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Phenyliodonium Diacetate Mediated Direct Synthesis of Benzonitriles from Styrenes through Oxidative Cleavage of C=C Bonds

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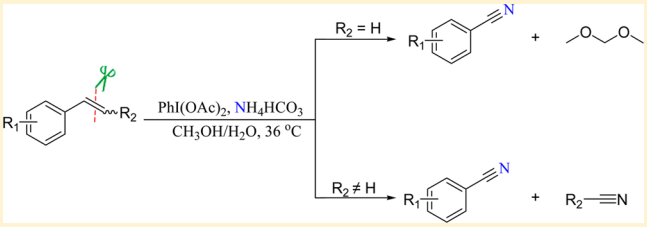
Supporting Information

ABSTRACT: A metal-free $PhI(OAc)_2$ mediated nitrogenation of alkenes through C=C bond cleavage using inorganic ammonia salt as nitrogen source under mild conditions was developed, affording nitriles in moderate to good yields. The advantages of this reaction are mild reaction conditions, operational simplicity, and use of an ammonium salt as nitrogen source. Based upon experimental observations, a plausible reaction mechanism is proposed.



INTRODUCTION

Carbon−carbon double bond cleavage represents a broad class of fundamental transformations in organic chemistry.[1,2] In this regard, both well-known and representative examples are the catalytic cleavage of C=C bonds to new C=C bonds (olefin metathesis)[1] and the oxidative cleavage of C=C bonds to C=O bonds.[2] In the past decades, olefin metathesis catalyzed by transition-metal carbene complexes has been developed as a powerful and straightforward synthetic approach in the manipulation of carbon−carbon double bonds, which has an important synthetic impact on fields ranging from materials science[3] to biochemistry[4] to natural-product synthesis.[5] Likewise, the oxidative cleavage of C=C bonds is among the most powerful and broadly applicable synthetic tools of modern organic chemistry,[2] resulting in the formation of carbonyl compounds that widely occur in natural and synthetic bioactive molecules.[6] While successful for olefin metathesis and the oxidative cleavage of C=C bonds to C=O bonds, the cleavage of C=C bonds to construct C≡N bonds is much underdeveloped.[7] In 1950, Denton et al. reported the alumina-supported molybdic oxide catalyzed C=C bond cleavage of styrenes to produce aromatic nitriles at elevated temperature (524−552 °C).[7a] Later on, Chow presented the C=C bond cleavage of olefins to form nitriles through the combination of photoaddition and Beckmann reaction using organic compounds as nitrogen sources, which caused the formation of organic wastes.[7b] More recently, significant progress was made by Jiao with TEMPO-catalyzed C=C double-bond cleavage to produce oxo nitriles using molecular oxygen as the terminal oxidant and $TMSN_3$ as the nitrogen source.[7c] Despite these advances, some challenges still remain in this promising field. Therefore, it is extraordinarily important to find new methods to broaden this area. Herein, we report a metal-free nitrogenation reaction of alkenes through C=C bond cleavage in the presence of phenyliodonium diacetate (PIDA) and NH_4HCO_3 in aqueous medium, which illustrates a convenient method toward the synthesis of nitriles from readily available starting materials.

Nitriles are an important class of structural motifs that frequently occur in agrochemically useful and pharmaceutically active compounds.[8] Also, their widespread synthetic utility is highlighted by a myriad of possible nitrile transformations,[9] including the synthesis of benzoic acids/esters, amides, amines, aldehydes, and nitrogen-containing heterocycles.[10] Generally, nitriles are prepared through the Sandmeyer reaction of aryldiazonium salts;[11] the transition-metal-mediated cyanation of aryl halides with a cyanide source that generally is toxic;[12] the dehydration approach of amines, alcohols, or oximes;[13] and other methods.[14] However, these reactions suffered from the harsh reaction conditions, multiple steps, poor functional group tolerance, or the use of expensive and toxic reagents. Therefore, the development of direct, mild, and environmentally benign processes to access nitriles from basic chemical materials is always highly desirable. To the best of our knowledge, no examples in which nitriles were prepared from direct oxidative C=C bond cleavage of alkenes using ammonium salt as nitrogen source under metal-free conditions have been reported.

RESULTS AND DISCUSSION

Inspired by recent reports that, using PIDA as the oxidant, alkenes can be oxidized to produce aldehydes[15] and the fact that the synthesis of nitriles from aldehydes is well documented in the literature,[16] we envisioned that nitriles could be generated directly from alkenes in the presence of PIDA. To test this hypothesis, we initially chose styrene in a model reaction to test different reaction conditions. Selected data from this study are listed in Table 1. First, when the reaction was

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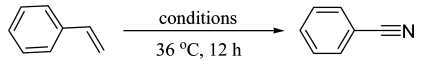
Table 1. Screening of Reaction Conditions[a]



1a 2a

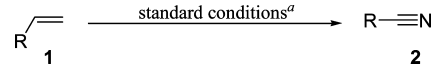
entry	PIDA (equiv)	NH_4HCO_3 (equiv)	solvent	convn (%)[b]	yield (%)[b]
1	1.2	6.0	CH_3CN	37	15
2	0	6.0	CH_3CN	0	0
3	1.2	0	CH_3CN	0	0
4	3.0	6.0	CH_3CN	70	43
5	5.0	6.0	CH_3CN	96	66
6	5.5	6.0	CH_3CN	>99	70
7	6.5	6.0	CH_3CN	>99	72
8	5.5	5.0	CH_3CN	98	69
9	5.5	3.0	CH_3CN	86	60
10	5.5	10	CH_3CN	>99	72
11	5.5	6.0	CH_2Cl_2	91	28
12	5.5	6.0	dioxane	87	21
13	5.5	6.0	EtOH	79	61
14	5.5	6.0	CH_3OH	90	77
15[c]	5.5	6.0	CH_3OH/H_2O	93	81
16[d]	5.5	6.0	CH_3OH/H_2O	94	86
17[e]	5.5	6.0	CH_3OH/H_2O	95	83
18[f]	5.5	6.0	CH_3OH/H_2O[d]	95	86
19[g]	5.5	6.0	CH_3OH/H_2O[d]	95	86

[a]Unless otherwise noted, the reaction was carried out with **1a** (0.2 mmol), PIDA, NH_4HCO_3, and solvent (2.0 mL) at 36 °C for 12 h. [b]Determined by GC. [c]0.1 mL water was added. [d]0.5 mL water was added. [e]1.0 mL water was added. [f]40 °C. [g]50 °C.

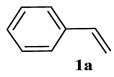
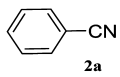
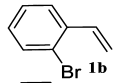
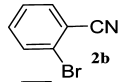
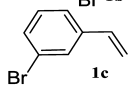
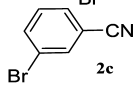
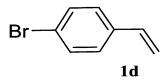
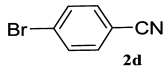
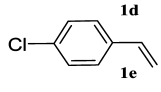
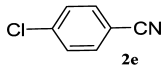
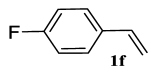
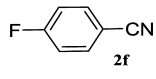
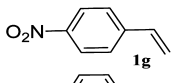
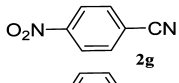
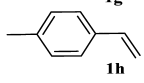
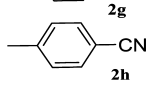
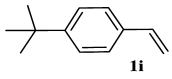
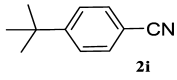
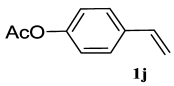
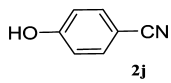
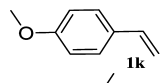
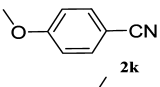
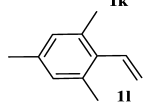
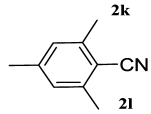
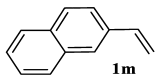
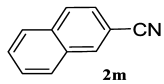
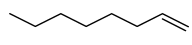
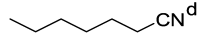
carried out in the presence of phenyliodonium diacetate (PIDA) and NH_4HCO_3 as the nitrogen source in acetonitrile at 36 °C for 12 h, much to our delight the desired nitrile product **2a** was produced in 15% yield (Table 1, entry 1). Control experiments showed that the reaction did not proceed in the absence of either PIDA or NH_4HCO_3 (Table 1, entries 2 and 3). Increasing the amount of PIDA increased the yield of **2a** and led to almost full conversion (Table 1, entries 4–7). Decreasing the amount of NH_4HCO_3 resulted in a slight drop in terms of product yield (Table 1, entries 8 and 9), while a comparable yield (72%) was obtained when the amount of NH_4HCO_3 was increased to 10 equiv (Table 1, entry 10). The influence of the solvent was also studied. When other solvents, such as CH_2Cl_2, dioxane, EtOH, and CH_3OH, were applied instead of CH_3CN, better yield (77%) was obtained in CH_3OH (Table 1, entries 11–14). The addition of water led to an increased yield (Table 1, entry 15). This promising result encouraged us to do further optimization with regard to the volume of water. Indeed, the best yield of 86% was obtained in the presence of 0.5 mL of water (Table 1, entries 16 and 17). A reaction temperature of 36 °C was selected because NH_4HCO_3 decomposes at this temperature and no further improvement was seen at higher temperatures (40–50 °C) (Table 1, entries 18 and 19). In addition, this reaction was repeated five times, and five runs were almost consistent in conversions and yields (see Figure S1 in the Supporting Information). From these experiments, we determined the optimized conditions to be PIDA (5.5 equiv), NH_4HCO_3 (6.0 equiv), CH_3OH (2 mL), H_2O (0.5 mL), 36 °C (this temperature is decomposition temperature of NH_4HCO_3), 12 h (for details, see Table S1 in the Supporting Information). However, when reaction of phenylacetylene was carried out under the optimized conditions, benzonitrile was obtained in only 10% yield.

With the optimized protocol in hand, we set out to explore the scope and limitation of the reaction with respect to various terminal alkenes (Table 2). We found that the reaction worked very well for a wide variety of substituted styrenes, affording the desired substituted benzonitriles in yields ranging from 65% to 93%. Styrene derivatives with electron-withdrawing substituents afforded the desired benzonitriles in 65–88% yield (Table 2, entries 2–7), while styrene derivatives bearing electron-donating substituents provided the desired benzonitriles in 83–93% yield (Table 2, entries 8 –12). It is worth pointing out that the C=C bond cleavage/hydrolyzation occurred in the

Table 2. Transformation of Terminal Olefins 1 to Nitriles 2



1 2

Entry	Substrate	Product	Yield(%)[b]
1	 1a	 2a	86[c]
2	 1b	 2b	65
3	 1c	 2c	72
4	 1d	 2d	88
5	 1e	 2e	82
6	 1f	 2f	85
7	 1g	 2g	82
8	 1h	 2h	88
9	 1i	 2i	93
10	 1j	 2j	83
11	 1k	 2k	92
12	 1l	 2l	90
13	 1m	 2m	89
14	 1n	 2n[d]	trace

[a]Standard conditions: alkenes (0.2 mmol), PIDA (5.5 equiv), NH_4HCO_3 (6 equiv), and CH_3OH/H_2O (2 mL/0.5 mL) at 36 °C for 12 h. [b]Isolated yield. [c]GC yield. [d]Determined by GC–MS.

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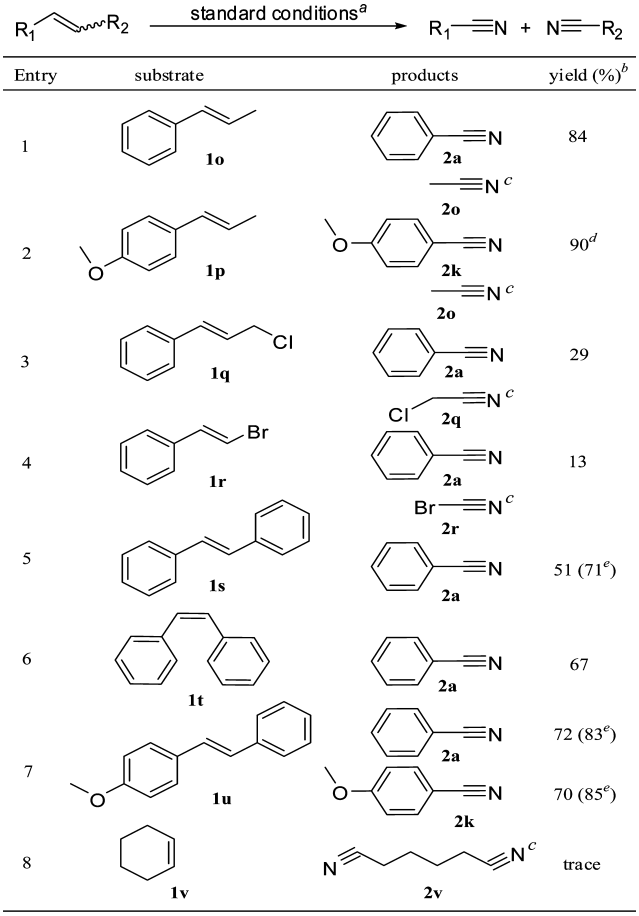
reaction of **1j** to produce **2j** in 83% yield (Table 2, entry 10). Notably, F, Cl, Br, and MeO substituents on the phenyl ring were well tolerated, which enables a potential application in further functionalization.[17] Additionally, a more bulky substrate, 2-vinylnaphthalene, also efficiently reacted to provide the product in 89% yield (Table 2, entry 13). While the results of styrenes were all favorable, the reactions of aliphatic alkenes were almost unreactive. For instance, when 1-octene was subjected to the same reaction conditions, only a trace amount of the desired product was detected by GC–MS (Table 2, entry 14). To investigate the possible on- carbon product, reaction of styrene was carried out under the optimized conditions. After the reaction, dimethoxymethane as another product was detected in the solvent by GC–MS (see Supporting Information).

Next, we applied our method to a range of internal alkenes (Table 3). Various β-substituted styrenes proceeded in a normal fashion to afford the desired nitriles in 13–90% yield (Table 3, entries 1–7). The reaction of *trans*- and *cis*-stilbene gave the same product benzonitrile in 51% and 67% yield, respectively (Table 3, entries 5 and 6). Moreover, better yields were obtained when **1s** and **1u** were used in this protocol (Table 3, entries 5 and 7). Unfortunately, cyclohexene did not proceed smoothly under the standard reaction conditions, and only trace amount of the desired product was detected by GC–MS (Table 3, entry 8).

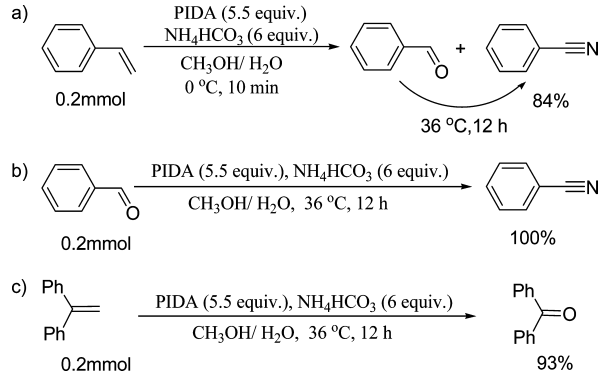
Table 3. Transformation of Internal Olefins to Nitriles



[a]Standard conditions: alkenes (0.2 mmol), PIDA (5.5 equiv), NH_4HCO_3 (6 equiv), and CH_3OH/H_2O (2 mL/0.5 mL) at 36 °C for 12 h. [b]GC yield. [c]**2o**, **2q**, and **2v** were detected by GC–MS; **2r** was not detected by GC–MS. [d]Isolated yield. [e]CH_3CN/H_2O (2 mL/0.5 mL).

To gain insight into the reaction mechanism, some information has been gathered. As shown in Scheme 1a, when the reaction was carried out at 0 °C, an intermediate benzaldehyde was detected by GC and GC–MS in the initial stage of the reaction. When the reaction temperature was increased to 36 °C and then reacted for 12 h under this conditions, benzaldehyde was completely consumed and benzonitrile was obtained in 84% yield (Scheme 1a). Also, we used NMR spectroscopy to monitor the reaction progress. An intermediate benzaldehyde was likewise observed in the initial stage of styrene reaction (see Supporting Information). To further support this, when benzaldehyde was reacted under the standard reaction condition, benzaldehyde was equally converted to benzonitrile (Scheme 1b). From this point, the 1,1-diphenylethylene would generate the corresponding ketone under the same reaction conditions. Unsurprisingly, the reaction of 1,1-diphenylethylene gave benzophenone in 93% yield (Scheme 1c). The data indicate that the reaction proceeds via the benzaldehyde as an intermediate. In addition, the bubbles generated during the reaction process were demonstrated to be CO_2 since it obviously could make limewater become turbid (see Figure S2 in the Supporting Information).

Scheme 1. Control Experiments



On the basis of these preliminary results and related reports,[15,16,18] a possible mechanism is proposed (Scheme 2). Initially, the alkene is oxidized to give the corresponding aldehydes (step a). Alternatively, the alkene undergoes dihydroxylation first to generate 1,2-diols, and its subsequent oxidative cleavage affords aldehydes.[18a] Next, the condensation of aldehyde with ammonia provides imine (step b). Finally, the imine is further oxidized to produce the desired nitrile (step c). However, when R_2 group was hydrogen, it would be trapped by methanol to provide dimethoxymethane (step d).

CONCLUSION

In summary, a novel way of synthesizing nitriles from alkenes through C=C bond cleavage was developed. By treating alkenes with NH_4HCO_3 in the presence of phenyliodonium diacetate (PIDA) in aqueous medium, the alkenes were found to proceed via the benzaldehyde as an intermediate, thus affording a variety of nitriles in moderate to good yields. This method features metal-free, mild reaction conditions, operational simplicity, good functional group tolerance, and use of NH_4HCO_3 as nitrogen source without the use of expensive and

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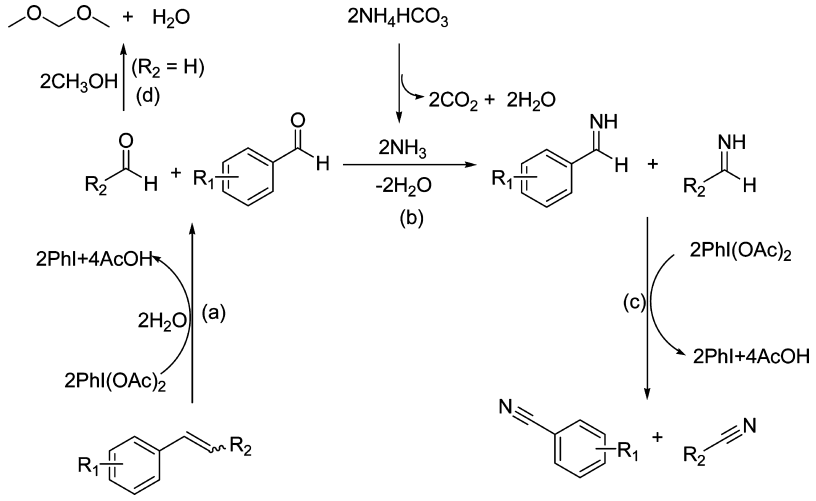
Scheme 2. Proposed Reaction Mechanism



toxic organic compounds as nitrogen source while avoiding the formation of organic wastes. From the results of the present study and on the basis of the proposed mechanism, it should be possible to develop novel chemical transformations through C−C bond cleavage, which should be of interest to both industrial and academic researchers.

EXPERIMENTAL SECTION

General Comments. All reagents and solvent used were obtained commercially and used without further purification unless indicated otherwise. Deionized water was used. $PhI(OAc)_2$ was prepared according to literature procedures.[19] All products were characterized by GC−MS, ^1H NMR, and ^{13}C NMR. Mass spectra were measured on a mass instrument (EI). Analyses of the yield and conversion of styrene were performed by gas phase chromatography, using a RTX-5 capillary column and a frame ionization detector (FID). ^1H NMR spectra were recorded on 400 MHz in $CDCl_3$, and ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$ using TMS as internal standard. Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quintet), and m (multiplet), and coupling constants (J) are reported in hertz. Copies of ^1H NMR and ^{13}C NMR spectra are provided as Supporting Information.

General Procedure for the Synthesis of Nitriles from Alkenes. A 10 mL sealed tube was charged with NH_4HCO_3 (1.2 mmol) and CH_3OH/H_2O (2 mL/0.5 mL). The mixture was stirred at room temperature until the solid was completely dissolved. Then alkene (0.2 mmol) was added. After stirring for 2 min, $PhI(OAc)_2$ (1.1 mmol) was added, and the reaction mixture was stirred at 36 °C for 12 h. After cooling to room temperature, the reaction mixture was diluted by addition of 20 mL ethyl acetate, dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was purified by column chromatography on silica gel to afford the desired product.

Reaction of Styrenes with NH_4HCO_3 in the Presence of Phenyliodonium Diacetate (PIDA) in CH_3OH/H_2O (as shown in Scheme 1a). In a 10 mL sealed tube, a mixture of 0.2 mmol styrene, 1.1 mmol $PhI(OAc)_2$, and 1.2 mmol NH_4HCO_3 in CH_3OH/H_2O(2 mL/0.5 mL) was stirred at 0 °C. After 10 min, an aliquot of sample was taken from the reaction mixture and analyzed by GC−MS. Then the reaction mixture was stirred at 36 °C for 12 h. The resulting mixture was analyzed by GC (bromobenzene as internal standard in GC analysis).

Reaction of Benzaldehyde with NH_4HCO_3 in the Presence of Phenyliodonium Diacetate (PIDA) in CH_3OH/H_2O (as shown in Scheme 1b). The reaction of benzaldehyde was performed according to the general procedure, and the resulting mixture was analyzed by GC (bromobenzene as internal standard in GC analysis).

Reaction of 1,1-Diphenylethylene with NH_4HCO_3 in the Presence of Phenyliodonium Diacetate (PIDA) in CH_3OH/H_2O (as shown in Scheme 1c). The reaction of 1,1-diphenylethylene was performed according to the general procedure. After cooling to room temperature, the reaction mixture was diluted with 20 mL ethyl acetate, dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was purified by column chromatography to afford the benzophenone in 93% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72−7.56 (m, 3H), 7.48 (dd, J = 7.9, 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.78, 137.61, 132.44, 130.08, 128.30.

Benzonitrile (2a). Following the general procedure, a colorless oil was obtained. The yield was determined by GC using bromobenzene as internal standard. Benzonitrile was obtained from **1a**, **1o**, **1q−u** in 86% (17.7 mg), 84% (17.3 mg), 29% (6.0 mg), 13% (2.7 mg), 51% (10.5 mg), 67% (13.8 mg), and 72% (14.8 mg) yield, respectively. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70−7.58 (m, 3H), 7.48 (dd, J = 7.9, 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.81, 132.15, 129.15, 118.87, 112.43. LRMS: m/z calcd for C_7H_5N (M + H) 104, found 104.

2-Bromobenzonitrile (2b).[20a] Following the general procedure, the product was isolated as a colorless solid in 65% yield (23.5 mg), mp = 53−55 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (m, 2H), 7.50−7.41 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.35, 133.90, 133.23, 127.64, 125.37, 117.16, 115.92. LRMS: m/z calcd for C_7H_4BrN (M + H) 183, found 183.

3-Bromobenzonitrile (2c).[20b] Following the general procedure, the product was isolated as a colorless solid in 72% yield (26.1 mg), mp = 38−40 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.61 (d, J = 7.7 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.15, 134.79, 130.73, 130.63, 122.94, 117.32, 114.23. LRMS: m/z calcd for C_7H_4BrN (M + H) 183, found 183.

4-Bromobenzonitrile (2d).[20c] Following the general procedure, the product was isolated as a colorless solid in 88% yield (32.0 mg), mp = 110−112 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.43, 132.66, 128.04, 118.08, 111.25. LRMS: m/z calcd for C_7H_4BrN (M + H) 183, found 183.

4-Chlorobenzonitrile (2e).[20d] Following the general procedure, the product was isolated as a colorless solid in 82% yield (22.5 mg), mp = 90−92 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.58, 133.40, 129.72, 117.99, 116.70, 110.80. LRMS: m/z calcd for C_7H_4ClN (M + H) 139, found 139.

4-Fluorobenzonitrile (2f).[20d] Following the general procedure, the product was isolated as a colorless solid in 85% yield (20.5 mg), mp = 33−35 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, J = 8.0 Hz, 2H), 7.69 (dd, J = 8.0, 4.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ165.05 (d, J = 256.5 Hz), 134.71 (d, J = 9.3 Hz), 118.05 (s), 116.88 (d, J = 22.7 Hz), 108.58 (d, J = 3.7 Hz). LRMS: m/z calcd for C_7H_4FN (M + H) 122, found 122.

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4-Nitrobenzonitrile (2g).[20g] Following the general procedure, the product was isolated as a colorless solid in 82% yield (24.2 mg), mp = 143−145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.58, 133.40, 129.72, 117.99, 116.70, 110.80. LRMS: m/z calcd for $C_7H_4N_2O_2$ (M + H) 149, found 149.

4-Methylbenzonitrile (2h).[20e] Following the general procedure, the product was isolated as a colorless solid in 88% yield (20.0 mg), mp = 28−30 °C. ^{1}H NMR (400 MHz, CDCl3) δ 7.47 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 7.9 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 143.70, 132.06, 129.85, 119.18, 109.33, 21.85. LRMS: m/z calcd for C_8H_4N (M + H) 118, found 118.

4-*Tert*-butylbenzonitrile (2i).[20f] Following the general procedure, the product was isolated as a colorless oil in 90% yield (28.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.66, 131.98, 126.18, 119.19, 109.31, 35.28, 30.96. LRMS: m/z calcd for $C_{11}H_4N$ (M + H) 160, found 160.

4-Hydroxybenzonitrile (2j).[20a] Following the general procedure, the product was isolated as a colorless solid in 78% yield (18.6 mg), mp = 110−112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 8.5 Hz, 2H), 6.79 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.16, 134.33, 119.28, 116.46, 103.20. LRMS: m/z calcd for C_7H_5ON (M + H) 120, found 120.

4-Methoxybenzonitrile (2k).[20a] Following the general procedure, the product was isolated as a colorless solid from **1k**, **1p**, **1u** in 92% (24.5 mg), 90% (23.9 mg) and 70% (18.6 mg) yield, respectively, mp = 57−59 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.85, 134.00, 119.26, 114.76, 103.97, 55.56. LRMS: m/z calcd for C_8H_7ON (M + H) 134, found 134.

2,4,6-Trimethylbenzonitrile (2l).[20f] Following the general procedure, the product was isolated as a colorless solid in 90% yield (25.8 mg), mp = 51−53 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (d, J = 0.5 Hz, 2H), 2.48 (s, 6H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.78, 141.99, 128.19, 117.62, 110.48, 21.56, 20.62. LRMS: m/z calcd for $C_{10}H_{11}N$ (M + H) 146, found 146.

2-Naphthonitrile (2m).[20c] Following the general procedure, the product was isolated as a colorless solid in 89% yield (27.1 mg), mp =63−65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.90 (t, J = 8.9 Hz, 3H), 7.67−7.58 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.66, 134.18, 132.26, 129.22, 129.07, 128.43, 128.08, 127.68, 126.36, 119.29, 109.38. LRMS: m/z calcd for $C_{11}H_7N$ (M + H) 154, found 154.

■ ASSOCIATED CONTENT

Supporting Information

Screening of reaction conditions and copies of ^{1}H and ^{13}C NMR spectra for the products. 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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