Supplementary Information
for
“Pyrrole Synthesis Catalyzed by AgOTf or Cationic Au(I) Complexes”

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1. General Experimental

All reactions were performed under an atmosphere of dry nitrogen. Glassware was flame-dried prior to use. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl prior to use. Dichloromethane, 1,2-dichloroethane and toluene were distilled from calcium hydride prior to use. Common reagents or materials were purchased from commercial sources and purified by standard distillation or recrystallization prior to use. Thin layer chromatography (TLC) was performed on DC-Fertigplatten SIL G-25 UV₂₅₄ pre-coated TLC plates. Triethylamine washed silica gel has been stirred with triethylamine prior to packing and then sequentially flushed with polar solvent component and the solvent system of choice. Melting points are uncorrected. Proton nuclear magnetic resonance (¹H NMR) spectra and carbon nuclear magnetic resonance (¹³C NMR) spectra were both recorded in deuteriochloroform. Chemical shifts are reported in parts per million (ppm) and are referenced to the centerline of deuteriochloroform (δ 7.24 ppm ¹H NMR; 77.0 ppm ¹³C NMR). Coupling constants (*J* values) are given in Hertz (Hz).

2. Experimental Procedures-Pyrrole Synthesis

a) Conversion of 3 to 4

(5,6,7,8-Tetrahydro-indolizin-3-yl)-acetic acid methyl ester (**4**)

To a tube charged with 35 mg of **3** (0.12 mmol), 1.7 mg of gold (III) chloride (0.006 mmol), 1.5 mg of silver (I) trifluoromethanesulfonate (0.0058 mmol) was added 1.2 mL of a 3:1 THF-dichloromethane mixture. The tube was sealed and the reaction mixture stirred at 100 °C for 11 h. The dark brown reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude brown residue.

Purification by column chromatography on triethylamine washed silica gel (10:1 hexanes:ethyl acetate) afforded 14 mg (59 %) of **4** as a colorless film.

IR (film): 2941, 1737, 1433 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 5.97 (d, *J* = 3.4 Hz, 1H), 5.78 (d, *J* = 3.4 Hz, 1H), 3.79 (t, *J* = 6.1 Hz, 2H), 3.68 (s, 3H), 3.58 (s, 2H), 2.75 (t, *J* = 6.4 Hz, 2H), 1.90-1.98 (m, 2H), 1.72-1.81 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 171.2, 129.6, 122.4, 107.6, 103.6, 52.0, 42.8, 32.3, 23.5, 23.6, 20.8. MS (ESI): 194 (M + H⁺).

b) Reactions Presented in Table 1

5-Heptyn-2-one was prepared as described in the literature.¹

IR (neat): 2922, 1718, 1368 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 2.60 (t, *J* = 7.3 Hz, 2H), 2.31-2.41 (m, 2H), 2.14 (s, 3H), 1.72 (t, *J* = 2.5 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 207.1, 77.6, 76.0, 42.8, 29.9, 13.3, 3.6

¹ Aitken, R. A.; Al-Awadi, N. A.; Balkovich, M. E.; Bestmann, H. J.; Clem, O.; Gibson, S.; Grob, A.; Kumar, A.; Roder, T. *Eur. J. Org. Chem.* **2003**, 840-847.

Catalyst systems:

method A: silver (I) trifluoromethanesulfonate

method B: triphenylphosphine gold (I) trifluoromethanesulfonate

1-Benzyl-2-ethyl-5-methyl-1H-pyrrole (**6a**)

Method A: To a solution of 3.7 mg of silver (I) trifluoromethanesulfonate (0.014 mmol) in 1.5 mL of 1,2-dichloroethane was added 31.3 mg of 5-heptyn-2-one (0.29 mmol) followed by 46 μ L of benzylamine (0.42 mmol) and the reaction was stirred at 50 °C for 3h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude brown oil. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 43 mg (76%) of **6a** as a colorless oil.

Method B: To a flask charged with 4.7 mg of triphenylphosphine (0.018 mmol), 4.2 mg of gold (I) chloride (0.018 mmol) and 4.8 mg of silver (I) trifluoromethanesulfonate (0.019 mmol) was added 2 mL of 1,2-dichloroethane and the mixture was stirred at rt for 5 min. To the resulting opaque solution was added 42 mg of 5-heptyn-2-one (0.38 mmol) followed by 40 μ L of benzylamine (0.37 mmol) and the reaction mixture was stirred at 50 °C for 12h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude brown oil. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 63 mg (87%) of **6a** as a colorless oil.

IR (film): 2070, 1419, 1300 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\square$ 7.28-7.41 (m, 3H), 6.97 (d, J = 7.3 Hz, 2H), 5.98-6.04 (m, 2H), 5.11 (s, 2H), 2.57 (quartet, J = 7.6 Hz, 2H), 2.24 (s, 3H), 1.29 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\square$ 138.6, 134.3, 128.6, 127.9, 126.9, 125.5, 105.4, 103.4, 46.4, 19.7, 12.8, 12.2. MS (ESI): 200 ($\text{M} + \text{H}^+$), 230 ($\text{M} + \text{K}^+$).

1-Allyl-2-ethyl-5-methyl-1H-pyrrole (6b)

Method A: To a solution of 5.9 mg of silver (I) trifluoromethanesulfonate (0.023 mmol) in 2.2 mL of 1,2-dichloroethane was added 50.9 mg of 5-heptyn-2-one (0.46 mmol) followed by 36 μ L of allylamine (0.48 mmol) and the reaction was stirred at 50 $^{\circ}$ C for 12h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude brown oil. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 45 mg (66%) of **6b** as a colorless oil.

Method B: To a flask charged with 5.0 mg of triphenylphosphine (0.019 mmol), 4.4 mg of gold (I) chloride (0.019 mmol) and 4.9 mg of silver (I) trifluoromethanesulfonate (0.019 mmol) was added 2 mL of 1,2-dichloroethane and the mixture was stirred at rt for 5 min. To the resulting opaque solution was added 42 mg of 5-heptyn-2-one (0.38 mmol) followed by 29 μ L of allylamine (0.39 mmol) and the reaction mixture was stirred at 50 $^{\circ}$ C for 18h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude brown oil. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 45 mg (80%) of **6b** as a colorless oil.

IR (film): 2970, 1645, 1419, 1303 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\square$ 5.80-5.96 (m, 3H), 5.11 (d, J = 10.4 Hz, 1H), 4.75 (d, J = 17.4 Hz, 1H), 4.37-4.41 (m, 2H), 2.54 (quartet, J = 7.6 Hz, 2H), 2.20 (s, 3H), 1.26 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\square$ 134.1, 127.7, 115.4, 105.0, 103.0, 45.4, 19.6, 13.0, 12.1. MS (ESI): 150 ($\text{M} + \text{H}^+$), 180 ($\text{M} + \text{K}^+$).

2-Ethyl-5-methyl-1-pentyl-1H-pyrrole (**6c**)

Method A: To a solution of 5.1 mg of silver (I) trifluoromethanesulfonate (0.020 mmol) in 2 mL of 1,2-dichloroethane was added 43 mg of 5-heptyn-2-one (0.39 mmol) followed by 46 μ L of *n*-amylamine (0.40 mmol) and the reaction was stirred at 50 °C for 12h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude orange oil. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 51 mg (77%) of **6c** as a colorless oil.

Method B: To a flask charged with 5.1 mg of triphenylphosphine (0.019 mmol), 4.3 mg of gold (I) chloride (0.019 mmol) and 4.7 mg of silver (I) trifluoromethanesulfonate (0.018 mmol) was added 2 mL of 1,2-dichloroethane and the mixture was stirred at rt for 5 min. To the resulting opaque solution was added 39 mg of 5-heptyn-2-one (0.36 mmol) followed by 42 μ L of *n*-amylamine (0.36 mmol) and the reaction mixture was stirred at 50 °C for 18h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude orange oil. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 44 mg (70%) of **6c** as a colorless oil.

IR (film): 2962, 1420, 1297 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\square$ 5.89 (s, 2H), 3.80 (t, J = 7.9 Hz, 2H), 2.65 (quartet, J = 7.6 Hz, 2H), 2.32 (s, 3H), 1.66-1.76 (m, 2H), 1.38-1.50 (m, 4H), 1.36 (t, J = 7.6 Hz, 3H), 1.02 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\square$ 133.6, 127.1, 104.9, 102.8, 43.4, 30.7, 29.1, 22.3, 19.7, 13.9, 12.8, 12.3. MS (ESI): 180 ($\text{M} + \text{H}^+$).

2-Ethyl-5-methyl-1-phenyl-1H-pyrrole (**6d**)

Method A: To a solution of 5.2 mg of silver (I) trifluoromethanesulfonate (0.020 mmol) in 2 mL of 1,2-dichloroethane was added 41 mg of 5-heptyn-2-one (0.37 mmol) followed by 34 μ L of aniline (0.40 mmol) and the reaction was stirred at 80 °C for 24h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude brown oil. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 9 mg (13%) of **6d** as a colorless oil.

Method B: To a flask charged with 5.2 mg of triphenylphosphine (0.020 mmol), 4.3 mg of gold (I) chloride (0.019 mmol) and 5.0 mg of silver (I) trifluoromethanesulfonate (0.019 mmol) was added 2 mL of 1,2-dichloroethane and the mixture was stirred at rt for 5 min. To the resulting opaque solution was added 40 mg of 5-heptyn-2-one (0.36 mmol) followed by 33 μ L of aniline (0.36 mmol) and the reaction mixture was stirred at 80 °C for 24h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude brown oil. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 39 mg (59%) of **6d** as a colorless oil.

IR (film): 2968, 1599, 1499, 1412 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\square$ 7.36-7.49 (m, 3H), 7.19-7.25 (m, 2H), 5.94 (s, 2H), 2.36 (quartet, $J = 7.6$ Hz, 2H), 2.02 (s, 3H), 1.09 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\square$ 139.0, 135.4, 129.0, 128.9, 128.4, 127.7, 105.5, 103.8, 20.3, 13.2, 12.8. MS (ESI): 186 ($\text{M} + \text{H}^+$).

1-Cyclohexyl-2-ethyl-5-methyl-1H-pyrrole (**6e**)

Method A: To a solution of 5.9 mg of silver (I) trifluoromethanesulfonate (0.023 mmol) in 2.3 mL of 1,2-dichloroethane was added 50 mg of 5-heptyn-2-one (0.46 mmol) followed by 53 μ L of cyclohexylamine (0.46 mmol) and the reaction was stirred at 80 °C for 24h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude brown oil. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 0.4 mg (1%) of **6e** as a colorless oil.

Method B: To a flask charged with 6.3 mg of triphenylphosphine (0.024 mmol), 5.3 mg of gold (I) chloride (0.023 mmol) and 5.8 mg of silver (I) trifluoromethanesulfonate (0.023 mmol) was added 2.3 mL of 1,2-dichloroethane and the mixture was stirred at rt for 5 min. To the resulting opaque solution was added 49 mg of 5-heptyn-2-one (0.44 mmol) followed by 52 μ L of cyclohexylamine (0.45 mmol) and the reaction mixture was stirred at 80 °C for 24h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude brown oil. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 23 mg (27%) of **6e** as a colorless oil.

IR (film): 2932, 1408, 1287 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\square$ 5.78 (s, 2H), 3.86-3.97 (m, 1H), 2.63 (q, $J=7.3$ Hz, 2H), 2.33 (s, 3H), 1.84-2.00 (m, 6H), 1.70-1.78 (m, 1H), 1.30-1.45 (m, 2H), 1.24 (t, $J=7.3$ Hz, 3H), 1.15-1.30 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): $\square$ 134.5, 127.7, 106.5, 103.4, 56.2, 32.4, 26.7, 25.6, 21.0, 14.8, 13.5. MS (EI): 191 (M^+).

2-Ethyl-5-methyl-1-(toluene-4-sulfonyl)-1H-pyrrole (**6f**)

Method A: To a flask charged with 4.8 mg of silver (I) trifluoromethanesulfonate (0.019 mmol) and 63 mg of *p*-toluenesulfonamide (0.37 mmol) was added 2 mL of 1,2-dichloroethane followed by 41 mg of 5-heptyn-2-one (0.38 mmol) and the reaction was stirred at 80 °C for 24h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude black residue. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether □ 20:1 petroleum ether:diethyl ether) afforded 36 mg (37%) of **6f** as a colorless oil which recrystallized upon storage.

Method B: To a flask charged with 5.1 mg of triphenylphosphine (0.019 mmol), 4.6 mg of gold (I) chloride (0.020 mmol), 5.0 mg of silver (I) trifluoromethanesulfonate (0.020 mmol) and 66 mg of *p*-toluenesulfonamide (0.39 mmol) was added 2 mL of 1,2-dichloroethane and the mixture was stirred at rt for 5 min. To the resulting opaque solution was added 42 mg of 5-heptyn-2-one (0.38 mmol) and the reaction mixture was stirred at 80 °C for 24h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude red residue. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether □ 20:1 petroleum ether:diethyl ether) afforded 34 mg (35%) of **6f** as a colorless oil which crystallized upon storage, mp: 74.5-75.5 °C.

IR (film): 2973, 1365, 1170, 1119 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): □ 7.50 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 5.85-5.89 (m, 2H), 2.79 (quartet, *J* = 7.3 Hz, 2H), 2.37 (s, 6H), 1.19 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): □ 144.2, 138.9, 137.5, 132.4, 129.9, 126.0, 111.8, 109.6, 22.1, 21.5, 15.6, 13.1. MS (ESI): 286 (M + Na⁺).

2-Ethyl-1-(4-methoxybenzyl)-5-methyl-1H-pyrrole (**6g**)

Method A: To a solution of 6.0 mg of silver (I) trifluoromethanesulfonate (0.023 mmol) in 3 mL of 1,2-dichloroethane was added 50 mg of 5-heptyn-2-one (0.45 mmol) followed by 59 μ L of 4-methoxybenzylamine (0.45 mmol) and the reaction was stirred at 50 °C for 16h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude brown oil. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 77 mg (74%) of **6g** as a colorless oil.

Method B: To a flask charged with 6.0 mg of triphenylphosphine (0.023 mmol), 5.0 mg of gold (I) chloride (0.022 mmol) and 6.0 mg of silver (I) trifluoromethanesulfonate (0.023 mmol) was added 3 mL of 1,2-dichloroethane and the mixture was stirred at rt for 5 min. To the resulting opaque solution was added 50 mg of 5-heptyn-2-one (0.45 mmol) followed by 60 μ L of 4-methoxybenzylamine (0.45 mmol) and the reaction mixture was stirred at 50 °C for 12h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude brown residue. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 71 mg (68%) of **6g** as a colorless oil.

IR (film): 2967, 2933, 2835, 1514, 1249 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\square$ 6.80-6.86 (m, 4H), 5.89 (s, 2H), 4.97 (s, 2H), 3.79 (s, 3H), 2.46 (quart, $J = 7.5$ Hz, 2H), 2.16 (s, 3H), 1.21 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): $\square$ 161.3, 134.6, 130.8, 128.1, 126.9, 114.3, 105.6, 103.6, 55.4, 46.2, 20.0, 13.1, 12.5. MS (ESI): 230 ($\text{M} + \text{H}^+$).

2-Ethyl-1-(4-methoxy-phenyl)-5-methyl-1H-pyrrole (**6h**)

Method A: To a solution of 6.0 mg of silver (I) trifluoromethanesulfonate (0.023 mmol) in 3 mL of 1,2-dichloroethane was added 50 mg of 5-heptyn-2-one (0.45 mmol) followed by 56 mg of *p*-anisidine (0.45 mmol) and the reaction was stirred at 80 °C for 24h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude brown oil. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether □ 20:1 petroleum ether:diethyl ether) afforded 40 mg (41%) of **6h** as a colorless oil.

Method B: To a flask charged with 6.0 mg of triphenylphosphine (0.023 mmol), 5.0 mg of gold (I) chloride (0.022 mmol) and 6.0 mg of silver (I) trifluoromethanesulfonate (0.023 mmol) was added 3 mL of 1,2-dichloroethane and the mixture was stirred at rt for 5 min. To the resulting opaque solution was added 50 mg of 5-heptyn-2-one (0.45 mmol) followed by 56 mg of *p*-anisidine (0.45 mmol) and the reaction mixture was stirred at 80 °C for 24h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude brown residue. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether □ 20:1 petroleum ether:diethyl ether) afforded 59 mg (60%) of **6h** as a colorless oil.

IR (film): 2967, 2934, 1515, 1247 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): □ 7.13 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 5.89 (s, 2H), 3.85 (s, 3H), 2.32 (quart, *J* = 7.4 Hz, 2H), 1.99 (s, 3H), 1.07 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): □ 158.8, 135.6, 131.6, 129.2, 128.9, 114.1, 105.1, 103.3, 55.3, 20.2, 13.1, 12.7. MS (ESI): 216 (M + H⁺).

c) Reactions Presented in Figure 1

1-Benzyl-2-methyl-4,5,6,7-tetrahydro-1H-indole (8)

Method A: To a solution of 3.8 mg of silver (I) trifluoromethanesulfonate (0.015 mmol) in 1.5 mL of 1,2-dichloroethane was added 40 mg of **7a** (0.30 mmol) followed by 33 μ L of benzylamine (0.30 mmol) and the reaction was stirred at 50 °C for 3.5h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude orange oil. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 52 mg (78%) of **8** as a colorless oil.

Method B: To a flask charged with 4.1 mg of triphenylphosphine (0.016 mmol), 3.4 mg of gold (I) chloride (0.015 mmol) and 3.9 mg of silver (I) trifluoromethanesulfonate (0.015 mmol) was added 2 mL of 1,2-dichloroethane and the mixture was stirred at rt for 5 min. To the resulting opaque solution was added 40 mg of **7a** (0.29 mmol) followed by 32 μ L of benzylamine (0.29 mmol) and the reaction mixture was stirred at 50 °C for 3.5h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude orange oil. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 49 mg (74%) of **8** as a colorless oil.

IR (film): 2926, 1439, 1402, 1298 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\square$ 7.23-7.36 (m, 3H), 6.97 (d, J = 7.6 Hz, 2H), 5.80 (s, 1H), 4.99 (s, 2H), 2.56 (t, J = 6.1 Hz, 2H), 2.46 (t, J = 6.1 Hz, 2H), 2.18 (s, 3H), 1.72-1.87 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3): $\square$ 138.8, 128.6, 127.1, 127.0, 126.9, 125.8, 116.2, 105.1, 46.3, 23.8, 23.5, 23.1, 22.0, 12.0. MS (ESI): 226 ($\text{M} + \text{H}^+$).

Method A: To a solution of 2.4 mg of silver (I) trifluoromethanesulfonate (0.010 mmol) in 1 mL of 1,2-dichloroethane was added 40 mg of **7b** (0.19 mmol) followed by 21 μ L of benzylamine (0.19 mmol) and the reaction was stirred at 50 °C for 3.5h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude orange oil. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 37 mg (86%) of **8** as a colorless oil.

Method B: To a flask charged with 2.5 mg of triphenylphosphine (0.010 mmol), 2.2 mg of gold (I) chloride (0.010 mmol) and 2.5 mg of silver (I) trifluoromethanesulfonate (0.010 mmol) was added 1 mL of 1,2-dichloroethane and the mixture was stirred at rt for 5 min. To the resulting opaque solution was added 39 mg of **7b** (0.19 mmol) followed by 21 μ L of benzylamine (0.19 mmol) and the reaction mixture was stirred at 50 °C for 3.5h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude orange oil. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 37 mg (86%) of **8** as a colorless oil.

1-Benzyl-2-methyl-1,4,5,6-tetrahydro-cyclopenta[b]pyrrole (**10**)

Method A: To a solution of 4.6 mg of silver (I) trifluoromethanesulfonate (0.018 mmol) in 1.8 mL of 1,2-dichloroethane was added 41 mg of **9** (0.33 mmol) followed by 37 μ L of benzylamine (0.34 mmol) and the reaction was stirred at 50 °C for 12h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude orange oil. Purification by gradient column chromatography on

triethylamine washed silica gel (20:1 petroleum ether:diethyl ether $\square$ 10:1 petroleum ether:diethyl ether) afforded 57 mg (81%) of **10** as a colorless oil.

Method B: To a flask charged with 4.5 mg of triphenylphosphine (0.017 mmol), 3.8 mg of gold (I) chloride (0.016 mmol) and 4.3 mg of silver (I) trifluoromethanesulfonate (0.017 mmol) was added 1.8 mL of 1,2-dichloroethane and the mixture was stirred at rt for 5 min. To the resulting opaque solution was added 39 mg of **9** (0.32 mmol) followed by 36 μ L of benzylamine (0.33 mmol) and the reaction mixture was stirred at 50 $^{\circ}$ C for 12h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude orange oil. Purification by gradient column chromatography on triethylamine washed silica gel (20:1 petroleum ether:diethyl ether $\square$ 10:1 petroleum ether:diethyl ether) afforded 54 mg (79%) of **10** as a colorless oil. IR (film): 2932, 2852, 1453, 1389 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.33-7.40 (m, 2H), 7.26-7.33 (m, 1H), 7.07 (d, J = 7.3 Hz, 2H), 5.82 (s, 1H), 5.00 (s, 2H), 2.67-2.73 (m, 2H), 2.63 (t, J = 6.9 Hz, 2H), 2.39-2.47 (m, 2H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 138.6, 137.4, 131.3, 128.6, 127.1, 126.3, 124.4, 101.8, 48.5, 28.7, 25.8, 24.9, 12.7. MS (ESI): 212 ($\text{M} + \text{H}^+$).

[4-(1-Benzyl-5-methyl-1H-pyrrol-2-yl)-butyl]-carbamic acid tert-butyl ester (12)

Method A: To a flask charged with 2.1 mg of silver (I) trifluoromethanesulfonate (0.0082 mmol) and 39 mg of **11** (0.15 mmol) was added 0.8 mL of 1,2-dichloroethane followed by 17 μ L of benzylamine (0.16 mmol) and the reaction was stirred at 50 $^{\circ}$ C for 17h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude orange oil. Purification by gradient column chromatography on triethylamine washed silica gel (5:1 $\square$ 3:1 petroleum ether:diethyl ether to elute product pyrrole $\square$ 1:1 petroleum ether:diethyl ether to elute starting material) afforded 48 mg (92%) of **12** as a colorless oil and 3.1 mg (8%) of **11** as a colorless residue.

Method B: To a flask charged with 2.0 mg of triphenylphosphine (0.008 mmol), 2.0 mg of gold (I) chloride (0.009 mmol), 2.1 mg of silver (I) trifluoromethanesulfonate (0.008 mmol) and 39 mg of **11** (0.15 mmol) was added 0.8 mL of 1,2-dichloroethane and the mixture was stirred at rt for 5 min. To the resulting opaque solution was added 17 μ L of benzylamine (0.16 mmol) and the reaction mixture was stirred at 50 °C for 17h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude orange oil. Purification by gradient column chromatography on triethylamine washed silica gel (5:1 $\square$ 3:1 petroleum ether:diethyl ether to elute product pyrrole $\square$ 1:1 petroleum ether:diethyl ether to elute starting material) afforded 46 mg (88%) of **12** as a colorless oil and 1.6 mg (4%) of **11** as a colorless residue.

IR (film): 3367, 2933, 1702, 1515 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.18-7.31 (m, 3H), 6.84 (d, J = 7.3 Hz, 2H), 5.87 (dd, J = 8.2 Hz, 3.4 Hz, 2H), 5.00 (s, 2H), 4.43 (s, 1H), 3.0-3.10 (m, 2H), 2.44 (t, J = 7.3 Hz, 2H), 2.12 (s, 3H), 1.42-1.59 (m, 4H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 155.9, 138.6, 132.2, 128.7, 128.0, 127.0, 125.5, 105.5, 104.5, 79.0, 46.5, 40.3, 26.9, 28.4, 26.2, 26.0, 12.3. MS (ESI): 365 ($\text{M} + \text{Na}^+$).

{1-[3-(1-Benzyl-5-methyl-1H-pyrrol-2-yl)-propyl]-but-3-enyl}-carbamic acid tert-butyl ester (14**)**

Method A: To a flask charged with 5.0 mg of silver (I) trifluoromethanesulfonate (0.020 mmol) and 149 mg of **13** (0.41 mmol) was added 3 mL of 1,2-dichloroethane followed by 89 μ L of benzylamine (0.82 mmol) and the reaction was stirred at 50 °C for 12h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude brown oil. Purification by column chromatography on triethylamine washed silica gel (petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 95 mg (65%) of **14** as a colorless oil.

Method B: To a flask charged with 2.0 mg of triphenylphosphine (0.008 mmol), 2.0 mg of gold (I) chloride (0.008 mmol), 2.0 mg of silver (I) trifluoromethanesulfonate (0.008 mmol) and 51 mg of **13** (0.16 mmol) was added 3 mL of 1,2-dichloroethane and the

mixture was stirred at rt for 5 min. To the resulting opaque solution was added 15 μ L of benzylamine (0.14 mmol) and the reaction mixture was stirred at 50 $^{\circ}$ C for 12h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude brown oil. Purification by gradient column chromatography on triethylamine washed silica gel (10:1 hexanes:ethyl acetate) afforded 18 mg (36%) of **14** as a colorless oil and 8 mg (16%) of **13** as a colorless residue.

IR (film): 3355, 3066, 2977, 2933, 1696, 1173 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.20-7.31 (m, 3H), 6.86 (d, J = 7.0 Hz, 2H), 5.87 (dd, J = 8.7 Hz, 3.5 Hz, 2H), 5.68-5.78 (m, 1H), 5.01-5.06 (m, 4H), 4.27 (d, J = 8.3 Hz, 1H), 2.36-2.49 (m, 2H), 2.11 (s, 3H), 1.59-1.66 (m, 2H), 1.41 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 155.4, 138.6, 134.4, 132.2, 128.6, 127.9, 126.9, 125.5, 117.5, 105.5, 104.5, 78.8, 49.8, 46.5, 39.4, 34.2, 28.3, 27.9, 26.4, 25.1, 12.3. MS (ESI): 388 ($\text{M} + \text{H}^+ + \text{MeOH}$).

[1-Benzyl-5-(4-tert-butoxycarbonylamino-butyl)-1H-pyrrol-2-yl]-acetic acid methyl ester (**16**)

Method A: To a flask charged with 1.8 mg of silver (I) trifluoromethanesulfonate (0.007 mmol) and 41 mg of **15** (0.13 mmol) was added 0.7 mL of 1,2-dichloroethane followed by 15 μ L of benzylamine (0.14 mmol) and the reaction was stirred at 50 $^{\circ}$ C for 18h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude orange oil. Purification by gradient column chromatography on triethylamine washed silica gel (3:1 petroleum ether:diethyl $\square$ 1:1 petroleum ether:diethyl ether to elute product pyrrole $\square$ 1:2 petroleum ether:diethyl ether to elute starting material) afforded 41 mg (78%) of **16** as a pale yellow film and 4.6 mg (11%) of **15** as a pale yellow film.

Method B: To a flask charged with 2.0 mg of triphenylphosphine (0.008 mmol), 1.7 mg of gold (I) chloride (0.007 mmol), 2.0 mg of silver (I) trifluoromethanesulfonate (0.008 mmol) and 45 mg of **15** (0.14 mmol) was added 0.8 mL of 1,2-dichloroethane and the

mixture was stirred at rt for 5 min. To the resulting opaque solution was added 16 μ L of benzylamine (0.15 mmol) and the reaction mixture was stirred at 50 $^{\circ}$ C for 18h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude orange oil. Purification by gradient column chromatography on triethylamine washed silica gel (3:1 petroleum ether:diethyl $\square$ 1:1 petroleum ether:diethyl ether to elute product pyrrole $\square$ 1:2 petroleum ether:diethyl ether to elute starting material) afforded 43 mg (74%) of **16** as a pale yellow film and 8.1 mg (18%) of **15** as a pale yellow film.

IR (film): 3377, 2934, 1737, 1708 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\square$ 7.16-7.33 (m, 3H), 6.80 (d, J = 7.3 Hz, 2H), 6.04 (d, J = 3.4 Hz, 1H), 5.90 (d, J = 3.4 Hz, 1H), 5.07 (s, 2H), 4.37-4.47 (m, 1H), 3.51 (s, 3H), 3.47 (s, 2H), 2.98-3.09 (m, 2H), 2.43 (t, J = 7.5 Hz, 2H), 1.41-1.60 (m, 4H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): $\square$ 171.1, 155.9, 138.2, 133.7, 128.7, 127.1, 125.4, 124.1, 108.1, 105.2, 79.0, 51.9, 46.7, 40.3, 32.9, 29.7, 28.4, 26.2, 25.8. MS (ESI): 423 ($\text{M} + \text{Na}^+$).

[3-(1-Benzyl-5-methyl-1H-pyrrol-2-yl)-propyl]-carbamic acid tert-butyl ester (**18**)

Method A: To a flask charged with 2.0 mg of silver (I) trifluoromethanesulfonate (0.008 mmol) and 25 mg of **17** (0.08 mmol) was added 1 mL of 1,2-dichloroethane followed by 10 μ L of benzylamine (0.092 mmol) and the reaction was stirred at 50 $^{\circ}$ C for 19h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude orange oil. Purification by gradient column chromatography on triethylamine washed silica gel (5:1 $\square$ 3:1 petroleum ether:diethyl ether to elute product pyrrole $\square$ 1:1 petroleum ether:diethyl ether to elute starting material) afforded 15 mg (57%) of **18** as a colorless oil and 8.3 mg (33%) of **17** as a colorless residue.

Method B: To a flask charged with 2.1 mg of triphenylphosphine (0.008 mmol), 2.1 mg of gold (I) chloride (0.009 mmol), 2.2 mg of silver (I) trifluoromethanesulfonate (0.009 mmol) and 51 mg of **17** (0.16 mmol) was added 1.2 mL of 1,2-dichloroethane and the

mixture was stirred at rt for 5 min. To the resulting opaque solution was added 18 μ L of benzylamine (0.17 mmol) and the reaction mixture was stirred at 50 $^{\circ}$ C for 19h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude orange oil. Purification by gradient column chromatography on triethylamine washed silica gel (5:1 $\square$ 3:1 petroleum ether:diethyl to elute product pyrrole $\square$ 1:1 petroleum ether:diethyl ether to elute starting material) afforded 40 mg (75%) of **18** as a colorless oil and 11.3 mg (22%) of **17** as a colorless residue. IR (film): 3367, 2932, 1702, 1516, 1171 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.27 (m, 3H), 6.85 (d, J = 6.9 Hz, 2H), 5.88 (s, 2H), 5.00 (s, 2H), 4.40 (s, 1H), 3.11 (quartet, J = 6.4 Hz, 2H), 2.47 (t, J = 7.5 Hz, 2H), 2.13 (s, 3H), 1.60-1.78 (m, 2H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 156.1, 138.7, 131.7, 128.9, 128.4, 127.2, 125.7, 105.8, 104.8, 79.2, 46.7, 40.3, 29.3, 28.5, 24.0, 12.5. MS (ESI): 351 ($\text{M} + \text{Na}^+$).

d) Reactions Presented in Scheme 2

3-Methyl-5,6,7,8-tetrahydro-indolizine (21)

Method A: To a solution of 3.9 mg of silver (I) trifluoromethanesulfonate (0.015 mmol) in 1.5 mL of 1,2-dichloroethane was added 41 mg of **19** (0.31 mmol) and the reaction was stirred at 50 $^{\circ}$ C for 3h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude red oil. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 26 mg (62%) of **21** as a colorless oil.

Method B: To a flask charged with 4.2 mg of triphenylphosphine (0.016 mmol), 3.6 mg of gold (I) chloride (0.016 mmol) and 4.0 mg of silver (I) trifluoromethanesulfonate (0.016 mmol) was added 1.5 mL of 1,2-dichloroethane and the mixture was stirred at rt for 5 min. To the resulting opaque solution was added 41 mg of **19** (0.31 mmol) and the black reaction mixture was stirred at 50 $^{\circ}$ C for 3h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a black residue. Purification by gradient column chromatography on triethylamine washed silica gel

(petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 20 mg (48%) of **21** as a colorless oil.

IR (film): 2936, 1514, 1420, 1392 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\square$ 5.84 (d, $J = 3.4$ Hz, 1H), 5.76 (d, $J = 3.4$ Hz, 1H), 3.77 (t, $J = 6.2$ Hz, 2H), 2.79 (t, $J = 6.4$ Hz, 2H), 2.20 (s, 3H), 1.94-2.02 (m, 2H), 1.76-1.84 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): $\square$ 128.2, 126.4, 105.0, 102.8, 42.6, 30.2, 23.7, 20.9, 11.6. MS (ESI): 136 ($\text{M} + \text{H}^+$).

5-Methyl-2,3-dihydro-1H-pyrrolizine (**22**)

Method A: To a solution of 7.8 mg of silver (I) trifluoromethanesulfonate (0.030 mmol) in 1.8 mL of 1,2-dichloroethane was added 0.39 mL of **20** (1.48 M in 1,2-dichloroethane prepared immediately before addition, 0.58 mmol) and the reaction was stirred at 50 $^{\circ}\text{C}$ for 1.5 h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude brown oil. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 45 mg (64%) of **22** as a colorless oil.

Method B: To a flask charged with 7.6 mg of triphenylphosphine (0.029 mmol), 6.5 mg of gold (I) chloride (0.028 mmol) and 7.6 mg of silver (I) trifluoromethanesulfonate (0.030 mmol) was added 1.8 mL of 1,2-dichloroethane and the mixture was stirred at rt for 5 min. To the resulting opaque solution was added 0.39 mL of **20** (1.48 M in 1,2-dichloroethane prepared immediately before addition, 0.58 mmol) and the reaction mixture was stirred at 50 $^{\circ}\text{C}$ for 10h. The reaction mixture was filtered through Celite and concentrated by rotary evaporation *in vacuo* to afford a crude brown oil. Purification by gradient column chromatography on triethylamine washed silica gel (petroleum ether $\square$ 20:1 petroleum ether:diethyl ether) afforded 35 mg (50%) of **22** as a colorless oil.

IR (film): 2873, 1509, 1420, 1291 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\square$ 5.91 (d, $J = 3.1$ Hz, 1H), 5.72 (d, $J = 3.1$ Hz, 1H), 3.84 (t, $J = 7.0$ Hz, 2H), 2.87 (t, $J = 7.3$ Hz, 2H), 2.47-2.56 (m, 2H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\square$ 135.1, 122.8, 108.9, 97.9, 44.1, 27.9, 24.5, 11.9. MS (ESI): 122 ($\text{M} + \text{H}^+$).

3. Experimental Procedures-Substrate Preparation

N-*tert*butylcarboxycarbamoyl-piperidin-2-one was prepared using the literature method.²

(5-Oxo-9-trimethylsilyl-non-8-ynyl)-carbamic acid *tert*-butyl ester

To a suspension of 1.48 g of magnesium (47.2 mmol) in 125 mL of THF was added 8.76 g of 4-trimethylsilyl-1-bromo-3-butyne (42.7 mmol). The reaction mixture was stirred for 45 min to give a green solution. This solution was transferred dropwise to a cold (-78°C) suspension of 3.10 g of *N*-*tert*butylcarboxycarbamoyl-piperidin-2-one (15.6 mmol) in 30 mL of THF. The green reaction mixture was stirred at -78°C for 1 h before being warmed to rt and stirred for 1 h. The reaction was diluted with diethyl ether and slowly quenched with 20 mL of water. The organic phase was washed with a saturated aqueous solution of sodium bicarbonate. The combined aqueous fractions were back extracted two times with diethyl ether. The combined organic fractions were dried over sodium sulfate, and concentrated by rotary evaporation *in vacuo* to afford 6.83 g of a pale yellow oil. Purification by column chromatography on triethylamine washed silica gel (10:1 hexanes:ethyl acetate to elute bromide byproduct □ 3:1 hexanes:ethyl acetate to elute product ketone) afforded 4.74 g (94 %) of the title compound as a colorless oil that solidifies in the freezer, mp: $38\text{--}40^\circ\text{C}$.

IR (film): 3386, 2961, 2177, 1713, 1520 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): □ 4.60 (s, 1H), 3.05 (quartet, $J = 6.4\text{ Hz}$, 2H), 2.55–2.61 (m, 2H), 2.37–2.44 (m, 4H), 1.50–1.60 (m, 2H), 1.34–1.48 (m, 2H), 1.38 (s, 9H), 0.07 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): □ 208.4, 155.9, 105.5, 85.0, 79.0, 42.1, 41.4, 40.0, 29.4, 28.3, 20.5, 14.3, -0.06 . MS (ESI): 348 ($\text{M} + \text{Na}^+$). Anal. Calcd for $\text{C}_{17}\text{H}_{31}\text{NO}_3\text{Si}$: C, 62.73; H, 9.60; N, 4.30. Found: C, 62.82; H, 9.74; N, 4.25.

² Williams, G. D.; Pike, R. A.; Wade, C. E.; Wills, M. *Org. Lett.* **2003**, 5(22), 4227–4230.

6-(4-Trimethylsilyl-but-3-ynyl)-3,4-dihydro-2H-pyridine-1-carboxylic acid tert-butyl ester

A solution of 2.44 g of (5-oxo-9-(trimethylsilyl)non-8-ynyl)-carbamic acid tert-butyl ester (7.51 mmol) and 44 mg of *p*-toluenesulfonic acid (0.23 mmol) in 30 mL of benzene was stirred at reflux with a Dean-Stark trap for 1 h. The orange reaction mixture was quenched with 1 mL of triethylamine and concentrated to afford a crude orange oil. Remaining starting material was recovered by column chromatography on triethylamine washed silica gel (10:1 hexanes:ethyl acetate to elute product to 2:1 hexanes:ethyl acetate to elute starting material) and resubjected to the reaction conditions two additional times for a total of three iterations. Purification of the combined product fractions by column chromatography on triethylamine washed silica gel (20:1 hexanes:ethyl acetate) afforded 1.80 g (78%) of the title compound as a colorless oil.

IR (film): 2960, 2176, 1700, 1367 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 4.93 (t, $J = 3.7$ Hz, 1H), 3.40-3.45 (m, 2H), 2.59 (t, $J = 7.2$ Hz, 2H), 2.21 (t, $J = 7.3$ Hz, 2H), 1.96-2.03 (m, 2H), 1.62-1.71 (m, 2H), 1.40 (s, 9H), 0.04 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 153.3, 137.9, 113.5, 106.8, 84.7, 80.3, 44.6, 34.6, 28.2, 23.3, 22.9, 18.5, 0.02. MS (ESI): 330 ($\text{M} + \text{Na}^+$). Anal. Calcd for $\text{C}_{17}\text{H}_{29}\text{NO}_2\text{Si}$: C, 66.40; H, 9.51; N, 4.55. Found: C, 66.49; H, 9.36; N, 4.95.

6-But-3-ynyl-3,4-dihydro-2H-pyridine-1-carboxylic acid tert-butyl ester

To a solution of 1.88 g of 6-(4-trimethylsilyl-but-3-ynyl)-3,4-dihydro-2H-pyridine-1-carboxylic acid tert-butyl ester (6.13 mmol) in 30 mL of methanol was added 1.70 g of potassium carbonate (12.3 mmol) and the suspension was stirred at rt for 10 h. Concentration by rotary evaporation *in vacuo* resulted in a yellow slurry that was taken

up in diethyl ether and water. The aqueous fraction was extracted with diethyl ether. The combined organic fractions were dried over magnesium sulfate and concentrated by rotary evaporation *in vacuo* to afford a crude yellow oil. Purification by column chromatography on triethylamine washed silica gel (6:1 hexanes:ethyl acetate) afforded 1.40 g (97%) of the title compound as a colorless oil that crystallized in the freezer, mp: 26-27.5 °C.

IR (film): 3376, 3302, 2934, 1708, 1520 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 4.67 (s, 1H), 3.01 (quartet, $J = 6.4$ Hz, 2H), 2.55 (t, $J = 7.0$ Hz, 2H), 2.31-2.41 (m, 4H), 1.86 (t, $J = 2.7$ Hz, 1H), 1.46-1.57 (m, 2H), 1.32-1.43 (m, 2H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 208.2, 155.9, 82.9, 78.8, 68.6, 42.0, 41.1, 39.9, 29.3, 28.3, 20.5, 12.8. MS (ESI): 276 ($\text{M} + \text{Na}^+$). Anal. Calcd for $\text{C}_{14}\text{H}_{23}\text{NO}_2$: C, 66.37; H, 9.15; N, 5.53. Found: C, 66.77; H, 9.32; N, 5.57.

6-(4-Methoxycarbonyl-but-3-ynyl)-3,4-dihydro-2H-pyridine-1-carboxylic acid tert-butyl ester (3)

A solution of *t*-butyllithium (0.13 mL, 0.19 mmol, 1.46 M in pentane) was added dropwise to a solution of 37 mg of 6-but-3-ynyl-3,4-dihydro-2H-pyridine-1-carboxylic acid tert-butyl ester (0.16 mmol) in 1 mL of THF at -78 °C. After the reaction mixture was stirred for 1 h at -78 °C, neat methyl chloroformate (60 μL , 0.78 mmol) was added. The reaction mixture was stirred at -78 °C for 20 min, then warmed to rt and stirred for 8 h. The reaction mixture was diluted with diethyl ether, and washed sequentially with water followed by an aqueous saturated brine solution. The combined aqueous washes were back extracted with diethyl ether. The combined organic phases were dried over sodium sulfate, filtered and concentrated by rotary evaporation *in vacuo* to afford 46 mg of a crude yellow residue. Purification by column chromatography on triethylamine washed silica gel, (10:1 hexanes:ethyl acetate) afforded 35 mg (74 %) of **3** as a colorless film.

IR (film): 2951, 2239, 1702, 1368, 1257 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 5.10 (t, $J = 3.7$ Hz, 1H), 3.78 (s, 3H), 3.52-3.58 (m, 2H), 2.78 (t, $J = 7.3$ Hz, 2H), 2.47 (t, $J = 7.3$ Hz, 2H), 2.07-2.15 (m, 2H), 1.74-1.83 (m, 2H), 1.51 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 154.0, 153.2, 137.2, 114.0, 89.0, 80.4, 73.2, 52.3, 44.8, 33.4, 28.2, 23.1, 22.9,

17.4. MS (ESI): 316 ($M + Na^+$). Anal. Calcd for $C_{16}H_{23}NO_4$: C, 65.51; H, 7.90; N, 4.77. Found: C, 65.64; H, 7.93; N, 4.90.

2-Prop-2-ynyl-cyclohexanone (7a)³

To a cold solution (-78°C) of 3 mL of diisopropylamine (21.4 mmol) in 50 mL of THF was added 13.9 mL of *n*-BuLi (1.46 M in hexanes, 20.3 mmol) dropwise. The colorless solution was stirred at -78°C for 15 min. before 2 mL of cyclohexanone (19.3 mmol) was added and the solution was stirred cold for an additional 30 min. This enolate solution was added to a stirred cold (-78°C) solution of 3.59 g of propargyl bromide (80% wt/wt in toluene, 24.1 mmol) in 50 mL of THF and the reaction mixture was stirred cold for 1.5h and then at rt for 5h. The orange reaction mixture was diluted with diethyl ether and washed sequentially with water followed by an aqueous saturated brine solution. The combined aqueous fractions were back extracted once with diethyl ether and the combined organic fractions were dried over sodium sulfate and concentrated by rotary evaporation *in vacuo* to afford a crude yellow oil. Purification by column chromatography on silica gel (10:1 petroleum ether:diethyl ether) afforded 1.86 g of a pale yellow oil. Further purification by Kugelrohr distillation (0.5 mm Hg, $95-120^\circ\text{C}$) afforded 1.22 g (47 %) of **7a** as a colorless liquid.

IR (film): 3290, 2939, 1712 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 2.58 (ddd, $J=17.1$ Hz, 4.6 Hz, 2.7 Hz, 1H), 2.34-2.52 (m, 3H), 2.23-2.34 (m, 1H), 2.16 (ddd, $J=17.1$ Hz, 8.5 Hz, 2.7 Hz, 1H), 2.03-2.11 (m, 1H), 1.93 (t, $J=2.7$ Hz, 1H), 1.86-1.94 (m, 1H), 1.55-1.74 (m, 2H), 1.39 (ddd, $J=25.3$ Hz, 12.8 Hz, 3.7 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 210.8, 82.5, 69.4, 49.5, 41.9, 33.2, 27.8, 25.1, 18.8. MS (ESI): 159 ($M + Na^+$).

2-(3-Trimethylsilylprop-2-ynyl)-cyclohexanone (7b)

To a cold solution (-78°C) of 0.74 mL of diisopropylamine (5.3 mmol) in 20 mL of THF was added 3.37 mL of *n*-BuLi (1.50 M in hexanes, 5.1 mmol) dropwise. The colorless

³ Trost, B. M.; Rudd, M. T. *J. Am. Chem. Soc.* **2005**, 127, 4763-4776.

solution was stirred at -78 °C for 30 min., warmed to 0 °C for 5 min and then cooled back down to -78 °C for 10 min. before 0.5 mL of cyclohexanone (4.8 mmol) was added and the solution was stirred cold for an additional 45 min. This enolate solution was added to a stirred cold (-78 °C) solution of 1.39 g of 3-trimethylsilyl-1-bromo-2-propyne (7.3 mmol) in 20 mL of THF and the reaction mixture was stirred cold for 1.5h and then at rt for 3h. The orange reaction mixture was diluted with diethyl ether and washed sequentially with water followed by an aqueous saturated brine solution. The combined aqueous fractions were back extracted once with diethyl ether and the combined organic fractions were dried over sodium sulfate and concentrated by rotary evaporation *in vacuo* to afford 1.08 g of a crude yellow oil. Purification by column chromatography on silica gel (Hexanes to elute bromide starting material □ 15:1 hexanes:ethyl acetate to elute product) afforded 0.839 g (83%) of **7b** as a colorless oil.

IR (film): 2941, 2177, 1714, 1250 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): □ 2.61 (dd, *J*=17.2 Hz, 4.2 Hz, 1H), 2.31-2.47 (m, 3H), 2.19-2.30 (m, 1H), 2.13 (dd, *J*= 17.4 Hz, 8.8 Hz, 1H), 1.99-2.07 (m, 1H), 1.82-1.91 (m, 1H), 1.51-1.71 (m, 2H), 1.25-1.38 (m, 1H), 0.07 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): □ 210.7, 105.2, 85.7, 49.5, 41.8, 33.1, 27.8, 25.0, 20.1, 0.04. MS (ESI): 231 (M + Na⁺). Anal. Calcd for C₁₂H₂₀OSi: C, 69.17; H, 9.67. Found: C, 68.90; H, 9.46.

2-Prop-2-ynyl-cyclopentanone (9)⁴

To a solution of 3 mL of cyclopentanone (33.9 mmol) and 3 mL of pyrrolidine (35.9 mmol) in 100 mL of benzene was added 68 mg of *p*-toluenesulfonic acid and the reaction mixture was stirred at reflux with a Dean-Stark trap for 1.5h. The orange reaction mixture was cooled to rt, quenched with 1 mL of triethylamine and concentrated by rotary evaporation *in vacuo*. To the resulting orange liquid was added 90 mL of acetonitrile followed by slow addition of 6.15 g of propargyl bromide (80% wt/wt in toluene, 41.4 mmol) and 2 mL of triethylamine and the maroon reaction mixture was stirred at rt for 15h before being concentrated by rotary evaporation *in vacuo* to a volume of 5-10 mL. The resulting slurry was diluted with 20 mL of water, 3 mL of 1N HCl and

⁴ Imagawa, H.; Kurisaki, T.; Nishizawa, M. *Org. Lett.* **2004**, 6(21), 3679-3681.

50 mL of diethyl ether and it was stirred at rt for 20 min. The aqueous phase was extracted with diethyl ether three times. The combined organic fractions were washed two times with a saturated aqueous ammonium chloride solution, dried over sodium sulfate and concentrated by rotary evaporation *in vacuo* to afford a crude maroon liquid. Purification by column chromatography on silica gel (10:1 hexanes:ethyl acetate) followed by Kugelrohr distillation (0.5 mm Hg, 35 °C) afforded 0.61 g (15 %) of **9** as a colorless liquid.

IR (film): 3290, 2967, 1742, 1158 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 2.49 (ddd, J = 16.8 Hz, 4.0 Hz, 2.7 Hz, 1H), 2.16-2.35 (m, 4H), 1.94-2.12 (m, 2H), 1.90 (t, J = 2.7 Hz, 1H), 1.67-1.82 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 218.6, 81.6, 69.4, 47.5, 37.9, 28.5, 20.3, 18.4.

(5-Oxo-non-8-ynyl)-carbamic acid tert-butyl ester (11**)**

To a solution of 0.303 g of (5-oxo-9-trimethylsilyl-non-8-ynyl)-carbamic acid tert-butyl ester (0.932 mmol) in 2 mL of methanol was added 0.314 g of potassium carbonate (2.27 mmol). The reaction mixture was stirred at rt for 3 h. Concentration by rotary evaporation *in vacuo* resulted in a yellow slurry that was taken up in diethyl ether and water. The aqueous fraction was extracted with diethyl ether. The combined organic fractions were dried over sodium sulfate and concentrated by rotary evaporation *in vacuo* to afford a crude yellow oil. Purification by column chromatography on triethylamine washed silica gel (3:1 hexanes:ethyl acetate) afforded 0.23 g (97%) of **11** as a colorless oil that crystallized in the freezer, mp: 63-65 °C.

IR (film): 3376, 3302, 2934, 1708, 1520 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 4.67 (s, 1H), 3.01 (quartet, J = 6.4 Hz, 2H), 2.55 (t, J = 7.0 Hz, 2H), 2.31-2.41 (m, 4H), 1.86 (t, J = 2.7 Hz, 1H), 1.46-1.57 (m, 2H), 1.32-1.43 (m, 2H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 208.2, 155.9, 82.9, 78.8, 68.6, 42.0, 41.1, 39.9, 29.3, 28.3, 20.5, 12.8. MS (ESI): 276 ($\text{M} + \text{Na}^+$). Anal. Calcd for $\text{C}_{14}\text{H}_{23}\text{NO}_2$: C, 66.37; H, 9.15; N, 5.53. Found: C, 66.77; H, 9.32; N, 5.57.

6-allyl-2-oxo-piperidine-1-carboxylic acid *tert*-butyl ester

To a cold (-78 °C) solution of 50 mg of 6-allylpiperidin-2-one (0.36 mmol) in 6 mL of THF was added 0.25 mL of *n*-butyllithium (1.6 M in hexanes, 0.40 mmol) drop-wise. The resulting cloudy, yellow reaction mixture was slowly warmed to rt and stirred for 12 h before the addition of a solution of 0.157 g of di-*t*-butyl-dicarbonate (0.72 mmol) in 6 mL of THF. The reaction was stirred at rt for 9 h before being diluted with diethyl ether and sequentially washed with water, a saturated aqueous solution of sodium bicarbonate and a saturated aqueous brine solution. The combined aqueous washes were extracted once with diethyl ether. The combined organic fractions were dried over magnesium sulfate, filtered, and concentrated by rotary evaporation *in vacuo* to afford 0.153 g of a pale yellow oil. Purification by column chromatography (5:1 hexanes:ethyl acetate) afforded 0.057 g (67 %) of the title compound as a colorless oil.

IR (film): 2978, 1769, 1714, 1642, 1290, 1252, 1158 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 5.63-5.75 (m, 1H), 5.10 (d, *J* = 6.0 Hz, 1H), 5.04 (s, 1H), 4.15-4.23 (m, 1H), 2.44-2.50 (m, 3H), 2.22-2.30 (m, 1H), 1.63-1.87 (m, 4H), 1.50 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 171.6, 152.9, 134.1, 118.2, 83.0, 55.3, 38.5, 34.4, 28.1, 25.4, 17.0. MS (ESI): 261 (M + Na⁺). Anal. Calcd for C₁₃H₂₁NO₃: C, 65.25; H, 8.84; N, 5.85. Found: C, 65.15; H, 8.99; N, 6.00.

(1-Allyl-5-oxo-9-trimethylsilyl-non-8-ynyl)-carbamic acid *tert*-butyl ester (13)

To a suspension of 0.145 g of magnesium (5.94 mmol) in 10 mL of THF was added 1.22 g of 4-trimethylsilyl-1-bromo-3-butyne (5.94 mmol). The reaction mixture was stirred at rt until the evolution of heat was detected and then was stirred at 0 °C for 1h. The resulting cloudy brown solution was transferred dropwise to a cold (-78 °C) suspension of 0.474 g of 6-allyl-2-oxo-piperidine-1-carboxylic acid *tert*-butyl ester (1.98 mmol) in 10 mL of THF. The reaction mixture was stirred at -78 °C for 1h before being warmed to rt and stirred for 12h. The reaction was diluted with diethyl ether and sequentially

washed with water, a saturated aqueous solution of sodium bicarbonate and a saturated aqueous brine solution. The combined aqueous fractions were back extracted with diethyl ether. The combined organic fractions were dried over magnesium sulfate, and concentrated by rotary evaporation *in vacuo* to afford 0.837 g of a yellow oil. Purification by column chromatography (5:1 hexanes:ethyl acetate) afforded 0.229 g (32 %) of **13** as a colorless oil.

IR (film): 3356, 2960, 2177, 1713, 1642, 1519, 1173, 844 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 5.67-5.78 (m, 1H), 5.01-5.09 (m, 2H), 4.31 (d, $J = 7.2$ Hz, 1H), 3.60 (d, $J = 7.2$ Hz, 1H), 2.59-2.64 (m, 2H), 2.39-2.47 (m, 4H), 2.14-2.21 (m, 2H), 1.53-1.69 (m, 3H), 1.41 (s, 9H), 0.11 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ 208.6, 155.7, 134.4, 117.9, 105.8, 85.2, 79.2, 49.8, 42.4, 41.7, 39.7, 34.1, 28.5, 20.1, 14.6, 0.2. MS (ESI): 388 ($\text{M} + \text{Na}^+$). Anal. Calcd for $\text{C}_{20}\text{H}_{35}\text{NO}_3\text{Si}$: C, 65.71; H, 9.65; N, 3.83. Found: C, 65.91; H, 9.30; N, 4.00.

10-tert-Butoxycarbonylamino-6-oxo-dec-2-ynoic acid methyl ester (**15**)

To a solution of 0.178 g of **3** (0.61 mmol) in 6 mL of THF and 0.1 mL of water was added 11 mg of *p*-toluenesulfonic acid (0.056 mmol) and the reaction mixture was stirred at rt for 24h. The reaction mixture was diluted with diethyl ether and washed with a saturated aqueous sodium bicarbonate solution. The combined aqueous fractions were back extracted with diethyl ether. The combined organic fractions were dried over sodium sulfate and concentrated by rotary evaporation *in vacuo* to afford 0.197 g of a crude yellow oil. Purification by column chromatography on silica gel (2:1 hexanes:ethyl acetate to 1:1 hexanes:ethyl acetate) to afford 186 mg (98%) of **15** as a colorless oil.

IR (film): 3397, 2935, 2241, 1713, 1257 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 4.61 (s, 1H), 3.68 (s, 3H), 3.04 (quartet, $J = 6.4$ Hz, 2H), 2.62-2.68 (m, 2H), 2.49-2.55 (m, 2H), 2.40 (t, $J = 7.3$ Hz, 2H), 1.50-1.60 (m, 2H), 1.35-1.46 (m, 2H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 207.2, 155.9, 153.9, 88.0, 79.0, 72.9, 52.5, 41.9, 39.9, 29.3, 28.3,

20.6, 12.9. MS (ESI): 334 (M + Na⁺). Anal. Calcd for C₁₆H₂₅NO₅: C, 61.72; H, 8.09; N, 4.50. Found: C, 61.89; H, 8.23; N, 4.78.

2-Oxo-pyrrolidine-1-carboxylic acid tert-butyl ester⁵

To a solution of 5.41 g of 2-pyrrolidinone (63.6 mmol) in 210 mL of acetonitrile was added 767 mg of DMAP (6.3 mmol) followed by a solution of 16.8 g of di-*tert*-butyl-dicarbonate (77.1 mmol) in 20 mL of acetonitrile. The colorless reaction mixture was stirred at rt for 1 h. The resulting dark yellow reaction mixture was concentrated by rotary evaporation *in vacuo* and the resulting oil was taken up in diethyl ether. The mixture was washed with an aqueous solution of 1N HCl and a saturated aqueous brine solution. The organic phase was dried over sodium sulfate, and concentrated by rotary evaporation *in vacuo* to afford a yellow oil. Purification by gradient column chromatography on triethylamine washed silica gel (5:1 □ 3:1 □ 1:1 hexanes:ethyl acetate) afforded 11.1 g (94 %) of the title compound as a pale yellow semi-solid.

IR (film): 2981, 1784, 1752, 1714, 1310, 1155 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): □ 3.61 (t, *J* = 7.3 Hz, 2H), 2.36 (t, *J* = 7.9 Hz, 2H), 1.86 (tt, *J* = 7.9 Hz, 7.3 Hz, 2H), 1.38 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): □ 174, 150, 82.4, 46.3, 132.7, 27.8, 17.2. MS (ESI): 208 (M + Na⁺).

(4-Oxo-8-trimethylsilyl-oct-7-ynyl)-carbamic acid tert-butyl ester

To a suspension of 0.403 g of magnesium (16.6 mmol) in 44 mL of THF was added 3.00 g of 4-trimethylsilyl-1-bromo-3-butyne (14.6 mmol). The reaction mixture was stirred for 1.5h to give a green solution. This solution was transferred dropwise to a cold (-78 °C) suspension of 0.990 g of 2-oxo-pyrrolidine-1-carboxylic acid tert-butyl ester (5.35 mmol) in 12 mL of THF. The green reaction mixture was stirred at -78 °C for 2h before being warmed to rt and stirred for 18h. The reaction was diluted with diethyl ether and slowly quenched with 20 mL of water. The organic phase was washed with a saturated aqueous solution of sodium bicarbonate. The combined aqueous fractions were back extracted

⁵ Same as footnote 1

two times with diethyl ether. The combined organic fractions were dried over sodium sulfate, and concentrated by rotary evaporation *in vacuo* to afford 3.56 g of a pale yellow oil. Purification by column chromatography on triethylamine washed silica gel (10:1 hexanes:ethyl acetate to elute bromide byproduct □ 3:1 hexanes:ethyl acetate to elute product ketone) afforded 1.43 g (86 %) of the title compound as a colorless oil that solidifies in the freezer, mp: 51-52 °C.

IR (film): 3384, 2964, 217, 1699, 1520 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): □ 4.60 (s, 1H), 3.09 (q, $J = 6.4$ Hz, 2H), 2.58-2.68 (m, 2H), 2.44 (t, $J = 7.3$ Hz, 4H), 1.73 (quintet, $J = 6.9$ Hz, 2H), 1.40 (s, 9H), 0.09 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): □ 208.2, 156.0, 105.6, 85.0, 79.1, 41.5, 39.8, 28.3, 24.0, 14.4, -0.02. MS (ESI): 334 ($\text{M} + \text{Na}^+$). Anal. Calcd for $\text{C}_{16}\text{H}_{29}\text{NO}_3\text{Si}$: C, 61.69; H, 9.38; N, 4.50. Found: C, 61.73; H, 9.69; N, 4.57.

4-Oxo-oct-7-ynyl)-carbamic acid tert-butyl ester (17)

To a solution of 1.84 g of (4-oxo-8-trimethylsilyl-oct-7-ynyl)-carbamic acid tert-butyl ester (5.93 mmol) in 10 mL of methanol was added 1.64 g of potassium carbonate (11.9 mmol). The reaction mixture was stirred at rt for 3 h. Concentration by rotary evaporation *in vacuo* resulted in a yellow slurry which was taken up in diethyl ether and water. The aqueous fraction was extracted with diethyl ether. The combined organic fractions were dried over sodium sulfate and concentrated by rotary evaporation *in vacuo* to afford a crude yellow oil. Purification by column chromatography on triethylamine washed silica gel (3:1 hexanes:ethyl acetate) afforded 1.28 g (91 %) of the title compound as a colorless oil that crystallized in the freezer, mp: 42.5-44 °C.

IR (film): 3374, 3307, 2978, 1708, 1521 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): □ 4.75 (s, 1H), 2.96-3.06 (m, 2H), 2.55 (t, $J = 7.3$ Hz, 2H), 2.38 (t, $J = 7.0$ Hz, 2H), 2.29-2.36 (m, 2H), 1.85 (s, 1H), 1.61-1.71 (m, 2H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): □ 207.9, 155.9, 82.8, 78.8, 68.6, 41.1, 39.6, 28.2, 23.8, 12.7. MS (ESI): 262 ($\text{M} + \text{Na}^+$). Anal. Calcd for $\text{C}_{13}\text{H}_{21}\text{NO}_3$: C, 65.25; H, 8.84; N, 5.85. Found: C, 65.39; H, 8.80; N, 6.10.

6-But-3-ynyl-2,3,4,5-tetrahydro-pyridine (19)

To a solution of 0.162 g of **11** (0.638 mmol) in 3 mL of dichloromethane was added 1 mL of trifluoroacetic acid and the yellow reaction mixture was stirred at rt for 1h before being cooled to 0 °C and treated with 15 mL of 1N NaOH. The aqueous phase was extracted four times with dichloromethane. The combined organic fractions were dried over magnesium sulfate and concentrated by rotary evaporation *in vacuo* to afford a crude yellow oil. Purification by gradient column chromatography on triethylamine washed silica gel (2:1 □ 1:1 □ 1:2 petroleum ether:diethyl ether) afforded 73 mg (84 %) of **19** as a yellow oil.

IR (film): 3296, 2932, 1667 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 3.51-3.57 (m, 2H), 2.39-2.45 (m, 2H), 2.31-2.37 (m, 2H), 2.07-2.14 (m, 2H), 1.92 (t, $J = 2.5$ Hz, 1H), 1.61-1.69 (m, 2H), 1.50-1.57 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 168.5, 84.2, 68.3, 49.2, 38.9, 29.7, 21.9, 19.5, 15.2. MS (ESI): 136 ($\text{M} + \text{H}^+$).

5-(But-3-ynyl)-3,4-dihydro-2H-pyrrole (20)

To a solution of 0.421 g of (4-oxo-oct-7-ynyl)-carbamic acid tert-butyl ester (1.76 mmol) in 4.5 mL of dichloromethane was added 1.5 mL of trifluoroacetic acid and the yellow reaction mixture was stirred at rt for 1h before being cooled to 0 °C and treated with 20 mL of 1N NaOH. The aqueous phase was extracted four times with dichloromethane. The combined organic fractions were dried over magnesium sulfate and concentrated by rotary evaporation *in vacuo* to afford a crude yellow oil. Purification by gradient column chromatography on triethylamine washed silica gel (2:1 □ 1:1 □ 1:2 petroleum ether:diethyl ether) afforded 0.190 g (89 %) of **20** as a yellow oil.

IR (film): 3294, 2921, 1646, 1434 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 3.78 (t, $J = 7.3$ Hz, 2H), 2.42-2.55 (m, 6H), 1.93 (t, $J = 2.4$ Hz, 1H), 1.79-1.89 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 176.0, 83.6, 68.4, 60.7, 37.4, 32.5, 22.4, 15.4. MS (ESI): 122 ($\text{M} + \text{H}^+$).