Electronic Supplementary Information

Intramolecular Nucleophilic Carbonyl Trapping of α-Ketenyl Radicals by an Amino Group

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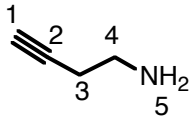
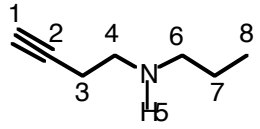
General information. ^{1}H NMR spectra were recorded with a JEOL JMN-500 (500 MHz) spectrometer in $CDCl_3$. Chemical shifts are reported in parts per million (δ) downfield from internal TMS at 0.00. ^{13}C NMR spectra were recorded with a JEOL JMN-500 (125 MHz) spectrometer and referenced to the solvent peak at 77.00 ppm. For ^{1}H-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 obtained on a JASCO FT/IR-5300 spectrometer; absorptions are reported in reciprocal centimeters. Both conventional and high resolution mass spectra were recorded with a JEOL MS700 spectrometer. Products were purificated by flash chromatography on silica gel (nacalai tesque int. Silica Gel 60, 230-400 mesh). **1a**, **1c**, and **1e** were prepared from corresponding methansulfonate by Gabriel amine synthesis. **1g** was prepared from 5-hexynenitrile by reduction using lithium aluminium hydride. **1b**, **1d**, and **1f** were prepared by reactions of the corresponding methansulfonate of alkynyl alcohol with propylamine. **1h** was prepared from piperidine-2-ethanol according to the literature (M. Ikeda, K. Kugo, T. Sato, *J. Chem. Soc., Perkin Trans. 1,* **1996**, 1819.). **1i** was prepared from (s)-(-)-1-formyl-2-hydroxymethylpyrrolidine and propargyl bromide (D. Enders, P. Fey, H. Kipphardt, *Org. Synth.* **1987**, *65*, 173.). **1j** was prepared according to the literature (R. L. Hillard, III, C. A. Parnell, K. P. Vollhardt, *Tetrahedron*, **1983**, *39*, 905.).

3-Butynylamine (1a).



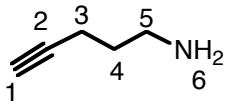
^{1}H NMR (270 MHz, $CDCl_3$) δ 1.44 (bs, 2H, H-5), 1.99 (t, *J* = 2.6 Hz, 1H, H-1), 2.31 (dt, 2H, *J* = 6.3 Hz, H-3), 2.83(t, *J* = 6.3 Hz, 2H, H-4).

***N*-Propyl-3-butynylamine (1b).**



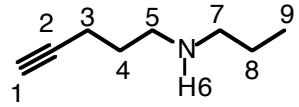
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.4 Hz, 3H, H-8), 1.37 (bs, 1H, H-5), 1.50 (sex, *J* = 7.3 Hz, 2H, H-7), 1.96-1.99 (m, 1H, H-1), 2.38 (dt, *J* = 6.9, 2.8 Hz, 2H, H-3), 2.58 (t, *J* = 7.3 Hz, 2H, H-6), 2.77 (t, *J* = 6.9 Hz, 2H, H-4); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.61, 19.43, 23.06, 47.83, 51.14, 69.32, 82.37; MS (EI) *m/z* (rel intensity)111 (M^+, 17), 82 (67), 72 (100), 53 (71).

4-Pentynylamine (1c).



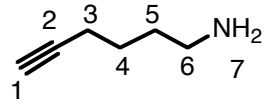
^{1}H NMR (270 MHz, $CDCl_3$) δ 1.55 (bs, 2H, H-6), 1.67 (qui, *J* = 6.9 Hz, 2H, H-4), 1.95 (t, *J* = 2.6 Hz, 1H, H-1), 2.26 (dt, *J* = 7.1, 2.6 Hz, 2H, H-3), 2.82 (t, *J* = 6.9 Hz, 2H, H-5).

***N*-Propyl-4-pentynylamine (1d).**



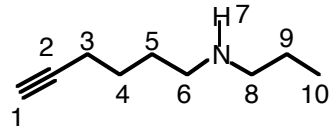
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.3 Hz, 3H, H-9), 1.05-1.25 (br, 1H, H-6), 1.49 (sex, *J* = 7.3 Hz, 2H, H-8), 1.70 (qui, *J* = 6.9 Hz, 2H, H-4), 1.94 (t, *J* = 2.3 Hz, 1H, H-1), 2.24 (dt, *J* = 7.3, 2.8 Hz, 2H, H-3), 2.56 (t, *J* = 6.9 Hz, 2H, H-7), 2.70 (t, *J* = 6.9 Hz, 2H, H-5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.72, 16.29, 23.20, 28.74, 48.68, 51.78, 68.45, 84.02; MS (EI) *m/z* (rel intensity) 125 (M^+, 46), 96 (100), 83 (78), 72 (83), 55 (75).

5-Hexynylamine (1e).



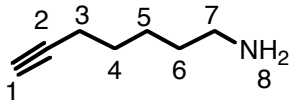
^{1}H NMR (270 MHz, $CDCl_3$) δ 1.40-1.70 (m, 6H, H-4, 5, 7), 1.99 (t, *J* = 2.7 Hz, 1H, H-1), 2.10-2.40 (m, 2H, H-3), 2.60-2.80 (m, 2H, H-6).

***N*-Propyl-5-hexynylmine (1f).**



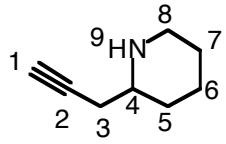
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.3 Hz, 3H, H-10), 1.10-1.40 (br, 1H, H-7), 1.49 (sex, *J* = 7.3 Hz, 2H, H-9), 1.53-1.63 (m, 4H, H-4, 5), 1.93 (t, *J* = 2.8 Hz, 1H, H-1), 2.20 (dt, *J* = 6.9, 2.7 Hz, 2H, H-3), 2.56 (t, *J* = 6.9 Hz, 2H, H-8), 2.61 (t, *J* = 6.9 Hz, 2H, H-6); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.77, 18.32, 23.22, 26.30, 29.26, 49.40, 51.93, 68.35, 84.28; MS (EI) *m/z* (rel intensity) 139 (M^+, 35), 110 (88), 97 (68), 82 (76), 72 (100), 53 (63).

6-Hepthynylamine (1g).



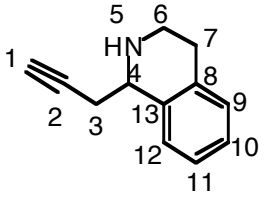
^{1}H NMR (270 MHz, $CDCl_3$) δ 1.40-1.60 (m, 8H, H-4, 5, 6, 8), 1.93 (t, *J* = 2.7 Hz, 1H, H-1), 2.19 (dt, *J* = 7.0, 2.7 Hz, 2H, H-3), 2.69 (t, *J* = 6.2 Hz, 2H, H-7).

2-Propynylpiperidine (1h).



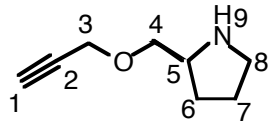
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.10-1.21 (m, 1H, H-5 or 6 or 7), 1.28-1.45 (m, 2H, H-5 or 6 or 7), 1.56-1.82 (m, 4H, H- 5 or 6 or 7 or 9), 2.01 (t, *J* = 2.7 Hz, 1H, H-1), 2.20 (ddd, *J* = 16.5, 7.3, 2.3 Hz, 1H, H-3), 2.28 (ddd, *J* = 16.5, 5.0, 2.8 Hz, 1H, H-3'), 3.05-3.11 (m, 1H, H-4).

1-(2-Propynyl)-1,2,3,4-tetrahydroisoquinoline (1i).



^{1}H NMR (500 MHz, $CDCl_3$) δ 2.06 (bs, 1H, H-5), 2.61-2.88 (m, 5H, H-1, 3, 6), 3.01-3.06 (m, 1H, H-7), 3.21-3.26 (m, 1H, H-7'), 4.17 (dd, *J* = 9.2, 3.7 Hz, 1H, H-4), 7.09-7.16 (m, 4H, H-9, 10, 11, 12).

[(2-Propynyloxy)methyl]pyrrolidine (1j).



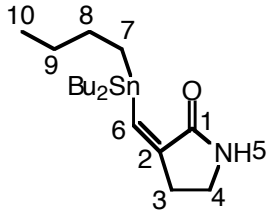
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34-1.48 (m, 1H, H-6 or 7), 1.64-1.78 (m, 2H, H-6 or 7), 1.79-1.88 (m, 1H, H-6 or 7), 1.99 (bs, 1H, H-9), 2.41 (t, *J* = 2.3 Hz, 1H, H-1), 2.83-2.89 (m, 1H, H-8), 2.93-3.00 (m, 1H, H-8'), 3.23-3.32 (m, 1H, H-5), 3.38 (dd, *J* = 8.7, 7.3 Hz, 1H, H-4), 3.52 (dd, *J* = 9.2, 4.6 Hz, 1H, H-4'), 4.10-4.20 (m, 2H, H-3).

Typical procedure for stannylcarbonylation of alkynylamine 1 (Method A).
A magnetic stirring bar, AIBN (2,2'-azobisisobutyronitrile, 16.2 mg, 0.1 mmol), benzene (50 mL), Bu_3SnH (170 mg, 0.58 mmol), and 4-pentynylpropylamine (65 mg, 0.52 mmol) were placed in a 100-mL stainless steel autoclave. The autoclave was closed, purged three times with carbon monoxide, pressurized with 75 atm of CO and then heated 90 °C for 3 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 (gradient from hexane to hexane/EtOAc = 5/1) to give (***Z***)**-2d** (77 mg, 33%), **4d** (14 mg, 6%), (***E***)**-2d** (4.3 mg, 2%), and **3d** (29 mg, 37%).

Typical procedure for protodestannylation (Method B).

After stannylcarbonylation (Method A), solvent was removed under reduced pressure. The residue was dissolved in MeOH (3.5 mL) and TMSCl (350 μL, 3.7 mmol) was added to the mixture. After stirring at room temperature for 10 min, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (gradient from hexane to hexane/EtOAc = 5/1) to give **3d** (58 mg, 71%).

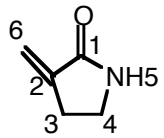
3-Tributylstannylmethylene-2-pyrrolidinone (2a).



E isomer: (R_f = 0.25, EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.76-1.05 (m, 15H, H-7, 10), 1.31 (sex, *J* = 7.3 Hz, 6H, H-9), 1.45-1.59 (m, 6H, H-8), 2.80-2.82 (m, 2H, H-3), 3.44 (t, *J* = 6.6 Hz, 2H, H-4), 7.11 (s, *J* ^{1}H-Sn = 56.0 Hz, H-6), 7.26 (bs, 1H, H-5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.31 (*J* ^{13}C-Sn = 332.1 Hz, C-7), 13.62 (C-10), 27.27 (*J* ^{13}C-Sn = 56.6 Hz, C-9), 28.26 (C-3), 29.10 (C-8), 137.18 (C-2), 146.85 (C-6), 169.84 (C-1); IR (neat) 2926, 2872, 1695, 1626; MS (EI) *m/z calculated from major ^{120}Sn isotope* (rel intensity) 330 (M^+-C_4H_9, 100), 269 (82), 216 (43); HRMS (EI) *m/z* calcd for $C_{17}H_{33}NO^{120}Sn$ (M^+-C_4H_9) 330.0880, found 330.0879.

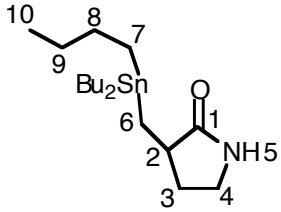
Z isomer: (R_f = 0.38, hexane/EtOAc = 3/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83-0.91 (m, 15H, H-7, 10), 1.27 (sex, *J* = 7.3 Hz, 6H, H-9), 1.44-1.54 (m, 6H, H-8), 2.84-2.87 (m, 2H, H-3), 3.37-3.40 (m, 2H, H-4), 6.51 (s, *J* ^{1}H-Sn = 61.4 Hz, H-6), 7.31 (bs, 1H, H-5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.50 (*J* ^{13}C-Sn = 346.5 Hz, C-7), 13.75 (C-10), 27.37 (*J* ^{13}C-Sn = 58.5 Hz, C-9), 28.87 (C-3), 29.25 (*J* ^{13}C-Sn = 20.2 Hz, C-8), 137.38 (C-2), 144.49 (C-6), 172.09 (C-1); IR (neat) 2955, 2926, 1651, 1581; MS (EI) *m/z calculated from major ^{120}Sn isotope* (rel intensity) 330 (M^+-C_4H_9, 100), 216 (42); HRMS (EI) *m/z* calcd for $C_{17}H_{33}NO^{120}Sn$ (M^+) 387.1512, found 387.1592.

3-Methylene-2-pyrrolidinone (3a).



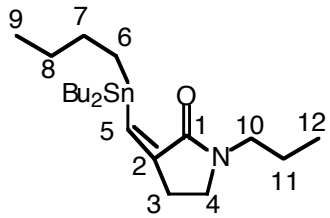
(R_f = 0.13, EtOAc/MeOH = 19/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.86-2.90 (m, 2H, H-3), 3.45 (t, *J* = 6.6 Hz, 2H, H-4), 5.39 (m, 1H, H-6), 6.01 (m, 1H, H-6), 6.46 (bs, 1H, H-5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.24 (C-3), 39.05 (C-4), 116.09 (C-6), 138.70 (C-2), 171.05 (C-1); IR (KBr) 2928, 2892, 1691, 1671, 1655; This product is a known compound and was identified by NMR with comparison of literature data (S. Klutchko *et al. J. Med. Chem.* **1981**, *24*, 104.).

3-Tributylstannylmethyl-2-pyrrolidinone (4a).



(R_f = 0.13, hexane/EtOAc = 3/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.73-0.91 (m, 15H, H-7, 10), 1.18-1.32 (m, 8H, H-6, 9), 1.34-1.53 (m, 6H, H-8), 1.56-1.74 (m, 1H, H-3), 2.26-2.32 (m, 1H, H-3'), 2.38-2.48 (m, 1H, H-2), 3.22-3.31 (m, 2H, H-4), 6.63 (bs, 1H, H-5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.54 (C-7), 13.66 (C-10), 27.39 (*J* ^{13}C-Sn = 54.7 Hz, C-9), 29.17 (C-8), 31.59 (C-3), 39.35 (C-2), 39.80 (C-4), 182.04 (C-1); IR (neat) 2924, 2870, 1651; MS (EI) *m/z calculated from major ^{120}Sn isotope* (rel intensity) 332 (M^+-C_4H_9, 100), 218 (21); HRMS (EI) *m/z* calcd for $C_{13}H_{26}NO^{120}Sn$ (M^+-C_4H_9) 332.1036, found 332.1035.

***N*-Propyl-3-tributylstannylmethylene-2-azacyclopentanone (2b).**

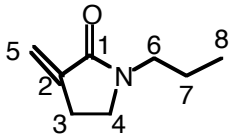


E isomer: (R_f = 0.6, hexane/EtOAc = 2/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83-1.03 (m, 18H, H-6, 9, 12), 1.25-1.34 (m, 6H, H-8), 1.43-1.63 (m, 8H, H-7, 11), 2.66-2.78 (m, 2H, H-3), 3.27-3.42 (m, 4H, H-4, 10), 7.05 (s, *J* ^{1}H-Sn = 57.7 Hz, 1H, H-5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.38 (C-12), 9.74 (*J* ^{13}C-Sn = 353.2 Hz, C-6), 13.71 (C-9), 20.55 (C-11), 26.46 (C-3), 27.37 (*J* ^{13}C-Sn = 56.6 Hz, C-8), 29.21 (*J* ^{13}C-Sn = 21.1 Hz, C-7), 43.54 (C-4), 45.13 (C-10), 131.96 (C-2), 147.75 (C-5), 166.64 (C-1); IR (neat)

1686, 1624; MS (EI), *m/z calculated from major ^{120}Sn isotope* (rel intensity) 372 (M^+-C_4H_9, 100), 316 (21), 258 (41); HRMS (EI) *m/z* calcd for $C_{16}H_{30}NO^{120}Sn$ (M^+-C_4H_9) 372.1350, found 372.1355.

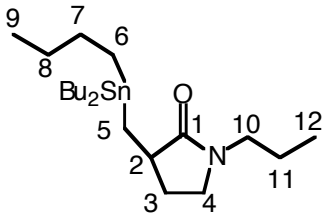
Z isomer: (R_f = 0.83, hexane/EtOAc = 2/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89-1.03 (m, 18H, H-6, 9, 12), 1.21-1.34 (m, 6H, H-8), 1.36-1.62 (m, 8H, H-7, 11), 2.71-2.82 (m, 2H, H-3), 3.26-3.38 (m, 4H, H-4, 10), 6.41 (s, *J* ^{1}H-Sn = 65.4 Hz 1H, H-5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.13 (C-12), 11.41 (C-6), 13.71 (C-9), 20.41 (C-11), 27.12 (C-3), 27.36 (C-8), 29.27 (C-7), 43.51 (C-4), 44.85 (C-10), 135.80 (C-2), 145.52 (C-5), 168.66 (C-1); IR (neat) 1683, 1620; MS (EI), *m/z calculated from major ^{120}Sn isotope* (rel intensity) 372 (M^+-C_4H_9, 100), 258 (30); HRMS (EI) *m/z* calcd for $C_{16}H_{30}NO^{120}Sn$ (M^+-C_4H_9) 372.1350, found 372.1344.

_N_-Propyl-3-methylene-2-azacyclopentanone (3b).



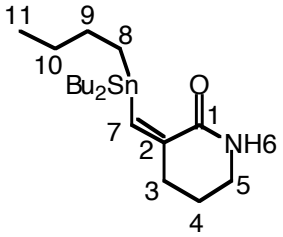
(R_f = 0.10, hexane/EtOAc = 2/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.3 Hz, 3H, H-8), 1.57 (sex, *J* = 7.5 Hz, 2H, H-7), 2.73 (m, 2H, H-3), 3.32 (t, *J* = 7.6 Hz, 2H, H-4), 3.37 (t, *J* = 6.6 Hz, 2H, H-6), 5.28 (s, 1H, H-5), 5.94 (s, 1H, H-5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.28 (C-8), 20.43 (C-7), 24.01 (C-3), 43.94 (C-4), 44.77 (C-6), 114.94 (C-2), 139.89 (C-5), 167.92 (C-1); IR (neat) 1686, 1659; MS (EI), *m/z* (rel intensity) 139 (M^+, 36), 124 (61), 110 (100); HRMS (EI) *m/z* calcd for $C_9H_{15}NO$ (M^+) 139.0997, found 139.0982.

_N_-Propyl-3-tributylstannylmethyl-2-azacyclopentanone (4b).



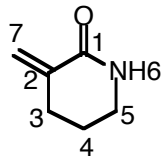
(R_f = 0.78, hexane/EtOAc = 2/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.71-0.96 (m, 19H, H-5, 6, 9, 12), 1.13-1.35 (m, 7H, H-5', 8), 1.36-1.58 (m, 10H, H-3, 7, 11), 2.17-2.26 (m, 1H, H-4), 2.42-2.56 (m, 1H, H-2), 3.14-3.29 (m, 4H, H-4, 10); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.66 (*J* ^{13}C-Sn = 317.2 Hz, C-6), 11.30 (C-12), 11.69 (C-5), 13.75 (C-9), 20.63 (C-11), 27.49 (*J* ^{13}C-Sn = 54.7 Hz, C-8), 29.29 (C-7), 40.53 (C-2), 44.49 (C-4), 44.85 (C-10), 177.95 (C-1); IR (neat) 1689; MS (EI) *m/z calculated from major ^{120}Sn isotope* (rel intensity) 374 (M^+-C_4H_9, 100), 260 (27); HRMS (EI) *m/z* calcd for $C_{16}H_{30}NO^{120}Sn$ (M^+-C_4H_9) 374.1505, found 374.1508.

3-Tributylstannylmethylene-2-piperidione (2c).



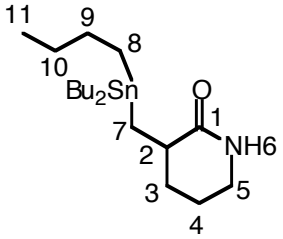
E isomer: (R_f = 0.38, EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87-0.90 (m, 15H, H-8, 11), 1.23-1.46 (m, 6H, H-10), 1.61 (qui, *J* = 7.6 Hz, 6H, H-9), 1.92-1.98 (m, 2H, H-4), 2.69-2.72 (m, 2H, H-3), 3.45-3.52 (m, 2H, H-5), 6.54 (bs, 1H, H-6), 7.05 (s, *J* ^{1}H-Sn = 90.7 Hz, 1H, H-7); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.61 (C-8), 20.23 (C-11), 22.85 (C-4), 26.63 (C-10), 27.98 (C-9), 30.22 (C-3), 42.92 (C-5), 140.55 (C-7), 154.86 (C-2), 169.19 (C-1); MS (EI) *m/z calculated from major ^{120}Sn isotope* (rel intensity) 344 (M^+-C_4H_9, 19), 322, (100), 230 (76), 149 (20); IR (neat) 3297, 3246, 2955, 2924, 2870, 1641, 1575; HRMS (EI) *m/z* calcd for $C_{15}H_{30}NO^{120}Sn$ (M^+-C_4H_9) 344.1037, found 344.1037.
Z isomer: (R_f = 0.20, hexane/EtOAc = 4/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.77-0.92 (m, 15H, H-8, 11), 1.28 (sex, *J* = 7.3 Hz, 6H, H-10), 1.40-1.49 (m, 6H, H-9), 1.66-1.95 (m, 2H, H-4), 2.63 (m, 2H, H-3), 3.35-3.38 (m, 2H, H-5), 6.45 (s, *J* ^{1}H-Sn = 69.2 Hz, 1H, H-7), 6.85 (bs, 1H, H-6); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.83 (C-8), 13.78 (C-11), 23.63 (C-4), 27.46 (*J* ^{13}C-Sn = 58.5 Hz, C-10), 29.33 (C-9), 33.29 (C-3), 42.80 (C-5), 142.85 (C-2), 146.17 (C-7), 166.81 (C-1); IR (neat) 3189, 2953, 1663, 1586; MS (EI) *m/z calculated from major ^{120}Sn isotope* (rel intensity) 344 (M^+-C_4H_9, 100), 230 (45); HRMS (EI) *m/z* calcd for $C_{14}H_{26}NO^{120}Sn$ (M^+-C_4H_9) 344.1037, found 344.1039.

3-Methylene-2-piperidione (3c).



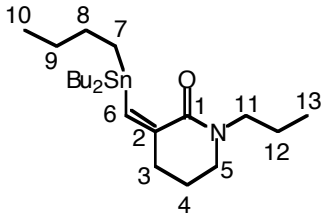
(R_f = 0.18, EtOAc/MeOH = 19/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.87 (qui, *J* = 6.0 Hz, 2H, H-4), 2.57-2.60 (m, 2H, H-3), 3.39-3.41 (m, 2H, H-5), 5.32 (d, *J* = 1.4 Hz, 1H, H-7), 6.21 (d, *J* = 1.8 Hz, 1H, H-7); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.08 (C-4), 29.75 (C-3), 42.63 (C-5), 122.07 (C-7), 137.51 (C-2), 166.04 (C-1); IR (neat) 2864, 1668, 1618; This product is a known compound and was identified by NMR with comparison of literature data (S. Klutchko *et al. J. Med. Chem.* **1981**, *24*, 104.).

3-Tributhylstannylmethyl-2-piperidione (4c).



(R_f = 0.13, hexane/EtOAc = 4/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0,78-0.89 (m, 15H, H-8, 11), 1.14-1.32 (m, 8H, H-7, 10), 1.35-1.50 (m, 7H, H-3 or 4, 9), 1.63-1.73 (m, 1H, H-3 or 4), 1.81-1.85 (m, 1H, H-3 or 4), 1.91-1.97 (m, 1H, H-3 or 4), 2.42 (qui, *J* = 7.8 Hz, 1H, H-2), 3.24-3.26 (m, 2H, H-5), 6.70 (bs, 1H, H-6); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.83 (*J* ^{13}C-Sn = 312.9 Hz, C-8), 12.93 (C-7), 13.65 (C-11), 21.67 (C-4), 27.40 (*J* ^{13}C-Sn = 54.7 Hz, C-10), 29.2 (*J* ^{13}C-Sn = 19.2 Hz, C-9), 31.27 (C-3), 39.49 (C-2), 42.50 (C-5), 176.71 (C-1); IR (neat) 3202, 3078, 1659; MS (EI) *m/z calculated from major ^{120}Sn isotope* (rel intensity) 346 (M^+- C_4H_9, 27), 324 (100), 230 (33), 198 (22), 151 (52); HRMS (EI) *m/z* calcd for $C_{14}H_{28}NO^{120}Sn$ (M^+) 346.1193, found 346.1195.

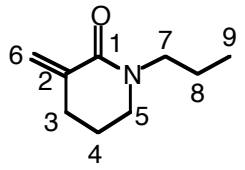
***N*-Propyl-3-tributylstannylmethylene-2-piperidinone (2d).**



E isomer: (R_f = 0.33, hexane/EtOAc = 5/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89-1.03 (m, 18H, H-7, 10, 13), 1.22-1.39 (m, 6H, H-9), 1.40-1.68 (m, 6H, H-8,12), 1.82-1.94 (m, 2H, H-4), 2.49-2.58 (m, 2H, H-3), 3.31-3.42 (m, 4H, H-5,11), 7.40 (s, *J* ^{1}H-Sn = 65.4 Hz 1H, H-6); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.09 (C-7), 11.49 (C-13), 13.73 (C-10), 20.45 (C-12), 23.80 (C-4), 27.37 (C-9), 29.22 (C-8), 32.67 (C-3), 48.58 (C-5), 49.78 (C-11), 139.71 (C-2), 144.77 (C-6), 163.46 (C-1); IR (neat) 1642, 1586; MS (EI), *m/z calculated from major ^{120}Sn isotope* (rel intensity) 386 (M^+-C_4H_9, 100), 272 (46); HRMS (EI) *m/z* calcd for $C_{17}H_{32}NO^{120}Sn$ (M^+-C_4H_9) 386.1506, found 386.1509.

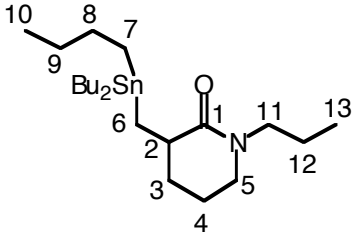
Z isomer: (R_f = 0.3, hexane/EtOAc = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.78-0.92 (m, 18H, H-7, 10, 13), 1.23-1.30 (sex, *J* = 7.3 Hz, 6H, H-9), 1.37-1.60 (m, 6H, H-8,12), 1.82-1.87 (m, 2H, H-4), 2.61-2.63 (m, 2H, H-3), 3.32-3.36 (m, 4H, H-5,11), 6.33 (s, *J* ^{1}H-Sn = 71.0 Hz 1H, H-6); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.3 (C-7), 11.9 (C-13), 13.9 (C-10), 20.42 (C-12), 23.83 (C-4), 27.57 (*J* ^{13}C-Sn = 59.5 Hz, C-9), 29.45 (*J* ^{13}C-Sn = 21.1 Hz, C-8), 33.85 (C-3), 48.68 (C-5), 49.27 (C-11), 143.87 (C-2), 144.22 (C-6), 165.09 (C-1); IR (neat) 1636, 1584; MS (EI), *m/z calculated from major ^{120}Sn isotope* (rel intensity); 386 (M^+-C_4H_9, 100), 272 (48); HRMS (EI) *m/z* calcd for $C_{17}H_{32}NO^{120}Sn$ (M^+-C_4H_9) 386.1506, found 386.1513.

***N*-Propyl-3-methylene-2-piperidinone (3d).**



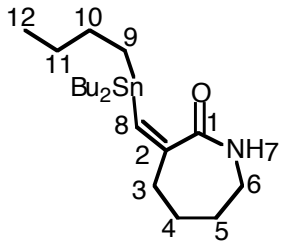
(R_f = 0.2, hexane/EtOAc = 5/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.3 Hz, 3H, H-9), 1.87 (sex, *J* = 7.3 Hz, 2H, H-8), 1.83 (qui, *J* = 6.0 Hz, 2H, H-4), 2.52 (t, *J* = 6.2 Hz, 2H, H-3), 3.30-3.38 (m, 4H, H-5, 7), 5.21 (s, 1H, H-6), 6.15 (s, 1H, H-6); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.29 (C-9), 20.25 (C-8), 23.19 (C-4), 30.06 (C-3), 48.36 (C-5), 49.26 (C-7), 121.16 (C-6), 137.79 (C-2), 163.91 (C-1); IR (neat) 1659, 1615; MS (EI) *m/z* (rel intensity) 153 (M^+, 22), 139 (36), 124 (61), 110 (100); HRMS (EI) *m/z* calcd for $C_9H_{15}NO$ (M^+) 153.1153, found 153.1159.

***N*-Propyl-3-tributylstannylmethyl-2-piperidinone (4d).**



(R_f = 0.3, hexane/EtOAc = 5/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.76-1.11 (m, 19H, H-6, 7, 10, 13), 1.24-1.32 (m, 7H, H-6', 9), 1.35-1.56 (m, 9H, H-3, 8, 12), 1.68-1.78 (m, 1H, H-4), 1.82-1.98 (m, 2H, H-3', 4'), 2.38-2.57 (m, 1H, H-2), 3.18-3.30 (m, 4H, H-5, 11); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.85 (*J* ^{13}C-Sn = 318.1 Hz, C-7), 11.38 (C-13), 13.67 (C-6), 13.78 (C-10), 20.38 (C-12), 21.85 (C-4), 27.53 (*J* ^{13}C-Sn = 56.6 Hz, C-9), 29.32 (*J* ^{13}C-Sn = 18.2 Hz, C-8), 31.36 (C-3), 40.00 (C-2), 48.21 (C-5), 49.00 (C-11), 173.85 (C-1); IR (neat) 1634; MS (EI), *m/z calculated from major ^{120}Sn isotope* (rel intensity); 388 (M^+-C_4H_9, 67), 350 (100); HRMS (EI) *m/z* calcd for $C_{17}H_{34}NO^{120}Sn$ (M^+-C_4H_9) 388.1662, found 388.1664.

3-Tributhylstannylmethylene-2-aszacycloheptanone (**2e**).

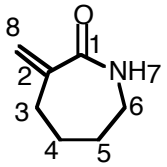


E isomer: (R_f = 0.5, EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86-1.03 (m, 15H, H-9, 12), 1.32 (sex, *J* = 6.9 Hz, 6H, H-11), 1.40-1.59 (m, 6H, H-10), 1.63-1.82 (m, 4H, H-4, 5), 2.05-2.49 (m, 2H, H-3), 3.17 (dd, *J* =10.1, 5.5 Hz, 2H, H-6), 6.41 (bs, 1H, H-7), 6.59 (s, *J* ^{1}H-Sn = 60.0 Hz, 1H, H-8); ^{13}C NMR (125

MHz, $CDCl_3$) δ 10.22 (C-9), 13.62 (C-12), 27.29 (C-11), 28.82 (C-4 or 5), 29.10 (C-10), 29.37 (C-4 or 5), 34.62 (C-3), 42.06 (C-6), 136.83 (C-8), 154.08 (C-2), 176.64 (C-1); IR (neat) 2926, 2853, 1653, 1464; MS (EI) *m/z calculated from major ^{120}Sn isotope* (rel intensity) 358 (M^+-C_4H_9, 100), 302 (46), 244 (59); HRMS (EI) *m/z* calcd for $C_{19}H_{37}NO^{120}Sn$ (M^+) 415.1897, found 415.1910.

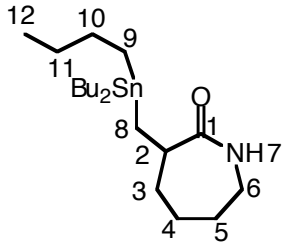
Z isomer: (R_f = 0.25, hexane/EtOAc = 4/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83-0.96 (m, 15H, H-9, 12), 1.28 (sex, *J* = 7.3 Hz, 6H, H-11) 1.41-1.54 (m, 6H, H-10), 1.66-1.76 (m, 4H, H-4, 5), 2.44-2.46 (m, 2H, H-3), 3.17 (m, 2H, H-6), 6.29 (s, *J* ^{1}H-Sn = 64.6 Hz, 1-H, H-8), 6.44 (bs, 1H, H-7); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.77 (C-9), 13.75 (C-12), 27.38 (*J* ^{13}C-Sn = 57.6 Hz, C-11), 28.62 (C-4 or 5), 29.04 (C-4 or 5), 29.08 (C-10), 36.44 (C-3), 42.54 (C-6), 140.89 (C-8), 152.98 (C-2), 176.02 (C-1); IR (neat) 2910, 2840, 1750, 1640 cm^{-1}; MS (EI) *m/z calculated from major ^{120}Sn isotope* (rel intensity) 358 (M^+- C_4H_9, 100), 244 (32); HRMS (EI) calcd for *m/z* $C_{15}H_{28}NO^{120}Sn$ (M^+-C_4H_9) 358.1193, found 358.1194.

3-Methylene-2-aszacycloheptanone (**3e**).



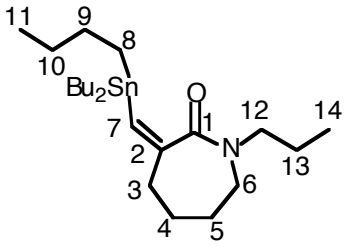
(R_f = 0.2, EtOAc/MeOH = 19/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.65-1.76 (m, 4H, H-4, 5), 2.33-2.36 (m, 2H, H-3), 3.14-2.36 (m, 2H, H-6), 5.25 (s, 1H, H-8), 5.56 (s, 1H, H-8), 6.66 (bs, 1H, H-7); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.80 (C-4 or 5), 29.53 (C-4 or 5), 32.60 (C-3), 42.66 (C-6), 120.23 (C-8), 146.24 (C-2), 175.94 (C-1); IR (neat) 3207, 2938, 1651, 1630; MS (EI) *m/z* (rel intensity) 125 (M^+, 50), 97 (100), 68 (57), 49 (28); HRMS (EI) *m/z* calcd for $C_7H_{11}NO$ (M^+) 125.0841, found 125.0842.

3-Tributylstannylmethyl-2-aszacycloheptanone (**4e**)**.**



(R_f = 0.2, hexane/EtOAc = 4/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.75-0.93 (m, 15H, H-9, 12), 1.04-1.11 (m, 1H, H-8), 1.23-1.34 (m, 7H, H-8', 11), 1.36-1.55 (m, 6H, H-10), 1.57-1.69 (m, 2H, H-5), 1.70-1.81 (m, 2H, H-4), 1.85-2.01 (m, 2H, H-3), 2.66-2.73 (m, 1H, H-2), 3.14-3.25 (m, 2H, H-6), 6.22 (bs, 1H, H-7); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.82 (C-9), 13.31 (C-8), 13.73 (C-12), 27.46 (C-11), 29.24 (C-10), 29.77 (C-5), 30.90 (C-4), 34.46 (C-3), 41,94 (C-2), 42.24 (C-6) 181.09 (C-1); IR (neat) 2910, 2840, 1660, 1480; MS (CI) *m/z calculated from major ^{120}Sn isotope* (relative intensity) 418 (M^++H, 81), 360 (100), 291 (15), 128 (31), 126 (31), 73 (13); HRMS (CI) *m/z* calcd for $C_{19}H_{39}NO^{120}Sn$ (M^++H) 418.2135, found 418.2131.

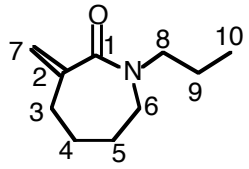
***N*-Propyl-3-tributylstannylmethylene-2-azacycloheptanone (2f).**



E isomer: (R_f = 0.58, hexane/EtOAc = 2/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85-1.01 (m, 18H, H-8, 11, 14), 1.25-1.37 (m, 6H, H-10), 1.42-1.60 (m, 8H, H-9, 13), 1.61-1.74 (m, 4H, H-4, 5), 2.25-2.36 (m, 2H, H-3), 3.23-3.29 (m, 2H, H-6), 3.31-3.38 (m, 2H, H-12), 6.37 (s, *J* ^{1}H-Sn = 60.9 Hz 1H, H-7); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.27 (C-8), 11.45 (C-14), 13.72 (C-11), 21.45 (C-13), 27.40 (C-9), 27.65 (C-4 or 5), 28.20 (C-4 or 5), 29.24 (C-10), 34.19 (C-3), 48.66 (C-6), 49.34 (C-12), 133.49 (C-7), 155.94 (C-2), 173.79 (C-1); IR (neat) 1636; MS (EI) *m/z calculated from major ^{120}Sn isotope* (relative intensity) 400 (M^+-C_4H_9, 100), 344 (24); HRMS (EI) *m/z* calcd for $C_{18}H_{34}NO^{120}Sn$ (M^+-C_4H_9) 400.1662, found 400.1668.

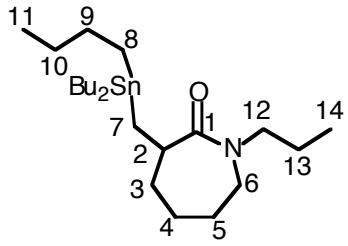
Z isomer: (R_f = 0.85, hexane/EtOAc = 2/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.70-0.96 (m, 18H, H-8, 11, 14), 1.27 (sex, *J* = 7.5 Hz, 6H, H-10), 1.37-1.60 (m, 8H, H-9, 13), 1.61-1.73 (m, 4H, H-4, 5), 2.36-2.42 (m, 2H, H-3), 3.23-3.34 (m, 2H, H-6, 12), 6.15 (s, *J* ^{1}H-Sn = 64.6 Hz 1H, H-7); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.50 (*J* ^{13}C-Sn = 344.5 Hz, C-8), 11.56 (C-14), 13.82 (C-11), 21.39 (C-13), 27.48 (*J* ^{13}C-Sn = 58.5 Hz, C-10), 27.77 (C-4 or 5), 28.72 (C-4 or 5), 29.31 (*J* ^{13}C-Sn = 20.2 Hz, C-9), 36.44 (C-3), 49.07 (C-6), 49.75 (C-12), 136.06 (C-7), 155.74 (C-2), 173.56 (C-1); IR (neat) 1630; MS (EI), *m/z calculated from major ^{120}Sn isotope* (relative intensity) 400 (M^+-C_4H_9, 100), 286 (27); HRMS (EI) *m/z* calcd for $C_{18}H_{34}NO^{120}Sn$ (M^+-C_4H_9) 400.1662, found 400.1665.

***N*-Propyl-3-methylene-2-azacycloheptanone (3f).**



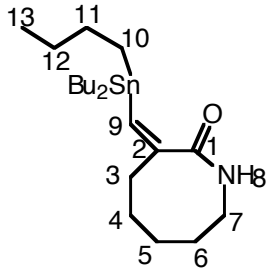
(R_f = 0.18, hexane/EtOAc = 1/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (t, *J* = 7.3 Hz, 3H, H-10), 1.50 (sex, *J* = 7.5 Hz, 2H, H-9), 1.56-1.72 (m, 4H, H-4, 5), 2.23-2.29 (m, 2H, H-3), 3.19-3.24 (m, 2H, H-6), 3.26-3.32 (m, 2H, H-8), 5.12 (s, 1H, H-7), 5.35 (s, 1H, H-7); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.35 (C-10), 21.28 (C-9), 27.82 (C-4 or 5), 28.87 (C-4 or 5), 32.36 (C-3), 48.97 (C-6), 49.48 (C-8), 117.99 (C-2), 147.78 (C-7), 172.95 (C-1); IR (neat) 1644; MS (EI) *m/z* (relative intensity), 167 (M^+, 52), 138 (100); HRMS (EI) *m/z* calcd for $C_9H_{15}NO$ (M^+) 167.1311, found 167.1305.

_N_-Propyl-3-tributylstannylmethyl-2-azacycloheptanone (4f).



(R_f = 0.78, hexane/EtOAc = 2/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.70-0.96 (m, 19H, H-7, 8, 11, 14), 1.08-1.15 (m, 1H, H-7'), 1.26 (sex, *J* = 7.5 Hz, 6H, H-10), 1.32-1.64 (m, 12H, H-3, 4, 5, 9, 13), 1.71-1.79 (m, 1H, H-4'), 1.86-1.92 (m, 1H, H-3'), 2.68-2.84 (m, 1H, H-2), 3.16-3.30 (dd, *J* = 15.1, 5.0 Hz, 1H, H-6), 3.25 (dt, *J* = 13.3, 7.8 Hz, 1H, H-12), 3.36 (dt, *J* = 13.3, 7.8 Hz, 1H, H-12), 3.49 (dd, *J* = 15.1, 5.0 Hz, 1H, H-6); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.88 (*J* ^{13}C-Sn = 314.8 Hz, C-8), 11.50 (C-14), 13.81 (C-11), 14.65 (C-7), 21.46 (C-13), 27.58 (*J* ^{13}C-Sn = 52.7 Hz, C-9), 28.32 (C-4 or 5), 29.37 (*J* ^{13}C-Sn = 19.2 Hz, C-10), 29.48 (C-4 or 5), 35.12 (C-3), 42.24 (C-2), 48.83 (C-6), 50.33 (C-12), 177.64 (C-1); IR (neat) 1642; MS (EI), *m/z calculated from major ^{120}Sn isotope* (relative intensity) 402 (M^+-C_4H_9, 100), 288 (25); HRMS (EI) *m/z* calcd for $C_{18}H_{36}NO^{120}Sn$ (M^+-C_4H_9) 402.1818, found 402.1823.

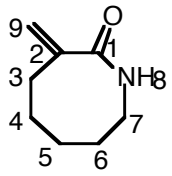
3-Tributhylstannylmethylene-2-azacyclooctanone (2g).



E isomer: (R_f = 0.25, hexane/EtOAc =1/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86-0.96 (m, 15H, H-10, 13), 1.30 (sex, *J* = 7.3 Hz, 6H, H-12), 1.45-1.64 (m, 12H, H-4, 5, 6, 11), 2.38-2.40 (m, 2H, H-3), 3.29-3.32 (m, 2H, H-7), 5.68 (bs, 1H, H-8), 5.87 (s, *J* ^{1}H-Sn = 60.5 Hz, 1H, H-9); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.41 (C-10), 13.62 (C-13), 24.94 (C-4 or 5 or 6), 26.50 (C-4 or 5 or 6), 27.31 (C-12), 29.18 (C-11), 31.94 (C-4 or 5 or 6), 39.36 (C-3), 41.89 (C-7), 128.91 (C-9), 154.15 (C-2), 177.44 (C-1); IR (neat) 2955, 2926, 1649, 1464; MS (EI) *m/z calculated from major ^{120}Sn isotope* (rel intensity) 372 (M^+- C_4H_9, 100), 316 (43), 269 (26), 258 (42), 149 (25); HRMS (EI) *m/z* calcd for $C_{16}H_{30}NO^{120}Sn$ (M^+-C_4H_9) 372.1350, found 372.1348.

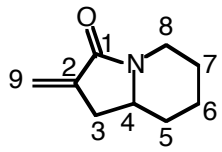
Z isomer: (R_f = 0.13, hexane/EtOAc = 4/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86-0.96 (m, 15H, H-10, 13), 1.28 (sex, *J* = 7.3 Hz, 6H, H-12), 1.40-1.51 (m, 6H, H-11), 1.55-1.75 (m, 6H, H-4, 5, 6), 2.49-2.50 (m, 2H, H-3), 3.28-3.32 (m, 2H, H-7), 5.89 (bs, 1H, H-8), 6.02 (s, *J* ^{1}H-Sn = 57.7 Hz, 1H, H-9); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.43 (C-10), 13.69 (C-13), 24.94 (C-4 or 5 or 6), 26.50 (C-4 or 5 or 6), 27.31 (C-12), 29.18 (C-11), 31.95 (C-4 or 5 or 6), 39.36 (C-3), 41.89 (C-7), 128.90 (C-9), 154.18 (C-2), 177.39 (C-1); IR (neat) 2953, 2930, 1645, 1464; MS (EI) *m/z calculated from major ^{120}Sn isotope* (rel intensity) 372 (M^+-C_4H_9, 100), 269 (48), 149 (66); HRMS (EI) *m/z* calcd for $C_{16}H_{30}NO^{120}Sn$ (M^+-C_4H_9) 372.1350, found 372.1350.

3-Methylene-2- azacyclooctanone (3g).



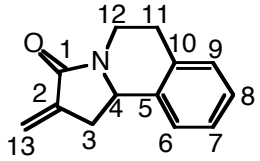
(R_f = 0.2, EtOAc/MeOH = 19/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.52-1.61 (m, 6H, H-4, 5, 6), 2.37-2.40 (m, 2H, H-3), 3.26-3.30 (m, 2H, H-7), 4.98-5.13 (m, 1H, H-9), 5.14-5.17 (m, 1H, H-9); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.53 (C-4 or 5 or 6), 26.22 (C-4 or 5 or 6), 31.59 (C-4 or 5 or 6), 37.36 (C-3), 41.54 (C-7), 114.34 (C-9), 145.75 (C-2), 176.31 (C-1); IR (neat) 2930, 2861, 1738, 1640, 1620; MS (EI) *m/z* (rel intensity) 139 (M^+, 14), 111 (100), 67 (62); HRMS (EI) *m/z* calcd for $C_{15}H_{30}N$ (M^+) 415.1901, found 415.1910.

1-Oxo-2-methyleneoctahydroindolizine (3h).



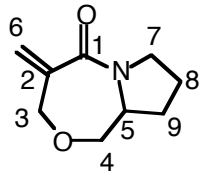
(R_f = 0.18, Hexane/EtOAc = 1/1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.08-1.20 (m, 1H, CH_2), 1.30-1.47 (m, 2H, CH_2), 1.66-1.69 (m, 1H, CH_2), 1.84-1.90 (m, 2H, CH_2), 2.27-2.30 (m, 1H, CH_2), 2.68-2.73 (m, 1H, CH_2), 2.86-2.90 (m, 1H, CH_2), 3,41-4.44 (m, 1H, CH_2), 4.18-4.20 (m, 1H, H-4), 5.21-5.28 (m, 1H, H-9), 5.88-5.91 (m, 1H, H-9); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.90 (C-3 or 5), 24.67 (C-3 or 5), 31.84 (C-6 or 7), 33.74 (C-6 or 7), 40.69 (C-8), 54.50 (C-4), 115.05 (C-9), 139.60 (C-2), 166.84 (C-1); IR (neat) 2932, 2854, 1685, 1658; MS (EI) *m/z* (rel intensity) 151 (M^+, 100), 122 (34), 110 (19), 95 (21); HRMS (EI) *m/z* calcd for $C_9H_{13}NO$ (M^+) 151.0997, found 151.0985.

Pyrrolo[2,1-a]isoquinolin-3(2H)-one (3i).



Carbonylation with tributyltin hydride was carried out with V-40 (1,1'-azobis(cyclohexane-1-carbonitrile)) as a radical initiator. (R_f = 0.18, Hexane/EtOAc = 1/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.68-2.83 (m., 2H, H-3), 2.98-3.06 (m, 1H, H-12), 3.16-3.23 (m, 1H, H-12'), 3.40 (ddd, *J* = 16.6, 7.8, 2.0 Hz, 1H, H-11), 4.39 (ddd, *J* = 12.9, 6.1, 2.2 Hz, 1H, H-11'), 5.36-5.37 (m, 1H, H-13), 5.98-6.02 (m, 1H, H-13), 7.11-7.26 (m, 4H, H-6, 7, 8, 9); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.35 (C-3 or 11), 33.43 (C-3 or 11), 37.69 (C-12), 54.05 (C-4), 115.17 (C-13), 124.92 (C-6 or 7 or 8 or 9), 126.80 (C-6 or 7 or 8 or 9), 126.98 (C-6 or 7 or 8 or 9), 129.07 (C-6 or 7 or 8 or 9), 133.64 (C-5 or 10), 137.22 (C-5 or 10), 139.61 (C-2), 166.33 (C-1); IR (KBr) 2934, 1686, 1433; MS (EI) *m/z* (rel intensity) 199 (M^+, 77), 198 (100), 149 (26), 130 (20); HRMS (EI) *m/z* calcd for $C_{13}H_{13}NO$ (M^+) 199.0997, found 199.0996.

Hexahydro-4-methylene-(9aS)-1H,5H-pyrrolo[2,1-c][1,4]oxazepine-5-one (3j).



^{1}H NMR (500 MHz, $CDCl_3$) δ 1.44-1.58 (m, 1H, H-9), 1.70-1.81 (m, 1H, H-8), 1.82-1.92 (m, 1H, H-8'), 2.25-2.42 (m, 1H, H-9'), 3.34 (dd, *J* = 11.9, 9.2 Hz, 1H, H-4), 3.40 (ddd, *J* = 15.6, 8.7, 6.8, 1H, H-7), 3.81 (ddd, *J* = 11.9, 7.8, 3.7, 1H, H-7'), 3.82-3.89 (m, 1H, H-5), 3.90 (dd, *J* = 12.4, 1.8 Hz, 1H, H-4'), 4.01 (d, *J* = 12.8 Hz, 1H, H-3), 4.30 (d, *J* = 12.8 Hz, 1H, H-3'), 5.50 (s, 1H, H-6), 5.90 (s, 1H, H-6); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.81 (C-8), 29.67 (C-9), 47.29 (C-7), 60.01 (C-5), 70.54 (C-3), 73.80 (C-4), 125.51 (C-2), 144.22 (C-6), 169.27 (C-1); IR (neat) 1647; MS (EI) *m/z* (rel intensity) 167 (M^+, 12), 149 (11), 137 (21), 109 (28), 83 (100); HRMS (EI) *m/z* calcd for $C_9H_{13}NO$ (M^+) 167.0946, found 167.0946.