

Carbinol Derivatives via Rhodium-Catalyzed 1,2-Addition of Potassium Trifluoro(organo)borates

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Supplementary Information

General: ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 300 or Avance 400 instruments; chemical shifts (δ) are reported in ppm relative to Me_4Si ; coupling constants (J) are reported in Hz and refer to apparent peak multiplicities. Mass spectra were determined on a Ribermag instrument. High resolution mass spectra were performed on a Varian MAT311 at the Université Pierre and Marie Curie (Paris). Elemental analyses were done at the Regional Service of Microanalysis (Université Pierre et Marie Curie). Thin layer chromatography was carried out on silica-gel plates (Merck F₂₅₄), spots were detected with UV light and revealed with KMnO_4 solution. GC analyses were performed on a Agilent 6850 Series instrument equipped with a capillary column HP-1 (30 m, $\varnothing = 0.25\ \mu\text{m}$), using an ionisation flame detector: program A = 70°C during 1 min then 20°C/min up to 210°C, program B = 70°C during 1 min then 20°C/min up to 250°C. Potassium trifluoro(organo)borates were prepared according to published procedures.¹ Toluene was distilled from CaH_2 .

General Procedure: A septum-capped vial equipped with a magnetic stirring bar was charged with trifluoro-(organo)borate (1 mmol), aryl aldehyde (0.5 mmol) and chlorobis(ethylene)rhodium(I) dimer (7.5 μmol , 2.9 mg). The vial was closed and evacuated under vacuum and placed under an argon atmosphere. Degassed toluene (1.5 ml) and water (1 ml) were added followed by a solution of tri-*tert*-butylphosphane in degassed toluene (15 μmol , 3M solution, 50 μL). The mixture was stirred in a preheated oil bath at 60°C for the indicated time. After cooling the vessel to room temperature, the reaction mixture was purified by silica gel column chromatography.

(4-fluorophenyl)-3-thienylmethanol: Colorless oil (102 mg, 97% yield) obtained from **2d** (1 mmol, 190 mg) and **1f** (0.5 mmol, 62 mg) according to the general procedure. $R_f = 0.24$ (cyclohexane/AcOEt, 9/1). GC (program B): $t_R = 7.1$ min. ^1H NMR (300 MHz, CDCl_3 , δ): 2.68 (1H, br s), 5.93 (1H, s), 7.06 (1H, dd, $J = 1.2$ Hz and 5.0 Hz), 7.13 (2H, dd, $J = 8.9$ Hz and 9.2 Hz), 7.26 (1H, dd, $J = 1.2$ Hz and 3.0 Hz), 7.38 (1H, dd, $J = 5.0$ Hz and 3.0 Hz), 7.44 (2H, dd, $J = 8.9$ Hz and 5.5 Hz). ^{13}C NMR (75 MHz, CDCl_3 , δ): 72.1, 115.3 (d, $J_{\text{C-F}} = 21.3$ Hz), 121.7, 126.3, 126.4, 128.2 (d, $J_{\text{C-F}} = 8.0$ Hz), 139.1 (d, $J_{\text{C-F}} = 2.8$ Hz), 145.2 (C_6), 165.3 (d, $J_{\text{C-F}} = 244$ Hz). MS (ICP, NH_3): 208 (5%, $[\text{M-H}_2\text{O}+\text{NH}_4]^+$), 191 (100%, $[\text{M-H}_2\text{O}+\text{H}]^+$).

(2,4,6-Trimethoxyphenyl)phenylmethanol:² White solid (131 mg, 96% yield) obtained from **2a** (1 mmol, 184 mg) and **1l** (0.5 mmol, 98 mg) according to the general procedure at 40°C. m.p. = 123°C, litt²: 124-125°C. $R_f = 0.41$ (CH_2Cl_2). GC (program A): $t_R = 10.0$ min. ^1H NMR (300 MHz, CDCl_3 , δ): 3.75 (6H, s), 3.81 (3H, s), 4.17 (1H, br s), 6.17 (2H, s), 6.36 (1H, s), 7.18–7.37 (5H, m). ^{13}C NMR (75 MHz, CDCl_3 , δ): 55.4, 55.8, 68.3, 91.3, 112.4, 125.7, 126.4, 127.9, 145.3, 158.5, 160.8. MS (EI, 70 eV, m/z): 274 (23%), 197 (100%), 179 (21%).

2,4,6-Trimethoxyphenyl-(2-methylphenyl)methanol: White solid (122.4 mg, 85% yield) obtained from **2f** (1 mmol, 198 mg) and **1l** (0.5 mmol, 98 mg) according to the general procedure at 40°C. m.p. = 120°C. $R_f = 0.49$ (CH_2Cl_2). GC (program A): $t_R = 10.2$ min. ^1H NMR (300 MHz, CDCl_3 , δ): 2.48 (3H, s), 3.76 (6H, s), 3.83 (3H, s), 4.10 (1H, br s), 6.19 (2H, s), 6.35 (1H, s), 7.10–7.16 (4H, m). ^{13}C NMR (75 MHz, CDCl_3 , δ): 55.4, 55.8, 66.9, 91.2, 110.9, 125.2, 126.4, 127.0, 130.4, 137.2, 141.7, 158.8, 160.7. MS (IE, 70 eV, m/z): 288 (6%), 197 (100%), 169 (89%). HRMS (m/z): calcd for $\text{C}_{17}\text{H}_{20}\text{O}_4$ 288.1362, found 288.1363.

2,4,6-Trimethoxyphenyl-(2,6-dimethylphenyl)methanol:³ White solid obtained from **2g** (1 mmol, 212 mg) and **1l** (0.5 mmol, 98 mg) according to the general procedure at 40°C (143.5 mg, 63% yield). m.p. = 122°C. R_f (CH_2Cl_2) = 0.52. GC (program A): $t_R = 10.4$ min. ^1H NMR (300 MHz, CDCl_3 , δ): 2.37 (6H, s), 3.71 (6H, s), 3.80 (3H, s), 4.80 (1H, br s), 6.15 (2H, s), 6.49 (1H, s), 6.96–7.00 (3H, m). ^{13}C NMR (75 MHz, CDCl_3 , δ): 55.4, 55.8,

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68.3, 91.3, 112.4, 125.7, 126.4, 127.9, 145.3, 158.5, 160.8. MS (IE, m/z) : 302 (4%), 197 (94%), 169 (100%). HRMS (m/z): calcd for C₁₈H₂₂O₄ 302.1518 found 302.1527.

All other products were identified by comparison of spectroscopic data with authentic sample or with those reported in the literature: entry 1⁴ [720-44-5], entry 2⁵ [33091-15-5], entry 3⁶ [87901-71-1], entry 4 [119-56-2], entry 5 [29334-16-5], entry 6⁷ [2795-76-8], entry 7⁸ [22788-49-4], entry 8⁹ [833-39-6], entry 9¹⁰ [7765-98-2], entry 10¹¹ [4484-57-5], entry 12¹² [104449-55-0], entry 13,¹³ and Eqn. 4¹⁴ [4471-05-0].

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