- Supporting Information -

Z-Selective Ring Opening of Vinyl Oxetanes with Dialkyl Dithiophosphate Nucleophiles

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General Information:
All reactions were carried out under a nitrogen atmosphere with flame-dried glassware. Commercially available reagents were used as received without further purification unless specified. Toluene, benzene, diethyl ether, dichloromethane, and tetrahydrofuran were dried through activated alumina columns. Flash chromatography was done with Silicycle SiliaFlash® F60 silica, and thin layer chromatography (TLC) was performed with EMD 250µm silica gel 60-F254 plates. \(^1\)H NMR data were recorded on Bruker (400, 500 or 600 MHz) spectrometers with tetramethylsilane (TMS) (0 ppm) as internal reference. Signals are reported as follows: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), dt (doublet of triplets), m (multiplet). Coupling constants are reported in hertz (Hz). \(^1^3\)C NMR spectra were recorded on spectrometers operating at 100 or 125 MHz with chloroform (CDCl\(_3\)) (77.0 ppm) as internal reference. Infrared spectra were obtained on an FT-IR spectrometer. High-resolution mass (HRMS) spectra were performed at the University of Arizona Mass Spectrometry Facility.
General Procedure A: Preparation of \( O,O \)-Dialkyl Dithiophosphates

\[
P_{4}S_{10} + ROH \xrightarrow{\text{toluene, heat}} HS\text{P}OR \text{ (OR)}
\]

The known \( O,O \)-dialkyl dithiophosphoric acids were prepared according to the reported procedures with minor modifications\(^1\). To a flame dried three-necked 250 mL rbf charged with condenser, 15 mL addition funnel and magnetic stir bar was introduced dry toluene (100 mL) and \( P_{4}S_{10} \) (13.36 g, 30 mmol). The above mixture was heated to 40 °C with stirring. At the same temperature, dry methanol (12.2 mL, 300 mmol) was added through addition funnel during a course of 30 minutes. The mixture was heated at 65 °C for 10 hours and then reflux for 1 hour at which point a clear homogenous solution was obtained. The excessive amount of toluene was removed under reduced pressure and the residue was distilled under high vacuum.

General Procedure B: Synthesis of vinyl oxetanes from \( \beta \)-chloro ketone

\[
\text{R}^1\text{C}==\text{CHCl} \xrightarrow{\text{CeCl}_3, \text{THF}, -78^\circ\text{C} \to \text{rt}} \text{R}^1\text{C}==\text{CH(OH)}\text{Cl} \xrightarrow{\text{NaH, DMSO, rt}} \text{R}^1\text{O}
\]

The preparation of vinyl oxetanes from the corresponding \( \beta \)-chloro ketone as precursor has been described in our previous publication\(^2\). The same procedures were followed for the preparation of vinyl oxetanes here except for \( 1r \).

Cerium chloride (\( \text{CeCl}_3 \cdot 7\text{H}_2\text{O} \)) (3.55mmol, 1.2 eq) was finely ground into a powder in a mortar and transferred into a 50 mL two-necked flame dried round bottom flask charged with a stir bar. The flask was heated gradually to 140 °C in an oil bath under high vacuum and maintained at the same temperature for 2 hs. Then the oil bath was removed and the flask was cooled to room temperature. THF (10 mL) was introduced with vigorous stirring. The suspension was well stirred under nitrogen at room temperature for 2 h. Then the flask placed in an acetone-dry ice bath for another 30 mins. The corresponding vinyl magnesium bromide (3.55 mmol, 1.2 eq) was added via syringe. After being stirred for 45 mins at -78 °C, the corresponding \( \beta \)-chloro ketone (2.96 mmol, 1 eq) in THF (15 mL) was added via syringe slowly. The reaction was maintained at -78 °C for 3 hrs, TLC indicated that all of the starting material was consumed. The reaction was quenched with 50 mL sat. NaHCO\(_3\). After separation, the
aqueous layer was extracted with ether (4 x 10 mL). The combined organic layers were washed sequentially with sat. NaHCO₃ (1 x 5 mL), water (1 x 5 mL) and brine (1 x 2 mL) then dried over MgSO₄. The crude product was purified by flash column chromatography on silica gel.

To a 50 mL flame-dried round bottom flask charged with a magnetic stir bar, was introduced 3 mL freshly distilled DMSO and the corresponding allylic alcohol (0.647 mmol, 1 eq). NaH (60% suspension in mineral oil, 1.30 mmol, 2 eq) was added in one portion. Reaction was stirred at room temperature for 30 minutes, during which course, a yellowish or brownish color appeared. The reaction was then chilled to 0 °C by standing in an ice bath, 3 mL sat. NaHCO₃ was added carefully. The organic layer was separated and washed with sat. NaHCO₃ (3 x 5 mL), H₂O (1 x 2 mL) and dried with MgSO₄. The crude product was purified by flash column chromatography.

**General procedure C: Ring opening with dialkyl dithiophosphate**

![Reaction Scheme](image)

To a flame dried 25 mL rbf charged with magnetic stir bar was introduced 5 mL dry DCM, vinyl oxetane (1 mmol), and O,O-diisopropyl dithiophosphoric acid (1.2 mmol, 1.2 eq.). The reaction was stirred at room temperature and monitored by TLC till all of oxetane was consumed. DCM was then removed under reduced pressure and the crude residue was purified by flash chromatography to afford the corresponding alcohol product.
**O,O-dimethyl dithiophosphoric acid (A₁)**

![Image](A1)

Known acid A₁ (reference 1) was prepared according to General Procedure A using P₄S₁₀ (13.36 g, 30 mmol) and MeOH (12.2 mL, 300 mmol). Distillation under high vacuum afforded A₁ (86%) as a clear liquid.

**¹H NMR** (400 MHz, CDCl₃) δ 3.90 (s, 3H), 3.86 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 54.33, 54.27; **³¹P NMR** (162 MHz, CDCl₃) δ 118.50.

**O,O-diisopropyl dithiophosphoric acid (A₃)**

![Image](A3)

Known acid A₃ (reference 1) was prepared according to general procedure A using P₄S₁₀ (10 g, 22.5 mmol) and i-PrOH (15.1 mL, 198 mmol). Distillation under high vacuum afforded A₃ (75%) as a clear liquid.

**¹H NMR** (600 MHz, CDCl₃) δ 4.94 – 4.87 (m, 2H), 1.38 (dd, J = 6.2, 2.4 Hz, 12H); **¹³C NMR** (101 MHz, CDCl₃) δ 73.95, 73.88, 23.54, 23.50; **³¹P NMR** (162 MHz, CDCl₃) δ 81.76.

**2-phenethyl-2-vinyloxetane (0a)**

![Image](0a)

For the preparation of oxetane 0a, please see reference 2

(5-hydroxy-3-phenylpent-2-en-1-yl) **O,O-dimethyl phosphorodithioate (1aa)**

![Image](1aa)

Compound 1aa was prepared according to General Procedure C using oxetane 0a (15 mg, 0.08 mmol) and acid A₁ (15 mg, 0.096 mmol). Purification by flash chromatography [30% EA/Hexanes] afforded 1aa (24 mg, 88%) as a clear liquid. The
Z/E isomers were inseparable and characterized as mixture. Only NMR-data was collected for this mixture since the isopropyl esters became the focus of our studies.

\[ ^1H \text{ NMR} (499 \text{ MHz, CDCl}_3) \delta 7.31 - 7.26 (m, 2H), 7.22 - 7.14 (m, 3H), 5.43 (dt, J = 34.3, 7.9 Hz, 1H), 3.76 (dd, J = 15.0, 6.9 Hz, 6H), 3.73 - 3.68 (m, 2H), 3.45 (dd, J = 23.2, 14.7, 7.9 Hz, 2H), 2.72 (td, J = 9.6, 7.1 Hz, 2H), 2.46 - 2.39 (m, 2H), 2.39 - 2.28 (m, 2H); \]
\[ ^13C \text{ NMR} (126 \text{ MHz, CDCl}_3) \delta 141.38, 140.44, 128.39, 128.34, 128.27, 125.95, 122.29, 122.23, 77.25, 77.00, 76.75, 60.73, 53.94, 53.90, 38.52, 34.47, 33.74, 31.33, 31.30; \]
\[ ^{31}P \text{ NMR} (162 \text{ MHz, CDCl}_3) \delta 99.21(\text{E isomer}) 99.16 (\text{Z isomer}). \]

(5-hydroxy-3-phenethylpent-2-en-1-yl) O,O-diethylphosphorodithioate (1ab)

\[ \text{HO} \]
\[ \text{Ph} \]
\[ \begin{array}{c}
\text{SP(S)(OEt)2} \\
\text{1ab}
\end{array} \]

Compound 1ab was prepared according to General Procedure C using oxetane 0a (23 mg, 0.122 mmol) and acid A2 (27 mg, 0.15 mmol). Purification by flash chromatography [30% EA/Hexanes] afforded 1ab (37.5 mg, 83%) as a clear liquid. The Z/E isomers were inseparable and characterized as mixture. Only NMR-data was collected for this mixture since the isopropyl esters became the focus of our studies.

\[ ^1H \text{ NMR} (400 \text{ MHz, CDCl}_3) \delta 7.30 - 7.25 (m, 2H), 7.21 - 7.13 (m, 3H), 5.44 (t, 7.8 Hz, 1H), 4.27 - 4.06 (m, 4H), 3.70 (q, J = 6.6 Hz, 2H), 3.57 (dd, J = 13.8, 8.0 Hz, 2H), 2.72 (dt, J = 8.1, 6.6 Hz, 2H), 2.48 - 2.39 (m, 2H), 2.39 - 2.32 (m, 2H), 1.36 (dq, J = 7.1, 0.8 Hz, 6H); \]
\[ ^13C \text{ NMR} (101 \text{ MHz, CDCl}_3) \delta 141.48, 140.30, 128.40, 128.32, 125.99, 122.52, 122.45, 63.98, 63.92, 60.79, 38.60, 34.50, 33.80, 31.30, 31.27, 15.92, 15.84; \]
\[ ^{31}P \text{ NMR} (162 \text{ MHz, CDCl}_3) \delta 94.14(\text{E isomer}) 93.99(\text{Z isomer}). \]

(5-hydroxy-3-phenethylpent-2-en-1-yl) O,O-diisopropyl phosphorodithioate (2a)

\[ \text{HO} \]
\[ \text{Ph} \]
\[ \begin{array}{c}
\text{SP(S)(OiPr)2} \\
\text{2a}
\end{array} \]

\[ \text{HO} \]
\[ \text{Ph} \]
\[ \begin{array}{c}
\text{SP(S)(OiPr)2} \\
\text{2a'}
\end{array} \]

Compound 2a was prepared according to General Procedure C using oxetane 1a (20 mg, 0.1 mmol) and acid A3 (27 mg, 0.12 mmol). Purification by flash chromatography [30% EA/Hexanes] afforded 2a + 2a' (35 mg, 87%) as a clear liquid.

2a: \[ ^1H \text{ NMR} (600 \text{ MHz, CDCl}_3) \delta 7.30 - 7.26 (m, 2H), 7.21 - 7.15 (m, 3H), 5.50 (t, J = 8.0 Hz, 1H), 4.83 (dhept, J = 12.4, 6.2 Hz, 2H), 3.70 (q, J = 6.5 Hz, 2H), 3.60 (dd, J = 13.2, 8.0 Hz, 2H), 2.73 (dd, J = 9.3, 6.9 Hz, 2H), 2.43 (t, J = 6.7 Hz, 2H), 2.35 (dd,
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**1H NMR** (600 MHz, CDCl₃) δ 7.30 – 7.26 (m, 2H), 7.20 – 7.15 (m, 3H), 5.10 (dd, J = 1.4, 0.7 Hz, 1H), 5.04 (p, J = 1.4 Hz, 1H), 3.60 (ddd, J = 10.8, 9.2, 7.0 Hz, 1H), 3.47 (ddd, J = 10.8, 9.1, 6.1 Hz, 1H), 2.63 (ddd, J = 13.7, 11.2, 6.2 Hz, 1H), 2.50 (ddd, J = 13.7, 11.1, 5.3 Hz, 1H), 2.13 – 2.07 (m, 2H), 1.93 – 1.85 (m, 2H), 1.79 – 1.76 (m, 3H), 1.74 (s, 1H); **13C NMR** (126 MHz, CDCl₃) δ 146.47, 141.88, 128.49, 128.31, 125.93, 112.33, 77.60, 42.12, 41.62, 40.17, 29.45, 19.67; **IR** (neat) ν max/cm⁻¹ 3548, 3070, 3035, 2943, 2890, 1498, 1460, 1227, 1029, 990, 737, 690; **HRMS** [ESI] 238.1120, 240.1071 [(M⁺)⁺; calcd for C₁₄H₁₉ClO 238.1124, 240.1095].

**2a**: **1H NMR** (600 MHz, CDCl₃) δ 7.30 – 7.26 (m, 2H), 7.22 – 7.17 (m, 3H), 5.43 (t, J = 7.9 Hz, 1H), 4.86 – 4.77 (m, 2H), 3.71 (t, J = 6.3 Hz, 2H), 3.41 (dd, J = 13.9, 7.9 Hz, 2H), 2.72 (dd, J = 9.0, 7.0 Hz, 2H), 2.41 (dd, J = 9.0, 7.0 Hz, 2H), 2.31 (t, J = 6.1 Hz, 2H), 1.34 (dd, J = 7.5, 6.2 Hz, 12H); **13C NMR** (126 MHz, CDCl₃) δ 141.32, 139.93, 128.41, 126.09, 123.00, 122.94, 73.44, 73.39, 60.49, 39.86, 34.74, 32.41, 31.11, 23.78, 23.75, 23.52, 23.48; **31P NMR** (162 MHz, CDCl₃) δ 91.07.

**5-chloro-2-methyl-3-phenethylpent-1-en-3-ol (0b)**

Alcohol 0b was prepared according to General Procedure B using 1-chloro-5-phenylpentan-3-one (300 mg, 1.53 mmol) and isopropenylmagnesium bromide (3.67 mL, 0.5M, 1.84 mmol). Purification by flash chromatography [1% EA/Hexanes] afforded 0b [313 mg, 86%] as a clear liquid.

**1H NMR** (499 MHz, CDCl₃) δ 7.30 – 7.26 (m, 2H), 7.20 – 7.15 (m, 3H), 5.10 (dd, J = 1.4, 0.7 Hz, 1H), 5.04 (p, J = 1.4 Hz, 1H), 3.60 (ddd, J = 10.8, 9.2, 7.0 Hz, 1H), 3.47 (ddd, J = 10.8, 9.1, 6.1 Hz, 1H), 2.63 (ddd, J = 13.7, 11.2, 6.2 Hz, 1H), 2.50 (ddd, J = 13.7, 11.1, 5.3 Hz, 1H), 2.13 – 2.07 (m, 2H), 1.93 – 1.85 (m, 2H), 1.79 – 1.76 (m, 3H), 1.74 (s, 1H); **13C NMR** (126 MHz, CDCl₃) δ 146.47, 141.88, 128.49, 128.31, 125.93, 112.33, 77.60, 42.12, 41.62, 40.17, 29.45, 19.67; **IR** (neat) ν max/cm⁻¹ 3548, 3070, 3035, 2943, 2890, 1498, 1460, 1227, 1029, 990, 737, 690; **HRMS** [ESI] 238.1120, 240.1071 [(M⁺)⁺; calcd for C₁₄H₁₉ClO 238.1124, 240.1095].

**2-phenethyl-2-(prop-1-en-2-yl) oxetane (1b)**

Oxetane 1b was prepared according to General Procedure B alcohol 0b (150 mg, 0.63 mmol) and NaH (60% suspension in mineral oil, 51 mg, 1.26 mmol). Purification by flash chromatography [0.5:0.5:99 EA/TEA/Hexanes] gave vinyl oxetane 1b as a clear liquid.
$^{1}$H NMR (400 MHz, CDCl$_3$) δ 7.29 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 5.20 – 5.18 (m, 1H), 4.98 (dq, $J = 3.1$, 1.5 Hz, 1H), 4.47 (m, 2H), 2.70 – 2.59 (m, 1H), 2.55 – 2.41 (m, 3H), 2.16 (ddd, $J = 13.7$, 12.3, 4.8 Hz, 1H), 1.99 (ddd, $J = 13.7$, 12.5, 4.8 Hz, 1H), 1.70 (dd, $J = 1.5$, 0.8 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 146.96, 142.29, 128.34, 128.32, 125.70, 110.18, 89.40, 64.48, 40.84, 31.82, 29.69, 29.28, 17.20; IR (neat) $\nu_{max}$/cm$^{-1}$ 3084, 3061, 3026, 2933, 2879, 1496, 1452, 1226, 1172, 991, 977, 750, 698; HRMS [ESI] 202.1360 ([M]$^+$; calcd for C$_{14}$H$_{18}$O 202.1358).

(5-hydroxy-2-methyl-3-phenethylpent-2-en-1-yl) O,O-diisopropyl phosphorodithioate (2b)

Compound 2b was prepared according to General Procedure C using oxetane 1b (57 mg, 0.28 mmol) and acid A$_3$ (90 mg, 0.42 mmol). Purification by flash chromatography [30% EA/Hexanes] afforded 2b + 2b' [107 mg, 92%] as a clear liquid.

2b: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.29 – 7.24 (m, 2H), 7.20 – 7.13 (m, 3H), 4.91 – 4.77 (m, 2H), 3.69 (t, $J = 6.8$ Hz, 2H), 3.63 (d, $J = 9.6$ Hz, 2H), 2.65 (dd, $J = 9.3$, 6.8 Hz, 2H), 2.42 (t, $J = 6.8$ Hz, 2H), 2.34 (dd, $J = 9.3$, 6.8 Hz, 2H), 1.71 (s, 3H), 1.37 (dd, $J = 6.2$, 1.2 Hz, 13H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 141.63, 134.45, 128.39, 127.63, 127.54, 125.96, 73.48, 73.41, 61.27, 38.02, 35.75, 34.78, 34.48, 23.79, 23.74, 23.52, 23.47, 17.92; $^{31}$P NMR (162 MHz, CDCl$_3$) δ 91.56; IR (neat) $\nu_{max}$/cm$^{-1}$ 3450, 3024, 2945, 2887, 1494, 1452, 1438, 1226, 1176, 1014, 910, 813, 732, 700, 655; HRMS [ESI] 416.1608 ([M]$^+$; calcd for C$_{20}$H$_{33}$O$_3$PS$_2$ 416.1609).

2b': $^1$H NMR (400 MHz, CDCl$_3$) δ 7.29 – 7.24 (m, 2H), 7.21 – 7.15 (m, 3H), 4.83 (dhept, $J = 12.4$, 6.2 Hz, 2H), 3.66 (dt, $J = 16.9$, 8.3 Hz, 2H), 3.50 (d, $J = 10.1$ Hz, 2H), 2.70 (dd, $J = 9.5$, 6.7 Hz, 2H), 2.45 – 2.35 (m, 4H), 1.82 (s, 3H), 1.34 (dd, $J = 6.2$, 4.9 Hz, 12H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 141.62, 134.27, 128.42, 128.37, 127.69, 127.61, 126.00, 73.40, 73.34, 61.07, 37.60, 35.84, 35.36, 34.82, 23.77, 23.73, 23.51, 23.46, 18.13; $^{31}$P NMR (162 MHz, CDCl$_3$) δ 91.09.
(E)-2-phenethyl-2-(prop-1-en-1-yl) oxetane (1c)

For the preparation of 1c please see reference 2.

(6-hydroxy-4-phenethylhex-3-en-2-yl) O,O-diisopropyl phosphorodithioate (2c)

Compound 2c was prepared according to General Procedure C using oxetane 1c (80 mg, 0.4 mmol) and acid A₃ (102 mg, 0.47 mmol). Purification by flash chromatography [30% EA/Hexanes] afforded 2c [129 mg, 78%] as a clear liquid. The E/Z isomers were inseparable by flash chromatography and characterized as a mixture.

¹H NMR (600 MHz, CDCl₃) δ 7.30 – 7.26 (m, 2H), 7.20 – 7.14 (m, 3H), 5.29 (dd, J = 15.7, 10.3 Hz, 1H), 4.90 – 4.73 (m, 2H), 4.37 – 4.09 (m, 1H), 3.83 – 3.66 (m, 2H), 2.78 – 2.62 (m, 2H), 2.56 – 2.45 (m, 2H), 2.41 – 2.26 (m, 2H), 1.44 (t, J = 7.4 Hz, 3H), 1.33 (ddd, J = 10.9, 6.1, 2.3 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 141.62, 141.50, 137.47, 136.78, 130.55, 130.47, 129.71, 129.62, 128.56, 128.40, 128.37, 128.33, 126.02, 125.91, 73.68, 73.60, 73.52, 73.48, 73.46, 73.41, 60.79, 60.33, 43.87, 43.84, 43.41, 43.37, 39.55, 38.35, 34.60, 34.44, 32.80, 24.23, 24.18, 23.78, 23.73, 23.70, 23.65, 23.61, 23.55, 23.51, 23.46, 23.43; ³¹P NMR (162 MHz, CDCl₃) δ 91.87, 90.93; IR (neat) νmax/cm⁻¹ 3453, 3022, 2941, 2884, 1495, 1451, 1428, 1226, 1177, 1010, 916, 810, 728, 700, 650; HRMS [ESI] 416.1600 [(M)+; calcld for C₂₀H₃₃O₃PS₂ 416.1609]

3-(2-chloroethyl)-4,4-dimethyl-5-phenylpent-1-en-3-ol (0d)

Alcohol 0d was prepared according to General Procedure B using 5-chloro-2,2-dimethyl-1-phenylpentan-3-one (synthesized as shown below) (200 mg, 0.89 mmol) and vinylmagnesium bromide (1.53 mL, 0.7M, 1.07 mmol). Purification by flash chromatography afforded 0d [204 mg, 91%] as a clear liquid.
$^1$H NMR (600 MHz, CDCl$_3$) δ 7.30 – 7.26 (m, 2H), 7.22 (ddt, $J$ = 6.4, 5.1, 2.5 Hz, 1H), 7.13 (dt, $J$ = 3.3, 1.9 Hz, 2H), 6.02 (dd, $J$ = 17.3, 11.0 Hz, 1H), 5.33 (m, 2H), 3.63 (td, $J$ = 10.5, 6.0 Hz, 1H), 3.53 (td, $J$ = 10.6, 4.9 Hz, 1H), 2.69 – 2.61 (m, 2H), 2.27 (ddd, $J$ = 13.7, 10.6, 6.1 Hz, 1H), 2.15 – 2.07 (m, 1H), 1.72 (dd, $J$ = 1.1 Hz, 1H), 0.87 (s, 3H), 0.82 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 139.38, 138.81, 131.07, 127.76, 126.01, 115.11, 79.95, 42.10, 41.72, 41.33, 37.14, 21.51, 21.15; IR (neat) ν$_{\text{max}}$/cm$^{-1}$ 3423, 3418, 2927, 1274, 1177, 1032, 909, 733, 704; HRMS [ESI] 252.1278 [(M)+; calcd for C$_{15}$H$_{21}$ClO 252.1281]

**Synthesis of β-Chloro Ketone Precursor:**

![Chemical structure diagram]

2-(2-methyl-1-phenylpropan-2-yl)-2-vinyloxetane (1d)

Oxetane 1d was prepared according to General Procedure B using alcohol 0d (133 mg, 0.53 mmol) and NaH (60% suspension in mineral oil, 42 mg, 1.05 mmol). Purification by flash chromatography [1% EA/Hexanes] gave oxetane 1d [104 mg, 93%] as a clear liquid.

$^1$H NMR (499 MHz, CDCl$_3$) δ 7.28 – 7.23 (m, 2H), 7.22 – 7.17 (m, 1H), 7.13 (dt, $J$ = 8.1, 2.5 Hz, 2H), 6.15 (dd, $J$ = 17.0, 10.8 Hz, 1H), 5.49 (dd, $J$ = 17.0, 2.0 Hz, 1H), 5.30 (dd, $J$ = 10.8, 2.0 Hz, 1H), 4.47 (ddd, $J$ = 8.8, 7.2, 5.8 Hz, 1H), 4.36 (dt, $J$ = 9.2, 5.9 Hz, 1H), 2.78 (ddd, $J$ = 11.1, 9.2, 7.2 Hz, 1H), 2.57 (s, 2H), 2.26 (ddd, $J$ = 11.1, 8.8, 6.0 Hz, 1H), 0.90 (s, 3H), 0.86 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 139.95, 138.90, 130.92, 127.64, 125.80, 113.58, 92.44, 64.43, 41.09, 40.45, 27.96, 20.14, 20.09; IR (neat) ν$_{\text{max}}$/cm$^{-1}$ 3080, 3071, 3020, 2930, 2881, 1495, 1450, 1226, 1171, 977, 750, 698; HRMS [ESI] 216.1520 [(M)+; calcd for C$_{15}$H$_{20}$O 216.1514].
(3-(2-hydroxyethyl)-4,4-dimethyl-5-phenylpent-2-en-1-yl) O,O-diisopropyl phosphorodithioate (2d)

Compound 2d was prepared according to General Procedure C using oxetane 1d (7 mg, 0.032 mmol) and acid A3 (8.3 mg, 0.038 mmol). Purification by flash chromatography [30% EA/Hexanes] afforded 2d [13 mg, 95%] as a clear liquid.

\[ \text{1H NMR (499 MHz, CDCl}_3) \delta 7.25 - 7.15 (m, 3H), 7.03 - 6.99 (m, 2H), 5.31 (t, J = 8.1 Hz, 1H), 4.82 (dhept, J = 12.4, 6.2 Hz, 2H), 3.70 - 3.63 (m, 2H), 3.60 (dd, J = 12.2, 8.1 Hz, 2H), 2.62 (s, 2H), 2.56 - 2.49 (m, 2H), 1.35 (dd, J = 6.2, 3.9 Hz, 12H), 1.03 (s, 6H); \]

\[ \text{13C NMR (126 MHz, CDCl}_3) \delta 146.12, 138.43, 130.45, 127.60, 125.99, 121.36, 121.30, 73.43, 73.38, 62.50, 47.47, 40.73, 32.35, 32.32, 32.04, 26.54, 23.75, 23.71, 23.49, 23.45; \]

\[ \text{31P NMR (162 MHz, CDCl}_3) \delta 91.66; \]

\[ \text{IR (neat) } v_{\text{max}}/\text{cm}^{-1} 3516, 3403, 3386, 2977, 2931, 1465, 1452, 1384, 1373, 1176, 1102, 1037, 989, 966, 775, 702, 651; \]

\[ \text{HRMS [ESI] 430.1760 [(M)+; calcd for C}_21\text{H}_35\text{O}_3\text{PS}_2 430.1765]. \]

1-chloro-5-methyl-3-phenethylhex-4-en-3-ol (0e)

Alcohol 0e was prepared according to General Procedure B using 1-chloro-5-phenylpentan-3-one (300 mg, 1.53 mmol) and 2-methyl propenylmagnesium bromide (3.67 mL, 0.5 M, 1.84 mmol). Purification by flash chromatography afforded 0e [340 mg, 88%] as a clear liquid.

\[ \text{1H NMR (600 MHz, CDCl}_3) \delta 7.30 - 7.26 (m, 2H), 7.20 - 7.16 (m, 4H), 5.16 - 5.15 (m, 1H), 3.70 - 3.65 (m, 1H), 3.64 - 3.58 (m, 1H), 2.75 - 2.63 (m, 2H), 2.12 (dd, J = 14.9, 7.2 Hz, 2H), 1.91 - 1.87 (m, 2H), 1.86 (d, J = 1.3 Hz, 3H), 1.76 (d, J = 1.4 Hz, 3H); \]

\[ \text{13C NMR (101 MHz, CDCl}_3) \delta 142.16, 135.57, 128.46, 128.33, 128.06, 125.87, 75.60, 44.89, 44.49, 40.66, 30.17, 27.59, 18.86; \]

\[ \text{IR (neat) } v_{\text{max}}/\text{cm}^{-1} 3555, 3518, 3448, 3442, 3025, 2965, 1700, 1250, 1186, 1035, 928, 907, 736, 704; \]

\[ \text{HRMS [ESI] 252.1280, 254.1244 [(M)+; calcd for C}_15\text{H}_3\text{ClO} 252.1281, 154.1251]. \]
2-(2-methylprop-1-en-1-yl)-2-phenethyloxetane (1e)

Oxetane 1e was prepared according to General Procedure B from using alcohol 0e (30 mg, 0.12 mmol) and NaH (60% suspension in mineral oil, 9.6 mg, 0.24 mmol). Purification by flash chromatography [0.5:0.5:99 EA:TEA:Hexanes] afforded oxetane 1b [24 mg, 96%] as a clear liquid.

$^{1}$H NMR (600 MHz, CDCl$_3$) δ 7.30 – 7.26 (m, 2H), 7.23 – 7.16 (m, 3H), 5.41 (dq, $J$ = 2.7, 1.3 Hz, 1H), 4.52 (dd, $J$ = 8.4, 7.1 Hz, 2H), 2.80 – 2.64 (m, 3H), 2.61 – 2.55 (m, 1H), 2.19 (ddd, $J$ = 13.5, 12.2, 4.8 Hz, 1H), 2.04 (ddd, $J$ = 13.5, 12.4, 5.0 Hz, 1H), 1.74 (d, $J$ = 1.4 Hz, 3H), 1.66 (d, $J$ = 1.2 Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 142.50, 132.04, 130.57, 128.32, 125.66, 87.86, 65.30, 43.88, 33.60, 29.78, 26.14, 18.67; IR (neat) $v_{\text{max}}$/cm$^{-1}$ 3419, 3413, 1469, 1399, 1250, 1231, 1035, 994, 968, 922; HRMS [ESI] 216.1510 [(M)$^+$; calcd for C$_{15}$H$_{21}$O 216.1514]

6, 6-dimethyl-4-phenethyl-3,6-dihydro-2H-pyran (2e')

Pyran 2e' was prepared according to General Procedure C using oxetane 1e (15 mg, 0.07 mmol) and acid A$_3$ (17.8 mg, 0.083 mmol). Purification by flash chromatography [1% EA/Hexanes] afforded 2e' [13 mg, 86%] as a clear sticky oil.

$^{1}$H NMR (600 MHz, CDCl$_3$) δ 7.30 – 7.27 (m, 2H), 7.21 – 7.16 (m, 3H), 5.26 (p, $J$ = 1.5 Hz, 1H), 3.79 (t, $J$ = 5.5 Hz, 2H), 2.73 (dd, $J$ = 8.9, 6.9 Hz, 2H), 2.30 – 2.25 (m, 2H), 2.03 – 1.98 (m, 2H), 1.19 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 141.93, 133.26, 129.15, 128.43, 128.24, 125.78, 71.69, 59.56, 38.95, 33.92, 28.31, 27.64; IR (neat) $v_{\text{max}}$/cm$^{-1}$ 3058, 3033, 2977, 2957, 2848, 1492, 1444, 1386, 1360, 1237, 1135, 968, 913, 699, 668; HRMS [ESI] 216.1514 [(M)$^+$; calcd for C$_{13}$H$_{21}$O 216.1514]
2-phenyl-2-vinylloxetane (1f)

For the preparation of oxetane 1f, please see reference 2.

(5-hydroxy-3-phenylpent-2-en-1-yl) \(O,O\)-diisopropyl phosphorodithioate (2f)

Compound 2f was prepared according to General Procedure C using oxetane 1f (6 mg, 0.037 mmol) and acid A \(_3\) (9.6 mg, 0.045 mmol). Purification by flash chromatography afforded 2f (12 mg, 90%). The \(E\) isomer was lost in mixture and only \(Z\) isomer was characterized.

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta 7.37 – 7.26\) (m, 6H), 5.95 (t, \(J = 8.1\) Hz, 1H), 4.90 – 4.81 (m, 2H), 3.78 (dd, \(J = 14.0, 8.1\) Hz, 2H), 3.65 (d, \(J = 5.9\) Hz, 2H), 2.88 (t, \(J = 6.7\) Hz, 2H), 1.36 (dd, \(J = 6.2, 4.6\) Hz, 13H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 141.35, 140.43, 128.46, 127.63, 126.44, 125.28, 125.21, 73.61, 73.54, 61.15, 33.39, 32.14, 32.10, 23.79, 23.74, 23.52, 23.47; \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta 91.08\); IR (neat) \(\nu_{\text{max}}/\text{cm}^{-1} 3441, 3418, 2979, 2933, 1602, 1509, 1385, 1373, 1225, 1102, 1041, 989, 837, 775, 651; HRMS [ESI] 374.1130 [(M)\(^+\); calcd for C\(_{17}\)H\(_{27}\)O\(_3\)PS\(_2\) 374.1139]

5-chloro-3-(4-fluorophenyl) pent-1-en-3-ol (0g)

Alcohol 0g was prepared according to General Procedure B using 3-chloro-4'-fluoropropiophenone (commercially available from Acros) (300 mg, 1.61 mmol) and vinylmagnesium bromide (2.76 mL, 1.93 mmol). Purification by flash chromatography afforded 0g [294 mg, 86%] as a clear liquid.

\(^1\)H NMR (499 MHz, CDCl\(_3\)) \(\delta 7.42 – 7.37\) (m, 2H), 7.07 – 7.01 (m, 2H), 6.14 (dd, \(J = 17.2, 10.7\) Hz, 1H), 5.32 (ddd, \(J = 17.3, 2.4, 0.8\) Hz, 1H), 5.23 (dd, \(J = 10.7, 0.8\) Hz, 1H), 3.60 – 3.54 (m, 1H), 3.44 – 3.37 (m, 1H), 2.42 (ddd, \(J = 14.0, 10.3, 5.6\) Hz, 1H),
2.33 (ddd, $J = 14.0, 10.3, 5.5$ Hz, 1H), 2.06 (s, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 162.94, 160.98, 142.86, 140.04, 140.01, 127.00, 126.93, 115.31, 115.14, 113.81, 76.17, 44.54, 39.99; IR (neat) $\nu_{\text{max}}$/cm$^{-1}$ 3559, 3551, 3518, 3064, 3025, 2965, 1460, 1489, 1250, 1186, 1035, 928, 907, 735, 703; HRMS [ESI] 214.0560, 216.0525 [(M)$^+$; calcd for C$_{11}$H$_{12}$ClFO 214.0561, 216.0531]

2-(4-fluorophenyl)-2-vinyloxetane (1g)

Oxetane 1g was prepared according to General Procedure B using alcohol 0g (160 mg, 0.75 mmol) and NaH (60% suspension in mineral oil, 45 mg, 1.12 mmol). Purification by flash chromatography [0.5:0.5:99 EA/TEA/Hexanes] afforded 1g [131 mg, 98%] as a clear liquid.

$^1$H NMR (499 MHz, CDCl$_3$) $\delta$ 7.38 – 7.32 (m, 2H), 7.08 – 7.01 (m, 2H), 6.18 (dd, $J = 17.1, 10.5$ Hz, 1H), 5.32 (dd, $J = 17.1, 1.4$ Hz, 1H), 5.21 (dt, $J = 2.7, 1.3$ Hz, 1H), 4.57 (m, 2H), 2.99 – 2.90 (m, 1H), 2.81 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 162.80, 160.84, 142.03, 141.04, 141.02, 126.27, 126.21, 115.10, 114.93, 113.29, 87.38, 64.93, 34.48; IR (neat) $\nu_{\text{max}}$/cm$^{-1}$ 3559, 3555, 3521, 3064, 3025, 2964, 1471, 1470, 1249, 1185, 1055, 934, 921, 730, 713; HRMS [ESI] 178.0793 [(M)$^+$; calcd for C$_{11}$H$_{11}$FO 178.0794]

(3-(4-fluorophenyl)-5-hydroxypent-2-en-1-yl) O,O-diisopropyl phosphorodithioate (2g)

Compound 2g was prepared according to General Procedure C using oxetane 1g (67 mg, 0.37 mmol) and acid A$_3$ (96.6 mg, 0.45 mmol). Purification by flash chromatography afforded 2g [137 mg, 93%] as a clear liquid. The E/Z isomers were inseparable and characterized as a mixture.
**1H NMR** (600 MHz, CDCl₃) δ 7.34 – 7.30 (m, 2H), 7.03 – 6.99 (m, 2H), 5.89 (dd, J = 9.9, 6.3 Hz, 1H), 4.85 (tq, J = 12.4, 6.2 Hz, 2H), 3.77 (dd, J = 14.2, 8.1 Hz, 2H), 3.64 (dd, J = 8.3, 5.2 Hz, 2H), 2.84 (t, J = 6.7 Hz, 2H), 1.35 (t, J = 6.0 Hz, 12H); **13C NMR** (101 MHz, CDCl₃) δ 163.55, 161.09, 139.43, 137.43, 137.40, 128.08, 128.00, 125.29, 125.23, 115.39, 115.17, 73.64, 73.57, 61.00, 33.47, 32.05, 32.02, 23.75, 23.71, 23.49, 23.44; **31P NMR** (162 MHz, CDCl₃) δ 91.08; **IR** (neat) ν max/cm⁻¹ 3418, 3406, 2979, 2933, 1509, 1385, 1373, 1225, 1178, 1161, 1102, 989, 970, 888, 835, 775, 651; **HRMS** [ESI] 392.1040 [(M)+; calcd for C₁₇H₂₆FO₃PS₃ 392.1045]

5-chloro-3-(4-chlorophenyl) pent-1-en-3-ol (0h)

Alcohol 0h was prepared according to General Procedure B using 3,4'-dichloropropiophenone (commercially available from Aldrich) (300 mg, 1.48 mmol) and vinylmagnesium bromide (2.54 mL, 0.7 M, 1.78 mmol). Purification by flash chromatography afforded 0h [272 mg, 78%] as a clear liquid.

**1H NMR** (499 MHz, CDCl₃) δ 7.38 – 7.31 (m, 4H), 6.13 (dd, J = 17.2, 10.7 Hz, 1H), 5.33 (dt, J = 17.3, 1.4 Hz, 1H), 5.24 (dd, J = 10.7, 0.4 Hz, 1H), 3.61 – 3.54 (m, 1H), 3.43 – 3.36 (m, 1H), 2.37 (dddd, J = 39.0, 14.0, 10.2, 5.6 Hz, 2H), 2.04 (d, J = 1.7 Hz, 1H); **13C NMR** (126 MHz, CDCl₃) δ 142.77, 142.68, 133.22, 128.58, 126.69, 114.01, 76.20, 44.44, 39.90; **IR** (neat) ν max/cm⁻¹ 3563, 3558, 3523, 3070, 3012, 2960, 1570, 1461, 1452, 1248, 1155, 1025, 927, 912, 730, 702; **HRMS** [ESI] 230.0261, 232.0228 [(M)+; calcd for C₁₁H₁₂Cl₂O 230.0265, 232.0236]

2-(4-chlorophenyl)-2-vinyloxetane (1h)

Oxetane 1h was prepared according to General Procedure B using alcohol 0h (73 mg, 0.32 mmol) and NaH (60% suspension in mineral oil, 19 mg, 0.47 mmol). Purification by flash chromatography [0.5:0.5:99 EA/TEA/Hexanes] afforded 1h [56 mg, 92%] as a clear liquid.
\textsuperscript{1}H NMR (499 MHz, CDCl\textsubscript{3}) \(\delta\) 7.35 – 7.30 (m, 4H), 6.17 (dd, \(J = 17.1, 10.5\) Hz, 1H), 5.32 (dd, \(J = 17.1, 1.3\) Hz, 1H), 5.22 (dd, \(J = 10.5, 1.3\) Hz, 1H), 4.57 (m, 2H), 2.95 (ddd, \(J = 10.7, 8.6, 6.6\) Hz, 1H), 2.80 (m, 1H); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 143.82, 141.79, 132.79, 128.38, 125.97, 113.54, 87.34, 65.01, 34.49; IR (neat) \(\nu_{\text{max}}/\text{cm}^{-1} 3561, 3553, 3517, 3043, 2960, 1478, 1471, 1244, 1255, 1034, 933, 920, 728, 713; HRMS [ESI] 194.0490 [(M)\textsuperscript{+}; calcd for C\textsubscript{11}H\textsubscript{11}ClO 194.0498]

(3-(4-chlorophenyl)-5-hydroxypent-2-en-1-yl) \(O,O\)-diisopropyl phosphorodithioate (2h)

Compound 2h was prepared according to General Procedure C using oxetane 1h (46 mg, 0.23 mmol) and acid A\textsubscript{3} (60 mg, 0.28 mmol). Purification by flash chromatography [30% EA/Hexanes] afforded 2h [89 mg, 92\%] as a clear liquid. The E/Z isomers were inseparable and characterized as a mixture.

\textsuperscript{1}H NMR (499 MHz, CDCl\textsubscript{3}) \(\delta\) 7.32 (s, 4H), 5.96 (t, \(J = 8.1\) Hz, 1H), 4.93 – 4.82 (m, 2H), 3.80 (dd, \(J = 14.5, 8.1\) Hz, 2H), 3.67 (t, \(J = 6.7\) Hz, 2H), 2.87 (t, \(J = 6.7\) Hz, 2H), 1.38 (dd, \(J = 6.1, 5.1\) Hz, 13H); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 139.83, 139.28, 133.44, 128.60, 127.74, 125.87, 125.82, , 73.67, 73.61, 61.02, 33.29, 32.04, 32.02, 23.77, 23.73, 23.51, 23.47; \textsuperscript{31}P NMR (162 MHz, CDCl\textsubscript{3}) \(\delta\) 91.06; IR (neat) \(\nu_{\text{max}}/\text{cm}^{-1} 3616, 3508, 3445, 3418, 1388, 1373, 1251, 1177, 1101, 989, 967, 775, 651; HRMS [ESI] 408.0749 [(M)\textsuperscript{+}; calcd for C\textsubscript{17}H\textsubscript{26}ClO\textsubscript{3}P\textsubscript{2} 408.0750]
Alcohol 0i was prepared according to General Procedure B using 3-chloro-4'-bromopropiophenone (commercially available from Acros) (300 mg, 1.2 mmol) and vinylmagnesium bromide (2 mL, 1.4 mmol). Purification by flash chromatography [1% EA/Hexanes] afforded 0i [264 mg, 80%] as a clear liquid.

\[ ^1H \text{ NMR} \ (600 \text{ MHz, CDCl}_3) \delta 7.50 - 7.47 \text{ (m, } 2\text{H}), \ 7.32 - 7.29 \text{ (m, } 2\text{H}), \ 6.13 \text{ (dd, } J = 17.2, 10.7 \text{ Hz, } 1\text{H}), \ 5.33 \text{ (dd, } J = 17.2, 2.7 \text{ Hz, } 1\text{H}), \ 5.25 \text{ (dd, } J = 9.2, 5.9 \text{ Hz, } 1\text{H}), \ 3.57 \text{ (td, } J = 10.5, 5.5 \text{ Hz, } 1\text{H}), \ 3.42 - 3.36 \text{ (m, } 1\text{H}), \ 2.44 - 2.29 \text{ (m, } 2\text{H}), \ 2.04 \text{ (s, } 1\text{H}); \]

\[ ^13C \text{ NMR} \ (101 \text{ MHz, CDCl}_3) \delta 143.31, 142.63, 131.54, 127.05, 121.37, 114.05, 76.25, 44.39, 39.88; \]

\[ \text{IR (neat) } v_{\max}/\text{cm}^{-1} 3545, 3550, 3512, 3049, 2958, 2948, 1546, 1459, 1444, 1240, 1154, 1023, 925, 910, 728, 714; \]

\[ \text{HRMS [ESI]} \ 273.9758, 275.9738 \ [(\text{M})^+; \text{calcd for } C_{11}H_{12}BrClO 273.9760, 275.9740] \]

Oxetane 1i was prepared according to General Procedure B using alcohol 0i (52 mg, 0.19 mmol) and NaH (60% suspension in mineral oil, 15 mg, 0.37 mmol). Purification by flash chromatography [0.5:0.5:99 EA/TEA/Hexanes] afforded 1i [42 mg, 94%] as a clear liquid.

\[ ^1H \text{ NMR} \ (499 \text{ MHz, CDCl}_3) \delta 7.51 - 7.45 \text{ (m, } 2\text{H}), \ 7.27 - 7.23 \text{ (m, } 2\text{H}), \ 6.16 \text{ (dd, } J = 17.1, 10.6 \text{ Hz, } 1\text{H}), \ 5.32 \text{ (dd, } J = 17.1, 1.3 \text{ Hz, } 1\text{H}), \ 5.21 \text{ (dd, } J = 10.5, 1.3 \text{ Hz, } 1\text{H}), \ 4.59 \text{ (ddd, } J = 8.6, 6.8, 5.8 \text{ Hz, } 1\text{H}), \ 4.53 \text{ (ddd, } J = 8.7, 6.5, 5.8 \text{ Hz, } 1\text{H}), \ 2.95 \text{ (ddd, } J = 10.7, 8.6, 6.6 \text{ Hz, } 1\text{H}); \]

\[ ^13C \text{ NMR} \ (126 \text{ MHz, CDCl}_3) \delta 144.45, 141.81, 131.36, 126.36, 120.95, 113.56, 87.39, 64.99, 34.54; \]

\[ \text{IR (neat) } v_{\max}/\text{cm}^{-1} 3550, 3548, 3502, 3043, 2960, 1468, 1461, 1254, 1251, 1024, 932, 921, 725, 712; \]

\[ \text{HRMS [ESI]} \ 237.9990 \ [(\text{M})^+; \text{calcd for } C_{11}H_{11}BrO 237.9993] \]
(3-(4-bromophenyl)-5-hydroxypent-2-en-1-yl) O,O-diisopropyl phosphorodithioate (2i)

![Chemical Structure of 2i](image)

Compound 2i was prepared according to General Procedure C using oxetane 1i (25 mg, 0.1 mmol) and acid A3 (27 mg, 0.12 mmol). Purification by flash chromatography [30% EA/Hexanes] afforded 2i [43 mg, 96%] as a clear liquid. The E/Z isomers were inseparable and characterized as a mixture.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.46 – 7.43 (m, 2H), 7.25 – 7.21 (m, 2H), 5.94 (dd, $J$ = 10.5, 5.6 Hz, 1H), 4.89 – 4.80 (m, 2H), 3.76 (dd, $J$ = 14.5, 8.1 Hz, 2H), 3.64 (dd, $J$ = 11.8, 6.5 Hz, 2H), 2.84 (t, $J$ = 6.7 Hz, 2H), 1.35 (dd, $J$ = 8.0, 4.4 Hz, 13H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.31, 139.33, 131.55, 128.08, 125.94, 125.87, 121.58, 73.68, 73.61, 61.02, 33.24, 32.04, 32.01, 23.77, 23.72, 23.51, 23.46; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 91.05, 90.88; IR (neat) $v_{\text{max}}$/cm$^{-1}$: 13418, 2978, 2931, 2876, 1486, 1466, 1379, 1373, 1250, 1177, 1141, 1076, 1042, 1007, 989, 969, 775, 651; HRMS [ESI] 452.0238 [(M$^+$) calcd for C$_{17}$H$_{26}$BrO$_3$PS$_2$ 452.0244]

5-chloro-3-mesitylpent-1-en-3-ol (0j)

![Chemical Structure of 0j](image)

Alcohol 0j was prepared according to General Procedure B using 3-chloro-1-mesitylpropan-1-one (synthesized from mesitylene and 3-chloropropionyl chloride) (322 mg, 1.53 mmol) and vinlylmagnesium bromide (2.6 mL, 1.8 mmol). Purification by flash chromatography [1% EA/Hexanes] afforded 0j [280 mg, 77%] as a clear liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.80 (dd, $J$ = 1.1, 0.6 Hz, 2H), 6.35 (dd, $J$ = 17.4, 10.6 Hz, 1H), 5.18 (ddd, $J$ = 6.8, 4.1, 0.7 Hz, 2H), 3.72 (ddd, $J$ = 11.1, 10.5, 5.4 Hz, 1H), 3.37 (ddd, $J$ = 11.1, 10.5, 5.0 Hz, 1H), 2.68 (ddddd, $J$ = 15.8, 11.1, 5.0, 0.6 Hz, 1H), 2.44 – 2.41 (m, 7H), 2.41 – 2.35 (m, 1H), 2.23 (s, 3H), 1.71 (d, $J$ = 0.5 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 145.34, 136.68, 136.34, 136.10, 131.98, 114.12, 79.40, 131.98, 114.12, 79.40
43.99, 40.57, 24.74, 20.35; IR (neat) νmax/cm⁻¹ 3543, 3439, 3088, 3061, 2976, 2873, 1492, 1446, 1105, 925, 769, 700; HRMS [ESI] 238.1121, 240.1087 [(M)+; calcd for C₁₁H₁₉ClO 238.1124, 240.1095]

2-mesityl-2-vinyloxetane (1j)

Oxetane 1j was prepared according to General Procedure B using alcohol 0j (300 mg, 1.27 mmol) and NaH (60% suspension in mineral oil, 202 mg, 2.55 mmol). Purification by flash chromatography [0.5:0.5:99 EA/TEA/Hexanes] afforded 1i [230 mg, 90%] as a clear liquid.

¹H NMR (400 MHz, CDCl₃) δ 6.78 (dt, J = 1.2, 0.6 Hz, 2H), 6.37 (dd, J = 17.0, 10.4 Hz, 1H), 5.18 (ddd, J = 13.7, 11.3, 1.6 Hz, 2H), 4.62 (ddd, J = 8.4, 7.7, 5.6 Hz, 1H), 4.38 (ddd, J = 9.4, 5.6, 4.8 Hz, 1H), 3.24 (ddd, J = 10.8, 9.4, 8.5 Hz, 1H), 2.80 (ddd, J = 10.8, 7.7, 4.8 Hz, 1H), 2.24 (s, 3H), 2.19 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 139.45, 137.89, 136.13, 129.98, 113.33, 91.12, 65.28, 36.65, 21.13, 20.60; IR (neat) νmax/cm⁻¹ 3084, 3059, 3024, 3001, 2956, 2883, 1490, 1446, 985, 966, 759, 700; HRMS [ESI] 202.1355 [(M)+; calcd for C₁₄H₁₈O 202.1358]

(5-hydroxy-3-mesitylpent-2-en-1-yl) O,O-diisopropyl phosphorodithioate (2j)

Thioate 2j was prepared according to General Procedure C using oxetane 1j (40 mg, 0.19 mmol) and acid A₃ (50 mg, 0.24 mmol). Purification by flash chromatography [30% EA/Hexanes] afforded 2j [67 mg, 85%] as a clear liquid. The E/Z isomers were inseparable and characterized as a mixture.

¹H NMR (600 MHz, CDCl₃) δ 6.86 (s, 2H), 5.76 (tt, J = 7.8, 1.3 Hz, 1H), 4.76 (dhept, J = 12.4, 6.2 Hz, 2H), 3.72 (t, J = 6.6 Hz, 2H), 3.21 (dd, J = 13.3, 7.8 Hz, 2H), 2.50 (td, J = 6.5, 0.9 Hz, 2H), 2.26 (s, 3H), 2.15 (s, 6H), 1.30 (d, J = 6.2 Hz, 6H), 1.24 (d, J = 6.2 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 140.69, 136.64, 135.02, 128.51, 123.07, 73.36, 73.30, 60.45, 40.93, 32.28, 23.73, 23.69, 23.29, 23.24, 20.89, 19.82;
$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 90.58, 90.32; IR (neat) $v_{\text{max}}$/cm$^{-1}$ 3516, 3508, 3470, 3442, 3384, 2979, 2921, 1384, 1178, 1141, 1102, 1034, 990, 966, 889, 850, 777, 652; HRMS [ESI] 416.1600 [(M)$^+$; calcd for C$_{20}$H$_{33}$O$_3$PS$_2$ 416.1609]

2-(2-methylprop-1-en-1-yl)-2-phenyloxetane (1k)

For the synthesis of oxetane 1k, please see reference 2.

6, 6-dimethyl-4-phenyl-3,6-dihydro-2H-pyran (2k)

Pyran 2k was prepared according to General Procedure C using oxetane 1k (15 mg, 0.8 mmol) and acid $A_3$ (20 mg, 0.95 mmol). Purification by flash chromatography [1% EA/Hexanes] afforded 2k [13.5 mg, 90%] as a clear liquid. For the spectroscopic data please see ref.2.

5-chloro-3-(1-phenylcyclobutyl)pent-1-en-3-ol (0l)

Alcohol 0l was prepared according to General Procedure B using 3-chloro-1-(1-phenylcyclobutyl) propan-1-one (prepared from 1-phenylcyclobutanecarbonitrile as described in 0d) (300 mg, 1.35 mmol) and vinylmagnesium bromide (2.3 mL, 1.62 mmol). Purification by flash chromatography [1% EA/Hexanes] afforded 0l [260 mg, 79%] as a clear liquid.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.34 – 7.30 (m, 2H), 7.24 – 7.20 (m, 3H), 5.81 (dd, $J = 17.3, 10.9$ Hz, 1H), 5.32 – 5.25 (m, 2H), 3.51 (td, $J = 10.6, 6.0$ Hz, 1H), 3.40 (td, $J = 10.6, 5.1$ Hz, 1H), 2.67 – 2.60 (m, 1H), 2.52 – 2.45 (m, 1H), 2.37 (m, 2H), 1.98 (ddd, $J = 13.8, 10.5, 6.0$ Hz, 1H), 1.91 – 1.85 (m, 2H), 1.79 (dtt, $J = 11.6, 10.0, 5.9$ Hz, 1H), 1.68 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 146.23, 138.41, 128.49, 127.61, 126.12, 115.27, 77.55, 53.65, 41.01, 37.44, 29.77, 29.57, 15.62; IR (neat) $v_{\text{max}}$/cm$^{-1}$ 3581,
Oxetane 11 was prepared according to General Procedure B using alcohol 0l (220 mg, 0.87 mmol) and NaH (60% suspension in mineral oil, 70 mg, 1.75 mmol). Purification by flash chromatography [0.5:0.5:99 EA/TEA/Hexanes] afforded 11 [178 mg, 95%] as a clear oil.

\(^1H\) NMR (600 MHz, CDCl\textsubscript{3}) \(\delta 7.31 - 7.27\) (m, 2H), \(7.24 - 7.18\) (m, 3H), \(5.64\) (dd, \(J = 17.0, 10.7\) Hz, 1H), \(5.36\) (dd, \(J = 17.0, 2.1\) Hz, 1H), \(5.14\) (dd, \(J = 10.7, 2.1\) Hz, 1H), \(4.45\) (td, \(J = 8.1, 5.7\) Hz, 1H), \(4.36\) (dt, \(J = 9.3, 5.5\) Hz, 1H), \(2.97 - 2.88\) (m, 1H), \(2.50 - 2.36\) (m, 2H), \(2.32 - 2.23\) (m, 1H), \(2.08\) (ddd, \(J = 10.9, 8.4, 5.3\) Hz, 1H), \(1.93\) (dtt, \(J = 11.2, 9.8, 6.0\) Hz, 1H), \(1.80\) (dtt, \(J = 11.2, 9.8, 6.7\) Hz, 1H); \(^{13}C\) NMR (101 MHz, CDCl\textsubscript{3}) \(\delta 145.20, 138.44, 127.81, 127.51, 125.83, 113.57, 90.02, 64.27, 52.24, 29.74, 27.90, 27.54, 15.32\); IR (neat) \(\nu_{\text{max}}/\text{cm}^{-1}\) \(3087, 3058, 3021, 2984, 2932, 2878, 1700, 1489, 1444, 1278, 1253, 1225, 1081, 980, 964, 924, 747, 703, 668, 651\); HRMS [ESI] 214.1358 [(M)+; calcd for C\(_{15}\)H\(_{18}\)O 214.1358]

(5-hydroxy-3-(1-phenylcyclobutyl)pent-2-en-1-yl) \(O,O\)-diisopropyl phosphorodithioate (2l)

Compound 2l was prepared according to General Procedure C using oxetane 11 (110 mg, 0.51 mmol) and acid A\textsubscript{3} (132 mg, 0.62 mmol). Purification by flash chromatography [30% EA/Hexanes] afforded 2l [198 mg, 91%] as a clear liquid.

\(^1H\) NMR (600 MHz, CDCl\textsubscript{3}) \(\delta 7.33 - 7.28\) (m, 4H), \(7.21 - 7.18\) (m, 1H), \(5.78\) (t, \(J = 8.0\) Hz, 1H), \(4.86\) (dhept, \(J = 12.4, 6.2\) Hz, 2H), \(3.66\) (dd, \(J = 13.3, 8.0\) Hz, 2H), \(3.07\) (d, \(J = 2.7\) Hz, 2H), \(2.45 - 2.34\) (m, 4H), \(2.21\) (t, \(J = 7.4\) Hz, 2H), \(1.88 - 1.75\) (m, 2H), \(1.38\) (d, \(J = 6.2\) Hz, 12H); \(^{13}C\) NMR (101 MHz, CDCl\textsubscript{3}) \(\delta 146.34, 145.74, 128.30, 126.38, 126.06, 120.20, 120.12, 73.47, 73.40, 61.63, 53.57, 32.58, 32.07, 31.79, 23.79, \)
23.75, 23.55, 23.49, 15.83; $^{31}$P NMR (162 MHz, CDCl₃) δ 91.44; IR (neat) $\nu_{\text{max}}$/cm⁻¹ 13423, 3419, 3406, 3384, 3055, 3021, 2977, 2871, 1492, 1444, 1384, 1178, 1141, 1103, 965, 936, 888, 797, 759, 701, 651; HRMS [ESI] 428.1600 [(M)⁺; calcd for C$_{21}$H$_{33}$O$_3$PS$_2$ 428.1609]

5-chloro-3-(1-phenylcyclopentyl)pent-1-en-3-ol (0m)

Alcohol 0m was prepared according to General Procedure B using 3-chloro-1-(1-phenylcyclopentyl) propan-1-one (prepared from 1-phenylcyclopentanecarbonitrile as described in 0d) (300 mg, 1.26 mmol) and vinylmagnesium bromide (2.1 mL, 1.5 mmol). Purification by flash chromatography [1% EA/Hexanes] afforded 0m [250 mg, 75%] as a clear liquid.

$^1$H NMR (600 MHz, CDCl₃) δ 7.42 (dt, $J$ = 8.6, 1.8 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.26 – 7.22 (m, 1H), 5.81 (dd, $J$ = 17.2, 11.0 Hz, 1H), 5.20 (ddd, $J$ = 13.6, 9.2, 1.4 Hz, 2H), 3.49 – 3.42 (m, 1H), 3.36 (td, $J$ = 10.5, 5.4 Hz, 1H), 2.27 – 2.14 (m, 2H), 2.04 (dt, $J$ = 12.9, 8.7 Hz, 1H), 2.01 – 1.89 (m, 3H), 1.68 – 1.59 (m, 3H), 1.45 – 1.32 (m, 2H);

$^{13}$C NMR (101 MHz, CDCl₃) δ 142.80, 139.61, 129.05, 127.88, 126.45, 114.81, 78.24, 59.60, 41.08, 39.30, 34.23, 32.83, 32.81, 23.77, 23.69, 23.66; IR (neat) $\nu_{\text{max}}$/cm⁻¹ 3595, 3551, 3518, 3442, 3091, 3025, 2965, 2959, 2874, 1700, 1250, 1186, 928, 907, 735, 704; HRMS [ESI] 264.1280, 266.1244 [(M)⁺; calcd for C$_{16}$H$_{21}$ClO 264.1281, 266.1251]

2-(1-phenylcyclopentyl)-2-vinyloxetane (1m)

Oxetane 1m was prepared according to General Procedure B using alcohol 0m (45 mg, 0.17 mmol) and NaH (60% suspension in mineral oil, 13 mg, 0.34 mmol). Purification by flash chromatography [0.5:0.5:99 EA/TEA/Hexanes] afforded 1m [36 mg, 93%] as a clear liquid.
1H NMR (499 MHz, CDCl3) δ 7.40 – 7.36 (m, 2H), 7.30 – 7.26 (m, 2H), 7.21 – 7.17 (m, 1H), 5.68 (dd, J = 17.0, 10.7 Hz, 1H), 5.26 (dd, J = 17.0, 2.0 Hz, 1H), 5.04 (dd, J = 10.7, 2.0 Hz, 1H), 4.40 (ddd, J = 8.3, 5.6 Hz, 1H), 4.28 (dt, J = 9.3, 5.5 Hz, 1H), 2.93 (ddd, J = 10.9, 9.3, 7.7 Hz, 1H), 2.28 – 2.14 (m, 3H), 2.10 – 1.93 (m, 2H), 1.81 – 1.63 (m, 2H), 1.55 – 1.47 (m, 2H); 13C NMR (126 MHz, CDCl3) δ 143.89, 140.47, 127.99, 127.71, 125.99, 112.64, 109.98, 91.10, 64.22, 57.67, 33.06, 31.28, 29.87, 24.13, 24.05; IR (neat) v max/cm−1 3419, 3413, 2960, 2875, 1250, 1231, 1035, 994, 968, 922; HRMS [ESI] 228.1514 [(M)+; calcd for C16H20O 228.1514]

(5-hydroxy-3-(1-phenylcyclopentyl)pent-2-en-1-yl) O,O-diisopropyl phosphorodithioate (2m)

Compound 2m was prepared according to General Procedure C using oxetane 1m (20 mg, 0.088 mmol) and acid A3 (22 mg, 0.11 mmol). Purification by flash chromatography [30% EA/Hexanes] afforded 2m [37 mg, 95%] as a clear liquid.

1H NMR (600 MHz, CDCl3) δ 7.27 (s, 2H), 7.27 (s, 2H), 7.18 (hept, J = 3.7 Hz, 1H), 5.77 (t, J = 8.0 Hz, 1H), 4.85 (dhept, J = 12.4, 6.2 Hz, 2H), 3.65 (dd, J = 12.9, 8.0 Hz, 2H), 3.13 (t, J = 7.6 Hz, 2H), 2.28 – 2.20 (m, 2H), 2.06 – 1.99 (m, 2H), 1.99 – 1.93 (m, 2H), 1.73 – 1.64 (m, 2H), 1.64 – 1.53 (m, 3H), 1.37 (d, J = 6.2 Hz, 12H); 13C NMR (101 MHz, CDCl3) δ 145.63, 145.34, 128.12, 126.97, 126.15, 120.31, 120.23, 73.46, 73.40, 62.13, 57.93, 36.25, 33.27, 32.21, 23.79, 23.75, 23.55, 23.49, 22.40; 31P NMR (162 MHz, CDCl3) δ 91.48; IR (neat) v max/cm−1 3419, 3058, 3021, 2976, 2959, 1492, 1466, 1454, 1444, 1384, 1378, 1176, 1141, 1103, 1023, 989, 962, 888, 776, 702, 651; HRMS [ESI] 442.1760 [(M)+; calcd for C22H35O3PS2 442.1765]

2-heptyl-2-vinylxetane (1n)

For the preparation of oxetane 1n, please see reference 2.
(3-(2-hydroxyethyl)dec-2-en-1-yl) O,O-diisopropyl phosphorodithioate (2n)

Compound 2n was prepared according to General Procedure C using oxetane 1n (18 mg, 0.045 mmol) and acid A3 (11 mg, 0.054 mmol). Purification by flash chromatography [30% EA/Hexanes] afforded 2n + 2n' [14 mg, 80%] as a clear liquid.

2n: $^1$H NMR (600 MHz, CDCl3) δ 5.46 (t, $J = 8.1$ Hz, 1H), 4.83 (dhept, $J = 12.4$, 6.2 Hz, 2H), 3.69 (t, $J = 6.7$ Hz, 2H), 3.60 (dd, $J = 13.1$, 8.1 Hz, 2H), 2.39 (t, $J = 6.7$ Hz, 2H), 2.05 – 2.00 (m, 2H), 1.40 (dd, $J = 14.7$, 7.4 Hz, 3H), 1.38 – 1.34 (m, 12H), 1.33 – 1.21 (m, 10H), 0.88 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl3) δ 141.12, 121.75, 121.69, 73.46, 73.41, 60.92, 36.89, 33.67, 31.84, 31.62, 29.34, 29.20, 27.99, 23.83, 23.80, 23.56, 23.52, 22.69, 14.13; $^{31}$P NMR (202 MHz, CDCl3) δ 100.00; IR (neat) νmax/cm$^{-1}$ 3421, 3405, 3054, 2998, 2967, 1499, 1480, 1454, 1444, 1321, 1122, 1100, 989, 960, 878, 773, 700, 650; HRMS [ESI] 396.1921 [(M)$^+$; calcd for C$_{18}$H$_{37}$O$_3$PS$_2$ 396.1922]

2n': $^1$H NMR (600 MHz, CDCl3) δ 5.39 (t, $J = 7.8$ Hz, 1H), 4.84 (tt, $J = 12.3$, 6.2 Hz, 2H), 3.68 (t, $J = 6.3$ Hz, 2H), 3.56 (dd, $J = 13.3$, 7.9 Hz, 2H), 2.29 (t, $J = 6.3$ Hz, 2H), 2.12 – 2.07 (m, 2H), 1.39 (s, 3H), 1.36 (dd, $J = 6.2$, 1.7 Hz, 12H), 1.28 (dd, $J = 13.8$, 7.5 Hz, 10H), 0.91 – 0.86 (m, 3H); $^{13}$C NMR (126 MHz, CDCl3) δ 141.41, 121.87, 121.82, 73.40, 73.34, 60.47, 39.84, 31.80, 31.28, 31.24, 30.21, 29.71, 29.17, 28.55, 23.78, 23.74, 23.49, 23.45, 22.64, 14.09; $^{31}$P NMR (162 MHz, CDCl3) δ 91.27

(E)-2-methyl-2-styryloxetane (1o)

For the preparation of oxetane 1o, please see reference 2.
(5-hydroxy-3-methyl-1-phenylpent-2-en-1-yl) O,O-diisopropyl phosphorodithioate (2o)

Compound 2o was prepared according to General Procedure C using oxetane 1o (33 mg, 0.19 mmol) and acid A3 (48 mg, 0.22 mmol). Purification by flash chromatography [30% EA/Hexanes] afforded 2o [45 mg, 65%] as a clear liquid. The E/Z isomers were inseparable and characterized as a mixture.

$^{1}$H NMR (600 MHz, CDCl$_3$) δ 7.43 – 7.39 (m, 2H), 7.33 – 7.29 (m, 2H), 7.25 – 7.21 (m, 1H), 5.73 – 5.67 (m, 1H), 5.42 – 5.29 (m, 1H), 4.91 – 4.55 (m, 2H), 3.81 – 3.65 (m, 2H), 2.62 – 2.24 (m, 2H), 1.85 – 1.78 (m, 3H), 1.32 (m, 3H), 1.25 (m, 4H), 1.16 (m, 6H);

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 141.64, 141.52, 137.49, 136.80, 130.57, 129.73, 129.65, 128.58, 128.42, 128.39, 128.35, 126.93, 73.70, 73.63, 73.55, 73.51, 73.48, 60.81, 60.35, 43.89, 43.86, 43.39, 39.57, 38.37, 34.62, 34.46, 32.82, 24.25, 24.20, 23.80, 23.75, 23.72, 23.67, 23.63, 23.58, 23.53, 23.49, 23.45; IR (neat) $v_{\max}$/cm$^{-1}$ 3556, 3503, 3486, 2957, 2941, 1469, 1465, 1455, 1453, 1342, 1235, 1102, 1037, 989, 966, 775, 702, 651; HRMS [ESI] 388.1290 [(M)$^+$; calcd for C$_{18}$H$_{29}$O$_3$PS$_2$ 388.1296].

2-(3-phenylprop-1-en-2-yl)oxetane (1p)

For the preparation of oxetane 1p, please see reference 2.

(2-benzyl-5-hydroxypent-2-en-1-yl) O,O-diisopropyl phosphorodithioate (2p)

Compound 2p was prepared according to General Procedure C using oxetane 1p (40 mg, 0.24 mmol) and acid A3 (60 mg, 0.27 mmol). Purification by flash chromatography [30% EA/Hexanes] afforded 2p (42 mg, 48%) as a clear liquid.

$^{1}$H NMR (600 MHz, CDCl$_3$) δ 7.30 – 7.26 (m, 2H), 7.23 – 7.17 (m, 3H), 5.57 (t, $J$ =7.4 Hz, 1H), 4.85 – 4.76 (m, 2H), 3.71 (dt, $J$ = 16.9, 6.4 Hz, 2H), 3.56 (s, 1H), 3.48 (ddd, $J$ = 14.6, 11.8, 6.0 Hz, 3H), 2.45 (tt, $J$ = 13.8, 6.5 Hz, 2H), 1.35 – 1.29 (m, 12H);

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 138.91, 138.75, 136.18, 129.06, 128.62, 128.56,
3-(2-chloroethyl)non-1-en-4-yn-3-ol (0q)

Alcohol 0q was prepared according to General Procedure B using 1-chloronon-4-yn-3-one (prepared according to known procedure) (153 mg, 0.87 mmol) and vinylmagnesium bromide (1.7 mL, 0.7M, 1.22 mmol). Purification by flash chromatography [1% EA/Hexanes] afforded 0q (128 mg, 74%) as a clear liquid.

$^1$H NMR (499 MHz, CDCl$_3$) $\delta$ 5.90 (dd, $J = 17.0, 10.2$ Hz, 1H), 5.53 (ddd, $J = 17.0, 2.8, 1.1$ Hz, 1H), 5.18 (dd, $J = 10.2, 1.1$ Hz, 1H), 3.74 – 3.62 (m, 2H), 2.28 – 2.10 (m, 4H), 1.54 – 1.46 (m, 2H), 1.46 – 1.35 (m, 2H), 0.92 (dd, $J = 8.0, 6.6$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.89, 114.87, 87.81, 79.68, 70.52, 44.96, 40.13, 30.63, 21.95, 18.31, 13.55; IR (neat) $\nu_{\text{max}}$/cm$^{-1}$ 13508, 3501, 3418, 3406, 3333, 3406, 3308, 3251, 2959, 2933, 1275, 1173, 1052, 986, 932, 689; HRMS [ESI] 200.0959, 202.0937 [(M)$^+$; calcd for C$_{11}$H$_{17}$ClO 200.0968, 202.0938]

2-(hex-1-yn-1-yl)-2-vinyloxetane (1q)

Oxetane 1q was prepared according to General Procedure B using alcohol 0q (70 mg, 0.35 mmol) and NaH (60% suspension in mineral oil, 28 mg, 0.7 mmol). Purification by flash chromatography [0.5:0.5:99 EA/TEA/Hexanes] afforded 1q (56 mg, 98%) as a clear liquid.
\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 6.16 (dd, \(J = 16.9, 10.2\) Hz, 1H), 5.54 (dd, \(J = 16.9, 1.3\) Hz, 1H), 5.30 – 5.14 (m, 1H), 4.63 (ddd, \(J = 8.7, 7.0, 5.8\) Hz, 1H), 4.46 (ddd, \(J = 8.7, 6.7, 5.8\) Hz, 1H), 2.93 (ddd, \(J = 10.9, 8.7, 6.7\) Hz, 1H), 2.74 (ddd, \(J = 10.9, 8.7, 7.0\) Hz, 1H), 2.35 – 2.25 (m, 2H), 1.59 – 1.50 (m, 2H), 1.50 – 1.36 (m, 2H), 0.92 (t, \(J = 7.2\) Hz, 4H); \(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 139.75, 114.61, 89.81, 80.09, 79.55, 65.39, 35.88, 30.61, 21.95, 18.62, 13.57; IR (neat) \(\nu_{\text{max}}/\text{cm}^{-1}\) 2958, 2932, 2886, 1598, 1588, 1274, 1228, 1183, 1033, 984, 959, 929; HRMS [ESI] 124.1200 [(M\(^+\); calcd for C\(_{11}\)H\(_{16}\)O 124.1201]

\((3-(2\text{-hydroxyethyl})\text{non}-2\text{-en}-4\text{-yn}-1\text{-yl})\ O,O\text{-diisopropyl phosphorodithioate} \ (2q)\)

![Image of 2q](image)

Compound 2q was prepared according to General Procedure C using oxetane 1q (25 mg, 0.15 mmol) and acid A\(_3\) (39 mg, 0.18 mmol). Purification by flash chromatography [30% EA/Hexanes] afforded 2q [48 mg, 85\%] as a clear liquid. The E/Z mixture was inseparable and characterized as a mixture.

\(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)) \(\delta\) 5.82 (t, \(J = 7.7\) Hz, 1H), 4.84 (tq, \(J = 12.4, 6.2\) Hz, 3H), 3.80 – 3.73 (m, 4H), 2.39 – 2.34 (m, 5H), 1.57 – 1.53 (m, 2H), 1.47 – 1.41 (m, 2H), 1.37 – 1.36 (m, 12H), 0.97 – 0.90 (m, 3H); \(^{13}\text{C NMR}\) (126 MHz, CDCl\(_3\)) \(\delta\) 132.11, 132.06, 123.81, 98.27, 73.43, 73.38, 60.96, 40.50, 33.27, 33.24, 30.75, 29.69, 23.78, 23.74, 23.47, 23.43, 22.02, 19.25, 13.59; \(^{31}\text{P NMR}\) (162 MHz, CDCl\(_3\)) \(\delta\) 90.86; IR (neat) \(\nu_{\text{max}}/\text{cm}^{-1}\) 3441, 3418, 3406, 2976, 2958, 2931, 1466, 1458, 1384, 1373, 1178, 1141, 1102, 989, 970, 889, 777, 652; HRMS [ESI] 378.2450 [(M\(^+\); calcd for C\(_{17}\)H\(_{31}\)O\(_3\)PS\(_2\) 378.1452]

\((E)-2-(1\text{-phenylprop}-1\text{-en}-2\text{-yl})\text{ oxetane} \ (1r)\)

![Image of 1r](image)

Oxetane 1r was prepared from oxetane 1p (15 mg, 0.086 mmol) and NaH (60\% suspension in mineral oil, 3.4 mg, 0.086 mmol) in DMSO as shown above.
Purification by flash chromatography [1% EA/Hexanes] afforded 1r (13.5 mg, 90%) as a clear liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 – 7.27 (m, 4H), 7.24 – 7.18 (m, 1H), 6.61 (s, 1H), 5.27 (t, $J$ = 7.6 Hz, 1H), 4.73 (ddd, $J$ = 8.3, 7.7, 5.9 Hz, 1H), 4.55 (ddd, $J$ = 8.3, 7.6, 5.9 Hz, 1H), 2.89 – 2.79 (m, 1H), 2.62 – 2.51 (m, 1H), 1.94 – 1.90 (m, 3H); $^1$C NMR (101 MHz, CDCl$_3$) $\delta$ 138.61, 137.47, 128.96, 128.12, 126.45, 124.51, 85.66, 67.93, 27.48, 12.62; IR (neat) $\nu_{\text{max}}$/cm$^{-1}$ 3058, 3024, 2962, 2932, 2879, 1449, 1440, 1250, 1228, 1035, 990, 968, 754, 747; HRMS [ESI] 174.1041 [(M)$^+$; calcd for C$_{12}$H$_{14}$O$_2$]

2-ethynyl-2-phenethyloxetane (1s)

Oxetane 1s was prepared from 1-chloro-5-phenylpentan-3-one as shown above.

5-chloro-3-phenethylpent-1-yn-3-ol (0s)

Clear liquid, yield 72%.

$^1$H NMR (499 MHz, CDCl$_3$) $\delta$ 7.32 – 7.26 (m, 2H), 7.24 – 7.17 (m, 3H), 3.81 (m, 2H), 2.93 – 2.84 (m, 2H), 2.60 (s, 1H), 2.25 – 2.15 (m, 3H), 2.04 – 1.92 (m, 2H); $^1$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.31, 128.55, 128.41, 126.10, 84.69, 74.15, 70.26, 44.31, 44.26, 40.20, 30.49; IR (neat) $\nu_{\text{max}}$/cm$^{-1}$ 3550, 3078, 3029, 2943, 2894, 1500, 1461, 1228, 1029, 991, 977, 750, 698; HRMS [ESI] 222.0810 [(M)$^+$; calcd for C$_{13}$H$_{15}$ClO$_2$]

2-ethynyl-2-phenethyloxetane (1s)

Clear liquid, yield 88%

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.31 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 4.70 (ddd, $J$ = 8.8, 7.2, 6.0 Hz, 1H), 4.51 – 4.46 (m, 1H), 2.87 – 2.82 (m, 2H), 2.82 (s, 1H), 2.77
(ddd, $J = 13.8$, 11.5, 5.6 Hz, 1H), 2.30 – 2.24 (m, 1H), 2.17 (ddd, $J = 13.4$, 11.7, 5.6 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.36, 128.43, 128.40, 125.96, 85.11, 80.05, 75.78, 66.03, 43.68, 34.16, 29.94; IR (neat) $v_{\text{max}}$/cm$^{-1}$ 2944, 2890, 1520, 1489, 1230, 1031, 987, 972, 754, 698; HRMS [ESI] 186.1040 [(M)$^+$; calcd for C$_{13}$H$_{14}$O 186.1045]
References


The diagram shows a spectroscopic analysis with peaks at various ppm values and chemical shifts. The spectrum is labeled with chemical shifts ranging from -36.65 to 21.13 ppm. The structure at the top of the page appears to be related to the analysis, possibly indicating the compound being studied.
The image contains an NMR spectrum, which is a graphical representation of the chemical shifts and peak areas of the nuclei in a sample. The spectrum is labeled with chemical structures and peak assignments, indicating the presence of specific functionalities in the sample. The peaks are labeled with their corresponding chemical shifts, which are critical for identifying the components of the sample. The spectrum is used to determine the molecular structure and functional groups present in the compound.