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m-CPBA Mediated Metal Free, Rapid Oxidation of Aliphatic Amines to Oximes

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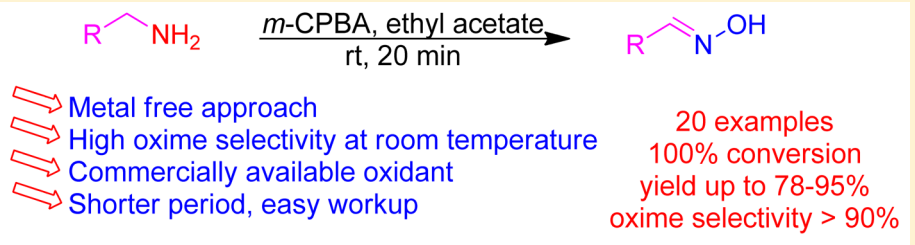
Supporting Information



ABSTRACT: An efficient, rapid oxidation of various aliphatic amines to oximes using *m*-CPBA as an oxidant in ethyl acetate is described. High conversion (100%) with >90% oxime selectivity is achieved at room temperature under catalyst-free conditions. Mild reaction conditions along with an easy work up procedure offer lower byproduct formation and high selectivity for oximes in good yield and purity.

INTRODUCTION

Oximes serve as important precursors for various commodity chemicals, pharmaceuticals, polymers, heterocycles, and fine chemicals. They can be easily transformed into various important functionalities such as carbonyl,[1−3] amide,[4−7] nitrile oxide (which are used as intermediate for the synthesis of substituted isoxazoles and isoxazolines),[8−11] thiohydroxamic and thiohydroxic acid derivatives,[12,13] nitriles,[14−17] *o*-ethers,[18] nitro compounds[19,20] and oxime esters[21] which serve as potential building blocks in organic synthesis. Oxidation of aliphatic amine is an alternative route for the conventional aldehyde-hydroxyl amine method[22−25] used for the synthesis of oxime. The main problem encountered during this transformation is the sensitivity of aliphatic amines toward oxidation. Owing to this, the reaction often results in a mixture of undesired side products such as aldehyde, nitrile, nitro, and imine which in turn reduces the selectivity for the desired product. Therefore, selective oxidation of aliphatic amines to oximes still remains one of the most stimulating tasks for researchers. Various oxidizing agents[26−30] such as dimethyldioxirane, sodium perborate, sulfonic peracid, metal catalysts with oxidants such as H_2O_2,[31−38] and TBHP[39] were used for this oxidative transformation.

However, the oxidant such as dimethyldioxirane is difficult to handle, excess use of oxidants give poor selectivity for oxime due to formation of side products such as nitrile, aldehyde, or imine which limits the scope for these systems. These shortcomings are compensated by environmentally a benign aerobic oxidation protocol, where molecular oxygen is used as an oxidant with transition metal catalysts such as gold-titania, DPPH and WO_3/Al_2O_3, $InCl_3$ with TEMPO, and acetaldoxime.[40−43] This approach offers various advantages over conventional protocols such as minimal waste generation, inexpensive source of oxidant, and recyclability of catalyst over several runs. However, these reactions require longer reaction time from 10 to 16 h, higher temperatures of 100−120 °C, and use expensive transition metal catalysts. Hence improvement in these aspects is still desirable.

As a part of our ongoing research on development of efficient, mild, and benign protocols for oxidation reactions,[44−46] we report a simple and effective route for selective oxidation of aliphatic amines to oximes using *m*-CPBA as an oxidant in ethyl acetate. The present protocol is found to be most effective with ethyl acetate solvent, as more than 90% oxime selectivity was achieved with easy product separation. To the best of our knowledge, this is the best route which offers high selectivity, purity, and yield in short time period avoiding harsh conditions and expensive catalysts.

RESULTS AND DISCUSSION

The reaction conditions were optimized by taking amine **1a** (0.935 mmol, 1 equiv), *m*-CPBA (1.86 mmol, 2 equiv) at room temperature. Solvent screening studies reveal that, in almost all solvents, the mixture of oxime and imine along with a small quantity of benzaldehyde and benzonitrile were formed (Table 1, entries **1**−**12**). In the case of nonpolar solvents such as pet ether and toluene, 51% and 72% selectivity for **4a** was observed along with **2a**, **3a** and **4a** (Table 1, entries **1**, **2**). Additionally, formation of *N*-benzylbenzamide in 7% and 6%, respectively, was also observed in these two solvents. Oxidation of **1a** using halogenated solvents such as chloroform and dichloromethane,

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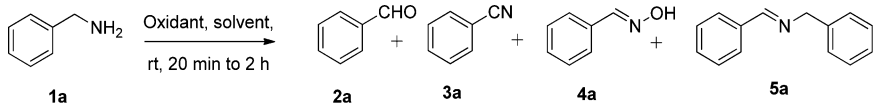
Table 1. Optimization of Reaction Parameters[a]



1a 2a 3a 4a 5a

entry	parameters	conversion[b] (%) 2a	3a	4a	5a
solvent study					
1	Pet ether	7	4	51	30
2	Toluene	3	1	79	8
3	Chloroform	3	1	74	13
4	DCM	6	6	56	22
5	Acetone	7	2	65	5
6	Acetonitrile	2		73	25
7	Ethanol	6	3	81	10
8	Methanol	9	6	70	15
9	Ethyl acetate	1	1	96	2
10	Glycerin	13	6	57	24
11	Water	9	5	43	43
12	DMF	16	20	45	19
temperature study					
13	40 °C	2		85	13
14	50 °C	1		80	19
m-CPBA molar ration study					
15[c]	1.75	2	1	72	10
16[d]	2.15	3		82	15
comparison with other oxidant					
17[e]	50% H_2O_2	4	2	12	75
18[e]	Oxone	14	5	77	2
19[e]	70% TBHP	2	2	0	16
20[e]	Sodium perborate	3	1	13	60
21[e]	Potasium peroxydisulfate		2	1	20
22[e]	Urea hydrogen peroxide	4	6	48	32
23[e]	Peracetic acid	2	1	39	21
24[f]	Peracetic acid			11	35
25[e]	No oxidant				

[a]Reaction conditions: **1a** (0.935 mmol, 1 equiv); *m*-CPBA (1.86 mmol, 2 equiv for entries 1−14), solvent: 2 mL; Temperature: 30−32 °C; time: 20 min. [b]Conversion determined by GC. [c]*m*-CPBA: 1.75 equiv and reaction kept for 2 h. [d]*m*-CPBA: 2.15 equiv and reaction kept for 20 min. [e]Oxidant (1.86 mmol, 2 equiv for entries 17−23) and reaction kept for 2 h. [f]4 equiv of peracetic acid was used.

resulted in 91% and 90% conversion with 9% and 10% of unreacted amine in 2 h, respectively (Table 1, entries **3**, **4**). In chloroform, 74% of **4a** and 13% of **5a** were formed while in dichloromethane 56% of **4a** and 22% of **5a** were formed, respectively. Liu, Jia et al.[47] have reported use of *m*-CPBA for oxidation of benzyl amine **1a** to respective oxime **4a** in acetone under reflux conditions to give only 60% yield after 10 h. Employing present conditions, we were successful in getting 100% conversion with acetone in 20 min for the conversion of benzyl amine **1a** to oxime **4a**. However, we could get only 60% of oxime **4a** selectivity along with 5% of **5a** (Table 1, entry **5**). It was also observed that, in the case of acetone as a solvent, benzyl amine undergoes reaction with acetone to give 21% of 1-phenyl-*N*-(propan-2-ylidene)methanamine, a condensation product of acetone with benzyl amine. Among the solvents studied, ethyl acetate was found to be most effective solvent to give 100% conversion, 96% selectivity for **4a** with 93% yield in 20 min (Table 1, entry **9**). Only in the case of ethyl acetate was minimum byproduct formation observed (only 2% **5a** formation was detected by GC). In the case of all other solvents, a mixture of products were obtained (Table 1, entries **6**−**8**,**10**−**12**). It was noticeable that, as we increased the reaction temperature from room temperature to 50 °C, **4a** selectivity was reduced from 96% to 80%, while **5a** formation was increased from 2% to 19% (Table 1, entries **13**, **14**). The oxidant molar ratio also serves as an important parameter to decide high or low selectivity for oxime. Oxidant equivalent study shows that, reducing the oxidant loading from 2 to 1.75 gives only 75% of **4a** (Table 1, entry **15**). When we increased oxidant loading from 2 to 2.15, it was observed that selectivity for **4a** get reduced from 96% to 82% (Table 1, entry **16**). This demonstrated that 2 equiv of *m*-CPBA were required to give high oxime selectivity.

Screening other oxidants under present condition gave mixture of products (Table 1, entries **17**−**23**). 50% H_2O_2 gives 93% conversion with higher selectivity of 75% for **5a** and only 12% for **4a** in 2 h (Table 1, entry **17**). Whereas Oxone gave 98% conversion with 77% selectivity for **4a**, 13% for benzaldehyde and only 2% for **5a** (Table 1, entry **18**). The oxidants, 70% TBHP and potassium peroxydisulfate showed lowest conversion of 20% and 23% in 2 h respectively with no or trace formation of **4a** (Table 1, entries **19**, **21**). Sodium perborate gave 77% conversion with 60% selectivity for **5a** and only 13% selectivity for **4a** (Table 1, entry **20**). Urea hydrogen

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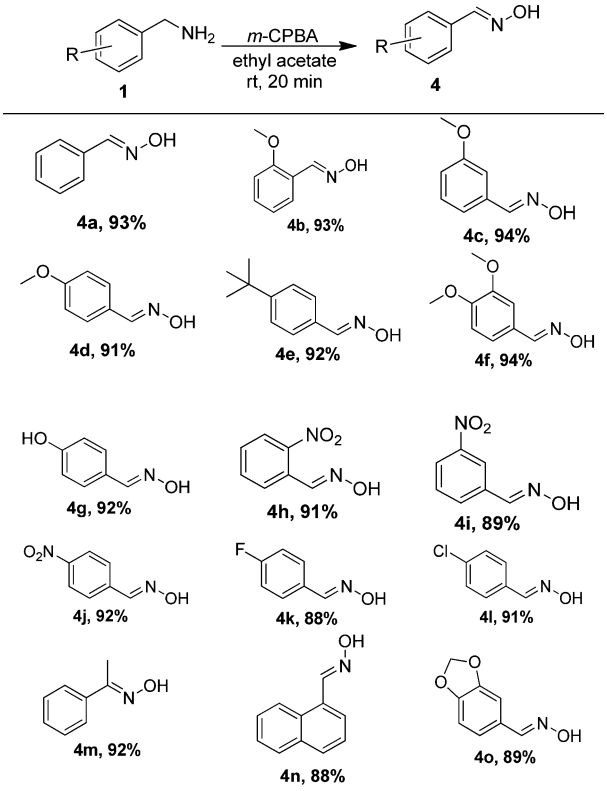
peroxide and peracetic acid gave 90% and 69% conversion with 48% and 39% selectivity for **4a**, respectively (Table 1, entries **22**, **23**). In the case of peracetic acid, it was observed that reaction rate as well as nature of products were affected by peracetic acid concentration. Employing 2 equiv of peracetic acid gives 69% conversion with 39% selectivity for **4a**. In addition, formation of 9% of *N*-benzylacetamide, an *N*-acyalted product of benzylamine, was also observed (Table 1, entry **23**). On increasing peracetic acid from 2 to 4 equiv, although the reaction gives 97% conversion, selectivity for **4a** was reduced from 39% to 11%, while that for *N*-benzylacetamide was increased from 11% to 51% along with 35% of **5a** (Table 1, entry **24**). No reaction occurred in the absence of oxidant (Table 1, entry **25**). Thus, we finalized reaction conditions employing ethyl acetate as a solvent, 2 equiv of *m*-CPBA at room temperature for 20 min.

The optimized conditions are screened for various benzyl amines and the results obtained are summarized in Table 2.

Table 2. Oxidation of Benzyl Amines to Oximes[a]



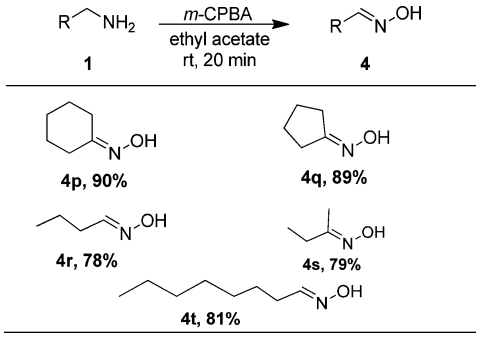
[a]Reaction conditions: 1 (1 equiv), *m*-CPBA (2 equiv), ethyl acetate 2 mL, Temperature: 30−32 °C; reaction time: 20 min; yield: isolated yield.

The oxidation of benzyl amine gave 100% conversion with 96% selectivity for **4a**, along with 2% of imine in 20 min at room temperature (Table 2, entry **4a**). Benzyl amines bearing electron donating groups such as *-o/-m* and *-p* methoxy, *p*-*tert*-butyl, 3,4-dimethoxy, and *p*-hydroxy were smoothly oxidized to corresponding oximes in 20 min (Table 2, entries **4b**−**4g**). Interestingly, benzyl amines possessing electron withdrawing groups such as *-o/-m* or *-p* nitro also undergo oxidation in 20 min to give corresponding oximes in high yields (Table 2, entries **4h**−**4j**). Benzyl amines substituted with halogens such as *p*-F and *p*-Cl along with 1-phenylethanamine, naphthalen-2-ylmethanamine, and benzo[d][1,3]dioxol-5-ylmethanamine gave the corresponding oxime in high yields (Table 2, entries **4k**−**4o**).

It was observed that **4a** obtained after oxidation of **1a** gives mixture of *E* and *Z* isomer. From GC analysis, the ratio of *E*:*Z* isomer was found to be 86:10. However, other substrates of benzyl amine selectively give *E* isomer which was further confirmed by ^{1}H NMR analysis.

Encouraged by these results, we applied optimized conditions to alicyclic amines and aliphatic amines which are summarized in Table 3. The alicyclic amines such as cyclohexyl

Table 3. Oxidation of Aliphatic Amines[a]



[a]Reaction conditions: 1 (1 equiv), *m*-CPBA (2 equiv), ethyl acetate 2 mL, Temperature: 30−32 °C; reaction time: 20 min; yield: isolated yield.

and cyclopentyl amines were oxidized to corresponding oximes in good yields with high purity (Table 3, entries **4p**, **4q**). Especially with cyclohexyl amine white needles are obtained after work up. The GC analysis of the crude product reveals 94% oxime selectivity with 90% yield (Table 3, entry **4p**). Oxidation of octyl amine to its corresponding oxime in dichloromethane gives good yield of 83% at room temperature.[48] However, the reaction was carried out in excess halogenated solvent (7 mL dichloromethane required for oxidation of 65 μL of amine with excess oxidizing agent in 1 h. Under the present conditions, aliphatic amines such as *n*-butyl, *iso*-butyl, and octyl amine gave corresponding oxime in good yield only in 20 min without employing excess solvent and oxidant (Table 3, entries **4s**−**4u**). The oximes obtained from aliphatic amines give a mixture of *E*- and *Z*-isomers.

On the basis of literature reports,[26,49] a plausible mechanism is as shown in Scheme 1. In the first step, *m*-chloro perbenzoic acid was reacted with aliphatic amine to give hydroxylamine which on further reaction with second mole of *m*-chloro perbenzoic acid results into nitroso compound. The nitroso compound formed isomerizes into oxime. This mechanistic pathway was further confirmed by carrying out a separate reaction on *N*-benzylhydroxylamine using one equivalent of *m*-chloro perbenzoic acid following optimized conditions. It was observed that the reaction selectively results in benzaldehyde oxime. From this, it was confirmed that the reaction proceeds through *N*-benzylhydroxylamine as an intermediate. It was also clear that under present conditions, formation of various side products arising due to hydrolysis of benzaldehyde oxime **4a** and *N*-benzylidene-1-phenylmethanamine **5a** or by reaction of benzyl amine **1a** with benzaldehyde oxime **4a** to give *N*-benzylidene-1-phenylmethanamine **5a** were greatly reduced which in turn resulted in high oxime selectivity.

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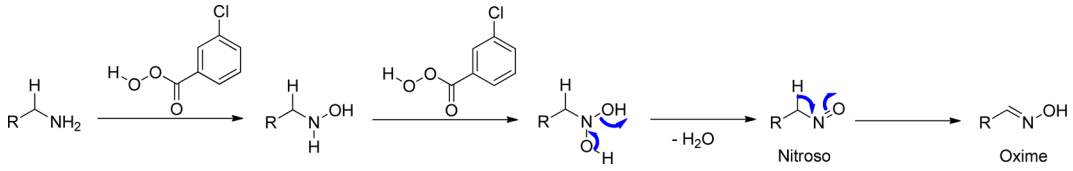
Scheme 1. Plausible Mechanism for Oxime Formation



CONCLUSIONS

In summary, we have developed a rapid and selective protocol for oxidation of various benzyl, alicyclic, and aliphatic amines to corresponding oximes using *m*-CPBA at room temperature. The oximes obtained from various benzyl amine derivatives selectively give *E*-isomer, whereas aliphatic amines give a mixture of *E*- and *Z*-isomers. The solvent used, ethyl acetate, was found to be most promising which offered easy separation of desired products from the reaction mixture.

EXPERIMENTAL SECTION

Chemicals and Instruments. The *m*-CPBA used was "Synthesis Grade" *m*-CPBA. The ethyl acetate used was AR grade "DRY" Ethyl Acetate. The ^{1}H NMR spectroscopic data were recorded on a 500 MHz, 400 MHz spectrometer with $CDCl_3$ and DMSO-d6 as solvent, and chemical shifts are expressed in δ ppm using TMS as an internal standard. GC analysis were carried out using column-TR-1, 30mX0.25 mm, IDX0.25um film, FID detector and sample size 0.11 μL. All melting points are uncorrected and are presented in Celsius.

General Procedure for the Oxidation of Benzylamine. An oven-dried round-bottom flask was charged with 2 mL of ethyl acetate and 100 μL of benzylamine (0.933 mmol, 1 equiv) at room temperature. The above mixture was stirred for 2 to 3 min. To this 320 mg of *m*-CPBA (0.187 mmol, 2 equiv) was added under constant stirring. The reaction mass was further stirred at room temperature, and the progress of reaction was monitored by TLC. After completion, the reaction was quenched by adding 3 mL of saturated sodium bicarbonate solution. The product was extracted by adding an extra 5 mL of ethyl acetate and stirred for 15 min. The aqueous layer was further extracted in ethyl acetate (3 × 5 mL). All organic layers were combined and washed with water until neutral pH, dried over anhydrous sodium sulfate, and concentrated to give crude product which was further purified by column chromatography using a hexane/ethyl acetate system.

Spectral Data for the Representative Compounds. *1. (E)-Benzaldehyde Oxime (**4a**).*[50,51] White solid; yield: 0.105 g, 93%; mp: 32−33 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.78 (s, 1H), 8.19 (s, 1H), 7.61−7.59 (m, 2H), 7.42−7.43 (m, 3H); ESI-MS *m*/*z* 121 $[M]^+$.

*2. (E)-2-Methoxybenzaldehyde Oxime (**4b**).*[52,53] White solid; yield: 0.101 g, 92%; mp: 88−90 °C; ^{1}H NMR (400 MHz, DMSO): δ 11.19 (s, 1H), 8.29 (s, 1H), 7.65 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.41−7.31 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 3.82 (s, 3H); ESI-MS *m*/*z* 151 $[M]^+$.

*3. (E)-3-Methoxybenzaldehyde Oxime (**4c**).*[52,54] White solid; yield: 0.104 g, 94%; mp: 39−40 °C; ^{1}H NMR (400 MHz, DMSO): δ 11.16 (s, 1H), 8.10 (s, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 7.5 Hz, 1H), 3.73 (s, 3H); ESI-MS *m*/*z* 151 $[M]^+$.

*4. (E)-4-Methoxybenzaldehyde Oxime (**4d**).*[50,55] White solid; yield: 0.10 g, 92%; mp: 63−64 °C; ^{1}H NMR (400 MHz, DMSO): δ 10.93 (s, 1H), 8.05 (s, 1H), 7.50 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 3H); ESI-MS *m*/*z* 151 $[M]^+$.

*5. (E)-4-(tert-Butyl)Benzaldehyde Oxime (**4e**).*[56] White solid; yield: 0.1 g, 92%; mp 105−106 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.72 (s, broad, 1H), 7.55−7.49 (m, 2H), 7.42 (dd, *J* = 8.3, 1.5 Hz, 2H), 1.34 (d, *J* = 1.7 Hz, 9H); ESI-MS *m*/*z* 177 $[M]^+$.

*6. (E)-3,4-Dimethoxybenzaldehyde Oxime (**4f**).*[57,58] White solid; yield: 0.102 g, 94%; mp 91−92 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.45 (s, 1H), 7.23 (s, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.2 Hz, 1H), 3.91 (s, 6H); ESI-MS *m*/*z* 181 $[M]^+$.

*7. (E)-4-Hydroxybenzaldehyde Oxime (**4g**).*[50,59] White solid; yield: 0.102 g, 92%; mp: 93−95 °C; ^{1}H NMR (500 MHz, DMSO): δ 10.824 (s, 1), 9.737 (s, 1H), 7.986 (s, 1H), 7.396−7.379 (d, *J* = 8.55, 2H), 6.765−6.748 (d, *J* = 8.55, 2H); ESI-MS *m*/*z* 137 $[M]^+$.

*8. (E)-2-Nitrobenzaldehyde Oxime (**4h**).*[60] White solid; yield: 0.099 g, 91%; mp: 99−100 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.73 (s, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.59−7.54 (m, 1H); ESI-MS *m*/*z* 166 $[M]^+$.

*9. (E)-3-Nitrobenzaldehyde Oxime (**4i**).*[50,61] White solid; yield: 0.097 g, 89%; mp: 120−122 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.451−8.444 (t, *J* = 2, 1H), 8.256−8.233 (dd, *J* = 8.5, 2.5, 1H), 8.215 (s, 1H), 7.926−7.913 (dd, *J* = 8.0, 1.5, 1H), 7.736 (s, 1H), 7.603−7.572 (t, *J* = 8, 7.5, 1H); ESI-MS *m*/*z* 166 $[M]^+$.

*10. (E)-4-Nitrobenzaldehyde Oxime (**4j**).*[50,62] Light yellow solid; yield: 0.10 g, 92%; mp: 126−128 °C; ^{1}H NMR (500 MHz, DMSO): δ 11.84 (s, 1H), 8.31 (s, 1H), 8.28−8.23 (m, 2H), 7.88−7.83 (m, 2H); ESI-MS *m*/*z* 166 $[M]^+$.

*11. (E)-4-Fluorobenzaldehyde Oxime (**4k**).*[50,63] White solid; yield: 0.098 g, 88%; mp: 87−88 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.127 (s, 1H), 7.856 (s, 1H), 7.589−7.560 (dd, *J* = 5.4, 5.5, 2H), 7.106−7.072 (t, *J* = 8.7, 8.65, 2H); ESI-MS *m*/*z* 139 $[M]^+$.

*12. (E)-4-Chlorobenzaldehyde Oxime (**4l**).*[50,54] White solid; yield: 0.10 g, 91%; mp: 108−110 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (s, 1H), 8.03 (s, 1H), 7.534−7.525 (d, *J* = 8.4, 2H), 7.385−7.359 (d, *J* = 8.55, 2H); ESI-MS *m*/*z* 155 $[M]^+$.

*13. (E)-Acetophenone Oxime (**4m**).*[64,65] White solid; yield: 0.103 g, 92%; mp: 58 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.984 (s, 1H), 7.650−7.630 (q, 2H); 7.408−7.393 (q, 3H), 2.319 (s, 3H); ESI-MS *m*/*z* 135 $[M]^+$.

*14. (E)-1-Naphthaldehyde Oxime (**4n**).*[50,66] White solid; yield: 0.096 g, 88%; mp: 94−96 °C; ^{1}H NMR (500 MHz, DMSO): δ 11.51 (s, 1H), 8.80 (s, 1H), 8.68 (d, *J* = 8.45 Hz, 1H), 7.95 (t, *J* = 7.5, 7.65 Hz, 2H), 7.81 (d, *J* = 6.6 Hz, 1H), 7.63−7.49 (m, 3H); ESI-MS *m*/*z* 171 $[M]^+$.

*15. (E)-Benzo[d][1,3]dioxole-5-carbaldehyde Oxime (**4o**).*[67] White solid; yield: 0.097 g, 89%; mp: 104−105 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.27 (d, *J* = 1.4 Hz, 1H), 7.17 (d, *J* = 1.3 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.00 (d, *J* = 1.4 Hz, 2H) ; ESI-MS *m*/*z* 165 $[M]^+$.

*16. Cyclohexanone Oxime (**4p**).*[42,68] White solid; yield: 0.103 g, 90%; mp: 106−108 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.546 (s, 1H), 2.522−2.497 (t, 2H), 2.228−2.203 (t, *J* = 6.0, 2H), 1.699−1.584 (m, *J* = 6.05, 6H); ESI-MS *m*/*z* 113 $[M]^+$.

*17. Cyclopentanone Oxime (**4q**).*[42,68] White solid; yield: 0.104 g, 89%; mp: 56−58 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, broad, 1H), 2.46 (t, *J* = 7.0 Hz, 2H), 2.37 (t, *J* = 6.9 Hz, 2H), 1.77 (dq, *J* = 11.3, 6.4 Hz, 4H); ESI-MS *m*/*z* 99 $[M]^+$.

*18. 1-Butyraldehyde Oxime (**4s**).*[69] Pale yellow liquid; yield: 0.093 g, 78%; bp:149−151 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.27 (t, *J* = 7.2 Hz, 1H), 1.92−1.81 (q, 2H), 1.47−1.35 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ESI-MS *m*/*z* 87 $[M]^+$.

*19. 2-Butyraldehyde Oxime (**4t**).*[68] Yellow liquid; yield: 0.094 g, 79%; bp: 150−152 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (s, 1H), 2.41−2.33 (m, 2H), 1.97 (s, 3H), 1.11−1.08 (m, 3H); ESI-MS *m*/*z* 87 $[M]^+$.

*20. 1-Octanal Oxime (**4u**).*[70] White solid; yield: 0.09 g, 81%; mp: 58−60 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.26 (t, *J* = 7.3 Hz, 1H), 1.87 (dd, *J* = 14.4, 6.8 Hz, 2H), 1.42−1.22 (m, 10H), 0.88 (t, *J* = 6.2 Hz, 3H) ; ESI-MS *m*/*z* 142 $[M\text{-}H]^+$.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01740.

Spectroscopic (Mass and ^{1}H NMR spectra) data of selected products in Tables 2 and 3 (PDF)

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Notes

The authors declare no competing financial interest.

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