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Supplementary Materials for

Highly Diastereoselective Pinacol Coupling of Aliphatic Secondary Aldehydes Induced by a Catalytic System Consisting of Vanadium Complex, Chlorosilane, and Zinc Metal

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General Comments.

^1H NMR spectra were recorded on JEOL JNM-GSX-400 (400 MHz), Varian INOVA 600 (600 MHz), and Varian Mercury 300 (300 MHz) spectrometers using CDCl_3 as the solvent. ^{13}C NMR spectra were taken on JEOL JNM-GSX-400 (100 MHz), Varian INOVA 600 (150 MHz), and Varian Mercury 300 (75 MHz) spectrometers using CDCl_3 as the solvent. IR spectra were determined on Perkin Elmer Model 1600 spectrometer. Melting points were determined on Yanagimoto micro melting point apparatus. Mass spectra were obtained on JEOL JMS-DX303 or Varian Saturn 3. Elemental analyses were performed in the analytical section of our department. Capillary gas layer chromatography (CGLC) analysis was carried out on Shimadzu GC8APF. Isolation was carried out by recycling preparative HPLC (Japan Analytical Industry, Model LC-908, JAIGEL-1H and-2H (GPC), length 600 mm, i.d. 20 mm, eluent CHCl_3). Zn powder (Aldrich) was activated by 1.5 N HCl, washed with EtOH, and dried over *in vacuo*. All substrates were obtained from commercial supplies. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were distilled from sodium benzophenone ketyl under dry argon. Chlorosilanes were purified by distillation according to the conventional procedure.

A Representative Procedure for the Coupling Reaction of Carbonyl Compounds.

To a suspension of vanadium catalyst (15.1 mg, 0.06 mmol) in THF (7 mL) was added Zn powder (261.6 mg, 4.0 mmol) and then chlorotrimethylsilane (434.6 mg, 4.0 mmol) under argon.

After 2-ethylbutanal (**1a**, 200.3 mg, 2.0 mmol) was added to the resulting suspension, the mixture was stirred at room temperature for 13 h. Ether (ca. 10 mL) was added to the resulting mixture, which was filtered, washed with brine, dried over MgSO_4 , and concentrated. Recrystallization of the obtained yellow solid from hexane gave **2a** as a colorless crystal (182.1 mg, 0.90 mmol, 90%). The ratio of the diastereomers was determined by ^1H NMR of crude products. The stereochemistry of the 1,2-diol (**2a**) was determined by the acetalization of **2a** to give the corresponding 1,3-dioxolane (**3a**), the stereochemistry of which had already been determined clearly in the literature.¹ For example, the acetalization of the stereoisomeric mixture (92/8) of 1,2-diol (**2a**) using *p*-toluenesulfonic acid monohydrate provided the stereoisomeric mixture of 1,3-dioxolane (**3a**, *dl*/*meso*=91/9). The result indicated that the major stereoisomer was *dl*-**2a**. In the case of the coupling products **2d** and **2e**, the ratio of the diastereomers was determined by CGLC.

A Representative Procedure for Intramolecular Pinacol Coupling Reaction.

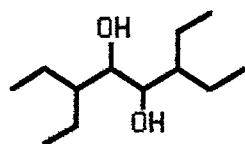
To a suspension of vanadium catalyst (47.9 mg, 0.19 mmol) in DME (10 mL) was added Zn powder (503.5 mg, 7.5 mmol) and then chlorotrimethylsilane (836.5 mg, 7.7 mmol) under argon. After 1,3-dibenzoylpropane (**1k**, 479.4 mg, 1.9 mmol) was added to the resulting suspension, the mixture was stirred at 50 °C for 24 h. Workup was carried out similarly as mentioned above. The ratio of the diastereomers was determined by ^{13}C NMR (150MHz) of crude products. During the purification by GPC, the silylated intramolecular pinacol coupling product (**4**) underwent desilylation to give the corresponding 1,2-diol as the single isomer. The 1,2-diol (mp 105 °C) was identified with the *dl*-isomer in comparison with the literature's analytical data (eg., lit. 104-105 °C, cf. 109-110 °C for the *meso*-isomer).²

A Representative Procedure for Intramolecular Cyclization of Olefinic Aldehyde.

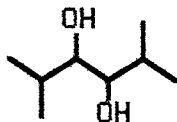
To a suspension of vanadium catalyst (47.9 mg, 0.19 mmol) in THF (10 mL) was added Zn powder (659.8 mg, 10.1 mmol) and then chlorotrimethylsilane (1095.1 mg, 10.1 mmol) under argon. After 2,6-dimethyl-5-heptenal (**1l**, 706.8 mg, 5.0 mmol) was added to the resulting suspension, the mixture was stirred at -20 °C for 24 h. Workup was carried out similarly as

mentioned above. The resulting yellow oil was purified by GPC to give 2-(1-chloro-1-methylethyl)-5-methyl-1-cyclopentanol (**5**, 752.6 mg, 84%) as pale yellow oil. The stereochemistry of the cyclized product was determined by the NOE experiments.

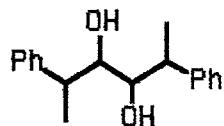
Spectral and Analytical Data



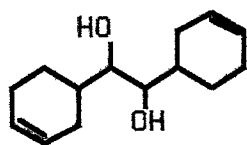
dl-3,6-Diethyl-4,5-octanediol (**2a**). Colorless solid; mp 88-89 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.08 (t, $J = 7.0$ Hz, 12 H), 1.45-1.70 (m, 10 H), 2.68 (br s, 2 H), 3.78 (br d, $J = 1.8$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 11.45, 11.61, 20.76, 22.28, 43.17, 72.88; IR (KBr) 3294, 2953, 1028 cm^{-1} ; MS (EI) $m/z = 202$ (M^+); Anal. Calcd for $\text{C}_{12}\text{H}_{26}\text{O}_2$: C, 71.23; H, 12.95. Found: C, 70.81; H, 12.74.



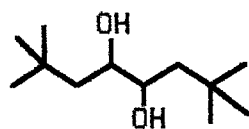
dl-2,5-Dimethyl-3,4-hexanediol (**2b**). Colorless solid (obtained as a single isomer); mp 114-115 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.96 (d, $J = 6.6$ Hz, 6 H), 0.97 (d, $J = 7.0$ Hz, 6 H), 1.81 (m, 2 H), 1.89 (br s, 2 H) 3.31 (br d, $J = 4.2$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.47, 19.52, 30.60, 76.41, 77.23; IR (KBr) 3338, 2963, 1000 cm^{-1} ; MS (EI) $m/z = 146$ (M^+); Anal. Calcd for $\text{C}_8\text{H}_{18}\text{O}_2$: C, 65.71; H 12.41. Found: C, 65.66; H, 12.37.



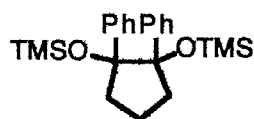
dl-2,5-Diphenyl-3,4-hexanediol (2d). Colorless solid (obtained as a stereoisomeric mixture (isomer A / isomer B = 60 / 40)); mp 114-115 °C; ^1H NMR (400 MHz, CDCl_3) [isomer A]: δ 1.17 (d, $J = 7.0$ Hz, 6 H), 1.40 (d, $J = 7.0$ Hz, 6 H), 1.99 (br d, $J = 8.8$ Hz, 4 H), 2.98 (m, 4 H), 3.33 (br d, $J = 8.1$ Hz, 2 H), 3.73 (m, 2 H), 7.13-7.33 (m, 20 H) [isomer B]: δ 1.24 (d, $J = 8.1$ Hz, 6 H), 1.93 (br d, $J = 5.1$ Hz, 2 H), 2.90 (dq, $J = 8.3, 8.1$ Hz, 2 H), 3.36 (dd, $J = 5.1, 8.3$ Hz, 2 H), 6.98 (dd, $J = 8.2, 1.8$ Hz, 4 H), 7.19-7.28 (m, 6 H); ^{13}C NMR (100 MHz, CDCl_3) [isomer A]: δ 18.09, 18.43, 42.87, 43.49, 74.67, 75.65, 126.44, 126.91, 127.67, 128.06, 128.63, 128.79, 143.40, 144.47 [isomer B]: δ 18.39, 43.30, 74.90, 126.47, 127.65, 128.58, 144.10; IR (KBr) 3697, 3545, 3025, 2954, 1696, 1009 cm^{-1} ; MS (EI) $m/z = 270$ (M^+); Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_2$: C, 79.96; H 8.20. Found: C, 79.61; H, 7.98.



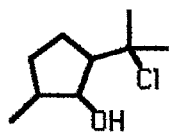
1,2-Di(3-cyclohexenyl)-1,2-ethanediol (2e). Colorless solid (obtained as a stereoisomeric mixture); mp 120-121 °C; ^1H NMR (400 MHz, CDCl_3) [stereoisomeric mixture] δ 1.31-2.20 (m, 16 H), 3.39-3.54 (m, 2 H), 5.65-5.73 (m, 4 H); ^{13}C NMR (100 MHz, CDCl_3) δ 24.20, 24.68, 24.95, 25.03, 25.07, 25.15, 25.51, 25.85, 26.37, 27.06, 28.20, 28.36, 36.11, 36.34, 36.48, 74.39, 74.53, 74.62, 74.96, 76.70, 77.02, 77.34, 125.71, 125.86, 126.22, 126.25, 126.87, 126.91, 127.35, 127.42; IR (KBr) 3307, 3022, 2912, 1419, 1067 cm^{-1} ; MS (EI) $m/z = 222$ (M^+); HRMS (CI, CH_4) Calcd for $\text{C}_{14}\text{H}_{22}\text{O}_2$: 222.1619. Found: 222.1612



2,2,7,7-Tetramethyl-4,5-octanediol (2i). Colorless solid (obtained as a stereoisomeric mixture (*dl meso* = 86/14)); mp 120-121 °C; ¹H NMR (400 MHz, CDCl₃) [*dl*-isomer]: δ 0.99 (s, 18 H), 1.26-1.42 (m, 4 H), 1.98 (br s, 2 H), 3.46 (br d, *J* = 5.5 Hz, 2 H). [*meso*-isomer]: δ 0.99 (s, 18 H), 1.26-1.45 (m, 4 H), 1.98 (br s, 2 H), 3.67 (br s, 2 H); ¹³C NMR (100 MHz, CDCl₃) [*dl*-isomer]: δ 30.12, 30.20, 47.51, 73.14. [*meso*-isomer]: 30.07, 30.20, 45.27, 73.61; IR(KBr) 3680, 2949, 1065 cm⁻¹; MS (EI) *m/z* = 202 (M⁺); Anal. Calcd for C₁₂H₂₆O₂: C, 71.23; H 12.95. Found: C, 70.93; H, 12.80.



1,2-Diphenyl-1,2-bis(trimethylsilyloxy)cyclopentane (4). Brown solid (obtained as a stereoisomeric mixture (*dl meso* = 90/10)); mp 101-102 °C; ¹H NMR (300 MHz, CDCl₃) [*dl*-isomer] δ 0.06 (s, 18 H), 2.01-2.13 (m, 1 H), 2.13-2.23 (m, 2 H), 2.28-2.52 (m, 1 H), 2.52-2.60 (m, 2 H), 7.01-7.15 (m, 10 H). [*meso*-isomer] δ 0.15 (s, 18 H), 2.01-2.13 (m, 1 H), 2.13-2.23 (m, 2 H), 2.28-2.52 (m, 1 H), 2.52-2.60 (m, 2 H), 7.01-7.15 (m, 10 H); ¹³C NMR (75 MHz, CDCl₃) [*dl*-isomer] δ 2.02, 20.06, 36.89, 85.52, 126.12, 126.64, 126.97, 142.35. [*meso*-isomer] δ 1.11, 18.73, 33.84, 87.77, 126.36, 126.46, 126.81, 144.03; MS (EI) *m/z* = 308 (M⁺-CH₃, 6).

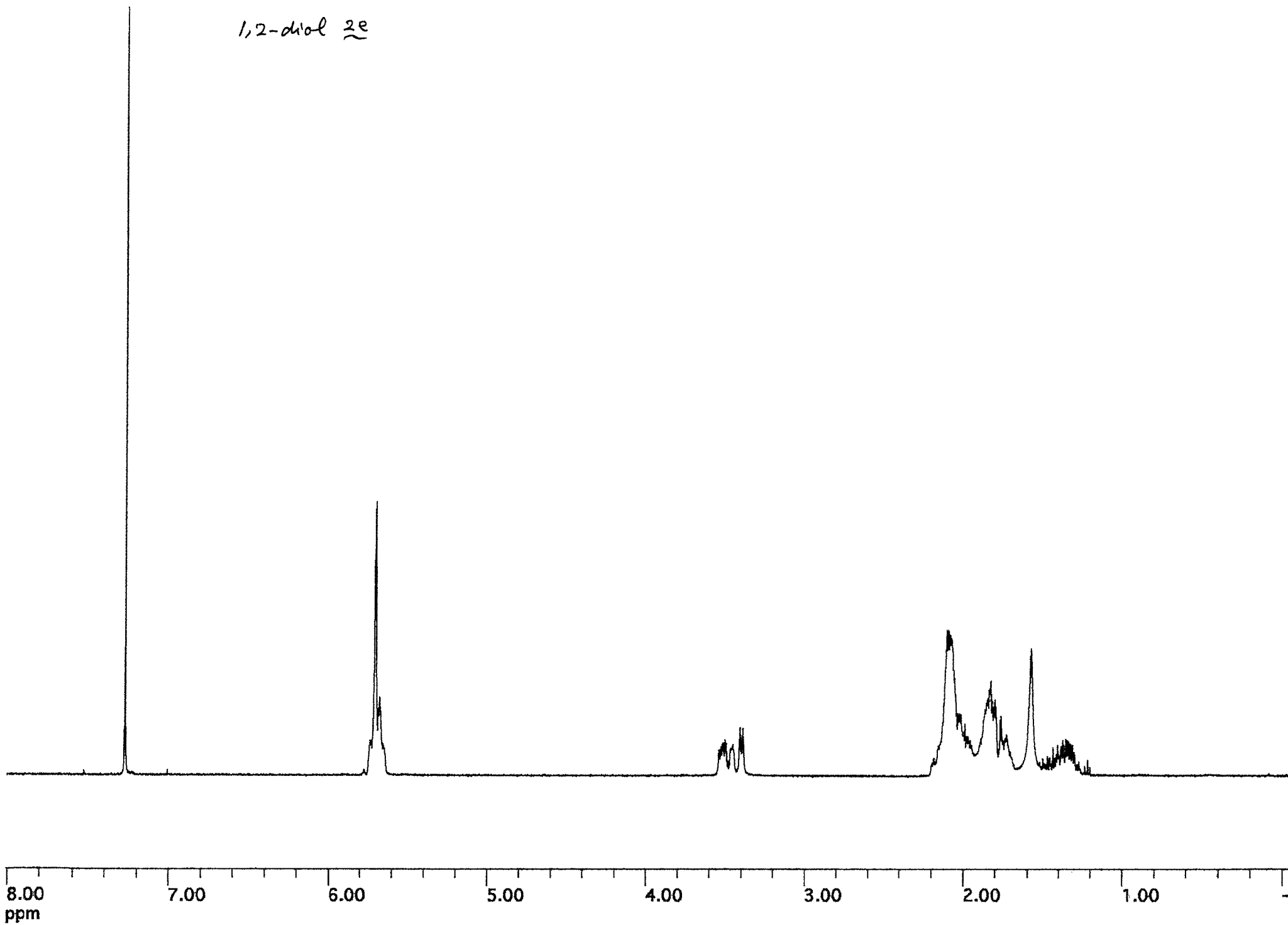


2-(1-Chloro-1-methylethyl)-5-methyl-1-cyclopentanol (5). Pale yellow oil (obtained as a stereoisomeric mixture (*α*-Me/*β*-Me = 77/23)); ¹H NMR (300 MHz, CDCl₃) [*α*-Me isomer] δ 1.04 (d, *J* = 6.3 Hz, 3 H), 1.09-1.41 (m, 2 H), 1.55 (s, 3 H), 1.63 (s, 3 H), 1.73-1.88 (m, 3 H), 2.02-2.08 (m, 1 H), 2.17 (br s, 1 H), 3.60 (t, *J* = 7.7 Hz, 1 H). [*β*-Me isomer]

d 1.00 (d, $J = 6.9$ Hz, 3 H), 1.09-1.41 (m, 2 H), 1.52 (s, 3 H), 1.65 (s, 3 H), 1.73-1.88 (m, 3 H), 2.02-2.08 (m, 1 H), 2.17 (br s, 1 H), 3.72 (t, $J = 7.7$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) [α -Me isomer] d 17.42, 25.60, 30.35, 30.69, 31.84, 42.88, 58.83, 74.66, 81.54. [β -Me isomer] d 13.25, 27.20, 30.81, 32.02, 39.71, 45.84, 61.09, 73.71, 76.76; IR (KBr) 3487, 2946, 1458, 1377, 1104, 911, 738 cm^{-1} ; MS (EI) $m/z = 140$ ($\text{M}^+ - 1\text{-Cl}$); Anal. Calcd for $\text{C}_9\text{H}_{17}\text{OCl}$: C, 61.18; H, 9.70. Found: C, 61.47; H, 9.87.

(1) Hirao, T.; Hasegawa, T.; Muguruma, Y.; Ikeda, I. *J. Org. Chem.* **1996**, *61*, 366. (2) Fujiwara, T.; Tsuruta, Y.; Arizono, K.; Takeda, T. *Synlett.* **1997**, 962.

1,2-diol 2e



1,2-diol, 2e

