Aryl- and Alkenyllithium Preparations and Copper-catalyzed Reaction between the Derived Magnesium Reagents and Monoacetate of 4-Cyclopentene-1,3-diol

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Compatibility of the Preparations of RLi

☐ Ar-X + Li	☐ Ar-SnBu ₃ + <i>n</i> -BuLi
☐ Ar-X + <i>n</i> -BuLi	☐ Ar-H + <i>n</i> -BuLi
☐ Ar-X + <i>t</i> -BuLi	

Typical procedures: p. 2–4

¹H NMR spectra of **2a**, **2b**, **2c**, **2d**, **2e**, **2f**, and ¹³C NMR spectrum of **2b**: p. 5-11

General:

Identity and purity of the products **2a**, **2c–f** were confirmed by comparison with the spectral data reported (Kobayashi, Y.; Muruges, M. G.; Nakano, M.; Takahisa, E.; Usmani, S. B.; Aina, T., *J. Org. Chem.*, **2002**, 67, 7110–7123), and those for **2b** were established by ^1H NMR and ^{13}C NMR spectra.

Phenylation with PhMgCl Derived from Pure PhLi :

To a mixture of Mg (29.2 mg, 1.20 mmol) and THF (0.5 mL) was added 1,2-dichloroethane (0.28 mL, 3.55 mmol) at room temperature under argon atmosphere. After being stirred at room temperature for 30 min, the mixture was diluted with THF (0.5 mL) and was stirred at the same temperature for 30 min to dissolve Mg completely. The resulting suspension was diluted with THF (1.5 mL) to prepare a clear solution and cooled to $0\text{ }^\circ\text{C}$. To the mixture were added PhLi (0.96 mL, 0.94 M in cyclohexane- Et_2O (2 : 1), 0.90 mmol), CuCN (8.1 mg, 0.09 mmol), and a solution of monoacetate **1** (42.3 mg, 0.30 mmol) in THF (1 mL), each after 15 min interval. The mixture was stirred for 1 h at the same temperature and then diluted with saturated NH_4Cl to quench the reaction. After extraction with EtOAc four times, combined extracts were dried over MgSO_4 and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane/ EtOAc = 4 : 1 to 1 : 1) to afford 4-phenyl-2-cyclopenten-1-ol (**2a**) (35.6 mg, 75%). The ^1H NMR spectrum of **2a** thus synthesized was identical with that previously reported (Tueting, D. R.; Echavarren, A. M., Stille, J. K. *Tetrahedron* **1989**, 45, 979–992) and a copy of the spectrum was attached to this supporting information.

Lithiation of Iodobenzene by $t\text{-BuLi}$ and Subsequent Phenylation with the Derived PhMgCl :

To a solution of PhI (0.101 mL, 0.90 mmol) in THF (1 mL) was added *t*-BuLi (1.26 mL, 1.43 M in pentane, 1.80 mmol) slowly at -78 °C. After 30 min at -78 °C, a solution of MgCl₂ (2.50 mL, 0.48 M in THF, 1.20 mmol) was added to the solution dropwise. The cooling bath (-78 °C) was changed to an ice-water bath, and stirring was continued for 20 min. To the resulting solution were added CuCN (8.1 mg, 0.09 mmol) and, after 15 min, **1** (42.6 mg, 0.30 mmol) in THF (1 mL). The whole mixture was stirred at the same temperature for 1 h, and diluted with saturated NH₄Cl with vigorous stirring. The products were extracted with EtOAc four times, and the combined layers were dried over MgSO₄. After concentration under reduced pressure, the residue was subjected to silica gel chromatography (hexane/EtOAc = 9 : 1 to 4 : 1) to give **2a** (43.7 mg, 91%).

Lithiation of Tributylstannylbenzene by *n*-BuLi and Subsequent Phenylation with the Derived PhMgCl:

To an ice-cold solution of PhSnBu₃ (397 mg, 1.08 mmol) in THF (1 mL) was added *n*-BuLi (0.74 mL, 1.45 M in hexane, 1.07 mmol) slowly, and the solution was stirred for 30 min at 0 °C. To the solution were added MgCl₂ (2.50 mL, 0.48 M in THF, 1.20 mmol), CuCN (8.1 mg, 0.09 mmol), and a solution of **1** (42.6 mg, 0.30 mmol) in THF (1 mL), each after 15 min interval. The resulting mixture was stirred at room temperature for 2 h, and diluted with saturated NH₄Cl with vigorous stirring. The products were extracted with EtOAc four times, and the combined layers were dried over MgSO₄. After concentration under reduced pressure, the residue was subjected to silica gel chromatography (hexane/EtOAc = 4 : 1 to

1 : 1) to give **2a** (35.6 mg, 74%).

Direct Lithiation of Methoxymethylbenzene by *n*-BuLi and Subsequent Reaction with the Derived Magnesium Reagent:

To an ice-cold solution of methoxymethyl phenyl ether (124 mg, 0.90 mmol) in THF (1 mL) was added *n*-BuLi (0.53 mL, 1.71 M in hexane, 0.91 mmol) slowly, and the solution was stirred for 30 min. To the solution were added MgCl_2 (2.50 mL, 0.48 M in THF, 1.20 mmol), CuCN (8.1 mg, 0.09 mmol), and a solution of **1** (42.6 mg, 0.30 mmol) in THF (1 mL), each after 15 min interval. The resulting mixture was stirred at the same temperature for 1 h, and diluted with saturated NH_4Cl with vigorous stirring. The products were extracted with EtOAc four times. The combined layers were dried over MgSO_4 and evaporated under reduced pressure to give an oil, which was purified by silica gel chromatography (hexane/EtOAc = 9 : 1 to 1 : 1) to afford **2b** (54.2 mg, 82%): IR (neat) 3348, 1078, 755 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.68 (br s, 1 H), 2.04 (ddd, J = 14, 7, 5.5 Hz, 1 H), 2.32 (ddd, J = 14, 8, 3 Hz, 1 H), 3.49 (s, 3 H), 4.54 (t, J = 6 Hz, 1 H), 5.01 (d, J = 6 Hz, 1 H), 5.21 (s, 2 H), 6.02–6.08 (m, 2 H), 6.93 (dt, J = 1, 7.5 Hz, 1 H), 7.03 (dd, J = 7.5, 2 Hz, 1 H), 7.06 (dd, J = 8, 1 Hz, 1 H), 7.16 (dt, J = 2, 8 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 42.7, 43.2, 56.1, 77.5, 94.4, 113.9, 121.8, 126.8, 127.4, 133.8, 134.2, 138.5, 154.7.

¹H NMR (300 MHz, CDCl₃)

¹H NMR (300 MHz, CDCl₃)

2b

¹³C NMR (75 MHz, CDCl₃)

^1H NMR (300 MHz, CDCl_3)

2c

¹H NMR (300 MHz, CDCl₃)

^1H NMR (300 MHz, CDCl_3)

2e

CC(C)(C)/C=C/[C@H]1C=CC[C@@H]1O