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Supporting Information

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Cobalt(II)-Catalyzed Cross-Coupling Between Polyfunctional Arylcopper Reagents and Aryl Bromides or Chlorides

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General All reactions were carried out under an argon 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. DME was distilled from sodium benzophenone ketyl under nitrogen. DMPU was refluxed for 6 h over calcium hydride and distilled. Yields refer to isolated yields of compounds estimated to be > 95% pure as determined by ^{1}H-NMR and capillary GC.

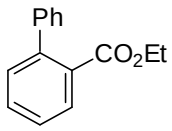
Typical procedure for the cobalt catalyzed cross-coupling reaction (TP 1)

A 25 mL Schlenk-tube, equipped with a magnetic stirring bar and a septum, was charged with the appropiate Grignard reagent, cooled to –20 °C and a solution of CuCN·2LiCl (1.9 mL, 1.9 mmol, 1 M in THF) was added. After stirring for 10 min at –20 °C DME (6.0 mL), DMPU (2.0 mL), Bu_4NI (370 mg, 1.00 mmol), 4-fluorostyrene (25 mg, 0.20 mmol), $Co(acac)_2$ (19.3 mg, 0.075 mmol) and the corresponding aryl bromide or chloride (1.00 mmol) were added. The reaction mixture was stirred at room temperature or heated to 80 °C. After full conversion (checked by GC-analysis) the suspension was quenched with sat. $NH_4Cl_{(aq.)}/NH_3$ (9:1) (50 mL). The organic fraction was washed a second time with sat. $NH_4Cl_{(aq.)}/NH_3$ (9:1) (50 mL) and the combined water phases were extracted with EtOAc (3x40 mL). The organic fractions were washed with brine (50 mL), dried over Mg_2SO_4, filtered and the solvent was evaporated *in vacuo*. Flash chromatographical purification on silica gel furnished the analytically pure products.

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

A 25 mL Schlenk-tube, equipped with a magnetic stirring bar and a septum, was charged with *i*PrMgCl or *i*PrMgCl·LiCl, cooled to the appropriate temperature and the aryl halide (1.70 mmol) was added. The reaction mixture was stirred at the same temperature or higher (as stated in the experiment) until full completion of the halogen/Mg exchange (checked by GC-analysis). Subsequent, a solution of CuCN·2LiCl (1.9 mL, 1.9 mmol, 1 M in THF) was added at –20 °C. After stirring for additional 10 min DME (6.0 mL), DMPU (2.0 mL), Bu_4NI (370 mg, 1.00 mmol), 4-fluorostyrene (25 mg, 0.20 mmol), $Co(acac)_2$ (19.3 mg, 0.075 mmol) and the corresponding aryl bromide or chloride (1.00 mmol) were added. The reaction mixture was stirred at room temperature or heated to 80 °C. After full conversion (checked by GC-analysis) the suspension was quenched with sat. $NH_4Cl_{(aq.)}/NH_3$ (9:1) (50 mL). The organic fraction was washed a second time with sat. $NH_4Cl_{(aq.)}/NH_3$ (9:1) (50 mL) and the combined water phases were extracted with EtOAc (3x40 mL). The organic fractions were washed with brine (50 mL), dried over Mg_2SO_4, filtered and the solvent was evaporated *in vacuo*. Flash chromatographical purification on silica gel furnished the analytically pure products.

Synthesis of ethyl [1,1'-biphenyl]-2-carboxylate (3a)



Prepared according to **TP 1** from ethyl 2-bromobenzoate **1a** (229 mg, 1.00 mmol) and PhMgCl **2a** (1.42 mL, 1.70 mmol, 1.20 M in THF). Reaction time: 0.25 h at 80 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 19:1) yielded product **3a** as a colourless oil (175 mg, 0.77 mmol, 77 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.81 (dd, *J* = 7.6 and 1.3 Hz, 1 H), 7.51(td, *J* = 7.5 and 1.3 Hz, 1 H), 7.44-7.27 (m, 7 H), 4.07 (q, *J* = 7.0 Hz, 2 H), 0.97 (t, *J* = 7.2 Hz, 3 H).

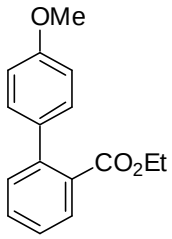
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 168.8, 142.4, 141.5, 131.3, 131.1, 130.6, 129.7, 128.4, 127.9, 127.1, 113.9, 60.9, 13.6.

MS (70 eV, EI): *m/z* (%): 226 (41) [M^+], 182 (15), 181 (100), 153 (22), 152 (34).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 3061 (w), 3027 (w), 2982 (m), 2936 (w), 1950 (vw), 1716 (vs), 1281 (s), 1243 (s), 747 (s), 700 (m).

HRMS for **$C_{15}H_{14}O_2$** (226.0994): found: 226.1008.

Synthesis of ethyl 4'-methoxy[1,1'-biphenyl]-2-carboxylate (3b)



Prepared according to **TP 1** from ethyl 2-bromobenzoate **1a** (230 mg, 1.00 mmol) and (4-methoxyphenyl)magnesium bromide **2b** (2.13 mL, 1.70 mmol, 0.80 M in THF). Reaction time: 0.25 h at 80 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 19:1) yielded product **3b** as a colourless oil (202 mg, 0.79 mmol, 79 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.77 (dd, *J* = 7.4 and 1.4 Hz, 1 H), 7.47(td, *J* = 7.5 and 1.2 Hz, 1 H), 7.35 (tt, *J* = 8.1 and 1.3 Hz, 2 H), 7.23 (d, *J* = 8.8 Hz, 2 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 4.10 (q, *J* = 7.0 Hz, 2 H), 3.82 (s, 3 H), 1.04 (t, *J* = 7.1 Hz, 3 H).

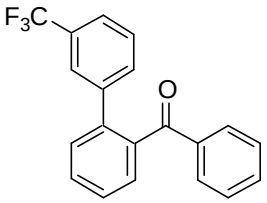
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 169.0, 159.0, 141.9, 133.8, 131.4, 131.0, 130.6, 129.6, 129.5, 126.8, 113.5, 60.9, 55.3, 13.8.

MS (70 eV, EI): *m/z* (%): 256 (100) [M^+], 228 (10), 212 (12), 211 (81), 168 (18), 139 (15).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 3064 (w), 3031 (w), 2981 (m), 2936 (w), 2837 (w), 1715 (s), 1612 (m), 1518 (s), 1283 (s), 1248 (vs), 833 (m), 764 (m).

HRMS for **$C_{16}H_{16}O_3$** (256.1099): found: 256.1089.

Synthesis of phenyl[3'-(trifluoromethyl)[1,1'-biphenyl]-2-yl]methanone (3c)



Prepared according to **TP 2** from 2-bromobenzophenone **1b** (260 mg, 1.00 mmol), 1-iodo-3-(trifluoromethyl)benzene (465 mg, 1.71 mmol) and *i*PrMgCl (2.15 mL, 1.79 mmol, 0.83 M in THF). The *i*PrMgCl-solution was added at -20 °C and the halogen/Mg exchange was complete after 0.5 h at -20 °C. Reaction time for cross-coupling: 3 h at 80 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 29:1) yielded product **3c** as a colourless oil (201 mg, 0.62 mmol, 62 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.67-7.20 (m, 13 H).

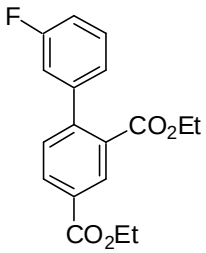
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 198.3, 141.0, 139.7, 139.0, 137.3, 133.0, 132.3 (q, *J* = 0.9 Hz), 130.6, 130.6 (q, *J* = 32.2 Hz), 130.0, 129.8, 129.1, 128.6, 128.2, 127.8, 125.8 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 3.4 Hz), 123.9 (q, *J* = 272.3 Hz).

MS (70 eV, EI): *m/z* (%): 326 (100) [M^+], 325 (24), 257 (21), 250 (13), 249 (94), 201 (36), 152 (17).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 4062 (vw), 3317 (vw), 3064 (m), 2927 (w), 1966 (vw), 1666 (s), 1335 (vs), 1283 (s), 1167 (s), 1127 (s), 929 (m), 761 (m), 700 (s), 639 (m).

HRMS for **$C_{20}H_{13}F_3O$** (326.0918): found: 326.0922.

Synthesis of diethyl 3'-fluoro[1,1'-biphenyl]-2,4-dicarboxylate (3d)



Prepared according to **TP 2** from diethyl 4-bromoisophthalate **1c** (299 mg, 0.99 mmol), 1-bromo-3-fluorobenzene (300 mg, 1.71 mmol) and *i*PrMgCl·LiCl (1.88 mL, 1.79 mmol, 0.95 M in THF). The *i*PrMgCl·LiCl-solution was added at -10 °C and the halogen/Mg exchange was complete after 3 h at 25 °C. Reaction time for the cross-coupling: 0.5 h at 80 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 4:1) yielded product **3d** as a colourless oil (202 mg, 0.64 mmol, 65 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 8.48 (d, *J* = 1.8 Hz, 1 H), 8.16 (dd, *J* = 8.4 and 2.2 Hz, 1 H), 7.44-730 (m, 2 H), 7.11-6.99 (m, 3 H), 4.40 (q, *J* = 7.1 Hz, 2 H), 4.13 (q, *J* = 7.1 Hz, 2 H), 1.40 (t, *J* = 7.1 Hz, 3 H), 1.05 (t, *J* = 7.1 Hz, 3 H).

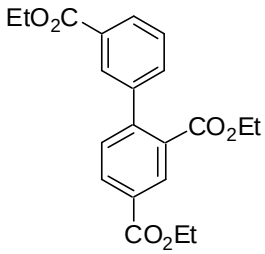
^{13}C-NMR (150 MHz, $CDCl_3$, 25 °C): d = 167.6, 165.5, 162.5 (q *J* = 247 Hz), 145.2 (q, *J* = 2.3 Hz), 142.7 (q, *J* = 8.2 Hz), 133.7, 132.0, 131.5, 131.1, 130.7, 129.7 (q, *J* = 8.3 Hz), 124.1 (q, *J* = 2.4 Hz), 115.4 (q, *J* = 22.3 Hz), 114.6 (q, *J* = 21.1 Hz), 61.4, 61.3, 14.3, 13.7.

MS (70 eV, EI): *m/z* (%): 316 (52) [M^+], 272 (19), 271 (100), 243 (28), 170 (26).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 3425 (vw), 3071 (w), 2983 (m), 2874 (vw), 1723 (vs), 1305 (s), 1247 (s), 769 (m).

HRMS for **$C_{18}H_{17}O_4F$** (316.1111): found: 316.1118.

Synthesis of triethyl [1,1'-biphenyl]-2,3',4-tricarboxylate (3e)



Prepared according to **TP 2** from diethyl 4-bromoisophthalate **1c** (300 mg, 1.00 mmol), ethyl 3-iodobenzoate (469 mg, 1.70 mmol) and *i*PrMgCl (1.82 mL, 1.78 mmol, 0.98 M in THF). The *i*PrMgCl-solution was added at -20 °C and the halogen/Mg exchange was complete after 0.5 h at -20 °C. Reaction time for cross-coupling: 18 h at 80 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 4:1) yielded product **3e** as a colourless oil (200 mg, 0.54 mmol, 54 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 8.51 (d, *J* = 1.8 Hz, 1 H), 8.18 (dd, *J* = 8.0 and 1.8 Hz, 1 H), 8.08-7.98 (m, 2 H), 7.51-7.41 (m, 3 H), 4.46-4.32 (m, 4 H), 4.12 (q, *J* = 7.1 Hz, 2 H), 1.45-1.34 (m, 6 H), 1.03 (t, *J* = 7.1 Hz, 3 H).

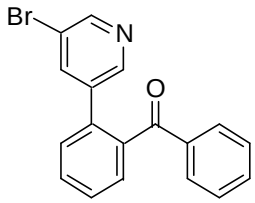
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 167.5, 166.2, 165.5, 145.6, 140.8, 132.6, 132.1, 131.3, 131.2, 130.9, 130.5, 129.9, 129.3, 128.9, 128.1, 61.4, 61.3, 61.1, 14.3, 13.7.

MS (70 eV, EI): *m/z* (%): 370 (74) [M^+], 326 (21), 325 (100), 297 (24), 280 (23), 279 (68), 253 (24).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 3423 (vw), 2982 (m), 1722 (vs), 1305 (s), 1243 (s), 1111 (s), 754 (m), 698 (w).

HRMS for **$C_{21}H_{22}O_6$** (370.1416): found: 370.1403.

Synthesis of [2-(5-bromo-3-pyridinyl)phenyl](phenyl)methanone (3f)



Prepared according to **TP 2** from 2-bromobenzophenone **1b** (260 mg, 1.00 mmol), 3,5-dibromopyridine (403 mg, 1.70 mmol) and *i*PrMgCl·LiCl (1.86 mL, 1.79 mmol, 0.96 M in THF). The *i*PrMgCl·LiCl-solution was added at -10 °C and the halogen/Mg exchange was complete after 0.25 h at -10 °C. Reaction time for the cross-coupling: 16 h at 80 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 29:1) yielded product **3f** as a light yellow oil (210 mg, 0.62 mmol, 62 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 8.42 (dd, *J* = 24.2 and 2.2 Hz, 2 H), 7.77-7.29 (m, 10 H).

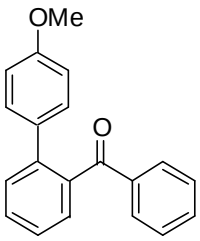
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 197.4, 149.1, 147.2, 139.0, 138.9, 137.6, 137.2, 136.0, 133.4, 130.9, 130.3, 129.9, 129.4, 128.4, 128.4, 120.3.

MS (70 eV, EI): *m/z* (%): 337 (19) [M^+], 311 (21), 310 (99), 309 (22), 308 (100), 261 (24), 259 (27), 153 (27), 105 (56), 77 (43).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 3312 (vw), 3060 (m), 1828 (vw), 1663 (vs), 1426 (m), 1285 (s), 928 (s), 701 (s), 639 (s).

HRMS for **$C_{18}H_{12}BrNO$** (337.0102): found: 337.0077.

Synthesis of (4'-methoxy[1,1'-biphenyl]-2-yl)(phenyl)methanone (3g)



Prepared according to **TP 1** from 2-bromobenzophenone **1b** (261 mg, 1.00 mmol) and (4-methoxyphenyl)magnesium bromide **2b** (2.13 mL, 1.70 mmol, 0.80 M in THF). Reaction time: 1 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 9:1) yielded product **3g** as a colourless oil (255 mg, 0.89 mmol, 89 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.65-7.59 (m, 2 H), 7.55-7.35 (m, 5 H), 7.27-7.21 (m, 2 H), 7.16 (d, *J* = 9.0 Hz, 2 H), 6.71 (d, *J* = 8.8 Hz, 2 H), 3.69 (s, 3 H).

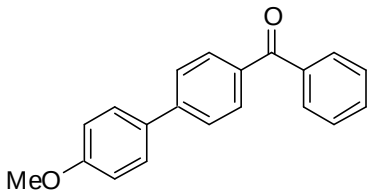
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 198.9, 158.9, 140.7, 138.8, 137.4, 132.8, 132.6, 130.2, 130.1, 129.9, 129.9, 128.6, 128.1, 126.6, 113.7, 55.1.

MS (70 eV, EI): *m/z* (%): 288 (100) [M^+], 287 (38), 273 (11), 257 (11), 211 (58), 168 (13), 105 (19), 77 (17).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 3060 (w), 2935 (w), 2837 (w), 1666 (s), 1517 (s), 1283 (s), 1249 (vs), 1179 (m), 927 (m), 707 (s).

HRMS for $\mathbf{C_{20}H_{16}O_2}$ (288.1150): found: 288.1147.

Synthesis of (4'-methoxy[1,1'-biphenyl]-4-yl)(phenyl)methanone (3h)



Prepared according to **TP 1** from 4-bromobenzophenone **1d** (261 mg, 1.00 mmol) and (4-methoxyphenyl)magnesium bromide **2b** (2.13 mL, 1.70 mmol, 0.80 M in THF). Reaction time: 7.5 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 9:1) yielded product **3h** as a colourless solid (210 mg, 0.73 mmol, 73 %, m.p.: 158.4 – 162.7 °C).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.90-7.76 (m, 4 H), 7.67-7.44 (m, 7 H), 7.00 (d, *J* = 8.8 Hz, 2 H), 3.85 (s, 3 H).

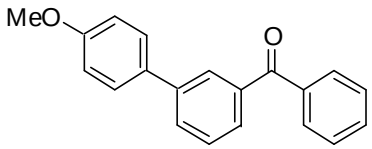
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 159.9, 144.8, 137.9, 135.6, 132.3, 132.2, 130.8, 129.9, 128.4, 128.3, 127.2, 126.4, 114.4, 55.4.

MS (70 eV, EI): *m/z* (%): 288 (100) [M^+], 212 (10), 211 (73), 139 (11), 105 (13), 77 (12).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 3058 (w), 3010 (w), 2842 (w), 1651 (s), 1600 (vs), 1277 (s), 1206 (m), 829 (s), 697 (m).

HRMS for $\mathbf{C_{20}H_{16}O_2}$ (288.1150): found: 288.1130.

Synthesis of (4'-methoxy[1,1'-biphenyl]-3-yl)(phenyl)methanone (3i)



Prepared according to **TP 1** from 3-bromobenzophenone **1e** (261 mg, 1.00 mmol) and (4-methoxyphenyl)magnesium bromide **2b** (2.13 mL, 1.70 mmol, 0.80 M in THF). Reaction time: 24 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 19:1) yielded product **3i** as a colourless solid (73 mg, 0.25 mmol, 25 %, m.p.: 68.2 – 69.7 °C).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.98-7.45 (m, 11 H), 6.98 (d, *J* = 8.9 Hz, 2 H), 3.83 (s, 3 H).

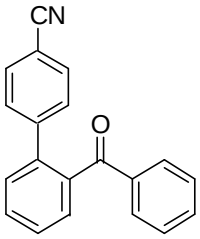
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 159.5, 141.0, 138.1, 137.6, 132.6, 132.4, 130.5, 130.1, 128.6, 128.3, 128.2, 128.1, 128.1, 114.3, 114.1, 55.3.

MS (70 eV, EI): *m/z* (%): 288 (100) [M^+], 211 (37), 183 (14), 105 (33), 77 (17).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 3056 (vw), 2955 (w), 2837 (vw), 1904 (vw), 1651 (vs), 1599 (s), 1517 (s), 1434 (m), 1249 (vs), 1026 (m), 837 (s), 700 (s), 647 (m), 574 (m).

HRMS for $\mathbf{C_{20}H_{16}O_2}$ (288.1150): found: 288.1138.

Synthesis of 2'-benzoyl[1,1'-biphenyl]-4-carbonitrile (3j)



Prepared according to **TP 2** from 2-bromobenzophenone **1b** (260 mg, 1.00 mmol), 4-bromobenzonitrile (309 mg, 1.70 mmol) and *i*PrMgCl·LiCl (1.73 mL, 1.70 mmol, 0.98 M in THF). The *i*PrMgCl·LiCl-solution was added at -20 °C and the halogen/Mg exchange was complete after 2 h at 0 °C. Reaction time for the cross-coupling: 0.5 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 4:1) yielded product **3j** as a light yellow solid (256 mg, 0.90 mmol, 90 %, m.p.: 91.4 – 92.3 °C).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.68-7.27 (m, 13 H).

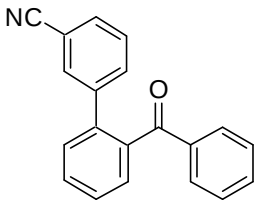
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d= 197.8, 145.0, 139.4, 138.8, 137.1, 133.3, 132.0, 130.7, 130.0, 129.9, 129.6, 129.2, 128.4, 128.1, 119.0, 111.5.

MS (70 eV, EI): *m/z* (%): 283 (100) [M^+], 282 (34), 206 (69), 178 (15), 177 (18), 151 (17), 105 (68), 77 (30).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 3086 (w), 2228 (m), 1666 (vs), 1596 (m), 1451 (m), 1285 (s), 938 (m), 838 (m), 765 (m), 704 (s), 636 (m), 562 (w).

HRMS for $\mathbf{C_{20}H_{13}NO}$ (283.0997): found: 283.0995.

Synthesis of 2'-benzoyl[1,1'-biphenyl]-3-carbonitrile (3k)



Prepared according to **TP 2** from 2-bromobenzophenone **1b** (262 mg, 1.00 mmol), 3-bromobenzonitrile (309 mg, 1.70 mmol) and *i*PrMgCl·LiCl (2.29 mL, 1.79 mmol, 0.78 M in THF). The *i*PrMgCl·LiCl-solution was added at -20 °C and the halogen/Mg exchange was complete after 3 h at 0 °C. Reaction time for the cross-coupling: 0.5 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 6:1) yielded product **3k** as a light yellow oil (227 mg, 0.80 mmol, 80 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.66-7.25 (m, 13 H).

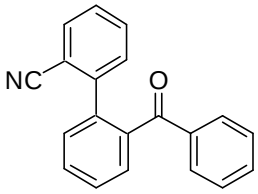
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d= 197.8, 141.5, 138.9, 138.8, 137.2, 133.4, 133.3, 132.2, 130.9, 130.7, 130.0, 129.8, 129.2, 129.0, 128.4, 128.0, 118.5, 112.5.

MS (70 eV, EI): *m/z* (%): 283 (100) [M^+], 282 (31), 254 (22), 206 (76), 178 (22), 177 (17), 151 (21), 105 (77), 77 (34).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 4058 (vw), 3313 (vw), 3063 (m), 2230 (s), 1666 (vs), 1596 (s), 1449 (m), 1287 (s), 929 (s), 761 (s), 693 (s), 640 (s), 493 (m).

HRMS for **$C_{20}H_{13}NO$** (283.0997): found: 283.0971.

Synthesis of 2'-benzoyl[1,1'-biphenyl]-2-carbonitrile (3l)



Prepared according to **TP 2** from 2-bromobenzophenone **1b** (261 mg, 1.00 mmol), 2-bromobenzonitrile (309 mg, 1.70 mmol) and *i*PrMgCl·LiCl (2.29 mL, 1.79 mmol, 0.78 M in THF). The *i*PrMgCl·LiCl-solution was added at -20 °C and the halogen/Mg exchange was complete after 1 h at 0 °C. Reaction time for the cross-coupling: 2.5 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 6:1) yielded product **3l** as a light red oil (208 mg, 0.74 mmol, 74 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.69-7.25 (m, 13 H).

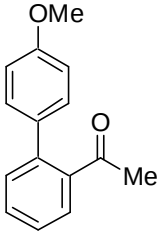
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d= 197.4, 144.2, 139.0, 137.8, 137.3, 132.9, 132.9, 132.1, 130.9, 130.7, 130.7, 129.9, 129.6, 128.5, 128.2, 127.7, 118.1, 112.1.

MS (70 eV, EI): *m/z* (%): 283 (100) [M^+], 282 (12), 206 (76), 178 (19), 177 (17), 151 (19), 105 (93), 77 (31).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 3062 (w), 2225 (m), 1663 (vs), 1596 (m), 1448 (m), 1287 (s), 1154 (w), 928 (m), 761 (s), 705 (s), 640 (m), 523 (w).

HRMS for **$C_{20}H_{13}NO$** (283.0997): found: 283.0971.

Synthesis of 1-(4'-methoxy[1,1'-biphenyl]-2-yl)ethanone (3m)



Prepared according to **TP 1** from 2-bromoacetophenone **1f** (200 mg, 1.01 mmol), (4-methoxyphenyl)magnesium bromide **2b** (2.13 mL, 1.70 mmol, 0.80 M in THF). Reaction

time: 0.5 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 9:1) yielded product **3m** as a colourless oil (203 mg, 0.90 mmol, 90 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.53-7.43 (m, 2 H), 7.39-7.32 (m, 2 H), 7.25 (d, *J* = 8.8 Hz, 2 H), 6.95 (d, *J* = 8.7 Hz, 2 H), 3.83 (s, 3 H), 2.00 (s, 3 H).

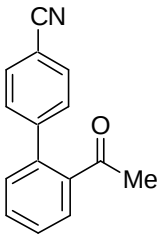
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 205.2, 159.5, 140.9, 140.1, 133.0, 130.6, 130.1, 130.0, 127.8, 127.0, 114.1, 55.3, 30.4.

MS (70 eV, EI): *m/z* (%): 226 (71) [M^+], 225 (15), 212 (14), 211 (100), 168 (26), 139 (16).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 3003 (vw), 2935 (vw), 2837 (vw), 1685 (s), 1610 (s), 1516 (s), 1248 (vs), 1179 (m), 1036 (m), 835 (m), 766 (m), 597 (w).

HRMS for **$C_{15}H_{14}O_2$** (226.0994): found: 226.0974.

Synthesis of 2'-acetyl[1,1'-biphenyl]-4-carbonitrile (3n)



Prepared according to **TP 2** from 2-bromoacetophenone **1f** (199 mg, 1.00 mmol), 4-bromobenzonitrile (309 mg, 1.70 mmol) and *i*PrMgCl·LiCl (2.29 mL, 1.79 mmol, 0.78 M in THF). The *i*PrMgCl·LiCl-solution was added at -20 °C and the halogen/Mg exchange was complete after 2 h at 0 °C. Reaction time for the cross-coupling: 1 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 6:1) yielded product **3n** as a colourless solid (170 mg, 0.77 mmol, 77 %, m.p.: 77.8 – 78.4 °C).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.23-7.30 (m, 8 H), 2.19 (s, 3 H).

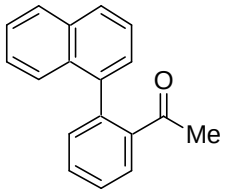
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 202.6, 145.8, 139.8, 138.9, 132.9, 132.2, 131.2, 130.4, 129.5, 128.5, 128.5, 111.5, 30.1.

MS (70 eV, EI): *m/z* (%): 221 (34) [M^+], 207 (13), 206 (100), 178 (27), 177 (17), 151 (18).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 3060 (vw), 2926 (vw), 2229 (m), 1685 (vs), 1608 (w), 1358 (w), 1269 (m), 845 (m), 776 (m), 597 (w), 576 (w).

HRMS for **$C_{15}H_{11}NO$** (221.0841): found: 221.0819.

Synthesis of 1-[2-(1-naphthyl)phenyl]ethanone (3o)



Prepared according to **TP 1** from 2-bromoacetophenone **1f** (200 mg, 1.01 mmol), naphthylmagnesium bromide **2j** (2.43 mL, 1.70 mmol, 0.70 M in THF). Reaction time: 15 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 9:1) yielded product **3o** as a light yellow oil (205 mg, 0.83 mmol, 83 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.89 (dd, *J* = 8.5 and 3.7 Hz, 2 H), 7.75 (dd, *J* = 7.4 and 1.7 Hz, 1 H), 7.63-7.31 (m, 8 H), 1.77 (s, 3 H).

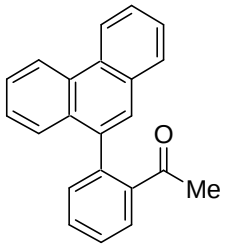
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d= 203.1, 141.2, 139.0, 138.7, 133.6, 131.9, 131.6, 130.8, 128.3, 128.3, 128.3, 127.8, 127.3, 126.5, 126.1, 125.6, 125.3, 29.7.

MS (70 eV, EI): *m/z* (%): 246 (77) [M^+], 245 (19), 132 (17), 231 (100), 203 (48), 202 (64), 201 (12), 200 (13), 101 (22).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 3058 (m), 1936 (vw), 1684 (vs), 1593 (w), 1355 (m), 1273 (m), 964 (w), 804 (m), 766 (s), 596 (w).

HRMS for **$C_{18}H_{14}O$** (246.1045): found: 246.1031.

Synthesis of 1-[2-(9-phenanthryl)phenyl]ethanone (3p)



Prepared according to **TP 2** from 2-bromoacetophenone **1f** (200 mg, 1.01 mmol), 9-bromophenanthrene (438 mg, 1.70 mmol) and *i*PrMgCl·LiCl (1.86 mL, 1.79 mmol, 0.96 M in THF). The *i*PrMgCl·LiCl-solution was added at -20 °C and the halogen/Mg exchange was complete after 17 h at 25 °C. Reaction time for the cross-coupling: 0.25 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 9:1) yielded product **3p** as a light yellow solid (209 mg, 0.70 mmol, 70 %, m.p.: 126.4 – 127.6 °C).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 8.78-8.70 (m, 2 H), 7.83 (ddd, *J* = 18.2 and 6.9 and 1.7 Hz, 2 H), 7.71-7.45 (m, 9 H), 1.88 (s, 3 H).

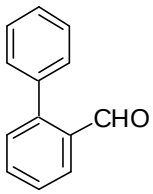
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d= 202.8, 141.2, 139.1, 137.4, 131.7, 131.3, 131.2, 130.9, 130.5, 130.1, 128.8, 128.4, 128.0, 127.9, 127.0, 127.0, 126.9, 126.8, 126.6, 123.0, 122.6, 29.8.

MS (70 eV, EI): *m/z* (%): 296 (100) [M^+], 282 (20), 281 (98), 253 (52), 252 (67), 250 (25), 126 (19).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 3063 (w), 1961 (vw), 1678 (vs), 1248 (m), 754 (m), 727 (m), 602 (w).

HRMS for **$C_{22}H_{16}O$** (296.1201): found: 296.1196.

Synthesis of [1,1'-biphenyl]-2-carbaldehyde (3q)



Prepared according to **TP 1** from 2-bromobenzaldehyde **1g** (184 mg, 0.99 mmol), phenylmagnesium bromide **2a** (1.42 mL, 1.70 mmol, 1.2 M in THF). Reaction time: 0.25 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 19:1) yielded product **3q** as a colourless oil (77 mg, 0.42 mmol, 42 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 9.97 (s, 1 H), 8.02 (dd, *J* = 7.5 and 1.8 Hz, 1 H), 7.63 (td, *J* = 7.5 and 1.4 Hz, 1 H), 7.51-7.34 (m, 7 H).

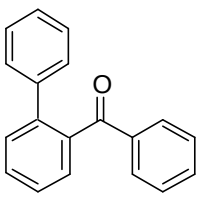
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 192.4, 146.0, 137.7, 133.7, 133.5, 130.7, 130.1, 128.4, 128.1, 127.8, 127.5.

MS (70 eV, EI): *m/z* (%): 182 (94) [M^+], 181 (100), 153 (83), 152 (85).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 3061 (w), 2849 (vw), 2753 (vw), 1692 (vs), 1597 (m), 1196 (m), 747 (s), 702 (m), 645 (w).

HRMS for **$C_{13}H_{10}O$** (182.0732): found: 182.0735.

Synthesis of [1,1'-biphenyl]-2-yl(phenyl)methanone (3r)



Prepared according to **TP 1** from 2-chlorobenzophenone **5** (216 mg, 1.00 mmol) and phenylmagnesium bromide **2a** (1.42 mL, 1.70 mmol, 1.20 M in THF). Reaction time: 0.25 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 19:1) yielded product **3r** as a light yellow solid (244 mg, 0.95 mmol, 95 %, m.p.: 87.6 – 88.5 °C).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.66-7.09 (m, 14 H).

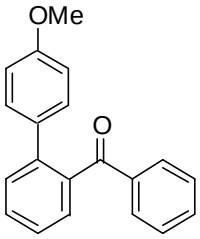
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 198.7, 141.1, 140.2, 139.0, 137.4, 132.8, 130.3, 130.0, 129.9, 129.0, 128.7, 128.2, 128.0, 127.3, 127.0.

MS (70 eV, EI): *m/z* (%): 258 (100) [M^+], 257 (83), 229 (15), 181 (86), 153 (27), 152 (44), 105 (34), 77 (31).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 4061 (vw), 3077 (w), 1665 (vs), 1595 (m), 1449 (m), 1314 (m), 1261 (m), 928 (m), 775 (s), 636 (m).

HRMS for **$C_{19}H_{14}O$** (258.1045): found: 258.1035.

Synthesis of (4'-methoxy[1,1'-biphenyl]-2-yl)(phenyl)methanone (3g)



Prepared according to **TP 1** from 2-chlorobenzophenone **5** (216 mg, 1.00 mmol) and (4-methoxyphenyl)magnesium bromide **2b** (2.13 mL, 1.70 mmol, 0.80 M in THF). Reaction time: 1 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 9:1) yielded product **3g** as a colourless oil (282 mg, 0.98 mmol, 98 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.65-7.59 (m, 2 H), 7.55-7.35 (m, 5 H), 7.27-7.21 (m, 2 H), 7.16 (d, *J* = 9.0 Hz, 2 H), 6.71 (d, *J* = 8.8 Hz, 2 H), 3.69 (s, 3 H).

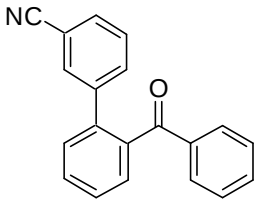
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 198.9, 158.9, 140.7, 138.8, 137.4, 132.8, 132.6, 130.2, 130.1, 129.9, 129.9, 128.6, 128.1, 126.6, 113.7, 55.1.

MS (70 eV, EI): *m/z* (%): 288 (100) [M^+], 287 (38), 273 (11), 257 (11), 211 (58), 168 (13), 105 (19), 77 (17).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 3060 (w), 2935 (w), 2837 (w), 1666 (s), 1517 (s), 1283 (s), 1249 (vs), 1179 (m), 927 (m), 707 (s).

HRMS for **$C_{20}H_{16}O_2$** (288.1150): found: 288.1147.

Synthesis of 2'-benzoyl[1,1'-biphenyl]-3-carbonitrile (3k)



Prepared according to **TP 2** from 2-chlorobenzophenone **5** (215 mg, 0.99 mmol), 3-bromobenzonitrile (309 mg, 1.70 mmol) and *i*PrMgCl·LiCl (1.88 mL, 1.79 mmol, 0.95 M in THF). The *i*PrMgCl·LiCl-solution was added at -20 °C and the halogen/Mg exchange was complete after 3 h at 0 °C. Reaction time for the cross-coupling: 1.5 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 6:1) yielded product **3k** as a light yellow oil (270 mg, 0.95 mmol, 96 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.66-7.25 (m, 13 H).

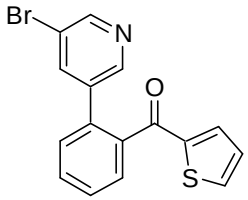
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d= 197.8, 141.5, 138.9, 138.8, 137.2, 133.4, 133.3, 132.2, 130.9, 130.7, 130.0, 129.8, 129.2, 129.0, 128.4, 128.0, 118.5, 112.5.

MS (70 eV, EI): *m/z* (%): 283 (100) [M^+], 282 (31), 254 (22), 206 (76), 178 (22), 177 (17), 151 (21), 105 (77), 77 (34).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 4058 (vw), 3313 (vw), 3063 (m), 2230 (s), 1666 (vs), 1596 (s), 1449 (m), 1287 (s), 929 (s), 761 (s), 693 (s), 640 (s), 493 (m).

HRMS for **$C_{20}H_{13}NO$** (283.0997): found: 283.0971.

Synthesis of [2-(5-bromo-3-pyridinyl)phenyl](2-thienyl)methanone (7a)



Prepared according to **TP 2** from (2-bromophenyl)-thiophen-2-yl-methanone **6a** (269 mg, 1.01 mmol), 3,5-dibromopyridine (403 mg, 1.70 mmol) and *i*PrMgCl·LiCl (1.88 mL, 1.79 mmol, 0.95 M in THF). The *i*PrMgCl·LiCl-solution was added at -10 °C and the halogen/Mg exchange was complete after 0.25 h at -10 °C. Reaction time for the cross-coupling: 1 h at 80 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 2:1) yielded product **7a** as a orange oil (257 mg, 0.75 mmol, 74 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 8.49 (dd, *J* = 27.9 and 2.3 Hz, 2 H), 7.82 (t, *J* = 2.1 Hz, 1 H), 7.69-7.33 (m, 6 H), 7.02 (dd, *J* = 4.9 and 3.9 Hz, 1 H).

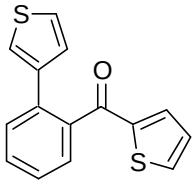
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d= 189.0, 149.1, 147.0, 144.2, 139.0, 138.8, 135.5, 135.5, 135.5, 130.9, 130.5, 128.9, 128.3, 128.2, 120.4, 113.7.

MS (70 eV, EI): *m/z* (%): 343 (50) [M^+], 316 (39), 314 (43), 311 (65), 309 (67), 283 (43), 282 (40), 153 (44), 126 (35), 111 (100).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 3036 (vw), 1639 (vs), 1410 (vs), 1295 (m), 1012 (m), 847 (m), 727 (m), 705 (m), 644 (w).

HRMS for **$C_{16}H_{10}BrNOS$** (342.9666): found: 342.9652.

Synthesis of 2-thienyl[2-(3-thienyl)phenyl]methanone (7b)



Prepared according to **TP 2** from (2-bromophenyl)-thiophen-2-yl-methanone **6a** (267 mg, 1.00 mmol), 3-bromothiophene (279 mg, 1.71 mmol) and *i*PrMgCl·LiCl (1.88 mL, 1.79 mmol, 0.95 M in THF). The *i*PrMgCl·LiCl-solution was added at -20 °C and the halogen/Mg exchange was complete after 8 h at 25 °C. Reaction time for the cross-coupling: 0.25 h at 80 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 9:1) yielded product **7b** as a light yellow solid (238 mg, 0.88 mmol, 88 %, m.p.: 65.3 – 67.0 °C).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.60-7.36 (m, 5 H), 7.26-7.16 (m, 3 H), 7.07 (dd, *J* = 4.8 and 1.7 Hz, 1 H), 6.93 (dd, *J* = 4.8 and 3.6 Hz, 1 H).

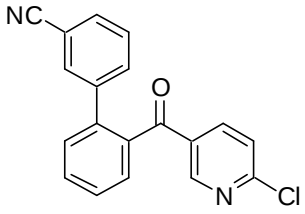
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 190.8, 144.6, 140.5, 138.7, 135.2, 134.8, 134.6, 130.3, 129.6, 128.2, 128.1, 127.9, 127.0, 125.8, 123.4.

MS (70 eV, EI): *m/z* (%): 270 (91) [M^+], 241 (39), 237 (100), 186 (16), 115 (49), 110 (50).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 3101 (w), 1643 (vs), 1411 (s), 1296 (m), 1044 (m), 844 (m), 754 (s), 727 (m), 642 (m).

HRMS for **$C_{15}H_{10}OS_2$** (270.0173): found: 270.0187.

Synthesis of 2'-[(6-chloro-3-pyridinyl)carbonyl][1,1'-biphenyl]-3-carbonitrile (7c)



Prepared according to **TP 2** from (2-bromophenyl)-(6-chloropyridin-3-yl)-methanone **6b** (892 mg, 3.01 mmol), 3-bromobenzonitrile (928 mg, 5.10 mmol) and *i*PrMgCl·LiCl (5.64 mL, 5.36 mmol, 0.95 M in THF). The *i*PrMgCl·LiCl-solution was added at -20 °C and the halogen/Mg exchange was complete after 3 h at 0 °C. Reaction time for the cross-coupling: 16.5 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 2:1) yielded product **7c** as a light yellow oil (788 mg, 2.47 mmol, 82 %).

^{1}H-NMR (600 MHz, $CDCl_3$, 25 °C): d = 8.47 (d, *J* = 2.2 Hz, 1 H), 7.91 (dd, *J* = 8.2 and 5.7 Hz, 1 H), 7.67-7.27 (m, 9 H).

^{13}C-NMR (150 MHz, $CDCl_3$, 25 °C): d = 195.1, 155.6, 151.3, 141.0, 139.0, 139.0, 137.2, 133.3, 132.2, 131.7, 131.3, 130.4, 129.4, 129.3, 128.5, 124.3, 118.1, 112.8, 104.2.

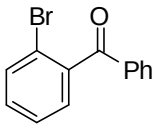
MS (70 eV, EI): *m/z* (%): 318 (67) [M^+], 317 (51), 289 (63), 206 (100), 139 (48), 111 (25).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 3062 (w), 2929 (vw), 2231 (m), 1668 (vs), 1580 (vs), 1456 (m), 1362 (m), 1294 (s), 1103 (vs), 928 (s), 761 (s), 693 (m), 514 (w).

HRMS for **$C_{19}H_{11}ClN_2O$** (318.0560): found: 318.0563.

Preparation of starting material:

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 evolution**). 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): d = 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): d = 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): $\tilde{n}$ (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).

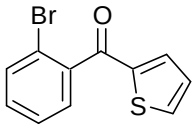
HRMS for **$C_{13}H_9OBr$** (259.9837): found: 259.9853.

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

Typical procedure for the preparation of starting materials (bromo-ketones from aryl magnesium chlorides and acid chlorides) (TP 3)

A 100 mL Schlenk-tube, equipped with a magnetic stirring bar and a septum, was charged with *i*PrMgCl·LiCl, cooled to the appropriate temperature and the aryl bromide was added. The reaction mixture was stirred at the same temperature or higher (as stated in the experiment) until full completion of the bromine/Mg exchange (checked by GC-analysis). Subsequent, a solution of CuCN·2LiCl was added at –20 °C. After stirring for additional 10 min the corresponding acid chloride was added. The reaction mixture was stirred at -10 °C. After full conversion (checked by GC-analysis) the suspension was quenched with sat. $NH_4Cl_{(aq.)}/NH_3$ (9:1) (50 mL). The organic fraction was washed a second time with sat. $NH_4Cl_{(aq.)}/NH_3$ (9:1) (50 mL) and the combined water phases were extracted with EtOAc (4x100 mL). The organic fractions were washed with brine (100 mL), dried over Mg_2SO_4, filtered and the solvent was evaporated *in vacuo*. Flash chromatographical purification on silica gel furnished the analytically pure products.

Synthesis of (2-bromophenyl)(2-thienyl)methanone (6a)



Prepared according to **TP 3** from 1,2-dibromobenzene (4.71 g, 19.98 mmol), *i*PrMgCl·LiCl (21.50 mL, 21.07 mmol, 0.98 M in THF) and thiophene-2-carbonyl chloride (3.82 g, 26.06 mmol). The *i*PrMgCl·LiCl-solution was added at -15 °C and the halogen/Mg exchange was complete after 2.5 h at -15 °C. Reaction time for coupling with acid chloride: 5.5 h. Purification by flash chromatography on silica gel (pentane/diethyl ether = 4:1) yielded product **6a** as a light yellow oil (3.53 g, 13.21 mmol, 66 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.74 (dd, *J* = 4.8 and 0.9 Hz, 1 H), 7.64 (dd, *J* = 7.1 and 0.9 Hz, 1 H), 7.42-7.30 (m, 4 H), 7.10 (dd, *J* = 4.9 and 4.0 Hz, 1 H).

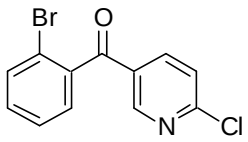
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d = 187.8, 143.4, 140.5, 136.0, 135.6, 133.4, 131.3, 128.7, 128.3, 127.0, 119.4.

MS (70 eV, EI): *m/z* (%): 266 (23) [M^+], 187 (18), 110 (100).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 1647 (vs), 1411 (s), 1296 (s), 1055 (m), 845 (m), 742 (m), 729 (m), 637 (w).

HRMS for **$C_{11}H_7BrSO$** (265.9401): found: 265.9378.

Synthesis of (2-bromophenyl)(6-chloro-3-pyridinyl)methanone (6b)



Prepared according to **TP 3** from 1,2-dibromobenzene (4.72 g, 20.02 mmol), *i*PrMgCl·LiCl (21.50 mL, 21.07 mmol, 0.98 M in THF) and 6-chloronicotinoyl chloride (4.57 g, 25.97 mmol). The *i*PrMgCl·LiCl-solution was added at -15 °C and the halogen/Mg exchange was complete after 2.5 h at -15 °C. Reaction time for coupling with acid chloride: 5.5 h. Purification by flash chromatography on silica gel (pentane/diethyl ether = 6:1) yielded product **6b** as a light yellow oil (3.90 g, 13.16 mmol, 66 %).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 8.67 (d, *J* = 1.9 Hz, 1 H), 8.08 (dd, *J* = 8.5 and 2.2 Hz, 1 H), 7.66 (dd, *J* = 7.5 and 1.0 Hz, 1 H), 7.48-7.33 (m, 4 H).

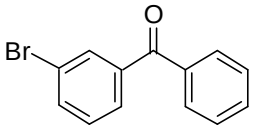
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d= 193.4, 156.1, 151.9, 139.4, 139.1, 133.5, 132.1, 130.6, 129.2, 127.7, 124.6, 119.5.

MS (70 eV, EI): *m/z* (%): 295 (20) [M^+], 219 (29), 217 (96), 185 (54), 183 (54), 142 (32), 140 (100), 112 (33).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 1674 (s), 1581 (s), 1362 (s), 1293 (s), 1105 (vs), 1023 (m), 927 (s), 752 (m), 526 (w).

HRMS for **$C_{12}H_7BrClNO$** (294.9400): found: 294.9404.

Synthesis of (3-bromophenyl)(phenyl)methanone (1e)



Prepared according to **TP 3** from 1,3-dibromobenzene (2.37 g, 10.03 mmol), *i*PrMgCl·LiCl (11.0 mL, 10.45 mmol, 0.95 M in THF) and benzoyl chloride (1.88 g, 13.37 mmol). The *i*PrMgCl·LiCl-solution was added at -20 °C and the halogen/Mg exchange was complete after 2 h at 25 °C. Reaction time for coupling with acid chloride: 1.25 h. Purification by flash chromatography on silica gel (pentane/diethyl ether = 29:1) yielded product **1e** as a colourless solid (2.40 g, 9.18 mmol, 92 %, m.p.: 76.6 – 77.6 °C).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): d = 7.93-7.31 (m, 9 H).

^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): d= 195.1, 139.5, 136.9, 135.2, 132.8, 132.8, 130.0, 129.8, 128.5, 128.4, 122.5.

MS (70 eV, EI): *m/z* (%): 260 (16) [M^+], 105 (100), 77 (38), 76 (16), 51 (19), 50 (12).

IR (KBr): $\tilde{n}$ (cm^{-1}) = 1661 (vs), 1564 (m), 1448 (m), 1419 (m), 1309 (s), 1071 (w), 946 (m), 715 (s), 668 (m).

HRMS for $\mathbf{C_{13}H_9BrO}$ (259.9837): found: 259.9843.

[i] P. J. Wagner, J. H. Sedon, A. Gudmundsdottir, *J. Am. Chem. Soc.* **1996**, *118*, 746-754.