Supporting Information

Cu-catalyzed atom transfer radical addition reactions of alkenes with

α-bromoacetonitrile

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1. General Information

Unless otherwise stated, starting materials were purchased from TCI or Energy-Chemical Limited and used as supplied without further purification. Solvents were used directly without further purification. All deuterated solvents were purchased from Cambridge Isotope Laboratories. ¹H NMR and ¹³C NMR spectra were recorded at 25 °C on a Brüker Advance 400 spectrometer (¹H: 400 MHz and ¹³C:100 MHz). ¹H NMR chemical shifts were determined relative to internal (CH₃)₄Si (TMS) at δ 0.00 ppm or to the signal of the residual protonated solvent: CDCl₃ at δ 7.26 ppm. ¹³C NMR chemical shifts were determined relative to the signal of the solvent: CDCl₃ at δ 7.26 ppm. ¹³C NMR chemical shifts were recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets), coupling constants (Hz) and integration. Melting points were obtained with a micro melting point XT4A Beijing Keyi electrooptic apparatus and are uncorrected. High-resolution mass data were recorded on a Waters LCT PremierxeTM (USA). All reactions were monitored by thin layer chromatography (TLC) with Taizhou GF254 silica gel coated plates. Flash column chromatography was carried out using 200-300 mesh silica gel at increased pressure.

2. General procedure for the preparation of 3

3a as an example



To a solution of the styrene **1a** (35 μ L, 0.3 mmol) in CH₃CN (1.0 ml) was added the α bromoacetonitrile **2a** (38 μ L, 0.60 mmol), Phen (10.8 mg, 0.06 mmol), and CuI (5.7 mg, 0.03 mmol) under N₂ in a Schlenck tube. The reaction mixture was stirred at 110 °C for 1.0 h. After the reaction finished, the reaction mixture was cooled to room temperature and quenched by water. The mixture was extracted with EtOAc (3.0 mL×3), the combined organic phases were dried over

anhydrous Na_2SO_4 and the solvent was evaporated under vacuum. The residue was purified by column chromatography (petroleum ether /ethyl acetate = 40:1) to give the corresponding products **3a** (61.1 mg, 91%).

3. General procedure for the preparation of 4

4a as an example

$$Ph + NC Br \xrightarrow{Cul (10 mol%)}{Phen (20 mol%)} Ph CN$$
1a 2a $CH_3CN, 110 °C, N_2$ 4a

To a solution of the styrene **1a** (35 μ L, 0.3 mmol) in CH₃CN (1.0 ml) was added the α bromoacetonitrile **2a** (38 μ L, 0.6 mmol), Phen (10.8 mg, 0.06 mmol), CuI (5.7 mg, 0.03 mmol), and DBU (91 μ L, 0.60 mmol) under N₂ in a Schlenck tube. The reaction mixture was stirred at 110 °C for 1.0 h. After the reaction finished, the reaction mixture was cooled to room temperature and quenched by water. The mixture was extracted with EtOAc (3.0 mL×3), the combined organic phases were dried over anhydrous Na₂SO₄ and the solvent was evaporated under vacuum. The residue was purified by column chromatography (petroleum ether /ethyl acetate = 40:1) to give the corresponding products **4a** (38.7 mg, 90%).

4. Analytical Data of Compounds 3, 4 and 6



4-bromo-4-phenylbutanenitrile 3a

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.38-2.62 (m, 4H), 5.04 (dd, J_1 = 5.6 Hz, J_2 = 8.8 Hz, 1H), 7.32-7.42 (s, 5H); ¹³C NMR (100 MHz, CDCl₃): δ = 16.3, 35.2, 52.1, 118.2, 127.1, 128.9, 140.0. HRMS(ESI-TOF) Calcd for C₁₀H₁₁BrN, [M+H]⁺ *m/z* 224.0075, 226.0054; Found 224.0079, 226.0057.



4-bromo-4-(4-fluorophenyl)butanenitrile 3b

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.36-2.49 (m, 1H), 2.49-2.58 (m, 3H), 5.03 (dd, J_I = 6.0 Hz, J_2 = 8.4 Hz, 1H), 7.06 (t, J = 8.4 Hz, 2H), 7.39 (dd, J_I = 5.2 Hz, J_2 = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 16.4, 35.4, 51.2, 116.0 (d, J = 22.0 Hz), 118.1, 129.0 (d, J = 8 Hz), 136.1 (d, J = 3.0 Hz), 162.6 (d, J = 247.0 Hz). HRMS(ESI-TOF) Calcd for C₁₀H₁₀BrFN, [M+H]⁺ *m*/z 241.9981, 243.9960; Found 241.9985, 243.9963.



4-bromo-4-(4-chlorophenyl)butanenitrile 3c

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.35-2.42 (m, 1H), 2.48-2.60 (m, 3H), 5.00 (dd, J_1 = 5.6 Hz, J_2 = 8.4 Hz, 1H), 7.34 (s, 4H); ¹³C NMR (100 MHz, CDCl₃): δ = 16.3, 35.1, 50.9, 118.1, 128.5, 129.2, 134.7, 138.6. HRMS(ESI-TOF) Calcd for C₁₀H₁₀BrClN, [M+H]⁺ *m/z* 257.9685, 259.9665; Found 257.9687, 259.9668.



4-bromo-4-(4-bromophenyl)butanenitrile 3d

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.34-2.39 (m, 1H), 2.48-2.58 (m, 3H), 4.98 (dd, J_1 = 5.6 Hz, J_2 = 8.4 Hz, 1H), 7.28 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 16.3, 35.1, 50.9, 118.1, 122.9, 128.8, 132.1, 139.2. HRMS(ESI-TOF) Calcd for C₁₀H₁₀Br₂N, [M+H]⁺ *m/z* 303.9160; Found 303.9165.



4-bromo-4-(4-nitrophenyl)butanenitrile 3e

Yellow solid. mp: 76-78 °C. Petroleum ether/ethyl acetate = 20/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.38-2.44 (m, 1H), 2.51-2.69 (m, 3H), 5.08 (dd, J_1 = 5.6 Hz, J_2 = 9.6 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 8.25 (d, J = 8.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 16.4, 34.9, 49.6, 117.8, 124.3, 128.3, 147.0, 148.0. HRMS(ESI-TOF) Calcd for C₁₀H₁₀BrN₂O₂, [M+H]⁺ *m/z* 268.9926, 270.9905; Found 268.9929, 270.9907.



4-bromo-4-(p-tolyl)butanenitrile 3f

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.36 (s, 3H), 2.39-2.58 (m, 4H), 5.02-5.05 (m, 1H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 16.4, 21.1, 35.3, 52.3, 118.3, 127.0, 129.6, 137.1, 139.0. HRMS(ESI-TOF) Calcd for C₁₁H₁₃BrN, [M+H]⁺ *m/z* 238.0231, 240.0211; Found 238.0237, 240.0215.



4-bromo-4-(4-(tert-butyl)phenyl)butanenitrile 3g

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 1.33 (s, 9H), 2.40-2.59 (m, 4H), 5.04-5.08 (m, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 16.3, 31.1, 34.6, 35.2, 52.3, 118.3, 125.8, 126.8, 137.0, 152.0. HRMS(ESI-TOF) Calcd for C₁₄H₁₉BrN, [M+H]⁺ *m/z* 280.0701, 282.0680; Found 280.0704, 282.0685.



4-bromo-4-(3-fluorophenyl)butanenitrile 3h

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.37-2.44 (m, 1H), 2.49-2.60 (m, 3H), 4.99-5.02 (m, 1H), 7.03 (t, *J* = 8.4 Hz, 1H), 7.12 (d, *J* = 9.6 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.35 (dd, *J*₁ = 7.6 Hz, *J*₂ = 14.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 16.3, 35.2, 50.8, 114.3 (d, *J* = 23.0 Hz), 116.0 (d, *J* = 21.0 Hz), 118.1, 122.8 (d, *J* = 3.0 Hz), 130.6 (d, *J* = 9.0 Hz), 142.5 (d, *J* = 8.0 Hz), 162.8 (d, *J* = 246.0 Hz). HRMS(ESI-TOF) Calcd for C₁₀H₁₀BrFN, [M+H]⁺ *m/z* 241.9981, 243.9960; Found 241.9983, 243.9958.



4-bromo-4-(3-chlorophenyl)butanenitrile 3i

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.35-2.44 (m, 1H), 2.49-2.60 (m, 3H), 4.96-4.99 (m, 1H), 7.28-7.32 (m, 3H), 7.40 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 16.4, 35.2, 50.8, 118.0, 125.4, 127.4, 129.2, 130.3, 134.9, 142.1. HRMS(ESI-TOF) Calcd for C₁₀H₁₀BrClN, [M+H]⁺ *m/z* 257.9685, 259.9665; Found 257.9687, 259.9669.



4-bromo-4-(3-bromophenyl)butanenitrile 3j

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.36-2.40 (m, 1H), 2.48-2.58 (m, 3H), 4.94-4.97 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.46 (dd, *J*₁ = 1.2 Hz, *J*₂ = 8.0 Hz, 1H), 7.55 (d, *J* = 1.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 16.3, 35.1, 50.6, 118.0, 122.8, 125.8, 130.2, 130.5, 132.0, 142.3. HRMS(ESI-TOF) Calcd for C₁₀H₁₀Br₂N, [M+H]⁺ *m/z* 303.9160; Found 303.9165.



4-bromo-4-(2-chlorophenyl)butanenitrile 3k

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.42-2.47 (m, 1H), 2.54-2.63 (m, 3H), 5.52 (dd, J_1 = 5.2 Hz, J_2 = 9.2 Hz, 1H), 7.27-7.33 (m, 2H), 7.39 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1H), 7.57 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 16.3, 34.6, 47.6, 118.1, 127.7, 128.8, 130.0, 132.7, 137.4. HRMS(ESI-TOF) Calcd for C₁₀H₁₀BrClN, [M+H]⁺ *m/z* 257.9685, 259.9665; Found 257.9688, 259.9669.



4-bromo-4-(2-bromophenyl)butanenitrile 31

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.40-2.47 (m, 1H), 2.51-2.62 (m, 3H), 5.50 (dd, J_1 = 5.2 Hz, J_2 = 8.8 Hz, 1H), 7.16-7.20 (m, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.56-7.59 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 16.2, 34.7, 50.5, 118.1, 123.0, 128.3, 128.9, 130.2, 133.2, 139.0. HRMS(ESI-TOF) Calcd for C₁₀H₁₀Br₂N, [M+H]⁺ *m/z* 303.9160; Found 303.9165.



4-(pyridin-2-yl)butanenitrile 3m

Colorless oil. Petroleum ether/ethyl acetate = 20/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.60-2.72 (m, 4H), 5.16 (dd, J_I = 5.2 Hz, J_2 = 8.4 Hz, 1H), 7.28 (dd, J_I = 2.4 Hz, J_2 = 4.0 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.72-7.76 (m, 1H), 8.63 (d, J = 4.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 16.1, 32.9, 51.6, 118.4, 122.8, 123.6, 137.2, 149.7, 158.1. HRMS(ESI-TOF) Calcd for C₉H₁₀BrN₂, [M+H]⁺ *m/z* 225.0027, 227.0007; Found 225.0024,

4-bromo-5-(3,4-dimethoxyphenyl)pentanenitrile 3n

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 1.97-2.23 (m, 2H), 2.58-2.61 (m, 2H), 3.05-3.25 (m, 2H), 3.86 (s, 3H), 3.87 (s, 3H), 4.18-4.25 (m, 1H), 6.71-6.82 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 16.1, 33.3, 44.9, 54.2, 55.8, 55.8, 111.1, 112.1, 118.6, 121.2, 129.7, 148.1, 148.9. HRMS(ESI-TOF) Calcd for C₁₃H₁₇BrNO₂, [M+H]⁺ *m/z* 298.0443, 300.0422; Found 298.0446, 300.0425.



3-bromo-5-cyanopentyl benzoate 30

Colorless oil. Petroleum ether/ethyl acetate = 30/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.15-2.37 (m, 4H), 2.63-2.68 (m, 2H), 4.22-4.29 (m, 1H), 4.45-4.61 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 8.02-8.04 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 16.0, 34.6, 37.8, 50.3, 62.3, 118.4, 128.4, 129.6, 129.8, 133.2, 166.3. HRMS(ESI-TOF) Calcd for C₁₃H₁₅BrNO₂, [M+H]⁺ *m/z* 296.0286, 298.0266; Found 296.0291, 298.0273.



4,6-dibromohexanenitrile 3p

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.12-2.59 (m, 4H), 2.61-2.70 (m, 2H), 3.57-3.60 (m, 2H), 4.22-4.29 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 15.9, 30.2, 34.3, 41.1, 52.0, 118.4. HRMS(ESI-TOF) Calcd for C₆H₁₀Br₂N, [M+H]⁺ *m/z* 255.9160; Found 255.9165.



4-iodo-4-phenylbutanenitrile 3q

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.30-2.68 (m, 4H), 5.15-5.19 (m, 1H), 7.28-7.41 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ = 18.0, 29.1, 36.8, 118.1, 127.0, 128.6, 129.1, 141.9. HRMS(ESI-TOF) Calcd for C₁₀H₁₁IN, [M+H]⁺ *m/z* 271.9936; Found 271.9939.



4-(4-chlorophenyl)-4-iodobutanenitrile 3r

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.25-2.61 (m, 4H), 5.13 (dd, J_1 = 6.4 Hz, J_2 = 8.8 Hz, 1H), 7.29-7.35 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ = 17.9, 27.6, 36.4, 117.8, 128.3, 129.1, 134.0, 140.5. HRMS(ESI-TOF) Calcd for C₁₀H₁₀ClIN, [M+H]⁺ *m/z* 305.9546; Found 305.9548.



4-(2-chlorophenyl)-4-iodobutanenitrile 3s

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.33-2.72 (m, 4H), 5.57 (dd, J_1 = 6.0 Hz, J_2 = 8.8 Hz, 1H), 7.22-7.37 (m, 3H), 7.53-7.55 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 17.8, 24.0, 35.7, 117.9, 127.8, 128.4, 129.6, 130.3, 132.2, 139.1. HRMS(ESI-TOF) Calcd for C₁₀H₁₀ClIN, [M+H]⁺ *m/z* 305.9546; Found 305.9543.



(E)-4-phenylbut-3-enenitrile 4a

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 3.30 (dd, J_1 = 1.6 Hz, J_2 = 5.6 Hz, 2H), 6.06 (dt, J_1 = 15.6, J_2 = 5.6 Hz, 1H), 6.75 (d, J = 15.6 Hz, 1H), 7.27-7.39 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ = 20.8, 116.7, 117.3, 126.5, 128.3, 128.7, 134.7, 135.6. HRMS(ESI-TOF) Calcd for C₁₀H₁₀N, [M+H]⁺ *m/z* 144.0813; Found 144.0811.



(E)-4-(4-fluorophenyl)but-3-enenitrile 4b

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 3.29 (dd, J_1 = 1.2 Hz, J_2 = 5.6 Hz, 2H), 5.98 (dt, J_1 = 15.6, J_2 = 5.6 Hz, 1H), 6.71 (d, J = 15.6 Hz, 1H), 7.03 (t, J = 8.8 Hz, 2H), 7.34 (dd, J_1 = 5.6, J_2 = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 20.7, 115.7 (d, J = 22.0 Hz), 116.5 (d, J = 2.0 Hz), 117.2, 128.1 (d, J = 8.0 Hz), 131.8 (d, J = 3.0 Hz), 133.5, 162.7 (d, J = 246.0 Hz). HRMS(ESI-TOF) Calcd for C₁₀H₉FN, [M+H]⁺ *m/z* 162.0719; Found 162.0725.



(E)-4-(4-chlorophenyl)but-3-enenitrile 4c

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 3.29 (dd, J_1 = 1.6 Hz, J_2 = 5.6 Hz, 2H), 6.04 (dt, J_1 = 16.0, J_2 = 5.6 Hz, 1H), 6.70 (dt, J_1 = 15.6, J_2 = 1.6 Hz, 1H), 7.27-7.34 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ = 20.7, 117.0, 117.4, 127.7, 128.9, 133.4, 134.0, 134.1. HRMS(ESI-TOF) Calcd for C₁₀H₉ClN, [M+H]⁺ *m/z* 178.0424; Found 178.0427.



(E)-4-(4-bromophenyl)but-3-enenitrile 4d

White solid. mp: 62-64 °C. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 3.29 (dd, J_1 = 1.6 Hz, J_2 = 5.6 Hz, 2H), 6.05

(dt, $J_1 = 15.6$, $J_2 = 5.6$ Hz, 1H), 6.68 (d, J = 16.0, 1H), 7.23 (d, J = 8.4, 2H), 7.46 (d, J = 8.4, 2H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 20.8$, 117.0, 117.5, 122.2, 127.9, 131.8, 133.4, 134.5. HRMS(ESI-TOF) Calcd for C₁₀H₉BrN, [M+H]⁺ *m*/*z* 221.9918, 223.9898; Found 221.9923, 223.9901.



(E)-4-(4-nitrophenyl)but-3-enenitrile 4e

White solid. mp: 50-51 °C. Petroleum ether/ethyl acetate = 20/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 3.38 (dd, J_1 = 1.6 Hz, J_2 = 5.2 Hz, 2H), 6.26 (dt, J_1 = 16.0, J_2 = 5.6 Hz, 1H), 6.83 (d, J = 16.0, 1H), 7.51 (d, J = 8.4, 2H), 8.20 (d, J = 8.8, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 20.9, 116.5, 121.7, 124.1, 127.1, 132.5, 141.8, 147.3. HRMS(ESI-TOF) Calcd for C₁₀H₉N₂O₂, [M+H]⁺ *m/z* 189.0664; Found 189.0667.



(E)-4-(p-tolyl)but-3-enenitrile 4f

White solid. mp: 50-52 °C. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.43 (s, 3H), 3.27-3.28 (m, 2H), 5.99 (dt, J_I = 16.0, J_2 = 5.6 Hz, 1H), 6.69 (d, J = 15.6, 1H), 7.14 (d, J = 8.0, 2H), 7.26 (d, J = 8.0, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 20.7, 21.2, 115.6, 117.4, 126.3, 129.4, 132.8, 134.5, 138.2. HRMS(ESI-TOF) Calcd for C₁₁H₁₂N, [M+H]⁺ *m/z* 158.0970; Found 158.0965.



(E)-4-(4-(tert-butyl)phenyl)but-3-enenitrile 4g

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 1.33 (s, 9H), 3.29 (dd, J_1 = 1.6 Hz, J_2 = 5.6 Hz, 2H), 6.02 (dt, J_1 = 15.6, J_2 = 5.6 Hz, 1H), 6.72 (d, J = 15.6, 1H), 7.32 (d, J = 8.4, 2H), 7.37 (d, J = 8.4, 2H); ¹³C NMR (100

MHz, CDCl₃): δ = 20.8, 31.2, 34.6, 115.8, 117.4, 125.6, 126.2, 132.9, 134.4, 151.5. HRMS(ESI-TOF) Calcd for C₁₄H₁₈N, [M+H]⁺ *m/z* 200.1439; Found 200.1435.



(*E*)-4-([1,1'-biphenyl]-4-yl)but-3-enenitrile 4h

White solid. mp: 86-88 °C. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 3.32 (d, *J* = 4.2, 2H), 6.10 (dt, *J*₁ = 15.6, *J*₂ = 5.6 Hz, 1H), 6.79 (d, *J* = 16.0, 1H), 7.37 (t, *J* = 7.2, 1H), 7.44-7.48 (m, 4H), 7.60 (t, *J* = 8.0, 4H); ¹³C NMR (100 MHz, CDCl₃): δ = 20.8, 116.7, 117.3, 126.9, 126.9, 127.4, 127.5, 128.8, 134.2, 134.6, 140.4, 141.0. HRMS(ESI-TOF) Calcd for C₁₆H₁₄N, [M+H]⁺ *m/z* 220.1126; Found 220.1123.



(E)-4-(3-cyanoprop-1-en-1-yl)phenyl acetate 4i

Colorless oil. Petroleum ether/ethyl acetate = 30/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.30 (s, 3H), 3.29 (dd, J_1 = 1.2 Hz, J_2 = 5.6 Hz, 2H), 6.01 (dt, J_1 = 16.0, J_2 = 5.6 Hz, 1H), 6.72 (d, J = 15.6 Hz 1H), 7.06 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 20.7, 21.1, 117.0, 117.2, 121.9, 127.4, 133.4, 133.6, 150.5, 169.3. HRMS(ESI-TOF) Calcd for C₁₂H₁₂NO₂, [M+H]⁺ *m/z* 202.0868; Found 202.0868.



(E)-4-(4-methoxyphenyl)but-3-enenitrile 4j

White solid. mp: 78-79 °C. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 3.26 (dd, J_1 = 1.6 Hz, J_2 = 5.6 Hz, 2H), 3.81 (s, 3H), 5.90 (dt, J_1 = 15.6, J_2 = 5.6 Hz, 1H), 6.66 (d, J = 16.0 Hz 1H), 6.87 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 20.7, 55.2, 114.0, 114.3, 117.5, 127.6, 128.4, 134.0, 159.6. HRMS(ESI-TOF) Calcd for C₁₁H₁₂NO, [M+H]⁺ *m/z* 174.0919; Found

(E)-4-(4-ethoxyphenyl)but-3-enenitrile 4k

White solid. mp: 81-82 °C. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 1.42 (t *J* = 6.8 Hz 3H), 3.26 (d, *J* = 5.2 Hz, 2H), 4.04 (q, *J* = 6.8 Hz, 2H), 5.90 (dt, *J*₁ = 15.2, *J*₂ = 5.6 Hz, 1H), 6.66 (d, *J* = 15.6 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 14.8, 20.8, 63.5, 114.2, 114.7, 117.5, 127.7, 128.3, 134.2, 159.1. HRMS(ESI-TOF) Calcd for C₁₂H₁₄NO, [M+H]⁺ *m/z* 188.1075; Found 188.1077.



(E)-4-(3-fluorophenyl)but-3-enenitrile 4l

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 3.31 (dd, J_1 = 1.6 Hz, J_2 = 5.6 Hz, 2H), 6.07 (dt, J_1 = 16.0, J_2 = 5.6 Hz, 1H), 6.72 (d, J = 15.6 Hz, 1H), 6.98 (dt, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.07 (d, J = 9.6 Hz, 1H), 7.13 (d, J = 7.6 Hz, 1H), 7.28-7.33 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 20.7, 112.9 (d, J = 22.0 Hz), 115.1 (d, J = 21.0 Hz), 117.0, 118.2, 122.4 (d, J = 3.0 Hz), 130.2 (d, J = 8.0 Hz), 133.5 (d, J = 2.0 Hz), 137.9 (d, J = 8.0 Hz), 163.0 (d, J = 245.0 Hz). HRMS(ESI-TOF) Calcd for C₁₀H₉FN, [M+H]⁺ *m/z* 162.0719; Found 162.0722.



(E)-4-(3-chlorophenyl)but-3-enenitrile 4m

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 3.30 (dd, J_1 = 1.6 Hz, J_2 = 5.6 Hz, 2H), 6.07 (dt, J_1 = 15.6, J_2 = 5.6 Hz,

1H), 6.69 (d, J = 16.0, 1H), 7.23-7.30 (m, 3H), 7.36 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 20.7, 116.9, 118.3, 124.7, 126.3, 128.2, 129.9, 133.3, 134.6, 137.4.$ HRMS(ESI-TOF) Calcd for C₁₀H₉ClN, [M+H]⁺ m/z 178.0424; Found 178.0427.



(E)-4-(3-bromophenyl)but-3-enenitrile 4n

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 3.30 (dd, J_1 = 1.6 Hz, J_2 = 5.6 Hz, 2H), 6.07 (dt, J_1 = 16.0, J_2 = 5.6 Hz, 1H), 6.68 (d, J = 16.0, 1H), 7.21 (t, J = 8.0, 1H), 7.28 (d, J = 8.0, 1H), 7.41 (d, J = 8.0, 1H), 7.52 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 20.7, 116.9, 118.3, 122.8, 125.2, 129.3, 130.2, 131.2, 133.2, 137.7. HRMS(ESI-TOF) Calcd for C₁₀H₉BrN, [M+H]⁺ *m/z* 221.9918, 223.9898; Found 221.9923, 223.9896.



(E)-4-(2-fluorophenyl)but-3-enenitrile 40

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 3.32 (dd, J_1 = 1.6 Hz, J_2 = 5.6 Hz, 2H), 6.18 (dt, J_1 = 16.0, J_2 = 5.6 Hz, 1H), 6.85 (d, J = 16.0 Hz, 1H), 7.04-7.14 (m, 2H), 7.23-7.29 (m, 1H), 7.40 (dt, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 21.2, 115.9 (d, J = 22.0 Hz), 117.1, 119.7 (d, J = 6.0 Hz), 123.4 (d, J = 13.0 Hz), 124.2 (d, J = 4.0 Hz), 127.7 (d, J = 3.0 Hz), 127.9 (d, J = 3.0 Hz), 129.6 (d, J = 9.0 Hz), 160.3 (d, J = 249.0 Hz). HRMS(ESI-TOF) Calcd for C₁₀H₉FN, [M+H]⁺ *m*/z 162.0719; Found 162.0715.



(E)-4-(2-chlorophenyl)but-3-enenitrile 4p

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 3.34 (dd, J_1 = 1.6 Hz, J_2 = 5.6 Hz, 2H), 6.05 (dt, J_1 = 15.6, J_2 = 6.0 Hz, 1H), 7.11 (d, J = 15.6, 1H), 7.21-7.25 (m, 2H), 7.36-7.38 (m, 1H), 7.46-7.49 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 21.0, 117.0, 119.7, 127.0, 127.0, 129.3, 129.8, 131.3, 133.1, 133.9. HRMS(ESI-TOF) Calcd for C₁₀H₉CIN, [M+H]⁺ *m/z* 178.0424; Found 178.0421.



(E)-4-(2-bromophenyl)but-3-enenitrile 4q

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 3.30 (dd, J_1 = 1.6 Hz, J_2 = 5.6 Hz, 2H), 6.07 (dt, J_1 = 15.6, J_2 = 5.6 Hz, 1H), 6.69 (d, J = 15.6, 1H), 7.22-7.29 (m, 3H), 7.36 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 20.7, 116.9, 118.3, 124.7, 126.4, 128.2, 129.9, 133.3, 134.7, 137.4. HRMS(ESI-TOF) Calcd for C₁₀H₉BrN, [M+H]⁺ *m/z* 221.9918, 223.9898; Found 221.9913, 223.9895.



(E)-4-(2,5-dimethylphenyl)but-3-enenitrile 4r

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.32 (s, 6H), 3.31 (dd, J_1 = 1.2 Hz, J_2 = 5.6 Hz, 2H), 5.93 (dt, J_1 = 15.6, J_2 = 5.6 Hz, 1H), 6.93 (d, J = 15.6, 1H), 7.02 (d, J = 8.0, 1H), 7.06 (d, J = 7.6, 1H), 7.21 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 19.2, 20.9, 21.0, 117.4, 117.7, 126.4, 128.9, 130.3, 132.5, 132.8, 134.6, 135.6. HRMS(ESI-TOF) Calcd for C₁₂H₁₄N, [M+H]⁺ *m/z* 172.1126; Found 172.1123.



4,4-diphenylbut-3-enenitrile 4s

White solid. mp: 76-78 °C. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 3.16 (d, *J* = 7.6, 2H), 6.05 (t, *J* = 7.6, 1H), 7.18-7.46 (m, 10H); ¹³C NMR (100 MHz, CDCl₃): δ = 18.3, 115.4, 118.1, 127.4, 128.1, 128.2, 128.3, 128.8, 129.3, 137.9, 140.6, 147.5. HRMS(ESI-TOF) Calcd for C₁₆H₁₄N, [M+H]⁺ *m/z* 220.1126; Found 220.1125.



2-(1H-inden-3-yl)acetonitrile 4t

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 3.43 (s, 2H), 3.57 (s, 2H), 6.87 (s, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 19.9, 40.7, 117.1, 121.0, 123.6, 125.1, 126.7, 130.9, 136.1, 142.8, 143.7. HRMS(ESI-TOF) Calcd for C₁₁H₁₀N, [M+H]⁺ *m/z* 156.0813; Found 156.0811.



(E)-4-(9H-carbazol-9-yl)but-3-enenitrile 4u

White solid. mp: 88-89 °C. Petroleum ether/ethyl acetate = 20/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 3.39 (dd, J_1 = 1.6 Hz, J_2 = 6.0 Hz, 2H), 5.94 (dt, J_1 = 14.0, J_2 = 6.0 Hz, 1H), 7.30-7.34 (m, 3H), 7.47-7.51 (m, 2H), 7.58 (t, J = 8.0 Hz, 2H), 8.07 (d, J = 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 19.0, 106.0, 110.2, 117.3, 120.3, 121.0, 124.1, 126.4, 127.7, 139.1. HRMS(ESI-TOF) Calcd for C₁₆H₁₃N₂, [M+H]⁺ *m/z* 233.1079; Found 233.1076.



4-(4-chlorophenyl)pent-4-enenitrile 4v and (E)-4-(4-chlorophenyl)pent-3-enenitrile 4v' (3:2) Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.07 (s, 3H), 2.47 (t, *J* = 7.2 Hz, 2H), 2.83 (t, *J* = 7.2 Hz, 2H), 3.25 (d, *J* = 6.8 Hz, 2H), 5.23 (s, 1H), 5.41 (s, 1H), 5.70 (dt, *J*₁ = 7.2 Hz, *J*₂ = 1.2 Hz, 1H), 7.29-7.35 (m, 8H); ¹³C NMR (100 MHz, CDCl₃): δ = 16.3, 16.4, 16.9, 31.1, 115.1, 115.4, 117.8, 118.8, 127.1, 127.4, 128.6, 128.8, 133.7, 134.0, 137.7, 140.3, 143.6. HRMS(ESI-TOF) Calcd for C₁₁H₁₁ClN, [M+H]⁺ *m/z* 192.0580; Found 192.0575.



7-bromo-4-phenylhept-4-enenitrile 6

Colorless oil. Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. ¹H NMR (400 MHz; CDCl₃): δ = 2.35 (t, *J* = 7.2 Hz, 2H), 2.83-2.91 (m, 4H), 3.51 (t, *J* = 6.8 Hz, 2H), 5.78 (t, *J* = 7.2 Hz, 1H), 7.29-7.40 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ = 16.2, 25.9, 31.8, 32.2, 119.0, 126.5, 127.7, 128.2, 128.6, 139.0, 140.3. HRMS(ESI-TOF) Calcd for C₁₃H₁₅BrN, [M+H]⁺ *m/z* 264.0388, 266.0367; Found 264.0385, 266.0363.

5. Mechanistic Study

5.1 Radical Inhibition Experiments

Ph → NC Br 1a 2a	Cul (10 mol%) Phen (20 mol%) CH ₃ CN, 110 °C, N ₂ NC Br Ph Br Ph 3a
Additive	3a , yield (%)
none	91
BHT (2 equiv)	10
TEMPO (2 equiv)	0

Reactions were carried out with 1a (0.3 mmol), 2a (0.60 mmol), CuI (10 mol %), and Phen (20 mol %) in CH₃CN

(1 mL) under N_2 atmosphere at 110 °C for 1.0 h. Yield of the isolated product.

Ph + NC Br - 1a 2a	Cul (10 mol%) Phen (20 mol%) DBU (2.0 equiv) CH ₃ CN, 110 °C w or w/o additive
Additive	4a , yield (%)
none	90
BHT (2 equiv)	16
TEMPO (2 equiv)	0

Reactions were carried out with 1a (0.3 mmol), 2a (0.6 mmol), CuI (10 mol %), Phen (20 mol %) and DBU (2.0

equiv) in CH₃CN (1 mL) under N₂ atmosphere at 110 °C for 1.0 h. Yield of the isolated product.

5.2 Radical Clock Experiment



To a solution of the styrene **5** (43.3 mg, 0.3 mmol) in CH₃CN (1.0 ml) was added the α bromoacetonitrile **2a** (38 µL, 0.60 mmol), Phen (10.8 mg, 0.06 mmol), and CuI (5.7 mg, 0.03 mmol) under N₂ in a Schlenck tube. The reaction mixture was stirred at 110 °C for 1.0 h. After the reaction finished, the reaction mixture was cooled to room temperature and quenched by water. The mixture was extracted with EtOAc (3.0 mL×3), the combined organic phases were dried over anhydrous Na₂SO₄ and the solvent was evaporated under vacuum. The residue was purified by column chromatography (petroleum ether /ethyl acetate = 40:1) to give the corresponding products **6** and **7** (59.6 mg, total yield 83%).

6. ¹H and ¹³C NMR Spectra of Compounds 3, 4 and 6

Product 3a

























Product 3k

84 86 86 86 86 86 86 83 83 83 83 83 83 83 83 83 83 83 83 83	5.517	6 5 7 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8



Product 31

887 571 558 558 558 558 558 558 558 558 558 55	515 502 493 481	802 802 803 805 805 805 805 805 805 805 805
666666666666666	5.5.5.5	2222222222222222222











210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10





S36



Product 3s





















S45











Product 41





Product 4n



Product 4o





Product 4p











 10 0 -10

210 200 190 180 170 160 150 140 130 120 110 100 90



S58















