An Efficient Method for the Preparation of Nitriles *via* the Dehydration of Aldoximes with Phthalic Anhydride

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A new and highly efficient method for the conversion of aldoximes to nitriles was established. By fusing with phthalic anhydride, aldoximes were efficiently and smoothly converted into nitriles, in high yields (over 85%) and in a short time (within 5 minutes). The mixture of phthalic anhydride, a cyclic anhydride, and aldoximes in fusing state set up an ideal transition state for a selective [3.3]-sigmatropic rearrangement of the acylated aldoximes to nitriles.

Keywords: Aldoximes; Phthalic anhydride; Nitriles.

INTRODUCTION

Nitriles, important reagents, have been widely used by chemists in many aspects for a long time. They can be reduced to furnish primary amines,[1] can be hydrolyzed to give either amides[2] or carboxylic acids,[3] can be attacked by organometallics to afford various ketones,[4] can be reacted with tertiary alcohols in acidic condition to undergo the Ritter reaction to afford *N*-alkyl amide,[5] etc. Although numerous dehydration methods for conversion of aldoximes to nitriles have been developed, it is still an interesting topic to current organic chemists. Among the strategies, much attention has been paid to the activation of the hydroxyl group in aldoxime as leaving group for the subsequent 1,2-elimination by base to give nitrile.[6] For the past development of methodologies including the use of trifluoromethane sulfonic anhydride,[7] trifluoroacetic anhydride,[8] phosphonium anhydride,[9] trichloromethyl carbonochloridate,[10] bis(trichloromethyl)carbonate,[11] and 2,2′-oxalyl-di(*O*-sulfobenzimide),[12] it was proposed to undergo decarboxylation by a 1,4-concerted elimination. Furthermore these methodologies have drawbacks of low yield, long reaction time, and harsh reaction conditions. In addition the reagents used in these preparations are corrosive, toxic, expensive or commercially unavailable, which are disadvantages. To the best of our knowledge, all previous reports have paid much attention to the use of acyclic anhydride as dehydration agent of aldoximes. Acetic anhydride was commonly used for this purpose,[13] but it may suffer from some limitations which were described in our previous study.[14] In order to facilitate the reaction, a thermal fusing condition, which has never been approached in the dehydration chemistry of aldoximes, was investigated in our laboratory (Scheme I). This concomitant acylation and dehydration of aldoximes, prepared from corresponding aldehydes and hydroxylamine, with fusing phthalic anhydride is expected to be a useful method for the preparation of nitriles.

RESULTS AND DISCUSSION

Aldoximes are prepared by a general method (using water as solvent), but with a little modification. Increasing the alcohol/water ratio to 1/5 to increase the solubility of aldehyde gave aldoximes (**2a-r**) in good yields. Without further separation, the mixture of *syn*- or (and) *anti*-aldoxime was directly used for dehydration studies. In order to overcome the drawback of low yield, or long reaction time, thus, a dehydration of aldoximes with phthalic anhydride in fusing state was studied. It turned out to be an effective and practical method for the preparation of nitriles in a very short reaction time, 5 minutes, and in yields of 85 to 90%. The rationale for using cyclic anhydride was the ability of forming the acylated aldoxime intermediate, which made it undergo efficiently a feasible [3.3]-sigmatropic rearrangement as the reaction

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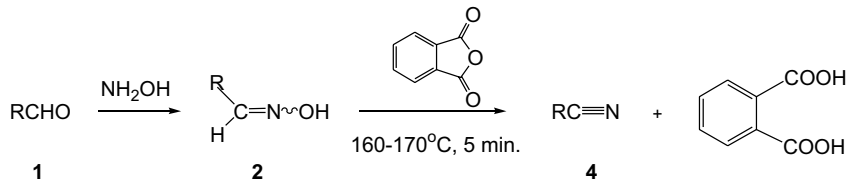
Scheme I



a. R=C_6H_5
b. R=3-BnOC_6H_4
c. R=4-BnOC_6H_4
d. R=4-AllylOC_6H_4
e. R=4-HO-3-MeOC_6H_3
f. R=3,4-di$MeOC_6H_3$
g. R=3-BnO-4-MeOC_6H_3
h. R=4-EtO-3-MeOC_6H_3
i. R=3,4-di$EtOC_6H_3$
j. R=2-$NO_2C_6H_4$
k. R=3-$NO_2C_6H_4$
l. R=4-$NO_2C_6H_4$
m. R=4-$CH_3C_6H_4$
n. R=4-AllylO-3-MeOC_6H_3
o. R=3,5-diMeO-4-HOC_6H_2
p. R= 
q. R= 
r. R= 

pathway *via* this proposed six-membered transition state (**3a-r**). Consequently it gave the nitrile (**4a-r**) in good yields, and without the requirement of using an external base (Scheme II). The results of fusing the mixtures of phthalic anhydride and aldoxime to give nitrile at 160-170 °C are summarized in Table 1.

In conclusion an interesting aspect of the conversion of aldoxime to nitrile using phthalic anhydride as a sole reagent at fusing condition has been illustrated. In the case of phenolic aldehydes with labile groups such as methoxymethyl, methoxyethylmethoxy were limited to our fusing process. But allyloxybenzaldoxime (**2d**) can be smoothly converted to allyoxybenzonitrile (**4d**), and without causing the Claisen rearrangement in such a short reaction time, 5 min. Furthermore heterocyclic aldoximes such as pyrrole (**2p**), thiophene (**2q**) and pyridine (**2r**), which are considered to be fragile and oxidizable, can be converted into corresponding nitriles, **4p**, **4q**, and **4r** by our fusing procedure. On the other hand this solvent free reaction with innocuous reagent is significant in this era of increased environmental concern. Furthermore our method has the following advantages: (1) it is applicable to aromatic, and heterocyclic aldoximes, (2) phthalic acid formed can be readily removed as it is nearly insoluble in cold chloroform and ethyl acetate or by washing with cold ammonium water, allowing easy workup, or by passing it through a short APS silica-gel (Daiso Co.) column, (3) a short reaction time was taken, within 5 minutes, but only a little/or no trace of aldoxime could be detected by either GC or TLC, (4) only a stochiometric amount of phthalic anhydride was consumed, (5) in fusing reaction, no solvent was required, (6) no limitation for *E*- and *Z*-aldoximes, which can be worked without any significant difference, and (7) furthermore, phthalic anhydride and aldoximes are thermally almost stable, and phthalic anhydride is nonhygroscopic, readily available, inexpensive and innocuous.

EXPERIMENTAL

Melting points (Yanaco micro melting-point apparatus) are uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a Varian Gemini-200 or Varian Unity plus 400 Spectrometer. Chemical shifts are measured in parts per million with respect to TMS. Elemental analyses were recorded on a Heraeus CHN-O Rapid analyzer. Mass spectra were recorded on a Chem/hp/middle instrument. Silica gel (70-230 mesh) for column chromatography and precoated silica gel plates (60 F-254) for TLC were purchased from E. Merck Co.

Scheme II

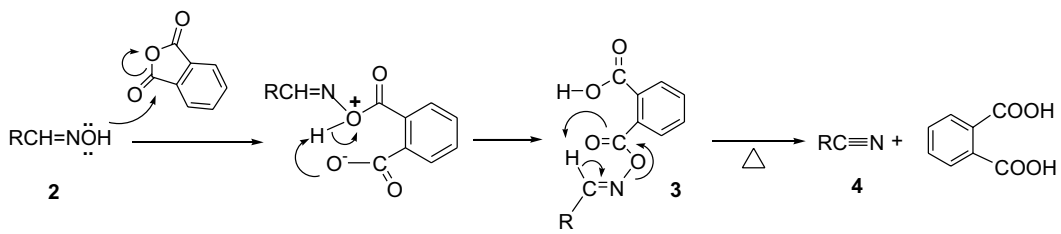
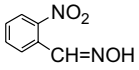
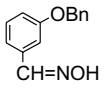
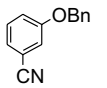
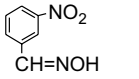
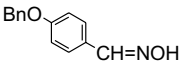
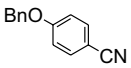
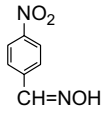
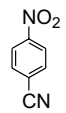
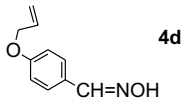
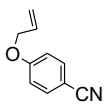
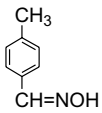
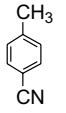
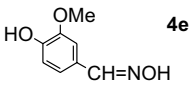
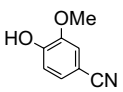
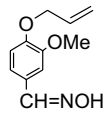
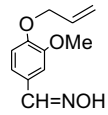
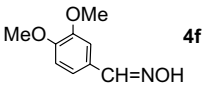
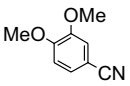
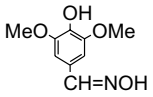
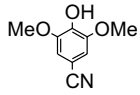
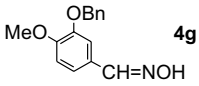
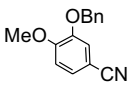
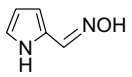
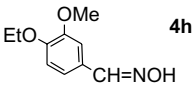
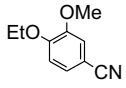
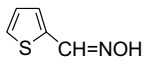
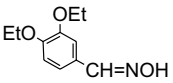
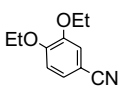
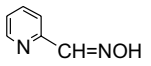


Table 1. The Results for the Fusion of Aldoximes[a] (5 mmol) with Phthalic Anhydride (5 mmol) at 160-170 °C within 5 Minutes

Entry	Substrate		Product	Yield (%)	Entry	Substrate		Product	Yield (%)
2a	$C_6H_5CH=NOH$	**4a**	C_6H_5CN	90	**2j**		**4j**		90
2b		**4b**		88	**2k**		**4k**		87
2c		**4c**		90	**2l**		**4l**		91
2d		**4d**		88	**2m**		**4m**		85
2e		**4e**		85	**2n**		**4n**		87
2f		**4f**		87	**2o**		**4o**		90
2g		**4g**		95	**2p**		**4p**		86
2h		**4h**		93	**2q**		**4q**		85
2i		**4i**		86	**2r**		**4r**		85

[a] The procedure for the preparation of aldoximes is described in the Experimental section.

APS silica-gel for column chromatography was supplied from Daiso Co. UV light (254 nm) was used to detect spots on TLC plates after development.

General procedure for the preparation of Aldoximes (2a-r)

A solution of water (100 mL), ethanol (20 mL) and NaOH (2 g, 50 mmol) was cooled with an ice-bath. To this cold solution was added hydroxylamine hydrochloride (3.5 g, 50 mmol), and subsequently added dropwise with a corresponding aldehyde (45 mmole) in ethanol (5 mL). The mixture was stirred at 0 °C for 4 h, and then continually stirred at room temperature for another h. Finally the reaction mixture was concentrated *in vacuo* to remove ethanol, and then immersed in an ice-bath to precipitate the corresponding aldoxime, which could be recrystallized from a mixing solvent, ethyl acetate and *n*-hexane to give aldoximes (**2a-r**). Without further purification, the given aldoximes were directly used for the following dehydration studies, respectively.

Benzaldehyde oxime (2a)[15]

Pure **2a** (5.17 g, 95%) was obtained as colorless crystals, mp 35-36 °C (lit.[15] 34-36 °C), R_f 0.50, and 0.40 (EA/*n*-

hexane = 1/3), ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.42 (m, 3H, ArH), 7.61 (m, 2H, ArH), 8.23 (s, 1H, ArCH=N-OH), 8.40 (br s, 1H, ArCH=N-OH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 127.00, 128.72, 130.03, 131.70, 150.24; EI-MS (70 eV) *m/z* 121 (M^+, 100), 94 (35), 78 (59), 77 (62), 66 (30), 51 (51).

_m_-Benzyloxybenzaldehyde oxime (2b)[16]

Pure **2b** (9.82 g, 96%) was obtained as colorless crystals, mp 53-54 °C, R_f 0.50 (EA/*n*-hexane = 1/3); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.10 (s, 2H, ArOCH_2Ph), 6.99 (m, 2H, ArH), 7.41 (m, 5H, ArOCH_2Ph), 7.53 (m, 2H, ArH), 7.96 (br s, 1H, OH), 8.10 (s, 1H, ArCH=N-OH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 70.08, 112.45, 117.16, 120.29, 127.43, 127.94, 128.50, 129.75, 133.28, 136.68, 150.23, 159.02; EI-MS (70 eV) *m/z* 227 (M^+, 4.7), 91 (100), 65 (15).

_p_-Benzyloxybenzaldehyde oxime (2c)[17]

Pure **2c** (9.62 g, 94%) was obtained as colorless crystals, mp 110-111 °C [lit.[17] 110-111.5 °C], R_f 0.50, and 0.36 (EA/*n*-hexane = 1/3); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.10 (s, 2H, ArOCH_2Ph), 6.99 (d, *J* = 8.8 Hz, 2H, ArH), 7.52 (d, *J* = 8.8 Hz, 2H, ArH), 7.40 (m, 5H, ArOCH_2Ph), 7.90 (br s, 1H, OH), 8.09 (s, 1H, ArCH=N-OH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 70.06, 115.12, 124.86, 127.42, 128.68, 128.48, 128.61, 136.50, 149.87, 160.19; EI-MS (70 eV) *m/z* 227 (M^+, 6), 221 (9), 92 (13), 91 (100), 65 (20).

_p_-Allyloxybenzaldehyde oxime (2d)

Pure **2d** (7.57 g, 95%) was obtained as colorless crystals, mp 88-89 °C, R_f 0.54, and 0.36 (EA/*n*-hexane = 1/3); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.57 (dt, *J* = 5.2 Hz, 1.4 Hz, 2H, ArOCH_2CH=CH_2), 5.31 (dd, $J_{cis\text{-}gem}$ = 10.6 Hz, 1.4 Hz, 1H, ArOCH$_2$CH=CH_2), 5.42 (dd, $J_{trans\text{-}gem}$ = 17.2 Hz, 1.4 Hz, 1H, ArOCH$_2$CH=CH_2), 6.02 (ddd, 17.2 Hz, 10.6 Hz, 5.2 Hz, 1H, ArOCH$_2$CH=CH$_2$), 6.92 (d, *J* = 8.8 Hz, 2H, ArH), 7.50 (d, *J* = 8.8 Hz, 2H, ArH), 7.80 (br s, 1H, OH), 8.09 (s, 1H, ArCH=N-OH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 29.71, 68.82, 114.97, 117.90, 128.42, 132.81, 149.81, 159.99; EI-MS (70 eV) *m/z* 177 (M^+, 100), 160 (12), 136 (21).

4-Hydroxy-3-methoxybenzaldehyde oxime (2e)[18]

Pure **2e** (6.69 g, 89%) was obtained as colorless crystals, mp 123-124 °C [lit.[18] 118.2 °C], R_f 0.15 (EA/*n*-hexane = 1/3); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.94 (s, 3H, OCH_3), 5.95 (br s, 1H, ArOH), 6.93 (d, *J* = 8.0 Hz, 1H, ArH), 7.02 (d, *J* = 8.0 Hz, 1H, ArH), 7.23 (s, 1H, ArH), 7.85 (br s, 1H, ArCH=N-OH), 8.09 (s, 1H, ArCH=N-OH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 55.97, 107.60, 114.39, 122.31, 124.36, 128.30, 147.58, 150.28; EI-MS (70 eV) *m/z* 167 (M^+, 100), 149 (27), 134 (33), 124 (58), 106 (33).

3,4-Dimethoxybenzaldehyde oxime (2f)[19]

Pure **2f** (7.49 g, 92%) was obtained as colorless crystals, mp 93-94 °C [lit.[19] 94-95 °C], R_f 0.23 and 0.18 (EA/*n*-hexane = 1/3), ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.91, 3.92 (each s, 3H, OCH_3), 6.85 (d, *J* = 8.4 Hz, 1H, ArH), 7.03 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H, ArH), 7.22 (d, *J* = 2.0 Hz, 1H, ArH), 7.99 (br s, 1H, ArCH=N-OH), 8.08 (s, 1H, ArCH=N-OH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 55.86, 55.91, 107.99, 110.76, 121.62, 124.84, 149.28, 150.13, 150.77; EI-MS (70 eV) *m/z* 181 (M^+, 100), 163 (67), 148 (23), 138 (37), 120 (27), 92 (24), 79 (26), 77 (34), 65 (28).

3-Benzyloxy-4-methoxybenzaldehyde oxime (2g)[20]

Pure **2g** (10.42 g, 90%) was obtained as colorless crystals, mp 102-103 °C [lit.[20] 96-97 °C], R_f 0.30 and 0.20 (EA/*n*-hexane = 1/3), ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.93 (s, 3H, OCH_3), 5.21 (s, 2H, OCH_2C$_6$H$_5$), 6.88 (d, *J* = 8.2 Hz, 1H, ArH), 6.99 (dd, *J* = 8.2 Hz, 2.0 Hz, 1H, ArH), 7.26 (d, *J* = 2.0 Hz, 1H, ArH), 7.41 (m, 5H, OCH$_2$C$_6$H$_5$), 8.09 (s, 1H, ArCH=N-OH), 8.40 (br s, 1H, OH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 55.94, 70.82, 97.08, 108.53, 113.25, 121.40, 125.21, 127.16, 127.91, 128.54, 136.60, 149.81, 150.04; EI-MS (70 eV) *m/z* 257 (M^+, 5), 105 (4), 92 (7), 91 (100), 77 (6), 65 (12).

4-Ethoxy-3-methoxybenzaldehyde oxime (2h)[21]

Pure **2h** (7.91 g, 90%) was obtained as colorless crystals, mp 102-103 °C [lit.[21] 100 °C], R_f 0.30 and 0.20 (EA/*n*-hexane = 1/3), ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.47 (t, *J* = 7.0 Hz, 3H, OCH$_2$CH_3), 3.89 (s, 3H, OCH_3), 4.12 (q, *J* = 7.0 Hz, 2H, OCH_2CH$_3$), 6.84 (d, *J* = 8.6 Hz, 1H, ArH), 7.01 (dd, *J* = 8.6 Hz, 2.0 Hz, 1H, ArH), 7.21 (d, *J* = 2.0 Hz, 1H, ArH), 8.08 (s, 1H, ArCH=N-OH), 8.44 (br s, 1H, OH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 14.66, 55.88, 64.29, 108.26, 111.89, 117.30, 121.56, 124.63, 149.43, 150.10; EI-MS (70 eV) *m/z* 195 (M^+, 100), 167 (56), 125 (22), 124 (75), 121 (15), 106 (15), 79 (23), 65 (17), 63 (16), 51 (27).

3,4-Diethoxybenzaldehyde oxime (2i)[22]

Pure **2i** (8.66 g, 92%) was obtained as colorless crystals, mp 99-100 °C [lit.[22] 98 °C], R_f 0.40 (EA/*n*-hexane = 1/3), ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.47 (m, 6H, 2 × OCH$_2$CH_3), 4.13 (m, 4H, 2 × OCH_2CH$_3$), 6.84 (d, *J* = 8.4 Hz, 1H, ArH), 7.01 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H, ArH), 7.21 (d, *J* = 2.0 Hz,

1H, ArH), 8.07 (s, 1H, ArCH=N-OH), 8.77 (br s, 1H, OH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 14.66, 64.43, 110.01, 112.47, 121.44, 124.69, 148.79, 150.07, 150.39; EI-MS (70 eV) *m/z* 209 (M^+, 100), 181 (20), 152 (55), 135 (42), 110 (50), 79 (28), 63 (16), 52 (30), 51 (31).

o-Nitrobenzaldehyde oxime (2j)[23]

Pure **2j** (6.36 g, 85%) was obtained as colorless crystals, mp 100-101 °C [lit.[23] 102-103 °C], R_f 0.40 (EA/*n*-hexane = 1/3), ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 8.0 Hz, 1.4 Hz, 1H, ArH), 7.54 (dd, *J* = 8.0 Hz, 1.4 Hz, 1H, ArH), 7.91 (t, *J* = 8.0 Hz, 1H, ArH), 7.92 (t, *J* = 8.0 Hz, 1H, ArH), 8.56 (s, 1H, ArCH=N-OH), 10.52 (br s, 1H, OH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 124.40, 127.53, 128.49, 129.68, 133.10, 145.40, 147.54; EI-MS (70 eV) *m/z* 166 (M^+, 12), 135 (100), 102 (27), 92 (20), 91 (40), 90 (21), 79 (30), 76 (50), 65 (59), 50 (50), 51 (31).

m-Nitrobenzaldehyde oxime (2k)[24]

Pure **2k** (6.43 g, 86%) was obtained as colorless crystals, mp 123-124 °C [lit.[24] 121-122 °C], R_f 0.50 (EA/*n*-hexane = 1/3), ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.50 (t, *J* = 8.0 Hz, 1H, ArH), 7.85 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H, ArH), 8.12 (s, 1H, ArCH=N-OH), 8.13 (t, *J* = 8.0 Hz, 1H, ArH), 8.39 (d, *J* = 2.0 Hz, 1H, ArH), 10.69 (br s, 1H, OH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 121.12, 123.56, 129.47, 132.29, 134.73, 146.73, 148.33; EI-MS (70 eV) *m/z* 166 (M^+, 100), 149 (67), 119 (69), 102 (65), 76 (69), 75 (68), 65 (71), 50 (37).

p-Nitrobenzaldehyde oxime (2l)[25]

Pure **2l** (6.36 g, 85%) was obtained as colorless crystals, mp 128-129 °C [lit.[25] 130-134 °C], R_f 0.5 (EA/*n*-hexane = 1/3), ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.39 (t, *J* = 8.8 Hz, 1H, ArH), 7.85 (d, *J* = 8.8 Hz, 1H, ArH), 8.13 (d, *J* = 8.8 Hz, 2H, ArH), 8.41 (s, 1H, ArCH=N-OH), 10.65 (br s, 1H, OH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 124.0, 127.59, 136.29, 138.73, 148.24; EI-MS (70 eV) *m/z* 166 (M^+, 100), 136 (19), 103 (20), 102 (27), 76 (37), 75 (39), 65 (46), 50 (31).

p-Methylbenzaldehyde oxime (2m)[25]

Pure **2m** (5.5 g, 91%) was obtained as colorless crystals, mp 74-75 °C [lit.[25], 70-75 °C] R_f 0.5 (EA/*n*-hexane = 1/3); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H, CH_3), 7.17, 7.46 (each d, *J* = 8.2 Hz, 2H, ArH), 8.14 (s, 1H, CH=NOH), 9.42 (br s, 1H, CH=NOH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.35 (CH_3), 126.98, 129.04, 129.12, 129.45, 140.25 (CH=NOH); EI-MS (70 eV) *m/z* 135 (31), 119 (45), 117 (100), 116 (64), 92 (25), 91 (40), 90 (46), 89 (29), 65 (14), 63 (86).

4-Allyloxy-3-methoxybenzaldehyde oxime (2n)[14]

Pure **2m** (8.3 g, 89%) was obtained as colorless crystals, mp 68-69 °C, R_f 0.34 (EA/*n*-hexane = 1/3), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3H, OCH_3), 4.65 (dd, *J* = 5.2 Hz, 1.4 Hz, 2H, $OCH_2CH=CH_2$), 5.32 (m, 1H, $OCH_2CH=CH_2$), 5.42 (m, 1H, $OCH_2CH=CH_2$), 6.08 (m, 1H, $OCH_2CH=CH_2$), 6.87 (d, *J* = 8.0 Hz, 1H, ArH), 7.02 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H, ArH), 7.24 (d, *J* = 2.0 Hz, 1H, ArH), 8.09 (s, 1H, CH=NOH), 10.52 (br s, 1H, OH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 55.88, 69.69, 108.38, 112.60, 118.25, 121.40, 125.01, 132.76, 149.57, 149.67, 150.04; EI-MS (70 eV) *m/z* 207 (56), 191 (32), 166 (100), 150 (48), 148 (28), 135 (14), 120 (28), 95 (38), 79 (35), 65 (31).

4-Hydroxy-3,5-dimethoxybenzaldehyde oxime (2o)[26]

Pure **2o** (8.28 g, 88%) was obtained as colorless crystals, mp 130-131 °C [lit.[26] 128-129 °C], R_f 0.08 (EA/*n*-hexane = 1/3); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 6H, 2 × OCH_3), 3.93 (s, 1H, OH), 6.83 (s, 2H, ArH), 8.04 (s, 1H, CH=NOH), 8.05 (s, 1H, CH=NOH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 56.44, 104.16, 123.42, 136.85, 147.32, 150.42; EI-MS (70 eV) *m/z* 197 (100), 179 (19), 155 (16), 154 (55), 67 (15), 65 (14).

Pyrrole-2-carboxaldehyde oxime (2p)[27]

Pure **2p** (4.22 g, 85%) was obtained as colorless crystals, mp 135-136 °C [lit.[27] 165-166 °C], R_f 0.25 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 6.27 (m, 1H), 6.52 (m, 1H), 6.98 (m, 1H), 7.21 (s, 1H), 7.30 (s, 1H), 10.14 (br s, 1H); ^{13}C-NMR (DMSO-d_6 + $CDCl_3$, 100 MHz) δ 108.84, 113.71, 120.85, 125.23, 138.05; EI-MS (70 eV) *m/z* 110 (100), 93 (26), 67 (73), 66 (60), 65 (29), 52 (31).

Thiophene-2-carboxaldehyde oxime (2q)[28]

Pure **2q** (4.98 g, 87%) was obtained as colorless crystals, mp 125-126 °C [lit.[28] 130-133 °C], R_f 0.45 (EA/*n*-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.05 (t, *J* = 4.5 Hz, 1H), 7.34 (dd, *J* = 5.0 Hz, 4.0 Hz, 1H), 7.49 (dd, *J* = 5.0 Hz, 4.0 Hz, 1H), 7.70 (s, 1H), 8.21 (br s, 1H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 126.23, 130.94, 131.62, 131.86, 141.18; EI-MS (70 eV) *m/z* 127 (M^+, 100), 109 (30), 100 (41), 84 (94), 58 (40).

Pyridine-2-carboxaldehyde oxime (2r)[29]

Pure **2r** (4.73 g, 86%) was obtained as colorless crystals, mp 111-112 °C [lit.[29] 113.5 °C], R_f 0.18 (EA/n-hexane = 1/3); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.73 (td, *J* = 7.7 Hz, 1.8 Hz, 1H), 7.72 (td, *J* = 7.7 Hz, 1.8 Hz, 1H), 7.87 (d, *J* = 8.0 Hz,

1H), 7.38 (s, 1H), 8.64 (d, J = 5.2 Hz, 1H), 10.83 (br s, 1H, OH); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 120.92, 123.93, 136.90, 149.08, 149.84, 151.83; EI-MS (70 eV) *m/z* 122 (M^+, 100), 121 (58), 92 (23), 79 (45), 78 (23), 77 (22), 65 (53), 52 (22), 51 (36).

General procedure for the preparation of nitriles (4a-s)

Aldoxime (10 mmol) and phthalic anhydride (1.5 g, 10.1 mmol) were mixed well in a mortar, and transferred into a sealed tube (9 × 1.8 cm), which was immersed into a pre-heated oil bath (160-170 °C). After fusing for 5 minutes, the reaction mixture was cooled to room temperature, and percolated with CH_2Cl_2. The combined CH_2Cl_2 solution was washed with cold 5% aq. ammonia to remove phthalic acid and phthalic anhydride. Then the solution was washed with water and brine, and dried with $MgSO_4$. Finally the solution was filtered, and the filtrate was concentrated under reduced pressure to provide the product, which showed a single spot in TLC (*n*-hexane/EtOAc = 3/1).

Benzonitrile (4a)[11]

Pure **4a** was obtained as colorless liquid (0.93 g, 90%); bp 95-97 °C (25 mmHg) [lit.[11] 35-40 °C (0.05 torr)]; R_f = 0.77 (EtOAc/*n*-hexane = 1/3); IR ν_{max} (neat) cm^{-1}: 2228.0 cm^{-1} (CN); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.42-7.61 (m, 5H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 111.57, 118.12, 128.49, 131.34, 132.15; MS (70 eV), *m/z* (relative intensity), 103 (M^+, 100), 76 (39), 75 (8), 50 (11); HRMS calcd for C_7H_5N: 103.0422. Found: 103.0424.

3-Benzyloxybenzonitrile (4b)[12]

Pure **4b** was obtained as colorless crystals (1.84 g, 88%); mp 38-39 °C (EtOAc + *n*-hexane) [lit.[12] 38-40 °C]; R_f = 0.63 (EtOAc/*n*-hexane = 1/3); IR ν_{max} (neat) cm^{-1}: 2227.4 cm^{-1} (CN); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 5.08 (s, 2H, $C\underline{H}_2C_6H_5$), 7.12-7.26 (m, 4H), 7.35-7.41 (m, 5H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 70.36, 113.26, 117.85, 118.65, 120.13, 124.76, 127.43, 128.35, 128.73, 130.36, 135.83, 158.78; MS (70 eV), *m/z* (relative intensity) 209 (M^+, 14), 92 (7), 91 (100), 65 (14), 51 (2); HRMS calcd for $C_{14}H_{11}NO$: 209.0841. Found: 209.0839.

4-Benzyloxybenzonitrile (4c)[13]

Pure **4c** was obtained as colorless crystals (1.88 g, 90%); mp 87-88 °C (EtOAc + *n*-hexane) [lit.[13] 62 °C]; R_f = 0.65 (EtOAc/*n*-hexane = 1/3); IR ν_{max} (neat) cm^{-1}: 2221.2 cm^{-1} (CN); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 5.12 (s, 2H, $C\underline{H}_2C_6H_5$), 7.02, 7.59 (each d, J = 8.8 Hz, 2H), 7.34-7.43 (m, 5H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 70.19, 104.14, 115.51, 119.07, 127.39, 128.33, 128.68, 133.91, 135.63, 161.89; MS (70 eV), *m/z* (relative intensity) 209 (M^+, 4), 92 (9), 91 (100), 89 (2), 65 (12); HRMS calcd for $C_{14}H_{11}NO$: 209.0841. Found: 209.0841.

4-Allyloxybenzonitrile (4d)[14]

Pure **4d** was obtained as colorless crystals (1.20 g, 88%); mp 43-44 °C (EtOAc + *n*-hexane) [lit.[14] 44-45 °C]; R_f = 0.66 (EtOAc/*n*-hexane = 1/3); IR ν_{max} (CH_2Cl_2) cm^{-1}: 2223.6 cm^{-1} (CN); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 4.43 (dt, J = 5.2 Hz, 1.4 Hz, 2H, $ArOC\underline{H}_2CH=CH_2$), 5.16 (dd, $J_{cis\text{-}gem}$ = 10.6 Hz, 1.4 Hz, 1H, $ArOCH_2CH=C\underline{H}_2$), 5.32 (dd, $J_{trans\text{-}gem}$ = 17.2 Hz, 1.4 Hz, 1H, $ArOCH_2CH=C\underline{H}_2$), 5.89 (ddd, 17.2 Hz, 10.6 Hz, 5.2 Hz, 1H, $ArOCH_2C\underline{H}=CH_2$), 6.95 (d, J = 8.2 Hz, 1H, Ar$\underline{H}$), 7.08 (d, J = 1.8 Hz, 1H, Ar$\underline{H}$), 7.22 (dd, J = 8.2 Hz, 1.8 Hz, 1H, Ar$\underline{H}$); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 56.18, 103.19, 113.73, 115.19, 119.20, 126.94, 146.61, 149.88 (CN); MS (70 eV), *m/z* (relative intensity), 159 (M^+, 100), 144 (15), 119 (23), 75 (14), 64 (25), 63 (21), 51 (14); HRMS calcd for $C_{10}H_9NO$: 159.0684. Found: 159.0687.

4-Hydroxy-3-methoxybenzonitrile (4e)[30]

Pure **4e** was obtained as colorless crystals (1.27 g, 85%); mp 86-87 °C (EtOAc + *n*-hexane) [lit.[30] 85-87 °C]; R_f = 0.24 (EtOAc/*n*-hexane = 1/3); IR ν_{max} (CH_2Cl_2) cm^{-1}: 2225.3 cm^{-1} (CN); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.92 (s, 3H, $OC\underline{H}_3$), 6.21 (br s, 1H, ArO$\underline{H}$), 6.95 (d, J = 8.2 Hz, 1H, Ar$\underline{H}$), 7.08 (d, J = 1.8 Hz, 1H, Ar$\underline{H}$), 7.22 (dd, J = 8.2 Hz, 1.8 Hz, 1H, Ar$\underline{H}$); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 56.18, 103.19, 113.73, 115.19, 119.20, 126.94, 146.61, 149.88 (CN); MS (70 eV), *m/z* (relative intensity), 149 (M^+, 100), 134 (89), 106 (82), 51 (49); HRMS calcd for $C_8H_7NO_2$: 149.0477. Found: 149.0477.

3,4-Dimethoxybenzonitrile (4f)[31]

Pure **4f** was obtained as colorless crystals (1.84 g, 87%); mp 65-66 °C (EtOAc + *n*-hexane) [lit.[31] 66-68 °C]; R_f = 0.37 (EtOAc/*n*-hexane = 1/3); IR ν_{max} (neat) cm^{-1}: 2226.2 cm^{-1} (CN); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.91 (s, 3H, $OC\underline{H}_3$), 3.94 (s, 3H, $OC\underline{H}_3$), 6.90 (d, J = 8.4 Hz, 1H, Ar$\underline{H}$-5), 7.08 (d, J = 2.0 Hz, 1H, Ar$\underline{H}$-2), 7.29 (dd, J = 8.4 Hz, 2.0 Hz, 1H, Ar$\underline{H}$-6); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 56.09, 56.14, 103.95, 111.26, 114.00, 119.19, 126.46, 149.24, 152.90; MS (70 eV), *m/z* (relative intensity): 164 (M^{+1}, 10.36), 163 (M^+, 100), 148 (41), 120 (14), 102 (8), 92 (23), 77 (20), 65 (21), 50 (8); HRMS calcd for $C_9H_9NO_2$: 163.0633. Found: 163.0635.

3-Benzyloxy-4-methoxybenzonitrile (4g)[32]

Pure **4g** was obtained as colorless crystals (1.84 g, 95%); mp 73-74 °C (EtOAc + *n*-hexane) [lit.[32] 75 °C]; R_f = 0.61 (EtOAc/*n*-hexane = 1/3); IR ν_{max} (neat) cm^{-1}: 2222.8 cm^{-1} (CN); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.93 (s, 3H, $OC\underline{H}_3$), 5.15 (s, 2H, $C\underline{H}_2C_6H_5$), 6.92 (d, *J* = 8.3 Hz, 1H, Ar<u>H</u>-5), 7.10 (d, *J* = 2.0 Hz, 1H, Ar<u>H</u>-2), 7.54 (m, 5H, $OCH_2C_6\underline{H}_5$), 8.17 (dd, *J* = 8.3 Hz, 2.0 Hz, 1H, Ar<u>H</u>-6); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 56.10, 71.23, 103.78, 111.64, 116.52, 118.52, 126.85, 127.33, 128.29, 128.74, 135.88, 148.26, 153.57; MS (70 eV), *m/z* (relative intensity): 239 (M^+, 15), 92 (9), 91 (100), 77 (2), 65 (13); HRMS calcd for $C_{15}H_{13}NO_2$: 239.0946. Found: 239.0945.

4-Ethoxy-3-methoxybenzonitrile (4h)[33]

Pure **4h** was obtained as colorless crystals (1.65 g, 93%); mp 103 °C [lit.[33] 102 °C]; R_f = 0.54 (EtOAc/*n*-hexane = 1/3); IR ν_{max} (neat) cm^{-1}: 2221.3 cm^{-1} (CN); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.50 (t, *J* = 6.8 Hz, 3H, $C\underline{H}_3CH_2O$), 3.89 (s, 3H, $OC\underline{H}_3$), 4.15 (q, *J* = 6.8 Hz, 2H, $CH_3C\underline{H}_2O$), 6.88 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 2.0 Hz, 1H), 7.26 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 14.51, 56.15, 64.59, 103.66, 112.17, 114.22, 119.29, 126.40, 149.36, 152.32; MS (70 eV), *m/z* (relative intensity): 177 (M^+, 64), 149 (100), 134 (68), 106 (20), 51 (9); HRMS: calcd for $C_{10}H_{11}NO_2$: 177.0790. Found: 177.0791.

3,4-Diethoxybenzonitrile (4i)[34]

Pure **4i** was obtained as colorless crystals (1.64 g, 86 %); mp 67-68 °C (EtOAc + *n*-hexane) [lit.[34] 68 °C]; R_f = 0.55 (EtOAc/*n*-hexane = 1/3); IR ν_{max} (neat) cm^{-1}: 2225.7 cm^{-1} (CN); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.43-1.52 (m, 6H, 2 × $CH_2C\underline{H}_3$), 4.04-4.19 (m, 4H, 2 × $C\underline{H}_2CH_3$), 6.88 (d, *J* = 8.0 Hz, 1H, Ar<u>H</u>), 7.08 (d, *J* = 2.0 Hz, 1H, Ar<u>H</u>), 7.24 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H, Ar<u>H</u>); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 14.54, 14.59, 64.64, 64.87, 103.62, 112.58, 115.81, 119.39, 126.34, 148.72, 152.70; MS (70 eV), *m/z* (relative intensity): 191 (M^+, 45), 163 (16), 136 (9), 135 (100), 134 (7), 106 (6), 51 (6); HRMS calcd for $C_{11}H_{13}NO_2$: 191.0946. Found: 191.0945.

2-Nitrobenzonitrile (4j)[35]

Pure **4j** was obtained as colorless crystals (1.33 g, 90%); mp 109-110 °C (EtOAc + *n*-hexane) [lit.[35] 111 °C], R_f = 0.28 (EtOAc/*n*-hexane = 1/3); IR ν_{max} (neat) cm^{-1}: 2231.6 cm^{-1} (CN); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 7.83-7.88 (m, 2H), 7.93-7.95 (m, 1H), 8.33-8.38 (m, 1H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 108.09, 114.90, 125.54, 133.67, 134.27, 135.58, 148.85; MS (70 eV), *m/z* (relative intensity): 148 (M^+, 99), 118 (18), 102 (100), 90 (52), 76 (45), 75 (78), 51 (29); HRMS calcd for $C_7H_4N_2O_2$: 148.0273. Found: 148.0273.

3-Nitrobenzonitrile (4k)[36]

Pure **4k** was obtained as colorless crystals (1.28 g, 87%); mp 117-118 °C (EtOAc + *n*-hexane) [lit.[36] 118 °C]; R_f = 0.50 (EtOAc/*n*-hexane = 1/3); IR ν_{max} (neat) cm^{-1}: 2235.1 cm^{-1} (CN); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.76 (t, *J* = 8.0 Hz, 1H, Ar<u>H</u>), 8.02 (dt, *J* = 8.0 Hz, 1.0 Hz, 1H, Ar<u>H</u>), 8.49 (dt, *J* = 8.0 Hz, 1.0 Hz, 1H, Ar<u>H</u>), 8.55 (br s 1H, Ar<u>H</u>); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 114.10, 116.48, 127.18, 127.48, 130.64, 137.57, 148.20 (CN); MS (70 eV), *m/z* (relative intensity): 148 (M^+, 100), 102 (65), 90 (30), 76 (23), 75 (48), 51 (29); HRMS calcd for $C_7H_4N_2O_2$: 148.0273. Found: 148.0276.

4-Nitrobenzonitrile (4l)[37]

Pure **4l** was obtained as colorless crystals (1.34 g, 91%); mp 148-149 °C (EtOAc + *n*-hexane) [lit.[37] 147-149 °C]; R_f = 0.58 (EtOAc/*n*-hexane = 1/3); IR ν_{max} (neat) cm^{-1}: 2230.1 cm^{-1} (CN); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.92, 8.38 (each d, *J* = 8.8 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 400 MHz) δ 116.74, 118.25, 124.22, 133.43, 149.98 (CN); MS (70 eV), *m/z* (relative intensity), 148 (M^+, 72), 118 (9), 102 (100), 90 (16), 76 (16), 75 (34), 51 (17); HRMS calcd for $C_7H_4N_2O_2$: 148.0273. Found: 148.0275.

4-Methylbenzonitirle (4m)[38]

Pure **4m** was obtained as liquid (1.0 g, 85 %); mp 39 °C (EtOAc + *n*-hexane) [lit.[38] 37-38 °C]; R_f = 0.66 (EtOAc/*n*-hexane = 1/3); IR ν_{max} (neat) cm^{-1}: 2227.5 cm^{-1} (CN), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 2.39 (s, 3H, $C\underline{H}_3$), 7.24, 7.48 (each d, *J* = 8.0 Hz, 2H, Ar<u>H</u>); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 21.29, 108.79, 118.65, 129.44, 131.50, 143.30 (CN); MS (70 eV), *m/z* (relative intensity): 117 (M^+, 100), 116 (63), 90 (46), 89 (24), 63 (9); HRMS calcd for C_8H_7N: 117.0578. Found: 117.0579.

4-Allyloxy-3-methoxybenzonitrile (4n)[39]

Pure **4n** was obtained as colorless crystals (1.64 g, 87%); mp 59-60 °C [lit.[39] 58-60 °C]; (EtOAc + *n*-hexane) [lit.[39]; R_f = 0.49 (EtOAc/*n*-hexane = 1/3); IR ν_{max} (neat) cm^{-1}: 2223.8 cm^{-1} (CN); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.89 (s, 3H, $OC\underline{H}_3$), 4.66 (dd, *J* = 5.4 Hz, 1.2 Hz, 2H), 5.33 (ddd, *J* = 10.7 Hz, 3.0 Hz, 1.2 Hz, 1H), 5.43 (ddd, *J* = 17.2 Hz, 3.0 Hz, 1.2 Hz, 1H), 6.06 (m, 1H), 6.90 (d, *J* = 8.4 Hz, 1H, Ar<u>H</u>), 7.09 (d, *J* = 2.0 Hz, 1H, Ar<u>H</u>), 7.24 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H, Ar<u>H</u>); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 55.94, 69.52, 103.78, 112.72, 114.12, 118.53, 118.97, 126.01, 131.90, 149.29 (CN), 151.68; MS (70 ev), *m/z* (relative intensity): 189 (M^+, 100), 149 (17),

148 (94), 146 (12), 134 (15), 120 (30), 102 (16), 92 (38), 77 (33), 65 (21), 51 (7); Anal calcd for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.48; H, 5.83; N, 7.31.

3,5-Dimethoxy-4-hydroxybenzonitrile (4o)[40]

Pure **4o** was obtained as colorless crystals (1.61 g, 90%); mp 121-122 °C (EtOAc + *n*-hexane) [lit.[40] 123-124 °C]; R_f = 0.13 (EtOAc/*n*-hexane = 1/3); IR ν_{max} (neat) cm^{-1}: 2230.3 cm^{-1} (CN); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 3.96 (s, 6H, 2 × OC<u>H</u>$_3$), 6.36 (s, 1H, O<u>H</u>), 6.87 (s, 2H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 56.51 (OCH_3), 102.16, 109.13, 119.24, 139.28, 147.12 (CN); MS (70 eV), *m/z* (relative intensity): 179 (M^+, 100), 164 (57), 136 (14), 121 (13), 118 (23), 93 (7), 90 (16), 53 (6); Anal calcd for $C_9H_9NO_3$: C, 60.33; H, 5.06; N, 7.82. Found: C, 60.56; H, 4.98; N, 7.71.

2-Cyanopyrrole (4p)[41]

Pure **4p** was obtained as colorless liquid (0.93 g, 86%); bp 143-150 °C (20 mmHg) [lit.[41] 120-123 °C (15 torr)]; R_f = 0.46 (EtOAc/*n*-hexane = 1/3); IR ν_{max} (neat) cm^{-1}: 2234.0 cm^{-1} (CN); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 6.24 (m, 1H), 6.86 (m, 1H), 6.94 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 100.23, 109.85, 114.84, 120.19, 123.89; MS (70 eV), *m/z* (relative intensity): 92 (M^+, 100), 70 (16), 65 (29), 64 (21), 61 (18), 45 (18), 43 (80); HRMS calcd for $C_5H_4N_2$: 92.0374. Found: 92.0376.

2-Cyanothiophene (4q)[42]

Pure **4q** was obtained as colorless liquid (0.93 g, 85%), bp 112 °C; R_f = 0.51 (EtOAc/*n*-hexane = 1/3); IR ν_{max} (neat) cm^{-1}: 2221.7 cm^{-1} (CN); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.14 (dd, *J* = 4.8 Hz, 4.0 Hz, 1H), 7.62-7.64 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 109.53, 114.03, 127.48, 132.50 137.23; MS (70 eV), *m/z* (relative intensity): 109 (M^{+1}, 100), 82 (10), 70 (11), 58 (6), 57 (16); HRMS calcd for C_5H_3NS: 108.9986. Found: 108.9989.

2-Cyanopyridine (4r)[43]

Pure **4r** was obtained as colorless liquid (0.88 g, 85%). R_f = 0.37 (EtOAc/*n*-hexane = 1/3); IR ν_{max} (neat) cm^{-1}: 2236.7 cm^{-1} (CN); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.51-7.55 (m, 1H), 7.70 (dt, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.85 (td, *J* = 7.8 Hz, 2.0 Hz, 1H), 8.72 (dd, *J* = 4.8 Hz, 0.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 117.11, 126.86, 128.48, 134.00, 136.97, 151.08; MS (70 eV), *m/z* (relative intensity): 104 (M^+, 100), 77 (45), 51 (11), 50 (12); HRMS calcd for $C_6H_4N_2$: 104.0374. Found: 104.0376.

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