Supporting Information

Rhodium-Catalyzed Cycloisomerization of *N*-Propargyl Enamine Derivatives

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General: Unless otherwise noted, all reactions were conducted as described under an argon atmosphere using anhydrous solvent (either distilled or passed through an activated alumina column or activated molecular sieves column). Commercially available reagents were used without further purification. Thin layer chromatography (TLC) was performed using EM Science silica gel 60 F_{254} plates and visualized by using UV light and/or anisaldehyde, ceric sulfate or potassium permanganate stains. Flash chromatography was performed on EM Science silica gel 60 (40-63 μm) using the indicated solvent system. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, unless otherwise noted, on a Varian Mercury 300 MHz or a Varian Inova 400 MHz or a Varian Inova 500 MHz spectrometer. Chemical shifts in ^{1}H NMR spectra were reported in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.27 ppm). Data for ^{1}H NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hertz (Hz) and integration. Data for ^{13}C

NMR spectra are reported in terms of chemical shift in ppm from the central peak of $CDCl_3$ (77.23 ppm). Infrared (IR) spectra were recorded on a Nicolet 730 FT-IR spectrometer and reported in frequency of the absorption (cm^{-1}). High resolution mass spectra (HRMS) were obtained from the Princeton University Mass Spectrometry Facility and the Scripps Center for Mass Spectrometry.

Preparation of Cyclization Substrates: Substrates **1**, **3a-c**, **4-6**, **10** and **11** were prepared by condensation of the appropriate ketone with the corresponding propargyl amine followed by acylation according to the procedure as described by Rutjes et al.[1] Substrates **7** and **8** were prepared similarly from the corresponding secondary amine and ethyl propiolate based on methods of Lee et al.[2] Substrate **9** was prepared from tetronic acid and the corresponding propargyl benzyl amine in a similar fashion as reported by Hsung et al.[3]

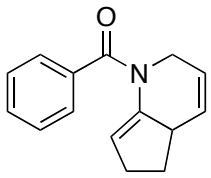
Representative cyclization procedure at room temperature: To a flame dried 1 dram glass vial equipped with a screw-cap and Teflon septum was added $[Rh(C_2H_2)_2Cl]_2$ (3.9 mg, 0.0099 mmol), $P(4\text{-}F\text{-}C_6H_4)_3$ (15.8 mg, 0.0499 mmol) and DMF (0.50 mL). This mixture was stirred for 15 min before *N*-propargyl enamine **1** (42 mg, 0.20 mmol) in DMF (0.50 mL) was added *via* syringe. DABCO (23 mg, 0.20 mmol) was then added to the reaction mixture in one portion. The syringe previously used for the addition was washed with DMF (0.50 mL * 2). After stirring for 24 h at room temperature, the reaction

[1] Kinderman, S. S.; van Maarseveen, J. H.; Schoemaker, H. E.; Hiemstra, H.; Rutjes, F. P. J. T. *Org. Lett.* **2001**, *3*, 2045.
[2] Lee, E.; Kang, T. S.; Joo, B. J.; Tae, J. S.; Li, K. S.; Chung, C. K. *Tetrahedron Lett.* **1995**, *36*, 417.
[3] Sydorenko, N.; Hsung, R. P.; Darwish, O. S.; Hahn, J. M.; Liu, J. *J. Org. Chem.* **2004**, *69*, 6732.

mixture was loaded directly onto a silica gel column. Purification *via* flash column chromatography (Hexanes: Ethyl Acetate = 8:1) yielded **2** (40 mg, 0.19 mmol) as a faint yellow, clear oil.

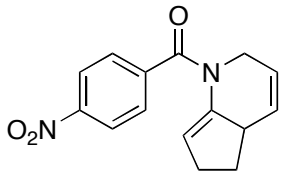
No reaction occurred in a control experiment which employed all of the above reagents except for the rhodium complex, $[Rh(C_2H_2)_2Cl]_2$.

Representative cyclization procedure at 85 ºC: To a flame dried 1 dram glass vial equipped with a screw-cap and Teflon septum was added $[Rh(C_2H_2)_2Cl]_2$ (3.9 mg, 0.0099 mmol), $P(4\text{-}F\text{-}C_6H_4)_3$ (15.8 mg, 0.0499 mmol) and DMF (0.50 mL). This mixture was stirred for 15 min before *N*-propargyl enamine **1** (42 mg, 0.20 mmol) in DMF (0.50 mL) was added *via* syringe. DABCO (23 mg, 0.20 mmol) was then added to the reaction mixture in one portion. The syringe previously used for the addition was washed with DMF (0.50 mL * 2). The vial was then moved to a pre-heated sand-bath at 85 ºC and stirred for 24 h. After 24 h, the reaction mixture was loaded directly onto a silica gel column. Purification *via* flash column chromatography (Hexanes: Ethyl Acetate = 8:1) yielded **2** (40 mg, 0.19 mmol) as a faint yellow, clear oil.

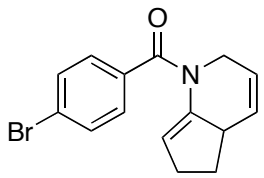


(5,6-Dihydro-2*H*-cyclopenta[*b*]pyridin-1(4a*H*)-yl)(phenyl)methanone (2, Table 1). IR (film) 3032, 2930, 2849, 1638, 1398, 1274, 790, 717, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51-7.48 (m, 2H), 7.42-7.31 (m, 3H), 5.85-5.81 (m, 1H), 5.72-5.68 (m, 1H), 4.66 (s, 1H), 4.46 (ddd, *J* = 18.8, 6.0, 3.2 Hz, 1H), 3.99-3.92 (m, 1H), 3.39-3.36 (m, 1H),

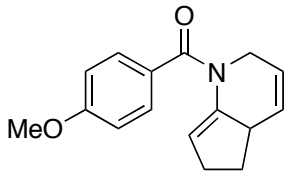
2.22-2.05 (m, 3H), 1.47-1.37 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 140.3, 135.6, 130.2, 129.5, 127.8, 121.6, 119.7, 88.8, 46.2, 42.0, 29.8, 29.5; HRMS (ESI-TOF) Calc'd for $C_{15}H_{16}NO$ [MH^+] 226.1226, Found 226.1225.



(5,6-Dihydro-2*H*-cyclopenta[*b*]pyridin-1(4a*H*)-yl)(4-nitrophenyl)methanone (12a, Table 2, entry 1). Following the room temperature procedure, $[Rh(C_2H_2)_2Cl]_2$ (3.9 mg, 0.0099 mmol), P(4-F-C_6H_4)$_3$ (15.8 mg, 0.0499 mmol), DABCO (23 mg, 0.20 mmol) and **3a** (54 mg, 0.20 mmol) were reacted in DMF (2.0 mL, 0.10 M) to give **12a** (44 mg, 0.16 mmol) as a thick, yellow clear oil after purification by flash column chromatography (Hexanes: Ethyl Acetate = 4:1): IR (film) 3072, 2931, 2850, 1639, 1522, 1346, 1107, 849, 725 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (dt, J = 9.1, 2.2 Hz, 2H), 7.65 (dt, J = 9.2, 2.4 Hz, 2H), 5.88-5.82 (m, 1H), 5.74-5.67 (m, 1H), 4.64 (s, 1H), 4.48 (dd, J = 18.7, 2.2 Hz, 1H), 4.01-3.92 (m, 1H), 3.40-3.36 (m, 1H), 2.25-2.03 (m, 3H), 1.53-1.38 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 148.6, 141.8, 139.9, 129.5, 128.8, 123.3, 121.2, 121.0, 46.2, 41.9, 29.8, 29.5; HRMS (ESI-TOF) Calc'd for $C_{15}H_{15}N_2O_3$ [MH^+] 271.1077, Found 271.1079.

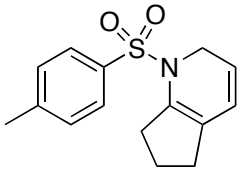


(4-Bromophenyl)(5,6-dihydro-2*H*-cyclopenta[*b*]pyridin-1(4a*H*)-yl)methanone (12b, Table 2, entry 1). Following the room temperature procedure, $[Rh(C_2H_2)_2Cl]_2$ (3.9 mg, 0.0099 mmol), P(4-F-C_6H_4)$_3$ (15.8 mg, 0.0499 mmol), DABCO (23 mg, 0.20 mmol) and **3b** (61 mg, 0.20 mmol) were reacted in DMF (2.0 mL, 0.10 M) to give **12b** (55 mg, 0.18 mmol) as a yellow, clear oil after purification by flash column chromatography (Hexanes: Ethyl Acetate = 8:1): IR (film) 3033, 2931, 2848, 1638, 1400, 1012, 838, 751 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49-7.45 (m, 2H), 7.39-7.35 (m, 2H), 5.86-5.80 (m, 1H), 5.72-5.66 (m, 1H), 4.67 (s, 1H), 4.46 (ddd, *J* = 18.8, 6.0, 3.2 Hz, 1H), 3.99-3.92 (m, 1H), 3.39-3.36 (m, 1H), 2.22-2.09 (m, 3H), 1.45-1.38 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 140.2, 134.4, 131.1, 129.6, 129.5, 124.6, 121.5, 120.2, 46.3, 42.0, 29.8, 29.5; HRMS (ESI-TOF) Calc'd for $C_{15}H_{15}BrNO$ [MH^+] 304.0331, Found 304.0330.

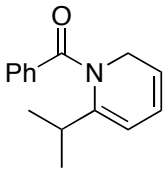


(5,6-Dihydro-2*H*-cyclopenta[*b*]pyridin-1(4a*H*)-yl)(4-methoxyphenyl)methanone (12c, Table 2, entry 1). Following the room temperature procedure, $[Rh(C_2H_2)_2Cl]_2$ (3.9 mg, 0.0099 mmol), P(4-F-C_6H_4)$_3$ (15.8 mg, 0.0499 mmol), DABCO (23 mg, 0.20 mmol) and **3c** (51 mg, 0.20 mmol) were reacted in DMF (2.0 mL, 0.10 M) to give **12c** (47 mg, 0.19 mmol) as a yellow, clear oil after purification by flash column chromatography (Hexanes: Ethyl Acetate = 4:1): IR (film) 3072, 2931, 2850, 1639, 1522, 1346, 1107, 849, 725 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.21 (dt, *J* = 9.1, 2.2 Hz, 2H), 7.65 (dt, *J* = 9.2, 2.4 Hz, 2H), 5.88-5.82 (m, 1H), 5.74-5.67 (m, 1H), 4.64 (s, 1H), 4.48 (dd, *J* = 18.7,

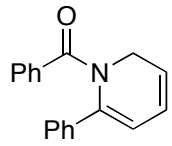
2.2 Hz, 1H), 4.01-3.92 (m, 1H), 3.40-3.36 (m, 1H), 2.25-2.03 (m, 3H), 1.53-1.38 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 148.6, 141.8, 139.9, 129.5, 128.8, 123.3, 121.2, 121.0, 55.2, 46.2, 41.9, 29.8, 29.5; HRMS (ESI-TOF) Calc'd for $C_{16}H_{18}NO_2$ [MH^+] 256.1332, Found 256.1329.



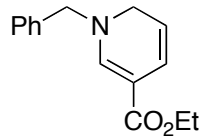
1-(Toluene-4-sulfonyl)-2,5,6,7-tetrahydro-1*H*-cyclopenta[*b*]pyridine (13, Table 2, entry 2). Following the room temperature procedure, $[Rh(C_2H_2)_2Cl]_2$ (3.9 mg, 0.0099 mmol), P(4-F-C_6H_4)$_3$ (15.8 mg, 0.0499 mmol), DABCO (23 mg, 0.20 mmol) and **4** (55 mg, 0.20 mmol) were reacted in DMF (2.0 mL, 0.10 M) to give **13** (46 mg, 0.17 mmol) as a yellow, clear oil after purification by flash column chromatography (Hexanes: Ethyl Acetate = 2:1): IR (film) 3064, 2925, 2854, 1595, 1352, 1165, 1087, 814, 668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 5.72 (d, J = 10 Hz, 1H), 5.25 (m, 1H), 4.34 (dd, J = 4.0, 0.8 Hz, 2H), 2.80 (t, J = 7.5 Hz, 2H), 2.40 (s, 3H), 2.36-2.32 (m, 2H), 1.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 136.9, 136.6, 129.3, 126.9, 123.7, 116.6, 46.8, 33.5, 30.6, 21.6, 21.5; HRMS (ESI-TOF) Calc'd for $C_{15}H_{18}NO_2S$ [MH^+] 276.1053, Found 276.1051.



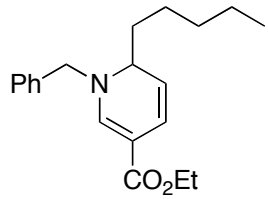
(6-Iso-propylpyridin-1(2*H*)-yl)(phenyl)methanone (14, Table 2, entry 3). Following the room temperature procedure, $[Rh(C_2H_2)_2Cl]_2$ (3.9 mg, 0.0099 mmol), P(4-F-$C_6H_4)_3$ (15.8 mg, 0.0499 mmol), DABCO (23 mg, 0.20 mmol) and **5** (45 mg, 0.20 mmol) were reacted in DMF (2.0 mL, 0.10 M) to give **14** (37 mg, 0.16 mmol) as a yellow, clear oil after purification by flash column chromatography (Hexanes: Ethyl Acetate = 8:1): IR (film) 3060, 2966, 2873, 1634, 1381, 1265, 1106, 711, 679 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.56-7.52 (m, 2H), 7.48-7.36 (m, 3H), 6.12-6.06 (m, 1H), 5.77-5.71 (m, 2H), 4.31 (d, *J* = 2.8 Hz, 2H), 2.40-2.20 (s, 1H), 0.99 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 148.9, 136.5, 130.7, 128.3, 128.1, 124.0, 121.5, 111.3, 44.7, 31.8, 21.9; HRMS (ESI-TOF) Calc'd for $C_{15}H_{18}NO$ $[MH^+]$ 228.1383, Found 228.1382.



Phenyl(6-phenylpyridin-1(2*H*)-yl)methanone (15, Table 2, entry 4). Following the room temperature procedure, $[Rh(C_2H_2)_2Cl]_2$ (3.9 mg, 0.0099 mmol), P(4-F-$C_6H_4)_3$ (15.8 mg, 0.0499 mmol), DABCO (23 mg, 0.20 mmol) and **6** (52 mg, 0.20 mmol) were reacted in DMF (2.0 mL, 0.10 M) to give **15** (35 mg, 0.13 mmol) as a yellow, clear oil after purification by flash column chromatography (Hexanes: Ethyl Acetate = 8:1): IR (film) 3059, 1715, 1650, 1637, 1268, 1110, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48-7.23 (m, 4H), 7.18-6.90 (m, 6H), 6.28-6.22 (m, 1H), 6.05-5.80 (m, 2H), 4.60 (s, 2H); ^{13}C NMR (100Hz, $CDCl_3$) δ 178.0, 148.2, 140.8, 130.2, 128.2, 128.1, 127.6, 126.6, 124.6, 114.2, 100.0, 44.6; HRMS (EI) Calc'd for $C_{18}H_{15}NO$ $[M^+]$ 261.1154, Found 261.1148.

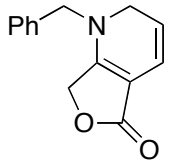


Ethyl 1-benzyl-1,6-dihydropyridine-3-carboxylate (16, Table 2, entry 5). Following the 85 ºC procedure, $[Rh(C_2H_2)_2Cl]_2$ (3.9 mg, 0.0099 mmol), P(4-F-$C_6H_4)_3$ (15.8 mg, 0.0499 mmol), DABCO (23 mg, 0.20 mmol) and **7** (49 mg, 0.20 mmol) were reacted in DMF (2.0 mL, 0.10 M) to give **16** (26 mg, 0.11 mmol) as a brown, clear oil after purification by flash column chromatography (Hexanes: Ethyl Acetate = 8:1): IR (film) 2990, 1678, 1594, 1395, 1285, 1161, 1076, 1028, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.25 (m, 5H), 7.13 (s, 1H), 5.69 (dd, *J* = 7.2, 1.2 Hz, 1H), 4.79 (dt, *J* = 7.5, 3.2 Hz, 1H), 4.30 (s, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.14 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 141.7, 137.3, 128.8, 128.3, 127.8, 127.0, 105.0, 97.7, 59.5, 57.3, 22.1, 14.5; HRMS (ESI-TOF) Calc'd for $C_{15}H_{18}NO_2$ [MH^+] 244.1332, Found 244.1334.

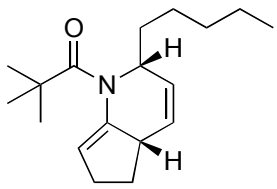


Ethyl 1-benzyl-6-pentyl-1,6-dihydropyridine-3-carboxylate (17, Table 2, entry 6). Following the 85 ºC procedure, $[Rh(C_2H_2)_2Cl]_2$ (3.9 mg, 0.0099 mmol), P(4-F-$C_6H_4)_3$ (15.8 mg, 0.0499 mmol), DABCO (23 mg, 0.20 mmol) and **8** (63 mg, 0.20 mmol) were reacted in DMF (2.0 mL, 0.10 M) to give **17** (43 mg, 0.14 mmol) as a brown, clear oil after purification by flash column chromatography (Hexanes: Ethyl Acetate = 8:1): IR (film) 2955, 2930, 2858, 1681, 1633, 1570, 1453, 1299, 1149, 730, 698 cm^{-1}; ^1H NMR

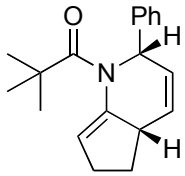
(500 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.37-7.34 (m, 2H), 7.32-7.31 (m, 1H), 7.28-7.26 (m, 2H), 6.43 (d, *J* = 9.7 Hz, 1H), 4.95-4.92 (m, 1H), 4.31 (q, *J* = 7.0 Hz, 2H), 4.16-4.15 (m, 2H), 4.00 (s, 1H), 1.69-1.67 (m, 1H), 1.35-1.21 (m, 3H), 1.29-1.25 (m, 7H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 147.2, 136.3, 128.8, 128.0, 127.4, 121.9, 112.3, 97.6, 59.1, 57.8, 56.3, 34.0, 31.8, 23.0, 22.6, 14.6, 14.0; HRMS (ESI-TOF) Calc'd for $C_{20}H_{28}NO_2$ [MH^+] 314.2114, Found 314.2118.



1-Benzyl-1,2-dihydrofuro[3,4-*b*]pyridin-5(7*H*)-one (18, Table 2, entry 7). Following the 85 ºC procedure, $[Rh(C_2H_2)_2Cl]_2$ (3.9 mg, 0.0099 mmol), P(4-F-C_6H_4)$_3$ (15.8 mg, 0.0499 mmol), DABCO (23 mg, 0.20 mmol) and **9** (45 mg, 0.20 mmol) were reacted in DMF (2.0 mL, 0.10 M) to give **18** (24 mg, 0.10 mmol) as a brown, clear oil after purification by flash column chromatography (Hexanes: Ethyl Acetate = 8:1): IR (film) 2924, 1735, 1675, 1601, 1451, 1233, 1027, 732, 668 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44-7.33 (m, 2H), 7.27-7.20 (m, 3H), 6.15 (dt, *J* = 10.0, 2.0 Hz, 1H), 5.11 (dt, *J* = 10.0, 3.3 Hz, 1H), 4.73 (s, 2H), 4.21 (dd, *J* = 3.2, 2.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4, 134.4, 133.5, 129.3, 128.5, 127.3, 117.9, 116.2, 113.7, 64.8, 54.3, 50.5; HRMS (EI) Calc'd for $C_{14}H_{13}NO_2$ [M^+] 227.0946, Found 227.0945.



2,2-Dimethyl-1-(2-pentyl-5,6-dihydro-2*H*-cyclopenta[*b*]pyridin-1(4a*H*)-yl)propan-1-one (19, Table 2, entry 8). Following the room temperature procedure, $[Rh(C_2H_2)_2Cl]_2$ (3.9 mg, 0.0099 mmol), P(4-F-C_6H_4)$_3$ (15.8 mg, 0.0499 mmol), DABCO (23 mg, 0.20 mmol) and **10** (55 mg, 0.20 mmol) were reacted in DMF (2.0 mL, 0.10 M) to give **19** (52 mg, 0.19 mmol) as a yellow, clear oil after purification by flash column chromatography (Hexanes: Ethyl Acetate = 8:1). The diastereomeric ratio was measured to be >98:2 by 400MHZ ^{1}H NMR analysis on the crude product mixture. The relative configuration was determined in analogy to the phenyl derivative **20**: IR (film) 2956, 2931, 2857, 1651, 1478, 1401, 1305, 1200, 1124, 1020, 729 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.75 (dd, *J* = 9.9, 0.6 Hz, 1H), 5.52 (dt, *J* = 10.1, 2.8 Hz, 1H), 5.04 (q, *J* = 2.2 Hz, 1H), 4.44-4.38 (m, 1H), 3.28-3.20 (m, 1H), 2.45-2.30 (m, 2H), 2.25-2.15 (m, 1H), 1.80-1.70 (m, 1H), 1.49-1.40 (m, 2H), 1.31-1.20 (m, 6H), 1.26 (s, 9H), 0.86 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.0, 142.3, 130.9, 127.2, 113.6, 56.9, 42.2, 41.8, 32.4, 31.9, 29.64, 29.56, 28.9, 28.7, 26.5, 23.6, 22.6, 14.0; HRMS (ESI-TOF) Calc'd for $C_{18}H_{30}NO$ [MH^+] 276.2322, Found 276.2324.

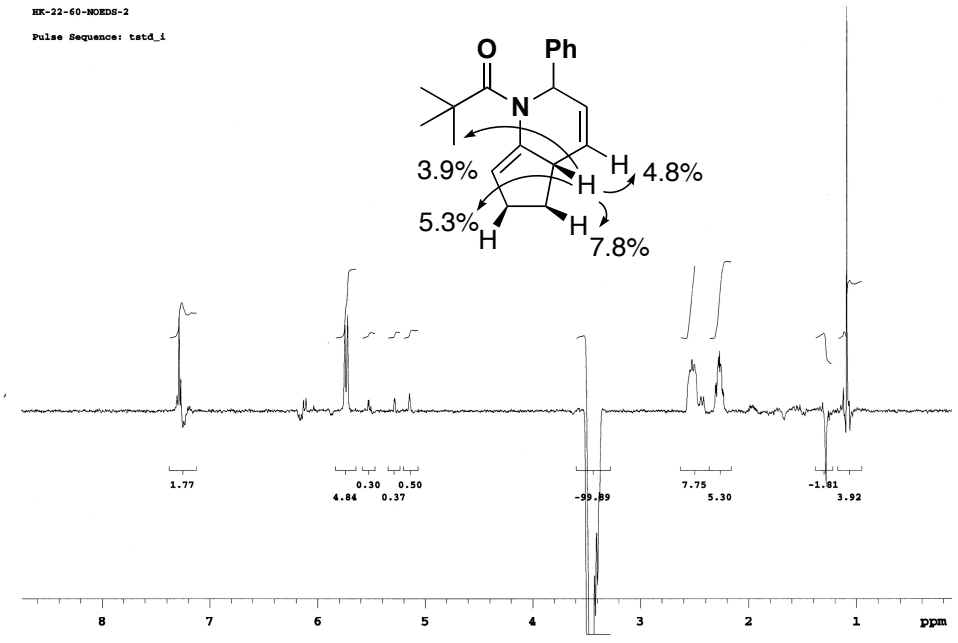


2,2-Dimethyl-1-(2-phenyl-5,6-dihydro-2*H*-cyclopenta[*b*]pyridin-1(4a*H*)-yl)propan-1-one (20, Table 2, entry 9). Following the room temperature procedure, $[Rh(C_2H_2)_2Cl]_2$ (3.9 mg, 0.0099 mmol), P(4-F-C_6H_4)$_3$ (15.8 mg, 0.0499 mmol), DABCO (23 mg, 0.20 mmol) and **11** (56 mg, 0.20 mmol) were reacted in DMF (2.0 mL, 0.10 M) to give **20** (56 mg, 0.20 mmol) as a yellow, clear oil after purification by flash column chromatography

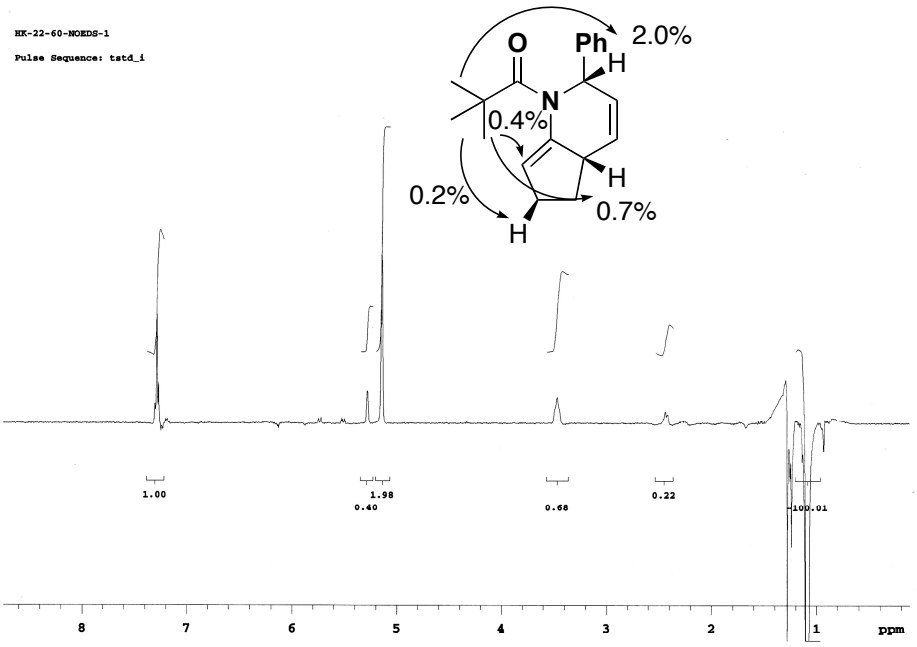
(Hexanes: Ethyl Acetate = 8:1). The diasteromeric ratio was measured to be >98:2 by 400MHZ ^{1}H NMR analysis on the crude product mixture. The relative configuration was determined by nOe analysis: IR (film) 3027, 2966, 2849, 1653, 1477, 1363, 1180, 851, 739, 697 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56-7.23 (m, 4H), 7.22-7.18 (m, 1H), 5.76-5.72 (m, 1H), 5.52 (dd, *J* = 10.0, 2.8 Hz, 1H), 5.30-5.28 (m, 1H), 5.15-5.14 (m, 1H), 3.51-3.45 (m, 1H), 2.47-2.42 (m, 2H), 2.32-2.24 (m, 1H), 1.53 (dt, *J* = 12.3, 9.6 Hz, 1H), 1.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.5, 142.3, 142.0, 129.0, 128.1, 127.8, 127.0, 114.6, 62.9, 41.9, 41.8, 29.6, 29.1, 28.9; HRMS (ESI-TOF) Calc'd for $C_{19}H_{24}NO$ [MH^+] 282.1852, Found 282.1852.

1D-NOESY Studies on **20**

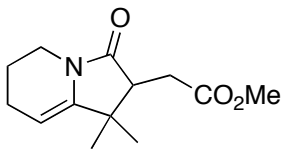
1.Irradiation at 3.50 ppm



2. Irradiation at 1.10 ppm

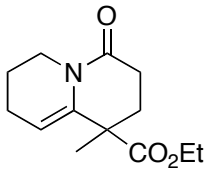


Preparation of cyclization substrate through multi-component coupling: Substrate **21** was prepared similarly from propargyl amine based on a report by Jabin et al.[4] Substrate **23** was prepared similarly from propargyl amine based on a report by Stille et al.[5]



[4] Jabin, I.; Netchitailo, P. *Tetrahedron Lett.* **2001**, *42*, 7823.
[5] Barta, N. S.; Brode, A.; Stille, J. R. *J. Am. Chem. Soc.* **1994**, *116*, 6201.

Methyl 2-(1,1-dimethyl-3-oxo-1,2,3,5,6,7-hexahydroindolizin-2-yl)acetate (22, Scheme 2). To a flame dried 1 dram glass vial equipped with a screw-cap and Teflon septum were added $[Rh(C_2H_2)_2Cl]_2$ (3.9 mg, 0.0099 mmol), P(4-F-C_6H_4)$_3$ (15.8 mg, 0.0499 mmol) and DMF (0.50 mL). This mixture was stirred for 15 minutes before **21** (47 mg, 0.20 mmol) in DMF (0.50 mL) was added *via* syringe at room temperature. DABCO (23 mg, 0.20 mmol) was then added to the reaction mixture in one portion. The syringe previously used for the addition was washed with DMF (0.50 mL * 2). After rapid stirring for 24 h, the vial was flushed with hydrogen three times and then placed under an atmosphere of H_2 (balloon pressure). Upon completion of the reduction as determined by TLC (~24 h), the reaction mixture was loaded directly onto a silica gel column. Purification *via* flash column chromatography (Hexanes: Ethyl Acetate = 4:1) yielded **22** (28 mg, 0.12 mmol) as a faint yellow, clear oil: IR (film) 2928, 1736, 1714, 1674, 1410, 1370, 1270, 1169, 1073 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.74 (t, J = 3.9 Hz, 1H), 3.72 (s, 3H), 3.71-3.66 (m, 1H), 3.38-3.32 (m, 2H), 2.87-2.75 (m, 2H), 2.40 (dd, J = 16.0, 8.8 Hz, 1H), 2.14-2.10 (m, 2H), 1.82-1.68 (m, 3H), 1.26 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 172.9, 147.1, 95.8, 51.9, 48.7, 39.2, 38.9, 30.8, 27.2, 24.6, 21.5, 20.6; HRMS (ESI-TOF) Calc'd for $C_{13}H_{20}NO_3$ [MH^+] 238.1438, Found 238.1434.



Ethyl 1-methyl-4-oxo-2,3,4,6,7,8-hexahydro-1*H*-quinolizine-1-carboxylate (24, Scheme 2). To a flame dried 1 dram glass vial equipped with a screw-cap and Teflon

septum were added $[Rh(C_2H_2)_2Cl]_2$ (3.9 mg, 0.0099 mmol), P(4-F-$C_6H_4)_3$ (15.8 mg, 0.0499 mmol) and DMF (0.50 mL). This mixture was stirred for 15 minutes before **23** (47 mg, 0.20 mmol) in DMF (0.50 mL) was added *via* syringe at room temperature. DABCO (23 mg, 0.20 mmol) was then added to the reaction mixture in one portion. The syringe previously used for the addition was washed with DMF (0.50 mL * 2). After rapid stirring for 24 h, the vial was flushed with hydrogen three times and then placed under an atmosphere of H_2 (balloon pressure). Upon completion of the reduction as determined by TLC (~24 h), the reaction mixture was loaded directly onto a silica gel column. Purification *via* flash column chromatography (Hexanes: Ethyl Acetate = 2:1) yielded **24** (39 mg, 0.17 mmol) as a faint yellow, clear oil: IR (film) 2934, 1727, 1643, 1462, 1386, 1225, 1180, 1115, 1021, 832, 782 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.96 (t, *J* = 4.2 Hz, 1H), 4.26 (ddd, *J* = 12.9, 5.8, 2.8 Hz, 1H), 4.14 (m, 1H), 3.25 (m, 2H), 2.56-2.46 (m, 2H), 2.25 (ddd, *J* = 13.3, 5.8, 4.2 Hz, 1H), 2.19-2.11 (m, 1H), 1.89-1.77 (m, 1H), 1.76-1.67 (m, 3H), 1.42 (s, 3H), 1.23 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.3, 167.3, 138.2, 106.1, 77.2, 61.2, 45.6, 40.5, 30.5, 29.6, 23.5, 22.6, 21.5; HRMS (ESI-TOF) Calc'd for $C_{13}H_{20}NO_3$ $[MH^+]$ 238.1438, Found 238.1443.