6H_4$	H	**2h**; 62 (21.2 : 1)	**3h**; 3
9	3-$OHCC_6H_4$	H	**2i**; 56 (single isomer)[d]	**3i**; 7
10	4-$(ClCH_2)C_6H_4$	H	**2j**; 60 (single isomer)[d]	**3j**; 7
11	4-MeC_6H_4	H	**2k**; 45 (10.8 : 1)	**3k**; 21
12	4-$MeOC_6H_4$	H	**2l**; 51 (single isomer)[d]	**3l**; 5
13	4-*t*-BuC_6H_4	H	**2m**; 59 (5.5 : 1)	**3m**; 8
14	4-$AcOC_6H_4$	H	**2n**; 71 (14.4 : 1)	**3n**; 9
15	C_6H_5	H	**2o**; 63 (single isomer)[d]	**3o**; 5
16	1-Naphthyl	H	**2p**; 44 (1.7 : 1)	**3p**; 15
17	C_6H_5	CH_3	**2q**; 52 (2.3 : 1)	**3q**; 12
18			**2r**; 56 (single isomer)[e]	**3r**; 0
19	1-Thienyl	H	**2s**; 73 (1 : 1)	**3s**; 0

[a] Reaction conditions: **1** (0.5 mmol), $NaNO_2$ (2 equiv.) and OXONE® (2 equiv.) were suspended in CH_3CN (1 mL), followed by the slow addition of water (2 mL). After the reaction was stirred at room temperature for 45 min, $NaNO_2$ (2 equiv.) was added and the reaction was further stirred for an additional 45 min. [b] Isolated yield; in most cases their corresponding nitroalkenes (*E* isomers) were isolated in the range of 2–21% yields. [c] The isomeric ratio was determined by ^1H NMR analysis. [d] ^1H NMR spectral data of the crude mixtures exhibited a mixture of two isomers; compound (isomer ratio): **2a** (11.0 : 1); **2i** (10.5 : 1); **2j** (10 : 1); **2l** (9.2 : 1); **2o** (9.9 : 1). [e] A ^1H NMR spectrum of the crude mixture exhibited a single isomer.

generating unstable peroxynitrous acid (HPN, HOONO). Under the reaction conditions (OXONE®, $pK_a \sim 2$), the peroxynitrous acid decomposes, leading to a reactive species which is believed to be nitrous anhydride (N_2O_3). Alternatively, sodium nitrite under relatively acidic conditions *in situ* generates nitrous acid (HNO_2) which undergoes decomposition to furnish several electrophilic species including NO, NO_2, N_2O_3 and N_2O_4. The nitrous anhydride reacts with styrene and its derivatives to generate a more stable benzylic radical **A** and nitric oxide (NO). Subsequent coupling of the benzylic radical **A** with nitric oxide then gives a *C*-nitroso derivative which easily undergoes tautomerization, leading to the observed α-nitrooxime **2**. It is believed that the major isomer of α-nitrooxime **2** that was obtained has a *Z* configuration (the methylnitro group *syn* to the hydroxy group). In comparison with a closely related system, the ^1H NMR signals of the methylene protons of the *Z* isomer resonate at a lower field than those of the *E* isomer due to the deshielding effect of the electronegative oxygen atom.[12] As the corresponding nitroalkene **3** was isolated as a by-product, it is



Scheme 2 Control experiments.



Scheme 3 Plausible reaction pathway.

likely to be derived from the benzylic radical **A** generating a benzyl cation *via* a one-electron oxidation with OXONE® followed by a deprotonation process. Although the radical mechanistic pathway shown in Scheme 3 can direct alkenes to α-nitrooximes, we cannot exclude the possibility of the ionic mechanism proceeding *via* the nitronium ion ($^{+}NO_2$) which acts as a nitrating species. The failure of aliphatic alkenes to undergo the reaction suggests the involvement of the cationic intermediate. The formation of nitroalkene **3** also suggests the involvement of the nitronium ion ($^{+}NO_2$) to serve as a reactive electrophile. Thus, the nitronium ion reacts with the styrene substrates, leading to a benzylic cation **B** which upon elimination of a proton yields nitroalkene **3** (Scheme 3).

Conclusion

In summary, we have developed a convenient synthesis of α-nitrooximes from styrene derivatives by employing a new combination of the inorganic salt OXONE® and sodium nitrite. The reaction readily proceeded at ambient temperature and conveniently employed inexpensive and environmentally benign reagents. The reaction offers easy access to the 1,2-difunctionalization of alkenes through the formation of C–N bonds, albeit limited to styrene derivatives.

Experimental

General information

^{1}H NMR spectra were recorded with a Bruker DPX-300 (300 MHz) or a Bruker Ascend™ 400 (400 MHz) spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard or in acetone-d_6 using a residual non-deuterated solvent peak as an internal standard. ^{13}C NMR spectra were recorded with a Bruker DPX-300 (75 MHz) or a Bruker Ascend™ 400 (100 MHz) spectrometer in $CDCl_3$ or acetone-d_6 using a residual non-deuterated solvent peak as an internal standard. IR spectra were recorded with a Perkin Elmer 683 GX FTIR System spectrometer. High resolution mass spectra were recorded with a Bruker micro TOF spectrometer. Melting points were recorded with a digital Electrothermal Melting 9100 apparatus and uncorrected. Column chromatography was performed using Merck silica gel (Art 7734). Other common solvents (dichloromethane, hexanes, ethyl acetate, and acetone) were distilled before use.

General procedure for the synthesis of α-nitrooxime

A mixture of the styrene derivative (0.5 mmol), sodium nitrite (68.9 mg, 1 mmol) and OXONE® (307.4 mg, 1 mmol) was suspended in acetonitrile (1 mL). To this mixture was slowly added H_2O (2 mL) at room temperature. After the reaction mixture was stirred at room temperature for 45 min, a second portion of sodium nitrite (68.9 mg, 1 mmol) was introduced and the resulting mixture was further stirred for an additional 45 min. The reaction mixture was diluted by the addition of water (5 mL) and was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with H_2O (20 mL) and brine (20 mL), dried (anhydrous $MgSO_4$), filtered and vacuumed (aspirator). The residue was purified by column chromatography (SiO_2) using acetone/hexanes as the eluent to provide the corresponding product.

1-(4-Bromophenyl)-2-nitroethanone oxime (2a). White solid (109.7 mg, 84% yield); mp = 97–98 °C (CH_2Cl_2/hexanes); TLC (30% acetone in hexanes) $R_f = 0.26$; ^{1}H NMR (400 MHz; $CDCl_3$) δ 9.18 (br s, 1H), 7.57 (dd, $J = 6.7$, 2.0 Hz, 2H), 7.49 (dd, $J = 6.7$, 2.0 Hz, 2H), 5.62 (s, 2H) ppm. ^{13}C NMR (100 MHz; $CDCl_3$) δ 147.8 (C), 132.3 (2 × CH), 131.9 (C), 127.7 (2 × CH), 125.0 (C), 68.1 (CH_2) ppm; IR (KBr) ν 3232 (O–H), 1636 (C=N), 1558 and 1375 (NO_2) cm^{-1}; MS *m*/*z* (%) relative intensity 258 (M^+, 55), 181 (57), 169 (100), 102 (59), 89 (73); HRMS (APCI-TOF) calcd for $C_8H_8BrN_2O_3$ $[M + H]^+$ 258.9718, found 258.9719.

1-(4-Chlorophenyl)-2-nitroethanone oxime (2b).[8a] Yellow viscous oil (79.6 mg, 73% yield); TLC (30% acetone in hexanes) $R_f = 0.29$; ^{1}H NMR (400 MHz; $CDCl_3$, isomeric ratio 27.6 : 1, minor isomer marked*) δ 9.87 (br s, 1H of major and minor isomers), 7.54 (dd, $J = 6.8$, 2.0 Hz, 2H of major and minor isomers), 7.38 (dd, $J = 6.8$, 2.0 Hz, 2H of major and minor isomers), 5.62 (s, 1.93H), 5.40* (s, 0.07H) ppm. ^{13}C NMR (100 MHz; $CDCl_3$) δ 147.4 (C), 136.4 (C), 131.4 (C), 129.7* (2 × CH), 129.2 (2 × CH), 128.9* (2 × CH), 127.3 (2 × CH), 77.8* (CH_2), 68.1 (CH_2) ppm (some peaks of the minor isomer could not be detected by ^{13}C NMR due to their low intensity); IR (KBr) ν 3235 (O–H), 1596 (C=N), 1562 and 1379 (NO_2) cm^{-1}; HRMS (APCI-TOF) *m*/*z* calcd for $C_8H_8ClN_2O_3$ $[M + H]^+$ 215.0223, found 215.0213.

1-(3-Chlorophenyl)-2-nitroethanone oxime (2c). Yellow viscous oil (79.9 mg, 74% yield); TLC (30% acetone in hexanes) $R_f = 0.31$; ^{1}H NMR (400 MHz; $CDCl_3$, isomeric ratio 14.4 : 1, minor isomer marked*) δ 9.39 (br s, 1H of major and minor isomers), 7.63 (t, $J = 1.8$ Hz, 0.94H), 7.60* (t, $J = 1.8$ Hz, 0.06H), 7.49–7.34 (m, 3H of major and minor isomers), 5.62 (s, 1.87H), 5.39* (s, 0.13H) ppm. ^{13}C NMR (100 MHz; $CDCl_3$) δ 147.6 (C), 135.1 (C), 134.7 (C), 130.5 (CH), 130.3 (CH), 130.0* (CH), 128.5* (CH), 126.3 (CH), 126.2* (CH), 124.5* (CH), 124.3 (CH), 77.8* (CH_2), 68.2 (CH_2) ppm (some peaks of the minor isomer could not be detected by ^{13}C NMR due to their low intensity); IR (KBr) ν 3274 (O–H), 1630 (C=N), 1559 and 1373 (NO_2) cm^{-1}; MS *m*/*z* (%) relative intensity 214 (M^+, 6), 137 (100), 125 (68), 102 (64), 75 (40); HRMS (APCI-TOF) calcd for $C_8H_7ClN_2NaO_3$ $[M + Na]^+$ 237.0043, found 237.0041.

1-(2-Chlorophenyl)-2-nitroethanone oxime (2d). Yellow viscous oil (64.0 mg, 59% yield); TLC (30% acetone in hexanes) $R_f = 0.31$; ^{1}H NMR (400 MHz; $CDCl_3$, isomeric ratio 1.7 : 1, minor isomer marked*) δ 9.71 (br s, 0.63H), 9.02* (br s, 0.37H), 7.53–7.33 (m, 4H of major and minor isomers), 5.60 (s, 1.25H), 5.42* (s, 0.75H) ppm. ^{13}C NMR (100 MHz; $CDCl_3$) δ 148.8 (C), 147.9* (C), 132.6* (C), 132.5 (C), 131.7 (CH), 131.5 (CH), 131.3 (C), 131.2* (CH), 130.6* (CH), 130.0 (CH), 129.8* (CH), 129.7* (C), 127.5 (CH), 127.0* (CH), 77.4* (CH_2), 70.2 (CH_2) ppm; IR (neat) ν 3272 (O–H), 1622 (C=N), 1558 and 1373 (NO_2) cm^{-1}; MS *m*/*z* (%) relative intensity 215 ($M^+ + 1$, 100), 137 (31), 102 (41), 75 (19); HRMS (APCI-TOF) calcd for $C_8H_7ClN_2NaO_3$ $[M + Na]^+$ 237.0043, found 237.0042.

1-(4-Fluorophenyl)-2-nitroethanone oxime (2e).[8a] Yellow viscous oil (70.0 mg, 69% yield); TLC (30% acetone in hexanes) R_f = 0.31; ^{1}H NMR (400 MHz; $CDCl_3$, isomeric ratio 11.5 : 1, minor isomer marked*) δ 9.57 (br s, 1H of major and minor isomers), 7.62–7.58 (m, 2H of major and minor isomers), 7.15–7.09 (m, 2H of major and minor isomers), 5.63 (s, 1.84H), 5.40* (s, 0.16H) ppm. ^{13}C NMR (100 MHz; $CDCl_3$) δ 164.0 (d, J = 249.9 Hz, C), 147.7 (d, J = 8.2 Hz, C), 130.6* (d, J = 8.5 Hz, 2 × CH), 129.1 (d, J = 3.1 Hz, C), 128.3 (d, J = 8.5 Hz, 2 × CH), 116.2 (d, J = 21.8 Hz, 2 × CH), 115.9* (d, J = 21.8 Hz, 2 × CH), 78.0* (CH_2), 68.5 (CH_2) ppm (some peaks of the minor isomer could not be detected by ^{13}C NMR due to their low intensity); IR (KBr) ν 3279 (O–H), 1602 (C=N), 1549 and 1376 (NO_2) cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_8H_7FN_2NaO_3$ $[M + Na]^+$ 221.0338, found 221.0337.

1-(3-Fluorophenyl)-2-nitroethanone oxime (2f). Yellow viscous oil (74.2 mg, 75% yield); TLC (30% acetone in hexanes) R_f = 0.31; ^{1}H NMR (400 MHz; $CDCl_3$, isomeric ratio 32.3 : 1, minor isomer marked*) δ 8.71 (br s, 1H of major and minor isomers), 7.45–7.38 (m, 3H of major and minor isomers), 7.18–7.13 (m, 1H of major and minor isomers), 5.64 (s, 1.94H), 5.40* (s, 0.06H) ppm. ^{13}C NMR (100 MHz; $CDCl_3$) δ 163.0 (d, J = 245.8 Hz, C), 147.5 (d, J = 2.6 Hz, C), 135.1 (d, J = 7.9 Hz, C), 130.7 (d, J = 8.2 Hz, CH), 121.8 (d, J = 2.9 Hz, CH), 117.4 (d, J = 21.2 Hz, CH), 113.2 (d, J = 23.5 Hz, CH), 77.9* (CH_2), 68.0 (CH_2) ppm (some peaks of the minor isomer could not be detected by ^{13}C NMR due to their low intensity); IR (KBr) ν 3274 (O–H), 1610 (C=N), 1558 and 1376 (NO_2) cm^{-1}; MS m/z (%) relative intensity 199 (M^+ + 1, 100), 198 (M^+, 31), 180 (3), 121 (82), 109 (59); HRMS (APCI-TOF) calcd for $C_8H_7FN_2NaO_3$ $[M + Na]^+$ 221.0338, found 221.0331.

1-(4-Nitrophenyl)-2-nitroethanone oxime (2g). Pale yellow solid (75.2 mg, 66% yield); mp = 123–124 °C (EtOAc/hexanes); TLC (30% acetone in hexanes) R_f = 0.21; ^{1}H NMR (400 MHz; acetone-d_6, isomeric ratio 19.0 : 1, minor isomer marked*) δ 11.99 (s, 1H of major and minor isomers), 8.23 (dd, J = 7.1, 2.0 Hz, 2H of major and minor isomers), 7.99 (dd, J = 7.1, 2.0 Hz, 2H of major and minor isomers), 5.89 (s, 1.90H), 5.68* (s, 0.10H) ppm. ^{13}C NMR (100 MHz; acetone-d_6) δ 149.0 (C), 147.4 (C), 141.0 (C), 130.6* (2 × CH), 127.7 (2 × CH), 124.4 (2 × CH), 124.0* (2 × CH), 78.6* (CH_2), 68.4 (CH_2) ppm (some peaks of the minor isomer could not be detected by ^{13}C NMR due to their low intensity); IR (KBr) ν 3364 (O–H), 1599 (C=N), 1567 and 1380 (NO_2) cm^{-1}; MS m/z (%) relative intensity 225 (M^+, 2), 147 (100), 102 (33), 89 (98); HRMS (ESI-TOF) calcd for $C_8H_7N_3NaO_5$ $[M + Na]^+$ 248.0283, found 248.0282.

1-(3-Nitrophenyl)-2-nitroethanone oxime (2h). Pale yellow solid (69.8 mg, 62% yield); mp = 98–99 °C (CH_2Cl_2/hexanes); TLC (30% acetone in hexanes) R_f = 0.26; ^{1}H NMR (400 MHz; acetone-d_6, isomeric ratio 21.2 : 1, minor isomer marked*) δ 11.93 (s, 0.95H), 11.51* (s, 0.05H), 8.63 (t, J = 1.7 Hz, 1H of major and minor isomers), 8.32–8.29 (m, 1H of major and minor isomers), 8.24–8.21 (m, 1H of major and minor isomers), 7.77 (t, J = 8.0 Hz, 1H of major and minor isomers), 6.00 (s, 1.91H), 5.81* (s, 0.09H) ppm. ^{13}C NMR (100 MHz; acetone-d_6) δ 149.5 (C), 147.5 (C), 137.0 (C), 135.6* (CH), 132.9 (CH), 131.0 (CH), 130.6* (CH), 125.0* (CH), 124.8 (CH), 124.4* (CH), 121.5 (CH), 78.7* (CH_2), 68.8 (CH_2) ppm (some peaks of the minor isomer could not be detected by ^{13}C NMR due to their low intensity); IR (KBr) ν 3314 (O–H), 1575 (C=N), 1533 and 1378 (NO_2) cm^{-1}; MS m/z (%) relative intensity 225 (M^+, 1), 148 (100), 102 (56), 89 (41); HRMS (ESI-TOF) calcd for $C_8H_7N_3NaO_5$ $[M + Na]^+$ 248.0283, found 248.0276.

3-(1-(Hydroxyimino)-2-nitroethyl)benzaldehyde (2i). Yellow solid (59.2 mg, 56% yield); mp = 118–119 °C (EtOAc/hexanes); TLC (30% acetone in hexanes) R_f = 0.19; ^{1}H NMR (400 MHz; acetone-d_6) δ 11.80 (s, 1H), 10.11 (s, 1H), 8.33 (t, J = 1.5 Hz, 1H), 8.13 (ddd, J = 7.8, 1.8, 1.2 Hz, 1H), 8.01 (dt, J = 7.6, 1.3 Hz, 1H), 7.71 (t, J = 7.7 Hz, 1H), 5.98 (s, 2H) ppm. ^{13}C NMR (100 MHz; acetone-d_6) δ 192.6 (CH), 148.0 (C), 137.9 (C), 136.2 (C), 132.3 (CH), 131.0 (CH), 130.3 (CH), 127.7 (CH), 68.8 (CH_2) ppm; IR (KBr) ν 3203 (O–H), 1610 (C=N), 1554 and 1381 (NO_2) cm^{-1}; MS m/z (%) relative intensity 208 (M^+, 6), 131 (90), 103 (76), 77 (100); HRMS (ESI-TOF) calcd for $C_9H_8N_2NaO_4$ $[M + Na]^+$ 231.0382, found 231.0375.

1-(4-(Chloromethyl)phenyl)-2-nitroethanone oxime (2j). Pale yellow solid (68.4 mg, 60% yield); mp = 83–84 °C (CH_2Cl_2/hexanes); TLC (30% acetone in hexanes) R_f = 0.24; ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.76 (br s, 1H), 7.64 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.3 Hz, 2H), 5.65 (s, 2H), 4.60 (s, 2H) ppm. ^{13}C NMR (100 MHz; $CDCl_3$) δ 148.0 (C), 139.7 (C), 133.0 (C), 129.2 (2 × CH), 126.5 (2 × CH), 68.1 (CH_2), 45.4 (CH_2) ppm; IR (KBr) ν 3227 (O–H), 1605 (C=N), 1574 and 1383 (NO_2) cm^{-1}; MS m/z (%) relative intensity 228 (M^+, 3), 151 (100), 115 (44), 100 (30); HRMS (APCI-TOF) calcd for $C_9H_{10}ClN_2O_3$ $[M + H]^+$ 229.0380, found 229.0375.

2-Nitro-1-(*p*-tolyl)ethanone oxime (2k).[8a] Yellow viscous oil (43.9 mg, 45% yield); TLC (30% acetone in hexanes) R_f = 0.36; ^{1}H NMR (400 MHz; $CDCl_3$, isomeric ratio 10.8 : 1, minor isomer marked*) δ 9.37 (br s, 1H of major and minor isomers), 7.42 (d, J = 8.1 Hz, 2H of major and minor isomers), 7.15 (d, J = 8.1 Hz, 2H of major and minor isomers), 5.56 (s, 1.83H), 5.31* (s, 0.17H), 2.30 (s, 3H of major and minor isomers) ppm. ^{13}C NMR (100 MHz; $CDCl_3$) δ 148.5 (C), 140.9 (C), 131.3* (C), 130.0 (C), 129.8 (2 × CH), 129.4* (2 × CH), 129.0* (C), 128.3* (2 × CH), 126.8* (C), 126.1 (2 × CH), 78.1* (CH_2), 68.5 (CH_2), 21.5* (CH_3), 21.4 (CH_3) ppm; IR (KBr) ν 3292 (O–H), 1611 (C=N), 1546 and 1377 (NO_2) cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_9H_{10}N_2NaO_3$ $[M + Na]^+$ 217.0589, found 217.0595.

1-(4-Methoxyphenyl)-2-nitroethanone oxime (2l).[8a] Pale yellow solid (56.0 mg, 51% yield); mp = 109–110 °C (CH_2Cl_2/hexanes); TLC (20% acetone in hexanes) R_f = 0.26; ^{1}H NMR (400 MHz; acetone-d_6) δ 11.22 (s, 1H), 7.72 (dd, J = 6.9, 2.2 Hz, 2H), 6.98 (dd, J = 6.9, 2.2 Hz, 2H), 5.84 (s, 2H), 3.83 (s, 3H) ppm. ^{13}C NMR (100 MHz; acetone-d_6) δ 161.7 (C), 148.2 (C), 128.2 (2 × CH), 127.5 (C), 114.8 (2 × CH), 68.9 (CH_2), 55.6 (CH_3) ppm; IR (KBr) ν 3229 (O–H), 1606 (C=N), 1559 and 1380 (NO_2) cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_9H_{11}N_2O_4$ $[M + H]^+$ 211.0719, found 211.0720.

1-(4-(*tert*-Butyl)phenyl)-2-nitroethanone oxime (2m). Yellow solid (70.3 mg, 59% yield); mp = 102–103 °C (CH_2Cl_2/hexanes); TLC (30% acetone in hexanes) R_f = 0.32; ^{1}H NMR (400 MHz; $CDCl_3$, isomeric ratio 5.5 : 1, minor isomer marked*) δ 9.27 (br s, 0.85H), 8.81* (br s, 0.15H), 7.57 (d, J = 8.5 Hz, 2H of major and

minor isomers), 7.46 (d, J = 8.5 Hz, 2H of major and minor isomers), 5.66 (s, 1.69H), 5.41* (s, 0.31H), 1.33 (br s, 9H of major and minor isomers) ppm. ^{13}C NMR (100 MHz; $CDCl_3$) δ 153.9 (C), 148.4 (C), 130.0 (C), 128.1* (2 × CH), 126.1 (2 × CH), 125.9 (2 × CH), 125.7* (2 × CH), 78.1* (CH_2), 68.4 (CH_2), 34.9 (C), 31.1 (3 × CH_3) ppm (some peaks of the minor isomer could not be detected by ^{13}C NMR due to their low intensity); IR (KBr) ν 3300 (O–H), 1608 (C=N), 1558 and 1374 (NO_2) cm^{-1}; MS m/z (%) relative intensity 236 (M^+, 6), 221 (52), 175 (35), 158 (100), 130 (40); HRMS (ESI-TOF) calcd for $C_{12}H_{16}N_2NaO_3$ $[M + Na]^+$ 259.1059, found 259.1058.

4-(1-(Hydroxyimino)-2-nitroethyl)phenyl acetate (2n). Yellow solid (85.7 mg, 71% yield); mp = 114–115 °C (EtOAc/hexanes); TLC (30% acetone in hexanes) R_f = 0.20; ^{1}H NMR (400 MHz; acetone-d_6, isomeric ratio 14.4 : 1, minor isomer marked*) δ 11.35 (s, 1H of major and minor isomers), 7.63 (d, J = 8.3 Hz, 2H of major and minor isomers), 7.03 (d, J = 8.3 Hz, 2H of major and minor isomers), 5.66 (br s, 1.87H), 5.44* (br s, 0.13H), 2.14 (br s, 3H of major and minor isomers) ppm. ^{13}C NMR (100 MHz; acetone-d_6) δ 169.5 (C), 152.9 (C), 148.0 (C), 132.6 (C), 130.7* (2 × CH), 128.0 (2 × CH), 122.9 (2 × CH), 122.5* (2 × CH), 79.2* (CH_2), 69.0 (CH_2), 20.9 (CH_3) ppm (some peaks of the minor isomer could not be detected by ^{13}C NMR due to their low intensity); IR (KBr) ν 3278 (O–H), 1604 (C=N), 1570 and 1369 (NO_2) cm^{-1}; MS m/z (%) relative intensity 238 (M^+, 7), 196 (21), 119 (31), 107 (100), 77 (25); HRMS (ESI-TOF) calcd for $C_{10}H_{10}N_2NaO_5$ $[M + Na]^+$ 261.0487, found 261.0480.

2-Nitro-1-phenylethanone oxime (2o).[13] Yellow solid (59.1 mg, 63% yield); mp = 95–96 °C (CH_2Cl_2/hexanes, lit.[13] mp 95 °C); TLC (30% acetone in hexanes) R_f = 0.24; ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.65 (br s, 1H), 7.65–7.63 (m, 2H), 7.47–7.43 (m, 3H), 5.66 (s, 2H) ppm. ^{13}C NMR (100 MHz; $CDCl_3$) δ 148.5 (C), 133.0 (C), 130.4 (CH), 129.0 (2 × CH), 126.2 (2 × CH), 68.3 (CH_2) ppm; IR (KBr) ν 3222 (O–H), 1636 (C=N), 1559 and 1383 (NO_2) cm^{-1}; MS m/z (%) relative intensity 180 (M^+, 3), 134 (11), 103 (100), 91 (65), 77 (42); HRMS (ESI-TOF) calcd for $C_8H_8N_2NaO_3$ $[M + Na]^+$ 203.0433, found 203.0434.

1-(Naphthalen-1-yl)-2-nitroethanone oxime (2p). Yellow viscous oil (51.1 mg, 44% yield); TLC (30% acetone in hexanes) R_f = 0.22; ^{1}H NMR (400 MHz; $CDCl_3$, isomeric ratio 1.7 : 1, minor isomer marked*) δ 9.61 (br s, 0.63H), 8.84* (br s, 0.37H), 8.01–7.88 (m, 3H of major and minor isomers), 7.68–7.37 (m, 4H of major and minor isomers), 5.63 (s, 1.26H), 5.46* (s, 0.74H) ppm. ^{13}C NMR (100 MHz; $CDCl_3$) δ 149.3* (C), 149.1 (C), 133.8 (C), 133.5* (C), 130.83 (C), 130.79* (C), 130.6 (CH), 130.5* (CH), 129.4 (C), 128.8 (CH), 128.7* (CH), 127.4* (CH), 127.3 (CH), 127.1* (CH), 126.9* (C), 126.57* (CH), 126.55 (CH), 125.4 (CH), 125.20 (CH), 125.18* (CH), 125.1* (CH), 124.5 (CH), 79.0* (CH_2), 71.6 (CH_2) ppm; IR (neat) ν 3273 (O–H), 1592 (C=N), 1558 and 1372 (NO_2) cm^{-1}; MS m/z (%) relative intensity 230 (M^+, 14), 184 (31), 166 (100), 152 (47), 115 (19); HRMS (ESI-TOF) calcd for $C_{12}H_{10}N_2NaO_3$ $[M + Na]^+$ 253.0589, found 253.0588.

2-Nitro-1-phenylpropan-1-one oxime (2q). Yellow solid (50.5 mg, 52% yield); mp = 96–97 °C (EtOAc/hexanes); TLC (30% acetone in hexanes) R_f = 0.29; ^{1}H NMR (400 MHz; acetone-d_6, isomeric ratio 2.3 : 1, minor isomer marked*) δ 11.29 (s, 0.70H), 10.86* (s, 0.30H), 7.64–7.39 (m, 5H of major and minor isomers), 6.10 (q, J = 6.9 Hz, 0.70H), 5.82* (q, J = 6.9 Hz, 0.30H), 1.86 (d, J = 6.9 Hz, 2.09H), 1.75* (d, J = 6.9 Hz, 0.91H) ppm. ^{13}C NMR (100 MHz; acetone-d_6) δ 153.3 (C), 152.3* (C), 134.8 (C), 132.1*(C), 130.2 (CH), 130.0* (CH), 129.4 (2 × CH), 129.1* (2 × CH), 129.0* (2 × CH), 127.4 (2 × CH), 86.2* (CH), 78.3 (CH), 17.1* (CH_3), 15.4 (CH_3) ppm; IR (KBr) ν 3237 (O–H), 1648 (C=N), 1546 and 1386 (NO_2) cm^{-1}; MS m/z (%) relative intensity 194 (M^+, 2), 130 (26), 117 (70), 115 (100), 103 (32), 77 (65); HRMS (ESI-TOF) calcd for $C_9H_{10}N_2NaO_3$ $[M + Na]^+$ 217.0589, found 217.0587.

2-Nitro-3,4-dihydronaphthalen-1(2*H*)-one oxime (2r).[14] Pale brown solid (57.7 mg, 56%); mp = 138–139 °C (CH_2Cl_2/hexanes, lit.[14] mp 140–142 °C); TLC (20% acetone in hexanes) R_f = 0.28; ^{1}H NMR (400 MHz; $CDCl_3$) δ 11.86 (br s, 1H), 10.61 (d, J = 7.9 Hz, 1H), 9.82–9.62 (m, 2H), 9.58 (d, J = 7.5 Hz, 1H), 8.09 (t, J = 4.7 Hz, 1H), 3.93–3.79 (m, 1H), 3.76–3.68 (m, 1H), 3.59–3.50 (m, 1H), 3.16–3.03 (m, 1H). ^{13}C NMR (100 MHz; $CDCl_3$) δ 147.8 (C), 137.4 (C), 130.3 (CH), 128.7 (CH), 128.1 (C), 127.3 (CH), 124.5 (CH), 76.9 (CH), 27.8 (CH_2), 25.0 (CH_2); IR (KBr) ν 3300 (O–H), 1598 (C=N), 1547 and 1375 (NO_2) cm^{-1}; MS m/z (%) relative intensity 206 (M^+, 1), 160 (10), 142 (23), 128 (36), 115 (100), 89 (31); HRMS (ESI-TOF) calcd for $C_{10}H_{10}N_2NaO_3$ $[M + Na]^+$ 229.0589, found 229.0584.

2-Nitro-1-(thiophen-2-yl)ethanone oxime (2s).[15] Yellow solid (51.2 mg, 73%); mp = 218–219 °C (CH_2Cl_2/hexanes, lit.[15] mp 218 °C); TLC (30% acetone in hexanes) R_f = 0.38; ^{1}H NMR (400 MHz; $CDCl_3$, isomeric ratio 1 : 1, minor isomer marked*) δ 9.29 (br s, 0.53H), 7.65 (d, J = 4.8 Hz, 0.51H), 7.48 (d, J = 3.9 Hz, 0.54H), 7.38* (d, J = 4.8 Hz, 0.49H), 7.28* (d, J = 3.9 Hz, 0.47H), 7.13 (dd, J = 4.8, 3.9 Hz, 0.54H), 7.07* (dd, J = 4.8, 3.9 Hz, 0.49H), 5.64 (s, 0.93H), 5.54 (s, 1H) (some peaks of the minor isomer could not be detected by ^{1}H NMR due to their low intensity). ^{13}C NMR (75 MHz; $CDCl_3$) δ 144.3* (C), 142.4 (C), 136.6* (C), 132.3* (CH), 129.6 (C), 129.4 (CH), 128.6* (CH), 127.6 (CH), 127.4* (CH), 126.2 (CH), 77.4 (CH_2), 68.0* (CH_2); IR (KBr) ν 3265 (O–H), 1637 (C=N), 1557 and 1375 (NO_2) cm^{-1}; MS m/z (%) relative intensity 186 (M^+, 11), 140 (14), 109 (37), 97 (100); HRMS (ESI-TOF) calcd for $C_6H_6N_2NaO_3S$ $[M + Na]^+$ 208.9997, found 208.9996.

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Notes and references

1 For selected dioxygenation, see: (*a*) C. J. R. Bataille and T. J. Donohoe, *Chem. Soc. Rev.*, 2011, **40**, 114; (*b*) Q. Xue, J. Xie, P. Xu, K. Hu, Y. Cheng and C. Zhu, *ACS Catal.*, 2013, **3**, 1365; (*c*) M. J. Rawling and N. C. O. Tomkinson, *Org. Biomol. Chem.*, 2013, **11**, 1434; (*d*) B. C. Giglio, V. A. Schmidt and E. J. Alexanian, *J. Am. Chem. Soc.*, 2011, **133**, 13320; (*e*) M.-K. Zhu, J.-F. Zhao and T.-P. Loh, *J. Am. Chem. Soc.*, 2010, **132**, 6284; (*f*) A. Wang, H. Jiang and

H. Chen, *J. Am. Chem. Soc.*, 2009, **131**, 3846; (*g*) Y. Li, D. Song and V. M. Dong, *J. Am. Chem. Soc.*, 2008, **130**, 2962.

2 For selected oxyamination, see: (*a*) Masruri, A. C. Willis and M. D. McLeod, *J. Org. Chem.*, 2012, **77**, 8480; (*b*) F. C. Sequeira and S. R. Chemler, *Org. Lett.*, 2012, **14**, 4482; (*c*) K. S. Williamson and T. P. Yoon, *J. Am. Chem. Soc.*, 2012, **134**, 12370; (*d*) U. Farid and T. Wirth, *Angew. Chem., Int. Ed.*, 2012, **51**, 3462; (*e*) T. de Haro and C. Nevado, *Angew. Chem., Int. Ed.*, 2011, **50**, 906; (*f*) T. J. Donohoe, C. K. A. Callens, A. Flores, A. R. Lacy and A. H. Rathi, *Chem.–Eur. J.*, 2011, **17**, 58; (*g*) D. E. Mancheno, A. R. Thornton, A. H. Stoll, A. Kong and S. B. Blakey, *Org. Lett.*, 2010, **12**, 4110; (*h*) D. J. Michaelis, C. J. Shaffer and T. P. Yoon, *J. Am. Chem. Soc.*, 2007, **129**, 1866; (*i*) E. J. Alexanian, C. Lee and E. J. Sorensen, *J. Am. Chem. Soc.*, 2005, **127**, 7690.

3 For selected oxysulfonylation and oxysulfenylation, see: (*a*) F.-L. Yang, F.-X. Wang, T.-T. Wang, Y.-J. Wang and S.-K. Tian, *Chem. Commun.*, 2014, **50**, 2111; (*b*) R. Chawla, A. K. Singh and L. D. S. Yadav, *Eur. J. Org. Chem.*, 2014, 2032; (*c*) A. Kariya, T. Yamaguchi, T. Nobuta, N. Tada, T. Miura and A. Itoh, *RSC Adv.*, 2014, **4**, 13191; (*d*) Q. Lu, J. Zhang, F. Wei, Y. Qi, H. Wang, Z. Liu and A. Lei, *Angew. Chem., Int. Ed.*, 2013, **52**, 7156; (*e*) W. Wei, C. Liu, D. Yang, J. Wen, J. You, Y. Suo and H. Wang, *Chem. Commun.*, 2013, **49**, 10239; (*f*) T. Taniguchi, A. Idota and H. Ishibashi, *Org. Biomol. Chem.*, 2011, **9**, 3151.

4 W. Wei and J.-X. Ji, *Angew. Chem., Int. Ed.*, 2011, **50**, 9097.

5 For selected diamination, see: (*a*) B. W. Turnpenny and S. R. Chemler, *Chem. Sci.*, 2014, **5**, 1786; (*b*) E. L. Ingalls, P. A. Sibbald, W. Kaminsky and F. E. Michael, *J. Am. Chem. Soc.*, 2013, **135**, 8854; (*c*) M.-K. Zhu, Y.-C. Chen and T.-P. Loh, *Chem.–Eur. J.*, 2013, **19**, 5250; (*d*) C. Röben, J. A. Souto, E. C. Escudero-Adán and K. Muñiz, *Org. Lett.*, 2013, **15**, 1008; (*e*) K. Muñiz and C. Martínez, *J. Org. Chem.*, 2013, **78**, 2168; (*f*) H. J. Kim, S. H. Cho and S. Chang, *Org. Lett.*, 2012, **14**, 1424.

6 (*a*) E. Bogatcheva, C. Hanrahan, B. Nikonenko, R. Samala, P. Chen, J. Gearhart, F. Barbosa, L. Einck, C. A. Nacy and M. Protopopova, *J. Med. Chem.*, 2006, **49**, 3045; (*b*) D. Lucet, T. Le Gall and C. Mioskowski, *Angew. Chem., Int. Ed.*, 1998, **37**, 2580; (*c*) W. Notz, F. Tanaka and C. F. Barbas III, *Acc. Chem. Res.*, 2004, **37**, 580; (*d*) I.-W. Kim and S.-H. Jung, *Arch. Pharmacal Res.*, 2002, **25**, 421.

7 (*a*) S. Prateeptongkum, I. Jovel, R. Jackstell, N. C. Weckbecker and M. Beller, *Chem. Commun.*, 2009, 1990; (*b*) K. Sugamoto, Y. Hamasuna, Y. Matsushita and T. Matsui, *Synlett*, 1998, 1270; (*c*) K. Kato and T. Mukaiyama, *Chem. Lett.*, 1992, **21**, 1137; (*d*) K. Kato and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 2948; (*e*) K. Kato and T. Mukaiyama, *Chem. Lett.*, 1990, **19**, 1395; (*f*) K. Kato and T. Mukaiyama, *Chem. Lett.*, 1990, **19**, 1917; (*g*) T. Okamoto, K. Kobayashi, S. Oka and S. Tanimoto, *J. Org. Chem.*, 1988, **53**, 4897; (*h*) T. Okamoto, K. Kobayashi, S. Oka and S. Tanimoto, *J. Org. Chem.*, 1987, **52**, 5089.

8 (*a*) A. Shaabani, H. R. Bijanzadeh, A. R. Karimi, M. B. Teimouri and K. Soleimani, *Can. J. Chem.*, 2008, **86**, 248; (*b*) L. Grossi, P. C. Montevecchi and S. Strazzari, *Eur. J. Org. Chem.*, 2001, 741; (*c*) M. L. Scheinbaum, *J. Org. Chem.*, 1970, **35**, 2790.

9 R. M. Uppu and W. A. Pryor, *Anal. Biochem.*, 1996, **236**, 242.

10 (*a*) C. Muangkaew, P. Katrun, P. Kanchanarugee, M. Pohmakotr, V. Reutrakul, D. Soorukram, T. Jaipetch and C. Kuhakarn, *Tetrahedron*, 2013, **69**, 8847; (*b*) T. Sawangphon, P. Katrun, K. Chaisiwamongkhol, M. Pohmakotr, V. Reutrakul, D. Soorukram, T. Jaipetch and C. Kuhakarn, *Synth. Commun.*, 2013, **43**, 1692; (*c*) N. Samakkanad, P. Katrun, T. Techajaroonjit, S. Hlekhlai, M. Pohmakotr, V. Reutrakul, T. Jaipetch, D. Soorukram and C. Kuhakarn, *Synthesis*, 2012, **44**, 1693; (*d*) P. Katrun, S. Chiampanichayakul, K. Korworapan, M. Pohmakotr, V. Reutrakul, D. Soorukram, T. Jaipetch and C. Kuhakarn, *Eur. J. Org. Chem.*, 2010, 5633.

11 (*a*) M. C. Marcotullio, F. Epifano and M. Curini, *Trends Org. Chem.*, 2003, **10**, 21; (*b*) K. Moriyama, M. Takemura and H. Togo, *Org. Lett.*, 2012, **14**, 2414; (*c*) B. Yu, A.-H. Liu, L.-N. He, B. Li, Z.-F. Diao and Y.-N. Li, *Green Chem.*, 2012, **14**, 957; (*d*) H. Hussain, I. R. Green and I. Ahmed, *Chem. Rev.*, 2013, **113**, 3329; (*e*) A. Yoshimura, K. R. Middleton, A. D. Todora, B. J. Kastern, S. R. Koski, A. V. Maskaev and V. V. Zhdankin, *Org. Lett.*, 2013, **15**, 4010; (*f*) B. Poladura, A. Martinez-Castaneda, H. Rodriguez-Solla, R. Llavona, C. Concellon and V. del Amo, *Org. Lett.*, 2013, **15**, 2810; (*g*) F. Drouet, G. Masson and J. Zhu, *Org. Lett.*, 2013, **15**, 2854; (*h*) A. C. Nelson, E. S. Kalinowski, N. J. Czerniecki, T. L. Jacobson and P. Grundt, *Org. Biomol. Chem.*, 2013, **11**, 7455; (*i*) X.-L. Lian, H. Lei, X.-J. Quan, Z.-H. Ren, Y.-Y. Wang and Z.-H. Guan, *Chem. Commun.*, 2013, **49**, 8196.

12 (*a*) H. Baji, M. Flammang, T. Kimny, F. Gasquez, P. L. Compagnon and A. Delcourt, *Eur. J. Med. Chem.*, 1995, **30**, 617; (*b*) A. Balsamo, M. C. Breschi, G. Chielini, L. Favero, M. Macchia, A. Martinelli, C. Martini, A. Rossello and R. Scatizzi, *Eur. J. Med. Chem.*, 1995, **30**, 743; (*c*) A. Karakurt, M. A. Alagöz, B. Sayoğlu, Ü. Çaliş and S. Dalkara, *Eur. J. Med. Chem.*, 2012, **57**, 275.

13 E. Duranti, C. Balsamini, G. Spadoni and S. Lamberto, *J. Org. Chem.*, 1988, **53**, 2870.

14 T. Kametani, H. Sugahara and H. Yagi, *J. Chem. Soc. C*, 1966, **7**, 717.

15 P. Fournari and J. P. Chane, *Bull. Soc. Chim. Fr.*, 1963, 479.

