Support Information

Highly Enantioselective Hydrogenation of Enol Acetates Catalyzed by Ru-TunaPhos Complexes

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Experimental Section

General Methods. All reactions and manipulations were performed in a nitrogen-filled glovebox or using standard Schlenk techniques. All solvents were purified and deoxygenated by the standard procedures before use. (*S*)-Cn-TunaPhos Ligands were prepared as previously described.¹ Gas chromatography was carried out on Hewlett-Packard 6890 gas chromatographs using the Chiral Select 1000 column [0.25 mm (i.d.) x 30 m]: carrier gas, He (1 mL/min)

General Procedure for Preparation of Ru-Cn-TunaPhos Dinuclear Catalysts. A solution of $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)]_2$ (0.050 g, 0.1 mmol) and (*S*)-Cn-TunaPhos ($n = 1 - 6$) (0.2 mmol) in CH_2Cl_2 (5 mL) and ethanol (5 mL) was stirred at 50 °C for 2 h. The solvent was removed under vacuum, then dimethylamine hydrochloride (16 mg, 0.2 mmol) and dioxane (20 mL) were added. The mixture was stirred under reflux for 16 h. The reaction solution was concentrated under vacuum to dryness to afford brown solid in quantitative yield. They were identified by comparison of their ^{31}P NMR with those of the related complexes² and directly used as catalysts for hydrogenation without further purification.

$[\text{NMe}_2\text{H}_2][\{\text{RuCl}((S)\text{-C1-TunaPhos})_2(\mu\text{-Cl})_3\}]$: ^{31}P NMR (146 MHz, CD_2Cl_2) δ 52.9 (d, $J = 39.7$ Hz), 50.2 (d, $J = 39.1$ Hz)

$[\text{NMe}_2\text{H}_2][\{\text{RuCl}((S)\text{-C2-TunaPhos})_2(\mu\text{-Cl})_3\}]$: ^{31}P NMR (146 MHz, CD_2Cl_2) δ 55.0 (d, $J = 38.6$ Hz), 51.3 (d, $J = 38.9$ Hz)

$[\text{NMe}_2\text{H}_2][\{\text{RuCl}((S)\text{-C3-TunaPhos})_2(\mu\text{-Cl})_3\}]$: ^{31}P NMR (146 MHz, CD_2Cl_2) δ 54.4 (d, $J = 39.0$ Hz), 51.2 (d, $J = 39.5$ Hz)

$[\text{NMe}_2\text{H}_2][\{\text{RuCl}((S)\text{-C4-TunaPhos})_2(\mu\text{-Cl})_3\}]$: ^{31}P NMR (146 MHz, CD_2Cl_2) δ 55.1 (d, $J = 38.8$ Hz), 51.1 (d, $J = 39.1$ Hz)

$[\text{NMe}_2\text{H}_2][\{\text{RuCl}((S)\text{-C5-TunaPhos})_2(\mu\text{-Cl})_3\}]$: ^{31}P NMR (146 MHz, CD_2Cl_2) δ 54.7 (d, $J = 38.6$ Hz), 50.9 (d, $J = 38.8$ Hz)

$[\text{NMe}_2\text{H}_2][\{\text{RuCl}((S)\text{-C6-TunaPhos})_2(\mu\text{-Cl})_3\}]$: ^{31}P NMR (146 MHz, CD_2Cl_2) δ 54.9 (d, $J = 38.3$ Hz), 50.6 (d, $J = 38.5$ Hz)

General Procedure for Asymmetric Hydrogenation. To a solution of enol acetate substrate (0.2 mmol) in ethanol (2.0 mL) in a glovebox was added a solution of $[\text{NMe}_2\text{H}_2][\{\text{RuCl}((S)\text{-C2-TunaPhos})_2(\mu\text{-Cl})_3\}]$ (0.0001 mmol) in CH_2Cl_2 (0.5 mL). The hydrogenation was performed at rt to 50 °C under 3 atm of hydrogen pressure for 12 - 48 h. After the hydrogen was released, the reaction mixture was passed through a short silica gel column to remove the catalyst. The enantiomeric excess was measured by GC.

References

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