Journal of the Korean Chemical Society
2013, *Vol. 57, No. 2*
Printed in the Republic of Korea
http://dx.doi.org/10.5012/jkcs.2013.57.2.295

단신 (Notes)

A Development of Rapid, Practical and Selective Process for Preparation of *Z*-Oximes

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(Received December 28, 2012; Accepted January 22, 2013)

Key words: Oxime, Oximation, Aldehyde, Ketone, Potassium carbonate

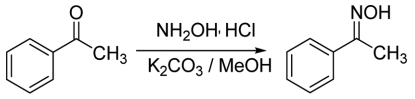
Oximes are important functional groups in organic chemistry due to their synthetic utility as protecting groups for carbonyl groups and their ability to form other functionalities,[1–4] and their biological activity.[5] Oximes are commonly prepared by condensing aldehydes and ketones with hydroxylamines. These reactions do not always go to completion and reaction times can be long, and therefore there has been interest in more convenient and efficient methods. To avoid the typical disadvantage, conversion of aldehydes and ketones to the corresponding oximes was accomplished by using various catalysts such as organic acid/bases,[1,2,6] AcONa, alumina,[7] TiO_2/SO_4^{2-},[2] silica gel,[8] Oxone®,[9] NaOH,[10] basic ionic liquid 1-butyl-3-methylimidazolium hydroxide,[11] polyoxometalates,[12] Na_2SO_4,[13] and $CuSO_4/K_2CO_3$ [14] under the solvent, the solvent-free or the microwave conditions. These are one and more drowbacks such as long reaction time, use of catalysts, inconvenients due to solid-sate reaction, low yields and limitaion of some carbonyl compounds. On the other hand, H. Sharghi, et al.,[14] reported the catalysis of the stereoselectivity of $CuSO_4$ and K_2CO_3 in the oximation of aldehydes and ketones under solvent-free conditions. Although this method show high selectivity, it is inconvenient for the large scale experiments and the industrial process due to the solvent-free condition. Therefore, we attempted to develop a more convenient and efficient solution method. According to the literatures,[15] treatment of potassium carbonate with methanol generates slightly the potassium methoxide, which may be useful for forming the free NH_2OH from its salts. We describe the oximation of aldehyde and ketone using $NH_2OH{\cdot}HCl/K_2CO_3$ in methanol solvent.

We selected oximation of acetophenone (**1a**) with hydroxylamine hydrochloride as a model and its behavior was investigated in seven solvents involving methanol (*Table* 1).

As shown in the Entry 2 in *Table* 1, compound **1a** was treated with hydroxylamine hydrochloride in the presence of potassium carbonate in refluxing 1,4-dioxane to afford the corresponding ketoxime **2a** in excellent yield.

Acetophenone oxime (**2a**) was also obtained by the use of ethanol or methanol as the solvent at room temperature or at reflux temperature in excellent yields (Entries 9–12 in *Table* 1), whereas the side reaction was detected for the

***Table* 1.** Screening of the solvents

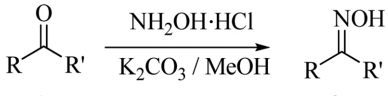


1a **2a**

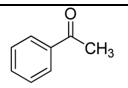
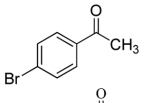
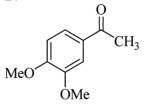
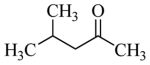
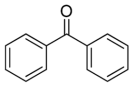
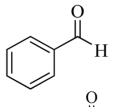
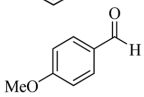
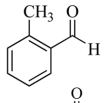
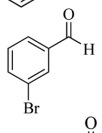
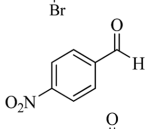
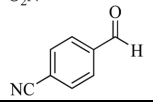
Entry	Solvent	Conditions	Time (h)	**2a** (Yield %)[a]
1	1,4-Dioxane	Room temp.	48	–[b]
2	1,4-Dioxane	Reflux	5	96
3	Diethyl Ether	Room temp.	48	–[b]
4	Diethyl Ether	Reflux	48	25
5	Chloroform	Room temp.	48	–[b]
6	Chloroform	Reflux	48	13
7	Tetrahydrofuran	Room temp.	48	–[b]
8	Tetrahydrofuran	Reflux	48	30
9	Ethanol	Room temp.	15	94
10	Ethanol	Reflux	6	92
11	Methanol	Room temp.	8.5	98
12	Methanol	Reflux	0.25	98
13	Water	Room temp.	48	trace
14	Water	Reflux	4.5	60[c]

[a]Isolated yield.
[b]Trace.
[c]Hydroxylamine was decomposed in hot water.

***Table* 2.** Oximation of aldehydes and ketones with hydroxylamine hydrochloride in the presence of potassium carbonate in methanol



1 **2**

Entry		Substrate **1**	Conditions[a]		Yield(%)[b]
1	**1a**		10 min/rf	**2a**	*E* (17) *Z* (73)
2	**1b**		30 min/rf	**2b**	*E* (12) *Z* (86)
3	**1c**		20 min/rf	**2c**	*E* (10) *Z* (84)
4	**1d**		40 min/rf	**2d**	*E* (10) *Z* (74)
5	**1e**		30 min/rf	**2e**	86
6	**1f**		6.5 h/rf	**2f**	97
7	**1g**		10 min/rt	**2g**	*E* (9) *Z* (82)
8	**1h**		10 min/rf	**2h**	*E* (4) *Z* (93)
9	**1i**		5 min/rf	**2i**	*E* (3) *Z* (87)
10	**1j**		5 min/rf	**2j**	*E* (6) *Z* (85)
11	**1k**		10 min/rf	**2k**	*E* (9) *Z* (91)
12	**1l**		20 min/rt	**2l**	*E* (3) *Z* (90)

[a]rf = reflux; rt = room temperature.
[b]Isolated yield.

reaction of **1a** with hydroxylamine hydrochloride in the presence of potassium carbonate in refluxing water. According to our preliminary results, we selected the methanol as the solvent due to short reaction time and low price.

As shown in *Table* 2, aliphatic and aromatic ketones **1b**–**1e** except for benzophenone (**1f**) were rapidly and selectively converted to the corresponding *Z*-oximes **2b**–**2e** in good yields. Also, various types of aromatic aldehydes **1g**–**1l** with electron donating and withdrawing groups were rapidly and selectively converted to the corresponding *Z*-aldoximes **2g**–**2l** in good to excellent yields. In our condition, the oximation of aldehydes is more *Z*-selective than the oximation of ketones. In order to evaluate the utility of industrial process, we examined the one mole scale reaction. Treatment of one mole acetophenone (**1a**) and benzaldehyde (**1g**) with hydroxylamine hydrochloride and potassium carbonate in methanol afforded the corresponding oximes **2a** (*E*/*Z* ratio = 15:85, 92%) and **2g** (*E*/*Z* ratio = 10:90, 92%).

The structures of the oximes were established by IR and NMR. In the case of ketoximes, we distinguished two isomers by using the carbon chemical shifts of C=NOH, that is, the chemical shifts of the *Z*-isomer are detected higher field than the chemical shifts of the *E*-isomer.[16] In the case of aldoximes, *E*/*Z*-isomers were distinguished by using the proton chemical shifts of HC=N for aldoximes, that is, the proton chemical shifts of the *Z*-isomer are detected lower field than the chemical shifts of the *E*-isomer.[17]

In summary, we have demonstrated the rapid and convenient oximation of ketones and aldehydes with potassium carbonate in methanol at room or reflux temperature in good to excellent yields. Our method has some advantages: use of cheap reagent, mild reaction conditions, high *Z*-selectivity, short reaction time, no side-reactions, good solubility of methanol for carbonyl compounds, the solution reaction and easy work-up.

EXPERIMENTAL

Melting points were determined with a capillary apparatus and uncorrected. NMR spectra were recorded on a 300 MHz spectrometer with chemical shift values reported in units (ppm) relative to an internal standard (TMS). IR spectra were obtained on SIMADZU FT-IR 8400s spectrophotometer. The open-bed chromatography was carried out on silica gel (70–230 mesh, Merck) using gravity flow. The column was packed with slurries made from the elution solvent.

General Procedure for the Conversion of Aldehydes and Ketones to Oximes

A mixture of carbonyl compound (**1a**–**1l**, 8.3 mmol), hydroxylamine hydrochloride (8.4 mmol), K_2CO_3 (9.1 mmol) and MeOH (40 ml) was stirred at until the carbonyl compound was disappeared at reflux temperature or at room temperature. After cooling to room temperature, ketoximes **2a**–**2f** were extracted with dichloromethane (30 × 5 mL). The organic layer was separated and dried over

anhydrous $MgSO_4$. After evaporating the solvent under reduced pressure at below 20 ºC, the isomers were then separated from the resulting residue by column chromatography [*n*-hexane : ethyl acetate = 3 : 1 (v/v)] to give the corresponding *E*- and *Z*-ketoximes. (*Caution: E*- ketoxime is evaporating the solvent below 20 ºC. And store in freezer).

In the case of aldoximes, the solvent was evaporated under reduced pressure. The resulting residue was washed with cold diethyl ether (150 mL). The ether solutions were combined, and evaporated under reduced pressure. The isomers were then separated by column chromatography [*n*-hexane : ethyl acetate = 3 : 1 (v/v)] to give the corresponding *E*- and *Z*-aldoximes.

(*E*)-Acetophenone oxime (*E*-2a)

Mp 75–76 ºC (lit.[18] 80–81 ºC); R_f = 0.23 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 3193, 3083, 3053, 3030, 2967, 2920, 2868, 1468, 1436, 1375, 1301, 1267, 1021, 950, 759, 693, 621 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.31 (s, 3H), 7.36–7.42 (m, 3H), 7.60–7.64 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.37, 126.0, 128.5, 129.3, 136.4, 156.1; HRMS(EI): *m*/*z* calcd for C_8H_9NO: 135.0684; found: 135.0684.

(*Z*)-Acetophenone oxime (*Z*-2a)

Mp 52–54 ºC (lit.[19] 52–55 ºC); R_f = 0.3 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 3292, 3245, 3064, 2926, 1496, 1446, 1370, 1302, 1265, 1079, 1006, 926, 762, 744 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.30 (s, 3H), 7.36 (m, 3H), 7.60–7.62 (m, 2H), 9.86 (s, OH, D_2O exchangeable); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.42, 126.0, 128.5, 129.2, 136.4, 155.9; HRMS (EI): *m*/*z* calcd for C_8H_9NO: 135.0684; found: 135.0684.

(*E*)-4-Bromoacetophenone oxime (*E*-2b)

Mp 115–116 ºC; R_f = 0.2 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 3199, 3087, 3054, 2090, 2869, 2838, 1585, 1488, 1460, 1423, 1392, 1264, 1089, 1029, 1010, 942, 820, 748 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) : δ 2.27 (s, 3H), 7.25–7.56 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.22, 123.6, 127.6, 131.6, 135.2, 155.2(9); HRMS (EI): *m*/*z* calcd for C_8H_8NOBr: 212.9789; found: 212.9793.

(*Z*)-4-Bromoacetophenone oxime (*Z*-2b)

Mp 124–126 ºC; R_f = 0.48 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 3286, 3246, 3082, 3009, 3956, 2914, 1484, 1394, 1309, 1274, 1182, 1069, 1008, 929, 825, 750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.27 (s, 3H), 7.24–7.52 (m, 4H), 8.72 (s, OH D_2O exchangeable); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.25, 123.6, 127.6, 131.7, 135.2, 155.2 (5); HRMS (EI): *m*/*z* calcd for C_8H_8NOBr: 212.9789; found: 212.9793.

(*E*)-3,4-Dimethoxyacetophenone oxime (*E*-2c)

Mp 45–47 ºC; R_f = 0.11 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 3249, 3005, 2954, 2921, 2851, 1517, 1463, 1416, 1367, 1274, 1260, 1225, 1175, 1148, 1024, 948, 869, 804, 764, 749 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) : δ 2.10 (s, 3H), 3.75 (d, 6H, *J* = 9.9 Hz), 6.95–7.31 (m, 3H), 10.59 (s, OH, D_2O exchangeable); ^{13}C NMR (75 MHz, DMSO-d_6) : δ 21.87, 55.39, 55.45, 110.9, 111.6, 112.3, 121.3, 147.7, 150.1, 158.1; HRMS(EI): *m*/*z* calcd for $C_{10}H_{13}NO_3$: 195.0895; found: 195.0899.

(*Z*)-3,4-Dimethoxyacetophenone oxime (*Z*-2c)

Mp 141–143 ºC; R_f = 0.17 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 3432, 3084, 3011, 2975, 2928, 2843, 1583, 1515, 1503, 1456, 1441, 1332, 1296, 1272, 1241, 1222, 1173, 1149, 1079, 1016, 998, 950, 869, 812, 766 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) : δ 2.14 (s, 3H), 3.77 (s, 6H), 6.93–6.95 (m, 1H), 7.14–7.17 (m, 1H), 7.28(2)–7.28(4) (m, 1H), 11.03 (s, OH D_2O exchangeable); ^{13}C NMR (75 MHz, DMSO-d_6): δ 11.33, 55.22, 55.38, 108.2, 111.1, 118.4, 129.5, 148.4, 149.4, 152.3; HRMS(EI): *m*/*z* calcd for $C_{10}H_{13}NO_3$: 195.0895; found: 195.0899.

(*E*)-4-Methylpentan-2-one oxime (*E*-2d)

Liquid; R_f = 0.35 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 1341, 1265, 1215, 1165, 1108, 1017, 955, 803, 751 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.94 (d, 6H, *J* = 6.6 Hz), 1.86(0)–1.86(9) (m, 4H), 2.25 (d, 2H, *J* = 7.5 Hz), 8.56 (s, OH, D_2O exchangeable); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.10, 25.73, 26.90, 37.44, 158.3; HRMS(EI): *m*/*z* calcd for $C_6H_{13}NO$: 115.0997; found: 115.1008.

(*Z*)-4-Methylpentan-2-one oxime (*Z*-2d)

Liquid; R_f = 0.55 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 3422, 2958, 2375, 1629, 1464, 1374, 1112, 974, 931, 875, 832, 736 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.91 (d, 6H, *J* = 6.6 Hz), 1.82–1.94 (m, 4H), 2.06 (d, 2H, *J* = 7.2 Hz), 9.74 (s, OH, D_2O exchangeable); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.56, 22.36, 25.85, 44.75, 157.9; HRMS (EI): *m*/*z* calcd for $C_6H_{13}NO$: 115.0997; found: 115.1008.

Cyclohexanone oxime (2e)

Mp 85–87 ºC (lit.[20] 85–87 ºC); R_f = 0.5 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 3232, 3114, 2933, 2856, 2729, 1600, 1477, 148, 1249, 1222, 991, 958, 896, 763, 655,

565, 474 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.56–1.71 (m, 6H), 2.20–2.25 (m, 2H), 2.49–2.53 (m, 2H), 8.54 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.51, 25.57, 25.77, 26.86, 32.08, 160.89; HRMS (EI): *m/z* calcd for $C_6H_{11}NO$: 113.0841; found: 113.0848.

Benzophenone oxime (2f)

Mp 136–137 °C (lit.[21] 138–142 °C); R_f = 0.45 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 3253, 3055, 2953, 2923, 2854, 1448, 1327, 1077, 1032, 997, 919, 766, 697 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 7.26–7.29 (m, 2H), 7.37–7.38 (m, 5H), 7.41–7.49 (m, 3H), 11.34 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 127.4, 128.6, 128.8(0), 128.8(4), 129.3, 133.9, 137.1, 147.3, 155.6; HRMS(EI): *m/z* calcd for $C_{13}H_{11}NO$: 197.0841; found: 197.0844.

(*E*)-Benzaldehyde oxime (*E*-2g)

Mp 113–115 °C; R_f = 0.4 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 3461, 3156, 2923, 2854, 1639, 1433, 1351, 1268, 954, 850, 754, 691 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) : δ 7.36 (s, 1H), 7.39–7.47 (m, 3H), 7.91–7.97 (m, 2H), 8.35 (s, OH, D_2O exchangeable); ^{13}C NMR (75 MHz, $CDCl_3$): δ 128.4, 130.1, 130.3, 130.8, 147.0; HRMS(EI): *m/z* calcd for C_7H_7NO: 121.0528; found: 121.0529.

(*Z*)-Benzaldehyde oxime (*Z*-2g)

Liquid; R_f = 0.57 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 3388, 2896, 2771, 1954, 1895, 1692, 1634, 1497, 1449, 1292, 1211, 956, 869, 756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) : δ 7.32–7.36 (m, 3H), 7.53–7.58 (m, 2H), 8.18 (s, 1H), 9.95 (s, OH, D_2O exchangeable); ^{13}C NMR (75 MHz, $CDCl_3$): δ 127.0, 128.7, 130.0, 131.6, 150.5; HRMS (EI): *m/z* calcd for C_7H_7NO: 121.0528; found: 121.0529.

(*E*)-4-Methoxybenzaldehyde oxime (*E*-2h)

Mp 84–85 °C (lit.[22] 74 °C); R_f = 0.38 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 3173, 3069, 3009, 2925, 2837, 2793, 1599, 1506, 1448, 1406, 1351, 1301, 1257, 1172, 1113, 1022, 951, 827, 743 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) : δ 3.83 (s, 3H), 6.90–6.96 (m, 2H), 7.31 (s, 1H), 7.92–7.96 (m, 2H), 8.98 (s, OH, D_2O exchangeable); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.31, 113.7, 132.0, 132.4, 146.3, 160.6; HRMS (EI): *m/z* calcd for $C_8H_9NO_2$: 151.0633; found: 151.0631.

(*Z*)-4-Methoxybenzaldehyde oxime (2h)

Mp 44–46 °C; R_f = 0.43 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 3301, 3005, 2963, 2937, 2910, 2838, 1607, 1575, 1515, 1463, 1418, 1304, 1252, 1109, 1029, 957, 874, 829 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) : δ 3.81 (s, 3H), 6.09 (d, 2H, *J* = 8.76 Hz), 7.51 (d, 2H, *J* = 8.7 Hz), 8.11 (s, 1H), 9.03 (s, OH, D_2O exchangeable); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.31, 114.2, 124.5, 128.5, 149.8, 161.0; HRMS (EI): *m/z* calcd for $C_8H_9NO_2$: 151.0633; found: 151.0631.

(*E*)-2-Methylbenzaldehyde oxime (*E*-2i)

Mp 88–89 °C; R_f = 0.28 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 3191, 3086, 3030, 2987, 2866, 1656, 1600, 1437, 1328, 1275, 1260, 1217, 1037, 956, 939, 854, 764 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) : δ 2.39 (s, 3H), 7.22–7.32 (m, 3H), 7.64 (s, 1H), 7.88–7.92 (m, 1H), 8.41 (s, OH, D_2O exchangeable); ^{13}C NMR (75 MHz, , $CDCl_3$): δ 19.88, 125.6, 129.2, 129.6, 129.7, 130.4, 136.8, 146.3; HRMS (EI): *m/z* calcd for C_8H_9NO: 135.0684; found: 135.0683.

(*Z*)-2-Methylbenzaldehyde oxime (*Z*-2i)

Mp 46–48 °C; R_f = 0.43 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 3317, 3069, 3022, 2984, 2922, 2779, 1622, 1489, 1457, 1433, 1312, 1292, 1226, 1125, 1034, 951, 871, 754, 716 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) : δ 2.38 (s, 3H), 7.14–7.28 (m, 3H), 7.65–7.68 (m, 1H), 8.44 (s, 1H), 9.72 (s, OH, D_2O exchangeable). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.77, 126.3, 126.6, 130.0, 130.1, 130.9, 136.2, 149.3; HRMS (EI): *m/z* calcd for C_8H_9NO: 135.0684; found: 135.0683.

(*E*)-3-Bromobenzaldehyde oxime (*E*-2j)

Mp 98–100 °C; R_f = 0.25 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 3170, 3069, 2840, 2746, 1949, 1685, 1644, 1559, 1463, 1415, 1330, 1269, 1191, 1073, 955, 917, 900, 877, 780, 749 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) : δ 7.31–7.33 (m, 2H), 7.53–7.56 (m, 1H), 7.78–7.81 (m, 1H), 8.15–8.16 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.3, 130.0, 133.1, 133.6, 145.4; HRMS (EI): *m/z* calcd for C_7H_6NOBr: 189.9633; found: 189.9635.

(*Z*)-3-Bromobenzaldehyde oxime (*Z*-2j)

Mp 57–59 °C; R_f = 0.43 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 3343, 3065, 2939, 2888, 2832, 2752, 1943, 1695, 1566, 1475, 1421, 1351, 1310, 1272, 1200, 1105, 1064, 976, 908, 875, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) : δ 7.23–7.28 (m, 1H), 7.47–7.53 (m, 2H), 7.74–7.75 (m, 1H), 8.08 (s, 1H), 8.19 (s, OH, D_2O exchangeable); ^{13}C NMR (75 MHz, $CDCl_3$): δ 125.6, 129.7, 130.2, 132.9, 149.0; HRMS(EI): *m/z* calcd for C_7H_6NOBr: 189.9633; found: 189.9635.

(*E*)-4-Nitrobenzaldehyde oxime (*E*-2k)

Mp 157–159 °C (lit.[23] 146 °C); R_f = 0.31 (*n*-hexane :

ethyl acetate = 3:1, v/v); IR (KBr): 3180, 3067, 3014, 2926, 2880, 2837, 2788, 1601, 1519, 1441, 1401, 1344, 1318, 1264, 1192, 1104, 1013, 967, 942, 909, 852, 840, 746 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 7.67 (s, 1H), 8.21–8.24 (m, 2H), 8.29–8.32 (m, 2H), 12.27 (s, OH, D_2O exchangeable); ^{13}C NMR (75 MHz, DMSO-d_6): δ 123.6, 131.3, 136.2, 143.0, 147.0; HRMS (EI): *m*/*z* calcd for $C_7H_6N_2O_3$: 166.0378; found: 166.0378.

(*Z*)-4-Nitrobenzaldehyde oxime (*Z*-2k)

Mp 128–129 °C (lit[24] 129 °C); R_f = 0.44 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 3335, 3079, 2938, 1925, 1803, 1602, 1535, 1347, 1213, 1105, 969, 845, 746 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) : δ 7.85–7.89 (m, 2H), 8.24–8.28 (m, 2H), 8.32 (s, 1H), 11.89 (s, OH, D_2O exchangeable); ^{13}C NMR (75 MHz, DMSO-d_6): δ 123.9, 127.2, 139.4, 146.7, 147.4; HRMS (EI): *m*/*z* calcd for $C_7H_6N_2O_3$: 166.0378; found: 166.0378.

(*E*)-4-Cyanobenzaldehyde oxime (*E*-2l)

Mp 138–140 °C; R_f = 0.1 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 3259, 2981, 2963, 2868, 2855, 2227, 1459, 1403, 1275, 1260, 1176, 1082, 916, 828, 763, 749, 704 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) : δ 7.58 (s, 1H), 7.74 (d, 2H, *J* = 8.19 Hz), 8.13 (d, 2H, *J* = 8.49 Hz), 12.15 (s, OH, D_2O exchangeable); ^{13}C NMR (75 MHz, DMSO-d_6): δ 111.5, 126.9, 130.7, 132.3, 132.6, 143.4; HRMS (EI): *m*/*z* calcd for $C_8H_6N_2O$: 146.0480; found: 146.0478.

(*Z*)-4-Cyanobenzaldehyde oxime (*Z*-2l)

Mp 171–173 °C; R_f = 0.2 (*n*-hexane : ethyl acetate = 3:1, v/v); IR (KBr): 3208, 3003, 2980, 2955, 2935, 2896, 2831, 2225, 1399, 1326, 1305, 1278, 1261, 1191, 1101, 1056, 971, 938, 873, 842, 824, 750, 702 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 7.78 (d, 2H, *J* = 8.1 Hz), 7.87 (d, 2H, *J* = 8.1 Hz), 8.25 (s, 1H), 11.7 (s, OH, D_2O exchangeable); ^{13}C NMR (75 MHz, DMSO-d_6): δ 111.2, 118.6, 126.9, 132.6, 137.5, 147.0; HRMS (EI): *m*/*z* calcd for $C_8H_6N_2O$: 146.0480; found: 146.0478.

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