

Stereoselectivity Control in the Rh(I)-Catalyzed Conjugate Additions of Aryl and Alkenylboronic Acids to Unprotected Hydroxycyclopentenones

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Supplementary material

General procedures and $^1$H, $^{13}$C-NMR and optical rotations of compounds 2-I and 2-II
(6 pages)
General Methods

All starting boronic acids were commercially available research-grade chemicals, and were used without further purification. [RhCl(COD)]₂ was commercially available. Dioxane and MeOH were research-grade chemicals used without further purification. (S)-4-hydroxy-2-phenylcyclopentenone was prepared as previously reported.¹ Deionized water was used as co-solvent. Silica gel 60 F₂₅₄ was used for TLC, and the spots were detected with UV or vanillin solution. Flash column chromatography was carried out on silica gel 60. IR spectra have been recorded as CHCl₃ solutions. ¹H NMR spectra were recorded at 200 MHz or 300 MHz as indicated, in CDCl₃ solution. ¹³C and ¹⁹F NMR spectra were recorded at 50.5 MHz and 141.2 MHz respectively in CDCl₃ solution. MS spectra were carried out by EI at 70 eV. Optical rotations were determined at 25°C with a Na lamp in a Perkin-Elmer 241 apparatus using 1 mL cuvettes.

Reactions with R²B(OH)₂

General procedure.

R²B(OH)₂ (0.20 mol) and [RhCl(COD)]₂ (0.005mol, 2.5 mg for Table 1, entries 1-17, 19-21 or 0.02 mol, 10 mg, entries 18, 21-24) were successively introduced in a flask and placed under Ar. A solution of 1a (30 mg, 0.17 mol) in the corresponding solvent mixture was added (Table 1: conditions A, 0.5 mL, dioxane-H₂O 4:1; conditions B, 0.5 mL, MeOH-H₂O 6:1; conditions C, 0.6 mL, dioxane-H₂O 2:1). Last, Cs₂CO₃, NaHCO₃, LiOH, Et₃N, Mg(OH)₂, Ba(OH)₂, Zr(OH)₄ or CsF were added (Eq given in Table 1). In the reactions with guanidine as base (Table 1, entries 15, 19-21), guanidinium hydrochloride (0.17 mmol, 16.4 mg) was added to the reaction mixture followed by LiOH (0.17 mmol, 7.2 mg). The reaction mixtures were stirred 16 h at rt. Evaporation under vacuum afforded the crude reaction products, which were purified by column chromatography (hexane-AcOEt, 20:80).
Characterization of compounds 2.

\((-\)\((2R,\ 3R,\ 4S)\)- 4-Hydroxy-2,3-diphenylcyclopentanone, 2a-I. \([\alpha]_D = -50\) (c 0.8, CHCl\(_3\)). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.31 - 7.02 (10H, m), 4.55 (1H, ddd, \(J = 7.6\) Hz, \(J = 9.2\) Hz, \(J = 9.7\) Hz), 3.67 (1H, d, \(J = 13.0\) Hz), 3.44 (1H, ddd, \(J = 13.0\) Hz, \(J = 9.2\) Hz), 3.07 (1H, ddd, \(J = 18.6\) Hz, \(J = 7.6\) Hz, \(J = 1.2\) Hz), 2.60 (1H, dd, \(J = 18.6\) Hz, \(J = 9.7\) Hz). \(^{13}\)C NMR (50.5 MHz, CDCl\(_3\)) \(\delta\) 211.4, 138.3, 135.6, 129.0, 128.6, 128.5, 127.6, 127.5, 127.3, 73.4, 62.4, 58.7, 46.6 Anal. Calcd for C\(_{17}\)H\(_{16}\)O\(_2\): C, 80.93; H, 6.39. Found: C, 81.09; H, 6.47.

\((-\)\((2R,\ 3R,\ 4S)\)- 4-Hydroxy-3-(4-methoxyphenyl)-2-phenylcyclopentanone, 2b-I. \([\alpha]_D = -38\) (c 0.2, CHCl\(_3\)). \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\) 7.40 - 6.72 (9H, m), 4.44 (1H, ddd, \(J = 7.4\) Hz, \(J = 9.7\) Hz, \(J = 9.1\) Hz), 3.70 (3H, s), 3.54 (1H, d, \(J = 13.2\) Hz), 3.30 (1H, dd, \(J = 13.2\) Hz, \(J = 9.1\) Hz), 2.98 (1H, ddd, \(J = 18.0\) Hz, \(J = 7.4\) Hz, \(J = 1.0\) Hz), 2.51 (1H, dd, \(J = 18.0\), \(J = 9.7\) Hz). \(^{13}\)C NMR (50.5 MHz, CDCl\(_3\)) \(\delta\) 212.3, 158.3, 136.1, 130.0, 129.0, 128.9, 127.7, 114.8, 73.9, 62.9, 58.3, 55.7, 47.0 Anal. Calcd for C\(_{18}\)H\(_{18}\)O\(_3\): C, 76.57; H, 6.43. Found: C, 76.71; H, 6.52.

\((-\)\((2R,\ 3R,\ 4S)\)- 4-Hydroxy-3-(3-methoxyphenyl)-2-phenylcyclopentanone, 2c-I. \([\alpha]_D = -43\) (c 1.0, CHCl\(_3\)). \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\) 7.30 - 6.62 (9H, m), 4.46 (1H, ddd, \(J = 7.5\) Hz, \(J = 9.1\) Hz, \(J = 9.8\) Hz), 3.69 (3H, s), 3.54 (1H, d, \(J = 13.2\) Hz), 3.33 (1H, dd, \(J = 13.2\) Hz, \(J = 9.1\) Hz), 2.98 (1H, ddd, \(J = 19.0\) Hz, \(J = 7.5\) Hz, \(J = 1.1\) Hz), 2.51 (1H, dd, \(J = 19.0\), \(J = 9.8\) Hz). \(^{13}\)C NMR (50.5 MHz, CDCl\(_3\)) \(\delta\) 211.5, 160.1, 140.1, 135.8, 130.1, 128.7, 128.6, 127.4, 119.8, 113.9, 112.6, 73.5, 62.4, 58.7, 55.3, 46.7 Anal. Calcd for C\(_{18}\)H\(_{18}\)O\(_3\): C, 76.57; H, 6.43. Found: C, 76.49; H, 6.34.

\((-\)\((2R,\ 3R,\ 4S)\)- 4-Hydroxy-3-(2-methoxyphenyl)-2-phenylcyclopentanone, 2d-I. \([\alpha]_D = -50\) (c 1.4, CHCl\(_3\)). \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\) 7.20 - 6.75 (9H, m), 4.60 (1H, ddd, \(J = 7.6\) Hz, \(J = 9.1\) Hz, \(J = 10.1\) Hz), 3.91 (1H, d, \(J = 13.3\) Hz), 3.74 (3H, s), 3.73 (1H, dd, \(J = 13.3\) Hz, \(J = 10.1\) Hz), 2.97 (1H, ddd, \(J = 18.7\) Hz, \(J = 7.6\) Hz, \(J = 1.1\) Hz), 2.49 (1H, dd, \(J = 18.7\), \(J = 9.1\) Hz). \(^{13}\)C NMR (50.5 MHz, CDCl\(_3\)) \(\delta\) 212.5,

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1 Csáký, A. G.; Mba, M.; Plumet, J. *Tetrahedron Asymm.* 2004, 15, 647
157.9, 136.3, 128.9, 128.6, 128.5, 127.1, 126.6, 121.3, 111.3, 72.6, 60.5, 55.5, 53.9, 47.2. Anal. Calcd for C_{18}H_{18}O_{3}: C, 76.57; H, 6.43. Found: C, 76.44; H, 6.28.

(-)-(2R, 3R, 4S)- 4-Hydroxy-2-phenyl-3-(4-trifluoromethylphenyl)cyclopentanone, 2e-I. $[\alpha]_D = -29$ (c 1.5, CHCl₃). $^1$H NMR (200 MHz, CDCl₃) δ 7.55 - 6.98 (9H, m), 4.49 (1H, ddd, $^3$J = 7.5 Hz, $^3$J = 8.7 Hz, $^3$J = 9.5 Hz), 3.58 (1H, d, $^3$J = 13.3 Hz), 3.44 (1H, dd, $^3$J = 13.3 Hz, $^3$J = 8.7 Hz), 3.00 (1H, ddd, $^2$J = 18.6 Hz, $^3$J = 7.5 Hz, $^3$J = 1.0 Hz), 2.53 (1H, dd, $^2$J = 18.6, $^3$J = 9.5 Hz). $^{13}$C NMR (50.5 MHz, CDCl₃) δ 210.6, 142.6, 135.1, 128.7, 128.4, 128.0, 127.5, 125.9, 125.8, 125.7, 125.6, 73.0, 62.3, 58.1, 46.7. Anal. Calcd for C_{18}H_{15}F_{3}O_{2}: C, 67.50; H, 4.72. Found: C, 67.61; H, 4.54.

(-)-E-(2R, 3S, 4S)- 4-Hydroxy-2-phenyl-3-styrylcyclopentanone, 2f-I. $[\alpha]_D = -58$ (c 0.3, CHCl₃). $^1$H NMR (200 MHz, CDCl₃) δ 7.33 - 7.01 (10H, m), 6.44 (1H, d, $^3$J = 15.8Hz), 6.10 (1H, dd, $^3$J = 15.8 Hz, $^3$J = 8.2 Hz), 4.28 (1H, m), 3.29 (1H, d, $^3$J = 12.7 Hz), 2.96 (2H, m), 2.44 (1H, dd, $^2$J = 18.6 Hz, $^3$J = 9.7 Hz). $^{13}$C NMR (50.5 MHz, CDCl₃) δ 211.3, 136.3, 135.5, 133.9, 128.9, 128.6, 128.5, 127.7, 127.5, 127.2, 126.2, 71.7, 61.5, 56.5, 46.2. Anal. Calcd for C_{19}H_{18}O_{2}: C, 81.99; H, 6.52. Found: C, 81.89; H, 6.44.

(+)-E-(2S, 3R, 4S)- 4-Hydroxy-2-phenyl-3-styrylcyclopentanone, 2f-II. $[\alpha]_D = +134$ (c 0.8, CHCl₃). $^1$H NMR (200 MHz, CDCl₃) δ 7.35 - 7.01 (10H, m), 6.44 (1H, d, $^3$J = 16.2 Hz), 6.33 (1H, dd, $^3$J = 16.2 Hz, $^3$J = 6.6 Hz), 4.57 (1H, m), 3.70 (1H, d, $^3$J = 14.5 Hz), 3.17 (1H, m), 2.63 (2H, m). $^{13}$C NMR (50.5 MHz, CDCl₃) δ 214.8, 136.7, 136.6, 134.17, 128.8, 128.7, 127.9, 127.3, 126.4, 126.1, 70.3, 55.9, 53.0, 47.5. Anal. Calcd for C_{19}H_{18}O_{2}: C, 81.99; H, 6.52. Found: C, 82.21; H, 6.47.

(-)-E-(2R, 3S, 4S)- 4-Hydroxy-2-phenyl-3-[2-(p-tolyl)vinyl]cyclopentanone, 2g-I. $[\alpha]_D = -69$ (c 0.7, CHCl₃). $^1$H NMR (200 MHz, CDCl₃) δ 7.35 - 6.95 (9H, m), 6.41 (1H, d, $^3$J = 15.9 Hz), 6.04 (1H, dd, $^3$J = 15.9, $^3$J = 8.2), 4.27 (1H, m), 3.28 (1H, d, $^3$J = 12.7 Hz), 2.94 (2H, m), 2.43 (1H, dd, $^2$J = 18.6 Hz, $^3$J = 9.7 Hz), 2.29 (3H, s). $^{13}$C NMR (50.5 MHz, CDCl₃) δ 211.5, 137.7, 135.7, 133.9, 133.6, 129.3, 128.7, 128.6, 127.3, 126.5, 126.2, 71.8, 61.7, 56.7, 46.3, 21.2. Anal. Calcd for C_{20}H_{20}O_{2}: C, 82.16; H, 6.89. Found: C, 82.25; H, 7.05.
(+)-E-(2S, 3R, 4S)- 4-Hydroxy-2-phenyl-3-[2-(p-tolyl)vinyl]cyclopentanone, 2g-II. [α]D = +93 (c 1.5, CHCl3). 1H NMR (200 MHz, CDCl3) δ 7.40 - 6.98 (9H, m), 6.41 (1H, d, 3J = 16.2 Hz), 6.27 (1H, dd, 3J = 16.2, 3J = 6.8), 4.57 (1H, m), 3.69 (1H, d, 3J = 12.5 Hz), 3.17 (1H, m), 2.58 (2H, m), 2.25 (3H, s). 13C NMR (50.5 MHz, CDCl3) δ 214.8, 137.7, 136.6, 133.9, 133.7, 129.3, 128.6, 127.1, 126.2, 124.8, 70.2, 55.8, 52.9, 47.4, 21.2. Anal. Calcd for C20H20O2: C, 82.16; H, 6.89. Found: C, 82.31; H, 6.74.

(-)-E-(2R, 3S, 4S)- 3-[2-(p-Chlorophenyl)vinyl]-4-hydroxy-2-phenylcyclopentanone, 2h-I. [α]D = -91 (c 1.1, CHCl3). 1H NMR (200 MHz, CDCl3) δ 7.27 - 7.05 (9H, m), 6.38 (1H, d, 3J = 15.8 Hz), 6.08 (1H, dd, 3J = 15.8, 3J = 8.0), 4.56 (1H, m), 3.28 (1H, d, 3J = 12.7 Hz), 2.94 (2H, m), 2.43 (1H, 2J = 18.6 Hz, 3J = 9.7 Hz). 13C NMR (50.5 MHz, CDCl3) δ 211.2, 135.6, 134.9, 133.5, 132.7, 128.8, 128.6, 128.4, 127.5, 127.4, 71.8, 61.4, 56.5, 46.4. Anal. Calcd for C19H17ClO2: C, 72.96; H, 5.48. Found: C, 72.78; H, 5.39.

(+)-E-(2S, 3R, 4S)- 3-[2-(p-Chlorophenyl)vinyl]-4-hydroxy-2-phenylcyclopentanone, 2h-II. [α]D = +123 (c 1.4, CHCl3). 1H NMR (200 MHz, CDCl3) δ 7.49 - 6.95 (9H, m), 6.37 (1H, d, 3J = 16.0 Hz), 6.32 (1H, dd, 3J = 16.2, 3J = 6.0), 4.57 (1H, m), 3.67 (1H, d, 3J = 12.5 Hz), 3.16 (1H, m), 2.59 (2H, m). 13C NMR (50.5 MHz, CDCl3) δ 214.2, 136.4, 134.9, 133.3, 132.6, 128.6, 128.5, 127.8, 127.4, 127.1, 126.7, 70.1, 55.8, 52.8, 47.5. Anal. Calcd for C19H17ClO2: C, 72.96; H, 5.48. Found: C, 73.11; H, 5.55.

(-)-E-(2R, 3S, 4S)- 4-Hydroxy-2-phenyl-3-[2-(p-trifluorophenyl)vinyl]cyclopentanone, 2i-I. [α]D = -38 (c 0.4, CHCl3). 1H NMR (200 MHz, CDCl3) δ 7.49 - 7.06 (9H, m), 6.46 (1H, d, 3J = 15.9 Hz), 6.23 (1H, dd, 3J = 7.8 Hz, 3J = 15.9 Hz), 4.33 (1H, m), 3.31 (1H, d, 3J = 13.0 Hz), 2.99 (2H, m), 2.46 (1H, dd, 3J = 18.6 Hz, 3J = 9.7 Hz). 13C NMR (50.5 MHz, CDCl3) δ 210.9, 138.6, 135.5, 132.6, 130.5, 128.8, 128.6, 127.5, 126.5, 125.6, 125.5, 71.7, 61.6, 56.4, 46.1. Anal. Calcd for C20H17F3O2: C, 69.36; H, 4.95. Found: C, 69.25; H, 4.79.

(+)-E-(2S, 3R, 4S)- 4-Hydroxy-2-phenyl-3-[2-(p-trifluorophenyl)vinyl]cyclopentanone, 2i-II. [α]D = +114 (c 1.2, CHCl3). 1H NMR (200 MHz, CDCl3) δ 7.48 - 7.03 (9H, m), 6.43 (2H, m), 4.60 (1H, m), 3.69 (1H, d, 3J = 12.4 Hz), 3.19 (1H, m), 2.59.
(2H, m). $^{13}$C NMR (50.5 MHz, CDCl$_3$) δ 214.5, 139.9, 136.4, 132.3, 129.1, 128.6, 128.5, 127.1, 126.3, 125.4, 125.3, 70.0, 55.9, 53.0, 47.6. Anal. Calcd for C$_{20}$H$_{17}$F$_3$O$_2$: C, 69.36; H, 4.95. Found: C, 69.44; H, 5.12.