Supporting Information

A Tandem Reaction of Organozinc Reagent Prepared from Palladium-catalyzed Umpolung Method: Diastereoselective Formation of Cyclohexene Derivatives Bearing Three Adjacent Stereocenters

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Instrumentation and Chemicals

Nuclear magnetic resonance spectra were taken on Varian UNITY INOVA 500 (\(^1\)H, 500 MHz; \(^{13}\)C, 125 MHz) spectrometer using tetramethylsilane for \(^1\)H NMR as an internal standard (\(\delta = 0\) ppm), CDCl\(_3\) for \(^{13}\)C NMR as an internal standard (\(\delta = 77.0\) ppm). \(^1\)H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. High-resolution mass spectra were obtained with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at Kyoto University Elemental Analysis Center. Infrared (IR) spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. Melting points were determined using a YANAKO MP-500D. TLC analyses were performed by means of Merck Kieselgel 60 F\(_{254}\) (0.25 mm) Plates. Visualization was accomplished with UV light (254 nm) and an aqueous vanillin solution followed by heating. Flash column chromatography was carried out using Kanto Chemical silica gel (spherical, 40–100 \(\mu\)m).

Unless otherwise noted, commercially available reagents were used without purification. Tetrahydrofuran, Dehydrated stabilizer free —Super— was purchased from Kanto Chemical Co., stored under argon, and used as it is.
X-ray Crystallographic Analysis

ORTEP drawing: 4a

Empirical formula: $\text{C}_{22}\text{H}_{22}\text{O}_4$

Formula weight: 350.40

Temperature: 293(2) K

Wavelength: 0.71073 Å

Crystal system: Triclinic

Space group: P-1

Unit cell dimensions:
- $a = 6.0102(6)$ Å, $\alpha = 81.280(2)^\circ$
- $b = 10.0194(9)$ Å, $\beta = 83.245(2)^\circ$
- $c = 15.9053(15)$ Å, $\gamma = 75.899(2)^\circ$

Volume: 914.94(15) Å$^3$

Z: 2

Density (calculated): 1.272 Mg/m$^3$

Absorption coefficient: 0.087 mm$^{-1}$

$F(000)$: 372

Crystal size: 1.00 x 0.50 x 0.20 mm$^3$

Theta range for data collection: 2.11 to 27.04°

Index ranges:
- $-7 \leq h \leq 6$, $-12 \leq k \leq 8$, $-19 \leq l \leq 20$

Reflections collected: 5637

Independent reflections: 3892 [R(int) = 0.0150]

Completeness to theta = 27.04°: 96.8%

Absorption correction: None

Refinement method: Full-matrix least-squares on F$^2$

Data / restraints / parameters: 3892 / 0 / 237

Goodness-of-fit on F$^2$: 0.823

Final R indices [I>2sigma(I)]: $R1 = 0.0541$, $wR2 = 0.1829$

R indices (all data): $R1 = 0.0625$, $wR2 = 0.1990$

Largest diff. peak and hole: 0.295 and -0.219 e.Å$^{-3}$
$^1$H NMR and $^{13}$C NMR Spectra of the Substrate and the Products
4'a