Supporting Information

Ruthenium-Catalyzed ROM-RCM of Cycloalkene-Yne

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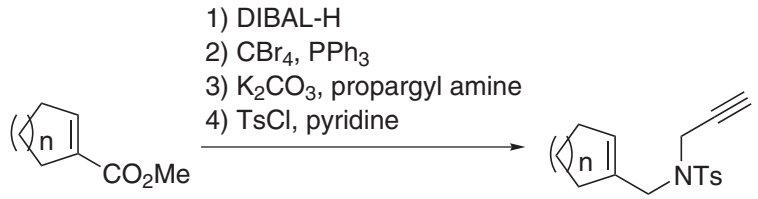
General Information:

The metathesis reactions were carried out under an atmosphere of ethylene (1 atm) unless otherwise mentioned, and all the reaction solutions were degassed through freeze-pump-thaw cycle. CH_2Cl_2 was distilled under an argon atmosphere from CaH_2. Toluene was distilled under an argon atmosphere from Na-benzophenone. Ethylene gas was purified by passage through the aqueous CuCl solution (2 g of CuCl in 180 ml of sat. NH_4Cl aq.) and conc. H_2SO_4 and then KOH tube. Ruthenium catalyst **1** was purchased from Strem Chemicals.

Typical Procedure for the Synthesis of Cycloalkene-yne 2.



9a (n = 2)
9b (n = 1)
9c (n = 3)

2a (n = 2, 45%)
2b (n = 1, 45%)
2c (n = 3, 18%)

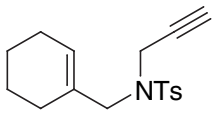
To a solution of **9a** (1.4 ml, 10 mmol) in CH_2Cl_2 (33 ml) was added DIBAL-H (28 ml, 26 mmol, 0.93 M in hexane), and the solution was stirred at –78 °C for 2.5 h. To this solution was added MeOH and 3N NaOH aq. at –78 °C and the aqueous layer was extracted with Et_2O. The organic layer was washed with brine, dried over Na_2SO_4 and evaporated.
To a solution of the crude alcohol in CH_2Cl_2 (19 ml) was added CBr_4 (4.4 g, 13 mmol) and PPh_3 (4.0 g, 15 mmol), and the solution was stirred at room temperature for 3 h.
To a solution of propargyl bromide (3.4 ml, 50 mmol) and K_2CO_3 (5.5 g, 40 mmol) in CH_3CN (75 ml) was added the above solution, and the whole solution was stired at room temperature for 16 h. Then the solution was filtered through celite. To this mother liquid was added pyridine (9.1 ml, 113 mmol) and p-toluenesulfonyl chloride (14.4 g, 75 mmol), and the solution was stirred at room temperature for 45 h. To this solution was added MeOH and the solution was diluted with ethyl acetate. The organic layer was washed with 10 % HCl aq., 10 % NaOH aq., and brine, dried over Na_2SO_4 and evaporated. After the solvent was removed, the residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate 20:1) to yield **2a** (1.37 g, 45%) as colorless crystals.
Ester **9c** was prepared according to the literature procedure. (Pawlak, J. L.; Berchtold, G. A. *J. Org. Chem.* **1988**, *53*, 4063.)

Typical Procedure for the Metathesis Reaction of 2b.

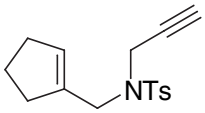
To a solution of **2b** (83.4 mg, 0.29 mmol) in CH_2Cl_2 (9.5 ml, 0.03 M) was added **1b** (26.1 mg, 30 μmol, 10 mol %), and the solution was refluxed under an atmosphere of ethylene for 26 h. To this solution was added an excess of ethyl vinyl ether. After the solvent was removed, the residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate 4:1) to yield **3b** (83 mg, quant.) as colorless crystals.

Spectral Data:

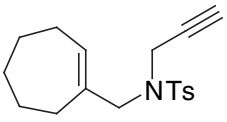
***N*-Cyclohex-1-enylmethyl-4-methyl-*N*-prop-2-ynyl-benzenesulfonamide (2a).** Colorless crystals. mp 54-54.5 °C. (ether/hexane); IR (nujol) ν 3292, 2926, 2853, 1596, 1346, 1158 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.57 (m, 4 H), 1.94 (t, *J* = 2.4 Hz, 1 H), 1.99 (m, 4 H), 2.42 (s, 3 H), 3.67 (s, 2 H), 4.02 (d, *J* = 2.4 Hz, 2 H), 5.68 (s, 1 H), 7.28 (*J* = 8.4 Hz, 2 H), 7.73 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 21.48 (CH_3), 22.19 (CH_2), 22.46 (CH_2), 25.20 (CH_2), 25.84 (CH_2), 35.19 (CH_2), 52.76 (CH_2), 73.44 (CH), 76.64 (C), 127.62 (CH), 127.75 (CH x 2), 129.31 (CH x 2), 131.61 (C), 136.17 (C), 143.29 (C); LRMS *m/z* 303 (M^+), 288, 222, 155, 148, 91; HRMS calcd for $C_{17}H_{21}NO_2S$ (M^+) 303.1293, found 303.1303; Anal. calcd for $C_{17}H_{21}NO_2S$: C, 67.29; H, 6.98; N, 4.62; S, 10.57. found: C, 67.11; H, 7.13; N, 4.47; S, 10.71.



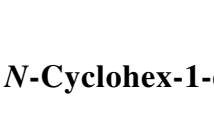
***N*-Cyclopent-1-enylmethyl-4-methyl-*N*-prop-2-ynyl-benzenesulfonamide (2b).** Colorless crystals. mp 55.5 °C. (ether/hexane); IR (nujol) ν 3259, 2923, 2114, 1654, 1596, 1343, 1160 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.89 (dt, *J* = 7.3 Hz, 2 H), 1.97 (t, *J* = 2.4 Hz, 1 H), 2.24-2.36 (m, 4 H), 2.42 (s, 3 H), 3.86 (s, 2 H), 4.04 (d, *J* = 2.4 Hz, 2 H), 5.69 (brs, 1 H), 7.28 (d, *J* = 8.1 Hz, 2 H), 7.74 (d, *J* = 8.1 Hz, 2 H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 21.51 (CH_3), 23.36 (CH_2), 32.46 (CH_2), 32.98 (CH_2), 35.64 (CH_2), 46.52 (CH_2), 73.50 (CH), 76.68 (C), 127.76 (CH x 2), 129.36 (CH x 2), 130.55 (CH), 136.14 (C), 138.20 (C), 143.38 (C); LRMS *m/z* 289 (M^+), 155, 134, 91; Anal. calcd for $C_{16}H_{19}NO_2S$: C, 66.41; H, 6.62; N, 4.84; S, 11.08. found: C, 66.42; H, 6.73; N, 4.79; S, 11.14.



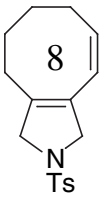
***N*-Cyclohept-1-enylmethyl-4-methyl-*N*-prop-2-ynyl-benzenesulfonamide (2c).** Colorless crystals. mp 72-73 °C. (ether/hexane); IR (nujol) ν 3304, 2922, 2852, 1654, 1597, 1348, 1163 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.48-1.54 (m, 4 H), 1.69 (m, 2 H), 1.92 (t, *J* = 2.4 Hz, 1 H), 2.08-2.21 (m, 4 H), 2.42 (s, 3 H), 3.65 (s, 2 H), 4.04 (d, *J* = 2.4 Hz, 2 H), 5.79 (m, 1 H), 7.28 (d, *J* = 8.4 Hz, 2 H), 7.74 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 21.51 (CH_3), 26.70 (CH_2), 26.96 (CH_2), 28.45 (CH_2), 30.01 (CH_2), 32.20 (CH_2), 35.13 (CH_2), 54.43 (CH_2), 73.55 (CH), 77.20 (C), 127.85 (CH x 2), 129.31 (CH x 2), 132.87 (CH), 136.15 (C), 137.66 (C), 143.32 (C); LRMS *m/z* 317 (M^+), 162, 155, 91; Anal. calcd for $C_{16}H_{19}NO_2S$: C, 68.10; H, 7.30; N, 4.41; S, 10.10. found: C, 68.00; H, 7.28; N, 4.46; S, 10.16.



***N*-Cyclohex-1-enylmethyl-4-methyl-*N*-(2-methylene-but-3-enyl)-benzenesulfonamide (3a).** Colorless oil. IR (neat) ν 1597, 1338, 1160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.46-1.51 (m, 4 H), 1.81 (br, 2 H), 1.90 (br, 2 H), 2.42 (s, 3 H), 3.64 (s, 2 H), 3.91 (s, 2 H), 5.05 (s, 1 H), 5.06 (d, *J* = 10.8 Hz, 1 H), 5.13 (s, 1 H), 5.29 (d, *J* = 18.0 Hz, 1 H), 5.46 (br, 1 H), 6.30 (dd, *J* = 18.0, 10.8 Hz, 1 H), 7.29 (d, *J* = 8.4 Hz, 2 H), 7.70 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.54 (CH_3), 22.13 (CH_2), 22.45 (CH_2), 25.17 (CH_2), 26.18 (CH_2), 48.61 (CH_2), 54.55 (CH_2), 114.28 (CH_2), 117.63 (CH_2), 126.80 (CH), 127.21 (CH x 2), 129.38 (CH x 2), 132.30 (C), 136.58 (CH), 137.02 (C), 140.27 (C), 142.89 (C); LRMS *m/z* 331 (M^+), 316, 302, 290, 276, 264, 249, 236, 198, 184, 176, 155, 148, 133, 119, 106; HRMS calcd for $C_{19}H_{25}NO_2S$ (M^+) 331.1606, found 331.1606; Anal. calcd for $C_{19}H_{25}NO_2S$: C, 68.85; H, 7.60; N, 4.23; S, 9.67. found: C, 68.73; H, 7.61; N, 4.29; S, 9.77.



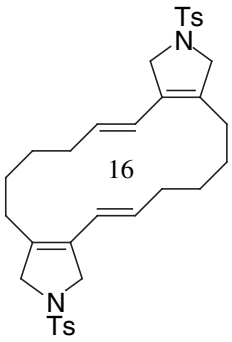
2-(Toluene-4-sulfonyl)-2,3,4,5,6,7-hexahydro-1*H*-cycloocta[*c*]pyrrole (4a). Colorless solid. IR (nujol) ν 2924, 2854, 1654, 1344, 1162 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.45-1.52 (m, 2 H), 1.59-1.67 (m, 2 H), 2.03-2.07 (m, 2 H), 2.13-2.17 (m, 2 H), 2.43 (s, 3 H), 4.03 (s, 4 H), 5.62-5.66 (m, 2 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 7.72 (d, *J* = 8.1 Hz, 2 H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 21.55 (CH_3), 21.55 (CH_2), 25.38 (CH_2), 27.01 (CH_2), 27.05 (CH_2), 58.15 (CH_2), 59.18 (CH_2), 122.34 (CH), 127.12 (C), 127.49 (CH x 2), 129.70 (CH x 2), 132.67 (CH), 132.92 (C), 134.27 (C), 143.34 (C); LRMS *m/z* 303 (M^+), 155, 148, 91; HRMS calcd for $C_{17}H_{21}NO_2S$ (M^+) 303.1293, found 303.1299.



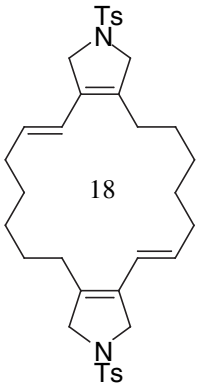
2-(Toluene-4-sulfonyl)-1,2,3,4,5,6-hexahydro-cyclohepta[*c*]pyrrole (4b). Colorless crystals. mp 111-113 °C. (ether); IR (nujol) ν 2924, 2854, 1654, 1344, 1163 cm^{-1}.
^1H NMR (400 MHz, $CDCl_3$) δ 1.78 (m, 2 H), 2.20 (br, 2 H), 2.31 (m, 2 H), 2.43 (s, 3 H), 4.10 (br, 4 H), 5.52 (d, *J* = 11.6 Hz, 1 H), 5.83 (dt, *J* = 11.6, 5.6 Hz, 1 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.72 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.56 (CH_3), 23.38

(CH_2), 29.47 (CH_2), 30.59 (CH_2), 58.41 (CH_2), 59.53 (CH_2), 120.32 (CH), 127.20 (C), 127.41 (CH x 2), 129.62 (CH x 2), 133.93 (C), 134.14 (C), 134.65 (CH), 143.24 (C); LRMS *m/z* 289 (M^+), 155, 134, 91; HRMS calcd for $C_{16}H_{19}NO_2S$ (M^+) 289.1136, found 289.1124.

Dimeric compound (5a). Colorless solid. IR (nujol) ν 2924, 2854, 1598, 1348, 1157 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29-1.39 (m, 8 H), 2.05-2.09 (m, 4 H), 2.12-2.16 (m, 4 H), 2.41 (s, 6 H), 4.06 (s, 4 H), 4.16 (s, 4 H), 5.34 (m, 2 H), 6.10 (d, *J* = 16.0 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 4 H), 7.70 (d, *J* = 8.0 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.52 (CH_3 x 2), 24.36 (CH_2 x 2), 25.57 (CH_2 x 2), 26.82 (CH_2 x 2), 30.94 (CH_2 x 2), 55.09 (CH_2 x 2), 57.48 (CH_2 x 2), 121.76 (CH x 2), 127.44 (CH x 4), 129.00 (C x 2), 129.72 (CH x 4), 131.63 (CH x 2), 133.24 (C x 2), 134.29 (C x 2), 143.37 (C x 2); LRMS *m/z* 606 (M^+), 518, 451, 295, 155, 91; HRMS calcd for $C_{34}H_{42}N_2O_4S_2$ (M^+) 606.2586, found 606.2581.



Dimeric compound (5c). Colorless solid. IR (nujol) ν 2923, 2854, 1598, 1348, 1157 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.99-1.38 (m, 12 H), 2.01-2.14 (m, 8 H), 2.42 (s, 6 H), 4.05 (s, 4 H), 4.19 (s, 4 H), 5.33 (m, 2 H), 6.02 (d, *J* = 15.6 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 4 H), 7.73 (d, *J* = 8.0 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.59 (CH_3 x 2), 25.31 (CH_2 x 2), 26.85 (CH_2 x 2), 27.00 (CH_2 x 2), 27.94 (CH_2 x 2), 33.12 (CH_2 x 2), 55.19 (CH_2 x 2), 57.00 (CH_2 x 2), 121.59 (CH x 2), 127.42 (CH x 4), 129.46 (C x 2), 129.64 (CH x 4), 132.08 (CH x 2), 132.43 (C x 2), 134.11 (CH x 2), 143.28 (C x 2); LRMS *m/z* 634 (M^+), 479. 451, 323, 155, 91; HRMS calcd for $C_{36}H_{46}N_2O_4S_2$ (M^+) 634.2899, found 634.2902.



3-Hex-5-enyl-1-(toluene-4-sulfonyl)-4-vinyl-2,5-dihydro-1*H*-pyrrole (6a). Colorless solid. IR (film) ν 2926, 2855, 1654, 1598, 1347, 1164 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26-1.40 (m, 4 H), 1.98-2.05 (m, 2 H), 2.12-2.15 (m, 2 H), 2.43 (s, 3 H), 4.11 (s, 2 H), 4.22 (s, 2 H), 4.93-4.99 (m, 3 H), 5.12 (d, *J* = 10.8 Hz, 1 H), 5.74 (m, 1 H), 6.43 (dd, *J* = 17.2, 10.8 Hz, 1 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 7.73 (d, J = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.58 (CH_3), 26.03 (CH_2), 27.30 (CH_2), 28.47 (CH_2), 33.42 (CH_2), 54.87 (CH_2), 57.61 (CH_2), 114.68 (CH_2), 115.31 (CH_2), 127.36 (CH x 2), 129.38 (CH), 129.71 (CH x 2), 130.80 (C), 133.90 (C), 135.84 (C), 138.28 (CH), 143.37 (C); LRMS *m/z* 331 (M^+), 248, 176, 155, 91; HRMS calcd for $C_{19}H_{25}NO_2S$ (M^+) 331.1606, found 331.1592.