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Palladium-Catalyzed Cyanation of Aryl Halides with CuSCN

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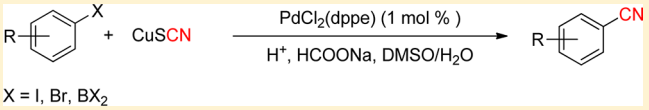
Supporting Information

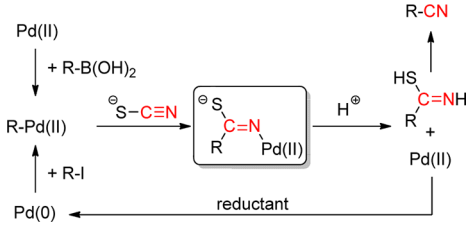
ABSTRACT: A palladium-catalyzed cyanation of aryl halides and borons has been developed by employing cuprous thiocyanate as a safe cyanide source. This protocol avoids the use of a highly toxic cyanide source, providing aromatic nitriles in moderate to good yields with good functional tolerance.



Nitriles have occupied pivotal positions in organic chemistry due to facile transformations of nitriles to aldehydes, amines, amidines, tetrazoles, amides, and their carboxyl derivatives.[1] Moreover, they are also versatile building blocks in the synthesis of natural products, pharmaceuticals, materials, agricultural chemicals, and dyes.[2] Recently, the transition-metal-catalyzed cyanation of aryl halides, borons, mesylates, and arene C−H bonds has become a common and powerful transformation in organic synthesis. With respect to the cyanide sources, MCN (M = Na, K, Cu, Zn, TMS),[3−11] acetone cyanohydrin,[12,13] BnSCN,[14] acetonitrile,[15−17] DDQ,[18] *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide,[19] ethyl cyanoacetate,[20] and $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$[21−24] have been successfully applied. However, except for the aforementioned last five types of cyanide sources, the toxicity of the cyanide source would greatly limit the utility of such transformations, especially in large scale. To circumvent this drawback, much attention has been paid to the development of safe cyanide sources for the cyanation reaction.[25] Recently, Chang pioneered a combination of ammonia and DMF as safe cyanide sources in cyanation of 2-aryl pyridine C−H bonds.[26,27] Theses reports presented a new concept that the cyano group could be generated from DMF and ammonium safely and conveniently in cyanation reactions. Subsequently, we found that the combination of ammonium and DMSO or DMF enabled cyanation of an indole[28] C−H bond or aryl halide.[29] Shortly afterward, Jiao reported the direct cyanation of an indole C−H bond using DMF.[30] Togo et al. also demonstrated conversion of aromatic bromides and aromatics into aromatic nitriles via aryllithiums and their DMF adducts.[31−35] Nevertheless, the aforementioned procedures suffered from limited substrate scope or harsh reaction conditions. Thus, the development of a new procedure with broad substrate scope would dramatically improve the practicality of safe cyanation reactions.

Larock[36,37] and Lu[38] have demonstrated that the nitrile group could produce imines via carbopalladation and subsequent protonation. We envisaged CuSCN would possess the potential similar chemistry leading to the formation of benzothioamide as a precursor to nitriles (Scheme 1). Thus, it may provide a new strategy for aryl nitrile synthesis.

Scheme 1. Design Plan



Importantly, CuSCN is low toxicity to humans and the environment.[39] Herein, we report our preliminary study in the cyanation reaction of aryl halides with CuSCN as a safe and new cyanide source.

Obviously, for the former route, an additional reductant might be needed to regenerate Pd(0) species in the catalytic cycle. With these considerations in mind, we initially conducted the reaction of *p*-iodoanisole **1b** (1.4 equiv) and CuSCN with sodium formate (3 equiv) as the reductant. The copper(I) could promote the cyanation reaction to some extent since the desired product was obtained in 21% yield with the combination of **1b**, CuSCN, formic acid, and sodium formate in DMSO/H_2O (entry 1, Table 1). To our delight, the reaction efficiency was improved by using $Pd(OAc)_2$ (entry 2, Table 1). Some palladium sources were tested. Gratifyingly, *p*-anisonitrile was isolated in 83% yield when $PdCl_2$(dppe) was employed as the catalyst (entry 6, Table 1). Under N_2, a comparable yield was obtained, indicating the O_2 should not take part in the reaction. Further study revealed that the acid was crucial for this transformation. HCOOH gave the best outcome and other acids, such as CF_3COOH, CH_3COOH, and PhCOOH, resulted in low yields (entries 11−13, Table 1). The acid was believed to accelerate the reaction since in the absence of acid, the reaction became sluggish. However, with prolonged reaction time, the cyanation product was still isolated in 81% yield (entry 7, Table 1). The sodium formate played an

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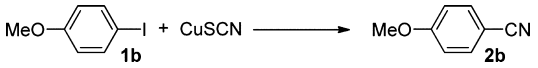
Table 1. Screening Conditions[a]



entry	Pd source	acid	additive	solvent	yield (%)
1		HCOOH	HCOONa	DMSO/H_2O	21
2	$Pd(OAc)_2$	HCOOH	HCOONa	DMSO/H_2O	48
3	$PdCl_2(PPh_3)_2$	HCOOH	HCOONa	DMSO/H_2O	53
4	$PdCl_2$	HCOOH	HCOONa	DMSO/H_2O	38
5	$Pd(dba)_2$	HCOOH	HCOONa	DMSO/H_2O	46
6	$PdCl_2$(dppe)	HCOOH	HCOONa	DMSO/H_2O	83 (80)[b]
7	$PdCl_2$(dppe)		HCOONa	DMSO/H_2O	36 (41)[c] (81)[d]
8	$PdCl_2$(dppe)			DMSO/H_2O	<5
9			HCOONa	DMSO/H_2O	<5
10				DMSO/H_2O	<5
11	$PdCl_2$(dppe)	CF_3COOH	HCOONa	DMSO/H_2O	52
12	$PdCl_2$(dppe)	CH_3COOH	HCOONa	DMSO/H_2O	56
13	$PdCl_2$(dppe)	PhCOOH	HCOONa	DMSO/H_2O	41
14	$PdCl_2$(dppe)	HCOOH	DMSO/H_2O		28
15	$PdCl_2$(dppe)	HCOOH	PhCOONa	DMSO/H_2O	40
16	$PdCl_2$(dppe)	HCOOH	CH_3COOK	DMSO/H_2O	57
17	$PdCl_2$(dppe)	HCOOH	$Na_2C_2O_4$	DMSO/H_2O	49
18	$PdCl_2$(dppe)	HCOOH	HCOONa	DMSO/H_2O	67[e]
19	$PdCl_2$(dppe)	HCOOH	HCOONa	DMSO	76
20	$PdCl_2$(dppe)	HCOOH	HCOONa	toluene/H_2O	0
21	PdCh(dppe)	HCOOH	HCOONa	DMF/H_2O	61

[a]Reaction conditions: *p*-iodoanisole **1b** (0.7 mmol), CuSCN (0.5 mmol), [Pd] (1 mol %), acid (10 mol %), additive (3.0 equiv), under air, solvent/H_2O = 8:1 (3 mL), 100 °C, 36 h. [b]N_2. [c]48 h. [d]48 h, DMSO = 3 mL. [e]DMSO/H_2O = 6/1 (3 mL).

important role on this transformation since removing or replacing sodium formate with other carboxylates dramatically decreased the reaction efficiency. Meanwhile, reaction in other solvents, such as toluene/H_2O and DMF/H_2O resulted in lower yield or no reaction (entries 20 and 21, Table 1). The ratio of DMSO/H_2O had some effect on the reaction. For example, the yield dropped to 67% in DMSO/H_2O = 6:1 (entry 18, Table 1). Finally, we identified the optimal reaction medium as an 8:1 DMSO/H_2O mixture. The dehalogenation byproduct was detected by GC−MS, but the thiocyanate coupled product or the diaryl sulfide was not found.[41] Thus, excess aryl iodides were required to fulfill the reaction.

After the establishment of optimized reaction conditions, we extended this new protocol to a range of aryl iodides. As illustrated in Figure 1, the procedure tolerated well some functional groups, such as methoxy, benzyloxy, acetyl, free phenolic hydroxyl, free amino, and acetamido, with good yields. The electronic nature of aryl iodides had some effect on the reaction. Generally, the aryl iodides with electron-withdrawing groups gave slightly lower yields than those electron-donating analogues (**2a−2i** vs **2p−2s**, Figure 1). This was consistent with Larock's procedure on the palladium-catalyzed cyclization of *ω*-(2-iodoaryl)alkanenitriles.[36] The low yield in the cyanation of the electron-poor aryl iodides may be at least partly due to the reduced nucleophilicity of the arylpalladium intermediate involved in the presumed carbopalladation of CN moiety in thiocyanate (vide infra). Importantly, the *ortho* group in aryl iodides hardly had an effect on the reaction efficiency (**2b**,**2c** vs **2d−2f**, Figure 1). Notably, the mono-, di-, and trimethoxy aryl iodides all worked well with excellent yields (**2b−2g**, Figure 1). Fortunately, free phenolic hydroxyl and amino groups were tolerated well in the standard procedure without any protection. However, *β*-iodo naphthalene afforded the cyanation products in moderate yields. Disappointingly, alkyl iodides failed to cyanate under the standard reaction conditions.

To extend the scope of our catalytic system, we also tested aryl bromides and borons under the standard procedure (Table 2). The nitriles were obtained in moderate yields. Aryl chloride did not work under this procedure. Since the cyanation of boronic acid is triggered by the transmetalation of Pd(II) with arylboronic acid, we reasoned the cyanation yield would improve in the absence of HCOONa. However, a serious homocoupling of arylboronic acid resulted in low yield in this cyanation reaction.

Other substrates containing the XCN (X = O, S) moiety were tested in the newly developed cyanation procedure (Scheme 2). However, in the absence of copper, no reaction took place for KSCN under the indicated conditions. Fortunately, in the presence of 1 equiv of CuI, KSCN ran smoothly to provide the cyanation products in moderate yield. Moreover, KOCN was a potential partner in such transformation, albeit the cyanated products was isolated in low yield. Notably, methyl thiocyanate and 1-methyl-4-thiocyanatobenzene also provided the cyanation products in good yields, respectively.

Next, we conducted the reaction of *p*-iodoanisole and CuSCN on a 10 mmol scale with elongated time, and anisonitrile was isolated in an acceptable 73% (0.97 g) yield, which greatly increased the practicality of this palladium-catalyzed cyanation reaction.

4-Methylbenzothioamide was subjected to the standard procedure, and the cyanation product was isolated in 51% yield in 20 h, while no cyanation product was detected for 4-methoxybenzamide in 36 h. Moreover, during the reaction of KOCN and *p*-iodoanisole, *p*-methoxybenzamide was detected as byproduct (Scheme 3). These results were all consistent with the possibility of a carbopalladation step and *p*-methylbenzo-

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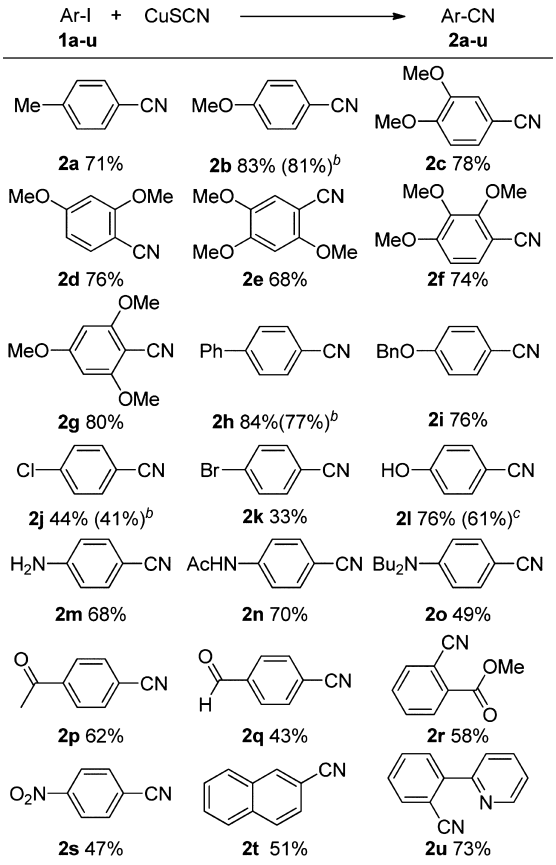
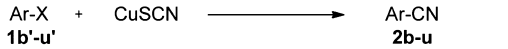
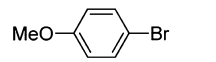
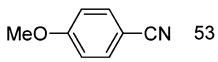
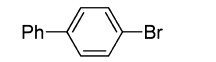
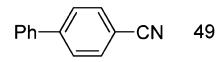
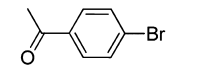
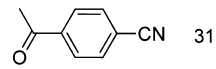
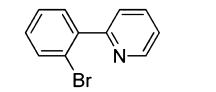
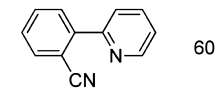
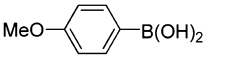
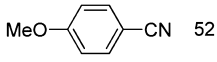
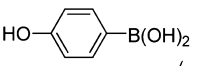
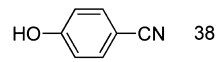
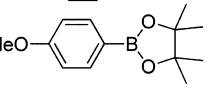
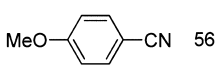


Figure 1. Palladium-catalyzed cyanation of aryl iodides. Reaction conditions: **1a−1u** (0.7 mmol), CuSCN (0.5 mmol), $PdCl_2$(dppe) (1 mol %), HCOOH (10 mol %), HCOONa (3.0 equiv), under air, DMSO/H_2O = 8:1 (3 mL), 100 °C, 36 h. Notes: [b]No HCOOH, 48 h, DMSO = 3 mL. [c] *p*-Iodophenyl acetate.

Table 2. Palladium-Catalyzed Cyanation of Aryl Bromides and Borons[a]

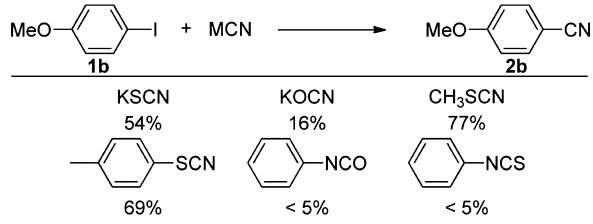


entry	substrate	product	yield (%)
1			53
2			49
3			31
4			60
5			52
6			38
7			56

[a]Reaction conditions were the same as in Figure 1.

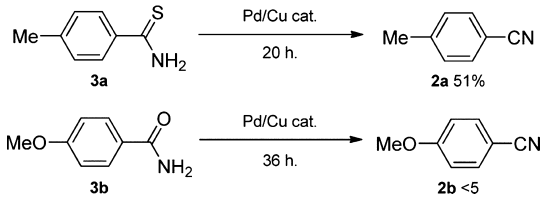
thioamide as the potential intermediate. The low yield of KOCN may be due to the low reactivity of benzamide to nitrile under the standard procedure.

Scheme 2. Pd-Catalyzed Cyanation of 1b with Other Cyanide Sources[a]



[a]Reaction conditions: **1b** (0.7 mmol), MCN (0.5 mmol), $PdCl_2$(dppe) (1 mol %), CuI (0.5 mmol), HCOOH (10 mol %), HCOONa (3.0 equiv), under air, DMSO (3 mL), 100 °C, 36 h.

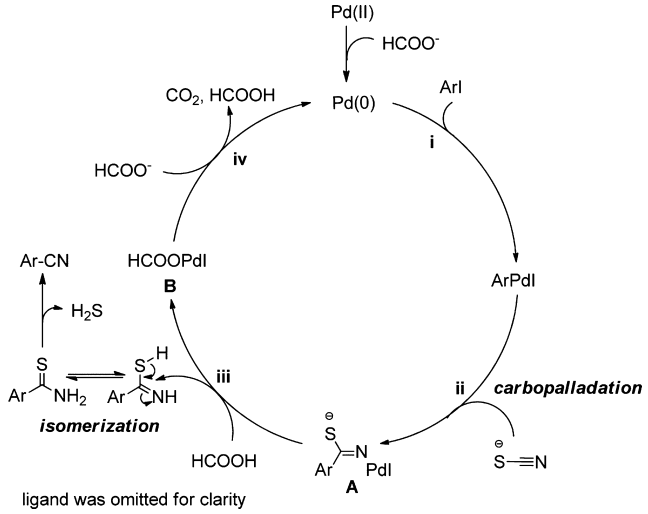
Scheme 3. Pd-Catalyzed Cyanation of 3a and 3b[a]



[a]Reaction conditions were the same as in Scheme 2.

A tentative mechanism is illustrated in Scheme 4. In step i, the oxidative addition of ArI to Pd(0), which derives from the

Scheme 4. Plausible Mechanism



reduction of Pd(II) with HCOONa,[41−43] forms ArPdI. Step ii involves the carbopalladation of ArPdI to form Pd(II) species **A**. Wang reported palladium-catalyzed cyanide metathesis of benzyl cyanide, where the carbopalladation of the cyano moiety was the key step in the catalytic cycle.[44] Then, in step iii, the hydrolysis of intermediate **A** by acid releases the Pd(II) species **B**, along with benzothioamide. Benzothioamide converts to the aryl nitrile via the loss of H_2S.[45,46] In step iv, the reaction of sodium formate with species **B** releases 1 equiv of CO_2 and formic acid, followed by the reductive elimination to regenerate Pd(0) species. Thus, a catalytic amount of formic acid is sufficient to promote the reaction. Notably, in the presence of palladium, 21% of cyanation product was isolated. This result implied Cu(I) could promote the cyanation reaction to some extent. In this case, aryl cuprate species may be formed as the

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intermediate in an Ullmann reaction,[47] and then the aryl cuprate species undergoes a similar process as the ArPd(II) does in steps ii−iv in Scheme 4 to yield the cyanation product. Meanwhile, an alternative pathway may involve the following steps: (1) the formation of PhSCN via the palladium-catalyzed reaction of aryl iodides with CuSCN; (2) cleavage of the S-CN bond; (3) the palladium-catalyzed cyanation.[47] However, in this pathway, 2 equiv of aryl iodides were required to form the cyanation product. The fact of high yields for some substrates in Figure 1 strongly argues against this pathway. However, the detailed mechanism is unclear at the current stage.

In conclusion, we have developed an unprecedented and simple procedure for the cyanation of aryl halides employing CuSCN as an inexpensive and nontoxic cyanide source. The procedure represents good functional tolerance as well as the capability for 10 mmol scale preparation. As such, it represents a novel and safe method to access aromatic nitriles.

EXPERIMENTAL SECTION

General Information. Chemicals were either purchased or purified by standard techniques. ^{1}H NMR and ^{13}C NMR spectra were measured on a 500 MHz spectrometer (^{1}H 500 MHz, ^{13}C 125 MHz), using $CDCl_3$ as the solvent at room temperature. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) or 7.26 ppm in $CDCl_3$ as an internal standard. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm). Chemical shifts are given in δ relative to TMS, the coupling constants J are given in hertz. Column chromatography was performed using EM silica gel 60 (300−400 mesh).

General Procedure for the Reaction of Aryl Iodides, Bromines, and Borons with CuSCN Leading to Nitriles. Under air, a Schlenk tube was charged with CuSCN (60.8 mg, 0.5 mmol), aryl iodides (0.7 mmol, 1.25 equiv), $PdCl_2$(dppe) (2.9 mg, 1 mol %), HCOONa (102.0 mg, 3.0 equiv), HCOOH (2.0 μL, 10 mol %), and DMSO/H_2O = 8:1 (3.0 mL). The mixture was stirred at 100 °C (oil bath temperature) for 36 h, or until complete consumption of starting material as monitored by TLC or GC−MS analysis. The color of the reaction solution started as muddy and ended as dark after the reaction was finished. The reaction mixture was allowed to cool to room temperature, poured into 20 mL of brine, and extracted with EtOAc (4 × 5 mL). The combined organic layers were washed with water and dried over $MgSO_4$, and the solvents were removed under vacuum. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to afford the desired product **2a**--**2u**.

4-Methylbenzonitrile (**2a**).[49] Colorless oil (41.6 mg, 71% yield); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.47 (d, J = 7.5 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.7, 132.0, 129.8, 119.1, 109.3, 21.8.

4-Methoxybenzonitrile (**2b**).[49] Colorless solid (55.2 mg, 83% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.58 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.5 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.8, 134.0, 119.2, 114.7, 103.9, 55.5.

3,4-Dimethoxybenzonitrile (**2c**).[50] Colorless solid (63.6 mg, 78% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.28 (d, J = 8.0 Hz, 1H), 6.90 (s, 1H), 6.90 (d, J = 8.5 Hz, 1H), 3.93 (s, 3H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.9, 149.2, 126.5, 119.2, 114.0, 111.2, 103.9, 56.1, 56.0.

2,4-Dimethoxybenzonitrile (**2d**).[50] Colorless solid (61.9 mg, 76% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.44 (d, J = 9.0 Hz, 1H), 6.50 (d, J = 8.5 Hz, 1H), 6.44 (s, 1H), 3.88 (s, 3H), 3.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.6, 162.8, 134.8, 116.9, 105.7, 98.4, 93.8, 55.9, 55.6.

2,4,5-Trimethoxybenzonitrile (**2e**).[29] Colorless solid (65.6 mg, 68% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.92 (s, 1H), 6.48 (s, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.6, 154.1, 143.0, 116.9, 114.7, 96.4, 91.4, 56.5, 56.1.

2,3,4-Trimethoxybenzonitrile (**2f**).[29] Colorless solid (71.4 mg, 74% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.20 (d, J = 8.5 Hz, 1H), 6.62 (d, J = 9.0 Hz, 1H), 3.98 (s, 3H), 3.84 (s, 3H), 3.79 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.9, 155.7, 141.7, 128.7, 116.5, 107.4, 99.0, 61.7, 61.0, 56.2.

2,4,6-Trimethoxybenzonitrile (**2g**).[50] Colorless solid (77.2 mg, 80% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.05 (s, 2H), 3.87 (s, 6H), 3.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.3, 163.7, 114.6, 90.3, 84.0, 56.0, 55.6.

(1,1′-Biphenyl)-4-carbonitrile (**2h**).[29] Colorless solid (75.2 mg, 84% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.74−7.68 (m, 4H), 7.59 (d, J = 7.5 Hz, 2H), 7.51−7.48 (m, 2H), 7.44−7.42 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 145.6, 139.1, 132.5, 129.1, 128.6, 127.7, 127.2, 118.9, 110.9.

4-(Benzyloxy)benzonitrile (**2i**).[29] Colorless solid (79.4 mg, 76% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.60−7.58 (m, 2H), 7.92−7.88 (m, 5H), 7.02−7.01 (m, 2H), 5.12 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.9, 135.6, 133.9, 128.7, 128.3, 127.4, 119.1, 115.5, 104.1, 70.2.

4-Chlorobenzonitrile (**2j**).[49] Colorless solid (30.1 mg, 44% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.60 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 139.5, 133.3, 129.7, 117.9, 110.7.

4-Bromobenzonitrile (**2k**).[49] Colorless solid (29.8 mg, 33% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.64 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 133.3, 132.6, 127.9, 118.0, 111.2.

4-Hydroxybenzonitrile (**2l**).[29] Colorless solid (45.2 mg, 76% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.55 (d, J = 8.5 Hz, 2H), 6.94 (d, J = 9.0 Hz, 2H), 6.77 (br, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.2, 134.3, 119.2, 116.4, 103.0.

4-Aminobenzonitrile (**2m**).[49] Colorless solid (40.1 mg, 68% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.39 (d, J = 8.0 Hz, 2H), 6.63 (d, J = 8.1 Hz, 2H), 4.23 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.5, 133.7, 120.1, 114.3, 99.9.

N-(4-Cyanophenyl)acetamide (**2n**).[49] Colorless solid (56.0 mg, 70% yield); ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.4 (s, 1H), 7.72 (s, 4H), 2.07(s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 169.4, 143.3, 133.2, 119.1, 119.0, 104.7, 24.0.

4-(Dibutylamino)benzonitrile (**2o**).[29] Colorless solid (56.3 mg, 49% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40 (d, J = 9.0 Hz, 2H), 6.56 (d, J = 9.0 Hz, 2H), 3.29 (t, J = 8.0 Hz, 4H). 1.59−1.52 (m, 4H), 1.39−1.31 (m, 4H), 0.96 (t, J = 7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.6, 133.4, 120.8, 111.0, 96.1, 50.6, 29.0, 20.1, 13.8.

4-Acetylbenzonitrile (**2p**).[29] Colorless solid (44.9 mg, 62% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.04 (d, J = 8.5 Hz, 2H), 7.78 (d, J = 8.5 Hz, 2H), 2.65 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 196.5, 139.9, 132.5, 128.7, 117.9, 116.4, 26.7.

4-Formylbenzonitrile (**2q**).[6] Colorless solid (28.2 mg, 43% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10.1 (s, 1H), 8.0 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 190.6, 138.8, 132.9, 129.9, 117.7, 117.6.

Methyl-2-cyanobenzoate (**2r**).[29] Colorless solid (46.7 mg, 58% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.14−8.13 (m, 1H), 7.81−7.80 (m, 1H), 7.70−7.64 (m, 2H), 4.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.4, 134.7, 132.6, 132.4, 132.3, 131.1, 117.4, 112.9, 52.8.

4-Nitrobenzonitrile (**2s**).[29] Yellow solid (34.8 mg, 47% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.36 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.0, 133.4, 124.3, 118.3, 116.8.

2-Naphthonitrile (**2t**).[29] Colorless solid (39.0 mg, 51% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.23 (s, 1H), 7.92−7.88 (m, 3H), 7.67−7.59 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 134.6, 134.1, 132.2, 129.2, 129.0, 128.4, 128.0, 127.6, 126.3, 119.2, 109.4.

2-(Pyridin-2-yl)benzonitrile (**2u**).[10] Colorless solid (65.7 mg, 73% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.76 (d, J = 4.5 Hz, 1H), 7.85−7.83 (m, 2H), 7.78 (t, J = 7.5 Hz, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 8.0 Hz, 1H), 7.37−7.35 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ

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155.0, 149.7, 143.1, 137.0, 134.0, 132.8, 129.9, 128.8, 123.3, 123.2, 118.6, 111.0.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of compounds **2a**−**2u**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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