Enantioselective Rhodium-Catalyzed [2 + 2 + 2] Cycloaddition of Alkenyl Isocyanates and Terminal Alkynes: Application to the Total Synthesis of (+)-Lasubine II.

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Supporting Information

General Methods. All reactions were carried out under an atmosphere of argon in flame-dried glassware with magnetic stirring. Toluene was degassed with argon and passed through one column of neutral alumina and one column of Q5 reactant. Triethylamine (peptide synthesis grade) was purchased from Fisher Scientific and used without further purification. Column chromatography was performed on EM Science silica gel 60 (230-400 mesh). Thin layer chromatography was performed on EM Science 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and KMnO₄ followed by heating.

Infrared spectra were obtained on a Nicolet Avatar 320 FT-IR spectrometer. ¹H NMR and spectra were recorded on a Varian 300 or 400 MHz spectrometers at ambient temperature. Data are reported as follows: chemical shift in parts per million (δ, ppm) from deuterated chloroform (CDCl₃) taken as 7.26 ppm (300 MHz) or 7.23 ppm (400 MHz), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, and coupling constant (Hz). ¹³C NMR and spectra were recorded on a Varian 300 or 400 MHz spectrometers at ambient temperature. Chemical shifts are reported in ppm from CDCl₃ taken as 77.0 ppm. Mass spectra were obtained on Fisons VG Autospec.

Alkynes **1a**, **1c** – **1g**, **1j**, **1l**, **1n** – **1s**, **1u**, and **1v** were all purchased from Aldrich Chemicals Co. and used without further purification. Alkyne **1b**,¹ isocyanates **2** and **5** were prepared according to the literature methods.² Alkyne **1t** was prepared by a typical TBS-protection of the corresponding alcohol, which was purchased from Aldrich Chemicals Co. Alkynes **1h**, **1k**, **1m** and ligands **L4** and **L5** are known compounds and can be synthesized by the procedure described within. Phosphorus trichloride and tris(4-methoxyphenyl) phosphine were purchased from Aldrich Chemicals Co. [Rh(ethylene)₂Cl]₂, PdCl₂(PPh₃)₂, ligands **L1** – **L3**, and trimethylsilylacetylene were purchased from Strem Chemical, Inc. and used without further purification. All racemates are obtained via the same cycloaddition using *rac*-**L3** as the ligand.

¹ Lawrence, N. J.; Ghani, F. A.; Hepworth, L. A.; Hadfield, J. A.; McGown, A. T.; Pritchard, R. G. *Synthesis* **1999**, 1656.

² Yu, R. T.; Rovis, T. *J. Am. Chem. Soc.* **2006**, 128, 2782.

General procedure for synthesis of terminal aryl alkynes (1h as the example):

5-ethynyl-1H-indole (1h). To a solution of 2.02 g of Boc-protected 5-iodoindole (5.886 mmol) and 0.84 ml of trimethylsilylacetylene (5.886 mmol) in 50 ml of Et₃N (ca. 0.12 M) at 0 °C was added 107 mg of PdCl₂(PPh₃)₂ (0.153 mmol) and 56 mg of CuI (0.294 mmol). The reaction mixture was stirred at ambient temperature for 12 h. The reaction mixture was then filtered and concentrated in vacuo. The resulting slurry was dissolved in 20 ml of MeOH (ca. 0.3 M), and treated with 1.62 g of K₂CO₃ (11.772 mmol). After stirring at ambient temperature for 2 h, the mixture was diluted with Et₂O, partitioned with H₂O, dried (MgSO₄), and concentrated in vacuo. The crude material was purified by flash column chromatography (1:10 EtOAc/Hexane) to give the free indole **1h** (400 mg, 48% overall yield): R_f = 0.13 (1:10 EtOAc/hex); ¹H NMR (400 MHz, CDCl₃) δ 8.20 (br s, 1H), 7.82 (s, 1H), 7.30 – 7.34 (m, 2H), 7.21 (dd, 1H, *J* = 2.6, 3.2 Hz), 6.52 (dd, 1H, *J* = 2.1, 3.0 Hz), 2.98 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 135.8, 127.8, 126.2, 125.5, 125.3, 113.4, 111.3, 103.1, 85.5, 74.8; IR (NaCl, CDCl₃) 3421, 3283, 1614, 1465, 1413, 1337, 1306 cm⁻¹; HRMS [C₁₀H₇N]⁺ calcd 141.0578. Found 141.0583 (FAB+).

tert-butyl 5-ethynyl-1H-indole-1-carboxylate (1i). To a solution of 270 mg of **1h** (1.91 mmol) and 7.0 mg of DMAP (0.057 mmol) in 2 ml of dry acetonitrile (ca. 0.96 M) was added 0.48 ml of (Boc)₂O (2.10 mmol) at ambient temperature. The reaction mixture was stirred at ambient temperature for 20 h. The reaction mixture was concentrated in vacuo, partitioned with EtOAc/H₂O, dried (MgSO₄), and concentrated in vacuo. The crude material was purified by flash column chromatography (1:10 EtOAc/Hexane) to give **1i** as a yellow oil (409 mg, 89% yield): R_f = 0.64 (1:10 EtOAc/hex); ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, 1H, *J* = 8.3 Hz), 7.69 (s, 1H), 7.58 (br s, 1H), 7.41 (d, 1H, *J* = 8.7 Hz), 6.51 (m, 1H), 3.03 (s, 1H), 1.66 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 149.7, 135.2, 130.6, 128.3, 127.1, 125.3, 116.3, 115.3, 107.2, 84.5, 84.3, 76.0, 28.4; IR (NaCl, CDCl₃) 3294, 2979, 1736, 1462, 1369, 1339, 1252, 1159, 1024 cm⁻¹; HRMS [C₁₅H₁₆NO₂]⁺ calcd 242.1181. Found 242.1183 (FAB+).

1-((3aR,8aR)-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-yl)piperidine (L4). To a flame-dried round bottom flask charged with a magnetic stir bar was added 4 Å molecular sieves, followed by 500 mg of (–)-TADDOL³ (1.072 mmol) and 4.6 ml of THF. To the reaction mixture was added 0.51 ml of Et₃N (3.644 mmol) and 0.112 ml of phosphorus trichloride (1.286 mmol) dropwise at 0 °C. The mixture was allowed to warm to ambient temperature and stirred for 40 minutes. A solution of piperidine (10.72 mmol) in 5.4 ml of THF was added slowly at 0 °C. The reaction was allowed to stir overnight at ambient temperature before it was diluted with

³ Seebach, D.; Beck, A. K.; Keckel, A. *Angew. Chem. Int. Ed.* **2001**, *40*, 92.

diethyl ether and filtered. The filtrate was concentrated in vacuo and the resulting crude material was purified by flash column chromatography (4:96 EtOAc/Hexane) to afford the desired phosphoramidite (400 mg, 65% yield): $R_f = 0.58$ (1:10 EtOAc/hex); ^1H NMR (300 MHz, CDCl_3) δ 7.78 (d, 2H, $J = 7.3$ Hz), 7.63 (d, 2H, $J = 7.0$ Hz), 7.48 (d, 2H, $J = 7.3$ Hz), 7.42 (d, 2H, $J = 7.3$ Hz), 7.14 – 7.36 (m, 12H), 5.16 (m, 1H), 4.76 (d, 1H, $J = 8.4$ Hz), 3.02 – 3.38 (m, 4H), 1.50 – 1.68 (m, 6H), 1.33 (s, 3H), 0.29 (s, 3H).

1-((3aR,8aR)-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-yl)pyrrolidine (L5). To a flame-dried round bottom flask charged with a magnetic stir bar was added 4 Å molecular sieves, followed by 1.20 g of (–)-TADDOL (2.572

mmol) and 11 ml of THF. To the reaction mixture was added 1.23 ml of Et_3N (8.745 mmol) and 0.27 ml of phosphorus trichloride (3.086 mmol) dropwise at 0 °C. The mixture was allowed to warm to ambient temperature and stirred for 40 minutes. A solution of piperidine (25.72 mmol) in 13 ml of THF was added slowly at 0 °C. The reaction was allowed to stir overnight at ambient temperature before it was diluted with diethyl ether and filtered. The filtrate was concentrated in vacuo and the resulting crude material was purified by flash column chromatography (4:96 EtOAc/Hexane) to afford the desired phosphoramidite (610 mg, 42% yield): $R_f = 0.50$ (1:10 EtOAc/hex); ^1H NMR (300 MHz, CDCl_3) δ 7.68 (d, 2H, $J = 7.0$ Hz), 7.54 (d, 2H, $J = 7.3$ Hz), 7.42 (d, 2H, $J = 7.3$ Hz), 7.35 (d, 2H, $J = 7.3$ Hz), 7.12 – 7.28 (m, 12H), 5.15 (dd, 1H, $J = 2.9, 8.4$ Hz), 4.76 (d, 1H, $J = 8.4$ Hz), 3.10 – 3.38 (m, 4H), 1.66 – 1.82 (m, 4H), 1.19 (s, 3H), 0.23 (s, 3H).

General procedure for the Rh-catalyzed [2+2+2] cycloaddition of alkenyl isocyanates and terminal alkynes: A flame-dried round bottom flask was charged with $[\text{Rh}(\text{ethylene})_2\text{Cl}]_2$ (0.05 eq) and the phosphoramidite ligand **L** (0.1 eq), and was fitted with a flame-dried reflux condenser in an inert atmosphere (N_2) glove box. Upon removal from the glove box, 1.0 ml toluene was added via syringe and the resulting yellow solution was stirred at ambient temperature under argon flow for 15 minutes. To this solution was added a solution of alkyne **1** (2.0 eq) and isocyanate **2** or **5** (0.270 mmol) in 2 ml of toluene via syringe or cannula. After an additional 1 ml of toluene to wash down the remaining residue, the resulting solution was heated to 110 °C in an oil bath, and maintained at reflux for *ca.* 16 h. The reaction mixture was cooled to ambient temperature, concentrated in vacuo, and purified by flash column chromatography (gradient elution typically 100% ethyl acetate). Evaporation of solvent afforded the analytically pure product.

(S)-7-phenyl-2,3,8,8a-tetrahydroindolizin-5(1H)-one (3a). According to the general procedure with ligand **L5**, alkyne **1a**, and isocyanate **2**. Upon purification 4.6 mg (8%) of the desired product was isolated: $R_f = 0.21$ (EtOAc); $[\alpha]_D^{20} = +166.9$ ($c = 0.16$, CHCl_3); HPLC analysis – Chiracel

AD-H column 90:10 hexane:iPrOH, 1.0 ml/min, Major: 24.4 minutes, Minor: 19.6 minutes, 254 nm detection light, *ee* = 89%; ^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.49 (m, 2H), 7.33 – 7.40 (m, 3H), 6.29 (d, 1H, $J = 2.8$ Hz), 3.81 (dddd, 1H, $J = 5.1, 5.1, 10.2, 14.9$ Hz), 3.67 (ddd, 1H, $J = 2.1, 9.0, 11.7$ Hz), 3.51 (ddd, 1H, $J = 7.7, 9.4, 11.5$ Hz), 2.90

(dd, 1H, $J = 4.7, 16.6$ Hz), 2.51 (ddd, 1H, $J = 2.8, 14.1, 16.6$ Hz), 2.27 (ddd, 1H, $J = 5.3, 5.3, 12.1$ Hz), 2.06 (m, 1H), 1.84 (dddd, 1H, $J = 6.6, 9.6, 9.6, 12.2, 12.2$ Hz), 1.70 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.2, 148.7, 138.1, 129.5, 129.0, 126.1, 121.0, 56.8, 44.2, 33.7, 33.4, 23.3; IR (NaCl, CH_2Cl_2) 1644, 1593, 1450, 1352, 1327 cm^{-1} ; HRMS $[\text{C}_{14}\text{H}_{16}\text{NO}]^+$ calcd 214.1232. Found 214.1233 (FAB+).

(R)-5-phenyl-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4a). According to the general procedure with ligand **L5**, alkyne **1a**, and isocyanate **2**. From the same reaction as above, upon purification 44 mg (79%) of the desired product was isolated: $R_f = 0.15$ (EtOAc); $[\alpha]_D^{20} = +640.0$ ($c = 1.0$, CHCl_3); HPLC analysis – Chiracel OD-H column 85:15 hexane:iPrOH, 0.3 ml/min, Major: 49.9 minutes, Minor: 48.9 minutes, 330 nm detection light, $ee = 94\%$; ^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.40 (m, 5H), 5.05 (s, 1H), 4.00 (dddd, 1H, $J = 7.2, 7.2, 7.2, 14.3$ Hz), 3.46 (ddd, 1H, $J = 4.5, 7.7, 11.5$ Hz), 3.23 (ddd, 1H, $J = 7.5, 7.5, 10.9$ Hz), 2.45 (dd, 1H, $J = 16.0, 16.0$ Hz), 2.40 (dd, 1H, $J = 6.7, 16.2$ Hz), 2.29 (m, 1H), 1.98 (m, 1H), 1.86 (m, 1H), 1.75 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.2, 163.1, 136.4, 130.0, 128.7, 127.8, 100.2, 59.1, 49.5, 41.7, 32.2, 24.7; IR (NaCl, CH_2Cl_2) 1624, 1532, 1460, 1332, 1260, 1235 cm^{-1} ; HRMS $[\text{C}_{14}\text{H}_{16}\text{NO}]^+$ calcd 214.1232. Found 214.1231 (FAB+).

(R)-5-(3,4-dimethoxyphenyl)-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4b). According to the general procedure with ligand **L5**, alkyne **1b**, and isocyanate **2**. Upon purification 53.2 mg (72%) of the desired product was isolated: $R_f = 0.05$ (EtOAc); $[\alpha]_D^{20} = +452.4$ ($c = 1.0$, CHCl_3); HPLC analysis – Chiracel AD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 24.2 minutes, Minor: 21.8 minutes, 330 nm detection light, $ee = 94\%$; ^1H NMR (400 MHz, CDCl_3) δ 6.96 (dd, 1H, $J = 1.7, 8.3$ Hz), 6.88 (br s, 1H), 6.85 (d, 1H, $J = 8.3$ Hz), 5.19 (s, 1H), 4.04 (dddd, 1H, $J = 7.0, 7.0, 7.0, 13.4$ Hz), 3.88 (s, 3H), 3.86 (s, 3H), 3.54 (ddd, 1H, $J = 6.6, 6.6, 11.7$ Hz), 3.27 (ddd, 1H, $J = 7.0, 7.0, 10.9$ Hz), 2.46 (dd, 1H, $J = 16.2, 16.2$ Hz), 2.38 (dd, 1H, $J = 5.8, 16.2$ Hz), 2.28 (dddd, 1H, $J = 6.4, 6.4, 6.4, 12.8$ Hz), 1.99 (m, 1H), 1.88 (m, 1H), 1.75 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.1, 163.1, 150.6, 149.0, 128.9, 121.0, 111.1, 110.9, 100.0, 58.9, 56.2, 56.2, 50.0, 41.6, 31.9, 24.9; IR (NaCl, CDCl_3) 1619, 1511, 1475, 1332, 1260, 1137, 922 cm^{-1} ; HRMS $[\text{C}_{16}\text{H}_{20}\text{NO}_3]^+$ calcd 274.1443. Found 274.1450 (FAB+).

(R)-5-(4-methoxyphenyl)-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4c). According to the general procedure with ligand **L5**, alkyne **1c**, and isocyanate **2**. Upon purification 45.8 mg (70%) of the desired product was isolated: $R_f = 0.05$ (EtOAc); $[\alpha]_D^{20} = +462.4$ ($c = 1.0$, CHCl_3); HPLC analysis – Chiracel OD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 10.6 minutes, Minor: 12.1 minutes, 210 nm detection light, $ee = 90\%$; ^1H NMR (400 MHz, CDCl_3) δ 7.31 (dm, 2H, $J = 8.7$ Hz), 6.88 (dm, 2H, $J = 8.9$ Hz), 5.06 (s, 1H), 4.02 (dddd, 1H, $J = 6.7, 6.7, 6.7, 13.5$ Hz), 3.80 (s, 3H), 3.53 (ddd, 1H, $J = 5.5, 7.3, 11.8$ Hz), 3.25 (ddd, 1H, $J = 7.0, 7.0, 10.7$ Hz), 2.44 (dd, 1H, $J = 16.2, 16.2$ Hz), 2.37 (dd, 1H, $J = 5.6, 16.2$ Hz), 2.27 (m, 1H), 1.97 (m, 1H), 1.86 (m, 1H), 1.74 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.1, 163.0, 161.1, 129.5, 128.8, 114.0, 100.0, 58.9, 55.6, 49.8, 41.7, 31.9, 24.8; IR

(NaCl, CDCl₃) 1624, 1603, 1511, 1465, 1245, 1173, 1030 cm⁻¹; HRMS [C₁₅H₁₈NO₂]⁺ calcd 244.1338. Found 244.1337 (FAB+).

(R)-5-(2-methoxyphenyl)-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4d).

According to the general procedure with ligand **L5**, alkyne **1d**, and isocyanate **2**. Upon purification 42 mg (64%) of the desired product was isolated: R_f = 0.11 (EtOAc); [α]_D²⁰ = +464.8 (c = 1.0, CHCl₃); HPLC analysis – Chiracel AD-H column 85:15 hexane:iPrOH, 1.0 ml/min, Major: 14.5 minutes, Minor: 13.9 minutes, 330 nm detection light, ee = 94%; ¹H NMR (400 MHz, CDCl₃) δ 7.36 (ddd, 1H, J = 1.5, 8.5, 8.5 Hz), 7.18 (m, 1H), 6.96 (dd, 1H, J = 7.5, 7.5 Hz), 6.90 (d, 1H, J = 8.3 Hz), 4.95 (s, 1H), 3.95 (m, 1H), 3.81 (s, 3H), 3.10 – 3.35 (m, 2H), 2.39 – 2.48 (m, 2H), 2.28 (dddd, 1H, J = 2.8, 6.4, 6.4, 8.7 Hz), 1.96 (m, 1H), 1.68 – 1.88 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 191.8, 160.8, 155.9, 131.2, 129.5, 125.4, 121.0, 111.2, 99.4, 59.2, 55.9, 48.1, 41.7, 32.8, 24.2; IR (NaCl, CDCl₃) 1619, 1527, 1475, 1332, 1240, 1132, 1015 cm⁻¹; HRMS [C₁₅H₁₈NO₂]⁺ calcd 244.1338. Found 244.1336 (FAB+).

(R)-5-(4-(dimethylamino)phenyl)-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4e).

According to the general procedure with ligand **L3**, alkyne **1e**, and isocyanate **2**. Upon purification 52.5 mg (78%) of the desired product was isolated: R_f = 0.05 (EtOAc); [α]_D²⁰ = +70.3 (c = 1.0, CHCl₃); HPLC analysis – Chiracel OD-H column 85:15 hexane:iPrOH, 1.0 ml/min, Major: 21.2 minutes, Minor: 24.4 minutes, 330 nm detection light, ee = 87%; ¹H NMR (400 MHz, CDCl₃) δ 7.28 (d, 2H, J = 9.0 Hz), 6.65 (d, 2H, J = 9.0 Hz), 5.11 (s, 1H), 4.04 (dddd, 1H, J = 6.4, 6.4, 6.4, 12.4 Hz), 3.60 (ddd, 1H, J = 6.6, 6.6, 10.9 Hz), 3.31 (ddd, 1H, J = 6.6, 6.6, 11.1 Hz), 2.98 (s, 6H), 2.45 (dd, 1H, J = 16.0, 16.0 Hz), 2.34 (dd, 1H, J = 4.9, 16.0 Hz), 2.25 (dddd, 1H, J = 6.8, 6.8, 6.8, 13.4 Hz), 1.96 (m, 1H), 1.86 (m, 1H), 1.73 (dddd, 1H, J = 6.9, 6.9, 6.9, 13.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 191.9, 163.8, 151.7, 129.5, 123.4, 111.5, 99.3, 58.7, 50.3, 41.7, 40.4, 31.6, 25.0; IR (NaCl, CDCl₃) 1603, 1557, 1496, 1358, 1240, 1189, 1132 cm⁻¹; HRMS [C₁₆H₂₁N₂O]⁺ calcd 257.1654. Found 257.1643 (FAB+).

(R)-5-m-tolyl-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4f).

According to the general procedure with ligand **L5**, alkyne **1f**, and isocyanate **2**. Upon purification 36.1 mg (59%) of the desired product was isolated: R_f = 0.14 (EtOAc); [α]_D²⁰ = +609.2 (c = 1.0, CHCl₃); HPLC analysis – Chiracel AD-H column 95:5 hexane:iPrOH, 1.0 ml/min, Major: 22.1 minutes, Minor: 21.9 minutes, 330 nm detection light, ee = 94%; ¹H NMR (400 MHz, CDCl₃) δ 7.26 (dd, 1H, J = 7.5, 7.5 Hz), 7.20 (d, 1H, J = 7.6 Hz), 7.17 (s, 1H), 7.14 (d, 1H, J = 7.5 Hz), 5.04 (s, 1H), 3.99 (dddd, 1H, J = 7.5, 7.5, 7.5, 14.7 Hz), 3.47 (ddd, 1H, J = 4.5, 7.7, 11.5 Hz), 3.23 (ddd, 1H, J = 7.5, 7.5, 10.9 Hz), 2.44 (dd, 1H, J = 16.2, 16.2 Hz), 2.39 (dd, 1H, J = 7.0, 16.2 Hz), 2.28 (dddd, 1H, J = 4.1, 6.4, 6.4, 10.9 Hz), 1.98 (m, 1H), 1.86 (m, 1H), 1.74 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 192.1, 163.3, 138.5, 136.4, 130.7, 128.6, 128.4, 124.8, 100.1, 59.1, 49.5, 41.6, 32.2, 24.7, 21.6; IR (NaCl, CDCl₃) 1624, 1527, 1470, 1337, 1260, 1235, 1127 cm⁻¹; HRMS [C₁₅H₁₈NO]⁺ calcd 228.1388. Found 228.1384 (FAB+).

From the same reaction mixture, 4 mg (6%) of **3f** was also isolated but not fully characterized due to its small quantity.

(R)-5-(thiophen-3-yl)-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4g).

According to the general procedure with ligand **L3**, alkyne **1g**, and isocyanate **2**. Upon purification 34.2 mg (58%) of the desired product was isolated: $R_f = 0.10$ (EtOAc); $[\alpha]_D^{20} = +455.0$ ($c = 1.0$, CHCl_3); HPLC analysis – Chiracel AD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 10.6 minutes, Minor: 10.1 minutes, 330 nm detection light, $ee = 86\%$; ^1H NMR (400 MHz, CDCl_3) δ 7.47 (dd, 1H, $J = 1.1, 3.0$ Hz), 7.33 (dd, 1H, $J = 3.0, 5.1$ Hz), 7.13 (dd, 1H, $J = 1.3, 5.1$ Hz), 5.15 (s, 1H), 3.99 (dddd, 1H, $J = 7.5, 7.5, 7.5, 14.5$ Hz), 3.59 (ddd, 1H, $J = 5.1, 7.7, 11.1$ Hz), 3.39 (ddd, 1H, $J = 7.2, 7.2, 10.9$ Hz), 2.43 (dd, 1H, $J = 16.2, 16.2$ Hz), 2.39 (dd, 1H, $J = 7.0, 16.2$ Hz), 2.28 (dddd, 1H, $J = 6.6, 6.6, 6.6, 11.9$ Hz), 2.02 (m, 1H), 1.89 (m, 1H), 1.75 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.2, 157.6, 137.1, 127.3, 126.5, 126.5, 99.8, 59.1, 49.8, 41.6, 31.9, 24.8; IR (NaCl, CDCl_3) 1619, 1521, 1470, 1332, 1265, 1240, 1127 cm^{-1} ; HRMS $[\text{C}_{12}\text{H}_{14}\text{NOS}]^+$ calcd 220.0796. Found 220.0797 (FAB+).

From the same reaction mixture, 3.8 mg (6%) of **3g** was also isolated but not fully characterized due to its small quantity.

(R)-5-(1H-indol-5-yl)-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4h).

According to the general procedure with ligand **L5**, alkyne **1h**, and isocyanate **2**. Upon purification 44.3 mg (65%) of the desired product was isolated: $R_f = 0.05$ (EtOAc); $[\alpha]_D^{20} = +290.2$ ($c = 1.0$, CHCl_3); HPLC analysis – Chiracel AD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 12.9 minutes, Minor: 15.5 minutes, 254 nm detection light, $ee = 90\%$; ^1H NMR (400 MHz, CDCl_3) δ 8.91 (br s, 1H), 7.67 (s, 1H), 7.40 (d, 1H, $J = 8.3$ Hz), 7.26 (dd, 1H, $J = 2.7, 2.7$ Hz), 7.16 (d, 1H, $J = 8.3$ Hz), 6.55 (m, 1H), 5.19 (s, 1H), 4.08 (dddd, 1H, $J = 6.8, 6.8, 6.8, 13.0$ Hz), 3.61 (ddd, 1H, $J = 6.4, 6.4, 11.7$ Hz), 3.29 (ddd, 1H, $J = 7.0, 7.0, 11.1$ Hz), 2.51 (dd, 1H, $J = 16.0, 16.0$ Hz), 2.42 (dd, 1H, $J = 5.5, 16.2$ Hz), 2.30 (dddd, 1H, $J = 6.2, 6.2, 6.2, 12.2$ Hz), 1.97 (m, 1H), 1.88 (m, 1H), 1.76 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.7, 165.3, 136.8, 127.8, 127.7, 125.9, 121.8, 120.8, 111.4, 103.2, 100.1, 59.0, 50.1, 41.5, 31.9, 24.8; IR (NaCl, CDCl_3) 1598, 1506, 1455, 1334, 1271, 1237, 1128 cm^{-1} ; HRMS $[\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}]^+$ calcd 253.1341. Found 253.1344 (FAB+).

(R)-tert-butyl 5-(7-oxo-1,2,3,7,8,8a-hexahydroindolizin-5-yl)-1H-indole-1-carboxylate (4i).

According to the general procedure with ligand **L5**, alkyne **1i**, and isocyanate **2**. Upon purification 80.6 mg (85%) of the desired product was isolated: $R_f = 0.12$ (EtOAc); $[\alpha]_D^{20} = +320.4$ ($c = 1.0$, CHCl_3); HPLC analysis – Chiracel OD-H column 90:10 hexane:iPrOH, 1.0 ml/min, Major: 24.9 minutes, Minor: 22.4 minutes, 230 nm detection light, $ee = 91\%$; ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, 1H, $J = 8.3$ Hz), 7.62 (d, 1H, $J = 3.6$ Hz), 7.58 (s, 1H), 7.30 (d, 1H, $J = 8.5$ Hz), 6.55 (d, 1H, $J = 3.6$), 5.15 (s, 1H), 4.05 (dddd, 1H, $J = 6.8, 6.8, 6.8, 13.9$ Hz), 3.54 (ddd, 1H, $J = 5.1, 7.5, 11.7$ Hz), 3.25 (ddd, 1H, $J = 7.3, 7.3, 11.1$ Hz), 2.48 (dd, 1H, $J = 16.0, 16.0$ Hz), 2.42 (dd, 1H, $J = 6.1, 16.2$ Hz), 2.30 (dddd, 1H, $J = 6.4, 6.4, 6.4, 11.5$ Hz), 1.99 (m, 1H), 1.88 (m, 1H), 1.77 (m, 1H), 1.65 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.0, 163.8, 149.7, 136.0, 130.9,

130.6, 127.3, 124.0, 120.7, 115.3, 107.5, 100.4, 84.4, 59.1, 49.7, 41.7, 32.1, 28.3, 24.8; IR (NaCl, CDCl₃) 1736, 1615, 1524, 1449, 1369, 1329, 1271, 1151, 1025 cm⁻¹; HRMS [C₂₁H₂₅N₂O₃]⁺ calcd 353.1865. Found 353.1852 (FAB+).

(S)-7-(4-bromophenyl)-2,3,8,8a-tetrahydroindolizin-5(1H)-one (3j).

According to the general procedure with ligand **L5**, alkyne **1j**, and isocyanate **2**. Upon purification 13.5 mg (17%) of the desired product was isolated: $R_f = 0.19$ (EtOAc); $[\alpha]_D^{20} = +102.0$ ($c = 1.0$, CHCl₃); HPLC analysis – Chiracel AD-H column 90:10 hexane:iPrOH, 1.0 ml/min, Major: 23.6 minutes, Minor: 25.0 minutes, 254 nm detection light, $ee = 90\%$; ¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, 2H, $J = 8.7$ Hz), 7.33 (d, 2H, $J = 8.7$ Hz), 6.27 (d, 1H, $J = 2.6$ Hz), 3.80 (dddd, 1H, $J = 5.1, 5.1, 10.2, 14.9$ Hz), 3.67 (m, 1H), 3.50 (m, 1H), 2.84 (dd, 1H, $J = 4.7, 16.4$ Hz), 2.50 (ddd, 1H, $J = 2.6, 14.1, 16.6$ Hz), 2.27 (ddd, 1H, $J = 5.8, 5.8, 11.9$ Hz), 2.06 (m, 1H), 1.84 (m, 1H), 1.71 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 147.6, 136.9, 132.1, 127.6, 123.7, 121.4, 56.7, 44.2, 33.7, 33.3, 23.2; IR (NaCl, CDCl₃) 1650, 1539, 1486, 1445, 1347, 1004, 835, 815 cm⁻¹; HRMS [C₁₄H₁₅NOBr]⁺ calcd 292.0337. Found 292.0333 (FAB+). X-ray data of this compound is attached at the end of this manuscript.

(R)-5-(4-bromophenyl)-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4j).

According to the general procedure with ligand **L5**, alkyne **1j**, and isocyanate **2**. From the same reaction as above, upon purification 43.4 mg (55%) of the desired product was isolated: $R_f = 0.13$ (EtOAc); $[\alpha]_D^{20} = +469.0$ ($c = 1.0$, CHCl₃); HPLC analysis – Chiracel OJ-H column 90:10 hexane:iPrOH, 1.0 ml/min, Major: 21.3 minutes, Minor: 19.7 minutes, 254 nm detection light, $ee = 89\%$; ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, 2H, $J = 8.3$ Hz), 7.24 (d, 2H, $J = 8.3$ Hz), 5.01 (s, 1H), 4.00 (dddd, 1H, $J = 7.9, 7.9, 7.9, 15.3$ Hz), 3.44 (ddd, 1H, $J = 4.5, 7.3, 11.3$ Hz), 3.22 (ddd, 1H, $J = 7.7, 7.7, 10.7$ Hz), 2.44 (dd, 1H, $J = 16.2, 16.2$ Hz), 2.42 (dd, 1H, $J = 7.8, 16.2$ Hz), 2.29 (m, 1H), 1.99 (m, 1H), 1.87 (m, 1H), 1.75 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 192.2, 161.8, 135.3, 132.0, 129.4, 124.4, 100.4, 59.2, 49.5, 41.6, 32.1, 24.7; IR (NaCl, CDCl₃) 1619, 1568, 1527, 1465, 1260, 1235, 1127, 1004 cm⁻¹; HRMS [C₁₄H₁₅NOBr]⁺ calcd 292.0337. Found 292.0330 (FAB+). X-ray of this compound is attached at the end of this manuscript.

(S)-7-(4-chlorophenyl)-2,3,8,8a-tetrahydroindolizin-5(1H)-one (3k).

According to the general procedure with ligand **L5**, alkyne **1k**, and isocyanate **2**. Upon purification 9.4 mg (14%) of the desired product was isolated: $R_f = 0.13$ (EtOAc); $[\alpha]_D^{20} = +93.5$ ($c = 0.52$, CHCl₃); HPLC analysis – Chiracel OD-H column 90:10 hexane:iPrOH, 1.0 ml/min, Major: 19.5 minutes, Minor: 18.1 minutes, 254 nm detection light, $ee = 93\%$; ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, 2H, $J = 8.5$ Hz), 7.34 (d, 2H, $J = 8.5$ Hz), 6.27 (d, 1H, $J = 2.8$ Hz), 3.81 (dddd, 1H, $J = 5.1, 5.1, 10.2, 14.7$ Hz), 3.67 (ddd, 1H, $J = 2.1, 9.2, 11.7$ Hz), 3.50 (ddd, 1H, $J = 7.7, 9.6, 11.5$ Hz), 2.85 (dd, 1H, $J = 4.7, 16.4$ Hz), 2.50 (ddd, 1H, $J = 2.6, 13.9, 16.4$ Hz), 2.27 (ddd, 1H, $J = 5.0, 5.0, 11.3$ Hz), 2.06 (m, 1H), 1.84 (m, 1H), 1.71 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 147.5, 136.5, 135.5, 129.2, 127.3, 121.3, 56.7,

44.2, 33.7, 33.3, 23.2; IR (NaCl, CDCl₃) 1650, 1598, 1489, 1443, 1345, 1087, 829 cm⁻¹; HRMS [C₁₄H₁₅NOCl]⁺ calcd 248.0842. Found 248.0853 (FAB+).

(R)-5-(4-chlorophenyl)-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4k).

According to the general procedure with ligand **L5**, alkyne **1k**, and isocyanate **2**. From the same reaction as above, upon purification 34.1 mg (51%) of the desired product was isolated: R_f = 0.08 (EtOAc); [α]_D²⁰ = +383.9 (c = 1.0, CHCl₃); HPLC analysis – Chiracel OJ-H column 95:5 hexane:iPrOH, 1.0 ml/min, Major: 23.3 minutes, Minor: 22.3 minutes, 330 nm detection light, ee = 90%; ¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, 2H, J = 8.3 Hz), 7.31 (d, 2H, J = 8.3 Hz), 5.03 (s, 1H), 4.01 (dddd, 1H, J = 7.9, 7.9, 7.9, 15.1 Hz), 3.45 (ddd, 1H, J = 4.5, 7.5, 11.7 Hz), 3.23 (ddd, 1H, J = 7.7, 7.7, 10.9 Hz), 2.45 (dd, 1H, J = 16.2, 16.2 Hz), 2.42 (dd, 1H, J = 8.0, 16.2 Hz), 2.29 (m, 1H), 1.99 (m, 1H), 1.88 (m, 1H), 1.76 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 192.2, 161.8, 136.1, 134.8, 129.2, 129.1, 100.4, 59.2, 49.5, 41.6, 32.1, 24.7; IR (NaCl, CDCl₃) 1624, 1572, 1527, 1470, 1265, 1240, 1086, 1004 cm⁻¹; HRMS [C₁₄H₁₅NOCl]⁺ calcd 248.0842. Found 248.0843 (FAB+).

(S)-7-(3-fluorophenyl)-2,3,8,8a-tetrahydroindolizin-5(1H)-one (3l).

According to the general procedure with ligand **L5**, alkyne **1l**, and isocyanate **2**. Upon purification 15.5 mg (25%) of the desired product was isolated: R_f = 0.21 (EtOAc); [α]_D²⁰ = +88.3 (c = 1.0, CHCl₃); HPLC analysis – Chiracel AD-H column 90:10 hexane:iPrOH, 1.0 ml/min, Major: 17.1 minutes, Minor: 12.9 minutes, 254 nm detection light, ee = 94%; ¹H NMR (400 MHz, CDCl₃) δ 7.33 (ddd, 1H, J = 6.0, 8.1, 8.1 Hz), 7.25 (m, 1H), 7.15 (ddd, 1H, J = 2.1, 2.1, 10.2 Hz), 7.04 (m, 1H), 6.29 (d, 1H, J = 2.8 Hz), 3.81 (dddd, 1H, J = 5.1, 5.1, 10.2, 14.9 Hz), 3.67 (ddd, 1H, J = 1.7, 8.7, 11.5 Hz), 3.50 (ddd, 1H, J = 7.7, 9.4, 11.9 Hz), 2.85 (dd, 1H, J = 4.7, 16.6 Hz), 2.51 (ddd, 1H, J = 2.8, 14.1, 16.6 Hz), 2.27 (ddd, 1H, J = 5.5, 5.5, 11.9 Hz), 2.07 (m, 1H), 1.84 (m, 1H), 1.70 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 164.4, 163.8, 161.9, 147.4, 130.5, 130.4, 121.9, 121.7, 116.4, 116.2, 113.1, 112.9, 56.7, 44.2, 33.7, 33.4, 23.2; IR (NaCl, CDCl₃) 1650, 1598, 1434, 1327, 1265, 1173, 1158, 876 cm⁻¹; HRMS [C₁₄H₁₅NOF]⁺ calcd 232.1138. Found 232.1141 (FAB+).

(R)-5-(3-fluorophenyl)-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4l).

According to the general procedure with ligand **L5**, alkyne **1l**, and isocyanate **2**. From the same reaction as above, upon purification 27.0 mg (43%) of the desired product was isolated: R_f = 0.15 (EtOAc); [α]_D²⁰ = +366.7 (c = 1.0, CHCl₃); HPLC analysis – Chiracel OJ-H column 97:3 hexane:iPrOH, 1.0 ml/min, Major: 25.6 minutes, Minor: 24.8 minutes, 330 nm detection light, ee = 94%; ¹H NMR (400 MHz, CDCl₃) δ 7.36 (ddd, 1H, J = 5.8, 7.9, 7.9 Hz), 7.05 – 7.16 (m, 3H), 5.05 (s, 1H), 4.00 (dddd, 1H, J = 8.8, 8.1, 8.1, 12.2 Hz), 3.45 (ddd, 1H, J = 4.5, 7.7, 11.3 Hz), 3.24 (ddd, 1H, J = 7.5, 7.5, 10.7 Hz), 2.46 (dd, 1H, J = 16.2, 16.2 Hz), 2.42 (dd, 1H, J = 7.5, 16.2 Hz), 2.30 (dddd, 1H, J = 4.1, 6.4, 6.4, 10.9 Hz), 2.01 (m, 1H), 1.88 (m, 1H), 1.75 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 192.2, 163.9, 161.6, 161.4, 138.4, 130.6, 130.5, 123.5, 117.1, 116.9, 115.1, 114.9, 100.4, 59.2, 49.5, 41.6, 32.2, 24.7; IR (NaCl, CDCl₃) 1629, 1527, 1470, 1260, 1239, 1122, 933 cm⁻¹; HRMS [C₁₄H₁₅NOF]⁺ calcd 232.1138. Found 232.1139 (FAB+).

(S)-7-(4-acetylphenyl)-2,3,8,8a-tetrahydroindolizin-5(1H)-one (3m). According to the general procedure with ligand **L5**, alkyne **1m**, and isocyanate **2**. Upon purification 17.8 mg (26%) of the desired product was isolated: $R_f = 0.07$ (EtOAc); $[\alpha]_D^{20} = +82.6$ ($c = 1.0$, CHCl_3); HPLC analysis – Chiracel AD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 23.0 minutes, Minor: 21.1 minutes, 254 nm detection light, $ee = 94\%$; ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, 2H, $J = 8.3$ Hz), 7.55 (d, 2H, $J = 8.3$ Hz), 6.36 (d, 1H, $J = 2.8$ Hz), 3.83 (dddd, 1H, $J = 5.1, 5.1, 10.0, 14.7$ Hz), 3.68 (ddd, 1H, $J = 2.3, 9.4, 11.7$ Hz), 3.51 (ddd, 1H, $J = 8.1, 9.6, 11.8$ Hz), 2.90 (dd, 1H, $J = 4.7, 16.6$ Hz), 2.59 (s, 3H), 2.57 (m, 1H), 2.29 (m, 1H), 2.07 (m, 1H), 1.84 (m, 1H), 1.72 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.6, 163.6, 147.5, 142.6, 137.5, 129.0, 126.2, 122.8, 56.7, 44.2, 33.7, 33.3, 26.9, 23.2; IR (NaCl, CDCl_3) 1672, 1649, 1598, 1445, 1360, 1269, 843 cm^{-1} ; HRMS $[\text{C}_{16}\text{H}_{18}\text{NO}_2]^+$ calcd 256.1338. Found 256.1327 (FAB+).

(R)-5-(4-acetylphenyl)-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4m). According to the general procedure with ligand **L5**, alkyne **1m**, and isocyanate **2**. From the same reaction as above, upon purification 26.8 mg (39%) of the desired product was isolated: $R_f = 0.04$ (EtOAc); $[\alpha]_D^{20} = +347.3$ ($c = 1.0$, CHCl_3); HPLC analysis – Chiracel OD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 21.3 minutes, Minor: 23.1 minutes, 254 nm detection light, $ca. ee = 81\%$; ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, 2H, $J = 8.3$ Hz), 7.46 (d, 2H, $J = 8.1$ Hz), 5.02 (s, 1H), 4.01 (m, 1H), 3.42 (ddd, 1H, $J = 4.3, 7.7, 11.3$ Hz), 3.23 (ddd, 1H, $J = 7.7, 7.7, 10.9$ Hz), 2.60 (s, 3H), 2.42 – 2.51 (m, 2H), 2.31 (m, 1H), 2.01 (m, 1H), 1.88 (m, 1H), 1.77 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.5, 192.1, 161.7, 140.7, 138.1, 128.7, 128.1, 100.6, 59.3, 49.4, 41.5, 32.2, 26.9, 24.7; IR (NaCl, CDCl_3) 1683, 1621, 1530, 1507, 1468, 1257, 1127 cm^{-1} ; HRMS $[\text{C}_{16}\text{H}_{18}\text{NO}_2]^+$ calcd 256.1338. Found 256.1336 (FAB+).

(S)-7-(4-(trifluoromethyl)phenyl)-2,3,8,8a-tetrahydroindolizin-5(1H)-one (3n). According to the general procedure with ligand **L5**, alkyne **1n**, and isocyanate **2**. Upon purification 27.2 mg (36%) of the desired product was isolated: $R_f = 0.20$ (EtOAc); $[\alpha]_D^{20} = +104.5$ ($c = 1.0$, CHCl_3); HPLC analysis – Chiracel OD-H column 90:10 hexane:iPrOH, 1.0 ml/min, Major: 17.0 minutes, Minor: 15.8 minutes, 254 nm detection light, $ee = 94\%$; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, 2H, $J = 8.3$ Hz), 7.56 (d, 2H, $J = 8.5$ Hz), 6.34 (d, 1H, $J = 2.6$ Hz), 3.83 (dddd, 1H, $J = 5.1, 5.1, 10.2, 14.7$ Hz), 3.69 (ddd, 1H, $J = 2.1, 9.2, 11.7$ Hz), 3.52 (ddd, 1H, $J = 7.7, 9.6, 11.7$ Hz), 2.88 (dd, 1H, $J = 4.7, 16.4$ Hz), 2.55 (ddd, 1H, $J = 2.6, 14.1, 16.6$ Hz), 2.29 (m, 1H), 2.08 (m, 1H), 1.85 (m, 1H), 1.73 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.6, 147.3, 141.6, 126.4, 125.9, 125.9, 122.8, 56.7, 44.2, 33.7, 33.4, 23.2; IR (NaCl, CDCl_3) 1654, 1601, 1450, 1410, 1328, 1152, 1124, 1071, 849 cm^{-1} ; HRMS $[\text{C}_{15}\text{H}_{15}\text{NOF}_3]^+$ calcd 282.1106. Found 282.1094 (FAB+).

(R)-5-(4-(trifluoromethyl)phenyl)-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4n). According to the general procedure with ligand **L5**, alkyne **1n**, and isocyanate **2**. From the same reaction as above, upon purification 10.6 mg

(14%) of the desired product was isolated: $R_f = 0.14$ (EtOAc); $[\alpha]_D^{20} = +318.9$ ($c = 1.0$, CHCl_3); ee is not determined since the racemate synthesis of **4n** has failed; ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, 2H, $J = 8.1$ Hz), 7.49 (d, 2H, $J = 8.1$ Hz), 5.08 (s, 1H), 4.02 (dddd, 1H, $J = 9.2, 9.2, 9.2, 9.2$ Hz), 3.42 (ddd, 1H, $J = 4.1, 7.9, 11.3$ Hz), 3.23 (ddd, 1H, $J = 7.5, 7.5, 10.4$ Hz), 2.42 – 2.52 (m, 2H), 2.32 (m, 1H), 2.02 (m, 1H), 1.89 (m, 1H), 1.78 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.0, 161.5, 150.8, 139.8, 128.2, 125.8, 100.6, 59.3, 49.4, 41.4, 32.2, 24.7; IR (NaCl, CDCl_3) 1625, 1538, 1514, 1461, 1322, 1164, 1124, 1065 cm^{-1} ; HRMS $[\text{C}_{15}\text{H}_{15}\text{NOF}_3]^+$ calcd 282.1106. Found 282.1115 (FAB+).

(R)-5-cyclohexenyl-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4o).

According to the general procedure with ligand **L5**, alkyne **1o**, and isocyanate **2**. Upon purification 56.3 mg (96%) of the desired product was isolated: $R_f = 0.12$ (EtOAc); $[\alpha]_D^{20} = +477.5$ ($c = 1.0$, CHCl_3); HPLC analysis – Chiracel AD-H column 85:15 hexane:iPrOH, 1.0 ml/min, Major: 10.9 minutes, Minor: 10.3 minutes, 330 nm detection light, $ee = 92\%$; ^1H NMR (400 MHz, CDCl_3) δ 5.83 (m, 1H), 4.88 (s, 1H), 3.80 (m, 1H), 3.46 (ddd, 1H, $J = 4.5, 8.1, 11.3$ Hz), 3.34 (ddd, 1H, $J = 7.7, 7.7, 10.9$ Hz), 2.27 – 2.35 (m, 2H), 2.21 (dddd, 1H, $J = 4.1, 6.6, 6.6, 12.6$ Hz), 2.05 – 2.11 (m, 4H), 2.00 (m, 1H), 1.84 (m, 1H), 1.54 – 1.72 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.4, 165.5, 134.7, 129.7, 97.8, 58.9, 48.6, 41.5, 32.1, 27.4, 25.2, 24.6, 22.5, 21.9; IR (NaCl, CDCl_3) 1621, 1512, 1466, 1329, 1260, 1231, 1122, 922 cm^{-1} ; HRMS $[\text{C}_{14}\text{H}_{20}\text{NO}]^+$ calcd 218.1545. Found 218.1541 (FAB+).

(S)-7-hexyl-2,3,8,8a-tetrahydroindolizin-5(1H)-one (3p).

According to the general procedure with ligand **L4**, alkyne **1p**, and isocyanate **2**. Upon purification 38.3 mg (64%) of the desired product was isolated: $R_f = 0.39$ (5% MeOH/ CH_2Cl_2); $[\alpha]_D^{20} = +95.3$ ($c = 1.0$, CHCl_3); HPLC analysis – Chiracel OD-H column 97:3 hexane:iPrOH, 1.0 ml/min, Major: 20.2 minutes, Minor: 21.9 minutes, 230 nm detection light, $ee = 80\%$; ^1H NMR (400 MHz, CDCl_3) δ 5.68 (m, 1H), 3.62 (dddd, 1H, $J = 5.1, 5.1, 10.2, 15.1$ Hz), 3.58 (ddd, 1H, $J = 2.1, 9.4, 11.7$ Hz), 3.42 (ddd, 1H, $J = 7.9, 9.8, 11.7$ Hz), 2.27 (dd, 1H, $J = 4.9, 16.6$ Hz), 2.06 – 2.19 (m, 4H), 1.98 (m, 1H), 1.75 (dddd, 1H, $J = 6.6, 9.6, 9.6, 12.2, 12.2$ Hz), 1.56 (m, 1H), 1.38 – 1.46 (m, 2H), 1.21 – 1.31 (m, 6H), 0.84 (t, 3H, $J = 6.7$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 164.4, 153.6, 120.4, 56.7, 44.0, 36.7, 34.8, 33.7, 31.8, 29.0, 26.9, 23.2, 22.7, 14.3; IR (NaCl, CH_2Cl_2) 1660, 1609, 1445, 1342, 1265 cm^{-1} ; HRMS $[\text{C}_{14}\text{H}_{24}\text{NO}]^+$ calcd 222.1858. Found 222.1853 (FAB+).

From the same reaction mixture, the minor product **4p** (8.5 mg, 14%) was also isolated, and its characterization data is available upon request.

(S)-methyl 5-(5-oxo-1,2,3,5,8,8a-hexahydroindolizin-7-yl)pentanoate (3q).

According to the general procedure with ligand **L4**, alkyne **1q**, and isocyanate **2**. Upon purification 37.8 mg (56%) of the desired product was isolated: $R_f = 0.12$ (EtOAc); $[\alpha]_D^{20} = +71.6$ ($c = 1.0$, CHCl_3); HPLC analysis – Chiracel AD-H column 90:10 hexane:iPrOH, 1.0 ml/min, Major: 16.3 minutes, Minor: 14.4 minutes, 254 nm detection light, $ee = 80\%$; ^1H NMR (400 MHz, CDCl_3) δ 5.70 (m, 1H), 3.64 (dddd, 1H, $J = 5.3, 5.3, 10.4, 15.3$ Hz),

3.63 (s, 3H), 3.58 (ddd, 1H, $J = 2.3, 9.4, 11.7$ Hz), 3.41 (ddd, 1H, $J = 7.9, 9.8, 11.7$ Hz), 2.29 (t, 2H, $J = 7.3$ Hz), 2.26 (dd, 1H, $J = 4.9, 16.6$ Hz), 2.06 – 2.20 (m, 4H), 1.98 (m, 1H), 1.76 (dddd, 1H, $J = 6.6, 9.4, 9.4, 12.2, 12.2$ Hz), 1.53 – 1.64 (m, 3H), 1.43 – 1.52 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.0, 164.2, 152.9, 120.6, 56.6, 51.8, 44.0, 36.3, 34.7, 33.9, 33.6, 26.3, 24.6, 23.2; IR (NaCl, CDCl_3) 1734, 1661, 1615, 1439, 1354, 1326, 1195, 1161, 866 cm^{-1} ; HRMS $[\text{C}_{14}\text{H}_{22}\text{NO}_3]^+$ calcd 252.1600. Found 252.1588 (FAB+).

From the same reaction mixture, the minor product **4q** (6.0 mg, 9%) was also isolated but not fully characterized due to its small quantity.

(S)-7-phenethyl-2,3,8,8a-tetrahydroindolizin-5(1H)-one (3r).

According to the general procedure with ligand **L4**, alkyne **1r**, and isocyanate **2**. Upon purification 32.6 mg (50%) of the desired product was isolated: $R_f = 0.38$ (5% MeOH/ CH_2Cl_2); $[\alpha]_D^{20} = +101.9$ ($c = 1.0$, CHCl_3); HPLC analysis – Chiracel AD-H column 90:10 hexane:iPrOH, 1.0 ml/min, Major: 15.0 minutes, Minor: 13.7 minutes, 210 nm detection light, $ee = 84\%$; ^1H NMR (400 MHz, CDCl_3) δ 7.27 (d, 1H, $J = 7.0$ Hz), 7.25 (d, 1H, $J = 7.7$ Hz), 7.13 – 7.19 (m, 3H), 5.74 (m, 1H), 3.63 (dddd, 1H, $J = 5.3, 5.3, 10.4, 15.4$ Hz), 3.59 (m, 1H), 3.42 (ddd, 1H, $J = 7.9, 9.8, 11.7$ Hz), 2.77 (dd, 1H, $J = 7.2, 7.2$ Hz), 2.77 (dd, 1H, $J = 8.5, 8.5$ Hz), 2.46 (dd, 1H, $J = 8.5, 8.5$ Hz), 2.46 (dd, 1H, $J = 7.4, 7.4$ Hz), 2.28 (dd, 1H, $J = 4.9, 16.6$ Hz), 2.08 – 2.20 (m, 2H), 1.99 (m, 1H), 1.76 (dddd, 1H, $J = 6.6, 9.6, 9.6, 12.2, 12.2$ Hz), 1.57 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.2, 152.5, 141.0, 128.7, 128.5, 126.4, 120.9, 56.6, 44.0, 38.4, 35.0, 33.6, 33.5, 23.2; IR (NaCl, CDCl_3) 1655, 1609, 1445, 1347, 1327, 1240, 856 cm^{-1} ; HRMS $[\text{C}_{16}\text{H}_{20}\text{NO}]^+$ calcd 245.1545. Found 245.1547 (FAB+).

(S)-7-benzyl-2,3,8,8a-tetrahydroindolizin-5(1H)-one (3s).

According to the general procedure with ligand **L4**, alkyne **1s**, and isocyanate **2**. Upon purification 28.6 mg (47%) of the desired product was isolated: $R_f = 0.13$ (EtOAc); $[\alpha]_D^{20} = +81.5$ ($c = 1.0$, CHCl_3); HPLC analysis – Chiracel AD-H column 95:5 hexane:iPrOH, 1.0 ml/min, Major: 30.3 minutes, Minor: 29.2 minutes, 210 nm detection light, $ee = 84\%$; ^1H NMR (400 MHz, CDCl_3) δ 7.12 – 7.32 (m, 5H), 5.75 (m, 1H), 3.55 – 3.66 (m, 2H), 3.37 – 3.50 (m, 3H), 2.25 (dd, 1H, $J = 4.9, 16.6$ Hz), 2.02 – 2.15 (m, 2H), 1.97 (m, 1H), 1.74 (dddd, 1H, $J = 6.8, 9.6, 9.6, 12.2, 12.2$ Hz), 1.52 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.1, 152.0, 137.4, 129.3, 128.9, 127.0, 122.1, 56.8, 44.0, 43.2, 34.2, 33.6, 23.2; IR (NaCl, CH_2Cl_2) 1664, 1605, 1445, 1347, 1320 cm^{-1} ; HRMS $[\text{C}_{15}\text{H}_{18}\text{NO}]^+$ calcd 228.1388. Found 228.1383 (FAB+).

(S)-7-(2-(tert-butyldimethylsilyloxy)ethyl)-2,3,8,8a-tetrahydroindolizin-5(1H)-one (3t).

According to the general procedure with ligand **L4**, alkyne **1t**, and isocyanate **2**. Upon purification 51.9 mg (65%) of the desired product was isolated: $R_f = 0.13$ (EtOAc); $[\alpha]_D^{20} = +75.4$ ($c = 1.0$, CHCl_3); HPLC analysis – Chiracel AD-H column 99:1 hexane:iPrOH, 1.0 ml/min, Major: 18.2 minutes, Minor: 16.1 minutes, 210 nm detection light, $ee = 87\%$; ^1H NMR (400 MHz, CDCl_3) δ 5.71 (m, 1H), 3.72 (t, 2H, $J = 6.6$ Hz), 3.64 (dddd, 1H, $J = 5.3, 5.3, 10.4, 15.1$ Hz), 3.59 (ddd, 1H, $J = 2.1, 9.2, 11.5$ Hz), 3.42 (ddd, 1H, $J = 7.7, 9.8, 11.7$ Hz), 2.38 (dd, 1H, $J = 4.7, 16.6$ Hz), 2.32 – 2.36 (m, 2H),

2.08 – 2.19 (m, 2H), 1.98 (m, 1H), 1.76 (dddd, 1H, $J = 6.6, 9.4, 9.4, 11.9, 11.9$ Hz), 1.56 (m, 1H), 0.84 (s, 9H), 0.01 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.1, 151.0, 121.9, 61.6, 56.6, 44.0, 39.8, 35.2, 33.6, 26.1, 23.2, 18.4, -5.2; IR (NaCl, CDCl_3) 1660, 1598, 1455, 1352, 1327, 1245, 1091, 1050, 835 cm^{-1} ; HRMS $[\text{C}_{16}\text{H}_{30}\text{NO}_2\text{Si}]^+$ calcd 296.2046. Found 296.2057 (FAB+).

(S)-7-(methoxymethyl)-2,3,8,8a-tetrahydroindolizin-5(1H)-one (3u).

According to the general procedure with ligand **L4**, alkyne **1u**, and isocyanate **2** (seal tube). Upon purification 22.6 mg (46%) of the desired product was isolated: $R_f = 0.07$ (EtOAc); $[\alpha]_D^{20} = +66.9$ ($c = 1.0$, CHCl_3); HPLC analysis – Chiracel OD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 9.1 minutes, Minor: 10.2 minutes, 210 nm detection light, $ee = 77\%$; ^1H NMR (400 MHz, CDCl_3) δ 5.91 (m, 1H), 3.98 (d, 1H, $J = 13.9$ Hz), 3.92 (d, 1H, $J = 13.9$ Hz), 3.67 (dddd, 1H, $J = 5.1, 5.1, 10.4, 15.1$ Hz), 3.61 (ddd, 1H, $J = 2.1, 9.2, 11.5$ Hz), 3.44 (m, 1H), 3.31 (s, 3H), 2.42 (dd, 1H, $J = 4.7, 16.6$ Hz), 2.19 (ddd, 1H, $J = 6.2, 6.2, 11.7$ Hz), 1.96 – 2.11 (m, 2H), 1.77 (dddd, 1H, $J = 6.8, 9.8, 9.8, 12.4, 12.4$ Hz), 1.60 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.7, 148.9, 121.4, 74.0, 58.6, 56.7, 44.1, 33.6, 31.5, 23.2; IR (NaCl, CDCl_3) 1667, 1610, 1449, 1340, 1191, 1105 cm^{-1} ; HRMS $[\text{C}_{10}\text{H}_{16}\text{NO}_2]^+$ calcd 182.1181. Found 182.1181 (FAB+).

(S)-7-cyclohexyl-2,3,8,8a-tetrahydroindolizin-5(1H)-one (3v).

According to the general procedure with ligand **L3**, alkyne **1v**, and isocyanate **2**. Upon purification 26.2 mg (44%) of the desired product was isolated: $R_f = 0.17$ (EtOAc); $[\alpha]_D^{20} = +68.9$ ($c = 1.0$, CHCl_3); HPLC analysis – Chiracel AD-H column 95:5 hexane:iPrOH, 1.0 ml/min, Major: 39.3 minutes, Minor: 29.3 minutes, 210 nm detection light, $ee = 76\%$; ^1H NMR (400 MHz, CDCl_3) δ 5.67 (m, 1H), 3.54 – 3.64 (m, 2H), 3.42 (ddd, 1H, $J = 7.7, 9.6, 11.7$ Hz), 2.32 (dd, 1H, $J = 4.7, 16.4$ Hz), 2.16 (ddd, 1H, $J = 5.5, 5.5, 11.9$ Hz), 2.09 (ddd, 1H, $J = 2.6, 14.5, 16.6$ Hz), 1.93 – 2.02 (m, 2H), 1.63 – 1.81 (m, 6H), 1.57 (m, 1H), 1.07 – 1.31 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.7, 158.2, 118.6, 56.8, 44.8, 44.0, 33.7, 33.5, 31.3, 30.9, 26.5, 26.4, 26.3, 23.2; IR (NaCl, CH_2Cl_2) 1655, 1603, 1445, 1332, 1163, 851 cm^{-1} ; HRMS $[\text{C}_{14}\text{H}_{22}\text{NO}]^+$ calcd 220.1701. Found 220.1712 (FAB+).

(R)-5-cyclohexyl-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4v).

From the same reaction as above, upon purification 22.4 mg (38%) of the desired product was isolated: $R_f = 0.07$ (EtOAc); $[\alpha]_D^{20} = +432.3$ ($c = 1.0$, CHCl_3); HPLC analysis – Chiracel AD-H column 90:10 hexane:iPrOH, 1.0 ml/min, Major: 16.5 minutes, Minor: 15.7 minutes, 330 nm detection light, $ee = 95\%$; ^1H NMR (400 MHz, CDCl_3) δ 4.96 (s, 1H), 3.68 (dddd, 1H, $J = 5.3, 5.3, 10.4, 15.8$ Hz), 3.59 (m, 1H), 3.42 (m, 1H), 2.35 (dd, 1H, $J = 4.7, 15.8$ Hz), 2.13 – 2.27 (m, 3H), 2.07 (m, 1H), 1.58 – 1.91 (m, 7H), 1.14 – 1.32 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.3, 169.0, 94.9, 59.4, 46.5, 41.9, 41.5, 32.6, 31.4, 31.3, 26.6, 26.4, 26.0, 24.0; IR (NaCl, CDCl_3) 1624, 1537, 1481, 1342, 1260, 1245, 1128 cm^{-1} ; HRMS $[\text{C}_{14}\text{H}_{22}\text{NO}]^+$ calcd 220.1701. Found 220.1699 (FAB+).

(R)-4-(4-methoxyphenyl)-7,8,9,9a-tetrahydro-1H-quinolizin-2(6H)-one (6c). According to the general procedure with ligand **L5**, alkyne **1c**, and isocyanate **5**. Upon purification 31.3 mg (45%) of the desired product was isolated: $R_f = 0.22$ (EtOAc); $[\alpha]_D^{20} = +52$ ($c = 1.0$, CHCl_3); HPLC analysis – Chiracel AD-H column 90:10 hexane:iPrOH, 1.0 ml/min, Major: 13.3 minutes, Minor: 15.8 minutes, 330 nm detection light, $ee = 98\%$; ^1H NMR (400 MHz, CDCl_3) δ 7.19 (br d, 2H, $J = 8.7$ Hz), 6.89 (br d, 2H, $J = 8.5$ Hz), 5.02 (s, 1H), 3.80 (s, 3H), 3.60 (m, 1H), 3.44 (dddd, 1H, $J = 6.0, 6.0, 11.3, 11.3$ Hz), 2.57 (dd, 1H, $J = 5.8, 16.4$ Hz), 2.56 (m, 1H), 2.40 (dd, 1H, $J = 11.3, 16.4$ Hz), 1.83 (m, 1H), 1.69 – 1.75 (m, 2H), 1.38 – 1.56 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.8, 166.1, 160.3, 129.2, 128.7, 114.2, 103.6, 58.8, 55.5, 50.6, 42.8, 31.6, 26.2, 24.1; IR (NaCl, CDCl_3) 1639, 1603, 1547, 1511, 1434, 1245, 1178, 1132 cm^{-1} ; HRMS $[\text{C}_{16}\text{H}_{20}\text{NO}_2]^+$ calcd 258.1494. Found 258.1484 (FAB+).

(R)-4-(3,4-dimethoxyphenyl)-7,8,9,9a-tetrahydro-1H-quinolizin-2(6H)-one (6b). According to the general procedure with ligand **L5**, alkyne **1b**, and isocyanate **5**. Upon purification 47.9 mg (62%) of the desired product was isolated: $R_f = 0.15$ (EtOAc); $[\alpha]_D^{20} = +54.5$ ($c = 1.0$, CHCl_3); HPLC analysis – Chiracel AD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 20.6 minutes, Minor: 22.4 minutes, 330 nm detection light, $ee = 98\%$; ^1H NMR (400 MHz, CDCl_3) δ 6.85 (d, 1H, $J = 8.1$ Hz), 6.82 (dd, 1H, $J = 1.7, 8.1$ Hz), 6.76 (d, 1H, $J = 1.7$ Hz), 5.07 (s, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.63 (m, 1H), 3.44 (dddd, 1H, $J = 6.0, 6.0, 11.3, 11.3$ Hz), 2.58 (m, 1H), 2.57 (dd, 1H, $J = 5.8, 16.2$ Hz), 2.40 (dd, 1H, $J = 11.1, 16.2$ Hz), 1.84 (m, 1H), 1.69 – 1.76 (m, 2H), 1.38 – 1.58 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.8, 166.1, 149.7, 149.1, 129.4, 119.9, 111.2, 110.4, 103.5, 58.9, 56.2, 56.1, 50.7, 42.7, 31.6, 26.2, 24.1; IR (NaCl, CDCl_3) 1634, 1547, 1511, 1440, 1342, 1250, 1137, 1025 cm^{-1} ; HRMS $[\text{C}_{17}\text{H}_{22}\text{NO}_3]^+$ calcd 288.1600. Found 288.1591 (FAB+).

4,6-bis(3,4-dimethoxyphenyl)-1-(hex-5-enyl)pyridin-2(1H)-one (7b). From the same reaction as above, the pyridone side product (*ca.* 27 mg, 22%) was isolated and characterized: $R_f = 0.41$ (EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 7.16 (dd, 1H, $J = 2.1, 8.5$ Hz), 7.08 (d, 1H, $J = 2.1$ Hz), 6.92 – 6.94 (m, 2H), 6.88 (d, 1H, $J = 8.5$ Hz), 6.85 (s, 1H), 6.74 (d, 1H, $J = 2.1$ Hz), 6.30 (d, 1H, $J = 2.1$ Hz), 5.66 (dddd, 1H, $J = 6.6, 6.6, 10.5, 16.8$ Hz), 4.84 – 4.92 (m, 2H), 3.93 (s, 3H), 3.89 (s, 3H), 3.89 (s, 3H), 3.88 (s, 3H), 1.90 (q, 2H, $J = 7.0$ Hz), 1.60 (m, 2H), 1.23 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.7, 150.4, 150.0, 149.8, 149.5, 149.4, 148.9, 138.5, 130.3, 128.5, 121.5, 119.7, 114.9, 114.8, 111.9, 111.4, 111.0, 109.8, 107.6, 56.3, 56.2, 45.8, 33.4, 28.7, 26.2; IR (NaCl, CDCl_3) 1650, 1603, 1583, 1506, 1455, 1265, 1137, 1025 cm^{-1} ; HRMS $[\text{C}_{27}\text{H}_{32}\text{NO}_5]^+$ calcd 450.2280. Found 450.2276 (FAB+).

Hydrogenation of 6b (8). A mixture of **6b** (66 mg, 0.23 mmol) and 34 mg of 10% Pd/C in 9 ml of MeOH was stirred at ambient temperature under hydrogen atmosphere (1 atm) for 30 hours. The reaction mixture was filtered through celite and concentrated in vacuo. Upon purification by column chromatography 53.5 mg (80%) of the desired product **8** was

isolated: $R_f = 0.07$ (EtOAc); $[\alpha]_D^{20} = +53.8$ ($c = 1.0$, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 6.60 – 7.10 (m, 3H), 3.91 (s, 3H), 3.87 (s, 3H), 3.75 (m, 1H), 2.93 (br d, 1H, $J = 10.8$ Hz), 2.70 (br d, 1H, $J = 10.9$ Hz), 1.88 – 2.08 (m, 3H), 1.33 – 1.80 (m, 9H), 1.26 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.2, 122.4, 110.8, 68.6, 68.5, 56.2, 56.1, 53.2, 45.4, 43.0, 33.8, 26.3, 24.8; IR (NaCl, CDCl_3) 2934, 1592, 1506, 1455, 1363, 1260, 1225, 1128, 1025, 910, 727 cm^{-1} ; HRMS $[\text{C}_{17}\text{H}_{26}\text{NO}_3]^+$ calcd 292.1913. Found 292.1914 (FAB+). Spectral properties were in agreement with literature values reported for the opposite enantiomer.⁴

(+)-Lasubine II. According to the literature procedure,⁴ a Mitsunobu reaction on **8** (42.0 mg, 0.144 mmol) provided 27.0 mg (64%) of the desired product: $R_f = 0.24$ (8:1 EtOAc/MeOH); $[\alpha]_D^{20} = +43.4$ ($c = 1.0$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 6.74 – 6.91 (m, 3H), 4.12 (br s, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 3.29 (br d, 1H, $J = 10.2$ Hz), 2.66 (br d, 1H, $J = 10.6$ Hz), 2.36 (m, 1H), 1.20 – 1.92 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.1, 148.0, 137.4, 119.9, 111.0, 107.0, 65.3, 63.6, 56.7, 56.2, 56.0, 53.4, 43.0, 40.5, 33.8, 26.3, 25.1; IR (NaCl, CDCl_3) 2930, 1588, 1516, 1460, 1414, 1260, 1132, 1025 cm^{-1} ; HRMS $[\text{C}_{17}\text{H}_{26}\text{NO}_3]^+$ calcd 292.1913. Found 292.1916 (FAB+). Spectral properties were in agreement with literature values reported for the (–)-lasubine II.⁵

^1H NMR and ^{13}C NMR spectra of new compounds are attached:

X-ray data of **3j** and **4j** are attached following the spectra

⁴ Ma, D.; Zhu, W. *Org. Lett.* **2001**, *3*, 3927.

⁵ Back, T. G.; Hamilton, M. D. *Org. Lett.* **2002**, *4*, 1779.

3a

STANDARD 1H OBSERVE

yu2-209-1
yu2-209-1

¹³C OBSERVE

yu2-209-1

4a

STANDARD 1H OBSERVE

yu2-209-2

13C OBSERVE

yu2-209-2

4b

STANDARD 1H OBSERVE

yu2-280

13C OBSERVE

yu2-280

4c

STANDARD 1H OBSERVE

yu2-252

13C OBSERVE

yu2-252

4d

STANDARD 1H OBSERVE

yu2-281

13C OBSERVE

yu2-281

4e

STANDARD 1H OBSERVE

yu2-273

13C OBSERVE

yu2-273

4f

STANDARD 1H OBSERVE

yu2-258-2

13C OBSERVE

yu2-258-2

4g

STANDARD 1H OBSERVE

yu2-260-2

13C OBSERVE

yu2-260-2

4h

STANDARD 1H OBSERVE

yu2-288

13C OBSERVE

yu2-288

4i

STANDARD 1H OBSERVE

yu2-291

13C OBSERVE

yu2-291

3j

STANDARD 1H OBSERVE

yu2-305-1

13C OBSERVE

yu2-305-1

4j
STANDARD 1H OBSERVE
yu2-305-2

¹³C OBSERVE
yu2-305-2

3k

STANDARD 1H OBSERVE

yu2-298-1

13C OBSERVE

yu2-298-1

4k
STANDARD 1H OBSERVE
yu2-253-2

13C OBSERVE
yu2-253-2

31

STANDARD 1H OBSERVE

yu2-257-1

¹³C OBSERVE

yu2-257-1

41

STANDARD 1H OBSERVE

yu2-257-2

13C OBSERVE

yu2-257-2

3m

STANDARD 1H OBSERVE

yu2-274-1

13C OBSERVE

yu2-274-1

4m

STANDARD 1H OBSERVE

yu2-274-2

13C OBSERVE

yu2-274-2

3n

STANDARD 1H OBSERVE

yu2-276-1

¹³C OBSERVE

yu2-276-1

4n

STANDARD 1H OBSERVE

yu2-276-2

13C OBSERVE

yu2-276-2

4o

STANDARD 1H OBSERVE

yu2-303
yu2-303

13C OBSERVE

yu2-303

3p

STANDARD 1H OBSERVE

yu2-208-1

13C OBSERVE

yu2-208-1

3q

STANDARD 1H OBSERVE

yu2-255

13C OBSERVE

yu2-255-1

3r

STANDARD 1H OBSERVE

yu2-215-1

¹³C OBSERVE

yu2-215-1

3s

STANDARD 1H OBSERVE

yu2-212-1

13C OBSERVE

yu2-212-1

3t

STANDARD 1H OBSERVE

yu2-214-1

13C OBSERVE

yu2-214-1

3u

STANDARD 1H OBSERVE

yu2-290

13C OBSERVE

yu2-290

3v

STANDARD 1H OBSERVE

yu2-211-1

13C OBSERVE

yu2-211-1

4v
STANDARD 1H OBSERVE
yu2-211-2

13C OBSERVE
yu2-211-2

6c

STANDARD 1H OBSERVE

yu2-261-2

13C OBSERVE

yu2-261-2

yu2-261-2

6b

STANDARD 1H OBSERVE

yu2-279-2

13C OBSERVE

yu2-279-2

7

STANDARD 1H OBSERVE

yu2-297-1

13C OBSERVE

yu2-297-1

8

STANDARD 1H OBSERVE

yu2-301

13C OBSERVE

yu2-301c

yu2-301

Table 1. Crystal data and structure refinement for **3j**.

Identification code	rovis22a	
Empirical formula	C ₁₄ H ₁₄ Br N O	
Formula weight	292.17	
Temperature	373(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 12.2073(5) Å	α = 90°.
	b = 7.8184(4) Å	β = 91.258(3)°.
	c = 12.9408(6) Å	γ = 90°.
Volume	1234.79(10) Å ³	
Z	4	
Density (calculated)	1.572 Mg/m ³	
Absorption coefficient	3.311 mm ⁻¹	
F(000)	592	
Crystal size	0.17 x 0.15 x 0.11 mm ³	
Theta range for data collection	1.57 to 35.41°.	
Index ranges	-19 ≤ h ≤ 19, -12 ≤ k ≤ 12, -21 ≤ l ≤ 19	
Reflections collected	50738	
Independent reflections	10905 [R(int) = 0.0466]	
Completeness to theta = 35.41°	99.1 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.7183 and 0.6062	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10905 / 1 / 308	
Goodness-of-fit on F ²	0.940	
Final R indices [I > 2σ(I)]	R1 = 0.0350, wR2 = 0.0719	
R indices (all data)	R1 = 0.0722, wR2 = 0.0811	
Absolute structure parameter	0.005(5)	
Largest diff. peak and hole	0.415 and -0.553 e.Å ⁻³	

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

	x	y	z	$U(\text{eq})$
Br(1A)	11295(1)	11742(1)	7916(1)	37(1)
N(1A)	17817(1)	11759(3)	11237(1)	23(1)
O(1A)	16938(1)	11933(3)	12752(1)	34(1)
C(1A)	17819(1)	11803(3)	10101(1)	22(1)
C(2A)	18879(1)	10840(3)	9887(2)	33(1)
C(3A)	19650(1)	11386(4)	10774(2)	36(1)
C(4A)	18903(1)	11572(3)	11703(2)	27(1)
C(5A)	16909(1)	11934(3)	11800(1)	24(1)
C(6A)	15870(1)	12096(2)	11199(1)	24(1)
C(7A)	15775(1)	11685(3)	10195(1)	18(1)
C(8A)	16776(1)	11087(3)	9635(1)	22(1)
C(9A)	14701(1)	11718(3)	9646(1)	19(1)
C(10A)	13749(1)	11235(2)	10149(2)	22(1)
C(11A)	12736(1)	11285(3)	9643(2)	26(1)
C(12A)	12675(1)	11793(3)	8623(2)	24(1)
C(13A)	13601(1)	12305(3)	8101(2)	27(1)
C(14A)	14611(1)	12256(2)	8618(2)	23(1)
Br(1)	8590(1)	9294(1)	7116(1)	34(1)
N(1)	2124(1)	9645(2)	3705(1)	24(1)
O(1)	3018(1)	9083(2)	2230(1)	31(1)
C(1)	2117(1)	10323(3)	4764(1)	24(1)
C(2)	996(1)	9774(3)	5120(2)	33(1)
C(3)	271(1)	9885(3)	4142(2)	31(1)
C(4)	1027(1)	9390(4)	3257(2)	29(1)
C(5)	3044(1)	9482(3)	3159(1)	24(1)
C(6)	4082(1)	9704(3)	3743(1)	24(1)
C(7)	4145(1)	9776(2)	4780(1)	20(1)
C(8)	3100(1)	9726(3)	5387(1)	25(1)
C(9)	5207(1)	9747(2)	5349(1)	20(1)
C(10)	6185(1)	10219(3)	4874(2)	25(1)
C(11)	7181(1)	10117(3)	5396(2)	27(1)

C(12)	7213(1)	9537(3)	6408(2)	25(1)
C(13)	6265(1)	9090(3)	6908(2)	26(1)
C(14)	5267(1)	9199(3)	6381(1)	24(1)

Table 3. Bond lengths [Å] and angles [°] for **3j**.

Br(1A)-C(12A)	1.9006(17)
N(1A)-C(5A)	1.346(2)
N(1A)-C(4A)	1.452(2)
N(1A)-C(1A)	1.471(2)
O(1A)-C(5A)	1.231(2)
C(1A)-C(8A)	1.505(2)
C(1A)-C(2A)	1.528(3)
C(2A)-C(3A)	1.529(3)
C(3A)-C(4A)	1.532(2)
C(5A)-C(6A)	1.480(2)
C(6A)-C(7A)	1.340(2)
C(7A)-C(9A)	1.477(2)
C(7A)-C(8A)	1.509(2)
C(9A)-C(10A)	1.396(2)
C(9A)-C(14A)	1.397(3)
C(10A)-C(11A)	1.387(2)
C(11A)-C(12A)	1.379(3)
C(12A)-C(13A)	1.388(3)
C(13A)-C(14A)	1.391(2)
Br(1)-C(12)	1.9053(17)
N(1)-C(5)	1.347(2)
N(1)-C(4)	1.461(2)
N(1)-C(1)	1.468(2)
O(1)-C(5)	1.242(2)
C(1)-C(8)	1.506(2)
C(1)-C(2)	1.515(2)
C(2)-C(3)	1.532(3)
C(3)-C(4)	1.536(3)
C(5)-C(6)	1.471(2)
C(6)-C(7)	1.344(3)
C(7)-C(9)	1.477(2)
C(7)-C(8)	1.512(2)
C(9)-C(14)	1.403(3)
C(9)-C(10)	1.404(2)

C(10)-C(11)	1.380(3)
C(11)-C(12)	1.386(3)
C(12)-C(13)	1.383(2)
C(13)-C(14)	1.385(2)
C(5A)-N(1A)-C(4A)	122.76(15)
C(5A)-N(1A)-C(1A)	123.94(14)
C(4A)-N(1A)-C(1A)	113.27(13)
N(1A)-C(1A)-C(8A)	111.81(14)
N(1A)-C(1A)-C(2A)	100.96(14)
C(8A)-C(1A)-C(2A)	117.18(17)
C(1A)-C(2A)-C(3A)	103.68(17)
C(2A)-C(3A)-C(4A)	104.38(14)
N(1A)-C(4A)-C(3A)	103.80(15)
O(1A)-C(5A)-N(1A)	122.35(16)
O(1A)-C(5A)-C(6A)	122.15(15)
N(1A)-C(5A)-C(6A)	115.50(16)
C(7A)-C(6A)-C(5A)	122.98(15)
C(6A)-C(7A)-C(9A)	121.29(15)
C(6A)-C(7A)-C(8A)	119.06(14)
C(9A)-C(7A)-C(8A)	119.57(15)
C(1A)-C(8A)-C(7A)	112.30(15)
C(10A)-C(9A)-C(14A)	118.43(15)
C(10A)-C(9A)-C(7A)	120.63(16)
C(14A)-C(9A)-C(7A)	120.94(15)
C(11A)-C(10A)-C(9A)	121.02(18)
C(12A)-C(11A)-C(10A)	119.19(16)
C(11A)-C(12A)-C(13A)	121.50(16)
C(11A)-C(12A)-Br(1A)	118.88(13)
C(13A)-C(12A)-Br(1A)	119.61(15)
C(12A)-C(13A)-C(14A)	118.71(19)
C(13A)-C(14A)-C(9A)	121.13(16)
C(5)-N(1)-C(4)	123.14(16)
C(5)-N(1)-C(1)	123.06(15)
C(4)-N(1)-C(1)	113.30(13)
N(1)-C(1)-C(8)	111.52(14)

N(1)-C(1)-C(2)	101.90(15)
C(8)-C(1)-C(2)	117.63(16)
C(1)-C(2)-C(3)	103.98(15)
C(2)-C(3)-C(4)	104.83(14)
N(1)-C(4)-C(3)	103.30(15)
O(1)-C(5)-N(1)	121.82(16)
O(1)-C(5)-C(6)	122.08(15)
N(1)-C(5)-C(6)	116.01(16)
C(7)-C(6)-C(5)	123.19(15)
C(6)-C(7)-C(9)	121.79(15)
C(6)-C(7)-C(8)	119.16(15)
C(9)-C(7)-C(8)	118.82(15)
C(1)-C(8)-C(7)	112.67(15)
C(14)-C(9)-C(10)	118.05(15)
C(14)-C(9)-C(7)	120.36(15)
C(10)-C(9)-C(7)	121.57(17)
C(11)-C(10)-C(9)	121.26(19)
C(10)-C(11)-C(12)	119.21(16)
C(13)-C(12)-C(11)	121.17(16)
C(13)-C(12)-Br(1)	119.26(15)
C(11)-C(12)-Br(1)	119.55(13)
C(12)-C(13)-C(14)	119.38(18)
C(13)-C(14)-C(9)	120.91(15)

Symmetry transformations used to generate equivalent atoms:

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1A)	19(1)	48(1)	45(1)	-8(1)	-6(1)	1(1)
N(1A)	19(1)	35(1)	15(1)	-1(1)	2(1)	2(1)
O(1A)	30(1)	59(1)	14(1)	-4(1)	4(1)	5(1)
C(1A)	21(1)	28(1)	16(1)	3(1)	4(1)	-2(1)
C(2A)	19(1)	58(1)	22(1)	-3(1)	6(1)	3(1)
C(3A)	18(1)	62(2)	28(1)	-1(1)	3(1)	-5(1)
C(4A)	20(1)	37(1)	24(1)	0(1)	-1(1)	0(1)
C(5A)	22(1)	34(1)	18(1)	-1(1)	4(1)	2(1)
C(6A)	21(1)	31(1)	20(1)	0(1)	6(1)	2(1)
C(7A)	18(1)	20(1)	17(1)	3(1)	4(1)	-1(1)
C(8A)	19(1)	29(1)	18(1)	-1(1)	3(1)	4(1)
C(9A)	18(1)	20(1)	20(1)	-1(1)	4(1)	0(1)
C(10A)	21(1)	23(1)	23(1)	2(1)	6(1)	1(1)
C(11A)	17(1)	22(1)	40(1)	-3(1)	8(1)	0(1)
C(12A)	17(1)	25(1)	31(1)	-5(1)	-1(1)	0(1)
C(13A)	22(1)	35(1)	22(1)	1(1)	-1(1)	-1(1)
C(14A)	20(1)	29(1)	21(1)	1(1)	2(1)	-2(1)
Br(1)	18(1)	47(1)	37(1)	-8(1)	-6(1)	0(1)
N(1)	18(1)	36(1)	16(1)	-3(1)	0(1)	4(1)
O(1)	27(1)	50(1)	17(1)	-2(1)	1(1)	7(1)
C(1)	20(1)	34(1)	18(1)	-2(1)	4(1)	3(1)
C(2)	20(1)	56(2)	22(1)	-1(1)	4(1)	1(1)
C(3)	18(1)	47(1)	29(1)	-5(1)	2(1)	5(1)
C(4)	18(1)	43(1)	26(1)	-8(1)	-3(1)	7(1)
C(5)	20(1)	31(1)	19(1)	2(1)	3(1)	5(1)
C(6)	18(1)	37(1)	18(1)	1(1)	5(1)	1(1)
C(7)	18(1)	22(1)	20(1)	2(1)	4(1)	0(1)
C(8)	18(1)	41(1)	16(1)	-3(1)	4(1)	0(1)
C(9)	17(1)	23(1)	21(1)	-2(1)	3(1)	0(1)
C(10)	20(1)	32(1)	23(1)	3(1)	6(1)	-1(1)
C(11)	18(1)	33(1)	30(1)	1(1)	6(1)	-2(1)

C(12)	15(1)	26(1)	32(1)	-6(1)	-2(1)	-1(1)
C(13)	20(1)	35(1)	23(1)	1(1)	-2(1)	-4(1)
C(14)	17(1)	35(1)	19(1)	2(1)	1(1)	-4(1)

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

	x	y	z	U(eq)
H(1AA)	17899	12992	9875	26
H(2AA)	19170	11168	9224	39
H(2AB)	18761	9614	9893	39
H(3AA)	20005	12463	10618	43
H(3AB)	20208	10525	10905	43
H(4AA)	18944	10566	12141	32
H(4AB)	19101	12570	12111	32
H(6AA)	15254	12501	11532	29
H(8AA)	16808	9847	9656	26
H(8AB)	16715	11432	8916	26
H(10A)	13795	10873	10833	27
H(11A)	12104	10981	9988	31
H(13A)	13546	12674	7419	32
H(14A)	15237	12588	8274	28
H(1A)	2133	11574	4729	29
H(2A)	733	10536	5652	39
H(2B)	1016	8616	5389	39
H(3A)	-11	11035	4046	37
H(3B)	-342	9098	4180	37
H(4A)	916	8208	3053	35
H(4B)	904	10121	2660	35
H(6A)	4726	9799	3377	29
H(8A)	2975	8564	5620	30
H(8B)	3188	10444	5994	30
H(10B)	6162	10608	4195	30
H(11B)	7823	10433	5072	32
H(13B)	6297	8719	7590	31
H(14B)	4628	8905	6716	29

Figure 1 Br1

Figure 2 br1a

Table 1. Crystal data and structure refinement for **4j**.

Identification code	rovis23a	
Empirical formula	C ₁₄ H ₁₄ Br N O	
Formula weight	292.17	
Temperature	373(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 12.5864(8) Å	$\alpha = 90^\circ$.
	b = 8.6454(6) Å	$\beta = 100.668(4)^\circ$.
	c = 17.4451(12) Å	$\gamma = 90^\circ$.
Volume	1865.5(2) Å ³	
Z	6	
Density (calculated)	1.560 Mg/m ³	
Absorption coefficient	3.288 mm ⁻¹	
F(000)	888	
Crystal size	0.13 x 0.09 x 0.09 mm ³	
Theta range for data collection	1.65 to 31.53°.	
Index ranges	-18 ≤ h ≤ 18, -12 ≤ k ≤ 12, -25 ≤ l ≤ 25	
Reflections collected	55388	
Independent reflections	12412 [R(int) = 0.0498]	
Completeness to theta = 31.53°	99.7 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.7541 and 0.6783	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	12412 / 1 / 461	
Goodness-of-fit on F ²	0.744	
Final R indices [I > 2σ(I)]	R1 = 0.0327, wR2 = 0.0806	
R indices (all data)	R1 = 0.0482, wR2 = 0.0895	
Absolute structure parameter	-0.006(5)	
Largest diff. peak and hole	0.583 and -0.511 e.Å ⁻³	

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

	x	y	z	U(eq)
Br(1)	1341(1)	7216(1)	6210(1)	28(1)
N(1)	-2477(2)	7614(2)	2761(1)	17(1)
O(1)	-992(2)	9676(2)	1119(1)	20(1)
C(1)	-1439(2)	8026(3)	2933(1)	16(1)
C(2)	-933(2)	8835(3)	2412(1)	18(1)
C(3)	-1423(2)	9005(3)	1610(1)	17(1)
C(4)	-2506(2)	8183(3)	1364(1)	19(1)
C(5)	-3156(2)	8132(3)	2016(1)	18(1)
C(6)	-4096(2)	6989(3)	1899(1)	20(1)
C(7)	-4206(2)	6535(3)	2730(2)	21(1)
C(8)	-3043(2)	6476(3)	3173(1)	20(1)
C(9)	-808(2)	7681(3)	3729(1)	17(1)
C(10)	-1182(2)	8187(3)	4394(1)	21(1)
C(11)	-539(2)	8024(3)	5129(1)	22(1)
C(12)	463(2)	7337(3)	5196(1)	20(1)
C(13)	849(2)	6772(3)	4552(1)	20(1)
C(14)	192(2)	6954(3)	3819(1)	18(1)
Br(1A)	2976(1)	5554(1)	13079(1)	20(1)
N(1A)	238(2)	7837(2)	9512(1)	14(1)
O(1A)	2189(2)	9322(2)	8017(1)	28(1)
C(1A)	1309(2)	7987(3)	9751(1)	15(1)
C(2A)	1974(2)	8625(3)	9283(1)	20(1)
C(3A)	1605(2)	8835(3)	8463(1)	21(1)
C(4A)	460(2)	8293(3)	8144(1)	20(1)
C(5A)	-288(2)	8421(3)	8735(1)	17(1)
C(6A)	-1326(2)	7471(3)	8553(1)	21(1)
C(7A)	-1598(2)	7136(3)	9353(1)	21(1)
C(8A)	-488(2)	6830(3)	9863(1)	17(1)
C(9A)	1764(2)	7455(3)	10557(1)	15(1)
C(10A)	1341(2)	8031(3)	11190(1)	17(1)
C(11A)	1734(2)	7483(3)	11940(1)	17(1)

C(12A)	2546(2)	6368(3)	12059(1)	17(1)
C(13A)	2998(2)	5823(3)	11437(1)	18(1)
C(14A)	2599(2)	6373(3)	10687(1)	17(1)
Br(1B)	5095(1)	7231(1)	9810(1)	41(1)
N(1B)	6128(2)	5254(2)	6176(1)	19(1)
O(1B)	3274(2)	4358(3)	4680(1)	30(1)
C(1B)	5172(2)	5403(3)	6412(1)	18(1)
C(2B)	4204(2)	5029(3)	5935(1)	23(1)
C(3B)	4132(2)	4687(3)	5123(1)	22(1)
C(4B)	5192(2)	4883(4)	4817(2)	29(1)
C(5B)	6177(2)	4495(4)	5430(2)	27(1)
C(6B)	7266(2)	4964(4)	5261(2)	29(1)
C(7B)	7955(2)	5175(4)	6078(2)	31(1)
C(8B)	7174(2)	5950(3)	6527(2)	24(1)
C(9B)	5165(2)	5896(3)	7230(1)	18(1)
C(10B)	5825(2)	5115(3)	7847(1)	20(1)
C(11B)	5780(2)	5502(4)	8614(1)	24(1)
C(12B)	5103(2)	6672(3)	8757(2)	24(1)
C(13B)	4435(2)	7461(3)	8163(2)	23(1)
C(14B)	4473(2)	7053(3)	7392(1)	22(1)

Table 3. Bond lengths [Å] and angles [°] for **4j**.

Br(1)-C(12)	1.906(2)
N(1)-C(1)	1.334(3)
N(1)-C(8)	1.477(3)
N(1)-C(5)	1.487(3)
O(1)-C(3)	1.240(3)
C(1)-C(2)	1.391(3)
C(1)-C(9)	1.496(3)
C(2)-C(3)	1.429(3)
C(3)-C(4)	1.527(3)
C(4)-C(5)	1.519(3)
C(5)-C(6)	1.526(3)
C(6)-C(7)	1.532(3)
C(7)-C(8)	1.525(4)
C(9)-C(14)	1.389(3)
C(9)-C(10)	1.400(3)
C(10)-C(11)	1.391(3)
C(11)-C(12)	1.380(4)
C(12)-C(13)	1.393(3)
C(13)-C(14)	1.397(3)
Br(1A)-C(12A)	1.896(2)
N(1A)-C(1A)	1.342(3)
N(1A)-C(8A)	1.475(3)
N(1A)-C(5A)	1.482(3)
O(1A)-C(3A)	1.239(3)
C(1A)-C(2A)	1.387(3)
C(1A)-C(9A)	1.490(3)
C(2A)-C(3A)	1.431(3)
C(3A)-C(4A)	1.520(4)
C(4A)-C(5A)	1.523(3)
C(5A)-C(6A)	1.526(3)
C(6A)-C(7A)	1.526(3)
C(7A)-C(8A)	1.533(3)
C(9A)-C(14A)	1.394(3)
C(9A)-C(10A)	1.403(3)

C(10A)-C(11A)	1.394(3)
C(11A)-C(12A)	1.392(3)
C(12A)-C(13A)	1.398(3)
C(13A)-C(14A)	1.396(3)
Br(1B)-C(12B)	1.902(3)
N(1B)-C(1B)	1.348(3)
N(1B)-C(5B)	1.469(3)
N(1B)-C(8B)	1.474(3)
O(1B)-C(3B)	1.239(3)
C(1B)-C(2B)	1.381(3)
C(1B)-C(9B)	1.490(3)
C(2B)-C(3B)	1.433(3)
C(3B)-C(4B)	1.535(4)
C(4B)-C(5B)	1.517(4)
C(5B)-C(6B)	1.510(4)
C(6B)-C(7B)	1.536(4)
C(7B)-C(8B)	1.521(4)
C(9B)-C(14B)	1.390(3)
C(9B)-C(10B)	1.405(3)
C(10B)-C(11B)	1.389(3)
C(11B)-C(12B)	1.375(4)
C(12B)-C(13B)	1.386(4)
C(13B)-C(14B)	1.400(3)
C(1)-N(1)-C(8)	127.5(2)
C(1)-N(1)-C(5)	119.77(19)
C(8)-N(1)-C(5)	112.06(19)
N(1)-C(1)-C(2)	122.3(2)
N(1)-C(1)-C(9)	119.0(2)
C(2)-C(1)-C(9)	118.6(2)
C(1)-C(2)-C(3)	121.7(2)
O(1)-C(3)-C(2)	124.0(2)
O(1)-C(3)-C(4)	120.4(2)
C(2)-C(3)-C(4)	115.3(2)
C(5)-C(4)-C(3)	112.31(19)
N(1)-C(5)-C(4)	111.21(19)

N(1)-C(5)-C(6)	103.15(19)
C(4)-C(5)-C(6)	115.5(2)
C(5)-C(6)-C(7)	104.08(19)
C(8)-C(7)-C(6)	104.01(19)
N(1)-C(8)-C(7)	103.60(19)
C(14)-C(9)-C(10)	119.0(2)
C(14)-C(9)-C(1)	120.6(2)
C(10)-C(9)-C(1)	120.3(2)
C(11)-C(10)-C(9)	120.3(2)
C(12)-C(11)-C(10)	119.2(2)
C(11)-C(12)-C(13)	122.2(2)
C(11)-C(12)-Br(1)	117.81(18)
C(13)-C(12)-Br(1)	120.01(19)
C(12)-C(13)-C(14)	117.6(2)
C(9)-C(14)-C(13)	121.7(2)
C(1A)-N(1A)-C(8A)	126.32(19)
C(1A)-N(1A)-C(5A)	120.21(19)
C(8A)-N(1A)-C(5A)	112.03(18)
N(1A)-C(1A)-C(2A)	122.5(2)
N(1A)-C(1A)-C(9A)	116.8(2)
C(2A)-C(1A)-C(9A)	120.6(2)
C(1A)-C(2A)-C(3A)	121.3(2)
O(1A)-C(3A)-C(2A)	123.4(2)
O(1A)-C(3A)-C(4A)	120.5(2)
C(2A)-C(3A)-C(4A)	115.9(2)
C(3A)-C(4A)-C(5A)	113.1(2)
N(1A)-C(5A)-C(4A)	111.56(19)
N(1A)-C(5A)-C(6A)	103.12(18)
C(4A)-C(5A)-C(6A)	115.6(2)
C(7A)-C(6A)-C(5A)	103.86(19)
C(6A)-C(7A)-C(8A)	103.26(19)
N(1A)-C(8A)-C(7A)	102.99(18)
C(14A)-C(9A)-C(10A)	119.7(2)
C(14A)-C(9A)-C(1A)	120.4(2)
C(10A)-C(9A)-C(1A)	119.9(2)
C(11A)-C(10A)-C(9A)	119.9(2)

C(12A)-C(11A)-C(10A)	119.9(2)
C(11A)-C(12A)-C(13A)	120.7(2)
C(11A)-C(12A)-Br(1A)	118.11(18)
C(13A)-C(12A)-Br(1A)	121.12(18)
C(14A)-C(13A)-C(12A)	119.1(2)
C(9A)-C(14A)-C(13A)	120.7(2)
C(1B)-N(1B)-C(5B)	120.0(2)
C(1B)-N(1B)-C(8B)	127.8(2)
C(5B)-N(1B)-C(8B)	111.7(2)
N(1B)-C(1B)-C(2B)	122.1(2)
N(1B)-C(1B)-C(9B)	118.9(2)
C(2B)-C(1B)-C(9B)	118.9(2)
C(1B)-C(2B)-C(3B)	122.1(2)
O(1B)-C(3B)-C(2B)	123.5(2)
O(1B)-C(3B)-C(4B)	121.4(2)
C(2B)-C(3B)-C(4B)	114.9(2)
C(5B)-C(4B)-C(3B)	112.4(2)
N(1B)-C(5B)-C(6B)	104.0(2)
N(1B)-C(5B)-C(4B)	111.3(2)
C(6B)-C(5B)-C(4B)	117.2(2)
C(5B)-C(6B)-C(7B)	103.2(2)
C(8B)-C(7B)-C(6B)	102.8(2)
N(1B)-C(8B)-C(7B)	102.7(2)
C(14B)-C(9B)-C(10B)	119.5(2)
C(14B)-C(9B)-C(1B)	121.1(2)
C(10B)-C(9B)-C(1B)	119.3(2)
C(11B)-C(10B)-C(9B)	119.9(2)
C(12B)-C(11B)-C(10B)	119.2(2)
C(11B)-C(12B)-C(13B)	122.5(2)
C(11B)-C(12B)-Br(1B)	118.4(2)
C(13B)-C(12B)-Br(1B)	119.1(2)
C(12B)-C(13B)-C(14B)	118.0(2)
C(9B)-C(14B)-C(13B)	120.8(2)

Symmetry transformations used to generate equivalent atoms:

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	33(1)	33(1)	14(1)	3(1)	-3(1)	-2(1)
N(1)	20(1)	19(1)	12(1)	2(1)	4(1)	1(1)
O(1)	25(1)	18(1)	18(1)	4(1)	7(1)	1(1)
C(1)	19(1)	16(1)	12(1)	-3(1)	2(1)	2(1)
C(2)	20(1)	18(1)	16(1)	-1(1)	5(1)	-3(1)
C(3)	18(1)	16(1)	17(1)	1(1)	6(1)	3(1)
C(4)	21(1)	24(1)	12(1)	2(1)	2(1)	-1(1)
C(5)	20(1)	20(1)	15(1)	3(1)	2(1)	2(1)
C(6)	16(1)	25(1)	18(1)	1(1)	4(1)	-1(1)
C(7)	22(1)	21(1)	21(1)	0(1)	8(1)	-2(1)
C(8)	21(1)	24(1)	17(1)	4(1)	8(1)	-1(1)
C(9)	20(1)	17(1)	14(1)	1(1)	2(1)	-2(1)
C(10)	23(1)	22(1)	17(1)	-1(1)	3(1)	3(1)
C(11)	31(1)	21(1)	15(1)	-1(1)	6(1)	-1(1)
C(12)	26(1)	19(1)	12(1)	2(1)	0(1)	-2(1)
C(13)	21(1)	20(1)	18(1)	3(1)	2(1)	1(1)
C(14)	24(1)	15(1)	14(1)	1(1)	4(1)	0(1)
Br(1A)	21(1)	25(1)	12(1)	3(1)	-1(1)	-1(1)
N(1A)	16(1)	14(1)	11(1)	1(1)	1(1)	0(1)
O(1A)	31(1)	34(1)	21(1)	7(1)	9(1)	-5(1)
C(1A)	18(1)	12(1)	13(1)	-2(1)	1(1)	0(1)
C(2A)	18(1)	23(1)	16(1)	2(1)	2(1)	-6(1)
C(3A)	25(1)	18(1)	20(1)	3(1)	6(1)	-2(1)
C(4A)	26(1)	22(1)	12(1)	3(1)	2(1)	0(1)
C(5A)	18(1)	16(1)	14(1)	2(1)	-1(1)	0(1)
C(6A)	19(1)	21(1)	19(1)	0(1)	-4(1)	0(1)
C(7A)	15(1)	22(1)	25(1)	1(1)	2(1)	2(1)
C(8A)	20(1)	14(1)	17(1)	1(1)	2(1)	-2(1)
C(9A)	17(1)	15(1)	13(1)	1(1)	2(1)	-2(1)
C(10A)	18(1)	16(1)	16(1)	-1(1)	0(1)	-1(1)
C(11A)	20(1)	20(1)	13(1)	-1(1)	3(1)	-3(1)

C(12A)	19(1)	19(1)	13(1)	2(1)	0(1)	-3(1)
C(13A)	17(1)	20(1)	17(1)	1(1)	1(1)	-1(1)
C(14A)	18(1)	21(1)	13(1)	1(1)	5(1)	-1(1)
Br(1B)	32(1)	72(1)	20(1)	-16(1)	7(1)	-9(1)
N(1B)	19(1)	22(1)	17(1)	-3(1)	4(1)	0(1)
O(1B)	28(1)	44(1)	16(1)	2(1)	-1(1)	-6(1)
C(1B)	19(1)	18(1)	17(1)	0(1)	5(1)	1(1)
C(2B)	19(1)	32(1)	16(1)	-3(1)	3(1)	-4(1)
C(3B)	25(1)	25(1)	15(1)	5(1)	2(1)	0(1)
C(4B)	28(2)	43(2)	17(1)	-1(1)	4(1)	3(1)
C(5B)	28(1)	37(2)	17(1)	-4(1)	7(1)	5(1)
C(6B)	24(1)	47(2)	18(1)	7(1)	8(1)	11(1)
C(7B)	24(1)	45(2)	26(1)	4(1)	8(1)	3(1)
C(8B)	18(1)	28(1)	27(1)	1(1)	5(1)	-1(1)
C(9B)	17(1)	19(1)	18(1)	-2(1)	4(1)	-2(1)
C(10B)	16(1)	23(1)	20(1)	0(1)	2(1)	-1(1)
C(11B)	20(1)	33(1)	16(1)	5(1)	-1(1)	-1(1)
C(12B)	22(1)	34(1)	18(1)	-7(1)	4(1)	-11(1)
C(13B)	24(1)	21(1)	25(1)	-6(1)	8(1)	-2(1)
C(14B)	22(1)	21(1)	22(1)	-1(1)	4(1)	1(1)

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

	x	y	z	U(eq)
H(2A)	-259	9277	2590	21
H(4A)	-2924	8713	918	23
H(4B)	-2378	7134	1205	23
H(5A)	-3434	9170	2088	22
H(6A)	-3937	6092	1606	24
H(6B)	-4754	7471	1626	24
H(7A)	-4622	7299	2955	25
H(7B)	-4554	5534	2736	25
H(8A)	-3001	6764	3715	24
H(8B)	-2738	5450	3150	24
H(10A)	-1864	8634	4344	25
H(11A)	-782	8375	5570	26
H(13A)	1520	6291	4607	24
H(14A)	429	6578	3381	21
H(2AA)	2672	8923	9507	23
H(4AA)	482	7224	7979	24
H(4AB)	165	8905	7688	24
H(5AA)	-478	9511	8785	20
H(6AA)	-1900	8054	8232	25
H(6AB)	-1211	6519	8285	25
H(7AA)	-2063	6238	9336	25
H(7AB)	-1949	8016	9545	25
H(8AA)	-483	7110	10402	20
H(8AB)	-284	5751	9839	20
H(10C)	799	8777	11109	20
H(11C)	1455	7862	12361	21
H(13C)	3557	5104	11522	22
H(14C)	2893	6014	10269	20
H(2BA)	3578	4999	6147	27
H(4BA)	5178	4215	4368	35

H(4BB)	5248	5943	4647	35
H(5BA)	6186	3374	5514	33
H(6BA)	7216	5921	4966	35
H(6BB)	7563	4164	4973	35
H(7BA)	8201	4187	6308	37
H(7BB)	8577	5828	6061	37
H(8BA)	7360	5721	7080	29
H(8BB)	7165	7062	6454	29
H(10B)	6292	4342	7743	24
H(11B)	6203	4975	9025	28
H(13B)	3974	8237	8274	27
H(14B)	4031	7564	6984	26