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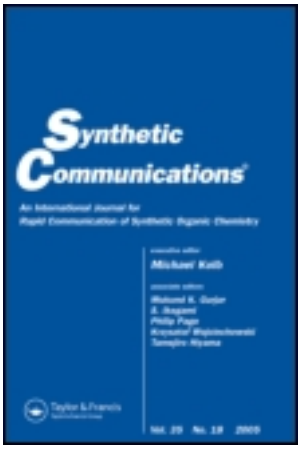

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Fe-HCl: An Efficient Reagent for Deprotection of Oximes as well as Selective Oxidative Hydrolysis of Nitroalkenes and Nitroalkanes to Ketones

Prasun K. Pradhan [a], Sumit Dey [a], Parasuraman Jaisankar [a] & Venkatachalam S. Giri [a]

[a] Department of Medicinal Chemistry, Indian Institute of Chemical Biology, Calcutta, India

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Fe-HCl: An Efficient Reagent for Deprotection of Oximes as well as Selective Oxidative Hydrolysis of Nitroalkenes and Nitroalkanes to Ketones

Prasun K. Pradhan, Sumit Dey, Parasuraman Jaisankar, and Venkatachalam S. Giri
Department of Medicinal Chemistry, Indian Institute of Chemical Biology, Calcutta, India

Abstract: Fe-HCl mixture was found to selectively perform oxidative hydrolysis of the nitroalkenes **1a–j** and nitroalkanes **2a–j** to the ketones **3a–j**. Also, the reagent was observed to deprotect the oximes **7a–j** to carbonyl compounds **8a–j** in excellent yields.

Keywords: Deprotection of oximes, Fe, HCl, hydrolysis, ketones, nitroalkanes, nitroalkenes, oxidation

INTRODUCTION

Nitro compounds are important intermediates in synthetic organic chemistry because they can be converted easily into other desired functional groups. The formation of ketones and aldehydes by oxidative hydrolysis from the corresponding nitroalkanes is one of the important transformations that has tremendous synthetic utility. Nef reaction[1] involves oxidative hydrolysis of the nitronate salts of primary or secondary nitroalkanes to aldehydes or ketones under strong acidic conditions. Kornblum et al. have used potassium permanganate

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Address correspondence to Venkatachalam S. Giri, Department of Medicinal Chemistry, Indian Institute of Chemical Biology, 4, Raja S. C. Mullick Road, Calcutta 700 032, India. Tel.: +91-33-24733491; Fax: +91-33-24735197; E-mail: vsgiri@iicb.res.in

for converting nitroparaffin salts to ketones and aldehydes in good yield.[2] It is also known that ozonolysis of the nitroalkenes results in the formation of the carbonyl compounds. Later it was observed by McMurry et al. that nitroalkanes upon treatment with Ti(III)chloride followed by hydrolysis, afford the aldehydes in good yield. In a recent review,[1b] Ballini et al. have given an up-to-date account of Nef reaction and its applications.

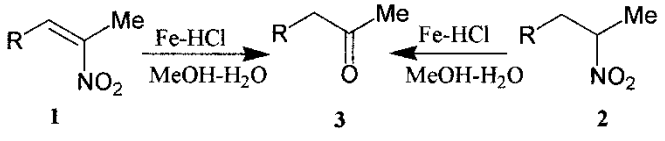
RESULTS AND DISCUSSION

In the course of preparation of some aryl ethylamine derivatives, we observed that Fe-HCl could bring about the oxidative hydrolysis of both secondary nitroalkenes **1a–j** and nitroalkanes **2a–j** to the ketones **3a–j** in very good yield (Scheme 1). Usually a mixture of iron and aqueous hydrochloric acid is used for reduction of nitro groups to amino groups. This is the first report of such an oxidative hydrolysis of both nitroalkanes and nitroalkenes to the ketones using Fe and hydrochloric acid. The results are summarized in Table 1.

Interestingly, the reagent selectively converts the nitroalkenes **1a–j** and nitroalkanes **2a–j** that have a methyl group α- to the NO_2 functionality to the ketones **3a–j**, whereas those having an α-hydrogen **4a–d** and **5a–d** are reduced to the corresponding amines **6a–d** (Scheme 2), and the yields are summarized in Table 2.

The nitroalkenes **1a–j** or **4a–d** obtained from the condensation by standard procedures of the aldehydes and nitroethane or nitromethane, respectively, are reduced to the corresponding nitroalkanes **2a–j** or **5a–d** by using $NaBH_4$-Dioxane-ethanol.[3]

Oximes are important derivatives used for both purification and isolation of carbonyl compounds. Carbonyl compounds are easily converted into oximes by refluxing with hydroxylamine hydrochloride in ethanol. The oximes are potential intermediates in organic synthesis.[4] Oximes not only serve as protecting groups for carbonyl compounds[4b] but also have other uses such as preparation of nitriles, preparation of amides *via* Beckmann rearrangement, or to activate the carbonyl groups. However, the methods so far developed to regenerate carbonyl compounds from oximes consist of oxidative or reductive reaction. Most of the methods involve reagents that are often hazardous or very toxic, expensive, or not readily available. Although deprotection of oximes is well known, our method is a very



1 3 2

Scheme 1.

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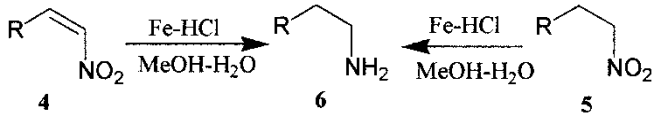
Table 1. Conversion of nitroalkenes **1a–j** and nitroalkanes **2a–j** to ketones **3a–j**

Entry	Substrates **1** or **2** **R** =	Products **3**	Percent of yield (isolated) From **1**	Percent of yield (isolated) From **2**
a	phenyl	1-phenyl-propan-2-one	82	85
b	4-methoxyphenyl	1-(4-methoxy-phenyl)-propan-2-one	80	82
c	4-hydroxy-3-methoxyphenyl	1-(4-hydroxy-3-methoxy-phenyl) propan-2-one	90	95
d	3,4,5–trimethoxyphenyl	1-(3,4,5-trimethoxy-phenyl)propan-2-one	80	85
e	4-hydroxyphenyl	1-(4-hydroxy-phenyl)-propan-2-one	81	84
f	3-indolyl	1-(1H-indol-3-yl) propan-2-one	78	85
g	1-benzo-(1,3)dioxole-5-yl	1-benzo-(1,3)-dioxole-5-yl propan-2-one	85	89
h	4-nitrophenyl	1-(4-amino-phenyl)propan-2-one	83	80
i	2- furyl	1-(furan-2-yl) propan-2-one	75	81
j	3-nitro-4-(methoxycarbonylmethoxy)-phenyl	6-(2-oxo-propyl)-4H-benzo-(1,4)-oxazin-3-one	92	95

simple, efficient, and facile method for deprotection of oximes (Scheme 3). The yields of carbonyl compounds **8a–j** from their oximes **7a–j** are summarized in Table 3. The reaction takes place only when a mixture of Fe and HCl is used but does not occur in the absence of one of them (Fe or HCl).

It is well known that reduction of nitro groups to the amines takes place through the intermediacy of the nitroso derivatives of the oximes. We believe that in the cases of nitroalkenes **1a–j** and nitroalkanes **2a–j**, because of the presence of a methyl group α to the NO_2 functionality, oximes are generated that subsequently undergo oxidative hydrolysis to the ketones **3a–j**. On the other hand, nitroalkenes **4a–d** and nitroalkanes **5a–d** are



Scheme 2.

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Table 2. Conversion of nitroalkenes **4a–d** and nitroalkanes **5a–d** to the amines **6a–d**

Entry	Substrate **4** or **5**	Percent yield of **6** (isolated)	
		From **4**	From **5**
a	3,4,5- trimethoxyphenyl	72	75
b	benzo-(1,3)-dioxole-5-yl	70	71
c	phenyl	63	65
d	3-indolyl	71	76

converted to the nitroso group, which spontaneously undergoes reduction to the corresponding amines **6a–d** through the intermediacy of the hydroxylamines.

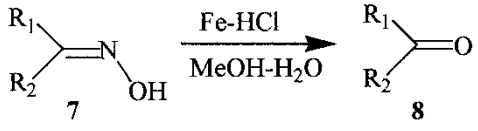
In conclusion, the Fe and aq. HCl system is an efficient reagent for deprotection of oximes and also for selective conversion of both nitroalkenes and nitroalkanes to the same ketones.

EXPERIMENTAL

All melting points were determined in open capillaries on SPAC-N-SERVICE (India) capillary melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO-FT-IR Model 410 using samples as KBr plates. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on a Bruker DPX 300 NMR instrument using TMS as internal standard. Elemental analyses were done on a PERKIN ELMER 2400 Series II CHNS/O analyzer. Mass spectra ESI and EI were recorded on Q-TOF Micro mass (LCMS) spectrometer and JEOL-AX-500 spectrometer respectively.

Typical Experimental Procedure for Conversion of Nitro Alkanes or Nitro Alkenes or Oximes to Carbonyl Compounds

To a solution of nitroalkane or nitroalkene or oxime (3 mmol) in a mixture of MeOH (5 mL), H_2O (2 mL), and conc. HCl (2 mL), iron dust (336 mg; 6 mmol) was added in portions and the resulting reaction mixture was



7 8

Scheme 3.

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Table 3. Conversion of oximes **7a–j** to the corresponding carbonyl compounds **8a–j**

Entry	Oximes **7**	Carbonyl compounds **8**	Percent yield of **8**
a	Benzaldehyde oxime	Benzaldehyde	94
b	Benzo(1,3)dioxole-5-carbaldehyde oxime	Benzo(1,3)dioxole-5-carbaldehyde	85
c	Chroman-4-one-oxime	Chroman-4-one	80
d	6-(2-Hydroxyamino-propyl)-4H-benzo(1,4)oxazine-3-one	6-(2-Oxo-propyl)-4H-benzo(1,4)oxazine-3-one	82
e	Furan-2-carbaldehyde oxime	Furan-2-aldehyde	81
f	4-Nitro-benzaldehyde oxime	4-amino-benzaldehyde	90
g	1-(4-Hydroxy-3-methoxy-phenyl)-propan-2-one oxime	1-(4-Hydroxy-3-methoxy-phenyl)-propan-2-one	82
h	1-Phenyl-ethanone oxime	1-Phenyl-ethanone	84
i	Diphenyl-methanone oxime	Diphenyl-methanone	81
j	4-Methoxy benzaldehyde oxime	4-Methoxy benzaldehyde	90

refluxed over a steam bath for 30 min. After complete disappearance of the starting material (monitored by TLC using 1% MeOH in $CHCl_3$), the reaction mixture was filtered over a bed of celite using MeOH. The filtrate was concentrated and diluted with H_2O (10 mL) either basified in the case of amine products or directly extracted with $CHCl_3$ (3×10 mL). The $CHCl_3$ layer was then dried (Na_2SO_4), the solvent was removed under reduced pressure, and the residue was chromatographed over silica gel using increasing concentrations of $CHCl_3$ in petroleum ether or direct crystallization to the desired ketone in pure form. The compounds have been characterized mainly from their physical data, particularly NMR, and confirmed by comparison with authentic specimens obtained by standard procedures.

The following compounds are already known in the literature: **1a**,[5] **1b**,[6] **1c**,[7] **1e**,[8] **1g**,[6] **1h**,[9] **1i**,[10] **2a**,[11] **2h**,[12] **3a**,[13] **3b**,[14] **3c**,[7] **3g**,[15] **4a**,[16] **4b**,[17] **4c**,[18] **4d**,[19] **5a**,[16] **5b**,[3] **5c**,[11] **5d**,[20] **6c**,[21] **6d**,[22] **7a**,[23] **7b**,[24] **7c**,[25] **7e**,[23] **7f**,[26] **7h**,[27] **7i**,[28] and **7j**.[29]

1,2,3-Trimethoxy-5-(2-nitro-propenyl)benzene (1d). Mp 66–68°C; IR (KBr): $\upsilon = 2940$, 2223, 1582, 943, 851 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.49$ (s, 3H), 3.90 (s, 9H), 6.66 (s, 2H), 6.86 (s, 1H); MS (ESI): 254 $(M + H)^+$. Anal. calcd. for $C_{12}H_{15}NO_5$: C, 56.91; H, 5.97; N, 5.53. Found: C, 56.79; H, 6.01; N, 5.60.

3-(2-Nitro-propenyl)-1H-indole (1f). Mp 186–188 °C; IR (KBr): $\upsilon = 3425$, 1627, 1525, 1478, 1269, 1222, 1126, 971, 857, 750 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.54$ (s, 3H), 7.27–7.36 (m, 2H), 7.46 (d, $J = 6.8$ Hz,

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1H), 7.57 (s, 1H), 7.83 (d, $J = 7.2$ Hz, 1H), 8.52 (s, 1H), 8.74 (brs, NH); MS (ESI): 203 $(M + H)^+$. Anal. calcd. for $C_{11}H_{10}N_2O_2$: C, 65.34; H, 4.98; N, 13.85. Found: C, 65.50; H, 5.02; N, 13.91.

[2-Nitro-4-(2-nitro-propenyl)-phenoxy]aceticacid methyl ester (1j). Liquid; IR (neat): $\upsilon = 3429$, 1641 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.46$ (s, 3H), 3.83 (s, 3H), 4.86 (s, 2H), 7.06 (d, $J = 8.7$ Hz, 1H), 7.59 (d, $J = 8.7$ Hz, 1H), 7.98 (s, 1H), 8.0 (d, $J = 5.1$ Hz, 1H); MS (ESI): 297$(M + H)^+$. Anal. calcd. for $C_{12}H_{12}N_2O_7$: C, 54.90; H, 4.61; N, 9.15. Found: C, 55.01; H, 4.67; N, 9.21.

1-Methoxy-4-(2-nitro-propyl)benzene (2b). Liquid; IR (neat): $\upsilon = 2937$, 1610, 1549, 757 cm^{-1}; ^{1}HNMR ($CDCl_3$): $\delta = 1.52$ (d, $J = 6.9$ Hz, 3H), 2.95 (dd, $J = 6.66$ Hz, 14.0 Hz, 1H), 3.24 (dd, $J = 6.65$ Hz, 14.0 Hz, 1H), 3.77 (s, 3H), 4.72 (sext, $J = 6.76$ Hz, 1H), 6.83 (d, $J = 8.56$ Hz, 2H), 7.07 (d, $J = 8.22$ Hz, 2H); MS (ESI): 196 $(M + H)^+$. Anal. calcd. for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71; N, 7.18. Found: C, 61.42; H, 6.78; N, 7.27.

2-Methoxy-4-(2-nitro-propyl)phenol (2c). Liquid; IR (neat): $\upsilon = 3471$, 1548, 1032, 797 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.53$ (d, $J = 6.64$ Hz, 3H), 2.94 (dd, $J = 6.66$ Hz, 14.01 Hz, 1H), 3.24 (dd, $J = 7.50$ Hz, 14.01 Hz, 1H), 3.86 (s, 3H), 4.73 (sext, $J = 6.70$ Hz, 1H), 5.61 (brs, OH), 6.56 (s, 1H), 6.65 (d, $J = 9.9$ Hz, 1H), 6.95 (d, $J = 8.2$ Hz, 1H); MS (ESI): 212 $(M + H)^+$. Anal. calcd. for $C_{10}H_{13}NO_4$: C, 56.86; H, 6.20; N, 6.63. Found: C, 56.68; H, 6.28; N, 6.71.

1,2,3-Trimethoxy-5-(2-nitro-propyl)benzene (2d). Liquid; IR (neat): $\upsilon = 3430$, 1549, 922 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.56$ (d, $J = 6.6$ Hz, 3H), 2.94 (dd, $J = 6.6$ Hz, 14.0 Hz, 1H), 3.28 (dd, $J = 6.6$ Hz, 14.0 Hz, 1H), 3.82 (s, 9H), 4.73 (sext, $J = 6.64$ Hz, 1H), 6.36 (s, 2H); MS (ESI): 256 $(M + H)^+$. Anal. calcd. for $C_{12}H_{17}NO_5$: C, 56.46; H, 6.71; N, 5.49. Found: C, 56.34; H, 6.80; N, 5.57.

4-(2-Nitropropyl)phenol (2e). Liquid; IR (neat): $\upsilon = 3390$, 1546, 770 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.53 (d, $J = 6.9$ Hz, 3H), 2.94 (dd, $J = 6.5$ Hz, 14.0 Hz, 1H), 3. 23 (dd, $J = 6.6$ Hz, 14.0 Hz, 1H), 4.73 (sext, $J = 6.5$ Hz, 1H), 5.29 (brs, OH), 6.78 (d, $J = 6.9$ Hz, 2H), 7.04 (d, $J = 6.9$ Hz, 2H); MS (ESI): 182 $(M + H)^+$. Anal. calcd. for $C_9H_{11}NO_3$: C, 59.66; H, 6.12; N, 7.73. Found: C, 59.54; H, 6.89; N, 7.81.

3-(2-Nitro-propyl)-1H-indole (2f). Liquid; IR (neat): $\upsilon = 3417$, 1546, 745 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.523$ (d, $J = 6.2$ Hz, 3H), 3.16 (dd, $J = 6.2$ Hz, 14.5 Hz, 1H), 3.44 (dd $J = 7.2$ Hz, 14.5 Hz, 1H), 4.85 (sext, $J = 6.3$ Hz, 1H), 6.91 (s, 1H), 7.08–7.17 (m, 2H), 7.30 (d, $J = 7.6$ Hz, 1H), 7.54 (d, $J = 7.6$ Hz, 1H), 8.03 (brs, NH); MS (ESI): 205 $(M + H)^+$. Anal. calcd. for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.54; H, 5.99; N, 13.83.

5-(2-Nitro-propyl)benzo(1,3)dioxole (2g). Liquid; IR (neat): $\upsilon = 2900$, 1550, 930 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.53$ (d, $J = 6.6$ Hz,

3H), 2.92 (dd, $J = 6.6$ Hz, 14.0 Hz, 1H), 3.22 (dd, $J = 7.6$ Hz, 14.0 Hz, 1H), 4.71 (sext, $J = 6.8$ Hz, 1H), 5.93 (s, 2H), 6.61 (d, $J = 7.8$ Hz, 1H), 6.63 (s, 1H), 6.74 (d, $J = 7.8$ Hz, 1H); MS (ESI): 210 $(M + H)^+$. Anal. calcd. for $C_{10}H_{11}NO_4$: C, 57.41; H, 5.30; N, 6.70. Found: C, 57.30; H, 5.39; N, 6.78.

2-(2-Nitro-propyl)furan (2i). Liquid; IR (neat): $\upsilon = 3420$, 1537, 756 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.57$ (d, $J = 6.7$ Hz, 3H), 2.37 (dd, $J = 7.2$ Hz, 15.2 Hz, 1H), 3.80 (dd, $J = 6.7$ Hz, 15.2 Hz, 1H), 4.84 (sext, $J = 6.8$ Hz, 1H), 6.13 (d, $J = 2.53$ Hz, 1H), 6.30 (d, $J = 2.8$ Hz, 1H), 7.33 (s, 1H); MS (ESI): 156 $(M + H)^+$. Anal. calcd. for $C_7H_9NO_3$: C, 54.19; H, 5.85; N, 9.03. Found: C, 54.05; H, 5.92; N, 9.10.

(2-Nitro-4-(2-nitro-propyl)phenoxy(acetic acid methyl ester (2j). Liquid; IR (neat): $\upsilon = 3439$, 1743, 1626, 814, 755 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.59$ (d, $J = 6.7$ Hz, 3H), 3.04 (dd, $J = 5.8$ Hz, 14.4 Hz, 1H), 3.30 (dd, $J = 8.3$ Hz, 14.4 Hz, 1H), 3.80 (s, 3H), 4.74 (s, 2H), 4.75–4.80 (m, 1H), 6.94 (d, $J = 8.6$ Hz, 1H), 7.30 (d, $J = 8.6$ Hz, 1H), 7.71 (s, 1H); MS (ESI): 299 $(M + H)^+$. Anal. calcd. for $C_{12}H_{14}N_2O_7$: C, 48.32; H, 4.73; N, 9.39. Found: C, 48.21; H, 4.80; N, 9.46.

1-(3,4,5-Trimethoxy-phenyl)propan-2-one (3d). Liquid; IR (neat): $\upsilon = 3513$, 1710, 1590, 917 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.18$ (s, 3H), 3.63 (s, 2H), 3.84 (s, 9H), 6.41 (s, 2H); MS (ESI): 225 $(M + H)^+$: Anal. calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.41; H, 7.26.

1-(4-Hydroxy–phenyl)propan-2-one (3e). Liquid; IR (neat): $\upsilon = 3357$, 1698, 1513, 757 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.16$ (s, 3H), 3.63 (s, 2H), 6.40 (brs, OH), 6.80 (d, $J = 8.30$ Hz, 2H), 7.02 (d, $J = 8.30$ Hz, 2H); MS (ESI): 151 $(M + H)^+$. Anal. calcd. for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.86; H, 6.77.

1-(1H-Indol-3-yl)propan-2-one (3f). Mp 104–106°C. IR (KBr): $\upsilon = 3327$, 1708, 752 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.15$ (s, 3H), 3.8 (s, 2H), 7.07 (s, 1H), 7.10–7.23 (m, 2H), 7.34 (d, $J = 7.71$ Hz, 1H), 7.52 (d, $J = 7.71$ Hz, 1H), 8.2 (brs, NH); MS (ESI): 174 $(M + H)^+$. Anal. calcd. for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.13; H, 6.46; N, 8.15.

1-(4-Amino-phenyl)propan-2-one (3h). Liquid; IR (neat): $\upsilon = 3363$, 1703, 1624, 1515 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.14$ (s, 3H), 3.57 (s, 2H), 4.17 (brs, NH_2), 6.49 (d, $J = 8.41$ Hz, 2H), 7.14 (d, $J = 7.95$ Hz, 2H); MS (ESI): 150 $(M + H)^+$. Anal. calcd. for $C_9H_{11}NO$: C, 72.46; H, 7.43; N, 9.39. Found: C, 72.33; H, 7.50; N, 9.48.

1-Furan-2-yl-propan-2-one(3i). Liquid; IR (neat): $\upsilon = 3282$, 2923, 1712, 743 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.88$ (s, 3H), 3.52 (s, 2H), 6.12 (d, $J = 2.22$ Hz, 1H), 6.20 (d, $J = 2.90$ Hz, 1H), 7.33 (s, 1H); MS (ESI): 125 $(M + H)^+$. Anal. calcd. for $C_7H_8O_2$: C, 67.73; H, 6.50. Found: C, 67.99; H, 6.58.

6-(2-Oxo-propyl)-4H-benzo(1,4(oxazine-3-one (3j). Mp 154–156°C; IR (KBr): $\upsilon = 3197$, 1710, 1688, 800 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.18$ (s, 3H), 3.64 (s, 2H), 4.61 (s, 2H), 6.67 (s, 1H), 6.79 (d, $J = 8.16$ Hz, 1H),

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6.93 (d, $J = 8.16$ Hz, 1H), 8.86 (brs, NH); ^{13}C NMR ($CDCl_3$): ($\delta = 29.82$, 50.25, 67.51, 117.28, 117.50, 125.56, 126.75, 129.08, 143.12, 166.80, and 206.79; MS (ESI): 206 $(M + H)^+$. Anal. calcd. for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.50; H, 5.59; N, 6.90.

2-(3,4,5-Trimethoxy-phenyl)ethylamine (6a). Liquid; IR (neat): $\upsilon = 3412$, 1645, 996, 826 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.73$ (t, $J = 6.78$ Hz, 2H), 2.98 (t, $J = 6.74$ Hz, 2H), 2.91 (brs, 2 × NH), 3.84 (s, 9 H), 6.43 (s, 2H); ^{13}C NMR ($CDCl_3$): ($\delta = 39.02$, 46.12, 61.27 (2 × C), 65.78, 111.01 (2 × C), 137.95, 141.82, 158.42 (2 × C); MS: 212 $(M + H)^+$. Anal. calcd. for $C_{11}H_{17}NO_3$: C, 62.54; H, 8.11; N, 6.63. Found: C, 62.42; H, 8.15: N, 6.69.

2-Benzo(1,3(dioxole-5-yl-ethylamine (6b). Liquid; IR (neat): $\upsilon = 3412$, 1653, 809 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.74 (brs, NH_2), 2.66 (t, $J = 6.69$ Hz, 2H), 2.91 (t, $J = 6.57$ Hz, 2H), 5.91 (s, 2H), 6.50–6.80 (m, 3H); MS (ESI): 166 $(M + H)^+$. Anal. calcd. for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.31; H, 6.78, N, 8.54.

6-(2-Hydroxyimino-propyl)-4H-benzo-(1,4)oxazine-3-one (7d). Mp 143–144°C; IR (KBr): $\upsilon = 3216$, 1688, 806 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.65$ (s, 3H), 3.16 (s, 2H), 3.18 (s, 2H), 6.70–7.06 (m, 3, H), 10.49 (brs, 1H), 10.66 (s, 1H); ^{13}C NMR (DMSO-d_6): ($\delta = 13.78$, 41.48, 67.59, 116.76, 116.89, 124.25, 128.11, 132.57, 142.77, 155.28, 165.83; MS (ESI): 221 $(M + H)^+$. Anal. calcd. for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49; N, 12.72. Found: C, 59.83; H, 5.54; N, 12.78.

1-(4-Hydroxy-3-methoxy-phenyl)propan-2-one oxime (7g). Liquid; IR (neat): $\upsilon = 3370$, 1661, 1514, 793 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.79$ (s, 3H), 3.41 (s, 2H), 3.79 (s, 3H), 3.85 (s, 1H), 6.66–6.90 (m, 4H); MS (ESI): 196 $(M + H)^+$. Anal. calcd. for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71; N, 7.18. Found: C, 61.42; H, 6.79; N, 7.24.

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