Electronic Supplementary Information

Copper-catalyzed cyanation of aryl iodides with α-cyanoacetates via

C-CN bond activation

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1. General experimental considerations

All the reactants and reagents were used upon received commercially without further purification. All the reactions were performed under air or O\textsubscript{2} atmosphere. \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded on a Bruker Avance III HD spectrometer (400 MHz for \textsuperscript{1}H NMR and 101 MHz for \textsuperscript{13}C NMR). Elemental analyses were performed using Elementar VARIOEL III. GC analyses were done using GC9790II equipment.

2. A typical procedure for copper-catalyzed cyanation of aryl halides with α-cyanoacetate

A Schlenk tube was charged with aryl halide (0.5 mmol), ethyl cyanoacetate (1.0 mmol), Cu\textsubscript{2}O (0.1 mmol), PPh\textsubscript{3} (0.1 mmol), AgNO\textsubscript{3} (0.5mmol) and NMP (2mL). The reaction mixture was stirred under O\textsubscript{2} at 130°C (oil bath) overnight. The reaction mixture was cooled and partitioned between ethyl acetate and saturated NH\textsubscript{4}Cl. The organic layer was then washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4} and concentrated in vacuum. The residue was purified by column chromatography on silica gel (eluent: V(petroleum ether)/V(EtOAC) = 20:1\textendash{}10:1) to provide pure products.
3. Spectroscopic characterization data for all the products

\[ \text{H}_3\text{CO} - \text{CN} \]

**4-methoxybenzonitrile (3a; 54 mg, 80%).** White solid; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.62 (d, \(J = 8.8\) Hz, 2H), 6.96 (d, \(J = 8.8\) Hz, 2H), 3.88 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): \(\delta\) 162.8, 134.0, 119.2, 114.8, 104.0, 55.5. Anal. Calcd for C\textsubscript{8}H\textsubscript{7}NO: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.28; H, 5.38; N, 10.47.

\[ \text{O}/\begin{array}{c} \text{CN} \\ \end{array} \]

**methyl 4-cyanobenzoate (3b; 61 mg, 76%).** White solid; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 8.15 (d, \(J = 8.1\) Hz, 2H), 7.77 (d, \(J = 8.1\) Hz, 2H), 3.98 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): \(\delta\) 165.4, 133.9, 132.2, 130.1, 117.9, 116.4, 52.7. Anal. Calcd for C\textsubscript{9}H\textsubscript{7}NO\textsubscript{2}: C, 67.07; H, 4.38; N, 8.69. Found: C, 67.12; H, 4.29; N, 8.73.

\[ \text{Cl} - \text{CN} \]

**4-chlorobenzonitrile (3c; 48 mg, 70%).** White solid; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.61 (d, \(J = 8.6\) Hz, 2H), 7.50 (d, \(J = 8.6\) Hz, 2H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): \(\delta\) 139.6, 133.4 129.7, 118.0, 110.8. Anal. Calcd for C\textsubscript{7}H\textsubscript{4}ClN: C, 61.12; H, 2.93; N, 10.18. Found: C, 61.23; H, 2.86; N, 10.03.

\[ \text{O}_2\text{N} - \text{CN} \]

**4-nitrobenzonitrile (3d; 55 mg, 75%).** White solid; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 8.38 (d, \(J = 8.8\) Hz, 2H), 7.91 (d, \(J = 8.8\) Hz, 2H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): \(\delta\) 150.1, 133.5, 124.3, 118.4, 116.8. Anal. Calcd for C\textsubscript{7}H\textsubscript{4}N\textsubscript{2}O\textsubscript{2}: C, 56.76; H, 2.72; N, 18.91. Found: C, 56.87; H, 2.65; N, 18.82.
3-nitrobenzonitrile (3e; 49 mg, 66%). White solid; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.52 (m, 2H), 8.02 (dt, $J = 7.7$, 1.3 Hz, 1H), 7.77 (t, $J = 8.0$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 148.2, 137.6, 130.7, 127.5, 127.2, 116.5, 114.2. Anal. Calcd for C$_7$H$_4$N$_2$O$_2$: C, 56.76; H, 2.72; N, 18.91. Found: C, 56.86; H, 2.66; N, 18.83.

2-nitrobenzonitrile (3f; 37 mg, 50%). Yellow solid; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.39 (m, 1H), 7.96 (m, 1H), 7.88 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 148.6, 135.6, 134.3, 133.7, 125.6, 114.9, 108.1. Anal. Calcd for C$_7$H$_4$N$_2$O$_2$: C, 56.76; H, 2.72; N, 18.91. Found: C, 56.83; H, 2.67; N, 18.87.

N-(4-cyanophenyl)acetamide (3g; 72 mg, 90%). White solid; $^1$H NMR (400 MHz, d$_6$-DMSO): $\delta$ 10.37 (s, 1H), 7.76 (s, 4H), 2.10 (s, 3H). $^{13}$C NMR (101 MHz, d$_6$-DMSO): $\delta$ 169.6, 143.9, 133.7, 119.5, 119.4, 105.1, 24.7. Anal. Calcd for C$_9$H$_8$N$_2$O: C, 67.49; H, 5.03; N, 17.49. Found: C, 67.62; H, 4.97; N, 17.38.

terephthalaronitrile (3h; 39 mg, 61%). Yellow solid; $^1$H NMR (400 MHz, d$_6$-DMSO): $\delta$ 8.09 (s, 4H). $^{13}$C NMR (101 MHz, d$_6$-DMSO): $\delta$ 133.7, 118.0, 116.2. Anal. Calcd for C$_8$H$_4$N$_2$: C, 74.99; H, 3.15; N, 21.86. Found: C, 74.86; H, 3.22; N, 21.92.

biphenyl-4-carbonitrile (3i; 80 mg, 89%). White solid; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.73 (q, $J = 8.4$ Hz, 4H), 7.62 (d, $J = 7.4$ Hz, 2H), 7.51 (t, $J = 7.4$ Hz, 2H), 7.45 (t, $J$
= 7.2 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 145.7, 139.2, 132.6, 129.1, 128.7, 127.7, 127.2, 118.9, 111.0. Anal. Calcd for C$_{13}$H$_9$N: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.28; H, 4.98; N, 7.94.

biphenyl-2-carbonitrile (3j; 46 mg, 51%). Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.80 (m, 1H), 7.67 (m, 1H), 7.59 (m, 2H), 7.53 (m, 5H). $^{13}$C NMR (101MHz, CDCl$_3$): $\delta$ 145.5, 138.2, 133.8, 132.8, 130.1, 128.7, 127.6, 118.7, 111.3. Anal. Calcd for C$_{13}$H$_9$N: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.21; H, 4.93; N, 7.86.

$\begin{array}{c} \text{O}_2\text{N} \end{array}$

4'-nitrobiphenyl-4-carbonitrile (3k; 108 mg, 96%). Yellow solid; $^1$H NMR (400 MHz, d$_6$-DMSO): $\delta$ 8.34 (d, $J$ = 8.8 Hz, 2H), 8.03 (m, 6H). $^{13}$C NMR (101MHz, d$_6$-DMSO): $\delta$ 147.9, 145.0, 142.7, 133.5, 129.0, 128.7, 124.6, 119.0, 112.0. Anal. Calcd for C$_{13}$H$_8$N$_2$O$_2$: C, 69.64; H, 3.60; N, 12.49. Found: C, 69.79; H, 3.54; N, 12.41.

$\begin{array}{c} \text{CN} \end{array}$

1-naphthonitrile (3l; 66 mg, 86%). White solid; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.22 (d, $J$ = 8.3 Hz, 1H), 8.06 (d, $J$ = 8.3 Hz, 1H), 7.91 (t, $J$ = 8.2 Hz, 2H), 7.68 (t, $J$ = 7.2 Hz, 1H), 7.62 (t, $J$ = 7.4 Hz, 1H), 7.51 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 133.3, 132.9, 132.6, 132.3, 128.7, 128.6, 127.6, 125.1, 124.9, 117.8, 110.1. Anal. Calcd for C$_{11}$H$_7$N: C, 86.25; H, 4.61; N, 9.14. Found: C, 86.28; H, 4.52; N, 9.20.
4. GC analyses of the crude product mixture

![Chemical Reaction]  

The product mixture for this model reaction was analyzed with GC technique. The signals are shown in Figure S1.

As shown in Figure S1, aside from the signals corresponding to the desired aryl nitrile product (with a retention time of 2.157 min) and reactants recovered (cyanoacetate at 1.574 min; aryl iodide at 2.291 min), there is no appreciable new organic compounds detected (Note: signal at 1.641 min corresponds to the solvent NMP whilst some minor impurity contained in NMP were detected at 1.403 and 1.453 min). The assignments of these signals were according to separate GC analyses of the corresponding organic compounds under similar conditions. Figures S2 to S5 show the signals appearing in GC analyses of the corresponding separate compounds.
Figure S2. GC analysis of the solvent NMP.

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Figure S3. GC analysis of NMP + ethyl cyanoacetate.
Figure S4. GC analysis of NMP + *para*-methoxyphenyl iodide.

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Figure S5. GC analysis of NMP + para-methoxybenzonitrile product.
5. $^1$H and $^{13}$C NMR spectra for all the products

4-methoxybenzonitrile (3a) ($^1$H NMR 400 MHz, CDCl$_3$; $^{13}$C NMR 101 MHz, CDCl$_3$).
methyl 4-cyanobenzoate (3b. $^1$H NMR 400 MHz, CDCl$_3$; $^{13}$C NMR 101 MHz, CDCl$_3$).
4-chlorobenzonitrile (3c. $^1$H NMR 400 MHz, CDCl$_3$; $^{13}$C NMR 101 MHz, CDCl$_3$).
4-nitrobenzonitrile (3d. $^1$H NMR 400 MHz, CDCl$_3$; $^{13}$C NMR 101 MHz, CDCl$_3$).
3-nitrobenzonitrile (3e. $^1$H NMR 400 MHz, CDCl$_3$; $^{13}$C NMR 101 MHz, CDCl$_3$).

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2-nitrobenzonitrile (3f. $^1$H NMR 400 MHz, CDCl$_3$; $^{13}$C NMR 101 MHz, CDCl$_3$).
N-(4-cyanophenyl)acetamide (3g. $^1$H NMR 400 MHz, d$_6$-DMSO; $^{13}$C NMR 101 MHz, d$_6$-DMSO).
terephthalonitrile (3h. $^1$H NMR 400 MHz, d$_6$-DMSO; $^{13}$C NMR 101 MHz, d$_6$-DMSO).
biphenyl-4-carbonitrile (3i. $^1$H NMR 400 MHz, CDCl$_3$; $^{13}$C NMR 101 MHz, CDCl$_3$).
biphenyl-2-carbonitrile(3j. $^1$H NMR 400 MHz, CDCl$_3$; $^{13}$C NMR 101 MHz, CDCl$_3$).
4′-nitrobiphenyl-4-carbonitrile (3k. $^1$H NMR 400 MHz, d$_6$-DMSO; $^{13}$C NMR 101 MHz, d$_6$-DMSO).
1-naphthonitrile (δH NMR 400 MHz, CDCl₃; δC NMR 101 MHz, CDCl₃).