Supplementary Information

C-H bond functionalisation with $[RuH(codyl)_2]BF_4$ catalyst precursor

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All reactions were carried out under an inert atmosphere of argon in closed Schlenck tube (P < 2-3 bar). In all cases a protection shield was used. NMP was purchased from Alfa Aesar and was freshly distilled and dried prior to use according to classical procedures, over CaH_2 under vacuum. All the organic reagents were commercially available and used as received. Potassium acetate was purchased from Acros Organics. Potassium pivalate was prepared by mixing an equimolar amount of pivalic acid and KOH in water followed by filtration. The white precipitate was filtrated and washed with diethylether. Sample products were characterised by NMR analysis using Bruker 200 dpx and Bruker avance 300 MHz NMR spectrometers. Gas chromatography analyses were performed on a Shimadzu 2014 gas chromatograph with internal calibration. GC/MS analyses were performed on a Shimadzu QP2010 apparatus.

General procedure for the catalytic transformations: A Schlenck tube was loaded with 10.2 mg (0.025 mol, 5 mol%) of $[RuH(codyl)_2]BF_4$ [1], 4.9 mg of KOAc/ 9.2 mg of KIP (0.05 mmol, 10 mol%), 198.3 mg of K_2CO_3 (1.5 mmol, 3 equiv.), 76 mg of 2-phenylpyridine (0.5 mmol, 1 equiv), aryl halide (1.25 mmol, 2.5 equiv) and 2 ml of NMP as solvent. The reaction mixture was then stirred for the appropriate reaction time and temperature. To the reaction mixture were added 15 ml of water and 10 ml of diethyl ether. The organic phase was separated and washed three times with 10 ml of water. The organic phase was dried over sodium sulphate and the solvent evaporated under vacuum.

***Purification method*:** When full conversion was achieved and the diarylated product obtained in more than 99% the product was purified by a simple filtration on a short plug of silica. In other cases, products were purified by column chromatography on silica gel using mixtures of petroleum ether and diethyl ether as the eluant.

2-(2,6-Diphenyl)-phenylpyridine **3:** NMR data were consistent with reported data.[2] ^{1}H NMR (200 MHz, CDCl3): δ=8.31 (d, 1H, J=4.8 Hz), 7.57–7.42 (m, 3H), 7.34–7.23 (m, 1H), 7.14–7.07 (m, 10H), 6.94–6.86 (m, 2H). ^{13}C NMR(75 MHz): δ=157.8, 147.4, 140.7, 140.5, 137.4, 133.8, 128.5, 128.4, 127.1, 126.6, 125.7, 125.2, 119.8.

2–(2,6–Di-(2-methylphenyl))–phenylpyridine **4:** NMR data were consistent with reported data.[3] ^{1}H NMR (200 MHz, CDCl3): δ = 8.18, (m, 1 H), 7.51-7.44 (m, 1 H), 7.44-7.29 (m, 2 H), 7.20-7.04 (m, 9 H), 6.79-6.73 (m, 2 H), 2.10 (s, 3 H), 2.03 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=158.6, 158.5, 148.1, 141.4, 141.4, 141.3, 139.5, 136.0, 135.8, 134.3, 130.7, 130.3, 129.4, 129.6, 129.1, 127.5, 127.5, 126.8, 125.7, 125.5, 124.7, 124.9, 120.7, 20.5, 20.5.

2-(2.6-di-2-thienylphenyl)pyridine **5:** NMR data were consistent with reported data.[4] ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.58 (d, 1H, J =5.0 Hz), 7.62-7.44 (m, 4H), 7.18-7.09 (m, 4H), 6.86-6.82 (m, 2H), 6.69 (d, 2H, J=2.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 158.9, 149.3, 143.1, 138.9, 136.2, 135.1, 130.5, 128.8, 127.6, 127.2, 126.7, 126.2, 122.5.

2'-pyridin-2-yl-1,1':3',1"-terphenyl-4,4"-dicarbonitrile **7:** NMR data were consistent with reported data.[5] ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.35 (ddd, 1H, J = 4.9 Hz, 1.8 Hz, 1.0 Hz), 7.62 (dd, 1H, J = 8.5Hz, J = 6.9 Hz), 7.52-7.46 (m, 6H), 7.40 (td, 1H, J = 7.7 Hz, J = 1.8 Hz), 7.24-7.18 (m, 4H), 7.03 (ddd, 1H, J = 7.6 Hz, 4.9 Hz, 1.0 Hz), 6.84 (dt, 1H, J = 7.8 Hz, J = 1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 157.4, 149.1, 145.6, 140.4, 138.4, 135.6, 131.6, 130.2, 130.1, 128.8, 126.6, 121.8, 118.8, 110.5.

Dimethyl 2'-(pyridin-2-yl)-[1,1':3',1"-terphenyl]-4,4"-dicarboxylate **8:** NMR data were consistent with reported data.[3] ^{1}H NMR (300 MHz, $CDCl_3$): δ =8.28 (1 H, d, J = 4.7 Hz), 7.83 (4 H, d, J = 8.3 Hz), 7.61 – 7.35 (3 H, m), 7.37 – 7.20 (1 H, m), 7.16 (4 H, d, J = 8.3 Hz), 7.02 – 6.69 (2 H, m), 3.84 (6 H, s).^{13}C NMR (75 MHz, $CDCl_3$):166.7, 157.8, 148.6, 145.9, 140.8, 138.2, 135.1, 129.6, 129.4, 128.8, 128.3, 127.9, 126.5, 121.2, 51.8.

2-(2,6-Diphenyl)-phenylpyrazole **12:** NMR data were consistent with reported data.[6] ^{1}H NMR (200 MHz, $CDCl_3$): δ =7.65-7.51 (m, 3 H), 7.41 (bs, 1 H), 7.28-7.26 (m, 6 H), 7.19-7.11 (m, 5 H), 6.10 (bs, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): 140.8, 139.8, 139.2, 136.9, 132.8, 130.5, 129.5, 128.7, 128.5, 127.6, 106.5.

2-(2, 6-Diphenyl)-phenyloxazoline **13:** NMR data were consistent with reported data.[6] ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.54 (dd, 1H, J = 8.4 Hz, J = 6.6 Hz), 7.32-7.50 (m, 12H), 3.90

(t, 2H, J = 9.0 Hz), 3.60 (t, 2H, J = 9.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 164.5, 142.8, 141.4, 130.1, 129.3, 129.0, 128.4, 127.9, 127.7, 67.7, 55.5

2-[4,4''-Dichloro-(1,1';3',1'')-terphen-2'-yl] pyridine **14:** NMR data were consistent with reported data. ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.35 (d, 1 H, J = 4.1 Hz,), 7.52 (t, 1 H, J = 7.1 Hz), 7.42 (d, 2 H, J =7.4 Hz), 7.35 (t, 1H, J = 7.7 Hz), 7.13 (d, 4 H, J = 6.5 Hz), 7.02 (d, 4 H, 8.5 Hz), 6.97 (t, 1 H, J = 5.0 Hz), 6.85 (d, 1 H, J = 7.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.4, 148.8, 140.8, 139.9, 138.5, 135.3, 132.6, 130.9, 129.7, 128.4, 127.9, 126.7, 121.3. . Compound **14** was previously produced via direct arylation of phenylpyridine with 4-iodophenylchloride in the presence of $RuCl_3$ catalyst in 69 % yield with K_2CO_3 at 120 °C for 22 h.[5]

References

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