Supporting Information

Broad-Spectrum Radical Cyclizations Boosted by Polarity Matching. Carbonylative Access to α -Stannylmethylene Lactams from Azaenynes and CO

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General Information. ^1H NMR spectra were recorded with a JEOL FT-NMR JNM-270EX (270 MHz) spectrometer or JEOL FT-NMR JMN-ECP 500 (500 MHz) spectrometer. Chemical shifts are reported in parts per million () downfield from internal TMS at 0.00. ^{13}C NMR spectra were recorded with a JEOL FT-NMR JMN 270EX (68 MHz) spectrometer or JEOL FT-NMR JMN-ECP 500 (125 MHz) spectrometer and referenced to the solvent peak at 77.00 ppm. For ^1H -Sn or ^{13}C -Sn coupling constants, the central signals are normally associated with two close pairs of satellites corresponding to both ^{117}Sn and ^{119}Sn isotopes, and average values of the two different coupling constants are reported. Infrared spectra were recorded with JASCO FT/IR-410 spectrometer, and absorptions were reported in reciprocal centimeters. Both conventional and high resolution mass spectra were recorded with a JEOL JMS-DX303HF spectrometer. The products were purified by flash chromatography on silica gel (Fuji Silysia BW-300) and, if necessary, were further purified by recycling preparative HPLC (JAI LC-908) equipped with a GPC column using CHCl_3 as eluant.

Preparation of Azaenyne (**1f**).

The mixture of 4-pentynylamine (11.1 mmol, 920 mg), isobutylaldehyde (22.3 mmol, 1.61 g), and K_2CO_3 (10 g) in Et_2O (50 mL) was stirred at room temperature for 12 h. After filtration, the solvent was evaporated. The residue was distilled under reduced pressure to give 1.21 g (69%) of **1f** (105 °C/10 mmHg). ^1H NMR (CDCl_3 , 270 MHz) 1.07 (d, $J = 6.9$ Hz, 6H, H-8), 1.82 (quint, $J = 6.9$ Hz, 2H, H-4), 1.95 (t, $J = 2.6$ Hz, 1H, H-1), 2.20 (dt, $J = 6.9$, 2.6 Hz, 2H, H-3), 2.40-2.44 (m, 1H, H-7), 3.45 (t, $J = 6.9$ Hz, 2H, H-5), 7.55 (d, $J = 5.3$ Hz, 1H, H-6); ^{13}C NMR (CDCl_3 , 68 MHz) 15.76 (C-4), 19.26 (C-8), 29.04 (C-3), 33.89 (C-7), 59.28 (C-5), 68.55 (C-1), 3.63 (C-2), 170.33 (C-6); IR (neat) 3308, 1672; MS (EI) m/z 137 (M^+ , 6), 136 (21), 122 (100), 94 (38), 67 (77); HRMS (EI) m/z calcd for $\text{C}_9\text{H}_{17}\text{N}$ (M^+) 137.1204, found 137.1179.

Azaenynes **1a**, **1b**, **1c**, **1d**, **1e**, **1g**, **1h**, and **1j** were prepared by a similar procedure from the corresponding amines and aldehydes. Azaenyne **1i** was prepared from 6-heptynylamine and 3-pentanone by azeotropic distillation using Dean-Stark tube (solvent C_6H_6).

Selected Spectral Data: **1a**: ^1H NMR (270 MHz, CDCl_3) 1.10 (d, $J = 6.9$ Hz, 6H), 2.43 (t, $J = 2.6$ Hz, 1H), 2.50 (dsept, $J = 6.9$, 4.9 Hz, 1H), 4.25 (d, $J = 2.6$ Hz, 2H), 7.84 (d, $J = 4.9$ Hz, 1H); ^{13}C NMR (68 MHz, CDCl_3) 18.94, 33.91, 46.79, 74.84, 79.16, 171.09; HRMS (EI) m/z calcd for $\text{C}_7\text{H}_{11}\text{N}$ (M^+) 109.0891, found 109.0883.

1b: ^1H NMR (270 MHz, CDCl_3) 0.89 (t, $J = 6.9$ Hz, 3H), 1.09 (d, $J = 6.9$ Hz, 6H), 1.24-1.43 (m, 6H), 1.60-1.81 (m, 2H), 2.46 (d, $J = 2.3$ Hz, 1H), 2.47 (m, 1H), 4.14 (t, $J = 7.3$ Hz, 1H), 7.77 (dd, $J = 6.6, 1.3$ Hz, 1H); ^{13}C NMR (68 MHz, CDCl_3) 13.94, 19.46, 22.48, 25.27, 31.38, 34.00, 36.63, 58.73, 74.64, 83.15, 169.85; HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{19}\text{N}$ (M^+) 179.1674, found 179.1673.

1c: ^1H NMR (270 MHz, CDCl_3) 0.91 (d, $J = 6.6$ Hz, 3H), 1.00 (d, $J = 6.9$ Hz, 3H), 1.10 (d, $J = 6.6$ Hz, 6H), 2.02 (dsept, $J = 5.3$ Hz, 1H), 2.46 (d, $J = 2.3$ Hz, 1H), 2.51 (m, 1H), 4.03 (d, $J = 2.3$ Hz, 1H), 7.76 (dd, $J = 6.6, 1.3$ Hz, 1H); ^{13}C NMR (68 MHz, CDCl_3) 17.56, 19.48, 33.33, 34.16, 64.93, 75.68, 81.54, 169.96; HRMS (EI) m/z calcd for $\text{C}_{10}\text{H}_{17}\text{N}$ (M^+) 151.1361, found 151.1368.

1d: ^1H NMR (270 MHz, CDCl_3) 1.07 (d, 6H, $J = 6.9$ Hz), 1.17-1.25 (m, 1H), 1.57-1.69 (m, 9H), 2.46 (dsept, $J = 6.9$ Hz, 1H), 2.58 (s, 1H), 7.94 (d, $J = 5.6$ Hz, 1H); ^{13}C NMR (68 MHz, CDCl_3) 19.46, 22.86, 25.20, 33.98, 39.45, 62.25, 76.61, 85.46, 167.06; HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{19}\text{N}$ (M^+) 177.1517, found 177.1518.

1e: ^1H NMR (270 MHz, CDCl_3) 1.08 (d, $J = 6.6$ Hz, 6H), 1.96 (t, $J = 2.6$ Hz, 1H), 2.45 (dsept, $J = 6.6, 5.3$ Hz, 1H), 2.48 (dt, $J = 2.6, 6.9$ Hz, 1H), 3.49 (t, $J = 6.9$ Hz, 2H), 7.56 (d, $J = 5.3$ Hz, 1H); ^{13}C NMR (68 MHz, CDCl_3) 19.25, 20.38, 33.91, 59.09, 69.31, 82.21, 171.34; HRMS (EI) m/z calcd for $\text{C}_8\text{H}_{14}\text{N}$ (M^+) 123.1956, found 123.1962.

1g: ^1H NMR (270 MHz, CDCl_3) 1.07 (d, $J = 6.9$ Hz, 6H), 1.50-1.58 (m, 2H), 1.65-1.76 (m, 2H), 1.94 (t, $J = 2.6$ Hz, 1H), 2.21 (dt, $J = 6.9, 2.6$ Hz, 2H), 2.42 (m, 1H), 3.36 (t, $J = 6.9$ Hz, 2H), 7.51 (td, $J = 5.0, 1.3$ Hz, 1H); ^{13}C NMR (68 MHz, CDCl_3) 18.22, 19.38, 26.09, 29.80, 33.94, 60.54, 68.26, 84.17, 169.57; HRMS (CI, CH_4) m/z calcd for $\text{C}_{10}\text{H}_{19}\text{N}$ ($\text{M}^+ + \text{H}$) 152.1439, found 152.1435.

1h: ^1H NMR (270 MHz, CDCl_3) 1.07 (d, $J = 6.9$ Hz, 6H), 1.33-1.71 (m, 6H), 1.94 (t, $J = 2.6$ Hz, 1H), 2.20 (dt, $J = 6.9, 2.6$ Hz, 2H), 2.42 (sept, $J = 6.9$ Hz, 1H), 3.35 (t, $J = 6.9$ Hz, 2H), 7.50 (d, $J = 5.0$ Hz, 1H); ^{13}C NMR (68 MHz, CDCl_3) 18.22, 19.29, 26.09, 28.09, 30.01, 33.82, 60.83, 68.11, 84.36, 169.77; HRMS (EI) m/z calcd for $\text{C}_{11}\text{H}_{19}\text{N}$ (M^+) 165.1517, found 165.1512.

1i: ^1H NMR (270 MHz, CDCl_3) 1.03 (t, $J = 7.8$ Hz, 3H), 1.07 (t, $J = 7.8$ Hz, 3H), 1.40-1.47 (m, 2H), 1.50-1.65 (m, 4H), 1.92 (t, $J = 2.8$ Hz, 1H), 2.15-2.28 (m, 6H), 3.28 (t, $J = 7.4$ Hz, 2H).

1j: ^1H NMR (270 MHz, CDCl_3) 1.07 (d, $J = 6.9$ Hz, 6H), 1.29-1.62 (m, 14H), 1.94 (t, $J = 2.6$ Hz, 1H), 2.18 (dt, $J = 6.9, 2.6$ Hz, 2H), 2.41 (sept, $J = 6.9$ Hz, 1H), 3.33 (t, $J = 6.9$ Hz, 2H), 7.48 (d, $J = 5.1$ Hz, 1H); ^{13}C NMR (68 MHz, CDCl_3) 18.44, 19.49, 27.14, 28.52, 28.77, 29.09, 29.35, 29.45, 30.78, 34.01, 61.29, 68.02, 84.70, 169.25.

Typical Procedure for the Stannylcarbonylation of Azaenynes: *N*-Isobutyl-3(*Z*)-tributylstannylmethylene-2-piperidinone (2f). A magnetic stirring bar, AIBN (32.9 mg, 0.2 mmol), benzene (50 mL), Bu₃SnH (345.0 mg, 1.15 mmol), and azaenylene **1f** (143.8 mg, 1.05 mmol) were placed in a 100-mL stainless autoclave lined with a glass liner. The autoclave was closed, purged three times with carbon monoxide, pressurized with 88 atm of CO and then heated at 90 °C for 8 h. Excess CO was discharged at room temperature. The solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (eluant hexane/EtOAc = 8/2) to give 357 mg (75%) of **2f**.

Colorless oil. (*E/Z* = 0/100): ¹H NMR (270 MHz, CDCl₃): 0.84-0.96 (m, 21H, H-7, 10, 13), 1.21-1.35 (m, 6H, H-9), 1.42-1.54 (m, 6H, H-8), 1.80-1.90 (m, 2H, H-4), 1.95 (sept, *J* = 7.6 Hz, 1H, H-12), 2.60-2.68 (m, 2H, H-3), 3.23 (d, *J* = 7.6 Hz, 2H, H-10), 3.33 (t, *J* = 6.8 Hz, 1H, H-5), 6.31 (t, *J* = 2.2 Hz, *J* ¹H-Sn = 58.9 Hz 1H, H-5); ¹³C NMR (68 MHz, CDCl₃) 11.81 (*J* ¹³C-Sn = 359.9 Hz, C-7), 13.79 (C-10), 19.95 (C-13), 23.67 (C-4), 26.49 (C-12), 27.51 (*J* ¹³C-Sn = 59.8 Hz, C-8), 29.36 (*J* ¹³C-Sn = 19.6 Hz, C-9), 33.73 (*J* ¹³C-Sn = 49.0 Hz, C-3), 49.02 (C-5), 54.66 (C-11), 143.65 (C-2), 144.46 (C-6), 165.09 (C1); IR (neat) 1636, 1584; MS *m/z* calculated from major ¹²⁰Sn isotope; (EI), 400 (M⁺-C₄H₉, 100), 286 (37), 230 (19); HRMS, (CI, CH₄) *m/z* calcd for C₂₂H₄₄NO¹²⁰Sn (M⁺+H) 458.2445, found 458.2429.

***N*-Isobutyl-3-tributylstannylmethylene-2-azetidinone (2a).**

Colorless oil. (*E/Z* = 32/68): ¹H NMR (270 MHz, CDCl₃) *E* isomer: 0.83-0.99 (m, 21H, H-5,8,11), 1.24-1.38 (m, 6H, H-7), 1.45-1.57 (m, 6H, H-6), 1.92 (sept, 1H, *J* = 6.8 Hz, H-10), 3.16 (d, 2H, *J* = 7.3 Hz, H-9), 3.72 (d, 2H, *J* = 1.7 Hz, H-3) 6.72 (t, 1H, *J* = 1.7 Hz, *J* ¹H-Sn = 47.5 Hz, H-4); *Z* isomer: 0.85-0.94 (m, 15H, H-8,11), 1.02-1.18 (m, 6H, H-5), 1.23-1.37 (m, 6H, H-7), 1.47-1.56 (m, 6H, H-6), 1.89 (sept, 1H, *J* = 6.9 Hz, H-10), 3.14 (d, 2H, *J* = 6.9 Hz, H-9), 3.71 (dd, 2H, *J* = 3.6, 3.0 Hz, H-3), 6.22 (s, 1H, *J* ¹H-Sn = 45.6, H-4); ¹³C NMR (68 MHz, CDCl₃) *E* isomer: 10.64 (C-5), 13.70 (C-8), 20.31 (C-11), 27.19 (C-7), 27.71 (C-10), 29.06 (C-6), 49.60 (C-9), 51.57 (C-3), 128.63 (C-4), 151.46 (C-2), 165.52 (C-1); *Z* isomer: 9.92 (C-5), 13.59 (C-8), 20.25 (C-11), 27.15 (C-7), 27.66 (C-10), 28.99 (C-6), 49.60 (C-9), 51.39 (C-3), 125.95 (C-4), 152.24 (C-2), 163.56 (C-1); IR (neat) *E* isomer: 1752; *Z* isomer: 1750; MS (EI) *m/z* calculated from major ¹²⁰Sn isotope; *E* isomer 372 (M⁺-C₄H₉, 100), 316 (46); *Z* isomer: 372 (M⁺-C₄H₉, 100), 258 (12); HRMS, *E* isomer (CI, CH₄) *m/z* calcd for C₂₀H₄₀NO¹²⁰Sn (M⁺+ H) 430.2132, found 430.2108; *Z* isomer (CI, CH₄) *m/z* calcd for C₂₀H₄₀NO¹²⁰Sn (M⁺+ H) 430.2132, found 430.2130.

***N*-Isobutyl-4-*n*-pentyl-3-tributylstannylmethylene-2-azetidinone (2b).**

Colorless oil. (*E/Z* = 9/91) Separated by HPLC: ^1H NMR (270 MHz, CDCl_3) *E* isomer: 0.87-1.00 (m, 24H, H-5, 8, 11, 16), 1.25-1.45 (m, 12H, H-6, 14, 15), 1.47-1.82 (m, 12H, H-7,12,13), 1.92 (sept, J = 6.6 Hz, 1H, H-10), 2.86 (dd, J = 13.8, 5.9 Hz, 1H, H-9), 3.35 (dd, J = 13.8, 8.6 Hz, 1H, H-9), 3.98-4.13 (m, 1H, H-3), 6.65 (s, J $^1\text{H-Sn}$ = 46.1 Hz, 1H, H-4); *Z* isomer: 0.85-0.95 (m, 18H, H-8, 11, 16), 0.95-1.18 (m, 6H, H-5), 1.23-1.44 (m, 12H, H-6,14,15), 1.46-1.80 (m, 12H, H-7, 12, 13), 1.90 (sept, J = 7.8 Hz, 1H, H-10), 2.88 (dd, J = 14.3, 6.5 Hz, 1H, H-9), 3.27 (dd, J = 14.3, 7.8 Hz, 1H, H-9), 3.93-3.98 (m, 1H, H-3), 6.15 (s, J $^1\text{H-Sn}$ = 45.2 Hz, 1H, H-4); ^{13}C NMR (68 MHz, CDCl_3) *E* isomer: 10.39 (J $^{13}\text{C-Sn}$ = 340.1 Hz, C-5), 13.72 (C-8), 14.08 (C-16), 20.42 (C-11), 20.58 (C-11), 22.66 (C-15), 24.11 (C-13), 27.3 (J $^{13}\text{C-Sn}$ = 58.2 Hz, C-6), 27.95 (C-10), 29.13 (J $^{13}\text{C-Sn}$ = 21.3 Hz, C-7), 31.21 (C-12), 32.12 (C-14), 48.37 (C-9), 62.72 (J $^{13}\text{C-Sn}$ = 22.9 Hz, C-3), 124.38 (J $^{13}\text{C-Sn}$ = 293.5 Hz, C-4), 155.99 (C-2), 163.48 (C-1); *Z* isomer: 10.67 (J $^{13}\text{C-Sn}$ = 342.2 Hz, C-5), 13.69 (C-8), 13.90 (C-16), 20.32 (C-11), 20.43 (C-11), 22.45 (C-15), 24.74 (C-13), 27.16 (J $^{13}\text{C-Sn}$ = 56.6 Hz, C-6), 27.92 (C-10), 29.07 (J $^{13}\text{C-Sn}$ = 21.3 Hz, C-7), 31.49 (C-12), 31.92 (C-14), 48.16 (C-9), 62.86 (C-3), 126.63 (C-4), 156.29 (C-2), 165.35 (C-1); IR (neat) *E* isomer: 1749; *Z* isomer: 1747; MS (CI, CH_4) m/z calculated from major ^{120}Sn isotope; *E* isomer: 500 ($\text{M}^+ + \text{H}$, 100), 442 (72); *Z* isomer: 500 ($\text{M}^+ + \text{H}$, 3), 442 (100); HRMS, *E* isomer (CI, CH_4) m/z calcd for $\text{C}_{25}\text{H}_{50}\text{NO}^{120}\text{Sn}$ ($\text{M}^+ + \text{H}$) 500.2914, found 500.2915; *Z* isomer (CI, CH_4) m/z calcd for $\text{C}_{25}\text{H}_{50}\text{NO}^{120}\text{Sn}$ ($\text{M}^+ + \text{H}$) 500.2914, found 500.2912.

***N*-Isobutyl-4-isopropyl-3-tributylstannylmethylene-2-azetidinone (2c).**

Colorless oil. (*E/Z* = 4/96) Separated by HPLC: ^1H NMR (270 MHz, CDCl_3) *E* isomer: 0.84-1.03 (m, 21H, H-5, 8, 11), 1.10 (d, J = 6.9 Hz, 6H, H-13), 1.24-1.38 (m, 6H, H-7), 1.45-1.60 (m, 6H, H-6), 1.95-2.04 (m, 2H, H-10,12), 2.91 (dd, J = 13.8, 5.9 Hz, 1H, H-9), 3.43 (dd, J = 13.8, 8.9 Hz, 1H, H-9), 4.04-4.08 (m, 1H, H-3), 6.66 (s, J $^1\text{H-Sn}$ = 42.9 Hz, 1H, H-4); *Z* isomer: 0.85-0.95 (m, 21H, H-8,11,13), 0.99-1.20 (m, 6H, H-5), 1.23-1.37 (m, 6H, H-7), 1.47-1.56 (m, 6H, H-6), 1.87-2.06 (m, 2H, H-10,12), 2.78 (dd, J = 13.8, 5.9 Hz, 1H, H-9), 3.33 (dd, J = 13.8, 8.6 Hz, 1H, H-9), 3.93 (d, J = 4.0 Hz, 1H, H-3), 6.15 (s, J $^1\text{H-Sn}$ = 47.5 Hz 1H, H-4); ^{13}C NMR (68 MHz, CDCl_3) *E* isomer: 10.45 (J $^{13}\text{C-Sn}$ = 348.0 Hz, C-5), 13.75 (C-8), 15.70 (C-13), 20.29, 20.53 and 20.92 (C-11 or C-13), 27.32 (J $^{13}\text{C-Sn}$ = 57.0 Hz, C-6), 27.46 (C-10), 29.13 (J $^{13}\text{C-Sn}$ = 21.0 Hz, C-7), 30.13 (C-12), 49.68 (C-9), 67.96 (C-3), 124.57 (C-4), 155.45 (C-2), 163.97 (C-1); *Z* isomer: 10.84 (J $^{13}\text{C-Sn}$ = 341.8 Hz, C-5), 13.79 (C-8), 17.01 (C-13), 18.86 (C-13), 20.34 (C-11), 20.53 (C-11), 27.25 (J $^{13}\text{C-Sn}$ = 60.5 Hz, C-6), 27.72 (C-10), 29.04 (C-12), 29.17 (C-7), 48.61 (C-9), 67.83 (J $^{13}\text{C-Sn}$ = 48.1 Hz, C-3), 127.70 (J $^{13}\text{C-Sn}$ = 292.1 Hz, C-4), 153.95 (C-2), 165.45 (C-1); IR (neat) *Z* isomer: 1747; MS m/z calculated from major ^{120}Sn isotope; *E* isomer (CI, CH_4), 472 ($\text{M}^+ + \text{H}$, 100), 414 (58); *Z* isomer (EI): 414 ($\text{M}^+ - \text{C}_4\text{H}_9$, 100), 300 (29); HRMS, *E* isomer (CI, CH_4) m/z calcd for $\text{C}_{23}\text{H}_{46}\text{NO}^{120}\text{Sn}$ ($\text{M}^+ + \text{H}$) 472.2601, found 472.2582; *E* isomer (EI) m/z calcd for $\text{C}_{19}\text{H}_{36}\text{NO}^{120}\text{Sn}$ ($\text{M}^+ - \text{C}_4\text{H}_9$) 414.1819, found 414.1826.

***N*-Isobutyl-3-tributylstannylmethylene-1-azaspiro[3,5]nonan-2-one (2d)**

Colorless oil. (*E/Z* = 0/100): ^1H NMR (270 MHz, CDCl_3): 0.85-0.91 (m, 15H, H-8, 11), 1.01-1.07 (m, 6H, H-5), 1.24-1.37 (m, 6H, H-7), 1.47-1.81 (m, 16H, H-6, 12, 13, 14), 1.95 (sept, $J = 6.6$ Hz, 1H, H-10), 2.95 (d, $J = 7.6$ Hz, 2H, H-9), 6.26 (s, J ^1H -Sn = 48.3 Hz, 1H, H-4); ^{13}C NMR (68 MHz, CDCl_3): 10.77 (J ^{13}C -Sn = 342.2 Hz, C-5), 13.70 (C-8), 20.47 (C-11), 24.51 (C-13), 25.16 (C-14), 27.14 (C-6), 28.63 (C-10), 29.06 (C-7), 34.41 (C-12), 47.06 (C-9), 68.36 (C-3), 125.23 (C-4), 161.72 (C-2), 165.05 (C-1); IR (neat): 1744, 1655 cm^{-1} ; MS, (CI, CH_4) m/z calculated from major ^{120}Sn isotope, 498 (M^+H , 4), 440 (100); HRMS (CI, CH_4) m/z calcd for $\text{C}_{25}\text{H}_{48}\text{NO}^{120}\text{Sn}$ (M^+H) 498.2758, found 498.2765.

***N*-Isobutyl-3-tributylstannylmethylene-2-azacyclopentanone (2e)**

Colorless oil. (*E/Z* = 4/96) Separated by HPLC: ^1H NMR (270 MHz, CDCl_3) *E* isomer: 0.86-1.00 (m, 21H, H-6, 9, 12), 1.24-1.38 (m, 6H, H-8), 1.45-1.57 (m, 6H, H-8), 1.97 (sept, $J = 7.3$ Hz, 1H, H-11), 2.73 (td, $J = 6.8, 2.7$ Hz, 2H, H-3), 3.19 (d, $J = 7.3$ Hz, 2H, H-10), 3.40 (t, $J = 6.8$ Hz, 2H, H-4), 7.08 (t, $J = 2.7$ Hz, J ^1H -Sn = 42.9 Hz, 1H, H-5); *Z* isomer: 0.84-0.96 (m, 21H, H-6, 9, 12), 1.21-1.35 (m, 6H, H-8), 1.42-1.54 (m, 6H, H-7), 1.95 (sept, $J = 7.6$ Hz, 1H, H-11), 2.79 (td, $J = 6.8, 2.2$ Hz, 1H, H-3), 3.19 (d, $J = 7.6$ Hz, 2H, H-10), 3.35 (t, $J = 6.8$ Hz, 1H, H-4), 6.45 (t, $J = 2.2$ Hz, J ^1H -Sn = 58.9 Hz 1H, H-5); ^{13}C NMR (68 MHz, CDCl_3) *E* isomer: 9.65 (J ^{13}C -Sn = 339.1 Hz, C-6), 13.64 (C-9), 20.09 (C-12), 26.44 (C-3), 26.63 (C-11), 27.28 (J ^{13}C -Sn = 41.5 Hz C-8), 29.13 (J ^{13}C -Sn = 20.7 Hz, C-7), 44.08 (C-4), 51.05 (C-10), 132.06 (C-5), 147.57 (C-2), 166.85 (C-1); *Z* isomer: 11.45 (J ^{13}C -Sn = 364.1 Hz, C-6), 14.00 (C-9), 19.86 (C-12), 26.54 (C-11), 27.23 (C-3), 27.41 (J ^{13}C -Sn = 60.5 Hz C-8), 29.29 (J ^{13}C -Sn = 19.6 Hz, C-7), 44.03 (C-4), 50.77 (C-10), 135.99 (C-5), 145.52 (C-2), 168.91 (C-1); IR (neat) *E* isomer: 1666, *Z* isomer: 1674; MS m/z calculated from major ^{120}Sn isotope; *E* isomer (CI, iso- C_4H_{10}), 444 (M^+H , 80), 307 (100); *Z* isomer (CI, iso- C_4H_{10}): 444 (M^+H , 25), 386 (50), 307 (53), 291 (27), 154 (100); HRMS, *E* isomer (CI, CH_4) m/z calcd for $\text{C}_{21}\text{H}_{42}\text{NO}^{120}\text{Sn}$ (M^+H) 444.2288, found 444.2272; Anal. *Z* isomer, Calcd for $\text{C}_{21}\text{H}_{41}\text{NOSn}$, 442.27; C, 57.03; H, 9.34; N, 3.17. Found C, 56.96; H, 9.24; N, 3.36.

***N*-Isobutyl-3-tributylstannylmethylene-2-azacycloheptanone (2g).**

Colorless oil. (*E/Z* = 19/81): ^1H NMR (270 MHz, CDCl_3) *E* isomer: 0.86-1.05 (m, 21H, H-8, 11, 14), 1.24-1.38 (m, 6H, H-10), 1.43-1.57 (m, 6H, H-9), 1.65-1.73 (m, 4H, H-4, 5), 1.91 (sept, 1H, $J = 6.9$ Hz, H-13), 2.29-2.36 (m, 2H, H-3), 3.21 (d, $J = 7.3$ Hz, 2H, H-12), 3.25-3.31 (m, 2H, H-6), 6.36 (s, J ^1H -Sn = 61.0 Hz, 1H, H-7); *Z* isomer: 0.85-0.91 (m, 15H, H-8, 11), 0.94 (d, 6H, $J = 6.6$ Hz, H-14), 1.22-1.36 (m, 6H, H-10), 1.42-1.54 (m, 6H, H-9), 1.66-1.75 (m, 4H, H-4, 5), 1.94 (sept, 1H, $J = 6.9$ Hz, H-13), 2.38-2.46 (m, 2H, H-3), 3.20 (d, $J = 7.3$ Hz, 2H, H-12), 3.27-3.34 (m, 2H, H-6), 6.17 (s, J ^1H -Sn = 64.4 Hz, 1H, H-7); ^{13}C NMR (68 MHz, CDCl_3) *E* isomer: 10.21 (J ^{13}C -Sn = 371.5 Hz, C-8), 13.66 (C-11), 20.18 (C-14), 27.33 (J ^{13}C -Sn = 57.5 Hz, C-9), 27.44 (C-13), 28.29 (C-4 or 5), 29.02 (C-4 or 5), 29.31 (C-10), 34.16 (C-3), 49.11 (C-6), 54.95 (C-12), 133.14 (C-7), 156.08 (C-2), 174.12 (C-1); *Z* isomer: 10.44 (J ^{13}C -Sn = 344.0 Hz, C-8), 13.76 (C-11), 20.32 (C-14), 27.42 (J ^{13}C -Sn = 57.4 Hz, C-9 and 13), 27.83 (C-4 or 5), 29.02 (C-4 or 5), 29.25 (C-10), 36.60 (C-3), 49.94 (C-6), 55.53 (C-12), 135.90 (C-7), 155.20 (C-2), 174.05 (C-1); IR (neat) *E* isomer: 1637; *Z* isomer: 1629; MS m/z calculated from major ^{120}Sn isotope; *E* isomer (CI, CH_4), 472 ($\text{M}^+\text{+H}$, 58), 414 (100); *Z* isomer (CI, CH_4): 472 ($\text{M}^+\text{+H}$, 14), 414 (100); HRMS, *E* isomer (CI, CH_4) m/z calcd for $\text{C}_{23}\text{H}_{46}\text{NO}^{120}\text{Sn}$ ($\text{M}^+\text{+H}$) 472.2301, found 472.2593; *Z* isomer: (CI, CH_4) m/z calcd for $\text{C}_{23}\text{H}_{46}\text{NO}^{120}\text{Sn}$ ($\text{M}^+\text{+H}$) 472.2601, found 470.2601.

***N*-Isobutyl-3-tributylstannylmethylene-2-azacyclooctanone (2h).**

Colorless oil. (*E/Z* = 52/48) Separated by HPLC: ^1H NMR (270 MHz, CDCl_3) *E* isomer: 0.82-1.01 (m, 21H, H-9, 15, 12), 1.25-1.50 (m, 6H, H-11), 1.50-1.58 (m, 12H, H-4, 5, 6, 10), 2.01 (sept, $J = 6.9$ Hz, 1H, H-14), 2.35-2.43 (m, 2H, H-3), 3.15 (d, $J = 7.3$ Hz, 2H, H-13), 3.43-3.47 (m, 2H, H-7), 5.74 (s, J ^1H -Sn = 64.0 Hz, 1H, H-8); *Z* isomer: 0.75-1.10 (m, 21H, H-9, 12, 15), 1.25-1.73 (m, 18H, H-4, 5, 6, 10, 11), 2.02 (sept, $J = 6.9$ Hz, 1H, H-14), 2.46-2.54 (m, 2H, H-3), 3.15 (d, 2H, $J = 7.3$ Hz, H-13), 3.46-3.53 (m, 2H, H-7), 5.91 (s, J ^1H -Sn = 56.1 Hz, 1H, H-8); ^{13}C NMR (68 MHz, CDCl_3) *E* isomer: 10.50 (J ^{13}C -Sn = 307.3 Hz, C-9), 13.78 (C-12), 20.27 (C-15), 24.60 (C-4 or 5 or 6), 27.06 (C-14), 27.20 (C-4 or 5 or 6), 27.41 (C-11), 28.72 (C-4 or 5 or 6), 29.28 (C-10), 39.95 (C-3), 46.97 (C-7), 50.63 (C-13), 126.60 (C-8), 156.35 (C-2), 175.06 (C-1); *Z* isomer: 9.68 (J ^{13}C -Sn = 336.6 Hz, C-9), 13.63 (C-12), 20.76 (C-15), 24.72 (C-4 or 5 or 6), 27.29 (J ^{13}C -Sn = 59.4 Hz, C-11), 27.38 (C-14), 27.44 (C-4 or 5 or 6), 28.73 (C-4 or 5 or 6), 29.07 (J ^{13}C -Sn = 20.2 Hz, C-10), 43.80 (J ^{13}C -Sn = 52.2 Hz, C-3), 47.73 (C-7), 52.10 (C-13), 127.71 (J ^{13}C -Sn = 350.9 Hz, C-8), 157.16 (C-2), 174.49 (C-1); IR (neat) *E* isomer: 1638 cm^{-1} ; *Z* isomer: 1640 cm^{-1} , 1597 cm^{-1} ; MS m/z calculated from major ^{120}Sn isotope; *E* isomer (CI, CH_4), 486 ($\text{M}^+\text{+H}$, 95), 428 (100); *Z* isomer (CI, CH_4): 486 ($\text{M}^+\text{+H}$, 43), 428 (100); HRMS *E* isomer (CI, CH_4), m/z calcd for $\text{C}_{24}\text{H}_{48}\text{NO}^{120}\text{Sn}$ ($\text{M}^+\text{+H}$) 486.2758, found 486.2740; *Z* isomer (CI, CH_4), m/z calcd for $\text{C}_{24}\text{H}_{48}\text{NO}^{120}\text{Sn}$ ($\text{M}^+\text{+H}$) 486.2758, found 486.2756.

***N*-(3-Pentyl)-3-tributylstannylmethylene-2-azacyclooctanone (2i).**

Colorless oil. (*E/Z* = 82/12): ^1H NMR (500 MHz, CDCl_3) *E* isomer: 0.85-1.00 (m, 21H, H-9, 12, 15), 1.25-1.38 (m, 6H, H-11), 1.40-1.70 (m, 16H, H-4, 5, 6, 10, 14), 2.35-2.43 (m, 2H, H-3), 3.37-3.43 (m, 2H, H-7), 4.28-4.35 (m, 1H, H-13), 5.71 (s, J ^1H -Sn = 62.3 Hz, 1H, H-8); *Z* isomer: 0.82-0.95 (m, 15H, H-9, 12), 0.97 (t, J = 7.3 Hz, 6 H, H-15), 1.30 (sext, J = 7.3 Hz, 6H, H-11), 1.40-1.55 (m, 6H, H-10), 1.55-1.70 (m, 10H, H-4, 5, 6, 14), 2.46-2.54 (m, 2H, H-3), 3.43-3.50 (m, 2H, H-7), 5.89 (s, J ^1H -Sn = 66.4 Hz, 1H, H-8); ^{13}C NMR (125 MHz, CDCl_3) *E* isomer: 10.24 (J ^{13}C -Sn = 334.9 Hz, C-9), 11.09 (C-15), 13.48 (C-12), 25.29 (C-4 or 5 or 6), 25.74 (C-14), 26.94 (C-4 or 5 or 6), 27.14 (C-11), 29.03 (C-10), 31.58 (C-4 or 5 or 6), 39.33 (C-3), 42.55 (C-7), 56.69 (C-13), 126.24 (C-8), 156.82 (C-2), 175.69 (C-1); *Z* isomer: 9.75 (J ^{13}C -Sn = 335.9 Hz, C-9), 12.11 (C-15), 13.66 (C-12), 25.28 (C-4 or 5 or 6), 25.59 (C-14), 27.29 (J ^{13}C -Sn = 57.6 Hz, C-11), 27.63 (C-4 or 5 or 6), 29.10 (C-10), 30.98 (C-4 or 5 or 6), 43.62 (C-3 or 7), 43.80 (C-3 or 7), 57.89 (C-13), 127.88 (C-8), 157.81 (C-2), 174.18 (C-1); IR (neat) *E* isomer: 1634; *Z* isomer: 1634, 1597; MS m/z calculated from major ^{120}Sn isotope; *E* isomer (EI), 442 (M^+ - C_4H_9 , 100), 386 (22); *Z* isomer (EI): 442 (M^+ - C_4H_9 , 100), 325 (11), 269 (12), 258 (11); HRMS *E* isomer (EI), m/z calcd for $\text{C}_{21}\text{H}_{40}\text{NO}^{120}\text{Sn}$ (M^+ - C_4H_9) 442.2132, found 442.2134; *Z* isomer (EI), m/z calcd for $\text{C}_{21}\text{H}_{40}\text{NO}^{120}\text{Sn}$ (M^+ +H) 442.2132, found 442.2128.

***N*-Isobutyl-3-tributylstannylmethylene-2-azacyclononanone (2j).**

Separated by HPLC (*E/Z* = 47/53): ^1H NMR (270 MHz, CDCl_3) *E* isomer: 0.85-0.99 (m, 21H, H-10, 13, 16), 1.32 (sext, J = 7.3, 6H, H-12), 1.47-1.62 (m, 12H, H-11, and H-4, 5, 6 or 7), 1.66-1.76 (m, 2H, H-4, 5, 6 or 7), 2.03 (sept, J = 6.93 Hz, 1H, H-15), 2.44-2.50 (m, 2H, H-3), 3.13 (d, J = 7.6 Hz, 2H, H-14), 3.54-3.60 (m, 2H, H-8), 5.80 (s, J ^1H -Sn = 54.0 Hz, 1H, H-9); *Z* isomer: 0.86-0.90 (m, 15H, H-10,13), 0.96 (d, J = 6.60 Hz, 6H, H-16), 1.30 (sext, 6H, J = 7.3 Hz, H-12), 1.47-1.51 (m, 6H, H-11), 1.56-1.60 (m, 6H, H-4, 5, 6 or 7), 1.68-1.74 (m, 2H, H-4, 5, 6 or 7), 2.03 (sept, 1H, J = 6.9 Hz, H-15), 2.43-2.49 (m, 2H, H-3), 3.15 (d, 2H, J = 7.6 Hz, H-14), 3.57 (t, 2H, J = 5.61 Hz, H-8), 5.96 (s, J ^1H -Sn = 54.1 Hz, 1H, H-9); ^{13}C NMR (68 MHz, CDCl_3) *E* isomer: 10.29 (C-10), 13.77 (C-13), 20.30 (C-16), 21.79 (C-4, 5, 6, 7 or 15), 24.72 (C-4, 5, 6, 7 or 15), 27.29 (C-11), 26.41 (C-4, 5, 6, 7 or 15), 26.65 (C-4, 5, 6, 7 or 15), 27.25 (C-4, 5, 6, 7 or 15), 27.42 (C-12), 29.29 (C-11), 34.80 (C-3), 47.56 (C-8), 50.33 (C-14), 128.03 (C-9), 156.54 (C-2), 175.30 (C-1); *Z* isomer: 9.72 (C-10), 13.70 (C-13), 20.28 (C-4, 5, 6, 7 or 15), 20.98 (C-16), 26.59 (C-4, 5, 6, 7 or 15), 26.88 (C-4, 5, 6, 7 or 15), 27.11 (C-4, 5, 6, 7 or 15), 27.16 (C-4, 5, 6, 7 or 15), 27.34 (C-12), 29.10 (C-11), 36.82 (C-3), 48.23 (C-8), 51.80 (C-14), 127.99 (C-9), 157.62 (C-2), 175.06 (C-1); IR (neat) *E* isomer: 1632; *Z* isomer: 1635; MS m/z calculated from major ^{120}Sn isotope; *E* isomer (CI, CH_4), 500 (M^+ +H, 3), 291 (23), 210 (100); *Z* isomer (CI, CH_4): 500 (M^+ +H, 2), 291 (42), 210 (100); HRMS *E* isomer (CI, CH_4), m/z calcd for $\text{C}_{25}\text{H}_{50}\text{NO}^{120}\text{Sn}$ (M^+ +H) 500.2914, found 500.2922; *Z* isomer (CI, CH_4), m/z calcd for $\text{C}_{25}\text{H}_{50}\text{NO}^{120}\text{Sn}$ (M^+ +H) 500.2914, found 500.2912.

Typical Procedure for Iodination of α -Stannylmethylene Lactams: *N*-isobutyl-3-(*Z*)-iodomethylene-2-azetidinone (4(Z)**).** The mixture of iodine (0.09 mmol, 22.9 mg) and lactam **2a(Z)** (0.09 mmol, 33.5 mg) in Et₂O was stirred at 0 °C for 1 h under N₂. After evaporation, the residue was purified by preparative HPLC equipped with a GPC column to give 31.6 mg (100%) of **4(Z)**.

Yellow oil. ¹H NMR (270 MHz, CDCl₃): 0.94 (d, *J* = 6.9 Hz, 6H, H-7), 1.90 (tsept, *J* = 6.9, 6.6 Hz, 1H, H-6), 3.15 (d, *J* = 6.3 Hz, 2H, H-5), 3.79 (d, *J* = 1.0 Hz, 2H, H-3), 6.43 (s, 1H, H-4); ¹³C NMR (68 MHz, CDCl₃) 20.28 (C-7), 27.54 (C-6), 49.78 (C-5), 52.22 (C-3), 69.55 (C-4), 145.68 (C-2), 162.91 (C-1); IR (neat): 1747; MS (EI) *m/z* 265 (M⁺, 44), 250 (22), 222 (100); HRMS (EI) *m/z* calcd for C₈H₁₂INO 264.9964, found 264.9963.

***N*-Isobutyl-3-(*E*)-iodomethylene-2-azetidinone (**4(E)**).**

Yellow oil. ¹H NMR (270 MHz, CDCl₃): 0.95 (d, *J* = 6.9 Hz, 6H, H-7), 1.92 (tsept, *J* = 6.9, 6.6 Hz, 1H, H-6), 3.15 (d, *J* = 6.3 Hz, 2H, H-5), 3.71 (d, *J* = 1.7 Hz, 2H, H-3), 7.08 (s, 1H, H-4); ¹³C NMR (68 MHz, CDCl₃) 20.37 (C-7), 27.62 (C-6), 49.96 (C-5), 52.68 (C-3), 76.29 (C-4), 149.94 (C-2), 160.20 (C-1); IR (neat): 1734; MS (EI) *m/z* 265 (M⁺, 32), 250 (4), 222 (100); HRMS (EI) *m/z* calcd for C₈H₁₂INO 264.9964, found 264.9964.

Typical Procedure for Stille Coupling Reaction of α -Stannylmethylene Lactams and Iodobenzene: 3-Benzylidene-1-isobutyl-2-azacycloheptanone (7(E)**).** The procedure reported by Buynak was used (Buynak, J. D.; Doppalapude, V. R.; Frotan, M.; Kumar, R. *Tetrahedron Lett.* **1999**, *40*, 1281.). (Pd₂(dba)₃ (0.007 mmol, 7.2 mg) was placed two-necked round bottom flask. The Pd catalyst was dried under vacuum, and Ar was introduced. DMF solution of **2g(E)** (0.062 mmol, 29.1 mg) and iodobenzene (0.1 mmol, 21.1 mg) were added, and the resulting mixture was stirred at room temperature for 12 h. After filtration, water was added and extracted with Et₂O (3 x 20 mL). The combined organic layer was washed with water, dried over MgSO₄. The solvent was evaporated. The residue was purified by flash chromatography on silica gel (hexane to hexane/EtOAc = 5/1) to afford 14.7 mg (92%) of **7(E)**.

Colorless oil. ¹H NMR (270 MHz, CDCl₃): 0.95 (d, *J* = 6.9 Hz, 6H, H-11), 1.63-1.69 (m, 2H, H-5), 1.85 (quint, *J* = 6.3 Hz, 2H, H-4), 1.98 (sept, *J* = 6.9 Hz, 1H, H-10), 2.37-2.42 (m, 2H, H-3), 3.30 (d, *J* = 7.6 Hz, 2H, H-9), 3.36-3.41 (m, 2H, H-6), 6.38 (s, 1H, H-7), 7.16-7.70 (m, 5H, Ar); ¹³C NMR (68 MHz, CDCl₃) 20.27 (C-11), 27.28 (C-5), 27.35 (C-10), 31.14 (C-4), 34.28 (C-3), 49.53 (C-6), 54.27 (C-9), 127.40 (Ar), 128.03 (Ar), 128.30 (Ar), 128.34 (C-7), 135.87 (Ar), 173.06 (C-1); IR (neat): 1635; MS (EI) *m/z* 257 (M⁺, 96), 214 (100); HRMS (EI) *m/z* calcd for C₁₇H₂₃NO (M⁺) 257.1780, found 257.1776.

3(Z)-Benzylidene-N-Isobutyl-4-pentyl-2-azetidinone (5(Z))

Colorless oil. $^1\text{H-NMR}$ (270 MHz, CDCl_3) 0.88-0.99 (m, 9H, H-9), 1.26-1.50(m, 6H, H-14, 15), 1.64-2.99 (m, 3H, H-10, 12, 13), 2.94 (dd, $J = 13.8, 6.2$, Hz, 1H, H-9), 3.32 (dd, $J = 13.8, 8.1$ Hz, 1H, H-9), 4.06 (t, $J = 5.4$ Hz, 1H, H-2), 6.30 (s, 1H, H-4), 7.27-7.40 (m, 3H, H7, 8), 8.01 (d, $J = 6.9$ Hz, H-6): $^{13}\text{C NMR}$ (68 MHz, CDCl_3) 14.08 (C-16), 29.54 (C-11), 22.57 (C-15), 24.89 (C-13), 28.06 (C-10), 31.88 (C-12), 32.06 (C-14), 48.52 (C-9), 59.30 (C-3), 127.12 (C-4), 128.42 (C-8), 128.70 (C-7), 129.61 (C-6), 134.31 (C-5), 140.82 (C-2), 162.73 (C-1); MS (EI) m/z 285 (M^+ , 16), 242 (100), 214 (47); HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{27}\text{NO}$ (M^+) 285.2093, found 285.2096.

3(Z)-Benzylidene-1-isobutyl-1-azaspiro[3,5]nonan-2-one (6(Z)).

Colorless oil. $^1\text{H-NMR}$ (270 MHz, CDCl_3) 0.97 (d, $J = 6.9$ Hz, 6H, H-11), 1.57-2.00 (m, 11H, H-19, 12, 13, 14), 3.03 (d, $J = 7.6$ Hz, 2H, H-9), 6.58 (s, 1H, H-4), 7.26-740 (m, 3H, H-7, 8), 8.02 (d, $J = 6.9$ Hz, 2H, H-6); $^{13}\text{C NMR}$ (68 MHz, CDCl_3) 20.65 (C-13), 24.26 (C-11), 25.04 (C-14), 28.82 (C-10), 34.35 (C-12), 47.27 (C-9), 64.38 (C-3), 126.28 (C-4), 128.36 (C-8), 128.58 (C-7), 129.69 (C-6), 134.59 (C-5), 146.67 (C-2), 162.54 (C-1); MS (EI) m/z 283 (M^+ , 29), 240 (100), 211 (59); HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{25}\text{NO}$ (M^+) 283.1936, found 283.1931.

Typical Procedure for Proto-Destannylation of α -Stannylmethylene Lactam. *N*-Isobutyl-3-methylene-2-azacyclooctanone (8**).** In a 20 mL round-bottom flask, lactam **2h** (0.07 mmol, 34.2 mg), TMSCl (0.075 mmol, 8.1 mg), and MeOH (0.5 mL) were placed, and the resulting mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure. The residue was purified by preparative HPLC equipped with a GPC column to give 15.9 mg (100%) of **8**.

Colorless oil. $^1\text{H-NMR}$ (270 MHz, CDCl_3) 0.93 (d, $J = 6.6$ Hz, 6H, H-11), 1.50-1.71 (m, 6H, H-4, 5, 6), 2.02 (sept, $J = 6.9$ Hz, 1H, H-10), 2.37-2.44 (m, 2H, H-3), 3.18 (d, $J = 7.6$ Hz, 2H, H-9), 3.45-3.54 (m, 2H, H-7), 4.93 (s, 1H, H-8), 5.06 (s, 2H, H-8): $^{13}\text{C NMR}$ (68 MHz, CDCl_3) 20.11 (C-11), 21.44 (C-10), 24.17 (C-4, 5, or 6), 26.91 (C-4, 5 or 6), 28.52 (C-4, 5, or 6), 38.05 (C-3), 46.71 (C-7), 50.66 (C-9), 112.89 (C-8), 147.90 (C-2), 173.89 (C-1); IR (neat) 1632.

***N*-(3-pentyl)-3-methylene-2-azacyclooctanone (**9**).**

Colorless oil. $^1\text{H-NMR}$ (500 MHz, CDCl_3) 0.83 (d, $J = 7.3$ Hz, 6H, H-11), 1.40-1.61 (m, 10H, H-4, 5, 6, 11), 2.30-2.38 (m, 2H, H-3), 3.30-3.34 (m, 2H, H-7), 4.2 (quint, $J = 7.4$ Hz, 1H, H-9), 4.81 (s, 1H, H-8), 4.98 (s, 1H, H-8): $^{13}\text{C NMR}$ (68 MHz, CDCl_3) 11.05 (C-11), 25.06 (C-4 or 5 or 6), 25.65 (C-4 or 5 or 6), 26.80 (C-4 or 5 or 6), 31.51 (C-3), 37.52 (C-10), 42.45 (C-7), 56.79 (C-9), 112.66 (C-8), 148.81 (C-2), 174.41 (C-1); IR (neat) 1628; MS (EI) m/z 209 (M^+ , 25), 180 (100), 166 (26), 152 (19), 67 (33), 55, (42).

***N*-Isobutyl-3-methylene-2-piperidinnone (**3**).**

Colorless oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) 0.91 (d, $J = 6.8$ Hz, 6H, 9), 1.87 (quint, $J = 6.0$ Hz, 2H, H-4), 2.03 (sept, $J = 6.8$ Hz, 1H, H-8), 2.58 (t, $J = 6.2$ Hz, 2H, H-3), 3.27 (d, $J = 6.9$ Hz, 1H, H-7), 3.36 (t, $J = 7.8$ Hz, 2H, H-5), 5.26 (s, 1H, H-6), 6.20 (s, 1H, H-6); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) 20.07 (C-9), 23.25 (C-4), 26.53 (C-8), 30.08 (C-3), 49.07 (C-5), 54.99 (C-7), 121.34 (C-6), 137.79 (C-2), 164.21 (C-1); MS m/z (EI), 167 (M^+ , 25), 125 (100); IR (neat) 1659, 1615; HRMS, (EI) m/z calcd for $\text{C}_{10}\text{H}_{17}\text{NO}$ (M^+) 167.1310, found 167.1306.

3-(Z)-Deuteriomethylene-N-Isobutyl- 2-piperidinone (3-d).

Colorless oil. ^1H NMR (500 MHz, CDCl_3) 0.91 (d, $J = 6.9$ Hz, 6H, 9), 1.87 (quint, $J = 6.0$ Hz, 2H, H-4), 2.04 (sept, $J = 6.9$ Hz, 1H, H-8), 2.57 (t, $J = 6.0$ Hz, 2H, H-3), 3.26 (d, $J = 6.9$ Hz, 1H, H-7), 3.36 (t, $J = 6.0$ Hz, 2H, H-5), 5.25 (s, 1H, H-6); ^{13}C NMR (125 MHz, CDCl_3) 20.13 (C-9), 23.31 (C-4), 26.60 (C-8), 30.08 (C-3), 49.12 (C-5), 55.05 (C-7), 121.13 (t, $J = 25.9$ Hz, C-6), 137.75 (C-2), 164.27 (C-1); MS m/z (EI), 168 (M^+ , 27), 125 (100); HRMS, (EI) m/z calcd for $\text{C}_{10}\text{H}_{16}\text{DNO}$ (M^+) 168.1372, found 168.1368.