Metal-Catalyzed [2+2+1] Cycloadditions of 1,3-Dienes, Allenes, and CO**

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Reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of carbon monoxide from a balloon, unless otherwise indicated. Liquids and solutions were transferred via syringe or stainless steel cannula. Reactions were run using Teflon-coated magnetic stir bars. Elevated temperatures were maintained in thermostat-controlled oil baths. Elevated carbon monoxide pressures were maintained using a pressure reaction vessel purchased from Andrew’s Glass Co. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. Thin layer chromatography plates were visualized by ultraviolet light and treatment with acidic p-anisaldehyde stain followed by gentle heating. Chromatographic purification of products was accomplished by flash chromatography. Silica gel 60, 230-400 mesh was purchased from EM Science. \([\text{RhCl(CO)}_2]_2\) and \([\text{RhCl(CO)(PPh}_3)_2]\) were purchased from Strem Chemicals. \(\text{AgSbF}_6\) and DCE (99%, ACS reagent grade) were purchased from Aldrich Chemical Co. and were used as received. Carbon monoxide (2.5 grade) was purchased from Praxair.

NMR spectra were measured on a Varian INOVA 500 (\(^1\text{H}\) at 500 MHz, \(^{13}\text{C}\) at 125 MHz), Varian Mercury 400 (\(^1\text{H}\) at 400 MHz, \(^{13}\text{C}\) at 100 MHz), or Varian Gem-300 (\(^1\text{H}\) at 300 MHz, \(^{13}\text{C}\) at 75 MHz) magnetic resonance spectrometer. Data for \(^1\text{H}\) NMR spectra are reported as follows: chemical shift (\(\delta\) ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, dqt = doublet of quartets, septd = septet of doublets, m = multiplet), coupling constant (Hz), and integration. Nuclear Overhauser effect (nOe) data were measured at 500 MHz and are reported as follows: \(\text{H (irradiated)} \rightarrow \text{H (observed)}\), \% enhancement. Data for \(^{13}\text{C}\) are reported in terms of chemical shift and quantity of carbons. Infrared spectra were recorded on a Perkin-Elmer Spectrum BX Fourier transform spectrometer (IR) and are reported as follows: wavenumbers (cm\(^{-1}\)), description (w = weak, m = medium, s = strong, b = broad). High-resolution mass spectra (HRMS) were recorded at the NIH regional mass spectrometry facility at the University of California, San Francisco. Reported mass values are with error limits of ±1 millimass unit.

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[2+2+1] and [4+2] Cycloadducts - Procedures and Characterization Data

Diene-allene 1 (17 mg, 0.051 mmol) was weighed into an oven-dried test tube equipped with a magnetic stir bar. [RhCl(CO)\(_2\)]\(_2\) (1 mg, 0.0026 mmol) was added in one portion and DCE (0.5 mL) was added in one portion via syringe. The test tube was capped with a rubber septum and the solution was stirred under a balloon of CO (balloon, 1 atm) vented to a bubbler for 10 min. The outlet needle was removed and the solution was then immersed into a thermostat-controlled oil bath preheated to 80 °C. The solution was stirred for 1 h at which time TLC indicated that the starting material was consumed. The solution was cooled to RT and was purified via flash chromatography on silica gel (gradient elution, 5% Et\(_2\)O/pentane → 30% Et\(_2\)O/pentane). Fractions containing alkylidenyl cyclopentanone 2 were combined and concentrated by rotary evaporation to yield 2 (7.8 mg, 43%) as a white solid. Fractions containing cyclohexene 3 were combined and concentrated by rotary evaporation to yield 3 (8.8 mg, 52%) as colorless oil. Compounds were chromatographically homogeneous.

Data for 3:

TLC: \(R_f = 0.46\) (16% EtOAc/pentane), one brown spot with \(p\)-anisaldehyde stain.

\(\text{\textsuperscript{1}H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta = 7.69-7.67 (\text{d}, J = 8.2\) Hz, 2H), 7.31-7.29 (m, 2H), 4.75 (s, 1H, C1-H), 3.44 (dd, \(J = 10.4, 6.1\) Hz, 1H, C7\(\beta\)-H), 3.32-3.21 (m, 3H, C3-H, C7\(\alpha\)-H, C6\(\beta\)-H), 2.85 (ddd, \(J = 9.3, 9.0, 1.2\) Hz, 1H, C6\(\alpha\)-H), 2.65 (d, \(J = 20.9\) Hz, 1H, C4\(\beta\)-H), 2.59-2.52 (m, 1H, C2-H), 2.42 (s, 3H, C10-Me), 2.36 (d, \(J = 20.9\) Hz, 1H, C4\(\alpha\)-H), 1.65 (d, \(J = 1.7\) Hz, 3H, C9-Me), 1.62 (s, 3H, C8-Me), 1.41 (s, 3H, C5-Me) ppm.

\(\text{\textsuperscript{13}C NMR}\) (125 MHz, CDCl\(_3\)): \(\delta = 143.1, 134.13, 134.11, 129.4\) (2C), 127.5 (2C), 126.8, 123.3, 121.4, 54.5, 49.3, 39.5, 39.2, 30.4, 23.2, 21.5, 20.5, 19.9 ppm.

\(\text{IR}\) (thin film): 2964 (m), 2912 (m), 2886 (m), 1598 (w), 1466 (w), 1444 (w), 1377 (w), 1344 (s), 1219 (w), 1163 (s), 1107 (m), 1090 (m), 1028 (m), 1010 (w), 992 (w), 905 (w), 815 (m), 785 (w), 729 (w), 708 (w), 664 (s) cm\(^{-1}\).

\(\text{HRMS}\) (EI, \(m/z\)): Calcd for C\(_{19}\)H\(_{25}\)NO\(_2\)S: 331.1606 g/mol (M\(^+\)). Found: 331.1604 g/mol.

\(\text{nOe}\):
Preparation of the catalyst solution: $[\text{RhCl(CO)}_2]_2$ was weighed into an oven-dried test tube equipped with a magnetic stir bar. TFE was added via syringe to make a 0.005 M solution. The test tube was capped with a septum and the solution was stirred under a balloon of CO (balloon, 1 atm), vented to a bubbler for 45 min.

Diene-allene 1 (21 mg, 0.063 mmol) was weighed into an oven-dried test tube equipped with a magnetic stir bar. TFE (0.114 mL) was added via syringe and the test tube was capped with a rubber septum. The solution was stirred under a balloon of CO (balloon, 1 atm), vented to a bubbler for 30 min. The catalyst solution (0.0127 mL, 0.00063 mmol of $[\text{RhCl(CO)}_2]_2$) was added via syringe and the reaction mixture was stirred under a balloon of CO for 8 h. The solution was concentrated by rotary evaporation and the residue was purified by column chromatography with silica gel (2% EtOAc/CH$_2$Cl$_2$). Product-containing fractions were combined and concentrated to give 2 (20.6 mg, 97%) as a white solid. Compound 2 was chromatographically homogeneous. CCDC-295976 contains the supplementary crystallographic data for this compound. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html.

Data for 2:

**TLC:** $R_f = 0.16$ (15% EtOAc/pentane), one blue spot with $p$-anisaldehyde stain.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.72-7.70$ (m, 2H), 7.35-7.33 (m, 2H), 4.91 (s, 1H, C1-E-H), 4.58 (s, 1H, C1-Z-H), 3.66 (dd, $J = 9.6, 9.6$ Hz, 1H, C6$\beta$-H), 3.45 (dd, $J = 16.5, 8.1$ Hz, 1H, C5-H), 3.36 (dd, $J = 10.4, 6.3$ Hz, 1H, C7$\beta$-H), 3.22 (dd, $J = 10.3, 1.8$ Hz, 1H, C7$\alpha$-H), 2.95 (dd, $J = 9.8, 7.4$ Hz, 1H, C6$\alpha$-H), 2.69-2.64 (m, 1H, C4-H), 2.52 (d, $J = 10.3$ Hz, 1H, C3-H), 2.44 (s, 3H, C10-Me), 2.19 (s, 3H, C8-Me), 1.84 (s, 3H, C9-Me), 1.62 (s, 3H, C2-Me) ppm.

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 203.3, 151.5, 143.8, 140.7, 132.7, 132.3, 129.8$ (2C), 127.7 (2C), 115.5, 62.1, 52.7, 52.2, 42.5, 41.1, 24.8, 21.5, 20.7, 19.6 ppm.

**IR** (thin film): 3074 (w), 2946 (m), 2857 (w), 1707 (s), 1632 (s), 1597 (m), 1493 (w), 1477 (w), 1437 (m), 1375 (m), 1346 (s), 1305 (m), 1290 (w), 1269 (w), 1184 (m), 1165 (s), 1126 (w), 1091 (m), 1029 (m), 1015 (m), 988 (m), 898 (m), 816 (m) cm$^{-1}$.

**HRMS** (EI, m/z): Calc'd for C$_{20}$H$_{25}$NO$_3$S: 359.1555 g/mol (M$^+$). Found: 359.1563 g/mol.

**Melting point:** 119-120°C.
nOe:

Figure 1. ORTEP Diagram of 2 (CCDC-295976); ellipsoids drawn at 50% probability level.

Diene-allene 4 (45.9 mg, 0.279 mmol) was weighed into an oven-dried test tube equipped with a magnetic stir bar. TFE (2.79 mL) was added via syringe and then [RhCl(CO)$_2$]$_2$ (2.7 mg, 0.00699 mmol) was added in one portion. The test tube was capped with a rubber septum and the resulting yellow solution was stirred under a balloon of CO (balloon, 1 atm) vented to a bubbler for 10 min. The outlet needle was removed and the reaction mixture was stirred at ambient temperature for 1.5 h. The mixture was concentrated by rotary evaporation and the residue was purified by column chromatography with silica gel (17% EtOAc/pentane). Fractions containing 5 were combined and concentrated by rotary evaporation to give alkylidenyl cyclopentanone 5 (38.5 mg, 72% yield) as a colorless oil. Fractions containing 6 were combined and concentrated by rotary evaporation to give alkylidenyl cyclopentanone 6 (13.3 mg, 25% yield) as a colorless oil. Compounds were chromatographically homogeneous.

Data for 5:

TLC: $R_f = 0.22$ (10% EtOAc/pentane), one blue spot with $p$-anisaldehyde stain.
\textbf{1H NMR} (500 MHz, CDCl\textsubscript{3}): \(\delta = 5.86\) (ddd, \(J = 17.0, 10.0, 7.0\) Hz, 1H, C2-H), 5.22 (d, \(J = 10.5\) Hz, 1H, C1\texttextit{trans}-H), 5.14 (d, \(J = 17.5\) Hz, 1H, C1\texttextit{cis}-H), 4.15 (dd, \(J = 8.5, 8.5\) Hz, 1H, C6\textbeta-\textit{H}), 3.90 (dd, \(J = 9.0, 5.5\) Hz, 1H, C7\textbeta-\textit{H}), 3.80 (dd, \(J = 9.0, 1.5\) Hz, 1H, C7\textalpha-\textit{H}), 3.63 (dd, \(J = 8.5, 6.0\) Hz, 1H, C6\textalpha-\textit{H}), 3.55-3.52 (m, 1H, C5-H), 2.91 (dd, \(J = 7.5, 8.0\) Hz 1H, C3-H), 2.72-2.67 (m, 1H, C4-H), 2.24 (s, 3H, C8-Me), 1.86 (s, 3H, C9-Me) ppm.

\textbf{13C NMR} (125 MHz, CDCl\textsubscript{3}): \(\delta = 204.9, 150.6, 134.9, 133.3, 117.5, 73.9, 73.0, 58.5, 44.2, 43.4, 24.9, 20.6\) ppm.

\textbf{IR} (thin film): 3394 (w), 3080 (w), 2929 (m), 2852 (m), 1705 (s), 1633 (s), 1434 (w), 1369 (m), 1268 (m), 1174 (m), 1152 (m), 1090 (w), 1059 (m), 962 (w), 914 (m), 806 (w), 701 (w) cm\textsuperscript{-1}.

\textbf{HRMS} (EI, \textit{m/z}): Calcd for C\textsubscript{12}H\textsubscript{16}O\textsubscript{2}: 192.1150 g/mol (M\textsuperscript{+}). Found: 192.1155 g/mol.

\textbf{nOe}:

Data for 6:

\textbf{TLC}: \(R_f = 0.11\) (10\% EtOAc/pentane), one blue spot with \(p\)-anisaldehyde stain.

\textbf{1H NMR} (500 MHz, CDCl\textsubscript{3}): \(\delta = 6.70\) (dq, \(J = 7.0, 2.5\) Hz, 1H, C2-H), 4.21 (dd, \(J = 8.5, 8.5\) Hz, 1H, C6\textbeta-\textit{H}), 4.20 (dd, \(J = 8.0, 8.0\) Hz, 1H, C7\textbeta-\textit{H}), 3.49-3.52 (m, 2H, C7\textalpha-\textit{H}, C6\textalpha-\textit{H}), 3.43-3.52 (m, 2H, C4-H, C5-H), 2.32 (s, 3H, C8-Me), 1.89 (s, 3H, C9-Me), 1.83 (dd, \(J = 7.5, 1.5\) Hz, 3H, C1-Me) ppm.

\textbf{13C NMR} (125 MHz, CDCl\textsubscript{3}): \(\delta = 193.8, 151.3, 143.3, 135.0, 133.2, 74.8, 74.2, 43.4, 40.4, 24.8, 20.8, 15.1\) ppm.

\textbf{IR} (thin film): 3499 (w), 2925 (s), 3851 (s), 1755 (m), 1697 (m), 1643 (s), 1621 (s), 1441 (m), 1369 (w), 1271 (m), 1226 (s), 1184 (w), 1092 (w), 1062 (w), 1044 (w), 965 (m), 925 (m), 864 (w), 827 (w), 785 (w), 735 (w) cm\textsuperscript{-1}.

\textbf{HRMS} (EI, \textit{m/z}): Calcd for C\textsubscript{12}H\textsubscript{16}O\textsubscript{2}: 192.1150 g/mol (M\textsuperscript{+}). Found: 192.1147 g/mol.
TFE, rt

\[ \text{[RhCl(CO)\textsubscript{2}]} \] was weighed into an oven-dried test tube equipped with a magnetic stir bar. TFE was added via syringe to make a 0.001 M solution. The test tube was capped with a septum and the solution was stirred under a balloon of CO (balloon, 1 atm), vented to a bubbler for 30 min.

Diene-allene 7 (22 mg, 0.069 mmol) was weighed into an oven-dried test tube equipped with a magnetic stir bar. The test tube was capped with a rubber septum and the catalyst solution (0.69 mL, 0.00069 mmol of [RhCl(CO)\textsubscript{2}]) was added via syringe. The reaction mixture was stirred under a balloon of CO (balloon, 1 atm) for 20 min. The solution was concentrated by rotary evaporation and the residue was purified by column chromatography with silica gel (gradient elution, 3% EtOAc/pentane \(\rightarrow\) 6% EtOAc/pentane \(\rightarrow\) 9% EtOAc/pentane). Product-containing fractions were combined and concentrated by rotary evaporation to give 8 (22 mg, 92%) as a colorless oil. Compound 8 was chromatographically homogeneous.

Data for 8:

**TLC:** \( R_f = 0.43 \) (20% EtOAc/pentane), one blue spot with \( p \)-anisaldehyde stain.

**\(^1\)H NMR** (400 MHz, CDCl\textsubscript{3}): \( \delta = 4.91 \) (s, 1H, C1 E-H), 4.67 (s, 1H, C1 Z-H), 3.77 (s, 3H, CO\textsubscript{2}Me), 3.71 (s, 3H, CO\textsubscript{2}Me), 3.46-3.38 (m, 1H, C7-H), 2.88 (ddd, \( J = 13.4, 8.2, 1.1 \) Hz, 1H, C8β-H), 2.82 (d, \( J = 6.3 \) Hz, 1H, C5-H), 2.67-2.60 (m, 2H, C6-H, C9β-H), 2.31 (sept, \( J = 6.8 \) Hz, 1H, C2-H), 2.19 (d, \( J = 1.5 \) Hz, 3H, C10-Me), 2.08 (dd, \( J = 16.7, 9.9 \) Hz, 1H, C9α-H), 1.94 (dd, \( J = 13.6, 9.4 \) Hz, 1H, C8α-H), 1.88 (s, 3H, C11-Me), 1.04 (d, \( J = 6.7 \) Hz, 3H, C4-Me), 1.03 (d, \( J = 6.7 \) Hz, 3H, C3-Me) ppm.

**\(^{13}\)C NMR** (125 MHz, CDCl\textsubscript{3}): \( \delta = 205.5, 172.4, 172.0, 154.5, 150.3, 134.6, 109.0, 61.6, 61.4, 52.9, 52.8, 43.3, 42.8, 40.7, 39.9, 33.4, 24.6, 22.2, 22.0, 20.8 ppm.

**IR** (thin film): 2956 (m), 2871 (w), 1734 (s), 1704 (m), 1630 (m), 1458 (w), 1435 (m), 1368 (w), 1328 (w), 1268 (s), 1199 (m), 1173 (m), 1097 (w), 1065 (w), 1030 (w), 972 (w), 892 (w), 821 (w) cm\textsuperscript{-1}.

**HRMS** (EI, \( m/z \)): Calcd for C\textsubscript{20}H\textsubscript{28}O\textsubscript{5}: 348.1937 g/mol (M\textsuperscript{+}). Found: 348.1936 g/mol.

noe:
Preparation of the catalyst solution: [RhCl(CO)$_2$]$_2$ was weighed into an oven-dried test tube equipped with a magnetic stir bar. DCE was added via syringe to make a 0.0005 M solution. The test tube was capped with a septum and the solution was stirred under a balloon of CO (balloon, 1 atm), vented to a bubbler for 20 min.

Diene-allene 9 (18.8 mg, 0.054 mmol) was weighed into an oven-dried test tube equipped with a magnetic stir bar. The test tube was capped with a rubber septum and the catalyst solution (1.09 mL, 0.00054 mmol of [RhCl(CO)$_2$]$_2$) was added via syringe. The reaction mixture was stirred under a balloon of CO (balloon, 1 atm) for 24 h. The mixture was purified by column chromatography with silica gel (18% EtOAc/pentane). Fractions containing 10 were combined and concentrated by rotary evaporation to give alkylidenyl cyclopentanone 10 (8.7 mg, 44%) as a colorless oil. Fractions containing 11 were combined and concentrated by rotary evaporation to give alkylidenyl cyclopentanone 11 (7.8 mg, 37%) as a colorless oil. Compounds were chromatographically homogeneous.

Data for 10:

**TLC:** $R_f = 0.47$ (20% EtOAc/pentane), one blue spot with $p$-anisaldehyde stain.

1H NMR (500 MHz, CDCl$_3$): δ = 7.72–7.70 (d, $J = 8.3$ Hz, 2H), 7.35–7.33 (d, $J = 8.5$ Hz, 2H), 6.69 (qd, $J = 7.2$, 2.2 Hz, 1H, C10-H), 4.96 (s, 1H, C1 E-H), 4.62 (s, 1H, C1 Z-H), 3.66 (dd, $J = 9.6$, 9.5 Hz, 1H, C8β-H), 3.52–3.44 (m, 1H, C7-H), 3.40 (dd, $J = 10.3$, 6.5 Hz, 1H, C9β-H), 3.16 (dd, $J = 10.3$, 2.7 Hz, 1H, C9α-H), 2.98 (dd, $J = 9.8$, 6.7 Hz, 1H, C8α-H), 2.75 (dd, $J = 8.9$, 6.6, 2.7 Hz, 1H, C6-H), 2.64 (d, $J = 8.8$, 1H, C5-H), 2.44 (s, 3H, C12-Me), 2.18 (sept, $J = 6.7$ Hz, 1H, C2-H), 1.82 (d, $J = 6.7$ Hz, 3H, C11-Me), 1.00 (d, $J = 6.7$ Hz, 3H, C3-Me) ppm.

13C NMR (125 MHz, CDCl$_3$): δ = 203.3, 152.5, 143.9, 139.6, 135.0, 132.5, 129.8 (2C), 127.7 (2C), 111.0, 59.0, 52.6, 52.5, 43.5, 40.2, 33.1, 22.2 (2C), 21.5, 15.4 ppm.

IR (thin film): 2961 (m), 2870 (m), 1720 (s), 1651 (m), 1597(w), 1463 (w), 1380 (w), 1346 (s), 1305 (w), 1289 (w), 1214 (m), 1184 (m), 1164 (s), 1090 (m), 1028 (m), 1015 (m), 974 (w), 949 (w), 898 (m), 816 (m) cm$^{-1}$.

HRMS (EI, m/z): Calcd for C$_{21}$H$_{27}$NO$_3$S: 373.1712 g/mol (M$^+$). Found: 373.1713 g/mol.
Data for 11:

**TLC:** R$_f$ = 0.59 (20% EtOAc/pentane), one blue spot with p-anisaldehyde stain.

**$^1$H NMR (500 MHz, CDCl$_3$):** $\delta$ = 7.70–7.69 (d, $J = 8.2$ Hz, 2H), 7.34–7.32 (d, $J = 7.9$ Hz, 2H), 6.08 (qd, $J = 7.4$, 1.6 Hz, 1H, C10-H), 4.94 (s, 1H, C1 E-H), 4.60 (s, 1H, C1 Z-H), 3.57 (dd, $J = 10.0$, 8.5 Hz, 1H, C8β-H), 3.42 (dd, $J = 10.3$, 7.0 Hz, 1H, C9β-H), 3.38–3.29 (m, 1H, C7-H), 3.13 (dd, $J = 10.0$, 5.5 Hz, 1H, C9α-H), 3.09 (dd, $J = 10.3$, 3.8 Hz, 1H, C8α-H), 2.75 (ddd, $J = 7.6$, 7.3, 4.0 Hz, 1H, C6-H), 2.64 (d, $J = 7.4$, 1H, C5-H), 2.44 (s, 3H, C12-Me), 2.21 (sept, $J = 6.7$ Hz, 1H, C2-H), 2.08 (dd, $J = 7.4$, 1.7 Hz, 3H, C11-Me), 1.00 (d, $J = 6.7$ Hz, 3H, C3-Me), 0.98 (d, $J = 6.7$ Hz, 3H, C4-Me) ppm.

**$^{13}$C NMR (125 MHz, CDCl$_3$):** $\delta$ = 205.3, 152.8, 143.8, 139.6, 137.0, 132.8, 129.7 (2C), 127.9 (2C), 110.4, 59.4, 53.8, 43.9, 43.4, 33.3, 22.1, 22.0, 21.5, 14.6 ppm.

**IR (thin film):** 2960 (m), 2870 (m), 1713 (s), 1639 (m), 1597 (w), 1493 (w), 1462 (w), 1379 (w), 1346 (s), 1305 (w), 1290 (w), 1164 (s), 1091 (m), 1030 (m), 1015 (m), 984 (w), 897 (w), 860 (w), 816 (m) cm$^{-1}$.

**HRMS (EI, m/z):** Calcd for C$_{21}$H$_{27}$NO$_3$S: 373.1712 g/mol (M$^+$). Found: 373.1704 g/mol.
Diene-allene 12 (26.7 mg, 0.139 mmol) was weighed into an oven-dried test tube equipped with a magnetic stir bar. TFE (1.39 mL) was added via syringe and then [RhCl(CO)₂]₂ (1.3 mg, 0.0035 mmol) was added in one portion. The test tube was capped with a rubber septum and the resulting yellow solution was stirred under a balloon of CO (balloon, 1 atm) vented to a bubbler for 10 min. The outlet needle was removed and the reaction mixture was stirred at ambient temperature for 24 h. The mixture was concentrated by rotary evaporation and the residue was purified by column chromatography with silica gel (17% EtOAc/pentane). Fractions containing 13 were combined and concentrated by rotary evaporation to give alkylidenyl cyclopentanone 13 (21.6 mg, 83% yield) as a colorless oil. Fractions containing 14 were combined and concentrated by rotary evaporation to give alkylidenyl cyclopentanone 14 (2.9 mg, 11% yield) as a colorless oil. Compounds were chromatographically homogeneous.

Data for 13:

TLC: R_f = 0.28 (10% EtOAc/pentane), one blue spot with p-anisaldehyde stain.

¹H NMR (500 MHz, CDCl₃): δ = 6.66 (d, J = 2.0 Hz, 1H, C8-H), 5.85 (ddd, J = 17.0, 10.5, 7.0 Hz, 1H, C2-H), 5.25 (dt, J = 10.5, 1.5 Hz, 1H, C1E-H), 5.19 (dt, J = 17.0, 1.5 Hz, 1H, C1Z-H), 4.16 (dd, J = 9.0, 9.0 Hz, 1H, C6β-H), 3.90 (m, 2H, C6α-H), 3.76 (ddd, J = 15.5, 7.0, 1.0 Hz, 1H, C5-H), 3.66 (dd, J = 8.5, 6.0 Hz, 1H, C7α-H), 2.85 (dd, J = 9.5, 8.5 Hz, 1H, C3-H), 2.70 (ddddd, J = 9.3, 8.3, 4.0, 2.5 Hz, 1H, C4-H), 1.15 (s, 9H, t-Bu) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 206.3, 148.6, 134.8, 134.1, 118.2, 74.6, 72.5, 55.8, 45.0, 42.2, 33.7, 29.7 (3C) ppm.

IR (thin film): 2961 (s), 2864 (m), 1718 (s), 1636 (s), 1465 (w), 1363 (m), 1275 (w), 1235 (m), 1200 (m), 1167 (m), 1092 (w), 1060 (m), 1000 (w), 915 (m), 876 (w) cm⁻¹.

HRMS (EI, m/z): Calcd for C_{18}H_{20}O₂: 220.1463 g/mol (M⁺). Found: 220.1462 g/mol.

nOe:
Data for 14:

**TLC**: $R_f = 0.18$ (10% EtOAc/pentane), one blue spot with $p$-anisaldehyde stain.

![TLC Image](image)

**$^1$H NMR** (500 MHz, CDCl$_3$): $\delta = 6.85$ (d, $J = 7.5$, 2.5 Hz, 1H, C2-H), 6.73 (d, $J = 2.5$ Hz, 1H, C8-H), 4.23 (dd, $J = 8.0$, 5.5 Hz, 1H, C6β-H), 4.21 (dd, $J = 8.5$, 6.0 Hz, 1H, C7β-H), 3.75 (dddd, $J = 10.0$, 10.0, 6.5, 2.0 Hz, 1H, C5-H), 3.60 (dd, $J = 9.0$, 5.0 Hz, 1H, C7α-H), 3.51-3.46 (m, 2H, C4-H, C6α-H), 1.86 (dd, $J = 7.0$, 2.0 Hz, 3H, C1-Me), 1.17 (s, 9H, t-Bu) ppm.

**$^{13}$C NMR** (125 MHz, CDCl$_3$): $\delta = 194.6, 149.3, 141.0, 134.8$ (2C), 75.6, 74.3, 41.7, 41.6, 34.0, 29.9, 15.3 (3C) ppm.

**IR** (thin film): 2960 (s), 2851 (m), 1706 (m), 1646 (s), 1634 (s), 1457 (w), 1362 (w), 1260 (m), 1237 (s), 1197 (m), 1174 (m), 1136 (w), 1093 (m), 1047 (w), 973 (w), 926 (m), 870 (w), 780 (w), 730 (w) cm$^{-1}$.

**HRMS** (EI, m/z): Calcd for C$_{14}$H$_{20}$O$_2$: 220.1463 g/mol (M$^+$). Found: 220.1459 g/mol.

**nOe:**

![nOe Image](image)

Preparation of the catalyst solution: [RhCl(CO)$_2$]$_2$ (2.4 mg, 0.006 mmol) was weighed into an oven-dried test tube equipped with a magnetic stir bar. DCE (1.2 mL) was added via syringe. The test tube was capped with a septum and the solution was stirred under a balloon of CO (balloon, 1 atm), vented to a bubbler for 20 min.

Diene-allene 15 (20 mg, 0.06 mmol) was weighed into an oven-dried test tube equipped with a magnetic stir bar. The test tube was capped with a rubber septum and the septum was then punctured with a disposable 16 G 1⅛ needle. The catalyst solution (0.6 mL, 0.003 mmol of [RhCl(CO)$_2$]$_2$) was added via syringe and the test tube was placed in the pressure vessel. The vessel was pressurized to four atmospheres of CO and was placed in a preheated thermostat-controlled oil bath at 60 °C. The reaction mixture was stirred at 60 °C for 30 min and was then cooled to ambient temperature. The mixture was purified by column chromatography with silica gel (gradient elution 10% EtOAc/pentane, 20% EtOAc/pentane).
Fractions containing 16 were combined and concentrated by rotary evaporation to give vinylcyclopentene 16 (9.3 mg, 43%) as a colorless oil. Fractions containing 17 were combined and concentrated by rotary evaporation to give cyclohexene 17 (3.8 mg, 19%) as a colorless oil. Compounds were chromatographically homogeneous.

Data for 16:

\[ R_f = 0.32 \text{ (25\% EtOAc/pentane), one blue spot with } p\text{-anisaldehyde stain.} \]

\[^1H\text{-NMR (400 MHz, CDCl}_3\text{):} \delta = 7.69 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 6.06 (d, J = 2.4 Hz, 1H, C10 Z-H), 5.35 (d, J = 1.9 Hz, 1H, C10 E-H), 4.95 (s, 1H, C1E-H), 4.62 (s, 1H, C1Z-H), 3.62 (dd, J = 9.9, 8.7 Hz, 1H, C8β-H), 3.46-3.40 (m, 2H, C7-H, C9β-H), 3.17 (dd, J = 10.1, 5.2 Hz, 1H, C9α-H), 3.09 (dd, J = 10.1, 4.1 Hz, 1H, C8α-H), 2.80 (ddd, J = 12.0, 7.9, 4.1 Hz, 1H, C6-H), 2.70 (d, J = 7.0 Hz, 1H, C5-H), 2.44 (s, 3H, C11-Me), 2.23 (sept, J = 6.9 Hz, 1H, C2-H), 1.01 (d, J = 6.9 Hz, 3H, C3-Me), 0.99 (d, J = 6.9 Hz, 3H, C4-Me) ppm.

\[^{13}C\text{-NMR (125 MHz, CDCl}_3\text{):} \delta = 204.2, 152.7, 145.9, 144.2, 132.9, 130.0 (2C), 127.9 (2C), 121.3, 110.9, 58.1, 53.6, 52.9, 43.6, 42.8, 33.5, 22.4, 22.3, 21.8 ppm.

\[ \text{IR (thin film): 2961 (m), 2871 (w), 1724 (m), 1638 (m), 1597 (w), 1465 (w), 1402 (w), 1346 (s), 1305 (w), 1163 (s), 1092 (m), 1017 (m), 949 (w), 899 (w), 815 (m) cm}^{-1}. \]

\[ \text{HRMS (EI, } m/z\text{): Calcd for } C_{20}H_{25}NO_3S: 359.1555 \text{ g/mol (M)}. \text{ Found: } 359.1556 \text{ g/mol.} \]

\[ n\text{Oe:} \]

Data for 17:

\[ \text{TLC: } R_f = 0.71 \text{ (25\% EtOAc/pentane).} \]

\[^1H\text{-NMR (400 MHz, CDCl}_3\text{):} \delta = 7.70-7.69 (d, J = 8.1 Hz, 2H), 7.31-7.29 (d, J = 8.3 Hz, 2H), 4.98 (s, 1H, C1-H), 4.79 (s, 1H, C8 E-H), 4.75 (s, 1H, C8 Z-H), 3.47 (dd, J = 9.8, 6.6 Hz, 1H, C10β-H), 3.35 (dd, J = 9.5, 8.1 Hz, 1H, C9β-H), 3.15 (dd, J = 9.9, 2.8 Hz, 1H, C10α-H), 3.11 (dd, J = 9.3, 9.3 Hz, 1H, C9α-H), 2.91 (dd, J = 15.1, 8.4 Hz, 1H, C3-H), 2.75-2.70 (m, 1H, C2-H), 2.66 (d, J = 19.3 Hz, 1H, C4β-H), 2.57 (d, J = 19.4 Hz, 1H, C4α-H), 2.42 (s, 3H, C11-Me), 2.02 (sept, J = 6.7 Hz, 1H, C5-H), 0.86 (d, J = 6.7 Hz, 3H, C6-Me), 0.85 (d, J = 6.7 Hz, 3H, C7-Me) ppm.
\(^{13}\text{C-NMR}\) (125 MHz, CDCl\(_3\)): \(\delta = 143.8, 143.2, 142.1, 134.0, 129.5\) (2C), 127.5 (2C), 118.7, 110.6, 53.7, 49.4, 44.6, 41.0, 34.4, 31.0, 21.5, 21.0, 20.7 ppm.

\(\text{IR}\) (thin film): 2960 (m), 2873 (m), 1648 (w), 1597 (w), 1466 (w), 1382 (w), 1345 (s), 1304 (m), 1182 (m), 1163 (s), 1091 (m), 1052 (m), 1017 (w), 984 (w), 894 (m), 815 (m) cm\(^{-1}\).

\(\text{HRMS}\): calc. for C\(_{19}\)H\(_{25}\)NO\(_2\)S 331.1606 g/mol (M\(^{+}\)). Found: 331.1611 g/mol.

\(\text{nOe}\):

Diene-allenes – Procedures and Characterization Data

Sulfonamide 1\text{I}\(^{i}\) (106 mg, 0.42 mmol) was weighed into a round bottom flask equipped with a magnetic stir bar. Dienol 1\text{Ii}\(^{ii}\) (37 mg, 0.38 mmol) and PPh\(_3\) (100 mg, 0.38 mmol) were each added in one portion. THF (2.5 mL) was added via syringe and the solution was stirred under a positive pressure of nitrogen. The solution was cooled using an ice/water bath. A solution of DIAD (75 \(\mu\)L, 0.38 mmol) in THF (1.5 mL) was added via syringe dropwise over the course of 5 min. The resulting yellow-orange solution was allowed to warm to ambient temperature and was stirred for 24 h. The reaction mixture was diluted with ether (20 mL) and was transferred to a separatory funnel. The organic layer was washed with brine (3x10 mL), dried over MgSO\(_4\), and vacuum filtered through a fritted funnel. The filtrate was concentrated by rotary evaporation and the residue was purified by flash chromatography with silica gel (gradient elution 100% pentane \(\rightarrow\) 5% Et\(_2\)O/pentane). Product-containing fractions were combined and concentrated by rotary evaporation to give 1 as a colorless oil (108 mg, 70%). Compound 1 was chromatographically homogeneous.

Data for 1:

\(\text{TLC}\): \(R_f = 0.76\) (15% EtOAc/pentane), one blue-green spot with \(p\)-anisaldehyde.

\(\text{TsN}\)
**1H NMR** (400 MHz, CDCl3): δ = 7.70 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 6.16 (d, J = 15.6 Hz, 1H, C7-H), 5.40 (dt, J = 15.4, 7.0 Hz, 1H, C6-H), 4.95 (s, 1H, C8-H), 4.90 (s, 1H, C8-H), 4.70 (sept, J = 6.7, 2.9 Hz, 1H, C1-H), 3.90 (d, J = 6.7 Hz, 2H, C2-H), 3.78 (d, J = 7.0 Hz, 2H, C5-H), 2.41 (s, 3H, C10-Me), 1.73 (s, 3H, C9-Me), 1.64 (d, J = 2.9 Hz, 6H, C3-Me, C4-Me) ppm.

**13C NMR** (125 MHz, CDCl3): δ = 203.3, 143.1, 141.1, 137.7, 136.7, 129.6 (2C), 127.2 (2C), 123.7, 116.9, 96.6, 84.2, 48.2, 46.5, 21.5, 20.3 (2C), 18.4 ppm.

**IR** (thin film): 2978 (w), 2911 (w), 1598 (w), 1442 (w), 1406 (w), 1346 (m), 1159 (s), 1095 (m), 1018 (w), 967 (w), 904 (m), 849 (w), 815 (w) cm⁻¹.

**LRMS** (ESI, m/z): Calcd for C₁₉H₂₅NO₂S: 331.2 g/mol (M⁺). Found: 332.2 g/mol (M⁺H⁺).

Allenyl alcohol 4i (132 mg, 1.3 mmol) was added drop wise over 5 min via syringe to a stirred suspension of sodium hydride (59 mg of 60% in mineral oil, 1.5 mmol) in THF (10 mL). The reaction mixture was heated to reflux in an oil bath for 10 minutes. The reaction was cooled to RT and 5-bromopenta-trans-1,3-diene 4ii (276 mg, 1.88 mmol) was added dropwise over 5 min via syringe. The resulting mixture was stirred for 3 h at RT and was then heated in a thermostat-controlled oil bath preheated to 60 °C for 7.5 hours. The reaction was cooled to RT and the reaction was quenced by the addition over 5 min of saturated aqueous ammonium chloride (10 mL). The organics were extracted with diethyl ether (3x5 mL). The organic layers were combined, washed with brine (20 mL), dried over sodium sulfate, filtered, and concentrated by rotary evaporation. The residue was purified via flash chromatography to yield diene-allene 4 (210 mg, 95%) as a clear colorless oil. Compound 4 was chromatographically homogeneous.

Data for 4:

**TLC:** Rf = 0.83 (10% EtOAc/pentane), one blue spot with p-anisaldehyde.

**1H NMR** (400 MHz, CDCl3): δ = 6.35 (dt, J = 17.0, 10.0 Hz, 1H, C8-H), 6.30-6.22 (m, 1H, C7-H), 5.78 (ddt, J = 15.0, 6.0, 1.0 Hz, 1H, C6-H), 5.21 (dd, J = 16.0, 0.5 Hz, 1H, C9cis-H), 5.09 (dd, J = 10.0, 0.5 Hz, 1H, C9trans-H), 5.09 - 5.03 (m, 1H, C1-H), 4.03 (dd, J = 6.0, 1.5 Hz, 2H, C5-CH₂), 3.96 (d, J = 7.0 Hz, 2H, C2-CH₂), 1.71 (d, J = 3.0 Hz, 6H, C3-Me, C4-Me) ppm.

**13C NMR** (125 MHz, CDCl3): δ = 203.0, 136.4, 133.2, 130.1, 117.4, 95.9, 86.2, 69.5, 68.9, 20.4 (2C) ppm.

**IR** (thin film): 3086 (w), 2980 (m), 2936 (m), 2909 (m), 2852 (m), 2868 (w), 1604 (w), 1448 (w), 1406 (w), 1362 (w), 1300 (w), 1239 (w), 1190 (w), 1106 (s), 1051 (m), 1004 (s), 953 (m), 903 (m), 799 (w) cm⁻¹.
HRMS (ESI, m/z): Calcd for C_{11}H_{16}O: 164.1201 g/mol (M^+). Found: 165.1238 g/mol (M+H^+).

NaH (60%, 3.1 g, 77.0 mmol) was added over 2 min to THF (150 mL) in a 500 mL 3-necked flask equipped with an overhead mechanical stirred, an internal thermometer, and 50 mL addition funnel. The solution was stirred, was kept under a positive pressure of nitrogen, and cooled in an ice/water bath. Triethyl phosphonoacetate (18.1 g, 81 mmol) in THF (10 mL) was added dropwise over 30 min via the addition funnel. An additional THF (5 mL) was used to rinse residual triethyl phosphonoacetate from the addition funnel into the reaction flask. After an additional 15 min, isopropylacrolein 7iv (6.0 g, 76 mmol) was added dropwise over 5 min via the addition funnel. The resulting cloudy yellow reaction mixture was stirred for 20 min. The reaction was quenched by the addition over 5 min of brine (50 mL) and then water (50 mL). The product was extracted with Et_2O (3x100 mL). The combined organic extracts were washed with water (50 mL) and then brine (50 mL), dried over MgSO_4, filtered through a fritted funnel, and concentrated by rotary evaporation. The residue was purified via short-path distillation (15 mm Hg, 76-79 °C) giving ester 7iii as a clear oil (6.4 g, 60%). Compound 7iii was chromatographically homogeneous.

Data for 7iii:

TLC: R_f = 0.67 (25% EtOAc/pentane), one blue spot with p-anisaldehyde stain.

^1H NMR (500 MHz, CDCl_3): δ = 7.10 (d, J = 15.9 Hz, 1H, C4-H), 5.77 (d, J = 15.9 Hz, 1H, C3-H), 5.15 (s, 1H, C1-H), 5.12 (s, 1H, C1-H), 4.02 (q, J = 7.1 Hz, 2H, C7-CH_2), 2.39 (sept, J = 6.6 Hz, 1H, C2-H), 1.11 (t, J = 7.2 Hz, 3H, C8-Me), 0.91 (d, J = 6.9 Hz, 6H, C5-Me, C6-Me) ppm.

^13C NMR (125 MHz, CDCl_3): δ = 167.0, 150.9, 146.4, 119.6, 117.5, 60.1, 28.8, 21.8 (2C), 14.1 ppm.

IR (thin film): 3095 (w), 2967 (s), 2906 (m), 2874 (m), 1717 (s), 1630 (s), 1602 (m), 1308 (s), 1278 (s), 1256 (s), 1242 (s), 1180 (s), 1155 (s), 1108 (m), 1095 (m), 1038 (m), 984 (m), 908 (m), 866 (m), 811 (w), 749 (w), 666 (w), 593 (w) cm^{-1}.

LRMS (EI, m/z): Calcd for C_{10}H_{16}O: 168 g/mol (M^+). Found: 168 g/mol.

Ester 7iii (2.0 g, 11.9 mmol) was dissolved in Et_2O (30 mL) in an oven-dried round bottom flask equipped with a magnetic stir bar. The solution was kept under a positive pressure of nitrogen and cooled using a dry ice/acetone bath. Diisobutylaluminum hydride (1.0 M in hexane, 29.8 mL, 29.8 mmol) was added dropwise via syringe over 15 min. The resulting solution was stirred for 1.5 h. The dry ice/acetone bath was removed and the reaction mixture was stirred for an additional 5 h. The reaction mixture was cooled in
an ice/water bath and the reaction was quenched by the portion-wise addition over 15 min of NaSO₄•10H₂O (20 g). The ice/water bath was removed and the reaction mixture was stirred for 1 h. The mixture was filtered through a plug of celite and the filtrate was concentrated by rotary evaporation. The residue was purified by column chromatography with silica gel (gradient elution, 5% Et₂O/pentane → 10% Et₂O/pentane). Product containing fractions were combined and concentrated by rotary evaporation to give 4-isopropyl-2,4-pentadien-1-ol 7ii as a colorless oil (1.20 g, 80%). Compound 7ii was chromatographically homogeneous.

Data for 7ii:

**TLC:** \( R_f = 0.25 \) (25% EtOAc/pentane), one blue spot with \( p \)-anisaldehyde stain.

\[ \begin{array}{c}
\text{HO} \\
\text{1} \\
\text{3} \\
\text{4} \\
\text{5} \\
\text{7} \\
\text{2} \\
\text{6}
\end{array} \]

\( ^1H \text{NMR} \) (500 MHz, CDCl₃): \( \delta = 6.23 \) (d, \( J = 15.9 \) Hz, 1H, C3-H), 5.91 (dt, \( J = 15.9 \) Hz, 5.9 Hz, 1H, C2-H), 5.01 (s, 1H, C4-H), 4.96 (s, 1H, C4-H), 4.21 (t, \( J = 5.8 \) Hz, 2H, C1-CH₂), 2.58 (sept, \( J = 6.8 \) Hz, 1H, C5-H), 1.58 (s, 1H, OH), 1.09 (d, \( J = 6.8 \) Hz, 6H, C6-Me, C7-Me) ppm.

\( ^13C \text{NMR} \) (125 MHz, CDCl₃): \( \delta = 151.9, 133.3, 127.2, 112.5, 63.9, 29.3, 22.1 \) (2C) ppm.

**IR** (thin film): 3338 (s, broad), 3090 (m), 3032 (m), 2962 (s), 2872 (s), 1787 (w), 1606 (m), 1460 (m), 1418 (m), 1380 (m), 1255 (w), 1157 (w), 1097 (m), 1019 (m), 969 (s), 890 (m), 806 (w) cm⁻¹.

**HRMS** (EI, \( m/z \)): Calcd for C₈H₁₄O: 126.1045 g/mol (M⁺). Found: 126.1044 g/mol.

\[ \begin{array}{c}
\text{MeO}_2\text{C} \\
\text{MeO}_2\text{C}
\end{array} \]

4-Isopropyl-2,4-pentadien-1-ol 7ii (4.77 g, 37.8 mmol) was dissolved in THF (100 mL) in an oven-dried round bottom flask equipped with a magnetic stir bar. The solution was kept under a positive pressure of nitrogen and was cooled using a dry ice/acetone bath. \( n \)-BuLi (2.5 M in hexane, 16.6 mL, 41.6 mmol) was added dropwise via syringe over 3 min. The resulting yellow solution was stirred for 5 min. MsCl (4.76 g, 41.6 mmol) was added via syringe over 5 min and the resulting colorless solution was stirred for 30 min. Meanwhile, into a separate oven-dried flask charged with a stir bar was added 4 Å molecular sieves (~2 g) and THF (100 mL). LiBr (16.4 g, 189 mmol) was added in one portion. The LiBr mixture was stirred for 15 min and was then cannulated over ~5 min into the reaction mixture. The reaction mixture was stirred for 30 min and then the dry ice/acetone bath was removed and the reaction mixture was stirred at ambient temperature for 1.5 h. Dimethyl malonate (1.99 g, 10.8 mmol) was added dropwise over 10 min via syringe to a suspension of sodium hydride (60% dispersion in mineral oil, 1.97 g, 49.14 mmol) in THF (100 mL). The mixture was stirred at ambient temperature under a positive pressure of nitrogen for 15 min and was then cooled using an ice/water bath. The solution containing the diene was cannulated over 10 min into the solution of the malonate and the reaction mixture was stirred overnight at ambient temperature. The reaction was quenched by the addition over 30 seconds of saturated aqueous NH₄Cl (100 mL) and the
product was extracted with Et<sub>2</sub>O (3x50 mL). The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered through a fritted funnel, and concentrated by rotary evaporation. The residue was purified by column chromatography with silica gel (gradient elution, 100% pentane → 2% Et<sub>2</sub>O/pentane → 5% Et<sub>2</sub>O/pentane). Product containing fractions were combined and concentrated by rotary evaporation to give diene 7i as a colorless oil (5.32 g, 59%). Compound 7i was chromatographically homogeneous.

Data for 7i:

**TLC**: R<sub>f</sub> = 0.28 (5% EtOAc/pentane), one blue spot with p-anisaldehyde stain.

**¹H NMR** (500 MHz, CDCl<sub>3</sub>): δ = 6.90 (d, J = 15.9 Hz, 1H, C1-H), 5.67 (dt, J = 15.6, 7.2 Hz, 1H, C4-H), 4.90 (s, 1H, C1-H), 4.89 (s, 1H, C1-H), 3.73 (s, 6H, CO<sub>2</sub>Me, CO<sub>2</sub>Me), 3.47 (t, J = 7.8 Hz, 1H, C6-H), 2.69 (dd, J = 7.8, 7.2 Hz, 2H, C5-CH<sub>2</sub>), 2.52 (sept, J = 6.6 Hz, 1H, C2-H), 1.05 (d, J = 6.9 Hz, C7-Me, C8-Me) ppm.

**¹³C NMR** (125 MHz, CDCl<sub>3</sub>): δ = 169.2 (2C), 152.0, 134.8, 123.8, 111.4, 52.3 (2C), 51.7, 32.1, 29.2, 21.9 (2C) ppm.

**IR** (thin film): 3090 (w), 2959 (m), 2873 (w), 1754 (s), 1738 (s), 1605 (w), 1436 (m), 1343 (m), 1267 (m), 1229 (m), 1201 (m), 1154 (m), 1107 (w), 1029 (w), 970 (w), 832 (w) cm<sup>-1</sup>.

**HRMS** (EI, m/z): Calcd for C<sub>13</sub>H<sub>20</sub>O<sub>4</sub>: 240.1362 g/mol (M<sup>+</sup>). Found: 240.1365 g/mol.

Allenol 4i: (100 mg, 1.02 mmol) was dissolved in THF (2 mL) in an oven-dried round bottom flask equipped with a magnetic stir bar. The solution was kept under a positive pressure of nitrogen and was cooled using a dry ice/acetone bath. n-BuLi (2.25 M in hexane, 0.5 mL, 1.12 mmol) was added dropwise via syringe over 2 min. The resulting yellow solution was stirred for 10 min. MsCl (95 µL, 1.22 mmol) was added via syringe over 1 min. and the resulting colorless solution was stirred for 15 min. Meanwhile, in a separate oven-dried flask charged with a stir bar was weighed 4 Å molecular sieves (300 mg). LiBr (443 mg, 5.1 mmol) was added in one portion and THF (2 mL) was added in one portion via syringe. The LiBr mixture was stirred for 5 min and was then cannulated over 3 min into the reaction mixture. The dry ice/acetone bath was removed and the reaction mixture was stirred at ambient temperature for 6 h. Diene-malonate 7i (233 mg, 0.97 mmol) was dissolved in THF (2 mL) in an oven-dried flask charged with a magnetic stir bar. Sodium hydride (60% dispersion in mineral oil, 44 mg, 1.12 mmol) was added all at once. The mixture was stirred at ambient temperature under a positive pressure of nitrogen for 20 min and was then cooled using an ice/water bath. The solution containing the allene was cannulated over 3 min into the solution of the diene and the reaction mixture was stirred overnight at ambient temperature. The reaction was quenched by the addition over 30 seconds of saturated aqueous NH<sub>4</sub>Cl (10 mL) and the
product was extracted with EtOAc (3x 4 mL). The combined organic extracts were washed with brine (3x 4 mL), dried over MgSO4, filtered through a fritted funnel, and concentrated by rotary evaporation. The residue was purified by column chromatography with silica gel (gradient elution, 100% pentane → 1% EtOAc/pentane, 2% EtOAc/pentane, 3% EtOAc/pentane). Product containing fractions were combined and concentrated by rotary evaporation to give diene-allene 7 as a colorless oil (77 mg, 24%). Compound 7 was chromatographically homogeneous.

Data for 7:

**TLC:** \( R_f = 0.58 \) (8% EtOAc/pentane), one blue spot with \( p \)-anisaldehyde stain.

![Diagram](image)

\[^1H\text{NMR}\] (500 MHz, CDCl3): \( \delta = 6.01 \) (d, \( J = 15.7 \) Hz, 1H, C7-H), 5.55 (dt, \( J = 15.5, 7.7 \) Hz, 1H, C6-H), 4.88 (s, 2H, C8-H, C8-H), 4.78 (tsept, \( J = 7.6, 2.8 \) Hz, 1H, C1-H), 3.71 (s, 6H, CO2Me, CO2Me), 2.73 (dd, \( J = 7.7, 1.1 \) Hz, 2H, C5-CH\(_2\)), 2.56 (d, \( J = 7.6 \) Hz, 2H, C2-CH\(_2\)), 2.51 (sept, \( J = 6.8 \) Hz, 1H, C9-H), 1.66 (d, \( J = 2.8 \) Hz, 6H, C3-Me, C4-Me), 1.05 (d, \( J = 6.8 \) Hz, 6H, C10-Me, C11-Me) ppm.

\[^{13}C\text{NMR}\] (125 MHz, CDCl3): \( \delta = 203.8, 171.2 \) (2C), 152.3, 136.0, 122.6, 111.4, 95.2, 82.7, 58.3, 52.4 (2C), 35.9, 32.8, 29.3, 22.1 (2C), 20.5 (2C) ppm.

**IR** (thin film): 2956 (m), 2872 (w), 1737 (s), 1605 (w), 1437 (m), 1363 (w), 1278 (m), 1243 (m), 1179 (m), 1079 (w), 970 (w), 891 (w), 765 (w) cm\(^{-1}\).

**LRMS** (ESI, m/z): Calcd for C\(_{19}\)H\(_{28}\)O\(_4\): 320.2 g/mol (M\(^+\)). Found: 321.2 g/mol (M+H\(^+\)).

Sulfonamide 9i (304 mg, 1.28 mmol) was weighed into a round bottom flask equipped with a magnetic stir bar. Dienol 7ii (170 mg, 1.35 mmol) and PPh\(_3\) (369 mg, 1.41 mmol) were each added in one portion. THF (10 mL) was added via syringe and the solution was stirred under a positive pressure of nitrogen. The solution was cooled using an ice/water bath. A solution of DEAD (246 mg, 1.41 mmol) in THF (5 mL) was added via syringe dropwise over the course of 30 min. The resulting yellow-orange solution was allowed to warm to ambient temperature and was stirred for 24 h. The reaction mixture was diluted with ether (40 mL) and was transferred to a separatory funnel. The organic layer was washed with brine (3x 15 mL), dried over MgSO4, and vacuum filtered through a fritted funnel. The filtrate was concentrated by rotary evaporation and the residue was purified by flash chromatography with silica gel (gradient elution 100% pentane → 5% Et\(_2\)O/pentane). Product-containing fractions were combined and concentrated by rotary evaporation to give 9 as a colorless oil (280 mg, 63%). Compound 9 was chromatographically homogeneous.
Data for 9:

**TLC:** $R_f = 0.71$ (15% EtOAc/pentane), one blue spot with $p$-anisaldehyde stain.

![TLC Diagram]

**$^1$H NMR** (400 MHz, CDCl$_3$): $\delta = 7.71$-$7.68$ (m, 2H), 7.30-$7.27$ (m, 2H), 6.05 (d, $J = 15.7$ Hz, 1H, C7-H), 5.47 (dt, $J = 15.9$, 6.7 Hz, 1H, C6-H), 5.08 (qdt, $J = 7.2$, 7.0, 2.3 Hz, 1H, C3-H), 4.93 (s, 1H, C8-H), 4.89 (s, 1H, C8-H), 4.70 (td, $J = 7.2$, 7.0, 3.2 Hz, 1H, C1-H), 3.94 (dd, $J = 14.2$, 6.7 Hz, 1H, C2-H), 3.87 (dd, $J = 14.2$, 6.7 Hz, 1H, C2-H), 3.84 (ddd, $J = 16.3$, 6.9, 2.1 Hz, C5-H), 3.76 (ddd, $J = 16.3$, 6.9, 2.1 Hz, 1H, C5-H), 2.41 (s, 3H, C12-Me), 2.40 (sept, $J = 6.9$ Hz, 1H, C9-H), 1.61 (d, $J = 7.2$, 3.2 Hz, 3H, C4-Me), 1.01 (d, $J = 6.9$ Hz, 6H, C10-Me, C11-Me) ppm.

**$^{13}$C NMR** (125 MHz, CDCl$_3$): $\delta = 206.1$, 151.7, 143.1, 137.6, 136.2, 129.6 (2C), 127.2 (2C), 122.3, 112.7, 87.1, 85.7, 48.6, 46.1, 29.2, 22.0 (2C), 21.5, 14.1 ppm.

**IR** (thin film): 3031 (w), 2962 (m), 2926 (m), 2871 (m), 1966 (w), 1598 (m), 1494 (w), 1460 (m), 1442 (m), 1411 (w), 1348 (s), 1305 (m), 1287 (w), 1236 (w), 1213 (w), 1184 (w), 1160 (s), 1119 (m), 1093 (m), 1019 (w), 970 (m), 913 (m), 815 (m), 801 (w) cm$^{-1}$.

**HRMS** (EI, $m/z$): Calcd for C$_{20}$H$_{27}$NO$_2$S: 345.1762 g/mol ($M^+$). Found: 345.1750 g/mol.

Allenyl alcohol $^{12i}$ (102 mg, 0.81 mmol) was added dropwise over 5 min via syringe to a stirred suspension of sodium hydride (60% dispersion in mineral oil, 36 mg, 0.9 mmol) in THF (8.1 mL). The reaction mixture was heated to reflux in an oil bath for 10 minutes. The reaction was cooled to RT and trans-1-bromopenta-2,4-diene $^{4ii}$ (166 mg, 1.13 mmol) was added dropwise over 5 min via syringe. The resulting mixture was stirred for 3 h at RT and was then heated in a thermostat-controlled oil bath preheated to 60 $^\circ$C for 7.5 hours. The reaction was cooled to RT and the reaction was quenched by the addition of saturated aqueous ammonium chloride (10 mL). The organics were extracted with diethyl ether (3x5 mL). The organic layers were combined, washed with brine (20 mL), dried over sodium sulfate, filtered, and concentrated by rotary evaporation. The residue was purified via flash chromatography to yield diene-allene $^{12}$ (53 mg, 34%) as a clear colorless oil. Compound $^{12}$ was chromatographically homogeneous.

Data for $^{12}$:

**TLC:** $R_f = 0.35$ (2% EtOAc/pentane), one blue spot with $p$-anisaldehyde.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 6.36$ (dt, $J = 17.2, 10.0$ Hz, 1H, C7-H), 6.30-6.23 (m, 1H, C6-H), 5.78 (dt, $J = 14.8, 6.4$ Hz, 1H, C5-H), 5.30-5.19 (m, 3H, C8cis-H, C8trans-H, C3-H), 5.11-5.08 (m, 1H, C1-H), 4.04 (d, $J = 5.6$ Hz, 2H, C2-CH$_2$), 4.00 (dd, $J = 2.4, 6.8$ Hz, 2H, C4-CH$_2$), 1.05 (s, 9H, t-Bu) ppm.

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 202.3, 136.3, 133.2, 130.0, 117.5, 103.8, 90.2, 69.7, 68.9, 31.8, 30.1$ (3C) ppm.

IR (thin film): 3087 (w), 2961 (s), 2903 (m), 2865 (m), 1961 (w), 1722 (w), 1651 (w), 1604 (w), 1459 (m), 1363 (m), 1253 (w), 1190 (w), 1108 (m), 1045 (m), 1004 (s), 953 (w), 903 (m), 870 (w), 741 (w) cm$^{-1}$.

LRMS (ESI, $m/z$): Calcd for C$_{13}$H$_{20}$O: 193.2 g/mol (M+H$^+$). Found: 215.2 g/mol (M+Na$^+$).

Sulfonamide 15i ($242$ mg, $1.09$ mmol) was weighed into a round bottom flask equipped with a magnetic stir bar. Dienol 7ii ($151$ mg, $1.19$ mmol) and PPh$_3$ ($356$ mg, $1.36$ mmol) were each added in one portion. THF ($10$ mL) was added via syringe and the solution was stirred under a positive pressure of nitrogen. The solution was cooled using an ice/water bath. A solution of DEAD ($246$ mg, $1.41$ mmol) in THF ($5$ mL) was added via syringe drop wise over the course of $30$ min. The resulting yellow-orange solution was allowed to warm to ambient temperature and was stirred for $24$ h. The reaction mixture was diluted with ether ($40$ mL) and was transferred to a separatory funnel. The organic layer was washed with brine ($3x15$ mL), dried over MgSO$_4$, and vacuum filtered through a fritted funnel. The filtrate was concentrated by rotary evaporation and the residue was purified by flash chromatography with silica gel (gradient elution 100% pentane $\rightarrow$ 5% Et$_2$O/pentane). Product-containing fractions were combined and concentrated by rotary evaporation to give 15 as a colorless oil ($263$ mg, 73%). Compound 15 was chromatographically homogeneous.

Data for 15:

TLC: $R_f = 0.75$ (25% EtOAc/pentane), one blue spot with $p$-anisaldehyde stain.
$^1$H NMR (500 MHz, CDCl$_3$); $\delta = 7.71-7.68$ (m, 2H), 7.30-7.28 (m, 2H), 6.06 (d, $J = 16.0$ Hz, 1H, C6-H), 5.47 (dt, $J = 9.0$, 6.9 Hz, 1H, C5-H), 4.93 (s, 1H, C7-H), 4.90 (s, 1H, C7-H), 4.92-4.87 (m, 1H, C1-H), 4.70-4.67 (m, 2H, C3-H, C3-H), 3.89 (d, $J = 7.0$ Hz, 2H, C4-CH$_2$), 3.86-3.83 (m, 2H, C2-CH$_2$), 2.42 (s, 3H, C11-Me), 2.40 (sept, $J = 6.7$ Hz, 1H, C8-H), 1.01 (d, $J = 6.9$ Hz, 6H, C9-Me, C10-Me) ppm.

$^{13}$C NMR (125 MHz, CDCl$_3$); $\delta = 209.6, 151.7, 143.2, 137.5, 136.3, 129.6$ (2C), 127.2 (2C), 122.2, 112.8, 85.7, 76.1, 48.9, 45.6, 29.2, 22.0 (2C), 21.5 ppm.

IR (thin film): 2962 (m), 2871 (w), 1955 (m), 1598 (w), 1495 (w), 1445 (m), 1344 (s), 1305 (m), 1160 (s), 1093 (m), 971 (m), 923 (m), 895 (m), 851 (m), 815 (m), 759 (w) cm$^{-1}$.

HRMS (EI, m/z): Calcd for C$_{19}$H$_{25}$NO$_2$S: 331.1606 g/mol (M$^+$). Found: 331.1593 g/mol.

5. Allenyl sulfonamide 9i was prepared using a procedure analogous to that described for 1i (ref. 1). Pentadien-1-ol was prepared according to a reported procedure: L. I. Olsson, A. Claesson, Acta Chemica Scand. B 1977, 7, 614-618.
7. Allenyl sulfonamide 15i was prepared using a procedure analogous to that described for 1i (ref. 1). Butadien-1-ol was prepared according to a reported procedure: L. Brandsma, H. D. Verkuijse, “Synthesis of Acetylenes, Allenes and Cumulenes, A Laboratory Manual” Elsevier Science Publishers, New York, 1981, pp. 188-189.