An Efficient Solvent-free Selective Monoalkylation of Arylacetonitriles with Mono, Bis- and Tris-Primary Alcohols Catalyzed by a Cp*Ir Complex

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Experimental Section

General. Unless otherwise noted all reagents were obtained from commercial suppliers and used without further purification. For ^1H and ^{13}C NMR spectra the deuterated solvents indicated were used. Chemical shifts (δ) are reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS). Mass spectrometric data (MS) were obtained by electrospray ionization (ESI) or electron ionization (EI). For preparative scale chromatography, silica gel (60 Å particle size 35 – 70 micron) was used. Infra-red spectra were recorded either as a thin film on sodium chloride plates or using the solids attachment. Thin films were prepared by the evaporation of a solution of the compound in chloroform. Melting points are uncorrected.

(A) General procedure for the $[\text{IrCp}^*\text{Cl}_2]_2$ catalyzed alkylation cascade of nitriles (1a-f) by alcohols (2a-o).

A mixture of nitrile (1 mmol), $[\text{IrCp}^*\text{Cl}_2]_2$ (2.5 mol% based on nitrile), KOH (15 mol%) and alcohol (1.5 or 3.0 mmol) was flushed with nitrogen. The reaction mixture was then magnetically stirred in a schlenk tube at 100 °C for 12-17 h. The progression of the reaction was monitored by TLC. After the reaction was complete, the crude mixture was analyzed by ^1H NMR and thereafter purified by column chromatography eluting with diethyl ether, diethyl ether/petroleum or methanol/diethyl ether.

(B) General procedure for the $[\text{IrCp}^*\text{Cl}_2]_2$ catalyzed alkylation cascade of nitriles (1b, e), by alcohols (2b-p) under microwave irradiation.

A mixture of nitrile (1 mmol), $[\text{IrCp}^*\text{Cl}_2]_2$ (2.5 mol% based on nitrile), KOH (15 mol%) and alcohol (1.5 or 3 mmol) was loaded and sealed under air in a microwave tube. The reaction mixture was then magnetically stirred under microwave irradiation (300 W) for 10 min at 110 °C. The crude reaction mixture was analyzed by ^1H NMR and thereafter purified by column chromatography eluting with diethyl ether, diethyl ether/petroleum or methanol/diethyl ether.

2,3-Diphenylpropanenitrile (3a)

Prepared by the general procedure **A** from phenylacetonitrile (0.117 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and benzyl alcohol (0.324 g, 3.00 mmol). Work up followed by column chromatography eluting with 1:9 v/v ether-petroleum ether gave **3a** (0.182 g, 88%) as colorless plates, mp 53-55 °C (lit.¹ 54 °C); (Found: C, 87.10; H, 6.20; N, 7.00; C₁₅H₁₃N requires: C, 86.92; H, 6.32; N, 6.76 %); $\nu_{\max}$ (film) 2236 (CN stretching) cm⁻¹; m/z (EI, %) 207 (M⁺, 12), 116 (PhCHCN⁺, 5), 91 (PhCH₂⁺, 100); δ_{H} (300 MHz, CDCl₃); 7.48-7.29 (m, 8H), 7.26-7.19 (m, 2H), 4.07 (dd, 1H, J = 8.2 and 6.7 Hz), 3.27 (dd, 1H, J = 13.6 and 8.2 Hz) and 3.20 (dd, 1H, J = 13.6 and 6.7 Hz); δ_{C} (75.5 MHz, CDCl₃); 136.8 (C), 135.7 (C), 129.7 (2 × CH), 129.5 (2 × CH), 129.1 (2 × CH), 128.7 (CH), 128.0 (2 × CH), 127.9 (CH), 120.9 (C), 42.7 (CH₂) and 40.2 (CH).

2-(4-Fluorophenyl)-3-phenylpropanenitrile (3b)

Prepared by the general procedure **A** from 4-fluorophenylacetonitrile (0.135 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and benzyl alcohol (0.324 g, 3.0 mmol). Work up followed by column chromatography eluting with 1:9 v/v ether-petroleum ether gave **3b** (0.206 g, 92%) as colorless plates, mp 84-86 °C; (Found: C, 79.75; H, 5.50; F, 8.30; N, 6.10; C₁₅H₁₂FN requires: C, 79.98; H, 5.37; F, 8.43; N, 6.22 %); $\nu_{\max}$ (film) 2236 (CN stretching) cm⁻¹; m/z (EI, %) 225 (M⁺, 10), 134 (4-F-PhCHCN⁺, 8), 91 (CH₂Ph⁺, 100); δ_{H} (300 MHz, CDCl₃); 7.33-7.23 (m, 3H), 7.18 (ddt, 2H, J = 8.7, 5.1 and 2.6 Hz), 7.13-7.06 (m, 2H), 7.00 (tt, 2H, J = 8.7 and 2.1 Hz), 3.99 (app. t, 1H, J = 7.3 Hz), 3.19 (dd, 1H, J = 13.6 and 7.9 Hz) and 3.10 (dd, 1H, J = 13.6 and 6.7 Hz); δ_{C} (75.5 MHz, CDCl₃); 162.9 (d, C, $^1J_{\text{CF}}$ = 247.6 Hz), 136.4 (C), 131.4 (d, C, $^4J_{\text{CF}}$ = 3.8 Hz), 129.8 (d, 2 × CH, $^3J_{\text{CF}}$ = 8.3 Hz), 129.7 (2 × CH), 129.2 (2 × CH), 127.9 (CH), 120.7 (C), 116.5 (d, 2 × CH, $^2J_{\text{CF}}$ = 21.9 HZ), 42.6 (CH₂) and 39.4 (CH).

3-Phenyl-2-(4-(trifluoromethyl)phenyl)propanenitrile (3c)

Prepared by the general procedure A from 4-(trifluoromethyl)phenylacetonitrile (0.185 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and benzyl alcohol (0.324 g, 3.0 mmol). Work up followed by column chromatography eluting with 1:9 v/v ether-petroleum ether gave **3c** (0.242 g, 88%) as colorless plates, mp 74-76 °C; (Found: C, 69.60; H, 4.45; F, 20.70; N, 5.15; C₁₆H₁₂F₃N requires: C, 69.81; H, 4.39; F, 20.70; N, 5.09 %); $\nu_{\max}$ (solid) 2244 (CN stretching) cm⁻¹; m/z (EI, %) 275 (M⁺, 100%), 256 (M⁺-F, 15); δ_{H} (300 MHz, CDCl₃); 7.60 (d, 2H, J = 8.1 Hz), 7.36 (d, 2H, J = 8.1 Hz), 7.33-7.24 (m, 3H), 7.10 (dd, 2H, J = 7.7 and 1.3 Hz), 4.06 (app. t, 1H, J = 7.3 Hz), 3.20 (dd, 1H, J = 13.7 and 7.9 Hz) and 3.13 (dd, 1H, J = 13.7 and 6.7 Hz); δ_{C} (75.5 MHz, CDCl₃); 139.5 (C), 136.0 (C), 131.2 (q, C, $^2J_{\text{CF}}$ = 33 Hz), 129.7 (2 × CH), 129.2 (2 × CH), 128.5 (2 × CH), 128.1 (CH), 126.4 (t, 2 × CH, $^3J_{\text{CF}}$ = 3.8 Hz), 124.3 (q, C, $^1J_{\text{CF}}$ = 273 Hz), 120.1 (C), 42.3 (CH₂) and 40.0 (CH).

2-(4-Methoxyphenyl)-3-phenylpropanenitrile (3d)

Prepared by the general procedure A from 4-methoxyphenylacetonitrile (0.147 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and benzyl alcohol (0.324 g, 3.0 mmol). Work up followed by column chromatography eluting with 1:9 v/v diethyl ether-petroleum ether gave **3d** (0.220 g, 93%) as colorless needles, mp 67.5-68.5 °C (lit.² 66-67 °C); (Found: C, 81.25; H, 6.35; N, 5.75; C₁₆H₁₅NO requires: C, 80.98; H, 6.37; N, 5.9 %); $\nu_{\max}$ (solid) 2236 (CN stretching) cm⁻¹; m/z (EI, %) 237 (M⁺, 15), 146 (4-CH₃O-PhCHCN⁺, 89), 91 (CH₂Ph⁺, 100); δ_{H} (300 MHz, CDCl₃); 7.41-7.28 (m, 3H), 7.26-7.13 (m, 2H), 7.21 (d, 2H, J = 8.8 Hz), 6.92 (dd, 2H, J = 8.8 and 2.0 Hz), 4.00 (dd, 1H, J = 8.0 and 6.8 Hz), 3.85 (s, 3H), 3.22 (dd, 1H, J = 13.6 and 8.0 Hz), 3.14 (dd, 1H, J = 13.6 and 6.8 Hz); δ_{C} (75.5 MHz, CDCl₃); 159.8 (C), 136.8 (C), 129.7 (2 × CH), 129.1 (2 × CH), 129.0 (2 × CH), 127.7 (CH), 127.6 (C), 121.1 (C), 114.8 (2 × CH), 55.8 (CH₃), 42.7 (CH₂) and 39.4 (CH).

3-Phenyl-2-(pyridin-3-yl)propanenitrile (3e)

Prepared by the general procedure A from 3-pyridylacetonitrile (0.118 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and benzyl alcohol (0.324 g, 3.0 mmol). Work up followed by column chromatography eluting with diethyl ether gave **3e** (0.183 g, 88%) as colorless plates, mp 61.5-62.5 °C (lit.³ 64-65 °C (benzene, petroleum ether)); (Found: C, 80.45; H, 5.65; N, 13.70; C₁₄H₁₂N₂ requires: C, 80.74; H, 5.81; N, 13.45 %); $\nu_{\max}$ (solid) 2242 (CN stretching) cm⁻¹; m/z (ESI, %) 209 (M+1, 50), 250 (M+42, 100); δ_{H} (300 MHz, CDCl₃); 8.55 (dd, 1H, J = 4.9 and 1.3 Hz), 8.45 (d, 1H, J = 2.1 Hz), 7.56 (dt, 1H, J = 7.9 and 1.9 Hz), 7.26 (m, 4H), 7.09 (m, 2H), 4.06 (app. t, 1H, J = 7.2 Hz), 3.19 (dd, 1H, J = 7.7 and 13.6 Hz) and 3.11 (dd, 1H, J = 13.6 and 6.7 Hz); δ_{C} (75.5 MHz, CDCl₃); 150.1 (CH), 149.3 (CH), 135.8 (C), 135.5 (CH), 131.4 (C), 129.7 (2 × CH), 129.2 (2 × CH), 128.11 (CH), 124.1 (CH), 119.9 (C), 42.1 (CH₂) and 37.6 (CH).

3-Phenyl-2-(pyridin-2-yl)propanenitrile (3f)

Prepared by the general procedure A from 2-pyridylacetonitrile (0.118 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and benzyl alcohol (0.324 g, 3.0 mmol). Work up followed by column chromatography eluting with diethyl ether gave **3f** (0.185 g, 89%) as colorless plates, mp 64.5-66.5 °C (lit.⁴ 66-67 °C); (Found: C, 80.45; H, 5.65; N, 13.70; C₁₄H₁₂N₂ requires: C, 80.74; H, 5.81; N, 13.45 %); $\nu_{\max}$ (solid) 2246 (CN stretching) cm⁻¹; m/z (ESI, %) 209 (M+1, 100); δ_{H} (300 MHz, CDCl₃); 8.63 (d, 1H, J = 4.6 Hz), 7.65 (td, 1H, J = 7.8 and 1.8 Hz), 7.32-7.21 (m, 5H), 7.19-7.14 (m, 2H), 4.20 (dd, 1H, J = 8.6 and 5.9 Hz), 3.36 (dd, 1H, J = 13.5 and 5.9 Hz) and 3.25 (dd, 1H, J = 13.5 and 8.6 Hz); δ_{C} (75.5 MHz, CDCl₃); 154.9 (C), 150.4 (CH), 137.6 (CH), 136.8 (C), 129.6 (2 × CH), 129.0 (2 × CH), 127.8 (CH), 123.5 (CH), 122.6 (CH), 120.1 (C), 42.4 (CH) and 40.4 (CH₂).

3-(3,4-Dimethoxyphenyl)-2-(pyridin-3-yl)propanenitrile (3g)

Prepared by general procedures **A** and **B** from 3-pyridylacetonitrile (0.118 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 3,4-dimethoxybenzyl alcohol (0.504 g, 3.0 mmol). Work up followed by column chromatography eluting with diethyl ether gave **3g** (0.230 g, 86% from **A** and 0.219 g, 82% from **B**) as colorless plates, mp 55-57 °C; (Found: C, 71.35; H, 5.85; N, 10.45; C₁₆H₁₆N₂O₂ requires: C, 71.62; H, 6.01; N, 10.44 %); $\nu_{\max}$ (solid) 2244 (CN stretching) cm⁻¹; m/z (ESI, %) 269 (M+1, 55), 310 (M+42, 100); δ_{H} (300 MHz, CDCl₃); 8.58 (dd, 1H, J = 4.7 and 1.4 Hz), 8.47 (d, 1H, J = 2.3 Hz), 7.55 (dt, 1H, J = 7.9 and 1.8 Hz), 7.29 (dd, 1H, J = 7.9 and 4.7 Hz), 6.78 (d, 1H, J = 8.2 Hz), 6.65 (dd, 1H, J = 8.2 and 2.0 Hz), 6.56 (d, 1H, J = 2.0 Hz), 4.07 (app. t, 1H, J = 7.0 Hz), 3.85 (s, 3H), 3.78 (s, 3H), 3.17 (dd, 1H, J = 13.6 and 7.4 Hz) and 3.10 (dd, 1H, J = 13.6 and 6.7 Hz); δ_{C} (75.5 MHz, CDCl₃); 149.9 (CH), 149.3 (C), 149.2 (CH), 148.9 (C), 135.5 (CH), 131.5 (C), 128.1 (C), 124.0 (CH), 122.0 (CH), 120.0 (C), 112.9 (CH), 111.7 (CH), 56.2 (2 x CH₃), 41.7 (CH₂) and 37.7 (CH).

3-(Methylene-3,4-di-oxy-phenyl)-2-(pyridin-3-yl)propanenitrile (3h)

Prepared by general procedures **A** and **B** from 3-pyridylacetonitrile (0.118 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol), 3,4-dioxymethylenebenzyl alcohol (0.228 g, 1.5 mmol) and toluene (1.0 mL). Work up followed by column chromatography eluting with diethyl ether gave **3h** (0.228 g, 90% from **A** and 0.218 g, 86% from **B**) as colorless prisms, mp 97-99 °C; (Found: C, 71.45; H, 4.65; N, 11.10; C₁₅H₁₂N₂O₂ requires: C, 71.42; H, 4.79; N, 11.1 %); $\nu_{\max}$ (film) 2241 (CN stretching) cm⁻¹; m/z (ESI, %) 253 (M+1, 93), 294 (M+42, 100); δ_{H} (300 MHz, CDCl₃); 8.58 (dd, 1H, J = 4.9 and 1.5 Hz), 8.46 (d, 1H, J = 2.3 Hz), 7.60 (dt, 1H, J = 7.9 and 2.0 Hz), 7.31 (dd, 1H, J = 7.9 and 4.9 Hz), 6.72 (d, 1H, J = 7.9 Hz), 6.59 (d, 1H, J = 1.5 Hz), 6.53 (dd, 1H, J = 7.9 and 1.5 Hz), 5.90 (s, 2H), 4.02 (app. t, 1H, J = 7.2 Hz), 3.14 (dd, 1H, J = 13.6 and 7.7 Hz) and 3.06 (dd, 1H, J = 13.6 and 6.7 Hz); δ_{C} (75.5 MHz, CDCl₃); 150.1 (CH), 149.3 (CH), 148.3 (C), 147.5 (C), 135.4 (CH), 131.3 (C), 129.3 (C), 124.2 (CH), 123.0 (CH), 119.9 (C), 109.8 (CH), 108.9 (CH), 101.6 (CH₂), 41.9 (CH₂) and 37.8 (CH).

3-(4-Fluorophenyl)-2-(pyridin-3-yl)propanenitrile (**3i**)

Prepared by general procedures **A** and **B** from 3-pyridylacetonitrile (0.118 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 4-fluorobenzyl alcohol (0.378 g, 3.0 mmol). Work up followed by column chromatography eluting with diethyl ether gave **3i** (0.201 g, 89% from **A** and 0.201 g, 89% from **B**) as colorless plates, mp 117-118 °C; (Found: M⁺, 226.0910. C₁₄H₁₁N₂F requires M⁺, 226.0906); $\nu_{\max}$ (film) 2241 (CN stretching) cm⁻¹; m/z (ESI, %) 227 (M+1, 89), 268 (M+42, 100); δ_{H} (300 MHz, CDCl₃); 8.58 (dd, 1H, J = 4.9 and 1.5 Hz), 8.46 (d, 1H, J = 2.3 Hz), 7.57 (dt, 1H, J = 7.9 and 2.0 Hz), 7.29 (dd, 1H, J = 7.9 and 4.9 Hz), 7.06 (ddt, 2H, J = 8.7, 5.4 and 2.6 Hz), 6.97 (tt, 2H, J = 8.7 and 2.6 Hz), 4.06 (app. t, 1H, J = 7.2 Hz), 3.19 (dd, 1H, J = 13.7 and 7.7 Hz) and 3.14 (dd, 1H, J = 13.7 and 6.7 Hz); δ_{C} (75.5 MHz, CDCl₃); 162.6 (d, C, $^1J_{\text{CF}}$ = 247 Hz), 150.2 (CH), 149.2 (CH), 135.5 (CH), 131.5 (d, C, $^4J_{\text{CF}}$ = 3.0 Hz), 131.4 (d, 2 × CH, $^3J_{\text{CF}}$ = 8.3 Hz), 131.2 (C), 124.2 (CH), 119.7 (C), 116.1 (2 × CH, $^2J_{\text{CF}}$ = 21.9 Hz), 41.3 (CH₂) and 37.6 (CH).

3-(4-Chlorophenyl)-2-(pyridin-3-yl)propanenitrile (**3j**)

Prepared by general procedures **A** and **B** from 3-pyridylacetonitrile (0.118 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 4-chlorobenzyl alcohol (0.427 g, 3.0 mmol). Work up followed by column chromatography eluting with diethyl ether gave **3j** (0.210 g, 87% from **A** and 0.205 g, 85% from **B**) as colorless plates, mp 93-95 °C; (Found: C, 69.30; H, 4.60; Cl, 14.50; N, 11.55; C₁₄H₁₁ClN₂ requires: C, 69.28; H, 4.57; Cl, 14.61; N, 11.54 %); $\nu_{\max}$ (film) 2243 (CN stretching) cm⁻¹; m/z (ESI, %) 243 (M+1, C₁₄H₁₁³⁵ClN₂, 28), 245 (M+1, C₁₄H₁₁³⁷ClN₂, 9); δ_{H} (300 MHz, CDCl₃); 8.59 (dd, 1H, J = 4.9 and 1.5 Hz), 8.46 (d, 1H, J = 2.3 Hz), 7.57 (dt, 1H, J = 7.9 and 1.9 Hz), 7.30 (dd, 1H, J = 7.9 and 4.9 Hz), 7.26 (d, 2H, J = 8.4 Hz), 7.03 (d, 2H, J = 8.4 Hz), 4.07 (app. t, 1H, J = 7.2 Hz), 3.18 (dd, 1H, J = 13.8 and 7.7 Hz) and 3.12 (dd, 1H, J = 13.8 and 6.9 Hz); δ_{C} (75.5 MHz, CDCl₃); 150.2 (CH), 149.2 (CH), 135.5 (CH), 134.2 (C), 134.1 (C), 131.1 (2 × CH), 131.1 (C), 129.4 (2 × CH), 124.2 (CH), 119.6 (C), 41.4 (CH₂) and 37.4 (CH).

3-(3,5-Difluorophenyl)-2-(pyridin-3-yl)propanenitrile (**3k**)

Prepared by general procedures **A** and **B** from 3-pyridylacetonitrile (0.118 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 3,5-difluorobenzyl alcohol (0.216 g, 1.5 mmol). Work up followed by column chromatography eluting with 1:1 v/v diethyl ether-petroleum ether gave **3k** (0.200 g, 82% from **A** and 0.209 g, 86% from **B**) as colorless plates, mp 87-88 °C; (Found: C, 68.65; H, 4.20; F, 15.65; N, 11.50; C₁₄H₁₀F₂N₂ requires: C, 68.85; H, 4.13; F, 15.56; N, 11.47 %); $\nu_{\max}$ (film) 2244 (CN stretching) cm⁻¹; m/z (ESI, %) 245 (M+1, 85), 286 (M+42, 100); δ_{H} (300 MHz, CDCl₃); 8.62 (dd, 1H, J = 4.9 and 1.5 Hz), 8.51 (d, 1H, J = 2.3 Hz), 7.62 (dt, 1H, J = 7.9 and 1.9 Hz), 7.34 (dd, 1H, J = 7.9 and 4.9 Hz), 6.75 (tt, 1H, J = 9.0 and 2.3 Hz), 6.69 (dt, 1H, J = 6.7 and 2.1 Hz), 6.65 (dt, 1H, J = 6.7 and 2.1 Hz), 4.09 (app. t, 1H, J = 7.2 Hz), 3.21 (dd, 1H, J = 13.7 and 7.9 Hz) and 3.14 (dd, 1H, J = 13.7 and 6.7 Hz); δ_{C} (75.5 MHz, CDCl₃); 161.8 (dd, 2 × C, $^{1,3}J_{\text{CF}}$ = 248 and 12.8 Hz), 150.4 (CH), 149.1 (CH), 139.4 (t, C, $^3J_{\text{CF}}$ = 9 Hz), 135.3 (CH), 130.8 (C), 124.3 (CH), 119.3 (C), 112.7 (dd, 2 × CH, $^{2,4}J_{\text{CF}}$ = 17.3 and 8.3 Hz), 103.8 (t, CH, $^2J_{\text{CF}}$ = 24.8 Hz), 41.5 (CH₂) and 37.0 (CH).

3-(3,5-Dichlorophenyl)-2-(pyridin-3-yl)propanenitrile (**3l**)

Prepared by general procedures **A** and **B** from 3-pyridylacetonitrile (0.118 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 3,5-dichlorobenzyl alcohol (0.261 g, 1.5 mmol) and toluene (1.0 mL). Work up followed by column chromatography eluting with diethyl ether gave **3l** (0.234 g, 85% from **A** and 0.239 g, 87% from **B**) as colorless needles, mp 118-119 °C; (Found: C, 60.40; H, 3.75; Cl, 25.70; N, 9.90; C₁₄H₁₀Cl₂N₂ requires: C, 60.67; H, 3.64; Cl, 25.58; N, 10.11 %); $\nu_{\max}$ (film) 2241 (CN stretching) cm⁻¹; m/z (ESI, %) 277 (M+1, C₁₄H₁₀³⁵Cl₂N₂, 38), 279 (M+1, C₁₄H₁₀³⁵Cl³⁷ClN₂, 22); δ_{H} (300 MHz, CDCl₃); 8.62 (dd, 1H, J = 4.9 and 1.5 Hz), 8.52 (d, 1H, J = 2.3 Hz), 7.62 (dt, 1H, J = 7.9 and 2.1 Hz), 7.34 (dd, 1H, J = 7.9 and 4.9 Hz), 7.27 (t, 1H, J = 2.1 Hz), 7.03 (d, 2H, J = 2.1 Hz), 4.11 (app. t, 1H, J = 7.3 Hz), 3.16 (dd, 1H, J = 13.7 and 7.9 Hz) and 3.10 (dd, 1H, J = 13.7 and 6.7 Hz); δ_{C} (75.5

MHz, CDCl₃); 150.4 (CH), 149.1 (CH), 139 (C), 135.7 (2 x C), 135.4 (CH), 130.7 (C), 128.5 (CH), 128.2 (2 x CH), 124.3 (CH), 119.2 (C), 41.3 (CH₂) and 37.1 (CH).

3-(3,5-Bis(trifluoromethyl)phenyl)-2-(pyridin-3-yl)propanenitrile (3m)

Prepared by general procedures **A** and **B** from 3-pyridylacetonitrile (0.118 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 3,5-bis(trifluoromethyl)benzyl alcohol (0.366 g, 1.5 mmol) and toluene (1.0 mL). Work up followed by column chromatography eluting with diethyl ether gave **3m** (0.268 g, 78% from **A** and 0.257 g, 75% from **B**) as colorless prisms, mp 87-89 °C; (Found: C, 55.75; H, 2.85; F, 32.85; N, 8.15; C₁₆H₁₀F₆N₂ requires: C, 55.82; H, 2.93; F, 33.11; N, 8.14 %); $\nu_{\max}$ (film) 2245 (CN stretching) cm⁻¹; m/z (ESI, %) 345 (M+1, 12), 386 (M+42, 100); δ_{H} (300 MHz, CDCl₃); 8.64 (dd, 1H, J = 4.9 and 1.5 Hz), 8.53 (d, 1H, J = 2.1 Hz), 7.84 (s, 1H), 7.61 (dt, 1H, J = 7.9 and 2.0 Hz), 7.57 (s, 2H), 7.35 (dd, 1H, J = 7.9 and 4.9 Hz), 4.18 (app. t, 1H, J = 7.3 Hz) and 3.34 (app. d, 2H, J = 7.3 Hz); δ_{C} (75.5 MHz, CDCl₃); 150.7 (CH), 149.1 (CH), 138 (C), 135.4 (CH), 132.5 (q, 2C, $^2J_{\text{CF}}$ = 33 Hz), 130.3 (C), 130 (2 x CH), 124.3 (CH), 123.3 (q, 2C, $^1J_{\text{CF}}$ = 273 Hz), 122.3 (t, 1C, $^3J_{\text{CF}}$ = 3.8 Hz), 118.8 (C), 41.5 (CH₂) and 37.1 (CH).

3-(2-Chlorophenyl)-2-(pyridin-3-yl)propanenitrile (3n)

Prepared by general procedures **A** and **B** from 3-pyridylacetonitrile (0.118 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 2-chlorobenzyl alcohol (0.427 g, 3.0 mmol). Work up followed by column chromatography eluting with diethyl ether gave **3n** (0.212 g, 88% from **A** and 0.202 g, 84% from **B**) as colorless prisms, mp 61-63 °C; (Found: C, 69.30; H, 4.60; Cl, 14.50; N, 11.55; C₁₄H₁₁ClN₂ requires: C, 69.28; H, 4.57; Cl, 14.61; N, 11.54 %); $\nu_{\max}$ (film) 2243 (CN stretching) cm⁻¹; m/z (ESI, %) 243 (M+1, C₁₄H₁₁³⁵ClN₂, 100), 245 (M+1, C₁₄H₁₁³⁷ClN₂, 48); δ_{H} (300 MHz, CDCl₃); 8.60 (dd, 1H, J = 4.8 and 1.5 Hz), 8.55 (d, 1H, J = 2.2 Hz), 7.70 (ddd, 1H, J = 8.0, 2.2 and 1.5 Hz), 7.40 (dd, 1H, J = 7.0 and 2.0 Hz), 7.33 (dd, 1H, J = 8.0 and 4.8 Hz), 7.30-7.17 (m, 3H), 4.22 (app. t, 1H, J = 7.7 Hz),

3.30 (app. d, 2H, $J = 7.7$ Hz); δ_{C} (75.5 MHz, CDCl_3); 150.2 (CH), 149.2 (CH), 135.2 (CH), 134.4 (C), 133.8 (C), 132.2 (CH), 131.4 (C), 130.3 (CH), 129.8 (CH), 127.7 (CH), 124.2 (CH), 119.6 (C), 40.4 (CH_2) and 35.7 (CH).

2,3-Di(pyridin-3-yl)propanenitrile (3o)

Prepared by general procedures **A** and **B** from 3-pyridylacetonitrile (0.118 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), $[\text{IrCp}^*\text{Cl}_2]_2$ (0.020 g, 0.025 mmol) and 3-pyridylcarbinol (0.164 g, 1.5 mmol). Work up followed by column chromatography eluting with 1:9 v/v methanol-diethyl ether gave **3o** (0.175 g, 84% from **A** and 0.168 g, 81% from **B**) as colorless plates, mp 85-87 °C; (Found: C, 74.65; H, 5.25; N, 19.90; $\text{C}_{13}\text{H}_{11}\text{N}_3$ requires: C, 74.62; H, 5.30; N, 20.08 %); ν_{max} (film) 2241 (CN stretching) cm^{-1} ; m/z (ESI, %) 210 ($\text{M}+1$, 100), 251 ($\text{M}+42$, 90); δ_{H} (300 MHz, CDCl_3); 8.60 (dd, 1H, $J = 4.8$ and 1.5 Hz), 8.54 (dd, 1H, $J = 4.8$ and 1.5 Hz), 8.51 (d, 1H, $J = 2.4$ Hz), 8.35 (d, 1H, $J = 2.0$ Hz), 7.59 (dt, 1H, $J = 7.9$ and 1.9 Hz), 7.49 (dt, 1H, $J = 7.9$ and 2.0 Hz), 7.32 (dd, 1H, $J = 7.9$ and 4.8 Hz), 7.25 (dd, 1H, $J = 7.9$ and 4.8 Hz), 4.14 (app. t, 1H, $J = 7.1$ Hz), 3.24 (dd, 1H, $J = 13.9$ and 7.6 Hz) and 3.19 (dd, 1H, $J = 13.9$ and 6.7 Hz); δ_{C} (75.5 MHz, CDCl_3); 150.8 (CH), 150.4 (CH), 149.6 (CH), 149.2 (CH), 137.2 (CH), 135.4 (CH), 131.3 (C), 130.8 (C), 124.2 (CH), 123.9 (CH), 119.3 (C), 39.1 (CH_2) and 37.1 (CH).

4-(1H-Indol-3-yl)-2-(pyridin-3-yl)butanenitrile (3p)

Prepared by general procedures **A** and **B** from 3-pyridylacetonitrile (0.118 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), $[\text{IrCp}^*\text{Cl}_2]_2$ (0.020 g, 0.025 mmol), tryptophol (0.242 g, 1.5 mmol) and toluene (1.0 mL). Work up followed by column chromatography eluting with 3:1 v/v diethyl ether-petroleum ether gave **3p** (0.200 g, 77% from **A** and 0.175 g, 67% from **B**) as pale yellow plates, mp 114-116 °C; (Found: C, 78.20; H, 5.75; N, 16.05; $\text{C}_{17}\text{H}_{15}\text{N}_3$ requires: C, 78.13; H, 5.79; N, 16.08 %); ν_{max} (solid) 3378 (indole NH), 2245 (CN stretching) cm^{-1} ; m/z (ESI, %) 262 ($\text{M}+1$, 100), 303 ($\text{M}+42$, 23); δ_{H} (300 MHz, CDCl_3); 8.55 (dd, 1H, $J = 4.9$ and 1.3 Hz), 8.49 (d, 1H, $J = 2.1$ Hz), 7.64 (dt, 1H, $J = 7.8$ and 1.8 Hz), 7.54 (d, 1H, $J = 7.9$ Hz),

7.34 (d, 1H, $J = 7.9$ Hz), 7.28 (dd, 1H, $J = 7.8$ and 4.9 Hz), 7.19 (td, 1H, $J = 7.9$ and 1.0 Hz), 7.11 (td, 1H, $J = 7.9$ and 1.0 Hz), 7.01 (d, 1H, $J = 2.1$ Hz), 3.76 (dd, 1H, $J = 9.1$ and 6.3 Hz), 2.97 (t, 2H, $J = 7.2$ Hz), 2.40-2.15 (m, 2H); δ_{C} (75.5 MHz, CDCl_3); 149.9 (CH), 149.1 (CH), 137.0 (C), 135.4 (CH), 132.3 (C), 127.4 (C), 124.4 (CH), 122.7 ($2 \times \text{CH}$), 120.4 (C), 120.0 (CH), 119.0 (CH), 113.5 (C), 112.0 (CH), 36.3 (CH_2), 34.5 (CH) and 23.1 (CH_2).

2-(Pyridin-3-yl)butanenitrile (**3q**)

Prepared by general procedures **A** and **B** from 3-pyridylacetonitrile (0.118 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), $[\text{IrCp}^*\text{Cl}_2]_2$ (0.020 g, 0.025 mmol) and ethanol (1.0 mL). Work up followed by column chromatography eluting with diethyl ether gave **3q** (0.131 g, 90% from **A** and 0.128 g, 88% from **B**) as a colorless oil; ν_{max} (film) 2244 cm^{-1} (CN stretching), (lit.⁵ ν_{max} (CHCl_3) 2250 cm^{-1}); m/z (ESI, %) 147 ($\text{M}+1$, 86), 188 ($\text{M}+42$, 100); δ_{H} (300 MHz, CDCl_3); 8.59 (m, 2H), 7.72 (dt, 1H, $J = 7.9$ and 2.0 Hz), 7.35 (ddd, 1H, $J = 7.9$, 4.9 and 0.5 Hz), 3.82 (t, 1H, $J = 7.3$ Hz), 1.97 (quintet, 2H, $J = 7.3$ Hz) and 1.10 (t, 3H, $J = 7.3$ Hz); δ_{C} (75.5 MHz, CDCl_3); 149.9 (CH), 149.1 (CH), 135.2 (CH), 132.0 (C), 124.2 (CH), 120.2 (C), 36.9 (CH) 29.4 (CH_2) and 11.8 (CH_3).

4-Methyl-2-(pyridin-3-yl)pentanenitrile (**3r**)⁶

Prepared by general procedures **A** and **B** from 3-pyridylacetonitrile (0.118 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), $[\text{IrCp}^*\text{Cl}_2]_2$ (0.020 g, 0.025 mmol) and 2-methylpropanol (1.0 mL). Work up followed by column chromatography eluting with diethyl ether gave **3r** (0.139 g, 80% from **A** and 0.151 g, 87% from **B**) as a colorless oil; ν_{max} (film) 2240 cm^{-1} (CN stretching); m/z (ESI, %) 175 ($\text{M}+1$, 99), 216 ($\text{M}+42$, 100); δ_{H} (300 MHz, CDCl_3); 8.59 (m, 2H), 7.72 (dt, 1H, $J = 7.9$ and 1.8 Hz), 7.35 (dd, 1H, $J = 7.9$ and 4.9 Hz), 3.88 (dd, 1H, $J = 9.7$ and 6.4 Hz), 1.93 (ddd, 1H, $J = 13.1$, 9.7 and 5.4 Hz), 1.63 (ddd, 1H, $J = 13.1$, 8.1 and 6.4 Hz), 1.95-1.75 (m, 1H) and 1.05-0.95 ($2 \times \text{d}$, 6H, $J = 6.4$ Hz); δ_{C} (75.5 MHz, CDCl_3);

149.9 (CH), 149.0 (CH), 135.1 (CH), 132.6 (C), 124.3 (CH), 120.4 (C), 45.0 (CH₂), 33.5 (CH) 26.5 (CH) and 22.9 (CH₃) and 21.9 (CH₃).

3-(3,4-Dimethoxyphenyl)-2-phenylpropanenitrile (3s)

Prepared by the general procedure **A** from phenylacetonitrile (0.117 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 3,4-dimethoxybenzyl alcohol (0.504 g, 3.0 mmol). Work up followed by column chromatography eluting with 1:1 v/v diethyl ether-petroleum ether gave **3s** (0.242 g, 91%) as colorless needles, mp 99-100 °C (lit.⁷ 98 °C); (Found: C, 76.15; H, 6.60; N, 5.30; C₁₇H₁₇NO₂ requires: C, 76.38; H, 6.41; N, 5.24 %); $\nu_{\max}$ (film) 2236 (CN stretching) cm⁻¹; m/z (EI, %) 267 (M⁺, 8), 265 (M⁺-H₂, 58), 151 (PhCHCN⁺, 100); δ_{H} (300 MHz, CDCl₃); 7.39-7.30 (m, 3H), 7.28-7.21 (m, 2H), 6.79 (d, 1H, J = 8.2 Hz), 6.70 (dd, 1H, J = 8.2 and 1.8 Hz), 6.52 (d, 1H, J = 1.8 Hz), 3.98 (app. t, 1H, J = 7.2 Hz), 3.86 (s, 3H), 3.76 (s, 3H), 3.15 (dd, 1H, J = 13.6 and 7.7 Hz) and 3.07 (dd, 1H, J = 13.6 and 6.7 Hz); δ_{C} (75.5 MHz, CDCl₃); 149.1 (C), 148.7 (C), 135.6 (C), 129.4 (2 × CH), 129.0 (C), 128.6 (CH), 128.0 (2 × CH), 121.9 (CH), 120.9 (C), 112.8 (CH), 111.5 (CH), 56.3 (CH₃), 56.2 (CH₃), 42.2 (CH₂) and 40.3 (CH).

3-(4-Fluorophenyl)-2-phenylpropanenitrile (3t)

Prepared by the general procedure **A** from phenylacetonitrile (0.117 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 4-fluorobenzyl alcohol (0.378 g, 3.0 mmol). Work up followed by column chromatography eluting with 1:7 v/v diethyl ether-petroleum ether gave **3t** (0.189 g, 84%) as colorless needles, mp 87-89 °C (lit.⁸ 85.5-87.5 °C); (Found: M⁺, 225.0953. C₁₅H₁₂FN requires M⁺, 225.0954); $\nu_{\max}$ (film) 2236 (CN stretching) cm⁻¹; m/z (EI, %) 225 (M⁺, 5); δ_{H} (300 MHz, CDCl₃); 7.39-7.30 (m, 3H), 7.27-7.19 (m, 2H), 7.06 (ddt, 2H, J = 8.7, 5.6 and 2.5 Hz), 6.96 (tt, 2H, J = 8.7 and 2.5 Hz), 4.95 (app. t, 1H, J = 7.2 Hz), 3.15 (dd, 1H, J = 13.8 and 7.7 Hz) and 3.10 (dd, 1H, J = 13.8 and 6.7 Hz); δ_{C} (75.5 MHz, CDCl₃); 162.5 (d, 1C, $^1J_{\text{CF}}$ = 246.1 Hz), 135.3 (C), 132.3 (d, 1C, $^4J_{\text{CF}}$ = 3.8 Hz), 131.3 (d, 2

$\times \text{CH}$, $^3J_{\text{CF}} = 8.3 \text{ Hz}$), 129.5 ($2 \times \text{CH}$), 128.7 (CH), 127.9 ($2 \times \text{CH}$), 120.7 (C), 115.9 (d, $2 \times \text{CH}$, $^2J_{\text{CF}} = 21.9 \text{ Hz}$), 41.7 (CH_2) and 40.2 (CH).

4-Methyl-2-phenylpentanenitrile (**3u**)⁹

Prepared by the general procedure **A** from phenylacetonitrile (0.117 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), $[\text{IrCp}^*\text{Cl}_2]_2$ (0.020 g, 0.025 mmol) and 2-methylpropanol (1.0 mL). Work up followed by column chromatography eluting with 1:20 v/v diethyl ether-petroleum ether gave **3u** (0.131 g, 76%) as a colorless oil; (Found: M^+ , 173.1206. $\text{C}_{12}\text{H}_{15}\text{N}$ requires M^+ , 173.1204); ν_{max} (film) 2236 (CN stretching) cm^{-1} ; m/z (EI, %) 173 (M^+ , 25), 146 ($\text{M}^+ - \text{HCN}$, 85), 116 (PhCHCN^+ , 65); δ_{H} (300 MHz, CDCl_3); 7.42-7.27 (m, 5H), 3.80 (dd, 1H, $J = 9.7$ and 6.7 Hz), 1.90 (ddd, 1H, $J = 13.1$, 9.7 and 5.4 Hz), 1.95-1.75 (m, 1H), 1.63 (ddd, 1H, $J = 13.1$, 6.4 and 4.9 Hz), 0.99 (d, 3H, $J = 6.4 \text{ Hz}$) and 0.97 (d, 3H, $J = 6.7 \text{ Hz}$); δ_{C} (75.5 MHz, CDCl_3); 136.8 (C), 129.5 ($2 \times \text{CH}$), 128.4 (CH), 127.7 ($2 \times \text{CH}$), 121.5 (C), 45.4 (CH_2), 35.9 (CH), 26.5 (CH), 23.0 (CH_3) and 22.1 (CH_3).

3-(3,4-Dimethoxyphenyl)-2-(4-methoxyphenyl)propanenitrile (**3v**)

Prepared by the general procedure **A** from 4-methoxyphenylacetonitrile (0.147 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), $[\text{IrCp}^*\text{Cl}_2]_2$ (0.020 g, 0.025 mmol) and 3,4-dimethoxybenzyl alcohol (0.504 g, 3.0 mmol). Work up followed by column chromatography eluting with 1:1 v/v diethyl ether-petroleum ether gave **3v** (0.261 g, 88%) as colorless prisms, mp 147-148 °C; (Found: C, 72.45; H, 6.45; N, 4.70; $\text{C}_{18}\text{H}_{19}\text{NO}_3$ requires: C, 72.71; H, 6.44; N, 4.71 %); ν_{max} (film) 2236 (CN stretching) cm^{-1} ; m/z (EI, %) 297 (M^+ , 5), 295 ($\text{M}^+ - \text{H}_2$, 15), 151 ($3,4\text{-di-MeO-PhCH}_2^+$, 100); δ_{H} (300 MHz, CDCl_3); 7.15 (dt, 2H, $J = 8.8$ and 2.6 Hz), 6.87 (dt, 2H, $J = 8.8$ and 2.6 Hz), 6.79 (d, 1H, $J = 8.1 \text{ Hz}$), 6.68 (dd, 1H, $J = 8.1$ and 2.0 Hz), 6.55 (d, 1H, $J = 2.0 \text{ Hz}$), 3.93 (dd, 1H, $J = 7.7$ and 6.6 Hz), 3.86 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 3.12 (dd, 1H, $J = 13.6$ and 7.7 Hz) and 3.04 (dd, 1H, $J = 13.6$ and 6.6 Hz); δ_{C} (75.5 MHz, CDCl_3); 159.4

(C), 148.7 (C), 148.2 (C), 128.7 ($2 \times \text{CH}$), 128.7 (C), 127.2 (C), 121.5 (CH), 120.8 (C), 114.3 ($2 \times \text{CH}$), 112.4 (CH), 111.1 (CH), 55.9 (CH_3), 55.8 (CH_3), 55.4 (CH_3), 41.9 (CH_2) and 39.2 (CH).

3-(4-Fluorophenyl)-2-(4-methoxyphenyl)propanenitrile (3w)

Prepared by the general procedure **A** from 4-methoxyphenylacetonitrile (0.147 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), $[\text{IrCp}^*\text{Cl}_2]_2$ (0.020 g, 0.025 mmol) and 4-fluorobenzyl alcohol (0.378 g, 3.0 mmol). Work up followed by column chromatography eluting with 1:7 v/v diethyl ether-petroleum ether gave **3w** (0.216 g, 85%) as colorless prisms, mp 104-105 °C; (Found: C, 75.00; H, 5.70; F, 7.60; N, 5.65; $\text{C}_{16}\text{H}_{14}\text{FNO}$ requires: C, 75.28; H, 5.53; F, 7.44; N, 5.49 %); ν_{max} (film) 2236 (CN stretching) cm^{-1} ; m/z (EI, %) 255 (M^+ , 50), 146 ($4\text{-CH}_3\text{O-PhCHCN}^+$, 100), 109 (4-F-PhCH_2^+ , 97); δ_{H} (300 MHz, CDCl_3); 7.13 (dt, 2H, $J = 8.7$ and 2.6 Hz), 7.06 (ddt, 2H, $J = 8.7$, 5.4 and 2.6 Hz), 6.96 (tt, 2H, $J = 8.7$ and 2.6 Hz), 6.86 (dt, 2H, $J = 8.7$ and 2.6 Hz), 3.93 (app.t, 1H, $J = 7.2$ Hz), 3.79 (s, 3H), 3.13 (dd, 1H, $J = 13.6$ and 7.8 Hz) and 3.07 (dd, 1H, $J = 13.6$ and 6.7 Hz); δ_{C} (75.5 MHz, CDCl_3); 162.5 (d, 1C, $^1J_{\text{CF}} = 245.4$ Hz), 159.9 (C), 132.5 (d, 1C, $^4J_{\text{CF}} = 3.8$ Hz), 131.3 (d, $2 \times \text{CH}$, $^3J_{\text{CF}} = 7.6$ Hz), 129.1 ($2 \times \text{CH}$), 127.2 (C), 120.9 (C), 115.9 (d, $2 \times \text{CH}$, $^2J_{\text{CF}} = 21.1$ Hz), 114.8 ($2 \times \text{CH}$), 55.8 (CH_3), 41.8 (CH_2) and 39.4 (CH).

4-Methyl-2-(4-methoxyphenyl)pentanenitrile (3x)

Prepared by the general procedure **A** from 4-methoxyphenylacetonitrile (0.147 g, 1.0 mmol), KOH (9 mg, 0.152 mmol), $[\text{IrCp}^*\text{Cl}_2]_2$ (0.020 g, 0.025 mmol) and 2-methylpropanol (1.0 mL). Work up followed by column chromatography eluting with 1:9 v/v diethyl ether-petroleum ether gave **3x** (0.188 g, 93%) as a colorless oil; (Found: C, 76.90; H, 8.55; N, 7.00; $\text{C}_{13}\text{H}_{17}\text{NO}$ requires: C, 76.81; H, 8.43; N, 6.89 %); ν_{max} (film) 2236 (CN stretching) cm^{-1} ; m/z (EI, %) 203 (M^+ , 100); δ_{H} (300 MHz, CDCl_3); 7.23 (dt, 2H, $J = 8.7$ and 2.6 Hz), 6.89 (dt, 2H, $J = 8.7$ and 2.6 Hz), 3.79 (s, 3H), 3.75 (dd, 1H, $J = 9.5$ and 6.7 Hz), 1.87 (ddd, 1H, $J = 13.1$, 9.5 and 5.4 Hz), 1.90-1.70 (m, 1H), 1.59 (ddd, 1H, $J = 13.1$, 7.8 and 6.7 Hz) and 1.01-

0.92 (2 × d, 6H, $J = 6.7$ Hz); δ_C (75.5 MHz, CDCl₃); 159.7 (C), 128.7 (2 × CH), 128.7 (C), 121.7 (C), 114.9 (2 × CH), 55.7 (CH₃), 45.4 (CH₂), 35.1 (CH), 26.4 (CH), 22.9 (CH₃) and 22.1 (CH₃).

3-[4-(2-Cyano-2-(4-fluorophenyl)ethyl)-phenyl]-2-(4-fluorophenyl)propanenitrile (4a)

Prepared by the general procedure **B** from 4-fluorophenylacetonitrile (0.149 g, 1.1 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 1,4-benzene-dimethanol (0.069 g, 0.500 mmol). Work up followed by column chromatography eluting with 1:2 v/v diethyl ether-petroleum gave **4a** as a mixture of (*R,R*), (*S,S*), (*R,S*) and (*S,R*) (0.138 g, 74%) as colorless prisms; (Found: C, 77.35; H, 4.65; F, 10.3; N, 7.25; C₂₄H₁₈F₂N₂ requires: C, 77.40; H, 4.87; F, 10.20; N, 7.52 %); $\nu_{\max}$ (film) 2241 (CN stretching) cm⁻¹; m/z (EI, %) 372 (M⁺, 10); δ_H (300 MHz, CDCl₃); 7.18 (ddd, 2 × 4H, $J = 8.5$, 5.1 and 1.8 Hz), 7.03 (t, 2 × 4H, $J = 8.5$ Hz), 7.02 (s, 2 × 4H), 3.97 (app. t, 4 × 1H, $J = 7.3$ Hz), 3.15 (dd, 4 × 2H, $J = 13.6$ and 7.7 Hz), 3.08 (dd, 4 × 2H, $J = 13.6$ and 6.9 Hz); δ_C (75.5 MHz, CDCl₃); 162.9 (d, 2 × 2C, $^1J_{CF} = 247.6$ Hz), 135.6 (2 × 2C), 131.2 (d, 2 × 2C, $^4J_{CF} = 3.0$ Hz), 130.0 (2 × 4CH), 129.65 (d, 2 × 4CH, $^3J_{CF} = 8.3$ Hz), 120.5 (2 × 2C), 116.5 (d, 2 × 4CH, $^2J_{CF} = 21.1$ Hz), 42.1 (2 × 2CH₂) and 39.3 (2 × 2CH).

3-[4-(2-Cyano-2-(4-methoxyphenyl)ethyl)-phenyl]-2-(4-methoxyphenyl)propanenitrile (4b)

Prepared by the general procedure **A** from 4-methoxyphenylacetonitrile (0.162 g, 1.1 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 1,4-benzene-dimethanol (0.069 g, 0.500 mmol). Work up followed by column chromatography eluting with 1:2 v/v diethyl ether-petroleum gave **4b** as a mixture of (*R,R*), (*S,S*), (*R,S*) and (*S,R*) (0.141 g, 71%) as a pale yellow solid; (Found: M⁺, 396.1828 C₂₆H₂₄N₂O₂ requires M⁺, 396.1838); $\nu_{\max}$ (film) 2236 (CN stretching) cm⁻¹; m/z (EI, %) 396 (M⁺, 60); δ_H (300 MHz, CDCl₃); 7.12 (d, 2 × 4H, $J = 8.1$ Hz), 7.02 (s, 2 × 4H), 6.86 (d, 2 × 4H, $J = 8.1$ Hz), 3.92 (app. t, 4 × 1H, $J = 7.3$ Hz), 3.80 (s, 2 × 6H), 3.14 (dd, 4 × 2H, $J = 13.7$ and 7.7 Hz), 3.07 (dd, 4 × 2H, $J = 13.7$ and 6.4 Hz); δ_C (75.5 MHz, CDCl₃); 159.8 (2 × 2C), 135.8 (2 × 2C), 129.9 (2 × 4CH), 129.0 (2 ×

4CH), 127.4 (2 × 2C), 120.9 (2 × 2C), 114.8 (2 × 4CH), 55.7 (2 × 2CH₃), 42.3 (2 × 2CH₂) and 39.3 (2 × 2CH).

3-[4-(2-Cyano-2-(pyridine-3-yl)ethyl)-phenyl]-2-(pyridine-3-yl)propanenitrile (4c)

Prepared by the general procedure **B** from 3-pyridylacetonitrile (0.130 g, 1.1 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 1,4-benzene-dimethanol (0.069 g, 0.5 mmol). Work up followed by column chromatography eluting with 1:9 v/v methanol-diethyl ether gave **4c** as a mixture of (*R,R*), (*S,S*), (*R,S*) and (*S,R*) (0.146 g, 86%) as colorless prisms; (Found: M+1, 339.1616 C₂₂H₁₉N₄ requires M+1, 339.1610); ν_{max} (film) 2236 (CN stretching) cm⁻¹; *m/z* (ESI, %) 339 (M+1, 48); δ_H (300 MHz, CDCl₃); 8.57 (dd, 2 × 2H, *J* = 4.9 and 1.2 Hz), 8.44 (s, 2 × 2H), 7.56 and 7.55 (2 × dt, 2 × 2H, *J* = 7.9 and 1.8 Hz), 7.32 and 7.31 (2 × dd, 2 × 2H, *J* = 7.9 and 4.9 Hz), 7.03 (2 × s, 2 × 4H), 4.08 and 4.07 (2 × app. t, 2 × 2H, *J* = 7.2 Hz), 3.20 and 3.19 (2 × dd, 2 × 2H, *J* = 13.6 and 7.7 Hz), 3.13 and 3.12 (2 × dd, 2 × 2H, *J* = 13.6 and 6.7 Hz); δ_C (75.5 MHz, CDCl₃); 150.1 (2 × 2CH), 149.2 (2 × 2CH), 135.5 (2 × 2CH), 135.2 (2 × 2C), 131.2 (2 × 2C), 130.1 (2 × 4CH), 124.2 (2 × 2CH), 119.8 (2 × 2C), 41.7 (2 × 2CH₂) and 37.4 (2 × 2CH).

3-[3-(2-Cyano-2-(pyridine-3-yl)ethyl)-phenyl]-2-(pyridine-3-yl)propanenitrile (4d)

Prepared by the general procedure **B** from 3-pyridylacetonitrile (0.130 g, 1.1 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 1,3-benzene-dimethanol (0.046 g, 0.333 mmol). Work up followed by column chromatography eluting with 1:9 v/v methanol-diethyl ether gave **4d** as a mixture of (*R,R*), (*S,S*), (*R,S*) and (*S,R*) (0.105 g, 62%) as colorless prisms; (Found: M+1, 339.1593 C₂₂H₁₉N₄ requires M+1, 339.1604); ν_{max} (film) 2241 (CN stretching) cm⁻¹; *m/z* (ESI, %) 339 (M+1, 20); δ_H (300 MHz, CDCl₃); 8.60 (dd, 2 × 2H, *J* = 4.9 and 1.4 Hz), 8.46 (s, 2 × 2H), 7.59 (dd, 2 × 2H, *J* = 7.9 and 2.1 Hz), 7.32 (dd, 2 × 2H, *J* = 7.9 and 4.9 Hz), 7.26-7.19 (2 × t, 2 × 1H, *J* = 7.7 Hz), 7.01 (dt, 2 × 2H, *J* = 7.7 and 2.1 Hz), 6.93 and 6.91 (2 × t, 2 × 1H, *J* = 2.1 Hz), 4.08 and 4.07 (2 × app. t, 2 × 2H, *J* = 7.4 Hz), 3.25-

3.05 (m, $2 \times 4\text{H}$); δ_{C} (75.5 MHz, CDCl_3); 150.2 ($2 \times 2\text{CH}$), 149.2 ($2 \times 2\text{CH}$), 136.4 ($2 \times 2\text{C}$), 135.5 ($2 \times 2\text{CH}$), 131.2 ($2 \times 2\text{C}$), 130.6 ($2 \times \text{CH}$), 129.7 ($2 \times \text{CH}$), 129.1 ($2 \times 2\text{CH}$), 124.2 ($2 \times 2\text{CH}$), 119.7 ($2 \times 2\text{C}$), 42.0 ($2 \times 2\text{CH}_2$), 37.6 (2CH) and 37.5 (2CH).

3,3',3''-benzene-1,3,5-triyltris(2-pyridin-3-ylpropanenitrile) (4e)

Prepared by the general procedure **B** from 3-pyridylacetonitrile (0.130 g, 1.1 mmol), KOH (9 mg, 0.152 mmol), $[\text{IrCp}^*\text{Cl}_2]_2$ (0.020 g, 0.025 mmol) and 1,3-benzene-dimethanol (0.046 g, 0.333 mmol). Work up followed by column chromatography eluting with 1:9 v/v methanol-diethyl ether gave **4e** as a mixture of (*R,R,R*), (*S,S,S*), (*R,R,S*) and (*S,S,R*) (0.112 g, 72%) as a colorless solid; (Found: $\text{M}+1$, 469.2123 $\text{C}_{30}\text{H}_{25}\text{N}_6$ requires $\text{M}+1$, 469.2135); ν_{max} (film) 2241 (CN stretching) cm^{-1} ; m/z (ESI, %) 469 ($\text{M}+1$, 20); δ_{H} (300 MHz, CDCl_3); 8.61 (dd, $2 \times 3\text{H}$, $J = 4.9$ and 1.5 Hz), 8.46 (t, $2 \times 3\text{H}$, $J = 2.3$ Hz), 7.64-7.56 (m, $2 \times 3\text{H}$), 7.35 (dd, $2 \times 3\text{H}$, $J = 7.7$ and 4.9 Hz), 6.82 and 6.78 ($2 \times \text{s}$, $2 \times 3\text{H}$ (major and minor)), 3.98 (app. t, 3H , $J = 7.7$ Hz (major)), 3.95 (app. t, 3H , $J = 7.7$ Hz (minor)), 3.22-3.01 (m, $2 \times 6\text{H}$, CHCH_2); δ_{C} (75.5 MHz, CDCl_3); 150.3 ($2 \times 3\text{CH}$), 149.2 ($2 \times 3\text{CH}$), 137.2 ($2 \times 3\text{C}$), 135.5 ($2 \times 3\text{CH}$), 131.1 ($2 \times 3\text{C}$), 130.1 ($2 \times 3\text{CH}$), 124.3 ($2 \times 3\text{CH}$), 119.6 ($2 \times 3\text{C}$), 41.8 ($2 \times 3\text{CH}_2$) and 37.5 ($2 \times 3\text{CH}$).

NMR Spectra on Selected Compounds

3-(4-Fluorophenyl)-2-(pyridin-3-yl)propanenitrile (3i)

^1H NMR (300 MHz, CDCl_3)

3-(4-Fluorophenyl)-2-(pyridin-3-yl)propanenitrile (3i)

^{13}C NMR (75.5 MHz, CDCl_3)

3-(4-Fluorophenyl)-2-(pyridin-3-yl)propanenitrile (3i)

DEPT 135 (75.5 MHz, CDCl₃)

3-[4-(2-Cyano-2-(pyridine-3-yl)ethyl)-phenyl]-2-(pyridine-3-yl)propanenitrile (4c)

^1H NMR (300 MHz, CDCl_3)

3-[4-(2-Cyano-2-(pyridine-3-yl)ethyl)-phenyl]-2-(pyridine-3-yl)propanenitrile (4c)

^{13}C NMR (75.5 MHz, CDCl_3)

3-[4-(2-Cyano-2-(pyridine-3-yl)ethyl)-phenyl]-2-(pyridine-3-yl)propanenitrile (4c)

DEPT 135 (75.5 MHz, CDCl₃)

3-[3-(2-Cyano-2-(pyridine-3-yl)ethyl)-phenyl]-2-(pyridine-3-yl)propanenitrile (4d)

^1H NMR (300 MHz, CDCl_3)

3-[3-(2-Cyano-2-(pyridine-3-yl)ethyl)-phenyl]-2-(pyridine-3-yl)propanenitrile (4d)

^{13}C NMR (75.5 MHz, CDCl_3)

3-[3-(2-Cyano-2-(pyridine-3-yl)ethyl)-phenyl]-2-(pyridine-3-yl)propanenitrile (4d)

DEPT 135 (75.5 MHz, CDCl₃)

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