SUPPORTING INFORMATION

Synthesis of Functionalized Diarylmethanes via a Cobalt-catalyzed Cross-coupling of Arylzinc Species with Benzyl Chlorides

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**General Information**

GC analysis were carried out using a gas chromatograph Varian 3300 provided with a 25-m CPSIL5CB capillary column. Mass spectra were recorded with a GCQ Thermoelectron spectrometer coupled to a gas chromatograph Varian (35-m CPSIL5CB/MS capillary column). Column chromatography was performed on silica gel 60, 70-230 mesh with pentane/ethyl acetate as eluent. $^1$H, $^{13}$C and $^{19}$F NMR spectra were recorded in CDCl$_3$, on a Bruker ARX 400 MHz. All solvents and reagents were purchased and used without further purification. No inert atmosphere was required.

Chemical shifts (δ) are quoted in parts per million (ppm) and coupling constants (J) are measured in hertz (Hz). The following abbreviations are used to describe multiplicities s=singlet, d=doublet, t=triplet, q=quartet, b=broad, m=multiplet.

**Typical procedure for synthesis of diarylmethanes starting from aromatic bromides using of CoBr$_2$/Zn system. (Procedure A) :**

To a solution of CoBr$_2$ (10 mol%, 0.75 mmol, 164 mg) and zinc powder (15 mmol, 1.00 g) in acetonitrile (5 mL) were successively added at room temperature allylchloride (3 mmol, 250 μL) and trifluoroacetic acid (100 μL), causing an immediate rise in temperature and color change to dark grey. After stirring the resulting mixture for 3 minutes, aryl bromide (7.5 mmol) and benzyl chloride (15 mmol) were added. The medium was then stirred at room temperature until aryl bromide was consumed. The amount of the corresponding coupling product was measured by GC (addition of iodine) using an internal reference (dodecane, 200 μL). The reaction mixture was poured into a solution of 2N HCl and extracted with diethylether. The organic layer was washed with a saturated solution of NaCl and dried over MgSO$_4$. Evaporation of solvent and purification by column chromatography on silica gel (pentane/diethylether) afforded the coupling product characterized by NMR ($^1$H, $^{13}$C) and mass spectrometry.

**Typical procedure for synthesis of diarylmethanes starting from aromatic bromides and 1-chloro,1-phenylethane using CoBr$_2$/Zn system :**

(a) **Synthesis of ArZnBr.** To a solution of CoBr$_2$ (10 mol%, 0.75 mmol, 164 mg) and zinc powder (15 mmol, 1g) in acetonitrile (5 mL) were successively added at room temperature allylchloride (3 mmol, 250 μL) and trifluoroacetic acid (100 μL), causing an immediate rise in temperature and color change to dark grey. After stirring the resulting mixture for 3 minutes, aryl bromide (7.5 mmol) was added. The medium was then stirred at room temperature until complete conversion of aryl bromide. (b) **Cross-coupling reaction.** 1-chloro,1-phenylethane was added and the medium
was stirred at room temperature until ArZnBr was consumed. The amounts of the corresponding ArZnBr and coupling product were measured by GC (addition of iodine) using an internal reference (dodecane, 200 μL). The reaction mixture was poured into a solution of 2N HCl and extracted with diethylether. The organic layer was washed with a saturated solution of NaCl and dried over MgSO₄. Evaporation of solvent and purification by column chromatography on silica gel (pentane/diethylether) afforded the coupling product characterized by NMR (¹H, ¹³C) and mass spectrometry.

Typical procedure for synthesis of diarylmethanes starting from aromatic chlorides and benzyl chloride using CoBr₂/Zn system: (a) Synthesis of ArZnCl. To a solution of CoBr₂ (10 mol%, 0.75 mmol, 164 mg) and zinc powder (22.5 mmol, 1,47 g) in acetonitrile (10 mL) were successively added at room temperature allylchloride (6 mmol, 500 μL) and trifluoroacetic acid (100 μL), causing an immediate rise in temperature and color change to dark grey. After stirring the resulting mixture for 3 minutes, pyridine (4 mL), CoBr₂ (23 mol%, 1.7 mmol, 372 mg) and aryl chloride (7.5 mmol) were added. The medium was then stirred at room temperature until complete conversion of aryl chloride. (b) Cross-coupling reaction. Benzyl chloride was added and the medium was stirred at 50°C until ArZnCl was consumed. The amounts of the corresponding ArZnCl and coupling product were measured by GC (addition of iodine) using an internal reference (dodecane, 200 μL). The reaction mixture was poured into a solution of 2N HCl and extracted with diethylether. The organic layer was washed with a saturated solution of NaCl and dried over MgSO₄. Evaporation of solvent and purification by column chromatography on silica gel (pentane/diethylether) afforded the coupling product characterized by NMR (¹H, ¹³C) and mass spectrometry.

Ethyl 4-benzylbenzoate C₁₆H₁₆O₂, CAS registry number 18908-74-2.

Isolated as a colourless oil (77%): IR(υmax/cm⁻¹) 3085, 3027, 2980, 1713, 1610, 1271; ¹H NMR (400 MHz, CDCl₃, 293 K, TMS) δ 7.92 (d, J = 8.1 Hz, 2H), 7.18 (m, 7H), 4.31 (q, J = 7.1 Hz, 2H), 3.98 (s, 2H), 1.33 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃, 293 K, TMS) δ 166.6, 146.4, 140.2, 129.8 (2C), 128.9 (3C), 128.6 (3C), 128.4, 126.4, 60.8, 41.9, 14.4; EI-MS m/z (rel. intensity) 240 (M, 47), 213 (7), 212 (35), 211 (7), 196 (12), 195 (73), 168 (17), 167 (100), 166 (20), 165 (56), 153 (7), 152 (40), 149 (5).
Ethyl 3-benzylbenzoate $\text{C}_{16}\text{H}_{16}\text{O}_2$, CAS registry number 134752-72-0.

Isolated as a golden oil (75%): IR($\nu_{\text{max}}$/cm$^{-1}$) 3062, 3028, 2980, 1715, 1601, 1276; $^1$H NMR (400 MHz, CDCl$_3$, 293 K, TMS) $\delta$ 7.93 (m, 2H), 7.37 (m, 2H), 7.30 (m, 2H), 7.21 (m, 3H), 4.38 (q, $J$ = 7.1 Hz, 2H), 4.04 (s, 2H), 1.40 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 293 K, TMS) $\delta$ 166.7, 141.4, 140.5, 133.5, 130.7, 130.0, 128.9 (2C), 128.6 (3C), 127.4, 126.3, 60.9, 41.7, 14.4; EI-MS m/z (rel. intensity) 240 (M, 91), 212 (32), 211 (42), 195 (77), 167 (100), 166 (30), 165 (63), 152 (38).

Ethyl 2-benzylbenzoate $\text{C}_{16}\text{H}_{16}\text{O}_2$, CAS registry number 1585-99-5.

Isolated as a colourless oil (75%): IR($\nu_{\text{max}}$/cm$^{-1}$) 3062, 3028, 2980, 1715, 1601, 1276; $^1$H NMR (400 MHz, CDCl$_3$, 293 K, TMS) $\delta$ 8.00 (d, 1H), 7.46 (t, 1H), 7.33 (m, 3H), 7.24 (m, 4H), 4.49 (s, 2H), 4.35 (q, 2H), 1.36 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 293 K, TMS) $\delta$ 167.7, 142.1, 141.1, 131.9, 131.6, 130.6, 128.9, 128.4, 126.3, 125.9, 60.9, 39.6, 14.3; EI-MS m/z (rel. intensity) 240 (M, 91), 211 (32), 195 (24), 193 (11), 166 (12), 165 (45), 152 (6), 133 (19), 105 (3).

Methyl 4-benzylbenzoate $\text{C}_{15}\text{H}_{14}\text{O}_2$, CAS registry number 23450-30-8.

Isolated as a yellow oil (68%): IR($\nu_{\text{max}}$/cm$^{-1}$) 3085, 3027, 2950, 1717, 1611, 1274; $^1$H NMR (400 MHz, CDCl$_3$, 293 K, TMS) $\delta$ 7.99 (d, $J$ = 8.3 Hz, 2H), 7.25 (m, 7H), 4.04 (s, 2H ), 3.91 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 293 K, TMS) $\delta$ 167.1, 146.6, 140.2, 129.9 (2C), 128.9 (4C), 128.6 (2C), 128.1, 126.4, 52.0, 41.9; EI-MS m/z (rel. intensity) 226 (M, 64), 195 (35), 168 (15), 167 (100), 166 (17), 165 (47), 152 (22).
4-benzylbenzonitrile C_{14}H_{11}N, CAS registry number 23450-31-9.

Isolated as a golden oil (71 and 57%): IR(\nu_{\text{max}}/\text{cm}^{-1}) 3086, 3028, 2923, 2852, 2227, 1603; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 293 K, TMS) \delta 7.56 (d, J = 8.3 Hz, 2H), 7.31 (m, 5H), 7.19 (d, J = 7.3 Hz, 2H), 4.04 (s, 2H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, 293 K, TMS) \delta 146.8, 139.4, 132.3 (2C), 129.7 (2C), 129.0 (2C), 128.8 (2C), 126.7, 119.1, 110.0, 42.0; EI-MS m/z (rel. intensity) 193 (M, 100), 192 (44), 191 (14), 190 (16), 178 (10), 166 (13), 165 (47), 164 (7), 152 (6).

3-benzylbenzonitrile C_{14}H_{11}N, CAS registry number 93717-55-6. Isolated as a golden oil (74%): IR(\nu_{\text{max}}/\text{cm}^{-1}) 3062, 3028, 2918, 2228, 1599; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 293 K, TMS) \delta 7.50 (m, 2H), 7.45 (m, 1H), 7.42 (m, 1H), 7.34 (m, 2H), 7.28 (m, 1H), 7.19 (m, 2H), 4.03 (s, 2H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, 293 K, TMS) \delta 142.6, 139.4, 133.4, 132.4, 129.9, 129.2, 128.9 (2C), 128.8 (2C), 126.7, 118.9, 112.5, 41.4; EI-MS m/z (rel. intensity) 193 (M, 100), 192 (60), 190 (21), 178 (10), 166 (17), 165 (41).

2-benzylbenzonitrile C_{14}H_{11}N, CAS registry number 56153-61-8.

Isolated as an orange oil (76 and 55%): IR(\nu_{\text{max}}/\text{cm}^{-1}) 3085, 3028, 2926, 2223, 1599; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 293 K, TMS) \delta 7.66 (m, 1H), 7.52 (m, 1H), 7.31 (m, 7H), 4.24 (s, 2H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, 293 K, TMS) \delta 144.9, 138.8, 132.8 (2C), 130.1, 129.0 (2C), 128.8 (2C), 126.7 (2C), 118.2, 112.6, 40.2; EI-MS m/z (rel. intensity) 193 (M, 100), 192 (33), 190 (7), 166 (9), 165 (37).

4’-benzylacetophenone C_{15}H_{14}O, CAS registry number 782-92-3.

Isolated as a yellow oil (22 and 83%): IR(\nu_{\text{max}}/\text{cm}^{-1}) 3084, 3027, 2922, 2854, 1679, 1602, 1266; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 293 K, TMS) \delta 7.89 (d, J = 8.3 Hz, 2H), 7.29 (m, 4H), 7.27 (m, 1H), 7.20 (m, 2H), 4.04 (s, 2H), 2.58 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, 293 K,
4-benzylbenzotrifluoride $C_{14}H_{11}F_3$, CAS registry number 34239-04-8.
Isolated as a golden oil (85%): IR($\nu_{\text{max}}$ cm$^{-1}$) 3087, 3029, 2922, 1619, 1322, 1107; $^1$H NMR (400 MHz, CDCl$_3$, 293 K, TMS) $\delta$ 7.58 (d, $J = 8.1$ Hz, 2H), 7.29 (m, 7H), 4.07 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$, 293 K, TMS) $\delta$ 145.3, 140.0, 129.2 (3C), 128.9 (3C), 128.7 (2C), 127.0 (q, $J = 263$ Hz, CF$_3$), 126.5, 125.4, 41.7; $^{19}$F NMR (377 MHz, CDCl$_3$, 293 K, TMS) $\delta$ -62.7 (s, 3F); EI-MS m/z (rel. intensity) 236 (M, 55), 217 (7), 215 (10), 168 (11), 167 (100), 166 (18), 165 (40), 152 (12).

1-Benzyl-4-chlorobenzene $C_{13}H_{11}Cl$, CAS registry number 831-81-2.
Isolated as a white solid (77%): $^1$H NMR (400 MHz, CDCl$_3$, 293 K, TMS) $\delta$ 7.30-7.42 (m, 5H), 7.26 (d, 2H), 7.20 (d, $J = 8.4$ Hz, 2H), 4.03 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$, 293 K, TMS) $\delta$ 140.7, 139.7, 132.0, 130.4, 129.0, 128.7, 126.4, 41.3, EI-MS m/z (rel. intensity) 202 (M, 39), 168 (14), 167 (100), 166 (23), 165 (49), 152 (24).

4-methoxydiphenylmethane $C_{14}H_{14}O$, CAS registry number 834-14-0.
Isolated as an orange oil (71%): IR($\nu_{\text{max}}$ cm$^{-1}$) 3083, 2952, 2835, 1509, 1243; $^1$H NMR (400 MHz, CDCl$_3$, 293 K, TMS) $\delta$ 7.30 (m, 2H), 7.19 (m, 3H), 7.12 (d, $J = 8.3$ Hz, 2H), 6.85 (d, $J = 8.6$ Hz, 2H), 3.94 (s, 2H), 3.79 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 293 K, TMS) $\delta$ 157.9, 141.6, 133.3, 129.9 (2C), 128.8 (2C), 128.4 (2C), 126.0, 113.9 (2C), 55.3, 41.0; $^{19}$F NMR (377 MHz, CDCl$_3$, 293 K, TMS) $\delta$ -114.7 (s, F); EI-MS m/z (rel. intensity) 198 (M, 100), 197
2-methoxydiphenylmethane C_{14}H_{14}O, CAS registry number 883-90-9.  
Isolated as a colourless oil (68%): IR(\nu_{max}/\text{cm}^{-1}) 3083, 2952, 2835, 1509, 1243; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 293 K, TMS) \delta 7.33-7.23 (m, 6H), 7.12 (m, 1H), 6.93 (m, 2H), 4.04 (s, 2H), 3.87 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, 293 K, TMS) \delta 157.4, 141.1, 130.4, 129.06, 128.35, 127.5, 125.8, 120.5, 110.4, 55.4, 35.9 EI-MS m/z (rel. intensity) 198 (M, 100), 197 (15), 183 (43), 168 (10), 167 (57), 166 (14), 165 (63), 155 (11), 154 (5), 153 (18), 91 (23).

Benzenamine, \textit{N,N}-dimethyl-4-(phenylmethyl) C_{15}H_{17}N, CAS registry number 46734-13-8.  
Isolated as a red oil (70%): IR(\nu_{max}/\text{cm}^{-1}) 3082, 2894, 2798, 1614, 1519, 1342; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 293 K, TMS) \delta 7.35 (m, 2H), 7.28 (m, 3H), 7.17 (d, J = 8.7 Hz, 2H), 6.79 (d, J = 8.7 Hz, 2H), 3.99 (s, 2H), 2.99 (s, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, 293 K, TMS) \delta 149.2, 142.1, 129.6 (2C), 129.3, 129.1, 128.9 (2C), 128.4 (2C), 125.9, 113.0 (2C), 41.4 (2C); EI-MS m/z (rel. intensity) 211 (M, 100), 210 (71), 195 (7), 194 (9), 168 (5), 167 (28), 166 (12), 165 (20), 152 (7), 134 (40), 118 (5), 91 (11).

4-(1-phenyl-ethyl)-benzoic acid ethyl ester C_{17}H_{18}O_{2}.  
Isolated as a colourless oil (75%): IR(\nu_{max}/\text{cm}^{-1}) 3083, 3027, 2971, 1713, 1271; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 293 K, TMS) \delta 8.02 (d, J = 8.6 Hz, 2H), 7.33 (m, 4H), 7.25 (m, 3H), 4.41 (q, J = 7.2 Hz, 2H), 4.25 (q, J = 7.3 Hz, 1H), 1.70 (d, J = 7.3 Hz, 3H), 1.42 (t, J = 7.2 Hz, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, 293 K, TMS) \delta 166.6, 151.6, 145.5, 129.7 (2C), 128.5
2-(1-phenyl-ethyl)benzoic acid ethyl ester C\textsubscript{17}H\textsubscript{18}O\textsubscript{2}, CAS registry number 855277-13-3. Isolated as a colourless oil (60%): IR(\(\nu\)\textsubscript{max}/cm\(^{-1}\)) 3083, 3027, 2971, 1713, 1271; \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}, 293 K, TMS) \(\delta\) 7.80 (d, \(J = 7.7\) Hz, 2H), 7.45-7.19 (m, 8H), 5.15 (q, \(J = 7.1\) Hz, 1H), 4.34 (q, \(J = 7.3\) Hz, 2H ), 1.66 (d, \(J = 7.1\) Hz, 3H), 1.35 (t, \(J = 7.1\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}, 293 K, TMS) \(\delta\) 168.3, 147.1, 146.1, 131.6, 130.6, 129.8, 128.5, 128.2, 127.9, 125.9, 125.8, 61.0, 39.8, 22.0, 14.2; EI-MS m/z (rel. intensity) 254 (M, 14), 210 (15), 209(47), 208 (100), 207 (36), 194 (16), 193 (54), 183 (15), 179 (16), 178 (31), 165 (26), 152 (12), 149 (17), 131 (24), 120 (14), 106 (16), 105 (27), 103 (10), 91 (13), 79 (12), 77 (13).

4-(1-phenylethyl)benzonitrile C\textsubscript{15}H\textsubscript{13}N, CAS registry number 125847-21-4. Isolated as a colourless oil (67%): \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}, 293 K, TMS) \(\delta\) 7.58 (d, \(J = 8\) Hz, 2H), 7.36-7.32 (m, 4H), 7.27-7.2 (m, 3H), 4.23 (q, \(J = 7.2\) Hz, 1H), 1.68 (d, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}, 293 K, TMS) \(\delta\) 151.9, 144.7, 132.6, 132.2, 129.1, 128.7, 128.5, 127.8, 127.6, 127.3, 126.7, 119.1, 109.9, 44.9, 21.5; EI-MS m/z (rel. intensity) 207 (M, 44), 193 (19), 192 (100), 191 (26), 190 (27), 165 (51), 152 (9), 149 (7),125 (7), 105 (9), 103 (8), 77 (7), 73 (9), 69 (8).
4-(1-phenylethyl)benzotrifluoride C$_{15}$H$_{13}$F$_3$.
Isolated as a colourless oil (70%): IR($\nu_{\text{max}}$/cm$^{-1}$) 3087, 3029, 2922, 1619, 1322, 1107; $^1$H NMR (400 MHz, CDCl$_3$, 293 K, TMS) $\delta$ 7.59 (d, $J$ = 7.9 Hz, 2H), 7.40-7.23 (m, 7H), 4.26 (q, $J$ = 7.1 Hz, 1H), 1.72 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 293 K, TMS) $\delta$ 150.5, 145.3, 128.6, 128.3, 128.0, 127.9, 127.6, 126.5, 126.1, 125.8, 125.4, 125.3, 44.7, 21.6. EI-MS m/z (rel. intensity) 250 (M, 41), 236 (13), 235 (100), 215 (36), 195 (8), 166 (38), 165(45).HRMS measured 250.0959 found 250.0969.

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\text{F}_3\text{C} & \quad \text{F}_3\text{C} \\
& \\
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1-(4-Methoxyphenyl)-1phenylethane C$_{15}$H$_{16}$O, CAS registry number 2605-18-7. Isolated as a colourless oil (65%): $^1$H NMR (400 MHz, CDCl$_3$, 293 K, TMS) $\delta$ 7.45-7.3 (m, 7H), 7.0 (d, $J$ = 8.5 Hz, 2H), 4.27 (q, $J$ = 6.8 Hz, 1H), 3.89 (s, 3H), 1.78 (d, $J$ = 8.7 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 293 K, TMS) $\delta$ 158.0, 146.9, 138.7, 128.7, 128.5, 128.2, 127.9, 127.8, 127.7, 126.1, 113.9, 55.3, 44.1, 22.3 EI-MS m/z (rel. intensity) 212 (M, 34), 198 (13), 197 (100), 182 (15), 166 (10), 165 (22), 154 (10), 153 (14), 152 (9).

\[ \begin{align*}
\text{MeO} & \quad \text{MeO} \\
& \\
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