LIST of SUPPORTING INFORMATION

Highly Enantioselective Conjugate Addition of Diethylzinc to Acyclic Enones with Fine-Tunable Phosphite–Pyridine Ligands

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Experimental Section

General. All experiments were carried out under an argon atmosphere. All solvents were dried before use according to standard procedures and stored under argon. Feringa's phosphorus amidite **5** was prepared according to a literature procedure.¹ Three 4-*trans*-aryl-3-buten-2-ones were prepared according to a literature procedure.² Racemic conjugate addition products were prepared with acyclic enones and EtMgBr in THF.

1. Hulst, R.; de Vries, N. K.; Feringa, B. L. *Tetrahedron: Asymmetry* **1994**, 5, 699.
2. Patt, W. C.; Edmunds, J. J.; Repine, J. T.; Berryman, K. A.; Reisdorph, B. R.; Lee, C.; Plummer, M. S.; Shahrpour, A.; Haleen, S. J.; Keiser, J. A.; Flynn, M. A.; Welch, K. M.; Reynolds, E. E.; Rubin, R.; Tobias, B.; Hallak, H.; Doherty, A. M. *J. Med. Chem.* **1997**, 40, 1063.

3. Determination of enantiomeric excesses

(±)-1,3-diphenyl-pentan-1-one: Daicel Chiralpak AD, 5.0 μm , 25 cm x 0.46 cm (i.d.), *i*-PrOH/hexanes = 5 : 95, 0.5 mL/min, T_R = 10.86 min and 12.78 min.

(±)-3-(4-chlorophenyl)-1-phenyl-pentan-1-one: Daicel Chiralpak AD, *i*-PrOH/hexanes = 5 : 95, 0.5 mL/min, T_R = 11.60 min and 15.62 min.

(±)-1-(4-chlorophenyl)-3-phenyl-pentan-1-one: Daicel Chiralpak AD, *i*-PrOH/hexanes = 5 : 95, 0.5 mL/min, T_R = 12.22 min and 14.81 min.

(±)-3-(4-methylphenyl)-1-phenyl-pentan-1-one: Daicel Chiralpak AD, *i*-PrOH/hexanes = 5 : 95, 0.5 mL/min, T_R = 10.10 min and 13.37 min.

(±)-1-(4-methylphenyl)-3-phenyl-pentan-1-one: Daicel Chiralpak AD, *i*-PrOH/hexanes = 5 : 95, 0.5 mL/min, T_R = 13.16 min and 18.32 min.

(±)-3-(4-methoxyphenyl)-1-phenyl-pentan-1-one: Daicel Chiralpak AD, *i*-PrOH/hexanes = 5 : 95, 0.5 mL/min, T_R = 13.93 min and 19.54 min.

(±)-1-(4-methoxyphenyl)-3-phenyl-pentan-1-one: Daicel Chiralpak AD, *i*-PrOH/hexanes = 10 : 90, 0.8 mL/min, T_R = 10.14 min and 14.82 min.

(±)-4-phenyl-hexan-2-one: Supelco γ -DEX 225, 30 m x 0.32 mm (i.d.), 110 °C, flow rate 1.0 mL / min, T_R = 25.0 min and 26.2 min.

(±)-4-(4-methyl-phenyl)-hexan-2-one: Supelco γ -DEX 225, 110 °C, flow rate 1.1 mL / min, T_R = 39.9 min and 41.4 min.

(±)-4-(4-methoxyl-phenyl)-hexan-2-one: Supelco γ -DEX 225, 120 °C, flow rate 1.1 mL / min, T_R = 62.7 min and 64.7 min.

(±)-4-(4-chloro-phenyl)-hexan-2-one: Supelco γ -DEX 225, 120 °C, flow rate 0.9 mL / min, T_R = 62.1 min and 64.0 min.

¹H NMR Spectrum of (S)-4a

¹³C NMR Spectrum of (S)-4a

¹H NMR Spectrum of (S)-4b

¹³C NMR Spectrum of (S)-4b

¹H NMR Spectrum of (S)-4c

¹³C NMR Spectrum of (S)-4c

¹H NMR Spectrum of (S)-4d

¹³C NMR Spectrum of (S)-4d

¹H NMR Spectrum of L1

¹³C NMR Spectrum of LI

³¹P NMR Spectrum of L1

¹H NMR Spectrum of L2

¹³C NMR Spectrum of L2

³¹P NMR Spectrum of L2

¹H NMR Spectrum of L3

¹³C NMR Spectrum of L3

³¹P NMR Spectrum of L3

¹H NMR Spectrum of **L4**

¹³C NMR Spectrum of L4

³¹P NMR Spectrum of L4