Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Gold(I)-Catalyzed Reaction of 1-(1-Alkynyl)-cyclopropyl Ketones with Nucleophiles: A Modular Entry to Highly Substituted Furans**

Junliang Zhang and Hans-Günther Schmalz*

Institut für Organische Chemie, Universität zu Köln, Greinstrasse 4, 50939, Koeln, Germany

General procedure for the synthesis of 1-(1-alkynyl)cyclopropyl ketones: [2]

1-Phenylethynyl-bicyclo[4.1.0]heptan-2-one (*rac*-2a):

To a solution of trimethylsulfoxonium iodide (3.30 g, 15 mmol) in 50 mL of DMSO was added NaH (60% in mineral oil, 600 mg, 15 mmol) in one portion at rt. After stirring for 0.5 h, 2-phenylethynyl-2-cyclohexen-1-one[1] (2.94 g, 15 mmol) was added and the mixture was stirred overnight. After addition of 50 ml of water the mixture was extracted with ether (3 x 50 mL) and the combined organic layers was washed once with 20 ml of water and dried over Na_2SO_4. After filtration and evaporation, the residue was purified by column chromatography on silica gel (cyclohexane/ ethyl acetate = 8:1) to afford 2.80 g (89%) of compound ***rac*-2a** as light yellow solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.50-7.40 (m, 2 H), 7.36-7.24 (m, 3 H), 2.48-2.34 (m, 1 H), 2.32-1.90 (m, 4 H), 1.84-1.64 (m, 4 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 203.77, 131.86, 128.06, 127.85, 123.18, 89.20, 79.75, 36.35, 29.39, 27.00, 21.29, 21.25, 18.27 ppm; MS (70 eV): *m*/*z* (%): 210 (100) [M^+]; IR (neat): ν = 3108, 2927, 2208, 1691, 1435, 1004, 915 cm^{-1}; Anal. calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71; found: C, 85.48; H, 6.76.

1-(Cyclohexenyl-ethynyl)-bicyclo[4.1.0]heptan-2-one (*rac*-2b):

Reaction of 2-(cyclohexenylethynyl)-cyclohexen-1-one[1] (1.50, 7.5 mmol) with trimethylsulfoxonium iodide (1.65 g, 7.5 mmol) and NaH (60%, 300 mg, 7.5 mmol) afforded 0.88g (55%) of ***rac*-2b** as a yellow oil**.** ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.16-6.08 (m, 1 H), 2.44-2.30 (m, 1 H), 2.30-1.90 (m, 8 H), 1.90-1.70 (m, 8 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 204.04, 134.78, 120.34, 86.26, 81.54, 36.28, 29.32, 26.93, 25.58, 22.29, 21.47, 21.25, 21.23, 21.09, 18.31 ppm; MS (70 eV): *m*/*z* (%): 214 (100) [M^+]; IR (neat): ν = 3108, 2927, 2208, 1691, 1435, 1004, 915 cm^{-1}; HRMS calcd for $C_{15}H_{18}O$: 214.1358, found: 214.136.

1-(Cyclopropylethynyl)-bicyclo[4.1.0]heptan-2-one (*rac*-2c):

The reaction of 2-(cyclopropylethynyl)-cyclohexen-1-one[1] (1.00g, 6.25 mmol) with trimethylsulfoxonium iodide (1.65 g, 7.5 mmol) and NaH (60%, 300 mg, 7.5 mmol) afforded 0.70 g (65%) of ***rac*-2c** as a yellow oil**.** ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.48-2.22(m, 1 H), 2.18-1.85 (m, 4 H), 1.82-1.48 (m, 3 H), 1.42 (dd, *J* = 8.4, 6.6 Hz, 1 H), 1.30-1.18 (m, 1 H), 0.78-0.58 (m, 4 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 204.55, 83.10, 74.08, 36.17, 28.96, 26.56, 21.14, 20.88, 18.28, 8.17, -0.42 ppm; MS (70 eV): *m*/*z* (%): 174 (32.0) [M^+], 117 (100) [M^+-CO-C_2H_5]; IR (neat): ν = 2940, 2208, 1688, 1341, 1007, 912 cm^{-1}; HRMS calcd for $C_{12}H_{14}O$: 174.1045, found: 174.104.

1-(1-Hexynyl)-bicyclo[4.1.0]heptan-2-one (*rac*-2d):

The reaction of 2-(1-hexynyl)-cyclohexen-2-one (528 mg, 3.0 mmol) with trimethyl-sulfoxonium iodide (660 mg, 3.0 mmol) and NaH (60%, 130 mg, 3.0 mmol) afforded 380 mg (67%) of ***rac*-2d** as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.33 (dt, *J* = 18.0, 4.5 Hz, 1 H), 2,19 (t, *J* = 7.2 Hz, 2 H), 2.20-1.88 (m, 4 H), 1.78-1.53 (m, 3 H), 1.52-1.1.32 (m, 5 H), 0.89 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 204.67, 80.14, 79.38, 36.17, 30.88, 28.96, 26.67, 21.90, 21.18, 20.91,18.51, 18.32, 13.57 ppm; MS (70 eV): *m*/*z* (%): 190 (8.5) [M^+], 91 (100); IR (neat): ν = 2229, 1703, 1491, 1356, 1276, 1136, 755 cm^{-1}; HRMS calcd for $C_{13}H_{18}O$: 190.1358, found: 174.136.

1-(Trimethylsilylethynyl)-bicyclo[4.1.0]heptan-2-one (*rac*-2f):

The reaction of 2-(trimethylsilylethynyl)-cyclohexen-1-one (1.44 g, 7.5 mmol), trimethyl-sulfoxonium iodide (1.65 g, 7.5 mmol) and NaH (60%, 300 mg, 7.5 mmol) afforded 0.78 g (51%) of ***rac*-2f.** ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2. 40-2.26 (m, 1 H), 2.22-1.90 (m, 4 H), 1.80-1.50 (m, 4 H), 0.15 (s, 9 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 203.36, 105.44, 83.95, 36.25, 29.31, 27.08, 21.27, 21.09, 18.11, 0.05 ppm; MS (70 eV): *m*/*z* (%): 206 (13.5) [M^+], 191 (100)[M^+-CH_3]; IR (neat): ν = 2166, 1693, 1247, 839 cm^{-1}.

1-Ethynyl-bicyclo[4.1.0]heptan-2-one (*rac*-2e):

To a solution of ***rac*-2f** (618 mg, 3.0 mmol) in MeOH (20 mL) was added Na_2CO_3 (350 mg, 3.3 mmol) and the mixture was stirred for 8 h. After filtration and evaporation, the residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate = 4:1) to afford 400 mg (99.5%) of ***rac*-2e** as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ =

2.35 (ddd, *J* = 18.3, 5.7, 3.9 Hz, 1 H), 2.24-2.08 (m, 3 H), 2.08-1.90 (m, 2 H), 1.80-1.66 (m, 3 H), 1.53 (dd, *J* = 8.4, 4.2 Hz, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 203.66, 83.44, 67.98, 36.05, 28.86, 26.19, 20.99, 20.74, 18.09 ppm; MS (70 eV): *m*/*z* (%): 134 (18.8) [M^+], 91 (100); IR (neat): ν = 2117, 1686, 1302, 1084, 1006, 917 cm^{-1}; HRMS calcd for $C_9H_{10}O$:134.0732, found: 174.073.

1-Phenylethynyl-bicyclo[5.1.0]heptan-2-one (*rac*-10):

The reaction of 2-phenylethynyl-cyclohept-2-en-1-one (1.05g, 5.0 mmol) with trimethylsulfoxonium iodide (1.21, 5.5 mmol) and NaH (60%, 220 mg, 5.5 mmol) afforded 0.67 (60%) of ***rac*-10** as a yellow oil**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.42-7.35 (m, 2 H), 7.30-7.25 (m, 3 H), 2.99-2.94 (m, 1 H), 2.65-2.55 (m, 1 H), 2.52-2.38 (M, 1 H), 1.80-1.40 (m, 7 H), 1.20-1.10 (m, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 204.94, 131.74, 128.19, 127.93, 123.20, 89.69, 79.69, 41.53, 30.17, 29.39, 28.11, 25.75, 25.31, 22.30 ppm; MS (70 eV): *m*/*z* (%): 224 (100) [M^+]; IR (neat): ν = 3108, 2927, 2207, 1692, 1437, 1005, 918 cm^{-1}

3-Phenylethynyl-2, 3-methanochromanone (*rac*-12):

The reaction of 3-phenylethynyl-chromone[1] (1.230 g, 5 mmol) with trimethyl-sulfoxonium iodide (1.100 g, 7.5 mmol) and NaH (60%, 200 mg, 5 mmol) afforded 0.363 g (28%) of **12** as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.97 (dd, *J* = 7.8, 1.8 Hz, 1 H), 7.55-7.46 (m, 3 H), 7.37-7.26 (m, 3 H), 7.15-6.97 (m, 1 H), 7.00 (d, *J* = 7. 8 Hz, 1 H), 4.88 (dd, *J* = 7.2, 4.8 Hz, 1 H), 2.02 (t, *J* = 7.2 Hz, 1 H), 1.91 (dd, *J* = 7.2, 4.8 Hz, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 186.30, 155.58, 135.75, 132.00, 128.37, 128.17,

127.66, 122.52, 122.37, 118.40, 117.78, 85.16, 81.89, 63.88, 27.32, 18.53 ppm; MS (70 eV): *m*/*z* (%): 260 (100) [M^+]; IR (neat): ν = 2229, 1672, 1605, 1460, 1290, 949, 751 cm^{-1}; HRMS calcd for $C_{18}H_{12}O_2$: 260.0837, found: 260.083.

1-Phenylethynylcyclopropyl methyl ketone (14).

To a solution of 1-cyclopropyl-2-phenylethyne (1.85 g, 13 mmol) in dry THF (100 ML) was added dropwise BuLi (2.5 M, 15 mmol) in hexane at 0°C. The mixture was stirred for 1 h at rt before acetaldehyde was added. After 1h, the reaction was quenched by addition of 50 mL of water. The mixture was neutralized with 1 N HCl and extracted with ether (3 x 50 ml). The combined organic layers were dried over Na_2SO_4. After filtration and evaporation, the crude product was dissolved in 100 ml of CH_2Cl_2 and oxidized by PCC (5.6 g) at rt overnight. After filtration through a short pad of silica gel and concentration, the residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate = 8/1) to afford 1.20 g (two steps overall yield 48%) of **14** as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.50-7.38 (m, 2 H), 7.36-7.27 (m, 3 H), 2.57 (s, 3 H), 1.66-1.60 (m, 2 H), 1.43-1.36 (m, 2 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 205.90, 131.53, 128.31, 128.09, 123.08, 90.21, 80.49, 29.44, 23.53, 23.21 ppm; MS (70 eV): *m*/*z* (%): 184 (100) [M^+]; IR (neat): ν = 2930, 1696, 1135, 914 cm^{-1}; HRMS calcd for $C_{13}H_{12}O$: 184.0888, 184.089.

1-Phenylethynyl-2-phenyl-cyclopropyl methyl ketone (*rac*-16):

The reaction of 3-benzylidene-5-phenyl-pent-4-yn-2-one (1.23 g, 5.0 mmol) with trimethylsulfoxonium iodide (1.21, 5.5 mmol) and NaH (60%, 220 mg, 5.5 mmol)

afforded 0.65 (50%) of ***rac*-16** as a yellow solid**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.08-7.06 (m, 2 H), 7.06-7.01 (m, 3 H), 7.01-6.94 (m, 3 H), 6.89-6.84 (m, 2 H), 2.78 (td, *J* = 9.0, 2.3 Hz, 1 H), 2.32 (s, 3 H), 1.95-1.85 (m, 1 H), 1.60-1.55 (m, 1 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 204.95, 135.86, 131.32, 128.68, 128.20, 128.07, 128.01, 127.98, 127.26, 122.96, 87.32, 84.38, 39.19, 33.31, 29.65, 26.47 ppm;

General procedure for the $Ph_3PAuOTf$-catalyzed ring expansion / cyclization:

2-Phenyl-5-methoxy-5, 6, 7, 8-tetrahydro-4*H*-cyclohepta[b]furan (*rac*-3aa): To a solution of cyclopropyl ketone ***rac*-2a** (105 mg, 0.5 mmol), methanol (32 mg, 1.0 mmol) in dry CH_2Cl_2 was added a solution of Ph_3AuOTf (generated by equal equivalent of Ph_3PAuCl and AgOTf, AgCl was filtered off) in CH_2Cl_2 (0.00625 M, 0.8 mL, 0.005 mmol). The mixture was stirred for 15 min at room temperature. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate = 10:1) to afford 110 mg of ***rac*-3aa** (91%) as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.63-7.59 (m, 2 H), 7.40-7.32 (m, 2 H), 7.25-7.18 (m, 1 H), 6.48 (s, 1 H), 3.41 (s, 3 H), 3.35 (tt, *J* = 9.3, 2.7 Hz, 1 H), 2.96-2.82 (m, 2 H), 2.81-2.70 (m, 1 H), 2.61 (dd, *J* = 15.6, 9.6 Hz, 1 H), 2.30-2.16 (m, 1 H), 2.08-1.96 (m, 1 H), 1.82-1.54 (m, 2 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 153.12, 150.23, 131.06, 128.52, 126.58, 123.17, 116.67, 108.90, 79.69, 56.18, 35.76, 31.17, 28.34, 22.77 ppm; MS (70 eV): *m*/*z* (%): 242 (100) [M^+]; IR (neat): ν = 2926, 2850, 1600, 1580, 1551, 1485, 1444, 1091, 757 cm^{-1}; HRMS calcd for $C_{16}H_{18}O_2$: 242.1307, found: 242.131.

2-Phenyl-5-*iso*-propyloxy-5, 6, 7, 8-tetrahydro-4*H*-cyclohepta[b]furan (*rac*-3ab):

The reaction of **2a** (105 mg, 0.5 mmol) with *iso*-propanol (60 mg, 1.0 mmol) in the presence of Ph_3AuOTf (0.00625 M, 0.8 mL, 0.005 mmol) afforded 122 mg (90%) of ***rac*-3ab**. ^1H NMR (300 MHz, $CDCl_3$) δ = 7.64-7.58 (m, 2 H), 7.39-7.32 (m, 2 H), 7.29-7.20 (m, 1 H), 6.46 (s, 1 H), 3.74 (7, *J* = 6.0 Hz, 1 H), 3.43 (tt, *J* = 9.9, 3.0 Hz, 1 H), 2.98-2.50 (m, 4 H), 2.28-2.16 (m, 1 H), 2.10-1.90 (m, 1 H), 1.78-1.50 (m, 2 H), 1.19 (d, *J* = 6.0 Hz, 3 H), 1.18 (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 153.26, 150.14, 131.07, 128.55, 126.59, 123.18, 116.94, 108.87, 75.89, 69.13, 37.68, 32.80, 28.29, 23.74, 22.87 ppm; MS (70 eV): *m*/*z* (%): 270 (75.3) [M^+], 210 (100) [M^+-C_3H_7OH]; IR (neat): ν = 2967, 2928, 1601, 1550, 1486, 1447, 1123, 1055, 758, 667 cm^{-1}; HRMS calcd for $C_{18}H_{22}O_2$: 270.1620, found: 270.162.

2-Phenyl-5-*tert* -butyloxy-5, 6, 7, 8-tetrahydro-4*H*-cyclohepta[b]furan (*rac*-3ac):

The reaction of ***rac*-2a** (105 mg, 0.5 mmol) with *tert*-butanol (74 mg, 1.0 mmol) in the presence of Ph_3AuOTf (0.00625 M, 0.8 mL, 0.005 mmol) afforded 121 mg (85%) of ***rac*-3ac**. ^1H NMR (300 MHz, $CDCl_3$) δ = 7.64-7.58 (m, 2 H), 7.40-7.32 (m, 2 H), 7,26-7.20 (m, 1 H), 3.54 (tt, *J* = 8.1, 4.5 Hz, 1 H), 2.96-2.84 (m, 1 H), 2.78-2.58 (m, 3 H), 2.20-2.10 (m, 1 H), 2.08-1.90 (m, 1 H), 1.80-1.60 (m, 2 H), 1.25 (s, 9 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 153.18, 150.09, 131.06, 128.52, 126.56, 123.16, 117.17, 108.87, 73.76, 70.91, 39.97, 34.98, 28.24, 23.97 ppm; MS (70 eV): *m*/*z* (%): 284 (65.9) [M^+], 227 (100) [M^+-C_4H_9]; IR (neat): ν = 2969, 2929, 1601, 1551, 1486, 1361, 1194, 1053, 758 cm^{-1}; HRMS calcd for $C_{19}H_{24}O_2$: 284.1776, found: 284.178.

2-Phenyl-5-(3-phenylprop-2-ynyloxy) -5, 6, 7, 8-tetrahydro-4*H*-cyclohepta[b]-furan (*rac*-3ad):

The reaction of ***rac*-2a** (105 mg, 0.5 mmol) with 3-phenyl-2-propyn-1-ol (132 mg, 1.0 mmol) in the presence of Ph_3AuOTf (0.00625 M, 0.8 mL, 0.005 mmol) afforded 132 mg (77%) of ***rac*-3ad**. ^{1}H NMR (250MHz, $CDCl_3$) δ = 7.64-7.56 (m, 2 H), 7.50-7.48 (m, 2 H), 7.38-7.28 (m, 5 H), 7.25-7.16 (m, 1 H), 6.46 (s, 1 H), 4.46 (s, 2 H), 3.75 (tt, *J* = 9.5, 3.0 Hz, 1 H), 3.0-2.60 (m, 4 H), 2.28-2.18 (m, 1 H), 2.12-1.94 (m, 1 H), 1.90-1.60 (m, 2 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 153.12, 150.25, 131.74, 131.02, 128.53, 128.36, 128.24, 126.60, 123.18, 122.68, 116.54, 108.92, 85.74, 85.58, 77.23, 56.44, 36.06, 31.47, 28.31, 22.84 ppm; MS (70 eV): *m*/*z* (%): 342 (25.9) [M^+], 105 (100); IR (neat): ν = 2928, 1598, 1550, 1488, 1070, 756 cm^{-1}; HRMS calcd for $C_{24}H_{22}O_2$: 342.1620, found: 342.162.

2-Phenyl-5-(4'-methoxyphenyloxy) -5, 6, 7, 8-tetrahydro-4*H*-cyclohepta[b]furan (*rac*-3ae):

The reaction of ***rac*-2a** (105 mg, 0.5 mmol) with 4-methoxyphenol (124 mg, 1.0 mmol) in the presence of Ph_3AuOTf (0.00625 M, 0.8 mL, 0.005 mmol) afforded 140 mg (84%) of ***rac*-3ae**. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 7. 8 Hz, 2 H), 7.37 (t, *J* = 7. 8 Hz, 2 H), 7.23 (t, *J* = 7. 8 Hz, 1 H), 6.88 (s, 4 H), 6.43 (s, 1 H), 4.26 (tt, *J* = 9.6, 2.7 Hz, 1 H), 3.81 (s, 3 H), 3.08-2.90 (m, 2 H), 2.88-1.68 (m, 2 H), 2.44-2.32 (m, 1 H), 2.16-2.00 (m, 1 H), 1.94-1.80 (m, 1 H), 1.80-1.63 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 154.02, 153.24, 151.35, 150.34, 130.95, 128.56, 126.69, 123.20, 117.59, 116.25, 114.69, 108.77, 77.47, 55.67, 36.32, 31.59, 28.26, 23.23 ppm; MS (70 eV): *m*/*z* (%): 334 (9.1) [M^+],

211 (100) [M^+-$MeOC_6H_4O$]; IR (neat): ν = 2929, 1600, 1550, 1503, 1486, 1226, 1036 cm^{-1}; HRMS calcd for $C_{22}H_{22}O_3$: 334.1569, found: 334.157.

2-Phenyl-5-acetoxy-5, 6, 7, 8-tetrahydro-4*H*-cyclohepta[b]furan (*rac*-3af):

The reaction of **2a** (105 mg, 0.5 mmol) with acetic acid (60 mg, 1.0 mmol) in the presence of Ph_3AuOTf (0.00625 M, 0.8 mL, 0.005 mmol) afforded 113 mg (84%) of ***rac*-3af**. ^1H NMR (300 MHz, $CDCl_3$) δ = 7.64-7.58 (m, 2 H), 7.40-7.32 (m, 2 H), 7.26-7.22 (m, 1 H), 6.45 (s, 1 H), 4.93 (tt, *J* = 9.6, 2.7 Hz, 1 H), 3.00-2.64 (m, 4 H), 2.24-2.12 (m, 1 H), 2.08 (s, 3 H), 2.06-1.68 (m, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 170.24, 152.99, 150.33, 130.91, 128.54, 126.69, 123.19, 115, 96, 108.76, 72.87, 26.07, 31.30, 28.23, 22.76, 21.38 ppm; MS (70 eV): *m*/*z* (%): 270 (26.6) [M^+], 210 (100) [M^+-HOAc]; IR (neat): ν = 2933, 1727, 1600, 1551, 1486, 1238, 1022, 758 cm^{-1}; HRMS calcd for $C_{17}H_{18}O_3$: 270.1256, found: 270.1257.

3-[2-Phenyl-5, 6, 7, 8-tetrahydro-4*H*-cyclohepta[b]furan-5-yl]-indol (*rac*-3ag):

The reaction of ***rac*-2a** (105 mg, 0.5 mmol) with indole (117 mg, 1.0 mmol) in the presence of Ph_3AuOTf (0.00625 M, 0.8 mL, 0.005 mmol) afforded 119 mg (73%) of **3ag**. ^1H NMR (300 MHz, $CDCl_3$) δ = 7.92 (s, 1 H), 7.72-7.62 (m, 3 H), 7.42-7.34 (m, 3 H), 7.30-7.12 (m, 3 H), 7.01 (d, *J* = 2.4 Hz, 1 H), 6.51 (s, 1 H), 3.26 (tt, *J* = 10.2, 2.4 Hz, 1 H), 3.18-2.82 (m, 4 H), 2.46-2.36 (m, 1 H), 2.18-1.95 (m, 2 H), 1.90-1.68 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 153.25, 149.89, 136.21, 131.19, 128.56, 126.51, 126.44, 123.17, 122.98, 121.97, 121.40, 119.81, 119.16, 119.10, 111.14, 108.89, 37.85, 36.64, 33.15, 28.84, 25.75 ppm; MS (70 eV): *m*/*z* (%): 327 (100) [M^+]; IR (neat): ν = 3415,

2922, 1599, 1548, 1485, 1455, 1336, 1225, 1093, 759, 740 cm^{-1}; HRMS calcd for $C_{23}H_{21}NO$: 327.1623, found: 327.162.

2-Cyclohex-1-enyl-5-methoxy-5, 6, 7, 8-tetrahydro-4*H*-cyclohepta[b]furan (*rac*-3ba): The reaction of ***rac*-2b** (107 mg, 0.5 mmol) with methanol (32 mg, 1.0 mmol) in the presence of Ph_3AuOTf (0.00625 M, 0.8 mL, 0.005 mmol) afforded 98 mg (80%) of ***rac*-3ba**. ^1H NMR (300 MHz, $CDCl_3$) δ = 6.20-6.12 (m, 1 H), 5.95 (s, 1 H), 3.36 (s, 3 H), 3.26 (tt, *J* = 9.3 Hz, 3.0 Hz, 1 H), 2.85-2.72 (m, 2 H), 2.70-2.58 (m, 1 H), 2.56-2.42 (m, 1 H), 2.36-2.10 (m, 5 H), 1.98-1.84 (m, 1 H), 1.78-1.66 (m, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 151.90, 151.85, 127.10, 120.78, 115.62, 107.55, 79.87, 56.12, 35.85, 31.14, 28.21, 25.09, 24.86, 22.94, 22.42, 22.30 ppm; MS (70 eV): *m*/*z* (%): 246 (100) [M^+]; IR (neat): ν = 3085, 3007, 2926, 2850, 1699, 1633, 1578, 1451, 1093, 968 cm^{-1}; HRMS calcd for $C_{16}H_{22}O_2$: 246.1620, found: 246.162.

2-Cyclopropyl -5-methoxy-5, 6, 7, 8-tetrahydro-4*H*-cyclohepta[b]furan (*rac*-3ca): The reaction of ***rac*-2c** (87 mg, 0.5 mmol) with methanol (32 mg, 1.0 mmol) in the presence of Ph_3AuOTf (0.00625 M, 0.8 mL, 0.005 mmol) afforded 84 mg (82%) of ***rac*-3ca**. ^1H NMR (300 MHz, $CDCl_3$) δ = 5.75 (s, 1 H), 3.38 (s, 3 H), 3.28 (tt, *J* = 9.3, 2.7 Hz, 1 H), 2.82-2.40 (m, 4 H), 2.20-2.10 (m, 1 H), 1.98-1.86 (m, 1 H), 1.85-1.42 (m, 3 H), 0.86-0.76 (m, 2 H), 0.74-0.68 (m, 2 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 153.68, 150.86, 114.74, 107.28, 79.99, 56.15, 35.77, 31.13, 28.14, 22.90, 8.45, 6.27 ppm; MS (70 eV): *m*/*z* (%): 206 (92.9) [M^+], 174 (100)[M^+-CH_3OH]; IR (neat): ν = 2926, 1578, 1451, 1093, 968 cm^{-1}; HRMS calcd for $C_{13}H_{18}O_2$: 206.1307, found: 206.131.

2-Cyclopropyl-5-(1'-pyrrolidinonyl)-5,6,7,8-tetrahydro-4*H*-cyclohepta-[b]furan (*rac*-3ch):

The reaction of ***rac*-2c** (87 mg, 0.5 mmol) with pyrrolidinone (85 mg, 1.0 mmol) in the presence of Ph_3AuOTf (0.00625 M, 0.8 mL, 0.005 mmol) afforded 85 mg (68%) of ***rac*-3ch**. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.72 (s, 1 H), 4.84 (tt, *J* = 10.0, 2,5 Hz, 1 H), 3.68 (t, *J* = 7.0 Hz, 2 H), 2.85 (dd, *J* = 15.0, 2.0 Hz, 1 H), 2.79-2.71 (m, 1 H), 2.64-2.54 (m, 2 H), 2.43 (t, *J* = 8.0 Hz, 2 H), 2.29-2.21 (m, 1 H), 2.05-1.96 (m, 2 H), 1.96-1.84 (m, 1 H), 1.83 -1.70 (m, 2 H), 1.70-1.58 (m, 1 H), 0.81 (dd, *J* = 8.5, 2.5 Hz, 2 H), 0.74-0.64 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.82, 153.54, 150.72, 114.15, 107.31, 76.18, 55.20, 35.90, 31.48,31.26, 28.08, 22.81, 8.37, 6.26, 6.13 ppm; MS (70 eV): *m*/*z* (%): 259 (12.9) [M^+], 174 (100)[M^+-C_4H_7NO]; IR (neat): ν = 2933, 1644, 1579, 1354, 1335, 1303, 969 cm^{-1}; HRMS calcd for $C_{16}H_{21}NO_2$: 259.1572, found: 259.157.

2-Butyl -5-methoxy-5, 6, 7, 8-tetrahydro-4*H*-cyclohepta-[b]furan (*rac*-3da):

The reaction of ***rac*-2d** (95 mg, 0.5 mmol) with methanol (32 mg, 1.0 mmol) in the presence of Ph_3AuOTf (0.00625 M, 0.8 mL, 0.005 mmol) afforded 95 mg (86%) of **3da**. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.73 (s, 1 H), 3.35 (s, 3 H), 3.25 (tt, *J* =9.5, 3.0 Hz, 1 H), 2.82-2.58 (m, 3 H), 2.50 (t, *J* = 7.2 Hz, 2 H), 2.50-38 (m, 1 H), 2.20-2.10 (m, 1 H), 1.96-1.80 (m, 1 H), 1.70-1.42 (m, 4 H), 1.41-1.20 (m, 2 H), 0.90 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 152.84, 150.93, 114.56, 108.35, 80.08, 56.15, 35.81, 31.19, 30.24, 28.15, 27.58, 22.99, 22.34, 13.83 ppm; MS (70 eV): *m*/*z* (%): 222 (47.9) [M^+], 147 (100)[M^+-C_4H_9-CH_3OH]; IR (neat): ν = 2927, 1573, 1455, 1370, 1094, 974 cm^{-1}; HRMS calcd for $C_{14}H_{22}O_2$: 222.1620, found: 222.162.

5-Methoxy-5, 6, 7, 8-tetrahydro-4*H*-cyclohepta-[b]furan (*rac*-3ea):

The reaction of ***rac*-2e** (67 mg, 0.5 mmol) with methanol (32 mg, 1.0 mmol) in the presence of Ph_3AuOTf (0.00625 M, 0.8 mL, 0.005 mmol) afforded 63 mg (76%) of ***rac*-3ea**. ^1H NMR (300 MHz, $CDCl_3$) δ = 7.17 (d, *J* = 1.8 Hz, 1 H), 6.19 (d, , *J* = 1.8 Hz, 1 H), 3.93 (s, 3 H), 3.30 (tt, *J* = 9.6, 3.0 Hz, 1 H), 2.92-2.77 (m, 2 H), 2.76-2.44 (m, 2 H), 2.28-2.14 (m, 2 H), 2.04-1.89 (m, 1 H), 1.78-1.50 (m, 2 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 153.23, 138.89, 114.29, 113.37, 79.82, 56.18, 35.85, 31.04, 28.18, 22.83 ppm; MS (70 eV): *m*/*z* (%): 166 (48.8) [M^+], 134 (100)[M^+ -CH_3OH]; IR (neat): ν = 2914, 2846, 1799, 1505, 1446, 1094, 912 cm^{-1}; HRMS calcd for $C_{10}H_{14}O_2$:166.0994, found: 166.099.

The reaction of ***rac*-2f** (103 mg, 0.5 mmol) with methanol (32 mg, 1.0 mmol) in the presence Ph_3AuOTf (0.00625 M, 0.8 mL, 0.005 mmol) afforded 29 mg (35%) of ***rac*-3ea** under desilylation.

2-Phenyl -5-methoxy-4, 5, 6, 7, 8, 9-hexahydrocycloocta-[b]furan (*rac*-11):

The reaction of ***rac*-10** (112 mg, 0.5 mmol) with methanol (32 mg, 1.0 mmol) in the presence of Ph_3AuOTf (0.00625 M, 0.8 mL, 0.005 mmol) afforded 114 mg (89%) of ***rac*-11** as oil. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.61-7.58 (m, 2 H), 7.35-7.30 (m, 2 H), 7.20-7.16 (m, 1 H), 6.44 (s, 1 H), 3.49-3.44 (m, 1 H), 3.38 (s, 1 H), 2.84-2.76 (m, 3 H), 2.68-2.62 (m, 1 H), 1.85-1.36 (m, 5 H), 1.50-1.38 (m, 1 H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 152.15, 150.60, 131.10, 128.46, 126.46, 123.10, 117.25, 108.48, 81.11, 56.19, 29.19, 28.60, 26.71, 26.21, 21.57 ppm; MS (70 eV): *m*/*z* (%): 256 (100) [M^+]; IR (neat): ν =

2926, 2850, 1600, 1580, 1551, 1485, 1444, 1091, 757 cm^{-1}; HRMS calcd for $C_{17}H_{20}O_2$: 256.1463, found: 256.1464.

2-Phenyl-5-methoxy-5*H*-benzo[*b*]furo[2,3*d*]oxepine (*rac*-13):

The reaction of ***rac*-12** (130 mg, 0.5 mmol) with methanol (32 mg, 1.0 mmol) in the presence of Ph_3AuOTf (0.00625 M, 0.8 mL, 0.005 mmol) afforded 126 mg (86%) of ***rac*-13** as yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ = 8.00-7.92 (m, 1 H), 7.78-7.72 (m, 2 H), 7.46-7.40 (m, 2 H), 7.34-1.16 (m, 4 H), 6.65 (s, 1 H), 4.98 (dd, *J* = 8.1, 2.1 Hz, 1 H), 3.63 (s, 3 H), 3.28 (dd, *J* = 16.8, 8.1 Hz, 1 H), 3.12 (dd, *J* = 16.8, 2.1 Hz, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 153.10, 152.12, 145.37, 130.38, 128.70, 127.87, 127.58, 124.59, 123.82, 123.24, 120.68, 118.54, 108.69, 104.34, 56.25, 34.03, 26.91 ppm; MS (70 eV): *m*/*z* (%): 292 (100) [M^+]; IR (neat): ν = 3055, 2909, 1595, 1569, 1484, 1441, 1225, 1188, 1131, 1072, 1006, 971, 889, 760 cm^{-1}; HRMS calcd for $C_{19}H_{16}O_3$: 292.1099, found:292.110.

2-Methyl -3-methoxyethyl-5-phenylfuran (15):

The reaction of **14** (92 mg, 1.0 mmol) with methanol (32 mg, 1.0 mmol) in the presence of Ph_3AuOTf (0.00625 M, 0.8 mL, 0.005 mmol) afforded 82 mg (76%) of **15** as a liquid. ^1H NMR (300 MHz, $CDCl_3$) δ = 7.66-7.61 (m, 2 H), 7.40-7.34 (m, 2 H), 7.26-7.22 (m, 1 H), 6.53 (s, 1 H), 3.56 (t, *J* = 7.2 Hz, 2 H), 3.41 (s, 3 H), 2.67 (t, *J* = 7.2 Hz, 2 H), 2.33 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 151.18, 147.91, 131.12, 128.51, 126.60, 123.19, 117.88, 107.20, 72.73, 58.66, 25.59, 11.64 ppm; MS (70 eV): *m*/*z* (%): 216 (88.2) [M^+],

171 (100) [M^+-CH_3OCH_2]; IR (neat): ν = 2916, 1600, 1551, 1486, 1447, 1113, 929, 758 cm^{-1}; HRMS calcd for $C_{14}H_{16}O_2$: 216.1150, found: 216.115.

2-Methyl -3-(2'-methoxy-phenyl-ethyl)-5-phenylfuran (*rac*-17):

The reaction of ***rac*-16** (130 mg, 0.5 mmol) with methanol (32 mg, 1.0 mmol) in the presence of Ph_3AuOTf (0.00625 M, 0.8 mL, 0.005 mmol) afforded 140 mg (96%) of ***rac*-15** as an oil. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.50-7.46 (m, 2 H), 7.26-7.09 (m, 4 H), 6.30 (s, 1 H), 4.16 (d, *J* = 6.6 Hz, 1 H), 3.16 (m, 3 H), 2.78 (dd, *J* = 14.2, 6.6 Hz, 1 H), 2.58 (dd, *J* = 14.2, 6.6 Hz, 1 H), 1.90 (s, 3 H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 150.81, 148.69, 141.51, 131.19, 128.54, 128.29, 127.62, 126.81, 126.54, 123.14, 117.22, 107.85, 84.31, 56.77, 34.11, 11.26 ppm; IR (neat): ν = 2916, 1600, 1551, 1485, 1447, 1112, 928, 758 cm^{-1}; HRMS calcd for $C_{20}H_{20}O_2$: 292.1463, found: 292.1458.

References

1. T. Yao, X. Zhang, R. C. Larock, *J. Am. Chem. Soc.* **2004**, *126*, 11164.

2. J. Cossy, N, Furet, S. Bouzbouz*, Tetrahedron* **1995**, *51*, 11751.