Synthesis of α,β-unsaturated Epoxy Ketones Utilizing a Bifunctional Sulfonium/Phosphonium Ylide

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General experimental details

All reactions were performed in oven-dried glassware, under an argon atmosphere with exclusion of moisture from reagents and solvents. Hexanoic-\(^{2}\)H\(_{11}\) acid (98 atom% \(^{2}\)H(D)) was purchased from Millipore Sigma (Miamisburg, OH). All other reagents were used as supplied by the chemical manufacturers. Exact molarity of \(n\)-butyllithium determined by titration prior the use each time with 2-propanol, Et\(_{2}\)O at 0 °C and 1,10-phenanthroline as indicator. Tetrahydrofuran was distilled from a purple solution of sodium benzophenone ketyl. All other solvent were used as purchased.

Ozonolysis was performed on ozone generator lab series (L21) (Pacific Ozone), using industrial grade compressed oxygen (purity 99.5%). Liquid chromatography was performed using a forced air-flow (flash chromatography) on silica gel (230-400 mesh), using eluting solvent (reported as V:V ratio mixture). Analytical thin layer chromatography (TLC) was performed on 0.25 mm glass-backed EMD Millipore 60 F254 plates. Visualization of the developed chromatogram was accomplished with UV light (254 nm) and stained with either ethanolic phosphomolybdic acid (PMA) or ceric ammonium molybdate. \(^{1}\)H and \(^{13}\)C-NMR spectra were either recorded on a Varian Inova spectrometer operating at 400 MHz and 100 MHz for the \(^{1}\)H and \(^{13}\)C-NMR spectra or Bruker Ascend Avance III HD\(^{TM}\) operating at 500 MHz and 125 MHZ for the \(^{1}\)H and \(^{13}\)C-NMR spectra (at the Department of Chemistry, Case Western Reserve University). Chemical shifts reported in \(\delta\) units, part per million (ppm) with reference to the residual solvent peak CDCl\(_{3}\) (\(\delta\) 7.26), CD\(_{3}\)OD (\(\delta\) 3.31) for \(^{1}\)H and (\(\delta\) 77.36), CD\(_{3}\)OD (\(\delta\) 49.00) for \(^{13}\)C spectra, respectively. NMR data are presented in the following order: chemical shift, peak multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, ddd = doublet of doublet of doublet, ddt = doublet of doublet of triplet, dq = doublet of quartet, dm = doublet of multiplet, br = broad), coupling constant (in Hz). Mass spectra were acquired on a LTQ-FT hybrid mass spectrometer consisting of a linear ion trap and a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR) (R. Marshall Wilson Mass Spectrometry Facility at University of Cincinnati) using electrospray ionization (positive mode).
Experimental Procedure and Characterization

1,3-dibromopropan-2-one (12) (C₃H₄Br₂O)

An oven-dried 2.0 L, round-bottomed flask equipped with a mechanical stirrer was charged with 1,3-dichloro-2-propanone (25 g, 196 mmol) in acetone (750 mL). Powdered lithium bromide (150 g, 1.73 mol) was added slowly using a funnel. The reaction mixture was stirred at ambient temperature for 48 h. Additional lithium bromide (100 g, 1.15 mol) and 250 mL acetone were added and stirring continued for an extra 24 h. Evaporation of the solvent gave a white solid which was transferred to a 2.0 L separatory funnel charged with 1.0 L of cold water. The aqueous phase was extracted with methylene chloride (3 × 500 mL), and the combined organic phases dried with anhydrous magnesium sulfate and concentrated under reduced pressure to give 42.1 g (99% crude yield) of the 1,3-dibromopropan-2-one as yellow syrup. Analysis of the crude product by ¹H NMR indicates conversion was > 90%. Identity and purity of the product were confirmed by ¹H NMR and ¹³C NMR. ¹H NMR (400 MHz, CDCl₃) δ 4.13; ¹³C NMR (100 MHz, CDCl₃) δ 31.18, 194.13.

1-bromo-3-(triphenylphosphoranylidene)propan-2-one (13) (C₂₁H₁₈BrOP)

An oven-dried 500-mL, two-necked round-bottomed flask containing a magnetic stirring bar was equipped with an equalizing dropping funnel and an argon inlet. The flask was charged with triphenylphosphine (49.8 g, 190 mmol) in toluene (125 mL). The solution of crude 1,3-dibromopropan-2-one (41.0 g, 190 mmol) in toluene (125 mL) was added through dropping funnel. Stirring continued overnight at ambient temperature. The white precipitate formed during the reaction was collected by filtration, washed with toluene, and concentrated under reduced pressure. To a stirred solution of dried salt
in 60% aqueous methanol (800 mL) was added powdered sodium bicarbonate (42 g, 0.5 mol). Stirring continued for extra 30 min and more water (200 mL) was added to the mixture. After being stirred for another 30 min, the solid was collected by filtration, washed thoroughly with water. The solid transferred to a 2.0 L separatory funnel charged with 1.0 L of cold water. The aqueous phase was extracted with methylene chloride (3 × 500 mL), and the combined organic phases dried with anhydrous sodium sulfate and concentrated under reduced pressure to give 62.6 g (83% crude yield) of the 1-bromo-3-(triphenylphosphoranylidene)propan-2-one as white solid. Analysis of the crude by $^1$H NMR indicates conversion was >60% (contaminated with 1-chloro-3-(triphenylphosphoranylidene)propan-2-one). Identity and purity of the product were confirmed by $^1$H and $^{13}$C NMR and HRMS: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.91 (d, 2H, $^4$J$_{HP}$ = 1.6), 4.26 (d, 1H, $^2$J$_{HP}$ = 24.0), 7.42-7.70 (15H, m) ; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 35.77 (d, $^3$J$_{CP}$ = 17.4 Hz), 52.67 (d, $^1$J$_{CP}$ = 109.0 Hz), 125.95 (d, $^1$J$_{CP}$ = 56 Hz, C-1'), 129.22 (d, $^3$J$_{CP}$ = 12.3 Hz, C-3') 132.65 (d, $^4$J$_{CP}$ = 2.8 Hz, C-4') 133.36 (d, $^2$J$_{CP}$ = 10.2 Hz, C-2'), 184.99 (d, $^2$J$_{CP}$ = 4.3 Hz) , HRMS (ESI) m/z calcd for C$_{21}$H$_{19}$BrOP+ (M+1)$^+$ 397.03514, found 397.03520.

**Dimethyl(2-oxo-3-(triphenylphosphoranylidene)propyl)sulfonium tetrafluoroborate [Bifunctional Sulfonium/Phosphonium ylide] (14) (C$_{23}$H$_{24}$BF$_4$OPS)**

An oven-dried 1.0 L, round-bottomed flask was equipped with a magnetic stirring bar. The flask was charged with sodium tetrafluoroborate (27.5 g, 0.25 mol) , methyl sulfide (15.5 g, 0.25 mol) , 1-bromo-3-(triphenylphosphoranylidene)propan-2-one (19.86 g, 50 mmol) and acetone (500 mL). The reaction mixture was continued stirring at ambient temperature for 48h. The filtrate was concentrated under reduced pressure. Purification by column chromatography (DCM: MeOH/95:5) afforded 17.95 g (77% yield) of bifunctional conjunctive ylide as white solid. Identity and purity of the product were confirmed by $^1$H and $^{13}$C NMR and HRMS. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.91 (s, 6H), 4.16 (d, 1H, $^2$J$_{HP}$ = 21.2 Hz), 4.42
(s, 2H), 7.47-7.64 (15H, m); $^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 25.01, 52.43 ($d$, $^3$J$_{CP}$ = 20.5 Hz), 56.71 ($d$, $^1$J$_{CP}$ = 104 Hz), 125.20 ($d$, $^1$J$_{CP}$ = 90.8 Hz, C-1$'$), 129.45 ($d$, $^3$J$_{CP}$ = 12.4 Hz, C-3$'$), 133.09 (bs, C-4$'$), 133.21 ($d$, $^2$J$_{CP}$ = 10.3 Hz, C-2$'$), 177.06 ($d$, $^2$J$_{CP}$ = 4.0 Hz); HRMS (ESI) m/z calcd for C$_{23}$H$_{24}$OPS$^+$ (M+1)$^+$ 379.12800, found 379.12807.

Methyl 9-oxononanoate (15) (C$_{10}$H$_{18}$O$_3$)

An oven-dried 0.5 L, two-necked, round-bottomed flask equipped with a mechanical stirrer. The flask was charged with methyl oleate (20.8 g, 70 mmol) in dichloromethane (250 mL), and methanol (100 mL). The vessel was cooled to −78 °C and ozone was bubbled through the solution using a Pasteur pipet until a persistent dark blue color appeared. The solution was purged with argon gas until the color had dissipated, and then the cold bath was removed. The ozonide was decomposed by adding glacial acetic acid (25 ml) in one portion, followed by powdered Zn (9 g, 0.14 mol) in small portions to control heat evolution. The mixture was continued to stir for half an hour and then filtered through Celite to remove unreacted Zn in the mixture. Water (100 ml) was added 44 to the mixture to prevent acetal formation. The solution was concentrated to about one-half initial volume in vacuo and slowly added to saturated NaHCO$_3$ (150 ml). The mixture was extracted with CH$_2$Cl$_2$ (3x200 ml). The organic phases were dried and concentrated. The crude product was distilled to produce nonanal (bp 41 °C, 0.6 Torr) and 9.82 (75%) of methyl 9-oxononanoate (15) as a colorless oil. (bp 103 °C/ 1 Torr) as a colorless oil. (lit.24 bp 105-108 °C/1 Torr) (Caution: Ozone is highly toxic and can react explosively with numerous oxidizable materials.)

Identity and purity of the product were confirmed by $^1$H NMR. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.28-1.36 (m, 6H) 1.58-1.66 (m, 4), 2.42 (td, 2H, J = 7.2, 2.0 Hz), 3.66 (s, 3H), 9.76 (t, 3H, J = 2 Hz).

\[ \text{COOMe} \]
Hexan-2,2,3,4,5,5,6,6,6-2H11-1-ol (C6H32H11O)

A flame-dried, 250-mL, three-necked, round-bottomed flask equipped with a glass stopper, dropping funnel, a reflux condenser topped with a drying tube, and a magnetic stir bar. The flask was charged with LiAlH₄ (1.4 g, 37 mmol) and anhydrous ether (50 mL). A solution of hexanoic-2H₁₁ acid (3.2 g, 25 mmol) in ether (50 mL) was transferred to the addition funnel and added over a 10-min period. The reaction mixture was refluxed for another 2 h, diluted with ether (50 mL), and quenched by dropwise addition of water (25 mL). Following, the mixture was extracted with EtOAc (3 × 50 mL), and the combined organic phases dried with anhydrous sodium sulfate and concentrated under reduced pressure afforded 2.75 g (97% yield) of product as colorless oil. Identity and purity of the product were confirmed by ¹H and ¹³C NMR and HRMS. ¹H NMR (400 MHz, CDCl₃) δ 1.81 (s, 1H, OH), 3.60 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 62.90

Hexanal-2,2,3,4,5,5,6,6,6-2H₁₁ (23) (C₆H₂H₁₁O)

A flame-dried, 250-mL, three-necked, round-bottomed flask was equipped with a magnetic stir bar, rubber septum, glass stopper, and an argon inlet. The flask was charged with pyridinium chlorochromate (8.6 g, 40 mmol) and 60 mL of dichloromethane. A solution of hexan-2,2,3,4,5,5,6,6,6-2H₁₁-1-ol (2.26 g, 20 mmol) in 10 mL of 67 dichloromethane was transferred into the reaction mixture via syringe over 5 min, and the resulting mixture was stirred at ambient temperature for 3 h. The reaction mixture was then charged with 50 mL of diethyl ether and silica gel (20 g), the solution was decanted, and the remaining dark brown resinous polymer was thoroughly washed with three 20-mL portions of diethyl
ether. The combined dark brown/black ether solution was washed successively with two 40-mL portions of 5% aqueous sodium hydroxide solution, 40 mL of 5% aqueous hydrochloric acid, and two 20-mL portions of saturated aqueous NaHCO₃ solution, dried over anhydrous magnesium sulfate, filtered, and concentrated by stream of argon gas at room temperature to give 1.51 g (68%) of the crude product as a yellow oil. The product was carried on with no further purification. Identity and purity of the product were confirmed by ¹H and ¹³C NMR. ¹H NMR (400 MHz, CDCl₃) δ 9.74 (1H, CHO) ¹³C NMR (100 MHz, CDCl₃) δ 203.66

Hex-2-yn-1-ol (26) (C₆H₁₀O)

An oven-dried 500 mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar was sealed under argon with two rubber septa, one of which contains a needle adapter to an argon-filled balloon. The flask was charged with propargyl alcohol (5.61g, 0.1 mol), tetrahydrofurane (THF, 150 ml) and hexamethylphosphoric triamide (HMPA, 40 ml). The solution was cooled in a dry ice-acetone bath at −78 °C, and n-butyllithium (84.4 mL, 2.37 M in hexane, 0.2 mol) was added slowly via syringe. The resulting solution was stirred for 5 min at −78 °C, after which slowly warmed to -30 °C. Following, 1-bromopropane (9.23 g, 75 mmol) was added slowly to the mixture via syringe and temperature increased slowly and stirred ambient temperature overnight. The reaction mixture was neutralized with aqueous saturated NH₄Cl (100 ml) and extracted with EtOAc (3 × 100 mL), and the combined organic phases dried with anhydrous sodium sulfate and concentrated under reduced pressure. Purification by column chromatography (EtOAc: Hexanes /85:15) afforded 6.50 g (57% yield) of product as colorless oil. Identity and purity of the product were confirmed by ¹H and ¹³C NMR. ¹H NMR (400 MHz, CDCl₃) δ 0.96 (t, 1H, J = 7.2 Hz), 1.51 (sextet, 2H, J = 7.2 Hz), 1.99 (bs, 1H), 2.17 (tt, 2H, J = 7.2, 2.0 Hz), 4.24 (dt, 2H, J = 5.6, 2.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 13.72, 20.96, 22.35, 51.41, 78.75, 86.44.
Hex-5-yn-1-ol (27) (C₆H₁₀O)

An oven-dried 500 mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar was sealed under argon with two rubber septa, one of which contains a needle adapter to an argon inlet. The flask was charged with Li (4.48 g, 0.64 mol) and 1,3-diaminopropane (240 ml). The mixture was stirred while heating in an oil bath at 70 °C until the blue color discharged (1 h). The prepared lithium amide suspension was cooled to room temperature. Following, potassium tert-butoxide (42.4 g, 384 mmol), was added to the flask using a powder funnel, the resulting pale-yellow solution was stirred for 20 min at room temperature, and then Hex-2-yn-1-ol (6.27 g, 64 mmol) was added over 10 min via syringe. The reddish-brown mixture was stirred for 3 h and then poured into 1 L of ice-water and extracted with Et₂O (3 × 300 mL). The ether extracts were combined and washed successively with 1 L each of water, 10% hydrochloric acid, and saturated sodium chloride solution. The ether solution was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. Purification by column chromatography (EtOAc: Hexanes /80:20) afforded 5.33 g (84%) of product as colorless oil. Identity and purity of the product were confirmed by ¹H and ¹³C NMR. ¹H NMR (400 MHz, CDCl₃) δ (400 MHz, CDCl₃) 1.54-1.68 (m, 4H), 1.93 (t, 1H, J = 2.8 Hz), 2.19 (td, 2H, J = 6.8, 2.8 Hz), 2.56 (bs, 1H), 3.60 (t, 2H, J = 6.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 18.40, 24.95, 31.82, 62.31, 68.82, 84.58

Hex-5-ynal (21) (C₆H₁₂O)

A flame-dried, 500-mL, three-necked, round-bottomed flask was equipped with a magnetic stir bar, rubber septum, glass stopper, and an argon inlet. The flask was charged with pyridinium chlorochromate (21.5 g, 100 mmol) and 150 mL of dichloromethane. A solution of Hex-5-yn-1-ol (4.9 g, 50 mmol) in 20
mL of dichloromethane was transferred into the reaction mixture via syringe over 5 min, and the resulting mixture was stirred at ambient temperature for 3h. The reaction mixture was then charged with 125 mL of diethyl ether and silica gel (50 g), the solution was decanted, and the remaining dark brown resinous polymer was thoroughly washed with three 50-mL portions of diethyl ether. The combined dark brown/black ether was filtered and concentrated by rotary evaporation at room temperature. The crude product was distilled to give 2.49 g (52%) of product (bp 29 °C, 0.6 Torr) as a colorless oil. Identity and purity of the product were confirmed by 1H and 13C NMR. 1H NMR (400 MHz, CDCl3) δ 1.85 (quintet, 2H, J = 7.2 Hz), 1.97 (t, 1H, J = 2.8 Hz), 2.26 (td, 2H, J = 7.2, 2.8 Hz), 2.60 (td, 2H, J = 7.2, 1.2 Hz), 9.80 (1H, bs); 13C NMR (100 MHz, CDCl3) δ 18.07, 21.09, 42.82, 69.68, 83.48, 202.13

**General procedure; Johnson–Corey–Chaykovsky reaction**

An oven-dried 50- mL, two-necked, round-bottomed flask, containing a magnetic stirring bar was sealed under argon with two rubber septa, one of which contains a needle adapter to an argon-inlet. The solution was cooled in a dry ice-ethanol bath at −30 °C. The flask was charged with 2 mmol of bifunctional Sulfonium/Phosphonium ylide and 2 mmol sodium hydride (80 mg, 60% in mineral oil) and 2 mmol of desired aldehyde and 30 mL acetonitrile. The reaction mixture was continued stirring while warming to room temperatures for 3 hours. The reaction mixture was neutralized with aqueous saturated NH4Cl (20 mL) and extracted with EtOAc (3 × 20 mL), and the combined organic phases dried with anhydrous sodium sulfate and concentrated under reduced pressure. Purification by column chromatography (DCM: methanol /98:2) afforded desired epoxy products.

**Methyl 8-(3-(2-(triphenyl- λ5-phosphanylidene)acetyl)oxiran-2-yl)octanoate (16) (C31H35O4P)**

![Methyl 8-(3-(2-(triphenyl- λ5-phosphanylidene)acetyl)oxiran-2-yl)octanoate (16) (C31H35O4P)](image)

Following the general procedure for the Johnson–Corey–Chaykovsky reaction, reaction of bifunctional Sulfonium/Phosphonium ylide (14) with methyl 9-oxononanoate performed. Purification by column
chromatography afforded 583 mg (58%) of product as yellow oil. Identity and purity of the product were confirmed by $^1$H, $^{13}$C NMR and HRMS. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.20-1.79 (m, 12H), 2.28 (t, 2H, $J = 7.6$ Hz), 3.05 (bm, 1H), 3.14 (t, 1H, $J = 2$ Hz), 3.65 (s, 3H), 3.94 (d, 1H, $^2J_{HP} = 25.6$ Hz), 7.41-7.71 (m, 15H);$^{13}$C NMR (100MHz, CDCl$_3$) $\delta$ 25.03, 26.11, 29.18, 29.26, 29.30, 32.23, 34.19, 48.26 (d, 1H, $^1J_{CP} = 98$ Hz), 51.58, 59.90, 60.04 (d, $J = 17$ Hz), 126.56 (d, $^1J_{CP} = 91$ Hz, C-1'), 129.05 (d, $^3J_{CP} = 12.3$ Hz, C-3'), 132.40 (d, $^4J_{CP} = 2.7$ Hz, C-4'), 133.17 (d, $^2J_{CP} = 10.3$ Hz, C-2'), 174.40, 188.11 (d, $^2J_{CP} = 4.0$ Hz); HRMS (ESI) m/z calcd for C$_{31}$H$_{36}$O$_4$P$^+$ (M+1)$^+$ 503.23457, found 503.23469.

1-(3-pentyloxiran-2-yl)-2-(triphenyl-$\lambda^5$-phosphanylidene)ethan-1-one (19) (C$_{27}$H$_{29}$O$_2$P)

Following the general procedure for the Johnson–Corey–Chaykovsky reaction, reaction of bifunctional ylide (14) with n-hexanal performed. Purification by column chromatography afforded 600 mg (72%) of product as yellow oil. Identity and purity of the product were confirmed by $^1$H, $^{13}$C NMR and HRMS. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.88 (t, 3H, $J = 6.5$ Hz), 1.22-1.82 (m, 8H), 3.05 (bm, 1H), 3.13 (t, 1H, $J = 2.0$ Hz), 3.94 (d, 1H, $^2J_{HP}= 24$ Hz), 7.35-7.73 (m, 15H), $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$14.24, 22.80, 25.95, 31.82, 32.35, 48.86 (d, $^1J_{CP} = 110$ Hz), 60.07, 60.17 (d, $J = 16.6$ Hz), 126.36 (d, $^1J_{CP} = 90.6$ Hz, C-1'), 129.15 (d, $^3J_{CP} = 12.3$ Hz, C-3'), 132.49 (d, $^4J_{CP} = 2.8$ Hz, C-4'), 133.31 (d, $^3J_{CP} = 10.2$ Hz, C-2'), 188.31 (d, $^2J_{CP} = 3.5$ Hz); HRMS (ESI) m/z calcd for C$_{27}$H$_{30}$O$_2$P$^+$ (M+1)$^+$ 417.19779, found 417.19787.

1-(3-(pent-4-yn-1-yl)oxiran-2-yl)-2-(triphenyl-$\lambda^5$-phosphanylidene)ethan-1-one (22) (C$_{27}$H$_{25}$O$_2$P)
Following the general procedure for the Johnson–Corey–Chaykovsky reaction, reaction of bifunctional Sulfonium/Phosphonium ylide (14) with compound 21 performed. Purification by column chromatography afforded 553 mg (67%) of product as yellow oil. Identity and purity of the product were confirmed by $^1$H, $^{13}$C NMR and HRMS. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.49-1.71 (m, 4H), 1.89 (t, 1H, $J = 2.0$ Hz), 2.16-2.24 (m, 2H), 3.05 (ddd, 1H, $J = 8.5, 4, 2.0$ Hz), 3.13 (t, 2H, $J = 2.0$ Hz), 3.99 (d, 1H, $^2$J$_{HP} = 23.5$ Hz), 7.34-7.63 (m, 15H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 18.25, 25.06, 31.06, 49.07 (d, 1H, $^1$J$_{CP} = 110$ Hz), 59.10, 59.72 (d, $J = 17$ Hz), 68.70, 84.03, 126.44 (d, $^1$J$_{CP} = 91$ Hz, C-1’), 129.01 (d, $^3$J$_{CP} = 12.4$ Hz, C-3’), 132.38 (d, $^4$J$_{CP} = 2.8$ Hz, C-4’), 133.15 (d, $^2$J$_{CP} = 10.3$ Hz, C-2’), 187.65 (d, $^2$J$_{CP} = 4.0$ Hz).

1-(3-(pentyl-$^2$H$_{11}$)oxiran-2-yl)-2-(triphenyl-$\lambda^5$-phosphanylidene)ethan-1-one (24) (C$_{27}$H$_{18}$O$_2$P)

Following the general procedure for the Johnson–Corey–Chaykovsky reaction, reaction of bifunctional Sulfonium/Phosphonium ylide (14) with hexanal-2,2,3,3,4,4,5,5,6,6,6-$^2$H$_{11}$ performed. Purification by column chromatography afforded 599 mg (70%) of product as brown oil. Identity and purity of the product were confirmed by $^1$H, $^{13}$C NMR and HRMS. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 3.04 (b, 1H), 3.04 (t, 1H, $J = 2.0$ Hz), 3.94 (d, 1H, $^2$J$_{HP} = 24.0$ Hz), 7.39-7.72 (m, 15H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 48.90 (d, $^1$J$_{CP} = 110$ Hz), 60.09, 60.13 (d, $J = 16.5$ Hz), 126.79 (d, $^1$J$_{CP} = 90.6$ Hz, C-1’), 129.48 (d, $^3$J$_{CP} = 12.3$ Hz, C-3’), 132.37 (d, $^4$J$_{CP} = 2.8$ Hz, C-4’) 133.36 (d, $^2$J$_{CP} = 10.3$ Hz, C-2’), 188.44 (d, $^2$J$_{CP} = 4.0$ Hz); HRMS (ESI) m/z calcd for C$_{27}$H$_{19}$O$_2$P+ (M+1)$^+$ 428.267, found 428.2669.

General procedure; Wittig reaction

An oven-dried 50- mL round-bottomed flask, containing a magnetic stirring bar charged with 1 mmol of desired epoxy from the previous reaction and 1 mmol of desired aldehyde, and 10 mL toluene. The
mixture was heated under reflux overnight, allowed to cool to room temperature. The reaction mixture was concentrated under reduced pressure. Purification by column chromatography (hexane: Et₂O/85:15) afforded α,β-unsaturated keto epoxide products.

**Methyl (E)-8-(3-(oct-2-enoyl)oxiran-2-yl)octanoate (18) (C₁₉H₃₂O₄)**

Following the general procedure for the Wittig reaction, reaction of aldehyde 17 and Methyl 8-(3-(2-(triphenyl-λ⁵-phosphanylidene)acetyl)oxiran-2-yl)octanoate (16) afforded product 18. Purification by column chromatography afforded 278 mg (86%) of product as yellow oil. Identity and purity of the product were confirmed by ¹H, ¹³C NMR and HMRS. ¹H NMR (500 MHz, CDCl₃) δ 0.87 (t, 3H, J = 7.2 Hz), 1.25-1.69 (m, 18H), 2.18 (dd, 2H, J = 15.0, 7.0 Hz), 2.30 (t, 2H, J = 7.5 Hz), 3.02 (t, 1H, J = 6 Hz), 3.32 (bs, 1H), 3.67 (s, 3H), 6.23 (d, 1H, J = 15.5 Hz), 7.08 (1H, dt, J = 15.5, 7.0 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 14.32, 22.76, 25.11, 26.07, 27.97, 29.31, 29.41, 29.42, 31.71, 32.14, 33.08, 34.38, 51.83, 58.66, 59.36, 124.27, 151.02, 174.61, 196.05; HRMS (ESI) m/z calcd for C₁₉H₃₂O₄Na⁺ (M+Na)⁺ 347.21928, found 347.21943.

**Methyl (E)-8-(3-(oct-2-en-7-ynoyl)oxiran-2-yl)octanoate (28) (C₁₉H₂₈O₄)**

Following the general procedure for the Wittig reaction, reaction of aldehyde 21 and Methyl 8-(3-(2-(triphenyl-λ⁵-phosphanylidene)acetyl)oxiran-2-yl)octanoate (16) afforded product 28. Purification by column chromatography afforded 260 mg (81%) of product as yellow oil. Identity and purity of the product were confirmed by ¹H, ¹³C NMR and HRMS. ¹H NMR (500 MHz, CDCl₃) δ 1.26-1.66 (m, 12H), 1.70 (quintet, 2H, J = 7.0 Hz), 1.98 (t, 1H, J = 2.5 Hz), 2.22 (td, 2H, J = 7.0, 2.5 Hz), 2.30 (t, 2H, J = 7.0 Hz), 2.36 (t, 2H, J = 7.0 Hz), 3.04 (td, 1H, J = 5.5, 2.0 Hz), 3.33 (d, 1H, J = 2 Hz), 3.66 (s, 3H), 6.27 (d, 1H, J = 16
(Hz), 7.06 (1H, dt, J = 16.0, 7.0 Hz); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 18.27, 25.20, 26.09, 29.30, 29.39, 29.41, 31.81, 32.12, 34.38, 51.82, 59.42, 69.49, 83.716, 124.76, 149.27, 174.59, 195.93; HRMS (ESI) m/z calcd for C$_{19}$H$_{28}$O$_4$Na$^+$ (M+Na)$^+$ 343.18798, found 343.1881.

**Methyl (E)-8-(3-(oct-2-enoyl-4,4,5,5,6,6,7,7,8,8,8-$^2$H$_{11}$)oxiran-2-yl)octanoate (29) (C$_{19}$H$_{21}$D$_{11}$O$_4$)**

Following the general procedure for the Wittig reaction, reaction of aldehyde 23 and Methyl 8-(3-(2-(triphenyl-$\lambda^5$-phosphanylidene)acetyl)oxiran-2-yl)octanoate (16) afforded product 29. Purification by column chromatography afforded 245 mg (73%) of product as yellow oil. Identity and purity of the product were confirmed by $^1$H and $^{13}$C NMR and HMRS. $^1$H NMR (500 MHz, CDCl$_3$) δ 1.27-1.71 (m, 12H), 2.30 (t, 2H, J = 7.5 Hz), 3.04 (t, 1H, J = 5.0 Hz), 3.33 (bs, 1H), 3.66 (s, 3H), 6.23 (d, 1H, J = 16.0 Hz), 7.07 (d, 1H, J = 16.0 Hz); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 25.20, 26.09, 29.30, 29.39, 29.41, 32.13, 34.37, 51.81, 58.64, 59.34, 124.34, 150.95, 174.59, 196.02; HRMS (ESI) m/z calcd for C$_{19}$H$_{25}$D$_{11}$NO$_4^+$ (M+NH$_4$)$^+$ 353.567, found 353.3331.

**Methyl (E)-11-oxo-11-(3-pentyloxiran-2-yl)undec-9-enoate (20) (C$_{19}$H$_{32}$O$_4$)**

Following the general procedure for the Wittig reaction, reaction of aldehyde 15 and 1-(3-pentyloxiran-2-yl)-2-(triphenyl-$\lambda^5$-phosphanylidene)ethan-1-one (19) afforded product 20. Purification by column chromatography afforded 234 mg (72%) of the product as yellow oil. Identity and purity of the product were confirmed by $^1$H, $^{13}$C NMR and HMRS. $^1$H NMR (500 MHz, CDCl$_3$) δ 0.87 (t, 3H, J = 7.2 Hz), 1.19-1.73 (m, 18H), 2.21 (dd, 2H, J = 7.0, 2 Hz), 2.30(t, 2H, J = 7.5 Hz), 3.05 (td, 1H, J = 5.5, 2.0 Hz), 3.34 (d, 1H, J =
2.0 Hz), 3.67 (s, 3H), 6.23 (d, 1H, J = 15.5 Hz), 7.07 (1H, dt, J = 15.5, 7.0 Hz); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 14.27, 22.83, 25.19, 25.83, 28.19, 29.22, 29.31 (2C), 31.76, 32.13, 33.04, 34.37, 51.83, 58.75, 59.38, 124.32, 150.82, 174.64, 196.11; HRMS (ESI) m/z calcd for C$_{19}$H$_{32}$O$_4$Na$^+$ (M+Na)$^+$ 347.21928, found 347.21942.

**Methyl (E)-11-oxo-11-(3-(pent-4-yn-1-yl)oxiran-2-yl)undec-9-enoate (30) (C$_{19}$H$_{28}$O$_4$)**

Following the general procedure for the Wittig reaction, reaction of aldehyde 15 and 1-(3-(pent-4-yn-1-yl)oxiran-2-yl)-2-(triphenyl-$\lambda^5$-phosphanylidene)ethan-1-one (22) afforded product 30. Purification by column chromatography afforded 208 mg (65%) of product as yellow oil. Identity and purity of the product were confirmed by $^1$H and $^{13}$C NMR. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.24-1.90 (m, 16H), 1.97 (t, 1H, J = 2.5 Hz), 2.18-2.25 (m, 2H), 2.30 (t, 2H, J = 7.5 Hz), 3.07 (dt, 1H, J = 5.0, 1.5 Hz), 3.38 (d, 1H, J = 1.5 Hz), 3.66 (s, 3H), 6.23 (d, 1H, J = 16 Hz), 7.08 (1H, dt, J = 16.0, 7.0 Hz); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 18.39, 24.99, 25.20, 28.19, 29.22, 29.31, 30.97, 33.06, 34.36, 51.80, 58.08, 59.06, 69.47, 83.72, 124.41, 151.03, 174.53, 195.76; HRMS (ESI) m/z calcd for C$_{19}$H$_{28}$O$_4$Na$^+$ (M+Na)$^+$ 343.18798, found 343.18812.

**Methyl (E)-11-oxo-11-(3-(pentyl-2H$_{11}$)oxiran-2-yl)undec-9-enoate (31) (C$_{19}$H$_{21}$H$_{11}$O$_4$)**

Following the general procedure for the Wittig reaction, reaction of aldehyde 15 and 1-(3-(pentyl-2H$_{11}$)oxiran-2-yl)-2-(triphenyl-$\lambda^5$-phosphanylidene)ethan-1-one (22) afforded product 31. Purification by column chromatography afforded 146 mg (62%) of product as yellow oil. The identity and purity of the product were confirmed by $^1$H and $^{13}$C NMR. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.23-1.67 (m, 10H), 2.20 (q, 2H,
$J = 7.0 \text{ Hz}$, 2.27 (t, 2H, $J = 7.0 \text{ Hz}$), 3.01 (s, 1H), 3.31 (s, 1H), 3.64 (s, 3H), 6.21 (d, 1H, $J = 15.5 \text{ Hz}$), 7.05 (dt, 1H, $J = 15.5, 7.0 \text{ Hz}$); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 25.15, 28.15, 29.26, 29.27 (2C), 32.89, 34.31, 51.75, 58.58, 59.30, 124.28, 150.66, 174.51, 196.00, HRMS (ESI) m/z calcd for C$_{19}$H$_{25}$NO$_4$ $^+$ (M+NH$_4$)$^+$ 353.567, found 353.3330.

**General procedure; Porcine Pancreas Lipase (PPL) hydrolysis**

An oven-dried 25-mL round-bottomed flask, equipped with a magnetic stirring bar, was charged with 0.1 mmol of the desired methyl ester EKODE-($E$) and PPL (20 mg) (lipase from porcine pancreas, Type II from Sigma) in acetone (1 mL) and phosphate buffer (pH 7, 5 mL, 0.2 M). The mixture was stirred vigorously at ambient temperature for 4 h and filtered through a pad of Celite with EtOAc. The two phases were separated, and the organic phase was concentrated under reduced pressure. Purification by column chromatography (hexane: EtOAc /50: 50) afforded carboxylic acid final products.

**(E)-8-(3-(oct-2-enoyl)oxiran-2-yl)octanoic acid (trans-EKODE-($E$)-IIa) (1) (C$_{18}$H$_{30}$O$_4$)**

Following the general procedure for PPL hydrolysis of methyl ($E$)-8-(3-(oct-2-enoyl)oxiran-2-yl)octanoate 18 afforded 146 mg (94%) of product as yellow oil. Identity and purity of the product were confirmed by $^1$H, $^{13}$C NMR and HRMS. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.89 (t, 3H, $J = 7.0 \text{ Hz}$), 1.21-1.74 (m, 18H), 2.17-2.24 (m, 2H), 2.34 (t, 2H, $J = 7.0 \text{ Hz}$), 3.04 (ddd, 1H, $J = 6.0, 5.0, 2.0 \text{ Hz}$), 3.33 (d, 1H, $J = 2.0 \text{ Hz}$), 6.23 (dt, 1H, $J = 15.5, 1.5 \text{ Hz}$), 7.07 (1H, dt, $J = 15.5, 7.0 \text{ Hz}$); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 14.27, 22.73, 24.91, 26.08, 27.94, 29.20, 29.36, 29.38, 31.68, 32.11, 33.06, 34.25, 58.66, 59.33, 124.26, 151.06, 179.81. 196.08; HRMS (FAB) calcd for C$_{18}$H$_{29}$O$_4^-$ (M-H)$^-$ 309.427, found 309.2072.
Following the general procedure for PPL hydrolysis of methyl (E)-8-(3-oct-2-en-7-ynoyl)oxiran-2-yl)octanoate 28 afforded 139 mg (91%) of product as yellow oil. Identity and purity of the product were confirmed by 1H, 13C NMR and HRMS. 1H NMR (500 MHz, CDCl₃) δ 1.22-1.88 (m, 12H), 1.70 (quintet, 2H, J = 7.0 Hz), 1.98 (t, 1H, J = 2.5 Hz), 2.17-2.29 (m, 4H), 2.30-2.40 (m, 2H), 3.05 (t, 1H, J = 2.5 Hz), 3.33 (bs, 1H), 6.27 (d, 1H, J = 15.5 Hz), 7.06 (1H, dt, J = 15.5, 7.0 Hz); 13C NMR (125 MHz, CDCl₃) δ 18.27, 24.92, 26.96, 29.20, 29.36, 29.38, 31.82, 32.09, 34.15, 58.62, 59.41, 69.50, 83.72, 124.75, 149.33, 179.28, 195.97; HRMS (ESI) m/z calcd for C₁₈H₂₅O₄- (M-H)- 305.395, found 305.1758.

Following the general procedure for PPL hydrolysis of methyl (E)-8-(3-oct-2-enoyl-4,4,5,5,6,6,7,7,8,8,8-²H₁₁)oxiran-2-yl)octanoate 29 afforded 150 mg (93%) of product as yellow oil. Identity and purity of the product were confirmed by 1H, 13C NMR and HRMS. 1H NMR (500 MHz, CDCl₃) δ 1.29-1.71 (m, 12H), 2.28 (t, 2H, J = 7.5 Hz), 3.01 (m, 1H), 3.52 (bs, 1H), 6.28 (d, 1H, J = 16 Hz), 7.10 (d, 1H, J = 16.0 Hz); 13C NMR (125 MHz, CDCl₃) δ 26.82, 26.03, 30.10, 30.23, 30.24, 32.82, 34.91, 59.43, 60.01, 126.55, 152.05, 177.68, 197.45; HRMS (ESI) m/z calcd for C₁₈H₁₈²H₁₁O₄- (M-H)- 320.493, found 320.2762.

(E)-11-oxo-11-(3-pentyloxiran-2-yl)undec-9-enoic acid(trans-EKODE-(E)-IIb) (2) (C₁₈H₃₀O₄)
Following the general procedure for PPL hydrolysis of methyl (E)-11-oxo-11-(3-pentyloxiran-2-yl)undec-9-enoate 20 afforded 143mg (92%) of product as yellow oil. Identity and purity of the product were confirmed by $^1$H, $^{13}$C NMR and HRMS. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.88 (t, 3H, $J$ = 7.2 Hz), 1.17-1.67 (m, 18H), 2.21 (dq, 2H, $J$ = 6.8, 1.6 Hz), 2.33 (t, 2H, $J$ = 7.6 Hz), 3.05 (ddd, 1H, $J$ = 6.0, 5.0, 2.0 Hz), 3.34 (d, 1H, $J$ = 2.0 Hz), 6.25 (dt, 1H, $J$ = 15.5, 1.5 Hz), 7.06 (1H, dt, $J$ = 15.5, 7.0 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.28, 22.84, 24.93, 25.83, 28.20, 29.22, 29.30 (2C), 31.77, 32.14, 33.04, 34.20, 58.74, 59.40, 124.32, 150.76, 179.44, 196.09, HRMS (FAB) calcd for C$_{18}$H$_{29}$O$_4^-$ (M-H)$^-$_2 309.427, found 309.2072.

(E)-11-oxo-11-(3-(pent-4-yn-1-yl)oxiran-2-yl)undec-9-enoic acid (hydrolyzed 30) (C$_{18}$H$_{26}$O$_4$)

Following the general procedure for PPL hydrolysis of methyl (E)-11-oxo-11-(3-(pent-4-yn-1-yl)oxiran-2-yl)undec-9-enoate 30 afforded 144mg (94%) of product as yellow oil. Identity and purity of the product were confirmed by $^1$H, $^{13}$C NMR and HRMS. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.22-1.88 (m, 12H), 1.97 (t, 1H, $J$ = 2.5 Hz), 2.17-2.32 (m, 4H), 2.35 (t, 2H, $J$ = 7.5 Hz), 3.08 (bs, 1H), 3.29(d, 1H, $J$ = 5 Hz), 6.26 (d, 1H, $J$ = 15.5 Hz), 7.08 (1H, dt, $J$ = 15.5, 7.0 Hz); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 18.39, 24.93, 24.99, 28.18, 29.21, 29.28, 29.35, 30.97, 33.06, 34.09, 58.11, 59.11, 69.49, 83.74, 124.43, 151.00, 178.90, 195.76; HRMS (ESI) m/z calcd for C$_{18}$H$_{25}$O$_4^-$ (M-H)$^-$_2 305.395, found 305.1758.

(E)-11-oxo-11-(3-(pentyl-$^2$H$_{11}$)oxiran-2-yl)undec-9-enoic acid (hydrolyzed 31) (C$_{18}$H$_{19}^2$H$_{11}$O$_4$)

Following the general procedure for PPL hydrolysis of methyl (E)-11-oxo-11-(3-(pentyl-$^2$H$_{11}$)oxiran-2-yl)undec-9-enoate 31 afforded 144mg (94%) of product as yellow oil. Identity and purity of the product were confirmed by $^1$H, $^{13}$C NMR and HRMS. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.22-1.88 (m, 12H), 1.97 (t, 1H, $J$ = 2.5 Hz), 2.17-2.32 (m, 4H), 2.35 (t, 2H, $J$ = 7.5 Hz), 3.08 (bs, 1H), 3.29(d, 1H, $J$ = 5 Hz), 6.26 (d, 1H, $J$ = 15.5 Hz), 7.08 (1H, dt, $J$ = 15.5, 7.0 Hz); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 18.39, 24.93, 24.99, 28.18, 29.21, 29.28, 29.35, 30.97, 33.06, 34.09, 58.11, 59.11, 69.49, 83.74, 124.43, 151.00, 178.90, 195.76; HRMS (ESI) m/z calcd for C$_{18}$H$_{25}$O$_4^-$ (M-H)$^-$_2 305.395, found 305.1758.
Following the general procedure for PPL hydrolysis of methyl (E)-11-oxo-11-(3-(pentyl-2H11)oxiran-2-yl)undec-9-enoate 31 afforded 144 mg (94%) of product as yellow oil. Identity and purity of the product were confirmed by $^1$H, $^{13}$C NMR and HRMS. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.20-1.71 (m, 10H), 2.22 (q, 2H, J = 6.5 Hz), 2.35 (t, 2H, J = 6.5 Hz), 3.04 (s, 1H), 3.34 (s, 1H), 6.23 (d, 1H, J = 15.5 Hz), 7.07 (dt, 1H, J = 15.5, 6.0 Hz); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 24.95, 28.20, 29.23, 29.30, 29.36, 33.04, 34.17, 58.67, 59.36, 124.40, 150.79, 179.08, 196.16 HRMS (ESI) m/z calcd for C$_{18}$H$_{18}$-2H$_{11}$O$_4^-$ (M-H)$^-$ 320.493, found 320.2762
$^1$H and $^{13}$C NMR Spectra

$^1$HNMR of 12

Br\[O\]Br

1,3-dibromopropan-2-one

(400 MHz, CDCl$_3$)
$^{13}$CNMR of 12

Br \quad \text{C} \quad \text{O} \quad \text{Br}

1,3-dibromopropan-2-one

(100 MHz, CDCl$_3$)
$^1$HNMR of 13

1-bromo-3-(triphenylphosphoranylidene)propan-2-one

(400 MHz, CDCl$_3$)
$^{13}$C NMR of 13

1-bromo-3-(triphenylphosphoranylidene)propan-2-one

(100 MHz, CDCl$_3$)
$^{1}$HNMR of 14

Ph$_3$P$\rightleftharpoons$S$^{+}$CH$_3$

Bifunctional sulfonium/Phosphonium ylide

(400 MHz, CDC$_3$)
$^1$HNMR

Hexan-2,2,3,3,4,4,5,5,6,6,6-$^2$H$_{11}$-ol

(400 MHz, CDCl$_3$)
$^{13}$CNMR

Hexan-2,2,3,3,4,4,5,5,6,6,6,6,6,6-H$_{11}$-1-ol

(100 MHz, CDCl$_3$)
$^1$HNMR of 23

Hexanal-2,2,3,3,4,4,5,5,6,6,6-$^2$H$_{11}$

(400 MHz, CDCl$_3$)
$^{13}$CNMR of Z3

Hexanal-2,2,3,3,4,4,5,5,6,6,6,6-\textsuperscript{2}$H_{11}$

(100 MHz, CDCl$_2$)
$^1$HNMR of 26

Hex-2-yn-1-ol

(400 MHz, CDCl$_3$)
$^{13}$C NMR of 26

HO\[\equiv\]
Hex-2-yn-1-ol

(100 MHz, CDCl$_3$)
'\textsuperscript{1}H NMR of 27

\textbf{Hex-5-yn-1-ol}

(400 MHz, CDCl\textsubscript{3})
$^{13}$CNMR of 27

Hex-5-yn-1-ol

(100 MHz, CDCl$_3$)
$^{13}$C NMR of 21

Hex-5-ynal

(100 MHz, CDCl$_3$)
$^13$CNMR of 16

Methyl 8-(3-((triphenyl-5-phosphanylidenecacetyl)oxiran-2-yl)octanoate

(100 MHz, CDCl$_3$)
Methyl 8-(3-(2-(triphenyl-1,5-phosphanylidene)acetyl)oxiran-2-yl)octanoate

(400 MHz, CDCl₃)
$^1$HNMR of 19

1-(3-pentyl/oxiran-2-y)-2-(triphenylyl - \( \lambda^5 \)-phosphanylidene)ethan-1-one

(500 MHz, CDCl$_3$)
$^{13}$C NMR of 19

1-(3-pentyloxyiran-2-yl)-2-(triphenyl-\(\lambda_5\)-phosphanylidene)ethan-1-one

(125 MHz, CDCl$_3$)
$^1$HNMR of 22

Ph₃P\(\text{=O}\)Ph₃P

1-(3-(pent-4-yn-1-yl)oxiran-2-yl)-2-(triphenylphosphanylidene)ethan-1-one

(500 MHz, CDCl₆)
$^{13}$CNMR of 22

1-(3-(pent-4-yn-1-yl)oxiran-2-yl)-2-(triphenyl-$\lambda^5$-phosphanylidene)ethan-1-one

(125 MHz, CDCl$_6$)
$^1$HNMR of 24

Ph$_3$P

1-(3-(pentyl-$^2$H$_{11}$)oxiran-2-yl)-2-(triphenyl-$^5$-phosphanidene)ethan-1-one

(500 MHz, CDCl$_3$)
$^{13}$CNMR of 24

1-(3-(pentyl-$^2$H$_{11}$)oxiran-2-yl)-2-(triphenyl-$\lambda_5$-phosphanyliden)ethan-1-one

(125 MHz, CDCl$_3$)
$^{13}$CNMR of 18

Methyl (E)-8-(3-oct-2-enoyloxy)iran-2-yl)octanoate

(125 MHz, CDCl$_3$)
Methyl (E)-8-(3-oct-2-ene-7-ynoyl)oxiran-2-yl)octanoate

(500 MHz, CDCl₃)
Methyl (E)-8-(3-(oct-2-en-7-ynoyl)oxiran-2-yl)octanoate

(125 MHz, CDCl₃)
Methyl (E)-8-(3-(oct-2-enoyl-4,4,5,6,6,7,7,8,8,8-^2\text{H}_4)oxiran-2-yl)octanoate

(500 MHz, CDCl_3)
Methyl (E)-8-(3-oxo-1,2,2,6-octadecadien-4-yl)octanoate

\[ \text{\( ^{13}C \)NMR of 29} \]

(D) 8-(3-oxo-1,2,2,6-octadecadien-4-yl)octanoate

(125 MHz, CDCl3)
$\text{H}_3C$\begin{array}{c}
\text{O} \\
\text{C} \\
\text{O} \\
\text{Me}
\end{array}$

Methyl (E)-11-oxo-11-(3-pentyloxiran-2-yl)undec-9-enoate

(125 MHz, CDCl$_3$)
Methyl (E)-11-oxo-11-((3-pent-4-yn-1-yl)oxiran-2-yl)undec-9-enoate

$^{13}$CNMR of 30

(125 MHz, CDCl$_3$)
Methyl (E)-11-oxo-11-(3-pentyl-\textsuperscript{2}H\textsubscript{11})oxiran-2-yl)undec-9-enoate

(500 MHz, CDCl\textsubscript{3})
Methyl (E)-11-oxo-11-(3-(pentyl-^2^H_{11})oxiran-2-yl)undec-9-enoate

(125 MHz, CDCl$_3$)
\[ ^1 \text{HNMR of 1} \]

\[
\begin{align*}
\text{H}_3C & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \ quad
\(^{13}C\) NMR of 1

(E)-8-(3-(oct-2-enoyl)oxiran-2-yl)octanoic acid (trans-EKODE-(E)-IIa)

(125 MHz, CDCl\(_3\))
$^1$H NMR of hydrolyzed 28

(E)-8-(3-(oct-2-en-7-ynoyl)oxiran-2-yl)octanoic acid

(125 MHz, CDCl$_3$)
$^1$H NMR of hydrolyzed 29

Methyl (E)-8-(3-(oct-2-enoyl)-4,4,5,6,6,7,7,8,8,8-$^2$H$_4$)oxiran-2-yl)octanoate

(500 MHz, CDCl$_3$)
$^{13}$C NMR of hydrolyzed 29

Methyl (E)-8-(3-oct-2-enoyl-4,4,5,5,6,6,7,7,8,8-\textsuperscript{2}H\textsubscript{11})oxiran-2-yl)octanoate

(125 MHz, CDCl\textsubscript{3})
\(^{13}\text{C} \text{NMR of } Z \)

(E)-11-oxo-11-(3-pentyloxiran-2-yl)undec-9-enoic acid (trans-EKODE-(E)-Ib)

(125 MHz, CDCl\(_3\))
$^{13}$CNMR of hydrolyzed 30

(\(E\))-11-oxo-11-(3-(pent-4-yn-1-yl)oxiran-2-yl)undec-9-enoic acid

(125 MHz, CDCl$_3$)
$^1$HNMR of hydrolyzed 31

(E)-11-oxo-11-(3-(pentyl-$^2$H$_{11}$)oxiran-2-yl)undec-9-enoic acid

(500 MHz, CDCl$_3$)
\(^{13}\)C NMR of hydrolyzed 31

\[(E)-11\text{-oxo-11-}(3\text{-pentyl-}^{2}\text{H}_{11}\text{)oxiran-2-yl)}\text{undec-3-enoic acid}\]

(125 MHz, CDCl\(_3\))