Supporting Information for Complexation-Initiated Intramolecular Diels-Alder Reaction

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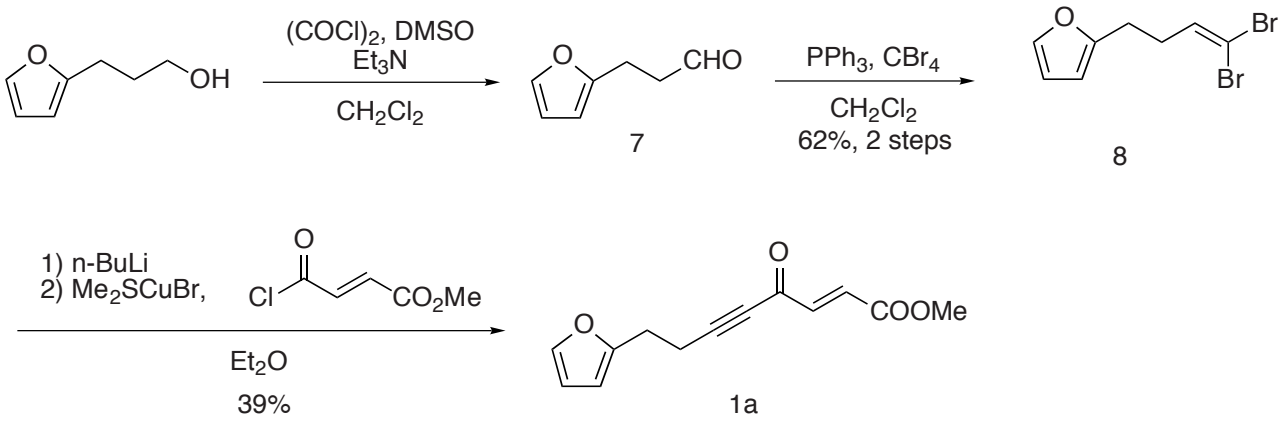
General. All operations were performed under an argon atmosphere. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker AM500 and a Bruker DRX500 spectrometers in $CDCl_3$ solutions using $CHCl_3$ (^{1}H, δ 7.24) and $CDCl_3$ (^{13}C, δ 77.0) as internal standards. IR spectra were recorded on a Horiba FT 300-S spectrophotometer. High-resolution mass spectra were obtained with a JMS-SX102A mass spectrometer at ionization energy of 70eV. Silica-gel column chromatography was carried out with Merck Kieselgel 60 Art.7734. Preparative TLC was performed on a silica-gel (Wakogel B-5F).

(1) Preparation of 1a.



3-(2-Furyl)-1-propanal (7)

To a CH_2Cl_2 solution (30 mL) of oxalyl chloride (2.02 g, 16.0 mmol) was added a CH_2Cl_2 solution (7.5 mL) of DMSO (2.21g, 28.3 mmol) at -78 °C. After 5 minutes, a CH_2Cl_2 solution (12.5 mL) of 3-(2-furyl)-1-propanol (1.64 g, 12.7 mmol) was added dropwise and the mixture was stirred for 15 minutes at -78 °C. Then 9.7 mL (70 mmol) of Et_3N was added at -78 °C and the mixture was warmed up to rt slowly. The reaction was quenched with water. The organic materials were extracted with Et_2O twice, and the combined extracts were washed with water twice, and then with brine. The organic phase was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was used in the next reaction without further purification.

1,1-Dibromo-4-(2-furyl)-1-butene (8)

To a CH_2Cl_2 solution (190 mL) of PPh_3 (27.14 g, 103.5 mmol) was added CBr_4 (21.19 g, 63.9 mmol) at 0 °C as a solid in one portion. After 10 minutes, a CH_2Cl_2 solution (100 mL) of **7** was added slowly. After the mixture was stirred for 30 minutes at 0 °C, the solvent was removed under reduced pressure. The organic materials were extracted from the solid residue with hexane 5 times

and the combined organic phase was filtered through Celite. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography (hexane) to give **8** (2.23 g, 62% for 2 steps).

IR (neat): 2918, 1506, 1011, 733, cm^{-1}.

^{1}H-NMR($CDCl_3$): 2.42 (2H, q, *J* =7.3 Hz), 2.74 (2H, t, *J* = 7.3 Hz), 6.01 (1H, d, *J* = 3.0 Hz), 6.28 (1H, d, *J* = 1.7 Hz), 6.40 (1H, t, *J* =7.1 Hz), 7.30 (1H, s).

^{13}C-NMR($CDCl_3$): 26.2, 31.6, 89.8, 105.6, 110.3, 137.3, 141.3, 154.2.

HRMS Found: m/z 277.8930

Calcd for $C_8H_8O^{79}Br_2$: 277.8941

Methyl 8-(2-furyl)-4-oxo-oct-2-en-5-ynoate (1a)

To a Et_2O solution (2 mL) of **8** (280 mg, 1.0 mmol) was added 1.39 mL of 1.5 M n-BuLi (2.1 mmol) dropwise at -78 °C. To this solution was added Me_2S•CuBr (174 mg, 0.8 mmol), 0.8 mL of Me_2S, and a Et_2O solution (2 mL) of 3-methoxycarbonylpropenoyl chloride (156 mg, 1.1 mmol), in this order at 0 °C. After the mixture was stirred for 1 hour at this temperature, the reaction was quenched with pH7 phosphate buffer. The organic materials were extracted with ethyl acetate three times, and the combined extracts were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by preparative TLC (hexane: ethyl acetate = 4: 1) to give **1a** (91.4 mg, 39 %).

IR (neat): 2214, 1722, 1647, 1628, 1257 cm^{-1}.

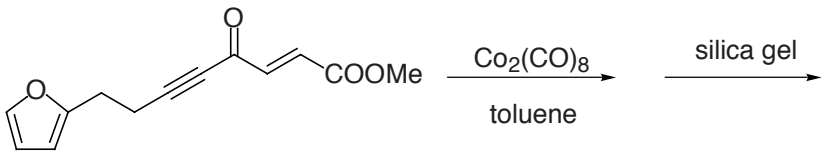
^{1}H-NMR($CDCl_3$): 2.76 (2H, t, *J* = 7.2 Hz), 2.94 (2H, t, *J* = 7.2 Hz), 3.82 (3H, s), 6.11 (1H, d, *J* = 3.4 Hz), 6.29 (1H, s), 6.85 (1H, d, *J* = 15.8 Hz), 6.97 (1H, d, *J* = 15.8 Hz), 7.33 (1H, d, *J* = 1.6 Hz).

^{13}C-NMR($CDCl_3$): 18.5, 26.4, 52.4, 79.5, 95.1, 106.3, 110.3, 135.0, 141.1, 141.7, 152.8, 165.5, 177.0.

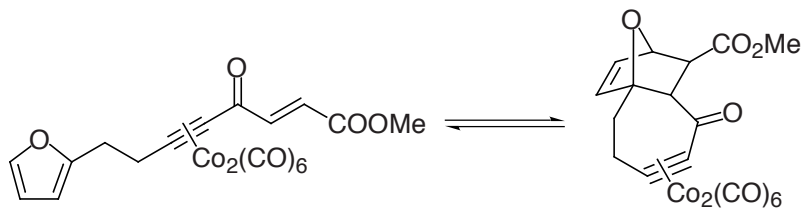
HRMS Found: m/z 232.0707

Calcd for $C_{13}H_{12}O_4$: 232.0736.

(2) Complexation Initiated Intramolecular Diels-Alder Reaction of 1a.



1a



2a 3a

A toluene solution (5 mL) of **1a** (24.8 mg, 0.11 mmol) was added to $Co_2(CO)_8$ (52.6 mg, 0.15 mmol) at rt. The mixture was stirred for 1h, and was adsorbed on silica-gel. After elution of excess $Co_2(CO)_8$ with pentane, it was left on silica-gel for 1h at rt. The complex was rapidly eluted with pentane-diethyl ether (= 4: 1) to give a mixture of **2a** and **3a** in a ratio of 3 : 1. **2a** and **3a** were separated by column chromatography without equilibrium by carrying out the chromatography at 0°C.

Hexacarbonyl-*μ*-[5-6-η-{methyl 8-(2-furyl)-4-oxo-oct-2-en-5-ynoate}] dicobalt(*Co -Co*) , (2a)

IR (neat): 2100, 2062, 2027, 1732, 1304 cm^{-1}.

^{1}H-NMR($CDCl_3$): 2.99 (1H, t, *J* = 8.3 Hz), 3.30 (2H, t, *J* = 8.3 Hz), 3.80 (3H, s), 6.06(1H, s), 6.26 (1H, s), 6.75 (1H, d, *J* = 16.7 Hz), 7.08 (1H, d, *J* = 16.7 Hz), 7.28 (1H, s) .

^{13}C-NMR($CDCl_3$): 29.5, 32.6, 52.2, 87.5, 98.5, 106.5, 110.4, 129.6, 138.5, 141.4, 153.1, 165.7, 190.9, 198.0.

HRMS Found: m/z 489.9146

Calcd for $C_{18}H_{12}O_9Co_2$: 489.9145 .

Hexacarbonyl-*μ*-[3-4-η-{(1R*, 7R*, 10S*, 11R*)-7,10-epoxy-11-methoxycarbonylbicyclo[5. 4. 0]undec-8-en-3-yn-2-one}] dicobalt(*Co -Co*), (3a)

IR (neat): 2102, 2062, 2034, 1735, 1680 cm^{-1}.

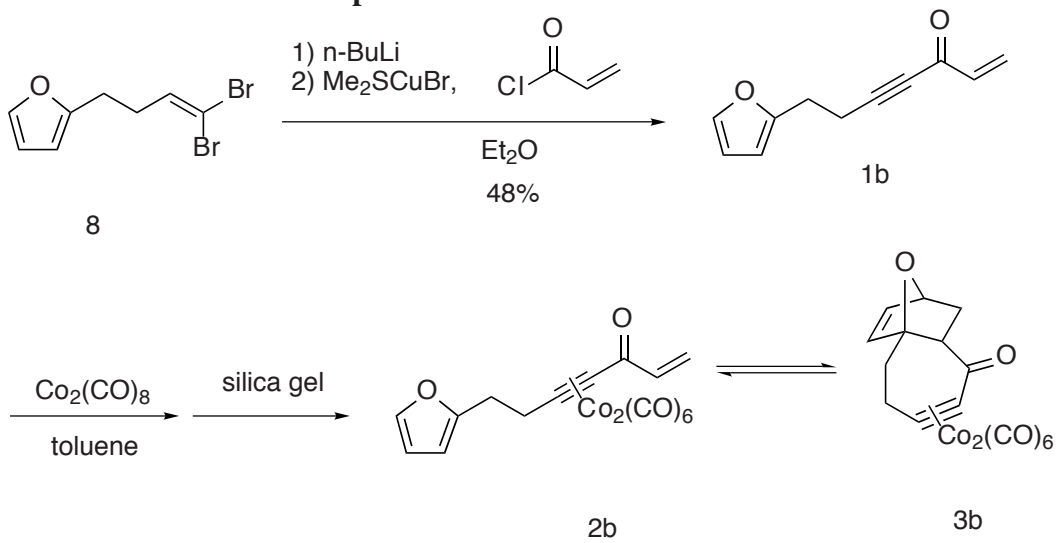
^{1}H-NMR($CDCl_3$): 2.48 (1H, dt, *J* = 4.1, 13.8 Hz), 2.54 (1H, ddd, *J* = 2.8, 5.0, 13.8 Hz), 3.22 (1H, ddd, *J* = 5.0, 13.8, 17.5 Hz), 3.27 (1H, d, *J* = 3.4 Hz), 3.56 (1H, ddd, *J* = 2.8, 4.1, 17.5 Hz), 3.66 (1H, d, *J* = 3.4 Hz), 3.73 (3H, s), 5.23 (1H, s), 6.16 (1H, d, *J* = 6.7 Hz), 6.58 (1H, d, J = 6.7 Hz) .

^{13}C-NMR($CDCl_3$): 30.7, 32.5, 46.8, 52.8, 60.7, 80.9, 81.6, 89.4, 95.9, 132.7, 138.5, 172.9, 197.6, 198.1.

HRMS Found: m/z 489.9112

Calcd for $C_{18}H_{12}O_9Co_2$: 489.9145(M^+-CO) .

(3) Preparation of 1b and Its Complexation Initiated Intramolecular Diels-Alder Reaction.



7-(2-Furyl)hept-1-en-4-yn-3-one (1b)

1b was prepared from **8** by employing acryloyl chloride instead of 3-methoxycarbonylpropenoyl chloride in 48% yield.

IR (neat): 2220, 1647, 1402, 1261 cm^{-1}.

^{1}H-NMR($CDCl_3$): 2.74 (2H, t, *J* = 7.3 Hz), 2.94 (2H, t, *J*= 7.3 Hz), 6.09 (1H, d, *J* = 3.0 Hz), 6.12 (1H, dd, *J* = 1.0, 10.0 Hz), 6.29 (1H, dd, *J* = 2.0, 3.0 Hz), 6.33 (1H, dd, *J* = 10.0, 17.4 Hz), 6.44 (1H, dd, *J* = 1.0, 17.4 Hz), 7.31 (1H, d, *J* = 2.0 Hz).

^{13}C-NMR($CDCl_3$): 18.3, 26.5, 79.0, 93.6, 106.1, 110.3, 133.6, 137.9, 141.5, 153.1, 178.9.

HRMS Found: m/z 174.0670

Calcd for $C_{11}H_{10}O_2$: 174.0681.

Complexation Initiated Intramolecular Diels-Alder Reaction of 1b.

1b was treated in the same procedure as **1a** to give a mixture of **2b** and **3b** in a ratio of 1: 10 (determined by ^{1}H-NMR analysis) in 91% yield.

Hexacarbonyl-*μ*-[4-5-η-{7-(2-furyl) hept-1-en-4-yn-3-one}] dicobalt (*Co -Co*) , (2b)

IR (neat): 2098, 2060, 2026, 1655, 1396 cm^{-1}.

^{1}H-NMR($CDCl_3$): 2.99 (2H, t, *J* = 8.1 Hz), 3.26 (2H, t, *J* = 8.0 Hz), 5.73 (1H, dd, *J* = 1.3, 10.2 Hz), 6.07 (1H, d, *J* = 2.9 Hz), 6.28 (1H, t, *J* = 3.0 Hz), 6.36 (1H, dd, *J* = 1.3, 17.1Hz), 6.52 (1H, dd, *J* = 10.2, 17.1 Hz), 7.30 (1H, d, *J* = 1.1 Hz).

^{13}C-NMR($CDCl_3$): 29.6, 32.5, 87.8, 98.3, 106.1, 110.4, 127.9, 134.7, 141.3, 153.5, 191.8, 198.3.

HRMS Found: m/z 459.9033

Calcd for $C_{17}H_{10}O_8Co_2$: 459.9040.

Hexacarbonyl-*μ*-[3-4-η-{(1R*, 7R*, 10R*)-7,10-epoxybicyclo[5. 4. 0]undec-8-en-3-yn-2-one}] dicobalt (*Co -Co*) , (3b)

IR (neat): 2100, 2048, 2027, 1676, 1560 cm^{-1}.

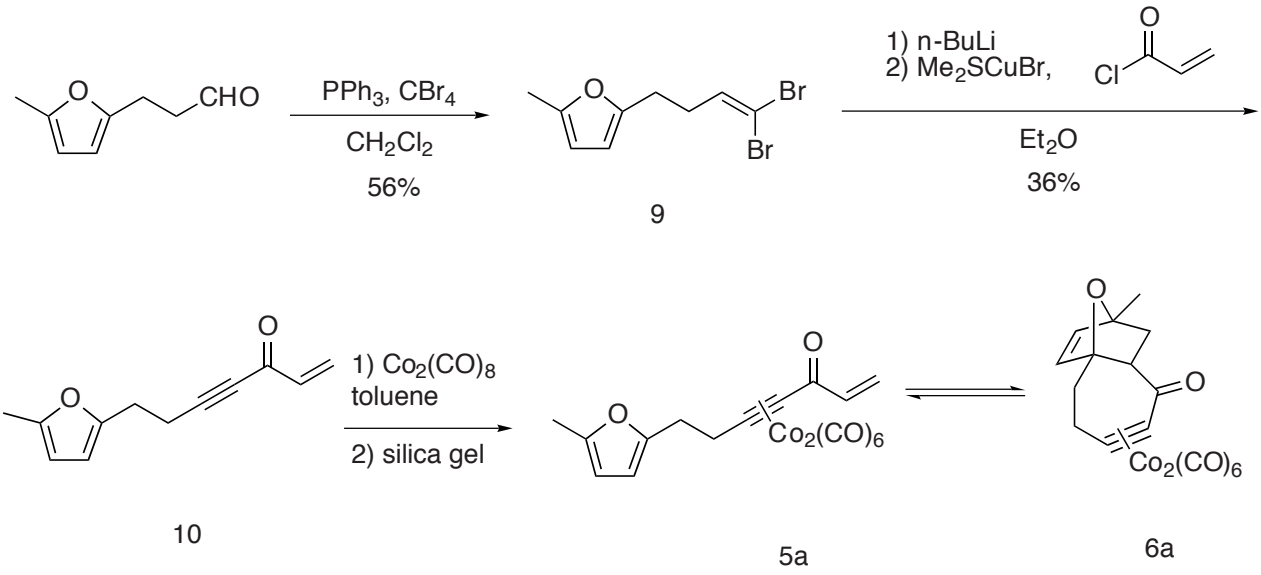
^{1}H-NMR($CDCl_3$): 2.03 (1H, dd, *J* = 3.5, 11.6 Hz), 2.13 (1H, ddd, *J* = 4.9, 8.3, 11.6 Hz), 2.42 (1H, dt, *J* = 4.0, 13.3 Hz), 2.52 (1H, ddd, *J* = 2.7, 4.9, 13.8 Hz), 3.18 (1H, dd, *J* = 3.5, 8.4 Hz), 3.24 (1H, ddd, *J* = 4.9, 13.2, 17.7 Hz), 3.55 (1H, ddd, *J* = 2.7, 4.3, 17.4 Hz), 5.00 (1H, dd, *J* = 1.6, 4.8 Hz), 6.02 (1H, d, *J* = 5.8 Hz), 6.50 (1H, d, *J* = 5.8 Hz) .

^{13}C-NMR($CDCl_3$): 28.3, 31.0, 33.0, 56.9, 78.7, 82.9, 88.8, 96.3, 130.3, 139.1, 198.0, 198.4 .

HRMS Found: m/z 459.9041

Calcd for $C_{17}H_{10}O_8Co_2$: 459.9040.

(4) Preparation of 10 and Its Complexation Initiated Intramolecular Diels-Alder Reaction.



1,1-Dibromo-4-[2-(5-methyl)furyl]-1-butene (9)

9 was prepared from 3-[2-(5-methyl)furyl]-1-propanal by the same procedure as **8** in 56% yield.

IR (neat): 2920,1570,1219,1022,783 cm^{-1}.

^{1}H-NMR($CDCl_3$): 2.25 (3H, s), 2.42 (2H, t, *J* = 7.1 Hz), 2.68 (2H, t, *J* = 6.9 Hz), 5.84 (1H, s), 5.88 (1H, s), 6.41 (1H, t, *J* = 6.8 Hz).

^{13}C-NMR($CDCl_3$): 26.8, 39.5, 39.8, 86.1, 107.7, 110.2, 141.4, 145.5, 152.9.

HRMS Found: m/z 291.9114

Calcd for $C_9H_{10}OBr_2$: 291.9098

7-[2-(5-Methyl)furyl]- hept-1-en-4-yn-3-one (10)

10 was prepared from **9** by the same procedure as **1a** in 36% yield.

IR (neat): 2224, 1647, 1400, 1263 cm^{-1}.

^{1}H-NMR($CDCl_3$): 2.24 (3H, s), 2.71 (2H, t, *J* = 7.5 Hz), 2.87 (2H, t, *J* = 7.5 Hz), 5.84 (1H, d, *J* = 1.5 Hz), 5.95 (1H, d, *J* = 3.0 Hz), 6.10 (1H, dd, *J* = 1.0, 10.5 Hz), 6.34 (1H, dd, *J* = 10.0, 17.5 Hz), 6.46 (1H, dd, *J* = 1.0, 17.5 Hz).

^{13}C-NMR($CDCl_3$): 13.5, 18.6, 26.7, 79.0, 93.9, 106.1, 106.8, 133.5, 138.1, 151.1, 151.3, 178.9.

HRMS Found: m/z 188.0835

Calcd for $C_{12}H_{12}O_2$: 188.0837.

Complexation Initiated Intramolecular Diels-Alder Reaction of 10.

10 was treated in the same procedure as **1a** to give a mixture of **5a** and **6a** in a ratio of 1: 34 (determined by ^{1}H-NMR analysis) in quantitative yield.

Hexacarbonyl-*μ*-[4-5-η-{7-[2-(5-methyl)furyl] hept-1-en-4-yn-3-one}] dicobalt(*Co -Co*), (5a)

IR (neat): 2096, 2031, 2013, 1658, 1396 cm^{-1}.

^{1}H-NMR($CDCl_3$): 2.24 (3H, s), 2.94 (2H, t, *J* = 7.5 Hz), 3.24 (2H, t, *J* = 7.5 Hz), 5.72 (1H, dd, *J* = 1.2, 10.2 Hz), 5.84 (1H, s), 5.92 (1H, s), 6.36 (1H, d, *J* = 17.1 Hz), 6.51 (1H, dd, *J* = 10.2, 17.1 Hz).

^{13}C-NMR($CDCl_3$): 13.4, 29.7, 32.7, 88.0, 98.5, 106.1, 106.8, 127.8, 134.8, 150.9, 151.6, 191.8, 198.4.

HRMS Found: m/z 445.9279

Calcd for $C_{17}H_{12}O_7Co_2$: 445.9247 (M^+-CO).

Hexacarbonyl-*μ*-[3-4-η-{(1R*, 7R*, 10R*)-7,10-epoxy-10-methylbicyclo[5. 4. 0]undec-8-en-3-yn-2-one}] dicobalt (*Co -Co*),(6a)

IR (neat): 2102, 2067, 2025, 1678, 1674 cm^{-1}.

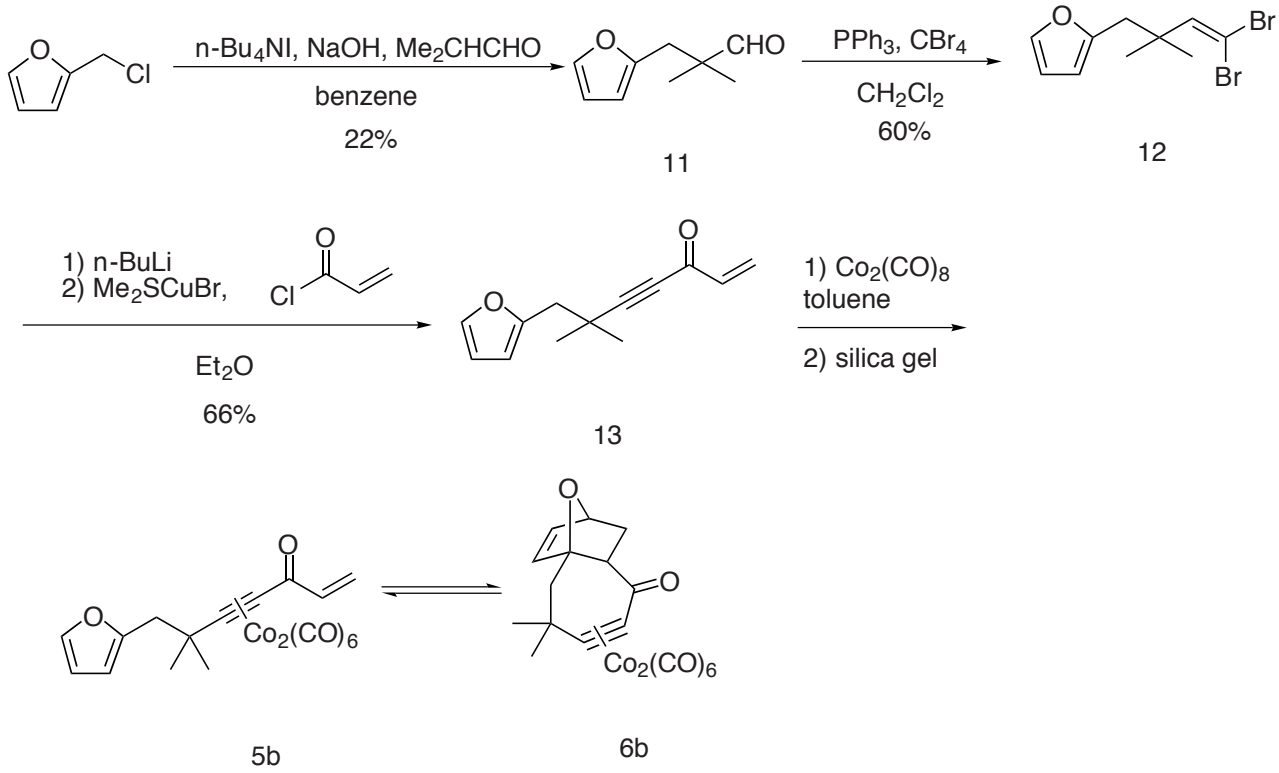
^{1}H-NMR($CDCl_3$): 1.62 (3H, s), 1.85 (1H, dd, *J* = 8.4, 11.7 Hz), 2.16 (1H, dd, *J* =3.3, 11.6 Hz), 2.40 (1H, dt, *J* = 4.1, 13.3 Hz), 2.49 (1H, ddd, *J* = 2.8, 4.9, 13.3 Hz), 3.23 (1H, ddd, *J* = 4.9, 13.1, 17.7 Hz), 3.33 (1H, dd, *J* = 3.3, 8.3 Hz), 3.53 (1H, ddd, *J* = 3.0, 3.9, 17.5 Hz), 6.02 (1H, d, *J* = 5.8 Hz), 6.33 (1H, d, *J* = 5.8 Hz) .

^{13}C-NMR($CDCl_3$): 18.7, 30.8, 33.2, 34.6, 60.1, 86.5, 88.8, 97.0, 107.8, 130.9, 142.0, 198.3, 198.5.

HRMS Found: m/z 473.9214

Calcd for $C_{18}H_{12}O_8Co_2$: 473.9196 .

(5) Preparation of 13 and Its Complexation Initiated Intramolecular Diels-Alder Reaction.



3-(2-Furyl)-2,2-dimethyl-1-propanal (11)

A benzene solution (6.8 mL) of tetra-*n*-butylammonium iodide (266 mg, 0.7 mmol) was added to powdered sodium hydroxide (2.88 g, 72.0 mmol) at rt. After 35 minutes, a mixture of isobutyraldehyde (5.19 g, 72.1 mmol) and 1-furfuryl chloride (10.44 g, 90.0 mmol) was added dropwise and the mixture was stirred overnight. The solvent was removed under reduced pressure and the organic materials were extracted with Et_2O twice. The combined extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by distillation (24 mm, 80 -90 °C) to give **11** (2.94 g, 22%).

1,1-Dibromo-4-(2-furyl)-3,3-dimethyl-1-butene (12)

12 was prepared from **11** by the same procedure as **8** in 60% yield.

IR (neat): 2964, 1504, 1011, 729 cm^{-1}.

^{1}H-NMR($CDCl_3$): 1.21 (6H, s), 2.80 (2H, s), 6.05 (1H, d, *J* = 2.4 Hz), 6.29 (1H, d, *J* = 2.4 Hz), 6.59 (1H, s), 7.31 (1H, s).

^{13}C-NMR($CDCl_3$): 13.5, 26.2, 31.7, 89.5, 105.9, 106.2, 137.4, 150.8, 152.3.

HRMS Found: m/z 305.9221

Calcd for $C_{10}H_{12}O^{79}Br_2$: 305.9254.

7-(2-Furyl)-6,6-dimethyl-hept-1-en-4-yn-3-one(13)

13 was prepared from **12** by the same procedure as **1a** in 66% yield.

IR (neat): 2214, 1651, 1610, 1400, 1255 cm^{-1}.

^{1}H-NMR($CDCl_3$): 1.31 (6H, s), 2.83 (2H, s), 6.10 (1H, dd, *J* = 0.8, 10.3 Hz), 6.14 (1H, d, *J* = 3.2 Hz), 6.30 (1H, dd, *J* = 2.4, 3.4 Hz), 6.33 (1H, dd, *J* = 10.1, 17.4 Hz), 6.44 (1H, d, *J* = 17.4 Hz), 7.31 (1H, d, *J* = 1.8 Hz).

^{13}C-NMR($CDCl_3$): 28.1, 32.4, 40.6, 78.5, 100.8, 108.1, 110.3, 133.4, 138.1, 141.5, 152.0, 179.2.

HRMS Found: m/z 202.0983

Calcd for $C_{13}H_{14}O_2$: 202.0994.

Complexation Initiated Intramolecular Diels-Alder Reaction of 13.

13 was treated in the same procedure as **1a** to give a mixture of **5b** and **6b** in a ratio of 5: 6 (determined by ^{1}H-NMR analysis) in 76% yield.

Hexacarbonyl-μ-[4-5-η-{7-(2-furyl)-6,6-dimethylhept-1-en-4-yn-3-one}] dicobalt(*Co-Co*), (5b)

IR (neat): 2096, 2046, 1655, 1396 cm^{-1}.

^{1}H-NMR($CDCl_3$): 1.29 (6H, s), 2.85 (1H, s), 5.70 (1H, d, *J* = 10.0 Hz), 6.08 (1H, d, J = 2.5 Hz), 6.29 (1H, s), 6.43 (1H, d, *J* = 17.0 Hz), 6.63 (1H, dd, *J* = 10.1, 17.0 Hz), 7.30(1H, s)

^{13}C-NMR($CDCl_3$): 30.2, 39.9, 42.6, 88.9, 108.6, 110.3, 112.6, 128.1, 134.3, 141.5, 152.4, 192.0, 198.8

HRMS Found: m/z 487.9344

Calcd for $C_{19}H_{14}O_8Co_2$: 487.9353.

Hexacarbonyl-μ-[3-4-η-{(1RS*, 7R*, 10R*)-7,10-epoxy-5,5-dimethylbicyclo[5. 4. 0]undec-8-en-3-yn-2-one}] dicobalt (*Co -Co*),(6b)

IR (neat): 2098, 2058, 2033, 1684, 1556 cm^{-1}.

^{1}H-NMR($CDCl_3$) major isomer: 1.51 (6H, s), 1.96 (1H, dd, *J* = 3.7, 11.6 Hz), 2.08 (1H, ddd, *J* = 4.9, 7.8, 11.8 Hz), 2.38 (1H, d, *J* = 13.7 Hz), 2.50 (1H, d, *J* = 13.6 Hz), 3.14 (1H, dd, *J* = 3.6, 8.3 Hz), 4.92 (1H, dd, *J* = 1.5, 4.8 Hz), 6.19 (1H, d, *J* = 5.9 Hz), 6.53 (1H, d, *J* = 5.9 Hz).

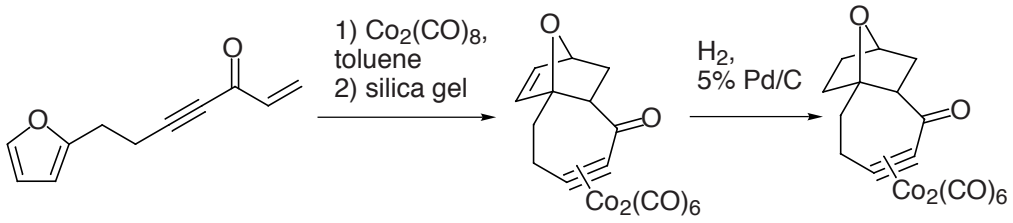
Minor isomer: 1.50 (6H, s), 1.97 (1H, d, *J* = 13.7 Hz), 2.38 (1H, d, *J* = 13.7 Hz), 2.76-2.85 (3H, m), 4.97 (1H, d, *J* = 3.4 Hz), 6.27 (1H, d, *J* = 5.7 Hz), 6.48 (1H, d, *J* = 5.6 Hz).

^{13}C-NMR($CDCl_3$): 27.9, 28.3, 31.8, 34.0, 34.6, 36.4, 36.5, 36.7, 44.5, 46.9, 53.2, 56.2, 76.2, 80.0, 88.3, 90.2, 108.5, 112.8, 130.9, 138.0, 139.1, 139.4, 198.3, 198.8, 201.0 .

HRMS Found: m/z 459.9420

Calcd for $C_{18}H_{14}O_7Co_2$: 459.9404(M^+-CO).

(6) Hydrogenation of 3b.



1b 3b 4

62% 2steps

Hexacarbonyl-μ-[3-4-η-{(1R*, 7R*, 10R*)-7,10-epoxybicyclo[5. 4. 0]undec-3-yn-2-one}] dicobalt (*Co -Co*),(4)

A toluene solution (10 mL) of **1b** (68.6 mg, 0.39 mmol) was added to $Co_2(CO)_8$ (205 mg, 0.60 mmol) at rt. The mixture was stirred for 1 h, and was adsorbed on silica-gel. After elution of excess $Co_2(CO)_8$ with pentane, it was left on silica-gel for 2 h at rt. The complex was rapidly eluted with pentane-diethyl ether (= 1: 1) at 0°C to give a mixture of **2b** and **3b**. The solvent was removed under reduced pressure at 0°C. To an EtOAc solution (30 mL) of the product was added 5% Pd/C (53 mg) and the mixture was stirred under H_2 atmosphere at 0°C. After 10 h, the mixture was separated from Pd/C by filtration. The solvent was removed under reduced pressure and the residue was purified by preparative TLC (hexane: ethyl acetate = 4: 1) to give **4** (112.5 mg, 62%).

IR (neat): 2069, 2056, 2011, 1653, 1128 cm^{-1}.

^{1}H-NMR($CDCl_3$): 1.44-1.50 (2H, m), 1.60-1.65 (1H, m), 1.80-1.88 (1H, m), 1.93-1.99 (1H, m), 2.29 (1H, dd, J = 4.7, 12.4 Hz), 2.33-2.44 (2H, m), 2.93 (1H, ddd, J = 5.5, 12.4, 17.6 Hz), 3.13 (1H, dd, J = 4.6, 11.1 Hz), 3.44 (1H, dt, J = 3.5, 17.2 Hz), 4.56 (1H, t, J = 5.4 Hz).

^{13}C-NMR($CDCl_3$): 30.1, 30.9, 31.1, 31.8, 35.6, 61.0, 77.3, 86.3, 97.6, 107.3, 198.2, 200.1

HRMS Found: m/z 461.9178

Calcd for $C_{17}H_{12}O_8Co_2$: 461.9196.