Direct Access to Ketones from Aldehydes via Rhodium-Catalyzed Cross-Coupling Reaction with Potassium Trifluoro(organo)borates

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Supporting Information

General Procedures

¹H NMR and ¹³C NMR spectra were recorded on a Avance 300 or Avance 400 instruments; chemical shifts (δ) are reported in ppm relative to Me₄Si; coupling constants (*J*) are reported in Hz and refer to apparent peak multiplicities. ²H NMR spectra were recorded on a Bruker Avance 400 instrument at 61.4 MHz using benzene-*d*₆ as an internal reference. Mass spectra were determined on a Ribermag instrument. High resolution mass spectra were performed on a Varian MAT311 at the Université Pierre et Marie Curie (Paris). Thin layer chromatography was carried out on silica-gel plates (Merck F254), spots were detected with UV light and revealed with KMnO₄ solution. GC analyses were performed on a Hewlett-Packard instrument equipped with a J&W Scientific HP-01 capillary column (30 m, Ø = 0.25 µm), using an ionization flame detector.

Potassium organotrifluoroborates¹ were prepared according to published procedures. Dioxane and acetone were freshly distilled from CaH₂.

Formation of deuteriated compounds.

2-deuteriopropen-2-ol, 1-deuteriodiphenylmethanol and 1-deuteriophenylmethanol were prepared by NaBD₄ reduction of acetone, benzophenone and benzaldehyde respectively.

2-deuteriopropen-2-ol:² ¹H NMR (CDCl₃, 300 MHz) δ = 0.95 (t, *J*_{D-H} = 7.0 Hz, 6H), 4.53 (s, 1H). ²H NMR (CDCl₃, 61.4 MHz) δ = 3.75 (hept, *J*_{D-H} = 0.8 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ = 24.6, 63.0 (t, *J*_{D-C} = 21.4 Hz).

1-deuteriodiphenylmethanol:³ ¹H NMR (CDCl₃, 300 MHz) δ = 2.65 (br s, 1H), 7.25-7.42 (m, 10H). ²H NMR (CDCl₃, 61.4 MHz) δ = 5.52 (s). ¹³C NMR (CDCl₃, 75 MHz) δ = 75.9 (t, *J*_{D-C} = 21.4 Hz), 126.8, 127.7, 128.7, 144.0.

1-deuteriophenylmethanol:⁴ ¹H NMR (CDCl₃, 300 MHz) δ = 3.6 (br s, 1H), 4.57 (br s, 1H), 7.25-7.33 (m, 5H). ²H NMR (CDCl₃, 61.4 MHz) δ = 4.34 (d, *J*_{D-H} = 2.0 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ = 64.4 (d, *J*_{D-C} = 22 Hz), 127.0, 127.4, 128.4, 141.1.

Typical procedure (conditions B) for carbonylation of potassium trifluoro(organo)borates: preparation of (4-hydroxy-3-methoxyphenyl)-2-methylphenylmethanone (entry 8):

To a mixture of potassium trifluoro(2-methylphenyl)borate **2d** (1 mmol, 198 mg), 4-hydroxy-3-methoxybenzaldehyde **1h** (0.5 mmol, 76 mg) and chlorobis(ethylene)rhodium(I) dimer (7.5 µmol, 2.9 mg) in degassed dioxane (2 mL) was added a solution of tri-*tert*-butylphosphane in degassed toluene (15 µmol, 3M solution, 50 µL), under an argon atmosphere. After 5 minutes stirring at room temperature, degassed acetone (0.5 mL) was added and the flask was placed in a preheated oil bath at 80°C. The mixture was stirred until completion of the reaction (followed by GC analysis). After concentration under reduced pressure, the crude mixture was purified by silica gel chromatography eluting with cyclohexane/ethyl acetate (4:1) to afford 141 mg of analytically pure ketone as a pale yellow oil (yield 94%).

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GC (HP-01, 30 m, 4 mL/min., 70°C during 1 min. then 20°C/min up to 250°C): T_R 9.21 min. Rf (cyclohexane/AcOEt 4/1): 0.23. 1H NMR ($CDCl_3$, 300 MHz) δ = 2.29 (s, 3H), 3.93 (s, 3H), 6.33 (s, 1H), 6.87 (d, J = 8.5 Hz, 1H), 7.18 (dd, J = 1.9 Hz, J = 8.5 Hz, 1H), 7.20-7.34 (m, 4H), 7.58 (d, J = 1.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 19.7, 56.1, 110.9, 113.8, 125.1, 126.8, 127.8, 129.8, 130.3, 130.8, 136.1, 139.1, 146.8, 150.7, 197.5. MS (70 eV): m/z (%) = 242 (91) $[M]^+$, 225 (62), 211 (82), 151 (67), 119 (37), 91 (100). HRMS for $C_{15}H_{14}O_3$ calculated 242.0943; found 242.0950.

(3-trifluoromethylphenyl)-2-thienylmethanone (entry 7):

Reaction of potassium 3-trifluoromethylphenyltrifluoroborate **2c** (1 mmol, 252 mg) and 2-thiophenecarboxaldehyde **1g** (0.5 mmol, 56 mg) afforded 106 mg of ketone as a colorless oil (yield 83%). GC (4 mL/min, 70°C during 1 min then 20°C/min up to 250°C): T_R 6.94 min. Rf (cyclohexane/ ethyl acetate 4/1): 0.34. 1H NMR ($CDCl_3$, 300 MHz) δ = 7.19 (dd, J = 3.9 Hz, J = 5.0 Hz, 1H), 7.61 (dd, J = 1.1 Hz, J = 5.0 Hz, 1H), 7.64 (t, J = 7.8 Hz, 1H), 7.77 (dd, J = 3.9 Hz, J = 1.1 Hz, 1H), 7.84 (dd, J = 0.5 Hz, J = 7.8 Hz, 1H), 8.03 (dd, J = 0.5 Hz, J = 7.8 Hz, 1H), 8.11 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 123.6 (q, J_{C-F} = 270.9 Hz), 125.9 (q, J_{C-F} = 3.7 Hz), 128.3, 128.67, 128.7, 129.1, 131.0 (q, J_{C-F} = 32.7 Hz), 132.2, 135.0 (q, J_{C-F} = 6.4 Hz), 138.8, 142.9, 186.7. MS (70 eV): m/z (%) = 256 (38) $[M]^+$, 173 (10), 145 (18), 111 (100). HRMS for $C_{12}H_7F_3OS$ calculated 256.0170; found 256.0174.

(3-bromophenyl)-2-furylmethanone (entry 6):

Reaction of potassium 3-bromophenyltrifluoroborate **2b** (1 mmol, 262 mg) and 2-furfural **1f** (0.5 mmol, 48 mg) afforded 114 mg of ketone as a pale yellow oil (yield 91%). GC (4 mL/min, 70°C during 1 min then 20°C/min up to 250°C): T_R 7.71 min. Rf (cyclohexane/ ethyl acetate 4/1): 0.27. 1H NMR ($CDCl_3$, 300 MHz) δ = 6.53 (dd, J = 3.6 Hz, J = 1.9 Hz, 1H), 7.15 (dd, J = 3.6 Hz, J = 0.8 Hz, 1H), 7.25 (dt, J = 0.4 Hz, J = 7.8 Hz, 1H), 7.57-7.61 (m, 2H), 7.79 (ddd, J = 1.2 Hz, J = 1.5 Hz, J = 7.8 Hz, 1H), 7.99 (dt, J = 0.8 Hz, J = 2.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 112.4, 120.9, 122.6, 127.8, 130.0, 132.2, 135.4, 138.9, 147.4, 151.9, 180.7. MS (70 eV): m/z (%) = 250 (2) $[M]^+$, 183 (15), 171 (13), 95 (100). HRMS for $C_{11}H_7BrO_2$ calculated 249.9629; found 249.9361.

All other products were identified by comparison of spectroscopic data with authentic sample or with those reported in the literature: diphenylmethanone [119-61-9], (4-methoxyphenyl)phenylmethanone [611-94-9], (2-methoxyphenyl)phenylmethanone [2553-04-0], (4-hydroxyphenyl)phenylmethanone [1137-42-4], (3-hydroxyphenyl)phenylmethanone [117-99-7], (4-fluorophenyl)phenylmethanone [345-83-5], 2-furylphenylmethanone⁵ and (4-hydroxyphenyl)-2,4,6-trimethylphenylmethanone⁶ and 1-(4-methoxyphenyl)propan-1-one.⁷

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