Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

C-C Bond Migration in the Cycloisomerization of Oxygen-Tethered 1,6-Enynes

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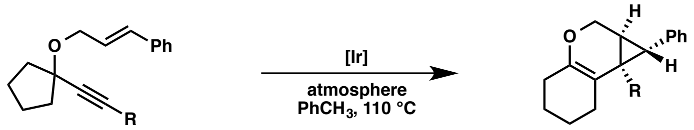
Materials and Methods: Reactions were performed under an argon atmosphere unless otherwise noted. Tetrahydrofuran, toluene, and benzene were purified by passing through activated alumina columns. All other reagents were used as received unless otherwise noted. Commercially available chemicals were purchased from Alfa Aesar (Ward Hill, MA), Sigma-Aldrich (St. Louis, MO), Oakwood Products, (West Columbia, SC), Strem (Newburport, MA) and TCI America (Portland, OR). Qualitative TLC analysis was performed on 250 mm thick, 60 Å, glass backed, F254 silica (Silicycle, Quebec City, Canada). Visualization was accomplished with UV light and exposure to *p*-anisaldehyde or ceric ammonium molybdate (CAM) solutions followed by heating. Flash chromatography was performed using Silicycle silica gel (230-400 mesh). ^{1}H NMR spectra were acquired on a Varian 400 MR (at 400 MHz) and are reported relative to $SiMe_4$ (δ 0.00). ^{13}C NMR spectra were acquired on a Varian 400 MR (at 100 MHz) and are reported relative to $SiMe_4$ (δ 0.0). All IR spectra were obtained on NaCl plates (film) with a Bruker Tensor 27. High resolution mass spectrometry data were acquired by the Colorado State University Central Instrument Facility on an Agilent 6210 TOF LC/MS.

Additional Iridium Optimization

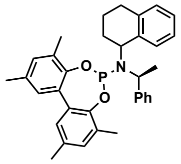
In our optimization of iridium conditions, we attempted the cycloisomerization with $Ir_4(CO)_{12}$, $Ir(CO)_2(acac)$, and $[Ir(dbcot)(L)]^+SbF_6^-$, as well as Vaska's complex ($IrCl(CO)(PPh_3)_2$), which Shibata and coworkers had achieved success with in the cycloisomerizations of heteroatom-tethered 1,6-enynes (Ref 10d), but none of these catalysts enabled full conversion, either under argon or CO, or when heated for several days (Table S1).

Table S1. Further iridium catalyst optimization.



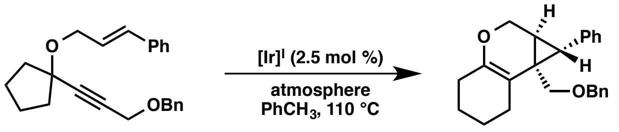
Entry	R	Catalyst (mol %)	Atmosphere	Time (h)	Result
1	*n*-Bu	$Ir_4(CO)_{12}$ (3)	CO, then Ar	40	1:1 SM:P
2	*n*-Bu	$Ir(CO)_2(acac)$ (5)	CO, then Ar	40	10:1 SM:P
3	*n*-Bu	$[Ir(dbcot)(L)]^+SbF_6^-$ (2.5)	CO	16	<5
4	CH_2OBn	$IrCl(CO)(PPh_3)_2$ (10)	Ar	16	<5
5	CH_2OBn	$IrCl(CO)(PPh_3)_2$ (5)	CO	16	<5

L =



Iridium dimers $[Ir(dbcot)Cl]_2$, $[Ir(cod)Cl]_2$, and $[Ir(coe)_2Cl]_2$, however, all produced the desired cycloisomerization product, with $[Ir(dbcot)Cl]_2$ performing the best. A comparison of these three iridium dimers is shown in Table S2. An increase in yield was observed when the catalysts were first exposed to CO, but the reactions were run under Ar, versus when the reactions were run under an atmosphere of CO.

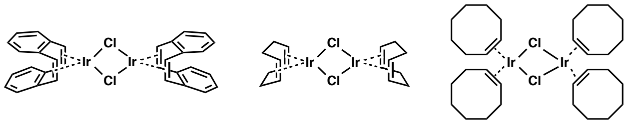
Table S2. Comparison of iridium dimers.



7i *8i*

Entry	$[Ir]^I$	Yield (%) CO (1 atm)	 CO, then Ar*
1	$[Ir(dbcot)Cl]_2$	72	87
2	$[Ir(cod)Cl]_2$	63	81
3	$[Ir(coe)_2Cl]_2$	47	50

*catalyst prepared under CO, but reaction run under Ar.



$[Ir(dbcot)Cl]_2$ $[Ir(cod)Cl]_2$ $[Ir(coe)_2Cl]_2$

Enyne Cycloisomerizations

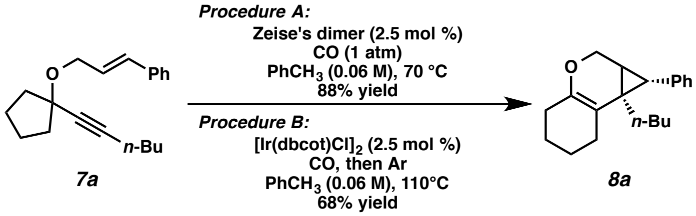
General Notes: All solvents used were anhydrous and all reactions were performed in flame-dried glassware. Without the addition of triethylamine to the flash chromatography eluent, decreased yields were observed. In the cycloisomerizations run with $[Ir(dbcot)Cl]_2$, dppp ((1,3-bis(diphenylphosphino)propane) was added in the work up to chelate the iridium. NMR spectra for the cycloisomerization products were taken in d_6-benzene, since the products were observed to decompose in $CDCl_3$.

A. General procedure for the cycloisomerization of oxygen-tethered 1,6-enynes catalyzed by Zeise's dimer ($[(C_2H_4)PtCl_2]_2$). To a solution of the 1,6-enyne (1 equiv) in toluene (0.06 M) in a 2-dram vial under argon was quickly added Zeise's dimer (2.5 mol %). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at the described temperature until all of the starting material was consumed, as determined by TLC. The reaction was allowed to cool to ambient temperature and diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography.

General procedure for the *scaled-up* cycloisomerization of oxygen-tethered 1,6-enynes catalyzed by Zeise's dimer ($[(C_2H_4)PtCl_2]_2$). To a solution of the 1,6-enyne (1 equiv) in toluene (0.15 M) in a 16 x 125 mm glass culture tube under argon was quickly added Zeise's dimer (2.5 mol %). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at the described temperature until all of the starting material was consumed, as determined by TLC. The reaction was allowed to cool to ambient temperature and the solvent was removed by rotary evaporation. The resulting residue was purified by flash chromatography.

B. General procedure for the cycloisomerization of oxygen-tethered 1,6-enynes catalyzed by $[Ir(dbcot)Cl]_2$. To a solution of the 1,6-enyne (1 equiv) in toluene (0.06 M) in a 16 x 125 mm glass culture tube under argon was quickly added $[Ir(dbcot)Cl]_2$ (2.5 mol %). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the solution turned a dark-blue/black color. The balloon was removed and argon was bubbled through the solution in the same manner. The septum was quickly replaced with a Teflon cap and the solution was stirred at 110 °C until all of the starting material was consumed, as determined by TLC. The reaction was allowed to cool to ambient temperature and diluted with an approximately equal amount of hexanes. 1,3-Bis(diphenylphosphino)propane (dppp) (0.25 equiv) was also added to the mixture. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography.

C. General procedure for the cycloisomerization of oxygen-tethered 1,6-enynes catalyzed by $PtCl_2$. To a solution of the 1,6-enyne (1 equiv) in toluene (0.06 M) in a 2-dram vial under argon was quickly added $PtCl_2$ (7 mol %). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at the described temperature until all of the starting material was consumed, as determined by TLC. The reaction was allowed to cool to ambient temperature and diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography.

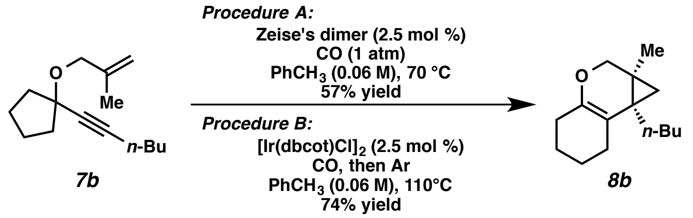


Tricycle 8a. ***Procedure A*****:** To a solution of enyne **7a** (16.0 mg, 56.7 µmol) in toluene (0.92 mL) in a 2-dram vial under argon was quickly added $[(C_2H_4)PtCl_2]_2$ (0.9 mg, 1.53 µmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 70 °C for 43 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 5:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8a** (14.1 mg, 88% yield, R_f = 0.70 in 2:1 CH_2Cl_2/hexanes, stained red with *p*-anisaldehyde) as a yellow oil.

Procedure B**:** To a solution of enyne **7a** (16.9 mg, 59.8 µmol) in toluene (0.92 mL) in a 16 x 125 mm glass culture tube under argon was quickly added $[Ir(dbcot)Cl]_2$ (1.3 mg, 1.53 µmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the solution turned a dark-blue/black color. The balloon was removed and argon was bubbled through the solution in the same manner. The septum was quickly replaced with a Teflon cap and the solution was stirred at 110 °C for 15.5 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. 1,3-Bis(diphenylphosphino)propane (dppp) (6.2 mg, 15.0 µmol) was also added to the mixture. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1

hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 5:1 hexanes/CH_2Cl_2w/ 0.5% Et_3N eluent) affording tricycle **8a** (11.5 mg, 68% yield) as a yellow oil.

Tricycle 8a: ^{1}H NMR (400 MHz; C_6D_6): δ 7.21-7.18 (m, 1H), 7.15 (d, *J* = 2.3 Hz, 1H), 7.09-7.04 (m, 3H), 4.08 (dd, *J* = 10.8, 4.5 Hz, 1H), 3.92 (dd, *J* = 10.9, 2.4 Hz, 1H), 2.29 (d, *J* = 5.5 Hz, 1H), 2.26-2.02 (m, 4H), 1.65-1.09 (m, 10H), 0.82 (d, *J* = 14.6 Hz, 3H), 0.62 (ddd, *J* = 14.0, 11.1, 5.7 Hz, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 147.8, 139.1, 129.4, 128.4, 126.2, 110.8, 64.5, 38.4, 30.2, 29.3, 28.1, 26.4, 25.6, 25.3, 23.8, 23.4, 23.3, 14.5; IR (film) 2929, 2858, 1673, 1447, 1145 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{26}O + H]^+$: 283.2056, found 283.2045.

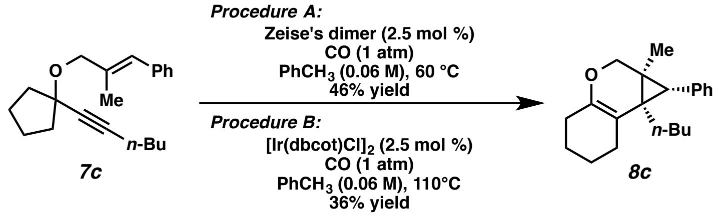


Tricycle 8b. ***Procedure A*****:** To a solution of enyne **7b** (31.5 mg, 0.143 mmol) in toluene (2.5 mL) in a 2-dram vial under argon was quickly added $[(C_2H_4)PtCl_2]_2$ (2.2 mg, 3.74 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 70 °C for 19 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 20:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8b** (17.9 mg, 57% yield, R_f = 0.81 in 2:1 CH_2Cl_2/hexanes, stained orange with *p*-anisaldehyde) as a colorless oil.

Procedure B**:** To a solution of enyne **7b** (13.3 mg, 60.4 μmol) in toluene (0.92 mL) in a 16 x 125 mm glass culture tube under argon was quickly added $[Ir(dbcot)Cl]_2$ (1.3 mg, 1.50 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the solution turned a dark-blue/black color. The balloon was removed and argon was bubbled through the solution in the same manner. The septum was quickly replaced with a Teflon cap and the solution was stirred at 110 °C for 15.5 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. 1,3-Bis(diphenylphosphino)propane (dppp) (6.2 mg, 15.0 μmol) was also added to the mixture. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 20:1

hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8b** (9.9 mg, 74% yield) as a colorless oil.

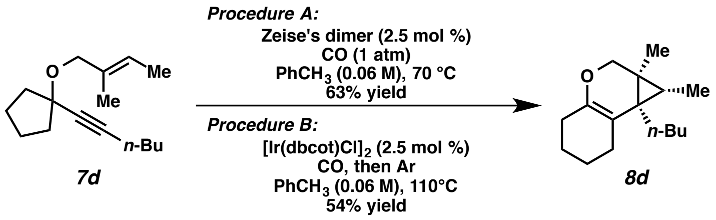
Tricycle 8b: ^{1}H NMR (400 MHz; C_6D_6): δ 3.74 (q, *J* = 12.4 Hz, 2H), 2.27-2.06 (m, 4H), 1.95-1.87 (m, 2H), 1.60-1.40 (m, 4H), 1.33-1.23 (m, 4H), 0.97 (d, *J* = 4.6 Hz, 3H), 0.93-0.91 (m, 3H), 0.41 (s, 1H), 0.35 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 147.5, 110.9, 70.5, 31.2, 30.6, 30.2, 28.1, 26.8, 25.5, 23.9, 23.8, 23.6, 23.3, 17.2, 14.4; IR (film) 2930, 2860, 1674, 1457, 1158 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{15}H_{24}O + H]^+$: 221.1900, found 221.1894.



Tricycle 8c. ***Procedure A***: To a solution of enyne **7c** (29.3 mg, 98.8 μmol) in toluene (1.5 mL) in a 2-dram vial under argon was quickly added $[(C_2H_4)PtCl_2]_2$ (1.5 mg, 2.55 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 60 °C for 24 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 6:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8c** (13.4 mg, 46% yield, R_f = 0.75 in 1:1 CH_2Cl_2/hexanes, stained orange with *p*-anisaldehyde) as a colorless oil.

Procedure B: To a solution of enyne **7c** (23.6 mg, 79.6 μmol) in toluene (1.2 mL) in a 16 x 125 mm glass culture tube under argon was quickly added $[Ir(dbcot)Cl]_2$ (1.7 mg, 1.97 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the solution turned a dark-blue/black color. The balloon was removed and argon was bubbled through the solution in the same manner. The septum was quickly replaced with a Teflon cap and the solution was stirred at 110 °C for 27 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 2:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8c** (8.4 mg, 36% yield) as a colorless oil.

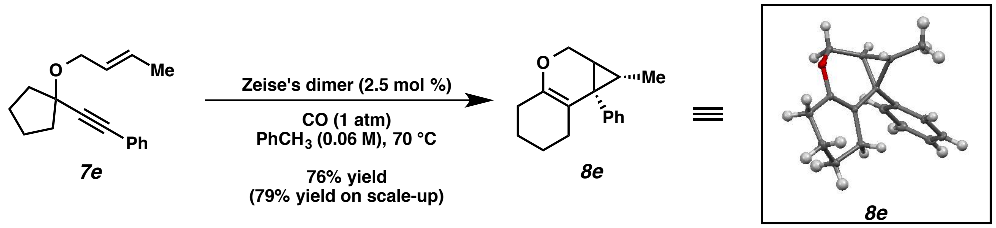
Tricycle 8c: ^{1}H NMR (400 MHz; C_6D_6): δ 7.27-7.07 (m, 5H), 3.86 (ABq, 2H, $\Delta\delta_{AB} = 0.12$, $J_{AB} = 10.8$ Hz), 2.31-2.24 (m, 1H), 2.22-2.12 (m, 2H), 1.90-1.80 (m, 1H), 1.65-1.42 (m, 6H), 1.39-1.27 (m, 1H), 1.22-1.12 (m, 2H), 0.99 (s, 3H), 0.98-0.91 (m, 1H), 0.83-0.79 (m, 3H); ^{13}C NMR (100 MHz; C_6D_6): δ 147.8, 138.0, 131.2, 130.2, 128.5, 126.4, 111.6, 71.2, 38.5, 29.9, 28.8, 28.1, 27.8, 27.4, 25.6, 23.9, 23.6, 23.3, 14.5, 14.4; IR (film) 2930, 2859, 1497, 1156, 1156 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{21}H_{28}O + H]^+$: 297.2213, found 297.2212.



Tricycle 8d. *Procedure A*: To a solution of enyne **7d** (15.5 mg, 66.1 μmol) in toluene (1.1 mL) in a 2-dram vial under argon was quickly added $[(C_2H_4)PtCl_2]_2$ (1.0 mg, 1.65 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 70 °C for 17 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 10:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8d** (9.8 mg, 63% yield, $R_f = 0.84$ in 2:1 CH_2Cl_2/hexanes, stained orange with *p*-anisaldehyde) as a colorless oil.

Procedure B: To a solution of enyne **7d** (14.4 mg, 61.4 μmol) in toluene (0.92 mL) in a 16 x 125 mm glass culture tube under argon was quickly added $[Ir(dbcot)Cl]_2$ (1.3 mg, 1.50 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the solution turned a dark-blue/black color. The balloon was removed and argon was bubbled through the solution in the same manner. The septum was quickly replaced with a Teflon cap and the solution was stirred at 110 °C for 15.5 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. 1,3-Bis(diphenylphosphino)propane (dppp) (6.2 mg, 15.0 μmol) was also added to the mixture. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 50:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8d** (7.8 mg, 54% yield) as a colorless oil.

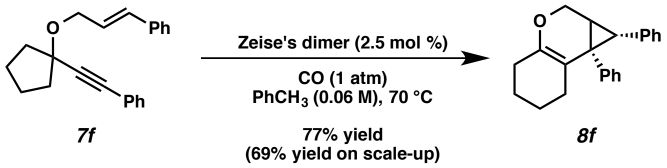
Tricycle 8d: ^{1}H NMR (400 MHz; C_6D_6): δ 3.74 (q, *J* = 10.8 Hz, 2H), 2.24-2.04 (m, 4H), 1.98-1.91 (m, 1H), 1.56-1.44 (m, 4H), 1.34-1.28 (m, 4H), 1.02 (t, *J* = 3.1 Hz, 2H), 0.92 (t, *J* = 7.0 Hz, 6H), 0.88 (s, 3H); ^{13}C NMR (100 MHz; C_6D_6): δ 147.2, 112.4, 71.2, 30.0, 28.2, 27.7, 26.9, 25.6, 24.9, 23.9, 23.8, 23.3, 20.6, 14.4, 12.0, 9.0; IR (film) 2926, 2956, 1457, 1157 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{16}H_{26}O + H]^+$: 235.2056, found 235.2050.



Tricycle 8e. ***Procedure A*****:** To a solution of enyne **7e** (36.7 mg, 0.153 mmol) in toluene (2.5 mL) in a 2-dram vial under argon was quickly added $[(C_2H_4)PtCl_2]_2$ (2.2 mg, 3.74 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 70 °C for 19 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 20:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8e** (27.9 mg, 76% yield, R_f = 0.81 in 2:1 CH_2Cl_2/hexanes, stained red with *p*-anisaldehyde) as a colorless oil.

Procedure A (Scale-up): To a solution of enyne **7e** (0.2715 g, 1.13 mmol) in toluene (7.5 mL) in a 16 x 125 mm glass culture tube under argon was quickly added $[(C_2H_4)PtCl_2]_2$ (16.6 mg, 28.3 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 70 °C for 20 h. The reaction was allowed to cool to ambient temperature and the solvent was removed by rotary evaporation. The resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 10:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8e** (0.2151 g, 79% yield) as a colorless oil.

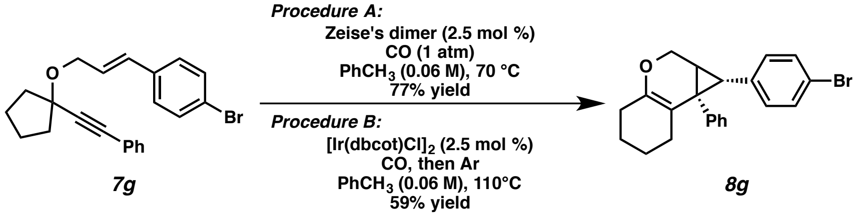
Tricycle 8e: ^{1}H NMR (400 MHz; C_6D_6): δ 7.22-7.17 (m, 4H), 7.10 (tt, *J* = 6.8, 2.2 Hz, 1H), 4.05-3.94 (m, 2H), 2.22-1.95 (m, 4H), 1.73 (dq, *J* = 15.4, 4.0 Hz, 1H), 1.45-1.35 (m, 4H), 1.13 (td, *J* = 4.9, 2.3 Hz, 1H), 0.86 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz; C_6D_6): δ 145.5, 141.0, 132.0, 128.3, 126.6, 112.3, 63.2, 31.8, 29.9, 28.2, 27.4, 25.8, 23.7, 23.3, 16.1; IR (film) 2928, 2858, 1670, 1445, 1150 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{17}H_{20}O + H]^+$: 241.1587, found 241.1583.



Tricycle 8f. ***Procedure A*:** To a solution of enyne **7f** (45.1 mg, 0.149 mmol) in toluene (2.5 mL) in a 2-dram vial under argon was quickly added $[(C_2H_4)PtCl_2]_2$ (2.2 mg, 3.75 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 70 °C for 18 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 20:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8f** (34.7 mg, 77% yield, $R_f = 0.80$ in 2:1 CH_2Cl_2/hexanes, stained red with *p*-anisaldehyde) as a yellow oil.

Procedure A (Scale-up): To a solution of enyne **7f** (0.1271 g, 0.420 mmol) in toluene (2.8 mL) in a 16 x 125 mm glass culture tube under argon was quickly added $[(C_2H_4)PtCl_2]_2$ (6.2 mg, 10.5 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 70 °C for 41 h. The reaction was allowed to cool to ambient temperature and the solvent was removed by rotary evaporation. The resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 20:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8f** (87.5 mg, 69% yield) as a yellow oil.

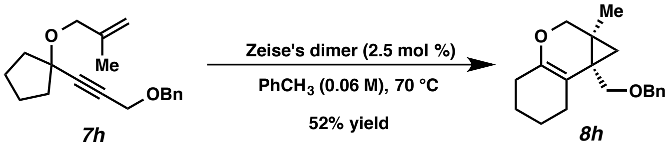
Tricycle 8f: ^{1}H NMR (400 MHz; C_6D_6): δ 6.99-6.91 (m, 8H), 6.65 (dd, *J* = 7.7, 1.6 Hz, 2H), 4.09-3.99 (m, 2H), 2.75 (d, *J* = 5.8 Hz, 1H), 2.28-2.07 (m, 2H), 2.02-1.95 (m, 2H), 1.72-1.66 (m, 1H), 1.46-1.38 (m, 3H), 1.31-1.25 (m, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 146.1, 139.2, 132.4, 128.1, 127.9, 126.7, 125.7, 112.3, 62.7, 36.7, 34.9, 31.3, 28.3, 27.2, 23.6, 23.2; IR (film) 2928, 1666, 1496, 1191 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{22}H_{22}O + H]^+$: 303.1743, found 303.1740.



Tricycle 8g. ***Procedure A*****:** To a solution of enyne **7g** (16.4 mg, 43.0 μmol) in toluene (0.70 mL) in a 2-dram vial under argon was quickly added $[(C_2H_4)PtCl_2]_2$ (0.6 mg, 1.02 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 70 °C for 18 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 20:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8g** (12.7 mg, 77% yield, $R_f = 0.79$ in 2:1 CH_2Cl_2/hexanes, stained red with *p*-anisaldehyde) as a colorless oil.

Procedure B**:** To a solution of enyne **7g** (20.5 mg, 53.8 μmol) in toluene (0.92 mL) in a 16 x 125 mm glass culture tube under argon was quickly added $[Ir(dbcot)Cl]_2$ (1.3 mg, 1.50 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the solution turned a dark-blue/black color. The balloon was removed and argon was bubbled through the solution in the same manner. The septum was quickly replaced with a Teflon cap and the solution was stirred at 110 °C for 6 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. 1,3-Bis(diphenylphosphino)propane (dppp) (7.4 mg, 17.9 μmol) was also added to the mixture. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 5:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8g** (12.0 mg, 59% yield, $R_f = 0.79$ in 2:1 CH_2Cl_2/hexanes, stained red with *p*-anisaldehyde) as a colorless oil.

Tricycle 8g: ^1H NMR (400 MHz; C_6D_6): δ 7.04-7.02 (m, 2H), 6.97-6.95 (m, 3H), 6.89-6.87 (m, 2H), 6.27-6.25 (m, 2H), 4.03-3.92 (m, 2H), 2.57 (d, J = 5.8 Hz, 1H), 2.26-2.05 (m, 2H), 1.98-1.89 (m, 1H), 1.83-1.79 (m, 1H), 1.70-1.60 (m, 1H), 1.46-1.37 (m, 3H), 1.30-1.21 (m, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 146.2, 138.6, 138.3, 132.3, 130.9, 129.7, 126.9, 119.5, 112.0, 62.5, 35.9, 35.0, 31.5, 28.2, 27.1, 23.5, 23.2; IR (film) 2928, 2858, 1668, 1491, 1145 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{22}H_{21}BrO + H]^+$: 381.0849, found 381.0842.



Tricycle 8h. ***Procedure A:*** To a solution of enyne **7h** (24.8 mg, 87.2 μmol) in toluene (1.3 mL) in a 2-dram vial under argon was quickly added $[(C_2H_4)PtCl_2]_2$ (1.3 mg, 2.21 μmol). The solution was stirred at 70 °C for 23 h. The reaction was allowed to cool to ambient temperature

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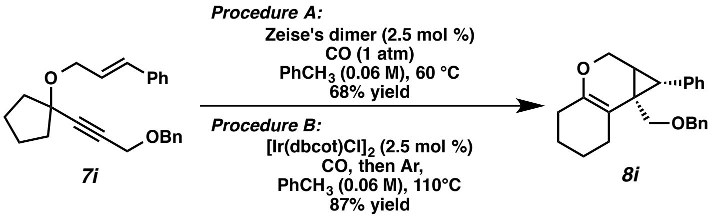
and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 2:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8h** (12.8 mg, 52% yield, $R_f = 0.30$ in 2:1 CH_2Cl_2/hexanes, stained blue with *p*-anisaldehyde) as a colorless oil.

Tricycle 8h: ^{1}H NMR (400 MHz; C_6D_6): δ 7.30-7.28 (m, 2H), 7.18-7.15 (m, 2H), 7.11-7.07 (m, 1H), 4.28 (ABq, 2H, $\Delta\delta_{AB} = 0.10$, $J_{AB} = 12.0$ Hz), 3.72 (ABq, 2H, $\Delta\delta_{AB} = 0.22$, $J_{AB} = 10.0$ Hz), 3.77 (d, $J = 10.4$ Hz, 1H), 2.91 (d, $J = 10.4$ Hz, 1H), 2.57-2.50 (m, 1H), 2.22-2.05 (m, 3H), 1.63-1.38 (m, 4H), 1.23-1.20 (m, 1H), 0.99 (s, 3H), 0.41-0.40 (m, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 146.2, 139.2, 128.5, 128.2, 127.7, 110.7, 73.1, 71.3, 68.0, 28.1, 28.0, 25.0, 24.5, 23.6, 23.2, 22.9, 16.0; IR (film) 2929, 2856, 1678, 1454, 1075 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{19}H_{24}O_2 + H]^+$: 285.1849, found 285.1848.

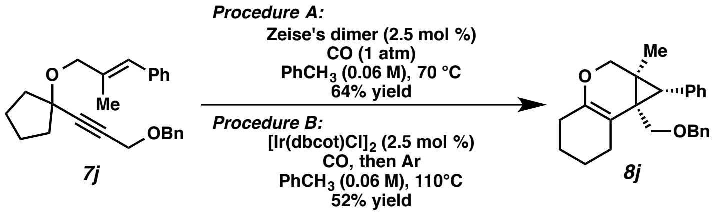


Tricycle 8i. ***Procedure A*****:** To a solution of enyne **7i** (34.5 mg, 99.6 μmol) in toluene (1.5 mL) in a 2-dram vial under argon was quickly added $[(C_2H_4)PtCl_2]_2$ (1.5 mg, 2.55 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 60 °C for 20 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 20:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8i** (23.4 mg, 68% yield, $R_f = 0.46$ (2:1 CH_2Cl_2/hexanes), stained blue with *p*-anisaldehyde) as a colorless oil.

Procedure B**:** To a solution of enyne **7i** (17.5 mg, 50.5 μmol) in toluene (0.77 mL) in a 16 x 125 mm glass culture tube under argon was quickly added $[Ir(dbcot)Cl]_2$ (1.1 mg, 1.25 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the solution turned a dark-blue/black color. The balloon was removed and argon was bubbled through the solution in the same manner. The septum was quickly replaced with a Teflon cap and the solution was stirred at 110 °C for 16 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. 1,3-

Bis(diphenylphosphino)propane (dppp) (6.2 mg, 1.50 μmol) was also added to the mixture. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 10:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8i** (15.2 mg, 87% yield, $R_f = 0.46$ (2:1 CH_2Cl_2/hexanes), stained blue with *p*-anisaldehyde) as a colorless oil.

Tricycle 8i: ^{1}H NMR (400 MHz; C_6D_6): δ 7.14-7.02 (m, 10H), 4.10 (ABq, 2H, $\Delta\delta_{AB} = 0.08$, $J_{AB} = 12.0$ Hz), 4.01-3.91 (m, 2H), 3.50 (d, $J = 10.5$ Hz, 1H), 2.94 (d, $J = 10.5$ Hz, 1H), 2.60 (d, $J = 5.9$ Hz, 1H), 2.57-2.50 (m, 1H), 2.31-2.07 (m, 3H), 1.80-1.77 (m, 1H), 1.61-1.49 (m, 4H); ^{13}C NMR (100 MHz; C_6D_6): δ 146.7, 139.3, 138.3, 129.3, 128.5, 128.2, 127.9, 127.5, 126.4, 111.2, 72.8, 71.1, 62.5, 35.2, 28.2, 27.3, 26.5, 25.4, 23.7, 23.3; IR (film) 3028, 2929, 2858, 1672, 1453, 1096 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{24}H_{26}O_2 + H]^+$: 347.2006, found 347.2009.

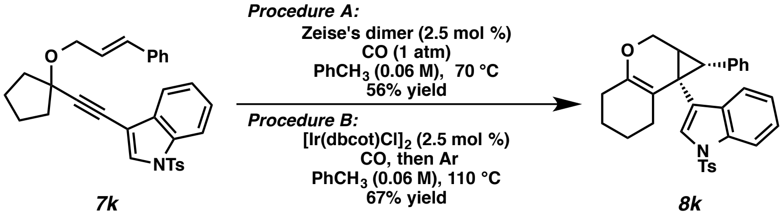


Tricycle 8j. ***Procedure A***: To a solution of enyne **7j** (52.9 mg, 0.148 mmol) in toluene (2.5 mL) in a 2-dram vial under argon was quickly added $[(C_2H_4)PtCl_2]_2$ (2.2 mg, 3.75 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 70 °C for 18 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 20:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8j** (34.1 mg, 64% yield, $R_f = 0.42$ in 2:1 CH_2Cl_2/hexanes, stained red with *p*-anisaldehyde) as a yellow oil.

Procedure B: To a solution of enyne **7j** (28.1 mg, 77.9 μmol) in toluene (1.2 mL) in a 16 x 125 mm glass culture tube under argon was quickly added $[Ir(dbcot)Cl]_2$ (1.7 mg, 1.97 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the solution turned a dark-blue/black color. The balloon was removed and argon was bubbled through the solution in the same manner. The septum was quickly replaced with a Teflon cap and the solution was stirred at 110 °C for 16 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1

hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 2:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8j** (14.5 mg, 52% yield) as a yellow oil.

Tricycle 8j: ^{1}H NMR (400 MHz; C_6D_6): δ 7.22 (d, J = 7.2 Hz, 2H), 7.13 (dt, J = 5.9, 2.1 Hz, 4H), 7.10-7.02 (m, 4H), 4.09 (ABq, 2H, $\Delta\delta_{AB}$ = 0.07, J_{AB} = 12.0 Hz), 3.85 (ABq, 2H, $\Delta\delta_{AB}$ = 0.30, J_{AB} = 10.0 Hz), 3.92 (d, J = 10.0 Hz, 1H), 3.00 (d, J = 10.0 Hz, 1H), 2.84 (s, 1H), 2.64-2.57 (m, 1H), 2.32-2.25 (m, 1H), 2.19-2.13 (m, 2H), 1.65-1.45 (m, 4H), 1.09 (s, 3H); ^{13}C NMR (100 MHz; C_6D_6): δ 146.5, 139.2, 137.6, 130.8, 128.6, 128.5, 127.9, 127.6, 126.5, 111.5, 73.3, 69.2, 68.4, 36.5, 31.9, 28.1, 27.7, 25.1, 23.7, 23.6, 23.1, 13.1; IR (film) 2930, 2856, 1678, 1445, 1155 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{25}H_{28}O_2 + H]^+$: 361.2162, found 361.2169.

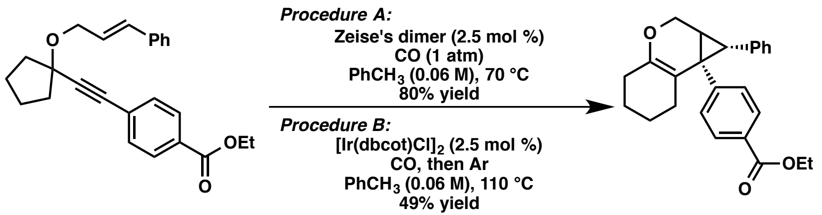


Tricycle 8k. ***Procedure A*****:** To a solution of enyne **7k** (78.0 mg, 0.157 mmol) in toluene (2.5 mL) in a 2-dram vial under argon was quickly added $[(C_2H_4)PtCl_2]_2$ (2.2 mg, 3.75 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 70 °C for 20.5 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 10:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8k** (43.6 mg, 56% yield, R_f = 0.67 in 2:1 CH_2Cl_2/hexanes, stained purple with *p*-anisaldehyde) as a colorless oil.

Procedure B**:** To a solution of enyne **7k** (49.7 mg, 99.9 μmol) in toluene (1.7 mL) in a 16 x 125 mm glass culture tube under argon was quickly added $[Ir(dbcot)Cl]_2$ (2.2 mg, 2.55 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the solution turned a dark-blue/black color. The balloon was removed and argon was bubbled through the solution in the same manner. The septum was quickly replaced with a Teflon cap and the solution was stirred at 110 °C for 15 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 9:1 hexanes/CH_2Cl_2 w/ 0.5%

Et_3N eluent) affording tricycle **8k** (33.1 mg, 67% yield, $R_f = 0.56$ in 2:1 CH_2Cl_2/hexanes, stained purple with *p*-anisaldehyde) as a colorless oil.

Tricycle 8k: ^1H NMR (400 MHz; C_6D_6): δ 8.15 (d, *J* = 8.2 Hz, 1H), 7.54-7.52 (m, 1H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.07-6.96 (m, 2H), 6.92-6.85 (m, 4H), 6.68 (d, *J* = 7.0 Hz, 2H), 6.51 (d, *J* = 8.1 Hz, 2H), 3.98-3.91 (m, 2H), 2.71 (d, *J* = 6.0 Hz, 1H), 2.19-2.00 (m, 3H), 1.84 (dt, *J* = 5.8, 2.8 Hz, 1H), 1.68 (s, 3H), 1.53-1.44 (m, 2H), 1.41-1.11 (m, 5H), 0.38-0.34 (m, 2H); ^{13}C NMR (100 MHz; C_6D_6): δ 179.4, 144.2, 138.8, 132.6, 129.7, 128.5, 128.2, 127.9, 127.2, 126.1, 124.9, 123.4, 114.2, 62.9, 28.2, 26.5, 23.6, 23.2, 21.1; IR (film) 2929, 2858, 1447, 1188 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{31}H_{29}NO_3S + H]^+$: 496.1941, found 496.1926.

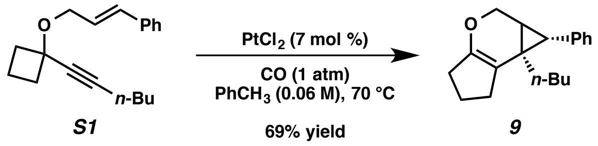


7l *8l*

Tricycle 8l. ***Procedure A*****:** To a solution of enyne **7l** (55.7 mg, 0.149 mmol) in toluene (2.5 mL) in a 2-dram vial under argon was quickly added $[(C_2H_4)PtCl_2]_2$ (2.2 mg, 3.75 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 70 °C for 20.5 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 10:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8l** (44.6 mg, 80% yield, $R_f = 0.55$ in 2:1 CH_2Cl_2/hexanes, stained purple with *p*-anisaldehyde) as a yellow oil.

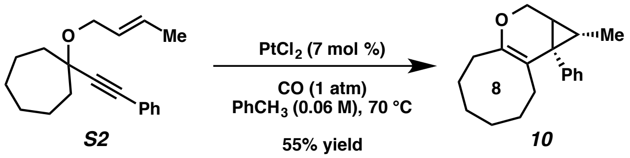
Procedure B**:** To a solution of enyne **7l** (34.6 mg, 99.6 μmol) in toluene (1.7 mL) in a 16 x 125 mm glass culture tube under argon was quickly added $[Ir(dbcot)Cl]_2$ (2.2 mg, 2.55 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the solution turned a dark-blue/black color. The balloon was removed and argon was bubbled through the solution in the same manner. The septum was quickly replaced with a Teflon cap and the solution was stirred at 110 °C for 15 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 2:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **8l** (16.8 mg, 49% yield) as a yellow oil.

Tricycle 8l: ^{1}H NMR (400 MHz; C_6D_6): δ 8.02 (d, *J* = 8.3 Hz, 2H), 6.97-6.91 (m, 5H), 6.59 (dd, *J* = 7.6, 1.9 Hz, 2H), 4.12-4.05 (m, 2H), 4.04-3.92 (m, 2H), 2.74 (d, *J* = 5.8 Hz, 1H), 2.27-2.05 (m, 2H), 1.93-1.91 (m, 1H), 1.90-1.86 (m, 1H), 1.61-1.58 (m, 1H), 1.46-1.39 (m, 3H), 1.31-1.23 (m, 1H), 0.98 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz; C_6D_6): δ 166.2, 146.5, 144.4, 138.6, 132.5, 129.4, 126.0, 111.4, 62.5, 60.7, 36.7, 34.7, 30.8, 28.2, 27.0, 23.5, 23.1, 14.3; IR (film) 2931, 2859, 1716, 1274, 1101 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{25}H_{26}O_3 + H]^+$: 375.1955, found 375.1943.



Tricycle 9. ***Procedure C*****:** To a solution of enyne **S1** (40.6 mg, 0.151 mmol) in toluene (2.5 mL) in a 2-dram vial under argon was quickly added $PtCl_2$ (2.8 mg, 1.05 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 70 °C for 16 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 2:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **9** (27.9 mg, 69% yield, R_f = 0.86 in 2:1 CH_2Cl_2/hexanes, stained brown with *p*-anisaldehyde) as a colorless oil.

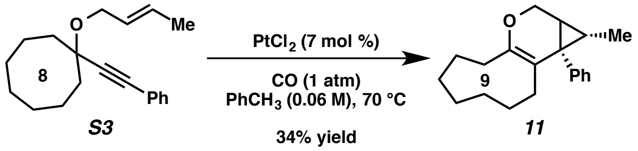
Tricycle 9: ^{1}H NMR (400 MHz; C_6D_6): δ 7.20-7.13 (m, 2H), 7.06 (dd, *J* = 7.3, 5.0 Hz, 3H), 4.19-4.16 (m, 1H), 4.01 (dd, *J* = 10.7, 2.9 Hz, 1H), 2.54-2.32 (m, 4H), 1.94-1.84 (m, 1H), 1.75-1.66 (m, 2H), 1.59-1.52 (m, 1H), 1.41-1.07 (m, 8H), 0.81 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz; C_6D_6): δ 150.3, 138.9, 129.2, 128.4, 126.2, 113.1, 64.2, 37.4, 31.8, 30.6, 29.9, 29.8, 26.5, 26.0, 23.2, 19.5, 14.4; IR (film) 3026, 2960, 1682, 1464, 1152, 698 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{19}H_{24}O + H]^+$: 269.1900, found 269.1910.



Tricycle 10. ***Procedure C*****:** To a solution of enyne **S2** (40.9 mg, 0.152 mmol) in toluene (2.5 mL) in a 2-dram vial under argon was quickly added $PtCl_2$ (2.8 mg, 1.05 μmol). CO was bubbled

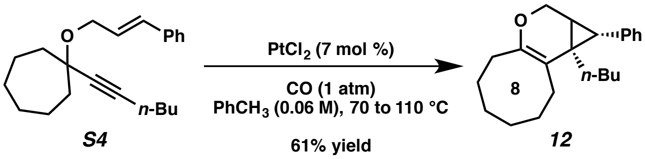
through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 70 °C for 16 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 1:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **10** (22.5 mg, 55% yield, $R_f = 0.85$ in 2:1 CH_2Cl_2/hexanes, stained blue with *p*-anisaldehyde) as a colorless oil.

Tricycle 10: ^{1}H NMR (400 MHz; C_6D_6): δ 7.26-7.24 (m, 2H), 7.16 (d, *J* = 14.8 Hz, 2H), 7.08 (dd, *J* = 8.5, 6.1 Hz, 1H), 4.05-3.93 (m, 2H), 2.33-2.16 (m, 2H), 2.08 (d, *J* = 6.3 Hz, 1H), 1.67-1.33 (m, 8H), 1.20-1.13 (m, 2H), 1.05 (dt, *J* = 5.3, 2.6 Hz, 1H), 0.90 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz; C_6D_6): δ 148.0, 141.6, 132.0, 127.9, 126.6, 112.9, 63.4, 31.7, 31.3, 30.3, 29.6, 29.3, 27.53, 27.51, 26.8, 25.8, 16.3; IR (film) 2923, 2851, 1658, 1493, 1164, 703 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{19}H_{24}O + H]^+$: 269.1900, found 269.1897.



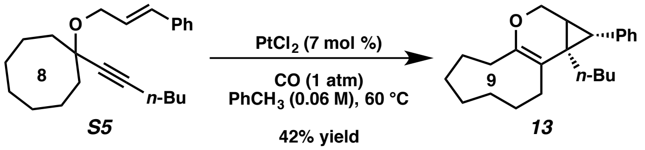
Tricycle 11. ***Procedure C*****:** To a solution of enyne **S3** (42.8 mg, 0.152 mmol) in toluene (2.5 mL) in a 2-dram vial under argon was quickly added $PtCl_2$ (2.8 mg, 1.05 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 70 °C for 20.5 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 10:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **11** (13.6 mg, 34% yield, $R_f = 0.85$ in 2:1 CH_2Cl_2/hexanes, stained blue with *p*-anisaldehyde) as a yellow oil.

Tricycle 11: ^{1}H NMR (400 MHz; C_6D_6): δ 7.28-7.26 (m, 2H), 7.18-7.15 (m, 2H), 7.11-7.06 (m, 1H), 3.99 (qd, *J* = 11.3, 3.2 Hz, 2H), 2.33-2.17 (m, 2H), 2.11 (dd, *J* = 4.2, 3.1 Hz, 1H), 1.69-1.59 (m, 2H), 1.51-1.30 (m, 10H), 1.08 (dd, *J* = 3.1, 2.1 Hz, 1H), 0.91 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz; C_6D_6): δ 148.6, 141.8, 132.1, 128.2, 126.6, 114.6, 64.2, 31.0, 30.4, 29.7, 28.2, 26.8, 26.5, 26.2, 25.7, 25.5, 25.4, 16.3; IR (film) 2926, 2853, 1653, 1493, 1146, 704 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{26}O + H]^+$: 283.2056, found 283.2056.



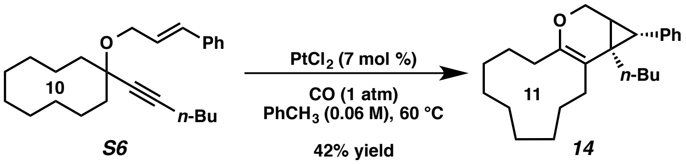
Tricycle 12. ***Procedure C*****:** To a solution of enyne **S4** (12.7 mg, 40.9 µmol) in toluene (0.67 mL) in a 2-dram vial under argon was quickly added $PtCl_2$ (0.7 mg, 2.63 µmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 70 °C for 21 h, then at 110 °C for 24 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 5:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **12** (7.7 mg, 61% yield, $R_f = 0.84$ in 2:1 CH_2Cl_2/hexanes, stained purple with *p*-anisaldehyde) as a yellow oil.

Tricycle 12: ^{1}H NMR (400 MHz; C_6D_6): δ 7.19-7.17 (m, 2H), 7.13-7.11 (m, 2H), 7.09-7.05 (m, 1H), 4.04-3.97 (m, 2H), 2.42 (d, *J* = 5.7 Hz, 1H), 2.39-2.14 (m, 4H), 1.79-1.10 (m, 14H), 0.82 (t, *J* = 7.3 Hz, 3H), 0.58 (ddd, *J* = 14.1, 11.1, 5.8 Hz, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 139.1, 129.3, 128.4, 126.2, 110.4, 63.5, 36.3, 31.6, 30.4, 30.3, 30.1, 29.5, 27.6, 26.9, 25.7, 25.6, 25.4, 23.2, 14.5; IR (film) 2924, 2854, 1660, 1447, 1128, 698 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{22}H_{30}O + H]^+$: 311.2369, found 311.2355.



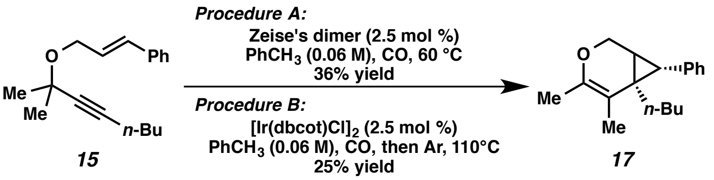
Tricycle 13. ***Procedure C*****:** To a solution of enyne **S5** (19.6 mg, 60.4 µmol) in toluene (1.0 mL) in a 2-dram vial under argon was quickly added $PtCl_2$ (1.2 mg, 4.51 µmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 60 °C for 21 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 20:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **13** (8.3 mg, 42% yield, $R_f = 0.87$ in 2:1 CH_2Cl_2/hexanes, stained blue with *p*-anisaldehyde) as a yellow oil.

Tricycle 13: ^{1}H NMR (400 MHz; C_6D_6): δ 7.20-7.17 (m, 1H), 7.15-7.13 (m, 2H), 7.10-7.06 (m, 1H), 4.04 (dd, J = 10.7, 4.0 Hz, 1H), 3.98-3.94 (m, 1H), 2.42 (d, J = 5.7 Hz, 1H), 2.39-2.30 (m, 3H), 2.21-2.15 (m, 1H), 1.81-1.08 (m, 19H), 0.82 (t, J = 7.3 Hz, 3H), 0.60 (ddd, J = 14.1, 11.2, 5.7 Hz, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 150.8, 139.1, 129.3, 128.4, 126.3, 111.3, 64.1, 37.0, 30.6, 30.4, 29.7, 27.1, 26.9, 26.5, 26.2, 25.6, 25.5, 24.9, 24.3, 23.3, 14.5; IR (film) 2926, 2856, 1654, 1497, 1183 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{23}H_{32}O + H]^+$: 325.2526, found 325.2517.



Tricycle 14. ***Procedure C*:** To a solution of enyne **S6** (21.1 mg, 59.8 μmol) in toluene (1.0 mL) in a 2-dram vial under argon was quickly added $PtCl_2$ (1.2 mg, 4.51 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 60 °C for 21 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 10:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording tricycle **14** (8.9 mg, 42% yield, R_f = 0.86 in 2:1 CH_2Cl_2/hexanes, stained brown/blue in *p*-anisaldehyde) as a colorless oil.

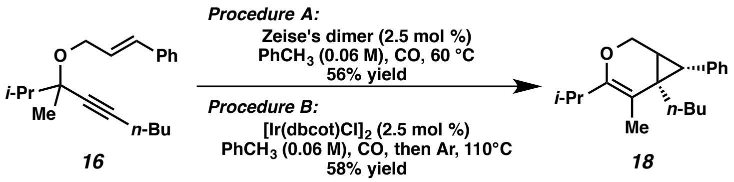
Tricycle 14: ^{1}H NMR (400 MHz; C_6D_6): δ 7.22-7.19 (m, 4H), 7.11-7.07 (m, 1H), 4.26 (dd, J = 11.3, 6.3 Hz, 1H), 3.62 (dd, J = 11.4, 4.6 Hz, 1H), 2.54-2.39 (m, 2H), 2.30-2.21 (m, 2H), 2.18 (d, J = 5.2 Hz, 1H), 2.00-1.89 (m, 2H), 1.74-1.08 (m, 18H), 0.80 (t, J = 7.3 Hz, 3H), 0.69 (ddd, J = 14.0, 11.1, 5.7 Hz, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 151.3, 139.1, 129.1, 128.4, 126.3, 112.4, 66.9, 39.5, 29.9, 29.7, 29.3, 27.8, 26.8, 26.44, 26.4, 26.3, 25.8, 25.53, 25.48, 25.2, 23.2, 22.4, 14.4; IR (film) 2927, 2857, 1498, 1154, 721 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{25}H_{36}O + H]^+$: 353.2839, found 353.2831.



Bicycle 17. ***Procedure A*****:** To a solution of enyne **15** (20.6 mg, 80.3 μmol) in toluene (1.2 mL) in a 2-dram vial under argon was quickly added $[(C_2H_4)PtCl_2]_2$ (1.2 mg, 2.04 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 60 °C for 19.5 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (50:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 2:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording bicycle **17** (7.5 mg, 36% yield, $R_f = 0.78$ in 2:1 CH_2Cl_2/hexanes, stained orange with *p*-anisaldehyde) as a yellow oil.

Procedure B**:** To a solution of enyne **15** (15.6 mg, 60.8 μmol) in toluene (0.92 mL) in a 16 x 125 mm glass culture tube under argon was quickly added $[Ir(dbcot)Cl]_2$ (1.3 mg, 1.50 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the solution turned a dark-blue/black color. The balloon was removed and argon was bubbled through the solution in the same manner. The septum was quickly replaced with a Teflon cap and the solution was stirred at 110 °C for 18 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. 1,3-Bis(diphenylphosphino)propane (dppp) (6.2 mg, 15.0 μmol) was also added to the mixture. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 50:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording bicycle **17** (3.9 mg, 25% yield) as a yellow oil.

Bicycle 17: ^1H NMR (400 MHz; C_6D_6): δ 7.16 (d, *J* = 14.7 Hz, 3H), 7.08-7.06 (m, 2H), 4.10 (dd, *J* = 11.0, 5.1 Hz, 1H), 3.80 (dd, *J* = 11.0, 3.4 Hz, 1H), 2.17 (d, *J* = 5.4 Hz, 1H), 1.79 (d, *J* = 0.9 Hz, 3H), 1.70 (d, *J* = 0.9 Hz, 3H), 1.65-1.58 (m, 1H), 1.47 (td, *J* = 5.3, 3.4 Hz, 1H), 1.36-1.09 (m, 4H), 0.81 (t, *J* = 7.3 Hz, 3H), 0.61 (ddd, *J* = 14.0, 10.9, 5.9 Hz, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 146.2, 139.1, 129.4, 126.2, 108.5, 65.4, 38.7, 30.0, 27.2, 25.4, 23.2, 16.8, 14.4, 14.0; IR (film) 2956, 2859, 2017, 1948, 1384, 1150 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{18}H_{24}O + H]^+$: 257.1900, found 257.1888.



Bicycle 18. ***Procedure A*****:** To a solution of enyne **16** (42.2 mg, 0.148 mmol) in toluene (2.5 mL) in a 2-dram vial under argon was quickly added $[(C_2H_4)PtCl_2]_2$ (2.2 mg, 3.74 μmol). CO was

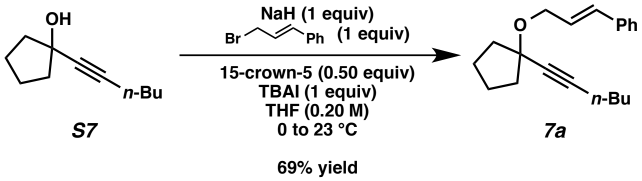
bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed and the solution was stirred at 60 °C for 20 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 9:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording bicycle **18** (23.8 mg, 56% yield, $R_f = 0.78$ in 2:1 CH_2Cl_2/hexanes, stained orange with *p*-anisaldehyde) as a yellow oil.

Procedure B: To a solution of enyne **16** (28.9 mg, 0.102 mmol) in toluene (1.5 mL) in a 16 x 125 mm glass culture tube under argon was quickly added $[Ir(dbcot)Cl]_2$ (2.2 mg, 2.55 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the solution turned a dark-blue/black color. The balloon was removed and argon was bubbled through the solution in the same manner. The septum was quickly replaced with a Teflon cap and the solution was stirred at 110 °C for 23 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. 1,3-Bis(diphenylphosphino)propane (dppp) (10.3 mg, 25.0 μmol) was also added to the mixture. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 20:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent) affording bicycle **18** (16.9 mg, 58% yield) as a yellow oil.

Bicycle 18: ^{1}H NMR (400 MHz; C_6D_6): δ 7.18-7.14 (m, 2H), 7.08-7.06 (m, 3H), 4.19 (ddd, *J* = 11.1, 5.9, 0.9 Hz, 1H), 3.65 (dd, *J* = 11.1, 4.1 Hz, 1H), 2.80-2.69 (m, 1H), 2.05 (d, *J* = 5.1 Hz, 1H), 1.73 (d, *J* = 1.0 Hz, 3H), 1.65-1.58 (m, 1H), 1.52-1.48 (m, 1H), 1.40-1.21 (m, 4H), 1.18 (dd, *J* = 6.8, 1.1 Hz, 3H), 1.13 (dd, *J* = 6.8, 1.0 Hz, 3H), 0.81 (t, *J* = 7.3 Hz, 3H), 0.64-0.57 (m, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 154.6, 139.1, 133.7, 129.4, 127.1, 126.2, 107.4, 67.3, 39.2, 30.2, 30.0, 29.8, 29.0, 27.4, 25.0, 23.1, 20.3, 20.2, 14.4, 13.3; IR (film) 2929, 2859, 1454, 1094, 698 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{28}O + H]^+$: 285.2213, found 285.2201.

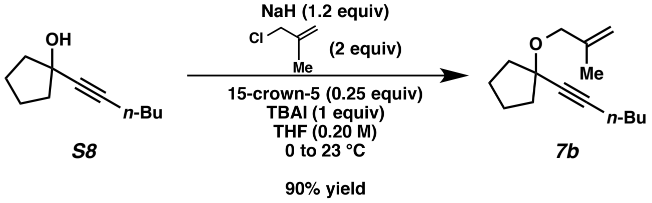
Substrate Synthesis

General procedure for the alkylation of tertiary propargyl alcohols to give oxygen-tethered 1,6-enyne starting materials. To a solution of the tertiary propargyl alcohol (1 equiv) in THF (0.20 M) in a flame-dried flask under argon at 0 °C was added NaH (1.2 equiv, 60% dispersion in mineral oil). The solution was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (0.25 equiv), tetrabutylammonium iodide (1 equiv), and the allylic halide (1 equiv). The resulting mixture was stirred at ambient temperature until completion, as determined by TLC. The reaction was quenched with sat. aq. NH_4Cl. The layers were separated, and the aqueous layer was extracted with Et_2O (3x). The combined organic layers were washed with brine, then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography.



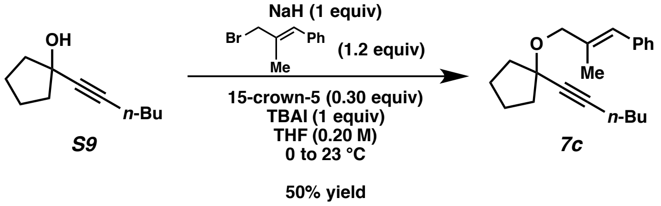
Enyne 7a. To a solution of tertiary propargyl alcohol **S7** (0.166 g, 1.00 mmol) in THF (5.0 mL) at 0 °C was added NaH (40.0 mg, 60% dispersion in mineral oil, 1.00 mmol). The solution was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (99.0 µL, 0.500 mmol), tetrabutylammonium iodide (0.369 g, 1.00 mmol), and cinnamyl bromide (0.197 g, 1.00 mmol). The resulting mixture was stirred at ambient temperature for 16 h. The reaction was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (25 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 → 2:1 hexanes/CH_2Cl_2 eluent), affording enyne **7a** (0.195 g, 69% yield, $R_f = 0.67$ in 1:1 hexanes/CH_2Cl_2, stained blue with *p*-anisidine) as a yellow oil.

Enyne 7a: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.39-7.37 (m, 2H), 7.32-7.28 (m, 2H), 7.24-7.19 (m, 1H), 6.61 (d, J = 15.9 Hz, 1H), 6.33 (dt, J = 15.9, 6.0 Hz, 1H), 4.23 (dd, J = 6.0, 1.5 Hz, 2H), 2.24 (t, J = 7.0 Hz, 2H), 2.06-1.99 (m, 2H), 1.92-1.85 (m, 2H), 1.80-1.69 (m, 4H), 1.55-1.40 (m, 4H), 0.92 (d, J = 14.5 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 137.2, 131.6, 128.6, 127.5, 127.3, 126.6, 85.6, 81.7, 80.8, 65.7, 39.9, 31.1, 23.5, 22.1, 18.6, 13.8; IR (film) 2959, 2872, 1496, 1053, 964 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{26}O + H]^+$: 283.2056, found 283.2056.



Enyne 7b. To a solution of tertiary propargyl alcohol **S8** (0.415 g, 2.49 mmol) in THF (13 mL) at 0 °C was added NaH (0.125 g, 60% dispersion in mineral oil, 3.14 mmol). The solution was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (0.120 mL, 0.625 mmol), tetrabutylammonium iodide (0.924 g, 2.50 mmol), and methallyl chloride (0.550 mL, 5.57 mmol). The resulting mixture was stirred at ambient temperature for 19.5 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 15 mL). The combined organic layers were washed with brine (40 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (100% hexanes → 5:1 hexanes/EtOAc eluent), affording enyne **7b** (0.470 g, 90% yield, $R_f = 0.85$ in 1:1 hexanes/CH_2Cl_2, stained blue with *p*-anisaldehyde) as a colorless oil.

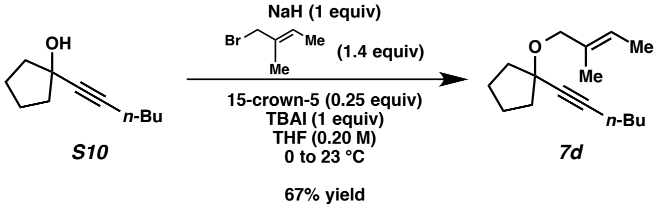
Enyne 7b: ^1H NMR (400 MHz; $CDCl_3$): δ 4.98 (dd, *J* = 2.2, 0.9 Hz, 1H), 4.84 (t, *J* = 1.1 Hz, 1H), 3.94 (s, 2H), 2.21 (t, *J* = 6.9 Hz, 2H), 2.03-1.96 (m, 2H), 1.88-1.78 (m, 2H), 1.75 (s, 3H), 1.74-1.65 (m, 4H), 1.53-1.38 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 143.3, 111.4, 85.2, 81.8, 80.6, 77.2, 68.7, 39.8, 31.1, 23.5, 22.1, 20.0, 18.6, 13.8; IR (film) 2960, 2873, 1452, 1094 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{15}H_{24}O + H]^+$: 221.1900, found 221.1902.



Enyne 7c. To a solution of tertiary propargyl alcohol **S9** (0.167 g, 1.00 mmol) in THF (5.0 mL) at 0 °C was added NaH (40.0 mg, 60% dispersion in mineral oil, 1.00 mmol). The solution was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (60.0 µL, 0.303 mmol),

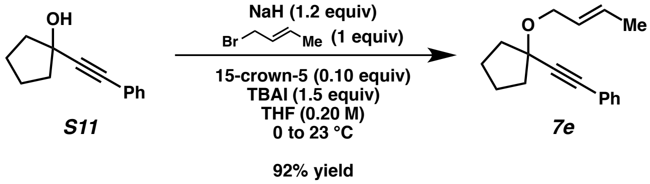
tetrabutylammonium iodide (0.369 g, 1.00 mmol), and 3-bromo-2-methyl-1-phenyl-1-propene (0.258 g, 1.22 mmol). The resulting mixture was stirred at ambient temperature for 20 h. The reaction was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (25 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (20:1 hexanes/CH_2Cl_2 → 1:1 hexanes/CH_2Cl_2 eluent), affording enyne **7c** (0.148 g, 50% yield, R_f = 0.63 in 1:1 hexanes/CH_2Cl_2, stained blue with *p*-anisaldehyde) as a colorless oil.

Enyne 7c: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.34-7.27 (m, 4H), 7.21-7.17 (m, 1H), 6.53 (s, 1H), 4.09 (s, 2H), 2.24 (t, *J* = 6.9 Hz, 2H), 2.08-2.01 (m, 2H), 1.90 (s, 3H), 1.88-1.84 (m, 2H), 1.82-1.69 (m, 4H), 1.53-1.40 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 138.1, 136.2, 129.1, 128.1, 126.3, 126.1, 98.8, 85.4, 81.8, 80.8, 70.9, 39.9, 31.1, 23.5, 22.1, 18.6, 15.9, 13.8; IR (film) 2959, 2872, 1446, 1047 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{21}H_{28}O + H]^+$: 297.2213, found 297.2208.



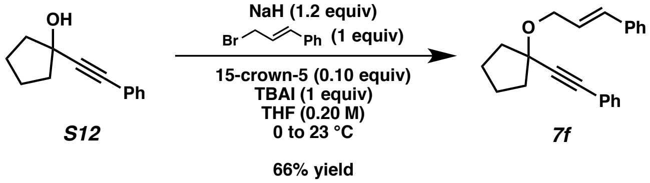
Enyne 7d. To a solution of tertiary propargyl alcohol **S10** (0.166 g, 0.996 mmol) in THF (5.0 mL) at 0 °C was added NaH (40.0 mg, 60% dispersion in mineral oil, 1.00 mmol). The solution was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (60.0 µL, 0.303 mmol), tetrabutylammonium iodide (0.369 g, 1.00 mmol), and 3-bromo-2-methyl-1-methyl-1-propene (0.208 g, 1.40 mmol). The resulting mixture was stirred at ambient temperature for 16 h. The reaction was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (40 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (hexanes → 1:1 hexanes/CH_2Cl_2 eluent), affording enyne **7d** (0.158 g, 67% yield, R_f = 0.71 in 1:1 hexanes/CH_2Cl_2, stained blue with *p*-anisaldehyde) as a colorless oil.

Enyne 7d: ^{1}H NMR (400 MHz; $CDCl_3$): δ 5.51 (dtdd, *J* = 8.3, 5.7, 2.6, 1.3 Hz, 1H), 3.90 (s, 2H), 2.22 (t, *J* = 6.9 Hz, 2H), 2.02-1.96 (m, 2H), 1.86-1.78 (m, 2H), 1.76-1.67 (m, 4H), 1.65 (d, *J* = 1.0 Hz, 3H), 1.61 (dt, *J* = 6.7, 0.9 Hz, 3H), 1.51-1.39 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 133.8, 121.9, 85.1, 82.0, 80.5, 70.9, 39.8, 31.1, 23.4, 22.1, 18.6, 14.0, 13.8, 13.4; IR (film) 2960, 2934, 2861, 1449, 1046 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{16}H_{26}O + H]^+$: 235.2056, found 235.2050.



Enyne 7e. To a solution of tertiary propargyl alcohol **S11** (0.150 g, 0.805 mmol) in THF (4.0 mL) at 0 °C was added NaH (38.9 mg, 60% dispersion in mineral oil, 0.973 mmol). The solution was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (16.0 µL, 81.0 µmol), tetrabutylammonium iodide (0.451 g, 1.22 mmol), and crotyl bromide (83.3 µL, 0.810 mmol). The resulting mixture was stirred at ambient temperature for 24 h. The reaction was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (30 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (100% hexanes → 9:1 hexanes/Et_2O eluent), affording enyne **7e** (0.179 g, 92% yield, $R_f = 0.71$ in 4:1 hexanes/EtOAc, stained blue with *p*-anisaldehyde) as a colorless oil.

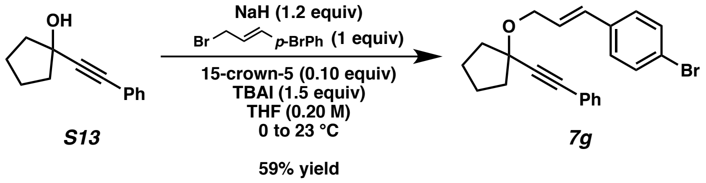
Enyne 7e: ^1H NMR (400 MHz; $CDCl_3$): δ 7.43 (td, *J* = 3.8, 1.7 Hz, 2H), 7.30 (t, *J* = 3.2 Hz, 3H), 5.79-5.60 (m, 2H), 4.08 (d, *J* = 6.1 Hz, 2H), 2.13-1.96 (m, 4H), 1.86-1.74 (m, 4H), 1.71 (dd, *J* = 6.2, 0.9 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 131.8, 129.1, 128.36, 128.35, 128.2, 126.6, 91.2, 84.9, 80.8, 66.1, 39.9, 23.6, 18.0; IR (film) 2965, 2857, 1443, 1088 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{17}H_{20}O + H]^+$: 241.1587, found 241.1587.



Enyne 7f. To a solution of tertiary propargyl alcohol **S12** (0.187 g, 1.00 mmol) in THF (5.0 mL) at 0 °C was added NaH (48.0 mg, 60% dispersion in mineral oil, 1.20 mmol). The solution was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (20.0 µL, 0.101 mmol), tetrabutylammonium iodide (0.369 g, 1.00 mmol), and cinnamyl bromide (0.198 g, 1.00 mmol). The resulting mixture was stirred at ambient temperature for 20 h. The reaction was quenched

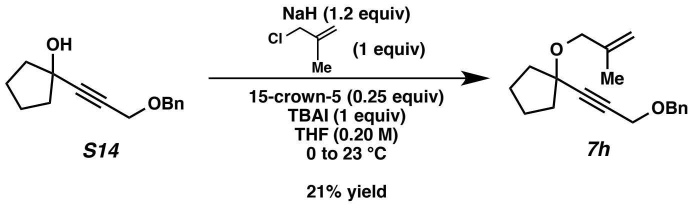
with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (30 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (100% hexanes → 1:1 hexanes/CH_2Cl_2 eluent), affording enyne **7f** (0.201 g, 66% yield, $R_f = 0.62$ in 1:1 hexanes/CH_2Cl_2, stained blue with *p*-anisaldehyde) as a colorless oil.

Enyne 7f: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.45-7.43 (m, 2H), 7.40-7.38 (m, 2H), 7.30 (dd, *J* = 8.5, 5.3 Hz, 5H), 7.24-7.20 (m, 1H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.36 (dt, *J* = 15.9, 5.9 Hz, 1H), 4.33 (dd, *J* = 6.0, 1.5 Hz, 2H), 2.19-2.01 (m, 4H), 1.89-1.76 (m, 4H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 137.2, 131.9, 131.8, 128.6, 128.4, 128.3, 127.6, 127.1, 126.6, 123.2, 91.0, 85.2, 81.1, 66.0, 39.9, 23.6; IR (film) 2965, 1598, 1445, 1048 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{22}H_{22}O + H]^+$: 303.1743, found 303.1743.



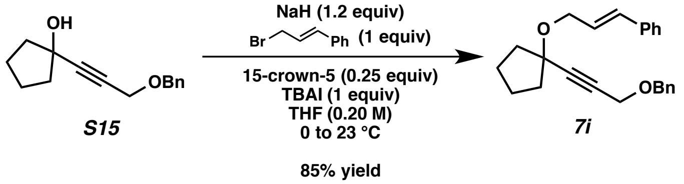
Enyne 7g. To a solution of tertiary propargyl alcohol **S13** (0.140 g, 0.750 mmol) in THF (3.8 mL) at 0 °C was added NaH (36.0 mg, 60% dispersion in mineral oil, 0.900 mmol). The solution was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (15.0 µL, 75.8 µmol), tetrabutylammonium iodide (0.420 g, 1.14 mmol), and *p*-bromocinnamyl bromide (0.207 g, 0.750 mmol). The resulting mixture was stirred at ambient temperature for 14 h. The reaction was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (30 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (100% hexanes → 1:1 hexanes/CH_2Cl_2 eluent), affording enyne **7g** (0.169 g, 59% yield, $R_f = 0.71$ in 4:1 hexanes/EtOAc, stained blue with *p*-anisaldehyde) as a colorless oil.

Enyne 7g: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.44-7.41 (m, 4H), 7.31 (t, *J* = 3.2 Hz, 3H), 7.24 (d, *J* = 8.5 Hz, 2H), 6.58 (d, *J* = 15.8 Hz, 1H), 6.35 (dt, *J* = 15.8, 5.9 Hz, 1H), 4.31 (dd, *J* = 5.8, 1.2 Hz, 2H), 2.17-1.99 (m, 4H), 1.85-1.76 (m, 4H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 136.1, 131.8, 131.7, 128.4, 128.3, 128.1, 128.0, 98.8, 77.4, 77.0, 69.9, 39.9, 23.6; IR (film) 2965, 1488, 1071 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{22}H_{21}BrO + H]^+$: 381.0849, found 381.0844.



Enyne 7h. To a solution of tertiary propargyl alcohol **S14** (0.150 g, 0.652 mmol) in THF (3.3 mL) at 0 °C was added NaH (31.2 mg, 60% dispersion in mineral oil, 0.780 mmol). The solution was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (32.0 µL, 0.163 mmol), tetrabutylammonium iodide (0.240 g, 0.650 mmol), and methallyl chloride (64.2 µL, 0.650 mmol). The resulting mixture was stirred at ambient temperature for 22 h. The reaction was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (30 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (100% hexanes → 10:1 hexanes/EtOAc eluent), affording enyne **7h** (38.3 mg, 21% yield, $R_f = 0.81$ in 3:1 hexanes/EtOAc, stained blue with *p*-anisaldehyde) as a colorless oil.

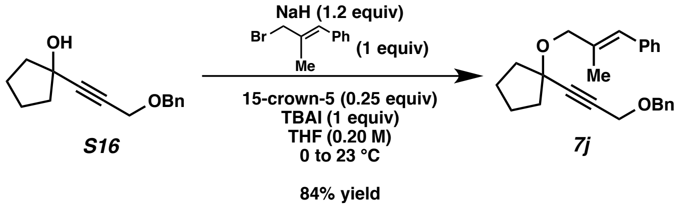
Enyne 7h: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.36 (d, *J* = 4.4 Hz, 4H), 7.31 (td, *J* = 6.6, 3.7 Hz, 1H), 5.00 (s, 1H), 4.86 (s, 1H), 4.61 (s, 2H), 4.23 (s, 2H), 3.97 (s, 2H), 2.06 (td, *J* = 10.8, 4.4 Hz, 2H), 1.95-1.88 (m, 2H), 1.81-1.70 (m, 7H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 143.0, 137.6, 128.6, 128.2, 128.0, 111.5, 88.5, 80.6, 80.5, 71.5, 68.9, 57.6, 39.7, 23.5, 20.0; IR (film) 2969, 2856, 1496, 1091 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{19}H_{24}O_2 + H]^+$: 285.1849, found 285.1851.



Enyne 7i. To a solution of tertiary propargyl alcohol **S15** (0.172 g, 0.749 mmol) in THF (3.8 mL) at 0 °C was added NaH (36.0 mg, 60% dispersion in mineral oil, 0.900 mmol). The solution was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (37.6 µL, 0.190 mmol), tetrabutylammonium iodide (0.280 g, 0.758 mmol), and cinnamyl bromide (0.147 g, 0.746 mmol). The resulting mixture was stirred at ambient temperature for 22 h. The reaction was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (30 mL),

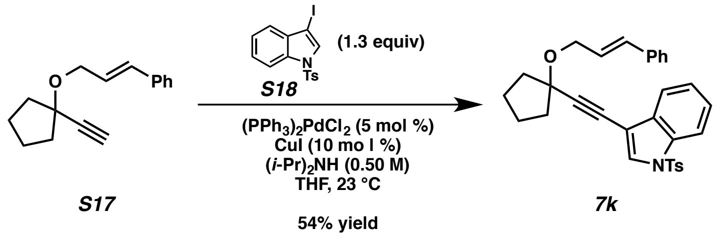
then dried over MgSO$_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (100% hexanes → 9:1 hexanes/EtOAc eluent), affording enyne **7i** (0.221 g, 85% yield, R$_f$ = 0.77 (3:1 hexanes/EtOAc), stained blue with *p*-anisaldehyde) as a colorless oil.

Enyne 7i: ^{1}H-NMR (400 MHz; CDCl$_3$): δ 7.39-7.34 (m, 5H), 7.31 (t, *J* = 7.5 Hz, 3H), 7.23 (dd, *J* = 8.3, 6.1 Hz, 2H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.33 (dt, *J* = 15.9, 5.9 Hz, 1H), 4.62 (s, 2H), 4.27-4.26 (m, 4H), 2.12-2.05 (m, 2H), 2.00-1.92 (m, 2H), 1.84-1.72 (m, 4H); ^{13}C NMR (100 MHz; CDCl$_3$): δ 137.6, 137.1, 131.8, 128.6, 128.2, 128.0, 127.6, 126.9, 126.6, 88.4, 80.9, 80.6, 71.6, 65.9, 57.7, 39.8, 23.5; IR (film) 2963, 2856, 1496, 1073 cm^{-1}; HRMS (ESI+) *m/z* calc'd for (M + H)$^+$ [C$_{24}$H$_{26}$O$_2$ + H]$^+$: 347.2006, found 347.2011.



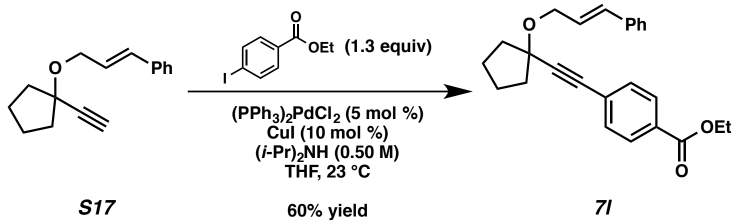
Enyne 7j. To a solution of tertiary propargyl alcohol **S16** (0.110 g, 0.475 mmol) in THF (2.4 mL) at 0 °C was added NaH (23.0 g, 60% dispersion in mineral oil, 0.571 mmol). The solution was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (23.8 µL, 0.120 mmol), tetrabutylammonium iodide (0.175 g, 0.475 mmol), and 3-bromo-2-methyl-1-phenyl-1-propene (0.101 g, 0.475 mmol). The resulting mixture was stirred at ambient temperature for 15 h. The reaction was quenched with sat. aq. NH$_4$Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et$_2$O (3 x 10 mL). The combined organic layers were washed with brine (30 mL), then dried over MgSO$_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (100% hexanes → 1:1 hexanes/CH$_2$Cl$_2$ eluent), affording enyne **7j** (0.144 g, 84% yield, R$_f$ = 0.55 in 1:1 hexanes/CH$_2$Cl$_2$, stained blue with *p*-anisaldehyde) as a colorless oil.

Enyne 7j: ^{1}H NMR (400 MHz; CDCl$_3$): δ 7.35 (dd, *J* = 6.0, 4.0 Hz, 3H), 7.30 (dt, *J* = 12.7, 6.1 Hz, 5H), 7.22-7.18 (m, 1H), 6.54 (s, 1H), 4.62 (s, 2H), 4.25 (s, 2H), 4.12 (s, 2H), 2.14-1.92 (m, 4H), 1.92 (s, 3H), 1.84-1.72 (m, 4H); ^{13}C NMR (100 MHz; CDCl$_3$): δ 138.0, 137.6, 135.9, 129.1, 128.6, 128.3, 128.2, 128.0, 126.4, 126.3, 88.5, 80.8, 80.6, 71.6, 71.2, 57.6, 39.8, 23.5, 15.9; IR (film) 2964, 2855, 1683, 1493, 1089 cm^{-1}; HRMS (ESI+) *m/z* calc'd for (M + H)$^+$ [C$_{25}$H$_{28}$O$_2$ + H]$^+$: 361.2162, found 361.2162.



Enyne 7k. To $(PPh_3)_2PdCl_2$ (52.7 mg, 75.1 μmol) and CuI (28.6 mg, 0.150 mmol) under argon was added $(i\text{-Pr})_2NH$ (3.0 mL). The mixture was stirred for 5 min, then 2-iodoindole **S18** (0.775 g, 1.95 mmol) was added and the mixture was stirred for 5 more min. Terminal alkyne **S17** (0.339 g, 1.50 mmol) was then added as a 0.50 M solution in THF. Additional THF (ca. 3.0 mL) was added to maintain dissolution. The mixture was stirred for 14 h, after which the reaction mixture was partitioned between 1 M HCl (10 mL) and Et_2O (5.0 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 5.0 mL). The combined organic layers were washed with brine (20 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (100% hexanes → 9:1 hexanes/EtOAc eluent), affording enyne **7k** (0.406 g, 54% yield, $R_f = 0.33$ in 9:1 hexanes/EtOAc, stained blue with *p*-anisaldehyde) as a brown amorphous solid.

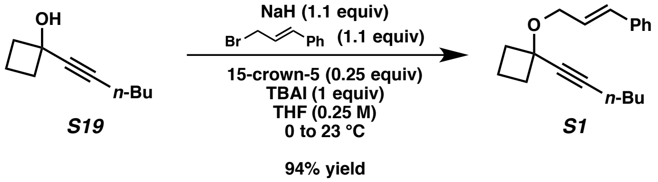
Enyne 7k: ^1H NMR (400 MHz; $CDCl_3$): δ 7.97 (d, $J = 8.3$ Hz, 1H), 7.79 (d, $J = 8.3$ Hz, 2H), 7.72 (s, 1H), 7.61 (d, $J = 7.7$ Hz, 1H), 7.38 (t, $J = 8.2$ Hz, 3H), 7.34-7.28 (m, 3H), 7.23 (t, $J = 8.3$ Hz, 3H), 6.65 (d, $J = 16.1$ Hz, 1H), 6.40-6.33 (m, 1H), 4.36-4.34 (m, 2H), 2.35 (s, 3H), 2.22-2.04 (m, 4H), 1.90-1.78 (m, 4H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 145.4, 135.1, 134.3, 131.9, 130.2, 128.8, 128.6, 127.7, 127.1, 127.0, 126.6, 125.6, 123.8, 120.6, 113.7, 95.5, 81.2, 77.4, 66.1, 40.1, 23.6, 21.7; IR (film) 2966, 1376, 1175, 964 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{31}H_{29}NO_3S + H]^+$: 496.1941, found 496.1960.



Enyne 7l. To $(PPh_3)_2PdCl_2$ (52.7 mg, 75.1 μmol) and CuI (28.6 mg, 0.150 mmol) under argon was added $(i\text{-Pr})_2NH$ (3.0 mL). The mixture was stirred for 5 min, then 4-iodoethylbenzoate (0.330 mL, 1.95 mmol) was added and the mixture was stirred for 5 min. Terminal alkyne **S17** (0.339 g, 1.50 mmol) was then added as a 0.50 M solution in THF. Additional THF (ca. 3.0 mL) was added to maintain dissolution. The mixture was stirred for 14 h, after which the reaction mixture was partitioned between 1 M HCl (10 mL) and Et_2O (5.0 mL). The layers were

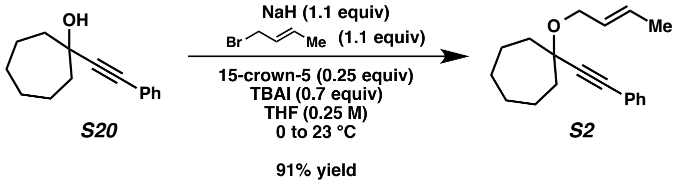
separated and the aqueous layer was extracted with Et_2O (3 x 5.0 mL). The combined organic layers were washed with brine (20 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (100% hexanes → 9:1 hexanes/EtOAc eluent), affording enyne **7l** (0.338 g, 60% yield, $R_f = 0.42$ in 9:1 hexanes/EtOAc, stained blue with *p*-anisaldehyde) as a colorless oil.

Enyne 7l: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.99-7.97 (m, 2H), 7.50-7.48 (m, 2H), 7.40-7.38 (m, 2H), 7.30 (dd, *J* = 8.1, 6.7 Hz, 2H), 7.24-7.20 (m, 1H), 6.63 (t, *J* = 14.3 Hz, 1H), 6.39-6.27 (m, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.32 (dd, *J* = 5.9, 1.4 Hz, 1H), 2.20-2.01 (m, 4H), 1.88-1.75 (m, 4H), 1.40 (d, *J* = 14.3 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 131.9, 131.7, 129.5, 128.6, 127.7, 126.6, 94.2, 84.6, 81.0, 66.1, 61.3, 39.9, 23.6, 14.5; IR (film) 2965, 1719, 1272, 1106 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{25}H_{26}O_3 + H]^+$: 375.1955, found 375.1935.



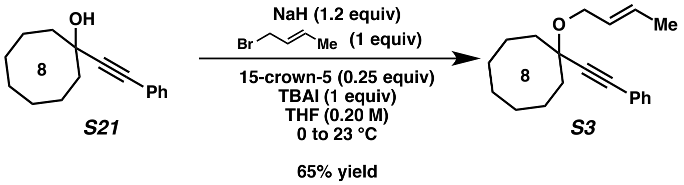
Enyne S1. To a solution of tertiary propargyl alcohol **S19** (0.378 g, 2.48 mmol) in THF (10 mL) at 0 °C was added NaH (0.111 g, 60% dispersion in mineral oil, 2.75 mmol). The solution was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (0.120 mL, 0.625 mmol), tetrabutylammonium iodide (0.646 g, 1.75 mmol), and cinnamyl bromide (0.542 g, 2.75 mmol). The resulting mixture was stirred at ambient temperature for 19 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (20 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (100% hexanes → 9:1 hexanes/EtOAc eluent), affording enyne **S1** (0.629 g, 94% yield, $R_f = 0.58$ in 9:1 hexanes/EtOAc, stained blue with *p*-anisaldehyde) as a colorless oil.

Enyne S1: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.40-7.38 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.24-7.20 (m, 1H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.33 (dt, *J* = 15.9, 6.1 Hz, 1H), 4.17 (dd, *J* = 6.1, 1.2 Hz, 2H), 2.35-2.24 (m, 6H), 1.93-1.78 (m, 2H), 1.57-1.40 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 137.1, 132.2, 128.6, 127.6, 126.7, 126.6, 85.8, 81.6, 73.1, 65.3, 36.5, 31.1, 22.1, 18.7, 13.8, 13.5; IR (film) 2935, 2861, 1450, 1128, 735 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{19}H_{24}O + H]^+$: 269.1900, found 269.1901.



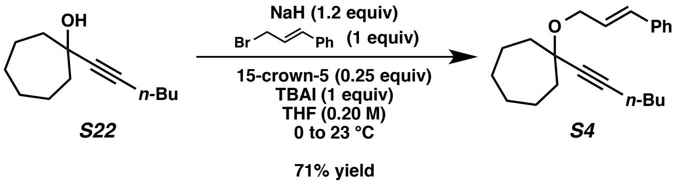
Enyne S2. To a solution of tertiary propargyl alcohol **S20** (2.14 g, 10.0 mmol) in THF (40 mL) at 0 °C was added NaH (0.442 g, 60% dispersion in mineral oil, 11.1 mmol). The solution was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (0.495 mL, 2.50 mmol), tetrabutylammonium iodide (2.58 g, 6.98 mmol), and crotyl bromide (1.13 mL, 11.0 mmol). The resulting mixture was stirred at ambient temperature for 19 h. The reaction was quenched with sat. aq. NH_4Cl (50 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 40 mL). The combined organic layers were washed with brine (100 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (100% hexanes → 9:1 hexanes/EtOAc eluent), affording enyne **S2** (2.44 g, 91% yield, $R_f = 0.75$ in 9:1 hexanes/EtOAc, stained blue with *p*-anisaldehyde) as a colorless oil.

Enyne S2: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.44-7.42 (m, 2H), 7.30 (t, *J* = 3.3 Hz, 3H), 5.79-5.60 (m, 2H), 4.10 (d, *J* = 6.0 Hz, 2H), 2.09 (dd, *J* = 13.9, 8.0 Hz, 2H), 1.98-1.92 (m, 2H), 1.71 (d, *J* = 6.2 Hz, 3H), 1.69-1.56 (m, 8H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 131.8, 128.8, 128.6, 128.4, 128.2, 123.3, 98.9, 92.0, 77.5, 65.0, 40.3, 28.5, 22.3, 18.0; IR (film) 2929, 2856, 1444, 1041, 755 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{19}H_{24}O + H]^+$: 269.1900, found 269.1900.



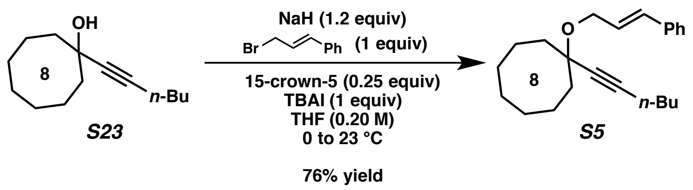
Enyne S3. To a solution of tertiary propargyl alcohol **S21** (0.505 g, 2.21 mmol) in THF (11 mL) at 0 °C was added NaH (0.104 g, 60% dispersion in mineral oil, 2.60 mmol). The solution was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (43.5 μL, 0.220 mmol), tetrabutylammonium iodide (0.815 g, 2.21 mmol), and crotyl bromide (0.235 mL, 2.28 mmol). The resulting mixture was stirred at ambient temperature for 18 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (30 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (hexanes → 4:1 hexanes/Et_2O eluent), affording enyne **S3** (0.406 g, 65% yield, R_f = 0.79 in 4:1 hexanes/EtOAc, stained blue with *p*-anisaldehyde) as a colorless oil.

Enyne S3: ^1H NMR (400 MHz; $CDCl_3$): δ 7.44-7.41 (m, 2H), 7.30 (t, *J* = 3.2 Hz, 3H), 5.78-5.60 (m, 2H), 4.08 (d, *J* = 6.0 Hz, 2H), 2.10-1.95 (m, 4H), 1.71 (dd, *J* = 6.2, 0.9 Hz, 3H), 1.68-1.56 (m, 10H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 131.8, 128.7, 128.6, 128.4, 128.2, 123.3, 91.9, 85.2, 77.3, 64.8, 35.1, 28.2, 24.7, 21.9, 18.0; IR (film) 2923, 2855, 1444, 1038, 755 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{26}O + H]^+$: 283.2056, found 283.2053.



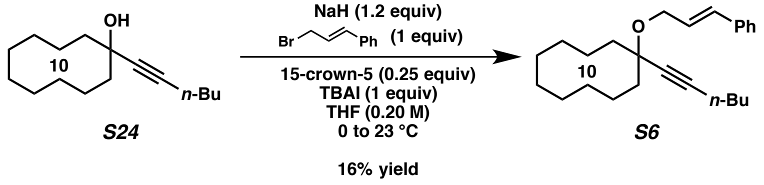
Enyne S4. To a solution of tertiary propargyl alcohol **S22** (0.194 g, 0.999 mmol) in THF (5.0 mL) at 0 °C was added NaH (48.0 mg, 60% dispersion in mineral oil, 1.20 mmol). The solution was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (49.5 µL, 0.250 mmol), tetrabutylammonium iodide (0.369 g, 1.00 mmol), and cinnamyl bromide (0.197 g, 1.00 mmol). The resulting mixture was stirred at ambient temperature for 14 h. The reaction was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (20 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (100% hexanes → 1:1 hexanes/CH_2Cl_2 eluent), affording enyne **S4** (0.220 g, 71% yield, R_f = 0.82 in 2:1 CH_2Cl_2/hexanes, stained blue with *p*-anisaldehyde) as a yellow oil.

Enyne S4: ^1H NMR (400 MHz; $CDCl_3$): δ 7.38 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.21 (dd, *J* = 8.2, 6.3 Hz, 1H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.33 (dt, *J* = 15.8, 5.9 Hz, 1H), 4.25 (dd, *J* = 5.9, 1.1 Hz, 2H), 2.24 (t, *J* = 6.9 Hz, 2H), 2.01-1.85 (m, 4H), 1.70-1.39 (m, 12H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 137.3, 131.3, 128.6, 127.7, 127.5, 126.6, 86.0, 82.6, 77.6, 64.6, 40.6, 31.1, 28.5, 22.2, 22.1, 18.6, 13.8; IR (film) 2932, 2859, 1496, 1058, 964 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{22}H_{30}O + H]^+$: 311.2369, found 311.2362.



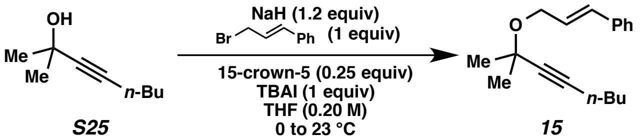
Enyne S5. To a solution of tertiary propargyl alcohol **S23** (0.209 g, 1.00 mmol) in THF (5.0 mL) at 0 °C was added NaH (48.0 g, 60% dispersion in mineral oil, 1.20 mmol). The solution was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (49.5 µL, 0.250 mmol), tetrabutylammonium iodide (0.369 g, 1.00 mmol), and cinnamyl bromide (0.197 g, 1.00 mmol). The resulting mixture was stirred at ambient temperature for 14 h. The reaction was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (20 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (100% hexanes → 1:1 hexanes/CH_2Cl_2 eluent), affording enyne **S5** (0.247 g, 76% yield, $R_f = 0.86$ in 2:1 CH_2Cl_2/hexanes, stained blue with *p*-anisaldehyde) as a yellow oil.

Enyne S5: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.39-7.37 (m, 2H), 7.31-7.27 (m, 2H), 7.23-7.19 (m, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.32 (dt, *J* = 15.9, 5.9 Hz, 1H), 4.23 (dd, *J* = 5.9, 1.5 Hz, 2H), 2.23 (t, *J* = 6.9 Hz, 2H), 2.03-1.84 (m, 4H), 1.69-1.40 (m, 14H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 137.3, 131.3, 128.6, 127.4, 126.6, 98.9, 85.7, 82.4, 64.4, 35.3, 31.1, 28.3, 24.7, 22.1, 21.9, 18.5, 13.8; IR (film) 2927, 2857, 1496, 1111, 963 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{23}H_{32}O + H]^+$: 325.2526, found 325.2517.



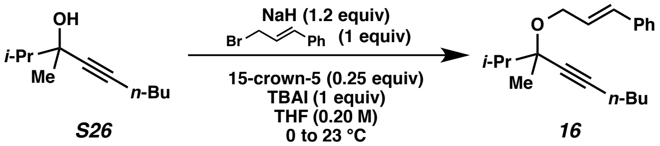
Enyne S6. To a solution of tertiary propargyl alcohol **S24** (0.298 g, 1.26 mmol) in THF (6.3 mL) at 0 °C was added NaH (60.4 mg, 60% dispersion in mineral oil, 1.51 mmol). The solution was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (63.3 µL, 0.320 mmol), tetrabutylammonium iodide (0.465 g, 1.26 mmol), and cinnamyl bromide (0.249 g, 1.26 mmol). The resulting mixture was stirred at ambient temperature for 14 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 15 mL). The combined organic layers were washed with brine (30 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (10:1 hexanes/CH_2Cl_2 → 1:1 hexanes/CH_2Cl_2 eluent), affording enyne **S6** (72.7 mg, 16% yield, R_f = 0.89 in 2:1 CH_2Cl_2/hexanes, stained blue with *p*-anisaldehyde) as a yellow oil.

Enyne S6: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.39-7.37 (m, 2H), 7.31-7.27 (m, 2H), 7.23-7.19 (m, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.33 (dt, *J* = 15.9, 5.9 Hz, 1H), 4.23 (dd, *J* = 5.9, 1.4 Hz, 2H), 2.23 (t, *J* = 6.9 Hz, 2H), 2.04-1.97 (m, 2H), 1.82 (dt, *J* = 14.2, 6.9 Hz, 2H), 1.71-1.38 (m, 18H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 137.3, 131.5, 128.6, 127.5, 126.6, 86.1, 82.0, 77.7, 64.3, 33.3, 31.2, 26.5, 26.0, 23.9, 22.1, 21.4, 18.5, 13.8; IR (film) 2924, 1446, 1054, 962 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{25}H_{36}O + H]^+$: 353.2839, found 353.2828.



Enyne 15. To a solution of tertiary propargyl alcohol **S25** (0.140 g, 0.998 mmol) in THF (5.0 mL) at 0 °C was added NaH (48.0 mg, 60% dispersion in mineral oil, 1.20 mmol). The solution was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (49.5 µL, 0.250 mmol), tetrabutylammonium iodide (0.369 g, 1.00 mmol), and cinnamyl bromide (0.197 g, 1.00 mmol). The resulting mixture was stirred at ambient temperature for 19 h. The reaction was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (25 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (hexanes → 1:1 hexanes/CH_2Cl_2 → 1:1:1 hexanes/CH_2Cl_2/EtOAc eluent), affording enyne **15** (0.183 g, 69% yield, R_f = 0.71 in 2:1 CH_2Cl_2/hexanes, stained blue with *p*-anisaldehyde) as a colorless oil.

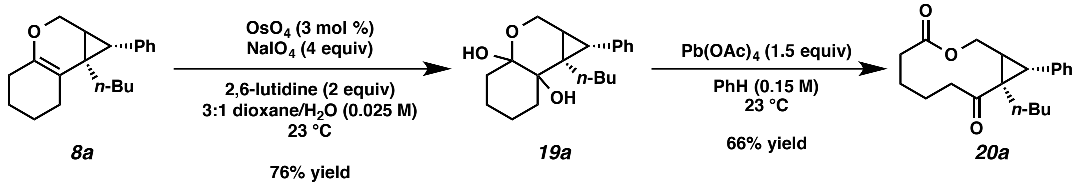
Enyne 15: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.40-7.38 (m, 2H), 7.30 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.24-7.22 (m, 1H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.33 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.26 (dd, *J* = 6.0, 1.5 Hz, 2H), 2.22 (t, *J* = 7.0 Hz, 2H), 1.49 (s, 6H), 1.54-1.39 (m, 10H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 137.2, 131.7, 128.6, 127.5, 127.3, 126.6, 84.9, 82.4, 70.7, 65.1, 31.0, 29.4, 22.1, 18.5, 13.8; IR (film) 2932, 2862, 1449, 1185 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{18}H_{24}O + H]^+$: 257.1900, found 257.1888.



Enyne 16. To a solution of tertiary propargyl alcohol **S26** (0.706 g, 4.20 mmol) in THF (21 mL) at 0 °C was added NaH (0.201 g, 60% dispersion in mineral oil, 5.04 mmol). The solution was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (0.208 mL, 1.05 mmol), tetrabutylammonium iodide (1.55 g, 4.20 mmol), and cinnamyl bromide (0.827 g, 4.20 mmol). The resulting mixture was stirred at ambient temperature for 16.5 h. The reaction was quenched with sat. aq. NH_4Cl (25 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with brine (50 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (100% hexanes → 1:1 hexanes/CH_2Cl_2 eluent), affording enyne **16** (0.800 g, 67% yield, $R_f = 0.86$ in 2:1 hexanes/CH_2Cl_2, stained blue with *p*-anisaldehyde) as a yellow oil.

Enyne 16: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.38 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.30 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.23-7.19 (m, 1H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.33 (dt, *J* = 15.9, 5.8 Hz, 1H), 4.32-4.19 (m, 2H), 2.24 (t, *J* = 6.9 Hz, 2H), 1.93 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.55-1.40 (m, 4H), 1.36 (s, 3H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 137.3, 131.1, 128.6, 127.7, 127.4, 126.6, 86.5, 80.8, 77.4, 64.6, 37.5, 31.1, 23.2, 22.1, 18.5, 18.3, 17.4, 13.8; IR (film) 2961, 2933, 1496, 1205, 964 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{28}O + H]^+$: 285.2213, found 285.2205.

Additional Reactions



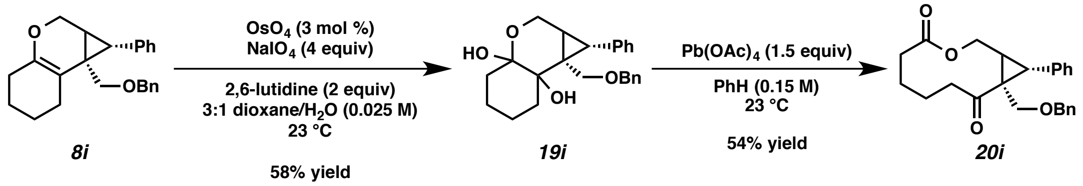
Diol 19a. To tricycle **8a** (67.6 mg, 0.239 mmol) in dioxane (7.5 mL) was added OsO_4 (50.0 µL, 4% solution in H_2O, 7.50 µmol), followed by 2,6-lutidine (57.6 µL, 0.500 mmol). The mixture was stirred for 5 min, then $NaIO_4$ (0.2139 g, 1.00 mmol) was added as a solution in H_2O (2.5 mL). The resulting mixture was stirred at ambient temperature for 1.5 d, after which the mixture was quenched with 1 M HCl (5 mL) and diluted with EtOAc (5 mL). The layers were separated and the aqueous layer was extracted with EtOAc (1 x 5 mL). The combined organic layers were washed with sat. $Na_2S_2O_3$ (10 mL) and brine (10 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (100% hexanes → 1:1 hexanes/CH_2Cl_2 → EtOAc eluent), affording diol **19a** (57.4 mg, 76% yield, $R_f = 0.77$ in 1:1 hexanes/EtOAc, stained with CAM) as a green oil.

Diol 19a: ^1H NMR (400 MHz; C_6D_6): δ 7.15-7.06 (m, 5H), 4.23 (dd, *J* = 10.6, 4.0 Hz, 1H), 3.69 (d, *J* = 10.6 Hz, 1H), 2.39 (d, *J* = 1.5 Hz, 1H), 2.20 (d, *J* = 6.1 Hz, 1H), 1.96-1.92 (m, 2H), 1.68-1.61 (m, 2H), 1.54-1.47 (m, 4H), 1.45-1.40 (m, 2H), 1.20 (dd, *J* = 6.0, 3.9 Hz, 1H), 1.16-0.90 (m, 3H), 0.69 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; C_6D_6): δ 139.2, 129.3, 126.1, 94.4, 70.7, 59.8, 36.5, 35.7, 35.6, 31.9, 31.5, 30.3, 23.7, 23.1, 21.6, 21.2, 14.0; IR (film) 3400, 2935, 2869, 1712, 1064 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M - H)^-$ $[C_{20}H_{28}O_3 - H]^-$: 315.1960, found 315.1959.

Macrolactone 20a. To diol **19a** (25.3 mg, 78.0 µmol) in benzene (0.70 mL) was added Pb(OAc)$_4$ (53.2 mg, 0.120 mmol). The mixture was stirred at ambient temperature for 3.5 h, after which ethylene glycol (1.0 mL) was added and the mixture was allowed to stir for 1 h. The reaction mixture was diluted with Et_2O (1.5 mL) and the layers were separated. The organic layer was washed with sat. $NaHCO_3$ (2 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (100% hexanes → 4:1 hexanes/EtOAc eluent), affording macrolactone **20a** (16.3 mg, 66% yield, $R_f = 0.83$ in 1:1 hexanes/EtOAc, stained with CAM) as a colorless oil.

Macrolactone 20a: ^1H NMR (400 MHz; C_6D_6): δ 7.09-7.01 (m, 3H), 6.96 (dd, *J* = 5.2, 3.2 Hz, 2H), 4.54 (dd, *J* = 11.6, 6.6 Hz, 1H), 3.80 (dd, *J* = 11.6, 6.6 Hz, 1H), 3.34 (d, *J* = 6.9 Hz, 1H), 2.63 (ddd, *J* = 16.8, 10.8, 2.4 Hz, 1H), 2.15 (m, 2H), 2.05-1.90 (m, 2H), 1.85-1.72 (m, 2H), 1.44-

1.31 (m, 4H), 0.96-0.74 (m, 4H), 0.51 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz; C_6D_6): δ 206.5, 172.0, 137.2, 128.9, 128.2, 126.5, 62.4, 44.3, 39.5, 34.6, 34.0, 31.1, 30.5, 28.7, 23.0, 22.8, 13.5; IR (film) 2933, 2872, 1737, 1698, 1233 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{26}O_3 + H]^+$: 315.1960, found 315.1962.



Diol 19i. To tricycle **8i** (34.5 mg, 90.7 μmol) in dioxane (3.0 mL) was added OsO_4 (19.0 μL, 4% solution in H_2O, 2.72 μmol), followed by 2,6-lutidine (20.9 μL, 19.4 μmol). The mixture was stirred for 5 min, then $NaIO_4$ (85.6 mg, 0.400 mmol) was added as a solution in H_2O (1.0 mL). The resulting mixture was stirred at ambient temperature for 3 d, after which the mixture was quenched with 1 M HCl (3 mL) and diluted with EtOAc (3 mL). The layers were separated and the aqueous layer was extracted with EtOAc (1 x 3 mL). The combined organic layers were washed with sat. $Na_2S_2O_3$ (5 mL) and brine (5 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (100% hexanes → 1:1 hexanes/EtOAc eluent), affording diol **19i** (20.0 mg, 58% yield, $R_f = 0.66$ in 1:1 hexanes/EtOAc, stained with CAM) as a green oil.

Diol 19i: ^{1}H NMR (400 MHz; C_6D_6): δ 7.14-6.95 (m, 10H), 4.42 (dd, $J = 11.1$, 4.5 Hz, 1H), 3.87-3.80 (m, 2H), 3.75 (d, $J = 11.2$ Hz, 2H), 3.36 (d, $J = 9.5$ Hz, 1H), 2.80 (d, $J = 9.5$ Hz, 1H), 2.32 (d, $J = 6.3$ Hz, 1H), 2.15-2.02 (m, 2H), 1.91-1.84 (m, 2H), 1.65-1.52 (m, 2H), 1.47-1.41 (m, 1H), 1.12 (dd, $J = 6.2$, 4.6 Hz, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 138.2, 137.9, 129.4, 128.7, 128.4, 128.0, 127.9, 126.6, 94.1, 73.1, 72.3, 71.0, 58.9, 36.2, 35.3, 33.5, 30.8, 22.9, 21.2, 19.9; IR (film) 3449, 2933, 2865, 1498, 1071 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + Na)^+$ $[C_{24}H_{28}O_4 + Na]^+$: 403.1885, found 403.1889.

Macrolactone 20i. To diol **19i** (25.3 mg, 78.0 μmol) in benzene (0.70 mL) was added $Pb(OAc)_4$ (53.2 mg, 0.120 mmol). The mixture was stirred at ambient temperature for 3.5 h, after which ethylene glycol (1.0 mL) was added and the mixture was allowed to stir for 1 h. The reaction mixture was diluted with Et_2O (1.5 mL) and the layers were separated. The organic layer was washed with sat. $NaHCO_3$ (2 mL), then dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the resulting residue was purified by flash chromatography (100% hexanes → 4:1 hexanes/EtOAc eluent), affording macrolactone **20i** (16.3 mg, 66% yield, $R_f =$ 0.83 in 1:1 hexanes/EtOAc, stained with CAM) as a colorless oil.

Macrolactone 20i: ^{1}H NMR (400 MHz; C_6D_6): δ 7.11-7.00 (m, 8H), 6.93-6.91 (m, 2H), 4.43 (dd, *J* = 11.7, 6.8 Hz, 1H), 3.93-3.81 (m, 3H), 3.57 (d, *J* = 6.9 Hz, 1H), 2.89 (ddd, *J* = 16.6, 9.2, 2.4 Hz, 1H), 2.61 (d, *J* = 10.5 Hz, 1H), 2.44 (ddd, *J* = 16.6, 9.2, 2.4 Hz, 1H), 2.13-2.06 (m, 1H), 2.01-1.88 (m, 1H), 1.84-1.74 (m, 1H), 1.71 (q, *J* = 6.8 Hz, 1H), 1.44-1.30 (m, 4H); ^{13}C NMR (100 MHz; C_6D_6): δ 205.5, 172.0, 136.9, 129.6, 128.5, 128.2, 127.9, 127.6, 126.9, 99.3, 73.1, 69.6, 62.1, 42.8, 39.8, 34.90, 34.87, 29.2, 22.93, 22.91, 13.4 IR (film) 2926, 2856, 1735, 1698, 1231, 1154 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + Na)^+$ $[C_{24}H_{26}O_4 + Na]^+$: 401.1729, found 401.1733.

Crystallographic Data

Table 1 Crystal data and structure refinement for 8e

Identification code	**8e**
Empirical formula	$C_{17}H_{20}O$
Formula weight	240.33
Temperature/K	100(2)
Crystal system	monoclinic
Space group	Cc
a/Å	16.9694(6)
b/Å	10.1758(6)
c/Å	7.7382(3)
α/°	90.00
β/°	92.801(3)
γ/°	90.00
Volume/Å^3	1334.61(11)
Z	4
ϱ_{calc}mg/mm^3	1.196
m/mm^{-1}	0.072
F(000)	520.0
Crystal size/mm^3	0.57 × 0.47 × 0.37
2Θ range for data collection	4.66 to 78.76°
Index ranges	$-30 \leq h \leq 30$, $-18 \leq k \leq 17$, $-13 \leq l \leq 13$
Reflections collected	28192
Independent reflections	7745[R(int) = 0.0359]
Data/restraints/parameters	7745/2/164
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	$R_1 = 0.0323$, $wR_2 = 0.0884$
Final R indexes [all data]	$R_1 = 0.0344$, $wR_2 = 0.0898$
Largest diff. peak/hole / e Å^{-3}	0.44/-0.21
Flack parameter	0.3(5)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 8e. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	2433.8(3)	3952.5(5)	7948.6(6)	17.52(8)
C1	2547.6(3)	2872.7(5)	6904.3(7)	14.09(8)
C2	1791.7(3)	2460.5(6)	5986.7(8)	19.35(9)
C3	1850.2(4)	1084.4(7)	5229.4(9)	22.48(11)
C4	2626.8(4)	936.6(7)	4327.2(9)	23.85(11)
C5	3338.8(3)	1121.1(6)	5597.0(7)	16.95(9)
C6	3249.0(3)	2268.5(5)	6809.1(6)	12.15(7)
C7	3942.0(3)	2700.0(5)	7954.2(6)	11.92(7)
C8	3837.1(3)	4030.3(5)	8789.1(7)	14.49(8)
C9	3109.2(4)	4787.4(5)	8212.4(7)	16.49(9)
C10	3797.7(3)	2817.6(5)	9894.9(7)	14.76(8)
C11	4442.3(4)	2563.0(7)	11270.5(8)	20.96(10)
C12	4740.9(3)	2293.9(5)	7406.4(6)	12.97(8)
C13	5046.6(3)	1060.0(5)	7863.3(7)	15.81(8)
C14	5767.5(3)	641.1(6)	7284.9(8)	19.55(10)
C15	6195.8(3)	1450.8(7)	6225.0(8)	21.97(11)
C16	5901.4(4)	2685.1(7)	5771.5(9)	22.63(11)
C17	5180.1(3)	3107.7(6)	6366.3(7)	18.19(9)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for 8e. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	14.84(16)	18.22(18)	19.61(17)	-2.34(13)	1.96(13)	5.73(13)
C1	12.34(17)	16.17(19)	13.70(18)	0.70(15)	0.04(14)	2.79(15)
C2	12.57(18)	24.7(2)	20.3(2)	1.57(19)	-3.27(16)	2.21(18)
C3	17.8(2)	25.2(3)	23.7(2)	-1.1(2)	-7.12(19)	-1.9(2)
C4	23.1(2)	29.3(3)	18.6(2)	-7.7(2)	-5.11(19)	1.3(2)
C5	16.23(19)	18.1(2)	16.3(2)	-5.30(16)	-0.91(16)	1.76(16)
C6	11.37(16)	13.34(17)	11.73(17)	-0.35(14)	0.27(13)	1.77(13)
C7	11.48(16)	12.08(17)	12.16(16)	-0.98(13)	0.32(13)	2.06(13)
C8	16.38(19)	12.38(18)	14.58(18)	-2.00(14)	-0.54(15)	2.79(15)
C9	20.1(2)	13.96(18)	15.4(2)	-0.88(15)	0.22(16)	5.40(16)
C10	15.80(18)	16.97(19)	11.42(17)	-0.03(15)	-0.25(14)	3.90(15)
C11	23.2(2)	23.6(2)	15.4(2)	-0.89(18)	-5.02(18)	6.3(2)
C12	11.34(16)	13.65(18)	13.90(18)	-1.38(14)	0.53(13)	0.99(14)
C13	13.53(18)	14.78(19)	19.1(2)	-0.92(16)	1.10(15)	2.91(15)
C14	15.02(19)	21.1(2)	22.5(2)	-5.00(19)	0.28(17)	5.70(17)
C15	13.24(19)	31.1(3)	21.9(2)	-7.8(2)	3.17(17)	1.79(19)
C16	19.0(2)	28.2(3)	21.3(3)	-2.0(2)	7.13(19)	-3.2(2)
C17	18.1(2)	18.3(2)	18.5(2)	1.32(17)	3.85(17)	0.02(17)

Table 4 Bond Lengths for 8e.

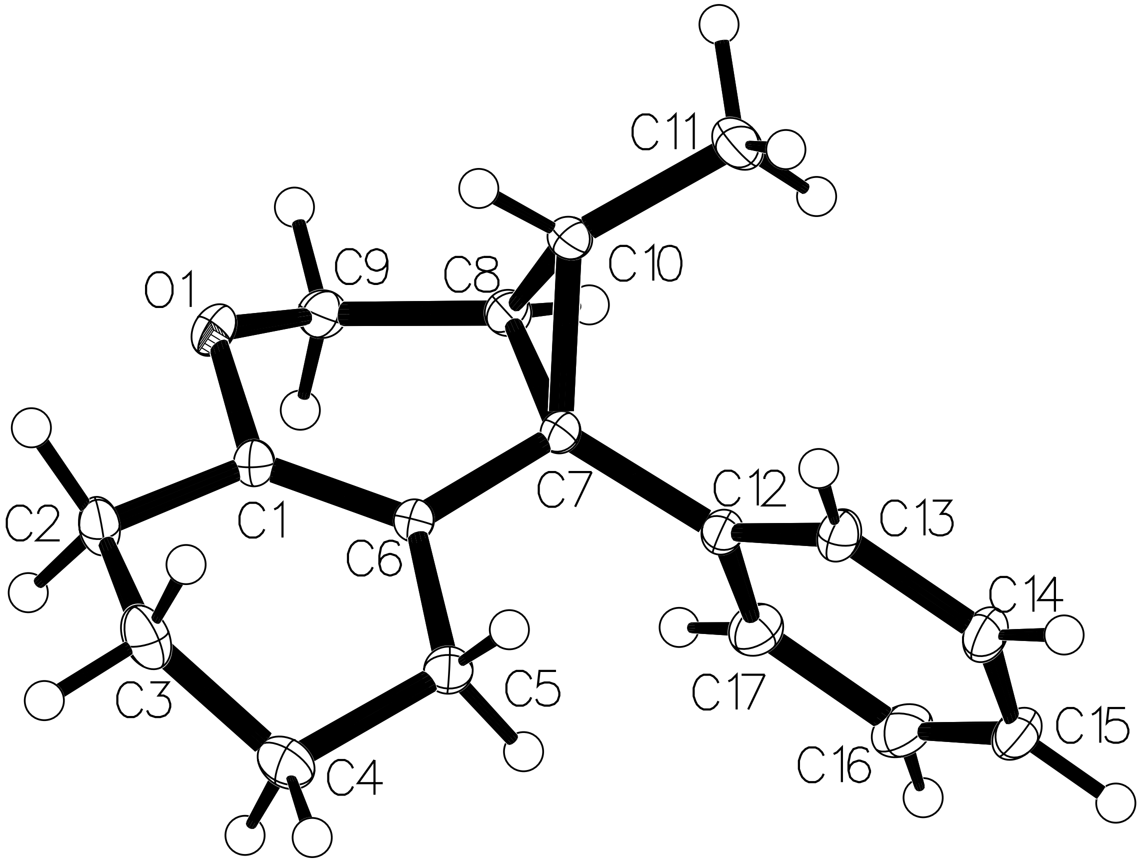
Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.3830(7)	C7	C12	1.4982(7)
O1	C9	1.4332(8)	C8	C9	1.5048(8)
C1	C2	1.4955(8)	C8	C10	1.5051(8)
C1	C6	1.3449(7)	C10	C11	1.5109(8)
C2	C3	1.5230(10)	C12	C13	1.3974(7)
C3	C4	1.5285(10)	C12	C17	1.3956(8)
C4	C5	1.5313(8)	C13	C14	1.3899(7)
C5	C6	1.5100(7)	C14	C15	1.3922(10)
C6	C7	1.5030(7)	C15	C16	1.3903(10)
C7	C8	1.5142(7)	C16	C17	1.3965(8)
C7	C10	1.5380(7)			

Table 5 Bond Angles for 8e.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	O1	C9	114.88(4)	C12	C7	C10	119.15(4)
O1	C1	C2	111.06(4)	C9	C8	C7	116.30(4)
C6	C1	O1	122.98(5)	C9	C8	C10	121.98(5)
C6	C1	C2	125.92(5)	C10	C8	C7	61.25(3)
C1	C2	C3	111.72(5)	O1	C9	C8	112.20(4)
C2	C3	C4	109.88(5)	C8	C10	C7	59.67(3)
C3	C4	C5	111.45(5)	C8	C10	C11	119.36(5)
C6	C5	C4	113.14(5)	C11	C10	C7	122.02(5)
C1	C6	C5	120.26(5)	C13	C12	C7	120.41(5)
C1	C6	C7	120.21(4)	C17	C12	C7	121.04(5)
C7	C6	C5	119.49(4)	C17	C12	C13	118.49(5)
C6	C7	C8	114.07(4)	C14	C13	C12	121.05(5)
C6	C7	C10	116.18(4)	C13	C14	C15	120.08(6)
C8	C7	C10	59.08(3)	C16	C15	C14	119.46(5)
C12	C7	C6	116.44(4)	C15	C16	C17	120.32(6)
C12	C7	C8	119.61(4)	C12	C17	C16	120.58(6)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 8e.

Atom	*x*	*y*	*z*	U(eq)
H2A	1657	3092	5045	23
H2B	1362	2481	6808	23
H3A	1401	929	4388	27
H3B	1824	424	6164	27
H4A	2648	1596	3390	29
H4B	2650	53	3797	29
H5A	3417	309	6288	20
H5B	3817	1256	4934	20
H8	4329	4565	8964	17
H9A	2998	5456	9097	20
H9B	3207	5253	7120	20
H10	3255	2567	10223	18
H11A	4946	2888	10872	31
H11B	4482	1617	11493	31
H11C	4317	3020	12338	31
H13	4757	499	8581	19
H14	5968	-199	7613	23
H15	6685	1162	5815	26
H16	6192	3244	5054	27
H17	4987	3957	6060	22


C11
C10
C9
C8
O1
C2
C1
C6
C7
C12
C13
C14
C3
C5
C17
C15
C16
C4