Supporting Information

Heterobimetallic Catalysis in Asymmetric 1,4-Addition of *O*-Alkylhydroxylamine to Enones

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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 ^{1}H NMR and 125.65 MHz for ^{13}C NMR. Chemical shifts in $CDCl_3$ were reported in the scale relative to $CHCl_3$ (7.24 ppm for ^{1}H 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, 880-PU or PU-980; detector, 875-UV or UV-970, measured at 254 nm; column, DAICEL CHIRALCEL OD, OD-H, OJ, OJ-H and DAICEL CHIRALPAK AD, AS, 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. $Y[N\{Si(CH_3)_3\}_2]_3$ was purchased from Aldrich Co. Ltd. The chiral ligand, (*S*)-1,1'-binaphth-2,2'-ol [(*S*)-BINOL], was recrystallized from diethylether and hexane before use. A hexanes solution of *n*-butyllithium (1.6 M) was purchased from Aldrich Co. Ltd. The nucleophile **3a** was prepared from *O*-methylhydroxylamine hydrochloride, which was purchased from Tokyo Chemical Industry (TCI). DRIERITE® (10–20 mesh, W. A. Hammond drierite company Ltd.) was purchased from Aldrich Co. Ltd and Wako Junyaku and grinded to powder before use. The *O*-benzylhydroxylamine (**3b**) THF solution was prepared using reported method [see, ref 3b in text].

Procedure for Preparation of the (*S*)-YLi_3[tris(binaphthoxide)] Complex [(*S*)-YLB 1a]:

To a stirred solution of (*S*)-BINOL (1.237 g, 4.32 mmol) in THF (20 mL) at 0 °C, was added BuLi (2.72 mL, 4.32 mmol, 1.59 M in hexanes). To the resulting suspended mixture was added a solution of $Y[N\{Si(CH_3)_3\}_2]_3$ (820 mg, 1.44 mmol) in THF (20 mL). After stirring for 10 min at room temperature, the solvent was removed under reduced pressure. The residue was dissolved in THF (24 mL) to give (*S*)-YLB solution (60 mM, in THF).

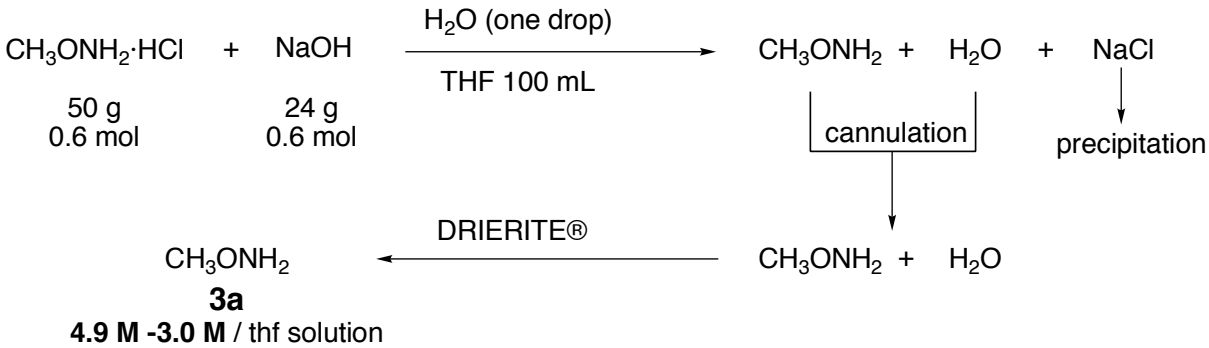
Procedure for Preparation of the (*S*)-YK_3[tris(binaphthoxide)] Complex [(*S*)-YPB 1b] :

(S)-YPB (**1b**) was prepared using same procedure used in preparation of (*S*)-YLB by changing *n*-butyllithium to potassium hexamethyldisilazide (KHMDS, 0.5 M in toluene). KHMDS solution was purchased from Aldrich Co. Ltd.

Procedure for Preparation of *O*-Methylhydroxylamine (3a) THF solution:

To *O*-methylhydroxylamine hydrochloride (50 g, 0.6 mol) and NaOH (24 g, 0.6 mol) in a round bottom flask equipped with stirring bar, tetrahydrofuran (100 mL) and a drop of water (ca. 3 μL) were added. The mixture was vigorously stirred for 12 h. Then the supernatant was transferred to another dried flask via a syringe to remove precipitated NaCl (Final conc. of **3a** ranged from 4.9 M–3.0 M depending on this step), and DRIERITE® (163 g) was added to the mixture. After vigorous stirring for 5 h, the supernatant was again transferred to another dried flask via a syringe. The remained precipitate was washed with THF (10 mL x 2). The collected THF solution (supernatant and washings) included free *O*-methylhydroxylamine (**3a**). The concentration of the *O*-methylhydroxylamine tetrahydrofuran solution was determined by NMR spectra; comparing the integral area of methyl group of *O*-methylhydroxylamine (**3a**) (3.33 ppm in $CDCl_3$) and methyl group of 1,3,5-trimethylbenzene (2.07 ppm in $CDCl_3$), which was added as an internal standard.

Figure : Preparation of free *O*-methylhydroxylamine (**3a**) /thf solution



Representative Procedure for Catalytic Asymmetric Conjugate Addition of *O*-Methylhydroxylamine (3a) to α,β-Unsaturated Ketone (2):

Procedure A (YLB 3 mol %: [enone 2] = 1.1 M)

To a mixture of chalcone (**2a**) (312 mg, 1.5 mmol) and grinded DRIERITE® (200 mg) in a dried test tube at room temperature, a THF solution of (*S*)-YLB (60 mM in THF, 0.75 mL, 0.045 mmol) was added. The orange-colored mixture was stirred at same temperature until **2a** dissolved. The mixture was cooled to –20 °C, and then a THF solution of *O*-methylhydroxylamine (**3a**) (3.0 M, 0.6 mL, 1.8 mmol) was added. After stirring for 42 h, small amount of acetaldehyde (ca. 30 μL) was added to trap the excess **3a**. The reaction mixture was diluted with diethyl ether (10 mL) and washed with water (5 mL x 3), brine (5 mL) and dried with Na_2SO_4. After removing the solvent, the residue was subjected on silica gel flash column chromatography [SiO_2, hexane/ether = 10/1 (to separate **2a** and **4a**) then hexane/acetone = 10/1 (to separate **4a** and BINOL)] to give (*S*)-3-(methoxyamino)-1,3-diphenyl-1-propanone (**4a**) (371 mg, 97% yield, 95% ee).

Procedure B (YLB 1 mol %: [enone 2] = 2.5 M)

Reaction procedure was same as shown in procedure A, except for concentration [2.5 M], and scale of reagents: **2a** (1.25 g, 6.00 mmol), DRIERITE® (500 mg), **3a** (4.88 M, 1.4 mL, 6.6 mmol) and (*S*)-YLB (60 mM in THF, 1 mL, 0.06 mmol). **4a** was obtained in 95% yield and 96% ee after 48 h.

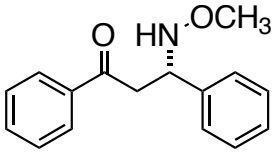
Procedure C (YLB 0.5 mol %: [enone 2] = 2.1 M)

Reaction procedure was same as shown in procedure A, except for concentration [2.1 M], and scale of reagents: **2a** (1.25 g, 6.00 mmol), DRIERITE® (500 mg), **3a** (3.0 M, 2.4 mL, 7.2 mmol) and (*S*)-YLB (60 mM in THF, 0.5 mL, 0.03 mmol). **4a** was obtained in 96% yield and 96% ee after 80 h.

Procedure D (YLB 1 mol %: [enone 2] = 2.1 M, 10 gram scale)

Reaction procedure was same shown in procedure A, except for reaction time (48 h), concentration [2.1 M], and scale of reagents: **2a** (10 g, 48 mmol), DRIERITE® (5.0 g), **3a** (3.9 M, 14.8 mL, 57.6 mmol) and (*S*)-YLB (60 mM in THF, 8.0 mL, 0.48 mmol). **4a** was obtained in 98% yield and 95% ee after 48 h.

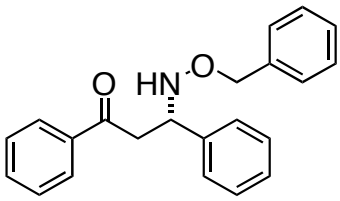
(*S*)-3-(Methoxyamino)-1,3-diphenyl-1-propanone (4a):



Colorless oil, IR (neat) ν 700, 749, 1001, 1206, 1275, 1448, 1682, 2597, 2936 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.29 (dd, *J* = 5.2 Hz, 17.2 Hz, 1H), 3.39 (s, 3H), 3.49 (dd, *J* = 8.0 Hz, 17.2 Hz, 1H), 4.66 (dd, *J* = 5.2 Hz, 8.0 Hz, 1H), 6.16 (s, 1H), 7.25-7.28 (m, 1H), 7.32-7.35 (m, 2H), 7.41-7.44 (m, 4H), 7.52-7.55 (m, 1H), 7.90-7.92 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 42.60, 60.99, 62.18, 127.54, 127.66, 128.02, 128.47, 128.56, 133.20, 136.76, 140.97, 198.33; LRMS (ESI, methanol) *m/z* 277.7 $[M+Na]^+$; HRMS (FAB) *m/z* 256.1334 $[M+H^+]$ calcd. for $C_{16}H_{18}NO_2$ = 256.1332; $[\alpha]_D^{23}$ –29.1 (*c* 1.00 , $CHCl_3$) (95% ee) [lit $[\alpha]_D^{23}$ –9.5 (*c* 1.00 , $CHCl_3$) 50% ee (*S*)]; HPLC condition DAICEL CHIRALCEL OD, hexane: 2-propanol = 19:1, flow rate = 0.5 mL/min, retention time 20.9 min (*S*) / 26.1 min (*R*).

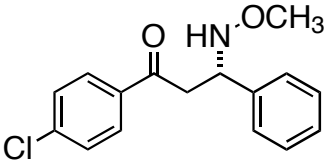
(Lit. Jin, X.-L.; Sugihara, H.; Daikai, K.; Takeishi, H.; Jin, Y.-Z.; Furuno, H.; Inanaga, J. *Tetrahedron* **2002**, *58*, 8321.)

(*S*)-3-(Benzyloxyamino)-1,3-diphenyl-1-propanone :



colorless oil; IR (neat) ν 698, 748, 1001, 1205, 1275, 1363, 1449, 1682, 2911, 3030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.21 (dd, *J* = 4.9 Hz, 17.1 Hz, 1H), 3.41 (dd, *J* = 8.2 Hz, 17.1 Hz, 1H), 4.45 (d, *J* = 11.6 Hz, 1H), 4.48 (d, *J* = 11.6 Hz, 1H), 4.63 (dd, *J* = 4.9 Hz, 8.2 Hz, 1H), 6.10 (brs, 1H), 7.11–7.12 (m, 2H), 7.17–7.22 (m, 4H), 7.25–7.28 (m, 2H), 7.33–7.37 (m, 4H), 7.44–7.48 (m, 1H), 7.80–7.82 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 42.66, 61.17, 76.54, 127.70, 127.76, 128.06, 128.25, 128.45, 128.45, 128.54, 133.17, 136.79, 137.63, 141.03, 198.30; LRMS (ESI, methanol) *m/z* 354.0 $[M+Na]^+$; HRMS (FAB) *m/z* 332.1642 $[M+H^+]$ calcd. for $C_{22}H_{22}NO_2$ = 332.1645; $[\alpha]_D^{24}$ –13.8 (*c* 1.00 , $CHCl_3$) (91% ee); HPLC condition DAICEL CHIRALCEL OJ-H, hexane:2-propanol = 4:1, flow rate = 1.0 mL/min, retention time 20.2 min (*R*) / 25.6 min (*S*). Absolute configuration was determined after transformation to 2-benzoyl-1-phenylaziridine (**5**) by treating with NaO-*t*-Bu. The spectrum data of **5** was shown in later section of this supporting information.

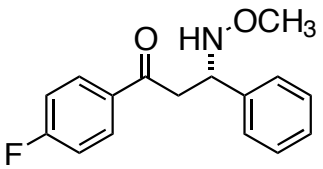
1-(4-Chlorophenyl)-3-(methoxyamino)-3-phenyl-1-propanone (4b):



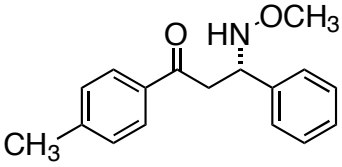
colorless oil; IR (neat) ν 527, 700, 759, 836, 1012, 1683, 1092, 1204, 1275, 1399, 1589, 2936 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.24 (dd, *J* = 17.0 Hz, 5.2 Hz, 1H), 3.39 (s, 3H), 3.47 (dd, *J* = 17.0 Hz, 8.0 Hz, 1H), 4.65 (dd, *J* = 8.0 Hz, 5.2 Hz, 1H), 6.11 (s, 1H), 7.25-7.28 (m, 1H), 7.31-7.34 (m, 2H), 7.38-7.41 (m, 4H), 7.83-7.85 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 42.58, 60.99, 62.15, 127.48, 127.73, 128.48, 128.83, 129.41, 135.07, 139.57, 140.66, 197.04; LRMS (ESI, methanol) *m/z* 313.9, 311.9 $[M+Na]^+$; HRMS (FAB) *m/z* 290.0950 $[M+H^+]$ calcd. for $C_{16}H_{17}ClNO_2$ = 290.0942; $[\alpha]_D^{24}$ –24.8 (*c* 0.19 , $CHCl_3$) (95% ee) HPLC, DAICEL CHIRALPAK AD-H, hexane:2-propanol = 19:1, flow rate = 1.0 mL/min, retention time 20.4 min (major) /22.5 min (minor).

1-(4-Fluorophenyl)-3-(methoxyamino)-3-phenyl-1-propanone (4c):

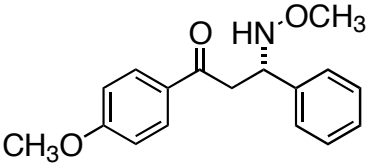
colorless oil; IR (neat) ν 577, 701, 763, 841, 989, 1157, 1205, 1229, 1410, 1507, 1597, 1683, 2937 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.25 (dd, J = 5.0 Hz, 17.1 Hz, 1H), 3.39 (s, 3H), 3.48 (dd, J = 7.9 Hz, 17.1 Hz, 1H), 4.64 (dd, J = 5.0 Hz, 7.9 Hz, 1H), 6.12 (brs, 1H), 7.07-7.11 (m, 2H), 7.25–7.28 (m, 1H), 7.31–7.34 (m, 2H), 7.39–7.42 (m, 2H), 7.93-7.95 (m 2H); ^{13}C NMR ($CDCl_3$) δ 42.58, 61.07, 62.26, 115.72 (d, $J_{C\text{-}F}$ = 21.6 Hz), 127.55, 127.79, 128.55, 130.73 (d, $J_{C\text{-}F}$= 9.4 Hz), 133.25 (d, $J_{C\text{-}F}$ = 2.0 Hz), 140.81, 165.3 (d, $J_{C\text{-}F}$ = 255.3 Hz), 196.76; LRMS (ESI, methanol) m/z 295.9 $[M+Na]^+$; HRMS (FAB) m/z 274.1246 $[M+H^+]$ calcd. for $C_{16}H_{17}FNO_2$ = 274.1238; $[\alpha]_D^{23}$ –26.9 (c 1.2 , $CHCl_3$) (96% ee) HPLC, DAICEL CHIRALPAK AD-H, hexane:2-propanol = 49:1, flow rate = 1.0 mL/min, retention time 29.3 min (minor) /31.5 min (major).



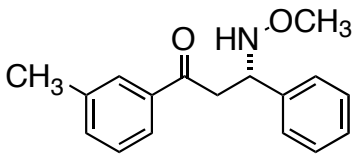
1-(4-Methylphenyl)-3-(methoxyamino)-3-phenyl-1-propanone (4d):
colorless oil; IR (neat) ν 578, 700, 764, 877, 997, 1181, 1202 1276, 1455, 1606, 1678, 2933 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.38 (s, 3H), 3.26 (dd, J = 4.9 Hz, 17.1 Hz, 1H), 3.39 (s, 3H), 3.44 (dd, J = 8.2 Hz, 17.1 Hz, 1H), 4.64 (dd, J = 4.9 Hz, 8.2 Hz, 1H), 6.19 (brs, 1H), 7.21-7.28 (m, 3H), 7.31-7.34 (m, 2H), 7.41-7.43 (m, 2H), 7.81-7.82 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.54, 42.44, 60.99, 62.12, 127.51, 127.6, 128.12, 128.39, 129.20, 134.29, 141.15, 143.97, 197.88; LRMS (ESI, methanol) m/z 291.9 $[M+Na]^+$; HRMS (FAB) m/z 270.1489 $[M+H^+]$ calcd. for $C_{17}H_{20}NO_2$ = 270.1489; $[\alpha]_D^{25}$ –32.1 (c 1.12 , $CHCl_3$) (94% ee); HPLC, DAICEL CHIRALCEL OD-H, hexane:2-propanol = 19:1, flow rate = 1.0 mL/min, retention time 7.6 min (major) /9.5 min (minor).



3-(Methoxyamino)-1-(4-methoxyphenyl)-3-phenyl-1-propanone (4e):
colorless solid; IR (KBr) ν 580, 7001, 762, 837, 1027, 1171, 1211, 1261, 1511, 1600, 1671, 2936 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.23 (dd, J = 4.9 Hz, 17.1 Hz, 1H), 3.38 (s, 3H), 3.41 (dd, J = 8.2 Hz, 17.1 Hz, 1H), 3.84 (s, 3H) 4.64 (dd, J = 4.9 Hz, 8.2 Hz, 1H), 6.21 (s, 1H), 6.88–6.91 (m, 2H), 7.25–7.27 (m, 1H), 7.31–7.34 (m, 2H), 7.31–7.43 (m, 2H), 7.89–7.91 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 42.23, 55.45, 61.09, 62.22, 113.72, 127.56, 127.60, 128.46, 129.87, 130.36, 141.28, 163.59, 196.83; LRMS (ESI, methanol) m/z 308.0 $[M+Na]^+$; HRMS (FAB) m/z 286.1448 $[M+H^+]$ calcd. for $C_{17}H_{20}NO_3$ = 286.1438; $[\alpha]_D^{23}$ –27.8 (c 2.650 , $CHCl_3$) (91% ee); HPLC DAICEL CHIRALPAK AD-H, hexane:2-propanol = 19:1, flow rate = 1.0 mL/min, retention time 36.2 min (major) /53.0 min (minor)

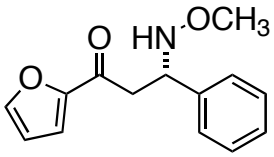


3-(Methoxyamino)-1-(3-methylphenyl)-3-phenyl-1-propanone (4f):
colorless oil; IR (neat) ν 700, 763, 999, 1160, 1278, 1455, 1682, 2932 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.37 (s, 3H) 3.27 (dd, J = 4.9 Hz, 17.4 Hz, 1H), 3.39 (s, 3H), 3.47 (dd, J = 8.3 Hz, 17.4 Hz, 1H), 4.65 (dd, J = 4.9 Hz, 8.3 Hz, 1H), 6.17 (brs, 1H), 7.24-7.36 (m, 5H), 7.43 (d, J = 7.9 Hz, 2H), 7.70- 7.72 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.29, 42.68, 61.02, 62.18,



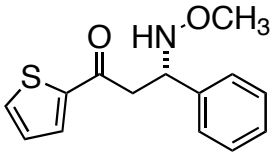
125.27, 127.56, 127.63, 128.19, 128.46, 128.57, 133.96, 136.84, 138.37, 141.13, 198.52; LRMS (ESI, methanol) *m/z* 292.0 [M+Na]$^+$; HRMS (FAB) *m/z* 270.1502 [M+H$^+$] calcd. for $C_{17}H_{20}NO_2$ = 270.1489; $[\alpha]_D^{25}$ –25.0 (*c* 1.13, $CHCl_3$) (92% ee) HPLC, DAICEL CHIRALCEL OD-H, hexane:2-propanol = 19:1, flow rate = 1.0 mL/min, retention time 6.9 min (major) /7.9 min (minor).

1-(2-Furyl)-3-(methoxyamino)-3-phenyl-1-propanone (4g):



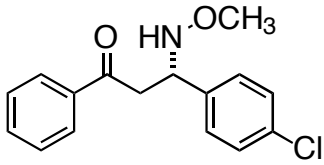
colorless oil; IR (neat) ν 596, 701, 763, 838, 883, 916, 1010, 1084, 1158, 1284, 1394, 1468, 1568, 1671, 2809, 2937 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ3.11 (dd, *J* = 5.2 Hz, 16.5 Hz, 1H), 3.31 (dd, *J* = 8.3 Hz, 16.5 Hz, 1H), 3.36 (s, 3H), 4.60 (dd, *J* = 5.2 Hz, 8.3 Hz, 1H), 6.05 (brs, 1H), 6.46-6.47 (m, 1H), 7.12 (d, *J* = 3.7 Hz, 1H), 7.22-7.24 (m, 1H), 7.28–7.31 (m, 2H), 7.36–7.38 (m, 2H) 7.52 (brs, 1H); ^{13}C NMR ($CDCl_3$) δ42.52, 60.98, 62.17, 112.28, 117.28, 127.51, 127.74, 128.48, 140.65, 146.46, 152.61, 187.22; LRMS (ESI, methanol) *m/z* 267.8 [M+Na]$^+$; HRMS (FAB) *m/z* 246.1123 [M+H$^+$] calcd. for $C_{14}H_{16}NO_3$ = 246.1125; $[\alpha]_D^{23}$ –28.3 (*c* 1.075, $CHCl_3$) (94% ee) HPLC, DAICEL CHIRALCEL OD-H, hexane:2-propanol = 19:1, flow rate = 0.5 mL/min, retention time 27.6 min (minor) /29.3 min (major).

3-(Methoxyamino)-3-phenyl-1-(2-thienyl)-1-propanone (4h):



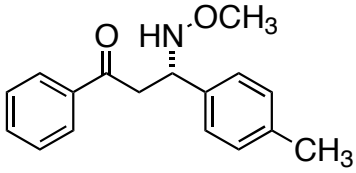
colorless oil; IR (neat) ν 701, 727, 859, 992, 1062, 1210, 1235, 1278, 1355, 1415, 1495, 1519, 1658, 2808, 2936, 3087 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ3.19 (dd, *J* = 5.2 Hz, 16.0 Hz, 1H), 3.37 (s, 3H), 3.40 (dd, *J* = 8.3 Hz, 16.0 Hz, 1H), 4.63 (dd, *J* = 5.2 Hz, 8.3 Hz, 1H), 6.12 (brs, 1H), 7.05 (dd, *J* = 3.2 Hz, 4.9 Hz, 1H), 7.22–7.26 (m, 1H), 7.29-7.32 (m, 2H), 7.39–7.41 (m, 2H), 7.56 (dd, *J* = 1.0 Hz, 4.9 Hz, 1H), 7.64 (dd, *J* = 1.0 Hz, 3.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ43.19, 61.07, 62.04, 127.39, 127.60, 128.00, 128.36, 132.02, 133.81, 140.63, 143.98, 190.93; LRMS (ESI, methanol) *m/z* 283.8 [M+Na]$^+$; HRMS (FAB) *m/z* 262.0900 [M+H$^+$] calcd. for $C_{17}H_{20}NO_2S$ = 262.0896; $[\alpha]_D^{26}$ –19.9 (*c* 1.035 , $CHCl_3$) (93% ee); HPLC, DAICEL CHIRALPAK AD-H, hexane:2-propanol = 19:1, flow rate = 0.5 mL/min, retention time 27.3 min (major) /29.0 min (minor).

3-(4-Chlorophenyl)-3-(methoxyamino)-1-phenyl-1-propanone (4i):



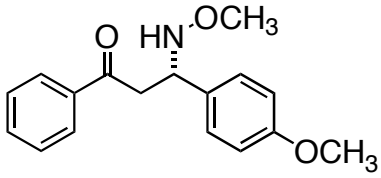
colorless oil; IR (neat) ν 689, 752, 823, 1014, 1089, 1181, 1205, 1448, 1491, 1597, 1683, 2936 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ3.25 (dd, *J* = 5.2 Hz, 17.4 Hz, 1H), 3.38 (s, 3H), 3.45 (dd, *J* = 8.0 Hz, 17.4 Hz, 1H), 4.62 (dd, *J* = 5.2 Hz, 8.0 Hz, 1H), 6.15 (brs, 1H), 7.28-7.29 (m, 2H), 7.35-7.37 (m, 2H), 7.42-7.45 (m, 2H), 7.53-7.56 (m, 1H), 7.89-7.91 (m, 2H); ^{13}C NMR ($CDCl_3$) δ42.42, 60.31, 62.31, 128.04, 128.64, 128.66, 128.98, 133.35, 133.40, 136.61, 139.69, 198.02; LRMS (ESI, methanol) *m/z* 314.0, 312.0 [M+Na]$^+$; HRMS (FAB) *m/z* 290.0952 [M+H$^+$] calcd. for $C_{16}H_{17}ClNO_2$ = 290.0942; $[\alpha]_D^{23}$ +12.3 (*c* 0.50, $CHCl_3$) (94% ee); HPLC, DAICEL CHIRALPAK AD-H, hexane:2-propanol = 19:1, flow rate = 1.0 mL/min, retention time 18.2 min (major) /20.4 min (minor)

3-(Methoxyamino)-3-(4-methylphenyl)-1-phenyl-1-propanone (4j):



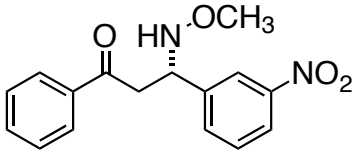
colorless oil; IR (neat) ν690, 758, 815, 1001, 1204, 1273, 1362, 1448, 1683, 2935 cm^{-1}; ^1H NMR ($CDCl_3$) δ2.31 (s, 3H), 3.27 (dd, *J* = 5.2 Hz, 17.1 Hz, 1H), 3.40 (s, 3H), 3.49 (dd, *J* = 7.9 Hz, 17.1 Hz, 1H), 4.63 (dd, *J* = 5.2 Hz, 7.9 Hz, 1H), 6.09 (brs, 1H), 7.13–7.15 (m, 2H), 7.29–7.31 (m, 2H), 7.41–7.44 (m, 2H), 7.52–7.55 (m, 1H), 7.90–7.92 (m, 2H); ^{13}C NMR ($CDCl_3$) δ21.11, 42.73, 60.80, 62.21, 127.46, 128.07, 128.58, 129.19, 133.16, 136.89, 137.36, 137.92, 198.44; LRMS (ESI, methanol) *m/z* 292.0 $[M+Na]^+$; HRMS (FAB) *m/z* 270.1494 $[M+H^+]$ calcd. for $C_{17}H_{20}NO_2$ = 270.1489; $[\alpha]_D^{25}$ –19.9 (*c* 1.07, $CHCl_3$) (96% ee); HPLC, DAICEL CHIRALCEL OD-H, hexane:2-propanol = 19:1, flow rate = 1.0 mL/min, retention time 6.5 min (major) /8.9 min (minor).

3-(Methoxyamino)-3-(4-methoxyphenyl)-1-phenyl-1-propanone (4k):



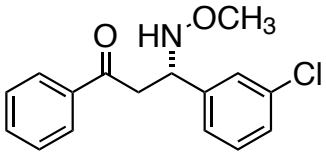
colorless oil; IR (neat) ν690, 757, 829, 1034, 1178, 1248, 1448, 1513, 1611, 1682, 2935 cm^{-1}; ^1H NMR ($CDCl_3$) δ3.27 (dd, *J* = 5.2 Hz, 17.1 Hz, 1H), 3.39 (s, 3H), 3.49 (dd, *J* = 8.0 Hz, 17.1 Hz, 1H), 3.78 (s, 3H) 4.61 (dd, *J* = 5.2 Hz, 8.0 Hz, 1H), 6.06 (brs, 1H), 6.85–6.87 (m, 2H), 7.32–7.34 (m, 2H), 7.41–7.44 (m, 2H), 7.52-7.55 (m, 1H), 7.90–7.91 (m, 2H); ^{13}C NMR ($CDCl_3$) δ42.72, 55.24, 60.51, 62.26, 113.88, 128.07, 128.59, 128.71, 132.92, 133.18, 136.89, 159.09, 198.48; LRMS (ESI, methanol) *m/z* 308.0 $[M+Na]^+$; HRMS (FAB) *m/z* 286.1445 $[M+H^+]$ calcd. for $C_{17}H_{20}NO_3$ = 286.1438; $[\alpha]_D^{24}$ –18.6 (*c* 2.975, $CHCl_3$) (95% ee); HPLC, DAICEL CHIRALCEL OD-H, hexane:2-propanol = 9:1, flow rate = 1.0 mL/min, retention time 10.2 (major) min /12.7 min (minor)

3-(3-Nitrophenyl)-3-(methoxyamino)-1-phenyl-1-propanone (4l):



colorless oil; IR (neat) ν668, 739, 754, 804, 1017, 1092, 1207, 1261, 1350, 1448, 1529, 1597, 1682, 2934 cm^{-1}; ^1H NMR ($CDCl_3$) δ3.30 (dd, *J* = 4.9 Hz, 17.7 Hz, 1H), 3.39 (s, 3H), 3.49 (dd, *J* = 8.3 Hz, 17.7 Hz, 1H), 4.76 (dd, *J* = 4.9 Hz, 8.3 Hz, 1H), 6.26 (brs, 1H), 7.43-7.46 (m, 2H), 7.49-7.52 (m, 1H), 7.55-7.58 (m, 1H), 7.77-7.78 (m, 1H), 7.90-7.92 (m, 2H), 8.12-8.14 (m, 1H), 8.33-8.34 (m, 1H); ^{13}C NMR ($CDCl_3$) δ42.07, 60.14, 62.35, 122.50, 122.68, 128.06, 128.75, 129.37, 133.63, 134.09, 136.36, 143.70, 148.42, 197.51; LRMS (ESI, methanol) *m/z* 322.9 $[M+Na]^+$; HRMS (FAB) *m/z* 301.1183 $[M+H^+]$ calcd. for $C_{16}H_{17}N_2O_4$ = 301.1183; $[\alpha]_D^{22}$ –25.3 (*c* 0.95, $CHCl_3$) (81% ee); HPLC, DAICEL CHIRALCEL OJ-H, hexane:2-propanol = 4:1, flow rate = 1.0 mL/min, retention time 28.6 (minor) min /35.8 min (major)

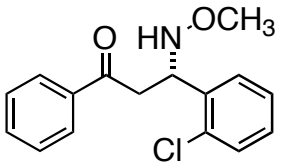
3-(3-Chlorophenyl)-3-(methoxyamino)-1-phenyl-1-propanone (4m):



colorless oil; IR (neat) ν689, 753, 785, 1001, 1205, 1448, 1683, 2933 cm^{-1}; ^1H NMR ($CDCl_3$) δ3.23 (dd, *J* = 4.9 Hz, 17.4 Hz, 1H), 3.39 (s, 3H), 3.44 (dd, *J* = 8.2 Hz, 17.4 Hz, 1H), 4.63 (dd, *J* = 4.9 Hz, 8.2 Hz, 1H), 6.20 (brs, 1H), 7.24-7.32 (m, 3H), 7.41-7.45 (m, 3H), 7.52-7.55 (m, 1H), 7.90-7.92 (m, 2H); ^{13}C NMR ($CDCl_3$) δ42.25, 60.35, 62.15, 125.77, 127.60,

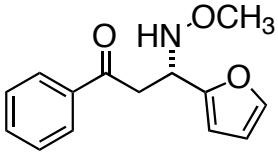
127.69, 127.94, 128.54, 129.54, 133.28, 134.18, 136.49, 143.36, 197.79; LRMS (ESI, methanol) *m/z* 313.9 (^{37}Cl), 311.9 (^{35}Cl) [M+Na]$^+$; HRMS (FAB) *m/z* 290.0944 [M+H$^+$] calcd. for $C_{16}H_{17}ClNO_2$ = 290.0942; $[\alpha]_D^{26}$ –28.1 (*c* 1.1 , $CHCl_3$) (92% ee); HPLC, DAICEL CHIRALCEL OD-H, hexane:2-propanol = 19:1, flow rate = 1.0 mL/min, retention time 7.7 min (major) /11.5 min (minor)

3-(2-Chlorophenyl)-3-(methoxyamino)-1-phenyl-1-propanone (4n):



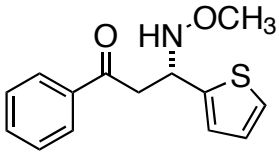
colorless oil; IR (neat) ν752, 1205, 1270, 1361, 1447, 1473, 1579, 1597, 1682, 2809, 2936, 3063, 3260 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ3.34–3.36 (m, 2H), 3.45 (s, 3H), 5.15 (dd, *J* = 5.5 Hz, 7.3 Hz, 1H), 6.38 (brs, 1H), 7.18–7.22 (m, 1H), 7.26–7.29 (m, 1H), 7.35–7.37 (m, 1H), 7.41–7.45 (m, 2H), 7.53–7.56 (m, 1H), 7.62–7.64 (m, 1H), 7.93–7.94 (m, 2H); ^{13}C NMR ($CDCl_3$) δ41.10, 57.09, 61.92, 126.84, 128.05, 128.35, 128.49, 128.57, 129.73, 133.26, 133.30, 136.50, 138.48, 198.01; LRMS (ESI, methanol) *m/z* 313.9 (^{37}Cl), 311.9 (^{35}Cl), [M+Na]$^+$; HRMS (FAB) *m/z* 290.0941 [M+H$^+$] calcd. for $C_{16}H_{17}ClNO_2$ = 290.0942; $[\alpha]_D^{24}$ –76.2 (*c* 2.27 , $CHCl_3$) (93% ee); HPLC, DAICEL CHIRALPAK AD-H, hexane:2-propanol = 19:1, flow rate = 1.0 mL/min, retention time 10.9 min (major) /15.0 min (minor)

3-(2-Furyl)-3-(methoxyamino)-1-phenyl-1-propanone (4o):



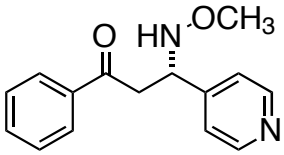
colorless oil; IR (neat) ν690, 757, 1011, 1210, 1282, 1360, 1448, 1597, 1683, 3265 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ3.39 (dd, *J* = 5.5 Hz, 17.4 Hz, 1H), 3.41 (s, 3H), 3.60 (dd, *J* = 8.0 Hz, 17.4 Hz, 1H), 4.75 (dd, *J* = 5.5 Hz, 8.0 Hz, 1H), 6.13 (brs, 1H), 6.28–6.29 (m, 1H), 6.31–6.32 (m, 1H), 7.35–7.36 (m, 1H), 7.45 (dd, *J* = 15.3 Hz, 15.3 Hz, 2H) 7.55 (t, *J* = 15.3 Hz, 1H) 7.95 (d, *J* = 15.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ39.17, 54.56, 62.27, 107.34, 110.31, 128.08, 128.63, 133.32, 136.70, 141.85, 153.69, 197.85; LRMS (ESI, methanol) *m/z* 267.9 [M+Na]$^+$; HRMS (FAB) *m/z* 246.1129 [M+H$^+$] calcd. for $C_{14}H_{16}NO_3$ = 246.1125; $[\alpha]_D^{24}$ –34.6 (*c* 1.9, $CHCl_3$) (92% ee); HPLC, DAICEL CHIRALCEL OJ-H, hexane:2-propanol = 49:1, flow rate = 1.0 mL/min, retention time 27.3 min (major) /30.8 min (minor)

3-(Methoxyamino)-1-phenyl-3-(2-thienyl)-1-propanone (4p):



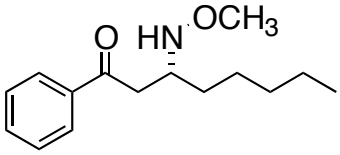
colorless oil; IR (neat) ν694, 758, 1216, 1282, 1353, 1448, 1682, 2934 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ3.36 (dd, *J* = 4.9 Hz, 17.1 Hz, 1H), 3.46 (s, 3H), 3.61 (dd, *J* = 7.9 Hz, 17.1 Hz, 1H), 4.96 (dd, *J* = 4.9 Hz, 7.9 Hz, 1H), 6.18 (brs, 1H) 6.93 (dd, *J* = 3.0 Hz, 4.0 Hz, 1H), 7.02 (d, *J* = 3.0 Hz, 1H), 7.21 (d, *J* = 4.0 Hz, 1H), 7.43 (dd, *J* = 7.3 Hz, 7.3 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.93 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ42.69, 56.58, 62.24, 124.59, 124.94, 126.44, 127.99, 128.55, 133.24, 136.64, 144.38, 197.88; LRMS (ESI, methanol) *m/z* 283.9 [M+Na]$^+$; HRMS (FAB) *m/z* 262.0902 [M+H$^+$] calcd. for $C_{17}H_{20}NO_2S$ = 262.0896; $[\alpha]_D^{26}$ –20.5 (*c* 1.30 , $CHCl_3$) (93% ee); HPLC condition DAICEL CHIRALCEL OD, hexane:2-propanol = 9:1, flow rate = 1.0 mL/min, retention time 8.7 min (major) / 11.7 min (minor).

3-(Methoxyamino)-1-phenyl-3-(4-pyridyl)-1-propanone (4q):



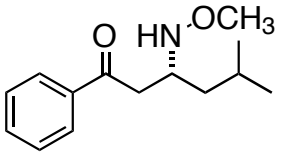
colorless oil; IR (neat) ν690, 754, 821, 1000, 1066, 1208, 1283, 1361, 1414, 1448, 1599, 1682, 2937, 3249 cm^{-1}; ^1H NMR ($CDCl_3$) δ3.19 (dd, J = 4.6 Hz, 17.4 Hz, 1H), 3.34 (s, 3H), 3.39 (dd, J = 8.6 Hz, 17.4 Hz, 1H), 4.58 (dd, J = 4.6 Hz, 8.6 Hz, 1H), 6.26 (brs, 1H), 7.30–7.32 (m, 2H), 7.35–7.39 (m, 2H), 7.47–7.50 (m, 1H), 7.83–7.85 (m, 2H), 8.49–8.50 (m, 2H); ^{13}C NMR ($CDCl_3$) δ41.51, 59.66, 62.03, 122.52, 127.84, 128.53, 133.39, 136.20, 149.71, 150.34, 197.37; LRMS (ESI, methanol) m/z 278.9 $[M+Na]^+$; HRMS (FAB) m/z 257.1299 $[M+H^+]$ calcd. for $C_{15}H_{17}N_2O_2$ = 257.1290; $[\alpha]_D^{22}$ –41.7 (c 0.99, $CHCl_3$) (85% ee); HPLC condition DAICEL CHIRALCEL OJ-H, hexane:2-propanol = 4:1, flow rate = 1.0 mL/min, retention time 15.0 min (minor) / 20.5 min (major).

3-(Methoxyamino)-1-phenyl-1-octanone (4r):



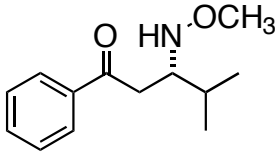
colorless oil; IR (neat) ν690, 752, 822, 1001, 1448, 1682, 2931 cm^{-1}; ^1H NMR ($CDCl_3$) δ0.86 (t, J = 6.9 Hz, 3H), 1.27–1.47 (m, 7H), 1.54–1.60 (m, 1H), 2.94 (dd, J = 4.9 Hz, 16.8 Hz, 1H), 3.26 (dd, J = 7.3 Hz, 16.8 Hz, 1H), 3.47 (s, 3H), 3.47–3.49 (m, 1H), 5.92 (brs, 1H), 7.44 (dd, J = 7.8 Hz, 7.8 Hz, 2H), 7.54 (t, J = 7.8 Hz, 1H), 7.95 (d, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ14.02, 22.56, 25.87, 31.89, 32.14, 40.67, 57.04, 62.15, 128.02, 128.54, 133.03, 137.19, 199.68; LRMS (ESI, methanol) m/z 271.7 $[M+Na]^+$; HRMS (FAB) m/z 250.1801 $[M+H^+]$ calcd. for $C_{15}H_{24}NO_2$ = 250.1802; $[\alpha]_D^{26}$ –14.6 (c 1.30 , $CHCl_3$) (84% ee); HPLC condition DAICEL CHIRALPAK AS-H, hexane:2-propanol = 99:1, flow rate = 0.5 mL/min, retention time 12.5 min (minor) / 13.5 min (major).

3-(Methoxyamino)-5-methyl-1-phenyl-1-hexanone (4s):



colorless oil; IR (neat) ν690, 752, 1363, 1448, 1682, 2954 cm^{-1}; ^1H NMR ($CDCl_3$) δ0.90 (d, J = 6.7 Hz, 3H), 0.92 (d, J = 6.4 Hz, 3H), 1.22–1.28 (m, 1H), 1.47–1.53 (m, 1H), 1.70–1.79 (m, 1H), 2.90 (dd, J = 4.9 Hz, 17.0 Hz, 1H), 3.31 (dd, J = 7.3 Hz, 17.0 Hz, 1H), 3.45 (s, 3H), 3.53–3.59 (m, 1H), 5.90 (brs, 1H), 7.44 (dd, J = 8.0 Hz, 8.0 Hz, 2H), 7.54 (t, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ22.51, 22.99, 24.96, 40.97, 41.39, 55.05, 62.15, 128.02, 128.56, 133.03, 137.24, 199.76; LRMS (ESI, methanol) m/z 257.9 $[M+Na]^+$; HRMS (FAB) m/z 236.1643 $[M+H^+]$ calcd. for $C_{14}H_{22}NO_2$ = 236.1645; $[\alpha]_D^{26}$ –13.4 (c 2.18 , $CHCl_3$) (93% ee); HPLC condition DAICEL CHIRALPAK AD-H, hexane:2-propanol = 19:1, flow rate = 1.0 mL/min, retention time 6.7 min (minor) / 8.1 min (major).

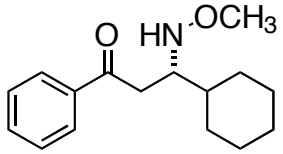
3-(Methoxyamino)-4-methyl-1-phenyl-1-pentanone (4t):



colorless oil; IR (neat) ν691, 751, 974, 1002, 1180, 1209, 1280, 1368, 1448, 1467, 1580, 1597, 1682, 2808, 2958 cm^{-1}; ^1H NMR ($CDCl_3$) δ0.95 (d, J = 7.0 Hz, 3H) 0.98 (d, J = 7.0 Hz, 3H) 1.95–2.01 (m, 1H), 2.96 (dd, J = 4.0 Hz, 16.5 Hz, 1H), 3.10 (dd, J = 8.5 Hz, 16.5 Hz, 1H), 3.31–3.35 (m, 1H), 3.42 (s, 3H), 5.90 (brs, 1H), 7.44 (dd, J = 7.7 Hz, 7.7 Hz, 2H), 7.54 (t, J = 7.7 Hz, 1H), 7.94 (d, J = 7.7 Hz,

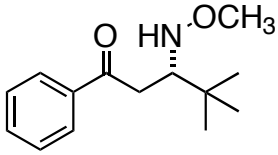
2H); ^{13}C NMR ($CDCl_3$) δ18.48, 19.31, 29.12, 37.25, 61.81, 62.04, 128.06, 128.56, 132.98, 137.29, 199.95; LRMS (ESI, methanol) *m/z* 243.6 [M+Na]$^+$; HRMS (FAB) *m/z* 222.1496 [M+H$^+$] calcd. for $C_{13}H_{20}NO_2$ = 222.1489; $[\alpha]_D^{26}$ –32.0 (*c* 1.12 , $CHCl_3$) (85% ee); HPLC condition DAICEL CHIRALPAK AD-H, hexane:2-propanol = 49:1, flow rate = 1.0 mL/min, retention time 10.2 min (minor) / 14.9 min (major).

3-Cyclohexane-3-(methoxyamino)-1-phenyl-1-propanone (4u):



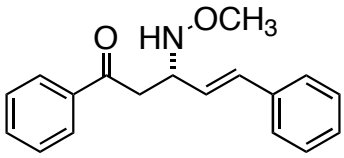
colorless oil; IR (neat) ν690, 752, 1210, 1279, 1358, 1448, 1682, 2851, 2926 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ1.01–1.26 (m, 4H), 1.59–1.86 (m, 7H), 2.98 (dd, *J* = 4.0 Hz, 16.5 Hz, 1H), 3.13 (dd, *J* = 13.2 Hz, 16.5 Hz, 1H), 3.31–3.36 (m, 1H). 3.40 (s, 3H), 5.88 (brs, 1H), 7.43 (dd, *J* = 7.7 Hz, 7.7 Hz, 2H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ26.39, 26.40, 26.55, 29.28, 29.79, 37.81, 39.37, 61.55, 61.71, 128.02, 128.50, 132.90, 137.30, 199.96; LRMS (ESI, methanol) *m/z* 283.9 [M+Na]$^+$; HRMS (FAB) *m/z* 262.1798 [M+H$^+$] calcd. for $C_{16}H_{23}NO_2$ = 262.1802; $[\alpha]_D^{24}$ –24.3 (*c* 1.06, $CHCl_3$) (82% ee); HPLC condition DAICEL CHIRALPAK AS-H, hexane:2-propanol = 99:1, flow rate = 1.0 mL/min, retention time 7.4 min (minor) / 8.0 min (major).

3-(Methoxyamino)-4,4-dimethyl-1-phenyl-1-pentanone (4v):



colorless oil; IR (neat) ν690, 760, 1043, 1218, 1293, 1364, 1448, 1598, 1682, 2954 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ0.98 (s, 9H), 2.92 (dd, *J* = 3.3 Hz, 16.1 Hz, 1H), 3.21 (dd, *J* = 8.9 Hz, 16.1 Hz, 1H), 3.30 (s, 3H), 3.34 (dd, *J* = 3.3 Hz, 8.9 Hz, 1H), 5.76 (s, 1H), 7.42–7.45 (m, 2H), 7.51–7.54 (m, 1H), 7.93–7.95 (m, 2H); ^{13}C NMR ($CDCl_3$) δ27.25, 33.69, 37.52, 61.03, 65.14, 128.02, 128.47, 132.68, 137.60, 200.11; LRMS (ESI, methanol) *m/z* 257.9 [M+Na]$^+$; HRMS (FAB) *m/z* 236.1643 [M+H$^+$] calcd. for $C_{14}H_{22}NO_2$ = 236.1645; $[\alpha]_D^{24}$ –12.5 (*c* 2.10, $CHCl_3$) (88% ee); HPLC condition DAICEL CHIRALPAK AS-H, hexane:2-propanol = 99:1, flow rate = 1.0 mL/min, retention time 7.0 min (minor) / 8.5 min (major).

3-(Methoxyamino)-1,5-diphenyl-4-penten-1-one (4w):



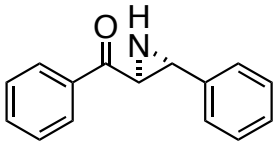
colorless oil; IR (neat) ν 691, 751, 967, 1362, 1448, 1682, 2934 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ3.21 (dd, *J* = 5.2 Hz, 11.8 Hz, 1H), 3.43 (dd, *J* = 7.4 Hz, 11.8 Hz, 1H), 3.55 (s, 3H), 4.31 (ddd, *J* = 5.2 Hz, 7.4 Hz, 7.6 Hz, 1H), 6.09 (brs, 1H), 6.30 (dd, *J* = 7.6 Hz, 15.9 Hz, 1H), 6.65 (d, *J* = 15.9 Hz, 1H), 7.23–7.27 (m, 1H), 7.30-7.33 (m, 2H), 7.38–7.40 (m, 2H), 7.45–7.48 (m, 2H), 7.55–7.58 (m, 1H), 7.98–7.99 (m, 2H); ^{13}C NMR ($CDCl_3$) δ40.96, 59.17, 62.19, 126.31, 127.52, 127.95, 128.39, 128.48, 128.55, 132.18, 133.07, 136.60, 136.85, 198.30; LRMS (ESI, methanol) *m/z* 303.8 [M+Na]$^+$; HRMS (FAB) *m/z* 282.1486 [M+H$^+$] calcd. for $C_{18}H_{20}NO_2$ = 282.1489; $[\alpha]_D^{26}$ +24.0 (*c* 1.14 , $CHCl_3$) (95% ee); HPLC condition DAICEL CHIRALPAK OD-H, hexane:2-propanol = 19:1, flow rate = 1.0 mL/min, retention time 15.6 min (major) / 18.4 min (minor).

Experimental procedure for transformation of 4a.

1) Aziridine ring forming reaction
Aziridine forming reaction was performed using reported procedure.

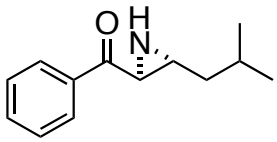
Reference Jin, X.-L.; Sugihara, H.; Daikai, K.; Takeishi, H.; Jin, Y.-Z.; Furuno, H.; Inanaga, J. *Tetrahedron* **2002**, *58*, 8321.

(2*S*,3*R*)-2-Benzoyl-3-phenylaziridine (5):



colorless solid, IR (KBr) ν697, 749, 813, 843, 1011, 129, 1259, 1352, 1411, 1449, 1495, 1597, 1666, 2925 cm^{-1}; ^1H NMR ($CDCl_3$) δ2.66 (dd, *J* = 8.0 Hz, 9.5 Hz, 1H), 3.16 (dd, *J* = 2.0 Hz, 9.5 Hz, 1H), 3.50 (dd, *J* = 2.0 Hz, 8.0 Hz, 1H), 7.28–7.39 (m, 5H), 7.47 (dd, *J* = 7.4 Hz, 7.6 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ43.50, 44.09, 126.17, 127.85, 128.30, 128.52, 128.79, 133.80, 135.86, 138.30, 195.68; LRMS (ESI, methanol) *m/z* 245.7 $[M+Na]^+$; HRMS (FAB) *m/z* 224.1076 $[M+H^+]$ calcd. for $C_{15}H_{14}NO$ = 224.1070; $[\alpha]_D^{22}$ +251.3 (*c* 0.85, $CHCl_3$) (95% ee) [lit. $[\alpha]_D^{19}$ +268.7 (*c* 1.00, $CHCl_3$) (>99% ee)] ; HPLC condition DAICEL CHIRALCEL OD, hexane:2-propanol = 19:1, flow rate = 0.5 mL/min, retention time 21.0 min (2*S*,3*R*) / 27.4 min (2*R*,3*S*).

2-Benzoyl-3-isobutylaziridine (6):



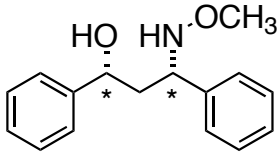
colorless oil, IR (neat) ν665, 704, 822, 863, 984, 1023, 1227, 1259, 1364, 1420, 1450, 1579, 1598, 1669, 2956, 3266 cm^{-1}; ^1H NMR ($CDCl_3$) δ0.94 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 6.7 Hz, 3H), 1.41–1.51 (m, 2H), 1.78–1.86 (m, 1H), 2.09 (brs, 1H), 2.16–2.18 (m, 1H), 3.22 (brs, 1H), 7.48–7.51 (m, 2H), 7.58–7.62 (m, 1H), 7.99–8.01 (m, 2H); ^{13}C NMR ($CDCl_3$) δ22.49, 22.74, 27.21, 39.84, 42.09, 42.38, 128.16, 128.79, 133.63, 136.18, 197.29; LRMS (ESI, methanol) *m/z* 225.7 $[M+Na]^+$; HRMS (FAB) *m/z* 204.1380 $[M+H^+]$ calcd. for $C_{14}H_{18}NO$ = 204.1383; $[\alpha]_D^{24}$ +28.3 (*c* 3.49 , $CHCl_3$) (94% ee); HPLC condition DAICEL CHIRALCEL OD–H, hexane:2-propanol = 19:1, flow rate = 0.5 mL/min, retention time 11.8 min (major) / 16.2 min (minor)

2) *syn* Selective reduction of **4a**

References (a) Pilli, R. A.; Russowsky, D.; Dias, L. C. *J. Chem. Soc., Perkin Trans. 1*, **1990**, 1213. (b) Kobayashi, S.; Matsubara, R.; Kitagawa, H. *Org. Lett.* **2002**, *4*, 143.

(1*R*,3*S*)-*syn*-3-(Methoxyamino)-1,3-diphenylpropan-1-ol (7)

An ether solution of $Zn(BH_4)_2$ was prepared using a known procedure and the reagent was immediately used after preparation.



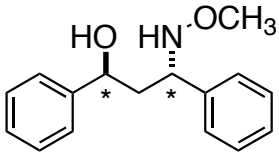
To **4a** (500 mg, 1.96 mmol) in diethylether (0.5 mL), a diethylether solution of $Zn(BH_4)_2$ was added at –78 °C. After stirred for 18 h at same temperature, the mixture was poured into ice-cooled water. The organic

compound was extracted with diethylether (10 mL x 2), and the combined organic layer was washed with small amount of water (2 mL x 2) and brine (2 mL), and then dried with Na_2SO_4. After removing the solvent, the residue was subjected on silica gel column chromatography [SiO_2, hexane/ether = 1/1] to give 3-(methoxyamino)-1,3-diphenylpropan-1-ol (**7**) as colorless oil (70% yield, *syn*/*anti* = 90/10)
colorless oil, IR (neat) ν700, 758, 914, 1009, 1058, 1454, 1494, 1603, 1886, 1952, 2937, 3030, 3061, 3252, 3387 cm^{-1}; ^1H NMR ($CDCl_3$) δ1.94 (ddd, *J* = 2.5 Hz, 4.6 Hz, 14.7 Hz, 1H), 2.13 (ddd, *J* = 9.1 Hz, 10.3 Hz, 14.7 Hz, 1H), 3.53 (s, 3H), 4.31 (dd, *J* = 4.6 Hz, 9.1 Hz, 1H), 4.85 (dd, *J* = 2.5 Hz, 10.3 Hz, 1H), 7.22–7.34 (m, 10H); ^{13}C NMR ($CDCl_3$) δ43.32, 62.21, 64.95, 73.99, 125.56, 127.05, 127.46, 127.69, 128.42, 128.60, 141.88, 144.52; LRMS (ESI, methanol) *m/z* 279.9 $[M+Na]^+$, 257.8 $[M+H]^+$; HRMS (FAB) *m/z* 258.1495 $[M+H^+]$ calcd. for $C_{16}H_{20}NO_2$ = 258.1489; $[\alpha]_D^{24}$ –29.1 (*c* 1.0 , $CHCl_3$) (95% ee); HPLC condition DAICEL CHIRALPAK AD–H, hexane:2-propanol = 9:1, flow rate = 1.0 mL/min, retention time 14.0 min (1*S*,3*R*) / 15.7 min (1*R*,3*S*).

3) *anti* Selective reduction of **4a**

Reference (a) Pilli, R. A.; Russowsky, D.; Dias, L. C. *J. Chem. Soc., Perkin Trans. 1*, **1990**, 1213.

(1*S*,3*S*)-*anti*-3-(Methoxyamino)-1,3-diphenylpropan-1-ol (8)

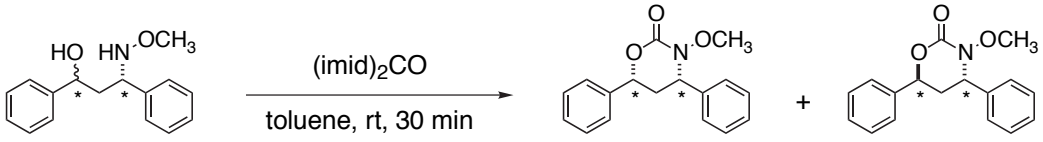


To a tetrahydrofuran (0.5 mL) solution of **4a** (500 mg, 1.96 mmol) at –78 °C, K-Selectride (1.0 M in THF, 3.9 mL, 3.9 mmol) was added slowly. Resulting orange-colored solution was stirred for 18 h at the same temperature, then further stirred for 6 h at room temperature. An aqueous H_2O_2 (3%) was added to the reaction mixture at 0 °C, the organic compound was extracted with diethylether. The organic layer was washed with brine and dried with Na_2SO_4. After removing the solvent, the residue was subjected on silica gel column chromatography [SiO_2, hexane/ether = 1/1] to give (1*S*,3*S*)-3-(methoxyamino)-1,3-diphenylpropan-1-ol (**8**) as colorless oil (93 % yield, *syn*/*anti* = 11/89): colorless oil, IR (neat) ν560, 700, 752, 1027, 1060, 1454, 1494, 2935, 3391 cm^{-1}; ^1H NMR ($CDCl_3$) δ2.15–2.22 (m, 2H), 3.53 (s, 3H), 4.12 (dd, *J* = 5.5 Hz, 7.0 Hz, 1H), 4.81 (dd, *J* = 5.2 Hz, 6.7 Hz, 1H), 7.22–7.36 (m, 10H); ^{13}C NMR ($CDCl_3$) δ42.14, 62.23, 62.23, 71.61, 125.74, 127.07, 127.33, 127.60, 128.41, 128.56, 141.07, 144.09; LRMS (ESI, methanol) *m/z* 257.9 $[M+H]^+$; HRMS (FAB) *m/z* 258.1489 $[M+H^+]$ calcd. for $C_{16}H_{20}NO_2$ = 258.1489.

Determination of relative configuration of β-amino alcohol

The *N*-Methoxy-1,3-aminoalcohols (**7** and **8**) were transformed to a cyclic carbonates in order to determine their relative configuration by 1H-NMR spectra. To a toluene solution of β-amino alcohols (**7** or **8**), 1.1-carbonylbis-1H-imidazol was added potionwisely at room temperature. After stirring the reaction mixture for 30 min, the solvent was removed under reduced pressure. The residue was subjected on silica gel column chromatography [SiO_2, hexane/ether = 1/1] to give cyclic carbamate in quantitative yield.

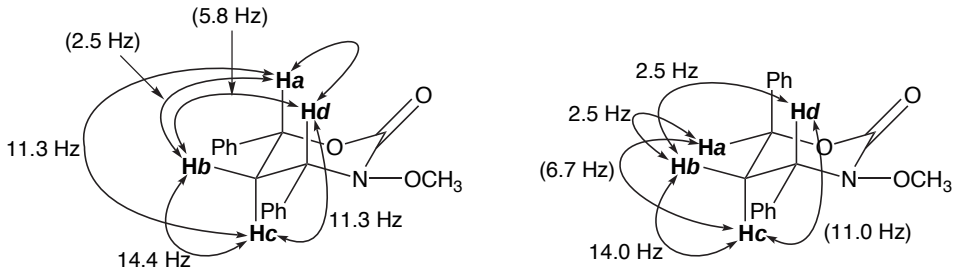
Scheme: Determination of relative conformation of β-amino alcohol (**7** and **8**)



(1*R*,3*S*)-*syn*-**7**
(1*S*,3*S*)-*anti*-**8**

(4*S*,6*R*)-syn

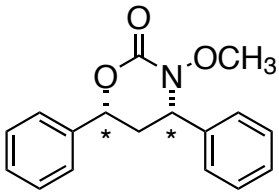
(4*S*,6*S*)-*anti*



(4*S*,6*R*)-syn

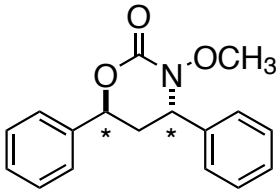
(4*S*,6*S*)-*anti*

(4*S*,6*R*)-*syn*-2-Oxo-3-methoxy-4,6-diphenyl-4*H*,5*H*,6*H*-trihydro-1,3-oxazine.



colorless solid, IR (KBr) ν696, 755, 984, 107 1178, 1306, 1369, 1399, 1456, 1705, 2926, 3038 cm^{-1}; ^1H NMR ($CDCl_3$) δ2.43 (ddd, *J* = 11.0 Hz, 11.3 Hz, 14.4 Hz, 1H), 2.51 (ddd, *J* = 2.5 Hz, 5.8 Hz, 14.4 Hz, 1H), 3.57 (s, 3H), 4.96 (dd, *J* = 5.8 Hz, 11.0 Hz, 1H), 5.36 (dd, *J* = 2.5 Hz, 11.3 Hz, 1H), 7.30–7.39 (m, 10H); ^{13}C NMR ($CDCl_3$) δ40.86, 62.64, 62.84, 77.66, 125.72, 127.09, 128.62, 128.67, 128.71, 128.81, 137.69, 138.41, 153.72; LRMS (ESI, methanol) *m/z* 306 $[M+Na]^+$; HPLC condition DAICEL CHIRALPAK AD-H, hexane:2-propanol = 4:1, flow rate = 1.0 mL/min, retention time 26.2 min / 50.7 min.

(4*S*,6*S*)-*anti*-2-Oxo-3-methoxy-4,6-diphenyl-4*H*,5*H*,6*H*-trihydro-1,3-oxazine.



colorless oil, IR (neat) ν700, 759, 1099, 1213, 1726, 2929 cm^{-1}; ^1H NMR ($CDCl_3$) δ2.29 (ddd, *J* = 2.5 Hz, 2.5 Hz, 14.0 Hz, 1H), 2.59 (ddd, *J* = 6.7 Hz, 11.0 Hz, 14.0 Hz, 1H), 3.73 (s, 3H), 4.94 (dd, *J* = 2.5 Hz, 6.7 Hz, 1H), 5.29 (dd, *J* = 2.5 Hz, 11.0 Hz, 1H), 7.26–7.45 (m, 10H); ^{13}C NMR ($CDCl_3$) δ38.94, 60.44, 62.35, 74.66, 125.70, 126.32, 128.30, 128.58, 128.64, 129.03, 137.80, 139.88, 153.19; LRMS (ESI, methanol) *m/z* 306.0 $[M+Na]^+$; HPLC condition DAICEL CHIRALPAK AD-H, hexane:2-propanol = 4:1, flow rate = 1.0 mL/min, retention time 12.6 min / 16.2 min.

Initial rate kinetics: experimental procedure

To a mixture of chalcone (**2a**) (312 mg, 1.5 mmol) and grinded DRIERITE® (200 mg) in a dried test tube at room temperature, a THF solution of (*S*)-YLB (60 mM, x mL, 0.06x mmol) and THF (y mL) was added [x + y = 4 mL]. The orange-colored mixture was stirred at same temperature until **2a** dissolved. The mixture was cooled to –20 °C, then a THF solution of *O*-methylhydroxylamine (**3a**) (5.7 M, 0.3 mL, 1.71 mmol) was added. After stirring for indicated period, small amount of reaction mixture was sampled via syringe and poured into diethylether containing acetaldehyde (ca. 30 μL) to quench the reaction. Diethylether was removed under reduced pressure and the residue was dissolved in $CDCl_3$ to measure the yield of product by NMR. Chemical yield of product was determined from NMR signal of **2a** (7.81 ppm) and **4a** (3.29 ppm). The results for initial rate kinetics on [YLB **1a**] are summarized in the following Chart. The results suggested that the present reaction is first order on [YLB **1a**].

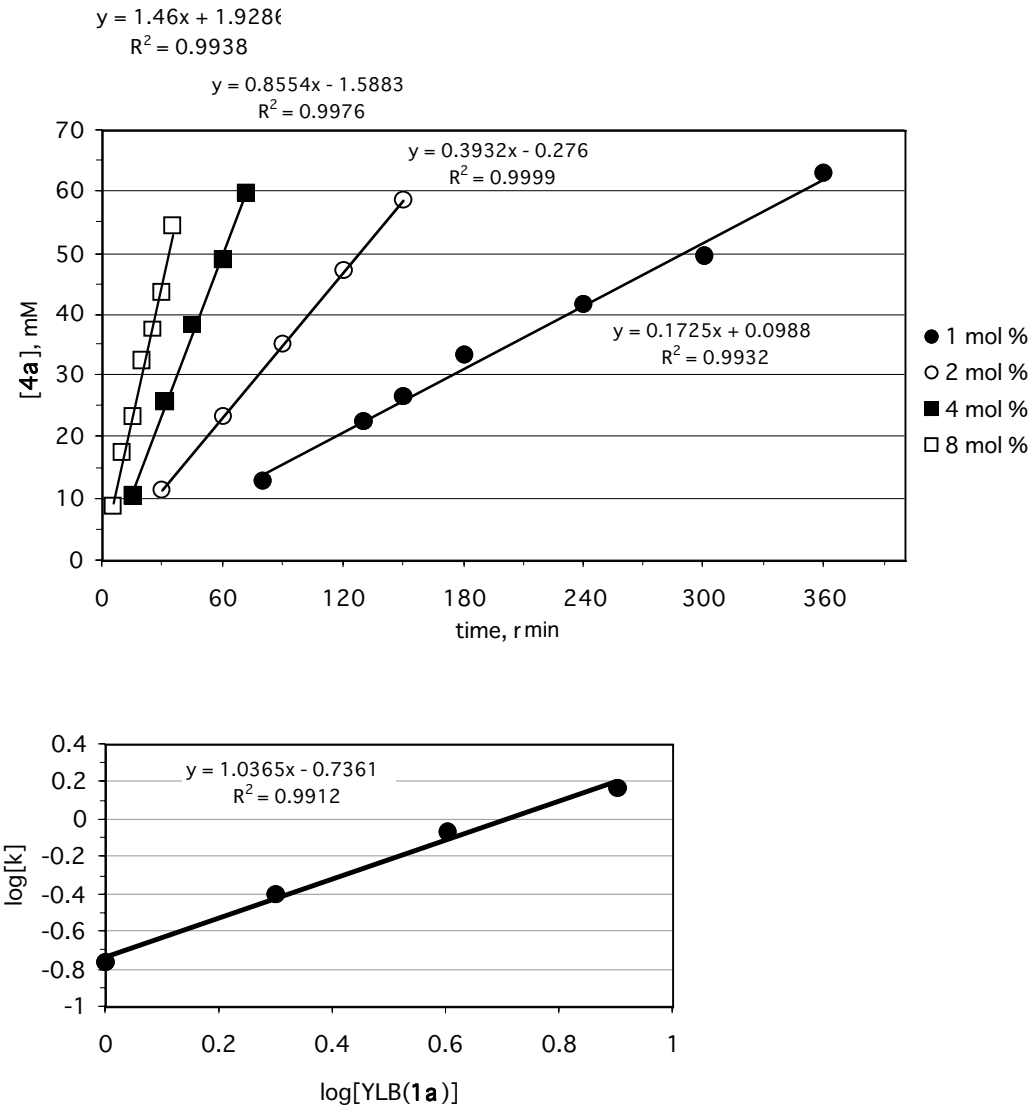


Chart. Reaction profiles with variant amount of catalyst (x = 1, 2, 4, and 8 mol %).