Efficient Cross-Coupling of Functionalized Arylzinc Halides Catalyzed by a Nickel Chloride-Diethyl Phosphite System

Andrei Gavryushin, Christiane Kofink, Georg Manolikakes and Paul Knochel*

Department Chemie, Ludwig-Maximilians-Universität, Butenandtstrasse 5-13, 81377, München (Germany).

Paul.Knochel@cup.uni-muenchen.de

Supporting Information

General considerations

Unless otherwise indicated, all reactions were carried out with magnetic stirring and in case of air- or moisture-sensitive compounds in flame-dried glassware under argon. Syringes were used to transfer the reagents and the solvents were purged with argon prior to use. Reactions were monitored by gas chromatography (GC and GC-MS) or thin layer chromatography.

Solutions of organomagnesium compounds were prepared, if not especially mentioned, by the reaction of Mg with aryl bromides in THF, titrated with a standard solution of I₂ in 0.5 M LiCl in THF and diluted with THF to the mentioned concentration. ZnBr₂ and ZnCl₂ were dried at 140 °C under high vacuum for 30 min and then dissolved in dry THF.

Typical Procedure 1 (TP 1).

The solution of the nickel catalyst was prepared as follows. In a 25 mL Schlenk tube under argon in dry degassed N-ethylpyrrolidinone (10.0 mL) were dissolved anhydrous NiCl₂ (8.2 mg, 0.063 mmol), (EtO)₂P(O)H (34.5 mg, 0.25 mmol) and DMAP (30.5 mg, 0.25 mmol).

In a dry and argon flushed 25 mL flask, equipped with a magnetic stirrer and a septum, the corresponding arylmagnesium reagent in THF (1.20 mmol) was added slowly with cooling to the solution of ZnBr₂ (0.67 mL of 1.5 M in THF, 1.00 mmol) and NEP (0.17 mL). To this mixture, the electrophile (aryl halide or sulfonate, 1.00 mmol) was added, followed by the solution of the catalyst (0.08 mL). The final THF-NEP volume ratio should be approximately 8:1. The mixture was stirred at the specified temperature until the GC of an aliquot showed the reaction completion, quenched with sat. NH₄Cl solution, extracted with ether, and the product was purified by column chromatography.

3-Fluoro-4'-methoxy-1,1'-biphenyl (**3a**):

Prepared according to the TP 1. To the ZnBr_2 solution (0.67 mL, 1.5 M in THF) and NEP (0.17 mL) was added dropwise 4-methoxyphenylmagnesium bromide (1.57 mL, 0.83 M in THF), then the catalyst solution (0.08 mL) and 3-bromofluorobenzene (175 mg, 1.00 mmol). Stirred 2 h at RT. The usual workup and purification by flash chromatography (pentane/ether 19:1) yielded **3a** as white solid (174 mg, 86%).

Mp.: 67-67.5 °C. (Lit.¹: 68 °C)

¹H-NMR (CDCl_3 , 300 MHz, 25 °C): δ = 7.39 (d, J = 8.9 Hz, 2H), 7.28-7.11 (m, 3H), 6.90-6.84 (m, 3H), 3.72 (s, 3H).

¹³C-NMR (CDCl_3 , 75 MHz, 25 °C): δ = 163.2 (q, $^1J(\text{C}, \text{F})$ = 245 Hz), 159.5, 143.1 (q, $^3J(\text{C}, \text{F})$ = 7.6 Hz), 132.4 (q, $^4J(\text{C}, \text{F})$ = 2.1 Hz), 130.1 (q, $^3J(\text{C}, \text{F})$ = 8.2 Hz), 128.1, 122.2 (q, $^4J(\text{C}, \text{F})$ = 2.6 Hz), 114.5, 113.5 (q, $^2J(\text{C}, \text{F})$ = 21.7 Hz), 113.3 (q, $^2J(\text{C}, \text{F})$ = 21.1 Hz), 55.3.

IR (KBr): 2963 (w), 2840 (w), 1610 (vs), 1589 (s), 1573 (m), 1522 (s), 1487 (s), 1447 (m), 1292 (s), 1264 (s), 1252 (s), 1189 (vs), 1162 (m), 1026 (m), 879 (m), 830 (vs), 782 (s).

MS (70 eV, EI), m/z (%): 209 (100, M^+), 187 (50), 159 (54), 133 (24), 107 (10), 77 (13).

HRMS m/z : calcd. for $\text{C}_{13}\text{H}_{11}\text{FO}$: 202.0794; found: 202.0790.

Ethyl 4'-methoxy-biphenyl-3-carboxylate (**3b**)

Prepared according to the TP 1. To the ZnBr_2 solution (0.67 mL, 1.5 M in THF) and NEP (0.17 mL) was added dropwise 4-methoxyphenylmagnesium bromide (1.57 mL, 0.83 M in THF), then the catalyst solution (0.08 mL), and ethyl 3-bromobenzoate (229 mg, 1.00 mmol). Stirred for 1 h at RT. The usual workup and purification by flash chromatography (pentane/ether 9:1) yielded **3b** as colourless oil (234 mg, 91%).

¹H-NMR (CDCl₃, 300 MHz, 25 °C): δ = 8.26 (s, 1H), 8.00-7.97 (m, 1H), 7.73-7.70 (m, 1H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H).

¹³C-NMR (CDCl₃, 75 MHz, 25 °C): δ = 166.5, 159.4, 140.9, 132.5, 130.9, 130.8, 128.6, 128.1, 127.6, 127.1, 114.2, 60.9, 55.2, 14.2.

IR (KBr): 2981 (w), 1717 (vs), 1610 (m), 1518 (s), 1439 (m), 1367 (w), 1300 (s), 1249 (vs), 1182 (m), 1109 (s), 1049 (m), 1030 (m), 834 (m), 758 (s), 574 (w).

MS (70 eV, EI), *m/z* (%): 256 (100, M⁺), 241 (9), 228 (11), 211 (20), 183 (10), 168 (6), 139 (12), 105 (3).

HRMS *m/z*: calcd. For C₁₆H₁₆O₃: 256.1099; found: 256.1097.

Ethyl 4'-methoxy-biphenyl-4-carboxylate (**3c**)

Prepared according to the TP 1. To the ZnBr₂ solution (0.67 mL, 1.5 M in THF) and NEP (0.17 mL) was added dropwise 4-methoxyphenylmagnesium bromide (1.57 mL, 0.83 M in THF), then the catalyst solution (0.08 mL) and ethyl 4-bromobenzoate (229 mg, 1.00 mmol) or ethyl 4-chlorobenzoate (185 mg, 1.00 mmol). The mixture was stirred for 1 h at RT (48 h for ethyl 4-chlorobenzoate). The usual workup and purification by flash chromatography (pentane-ether 9:1) yielded **3c** as white solid (224 mg or 87% for the reaction with ethyl 4-bromobenzoate and 214 mg or 83% for ethyl 4-chlorobenzoate). The analytical data are in accordance with the literature.³

Mp.: 100-101 °C.

¹H-NMR (CDCl₃, 300 MHz, 25 °C): δ = 8.09 (d, *J* = 8.7 Hz, 2H), 7.62-7.55 (m, 4H), 6.99 (d, *J* = 8.7 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H).

¹³C-NMR (CDCl₃, 75 MHz, 25 °C): δ = 166.5, 159.8, 145.0, 132.4, 130.0, 128.6, 128.3, 126.4, 114.3, 60.8, 55.3, 14.3.

(4'-Methoxy-[1,1'-biphenyl]-4-yl)-(phenyl)-methanone (3d)

Prepared according to the TP 1. To the ZnBr_2 solution (0.67 mL, 1.5 M in THF) and NEP (0.17 mL) was added dropwise 4-methoxyphenylmagnesium bromide (1.57 mL, 0.83 M in THF), then the catalyst solution (0.08 mL) and 4-bromobenzophenone (261 mg, 1.00 mmol). Stirred for 3 h at RT. The usual workup and purification by flash chromatography (pentane-ether 19:1) yielded **3c** as a white solid (210 mg, 73%). The analytical data are in accordance with the literature.²

Mp.: 167-168 °C.

¹H-NMR (CDCl_3 , 600 MHz, 25 °C): δ = 7.87 (d, J = 8.1 Hz, 2H), 7.83 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 8.3 Hz, 2H), 7.60-7.57 (m, 3H), 7.49 (t, J = 7.6 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H).

¹³C-NMR (CDCl_3 , 151 MHz, 25 °C): δ = 196.3, 159.9, 144.8, 137.9, 135.6, 132.4, 132.2, 130.8, 129.9, 128.4, 128.3, 126.4, 114.4, 55.4.

IR (KBr): 1651 (vs), 1600 (vs), 1529 (w), 1446 (w), 1316 (m), 1288 (s), 1276 (s), 1256 (m), 1206 (vs), 1182 (w), 1033 (w), 939 (w), 829 (s), 794 (w), 697 (m).

MS (70 eV, EI), m/z (%): 288 (100, M^+), 211 (76), 183 (6), 168 (8), 139 (8), 105 (11), 77 (10), 51 (1).

HRMS m/z : calcd. for $\text{C}_{20}\text{H}_{16}\text{O}_2$: 288.1150; found: 288.1146.

3-(4-Methoxyphenyl)-pyridine (3e)

Prepared according to the TP 1. To the ZnBr_2 solution (0.67 mL, 1.5 M in THF) and NEP (0.17 mL) was added dropwise 4-methoxyphenylmagnesium bromide (1.57 mL, 0.83 M in

THF), then the catalyst solution (0.08 mL) and 3-bromopyridine (159 mg, 1.00 mmol) or 3-Chloro-pyridine (114 mg, 1.00 mmol). Stirred for 2 h at RT (12 h for 3-chloropyridine). The usual workup and purification by flash chromatography (pentane-ether 1:1) yielded **3e** as a white solid (150 mg or 81% for 3-bromopyridine and 126 mg, 68% for 3-chloropyridine). The analytical data are in accordance with the literature.⁴ The same reaction performed on 20 mmol scale gave the yield of 82%.

Mp.: 62-63 °C.

¹H-NMR (CDCl₃, 600 MHz, 25 °C): δ = 8.81-8.80 (m, 1H), 8.53 (dd, *J*₁ = 4.8 Hz, *J*₂ = 1.6 Hz, 1H), 7.84-7.80 (m, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.34-7.30 (m, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H).

¹³C-NMR (CDCl₃, 151 MHz, 25 °C): δ = 159.7, 148.0, 147.9, 136.3, 133.8, 130.3, 128.2, 123.5, 114.6, 55.4.

IR (KBr): 2964 (w), 1608 (s), 1578 (w), 1564 (w), 1520 (s), 1478 (s), 1434 (m), 1283 (s), 1254 (vs), 1183 (s), 1030 (s), 838 (m), 803 (vs), 706 (m), 619 (w), 552 (w).

MS (70 eV, EI), *m/z* (%): 185 (100, M⁺), 170 (44), 142 (46), 115 (17), 89 (11), 63 (8).

HRMS *m/z*: calcd. for C₁₂H₁₁NO: 185.0841; found: 185.0837.

6-(3-Methoxy-phenyl)-nicotinic acid methyl ester (**3f**)

Prepared according to the TP 1. To the ZnBr₂ solution (0.67 mL, 1.5 M in THF) and NEP (0.17 mL) was added dropwise 3-methoxy-magnesium bromide (1.57 mL, 0.83 M in THF), then the catalyst solution (0.08 mL in NEP) and 6-chloronicotinic acid methyl ester (172 mg, 1.00 mmol). Stirred for 24 h at RT, standard workup and purification by flash chromatography (CH₂Cl₂-pentane 1:1) yielded **3f** as colourless solid (180 mg, 74%).

Mp.: 89.5-90 °C.

¹H-NMR (CDCl₃, 600 MHz, 25 °C): δ = 9.24 (s, 1H), 8.31 (dd, *J*₁ = 8.3 Hz, *J*₂ = 1.9 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.63-7.62 (m, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 8.1 Hz, 1H), 6.99 (dd, *J*₁ = 8.1 Hz, *J*₂ = 2.4 Hz, 1H), 3.94 (s, 3H), 3.88 (s, 3H).

^{13}C -NMR (CDCl_3 , 151 MHz, 25 °C): δ = 165.9, 160.7, 160.2, 151.0, 139.7, 137.9, 129.9, 124.3, 120.0, 119.7, 116.1, 112.5, 55.4, 52.3.

IR (KBr): 3059 (w), 3013 (w), 2954 (m), 2925 (m), 1715 (vs), 1596 (vs), 1562 (m), 1480 (s), 1433 (s), 1288 (vs), 1267 (s), 1231 (s), 1117 (s), 1030 (s), 1021 (s).

MS (70 eV, EI), m/z (%): 243 (65, M^+), 242 (100), 213 (38), 182 (9), 154 (10), 106 (11).

HRMS m/z : calcd. for $\text{C}_{14}\text{H}_{13}\text{NO}_3$: 243.0895; found: 243.0867.

1-(3'-Methoxy-biphenyl-4-yl)-ethanone (3g).

Prepared according to the TP 1. To the ZnBr_2 solution (0.67 mL, 1.5 M in THF) and NEP (0.17 mL) was added dropwise 3-methoxy-magnesium bromide (1.57 mL, 0.83 M in THF), then the catalyst solution (0.08 mL) and 4-bromoacetophenone (199 mg, 1.00 mmol). Stirred 2.5 h at RT. The standard workup and purification by flash chromatography (CH_2Cl_2 -pentane 1:1) yielded **3g** as a yellow solid (175 mg, 77%).

Mp.: 35 -36 °C. ⁵

^1H -NMR (CDCl_3 , 300 MHz, 25 °C): δ = 8.00 (ddd, J_1 = 8.5 Hz, J_2 = 2.9 Hz, J_3 = 1.9 Hz, 2H), 7.65 (ddd, J_1 = 8.6 Hz, J_2 = 2.0 Hz, J_3 = 1.9 Hz, 2H), 7.38-7.31 (m, 1H), 7.20-7.17 (m, 1H), 7.13-7.12 (m, 1H), 6.94-6.90 (m, 1H), 3.85 (s, 3H), 2.61 (s, 3H).

^{13}C -NMR (CDCl_3 , 75 MHz, 25 °C): δ = 198.1, 160.4, 146.0, 141.8, 136.4, 130.4, 129.3, 127.7, 120.1, 113.9, 113.5, 55.8, 27.0.

MS (70 eV, EI), m/z (%): 226 (56, M^+), 211 (100), 168 (14), 152 (11), 139 (21).

2-(3-Pyridino)-benzophenone (3h)

Prepared according to the TP 1. To the ZnBr_2 solution (0.67 mL, 1.5 M in THF) and NEP (0.17 mL) was added dropwise 3-pyridylmagnesium bromide⁸ (1.57 mL, 0.83 M in THF),

then the catalyst solution (0.08 mL) and 2-bromobenzophenone (270 mg, 1.00 mmol). Stirred for 3 h at 50 °C. The standard workup and purification by flash chromatography (pentan-CH₂Cl₂) yielded **3h** as a white solid (197 mg, 76%). The analytical data are in accordance with the literature.¹²

Mp.: 106-106.5 °C.

¹H-NMR (CDCl₃, 300 MHz, 25 °C): 8.56-8.52 (m, 1H), 8.44-8.40 (m, 1H), 7.72-7.10 (m, 11H).

¹³C-NMR (CDCl₃, 75 MHz, 25 °C): 198.3, 149.8, 148.8, 139.5, 137.9, 137.6, 136.6, 136.3, 133.6, 131.1, 130.6, 130.3, 129.5, 128.7, 128.2, 123.3.

MS (70 eV, EI), *m/z* (%): 77 (27), 105 (25), 127 (20), 182 (36), 230 (100), 231 (26), 259 (19, M⁺).

5-(3-Fluorophenyl)-pyrimidine (**3i**)

Prepared according to the TP 1. To the ZnBr₂ solution (0.67 mL, 1.5 M in THF) and NEP (0.17 mL) was added dropwise 3-fluorophenylmagnesium bromide (1.57 mL, 0.83 M in THF), then the catalyst solution (0.08 mL) and 5-bromopyrimidine (159 mg, 1.00 mmol). Stirred for 1 h at RT. The standard work up and purification by flash chromatography (pentan-Et₂O) yielded **3i** as a white solid (143 mg, 82%).

Mp.: 63-63.5 °C.

¹H-NMR (CDCl₃, 300 MHz, 25 °C): 9.13 (s, 1H), 8.85 (s, 2H), 7.44-7.23 (m, 1H), 7.29-7.26 (m, 1H), 7.22-7.17 (m, 1H), 7.10-7.03 (m, 1H).

¹³C-NMR (CDCl₃, 75 MHz, 25 °C): 163.7 (d, *J* = 248 Hz), 158.3, 155.2, 136.8 (d, *J* = 7.9 Hz), 133.5, 131.5 (d, *J* = 8.5 Hz), 123.0, 116.3 (d, *J* = 21.1 Hz), 114.3 (d, *J* = 21.1 Hz).

IR (KBr): 2239 (w), 1591 (s), 1416 (s), 909 (vs), 734 (vs).

MS (70 eV, EI), *m/z* (%): 94 (12), 105 (25), 120 (100), 173 (21), 174 (96, M⁺).

HRMS *m/z*: calcd. for C₁₀H₇N₂F: 174.0593; found: 174.0577.

4-Pyrimidin-5-yl-benzoic acid ethyl ester (**3j**)

Prepared according to the TP 1. To the ZnBr₂ solution (0.67 mL, 1.5 M in THF) and NEP

(0.17 mL) was added dropwise cold 4-carboethoxyphenylmagnesium bromide (prepared by iodine-magnesium exchange from ethyl 4-iodobenzoate and *i*PrMgCl-LiCl⁸ at -40 °C for 30 min) (1.57 mL, 0.83 M in THF), then the catalyst solution (0.08 mL) in NEP), and 5-bromopyrimidine (159 mg, 1.00 mmol). The mixture was stirred for 24 h at RT, standard work up and purification by flash chromatography (CH₂Cl₂-pentane) yielded **3j** as pale yellow crystals (137 mg, 60%). Analytical data are in accordance with literature.¹⁴

Mp.: 118-119 °C.

¹H-NMR (CDCl₃, 600 MHz, 25 °C): δ = 9.25 (s, 1H), 8.99 (s, 2H), 8.19 (m, 2H), 7.66 (m, 2H), 4.42 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H).

¹³C-NMR (CDCl₃, 150 MHz, 25 °C): δ = 164.9, 157.2, 157.0, 154.1, 154.0, 137.5, 132.4, 130.0, 129.6, 125.9, 60.3, 13.3.

MS (70 eV, EI, *m/z* (%): 228 (21, M⁺), 200 (33), 183 (100), 128 (40), 101 (32).

8-(1-Naphthyl)-quinoline (3k)

Prepared according to the TP 1. To the ZnBr₂ solution (0.67 mL, 1.5 M in THF) and NEP (0.17 mL) was added dropwise 1-naphthylmagnesium bromide (1.57 mL, 0.83 M in THF), then the catalyst solution (0.08 mL) and 8-quinolyl nonaflate¹³ (427 mg, 1.00 mmol). Stirred for 24 h at RT. The standard workup and purification by flash chromatography (CH₂Cl₂-pentan) yielded **3k** as a white solid (224 mg, 88 %).

Mp.: 163-164 °C.

¹H-NMR (CDCl₃, 300 MHz, 25 °C): 8.76-8.74 (m, 1H); 8.16-8.13 (m, 1H); 7.89-7.82 (m, 3H); 7.69-7.66 (m, 1H), 7.60-7.46 (m, 3H), 7.41-7.18 (m, 4H).

¹³C-NMR (CDCl₃, 75 MHz, 25 °C): δ = 150.9, 147.7, 140.6, 138.5, 136.6, 134.1, 133.3, 132.0, 128.9, 128.7, 128.5, 128.4, 128.3, 127.1, 126.6, 126.1, 126.0, 125.8, 121.5.

IR: (KBr) (cm⁻¹): 3042 (w), 1593 (w), 1492 (s), 829 (s), 797 (vs), 782 (vs), 773 (vs).

MS (70 eV, EI, *m/z* (%): 127 (9), 226 (9), 252 (14), 254 (100), 255 (47, M⁺).

HRMS *m/z*: calcd. for C₁₉H₁₃N: 255.1048; found: 255.1020.

3-(1-Methyl-1H-pyrrol-2-yl)-pyridine (3l).

Prepared according to the TP 1. To the ZnBr_2 solution (0.67 mL, 1.5 M in THF) and NEP (0.26 mL) was added dropwise 1-methyl-2-pyrrolyllithium⁶ (2.4 mL, 0.5 M in THF), then the catalyst solution (0.08 mL) and 3-bromopyridine (158 mg, 1.00 mmol). The reaction mixture was stirred for 22 h at 70 °C, the standard workup and purification by flash chromatography ($\text{Et}_2\text{O}-\text{CH}_2\text{Cl}_2$ 1:1) yielded **3l** as yellow oil (98 mg, 62%). The analytical data are in accordance with the literature.⁷

¹H-NMR (CDCl_3 , 300 MHz, 25 °C): δ = 8.66 (d, J = 1.8 Hz, 1H), 8.50 (dd, J_1 = 4.8 Hz, J_2 = 1.6 Hz, 1H), 7.70 (ddd, J_1 = 7.9 Hz, J_2 = 1.8 Hz, J_3 = 1.6 Hz, 1H), 7.31 (ddd, J_1 = 7.9 Hz, J_2 = 4.8 Hz, J_3 = 0.8 Hz, 1H), 6.74 (dd, J_1 = 2.5 Hz, J_2 = 1.9 Hz, 1H), 6.27 (dd, J_1 = 3.6 Hz, J_2 = 1.9 Hz, 1H), 6.20 (dd, J_1 = 3.6 Hz, J_2 = 2.8 Hz, 1H), 3.65 (s, 3H).

¹³C-NMR (CDCl_3 , 75 MHz, 25 °C): δ = 149.3, 147.8, 136.1, 131.1, 129.8, 125.2, 123.7, 110.3, 108.7, 35.5.

MS (70 eV, EI), m/z (%): 158 (100, M^+), 143 (7), 130 (19), 116 (6), 89 (5).

1-(3'-Trifluoromethyl-biphenyl-4-yl)-ethanone (3m).

Prepared according to the TP 1. To the ZnBr_2 solution (0.67 mL, 1.5 M in THF) and NEP (0.17 mL) was added dropwise 3-trifluoromethyl-phenyl-magnesium bromide⁸ (1.57 mL, 0.83 M in THF), then the catalyst solution (0.08 mL) and 4-bromoacetophenone (199 mg, 1.00 mmol). Stirred for 18 h at RT, the standard workup and purification by flash chromatography (CH_2Cl_2 -pentane 1:1) yielded **3m** as colourless oil (180 mg, 68%). The

analytical data are in accordance with the literature.⁹

¹H-NMR (CDCl₃, 300 MHz, 25 °C): δ = 8.06 (ddd, J_1 = 8.6 Hz, J_2 = 2.4 Hz, J_3 = 2.0 Hz, 2H), 7.87-7.78 (m, 2H), 7.73-7.57 (m, 4H), 2.65 (s, 3H).

¹³C-NMR (CDCl₃, 75 MHz, 25 °C): δ = 197.9, 144.6, 141.1, 136.9, 132.2, 132.0, 131.6, 130.9, 130.2, 129.9, 129.5, 127.4, 125.3, 124.4, 27.1.

MS (70 eV, EI), m/z (%): 264 (35, M⁺), 249 (100), 221 (6), 201 (34), 152 (21).

Ethyl 4-(1,3-benzodioxol-5-yl)benzoate (3n)

Prepared according to the TP 1. To the ZnBr₂ solution (0.67 mL, 1.5 M in THF) and NEP (0.17 mL) was added dropwise 1,3-benzodioxol-5-yl-magnesium bromide (1.57 mL, 0.83 M in THF), then the catalyst solution (0.08 mL) and ethyl 4-bromobenzoate (229 mg, 1.00 mmol). Stirred for 5 h at RT. The usual workup and purification by flash chromatography (pentane-ether 1:1) chromatography yielded **3n** as white solid (253 mg, 94%).
Mp.: 92.5-93.5 °C.

¹H-NMR (CDCl₃, 300 MHz, 25 °C): δ = 8.07 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 8.7 Hz, 2H), 7.11-7.07 (m, 2H), 6.89 (d, J = 8.6 Hz, 1H), 5.00 (s, 2H), 4.39 (q, J = 7.1 Hz, 2H), 1.40 (d, J = 7.2 Hz, 3H).

¹³C-NMR (CDCl₃, 75 MHz, 25 °C): δ = 166.4, 148.3, 147.7, 145.1, 134.3, 130.0, 128.8, 126.6, 121.0, 108.6, 107.6, 101.3, 60.9, 14.3.

IR (KBr): 2904 (w), 1707 (vs), 1606 (m), 1522 (w), 1503 (m), 1486 (s), 1410 (s), 1274 (vs), 1256 (s), 1235 (m), 1182 (s), 1107 (s), 1036 (s), 932 (m), 858 (m), 772 (s), 702 (w).

MS (70 eV, EI), m/z (%): 270 (100, M⁺), 242 (32), 225 (70), 139 (40), 112 (5), 63 (2).

HRMS m/z : calcd. for C₁₆H₁₄O₄: 270.0892; found: 270.0888.

3-(1,3-benzodioxol-5-yl)pyridine (3o)

Prepared according to the TP 1. To the ZnBr_2 solution (0.67 mL, 1.5 M in THF) and NEP (0.17 mL) was added dropwise 1,3-benzodioxol-5-yl-magnesium bromide (1.57 mL, 0.83 M in THF), then the catalyst solution (0.08 mL in NEP) and 3-bromopyridine (158 mg, 1.00 mmol). Stirred for 5 h at RT. The standard workup and purification by flash chromatography yielded **3o** as a white solid (165 mg, 83 %).

Mp.: 92-92.5 °C.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz, 25 °C): δ = 8.76 (d, J = 1.9 Hz, 1H), 8.54-8.51 (m, 1H), 7.78-7.74 (m, 1H), 7.32-7.27 (m, 1H), 7.04-7.00 (m, 2H), 6.90-6.87 (m, 1H), 5.99 (s, 2H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz, 25 °C): δ = 148.4, 148.1, 148.0, 147.7, 136.3, 133.9, 131.9, 123.4, 120.8, 108.8, 107.5, 101.3.

IR (KBr): 2912 (w), 1512 (s), 1479 (vs), 1420 (s), 1294 (w), 1266 (m), 1238 (s), 1111 (w), 1037 (s), 931 (m), 806 (s), 706 (m).

MS (70 eV, EI), m/z (%): 199 (100, M^+), 140 (10), 114 (11), 88 (4), 63 (3).

HRMS m/z : calcd. for $\text{C}_{12}\text{H}_9\text{NO}_2$: 199.0633; found: 199.0602.

1-(3,4-methylenedioxyphenyl)-naphthalene (3p)

Prepared according to the TP 1. To ZnBr_2 or ZnCl_2 solution (0.67 mL, 1.5 M in THF) and NEP (0.17 mL) was added dropwise 1-naphthylmagnesium bromide (1.57 mL, 0.83 M in THF), then the catalyst solution (0.08 mL) and 3,4-methylenedioxyphenyl triflate¹⁰ (270 mg, 1.00 mmol). Stirred for 24 h at RT. The standard workup and purification by flash chromatography (pentane-Et₂O 9:1) yielded **3p** as colourless oil (196 mg, 79%, for the reaction with ZnCl_2 77% yield). The analytical data are in accordance with the literature.¹¹

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz, 25 °C): δ = 7.99-7.85 (m, 3H), 7.55-7.41 (m, 4H), 7.02-6.94 (m,

3H), 6.06 (s, 2H).

¹³C-NMR (CDCl₃, 75 MHz, 25 °C): δ = 147.9, 174.3, 140.2, 135.1, 134.2, 132.2, 128.7, 128.0, 127.3, 126.4, 126.2, 125.8, 123.8, 111.1, 108.6, 101.5.

MS (70 eV, EI), *m/z* (%): 248 (100, M⁺), 217 (19), 208 (10), 189 (52), 94 (20).

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7 Jul 2005

Acquisition Time (sec)	9.0440	Comment	Ak Knoche	Date	16/12/2004 17:57:44	Frequency (MHz)	300.13
Nucleus	¹ H	Original Points Count	32768	Points Count	32768	Sweep Width (Hz)	3623.19
						Temperature (grad C)	0.000

7 Jul 2005

Acquisition Time (sec)	3.4079	Comment	Ak Knoche	Date	16/12/2004 19:42:44	Frequency (MHz)	75.47
Nucleus	¹³ C	Original Points Count	65536	Points Count	65536	Sweep Width (Hz)	19230.77
						Temperature (grad C)	0.000

S13

7 Jul 2005

Acquisition Time (sec)	4.1943	Comment	Ak Knochel	Date	19/04/2005 10:55:40	Frequency (MHz)	599.80
Nucleus	¹ H	Original Points Count	32768	Points Count	32768	Sweep Width (Hz)	7812.50
						Temperature (grad C)	0.000

7 Jul 2005

Acquisition Time (sec)	1.7039	Comment	Ak Knochel	Date	19/04/2005 11:25:40	Frequency (MHz)	150.82
Nucleus	¹³ C	Original Points Count	65536	Points Count	65536	Sweep Width (Hz)	38461.54
						Temperature (grad C)	0.000

S14

7 Jul 2005

Acquisition Time (sec)	9.0440	Comment	Ak Knochel	Date	07/06/2005 21:00:50	Frequency (MHz)	300.13
Nucleus	¹ H	Original Points Count	32768	Points Count	32768	Sweep Width (Hz)	3623.19
						Temperature (grad C)	0.000

7 Jul 2005

Acquisition Time (sec)	3.4079	Comment	Ak Knochel	Date	07/06/2005 23:01:06	Frequency (MHz)	75.47
Nucleus	¹³ C	Original Points Count	65536	Points Count	65536	Sweep Width (Hz)	19230.77
						Temperature (grad C)	0.000

S15

7 Jul 2005

Acquisition Time (sec)	9.0440	Comment	Ak Knochel	Date	07/06/2005 15:00:50	Frequency (MHz)	300.13
Nucleus	¹ H	Original Points Count	32768	Points Count	32768	Sweep Width (Hz)	3623.19
						Temperature (grad C)	0.000

7 Jul 2005

Acquisition Time (sec)	3.4079	Comment	Ak Knochel	Date	07/06/2005 16:45:58	Frequency (MHz)	75.47
Nucleus	¹³ C	Original Points Count	65536	Points Count	65536	Sweep Width (Hz)	19230.77
						Temperature (grad C)	0.000

S16

Acquisition Time (sec) 9.0440		Comment Ak Knoche		Date 27/05/2005 15:15:34		Frequency (MHz) 300.13
Nucleus	¹ H	Original Points Count	32768	Points Count	32768	Sweep Width (Hz) 3623.19
				Temperature (grad C) 0.000

Acquisition Time (sec) 3.4079		Comment Ak Knoche		Date 27/05/2005 17:00:34		Frequency (MHz) 75.47
Nucleus	¹³ C	Original Points Count	65536	Points Count	65536	Sweep Width (Hz) 19230.77
				Temperature (grad C) 0.000

S17

Acquisition Time (sec)	9.0440	Comment	Ak Knoche	Date	27/05/2005 12:45:40	Frequency (MHz)	300.13
Nucleus	1H	Original Points Count	32768	Points Count	32768	Sweep Width (Hz)	3623.19
						Temperature (grad C)	0.000

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10. Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478.
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