Triple Ring Closing Metathesis Reaction: Synthesis of Adjacent Cyclic Ethers

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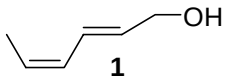
SUPPORTING INFORMATION

General Methods: All reagents are commercial grade and were used as received. Bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride **A** was purchased from Strem Chemical INC. 1,3-dimesitylimidazol-2-ylidene ruthenium benzylidene **B** was prepared according to the literature procedure.(3h) All reactions were performed under inert atmosphere using anhydrous solvents which were dried and distilled before use. Thin-layer chromatograms (TLC) and flash chromatography separations were respectively performed on precoated silica gel 60 F254 plates (Merck, 0.25 mm) and on Merck silica gel 60 (230-400 mesh). ^{1}H NMR spectra were recorded at 300 MHz in $CDCl_3$; shifts are relative to internal TMS. ^{13}C NMR spectra were obtained at 75 MHz with $CDCl_3$ as internal reference. Mass spectra were recorded at 70 eV using chemical ionization mode (CI-NH_3) or electrospray mode (ESI/TOF Mariner).

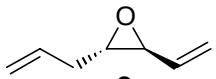


1

(E) 2,5 Hexadien-1 ol (1) was prepared by a two steps process according to the literature: the coupling reaction of propargyl alcohol(7a) with allyl bromide gave 5-hexen-2-yn-1 ol which was reduced with lithium aluminum hydride to yield to **(1)**.(7b)

2

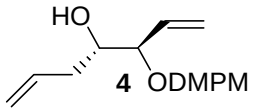
(S,S)-(3-allyl-oxiranyl)-methanol (2). To a cooled (-25°C) mixture of (+) diethyl-D-tartrate (0.88 ml, 5.1 mmol) in CH_2Cl_2 (250 ml) and 4Å molecular sieves (4g) was added dropwise titanium (IV) isopropoxide (1.3 ml, 4.3 mmol). The mixture was stirred 30 min at -25°C and *tert*-butylhydroperoxide (45 ml, 75 mmol, 5 M in CH_2Cl_2) was slowly added and stirred for further 30 min. A solution of alcohol **1** (8.42 g, 85.6 mmol) in CH_2Cl_2 (50 ml) was added using a syringe pump (addition during 1 hour), and the resulting reaction mixture was stirred at -25°C for 2 days. The mixture was warmed to 0°C and treated with a solution of iron (II) sulfate heptahydrate (15 g) and tartaric acid (5 g) in water (100 ml). After 30 min of stirring at room temperature, the reaction mixture was filtered through a celite pad. The organic layer was separated and the aqueous layer was extracted with Et_2O (5 x 75 ml). The organic layers were collected, dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography (pentane/ether 1/1) to yield **2** (8 g, 82% yield, ee>99%). ^{1}H NMR ($CDCl_3$) δ 5.80 (ddt, *J* = 2.3, 8.0, 15.5 Hz, 1H), 5.14 (dd, *J*= 1.5, 15.5 Hz, 1H), 5.09 (dd, *J* = 1.5, 8.0 Hz, 1H), 3.90 (dd, *J* = 5.3, 17.7 Hz, 1H), 3.62 (dd, *J* = 5.3, 12.1 Hz, 1H), 3.07-3.01 (m, 1H), 2.99-2.90 (m, 1H), 2.35 (tapp, *J* = 6.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 132.8, 117.7, 61.7, 58.1, 54.8, 35.6; IR (neat, cm^{-1}) 3423, 2982, 2922, 1642, 1007, 919; MS (DCI/NH_3) *m/z* (MNH_4^+) = 132.



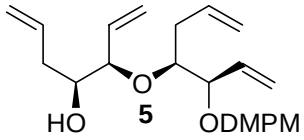
3

2-Allyl-3-vinyl-oxirane (3). To a stirred mixture of alcohol **2** (6.1 g, 53.4 mmol) in CH_2Cl_2 (150 ml), dry DMSO (30 ml, 423 mmol) and triethylamine (37.2 ml, 267, 2 mmol) at 0°C, was added trioxide-pyridine complex (1.92 g, 12.0 mmol) in four portions. After 45 min of stirring at 0°C, the reaction mixture was diluted with Et_2O (200 ml), washed with saturated aqueous ammonium chloride (2 x 75 ml), and with 1 N HCl (2 x 20 ml), dried over $MgSO_4$ and concentrated to give the corresponding aldehyde which was used directly. To a stirred suspension of methyltriphenylphosphonium bromide (28.6 g, 80.2 mmol) in THF (250 ml) at 0°C was dropwise added sodium bis(trimethylsilyl)amide (64 ml, 64 mmol, 1M in THF) over 20 min. After stirring for 45 min at 0°C, the bright yellow ylide was treated with the crude aldehyde (6.2 g, 55.3 mmol) in THF (50 ml) dropwise over a period of 15 min. After 90 min of stirring at 0°C, the brown solution was quenched with acetone (20 ml) and Et_2O (150 ml). The organic layer was separed, washed with a saturated aqueous NH_4Cl solution, dried over

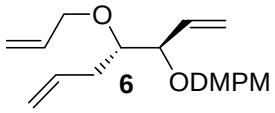
$MgSO_4$ and concentrated (keeping the bath beetween 0-5°C, epoxide extremely volatile). The crude residue was distilled to give epoxide **3** as a colorless oil (bp_{760} = 92°C, m = 3.6 g, 60% yield. ^{1}H NMR ($CDCl_3$) δ 5.78 (ddt, *J* = 6.7, 10.4, 17.0 Hz, 1H), 5.56 (ddt, *J* = 9.7, 7.5, 17.1 Hz, 1H), 5.42 (dd, *J* = 1.6, 17.3 Hz, 1H), 5.25 (dd, *J* = 1.6, 6.8 Hz, 1H), 5.18 (td, *J* = 1.6, 19.2 Hz, 1H), 3.19 (dd, *J* = 1.6, 9.7 Hz, 1H), 2.36 (dd, *J* = 2.0, 7.1 Hz, 2H), 2.88 (dd, *J* = 2.0, 10.5 Hz, 2H), 2.33 (t app, *J* = 6.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 135.6, 132.9, 119.1, 117.6, 59.2, 58.1, 36.0; IR (neat, cm^{-1}) 3084, 2980, 1642, 1256, 919, 872, 841; MS (DCI/NH_3) *m/z* (MNH_4^+) = 128, $(M+N_2H_7)^+$= 145.



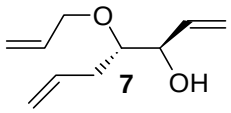
3-(3,4-Dimethoxy-benzyloxy)-hepta-1,6-dien-4-ol (4). To a solution of epoxide **3** (500 mg, 4.46 mmol) and 3,4-dimethoxybenzyl alcohol (2.6 ml, 18 mmol) in CH_2Cl_2 (8 ml) was added $BF_3.Et_2O$ (17 µl, 0.13 mmol). The mixture was stirred at room temperature for 3 hours, and was hydrolyzed with H_2O (5 ml), and extracted with CH_2Cl_2 (2 x 10 ml). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated. Purification by flash column chromatography (pentane/ether 6/4) provided alcohol **4** (745 mg, 60% yield). ^{1}H NMR ($CDCl_3$) δ 6.85-6.79 (m, 3H), 5.87-5.76 (m, 2H), 5.42-5.05 (m, 4H), 4.55 (d, *J* = 11.5 Hz, 1H), 4.30 (d, *J* = 11.5 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.78-3.69 (m, 2H), 2.32-2.14 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 149.1, 148.8, 134.8, 134.7, 130.8, 120.5, 120.3, 117.6, 111.4, 111.1, 82.8, 72.6, 70.3, 56.0, 55.9, 37.0; IR (neat, cm^{-1}) 3525, 1517, 1266, 1030; MS (DCI/NH_3) *m/z* (MNH_4^+) = 296.



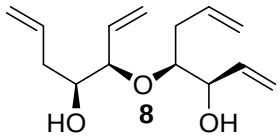
3-[1-Allyl-2-(3,4-dimethoxy-benzyloxy)-but-enyloxy]-hepta-1,6-dien-4-ol (5). During the formation of compound **4**, the alcohol **5** was formed, and isolated (264 mg, 15% yield). ^{1}H NMR ($CDCl_3$) δ 6.88-6.84 (m, 3H), 5.95-5.73 (m, 4H), 5.44-5.01 (m, 8H), 4.58 (d, *J* = 11.5 Hz, 1H), 4.30 (d, *J* = 11.5 Hz, 1H), 4.01-3.96 (m, 1H), 3.89 (s, 6H), 3.78-3.69 (m, 3H), 3.15 (d, *J* = 5.8 Hz, 1H), 2.29-2.16 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 149.0, 148.7, 135.5, 134.9, 134.8, 130.7, 120.4, 120.0, 119.9, 118.5, 117.2, 116.7, 111.4, 111.0, 84.3, 82.3, 79.7, 72.8, 70.2, 56.0, 36.8, 36.3; IR (neat, cm^{-1}) 3457, 2934, 1516, 1267, 1030, 996, 920; MS (DCI/NH_3) *m/z* (MNH_4^+) = 406.



4-(2-Allyloxy-1-vinyl-pent-4-enyloxymethyl-)1,2-dimethoxybenzene (6). To a stirred solution of alcohol **4** (745 mg, 2.68 mmol) in dry THF/DMF (22ml/6ml) at 0°C was added sodium hydride (320 mg, 8.05 mmol, 60% dispersion in mineral oil). The reaction mixture was stirred at room temperature for 15 min and was cooled to 0°C and allyl bromide (0.70 ml, 8.05 mmol) was added. The reaction was stirred for 12 hours at room temperature and was hydrolyzed with saturated aqueous NH_4Cl (20ml), extracted with Et_2O (2 x 20 ml). The organic layers were collected and dried ($MgSO_4$). After concentration, the crude product was purified on column chromatography (pentane/ether 8/2) to give **6** (818 mg, 96% yield). ^1H NMR ($CDCl_3$) δ 6.88-6.78 (m, 3H), 5.95-5.75 (m, 2H), 5.35-5.00 (m, 4H), 4.55 (d, *J* = 11.6 Hz, 1H), 4.30 (d, *J* = 11.6 Hz, 1H), 4.08 (dd, *J* = 1.0, 4.5 Hz, 1H), 4.05 (dd, *J* = 1.0, 4.5 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.77 (dd, *J* = 4.8, 7.4 Hz, 1H), 3.46 (dt, *J* = 4.8, 5.7 Hz, 1H), 2.34-2.29 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 149.0, 148.6, 135.8, 135.3, 135.2, 131.2, 120.2, 119.0, 116.9, 116.6, 111.2, 111.0, 81.8, 81.0, 71.7, 70.4, 56.0, 55.9, 35.7; IR (neat, cm^{-1}) 2958, 2936, 1516, 1265, 1031; MS (DCI/NH_3) *m/z* (MNH_4^+) = 336.

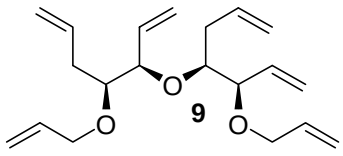


4-Allyloxy-hepta-1,6-dien-3-ol (7). A solution of ether **6** (818 mg, 2.56 mmol) in MeOH/H_2O (25ml/1.4ml) was treated with 2,3-dichloro-5,6-dicyanobenzoquinone (697 mg, 3.07 mmol) at room temperature and stirred for 15 min. The mixture was filtered through a celite pad, dried over $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography (pentane/ether 7/3) to give alcohol **7** (336 mg, 78% yield). ^1H NMR ($CDCl_3$) δ 5.93-5.80 (m, 2H), 5.32-5.00 (m, 4H), 4.05 (dd, *J* = 1.0, 4.5 Hz, 2H), 3.45-3.37 (m, 2H), 2.38-2.15 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 136.6, 135.0, 134.9, 117.1, 116.6, 81.6, 73.6, 71.3, 34.3; IR (neat, cm^{-1}) 3445, 2956, 2874, 1083, 995, 922; MS (DCI/NH_3) *m/z* (MNH_4^+) = 186.



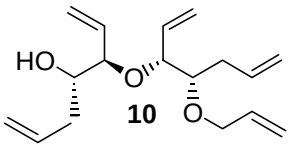
8

4-(2-Hydroxy-1-vinyl-pent-4-enyloxy)-hepta-1,6-dien-3-ol (8). A solution of alcohol **5** (20 mg, 0.05 mmol) in MeOH/H_2O (0.5ml/30μl) was treated with 2,3-dichloro-5,6-dicyanobenzoquinone (13 mg, 0.06 mmol) at room temperature, and stirred for 15 min. The mixture was filtered through a celite pad, dried over $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography (pentane/ether 95/5) to give diol **8** (12 mg, 90% yield). ^{1}H NMR ($CDCl_3$) δ 5.94-5.73 (m, 4H), 5.36-5.03 (m, 8H), 4.25-4.22 (m, 1H), 4.05 (dd, *J* = 3.1, 7.3 Hz, 1H), 3.79-3.73 (m, 1H), 3.63-3.57 (m, 3H), 2.75 (br s, 1H), 2.65 (br s, 1H), 2.35-2.18 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 136.4, 135.2, 135.0, 118.8, 117.8, 117.0, 83.2, 80.4, 73.9, 72.8, 36.0, 35.5; MS (DCI/NH_3) *m/z* (MNH_4^+) = 256.



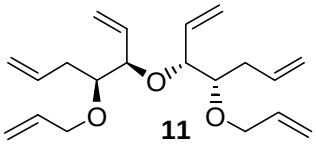
9

3-(1-Allyl-2-allyloxy-but-3-enyloxy)-4-allyloxy-hepta-1,6-diene (9). To a stirred solution of diol **8** (12 mg, 0.05 mmol) in dry THF (1 ml) at 0°C, was added NaH (10 mg, 0.26 mmol, 60% dispersion in mineral oil). The reaction mixture was stirred at room temperature for 15 min and was cooled to 0°C and allyl bromide (22 μl, 0.25 mmol) in DMF (1 ml) was added. The reaction was stirred for 12 hours at room temperature and was hydrolyzed with saturated aqueous NH_4Cl (2 ml), extracted with Et_2O (2 x 5 ml). The organic layers were collected and dried ($MgSO_4$) and concentrated. The crude product was purified on column chromatography (pentane/ether 9/1) to give **9** (13 mg, 80% yield). ^{1}H NMR ($CDCl_3$) δ 5.91-5.79 (m, 6H), 5.33-5.01 (m, 12H), 4.26 (dd, *J* = 5.5, 17.5 Hz, 1H), 4.10-4.02 (m, 3H), 3.90 (dd, *J* = 5.5, 7.5 Hz, 1H), 3.74 (dd, *J* = 3.7, 7.7 Hz, 1H), 3.64-3.58 (m, 1H), 3.52-3.46 (m, 1H), 2.32-2.20 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 136.2, 135.7, 135.6, 135.1, 119.0, 118.7, 116.5, 116.2, 83.1, 82.6, 81.1, 78.1, 71.9, 69.4, 36.4, 36.1; IR (neat, cm^{-1}) 2925, 2855, 1459, 1086, 994, 924; MS (DCI/NH_3) *m/z* (MH^+) = 319, (MNH_4^+) = 336.



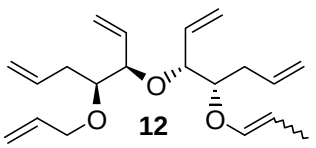
10

3-(2-Allyloxy-1-vinyl-pent-4-enyloxy)-hepta-1,6-dien-4-ol (10). To a stirred solution of alcohol **7** (46 mg, 0.27 mmol) and epoxide **3** (46 mg, 0.41 mmol) in CH_2Cl_2 (2 ml) was added $BF_3.Et_2O$ (5 µl, 0.04 mmol). The mixture was stirred at room temperature for 3 hours, and was concentrated. Purification by flash column chromatography (pentane/ether 8/2) afforded alcohol **10** (26 mg, 35% yield). ^{1}H NMR ($CDCl_3$) δ 5.90-5.71 (m, 5H), 5.40-5.04 (m, 10H), 4.15 (dd, *J* = 5.5, 12.5 Hz, 2H), 4.05 (dd, *J* = 5.5, 12.5 Hz, 2H), 3.91-3.85 (m,1H), 3.83-3.71 (m, 2H), 3.48-3.42 (m, 1H), 2.32-2.18 (m, 4H), 2.14 (d, *J* = 3.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 135.3, 135.2, 134.9, 134.6, 120.6, 119.7, 117.4, 116.9, 116.6, 81.0, 80.3, 79.6, 72.8, 71.9, 36.9, 35.9; MS (DCI/NH_3) *m/z* (MNH_4^+) = 296.



11

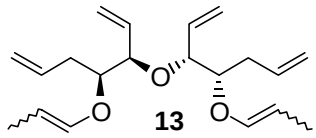
4-Allyloxy-3-(2-allyloxy-1-vinyl-pent-4-enyloxy)-hepta-1,6-diene (11). To a stirred solution of alcohol **10** (7 mg, 0.03 mmol) in dry THF/DMF (1 ml/1.5 ml) at 0°C, was added NaH (5 mg, 0.10 mmol, 60% dispersion in mineral oil). The reaction mixture was stirred at room temperature for 15 min, and was cooled to 0°C and allyl bromide (8 µl, 0.1 mmol) in DMF (0.5 ml) was added. The reaction was stirred for 12 hours at room temperature and was hydrolyzed with saturated NH_4Cl (2 ml), extracted with Et_2O (2 x 5 ml). The organic layers were collected, dried ($MgSO_4$) and concentrated. The crude product was purified on column chromatography (pentane/ether 9/1) to give **11** (7 mg, 88% yield). ^{1}H NMR ($CDCl_3$) δ 5.95-5.69 (m, 6H), 5.34-5.03 (m, 12H), 4.16 (dd, *J* = 5.5, 12.7 Hz, 2H), 4.05 (dd, *J* = 5.5, 12.7 Hz, 2H), 3.84 (dd, *J* = 4.3, 8.2 Hz, 2H), 4.46 (dt, *J* = 5.2, 6.4 Hz, 2H), 2.33-2.27 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 135.5, 135.3, 135.2, 119.4, 116.7, 116.4, 81.1, 79.4, 71.8, 35.8; MS (DCI/NH_3) *m/z* (MNH_4^+) = 336.



12

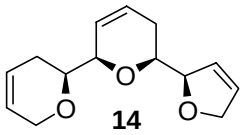
Compound (**12**). **4-Allyloxy-3-[2-((Z)-propenyloxy)-1-vinyl-pent-4-enyloxy]-hepta-1,6-diene** To a stirred solution of hexaene **11** (13.5 mg, 0.04 mmol) in dry MeOH (1.5 ml) was

added Wilkinson's catalyst (chlorotris(triphenylphosphine) rhodium (I) (3 mg, 2.97 μmol) and the resulting mixture was heated at 50° C for 12 hours. The solution was concentrated under vacuum, and the crude product was purified on silica gel (pentane/Et_2O 8.5/0.5) to give **12** (6.8 mg, 55% yield). ^{1}H NMR ($CDCl_3$) δ 6.11 (dd, *J* = 1.4, 10.8 Hz, 1H), 5.90-5.69 (m, 5H), 5.35-5.05 (m, 10H), 4.91-4.88 (m, 1H), 4.12 (dd, *J* = 5.5, 12.5 Hz, 1H), 4.08 (dd, *J* = 5.5, 12.5 Hz, 1H), 3.88-3.80 (m, 2H), 3.71-3.67 (m, 1H), 3.46-3.41 (m, 1H), 2.35-2.27 (m, 4H), 1.52 (dd, *J* = 1.5, 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 146.9, 135.5, 135.4, 135.3, 135.0, 134.6, 119.9, 119.6, 117.2, 116.8, 116.5, 100.6, 82.4, 81.1, 79.9, 78.9, 71.9, 35.9, 13.7; MS (DCI/NH_3) *m/z* (MNH_4^+) = 336.



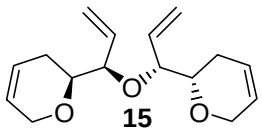
13

4-((E)-Propenyloxy)-3-[2-((Z)-propenyloxy)-1-vinyl-pent-4-enyloxy]-hepta-1,6-diene(13). During the preparation of compound **11**, the hexaene **13** was formed, and was isolated (2 mg, 20% yield). ^{1}H NMR ($CDCl_3$) δ 6.12 (d, *J* = 9.8 Hz, 1H), 6.02 (dd, *J* = 1.7, 6.1 Hz, 1H), 5.84-5.65 (m, 4H), 5.34-5.04 (m, 8H), 4.91-4.88 (m, 1H), 4.33-4.29 (m, 1H), 3.88-3.84 (m, 2H), 3.82-3.60 (m, 2H), 2.43-2.27 (m, 4H), 1.62 (dd, *J* = 1.3, 6.7 Hz, 3H), 1.44 (dd, *J* = 1.4, 8.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 147.2, 146.1, 134.9, 134.6, 135.4, 135.3, 119.9, 117.2, 100.5, 100.1, 83.4, 82.3, 79.1, 78.9, 35.8, 35.3, 12.4; MS (DCI/NH_3) *m/z* (MNH_4^+) = 336.



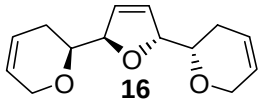
14

6'-(2,5-Dihydrofuran-2-yl)-3,6,5',6'-tetrahydro-2H,2H'-[2,2']-bipyranyl (14). To a solution of hexaene **9** (10 mg, 0.04 mmol) in dry benzene (1 ml) at room temperature was added a solution of bis(tricyclohexylphosphine)benzylidine ruthenium (IV) dichloride (2 mg, 0.002 mmol) in 1 ml of dry benzene. The reaction mixture was stirred for 2 hours at room temperature and was concentrated under vacuum. The crude product was purified by flash column chromatography (pentane/ether 8/2) to yield the tri-cyclic compound **14** (5 mg, 65% yield). ^{1}H NMR ($CDCl_3$) δ 5.99-5.68 (m, 6H), 4.84 (dd, *J* = 1.6, 5.0 Hz, 1H), 4.69-4.66 (m, 2H), 4.23-4.20 (m, 2H), 4.11-4.07 (m, 1H), 3.61-3.54 (m, 1H), 3.52-3.46 (m, 1H), 2.28-2.00 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 127.6, 127.2, 126.0, 125.2, 124.2, 88.3, 77.2, 76.5, 75.9, 75.7, 66.1, 29.7, 27.1; MS (DCI/NH_3) *m/z* (MNH_4^+) = 252.



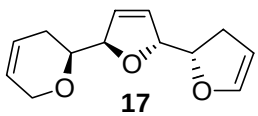
15

Compound (15). To a solution of hexaene **10** (10 mg, 0.031 mmol) in dry benzene (1 ml) at room temperature was added a solution of bis(tricyclohexylphosphine)benzylidine ruthenium (IV) dichloride (1.5 mg, 0.002 mmol) in 0.5 ml of dry benzene. The reaction mixture was stirred for 2 hours at room temperature and was concentrated under vacuum. The crude product was purified by flash column chromatography (pentane/ether 9/1) to yield the bi-cyclic compound **15** (5.2 mg, 69% yield). ^{1}H NMR ($CDCl_3$) δ 5.85-5.68 (m, 6H), 5.36 (dd, *J* = 1.6, 10.4 Hz, 2H), 5.27 (dd, *J* = 1.6, 15.9 Hz, 2H), 4.21 (br s, 4H), 3.81 (dd, *J* = 5.7, 8.1 Hz, 2H), 3.60 (dt, *J* = 5.5 Hz, 8.1 Hz, 2H), 2.17-2.12 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 135.8, 128.3, 126.0, 119.6, 116.4, 80.0, 75.6, 66.1, 27.2; MS (TOF/ *m/z*) (MNa^+) = 284.



16

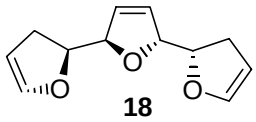
Compound (16). To a stirred solution of **15** (10 mg, 0.031 mmol) in dry toluene (1 ml) was added a solution of 1,3-dimesitylimidazol-2-ylidene ruthenium benzylidene (1 mg, 0.0011 mmol) in toluene (1 ml). The reaction mixture was heated at 70°C for 4 hours and then concentrated and purified on silicagel (pentane/Et_2O 5/5) to yield to the tri-cyclic compound **16** (5.5 mg, 75% yield). ^{1}H NMR ($CDCl_3$) δ 6.00 (br s, 2H), 5.87-5.80 (m, 2H), 5.75-5.65 (m, 2H), 4.90 (dd, *J* = 5.7, 8.1 Hz, 2H), 4.21 (br s, 4H), 3.58 (dt, *J* = 3.8, 10.4 Hz, 2H), 2.24-2.00 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 128.4, 126.2, 123.9, 88.6, 75.9, 66.1, 26.6; MS (DCI/NH_3) *m/z* (MNH_4^+) = 252.



17

5'-(3,6-Dihydro-2H-pyran-2-yl)-2,3,2',5'-tetrahydro-[2,2']bifuranyl (17). The hexaene **12** (5.1 mg, 0.016 mmol) was weighted in a NMR tube and dissolved in toluene d_8 (0.5 ml). A solution of 1,3-dimesitylimidazol-2-ylidene ruthenium benzylidene in toluene d_8 (64 µl, 12.5 mmol/L in toluene d_8) was added, and the NMR tube was heated at 70°C for 4 hours. The tricyclic product formation was monitored by NMR ^{1}H. After disappearance of the allylic methylene, the solution was filtered on a celite pad, and concentrated to give the tri-cyclic compound **17** (2 mg, 55% yield). ^{1}H NMR (C_7D_8) δ 6.48-6.44 (m, 1H), 6.07 (br s, 2H), 5.83-

5.63(m, 1H), 5.36-5.30 (m, 1H), 5.23-5.01 (m, 3H), 4.65-4.50 (m, 1H), 4.24 (br s, 2H), 3.68 (m, 1H), 2.83-2.75 (m, 2H), 2.34-2.10 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 141.6, 132.6, 130.5, 99.1, 89.5, 82.9, 73.7, 63.5, 31.9, 26.5; MS (DCI/NH_3) *m/z* (MNH_4^+) = 238.



18

2,3,2',5',2'',3''-Hexahydro-[2,2',5',2'']terfuran (18). The hexaene **13** (1.5 mg, 4.17 μmol) was weighted in a NMR tube and dissolved in toluene d_8 (0.5 ml). A solution of 1,3-dimesitylimidazol-2-ylidene ruthenium benzylidene in toluene d_8 (18 μl, 12.5 mmol/L in toluene d_8) was added, and the NMR tube was heated at 70°C for 6 hours. The tri-cyclic product formation was monitored by NMR ^{1}H. After disappearance of the allylic methylene, the solution was filtered on a celite pad, and concentrated to give the tricyclic compound **18** (0.61 mg, 62% yield). ^{1}H NMR (C_7D_8) δ 6.52-6.49 (m, 1H), 6.07 (br s, 1H), 5.10-4.98 (m, 2H), 4.61-4.59 (m, 1H), 2.84-2.71 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 143.1, 124.5, 99.2, 76.7, 88.7, 32.1; MS (DCI/NH_3) *m/z* (MNH_4^+) = 224.

References:

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