Cobalt(II)-Catalyzed Cross-Coupling Between Polyfunctional
Arylcopper Reagents and Aryl Fluorides or Tosylates

Supporting Information

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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 ¹H-NMR and capillary GC.

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

A 25 mL Schlenk-flask, equipped with a magnetic stirring bar and a septum, was charged with the appropriate Grignard reagent (3.00 mmol), cooled to -20 °C and a solution of CuCN·2LiCl (3.2 mL, 3.2 mmol, 1 M in THF) was added. After stirring for 10 min at -20 °C DME (6.0 mL), DMPU (2.0 mL), Bu₄NI (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 fluoride or tosylate (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. $\text{NH}_4\text{Cl}_{(\text{aq.})}/\text{NH}_3$ (9:1) (50 mL). The organic fraction was washed a second time with sat. $\text{NH}_4\text{Cl}_{(\text{aq.})}/\text{NH}_3$ (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-flask, equipped with a magnetic stirring bar and a septum, was charged with $i\text{PrMgCl}\cdot\text{LiCl}$ (3.15 mmol), cooled to the appropriate temperature and the aryl halide (3.00 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). Subsequently, a solution of $\text{CuCN}\cdot 2\text{LiCl}$ (3.2 mL, 3.2 mmol, 1 M in THF) was added at $-20\text{ }^\circ\text{C}$. 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), $\text{Co}(\text{acac})_2$ (19.3 mg, 0.075 mmol) and the corresponding aryl fluoride or tosylate (1.00 mmol) were added. The reaction mixture was stirred at room temperature or heated to $80\text{ }^\circ\text{C}$. After full conversion (checked by GC-analysis) the suspension was quenched with sat. $\text{NH}_4\text{Cl}_{(\text{aq.})}/\text{NH}_3$ (9:1) (50 mL). The organic fraction was washed a second time with sat. $\text{NH}_4\text{Cl}_{(\text{aq.})}/\text{NH}_3$ (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 (4'-methoxy[1,1'-biphenyl]-2-yl) (phenyl) methanone (3a)

Prepared according to **TP 1** from 2-fluorobenzophenone (**1a**) (101 mg, 0.50 mmol) and 4-methoxyphenylmagnesium bromide (1.88 mL, 1.50 mmol, 0.80 M in THF). Reaction time: 2 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 9:1) yielded product **3a** as a colourless oil (140 mg, 0.49 mmol, 98%).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 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).

¹³C-NMR (75 MHz, CDCl₃, 25 °C): δ = 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): $\tilde{\nu}$ (cm⁻¹) = 3060 (w), 2935 (w), 2837 (w), 1666 (s), 1517 (s), 1283 (s), 1249 (vs), 1179 (m), 927 (m), 707 (s).

HRMS for C₂₀H₁₆O₂ (288.1150): found: 288.1147.

^1H -NMR of pure product (3a):

^{13}C -NMR of pure product (3a):

Synthesis of (3',4'-dichloro[1,1'-biphenyl]-2-yl)phenyl methanone (**3b**)

Prepared according to **TP 2** from 2-fluorobenzophenone (**1a**) (202 mg, 1.01 mmol), 4-bromo-1,2-dichlorobenzene (678 mg, 3.00 mmol) and *i*PrMgCl·LiCl (2.86 mL, 3.15 mmol, 1.1 M in THF). The *i*PrMgCl·LiCl-solution was added at -20 °C and the Br/Mg exchange was complete after 1 h at 25 °C. Reaction time for cross-coupling: 0.5 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 9:1) yielded product **3b** as a colourless solid (286 mg, 0.88 mmol, 87%, mp: 68.3 – 73.0 °C).

$^1\text{H-NMR}$ (300 MHz, CDCl_3 , 25 °C): δ = 7.67-7.23 (m, 11 H), 7.08-7.03 (m, 1 H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , 25 °C): δ = 198.0, 140.2, 138.8, 138.7, 137.2, 133.2, 132.4, 131.6, 130.7, 130.6, 130.1, 129.9, 129.8, 129.0, 128.3, 128.3, 127.8.

MS (70 eV, EI): m/z (%): 326 (100) [M^+], 325 (21), 291 (30), 251 (32), 249 (54), 186 (36), 105 (49).

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3062 (w), 3026 (vw), 2962 (vw), 2926 (vw), 1667 (vs), 1596 (m), 1463 (s), 1449 (s), 1315 (s), 1286 (s), 1134 (m), 1030 (m), 928 (s), 825 (m), 763 (s), 700 (s), 637 (m), 515 (w).

HRMS for $\text{C}_{19}\text{H}_{12}\text{Cl}_2\text{O}$ (326.0265): found: 326.0291.

$^1\text{H-NMR}$ of pure product (3b):

^{13}C -NMR of pure product (3b) :

Synthesis of 2,2-dimethyl-4-[2-(1,3-benzodioxol-5-yl)benzoyl]phenyl propanoic acid ester (3c)

Prepared according to **TP 1** from 2,2-dimethyl-4-(2-fluorobenzoyl)phenyl propanoic acid ester (**1b**) (304 mg, 1.01 mmol) and 1,3-benzodioxol-5-ylmagnesium bromide (3.75 mL, 3.00 mmol, 0.8 M in THF). Reaction time for the cross-coupling: 16 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 9:1) yielded product **3c** as a colourless solid (291 mg, 0.72 mmol, 72%, mp: 94.5 – 95.8 °C).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 7.67 (d, *J* = 8.9 Hz, 2 H), 7.56-7.39 (m, 4 H), 7.00 (d, *J* = 8.8 Hz, 2 H), 6.74-6.62 (m, 3 H), 5.89 (s, 2 H), 1.33 (s, 9 H).

¹³C-NMR (75 MHz, CDCl₃, 25 °C): δ = 197.5, 176.4, 154.7, 147.7, 147.1, 140.6, 138.7, 134.7, 131.4, 130.4, 129.9, 128.6, 126.9, 122.8, 121.3, 109.3, 108.2, 101.1, 39.2, 27.4.

MS (70 eV, EI): *m/z* (%): 402 (29) [M⁺], 318 (21), 202 (11), 139 (15), 121 (16), 57 (100), 41 (10).

IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2975 (m), 2907 (w), 1752 (s), 1664 (s), 1597 (s), 1505 (m), 1475 (s), 1284 (m), 1241 (s), 1223 (s), 1150 (s), 1109 (vs), 1039 (s), 931 (s), 761 (s), 628 (m).

HRMS for C₂₅H₂₂O₅ (402.1467): found: 402.1478.

^1H -NMR of pure product (3c) :

^{13}C -NMR of pure product (3c) :

Synthesis of [2-(1,3-benzodioxol-5-yl)phenyl] (4-methoxyphenyl) methanone (**3d**)

Prepared according to **TP 1** from (2-fluorophenyl) (4-methoxyphenyl)methanone (**1c**) (232 mg, 1.01 mmol) and 1,3-benzodioxol-5-ylmagnesium bromide (3.75 mL, 3.00 mmol, 0.8 M in THF). Reaction time for the cross-coupling: 3 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 4:1) yielded product **3d** as a colourless oil which solidifies slowly upon standing (326 mg, 0.99 mmol, 98%, mp: 98.8 – 101.0 °C).

^1H -NMR (300 MHz, CDCl_3 , 25 °C): δ = 7.65 (d, J = 8.8 Hz, 2 H), 7.53-7.39 (m, 4 H), 6.80-6.61 (m, 5 H), 5.87 (s, 2 H), 3.80 (s, 3 H).

^{13}C -NMR (75 MHz, CDCl_3 , 25 °C): δ = 197.3, 163.4, 147.5, 146.9, 140.3, 139.2, 134.3, 132.3, 130.3, 129.9, 129.9, 128.4, 126.8, 122.7, 113.4, 109.3, 108.2, 101.0, 55.4.

MS (70 eV, EI): m/z (%): 332 (100) [M^+], 331 (11), 135 (21).

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3060 (vw), 2898 (w), 2779 (vw), 2053 (vw), 1658 (s), 1599 (vs), 1506 (s), 1475 (vs), 1258 (vs), 1150 (s), 1039 (s), 932 (s), 846 (m), 764 (m), 610 (m).

HRMS for $\text{C}_{21}\text{H}_{16}\text{O}_4$ (332.1049): found: 332.1033.

^1H -NMR of pure product (3d):

^{13}C -NMR of pure product (3d) :

Synthesis of [2-(1,3-benzodioxol-5-yl)phenyl] [4-(dimethylamino)phenyl] methanone (3e)

Prepared according to **TP 1** from [4-(dimethylamino)phenyl] (2-fluorophenyl)methanone (**1d**) (243 mg, 1.00 mmol) and 1,3-benzodioxol-5-ylmagnesium bromide (3.75 mL, 3.00 mmol, 0.8 M in THF). Reaction time for the cross-coupling: 3 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 2:1) yielded product **3e** as a light yellow solid (329 mg, 0.95 mmol, 95%, mp: 62.6 – 64.5 °C).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 7.62 (d, *J* = 9.3 Hz, 2 H), 7.49–7.35 (m, 4 H), 6.82–6.76 (m, 2 H), 6.66 (d, *J* = 8.0 Hz, 1 H), 6.53 (d, *J* = 8.9 Hz, 2 H), 5.87 (s, 2 H), 3.01 (s, 6 H).

¹³C-NMR (75 MHz, CDCl₃, 25 °C): δ = 196.6, 153.3, 147.4, 146.8, 140.0, 139.9, 134.6, 132.4, 129.8, 129.3, 128.2, 126.6, 125.2, 122.6, 110.4, 109.3, 108.1, 100.9, 39.9.

MS (70 eV, EI): *m/z* (%): 345 (100) [M⁺], 328 (16), 316 (3), 301 (3), 148 (29), 139 (5).

IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 3056 (vw), 2897 (w), 2821 (vw), 1590 (vs), 1474 (s), 1372 (m), 1293 (m), 1224 (m), 1148 (m), 1038 (m), 930 (m), 762 (m), 598 (w).

HRMS for C₂₂H₁₉NO₃ (345.1365): found: 345.1379.

^1H -NMR of pure product (3e):

^{13}C -NMR of pure product (3e):

Synthesis of 2,2-dimethyl-4-[(3'-cyano[1,1'-biphenyl]-2-yl)carbonyl]phenyl propanoic acid ester (3f)

Prepared according to **TP 2** from 2,2-dimethyl-4-(2-fluorobenzoyl)phenyl propanoic acid ester (**1b**) (300 mg, 1.00 mmol), 3-bromobenzonitrile (546 mg, 3.00 mmol) and *i*PrMgCl·LiCl (2.63 mL, 3.15 mmol, 1.2 M in THF). The *i*PrMgCl·LiCl-solution was added at -20 °C and the Br/Mg exchange was complete after 3 h at 0 °C. Reaction time for the cross-coupling: 0.25 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 7:1) yielded product **3f** as a colourless solid (199 mg, 0.52 mmol, 52%, mp: < 25 °C)

$^1\text{H-NMR}$ (300 MHz, CDCl_3 , 25 °C): δ = 7.69 (d, J = 8.9 Hz, 2 H), 7.62-7.42 (m, 7 H), 7.35-7.30 (m, 1 H), 7.03 (d, J = 8.8 Hz, 2 H), 1.34 (s, 9 H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , 25 °C): δ = 196.5, 176.3, 155.0, 141.4, 138.9, 138.6, 134.5, 133.3, 132.2, 131.4, 131.0, 130.8, 130.1, 129.1, 128.0, 121.6, 118.5, 112.6, 39.2, 27.0.

MS (70 eV, EI): m/z (%): 383 (5) [M^+], 299 (100), 206 (9), 121 (36), 85 (12), 57 (45).

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3065 (vw), 2976 (w), 2874 (vw), 2230 (w), 1753 (s), 1665 (s), 1597 (s), 1480 (w), 1276 (m), 1205 (s), 1108 (vs), 932 (s), 762 (m), 630 (w).

HRMS for $\text{C}_{25}\text{H}_{21}\text{NO}_3$ (383.1521): found: 383.1516.

$^1\text{H-NMR}$ of pure product (3f):

^{13}C -NMR of pure product (3f) :

Synthesis of 2'-(4-methoxybenzoyl)-[1,1'-biphenyl]-4-carbonitrile (3g)

Prepared according to **TP 2** from (2-fluorophenyl) (4-methoxyphenyl)methanone (**1c**) (230 mg, 1.00 mmol), 4-bromobenzonitrile (544 mg, 2.99 mmol) and *i*PrMgCl·LiCl (2.63 mL, 3.15 mmol, 1.2 M in THF). The *i*PrMgCl·LiCl-solution was added at -20 °C and the Br/Mg exchange was complete after 2 h at 0 °C. Reaction time for cross-coupling: 0.25 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 4:1) yielded product **3g** as a colourless solid (271 mg, 0.87 mmol, 87%, mp: 120.8 - 122.9 °C).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 7.73 (dd, *J* = 52.0 and 8.1 Hz, 1 H), 7.64 (d, *J* = 8.1 Hz, 2 H), 7.60-7.56 (m, 1 H), 7.51-7.49 (m, 4 H), 7.44 (d, *J* = 7.6 Hz, 1 H), 7.38 (d, *J* = 8.1 Hz, 2 H), 6.80 (d, *J* = 8.1 Hz, 2 H), 3.82 (s, 3 H).

¹³C-NMR (75 MHz, CDCl₃, 25 °C): δ = 196.4, 163.7, 145.0, 139.2, 132.9, 132.3, 132.0, 130.3, 130.0, 129.9, 129.5, 128.8, 128.1, 127.9, 118.7, 113.7, 111.1, 55.5.

MS (70 eV, EI): *m/z* (%): 313 (100) [M⁺], 312 (12), 135 (78).

IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 3078 (vw), 2962 (vw), 2839 (vw), 2230 (m), 1655 (s), 1598 (s), 1424 (w), 1278 (m), 1255 (vs), 1150 (s), 1025 (m), 928 (m), 847 (m), 771 (m), 610 (m), 570 (m).

HRMS for C₂₁H₁₅NO₂ (313.1103): found: 313.1117.

^1H -NMR of pure product (3g) :

^{13}C -NMR of pure product (3g) :

Synthesis of (2-benzo[*b*]thien-3-ylphenyl)phenyl methanone (3h)

Prepared according to **TP 2** from 2-fluorobenzophenone (**1a**) (200 mg, 1.00 mmol), 3-bromo benzo[*b*]thiophene (639 mg, 3.00 mmol) and *i*PrMgCl·LiCl (1.74 mL, 3.31 mmol, 1.90 M in THF). The *i*PrMgCl·LiCl-solution was added at -20 °C and the Br/Mg exchange was complete after 2 h at 25 °C. Reaction time for the cross-coupling: 1 h at 80 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 19:1) yielded product **3h** as a light yellow solid (294 mg, 0.94 mmol, 94%, mp: 123.2 – 125.0 °C).

$^1\text{H-NMR}$ (300 MHz, CDCl_3 , 25 °C): δ = 7.71-7.44 (m, 8 H), 7.34-7.04 (m, 6 H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , 25 °C): δ = 198.5, 140.1, 139.9, 138.2, 137.2, 135.5, 134.5, 132.4, 130.4, 130.3, 129.1, 129.0, 127.8, 127.7, 126.0, 124.3, 124.2, 122.7, 122.5.

MS (70 eV, EI): m/z (%): 314 (87) [M^+], 313 (24), 285 (28), 237 (100), 208 (32), 165 (72), 164 (24), 105 (52), 77 (88).

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3057 (vw), 1664 (vs), 1594 (w), 1449 (vw), 1286 (m), 1256 (m), 945 (w), 926 (m), 765 (m), 734 (m), 718 (m), 641 (m), 430 (vw).

HRMS for $\text{C}_{21}\text{H}_{14}\text{OS}$ (314.0765): found: 314.0790.

$^1\text{H-NMR}$ of pure product (3h):

^{13}C -NMR of pure product (3h) :

Synthesis of [4-(dimethylamino)phenyl] [2-(3-thienyl)phenyl] methanone (3i**)**

Prepared according to **TP 2** from [4-(dimethylamino)phenyl] (2-fluorophenyl)methanone (**1d**) (243 mg, 1.00 mmol), 3-bromothiophene (489 mg, 3.00 mmol) and *i*PrMgCl·LiCl (2.63 mL, 3.15 mmol, 1.2 M in THF). The *i*PrMgCl·LiCl-solution was added at 0 °C and the Br/Mg exchange was complete after 6 h at 25 °C. Reaction time for cross-coupling: 1 h at 80 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 20:1) yielded product **3i** as a grey solid (130 mg, 0.42 mmol, 42%, mp: 165.5 – 167.4 °C).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 7.63 (d, *J* = 9.3 Hz, 2 H), 7.53-7.42 (m, 2 H), 7.38-7.35 (m, 2 H), 7.21 (dd, *J* = 2.6 Hz und *J* = 1.3 Hz, 1 H), 7.15 (dd, *J* = 5.3 Hz und *J* = 3.1 Hz, 1 H), 7.08 (dd, *J* = 4.9 Hz und *J* = 1.3 Hz, 1 H), 6.52 (d, *J* = 9.3 Hz, 2 H), 3.00 (s, 6 H).

¹³C-NMR (75 MHz, CDCl₃, 25 °C): δ = 196.8, 153.4, 140.7, 139.9, 134.5, 132.3, 129.3, 129.2, 128.3, 127.9, 126.8, 125.3, 125.1, 123.1, 110.4, 39.9.

MS (70 eV, EI): *m/z* (%): 307 (100) [M⁺], 274 (11), 148 (27), 115 (6).

IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 3103 (vw), 2920 (vw), 1633 (m), 1585 (vs), 1542 (m), 1380 (m), 1318 (m), 1300 (s), 1200 (s), 1148 (s), 930 (m), 764 (m), 752 (m), 596 (w).

HRMS for C₁₉H₁₇NOS (307.1031): found: 307.1016.

^1H -NMR of pure product (3i):

^{13}C -NMR of pure product (3i):

Synthesis of 2,2-dimethyl-1-(3',4',5'-trimethoxy[1,1'-biphenyl]-2-yl)-1-propanone (3j)

Prepared according to **TP 1** from 1-(2-fluorophenyl)-2,2-dimethyl-1-propanone (**1e**) (180 mg, 1.00 mmol) and (3,4,5-trimethoxyphenyl)magnesium bromide (3.00 mL, 3.00 mmol, 1.0 M in THF). Reaction time for the cross-coupling: 1 h at 80 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 9:1) yielded product **3j** as a colourless solid (233 mg, 0.71 mmol, 71%, mp: < 30 °C).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 7.43-7.32 (m, 3 H), 7.11 (d, *J* = 7.5 Hz, 1 H), 6.59 (s, 2 H), 3.86 (s, 3 H), 3.85 (s, 6 H), 0.89 (s, 9 H).

^{13}C -NMR (75 MHz, CDCl_3 , 25 °C): δ = 217.1, 153.1, 141.1, 137.9, 137.7, 136.5, 129.3, 128.7, 126.8, 125.8, 106.8, 61.0, 56.2, 45.1, 27.3.

MS (70 eV, EI): m/z (%): 283 (36) [M^+], 271 (100), 256 (18), 241 (16), 211 (11), 197 (8), 170 (7), 114 (6).

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3011 (vw), 2969 (w), 2837 (vw), 1681 (s), 1586 (s), 1479 (s), 1408 (m), 1348 (m), 1238 (s), 1133 (vs), 1009 (m), 968 (w), 843 (w), 763 (m), 692 (m).

HRMS for $\text{C}_{20}\text{H}_{24}\text{O}_4$ (328.1675): found: 328.1651.

^1H -NMR of pure product (3j):

^{13}C -NMR of pure product (3j):

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

Prepared according to **TP 1** from ethyl 2-fluorobenzoate (170 mg, 1.01 mmol) and 4-methoxyphenylmagnesium bromide (**2a**) (3.33 mL, 3.00 mmol, 0.9 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 **3k** as a light yellow oil (132 mg, 0.52 mmol, 51%).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 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).

¹³C-NMR (75 MHz, CDCl₃, 25 °C): δ = 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): $\tilde{\nu}$ (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 C₁₆H₁₆O₃ (256.1099): found: 256.1089.

^1H -NMR of pure product (3k):

^{13}C -NMR of pure product (3k):

Synthesis of Synthesis of phenyl-(3,4,3'',4''-tetrachloro-4',5',6'-trifluoro-[1,1';3',1'']terphenyl-2'-yl)methanone (31)

Prepared according to **TP 2** (except: double amount of CuCN·2LiCl-solution, Co(acac)₂ and 4-fluorostyrene) from (2,3,4,5,6-pentafluorophenyl) (phenyl)methanone (**1g**) (270 mg, 0.99 mmol), 4-bromo-1,2-dichlorobenzene (1.356 g, 6.00 mmol) and *i*PrMgCl·LiCl (5.25 mL, 6.30 mmol, 1.2 M in THF). The *i*PrMgCl·LiCl-solution was added at -20 °C and the Br/Mg exchange was complete after 1 h at 25 °C. Reaction time for

cross-coupling: 0.5 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 39:1) yielded product **31** as a colourless solid (262 mg, 0.50 mmol, 50%, mp: 148.4 – 153.0 °C).

¹H-NMR (600 MHz, CDCl₃, 25 °C): δ = 7.45-7.39 (m, 3 H), 7.31-7.24 (m, 6 H), 7.02 (dd, *J* = 8.6 and 2.4 Hz, 2 H).

¹³C-NMR (150 MHz, CDCl₃, 25 °C): δ = 193.9, 148.0 (ddd, *J* = 254.7, 10.6 and 3.5 Hz), 140.6 (dt, *J* = 257.1 and 15.3 Hz), 136.8-128.5 (m).

MS (70 eV, EI): *m/z* (%): 524 (52) [M⁺], 508 (17), 506 (14), 491 (24), 489 (25), 451 (17), 449 (32), 447 (26), 379 (13), 377 (17), 105 (100), 77 (27).

IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 3064 (vw), 2970 (vw), 2357 (vw), 1901 (vw), 1666 (m), 1594 (w), 1476 (m), 1374 (m), 1319 (m), 1225 (m), 1132 (m), 1035 (s), 820 (vs), 751 (m), 656 (s).

HRMS for C₂₅H₁₁Cl₄F₃O (523.9516): found: 523.9527.

¹H-NMR of pure product (31):

^{13}C -NMR of pure product (31):

Synthesis of Synthesis of 2'-benzoyl-4',5',6'-trifluoro-[1,1';3',1'']terphenyl-3,3''-dicarbonitrile (3m)

Prepared according to **TP 2** (except: double amount of CuCN·2LiCl-solution, Co(acac)₂ and 4-fluorostyrene) from (2,3,4,5,6-pentafluorophenyl) (phenyl)methanone (**1g**) (270 mg, 0.99 mmol), 3-bromobenzonitrile (1.093 g, 6.00 mmol) and *i*PrMgCl·LiCl (5.25 mL, 6.30 mmol, 1.2 M in THF). The *i*PrMgCl·LiCl-solution was added at -20 °C and the Br/Mg exchange was complete after 3 h at 0 °C. Reaction time for cross-coupling: 0.5 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 3:1) yielded product **3m** as a colourless solid (169 mg, 0.39 mmol, 39%, mp: 168.8 – 171.3 °C).

¹H-NMR (600 MHz, CDCl₃, 25 °C): δ = 7.54-7.20 (m, 13 H).

¹³C-NMR (150 MHz, CDCl₃, 25 °C): δ = 193.7, 148.2 (ddd, *J* = 254.7, 10.6 and 3.5 Hz), 140.5 (dt, *J* = 257.1 and 15.3 Hz), 136.6-100.0 (m).

MS (70 eV, EI): *m/z* (%): 438 (88) [M⁺], 420 (20), 361 (39), 105 (100), 77 (27).

IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 3071 (vw), 2235 (s), 1672 (vs), 1597 (m), 1478 (s), 1409 (m), 1368 (m), 1319 (s), 1226 (s), 1060 (s), 908 (w), 785 (m), 694 (vs).

HRMS for C₂₇H₁₃F₃N₂O (438.0980): found: 438.0975.

^1H -NMR of pure product (3m) :

^{13}C -NMR of pure product (3m) :

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

Prepared according to **TP 1** from 2-benzoylphenyl 4-methylbenzenesulfonate (**5a**) (336 mg, 0.95 mmol) and 4-methoxyphenylmagnesium bromide (3.75 mL, 3.00 mmol, 0.80 M in THF). Reaction time: 3 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 9:1) yielded product **3a** as a colourless oil (236 mg, 0.82 mmol, 86 %).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 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): δ = 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): $\tilde{\nu}$ (cm^{-1}) = 3060 (w), 2935 (w), 2837 (w), 1666 (s), 1517 (s), 1283 (s), 1249 (vs), 1179 (m), 927 (m), 707 (s).

HRMS for $\text{C}_{20}\text{H}_{16}\text{O}_2$ (288.1150): found: 288.1147.

^1H -NMR of pure product (3a):

^{13}C -NMR of pure product (3a):

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

Prepared according to **TP 2** from 2-benzoylphenyl 4-methylbenzenesulfonate (**5a**) (352 mg, 1.00 mmol), 1-bromo-3-fluorobenzene (525 mg, 3.00 mmol) and *i*PrMgCl·LiCl (2.63 mL, 3.15 mmol, 1.2 M in THF). The *i*PrMgCl·LiCl-solution was added at -20 °C and the Br/Mg exchange was complete after 6 h at 25 °C. Reaction time for cross-coupling: 0.25 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 19:1) yielded product **3n** as a colourless solid (214 mg, 0.78 mmol, 78%, mp: 74.3 – 75.3 °C).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 7.66-7.39 (m, 7 H), 7.31-7.25 (m, 2 H), 7.18-7.10 (m, 1 H), 7.02-6.95 (m, 2 H), 6.87-6.80 (m, 1 H).

¹³C-NMR (75 MHz, CDCl₃, 25 °C): δ = 198.4, 162.5 (d, *J* = 246.5 Hz), 142.4 (d, *J* = 8.2 Hz), 139.8 (d, *J* = 1.8 Hz), 138.9, 137.3, 133.0, 130.4, 129.9, 129.8, 129.8 (d, *J* = 8.2 Hz), 128.9, 128.2, 127.5, 124.8 (d, *J* = 2.9 Hz), 115.9 (d, *J* = 21.7 Hz), 114.2 (d, *J* = 21.1 Hz).

MS (70 eV, EI): *m/z* (%): 276 (100) [M⁺], 247 (9), 199 (68), 170 (31), 105 (40).

IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 4060 (vw), 3063 (m), 1937 (w), 1667 (vs), 1587 (s), 1450 (s), 1287 (vs), 1185 (s), 1156 (s), 1026 (w), 929 (s), 879 (s), 759 (s), 693 (s), 520 (w), 468 (w).

HRMS for C₁₉H₁₃FO (276.0950): found: 276.0961.

^1H -NMR of pure product (3n):

^{13}C -NMR of pure product (3n):

Synthesis of 2'-benzoyl-5'-ethoxy-[1,1'-biphenyl]-4-carbonitrile (3o)

Prepared according to **TP 2** from 2-benzoyl-5-ethoxyphenyl benzenesulfonate (**5b**) (396 mg, 1.00 mmol), 4-bromobenzonitrile (546 mg, 3.00 mmol) and *i*PrMgCl·LiCl (2.63 mL, 3.15 mmol, 1.2 M in THF). The *i*PrMgCl·LiCl-solution was added at -20 °C and the Br/Mg exchange was complete after 2 h at 0 °C. Reaction time for the cross-coupling: 0.25 h at 25 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 7:1) yielded product **3o** as a colourless solid (256 mg, 0.78 mmol, 78%, mp 105.9 – 106.5 °C).

$^1\text{H-NMR}$ (300 MHz, CDCl_3 , 25 °C): δ = 7.65-7.62 (m, 2 H), 7.54-7.42 (m, 4 H), 7.36-7.28 (m, 4 H), 6.99-6.91 (m, 2 H), 4.14 (q, J = 7.1 Hz, 2 H), 1.46 (t, J = 7.1 Hz, 3 H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , 25 °C): δ = 197.0, 160.8, 145.3, 142.2, 137.9, 132.9, 132.1, 131.9, 129.9, 129.5, 128.2, 118.7, 116.5, 113.3, 112.6, 111.1, 63.9, 14.7.

MS (70 eV, EI): m/z (%): 327 (100) [M^+], 298 (13), 250 (99), 222 (44), 105 (16).

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3064 (vw), 2981 (w), 2933 (vw), 2898 (vw), 2230 (s), 1656 (vs), 1600 (vs), 1470 (m), 1326 (s), 1282 (s), 1224 (vs), 1044 (m), 846 (m), 708 (m), 636 (m).

HRMS for $\text{C}_{22}\text{H}_{17}\text{NO}_2$ (327.1259): found: 327.1242.

$^1\text{H-NMR}$ of pure product (3o):

^{13}C -NMR of pure product (3o):

Synthesis of (4'-chloro-5-ethoxy[1,1'-biphenyl]-2-yl)phenyl methanone (3p)

Prepared according to **TP 2** from 2-benzoyl-5-ethoxyphenyl benzenesulfonate (**5b**) (396 mg, 1.00 mmol), 1-bromo-4-chlorobenzene (574 mg, 3.00 mmol) and *i*PrMgCl·LiCl (2.63 mL, 3.15 mmol, 1.2 M in THF). The *i*PrMgCl·LiCl-solution was added at -10 °C and the Br/Mg exchange was complete after 20 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 = 19:1) yielded product **3p** as a colourless solid (323 mg, 0.96 mmol, 96%, mp: 66.8 – 68.6 °C).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 7.64-7.61 (m, 2 H), 7.50-7.39 (m, 2 H), 7.31-7.25 (m, 2 H), 7.16 (s, 4 H), 6.96-6.91 (m, 2 H), 4.13 (q, *J* = 7.1 Hz, 2 H), 1.46 (s, *J* = 7.1 Hz, 3 H).

¹³C-NMR (75 MHz, CDCl₃, 25 °C): δ = 197.7, 160.6, 142.6, 138.9, 138.0, 133.5, 132.6, 131.6, 131.1, 130.1, 129.9, 128.4, 128.1, 116.3, 112.8, 63.8, 14.8.

MS (70 eV, EI): *m/z* (%): 336 (100) [M⁺], 335 (42), 307 (11), 261 (29), 259 (84), 233 (11), 231 (32), 168 (15), 139 (10), 105 (13), 77 (17).

IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2978 (vw), 2926 (vw), 1738 (w), 1647 (m), 1594 (m), 1281 (s), 1213 (vs), 1090 (w), 928 (m), 836 (s), 797 (m), 752 (m), 702 (s), 617 (s).

HRMS for C₂₁H₁₇ClO₂ (336.0917): found: 336.0888.

^1H -NMR of pure product (3p):

^{13}C -NMR of pure product (3p):

Synthesis of phenyl (2',4',6'-trimethyl[1,1'-biphenyl]-2-yl) methanone (3q)

Prepared according to **TP 1** from 2-benzoylphenyl 4-methylbenzenesulfonate (**5a**) (352 mg, 1.00 mmol) and mesitylmagnesium bromide (4.29 mL, 3.00 mmol, 0.7 M in THF). Reaction time: 48 h at 80 °C. Purification by flash chromatography on silica gel (pentane/diethyl ether = 99:1) yielded product **3q** as a colourless solid (161 mg, 0.54 mmol, 54%, mp: 121.0 – 124.4 °C).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 7.70-7.23 (m, 9 H), 6.78 (s, 2 H), 2.23 (s, 3 H), 196 (s, 6 H).

^{13}C -NMR (75 MHz, CDCl_3 , 25 °C): δ = 197.0, 140.9, 138.5, 137.4, 136.6, 136.6, 135.8, 132.6, 131.1, 130.5, 129.9, 129.2, 128.0, 127.7, 126.1, 21.0, 20.8.

MS (70 eV, EI): m/z (%): 300 (100) [M^+], 285 (79), 223 (33), 195 (24), 179 (14), 165 (17), 105 (14), 77 (19).

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3070 (vw), 2917 (w), 2855 (vw), 1662 (vs), 1596 (w), 1444 (m), 1311 (m), 1276 (m), 1258 (s), 1156 (w), 926 (m), 856 (w), 762 (s), 710 (s), 640 (m).

HRMS for $\text{C}_{22}\text{H}_{20}\text{O}$ (300.1514): found: 300.1537.

^1H -NMR of pure product (3q):

^{13}C -NMR of pure product (3q):

Synthesis of [4-ethoxy-2-(3-thienyl)phenyl]phenyl methanone (3r)

Prepared according to **TP 2** from 2-benzoyl-5-ethoxyphenyl benzenesulfonate (**5b**) (396 mg, 1.00 mmol), 3-bromothiophene (489 mg, 3.00 mmol) and *i*PrMgCl·LiCl (2.63 mL, 3.15 mmol, 1.2 M in THF). The *i*PrMgCl·LiCl-solution was added at -20 °C and the Br/Mg exchange was complete after 6 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 = 16:1) yielded product **3r** as a light yellow oil (228 mg, 0.74 mmol, 74%).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 7.65-7.62 (m, 2 H), 7.49-7.37 (m, 2 H), 7.29-7.24 (m, 2 H), 7.12-7.10 (m, 2 H), 7.00-6.91 (m, 3 H), 4.13 (q, *J* = 7.1 Hz, 2 H), 1.46 (t, *J* = 7.1 Hz, 3 H).

¹³C-NMR (75 MHz, CDCl₃, 25 °C): δ = 198.2, 160.5, 140.8, 137.9, 137.7, 132.5, 131.3, 131.0, 129.7, 128.3, 128.0, 125.6, 123.6, 115.5, 112.9, 63.7, 14.8.

MS (70 eV, EI): *m/z* (%): 308 (100) [M⁺], 279 (22), 251 (17), 231 (36), 203 (28).

IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 3101 (vw), 3061 (vw), 2980 (w), 2930 (vw), 1659 (s), 1600 (vs), 1447 (m), 1315 (s), 1277 (s), 1222 (s), 1046 (m), 926 (w), 793 (m), 711 (m), 658 (m), 625 (w).

HRMS for C₁₉H₁₆O₂S (308.0871): found: 308.0877.

^1H -NMR of pure product (3r):

^{13}C -NMR of pure product (3r):

Preparation of starting material:

Synthesis of 2,2-Dimethyl-propionic acid 4-(2-fluorobenzoyl)-phenyl ester (1b)

A 50 mL Schlenk-tube, equipped with a magnetic stirring bar and a septum, was charged with 2,2-dimethyl-4-iodophenyl propanoic acid ester (2.96 g, 9.73 mmol) and dry THF (20 mL). The mixture was cooled to $-20\text{ }^{\circ}\text{C}$ and *i*PrMgCl (11.34 mL, 10.23 mmol, 0.90 M in THF) was added. The reaction mixture was stirred at the same temperature for 30 min until full completion of the iodine/Mg exchange (checked by GC-analysis). Subsequent, a solution of $\text{CuCN}\cdot 2\text{LiCl}$ (10.8 mL, 10.8 mmol, 1.0 M in THF) was added at $-20\text{ }^{\circ}\text{C}$. After stirring for additional 10 min 2-fluorobenzoyl chloride (1.86 g, 11.70 mmol) was

added. The reaction mixture was stirred at -10 °C. After full conversion (2 h, checked by GC-analysis) the suspension was quenched with sat. $\text{NH}_4\text{Cl}_{(\text{aq.})}/\text{NH}_3$ (9:1) (50 mL). The organic fraction was washed a second time with sat. $\text{NH}_4\text{Cl}_{(\text{aq.})}/\text{NH}_3$ (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 (pentane/diethyl ether = 6:1) yielded product **1b** as a colourless solid (2.75 g, 9.16 mmol, 94%, mp: 48.4 - 49.6 °C).

^1H -NMR (300 MHz, CDCl_3 , 25 °C): δ = 7.86 (d, J = 8.8 Hz, 2 H), 7.56-7.48 (m, 2H), 7.28-7.12 (m, 4 H), 1.36 (s, 9 H).

^{13}C -NMR (75 MHz, CDCl_3 , 25 °C): δ = 192.2, 176.4, 160.0 (d, J = 252.4 Hz), 155.2, 134.2, 133.1 (d, J = 8.2 Hz), 131.4, 130.7 (d, J = 2.9 Hz), 126.9 (d, J = 14.7 Hz), 124.3 (d, J = 3.5 Hz), 121.6, 116.3 (d, J = 21.7 Hz), 39.2, 27.1.

MS (70 eV, EI): m/z (%): 300 (3) [M^+], 216 (34), 123 (36), 121 (58), 95 (11), 85 (35), 57 (100).

IR (Film): $\tilde{\nu}$ (cm^{-1}) = 2976 (m), 2936 (w), 2874 (vw), 1753 (s), 1668 (s), 1599 (m), 1482 (m), 1451 (m), 1294 (m), 1205 (s), 1158 (m), 1109 (vs), 932 (s), 756 (m), 627 (w).

HRMS for $\text{C}_{18}\text{H}_{17}\text{FO}_3$ (300.1162): found: 300.1169.

^1H -NMR of pure product (1b):

^{13}C -NMR of pure product (1b):

Synthesis of [4-(dimethylamino)phenyl] (2-fluorophenyl)methanone (1d)

A 50 mL Schlenk-tube, equipped with a magnetic stirring bar and a septum, was charged with 4-(dimethylamino)phenyl magnesium bromide (11.1 mL, 7.23 mmol, 0.65 M in THF) and was cooled to -10 °C. Subsequent, a solution of CuCN·2LiCl (8.0 mL, 8.0 mmol, 1.0 M in THF) was added. After stirring for additional 10 min 2-fluorobenzoyl chloride (1.49 g, 9.40 mmol) was added. The reaction mixture was stirred at -10 °C. After full conversion (4.5 h, checked by GC-analysis) the suspension was quenched with sat. NH₄Cl_(aq.)/NH₃ (9:1) (50 mL). The organic fraction was washed a second time with sat. NH₄Cl_(aq.)/NH₃ (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 (pentane/diethyl ether = 4:1) yielded product **1d** as a greenish solid (1.76 g, 7.23 mmol, 100%, mp: 92.0 – 92.7 °C).

^1H -NMR (300 MHz, CDCl_3 , 25 °C): δ = 7.76 (dd, J = 8.8 and 1.3 Hz, 2 H), 7.49–7.40 (m, 2 H), 7.24–7.07 (m, 2 H), 6.65 (d, J = 9.3 Hz, 2 H), 3.06 (s, 6 H).

^{13}C -NMR (75 MHz, CDCl_3 , 25 °C): δ = 191.2, 159.5 (d, J = 249.4 Hz), 132.4, 131.7 (d, J = 8.2 Hz), 130.2 (d, J = 3.5 Hz), 128.3 (d, J = 16.4 Hz), 124.9, 124.0 (d, J = 3.5 Hz), 115.9 (d, J = 21.7 Hz), 112.6, 110.6, 40.0.

MS (70 eV, EI): m/z (%): 243 (100) [M^+], 242 (23), 148 (99), 123 (14).

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2913 (vw), 1600 (vs), 1454 (w), 1380 (m), 1320 (s), 1194 (m), 1146 (m), 930 (w), 831 (m), 761 (m), 598 (w).

HRMS for $\text{C}_{15}\text{H}_{14}\text{FNO}$ (243.1059): found: 243.1051.

^1H -NMR of pure product (1d):

^{13}C -NMR of pure product (1d):

Synthesis of 1-(2-fluorophenyl)-2,2-dimethyl-1-propanone (1e)

A 50 mL Schlenk-tube, equipped with a magnetic stirring bar and a septum, was charged with $t\text{BuMgCl}\cdot\text{LiCl}$ (20.0 mL, 20.0 mmol, 1.0 M in THF) and was cooled to $-20\text{ }^{\circ}\text{C}$. Subsequent, a solution of $\text{CuCN}\cdot 2\text{LiCl}$ (22.0 mL, 22.0 mmol, 1.0 M in THF) was added. After stirring for additional 10 min 2-fluorobenzoyl chloride (4.13 g, 26.05 mmol) was added. The reaction mixture was stirred at $-20\text{ }^{\circ}\text{C}$ for 1 h and then was warmed to rt over night. After full conversion (checked by GC-analysis) the suspension was quenched with sat. $\text{NH}_4\text{Cl}_{(\text{aq.})}/\text{NH}_3$ (9:1) (50 mL). The organic fraction was washed a second time with sat. $\text{NH}_4\text{Cl}_{(\text{aq.})}/\text{NH}_3$ (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 (pentane/diethyl ether = 19:1) yielded product **1e** as a colourless oil (3.59 g, 19.93 mmol, 100%).

^1H -NMR (300 MHz, CDCl_3 , 25 °C): δ = 7.40-7.31 (m, 1 H), 7.20-7.04 (m, 3 H), 1.24-1.23 (m, 9 H).

^{13}C -NMR (75 MHz, CDCl_3 , 25 °C): δ = 210.1 (d, J = 1.2 Hz), 157.9 (d, J = 245.9 Hz), 130.8 (d, J = 8.2 Hz), 129.0 (d, J = 20.0 Hz), 127.7 (d, J = 4.7 Hz), 123.8 (d, J = 2.9 Hz), 115.9 (d, J = 22.3 Hz), 45.0, 26.6, 26.5.

MS (70 eV, EI): m/z (%): 180 (2) [M^+], 125 (17), 123 (100), 57 (11).

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2974 (m), 2873 (w), 1697 (vs), 1614 (m), 1479 (m), 1449 (m), 1367 (w), 1285 (m), 1224 (m), 1188 (m), 1104 (w), 966 (s), 830 (w), 757 (s), 535 (w).

HRMS for $\text{C}_{11}\text{H}_{13}\text{FO}$ (180.0950): found: 180.0947.

^1H -NMR of pure product (1e):

^{13}C -NMR of pure product (1e):

Synthesis of 2-benzoylphenyl 4-methylbenzenesulfonate (5a)

A 100 mL round-bottom flask, equipped with a magnetic stirring bar, was charged with 2-hydroxybenzophenone (4.16 g, 21.0 mmol) and dry pyridine (20 mL) was added. The solution was cooled to 0 °C and 4-methylbenzenesulfonyl chloride (4.95 g, 26.0 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), 2 M HCl (30 mL) was added and the phases were separated. The water phase was extracted with EtOAc (4x100 mL). The organic phases were washed with 2 M HCl (30 mL), saturated NaHCO₃-solution (50 mL), brine (50 mL), dried over Mg₂SO₄, filtered and

concentrated in vacuo. Recrystallization from CH_2Cl_2 yielded product **5a** as a colourless solid (7.30 g, 20.71 mmol, 99%, mp: 95.4-96.8 °C).

^1H -NMR (300 MHz, CDCl_3 , 25 °C): δ = 7.63-7.33 (m, 11 H), 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 $\text{C}_{20}\text{H}_{16}\text{O}_4\text{S}$ (352.0769): found: 352.0774.

^1H -NMR of pure product (5a):

^{13}C -NMR of pure product (5a) :

Synthesis of [4-ethoxy-2-[[[(4-methylphenyl)sulfonyl]oxy]-phenyl]phenyl methanone (5b)

A 100 mL round-bottom flask, equipped with a magnetic stirring bar, was charged with (4-ethoxy-2-hydroxyphenyl)phenyl methanone (1.28 g, 5.30 mmol) and dry pyridine (20 mL) was added. The solution was cooled to 0 °C and 4-methylbenzenesulfonyl chloride (1.32 g, 6.92 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), 2 M HCl (30 mL) was added and the phases were separated. The water phase was extracted with EtOAc (4x100 mL). The organic phases were washed with 2 M HCl (30 mL), saturated NaHCO₃-solution (50 mL), brine (50 mL), dried over Mg₂SO₄, filtered and concentrated *in vacuo*. Recrystallization from CH₂Cl₂ yielded product **5b** as a colourless solid (1.55 g, 3.92 mmol, 74%, mp: 104.2 – 106.9 °C).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 7.58-7.34 (m, 8 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 6.89-6.83 (m, 2 H), 4.07 (q, *J* = 7.1 Hz, 2 H), 2.33 (s, 3 H), 1.43 (t, *J* = 7.1 Hz, 3 H).

¹³C-NMR (75 MHz, CDCl₃, 25 °C): δ = 192.7, 162.0, 148.0, 145.4, 137.4, 132.7, 132.2, 131.9, 130.0, 129.6, 128.5, 128.0, 125.1, 113.2, 109.8, 64.2, 21.6, 14.5.

MS (70 eV, EI): *m/z* (%): 396 (45) [M⁺], 319 (25), 242 (17), 241 (100), 240 (22), 213 (30), 155 (20), 105 (14), 91 (44), 77 (13).

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3089 (vw), 2987 (vw), 2940 (vw), 1660 (vs), 1609 (vs), 1501 (m), 1375 (vs), 1271 (vs), 1243 (m), 1192 (s), 1182 (s), 1086 (s), 984 (m), 889 (m), 818 (s), 703 (s), 630 (m), 561 (m), 551 (m).

HRMS for $\text{C}_{22}\text{H}_{20}\text{O}_5\text{S}$ (396.1031): found: 396.1039.

^1H -NMR of pure product (5b):

^{13}C -NMR of pure product (5b) :