Supporting Information for Highly Alkyl-Selective Addition to Ketones with Magnesium Ate Complexes Derived from Grignard Reagents

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General Methods. Infrared (IR) spectra were recorded on a JASCO FT/IR 460 plus spectrometer. ^1H NMR spectra were measured on a Varian Gemini-2000 spectrometer (300 MHz) at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the TM scale, multiplicity (s=singlet; d=doublet; t=triplet; m=multiplet), coupling constant (Hz), integration, and assignment. ^{13}C NMR spectra were measured on Varian Gemini-2000 (75 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuteriochloroform at 77.00 ppm). Low-resolution mass analysis (LRMS) and GC analysis were performed with a Shimadzu GC/MS instrument [GC-17A/QP-5050A; column: TC-1 (0.25 mm x 30 m)] by direct insertion for chemical ionization (CI) with isobutane.

All experiments were carried out under an atmosphere of dry nitrogen. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60GF254 0.25 mm) were used. The products were purified by column chromatography on silica gel (E. Merck Art. 9385). Visualization was accomplished by UV light (254 nm), anisaldehyde, KMnO_4 and phosphomolybdic acid.

In experiments that required dry solvents, diethyl ether (dehydrate), toluene (dehydrate), dichloromethane (dehydrate), tetrahydrofuran (dehydrate) and hexane (dehydrate) were purchased from Kanto Chemical Co., Inc. MeLi (0.98 M in diethylether, Kanto Chemical Co., Inc.; 1.60 M in diethylether, Acros or Kanto Chemical Co., Inc.). *n*-BuLi (1.60 M in *n*-hexane, Kanto Chemical Co., Inc.). *n*-BuMgCl (0.90 M in THF, Kanto Chemical Co., Inc.). *t*-BuLi (1.48 M in pentane, Kanto Chemical Co., Inc.). EtMgBr (0.96 M in THF, Kanto Chemical Co., Inc.). *i*-PrMgBr (0.65 M in THF, Kanto Chemical Co., Inc.). *n*-PrMgBr (1.04 M in THF, Kanto Chemical Co., Inc.). *n*-Bu₂Mg (1.00 M in heptane, Aldrich). PhLi (1.05 M in cyclohexane-diethylether, Kanto Chemical Co., Inc.). PhMgBr (1.02 M in THF, Kanto Chemical Co., Inc.)

Representative procedure: For addition to acetophenone **5 by *n*-Bu₃MgLi/Bpy reagents (Table 2).**

To a solution of 2,2'-bipyridyl in 1.5 mL of THF was added *n*-Bu₂Mg (1.06 mmol, 1.0 *M* in *n*-heptane solution) and *n*-BuLi (1.0 mmol, 1.60 *M* in *n*-hexane solution) at – 78 °C under nitrogen atmosphere. This suspension was stirred at that temperature for 1 h. Then acetophenone **5** (1.0 mmol) in 1.5 mL of THF was added. The mixture was stirred at – 78 °C for 5 h, quenched by saturated aqueous NH₄Cl (10 mL), extracted with ether (10 mL^[3]) and washed by brine (10 mL). The combined organic layer was evaporated *in vacuo* and the residue was purified by short column chromatography (hexane/AcOEt = 5/1) to afford **8** in 96% yield.

Representative procedure: For ethylation to acetophenone **5 by EtMe₂MgLi reagents (Table 5).**

To 1.5 mL of THF was added MeLi (2.0 mmol, 1.60 *M* in diethylether solution) and EtMgBr (1.2 mmol, 0.98 *M* in THF solution) at – 78 °C under nitrogen atmosphere. This solution was stirred at that temperature for 1 h. Then acetophenone **5** (1.0 mmol) in 1.5 mL of THF was added. The mixture was stirred at – 78 °C for 5 h, quenched by saturated aqueous NH₄Cl (10 mL), extracted with ether (10 mL^[3]) and washed by brine (10 mL). The combined organic layer was evaporated *in vacuo* and the residue was purified by short column chromatography (hexane/AcOEt = 5/1) to afford the product **11** in 93% yield.

2-phenyl-2-hexanol (**2**, Table 1)^{1,2,3}
 3-hydroxy-1,3-diphenyl-1-butanone (**3**, Table 1)^{4,5}
 3-phenyl-3-heptanol (**6**, Table 2, entry 2)³
 2-methyl-3-phenyl-3-heptanol (**6**, Table 2, entry 3)⁶
 1,1-diphenylpentan-1-ol (**6**, Table 2, entry 6)^{3,7}
 1-butyl-1,2,3,4-tetrahydro-1-naphthol (**6**, Table 2, entry 7)⁸
 1,1-dicyclohexyl-1-pentanol (**6**, Table 2, entry 8)⁹
 1,1-diphenyl-1-pentanol (**9**, Table 3, entry 1; Table 6, entry 4)³
 triphenylmethanol (**9**, Table 3, entry 2)^{10,11}
 1,1-diphenylethanol (**9**, Table 3, entry 3; **10**, Table 4 entries 2 and 4; **15**, Table 6)^{10,12,13}
 1,1-diphenyl-1-propanol (**9**, Table 3, entry 4; Table 6, entry 1; **11**, Table 5, entry 7)^{10,14}
 2-phenyl-2-propanol (**10**, Table 4, entries 1 and 3; **13**, Table 5, entry 1)^{1,15,16,17}
 3,3-dimethyl-2-phenyl-2-butanol (**10**, Table 4, entry 5; **13**, Table 5, entry 4)^{18,19,20,21}
 2-phenyl-2-butanol (**11**, Table 5, entry 1; **13**, Table 5, entry 2)^{1,2}
 3-phenyl-3-pentanol (**11**, Table 5, entry 2)²²
 2-methyl-3-phenyl-3-pentanol (**11**, Table 5, entry 3)²³
 2,2-dimethyl-3-phenyl-3-pentanol (**11**, Table 5, entry 4)²⁴
 2-(1-naphthyl)-2-butanol (**11**, Table 5, entry 5)²⁵
 2-(2-naphthyl)-2-butanol (**11**, Table 5, entry 6)²⁶
 1-ethyl-1,2,3,4-tetrahydro-1-naphthol (**11**, Table 5, entry 8)²⁷
 2-(3-pyridinyl)-2-butanol (**11**, Table 5, entry 9)²⁷
 2-(4-pyridinyl)-2-butanol (**11**, Table 5, entry 10)²⁷
 1-(3-pyridinyl)ethanol (**12**, Table 5, entry 9)²⁸
 3-methyl-2-phenyl-2-butanol (**13**, Table 5, entry 3)¹⁸
 2-(1-naphthyl)-2-propanol (**13**, Table 5, entry 5)²⁹
 2-(2-naphthyl)-2-propanol (**13**, Table 5, entry 6)³⁰
 1-methyl-1,2,3,4-tetrahydro-1-naphthol (**13**, Table 5, entry 8)^{31,32,33}
 2-(3-pyridinyl)-2-propanol (**13**, Table 5, entry 9)³⁴
 2-(4-pyridinyl)-2-propanol (**13**, Table 5, entry 10)³⁴
 2-(1-naphthyl)-2-propanol (**13**, Table 5, entry 5)²⁶
 2-methyl-1,1-diphenyl-1-propanol (**9**, Table 6, entry 2)¹⁰
 1,1-diphenyl-1-butanol (**9**, Table 6, entry 3)³⁵
4 and **12** are commercially available from Aldrich.

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