

Supporting Information

Silver-Catalyzed Cycloisomerization of 1,n-Allenynamides

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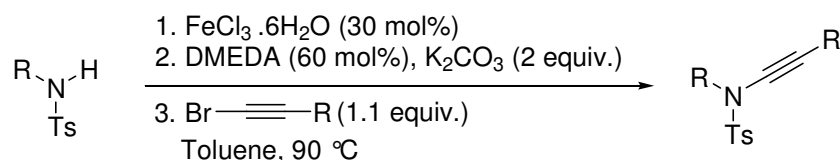
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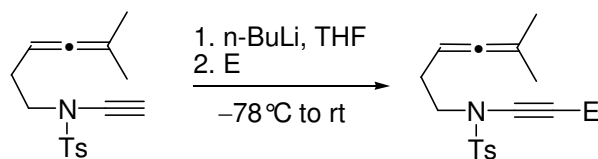
1. General Remarks

Reactions were carried out under argon, with magnetic stirring and redistilled solvents. CH_2Cl_2 was distilled from CaH_2 . THF and toluene was distilled from Na/benzophenone. Thin layer chromatography (TLC) was performed on Merck 60 F254 silica gel. Merck Geduran SI 60 A silica gel (35–70 mm) was used for column chromatography. The melting points reported were measured with a Reichert hot stage apparatus and are uncorrected. IR spectra were recorded with a Bruker Tensor 27 ATR diamant PIKE spectrometer. ^1H , ^{13}C NMR spectra were recorded at 400 and 100 MHz respectively, using a Bruker 400 AVANCE spectrometer fitted with a BBFO probehead. Chemical shifts are given in ppm using the CDCl_3 or the CD_2Cl_2 signal as reference ($^1\text{H} = 7.26$ ppm, $^{13}\text{C} = 77.16 \pm 0.06$ ppm and $^1\text{H} = 5.26$ ppm, $^{13}\text{C} = 53.3$ ppm respectively). Unless noted, NMR spectra were recorded in CDCl_3 at 300 K. The terms m, s, d, t, q and quint. represent multiplet, singlet, doublet, triplet, quadruplet and quintuplet, respectively, and the term br means a broad signal. High resolution mass spectra (HRMS) (electrospray source) were recorded at the Institut Parisien de Chimie Moléculaire (UMR 7201) of our university.

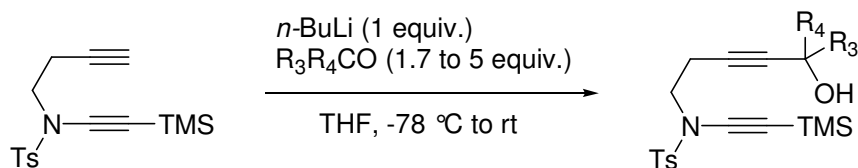
2. Synthesis of Allenynamides



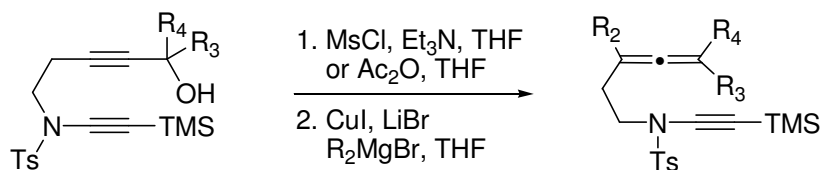
General procedure 1 (GP1):¹ *Synthesis of tosylynamides from the corresponding tosylamines.* To a suspension of finely crushed $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.5 g, 9.27 mmol), K_2CO_3 (8.5 g, 61.8 mmol) and the tosylamine (30.9 mmol) in toluene (80 mL) was added a solution of N,N'-dimethylethylenediamine (DMEDA) (85% purity, 1.92 g, 18.5 mmol) and the bromoalkyne (37.1 mmol) in toluene (40 mL). After 16 h at 90°C , the mixture was cooled to rt, filtered over a short pad of silica gel (EtOAc/Petroleum Ether (PE), 3:7) and concentrated under reduced pressure. Purification of the crude was performed by flash column chromatography (EtOAc/PE, 95:5) and afforded the corresponding pure tosylynamide.



General procedure 2 (GP2): At -78°C , *n*-BuLi (2.5 M in hexanes, 0.8 mL, 2 mmol) was added to a solution of alkyne derivative (2 mmol) in dry THF (15 mL). After 1 h, the corresponding electrophile (CH_3I (8 mmol), formaldehyde (20 mmol), acetaldehyde (5 mmol), acetone (3.5 mmol), ArCHO ($\text{Ar} = \text{Ph}$, PMP) (2.4 mmol), or ClCO_2Et (2.4 mmol)) was added, the mixture is kept at -78°C during 1 h and then allowed to warm to rt for 12 h. The mixture was quenched with saturated NH_4Cl solution and extracted with Et_2O . The combined organic extracts were washed with brine, dried over MgSO_4 and concentrated *in vacuo* to give the crude product. The residue was purified by flash column chromatography (Silica gel, $\text{PE}/\text{Et}_2\text{O}$ gradient) to give the desired product.



General procedure 3 (GP3): To a solution of N-(2-(trimethylsilyl)ethynyl)-N-tosylbut-3-yn-1-amine (1 g, 3.1 mmol), prepared from N-tosylbut-3-yn-1-amine and 2-bromoethynyl(trimethyl)silane following **GP1**, in THF (20 mL) at -78°C was added *n*-BuLi (2.1 M in hexanes, 1.5 mL, 3.1 mmol). After 30 min, dry formaldehyde (0.47 g, 15.6 mmol), acetaldehyde (0.24 g, 5.4 mmol), benzaldehyde (0.57 g, 5.4 mmol) or acetone (0.31 g, 5.4 mmol) was added and the reaction mixture warmed to rt for 3 h. The mixture was quenched with water, extracted with Et_2O and the combined organic extracts were washed with brine and dried over MgSO_4 . After removal of the volatiles under reduced pressure, the residue was purified by flash column chromatography (EtOAc/PE , 2:8) to afford the expected propargylic alcohol.



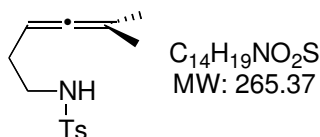
General procedure 4 (GP4): The corresponding ynamide-ynols were prepared by using **General procedure 3 (GP3)**.

From the acetate: At -78°C , *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1 mmol) was added to a solution of ynamide-ynol (1 mmol) in THF (8 mL). After 1 h, Ac₂O (160 μL , 1.7 mmol) was added. The mixture was quenched with water and extracted with EtOAc. The combined organic extracts were washed with brine, dried over MgSO₄ and concentrated under reduced pressure. The crude was purified by FC using a gradient of EtOAc/EP as eluent.

From the mesylate: At 0°C , methanesulfonyl chloride (85 μL , 1.1 mmol) and triethylamine (153 μL , 1.1 mmol) were added to a solution of ynamide-ynol (1 mmol) in THF (30 mL). After 20 min, the mixture was filtered over silica (Et₂O) and concentrated under reduced pressure to afford pure mesylate as observed by TLC and ¹H NMR.

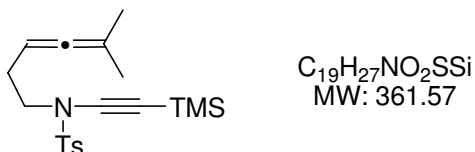
After being dried under reduced pressure for 2 h, LiBr (260 mg, 3 mmol) was added to a solution of CuI (571 mg, 3 mmol) in THF (30 mL), then RMgBr in THF (or toluene) (3 mmol) was added at -78°C and the mixture was stirred for 2 h. To this mixture, a solution of the mesylate (or acetate) (1 mmol) in THF (1 mL) was added and the cold bath removed. The resulting mixture was stirred at rt until completion of the reaction (monitored by TLC). The reaction mixture was quenched with a 1:1 NH₄Cl/NH₄OH solution, extracted with Et₂O, washed with brine and dried over MgSO₄. The volatiles were removed and the crude was purified over silica gel using a gradient of EtOAc/PE as eluent.

5-Methyl-N-tosylhexa-3,4-dien-1-amine



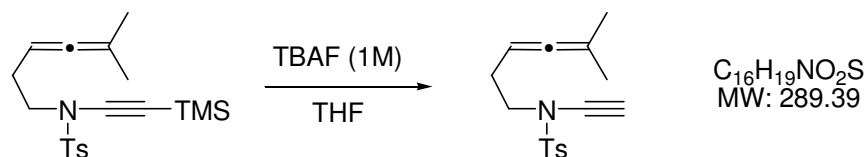
A mixture of 2-methyl-but-3-yn-2-ol (28 g, 333 mmol), 1,1,1-triethoxyethane (90.8 g, 560 mmol) and propionic acid (3.3 g, 45 mmol) was stirred for 20 min at rt, then at 145°C with a Dean-Stark. After 3 h, the mixture was cooled and distilled at 5 mbar (Bp = 54-56°C) to give 5-methyl-hexa-3,4-dienoic acid ethyl ester (13.3 g, 26%). The ester (12.7 g, 82.7 mmol) was reduced in Et₂O (800 mL) at 0°C for 1 h in the presence of LiAlH₄ (5 g, 132 mmol). Once back to room temperature, the mixture was quenched with water, dried over MgSO₄, filtered over a short pad of silica gel and concentrated under reduced pressure to afford the corresponding pure alcohol (8.8 g, 95%). To a solution of this alcohol (8 g, 63.6 mmol) in THF (800 mL) at 0°C was added methanesulfonyl chloride (6 mL, 77.5 mmol) and triethylamine (14 mL, 100 mmol). After 1 h, the solution was filtered and the filtrate concentrated under reduced pressure to give the mesylated product (10.9 g, 90%). Finally, a solution of this mesylate (4 g, 21 mmol), tosylamide (5.4 g, 31.5 mmol) and K₂CO₃ (5.8 g, 42 mmol) was stirred in CH₃CN (150 mL) at reflux. After 16 h, the solvent was evaporated under reduced pressure and the crude was extracted with EtOAc, filtered over silica gel and concentrated *in vacuo*. The crude was purified over silica gel using EtOAc/PE 1:5 as eluent to give the corresponding 5-methyl-N-tosylhexa-3,4-dien-1-amine (3.79 g, 68%). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 4.84-4.79 (m, 1H), 4.68 (br, 1H), 3.00 (q, *J* = 6.5 Hz, 2H), 2.41 (s, 3H), 2.07 (q, *J* = 6.5 Hz, 2H), 1.63 (d, *J* = 2.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 202.4, 143.4, 137.1, 129.7 (2C), 127.2 (2C), 96.5, 85.2, 42.6, 29.1, 21.6, 20.7 (2C).

5-Methyl-N-(2-(trimethylsilyl)ethynyl)-N-tosylhexa-3,4-dien-1-amine (1a)



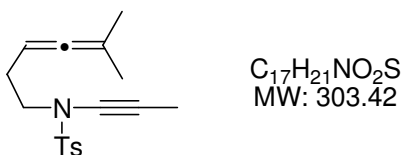
Compound **1a** was prepared according to (**GP1**), from 5-methyl-N-tosylhexa-3,4-dien-1-amine and 2-bromoethynyl(trimethyl)silane. White solid (80%). Mp = 59-61°C. IR (neat) ν 2922, 2229, 1594, 1355, 1201 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 4.88-4.83 (m, 1H), 3.35 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 2.24 (q, *J* = 7.2 Hz, 2H), 1.66 (d, *J* = 2.8 Hz, 6H), 0.15 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 202.6, 144.5, 134.6, 129.6 (2C), 127.8 (2C), 96.1, 94.9, 84.5, 73.4, 50.9, 27.7, 21.6, 20.5 (2C), 0.1 (3C). HRMS (ES⁺) calculated for C₁₉H₂₇NO₂SSi (M+H⁺): 362.1604; found: 362.1605.

N-Ethynyl-5-methyl-N-tosylhexa-3,4-dien-1-amine (1b)



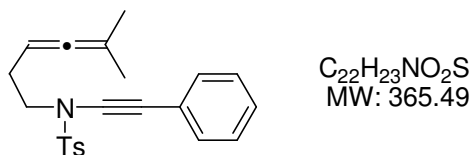
Tetra-*n*-butylammonium fluoride (1M in THF, 1.1 mL, 1.1 mmol) was added to a solution of **1a** (361 mg, 1 mmol) in THF (5 mL). After 1 h at rt, the mixture was quenched with saturated NH_4Cl solution and extracted with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* to give crude product. The residue was purified by flash column chromatography (Silica gel, EtOAc/PE : 1/3) to give the desired product **1b**. Yellow oil (90 %). IR (neat) ν 2917, 2238, 1588, 1373, 1261 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 4.88-4.83 (m, 1H), 3.36 (t, J = 7.6 Hz, 2H), 2.73 (s, 1H), 2.44 (s, 3H), 2.26 (q, J = 6.8 Hz, 2H), 1.66 (d, J = 2.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 144.7, 134.6, 129.8 (2C), 127.7 (2C), 96.3, 84.3, 75.9, 59.3, 50.8, 27.6, 21.6, 20.6 (2C).

5-Methyl-N-(prop-1-ynyl)-N-tosylhexa-3,4-dien-1-amine (1c)



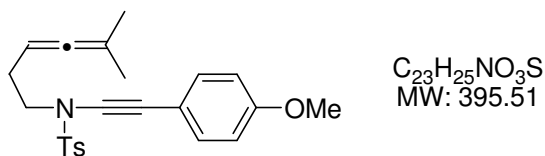
Compound **1c** was prepared according to (GP2), from **1b** and iodomethane. Colorless oil (85%). IR (neat) ν 2908, 2234, 1604, 1510, 1360, 811 cm^{-1} . 1H NMR (400 MHz, CD_2Cl_2) δ 7.72 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 4.85-4.81 (m, 1H), 3.25 (t, J = 7.6 Hz, 2H), 2.41 (s, 3H), 2.19 (q, J = 7.0 Hz, 2H), 1.85 (s, 3H), 1.63 (d, J = 2.8 Hz, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 202.4, 144.5, 134.7, 129.6 (2C), 127.5 (2C), 96.0, 84.5, 71.7, 65.7, 51.0, 27.7, 21.3, 20.2 (2C), 2.8. HRMS (ES+) calculated for $C_{17}H_{21}NO_2S$ ($M+Na^+$): 326.1185; found: 326.1186.

5-Methyl-N-(2-phenylethynyl)-N-tosylhexa-3,4-dien-1-amine (1d)



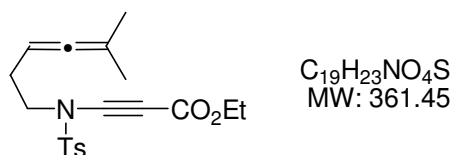
Compound **1d** was prepared according to (**GP1**), from 5-methyl-N-tosylhexa-3,4-dien-1-amine and 1-(2-bromoethynyl)benzene. Yellow oil (85%). IR (neat) ν 2908, 2233, 1597, 1361, 1166 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.3 Hz, 2H), 7.36-7.34 (m, 4H), 7.28-7.26 (m, 3H), 4.91-4.87 (m, 1H), 3.46 (t, J = 7.2 Hz, 2H), 2.45 (s, 3H), 2.33 (q, J = 6.8 Hz, 2H), 1.66 (d, J = 2.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 144.6, 134.7, 131.4 (2C), 129.7 (2C), 128.3 (2C), 127.7 (3C), 123.0, 96.2, 84.5, 82.3, 70.9, 51.1, 27.9, 21.6, 20.5 (2C). HRMS (ES+) calculated for $C_{22}H_{23}NO_2S$ ($M+H^+$): 366.1522; found: 366.1523.

N-(2-(4-Methoxyphenyl)ethynyl)-5-methyl-N-tosylhexa-3,4-dien-1-amine (1e)



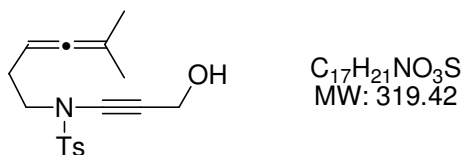
Compound **1e** was prepared according to (**GP1**), from 5-methyl-N-tosylhexa-3,4-dien-1-amine and 1-(2-bromoethynyl)-4-methoxybenzene. Yellow oil (83%). IR (neat) ν 2917, 2258, 1596, 1358, 1185 cm^{-1} . 1H NMR (400 MHz, CD_2Cl_2) δ 7.79 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 6.81 (d, J = 8.3 Hz, 2H), 4.90-4.85 (m, 1H), 3.77 (s, 3H), 3.40 (t, J = 7.2 Hz, 2H), 2.43 (s, 3H), 2.28 (q, J = 7.0 Hz, 2H), 1.64 (d, J = 2.8 Hz, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 202.5, 159.6, 144.8, 134.6, 133.2 (2C), 129.7 (2C), 127.6 (2C), 114.6, 113.9 (2C), 96.1, 84.5, 80.8, 70.3, 55.2, 51.2, 27.9, 21.3, 20.2 (2C). HRMS (ES+) calculated for $C_{23}H_{25}NO_3S$ ($M+Na^+$): 418.1447; found: 418.1448.

Ethyl 3-(N-(5-methylhexa-3,4-dienyl)-N-tosylamino)propiolate (1f)



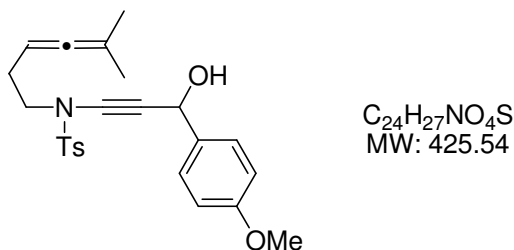
Compound **1f** was prepared according to (GP2), from **1b** and ethyl chloroformate. White solid (93%). Mp = 109-111 °C. IR (neat) ν 2910, 2213, 1704, 1327, 1027 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 4.86-4.80 (m, 1H), 4.22 (q, J = 7.2 Hz, 2H), 3.47 (t, J = 7.2 Hz, 2H), 2.46 (s, 3H), 2.28 (q, J = 7.2 Hz, 2H), 1.65 (d, J = 2.8 Hz, 6H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 202.7, 154.2, 145.5, 134.3, 130.0 (2C), 127.8 (2C), 96.7, 84.0, 82.5, 68.0, 61.6, 50.9, 27.9, 21.7, 20.5 (2C), 14.2. HRMS (ES+) calculated for $\text{C}_{19}\text{H}_{23}\text{NO}_4\text{S}$ ($\text{M}+\text{H}^+$): 362.1421; found: 362.1422.

3-(N-(5-Methylhexa-3,4-dienyl)-N-tosylamino)prop-2-yn-1-ol (**1g**)



Compound **1g** was prepared according to (GP2), from **1b** and formaldehyde. Colorless oil (81%). IR (neat) ν 3321, 2966, 2240, 1343, 1205 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.3 Hz, 2H), 4.84-4.80 (m, 1H), 4.35 (s, 2H), 3.33 (t, J = 7.6 Hz, 2H), 2.42 (s, 3H), 2.31 (br, 1H), 2.23 (q, J = 7.0 Hz, 2H), 1.63 (d, J = 2.8 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 202.5, 144.7, 134.6, 129.8 (2C), 127.5 (2C), 96.2, 84.3, 78.7, 69.9, 51.1, 50.9, 27.7, 21.6, 20.5 (2C). HRMS (ES+) calculated for $\text{C}_{17}\text{H}_{21}\text{NO}_3\text{S}$ ($\text{M}+\text{Na}^+$): 342.1135; found: 342.1136.

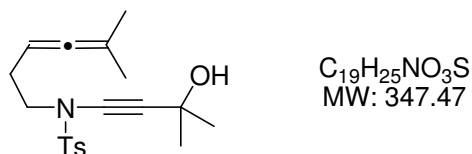
3-(N-(5-Methylhexa-3,4-dienyl)-N-tosylamino)-1-(4-methoxyphenyl)prop-2-yn-1-ol (**1h**)



Compound **1h** was prepared according to (GP2), from **1b** and 4-methoxy-benzaldehyde. Colorless oil (89%). IR (neat) ν 3390, 2908, 2241, 1443, 1165 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 6.88 (d, J = 8.3 Hz, 2H), 5.50 (s, 1H), 4.87-4.82 (m, 1H), 3.80 (s, 3H), 3.37 (td, J = 6.8, 2.8 Hz, 2H), 2.60 (br, 1H), 2.41 (s, 3H), 2.25 (q, J = 7.0 Hz, 2H),

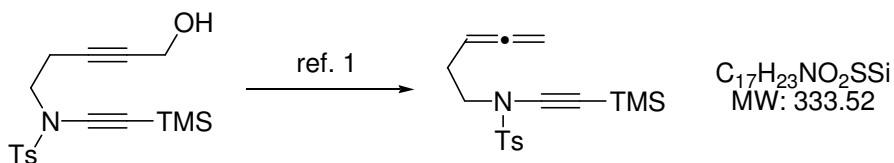
1.64 (d, $J = 2.8$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 202.6, 159.5, 144.6, 134.5, 133.3, 129.8 (2C), 128.1 (2C), 127.7 (2C), 113.9 (2C), 96.3, 84.4, 79.7, 71.4, 64.4, 55.3, 50.9, 27.8, 21.6, 20.5 (2C). HRMS (ES+) calculated for $\text{C}_{24}\text{H}_{27}\text{NO}_4\text{S}$ ($\text{M}+\text{Na}^+$): 448.1553; found: 448.1555.

4-(N-(5-Methylhexa-3,4-dienyl)-N-tosylamino)-2-methylbut-3-yn-2-ol (**1i**)



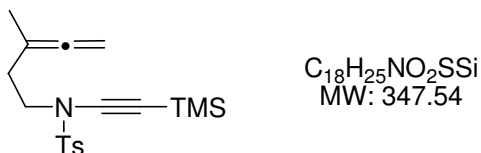
Compound **1i** was prepared according to (**GP2**), from **1b** and propan-2-one. Colorless oil (76% contaminated by an unknown product (~15%)). IR (neat) ν 3289, 2959, 2245, 1365, 1272 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 8.3$ Hz, 2H), 7.33 (d, $J = 8.3$ Hz, 2H), 4.87-4.83 (m, 1H), 3.33 (t, $J = 7.2$ Hz, 2H), 2.44 (s, 3H), 2.23 (q, $J = 7.0$ Hz, 2H), 2.08 (br s, 1H), 1.65 (d, $J = 2.8$ Hz, 6H), 1.50 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 202.5, 144.5, 134.4, 129.7 (2C), 127.6 (2C), 96.1, 84.5, 75.6, 65.3, 50.8, 31.4 (2C), 27.7, 21.6, 20.5 (2C). One C overlapped. HRMS (ES+) calculated for $\text{C}_{19}\text{H}_{25}\text{NO}_3\text{S}$ ($\text{M}+\text{Na}^+$): 370.1447; found: 370.1448.

N-(2-(Trimethylsilyl)ethynyl)-N-tosylpenta-3,4-dien-1-amine (**1j**)



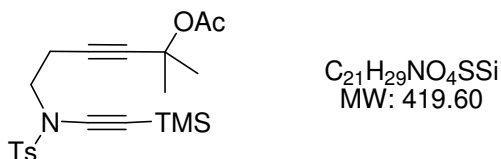
The ynamide-ynol, 5-(N-(2-(trimethylsilyl)ethynyl)-N-tosylamino)pent-2-yn-1-ol, was prepared by using **GP3** from N-(2-(trimethylsilyl)ethynyl)-N-tosylbut-3-yn-1-amine and formaldehyde converted to the desired monosubstituted allene **1j** according to a literature procedure on 0.85 mmol scale.² Yellow oil (55%). IR (neat) ν 2958, 2160, 1370, 1171, 844 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 8.3$ Hz, 2H), 7.35 (d, $J = 8.3$ Hz, 2H), 5.05 (quint., $J = 6.6$ Hz, 1H), 4.71-4.68 (m, 2H), 3.41 (t, $J = 7.2$ Hz, 2H), 2.47 (s, 3H), 2.37-2.29 (m, 2H), 0.17 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 209.2, 144.7, 134.7, 129.7 (2C), 127.9 (2C), 94.9, 86.0, 75.8, 73.7, 50.7, 26.9, 21.8, 0.2 (3C). HRMS (ES+) calculated for $\text{C}_{17}\text{H}_{23}\text{NO}_2\text{SSi}$ ($\text{M}+\text{Na}^+$): 356.1111; found: 356.1109.

3-Methyl-N-(2-(trimethylsilyl)ethynyl)-N-tosylpenta-3,4-dien-1-amine (1k)



Compound **1k** was prepared according to (**GP4**), from the mesylate of 5-(N-(2-(trimethylsilyl)ethynyl)-N-tosylamino)pent-2-yn-1-ol¹ and MeMgBr. The corresponding ynamide-ynol was obtained from N-(2-(trimethylsilyl)ethynyl)-N-tosylbut-3-yn-1-amine and formaldehyde by using **GP3**. Colorless oil (85%). IR (neat) ν 2957, 2160, 1366, 1168, 839 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 4.57-4.55 (m, 2H), 3.39 (t, J = 7.5 Hz, 2H), 2.42 (s, 3H), 2.24-2.19 (m, 2H), 1.64 (t, J = 3.1 Hz, 3H), 0.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 144.6, 134.5, 129.6 (2C), 127.7 (2C), 94.9, 94.6, 75.1, 73.3, 49.4, 31.4, 21.6, 18.6, 0.1 (3C). HRMS (ES+) calculated for $C_{18}H_{25}NO_2SSi$ ($M+Na^+$): 370.1267; found: 370.1271.

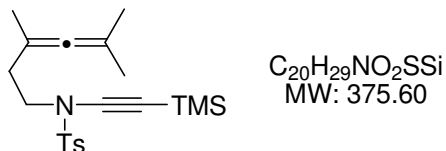
6-(N-(2-(Trimethylsilyl)ethynyl)-N-tosylamino)-2-methylhex-3-yn-2-yl acetate (1p)



To a solution of N-(2-(trimethylsilyl)ethynyl)-N-tosylbut-3-yn-1-amine (1 g, 3.1 mmol) in THF (20 mL) at $-78^\circ C$ was added *n*-BuLi (2.1 M in hexanes, 1.5 mL, 3.1 mmol). After 30 min, dry acetone (0.4 mL, 5.4 mmol) was added and the solution was stirred 15 min. Then, Ac_2O (0.5 mL, 5.3 mmol) was added and the reaction mixture was warmed to rt for 15 min. The mixture was quenched with water, extracted with Et_2O and the combined organic extracts were washed with brine and dried over $MgSO_4$. After removal of the volatiles under reduced pressure, the residue was purified by flash column chromatography ($EtOAc/PE$, 1:9) to afford the expected propargylic acetate **1p** (0.94 g, 71%) as a colorless oil. IR (neat) ν 2957, 2156, 1740, 1364, 1186 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 3.42 (t, J = 7.6 Hz, 2H), 2.51 (t, J = 7.6 Hz, 2H), 2.42 (s, 3H), 1.97 (s, 3H), 1.58 (s, 6H), 0.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 144.8, 134.5, 129.7 (2C), 127.7 (2C), 94.5, 83.5, 79.7,

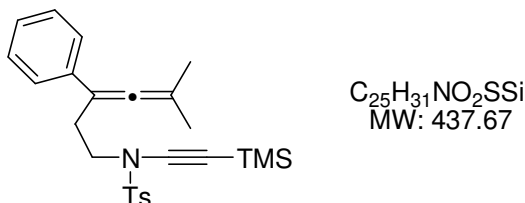
73.6, 72.1, 50.0, 29.1 (2C), 22.0, 21.7, 18.7, 0.1 (3C). HRMS (ES+) calculated for $C_{21}H_{29}NO_4SSi$ ($M+Na^+$): 442.1679; found: 442.1478.

3,5-Dimethyl-N-(2-(trimethylsilyl)ethynyl)-N-tosylhexa-3,4-dien-1-amine (1l)



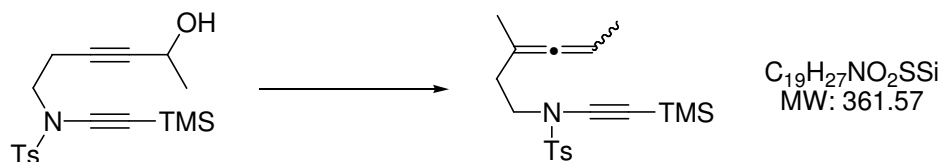
Compound **1l** was prepared according to (GP4) from **1p** and MeMgBr. White solid (95%). Mp = 67-69°C. IR (neat) ν 2948, 2144, 1621, 1414, 1129 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 3.35 (t, J = 7.6 Hz, 2H), 2.45 (s, 3H), 2.19 (t, J = 7.6 Hz, 2H), 1.63 (s, 6H), 1.62 (s, 3H), 0.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 144.5, 134.6, 129.5 (2C), 127.7 (2C), 95.4, 95.1, 93.0, 73.1, 49.7, 32.3, 21.6, 20.8 (2C), 19.4, 0.1 (3C). HRMS (ES+) calculated for $C_{20}H_{29}NO_2SSi$ ($M+H^+$): 376.1761; found: 376.1763.

5-Methyl-N-(2-(trimethylsilyl)ethynyl)-3-phenyl-N-tosylhexa-3,4-dien-1-amine (1m)



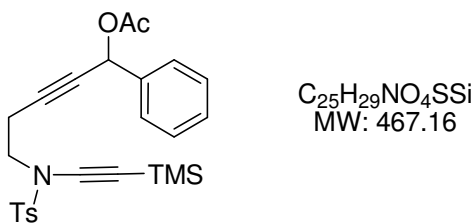
Compound **1m** was prepared according to (GP4) from **1p** and PhMgBr. White solid (80%). Mp = 80°C. IR (neat) ν 2956, 2165, 1356, 1165 cm^{-1} . 1H NMR (400 MHz, CD_2Cl_2) δ 7.76 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.31-7.15 (m, 5H), 3.46 (t, J = 7.5 Hz, 2H), 2.69 (t, J = 7.5 Hz, 2H), 2.45 (s, 3H), 1.79 (s, 6H), 0.15 (s, 9H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 202.1, 145.3, 137.6, 134.7, 130.0 (2C), 128.6 (2C), 128.0, 126.7 (2C), 126.1 (2C), 100.2, 99.9, 95.3, 73.5, 50.5, 28.8, 21.7, 20.4 (2C), 0.1 (3C). HRMS (ES+) calculated for $C_{25}H_{31}NO_2SSi$ ($M+H^+$): 438.1845; found: 438.1951.

3-Methyl-N-(2-(trimethylsilyl)ethynyl)-N-tosylhexa-3,4-dien-1-amine (1n)



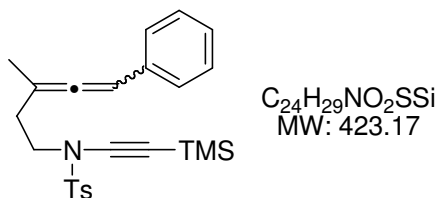
Compound **1n** was prepared according to (**GP4**) from the mesylate of 6-(N-(2-(trimethylsilyl)ethynyl)-N-tosylamino)hex-3-yn-2-ol and MeMgBr. Yellow oil (92%). The corresponding ynamide-ynol was obtained from N-(2-(trimethylsilyl)ethynyl)-N-tosylbut-3-yn-1-amine and acetaldehyde by using **GP3**. Yellow oil (92%). IR (neat) ν 2956, 2160, 1367, 1168, 839 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.3 Hz, 2H), 5.00-4.95 (m, 2H), 3.40-3.35 (m, 2H), 2.43 (s, 3H), 2.23-2.18 (m, 2H), 1.64 (d, J = 2.8 Hz, 3H), 1.58 (d, J = 7.0 Hz, 3H), 0.14 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 202.3, 144.6, 134.6, 129.6 (2C), 127.8 (2C), 95.0, 94.8, 86.1, 73.3, 49.6, 32.1, 21.7, 19.2, 14.7, 0.1 (3C). HRMS (ES⁺) calculated for $\text{C}_{19}\text{H}_{27}\text{NO}_2\text{SSi}$ ($\text{M}+\text{Na}^+$): 384.1424; found: 384.1428.

5-(N-(2-(Trimethylsilyl)ethynyl)-N-tosylamino)-1-phenylpent-2-ynyl acetate (1o')



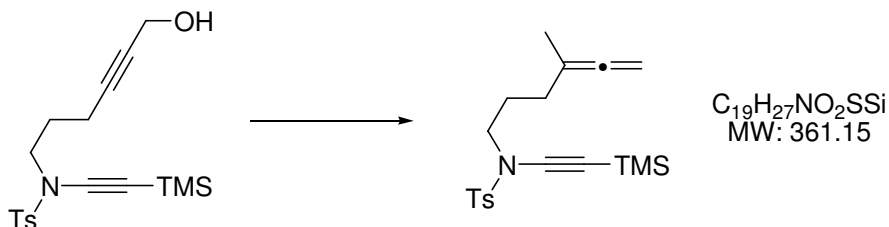
Compound **1o'** was obtained by acetylation of 5-(N-(2-(trimethylsilyl)ethynyl)-N-tosylamino)-1-phenylpent-2-yn-1-ol. The corresponding ynamide-ynol was obtained from N-(2-(trimethylsilyl)ethynyl)-N-tosylbut-3-yn-1-amine and benzaldehyde by using **GP3**. Colorless oil (89%). IR (neat) ν 2962, 2177, 1753, 1362, 1256 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, J = 8.3 Hz, 2H), 7.50-7.48 (m, 2H), 7.38-7.32 (m, 5H), 6.40 (s, 1H), 3.50 (t, J = 7.6 Hz, 2H), 2.62 (td, J = 6.8, 1.6 Hz, 2H), 2.45 (s, 3H), 2.09 (s, 3H), 0.15 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.7, 144.9, 137.0, 134.4, 129.7 (2C), 128.9, 128.6 (2C), 127.7 (2C), 127.7 (2C), 94.3, 83.2, 78.9, 73.9, 65.6, 49.7, 21.6, 21.0, 18.7, 0.1 (3C). HRMS (ES⁺) calculated for $\text{C}_{25}\text{H}_{29}\text{NO}_4\text{SSi}$ ($\text{M}+\text{Na}^+$): 490.1479; found: 490.1475.

3-Methyl-N-(2-(trimethylsilyl)ethynyl)-5-phenyl-N-tosylpenta-3,4-dien-1-amine (1o)



Compound **1o** was prepared according to (**GP4**) from **1o'** and MeMgBr. White solid (61%). Mp = 91-93°C. IR (neat) ν 2956, 2165, 1356, 1165 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.3 Hz, 2H), 7.34-7.28 (m, 6H), 7.26-7.19 (m, 1H), 6.08-6.06 (m, 1H), 3.56-3.42 (m, 2H), 2.44 (s, 3H), 2.46-2.42 (m, 2H), 1.84 (d, J = 2.8 Hz, 3H), 0.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8, 144.6, 135.2, 134.4, 129.6 (2C), 128.5 (2C), 127.8 (2C), 126.8 (3C), 99.8, 95.0, 94.9, 73.4, 49.5, 32.3, 21.6, 18.8, 0.1 (3C). HRMS (ES+) calculated for $C_{24}H_{29}NO_2SSi$ ($M+Na^+$): 446.1580; found: 446.1582.

4-Methyl-N-(2-(trimethylsilyl)ethynyl)-N-tosylhexa-4,5-dien-1-amine (1q)



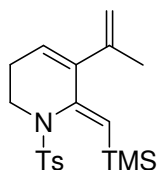
Compound **1q** was prepared according to (**GP4**) from the mesylate of 6-(N-(2-(trimethylsilyl)ethynyl)-N-tosylamino)hex-2-yn-1-ol and MeMgBr. The corresponding ynamide-ynol was obtained from N-(2-(trimethylsilyl)ethynyl)-N-tosylpent-3-yn-1-amine and formaldehyde. Yellow oil (100%). IR (neat) ν 2956, 2158, 1365, 1168, 839 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 4.59-4.56 (m, 2H), 3.30 (t, J = 7.0 Hz, 2H), 2.42 (s, 3H), 1.93-1.89 (m, 2H), 1.74 (quint., J = 7.2 Hz, 2H), 1.63-1.61 (t, J = 3.0 Hz, 3H), 0.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.9, 144.6, 134.6, 129.6 (2C), 127.7 (2C), 97.4, 95.2, 74.9, 73.1, 50.9, 29.8, 25.5, 21.6, 18.8, 0.1 (3C). HRMS (ES+) calculated for $C_{19}H_{27}NO_2SSi$ ($M+Na^+$): 384.1424; found: 384.1426.

3. Cycloisomerization Reactions

General procedure 5 (GP5): A dried schlenk flask equipped with a stir bar was charged with catalyst (0.1 mmol). The schlenk was evacuated and backfilled with argon three times, before allenynamide (1 mmol) in CH_2Cl_2 (10 mL) was added under argon. The resulting mixture was stirred at rt until completion of the reaction (monitored by TLC). The mixture was filtered through a short pad of silica gel, washed with Et_2O and concentrated *in vacuo*. Then, the crude was purified by flash chromatography over silica gel (gradient elution of EtOAc/Petroleum Ether).

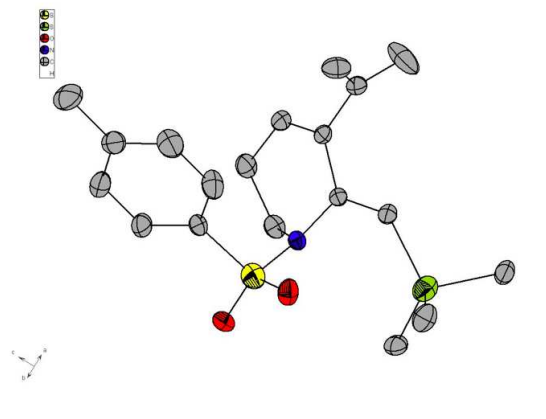
General procedure 6 (GP6): A dried schlenk flask equipped with a stir bar was charged with AgOTf (6.5 mg, 0.025 mmol). The schlenk was evacuated and backfilled with argon three times, before toluene (10 mL) was added under argon. The mixture was heated to reflux, and then a solution of allenynamide (0.25 mmol) in toluene (1 ml) was added. The resulting mixture was stirred until completion of the reaction (monitored by TLC). The mixture was filtered through a short pad of silica gel, washed with Et_2O and concentrated *in vacuo*. Then, the crude was purified by flash chromatography over silica gel (gradient elution of EtOAc/Petroleum Ether).

(2Z)-1,2,5,6-Tetrahydro-2-((trimethylsilyl)methylene)-3-(prop-1-en-2-yl)-1-tosylpyridine (**2a**)

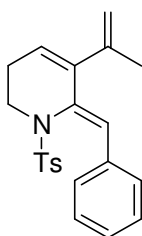


$\text{C}_{19}\text{H}_{27}\text{NO}_2\text{SSi}$
MW: 361.57

Compound **2a** was prepared according to (GP5) from **1a** (361 mg, 1 mmol) and AgOTf (25.7 mg, 0.1 mmol). White solid (61%). Mp = 123°C. IR (neat) ν 2924, 1584, 1351, 1162 838 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, J = 8.3 Hz, 2H), 7.17 (d, J = 8.3 Hz, 2H), 5.70 (s, 1H), 5.18 (t, J = 4.0 Hz, 1H), 4.98-4.96 (m, 1H), 4.86-4.85 (m, 1H), 3.77 (br, 2H), 2.38 (s, 3H), 1.82 (s, 3H), 1.78-1.74 (m, 2H), 0.23 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.1, 143.4, 143.3, 141.6, 138.3, 132.4, 128.9 (2C), 127.9 (2C), 123.2, 115.7, 45.3, 22.8, 22.7, 21.7, -0.1 (3C). HRMS (ES+) calculated for $\text{C}_{19}\text{H}_{27}\text{NO}_2\text{SSi}$ ($\text{M}+\text{Na}^+$): 384.1532; found: 384.1424. CCDC794305.



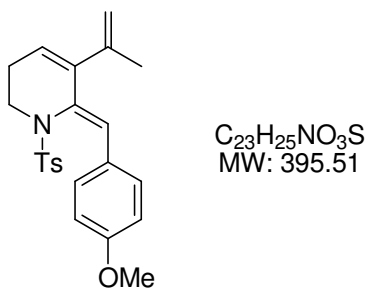
(2Z)-2-Benzylidene-1,2,5,6-tetrahydro-4-methyl-3-(prop-1-en-2-yl)-1-tosylpyridine (2d)



C₂₂H₂₃NO₂S
MW: 365.48

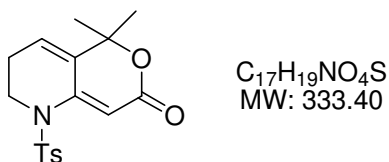
Compound **2d** was prepared according to (GP5) from **1d** (365 mg, 1 mmol) and **AgOTf** (25.7 mg, 0.1 mmol). White solid (90%). Mp = 93-95°C. IR (neat) ν 2917, 1596, 1350, 1182 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.64-7.58 (m, 4H), 7.29-7.21 (m, 3H), 7.11 (d, J = 8.3 Hz, 2H), 6.43 (s, 1H), 5.40 (br t, J = 3.6 Hz, 1H), 5.07 (s, 1H), 4.97 (s, 1H), 4.50-3.50 (br, 2H), 2.36 (s, 3H), 1.98 (s, 3H), 1.98 (br, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 143.8, 143.4, 141.1, 137.3, 135.7, 131.9, 129.7 (2C), 129.0 (2C), 128.7, 128.0 (2C), 127.9 (2C), 127.7, 123.5, 115.9, 45.1, 23.3, 22.7, 21.5. HRMS (ES+) calculated for C₂₂H₂₃NO₂S (M+Na⁺): 388.1341; found: 388.1342.

(2Z)-2-(4-Methoxybenzylidene)-1,2,5,6-tetrahydro-3-(prop-1-en-2-yl)-1-tosylpyridine (2e)



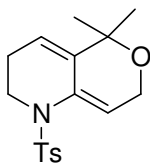
Compound **2e** was prepared according to (**GP5**) from **1e** (395 mg, 1 mmol) and **AgOTf** (25.7 mg, 0.1 mmol). White solid (95%). Mp = 89-91°C. IR (neat) ν 2921, 1591, 1330, 1179 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 9.2 Hz, 2H), 7.13 (d, J = 8.3 Hz, 2H), 6.81 (d, J = 9.2 Hz, 2H), 6.37 (s, 1H), 5.31 (t, J = 4.4 Hz, 1H), 5.05-5.04 (m, 1H), 4.96-4.95 (m, 1H), 4.50 (br, 1H), 3.80 (s, 3H), 3.50-3.45 (br, 1H), 2.36 (s, 3H), 1.96 (s, 3H), 1.96 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 143.8, 143.3, 141.0, 137.4, 131.1 (2C), 130.0, 128.9 (2C), 128.2 (2C), 127.8 (2C), 122.5, 115.7, 113.4 (2C), 55.1, 45.0, 23.1, 22.6, 21.4. HRMS (ES+) calculated for $C_{23}H_{25}NO_3S$ ($M+Na^+$): 418.1447; found: 418.1447.

2,3-Dihydro-5,5-dimethyl-1-tosyl-1H-pyrano[4,3-b]pyridin-7(5H)-one (3f)



Compound **3f** was prepared according to (**GP5**) from **1f** (333 mg, 1 mmol) and **AgOTf** (25.7 mg, 0.1 mmol). White solid (99%). Mp = 130-132°C. IR (neat) ν 2953, 1703, 1641, 1455, 1223 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 6.18-6.14 (m, 1H), 6.14 (s, 1H), 3.85 (t, J = 6.0 Hz, 2H), 2.40 (s, 3H), 2.36 (br q, J = 5.6 Hz, 2H), 1.46 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 145.1, 144.0, 135.4, 134.1, 130.1 (2C), 127.9, 127.4 (2C), 100.9, 80.2, 43.8, 28.7 (2C), 25.0, 21.6. HRMS (ES+) calculated for $C_{17}H_{19}NO_4S$ ($M+H^+$): 334.1108; found: 334.1108.

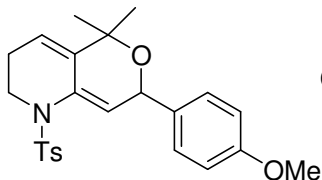
2,3,5,7-Tetrahydro-5,5-dimethyl-1-tosyl-1H-pyrano[4,3-b]pyridine (3g)



C₁₇H₂₁NO₃S
MW: 319.41

Compound **3g** was prepared according to (GP5) from **1g** (319 mg, 1 mmol) and **AgOTf** (25.7 mg, 0.1 mmol). White solid (65%). Mp = 77-79°C. IR (neat) ν 2927, 1665, 1454, 1158 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 6.74 (s, 1H), 5.49 (t, J = 5.0 Hz, 1H), 4.49 (br d, J = 1.2 Hz, 2H), 3.57-3.53 (m, 2H), 2.42 (s, 3H), 2.31 (q, J = 5.0 Hz, 2H), 1.26 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 144.4, 143.9, 136.0, 129.9 (2C), 127.0 (2C), 120.5, 120.3, 120.2, 84.7, 68.3, 46.2, 31.9, 27.4 (2C), 21.6. HRMS (ES⁺) calculated for C₁₇H₂₁NO₃S (M+Na⁺): 342.1134; found: 342.1137.

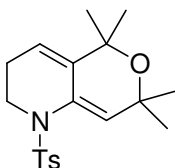
2,3,5,7-Tetrahydro-7-(4-methoxyphenyl)-5,5-dimethyl-1-tosyl-1H-pyrano[4,3-b]pyridine (3h)



C₂₄H₂₇NO₄S
MW: 425.54

Compound **3h** was prepared according to (GP5) from **1h** (425 mg, 1 mmol) and **AgOTf** (25.7 mg, 0.1 mmol). Colorless oil (76%). IR (neat) ν 2930, 1601, 1458, 1161 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.13 (s, 1H), 5.53-5.50 (m, 1H), 5.28 (s, 1H), 3.80 (s, 3H), 3.83-3.77 (m, 2H), 2.41 (s, 3H), 2.01 (br q, J = 5.0 Hz, 2H), 1.34 (s, 3H), 1.31 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 159.4, 143.5, 137.6, 135.9, 133.3, 129.5 (2C), 128.8 (2C), 128.6, 127.4 (2C), 122.6, 117.8, 114.0 (2C), 74.3, 71.3, 55.3, 43.8, 27.3, 25.9, 23.7, 21.5. HRMS (ES⁺) calculated for C₂₄H₂₇NO₄S (M+Na⁺): 448.1553; found: 448.1555.

2,3,5,7-Tetrahydro-5,5,7,7-tetramethyl-1-tosyl-1H-pyrano[4,3-b]pyridine (3i)

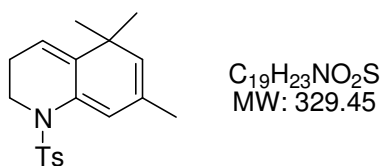


C₁₉H₂₅NO₃S
MW: 347.47

Compound **3i** and **4** were prepared according to (GP5) from **1i** (347 mg, 1 mmol) and **AgOTf** (25.7 mg, 0.1 mmol) and isolated from a 1.9 : 1 separable mixture of **3i** / **4** (53%).

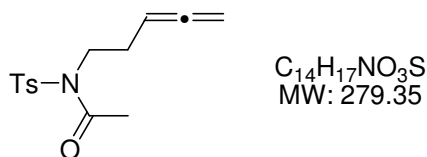
3i: White solid. Mp = 94-96°C IR (neat) ν 2931, 1668, 1463, 1134 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 6.04 (s, 1H), 5.42-5.40 (m, 1H), 3.75 (t, J = 6.1 Hz, 2H), 2.38 (s, 3H), 2.04-1.99 (br q, 2H), 1.32 (s, 6H), 1.23 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.5, 137.4, 135.7, 129.3 (2C), 127.7, 127.5 (2C), 126.1, 117.1, 74.0, 71.9, 43.7, 30.5 (2C), 30.2 (2C), 23.7, 21.5. HRMS (ES+) calculated for $\text{C}_{19}\text{H}_{25}\text{NO}_3\text{S}$ ($\text{M}+\text{Na}^+$): 370.1447; found: 370.1449.

1,2,3,5-Tetrahydro-5,5,7-trimethyl-1-tosylquinoline (**4**)



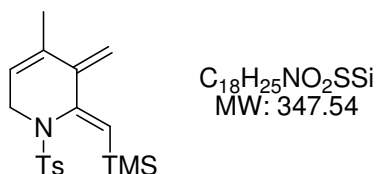
4: White solid. Mp = 86-88°C. IR (neat) ν 2949, 1657, 1444, 1188 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 8.3 Hz, 2H), 6.00 (s, 1H), 5.44-5.41 (m, 2H), 3.75 (t, J = 5.9 Hz, 2H), 2.38 (s, 3H), 2.05 (q, J = 5.9 Hz, 2H), 1.69 (br d, J = 1.1 Hz, 3H), 1.11 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.1, 137.8, 134.8, 131.8, 129.2 (2C), 129.1, 128.4, 127.4 (2C), 127.2, 117.3, 43.7, 36.4, 29.6 (2C), 23.9, 21.5, 18.8. HRMS (ES+) calculated for $\text{C}_{19}\text{H}_{23}\text{NO}_2\text{S}$ ($\text{M}+\text{Na}^+$): 352.1342; found: 352.1341.

N-(Penta-3,4-dienyl)-N-tosylacetamide (**5**)

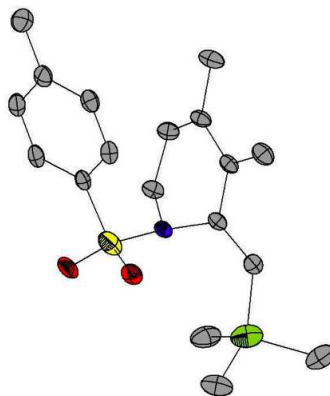


Compound **5** was prepared according to (GP5) from **1j** (333 mg, 1 mmol) and **AgOTf** (25.7 mg, 0.1 mmol). Yellow gel (21%). ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), 5.12 (quint, J = 7.2 Hz, 1H), 4.76-4.72 (m, 2H), 3.90-3.86 (m, 2H), 2.47 (s, 3H), 2.42-2.38 (m, 2H), 2.35 (s, 3H). ^{13}C (100 MHz, CDCl_3) δ 209.2, 170.2, 145.1, 136.9, 130.1 (2C), 127.6 (2C), 86.4, 75.8, 46.4, 28.5, 25.1, 21.8.

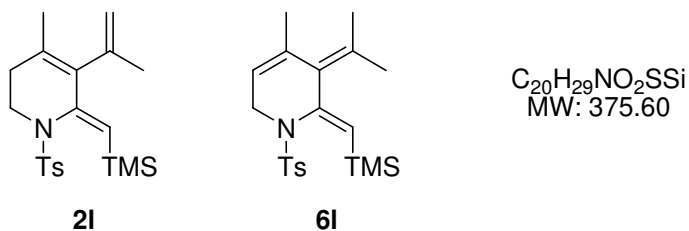
(2Z)-1,2,3,6-Tetrahydro-4-methyl-3-methylene-2-((trimethylsilyl)methylene)-1-tosylpyridine (6k)



Compound **6k** was prepared according to (**GP5**) from **1k** (347 mg, 1 mmol) and **AgOTf** (25.7 mg, 0.1 mmol). White solid (74%). Mp = 117-119°C. IR (neat) ν 2950, 1349, 1160 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.3 Hz, 2H), 7.12 (d, J = 8.3 Hz, 2H), 6.18 (br s, 1H), 5.34 (s, 1H), 5.18 (br s, 1H), 4.81 (s, 1H), 4.09 (br, 2H), 2.36 (s, 3H), 1.36 (d, J = 1.5 Hz, 3H), 0.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 143.1, 140.9, 136.4, 132.4, 132.3, 128.8 (2C), 128.3 (2C), 121.9, 110.8, 47.9, 21.5, 18.5, -0.2 (3C). HRMS (ES+) calculated for $C_{18}H_{25}NO_2SSi$ ($M+Na^+$): 370.1267; found: 370.1271. CCDC 794304.



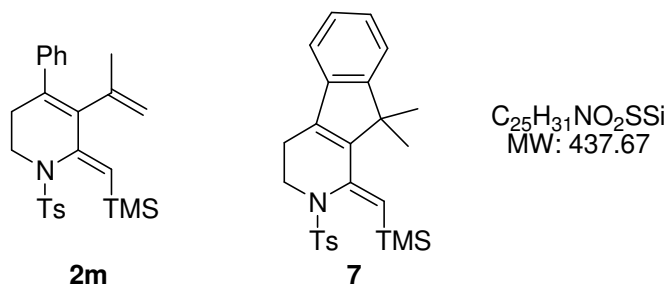
(2Z)-1,2,5,6-Tetrahydro-4-methyl-2-((trimethylsilyl)methylene)-3-(prop-1-en-2-yl)-1-tosylpyridine (2l) and (2Z)-1,2,3,6-tetrahydro-4-methyl-2-((trimethylsilyl)methylene)-3-(propan-2-ylidene)-1-tosylpyridine (6l)



Compound **2l** and **6l** were prepared according to (GP5) from **1l** (375 mg, 1 mmol) and **AgOTf** (25.7 mg, 0.1 mmol) and isolated as a 5.3 : 1 unseparable mixture of **2l** / **6l** (85%).

White solid. IR (neat) ν 2927, 1589, 1374, 1229 cm^{-1} . **2l**: ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, J = 8.3 Hz, 2H), 7.17 (d, J = 8.3 Hz, 2H), 5.60 (s, 1H), 5.13-5.11 (m, 1H), 4.64-4.62 (m, 1H), 3.70 (br, 2H), 2.38 (s, 3H), 1.77 (s, 3H), 1.61 (t, J = 6.4 Hz, 2H), 1.28 (s, 3H), 0.21 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.5, 143.2, 142.3, 138.1, 135.7, 129.5, 128.9 (2C), 128.7, 127.7 (2C), 116.6, 44.3, 27.8, 22.7, 21.6, 20.3, -0.0 (3C). **6l**: ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, J = 8.3 Hz, 2H), 7.14 (d, J = 8.3 Hz, 2H), 5.50 (s, 1H), 5.02 (br s, 1H), 4.13 (br s, 2H), 2.36 (s, 3H), 1.93 (s, 3H), 1.68-1.66 (m, 3H), 1.57 (s, 3H), 0.24 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.4, 142.9, 136.6, 134.8, 133.3, 131.7, 130.4, 128.6 (2C), 127.9 (2C), 120.4, 50.3, 25.7, 25.4, 22.4, 21.5, -0.1 (3C). HRMS (ES+) calculated for $\text{C}_{20}\text{H}_{29}\text{NO}_2\text{SSi}$ ($\text{M}+\text{H}^+$): 376.1761; found: 376.1763.

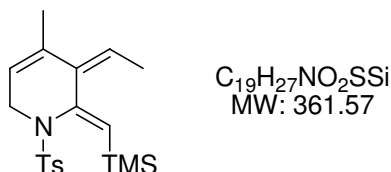
(2Z)-1,2,5,6-Tetrahydro-2-((trimethylsilyl)methylene)-4-phenyl-3-(prop-1-en-2-yl)-1-tosylpyridine (2m) and **(1Z)-2,3,4,9-tetrahydro-9,9-dimethyl-1-((trimethylsilyl)methylene)-2-tosyl-1H-indeno[2,1-c]pyridine (7)**



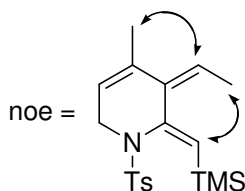
Compound **2m** and **7** were prepared according to (GP5) from **1m** (437 mg, 1 mmol) and **AgOTf** (25.7 mg, 0.1 mmol) and isolated as a 1.2 : 1 unseparable mixture of **2m** / **7** (70%). White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 8.0 Hz, 2H, **2m**), 7.57 (d, J = 8.0 Hz, 2H, **7**), 7.24-7.09 (m, 8H, **2m** and **7**), 6.97-6.91 (m, 3H, **2m** and/or **7**), 6.56-6.54 (m, 2H, **2m** and/or **7**), 5.84 (s, 1H, **2m**), 5.73 (s, 1H, **7**), 4.90 (s, 1H, **2m**), 4.57 (s, 1H, **2m**), 3.87 (br, 4H, **2m** and **7**), 2.39 (s, 3H, **2m**), 2.18 (s, 3H, **7**), 2.12 (t, J = 5.9 Hz, 2H, **7**), 2.07 (t, J = 6.4 Hz, 2H, **2m**), 1.65 (s, 3H, **2m**), 1.34 (s, 6H, **7**), 0.29 (s, 9H, **7**), 0.24 (s, 9H, **2m**). ^{13}C NMR (100 MHz, CDCl_3) δ 155.12, 144.5, 143.3 (2C), 143.1, 141.9, 141.6, 141.2, 140.2, 138.4, 138.0, 137.6, 135.1, 133.9, 131.9, 129.4, 129.3 (2C), 129.0 (2C), 127.9 (2C), 127.6 (2C), 127.4 (2C), 127.3 (2C), 126.7, 126.5, 126.2, 120.9, 119.1, 118.9 (**2m**), 48.9 (**7**), 44.8 (**2m**), 44.7 (**7**), 28.7 (**2m**),

23.5, 21.4, 21.3, 20.4 (**7**), 0.2 (3C, **7**), -0.2 (3C, **2m**). Two C overlapped. HRMS (ES+) calculated for $C_{25}H_{31}NO_2SSi$ ($M+Na^+$): 460.1845; found: 460.1737.

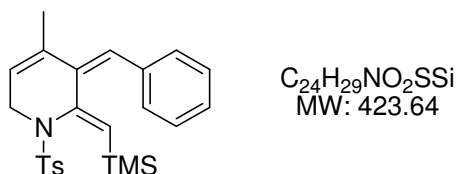
(2Z,3Z)-3-Ethylidene-1,2,3,6-tetrahydro-4-methyl-2-((trimethylsilyl)methylene)-1-tosylpyridine (6n)



Compound **6n** was prepared according to (GP5) from **1n** (361 mg, 1 mmol) and **AgOTf** (25.7 mg, 0.1 mmol). Yellow oil (79%). IR (neat) ν 2950, 2160, 1615, 1158, 855 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, $J = 8.3$ Hz, 2H), 7.10 (d, $J = 8.3$ Hz, 2H), 5.72 (s, 1H), 5.37 (q, $J = 6.8$ Hz, 1H), 5.06 (br s, 1H), 4.08 (br, 2H), 2.34 (s, 3H), 1.91 (d, $J = 7.2$ Hz, 3H), 1.34 (d, $J = 1.3$ Hz, 3H), 0.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 143.0, 136.4, 136.2, 134.9, 133.6, 128.6 (2C), 128.1 (2C), 123.0, 118.9, 49.1, 21.5, 18.7, 15.8, -0.1 (3C). HRMS (ES+) calculated for $C_{19}H_{27}NO_2SSi$ ($M+Na^+$): 384.1424; found: 384.1426.



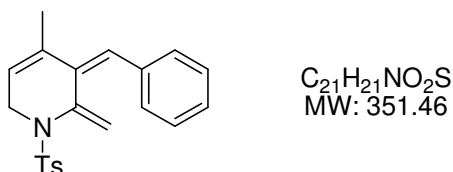
(2Z,3Z)-3-Benzylidene-1,2,3,6-tetrahydro-4-methyl-2-((trimethylsilyl)methylene)-1-tosylpyridine (6o)



Compound **6o** and **8** were prepared according to (GP5) from **1o** (423 mg, 1 mmol) and **AgOTf** (25.7 mg, 0.1 mmol) and isolated as a 3.3 : 1 separable mixture of **6o** / **8** (75%). The Z,Z configuration of **6o** has been assigned by analogy with **6n**.

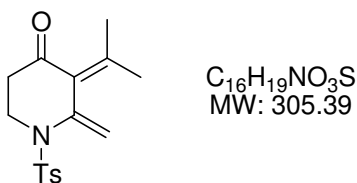
6o: White solid. Mp = 121-123 °C. IR (neat) ν 2914, 1601, 1332, 1177, 917 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, J = 7.7 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.35 (t, J = 7.7 Hz, 2H), 7.26-7.24 (m, 1H), 7.10 (d, J = 8.2 Hz, 2H), 6.21 (s, 1H), 6.07 (s, 1H), 5.20 (br s, 1H), 4.24 (br, 2H), 2.34 (s, 3H), 1.49 (s, 3H), 0.19 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.3, 143.1, 137.5, 136.2, 136.1, 134.0, 133.3, 129.5 (2C), 128.8 (2C), 128.3 (2C), 128.1 (2C), 127.5, 126.1, 121.9, 49.1, 21.4, 19.0, -0.8 (3C). HRMS (ES+) calculated for $\text{C}_{24}\text{H}_{29}\text{NO}_2\text{SSi}$ ($\text{M}+\text{H}^+$): 424.1761; found: 424.1763.

(3Z)-3-Benzylidene-1,2,3,6-tetrahydro-4-methyl-2-methylene-1-tosylpyridine (8)



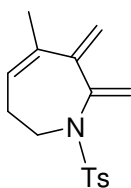
Colorless oil. IR (neat) ν 2922, 1657, 1299, 1203, 897 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.3 Hz, 2H), 7.29-7.21 (m, 5H), 6.40 (s, 1H), 5.49 (br s, 1H), 5.46 (s, 1H), 5.21 (s, 1H), 4.24 (br s, 2H), 2.42 (s, 3H), 1.78 (d, J = 1.6 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.6, 137.7, 136.7, 136.6, 133.4, 131.8, 129.5 (2C), 129.4 (2C), 128.5 (2C), 128.1 (2C), 127.4, 126.1, 122.0, 118.0, 47.9, 21.6, 19.4. HRMS (ES+) calculated for $\text{C}_{21}\text{H}_{21}\text{NO}_2\text{S}$ ($\text{M}+\text{H}^+$): 352.1366; found: 352.1368.

2-Methylene-3-(propan-2-ylidene)-1-tosylpiperidin-4-one (6p)



Compound **6p** was prepared according to (**GP6**) from **1p** (42 mg, 0.1 mmol) and **AgOTf** (2.6 mg, 0.01 mmol). Yellow gel (51%). IR (neat): ν = 3920, 2357, 1667, 1360, 1163 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.70 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.3 Hz, 2H), 5.69 (s, 1H), 4.68 (s, 1H), 3.74 (t, J = 6.0 Hz, 2H), 2.54 (t, J = 6.2 Hz, 2H), 2.41 (s, 3H), 2.03 (s, 3H), 1.69 (s, 3H). ^{13}C (100 MHz, CDCl_3) δ 197.6, 151.1, 144.1, 137.7, 135.8, 131.3, 129.6 (2C), 127.7 (2C), 111.1, 42.7, 39.7, 24.6, 22.4, 21.5. One C overlapped. HRMS (ES+) calculated for $\text{C}_{16}\text{H}_{19}\text{NO}_3\text{S}$ ($\text{M}+\text{Na}^+$): 328.09779; found: 328.09770.

(2,3,6,7-Tetrahydro-4-methyl-2,3-dimethylene-1-tosyl-1H-azepine (9))

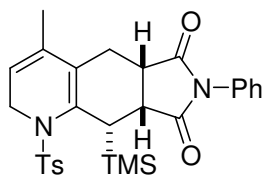


C₁₆H₁₉NO₂S
MW: 289.39

Compound **9** was prepared according to (GP6) from **1q** (90 mg, 0.250 mmol) and **AgOTf** (6.5 mg, 0.025 mmol). Yellow gel (58%). IR (neat): $\nu = 2924, 1340, 1158 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, $J = 8.3 \text{ Hz}$, 2H), 7.22 (d, $J = 8.3 \text{ Hz}$, 2H), 5.44 (br t, $J = 6.2 \text{ Hz}$, 1H), 5.33 (s, 1H), 5.27 (s, 1H), 5.18 (s, 1H), 4.97 (s, 1H), 3.69 (br t, $J = 5.9 \text{ Hz}$, 2H), 2.39 (s, 3H), 2.34-2.37 (m, 2H), 1.58 (d, $J = 0.9 \text{ Hz}$, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 146.9, 146.2, 143.1, 137.2, 134.6, 129.2 (2C), 127.9 (2C), 125.7, 116.3, 114.1, 49.0, 26.7, 22.7, 21.6. HRMS (ES⁺) calculated for C₁₆H₁₉NO₂S (M+Na⁺): 312.1029; found: 312.1031.

4. Tandem Alder-Ene/Diels-Alder Reaction

(5a*S*,8a*R*^{*},9*S*^{*})-1,2,5,5a,8a,9-hexahydro-4-methyl-9-(trimethylsilyl)-7-phenyl-1-tosyl-7H-pyrrolo[3,4-*g*]quinoline-6,8-dione (10)



C₂₈H₃₂N₂O₄SSi
MW: 520.71

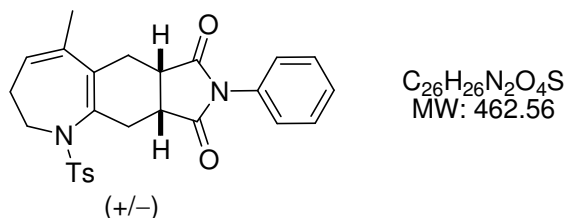
(+/-)

A dried schlenk flask equipped with a stir bar was charged with **AgOTf** (4.9 mg, 0.019 mmol). The schlenk was evacuated and backfilled with argon three times, before allenynamide **1k** (66 mg, 0.19 mmol) and *N*-phenylmaleimide (33 mg, 0.19 mmol) in CH₂Cl₂ (2 mL) was added under argon. The resulting mixture was stirred at rt until completion of the reaction (monitored by TLC). The mixture was filtered

through a short pad of silica gel, washed with Et₂O and concentrated *in vacuo*. Then, the crude was purified by flash chromatography over silica gel (gradient elution of EtOAc/Petroleum Ether).

10. Yellow gel (50%). IR (neat) ν 2920, 1705, 1150, 839 cm⁻¹. Mp = 104°C. ¹H NMR (400 MHz, CD₂Cl₂) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.53-7.49 (m, 2H), 7.47-7.41 (m, 1H), 7.35-7.32 (m, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 5.00-4.96 (m, 1H), 4.55 (dd, *J* = 17.5, 5.9 Hz, 1H), 3.85-3.77 (m, 1H), 3.60 (dd, *J* = 10.3, 8.7 Hz, 1H), 3.37 (d, *J* = 8.7 Hz, 1H), 3.12-3.08 (m, 1H), 2.89 (dd, *J* = 15.9, 7.8 Hz, 1H), 2.40 (s, 3H), 2.14-2.08 (m, 1H), 1.41 (s, 3H), 0.11 (s, 9H). ¹³C NMR (100 MHz, CD₂Cl₂) δ 178.3, 177.5, 144.3, 137.2, 136.7, 132.4, 132.1, 129.4 (2C), 129.4 (2C), 128.9, 127.8 (2C), 126.7 (2C), 126.5, 115.4, 45.7, 42.7, 41.9, 32.1, 23.8, 21.6, 18.0, 1.0 (3C). HRMS (ES+) calculated for C₂₈H₃₂N₂O₄SSi (M+Na⁺): 543.1852; found: 543.1744.

(6aS*,9aR*)-2,3,6,6a,9a,10-Hexahydro-5-methyl-8-phenyl-1-tosylazepino[3,2-f]isoindole-7,9(1H,8H)-dione (11)



A dried schlenk flask equipped with a stir bar was charged with AgOTf (6.5 mg, 0.025 mmol). The schlenk was evacuated and backfilled with argon three times, before toluene (10 mL) was added under argon. The mixture was heated to reflux, and then a solution of allenynamide **1q** (90 mg, 0.25 mmol) and *N*-phenylmaleimide (43 mg, 0.25 mmol) in toluene (1 ml) was added. The resulting mixture was stirred until completion of the reaction (monitored by TLC). The mixture was filtered through a short pad of silica gel, washed with Et₂O and concentrated *in vacuo*. Then, the crude was purified by flash chromatography over silica gel (gradient elution of EtOAc/Petroleum Ether).

11. Yellow gel (43%). IR (neat) ν 2924, 1707, 1156 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.46-7.41 (m, 2H), 7.37-7.34 (m, 1H), 7.32-7.28 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 5.47 (td, *J* = 6.1, 1.3 Hz, 1H), 3.97-3.91 (m, 1H), 3.79-3.74 (m, 1H), 3.43-3.38 (m, 1H), 3.32-3.27 (m, 1H), 3.11-3.06 (m, 1H), 2.88-2.80 (m, 2H), 2.37 (s, 3H), 2.40-2.33 (m, 1H), 2.05-1.94 (m, 2H), 1.38 (d, *J* = 0.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 178.5, 178.2, 143.1, 137.9, 136.6, 136.4, 133.8, 132.1, 129.4 (2C), 129.2

(2C), 128.6, 127.5, 127.4 (2C), 126.2 (2C), 58.5, 40.7, 39.7, 32.1, 27.2, 26.8, 21.6, 20.6. HRMS (ES+) calculated for C₂₆H₂₆N₂O₄S (M+Na⁺): 485.1505; found: 485.1498.

¹ Yao, B.; Liang, Z.; Niu, T.; Zhang, Y. *J. Org. Chem.* **2009**, *74*, 4630.

² Myers, A. G.; Zheng, B.; *J. Am. Chem. Soc.* **1996**, *118*, 4492.