Pd(II)-Catalyzed Enantioselective Oxidative Tandem Cyclization Reactions.

Synthesis of Indolines through C–N and C–C Bond Formation**

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General methods:

All reactions were performed in oven-dried flasks. Palladium(II) acetate was purchased from the Precious Metals and was used as received. All other commercially available chemicals were used as received. Toluene was distilled over calcium hydride and stored over activated 4Å molecular sieve (beads). 4Å (beads) and 3Å (powder) molecular sieves were activated by heating to 300 °C in oven for 6 hours and stored in a septum-sealed flask under an argon atmosphere. Reactions were monitored by thin-layer chromatography (TLC) using E. Merck silica gel 60 precoated glass plates with 0.25 mm thickness. Components were visualized by illumination with a short-wavelength ultra-violet light and/or staining in phosphomolybdic acid (PMA) solution followed by heating. Flash column chromatography were performed on E. Merck silica gel 60 (230–400 mesh ASTM) using ethyl acetate/*n*-hexane as eluting solvents.

¹H and ¹³C NMR spectra were recorded in deuteriochloroform (CDCl₃) with tetramethylsilane (TMS) as internal standard at ambient temperature unless otherwise indicated on a Bruker Avance DPX 300 Fourier Transform Spectrometer operating at 300 MHz for ¹H and 75 MHz for ¹³C, a Bruker Avance DPX 400 Fourier Transform Spectrometer operating at 400 MHz for ¹H and 100 MHz for ¹³C, or a Bruker Avance DPX 500 Fourier Transform Spectrometer operating at 500 MHz for ¹H and 125 MHz for ¹³C. Infrared absorption spectra were recorded as a solution in CH₂Cl₂ with a Bio-Rad FTS 165 Fourier Transform spectrophotometer. Mass spectra were recorded with a Finnigan MAT 95 mass spectrometer for both low resolution and high resolution mass spectra. Melting points were determined by Axiolab ZEISS microscope apparatus and were uncorrected.

Substrates 1a–l for Oxidative Tandem Cyclizations:

Overall synthetic scheme for substrates 1a–l:

Typical procedure for the preparation of *o*-allylaniline **6**:¹

In a 100-mL seal-tube, a cold solution (at $-78\text{ }^{\circ}\text{C}$) of *N*-allylaniline **7a** (2.66 g, 20.0 mmol) in *m*-xylene (40 mL) was added boron trifluoride etherate (3.0 mL, 24.0 mmol) under an argon atmosphere. After 5 min, the solution was warmed to room temperature. After 15 min, the seal-tube was sealed and heated to $180\text{ }^{\circ}\text{C}$. After 17 h, the reaction was cooled down to room temperature and quenched with 2M NaOH solution (30 mL) at $0\text{ }^{\circ}\text{C}$. The organic layer was separated and the aqueous layer was extracted with diethyl ether (30 mL $\times$ 2). The combined organic layers were filtered via a short pad of celite and concentrated in vacuo. The residue was purified by flash column chromatography to give **6a**² (2.04 g, 15.3 mmol, 77% yield) as a yellow oil.

6a:² 77% Yield; a yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-hexane, $R_f = 0.45$; ^1H NMR (300 MHz, CDCl_3) δ 7.06–7.03 (m, 2H) 6.74 (t, $J = 7.2\text{ Hz}$, 1H), 6.67 (d, $J = 7.8\text{ Hz}$, 1H), 6.01–5.88 (m, 1H), 5.13–5.06 (m, 2H), 3.64 (bs, 2H), 3.30 (d, $J = 6.1\text{ Hz}$, 2H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 145.1, 136.3, 130.5, 127.8, 124.3, 119.2, 116.4, 116.1, 36.8.

6b:² Yield 67%; yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-hexane, $R_f = 0.40$; ^1H NMR (400 MHz, CDCl_3) δ 7.01 (s, 1H), 6.99 (d, $J = 6.9\text{ Hz}$, 1H), 6.56 (d, $J = 6.6\text{ Hz}$, 1H), 5.94–5.84 (m, 1H), 5.15–5.06 (m, 2H), 3.63 (bs, 2H), 3.22 (d, $J = 6.1\text{ Hz}$, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.7, 135.2, 130.0, 127.5, 125.9, 123.4, 117.1, 117.0, 36.3.

(one quaternary carbon peak overlapped with δ 128.1 ppm in ^{13}C)

6c:² Yield 49%; yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-hexane, R_f = 0.39; ^1H NMR (300 MHz, CDCl_3) δ 6.86 (d, J = 8.0 Hz, 1H), 6.83 (s, 1H), 6.54 (d, J = 8.1 Hz, 1H), 5.98–5.85 (m, 1H), 5.11–5.03 (m, 2H), 3.48 (bs, 2H), 3.24 (d, J = 6.1 Hz, 2H), 2.21 (s, 3H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 142.5, 136.3, 130.9, 128.1, 124.3, 116.2, 116.1, 36.6, 20.6.

6d:² Yield 59%; yellow oil; analytical TLC (silica gel 60), 30% EtOAc in *n*-hexane, R_f = 0.42; ^1H NMR (300 MHz, CDCl_3) δ 6.65–6.54 (m, 3H), 5.99–5.85 (m, 1H), 5.12–5.04 (m, 2H), 3.71 (s, 3H), 3.35 (bs, 2H), 3.26 (d, J = 6.2 Hz, 2H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 153.7, 138.6, 135.9, 125.9, 117.1, 116.9, 116.1, 112.8, 55.9, 36.7.

6e:³ Yield 84%; yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-hexane, R_f = 0.41; ^1H NMR (400 MHz, CDCl_3) δ 6.47 (s, 1H), 6.38 (s, 1H), 5.94–5.84 (m, 1H), 5.04–4.96 (m, 2H), 3.54 (bs, 2H), 3.29 (d, J = 5.6 Hz, 2H), 2.22 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.0, 137.2, 136.5, 135.3, 122.0, 119.6, 115.1, 114.8, 31.6, 21.1, 19.9.

Typical procedure for the preparation of **1**:

To a solution of *o*-allylaniline **6a** (1.0 g, 7.5 mmol) in CH₂Cl₂ (35 mL) was added pyridine (0.67 mL, 8.3 mmol). At 0 °C, the reaction mixture was added acryloyl chloride (0.68 mL, 8.3 mmol) in CH₂Cl₂ (15 mL). After 12 h, the mixture was quenched with saturated NH₄Cl solution (40 mL). The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (40 mL × 2). The combined organic layers were dried over MgSO₄, filtered and concentrated in vacuo. The residue was purified by flash column chromatography to give **1a** (1.03 g, 5.5 mmol, 73% yield) as a white solid.

(one quaternary carbon peak overlapped in ¹³C)

1a: Yield 73%; white solid, m.p. 84–85 °C; analytical TLC (silica gel 60), 30% EtOAc in *n*-hexane, *R_f* = 0.28; ¹H NMR (300 MHz, CDCl₃) δ 7.88 (d, *J* = 7.4 Hz, 1H), 7.62 (bs, 1H), 7.27–7.09 (m, 3H), 6.37 (d, *J* = 16.7 Hz, 1H), 6.21 (dd, *J* = 16.9, 10.0 Hz, 1H), 6.01–5.88 (m, 1H), 5.72 (dd, *J* = 10.0, 1.4 Hz, 1H), 5.17 (d, *J* = 10.1 Hz, 1H), 5.09 (d, *J* = 17.2 Hz, 1H), 3.38 (d, *J* = 6.2 Hz, 2H); ¹³C NMR (75.5 MHz, CDCl₃) δ 164.0, 136.5, 136.1, 131.6, 130.4, 127.7, 127.6, 125.7, 124.0, 116.9, 37.1; IR (CH₂Cl₂) 3413, 3055, 2988, 1689, 1635, 1588, 1453 cm⁻¹; LRMS (EI, 20 eV) *m/z* 187 (M⁺, 32), 186 (15), 146 (31), 132 (100); HRMS (EI) for C₁₂H₁₃NO (M⁺): calcd 187.0997, found 187.0998.

1b: Yield 63%; white solid, m.p. 121–122 °C; analytical TLC (silica gel 60), 30% EtOAc in *n*-hexane, *R_f* = 0.20; ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 7.5 Hz, 1H), 7.63 (bs, 1H), 7.19–7.15 (m, 2H), 6.36 (d, *J* = 16.9 Hz, 1H), 6.20 (dd, *J* = 16.9, 10.2 Hz, 1H), 5.95–5.85 (m, 1H), 5.73 (d, *J* = 10.2 Hz, 1H), 5.19 (d, *J* = 9.9 Hz, 1H), 5.10 (d, *J* = 17.1 Hz, 1H), 3.32 (d, *J* = 6.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 164.1,

135.6, 134.6, 132.7, 131.3, 130.9, 130.2, 128.0, 127.6, 125.4, 117.6, 36.7; IR (CH₂Cl₂) 3399, 3055, 2988, 1691, 1635, 1583, 1422 cm⁻¹; LRMS (EI, 20 eV) *m/z* 221 (M⁺, 39), 220 (19), 180 (64), 166 (100); HRMS (EI) for C₁₂H₁₂ClNO (M⁺): calcd 221.0607, found 221.0602.

1c: Yield 99%; white solid, m.p. 109–110 °C; analytical TLC (silica gel 60), 50% EtOAc in *n*-hexane, *R_f* = 0.29; ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.45 (bs, 1H), 7.05–6.98 (m, 2H), 6.35 (d, *J* = 16.9 Hz, 1H), 6.20 (dd, *J* = 16.9, 10.2 Hz, 1H), 5.99–5.89 (m, 1H), 5.71 (d, *J* = 10.1 Hz, 1H), 5.15 (d, *J* = 9.4 Hz, 1H), 5.09 (d, *J* = 17.2 Hz, 1H), 3.34 (d, *J* = 6.1 Hz, 2H), 2.30 (s, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 164.4, 136.5, 135.8, 132.9, 132.3, 131.4, 130.5, 127.6, 126.9, 125.0, 116.3, 36.4, 21.0; IR (CH₂Cl₂) 3413, 3055, 2988, 2924, 1687, 1634, 1595, 1517, 1485 cm⁻¹; LRMS (EI, 20 eV) *m/z* 201 (M⁺, 50), 200 (7), 160 (35), 146 (100); HRMS (EI) for C₁₃H₁₅NO (M⁺): calcd 201.1154, found 201.1143.

1d: Yield 84%; white solid, m.p. 127–128 °C; analytical TLC (silica gel 60), 40% EtOAc in *n*-hexane, *R_f* = 0.32; ¹H NMR (300 MHz, CDCl₃) δ 7.67 (d, *J* = 8.7 Hz, 1H), 7.36 (bs, 1H), 6.80–6.73 (m, 2H), 6.36 (d, *J* = 16.9 Hz, 1H), 6.21 (dd, *J* = 16.9, 10.0 Hz, 1H), 5.99–5.90 (m, 1H), 5.72 (d, *J* = 10.0 Hz, 1H), 5.16 (d, *J* = 10.1 Hz, 1H), 5.09 (d, *J* = 17.2 Hz, 1H), 3.79 (s, 3H), 3.33 (d, *J* = 6.1 Hz, 2H); ¹³C NMR (75.5 MHz, CDCl₃) δ 164.1, 157.6, 136.4, 133.3, 131.6, 129.0, 127.3, 126.1, 117.0, 116.0, 112.4, 55.7, 37.2; IR (CH₂Cl₂) 3413, 3053, 2985, 1684, 1636, 1615, 1515, 1487 cm⁻¹; LRMS (EI, 20 eV) *m/z* 217 (M⁺, 72), 216 (7), 176 (43), 162 (100); HRMS (EI) for C₁₃H₁₅NO₂ (M⁺): calcd 217.1103, found 217.1099.

1e: Yield 82%; white solid, m.p. 134–135 °C; analytical TLC (silica gel 60), 30% EtOAc in *n*-hexane, R_f = 0.56; ^1H NMR (300 MHz, CDCl_3) δ 8.04 (bs, 1H) 7.76 (d, J = 15.6 Hz, 1H), 7.55 (m, 2H), 7.49 (bs, 1H), 7.45–7.40 (m, 3H), 7.35–7.29 (m, 1H), 7.25–7.15 (m, 2H), 6.52 (d, J = 15.6 Hz, 1H), 6.09–5.98 (m, 1H), 5.25 (d, J = 10.1 Hz, 1H), 5.17 (d, J = 17.2 Hz, 1H), 3.46 (d, J = 6.0 Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.0, 142.2, 136.3, 136.2, 134.7, 130.3, 130.0, 129.8, 128.8, 128.0, 127.6, 125.3, 123.5, 120.9, 116.8, 36.9; IR (CH_2Cl_2) 3409, 3059, 3053, 2988, 1683, 1633, 1588, 1519, 1451 cm^{-1} ; LRMS (EI, 20 eV) m/z 263 (M^+ , 13), 172 (40), 131 (100); HRMS (EI) for $\text{C}_{18}\text{H}_{17}\text{NO}$ (M^+): calcd 263.1310, found 263.1303.

1f: Yield 78%; white solid, m.p. 140–141 °C; analytical TLC (silica gel 60), 30% EtOAc in *n*-hexane, R_f = 0.26; ^1H NMR (300 MHz, CDCl_3) δ 7.98 (bs, 1H) 7.66 (d, J = 15.5 Hz, 1H), 7.53 (bs, 1H), 7.49 (s, 1H), 7.35–7.26 (m, 4H), 7.22–7.14 (m, 2H), 6.49 (d, J = 15.5 Hz, 1H), 6.06–5.97 (m, 1H), 5.22 (d, J = 10.0 Hz, 1H), 5.13 (d, J = 17.2 Hz, 1H), 3.43 (d, J = 5.9 Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 163.5, 140.7, 136.5, 136.3, 136.0, 134.9, 130.3, 130.1, 129.8, 127.6, 127.6, 127.5, 126.3, 125.5, 123.7, 122.3, 116.8, 36.8; IR (CH_2Cl_2) 3421, 3055, 2988, 1685, 1634, 1588, 1519, 1450 cm^{-1} ; LRMS (EI, 20 eV) m/z 297 (M^+ , 15), 165 (100), 132 (83); HRMS (EI) for $\text{C}_{18}\text{H}_{16}\text{ClNO}$ (M^+): calcd 297.0920, found 297.0912.

1g

1g: Yield 48%; white solid, m.p. 173–174 °C; analytical TLC (silica gel 60), 30% EtOAc in *n*-hexane, R_f = 0.37; ^1H NMR (300 MHz, CDCl_3) δ 8.03 (bs, 1H) 7.72 (d, J = 15.5 Hz, 1H), 7.44 (d, J = 7.8 Hz, 2H), 7.38 (bs, 1H), 7.32–7.27 (m, 1H), 7.26–7.12 (m, 4H), 6.43 (d, J = 15.5 Hz, 1H), 6.07–5.96 (m, 1H), 5.23 (d, J = 10.0 Hz, 1H), 5.15 (d, J = 17.2 Hz, 1H), 3.44 (d, J = 6.0 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 164.6, 142.6, 140.6, 136.6, 132.3, 130.6, 129.9, 129.7, 128.3, 128.1, 127.9, 125.6, 123.9, 120.1, 117.1, 37.2, 21.8; IR (CH_2Cl_2) 3413, 3055, 2988, 2940, 1683, 1631, 1588, 1515, 1451 cm^{-1} ; LRMS (EI, 20 eV) m/z 277 (M^+ , 9), 145 (100); HRMS (EI) for $\text{C}_{19}\text{H}_{19}\text{NO}$ (M^+): calcd 277.1467, found 277.1471.

1h

1h: Yield 73%; white solid, m.p. 113–114 °C; analytical TLC (silica gel 60), 30% EtOAc in *n*-hexane, R_f = 0.30; ^1H NMR (400 MHz, CDCl_3) δ 7.97 (bs, 1H), 7.33–7.11 (m, 4H), 6.99 (dq, J = 15.1, 6.9 Hz, 1H), 6.07–5.96 (m, 1H), 5.92 (dd, J = 15.1, 1.6 Hz, 1H), 5.22 (d, J = 10.1 Hz, 1H), 5.13 (d, J = 17.3 Hz, 1H), 3.42 (d, J = 6.1 Hz, 2H), 1.93 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 163.9, 141.3, 136.3, 130.2, 129.6, 128.9, 127.5, 125.5, 125.1, 123.5, 116.7, 37.0, 17.8; IR (CH_2Cl_2) 3413, 3055, 2988, 1687, 1650, 1588, 1519, 1451 cm^{-1} ; LRMS (EI, 20 eV) m/z 201 (M^+ , 48), 200 (6), 160 (9), 132 (100); HRMS (EI) for $\text{C}_{13}\text{H}_{15}\text{NO}$ (M^+): calcd 201.1154, found 201.1148.

1i: Yield 80%; white solid, m.p. 86–87 °C; analytical TLC (silica gel 60), 30% EtOAc in *n*-hexane, R_f = 0.25; ^1H NMR (300 MHz, CDCl_3) δ 7.99 (d, J = 8.1 Hz, 1H), 7.52 (bs, 1H), 7.31–7.25 (m, 1H), 7.18 (dd, J = 7.4, 1.5 Hz, 1H), 7.10 (td, J = 7.4, 1.1 Hz, 1H), 6.55 (q, J = 6.9 Hz, 1H), 6.06–5.93 (m, 1H), 5.20 (dd, J = 10.1, 1.6 Hz, 1H), 5.08 (dd, J = 17.2, 1.7 Hz, 1H), 3.40 (d, J = 5.9 Hz, 2H), 1.93 (s, 3H), 1.81 (dd, J = 6.9, 0.9 Hz, 3H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 167.7, 136.7, 136.5, 132.9, 131.9, 130.6, 129.8, 127.9, 125.2, 123.6, 117.0, 37.3, 14.5, 12.9; IR (CH_2Cl_2) 3428, 3055, 2987, 2924, 1677, 1643, 1587, 1514, 1451 cm^{-1} ; LRMS (EI, 20 eV) m/z 215 (M^+ , 34), 132 (60), 83 (100); HRMS (EI) for $\text{C}_{14}\text{H}_{17}\text{NO}$ (M^+): calcd 215.1310, found 215.1295.

1j:⁴ Yield 56% (2 steps from **10**); white solid; ^1H NMR (300 MHz, CDCl_3) δ 8.06 (d, J = 7.1 Hz, 1H), 7.58 (bs, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 7.2 Hz, 1H), 7.11 (t, J = 7.2 Hz, 1H), 6.38 (d, J = 16.9 Hz, 1H), 6.17 (dd, J = 16.9, 10.2 Hz, 1H), 5.75 (dd, J = 10.2, 1.0 Hz, 1H), 4.97 (s, 1H), 4.82 (s, 1H), 3.38 (s, 2H), 1.72 (s, 3H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 163.7, 144.9, 136.8, 131.8, 131.2, 129.1, 127.9, 127.5, 125.3, 123.3, 112.8, 42.2, 22.4.

1k: Yield 63%; white solid, m.p. 89–90 °C; analytical TLC (silica gel 60), 30% EtOAc in *n*-hexane, R_f = 0.25; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (s, 1H), 7.26 (s,

1H), 6.86 (s, 1H), 6.37 (d, $J = 16.9$ Hz, 1H), 6.20 (dd, $J = 16.9, 10.2$ Hz, 1H), 5.98–5.91 (m, 1H), 5.76 (d, $J = 10.1$ Hz, 1H), 5.11 (d, $J = 9.9$ Hz, 1H), 4.97 (d, $J = 16.9$ Hz, 1H), 3.36 (d, $J = 5.5$ Hz, 2H), 2.30 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 163.8, 136.8, 136.3, 135.5, 135.4, 131.4, 128.5, 126.9, 126.2, 122.8, 115.5, 31.8, 20.9, 19.8; IR (CH_2Cl_2) 3413, 3054, 2988, 2920, 1685, 1630, 1598, 1517, 1489 cm^{-1} ; LRMS (EI, 20 eV) m/z 215 (M^+ , 59), 160 (100), 146 (99); HRMS (EI) for $\text{C}_{14}\text{H}_{17}\text{NO}$ (M^+): calcd 215.1310, found 215.1308.

11: Yield 48%; white solid, m.p. 150–151 °C; analytical TLC (silica gel 60), 30% EtOAc in *n*-hexane, $R_f = 0.34$; ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, $J = 15.5$ Hz, 1H), 7.60–7.43 (m, 2H), 7.43–7.25 (m, 4H), 6.89 (s, 1H), 6.48 (d, $J = 15.5$ Hz, 1H), 6.10–5.92 (m, 1H), 5.13 (d, $J = 9.4$ Hz, 1H), 4.98 (d, $J = 16.7$ Hz, 1H), 3.90 (d, $J = 5.4$ Hz, 2H), 2.31 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.6, 140.6, 137.0, 136.6, 135.8, 135.5, 134.9, 130.1, 129.8, 128.6, 127.5, 126.4, 125.7, 122.8, 122.6, 122.4, 115.8, 31.9, 21.1, 20.0; IR (CH_2Cl_2) 3418, 3055, 2988, 1683, 1633, 1588, 1516, 1451 cm^{-1} ; LRMS (EI, 20 eV) m/z 325 (M^+ , 12), 160 (100); HRMS (EI) for $\text{C}_{20}\text{H}_{20}\text{ClNO}$ (M^+): calcd 325.1233, found 325.1226.

Typical procedure for the preparation of **7**:

To a solution of *p*-anisidine **8d** (6.16 g, 50 mmol) and triethylamine (7.7 mL, 55 mmol) in THF (150 mL) was slowly added di-*tert*-butyl dicarbonate (12.0 g, 55 mmol). The resulting solution was stirred at room temperature for 14 h. The solvent was then evaporated. The residue was dissolved with diethyl ether (150 mL) and the solution was passed through a short pad of silica gel. The filtrate was concentrated in vacuo. The crude product was used for the next step directly without further purification.

To a suspension of sodium hydride (60% dispersion in oil, 1.08 g, 27.1 mmol) in THF (80 mL) was added a THF solution (20 mL) of the crude product slowly at 0 °C. After 30 min, allyl bromide (2.4 mL, 27.1 mmol) was added and the mixture was heated to reflux (66 °C). After 16 h, the reaction mixture was cooled to 0 °C, and 10% HCl solution (60 mL) was added and followed by reflux.

After 16 h, the reaction mixture was cooled and THF was evaporated. To this aqueous mixture was added 1.3 M NaOH solution (100 mL) was added slowly at 0 °C and the mixture was extracted with diethyl ether (100 mL $\times$ 3). The combined organic layers were dried over MgSO₄, filtered and concentrated in vacuo. The residue was purified by flash column chromatography to give **7d** (3.61 g, 22.1 mmol, yield 90% from **8d**) as an orange oil.

7d:⁵ Yield 90% (from **8d**); orange oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-hexane, R_f = 0.50; ^1H NMR (300 MHz, CDCl_3) δ 6.76 (d, J = 8.9 Hz, 2H), 6.56 (d, J = 8.9 Hz, 2H), 5.97–5.86 (m, 1H), 5.25 (dd, J = 17.2, 1.5 Hz, 1H), 5.13 (dd, J = 10.3, 1.3 Hz, 1H), 3.70 (s, 1H), 3.68 (d, J = 5.5 Hz, 2H), 3.50 (bs, 1H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 152.3, 142.5, 136.1, 116.2, 115.0, 114.5, 55.9, 47.7.

7b:⁵ Yield 86% (from **8b**); yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-hexane, R_f = 0.55; ^1H NMR (300 MHz, CDCl_3) δ 7.10 (d, J = 8.9 Hz, 2H), 6.51 (d, J = 8.8 Hz, 2H), 5.97–5.84 (m, 1H), 5.25 (dd, J = 17.2, 1.4 Hz, 1H), 5.16 (dd, J = 10.2, 1.3 Hz, 1H), 3.79 (bs, 1H), 3.71 (bs, 2H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 146.9, 135.2, 129.3, 122.2, 116.7, 114.3, 46.8.

7c:⁵ Yield 99% (from **8c**); yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-hexane, R_f = 0.59; ^1H NMR (400 MHz, CDCl_3) δ 6.98 (d, J = 8.4 Hz, 2H), 6.54 (d, J = 8.4 Hz, 2H), 5.99–5.90 (m, 1H), 5.27 (dd, J = 17.3, 1.5 Hz, 1H), 5.15 (dd, J = 10.3, 1.4 Hz, 1H), 3.73 (dd, J = 5.3, 1.5 Hz, 2H), 3.62 (bs, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.1, 136.0, 130.0, 127.0, 116.4, 113.5, 47.2, 20.7.

Typical Procedure of Preparation 10:

For preparation of **9**, see ref. 6; For preparation of the reagent, 1.0 M THF solution of *i*-PrMgCl·LiCl, see ref. 7.

At $-10\text{ }^\circ\text{C}$, a THF solution of *i*-PrMgCl·LiCl (1.0 M, 21 mL, 21.1 mmol) was charged with **9** (6.0 g, 20.1 mmol). After 30 min, the solution was added 3-chloro-2-methylpropene (2.6 mL, 24.1 mmol) and CuCN·LiCl (1.0 M, 1.0 mL, 1.0 mmol), respectively. The reaction temperature was slowly increased to room temperature for 12 h. The reaction mixture was quenched with saturated NH_4Cl solution (40 mL). After 5 min, the aqueous layer was washed with diethyl ether (40 mL $\times$ 3). The combined organic layers were dried over MgSO_4 , filtered and concentrated in vacuo. The residue was purified by flash column chromatography to give **10** (4.6 g, 20.0 mmol, quantitative yield) as a colorless oil.

10: Quantitative yield; colorless oil; analytical TLC (silica gel 60), 100% *n*-hexane, $R_f = 0.45$; ^1H NMR (300 MHz, CDCl_3) δ 7.19–7.11 (m, 2H), 7.06–6.98 (m, 2H), 5.84–5.71 (m, 2H), 5.13 (d, $J = 17.2$ Hz, 2H), 5.06 (d, $J = 10.2$ Hz, 2H), 4.82 (s, 1H), 4.64 (s, 1H), 3.54 (d, $J = 6.1$ Hz, 4H), 3.45 (s, 2H), 1.70 (s, 3H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 150.4, 146.9, 137.0, 136.7, 130.8, 126.6, 123.9, 123.0, 117.3, 112.0, 56.8, 39.0, 23.0; IR (CH_2Cl_2) 3083, 3023, 2977, 2929, 2828, 1644, 1590, 1490, 1443, 1416 cm^{-1} ; LRMS (EI, 20 eV) m/z 227 (M^+ , 3), 186 (36), 144 (100); HRMS (EI) for $\text{C}_{16}\text{H}_{21}\text{N}$ (M^+): calcd 227.1674, found 227.1671.

Typical Procedure of Preparation 11:

A dry and argon-flushed 100-mL round-bottomed flask was added with $\text{Pd(PPh}_3)_4$ (231 mg, 0.2 mmol) and *N, N*-dimethylbarbituric acid (18.8g, 120.3 mmol). The mixture was added with a degassed solution of **10** (4.6g, 20.1 mmol) in CH_2Cl_2 (60 mL) via cannula and was heated to 35 °C. After 16 h, the reaction mixture was cooled and CH_2Cl_2 was evaporated. The solid residue was dissolved by a saturated solution of Na_2CO_3 (100 mL) and diethyl ether (100 mL). The ethereal layer was washed by another 100 mL of saturated Na_2CO_3 solution and then brine (100 mL). The organic layer was concentrated, filtered through a short of silica gel (20% ethyl acetate/ *n*-hexane as eluent) and then concentrated to afford crude product **11** as an orange oil. The crude product **11** was used directly for the preparation of **1j**.

Typical procedure for Pd(II)-Catalyzed Oxidative Tandem Cyclizations (Table 1, entry 3):

In a 5-mL round-bottomed flask equipped with a magnetic stir bar, a mixture of $\text{Pd}(\text{OAc})_2$ (6.7 mg, 0.03 mmol) and pyridine (9.7 μL , 0.12 mmol) in dry toluene (3 mL) was stirred at room temperature. After 30 min (or until all $\text{Pd}(\text{OAc})_2$ was dissolved), substrate **1b** (66.5 mg, 0.3 mmol) was added. The reaction flask was assembled with an air condenser, sealed with septa, connected to oxygen atmosphere and heated to $50\text{ }^\circ\text{C}$. After 19 h, the reaction mixture was cooled, filtered through a short pad of silica gel (EtOAc as eluent) and concentrated in vacuo. The crude residue was purified by flash column chromatography (EtOAc and *n*-hexane as eluents) to give **2b** in 83% yield.

Typical procedure for Pd(II)-Catalyzed Enantioselective Oxidative Tandem Cyclizations (Table 3, entry 2):

In a 25 mL round-bottomed flask equipped with a magnetic stir bar, a mixture of Pd(TFA)₂ (33.2 mg, 0.1 mmol), (–)-sparteine (92 μL, 0.4 mmol) and activated 3 Å molecular sieves (500 mg) in dry toluene (10 mL) was stirred at room temperature. After 30 min, substrate **1a** (187 mg, 1 mmol) and N(*i*Pr)₂Et (348 μL, 2 equiv) were added subsequently. The reaction flask was assembled with an air condenser, sealed with septum, connected to oxygen atmosphere and heated to 80 °C. After 26 h, the reaction mixture was cooled, filtered through a short pad of silica gel (EtOAc as eluent) and concentrated in vacuo. The crude residue was purified by flash column chromatography (EtOAc and *n*-hexane as eluents) to give (+)-**2a** in 78% yield (86% ee).

Chiral Ligands Screened for Enantioselective Oxidative Tandem Cyclizations

2a

2a: White solid, m.p. 83–84 °C; analytical TLC (silica gel 60), 30% EtOAc in *n*-hexane, R_f = 0.30; ^1H NMR (300 MHz, CDCl_3) δ 7.67 (d, J = 7.7 Hz, 1H), 7.25–7.17 (m, 2H), 7.04 (dt, J = 7.5, 0.9 Hz, 1H), 6.04 (dd, J = 3.3, 1.6 Hz, 1H), 5.40 (dd, J = 2.8, 1.3 Hz, 1H), 4.61–4.50 (m, 1H), 3.23–3.10 (m, 2H), 2.87 (dd, J = 15.4, 10.7 Hz, 1H), 2.75–2.65 (m, 1H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 164.5, 143.9, 139.8, 134.2, 127.9, 125.5, 124.9, 117.4, 115.2, 60.2, 36.3, 34.2; IR (CH_2Cl_2) 3055, 2987, 2915, 1693, 1658, 1606, 1484, 1442 cm^{-1} ; LRMS (EI, 20 eV) m/z 185 (M^+ , 100); HRMS (EI) for $\text{C}_{12}\text{H}_{11}\text{NO}$ (M^+): calcd 185.0841, found 185.0844.

2b

2b: White solid, m.p. 123–124 °C; analytical TLC (silica gel 60), 30% EtOAc in *n*-hexane, R_f = 0.33; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, J = 8.3 Hz, 1H), 7.21 (d, J = 8.3 Hz, 1H), 7.18 (s, 1H), 6.07 (dd, J = 3.4, 1.7 Hz, 1H), 5.44 (dd, J = 3.0, 1.5 Hz, 1H), 4.65–4.56 (m, 1H), 3.24–3.14 (m, 2H), 2.90 (dd, J = 15.4, 10.7 Hz, 1H), 2.77–2.69 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.7, 143.4, 138.5, 136.1, 130.0, 128.2, 125.9, 117.8, 116.1, 60.5, 36.4, 34.3; IR (CH_2Cl_2) 3055, 2987, 2916, 1696, 1658, 1604, 1481, 1442 cm^{-1} ; LRMS (EI, 20 eV) m/z 219 (M^+ , 100); HRMS (EI) for $\text{C}_{12}\text{H}_{10}\text{ClNO}$ (M^+): calcd 219.0451, found 219.0451.

2c

2c: Orange oil; analytical TLC (silica gel 60), 50% EtOAc in *n*-hexane, R_f = 0.57; ^1H NMR (500 MHz, CDCl_3) δ 7.56 (d, J = 7.9 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 7.02 (s, 1H), 6.05 (dd, J = 3.4, 1.6 Hz, 1H), 5.40 (dd, J = 3.0, 1.4 Hz, 1H), 4.60–4.54 (m, 1H),

3.18–3.12 (m, 2H), 2.86 (dd, $J = 15.3, 10.7$ Hz, 1H), 2.74–2.68 (m, 1H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.1, 143.7, 137.2, 134.5, 134.1, 128.2, 126.0, 116.6, 114.8, 60.2, 36.2, 34.1, 21.2; IR (CH_2Cl_2) 3055, 2988, 2917, 1690, 1658, 1492, 1422, 1403 cm^{-1} ; LRMS (EI, 20 eV) m/z 199 (M^+ , 100); HRMS (EI) for $\text{C}_{13}\text{H}_{13}\text{NO}$ (M^+): calcd 199.0997, found 199.0998.

2d

2d: White solid, m.p. 85–86 °C; analytical TLC (silica gel 60), 50% EtOAc in *n*-hexane, $R_f = 0.39$; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 8.4$ Hz, 1H), 6.79–6.76 (m, 2H), 6.05 (dd, $J = 3.4, 1.7$ Hz, 1H), 5.40 (dd, $J = 2.9, 1.4$ Hz, 1H), 4.63–4.57 (m, 1H), 3.79 (s, 3H), 3.20–3.12 (m, 2H), 2.89 (dd, $J = 15.4, 10.7$ Hz, 1H), 2.76–2.70 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.2, 157.6, 143.9, 136.0, 133.5, 116.9, 115.6, 112.5, 112.3, 60.7, 56.1, 36.8, 34.2; IR (CH_2Cl_2) 3055, 2988, 2917, 1687, 1657, 1595, 1491, 1422 cm^{-1} ; LRMS (EI, 20 eV) m/z 215 (M^+ , 100), 200 (54); HRMS (EI) for $\text{C}_{13}\text{H}_{13}\text{NO}_2$ (M^+): calcd 215.0946, found 215.0939.

2e

(*Z*)-form only

(one quaternary carbon peak overlapped in ^{13}C)

2e: White solid, m.p. 115–116 °C; analytical TLC (silica gel 60), 30% EtOAc in *n*-hexane, $R_f = 0.51$; ^1H NMR (500 MHz, CDCl_3) δ 7.88 (d, $J = 7.4$ Hz, 2H), 7.71 (d, $J = 7.8$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 2H), 7.29 (t, $J = 7.4$ Hz, 1H), 7.24–7.20 (m, 2H), 7.05 (dt, $J = 7.5, 0.9$ Hz, 1H), 6.79 (d, $J = 2.4$ Hz, 1H), 4.68–4.62 (m, 1H), 3.25–3.18 (m, 2H), 2.99–2.90 (m, 2H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 164.1, 140.3, 135.6, 134.8, 134.1, 130.7, 128.9, 128.3, 128.1, 125.7, 124.8, 115.5, 59.8, 39.1, 36.5; IR

(CH₂Cl₂) 3055, 2988, 2925, 1687, 1651, 1604, 1483, 1422 cm⁻¹; LRMS (EI, 20 eV) *m/z* 261 (M⁺, 80), 170 (7); HRMS (EI) for C₁₈H₁₅NO (M⁺): calcd 261.1154, found 261.1155.

2f
(Z)-form only

(one quaternary carbon peak overlapped in ¹³C)

2f: White solid, m.p. 112–113 °C; analytical TLC (silica gel 60), 30% EtOAc in *n*-hexane, *R_f* = 0.68; ¹H NMR (300 MHz, CDCl₃) δ 7.85 (s, 1H), 7.82–7.79 (m, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.36–7.19 (m, 4H), 7.06 (dt, *J* = 7.5, 0.9 Hz, 1H), 6.70 (d, *J* = 2.2 Hz, 1H), 4.71–4.60 (m, 1H), 3.27–3.16 (m, 2H), 3.00–2.88 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 163.4, 139.8, 136.2, 136.1, 133.8, 133.5, 130.2, 129.2, 128.6, 128.4, 127.8, 125.2, 124.7, 115.2, 59.6, 38.7, 36.1; IR (CH₂Cl₂) 3055, 2988, 2917, 1685, 1483, 1422, 1404 cm⁻¹; LRMS (EI, 20 eV) *m/z* 295 (M⁺, 100); HRMS (EI) for C₁₈H₁₄ClNO (M⁺): calcd 295.0764, found 295.0762.

2g

(Z)-form only

2g: White solid, m.p. 178–180 °C; analytical TLC (silica gel 60), 30% EtOAc in *n*-hexane, *R_f* = 0.51; ¹H NMR (300 MHz, CDCl₃) δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 1H), 7.26–7.16 (m, 4H), 7.05 (dt, *J* = 7.5, 0.9 Hz, 1H), 6.76 (d, *J* = 2.3 Hz, 1H), 4.68–4.63 (m, 1H), 3.28–3.16 (m, 2H), 3.01–2.89 (m, 2H), 2.36 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 164.6, 140.4, 139.0, 135.7, 134.1, 133.8, 132.1, 130.8,

129.0, 128.1, 125.5, 124.7, 115.4, 59.8, 39.2, 36.6, 21.8; IR (CH₂Cl₂) 3055, 2987, 2916, 1683, 1651, 1604, 1482, 1402 cm⁻¹; LRMS (EI, 20 eV) *m/z* 275 (M⁺, 6), 117 (21); HRMS (EI) for C₁₉H₁₇NO (M⁺): calcd 275.1310, found 275.1309.

2h

Mixture of (*E*)- and (*Z*)-forms.

2h: White solid, m.p. 118–119 °C; analytical TLC (silica gel 60), 30% EtOAc in *n*-hexane, *R_f* = 0.32; ¹H NMR (300 MHz, CDCl₃) δ 7.66 (d, *J* = 7.7 Hz, 1H), 7.26–7.19 (m, 2H), 7.05 (dt, *J* = 7.5, 0.8 Hz, 1H), 6.65–6.57 (m, 1H), 4.65–4.53 (m, 1H), 3.26–3.11 (m, 2H), 2.91 (dd, *J* = 15.3, 10.8 Hz, 1H), 2.62–2.52 (m, 1H), 1.84–1.81 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 165.1, 140.0, 136.0, 133.9, 129.8, 127.8, 125.1, 124.4, 115.1, 60.1, 36.5, 31.0, 14.9; IR (CH₂Cl₂) 3055, 2988, 1694, 1671, 1483, 1423 cm⁻¹; LRMS (EI, 20 eV) *m/z* 199 (M⁺, 100); HRMS (EI) for C₁₃H₁₃NO (M⁺): calcd 199.0997, found 199.1001.

3h

3h: White solid, m.p. 74–75 °C; analytical TLC (silica gel 60), 30% EtOAc in *n*-hexane, *R_f* = 0.07; ¹H NMR (500 MHz, CDCl₃) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.03 (dt, *J* = 7.5, 1.0 Hz, 1H), 6.06–5.99 (m, 1H), 5.26–5.19 (m, 1H), 4.60–4.53 (m, 1H), 3.60–3.54 (m, 1H), 3.21 (dd, *J* = 15.7, 8.5 Hz, 1H), 2.90 (dd, *J* = 15.7, 9.8 Hz, 1H), 2.71–2.66 (m, 1H), 1.92 (dt, *J* = 12.1, 10.1 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 171.4, 139.3, 134.5, 133.9, 127.8, 125.3,

124.2, 117.6, 114.8, 60.4, 50.8, 36.0, 35.7; IR (CH₂Cl₂) 3055, 2988, 2934, 1698, 1486, 1422, 1405 cm⁻¹; LRMS (EI, 20 eV) *m/z* 199 (M⁺, 100); HRMS (EI) for C₁₃H₁₃NO (M⁺): calcd 199.0997, found 199.0999.

minor diastereomer: brown solid, m.p. 66–67 °C; analytical TLC (silica gel 60), 30% EtOAc in *n*-hexane, *R_f* = 0.18; ¹H NMR (500 MHz, CDCl₃) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.04 (dt, *J* = 7.5, 0.9 Hz, 1H), 6.05–5.98 (m, 1H), 5.36 (dt, *J* = 17.2, 1.3 Hz, 1H), 5.24 (dt, *J* = 10.4, 1.2 Hz, 1H), 4.76–4.69 (m, 1H), 3.44 (m, 1H), 3.18 (dd, *J* = 15.6, 8.5 Hz, 1H), 2.91 (dd, *J* = 15.6, 10.1 Hz, 1H), 2.42 (dd, *J* = 12.5, 6.0 Hz, 1H), 2.26–2.20 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 171.5, 139.1, 134.3, 133.9, 127.8, 125.2, 124.4, 116.6, 115.1, 61.2, 52.3, 35.7, 34.7; IR (CH₂Cl₂) 3055, 2988, 2933, 1695, 1485, 1422, 1404 cm⁻¹; LRMS (EI, 20 eV) *m/z* 199 (M⁺, 100); HRMS (EI) for C₁₃H₁₃NO (M⁺): calcd 199.0997, found 199.1002.

3i

major diastereomer

3i: Yellow oil; analytical TLC (silica gel 60), 30% EtOAc in *n*-hexane, *R_f* = 0.44; ¹H NMR (500 MHz, CDCl₃) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.18 (d,

$J = 7.4$ Hz, 1H), 7.03 (dt, $J = 7.5, 0.9$ Hz, 1H), 5.93 (dd, $J = 17.4, 10.5$ Hz, 1H), 5.26 (d, $J = 17.4$ Hz, 1H), 5.16 (d, $J = 10.5$ Hz, 1H), 4.58–4.51 (m, 1H), 3.17 (dd, $J = 15.6, 8.5$ Hz, 1H), 2.87 (dd, $J = 15.6, 10.0$ Hz, 1H), 2.55 (dd, $J = 12.2, 5.6$ Hz, 1H), 1.89 (dd, $J = 12.3, 10.1$ Hz, 1H), 1.33 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.6, 139.4, 139.3, 134.2, 127.8, 125.3, 124.2, 115.0, 113.9, 58.6, 53.8, 43.0, 35.5, 23.1; IR (CH_2Cl_2) 3055, 2987, 2932, 1698, 1605, 1485, 1402 cm^{-1} ; LRMS (EI, 20 eV) m/z 213 (M^+ , 100); HRMS (EI) for $\text{C}_{14}\text{H}_{15}\text{NO}$ (M^+): calcd 213.1154, found 213.1154.

2j

2j:⁴ Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 7.8$ Hz, 1H), 7.26 (t, $J = 7.7$ Hz, 1H), 7.22 (d, $J = 7.5$ Hz, 1H), 7.08 (dt, $J = 7.5, 0.9$ Hz, 1H), 6.10 (t, $J = 2.5$ Hz, 1H), 5.45 (t, $J = 2.2$ Hz, 1H), 3.11 (d, $J = 15.4$ Hz, 1H), 2.94 (d, $J = 15.5$, 1H), 2.89 (d, $J = 2.2$ Hz, 2H), 1.35 (s, 3H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 164.4, 143.7, 138.8, 133.5, 128.2, 125.9, 125.0, 118.1, 115.9, 66.8, 43.1, 41.8, 27.5.

2k

2k: White solid, m.p. 89–90 °C; analytical TLC (silica gel 60), 30% EtOAc in *n*-hexane, $R_f = 0.31$; ^1H NMR (300 MHz, CDCl_3) δ 7.37 (s, 1H), 6.72 (s, 1H), 6.05 (s, 1H), 5.39 (s, 1H), 4.61–4.50 (m, 1H), 3.19–3.08 (m, 2H), 2.74–2.67 (m, 2H), 2.32 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 164.2, 143.8, 139.3, 137.9, 134.3, 129.6, 126.5, 116.6, 113.2, 60.2, 34.5, 34.3, 21.3, 18.6; IR (CH_2Cl_2) 3055, 2989, 2918, 1687, 1658, 1494, 1423, 1405 cm^{-1} ; LRMS (EI, 20 eV) m/z 213 (M^+ , 100), 198 (26); HRMS (EI) for $\text{C}_{14}\text{H}_{15}\text{NO}$ (M^+): calcd 213.1154, found 213.1151.

2l: Yellow solid, m.p. 117–118 °C; TLC (silica gel 60), 20% EtOAc in *n*-hexane, R_f = 0.49; ^1H NMR (400 MHz, CDCl_3) δ 7.85 (s, 1H), 7.80 (d, J = 6.6 Hz, 1H), 7.40 (s, 1H), 7.32–7.23 (m, 2H), 6.70 (s, 1H), 6.63 (d, J = 2.2 Hz, 1H), 4.59 (m, 1H), 3.17–3.07 (m, 2H), 2.94–2.87 (m, 1H), 2.73–2.67 (m, 1H), 2.30 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 163.2, 139.5, 137.9, 136.4, 136.2, 134.3, 133.7, 133.1, 130.2, 129.4, 129.1, 128.6, 128.3, 126.5, 113.2, 59.7, 38.8, 34.4, 21.2, 18.6; IR (CH_2Cl_2) 3055, 2988, 2919, 1687, 1486, 1423, 1406 cm^{-1} ; LRMS (EI, 20 eV) m/z 323 (M^+ , 100), 198 (70), 146 (83); HRMS (EI) for $\text{C}_{20}\text{H}_{18}\text{ClNO}$ (M^+): calcd 323.1077, found 323.1069.

Characterization data of chiral products:

chiral product	ee (%) ^a	retention time, t_R (min) ^b		optical rotation, $[\alpha]^{20}_D$
		t_R (major)	t_R (minor)	
2a	86	17.6	20.0	+ 196 °
2b	75	22.1	24.3	+ 224 °
2f	80	21.3	23.2	+ 331 °
2h	82	35.6	39.6	N.D.
3h	80	24.9	21.3	+ 7.3 °
minor diastereomer of 3h	86	18.9	28.8	+ 3.3 °
2k	91	17.8	32.0	+ 259 °
2l	87	18.5	29.8	+ 353 °

^a Enantiomeric excess of the chiral products were determined by HPLC using a Chiralcel OD column with guard column. ^b Retention time of major and minor peaks.

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Current Data Parameters
NAME y10-9-150-F1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050501
Time 9:17
INSTRUM av400
PROBHD 5 mm DPX13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 0
DS 0
SWH 8155.177 Hz
FIDRES 0.260462 Hz
AQ 1.788293 sec
RG 256
DM 54.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.8000000 sec
D11 1.8000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 13.20 usec
PL1 -4.00 dB
SFO1 400.1300000 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 27.00 cm
CY 5.75 cm
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F1 3001.17 Hz
F2P -0.500 dpm
F2 -950.37 Hz
PRMC 0.20148 sec/cm
HSCN 140.78648 Hz/cm

Current Data Parameters
NAME y10-9-168-F1C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
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SOLVENT CDCl3
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DS 0
SWH 25125.829 Hz
FIDRES 0.760773 Hz
AQ 0.6521332 sec
RG 514.7
DM 19.900 usec
DE 6.00 usec
TE 300.0 K
D1 2.5000000 sec
D11 0.0300000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 9.10 usec
PL1 -5.00 dB
SFO1 100.628364 MHz

===== CHANNEL f2 =====
CHRGD2 mltir16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 12.00 dB
SFO2 400.1300007 MHz

F2 - Processing parameters
SI 32768
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GB 0
PC 1.40

1D NMR plot parameters
CX 25.00 cm
CY 5.75 cm
F1P 230.000 dpm
F1 20134.80 Hz
F2P -10.000 dpm
F2 -1006.13 Hz
PRMC 0.20000 dpm/cm
HSCN 925.63723 Hz/cm

Current Data Parameters
NAME yip-B-115-F1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050413
Time 23.20
INSTRUM dpX300
PROBHD DUAL 5mm

PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 4
DS 2
SWH 7812.500 Hz
FIDRES 0.238419 Hz
AQ 2.0912021 sec
RG 181
DM 64.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

***** CHANNEL f1 *****
NUC1 1H
P1 9.00 usec
PL1 -6.00 dB
SF01 300.1318934 MHz

F2 - Processing parameters
SI 32768
SF 300.1300054 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 23.00 cm
F1P 9.000 ppm
F1 2701.17 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPHCH 0.41304 ppm/cm
H2CM 123.96674 Hz/cm

Current Data Parameters
NAME yip-B-115-F1C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050413
Time 23.41
INSTRUM dpX300
PROBHD DUAL 5mm

PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 814
DS 1
SWH 18832.393 Hz
FIDRES 0.574719 Hz
AQ 0.8700404 sec
RG 8192
DM 26.550 usec
DE 4.50 usec
TE 300.0 K
D1 2.50000000 sec
D11 0.03000000 sec

***** CHANNEL f1 *****
NUC1 13C
P1 7.00 usec
PL1 -6.00 dB
SF01 75.4750204 MHz

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 18.00 dB
SF02 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677253 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 25.00 cm
F1P 220.000 ppm
F1 16602.90 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPHCH 9.20000 ppm/cm
H2CM 694.30310 Hz/cm

Current Data Parameters
NAME y10-9-105-F1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050427
Time 23.44
INSTRUM mv400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 9139.177 Hz
FIDRES 0.2004602 Hz
AQ 1.7800000 sec
RG 408.4
DM 54.400 usec
DE 8.00 usec
TE 300.0 K
D1 1.8000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 13.20 usec
PL1 -4.00 dB
SFO1 400.1300000 MHz

F2 - Processing parameters
SI 32768
SF 400.1300700 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 27.00 cm
CY 10.24 cm
FIP 8.000 cm
F1 3001.17 Hz
F2 -9.500 cm
F2 -200.87 Hz
PPHCK 0.32185 cm/c
H2CK 146.78848 Hz/c

Current Data Parameters
NAME y10-9-105-F1C
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050428
Time 2.11
INSTRUM mv400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 25195.829 Hz
FIDRES 0.7807773 Hz
AQ 0.6501332 sec
RG 256
DM 19.900 usec
DE 8.00 usec
TE 300.0 K
D1 2.5000000 sec
d11 0.8300000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 9.10 usec
PL1 -5.00 dB
SFO1 100.6280364 MHz

===== CHANNEL f2 =====
CPROG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 12.00 dB
SFO2 400.1320007 MHz

F2 - Processing parameters
SI 32768
SF 100.6127350 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 25.00 cm
CY 14.00 cm
FIP 200.000 cm
F1 20122.50 Hz
F2 -1500.13 Hz
PPHCK 8.40000 cm/c
H2CK 845.14703 Hz/c

Current Data Parameters
NAME y10-B-128-1-F3
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050421
Time 9.44
INSTRUM spect
PROBHD BBO 5mm
PULPROG cosy45
TD 32768
SOLVENT CDCl3
NS 4
DS 16
SWH 3633.725 Hz
FIDRES 3.548656 Hz
AQ 0.1409524 sec
RG 287.4

2e

PC 1.00
F1 - Processing parameters
SI 512
HC2 512
SF 500.127513 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
F2 - Acquisition Parameters
CQ2 15.00 cm
CQ1 15.00 cm
F2PQD 0.412 ppm
F2Q 4207.18 Hz
F2PH1 1.147 ppm
F2H1 573.45 Hz
F2PQD 0.408 ppm
F2Q 4205.51 Hz
F2PH1 1.143 ppm
F2H1 571.78 Hz
F2PQMW 0.40437 ppm/cm
F2H2CM 242.24876 Hz/cm

Current Data Parameters
NAME y10-B-128-1-F3
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050421
Time 16.54
INSTRUM spect
PROBHD BBO 5mm
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 8
DS 16
SWH 14780.860 Hz
FIDRES 14.448191 Hz
AQ 0.206512 sec
RG 655.2
SW 33.860 MHz
SE 4.50 MHz
TE 300.2 K
CQ2 145.000000 MHz
CQ1 145.000000 MHz
F2PQD 3.000000 ppm/cm
F2H2CM 401.80776 Hz/cm

2e

SF 125.757708 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00
F1 - Processing parameters
SI 512
HC2 512
SF 500.130073 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
F2 - Acquisition Parameters
CQ2 18.00 cm
CQ1 18.00 cm
F2PQD 1.465731 ppm
F2Q 18388.58 Hz
F2PH1 28.161 ppm
F2H1 1408.57 Hz
F2PQD 0.411 ppm
F2Q 4206.37 Hz
F2PH1 1.145 ppm
F2H1 572.85 Hz
F2PQMW 0.40400 ppm/cm
F2H2CM 401.80776 Hz/cm
F2H2CM 242.24876 Hz/cm

Current Data Parameters
NAME yip-B-164-F1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050505
Time 23.26
INSTRUM spect
PROBHD DUAL 5mm
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 7
DS 2
SWH 7812.500 Hz
FIDRES 0.238419 Hz
AQ 2.0972021 sec
RG 287.4
DM 64.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

***** CHANNEL f1 *****
NUC1 1H
P1 9.00 usec
PL1 -6.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300081 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 23.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCH 0.45652 ppm/cm
HZCH 137.01587 Hz/cm

Current Data Parameters
NAME vis-B-188-F21
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050620
Time 22.12
INSTRUM opx300
PROBHD DUAL 5mm
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 3
DS 2
SWH 7812.500 Hz
FIDRES 0.238419 Hz
AQ 2.0972021 sec
RG 409.4
DM 64.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

***** CHANNEL f1 *****
NUC1 1H
P1 9.00 usec
PL1 -6.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300664 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 23.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPhCM 0.45652 ppm/cm
H2CM 137.01587 Hz/cm

Current Data Parameters
NAME vis-B-188-F22C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050620
Time 22.26
INSTRUM opx300
PROBHD DUAL 5mm
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 813
DS 1
SWH 16832.393 Hz
FIDRES 0.574719 Hz
AQ 0.8703404 sec
RG 4096
DM 26.550 usec
DE 4.50 usec
TE 300.0 K
D1 2.50000000 sec
D11 0.03000000 sec

***** CHANNEL f1 *****
NUC1 13C
P1 7.00 usec
PL1 -6.00 dB
SFO1 75.4760204 MHz

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 18.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677236 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 25.00 cm
F1P 220.000 ppm
F1 16602.90 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPhCM 9.20000 ppm/cm
H2CM 694.39298 Hz/cm

Current Data Parameters
NAME y1D-B-188-F2
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050530
Time 17.42
INSTRUM spect
PROBHD BBO 5mm

PULPROG cosy45
TD 32768
SOLVENT ccd13
AQ 4
DS 16
SWH 1646.400 MHz

PC 1.00

F1 - Processing parameters
SI 512
SF 500.1377033 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0

2D NMR list parameters
CX2 15.00 cm
CX1 15.00 cm
F2PLD 8.456 ppm
F2LO 4229.02 Hz
F2H1 0.742 ppm
F2H2 370.99 Hz
F2PLD 0.449 ppm
F2LO 4229.70 Hz
F2H1 0.725 ppm
F2H2 367.68 Hz
F2H3 0.51407 ppm/cm
F2H4 357.20166 Hz/cm
F2H5 0.51407 ppm/cm

Current Data Parameters
NAME y1D-B-188-F2
EXPNO 8
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050530
Time 20.54
INSTRUM spect
PROBHD BBO 5mm

PULPROG zgpg30
TD 65536
SOLVENT dms
AQ 18
DS 18
SWH 16178.543 Hz
F2H3 15.36657 Hz
AQ 0.630562 sec
RG 512
CW 25.800 kHz
DE 4.545 kHz

F1 - Processing parameters
SI 512
SF 500.1377033 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0

2D NMR list parameters
CX2 15.00 cm
CX1 15.00 cm
F2PLD 8.456 ppm
F2LO 4229.02 Hz
F2H1 0.742 ppm
F2H2 370.99 Hz
F2PLD 0.449 ppm
F2LO 4229.70 Hz
F2H1 0.725 ppm
F2H2 367.68 Hz
F2H3 0.51407 ppm/cm
F2H4 357.20166 Hz/cm
F2H5 0.51407 ppm/cm

Current Data Parameters
 Name: 10-15-15
 Date: 10/05/13
 Time: 17:11
 Instrument: spect
 Processed: 800 MHz

F2 - Acquisition Parameters
 Date: 10/05/13
 Time: 17:11
 Instrument: spect
 Processed: 800 MHz

Parameters
 FID: 1000
 TO: 32768
 SCA: 100
 MS: 1
 SW: 1400.000 MHz
 FIDRES: 0.200000 Hz
 AQ: 2.000000 sec
 RG: 327.5
 DW: 80.000 nsec
 DE: 4.50 nsec
 TE: 300.0 K
 RT: 1.0000000 sec

===== CHANNEL f1 =====
 NUC1: 1H
 P1: 10.00 nsec
 PL1: -0.00 dB
 SFO1: 500.135060 MHz

F2 - Processing parameters
 SI: 32768
 SF: 500.135060 MHz
 WDW: EM
 SSB: 0
 LB: 0.30 Hz
 GB: 0
 PC: 1.00

===== CHANNEL f2 =====
 NUC2: 13C
 P2: 8.00 nsec
 PL2: -2.00 dB
 SFO2: 125.760350 MHz

F2 - Processing parameters
 SI: 32768
 SF: 125.760350 MHz
 WDW: EM
 SSB: 0
 LB: 1.20 Hz
 GB: 0
 PC: 1.00

===== CHANNEL f3 =====
 NUC3: 13C
 P3: 8.00 nsec
 PL3: -2.00 dB
 SFO3: 125.760350 MHz

F2 - Processing parameters
 SI: 32768
 SF: 125.760350 MHz
 WDW: EM
 SSB: 0
 LB: 1.20 Hz
 GB: 0
 PC: 1.00

===== CHANNEL f4 =====
 NUC4: 13C
 P4: 8.00 nsec
 PL4: -2.00 dB
 SFO4: 125.760350 MHz

F2 - Processing parameters
 SI: 32768
 SF: 125.760350 MHz
 WDW: EM
 SSB: 0
 LB: 1.20 Hz
 GB: 0
 PC: 1.00

3h
major diastereomer

Current Data Parameters
 Name: 10-15-15
 Date: 10/05/13
 Time: 17:11
 Instrument: spect
 Processed: 800 MHz

F2 - Acquisition Parameters
 Date: 10/05/13
 Time: 17:11
 Instrument: spect
 Processed: 800 MHz

Parameters
 FID: 1000
 TO: 32768
 SCA: 100
 MS: 1
 SW: 1400.000 MHz
 FIDRES: 0.200000 Hz
 AQ: 2.000000 sec
 RG: 327.5
 DW: 80.000 nsec
 DE: 4.50 nsec
 TE: 300.0 K
 RT: 1.0000000 sec

===== CHANNEL f1 =====
 NUC1: 13C
 P1: 8.00 nsec
 PL1: -2.00 dB
 SFO1: 125.760350 MHz

F2 - Processing parameters
 SI: 32768
 SF: 125.760350 MHz
 WDW: EM
 SSB: 0
 LB: 1.20 Hz
 GB: 0
 PC: 1.00

===== CHANNEL f2 =====
 NUC2: 13C
 P2: 8.00 nsec
 PL2: -2.00 dB
 SFO2: 125.760350 MHz

F2 - Processing parameters
 SI: 32768
 SF: 125.760350 MHz
 WDW: EM
 SSB: 0
 LB: 1.20 Hz
 GB: 0
 PC: 1.00

===== CHANNEL f3 =====
 NUC3: 13C
 P3: 8.00 nsec
 PL3: -2.00 dB
 SFO3: 125.760350 MHz

F2 - Processing parameters
 SI: 32768
 SF: 125.760350 MHz
 WDW: EM
 SSB: 0
 LB: 1.20 Hz
 GB: 0
 PC: 1.00

3h
major diastereomer

Current Data Parameters
NAME γ10-B-167-F5
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050613
Time 12.30
INSTRUM spect
PROBHD BBO 5mm
PULPROG cosy45
TD 32768
SOLVENT CDCl3
NS 4
DS 16
SWH 3342.246 Hz
FIDRES 0.203512 Hz
AQ 0.1532404 sec
RG 322.5

3h
major diastereomer

F1 - Processing parameters
SI 512
MC2 512
SF 500.1278107 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
F2 - Acquisition Parameters
Date_ 20050613
Time 12.30
INSTRUM spect
PROBHD BBO 5mm
PULPROG hacc
TD 32768
SOLVENT CDCl3
NS 4
DS 16
SWH 3342.246 Hz
FIDRES 0.203512 Hz
AQ 0.1532404 sec
RG 322.5

3h
major diastereomer

F1 - Processing parameters
SI 512
MC2 512
SF 500.1278107 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
F2 - Acquisition Parameters
Date_ 20050613
Time 12.30
INSTRUM spect
PROBHD BBO 5mm
PULPROG hacc
TD 32768
SOLVENT CDCl3
NS 4
DS 16
SWH 3342.246 Hz
FIDRES 0.203512 Hz
AQ 0.1532404 sec
RG 322.5

Current Data Parameters
NAME y10-B-167-F5
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050517
Time 11.15
INSTRUM spect
PROBHD 500 Sma
PULPROG zgpg30
TD 32768
SOLVENT cdc13
DS 8
SS 1
SB 7485.530 Hz
FIDRES 0.108450 Hz
AQ 2.1889574 sec
RG 124.1
DM 68.800 usec
DE 4.50 usec
TE 300.2 K
D1 1.0000000 sec

***** CHANNEL f1 *****
NUC1 1H
P1 10.00 usec
PL1 -6.00 dB
SFO1 500.132606 MHz

F2 - Processing parameters
SI 32768
SF 500.1300124 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CH 30.00 cm
FAP 10.500 usec
FI 500.10 Hz
FAP -0.500 dB
FD 0.40000000 Hz
HCH 200.05721 MHz

minor diastereomer

```

MC2          OF
SF          500.1278110 MHz
WOW          SINE
SSB          0
LB           0.00 Hz
GB           0

```

2D NMR plot parameters

```

CA2          15.00 cm
CA1          15.00 cm
F2PL0        8.035 ppm
F2L0         4018.59 Hz
F2PH1        0.727 ppm
F2H1         363.62 Hz
F1PL0        8.031 ppm
F1L0         4016.52 Hz
F1PH2        0.723 ppm
F1H2         361.54 Hz
F2PRCH       0.48720 ppm/cm
F2HCH        743.66470 Hz/cm
F2PRCH       0.48720 ppm/cm

```

SGB	0
LB	3.00 Hz
GB	0
PC	1.00

F1 - Processing parameters

SI	512
HC2	GF
SF	500.1300147 MHz
WDW	SINE
SGB	2
LB	0.00 Hz
GB	0

2D NMR plot parameters

CH2	18.00 cm
CH1	18.00 cm
F2PL0	146.624 ppm
F2L0	18429.17 Hz
F2PH1	15.830 ppm
F2H1	1991.86 Hz
F1PL0	8.620 ppm
F1L0	1125.70 Hz
F1PH2	0.723 ppm
F1H2	361.76 Hz
F2PRCH	7.70388 ppm/cm
F2HCH	143.74388 Hz/cm

Current Data Parameters
NAME ym004-0-9
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050602
Time 21.32
INSTRUM mv400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 0
DS 0
SWH 8012.820 Hz
F2RES 0.244532 Hz
AQ 2.0447731 sec
RG 428
DM 62.400 usec
DE 8.00 usec
TE 300.2 K
DQ 1.0000000 sec

***** CHANNEL f1 *****
NUC1 13C
P1 13.00 usec
PL1 -4.00 dB
SFO1 400.1304000 MHz

F2 - Processing parameters
SI 32768
SF 400.1300176 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 25.00 cm
CY 6.69 cm
FIDP 10.000 ppm
F1 4001.30 Hz
F2P -0.200 ppm
F2 80.03 Hz
PRNCH 0.40800 ppm/cm
HDCN 163.25304 Hz/cm

Current Data Parameters
NAME ym004-0-9
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050602
Time 22.33
INSTRUM mv400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 0
DS 0
SWH 18852.960 Hz
F2RES 0.518719 Hz
AQ 1.8708404 sec
RG 428
DM 62.400 usec
DE 8.00 usec
TE 300.2 K
DQ 1.0000000 sec
D1 0.5000000 sec

***** CHANNEL f1 *****
NUC1 13C
P1 13.00 usec
PL1 -4.00 dB
SFO1 400.1304000 MHz

***** CHANNEL f2 *****
NUC2 13C
P2 13.00 usec
PL2 -4.00 dB
SFO2 100.6261250 MHz

F2 - Processing parameters
SI 32768
SF 400.1300176 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 25.00 cm
CY 6.69 cm
FIDP 10.000 ppm
F1 4001.30 Hz
F2P -0.200 ppm
F2 80.03 Hz
PRNCH 0.40800 ppm/cm
HDCN 163.25304 Hz/cm

21

NOESY spectrum of 21

HPLC conditions of 2a:

Column: Chiralcel OD

Eluent: i-Propanol/n-Hexane (6/94)

Flow rate: 0.8 mL/min; Detection: UV 278 nm

=====
 Area Percent Report
 =====

Sorted by Signal

Multiplier : 1.000000
 Dilution : 1.000000
 Sample Amount : 1.000000 [ng/ul] (not used in calc.)

Signal 1: MWD1 A, Sig=278,5 Ref=550,100

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.621	BV	0.539	5261.55957	144.28719	49.9238
2	19.970	VB	0.621	5277.61230	125.85117	50.0762

Totals : 10539.17188 270.13837

=====
 Area Percent Report
 =====

Sorted by Signal

Multiplier : 1.000000
 Dilution : 1.000000
 Sample Amount : 1.000000 [ng/ul] (not used in calc.)

Signal 1: MWD1 A, Sig=278,5 Ref=550,100

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.588	BB	0.546	3111.65015	84.69422	92.7808
2	19.957	BB	0.593	241.58241	5.92423	7.2192

Totals : 3360.23267 90.61845

HPLC conditions of 2b:

Column: Chiralcel OD

Eluent: i-Propanol/n-Hexane (6/94)

Flow rate: 0.6 mL/min, Detection: UV 290 nm

=====
Area Percent Report
=====

Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000
Sample Amount : 1.000000 [ng/ul] (not used in calc.)

Signal 1: MWD1 A, Sig=290,5 Ref=550,100

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.938	BV	0.661	5611.48682	126.89655	49.8687
2	24.171	VB	0.728	5641.03027	115.34396	50.1313

Totals : 11252.51758 242.24051

=====

=====
Area Percent Report
=====

Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000
Sample Amount : 1.000000 [ng/ul] (not used in calc.)

Signal 1: MWD1 A, Sig=290,5 Ref=550,100

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.057	BV	0.756	6751.21289	137.49324	87.3256
2	24.335	VB	0.996	915.67633	15.73150	12.6744

Totals : 7776.88916 153.22473

=====

HPLC conditions of 2f:

Column: Chiralcel OD

Eluent: i-Propanol/n-Hexane (6/94)

Flow rate: 0.8 mL/min; Detection: UV 316 nm

=====
 Area Percent Report
 =====

Sorted by Signal

Multiplier : 1.000000
 Dilution : 1.000000
 Sample Amount : 1.000000 [ng/ul] (not used in calc.)

Signal 1: MWD1 A, Sig=316,5 Ref=550,100

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.377	MF	0.763	4140.98486	90.49113	49.5768
2	23.183	FM	0.866	4211.67871	81.07754	50.4232

Totals : 8352.66406 171.56866

=====
 Area Percent Report
 =====

Sorted by Signal

Multiplier : 1.000000
 Dilution : 1.000000
 Sample Amount : 1.000000 [ng/ul] (not used in calc.)

Signal 1: MWD1 A, Sig=316,5 Ref=550,100

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.271	BF	0.685	3594.59082	78.52209	89.9333
2	23.162	FB	0.817	402.36331	6.91280	10.0667

HPLC conditions of 2h:

Column: Chiralcel OD, No. 578-028-50904

Eluent: i-Propanol/n-Hexane (6/94)

Flow rate: 0.6 mL/min; Detection: UV 278 nm

Area Percent Report

Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000
Sample Amount : 1.000000 [ng/ul] (not used in calc.)

Signal 1: MWD1 B, Sig=278,5 Ref=550,100

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.544	BV	1.165	3557.57837	45.29564	49.9544
2	39.447	VB	1.327	3564.06934	40.96814	50.0456

Totals : 7121.64746 86.26378

Area Percent Report

Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000
Sample Amount : 1.000000 [ng/ul] (not used in calc.)

Signal 1: MWD1 B, Sig=278,5 Ref=550,100

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.587	BV	1.234	9373.69922	115.72026	90.7950
2	39.586	VB	1.315	950.32135	10.81104	9.2050

Totals : 10324.02051 126.53130

HPLC conditions of 3h:

Column: Chiralcel OD

Eluent: i-Propanol/n-Hexane (6/94)

Flow rate: 0.6 mL/min; Detection: UV 278 nm

Area Percent Report

Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000
Sample Amount : 1.000000 [ng/ul] (not used in calc.)

Signal 1: MWD1 A, Sig=278,5 Ref=550,100

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.146	PV	0.676	3624.65161	80.64568	49.9860
2	24.801	VV	0.776	3626.67920	70.66043	50.0140

Totals : 7251.33105 151.30612

Area Percent Report

Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000
Sample Amount : 1.000000 [ng/ul] (not used in calc.)

Signal 1: MWD1 A, Sig=278,5 Ref=550,100

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.326	BB	0.712	949.57349	20.48109	10.2858
2	24.857	BV	0.830	8282.28613	149.95009	89.7142

Totals : 9231.85938 170.43118

HPLC conditions of 3h (minor diastereomer):

Column: Chiralcel OD

Eluent: i-Propanol/n-Hexane (6/94)

Flow rate: 0.6 mL/min; Detection: UV 278 nm

Area Percent Report

Sorted by Signal

Multiplier : 1.000000
 Dilution : 1.000000
 Sample Amount : 1.000000 [ng/ul] (not used in calc.)

Signal 1: MWD1 A, Sig=278,5 Ref=550,100

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.929	BF	0.600	8365.28418	207.51295	50.0092
2	28.766	FF	0.927	8362.21680	131.97887	49.9908

Totals : 16727.50000 339.49182

Area Percent Report

Sorted by Signal

Multiplier : 1.000000
 Dilution : 1.000000
 Sample Amount : 1.000000 [ng/ul] (not used in calc.)

Signal 1: MWD1 A, Sig=278,5 Ref=550,100

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.899	FF	0.646	16293.44434	380.51193	92.8767
2	28.778	BB	0.932	1250.03455	20.14201	7.1233

Totals : 17543.47852 400.65393

HPLC conditions of 2k:

Column: Chiralcel OD

Eluent: i-Propanol/n-Hexane (6/94)

Flow rate: 0.6 mL/min; Detection: UV 304 nm

Area Percent Report

Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000
Sample Amount : 1.000000 [ng/ul] (not used in calc.)

Signal 1: MWD1 A, Sig=304,5 Ref=550,100

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.775	BB	0.599	3511.46509	88.70679	49.8218
2	31.850	BB	1.066	3535.58325	49.79722	50.1782

Totals : 7047.04834 138.50401

Area Percent Report

Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000
Sample Amount : 1.000000 [ng/ul] (not used in calc.)

Signal 1: MWD1 A, Sig=304,5 Ref=550,100

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.752	BB	0.627	15275.08398	369.74695	95.7475
2	31.961	BB	1.069	67.42548	9.37937	4.2525

Totals : 15943.50977 379.12631

HPLC conditions of 2l:

Column: Chiralcel OD

Eluent: i-Propanol/n-Hexane (6/94)

Flow rate: 0.8 mL/min; Detection: UV 323 nm

Area Percent Report

Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000
Sample Amount : 1.000000 [ng/ul] (not used in calc.)

Signal 1: MWD1 B, Sig=278,5 Ref=550,100

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.755	BF	0.702	4592.14209	98.80494	50.1018
2	30.326	BB	1.073	4573.47314	63.57880	49.8982

Totals : 9165.61523 162.38374

Area Percent Report

Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000
Sample Amount : 1.000000 [ng/ul] (not used in calc.)

Signal 1: MWD1 A, Sig=323,5 Ref=550,100

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.480	BF	0.644	12420.20508	292.09891	93.6953
2	29.768	BB	0.953	833.08661	12.17957	6.3047

Totals : 13261.29199 304.27847

Figure 1. ORTEP representation of racemic compound **2a**

Crystal data: [C₁₂ H₁₁ N O] ; formula weight = 185.22, Monoclinic, P 2₁/n, a = 8.694(2) Å, b = 10.418(2) Å, c = 11.275(2) Å, β = 110.91(3)°, V = 954.0(3) Å³, Z = 4, D_c = 1.290 g cm⁻³, μ(Mo-Kα) = 0.083 mm⁻¹, F(000) = 392, T = 253 K.

Data collection: A crystal of dimensions 0.60 x 0.40 x 0.30 mm mounted on a glass fibre was used for data collection at -20°C on a MAR diffractometer with a 300 mm image plate detector using graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å). Data collection was made with 3° oscillation step of φ, 300 seconds exposure time and scanner distance at 120 mm. 60 images were collected.

Data reduction: The images were interpreted and intensities integrated using program DENZO¹.

Structure solution: The structure was solved by direct methods employing SHELXS-97 program² on PC. Almost all atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using program SHELXL-97³ on PC.

Structure refinement: According to the SHELXL-97 program³, all 1648 independent reflections (R_{int}⁴ equal to 0.0495, 1193 reflections larger than 4σ(F_o)) from a total 4969 reflections were participated in the full-matrix least-square refinement against F². These reflections were in the range -10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -13 ≤ l ≤ 11 with 2θ_{max} equal to 51.12°.

One crystallographic asymmetric unit consists of one formula unit. In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically. H atoms are generated by program SHELXL-97. The positions of H atoms are calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final R-indices⁵.

Convergence ((Δ/σ)_{max} = 0.001, av. 0.001) for 127 variable parameters by full-matrix least-squares refinement on F² reaches to R₁ = 0.0565 and wR₂ = 0.165 with a goodness-of-fit of 1.167, the parameters a and b for weighting scheme are 0.0984 and 0.0109. The final difference Fourier map shows maximum rest peaks and holes of 0.435 and -0.200 eÅ⁻³ respectively.

Drawing: The ORTEP⁶ drawing of the molecule was made with thermal ellipsoids at the 30 % probability level. Screen drawing is provided for reference. The drawing with high quality can be provided upon request.

Tables: Table (1) of Crystallographic and refinement data, table (3) of full bond lengths and bond angles and this report are provided. The other supplementary materials, such as table of atomic coordinates with thermal parameters, table of anisotropic displacement parameters, table of hydrogen coordinates and/or other tables and/or CIF, RES-files, can be provided under request by notifying the identification code.

¹ Otwinowski, Z. and Minor, W., "Processing of X-ray Diffraction Data Collected in Oscillation Mode", Methods in Enzymology, Volume 276: Macromolecular Crystallography, part A, p. 307-326, 1997. Carter C. W., Sweet Jr. & R. M., Eds., Academic Press.

² SHELXS97, Sheldrick, G. M. (1997). SHELX97. Programs for Crystal Structure Analysis (Release 97-2). University of Goettingen, Germany.

³ SHELXL97, Sheldrick, G. M. (1997). SHELX97. Programs for Crystal Structure Analysis (Release 97-2). University of Goettingen, Germany.

⁴ $R_{int} = \sum |F_o^2 - F_o^2(\text{mean})| / \sum [F_o^2]$

⁵ Since the structure refinements are against F², R-indices based on F² are larger than (more than double) those based on F. For comparison with older refinements based on F and an OMIT threshold, a conventional index R₁ based on observed F values larger than 4σ(F_o) is also given (corresponding to Intensity ≥ 2σ(I)). $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$, $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. The Goodness of Fit is always based on F²: $\text{Goof} = S = \{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined. The weighting scheme is: $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, where P is $[2 F_c^2 + \text{Max}(F_o^2, 0)] / 3$.

⁶ ORTEP3 for Windows - Farrugia, L. J. (1997) J. Appl. Cryst. 30, 565.

Table 1. Crystal data and structure refinement for mar1512.

Identification code	mar1512	
Empirical formula	C ₁₂ H ₁₁ N O	
Formula weight	185.22	
Temperature	253(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /n	
Unit cell dimensions	a = 8.694(2) Å	= 90°.
	b = 10.418(2) Å	= 110.91(3)°.
	c = 11.275(2) Å	= 90°.
Volume	954.0(3) Å ³	
Z	4	
Density (calculated)	1.290 Mg/m ³	
Absorption coefficient	0.083 mm ⁻¹	
F(000)	392	
Crystal size	0.60 x 0.40 x 0.30 mm ³	
Theta range for data collection	2.75 to 25.56°.	
Index ranges	-10<=h<=10, -12<=k<=12, -13<=l<=11	
Reflections collected	4969	
Independent reflections	1648 [R(int) = 0.0495]	
Completeness to theta = 25.56°	92.0 %	
Absorption correction	None	
Max. and min. transmission	0.9756 and 0.9521	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1648 / 0 / 127	
Goodness-of-fit on F ²	1.167	
Final R indices [I>2sigma(I)]	R1 = 0.0565, wR2 = 0.1650	
R indices (all data)	R1 = 0.0747, wR2 = 0.1737	
Largest diff. peak and hole	0.435 and -0.200 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mar1512. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	1206(2)	312(2)	7383(1)	67(1)
N(1)	689(2)	-1585(2)	6284(2)	58(1)
C(1)	1491(2)	-471(2)	6674(2)	51(1)
C(2)	2753(3)	-411(2)	6067(2)	58(1)
C(3)	2374(3)	-1457(2)	5082(2)	62(1)
C(4)	1362(3)	-2387(2)	5498(2)	61(1)
C(5)	3936(3)	456(3)	6388(2)	85(1)
C(6)	-160(3)	-3087(2)	4623(2)	59(1)
C(7)	-1320(3)	-3039(2)	5355(2)	52(1)
C(8)	-818(3)	-2087(2)	6278(2)	52(1)
C(9)	-1703(3)	-1775(2)	7039(2)	64(1)
C(10)	-3138(3)	-2455(2)	6851(2)	67(1)
C(11)	-3637(3)	-3422(2)	5966(2)	69(1)
C(12)	-2741(3)	-3705(2)	5198(2)	67(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for mar1512.

O(1)-C(1)	1.228(3)
N(1)-C(1)	1.345(3)
N(1)-C(8)	1.408(3)
N(1)-C(4)	1.481(3)
C(1)-C(2)	1.487(3)
C(2)-C(5)	1.319(3)
C(2)-C(3)	1.506(3)
C(3)-C(4)	1.493(3)
C(4)-C(6)	1.524(3)
C(6)-C(7)	1.515(3)
C(7)-C(12)	1.372(3)
C(7)-C(8)	1.391(3)
C(8)-C(9)	1.380(3)
C(9)-C(10)	1.384(3)

C(10)-C(11)	1.374(4)
C(11)-C(12)	1.388(4)
C(1)-N(1)-C(8)	134.04(18)
C(1)-N(1)-C(4)	114.37(18)
C(8)-N(1)-C(4)	110.68(17)
O(1)-C(1)-N(1)	125.8(2)
O(1)-C(1)-C(2)	128.70(19)
N(1)-C(1)-C(2)	105.54(18)
C(5)-C(2)-C(1)	122.3(2)
C(5)-C(2)-C(3)	129.9(2)
C(1)-C(2)-C(3)	107.80(17)
C(4)-C(3)-C(2)	103.64(18)
N(1)-C(4)-C(3)	102.98(17)
N(1)-C(4)-C(6)	102.71(18)
C(3)-C(4)-C(6)	125.4(2)
C(7)-C(6)-C(4)	102.98(16)
C(12)-C(7)-C(8)	119.0(2)
C(12)-C(7)-C(6)	131.1(2)
C(8)-C(7)-C(6)	109.80(18)
C(9)-C(8)-C(7)	122.5(2)
C(9)-C(8)-N(1)	129.3(2)
C(7)-C(8)-N(1)	108.14(18)
C(8)-C(9)-C(10)	117.1(2)
C(11)-C(10)-C(9)	121.4(2)
C(10)-C(11)-C(12)	120.4(2)
C(7)-C(12)-C(11)	119.5(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mar1512. The anisotropic displacement factor exponent takes the form: $-2 \text{ }^2 [h^2 a^* U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	78(1)	64(1)	61(1)	-14(1)	28(1)	-10(1)
N(1)	59(1)	61(1)	63(1)	-11(1)	32(1)	-9(1)
C(1)	55(1)	51(1)	46(1)	-2(1)	15(1)	-3(1)
C(2)	54(1)	66(1)	52(1)	3(1)	17(1)	-8(1)
C(3)	54(1)	74(1)	64(1)	-6(1)	27(1)	-5(1)
C(4)	66(1)	57(1)	70(1)	-6(1)	35(1)	-1(1)
C(5)	88(2)	99(2)	75(2)	-14(1)	39(1)	-38(2)
C(6)	64(1)	53(1)	66(1)	-9(1)	29(1)	-5(1)
C(7)	54(1)	47(1)	54(1)	4(1)	18(1)	1(1)
C(8)	53(1)	53(1)	51(1)	3(1)	21(1)	-2(1)
C(9)	65(1)	74(1)	58(1)	-3(1)	30(1)	-3(1)
C(10)	59(1)	85(2)	64(1)	14(1)	32(1)	4(1)
C(11)	56(1)	71(1)	82(2)	11(1)	25(1)	-9(1)
C(12)	63(1)	60(1)	78(2)	-1(1)	25(1)	-9(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mar1512.

	x	y	z	U(eq)
H(3A)	1760	-1122	4243	75
H(3B)	3377	-1856	5070	75
H(4)	2105	-3024	6053	73
H(5A)	4001	1058	7013	102
H(5B)	4706	466	5989	102
H(6A)	-628	-2651	3813	71
H(6B)	97	-3965	4478	71
H(9)	-1350	-1135	7652	76
H(10)	-3778	-2254	7333	80
H(11)	-4582	-3889	5882	83
H(12)	-3101	-4342	4582	80

Figure 2. ORTEP representation of chiral compound (S)-**2f**

Crystal data: [C₁₈H₁₄ClNO]; formula weight = 295.75, Orthorhombic, P 2₁ 2₁ 2₁, a = 5.605(1) Å, b = 11.220(2) Å, c = 22.945(5) Å, V = 1443.0(5) Å³, Z = 4, D_c = 1.361 g cm⁻³, μ(Mo-Kα) = 0.262 mm⁻¹, F(000) = 616, T = 301 K.

Data collection: A cut crystal of dimensions 0.6 x 0.4 x 0.15 mm mounted in glass capillary was used for data collection at 28°C on a MAR diffractometer with a 300 mm image plate detector using graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å). Data collection was made with 3° oscillation step of φ, 300 seconds exposure time and scanner distance at 120 mm. 60 images were collected.

Data reduction: The images were interpreted and intensities integrated using program DENZOⁱ.

Structure solution: The structure was solved by direct methods employing SHELXS-97 programⁱⁱ on PC. Almost all atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using program SHELXL-97ⁱⁱⁱ on PC. The absolute structure was assisted by the Flack absolute structure parameter, which is equal to -0.01(8).

Structure refinement: According to the SHELXL-97 program, all 1980 independent reflections (R_{int}^{iv} equal to 0.0437, 1335 reflections larger than 4σ(F_o)) from a total 5421 reflections were participated in the full-matrix least-square refinement against F². These reflections were in the range -5 ≤ h ≤ 5, -12 ≤ k ≤ 13, -26 ≤ l ≤ 26 with 2θ_{max} equal to 50.66°.

One crystallographic asymmetric unit consists of one formula unit. In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically. H atoms are generated by program SHELXL-97. The positions of H atoms are calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final R-indices^v.

Convergence ((Δ/σ)_{max} = 0.001, av. 0.001) for 190 variable parameters by full-matrix least-squares refinement on F² reaches to R₁ = 0.0330 and wR₂ = 0.0699 with a goodness-of-fit of 0.845, the parameters a and b for weighting scheme are 0.0 and 0.0. The final difference Fourier map shows maximum rest peaks and holes of 0.113 and -0.160 eÅ⁻³, respectively.

Drawing: The ORTEP^{vi} drawing of the molecule was made with thermal ellipsoids at the 30 % probability level. Screen drawing is provided for reference. The drawing with high quality can be provided upon request.

Tables: Table (1) of Crystallographic and refinement data, table (3) of full bond lengths and bond angles and this report are provided. The other supplementary materials, such as table of atomic coordinates with thermal parameters, table of anisotropic displacement parameters, table of hydrogen coordinates and/or other tables and/or CIF, RES-files, can be provided under request by notifying the identification code.

Table 1. Crystal data and structure refinement for mar1620.

Identification code	mar1620	
Empirical formula	C ₁₈ H ₁₄ Cl N O	
Formula weight	295.75	
Temperature	301(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 5.605(1) Å	= 90°.
	b = 11.220(2) Å	= 90°.
	c = 22.945(5) Å	= 90°.
Volume	1443.0(5) Å ³	
Z	4	
Density (calculated)	1.361 Mg/m ³	
Absorption coefficient	0.262 mm ⁻¹	
F(000)	616	
Crystal size	0.6 x 0.4 x 0.15 mm ³	
Theta range for data collection	2.02 to 25.33°.	
Index ranges	-5<=h<=5, -12<=k<=13, -26<=l<=26	
Reflections collected	5421	
Independent reflections	1980 [R(int) = 0.0437]	
Completeness to theta = 25.33°	80.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1980 / 0 / 190	
Goodness-of-fit on F ²	0.845	
Final R indices [I>2sigma(I)]	R1 = 0.0330, wR2 = 0.0699	
R indices (all data)	R1 = 0.0545, wR2 = 0.0742	
Absolute structure parameter	-0.01(8)	
Largest diff. peak and hole	0.113 and -0.160 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mar1620. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Cl(1)	886(2)	4778(1)	416(1)	86(1)
O(1)	2885(3)	3980(2)	2381(1)	67(1)
N(1)	4183(4)	2606(2)	3051(1)	51(1)
C(1)	2680(5)	3010(3)	2626(1)	54(1)
C(2)	777(6)	2079(2)	2571(1)	52(1)
C(3)	942(5)	1287(2)	3104(1)	63(1)
C(4)	3521(5)	1440(2)	3307(1)	56(1)
C(5)	4082(6)	1601(2)	3956(1)	69(1)
C(6)	5856(5)	2615(2)	3958(1)	55(1)
C(7)	7354(6)	3002(3)	4387(1)	70(1)
C(8)	8821(6)	3979(3)	4273(2)	76(1)
C(9)	8749(6)	4545(3)	3741(2)	76(1)
C(10)	7230(6)	4165(3)	3303(1)	66(1)
C(11)	5802(6)	3187(2)	3416(1)	52(1)
C(12)	-914(6)	1922(2)	2168(1)	57(1)
C(13)	-1537(5)	2472(3)	1610(1)	55(1)
C(14)	-138(5)	3320(2)	1319(1)	56(1)
C(15)	-872(6)	3729(2)	780(1)	61(1)
C(16)	-2942(7)	3373(3)	515(1)	71(1)
C(17)	-4322(6)	2548(3)	805(1)	78(1)
C(18)	-3654(6)	2114(3)	1340(1)	70(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for mar1620.

Cl(1)-C(15)	1.747(3)
O(1)-C(1)	1.230(3)
N(1)-C(1)	1.367(3)
N(1)-C(11)	1.396(3)
N(1)-C(4)	1.481(3)
C(1)-C(2)	1.498(4)
C(2)-C(12)	1.335(4)
C(2)-C(3)	1.514(3)
C(3)-C(4)	1.529(4)
C(4)-C(5)	1.534(4)
C(5)-C(6)	1.511(4)
C(6)-C(7)	1.365(4)
C(6)-C(11)	1.399(3)
C(7)-C(8)	1.396(4)
C(8)-C(9)	1.377(4)
C(9)-C(10)	1.385(4)
C(10)-C(11)	1.383(4)
C(12)-C(13)	1.463(4)
C(13)-C(18)	1.398(4)
C(13)-C(14)	1.404(4)
C(14)-C(15)	1.381(4)
C(15)-C(16)	1.369(4)
C(16)-C(17)	1.378(4)
C(17)-C(18)	1.373(4)
C(1)-N(1)-C(11)	132.4(2)
C(1)-N(1)-C(4)	114.9(2)
C(11)-N(1)-C(4)	109.7(2)
O(1)-C(1)-N(1)	124.2(3)
O(1)-C(1)-C(2)	130.2(3)
N(1)-C(1)-C(2)	105.5(2)
C(12)-C(2)-C(1)	130.9(2)
C(12)-C(2)-C(3)	121.7(3)
C(1)-C(2)-C(3)	107.3(2)
C(2)-C(3)-C(4)	103.8(2)
N(1)-C(4)-C(3)	102.4(2)

N(1)-C(4)-C(5)	103.3(2)
C(3)-C(4)-C(5)	120.2(2)
C(6)-C(5)-C(4)	103.0(2)
C(7)-C(6)-C(11)	120.6(3)
C(7)-C(6)-C(5)	130.2(3)
C(11)-C(6)-C(5)	109.2(2)
C(6)-C(7)-C(8)	118.5(3)
C(9)-C(8)-C(7)	120.7(3)
C(8)-C(9)-C(10)	121.4(3)
C(11)-C(10)-C(9)	117.6(3)
C(10)-C(11)-N(1)	129.3(3)
C(10)-C(11)-C(6)	121.3(3)
N(1)-C(11)-C(6)	109.5(3)
C(2)-C(12)-C(13)	136.0(3)
C(18)-C(13)-C(14)	117.2(3)
C(18)-C(13)-C(12)	118.0(3)
C(14)-C(13)-C(12)	124.8(3)
C(15)-C(14)-C(13)	119.1(3)
C(16)-C(15)-C(14)	123.6(3)
C(16)-C(15)-Cl(1)	117.6(3)
C(14)-C(15)-Cl(1)	118.9(3)
C(15)-C(16)-C(17)	117.2(3)
C(18)-C(17)-C(16)	121.1(3)
C(17)-C(18)-C(13)	121.7(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mar1620. The anisotropic displacement factor exponent takes the form: $-2 \text{ [} h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12} \text{]}$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	95(1)	84(1)	80(1)	17(1)	-5(1)	1(1)
O(1)	80(2)	47(1)	75(1)	10(1)	-13(1)	-6(1)
N(1)	52(2)	46(1)	55(1)	6(1)	-3(1)	-2(2)
C(1)	60(2)	50(2)	52(2)	-4(2)	5(2)	2(2)
C(2)	55(2)	49(2)	53(2)	-2(1)	0(2)	1(2)
C(3)	63(2)	59(2)	66(2)	4(1)	3(2)	-8(2)
C(4)	62(2)	46(2)	59(2)	4(1)	4(2)	1(2)
C(5)	67(2)	78(2)	62(2)	17(2)	-5(2)	-5(2)
C(6)	53(2)	57(2)	55(2)	4(2)	2(2)	1(2)
C(7)	80(3)	71(2)	59(2)	2(2)	-2(2)	2(2)
C(8)	82(3)	72(2)	75(2)	-8(2)	-17(2)	-9(2)
C(9)	82(3)	63(2)	83(2)	5(2)	-10(2)	-17(2)
C(10)	73(2)	59(2)	66(2)	9(2)	-8(2)	-5(2)
C(11)	49(2)	51(2)	56(2)	1(1)	-1(2)	2(2)
C(12)	57(2)	53(2)	62(2)	-2(1)	3(2)	-3(2)
C(13)	49(2)	56(2)	61(2)	-12(2)	-4(2)	6(2)
C(14)	52(2)	55(2)	60(2)	-9(1)	-4(2)	6(2)
C(15)	61(2)	58(2)	63(2)	-6(2)	1(2)	10(2)
C(16)	68(2)	84(2)	60(2)	-9(2)	-9(2)	17(2)
C(17)	61(2)	99(2)	73(2)	-20(2)	-15(2)	4(3)
C(18)	57(2)	83(2)	71(2)	-11(2)	-1(2)	-3(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mar1620.

	x	y	z	U(eq)
H(3A)	613	463	3004	75
H(3B)	-169	1542	3403	75
H(4)	4523	808	3142	67
H(5A)	2658	1807	4174	83
H(5B)	4774	883	4120	83
H(7)	7396	2622	4747	84
H(8)	9859	4251	4560	92
H(9)	9740	5195	3674	91
H(10)	7172	4553	2945	79
H(12)	-1957	1310	2267	69
H(14)	1264	3603	1485	67
H(16)	-3397	3676	155	85
H(17)	-5731	2281	635	93
H(18)	-4637	1567	1528	84