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Supporting Information

General. All reactions were run under an atmosphere of nitrogen at room temperature. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-EX-90 or JNM-EX-400 spectrometers. All ^1H NMR spectra are reported in δ units, parts per million (ppm) downfield from tetramethylsilane. ^{13}C NMR spectra are reported in ppm relative to deuteriochloroform. Melting points were measured using a Yanaco micro melting point apparatus. Flash chromatography was performed on Wakogel C-200 (100-200 mesh).

Tetrahydrofuran (THF) was distilled under nitrogen from sodium-benzophenone prior to use. A solution of SmI_2 in THF was prepared according to the Kagan's report.¹ Chlorotrimethylsilane (TMSCl) was distilled under nitrogen from CaH_2 . Magnesium turnings was purchased from Nacalai tesque and used without purification. Benzaldehyde, hydrocinnamaldehyde, benzylacetone, *p*-anisaldehyde, acetophenone, and 4-methoxyacetophenone were distilled from CaH_2 under reduced pressure. Methyl 4-formylbenzoate, 4-cyanobenzaldehyde, and 4-(dimethylamino)benzaldehyde were used without purification. 1,5-diphenyl-1,5-pentanedione was prepared by a procedure similar to that of 1,4-dibenzoylbutane²; ^1H NMR (400 MHz, CDCl_3) δ 2.10 - 2.24 (m, 2H), 2.85 - 3.26 (m, 4H), 7.35 - 7.66 (m, 6H), 7.88 - 8.20 (m, 4H); mp 66 - 67.5 °C (Lit.³ 65 °C).

Pinacol coupling of benzaldehyde. A test tube is charged with 400 mg of magnesium turnings. After a vigorous stirring for 1 hr under nitrogen to activate magnesium turnings, a 0.1 M solution of SmI_2 in dry THF (2 mL) and 1 mmol of TMSCl was added to the test tube at rt. Into the mixture was added dropwise a mixture of benzaldehyde (2 mmol) and TMSCl (2 mmol) at the rate to remain the blue color of SmI_2 (ca. 2h). After the complete consumption of benzaldehyde (ca. several min after the addition was completed), the mixture was acidified with 1N HCl (ca. 20 mL). The mixture was extracted with ether, and the ether layer was washed by brine, dried over MgSO_4 , and concentrated. The purification of the crude product by a SiO_2 column chromatography (eluent; hexane-ethyl acetate) gave the mixture (*dl* and *meso*) of the

pinacol. The reactions of hydrocinnamaldehyde, *p*-anisaldehyde, acetophenone, and 4-methoxyacetophenone were carried out by the same way.

Pinacol coupling of methyl 4-formylbenzoate. Into a mixture of a 0.1 M solution of SmI_2 in dry THF (2 mL), 1 mmol of TMSCl and 400 mg of activated magnesium was added a solution of methyl 4-formylbenzoate (2 mmol) and TMSCl (2 mmol) in THF (3 mL) in one portion at rt. After the 24 h stirring at rt, the mixture was acidified by 1N HCl . The mixture was extracted with ether, and the ether layer was washed by brine, dried over MgSO_4 , and concentrated. The purification of the crude product by a SiO_2 column chromatography (eluent; hexane-ethyl acetate) gave the pinacol. The reactions of 1,5-diphenyl-1,5-pentanedione and 4-cyanobenzaldehyde was carried out in the same way. In the case of 4-(dimethylamino)benzaldehyde, the reaction mixture was extracted with ether after quenching by saturated NaHCO_3 solution. The reaction of 1,5-diphenyl-1,5-pentanedione gave a single isomer (meso) of the pinacol.

Spectra data of the pinacol from 1,5-diphenyl-1,5-pentanedione were as follows; ^1H NMR (400 MHz, CDCl_3) δ 1.83 - 2.36 (m, 4H), 2.45 - 2.60 (m, 2H), 3.43 (brs, 2H), 6.83 - 7.21 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.0, 36.9, 85.6, 126.2, 126.8, 127.1, 142.5; mp 105 - 105.5 °C (Lit.⁴ 106 °C).

Pinacol coupling of benzylacetone. Into a mixture of a 0.1 M solution of SmI_2 in dry THF (2 mL), 1 mmol of TMSCl and 400 mg of magnesium metal which was activated by a vigorous stirring for 1 hour was added a mixture of benzylacetone (2 mmol) and TMSCl (2 mmol) in one portion. After 48 h stirring at rt, the mixture was acidified by 1N HCl . The mixture was extracted with ether, and the ether layer was washed by brine, dried over MgSO_4 , and concentrated. SiO_2 column chromatography (eluent; hexane-ethyl acetate) gave the diastereo-mixture of the pinacol.

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