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Supporting Information

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Supporting Information

Cyclization of Allenyne-1,6-diols Catalyzed by Gold and Silver Salts: An Efficient Selective Synthesis of Dihydrofuran and Furan Derivatives

Sundae Kim and Phil Ho Lee*

National Research Laboratory for Catalytic Organic Reaction, Department of Chemistry
and Institute for Basic Science, Kangwon National University, Chunchon 200-701
Republic of Korea

Fax: (+82)-33-253-7582, E-mail: phlee@kangwon.ac.kr

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Data of compounds: S2 – S10

Experimental Section

General: Reactions were carried out in oven-dried glassware under nitrogen atmosphere. All commercial reagents were used without purification, and all solvents were reaction grade. CH₂Cl₂ was freshly distilled from calcium hydride. All reaction mixtures were stirred magnetically and were monitored by thin-layer chromatography using Merck silica gel 60 F₂₅₄ precoated glass plates, which were visualized with UV light and then, developed using either iodine or a solution of anisaldehyde. Flash column chromatography was carried out using Merck silica gel 60 (0.040-0.063 mm, 230-400 mesh). ¹H NMR and ¹³C NMR spectra were recorded on a Bruker DPX FT(400 MHz) spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent (δ 7.24 for ¹H and δ 77.0 for ¹³C). Infrared spectra were recorded on a JASCO FT/IR-460 plus FT-IR spectrometer as either a thin film pressed between two sodium chloride plates or as a solid suspended in a potassium bromide disk. High-resolution mass spectra were recorded on an Autospec M363 series (Micromass).

Typical experimental procedures for intramolecular cyclization catalyzed by

AuCl₃: AuCl₃ (9.8 mg, 0.032 mmol) was added to a solution of 1,6-diphenyl-2-

vinylidenehex-3-yne-1,6-diol (63.0 mg, 0.217 mmol) in methylene chloride (1.5 mL). After the reaction mixture was stirred for 10 min, the solvent was removed under the reduced pressure. The crude product was purified by silica gel column chromatography to give 3-(4-hydroxy-4-phenyl-1-butyn-1-yl)-2-phenyl-2,5-dihydrofuran (**2a**) (38.0 mg, 60%) using EtOAc/hexane = 1/3, R_f = 0.3 and 5-(2-hydroxy-2-phenylethyl)-2-phenyl-3-vinylfuran (**3a**) using EtOAc/hexane = 1/5, R_f = 0.3.

3-(4-Hydroxy-4-phenyl-1-butyn-1-yl)-2-phenyl-2,5-dihydrofuran (2a): ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS) δ 7.39-7.21 (m, 10H), 6.18 (s, 1H), 5.61 (s, 1H), 4.94 (dd, J = 5.99, 5.99 Hz, 1H), 4.83 (d, J = 14.4 Hz, 1H), 4.74-4.68 (m, 1H), 2.73-2.60 (m, 2H), 2.21 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C, TMS) **Isomer A** δ 142.34, 140.65, 130.80, 128.44, 128.40, 128.21, 127.89, 126.67, 125.61, 125.11, 91.17, 89.09, 75.97, 75.77, 72.30, 30.47. **Isomer B** δ 142.30, 140.69, 130.80, 128.44, 128.40, 128.24, 127.85, 126.67, 125.68, 125.61, 91.11, 89.12, 76.08, 75.77, 72.13, 30.54; IR (film) 3433, 3062, 3028, 2921, 1972, 1884, 1817, 1601, 1491 cm^{-1} ; HRMS (EI) : m/z calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_2$: 290.1307; found: 290.1309.

3-(4-Hydroxy-1-octyn-1-yl)-2-propyl-2,5-dihydrofuran (2b): ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS) δ 6.05 (s, 1H), 4.76-4.63 (m, 1H), 4.68-4.63 (m, 2H), 3.79 (q, , J =

4.90 Hz, 1H), 2.59 (dd, , $J = 4.90, 4.90$ Hz, 1H), 2.49 (dd, , $J = 6.55, 6.55$ Hz, 1H), 1.84 (d, $J = 4.43$ Hz, 1H), 1.77-1.34 (m, 8H), 0.95 (t, $J = 7.35$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C, TMS) **Isomer A** δ 130.79, 124.97, 90.76, 86.90, 75.95, 74.90, 69.85, 38.51, 36.76, 28.47, 18.82, 18.11, 14.17, 14.01. **Isomer B** δ 130.77, 124.97, 90.76, 86.90, 75.95, 74.90, 69.83, 38.51, 36.76, 28.47, 18.82, 18.11, 14.17, 14.01; IR (film) 3432, 2960, 2933, 2227, 1636, 1014 cm^{-1} .

3-(4-Hydroxy-4-cyclohexyl-1-butyn-1-yl)-2-cyclohexyl-2,5-dihydrofuran (2c): ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ 6.09 (s, 1H), 4.66-4.61 (m, 3H), 3.54-3.51 (m, 1H), 2.66-2.49 (m, 2H), 1.90-1.76 (m, 12H), 1.37-1.06 (m, 11H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C): **Isomer A** δ 131.46, 123.49, 91.18, 76.16, 75.54, 74.16, 42.62, 41.86, 29.76, 29.11, 28.09, 26.62, 26.45, 26.37, 26.32, 26.18, 26.01, 25.75, 25.68. **Isomer B** δ 131.51, 123.49, 90.99, 76.16, 75.54, 74.16, 42.62, 41.86, 29.76, 29.11, 28.09, 26.62, 26.45, 26.37, 26.32, 26.18, 26.01, 25.75, 25.68; IR (film) 3854, 2927, 2853, 2102, 1644, 1027 cm^{-1} .

3-[4-Hydroxy-4-(4-chlorophenyl)-1-butyn-1-yl]-2-(4-chlorophenyl)-2,5-dihydrofuran (2d): ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ 7.33 (d, $J = 6.54$ Hz, 2H), 7.28 (d, $J = 8.48$ Hz, 2H), 7.22 (d, $J = 6.54$ Hz, 2H), 7.17 (d, $J = 8.48$ Hz, 2H), 6.19 (s, 1H), 5.58-5.54 (m, 1H), 4.91 (dd, $J = 5.72, 5.72$ Hz, 1H), 4.81 (dd, $J = 2.18, 2.37$ Hz, 1H),

4.75-4.69 (m, 1H), 2.73-2.61 (m, 2H), 2.17 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$):

Isomer A δ 140.74, 139.14, 133.94, 133.61, 131.39, 128.58, 128.53, 128.06, 127.04, 124.62, 90.72, 88.32, 75.97, 75.77, 71.46, 30.31. **Isomer B** δ 140.74, 139.14, 133.92, 133.63, 131.34, 128.58, 128.53, 128.06, 127.12, 124.62, 90.80, 88.32, 75.87, 75.77, 71.67, 30.27; IR (film) 3419, 2852, 1596, 1490, 1090, 1064 cm^{-1} .

3-[4-Hydroxy-4-(3-methoxyphenyl)-1-butyn-1-yl]-2-(3-methoxyphenyl)-2,5-dihydrofuran (2e): ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ 7.30-7.20 (m, 2H), 6.93-6.80 (m, 6H), 6.18 (s, 1H), 5.63-5.58 (m, 1H), 4.94 (dd, $J = 5.95, 5.50$ Hz, 1H), 4.85-4.81 (m, 1H), 4.75-4.69 (m, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 2.70-2.66 (m, 2H), 2.17 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$): **Isomer A** δ 159.75, 159.69, 144.11, 142.31, 130.82, 129.41, 125.07, 118.91, 118.00, 117.94, 113.60, 113.38, 112.15, 111.11, 91.34, 88.90, 75.93, 75.80, 72.25, 56.22, 30.57. **Isomer B** δ 159.75, 159.69, 144.05, 142.35, 130.82, 129.45, 125.07, 118.89, 118.00, 117.94, 113.65, 113.36, 112.12, 111.11, 91.23, 88.93, 76.05, 75.80, 72.10, 55.22, 30.60; IR (film) 3431, 2938, 2836, 2228, 1601, 1261, 1045 cm^{-1} .

3-[4-Hydroxy-4-(4-methoxyphenyl)-1-butyn-1-yl]-2-(4-methoxyphenyl)-2,5-dihydrofuran (2f): ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ 7.24-7.15 (m, 4H), 6.90 (d, $J = 8.67$ Hz, 2H), 6.83 (d, $J = 8.67$ Hz, 2H), 6.25 (s, 1H), 5.61-5.57 (m, 1H), 4.91 (dd, J

= 5.73, 4.93 Hz, 1H), 4.82-4.78 (m, 1H), 4.73-4.68 (m, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 2.66 (d, $J = 5.99$ Hz, 2H), 2.18 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C): **Isomer A** δ 159.59, 159.23, 134.57, 132.81, 130.89, 128.11, 126.97, 126.91, 125.17, 113.85, 113.76, 91.02, 88.78, 76.17, 75.45, 71.81, 55.28, 30.49. **Isomer B** δ 159.56, 159.26, 134.57, 132.81, 130.89, 128.11, 126.97, 126.91, 125.17, 113.82, 113.76, 91.07, 88.78, 76.06, 75.45, 71.96, 55.28, 30.44; IR (film) 3432, 2935, 1636, 1247, 1030 cm^{-1} .

3-[4-Hydroxy-4-(4-acetylphenyl)-1-butyn-1-yl]-2-(4-acetylphenyl)-2,5-dihydrofuran (2g): ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ 7.93 (d, $J = 8.22$ Hz, 2H), 7.88 (d, $J = 8.22$ Hz, 2H), 7.40 (d, $J = 8.22$ Hz, 2H), 7.34 (d, $J = 8.22$ Hz, 2H), 6.20 (s, 1H), 5.67-5.62 (m, 1H), 4.96 (dd, $J = 5.73, 5.87$ Hz, 1H), 4.87-4.80 (m, 2H), 2.78-2.69 (m, 2H), 2.60 (s, 3H), 2.59 (s, 3H), 2.46 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C): **Isomer A** δ 197.95, 197.80, 147.59, 145.93, 136.84, 136.65, 131.49, 128.50, 128.46, 126.67, 125.91, 125.84, 90.91, 88.37, 75.92, 71.83, 30.27, 26.70, 26.66. **Isomer B** δ 197.95, 197.80, 147.55, 145.93, 136.84, 136.62, 131.54, 128.50, 128.46, 126.67, 125.84, 124.41, 90.82, 88.37, 76.02, 71.62, 30.27, 26.70, 26.66; IR (film) 3430, 2924, 2228, 1680, 1269 cm^{-1} .

3-[4-Hydroxy-4-(2-furyl)-1-butyn-1-yl]-2-(2-furyl)-2,5-dihydrofuran (2h): ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ 7.42 (s, 1H), 7.36 (s, 1H), 6.36-6.30 (m, 3H),

6.26 (d, $J = 1.79$ Hz, 1H), 6.22 (d, $J = 3.13$ Hz, 1H), 5.68-5.65 (m, 1H), 4.85 (dd, $J = 5.69$, 5.69 Hz, 1H), 4.78 (dd, $J = 6.12$, 6.12 Hz, 1H), 4.77-4.73 (m, 1H), 2.85 (d, $J = 6.12$ Hz, 2H), 2.23 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$): **Isomer A** δ 154.48, 152.76, 143.03, 142.20, 132.52, 121.74, 110.29, 110.27, 110.22, 108.52, 106.59, 90.14, 81.94, 75.69, 75.23, 66.04, 27.16. **Isomer B** δ 154.48, 152.76, 143.03, 142.20, 132.52, 121.74, 110.29, 110.27, 110.22, 108.52, 106.59, 90.14, 81.94, 75.69, 75.23, 66.04, 27.16; IR (film) 3405, 2856, 1627, 1058 cm^{-1} .

Typical experimental procedures for intramolecular cyclization catalyzed by AgOTf: AgOTf (8.4 mg, 0.032 mmol) was added to a solution of 1,6-diphenyl-2-vinylidenehex-3-yne-1,6-diol (63.0 mg, 0.217 mmol) in methylene chloride (1.5 mL). After the reaction mixture was stirred for 1.5 h, the solvent was removed under the reduced pressure. The crude product was purified by silica gel column chromatography to give 5-(2-hydroxy-2-phenylethyl)-2-phenyl-3-vinylfuran (**3a**) (51.0 mg, 80%) using EtOAc/hexane=1/5, ($R_f = 0.3$).

5-(2-Hydroxy-2-phenylethyl)-2-phenyl-3-vinylfuran (3a): ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ 7.43-7.34 (m, 6H), 7.32-7.27 (m, 2H), 6.84 (dd, $J = 17.3$, 10.8 Hz, 1H), 6.39 (s, 1H), 5.50 (d, $J = 17.3$ Hz, 1H), 5.20 (d, $J = 10.8$ Hz, 1H), 5.05 (t, $J =$

6.50 Hz, 1H), 3.07 (d, $J = 6.50$ Hz, 2H), 2.29 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 151.73, 149.39, 143.30, 131.05, 128.57, 128.52, 127.79, 127.65, 127.52, 126.54, 125.78, 121.09, 114.50, 107.35, 72.74, 38.42; IR (film) 3419, 3061, 3029, 2923, 1954, 1668, 1598, 1491, 1261 cm^{-1} ; HRMS (EI) : m/z calcd. For $\text{C}_{20}\text{H}_{18}\text{O}_2$: 290.1307; found: 290.1308.

5-(2-Hydroxy-2-propylethyl)-2-propyl-3-vinylfuran (3b): ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ 6.50 (dd, $J = 17.4, 10.9$ Hz, 1H), 6.21 (s, 1H), 5.32 (d, $J = 17.4$ Hz, 1H), 5.05 (d, $J = 10.9$ Hz, 1H), 3.91-3.84 (m, 1H), 2.78 (dd, $J = 4.02, 4.02$ Hz, 1H), 2.65 (dd, $J = 7.92, 7.92$ Hz, 1H), 2.59 (t, $J = 7.30$ Hz, 2H), 1.80 (d, $J = 4.02$ Hz, 1H), 1.68-1.60 (m, 2H), 1.55-1.36 (m, 4H), 0.92 (t, $J = 7.30$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 152.68, 151.11, 127.05, 119.70, 111.60, 104.84, 70.11, 38.85, 36.22, 28.03, 21.97, 18.86, 14.06, 13.69; IR (film) 3452, 2961, 2933, 1652 cm^{-1} .

5-(2-Hydroxy-2-cyclohexylethyl)-2-cyclohexyl-3-vinylfuran (3c): ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ 6.49 (dd, $J = 17.4, 10.8$ Hz, 1H), 6.14 (s, 1H), 5.24 (d, $J = 17.4$ Hz, 1H), 4.96 (d, $J = 10.8$ Hz, 1H), 3.57-3.52 (m, 1H), 2.76-2.54 (m, 3H), 1.81-1.30 (m, 12H), 1.27-1.10 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 156.63, 151.10, 126.98, 117.94, 111.39, 104.73, 74.46, 43.04, 36.08, 33.19, 31.68, 26.16, 25.88; IR (film) 3451, 2927, 2853, 1662 cm^{-1} .

5-[2-Hydroxy-2-(4-chlorophenyl)]-2-(4-chlorophenyl)-3-vinylfuran (3d): ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ 7.45 (d, J = 8.59 Hz, 2H), 7.38 (d, J = 8.59 Hz, 2H), 7.33 (s, 4H), 6.77 (dd, J = 17.4, 10.8 Hz, 1H), 6.38 (s, 1H), 5.52 (d, J = 17.4 Hz, 1H), 5.24 (d, J = 10.8 Hz, 1H), 5.02 (t, J = 6.51 Hz, 1H), 3.04 (d, J = 6.51 Hz, 2H), 2.25 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 151.50, 148.24, 141.69, 133.49, 133.36, 129.40, 128.83, 128.66, 127.58, 127.17, 121.53, 115.25, 107.75, 72.08, 38.34; IR (film) 3452, 3092, 2923, 2251, 1651, 1487, 1092 cm^{-1} .

5-[2-Hydroxy-2-(3-methoxyphenyl)]-2-(3-methoxyphenyl)-3-vinylfuran (3e): ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ 7.35-7.26 (m, 1H), 7.16 (d, J = 7.83 Hz, 1H), 7.10-7.09 (m, 1H), 6.99-6.97 (m, 2H), 6.89-6.82 (m, 4H), 6.41 (s, 1H), 5.51 (d, J = 17.4 Hz, 1H), 5.21 (d, J = 10.8 Hz, 1H), 5.04 (t, J = 6.50 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.39 (s, 1H), 3.08 (d, J = 6.50 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 159.80, 159.72, 151.69, 149.19, 145.01, 132.28, 129.62, 129.57, 127.63, 121.34, 119.14, 118.05, 114.63, 113.47, 113.27, 111.96, 111.09, 107.47, 72.67, 55.34, 55.25, 38.41; IR (film) 3434, 2938, 2835, 1601, 1264, 1044 cm^{-1} .

5-[2-Hydroxy-2-(4-acetylphenyl)]-2-(4-acetylphenyl)-3-vinylfuran (3g): ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ 7.96 (dd, J = 7.02, 7.02 Hz, 4H), 7.63 (d, J = 8.37 Hz, 2H), 7.51 (d, J = 8.25 Hz, 2H), 6.86 (dd, J = 17.3, 10.8 Hz, 1H), 6.43 (s, 1H), 5.57 (d, J

= 17.3 Hz, 1H), 5.30 (d, J = 10.8 Hz, 1H), 5.16 (t, J = 6.48 Hz, 1H), 3.11 (d, J = 6.48 Hz, 2H), 2.61 (s, 3H), 2.60 (s, 3H), 1.90 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$): d 198.25, 197.91, 152.70, 148.95, 148.34, 136.99, 135.83, 135.61, 129.15, 129.04, 127.56, 126.33, 123.76, 116.60, 108.73, 72.62, 38.73, 27.07, 27.00; IR (film) 3433, 2347, 1676, 1269 cm^{-1} .