Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Synthesis of $[RhCl(CO)(cyclopentadienone)]_2$ from $[RhCl(cod)]_2$ and a 1,6-diyne under CO: Application to Rh(I)-catalyzed tandem [2+2+1] carbonylative cycloaddition of diynes and Claisen rearrangement

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Contents

1. General information

^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JMN-270 spectrometer in $CDCl_3$ with TMS (TMS= tetramethylsilane) or residual $CHCl_3$ as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and c = complex), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on a Horiba FT-700 spectrometer; absorptions are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained on a Shimadzu GCMS-QP 5000 instrument with ionization voltages of 70 eV. Elemental analyses were performed by the Elemental Analysis Section of Osaka University. Analytical gas chromatography (GC) was carried out on a Shimadzu GC-14A gas chromatography, equipped with a flame ionization detector. Column chromatography was performed with SiO_2 (Merck SilicaGel 60 (230-400 mesh)).

Solvents are purified according to standard purification methods. TCE was distilled over $CaCl_2$. Toluene was distilled over CaH_2. 1,4-Dioxane was distilled over Na/ Benzophenone. $[RhCl(cod)]_2$ and $Ru_3(CO)_{12}$ were prepared according to the literature.[1,2] $[RhCl(CO)_2]_2$, $[IrCl(cod)]_2$, and $Co_2(CO)_8$ were purchased from Strem Chemicals. Co.

2. Experimental procedures

1) Experimental procedure for the $[RhCl(cod)]_2$-catalyzed carbonylative cycloaddition of 1,6-diyne (eq 1)

To a 10-mL two-necked round-bottomed flask equipped with a reflux condenser, was introduced **5** (244mg, 1 mmol) and $[RhCl(cod)]_2$ (25 mg, 0.025 mmol) and dissolved in anhydrous 2-methylanisole (3 mL) under N_2 flow. After CO blowing from a CO balloon to the flask for 10 min (x2), the flask was sealed under CO atmosphere. The flask was immersed in an oil bath at 120 °C. After 12 h, the flask was cooled to room temperature. The resulting red wine solution was evaporated under reduced pressure. CH_2Cl_2 (20 mL) was added to the flask, CH_2Cl_2 solution was extracted carefully with pipette and a residual solid **6** in the flask was dried under vacuum (35 mg). After evaporation of the CH_2Cl_2 solution under reduced pressure, flask column chromatography gave **7** in 14 % yield (37.5 mg, R_f = 0.37) and **5** was recovered in 70 % (171 mg).

2) Experimental procedure for the preparation of $[RhCl(CO)(cpd)]_2$ (**6**) in a large scale

To a 30-mL two-necked round-bottomed flask equipped with a reflux condenser, **5** (1g, 4.1 mmol) and $[RhCl(cod)]_2$ (1g, 2 mmol) was introduced and dissolved in anhydrous DCE (1,2-dichloroethane, 10 mL) under N_2 flow. After CO blowing from a CO balloon to the flaks for 10 min (x2), the flask was sealed under CO atmosphere. After 12 h, the resulting red wine solution was evaporated under reduced pressure. A precipitate was filtered through glass filter, washed with CH_2Cl_2 (20 mL), and dried under vacuum.

3) Experimental procedure for equation 2

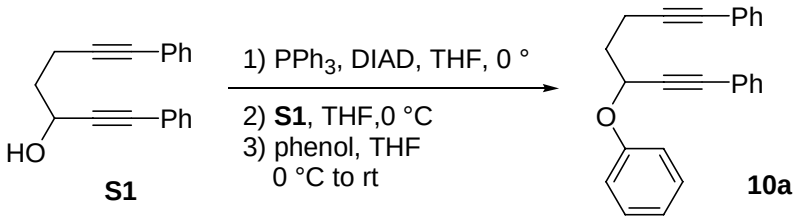
To a 50-mL glass vial, $[RhCl(CO)_2]_2$ (**1)** (0.5 g, 1.29 mmol) and anhydrous DCE (15 mL) was added under N_2. The vial was sealed with cap. After dissolving completely by supersonic wave, Et_2O (10 mL) was slowly added to the DCE solution under N_2. Using pipette, 5 mL ethereal solution of **5** (0.7 g, 2.87 mmol) was slowly added to the solution of **1** under N_2 flow. After sealing the vial with cap, it was placed on cotton-layered box at room temperature (Care should be taken not to mix two layers suddenly!). After 1 week later, red crystal was precipitated on the bottom of vial. The red solid precipitate was filtered and washed with CH_2Cl_2. Yield 1.069 g (1.22 mmol). ^{1}H NMR and GC analysis of the mother liquor showed only residual **5**. IR spectrum showed no carbonyl peak.

4) Experimental procedure for the formation of pyridine coordinated complex **8** (Scheme 2)
To a 10-mL two-necked round bottomed flask connected with venting line, pyridine (5 mL) and **6** (100 mg, 1.14 mmol) was added under N_2. Flask was immersed into an oil bath (40 °C) and **6** was slowly dissolved into pyridine. (Warning! CO was generated in the process. Flask should be connected with venting line.) After 1 hr, pyridine was evaporated under vacuum. Dissolving in 3 mL CH_2CL_2, the complex **8** was recrystallized with Hex/Et_2O (v/v= 10/1). Yield 124 mg (0.224 mmol).

5) Crystal growing of complex **8**
Into the CH_2Cl_2 solution of the complex **8**, Et_2O was slowly added in a refrigerator. Crystal is gradually decomposed in the absence of mother liquor. X-ray diffraction pattern of **8** was collected with mother liquor in capillary.

6) Representative procedure for the Rh(I) catalyzed tandem [2+2+1] carbonylative cycloaddition and Claisen rearrangement (eq 3 and Table 1)
To a 10-mL two-necked round flask connected with reflux condenser, diyne **10** (0.5 mmol) and $[RhCl(cod)]_2$ (0.025 mmol) was introduced and dissolved in anhydrous TCE (TCE= 1,1,2,2-tetrahchloroethane) (2.5 mL) under N_2 flow. After CO blowing from a CO balloon for 30 min, the flask was immersed into an oil bath at 130 °C. The reaction was monitored by TLC. After **10** was disappeared, the solvent was evaporated, and the product was separated by flash column chromatography.

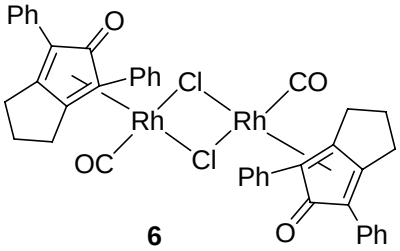
7) Representative synthetic procedure of phenoxy-substituted diynes **10**[3]



To a 200-mL three-necked round-bottomed flask, anhydrous THF (100 mL) was introduced. PPh_3 (6g, 22.88 mmol) and then DIAD (4.66g, 23 mmol) were added to the flask. After stirring at 0 °C for 10 min, white solid was precipitated. Propargyl alcohol **S1** (6g, 23.07 mmol) in THF (20 mL) was added to the solution of PPh_3/DIAD dropwise at 0 °C. After 30 min stirring, phenol (2.17g, 23 mmol) in 30 mL THF was added dropwise for 1 h. After stirring 1 h at 0 °C, the solution was raised to room temperature. After disappearance (2 h), the solvent was evaporated under reduced pressure. Flash column chromatography gave product **10a** (6.87g, 20.52 mmol). Yield 89%.

3. Characterization of Compounds

$[Rh(I)Cl(CO)(cpd)]_2$ (**6**)



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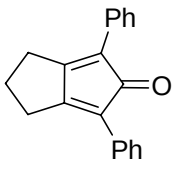

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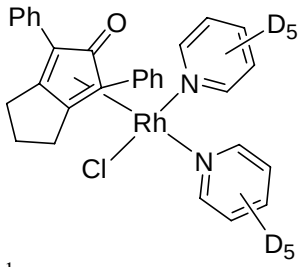
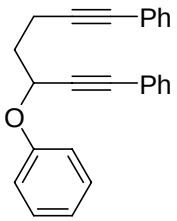
IR (KBr) 3057(m), 2991(m), 2958(m), 2090(m), 2057(s), 2023(m), 1668(s), 1576(m), 1504(m), 1471(m), 1452(s), 1437(s), 1421(m), 1377(m), 1354(m), 1335(m), 1296(m), 1228(m), 1186(m), 1159(m), 1113(w), 1080(m), 1030(m), 1005(w), 985(m), 842(w), 795(m), 773(s), 692(s), 642(m), 617(m), 552(s), 532(w9, 505(w), 486(m) cm^{-1}; MS m/z (relative intensity %) 820(M(**6**)-2[CO], 7), 649(24), 648(M(**6**)-[$RhCl_2(CO)_2$], 58), 647(14), 342(13), 273(M(**7**)$^+$+1, 22), 272(M(**7**)$^+$-1, 100), 243(13), 239(11), 228(11), 215(13), 167(10), 165(12); HRMS Calcd for $C_{40}H_{32}Cl_2O_2Rh_2$ (**6**-2[CO]): 819.9889. Found 819.9881.

Rh(I)Cl(cpd)(pyridine)$_2$ (**8**)



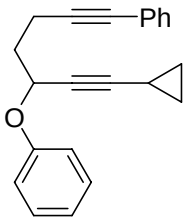
^{1}H NMR (270 MHz, d_5-pyr) δ 8.42-8.40 (m, 4H), 7.27-7.19 (m, 6H), 2.61 (m, 2H), 2.52-2.48 (m, 1H), 2.23-2.19 (m, 1H), 2.08-1.96 (m, 2H); IR (KBr) 3105(m), 3080(s), 3039(m), 2997(m), 2972(m), 1599(s), 1568(s), 1500(s), 1487(s), 1446(s), 1396(m), 1333(m), 1296(m), 1217(s), 1180(m), 1153(s), 1068(s), 1038(s), 1012(m), 922(w), 777(s), 760(s), 748(s), 696(s), 648(sh), 634(m), 619(m), 552(s), 507(w), 453(w); HRMS (FAB) Calcd for $C_{30}H_{26}N_2OClRh$: 568.0789. Found 568.0794.

(3-Phenoxyhepta-1,6-diyne-1,7-diyl)dibenzene (**10a**)



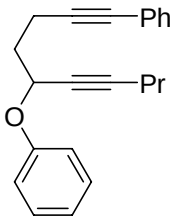
Yellowish liquid, R_f= 0.66 (hexane:EtOAc = 3:1); ^{1}H NMR (270 MHz, CD_2Cl_2) δ 7.17-7.33 (m, 12H), 7.01 (d, *J*= 8.6 Hz, 2H), 6.90 (t, *J*= 7.6 Hz, 1H), 5.10 (t, *J*= 5.9Hz, 1H), 2.70 (t, *J*= 6.2 Hz, 2H), 2.17-2.28 (m, 2H); ^{13}C NMR (67.5 MHz, CD_2Cl_2) δ 158.3, 132.3, 132.1, 129.9, 129.2, 128.89, 128.82, 128.3, 124.3, 122.8, 122.0, 116.4, 89.2, 87.4, 87.2, 81.8, 67.7, 35.5, 16.1; IR (neat) 3079(m), 3060(m), 3035(m), 2964(m), 2937(m), 2248(m), 1597(s), 1492(s), 1442(m), 1340(m), 1301(m), 1288(m), 1232(m), 1174(m), 1074(m), 1051(s), 1029(m), 1010(m), 950(m), 908(s), 755(s), 731(s), 690(s), 649(m); MS, *m/z* (relative intensity, %) 336(M^+, 15), 243(23), 241(13), 228(11), 165(25), 128(10), 115(100); HRMS (EI) Calcd for $C_{25}H_{20}O$: 336.1514. Found 336.1511.

(7-Cyclopropyl-5-phenoxyhepta-1,6-diynyl)benzene (**10b**)



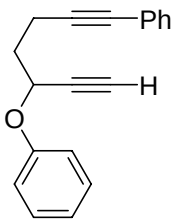
Colorless liquid, R_f= 0.57 (hexane:EtOAc = 3:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.28-7.25 (m, 2H), 7.18-7.13 (m, 5H), 6.94-6.83 (m, 3H), 4.80 (m, 1H), 2.60-2.54 (m, 2H), 2.17-2.00 (m, 2H), 1.12-1.07 (m, 1H), 0.65-0.51 (m, 4H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 158.3, 132.2, 129.9, 128.8, 128.3, 124.3, 121.8, 116.4, 91.4, 89.4, 81.9, 73.6, 67.5, 35.8, 16.2, 9.0, 0.1; IR (neat) 3060(m), 3014(m), 2960(m), 2935(m), 2240(m), 1599(s), 1493(s), 1442(m), 1429(m), 1360(m), 1336(m), 1300(m), 1290(m), 1234(s), 1174(m), 1157(m), 1076(m), 1053(s), 1030(s), 987(m), 947(m), 930(m), 883(m), 814(m), 754(s), 692(s); MS, *m*/*z* (relative intensity, %) 300(M^+, 1.5), 192(16), 191(18), 179(14), 178(18), 165(14), 116(11), 115(100), 91(16); HRMS (CI) Calcd for $C_{22}H_{20}O$: 300.1590. Found 300.1592.

(5-Phenoxydeca-1,6-diynyl)benzene (**10c**)



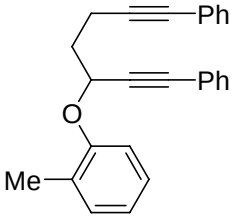
Colorless liquid, R_f= 0.60 (hexane:EtOAc = 3:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.38-7.36 (m, 2H), 7.29-7.26 (m, 5H), 7.07-6.95 (m, 3H), 4.94 (m, 1H), 2.72-2.67 (t, *J*= 7.4 Hz, 2H), 2.30-2.15 (m, 4H), 1.55-1.44 (m, 2H), 0.94 (t, *J*= 7.3 Hz, 3H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 158.0, 131.8, 129.5, 128.4, 127.9, 124.0, 121.4, 116.1, 89.1, 87.9, 81.4, 78.2, 67.2, 35.5, 22.2, 20.9, 15.9, 13.6; IR (neat) 3060(m), 3037(m), 2962(s), 2933(s), 2871(m), 2839(w), 2237(w), 1599(s), 1492(s), 1442(m), 1429(m), 1379(w), 1338(m), 1300(m), 1236(s), 1196(m), 1173(m), 1142(m), 1076(m), 1043(s), 1011(m), 989(m), 947(m), 885(m), 812(m), 754(s), 692(s), 619(w), 526(w), 507(w); MS, *m*/*z* (relative intensity, %) 302(M^+, 2), 301(M^+-1, 2), 211(29), 179(26), 178(18), 165(14), 116(10), 115(100); HRMS (EI) Calcd for $C_{22}H_{22}O$: 302.1671. Found 302.1666.

(5-Phenoxyhepta-1,6-diynyl)benzene (**10d**)



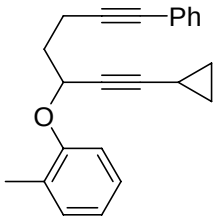
Colorless liquid, R_f= 0.59 (hexane:EtOAc = 3:1); ^{1}H NMR (270 MHz, CD_2Cl_2) δ 7.38-7.26 (m, 7H), 7.05-6.96 (m, 3H), 5.01-4.96 (m, 1H), 2.73-2.68 (m, 2H), 2.57 (d, *J*= 1.9Hz, 1H), 2.32-2.15 (m, 2H); ^{13}C NMR (67.5 MHz, CD_2Cl_2) δ 157.6, 131.6, 129.5, 128.3, 127.9, 123.7, 121.7, 115.9, 88.5, 81.6, 81.3, 74.9, 66.4, 34.9, 15.5; IR (neat) 3097(m), 3078(m), 3062(m), 2966(m), 2939(m), 2115(w), 1597(s), 1493(s), 1442(m), 1335(m), 1290(m), 1232(s), 1174(m), 1155(m), 1105(m), 1078(m), 1053(m), 1030(m), 1012(m), 949(m), 912(m), 883(m), 816(m), 754(s), 690(s), 528(m), 507(m); MS, *m*/*z* (relative intensity, %) 261(M^++1, 1), 260(M^+, 6), 259(M^+-1, 14), 167(17), 166(17), 165(67), 152(16), 116(11), 115(100); HRMS (CI) Calcd for $C_{19}H_{17}O$ (M^++H): 261.1279. Found 261.1279.

(3-(*o*-Tolyloxy)hepta-1,6-diyne-1,7-diyl)dibenzene (**10e**)



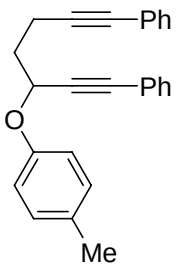
Colorless liquid, R_f= 0.57 (hexane:EtOAc = 3:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.42-7.36 (m, 4H), 7.30-7.26 (m, 6H), 7.19-7.16 (m, 3H), 6.94-6.91 (m, 1H), 5.17-5.13 (m, 1H), 2.82-2.77 (m, 2H), 2.43-2.29 (m, 5H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 155.9, 131.8, 131.6, 130.7, 128.5, 128.23, 128.20, 127.7, 127.6, 126.7, 123.6, 122.3, 121.2, 113.4, 88.7, 87.1, 86.6, 81.4, 67.4, 35.2, 16.4, 15.7; IR (neat) 3078(m), 3024(m), 2960(m), 2914(m), 2231(w), 1948(w), 1886(w), 1809(w), 1670(w), 1599(s), 1491(s), 1462(s), 1442(s), 1340(s), 1303(s), 1240(s), 1190(s), 1174(m), 1159(m), 1119(s), 1068(s), 1051(s), 1011(s), 987(m), 958(m), 955(m), 916(m), 839(m), 750(s), 712(w), 692(s), 528(s); MS, *m*/*z* (relative intensity, %) 350(M^+, 16), 243(30), 241(15), 228(11), 165(16), 116(10), 115(100); HRMS (EI) Calcd for $C_{26}H_{22}O$: 350.1671. Found 350.1662.

1-(1-Cyclopropyl-7-phenylhepta-1,6-diyn-3-yloxy)-2-methylbenzene (**10f**)



Colorless liquid, R_f= 0.56 (hexane:EtOAc = 3:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.38-7.36(m, 2H), 7.29-7.27 (m, 3H), 7.20-7.14 (m, 2H), 7.08 (d, *J*= 7.8Hz, 1H), 6.90 (t, *J*= 7.3 Hz, 1H), 4.88 (m, 1H), 2.73-2.68 (m, 2H), 2.32-2.15 (m, 5H), 1.28-1.25 (m, 1H), 0.77-0.64 (m, 4H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 156.1, 131.7, 130.8, 128.3, 127.8, 127.6, 126.7, 123.9, 121.1, 113.4, 90.7, 89.1, 81.4, 73.5, 67.3, 35.6, 16.6, 15.8, 8.5, -0.3; IR (neat) 3057(m), 3020(m), 2960(m), 2933(m), 2241(m), 1949(w), 1886(w), 1739(w), 1675(w), 1600(s), 1490(s), 1462(m), 1441(s), 1429(m), 1360(m), 1336(m), 1303(m), 1290(m), 1238(s), 1190(s), 1159(w), 1119(s), 1088(w), 1053(s), 1030(s), 985(m), 951(m), 930(m), 899(m), 883(m), 864(m), 839(m), 812(m), 754(s), 714(s), 692(s), 621(w), 528(w), 490(w), 442(w); MS, *m*/*z* (relative intensity, %) 314(M^+, 4), 192(19), 191(20), 179(15), 178(18), 165(14), 116(11), 115(100), 91(17); HRMS (CI) Calcd for $C_{23}H_{23}O$ (M^++H): 315.1749. Found 315.1753.

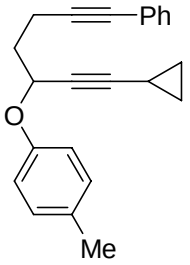
(3-(*p*-Tolyloxy)hepta-1,6-diyne-1,7-diyl)dibenzene (**10g**)



Colorless liquid, R_f= 0.60 (hexane:EtOAc = 3:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.57-7.56(m, 4H), 7.41(m, 6H), 7.26(d, *J*= 8.1Hz, 2H), 7.18(d, *J*=8.6 Hz, 2H), 5.33-5.28(m, 1H), 2.95-2.90(m, 2H), 2.55-2.45(m, 5H); ^{13}C NMR (67.5 MHz, CD_2Cl_2) δ 155.7, 131.9, 131.7, 131.0,

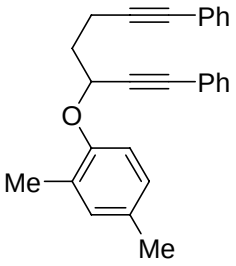
130.0, 128.7, 128.3, 127.8, 123.8, 122.4, 116.1, 88.9, 87.2, 86.9, 81.6, 67.6, 35.1, 20.7, 15.8; IR (neat) 3078(m), 3057(m), 3031(m), 2962(m), 2870(m), 2231(w), 1878(w), 1612(m), 1600(m), 1510(s), 1491(s), 1442(m), 1362(m), 1340(m), 1288(m), 1228(m), 1176(m), 1068(sh), 1051(s), 1012(m), 953(m), 916(m), 841(m), 818(m), 808(m), 756(s), 692(s), 528(m), 509(m); MS, *m*/*z* (relative intensity, %) 350(M^+, 20), 243(269, 242(10), 241(25), 228(11), 165(16), 115(100); HRMS (EI) Calcd for $C_{26}H_{22}O$: 350.1671. Found 350.1673.

1-(1-Cyclopropyl-7-phenylhepta-1,6-diyn-3-yloxy)-4-methylbenzene (**10h**)



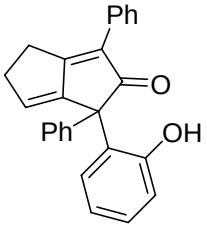
Colorless liquid, R_f= 0.59 (hexane:EtOAc = 3:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 7.20-7.16 (m, 3H), 7.00 (d, *J*= 8.1Hz, 2H), 6.84 (d, *J*= 8.6 Hz, 2H), 4.80-4.75 (m, 1H), 2.61-2.55 (m, 2H), 2.21 (s, 3H), 2.15-2.02 (m, 2H), 1.46-1.12 (m, 1H), 0.69-0.54 (m, 4H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 156.3, 132.2, 131.2, 130.4, 128.9, 128.3, 124.4, 116.5, 91.3, 89.6, 81.8, 73.8, 67.8, 35.9, 21.2, 16.3, 9.0, 0.2; IR (neat) 3078(m), 3055(m), 3020(m), 2958(m), 2933(m), 2916(m), 2241(m), 1601(s), 1589(m), 1493(s), 1462(m), 1442(s), 1429(m), 1379(w), 1358(m), 1336(m), 1304(m), 1288(m), 1236(s), 1190(s), 1159(m), 1119(s), 1089(w), 1053(s), 1030(s), 985(m), 953(m), 930(m), 899(m), 883(m), 864(m), 839(w), 814(m), 7568(s), 712(m), 692(s), 526(m), 440(w); MS, *m*/*z* (relative intensity, %) 314(M^+, 1), 313(M^+-1, 4), 205(12), 192(18), 191(24), 179(13), 178(18), 165(15), 116(10), 115(100), 91(17); HRMS (CI) Calcd for $C_{23}H_{23}O$: 315.1749. Found 315.1745.

(3-(2,4-Dimethylphenoxy)hepta-1,6-diyne-1,7-diyl)dibenzene (10i).



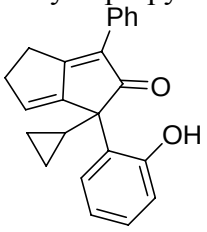
Brown oil; *Rf* 0.34 (hexane/EtOAc = 10/1); mp; ^{1}H NMR ($CDCl_3$) δ 7.29-7.34 (m, 4H), 7.18-7.22 (m, 6H), 6.99-7.02 (m, 1H), 6.88-6.91 (m, 2H), 5.02 (t, *J* = 6.3 Hz, 1H), 2.68-2.73 (m, 2H), 2.19-2.36 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 153.8, 131.68, 131.66, 131.5, 130.4, 128.4, 128.2, 127.7, 127.3, 126.90, 126.88, 122.3, 113.6, 88.8, 87.3, 86.4, 81.4, 67.6, 35.1, 20.5, 16.3 15.7; IR (neat) 3078 w, 3055 m, 3018 m, 2960 m, 2922 m, 2868 w, 2229 w, 1950 w, 1880 w, 1803 w, 1749 w, 1670 w, 1612 w, 1599 m, 1572 w, 1500 s, 1442 m, 1377 w, 1338 m, 1296 m, 1252 s, 1219 s, 1190 w, 1155 w, 1130 s, 1051 s, 1011 m, 958 m, 914 w, 876 w, 802 m, 756 s, 692 s, 669 w, 611 w, 553 w, 526 w; MS, *m*/*z* (relative intensity, %) 363 (M^+-1, 29), 362 (100), 361 (85); HRMS Calcd for $C_{27}H_{24}O$: 364.1827. Found: 364.1820.

1-(2-Hydroxyphenyl)-1,3-diphenyl-4,5-dihydropentalen-2(1*H*)-one (**11a**)



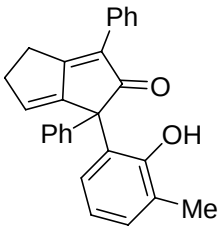
Colorless sticky liquid, R_f= 0.47 (hexane:EtOAc = 3:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.15 (s, 1H), 7.90 (d, *J*= 7.3 Hz, 2H), 7.45 (t, *J*= 7.3 Hz, 2H), 7.37-7.22 (m, 6H), 7.13-7.09 (m, 2H), 7.00 (d, *J*= 8.1 Hz, 1H), 6.88 (t, *J*=8.6 Hz, 1H), 6.32 (t, *J*= 2.8 Hz, 1H), 3.27-2.95(m, 4H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 210.9, 182.6, 156.8, 152.3, 141.0, 136.6, 131.5, 129.8, 128.7, 128.5, 128.0, 127.6, 127.2, 126.5, 125.0, 120.1, 119.7, 61.8, 36.3, 28.3; IR (neat) 3473(m), 3435(m), 3192(m), 3060(m), 2922(w), 1658(s), 1585(s), 1481(m), 1442(m), 1385(m), 1360(m), 1327(m), 1294(m), 1279(m), 1240(s), 1136(m), 984(m), 897(w), 837(w), 791(m), 752(s), 725(m), 692(s), 652(m), 633(m), 548(w), 523(w); MS, *m*/*z* (relative intensity, %) 365(M^++1, 27), 364(M^+, 98), 336(28), 335(11), 309(11), 259(11), 248(19), 247(100), 239(11), 215(11), 151(11); HRMS (EI+, $C_{26}H_{20}O_2$) (calc) 364.1463, (found) 364.1465.

1-Cyclopropyl-1-(2-hydroxyphenyl)-3-phenyl-4,5-dihydropentalen-2(1*H*)-one (**11b**)



Colorless liquid, R_f= 0.23 (hexane/EtOAc = 3:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.80 (d, *J*= 7.3 Hz, 2H), 7.44-7.15(m, 5H), 6.97 (d, J= 8.4 Hz, 1H), 6.84-6.79 (m, 1H), 6.36 (t, *J*= 2.4Hz, 1H), 3.15-3.06 (m, 4H), 2.08-2.02 (m, 1H), 0.58-0.31 (m, 3H), 0.07-0 (m, 1H); ^{13}C NMR (67.5 MHz, CD_2Cl_2) δ 211.5, 182.6, 156.3, 147.0, 136.1, 132.1, 130.0, 128.92, 128. 88, 128.4, 127.7, 126.8, 125.6, 119.8, 118.8, 57.3, 36.3, 27.5, 14.7, 3.0, 1.4; IR (neat) 3384 (br), 3080(m), 3006(m), 2918(m), 1680(s), 1591(s), 1491(m), 1452(m), 1358(m), 1323(m), 1261(m), 1234(m), 1159(m), 1128(m), 1105(m), 1076(m), 1049(m), 1024(m), 995(m), 984(m), 953(m), 908(m), 881(m), 827(m), 781(sh), 754(s), 710(s), 694(s), 642(m), 619(m), 580(m); MS, *m*/*z* (relative intensity, %) 329(M^++1, 13), 328(M^+, 49), 301(23), 300(100), 299(90), 283(11), 272(20), 271(14), 165(11), 115(11); HRMS (EI) Calcd for $C_{23}H_{20}O_2$: 328.1463. Found 328.1463.

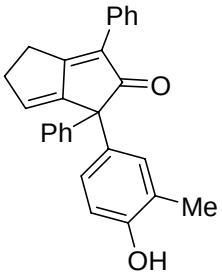
1-(2-Hydroxy-3-methylphenyl)-1,3-diphenyl-4,5-dihydropentalen-2(1*H*)-one (**11e**)



Colorless liquid, R_f= 0.26 (hexane/EtOAc = 3:1); ^{1}H NMR (270 MHz, CD_2Cl_2) δ 9.16 (s, 1H), 7.86 (d, *J*= 7.8Hz, 2H), 7.43 (t, *J*= 7.8Hz, 2H), 7.34-7.17 (m, 5H), 7.16-7.06 (m, 3H), 6.76 (t, *J*= 7.8Hz, 1H), 6.30 (t, *J*= 2.7Hz, 1H), 3.24-2.91 (m, 4H), 2.17 (s, 3H); ^{13}C NMR (67.5 MHz, CD_2Cl_2) δ 211.2, 183.5, 154.9, 152.4, 141.6, 137.4, 131.7, 131.1, 128.6, 128.5, 128.0, 127.7, 127.5, 127.1, 126.7, 126.5, 124.7, 123.3, 119.2, 62.0, 36.5, 28.5, 16.3; IR (neat) 3199(m),

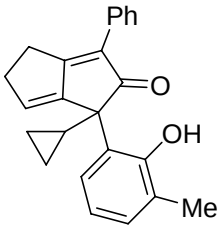
3089(m), 3060(m), 3028(m), 2918(m), 2251(w), 1666(s), 1624(m), 1591(m), 1495(m), 1466(m), 1381(m), 1360(m), 1327(m), 1282(m), 1252(m), 1213(m), 1169(w), 1144(m), 1107(sh), 1084(m), 1070(sh), 1034(w), 1005(w), 989(w), 835(m), 804(m), 779(m), 733(s), 694(m), 650(m), 619(w), 565(w), 532(w); MS, *m*/*z* (relative intensity, %) 379(M^++1, 19), 378(M^+, 63), 309(19), 262(20), 261(100); HRMS (EI) Calcd for $C_{27}H_{22}O_2$: 378.1620. Found 378.1622.

1-(4-Hydroxy-3-methylphenyl)-1,3-diphenyl-4,5-dihydropentalen-2(1*H*)-one (**12e**)



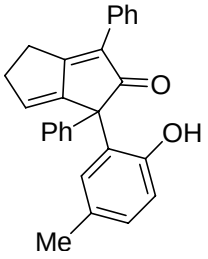
Colorless liquid, R_f= 0.08 (hexane/EtOAc = 3:1); ^{1}H NMR (270 MHz, CD_2Cl_2) δ 7.88 (d, *J*= 7.6Hz, 2H), 7.42 (t, *J*= 7.6Hz, 2H), 7.33-7.27 (m, 6H), 7.04 (s, 1H), 6.97 (d, *J*= 8.1Hz, 1H), 6.67 (d, *J*= 8.1Hz, 1H), 6.35 (s, 1H), 5.13 (s, 1H), 3.20-3.19 (m, 2H), 3.06-3.05 (m, 2H), 2.17 (s, 3H); ^{13}C NMR (67.5 MHz, CD_2Cl_2) δ 206.1, 180.4, 153.6, 153.1, 142.3, 134.0, 133.6, 132.6, 131.0, 128.43, 128.36, 128.2, 127.8, 127.6, 127.3, 127.2, 126.8, 123.7, 114.5, 61.3, 36.2, 28.0, 15.7; IR (neat) 3466(br), 3060(m), 3024(m), 1693(s), 1678(s), 1626(m), 1595(m), 1504(m), 1495(m), 1412(m), 1356(m), 1323(m), 1267(m), 1248(m), 1186(m), 1159(m), 1117(m), 1055(m), 1034(m), 987(m), 953(m), 912(m), 872(m), 823(m), 783(m), 731(m), 696(m), 631(m), 584(m); MS, m/z (relative intensity, %) 379(M^++1, 31), 378(M^+, 100), 351(14), 350(48), 349(13), 335(31), 273(16); HRMS (EI) Calcd for $C_{27}H_{22}O$: 378.1620. Found 378.1622.

1-Cyclopropyl-1-(2-hydroxy-3-methylphenyl)-3-phenyl-4,5-dihydropentalen-2(1*H*)-one (**11f**)



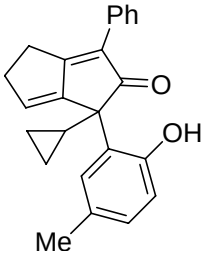
Colorless liquid, R_f= 0.26 (hexane/EtOAc = 3:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.49 (d, *J*= 7.3 Hz, 2H), 7.09 (t, *J*= 7.3Hz, 2H), 7.00-6.95 (m, 1H), 6.86 (d, *J*= 7.6Hz, 1H), 6.75 (d, *J*= 7.6Hz, 1H), 6.40 (t, *J*= 7.6Hz, 1H), 6.04 (t, *J*= 2.7Hz, 1H), 2.85-2.74 (m, 4H), 1.97 (s, 3H), 1.81-1.75 (m, 1H), 0.25-0.13 (m, 2H), 0.06-0 (m, 1H), -0.24-(-0.32) (m, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 211.8, 182.1, 154.6, 147.3, 135.7, 131.7, 130.4, 128.4, 127.9, 127.8, 127.7, 126.2, 124.5, 119.2, 57.6, 36.2, 27.4, 16.7, 14.6, 3.3, 1.8; IR (neat) 3084(m), 2916(m), 2860(m), 2249(w), 1698(s), 1662(s), 1597(s), 1493(m), 1464(m), 1444(m), 1427(m), 1360(m), 1327(m), 1282(m), 1250(m), 1203(m), 1132(m), 1090(m), 1050(m), 1024(m), 993(m), 910(s), 829(m), 804(m), 733(s), 694(s), 644(w), 596(m), 552(m), 530(m); MS, *m*/*z* (relative intensity, %) 343(M^++1, 22), 342(M^+, 83), 315(23), 314(100), 313(96), 299(11), 297(11), 286(17), 285(13); HRMS (EI) Calcd for $C_{24}H_{22}O_2$: 342.1620. Found 342.1621.

1-(2-Hydroxy-5-methylphenyl)-1,3-diphenyl-4,5-dihydropentalen-2(1*H*)-one (**11g**)



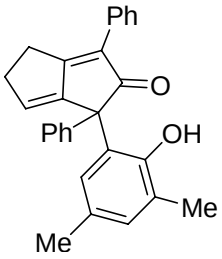
Colorless liquid, R_f= 0.37 (hexane/EtOAc = 3:1); ^{1}H NMR (270 MHz, CD_2Cl_2) δ 8.91 (s, 1H), 7.94-7.90 (m, 2H), 7.51-7.45 (m, 2H), 7.40-7.27 (m, 5H), 7.20-7.06 (m, 3H), 6.84 (d, *J*= 8.4Hz, 1H), 6.37 (t, *J*= 2.7Hz, 1H), 3.29-2.95 (m, 4H), 2.28 (s, 3H); ^{13}C NMR (67.5 MHz, CD_2Cl_2) δ 211.0, 183.5, 154.4, 152.2, 141.5, 137.4, 131.7, 130.3, 129.2, 129.1, 128.6, 128.5, 128.0, 127.7, 127.5, 127.1, 126.7, 125.0, 119.5; IR (neat) 3432(br), 3059(w), 1655(s), 1583(m), 1566(m), 1489(s), 1444(m), 1363(w), 1322(m), 1282(m), 1240(m), 1217(m), 1186(w), 1157(w), 1136(m), 1110(m), 1082(m), 1034(m), 991(m), 935(m), 906(m), 868(m), 831(m), 787(m), 754(m), 731(w), 694(s), 633(m), 571(w), 536(w); MS, *m*/*z* (relative intensity, %) 379(M^++1, 14), 378(M^+, 47), 334(16), 262(21), 261(100); HRMS (EI) Calcd for $C_{27}H_{22}O_2$: 378.1620. Found 378.1624.

1-Cyclopropyl-1-(2-hydroxy-5-methylphenyl)-3-phenyl-4,5-dihydropentalen-2(1*H*)-one (**11h**)



Colorless liquid, R_f= 0.31 (hexane/EtOAc = 3:1); ^{1}H NMR (270 MHz, CD_2Cl_2) δ 9.03 (s, 1H), 7.78 (d, *J*= 7.3 Hz, 2H), 7.41 (t, *J*= 7.3 Hz, 2H), 7.32-7.30 (m, 1H), 7.20 (s, 1H), 6.98 (d, *J*= 8.4 Hz, 1H), 6.77 (d, *J*= 8.4Hz, 1H), 6.33 (s, 1H), 3.15-3.03 (m, 4H), 2.24 (s, 3H), 1.99-1.93 (m, 1H), 0.57-0.54 (m, 1H), 0.52-0.33 (m, 2H), 0.03-(-0.02) (m, 1H); ^{13}C NMR (67.5 MHz, CD_2Cl_2) δ 212.0, 183.0, 154.3, 147.5, 136.5, 132.6, 129.82, 129.81, 129.50, 128.9, 128.7, 128.6, 128.20, 128.16, 127.3, 125.7, 119.1; IR (neat) 3346(br), 3080(w), 3059(w), 3008(w), 2918(w), 2860(w), 1682(s), 1610(m), 1597(m), 1510(m), 1493(m), 1444(m), 1421(w), 1358(m), 1325(m), 1267(m), 1238(m), 1174(w), 1117(m), 1078(w), 1024(w), 989(w), 953(w), 895(w), 818(m), 775(m), 746(m), 710(m), 694(m), 642(w), 625(w), 567(w), 542(w), 511(w); MS, *m*/*z* (relative intensity, %) 343(M^++1, 21), 342(M^+, 79), 315(22), 314(97), 313(100), 299(16), 297(13), 286(15), 285(14), 225(10), 115(10); HRMS (EI) Calcd for $C_{24}H_{22}O_2$: 342.1620. Found 342.1617.

1-(2-Hydroxy-3,5-dimethylphenyl)-1,3-diphenyl-4,5-dihydropentalen-2(1*H*)-one (**11i**)



Brown solid; R_f 0.20 (hexane/EtOAc = 10/1); mp; ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 3H), 2.32 (s, 3H), 2.99-3.01 (m, 1H), 3.11-3.14 (m, 1H), 3.21-3.24 (m, 2H), 6.29 (t, J = 2.7 Hz, 1H), 6.94 (s, 2H), 7.10-7.13 (m, 2H), 7.23-7.34 (m, 4H), 7.39-7.45 (m, 2H), 7.89 (d, J = 7.8 Hz, 2H), 8.87 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 16.5, 20.7, 28.2, 36.2, 61.8, 124.4, 126.47, 126.52, 127.1, 127.6, 127.7, 127.9, 128.1, 128.46, 128.55, 128.58, 131.6, 131.8, 136.4, 141.3, 152.5, 152.8, 182.3; IR (neat) 3213(w), 3057(w), 3020(w), 2918(m), 2854(w), 2360(w), 1747(w), 1664(s), 1589(s), 1541(w), 1493(m), 1475(m), 1444(m), 1412(m), 1360(m), 1325(m), 1294(w), 1252(m), 1227(m), 1174(w), 1142(m), 1082(w), 1034(w), 1016(w), 987(w), 958(w), 908(w), 861(w), 839(w), 808(w), 785(w), 754(m), 731(m), 710(m), 694(s), 636(w), 571 w, 517 w; MS, *m*/*z* (relative intensity, %) 393 (M^++1, 33), 392 (M+, 100), 364 (41), 275 (28), 235 (67), 58 (31); HRMS for $C_{28}H_{24}O_2$: 392.1776. Found: 392.1774.

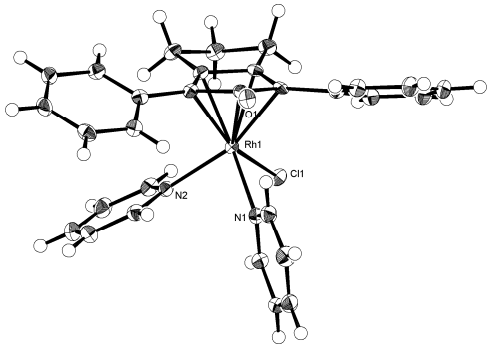
4. X-ray Crystallographic Structure Analysis

X-ray Crystallographic Structure Analysis of **6**

X-ray crystallography was performed on Rigaku RAXIS RAPID imaging plate diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71075 Å). The data were collected at 123 K using ω scan in the 2θ range of 3.01–27.45 deg. A total of 16585 reflections were measured, of which 3871 were independent reflections (R_{int} = 0.0440). The structure was solved by direct methods (Sir97) and refined by the full-matrix least-squares on F^2 (SHELXL-97).[1] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: (**6**_CCDC 752605): $C_{42}H_{32}Cl_2O_4Rh_2$, FW = 877.40, crystal size 0.19 × 0.18 × 0.06 mm^3, monoclinic, space group P21/c, a = 10.2579 (3) Å, b = 11.3113 (3) Å, c = 15.1156 (4) Å, α = 90 °, β = 104.6735 (9)°, γ = 90 °, V = 1696.66 (8) Å^3, Z = 2, D_c = 1.717 g cm^{-1}. The refinement converged to R_1 = 0.0657 for $I > 2\sigma(I)$, wR_2 = 0.1667 for $I > 2\sigma(I)$, wR_2 = 0.1769, GOF = 1.072 for all data. CCDC-752605 contains the supplementary crystallographic data.

X-ray Crystallographic Structure Analysis of **8**

X-ray crystallography was performed on Rigaku RAXIS RAPID imaging plate diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71075 Å). The data were collected at 123 K using ω scan in the 2θ range of 3.10–27.48 deg. A total of 13659 reflections were measured, of which 6240 were independent reflections (R_{int} = 0.0441). The structure was solved by direct methods (Sir97) and refined by the full-matrix least-squares on F^2 (SHELXL-97).[4] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: (**8**_CCDC 752604): $C_{31}H_{28}Cl_3N_2ORh$, FW = 653.81, crystal size 0.25 × 0.22 × 0.12 mm^3, brown prism, triclinic, space group P-1, a = 9.1035 (5) Å, b = 12.2818 (7) Å, c = 13.9760 (7) Å, α = 112.1714 (17) °, β = 97.0413 (16)°, γ = 100.9423 (18) °, V = 1387.97 (13) Å^3, Z = 2, D_c = 1.564 g cm^{-1}. The refinement converged to R_1 = 0.0343 for $I > 2\sigma(I)$, wR_2 = 0.0841 for $I > 2\sigma(I)$, wR_2 = 0.1012, GOF = 1.175 for all data. CCDC-752604 contains the supplementary crystallographic data.



5. References

(1) J. Chatt and L. M. Venanzi, *J. Chem. Soc*., 1957, 4735.
(2) M. I. Bruce, C. N. Jensen and N. L. Jones, *Inorg. Synth*., 1989, **26**, 259.
(3) A. J. Pearson, R. J. Shively, Jr. and R. A. Dubbert, *Organometallics*, 1992, **11**, 4096.
(4) Sheldrick, G.. M. SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.