Asymmetric 1,4-Addition of Organosiloxanes to α,β -Unsaturated Carbonyl Compounds Catalyzed by a Chiral Rhodium Complex

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Supporting Information

General Information

All reactions were carried out in Schlenk tubes under N₂. 1,4-dioxane was distilled and stored under N₂. NMR spectra were recorded using CDCl₃ as the solvent. Spherical silica gel (40-100 μ m, Kanto Chemical) was used for flash chromatography. The cationic rhodium complex, [Rh(cod)(MeCN)₂][BF₄], was prepared as described in the literature.¹ Phenyltrimethoxysilane (**1a**) and vinyltriethoxysilane (**1d**) was purchased from TCI Co., Ltd. *p*-Chlorophenyltriethoxysilane (**1b**) and *p*-methoxyphenyltriethoxysilane (**1c**) were prepared by cross coupling reaction of corresponding aryl bromide with triethoxysilane as described in the literature.² *E*-styryltriethoxysilane (**1e**)³ and *Z*-styryltriethoxysilane (**1f**)⁴ were prepared by hydrosilylation as described in the literatures.

Catalytic Asymmetric 1,4-addition of organosilicon compounds

To a mixture of [Rh(cod)(MeCN)₂][BF₄] (15.2 mg, 0.04 mmol) and (*S*)-BINAP (37.4 mg, 0.06 mmol) in 1,4-dioxane (2 mL) was added cyclohexenone (**2a**, 96.1 mg, 1.0 mmol), phenyltrimethoxysilane (**1a**, 397 mg, 2.0 mmol), and then water (0.2 mL) and the mixture was stirred at 90 °C for 20 h. Hexane (100-150 mL) was added to the reaction mixture and the resulting precipitate was removed by filtration. The solvent was removed *in vacuo* and the residue was purified by flash chromatography (hexane/AcOEt = 10:1) to give (*S*)-3-phenylcyclohexanone ((*S*)-**3a**, 132 mg, 76%). The spectroscopic data matched those reported in the literature.⁵ Optical purity was determined by HPLC using Daicel Chiralcel OD-H eluting with hexane/2-propanol 98/2. $[\alpha]^{25}_{\text{D}} = -20^{\circ}$ (c 1.08, CHCl₃) 98%ee (*S*) (lit.⁶ $[\alpha]^{20}_{\text{D}} = -21^{\circ}$ (c 0.96, CHCl₃) 97%ee (*S*)). Characterization data for the other products follow.

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(S)-3-Phenylcyclopentenone. The spectroscopic data matched those reported in the literature.⁵ Optical purity was determined by HPLC using Daicel Chiralcel OB-H eluting with hexane/2-propanol 99.5/0.5. $[\alpha]_{\text{D}}^{25} = -88^{\circ}$ (c 1.08, CHCl_3) 94%ee (*S*) (lit.⁶ $[\alpha]_{\text{D}}^{20} = -92^{\circ}$ (c 0.82, CHCl_3) 97%ee (*S*)).

(R)-4-phenylpentan-2-one (3c). The spectroscopic data matched those reported in the literature.⁷ Optical purity was determined by HPLC using Daicel Chiralcel OJ eluting with hexane/2-propanol 99/1. $[\alpha]_{\text{D}}^{23} = -37^{\circ}$ (c 1.01, CHCl_3) 75%ee (*R*) (lit.⁷ $[\alpha]_{\text{D}}^{20} = +40^{\circ}$ (c 0.5, CHCl_3) (*S*)).

(R)-1,3-Diphenylbutan-1-one (3d). The spectroscopic data matched those reported in the literature.⁵ Optical purity was determined by HPLC using Daicel Chiralcel OJ eluting with hexane/2-propanol 98/2. $[\alpha]_{\text{D}}^{24} = -13^{\circ}$ (c 1.02, CCl_4) 75%ee (*R*) (lit.⁸ $[\alpha]_{\text{D}}^{20} = -14.8^{\circ}$ (c 1.2, CCl_4) (*R*)).

4-Phenylheptan-2-one (3e). The spectroscopic data matched those reported in the literature.⁵ Optical purity was determined by HPLC using Daicel Chiralcel OD-H eluting with hexane/2-propanol 99.5/0.5. $[\alpha]_{\text{D}}^{27} = -32^{\circ}$ (c 0.99, CHCl_3) 91%ee.

5-Methyl-4-phenylhexan-2-one (3f). The spectroscopic data matched those reported in the literature.⁵ Optical purity was determined by HPLC using Daicel Chiralcel OD-H eluting with hexane/2-propanol 98/2. $[\alpha]_{\text{D}}^{22} = -35^{\circ}$ (c 1.04, CHCl_3) 98%ee (lit.⁶ $[\alpha]_{\text{D}}^{20} = -33^{\circ}$ (c 1.12, CHCl_3) 97%ee).

3-(4-Chlorophenyl)cyclohexanone (3g). The spectroscopic data matched those reported in the literature.⁹ Optical purity was determined by HPLC using Daicel Chiralcel OJ eluting with hexane/2-propanol 99.5/0.5. $[\alpha]_{\text{D}}^{25} = -6^{\circ}$ (c 1.00, CHCl_3) 96%ee.

3-(4-Methoxyphenyl)cyclohexanone (3h). The spectroscopic data matched those reported in the literature.⁹ Optical purity was determined by HPLC using Daicel Chiralcel OJ eluting with hexane/2-propanol 99.5/0.5. $[\alpha]_{\text{D}}^{24} = -18^{\circ}$ (c 1.01, CHCl_3) 96%ee (lit.¹⁰ $[\alpha]_{\text{D}}^{20} = -15^{\circ}$ (c 0.94, CHCl_3) 98%ee).

(S)-3-vinylcyclohexanone (3i). The spectroscopic data matched those reported in the literature.¹¹ Optical purity was determined by GLC using Chiraldex B-DM (100°C, N_2 , 60 kPa). $[\alpha]_{\text{D}}^{22} = -23^{\circ}$ (c 0.98, CHCl_3) 96%ee (*S*) (lit.¹² $[\alpha]_{\text{D}}^{25} = +8.51^{\circ}$ (c 0.94, CHCl_3) 41%ee (*R*)).

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(S)-3-((E)-2-Phenylethenyl)cyclohexanone (3j). The spectroscopic data matched those reported in the literature.¹³ Optical purity was determined by HPLC using Daicel Chiralcel OD-H eluting with hexane/2-propanol 98/2. $[\alpha]_{\text{D}}^{25} = +7.4^{\circ}$ (c 1.04, CHCl₃) 91%ee (S) (lit.¹³ $[\alpha]_{\text{D}}^{20} = +7.6^{\circ}$ (c 0.86, CHCl₃) 92%ee (S)).

3-((Z)-2-Phenylethenyl)cyclohexanone (3k). The spectroscopic data matched those reported in the literature.¹⁴ Optical purity was determined by HPLC using Daicel Chiralcel OD-H eluting with hexane/2-propanol 98/2. $[\alpha]_{\text{D}}^{24} = -141^{\circ}$ (c 1.00, CHCl₃) 87%ee.

(R)-3-Phenylbutanoic acid methyl ester (3l). The spectroscopic data matched those reported in the literature.¹⁵ Optical purity was determined by HPLC using Daicel Chiralcel OD-H eluting with hexane/2-propanol 99.5/0.5. $[\alpha]_{\text{D}}^{26} = -26^{\circ}$ (c 1.00, CHCl₃) 90%ee (R) (lit.¹⁶ $[\alpha]_{\text{D}}^{24} = -25.3^{\circ}$ (c 1.07, CHCl₃) 95%ee (R)).

(R)-3-Phenylbutyramide (3m). The spectroscopic data matched those reported in the literature.⁵ Optical purity was determined by HPLC using Daicel Chiralpak AD eluting with hexane/2-propanol 90/10. $[\alpha]_{\text{D}}^{24} = -36^{\circ}$ (c 1.01, CHCl₃) 81%ee (R) (lit.¹⁷ $[\alpha]_{\text{D}}^{20} = -30.9^{\circ}$ (c 1.01, CHCl₃) 89%ee (R)).

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