Synthesis of Optically Active $C_1$ Symmetric Al(salalen) Complex and Its Application to Catalytic Hydrophosphonylation of Aldehydes

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1. General

All reagents and solvents were used as supplied commercially, except for THF that was distilled from Na/Ph$_2$CO, before use. $^1$H and $^{13}$C NMR spectra were measured on a JEOL GX-400 spectrometer at 400 and 100 MHz, respectively. All chemical shifts were recorded in $\delta$ (ppm) relative to tetramethylsilane (TMS). Melting points were measured with a BÜCHI Melting Point B-545 apparatus and uncorrected. Infrared spectra were measured as a KBr disc or as a thin film using NaCl plate on a SHIMADZU FTIR-8600 spectrophotometer, and only diagnostic absorptions are listed below. UV/visible spectra were measured on SHIMADZU MultiSpec-1500. Optical rotation was measured with a JASCO P-1020 polarimeter. High resolution FAB mass spectra were obtained from JEOL JMX-SX/SX 102A spectrometer. Enantiomeric excesses were determined by HPLC analysis using SHIMADZU LC-10AT-VP equipped with an appropriate optically active column, as described in the footnotes to the corresponding Tables. TLC analysis was performed on Silica gel 60 F$_{254}$-coated glass plates (Merck). Visualization was accomplished with irradiation of 254 nm UV light or spray of a 12-molybdo(VI)phosphoric acid ethanol solution as the developing agent.

2. Synthesis of salalen ligand


To a solution of (1$R$, 2$R$)-1,2-cyclohexanediamine monohydrochloride (1, 3.40 g, 22.56 mmol) in dry methanol (ca. 100 ml) was added 3,5-di-tert-butyl salicylaldehyde (2, 5.03 g, 21.48 mmol) and the resulting mixture was stirred for 3 h at room temperature. After cooling to 0 °C, sodium borohydride
(2.03 g, 53.7 mmol) was added to the solution and stirred for 2 h at room temperature. The reaction was quenched with H$_2$O and extracted with Et$_2$O three times. The combined organic phases were washed with brine and dried over Na$_2$SO$_4$. After filtration, the solution was concentrated in vacuo, and re-dissolved in dry ethanol (100 ml). To the mixture was added di-tert-butyl dicarbonate (5.45 ml, 23.6 mmol) at room temperature and stirred for 1.5 h. The solution was concentrated under reduced pressure and submitted to silica gel column chromatography (hexane/ethyl acetate = 9/1-4/1) to give 3 (6.24 g, 67%).

Colorless solid (hygroscopic). [α]$_D^{22}$ + 8.85 (c 1.33, CHCl$_3$), IR (KBr): 3317, 2955, 2862, 1701, 1510, 1481, 1454, 1391, 1363, 1236, 1171, 1107, 1016, 872 cm$^{-1}$; $^1$H NMR (CDCl$_3$): δ 7.21 (d, $J$ = 2.4 Hz, 1H), 6.85 (d, $J$ = 2.4 Hz, 1H), 4.42 (br d, $J$ = 10.3 Hz, 1H), 4.08 (d, $J$ = 13.43 Hz, 1H), 3.87 (d, $J$ = 13.43 Hz, 1H), 3.40 (m, 1H), 2.23-2.32 (m, 2H), 2.00 (m, 1H), 1.69-1.76 (m, 2H), 1.46 (s, 9H), 1.42 (s, 9H), 1.28 (s, 9H), 1.12-1.40 (m, 4H); $^{13}$C NMR (CDCl$_3$): δ 155.7, 154.5, 140.1, 135.7, 123.0, 122.7, 122.1, 79.5, 60.4, 54.1, 50.4, 34.2, 33.5, 31.8, 31.4, 29.8, 28.5, 25.1, 24.7; HRFABMS m/z. Calcd for [C$_{26}$H$_{44}$N$_2$O$_3$]$^+$: m/z = 432.3352. Found: m/z = 432.3349.

2.2. Synthesis of salalen ligand 4.

To a solution of 3 (5.63 g, 13.01 mmol) in methanol (ca. 80 ml) were added aq. CH$_2$O (ca. 37%, 1.21 ml, 16.27 mmol) and 10% Pd/C (1.03 g) at room temperature. The flask was purged with H$_2$ and installed with a rubber balloon filled with H$_2$. After stirring for about 5 h at room temperature, the mixture was filtered through a pad of Celite and subsequently washed with MeOH. The solution was concentrated in vacuo and re-dissolved in MeOH (30 ml). To the solution 3M HCl (30 ml) was added and stirred for 36 h at room temperature. The reaction was quenched with 3M NaOH (35 ml) and the resulting mixture was extracted with Et$_2$O three times. The combined organic phases were washed with brine and dried over Na$_2$SO$_4$. After filtration, the solution was concentrated in vacuo and re-dissolved in methanol (ca. 100 ml). To the solution was added 3,5-di-tert-butyl salicylaldehyde (2, 3.04 g, 13.0 mmol) and stirred for 3.5 h at room temperature. The precipitate was filtered off and washed with methanol to give the ligand 4 (5.54 g, 76%).
Yellow solid. \([\alpha]^{D}_{D} = 100.4 (c 1.00, \text{CHCl}_3)\), IR (KBr): 2955, 2864, 1628, 1477, 1447, 1393, 1362, 1244, 1204, 1171, 1030, 876, 826 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)): \(\delta 13.56\) (s, 1H), 10.58 (br s, 1H), 8.37 (s, 1H), 7.38 (d, \(J = 2.4\) Hz, 1H), 7.10 (d, \(J = 2.4\) Hz, 1H), 7.02 (d, \(J = 2.4\) Hz, 1H), 6.79 (d, \(J = 2.4\) Hz, 1H), 3.79 (br ABq, 2H), 3.29 (m, 1H), 2.96 (m, 1H), 2.22 (s, 3H), 1.63-2.00 (m, 5H), 1.29-1.43 (m, 3H), 1.47 (s, 9H), 1.29 (s, 9H), 1.25 (s, 9H), 1.12 (s, 9H); \(^1\)C NMR (CDCl\(_3\)): \(\delta 165.5, 157.9, 154.5, 139.6, 139.6, 136.4, 135.2, 126.7, 125.6, 123.1, 122.3, 120.8, 117.9, 70.2, 66.6, 35.3, 35.1, 34.8, 34.2, 31.8, 31.6, 29.7, 29.5, 25.3, 24.8; Anal. Calcd for C\(_{37}\)H\(_{58}\)N\(_2\)O\(_2\): C, 78.95; H, 10.39; N, 4.98%. Found: C, 78.94; H, 10.40; N, 4.92%.


To a solution of salalen ligand 4 (453 mg, 0.806 mmol) in dry toluene (10 ml) was added diethylaluminum chloride (0.92 M in hexane, 876 µl) at 0 °C and the solution was stirred for overnight at room temperature. The yellow suspension was concentrated in vacuo and re-suspended in hexane. The yellow precipitate was filtered off and washed with hexane to give complex 5 (468 mg, 93%).

Yellow solid. IR (KBr): 2951, 2909, 2864, 1620, 1543, 1483, 1441, 1420, 1389, 1360, 1304, 1256, 1204, 1177, 1130, 1011, 962, 851, 761, 635, 600, 577 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)): \(\delta 8.44\) (s, 1H), 7.57 (d, \(J = 2.4\) Hz, 1H), 7.30 (d, \(J = 2.4\) Hz, 1H), 7.00 (d, \(J = 2.4\) Hz, 1H), 6.82 (d, \(J = 2.4\) Hz, 1H), 4.57 (d, \(J = 13.2\) Hz, 1H), 3.40 (m, 1H), 3.37 (d, \(J = 13.2\) Hz, 1H), 2.54 (m, 1H), 2.45 (s, 3H), 2.27-2.36 (m, 1H), 1.77-1.84 (m, 3H), 1.52 (s, 9H), 1.38 (s, 9H), 1.29 (s, 9H), 1.27 (s, 9H), 1.12-1.57 (m, 3H), 0.94-1.00 (m, 1H); Anal. Calcd for C\(_{37}\)H\(_{58}\)N\(_2\)O\(_2\)AlCl: C, 71.30; H, 9.06; N, 4.49%. Found: C, 71.35; H, 9.03; N, 4.53%.