Supporting information for
Palladium-catalyzed cyanation of aryl bromides with malononitrile through Carbon-Nitrile Bond Cleavage Mediated by Copper

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1 Experimental

1.1 General

All chemical reagents are obtained from commercial suppliers and used without further purification. All products are known compounds, which are identified by \(^1\)H NMR, \(^{13}\)C NMR and MS, and compared with previously reported data. Analytical thin-layer chromatography are performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. Mass spectra are taken on a Finnigan TSQ Quantum - MS instrument in the electrospray ionization (ESI) mode. \(^1\)H NMR and \(^{13}\)C NMR spectra are recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz and 125 MHz in CDCl\(_3\), respectively, and chemical shifts are reported in ppm. Elemental analyses are performed on a Yanagimoto MT3CHN recorder. GC analyses are performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m × 320 μm × 0.25 μm, carrier gas: H\(_2\), FID detection).

1.2 Experimental Procedure

**General procedure for the palladium-catalyzed cyanation of aryl bromides with malononitrile**: A mixture of aryl bromides (0.250 mmol), malononitrile (0.500 mmol), palladium catalyst (0.005 mmol), CuI (0.125 mmol), 1,10-phenanthroline (0.063 mmol), t-BuONa (0.500 mmol) and KF (0.500 mmol) in DMF or NMP (1 mL) is stirred at 130 °C for 24 h. Upon completion, the reaction mixture is diluted with EtOAc (4.0 mL), filtered through a bed of silica gel layered over Celite, The volatiles are removed in vacuo to afford the crude product. The extent of conversions is determined by GC. Further column chromatography on silica gel affords the pure desired product.
2. Characterization Data

Benzonitrile 2a\(^1\) colorless oil (17.5 mg, 68% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.46-7.49 (m, 2H), 7.60-7.66 (m, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 111.4, 117.9, 128.2, 131.1, 131.8. MS (ESI) \(m/z\): 103 (M\(^+\)).

4-Methoxybenzonitrile 2b\(^1\) colorless solid (23.3 mg, 70% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 3.87 (s, 3H), 6.95 (d, \(J = 9.0\) Hz, 2H), 7.59 (d, \(J = 9.0\) Hz, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 54.6, 103.8, 118.2, 133.0, 161.9. MS (ESI) \(m/z\): 133 (M\(^+\)).

4-(Trifluoromethyl)benzonitrile 2c\(^2\) colorless oil (31.2 mg, 73% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.77 (d, \(J = 8.0\) Hz, 2H), 7.82 (d, \(J = 8.0\) Hz, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 115.1, 116.4, 118.8-125.1 (q, \(J = 121.0\) Hz, 1C), 125.2, 131.7, 133.1-133.9 (q, \(J = 13.0\) Hz, 1C). MS (ESI) \(m/z\): 171 (M\(^+\)).

4-Methylbenzonitrile 2d\(^1\) colorless oil (22.8 mg, 78% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.43 (s, 3H), 7.28 (d, \(J = 8.0\) Hz, 2H), 7.55 (d, \(J = 8.0\) Hz, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 20.8, 108.3, 118.1, 128.9, 131.0, 142.7. MS (ESI) \(m/z\): 117 (M\(^+\)).

2-Naphthonitrile 2e\(^1\) white solid (28.7 mg, 75% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.62-7.69 (m, 3H), 7.91-7.95 (m, 3H), 8.26 (s, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 108.4, 118.2, 125.4, 126.7, 127.1, 127.4, 128.0, 128.2, 131.3, 133.2, 133.7. MS (ESI) \(m/z\): 153 (M\(^+\)).

1-Naphthonitrile 2f\(^3\) white solid (23.0 mg, 60% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.53-7.56 (t, \(J = 7.8\) Hz, 1H), 7.62-7.65 (t, \(J = 7.5\) Hz, 1H), 7.70-7.73 (t, \(J = 7.5\) Hz, 1H), 7.92-7.95 (t, \(J = 6.3\) Hz, 2H), 8.09 (d, \(J = 8.5\) Hz, 1H), 8.25 (d, \(J = 8.0\) Hz, 1H).
13C NMR (125 MHz, CDCl3) δ 109.3, 116.8, 123.9, 124.2, 126.6, 127.6, 131.4, 131.6, 132.0, 132.3. MS (ESI) m/z: 153 (M+).

Biphenyl-4-carbonitrile 2g[1] white solid (31.3 mg, 70% yield). 1H NMR (500 MHz, CDCl3) δ 7.43-7.45 (t, J = 7.3 Hz, 1H), 7.48-7.51 (t, J = 7.5 Hz, 2H), 7.60 (d, J = 7.0 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.5 Hz, 2H). 13C NMR (125 MHz, CDCl3) δ 110.0, 117.9, 126.2, 126.8, 127.7, 128.1, 131.6, 138.2, 144.7. MS (ESI) m/z: 179 (M+).

3,4-Dimethoxybenzonitrile 2h[1] colorless solid (26.5 mg, 65% yield). 1H NMR (500 MHz, CDCl3) δ 3.91 (s, 3H), 3.94 (s, 3H), 6.91 (d, J = 8.5 Hz, 1H), 7.09 (d, J = 1.5 Hz, 1H), 7.29-7.31 (dd, J = 8.3, 1.8 Hz, 1H). 13C NMR (125 MHz, CDCl3) δ 55.1, 102.9, 110.3, 113.0, 118.2, 125.5, 148.2, 151.9. MS (ESI) m/z: 163 (M+).

4-Hydroxybenzonitrile 2i[1] colorless solid (23.5 mg, 79% yield). 1H NMR (500 MHz, CDCl3) δ 6.20 (br, 1H), 6.91 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H). 13C NMR (125 MHz, CDCl3) δ 102.9, 115.4, 118.1, 133.3, 158.7. MS (ESI) m/z: 119 (M+).

4-Aminobenzonitrile 2j[1] colorless solid (22.4 mg, 76% yield). 1H NMR (500 MHz, CDCl3) δ 4.16 (br, 2H), 6.65 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H). 13C NMR (125 MHz, CDCl3) δ 99.4, 113.5, 119.0, 132.8, 149.3. MS (ESI) m/z: 118 (M+).

4-(Dimethylamino)benzonitrile 2k[4] colorless solid (22.3 mg, 61% yield). 1H NMR (500 MHz, CDCl3) δ 3.04 (s, 6H), 6.64 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 9.0 Hz, 2H). 13C NMR (125 MHz, CDCl3) δ 38.9, 96.4, 110.4, 119.7, 132.4, 151.5. MS (ESI) m/z: 146 (M+).

2-Aminobenzonitrile 2l[5] colorless solid (21.2 mg, 72% yield). 1H NMR (500 MHz, CDCl3) δ 4.40 (br, 2H), 6.73-6.76 (m, 2H), 7.32-7.35 (m, 1H), 7.38-7.40 (m, 1H). 13C
NMR (125 MHz, CDCl₃) δ 95.1, 114.2, 116.6, 117.1, 131.4, 133.0, 148.6. MS (ESI) m/z: 118 (M⁺).

4-nitrobenzonitrile 2m[1] yellow solid (14.8 mg, 40% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.91 (d, J = 8.5 Hz, 2H), 8.38 (d, J = 9.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 115.8, 117.4, 123.3, 132.5, 149.1. MS (ESI) m/z: 148 (M⁺).

4-Hydroxy-3,5-dimethylbenzonitrile 2s[6] colorless solid (26.5 mg, 72% yield). ¹H NMR (500 MHz, CDCl₃) δ 2.27 (s, 6H), 5.39 (br, 1H), 7.30 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 14.7, 102.4, 118.5, 123.3, 131.6, 155.2. MS (ESI) m/z: 147 (M⁺).

3. NMR Spectra of All Products

![NMR spectra image]