Supporting Information

Syn-Selective Direct Catalytic Asymmetric Mannich-type Reactions of Hydroxyketones Using $Y\{N(SiMe_3)_2\}_3$ /linked-BINOL Complexes

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Experimental Section

General: Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. NMR spectra were recorded on a JEOL JNM-LA500 spectrometer, operating at 500 MHz for 1H NMR and 125.65 MHz for ^{13}C NMR. Chemical shifts in $CDCl_3$ were reported in the scale relative to $CHCl_3$ (7.26 ppm for 1H NMR) and $CDCl_3$ (77.0 ppm for ^{13}C NMR) as an internal reference. Optical rotations were measured on a JASCO P-1010 polarimeter. ESI mass spectra (for LRMS) were measured on a Waters ZQ4000 spectrometer. FAB mass spectra (for HRMS) were measured on a JEOL JMS-700 spectrometer. Column chromatography was performed with silica gel Merck 60 (230-400 mesh ASTM). The enantiomeric excess (ee) was determined by HPLC analysis (JASCO HPLC systems consisting of the following: pump, PU-2080; detector, UV-2075, measured at 254 nm; column, DAICEL CHIRALCEL OD-H and DAICEL CHIRALPAK AD-H, AS-H). Reactions were carried out in dry solvents under an argon atmosphere, unless otherwise stated. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. $Y\{N(SiMe_3)_2\}_3$ was purchased from Aldrich.

General procedure of Mannich-type reaction (Tables 2 and 3): To a stirred solution of linked-binol **1a** or **1b** (8.8 μ mol, 5.86 mol %) in THF (0.5 mL) at room temperature was added $Y\{N(SiMe_3)_2\}_3$ (8.55 mg, 0.015 mmol, 10 mol %) in THF (1.0 mL). The mixture was stirred at room temperature for 10 min, then THF was removed in vacuo. THF (0.4 mL) was added and cooled to $-20\text{ }^{\circ}\text{C}$. To the mixture solution at $-20\text{ }^{\circ}\text{C}$ were added imine **2** (45.8 mg, 0.15 mmol) and hydroxyketone **3** (20.4 mg, 0.15 mmol) in THF (1.2 mL). The resulting mixture was stirred at $-20\text{ }^{\circ}\text{C}$ for indicated time in Tables and quenched with 1 M HCl. The mixture was extracted with ethyl acetate (x 3). The combined organic layers were washed with brine and dried over Na_2SO_4 . After removing solvent under reduced pressure, the residue was purified by flash silica gel column chromatography to afford Mannich adducts **7**. Diastereomeric ratio of Mannich adducts was determined by ^1H -NMR analysis of the crude mixture before purification. Ee of *syn*-isomer was determined by chiral HPLC analysis.

Relative and absolute configuration of Mannich adducts:

The relative and absolute configuration of Mannich adducts **7ab**, **7ac**, **7ae**, **7ag**, and **7bb** were determined after conversion into dibenzoate **8** as shown in the scheme below. ^1H NMR and sign of optical rotation (+ or $-$) were compared with those of authentic sample prepared from chiral aziridine **10** (ref. S-2: synthesis of chiral aziridine: a) X. L. Jin, H. Sugihara, K. Daikai, H. Takeishi, Y. Z. Jin, H. Furuno, J. Inanaga, *Tetrahedron* **2002**, 58, 8321; b) N. Yamagiwa, S. Matsunaga, M. Shibasaki, *J. Am. Chem. Soc.* **2003**, 125, 16178). **9** was synthesized from aziridine **10** by the reported method in three steps (ref. S-3: a) N. Furukawa, T. Yoshimura, M. Ohtsu, T. Akasaka, S. Oae, *Tetrahedron* **1980**, 36, 73; b) A. Padwa, W. Eisenhardt, *J. Org. Chem.* **1970**, 35, 2472); i) protection with benzoyl group; ii) NaI catalyzed ring opening of aziridine followed by formation of an oxazoline ring; iii) hydrolysis of the oxazoline ring to afford **9**. Protection of the hydroxyl group of **9** with benzoyl chloride afforded **8**. Absolute configurations of **7ac** and **7ad** were determined by Mosher's method. Relative configuration of **7ae** was also confirmed by NOE analysis of corresponding cyclic carbamate.

1,3-Diphenyl-3-(*N*-diphenylphosphinoylamino)-2-triethylsiloxy-propan-1-one (7ab- TES ether):

7ab was purified as TES ether for chiral HPLC analysis, because enantiomers of **7ab** itself was not separable by chiral HPLC.

colorless oil: IR (KBr) ν 566, 696, 725, 749, 939, 987, 1122, 1213, 1409, 1432, 1595, 1696, 2875, 2954 cm⁻¹; ¹H NMR (CDCl₃) δ 0.23-0.36 (m, 6H), 0.66 (t, *J* = 8.0 Hz, 9H), 4.27-4.31 (m, 1H), 4.42-4.46 (m, 1H), 5.13 (brs, 1H), 7.05 (dt, *J* = 3.1, 7.6 Hz, 2H), 7.16-7.28 (m, 8H), 7.34-7.55 (m, 6H), 7.70 (dd, *J* = 7.3, 12.0 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (CDCl₃) δ 4.4, 6.5, 57.7, 79.4, 126.9, 127.5, 128.0, 128.1, 128.2, 128.2, 128.3, 128.5, 128.7, 130.9, 131.4, 131.4, 131.7, 131.7, 131.9, 131.9, 132.1, 132.2, 133.2, 133.3, 135.1, 141.2, 198.4; ESI-MS *m/z* 578 [M+Na]⁺ [α]_D²⁵ +27.7 (*c* 1.39, CHCl₃); HRMS (FAB): *m/z* calcd. for C₃₃H₃₈CsNO₃PSi [M+Cs]⁺: 688.1407; found: 688.1423; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 20/80, flow 0.5 mL/min, detection at 254 nm) *t*_R 9.2 min (minor) and 10.2 min (major).

2-Hydroxy-1-(4-methoxyphenyl)-3-(*N*- diphenylphosphinoylamino)-3-phenylpropan-1-one (7ac):

colorless solid: IR (KBr) ν 1027, 1113, 1184, 1256, 1309, 1437, 1509, 1572, 1604, 1685, 2845, 2927, 3060, 3291 cm⁻¹; ¹H NMR (CDCl₃) δ 3.90 (s, 3H), 3.95 (dd, *J* = 7.6, 11.2 Hz, 1H), 4.48 (d, *J* = 4.5 Hz, 1H), 4.61 (ddd, *J* = 1.8, 8.9, 11.2 Hz, 1H), 5.20 (dd, *J* = 1.8, 4.5 Hz, 1H), 6.94 (d, *J* = 2.2 Hz, 2H), 7.18-7.23 (m, 2H), 7.26-7.38 (m, 8H), 7.41-7.45 (m, 1H), 7.55 (ddd, *J* = 1.2, 8.3, 12.2 Hz, 2H), 7.70

(ddd, $J = 1.3, 8.3, 11.9$ Hz, 2H), 7.92 (d, $J = 8.9$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 55.6, 57.9, 76.8, 114.2, 126.3, 126.8, 127.7, 128.1, 128.2, 128.3, 128.6, 131.2, 131.6, 131.6, 131.8, 131.8, 131.8, 131.9, 132.2, 132.3, 141.5, 141.5, 164.3, 197.3; ESI-MS m/z 494 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{26.9} +15.3$ (c 0.73, CHCl_3); HRMS (FAB): m/z calcd. for $\text{C}_{28}\text{H}_{26}\text{CsNO}_4\text{P}$ $[\text{M}+\text{Cs}]^+$: 604.0648; found: 604.0652; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 50/50, flow 0.3 mL/min, detection at 254 nm) t_{R} 25.4 min (minor) and 30.4 min (major).

2-Hydroxy-1-(4-methylphenyl)-3-(*N*-diphenylphosphinoylamino)-3-phenylpropan-1-

one (7ad): colorless foam: IR (neat) ν 1107, 1181, 1439, 1606, 1685,

2923, 3057, 3342 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.43 (s, 3H), 3.97 (dd, $J =$ 7.6, 11.3 Hz, 1H), 4.48 (brd, $J = 4.6$ Hz, 1H), 4.59-4.63 (m, 1H), 5.22 (brs, 1H), 7.17-7.22 (m, 2H), 7.25-7.75 (m, 10H), 7.40-7.44 (m, 1H),

7.51-7.56 (m, 2H), 7.59-7.64 (m, 2H), 7.82 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 21.7, 57.7, 77.1, 126.8, 127.7, 128.1, 128.2, 128.3, 128.6, 128.9, 129.6, 130.9, 131.2, 131.5, 131.6, 131.8, 131.8, 131.8, 131.9, 132.2, 132.3, 132.6, 141.4, 141.5, 145.1, 198.6; ESI-MS m/z 478 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{26.4} +18.1$ (c 1.11, CHCl_3); HRMS (FAB): m/z calcd. for $\text{C}_{28}\text{H}_{26}\text{CsNO}_3\text{P}$ $[\text{M}+\text{Cs}]^+$: 588.0699; found: 588.0704; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 50/50, flow 0.25 mL/min, detection at 254 nm) t_{R} 31.3 min (minor) and 38.6 min (major).

1-(4-chlorophenyl)-2-hydroxy-3-(*N*-diphenylphosphinoylamino)-

3-phenylpropan-1-one (7ae): colorless solid: IR (KBr) ν 1069, 1089,

1123, 1168, 1243, 1283, 1348, 1399, 1438, 1457, 1490, 1543, 1590, 1678, 1896, 1956, 2854, 2922, 3029, 3057, 3198, 3306 cm^{-1} ; ^1H NMR

(CDCl_3) δ 3.93 (dd, $J = 7.6, 11.0$ Hz, 1H), 4.56-4.61 (m, 2H), 5.19 (dd, $J = 3.1, 3.7$ Hz, 1H), 7.26-7.35 (m, 9H), 7.40-7.45 (m, 4H), 7.58 (d, $J = 7.0$ Hz, 2H), 7.60 (d, $J = 7.0$ Hz, 2H), 7.85 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 57.6, 77.3, 77.4, 126.8, 127.9, 128.3, 128.4, 128.8, 129.2, 130.3, 131.0, 131.4, 131.7, 131.8, 131.9, 131.9, 132.0, 132.1, 132.3, 132.3, 132.4, 140.5, 141.0, 141.0, 197.9; ESI-MS m/z 498 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{27.5} -7.4$ (c 0.25, CHCl_3); HRMS (FAB): m/z calcd. for $\text{C}_{27}\text{H}_{23}\text{ClCsNO}_3\text{P}$ $[\text{M}+\text{Cs}]^+$: 608.0153; found: 608.0156;

HPLC (DAICEL CHIRALPAK OD-H, 2-propanol/hexane 50/50, flow 0.3 mL/min, detection at 254 nm) t_R 14.8 min (minor) and 28.2 min (major).

1-(2-Furyl)-2-hydroxy-3-(*N*-diphenylphosphinoylamino)-3-phenylpropan-1-one (7af):

colorless foam: IR (neat) ν 1179, 1465, 1644, 2922, 3423 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.16 (brs, 1H), 4.08-4.15 (m, 1H), 4.75-4.82 (m, 1H), 5.00 (dd, $J = 0.9, 2.5$ Hz, 1H), 5.54 (dd, $J = 1.5, 3.7$ Hz, 1H), 7.23-7.28 (m, 3H), 7.31-7.47 (m, 9H), 7.52 (dd, $J = 0.7, 1.5$ Hz, 1H), 7.59-7.64 (m, 2H), 7.69-7.75 (m, 2H); ^{13}C NMR (CDCl_3) δ 57.3, 77.9, 112.7, 119.7, 126.9, 127.6, 128.2, 128.4, 128.5, 128.5, 131.7, 131.7, 131.8, 131.9, 131.9, 131.9, 132.3, 132.3, 140.9, 140.9, 141.0, 147.1, 150.5, 187.4; ESI-MS m/z 454 $[\text{M}+\text{Na}]^+$; $[\alpha]_D^{26.8} +67.1$ (c 0.65, CHCl_3); HRMS (FAB): m/z calcd. for $\text{C}_{25}\text{H}_{22}\text{NO}_4\text{P}$ $[\text{M}+\text{Cs}]^+$: 564.0335; found: 564.0334; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 50/50, flow 0.2 mL/min, detection at 254 nm) t_R 32.2 min (minor) and 36.7 min (major).

2-Hydroxy-3-(*N*-diphenylphosphinoylamino)-3-phenyl-1-(2-Thienyl)propan-1-one (7ag):

colorless foam: IR (neat) ν 753, 1107, 1181, 1411, 1438, 1454, 1660, 2921, 3015, 3358 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.73 (brs, 1H), 4.31 (dd, $J = 7.0, 11.0$ Hz, 1H), 4.59-4.66 (m, 1H), 5.00 (dd, $J = 0.9, 3.4$ Hz, 1H), 7.06 (dd, $J = 3.8, 4.8$ Hz, 1H), 7.21-7.38 (m, 10H), 7.41-7.46 (m, 1H), 7.57-7.63 (m, 2H), 7.66-7.77 (m, 4H); ^{13}C NMR (CDCl_3) δ 58.9, 78.7, 127.0, 127.7, 128.2, 128.3, 128.3, 128.4, 128.5, 130.8, 131.4, 131.8, 131.8, 131.9, 131.9, 132.3, 132.4, 133.5, 134.9, 140.3, 140.6, 140.6, 191.9; ESI-MS m/z 470 $[\text{M}+\text{Na}]^+$; $[\alpha]_D^{24.5} +21.7$ (c 0.80, CHCl_3); HRMS (FAB): m/z calcd. for $\text{C}_{25}\text{H}_{22}\text{NO}_3\text{PS}$ $[\text{M}+\text{Cs}]^+$: 580.0107; found: 588.0103; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 50/50, flow 0.3 mL/min, detection at 254 nm) t_R 25.5 min (minor) and 29.2 min (major).

3-(4-Chlorophenyl)-2-hydroxy-3-(*N*-diphenylphosphinoylamino)-1-phenylpropan-1-one (7bb):

colorless foam: IR (neat) ν 1090, 1182, 1316, 1439, 1491, 1686, 2923, 3375 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.01 (dd,

$J = 7.1, 11.0$ Hz, 1H), 4.54-4.59 (m, 2H), 5.20 (dd, $J = 1.2, 2.4$ Hz, 1H), 7.17-7.21 (m, 2H), 7.30-7.36 (m, 7H), 7.43-7.52 (m, 5H), 7.57-7.64 (m, 3H), 7.91 (dd, $J = 1.1, 8.6$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 57.1, 76.9, 128.2, 128.3, 128.4, 128.4, 128.8, 128.8, 129.0, 130.8, 131.4, 131.8, 131.8, 131.9, 131.9, 132.1, 132.2, 132.4, 133.4, 133.6, 134.2, 139.9, 139.9, 198.8; ESI-MS m/z 498, 500 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{24.5} +32.3$ (c 0.59, CHCl_3); HRMS (FAB): m/z calcd. for $\text{C}_{27}\text{H}_{23}^{37}\text{ClCsNO}_3\text{P}$ $[\text{M}+\text{Cs}]^+$: 610.0129; found: 610.0137; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 50/50, flow 0.5 mL/min, detection at 254 nm) t_{R} 15.1 min (minor) and 16.2 min (major).

2-Hydroxy-3-(4-methoxyphenyl)-3-(*N*-diphenylphosphinoylamino)-1-phenylpropan-1-one (7cb): colorless foam: IR (neat) ν 1248, 1439, 1513, 1636, 3436 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.78 (s, 3H), 3.91 (dd, $J = 7.3, 11.0$ Hz, 1H), 4.50 (d, $J = 4.9$

Hz, 1H), 4.53 (ddd, $J = 2.2, 8.9, 11.0$ Hz, 1H), 5.21 (brs, 1H), 6.81-6.85 (m, 2H), 7.15-7.20 (m, 2H), 7.25-7.34 (m, 5H), 7.39-7.45 (m, 3H), 7.50-7.54 (m, 2H), 7.57-7.63 (m, 3H), 7.89 (dd, $J = 1.1, 8.1$ Hz,

2H); ^{13}C NMR (CDCl_3) δ 55.3, 57.2, 77.3, 114.0, 128.0, 128.2, 128.3, 128.4, 128.9, 131.1, 131.4, 131.6, 131.7, 131.8, 131.8, 131.8, 131.9, 132.1, 132.2, 132.3, 132.5, 132.5, 133.5, 133.5, 133.6, 134.0, 159.0, 199.1; ESI-MS m/z 494 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{24.1} +24.5$ (c 0.43, CHCl_3); HRMS (FAB): m/z calcd. for $\text{C}_{28}\text{H}_{26}\text{CsNO}_3\text{P}$ $[\text{M}+\text{Cs}]^+$: 604.0648; found: 604.0652; HPLC (DAICEL CHIRALPAK AS-H, 2-propanol/hexane 50/50, flow 0.5 mL/min, detection at 254 nm) t_{R} 14.5 min (minor) and 19.7 min (major).

3-(2-Furyl)-2-hydroxy-3-(*N*-diphenylphosphinoylamino)-1-phenylpropan-1-one (7db): colorless foam: IR (neat) ν 1095, 1182, 1439, 1594, 1685, 2852, 2921,

3058, 3330 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.79 (dd, $J = 7.4, 10.7$ Hz, 1H), 4.47 (brd, $J = 4.9$ Hz, 1H), 4.67-4.71 (m, 1H), 5.51 (brs, 1H), 6.33-6.34 (m, 1H), 6.50-6.51 (m, 1H), 7.16-7.20 (m, 2H), 7.30-7.33 (m, 1H), 7.36-7.40

(m, 3H), 7.43-7.48 (m, 3H), 7.54-7.61 (m, 3H), 7.70-7.74 (m, 2H), 7.95 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 52.7, 74.7, 74.7, 108.3, 110.7, 128.2, 128.3, 128.4, 128.5, 128.9, 129.0, 130.6, 131.3, 131.7, 131.8, 131.8, 131.9, 132.0, 132.1, 132.2, 132.4, 133.2, 134.2, 142.1,

153.3, 198.6; ESI-MS m/z 454 $[M+Na]^+$ $[\alpha]_D^{25.0} +35.6$ (c 0.20, $CHCl_3$); HRMS (FAB): m/z calcd. for $C_{25}H_{22}CsNO_4P$ $[M+Cs]^+$: 564.0335; found: 564.0326; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 50/50, flow 0.5 mL/min, detection at 254 nm) t_R 16.3 min (minor) and 18.5 min (major).

2-Hydroxy-3-(*N*-diphenylphosphinoylamino)-1-phenyl-3-(2-

Thienyl)propan-1-one (7eb): colorless solid: IR (KBr) ν 945, 1263, 1596, 1685, 2922, 3201 cm^{-1} ; 1H NMR ($CDCl_3$) δ 3.84 (dd, $J = 7.5, 11.1$ Hz, 1H), 4.56 (d, $J = 4.3$ Hz, 1H), 4.91 (ddd, $J = 1.5, 9.5, 11.0$ Hz, 1H), 5.35 (brs, 1H), 6.93 (dd, $J = 3.5, 5.1$ Hz, 1H), 7.02-7.04 (m, 1H), 7.21-7.25 (m, 4H), 7.27-7.31 (m, 2H), 7.34-7.37 (m, 1H), 7.39-7.46 (m, 3H), 7.57-7.61 (m, 1H), 7.89 (d, $J = 1.2, 8.2$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 53.8, 76.9, 125.2, 125.4, 126.8, 128.3, 128.3, 128.4, 128.4, 128.9, 131.0, 131.0, 131.9, 131.9, 131.9, 131.9, 132.0, 132.0, 132.0, 132.1, 132.1, 132.2, 132.3, 134.2, 144.8, 198.3; ESI-MS m/z 470 $[M+Na]^+$ $[\alpha]_D^{25.3} +20.7$ (c 0.54, $CHCl_3$); HRMS (FAB): m/z calcd. for $C_{25}H_{22}CsNO_3PS$ $[M+Cs]^+$: 580.0107; found: 588.0103; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 50/50, flow 0.3 mL/min, detection at 254 nm) t_R 30.7 min (minor) and 33.4 min (major).

4*E*-1,5-Diphenyl-2-hydroxy-3-(*N*-diphenylphosphinoylamino)-4-penten-1-one (7fb):

colorless foam: IR (KBr) ν 725, 1122, 1179, 1438, 1594, 1682, 3229 cm^{-1} ; 1H NMR ($CDCl_3$) δ 3.48-3.60 (m, 1H), 4.18-4.26 (m, 1H), 5.19-5.22 (m, 1H), 6.40 (dd, $J = 6.7, 15.9$ Hz, 1H), 6.50 (d, $J = 15.9$ Hz, 1H), 7.18-7.40 (m, 10H), 7.44-7.49 (m, 3H), 7.55-7.61 (m, 3H), 7.70-7.73 (m, 2H), 7.92 (d, $J = 7.3$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 57.0, 76.2, 126.6, 127.7, 128.1, 128.2, 128.3, 128.4, 128.7, 128.7, 128.8, 131.0, 131.6, 131.6, 131.6, 131.8, 131.8, 131.8, 132.0, 132.1, 132.2, 132.6, 133.7, 134.0, 136.3, 199.3; ESI-MS m/z 490 $[M+Na]^+$ $[\alpha]_D^{25.2} +31.5$ (c 0.30, $CHCl_3$); HRMS (FAB): m/z calcd. for $C_{29}H_{26}CsNO_3P$ $[M+Cs]^+$: 600.0705; found: 600.0705; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 50/50, flow 0.3 mL/min, detection at 254 nm) t_R 24.2 min (minor) and 27.1 min (major).

4E-5-(4-Chlorophenyl)-2-hydroxy-3-(N-

diphenylphosphinoylamino)-1-phenyl-4-penten-1-one (7gb):

colorless foam: IR (KBr) ν 693, 725, 1089, 1107, 1123, 1179, 1438, 1490, 1686, 2924, 3057, 3212 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.60

(dd, $J = 6.1, 10.7$ Hz, 1H), 4.16-4.24 (m 1H), 4.49 (brd, $J = 4.9$ Hz, 1H), 5.19 (brs, 1H), 6.37 (dd, $J = 6.7, 15.9$ Hz, 1H), 6.47 (d, $J = 15.9$ Hz, 1H), 7.15-7.18 (m, 2H), 7.24-7.26 (m, 4H), 7.29-7.37 (m, 3H), 7.42-7.47 (m, 3H), 7.52 (dd, $J = 8.0, 12.2$ Hz, 2H), 7.58-7.62 (m, 1H), 7.70-7.75 (dd, $J = 8.2, 11.9$ Hz, 2H), 7.90 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 56.8, 76.1, 99.9, 127.9, 128.2, 128.3, 128.4, 128.5, 128.6, 128.8, 129.0, 129.5, 129.5, 130.6, 130.8, 131.7, 131.7, 131.8, 131.8, 131.9, 131.9, 132.0, 132.1, 132.1, 132.1, 132.7, 133.4, 133.4, 134.2, 134.8, 134.8, 134.8, 199.1; ESI-MS m/z 524 $[\text{M}+\text{Na}]^+$ $[\alpha]_D^{25.0} +39.5$ (c 1.0, CHCl_3); HRMS (FAB): m/z calcd. for $\text{C}_{29}\text{H}_{25}\text{ClC}_6\text{H}_5\text{NO}_3\text{P}$ $[\text{M}+\text{Cs}]^+$: 634.0309; found: 634.0305; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 50/50, flow 0.5 mL/min, detection at 254 nm) t_R 17.3 min (major) and 24.1 min (minor).

4E-5-(4-Methylphenyl)-3-(N-diphenylphosphinoylamino)-1-phenyl-2-triethylsiloxy-4-penten-1-one (7hb-TES ether): 7hb was purified as TES ether

for chiral HPLC analysis; colorless foam: IR (neat) ν 698, 724, 1122, 1202, 1697, 2875, 2954, 3364 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.53-0.63 (m, 6H), 0.90 (t, $J = 8.0$ Hz, 9H), 2.32 (s, 3H),

3.85-3.92 (m, 1H), 4.05-4.12 (m, 1H), 5.20 (s, 1H), 7.08 (d, $J = 8.1$ Hz, 2H), 7.14-7.20 (m, 4H), 7.29-7.34 (m, 1H), 7.36-7.49 (m, 5H), 7.54-7.60 (m, 3H), 7.81-7.87 (m, 2H), 7.94 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 4.7, 6.7, 21.2, 57.4, 78.5, 126.5, 128.0, 128.0, 128.1, 128.2, 128.3, 128.4, 128.6, 128.7, 129.1, 131.2, 131.4, 131.4, 138.5, 131.5, 131.7, 131.7, 131.9, 132.0, 132.2, 132.3, 132.4, 133.3, 133.5, 133.5, 133.7, 135.3, 137.4, 137.4, 198.6; ESI-MS m/z 618 $[\text{M}+\text{Na}]^+$ $[\alpha]_D^{24.7} +18.2$ (c 0.96, CHCl_3); HRMS (FAB): m/z calcd. for $\text{C}_{36}\text{H}_{42}\text{CsNO}_3\text{PSi}$ $[\text{M}+\text{Cs}]^+$: 728.1720; found: 728.1722; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 10/90, flow 1 mL/min, detection at 254 nm) t_R 13.0 min (minor) and 14.8 min (major).

4E-5-Furyl-3-(N-diphenylphosphinoylamino)-1-phenyl-2-triethylsiloxy-4-penten-1-one

(7ib-TES ether): **7ib** was purified as TES ether for chiral HPLC analysis; colorless foam: IR (neat) ν 1123, 1438, 1696, 2876, 2956 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.56 (m, 6H) 0.86 (t, J = 8.0 Hz, 9H), 2.32 (s, 3H), 3.85 (dd, J = 7.5, 10.3 Hz, 1H), 4.04 (m, 1H), 5.31 (brs, 1H), 6.20 (d, J = 3.4 Hz, 1H), 6.26 (dd, J = 6.3, 16.0 Hz, 1H), 6.32 (dd, J = 1.7, 3.4 Hz, 1H), 6.42 (d, J = 16.0 Hz, 1H), 7.10-7.15 (m, 2H), 7.25-7.30 (m, 2H), 7.36-7.47 (m, 5H), 7.50-7.58 (m, 3H), 7.81-7.86 (m, 2H), 7.90 (d, J = 7.4 Hz, 2H); ^{13}C NMR (CDCl_3) δ 4.7, 6.6, 56.8, 78.1, 108.3, 111.2, 120.3, 127.7, 128.1, 128.2, 128.4, 128.5, 128.6, 128.7, 130.9, 131.4, 131.5, 131.8, 131.8, 131.9, 131.9, 132.2, 132.3, 132.3, 133.3, 133.4, 135.1, 152.2, 198.4; ESI-MS m/z 594 $[\text{M}+\text{Na}]^{+}$; $[\alpha]_{\text{D}}^{22.6}$ +31.2 (c 0.41, CHCl_3); HRMS (FAB): m/z calcd. for $\text{C}_{33}\text{H}_{38}\text{CsNO}_4\text{PSi}$ $[\text{M}+\text{Cs}]^{+}$: 704.1357; found: 704.1352; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) t_{R} 5.3 min (minor) and 9.6 min (major).

<Synthesis of ligand 1b> Harada, S.; Handa, S.; Matsunaga, S.; Shibasaki, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4365.

Reagents and conditions: a) 1. BuLi (1.1 equiv), TMEDA (1.2 equiv), THF, 0 °C, 1 h; then DMF (1.05 equiv), -78 °C, 3 h; 2. NaBH₄ (1.0 mol equiv), THF/MeOH, 0 °C, 30 min, 76% (2 steps); b) Ms₂O (1.5 equiv), *i*Pr₂NEt (1.6 equiv), 25 °C, 1 h; then LiBr (5 equiv), DMF, 0 °C, 10 h, 99%; c) **B** (1.0 equiv), NaH (1.2 equiv), 25 °C, 3.5 h, 89%; d) *p*TsOH•H₂O (0.2 equiv), CH₂Cl₂/MeOH, 35 °C, 14 h, 66%.

ref. S-1: Yamashita, Y.; Ishitani, H.; Shimizu, H.; Kobayashi, S. *J. Am. Chem. Soc.* **2002**, *124*, 3292.

3-Hydroxymethyl-2,2'-bis(methoxymethoxy)-6,6'-bis(trimethylsilyl)-1,1'-binaphthalene (**B**):

To a solution of **A** (16.1 g, 31.1 mmol) in THF (310 mL) at -78 °C were added TMEDA (5.63 mL, 37.3 mmol) and BuLi (21.9 mL, 34.2

mmol, 1.56 M in hexane). The mixture was stirred for 1 h at 0 °C. Then DMF (2.53 mL, 32.6 mmol) was added at -78 °C. After stirring for 3 h at -78 °C, sat. *aq.* NH₄Cl was added. The mixture was extracted with ethyl acetate. The organic layer was washed with brine and was dried over Na₂SO₄. After evaporation under reduced pressure, the residue was used in the next step without purification. To a solution of the crude mixture in THF (194 mL) and MeOH (75 mL) at 0 °C was added NaBH₄ (1.18 mg, 31.1 mmol). After 30 min stirring at the same temperature, H₂O was added. The mixture was extracted with diethyl ether. The organic layer was washed with brine and was dried over Na₂SO₄. After evaporation under reduced pressure, the residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 4/1) to give **B** (13.0 g, 23.7 mmol, yield 76 %) as colorless foam; IR (neat) ν 1150, 1250, 1470, 1620, 3450 cm⁻¹; ¹H NMR (CDCl₃) δ 0.29 (s, 18H), 3.18 (s, 3H), 3.27 (s, 1H), 3.48 (dd, *J* = 6.7, 6.7 Hz, 1H), 4.48 (d, *J* = 6.1 Hz, 1H), 4.69 (d, *J* = 6.1 Hz, 1H), 4.89 (dd, *J* = 6.4, 12.2 Hz, 1H), 4.94 (dd, *J* = 6.4, 12.2 Hz, 1H), 5.05 (d, *J* = 7.0 Hz, 1H), 5.10 (d, *J* = 7.0 Hz, 1H), 7.10 (d, *J* = 8.6 Hz, 1H), 7.12 (d, *J* = 9.1 Hz, 1H), 7.34 (dd, *J* = 1.0, 8.3 Hz, 1H), 7.37 (dd, *J* = 1.0, 7.6 Hz, 1H), 7.98 (s, 1H), 7.98 (d, *J* = 9.2 Hz, 1H), 8.03 (brs, 1H), 8.05 (brs, 1H); ¹³C NMR (CDCl₃) δ -1.2, -1.1, 56.0, 57.2, 62.1, 94.9, 99.4, 116.3, 120.2, 124.2, 124.6, 125.2, 129.2, 129.3, 130.2, 130.3, 130.5, 130.9, 133.8, 133.8, 133.9, 134.2, 135.8, 136.9, 153.0, 153.5; ESI-MS *m/z* 571 [M+Na]⁺; [α]_D^{24.5} +5.76 (*c* 1.91, CDCl₃); HRMS (FAB): *m/z* calcd. for C₃₁H₄₁O₅Si₂ [M+H]⁺: 549.2496; found: 549.2493.

3-Bromomethyl-2,2'-bis(methoxymethoxy)-6,6'-bis(trimethylsilyl)-1,1'-binaphthalene (C):

To a solution of **C** (549 mg, 1.00 mmol) in CH₂Cl₂ (10 mL) at 0 °C were added diisopropyl ethyl amine (207 mg, 1.60 mmol) and mesyl anhydride (261 mg, 1.50 mmol). After stirring for 1 h at the same temperature, LiBr (434 mg, 5.00 mmol) and DMF (2 mL) were added

at 0 °C. After stirring for 10 h at 0 °C, H₂O was added. The mixture was extracted with CH₂Cl₂. The organic layer was washed with H₂O and brine. Then the organic layer was dried over Na₂SO₄. After evaporation under reduced pressure, the residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 4/1) to give **C** (608 mg,

0.99 mmol, yield 99 %) as pale yellow foam; IR (neat) ν 1150, 1250, 1470, 1620, 3410 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.33 (s, 18H), 3.03 (s, 3H), 3.18 (s, 3H), 4.58 (d, J = 5.8 Hz, 1H), 4.68 (d, J = 5.8 Hz, 1H), 4.98 (s, 2H), 5.07 (d, J = 7.0 Hz, 1H), 5.10 (d, J = 7.0 Hz, 1H), 7.11, (d, J = 8.6 Hz, 1H), 7.13 (d, J = 8.6 Hz, 1H), 7.35 (dd, J = 1.1, 8.6 Hz, 1H), 7.38 (dd, J = 1.1, 8.6 Hz, 1H), 7.58 (d, J = 9.1 Hz, 1H), 8.01 (s, 1H), 8.04 (s, 1H), 8.09 (s, 1H); ^{13}C NMR (CDCl_3) δ -1.1, -1.1, 42.6, 56.0, 56.9, 94.9, 99.5, 116.3, 120.0, 124.3, 124.7, 125.7, 129.2, 130.2, 130.2, 130.8, 131.0, 131.2, 133.8, 134.1, 134.4, 135.8, 137.2, 152.4, 153.2; ESI-MS m/z 633 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{24.4}$ +2.50 (c 0.40, CHCl_3); HRMS (FAB): m/z calcd. for $\text{C}_{31}\text{H}_{39}\text{O}_4\text{BrSi}_2$ $[\text{M}^+]$: 610.1570; found: 610.1562.

(*S,S*)-3,3''-[Oxybis(methylene)]-bis-[2,2'-bis(methoxymethoxy)-6,6'-bis(trimethylsilyl)-1,1'-bi-2-naphthalene] (D):

To a solution of **B** (474 mg, 0.863 mmol) in DMF (8.7 mL) at 0 °C was added NaH (24.9 mg, 1.04 mmol). After stirring for 30 min at the same temperature, **C** (528 mg, 0.863 mmol) was added. The mixture was stirred for 3.5

h at room temperature. Then sat. *aq.* NH_4Cl was added. The mixture was extracted with diethyl ether. The organic layer was washed with brine and was dried over Na_2SO_4 . After evaporation under reduced pressure, the residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 4/1) to give **D** (828 mg, 0.767 mmol, yield 89 %) as pale yellow foam; IR (neat) ν 1160, 1250, 1470, 1620, 3450 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.29 (s, 36H), 2.90 (s, 6H), 3.18 (s, 6H), 4.61 (d, J = 5.5 Hz, 2H), 4.70 (d, J = 5.5 Hz, 2H), 5.05 (d, J = 7.0 Hz, 2H), 5.10 (brs, 4H), 5.11 (d, J = 7.0 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 7.17 (d, J = 8.3 Hz, 2H), 7.34 (dd, J = 1.0, 8.3 Hz, 2H), 7.38 (dd, J = 1.3, 8.3 Hz, 2H), 7.59 (d, J = 9.2 Hz, 2H), 7.97 (d, J = 9.2 Hz, 2H), 8.01 (brs, 2H), 8.09 (brs, 2H), 8.21 (s, 2H); ^{13}C NMR (CDCl_3) δ -1.1, -1.1, 56.0, 56.6, 68.7, 94.9, 99.4, 116.6, 120.5, 124.5, 124.7, 125.0, 128.5, 129.2, 130.0, 130.0, 130.4, 130.8, 131.9, 133.7, 133.7, 133.9, 134.2, 135.6, 136.6, 152.2, 153.2; $[\alpha]_{\text{D}}^{24.3}$ -2.87 (c 1.40, CHCl_3); ESI-MS m/z 1101 $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd. for $\text{C}_{62}\text{H}_{78}\text{O}_9\text{Si}_4\text{Cs}$ $[\text{M}+\text{Cs}]^+$: 1211.3778; found: 1211.3787.

(*S,S*)-3,3''-[Oxybis(methylene)]-bis-[6,6'-bis(trimethylsilyl)-1,1'-bi-2-naphthol] (1b**):**

To a solution of **D** (786 mg, 0.728 mmol) in CH₂Cl₂ (7.5 mL) and MeOH (7.5 mL) at room temperature was added *p*-toluenesulfonic acid monohydrate (28 mg, 0.146 mmol). After stirring for 14 h at 35 °C, sat. *aq.* NaHCO₃ was

added. The mixture was extracted with ethyl acetate. The organic layer was washed with brine and was dried over Na₂SO₄. After evaporation under reduced pressure, the residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 10/1) to give **1b** (433mg, 0.479 mmol, yield 66 %) as pale yellow foam; IR (neat) ν 1250, 1470, 1620, 3410, 3530 cm⁻¹; ¹H NMR (CDCl₃) δ 0.29 (s, 36H), 4.98 (s, 2H), 5.03 (d, *J*= 12.7 Hz, 2H), 5.09 (d, *J*= 12.7 Hz, 2H), 6.29 (s, 2H), 7.10 (d, *J*= 8.2 Hz, 2H), 7.12 (d, *J*= 8.2 Hz, 2H), 7.32 (d, *J*= 8.9 Hz, 2H), 7.38 (dd, *J*= 1.2, 8.3 Hz, 2H), 7.40 (dd, *J*= 1.3, 8.2 Hz, 2H), 7.94 (d, *J*= 8.9 Hz, 2H), 8.00 (brs, 2H), 8.02 (brs, 2H), 8.03 (s, 2H); ¹³C NMR (CDCl₃) δ -1.1, -1.1, 70.1, 111.8, 112.1, 117.6, 123.4, 123.4, 125.4, 128.5, 128.8, 130.21, 131.1, 131.3, 131.5, 133.6, 133.7, 134.1, 134.2, 135.2, 136.0, 152.1, 152.5; ESI-MS *m/z* 925 [M+Na]⁺; [α]_D^{24.4} +24.2 (*c* 0.92, CHCl₃); HRMS (FAB): *m/z* calcd. for C₅₄H₆₂O₅Si₄ [M⁺]: 902.3674; found: 902.3663.

S-15

1H Line

157.28
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141.522
141.497
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132.194
131.906
131.832
131.807
131.783
131.602
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INIWT : 1000.0000 msec
RESOL : 1.03 Hz
PW1 : 6.25 usec
OBNUC : ¹³C
OBFRQ : 125.65 MHz
OBSET : 127958.00 Hz
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IRFRQ : 500.00 MHz
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IRRNS : 0

SCANS : 1024 times

SLVNT : CDCL3
SPINNING : 13 Hz
TEMP : 27.8 C

7af

Date : Tue Jul 26 12:22:39 2005

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INIWT : 1000.0000 msec
RESOL : 1.03 Hz
PWI : 6.25 usec
13C :
OBNUC : 125.55 MHz
OBFRQ : 127958.00 Hz
OBSET : 30
RGAIN : 1H
IRNUC : 500.00 MHz
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SLVNT : CDCL3
SPINNING : 12 Hz
TEMP : 28.5 C

7bb

DFILE
COMNT
DAFIM
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EXMOD
OBFRO
OBSET
OBFIN
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SCANS
ACQTM
PD
PW1
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CTEMP
SLVNT
EXREF
BF
RGAIN

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0.12 Hz
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S-21

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OBSET
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POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

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33898.3 Hz
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0.12 Hz
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S-22

7db

DFILE
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EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

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0.12 Hz
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7eb

13C

Date : Thu Jun 30 22:21:47 2005

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 PREDL 0.01000 msec
 INIWT 1000.0000 msec
 RESOL 1.03 Hz
 PW1 6.25 usec
 13C
 OBNUC 125.65 MHz
 OBFREQ 127958.00 Hz
 OBSET 30
 RGAIN
 IRNUC 500.00 MHz
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 IRAPW 50.0 usec
 IRRNS 0
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SLVNT : CDCL3
 SPINNING 11 Hz
 TEMP 27.9 C

7fb

S-24

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single pulse decoupled gated NOE

DFILE
COMNT
DATIM
OENUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
FW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

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13C
single pu
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PPM

0

50

100

150

200

S-25

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RGAIN 58

S-26

DFILE C:\My Doc
COMNT single pu
DATIM 23-08-20
OENUC 13C
EXMOD single pu
OBFRO 124.
OBFIN 3
POINT 32
FREQU 3906.
SCANS 4
ACQTM 0.8
PD 2.0
FWI 1H
IRNUC 2
CTEMP CDCL3
SLVNT 77.
EXREF BF
RGAIN 0