Rhodium-Catalyzed [2+2+2] Cycloaddition of Alkenyl Isocyanates and Alkynes

Robert T. Yu and Tomislav Rovis*

*Department of Chemistry, Colorado State University
Fort Collins, Colorado 80523*

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. Acetonitrile (certified ACS grade) and triethylamine (peptide synthesis grade) were 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**, **1l**, and **1m** were all purchased from Aldrich Chemicals Co. and used without further purification. Alkynes **1b** – **1k** were prepared according to the literature method.¹ Alkyne **1n** was prepared by a typical TBS-protection of the corresponding diol, which was prepared by the literature method.² Alkenyl isocyanates **2** and **5** are known compounds and can be synthesized by the procedure described within. 5-hexenoic acid, 6-heptenoic acid, and diphenyl phosphoryl azide were purchased from Aldrich Chemicals Co. RhCl(PPh₃)₃, [Rh(COD)Cl]₂, and [Rh(ethylene)₂Cl]₂ were purchased from Strem Chemical, Inc. and used without further purification. Tris(4-methoxyphenyl) phosphine was purchased from Aldrich Chemicals Co. and used without further purification.

5-isocyanatopent-1-ene (2). To a solution of 2.23 g of 5-hexenoic acid (19.54 mmol) in 20 ml of MeCN (ca. 1 M) was added 2.9 ml of Et₃N (20.71 mmol) slowly, followed by 4.5 ml of diphenyl phosphoryl azide (20.71 mmol) dropwise at ambient temperature. The reaction mixture was stirred at ambient temperature for another 20 minutes. The reaction mixture directly underwent distillation

¹ Mio, M. J.; Kopel, L. C.; Gadzikwa, T. L.; Hull, K. L.; Brisbois, R. G.; Markworth, C. J.; Grieco, P. A. *Org. Lett.* **2002**, 4, 3199.

² Malacria, M.; Vollhardt, K. P. C. *J. Org. Chem.* **1984**, 49, 5010.

under reduced pressure. MeCN and Et₃N were first collected at *ca.* 150 mmHg. The isocyanate was collected at 30 mmHg as a colorless oil (1.135 g, 52%): bp 60 °C (30 mmHg); ¹H NMR (400 MHz, CDCl₃) δ 5.75 (ddt, 1H, *J* = 6.8, 10.2, 17.1 Hz), 5.05 (dm, 1H, *J* = 17.1 Hz), 5.00 (dm, 1H, *J* = 10.2 Hz), 3.29 (t, 2H, *J* = 6.6 Hz), 2.14 (dt, 2H, *J* = 7.0, 7.0 Hz), 1.69 (tt, 2H, *J* = 7.0, 7.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 137.0, 116.1, 42.4, 30.7, 30.4; IR (NaCl, CHCl₃) 2955, 2279, 1644, 1516, 1434, 1358 cm⁻¹.

6-isocyanatohex-1-ene (5) To a solution of 706 mg of 6-heptenoic acid (5.508 mmol) in 6 ml of MeCN (*ca.* 1 M) was added 0.82 ml of Et₃N (5.840 mmol) slowly, followed by 1.3 ml of diphenyl phosphoryl azide (5.840 mmol) dropwise at ambient temperature. The reaction mixture was stirred at ambient temperature for another 20 minutes. The reaction mixture directly underwent distillation under reduced pressure. MeCN and Et₃N were first collected at *ca.* 150 mmHg. The isocyanate was collected at 30 mmHg as a colorless oil (497 mg, 72%): bp 70 – 75 °C (30 mmHg); ¹H NMR (300 MHz, CDCl₃) δ 5.79 (ddt, 1H, *J* = 6.6, 10.3, 16.9 Hz), 5.02 (dm, 1H, *J* = 16.9 Hz), 4.98 (dm, 1H, *J* = 9.9 Hz), 3.31 (t, 2H, *J* = 6.4 Hz), 2.08 (dt, 2H, *J* = 7.0, 7.0 Hz), 1.63 (m, 2H), 1.48 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 138.2, 115.2, 43.2, 33.3, 31.0, 26.1; IR (NaCl, CHCl₃) 2940, 2274, 1634, 1527, 1440, 1363 cm⁻¹.

General procedure for the Rh-catalyzed [2+2+2] cycloaddition of alkenyl isocyanates and alkynes: A flame-dried round bottom flask was charged with [Rh(ethylene)₂Cl]₂ (0.05 eq) and tris(4-methoxyphenyl) phosphine (0.1 eq), and was fitted with a flame-dried reflux condenser in an inert atmosphere (N₂) glove box. Upon removal from the glove box, 1.0 ml toluene was added via syringe and the resulting orange 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.* 23 h. The reaction mixture was cooled to ambient temperature and a small amount of silica gel was added. The reaction mixture was concentrated in vacuo and purified by flash column chromatography (gradient elution typically 3:7 ethyl acetate/hexane). Evaporation of solvent afforded the analytically pure product.³

5,6-diphenyl-2,3,8a-tetrahydroindolizin-7(1H)-one (4a). According to the general procedure, in the presence of 5.5 mg (0.014 mmol) of [Rh(ethylene)₂Cl]₂ and 9.8 mg (0.028 mmol) of tris(4-methoxyphenyl) phosphine, 30.0 mg (0.270 mmol) of **2** and 96.2 mg (0.540 mmol) of **1a** were reacted in 4 ml of toluene at 110 °C for 23 hours. Upon purification 58.1 mg (74%) of the desired product was isolated as a waxy yellow solid: R_f = 0.13 (1:1 EtOAc/hex); ¹H NMR (400 MHz, CDCl₃) δ 7.04 – 7.30 (m, 5H), 7.00 (m, 2H), 6.88 – 6.94 (m, 3H), 4.14 (dddd, 1H, *J* = 6.8, 6.8, 6.8, 13.6 Hz), 3.40 (ddd, 1H, *J* = 4.0, 7.5, 11.5 Hz), 3.11 (ddd, 1H, *J* = 7.5, 7.5, 10.9 Hz), 2.67 (dd, 1H, *J* = 15.6, 15.6 Hz), 2.59 (dd, 1H,

³ Many vinylogous amide bicyclic products exist as rotamers, especially in the aromatic region. Therefore proton-coupling constants are not resolved in some cases.

$J = 5.3, 16.0$ Hz), 2.35 (m, 1H), 1.94 – 2.03 (m, 1H), 1.73 – 1.93 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 189.9, 161.1, 136.7, 135.9, 132.2, 128.9, 128.2, 127.4, 125.3, 112.4, 57.8, 50.1, 42.1, 32.5, 24.4; IR (NaCl, CDCl_3) 1617, 1528, 1450, 1383, 1304, 1091 cm^{-1} ; HRMS $[\text{C}_{20}\text{H}_{20}\text{NO}]^+$ calcd 290.1545. Found 290.1545 (FAB+). X-ray data is attached at the end of this manuscript.

5,6-dip-tolyl-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4b). According to the general procedure, in the presence of 5.4 mg (0.014 mmol) of $[\text{Rh}(\text{ethylene})_2\text{Cl}]_2$ and 9.8 mg (0.028 mmol) of tris(4-methoxyphenyl) phosphine, 30.0 mg (0.270 mmol) of **2** and 61.3 mg (0.297 mmol) of **1b** were reacted in 4 ml of toluene at 110 °C for 23 hours. Upon purification 54.3 mg (63%) of the desired product was isolated as a yellow oil, which becomes a waxy solid upon standing: $R_f = 0.34$ (EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 6.80 – 7.20 (m, 8H), 4.10 (dddd, 1H, $J = 7.1, 7.1, 7.1, 12.2$ Hz), 3.38 (ddd, 1H, $J = 4.5, 7.2, 11.7$ Hz), 3.08 (ddd, 1H, $J = 7.5, 7.5, 11.1$ Hz), 2.64 (dd, 1H, $J = 15.8, 15.8$ Hz), 2.54 (dd, 1H, $J = 4.9, 15.8$ Hz), 2.32 (m, 1H), 2.24 (s, 3H), 2.15 (s, 3H), 1.92 – 2.01 (m, 1H), 1.71 – 1.89 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.1, 161.1, 138.7, 134.5, 133.8, 133.1, 132.0, 129.0, 128.2, 112.2, 57.7, 50.1, 42.2, 32.5, 24.4, 21.5, 21.3; IR (NaCl, CHCl_3) 1609, 1527, 1445, 1301, 1040 cm^{-1} ; HRMS $[\text{C}_{22}\text{H}_{24}\text{NO}]^+$ calcd 318.1858. Found 318.1845 (FAB+).

5,6-bis(4-methoxyphenyl)-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4c). According to the general procedure, in the presence of 5.7 mg (0.015 mmol) of $[\text{Rh}(\text{ethylene})_2\text{Cl}]_2$ and 9.7 mg (0.028 mmol) of tris(4-methoxyphenyl) phosphine, 30.0 mg (0.270 mmol) of **2** and 129.0 mg (0.540 mmol) of **1c** were reacted in 4 ml of toluene at 110 °C for 23 hours. Upon purification 68.0 mg (72%) of the desired product was isolated as a yellow oil: $R_f = 0.21$ (EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 6.54 – 7.20 (m, 8H), 4.11 (dddd, 1H, $J = 6.5, 6.5, 6.5, 12.9$ Hz), 3.71 (s, 3H), 3.65 (s, 3H), 3.43 (m, 1H), 3.10 (m, 1H), 2.64 (dd, 1H, $J = 15.8, 15.8$ Hz), 2.55 (dd, 1H, $J = 4.5, 15.8$ Hz), 2.31 (m, 1H), 1.91 – 2.01 (m, 1H), 1.71 – 1.90 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 189.9, 161.0, 159.8, 157.1, 133.0, 130.6, 129.3, 128.2, 113.6, 113.1, 111.8, 57.5, 55.3, 55.2, 50.3, 42.0, 32.3, 24.5; IR (NaCl, CHCl_3) 1598, 1521, 1440, 1301, 1030 cm^{-1} ; HRMS $[\text{C}_{22}\text{H}_{24}\text{NO}_3]^+$ calcd 350.1756. Found 350.1761 (FAB+).

5,6-bis(3-methoxyphenyl)-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4d). According to the general procedure, in the presence of 5.6 mg (0.014 mmol) of $[\text{Rh}(\text{ethylene})_2\text{Cl}]_2$ and 9.9 mg (0.028 mmol) of tris(4-methoxyphenyl) phosphine, 30.0 mg (0.270 mmol) of **2** and 129.0 mg (0.540 mmol) of **1d** were reacted in 4 ml of toluene at 110 °C for 23 hours. Upon purification 66.1 mg (70%) of the desired product was isolated as a yellow oil: $R_f = 0.21$ (EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 6.46 – 7.18 (m, 8H), 4.12 (dddd, 1H, $J = 6.8, 6.8, 6.8, 13.6$ Hz), 3.50 – 3.76 (m, 6H), 3.43 (m, 1H), 3.14 (ddd, 1H, $J = 7.5, 7.5, 10.9$ Hz), 2.65 (dd, 1H, $J = 15.7, 15.7$ Hz), 2.57 (dd, 1H, $J = 5.3, 15.9$ Hz), 2.34 (m, 1H), 1.94 – 2.03 (m, 1H), 1.73 – 1.92 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 189.9, 160.7, 159.4, 158.9, 138.2, 137.1, 129.4, 128.3, 124.8, 121.4, 117.2, 114.6, 111.8, 57.9,

55.4, 55.2, 50.1, 42.1, 32.5, 24.4; IR (NaCl, CHCl₃) 1614, 1521, 1460, 1419, 1312, 1045 cm⁻¹; HRMS [C₂₂H₂₃NO₃]⁺ calcd 349.1678. Found 349.1667 (EI+).

1,1'-(4,4'-(7-oxo-1,2,3,7,8,8a-hexahydroindolizine-5,6-diyl))bis(4,1-phenylene))diethanone (4g). According to the general procedure, in the presence of 5.6 mg (0.014 mmol) of [Rh(ethylene)₂Cl]₂ and 10.1 mg (0.029 mmol) of tris(4-methoxyphenyl) phosphine, 30.0 mg (0.270 mmol) of **2** and 142.0 mg (0.540 mmol) of **1g** were reacted in 4 ml of toluene at 110 °C for 23 hours. Upon purification 34.6 mg (34%) of the desired product was isolated as a yellow oil: R_f = 0.13 (EtOAc); ¹H NMR (400 MHz, CDCl₃) δ 7.89 (broad d, 1H, *J* = 7.0), 7.67 (broad d, 1H, *J* = 7.2), 7.59 (d, 2H, *J* = 8.3), 7.39 (broad d, 1H, *J* = 6.8), 7.03 (broad d, 1H, *J* = 7.5), 6.98 (d, 2H, *J* = 8.3), 4.17 (dddd, 1H, *J* = 7.0, 7.0, 7.0, 14.1 Hz), 3.40 (ddd, 1H, *J* = 4.3, 7.5, 11.6 Hz), 3.08 (ddd, 1H, *J* = 7.5, 7.5, 11.1 Hz), 2.67 (dd, 1H, *J* = 15.3, 15.3 Hz), 2.61 (dd, 1H, *J* = 6.1, 15.8 Hz), 2.52 (s, 3H), 2.44 (s, 3H), 2.38 (dddd, 1H, *J* = 4.3, 6.6, 6.6, 6.6 Hz), 2.01 (m, 1H), 1.75 – 1.96 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 198.3, 197.4, 189.6, 159.9, 142.0, 140.0, 137.5, 134.1, 132.1, 129.6, 129.4, 128.8, 128.3, 127.7, 111.7, 58.1, 50.3, 41.8, 32.4, 26.8, 26.7, 24.5; IR (NaCl, CHCl₃) 1680, 1619, 1521, 1429, 1301, 1040 cm⁻¹; HRMS [C₂₄H₂₄NO₃]⁺ calcd 374.1756. Found 374.1739 (FAB+).

5,6-bis(4-(dimethylamino)phenyl)-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4e). According to the general procedure, in the presence of 5.3 mg (0.014 mmol) of [Rh(ethylene)₂Cl]₂ and 9.6 mg (0.027 mmol) of tris(4-methoxyphenyl) phosphine, 30.0 mg (0.270 mmol) of **2** and 143.0 mg (0.540 mmol) of **1e** were reacted in 4 ml of toluene at 110 °C for 23 hours. Upon purification 61.0 mg (61%) of the desired product was isolated as a yellow oil, which becomes an orange-yellow waxy solid upon standing: R_f = 0.15 (EtOAc); ¹H NMR (400 MHz, CDCl₃) δ 6.42 – 7.02 (m, 8H), 4.12 (m, 1H), 3.49 (m, 1H), 3.13 (m, 1H), 2.87 – 2.93 (m, 6H), 2.79 (s, 6H), 2.64 (dd, 1H, *J* = 15.9, 15.9 Hz), 2.46 (dd, 1H, *J* = 4.4, 15.7 Hz), 2.28 (m, 1H), 1.94 (m, 1H), 1.70 – 1.89 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 190.3, 161.4, 150.3, 132.6, 130.8, 123.7, 112.8, 111.8, 111.2, 57.1, 50.7, 42.3, 41.2, 40.3, 32.0, 24.6; IR (NaCl, CHCl₃) 1603, 1516, 1470, 1434, 1358, 1306, 1045 cm⁻¹; HRMS [C₂₄H₃₀N₃O]⁺ calcd 376.2389. Found 376.2379 (FAB+).

5,6-bis(4-chlorophenyl)-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4f). According to the general procedure, in the presence of 5.4 mg (0.014 mmol) of [Rh(ethylene)₂Cl]₂ and 10.0 mg (0.028 mmol) of tris(4-methoxyphenyl) phosphine, 30.0 mg (0.270 mmol) of **2** and 133.5 mg (0.540 mmol) of **1f** were reacted in 4 ml of toluene at 110 °C for 23 hours. Upon purification 58.2 mg (60%) of the desired product was isolated as a yellow oil, which becomes a yellow waxy solid upon standing: R_f = 0.25 (EtOAc); ¹H NMR (400 MHz, CDCl₃) δ 6.76 – 7.32 (m, 8H), 4.12 (dddd, 1H, *J* = 7.2, 7.2, 7.2, 14.4 Hz), 3.39 (ddd, 1H, *J* = 4.3, 7.5, 11.5 Hz), 3.09 (ddd, 1H, *J* = 7.5, 7.5, 11.1 Hz), 2.63 (dd, 1H, *J* = 16.0, 16.0 Hz), 2.61 (dd, 1H, *J* = 6.6, 16.0 Hz), 2.35 (dddd, 1H, *J* = 4.3, 6.7, 6.7, 6.7 Hz), 1.95 – 2.04 (m, 1H), 1.73 – 1.93 (m, 2H); ¹³C NMR (100 MHz,

CDCl₃) δ 189.5, 160.0, 135.3, 134.9, 133.9, 133.3, 131.2, 130.6, 130.3, 128.8, 127.8, 111.4, 57.9, 50.3, 41.7, 32.4, 24.4; IR (NaCl, CHCl₃) 1614, 1516, 1440, 1301, 1086 cm⁻¹; HRMS [C₂₀H₁₈Cl₂NO]⁺ calcd 358.0765. Found 358.0755 (FAB+).

6,7-di(thiophen-2-yl)-2,3,8,8a-tetrahydroindolizin-5(1H)-one (3h) & 5,6-di(thiophen-2-yl)-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4h).

According to the general procedure, in the presence of 5.3 mg (0.014 mmol) of [Rh(ethylene)₂Cl]₂ and 9.7 mg (0.028 mmol) of tris(4-methoxyphenyl) phosphine, 30.0 mg (0.270 mmol) of **2** and 103.0 mg (0.540 mmol) of **1h** were reacted in 4 ml of toluene at 110 °C for 23 hours. Upon purification 59.1 mg (72%) of the desired products (**3h** and **4h**) were isolated as an inseparable mixture as a yellow oil, which becomes a yellow waxy solid upon standing: R_f = 0.50 (EtOAc); See spectra for its ¹H NMR (400 MHz, CDCl₃); ¹³C NMR (100 MHz, CDCl₃) δ 189.2, 172.8, 163.3, 154.2, 141.4, 139.8, 138.3, 136.2, 136.1, 130.4, 129.7, 129.6, 129.3, 129.2, 128.8, 128.0, 127.1, 127.1, 127.0, 126.7, 126.4, 125.9, 124.5, 124.3, 106.8, 57.3, 55.5, 50.9, 45.1, 42.0, 37.3, 33.8, 31.9, 24.5, 23.4; IR (NaCl, CHCl₃) 1629, 1521, 1496, 1429, 1281, 1040 cm⁻¹; HRMS [C₁₆H₁₆S₂NO]⁺ calcd 302.0673. Found 302.0662 (FAB+).

6,7-di(furan-3-yl)-2,3,8,8a-tetrahydroindolizin-5(1H)-one (3i).

According to the general procedure, in the presence of 5.3 mg (0.014 mmol) of [Rh(ethylene)₂Cl]₂ and 9.5 mg (0.027 mmol) of tris(4-methoxyphenyl) phosphine, 30.0 mg (0.270 mmol) of **2** and 45.0 mg (0.284 mmol) of **1i** were reacted in 4 ml of toluene at 110 °C for 23 hours. Upon purification 22.7 mg (31%) of **3i** was isolated as a yellow oil: R_f = 0.44 (EtOAc); ¹H NMR (400 MHz, CDCl₃) δ 7.60 (m, 1H), 7.41 (m, 1H), 7.35 (dd, 1H, *J* = 1.6, 2.9 Hz), 7.26 (dd, 1H, *J* = 1.5, 3.0 Hz), 6.24 (m, 1H), 6.11 (m, 1H), 3.83 (dddd, 1H, *J* = 5.1, 5.1, 9.9, 14.4 Hz), 3.64 (ddd, 1H, *J* = 2.1, 8.7, 11.5 Hz), 3.54 (ddd, 1H, *J* = 7.5, 9.8, 12.0 Hz), 2.76 (dd, 1H, *J* = 4.5, 16.8 Hz), 2.47 (dd, 1H, *J* = 13.7, 16.8 Hz), 2.27 (ddd, 1H, *J* = 6.0, 6.0, 6.0 Hz), 2.04 (m, 1H), 1.83 (m, 1H), 1.67 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 163.8, 143.1, 142.7, 142.4, 142.0, 135.9, 124.9, 123.4, 119.4, 112.6, 110.6, 55.6, 45.0, 36.6, 33.8, 23.4; IR (NaCl, CHCl₃) 1639, 1614, 1516, 1434, 1035 cm⁻¹; HRMS [C₁₆H₁₆NO₃]⁺ calcd 270.1130. Found 270.1129 (FAB+).

5,6-di(furan-3-yl)-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4i).

From the same reaction, 25.3 mg (35%) of **4i** was also isolated as a yellow oil: R_f = 0.38 (EtOAc); ¹H NMR (400 MHz, CDCl₃) δ 7.39 (m, 2H), 7.32 (m, 1H), 7.15 (m, 1H), 6.30 (m, 1H), 5.90 (m, 1H), 4.03 (dddd, 1H, *J* = 6.7, 6.7, 6.7, 13.7 Hz), 3.57 (ddd, 1H, *J* = 5.1, 7.5, 11.7 Hz), 3.30 (ddd, 1H, *J* = 7.5, 7.5, 11.3 Hz), 2.56 (dd, 1H, *J* = 15.4, 15.4 Hz), 2.50 (dd, 1H, *J* = 6.0, 16.0 Hz), 2.31 (dddd, 1H, *J* = 6.7, 6.7, 6.7, 6.7 Hz), 2.01 (m, 1H), 1.91 (m, 1H), 1.74 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 189.4, 152.6, 143.3, 143.1, 141.4, 141.0, 120.6, 119.7, 112.1, 111.3, 103.6, 57.3, 50.3, 42.1, 32.1, 24.4; IR (NaCl, CHCl₃) 1609, 1588, 1516, 1491, 1434, 1311, 1045 cm⁻¹; HRMS [C₁₆H₁₆NO₃]⁺ calcd 270.1130. Found 270.1133 (FAB+).

5,6-dicyclohexenyl-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4j).

According to the general procedure, in the presence of 5.4 mg (0.014 mmol) of $[\text{Rh}(\text{ethylene})_2\text{Cl}]_2$ and 9.7 mg (0.028 mmol) of tris(4-methoxyphenyl) phosphine, 30.0 mg (0.270 mmol) of **2** and 101.0 mg (0.540 mmol) of **1j** were reacted in 4 ml of toluene at 110 °C for 23 hours.

Upon purification 60.1 mg (75%) of the desired product was isolated as a waxy pale yellow solid: $R_f = 0.29$ (EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 5.58 (m, 1H), 5.32 (m, 1H), 3.73 (dddd, 1H, $J = 9.6, 9.6, 9.6, 16.9$ Hz), 3.24 – 3.52 (m, 2H), 2.28 – 2.36 (m, 2H), 2.21 (dddd, 2H, $J = 2.9, 6.5, 6.5, 12.7$ Hz), 1.92 – 2.08 (m, 7H), 1.79 (m, 2H), 1.44 – 1.66 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.2, 162.5, 134.3, 126.8, 57.6, 48.4, 42.3, 32.7, 30.2, 28.6, 26.0, 25.1, 24.3, 23.5, 22.6, 22.6, 22.1; IR (NaCl, CHCl_3) 1598, 1511, 1475, 1440, 1296, 1040 cm^{-1} ; HRMS $[\text{C}_{20}\text{H}_{28}\text{NO}]^+$ calcd 298.2171. Found 298.2175 (FAB+).

5,6-dicyclopentenyl-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4k).

According to the general procedure, in the presence of 5.3 mg (0.014 mmol) of $[\text{Rh}(\text{ethylene})_2\text{Cl}]_2$ and 9.5 mg (0.027 mmol) of tris(4-methoxyphenyl) phosphine, 30.0 mg (0.270 mmol) of **2** and 85.4 mg (0.540 mmol) of **1k** were reacted in 4 ml of toluene at 80 °C for 23 hours. Upon purification 36.5 mg (50%) of the desired product was isolated as a yellow oil: $R_f = 0.24$ (EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 5.71 (m, 1H), 5.38 (m, 1H), 3.80 (dddd, 1H, $J = 7.9, 7.9, 7.9, 15.1$ Hz), 3.45 (ddd, 1H, $J = 4.0, 8.1, 11.3$ Hz), 3.29 (ddd, 1H, $J = 8.1, 8.1, 10.8$ Hz), 2.61 (dddddd, 1H, $J = 2.4, 2.4, 2.4, 6.5, 6.5, 13.5$ Hz), 2.32 – 2.42 (m, 6H), 2.18 – 2.31 (m, 3H), 2.09 (m, 1H), 1.97 (m, 1H), 1.75 – 1.90 (m, 5H), 1.65 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 189.9, 158.3, 139.6, 139.2, 132.8, 129.2, 107.8, 57.5, 49.0, 42.2, 36.2, 35.8, 33.3, 32.9, 32.5, 24.2, 24.2, 23.9; IR (NaCl, CHCl_3) 1603, 1511, 1475, 1419, 1040 cm^{-1} ; HRMS $[\text{C}_{18}\text{H}_{24}\text{NO}]^+$ calcd 270.1858. Found 270.1848 (FAB+).

6,7-dipropyl-2,3,8,8a-tetrahydroindolizin-5(1H)-one (3l).

According to the general procedure, in the presence of 5.4 mg (0.014 mmol) of $[\text{Rh}(\text{ethylene})_2\text{Cl}]_2$ and 9.8 mg (0.028 mmol) of tris(4-methoxyphenyl) phosphine, 30.0 mg (0.270 mmol) of **2** and 60.0 mg (0.540 mmol) of **1l** were reacted in 4 ml of toluene at 80 °C for 23 hours. Upon purification 35.9 mg (60%) of the desired product was isolated as a yellow oil: $R_f = 0.30$ (EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 3.59 (dm, 1H, $J = 2.1$ Hz), 3.52 (m, 1H), 3.45 (ddd, 1H, $J = 7.5, 9.8, 11.9$ Hz), 2.42 (m, 1H), 2.26 (dd, 1H, $J = 4.4, 16.0$ Hz), 2.05 – 2.20 (m, 5H), 1.96 (m, 1H), 1.74 (dddd, 1H, $J = 6.6, 9.5, 9.5, 12.3, 12.3$ Hz), 1.54 (dddd, 1H, $J = 7.1, 10.4, 11.7, 11.7$ Hz), 1.42 (m, 2H), 1.39 (m, 2H), 0.91 (t, 3H, $J = 7.4$ Hz), 0.89 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 165.1, 144.9, 130.8, 55.6, 44.7, 35.9, 35.2, 33.9, 28.4, 23.4, 23.3, 21.2, 14.4, 14.3; IR (NaCl, CHCl_3) 1655, 1603, 1521, 1419, 1045 cm^{-1} ; HRMS $[\text{C}_{14}\text{H}_{24}\text{NO}]^+$ calcd 222.1858. Found 222.1865 (FAB+).

6,7-dibutyl-2,3,8,8a-tetrahydroindolizin-5(1H)-one (3m).

According to the general procedure, in the presence of 5.3 mg (0.014 mmol) of $[\text{Rh}(\text{ethylene})_2\text{Cl}]_2$ and 9.5 mg (0.027 mmol) of tris(4-methoxyphenyl)

phosphine, 30.0 mg (0.270 mmol) of **2** and 75.0 mg (0.540 mmol) of **1m** were reacted in 4 ml of toluene at 80 °C for 23 hours. Upon purification 47.4 mg (70%) of the desired product was isolated as a yellow oil: $R_f = 0.64$ (EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 3.58 (dm, 1H, $J = 2.1$ Hz), 3.51 (m, 1H), 3.45 (ddd, 1H, $J = 7.7, 10.0, 11.9$ Hz), 2.41 (m, 1H), 2.25 (dd, 1H, $J = 4.7, 16.2$ Hz), 2.05 – 2.20 (m, 5H), 1.95 (m, 1H), 1.74 (dddd, 1H, $J = 6.6, 9.5, 9.5, 12.3, 12.3$ Hz), 1.53 (dddd, 1H, $J = 7.1, 10.0, 11.7, 11.7$ Hz), 1.27 – 1.38 (m, 8H), 0.89 (t, 3H, $J = 7.0$ Hz), 0.87 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 165.1, 144.8, 130.8, 55.6, 44.6, 35.3, 33.9, 33.6, 32.5, 30.2, 26.2, 23.3, 23.1, 22.9, 14.2; IR (NaCl, CHCl_3) 1644, 1598, 1521, 1440, 1045 cm^{-1} ; HRMS $[\text{C}_{16}\text{H}_{28}\text{NO}]^+$ calcd 250.2171. Found 250.2163 (FAB+).

5,6-dibutyl-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4m). From the same reaction, 8.2 mg (12%) of **4m** was also isolated as an oil: $R_f = 0.35$ (EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 3.60 (m, 1H), 3.54 (dm, 1H, $J = 2.3$ Hz), 3.45 (ddd, 1H, $J = 7.5, 9.8, 9.8$ Hz), 2.39 (dd, 1H, $J = 4.5, 15.8$ Hz), 2.26 – 2.33 (m, 2H), 2.18 (m, 3H), 2.03 (m, 1H), 1.81 (dddd, 1H, $J = 6.9, 9.2, 9.2, 12.2, 12.2$ Hz), 1.61 (dddd, 1H, $J = 7.2, 10.3, 11.8, 11.8$ Hz), 1.41 (m, 4H), 1.29 (m, 4H), 0.93 (t, 3H, $J = 7.0$ Hz), 0.87 (t, 3H, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 190.0, 161.8, 108.5, 58.2, 47.5, 42.1, 33.5, 32.8, 30.6, 30.3, 25.0, 23.8, 23.2, 23.1, 14.3, 14.0; IR (NaCl, CHCl_3) 1532, 1475, 1424, 1045 cm^{-1} ; HRMS $[\text{C}_{16}\text{H}_{28}\text{NO}]^+$ calcd 250.2171. Found 250.2159 (FAB+).

6,7-bis(2-(tert-butyldimethylsilyloxy)ethyl)-2,3,8,8a-tetrahydroindolizin-5(1H)-one (3n). According to the general procedure, in the presence of 5.3 mg (0.014 mmol) of $[\text{Rh}(\text{ethylene})_2\text{Cl}]_2$ and 9.5 mg (0.027 mmol) of tris(4-methoxyphenyl) phosphine, 30.0 mg (0.270 mmol) of **2** and 185.0 mg (0.540 mmol) of **1n** were reacted in 4 ml of toluene at 110 °C for 23 hours. Upon purification 68.4 mg (56%) of the desired product was isolated as a yellow oil: $R_f = 0.36$ (3:7 EtOAc/hex); ^1H NMR (400 MHz, CDCl_3) δ 3.67 (m, 4H), 3.56 (m, 1H), 3.52 (m, 1H), 3.44 (ddd, 1H, $J = 7.7, 9.8, 11.7$ Hz), 2.66 (m, 1H), 2.54 (dt, 1H, $J = 6.5, 13.0$ Hz), 2.48 (dt, 1H, $J = 7.2, 13.6$ Hz), 2.39 (dd, 1H, $J = 4.3, 15.8$ Hz), 2.38 (dd, 1H, $J = 13.2, 13.2$ Hz), 2.13 (m, 2H), 1.95 (m, 1H), 1.73 (dddd, 1H, $J = 6.6, 9.4, 9.4, 11.9, 11.9$ Hz), 1.53 (dddd, 1H, $J = 7.1, 10.0, 11.8, 11.8$ Hz), 0.85 (dm, 18H, $J = 1.9$ Hz), 0.01 (dm, 12H, $J = 2.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 164.6, 144.4, 128.5, 62.9, 61.9, 55.6, 44.6, 37.5, 36.2, 33.9, 30.4, 26.2, 26.1, 23.2, 18.5, 18.4, -5.1, -5.2; IR (NaCl, CHCl_3) 1650, 1609, 1527, 1419, 1086 cm^{-1} ; HRMS $[\text{C}_{24}\text{H}_{48}\text{Si}_2\text{NO}_3]^+$ calcd 454.3173. Found 454.3167 (FAB+).

2,3-dibutyl-7,8,9,9a-tetrahydro-1H-quinolizin-4(6H)-one (6m). According to the general procedure, in the presence of 5.3 mg (0.014 mmol) of $[\text{Rh}(\text{ethylene})_2\text{Cl}]_2$ and 9.5 mg (0.027 mmol) of tris(4-methoxyphenyl) phosphine, 30.0 mg (0.270 mmol) of **5** and 74.7 mg (0.540 mmol) of **1m** were reacted in 4 ml of toluene at 110 °C for 23 hours. Upon purification 44.1 mg (62%) of the desired product was isolated as a yellow oil: $R_f = 0.64$ (3:7 EtOAc/hex); ^1H NMR (400 MHz, CDCl_3) δ 4.44 (dm, 1H, $J = 13.6$ Hz), 3.23 (dddd, 1H, $J = 3.3, 5.6, 10.3, 10.3$ Hz), 2.47 (ddd, 1H, $J = 3.0, 13.0, 13.0$ Hz), 2.19 (dd, 1H, $J =$

5.8, 17.3 Hz), 2.28 (m, 2H), 2.07 – 2.15 (m, 3H), 1.76 (m, 1H), 1.70 (m, 1H), 1.68 (m, 1H), 1.26 – 1.43 (m, 11H), 0.89 (t, 3H, $J = 7.1$ Hz), 0.87 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 167.5, 145.5, 129.3, 54.1, 43.4, 35.5, 33.6, 33.4, 32.6, 30.1, 26.6, 25.0, 23.9, 23.2, 23.0, 14.2, 14.2; IR (NaCl, CHCl_3) 1660, 1609, 1521, 1429, 1332, 1045 cm^{-1} ; HRMS $[\text{C}_{17}\text{H}_{30}\text{NO}]^+$ calcd 264.2327. Found 264.2326 (FAB+).

3,4-dibutyl-7,8,9,9a-tetrahydro-1H-quinolizin-2(6H)-one (7m). From the same reaction, 13.2 mg (18%) of **7m** was also isolated as a yellow oil: $R_f = 0.24$ (3:7 EtOAc/hex); ^1H NMR (400 MHz, CDCl_3) δ 3.74 (dm, 1H, $J = 13.0$ Hz), 3.15 (dddd, 1H, $J = 3.6, 5.1, 11.1, 11.1$ Hz), 2.69 (ddd, 1H, $J = 2.6, 12.6, 12.6$ Hz), 2.44 (dd, 1H, $J = 5.4, 16.1$ Hz) 2.21 – 2.38 (m, 4H), 2.13 (m, 1H), 1.79 (m, 1H), 1.70 (m, 1H), 1.48 – 1.60 (m, 3H), 1.41 (m, 5H), 1.27 (m, 4H), 0.93 (t, 3H, $J = 7.0$ Hz), 0.87 (t, 3H, $J = 6.9$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 191.3, 163.6, 112.4, 58.2, 49.0, 43.3, 33.2, 31.7, 30.9, 29.4, 26.4, 25.4, 24.0, 23.2, 23.1, 14.3, 14.0; IR (NaCl, CHCl_3) 1603, 1527, 1419, 1040 cm^{-1} ; HRMS $[\text{C}_{17}\text{H}_{30}\text{NO}]^+$ calcd 264.2327. Found 264.2331 (FAB+).

2,3-bis(2-(tert-butyl)dimethylsilyloxy)ethyl-7,8,9,9a-tetrahydro-1H-quinolizin-4(6H)-one (6n). According to the general procedure, in the presence of 5.3 mg (0.014 mmol) of $[\text{Rh}(\text{ethylene})_2\text{Cl}]_2$ and 9.5 mg (0.027 mmol) of tris(4-methoxyphenyl) phosphine, 30.0 mg (0.270 mmol) of **5** and 185.0 mg (0.540 mmol) of **1n** were reacted in 4 ml of toluene at 110 °C for 23 hours. Upon purification 71.1 mg (56%) of the desired product was isolated as an oil: $R_f = 0.74$ (3:7 EtOAc/hex); ^1H NMR (400 MHz, CDCl_3) δ 4.43 (dm, 1H, $J = 13.4$ Hz), 3.69 (m, 2H), 3.63 (m, 2H), 3.23 (dddd, 1H, $J = 3.2, 5.6, 10.5, 10.5$ Hz), 2.36 – 2.61 (m, 6H), 2.18 (dd, 1H, $J = 10.9, 17.3$ Hz), 1.76 (m, 1H), 1.71 (m, 1H), 1.68 (m, 1H), 1.30 – 1.46 (m, 3H), 0.85 (dm, 18H, $J = 3.2$ Hz), 0.08 (dm, 12H, $J = 6.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 167.1, 145.2, 127.0, 62.9, 61.7, 54.0, 43.3, 37.5, 36.5, 33.4, 30.7, 26.2, 26.1, 25.0, 23.8, 18.5, 18.4, -5.1, -5.2; IR (NaCl, CHCl_3) 1660, 1609, 1521, 1475, 1424, 1086, 1045 cm^{-1} ; HRMS $[\text{C}_{25}\text{H}_{50}\text{Si}_2\text{NO}_3]^+$ calcd 468.3329. Found 468.3324 (FAB+).

6-methyl-7-phenyl-2,3,8,8a-tetrahydroindolizin-5(1H)-one (3o). According to the general procedure, in the presence of 6.7 mg (0.0135 mmol) of $[\text{Rh}(\text{COD})\text{Cl}]_2$ and 9.5 mg (0.027 mmol) of tris(4-methoxyphenyl) phosphine, 30.0 mg (0.270 mmol) of **2** and 63.0 mg (0.540 mmol) of **1o** were reacted in 4 ml of toluene at 110 °C for 23 hours. Upon purification 21.2 mg (34%) of **3o** was isolated as a yellow oil: $R_f = 0.30$ (EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 7.34 (br t, 2H, $J = 7.5$ Hz), 7.27 (m, 1H), 7.17 (m, 2H), 3.77 (dddd, 1H, $J = 5.1, 5.1, 10.2, 14.9$ Hz), 3.64 (ddd, 1H, $J = 2.1, 9.2, 11.4$ Hz), 3.52 (ddd, 1H, $J = 7.6, 10.0, 11.8$ Hz), 2.60 (dd, 1H, $J = 4.7, 16.2$ Hz), 2.49 (ddq, 1H, $J = 2.1, 4.8, 16.4$ Hz), 2.19 (m, 1H), 2.02 (m, 1H), 1.85 (d, 3H, $J = 2.1$), 1.79 (m, 1H), 1.60 (dddd, 1H, $J = 7.0, 9.8, 11.7, 11.7$); ^{13}C NMR (100 MHz, CDCl_3) δ 165.3, 143.6, 141.0, 130.5, 128.5, 127.9, 127.7, 127.1, 56.0, 44.8, 37.5, 33.9, 23.3, 14.0; IR (NaCl, CHCl_3) 1644, 1608, 1445, 1378, 1091 cm^{-1} ; HRMS $[\text{C}_{15}\text{H}_{18}\text{NO}]^+$ calcd 228.1388. Found 228.1400 (FAB+).

Regiochemistry: Isolated as a single regioisomer. Assigned based on the observation of the proton coupling between the methyl group and the hydrogen at 2.49 ppm, and the 2D-NOESY.

6-methyl-5-phenyl-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4o). From the same reaction, 15.7 mg (26%) of **4o** was also isolated as a waxy yellow solid: $R_f = 0.16$ (EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 7.39 (m, 3H), 7.18 (dm, 2H, $J = 6.4$ Hz), 3.88 (dddd, 1H, $J = 6.6, 6.6, 6.6, 14.9$ Hz), 3.17 (ddd, 1H, $J = 3.4, 7.7, 10.9$ Hz), 3.03 (ddd, 1H, $J = 7.9, 7.9, 10.7$ Hz), 2.51 (dd, 1H, $J = 6.2, 16.0$ Hz), 2.46 (dd, 1H, $J = 16.0, 16.0$ Hz), 2.27 (m, 1H), 1.90 (m, 1H), 1.64 – 1.81 (m, 2H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.5, 160.4, 136.1, 129.0, 128.9, 127.8, 125.9, 104.2, 58.0, 49.5, 41.9, 32.8, 24.2, 11.9; IR (NaCl, CHCl_3) 1615, 1535, 1469, 1375, 1295, 1098 cm^{-1} ; HRMS $[\text{C}_{15}\text{H}_{18}\text{NO}]^+$ calcd 228.1388. Found 228.1387 (FAB+).

Regiochemistry: Regiochemistry > 95:5 indicated by ^1H NMR and GC-MS. Assigned based on 2D-NOESY.

6-ethyl-7-phenyl-2,3,8,8a-tetrahydroindolizin-5(1H)-one (3p). According to the general procedure, in the presence of 6.7 mg (0.014 mmol) of $[\text{Rh}(\text{COD})\text{Cl}]_2$ and 9.5 mg (0.027 mmol) of tris(4-methoxyphenyl) phosphine, 30.0 mg (0.270 mmol) of **2** and 70.3 mg (0.540 mmol) of **1p** were reacted in 4 ml of toluene at 110 $^\circ\text{C}$ for 23 hours. Upon purification 13.7 mg (21%) of **3p** was isolated as a yellow oil: $R_f = 0.45$ (EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 7.35 (tm, 2H, $J = 7.3$ Hz), 7.27 (m, 1H), 7.16 (m, 2H), 3.78 (dddd, 1H, $J = 5.8, 7.9, 10.5, 10.5$ Hz), 3.67 (ddd, 1H, $J = 2.2, 9.0, 11.7$ Hz), 3.53 (ddd, 1H, $J = 7.5, 10.0, 11.9$ Hz), 2.52 (m, 2H), 2.44 (m, 1H), 2.10 – 2.22 (m, 2H), 2.02 (dddd, 1H, $J = 2.1, 2.1, 7.5, 7.5, 14.7$ Hz), 1.80 (dddd, 1H, $J = 6.6, 9.8, 9.8, 11.9, 11.9$ Hz), 1.60 (dddd, 1H, $J = 7.0, 10.0, 11.7, 11.7$), 0.97 (t, 3H, $J = 7.5$); ^{13}C NMR (100 MHz, CDCl_3) δ 164.6, 143.6, 141.2, 134.3, 128.6, 127.6, 127.4, 55.8, 44.8, 37.9, 33.9, 23.3, 20.9, 14.9; IR (NaCl, CHCl_3) 1644, 1609, 1521, 1450, 1045 cm^{-1} ; HRMS $[\text{C}_{16}\text{H}_{20}\text{NO}]^+$ calcd 242.1545. Found 242.1544 (FAB+).

Regiochemistry: Assigned based on **3o**.

6-ethyl-5-phenyl-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4p). From the same reaction, 27.5 mg (42%) of **4p** was also isolated as a waxy yellow solid: $R_f = 0.30$ (EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 7.39 (m, 3H), 7.19 (m, 2H), 3.85 (dddd, 1H, $J = 6.0, 6.0, 9.0, 12.2$ Hz), 3.09 (ddd, 1H, $J = 3.0, 7.9, 11.1$ Hz), 3.00 (m, 1H), 2.51 (dd, 1H, $J = 6.0, 16.0$ Hz), 2.46 (dd, 1H, $J = 15.8, 15.8$ Hz), 2.26 (m, 1H), 1.81 – 2.00 (m, 3H), 1.72 (m, 1H), 0.77 (t, 3H, $J = 7.5$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 191.0, 160.6, 136.0, 129.0, 128.9, 128.8, 127.5, 126.1, 111.1, 58.1, 49.3, 42.2, 33.0, 24.0, 19.4, 15.6; IR (NaCl, CHCl_3) 1614, 1527, 1455, 1414, 1265, 1158 cm^{-1} ; HRMS $[\text{C}_{16}\text{H}_{20}\text{NO}]^+$ calcd 242.1545. Found 242.1543 (FAB+).

Regiochemistry: Assigned based on **4o**. Regioselectivity of both **3p** and **4p** ~ 10 :1. Two minor isomers isolated with the **4p** batch. According to GC-MS and proton NMR, ratio of **3p** : **4p** : isomer 1 : isomer 2 = 8.9 : 15 : 1.5 : 1.

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

X-ray data of **4a** is attached following the spectra:

STANDARD 1H OBSERVE

yul-280

13C OBSERVE

yul-280

STANDARD 1H OBSERVE

yu2-86

13C OBSERVE

yu2-86

4a

yul-272-cosy_07Dec2004
yul-272

¹³C OBSERVE
yul-272

STANDARD 1H OBSERVE

yul-456

13C OBSERVE

yul-456

STANDARD 1H OBSERVE

yul-385

13C OBSERVE

yul-385

yu1-475

¹³C OBSERVE

yu1-475

STANDARD 1H OBSERVE

yu1-441

13C OBSERVE

yu1-441

STANDARD 1H OBSERVE
yu1-502

13C OBSERVE
yu1-502

STANDARD 1H OBSERVE

yul-396

13C OBSERVE

yul-396

3h/4h 1 : 1.3

STANDARD 1H OBSERVE

yu1-421

13C OBSERVE

yu1-421

¹³C OBSERVE
 yu1-463-1

STANDARD 1H OBSERVE

yu1-463-2

13C OBSERVE

yu1-463-2

4j

STANDARD 1H OBSERVE

yul-503

13C OBSERVE

yul-503

4k

STANDARD 1H OBSERVE

yu2-50

13C OBSERVE

yu2-50

STANDARD 1H OBSERVE

yu1-403

¹³C OBSERVE

yu1-403

STANDARD 1H OBSERVE

yu1-425

13C OBSERVE

yu1-425

STANDARD 1H OBSERVE

yu2-112-2

13C OBSERVE

yu2-112-2

STANDARD 1H OBSERVE

yu2-88-1

13C OBSERVE

yu2-88-1

STANDARD 1H OBSERVE

yu2-88-2

13C OBSERVE

yu2-88-2

yu1-341-1

13C OBSERVE

yu1-341-1c

yu2-177-lnosey_13Jan2006

Automation directory:

Pulse Sequence: NOESY

4o

STANDARD 1H OBSERVE

yul-341-2

13C OBSERVE

yul-341-2c

yu2-177-2noscy_13Jan2006-14:06:02

Automation directory:

Pulse Sequence: NOESY

¹³C OBSERVE
 yu1-379-1c

¹³C OBSERVE
 yu1-379-2c

X-ray data of **4a**:

Table 1. Crystal data and structure refinement for rovis11m.

Identification code	rovis11m	
Empirical formula	C ₂₀ H ₁₉ N O	
Formula weight	289.36	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P2(1)/C	
Unit cell dimensions	a = 9.656(2) Å	α = 90°.
	b = 10.634(2) Å	β = 103.175(5)°.
	c = 15.602(4) Å	γ = 90°.
Volume	1559.9(6) Å ³	
Z	4	
Density (calculated)	1.232 Mg/m ³	
Absorption coefficient	0.075 mm ⁻¹	
F(000)	616	
Crystal size	0.08 x 0.20 x 0.40 mm ³	
Theta range for data collection	2.17 to 17.99°.	
Index ranges	-8 ≤ h ≤ 8, -9 ≤ k ≤ 9, -13 ≤ l ≤ 13	
Reflections collected	5581	
Independent reflections	1077 [R(int) = 0.0845]	
Completeness to theta = 17.99°	100.0 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1077 / 0 / 200	
Goodness-of-fit on F ²	1.025	
Final R indices [I > 2σ(I)]	R1 = 0.0504, wR2 = 0.1195	
R indices (all data)	R1 = 0.0869, wR2 = 0.1404	
Extinction coefficient	0.0008(13)	
Largest diff. peak and hole	0.174 and -0.158 e. Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\approx^2 \times 10^3$) for rovis11m. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	2611(5)	1843(5)	-469(3)	87(2)
N(1)	3157(5)	4609(5)	1339(4)	54(2)
C(1)	2597(8)	6282(7)	290(3)	38(2)
C(2)	3763(7)	7055(8)	391(3)	54(2)
C(3)	3573(9)	8326(8)	206(4)	66(2)
C(4)	2248(12)	8832(7)	-65(4)	70(2)
C(5)	1102(8)	8062(8)	-156(4)	65(2)
C(6)	1270(8)	6792(7)	14(4)	54(2)
C(7)	2770(6)	4908(7)	477(6)	40(2)
C(8)	2514(6)	4012(7)	-178(4)	41(2)
C(9)	2065(8)	4333(7)	-1114(5)	47(2)
C(10)	2741(7)	5229(7)	-1522(5)	60(2)
C(11)	2251(10)	5533(6)	-2396(6)	76(2)
C(12)	1075(11)	4954(8)	-2893(5)	79(2)
C(13)	393(7)	4043(8)	-2515(6)	76(2)
C(14)	881(8)	3736(6)	-1639(6)	62(2)
C(15)	2753(7)	2708(8)	65(4)	59(2)
C(16)	3316(9)	2434(7)	1018(6)	103(3)
C(17)	3123(9)	3309(8)	1622(5)	99(3)
C(18)	3677(7)	3332(6)	2583(4)	70(2)
C(19)	3399(8)	4625(7)	2871(4)	100(3)
C(20)	3353(7)	5465(6)	2092(4)	66(2)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for rovisl1m.

O(1)-C(15)	1.228(7)
N(1)-C(7)	1.349(6)
N(1)-C(17)	1.453(7)
N(1)-C(20)	1.465(7)
C(1)-C(6)	1.367(7)
C(1)-C(2)	1.374(7)
C(1)-C(7)	1.492(8)
C(2)-C(3)	1.386(8)
C(3)-C(4)	1.363(8)
C(4)-C(5)	1.358(8)
C(5)-C(6)	1.379(8)
C(7)-C(8)	1.377(7)
C(8)-C(15)	1.442(8)
C(8)-C(9)	1.466(8)
C(9)-C(10)	1.389(7)
C(9)-C(14)	1.399(7)
C(10)-C(11)	1.376(8)
C(11)-C(12)	1.367(8)
C(12)-C(13)	1.378(8)
C(13)-C(14)	1.379(8)
C(15)-C(16)	1.492(9)
C(16)-C(17)	1.367(8)
C(17)-C(18)	1.472(8)
C(18)-C(19)	1.490(7)
C(19)-C(20)	1.501(7)
C(7)-N(1)-C(17)	120.5(5)
C(7)-N(1)-C(20)	127.5(6)
C(17)-N(1)-C(20)	110.8(6)
C(6)-C(1)-C(2)	118.9(6)
C(6)-C(1)-C(7)	120.3(7)
C(2)-C(1)-C(7)	120.7(7)
C(1)-C(2)-C(3)	119.5(6)
C(4)-C(3)-C(2)	121.4(7)

C(5)-C(4)-C(3)	118.6(7)
C(4)-C(5)-C(6)	120.9(7)
C(1)-C(6)-C(5)	120.6(6)
N(1)-C(7)-C(8)	122.6(6)
N(1)-C(7)-C(1)	114.8(6)
C(8)-C(7)-C(1)	122.6(7)
C(7)-C(8)-C(15)	118.7(6)
C(7)-C(8)-C(9)	122.7(7)
C(15)-C(8)-C(9)	118.6(6)
C(10)-C(9)-C(14)	116.7(6)
C(10)-C(9)-C(8)	123.6(7)
C(14)-C(9)-C(8)	119.7(7)
C(11)-C(10)-C(9)	121.7(6)
C(12)-C(11)-C(10)	120.6(7)
C(11)-C(12)-C(13)	119.4(7)
C(12)-C(13)-C(14)	120.1(7)
C(13)-C(14)-C(9)	121.5(6)
O(1)-C(15)-C(8)	123.8(6)
O(1)-C(15)-C(16)	119.2(7)
C(8)-C(15)-C(16)	116.7(6)
C(17)-C(16)-C(15)	118.6(6)
C(16)-C(17)-N(1)	115.0(6)
C(16)-C(17)-C(18)	129.6(8)
N(1)-C(17)-C(18)	105.4(6)
C(17)-C(18)-C(19)	105.9(5)
C(18)-C(19)-C(20)	106.1(5)
N(1)-C(20)-C(19)	104.8(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\approx 2 \times 10^3$) for rovis11m. 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}
O(1)	150(5)	44(3)	69(4)	-10(3)	28(3)	-6(3)
N(1)	74(4)	37(5)	46(5)	0(4)	3(3)	-3(3)
C(1)	44(6)	33(6)	34(4)	-4(3)	5(4)	-9(5)
C(2)	62(6)	48(6)	50(5)	2(4)	7(4)	-5(5)
C(3)	84(8)	52(7)	58(5)	-4(4)	7(5)	-22(5)
C(4)	116(8)	31(5)	59(5)	2(4)	12(5)	-3(6)
C(5)	80(7)	46(6)	65(5)	5(4)	7(4)	12(5)
C(6)	57(6)	47(6)	57(5)	8(4)	10(4)	0(5)
C(7)	38(4)	34(6)	47(6)	4(5)	8(4)	-7(4)
C(8)	49(4)	30(6)	41(6)	0(5)	7(4)	-4(3)
C(9)	51(5)	42(5)	45(6)	-8(5)	7(5)	1(4)
C(10)	75(5)	50(5)	55(6)	-1(4)	17(5)	-5(4)
C(11)	110(7)	73(5)	46(6)	8(5)	23(5)	-9(6)
C(12)	94(7)	89(7)	50(5)	-7(5)	8(6)	8(5)
C(13)	64(6)	100(7)	61(7)	-11(5)	12(5)	-8(5)
C(14)	68(6)	76(5)	46(6)	-5(5)	23(4)	4(5)
C(15)	85(6)	56(7)	40(6)	3(5)	23(4)	-12(5)
C(16)	189(9)	41(5)	81(7)	5(6)	36(6)	6(5)
C(17)	188(9)	46(7)	54(7)	14(5)	9(5)	19(5)
C(18)	91(6)	62(6)	55(6)	17(4)	14(4)	2(4)
C(19)	166(8)	76(6)	54(5)	17(5)	18(5)	26(6)
C(20)	90(6)	54(5)	50(5)	1(5)	7(4)	-3(4)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\approx^2 \times 10^{-3}$) for rovis11m.

	x	y	z	U(eq)
H(2)	4674	6727	582	65
H(3)	4365	8844	267	80
H(4)	2131	9687	-186	84
H(5)	191	8396	-334	78
H(6)	473	6277	-61	65
H(10)	3544	5633	-1197	72
H(11)	2725	6139	-2651	91
H(12)	739	5173	-3481	95
H(13)	-398	3634	-2851	91
H(14)	412	3117	-1393	74
H(16A)	2886	1654	1151	123
H(16B)	4329	2283	1109	123
H(17)	2104	3207	1590	118
H(18A)	4688	3152	2730	83
H(18B)	3194	2712	2865	83
H(19A)	4151	4887	3364	120
H(19B)	2501	4654	3050	120
H(20A)	2568	6054	2021	79
H(20B)	4233	5933	2159	79