Supporting Information

Catalytic Asymmetric 1,4-Addition Reactions Using α,β -Unsaturated *N*-Acylpyrrole as Highly Reactive Monodentate α,β -Unsaturated Ester Surrogate

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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 downfield from TMS (= 0) or in the scale relative to CHCl_3 (7.24 ppm) for ^1H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to CHCl_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 were measured on Waters-ZQ4000. EI mass spectra were measured on JMS-BU20 GCmate. Column chromatography was performed with silica gel Merck 60 (230–400 mesh ASTM). The enantiomeric excess (ee) was determined by HPLC analysis. HPLC was performed on JASCO HPLC systems consisting of the following: pump, PU-980 OR PU-2080; detector, UV-970 or UV-2075, measured at 254 nm; column, DAICEL CHIRALCEL OD, OD-H, OJ, OJ-H, CHIRALPAK AD, AS, AD-H, AS-H; mobile phase, hexane–2-propanol; flow rate, 0.75–1.0 mL/min. Reactions were carried out in dry solvents under an argon atmosphere, unless otherwise stated. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. $\text{Sm}(\text{O}-i\text{-Pr})_3$ was purchased from Kojundo Chemical Laboratory Co., Ltd. (Fax: +81-492-84-1351, sales@kojundo.co.jp). Other reagents were purified by the usual methods.

(A) Synthesis of α,β -unsaturated *N*-acylpyrrole:

Synthesis of Pyrrolylmethylenetriphenylphosphorane (ylide: 2)

To a suspension of methyltriphenylphosphonium bromide (12.9 g, 36 mmol) in THF (14 mL) at 0 °C was added PhLi (Et₂O solution, 28.1 mL, 36 mmol). The mixture was stirred at 25 °C for 60 min to afford methylenetriphenylphosphorane. Then, the mixture was cooled down to -78 °C, and the solution of 1,1'-carbonyl-dipyrrole (1.92 g, 12 mmol) in THF (18 mL) was added. The cooling bath was removed and the reaction mixture was stirred overnight at 25 °C. H₂O was added and the mixture was extracted with ethyl acetate/CH₂Cl₂ = 5/1 (x3). The organic layers were washed with brine and dried over MgSO₄. After evaporation, the residue was purified by silica gel flash column chromatography to afford ylide 3 (4.33 g, 11.7 mmol, y. 98%); IR (KBr) ν 3434, 3048, 1601, 1438 cm⁻¹; ¹H NMR (CDCl₃) δ 7.68 (ddd, *J* = 12.5, 7.4, 1.3 Hz, 6H), 7.56 (td, *J* = 7.4, 1.3 Hz, 3H), 7.47 (ddd, *J* = 7.4, 7.4, 2.8 Hz, 6H), 7.33-7.35 (m, 2H), 6.15-6.18 (m, 2H), 3.71 (d, *J* = 9.3 Hz, 1H); ¹³C NMR (CDCl₃) δ 38.0 (d, *J* = 125 Hz), 109.3, 118.3, 126.4 (d, *J* = 91.5 Hz), 128.8 (d, *J* = 12.4 Hz), 132.1 (d, *J* = 2.1 Hz), 132.9 (d, *J* = 10.3 Hz); ESI-MS *m/z* 370 [M+H]⁺; HRMS (FAB): *m/z* calcd for C₂₄H₂₁ONP [M+H]⁺: 370.1361; found: 370.1369.

General Procedure of Wittig Reaction for the Synthesis of α,β -Unsaturated *N*-Acylpyrroles 1: To the suspension of ylide 2 (240 mg, 0.65 mmol) in toluene (1.25 mL) was added benzaldehyde 10a (50.8 μ L, 0.5 mmol). The suspension was stirred for 48 h at 100 °C, and cooled down to rt. The reaction mixture was dried in vacuo and purified with column chromatography (hexane:ethyl acetate = 20:1) to give 1a in 97% yield.

(2*E*)-3-Phenyl-1-pyrrol-1-yl-2-propen-1-one (1a): colorless solid; IR (KBr) ν 1688, 1624, 1467, 1351 cm⁻¹; ¹H NMR (CDCl₃): δ = 7.98 (d, *J* = 15.6 Hz, 1H), 7.61 (dd, *J* = 3.7, 3.4 Hz, 2H), 7.40-7.49 (m, 4H), 7.13 (d,

$J = 15.6$ Hz, 1H); ^{13}C NMR (CDCl_3): $\delta = 162.9, 147.5, 134.2, 130.9, 129.0, 128.4, 119.2, 115.7, 113.3$; ESI-MS: m/z 219.7 $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{13}\text{H}_{12}\text{ON}$ $[\text{M}+\text{H}]^+$: 198.0920; found: 198.0919.

(2E)-3-(2-naphthyl)-1-pyrrol-1-yl-2-propen-1-one (1b): colorless

solid; IR (KBr)v 1680, 1617, 1466, 1300 cm^{-1} ; ^1H NMR(CDCl_3): $\delta = 8.15$ (d, $J = 15.3$ Hz, 1H), 8.03 (s, 1H), 7.84-7.91

(m, 3H), 7.75 (m, 1H), 7.51-7.57 (m, 4H), 7.26 (d, $J = 15.3$ Hz, 1H), 6.30-6.35 (m, 2H); ^{13}C NMR (CDCl_3): $\delta = 163.0, 147.6, 134.5, 133.3, 131.7, 130.8, 128.8, 128.7, 127.6, 126.9, 123.4, 119.3, 115.8, 113.3$; ESI-MS: m/z 270 $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{17}\text{H}_{14}\text{ON}$ $[\text{M}+\text{H}]^+$: 248.1075; found: 248.1075.

(2E)-3-(4-methylphenyl)-1-pyrrol-1-yl-2-propen-1-one (1c):

colorless solid; IR (KBr)v 1686, 1621, 1467, 1352 cm^{-1} ; ^1H NMR(CDCl_3): $\delta = 7.96$ (d, $J = 15.6$ Hz, 1H), 7.51 (d, $J = 8.0$ Hz,

2H), 7.45 (brs, 2H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.09 (d, $J = 15.6$ Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (CDCl_3): $\delta = 163.1, 147.6, 141.6, 131.5, 129.7, 128.5, 119.2, 114.5, 113.2, 21.5$; ESI-MS: m/z 234 $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{14}\text{H}_{14}\text{NO}$ $[\text{M}+\text{H}]^+$: 212.1075; found: 212.1076.

(2E)-3-(4-Methoxyphenyl)-1-pyrrol-1-yl-2-propen-1-one (1d):

colorless solid; IR (KBr)v 1687, 1625, 1603, 1512, 1466, 1248 cm^{-1} ; ^1H NMR(CDCl_3): δ 7.94 (d, $J = 15.3$ Hz, 1H), 7.57 (d, $J = 8.5$ Hz,

2H), 7.45 (brs, 2H), 6.99 (d, $J = 15.3$ Hz, 1H), 6.93 (d, $J = 8.5$ Hz, 2H), 6.33 (brs, 2H), 3.85 (s, 3H); ^{13}C NMR (CDCl_3): $\delta = 163.2, 161.9, 147.3, 130.2, 127.0, 119.2, 114.4, 113.0, 55.4$; ESI-MS: m/z 250 $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2\text{N}$ $[\text{M}+\text{H}]^+$: 228.1024; found: 228.1020.

(2E)-3-(4-Bromophenyl)-1-pyrrol-1-yl-2-propen-1-one (1e): colorless solid; IR (KBr) ν 2922, 1685, 1622, 1471 cm^{-1} ; ^1H NMR(CDCl_3): δ 7.92 (d, J = 15.6 Hz, 1H), 7.45-7.59 (m, 6H), 7.13 (d, J = 15.6 Hz, 1H), 6.36-6.38 (m, 2H); ^{13}C NMR (CDCl_3): δ 162.7, 146.1, 133.1, 132.3, 129.8, 125.3, 119.2, 116.3, 113.5; ESI-MS: m/z 298, 300 $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{13}\text{H}_{11}\text{ONBr}$ $[\text{M}+\text{H}]^+$: 276.0014; found 276.0019.

(2E)-3-(4-Chlorophenyl)-1-pyrrol-1-yl-2-propen-1-one (1f): colorless solid; IR (KBr) ν 1674, 1620, 1469, 1352, 1255 cm^{-1} ; ^1H NMR(CDCl_3): δ = 7.87 (d, J = 15.6 Hz, 1H), 7.49 (d, J = 8.6 Hz, 2H), 7.39 (dd, J = 2.5, 2.2 Hz, 2H), 7.34 (d, J = 8.6 Hz, 2H), 7.04 (d, J = 15.6 Hz, 1H), 6.30 (dd, J = 2.5, 2.2 Hz, 2H); ^{13}C NMR (CDCl_3): δ = 162.6, 146.0, 136.9, 132.7, 129.6, 129.3, 119.2, 116.2, 113.5; ESI-MS: m/z 254 $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{13}\text{H}_{11}\text{ONCl}$ $[\text{M}+\text{H}]^+$: 232.0529; found 232.0529.

(2E)-3-(3-Chlorophenyl)-1-pyrrol-1-yl-2-propen-1-one (1g): colorless solid; IR (KBr) ν 1685, 1623, 1466 cm^{-1} ; ^1H NMR(CDCl_3): δ 7.90 (d, J = 15.6 Hz, 1H), 7.60 (s, 1H), 7.35-7.49 (m, 5H), 7.14 (d, J = 15.6 Hz, 1H), 6.36-6.39 (m, 2H); ^{13}C NMR (CDCl_3): δ 162.5, 145.8, 136.0, 135.0, 130.7, 130.3, 127.9, 126.8, 119.2, 117.1, 113.6 ESI-MS: m/z 254, 256 $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{13}\text{H}_{11}\text{ONCl}$ $[\text{M}+\text{H}]^+$: 232.0529; found 232.0534.

(2E)-3-(2-Chlorophenyl)-1-pyrrol-1-yl-2-propen-1-one (1h): colorless solid; IR (KBr) ν 1685, 1621, 1469, 1349, 1285 cm^{-1} ; ^1H NMR(CDCl_3): δ = 8.30 (d, J = 15.6 Hz, 1H), 7.64 (d, J = 5.8 Hz, 1H), 7.39 (brs, 3H), 7.28 (m, 2H), 7.09 (d, J = 15.6 Hz, 1H), 6.30 (brs, 2H); ^{13}C NMR (CDCl_3): δ = 162.5, 143.3, 135.4, 132.6, 131.5, 130.4, 127.9, 127.1, 119.3, 118.6, 113.5; ESI-MS: m/z 254 $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{13}\text{H}_{11}\text{ONCl}$ $[\text{M}+\text{H}]^+$: 232.0529; found: 232.0526.

(2E)-3-(1-Naphthyl)-1-pyrrol-1-yl-2-propen-1-one (1i): colorless

solid; IR (KBr) ν 1682, 1616, 1471, 1357 cm^{-1} ; ^1H NMR(CDCl_3): δ =8.76 (d, J = 15.0 Hz, 1H), 8.18 (d, J = 8.3 Hz, 1H),

7.88 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 7.0 Hz, 1H), 7.42-7.57 (m, 5H), 6.31 (brs, 2H); ^{13}C NMR (CDCl_3): δ =162.8, 144.6, 133.7, 131.7, 131.5, 131.2, 128.8, 127.1, 126.4, 125.4, 125.2, 123.3, 119.3, 118.4, 113.4, 113.2; ESI-MS: m/z 267 $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{17}\text{H}_{14}\text{ON}$ $[\text{M}+\text{H}]^+$: 248.1075; found: 248.1077.

(2E)-3-(2-Furyl)-1-pyrrol-1-yl-2-propen-1-one (1j): colorless solid; IR

(KBr) ν 1688, 1618, 1468 cm^{-1} ; ^1H NMR(CDCl_3): δ 7.73 (d, J = 15.3 Hz, 1H), 7.55 (brs, 1H), 7.45-7.48 (m, 2H), 7.04 (d, J = 15.3 Hz, 1H), 6.74 (d,

J = 3.1 Hz, 1H), 6.53 (dd, J = 1.9, 3.1 Hz, 1H), 6.34-6.37 (m, 2H); ^{13}C NMR (CDCl_3): δ 162.8, 150.9, 145.2, 133.1, 119.1, 116.6, 113.2, 113.0, 112.7; ESI-MS: m/z 210 $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{11}\text{H}_{10}\text{O}_2\text{N}$ $[\text{M}+\text{H}]^+$: 188.0711; found: 188.0716.

(2E)-1-Pyrrol-1-yl-3-(2-thienyl)-2-propen-1-one (1k): colorless solid;

IR (KBr) ν 1686, 1609, 1466 cm^{-1} ; ^1H NMR(CDCl_3): δ 8.10 (d, J = 15.0 Hz, 1H), 7.43-7.47 (m, 3H), 7.37 (d, J = 3.4 Hz, 1H), 7.10 (dd, J = 3.4,

4.5 Hz, 1H), 6.92 (d, J = 15.0 Hz, 1H), 6.34-6.38 (m, 2H); ^{13}C NMR (CDCl_3): δ 162.7, 139.8, 139.5, 132.4, 129.3, 128.4, 119.1, 114.2, 113.3; ESI-MS: m/z 226 $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{11}\text{H}_{10}\text{ONS}$ $[\text{M}+\text{H}]^+$: 204.0483; found: 204.0489.

(2E)-3-(4-Pyridyl)-1-pyrrol-1-yl-2-propen-1-one (1l): colorless solid;

IR (KBr) ν 1687, 1466 cm^{-1} ; ^1H NMR(CDCl_3): δ 8.70 (d, J = 4.9 Hz, 1H), 7.87 (d, J = 15.5 Hz, 1H), 7.43-7.46 (m, 4H), 7.29 (d, J = 15.5 Hz, 1H),

6.36-6.38 (m, 2H); ^{13}C NMR (CDCl_3): δ 162.0, 150.7, 144.4, 141.2, 121.9, 120.3, 119.2, 113.9; ESI-MS: m/z 199 $[\text{M}+\text{H}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{12}\text{H}_{11}\text{ON}_2$ $[\text{M}+\text{H}]^+$: 199.0871; found: 199.0871.

(2E)-5-Phenyl-1-pyrrol-1-yl-2-penten-1-one (1m) colorless oil; IR

(neat) ν 1694, 1643, 1467, 1363, 1280 cm^{-1} ; ^1H NMR(CDCl_3): δ =7.38-

7.16 (m, 8H), 6.53 (d, J = 15.0 Hz, 1H), 6.31 (dd, J = 2.5, 2.2 Hz, 2H),

2.85 (t, J = 7.6 Hz, 2H), 2.71-2.62 (m, 2H); ^{13}C NMR (CDCl_3): δ =162.6, 151.2, 140.4,

128.5, 128.3, 126.2, 120.1, 119.1, 113.1, 34.3, 34.2; ESI-MS: m/z 308 $[\text{M}+\text{Na}]^+$; HRMS

(FAB): m/z calcd for $\text{C}_{15}\text{H}_{16}\text{ON}$ $[\text{M}+\text{H}]^+$: 226.1232; found: 226.1234.

(2E)-7-Phenyl-1-pyrrol-1-yl-2-hepten-1-one (1n): colorless oil; IR

(KBr) ν 2933, 1696, 1642, 1468, 1353, 1287 cm^{-1} ; ^1H

NMR(CDCl_3): δ =7.36 (dd, J = 2.4, 2.1 Hz, 2H), 7.22- 7.34 (m,

3H), 7.15-7.21 (m, 3H), 6.54 (d, J = 15.0 Hz, 1H), 2.64 (t, J = 7.6 Hz, 2H), 2.36 (m, 2H),

1.69(m, 2H), 1.58 (m, 2H); ^{13}C NMR (CDCl_3): δ =162.7, 152.5, 142.0, 128.3, 128.3, 125.8,

119.1, 113.1, 35.6, 32.6, 30.9, 27.5; ESI-MS: m/z 276 $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd

for $\text{C}_{17}\text{H}_{20}\text{ON}$ $[\text{M}+\text{H}]^+$: 254.1545; found: 254.1538.

(2E)-3-Cyclohexyl-1-pyrrol-1-yl-2-propen-1-one (1o): colorless oil; IR

(neat) ν 2926, 2852, 1696, 1634, 1468, 1346, 1286 cm^{-1} ; ^1H

NMR(CDCl_3): δ =7.38 (dd, J = 2.5, 2.2 Hz, 2H), 7.22 (dd, J = 15.3, 7.1 Hz, 1H), 6.50 (dd, J

= 15.3, 1.3 Hz, 1H), 6.32 (dd, J = 2.5, 2.2 Hz, 2H), 2.26 (m, 1H), 1.65-1.90 (m, 5H), 1.15-

1.40 (m, 5H); ^{13}C NMR (CDCl_3): δ =163.1, 157.6, 119.1, 116.9, 113.0, 41.0, 31.6, 25.8,

25.6; ESI-MS: m/z 225.7 $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{15}\text{H}_{23}\text{O}_4$ $[\text{M}+\text{H}]^+$:

204.1388; found: 204.1382.

(2E)-4,4-Dimethyl-5-phenyl-1-pyrrol-1-yl-2-penten-1-one (1p): IR

(KBr) ν 2956, 1682, 1629, 1469, 1349, 1297 cm^{-1} ; ^1H

NMR(CDCl_3): δ =7.05-7.38(m, 8H), 6.25-6.29 (m, 3H), 2.71 (s, 2H),

1.12 (s, 6H); ^{13}C NMR (CDCl_3): δ =163.0, 160.7, 137.4, 130.4, 130.2, 128.1, 127.9, 126.4, 119.2, 116.3, 113.1, 48.5, 38.5, 26.1; ESI-MS: m/z 276 $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{17}\text{H}_{20}\text{ON}$ $[\text{M}+\text{H}]^+$: 254.1545; found: 254.1542.

(2E)-5-Benzyloxy-4,4-dimethyl-1-pyrrol-1-yl-2-penten-1-one (1q):

pale yellow oil; IR (neat) ν 2963, 2868, 1697, 1637, 1467, 1344, 1305, 1267 cm^{-1} ; ^1H NMR(CDCl_3): δ =7.22-7.36 (m, 8H), 6.50 (d, J = 15.6 Hz, 1H), 6.29 (dd, J = 2.5, 2.2 Hz, 2H), 4.51 (s, 2H), 3.31 (s, 2H), 1.15 (s, 6H); ^{13}C NMR (CDCl_3): δ =163.1, 158.8, 138.2, 128.3, 127.5, 127.4, 119.2, 117.0, 113.0, 77.9, 73.3, 38.8, 23.9; ESI-MS: m/z 306 $[\text{M}+\text{Na}]^+$; HRMS: m/z calcd for $\text{C}_{18}\text{H}_{21}\text{O}_2\text{N}$ $[\text{M}+\text{H}]^+$: 284.1650; found: 284.1647.

(2E)-5-(4-Methoxybenzyloxy)-1-pyrrol-1-yl-2-penten-1-one (1r):

pale yellow oil; IR (neat) ν 2858, 1697, 1643, 1513, 1468, 1353, 1291, 1247 cm^{-1} ; ^1H NMR(CDCl_3): δ =7.35 (dd, J = 2.4, 2.1 Hz, 2H), 7.23-7.33 (m, 3H), 6.68 (d, J = 8.6 Hz, 2H), 6.63 (d, J = 15.3 Hz, 1H), 4.47 (s, 2H), 3.81 (s, 3H), 3.61 (t, J = 6.4 Hz, 2H), 2.60-2.64 (m, 2H); ^{13}C NMR (CDCl_3): δ =162.5, 159.2, 129.9, 129.3, 120.9, 119.1, 113.7, 113.1, 72.7, 67.6, 55.1, 33.0; ESI-MS: m/z 308 $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3\text{N}$ $[\text{M}+\text{H}]^+$: 286.1443; found: 286.1440.

(2E)-5-(benzyloxymethyloxy)-1-pyrrol-1-yl-2-penten-1-one (1s):

colorless oil; IR (neat) ν 2878, 1698, 1644, 1467 cm^{-1} ; ^1H NMR(CDCl_3): δ 7.25-7.39 (m, 8H), 6.66 (d, J = 15.2 Hz, 1H), 6.31-6.34 (m, 2H), 4.79 (s, 2H), 4.62 (s, 2H), 3.77 (t, J = 6.1 Hz, 2H), 2.60-2.65 (m, 2H); ^{13}C NMR (CDCl_3): δ 162.3, 148.9, 137.6, 128.4, 127.8, 127.7, 121.1, 119.2, 113.2, 94.7, 69.5, 65.8, 33.1; ESI-MS: m/z 308 $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3\text{N}$ $[\text{M}+\text{H}]^+$: 286.1443; found: 286.1439.

(2E)-9-tert-Butyldimethylsilyloxy-1-pyrrol-1-yl-2-nonen-1-one

(1t): Oil; IR (neat) ν 2930, 2857, 1702, 1641, 1468, 1351, 1291, 1255, 1101 cm^{-1} ; ^1H NMR(CDCl_3): δ =7.38 (dd, J = 2.5, 2.1 Hz, 2H), 7.27 (dt, J = 15.0, 7.3 Hz, 1H), 6.55 (d, J = 15.0 Hz, 1H), 6.32 (dd, J = 2.4, 2.1 Hz, 1H), 3.61 (t, J = 6.4 Hz, 2H), 2.34 (m, 2H), 1.52 (m, 4H), 1.37 (m, 4H), 0.87 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (CDCl_3): δ =162.8, 152.8, 119.4, 119.2, 113.1, 63.1, 32.7, 32.7, 28.9, 28.0, 25.9, 25.6, 18.3, -5.3; ESI-MS: m/z 358 $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{19}\text{H}_{34}\text{O}_2\text{NSi}$ $[\text{M}+\text{H}]^+$: 336.2359; found: 336.2359.

(2E)-1-Pyrrol-1-yl-2-hepten-1,6-dione (1u): colorless oil; IR (neat) ν

1712, 1697, 1643, 1469, 1351, 1293 cm^{-1} ; ^1H NMR(CDCl_3): δ =7.36 (dd, J = 2.5, 2.2 Hz, 2H), 7.20 (dt, J = 15.3, 6.7 Hz, 1H), 6.60 (d, J = 15.3 Hz, 1H), 6.30 (dd, J = 2.5, 2.2 Hz, 2H), 2.67 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (CDCl_3): δ =206.4, 162.4, 150.3, 120.3, 119.1, 113.1, 41.2, 29.8, 26.4; ESI-MS: m/z 214 $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{11}\text{H}_{14}\text{O}_2\text{N}$ $[\text{M}+\text{H}]^+$: 192.1024; found: 192.1023.

(2E)-1-Pyrrol-1-yl-tridec-2,12-dien-1-one (1v) : colorless oil; IR

(neat) ν 2926, 2854, 1702, 1642, 1467, 1351, 1291 cm^{-1} ; ^1H NMR(CDCl_3): δ =7.38 (t, J = 2.4 Hz, 2H), 7.27 (m, 1H), 6.55 (d, J = 15.0 Hz, 1H), 6.32 (dd, J = 2.5, 2.2 Hz, 2H), 5.81 (m, 1H), 4.99 (d, J = 16.9 Hz, 1H), 4.93 (d, J = 10.1 Hz, 1H), 2.33 (m, 2H), 2.03 (m, 2H), 1.25-1.59 (m, 12H); ^{13}C NMR (CDCl_3): δ =167.8, 152.9, 139.1, 119.3, 119.2, 114.1, 113.1, 33.7, 32.8, 29.3, 29.3, 29.1, 29.0, 28.8, 28.0; ESI-MS: m/z 282 $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{17}\text{H}_{26}\text{ON}$ $[\text{M}+\text{H}]^+$: 260.2014; found: 260.2014.

(2E,4E)-1-Pyrrol-1-yl-oct-2,4-dien-1-one (1w): orange oil; IR

(neat) ν 2960, 1694, 1633, 1606, 1469, 1358, 1285 cm^{-1} ; ^1H NMR(CDCl_3): δ =7.58 (dd, J = 14.7, 10.1 Hz, 1H), 7.39 (dd, J = 2.5, 2.5 Hz, 2H), 6.52 (d, J = 14.7 Hz, 1H), 6.28-6.34 (m, 4H), 2.21 (m, 2H), 1.51 (m, 2H), 0.95 (t, J = 7.7 Hz, 3H); ^{13}C NMR (CDCl_3): δ =163.2, 148.0, 147.0, 128.6, 119.1, 116.7, 113.0, 35.1, 21.8, 13.6; ESI-

MS: m/z 212 $[M+Na]^+$; HRMS: m/z calcd for $C_{12}H_{16}ON$ $[M+H]^+$: 190.1232; found: 190.1236.

(2E)-(4R)-4-(tert-Butoxycarbonyl)amino-5-hydroxy-4,5-N,O-

isopropylidene-1-pyrrol-1-yl-2-penten-1-one (1x): IR (neat) ν 2980, 1698, 1647, 1469, 1366, 1292, 1171 cm^{-1} ; 1H NMR($CDCl_3$): δ =7.36 (brs, 2H), 7.12 (brs, 1H), 6.71 and 6.62 (brd, J = 15.6 Hz, 1H), 6.32 and 6.34 (brs, 2H), 4.54 and 4.65 (brs, 1H), 4.14 (brs, 1H), 3.85 and 3.87 (brs, 1H), 1.42, 1.50, 1.53, 1.57, 1.65 and 1.68 (brs, 15H); ^{13}C NMR ($CDCl_3$): δ =162.4, 162.2, 152.0, 151.5, 149.3, 148.0, 120.9, 120.0, 119.2, 113.5, 113.4, 94.7, 94.0, 80.8, 80.3, 67.1, 58.3, 58.2, 28.3, 28.2, 27.4, 26.4, 24.6, 23.5; ESI-MS: m/z 343 $[M+Na]^+$; HRMS: m/z calcd for $C_{17}H_{25}O_4N_2$ $[M+H]^+$: 321.1814; found: 321.1814; $[\alpha]_D^{26}$ -34 (c 1.1, $CHCl_3$).

(2E)-(4S)-4,5-Dihydroxy-4,5-O-isopropylidene-1-pyrrol-1-yl-2-penten-

1-one (1y): orange oil; IR (neat) ν 3444, 2931, 2849, 1472, 1378, 1253, 1164, 1090, 837 cm^{-1} ; 1H NMR($CDCl_3$): δ =7.38 (t, J = 2.5 Hz, 2H), 7.19 (dd, J = 15.3, 4.9 Hz, 1H), 6.88 (dd, J = 15.0, 1.6 Hz, 1H), 6.34 (t, J = 2.5 Hz, 2H), 4.80 (m, 1H), 4.26 (dd, J = 8.3, 6.7 Hz, 1H), 3.74 (dd, J = 8.3, 7.4 Hz, 1H), 1.49 (s, 3H), 1.45 (s, 3H); ^{13}C NMR ($CDCl_3$): δ =162.2, 147.6, 119.8, 119.2, 113.5, 110.3, 68.6, 26.4, 25.7; ESI-MS: m/z 244 $[M+Na]^+$; HRMS: m/z calcd for $C_{12}H_{16}O_3N$ $[M+H]^+$: 222.1130; found: 222.1125; $[\alpha]_D^{26}$ +4.8 (c 1.0, $CHCl_3$).

(2E)-(5R,6R)-7-Benzyloxy-5,6-dihydroxy-5,6-O-isopropylidene-1-pyrrol-1-yl-2-hepten-1-one (1z):

To a 14 mL test tube, was placed aldehyde (367 mg, 1.39 mmol), ylide (563 mg, 1.53 mmol) and toluene (5.0 mL). The mixture was heated to 65 °C for 36 h. Reaction mixture was concentrated, and served to SiO_2 column chromatography (hexane:Et₂O 5:1) to give titled compound (422 mg, 1.19 mmol, 86% yield); pale yellow oil; IR (neat): 3149, 2986, 2865, 1698, 1645, 1467, 1354, 1291, 1074, 938, 743 cm^{-1} ; 1H NMR($CDCl_3$): δ = 7.20-7.40 (m,

7H), 6.65 (d, $J = 15.3$ Hz, 1H), 6.32 (t, $J = 2.4$ Hz, 1H), 4.58 (s, 2H), 4.00-4.06 (m, 1H), 3.87-3.92 (m, 1H), 3.64 (dd, $J = 10.1, 5.2$ Hz, 1H), 3.57 (dd, $J = 10.1, 4.9$ Hz, 1H), 2.65-2.75 (m, 1H), 2.55-2.65 (m, 1H), 1.43 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (CDCl_3): $\delta = 162.3, 147.3, 137.7, 128.4, 127.8, 127.6, 121.8, 119.2, 113.3, 109.3, 79.1, 73.6, 70.2, 36.0, 27.2, 26.9$; ESI-MS: m/z 378 for $[\text{M}+\text{Na}]^+$; HRMS: m/z calcd for $\text{C}_{21}\text{H}_{26}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 356.1862; found: 356.1852; $[\alpha]_{\text{D}}^{23} +15.2$ (c 1.06, CDCl_3).

(B) Application to catalytic asymmetric epoxidation:

General Procedure for Catalytic Asymmetric Epoxidation Reaction with Reduced Catalyst Loading (0.02 mol %): MS 4A (1000 mg, powdered) in a flask was dried prior to use at 160 °C under reduced under vacuum (0.7 KPa) for 3 h. To a stirred suspension of **1a** (1.97 g, 10 mmol), $\text{Ph}_3\text{As}(\text{O})$ (0.644 mg, 0.002 mmol), and (*R*)- H_8 -BINOL (0.589 mg, 0.002 mmol) in THF (2.0 mL) at 25 °C was added $\text{Sm}(\text{O-}i\text{-Pr})_3$ (10 μL , 0.002 mmol, 0.2 M in THF). The mixture was stirred for 15 min at 25 °C and the mixture was cooled to 0 °C. *tert*-Butyl hydroperoxide (TBHP) (15 mmol, 4.5 M in toluene, dried with MS 4A) was added slowly over 60 min (45 min at 0 °C, then 15 min at 25 °C). The stirring was continued for additional 30 min at 25 °C and quenched with 2.5% aqueous citric acid. The mixture was filtered through Celite and the filtrate was extracted with ethyl acetate. Then combined organic layers were washed successively with sat. aq. NaHCO_3 and brine, and was dried over MgSO_4 . The solvent was evaporated and the resulting crude residue was purified by flash silica gel column chromatography (ethyl acetate/hexane = 1/15) to afford **11a** (2.01 g, 94.2% yield, 99% ee).

(C) Sequential Wittig olefination-catalytic asymmetric epoxidation:

Preparation of Sm-(*R*)- H_8 -BINOL Catalyst in THF: To a stirred suspension of MS4A (500 mg) and (*R*)- H_8 -BINOL (7.4 mg, 0.025 mmol) in THF (2.14 mL), $\text{Sm}(\text{O-}i\text{-Pr})_3$ (125 μL , 0.025 mmol, 0.2 M in THF) was added at 25 °C. After stirring for 20 min at this temperature, cumene hydroperoxide (CMHP) (231 μL , 0.75 mmol, 3.25M in toluene) was added. The stirring was continued for another 20 min at 25 °C to afford Sm-(*R*)- H_8 -BINOL

catalyst in THF. The resulting suspension was used for the second catalytic asymmetric epoxidation immediately.

General Procedure for Sequential Wittig-Catalytic Asymmetric Epoxidation Reaction (with 5 mol % Catalyst): To a stirred suspension of ylide **2** (139.1 mg, 0.65 mmol) in toluene (1.25 mL) at 25 °C was added benzaldehyde (**10a**) (50.8 μ L, 0.5 mmol). The stirring was continued for 36 h at 100 °C and cooled to 25 °C. To the reaction solution at 25 °C was added toluene (1.25 mL) and catalyst suspension prepared from Sm(O-*i*-Pr)₃ (125 μ L, 0.025 mmol, 0.2 M in THF), (*R*)-H₈-BINOL (7.4 mg, 0.025 mmol), cumene hydroperoxide (CMHP) (231 μ L, 0.75 mmol, 3.25M in toluene) and MS 4A (2.5 mL) by the above-mentioned procedure. The stirring was continued for 30 min and quenched with 2.5% aqueous citric acid. The mixture was filtered through Celite and the filtrate was extracted with ethyl acetate. Then combined organic layers were washed successively with sat. aq. NaHCO₃ and brine, and was dried over MgSO₄. The solvent was evaporated and the resulting crude residue was purified by flash silica gel column chromatography (ethyl acetate/hexane = 1/20) to afford **11a** (102.4 mg, 96% yield, >99.5% ee).

Scheme S1. Procedure for a sequential Wittig-catalytic asymmetric epoxidation reaction

Absolute configuration of **11a** and **11n** were determined after conversion into known compound by comparison of optical rotation. See, section for the transformation of *N*-acylpyrrole unit. Others were assigned by analogy.

(2*S*,3*R*)-trans-2,3-Epoxy-3-phenyl-1-pyrrol-1-yl-propan-1-one

(11a): IR (KBr) ν 3149, 1714, 1287, 904 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.32-7.42 (m, 7H), 6.33-6.36 (m, 2H), 4.20 (d, $J = 1.9$ Hz, 1H), 4.01 (d, $J = 1.9$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 57.3, 58.8, 114.1, 119.0, 125.7, 128.8, 129.2, 134.4, 164.3; ESI-MS m/z 236 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{24} +150$ (c 1.07, CHCl_3) (>99.5% ee); HRMS calcd. for $\text{C}_{13}\text{H}_{12}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 213.0868, found 213.0870; HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane 2/98, flow 1.0 mL/min, detection at 254 nm) t_{R} 28.0 min (minor) and 36.0 min (major).

(2S,3R)-trans-2,3-Epoxy-3-(2-naphthyl)-1-pyrrol-1-yl-propan-1-one (11b):

IR (KBr) ν 1716, 1288, 910, 818 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.82-7.89 (m, 4H), 7.50-7.53 (m, 2H), 7.41 (br, 1H), 7.37 (dd, $J = 8.3$, 1.2 Hz, 1H), 6.33-6.36 (m, 2H), 4.37 (br, 1H), 4.11 (d, $J = 1.8$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 57.5, 59.1, 114.2, 119.1, 122.2, 125.9, 126.8, 126.8, 127.9, 127.9, 128.9, 131.8, 133.0, 133.7, 164.3; ESI-MS m/z 286 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{24} +169$ (c 1.01, CHCl_3) (99% ee); HRMS calcd. for $\text{C}_{17}\text{H}_{14}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 264.1024, found 264.1023; HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane 2/98, flow 1.0 mL/min, detection at 254 nm) t_{R} 31.4 min (minor) and 40.0 min (major).

(2S,3R)-trans-2,3-Epoxy-3-(4-methylphenyl)-1-pyrrol-1-yl-propan-1-one (11c):

IR (KBr) ν 3152, 1713, 1284, 800 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.20-7.26 (m, 2H), 6.35-6.37 (m, 2H), 4.18 (d, $J = 1.7$ Hz, 1H), 4.02 (d, $J = 1.7$ Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (CDCl_3) δ 21.2, 57.3, 58.9, 114.1, 119.0, 125.7, 129.5, 131.4, 139.3, 164.5; ESI-MS m/z 250 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{25} +153$ (c 1.22, CHCl_3) (99% ee); HRMS calcd. for $\text{C}_{14}\text{H}_{14}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 228.1024, found 228.1026; HPLC (DAICEL CHIRALCEL OJ, 2-propanol/hexane 2/98, flow 1.0 mL/min, detection at 254 nm) t_{R} 33.1 min (major) and 50.2 min (minor).

(2S,3R)-trans-2,3-Epoxy-3-(4-methoxyphenyl)-1-pyrrol-1-yl-propan-1-one (11d):

IR (KBr) ν 1715, 1288, 910, 818 cm^{-1} ; ^1H

NMR (CDCl₃) δ 7.39 (br, 2H), 7.26 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 6.33-6.35 (m, 2H), 4.14 (d, J = 1.9 Hz, 1H), 4.00 (d, J = 1.9 Hz, 1H), 3.81 (s, 3H); ¹³C NMR (CDCl₃) δ 55.4, 57.3, 58.8, 114.1, 114.3, 119.0, 126.3, 127.2, 160.5, 164.5; ESI-MS m/z 266 [M+Na]⁺; [α]_D²⁵ +163 (c 0.93, CHCl₃) (98% ee); HRMS calcd. for C₁₄H₁₄NO₃ [M+H]⁺: 244.0973, found 244.0968; HPLC (DAICEL CHIRALPAK AS-H, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) t_R 20.2 min (minor) and 37.1 min (major).

(2S,3R)-3-(4-Chlorophenyl)-trans-2,3-epoxy-1-pyrrol-1-yl-

propan-1-one (11f): IR (KBr) ν 1740, 1288, 798 cm⁻¹; ¹H NMR (CDCl₃) δ 7.35-7.39 (m, 4H), 7.26-7.28 (m, 2H), 6.34-6.36 (m, 2H), 4.18 (d, J = 1.7 Hz, 1H), 3.96 (d, J = 1.7 Hz, 1H); ¹³C NMR (CDCl₃) δ 56.5, 57.4, 113.5, 118.2, 126.3, 128.3, 132.2, 134.5, 163.2; ESI-MS m/z 270 (for ³⁵Cl), 272 (for ³⁷Cl) [M+Na]⁺; [α]_D²⁵ +153 (c 1.11, CHCl₃) (99% ee); HRMS calcd. for C₁₃H₁₁ClNO₂ [M+H]⁺: 248.0478, found 248.0474; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 5/95, flow 1.0 mL/min, detection at 254 nm) t_R 15.9 min (major) and 18.3 min (minor).

(2S,3R)-3-(2-Chlorophenyl)-trans-2,3-epoxy-1-pyrrol-1-yl-propan-

1-one (11h): IR (KBr) ν 1713, 1294, 903 cm⁻¹; ¹H NMR (CDCl₃) δ 7.37-7.43 (m, 3H), 7.29-7.36 (m, 3H), 6.35-6.37 (m, 2H), 4.52 (d, J = 1.8 Hz, 1H), 3.90 (d, J = 1.8 Hz, 1H); ¹³C NMR (CDCl₃) δ 56.4, 56.6, 114.2, 119.1, 126.1, 127.3, 129.4, 130.0, 132.9, 133.3, 164.1; ESI-MS m/z 270 (for ³⁵Cl), 272 (for ³⁷Cl) [M+Na]⁺; [α]_D²⁵ -74.3 (c 1.15, CHCl₃) (97% ee); HRMS calcd. for C₁₃H₁₁ClNO₂ [M+H]⁺: 248.0478, found 248.0476; HPLC (DAICEL CHIRALPAK AS, 2-propanol/hexane 10/90, flow 1.0 mL/min, detection at 254 nm) t_R 10.8 min (major) and 16.9 min (minor).

(2S,3R)-trans-2,3-Epoxy-3-(1-naphthyl)-1-pyrrol-1-yl-propan-1-one (11i): IR (KBr) ν 1711, 1292, 901, 801 cm⁻¹; ¹H NMR (CDCl₃)

δ 7.99-8.02 (m, 1H), 7.89-7.92 (m, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.47-7.58 (m, 4H), 7.44 (br, 2H), 6.35-6.38 (m, 2H), 4.84 (d, J = 1.7 Hz, 1H), 4.02 (d, J = 1.7 Hz, 1H); ^{13}C NMR (CDCl_3)

δ 56.6, 57.3, 114.2, 119.1, 122.4, 122.6, 125.4, 126.3, 126.9, 128.9, 129.2, 130.7, 131.0, 133.2, 164.6; ESI-MS m/z 286 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{24}$ -157 (c 1.12, CHCl_3) (99% ee); HRMS calcd. for $\text{C}_{17}\text{H}_{14}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 264.1024, found 264.1024; HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane 2/98, flow 1.0 mL/min, detection at 254 nm) t_{R} 16.6 min (minor) and 24.6 min (major).

(2*S*,3*R*)-*trans*-2,3-Epoxy-5-phenyl-1-pyrrol-1-yl-pentan-1-one

(11m): IR (neat) ν 1723, 1288 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.25-7.30 (m, 2H), 7.16-7.23 (m, 5H), 6.28-6.31 (m, 2H), 3.69 (d, J = 1.9 Hz, 1H), 3.30 (dt, J = 5.8, 1.9 Hz, 1H), 2.85-2.91 (m, 1H), 2.75-2.82 (m, 1H), 2.00-2.11 (m, 2H); ^{13}C NMR (CDCl_3) δ 31.7, 33.0, 53.7, 58.8, 113.9, 118.9, 126.4, 128.3, 128.7, 140.2, 165.4; ESI-MS m/z 264 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{24}$ +3.74 (c 0.98, CHCl_3) (97% ee); HRMS calcd. for $\text{C}_{15}\text{H}_{16}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 242.1181, found 242.1178; HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane 2/98, flow 1.0 mL/min, detection at 254 nm) t_{R} 22.3 min (minor) and 29.6 min (major).

(2*S*,3*R*)-*trans*-2,3-Epoxy-7-phenyl-1-pyrrol-1-yl-pentan-1-one

(11n): IR (neat) ν 2934, 1729, 1470, 1360, 1287, 1238 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.40 (brs, 2H), 7.25-7.35 (m, 3H), 7.15-7.24 (m, 2H), 6.34-6.40 (m, 2H), 3.75 (d, J = 1.9 Hz, 1H), 3.27 (ddd, J = 6.4, 4.6, 1.9 Hz, 1H), 2.65 (dd, J = 8.3, 7.0 Hz, 2H), 1.50-1.84 (m, 6H); ^{13}C NMR (CDCl_3) δ 25.3, 30.9, 31.4, 35.6, 53.7, 59.3, 113.9, 119.0, 125.8, 128.3, 128.3, 141.9, 165.5; ESI-MS m/z 292 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{24}$ +1.7 (c 1.1, CHCl_3) (96% ee); HRMS calcd. for $\text{C}_{17}\text{H}_{20}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 270.1494, found 270.1499.

(2*S*,3*R*)-3-Cyclohexyl-*trans*-2,3-epoxy-1-pyrrol-1-yl-propan-1-one

(11o): IR (KBr) ν 3147, 2926, 1718, 1290, 901 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.38-7.41 (m, 2H), 6.32-6.35 (m, 2H), 3.82 (d, $J = 2.2$ Hz, 1H), 3.07 (dd, $J = 2.2, 6.7$ Hz, 1H), 1.86-1.91 (m, 1H), 1.73-1.80 (m, 3H), 1.65-1.70 (m, 1H), 1.38-1.47 (m, 1H), 1.11-1.31 (m, 5H); ^{13}C NMR (CDCl_3) δ 25.3, 25.4, 25.9, 28.7, 29.3, 39.6, 52.7, 63.5, 113.8, 118.9, 165.8; ESI-MS m/z 242 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{24} -26.1$ ($c = 1.02$, CHCl_3) (98% ee); HRMS calcd. for $\text{C}_{13}\text{H}_{18}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 220.1337, found 220.1336; HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane 2/98, flow 1.0 mL/min, detection at 254 nm) t_{R} 11.9 min (minor) and 15.9 min (major).

(2S,3R)-trans-2,3-Epoxy-5-(4-methoxybenzyloxy)-1-pyrrol-1-yl-

pentan-1-one (11r): IR (neat) ν 3145, 1727, 925, 820 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.36-7.38 (m, 2H), 7.21 (d, $J = 8.6$ Hz, 2H), 6.85 (d, $J = 8.6$ Hz, 2H), 6.23-6.25 (m, 2H), 4.44 (d, $J = 11.5$ Hz, 1H), 4.43 (d, $J = 11.5$ Hz, 1H), 3.89 (d, $J = 2.0$ Hz, 1H), 3.79 (s, 3H), 3.56-3.62 (m, 2H), 3.32 (ddd, $J = 4.6, 4.6, 2.0$ Hz, 1H), 2.09-2.16 (m, 1H), 1.87-1.97 (m, 1H); ^{13}C NMR (CDCl_3) δ 31.9, 53.9, 55.3, 57.3, 65.4, 73.0, 113.7, 113.8, 119.1, 129.5, 129.8, 159.3, 165.6; ESI-MS m/z 324 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{25} +163$ ($c = 0.93$, CHCl_3) (97% ee); HRMS calcd. for $\text{C}_{17}\text{H}_{20}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 302.1392, found 302.1388; HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane 2/98, flow 1.0 mL/min, detection at 254 nm) t_{R} 35.3 min (minor) and 43.1 min (major).

(2S,3R)-trans-2,3-epoxy-1-pyrrol-1-yl-heptan-1,6-dione (11u): IR (KBr) ν 1732, 1704, 1295, 909 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.39-7.41 (m, 2H), 6.32-6.34 (m, 2H), 3.82 (d, $J = 1.9$ Hz, 1H), 3.25 (dt, $J = 1.9, 5.8$ Hz, 1H), 2.65 (t, $J = 6.1$ Hz, 2H), 2.16 (s, 3H), 2.06-2.14 (m, 1H), 1.85-1.92 (m, 1H); ^{13}C NMR (CDCl_3) δ 25.1, 30.0, 38.6, 54.0, 58.4, 114.0, 119.0, 165.3, 206.9; ESI-MS m/z 230 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{25} -9.81$ ($c = 1.09$, CHCl_3) (96% ee); HRMS calcd. for $\text{C}_{11}\text{H}_{14}\text{NO}_3$ $[\text{M}+\text{Cs}]^+$: 339.9949, found 339.9952; HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) t_{R} 8.6 min (minor) and 14.2 min (major).

(2*S*,3*R*)-trans-2,3-Epoxy-1-pyrrol-1-yl-tridec-12-en-1-one (11v):

IR (KBr) ν 2918, 1719, 1296, 922 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.39-7.41 (m, 2H), 6.33-6.35 (m, 2H), 5.74-5.83 (m, 1H), 4.94-5.00 (m, 1H), 4.89-4.93 (m, 1H), 3.75 (d, $J = 1.8$ Hz, 1H), 3.25 (ddd, $J = 4.9, 3.1, 1.8$ Hz, 1H), 1.99-2.04 (m, 2H), 1.63-1.78 (m, 2H), 1.42-1.53 (m, 2H), 1.22-1.39 (m, 10H); ^{13}C NMR (CDCl_3)

δ 25.7, 28.9, 29.0, 29.2, 29.3, 29.3, 31.6, 33.8, 53.8, 59.5, 113.9, 114.2, 119.0, 139.1, 165.7; ESI-MS m/z 298 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{25} +0.84$ (c 1.05, CHCl_3) (96% ee); HRMS calcd. for $\text{C}_{17}\text{H}_{26}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 276.1963, found 276.1960; HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane 2/98, flow 1.0 mL/min, detection at 254 nm) t_{R} 15.8 min (minor) and 18.6 min (major).

(2*S*,3*R*)-trans-2,3-epoxy-1-pyrrol-1-yl-4-octen-1-one (11w): IR

(KBr) ν 2950, 1722, 1290, 903 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.37-7.40 (m, 2H), 6.32-6.34 (m, 2H), 6.06 (dt, $J = 15.6, 7.2$ Hz, 1H), 5.24 (ddt, $J = 15.6, 8.2, 1.1$ Hz, 1H), 3.89 (d, $J = 1.8$ Hz, 1H), 3.64 (dd, $J = 8.2, 1.8$ Hz, 1H), 2.07 (ddd, $J = 7.3, 7.2, 1.1$ Hz, 2H), 1.42 (dt, $J = 7.3, 7.3$ Hz, 2H), 0.90 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 13.6, 21.8, 34.4, 55.4, 59.2, 113.9, 119.0, 124.6, 140.2, 165.1; ESI-MS m/z 228 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{25} +4.59$ (c 1.02, CHCl_3) (96% ee); HRMS calcd. for $\text{C}_{12}\text{H}_{16}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 206.1181, found 206.1181; HPLC (DAICEL CHIRALPAK AS, 2-propanol/hexane 2/98, flow 1.0 mL/min, detection at 254 nm) t_{R} 13.4 min (major) and 21.3 min (minor).

(2*S*,3*R*,5*R*,6*R*)-7-Benzoyloxy-trans-2,3-epoxy-5,6-dihydroxy-

5,6-*O*-isopropylidene-1-pyrrol-1-yl-1-heptanone (14): Ylide **2** (1.176 g, 3.183 mmol) and chiral aldehyde **10z** (755 mg, 2.856 mmol) in toluene (11.3 mL) was stirred at 65 °C for 36 h, and then

the mixture was cooled to 25 °C. MS4A (2.32 g) and toluene (7.3 mL) was added to the reaction mixture. To this mixture at 25 °C was added a catalyst suspension mixture

prepared from $\text{Sm}(\text{O-}i\text{-Pr})_3$ (0.2 M in THF, 0.727 ml, 0.1454 mmol), (*R*)- H_8 -BINOL (42.9 mg, 0.1454 mmol), MS 4A (580 mg), THF (5.8 ml), and CMHP (2.5 M in toluene, 1.63 ml, 4.07 mmol). After stirring for 40 min at 25 °C, the mixture was cooled to 0 °C, 5% citric acid (12.5 mL) was added, then diluted with ethyl acetate (30 mL). MS4A was filtered off, organic layer was washed with sat. aq. NaHCO_3 (5 mL x 2), brine (5 mL x 2), and was dried over Na_2SO_4 . After evaporation, the residue oil was purified by silica gel column chromatography (hexane/diethyl ether = 4/1) to give **14** (853 mg, 2.30 mmol, 80% yield) as pale yellow oil: IR (neat) 3144, 2985, 2867, 1731, 1599, 1545, 1472, 1361, 1289, 1094, 916 cm^{-1} ; ^1H NMR(CDCl_3) δ 7.51 (t, J = 2.5 Hz, 2H), 7.25-7.40 (m, 5H), 6.34 (t, J = 2.5 Hz, 2H), 4.57 (s, 2H), 4.03 (m, 1H), 3.89 (d, J = 1.9 Hz, 1H), 3.85 (m, 1H), 3.66 (dd, J = 10.1, 4.9 Hz, 1H), 3.57 (dd, J = 10.1, 5.2 Hz, 1H), 3.37 (m, 1H), 2.25 (ddd, J = 14.1, 5.2, 2.5 Hz, 1H), 1.69 (ddd, J = 14.1, 10.0, 7.0 Hz, 1H), 1.45 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (CDCl_3) δ 165.2, 137.6, 128.4, 127.8, 127.6, 119.1, 113.7, 109.3, 79.4, 75.4, 73.6, 69.8, 56.7, 54.1, 35.9, 27.3, 26.8; $[\alpha]_D^{22}$ -17.4 (c 1.01, CHCl_3); HRMS calcd. for $\text{C}_{21}\text{H}_{26}\text{NO}_{5.5}$ $[\text{M}+\text{H}]^+$ 372.1811, found 372.1808.

(2*R*,3*S*,5*R*,6*R*)-7-Benzoyloxy-*trans*-2,3-epoxy-5,6-dihydroxy-

5,6-*O*-isopropylidene-1-pyrrol-1-yl-1-heptanone (2o): Ylide **2** (235 mg, 0.636 mmol) and chiral aldehyde **10z** (138 mg, 0.522

mmol) in toluene (2.0 mL) was stirred at 65 °C for 36 h, and then the mixture was cooled to 25 °C. MS4A (418 mg) and toluene (1.7 mL) was added to the reaction mixture. To this mixture at 25 °C was added a catalyst suspension mixture prepared from $\text{Sm}(\text{O-}i\text{-Pr})_3$ (0.2 M in THF, 0.13 ml, 0.026 mmol), (*S*)- H_8 -BINOL (7.7 mg, 0.026 mmol), MS4A (104 mg), THF (1.0 mL), and TBHP (5 M in decane, 0.235 ml, 1.17 mmol). After stirring for 40 min at 25 °C, the mixture was cooled to 0 °C, 5% citric acid (2.4 mL) was added, then diluted with ethyl acetate (30 mL). MS4A was filtered off, organic layer was washed with sat. aq. NaHCO_3 (3 mL x 2), brine (3 mL x 2), and was dried over Na_2SO_4 . After evaporation, the residue oil was purified by silica gel column chromatography (hexane/diethyl ether = 4/1) to give **15** (153.1 mg, 0.412 mmol, 78% yield) as pale yellow oil: IR (neat) 3147, 2985, 2865, 1729, 1599, 1546, 1471, 1406, 1363, 1289, 1076, 919 cm^{-1} ; ^1H NMR(CDCl_3) δ 7.44

(brs, 2H), 7.20-7.39(m, 5H), 6.36 (dd, $J = 2.5, 2.5$ Hz, 2H), 4.57 (s, 2H), 4.00 (d, $J = 1.9$ Hz, 1H), 3.95 (m, 2H), 3.64 (dd, $J = 10.1, 4.6$ Hz, 1H), 3.55 (dd, $J = 10.1, 4.9$ Hz, 1H), 3.45 (dt, $J = 1.8, 4.3$ Hz, 1H), 2.15-2.21 (m, 1H), 2.04-2.11 (m, 1H), 1.41 (s, 6H); ^{13}C NMR (CDCl_3) δ 165.4, 137.7, 128.4, 127.8, 127.7, 119.0, 113.9, 109.4, 78.8, 74.7, 73.6, 70.0, 56.1, 53.4, 33.6, 27.1, 27.0; $[\alpha]_{\text{D}}^{22} -4.19$ (c 1.04, CHCl_3); HRMS (FAB) calcd. for $\text{C}_{21}\text{H}_{26}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 372.1811, found 372.1813.

(D) Application of α,β -unsaturated *N*-acylpyrrole to direct catalytic asymmetric Michael reaction:

General Procedure for Direct Asymmetric Michael Reaction of 2-Hydroxy-2'-methoxyacetophenone (4**) with α,β -Unsaturated *N*-Acylpyrrole **1** Promoted by $\text{Et}_2\text{Zn}/(S,S)\text{-linked-BINOL} = 4/1$:**

MS3A (70 mg) in a test tube was dried at 160 °C under vacuum (0.7 KPa) for 3h. After cooling down to room temperature, argon gas was refilled to the test tube and a solution of (*S,S*)-linked-BINOL **5** (20.3 mg, 9.44 w/w% diethyl ether and hexane included, 0.03 mmol) in THF (0.3 mL) was charged. The resulting mixture was cooled to -20 °C, and was added Et_2Zn (120 μL , 0.12 mmol, 1.0M in hexanes). After stirring for 15 min at -20 °C, a mixture solution of α,β -unsaturated *N*-acylpyrrole **1a** (59.2 mg, 0.3 mmol) and hydroxyketone **4** (99.7 mg, 0.6 mmol) in THF (1 mL) was added. The stirring was continued for 5-10 min at -20 °C, and then, the mixture was stirred at 0 °C for 17 h. After addition of saturated aqueous NH_4Cl , the mixture was extracted with ethyl acetate. The combined organic layers were washed with brine and dried over MgSO_4 . The solvent was evaporated and the crude residue was purified by flash silica gel column chromatography (ethyl acetate/hexane = 1/10–1/6) to afford **16a** (92.9 mg, 85% yield, dr = 91/9, *syn* = 91% ee).

Diastereomeric ratio was determined by ^1H NMR analysis. Absolute configuration of **16k** was determined by Mosher's method. Absolute configurations of others were assigned by analogy.

(2*R*,3*R*)-2-Hydroxy-1-(2-methoxyphenyl)-3-phenyl-5-(pyrrol-1-yl)-1,5-pentanedione

(16a): IR (KBr) ν 3453, 1715, 1668, 1598 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.55 (dd, $J = 7.6, 7.6$ Hz, 1H), 7.44 (d, $J = 7.6$ Hz, 1H), 7.41 (brs, 2H), 6.90-7.20 (m, 7H), 6.29-6.32 (m, 2H), 5.54 (dd, $J = 1.9, 5.5$ Hz, 1H), 3.97 (d, $J = 5.5$ Hz, 1H), 3.92 (s, 3H), 3.81-3.87 (m, 1H), 3.70 (dd, $J = 8.6, 16.2$ Hz, 1H), 3.25 (dd, $J = 5.8, 16.2$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 37.8, 44.1, 55.5, 60.3, 78.0, 111.5, 113.2, 119.1, 120.8, 124.2, 127.3, 127.9, 128.5, 131.6, 134.9, 137.9, 158.6, 169.1, 200.8; ESI-MS m/z 386 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{22} +126$ (c 0.99, CHCl_3) (91% ee); HRMS calcd. for $\text{C}_{22}\text{H}_{22}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 364.1550, found 364.1545; HPLC (DAICEL CHIRALPAK OD-H, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) t_{R} 6.4 min (minor) and 7.4 min (major).

(2R,3R)-2-Hydroxy-3-(4-methylphenyl)-1-(2-methoxyphenyl)-5-(pyrrol-1-yl)-1,5-pentanedione (16c): IR (neat) ν 3454, 2942, 1715, 1666, 1597 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.55 (ddd, $J = 1.8, 7.7, 7.7$ Hz, 1H), 7.48 (dd, $J = 1.8, 7.7$ Hz, 1H), 7.40 (brs, 2H), 6.99-7.04 (m, 2H), 6.95 (d, $J = 7.9$ Hz, 2H), 6.81 (d, $J = 7.9$ Hz, 2H), 6.29-6.32 (m, 2H), 5.52 (dd, $J = 2.5, 6.1$ Hz, 1H), 3.92 (d, $J = 6.1$ Hz, 1H), 3.92 (s, 3H), 3.78-3.83 (m, 1H), 3.67 (dd, $J = 8.2, 15.7$ Hz, 1H), 3.24 (dd, $J = 6.1, 15.7$ Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (CDCl_3) δ 21.0, 37.9, 43.7, 55.5, 78.1, 111.5, 113.2, 119.1, 120.9, 124.2, 128.4, 128.6, 131.7, 134.7, 134.9, 136.8, 158.7, 169.2, 200.9; ESI-MS m/z 400 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{22} +144$ (c 1.8, CHCl_3) (93% ee); HRMS calcd. for $\text{C}_{23}\text{H}_{24}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 378.1706, found 378.1693; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 10/90, flow 1.0 mL/min, detection at 254 nm) t_{R} 15.0 min (minor) and 18.8 min (major).

(2R,3R)-2-Hydroxy-1-(2-methoxyphenyl)-3-(4-methoxyphenyl)-5-(pyrrol-1-yl)-1,5-pentanedione (16d): IR (neat) ν 3447, 2938, 1715, 1667 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.54-7.58 (m, 1H), 7.45 (dd, $J = 1.5, 7.6$ Hz, 1H), 7.39 (brs, 2H), 6.98-7.05 (m, 2H), 6.82-6.85 (m, 2H), 6.65-6.67 (m, 2H), 6.29-6.31 (m, 2H), 5.49 (dd, $J = 2.5, 6.1$ Hz, 1H), 3.92 (d, $J = 6.1$ Hz, 1H), 3.92 (s, 3H), 3.76-3.81 (m, 1H), 3.74 (s, 3H), 3.64 (dd, $J = 8.0, 16.0$ Hz, 1H),

3.22 (dd, $J = 6.1, 16.0$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 38.1, 43.3, 55.0, 55.5, 78.2, 111.5, 113.2, 113.3, 119.1, 120.9, 124.2, 129.6, 129.9, 131.6, 134.9, 158.6, 169.2, 201.0; ESI-MS m/z 416 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{23} +145$ ($c = 1.4$, CHCl_3) (95% ee); HRMS calcd. for $\text{C}_{23}\text{H}_{24}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 394.1655, found 394.1665; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 10/90, flow 1.0 mL/min, detection at 254 nm) t_{R} 13.5 min (minor) and 16.2 min (major).

(2*R*,3*R*)-3-(4-Bromophenyl)-1-(2-methoxyphenyl)-5-(pyrrol-1-yl)-2-triethylsilyloxy-1,5-pentanedione (16e): Diastereomers were

separated after conversion into TES ether. IR (neat) ν 2953, 1717, 1699, 1467 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.45 (ddd, $J = 1.6, 7.6, 7.6$ Hz, 1H), 7.23-7.30 (m, 4H), 7.13 (dd, $J = 1.6, 7.6$ Hz, 1H), 6.90-6.95 (m, 4H), 6.26-6.29 (m, 2H), 5.76 (d, $J = 3.7$ Hz, 1H), 3.89 (s, 3H), 3.68-3.74 (m, 1H), 3.49 (dd, $J = 7.9, 16.8$ Hz, 1H), 3.11 (dd, $J = 6.1, 16.8$ Hz, 1H), 0.95-0.99 (m, 9H), 0.57-0.70 (m, 6H); ^{13}C NMR (CDCl_3) δ 4.92, 6.90, 37.8, 43.5, 55.5, 79.6, 111.1, 113.2, 118.9, 120.8, 121.1, 127.1, 130.6, 130.8, 130.9, 133.4, 138.1, 157.5, 168.7, 201.1; ESI-MS m/z 578, 580 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{23} +66$ ($c = 0.94$, CHCl_3) (93% ee); HRMS calcd. for $\text{C}_{28}\text{H}_{35}\text{BrNO}_4\text{Si}$ $[\text{M}+\text{H}]^+$: 556.1518, found 556.1517; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 1/99, flow 1.0 mL/min, detection at 254 nm) t_{R} 5.9 min (minor) and 10.3 min (major).

(2*R*,3*R*)-3-(4-Chlorophenyl)-2-hydroxy-1-(2-methoxyphenyl)-5-(pyrrol-1-yl)-1,5-pentanedione (16f): IR (neat) ν 3450, 2942, 1716,

1666, 1597 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.57 (dd, $J = 7.5, 7.5$ Hz, 1H), 7.45 (d, $J = 7.5$ Hz, 1H), 7.38 (brs, 2H), 7.10 (d, $J = 8.1$ Hz, 1H), 6.98-7.05 (m, 2H), 6.86 (d, $J = 8.1$ Hz, 1H), 6.31 (brs, 2H), 5.49 (dd, $J = 2.1, 5.5$ Hz, 1H), 3.99 (d, $J = 5.5$ Hz, 1H), 3.93 (s, 3H), 3.79-3.86 (m, 1H), 3.64 (dd, $J = 7.9, 16.5$ Hz, 1H), 3.24 (dd, $J = 6.4, 16.5$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 37.8, 43.4, 55.6, 78.0, 115.7, 113.3, 119.1, 121.0, 124.0, 128.1, 129.9, 131.6, 133.1, 135.1, 136

.4, 158.7, 168.8, 200.6; ESI-MS m/z 420, 422 $[M+Na]^+$; $[\alpha]_D^{22} +173$ (c 1.5, $CHCl_3$) (90% ee); HRMS calcd. for $C_{22}H_{21}ClNO_4$ $[M+H]^+$: 398.1159, found 398.1159; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 10/90, flow 1.0 mL/min, detection at 254 nm) t_R 17.6 min (minor) and 20.1 min (major).

(2*R*,3*R*)-3-(3-Chlorophenyl)-2-hydroxy-1-(2-methoxyphenyl)-5-

(pyrrol-1-yl)-1,5-pentanedione (16g): IR (neat) ν 3447, 2947, 1716,

1669, 1597 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.58 (ddd, J = 1.4, 8.0, 8.0 Hz, 1H), 7.44 (dd, J = 1.4, 8.0 Hz, 1H), 7.39 (brs, 2H), 7.14 (dd, J = 1.0,

8.0 Hz, 1H), 7.01-7.08 (m, 3H), 6.89 (s, 1H), 6.79 (brd, J = 7.6 Hz, 1H), 6.30-6.33 (m, 2H), 5.50 (dd, J = 2.5, 5.8 Hz, 1H), 3.99 (d, J = 5.8 Hz, 1H), 3.93 (s, 3H), 3.78-3.83 (m, 1H), 3.66 (dd, J = 7.9, 16.5 Hz, 1H), 3.23 (dd, J = 6.1, 16.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 37.5, 43.7, 55.6, 77.8, 111.6, 113.3, 119.1, 121.0, 124.1, 126.7, 127.5, 128.8, 129.1, 131.5, 133.7, 135.1, 139.9, 158.6, 168.8, 200.6; ESI-MS m/z 420, 422 $[M+Na]^+$; $[\alpha]_D^{23} +111$ (c 0.65, $CHCl_3$) (88% ee); HRMS calcd. for $C_{22}H_{21}ClNO_4$ $[M+H]^+$: 398.1159, found 398.1159; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 10/90, flow 1.0 mL/min, detection at 254 nm) t_R 11.8 min (minor) and 13.9 min (major).

(2*R*,3*S*)-3-(2-Furyl)-2-hydroxy-1-(2-methoxyphenyl)-5-(pyrrol-1-yl)-1,5-pentanedione (16j): IR (neat) ν 3462, 1715, 1667, 1598,

1469 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.67 (d, J = 7.6 Hz, 1H), 7.55 (dd, J = 7.6, 7.6 Hz, 1H), 7.40 (brs, 2H), 7.19 (brs, 1H), 7.00-7.06 (m,

2H), 6.30-6.33 (m, 2H), 6.17-6.21 (m, 1H), 5.85 (brs, 1H), 5.41 (dd, J = 3.0, 6.7 Hz, 1H), 4.02-4.08 (m, 1H), 3.93 (s, 3H), 3.90 (d, J = 6.7 Hz, 1H), 3.57 (dd, J = 7.9, 16.5 Hz, 1H), 3.34 (dd, J = 6.4, 16.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 35.9, 38.5, 55.6, 77.6, 107.3, 110.0, 111.6, 113.3, 119.2, 121.0, 124.0, 131.6, 134.9, 141.6, 152.0, 158.6, 168.7, 200.7; ESI-MS m/z 376 $[M+Na]^+$; $[\alpha]_D^{22} +157$ (c 1.9, $CHCl_3$) (90% ee); HRMS calcd. for $C_{20}H_{20}NO_5$ $[M+H]^+$: 354.1341, found 354.1343; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 10/90, flow 1.0 mL/min, detection at 254 nm) t_R 19.0 min (minor) and 28.3 min (major).

(2*R*,3*S*)-2-Hydroxy-1-(2-methoxyphenyl)-5-(pyrrol-1-yl)-3-(2-

thienyl)-1,5-pentanedione (16k): IR (neat) ν 3448, 2942, 1714, 1667, 1468 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.55 (d, $J = 7.8$, 7.8 Hz, 1H), 7.50 (d, $J = 7.8$ Hz, 1H), 7.39 (brs, 2H), 7.10 (d, $J = 4.9$ Hz, 1H), 6.98-7.05 (m, 2H), 6.78 (dd, $J = 3.1$, 4.9 Hz, 1H), 6.46 (d, $J = 3.1$ Hz, 1H), 6.29-6.34 (m, 2H), 5.47 (dd, $J = 2.3$, 5.8 Hz, 1H), 4.20-4.27 (m, 1H), 4.13 (d, $J = 5.8$ Hz, 1H), 3.943 (s, 3H), 3.62 (dd, $J = 8.3$, 16.5 Hz, 1H), 3.24 (dd, $J = 6.0$, 16.5 Hz, 1H); ^{13}C NMR (CDCl_3) δ 39.4, 40.3, 55.6, 77.6, 114.5, 113.3, 119.1, 120.9, 123.8, 124.7, 125.9, 131.6, 134.9, 139.7, 158.6, 168.6, 200.5; ESI-MS m/z 392 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{23} +71$ (c 4.5, CHCl_3) (90% ee); HRMS calcd. for $\text{C}_{20}\text{H}_{20}\text{NO}_4\text{S}$ $[\text{M}+\text{H}]^+$: 370.1114, found 370.1118; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 10/90, flow 1.0 mL/min, detection at 254 nm) t_{R} 15.9 min (minor) and 18.8min (major).

(2*R*,3*R*)-2-Hydroxy-1-(2-methoxyphenyl)-3-(4-pyridyl)-5-

(pyrrol-1-yl)-1,5-pentanedione (16l): IR (nujol) ν 3438, 1717, 1669, 1463 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.37 (d, $J = 4.9$ Hz, 2H), 7.59 (dd, $J = 7.6$, 7.6 Hz, 1H), 7.45 (d, $J = 7.6$ Hz, 1H), 7.38 (brs, 2H), 7.00-7.06 (m, 2H), 6.85 (d, $J = 4.9$ Hz, 2H), 6.31-6.33 (m, 2H), 5.51 (dd, $J = 2.4$, 4.9 Hz, 1H), 4.05 (d, $J = 4.9$ Hz, 1H), 3.95 (s, 3H), 3.80-3.85 (m, 1H), 3.67 (dd, $J = 7.6$, 16.2 Hz, 1H), 3.29 (dd, $J = 6.1$, 16.2 Hz, 1H); ^{13}C NMR (CDCl_3) δ 37.1, 43.4, 55.6, 77.7, 111.6, 113.5, 119.0, 121.1, 123.8, 131.5, 135.3, 146.9, 149.4, 158.6, 168.4, 200.1; ESI-MS m/z 387 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{23} +114$ (c 0.53, CHCl_3) (90% ee); HRMS calcd. for $\text{C}_{21}\text{H}_{21}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 365.1501, found 365.1513; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 20/80, flow 0.75 mL/min, detection at 254 nm) t_{R} 28.3 min (major) and 31.7 min (minor).

(2*R*,3*R*)-3-[2-(Benzyloxymethyloxy)-ethyl]-2-hydroxy-1-(2-methoxyphenyl)-5-(pyrrol-1-yl)-1,5-pentanedione (16s): IR (neat) ν 3463, 2937, 1715, 1661, 1597 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.76 (dd,

$J = 1.5, 7.6$ Hz, 1H), 7.54 (ddd, $J = 1.5, 7.6, 8.3$ Hz, 1H), 7.26-7.35 (m, 5H), 7.14 (brs, 2H), 7.04 (dd, $J = 7.6, 7.6$ Hz, 1H), 6.97 (d, $J = 8.3$ Hz, 1H), 6.20-6.22 (m, 2H), 5.30 (brd, $J = 4.9$ Hz, 1H), 4.72 (d, $J = 7.0$ Hz, 1H), 4.71 (d, $J = 7.0$ Hz, 1H), 4.56 (d, $J = 12.6$ Hz, 1H), 4.56 (d, $J = 12.6$ Hz, 1H), 3.99 (d, $J = 4.9$ Hz, 1H), 3.85 (s, 3H), 3.72-3.83 (m, 2H), 2.74-2.82 (m, 2H), 2.47-2.53 (m, 1H), 1.98-2.06 (m, 1H), 1.85-1.93 (m, 1H); ^{13}C NMR (CDCl_3) δ 32.1, 33.4, 35.2, 55.4, 65.8, 69.3, 77.9, 94.4, 111.7, 112.9, 118.9, 121.1, 124.0, 127.6, 127.8, 128.3, 131.1, 135.0, 137.8, 158.5, 169.3, 202.8; ESI-MS m/z 474 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{22} +58$ (c 1.4, CHCl_3) (73% ee); HRMS calcd. for $\text{C}_{26}\text{H}_{30}\text{NO}_6$ $[\text{M}+\text{H}]^+$: 452.2073, found 452.2080; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) t_{R} 12.1 min (minor) and 22.8 min (major).

(F) Transformation of *N*-acylpyrrole unit:

***tert*-Butyl (4*R*,5*S*)-*trans*-4,5-epoxy-3-oxo-5-phenylpentanoate (**22**):** To a solution of 0.75 M LDA in THF-hexane (1.0 mL, 0.75 mmol) at -78 °C was added *t*-butyl acetate (0.10 mL, 0.742 mmol) slowly over 4 min. The mixture was stirred for 20 min at -78 °C. A solution of **11a** (56 mg, 0.262 mmol) in THF (0.8 mL) was added at -78 °C. After stirring for 10 min at -78 °C, sat. aq. NH_4Cl (1 mL) was added. The mixture was extracted with ethyl acetate. Organic layer was washed with 1M HCl, pH 7 phosphate buffer, brine, and was dried over Na_2SO_4 . After evaporation, the residue oil was dissolved in CH_2Cl_2 (5 mL), DBU (90 mg, in CH_2Cl_2 1 mL) was added and stirred for 20 min at 25 °C. To the reaction mixture was added CHCl_3 , and then 1M HCl. The organic layer was washed with pH 7 phosphate buffer, brine, and was dried over Na_2SO_4 , filtered and concentrated. After evaporation, the residue was purified by silica gel column chromatography (hexane/diethyl ether = 15/1 to 10/1) to give **22** (51.5 mg, 0.196 mmol, 74% yield) as pale yellow oil: IR (neat) 3437, 2979, 2932, 1733, 1713, 1652, 1457, 1369, 1325, 1253, 1154 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.24-7.43 (m, 5H), 4.06 (d, $J = 1.7$ Hz, 1H), 3.60 (d, $J = 1.7$ Hz, 1H), 3.43 (d, $J = 3.1$ Hz, 2H), 1.47 (s, 9H); ^{13}C NMR (CDCl_3) major peaks δ 198.8, 165.6, 134.7, 129.1, 128.7, 128.6, 125.6, 91.7, 82.5, 63.0, 58.0, 45.3, 28.2, 28.1, 27.9, minor peaks 172.0, 170.2, 135.7, 81.6, 59.3, 59.1, 31.1; ESI-MS m/z 285 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{24} +40.5$ (c 0.7, CHCl_3); HRMS (FAB): m/z calcd for $\text{C}_{15}\text{H}_{19}\text{O}_4$ $[\text{M}+\text{H}]^+$:

263.1283; found: 263.1283.

(2S,3R)-trans-2,3-epoxy-1,3-diphenylpentan-1-one (23): To a solution of bromobenzene (116 mg, 0.738 mmol) in THF (1.2 mL) at -78°C was added BuLi (1.58 M in hexane, 0.47 mL, 0.695 mmol). The mixture was stirred for 10 min at the same temperature. A solution of **11a** (96 mg, 0.45 mmol) in THF (1.2 mL) was added at -78°C . After stirring for 10 min at -78°C , sat. aq. NH_4Cl (1.5 mL) was added. The mixture was extracted with ethyl acetate. The organic layer was washed with aq. NaH_2PO_4 , sat. aq. NaHCO_3 , brine, and was dried over Na_2SO_4 . After evaporation, the residue was dissolved in CH_2Cl_2 , DBU (50 μL) was added, and the mixture was stirred for 20 min at 25°C . The mixture was diluted with CHCl_3 , washed with 1 M HCl, sat. aq. NaHCO_3 , brine, and was dried over Na_2SO_4 . After evaporation, the residue was purified by silica gel column chromatography (hexane/diethyl ether = 10/1) to give **23** (89 mg, 0.3968 mmol, y. 88%) as colorless oil: IR (neat) 1687, 1597, 1449, 1231, 1008 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.01 (d, $J = 7.0$ Hz, 2H), 7.30-7.68 (m, 8H), 4.30 (d, $J = 1.8$ Hz, 1H), 4.08 (d, $J = 1.8$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 193.0, 135.4, 134.0, 129.0, 128.8, 128.7, 128.3, 125.7, 70.0, 59.3; ESI-MS m/z 247 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{24} +209$ (c 1.0, CH_2Cl_2). Analytical data was identical to that of reported: lit. Marsman, B.; Wynberg, H. *J. Org. Chem.* **1979**, *44*, 2312.

(1S,2R)-trans-1,2-epoxy-3-oxo-1-phenyl-4-octyne (24): To a solution of 1-pentyne (0.167 mL, 1.7 mmol) in THF (1.4 mL) at -78°C was added BuLi (1.56 M in hexane, 0.96 mL, 1.5 mmol). The mixture was stirred for 30 min at the same temperature. A solution of **11a** (105 mg, 0.492 mmol) in THF (1.4 mL) was added at -78°C . After stirring for 10 min at -78°C , sat. aq. NH_4Cl (2 mL) was added. The mixture was extracted with ethyl acetate. The organic layer was washed with 1 M HCl, sat. aq. NaHCO_3 , brine, and was dried over Na_2SO_4 . After evaporation, obtained residue was dissolved in CH_2Cl_2 (15 mL), DBU (0.184 M in CH_2Cl_2 , 0.1 mL, 0.0184 mmol) was added, stirred for 10 min at 0°C . The mixture was diluted with CHCl_3 , washed with 1 M HCl, sat. aq. NaHCO_3 , brine, and was dried over Na_2SO_4 . After evaporation, the residue was purified by silica gel column chromatography (hexane/diethyl

ether = 15/1 to 10/1) to give **24** (88.7 mg, 0.414 mmol, 84% yield) as yellow oil: IR (neat) 2965, 2935, 2875, 2210, 1667, 1457, 1405, 1257, 1179 cm^{-1} ; ^1H NMR(CDCl_3) δ 7.27-7.50 (m, 5H), 4.17 (d, J = 1.5 Hz, 1H), 3.61 (d, J = 1.8 Hz, 1H), 2.41 (t, J = 7.3 Hz, 2H), 1.65 (dq, J = 7.3, 7.3 Hz, 2H), 1.04 (t, J = 7.3 Hz, 3H); ^{13}C NMR (CDCl_3) δ 182.6, 134.8, 129.0, 128.7, 125.7, 98.8, 78.3, 63.6, 58.6, 21.1, 13.4; ESI-MS m/z 237 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{24} +166$ (c 0.95, CHCl_3); HRMS (FAB): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{O}_2$ $[\text{M}+\text{H}]^+$: 215.1072; found: 215.1074.

(2R,3R)-trans-2,3-epoxy-5-phenyl-1-pentanol (25): To a suspension of LiBH_4 (15.6 mg, 0.72 mmol) in THF(0.8 mL) at 0 $^\circ\text{C}$, was added a solution of **2a** (50.5 mg, 0.209 mmol) in THF(0.8 mL). The mixture was stirred for 20 min at 0 $^\circ\text{C}$, then at 25 $^\circ\text{C}$ for 40 min. The reaction mixture was poured to ethyl acetate-sat. aq. NH_4Cl mixture at 0 $^\circ\text{C}$. The organic layer was separated, washed with pH 7 phosphate buffer, brine, and was dried over Na_2SO_4 . After evaporation, the residue oil was dissolved in THF (1 mL), and the solution was added to the suspension of NaBH_4 (27 mg, 0.71 mmol) in THF (1.5 mL) at 25 $^\circ\text{C}$. After stirring for 4 h, the reaction mixture was poured to ethyl acetate-sat.aq. NH_4Cl mixture at 0 $^\circ\text{C}$. Organic layer was separated, washed with pH 7 phosphate buffer, brine, and was dried over Na_2SO_4 . After evaporation, the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 3/1) to give **8** (0.151 mmol, 72% yield) as colorless oil: IR (neat) 3409, 2926, 1603, 1496, 1454, 1231, 1087, 878 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.18-7.32(m, 5H), 3.81-3.88 (m, 1H), 3.54-3.60 (m, 1H), 2.98-3.02 (m,1H), 2.80-2.88 (m, 2H), 2.70-2.78 (m, 1H), 1.84-1.97 (m, 2H); ^{13}C NMR (CDCl_3) δ 141.0, 128.4, 128.3, 126.0, 61.6, 58.7, 55.3, 33.2, 32.1; ESI-MS m/z 201 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{25} +42.6$ (c 2.41, CHCl_3); HRMS (FAB): m/z calcd for $\text{C}_{11}\text{H}_{15}\text{O}_2$ $[\text{M}+\text{H}]^+$: 179.1072; found: 179.1073.

(2E,4R,5R)-Ethyl trans-4,5-Epoxy-6-(4-methoxybenzyloxy)-2-heptenoate (26): To a solution of epoxide **11r** (29.2 mg, 0.097 mmol) in THF (0.4 mL) at 0 $^\circ\text{C}$ was added LiBH_4 (8.2 mg, 0.339 mmol) in THF (0.4 mL). The mixture was stirred at 25 $^\circ\text{C}$ for 5 min, then, sat. aq NH_4Cl was added. The mixture was extracted with AcOEt (x 3 times), and the organic layer was

washed with brine, dried over Na₂SO₄. After evaporation, the residue (pyrrole carbinol) was used in next step without purification. To a mixture of LiCl (7.4 mg, 0.174 mmol), DBU (21.7 μ L, 0.145 mmol), and (EtO)₂P(O)CH₂CO₂Et (35.7 μ L, 0.174 mmol) in CH₃CN (0.9 mL) at 25 °C was pyrrole carbinol in CH₃CN (0.6 mL). The mixture was stirred at 25 °C for 4 h, then, sat. aq NH₄Cl was added. The mixture was extracted with AcOEt (x 2 times), and the organic layer was washed with brine, dried over Na₂SO₄. After evaporation, the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 10/1 to 5/1) to give **26** (20.4 mg 0.067mmol, 69% yield) as pale yellow oil. IR (neat) ν 2927, 1718, 1512, 1249 cm⁻¹; ¹H NMR (CDCl₃) δ 7.25 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.67 (dd, *J* = 7.0, 15.6 Hz, 1H), 6.11 (d, *J* = 15.6 Hz, 2H), 4.45 (s, 2H), 4.20 (q, *J* = 7.0 Hz, 2H), 3.81 (s, 3H), 3.58 (dd, *J* = 5.5, 6.5 Hz, 2H), 3.26 (dd, *J* = 1.6, 7.0 Hz, 1H), 3.02-3.05 (m, 1H), 1.83-1.97 (m, 2H), 1.29 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (CDCl₃) δ 14.2, 32.4, 55.3, 56.3, 59.1, 60.6, 66.2, 72.8, 113.8, 123.8, 129.2, 130.2, 144.5, 159.2, 165.6; ESI-MS *m/z* 329 [M+Na]⁺; [α]_D²³ +10 (*c* 0.27, CHCl₃).

(3*R*,4*R*)-Ethyl 5-(2-Methoxyphenyl)-5-oxo-3-phenyl-4-(triethylsilyloxy) pentanoate (28): To a solution of **27** (22.9 mg, 0.479mmol) in EtOH (0.15 mL) at 0 °C was added a solution of EtSLi (0.101 mmol, prepared from EtSH and BuLi) in EtOH (0.2 mL). The mixture was stirred at 25 °C for 2 h, then, sat. aq NH₄Cl was added. The mixture was extracted with AcOEt (x 3 times), and the organic layer was washed with brine, dried over Na₂SO₄. After evaporation, the residue was purified by silica gel column chromatography (hexane/diethyl ether= 10/1) to give **28** (20.9 mg 0.458mmol, 96% yield) as colorless oil. IR (neat) ν 2953, 2875, 1734, 1692, 1246 cm⁻¹; ¹H NMR (CDCl₃) δ 7.41-7.44 (m, 1H), 7.01-7.02 (m, 2H), 6.89-6.93 (m, 2H), 5.61 (d, *J* = 3.7 Hz, 1H), 4.00-4.07 (m, 2H), 3.90 (s, 3H), 3.52 (ddd, *J* = 3.7, 7.6, 7.6 Hz, 1H), 2.94 (dd, *J* = 7.6, 15.9 Hz, 1H), 2.68 (dd, *J* = 7.6, 15.9 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H), 0.98 (t, *J* = 8.3 Hz, 9H), 0.58-0.70 (m, 6H); ¹³C NMR (CDCl₃) δ 4.9, 6.9, 14.1, 37.9, 44.8, 55.5, 60.2, 80.0, 111.0, 120.7, 126.8, 127.5, 127.6, 129.0, 130.9, 133.1, 139.1, 157.5, 172.2, 201.8; ESI-MS *m/z* 479 [M+Na]⁺; [α]_D²² +37 (*c* 0.43, CHCl₃).

(4*R*,5*S*)-4,5-Epoxy-1-methylmethoxyamino-9-phenyl-

nonan-1,3-dione (29): To a solution of Weinreb acetamide

(159 mg, 1.5 mmol) in THF (1.4 mL) was added 1.0 M LiHMDS/THF (1.5 mL, 1.5 mmol) at -78°C , and stirred for 20 min at the same temperature. To the mixture, epoxide ent-**11n** (113.6 mmol, 0.42 mmol) in THF (1.2 mL) was added at -78°C , and stirred for 45 min at the same temperature. Sat. aq NH_4Cl was added at -78°C , then warmed to rt. EtOAc and pH 7 phosphate buffer were added. Organic layer was washed with brine, dried over Na_2SO_4 , and concentrated. Obtained oil was dissolved in CH_2Cl_2 (5 mL). To this solution, DBU (9.1 mg, 0.06 mmol) in CH_2Cl_2 (0.3 mL) was added at rt. The mixture was stirred for 40 min at rt. Reaction mixture was quenched with 0.5 M aq KH_2PO_4 , diluted with CHCl_3 . Organic layer was washed with brine, dried over Na_2SO_4 and concentrated. Residue was served to SiO_2 column chromatography (hexane:EtOAc 3:1) to give **29** (75.6 mg, 0.2475 mmol, 63%) as pale yellow oil; $[\alpha]_{\text{D}}^{24}$: +20.6 (c 0.92, CHCl_3); IR (neat) ν 2934, 2858, 1724, 1661, 1644, 1586, 1185, 1010 cm^{-1} ; ^1H NMR(CDCl_3): δ =7.27 (m, 2H), 7.17 (m, 3H), 3.66 (s, 3H), 3.59 (d, J = 16 Hz, 1H), 3.41(d, J = 16 Hz, 1H), 3.30 (d, J = 1.5 Hz, 1H), 3.20 (s, 3H), 3.15 (m, 1H), 2.62 (t, J = 7.5 Hz, 2H), 1.46-1.74 (m, 6H); ^{13}C NMR (CDCl_3): δ =209.9, 167.6, 142.0, 128.3, 128.3, 125.8, 61.3, 59.6, 58.1, 42.3, 35.6, 32.1, 31.6, 30.9, 25.3; ESI-MS: m/z 328 for $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4\text{N}$ $[\text{M}+\text{H}]^+$: 306.1705; found: 306.1703.

(3*R*,5*R*,6*R*)-7-Benzyloxy-3-hydroxy-5,6-dihydroxy-5,6-*O*-

isopropylidene-1-pyrrol-1-yl-heptan-1-one (30): In a 300 mL

round flask was placed NaBH_4 (295 mg, 7.786 mmol), and PhSeSePh (1.214 g, 3.893 mmol). EtOH (13.8 mL) was added at 0°C , under Ar atmosphere. The mixture was stirred at rt for 40 min, followed by addition of AcOH (0.075 mL, 1.3 mmol) in EtOH (1 mL). Epoxide **7t** (853 mg, 2.29 mmol) / EtOH (12 mL) solution was added to the mixture in one portion at rt, and resulting mixture was stirred for 15 min at rt. Reaction mixture was cooled to 0°C , diluted with EtOAc(160 mL), washed with brine (3 x 30 mL), dried over Na_2SO_4 , and concentrated. Obtained solid was dissolved in CHCl_3 (6 mL), and was served to SiO_2 column chromatography (hexane-EtOAc 4:1 to 1:1) to give

30 (809 mg, 2.166 mmol, 94.5% yield); pale yellow oil; IR (neat) ν 3480, 3147, 2985, 2865, 1716, 1470, 1408, 1370, 1256, 1077, 923 cm^{-1} ; ^1H NMR(CDCl_3): δ 7.05-7.36 (m, 7H), 6.31 (t, J = 2.4, 2H), 4.59 (ABq, J = 12.2 Hz, 2H), 4.44 (m, 1H), 4.09 (dt, J = 3.1, 8.6 Hz, 1H), 3.91 (dt, J = 8.3, 5.2 Hz, 1H), 3.62 (dd, J = 10.4, 5.5 Hz, 1H), 3.58 (dd, J = 10.1, 4.9 Hz, 1H), 3.41 (d, J = 4.3 Hz, 1H), 3.06 (dd, J = 16.8, 3.7 Hz, 1H), 3.00 (dd, J = 16.8, 8.5 Hz, 1H), 1.93 (ddd, J = 14.3, 8.5, 3.1 Hz, 1H), 1.77 (ddd, J = 14.4, 8.8, 3.7 Hz, 1H), 1.40 (brs, 6H); ^{13}C NMR (CDCl_3): δ = 169.8, 137.7, 128.3, 127.7, 118.9, 113.4, 109.0, 79.7, 75.6, 73.5, 70.2, 65.5, 41.6, 39.5, 27.2, 26.9; ESI-MS: m/z 396 for $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{21}\text{H}_{28}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 373.1967; found: 374.1977; $[\alpha]_{\text{D}}^{21}$: +2.07 (c 1.00, CDCl_3).

Ethyl (3*R*,5*R*,6*R*)-7-Benzyloxy-3-hydroxy-5,6-dihydroxy-5,6-*O*-isopropylidene heptanoate (31): Alcohol **30** (809 mg, 2.166 mmol)

was dissolved in EtOH (8.8 mL), and was added a solution of 0.5 M

EtSLi in EtOH (4.3 mL) at rt. The mixture was stirred for 40 min. at rt. Reaction mixture was diluted with EtOAc (100 mL). Organic layer was washed with mixture of [0.5 M pH 7 aq phosphate buffer (10 mL) and 10% aq NaCl (10 mL)], [1 M KH_2PO_4 (10 mL) and 10% NaCl (10 mL)], [10 % CuSO_4 (5 mL) and brine (5 mL)] 3 times, [sat. aq NaHCO_3 (5 mL) and brine (5 mL)] 2 times, dried over Na_2SO_4 , filtered and concentrated. Obtained residue was served to silica gel column chromatography (hexane:Et₂O 2:1 to Et₂O) to give **31** (708.2 mg, 2.009 mmol, 92% yield); pale yellow oil; IR (neat) ν 3482, 2984, 2934, 1733, 1455, 1371, 1254, 1215, 1164, 1089, 835 cm^{-1} ; ^1H NMR(CDCl_3): δ 7.20-7.40 (m, 5H), 4.58 (AB q, J = 12.2 Hz, 2H), 4.25 (m, 1H), 4.14 (q, J = 7.1 Hz, 2H), 4.06 (dt, J = 3.1, 8.6 Hz, 1H), 3.89 (ddd, J = 8.3, 5.8, 4.3 Hz, 1H), 3.61 (dd, J = 10.1, 5.5 Hz, 1H), 3.56 (dd, J = 10.1, 4.6 Hz, 1H), 3.28 (d, J = 4.3 Hz, 1H), 2.54 (dd, J = 16.5, 3.7 Hz, 1H), 2.47 (dd, J = 16.5, 8.9 Hz, 1H), 1.81 (ddd, J = 14.4, 9.2, 3.4 Hz, 1H), 1.68 (ddd, J = 14.1, 8.6, 3.4 Hz, 1H), 1.41 (s, 3H), 1.40 (s, 3H), 1.27 (t, J = 7.4 Hz, 3H); ^{13}C NMR (CDCl_3): δ = 172.5, 137.8, 128.4, 127.7, 109.0, 79.8, 75.6, 73.5, 70.3, 65.6, 60.6, 41.6, 39.5, 27.2, 26.9, 14.1; ESI-MS: m/z 375 for $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{19}\text{H}_{29}\text{O}_6$ $[\text{M}+\text{H}]^+$: 353.1964; found: 353.1963; $[\alpha]_{\text{D}}^{24}$: +6.09 (c 2.55, CDCl_3).

Ethyl (3*R*,5*R*,6*R*)-7-Benzyloxy-5,6-dihydroxy-5,6-*O*-isopropylidene-3-methoxy heptanoate:

Ag₂O (4.06 g, 17.57 mmol) and MS 3A (7.98 g) in a 300 mL round flask was heated at 150 °C at 5 mmHg for 1 h, then cooled to rt. To this mixture, toluene (80 mL), Ethyl ester **31** (708 mg, 2.009 mmol) dissolved in toluene (30 mL), and MeI (14 mL) in toluene (20 mL) was added. The mixture was heated at 45 °C for 36 h. Solids were filtered off, washed with toluene. Filtrate and washing were concentrated, residue was served to silica gel column chromatography (hexane:Et₂O 2:1 to Et₂O) to afford methyl ether (686.3 mg, 1.872 mmol, 93% yield); pale yellow oil; IR (neat)_v 2984, 2934, 1735, 1455, 1371, 1240, 1222, 1171, 1097, 1029 cm⁻¹; ¹H NMR(CDCl₃): δ 7.23-7.37 (m, 5H), 4.58 (ABq, *J* = 12.2 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.95 (m, 1H), 3.83 (m, 2H), 3.58 (dd, *J* = 10.1, 5.5 Hz, 1H), 3.54 (dd, *J* = 10.1, 4.3 Hz, 1H), 3.36 (s, 3H), 2.54 (dd, *J* = 15.3, 6.5 Hz, 1H), 2.52 (dd, *J* = 15.3, 5.8 Hz, 1H), 1.82 (ddd, *J* = 14.0, 8.9, 2.7 Hz, 1H), 1.66 (ddd, *J* = 14.4, 9.5, 4.3 Hz, 1H), 1.40 (s, 3H), 1.39 (s, 3H), 1.26 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (CDCl₃): δ 171.4, 137.9, 128.3, 127.7, 127.6, 109.0, 80.1, 75.3, 75.2, 73.5, 70.4, 60.4, 57.5, 40.0, 38.7, 27.3, 27.0, 14.2; ESI-MS: *m/z* 389 for [M+Na]⁺; HRMS (FAB): *m/z* calcd for C₂₀H₃₁O₆ [M+H]⁺: 367.2120; found: 367.2128; [α]_D²⁰: +18.9 (c 1.45, CDCl₃).

(3*S*,5*R*,6*R*)-7-Benzyloxy-5,6-dihydroxy-5,6-*O*-isopropylidene-3-methoxy-heptan-1-ol :

To a suspension of LiAlH₄ (114 mg, 3.01 mmol) in ether (5 mL), solution of ethyl (3*R*,5*R*,6*R*)-7-benzyloxy-5,6-dihydroxy-5,6-*O*-isopropylidene-3-methoxy-heptanoate (221 mg, 0.603 mmol) in ether (6 mL) was added for 3 min. at 0 °C. the mixture was stirred for 30 min at rt, and then refluxed for 40 min. Reaction mixture was cooled to 0 °C, diluted with ether (5 mL). H₂O (0.11 mL) was added slowly, followed by addition of 1N aq NaOH (0.45 mL), stirred for 30 min at rt, filtered, and washed with EtOAc. Filtrate and washing were concentrated, and residue was served to SiO₂ column chromatography (hexane:Et₂O 1:1 to 1:2) to give titled compound (166.3 mg, 0.5126 mmol, 85%); pale yellow oil; IR (neat)_v 3421, 2991,

2934, 1447, 1370, 1215, 1082, 742 cm^{-1} ; ^1H NMR(CDCl_3): δ 7.26-7.36 (m, 5H), 4.59 (AB q, J = 12.3 Hz, 2H), 3.95 (m, 1H), 3.83 (td, J = 9.8, 2.5 Hz, 1H), 3.83 (m, 1H), 3.74 (m, 1H), 3.53-3.63 (m, 3H), 3.37 (s, 3H), 1.82-1.93 (m, 2H), 1.68-1.78 (m, 1H), 1.66 (ddd, J = 14.4, 9.5, 4.3 Hz, 1H), 1.41 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (CDCl_3): δ 137.9, 128.4, 108.9, 80.1, 78.0, 75.6, 73.5, 70.3, 60.2, 57.2, 38.1, 36.1, 27.3, 26.9; ESI-MS: m/z 347 for $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{18}\text{H}_{29}\text{O}$ $[\text{M}+\text{H}]^+$: 325.2015; found: 325.2010; $[\alpha]_{\text{D}}^{24}$: +8.05 (c 2.58, CDCl_3).

(2*R*,3*R*,5*S*)-1-Benzyloxy-7-(*tert*-butyldimethylsilyloxy)-2,3-dihydroxy-2,3-*O*-isopropylidene-5-methoxy-heptane:

(3*S*,5*R*,6*R*)-7-Benzyloxy-5,6-dihydroxy-5,6-*O*-isopropylidene-3-

methoxy-heptan-1-ol (166.3 mg, 0.5126 mmol) was dissolved in dry CH_2Cl_2 (7 mL), imidazole (150 mg, 4.3 mmol) was added at rt, TBSCl (127 mg, 0.843 mmol) was added at 0 $^\circ\text{C}$. Reaction mixture was stirred for 50 min. at rt, and then diluted with CHCl_3 . Organic layer was washed with dil. HCl, sat. aq NaHCO_3 , brine, dried over Na_2SO_4 , filtered and concentrated. Obtained residue was served to silica gel column chromatography (hexane:EtOAc 20:1 to 5:1) to give corresponding TBS ether (219.1 mg, 0.499 mmol, 97% yield); pale yellow oil; IR (neat) ν 3372, 2930, 2856, 1455, 1369, 1253, 1090, 836, cm^{-1} ; ^1H NMR(CDCl_3): δ 7.25-7.34 (m, 5H), 4.58 (AB q, J = 12.2 Hz, 2H), 3.95 (ddd, J = 8.3, 4.0, 3.7 Hz, 1H), 3.81 (ddd, J = 8.3, 5.2, 4.6 Hz, 1H), 3.68 (m, 1H), 3.48-3.59 (m, 3H), 3.32 (s, 3H), 1.64-1.79 (m, 4H), 1.40 (s, 3H), 1.39 (s, 3H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (CDCl_3): δ 138.0, 128.3, 127.7, 127.6, 108.8, 80.4, 75.5, 75.3, 73.5, 70.5, 59.4, 57.1, 38.9, 37.4, 27.3, 27.0, 25.9, 18.3, -5.4; ESI-MS: m/z 461 for $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{24}\text{H}_{43}\text{O}_5\text{Si}$ $[\text{M}+\text{H}]^+$: 439.2880; found: 439.2874; $[\alpha]_{\text{D}}^{24}$: +14.1 (c 1.16, CDCl_3).

(2*R*,3*R*,5*S*)-7-*tert*-Butyldimethylsilyloxy-2,3-dihydroxy-2,3-*O*-isopropylidene-5-methoxy -heptan-1-ol (32):

TBS ether (199 mg, 0.453 mmol) was dissolved in EtOAc (3.5 mL), followed by addition of EtOH (0.4 mL), NaHCO_3 (41 mg, 0.5 mmol), 20% $\text{Pd}(\text{OH})_2$ (wet type) (82 mg).

The mixture was stirred under H₂ (5 atm) at rt for 18 h. Solids were filtered off, and washed with EtOAc. Filtrate and washing were concentrated. Residue was served to silica gel column chromatography (hexane:EtOAc 4:1 to 1: 1) gave **32** (153.1 mg, 0.439 mmol, 96% yield); pale yellow oil; IR (neat) ν 3444, 2931, 2849, 1472, 1378, 1253, 1164, 1090, 837 cm⁻¹; ¹H NMR(CDCl₃): δ 4.03 (m, 1H), 3.60-3.80 (m, 5H), 3.53 (m, 1H), 3.37 (s, 3H), 2.22 (brs, 1H), 1.65-1.82 (m, 4H), 1.41 (s, 6H), 0.90 (s, 9H), 0.06 (s, 6H); ¹³C NMR (CDCl₃): δ 108.5, 81.8, 75.8, 74.7, 62.0, 59.4, 57.1, 38.7, 37.2, 27.3, 27.0, 25.9, 18.3, -5.4; ESI-MS: m/z 371 for [M+Na]⁺; HRMS (FAB): m/z calcd for C₂₄H₄₃O₅Si [M+H]⁺: 349.2410; 349.2416; [α]_D²⁴ +22.3 (c 2.2, CDCl₃).

(3R,4R,6S)-8-tert-Butyldimethylsilyloxy-3,4-dihydroxy-3,4-O-isopropylidene-6-methoxy-1-octyne: To a suspension of AcONa (553 mg, 6.74 mmol), MS 3A (800 mg), PCC (363 mg, 1.69 mmol)

in dry CH₂Cl₂ (16 mL), solution of **32** (103 mg, 0.296 mmol) in CH₂Cl₂ (5 mL) was added at rt. and stirred for 20 min at rt. The mixture was diluted with ether (15 mL), filtered with short plug of silica gel, washed with ether (150 mL). Filtrate and washing were combined, concentrated to give crude aldehyde. In 50 mL round flask, K₂CO₃ (254 mg, 1.847 mmol) was added to a solution of dimethyl (1-diazo-2-oxopropyl)phosphonate (253 mg, 1.273 mmol) in dry MeOH (8 mL) at rt. and stirred for 80 min at the same temperature. Crude aldehyde in dry MeOH (5 mL) was added to the reagent above mentioned. The mixture was stirred for 4 h at rt, diluted with EtOAc, washed with brine, dried over Na₂SO₄ and MgSO₄, filtered and concentrated. Residue was served to silica gel column chromatography (hexane:EtOAc 35:1 to 20:1) to give corresponding alkyne (57.7 mg, 0.168 mmol, 57% yield); pale yellow oil; IR (neat) ν 3312, 2931, 2857, 2123, 1472, 1380, 1254, 1161, 1090, 1051 cm⁻¹; ¹H NMR(CDCl₃): δ 4.25 (dd, J = 7.6, 1.8 Hz, 1H), 4.21 (ddd, J = 7.9, 4.3, 4.3 Hz, 1H), 3.70 (m, 2H), 3.53 (m, 1H), 3.37 (s, 3H), 2.50 (d, J = 1.9 Hz, 1H), 1.67-1.86 (m, 4H), 1.47 (s, 6H), 1.41 (s, 3H), 0.90 (s, 9H), 0.06 (s, 6H); ¹³C NMR (CDCl₃): δ 109.9, 80.8, 78.9, 75.2, 74.4, 70.5, 59.4, 57.1, 37.8, 37.2, 27.2, 26.1, 25.9, 18.3, -5.3; ESI-MS: m/z 365 for [M+Na]⁺; HRMS (FAB): m/z calcd for C₂₄H₄₃O₅Si [M+H]⁺: 343.2304; found: 343.2300; [α]_D²³: +13.4 (c 1.5, CDCl₃).

(4*R*,5*R*,7*S*)-9-*tert*-Butyldimethylsilyloxy-4,5-dihydroxy-4,5-*O*-isopropylidene-7-methoxy -2-nonyne: Alkyne (57.7 mg,

0.168 mmol) (azeotroped with toluene 2 times) in THF (1.4 mL) was added 1.48 M *n*-BuLi/hexane (0.150 mL, 0.222 mmol) at -78°C until yellow color persisted. Methyl iodide (0.20 mL, 3.23 mmol) was added at the same temperature. The mixture was stirred at -78°C for 7 h then allowed to rt for overnight. To the reaction mixture, brine and EtOAc were added. Organic layer was washed sat. aq NaHCO_3 , brine, dried over Na_2SO_4 , filtered and concentrated. Obtained residue was served to silica gel column chromatography (hexane:EtOAc 35:1 to 15:1) to give corresponding methylalkyne (55.2 mg, 0.154 mmol, 91% yield); pale yellow oil; IR (neat) ν 3366, 2986, 2930, 2857, 2247, 1472, 1378, 1254, 1159, 1089, 1048 cm^{-1} ; ^1H NMR(CDCl_3): δ 4.19 (dq, $J = 7.9, 2.2$ Hz, 1H), 4.09 (ddd, $J = 8.9, 8.2, 3.6$ Hz, 1H), 3.66-3.75 (m, 2H), 3.50-3.56 (m, 1H), 3.38 (s, 3H), 1.86 (d, $J = 2.1$ Hz, 1H), 1.63-1.83 (m, 4H), 1.46 (s, 6H), 1.39 (s, 3H), 0.90 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (CDCl_3): δ 109.2, 83.0, 78.6, 75.4, 75.3, 71.1, 59.4, 57.2, 37.6, 37.4, 27.2, 26.4, 25.9, 18.3, 3.8, -5.3 ; ESI-MS: m/z 379 for $[\text{M}+\text{Na}]^+$; HRMS (FAB): m/z calcd for $\text{C}_{24}\text{H}_{43}\text{O}_5\text{Si}$ $[\text{M}+\text{H}]^+$: 357.2461; found: 357.2460; $[\alpha]_{\text{D}}^{22} +14.9$ (c 1.6, CDCl_3).

(3*S*,5*R*,6*R*)-5,6-dihydroxy-5,6-*O*-isopropylidene-3-methoxy-non-7-yn-1-ol (33**):** To a solution of methylalkyne (55.2 mg, 0.1548 mmol) in THF (2 mL), was added 1.0 M TBAF/THF (0.60

mL, 0.6 mmol). The mixture was stirred for 2.5 h at rt, diluted with CHCl_3 (15 mL). Organic layer was washed with brine (3 x 3 mL), dried over Na_2SO_4 , and concentrated. Obtained oil was served to SiO_2 column chromatography (hexane:EtOAc 1:1 to 1:4) to give **33** (33.3 mg, 0.1374 mmol, 88 %); pale yellow oil; IR (neat) ν 3443, 2986, 2937, 2825, 2245, 1456, 1373, 1237, 1159, 1078, 1047 cm^{-1} ; ^1H NMR(CDCl_3): δ 4.19 (dq, $J = 8.2, 2.1$ Hz, 1H), 4.05 (ddd, $J = 8.9, 8.3, 3.7$ Hz, 1H), 3.73-3.87 (m, 2H), 3.61-3.67 (m, 1H), 3.43 (s, 3H), 2.33 (t, $J = 4.9$ Hz, 1H), 1.90-2.00 (m, 2H), 1.87 (d, $J = 2.2$ Hz, 3H), 1.70-1.78 (m, 1H), 1.65 (ddd, $J = 14.0, 8.9, 4.8$ Hz, 1H), 1.46 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (CDCl_3): δ

= 109.3, 83.3, 78.5, 77.6, 75.1, 71.1, 60.1, 57.3, 36.8, 36.1, 27.1, 26.4, 3.7; ESI-MS: m/z 265 for $[M+Na]^+$; HRMS (FAB): m/z calcd for $C_{24}H_{43}O_5Si$ $[M+H]^+$: 243.1596; found: 243.1596; $[\alpha]_D^{22} +7.97$ (c 1.7, $CDCl_3$).