Novel Alkenylative Cyclization Using a Ruthenium Catalyst

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General Procedure. Toluene was distilled under an argon atmosphere from Na/benzophenone. All the solvents using the organometallic agents were degassed through a freeze-pump-thaw cycle. Ethylene gas was purified by passing through the aqueous CuCl solution (2g of CuCl in 180 mL of saturated aqueous NH₄Cl), concentrated H₂SO₄, and a KOH tube.

General procedure for cyclization of Enyne: A toluene solution of enyne and a catalytic amount of Cp*RuCl(cod) was stirred at room temperature or 60 °C under ethylene gas (1 atm). After removal of the solvent, the residue was purified by column chromatography on silica gel.

3-Allylidene-4-methyl-1-(toluene-4-sulfonyl)pyrrolidine (4a)

According to the general procedure, a solution of **1a** (74.8 mg, 0.30 mmol) and Cp*RuCl(cod) (5.7 mg, 5 mol %) in toluene (10 mL, 0.03 M) was stirred at room temperature for 1 h under an ethylene. The crude residue was purified by column chromatography on silica gel (Hexane/AcOEt, 3/1) to yield **4a** (69.2 mg, 83%) as a brown oil. IR (CHCl₃) 1654, 1597, 1346, 1164 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.11 (d, *J* = 7.0 Hz, 3 H), 2.43 (s, 3 H), 2.98-3.03 (m, 1 H), 3.13 (dd, *J* = 6.2, 9.2 Hz, 1 H), 3.22 (dd, *J* = 2.2, 9.2 Hz, 1 H), 3.61 (d, *J* = 14.9 Hz, 1 H), 4.05 (d, *J* = 14.9 Hz, 1 H), 5.01 (d, *J* = 10.5 Hz, 1 H), 5.07 (d, *J* = 16.8 Hz, 1 H), 5.84 (d, *J* = 10.5 Hz, 1 H), 6.35 (ddd, *J* = 16.8, 10.5, 10.5 Hz, 1 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 7.70 (d, *J* = 8.4 Hz, 2 H); ¹³C NMR (67.5 MHz, CDCl₃) δ 19.8, 21.4, 35.0, 51.7, 55.2, 117.2, 122.3, 127.8, 129.6,

132.3, 132.3, 142.9, 143.6; LRMS (EI) m/z 277 (M^+), 262, 155, 122, 91; HRMS (EI) calcd for $C_{15}H_{19}NO_2S$ 277.1136, found 277.1146.

3-Allylidene-4-methylcyclopentane-1,1-dicarboxylic acid dimethyl ester (4b)

IR (neat) 1736, 1656, 1601 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 1.14 (d, $J = 6.4$ Hz, 3 H), 1.86 (dd, $J = 13.3, 6.5$ Hz, 1 H), 2.73 (dd, $J = 13.6, 8.4$ Hz, 1 H), 2.83 (d, $J = 16.2$ Hz, 1 H), 2.94-3.03 (m, 1 H), 3.14 (d, $J = 16.3$ Hz, 1 H), 3.70 (s, 3 H), 3.75 (s, 3 H), 5.01 (d, $J = 10.5$ Hz, 1 H), 5.07 (d, $J = 16.8$ Hz, 1 H), 5.93 (d, $J = 10.5$ Hz, 1 H), 6.44 (ddd, $J = 16.8, 10.5, 10.5$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 34.3, 41.6, 42.1, 52.7, 59.1, 115.4, 122.9, 133.0, 147.0, 171.7, 172.0; LRMS (EI) m/z 238 (M^+), 207, 178, 163, 119, 91; HRMS (EI) calcd for $C_{13}H_{18}O_4$ 238.1205, found 238.1204.

1,1-Bisbenzyloxymethyl-3-allylidene-4-methylcyclopentane (4c)

IR ($CHCl_3$) 1654, 1600, 1101 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 1.12 (d, $J = 7.2$ Hz, 1 H), 1.29 (dd, $J = 6.8, 13.2$ Hz, 1 H), 1.99 (dd, $J = 8.8, 13.2$ Hz, 1 H), 2.55 (d, $J = 16$ Hz, 1 H), 2.41 (d, $J = 16$ Hz, 1 H), 2.81-2.87 (m, 1 H), 3.27 (s, 2 H), 3.45 (d, $J = 8.8$ Hz, 1 H), 3.48 (d, $J = 8.8$ Hz, 1 H), 4.47 (s, 2 H), 4.52 (s, 2 H), 4.95 (d, $J = 10.0$ Hz, 1 H), 5.03 (d, $J = 16.8$ Hz, 1 H), 5.88 (d, $J = 10.8$ Hz, 1 H), 6.49 (ddd, $J = 10.0, 16.8, 10.8$ Hz, 1 H), 7.23-7.34 (m, 10 H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 22.9, 34.2, 40.8, 47.5, 72.7, 73.6, 73.7, 75.2, 114.5, 122.8, 127.8, 127.8, 128.7, 134.2, 139.4, 151.8; LRMS (EI) m/z 362 (M^+), 271, 254, 241, 91; HRMS (EI) calcd for $C_{25}H_{30}O_2$ 362.2246, found 362.2240. *Anal.* Calcd for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34. Found: C, 82.78; H, 8.31.

2-Allylidene-3,8,8-trimethyl-7,9-dioxaspiro[4.5]decane (4d)

IR (neat) 1654, 1600, 1067 cm^{-1} ; 1H NMR (270 MHz, $CDCl_3$) δ 1.10-1.17 (m, 4 H), 1.40 (s, 3 H), 1.42 (s, 3 H), 1.98 (dd, $J = 13.5, 8.6$ Hz, 1 H), 2.24-2.47 (m, 2 H), 2.83-2.91 (m, 1 H), 3.45-3.75 (m, 4 H), 4.98 (d, $J = 10.5$ Hz, 1 H), 5.08 (d, $J = 17.0$ Hz, 1 H), 5.94 (d, $J = 10.5$ Hz, 1 H), 6.49 (ddd, $J = 17.0, 10.5, 10.5$ Hz, 1 H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 22.4, 22.5, 33.4, 40.8, 41.2, 41.3, 67.6, 69.7, 97.8, 114.7, 123.2, 133.4, 149.7; LRMS (EI) m/z 222 (M^+), 207, 164, 147, 133, 91.

(3-Allylidene-4-methylpyrrolidin-1-yl)-phenylmethanone (4e)

IR (neat) 1624, 1576 cm^{-1} ; ^1H NMR (270 MHz, DMSO, 100 $^\circ\text{C}$) δ 1.10 (d, J = 6.8 Hz, 3 H), 3.16 (d, J = 11.1 Hz, 1 H), 3.38 (d, J = 11.1 Hz, 1 H), 3.66 (dd, J = 11.1, 6.8 Hz, 1 H), 4.04 (d, J = 16.7 Hz, 1 H), 4.34 (d, J = 16.7 Hz, 1 H), 5.10 (d, J = 11.1 Hz, 1 H), 5.15 (d, J = 17.8 Hz, 1 H), 5.98 (d, J = 10.8 Hz, 1 H), 6.50 (ddd, J = 17.8, 11.1, 10.8 Hz, 1 H), 7.42-7.49 (m, 5 H); LRMS (EI) m/z 227 (M^+), 212, 198, 149, 134, 122, 105; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{17}\text{NO}$ 227.1310, found 227.1315.

3-Allylidene-1-benzyl-4-methylpyrrolidin-2-one (4f)

IR (CHCl_3) 1683, 1604 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 1.19 (d, J = 5.9 Hz, 1 H), 2.83 (dd, J = 10.0, 1.6 Hz, 1 H), 3.09-3.15 (m, 1 H), 3.45 (dd, J = 10.0, 7.6 Hz, 1 H), 4.52 (d, J = 14.6 Hz, 1 H), 4.60 (d, J = 14.6 Hz, 1 H), 5.44 (d, J = 11.9 Hz, 1 H), 5.56 (d, J = 16.5 Hz, 1 H), 6.55 (ddd, J = 16.5, 11.9, 11.6 Hz, 1 H), 6.94 (d, J = 11.6 Hz, 1 H), 7.23-7.36 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.6, 29.1, 47.1, 52.2, 123.3, 127.3, 127.9, 128.4, 130.0, 131.5, 136.1, 137.7, 167.8; LRMS (EI) m/z 227 (M^+), 212, 91; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{17}\text{NO}$ 227.1310, found 227.1307.

3-Allylidene-1-benzyl-4-methylpyrrolidine (4g)

IR (neat) 1663, 1602, 1122 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 1.20 (d, J = 7.0 Hz, 3 H), 2.39 (dd, J = 8.6, 4.1 Hz, 1 H), 2.78 (dd, J = 8.6, 7.0 Hz, 1 H), 2.92-3.00 (m, 1 H), 3.07 (d, J = 13.5 Hz, 1 H), 3.32 (d, J = 13.5 Hz, 1 H), 3.60 (s, 2 H), 5.04 (d, J = 9.7 Hz, 1 H), 5.06 (d, J = 18.4 Hz, 1 H), 5.89 (d, J = 11.1 Hz, 1 H), 6.48 (ddd, J = 18.4, 11.1, 9.7 Hz, 1 H), 7.24-7.33 (m, 5 H); ^{13}C NMR (67.5 MHz, CDCl_3) δ 20.4, 35.3, 59.8, 60.4, 62.3, 114.9, 120.7, 126.7, 127.9, 128.4, 133.2, 138.7, 147.8; LRMS (EI) m/z 213 (M^+), 198, 184, 170, 91; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{19}\text{N}$ 213.1517, found 213.1509.

4-Allylidene-3,3-dimethylcyclopentane-1,1-dicarboxylic acid dimethyl ester (4h)

IR (neat) 1737, 1648, 1595 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.25 (s, 6 H), 2.06 (s, 2 H), 2.36 (s, 2 H), 3.72 (s, 6 H), 5.01 (d, J = 9.1 Hz, 1 H), 5.04 (d, J = 15.8 Hz, 1 H), 5.89 (d, J = 11.4 Hz, 1 H), 6.66 (ddd, J = 15.8, 11.4, 9.1 Hz, 1 H); ^{13}C NMR (67.5 MHz, CDCl_3) δ 29.5, 41.5, 43.6, 51.2, 52.7, 58.0, 116.0, 122.9, 132.6, 149.7, 172.2; LRMS (EI) m/z 252 (M^+), 221, 192, 177, 160, 133; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{20}\text{O}_4$ 252.1361, found 252.1350. *Anal.* Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_4$: C, 66.65; H, 7.99. Found: C, 66.80; H, 8.17.

2-(4,4-Bisbenzyloxymethyl-2-methylcyclopentylidene)-but-3-enoic acid methyl ester (4i)

IR (neat) 1723, 1636, 1098 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.14 (d, $J = 7.0$ Hz, 3 H), 1.36 (dd, $J = 6.8, 13.5$ Hz, 1 H), 2.02 (dd, $J = 8.6, 13.5$ Hz, 1 H), 2.52 (s, 2 H), 2.90-3.00 (m, 1 H), 3.24 (s, 2 H), 3.46 (s, 2 H), 3.74 (s, 3 H), 4.45 (s, 2 H), 4.51 (s, 2 H), 5.16 (d, $J = 11.2$ Hz, 1 H), 5.20 (d, $J = 17.2$ Hz, 1 H), 6.44 (dd, $J = 11.2, 17.2$ Hz, 1 H), 7.23-7.34 (m, 10 H); ^{13}C NMR (67.5 MHz, CDCl_3) δ 21.9, 35.3, 39.2, 39.3, 47.4, 51.5, 72.5, 73.2, 73.3, 74.4, 115.3, 126.2, 127.3, 127.3, 127.4, 128.2, 130.8, 138.7, 157.1, 169.0; LRMS (EI) m/z 420 (M^+), 388, 312, 191, 91; HRMS (EI) calcd for $\text{C}_{27}\text{H}_{32}\text{O}_4$ 420.2300, found 420.2312. Anal. Calcd for $\text{C}_{27}\text{H}_{32}\text{O}_4$: C, 77.11; H, 7.67. Found: C, 77.04; H, 7.87.

3-Allylidene-4-methoxycarbonylmethylcyclopentane-1,1-dicarboxylic acid dimethyl ester (4j)

IR (neat) 1734, 1654, 1601 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 2.04 (dd, $J = 14.0, 5.7$ Hz, 1 H), 2.33 (dd, $J = 15.7, 10.5$ Hz, 1 H), 2.61 (dd, $J = 15.7, 4.6$ Hz, 1 H), 2.79 (dd, $J = 14.0, 8.6$ Hz, 1 H), 2.86 (d, $J = 16.5$ Hz, 1 H), 3.13 (d, $J = 16.5$ Hz, 1 H), 3.31-3.40 (m, 1 H), 3.68 (s, 3 H), 3.71 (s, 3 H), 3.74 (s, 3 H), 5.06 (d, $J = 10.3$ Hz, 1 H), 5.12 (d, $J = 17.3$ Hz, 1 H), 5.99 (d, $J = 11.3$ Hz, 1 H), 6.39 (ddd, $J = 17.3, 11.3, 10.3$ Hz, 1 H); ^{13}C NMR (67.5 MHz, CDCl_3) δ 36.2, 39.7, 39.9, 41.4, 51.6, 52.8, 58.8, 116.8, 124.1, 132.5, 143.9, 171.6, 171.9, 172.3; LRMS (EI) m/z 296 (M^+), 265, 236, 204, 176, 117; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{20}\text{O}_6$ 296.1260, found 296.1255.

Propynoic acid allylbenzylamide (1f)

IR (neat) 2103, 1634 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 3.11 (s, 0.5 H), 3.12 (s, 0.5 H), 3.93 (d, $J = 5.9$ Hz, 1 H), 4.10 (d, $J = 5.9$ Hz, 1 H), 4.61 (s, 1 H), 4.78 (s, 1 H), 5.10-5.30 (m, 2 H), 5.66-5.79 (m, 1 H), 7.23-7.38 (m, 5 H); ^{13}C NMR (67.5 MHz, CDCl_3) δ 45.9, 46.7, 50.3, 51.5, 75.7, 75.9, 78.9, 79.0, 118.5, 127.5, 127.7, 128.0, 128.3, 128.7, 128.8, 131.5, 132.2, 135.8, 136.1, 153.3, 153.8; LRMS (EI) m/z 199 (M^+), 158, 91; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{13}\text{NO}$ 199.0997, found 199.0997.

5,5-Bisbenzyloxymethyloct-7-en-2-ynoic acid methyl ester (1i)

IR (neat) 2235, 1715, 1637, 1097 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.24 (d, $J = 7.6$ Hz, 2 H), 2.44 (s, 2 H), 3.38 (s, 4 H), 3.75 (s, 3 H), 4.49 (s, 4 H), 5.03-5.11 (m, 2 H), 5.68-5.79 (m, 1 H), 7.22-7.37 (m, 10

H); ^{13}C NMR (67.5 MHz, CDCl_3) δ 22.6, 36.4, 42.4, 52.5, 71.6, 73.3, 74.7, 87.1, 118.6, 127.4, 128.2, 133.2, 138.4, 154.1; LRMS (EI) m/z 392 (M^+), 361, 332, 301, 107, 91; HRMS (EI) calcd for $\text{C}_{25}\text{H}_{28}\text{O}_4$ 392.1987, found 392.1978. *Anal.* Calcd for $\text{C}_{25}\text{H}_{28}\text{O}_4$: C, 76.50; H, 7.19. Found: C, 76.71; H, 7.40.

Registry No.

4-Methyl-N-(prop-2-enyl)-N-(prop-2-ynyl)benzenesulfonamide (**1a**), 133886-40-5; Dimethyl 4-butenylpropargylmalonate (**1b**), 107428-06-8; 1,1'-[[2-(2-Propenyl)-2-(2-propynyl)-1,3-propanediyl]bis(oxymethylene)]bisbenzene (**1c**), 169123-62-0; 2,2-Dimethyl-5-(2-propenyl)-5-(2-propynyl)-1,3-dioxane (**1d**), 233665-77-5; *N*-Allyl-*N*-benzoyl-*N*-prop-2-ynylamine (**1e**), 119548-48-0; 4-Benzylazahept-1-ene-6-yne (**1g**), 119548-50-4; 2-(2-Methyl-allyl)-2-prop-2-ynylmalonic acid dimethyl ester (**1h**), 109468-75-9; 5-Methoxycarbonyl-5-prop-2-ynylhex-2-enedioic acid dimethyl ester (**1j**), 113704-39-5, 121497-81-2; 2-Butynyl-2-propenylpropanedioic acid dimethyl ester (**1k**), 109468-67-9; 2-But-2-enyl-2-prop-2-ynylmalonic acid dimethyl ester (**1l**), 109433-00-3, 109433-01-4, 113704-38-4.