Supporting information

Palladium–Catalyzed Cross–Coupling Reactions of Triorganoindium Compounds with Vinyl and Aryl Triflates or Iodides

Ignacio Pérez, José Pérez Sestelo, and Luis A. Sarandeses*

Departamento de Química Fundamental e Industrial, Universidade da Coruña, E-15071 A Coruña, Spain.

General Considerations. All reactions were conducted in a flame-dried glassware under a positive pressure of argon. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were dried by distillation from the sodium ketyl of benzophenone. Thin layer chromatography was effected on silica gel 60 F_{254} (layer thickness 0.2 mm), and components were located by observation under UV light and/or by treatment of the plates with a phosphomolybdic acid reagent followed by heating. Flash chromatography was performed on silica gel 60 (230-400 mesh) by Still's method.[1]

Organoindium Reagents. A 25 mL round-bottomed flask with a stir bar was charged with $InCl_3$ (0.37 mmol) and dried under vacuum with a heat gun. After the mixture was cooled and a positive argon pressure was established, dry THF (4 mL) was added. The resulting solution was cooled to –78 °C, and a solution of RLi or RMgBr (1.1 mmol, 1.0–1.8 M in hexanes, THF, or Et_2O) was slowly added (15–30 min). After the mixture was stirred for 30 min, the cooling bath was removed, and the reaction mixture was warmed to room temperature.

Phenyllithium, *n*-butyllithium, methyllithium, and vinylmagnesium bromide were purchased from Aldrich and used after titration by known procedures.[2]

(2-Phenyl)ethynyllithium and 2-(trimethylsilyl)ethynyllithium were prepared from phenylacetylene and trimethylsilylacetylene, respectively: To a cold (–78 °C) solution of the previous cited acetylenes (1 mmol, freshly distilled) in dry THF (3 mL), was slowly added a commercial solution of *n*-BuLi in hexanes (1.05 mmol, 1.3 M). After the mixture was stirred for 10 min, the cooling bath was removed, the reaction mixture was warmed

---

(1) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

(2) Brown, H. C. *Organic Synthesis via Boranes*; Wiley: New York, 1975; p 248–249.

to room temperature, and used immediately for the preparation of the organoindium compounds.

Cyclopropyllithium was prepared from cyclopropyl bromide: A commercial solution of *t*-BuLi in pentane (1.8 mL, 3.1 mmol, 1.7 M) was diluted with dry Et_2O (3 mL) and cooled to –78 °C. To the resulting solution was added a solution of cyclopropyl bromide (0,18 mL, 1.5 mmol, freshly distilled) in dry Et_2O (3 mL). After the mixture was stirred for 15 min, the cooling bath was removed, the reaction mixture was warmed to room temperature, and used immediately for the preparation of the tricyclopropylindium.

General Procedure for the Cross–Coupling Reaction. A solution of R_3In (0.34 mmol, ca. 0.1 M in dry THF) was added to a refluxing mixture of the electrophile (1 mmol) and $Pd(Ph_3P)_2Cl_2$ (0.03 mmol) in dry THF (4 mL). The resulting mixture was refluxed under argon atmosphere until consumption of the starting material (0.5–7 h), and the reaction quenched by addition of few drops of MeOH. The mixture was concentrated in vacuo, and Et_2O (30 mL) was added. The organic phase was washed with aqueous HCl (5%, 10 mL), saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography to afford, after concentration and high-vacuum drying, the cross–coupling product in 82–97% yield.

Compounds Prepared. The products prepared are already known. Products **3a**, **3b**, **3e**, **3f**, **5a**, **5e**, and **5f** are commercial materials. Additional data are reported below.

4-Phenyltoluene (3a).[3] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.44 (s, 3 H), 7.27–7.66 (m, 9 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.1 (CH_3), 127.0 (CH), 127.2 (CH), 127.3 (CH), 128.8 (CH), 129.5 (CH), 137.0 (C), 138.4 (C), 141.2 (C). MS (EI) *m*/*z* (%) 168 (M^+, 100), 167 (M^+–1, 94), 153 (M^+–CH_3, 49).

4-Methylstyrene (3b).[4] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.37 (s, 3 H), 5.21 (d, *J* = 10.7 Hz, 1 H), 5.72 (d, *J* = 17.4 Hz, 1 H), 6.72 (dd, *J* = 17.7, 11.0 Hz, 1 H), 7.16 (d, *J* = 8.2 Hz, 2 H), 7.34 (d, *J* = 8.2 Hz, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.2 (CH_3), 112.8 (CH_2), 126.1 (CH), 129.2 (CH), 134.8 (C), 136.7 (CH), 137.6 (C). MS (EI) *m*/*z* (%) 118 (M^+, 73), 117 (M^+–1, 100), 103 (M^+–CH_3, 13).

---

(3) Available from Aldrich Chemical Co., Ref. P3,660-6.

(4) Available from Aldrich Chemical Co., Ref. M8,080-6.

4-((2-Phenyl)ethynyl)toluene (3c).[5] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.29 (s, 3 H), 7.17 (d, *J* = 7.9 Hz, 2 H), 7.33–7.57 (m, 7 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.5 (CH_3), 88.7 (C), 89.5 (C), 120.2 (C), 123.5 (C), 128.1 (CH), 128.3 (CH), 129.1 (CH), 131.5 (CH), 131.6 (CH), 138.4 (C). MS (EI) *m/z* (%) 192 (M, 100), 191 (M^+–1, 69).

1-(2-(Trimetylsilyl)ethynyl)toluene (3d).[6] ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.26 (s, 9 H), 2.35 (s, 3 H), 7.10 (d, *J* = 8.1 Hz, 2 H), 7.36 (d, *J* = 8.1 Hz, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.0 (CH_3), 21.5 (CH_3), 93.2 (C), 105.3 (C), 120.0 (C), 128.9 (CH), 131.8 (CH), 138.6 (C). MS (EI) *m/z* (%) 188 (M^+, 27), 173 (M^+–CH_3, 100), 115 (M^+–TMS, 6).

4-*n*-Butyltoluene (3e).[7] ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.3 Hz, 3 H), 1.32 (m, 2 H), 1.60 (m, 2 H), 2.34 (s, 3 H), 2.60 (t, *J* = 7.3 Hz, 2 H), 7.11 (s, 4 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0 (CH_3), 21.0 (CH_3), 22.4 (CH_2), 33.8 (CH_2), 35.2 (CH_2), 128.3 (CH), 128.9 (CH), 134.9 (C), 139.8 (C). MS (EI) *m/z* (%) 148 (M^+, 23), 105 (M^+–C_3H_7, 100).

***p*-Xylene (3f).**[8] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.34 (s, 6 H), 7.10 (s, 4 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.9 (CH_3), 128.9 (CH), 134.7 (C).

4-Cyclopropyltoluene (3g).[9] ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.64–0.73 (m, 2 H), 0.91–1.00 (m, 2 H), 1.83–1.94 (m, 1 H), 2.34 (s, 3 H), 7.00 (d, *J* = 8.2 Hz, 2 H), 7.10 (d, *J* = 8.2 Hz, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 8.9 (CH_2), 15.0 (CH), 20.9 (CH_3), 125.6 (CH), 128.9 (CH), 134.8 (C), 140.8 (C). MS (EI) *m/z* (%) 132 (M^+, 33), 117 (M^+–CH_3, 80), 91 (M^+–C_3H_5, 100).

4-Acetylbiphenyl (5a).[10] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.65 (s, 3 H), 7.47 (m, 3 H), 7.67 (m, 4 H), 8.05 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.7 (CH_3), 127.2 (CH), 127.3 (CH), 128.2 (CH), 128.9 (CH), 129.0 (CH), 135.8 (C), 139.9 (C), 145.8 (C), 197.8 (C). MS (EI) *m/z* (%) 196 (M^+, 68), 181 (M^+–CH_3, 100), 152 (M^+–Ac, 45).

---

(5) Okuro, K.; Furuune, M.; Enna, M.; Miura, M.; Nomura, M. *J. Org. Chem.* **1993**, *58*, 4716–4721.

(6) Takeuchi, R.; Yasue, H. *J. Org. Chem.* **1993**, *58*, 5386–5392.

(7) Available from Aldrich Chemical Co., Ref. B10,262-8.

(8) Available from Aldrich Chemical Co., Ref. 31,719-5.

(9) Schlosser, M.; Schneider, P. *Helv. Chim. Acta* **1980**, *63*, 2404–2410.

(10) Available from Aldrich Chemical Co., Ref. 12,272-6.

4'-Vinylacetophenone (5b).[11] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.60 (s, 3 H), 5.41 (d, *J* = 10.7 Hz, 1 H), 5.88 (d, *J* = 17.7 Hz, 1 H), 6.76 (dd, *J* = 17.5, 11.0 Hz, 1 H), 7.47 (d, *J* = 8.4 Hz, 2 H), 7.92 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.5 (CH_3), 116.7 (CH_2), 126.3 (CH), 128.7 (CH), 135.9 (CH), 136.3 (C), 142.0 (C), 197.5 (C). MS (EI) *m/z* (%) 146 (M^+, 44), 131 (M^+–CH_3, 100), 103 (M^+–Ac, 51).

4'-((2-Phenyl)ethynyl)acetophenone (5c).[12] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.63 (s, 3 H), 7.38 (m, 3 H), 7.55 (m, 2 H), 7.62 (d, *J* = 8.4 Hz, 2 H), 7.95 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.6 (CH_3), 88.6 (C), 92.7 (C), 122.6 (C), 128.2 (C), 128.3 (CH), 128.5 (CH), 128.8 (CH), 131.69 (CH), 131.73 (CH), 136.2 (C), 197.3 (C). MS (EI) m/z (%) 220 (M^+, 72), 205 (M^+–CH_3, 100)

4'-((2-Trimethylsilyil)ethynyl)acetophenone (5d).[13] ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.27 (s, 9 H), 2.60 (s, 3 H), 7.54 (d, *J* = 8.4 Hz, 2 H), 7.89 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ –0.2 (CH_3), 26.6 (CH_3), 98.1 (C), 104.0 (C), 127.9 (C), 128.1 (CH), 132.0 (CH), 136.3 (C), 197.3 (C). MS (EI) *m/z* (%) 216 (M^+, 23), 201 (M^+–CH_3, 100), 143 (M^+–TMS, 7).

4'-*n*-Butylacetophenone (5e).[14] ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.7 Hz, 3 H), 1.33 (m, 2 H), 1.61 (m, 2 H), 2.58 (s, 3 H), 2.66 (t, *J* = 7.7 Hz, 2 H), 7.26 (d, *J* = 8.4 Hz, 2 H), 7.87 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.9 (CH_3), 22.3 (CH_2), 26.5 (CH_3), 33.2 (CH_2), 35.7 (CH_2), 128.4 (CH), 128.6 (CH), 134.9 (C), 148.8 (C), 197.8 (C). MS (EI) *m/z* (%) 176 (M^+, 36), 161 (M^+–CH_3, 100).

4'-Methylacetophenone (5f).[15] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.41 (s, 3 H), 2.58 (s, 3 H), 7.25 (d, *J* = 8.2 Hz, 2 H), 7.85 (d, *J* = 8.2 Hz, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.6 (CH_3), 26.5 (CH_3), 128.4 (CH), 129.2 (CH), 134.7 (C), 143.9 (C), 197.9 (C). MS (EI) *m/z* (%) 134 (M^+, 42), 119 (M^+–CH_3, 100), 91 (M^+–Ac, 76).

4'-Cyclopropylacetophenone (5g).[16] ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.74–0.83 (m, 2 H), 1.02–1.11 (m, 2 H), 1.88–1.99 (m, 1 H), 2.57 (s, 3 H), 7.12 (d, *J* = 8.4 Hz, 2 H), 7.85 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 10.3 (CH_2), 15.7 (CH), 26.4 (CH_3), 125.4 (CH), 128.5 (CH), 134.6 (C), 150.3 (C), 197.6 (C). MS (EI) *m/z* (%)160 (M^+, 41), 145 (M^+–CH_3, 100), 117 (M^+–Ac, 13).

---

(11) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478–5486.

(12) Nomoto, T.; Tanaka, F.; Suzuki, N. *Chem. Express* **1991**, *6*, 319–322.

(13) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627–630.

(14) Available from Aldrich Chemical Co., Ref. 38,925-0.

(15) Available from Aldrich Chemical Co., Ref.M2,661-5.

(16) Hart, H.; Levit, G. *J. Org. Chem.* **1959**, *24*, 1261–1267.

4-*tert*-Butyl-1-cyclohexen-1-yl Trifluoromethanosulfonate (6).[17] ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (s, 9 H), 1.36 (m, 2 H), 1.95 (m, 2 H), 2.18 (m, 1 H), 2.30 (m, 2 H), 5.75 (br s, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.0 (CH_2), 25.3 (CH_2), 27.2 (CH_3), 28.5 (CH_2), 32.0 (C), 42.9 (CH), 118.4 (CH), 149.2 (C). MS (EI) *m*/*z* (%) 286 (M^+, 5).

1-Phenyl-4-*tert*-butyl-1-cyclohexene (7a).[12] ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95 (s, 9 H), 1.20–1.47 (m, 2 H), 1.90–2.09 (m, 2 H), 2.21–2.54 (m, 3 H), 6.15 (br s, 1 H), 7.30 (m, 5 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.4 (CH_2), 27.2 (CH_3), 27.5 (CH_2), 28.8 (CH_2), 32.2 (C), 43.8 (CH), 124.9 (CH), 126.5 (CH), 128.2 (CH), 136.3 (C), 142.3 (C). MS (EI) *m*/*z* (%) 214 (M^+, 39), 157 (M^+–*t*-Bu, 26).

1-Vinyl-4-*tert*-Butyl-1-cyclohexene (7b).[12] ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (s, 9 H), 1.07–1.55 (m, 2 H), 1.84–2.40 (m, 5 H), 4.91 (d, *J* = 10.7 Hz, 1 H), 5.06 (d, *J* = 17.5 Hz, 1 H), 5.77 (br s, 1 H), 6.37 (dd, *J* = 17.7, 10.7 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.7 (CH_2), 25.1 (CH_2), 27.2 (CH_3), 27.4 (CH_2), 32.2 (C), 44.3 (CH), 109.8 (CH_2), 130.0 (CH), 135.9 (C), 139.7 (CH). MS (EI) *m*/*z* (%) 164 (M^+, 25), 107 (M^+–*t*-Bu, 33).

1-((2-Phenyl)ethynyl)-4-*tert*-butyl-1-cyclohexene (7c).[18] ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (s, 9 H), 1.18–1.33 (m, 2 H), 1.86–1.98 (m, 2 H), 2.11–2.21 (m, 1 H), 2.26–2.30 (m, 2 H), 6.22 (br s, 1 H), 7.28–7.33 (m, 3 H), 7.41–7.46 (m, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.8 (CH_2), 27.1 (CH_3), 27.5 (CH_2), 30.7 (CH_2), 32.2 (C), 43.2 (CH), 87.0 (C), 91.0 (C), 120.5 (C), 123.7 (C), 127.7 (CH), 128.2 (CH), 131.4 (CH), 135.5 (CH). MS (EI) *m*/*z* (%) 238 (M^+, 81), 223 (M^+– CH_3, 21), 181 (M^+–*t*-Bu, 52).

1-(2-(Trimetylsilyl)ethynyl)-4-*tert*-butyl-1-cyclohexene (7d).[12] ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.18 (s, 9 H), 0.86 (s, 9 H), 1.10–1.25 (m, 2 H), 1.77–1.93 (m, 2 H), 2.07–2.16 (m, 1 H), 2.17–2.23 (m, 2 H), 6.19 (br s, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.1 (CH_3), 23.7 (CH_2), 27.1 (CH_3), 27.4 (CH_2), 30.6 (CH_2), 32.2 (C), 43.1 (CH), 91.0 (C), 107.0 (C), 120.5 (C), 136.6 (CH). MS (EI) *m*/*z* (%) 234 (M^+, 23), 219 (M^+–CH_3, 50), 161 (M^+–TMS, 21).

1-*n*-Butyl-4-*tert*-butyl-1-cyclohexene (7e).[12] ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (s, 9 H), 0.90–0.94 (m, 2 H), 1.15-1.44 (m, 6 H), 1.70–2.05 (m, 8 H), 5.40 (br s, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0 (CH_3), 22.5 (CH_2), 24.3 (CH_2), 26.8

---

(17) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033–3040.

(18) Scott, W. J.; Peña, M. R.; Swärd, K.; Stoessel, S. J.; Stille, J. K. *J. Org. Chem.* **1985**, *50*, 2302–2308.

(CH_2), 27.2 (CH_3), 29.8 (CH_2), 30.0 (CH_2), 32.2 (C), 37.2 (CH_2), 44.2 (CH), 120.7 (CH), 137.9 (C). MS (EI) *m*/*z* (%) 194 (M^+, 17), 137 (M^+–*t*-Bu, 13).

1-Methyl-4-*tert*-butyl-1-cyclohexene (7f).[12] ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (s, 9 H), 1.18–1.24 (m, 2 H), 1.65 (s, 3 H), 1.77–1.84 (m, 2 H), 1.95–1.99 (m, 3 H), 5.39 (br s, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.3 (CH), 24.2 (CH_2), 26.8 (CH_2), 27.2 (CH_3), 31.5 (CH_2), 32.2 (C), 44.0 (CH_3), 121.3 (CH), 133.9 (C). MS (EI) *m*/*z* (%) 152 (M^+, 4), 151 (M^+–1, 30), 95 (M^+–*t*-Bu, 100).

1-Cyclopropyl-4-*tert*-Butyl-1-cyclohexene (7g).[19] ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.36–0.55 (m, 4 H), 0.86 (s, 9 H), 1.13–1.54 (m, 3 H), 1.79–2.05 (m, 5 H), 5.44 (br s, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 3.6 (CH_2), 4.5 (CH_2), 16.9 (CH), 24.1 (CH_2), 26.7 (CH_2), 27.2 (CH_3), 27.7 (CH_2), 32.2 (C), 44.4 (CH), 119.8 (CH), 138.0 (C). MS (EI) *m*/*z* (%) 178 (M^+, 14), 121 (M^+–*t*-Bu, 34).

---

(19) McMurry, J. E.; Scott, W. J. *Tetrahedron Lett.* **1980**, *21*, 4313–4316.