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Supporting Information

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Iron-Catalyzed Aryl-Aryl Cross-Couplings Using Magnesium-Derived Copper Reagents**

I. Sapountzis, W. Lin, C. C. Kofink, C. Despotopoulou and P. Knochel*
Ludwig-Maximilians-Universität München, Department Chemie
Butenandtstrasse 5-13, Haus F, 81377 München (Germany)
Fax: (+49) 089 21 80 776 80
e-mail: paul.knochel@cup.uni-muenchen.de

General All reactions were carried out under a nitrogen atmosphere in dried glassware. Commercially available starting materials were used without further purification. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Yields refer to isolated yields of compounds estimated to be > 95% pure as determined by ^{1}H-NMR and capillary GC.

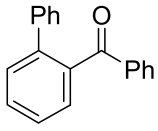
Typical procedure for the iron catalyzed cross-coupling reaction (TP 1)

A 25 mL Schlenk-flask, equipped with a magnetic stirring bar, was charged with DME (5 mL), cooled to −20 °C and PhMgCl (2.1 mL, 3.0 mmol, 1.4 M in THF) was added. Subsequently, a solution of CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF) was added and the reaction mixture was stirred for 10 min. A solution of the corresponding iodide (1 mmol) and $Fe(acac)_3$ (35 mg, 0.10 mmol) dissolved in DME (3 mL) was added at once and the reaction mixture was allowed to come to rt or was heated to the appropriate temperature. The reaction was quenched with sat. $NH_4Cl_{(aq.)}$ and was extracted with CH_2Cl_2 (3x40 mL). The organic fractions were washed with sat. $NH_4Cl_{(aq.)}/NH_3$ (9:1) (50 mL) and brine (50 mL), dried over Na_2SO_4, filtered and the solvent was evaporated *in vacuo*. Flash chromatography furnished the analytically pure products.

Typical procedure for the iron catalyzed cross-coupling reaction (TP 2)

A 25 mL Schlenk-flask, equipped with a magnetic stirring bar, was charged with the appropriate aryl halide (3.1 mmol), DME (5 mL) was added and the solution cooled to −20 °C. Then, *i*PrMgCl (3.0 mL, 3.0 mmol, 1.0 M in THF) was added and the reaction mixture was stirred at this temperature until GC analysis of reaction aliquots indicated complete exchange. Subsequently, a solution of CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF) was added and the reaction mixture was stirred for 10 min. A solution of the corresponding iodide (1 mmol) and $Fe(acac)_3$ (35 mg, 0.10 mmol) dissolved in DME (3 mL) was added at once and the reaction mixture was allowed to come to rt or was heated to the appropriate temperature. The reaction was quenched with sat. $NH_4Cl_{(aq.)}$ and was extracted with CH_2Cl_2 (3x40 mL). The organic fractions were washed with sat. $NH_4Cl_{(aq.)}/NH_3$ (9:1) (50 mL) and brine (50 mL), dried over Na_2SO_4, filtered and the solvent was evaporated *in vacuo*. Flash chromatography furnished the analytically pure products.

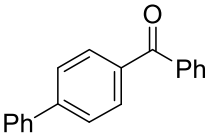
Synthesis of 2-phenylbenzophenone (4a)



Prepared according to **TP 1** from 2-iodobenzophenone **3a** (308 mg, 1.0 mmol), PhMgCl (1.82 mL, 3.0 mmol, 1.65 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF) and Fe(acac)$_3$ (36 mg, 0.1 mmol). Reaction time: 0.5 h at 25 °C. Purification by flash chromatography (pentane/diethyl ether = 29:1) yielded product **4a** as a colourless oil (240 mg, 93 %).

^{1}H-NMR (300 MHz, CDCl$_3$, 25 °C): δ = 7.65-7.60 (m, 2H), 7.59-7.34 (m, 5H), 7.28-7.08 (m, 7H). **^{13}C-NMR** (75 MHz, CDCl$_3$, 25 °C): δ = 198.71, 141.10, 140.13, 138.94, 137.37, 132.73, 130.30, 130.01, 129.84, 128.95, 128.71, 128.18, 128.01, 127.26, 127.01. **MS** (70 eV, EI): *m/z* (%): 258 (76) [M$^+$], 182 (13), 181 (100), 153 (16), 152 (26), 105 (17), 77 (13). **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 1665 (vs), 1595 (w), 1579 (w), 1477 (w), 1449 (w), 1314 (m), 1280 (m), 1261 (m), 1075 (m), 1024 (w), 999 (w), 928 (w), 847 (w), 806 (w), 775 (m), 758 (w), 744 (m), 698 (m), 636 (w). **HRMS** for **$C_{19}H_{14}O$** (258.1045): found: 258.1030.

Synthesis of 4-phenylbenzophenone (4b)

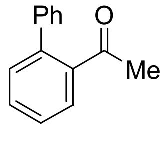


Prepared according to **TP 1** from 4-iodobenzophenone **3b** (308 mg, 1.0 mmol), PhMgCl (1.82 mL, 3.0 mmol, 1.65 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF) and Fe(acac)$_3$ (36 mg, 0.1 mmol). Reaction time: 4 at 25 °C. Purification by flash chromatography (pentane/diethyl ether = 150:1) yielded product **4b** as a white solid (207 mg, 80 %).

mp.: 101.3-102.0 °C. **^{1}H-NMR** (300 MHz, CDCl$_3$, 25 °C): δ = 7.94-7.88 (m, 2H), 7.88-7.83 (m, 2H), 7.75-7.69 (m, 2H), 7.69-7.64 (m, 2H), 7.64-7.58 (m, 1H), 7.55-7.47 (m, 4H), 7.46-7.38 (m, 1H). **^{13}C-NMR** (75 MHz, CDCl$_3$, 25 °C): δ = 196.25, 145.16, 139.91, 137.71, 136.18, 132.30, 130.66, 129.93, 128.91, 128.24, 128.13, 127.23, 126.90. **MS** (70 eV, EI): *m/z* (%): 258 (76) [M$^+$], 182 (13), 181 (100), 153 (16), 152 (26), 105 (17), 77 (13). **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3054 (w), 2926 (w), 1645 (vs), 1603 (m), 1485 (w), 1446 (w), 1402 (w), 1318 (m), 1291 (m), 1281 (m), 730 (m), 695 (s). **HRMS** for **$C_{19}H_{14}O$** (258.1045): found: 258.1051.

Spectral data match those reported in the literature.[i]

Synthesis of 2-phenylacetophenone (4c)

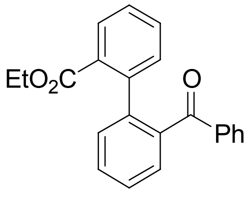


Prepared according to **TP 1** from 2-iodoacetophenone **3c** (246 mg, 1.0 mmol), PhMgCl (1.82 mL, 3.0 mmol, 1.65 M in THF), CuCN•2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF) and Fe(acac)$_3$ (36 mg, 0.1 mmol). Reaction time: 1 h at 25 °C. Purification by flash chromatography (pentane/diethyl ether = 150:1) yielded product **4c** as a colourless oil (169 mg, 86 %).

^{1}H-NMR (300 MHz, CDCl$_3$, 25 °C): δ = 7.58-7.54 (m, 1H), 7.54-7.48 (td, ^{3}J(H,H) = 7.52 Hz, ^{4}J(H,H) = 1.77 Hz, 1H), 7.46-7.33 (m, 7H), 2.01 (s, 3H). **^{13}C-NMR** (75 MHz, CDCl$_3$, 25 °C): δ = 204.74, 140.83, 140.66, 140.44, 130.63, 130.16, 128.78, 128.59, 127.81, 127.79, 127.36, 30.34. **MS** (70 eV, EI): *m/z* (%): 196 (40) [M$^+$], 195 (36), 182 (13), 181 (100), 153 (47), 152 (52), 151 (14). **IR** (Film): $\tilde{\nu}$ (cm^{-1}) = 1688 (vs), 1595 (m), 1472 (m), 1450 (m), 1434 (m), 1354 (m), 1269 (s), 1234 (s), 1076 (m), 1008 (m), 967 (w), 774 (m), 759 (s), 744 (s), 702 (s), 618 (w), 594 (m). **HRMS** for **$C_{14}H_{12}O$** (196.0888): found: 196.0874.

Spectral data match those reported in the literature [ii]

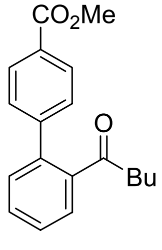
Synthesis of ethyl 2'-benzoyl[1,1'-biphenyl]-2-carboxylate (4d)



Prepared according to **TP 2** from ethyl 2-iodobenzoate (855 mg, 3.1 mmol), *i*PrMgCl (3.3 mL, 3.0 mmol, 0.90 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF) and 2-iodobenzophenone (308 mg, 1.0 mmol). Reaction time 12 h at 25 °C. Purification by flash chromatography (pentane/ethylacetate/methanol = 19:1:0.1) yielded **4d** as a colourless oil (250 mg, 75%).

^{1}H-NMR (300 MHz, CDCl$_3$, 25 °C): δ = 7.81 (dd, ^{3}J(H,H) = 7.5 Hz, ^{4}J(H,H) = 1.4 Hz, 1 H), 7.74-7.69 (m, 2 H), 7.59-7.52 (m, 2 H), 7.49-7.22 (m, 8 H), 4.19-4.05 (m, 2 H), 1.10 (t, ^{3}J(H,H) = 7.1 Hz, 3 H). **^{13}C-NMR** (75 MHz, CDCl$_3$, 25 °C): δ = 197.8, 167.1, 141.2, 141.1, 138.3, 137.6, 132.6, 131.5, 131.1, 130.3, 130.2, 130.1, 130.0, 129.9, 128.9, 127.9, 127.4, 126.7, 60.8, 13.8. **MS** (70 eV, EI): *m/z* (%): 330 (14) [M$^+$], 301 (21), 257 (100), 225 (32), 197 (30), 152 (8), 105 (14), 77 (14). **IR** (KBr): $\tilde{\nu}$ = 3061 (m), 2981 (m), 1715 (vs), 1666 (vs), 1597 (s), 1579 (s),1472 (m), 1448 (s), 1314 (s), 1286 (vs), 1257 (vs), 1134 (s), 1084 (s), 928 (s), 751 (vs), 701 (vs), 663 (m), 639 (vs). **HRMS** for **$C_{22}H_{18}O_3$** (330.1256): found: 330.1249.

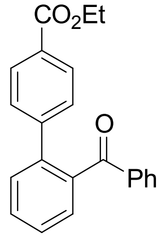
Synthesis of methyl 2'-pentanoyl[1,1'-biphenyl]-4-carboxylate (4e)



Prepared according to **TP 2** from 2-iodobutanophenone **3d** (288 mg, 1.0 mmol), methyl 4-iodobenzoate (786mg, 3.0 mmol), *i*PrMgCl (4.0 mL, 3.0 mmol, 0.75 M in THF), CuCN•2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF) and Fe(acac)$_3$ (36 mg, 0.1 mmol). Reaction time: 4 h at 25 °C. Purification by flash chromatography (pentane/diethyl ether = 20:1) yielded product **4e** as a pale-yellow oil (202 mg, 68%).

^{1}H-NMR (300 MHz, CDCl$_3$, 25 °C): δ = 8.09-8.04 (m, 2H), 7.52-7.33 (m, 6H), 3.92 (s, 3H), 2.33-2.27 (t, ^3J(H,H) = 7.52 Hz, 2H), 1.46-1.35 (m, 2H), 1.17-1.03 (m, 2H), 0.75-0.68 (t, ^3J(H,H) = 7.52 Hz, 3H). **^{13}C-NMR** (75 MHz, CDCl$_3$, 25 °C): δ = 207.03, 166.62, 145.36, 140.83, 138.93, 130.38, 130.01, 129.71, 129.29, 128.74, 127.96, 127.68, 52.05, 42.44, 26.39, 21.95, 13.54. **MS** (70 eV, EI): *m/z* (%): 296 (5) [M$^+$], 265 (11), 254 (47), 240 (9), 239 (51), 207 (14), 196 (16), 195 (100), 180 (31), 167 (10), 165 (13), 152 (33), 151 (12), 76 (9), 59 (10). **IR** (Film): $\tilde{\nu}$ (cm^{-1}) = 2957 (m), 2932 (m), 2873 (w), 1725 (vs), 1693 (s), 1610 (m), 1596 (w), 1436 (m), 1404 (w), 1312 (m), 1280 (vs), 1181 (m), 1113 (m), 1103 (m), 1022 (w), 1006 (w), 968 (w), 860 (w), 781 (w), 754 (m), 707 (w). **HRMS** for **$C_{19}H_{20}O_3$** (296.1412): found: 296.1404.

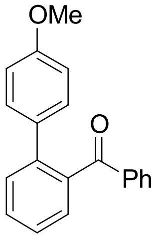
Synthesis of ethyl 2'-benzoyl[1,1'-biphenyl]-4-carboxylate (4f)



Prepared according to **TP 2** from ethyl 4-iodobenzoate (855 mg, 3.1 mmol), *i*PrMgCl (3.3 mL, 3.0 mmol, 0.90 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF) and 2-iodobenzophenone (308 mg, 1.0 mmol). Reaction time 2 h at rt. Purification by flash chromatography (pentane/diethyl ether = 29:1) yielded **4f** as a light yellow oil (284 mg, 86%).

^{1}H-NMR (300 MHz, CDCl$_3$, 25 °C): δ = 7.91 (d, ^3J(H,H) = 8.4 Hz, 2 H), 7.70-7.59 (m, 3 H), 7.56-7.42 (m, 4 H), 7.34-7.28 (m, 4 H), 4.35 (q, ^3J(H,H) = 7.1 Hz, 2 H), 1.37 (t, ^3J(H,H) = 7.1 Hz, 3 H). **^{13}C-NMR** (75 MHz, CDCl$_3$, 25 °C): δ = 198.2, 166.2, 144.7, 140.1, 138.9, 137.2, 133.1, 130.4, 130.0, 129.9, 129.5, 129.3, 128.89, 128.87, 128.2, 127.6, 60.9, 14.3. **MS** (70 eV, EI): *m/z* (%): 330 (100) [M$^+$], 301 (58), 285 (43), 257 (70), 228 (13), 202 (4), 181 (46), 152 (35), 105 (54), 77 (33). **IR** (KBr): $\tilde{\nu}$ = 1715 (vs), 1667 (vs), 1610 (s), 1597 (s), 1580 (s), 1467 (m), 1449 (s), 1405 (s), 1367 (s), 1277 (vs), 1102 (vs), 1025 (s), 928 (s), 781 (s), 770 (s), 699 (vs), 651 (m), 638 (m). **HRMS** for **$C_{22}H_{18}O_3$** (330.1256): found: 330.1234.

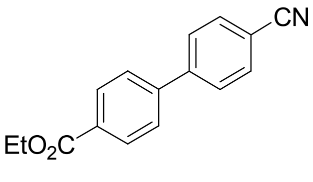
Synthesis of (4'-methoxy[1,1'-biphenyl]-2-yl)(phenyl)methanone (4g)



Prepared according to **TP 1** from 4-methoxyphenylmagnesium bromide (3.8 mL, 3.0 mmol, 0.8 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF) and 2-iodobenzophenone (308 mg, 1.0 mmol). Reaction time 2 h at 25 °C. Purification by flash chromatography (pentane/diethyl ether = 29:1) yielded **4g** as a colourless solid (219 mg, 76%).

mp.: 84-85 °C. **^{1}H-NMR** (600 MHz, $CDCl_3$, 25 °C): δ = 7.64-7.63 (m, 2 H), 7.54 (dt, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 1.1 Hz, 1 H), 7-48-7.39 (m, 4 H), 7.28-7.25 (m, 2 H), 7.17 (d, ^3J(H,H) = 8.6 Hz, 2 H), 6.72 (d, ^3J(H,H) = 8.6 Hz, 2 H), 3.71 (s, 3 H). **^{13}C-NMR** (150 MHz, $CDCl_3$, 25 °C): δ = 199.0, 158.9, 140.7, 138.9, 137.4, 132.8, 132.7, 130.3, 130.1, 130.0, 129.9, 128.7, 128.1, 126.6, 113.8, 55.2. **MS** (70 eV, EI): *m/z* (%): 288 (100) [M$^+$], 273 (11), 257 (12), 211 (66), 168 (20), 152 (9), 139 (26), 105 (31), 77 (30). **IR** (KBr): $\tilde{\nu}$ = 1666 (vs), 1612 (s), 1596 (m), 1517 (s), 1477 (m), 1449 (s), 1441 (m), 1315 (s), 1283 (s), 1249 (vs), 1179 (s), 834 (m), 763 (s), 707 (s). **HRMS** for **$C_{20}H_{16}O_2$** (288.1150): found: 288.1145.

Synthesis of 4'-cyano-biphenyl-4-carboxylic acid ethyl ester (4h)



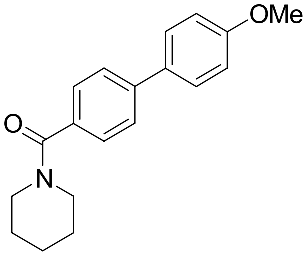
Prepared according to **TP 2** from ethyl 4-iodobenzoate (855 mg, 3.1 mmol), *i*PrMgCl (3.3 mL, 3.0 mmol, 0.90 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF) and 4-iodobenzonitrile (229 mg, 1.0 mmol). Reaction time 3 h at 80 °C. Purification by flash chromatography (pentane/diethyl ether = 9:1) yielded **4h** as a colourless solid (181 mg, 72%).

mp.: 123-124.5 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 8.14 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.76-7.68 (m, 4H), 7.64 (d, ^3J(H,H) = 8.4 Hz, 2H), 4.40 (q, ^3J(H,H) = 7.1 Hz, 2H), 1.41 (t,

^3J(H,H) = 7.1 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): δ = 166.1, 144.4, 143.3, 132.7, 130.5, 130.3, 127.9, 127.1, 118.6, 111.8, 61.2, 14.3. **MS** (70 eV, EI): *m/z* (%): 251 (35) [M^+], 223 (34), 206 (100), 178 (20), 151 (17). **HRMS** for **$C_{16}H_{13}NO_2$** (295.0946): found: 295.1550.

Spectral data match those reported in the literature.[iii]

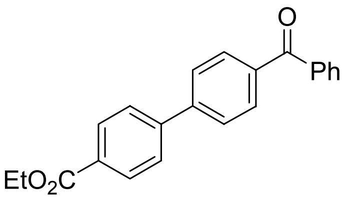
Synthesis of 1-[(4'-methoxy[1,1'-biphenyl]-4-yl)carbonyl]piperidine (4i)



Prepared according to **TP 1** from 4-methoxyphenylmagnesium bromide (3.8 mL, 3.0 mmol, 0.8 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF) and 1-(4-iodobenzoyl)piperidine (315 mg, 1.0 mmol). Reaction time 2 h at 25 °C. Purification by flash chromatography (pentane/diethyl ether = 29:1) yielded **4g** as a colourless solid (171 mg, 58%).

mp.: 103-104.5 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 7.56 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.53 (d, ^3J(H,H) = 8.9 Hz, 2H), 7.42 (d, ^3J(H,H) = 8.4 Hz, 2H), 6.98 (d, ^3J(H,H) = 8.9 Hz, 2H), 3.85 (s, 3 H), 3.78-3.66 (br_m, 2H), 3.51-3.33 (br_m, 2H), 1.78-1.48 (br_m, 6H).**^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): δ = 170.3, 159.5, 141.9, 134.7, 132.9, 128.2, 127.4, 126.6, 114.3, 55.4, 48.8, 43.2, 26.5, 25.8, 24.7. **MS** (70 eV, EI): *m/z* (%): 295 (52) [M^+], 294 (90), 211 (100), 183 (8), 168 (12), 152 (7), 140 (9), 105 (5). **IR** (KBr): $\tilde{\nu}$ = 3436 (m), 1605 (vs), 1621 (s), 1441 (s), 1285 (s), 1250 (s), 1183 (m), 1035 (m), 1003 (m), 833 (s). **HRMS** for **$C_{19}H_{21}NO_2$** (295.1572): found: 295.1550.

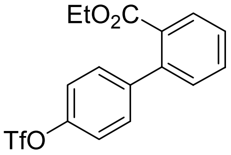
Synthesis of ethyl 4'-benzoyl[1,1'-biphenyl]-4-carboxylate (4j)



Prepared according to **TP 2** from 4-iodobenzophenone **3b** (308 mg, 1.0 mmol), ethyl 4-iodobenzoate (828mg, 3.0 mmol), *i*-PrMgCl (4.0 mL, 3.0 mmol, 0.75 M in THF), CuCN•2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF) and Fe(acac)$_3$ (36 mg, 0.1 mmol). Reaction time: 4 h (room temperature). Purification by flash chromatography (pentane/diethyl ether = 50:1) yielded product **4j** as a white solid (166 mg, 50%).

mp.: 98.5-100.5 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 8.18-8.12 (m, 2H), 7.93-7.88 (m, 2H), 7.86-7.81 (m, 2H), 7.76-7.68 (m, 4H), 7.64-7.57 (m, 1H), 7.54- 7.46 (m, 2H), 4.46-4.37 (q, ^3J(H,H) = 7.08 Hz, 2H), 1.45-1.39 (t, ^3J(H,H) = 7.08 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): δ = 196.10, 166.25, 144.16, 143.89, 137.54, 136.95, 132.47, 130.69, 130.16, 130.06, 129.96, 128.31, 127.16, 127.12, 61.05, 14.31. **MS** (70 eV, EI): *m/z* (%): 331 (23), 330 (100) [M$^+$], 285 (32), 254 (13), 253 (72), 225 (11), 152 (10), 105 (12), 77 (8). **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 1716 (vs), 1647 (vs), 1607 (m), 1578 (w), 1444 (w), 1396 (m), 1370 (w), 1284 (vs), 1180 (m), 1110 (s), 1025 (w), 941 (m), 925 (w), 844 (m), 773 (m), 760 (m), 736 (m), 693 (m), 650 (m). **HRMS** for **$C_{22}H_{18}O_3$** (330.1256): found: 330.1260.

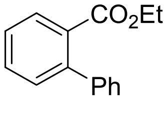
Synthesis of ethyl 4'-{[(trifluoromethyl)sulfonyl]oxy}[1,1'-biphenyl]-2-carboxylate (4k)



Prepared according to **TP 2** from ethyl 2-iodobenzoate **3g** (276 mg, 1.0 mmol), trifluoromethanesulfonic acid 4-iodo-phenyl ester (1.056 g, 3.0 mmol), *i*PrMgCl (4.0 mL, 3.0 mmol, 0.75 M in THF), CuCN•2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF) and Fe(acac)$_3$ (36 mg, 0.1 mmol). Reaction time: 2 h at 80 °C. Purification by flash chromatography (pentane/diethyl ether = 100:1) yielded product **4k** as a colourless oil (233 mg, 62%).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.93-7.88 (dd, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.33 Hz, 1H), 7.58-7.51 (td, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.77 Hz, 1H), 7.49-7.43 (td, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.77 Hz, 1H), 7.41-7.35 (m, 2H), 7.35-7.27 (m, 3H), 4.13-4.05 (q, ^3J(H,H) = 7.08 Hz, 2H), 1.04-0.98 (t, ^3J(H,H) = 7.08 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): δ = 168.00, 148.78, 142.19, 140.56, 131.40, 130.94, 130.50, 130.22, 130.20, 127.91, 120.82, 118.76 (q, ^1J(F,C) = 321 Hz), 61.05, 13.49. **MS** (70 eV, EI): *m/z* (%): 375 (12), 374 (68) [M$^+$], 329 (29), 242 (16), 241 (88), 214 (15), 213 (100), 195 (20), 185 (9), 169 (20), 168 (27), 167 (58), 141 (17), 140 (15), 139 (36), 129 (11), 128 (11). **IR** (Film): $\tilde{\nu}$ (cm^{-1}) = 1721 (s), 1600 (w), 1506 (w), 1480 (m), 1448 (w), 1426 (s), 1367 (w), 1281 (s), 1250 (s), 1214 (vs), 1180 (m), 1141 (vs), 1099 (m), 1048 (w), 1020 (w), 1008 (w), 888 (s), 843 (m), 764 (m), 706 (w), 637 (w), 607 (m), 574 (w), 527 (w). **HRMS** for **$C_{16}H_{13}F_3O_5S$** (374.0436): found: 374.0437.

Synthesis of ethyl 2-phenylbenzoate (4l)

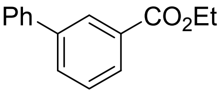


Prepared according to **TP 1** from ethyl 2-iodobenzoate **3g** (276 mg, 1.0 mmol), PhMgCl (1.82 mL, 3.0 mmol, 1.65 M in THF), CuCN•2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF) and Fe(acac)$_3$ (36 mg, 0.1 mmol). Reaction time: 2 h at 80 °C. Purification by flash chromatography (pentane/diethyl ether = 100:1) yielded product **4l** as a colourless oil (132 mg, 58%).

^{1}H-NMR (300 MHz, CDCl$_3$, 25 °C): δ = 7.87-7.82 (dd, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.33 Hz, 1H), 7.56-7.49 (td, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.33 Hz, 1H), 7.45-7.30 (m, 7H), 4.14-4.05 (q, ^3J(H,H) = 7.08 Hz, 2H), 1.03-0.97 (t, ^3J(H,H) = 7.08 Hz, 3H). **^{13}C-NMR** (75 MHz, CDCl$_3$, 25 °C): δ = 168.77, 142.37, 141.49, 131.32, 131.03, 130.54, 129.65, 128.34, 127.92, 127.09, 127.08, 60.83, 13.59. **MS** (70 eV, EI): *m/z* (%): 226 (33) [M$^+$], 198 (9), 182 (13), 181 (100), 153 (32), 152 (42), 151 (12), 76 (6), 44 (11). **IR** (Film): $\tilde{\nu}$ (cm^{-1}) = 3061 (w), 3027 (w), 2982 (m), 2937 (w), 2903 (w), 1716 (vs), 1598 (m), 1568 (w), 1477 (m), 1451 (m), 1391 (w), 1366 (m), 1281 (vs), 1243 (s), 1173 (w), 1130 (s), 1099 (m), 1049 (m), 1009 (m), 845 (w), 777 (m), 747 (s), 700 (s), 664 (w). **HRMS** for **$C_{15}H_{14}O_2$** (226.0994): found: 226.0970.

Spectral data match those reported in the literature. [iv]

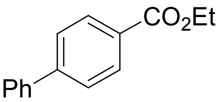
Synthesis of ethyl 3-phenylbenzoate (4m)



Prepared according to **TP 1** from ethyl 3-iodobenzoate **3h** (276 mg, 1.0 mmol),), PhMgCl (1.82 mL, 3.0 mmol, 1.65 M in THF), CuCN•2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF) and Fe(acac)$_3$ (36 mg, 0.1 mmol). Reaction time: 10 h at 80 °C. Purification by flash chromatography (pentane/diethyl ether = 100:1) yielded product **4m** as a colourless oil (159 mg, 70%).

^{1}H-NMR (300 MHz, CDCl$_3$, 25 °C): δ = 8.32-8.30 (m, 1H), 8.08-8.02 (m, 1H), 7.81-7.76 (m, 1H), 7.67-7.62 (m, 2H), 7.55-7.44 (m, 3H), 7.43-7.35 (m, 1H), 4.47-4.39 (q, ^3J(H,H) = 7.08 Hz, 2H), 1.46-1.40 (t, ^3J(H,H) = 7.08 Hz, 3H). **^{13}C-NMR** (75 MHz, CDCl$_3$, 25 °C): δ = 166.50, 141.39, 140.14, 131.37, 131.01, 128.82, 128.73, 128.27, 128.17, 127.65, 127.12, 61.00, 14.30. **MS** (70 eV, EI): *m/z* (%): 227 (11), 226 (67) [M$^+$], 198 (29), 182 (17), 181 (100), 154 (11), 153 (54), 152 (55), 151 (14), 76 (13). **IR** (Film): $\tilde{\nu}$ (cm^{-1}) = 3063 (w), 3034 (w), 2981 (m), 2936 (w), 2905 (w), 1717 (vs), 1602 (w), 1587 (w), 1479 (m), 1454 (m), 1422 (m), 1391 (w), 1367 (m), 1306 (s), 1273 (s), 1241 (vs), 1172 (m), 1109 (s), 1084 (m), 1050 (m), 1028 (m), 906 (w), 772 (w), 743 (s), 714 (m), 697 (s), 672 (w), 615 (w). **HRMS** for **$C_{15}H_{14}O_2$** (226.0994): found: 226.0986.

Synthesis of ethyl 4-phenylbenzoate (4n)

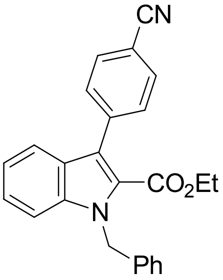


Prepared according to **TP 1** from ethyl 4-iodobenzoate **3i** (276 mg, 1.0 mmol), PhMgCl (1.82 mL, 3.0 mmol, 1.65 M in THF), CuCN•2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF) and Fe(acac)$_3$ (36 mg, 0.1 mmol). Reaction time: 2 h at 80 °C. Purification by flash chromatography (pentane/diethyl ether = 29:1) yielded product **4n** as a colourless solid (188 mg, 82%).

^{1}H-NMR (300 MHz, CDCl$_3$, 25 °C): δ = 8.14 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.69-7.63 (m, 4H), 7.48-7.40 (m, 3H), 4.43 (q, ^3J(H,H) = 7.1 Hz, 2H), 1.44 (t, ^3J(H,H) = 7.1 Hz, 3H). **^{13}C-NMR** (75 MHz, CDCl$_3$, 25 °C): δ = 166.4, 145.4, 139.9, 130.0, 129.2, 128.8, 128.0, 127.2, 126.9, 60.9, 14.3. **MS** (70 eV, EI): *m/z* (%): 226 (100) [M$^+$], 181 (80), 152 (47).

Spectral data match those reported in the literature.[v]

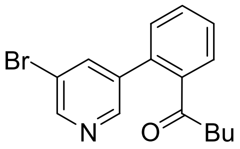
Synthesis of ethyl 1-benzyl-3-(4-cyanophenyl)-1*H*-indole-2-carboxylate (4o)



Prepared according to **TP 2** from ethyl 1-benzyl-3-iodo-1*H*-indole-2-carboxylate (1.26 g, 3.1 mmol), *i*PrMgCl (3.3 mL, 3.0 mmol, 0.90 M in THF), CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF) and 4-iodobenzonitrile (229 mg, 1.0 mmol). Reaction time 6 h at 80 °C. Purification by flash chromatography (pentane/diethyl ether = 4:1) yielded **4o** as a yellow oil (323 mg, 85%).

^{1}H-NMR (300 MHz, CDCl$_3$, 25 °C): δ = 7.78 (d, ^3J(H,H) = 8.2 Hz, 2H), 7.62 (d, ^3J(H,H) = 8.2 Hz, 2H), 7.56 (d, ^3J(H,H) = 8.2 Hz, 1H), 7.49-7.12 (m, 8H), 5.58 (s, 2H), 4.18 (q, ^3J(H,H) = 7.1 Hz, 2H), 1.05 (t, ^3J(H,H) = 7.1 Hz, 3H). **^{13}C-NMR** (75 MHz, CDCl$_3$, 25 °C): δ = 161.38, 140.16, 138.18, 137.87, 131.52, 131.34, 128.62, 127.30, 126.33, 126.29, 125.76, 125.32, 122.62, 121.52, 120.86, 119.14, 110.87, 110.45, 68.83, 48.28, 21.39. **MS** (70 eV, EI): *m/z* (%): 380 (89) [M$^+$], 334 (8), 305 (5), 245 (6), 190 (5), 91 (100). **IR** (KBr): $\tilde{\nu}$ = 2978 (s), 2871 (m), 2228 (vs), 1705 (vs), 1608 (s), 1541 (s), 1495 (s), 1454 (vs), 1418 (s), 1350 (s), 1270 (vs), 1245 (vs), 1175 (vs), 1152 (s), 1128 (vs), 1023 (m), 909 (vs), 842 (m), 732 (vs), 697 (s), 648 (m), 552 (m). **HRMS** for **$C_{25}H_{20}N_2O_2$** (380.1525): found: 380.1530.

Synthesis of 1-[2-(5-bromo-pyridin-3-yl)-phenyl]-pentan-1-one (4p)

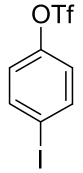


Prepared according to **TP 2** from 2-iodobutanophenone **3d** (288 mg, 1.0 mmol), 3,5-dibromopyridine (711 mg, 3.0 mmol), *i*PrMgCl•LiCl (3.13 mL, 3.0 mmol, 0.96 M in THF), CuCN•2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF) and Fe(acac)$_3$ (36 mg, 0.1 mmol). Reaction time: 22 h at 25 °C. Purification by flash chromatography (pentane/diethyl ether = 20:1) yielded product **4** as a yellow oil (182 mg, 57%).

^{1}H-NMR (300 MHz, CDCl$_3$, 25 °C): δ = 8.67-8.64 (d, ^4J(H,H) = 2.21 Hz, 1H), 8.45-8.42 (d, ^4J(H,H) = 2.21 Hz, 1H), 7.78-7.75 (t, ^4J(H,H) = 2.21 Hz, 1H), 7.64-7.59 (dd, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.77 Hz, 1H), 7.57-7.45 (m, 2H), 7.34-7.30 (dd, ^3J(H,H) = 7.52 Hz, ^4J(H,H) = 1.77 Hz, 1H), 2.59-2.53 (t, ^3J(H,H) = 7.08 Hz, 2H), 1.58-1.47 (m, 2H), 1.30-1.15 (m, 2H), 0.85-0.79 (t, ^3J(H,H) = 7.08 Hz, 3H). **^{13}C-NMR** (75 MHz, CDCl$_3$, 25 °C): δ = 205.04, 149.55, 147.30, 140.09, 138.40, 138.23, 135.31, 130.95, 130.79, 128.63, 128.17, 120.37, 42.03, 26.25, 22.13, 13.69. **MS** (70 eV, EI): *m/z* (%): 319 (4), 317 (5) [M$^+$], 277 (33), 276 (27), 275 (37), 274 (23), 263 (12), 262 (94), 261 (13), 260 (100), 181 (42), 153 (45), 126 (15), 77 (8), 57 (10). **IR** (Film): $\tilde{\nu}$ (cm^{-1}) = 3037 (w), 2958 (s), 2930 (m), 2872 (m), 1691 (vs), 1596 (w), 1579 (w), 1547 (w), 1465 (w), 1425 (m), 1408 (m), 1260 (m), 1206 (m), 1098 (w), 1011 (m), 888 (w), 761 (m), 707 (m). **HRMS** for **$C_{16}H_{16}NOBr$** (317.0415): found: 317.0393.

Preparation of starting material:

Synthesis of 4-iodophenyl trifluoromethanesulfonate

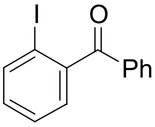


A 50 mL round-bottom flask, equipped with a magnetic stirring bar, was charged with 4-iodophenol (2.19 g, 10.0 mmol) and dry pyridine (20 mL) was added. The solution was cooled to 0 °C and trifluoromethylsulfonic acid anhydride (1.92 mL, 11.0 mmol) was added dropwise. On completion of the addition, the reaction mixture was stirred for additional 15 min at 0 °C and was then allowed to warm to room temperature and was stirred overnight. The reaction mixture was poured onto ice (50 g) and ethyl acetate (100 mL), 2M HCl (30 mL) was added and the phases were separated. The organic phase was washed with 2M HCl (30 mL), saturated NaHCO$_3$-solution (50 mL), brine (50 mL), dried over Na$_2$SO$_4$, filtered and concentrated *in vacuo*. Purification by flash chromatography (pentane) furnished the title compound as a colourless oil (2.63 g, 75%).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.81$-7.75 (m, 2H), 7.07-7.00 (m, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): $\delta = 149.39$, 139.41, 123.29, 118.67 (q, ^1J(F,C) = 321 Hz), 93.12. **MS** (70 eV, EI): *m/z* (%): 352 (80) [M^+], 219 (100), 191 (31), 95 (14), 92 (23), 69 (11), 64 (34), 63 (21). **IR** (Film): $\tilde{\nu}$ (cm^{-1}) = 1479 (s), 1428 (vs), 1395 (m), 1299 (w), 1251 (s), 1215 (vs), 1179 (m), 1141 (vs), 1098 (w), 1057 (w), 1010 (s), 940 (w), 886 (s), 829 (s), 778 (w), 747 (s), 698 (w), 635 (w), 626 (m), 606 (s), 573 (w), 522 (m), 482 (w). **HRMS** for **$C_7H_4F_3IO_3S$** (351.8878): found: 351.8869.

Spectral data match those reported in the literature.[v]

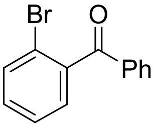
Synthesis of 2-iodobenzophenone (3a)



2-Aminobenzophenone (3.92 g, 20.0 mmol) was dissolved in a solution acetic acid (15 mL) and H_2SO_4 (50% in H_2O) in glacial acidic acid, cooled to 0 °C, and an aqueous solution (5 mL) of KNO_2 (1.82 g, 22.0 mmol) was added dropwise. After 30 min the reaction mixture was allowed to warm to rt, stirred for an additional hour and cooled again to 0 °C. Subsequent, KI (3.98 g, 24.0 mmol) dissolved in 5 mL of water was added with vigorous stirring (Caution! gas evaluation). The reaction mixture was stirred for 30 min at this temperature and was then allowed to warm to rt. Stirring was continued for 1 h, the reaction mixture afterwards poured on iced-water (100 mL) and extracted with diethyl ether (3x100 mL). The combined organic fractions were washed with brine (100 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by flash chromatography (pentane/diethyl ether = 49:1) yielded title compound **3a** as a yellow oil (4.50 g, 73%).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.95$-7.89 (m, 1H), 7.84-7.79 (m, 2H), 7.65-7.57 (m, 1H), 7.51-7.41 (m, 3H), 7.31-7.14 (m, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): $\delta = 197.2$, 144.4, 139.7, 135.6, 133.7, 131.1, 130.5, 128.7, 128.5, 127.8, 92.2. **MS** (70 eV, EI): *m/z* (%): 308 (100) [M^+], 231 (60), 203 (29), 181 (26), 152 (67), 126 (7), 105 (92), 77 (62), 51 (27). **IR** (Film): $\tilde{\nu}$ (cm^{-1}) = 1668 (vs), 1595 (m), 1580 (m), 1462 (w), 1448 (m), 1427 (m), 1315 (m), 1286 (vs), 1251 (m), 1154 (w), 1073 (w), 1014 (m), 927 (m), 800 (w), 763 (m), 734 (m), 703 (m), 654 (m), 632 (m). **HRMS** for **$C_{13}H_9OI$** (307.9698): found: 307.9699.

Synthesis of of 2-bromobenzophenone

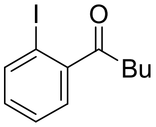


2-Aminobenzophenone (3.92 g, 20.0 mmol) was dissolved in HBr (20 mL, 47% in H_2O), cooled to 0 °C, and an aqueous solution (5 mL) of KNO_2 (1.82 g, 22 mmol) was added dropwise. After 30 min the reaction mixture was allowed to warm to rt, stirred for an additional hour. This suspension was then added with vigorous stirring to CuBr (3.59 g, 25 mmol) dissolved in 15 mL of HBr (Caution! gas evaluation). The reaction mixture was heated to 60 °C for 1 hour, the reaction mixture afterwards poured on iced-water (100 mL) and extracted with diethyl ether (3x100 mL). The combined organic fractions were washed with brine (100 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by flash chromatography (pentane/diethyl ether = 49:1) yielded title compound as a yellow oil (3.53 g, 68%).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.84-7.79 (m, 2H), 7.68-7.57 (m, 2H), 7.50-7.32 (m, 5H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): δ = 195.83, 140.67, 136.11, 133.69, 133.17, 131.12, 130.19, 128.96, 128.61, 127.16, 119.51. **MS** (70 eV, EI): *m/z* (%): 262 (17), 260 (15) [M^+], 185 (19), 183 (22), 182 (28), 157 (9), 155 (9), 152 (13), 105 (100), 77 (52), 76 (20), 75 (11), 51 (11). **IR** (Film): $\tilde{\nu}$ (cm^{-1}) = 1671 (vs), 1596 (s), 1581 (m), 1467 (w), 1449 (s), 1431 (m), 1315 (s), 1288 (vs), 1251 (s), 1154 (m), 1047 (w), 1025 (m), 928 (s), 800 (w), 763 (s), 738 (s), 722 (m), 702 (s), 665 (m), 632 (s). **HRMS** for **$C_{13}H_9OBr$** (259.9837): found: 259.9853.

Spectral data match those reported in the literature.[vi]

Synthesis of 1-iodophenyl-1-pentanone (3d)

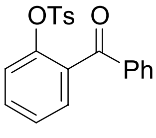


Prepared according to the procedure reported by F. M. Beringer.[vii]

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.92-7.88 (dd, ^3J(H,H) = 7.96 Hz, ^4J(H,H) = 0.89 Hz, 1H), 7.43-7.32 (m, 2H), 7.14-7.07 (m, 1H), 2.91-2.85 (t, ^3J(H,H) = 7.52 Hz, 2H), 1.76-1.65 (m, 2H), 1.48-1.34 (m, 2H), 0.97-0.91 (t, ^3J(H,H) = 7.52 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): δ = 205.22, 145.04, 140.44, 131.33, 127.97, 127.56, 90.88, 41.83, 26.13, 22.31, 13.85. **MS** (70 eV, EI): *m/z* (%): 288 (6) [M^+], 246 (57), 232 (7), 231 (100), 203 (20), 76 (11). **IR** (Film): $\tilde{\nu}$ (cm^{-1}) = 1699 (vs), 1582 (m), 1561 (w), 1462 (m), 1428 (m), 1278 (m), 1251 (m), 1208 (m), 1013 (m), 755 (s), 729 (m). **HRMS** for **$C_{11}H_{13}OI$** (288.0011): found: 288.0017.

Spectral data match those reported in the literature.[vii]

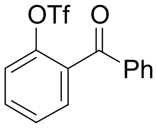
Synthesis of 2-benzoylphenyl 4-methylbenzenesulfonate



A 50 mL round-bottom flask, equipped with a magnetic stirring bar, was charged with 2-hydroxybenzophenone (1.98 g, 10.0 mmol) and dry pyridine (20 mL) was added. The solution was cooled to 0 °C and 4-methylbenzenesulfonyl chloride (2.54 g, 13.0 mmol) was added portionwise. On completion of the addition, the reaction mixture was stirred for additional 15 min at 0 °C and was then allowed to warm to room temperature and was stirred overnight. The reaction mixture was poured onto ice (50 g) and ethyl acetate (100 mL), 2M HCl (30 mL) was added and the phases were separated. The organic phase was washed with 2M HCl (30 mL), saturated $NaHCO_3$-solution (50 mL), brine (50 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Recrystallization from ethanol furnished the title compound as a colourless solid (3.27 g, 93%).

mp.: 98.0-99.4 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 7.63-7.33 (m, 10H), 7.15-7.11 (m, 2H), 2.34 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): δ = 193.8, 146.5, 145.4, 136.6, 133.2, 133.1, 132.1, 131.9, 130.5, 130.1, 129.6, 128.4, 128.2, 126.9, 123.8, 21.7. **MS** (70 eV, EI): *m/z* (%): 352 (0.1) [M^+], 197 (100), 168 (7), 155 (40), 91 (65), 77 (11). **IR** (Film): $\tilde{\nu}$ (cm^{-1}) = 1666 (vs), 1600 (s), 1372 (vs), 1298 (m), 1270 (s), 1199 (s), 1172 (s), 1089 (s), 938 (m), 790 (m), 698 (s), 557 (m), 549 (m). **HRMS** for **$C_{20}H_{16}O_4S$** (352.0769): found: 352.0774.

Synthesis of 2-benzoylphenyl trifluoromethanesulfonate

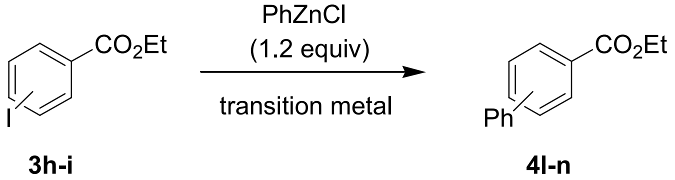


A 50 mL round-bottom flask, equipped with a magnetic stirring bar, was charged with 2-hydroxybenzophenone (1.98 g, 10.0 mmol) and dry pyridine (20 mL) was added. The solution was cooled to 0 °C and trifluoromethylsulfonic acid anhydride (1.92 mL, 11.0 mmol) was added dropwise. On completion of the addition, the reaction mixture was stirred for additional 15 min at 0 °C and was then allowed to warm to room temperature and was stirred overnight. The reaction mixture was poured onto ice (50 g) and ethyl acetate (100 mL), 2M HCl (30 mL) was added and the phases were separated. The organic phase was washed with 2M HCl (30 mL), saturated $NaHCO_3$-solution (50 mL), brine (50 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by flash chromatography (pentane/diethyl ether = 19:1) furnished the title compound as a colourless oil (3.10 g, 94%).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.82-7.79 (m, 2H), 7.66-7.56 (m, 3H), 7.51-7.41 (m, 4H). **^{13}C-NMR** (75 MHz, $CDCl_3$, 25 °C): δ = 192.6, 146.8, 136.5, 133.8, 132.6, 132.5, 131.2, 130.2, 128.6, 128.0, 122.4, 118.7 (^1J(C,F) = 321 Hz). **MS** (70 eV, EI): *m/z* (%): 330 (39) [M^+], 265 (6), 252 (16), 197 (32), 168 (8), 105 (100), 77 (31). **IR** (Film): $\tilde{\nu}$ (cm^{-1}) = 1670 (vs), 1607 (m), 1448 (m), 1425 (vs), 1294 (s), 1273 (s), 1248 (s), 1212 (vs), 1139 (vs), 1090 (vs), 940 (s), 884 (vs), 782 (m), 704 (m), 633 (w), 619 (m), 604 (w), 594 (m). **HRMS** for **$C_{14}H_9F_3O_4S$** (330.0174): found: 330.0175.

Comparison of the reactivity of ethyl 2-, 3- and 4-iodobenzoate with different transition metal catalysts

In order to compare the reactivities, three Schlenk-tubes (10 mL) were used, each loaded with the appropriate iodide (276 mg, 1 mmol) and literature procedures were followed for the performance of the cross-coupling.



Pd-catalyzed cross-coupling reactions:
A dry and argon flushed 10 mL Schlenk-tube, equipped with a magnetic stirrer and a septum, was charged phenylmagnesium chloride (0.73 mL, 1.20 mmol, 1.65 M in THF) and zinc chloride (1.2 mL, 1.2 mmol, 1.0 M in THF) was added dropwise. The appropriate iodide (276 mg, 1.00 mmol) and *n*-decane (50 mg) dissolved in dry THF (1 mL) were added subsequently and the mixture cooled to –5 °C. Another dry two-necked flask equipped with a magnetic stirrer and a septum was charged with *bis*-(dibenzylideneacetone)palladium(0) ($Pd(dba)_2$) (29 mg, 5mol%) and *tris*-*o*-furylphosphine (tfp) (25 mg, 10mol%) followed by THF (2 mL). The initial red colour disappeared after 2 min leading to a yellow solution and this solution was added *via cannula* to the reaction mixture. The reaction mixture was stirred for 3 h at –5 °C, a reaction aliquot was taken every 10 min and analyzed with GC/GCMS until 50% conversion was observed.

Ethyl 2-iodobenzoate (**3g**) 50% conversion after **2 h 10 min** at –5 °C.

Ethyl 3-iodobenzoate (**3h**) 50% conversion after **1 h 30 min** at –5 °C.

Ethyl 4-iodobenzoate (**3i**) 50% conversion after **30 min** at –5 °C.

Ni-catalyzed cross-coupling reactions:
Prepared according to the procedure reported by Miyaura[viii] from phenylmagnesium chloride (0.73 mL, 1.20 mmol, 1.65 M in THF), zinc chloride (1.2 mL, 1.2 mmol, 1.0 M in THF), the appropriate iodide (276 mg, 1.00 mmol), *n*-decane (50 mg) and $NiCl_2(dppe)$ (52.8 mg, 10 mol%). The reaction mixture was stirred for 2 h at 25 °C, a reaction aliquot was taken every 10 min and analyzed with GC/GCMS until 50% conversion was observed.

Ethyl 2-iodobenzoate (**3g**) 50% conversion after **30 min** at 25 °C.

Ethyl 3-iodobenzoate (**3h**) 50% conversion after **10 min** at 25 °C.

Ethyl 4-iodobenzoate (**3i**) 50% conversion after **20 min** at 25 °C.

The procedure for the iron catalyzed cross-coupling reaction with the copper reagent made from phenyllithium

A 25 mL Schlenk-flask, equipped with a magnetic stirring bar, was charged with DME (5 mL), cooled to −20 °C and PhLi (2.1 mL, 3.0 mmol, 1.4 M in THF) was added. Subsequently, a solution of CuCN·2LiCl (2.8 mL, 2.8 mmol, 1.0 M in THF) was added and the reaction mixture was stirred for 10 min. A solution of 2-iodobenzophenone **3a** (308 mg, 1.0 mmol) and $Fe(acac)_3$ (35 mg, 0.10 mmol) dissolved in DME (3 mL) was added at once and the reaction mixture was warmed up to room temperature for 30 min. The reaction was quenched with sat. $NH_4Cl_{(aq.)}$ and was extracted with CH_2Cl_2 (3x40 mL). The organic fractions were washed with sat. $NH_4Cl_{(aq.)}/NH_3$ (9:1) (50 mL) and brine (50 mL), dried over Na_2SO_4, filtered and the solvent was evaporated *in vacuo*. Purification by flash chromatography (pentane/diethyl ether = 29:1) yielded product **4a** as a colourless oil (233 mg, 90 %).

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