One-Pot Conversion of Aromatic Bromides and Aromatics into Aromatic Nitriles

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Abstract: Various aromatic bromides and iodides were smoothly converted into the corresponding aromatic nitriles in good to moderate yields by the treatment with butyllithium and subsequently DMF, followed by treatment with molecular iodine in aqueous ammonia. The same treatment of typical aromatics and heteroaromatics with butyllithium and subsequently DMF, followed by treatment with molecular iodine in aqueous ammonia also provided the corresponding aromatic nitriles in good yields. The present reactions are novel one-pot methods for the preparation of aromatic nitriles from aromatic bromides and aromatics, respectively, through the formation of aryllithiums and their DMF adducts.

Key words: aromatics, butyllithium, aryllithium, aromatic nitrile, molecular iodine, aqueous ammonia, aromatic bromide, aromatics

Aromatic nitriles are one of the most important synthetic transformation precursors because they can be easily converted into esters, amides, carboxylic acids, amines, and nitrogen-containing heterocycles, such as tetrazoles, and are used as synthetic intermediates for agricultural chemicals, pharmaceuticals, and functional materials.[1] For example, Citalopram hydrobromide® (treatment of alcohol dependency), Periciazine® (antipsychotic drug), Fadrozole® (oncolytic drug), and Letrozole® (breast cancer therapy) are pharmaceutically important aromatic nitriles.[2] The most typical methods for the preparation of aromatic nitriles are the dehydration of aromatic amides with $SOCl_2$, TsCl/pyridine, P_2O_5, $POCl_3$, $COCl_2$, or Ph_3P/CCl_4, the reaction of carboxylic acids with chlorosulfonylisocyanate ($ClSO_2NCO$) and DMF,[3] the reaction of esters with Me_2AlNH_2,[3] and the Sandmeyer reaction of aromatic diazonium ion with toxic CuCN.[3,4] Recently, the direct conversion of aromatic bromides into the corresponding aromatic nitriles has been actively studied with CuCN at DMF refluxing temperature,[5a] $Pd(OAc)_2{\cdot}K_4[Fe(CN)_6]$ at 120 °C,[5b] Pd·(binaphthyl)P(*t*-Bu)$_2{\cdot}Zn(CN)_2{\cdot}$Zn at 80–95 °C,[5c] $Pd_2(dba)_3{\cdot}Zn(CN)_2{\cdot}$DPPF at 80–120 °C,[5d] $Pd(tmhd)_2{\cdot}K_4[Fe(CN)_6]$ at 80 °C,[5e] $Zn(CN)_2{\cdot}Pd_2(dba)_3$ at 100 °C,[5f] Pd/C·CuI·$K_4[Fe(CN)_6]{\cdot}3H_2O$ at 130–140 °C,[5g] CuI·alkylimidazole·Pd/C·CuI·$K_4[Fe(CN)_6]$ at 140–180 °C,[5h] $Zn(CN)_2{\cdot}Pd_2(dba)_3{\cdot}$dppf·Zn·$ZnBr_2$ at 95 °C,[5i] CuO·Pd·$K_4[Fe(CN)_6]$ at 120 °C,[5j] and $Pd(OAc)_2{\cdot}Cu(OAc)_2{\cdot}K_4[Fe(CN)_6]$,[5k] at 130 °C all of which require toxic metal cyanides. More recently, the direct and catalytic cyanation of aromatics containing a 2-pyridyl group via C–H bond cleavage with $Cu(OAc)_2{\cdot}$TMSCN[6a] and $Pd(OAc)_2{\cdot}$CuBr·CuCN[6b] at 130 °C, which requires toxic metal cyanides again, was reported. To the best of our knowledge, methods for the one-pot preparation of aromatic nitriles from aromatics are extremely limited, and one established method is the reaction of highly electron-rich aromatics with $ClSO_2NCO$ to form *N*-chlorosulfonyl amides and the subsequent treatment with DMF to provide aromatic nitriles, together with the evolution of SO_3 and HCl.[7] Clearly, there are no reliable methods for the environmentally benign and efficient preparation of aromatic nitriles from aromatic bromides and aromatics directly. It is evident that an environmentally benign, economical, and efficient approach for the conversion of aromatic bromides and aromatics into aromatic nitriles is required. On the other hand, molecular iodine is one of the simplest oxidants currently available. It is highly affordable and has very low toxicity. Therefore, in view of environmentally benign organic synthesis, molecular iodine is used in various organic reactions, including the oxidation of alcohols or aldehydes to esters, the oxidation of sulfides to sulfoxides, the oxidation of cyclohexenones to benzene rings, the introduction of protecting groups, the deprotection of protecting groups, iodocyclization, carbon–carbon bond formation, and the formation of heterocycles.[8]

Recently, we have reported the direct, efficient, practical, and low-toxicity oxidative conversion of benzylic halides into the corresponding aromatic nitriles using molecular iodine in aqueous ammonia.[9h,i] In that reaction, aromatic aldehydes could be also smoothly converted into the corresponding aromatic nitriles with molecular iodine in aqueous ammonia.[9b,g,10] As part of our ongoing studies on the use of molecular iodine for organic synthesis,[9] we would like to report herein the one-pot conversion of typical aromatic bromides and aromatics into the corresponding aromatic nitriles directly. Very recently, we have reported the metal-free one-pot conversion of electron-rich aromatics into the corresponding aromatic nitriles in good yields, via the formation of aromatic *N*,*N*-dimethyliminium salts with $POCl_3$ and DMF, followed by the treatment with molecular iodine in aqueous ammonia.[11] However, that reaction required highly electron-rich aromatics, such as dimethoxybenzenes, trimethoxybenzenes, methoxynaphthalenes, indoles, 2-alkylfurans, and 2-alkylthiophenes, because the first step involves the formation of aromatic *N*,*N*-dimethyliminium salts via electrophilic

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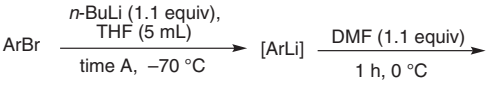
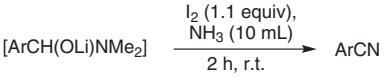
substitution on aromatics, with $POCl_3$ and DMF (the Vilsmeier–Haack reaction). Therefore, we designed an environmentally benign one-pot conversion of aromatic bromides and aromatics into the corresponding aromatic nitriles via aryllithium, using DMF and molecular iodine in aqueous ammonia. The reaction was carried out as follows:[12] butyllithium (1.67 M solution in hexane, 3.3 mL) was added dropwise to a solution of 4-bromotoluene (855 mg, 5 mmol) in THF (5 mL) at –70 °C. After 30 minutes, the resulting mixture was warmed at 0 °C and stirred for five minutes. Then, DMF (0.43 mL, 5.5 mmol) was added, and the obtained mixture was stirred at 0 °C. After one hour at the same temperature, aqueous NH_3 (10 mL, 150 mmol) and I_2 (1396 mg, 5.5 mmol) were added, and the obtained mixture was stirred for two hours at room temperature to provide 4-methylbenzonitrile in 80% yield, as shown in Table 1 (entry 1). The same treatment of 3-methylbromobenzene, 2-methylbromobenzene, 2,4-dimethylbromobenzene, 3,4-dimethylbromobenzene, 2,5-dimethylbromobenzene, 2,4,6-trimethylbromobenzene, *p*-bromoanisole, 2,4-dimethoxybromobenzene, 2,4,6-trimethoxybromobenzene, and 4-(dimethylamino)-bromobenzene gave the corresponding aromatic nitriles in good to moderate yields (entries 2–11). Using the same procedure, 1-bromonaphthalene, 2-bromonaphthalene, and 4-bromobiphenyl also provided the corresponding aromatic nitriles in good yields (entries 12–14). The same treatment of electron-deficient 2-bromopyridine gave 2-cyanopyridine in good yield (entry 15). Under the present conditions, *p*-chlorotoluene did not provide 4-methylbenzonitrile at all, while the same treatment of *p*-iodotoluene gave 4-methylbenzonitrile in good yield (entries 16, 17). The direct conversion of dialkylbenzenes, trialkylbenzenes, anisoles, benzothiophene, benzofuran, and pyridine into the corresponding aromatic nitriles with the previous methods did not generate the corresponding aromatic nitriles at all.[7,11] Therefore, the present method should be very useful for the conversion of aromatic bromides and iodides into the corresponding aromatic nitriles, using butyllithium, DMF, and molecular iodine in aqueous ammonia, since aromatic bromides and iodides can be prepared directly from aromatics. Moreover, known one-pot methods for the preparation of aromatic nitriles from aromatic bromides requires expensive Pd and toxic metal cyanide, and the reactions are conducted at high temperature.[5]

Then, butyllithium (1.67 M solution in hexane, 2.9 mL, 4.8 mmol) was added dropwise into a solution of 1,3-dimethoxybenzene (553 mg, 4 mmol) in THF (5 mL) at 0 °C, and the obtained mixture was stirred for two hours at the same temperature. Then, DMF (0.34 mL, 4.4 mmol) was added, and the obtained mixture was stirred at 0 °C. After 2 hours at the same temperature, aqueous NH_3 (8 mL, 120 mmol) and I_2 (1117 mg, 4.4 mmol) were added, and the reaction mixture was stirred for two hours at room temperature to give 2,6-dimethoxybenzonitrile in 91% yield, as shown in Table 2 (entry 2). Under the same conditions, anisole, 1,3,5-trimethoxybenzene, 1,4-dimethoxybenzene, 1,2-dimethoxybenzene, indoles, benzofuran, benzothiophene, and 2-decylfuran could be converted into the corresponding aromatic nitriles in good to moderate yields (entries 1, 3–10). Therefore, the present method can be used for the direct preparation of typical aromatic and heteroaromatic cycanides from aromatics and heteroaromatics, using butyllithium and subsequently DMF, followed by treatment with molecular iodine in aqueous ammonia.

Table 1 Conversion of Aromatic Bromides into Aromatic Nitriles





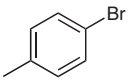
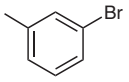
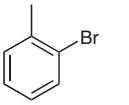
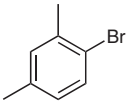
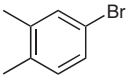
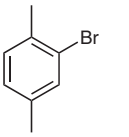
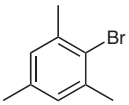
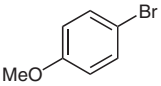
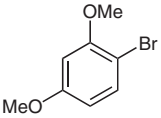
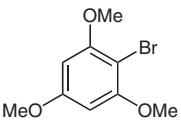
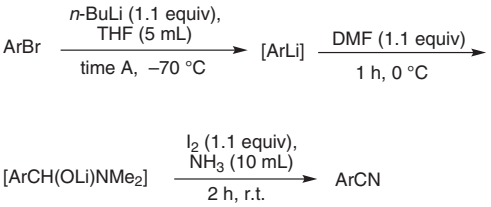
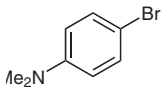
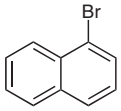
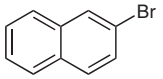
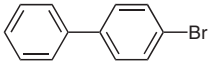
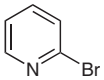
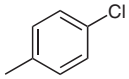
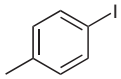
Entry[a]	ArBr	Time A (h)	Yield (%)[a]
1		0.5	80
2		0.5	76
3		0.5	68
4		0.5	62 (15)[b]
5		0.25	74 (20)[c]
6		0.5	62
7		0.5	99[d]
8		0.5	76
9		0.5	95[d]
10		0.5	59

Table 1 Conversion of Aromatic Bromides into Aromatic Nitriles (continued)



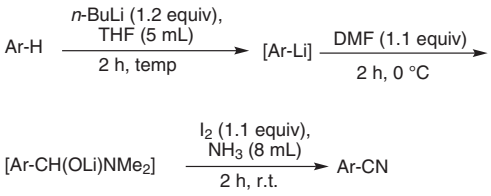
Entry[a]	ArBr	Time A (h)	Yield (%)[a]
11		0.5	44
12		0.5	60[d]
13		0.5	83
14		0.5	64
15		0.5	66
16		0.5	0
17		0.25	70

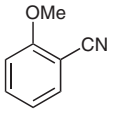
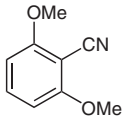
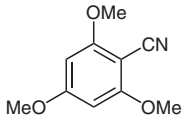
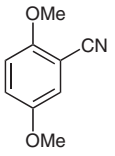
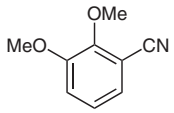
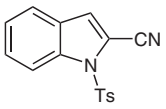
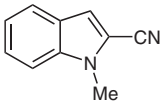
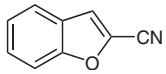
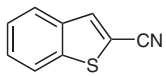
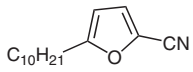
[a] Reaction was performed on a 5 mmol scale. Isolated yield.
[b] Yield of 2,6-dimethylbenzonitrile.
[c] Yield of 2,3-dimethylbenzonitrile.
[d] DMF (1.5 equiv) was added.

The plausible reaction mechanism is shown in Scheme 1. The initial step is the formation of aryllithium **a** by the reaction of aromatic bromide or aromatics with butyllithium. Then, aryllithium **a** reacts with DMF to generate adduct **b**. The addition of molecular iodine and aqueous ammonia induces the formation of aromatic imine **c**, which further reacts with molecular iodine to form *N*-iodo aromatic imine **d**. Once *N*-iodo aromatic imine **d** is formed, HI elimination smoothly occurs by ammonia to generate aromatic nitrile.[9g–j]

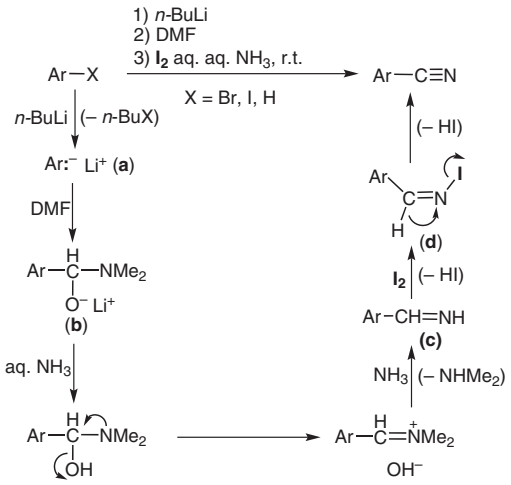
In conclusion, various electron-rich and electron-deficient aromatics, such as bromotoluenes, bromodimethylbenzenes, bromotrimethylbenzene, bromoanisole, bromonaphthalenes, bromobiphenyl, and bromopyridine could be smoothly converted into the corresponding aromatic nitriles in good to moderate yields by treatment with butyllithium and subsequently DMF, followed by treatment with molecular iodine in aqueous ammonia. The same treatment of typical aromatics and heteroaromatics, such as anisole, dimethoxybenzenes, trimethoxybenzenes, benzothiophene, benzofuran, and alkylfuran with butyllithium and subsequently DMF, followed by treatment with molecular iodine in aqueous ammonia provided the corresponding aromatic nitriles in good yields. The present reactions are novel one-pot methods for the preparation of aromatic nitriles from aromatic bromides and aromatics through the formation of aryllithiums and their DMF adducts. Further synthetic study and application of the present methods is under way in this laboratory.

Table 2 Conversion of Aromatics into Aromatic Nitriles



Entry[a]	ArCN	Temp (°C)	Yield (%)[a]
1		0	74
2		0	91
3		0	61
4		0	92
5		0	76
6		0 to r.t.	65
7		0	68
8		0	70
9		0	49 (20)[b]
10		0	90

[a] Reaction was performed on a 4 mmol scale. Isolated yield.
[b] Yield of starting material.



Scheme 1 Possible reaction pathway for nitrile

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(12) **Typical Experimental Procedure for the Conversion of Aromatic Bromides into Aromatic Nitriles**
Butyllithium (1.67 M solution in hexane, 3.3 mL, 5.5 mmol) was added dropwise to a solution of 4-bromotoluene (855 mg, 5 mmol) in THF (5 mL) at –70 °C. After 30 min, the resulting mixture was warmed and stirred for 5 min at 0 °C. Then, DMF (0.43 mL, 5.5 mmol) was added to the mixture, and the obtained mixture was stirred at 0 °C. After 1 h at the same temperature, aq NH_3 (10 mL, 150 mmol) and I_2 (1396 mg, 5.5 mmol) were added, and the obtained mixture was stirred for 2 h at r.t. The reaction mixture was quenched with sat. aq Na_2SO_3 (15 mL) and was extracted with Et_2O (3 × 20 mL). The organic layer was washed with brine and dried over Na_2SO_4 to provide 4-methylbenzonitrile in 80% yield. If necessary, the product was purified by a short column chromatography on silica gel (hexane–EtOAc = 9:1) to give pure 4-methylbenzonitrile as a colorless solid.
Most aromatic nitriles mentioned in this work are commercially available and were identified by comparison with the authentic samples.
4-Methylbenzonitrile
Mp 26–28 °C (commercial, mp 26–28 °C). IR: 2227 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 7.26 (d, *J* = 8.1 Hz, 2 H), 7.52 (d, *J* = 8.1 Hz, 2 H).
3-Methylbenzonitrile
Oil (commercial). IR: 2229 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.38 (s, 3 H), 7.32–7.47 (m, 4 H).
2-Methylbenzonitrile
Oil (commercial). IR: 2225 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.54 (s, 3 H), 7.26 (t, *J* = 7.6 Hz, 1 H), 7.31 (d, *J* = 7.6 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 1 H), 7.58 (d, *J* = 7.6 Hz, 1 H).
2,4-Dimethylbenzonitrile
Mp 23–24 °C (commercial, mp 23–25 °C). IR: 2221 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.36 (s, 3 H), 2.47 (s, 3 H), 7.05 (d, *J* = 8.0 Hz, 1 H), 7.10 (s, 1 H) 7.43 (d, *J* = 8.0 Hz, 1 H).
3,4-Dimethylbenzonitrile
Mp 63–64 °C (commercial, mp 64–67 °C). IR: 2224 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.29 (s, 3 H), 2.32 (s, 3 H), 7.21 (d, *J* = 7.8 Hz, 1 H), 7.39 (d, *J* = 7.8 Hz, 1 H), 7.41 (s, 1 H).
2,5-Dimethylbenzonitrile
Oil (commercial). IR: 2227 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.33 (s, 3 H), 2.48 (s, 3 H), 7.18 (d, *J* = 7.9 Hz, 1 H), 7.27 (d, *J* = 7.9 Hz, 1 H), 7.36 (s, 1 H).

2,4,6-Trimethylbenzonitrile
Mp 50–51 °C (lit.[9i] mp 54–55 °C). IR: 2218 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.32 (s, 3 H), 2.47 (s, 6 H), 6.92 (s, 2 H).
4-Methoxybenzonitrile
Mp 54–55 °C (commercial, mp 57–59 °C). IR: 2216 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 6.95 (d, *J* = 8.9 Hz, 2 H), 7.59 (d, *J* = 8.9 Hz, 2 H).
2,4-Dimethoxybenzonitrile
Mp 93–94 °C (commercial, mp 93–94 °C). IR: 2219 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 3.90 (s, 3 H), 6.46 (s, 1 H), 6.51 (d, *J* = 8.5 Hz, 1 H), 7.48 (d, *J* = 8.5 Hz, 1 H).
2,4,6-Trimethoxybenzonitrile
Mp 139–140 °C (commercial, mp 143–145 °C. IR: 2212 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 3.89 (s, 6 H), 6.07 (s, 2 H).
4-(*N*,*N*-Dimethyamino)benzonitrile
Mp 75 °C (commercial, mp 75 °C). IR: 2210 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.04 (s, 6 H), 6.64 (d, *J* = 9.1 Hz, 2 H), 7.47 (d, *J* = 9.1 Hz, 2 H).
1-Naphthonitrile
Mp 35–36 °C (commercial, mp 36–38 °C). IR: 2219 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.49 (t, *J* = 7.9 Hz, 1 H), 7.59 (t, *J* = 8.2 Hz, 1 H), 7.67 (t, *J* = 8.2 Hz, 1 H), 7.89 (d, *J* = 7.9 Hz, 1 H), 7.91 (d, *J* = 7.9 Hz, 1 H), 8.05 (d, *J* = 8.2 Hz, 1 H), 8.22 (d, *J* = 8.2 Hz, 1 H).
2-Naphthonitrile
Mp 68–70 °C (commercial, mp 66–70 °C). IR: 2225 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.58–7.68 (m, 3 H), 7.88–7.93 (m, 3 H), 8.24 (s, 1 H).
4-Cyanobiphenyl
Mp 85–88 °C (commercial, mp 85–87 °C). IR: 2225 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.44 (t, *J* = 7.3 Hz, 1 H), 7.49 (t, *J* = 7.3 Hz, 2 H), 7.59 (d, *J* = 7.3 Hz, 2 H), 7.69 (d, *J* = 8.8 Hz, 2 H), 7.73 (d, *J* = 8.8 Hz, 2 H).
2-Cyanopyridine
Mp 24–25 °C (commercial, mp 24–27 °C). IR: 2236 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.56 (dd, *J* = 7.8, 4.6 Hz, 1 H), 7.73 (d, *J* = 7.8 Hz, 1 H), 7.88 (t, *J* = 7.8 Hz, 1 H), 8.74 (d, *J* = 4.6 Hz, 1 H).

Typical Experimental Procedure for the Conversion of Aromatics into Aromatic Nitriles

Butyllithium (1.67 M solution in hexane, 2.9 mL, 4.8 mmol) was added dropwise into a solution of 1,3-dimethoxybenzene (552 mg, 4 mmol) in THF (5 mL) at 0 °C, and the mixture was stirred for 2 h at the same temperature. Then, DMF (0.34 mL, 4.4 mmol) was added to the mixture, and the obtained mixture was stirred at 0 °C. After 2 h at the same temperature, aq NH_3 (8 mL, 120 mmol) and I_2 (1117 mg, 4.4 mmol) were added and stirred for 2 h at r.t. The reaction mixture was quenched with sat. aq Na_2SO_3 (15 mL) and was extracted with Et_2O (3 × 20 mL). The organic layer was washed with brine and dried over Na_2SO_4 to provide 2,6-dimethoxybenzonitrile in 91% yield. If necessary, the product was purified by a short column chromatography on silica gel (hexane–EtOAc = 3:1) to give pure 2,6-dimethoxybenzonitrile as a colorless solid.

2,6-Dimethoxybenzonitrile
Mp 117–119 °C (commercial, mp 119–123 °C). IR: 2220 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.90 (s, 6 H), 6.56 (d, *J* = 8.5 Hz, 2 H), 7.44 (t, *J* = 8.5 Hz, 1 H).
2-Methoxybenzonitrile
Oil (commercial). IR: 2230 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.91 (s, 3 H), 7.02–6.97 (m, 2 H), 7.59–7.52 (m, 2 H).
2,5-Dimethoxybenzonitrile
Mp 79–82 °C (commercial, mp 81–85 °C). IR: 2224 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.78 (s, 3 H), 3.89 (s, 3 H), 6.91 (d, *J* = 9.0 Hz, 1 H), 7.05–7.11 (m, 2 H).
2,3-Dimethoxybenzonitrile
Mp 41–42 °C (commercial, mp 43–46 °C). IR: 2228 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.89 (s, 3 H), 4.03 (s, 3 H), 7.07–7.16 (m, 3 H).
2-Cyano-*N*-methylindole
Mp 70–75 °C. IR: 2223 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.91 (s, 3 H), 7.16 (s, 1 H), 7.21 (t, *J* = 6.8, 1 H), 7.34–7.44 (m, 2 H), 7.66 (d, *J* = 8.2 Hz, 1 H).
***N*-Tosylindole-2-carbonitrile**
Mp 160–161 °C (lit.[13] mp 160–162 °C). IR: 2227 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 7.27 (d, *J* = 8.2 Hz, 1 H), 7.32 (d, *J* = 7.2 Hz, 1 H) 7.36 (s, 1 H), 7.52 (t, *J* = 7.2 Hz, 1 H), 7.58 (d, *J* = 8.2 Hz, 1 H), 7.90 (d, *J* = 8.4 Hz, 2 H), 8.21 (d, *J* = 8.4 Hz, 1 H).
2,4,6-Trimethoxybenzonitrile
Mp 139–140 °C (commercial, mp 143–145 °C). IR: 2212 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 3.89 (s, 6 H), 6.07 (s, 2 H).
Benzofuran-2-carbonitrile
Oil (lit.[14]). IR: 2227 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.36 (t, *J* = 7.5 Hz, 1 H), 7.46 (s, 1 H), 7.49–7.58 (m, 2 H), 7.68 (d, *J* = 7.9 Hz, 1 H).
Benzothiophene-2-carbonitrile
Oil (commercial, mp 24–28 °C). IR: 2217 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.43 (t, *J* = 7.6 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 1 H), 7.77–7.85 (m, 3 H).
5-Decylfuran-2-carbonitrile
Oil. IR: 2229 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.0 Hz, 3 H), 1.21–1.38 (m, 14 H), 1.65 (quint, *J* = 7.1 Hz, 2 H), 2.66 (t, *J* = 7.1 Hz, 2 H), 6.11 (d, *J* = 3.4 Hz, 1 H), 6.99 (d, *J* = 3.4 Hz, 1 H). HRMS–FAB: *m/z* calcd for $C_{15}H_{24}NO$ $[M + H]^+$: 234.1858; found: 234.1861.

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