

Electronic Supplementary Information

Gold(I)-catalyzed Cycloisomerization of Alkynyl Hydroxyallyl Tosylamides to 4-Oxa-6-azatricyclo[3.3.0.0^{2,8}]octanes

Yujung Park,^a Sun Young Kim,^a Ji Hoon Park,^a Jieun Cho,^b Youn Kyung Kang^b and Young Keun Chung^{*a}

^a *Intelligent Textile System Research Center, Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul, Korea*

^b *Division of Chemistry and Molecular Engineering, Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul, Korea.*

I. General information

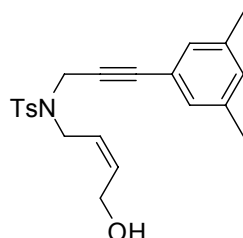
All solvents were dried and distilled according to standard methods before use. Au(PPh₃)Cl was prepared according to the literature procedures. Commercially available reagents were used as received without further purification. Reactions were carried out in a flame-dried glassware equipped with a stirring bar and sealed with a rubber septum under N₂, unless otherwise indicated. Elevated temperatures were maintained in thermostat-controlled oil baths. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as a visualizing agent and acidic *p*-anisaldehyde, and heat as a developing agent. Flash chromatography was carried out on Merck 60 silica gel (230 – 400 mesh). ¹H and ¹³C NMR spectra were recorded with Bruker (300 MHz) spectrometer and Varian spectrometer (500 MHz). ¹H NMR spectra were referenced to residual TMS (0 ppm) and reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet). Chemical shifts of the ¹³C NMR spectra were measured relative to CDCl₃ (77.00 ppm). Mass spectral data were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer. Single crystal data for **1a** were collected on an Enraf-Nonius CCD single crystal X-ray diffractometer at room temperature using graphite-monochromated Mo K α radiation (λ = 0.71073 Å). Structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares with SHELXL-97. Compounds **1**, **2**, **3**, **6**, **1b**, **2b**, **3b**, and **6b** were known.¹

1 M.-C. P. Yeh, M.-N. Lin, W.-J. Chang, J.-L. Liou and Y.-F. Shih, *J. Org. Chem.* **2010**, 75, 6031-6034.

II. General Procedure for Au(I)-Catalyzed Cycloisomerization

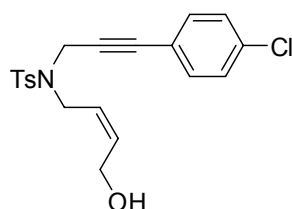
To a flame-dried 15 ml Schlenk flask capped with a rubber septum was injected 6 ml of dichloromethane via syringe under N₂ flow. Au(PPh₃)Cl (7 mg, 10 mol%) and AgSbF₆ (7 mg, 14 mol %) were added sequentially. The Au solution was stirred for 10 min at 85 °C. A alkynyl allyl alcohols (0.15 mmol) was put into the flask under N₂ flow. The reaction was monitored by thin-layer chromatography. After reactant disappeared, solvent was removed under reduced pressure. Flash chromatography on silica gel eluting with hexane and ethyl acetate (v/v = 6:1) gave the product.

III. Characterization Data



(Z)-N-(3-(3,5-dimethylphenyl)prop-2-ynyl)-N-(4-hydroxybut-2-enyl)-4-methylbenzenesulfonamide (4)

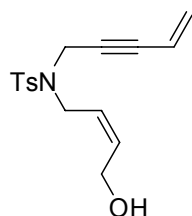
¹H NMR (300 MHz, CDCl₃) δ 1.63 (s, 1 H), 2.25 (s, 6 H), 2.37 (s, 3 H), 3.95 (d, *J* = 7.3 Hz, 2 H), 4.22 (d, *J* = 6.5 Hz, 2 H), 4.30 (s, 2 H), 5.57 (dt, *J* = 10.9, 7.3 Hz, 1 H), 5.90 (dt, *J* = 10.9, 6.5 Hz, 1 H), 6.69 (s, 2 H), 6.92 (s, 1 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 7.78 (d, *J* = 8.1 Hz, 2 H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 21.0, 21.5, 36.9, 43.0, 58.0, 80.7, 86.2, 121.5, 125.6, 127.9, 129.1, 129.6, 130.5, 134.3, 135.7, 137.7, 143.5 ppm. HRMS (EI) calc. for [C₂₂H₂₅NO₃S]⁺: 383.1555, found: 383.1552.



(Z)-N-(3-(4-chlorophenyl)prop-2-ynyl)-N-(4-hydroxybut-2-enyl)-4-methylbenzenesulfonamide (5)

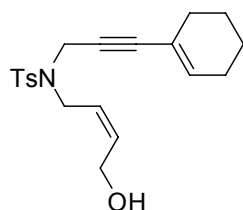
¹H NMR (300 MHz, CDCl₃) δ 1.65 (s, 1 H), 2.35 (s, 3 H), 3.95 (d, *J* = 7.3 Hz, 2 H), 4.23 (d, *J* = 6.6 Hz, 2 H), 4.29 (s, 2 H), 5.56 (dt, *J* = 10.9, 7.4 Hz, 1 H), 5.90 (dt, *J* = 10.9, 6.6 Hz, 1 H), 7.00 (d, *J* =

8.4 Hz, 2 H), 7.22 (d, J = 8.4 Hz, 2 H), 7.27 (d, J = 8.1 Hz, 2 H), 7.76 (d, J = 8.1 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 21.4, 36.8, 43.2, 58.0, 82.7, 84.6, 120.3, 125.6, 127.8, 128.5, 129.6, 132.7, 134.3, 134.6, 135.6, 143.7 ppm. HRMS (EI) calc. for $[\text{C}_{20}\text{H}_{20}\text{ClNO}_3\text{S}]^+$: 389.0852, found: 389.0855



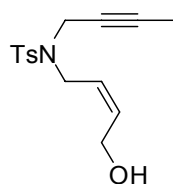
(Z)-N-(4-hydroxybut-2-enyl)-4-methyl-N-(pent-4-en-2-ynyl)benzenesulfonamide (7)

^1H NMR (300 MHz, CDCl_3) δ 1.78 (s, 1 H), 2.42 (s, 3 H), 3.88 (d, J = 7.3 Hz, 2 H), 4.19 (br s, 4 H) ppm. 5.33 (dd, J = 16.9, 2.5 Hz, 1 H), 5.39 (dd, J = 11.2, 2.5 Hz, 1 H), 5.46 – 5.56 (m, 2 H), 5.88 (dt, J = 11.0, 6.8 Hz, 1 H), 7.30 (d, J = 8.1 Hz, 2 H), 7.74 (d, J = 8.2 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 21.5, 36.8, 43.0, 58.0, 82.3, 84.4, 115.9, 125.7, 127.7, 127.8, 129.5, 134.2, 135.5, 143.6 ppm. HRMS (EI) calc. for $[\text{C}_{16}\text{H}_{19}\text{NO}_3\text{S}]^+$: 305.1086, found: 305.1087.



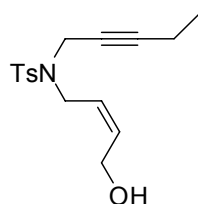
(Z)-N-(3-cyclohexenylprop-2-ynyl)-N-(4-hydroxybut-2-enyl)-4-methylbenzenesulfonamide (8)

^1H NMR (300 MHz, CDCl_3) δ 1.52 (br s, 4 H), 1.79 (br s, 2 H), 2.01 (br s, 2 H), 2.26 (br s, 1 H), 2.41 (s, 3 H), 3.88 (d, J = 7.3 Hz, 2 H), 4.18 (s, 2 H), 4.20 (d, J = 7.0 Hz, 2 H), 5.50 (dt, J = 10.6, 7.3 Hz, 1 H), 5.78 (br s, 1 H), 5.86 (dt, J = 10.6, 7.0 Hz, 1 H), 7.30 (d, J = 8.1 Hz, 2 H), 7.72 (d, J = 8.1 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 21.2, 21.4, 22.0, 25.4, 28.6, 36.7, 42.8, 57.8, 78.5, 87.6, 119.4, 125.4, 127.7, 129.4, 134.2, 135.4, 135.5, 143.4 ppm. HRMS (FAB) calc. for $[\text{C}_{20}\text{H}_{26}\text{NO}_3\text{S}]^+$: 360.1633, found: 360.1635.



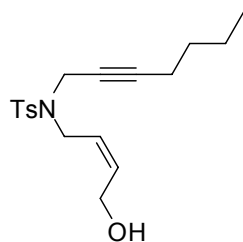
(Z)-N-(but-2-ynyl)-N-(4-hydroxybut-2-enyl)-4-methylbenzenesulfonamide (9)

¹H NMR (300 MHz, CDCl₃) δ 1.55 (t, *J* = 2.2 Hz, 3 H), 2.04 (s, 1 H), 2.43 (s, 3 H), 3.86 (d, *J* = 7.3 Hz, 2 H), 4.01 (d, *J* = 2.2 Hz, 2 H), 4.20 (s, 2 H), 5.49 (dt, *J* = 10.9, 7.3 Hz, 1 H), 5.86 (dt, *J* = 10.9, 6.8 Hz, 1 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 7.73 (d, *J* = 8.1 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 3.1, 21.4, 36.4, 42.8, 57.8, 71.6, 81.8, 125.6, 127.8, 129.3, 134.0, 135.6, 143.4 ppm. **HRMS (FAB)** calc. for [C₁₅H₂₀NO₃S]⁺: 294.1164, found: 294.1161.



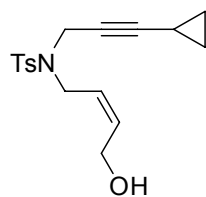
(Z)-N-(4-hydroxybut-2-enyl)-4-methyl-N-(pent-2-ynyl)benzenesulfonamide (10)

¹H NMR (300 MHz, CDCl₃) δ 0.90 (t, *J* = 7.5 Hz, 3 H), 1.74 – 1.79 (m, 1 H), 1.92 (q, *J* = 7.5 Hz, 2 H), 2.43 (s, 3 H), 3.88 (d, *J* = 7.3 Hz, 2 H), 4.05 (s, 2 H), 4.21 (dt, *J* = 6.6, 5.9 Hz, 2 H), 5.51 (dt, *J* = 11.0, 7.3 Hz, 1 H), 5.87 (dd, *J* = 11.0, 6.6 Hz, 1 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 7.73 (d, *J* = 8.1 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 12.0, 13.4, 21.5, 36.4, 42.7, 57.9, 71.7, 87.7, 125.8, 127.8, 129.4, 134.0, 135.7, 143.4 ppm. **HRMS (FAB)** calc. for [C₁₆H₂₂NO₃S]⁺: 308.1320, found: 308.1324.



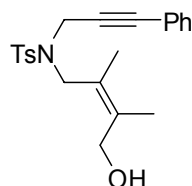
(Z)-N-(hept-2-ynyl)-N-(4-hydroxybut-2-enyl)-4-methylbenzenesulfonamide (11)

¹H NMR (300 MHz, CDCl₃) δ 0.85 (t, *J* = 6.8 Hz, 3 H), 1.16 – 1.28 (m, 4 H), 1.55 – 1.58 (m, 1 H), 1.90 – 1.95 (m, 2 H), 2.43 (s, 3 H), 3.89 (d, *J* = 7.3 Hz, 2 H), 4.07 (t, *J* = 2.0 Hz, 2 H), 4.21 (t, *J* = 6.9 Hz, 2 H), 5.52 (dt, *J* = 10.9, 7.4 Hz, 1 H), 5.88 (dt, *J* = 10.9, 6.9 Hz, 1 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 7.73 (d, *J* = 8.1 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 13.5, 18.1, 21.5, 21.9, 30.4, 36.5, 42.7, 58.0, 86.5, 90.1, 126.0, 127.8, 129.4, 133.9, 143.4, 151.9 ppm. **HRMS (FAB)** calc. for [C₁₈H₂₆NO₃S]⁺: 336.1633, found: 336.1630.



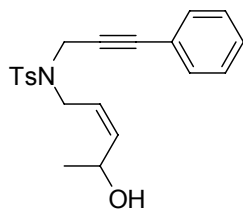
(Z)-N-(3-cyclopropylprop-2-ynyl)-N-(4-hydroxybut-2-enyl)-4-methylbenzenesulfonamide (12)

¹H NMR (500 MHz, CDCl₃) δ 0.30 - 0.36 (m, 2 H), 0.60 – 0.66 (m, 2 H), 0.93 – 1.02 (m, 1 H), 2.45 (s, 3 H), 3.87 (d, *J* = 7.4 Hz, 2 H), 4.03 (s, 2 H), 4.21 (d, *J* = 6.8 Hz, 2 H), 5.51 (dt, *J* = 11.0, 7.4 Hz, 1 H), 5.88 (dt, *J* = 11.0, 6.9 Hz, 1 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 7.72 (d, *J* = 8.1 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ -1.0, 7.8, 21.5, 36.5, 42.7, 58.0, 67.7, 80.6, 89.5, 125.9, 127.8, 129.4, 134.0, 135.7, 143.5 ppm. **HRMS (FAB)** calc. for [C₁₇H₂₂NO₃S]⁺: 320.1320, found: 320.1318.



(Z)-N-(4-hydroxy-2,3-dimethylbut-2-enyl)-4-methyl-N-(3-phenylprop-2-ynyl)benzenesulfonamide (13)

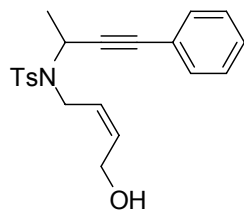
¹H NMR (500 MHz, CDCl₃) δ 1.50 (s, 1 H), 1.79 (s, 3 H), 1.83 (s, 3 H), 2.32 (s, 3 H), 3.94 (s, 2 H), 4.16 (s, 2 H), 4.20 (s, 2 H), 7.04 (d, *J* = 7.0 Hz, 2 H), 7.21 – 7.26 (m, 5 H), 7.78 (d, *J* = 7.9 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 16.7, 17.5, 21.4, 36.1, 47.9, 62.5, 81.9, 85.9, 121.8, 126.5, 127.8, 128.2, 128.6, 129.5, 131.5, 135.6, 135.8, 143.5 ppm. **HRMS (EI)** calc. for [C₂₂H₂₅NO₃S]⁺: 383.1555, found: 383.1558.



(Z)-N-(4-hydroxypent-2-enyl)-4-methyl-N-(3-phenylprop-2-ynyl)benzenesulfonamide (14)

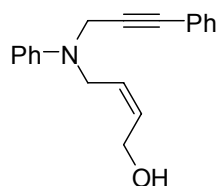
¹H NMR (300 MHz, CDCl₃) δ 1.24 (d, *J* = 6.3 Hz, 3 H), 2.34 (s, 3 H), 3.98 (d, *J* = 7.4 Hz, 2 H), 4.31 (s, 2 H), 4.70 (br s, 1 H), 5.46 (dt, *J* = 10.9, 7.4 Hz, 1 H), 5.72 (dd, *J* = 10.9, 9.0 Hz, 1 H), 7.07 (d, *J* = 7.9 Hz, 2 H), 7.25 (m, 5 H), 7.78 (d, *J* = 8.1 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 21.4, 23.3, 36.9, 43.3, 63.2, 81.6, 85.8, 121.8, 124.0, 127.8, 128.2, 128.6, 129.6, 131.5, 135.6, 139.3, 143.7 ppm.

HRMS (EI) calc. for $[C_{21}H_{23}NO_3S]^+$: 369.1399, found: 369.1396.



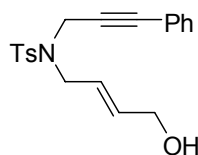
(Z)-N-(4-hydroxybut-2-enyl)-4-methyl-N-(4-phenylbut-3-yn-2-yl)benzenesulfonamide (15)

1H NMR (300 MHz, $CDCl_3$) δ 1.51 (d, J = 7.1 Hz, 3 H), 2.34 (s, 3 H), 2.67 (br s, 1 H), 3.87 (dd, J = 16.2, 5.9 Hz, 1 H), 4.02 (dd, J = 16.2, 5.3 Hz, 1 H), 4.18 – 4.29 (m, 2 H), 5.06 (q, J = 7.1 Hz, 1 H), 5.62 – 5.76 (m, 2 H), 7.09 (d, J = 7.8 Hz, 2 H), 7.20 – 7.30 (m, 5 H), 7.76 (d, J = 8.1 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.5, 22.6, 41.5, 46.9, 58.1, 85.1, 86.4, 122.0, 127.6, 128.2, 128.5, 129.6, 129.9, 130.4, 131.5, 136.0, 143.5 ppm. **HRMS (EI)** calc. for $[C_{21}H_{23}NO_3S]^+$: 369.1399, found: 369.1403.



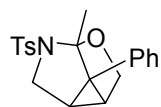
(Z)-4-(phenyl(3-phenylprop-2-ynyl)amino)but-2-en-1-ol (16)

1H NMR (300 MHz, $CDCl_3$) δ 1.86 (s, 1 H), 4.07 (d, J = 6.4 Hz, 2 H), 4.22 (s, 2 H), 4.31 (d, J = 6.4 Hz, 2 H), 5.71 (dt, J = 11.3, 6.4 Hz, 1 H), 5.85 (dt, J = 11.3, 6.4 Hz, 1 H), 6.85 (t, J = 7.3 Hz, 1 H), 6.96 (d, J = 8.1 Hz, 2 H), 7.24-7.31 (m, 5 H), 7.36-7.39 (m, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 40.8, 47.9, 58.5, 84.4, 85.0, 115.6, 119.1, 122.7, 128.20, 128.23, 128.7, 129.1, 131.6, 132.0, 148.5 ppm. **HRMS (FAB)** calc. for $[C_{19}H_{20}NO]^+$: 278.1545, found: 278.1547.



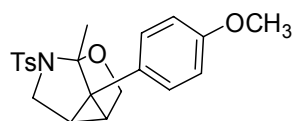
(E)-N-(4-hydroxybut-2-enyl)-4-methyl-N-(3-phenylprop-2-ynyl)benzenesulfonamide (1-trans)

1H NMR (300 MHz, $CDCl_3$) δ 1.61 (t, J = 5.1 Hz, 1 H), 2.33 (s, 3 H), 3.90 (d, J = 6.3 Hz, 2 H), 4.16 (br s, 2 H), 4.30 (s, 2 H), 5.71 (dt, J = 6.3, 15.5 Hz, 1 H), 5.92 (dt, J = 15.4, 5.1 Hz, 1 H), 7.06 (dd, J = 7.8, 1.3 Hz, 2 H), 7.21 – 7.31 (m, 5 H), 7.77 (d, J = 8.1 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.4, 36.8, 48.0, 62.7, 81.6, 85.7, 122.1, 124.9, 127.8, 128.1, 128.4, 129.5, 131.4, 134.6, 135.8, 143.5 ppm. **HRMS (EI)** calc. for $[C_{20}H_{21}NO_3S]^+$: 355.1242, found: 355.1238



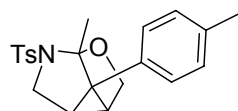
(1a)

¹H NMR (300 MHz, CDCl₃) δ 1.60 (s, 3 H), 2.06 – 2.17 (m, 2 H), 2.44 (s, 3 H), 2.82 (dd, *J* = 9.8, 1.3 Hz, 1 H), 3.44 (d, *J* = 10.2 Hz, 1 H), 3.97 (dd, *J* = 9.8, 5.4 Hz, 1 H), 4.14 (dd, *J* = 10.2, 5.4 Hz, 1 H), 7.26 – 7.37 (m, 7 H), 7.83 (d, *J* = 8.1 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 21.6, 22.8, 28.7, 32.2, 48.7, 53.5, 65.1, 105.9, 127.9, 128.5, 128.7, 128.9, 130.4, 135.6, 136.4, 143.2 ppm. **HRMS (EI)** calc. for [C₂₀H₂₁NO₃S]⁺: 355.1242, found: 355.1246.



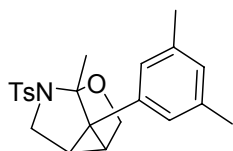
(2a)

¹H NMR (300 MHz, CDCl₃) δ 1.59 (s, 3 H), 2.02 – 2.12 (m, 2 H), 2.43 (s, 3 H), 2.81 (dd, *J* = 9.8, 1.3 Hz, 1 H), 3.42 (d, *J* = 10.1 Hz, 1 H), 3.80 (s, 3 H), 3.95 (dd, *J* = 9.8, 5.4 Hz, 1 H), 4.12 (dd, *J* = 10.1, 5.4 Hz, 1 H), 6.86 (d, *J* = 8.6 Hz, 2 H), 7.21 (d, *J* = 8.6 Hz, 2 H), 7.28 (d, *J* = 8.1 Hz, 2 H), 7.82 (d, *J* = 8.1 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 21.5, 22.8, 28.8, 32.3, 48.7, 52.8, 55.3, 65.1, 105.9, 113.9, 128.5, 128.7, 128.9, 131.5, 135.6, 143.2, 159.3 ppm. **HRMS (EI)** calc. for [C₂₁H₂₃NO₃S]⁺: 385.1348, found: 385.1347.



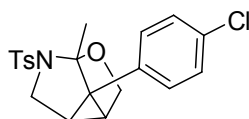
(3a)

¹H NMR (300 MHz, CDCl₃) δ 1.60 (s, 3 H), 2.03 – 2.13 (m, 2 H), 2.35 (s, 3 H), 2.43 (s, 3 H), 2.81 (dd, *J* = 9.8, 1.3 Hz, 1 H), 3.42 (d, *J* = 10.2 Hz, 1 H), 3.95 (dd, *J* = 9.8, 5.3 Hz, 1 H), 4.12 (dd, *J* = 10.1, 5.6 Hz, 1 H), 7.14 (d, *J* = 8.1 Hz, 2 H), 7.19 (d, *J* = 8.1 Hz, 2 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 7.82 (d, *J* = 8.1 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 21.1, 21.5, 22.8, 28.7, 32.2, 48.7, 53.1, 65.1, 105.9, 128.7, 128.9, 129.2, 130.3, 133.3, 135.5, 137.7, 143.2 ppm. **HRMS (EI)** calc. for [C₂₁H₂₃NO₃S]⁺: 369.1399, found: 369.1402.



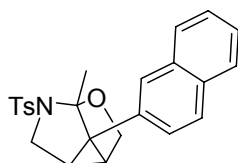
(4a)

¹H NMR (300 MHz, CDCl₃) δ 1.61 (s, 3 H), 2.02 – 2.13 (m, 2 H), 2.30 (s, 6 H), 2.43 (s, 3 H), 2.81 (dd, *J* = 9.8, 1.3 Hz, 1 H), 3.41 (d, *J* = 10.1 Hz, 1 H), 3.96 (dd, *J* = 9.8, 5.5 Hz, 1 H), 4.12 (dd, *J* = 10.1, 5.5 Hz, 1 H), 6.91 (s, 2 H), 6.93 (s, 1 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 7.83 (d, *J* = 8.1 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 21.1, 21.5, 22.8, 28.6, 32.1, 48.7, 53.3, 65.1, 106.0, 128.1, 128.7, 128.9, 129.5, 135.6, 136.2, 138.1, 143.2 ppm. **HRMS (EI)** calc. for [C₂₂H₂₅NO₃S]⁺: 383.1555, found: 383.1559.



(5a)

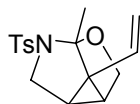
¹H NMR (300 MHz, CDCl₃) δ 1.59 (s, 3 H), 2.05 – 2.16 (m, 2 H), 2.44 (s, 3 H), 2.81 (dd, *J* = 9.9, 1.2 Hz, 1 H), 3.43 (d, *J* = 10.2 Hz, 1 H), 3.96 (dd, *J* = 9.9, 5.4 Hz, 1 H), 4.12 (dd, *J* = 10.2, 5.5 Hz, 1 H), 7.24 (d, *J* = 8.4 Hz, 2 H), 7.27 - 7.33 (m, 4 H), 7.82 (d, *J* = 8.1 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 21.6, 22.8, 28.8, 32.3, 48.6, 52.8, 65.1, 105.7, 128.7, 128.8, 129.0, 131.7, 134.9, 135.4, 143.3, 153.3 ppm. **HRMS (EI)** calc. for [C₂₀H₂₀ClNO₃S]⁺: 389.0852, found: 389.0851.



(6a/6a' = 1/1)

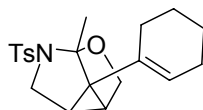
¹H NMR (300 MHz, CDCl₃) δ 1.55 (s, 3 H), 1.59 (s, 3 H), 2.11 (dd, *J* = 7.4, 5.7 Hz, 1 H), 2.18 – 2.33 (m, 3 H), 2.45 (s, 6 H), 2.92 (d, *J* = 11.2 Hz, 1 H), 2.97 (d, *J* = 9.8 Hz, 1 H), 3.55 (d, *J* = 10.2 Hz, 1 H), 3.66 (d, *J* = 10.4 Hz, 1 H), 4.06 (dd, *J* = 9.8, 5.6 Hz, 1 H), 4.23 – 4.29 (m, 2 H), 4.40 (dd, *J* = 10.4, 5.6 Hz, 1 H), 7.32 (d, *J* = 8.0 Hz, 4 H), 7.38 – 7.60 (m, 8 H), 7.81 – 7.89 (m, 8 H), 7.99 - 8.05 (m, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 21.6, 21.7, 22.6, 28.8, 29.7, 31.6, 32.4, 33.3, 48.7, 49.0, 51.4, 52.0, 64.8, 65.3, 106.1, 106.3, 124.7, 124.9, 125.2, 125.5, 125.9, 126.1, 126.7, 126.9, 128.6, 128.73, 128.75, 128.8, 129.0, 129.1, 133.15, 133.24, 133.36, 133.43, 133.7, 133.8, 135.7, 135.8, 143.3, 143.4

ppm. **HRMS (EI)** calc. for $[C_{24}H_{23}NO_3S]^+$: 405.1399, found: 405.1394



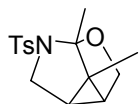
(7a)

1H NMR (300 MHz, $CDCl_3$) δ 1.89 (s, 3 H), 1.94 – 2.05 (m, 2 H), 2.43 (s, 3 H), 2.74 (dd, J = 9.7, 1.4 Hz, 1 H), 3.31 (d, J = 10.1 Hz, 1 H), 3.79 (dd, J = 9.7, 5.5 Hz, 1 H), 3.92 (dd, J = 10.1, 5.5 Hz, 1 H), 5.03 (dd, J = 17.0, 1.2 Hz, 1 H), 5.13 (dd, J = 10.3, 1.2 Hz, 1 H), 6.27 (dd, J = 17.0, 10.3 Hz, 1 H), 7.27 (d, J = 8.1 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.5, 21.9, 29.6, 32.8, 48.2, 50.9, 64.6, 104.7, 116.1, 128.7, 128.9, 132.1, 134.1, 143.2 ppm. **HRMS (EI)** calc. for $[C_{16}H_{19}NO_3S]^+$: 305.1086, found: 305.1090.



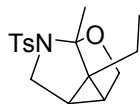
(8a)

1H NMR (300 MHz, $CDCl_3$) δ 1.56 – 1.63 (m, 4 H), 1.75 – 1.90 (m, 2H), 1.83 (s, 3 H), 1.98 - 2.08 (m, 4 H), 2.42 (s, 3 H), 2.66 (dd, J = 9.7, 1.3 Hz, 1 H), 3.29 (d, J = 10.1 Hz, 1 H), 3.78 (dd, J = 9.7, 5.6 Hz, 1 H), 3.95 (dd, J = 10.1, 5.6 Hz, 1 H), 5.70 (br s, 1 H), 7.26 (d, J = 8.1 Hz, 2 H), 7.79 (d, J = 8.1 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.3, 21.5, 22.1, 22.7, 25.3, 27.7, 28.5, 31.5, 48.7, 54.4, 64.9, 105.4, 128.7, 128.8, 129.1, 132.9, 135.6, 143.1 ppm. **HRMS (EI)** calc. for $[C_{20}H_{25}NO_3S]^+$: 359.1555, found: 359.1552.



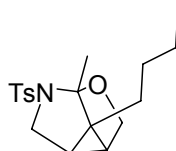
(9a)

1H NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 3 H), 1.65 (br s, 2 H), 1.86 (s, 3 H), 2.42 (s, 3 H), 2.65 (d, J = 9.8 Hz, 1 H), 3.24 (d, J = 10.0 Hz, 1 H), 3.73 (ddd, J = 9.8, 3.4, 2.0 Hz, 1 H) ppm. 3.86 (ddd, J = 10.0, 3.4, 2.0 Hz, 1 H), 7.27 (d, J = 8.0 Hz, 2 H), 7.79 (d, J = 8.2 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 14.9, 21.1, 21.5, 28.8, 32.2, 43.8, 48.1, 64.5, 105.1, 128.6, 128.9, 135.5, 143.1 ppm. **HRMS (EI)** calc. for $[C_{15}H_{19}NO_3S]^+$: 293.1086, found: 293.1082.



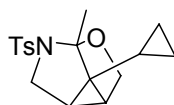
(10a)

¹H NMR (300 MHz, CDCl₃) δ 0.83 (t, *J* = 7.4 Hz, 3 H), 1.68 – 1.80 (m, 1 H), 1.73 (br s, 2H), 1.82 – 1.92 (m, 1 H), 1.90 (s, 3 H), 2.42 (s, 3 H), 2.67 (d, *J* = 9.7 Hz, 1 H), 3.27 (d, *J* = 10.0 Hz, 1 H), 3.70 (ddd, *J* = 9.7, 3.5, 1.9 Hz, 1 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 10.6, 20.0, 20.8, 21.5, 25.7, 29.6, 48.3, 64.7, 105.2, 128.7, 128.9, 135.6, 143.1 ppm. **HRMS (EI)** calc. for [C₁₆H₂₁NO₃S]⁺: 307.1242, found: 307.1238.



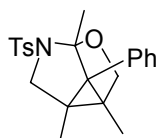
(11a)

¹H NMR (300 MHz, CDCl₃) δ 0.90 (t, *J* = 7.2 Hz, 3 H), 1.07- 1.39 (m, 4 H), 1.62 – 1.74 (m, 1 H), 1.71 – 1.74 (m, 2 H), 1.79 – 1.93 (m, 1 H), 1.90 (s, 3 H), 2.42 (s, 3 H), 2.66 (d, *J* = 9.7 Hz, 1 H), 3.27 (d, *J* = 10.0 Hz, 1 H), 3.70 (ddd, 9.7, 3.5, 2.0 Hz, 1 H), 3.85 (ddd, *J* = 10.0, 3.4, 2.0 Hz, 1 H), 7.26 (d, *J* = 8.1 Hz, 2 H), 7.79 (d, *J* = 8.1 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 14.0, 21.0, 21.5, 22.8, 26.4, 27.2, 28.8, 30.3, 48.2, 48.3, 64.6, 105.4, 128.7, 128.9, 135.7, 143.1 ppm. **HRMS (EI)** calc. for [C₁₈H₂₅NO₃S]⁺: 335.1555, found: 335.1551.



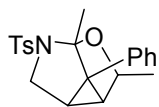
(12a)

¹H NMR (300 MHz, CDCl₃) δ -0.02 - 0.1 (m, 2 H), 0.49 – 0.61 (m, 2 H), 1.24 – 1.32 (m, 1 H), 1.53 – 1.62 (m, 2 H), 2.02 (s, 3 H), 2.42 (s, 3 H), 2.62 (d, *J* = 9.7 Hz, 1 H), 3.23 (d, *J* = 10.1 Hz, 1 H), 3.66 (dd, *J* = 9.7, 4.9 Hz, 1 H), 3.82 (dd, *J* = 10.1, 5.1 Hz, 1 H), 7.26 (d, *J* = 7.9 Hz, 2 H), 7.79 (d, *J* = 8.1 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 2.7, 3.3, 7.9, 21.2, 21.5, 26.3, 29.3, 48.2, 51.2, 64.5, 105.4, 128.6, 128.8, 135.5, 143.1 ppm. **HRMS (EI)** calc. for [C₁₇H₂₁NO₃S]⁺: 319.1242, found: 319.1241



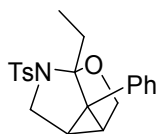
(13a)

¹H NMR (300 MHz, CDCl₃) δ 1.05 (s, 3 H), 1.08 (s, 3 H), 1.49 (s, 3 H), 2.44 (s, 3 H), 2.97 (d, *J* = 9.6 Hz, 1 H), 3.57 (d, *J* = 9.9 Hz, 1 H), 3.63 (d, *J* = 9.6 Hz, 1 H), 3.84 (d, *J* = 9.9 Hz, 1 H), 7.15 (d, *J* = 6.6 Hz, 2 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 7.28 – 7.40 (m, 3 H), 7.83 (d, *J* = 8.2 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 13.9, 14.7, 21.6, 23.1, 29.7, 35.4, 40.0, 56.2, 72.6, 107.6, 127.7, 128.7, 128.8, 128.9, 129.5, 131.8, 135.6, 143.2 ppm. **HRMS (EI)** calc. for [C₂₂H₂₅NO₃S]⁺: 383.1555, found: 383.1558.



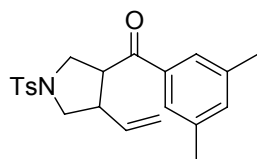
(14a)

¹H NMR (300 MHz, CDCl₃) δ 1.18 (d, *J* = 6.1 Hz, 3 H), 1.60 (s, 3 H), 1.79 (dd, *J* = 7.6, 0.9 Hz, 1 H), 2.03 (dd, *J* = 7.6, 5.7 Hz, 1 H), 2.44 (s, 3 H), 3.04 (q, *J* = 6.1 Hz, 1 H), 3.44 (d, *J* = 10.1 Hz, 1 H), 4.12 (dd, *J* = 10.1, 5.7 Hz, 1 H), 7.27 – 7.35 (m, 7 H), 7.84 (d, *J* = 8.1 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 21.0, 21.6, 23.2, 28.3, 37.8, 49.2, 53.9, 72.0, 105.5, 127.9, 128.5, 128.6, 128.75, 128.79, 130.5, 136.4, 143.2 ppm. **HRMS (EI)** calc. for [C₂₁H₂₃NO₃S]⁺: 369.1399, found: 369.1396.



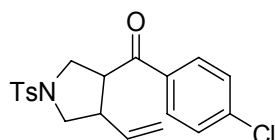
(15a)

¹H NMR (300 MHz, CDCl₃) δ 0.66 (t, *J* = 7.3 Hz, 3 H), 1.92 – 2.05 (m, 2 H), 2.16 (dd, *J* = 7.2, 5.7 Hz, 1 H), 2.44 (s, 3 H), 2.48 – 2.55 (m, 1 H), 2.67 (dd, *J* = 10.1, 1.4 Hz, 1 H), 3.48 (d, *J* = 10.0 Hz, 1 H), 3.93 (dd, *J* = 10.1, 5.7 Hz, 1 H), 4.12 (dd, *J* = 10.0, 5.6 Hz, 1 H), 7.26 – 7.33 (m, 7 H), 7.85 (d, *J* = 8.1 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 8.8, 21.6, 26.7, 28.4, 33.4, 49.1, 52.2, 64.7, 109.2, 127.8, 128.3, 128.9, 129.0, 140.7, 135.4, 136.5, 143.3 ppm. **HRMS (EI)** calc. for [C₂₁H₂₃NO₃S]⁺: 369.1399, found: 369.1396.



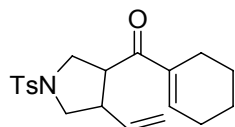
(3,5-Dimethylphenyl)(1-tosyl-4-vinylpyrrolidin-3-yl)methanone (4b)

¹H NMR (300 MHz, CDCl₃) δ 2.34 (s, 6 H), 2.46 (s, 3 H), 3.13 – 3.23 (m, 1 H), 3.26 (dd, *J* = 9.7, 5.1 Hz, 1 H), 3.59 – 3.70 (m, 3 H), 4.07 (dd, *J* = 15.2, 7.7 Hz, 1 H), 4.75 (d, *J* = 16.9 Hz, 1 H), 4.80 (d, *J* = 10.1 Hz, 1 H), 5.27 (ddd, *J* = 16.9, 10.1, 9.0 Hz, 1 H), 7.19 (s, 1 H), 7.36 (d, *J* = 8.1 Hz, 2 H), 7.40 (s, 2 H), 7.77 (d, *J* = 8.2 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 21.2, 21.6, 46.1, 48.5, 49.1, 52.8, 117.8, 126.0, 127.6, 129.7, 133.6, 133.8, 135.1, 136.7, 138.3, 143.6, 197.8 ppm. **HRMS (FAB)** calc. for [C₂₂H₂₆NO₃S]⁺: 384.1633, found: 384.1635.



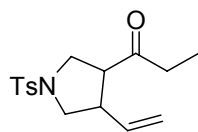
(4-Chlorophenyl)(1-tosyl-4-vinylpyrrolidin-3-yl)methanone (5b)

¹H NMR (300 MHz, CDCl₃) δ 2.46 (s, 3 H), 3.14 – 3.25 (m, 2 H), 3.60 – 3.72 (m, 3 H), 4.01 – 4.12 (m, 1 H), 4.75 (d, *J* = 16.6 Hz, 1 H), 4.79 (d, *J* = 9.2 Hz, 1 H), 5.17 – 5.29 (m, 1 H), 7.36 (d, *J* = 8.1 Hz, 2 H), 7.41 (d, *J* = 8.5 Hz, 2 H), 7.75 (d, *J* = 8.5 Hz, 2 H), 7.76 (d, *J* = 8.1 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 21.6, 46.2, 48.4, 49.1, 52.9, 118.2, 127.7, 129.1, 129.6, 129.8, 133.55, 133.64, 134.9, 140.0, 143.7, 196.3 ppm. **HRMS (EI)** calc. for [C₂₀H₂₀ClNO₃S]⁺: 389.0852, found: 389.0850.



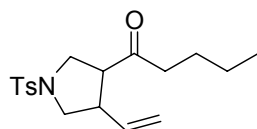
Cyclohexenyl(1-tosyl-4-vinylpyrrolidin-3-yl)methanone (8b)

¹H NMR (300 MHz, CDCl₃) δ 1.57 – 1.59 (m, 4 H), 2.02 (br s, 1 H), 2.16 (br s, 1 H), 2.23 (br s, 2 H), 2.45 (s, 3 H), 3.03 (td, *J* = 13.8, 7.1 Hz, 1 H), 3.15 (dd, *J* = 9.8, 5.2 Hz, 1 H), 3.52 (dd, *J* = 7.7, 1.9 Hz, 2 H), 3.59 (dd, *J* = 9.8, 6.6 Hz, 1 H), 3.81 (q, *J* = 7.7 Hz, 1 H), 4.87 (d, *J* = 11.7 Hz, 1 H), 4.88 (d, *J* = 15.3 Hz, 1 H), 5.17 – 5.30 (m, 1 H), 6.78 (s, 1 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 7.74 (d, *J* = 8.1 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 21.1, 21.6, 21.7, 23.0, 26.1, 46.4, 47.6, 48.6, 52.8, 117.3, 127.6, 129.7, 133.4, 134.4, 139.5, 140.8, 143.5, 198.2 ppm. **HRMS (EI)** calc. for [C₂₀H₂₅NO₃S]⁺: 359.1555, found: 359.1554.



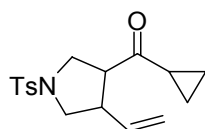
1-(1-Tosyl-4-vinylpyrrolidin-3-yl)propan-1-one (10b)

¹H NMR (300 MHz, CDCl₃) δ 0.95 (t, *J* = 7.2 Hz, 3 H), 2.25 - 2.41 (m, 2 H), 2.44 (s, 3 H), 3.03 - 3.12 (m, 1 H), 3.16 - 3.27 (m, 2 H), 3.45 - 3.57 (m, 3 H), 4.98 (dd, *J* = 10.1, 1.0 Hz, 1 H), 5.04 (d, *J* = 16.8 Hz, 1 H), 5.25 - 5.37 (ddd, *J* = 16.8, 10.1, 9.7, 1 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 7.73 (d, *J* = 8.2 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 7.1, 36.4, 43.4, 45.3, 47.5, 52.9, 53.5, 118.1, 127.6, 129.7, 133.5, 134.1, 143.6, 208.2 ppm. **HRMS (FAB)** calc. for [C₁₆H₂₂NO₃S]⁺: 308.1320, found: 308.1324.



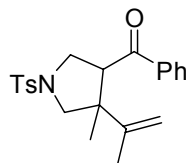
1-(1-Tosyl-4-vinylpyrrolidin-3-yl)pentan-1-one (11b)

¹H NMR (300 MHz, CDCl₃) δ 0.86 (t, *J* = 7.3 Hz, 3 H), 1.17 - 1.29 (m, 4 H), 1.37 - 1.53 (m, 2 H), 2.31 (dt, *J* = 7.6, 1.4 Hz, 2 H), 2.44 (s, 3 H), 3.03 - 3.12 (m, 1 H), 3.16 - 3.25 (m, 2 H), 3.44 - 3.56 (m, 3 H) ppm 4.98 (dd, *J* = 10.2, 1.0 Hz, 1 H), 5.04 (d, *J* = 16.9 Hz, 1 H), 5.31 (ddd, *J* = 16.9, 10.2, 9.8 Hz, 1 H), 7.34 (d, *J* = 8.0 Hz, 1 H), 7.73 (d, *J* = 8.2 Hz, 1 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 13.8, 21.5, 22.2, 25.1, 42.9, 45.3, 47.5, 52.9, 53.5, 118.1, 127.6, 129.7, 133.5, 134.1, 143.6, 207.8 ppm. **HRMS (FAB)** calc. for [C₁₈H₂₆NO₃S]⁺: 336.1633, found: 336.1631.



Cyclopropyl(1-tosyl-4-vinylpyrrolidin-3-yl)methanone (12b)

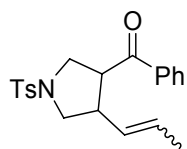
¹H NMR (300 MHz, CDCl₃) δ 0.75 - 0.84 (m, 2 H), 0.86 - 0.94 (m, 2 H), 1.71 - 1.79 (m, 1 H), 2.44 (s, 3 H), 3.07 - 3.17 (m, 2 H), 3.35 - 3.43 (m, 1 H), 3.46 - 3.59 (m, 3 H), 4.99 (d, *J* = 9.9 Hz, 1 H), 5.05 (d, *J* = 17.2 Hz, 1 H), 5.37 (ddd, 1H, *J* = 17.2, 9.9, 8.9 Hz, 1 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 7.73 (d, *J* = 8.1 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 11.5, 11.7, 20.9, 21.5, 45.1, 47.5, 52.7, 55.0, 117.9, 127.6, 129.7, 133.6, 134.3, 143.6, 207.5 ppm. **HRMS (EI)** calc. for [C₁₇H₂₁NO₃S]⁺: 319.1242, found: 319.1241



(4-Methyl-4-(prop-1-en-2-yl)-1-tosylpyrrolidin-3-yl)(phenyl)methanone (13b)

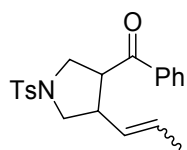
¹H NMR (300 MHz, CDCl₃) δ 1.25 (s, 3 H), 1.49 (s, 3 H), 2.44 (s, 3 H), 3.40 – 3.47 (m, 2 H), 3.79 – 3.90 (m, 3 H), 4.54 (s, 1 H), 4.69 (s, 1 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 7.40 – 7.45 (m, 2 H), 7.55 (t, *J* = 7.3 Hz, 1 H), 7.70 (d, *J* = 7.9 Hz, 4 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 20.6, 21.5, 27.0, 28.5, 49.8, 51.7, 60.0, 111.5, 127.4, 128.1, 128.7, 129.6, 133.3, 134.2, 136.6, 143.3, 146.2, 199.2 ppm.

HRMS (FAB) calc. for [C₂₂H₂₆NO₃S]⁺: 384.1633, found: 384.1631.



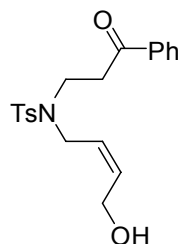
Phenyl(4-(prop-1-enyl)-1-tosylpyrrolidin-3-yl)methanone (14b)

¹H NMR (300 MHz, CDCl₃) δ 1.30 (dd, *J* = 6.4, 1.3 Hz, 3 H), 2.46 (s, 3 H), 3.09 – 3.21 (m, 2 H), 3.58 – 3.72 (m, 3 H), 4.04 (q, *J* = 7.6 Hz, 1 H), 4.76 (ddd, *J* = 15.2, 9.0, 1.3 Hz, 1 H), 5.09 (dq, *J* = 15.2, 6.4 Hz, 1 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.40 – 7.45 (m, 2 H), 7.55 (t, *J* = 7.3 Hz, 1 H), 7.77 (d, *J* = 7.9 Hz, 4 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 17.6, 21.6, 45.3, 48.4, 49.4, 53.5, 126.4, 127.7, 128.1, 128.6, 128.8, 129.7, 133.3, 133.5, 136.8, 143.6, 197.8 ppm. **HRMS (FAB)** calc. for [C₂₁H₂₄NO₃S]⁺: 370.1477, found: 370.1479.



Phenyl(4-(prop-1-enyl)-1-tosylpyrrolidin-3-yl)methanone (14b')

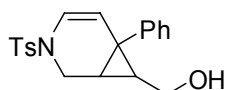
¹H NMR (300 MHz, CDCl₃) δ 1.55 (d, *J* = 6.3 Hz, 3 H), 2.46 (s, 3 H), 2.99 – 3.09 (m, 1 H), 3.20 (dd, *J* = 9.8, 7.7 Hz, 1 H), 3.29 – 3.37 (m, 1 H), 3.45 (dd, *J* = 9.8, 7.8 Hz, 1 H), 3.67 – 3.78 (m, 2 H), 5.26 (ddd, *J* = 15.2, 8.0, 1.2 Hz, 1 H), 5.45 (dq, *J* = 15.2, 6.3 Hz, 1 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.45 (t, *J* = 7.3 Hz, 2 H), 7.58 (t, *J* = 7.4 Hz, 1 H), 7.72 (d, *J* = 8.1 Hz, 2 H), 7.83 (d, *J* = 7.3 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 17.8, 21.6, 44.9, 50.6, 50.9, 52.6, 127.6, 128.4, 128.5, 128.7, 128.9, 129.8, 133.4, 133.6, 136.1, 143.7, 197.8 ppm. **HRMS (EI)** calc. for [C₂₁H₂₄NO₃S]⁺: 370.1477, found: 370.1481.



(Z)-N-(4-hydroxybut-2-enyl)-4-methyl-N-(3-oxo-3-phenylpropyl)benzenesulfonamide (1c)

¹H NMR (500 MHz, CDCl₃) δ 2.24 (s, 1 H), 2.43 (s, 3 H), 3.36 (t, *J* = 6.7 Hz, 2 H), 3.55 (t, *J* = 6.7 Hz, 2 H), 3.94 (d, *J* = 7.1 Hz, 2 H), 4.18 (d, *J* = 6.9 Hz, 2 H), 5.39 (dt, *J* = 11.0, 7.2 Hz, 1 H), 5.78 (dt, *J* = 11.0, 6.9 Hz, 1 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.60 (t, *J* = 7.3 Hz, 1 H), 7.71 (d, *J* = 8.1 Hz, 2 H), 7.94 (d, *J* = 7.4 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 21.5, 39.2, 43.2, 45.9, 57.8, 126.8, 127.1, 128.2, 128.7, 129.8, 132.9, 133.6, 136.3, 136.4, 143.6, 199.0 ppm.

HRMS (FAB) calc. for [C₂₀H₂₄NO₄S]⁺: 374.1426, found: 374.1423.

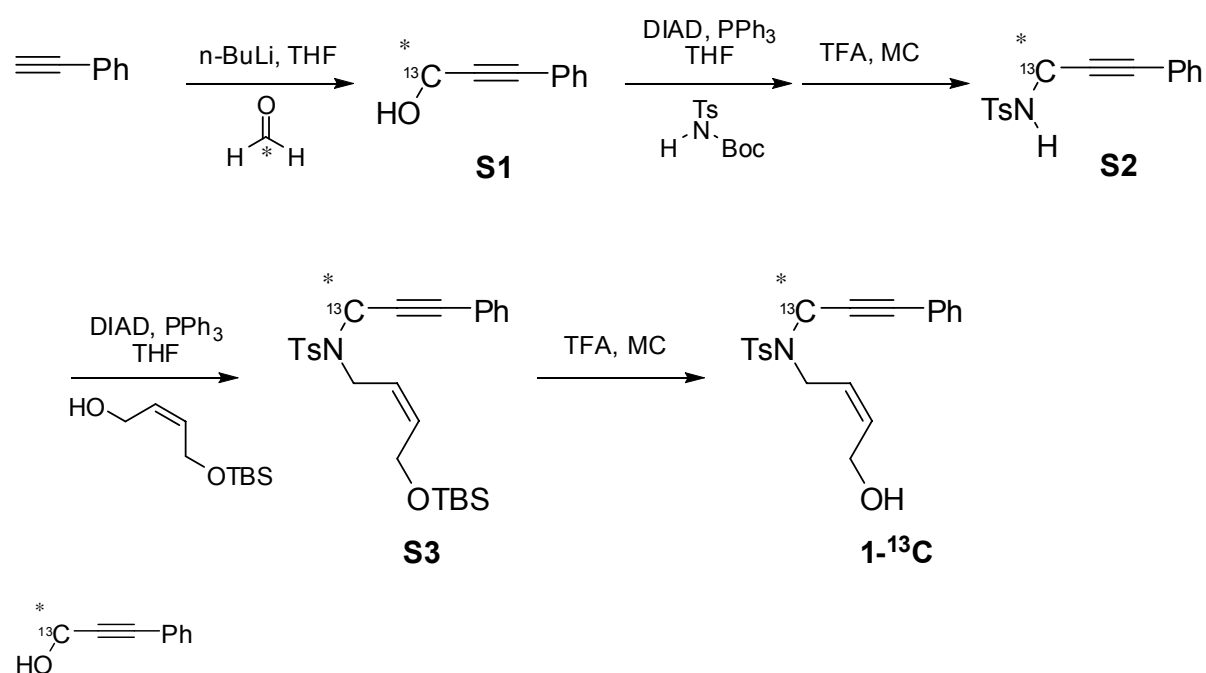


(6-Phenyl-3-tosyl-3-azabicyclo[4.1.0]hept-4-en-7-yl)methanol

¹H NMR (300 MHz, CDCl₃) δ 1.41 (dd, *J* = 13.4, 5.6 Hz, 1 H), 1.57 (s, 1 H), 1.96 – 1.98 (m, 1 H), 2.44 (s, 3 H), 3.12 (dd, *J* = 11.8, 7.8 Hz, 1 H), 3.17 (dd, *J* = 11.7, 2.6 Hz, 1 H), 3.30 (dd, *J* = 11.8, 5.6 Hz, 1 H), 4.09 (d, *J* = 11.7 Hz, 1 H), 5.45 (d, *J* = 8.3 Hz, 1 H), 6.38 (d, *J* = 8.2 Hz, 1 H), 7.20 – 7.36 (m, 5 H), 7.34 (d, *J* = 8.3 Hz, 2 H), 7.69 (d, *J* = 8.1 Hz, 2 H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 21.6, 27.1, 27.4, 34.6, 40.3, 62.1, 116.3, 120.4, 127.1, 127.8, 128.8, 129.9, 131.5, 134.6, 139.7, 144.0 ppm.

HRMS (EI) calc. for [C₂₀H₂₁NO₃S]⁺: 355.1242, found: 355.1240

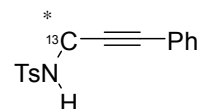
IV. General procedure for preparation of C-13 labeled reactant.



3-Phenylprop-2-yn-1-ol (S1)

A 100 mL schlenk equipped with magnetic stirring bar and rubber septum was charged with phenyl acetylene (0.6 mL, 5.5 mmol) and 20 mL of tetrahydrofuran. The resulting mixture was cooled to -78°C and 2.2 mL of $n\text{-BuLi}$ (5.5 mmol, 2.5 M in hexane solution) was added dropwise. The solution was stirred for 30 min. Then ^{13}C -labeled paraformaldehyde (0.16 g, 5 mmol) was added and the reaction mixture allowed to warm to room temperature. After stirring at room temperature overnight, the solution was washed with saturated NH_4Cl solution and extracted with three 10 mL portion of diethyl ether. The combined ether extracts were dried over anhydrous magnesium sulfate. After filtration, the solvent was removed by rotoevaporation to give crude product. The crude product was purified by flash column chromatography (hexane/ethyl acetate=5/1) and 3-phenylprop-2-yn-1-ol was obtained in 93 % yield. (0.61 g, 4.63 mmol) ^1H NMR (500 MHz, CDCl_3) δ 1.81 (s, 1 H), 4.50 (d, $J = 148.3$ Hz, 2 H), 7.32 - 7.33 (m, 3 H), 7.44 - 7.46 (m, 2 H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ 51.6 ppm.

HRMS (EI) calc. for $[\text{C}_9\text{H}_8\text{O}]^+$: 133.0609, found: 133.0612

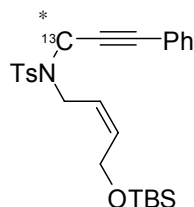


4-Methyl-N-(3-phenylprop-2-ynyl)benzenesulfonamide (S2)

1.21 g of triphenylphosphine (4.63 mmol), 0.92 mL of diisopropylazodicarboxylate (4.63 mmol) and 20 mL of tetrahydrofuran was added to flame dried 100 mL schlenk, and stirred for 10 min. Then tert-

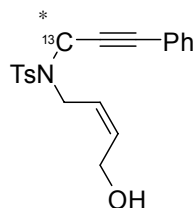
butyl tosylcarbamate (1.26 g, 4.63 mmol) was added and 0.61 g of 3-phenylprop-2-yn-1-ol **S1** was injected another 10 min later. The reaction mixture was stirred overnight and solvent was removed by rotoevaporation. Flash column chromatography with hexane and ethyl acetate (10/1) give 1.73 g of tert-butyl 3-phenylprop-2-ynyl(tosyl)carbamate.

The purified tert-butyl 3-phenylprop-2-ynyl(tosyl)carbamate (1.73 g, 4.5 mmol) was treated with trifluoroacetic acid (1.7 mL, 22.5 mmol) in 20 mL of dichloromethane. After 1 hr, the mixture was washed with NaHCO₃. The organic layer was combined and dried over anhydrous magnesium sulfate. After Flash column chromatography(hexane/ethyl acetate=3/1), 1.04 g (3.96 mmol) of 4-methyl-N-(3-phenylprop-2-ynyl)benzenesulfonamide **S2** was obtained. ¹H NMR (500 MHz, CDCl₃) δ 2.36 (s, 3 H), 4.09 (dd, *J* = 145.1, 6.2 Hz, 2 H), 4.60 (s, 1 H), 7.13 (d, *J* = 8.2 Hz, 2 H), 7.24 – 7.30 (m, 5 H), 7.82 (d, *J* = 8.2 Hz, 2 H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 33.8 ppm. HRMS (EI) calc. for [¹³C₁C₁₅H₁₅NO₂S]⁺: 286.0857, found: 286.0858.



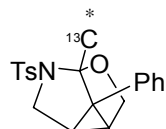
(Z)-N-(4-(tert-butyldimethylsilyloxy)but-2-enyl)-4-methyl-N-(3-phenylprop-2-ynyl)benzenesulfonamide (S3)

To 100 ml Schlenk flask, 1.04 g of triphenylphosphine (3.96 mmol), 0.79 mL of diisopropylazodicarboxylate (3.96 mmol) and 20 mL of tetrahydrofuran was added and stirred for 10 min. 4-methyl-N-(3-phenylprop-2-ynyl)benzenesulfonamide **S2** (1.13 g, 3.96 mmol) was then added. After 10 min, (Z)-4-(tert-butyldimethylsilyloxy)but-2-en-1-ol(0.8 g, 3.96 mmol) was injected. The reaction mixture was stirred overnight and solvent was removed by rotoevaporation. Flash column chromatography with hexane and ethyl acetate (8/1) give 1.7 g (3.6 mmol) of (Z)-N-(4-(tert-butyldimethylsilyloxy)but-2-enyl)-4-methyl-N-(3-phenylprop-2-ynyl)benzenesulfonamide **S3**. ¹H NMR (500 MHz, CDCl₃) δ 0.85 (s, 9 H), 2.36 (s, 3 H), 3.94 – 3.97 (m, 2 H), 4.28 (d, *J* = 5.6Hz, 2 H), 4.32 (d, *J* = 145.8 Hz, 2 H), 5.44 – 5.52 (m, 1 H), 5.82 (dt, *J* = 11.3, 5.6 Hz, 1 H), 7.06 (d, *J* = 6.6 Hz, 2 H), 7.23 – 7.33 (m, 5 H), 7.80 (d, *J* = 8.2 Hz, 2 H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 36.7 ppm. HRMS (FAB) calc. for [¹³C₁C₂₅H₃₆NO₂S]⁺: 471.2219, found: 471.2217.



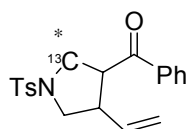
(Z)-N-(4-hydroxybut-2-enyl)-4-methyl-N-(3-phenylprop-2-ynyl)benzenesulfonamide (1-¹³C)

To a solution of tetrabutylammonium fluoride (1.14 g, 3.6 mmol) in 20 mL of tetrahydrofuran, 1.7 g (3.6 mmol) of (Z)-N-(4-(tert-butyldimethylsilyloxy)but-2-enyl)-4-methyl-N-(3-phenylprop-2-ynyl)benzenesulfonamide **S3** was added. The reaction mixture was stirred for 1 hr and the solvent was removed by rotoevaporation. The crude product was purified by flash column chromatography (hexane/ethyl acetate=2/1), then (Z)-N-(4-hydroxybut-2-enyl)-4-methyl-N-(3-phenylprop-2-ynyl)benzenesulfonamide **S4** was obtained in 80 % yield. (1.03 g, 2.88 mmol) ¹H NMR (500 MHz, CDCl₃) δ 1.64 (t, *J* = 5.7 Hz, 1 H), 2.34 (s, 3 H), 3.96 (dd, *J* = 6.6, 4.5 Hz, 2 H), 4.23 (t, *J* = 5.8 Hz, 2 H), 4.30 (d, *J* = 145.9 Hz, 2 H), 5.57 (dt, *J* = 10.9, 7.4 Hz, 1 H), 5.91 (dt, *J* = 10.9, 6.7 Hz, 1 H), 7.07 (dd, *J* = 7.8, 1.3 Hz, 2 H), 7.22 – 7.28 (m, 5 H), 7.77 (d, *J* = 8.2 Hz, 2 H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 36.8 ppm. HRMS (EI) calc. for [¹³C₁C₁₉H₂₁NO₃S]⁺: 356.1276, found: 356.1273.



(1a-¹³C)

¹H NMR (500 MHz, CDCl₃) δ 1.60 (d, *J* = 129.5 Hz, 3 H), 2.06 – 2.17 (m, 2 H), 2.44 (s, 3 H), 2.82 (dd, *J* = 9.8, 1.4 Hz, 1 H), 3.44 (d, *J* = 10.2 Hz, 1 H), 3.97 (dd, *J* = 9.8, 5.4 Hz, 1 H), 4.14 (dd, *J* = 10.2, 5.4 Hz, 1 H), 7.26 – 7.37 (m, 7 H), 7.83 (d, *J* = 8.2 Hz, 2 H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 22.8 ppm. HRMS (EI) calc. for [¹³C₁C₁₉H₂₁NO₃S]⁺: 356.1276, found: 356.1278.



Phenyl(1-tosyl-4-vinylpyrrolidin-3-yl)methanone (1b-¹³C)

¹H NMR (500 MHz, CDCl₃) δ 2.46 (s, 3 H), 3.14 – 3.26 (m, 2 H), 3.37 – 3.48 (m, 1 H), 3.64 – 3.70 (m, 1 H), 3.85 – 3.93 (m, 1 H), 4.05 – 4.13 (m, 1 H), 4.72 (d, *J* = 17.3 Hz, 1 H), 4.78 (d, *J* = 10.4 Hz, 1 H), 5.25 (ddd, *J* = 17.3, 10.4, 9.1 Hz, 1 H), 7.36 (d, *J* = 8.2 Hz, 2 H), 7.41 – 7.47 (m, 2 H), 7.56 (t, *J*

= 7.3 Hz, 1 H), 7.77 (d, J = 8.8 Hz, 2 H), 7.81 (d, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 48.4 ppm. HRMS (EI) calc. for $[\text{C}_{19}\text{H}_{21}\text{NO}_3\text{S}]^+$: 356.1276, found: 356.1281.

V. X-ray analysis

Diffraction data were measured by a Bruker-Nonius CCD single-crystal X-ray diffractometer at room temperature by using graphite-monochromated Mo $\text{K}\alpha$ radiation (λ = 0.71073 Å). Preliminary orientation matrices and unit cell parameters were obtained from the peaks of the first 10 frames and then refined using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects using DENZO. The structure was solved by direct methods using SHELXS-97, and refined by full-matrix least-squares with SHELXL-97. All non-hydrogen atoms were refined anisotropically and hydrogen atoms except some were treated as idealized contributions.

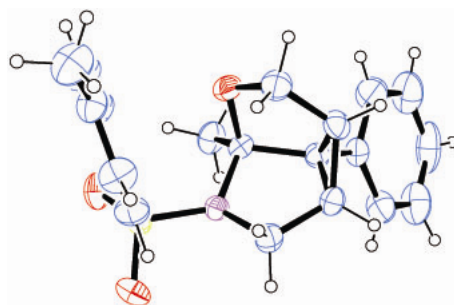


Figure S_A1. An ORTEP drawing of **1a** with 30% probability of thermal ellipsoids.

Table S_A1. Crystal data and structure refinement for **1a**.

Identification code	1a	
Empirical formula	$\text{C}_{20}\text{H}_{21}\text{NO}_3\text{S}$	
Formula weight	355.44	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/a	
Unit cell dimensions	$a = 7.8824(4)$ Å	$a = 90^\circ$.
	$b = 13.2869(7)$ Å	$b = 98.799(3)^\circ$.
	$c = 17.5082(9)$ Å	$c = 90^\circ$.
Volume	$1812.10(16)$ Å ³	

Z	4
Density (calculated)	1.303 Mg/m ³
Absorption coefficient	0.197 mm ⁻¹
F(000)	752
Crystal size	0.2 x 0.2 x 0.2 mm ³
Theta range for data collection	3.07 to 27.47°.
Index ranges	-10<=h<=10, -17<=k<=15, -22<=l<=22
Reflections collected	7365
Independent reflections	4130 [R(int) = 0.0414]
Completeness to theta = 27.47°	99.4 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4130 / 0 / 310
Goodness-of-fit on F ²	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0516, wR2 = 0.1192
R indices (all data)	R1 = 0.0996, wR2 = 0.1383
Largest diff. peak and hole	0.178 and -0.215 e.Å ⁻³

VI. NMR Spectra

