Supplementary Information
For
“Platinum(II)-Catalyzed Cyclizations Forming Quaternary Carbon Centers Using
Enesulfonamides, Enecarbamates or Enamides as Nucleophiles”

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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 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. pH 8 buffered saturated aqueous ammonium chloride was prepared by adding 50 mL of NH₄OH to 950 mL of saturated aqueous ammonium chloride solution. Melting points are uncorrected. Proton nuclear

magnetic resonance (^1H NMR) spectra and carbon nuclear magnetic resonance (^{13}C 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 ^{13}C NMR). Coupling constants (J values) are given in Hertz (Hz).

Experimental Procedures for Scheme 2:

3-(5-Trimethylsilyl-pent-4-ynyl)-piperidin-2-one

To a solution of 2.21 g of δ -valerolactam (22.3 mmol) in 100 mL of THF at $-78\text{ }^\circ\text{C}$ was added 31.0 mL of a solution of *n*-butyllithium (1.50 M in hexanes, 46.5 mmol) dropwise. The yellow reaction mixture was warmed to $0\text{ }^\circ\text{C}$ and stirred for 1 h. To this reaction mixture was added 7.27 g of (4-Bromo-but-1-ynyl)-trimethyl-silane (33.2 mmol) and stirring was continued at $0\text{ }^\circ\text{C}$ for 1.5 h. The reaction was quenched with 25 mL of a saturated aqueous solution of ammonium chloride and 5 mL of water, warmed to rt and extracted three times with dichloromethane. The combined organic fractions were dried over sodium sulfate and concentrated by rotary evaporation *in vacuo* to afford a crude pale yellow oil. Purification of the crude material by column chromatography on a silica gel plug (1:2 hexanes:ethyl acetate) afforded 4.12 g (78%) of the title compound as a white solid, mp: $63\text{--}64\text{ }^\circ\text{C}$.

IR (film): $3210, 2173, 1657\text{ cm}^{-1}$. ^1H NMR (400 MHz, CDCl_3): δ 7.25 (s, 1H), 3.10-3.22 (m, 2H), 2.08-2.20 (m, 3H), 1.78-1.90 (m, 2H), 1.68-1.78 (m, 1H), 1.35-1.65 (m, 5H), 0.015 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 175.0, 107.0, 84.2, 41.9, 40.3, 30.7, 26.0, 25.9, 21.0, 19.8, -0.09. MS (ESI): 260 ($\text{M} + \text{Na}^+$). Anal. Calcd for $\text{C}_{13}\text{H}_{23}\text{NOSi}$: C, 65.77; H, 9.76; N, 5.90. Found: C, 65.99; H, 9.88; N, 6.20.

1-(Toluene-4-sulfonyl)-3-(5-trimethylsilyl-pent-4-ynyl)-piperidin-2-one

To a solution of 3.21 g of 3-(5-trimethylsilyl-pent-4-ynyl)-piperidin-2-one (13.5 mmol) in 40 mL of THF at $-78\text{ }^{\circ}\text{C}$ was added 9.7 mL of a solution of *n*-butyllithium (1.53 M in hexanes, 14.8 mmol) dropwise. The reaction mixture was stirred for 1 h before the addition of 5.19 g of *p*-toluenesulfonyl chloride (27.2 mmol) in 30 mL of THF. Stirring was continued at $-78\text{ }^{\circ}\text{C}$ for 30 min before being allowed to stir and warm to rt for 1h. The pale yellow 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 magnesium sulfate and concentrated by rotary evaporation *in vacuo* to afford a crude yellow oil. Purification of the crude material by gradient column chromatography on silica gel column (10:1 $\rightarrow$ 5:1 hexanes:ethyl acetate to elute product) afforded 5.22 g (99 %) of the title compound as a colorless syrup.

IR (film): 2956, 2173, 1694 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.84 (d, $J = 8.5$ Hz, 2H), 7.26 (d, $J = 8.3$ Hz, 2H), 3.80-3.94 (m, 2H), 2.37 (s, 3H), 2.25-2.33 (m, 1H), 2.11 (td, $J = 7.0$ Hz, 1.8 Hz, 2H), 1.88-2.00 (m, 2H), 1.73-1.85 (m, 2H), 1.37-1.49 (m, 4H), 0.08 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 172.9, 144.5, 136.1, 129.2, 128.4, 106.7, 84.6, 46.5, 43.0, 30.1, 25.8, 25.6, 22.2, 21.5, 19.7, 0.02. MS (ESI): 414 ($\text{M} + \text{Na}^+$). Anal. Calcd for $\text{C}_{20}\text{H}_{29}\text{NO}_3\text{SSi}$: C, 61.34; H, 7.46; N, 3.58. Found: C, 60.94; H, 7.42; N, 3.75.

1-(Toluene-4-sulfonyl)-5-(5-trimethylsilyl-pent-4-ynyl)-1,2,3,4-tetrahydro-pyridine

To a solution of 5.22 g of 1-(toluene-4-sulfonyl)-3-(5-trimethylsilyl-pent-4-ynyl)-piperidin-2-one (13.4 mmol) in 70 mL of dichloromethane at $-78\text{ }^{\circ}\text{C}$ was added 26 mL of a solution of diisobutylaluminum hydride (1M in hexanes, 26 mmol) slowly. The

reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 2 h before being slowly quenched with 6.5 mL of a pH 8 buffered saturated aqueous solution of ammonium chloride and allowed to stir and warm to rt for 1 h. To the reaction was added 20 g of magnesium sulfate and stirring was continued at rt for 1 h. The resulting white suspension was filtered through celite and concentrated by rotary evaporation *in vacuo* to afford a crude colorless syrup. The crude syrup was taken up in 70 mL of dichloromethane and to this solution was added 7.5 mL of triethylamine (53.8 mmol) followed by 81 mg of *N,N*-dimethyl-4-aminopyridine (0.67 mmol). The reaction was cooled to $0\text{ }^{\circ}\text{C}$ and 2.1 mL of methanesulfonyl chloride (27.1 mmol) was added slowly to give a pale yellow reaction mixture which was let stir and warm to rt for 14 h. The resulting orange reaction mixture was washed with water followed by a saturated aqueous brine solution. The combined aqueous washes were back extracted with dichloromethane. The combined organic phases were dried over magnesium sulfate and concentrated by rotary evaporation *in vacuo* to afford a crude yellow solid. Purification of the crude material by column chromatography on triethylamine washed silica gel (10:1 hexanes:ethyl acetate) afforded 3.96 g (79 %) of the title compound as a white powder, mp: $81\text{--}83\text{ }^{\circ}\text{C}$.

IR (film): 2935, 2173, 1352, 1166 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.65 (d, $J = 8.2$ Hz, 2H), 7.28 (d, $J = 8.2$ Hz, 2H), 6.46 (s, 1H), 3.24–3.29 (m, 2H), 2.40 (s, 3H), 2.10 (t, $J = 7.3$ Hz, 2H), 2.04 (t, $J = 7.3$ Hz, 2H), 1.79 (t, $J = 6.1$ Hz, 2H), 1.50–1.62 (m, 4H), 0.15 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 143.4, 134.8, 129.6, 127.0, 120.4, 119.9, 106.8, 85.0, 43.5, 33.9, 26.3, 24.2, 21.5, 20.7, 18.9, 0.11. MS (ESI): 398 ($\text{M} + \text{Na}^+$). Anal. Calcd for $\text{C}_{20}\text{H}_{29}\text{NO}_2\text{SSi}$: C, 63.95; H, 7.78; N, 3.73. Found: C, 64.00; H, 7.86; N, 4.00.

5-Pent-4-ynyl-1-(toluene-4-sulfonyl)-1,2,3,4-tetrahydro-pyridine (1)

To a solution of 3.80 g of 1-(toluene-4-sulfonyl)-5-(5-trimethylsilyl-pent-4-ynyl)-1,2,3,4-tetrahydro-pyridine (10.1 mmol) in 50 mL of methanol was added 4.23 g of potassium carbonate (30.6 mmol) and the reaction was stirred at rt for 14 h. The resulting white

suspension was concentrated by rotary evaporation *in vacuo*. The resulting pale yellow slurry was taken up in 50 mL of diethyl ether and 20 mL of water. The aqueous phase was extracted three times with diethyl ether. The combined organic phases were dried over magnesium sulfate and concentrated by rotary evaporation *in vacuo* to afford a crude yellow oil. Purification of the crude material by column chromatography on triethylamine washed silica gel (8:1 hexanes:ethyl acetate) afforded 2.80 g (92 %) of the title compound **1** as a white solid, mp: 55-56 °C.

IR (film): 3291, 2935, 1349, 1165 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.62 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 6.45 (s, 1H), 3.23-3.29 (m, 2H), 2.39 (s, 3H), 2.01-2.10 (m, 4H), 1.94 (t, J = 2.5 Hz, 1H), 1.78 (t, J = 6.1 Hz, 2H), 1.50-1.63 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 143.3, 134.7, 129.5, 126.9, 120.3, 119.9, 83.7, 68.6, 43.4, 33.8, 26.1, 24.2, 21.4, 20.6, 17.4. MS (ESI): 326 ($\text{M} + \text{Na}^+$).

1-Methylene-7-(toluene-4-sulfonyl)-7-aza-spiro[4.5]decane (**2**)

To a flask charged with 61 mg of **1** (0.20 mmol) and 2.7 mg of PtCl_2 (0.01 mmol) was added 2 mL of toluene followed by 17 μL of methanol (0.42 mmol) and the reaction was stirred for 3 h at 80 °C before being cooled to rt. To the resulting brown reaction mixture was added 49 μL of triethylsilane (0.31 mmol) followed by 26 μL of borontrifluoride diethyletherate (0.21 mmol) and stirring was continued at rt for 30 min. The resulting black reaction mixture was diluted with diethyl ether, filtered through a pipette of silica gel and concentrated by rotary evaporation *in vacuo* to afford a crude brown oil.

Purification of the crude material by column chromatography on silica gel (8:1 hexanes:ethyl acetate) afforded 49 mg (80 %) of the title compound **2** as a colorless film. IR (film): 2942, 1340, 1160 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.59 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 4.90 (t, J = 2.1 Hz, 1H), 4.67 (t, J = 2.1 Hz, 1H), 3.68 (d, J = 11.6 Hz, 1H), 3.31 (d, J = 11.6 Hz, 1H), 2.40 (s, 3H), 2.29-2.44 (m, 2H), 2.22 (td, J = 11.6 Hz, 3.7 Hz, 1H), 2.08 (dt, J = 12.2 Hz, 5.8 Hz, 1H), 1.97 (d, J = 11.3 Hz, 1H), 1.57-

1.77 (m, 4H), 1.38-1.50 (m, 2H), 1.24-1.33 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 157.9, 143.2, 133.6, 129.5, 127.5, 105.5, 54.9, 46.5, 45.4, 35.7, 35.1, 33.7, 22.7, 22.4, 21.5. MS (ESI): 328 ($\text{M} + \text{Na}^+$).

1-Methyl-7-(toluene-4-sulfonyl)-7-aza-spiro[4.5]dec-1-ene (3)

Representative procedure for use of PtCl_2 with silver salts:

To a flask charged with 55 mg of **1** (0.18 mmol), 2.5 mg of PtCl_2 (0.0094 mmol) and 2.5 mg of silver (I) trifluoromethanesulfonate (0.0097 mmol) was added 1.8 mL of toluene followed by 15 μL of methanol (0.37 mmol) and the reaction was stirred for 6.5 h at 50 $^\circ\text{C}$ before being cooled to rt. To the resulting brown reaction mixture was added 35 μL of triethylsilane (0.22 mmol) followed by 23 μL of borontrifluoride diethyletherate (0.18 mmol) and stirring was continued at rt for 45 min. The resulting black reaction mixture was diluted with diethyl ether, filtered through a pipette of silica gel and concentrated by rotary evaporation *in vacuo* to afford a crude brown oil. Purification of the crude material by column chromatography on silica gel (5:1 hexanes:ethyl acetate) afforded 45 mg (80 %) of the title compound **3** as a colorless oil.

IR (film): 2932, 1445, 1341, 1160 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.60 (d, $J = 8.2$ Hz, 2H), 7.29 (d, $J = 8.2$ Hz, 2H), 5.39 (s, 1H), 3.73 (d, $J = 11.6$ Hz, 1H), 3.21 (d, $J = 11.0$ Hz, 1H), 2.41 (s, 3H), 2.07-2.31 (m, 5H), 1.56-1.81 (m, 3H), 1.50 (d, $J = 1.8$ Hz, 3H), 1.27-1.41 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 143.1, 142.9, 133.5, 129.4, 127.5, 126.6, 52.0, 49.5, 46.1, 33.9, 32.5, 28.7, 22.3, 21.4, 12.7. MS (ESI): 306 ($\text{M} + \text{H}^+$).

Experimental Procedures for Scheme 3:

2-(Toluene-4-sulfonyl)-2-aza-spiro[5.5]undec-8-en-7-one

A stream of O₃/O₂ was bubbled through a solution of 0.166 g of **3** (0.543 mmol) in 10 mL of dichloromethane at -78 °C until persistence of blue color was observed in the reaction mixture or two minutes (7 min total) at which point the reaction was let stand and warm to rt. To the resulting colorless solution was added 1 mL of dimethyl sulfide (13.6 mmol) and the reaction was stirred for 3 h at rt. An additional 1 mL of dimethyl sulfide (13.6 mmol) was added and the reaction was stirred at reflux for 20 h before being concentrated by rotary evaporation *in vacuo* to afford 3-[3-acetyl-1-(toluene-4-sulfonyl)-piperidin-3-yl]-propionaldehyde as a crude yellow oil.

IR (film): 2933, 1724, 1704 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 9.68 (s, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 3.47 (d, *J* = 12.2 Hz, 1H), 3.08-3.16 (m, 1H), 2.58 (d, *J* = 12.4 Hz, 2H), 2.40 (s, 3H), 2.33 (ddd, *J* = 15.8 Hz, 9.5 Hz, 5.9 Hz, 2H), 2.21 (s, 3H), 1.89-1.99 (m, 2H), 1.54-1.71 (m, 3H), 1.08 (ddd, *J* = 13.5 Hz, 9.4 Hz, 4.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 210.2, 200.4, 143.7, 132.4, 129.7, 127.6, 52.2, 50.3, 46.6, 37.9, 30.0, 26.4, 25.6, 21.5, 21.4. MS (ESI): 338 (M + H⁺).

The crude yellow oil was taken up in 8 mL of benzene. To this solution was added 30 mg of *p*-toluenesulfonic acid monohydrate (0.16 mmol) and the reaction mixture was stirred at reflux with a Dean-Stark trap for 4 h. The reaction mixture was cooled to rt and concentrated by rotary evaporation *in vacuo* to afford a crude yellow oil. Purification of the crude material by column chromatography on silica gel (4:1 hexanes:ethyl acetate) afforded 0.113 g (65 %) of the title compound as a colorless film.

IR (film): 2927, 1673, 1341, 1161 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 6.94 (dt, *J* = 10.0 Hz, 4.0 Hz, 1H), 5.91 (dt, *J* = 10.0 Hz, 2.1 Hz, 1H), 3.74 (d, *J* = 11.3 Hz, 1H), 3.57 (d, *J* = 11.9 Hz, 1H), 2.47-2.58 (m, 1H),

2.40 (s, 3H), 2.34 (d, $J = 11.9$ Hz, 1H), 2.29-2.40 (m, 1H), 2.19-2.27 (m, 1H), 2.15 (td, $J = 11.9$ Hz, 3.0 Hz, 1H), 2.01 (ddd, $J = 14.0$ Hz, 7.3 Hz, 4.9 Hz, 1H), 1.72-1.86 (m, 1H), 1.50-1.67 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 201.4, 150.0, 143.5, 133.2, 129.7, 128.3, 127.4, 50.4, 46.6, 44.5, 28.6, 27.7, 22.6, 21.5, 20.5. MS (ESI): 320 ($\text{M} + \text{H}^+$), 342 ($\text{M} + \text{Na}^+$).

2-(Toluene-4-sulfonyl)-2-aza-spiro[5.5]undecan-7-one

To a solution of 73 mg of 2-(toluene-4-sulfonyl)-2-aza-spiro[5.5]undec-8-en-7-one (0.22 mmol) in 4 mL of ethyl acetate was added 14 mg of palladium on charcoal (5 wt. %) and the reaction was stirred under atmospheric pressure of hydrogen gas for 24 h. The reaction mixture was then filtered through celite and concentrated by rotary evaporation *in vacuo* to afford a crude colorless oil. Purification of the crude material by column chromatography on silica gel (3:1 hexanes:ethyl acetate) afforded 68 mg (92 %) of the title compound as a colorless oil.

IR (film): 2937, 1707, 1341 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.57 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 3.14-3.22 (m, 1H), 3.12 (d, $J = 12.0$ Hz, 1H), 2.98 (d, $J = 12.0$ Hz, 1H), 2.50-2.59 (m, 1H), 2.37 (s, 3H), 2.27-2.46 (m, 2H), 1.58-1.90 (m, 8H), 1.40-1.58 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 213.5, 143.4, 133.1, 129.6, 127.4, 52.1, 48.1, 46.6, 38.5, 34.6, 30.0, 27.5, 21.4, 20.6, 20.3. MS (ESI): 344 ($\text{M} + \text{Na}^+$).

2-Aza-spiro[5.5]undecan-7-ol

To a solution of 10.9 mg of 2-(toluene-4-sulfonyl)-2-aza-spiro[5.5]undecan-7-one (0.034 mmol) in 0.34 mL of THF at -78°C was condensed approximately 5 mL of ammonia. To this solution was added 7 mg of lithium metal to give a dark blue reaction mixture which was stirred at -78°C for 1 h. The reaction was quenched with 0.120 mg of ammonium chloride (2.24 mmol) and allowed to stir and warm to rt. The reaction mixture was diluted with dichloromethane, filtered through celite and concentrated by rotary evaporation *in vacuo* to afford a crude colorless residue. Purification of the crude material by gradient column chromatography on silica gel (dichloromethane $\rightarrow$ 20:20:1 $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}:\text{NH}_4\text{OH}$) afforded 2.8 mg (45 %) of the title compound as a 2:1 mixture of isonitramine:nitramine.

($\pm$)-Isonitramine and ($\pm$)-Nitramine:

IR (film): 3370, 2932, 1455 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): ($\pm$)-Isonitramine: δ 3.64 (dd, $J = 10.9$ Hz, 3.5 Hz, 1H), 2.99-3.07 (m, 1H), 2.93 (d, $J = 11.3$ Hz, 1H), 2.7-3.3 (bs, 2H), 2.60 (td, $J = 11.3$ Hz, 3.5 Hz, 1H), 2.50 (d, $J = 11.3$ Hz, 1H), 2.22 (d, $J = 14.0$ Hz, 1H), 0.80-2.10 (m, 11H). ($\pm$)-Nitramine: δ 3.58-3.62 (m, 1H), 3.47 (d, $J = 11.9$ Hz, 1H), 2.98-3.07 (m, 1H), 2.7-3.3 (bs, 2H), 2.58-2.67 (m, 1H), 2.40 (d, $J = 11.8$ Hz, 1H), 0.80-2.10 (m, 12 H). ^{13}C NMR (100 MHz, CDCl_3): ($\pm$)-Isonitramine: δ 80.3, 60.5, 47.1, 36.7, 36.2, 29.7, 28.6, 24.3, 22.9, 20.2. ($\pm$)-Nitramine: δ 77.2, 51.8, 46.3, 37.1, 36.4, 35.9, 31.9, 23.6, 22.7, 20.9. MS (ESI): 170 ($\text{M} + \text{H}^+$).

Experimental Procedures for Scheme 4:

6-Methylene-2-(toluene-4-sulfonyl)-2-aza-spiro[4.4]nonane (9)

To a flask charged with 60 mg of **4** (0.21 mmol) and 2.9 mg of PtCl₂ (0.011 mmol) was added 2 mL of toluene followed by 17 μ L of methanol (0.42 mmol) and the reaction was stirred for 2 h at 80 °C before being cooled to rt. To the resulting brown reaction mixture was added 50 μ L of triethylsilane (0.31 mmol) followed by 27 μ L of borontrifluoride diethyletherate (0.21 mmol) and stirring was continued at rt for 45 min. The resulting black reaction mixture was diluted with diethyl ether, filtered through a pipette of silica gel and concentrated by rotary evaporation *in vacuo* to afford a crude brown oil.

Purification of the crude material by column chromatography on silica gel (8:1 hexanes:ethyl acetate) afforded 49 mg (80 %) of the title compound **9** as a colorless oil. IR (film): 2953, 1347, 1161 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 4.83 (t, *J* = 2.1 Hz, 1H), 4.62 (t, *J* = 2.4 Hz, 1H), 3.40 (ddd, *J* = 9.7 Hz, 8.2 Hz, 4.3 Hz, 1H), 3.27 (ddd, *J* = 9.7 Hz, 8.2 Hz, 7.3 Hz, 1H), 3.19 (d, *J* = 9.7 Hz, 1H), 3.05 (d, *J* = 9.7 Hz, 1H), 2.41 (s, 3H), 2.31 (tt, *J* = 7.3 Hz, 2.1 Hz, 2H), 1.75 (dt, *J* = 12.5, 8.2 Hz, 1H), 1.58-1.66 (m, 1H), 1.49-1.57 (m, 2H), 1.33-1.48 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 155.4, 143.3, 134.1, 129.6, 127.4, 105.4, 59.1, 52.2, 47.2, 38.4, 38.2, 33.1, 22.9, 21.5. MS (ESI): 314 (M + Na⁺).

1-Methylene-7-(toluene-4-sulfonyl)-7-aza-spiro[4.6]undecane (10)

To a flask charged with 52 mg of **5** (0.16 mmol) and 2.2 mg of PtCl₂ (0.0083 mmol) was added 1.7 mL of toluene followed by 14 μ L of methanol (0.35 mmol) and the reaction

was stirred for 5.5 h at 80 °C before being cooled to rt. To the resulting brown reaction mixture was added 40 μ L of triethylsilane (0.25 mmol) followed by 21 μ L of borontrifluoride diethyletherate (0.17 mmol) and stirring was continued at rt for 30 min. The resulting black reaction mixture was diluted with diethyl ether, filtered through a pipette of silica gel and concentrated by rotary evaporation *in vacuo* to afford a crude brown oil. Purification of the crude material by column chromatography on silica gel (8:1 hexanes:ethyl acetate) afforded 27 mg (50 %) of the title compound **10** as a colorless film.

IR (film): 2932, 1455, 1338, 1159 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.62 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 4.86 (t, J = 2.1 Hz, 1H), 4.68 (t, J = 2.1 Hz, 1H), 3.55-3.63 (m, 1H), 3.46 (d, J = 14.0 Hz, 1H), 2.67-2.76 (m, 1H), 2.48 (d, J = 14.0 Hz, 1H), 2.35-2.44 (m, 2H), 2.39 (s, 3H), 2.17-2.25 (m, 1H), 1.85-1.95 (m, 1H), 1.43-1.76 (m, 8H). ^{13}C NMR (100 MHz, CDCl_3): δ 159.7, 142.9, 135.8, 129.5, 127.2, 104.9, 56.9, 49.8, 49.7, 40.4, 36.3, 33.9, 28.6, 22.4, 22.3, 21.4. MS (ESI): 342 ($\text{M} + \text{Na}^+$).

1-Methylene-7-aza-spiro[4.5]decane-7-carboxylic acid tert-butyl ester (11)

To a flask charged with 58 mg of **6** (0.23 mmol) and 3.1 mg of PtCl_2 (0.012 mmol) was added 2.2 mL of toluene followed by 19 μ L of methanol (0.44 mmol) and the reaction was stirred for 2 h at 80 °C before being cooled to 0 °C. To the resulting brown reaction mixture was added 40 μ L of triethylsilane (0.25 mmol) followed by 30 μ L of borontrifluoride diethyletherate (0.24 mmol) and stirring was continued at 0 °C for 1 h. The resulting black reaction mixture was diluted with diethyl ether, filtered through a pipette of silica gel and concentrated by rotary evaporation *in vacuo* to afford a crude brown oil. Purification of the crude material by column chromatography on silica gel (10:1 hexanes:ethyl acetate) afforded 41 mg (69 %) of the title compound **11** as a colorless oil.

IR (film): 2933, 1695, 1425, 1157 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 4.90 (s, 1H), 4.75 (s, 1H), 3.60-4.20 (bm, 2H), 2.56-2.80 (bs, 1H), 2.26-2.50 (m, 3H), 1.80 (dt, J = 12.5 Hz, 5.2 Hz, 1H), 1.40 (s, 9H), 1.24-1.68 (m, 7H). ^{13}C NMR (100 MHz, CDCl_3): δ 158.1, 154.8, 104.7, 79.0, 52.9, 52.1, 46.3, 43.6, 36.2, 35.0, 33.8, 28.4, 22.7. MS (ESI): 274 ($\text{M} + \text{Na}^+$).

1-Methylene-7-aza-spiro[4.5]decane-7-carboxylic acid methyl ester (12**)**

To a flask charged with 26 mg of **7** (0.12 mmol) and 1.8 mg of PtCl_2 (0.0068 mmol) was added 1 mL of toluene followed by 10 μL of methanol (0.25 mmol) and the reaction was stirred for 2 h at 80 $^\circ\text{C}$ before being cooled to rt. To the resulting brown reaction mixture was added 24 μL of triethylsilane (0.15 mmol) followed by 16 μL of borontrifluoride diethyletherate (0.13 mmol) and stirring was continued at rt for 45 min. The resulting black reaction mixture was diluted with diethyl ether, filtered through a pipette of silica gel and concentrated by rotary evaporation *in vacuo* to afford a crude brown residue. Purification of the crude material by column chromatography on silica gel (10:1 hexanes:ethyl acetate) afforded 19 mg (73 %) of the title compound **12** as a colorless film in a 12.5:1 mixture of the desired exocyclic alkene and corresponding structural isomer with internal alkene.

IR (film): 2951, 1703, 1446, 1272 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 4.91 (s, 1H), 4.75 (s, 1H), 3.60-4.20 (bm, 2H), 3.65 (s, 3H), 2.66-2.82 (bs, 1H), 2.27-2.58 (m, 3H), 1.70-1.87 (bs, 1H), 1.30-1.66 (m, 7H). Alkene peak of migrated double bond: 5.37 (s). ^{13}C NMR (100 MHz, CDCl_3): δ 158.2, 156.3, 104.9, 52.8, 52.4, 46.0, 44.3, 36.0, 35.2, 33.8, 22.7, 22.5. MS (ESI): 210 ($\text{M} + \text{H}^+$), 232 ($\text{M} + \text{Na}^+$).

5-(5-Iodo-pent-4-ynyl)-1-(toluene-4-sulfonyl)-1,2,3,4-tetrahydro-pyridine (8)

To a solution of 64 mg of **1** (0.21 mmol) in 1.5 mL of THF at $-78\text{ }^{\circ}\text{C}$ was added 0.15 mL of a solution of *n*-butyllithium (1.50 M in hexanes, 0.23 mmol) dropwise. The reaction was warmed to $-42\text{ }^{\circ}\text{C}$ and stirred for 1 h before the addition of 73 mg of iodine (0.28 mmol) in 0.5 mL of THF. The red reaction was allowed to stir and warm to rt for 1 h. The reaction mixture was diluted with diethyl ether and washed sequentially with 20 % aqueous sodium thiosulfate solution followed by a saturated aqueous brine solution. The combined aqueous washes were back extracted with diethylether. The combined organic phases were dried over magnesium sulfate and concentrated by rotary evaporation *in vacuo* to afford a crude yellow oil. Purification of the crude material by column chromatography on triethylamine washed silica gel (8:1 hexanes:ethyl acetate) afforded 77 mg (85 %) of the title compound **8** as a colorless oil.

IR (film): 2932, 1348, 1164 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.65 (d, $J = 8.3$ Hz, 2H), 7.30 (d, $J = 8.3$ Hz, 2H), 6.46 (s, 1H), 3.26-3.32 (m, 2H), 2.43 (s, 3H), 2.26 (t, $J = 7.0$ Hz, 2H), 2.04 (t, $J = 7.4$ Hz, 2H), 1.80 (t, $J = 6.1$ Hz, 2H), 1.52-1.66 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 143.4, 134.8, 129.6, 127.0, 120.4, 119.7, 94.0, 43.5, 34.0, 26.2, 24.3, 21.5, 20.8, 19.9, -6.8. MS (ESI): 452 ($\text{M} + \text{Na}^+$).

1-Iodomethylene-7-(toluene-4-sulfonyl)-7-aza-spiro[4.5]decane (13)

To a flask charged with 37 mg of **8** (0.086 mmol) and 1.2 mg of PtCl_2 (0.0045 mmol) was added 0.9 mL of toluene followed by 7 μL of methanol (0.17 mmol) and the reaction was stirred for 7 h at $65\text{ }^{\circ}\text{C}$ before being cooled to rt. To the resulting brown reaction mixture was added 15 μL of triethylsilane (0.094 mmol) followed by 11 μL of borontrifluoride diethyletherate (0.087 mmol) and stirring was continued at rt for 15 min.

The resulting black reaction mixture was directly columned on triethylamine washed silica gel (8:1 hexanes:ethyl acetate) afforded 27 mg (74 %) of the title compound **13** as a colorless film which solidified upon storage to give white needles. Crystals of X-ray diffraction quality (needles) were obtained from methanol, mp: 151-153 °C.

IR (film): 2943, 1341, 1160 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.62 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 5.94 (t, J = 2.6 Hz, 1H), 3.55-3.63 (m, 1H), 3.29 (d, J = 11.8 Hz, 1H), 2.44 (s, 3H), 2.31-2.43 (m, 2H), 2.26 (dt, J = 12.6 Hz, 6.1 Hz, 2H), 2.12 (d, J = 11.3 Hz, 1H), 1.54-1.80 (m, 5H), 1.33-1.50 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 160.3, 143.4, 133.4, 129.7, 127.5, 72.3, 53.9, 48.5, 46.4, 38.3, 37.3, 34.5, 22.2, 21.5, 21.3. MS (ESI): 304 ($\text{M} - \text{I}$), 454 ($\text{M} + \text{Na}^+$).

Structure of product **13** as determined from X-ray diffraction

1-Methyl-5-pent-4-ynyl-3,4-dihydro-1H-pyridin-2-one (**14**)

To a solution of 0.570 g of 4-formyl-non-8-ynoic acid methyl ester (2.91 mmol) in 6 mL of toluene was added 3.0 mL of methyl amine solution (2.0 M in THF, 6.0 mmol) and the reaction was allowed to stir and warm to reflux with a Dean-Stark trap. After stirring for 4 h at reflux, the reaction mixture was cooled to rt and concentrated by rotary evaporation

in vacuo to afford a crude yellow oil. Purification by column chromatography on triethylamine washed silica gel (1:1 hexanes:ethyl acetate) afforded 0.397 g (77 %) of the title compound **14** as a colorless oil.

IR (film): 3293, 2939, 1662, 1392 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 5.70 (t, J = 1.2 Hz, 1H), 2.92 (s, 3H), 2.38 (dd, J = 8.5 Hz, 7.6 Hz, 2H), 2.02-2.17 (m, 6H), 1.89 (t, J = 2.7 Hz, 1H), 1.54 (quintet, J = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 168.7, 125.8, 118.2, 83.7, 68.7, 33.4, 32.3, 30.8, 26.2, 23.9, 17.6. MS (ESI): 200 ($\text{M} + \text{Na}^+$).

1:1 mixture of diastereomers

6-Methoxy-7-methyl-1-methylene-7-aza-spiro[4.5]decan-8-one (15)

To a flask charged with 32 mg of **14** (0.18 mmol) and 2.5 mg of PtCl_2 (0.0094 mmol) was added 1.8 mL of toluene followed by 15 μL of methanol (0.37 mmol) and the reaction was stirred for 3 h at 80 $^\circ\text{C}$ before being cooled to rt, diluted with ethyl acetate, filtered through a pipette of triethyl amine washed silica gel and concentrated by rotary evaporation *in vacuo* to afford a crude colorless oil. Purification of the crude material by column chromatography on triethylamine washed silica gel (1:2 hexanes:ethyl acetate) afforded 31 mg (81 %) of the title compound **15** as a 1:1 mixture of diastereomers in the form of a colorless oil.

IR (film): 2952, 1652, 1078 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 5.04 (s, 1H), 5.01 (s, 1H), 4.92 (t, J = 2.1 Hz, 1H), 4.66 (t, J = 2.1 Hz, 1H), 4.10 (s, 1H), 3.96 (s, 1H), 3.45 (s, 3H), 3.40 (s, 3H), 3.01 (s, 3H), 3.00 (s, 3H), 2.22-2.51 (m, 9H), 1.78-1.95 (m, 2H), 1.52-1.69 (m, 8H), 1.34-1.42 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 171.1, 170.7, 154.4, 153.5, 109.4, 107.0, 97.0, 95.7, 59.4, 58.8, 49.3, 48.6, 36.6, 36.1, 35.1, 34.8, 33.8, 33.1, 29.5, 28.9, 27.3, 26.6, 22.1, 21.3. MS (ESI): 210 ($\text{M} + \text{H}^+$), 232 ($\text{M} + \text{Na}^+$).

Experimental Procedures for Scheme 5:

5-(5-Phenyl-pent-4-ynyl)-1-(toluene-4-sulfonyl)-1,2,3,4-tetrahydro-pyridine (16a)

To a flask charged with 16 mg of bis(triphenylphosphine)palladium (II) dichloride (0.023 mmol) and 4.3 mg of copper (I) iodide (0.023 mmol) was added 1.5 mL triethylamine. To the resulting bright yellow mixture was added a solution of 0.192 g of **1** (0.63 mmol) and 85 μ L of iodobenzene (0.76 mmol) in 1.7 mL of triethylamine and 0.2 mL of dichloromethane and the reaction was stirred for 4 h at rt, wrapped in aluminum foil. The yellow reaction mixture was filtered through a pipette of triethylamine washed silica gel using diethyl ether eluant and then concentrated by rotary evaporation *in vacuo* to afford a crude orange syrup. Purification of the crude material by column chromatography on triethylamine washed silica gel (5:1 hexanes:ethyl acetate) afforded 0.230 g (96 %) of the title compound **16a** as an orange oil which solidified upon storage in the freezer, mp: 84-86 °C.

IR (film): 2933, 1491, 1351, 1165 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.65 (d, J = 8.2 Hz, 2H), 7.37-7.42 (m, 2H), 7.23-7.30 (m, 5H), 6.51 (s, 1H), 3.26-3.31 (m, 2H), 2.39 (s, 3H), 2.30 (t, J = 7.0 Hz, 2H), 2.11 (t, J = 7.3 Hz, 2H), 1.82 (t, J = 6.1 Hz, 2H), 1.56-1.69 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 143.4, 134.8, 131.4, 129.6, 128.2, 127.5, 127.0, 123.8, 120.3, 120.0, 89.5, 81.1, 43.5, 34.1, 26.4, 24.3, 21.4, 20.7, 18.5. MS (ESI): 402 ($\text{M} + \text{Na}^+$).

1-Methyl-5-(5-phenyl-pent-4-ynyl)-3,4-dihydro-1H-pyridin-2-one (16b)

To a flask charged with 38 mg of bis(triphenylphosphine)palladium (II) dichloride (0.054 mmol) and 12 mg of copper (I) iodide (0.062 mmol) was added 5 mL triethylamine. To

the resulting bright yellow mixture was added a solution of 0.269 g of **14** (1.52 mmol) and 0.20 mL of iodobenzene (1.79 mmol) in 3.0 mL of dichloromethane and the reaction was stirred for 4 h at rt, wrapped in aluminum foil. The reaction mixture was filtered through celite using dichloromethane eluant and then concentrated by rotary evaporation *in vacuo* to afford a crude orange syrup. Purification of the crude material by column chromatography on triethylamine washed silica gel (1:1 hexanes:ethyl acetate) afforded 0.355 g (92 %) of the title compound **16b** as an orange oil.

IR (film): 2936, 1667, 1392 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.32-7.36 (m, 2H), 7.20-7.25 (m, 3H), 5.75 (s, 1H), 2.96 (s, 3H), 2.40-2.46 (m, 2H), 2.36 (t, $J = 7.0$ Hz, 2H), 2.16-2.22 (m, 2H), 2.14 (t, $J = 7.3$ Hz, 2H), 1.65 (quintet, $J = 7.3$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 168.8, 131.3, 128.0, 127.5, 125.8, 123.6, 118.3, 89.4, 81.0, 33.4, 32.5, 30.9, 26.5, 24.0, 18.7. MS (ESI): 276 ($\text{M} + \text{Na}^+$).

5-[5-(4-Methoxy-phenyl)-pent-4-ynyl]-1-(toluene-4-sulfonyl)-1,2,3,4-tetrahydropyridine (16c**)**

To a flask charged with 16 mg of bis(triphenylphosphine)palladium (II) dichloride (0.023 mmol) and 4.7 mg of copper (I) iodide (0.025 mmol) was added 3 mL triethylamine. To the resulting bright yellow mixture was added a solution of 0.205 g of **1** (0.68 mmol) and 0.174 g of 4-iodoanisole (0.74 mmol) in 1.0 mL of dichloromethane and the reaction was stirred for 5.5 h at rt, wrapped in aluminum foil. The orange reaction mixture was filtered through celite using diethyl ether eluant and then concentrated by rotary evaporation *in vacuo* to afford a crude orange oil. Purification of the crude material by column chromatography on triethylamine washed silica gel (3:1 hexanes:ethyl acetate) afforded 0.245 g (89 %) of the title compound **16c** as an orange syrup.

IR (film): 2934, 1607, 1510, 1165 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.66 (d, $J = 8.3$ Hz, 2H), 7.34 (d, $J = 8.7$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 6.81 (d, $J = 8.7$ Hz, 2H), 6.52 (s, 1H), 3.76 (s, 3H), 3.26-3.31 (m, 2H), 2.39 (s, 3H), 2.29 (t, $J = 7.1$ Hz, 2H), 2.11 (t, $J =$

7.1 Hz, 2H), 1.79-1.84 (m, 2H), 1.55-1.68 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 158.9, 143.3, 134.7, 132.7, 129.5, 126.9, 120.2, 120.0, 115.8, 113.7, 87.8, 80.7, 55.0, 43.4, 33.9, 26.4, 24.2, 21.3, 20.6, 18.3. MS (ESI): 432 ($\text{M} + \text{Na}^+$).

1-(Toluene-4-sulfonyl)-5-[5-(4-trifluoromethyl-phenyl)-pent-4-ynyl]-1,2,3,4-tetrahydro-pyridine (16d)

To a flask charged with 9.6 mg of bis(triphenylphosphine)palladium (II) dichloride (0.014 mmol) and 2.5 mg of copper (I) iodide (0.013 mmol) was added 3 mL triethylamine. To the resulting bright yellow mixture was added a solution of 0.116 g of **1** (0.38 mmol) and 62 μL of 4-iodobenzotrifluoride (0.42 mmol) in 1.0 mL of dichloromethane and the reaction was stirred for 8 h at rt, wrapped in aluminum foil. The yellow reaction mixture was filtered through celite using diethyl ether eluant and then concentrated by rotary evaporation *in vacuo* to afford a crude orange oil. Purification of the crude material by column chromatography on triethylamine washed silica gel (8:1 hexanes:ethyl acetate) afforded 0.159 g (93 %) of the title compound **16d** as a yellow film which solidified upon storage in the freezer, mp: 72-73 $^{\circ}\text{C}$.

IR (film): 2935, 1616, 1325, 1165 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.67 (d, $J = 8.3$ Hz, 2H), 7.54 (d, $J = 8.7$ Hz, 2H), 7.50 (d, $J = 8.7$ Hz, 2H), 7.24 (d, $J = 8.3$ Hz, 2H), 6.54 (s, 1H), 3.28-3.33 (m, 2H), 2.41 (s, 3H), 2.34 (t, $J = 7.0$ Hz, 2H), 2.13 (t, $J = 7.4$ Hz, 2H), 1.84 (t, $J = 6.1$ Hz, 2H), 1.58-1.73 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 143.4, 134.9, 131.7, 129.6, 129.3 (quartet, $J = 32$ Hz), 127.7, 127.0, 125.1 (quartet, $J = 4$ Hz), 124.0 (quartet, $J = 270$ Hz), 120.5, 119.8, 92.5, 80.0, 43.5, 34.1, 26.2, 24.3, 21.5, 20.7, 18.5. ^{19}F NMR (282.4 MHz, CDCl_3): δ -63.1. MS (ESI): 470 ($\text{M} + \text{Na}^+$).

1-(Toluene-4-sulfonyl)-1,2,3,4,5,6,7,12b-octahydro-1-aza-benzo[k]fluorine (17a) + 12b-Methyl-1-(toluene-4-sulfonyl)-1,2,3,4,5,6,7,12b-octahydro-1-aza-cyclopenta[k]phenanthrene (18a)

A solution of 32 mg of **16a** (0.085 mmol) and 2.3 mg of PtCl₂ (0.0086 mmol) in 1 mL of toluene was stirred in a sealed tube at 110 °C for 12 h. The reaction mixture was cooled to rt and directly columned on triethylamine washed silica gel (8:1 hexanes:ethyl acetate) to afford 25 mg (78 %) of a 4:1 mixture of **17a** and **18a** as a colorless film which solidified into a white solid upon storage. X-ray quality crystals (prisms) were obtained from dichloromethane and hexanes, mp: 146-148 °C.

IR (film): 2938, 1463, 1331, 1161 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.27-7.35 (m, 3H), 7.09-7.23 (m, 3H), 5.96 (t, *J* = 3.7 Hz, 1H), 4.91 (s, 1H), 3.84 (d, *J* = 13.7 Hz, 1H), 2.83-2.92 (m, 1H), 2.43 (s, 3H), 2.10-2.18 (m, 2H), 1.13-1.80 (m, 8H). Additional peaks associated with the minor isomer **18a**: δ 7.04 (td, *J* = 7.6 Hz, 1.5 Hz, 1H), 6.93-7.00 (m, 1H), 6.15 (s, 1H), 5.16 (s, 1H), 3.75 (dd, *J* = 13.7 Hz, 4.6 Hz, 1H), 3.02 (td, *J* = 13.7 Hz, 3.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 143.9, 143.0, 140.3, 139.9, 138.8, 129.6, 127.8, 127.6, 127.1, 123.9, 120.7, 119.1, 66.2, 44.2, 41.5, 29.1, 28.8, 24.6, 21.5, 20.7, 18.1. Additional peaks associated with the minor isomer **18a**: δ 152.1, 142.9, 139.0, 135.4, 131.9, 129.5, 127.3, 127.0, 126.6, 126.0, 118.0, 63.5, 45.3, 40.9, 35.5, 29.8, 26.0, 22.4, 21.3. MS (ESI): 380 (M + H⁺), 402 (M + Na⁺).

Structure of product **17a** as determined from X-ray diffraction

Structure of product **18a** as determined from X-ray diffraction

1-Methyl-3,4,5,6,7,12b-hexahydro-1H-1-aza-benzo[k]fluoren-2-one (17b**) + 1,12b-Dimethyl-3,4,5,6,7,12b-hexahydro-1H-1-aza-cyclopenta[k]phenanthren-2-one (**18b**)**

A solution of 44 mg of **16b** (0.17 mmol) and 4.7 mg of PtCl_2 (0.018 mmol) in 1.8 mL of toluene was stirred in a sealed tube at 110 °C for 12 h. The reaction mixture was cooled to rt and directly columned on triethylamine washed silica gel (1:2 hexanes:ethyl acetate) to afford 34 mg (78 %) of a 3:1 mixture of **17b** and **18b** as a colorless film.

IR (film): 2936, 1646 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.38 (d, $J = 7.0$ Hz, 1H), 7.30 (d, $J = 7.4$ Hz, 1H), 7.13-7.28 (m, 2H), 6.00 (t, $J = 3.7$ Hz, 1H), 4.35 (s, 1H), 3.33 (s, 3H), 2.21-2.37 (m, 2H), 2.17 (dt, $J = 12.5$ Hz, 3.4 Hz, 1H), 2.02-2.13 (m, 2H), 1.65-1.87 (m, 4H), 1.52-1.64 (m, 1H). Additional peaks associated with the minor isomer **18b**: δ 7.00-7.07 (m, 1H), 6.24 (s, 1H), 4.29 (s, 1H), 3.23 (s, 3H), 1.37-1.47 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): all peaks for the mixture of **17b** and **18b**: δ 171.0, 170.3, 151.9, 143.6, 143.2, 139.4, 134.9, 134.1, 128.4, 128.1, 127.6, 126.9, 125.8, 124.5, 123.5, 120.5, 118.7, 118.2, 73.0, 69.4, 45.5, 45.3, 37.5, 37.0, 34.9, 31.1, 30.0, 29.19, 29.17, 28.5, 24.5, 23.1, 22.9, 17.9. MS (ESI): 254 ($\text{M} + \text{H}^+$), 276 ($\text{M} + \text{Na}^+$).

11-Methoxy-1-(toluene-4-sulfonyl)-1,2,3,4,5,6,7,12b-octahydro-1-azabenzok[fluorine] (17c) + 11-Methoxy-1-(toluene-4-sulfonyl)-1,2,3,4,5,6,7,12b-octahydro-1-azacyclopenta[k]phenanthrene (18c)

A solution of 40 mg of **16c** (0.098 mmol) and 2.7 mg of PtCl_2 (0.010 mmol) in 1 mL of toluene was stirred in a sealed tube at 110 °C for 12 h. The reaction mixture was cooled to rt and directly columned on triethylamine washed silica gel (8:1 $\rightarrow$ 5:1 hexanes:ethyl acetate) to afford 26 mg (65 %) of a 19:1 mixture of **17c** and **18c** as a colorless film which solidified into a white solid upon storage. The solid was recrystallized from diethyl ether, mp: 121-123 °C.

IR (film): 2938, 1608, 1484, 1154 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.81 (d, $J = 8.3$ Hz, 2H), 7.35 (d, $J = 8.3$ Hz, 2H), 7.25 (d, $J = 8.3$ Hz, 1H), 6.76 (dd, $J = 8.3$ Hz, 2.2 Hz, 1H), 6.60 (s, 1H), 5.83 (t, $J = 3.6$ Hz, 1H), 4.89 (s, 1H), 3.91 (d, $J = 14.0$ Hz, 1H), 3.71 (s, 3H), 2.91 (td, $J = 12.6$ Hz, 2.2 Hz, 1H), 2.44 (s, 3H), 2.10-2.17 (m, 2H), 1.53-1.79 (m, 4H), 1.16-1.50 (m, 4H). Additional peaks associated with the minor isomer **18c**: δ 6.90 (d, $J = 8.3$ Hz, 1H), 6.67 (dd, $J = 8.3$ Hz, 2.6 Hz, 1H), 6.55 (s, 1H), 6.11 (s, 1H), 5.17 (s, 1H), 3.61 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) for **17c**: δ 159.9, 143.3, 143.0, 142.1, 138.9, 132.6, 129.6, 127.0, 121.7, 116.9, 114.8, 108.3, 66.2, 55.4, 44.5, 41.7, 29.1, 28.9, 24.5, 21.5, 20.8, 18.1. MS (ESI): 410 ($\text{M} + \text{H}^+$), 432 ($\text{M} + \text{Na}^+$).

1-(Toluene-4-sulfonyl)-11-trifluoromethyl-1,2,3,4,5,6,7,12b-octahydro-1-aza-benzo[k]fluorine (17d) + 1-(Toluene-4-sulfonyl)-11-trifluoromethyl-1,2,3,4,5,6,7,12b-octahydro-1-aza-cyclopenta[k]phenanthrene (18d)

A solution of 38 mg of **16d** (0.085 mmol) and 2.3 mg of PtCl_2 (0.0086 mmol) in 0.8 mL of toluene was stirred in a sealed tube at 110 °C for 72 h. The reaction mixture was cooled to rt and directly columned on triethylamine washed silica gel (8:1 hexanes:ethyl acetate) to afford 26 mg (67 %) of a 1:1 mixture of **17d** and **18d** as a colorless film.

IR (film): 2942, 1328, 1162 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) for the mixture of **17d** and **18d**: δ 7.80 (d, $J = 8.3$ Hz, 2H), 7.75 (d, $J = 8.3$ Hz, 2H), 7.39-7.47 (m, 2H), 7.28-7.38 (m, 5H), 7.04 (d, $J = 7.8$ Hz, 1H), 6.99 (s, 1H), 6.82 (s, 1H), 6.20 (s, 1H), 6.11 (t, $J = 3.5$ Hz, 1H), 5.21 (s, 1H), 4.94 (s, 1H), 3.97 (d, $J = 13.5$ Hz, 1H), 3.87 (d, $J = 13.5$ Hz, 1H), 2.80-2.96 (m, 2H), 2.45-2.66 (m, 2H), 2.46 (s, 3H), 2.44 (s, 3H), 2.15-2.24 (m, 2H), 2.00-2.09 (m, 1H), 1.82-1.91 (m, 2H), 1.67-1.80 (m, 5H), 1.48-1.67 (m, 2H), 1.37-1.48 (m, 3H), 1.23-1.36 (m, 2H), 1.15 (td, $J = 13.5$ Hz, 3.5 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) for the mixture of **17d** and **18d**: δ 155.9, 143.5, 143.44, 143.39, 142.8, 141.1, 139.0, 138.6, 138.5, 132.8, 129.8, 129.6 (quartet, $J = 32$ Hz), 128.3 (quartet, $J = 32$ Hz), 126.9, 126.6, 126.1, 125.2 (quartet, $J = 3.8$ Hz), 124.4 (quartet, $J = 3.8$ Hz), 124.2 (quartet, $J = 271$ Hz), 124.1 (quartet, $J = 271$ Hz), 122.7 (quartet, $J = 3.8$ Hz), 122.0, 121.0, 120.9 (quartet, $J = 3.8$ Hz), 117.1, 65.9, 62.8, 45.3, 44.5, 41.5, 40.9, 35.1, 30.2, 28.9, 28.7, 26.1, 24.8, 22.4, 21.5, 21.4, 21.3, 20.8, 18.0. MS (ESI): 470 ($\text{M} + \text{Na}^+$).

Experimental Procedures for Scheme 6:

1-Allyl-5-but-3-ynyl-3,4,5,6,7,8-hexahydro-1H-quinolin-2-one (19a)

To a solution of 58 mg of 3-(2-but-3-ynyl-6-oxo-cyclohexyl)-propionic acid methyl ester (0.24 mmol) in 2 mL of toluene was added 0.2 mL of glacial acetic acid followed by 87 μ L of allylamine (1.2 mmol) and the reaction was let stir and warm to reflux for 2 h with a Dean-Stark trap. The resulting reaction mixture was cooled to rt, diluted with diethyl ether, washed two times with a saturated aqueous solution of sodium bicarbonate, dried over magnesium sulfate and concentrated by rotary evaporation *in vacuo* to afford a crude yellow oil. Purification of the crude material on triethylamine washed silica gel (3:1 hexanes:ethyl acetate) afforded 56 mg (96 %) of the title compound **19a** as a colorless oil.

IR (film): 3303, 2936, 1666, 1395 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 5.73 (ddt, J = 16.8 Hz, 10.1 Hz, 5.2 Hz, 1H), 4.94-5.11 (m, 2H), 4.26 (dd, J = 16.8 Hz, 4.6 Hz, 1H), 4.09 (dd, J = 16.8 Hz, 4.6 Hz, 1H), 2.38-2.46 (m, 2H), 1.95-2.28 (m, 7H), 1.91 (t, J = 2.6 Hz, 1H), 1.50-1.80 (m, 4H), 1.28-1.41 (m, 2H). Additional peaks associated with the minor isomer: δ 4.59 (d, J = 16.4 Hz, 1H), 3.93 (d, J = 16.4 Hz, 1H), 2.61 (dd, J = 18.0 Hz, 5.5 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): major isomer: δ 169.8, 134.2, 132.5, 118.0, 114.9, 84.0, 68.5, 42.5, 36.7, 31.8, 31.3, 26.0, 25.3, 23.7, 19.8, 16.2. minor isomer: δ 168.4, 138.5, 133.2, 115.5, 105.1, 84.0, 68.5, 46.0, 40.0, 38.6, 32.6, 32.1, 26.2, 25.0, 24.0, 15.8. MS (ESI): 266 ($\text{M} + \text{Na}^+$).

1-Benzyl-5-but-3-ynyl-3,4,5,6,7,8-hexahydro-1H-quinolin-2-one (**19b**)

To a solution of 0.116g of 3-(2-but-3-ynyl-6-oxo-cyclohexyl)-propionic acid methyl ester (0.466 mmol) in 3.6 mL of toluene was added 0.4 mL of glacial acetic acid followed by 0.26 mL of benzylamine (2.4 mmol) and the reaction was let stir and warm to reflux for 2 h with a Dean-Stark trap. The resulting reaction mixture was cooled to rt, diluted with diethyl ether, washed two times with a saturated aqueous solution of sodium bicarbonate, dried over magnesium sulfate and concentrated by rotary evaporation *in vacuo* to afford a crude red oil. Purification of the crude material on triethylamine washed silica gel (3:1 hexanes:ethyl acetate) afforded 0.132 (96 %) of the title compound **19b** as a colorless film.

IR (film): 3296, 2935, 1666 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.23-7.29 (m, 2H), 7.15-7.20 (m, 1H), 7.08-7.13 (m, 2H), 4.93 (d, $J = 16.1$ Hz, 1H), 4.76 (d, $J = 16.1$ Hz, 1H), 2.49-2.56 (m, 2H), 1.97-2.36 (m, 7H), 1.93 (t, $J = 2.6$ Hz, 1H), 1.73-1.82 (m, 1H), 1.22-1.64 (m, 5H). Additional peaks associated with the minor isomer: δ 5.26 (d, $J = 15.8$ Hz, 1H), 5.01-5.05 (m, 1H), 4.56 (d, $J = 15.8$ Hz, 1H), 2.74 (ddd, $J = 18.0$ Hz, 5.2 Hz, 1.8 Hz, 1H), 1.00-1.12 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.4, 138.3, 132.7, 128.4, 126.7, 126.1, 118.6, 84.0, 68.5, 43.7, 36.7, 31.9, 31.3, 25.8, 25.6, 23.9, 19.7, 16.1. Additional peaks associated with the minor isomer: δ 169.0, 138.5, 137.6, 126.5, 105.8, 68.5, 47.1, 40.1, 38.5, 32.7, 32.1, 26.2, 24.9, 23.9, 15.8. MS (ESI): 294 ($\text{M} + \text{H}^+$).

1-But-3-enyl-5-but-3-ynyl-3,4,5,6,7,8-hexahydro-1H-quinolin-2-one (19c)

To a solution of 82 mg of 3-(2-but-3-ynyl-6-oxo-cyclohexyl)-propionic acid methyl ester (0.35 mmol) in 2 mL of toluene was added 0.2 mL of glacial acetic acid followed by 0.114 g of but-3-enylamine (1.6 mmol) and the reaction was let stir and warm to reflux for 1 h with a Dean-Stark trap. The resulting reaction mixture was cooled to rt, diluted with diethyl ether, washed two times with a saturated aqueous solution of sodium bicarbonate, dried over magnesium sulfate and concentrated by rotary evaporation *in vacuo* to afford a crude yellow oil. Purification of the crude material on triethylamine washed silica gel (4:1 hexanes:ethyl acetate) afforded 85 mg (95 %) of the title compound **19c** as a colorless oil.

IR (film): 3300, 2933, 1663, 1397 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 5.72 (ddt, J = 17.1 Hz, 10.1 Hz, 7.0 Hz, 1H), 4.94-5.05 (m, 2H), 3.70-3.78 (m, 1H), 3.46 (ddd, J = 14.2 Hz, 8.2 Hz, 6.1 Hz, 1H), 2.34-2.40 (m, 2H), 2.06-2.28 (m, 8H), 1.92 (t, J = 2.7 Hz, 1H), 1.52-1.88 (m, 5H), 1.26-1.43 (m, 2H). Additional peaks associated with the minor isomer: δ 5.11 (broad s, 1H), 3.78-3.85 (m, 1H), 3.55-3.64 (m, 1H), 2.58 (ddd, J = 18.0 Hz, 5.5 Hz, 1.8 Hz, 1H), 1.04-1.14 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.1, 135.1, 132.2, 119.1, 116.6, 84.1, 68.6, 39.7, 37.0, 33.6, 32.0, 31.4, 26.3, 25.8, 23.6, 20.1, 16.2. Additional peaks associated with the minor isomer: δ 168.6, 138.2, 135.3, 116.3, 104.5, 68.5, 42.3, 40.1, 38.7, 32.7, 32.2, 31.4, 26.3, 24.9, 24.1, 15.9. MS (ESI): 280 ($\text{M} + \text{Na}^+$).

1-[2-(tert-Butyl-diphenyl-silanyloxy)-ethyl]-5-but-3-ynyl-3,4,5,6,7,8-hexahydro-1H-quinolin-2-one (19d)

To a solution of 65 mg of 3-(2-but-3-ynyl-6-oxo-cyclohexyl)-propionic acid methyl ester (0.28 mmol) in 2 mL of toluene was added 0.2 mL of glacial acetic acid followed by 0.169 g of 2-(tert-butyl-diphenyl-silanyloxy)-ethylamine (0.57 mmol) and the reaction was let stir and warm to reflux for 2 h with a Dean-Stark trap. The resulting reaction mixture was cooled to rt, diluted with diethyl ether, washed two times with a saturated aqueous solution of sodium bicarbonate, dried over magnesium sulfate and concentrated by rotary evaporation *in vacuo* to afford a crude pale yellow oil. Purification of the crude material on triethylamine washed silica gel (5:1 hexanes:ethyl acetate) afforded 0.132 g (99 %) of the title compound **19d** as a colorless oil.

IR (film): 3308, 2932, 1657 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.62-7.70 (m, 4H), 7.34-7.45 (m, 6H), 3.63-3.87 (m, 4H), 2.40-2.46 (m, 2H), 2.00-2.32 (m, 7H), 1.96 (t, $J = 2.6$ Hz, 1H), 1.74-1.86 (m, 1H), 1.52-1.72 (m, 3H), 1.26-1.43 (m, 2H), 1.05 (s, 9H).

Additional peaks associated with the minor isomer: δ 5.08 (broad s, 1H), 4.04-4.11 (m, 1H), 2.59 (ddd, $J = 17.9$ Hz, 5.2 Hz, 1.7 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.1, 135.5, 133.3, 132.9, 129.6, 127.6, 117.4, 84.0, 68.6, 62.3, 42.7, 36.9, 31.8, 31.4, 26.8, 26.0, 25.9, 23.7, 19.9, 19.0, 16.4. Additional peaks associated with the minor isomer: δ 168.6, 138.6, 135.5, 133.5, 133.4, 127.5, 105.2, 68.5, 60.6, 45.5, 39.9, 38.7, 32.6, 32.2, 26.2, 24.9, 24.0, 15.9. MS (ESI): 508 ($\text{M} + \text{Na}^+$).

7-Allyl-1-methylene-2,3,3a,4,5,7,9,10-octahydro-1H-7-aza-cyclopenta[d]naphthalen-8-one (20a)

To a flask charged with 55 mg of **19a** (0.23 mmol) and 3.2 mg of PtCl₂ (0.012 mmol) was added 2 mL of toluene and the reaction was stirred for 2 h at 80 °C before being cooled to rt. The resulting yellow reaction mixture was diluted with diethyl ether, filtered through a pipette of triethylamine washed silica gel and concentrated by rotary evaporation *in vacuo* to afford a crude yellow oil. Purification of the crude material by column chromatography on triethylamine washed silica gel (3:1 hexanes:ethyl acetate) afforded 46 mg (83 %) of the title compound **20a** as a colorless oil.

IR (film): 2923, 1667, 1640 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 5.81 (ddt, *J* = 17.1 Hz, 10.6 Hz, 5.2 Hz, 1H), 5.06-5.16 (m, 3H), 4.90 (s, 1H), 4.67-4.76 (m, 2H), 3.93 (dd, *J* = 16.0 Hz, 5.4 Hz, 1H), 2.32-2.61 (m, 4H), 1.96-2.14 (m, 3H), 1.76-1.85 (m, 2H), 1.57 (td, *J* = 12.8 Hz, 6.4 Hz, 1H), 1.24-1.49 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 168.5, 153.3, 139.5, 133.5, 115.9, 108.3, 105.4, 48.5, 46.7, 45.0, 29.2, 28.3, 28.2, 26.5, 25.7, 24.1. MS (ESI): 244 (M + H⁺), 266 (M + Na⁺).

7-Benzyl-1-methylene-2,3,3a,4,5,7,9,10-octahydro-1H-7-aza-cyclopenta[d]naphthalen-8-one (20b)

To a flask charged with 55 mg of **19b** (0.19 mmol) and 2.5 mg of PtCl₂ (0.0094 mmol) was added 1.8 mL of toluene and the reaction was stirred for 2 h at 80 °C before being cooled to rt. The resulting yellow reaction mixture was diluted with diethyl ether, filtered through a pipette of triethylamine washed silica gel and concentrated by rotary

evaporation *in vacuo* to afford a crude yellow oil. Purification of the crude material by column chromatography on triethylamine washed silica gel (5:1 hexanes:ethyl acetate) afforded 45 mg (81 %) of the title compound **20b** as a colorless film.

IR (film): 2923, 1668, 1641 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.25-7.32 (m, 2H), 7.15-7.22 (m, 3H), 5.51 (d, $J = 15.8$ Hz, 1H), 5.04 (dd, $J = 4.9$ Hz, 3.4 Hz, 1H), 4.93 (s, 1H), 4.74 (s, 1H), 4.37 (d, $J = 15.8$ Hz, 1H), 2.57-2.72 (m, 2H), 2.33-2.55 (m, 2H), 1.96-2.11 (m, 3H), 1.78-1.91 (m, 2H), 1.61-1.70 (m, 1H), 1.38-1.47 (m, 2H), 1.23-1.36 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 169.1, 153.4, 139.8, 137.9, 128.5, 126.6, 126.4, 108.6, 105.9, 48.7, 48.2, 44.9, 29.4, 28.3, 28.2, 26.5, 25.7, 24.2. MS (ESI): 294 ($\text{M} + \text{H}^+$), 316 ($\text{M} + \text{Na}^+$).

7-But-3-enyl-1-methylene-2,3,3a,4,5,7,9,10-octahydro-1H-7-aza-cyclopenta[d]naphthalen-8-one (20c)

To a flask charged with 80 mg of **19c** (0.31 mmol) and 4.1 mg of PtCl_2 (0.015 mmol) was added 3.1 mL of toluene followed by 26 μL of methanol (0.64 mmol) and 5 μL of 2,6-lutidine (0.043 mmol) and the reaction was stirred for 15 h at 80 $^\circ\text{C}$ before being cooled to rt. The resulting yellow reaction mixture was diluted with diethyl ether, filtered through a pipette of triethylamine washed silica gel and concentrated by rotary evaporation *in vacuo* to afford a crude yellow oil. Purification of the crude material by column chromatography on triethylamine washed silica gel (5:1 hexanes:ethyl acetate) afforded 54 mg (68 %) of the title compound **20c** as a colorless oil.

IR (film): 2923, 1667, 1640 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 5.79 (ddt, $J = 17.1$ Hz, 10.4 Hz, 6.7 Hz, 1H), 4.97-5.11 (m, 3H), 4.89 (s, 1H), 4.69 (s, 1H), 3.85 (ddd, $J = 13.7$ Hz, 10.4 Hz, 5.5 Hz, 1H), 3.63 (ddd, $J = 13.7$ Hz, 10.4 Hz, 5.5 Hz, 1H), 2.30-2.58 (m, 5H), 1.95-2.30 (m, 4H), 1.73-1.86 (m, 2H), 1.24-1.70 (m, 4H). ^{13}C NMR (100 MHz,

CDCl₃): δ 168.6, 153.4, 138.9, 135.3, 116.3, 108.5, 104.4, 48.5, 45.0, 42.7, 31.4, 29.4, 28.3, 28.1, 26.6, 25.7, 24.3. MS (ESI): 258 (M + H⁺), 280 (M + Na⁺).

7-[2-(tert-Butyl-diphenyl-silanyloxy)-ethyl]-1-methylene-2,3,3a,4,5,7,9,10-octahydro-1H-7-aza-cyclopenta[d]naphthalen-8-one (20d)

To a flask charged with 39 mg of **19d** (0.080 mmol) and 1.1 mg of PtCl₂ (0.0041 mmol) was added 0.8 mL of toluene and the reaction was stirred for 3 h at 65 °C before being cooled to rt. The resulting yellow reaction mixture was directly purified by column chromatography on triethylamine washed silica gel (5:1 hexanes:ethyl acetate) to afford 27 mg (69 %) of the title compound **20d** as a colorless film.

IR (film): 2930, 1668, 1642 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.65-7.72 (m, 4H), 7.35-7.46 (m, 6H), 5.08 (dd, *J* = 5.2 Hz, 3.1 Hz, 1H), 4.90 (s, 1H), 4.70 (s, 1H), 4.12-4.21 (m, 1H), 3.77-3.92 (m, 2H), 3.60 (dt, *J* = 13.5 Hz, 7.0 Hz, 1H), 2.33-2.58 (m, 4H), 1.93-2.10 (m, 3H), 1.70-1.84 (m, 2H), 1.39-1.55 (m, 3H), 1.23-1.36 (m, 1H), 1.06 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 168.8, 153.2, 139.6, 135.6, 133.6, 129.6, 127.6, 108.5, 105.6, 60.9, 48.6, 46.4, 45.1, 29.3, 28.3, 28.2, 26.8, 26.6, 25.7, 24.2, 19.1. MS (ESI): 508 (M + Na⁺).