Cyclopentadienone Synthesis by Rhodium(I)-Catalyzed [3 + 2] Cycloaddition Reactions of Cyclopropenones and Alkynes

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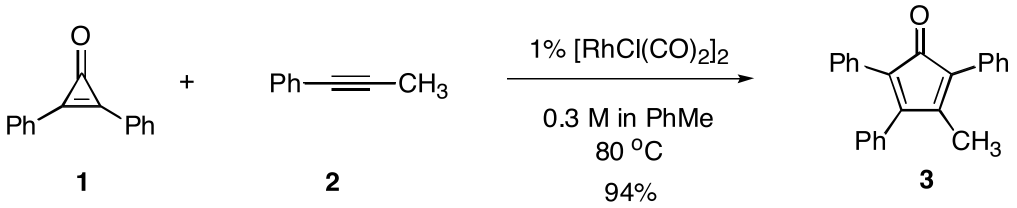
I. General Procedures.

General methods: air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry nitrogen from a manifold unless otherwise indicated. Sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Reactions were run using Teflon™-coated magnetic stir bars. Elevated temperatures were maintained in temperature regulated oil baths. Unless otherwise indicated, cycloadditions were run in borosilicate test tubes. Organic solutions were concentrated using a Buchi or Heildoph rotary evaporator. Thin layer chromatography plates were visualized (as needed) by ultraviolet light and treatment with acidic *p*-anisaldehyde stain or potassium permanganate stain followed by gentle heating. Chromatographic purification of products was accomplished by flash chromatography. Silica gel 60, 230-400 mesh was purchased from EM Science. 1,2-dichloroethane was freshly distilled over calcium hydride. Tetrahydrofuran, toluene, and dichloromethane were purified with a Solvtek™ solvent purification system using alumina columns. Where indicated, tetrahydrofuran was distilled over benzophenone ketyl (benzophenone plus sodium metal). Other solvents were used directly from commercial suppliers, unless otherwise specified. $[RhCl(CO)_2]_2$ was purchased from Strem Chemicals. Diphenylcyclopropenone (**1**), alkynes, and other materials were purchased from Aldrich Chemical Co. and used without further purification unless otherwise noted. Copper(I) iodide was purified prior to use by the method of Kauffman.[1]

NMR spectra were measured on a Varian INOVA 500 (^{1}H at 500 MHz, ^{13}C at 125 MHz), Varian Mercury 400 (^{1}H at 400 MHz, ^{13}C at 100 MHz), Varian Gemini 200 (^{1}H at 200 MHz, ^{13}C at 50 MHz) magnetic resonance spectrometer. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, qd = quartet of doublets, ddd = doublet of doublet of doublets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C are reported in terms of chemical shift and quantity of carbons. Infrared spectra were recorded on a Perkin-Elmer Spectrum BX or ThermoNicolet IR300 Fourier transform spectrometer (FTIR) and are reported as follows: wavenumbers (cm^{-1}), description (w = weak, m = medium, s = strong, b = broad). High-resolution mass spectra (HRMS) were recorded at the NIH regional mass spectrometry facility at the University of California, San Francisco. Reported mass values are with error limits of ±4 millimass unit. MALDI data was recorded on an Voyager Biosystems MALDI apparatus. Melting points were measured with a Thomas-Hoover Unimelt™ apparatus. Elemental analyses (%C, %H, %N, %F) were determined by Desert Analytics laboratory of Tucson, Arizona. X-ray data collection was accomplished by CHEXRAY (University of California, Berkeley). X-ray data was solved at Stanford by Xavier Ottenwaelder, Prateek Verma, and T. D. P. Stack.

II. Preparative and Experimental Details for New Compounds.



Cyclopentadienone **3**:

Diphenylcyclopropenone (**1**, 375 μmol, 77.3 mg) and 1-phenyl-1-propyne (**2**, 250 μmol, 25.1 mg, 27 μL) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (Solvtek™, 750 μL) and $[RhCl(CO)_2]_2$ (1.0 mg, 2.5 μmol). The tube was capped with a septum and heated at 80 °C for 2 hours under nitrogen. The resulting solution was cooled to room temperature and then purified by flash column chromatography eluting with 100 mL petroleum ether followed by 150 mL 5% diethyl ether/petroleum ether. Product-containing fractions were concentrated under reduced pressure to leave cyclopentadienone **3** as a deep purple solid (76 mg, 94%).

Large-Scale: Diphenylcyclopropenone (**1**, 12 mmol, 2.47 g) and $[RhCl(CO)_2]_2$ (46.7 mg, 0.12 mmol, 1.5 mol%) were weighed out into a round-bottom flask with stir bar under nitrogen and capped with a septum. To this was added toluene (Solvtek™, 27 mL) and 1-phenyl-1-propyne (**2**, 8 mmol, 929 mg, 1.00 mL). The reaction was heated at 80 °C for 6.5 hours under nitrogen. At this point, TLC indicated complete consumption of **2**. The reaction was cooled to room temperature and then concentrated under reduced pressure. The concentrate was purified by flash column chromatography eluting with 500 mL pentane followed by 500 mL 5% ethyl acetate/pentane. Product-containing fractions were concentrated under reduced pressure to leave cyclopentadienone **3** as a deep purple solid (2.19 g, 85%).

R_f: 0.57 in 19:1, pentane: ether (appears red in visible light).

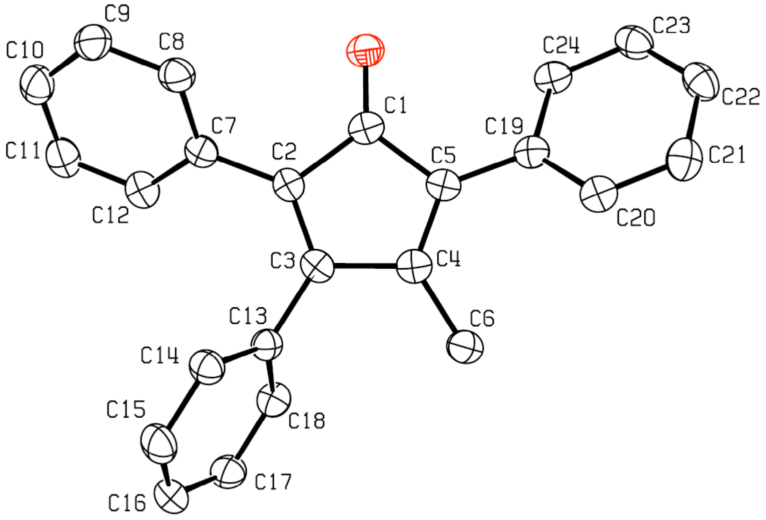
m. p. 145-148 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46-7.20 (m, 15 H), 2.12 (s, 3H).

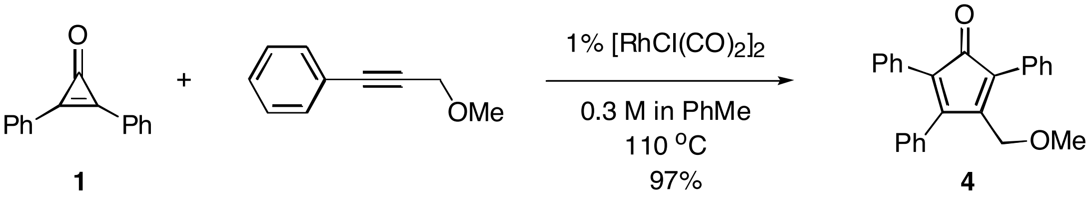
^{13}C NMR ($CDCl_3$, 100 MHz) δ: 200.7, 154.7, 154.4, 134.0, 131.6, 130.9, 130.1 (2C), 129.8 (2C), 128.9 (2C), 128.9 (2C), 128.8, 128.5 (2C), 128.2 (2C), 127.6, 127.6, 125.9, 124.9, 14.9.

FTIR ($CDCl_3$ film): 3054 (w), 1712 (m), 1596 (w), 1492 (w), 1442 (w), 1380 (w), 1348 (w), 1298 (w), 1113 (w), 1073 (w), 1002 (w), 989 (w), 910 (w), 796 (w), 738 (m), 695 (s) cm^{-1}.

HRMS for $C_{24}H_{18}O$ calc'd: 322.1358 g/mol, found: 322.1356 g/mol.



ORTEP diagram of **3**. Ellipsoids drawn at the 50% probability level.



Cyclopentadienone **4**:

Phenylpropargyl methyl ether[2] (147 mg, 1 mmol), diphenylcyclopropenone (**1**, 1.51 mmol, 310 mg), and $[RhCl(CO)_2]_2$ (10.0 µmol, 3.9 mg) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (Solvtek^{TM}, 3.3 mL). The tube was capped with a septum and heated in an oil bath for 4 hours at 110 °C under nitrogen. The resulting solution was then purified by flash column chromatography eluting with 300 mL petroleum ether followed by 500 mL 5% diethyl ether/petroleum ether. Product-containing fractions were concentrated under reduced pressure to leave cyclopentadienone **4** as a purple solid (340 mg, 97%).

R_f: 0.41 in 19:1, petroleum ether: ether (appears red in visible light).

m. p. 114-118 °C.

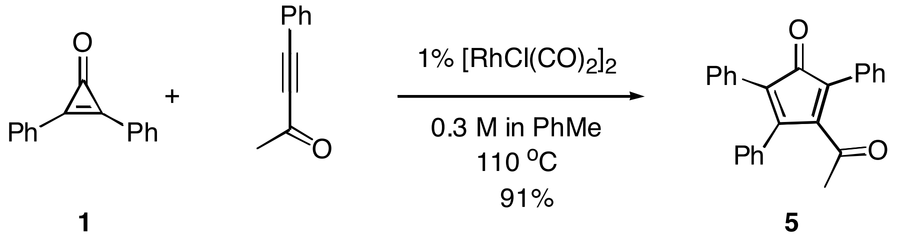
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.56-7.54 (m, 2H), 7.47-7.37 (m, 8H), 7.22-7.20 (m, 5H), 4.11 (s, 2H), 3.28 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ: 200.6, 155.6, 150.1, 133.6, 130.7, 130.5, 129.9 (2C), 129.8 (2C), 129.5, 128.8, 128.6 (2C), 128.6 (2C), 128.4 (2C), 128.3, 128.0 (2C), 127.4, 124.8, 65.5, 58.4.

FTIR ($CDCl_3$ film): 3054 (w), 2917 (m), 2848 (w), 1712 (s), 1493 (w), 1443 (m), 1392 (w), 1347 (w), 1302 (w), 1189 (w), 1156 (w), 1091 (s), 1028 (m), 942 (w), 797 (w), 739 (w), 695 (s) cm^{-1}.

HRMS for $C_{25}H_{20}O_2$ calc'd: 352.1463 g/mol, found: 352.1461 g/mol.

Elemental Analysis for $C_{25}H_{20}O_2$ calc'd: 85.20% C, 5.72% H, 9.08% O; found 84.80% C, 5.84% H.



1 **5**

Cyclopentadienone **5**:

Diphenylcyclopropenone (**1**, 77.3 mg, 375 μmol) and 4-phenyl-but-3-yn-2-one (36 mg, 250 μmol) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (750 μL, Solvtek^{TM}) and $[RhCl(CO)_2]_2$ (1.0 mg, 2.5 μmol). The tube was then capped with a septum and then heated at 110 °C for 18 hours under nitrogen. The crude reaction mixture was then cooled to room temperature and then purified by flash column chromatography eluting with diethyl ether and pentane (1:19). Product-containing fractions were collected and concentrated under reduced pressure to give a purple solid **5** (80 mg, 91% yield).

m. p. 132-134 °C.

R_f: 0.33 in 24:1, pentane: ethyl acetate (appears red in visible light).

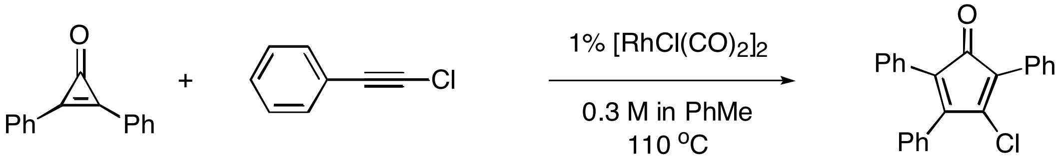
^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.49-7.45 (m, 2H), 7.45-7.32 (m, 6H), 7.27-7.19 (m, 7H), 2.13 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ: 201.7, 199.6, 153.6, 152.2, 132.8, 130.0, 129.9 (2C), 129.5 (2C), 129.3, 129.2, 129.1, 128.7 (2C), 128.5 (2C), 128.1 (2C), 128.0 (2C), 127.8, 126.5, 124.9, 31.4.

FTIR (thin film): 3727 (w), 3054 (w), 2360 (s), 2341 (s), 1717 (s), 1699 (s), 1694 (m), 1490 (w), 1443 (m), 1352 (m), 1181 (w), 1112 (m), 694 (s), 668 (m) cm^{-1}.

HRMS for $C_{25}H_{18}O_2$ calc'd: 350.1307 g/mol, found 350.1312 g/mol.

Elemental Analysis for $C_{25}H_{18}O_2$ calc'd: 85.69% C; 5.19% H; 9.13% O; found 85.62% C; 5.37% H.



1 **6**

Cyclopentadienone **6**:

Chloroethynyl benzene[3] (20.0 mg, 146 μmol), diphenylcyclopropenone (**1**, 45.2 mg, 220 μmol), and $[RhCl(CO)_2]_2$ (1.5 μmol, 0.6 mg) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (Solvtek^{TM}, 440 μL). The tube was capped with a septum and heated in an oil bath for 6 hours at 110 °C under nitrogen. The resulting solution was purified by flash column chromatography eluting with 1% diethyl ether/pentane. Product fractions were collected and concentrated under reduced pressure to give cyclopentadienone **6** as a red solid (35.4 mg, 71%).

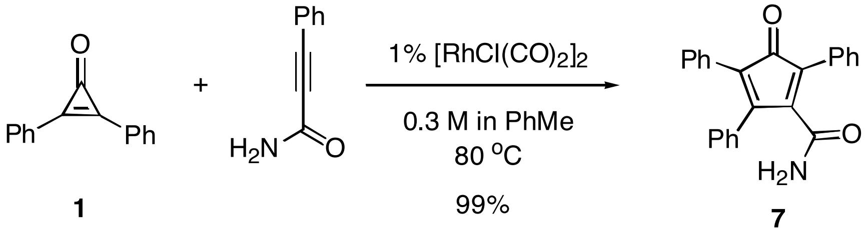
m. p. 147-150 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (apparent dd, J_1 = 8.5 Hz, J_2 = 1.3 Hz, 2H), 7.49-7.40 (m, 8H), 7.25 (apparent s, 5H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 196.7, 149.8, 149.5, 131.2, 130.1 (2C), 129.6, 129.5 (2C), 129.4 (2C), 129.3, 129.2, 128.4 (2C), 128.4, 128.3 (2C), 128.2 (2C), 128.0, 125.3, 123.8.

FTIR ($CDCl_3$ film): 3055 (w), 1717 (s), 1598 (w), 1490 (m), 1443 (m), 1346 (m), 1256 (m), 1156 (w), 1115 (s), 1073 (w), 1027 (m), 906 (w), 792 (m), 738 (m), 713 (s) cm^{-1}.

HRMS for $C_{23}H_{15}Cl$ calc'd: 342.0811 g/mol, found: 342.0805 g/mol.



Cyclopentadienone **7**:

Diphenylcyclopropenone (**1**, 77.3 mg, 375 μmol) and 3-phenyl-propynoic acid amide (36.3 mg, 250 μmol) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (1.250 mL, Solvtek™) and $[RhCl(CO)_2]_2$ (1.0 mg, 2.5 μmol). The tube was capped with a septum and the reaction was heated at 80 °C for 12 hours under nitrogen. The crude reaction mixture was then cooled to room temperature and then purified by flash column chromatography eluting with methanol and chloroform (1:99). Product-containing fractions were collected and concentrated under reduced pressure to give cyclopentadienone **7** as a purple solid (87 mg, 99% yield).

m. p. 202-204 °C.

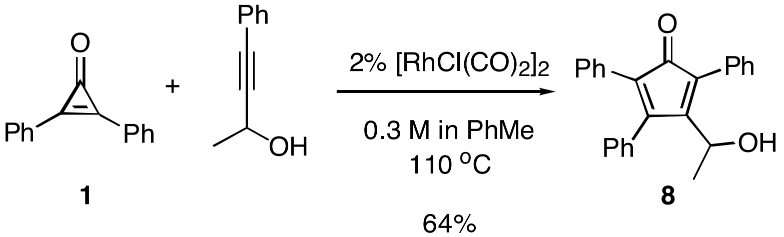
R_f: 0.68 in 6:5, ethyl acetate: pentane (appears purple in visible light).

^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.63-7.60 (m, 2H), 7.46-7.31 (m, 8H), 7.27-7.23 (m, 3H), 7.21-7.18 (m, 2H), 5.73 (s, 1H), 5.60 (s, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ: 199.5, 166.9, 160.4, 153.0, 147.0, 132.5, 130.1, 130.0 (2C), 129.5 (2C), 129.3 (2C), 129.1 (2C), 128.6 (3C), 128.2 (3C), 127.9, 126.4, 124.8.

FTIR (thin film): 3402 (m), 3339 (w), 3081 (w), 3057 (w), 1716 (s), 1661 (s), 1597 (m), 1493 (w), 1443 (m), 1344 (w), 1344 (w), 1261 (w), 1130 (w), 1114 (w), 909 (w), 796 (w), 735 (m), 715 (m), 694 (s) cm^{-1}.

HRMS for $C_{24}H_{17}NO_2$ calc'd: 351.1259 g/mol, found 351.1249 g/mol.



Alcohol **8**:

Diphenylcyclopropenone (**1**, 186 mg, 903 μmol) and 4-phenyl-but-3-yn-2-ol (88 mg, 602 μmol) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (2.0 mL, Solvtek™) and $[RhCl(CO)_2]_2$ (2.4 mg, 6.0 μmol). The tube was then capped with a septum and then heated at 110 °C for 12 hours under nitrogen. TLC indicated incomplete conversion. To this was added more

$[RhCl(CO)_2]_2$ (2.4 mg, 6.0 μmol) and the reaction was heated at 110 °C for an additional 11 hours under nitrogen. The crude reaction mixture was then cooled to room temperature and then purified by flash column chromatography eluting with using ethyl acetate and pentane (1:6). Product-containing fractions were collected and concentrated under reduced pressure to give a red solid **8** (135 mg, 64% yield).

m. p. 59-61 °C.

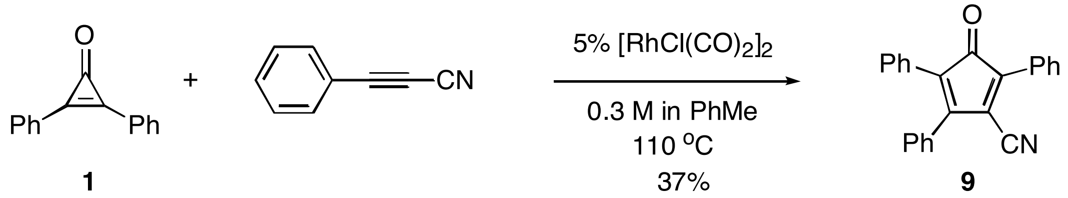
R$_f$: 0.30 in 6:1, pentane: ethyl acetate (appears red spot on plate).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.46-7.34 (m, 10H), 7.20-7.13 (m, 5H), 4.93 (dq, J_{quart} = 6.6 Hz, J_{double} = 6.5 Hz, 1H), 1.60 (d, J = 6.4 Hz, 1H), 1.26 (d, J = 6.7 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 200.6, 157.4, 154.6, 134.7, 130.7, 130.4, 130.1 (2C), 129.8 (2C), 128.8 (2C), 128.7 (2C), 128.6, 128.3 (2C), 128.1, 127.9 (2C), 127.4, 126.4, 125.5, 65.3, 22.7.

FTIR (thin film): 3523 (b, m), 3054 (w), 2929 (w) 2360 (m), 2341 (m), 1710 (s), 1596 (w), 1491 (m), 1443 (m), 1347 (w), 1263 (w), 1158 (w), 1090 (m), 1072 (m), 1029 (m), 1015 (m), 910 (m), 796 (m), 740 (m), 697 (s) cm^{-1}.

HRMS for $C_{25}H_{20}O_2$ calc'd: 352.1463 g/mol, found 352.1460 g/mol.



Cyclopentadienone **9**:

Phenylpropynenitrile[4] (38.1 mg, 300 μmol), diphenylcyclopropenone (**1**, 92.8 mg, 450 μmol), and $[RhCl(CO)_2]_2$ (15 μmol, 5.8 mg) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (Solvtek^{TM}, 900 μL). The tube was capped with a septum and heated in an oil bath for 11 hours at 110 °C under nitrogen. The resulting solution was purified by flash column chromatography eluting with 100 mL petroleum ether followed by 200 mL 5% diethyl ether/petroleum ether. Product-containing fractions were collected and concentrated under reduced pressure to leave cyclopentadienone **9** as a purple solid (36.6 mg, 37%).

m. p. 128 °C.

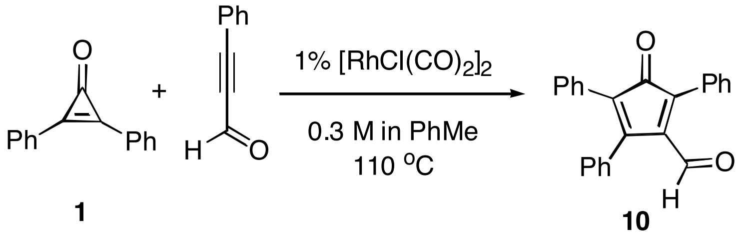
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98-7.96 (m, 2H), 7.52-7.42 (m, 8H), 7.30-7.22 (m, 5H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 197.6, 150.2, 138.6, 131.1, 131.0, 130.4, 129.9 (2C), 129.6 (2C), 129.3, 129.0 (2C), 128.9 (2C), 128.6 (2C), 128.4 (2C), 128.4, 128.3, 124.6, 122.1, 115.0.

FTIR ($CDCl_3$ film): 3056 (w), 2210 (w), 1716 (s), 1621 (w), 1598 (w), 1574 (w), 1492 (w), 1444 (m), 1355 (w), 1297 (m), 1114 (m), 1074 (w), 1028 (w), 910 (w), 795 (w), 761 (w), 727 (s), 693 (s) cm^{-1}.

HRMS for $C_{24}H_{15}NO$ calc'd: 333.1154 g/mol, found: 333.1151 g/mol.

Elemental Analysis for $C_{24}H_{15}NO$ calc'd: 86.46% C, 4.54% H, 4.20% N; found 86.36% C, 4.76% H, 4.09% N.



1 **10**

Cyclopentadienone **10**:

Diphenylcyclopropenone (**1**, 77.3 mg, 0.375 μmol) and 3-phenylpropynal (32.6 mg, 250 μmol) were weighed out into a test tube under nitrogen. To this was added toluene (750 μL, Solvtek^{TM}) and $[RhCl(CO)_2]_2$ (1.0 mg, 2.5 μmol). The tube was then capped with a septum and heated at 110 ºC for 3 hours under nitrogen. The crude reaction mixture was then cooled to room temperature and then purified by flash column chromatography eluting with diethyl ether and pentane (1:19). Product-containing fractions were collected and concentrated under reduced pressure to give a purple solid (35.4 mg, 42% yield).

m. p. 171-173 ºC.

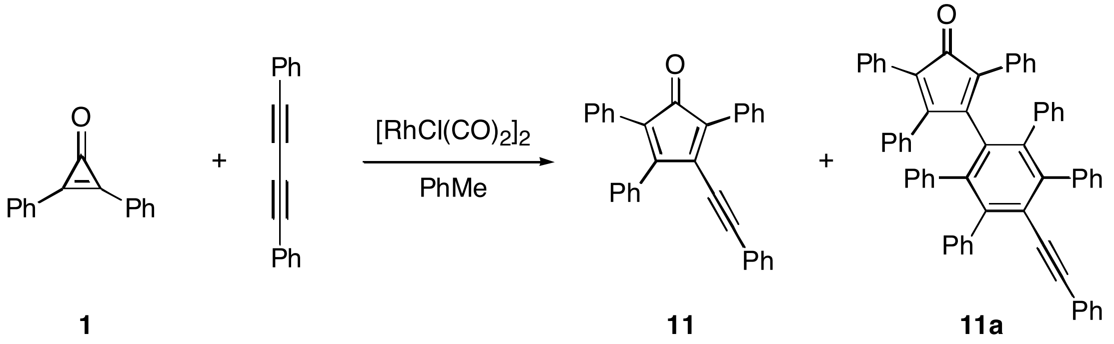
R$_f$: 0.38 in 24:1, pentane: ethyl acetate (appears purple in visible light).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 10.19 (s, 1H), 7.59-7.54 (m, 2H), 7.54-7.47 (m, 3H), 7.42-7.32 (m, 3H), 7.26-7.21 (m, 5H), 7.19-7.14 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ: 199.9, 189.1, 155.3, 152.7, 143.9, 138.5, 132.8, 131.1 (2C), 130.4, 130.0 (2C), 129.9, 129.1, 128.6 (2C), 128.5 (2C), 128.12 (2C), 128.09 (2C), 127.9, 126.6.

FTIR (thin film): 3054 (w), 2849 (w), 2360 (s), 2341 (s), 1713 (s), 1679 (m), 1598 (w), 1575 (w), 1489 (w), 1443 (m), 1354 (m), 1116 (m), 1074 (w), 1001 (w), 798 (m), 729 (m), 694 (s) cm^{-1}.

HRMS for $C_{24}H_{16}O_2$ calc'd: 336.1150 g/mol, found 336.1152 g/mol.



1 **11** **11a**

Cyclopentadienones **11** and **11a**:

Table 1. [3+2] Reactions of Diphenylbutadiyne.

Entry	Conditions	**11**	**11a**
1	1 mol% $[RhCl(CO)_2]_2$, 9.5 h, 110 ºC	10%	10%
2	1 mol% $[RhCl(CO)_2]_2$, 14.5 h, 80 ºC	5%	17%
3	10 mol% $[RhCl(CO)_2]_2$, 21 h, 60 ºC	35%	Trace

Diphenylbutadiyne (75.0 mg, 371 μmol), diphenylcyclopropenone (**1**, 556 μmol, 115 mg) and $[RhCl(CO)_2]_2$ (3.7 μmol, 1.4 mg) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (Solvtek^{TM}, 1.1 mL). The tube was capped with a septum and heated in an oil bath for

9.5 hours at 110 ºC under nitrogen. The resulting solution was purified by flash column chromatography eluting with 300 mL 3% diethyl ether/petroleum ether followed by 200 mL 5% then 100 mL 10%. The resulting blue fraction (high R_f) was concentrated under reduced pressure to leave (**11**) as a blue solid (15.1 mg, 10%). The resulting brown fraction (low R_f) was concentrated under reduced pressure to leave (**11a**) as a blue solid (15.3 mg, 10%).

Data for **11**:

m. p. 144-146 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13-8.10 (dd, 2H), 7.56-7.28 (m, 18H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 200.1, 151.1, 135.5, 132.6, 131.7 (2C), 131.1, 131.0, 130.4, 130.0 (2C), 129.9, 129.7, 129.4 (2C), 129.2, 129.1 (2C), 128.5 (2C), 128.3 (2C), 128.1 (2C), 128.1 (2C), 127.7, 125.0, 122.4, 110.8, 86.5.

FTIR ($CDCl_3$ film): 3056 (m), 2185 (m), 1705 (s), 1576 (w), 1599 (w), 1495 (m), 1486 (m), 1443 (m), 1365 (m), 1327 (m), 1128 (m), 1116 (m), 1073 (w), 1006 (w), 910 (m), 795 (w), 756 (m), 727 (m), 689 (m) cm^{-1}.

HRMS for $C_{31}H_{20}O$ calc'd: 408.1514 g/mol, found: 408.1510 g/mol.

Data for **11a**:

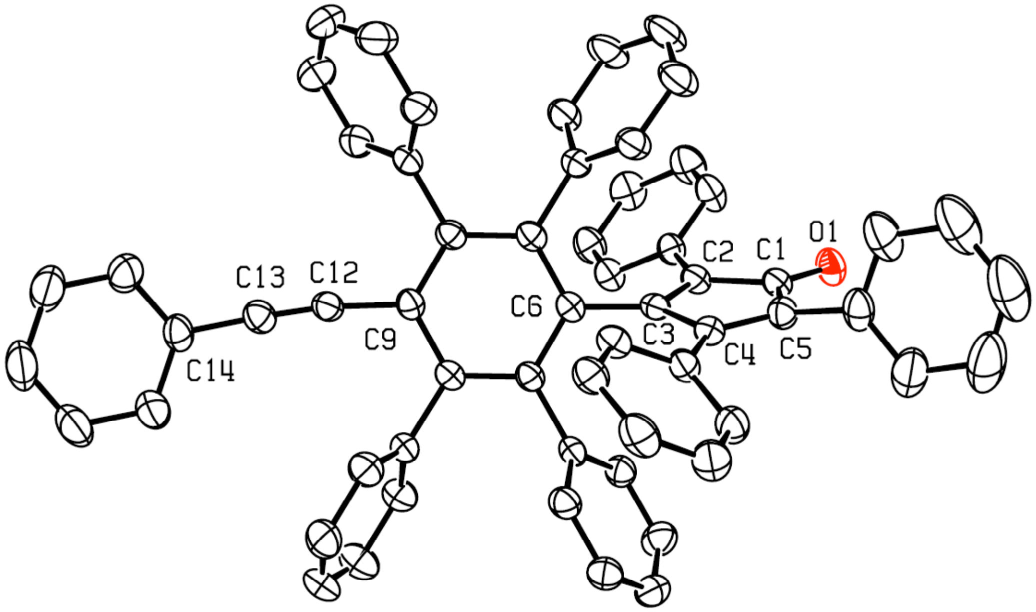
m. p. 300-302 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.28 (s, 1H), 7.26-7.10 (m, 19H), 7.06 (t, J = 8.1 Hz, 4H), 6.89 (t, J = 7.8 Hz, 4H), 6.75 (apparent dd, J_1 = 13.9 Hz, J_2 = 7.8 Hz, 8H), 6.67 (s, broad, 2H), 6.46 (s, broad, 2H).

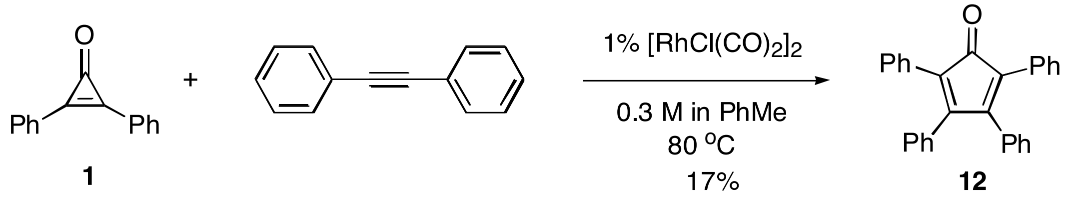
^{13}C NMR ($CDCl_3$, 125 MHz) δ: 199.6, 154.5, 154.1, 144.2, 139.7, 139.3, 138.3, 133.5, 132.7, 131.2, 131.0, 130.9, 130.9, 130.1, 129.5, 129.1, 128.7, 128.0, 128.0, 127.9, 127.9, 127.6, 127.5, 127.2, 127.1, 127.0, 127.0, 126.5, 126.5, 126.2, 125.0, 124.6, 123.1, 98.1, 89.2. Because of dispersity problems in the region between 126 and 132 ppm, 8 carbon signals could not been unambiguously identified.

FTIR ($CDCl_3$ film): 3056 (m), 2248 (w), 1947 (w), 1879 (w), 1707 (s), 1599 (m), 1492 (m), 1442 (m), 1405 (w), 1361 (m), 1327 (m), 1269 (w), 1117 (m), 1074 (m), 1027 (m), 909 (s), 757 (m), 732 (s), 697 (s) cm^{-1}.

MALDI for $C_{61}H_{40}O$ calc'd: 788.3 g/mol, found: 790.4 g/mol (M+2H), 813.5 g/mol (M+H+Na).



ORTEP diagram for **11a**. Elipsoids drawn at the 50% probability level.



Tetracyclone (**12**):

Diphenylacetylene (44.6 mg, 250 μmol), diphenylcyclopropenone (**1**, 250 μmol, 53.1 mg) and $[RhCl(CO)_2]_2$ (2.5 μmol, 1.0 mg) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (Solvtek^{TM}, 1.67 mL). The tube was capped with a septum and heated in an oil bath for 65 hours at 80 °C under nitrogen. The resulting solution was purified by flash column chromatography eluting with 100 mL petroleum ether followed by 150 mL 5% diethyl ether/petroleum ether. Product-containing fractions were collected and concentrated under reduced pressure to leave tetracyclone (**12**) as a purple solid (16.5 mg, 17%).

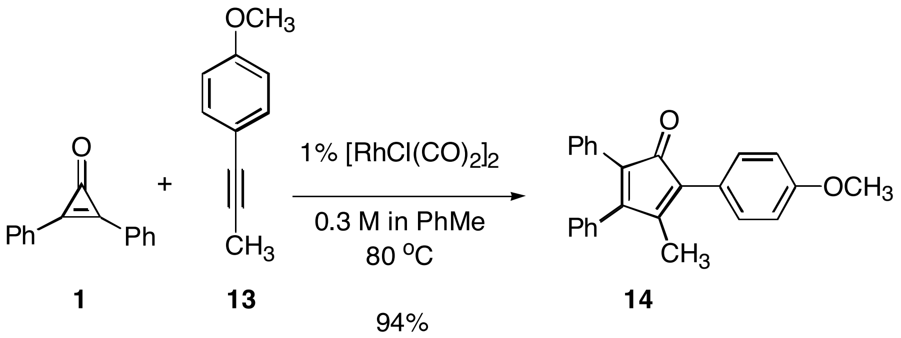
m. p. 218-219 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25-7.23 (m, 12H), 7.19-7.16 (m, 4H), 6.94-6.92 (m, 4H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 200.3, 154.5 (2C), 133.0 (2C), 130.7 (2C), 130.1 (4C), 129.3 (4C), 128.5 (2C), 128.0 (4C), 128.0 (4C), 127.4 (2C), 125.3 (2C).

FTIR ($CDCl_3$ film): 3056 (w), 1711 (s), 1598 (w), 1488 (w), 1443 (m), 1354 (w), 1300 (m), 1116 (w), 1090 (w), 1075 (w), 1027 (w), 913 (w), 809 (m), 793 (w), 750 (w), 738 (w), 717 (s), 696 (s), 689 (s) cm^{-1}.

HRMS for $C_{29}H_{20}O$ calc'd: 384.1514 g/mol, found: 384.1515 g/mol.



Cyclopentadienone **14**:

Diphenylcyclopropenone (**1**, 79.4 mg, 385 μmol) and alkyne **13**[5] (37.5 mg, 257 μmol) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (800 μL, Solvtek™) and $[RhCl(CO)_2]_2$ (1.0 mg, 2.5 μmol). The tube was capped with a septum and heated at 80 °C for 2.5 hours under nitrogen. The crude reaction mixture was then cooled to room temperature and then purified by flash column chromatography eluting with diethyl ether and pentane (1:19). Product-containing fractions were collected and concentrated under reduced pressure to give **14** as a purple solid (85 mg, 94% yield).

m. p. 57-59 °C.

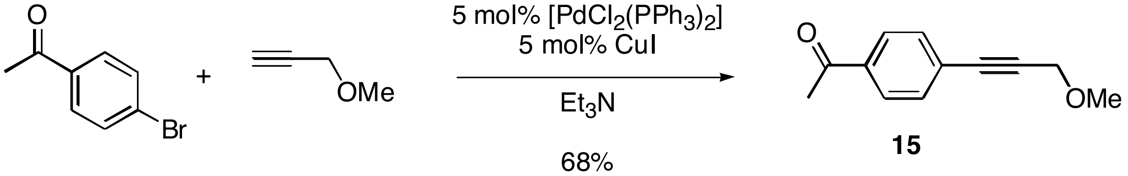
R$_f$: 0.31 in 19:1 pentane: ethyl acetate (appears purple in visible light).

^{1}H NMR ($CDCl_3$, 500 MHz): δ: 7.44-7.36 (m, 5H), 7.31-7.27 (m, 2H), 7.25-7.16 (m, 5H), 7.01-6.97 (m, 2H), 3.85 (s, 3H), 2.09 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ: 200.9, 158.9, 154.9, 152.4, 133.9, 130.8 (2C), 129.8 (2C), 128.6 (3C), 128.5 (2C), 127.9 (2C), 127.2 (2C), 125.2, 124.3, 123.8, 113.8 (2C), 55.2, 14.5.

FTIR (thin film): 3054 (w), 2933 (w), 2835 (s), 2361 (s), 1708 (s), 1603 (m), 1569 (w), 1509 (s), 1441 (m), 1285 (m), 1249 (s), 1179 (m), 1112 (w), 1036 (w), 833 (m), 697 (m) cm^{-1}.

HRMS for $C_{25}H_{20}O_2$ calc'd: 352.1463 g/mol, found 352.1466 g/mol.



Alkyne **15**:

Methyl propargyl ether (0.489 g, 4.8 mmol, 406 μL) was added to a stirring solution of 4'-bromoacetophenone (0.796 g, 4.0 mmol), copper(I) iodide (38 mg, 0.200 mmol), and bistriphenylphosphinopalladium(II) dichloride (140 mg, 0.200 mmol) in triethylamine (12 mL) under nitrogen. The suspension was stirred for 1 day at 50 °C under nitrogen and then poured over 25 mL water and 10 mL diethyl ether. The layers were separated and the aqueous layer was extracted with ether (2 x 20 mL). Combined organic fractions were washed with 1 N HCl (aq), saturated $NaHCO_3$ (aq), water, and brine (30 mL each), dried over magnesium sulfate, filtered and concentrated by rotary evaporation. Further purification was accomplished by flash column chromatography eluting with 17% ether in pentane up to 33% ether in pentane. Product-containing fractions were concentrated to leave alkyne **15** (512 mg, 68%).

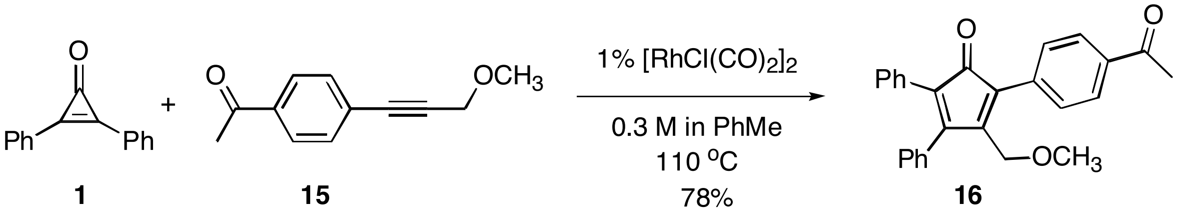
R$_f$: 0.63 in 1:1, pentane:ether (potassium permanganate stain).

^{1}H NMR (200 MHz, CDCl$_3$) δ: 7.91 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 4.35 (s, 2H), 3.47 (s, 3H), 2.60 (s, 3H).

^{13}C NMR (CDCl$_3$, 125 MHz) δ: 197.3, 136.4, 131.8 (2C), 128.2 (2C), 127.4, 88.3, 85.5, 60.3, 57.9, 26.6.

FTIR (CDCl$_3$ film): 3042 (w), 2932 (m), 2822 (w), 1685 (s), 1602 (s), 1555 (w), 1404 (m), 1357 (m), 1264 (s), 1186 (m), 1100 (s), 958 (m), 901 (m), 838 (m), 647 (m) cm^{-1}.

HRMS for $C_{12}H_{12}O_2$ calc'd: 188.0837 g/mol, found 188.0840 g/mol.



Cyclopentadienone **16**:

Alkyne **15** (32.0 mg, 170 μmol), diphenylcyclopropenone (**1**, 53.0 mg, 255 μmol), and [RhCl(CO)$_2$]$_2$ (1.7 μmol, 1.0 mg) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (Solvtek^{TM}, 510 μL). The tube was capped with a septum and heated in an oil bath for 5 hours at 110 °C under nitrogen. The resulting solution was purified by flash column chromatography eluting with 100 mL pentane followed by 200 mL 33% diethyl ether/pentane. The product-containing fractions were concentrated under reduced pressure to leave cyclopentadienone **16** as a red solid (52.5 mg, 78%).

m. p. 155-157 °C.

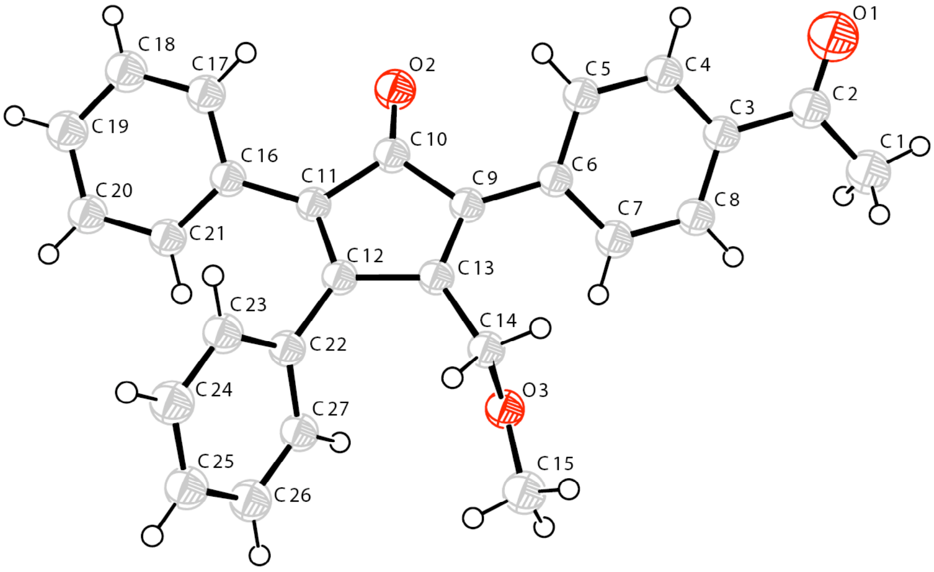
R$_f$: 0.52 in 3:2, pentane: ether (appears red in visible light).

^{1}HNMR (CDCl$_3$, 500 MHz): δ: 8.04-8.00 (m, 2H), 7.68-7.63 (m, 2H), 7.57-7.01 (m, 10H), 4.07 (s, 2H), 3.27 (s, 3H), 2.59 (s, 3H).

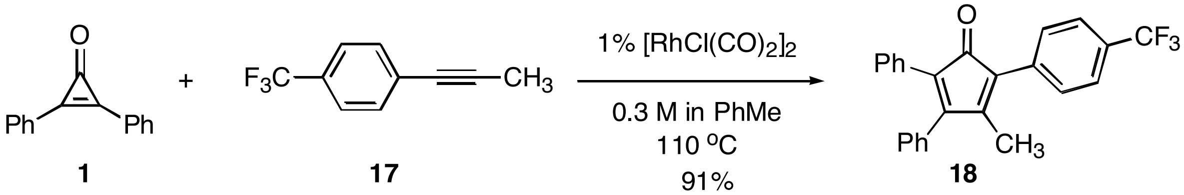
^{13}CNMR (CDCl$_3$, 50 MHz): δ: 200.0, 197.7, 155.3, 152.0, 136.3, 135.2, 133.1, 130.5, 130.4, 129.9 (2C), 129.8 (2C), 128.7 (2C), 128.5 (2C), 128.3 (2C), 128.1 (2C), 125.9, 125.3, 116.3, 65.5, 58.6, 26.6.

FTIR (thin film): 3407 (w), 3351 (w), 3058 (m), 2925 (m), 1738 (s), 1713 (s), 1682 (s), 1601 (m), 1485 (w), 1446 (m), 1356 (m), 1265 (m), 1170 (m), 1091 (m), 977 (m), 948 (m), 911 (m), 858 (m), 848 (m), 758 (m), 732 (m), 692 (m) cm^{-1}.

HRMS for $C_{27}H_{22}O_3$ calc'd: 394.1569 g/mol, found 394.1582 g/mol.



ORTEP diagram of **16**. Ellipsoids drawn at the 50% probability level.



Cyclopentadienone **18**:

4-Propynyltrifluoromethylbenzene[6] (**17**, 13.7 mg, 74.4 μmol), diphenylcyclopropenone (**1**, 23.1 mg, 112 μmol), and $[RhCl(CO)_2]_2$ (0.744 μmol, 0.5 mg) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (Solvtek™, 410 μL). The tube was capped with a septum and heated in an oil bath for 6.5 hours at 110 °C under nitrogen. The resulting solution was purified by flash column chromatography eluting with 10% diethyl ether/petroleum ether. Product-containing fractions were concentrated under reduced pressure to leave cyclopentadienone **18** as a red solid (26.3 mg, 91%).

m. p. 134-136 °C.

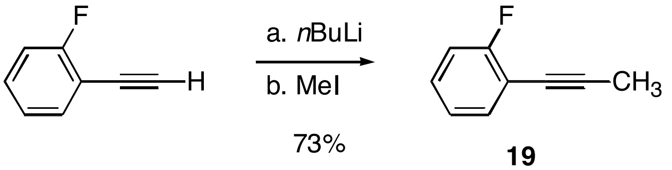
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, J = 8.1 Hz, 2H), 7.57 (d, J = 8.1 Hz, 2H), 7.43-7.41 (m, 3H), 7.31-7.29 (m, 2H), 7.26-7.21 (m, 5H), 2.13 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 199.8, 156.2, 154.2, 135.0 (q, J_{CF} = 1.5 Hz), 133.4, 130.4, 129.9 (2C), 129.8 (2C), 129.1 (q, J_{CF} = 32.8 Hz), 128.8 (m, 3C), 128.7, 128.6 (2C), 128.1, (2C), 127.6, 125.2 (q, J_{CF} = 3.8 Hz, 2C), 124.5, 124.2 (q, J_{CF} = 271.6 Hz), 14.7.

FTIR ($CDCl_3$ film): 3058 (m), 2926 (m), 2853 (w), 1713 (s), 1614 (s), 1485 (m), 1443 (m), 1408 (m), 1380 (m), 1324 (s), 1166 (s), 1121 (s), 1068 (s), 1018 (s), 993 (m), 945 (w), 915 (w), 842 (s), 794 (s), 774 (s), 738 (s), 702 (s) cm^{-1}.

HRMS for $C_{25}H_{17}F_3O$ calc'd: 390.1232 g/mol, found: 390.1229 g/mol.

Elemental Analysis for $C_{25}H_{17}F_3O$ calc'd: 76.91% C, 4.39% H, 14.60% F; found 76.41% C, 4.70% H, 14.50% F.



2-Propynylfluorobenzene (**19**):

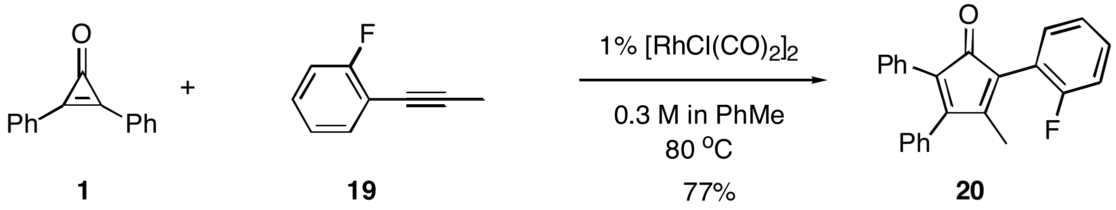
2-Ethynylfluorobenzene (120 mg, 1.00 mmol) was weighed out into a test tube with a stir bar under nitrogen and capped with a septum. Tetrahydrofuran (Solvtek^{TM}, 3.0 mL) was added and the solution was cooled to –78 °C. *n*-Butyllithium (2.5 M in hexanes, 800 μL, 2.00 mmol) was added and the reaction was stirred for 10 minutes. Iodomethane (710 mg, 312 μL, 5.00 mmol) was then added and the reaction was warmed to room temperature. Saturated aqueous sodium thiosulfate (10 mL) was added, and the organic layer was extracted. The aqueous layer was extracted once with 10 mL pentane, the combined organic layers were concentrated and purified by flash column chromatography eluting with pentane. Product-containing fractions were identified and concentrated under reduced pressure to yield 2-propynylfluorobenzene (**19**, 98.3 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41-7.37 (m, 1H), 7.27-7.22 (m, 1H), 7.08-7.02 (m, 2H), 2.10 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 162.8 (d, J_{CF} = 250.2 Hz), 133.5, 129.1 (d, J_{CF} = 7.6 Hz), 123.8 (d, J_{CF} = 3.8 Hz), 115.3 (d, J_{CF} = 21.4 Hz), 112.4 (d, J_{CF} = 16.0 Hz), 91.3 (d, J_{CF} 3.1 = Hz), 73.0, 4.6.

FTIR ($CDCl_3$ film): 2918 (m), 2849 (w), 2242 (w), 1575 (w), 1492 (s), 1446 (m), 1259 (m), 1216 (m), 1154 (w), 1102 (m), 1029 (m), 941 (w), 817 (m), 755 (s) cm^{-1}.

HRMS for C_9H_7F calc'd: 134.0528 g/mol, found: 134.0532 g/mol.



Cyclopentadienone **20**:

2-Propynylfluorobenzene (**19**, 46.3 mg, 345 μmol), diphenylcyclopropenone (**1**, 100 mg, 487 μmol), and $[RhCl(CO)_2]_2$ (3.45 μmol, 1.3 mg) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (Solvtek^{TM}, 975 μL). The tube was capped with a septum and heated in an oil bath for 20 hours at 80 °C under nitrogen. The resulting solution was purified by flash column chromatography eluting with 50 mL pentane followed by 100 mL 1% diethyl ether/pentane, 100 mL 2%, 100 mL 3%, and 50 mL 4%. Product-containing fractions were identified and concentrated under reduced pressure to leave cyclopentadienone **20** as a red solid (90.0 mg, 77%).

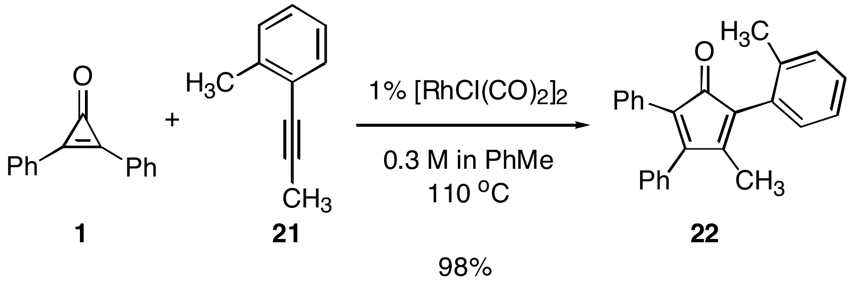
m. p. 133-135 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43-7.14 (m, 14H), 2.00 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ: 199.4, 160.3 (d, J_{CF} = 247.8 Hz), 157.4, 153.9, 133.5, 131.9 (d, J_{CF} = 3.0 Hz), 130.6, 129.9, 129.5 (d, J_{CF} = 8.1 Hz), 128.7 (2C), 128.6 (2C), 128.6, 128.0 (2C), 127.4, 125.4, 123.9 (d, J_{CF} = 3.0 Hz), 121.0, 119.1 (d, J_{CF} = 16.1 Hz, 2C), 115.8 (d, J_{CF} = 22.7 Hz), 15.1 (d, J_{CF} = 4.5 Hz).

FTIR ($CDCl_3$ film): 3058 (w), 2975 (w), 2865 (w), 1713 (s), 1574 (w), 1488 (s), 1443 (m), 1381 (m), 1347 (w), 1303 (m), 1261 (w), 1214 (m), 1118 (m), 1099 (m), 1073 (w), 1027 (w), 1000 (w), 993 (w), 913 (w), 824 (w), 793 (m), 755 (s), 741 (w), 696 (s) cm^{-1}.

HRMS for $C_{24}H_{17}FO$ calc'd: 340.1264 g/mol, found: 340.1260 g/mol.



Cyclopentadienone **22**:

Diphenylcyclopropenone (**1**, 87.9 mg, 426 μmol) and alkyne **21** (37 mg, 284 μmol) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (860 μL, Solvtek™) and $[RhCl(CO)_2]_2$ (1.0 mg, 2.5 μmol). The tube was capped with a septum and the reaction was heated at 110 °C for 5 hours under nitrogen. The crude reaction mixture was then cooled to room temperature and purified by flash column chromatography eluting with diethyl ether and pentane (1:19). Product-containing fractions were collected and concentrated under reduced pressure to give **22** as a purple solid (94 mg, 98% yield).

m. p. 50-53 °C.

$\mathbf{R_f}$: 0.52 in 24:1, pentane: ethyl acetate (appears red in visible light).

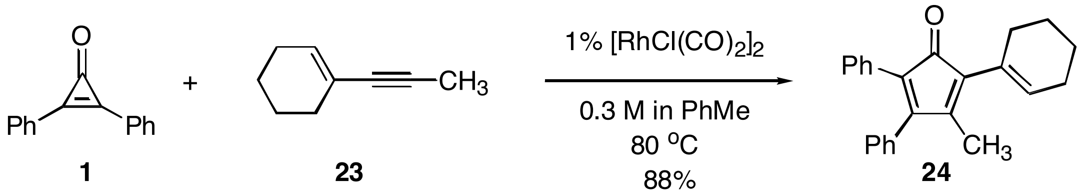
^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.42-7.34 (m, 2H), 7.32-7.12 (m, 11H), 6.94-6.91 (m, 1H), 2.27 (s, 3H), 1.88 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ: 200.2, 155.4, 153.6, 137.5, 133.7, 131.1, 130.7, 130.4, 130.2, 130.1, 129.8 (2C), 129.3, 128.6 (2C), 128.5, 128.0 (2C), 127.9 (2C), 127.3, 125.5, 124.9, 20.5, 14.5.

FTIR (thin film): 3056 (w), 3018 (w), 2923 (w), 1710 (s), 1486 (m), 1443 (m), 1380 (w), 1345 (w), 1301 (w), 990 (w), 910 (w), 795 (w), 747 (m), 738 (m), 696 (s) cm^{-1}.

HRMS for $C_{25}H_{20}O$ calc'd: 336.1514 g/mol, found 336.1510 g/mol.

Elemental Analysis for $C_{25}H_{20}O$ calc'd: 89.25% C; 5.99% H; 4.76% O; found 89.04% C; 6.10% H.



Cyclopentadienone **24**:

1-propynylcyclohexene[7] (**23**, 35.0 mg, 291 μmol), diphenylcyclopropenone (**1**, 90.1 mg, 437 μmol), and $[RhCl(CO)_2]_2$ (1.1 mg, 2.9 μmol) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (Solvtek™, 874 μL). The tube was capped with a septum and heated in an oil bath for 3 hours at 80 °C under nitrogen. The resulting solution was purified by flash column chromatography eluting with 100 mL petroleum ether followed by 200 mL 5% diethyl ether/petroleum ether. Product-containing fractions were collected and concentrated under reduced pressure to leave cyclopentadienone **24** as a red solid (83.7 mg, 88%).

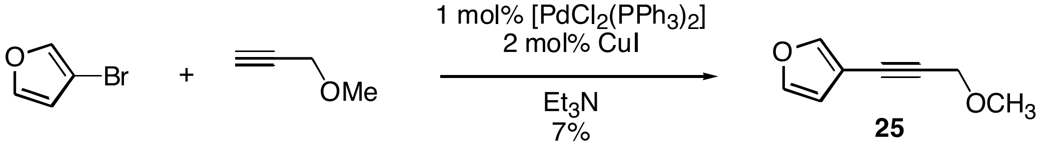
m. p. 85-88 °C.

^{1}**H NMR** (500 MHz, CDCl$_3$) δ: 7.40-7.37 (m, 3H), 7.26-7.24 (m, 2H), 7.20-7.17 (m, 5H), 5.82 (dd, J_1 = 3.8 Hz, J_2 = 2.0 Hz, 1H), 2.34-2.31 (m, 2H), 2.24-2.22 (m, 2H), 1.98 (s, 3H), 1.77-1.74 (m, 2H), 1.73-1.68 (m, 2H); assigned by COSY.

^{13}**C NMR** (CDCl$_3$, 125 MHz) δ: 201.4, 154.6, 151.7, 134.1, 130.9, 129.8, 129.7 (2C), 129.7, 128.6 (2C), 128.6 (2C), 128.5, 128.3, 127.9 (2C), 127.0, 124.3, 28.2, 25.7, 22.8, 22.0, 14.5.

FTIR (CDCl$_3$ film): 3055 (w), 3029 (w), 2930 (m), 2856 (w), 1709 (m), 1597 (w), 1484 (w), 1442 (m), 1380 (m), 1347 (m), 1288 (m), 1264 (w), 1157 (w), 1136 (w), 1101 (m), 1072 (w), 1000 (w), 911 (m), 855 (w), 790 (m), 768 (m), 733 (m), 715 (m), 699 (s) cm^{-1}.

HRMS for $C_{24}H_{22}O$ calc'd: 326.1671 g/mol, found: 326.1673 g/mol.



3-(3-Methoxypropynyl)furan (**25**):

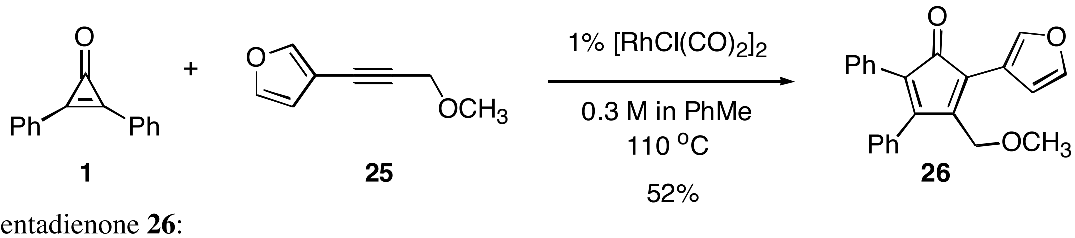
3-Bromofuran (2.21 g, 15.0 mmol) was weighed out in an oven-dried 50 mL round bottom flask with a stir bar. Triethylamine (5 mL), methyl propargyl ether (1.58 g, 22.5 mmol, 1.90 mL), copper(I) iodide (57.2 mg, 0.300 mmol), and bistriphenylphosphinopalladium(II) dichloride (106 mg, 300 mmol) were then added and the flask was flushed with nitrogen. The suspension was stirred for 2 days at 50 °C under nitrogen and then poured over 20 mL saturated ammonium chloride and 10 mL diethyl ether. The organic layer was extracted and the aqueous layer was extracted with ether (2 x 10 mL). Combined organic fractions were dried over sodium sulfate and filtered through fluorosil. The resulting solution was concentrated by rotary evaporation and then purified by flash column chromatography eluting with 200 mL pentane, 200 mL 5% diethyl ether/pentane, followed by 100 mL 10% diethyl ether/pentane. Product-containing fractions were identified and concentrated to yield furan **25** (149 mg, 7%).

^{1}**H NMR** (500 MHz, CDCl$_3$) δ: 7.62 (m, 1H), 7.36 (dd, $J_1 = J_2$ = 1.7 Hz, 1H), 6.44 (dd, J_1 = 1.9 Hz, J_2 = 0.8 Hz, 1H), 4.28 (s, 2H), 3.43 (s, 3H).

^{13}**C NMR** (CDCl$_3$, 125 MHz) δ: 145.9, 142.8, 112.5, 107.0, 86.8, 77.6, 60.4, 57.7.

FTIR (CDCl$_3$ film): 3147 (w), 2929 (m), 2822 (w), 2233 (w), 1450 (w), 1357 (m), 1286 (w), 1187 (w), 1163 (m), 1100 (s), 1031 (m), 1006 (m), 871 (m), 792 (m) cm^{-1}.

HRMS for $C_8H_8O_2$ calc'd: 136.054230 g/mol, found: 136.052513 g/mol.



Cyclopentadienone **26**:

Furan (**25**, 27.1 mg, 199 μmol), diphenylcyclopropenone (**1**, 61.5 mg, 299 μmol), and $[RhCl(CO)_2]_2$ (2.0 μmol, 0.8 mg) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (Solvtek^{TM}, 600 μL). The tube was capped with a septum and heated in an oil bath for 17.5 hours at 110 °C under nitrogen. The resulting solution was purified twice by flash column chromatography eluting with 5% diethyl ether/ petroleum ether. Product-containing fractions were identified and concentrated under reduced pressure to leave cyclopentadienone **26** as a purple solid (35.4 mg, 52%).

m. p. 128-131 °C.

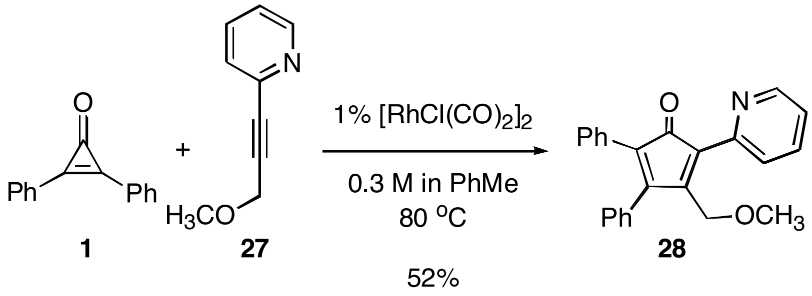
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.99-7.98 (m, 1H), 7.49 (m, 1H), 7.40-7.35 (m, 5H), 7.22-7.17 (m, 5H), 6.80-6.79 (m, 1H), 4.14 (s, 2H), 3.37 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ: 200.5, 156.5, 146.7, 143.2, 143.1, 133.3, 130.7, 129.7 (2C), 128.9, 128.7 (2C), 128.4 (2C), 128.0 (2C), 127.3, 124.8, 122.2, 115.7, 110.0, 65.3, 58.5.

FTIR ($CDCl_3$ film): 2923 (m), 1713 (s), 1443 (m), 1346 (w), 1306 (w), 1159 (m), 1126 (m), 1089 (m), 1025 (w), 945 (m), 871 (m), 803 (m), 777 (w), 730 (m), 695 (m) cm^{-1}.

HRMS for $C_{23}H_{18}O_3$ calc'd: 342.125595 g/mol, found: 342.126090 g/mol.

Elemental Analysis for $C_{23}H_{18}O_3$ calc'd: 80.68% C, 5.30% H, 14.02% O; found 80.79% C, 5.52% H.



1 **27** **28**

Cyclopentadienone **28**:

Diphenylcyclopropenone (**1**, 70.8 mg, 345 μmol) and alkyne **27**^{8} (33.7 mg, 229 μmol) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (Solvtek^{TM}, 690 μL) and $[RhCl(CO)_2]_2$ (1.0 mg, 2.5 μmol). The tube was capped with a septum and then heated at 80 °C for 20 hours under nitrogen. The crude reaction mixture was then cooled to room temperature and purified by flash column chromatography eluting with diethyl ether and pentane (2:3). Product-containing fractions were collected and concentrated under reduced pressure to give **28** as a yellow solid (42 mg, 52% yield).

m. p. 81-83 °C.

R_f: 0.39 in 3:2, pentane: ethyl acetate (appears yellow in visible light).

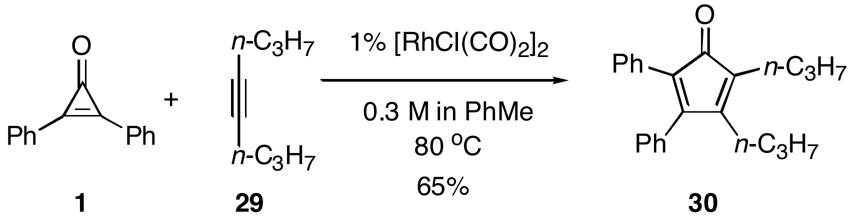
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.52-7.42 (m, 3H), 7.39-7.34 (m, 2H), 7.19-7.11 (m, 5H), 6.37 (dq, J = 7.2 Hz, J = 0.6 Hz, 1H), 6.08 (qd, J = 4.8 Hz, J = 0.5 Hz, 1H), 6.03 (dt, J = 8.8 Hz, J = 1.3 Hz, 1H), 5.44 (qd, J = 4.1 Hz, J = 1.5 Hz, 1H), 4.17 (d, J = 16 Hz, 1H), 4.12 (d, J = 16 Hz, 1H), 3.35 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 194.6, 169.1, 130.6, 130.2, 129.0 (2C), 128.7 (2C), 128.5, 127.8 (2C), 126.2 (2C), 123.8, 123.6, 119.9, 110.2, 108.9, 82.4, 81.4, 77.2, 62.5, 59.9, 57.5.

FTIR (thin film): 3369 (w), 3055 (w), 2929 (w), 2360 (m), 2341 (m), 1845 (w), 1685 (s), 1602 (m), 1581 (m), 1543 (s), 1448 (m), 1419 (m), 1358 (m), 1323 (m), 1098 (s), 1009 (m), 756 (m), 697 (m) cm^{-1}.

HRMS for $C_{24}H_{19}NO_2$ calc'd: 353.1416 g/mol, found 353.1400 g/mol.

Elemental Analysis for $C_{24}H_{19}NO_2$ calc'd: 81.56% C, 5.42% H, 3.96 %N; found 81.51% C, 5.10% H, 3.83 %N.



Cyclopentadienone **30**:

Diphenylcyclopropenone (**1**, 53.0 mg, 256 μmol), 4-octyne (**29**, 18.8 mg, 170 μmol), and $[RhCl(CO)_2]_2$ (1.0 mg, 2.3 μmol) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (Solvtek™, 600 μL). The reaction was capped with a septum and heated at 80 °C for 7.5 hours under nitrogen. The crude reaction mixture was then cooled to room temperature and purified by flash column chromatography using ether and pentane (1:30). Product-containing fractions were collected and concentrated under reduced pressure to give **30** as an orange-red oil (34.8 mg, 65% yield).

R_f: 0.37 in pentane: ether, 49:1 (appears orange in visible light).

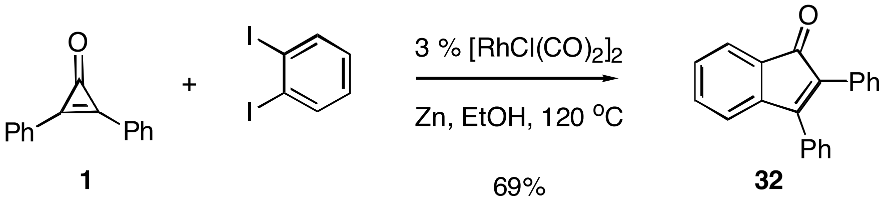
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.40-7.31 (m, 3H), 7.23-7.10 (m, 7H), 2.33 (t, J = 8.0 Hz, 2H), 2.23 (t, J = 8.4 Hz, 2H), 1.52 (m, 2H), 1.15 (m, 2H), 0.97 (t, J =7.6 Hz, 3H), 0.78 (t, J = 7.2 Hz. 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 202.6, 156.4, 154.1, 134.6, 131.0, 129.7 (2C), 128.6 (2C), 128.2, 128.1 (2C), 127.8 (2C), 126.9, 126.5, 124.7, 28.5, 25.9, 22.9, 21.6, 14.3, 14.1.

FTIR (thin film): 3396 (w), 3056 (m), 2960 (m), 2931 (m), 2870 (m), 1949 (w), 1881 (w), 1805 (w), 1707 (s), 1600 (m), 1573 (w), 1498 (m), 1463 (m), 1443 (m), 1357 (w), 1339 (w), 1307 (w), 1090 (m), 1071 (m), 1027 (w), 970 (w), 914 (w), 756 (m), 691 (m) cm^{-1}.

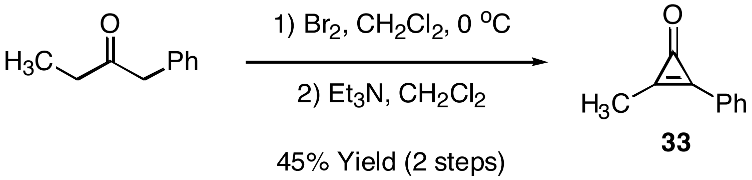
HRMS Calculated for $C_{23}H_{24}NaO^+$ $(M+Na)^+$: 339.1725, found: 339.1731.

Elemental Analysis for $C_{23}H_{24}O$ calc'd: 87.30% C, 7.64% H; found 87.34% C, 7.49% H.



2,3-Diphenyl-1-indenone[9] (**32**):

Diphenylcyclopropenone (**1**, 206 mg, 1.0 mmol), 1,2-diiodobenzene (165 mg, 0.5 mmol), and activated zinc[10] (36 mg, 0.55 mmol) were added to an oven dried borosilicate vial with stir bar. $[RhCl(CO)_2]_2$ (6.0 mg, 1.5 μmol) and ethanol (300 μL) were then added. The vial was flushed with argon, sealed tightly and heated at 120 °C for 3.5 hours before cooling back to room temperature. Ethanol was removed by blowing nitrogen into the vial. The reaction was purified by flash column chromatography eluting with ethyl acetate and pentane (1:20). Product-containing fractions were collected and concentrated under reduced pressure to give **32** as a red solid (97 mg, 69%). **32** prepared in this manner was identical (^{1}H NMR) to commercially available **32** (Aldrich®).



Methylphenylcyclopropenone[11] (**33**):

1-phenyl-2-butanone (1.32 g, 8.9 mmol) and dichloromethane (18 mL, 0.5 M) were added to an oven-dried flask with a stir bar under nitrogen. The solution was cooled to 0 °C and bromine (3.56 g, 22.3 mmol) was added dropwise via syringe over 30 minutes. After addition was completed the reaction was stirred at room temperature for another 30 minutes. The reaction was poured into a separatory funnel containing 20 mL sat. aq. $Na_2S_2O_3$. The layers were separated and the aqueous layer was extracted with ether (2 x 15 mL). The combined organics were washed with sat. aq. $NaHCO_3$ (20 mL) and brine (20 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. The yellowish oil was dissolved in dichloromethane (18 mL) and triethylamine (9 mL) and stirred at room temperature for 8 hours under nitrogen. The reaction was then diluted with ether (100 mL). The organics were washed with sat. aq. $CuSO_4$ and brine (100 mL each), dried over sodium sulfate, filtered, and concentrated in vacuo. Further purification was accomplished by flash column chromatography eluting with ether. Product-containing fractions were concentrated to give light-brown solid **33** (572 mg, 45%).

m. p. 66-68 °C.

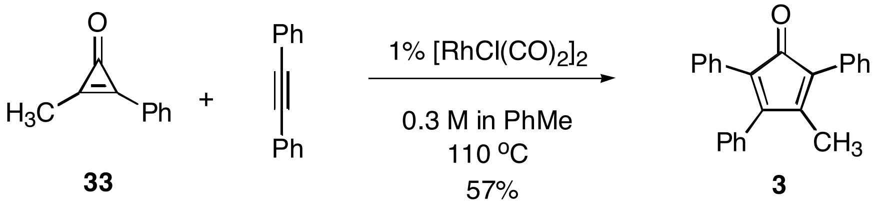
R$_f$: 0.25 in ether (uv).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.78-7.72 (m, 2H), 7.58-7.48 (m, 3H), 2.47 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 155.9, 154.0, 151.2, 131.9, 130.3 (2C), 128.6 (2C), 123.1, 10.9.

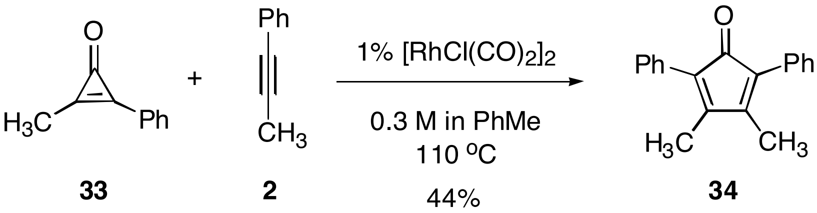
FTIR (thin film): 3467 (b), 3059 (w), 2960 (w), 2922 (w), 1856 (s), 1626 (s), 1448 (m), 1333 (w), 1021 (w), 770 (m), 692 (m), 678 (w) cm^{-1}.

HRMS for $C_{10}H_8NaO^+$ $(M+Na)^+$ cac'd: 167.0473, found: 167.0467.



Cyclopentadienone **3**:

Methylphenylcyclopropenone (**33**, 220 μmol, 31.7 mg), diphenylacetylene (35.7 mg, 200 μmol and $[RhCl(CO)_2]_2$ (1 mg, 2.6 μmol) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (Solvtek^{TM}, 540 μL). The tube was capped with a septum and heated at 110 °C for 17.5 hours under nitrogen. The resulting solution was purified by flash column chromatography eluting with 100 mL petroleum ether followed by 150 mL 5% diethyl ether/petroleum ether. Product-containing fractions were concentrated under reduced pressure to leave cyclopentadienone **3** as a deep purple solid (36.6 mg, 57%). **3** prepared in this manner is identical (^{1}H NMR) to **3** prepared in the manner described on page S2.



Cyclopentadienone **34**:

Methylphenylcyclopropenone (**33**, 31.7 mg, 220 μmol), 1-phenyl-1-propyne (**2**, 23.2 mg, 200 μmol), and $[RhCl(CO)_2]_2$ (1.0 mg, 2.6 μmol) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (Solvtek^{TM}, 440 μL). The tube was capped with a septum and heated at 110 °C for 7.5 hours under nitrogen. The crude reaction mixture was then cooled to room temperature and purified by flash column chromatography eluting with ethyl acetate and pentane (1:24). Product fractions were collected and concentrated under reduced pressure to give **34** as a red solid (23 mg, 44% yield).

mp: 131-133 °C.

R$_f$: 0.50 in pentane: ether, 19:1 (appears red-orange in visible light).

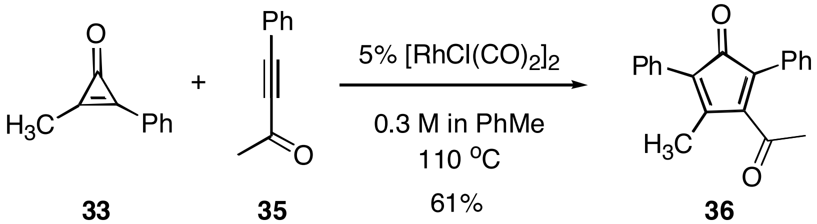
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.44-7.35 (m, 8H), 7.33-7.28 (m, 2H), 2.23 (s, 6H).

^{13}C NMR ($CDCl_3$, 50 MHz) δ: 200.5, 153.2 (2C), 131.3 (2C), 129.5 (4C), 128.2 (4C), 127.2 (2C), 125.0 (2C), 13.0 (2C).

FTIR (thin film): 3398 (w), 3047 (w), 2951 (w), 2920 (w), 2360 (w), 2342 (w), 1956 (w), 1892 (w), 1855 (w), 1703 (s), 1442 (m), 1377 (m), 1297 (m), 1275 (w), 1081 (w), 977 (w), 922 (w), 846 (w), 795 (m), 740 (m), 701 (s) cm^{-1}.

HRMS for $C_{19}H_{16}O$ calc'd: 260.1201 g/mol, found 260.1192 g/mol.

Elemental Analysis for $C_{19}H_{16}O$ calc'd: 87.66% C, 6.19% H; found 87.34% C, 6.07% H.



Cyclopentadienone **36**:

Methylphenylcyclopropenone (**33**, 19.9 mg, 138 μmol), 4-phenyl-but-3-yn-2-one (**35**, 15.3 mg, 106 μmol), and $[RhCl(CO)_2]_2$ (2.1 mg, 5.4 μmol) were weighed out into a test tube with stir bar under nitrogen. To this was added toluene (Solvtek^{TM}, 600 μL). The tube was capped with a septum and heated at 110 °C for 5 hours under nitrogen. The crude reaction mixture was then cooled to room temperature and purified by flash column chromatography eluting with ethyl acetate and pentane (1:24). Product fractions were collected and concentrated under reduced pressure to give **36** as a red oil (18.6 mg, 61% yield).

R$_f$: 0.33 in 9:1, pentane: ether (appears red in visible light).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.47-7.31 (m, 10H), 2.24 (s, 3H), 2.23 (s, 3H).

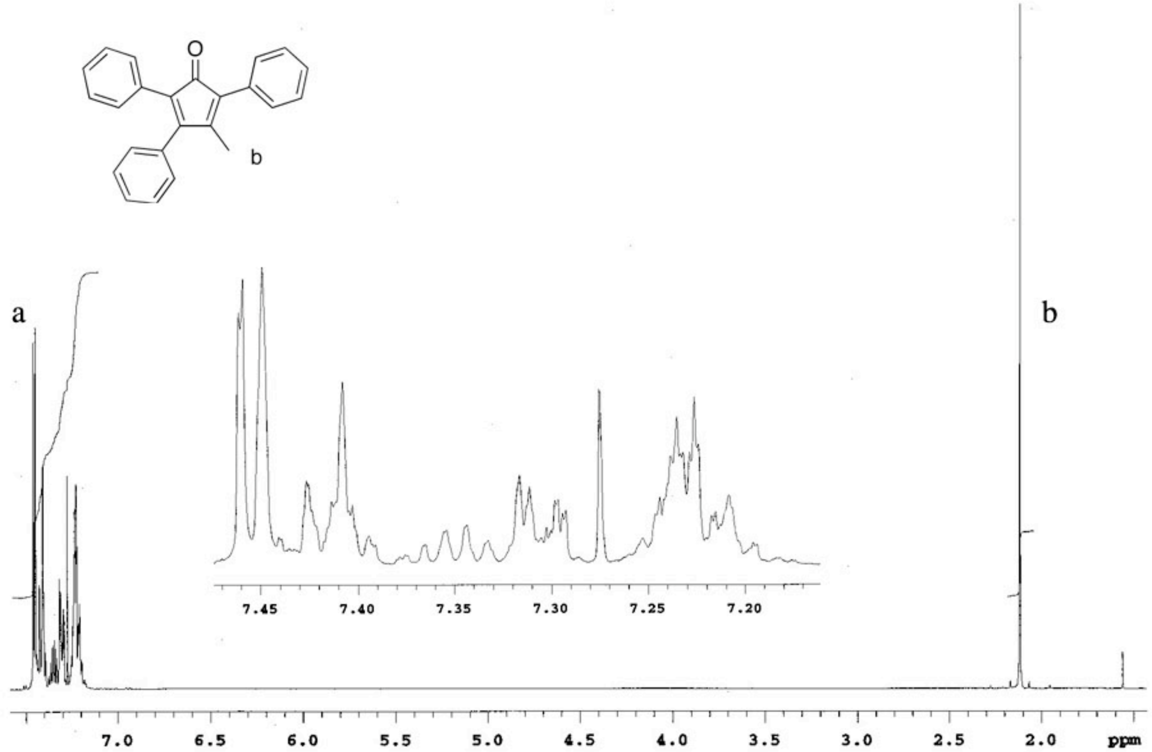
^{13}C NMR ($CDCl_3$, 100 MHz) δ: 202.1, 199.8, 154.2, 149.6, 130.5, 129.54 (2C), 129.52 (2C), 129.3, 128.6 (2C), 128.3 (2C), 128.1, 127.7, 125.9, 77.2, 30.9, 14.3.

FTIR (thin film): 3055 (w), 2920 (w), 1717 (s), 1684 (s), 1492 (m), 1443 (m), 1380 (m), 1358 (m), 1298 (w), 1175 (m), 1112 (m), 1077 (w), 1025 (w), 974 (w), 933 (w), 796 (m), 755 (w), 739 (m), 697 (m) cm^{-1}.

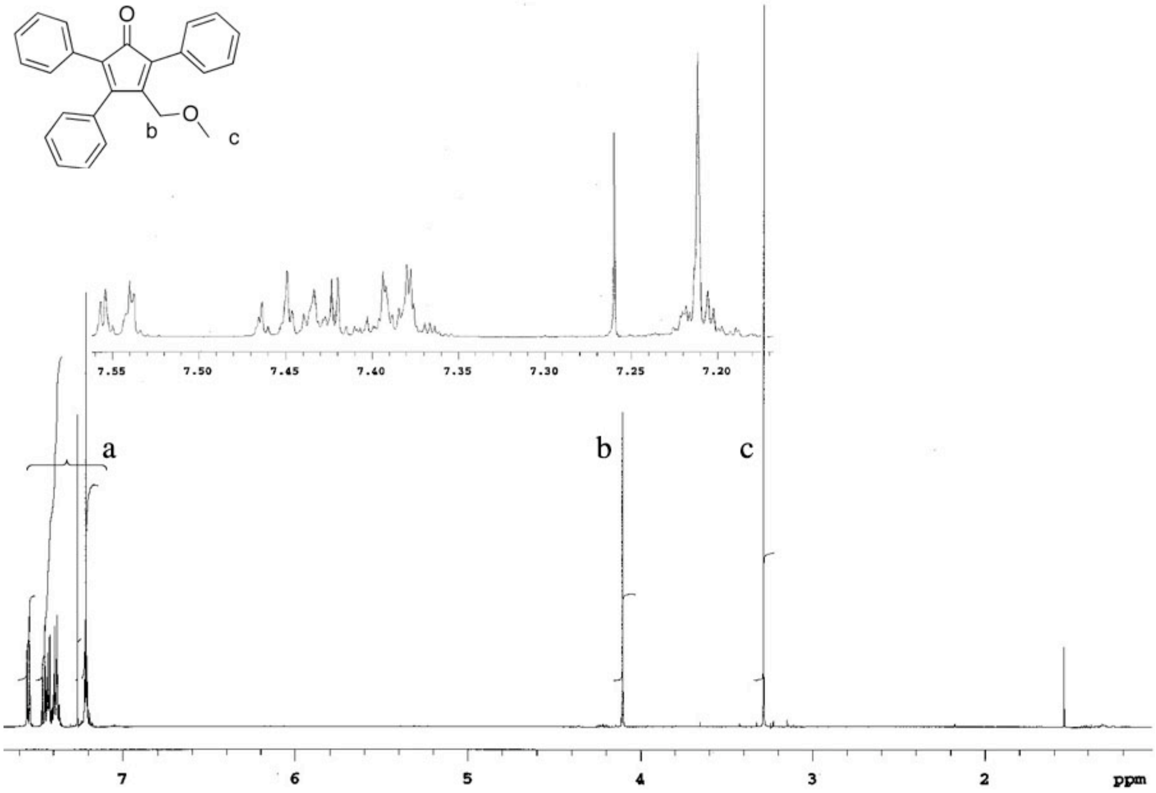
HRMS for $C_{20}H_{16}O_2$ calc'd: 288.1150 g/mol, found 288.1144 g/mol.

III. Selected ^{1}H NMR Spectra for New Compounds.

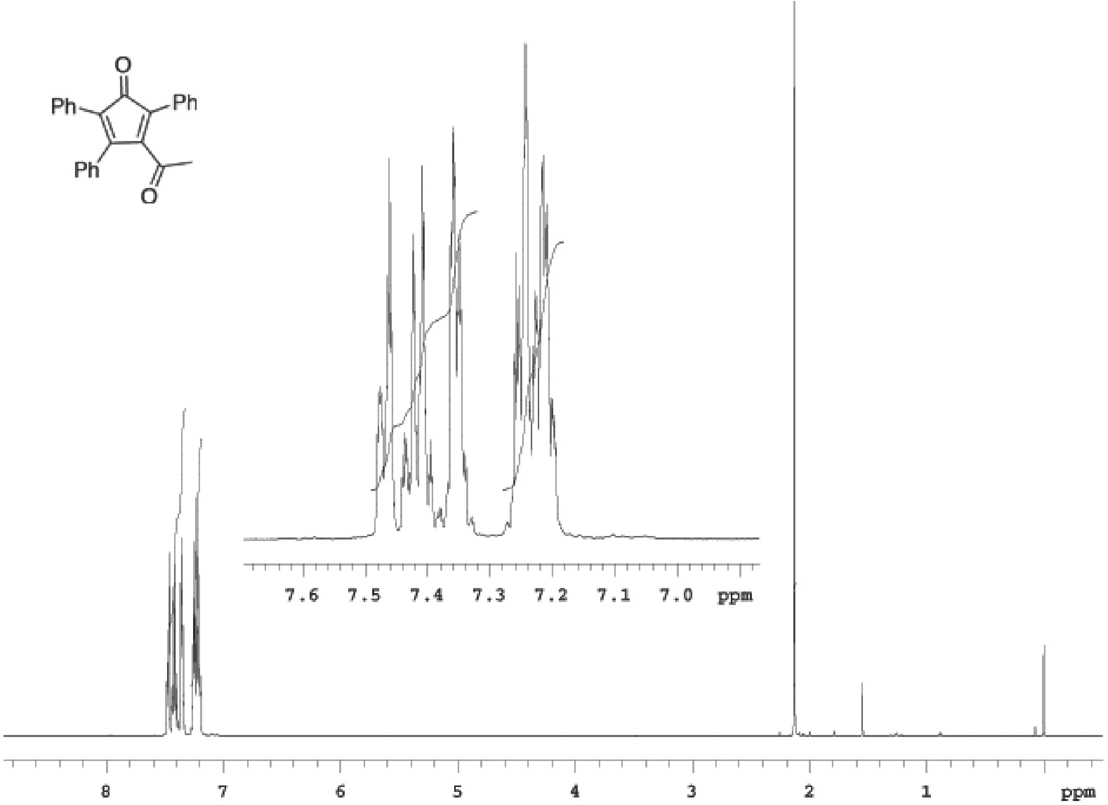
Cyclopentadienone **3**:



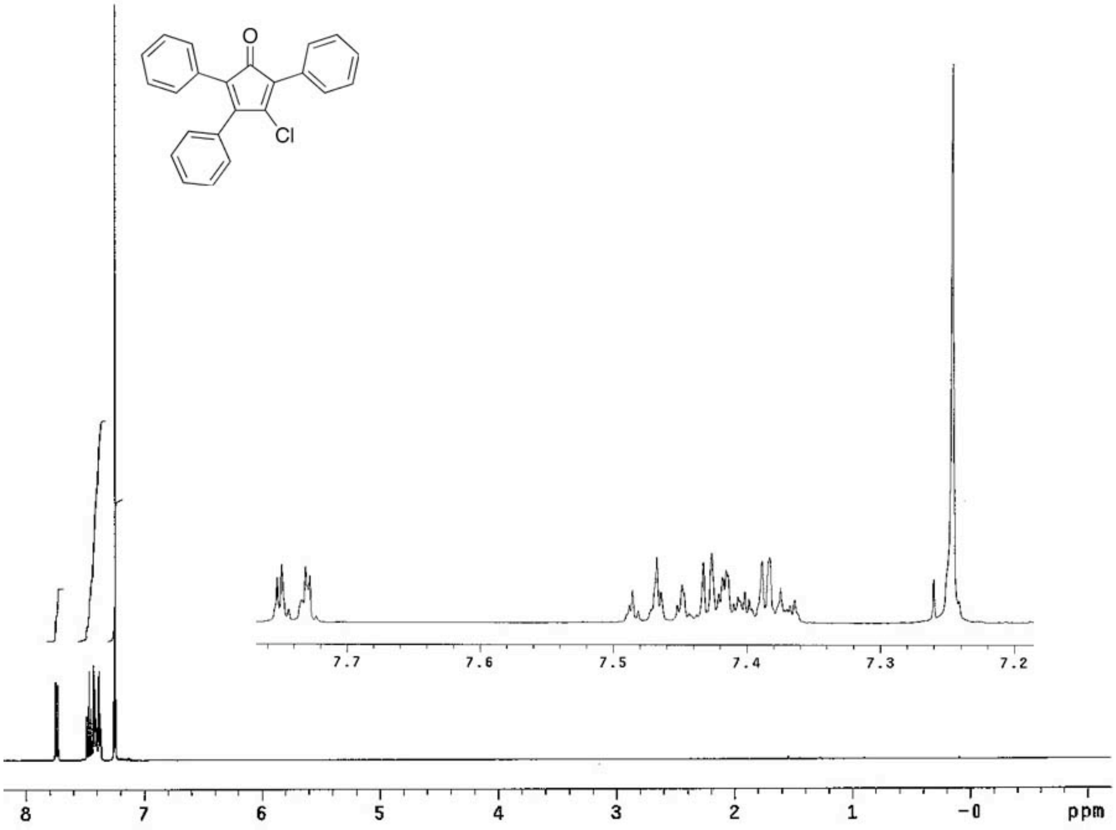
Cyclopentadienone **4**:



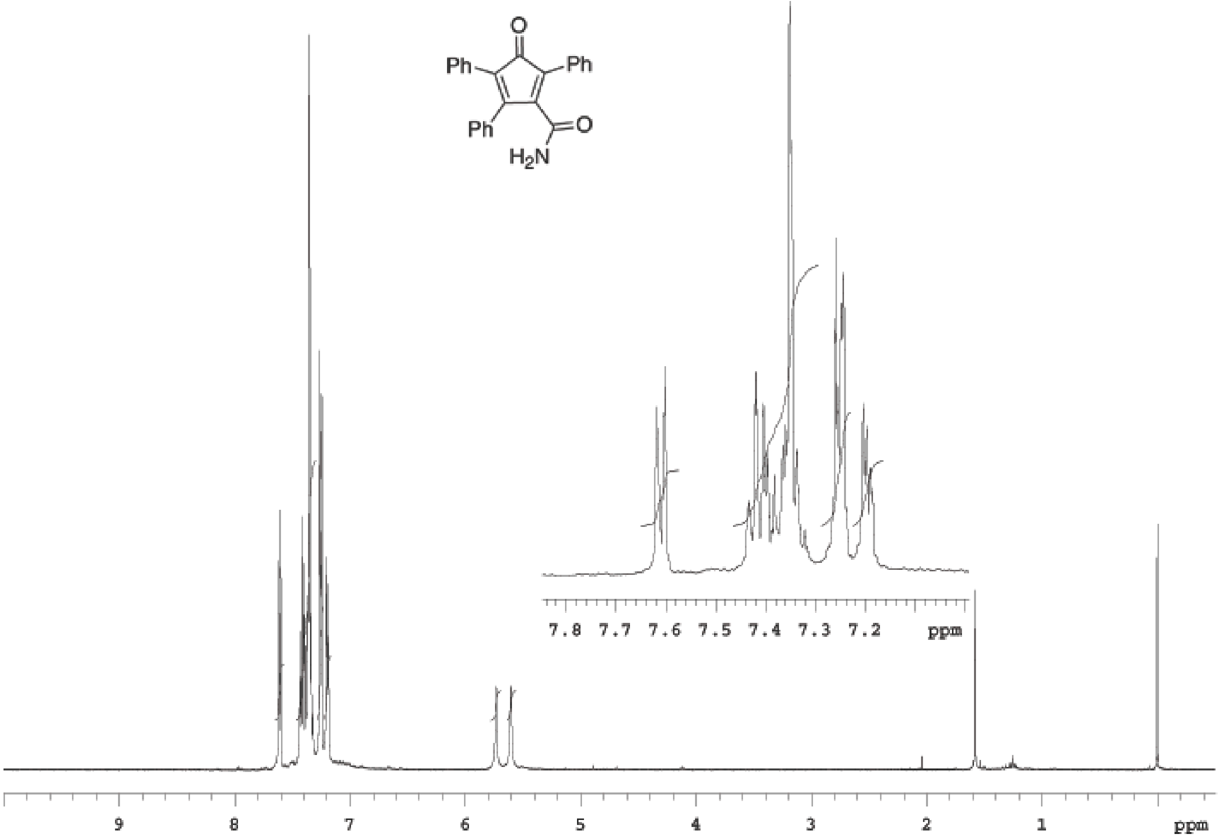
Cyclopentadienone **5**:



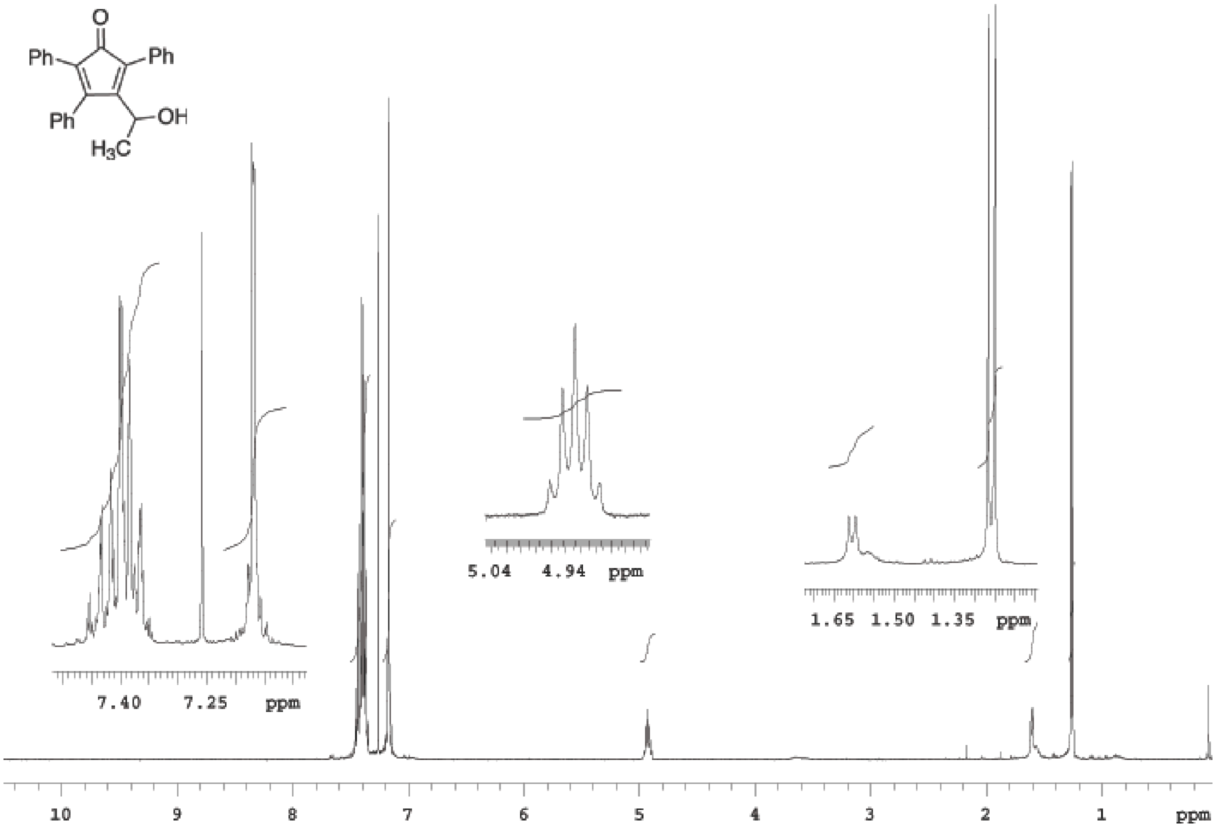
Cyclopentadienone **6**:



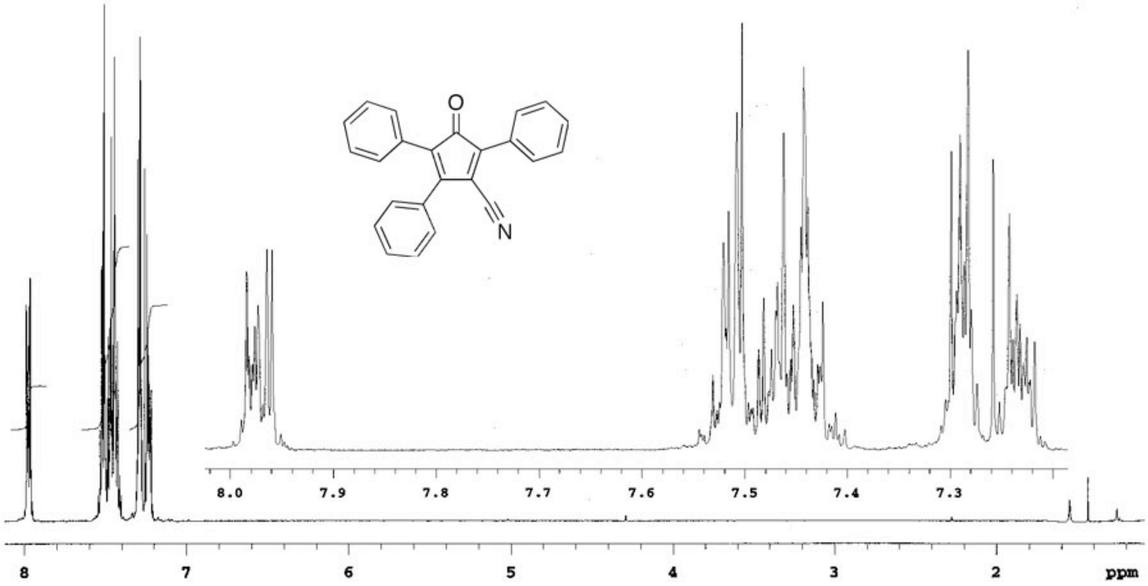
Cyclopentadienone **7**:



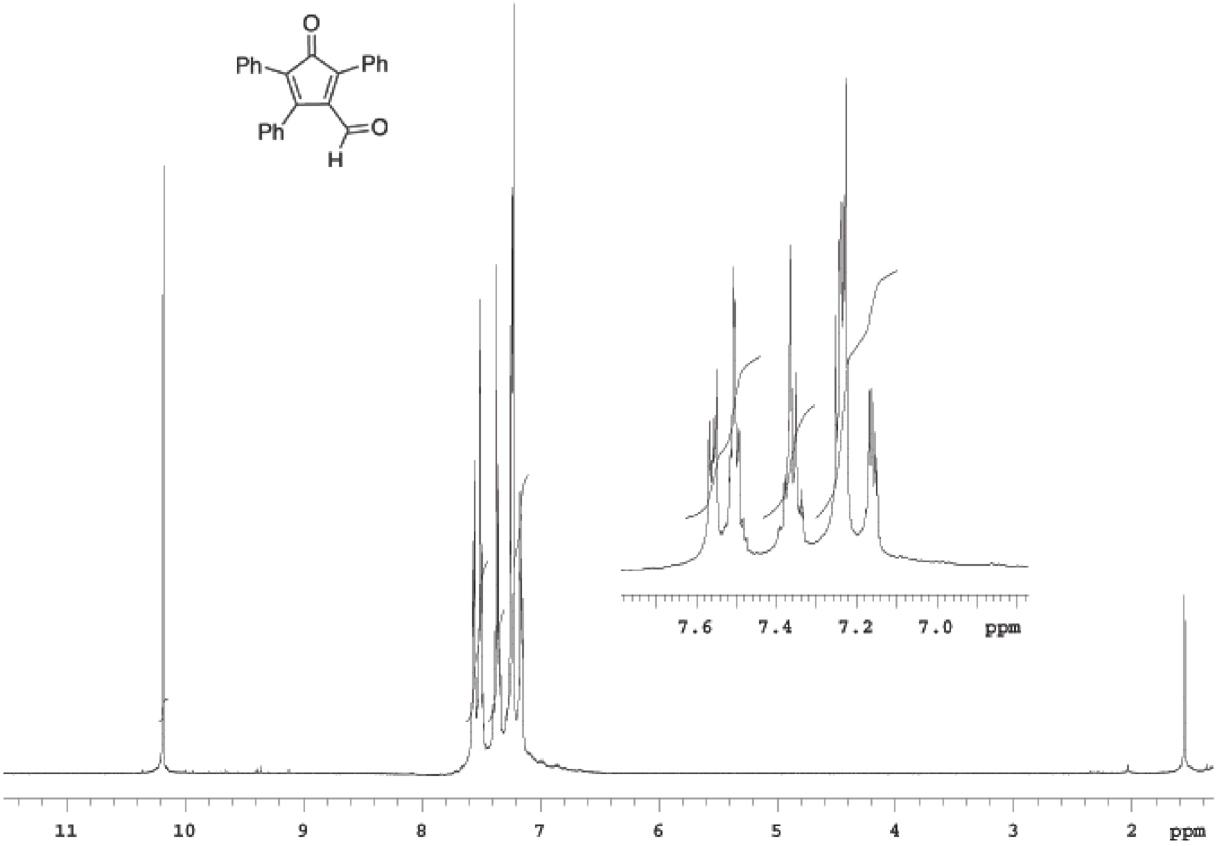
Cyclopentadienone **8**:



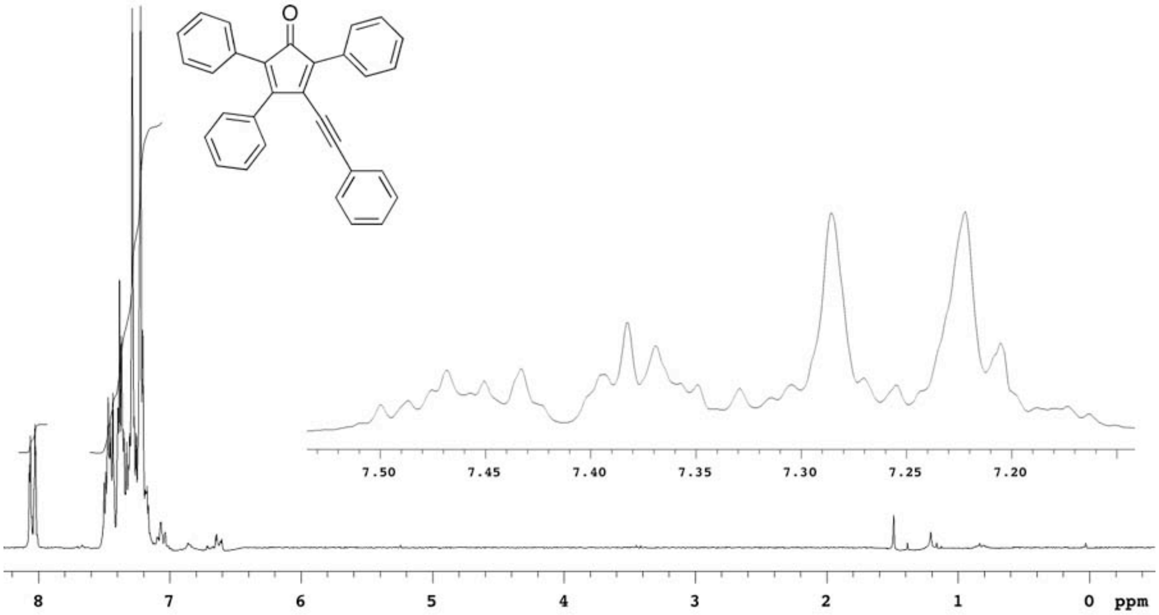
Cyclopentadienone **9**:



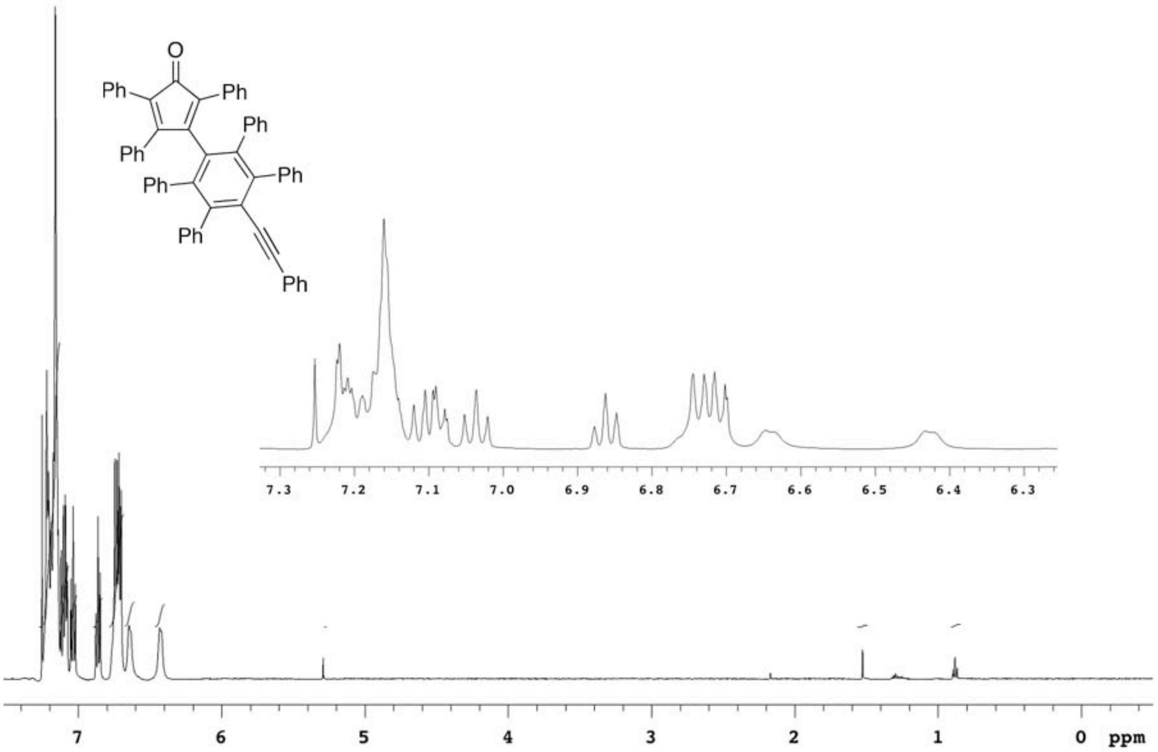
Cyclopentadienone **10**:



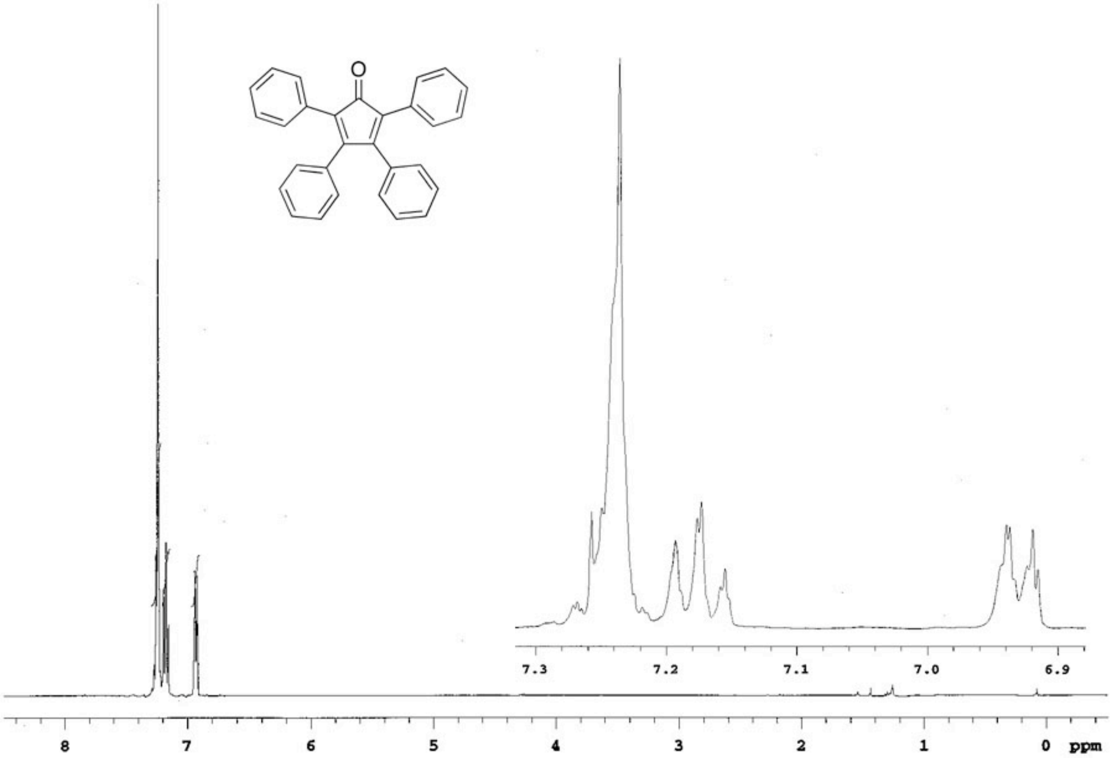
Cyclopentadienone **11**:



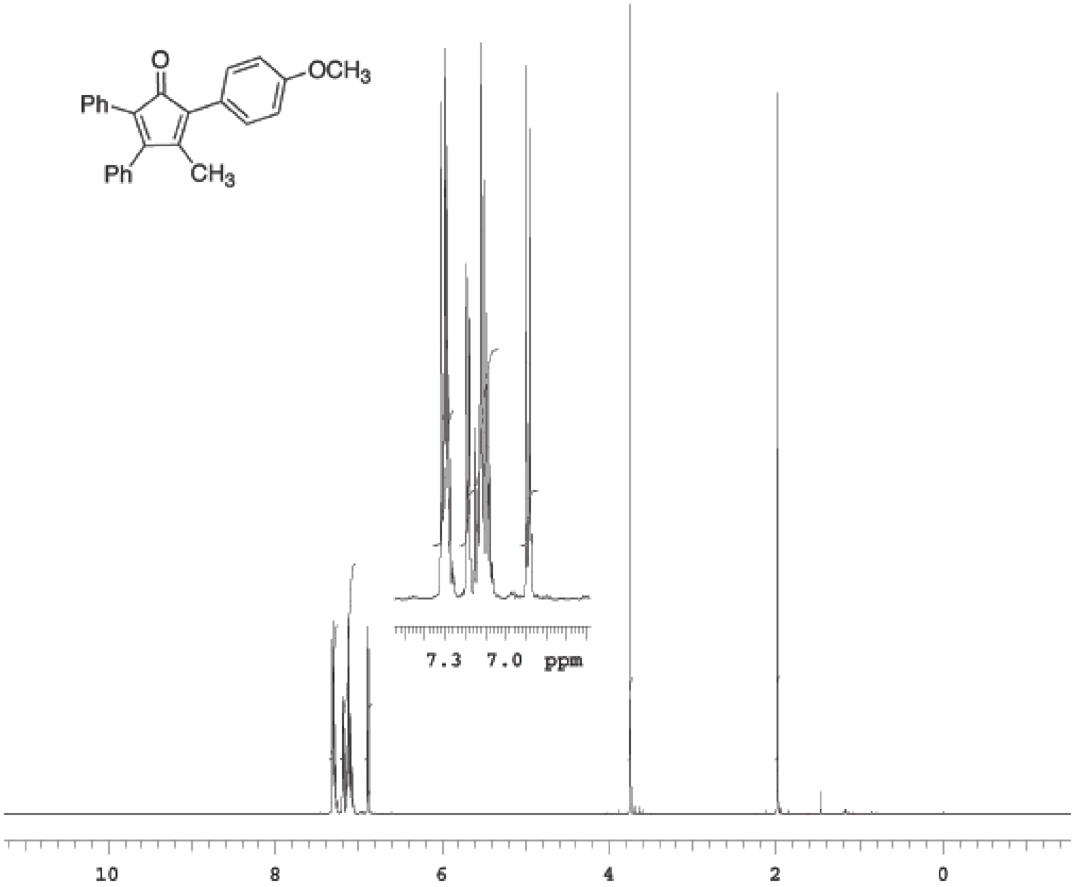
Cyclopentadienone **11a**:



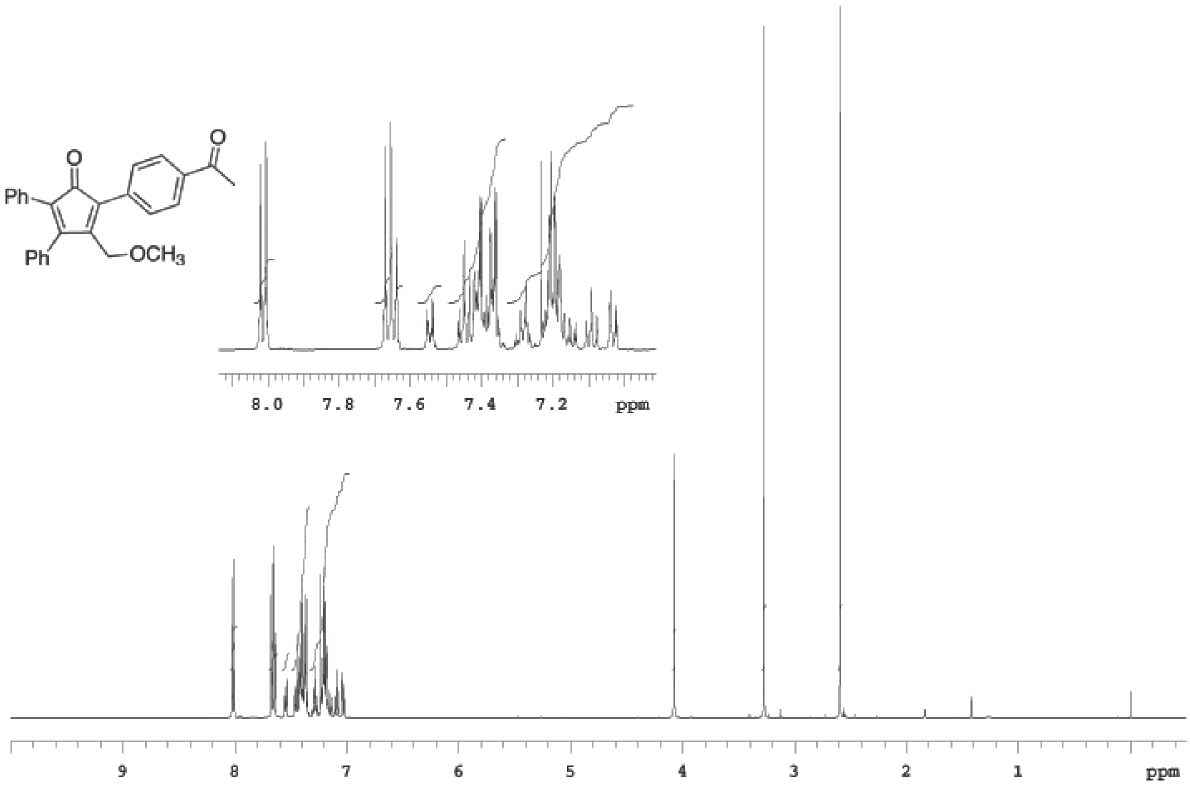
Cyclopentadienone **12**:



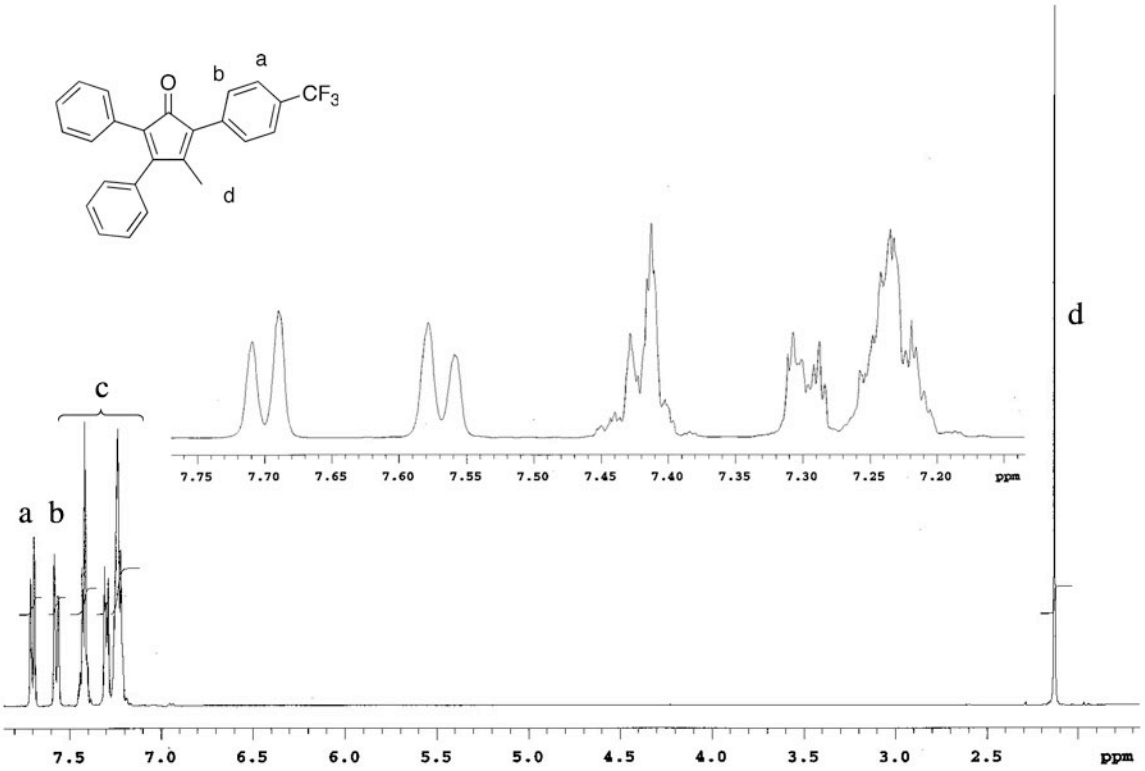
Cyclopentadienone **14**:



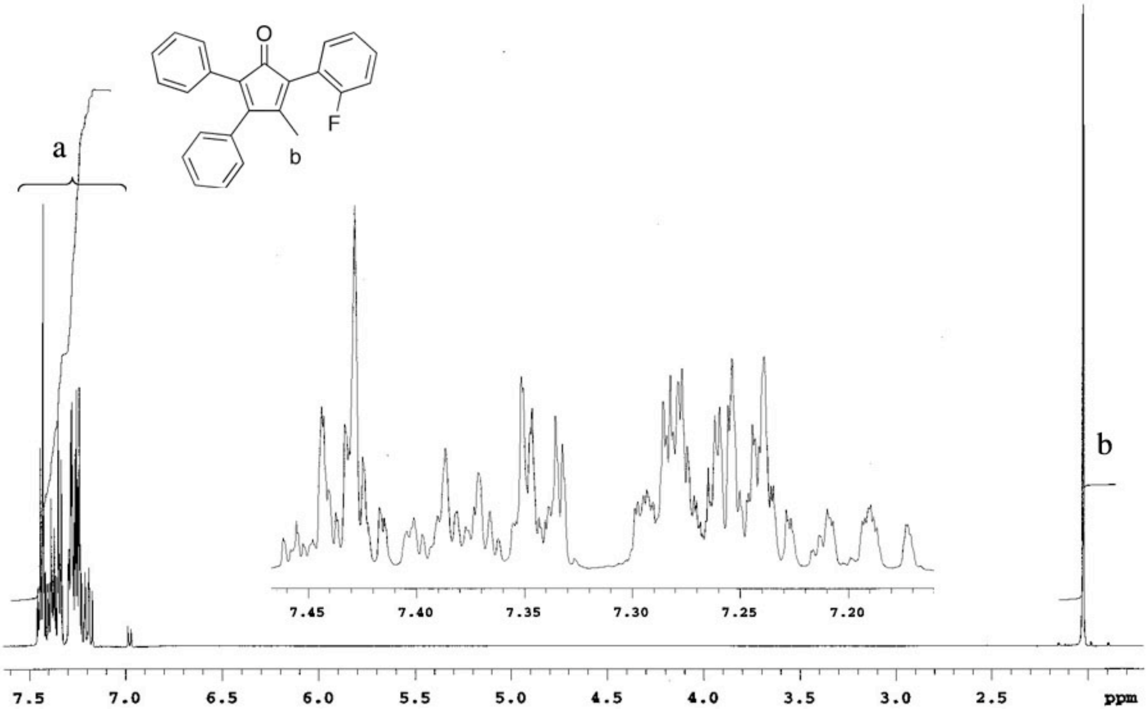
Cyclopentadienone **16**:



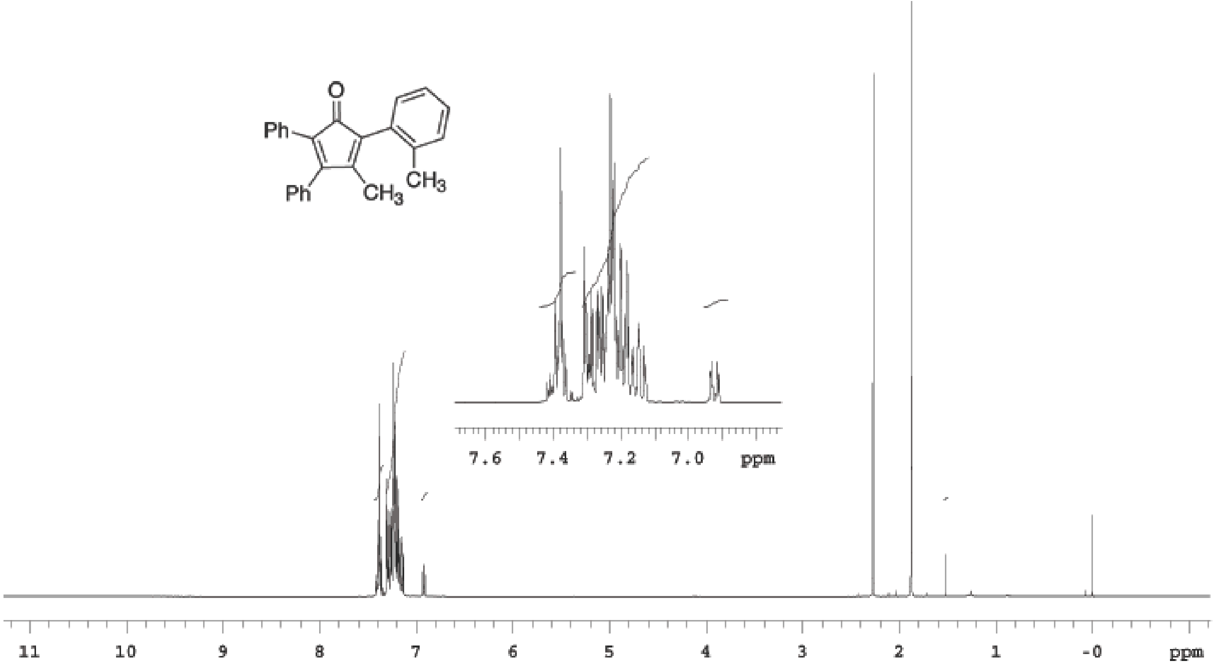
Cyclopentadienone **18**:



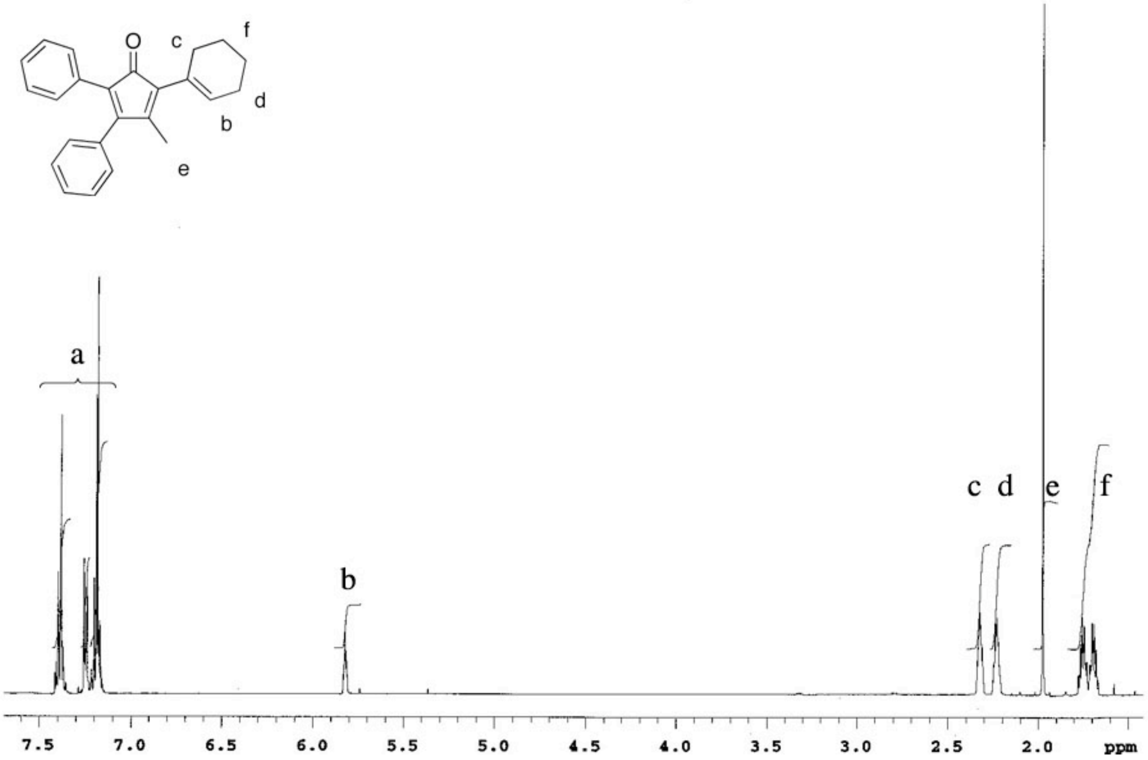
Cyclopentadienone **20**:



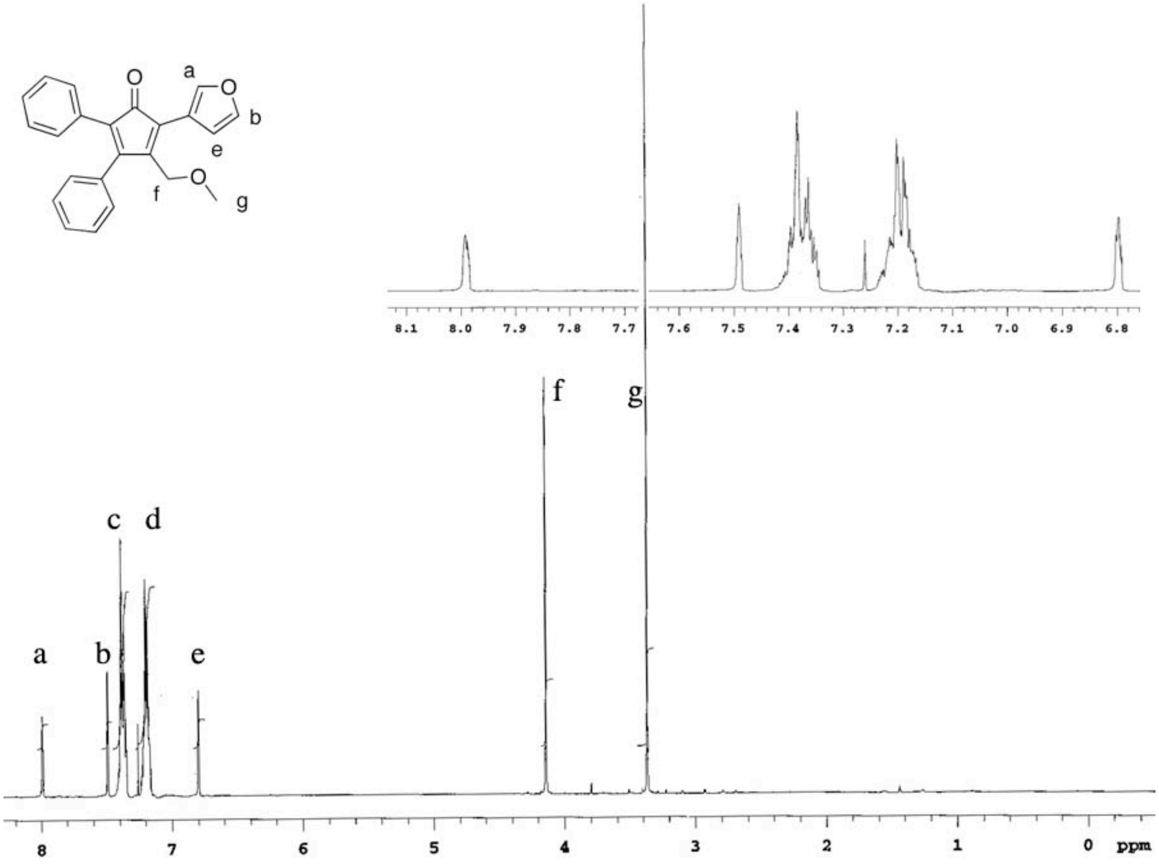
Cyclopentadienone **22**:



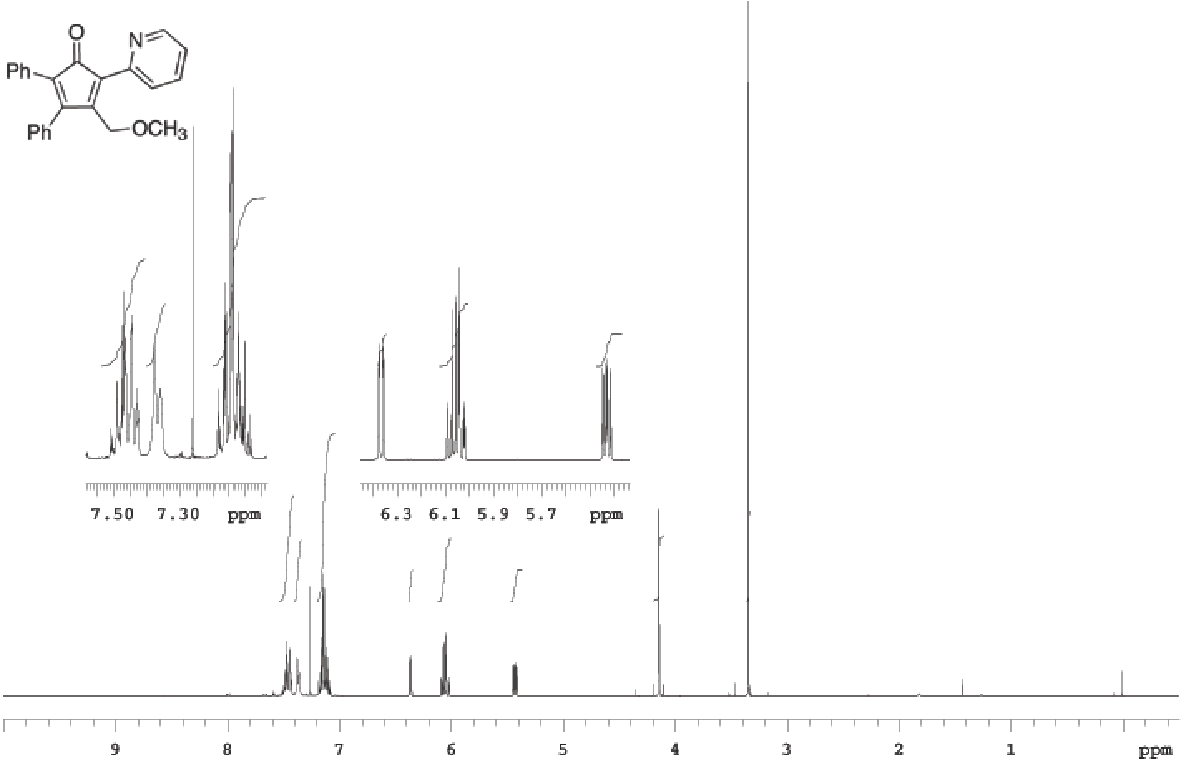
Cyclopentadienone **24**:



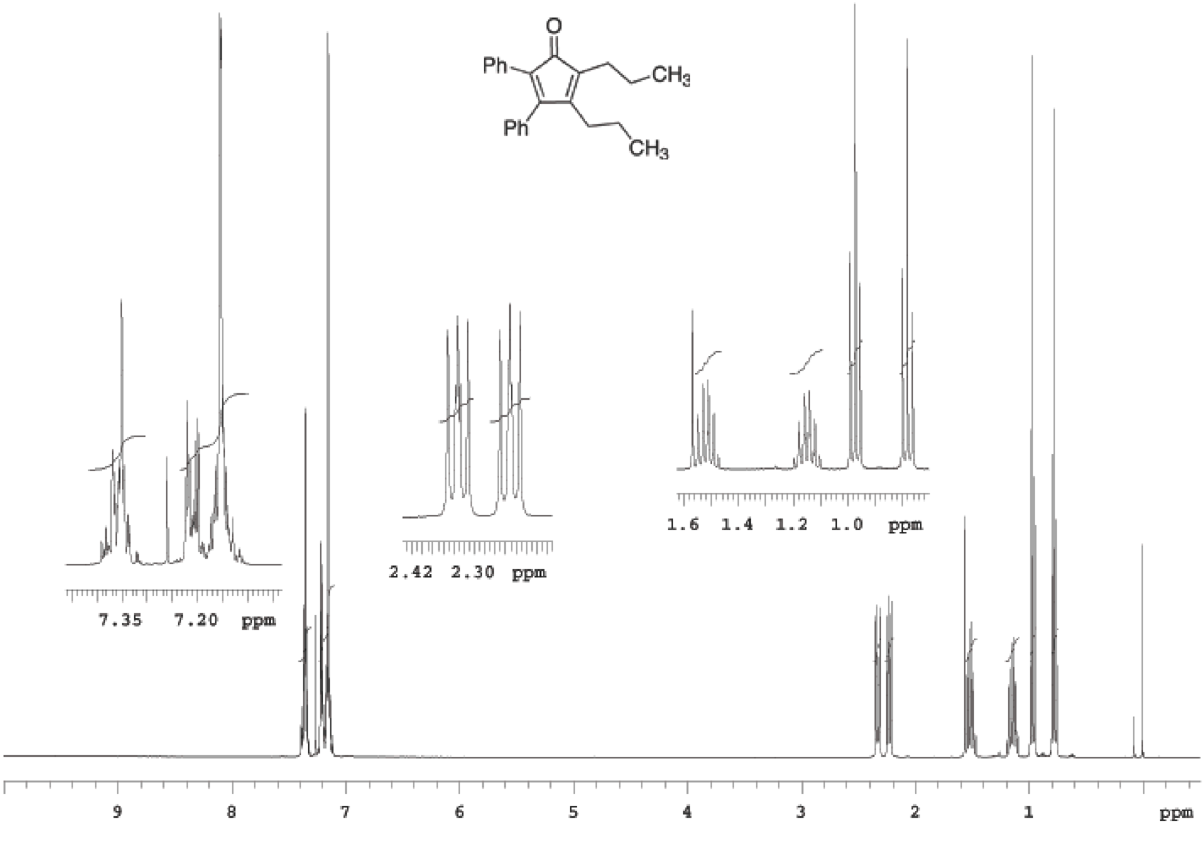
Cyclopentadienone **26**:



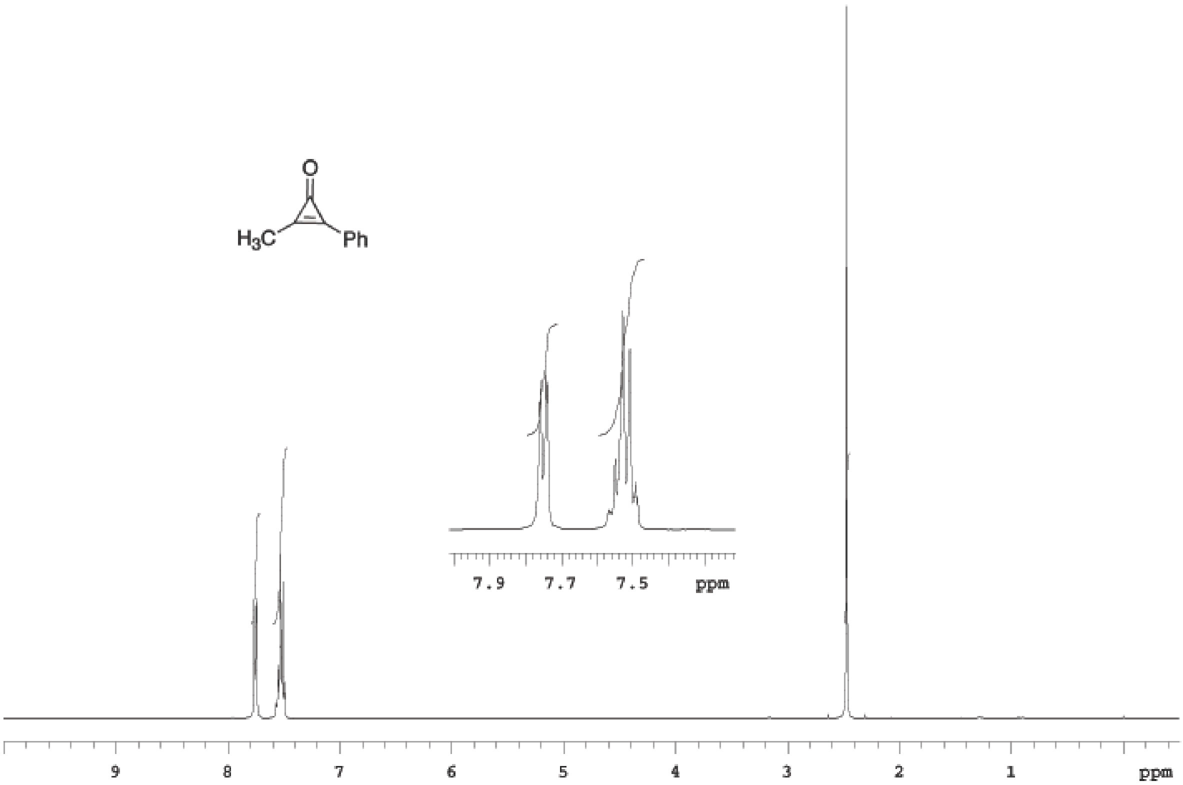
Cyclopentadienone **28**:



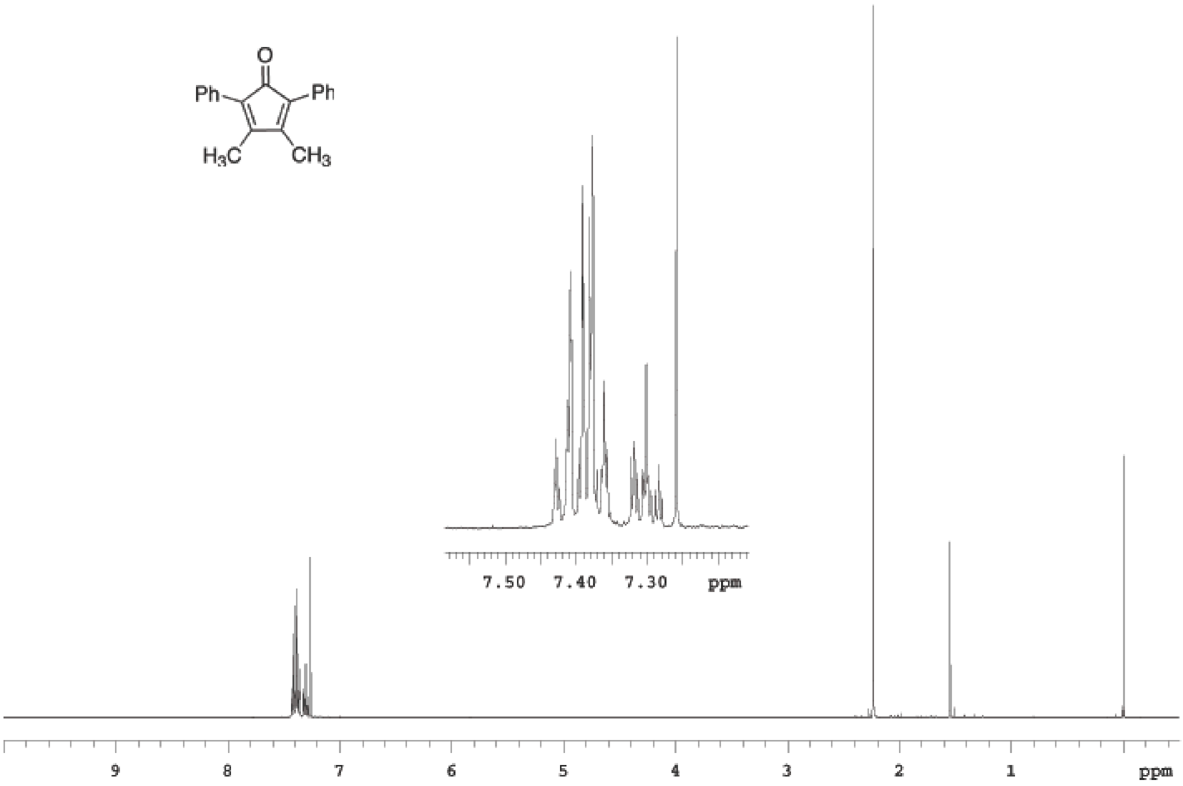
Cyclopentadienone **30**:



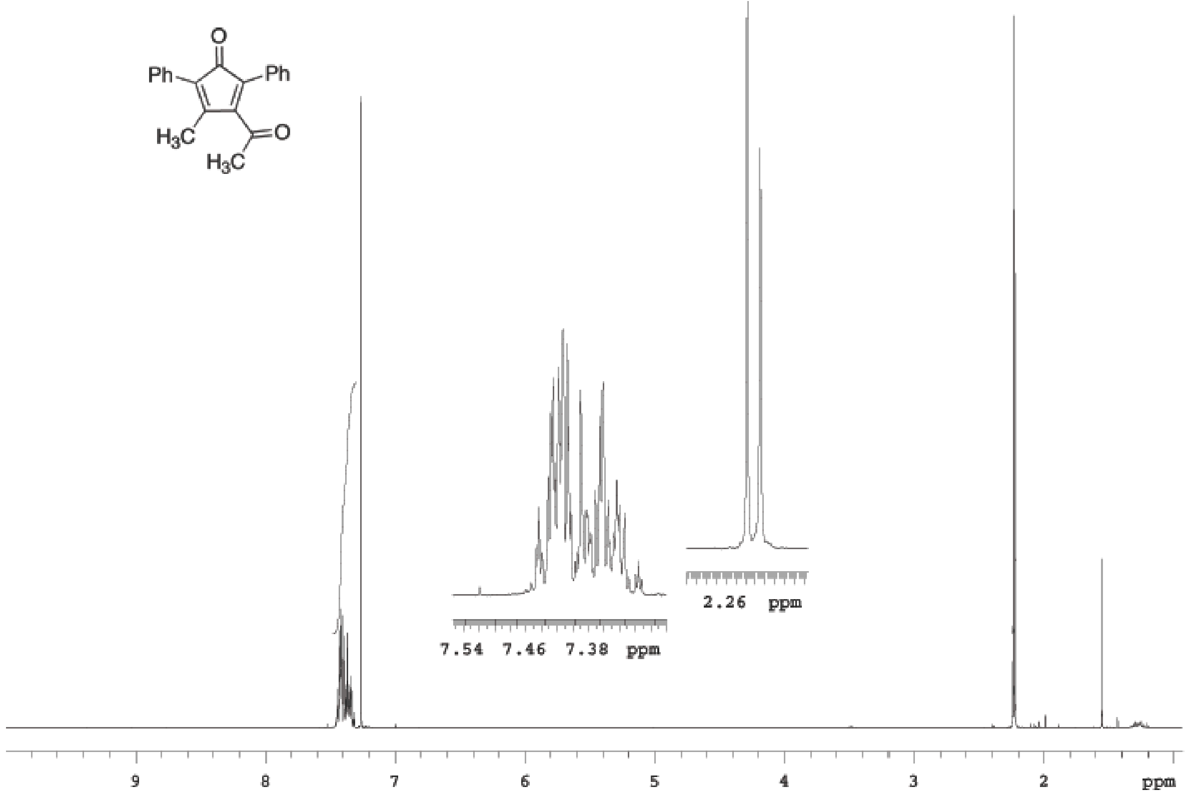
Methylphenylcyclopropenone (**33**):



Cyclopentadienone **34**:



Cyclopentadienone **36**:



IV. X-Ray Crystallographic Data for Compound **3**.

A purple plate crystal of $C_{24}H_{18}O$ having approximate dimensions of 0.25 x 0.17 x 0.01 mm was mounted on a quartz fiber using Paratone N hydrocarbon oil. All measurements were made on a Bruker-Siemens SMART CCD area detector with monochromatic radiation of wavelength 0.71073 Å.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the measured positions of 1166 centered reflections with $I > 10\sigma(I)$ in the range $2.38° < \theta < 23.29°$, corresponded to a primitive monoclinic cell with dimensions:

a = 8.983(2) Å	$\alpha = 90°$	V = 1693.6(7) Å^3
b = 16.458(4) Å	$\beta = 108.031(4)°$	
c = 12.047(3) Å	$\gamma = 90°$	

For $Z = 4$ and $F.W. = 322.38$, the calculated density is 1.264 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P\,2_1/c$. The data were collected at a temperature of 133 K. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3° counted for a total of 40 seconds per frame.

Data were integrated by the program SAINT with box parameters of 1.6 x 1.6 x 1.0° to a maximum θ value of 24.96°. The data were corrected for Lorentz and polarization effects. The linear absorption coefficient, μ, for 0.71073 Å radiation is 0.076 mm^{-1}. Data were analyzed for agreement and possible absorption using SADABS.[3] A semi-empirical absorption correction based on 7.07 reflections with $I > 5\sigma(I)$ was applied that resulted in normalized transmission factors ranging from 0.39 to 1. Of the 7336 reflections that were collected, 2746 were unique ($R_{\text{int}} = 0.0821$); equivalent reflections were merged. A correction for secondary extinction[3a] was applied having a refined coefficient of 0.012(3). No decay correction was deemed necessary.

The structure was solved by direct methods (SIR-97) and expanded using Fourier techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located on the difference Fourier map, but were positioned using the HFIX command (idealized positions via a riding refinement). A single torsional parameter about the C-C bond was refined in the case of the methyl group. The final cycle of full-matrix least-squares refinement was based on 2746 reflections (all data) and 228 variable parameters and converged (largest parameter shift was 0.000 times its esd) with conventional unweighted and weighted agreement factors of $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o| = 0.0577$ for 1687 data with $F_o > 4\sigma(F_o)$, and $wR_2 = [(\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w |F_o|^2)]^{1/2} = 0.1716$.

The standard deviation of an observation of unit weight (S)[7] was 0.940. Sheldrick weights[6] were used; where applicable, weights were refined to convergence. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.29 and -0.23 $e^-/Å^3$, respectively.

Table 2. Crystal Data.

Empirical Formula	$C_{24}H_{18}O$
Formula Weight	322.38
Crystal Color, Habit	Purple, plate
Crystal Dimensions	0.25 x 0.17 x 0.01 mm
Crystal System	Monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 8.983(2) Å; b = 16.458(4) Å; c = 12.047(3) Å $\alpha = 90^o$; $\beta = 108.031(4)^o$; $\gamma = 90^o$ V = 1693.6(7) $Å^3$
Space Group	$P\ 2_1/c$
Z value	4
D_{calc}	1.264 g/cm^3
F_{000}	680
μ(0.71073 Å radiation)	0.08 cm^{-1}

Table 3. Intensity Measurements.

Diffractometer	Siemens SMART APEX CCD
Radiation	λ = 0.71073 Å, graphite monochromated
Temperature	133 K
Scan Type	$\omega(0.3^o$/frame)
Exposure Time	40 seconds per frame
θ_{max}	24.96°
No. of Reflections Measured	Total: 7336; Unique: 2746 (R_{int} = 0.0821)
Corrections	Lorentz-polarization Absorption: $T_{max} = 1$, $T_{min} = 0.39$

Table 4. Structure Solution and Refinement.

Structure Solution	Direct (SIR-97)
Refinement	Full-matrix least-squares (SHELXL-97)
Function Minimized	$\Sigma w(|F_o|^2 - |F_c|^2)^2$
Least Squares Weight Scheme	$w=1/[\sigma^2(F_o^2)+(0.0722P)^2]$ where $P=(F_o^2+2F_c^2)/3$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($F_o > 4\sigma(F_o)$)	1687
No. Variables	228
Reflection/Parameter Ratio	12.04
Residuals: R_1; wR_2	0.0577; 0.11716
Goodness of Fit Indicator (S)	0.940

Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.29 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.23 $e^-/Å^3$

Table 5. Bond Lengths (Å).

Atom	Atom	Distance	Atom	Atom	Distance
O1	C1	1.217(3)	C1	C5	1.502(4)
C1	C2	1.508(4)	C2	C3	1.348(4)
C2	C7	1.467(4)	C3	C13	1.469(4)
C3	C4	1.516(4)	C4	C5	1.352(4)
C4	C6	1.492(4)	C5	C19	1.467(4)
C7	C8	1.396(4)	C7	C12	1.398(4)
C8	C9	1.386(4)	C9	C10	1.372(4)
C10	C11	1.382(4)	C11	C12	1.375(4)
C13	C18	1.398(4)	C13	C14	1.398(4)
C14	C15	1.376(4)	C15	C16	1.385(4)
C16	C17	1.378(4)	C17	C18	1.376(4)
C19	C24	1.397(4)	C19	C20	1.401(4)
C20	C21	1.384(4)	C21	C22	1.378(4)
C22	C23	1.381(4)	C23	C24	1.382(4)

Table 6. Bond Angles (°).

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
O1	C1	C5	127.2(3)	O1	C1	C2	125.5(3)
C5	C1	C2	107.3(2)	C3	C2	C7	130.5(3)
C3	C2	C1	106.6(2)	C7	C2	C1	122.7(3)
C2	C3	C13	127.8(3)	C2	C3	C4	109.7(2)
C13	C3	C4	122.5(3)	C5	C4	C6	128.0(3)
C5	C4	C3	109.6(3)	C6	C4	C3	122.3(3)
C4	C5	C19	130.3(3)	C4	C5	C1	106.6(3)
C19	C5	C1	123.0(2)	C8	C7	C12	117.8(3)
C8	C7	C2	120.3(3)	C12	C7	C2	121.9(3)
C9	C8	C7	120.7(3)	C10	C9	C8	120.4(3)
C9	C10	C11	119.8(3)	C12	C11	C10	120.2(3)
C11	C12	C7	121.1(3)	C18	C13	C14	117.6(3)
C18	C13	C3	122.0(2)	C14	C13	C3	120.5(2)
C15	C14	C13	120.9(3)	C14	C15	C16	120.3(3)
C17	C16	C15	119.8(3)	C18	C17	C16	119.8(3)
C17	C18	C13	121.6(3)	C24	C19	C20	117.2(3)
C24	C19	C5	121.4(3)	C20	C19	C5	121.3(2)
C21	C20	C19	121.0(3)	C22	C21	C20	120.5(3)
C21	C22	C23	119.6(3)	C22	C23	C24	120.1(3)
C23	C24	C19	121.5(3)				

Table 7. Torsion Angles (°).

Atom	Atom	Atom	Atom	Angle	Atom	Atom	Atom	Atom	Angle
O1	C1	C2	C3	175.1(2)	C5	C1	C2	C3	-2.7(3)
O1	C1	C2	C7	-1.9(4)	C5	C1	C2	C7	-179.8(2)
C7	C2	C3	C13	-4.6(5)	C1	C2	C3	C13	178.7(2)
C7	C2	C3	C4	178.0(2)	C1	C2	C3	C4	1.3(3)
C2	C3	C4	C5	0.8(3)	C13	C3	C4	C5	-176.8(2)
C2	C3	C4	C6	179.3(2)	C13	C3	C4	C6	1.6(4)
C6	C4	C5	C19	-3.7(5)	C3	C4	C5	C19	174.6(2)
C6	C4	C5	C1	179.2(2)	C3	C4	C5	C1	-2.5(3)
O1	C1	C5	C4	-174.6(2)	C2	C1	C5	C4	3.3(3)

O1	C1	C5	C19	8.0(4)	C2	C1	C5	C19	-174.2(2)
C3	C2	C7	C8	145.0(3)	C1	C2	C7	C8	-38.8(4)
C3	C2	C7	C12	-37.0(4)	C1	C2	C7	C12	139.3(3)
C12	C7	C8	C9	1.9(4)	C2	C7	C8	C9	180.0(3)
C7	C8	C9	C10	-1.4(4)	C8	C9	C10	C11	0.0(4)
C9	C10	C11	C12	0.8(4)	C10	C11	C12	C7	-0.3(4)
C8	C7	C12	C11	-1.0(4)	C2	C7	C12	C11	-179.1(3)
C2	C3	C13	C18	120.8(3)	C4	C3	C13	C18	-62.1(4)
C2	C3	C13	C14	-59.1(4)	C4	C3	C13	C14	118.1(3)
C18	C13	C14	C15	1.2(4)	C3	C13	C14	C15	-178.9(3)
C13	C14	C15	C16	-0.5(5)	C14	C15	C16	C17	-0.4(5)
C15	C16	C17	C18	0.6(5)	C16	C17	C18	C13	0.1(5)
C14	C13	C18	C17	-1.0(4)	C3	C13	C18	C17	179.1(3)
C4	C5	C19	C24	147.4(3)	C1	C5	C19	C24	-35.8(4)
C4	C5	C19	C20	-35.6(4)	C1	C5	C19	C20	141.1(3)
C24	C19	C20	C21	0.1(4)	C5	C19	C20	C21	-177.0(2)
C19	C20	C21	C22	2.3(4)	C20	C21	C22	C23	-2.3(4)
C21	C22	C23	C24	0.0(4)	C22	C23	C24	C19	2.5(4)

V. X-Ray Crystallographic Data for Compound **11a**.

A brown rhombic crystal of $C_{61}H_{40}O$ having approximate dimensions of 0.20 x 0.11 x 0.07 mm was mounted on a quartz fiber using Paratone N hydrocarbon oil. All measurements were made on a Siemens SMART-APEX[1] CCD area detector with monochromatic radiation of wavelength 0.71073 Å.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the measured positions of 2608 centered reflections with $I > 10\sigma(I)$ in the range $2.22^\circ < \theta < 23.04^\circ$, corresponded to a primitive monoclinic cell with dimensions:

$a = 12.459(2)$ Å $\alpha = 90^\circ$ $V = 4290.5(10)$ Å^3
$b = 23.392(3)$ Å $\beta = 99.347(3)^\circ$
$c = 14.920(2)$ Å $\gamma = 90^\circ$

For $Z = 4$ and $F.W. = 788.93$, the calculated density is 1.221 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be P 21/c. The data were collected at a temperature of 148 K. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3° counted for a total of 30 seconds per frame.

Data were integrated by the program SAINT with box parameters of 1.6 x 1.6 x 1.0° to a maximum θ value of 23.29°. The data were corrected for Lorentz and polarization effects. The linear absorption coefficient, μ, for 0.71073 Å radiation is 0.071 mm^{-1}. Data were analyzed for agreement and possible absorption using SADABS. A semi-empirical absorption correction based on 2.57 reflections with $I > 5\sigma(I)$ was applied that resulted in normalized transmission factors ranging from 0.91 to 1. Of the 18844 reflections that were collected, 6159 were unique ($R_{\mathrm{int}} = 0.0430$); equivalent reflections were merged. No decay correction was deemed necessary.

The structure was solved by direct methods (SIR-97) and expanded using Fourier techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located on the difference Fourier map, but were positioned using the HFIX command (idealized positions via a riding refinement). The final cycle of full-matrix least-squares refinement[6] was based on 6159 reflections (all data) and 559 variable parameters and converged (largest parameter shift was 0.000 times its esd) with conventional unweighted and weighted agreement factors of $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o| = 0.0432$ for 4303 data with $F_o > 4\sigma(F_o)$, and $wR_2 = [(\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w |F_o|^2)]^{1/2} = 0.1108$

The standard deviation of an observation of unit weight (S)[7] was 1.017. Sheldrick weights[6] were used; where applicable, weights were refined to convergence. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.28 and -0.21 $e^-/Å^3$, respectively.

Table 8. Crystal Data.

Empirical Formula	$C_{61}H_{40}O$
Formula Weight	788.93
Crystal Color, Habit	brown, rhombic
Crystal Dimensions	0.20 x 0.11 x 0.07 mm
Crystal System	monoclinic
Lattice Type	primitive
Lattice Parameters	a = 12.459(2) Å; b = 23.392(3) Å; c = 14.920(2) Å $\alpha = 90^o$; $\beta = 99.347(3)^o$; $\gamma = 90^o$ V = 4290.5(10) $Å^3$
Space Group	P 21/c
Z value	4
d_{calc}	1.221 g/cm^3
F_{000}	1656
μ(0.71073 Å radiation)	0.07 cm^{-1}

Table 9. Intensity Measurements.

Diffractometer	Siemens SMART-APEX CCD
Radiation	λ = 0.71073 Å, graphite monochromated
Exposure Time	30 seconds per frame.
Scan Type	ω (0.3 degrees per frame)
θ_{max}	23.29^o
Data Collection Temperature	148 K
No. of Reflections Measured	Total: 18844, Unique: 6159 (R_{int} = 0.0430)
Corrections	Lorentz-polarization Absorption: T_{max} = 1, T_{min} = 0.91

Table 10. Structure Solution and Refinement.

Structure Solution	Direct (SIR-97)
Refinement	Full-matrix least-squares (SHELXL-97)
Function Minimized	$\Sigma w(\lvert F_o\rvert^2 - \lvert F_c\rvert^2)^2$
Least Squares Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0510P)^2+0.5992P]$ where $P=(F_o^2+2F_c^2)/3$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($F_o > 4\sigma(F_o)$)	4303
No. Variables	559
Reflection/Parameter Ratio	11.02
Residuals: R_1; wR_2	0.0432; 0.1108
Goodness of Fit Indicator (S)	1.017
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.28 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.21 $e^-/Å^3$

Table 11. Bond Lengths (Å).

Atom	Atom	Distance	Atom	Atom	Distance
O1	C1	1.217(2)	C1	C5	1.491(3)
C1	C2	1.493(3)	C2	C3	1.348(3)
C2	C20	1.470(3)	C3	C6	1.484(3)
C3	C4	1.521(3)	C4	C5	1.346(3)
C4	C32	1.476(3)	C5	C26	1.477(3)
C6	C11	1.406(3)	C6	C7	1.414(3)

C7	C8	1.403(3)	C7	C38	1.496(3)
C8	C9	1.405(3)	C8	C44	1.498(3)
C9	C10	1.416(3)	C9	C12	1.440(3)
C10	C11	1.394(3)	C10	C50	1.492(3)
C11	C56	1.500(3)	C12	C13	1.197(3)
C13	C14	1.441(3)	C14	C15	1.382(3)
C14	C19	1.392(3)	C15	C16	1.375(3)
C16	C17	1.372(4)	C17	C18	1.369(4)
C18	C19	1.390(3)	C20	C25	1.391(3)
C20	C21	1.398(3)	C21	C22	1.377(3)
C22	C23	1.374(3)	C23	C24	1.378(3)
C24	C25	1.372(3)	C26	C27	1.375(3)
C26	C31	1.392(4)	C27	C28	1.418(4)
C28	C29	1.365(5)	C29	C30	1.346(5)
C30	C31	1.381(4)	C32	C33	1.396(3)
C32	C37	1.399(3)	C33	C34	1.377(3)
C34	C35	1.375(3)	C35	C36	1.379(3)
C36	C37	1.377(3)	C38	C43	1.386(3)
C38	C39	1.390(3)	C39	C40	1.376(3)
C40	C41	1.382(3)	C41	C42	1.367(3)
C42	C43	1.380(3)	C44	C49	1.380(3)
C44	C45	1.392(3)	C45	C46	1.394(3)
C46	C47	1.377(4)	C47	C48	1.371(4)
C48	C49	1.385(3)	C50	C51	1.380(3)
C50	C55	1.384(3)	C51	C52	1.385(3)
C52	C53	1.365(4)	C53	C54	1.364(4)
C54	C55	1.375(3)	C56	C57	1.388(3)
C56	C61	1.388(3)	C57	C58	1.382(3)
C58	C59	1.375(3)	C59	C60	1.378(3)
C60	C61	1.385(3)			

Table 12. Bond Angles (°).

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
O1	C1	C5	125.2(2)	O1	C1	C2	127.3(2)
C5	C1	C2	107.50(17)	C3	C2	C20	130.6(2)
C3	C2	C1	106.52(18)	C20	C2	C1	122.84(18)
C2	C3	C6	126.33(19)	C2	C3	C4	109.86(18)
C6	C3	C4	123.45(17)	C5	C4	C32	126.55(19)
C5	C4	C3	108.49(18)	C32	C4	C3	124.90(18)
C4	C5	C26	132.1(2)	C4	C5	C1	107.48(18)
C26	C5	C1	119.81(18)	C11	C6	C7	120.88(18)
C11	C6	C3	120.40(18)	C7	C6	C3	118.67(17)
C8	C7	C6	119.66(18)	C8	C7	C38	120.81(18)
C6	C7	C38	119.53(18)	C7	C8	C9	119.39(18)
C7	C8	C44	121.21(18)	C9	C8	C44	119.33(18)
C8	C9	C10	120.61(19)	C8	C9	C12	121.78(19)
C10	C9	C12	117.52(18)	C11	C10	C9	120.07(18)
C11	C10	C50	121.12(18)	C9	C10	C50	118.75(18)
C10	C11	C6	119.33(19)	C10	C11	C56	120.45(18)
C6	C11	C56	120.21(18)	C13	C12	C9	171.6(2)
C12	C13	C14	173.0(2)	C15	C14	C19	119.2(2)
C15	C14	C13	121.0(2)	C19	C14	C13	119.7(2)
C16	C15	C14	120.7(2)	C17	C16	C15	120.2(3)
C18	C17	C16	119.9(2)	C17	C18	C19	120.7(3)
C18	C19	C14	119.4(2)	C25	C20	C21	117.9(2)
C25	C20	C2	122.32(19)	C21	C20	C2	119.76(19)
C22	C21	C20	120.9(2)	C23	C22	C21	120.1(2)
C22	C23	C24	119.8(2)	C25	C24	C23	120.4(2)

C24	C25	C20	120.8(2)	C27	C26	C31	118.2(2)
C27	C26	C5	123.9(2)	C31	C26	C5	117.8(2)
C26	C27	C28	119.3(3)	C29	C28	C27	119.6(3)
C30	C29	C28	122.0(3)	C29	C30	C31	118.5(3)
C30	C31	C26	122.3(3)	C33	C32	C37	117.4(2)
C33	C32	C4	122.80(19)	C37	C32	C4	119.81(19)
C34	C33	C32	121.1(2)	C35	C34	C33	120.3(2)
C34	C35	C36	119.9(2)	C37	C36	C35	119.9(2)
C36	C37	C32	121.4(2)	C43	C38	C39	118.30(19)
C43	C38	C7	120.36(19)	C39	C38	C7	121.32(19)
C40	C39	C38	120.6(2)	C39	C40	C41	120.3(2)
C42	C41	C40	119.5(2)	C41	C42	C43	120.5(2)
C42	C43	C38	120.7(2)	C49	C44	C45	118.6(2)
C49	C44	C8	121.4(2)	C45	C44	C8	119.9(2)
C44	C45	C46	120.7(2)	C47	C46	C45	119.4(3)
C48	C47	C46	120.3(2)	C47	C48	C49	120.3(3)
C44	C49	C48	120.7(2)	C51	C50	C55	118.8(2)
C51	C50	C10	119.6(2)	C55	C50	C10	121.6(2)
C50	C51	C52	120.2(2)	C53	C52	C51	120.2(3)
C54	C53	C52	119.9(2)	C53	C54	C55	120.6(3)
C54	C55	C50	120.3(2)	C57	C56	C61	118.02(19)
C57	C56	C11	120.18(18)	C61	C56	C11	121.79(18)
C58	C57	C56	121.3(2)	C59	C58	C57	120.0(2)
C58	C59	C60	119.7(2)	C59	C60	C61	120.3(2)
C60	C61	C56	120.7(2)				

Table 13. Torsion Angles (º).

Atom	Atom	Atom	Atom	Angle	Atom	Atom	Atom	Atom	Angle
O1	C1	C2	C3	176.5(2)	C5	C1	C2	C3	-1.9(2)
O1	C1	C2	C20	-5.8(3)	C5	C1	C2	C20	175.75(19)
C20	C2	C3	C6	-4.4(4)	C1	C2	C3	C6	173.04(18)
C20	C2	C3	C4	-177.7(2)	C1	C2	C3	C4	-0.3(2)
C2	C3	C4	C5	2.6(2)	C6	C3	C4	C5	-170.90(19)
C2	C3	C4	C32	179.96(19)	C6	C3	C4	C32	6.4(3)
C32	C4	C5	C26	-10.1(4)	C3	C4	C5	C26	167.2(2)
C32	C4	C5	C1	179.01(19)	C3	C4	C5	C1	-3.7(2)
O1	C1	C5	C4	-174.8(2)	C2	C1	C5	C4	3.6(2)
O1	C1	C5	C26	12.9(3)	C2	C1	C5	C26	-168.65(19)
C2	C3	C6	C11	119.0(2)	C4	C3	C6	C11	-68.5(3)
C2	C3	C6	C7	-63.7(3)	C4	C3	C6	C7	108.8(2)
C11	C6	C7	C8	-1.5(3)	C3	C6	C7	C8	-178.83(18)
C11	C6	C7	C38	178.43(18)	C3	C6	C7	C38	1.1(3)
C6	C7	C8	C9	-0.8(3)	C38	C7	C8	C9	179.24(19)
C6	C7	C8	C44	175.90(19)	C38	C7	C8	C44	-4.1(3)
C7	C8	C9	C10	2.1(3)	C44	C8	C9	C10	-174.61(19)
C7	C8	C9	C12	178.48(19)	C44	C8	C9	C12	1.7(3)
C8	C9	C10	C11	-1.2(3)	C12	C9	C10	C11	-177.66(19)
C8	C9	C10	C50	176.21(19)	C12	C9	C10	C50	-0.3(3)
C9	C10	C11	C6	-1.1(3)	C50	C10	C11	C6	-178.47(19)
C9	C10	C11	C56	177.23(19)	C50	C10	C11	C56	-0.1(3)
C7	C6	C11	C10	2.5(3)	C3	C6	C11	C10	179.75(19)
C7	C6	C11	C56	-175.87(19)	C3	C6	C11	C56	1.4(3)
C8	C9	C12	C13	-145.4(15)	C10	C9	C12	C13	31.0(16)
C9	C12	C13	C14	35(3)	C12	C13	C14	C15	107.1(19)
C12	C13	C14	C19	-68(2)	C19	C14	C15	C16	1.2(4)
C13	C14	C15	C16	-174.3(2)	C14	C15	C16	C17	-0.6(5)
C15	C16	C17	C18	-0.5(5)	C16	C17	C18	C19	1.1(5)
C17	C18	C19	C14	-0.5(4)	C15	C14	C19	C18	-0.6(4)

C13	C14	C19	C18	175.0(2)	C3	C2	C20	C25	-33.7(4)
C1	C2	C20	C25	149.3(2)	C3	C2	C20	C21	145.3(2)
C1	C2	C20	C21	-31.8(3)	C25	C20	C21	C22	0.6(3)
C2	C20	C21	C22	-178.5(2)	C20	C21	C22	C23	0.2(4)
C21	C22	C23	C24	-1.4(4)	C22	C23	C24	C25	1.8(4)
C23	C24	C25	C20	-1.0(3)	C21	C20	C25	C24	-0.1(3)
C2	C20	C25	C24	178.9(2)	C4	C5	C26	C27	90.5(3)
C1	C5	C26	C27	-99.5(3)	C4	C5	C26	C31	-94.2(3)
C1	C5	C26	C31	75.9(3)	C31	C26	C27	C28	0.6(4)
C5	C26	C27	C28	175.9(2)	C26	C27	C28	C29	-0.6(5)
C27	C28	C29	C30	0.4(5)	C28	C29	C30	C31	-0.2(5)
C29	C30	C31	C26	0.2(5)	C27	C26	C31	C30	-0.4(4)
C5	C26	C31	C30	-176.0(2)	C5	C4	C32	C33	140.1(2)
C3	C4	C32	C33	-36.7(3)	C5	C4	C32	C37	-38.2(3)
C3	C4	C32	C37	144.9(2)	C37	C32	C33	C34	0.0(3)
C4	C32	C33	C34	-178.37(19)	C32	C33	C34	C35	0.6(3)
C33	C34	C35	C36	-1.1(4)	C34	C35	C36	C37	0.9(4)
C35	C36	C37	C32	-0.3(4)	C33	C32	C37	C36	-0.2(3)
C4	C32	C37	C36	178.3(2)	C8	C7	C38	C43	-60.2(3)
C6	C7	C38	C43	119.8(2)	C8	C7	C38	C39	121.6(2)
C6	C7	C38	C39	-58.4(3)	C43	C38	C39	C40	-2.9(3)
C7	C38	C39	C40	175.3(2)	C38	C39	C40	C41	0.8(4)
C39	C40	C41	C42	1.9(4)	C40	C41	C42	C43	-2.4(4)
C41	C42	C43	C38	0.2(4)	C39	C38	C43	C42	2.4(3)
C7	C38	C43	C42	-175.9(2)	C7	C8	C44	C49	121.0(2)
C9	C8	C44	C49	-62.3(3)	C7	C8	C44	C45	-60.1(3)
C9	C8	C44	C45	116.6(2)	C49	C44	C45	C46	0.3(3)
C8	C44	C45	C46	-178.7(2)	C44	C45	C46	C47	-0.8(3)
C45	C46	C47	C48	0.7(4)	C46	C47	C48	C49	-0.1(4)
C45	C44	C49	C48	0.4(3)	C8	C44	C49	C48	179.3(2)
C47	C48	C49	C44	-0.5(4)	C11	C10	C50	C51	107.1(2)
C9	C10	C50	C51	-70.3(3)	C11	C10	C50	C55	-72.3(3)
C9	C10	C50	C55	110.4(2)	C55	C50	C51	C52	0.7(3)
C10	C50	C51	C52	-178.7(2)	C50	C51	C52	C53	0.1(4)
C51	C52	C53	C54	-1.1(4)	C52	C53	C54	C55	1.3(4)
C53	C54	C55	C50	-0.5(4)	C51	C50	C55	C54	-0.5(3)
C10	C50	C55	C54	178.8(2)	C10	C11	C56	C57	-59.2(3)
C6	C11	C56	C57	119.1(2)	C10	C11	C56	C61	122.0(2)
C6	C11	C56	C61	-59.6(3)	C61	C56	C57	C58	-0.6(3)
C11	C56	C57	C58	-179.4(2)	C56	C57	C58	C59	0.4(3)
C57	C58	C59	C60	-0.2(4)	C58	C59	C60	C61	0.2(4)
C59	C60	C61	C56	-0.4(3)	C57	C56	C61	C60	0.6(3)
C11	C56	C61	C60	179.4(2)					

VI. X-Ray Crystallographic Data for Compound **16**.

A purple rhombic crystal of $C_{27}H_{22}O_3$ having approximate dimensions of 0.20 x 0.12 x 0.10 mm was mounted on a quartz fiber using Paratone N hydrocarbon oil. All measurements were made on a Bruker-Siemens SMART[1] CCD area detector with monochromatic radiation of wavelength 0.71073 Å.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the measured positions of 1563 centered reflections with $I > 10\sigma(I)$ in the range $3.33° < \theta < 22.4°$, corresponded to a primitive monoclinic cell with dimensions:

$a = 8.976(4)$ Å $\alpha = 90°$ $V = 2033.9(17)$ Å^3
$b = 24.230(12)$ Å $\beta = 111.058(6)°$
$c = 10.021(5)$ Å $\gamma = 90°$

For $Z = 4$ and $F.W. = 394.45$, the calculated density is 1.288 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be P 2_1/a (#14). The data were collected at a temperature of 143 K. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3° counted for a total of 40 seconds per frame.

Data were integrated by the program SAINT with box parameters of 1.6 x 1.6 x 1.0° to a maximum θ value of 23.44°. The data were corrected for Lorentz and polarization effects. The linear absorption coefficient, μ, for 0.71073 Å radiation is 0.083 mm^{-1}. Data were analyzed for agreement and possible absorption using SADABS. A semi-empirical absorption correction based on 6.09 reflections with $I > 5\sigma(I)$ was applied that resulted in normalized transmission factors ranging from 0.87 to 0.99. Of the 9074 reflections that were collected, 2907 were unique ($R_{\text{int}} = 0.0655$); equivalent reflections were merged. No decay correction was deemed necessary.

The structure was solved by direct methods (SIR-2002) and expanded using Fourier techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located using the HFIX command (idealized positions via a riding refinement). A single torsional parameter about the X-C or X-O bond was refined in the case of methyl or hydroxyl groups. The final cycle of full-matrix least-squares refinement[6] was based on 2907 reflections (all data) and 274 variable parameters and converged (largest parameter shift was 0.000 times its esd) with conventional unweighted and weighted agreement factors of $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o| = 0.0511$ for 1967 data with $F_o > 4\sigma(F_o)$, and $wR_2 = [(\Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w |F_o|^2)]^{1/2} = 0.1419$.

The standard deviation of an observation of unit weight (S)[7] was 0.975. Sheldrick weights[6] were used; where applicable, weights were refined to convergence. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.19 and -0.20 $e^-/\text{Å}^3$, respectively.

Table 14. Crystal Data.

Empirical Formula	$C_{27}H_{22}O_3$
Formula Weight	394.45
Crystal Color, Habit	purple, rhombic
Crystal Dimensions	0.20 x 0.12 x 0.10 mm
Crystal System	Monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 8.976(4) Å; b = 24.230(12) Å; c = 10.021(5) Å α = 90°; β = 111.058(6)°; γ = 90° V = 2033.9(17) Å^3
Space Group	P 21/a
Z value	4
d_{calc}	1.288 g/cm^3
F_{000}	832
μ(0.71073 Å radiation)	0.08 cm^{-1}

Table 15. Intensity Measurements.

Diffractometer	Bruker-Siemens SMART CCD
Radiation	λ = 0.71073 Å, graphite monochromated
Exposure Time	40 seconds per frame.
Scan Type	ω (0.3 degrees per frame)
θ_{max}	23.44°
Data Collection Temperature	143 K
No. of Reflections Measured	Total: 9074; Unique: 2907 ($R_{\text{int}} = 0.0655$)
Corrections	Lorentz-polarization Absorption: $T_{\text{max}} = 0.99$, $T_{\text{min}} = 0.87$

Table 16. Structure Solution and Refinement.

Structure Solution	Direct (SHELXS-97)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(|F_o|^2 - |F_c|^2)^2$

Least Squares Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0000P)^2]$ where $P=(F_o^2+2F_c^2)/3$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($F_o > 4\sigma(F_o)$)	1967
No. Variables	274
Reflection/Parameter Ratio	10.61
Residuals: R_1; wR_2	0.0511; 0.1419
Goodness of Fit Indicator (S)	0.975
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.19 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.20 $e^-/Å^3$

Table 17. Bond Lengths (Å).

Atom	Atom	Distance	Atom	Atom	Distance
O1	C2	1.208(3)	O2	C10	1.216(3)
O3	C14	1.420(3)	O3	C15	1.428(3)
C1	C2	1.505(4)	C2	C3	1.503(4)
C3	C8	1.389(4)	C3	C4	1.391(4)
C4	C5	1.379(4)	C5	C6	1.391(4)
C6	C7	1.397(3)	C6	C9	1.469(4)
C7	C8	1.381(4)	C9	C13	1.344(3)
C9	C10	1.514(4)	C10	C11	1.511(4)
C11	C12	1.354(3)	C11	C16	1.473(4)
C12	C22	1.477(4)	C12	C13	1.511(4)
C13	C14	1.497(4)	C16	C21	1.388(3)
C16	C17	1.397(3)	C17	C18	1.379(4)
C18	C19	1.380(4)	C19	C20	1.379(4)
C20	C21	1.388(4)	C22	C23	1.386(4)
C22	C27	1.393(4)	C23	C24	1.384(4)
C24	C25	1.383(4)	C25	C26	1.376(4)
C26	C27	1.379(4)			

Table 18. Bond Angles (°).

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C14	O3	C15	111.3(2)	O1	C2	C3	120.5(3)
O1	C2	C1	120.8(3)	C3	C2	C1	118.8(3)
C8	C3	C4	118.5(2)	C8	C3	C2	122.2(3)
C4	C3	C2	119.3(3)	C5	C4	C3	120.9(3)
C4	C5	C6	121.0(2)	C5	C6	C7	117.9(2)
C5	C6	C9	122.4(2)	C7	C6	C9	119.7(2)
C8	C7	C6	121.1(2)	C7	C8	C3	120.6(3)
C13	C9	C6	129.5(2)	C13	C9	C10	106.3(2)
C6	C9	C10	124.1(2)	O2	C10	C11	127.5(2)
O2	C10	C9	125.5(2)	C11	C10	C9	107.0(2)
C12	C11	C16	129.1(2)	C12	C11	C10	106.8(2)
C16	C11	C10	124.0(2)	C11	C12	C22	129.0(2)
C11	C12	C13	109.2(2)	C22	C12	C13	121.6(2)
C9	C13	C14	127.4(2)	C9	C13	C12	110.6(2)
C14	C13	C12	121.9(2)	O3	C14	C13	108.8(2)
C21	C16	C17	117.9(2)	C21	C16	C11	120.8(2)
C17	C16	C11	121.3(2)	C18	C17	C16	120.8(3)
C17	C18	C19	120.4(3)	C20	C19	C18	119.7(3)
C19	C20	C21	119.8(3)	C20	C21	C16	121.2(2)
C23	C22	C27	118.3(2)	C23	C22	C12	120.4(2)
C27	C22	C12	121.3(2)	C24	C23	C22	120.9(2)
C25	C24	C23	120.1(3)	C26	C25	C24	119.5(3)
C25	C26	C27	120.6(3)	C26	C27	C22	120.7(3)

Table 19. Torsion Angles (°).

Atom	Atom	Atom	Atom	Angle	Atom	Atom	Atom	Atom	Angle
O1	C2	C3	C8	-173.3(3)	C1	C2	C3	C8	6.0(4)
O1	C2	C3	C4	5.0(4)	C1	C2	C3	C4	-175.7(3)
C8	C3	C4	C5	-0.2(4)	C2	C3	C4	C5	-178.5(2)
C3	C4	C5	C6	0.9(4)	C4	C5	C6	C7	-1.0(4)
C4	C5	C6	C9	-179.5(2)	C5	C6	C7	C8	0.2(4)
C9	C6	C7	C8	178.8(2)	C6	C7	C8	C3	0.5(4)
C4	C3	C8	C7	-0.5(4)	C2	C3	C8	C7	177.8(2)
C5	C6	C9	C13	-145.0(3)	C7	C6	C9	C13	36.5(4)
C5	C6	C9	C10	38.1(4)	C7	C6	C9	C10	-140.4(3)
C13	C9	C10	O2	-177.1(3)	C6	C9	C10	O2	0.4(4)
C13	C9	C10	C11	1.0(3)	C6	C9	C10	C11	178.5(2)
O2	C10	C11	C12	177.0(3)	C9	C10	C11	C12	-1.1(3)
O2	C10	C11	C16	1.1(4)	C9	C10	C11	C16	-176.9(2)
C16	C11	C12	C22	-7.8(5)	C10	C11	C12	C22	176.6(3)
C16	C11	C12	C13	176.3(2)	C10	C11	C12	C13	0.7(3)
C6	C9	C13	C14	5.3(5)	C10	C9	C13	C14	-177.4(2)
C6	C9	C13	C12	-177.9(2)	C10	C9	C13	C12	-0.6(3)
C11	C12	C13	C9	-0.1(3)	C22	C12	C13	C9	-176.3(2)
C11	C12	C13	C14	176.9(2)	C22	C12	C13	C14	0.7(4)
C15	O3	C14	C13	-158.9(2)	C9	C13	C14	O3	-92.0(3)
C12	C13	C14	O3	91.6(3)	C12	C11	C16	C21	-26.7(4)
C10	C11	C16	C21	148.3(3)	C12	C11	C16	C17	152.8(3)
C10	C11	C16	C17	-32.2(4)	C21	C16	C17	C18	1.3(4)
C11	C16	C17	C18	-178.2(2)	C16	C17	C18	C19	0.3(4)
C17	C18	C19	C20	-1.2(4)	C18	C19	C20	C21	0.4(4)
C19	C20	C21	C16	1.2(4)	C17	C16	C21	C20	-2.0(4)
C11	C16	C21	C20	177.5(2)	C11	C12	C22	C23	-54.7(4)
C13	C12	C22	C23	120.7(3)	C11	C12	C22	C27	126.4(3)
C13	C12	C22	C27	-58.2(4)	C27	C22	C23	C24	0.5(4)
C12	C22	C23	C24	-178.4(2)	C22	C23	C24	C25	-0.2(4)
C23	C24	C25	C26	-0.3(4)	C24	C25	C26	C27	0.5(4)
C25	C26	C27	C22	-0.2(4)	C23	C22	C27	C26	-0.3(4)
C12	C22	C27	C26	178.6(2)					

VII. References.

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