Supporting Information for:

Platinum Dichloride-Catalyzed Cycloisomerization of Ene-ynamides

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1. Synthesis of precursors: a representative example.

N-tert-butoxycarbonyl-*N*-(4-methylpent-4-enyl)-4-methylbenzenesulfonamide **20**.

$\text{C}_{18}\text{H}_{27}\text{O}_4\text{NS}$
 $M = 353.48 \text{ g/mol}$

Ts-NH-Boc (12.25 g, 45.2 mmol, 1 equiv.), PPh_3 (11.86 g, 45.2 mmol, 1 equiv.) and 4-methylpent-4-en-1-ol (4.52 g, 45.2 mmol, 1 equiv.) were introduced in 100 mL of THF. The mixture was cooled to 0°C and 8.96 mL (45.2 mmol, 1 equiv.) of DIAD were added dropwise. After stirring for 5 minutes, the mixture was allowed to warm up to r.t. and stirred for 1h. The solvent was removed and the residue was purified by flash column chromatography on silica gel (PE/Et₂O-9/1 to 4/1) to give **20** (14.43 g, 90 %) as a yellow oil.

¹H NMR (400 MHz, CDCl₃):

δ 1.35 (s, 9H, Boc), 1.77 (s, 3H, $\text{CH}_2=\text{C}(\text{CH}_3)-$), 1.91-1.95 (m, 2H, N-CH₂-CH₂), 2.08-2.12 (m, 2H, N-CH₂-CH₂-CH₂), 2.44 (s, 3H, Ts), 3.83 (t, $J = 7.6 \text{ Hz}$, 2H, N-CH₂), 4.76 (br s, 2H, $\text{CH}_2=$), 7.31 (d, $J = 8.2 \text{ Hz}$, 2H, Ts), 7.79 (d, $J = 8.2 \text{ Hz}$, 2H, Ts).

¹³C NMR (100 MHz, CDCl₃):

δ 21.5 and 22.2 (Ts + $\text{CH}_2-\text{C}(\text{CH}_3)-$), 27.8 (3C, Boc), 31.8 (N-CH₂-CH₂), 34.7 (N-CH₂-CH₂-CH₂), 46.9 (N-CH₂), 83.9 ($\text{C}(\text{CH}_3)_3$), 110.4 ($\text{CH}_2=$), 127.7 (2 CH, Ts), 129.2 (2 CH, Ts), 137.5 (SO_2-C), 144.0 and 144.4 ($\text{CH}_2=\text{C}(\text{CH}_3)-$ + CH_3-C), 150.9 (C=O).

IR (ATR):

2984, 1718, 1649, 1350, 1152 cm^{-1} .

Elemental analysis:

Calculated for $C_{18}H_{27}O_4NS$: C, 61.17 ; H, 7.69 ; N, 3.96. Found: C, 61.00 ; H, 7.77 ; N, 4.10.

***N*-(4-methylpent-4-enyl)-4-methylbenzenesulfonamide 21:** consistent with literature (Larock, R. C.; Yang, H.; Weinreb, S. M.; Herr, R. J. *J. Org. Chem.* **1994**, 59, 4172).

$C_{13}H_{19}O_2NS$
M = 253.36 g/mol

In a flask containing a solution of **I** (13.94 g, 39.49 mmol, 1 equiv.) in methanol (400 mL) was added K_2CO_3 (27.29 g, 197.45 mmol, 5 equiv.). After refluxing for 3 h, water (100 mL) was introduced and the aqueous layer was extracted with CH_2Cl_2 . The organic layer was washed with brine, dried over $MgSO_4$ and concentrated to give **II** (9.99 g, 100 %) as a yellow oil.

***N*-formyl-*N*-(4-methylpent-4-enyl)-4-methylbenzenesulfonamide 22.**

$C_{14}H_{19}O_3NS$
M = 281.37 g/mol

Under argon, *n*-BuLi (18.8 mL, 2.3 M solution in hexane, 43.16 mmol, 1.1 equiv.) was added to a solution of **II** (9.93 g, 39.23 mmol, 1 equiv.) in THF (200 mL) at 0°C. After stirring for 5 minutes, *N*-formylbenzotriazole (6.92 g, 47.08 mmol, 1.2 equiv.) was added, and the mixture was stirred at r.t. for 1 h. After addition of saturated $NaHCO_3$ aq., the aqueous layer was extracted with Et_2O . The organic layer was washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography on silica gel (PE/ Et_2O -9/1 to 4/1) to give **III** (9.85 g, 89 %) as a colorless oil.

 1H NMR (200 MHz, $CDCl_3$):

δ 1.66 (s, 3H, $CH_2=C(CH_3)-$), 1.58-1.70 (m, 2H, N- CH_2-CH_2), 1.95 (t, J = 8.3 Hz, 2H, N- $CH_2-CH_2-CH_2$), 2.44 (s, 3H, Ts), 3.40 (t, J = 7.8 Hz, 2H, N- CH_2), 4.62 (br s, 1H, $CHH=$), 4.69 (br s, 1H, $CHH=$), 7.36 (d, J = 8.0 Hz, 2H, Ts), 7.74 (d, J = 8.0 Hz, 2H, Ts), 9.09 (s, 1H, CHO).

 ^{13}C NMR (50 MHz, $CDCl_3$):

δ 21.6 and 22.1 (Ts + $CH_2-C(CH_3)-$), 25.7 (N- CH_2-CH_2), 34.6 (N- $CH_2-CH_2-CH_2$), 42.4 (N- CH_2), 110.6 ($CH_2=$), 127.3 (2 CH, Ts), 130.3 (2 CH, Ts), 135.0 (SO_2-C), 144.0 and 145.4 ($CH_3-C + CH_2=C(CH_3)-$), 161.2 ($C=O$).

IR (ATR):

3072, 2935, 1697, 1650, 1596, 1355, 1161 cm^{-1} .

Elemental analysis:

Calculated for $C_{14}H_{19}O_3NS$: C, 59.77 ; H, 6.80 ; N, 4.98. Found: C, 59.67 ; H, 6.89 ; N, 5.15.

***N*-(2,2-dichlorovinyl)-*N*-(4-methylpent-4-enyl)-4-methylbenzenesulfonamide 23.**

C₁₅H₁₉O₂NSCl₂
 M = 348.29 g/mol
 Solid, m.p. = 85°C

To a solution of **III** (9.79 g, 34.83 mmol, 1 equiv.) and PPh₃ (27.41 g, 104.49 mmol, 3 equiv.) in THF (350 mL) at 60°C was added 33.7 mL of CCl₄ (348.29 mmol, 10 equiv.) over 6 h. After addition of saturated NaHCO₃ aq., the aqueous layer was extracted with Et₂O. The organic layer was washed with brine, dried over MgSO₄, and concentrated. The residue was purified by flash column chromatography on silica gel (PE/Et₂O-9/1, then PE/EA-9/1 to 4/1) to give **IV** (12.12 g, 100 %) as a yellow solid.

¹H NMR (400 MHz, CDCl₃):

δ 1.60-1.68 (m, 2H, N-CH₂-CH₂), 1.68 (s, 3H, CH₂=C(CH₃)-), 2.01 (t, *J* = 7.5 Hz, 2H, N-CH₂-CH₂-CH₂), 2.42 (s, 3H, Ts), 3.29 (t, *J* = 7.3 Hz, 2H, N-CH₂), 4.65 (br s, 1H, CHH=), 4.71 (br s, 1H, CHH=), 6.25 (s, 1H, CH-CCl₂), 7.31 (d, *J* = 8.1 Hz, 2H, Ts), 7.67 (d, *J* = 8.1 Hz, 2H, Ts).

¹³C NMR (100 MHz, CDCl₃):

δ 21.6 and 22.4 (Ts + CH₂-C(CH₃)-), 26.4 (N-CH₂-CH₂), 34.6 (N-CH₂-CH₂-CH₂), 49.0 (N-CH₂), 110.7 (CH₂=), 124.8 (CCl₂), 125.0 (CH-CCl₂), 127.3 (2 CH, Ts), 130.0 (2 CH, Ts), 135.4 (SO₂-C), 144.2 and 144.4 (CH₃-C + CH₂=C(CH₃)-).

IR (ATR):

3067, 2969, 1650, 1598, 1353, 1164 cm⁻¹.

Ynamide 15.

C₁₅H₁₉O₂NS
 M = 277.38 g/mol
 Solid, m.p. = 49°C

Under argon, *n*-BuLi (9.57 mL, 2.3 M solution in hexane, 22 mmol, 2.2 equiv.) was added to a solution of **IV** (3.48 g, 10 mmol, 1 equiv.) in anhydrous THF (50 mL) at -78°C and the mixture was stirred during 45 min. 80 μL (2 mmol, 0.2 equiv.) of MeOH was then added and the mixture was allowed to warm up to r.t. over 1 h 30. After addition of saturated NaHCO₃ aq., and the aqueous layer was extracted with Et₂O. The organic layer was washed with brine, dried over MgSO₄, and concentrated. The residue was purified by flash column chromatography on silica gel (pentane/EA/NEt₃-90/10/1) to give **15** (1.97 g, 71 %) as a yellow solid.

¹H NMR (400 MHz, CDCl₃):

δ 1.66 (s, 3H, CH₂=C(CH₃)-), 1.72-1.80 (m, 2H, N-CH₂-CH₂), 1.98-2.01 (m, 2H, N-CH₂-CH₂-CH₂), 2.41 (s, 3H, Ts), 2.74 (s, 1H, C≡CH), 3.27 (t, *J* = 6.4 Hz, 2H, N-CH₂), 4.64 (s, 1H, CHH=), 4.70 (s, 1H, CHH=), 7.33 (d, *J* = 7.8 Hz, 2H, Ts), 7.77 (d, *J* = 7.8 Hz, 2H, Ts).

¹³C NMR (100 MHz, CDCl₃):

δ 21.5 and 22.4 (Ts + CH₂-C(CH₃)-), 25.4 (N-CH₂-CH₂), 34.0 (N-CH₂-CH₂-CH₂), 50.7 (N-CH₂), 59.1 (C≡CH), 75.9 (C≡CH), 110.6 (CH₂=), 127.5 (2 CH, Ts), 129.7 (2 CH, Ts), 134.4 (SO₂-C), 144.0 and 144.7 (CH₃-C + CH₂=C(CH₃)-).

IR (ATR):

3294, 3073, 2933, 2132, 1650, 1596, 1362, 1166 cm^{-1} .

Elemental analysis:

Calculated for $\text{C}_{15}\text{H}_{19}\text{O}_2\text{NS}$: C, 64.95 ; H, 6.90 ; N, 5.05. Found: C, 64.82 ; H, 7.05 ; N, 5.09.

Ynamides **3**, **5**, **7** and **17** were prepared according to this method.

Ynamide 3: consistent with literature (ref. 2a). Yield = 82 %.

$\text{C}_{14}\text{H}_{17}\text{O}_2\text{NS}$
M = 263,36 g/mol

Elemental analysis:

Calculated for $\text{C}_{14}\text{H}_{17}\text{O}_2\text{NS}$: C, 63.85 ; H, 6.51 ; N, 5.32. Found: C, 63.73 ; H, 6.70 ; N, 5.38.

Ynamide 5: consistent with literature (ref. 2a). Yield = 69 %.

$\text{C}_{16}\text{H}_{21}\text{O}_2\text{NS}$
M = 291,41 g/mol
Solid, m.p. = 53°C

Ynamide 7.

$\text{C}_{17}\text{H}_{23}\text{O}_2\text{NS}$
M = 305.44 g/mol
Solid, m.p. = 38°C

Yield = 56 %.

 ^1H NMR (200 MHz, CDCl_3):

δ 1.03 (s, 6H, 2 CH_3), 1.41-1.50 (m, 2H, $=\text{CH}-\text{CH}_2-\text{CH}_2$), 1.99-2.11 (m, 2H, $=\text{CH}-\text{CH}_2$), 2.46 (s, 3H, Ts), 2.70 (s, 1H, $\text{C}\equiv\text{CH}$), 3.15 (s, 2H, N- CH_2), 4.92-5.07 (m, 2H, $\text{CH}_2=$), 5.81 (ddt, $J=17.0, 10.1, 6.4$ Hz, 1H, $\text{CH}_2=\text{CH}$), 7.37 (d, $J=8.2$ Hz, 2H, Ts), 7.82 (d, $J=8.2$ Hz, 2H, Ts).

 ^{13}C NMR (50 MHz, CDCl_3):

δ 21.6 (Ts), 25.2 (2C, 2 CH_3), 28.2 ($=\text{CH}-\text{CH}_2-\text{CH}_2$), 35.7 ($\text{C}(\text{CH}_3)_2$), 38.8 ($=\text{CH}-\text{CH}_2$), 58.3 ($\text{C}\equiv\text{CH}$), 61.5 (N- CH_2), 78.7 ($\text{C}\equiv\text{CH}$), 114.2 ($\text{CH}_2=$), 127.8 (2 CH , Ts), 129.7 (2 CH , Ts), 134.3 (SO_2-C), 138.9 ($=\text{CH}$), 144.7 (CH_3-C).

IR (ATR):

3276, 3081, 2968, 2133, 1643, 1598, 1355, 1168 cm^{-1} .

Elemental analysis:

Calculated for $\text{C}_{17}\text{H}_{23}\text{O}_2\text{NS}$: C, 66.85 ; H, 7.59 ; N, 4.59. Found: C, 66.67 ; H, 7.78 ; N, 4.62.

Ynamide 13.

$C_{17}H_{23}O_2NS$
 $M = 305.44 \text{ g/mol}$

To a solution of LiHMDS (343 mg, 2.13 mmol, 1.3 equiv.) in THF (8 mL) at -78°C was added *n*-BuLi (0.92 mL, 2.3 M solution in hexane, 2.13 mmol, 1.3 equiv.). The mixture was stirred for 10 min, then a solution of ynamide **5** (476 mg, 1.64 mmol, 1 equiv.) in THF (8 mL) was cannulated. The reaction medium was allowed to warm up to -40°C and was stirred for 1 h, and then 0.51 mL of MeI (8.18 mmol, 5 equiv.) was slowly added. The mixture was stirred for 30 min. at -40°C , then allowed to warm up to r.t. and stirred for 20 h. To the mixture was added saturated NaHCO_3 aq., and the aqueous layer was extracted with Et_2O . The organic layer was washed with brine, dried over MgSO_4 , and concentrated. The residue was purified by flash column chromatography on silica gel (pentane/EA-95/5) to give **13** (420 mg, 84 %).

^1H NMR (400 MHz, CDCl_3):

δ 0.98 (s, 6H, 2 CH_3), 1.84 (s, 3H, $\text{CH}_3\text{-C}\equiv\text{C}$), 2.08 (d, $J = 7.6 \text{ Hz}$, 2H, $\text{N-CH}_2\text{-C}(\text{CH}_3)_2\text{-CH}_2$), 2.44 (s, 3H, Ts), 3.06 (s, 2H, N-CH_2), 4.99-5.06 (m, 2H, $\text{CH}_2=$), 5.80 (m, $J = 16.9, 10.4, 7.3 \text{ Hz}$, 1H, $\text{CH}_2\text{-CH-}$), 7.33 (d, $J = 8.2 \text{ Hz}$, 2H, Ts), 7.76 (d, $J = 8.2 \text{ Hz}$, 2H, Ts).

^{13}C NMR (100 MHz, CDCl_3):

δ 3.3 ($\text{CH}_3\text{-C}\equiv\text{C}$), 21.7 (Ts), 25.2 (2C, 2 CH_3), 35.8 ($\text{C}(\text{CH}_3)_2$), 44.5 ($\text{N-CH}_2\text{-C}(\text{CH}_3)_2\text{-CH}_2$), 61.8 (N-CH_2), 64.8 ($\text{CH}_3\text{-C}\equiv\text{C}$), 74.9 ($\text{CH}_3\text{-C}\equiv\text{C}$), 117.8 ($\text{CH}_2=$), 127.8 (2 CH, Ts), 129.7 (2 CH, Ts), 134.6 and 134.7 ($\text{CH}_2=\text{CH-} + \text{SO}_2\text{-C}$), 144.3 ($\text{CH}_3\text{-C}$).

IR (ATR):

3074, 2966, 2259, 1638, 1597, 1363, 1170 cm^{-1} .

Elemental analysis:

Calculated for $C_{17}H_{23}O_2NS$: C, 66.85 ; H, 7.59 ; N, 4.59. Found: C, 67.21 ; H, 7.69 ; N, 4.26.

Ynamide 17.

$C_{17}H_{23}O_2NS$
 $M = 305.44 \text{ g/mol}$
 Solid, m.p. = 77°C

Yield = 66 %.

^1H NMR (400 MHz, CDCl_3):

δ 1.05 (s, 6H, 2 CH_3), 1.78 (s, 3H, $\text{CH}_2=\text{C}(\text{CH}_3)\text{-}$), 2.07 (s, 2H, $\text{N-CH}_2\text{-C}(\text{CH}_3)_2\text{-CH}_2$), 2.45 (s, 3H, Ts), 2.68 (s, 1H, $\text{C}\equiv\text{CH}$), 3.16 (s, 2H, N-CH_2), 4.67 (br s, 1H, CHH=), 4.88 (br s, 1H, CHH=), 7.35 (d, $J = 8.2 \text{ Hz}$, 2H, Ts), 7.80 (d, $J = 8.2 \text{ Hz}$, 2H, Ts).

^{13}C NMR (100 MHz, CDCl_3):

δ 21.8 (Ts), 25.6 (3C, 3 CH_3), 36.7 ($\text{C}(\text{CH}_3)_2$), 48.0 ($\text{N-CH}_2\text{-C}(\text{CH}_3)_2\text{-CH}_2$), 58.5 ($\text{C}\equiv\text{CH}$), 63.0 (N-CH_2), 79.0 ($\text{C}\equiv\text{CH}$), 115.3 ($\text{CH}_2=$), 128.0 (2 CH, Ts), 129.9 (2 CH, Ts), 134.5 ($\text{SO}_2\text{-C}$), 142.5 and 144.8 ($\text{CH}_2=\text{C}(\text{CH}_3)\text{-} + \text{CH}_3\text{-C}$).

IR (ATR):

3274, 3070, 2964, 2133, 1638, 1597, 1355, 1168 cm⁻¹.

Elemental analysis:

Calculated for C₁₇H₂₃O₂NS: C, 66.85 ; H, 7.59 ; N, 4.59. Found: C, 67.00 ; H, 7.82 ; N, 4.38.

2. Cycloisomerizations

General procedure: In a dry schlenk under argon was introduced 0.5 mmol of ynamide in 20 mL of anhydrous toluene. The reaction medium was degassed by the freeze-pump-thaw method and the reaction vessel was plunged in a pre-heated oil bath (80°C). PtCl₂ (7 mg, 0.025 mmol, 0.05 equiv.) was then added, and the mixture was stirred until the IR spectrum indicated the vanishing of the C≡C bond. The solvent was removed and the residue was purified by flash chromatography (PE/Et₂O/NEt₃-85/15/1) to give the desired cyclization product.

Dienamide 2: consistent with literature (ref. 2a). Yield = 98 %.

C₁₃H₁₅O₂NS
M = 249.33 g/mol

Bicyclic enamide 4.

C₁₄H₁₇O₂NS
M = 263.36 g/mol

Yield = 44 %.

¹H NMR (400 MHz, C₆D₆):

δ 1.18-1.21 (m, 2H, N-CH₂-CH₂), 1.35-1.38 (m, 2H, N-CH₂-CH₂-CH₂), 1.86 (s, 3H, Ts), 2.15-2.18 (m, 2H, N-C-CH₂), 3.09 (quint., J=3.2 Hz, 2H, N-C-CH₂-CH₂), 3.20-3.22 (m, 2H, N-CH₂), 6.77 (d, J=8.1 Hz, 2H, Ts), 7.72 (d, J=8.1 Hz, 2H, Ts).

¹³C NMR (100 MHz, C₆D₆):

δ 21.1 (Ts), 22.0 (N-CH₂-CH₂-CH₂), 22.5 (N-CH₂-CH₂), 28.7 (N-C-CH₂), 33.1 (N-C-CH₂-CH₂), 45.7 (N-CH₂), 122.3 (N-C=C), 127.6 (2 CH, Ts), 129.8 (2 CH, Ts), 134.2, 136.8 (N-C=C + SO₂-C), 143.1 (CH₃-C).

IR (ATR):

3074, 2920, 1691, 1597, 1353, 1166 cm⁻¹.

Bicyclic enamide 6.

C₁₆H₂₁O₂NS
M = 291.41 g/mol

Yield = 71 %.

¹H NMR (400 MHz, C₆D₆):

δ 0.69 (s, 6H, 2 CH₃), 1.31 (bs, 2H, N-CH₂-C(CH₃)₂-CH₂), 1.84 (s, 3H, Ts), 2.20 (bs, 2H, N-C-CH₂), 2.94 (s, 2H, N-CH₂), 3.11 (m, *J*=2.8 Hz, 2H, N-C-CH₂-CH₂), 6.79 (d, *J*=8.2 Hz, 2H, Ts), 7.76 (d, *J*=8.2 Hz, 2H, Ts).

¹³C NMR (100 MHz, C₆D₆):

δ 21.1 (Ts), 26.6 (2C, 2 CH₃), 28.5 (N-C-CH₂), 31.6 (C-(CH₃)₂), 32.0 (N-C-CH₂-CH₂), 36.6 (N-CH₂-C(CH₃)₂-CH₂), 55.9 (N-CH₂), 118.9 (N-C=C), 127.6 (2 CH, Ts), 129.8 (2 CH, Ts), 132.6, 137.2 (N-C=C + SO₂-C), 143.1 (CH₃-C).

IR (ATR):

2958, 2927, 1696, 1598, 1356, 1163 cm⁻¹.

3. Ozonolysis

General one-pot procedure (cycloisomerization-ozonolysis): in a dry schlenk under argon was introduced 0.5 mmol of ynamide in 20 mL of anhydrous toluene. The reaction medium was degassed by the freeze-pump-thaw method and the reaction vessel was plunged in a pre-heated oil bath (80°C). PtCl₂ (7 mg, 0.025 mmol, 0.05 equiv.) was then added, and the mixture was stirred until the IR spectrum indicated the end of the reaction. The solvent was removed and CH₂Cl₂ (20 mL) was added. The mixture was cooled down to -78°C and O₃ was allowed to bubble in the solution until the mixture becomes blue. 1 mL of SMe₂ was then added and the mixture was allowed to warm up to r.t. over 2 h. The solvent was removed and the residue was purified by flash chromatography (pentane/EA-9/1 to 1/1) to give the desired lactam.

Ketolactam 8.

C₁₄H₁₇O₄NS
M = 295.35 g/mol

¹H NMR (400 MHz, CDCl₃):

δ 2.13-2.20 (m, 2H, N-CH₂-CH₂), 2.46 (s, 3H, Ts), 2.54 (t, *J*=6.4 Hz, 2H, N-CH₂-CH₂-CH₂), 2.68-2.76 (m, 4H, O=C-CH₂-CH₂-C=O), 4.00 (t, *J*=5.7 Hz, 2H, N-CH₂), 7.35 (d, *J*=8.2 Hz, 2H, Ts), 7.91 (d, *J*=8.2 Hz, 2H, Ts).

¹³C NMR (100 MHz, CDCl₃):

δ 21.9 (Ts), 27.9 (N-CH₂-CH₂), 33.0 + 46.6 (O=C-CH₂-CH₂-C=O), 37.8 (N-CH₂-CH₂-CH₂), 46.6 (N-CH₂), 129.3 (2 CH, Ts), 129.4 (2 CH, Ts), 135.6 (SO₂-C), 145.3 (CH₃-C), 172.3 (N-C=O), 211.4 (C=O).

IR (ATR):

2924, 2854, 1694, 1597, 1340, 1157 cm⁻¹.

HRMS:

m/z calcd for $C_{14}H_{17}O_4NS$ (MH⁺) 318.0776; found 318.0792.

Ketolactam 9.

$C_{16}H_{21}O_4NS$
M = 323.41 g/mol

¹H NMR (400 MHz, CDCl₃):

δ 1.19 (s, 6H, 2 CH₃), 2.42 (s, 3H, Ts), 2.44 (s, 2H, C(CH₃)₂-CH₂-C=O), 2.65 (s, 4H, O=C-CH₂-CH₂-C=O), 3.87 (bs, 2H, N-CH₂), 7.29 (d, J =8.2 Hz, 2H, Ts), 7.84 (d, J =8.2 Hz, 2H, Ts).

¹³C NMR (100 MHz, CDCl₃):

δ 21.8 (Ts), 27.2 (2C, 2 CH₃), 32.5 + 43.7 (2C, O=C-CH₂-CH₂-C=O), 37.5 (C(CH₃)₂), 51.0 (C(CH₃)₂-CH₂-C=O), 56.5 (N-CH₂), 129.2 (2 CH, Ts), 129.3 (2 CH, Ts), 136.1 (SO₂-C), 145.0 (CH₃-C), 172.7 (N-C=O), 208.5 (C=O).

IR (ATR):

2966, 1698, 1597, 1345, 1167 cm⁻¹.

Ketolactam 10.

$C_{17}H_{23}O_4NS$
M = 337.43 g/mol

¹H NMR (400 MHz, CDCl₃):

δ 1.11 (s, 6H, 2 CH₃), 1.66 (t, J =6.7 Hz, 2H, C(CH₃)₂-CH₂-CH₂-C=O), 2.40 (s, 3H, Ts), 2.47 (t, J =6.7 Hz, 2H, C(CH₃)₂-CH₂-CH₂-C=O), 2.60-2.67 (m, 4H, O=C-CH₂-CH₂-C=O), 3.74 (s, 2H, N-CH₂), 7.28 (d, J =8.2 Hz, 2H, Ts), 7.79 (d, J =8.2 Hz, 2H, Ts).

¹³C NMR (100 MHz, CDCl₃):

δ 21.8 (Ts), 26.8 (2C, 2 CH₃), 31.3 (C(CH₃)₂-CH₂-CH₂-C=O), 33.9 + 36.9 (2C, O=C-CH₂-CH₂-C=O), 36.6 (C(CH₃)₂), 39.7 (C(CH₃)₂-CH₂-CH₂-C=O), 54.7 (N-CH₂), 129.1 (2 CH, Ts), 129.4 (2 CH, Ts), 136.2 (SO₂-C), 144.9 (CH₃-C), 174.3 (N-C=O), 212.6 (C=O).

IR (ATR):

2957, 2871, 1688, 1596, 1348, 1164 cm⁻¹.

4. Hydrolysis

General one-pot procedure (cycloisomerization-hydrolysis): in a dry schlenk under argon was introduced 0.5 mmol of ynamide in 20 mL of anhydrous toluene. The reaction medium was degassed during 10 minutes. 7 mg of PtCl₂ (0.025 mmol, 0.05 equiv.) were

added and the reaction vessel was plunged in a pre-heated oil bath (80°C). At the end of 10 min., 7 mg of PtCl₂ (0.025 mmol, 0.05 equiv.) were added. The mixture was stirred until the IR spectrum indicated the end of the reaction. Then, the mixture was fastly cooled to r.t. with a water bath, and 2.5 mL (2.5 mmol, 5 equiv.) of HCl 1M were added with 20 mL of ethyl acetate. The resulting mixture was stirred during 2 hours. The mixture was then neutralized with a saturated solution of NaHCO₃, the organic layer was washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography (pentane/EA-6/4) to give the desired cyclobutanone.

Cyclobutanone 11.

C₁₄H₁₉O₃NS
M = 281.37 g/mol

¹H NMR (400 MHz, CDCl₃):

δ 1.47-1.66 (m, 5H, N-CH₂-CH₂-CH₂ + O=C-CH₂-CHH), 2.16 (m, 1H, O=C-CH₂-CHH), 2.42 (s, 3H, Ts), 2.83-3.08 (m, 4H, N-CH₂ + O=C-CH₂), 3.22 (m, 1H, CH-C=O), 4.63 (t, *J* = 6.3 Hz, 1H, NH), 7.31 (d, *J* = 8.5 Hz, 2H, Ts), 7.73 (d, *J* = 8.5 Hz, 2H, Ts).

¹³C NMR (100 MHz, CDCl₃):

δ 16.8 (N-CH₂-CH₂), 21.5 (Ts), 26.4 and 27.1 (O=C-CH₂-CH₂-CH₂), 42.8 (N-CH₂), 44.4 (O=C-CH₂), 59.6 (C-C=O), 127.0 (2 CH, Ts), 129.7 (2 CH, Ts), 136.8 (SO₂-C), 143.4 (CH₃-C), 212.1 (C=O).

IR (ATR):

3282, 2925, 1772, 1598, 1325, 1157 cm⁻¹.

Cyclobutanone 12.

C₁₆H₂₃O₃NS
M = 309.42 g/mol

¹H NMR (400 MHz, CDCl₃):

δ 0.84 (s, 3H, CH₃), 0.91 (s, 3H, CH₃), 1.30 (dd, *J*=14.6, 6.4 Hz, 1H, N-CH₂-C(CH₃)₂-CHH), 1.58 (m, 1H, O=C-CH₂-CHH), 1.73 (dd, *J*=14.6, 6.8 Hz, 1H, N-CH₂-C(CH₃)₂-CHH), 2.22 (m, 1H, O=C-CH₂-CHH), 2.58 (ABX, 1H, N-CHH), 2.66 (ABX, 1H, N-CHH), 2.85 (m, 1H, O=C-CHH), 3.04 (m, 1H, O=C-CHH), 3.25 (m, 1H, O=C-CH), 5.22 (t, *J*=7.2 Hz, 1H, NH), 7.30 (d, *J*=8.1 Hz, 2H, Ts), 7.74 (d, *J*=8.1 Hz, 2H, Ts).

¹³C NMR (100 MHz, CDCl₃):

δ 18.9 (O=C-CH₂-CH₂), 21.6 (Ts), 24.9 (CH₃), 26.1 (CH₃), 34.1 (C(CH₃)₂), 39.0 (N-CH₂-C(CH₃)₂-CH₂), 44.7 (O=C-CH₂), 52.6 (N-CH₂), 56.4 (C*), 127.1 (2 CH, Ts), 129.8 (2 CH, Ts), 137.3 (SO₂-C), 143.3 (CH₃-C), 212.6 (C=O).

IR (ATR):

3281, 3064, 2959, 1772, 1598, 1327, 1157 cm⁻¹.

Elemental analysis:

Calculated for C₁₆H₂₃O₃NS: C, 62.11 ; H, 7.48 ; N, 4.53. Found: C, 61.97 ; H, 7.58 ; N, 4.51.

Cyclobutanone 14.

C₁₇H₂₅O₃NS
M = 323.45 g/mol

¹H NMR (400 MHz, CDCl₃):

δ 0.83 (s, 3H, CH₃), 0.88 (s, 3H, CH₃), 1.18 (d, *J* = 7.6 Hz, 3H, O=C-CH(CH₃)-), 1.37 (dd, *J* = 14.5, 7.1 Hz, 1H, N-CH₂-C(CH₃)₂-CHH), 1.69 (dd, *J* = 14.5, 7.1 Hz, 1H, N-CH₂-C(CH₃)₂-CHH), 1.82 (t, *J* = 8.1 Hz, 2H, O=C-CH(CH₃)-CH₂), 2.41 (s, 3H, Ts), 2.60 (ABX, 1H, N-CHH), 2.65 (ABX, 1H, N-CHH), 3.14-3.30 (m, 2H, O=C-CH(CH₃)- + O=C-CH(CH₃)-CH₂-CH), 5.25 (t, *J* = 7.1 Hz, 1H, NH), 7.29 (d, *J* = 8.2 Hz, 2H, Ts), 7.74 (d, *J* = 8.2 Hz, 2H, Ts).

¹³C NMR (100 MHz, CDCl₃):

δ 15.3 (O=C-CH(CH₃)-), 21.6 (Ts), 24.9 and 25.8 (2C, 2 CH₃), 21.2 (O=C-CH(CH₃)-CH₂), 34.2 (N-CH₂-C(CH₃)₂-), 39.8 (N-CH₂-C(CH₃)₂-CH₂), 52.7 (N-CH₂), 52.2 and 53.5 (O=C-CH(CH₃)- + O=C-CH(CH₃)-CH₂-CH), 127.0 (2 CH, Ts), 129.7 (2 CH, Ts), 137.1 (SO₂-C), 143.3 (CH₃-C), 216.8 (C=O).

IR (ATR):

3283, 2960, 1768, 1599, 1327, 1158 cm⁻¹.

Cyclobutanone 16.

C₁₅H₂₁O₃NS
M = 295.40 g/mol

¹H NMR (400 MHz, CDCl₃):

δ 1.10 (s, 3H, CH₃-C-C=O), 1.37-1.56 (m, 4H, N-CH₂-CH₂-CH₂), 1.68 (m, 1H, O=C-CH₂-CHH), 1.81 (m, 1H, O=C-CH₂-CHH), 2.41 (s, 3H, Ts), 2.85-3.02 (m, 4H, N-CH₂ + O=C-CH₂), 5.22 (t, *J* = 6.1 Hz, 1H, NH), 7.29 (d, *J* = 7.9 Hz, 2H, Ts), 7.73 (d, *J* = 7.9 Hz, 2H, Ts).

¹³C NMR (100 MHz, CDCl₃):

δ 20.4 (CH₃-C-C=O), 21.5 (Ts), 24.0 (O=C-CH₂-CH₂), 24.7 (N-CH₂-CH₂), 32.8 (N-CH₂-CH₂-CH₂), 42.2 (O=C-CH₂), 43.3 (N-CH₂), 63.4 (CH₃-C-C=O), 127.1 (2 CH, Ts), 129.7 (2 CH, Ts), 136.9 (SO₂-C), 143.4 (CH₃-C), 215.7 (C=O).

IR (ATR):

3277, 2925, 1769, 1598, 1325, 1155 cm⁻¹.

Elemental analysis:

Calculated for C₁₅H₂₁O₃NS: C, 60.99 ; H, 7.17 ; N, 4.74. Found: C, 61.01 ; H, 7.27 ; N, 4.55.

Aminal 18.

C₁₇H₂₅O₃NS
M = 323.45 g/mol

¹H NMR (400 MHz, CDCl₃):

δ 0.90 (s, 3H, CH₃), 0.91 (s, 3H, CH₃), 1.17 (s, 3H, CH₃), 1.27 (d, *J* = 14.4 Hz, 1H, N-CH₂-C(CH₃)₂-CHH), 1.35 (d, *J* = 14.4 Hz, 1H, N-CH₂-C(CH₃)₂-CHH), 1.52 (m, 1H, N-C(OH)-CH₂-CHH), 1.72 (m, 1H, N-C(OH)-CH₂-CHH), 2.35 (m, 1H, N-C(OH)-CHH), 2.45 (s, 3H, Ts), 2.75 (d, *J* = 12.9 Hz, 1H, N-CHH), 2.81 (m, 1H, N-C(OH)-CHH), 3.01 (d, *J* = 12.9 Hz, 1H, N-CHH), 3.33 (s, 1H, OH), 7.32 (d, *J* = 8.5 Hz, 2H, Ts), 7.81 (d, *J* = 8.5 Hz, 2H, Ts).

¹³C NMR (100 MHz, CDCl₃):

δ 21.6 (Ts), 24.7 (CH₃), 27.8 and 29.2 (2C, 2 CH₃), 28.1 (N-C(OH)-CH₂-CH₂), 31.4 (N-CH₂-C(CH₃)₂-), 33.8 (N-C(OH)-CH₂), 44.2 (N-C(OH)-C), 45.7 (N-CH₂-C(CH₃)₂-CH₂), 52.1 (N-CH₂), 87.3 (N-C(OH)), 127.7 and 129.5 (2 CH, Ts), 137.8 (SO₂-C), 143.4 (CH₃-C).

IR (ATR):

3506, 3027, 2958, 1603, 1347, 1163 cm⁻¹.

Cyclobutanone 19.

C₁₇H₂₅NO₃S
M = 323,45 g/mol

¹H NMR (400 MHz, CDCl₃):

δ 1.23-1.27 (m, 2H, N-CH₂-C(CH₃)₂-CH₂), 1.35 (m, 1H, N-CH₂-C(CH₃)₂-CH₂-CHH), 1.51 (m, 1H, N-CH₂-C(CH₃)₂-CH₂-CHH), 1.56 (m, 1H, O=C-CH₂-CHH), 2.15 (m, 1H, O=C-CH₂-CHH), 2.42 (s, 3H, Ts), 2.59-2.70 (ABX, 2H, N-CH₂), 2.87 (m, 1H, O=C-CHH), 3.00 (m, 1H, O=C-CHH), 3.18 (m, 1H, O=C-CH), 4.78 (t, *J*=6.9 Hz, 1H, NH), 7.30 (d, *J*=8.2 Hz, 2H, Ts), 7.73 (d, *J*=8.2 Hz, 2H, Ts).

¹³C NMR (100 MHz, CDCl₃):

δ 16.9 (O=C-CH₂-CH₂), 21.7 (Ts), 23.8 (N-CH₂-C(CH₃)₂-CH₂-CH₂), 25.0 (2C, 2 CH₃), 33.8 (N-CH₂-C(CH₃)₂-), 36.4 (N-CH₂-C(CH₃)₂-CH₂), 44.6 (O=C-CH₂), 52.6 (N-CH₂), 60.7 (O=C-CH), 127.2 (2 CH, Ts), 129.9 (2 CH, Ts), 137.1 (SO₂-C), 143.4 (CH₃-C), 212.5 (C=O).

IR (ATR):

3284, 2958, 1773, 1598, 1326, 1158 cm⁻¹.