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

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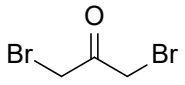
General experimental details

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_2O 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 δ units, part per million (ppm) with reference to the residual solvent peak $CDCl_3$ (δ 7.26), CD_3OD (δ 3.31) for ^{1}H and (δ 77.36), CD_3OD (δ 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).

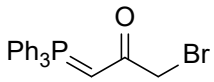
Experimental Procedure and Characterization

1,3-dibromopropan-2-one (12) ($C_3H_4Br_2O$)



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 48h. 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 ^{1}H NMR indicates conversion was > 90%. Identity and purity of the product were confirmed by ^{1}H NMR and ^{13}C NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13; ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.18, 194.13.

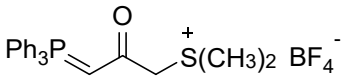
1-bromo-3-(triphenylphosphoranylidene)propan-2-one (13) ($C_{21}H_{18}BrOP$)



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, $CDCl_3$) δ 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, $CDCl_3$) δ 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.

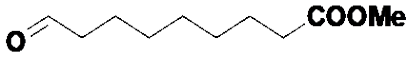
Dimethyl(2-oxo-3-(triphenylphosphoranylidene)propyl)sulfonium tetrafluoroborate [Bifunctional Sulfonium/Phosphonium ylide] (14) ($C_{23}H_{24}BF_4OPS$)



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, $CDCl_3$) δ 2.91 (s, 6H), 4.16 (d, 1H, $^{2}J_{HP}$ = 21.2 Hz), 4.42

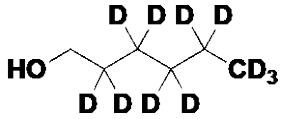
(s, 2H), 7.47-7.64 (15H, m) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.01, 52.43 (d, $^3J_{CP}$ = 20.5 Hz), 56.71 (d, $^1J_{CP}$ = 104 Hz), 125.20 (d, $^1J_{CP}$ = 90.8 Hz, C-1'), 129.45 (d, $^3J_{CP}$ = 12.4 Hz, C-3'), 133.09 (bs, C-4'), 133.21 (d, $^2J_{CP}$ = 10.3 Hz, C-2'), 177.06 (d, $^2J_{CP}$ = 4.0 Hz) ; HRMS (ESI) m/z calcd for $C_{23}H_{24}OPS^+$ $(M+1)^+$ 379.12800, found 379.12807.

Methyl 9-oxononanoate (15) ($C_{10}H_{18}O_3$)



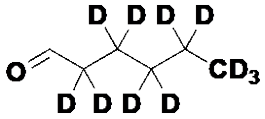
An oven-dried 0.5 L, two-necked, round-bottomed flask equipped with a mechanical stirrer. The flask was charged with methyl oleate (20.8 g, 70 mmol) in dichloromethane (250 mL), and methanol (100 mL). The vessel was cooled to −78 ° C and ozone was bubbled through the solution using a Pasteur pipet until 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_2Cl_2 (3x200 ml). The organic phases were dried and concentrated. The crude product was distilled to produce nonanal (bp 41 ^oC, 0.6 Torr) and 9.82 (75%) of methyl 9-oxononanoate **(15)** as a colorless oil. (bp 103 ^oC/ 1 Torr) as a colorless oil. (lit.24 bp 105-108 ^oC/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, $CDCl_3$) δ 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).

Hexan-2,2,3,3,4,4,5,5,6,6,6-$^{2}H_{11}$-1-ol ($C_6H_3{}^{2}H_{11}O$)



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 $LiAlH_4$ (1.4 g, 37 mmol) and anhydrous ether (50 mL). A solution of hexanoic-$^{2}H_{11}$ 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 ^{1}H and ^{13}C NMR and HRMS. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81 (s, 1H, OH), 3.60 (s, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 62.90

Hexanal-2,2,3,3,4,4,5,5,6,6,6-$^{2}H_{11}$ (23) ($C6H^{2}H_{11}O$)



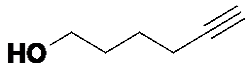
A flame-dried, 250-mL, three-necked, round-bottomed flask was equipped with a magnetic stir bar, rubber septum, glass stopper, and an argon inlet. The flask was charged with pyridinium chlorochromate (8.6 g, 40 mmol) and 60 mL of dichloromethane. A solution of hexan-2,2,3,3,4,4,5,5,6,6,6-$^{2}H_{11}$-1-ol (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 ^{1}H and ^{13}C NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (1H, CHO) ^{13}C NMR (100 MHz, CDCl3) δ 203.66

Hex-2-yn-1-ol (26) ($C_6H_{10}O$)

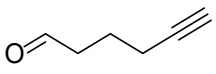
An oven-dried 500 mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar was sealed under argon with two rubber septa, one of which contains a needle adapter to an argon-filled balloon. The flask was charged with propargyl alcohol (5.61g, 0.1 mol), tetrahydrofurane (THF, 150 ml) and 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 NH_4Cl (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 ^{1}H and ^{13}C NMR. ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.72, 20.96, 22.35, 51.41, 78.75, 86.44 .

Hex-5-yn-1-ol (27) ($C_6H_{10}O$)



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 Et_2O (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 ^{13}C NMR. ^1H NMR (400 MHz, $CDCl_3$) δ (400 MHz, $CDCl_3$) *δ* 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); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 18.40, 24.95, 31.82, 62.31, 68.82, 84.58

Hex-5-ynal (21) ($C_6H_{12}O$)



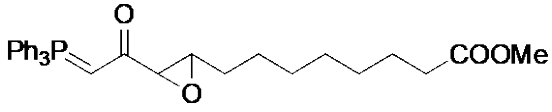
A flame-dried, 500-mL, three-necked, round-bottomed flask was equipped with a magnetic stir bar, rubber septum, glass stopper, and an argon inlet. The flask was charged with pyridinium chlorochromate (21.5 g, 100 mmol) and 150 mL of dichloromethane. A solution of Hex-5-yn-1-ol (4.9 g, 50 mmol) in 20

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 ^{o}C, 0.6 Torr) as a colorless oil. Identity and purity of the product were confirmed by ^{1}H and ^{13}C NMR. ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 NH_4Cl (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.

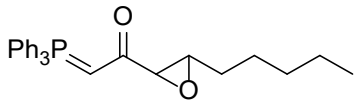
Methyl 8-(3-(2-(triphenyl- λ^{5}-phosphanylidene)acetyl)oxiran-2-yl)octanoate (16) ($C_{31}H_{35}O_4P$)



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

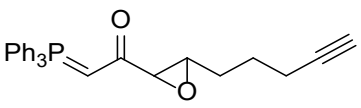
chromatography afforded 583 mg (58%) of product as yellow oil. Identity and purity of the product were confirmed by ^{1}H, ^{13}C NMR and HRMS. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20-1.79 (m, 12H), 2.28 (t, 2H, J = 7.6 Hz), 3.05 (bm, 1H), 3.14 (t, 1H, J = 2 Hz), 3.65 (s, 3H), 3.94 (d, 1H, $^{2}J_{HP}$ = 25.6 Hz), 7.41-7.71 (m, 15H);^{13}C NMR (100MHz, $CDCl_3$) δ 25.03, 26.11, 29.18, 29.26, 29.30, 32.23, 34.19, 48.26 (d, 1H, $^{1}J_{CP}$ = 98 Hz), 51.58, 59.90, 60.04 (d, J = 17 Hz), 126.56 (d, $^{1}J_{CP}$ = 91 Hz, C-1'), 129.05 (d, $^{3}J_{CP}$ = 12.3 Hz, C-3'), 132.40 (d, $^{4}J_{CP}$ = 2.7 Hz, C-4'), 133.17 (d, $^{2}J_{CP}$ = 10.3 Hz, C-2'), 174.40, 188.11 (d, $^{2}J_{CP}$ = 4.0 Hz) ; HRMS (ESI) m/z calcd for $C_{31}H_{36}O_4P^+$ $(M+1)^+$ 503.23457, found 503.23469.

1-(3-pentyloxiran-2-yl)-2-(triphenyl-λ^5-phosphanylidene)ethan-1-one (19) ($C_{27}H_{29}O_2P$)



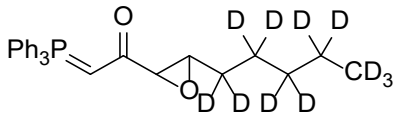
Following the general procedure for the Johnson–Corey–Chaykovsky reaction, reaction of bifunctional ylide (**14**) with *n*-hexanal performed. Purification by column chromatography afforded 600 mg (72%) of product as yellow oil. Identity and purity of the product were confirmed by ^{1}H, ^{13}C NMR and HRMS. ^{1}H NMR (500 MHz, $CDCl_3$) δ 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, $^{2}J_{HP}$= 24 Hz), 7.35-7.73 (m, 15H) , ^{13}C NMR (125 MHz, $CDCl_3$) δ14.24, 22.80, 25.95, 31.82, 32.35, 48.86 (d, $^{1}J_{CP}$ = 110 Hz) , 60.07, 60.17 (d, J = 16.6 Hz), 126.36 (d, $^{1}J_{CP}$ = 90.6 Hz, C-1'), 129.15 (d, $^{3}J_{CP}$ = 12.3 Hz, C-3'), 132.49 (d, $^{4}J_{CP}$ = 2.8 Hz, C-4'), 133.31 (d, $^{2}J_{CP}$ = 10.2 Hz, C-2'), 188.31 (d, $^{2}J_{CP}$ = 3.5 Hz); HRMS (ESI) m/z calcd for $C_{27}H_{30}O_2P^+$ $(M+1)^+$ 417.19779, found 417.19787.

1-(3-(pent-4-yn-1-yl)oxiran-2-yl)-2-(triphenyl- λ^5-phosphanylidene)ethan-1-one (22) ($C_{27}H_{25}O_2P$)



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, $CDCl_3$) δ 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, $CDCl_3$) δ 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- λ^{5}-phosphanylidene)ethan-1-one (24) ($C_{27}H_{18}{}^{2}H_{11}O_2P$)



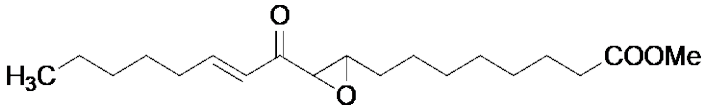
Following the general procedure for the Johnson–Corey–Chaykovsky reaction, reaction of bifunctional Sulfonium/Phosphonium ylide (**14**) with hexanal-2,2,3,3,4,4,5,5,6,6,6-$^{2}H_{11}$ performed. Purification by column chromatography afforded 599 mg (70%) of product as brown oil. Identity and purity of the product were confirmed by ^{1}H, ^{13}C NMR and HRMS. ^{1}H NMR (500 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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 $C_{27}H_{19}{}^{2}H_{11}O_2P^{+}$ $(M+1)^{+}$ 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

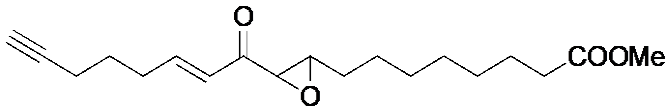
mixture was heated under reflux overnight, allowed to cool to room temperature. The reaction mixture was concentrated under reduced pressure. Purification by column chromatography (hexane: Et_2O /85:15) afforded α,β-unsaturated keto epoxide products.

Methyl (*E*)-8-(3-(oct-2-enoyl)oxiran-2-yl)octanoate (18) ($C_{19}H_{32}O_4$)



Following the general procedure for the Wittig reaction, reaction of aldehyde **17** and Methyl 8-(3-(2-(triphenyl- λ^5-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 ^{1}H, ^{13}C NMR and HMRS. ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_{19}H_{32}O_4Na^+$ $(M+Na)^+$ 347.21928, found 347.21943.

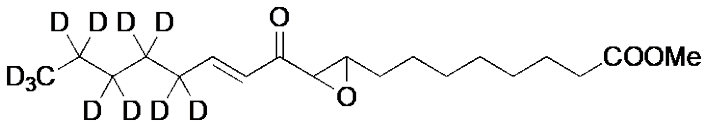
Methyl (*E*)-8-(3-(oct-2-en-7-ynoyl)oxiran-2-yl)octanoate (28) ($C_{19}H_{28}O_4$)



Following the general procedure for the Wittig reaction, reaction of aldehyde **21** and Methyl 8-(3-(2-(triphenyl- λ^5-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 ^{1}H, ^{13}C NMR and HRMS. ^{1}H NMR (500 MHz, $CDCl_3$) 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

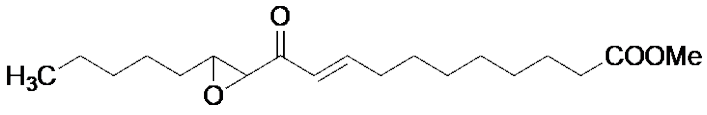
Hz), 7.06 (1H, dt, *J* = 16.0, 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.27, 25.20, 26.09, 29.30, 29.39, 29.41, 31.81, 32.12, 34.38, 51.82, 58.61, 59.42, 69.49, 83.716, 124.76, 149.27, 174.59, 195.93; HRMS (ESI) m/z calcd for $C_{19}H_{28}O_4Na^+$ $(M+Na)^+$ 343.18798, found 343.1881.

Methyl *(E)*-8-(3-(oct-2-enoyl-4,4,5,5,6,6,7,7,8,8,8-$^2H_{11}$)oxiran-2-yl)octanoate (29) ($C_{19}H_{21}{}^2H_{11}O_4$)



Following the general procedure for the Wittig reaction, reaction of aldehyde **23** and Methyl 8-(3-(2-(triphenyl- λ^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 $C_{19}H_{25}{}^2H_{11}NO_4^+$ $(M+NH_4)^+$ 353.567, found 353.3331.

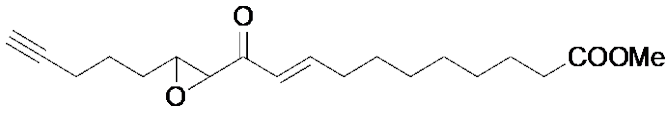
Methyl (*E*)-11-oxo-11-(3-pentyloxiran-2-yl)undec-9-enoate (20) ($C_{19}H_{32}O_4$)



Following the general procedure for the Wittig reaction, reaction of aldehyde **15** and 1-(3-pentyloxiran-2-yl)-2-(triphenyl-λ^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* =

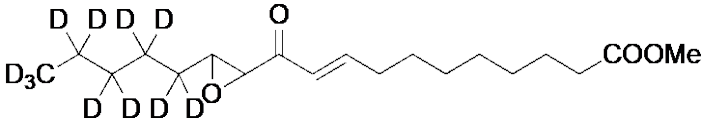
2.0 Hz), 3.67 (s, 3H), 6.23 (d, 1H, *J* = 15.5 Hz), 7.07 (1H, dt, *J* = 15.5, 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.27, 22.83, 25.19, 25.83, 28.19, 29.22, 29.31 (2C), 31.76, 32.13, 33.04, 34.37, 51.83, 58.75, 59.38, 124.32, 150.82, 174.64, 196.11; HRMS (ESI) m/z calcd for $C_{19}H_{32}O_4Na^+$ $(M+Na)^+$ 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- λ^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, $CDCl_3$) δ 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, $CDCl_3$) δ 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 $C_{19}H_{28}O_4Na^+$ $(M+Na)^+$ 343.18798, found 343.18812.

Methyl (*E*)-11-oxo-11-(3-(pentyl-$^2H_{11}$)oxiran-2-yl)undec-9-enoate (31) (C_{19} $H_{21}{}^2H_{11}O_4$)



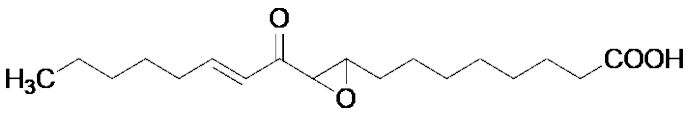
Following the general procedure for the Wittig reaction, reaction of aldehyde **15** and 1-(3-(pentyl-$^2H_{11}$)oxiran-2-yl)-2-(triphenyl-l5-phosphanylidene)ethan-1-one **(22)** afforded product **31.** Purification by column chromatography afforded 146 mg (62%) of product as yellow oil. The identity and purity of the product were confirmed by ^{1}H and ^{13}C NMR. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23-1.67 (m, 10H), 2.20 (q, 2H,

J = 7.0 Hz), 2.27 (t, 2H, *J* = 7.0 Hz), 3.01 (s, 1H), 3.31 (s, 1H), 3.64 (s, 3H), 6.21 (d, 1H, *J* = 15.5 Hz), 7.05 (dt, 1H, *J* = 15.5, 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 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 $C_{19}H_{25}{}^2H_{11}NO_4{}^+$ $(M+NH_4)^+$ 353.567, found 353.3330.

General procedure; Porcine Pancreas Lipase (PPL) hydrolysis

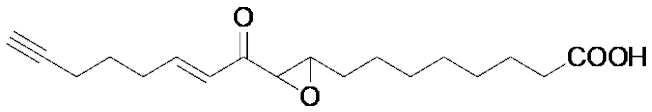
An oven-dried 25-mL round-bottomed flask, equipped with a magnetic stirring bar, was charged with 0.1 mmol of the desired methyl ester EKODE-(*E*) and PPL (20 mg) (lipase from porcine pancreas, Type II from Sigma) in acetone (1 mL) and phosphate buffer (pH 7, 5 mL, 0.2 M). The mixture was stirred vigorously 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) ($C_{18}H_{30}O_4$)



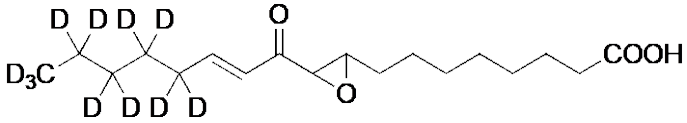
Following the general procedure for PPL hydrolysis of methyl (*E*)-8-(3-(oct-2-enoyl)oxiran-2-yl)octanoate **18** afforded 146 mg (94%) of product as yellow oil. Identity and purity of the product were confirmed by ^{1}H, ^{13}C NMR and HRMS. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, 3H, *J* = 7.0 Hz), 1.21-1.74 (m, 18H), 2.17-2.24 (m, 2H), 2.34 (t, 2H, *J* = 7.0 Hz), 3.04 (ddd, 1H, *J* = 6.0, 5.0, 2.0 Hz), 3.33 (d, 1H, *J* = 2.0 Hz), 6.23 (dt, 1H, *J* = 15.5, 1.5 Hz), 7.07 (1H, dt, *J* = 15.5, 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 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.

(*E*)-8-(3-(oct-2-en-7-ynoyl)oxiran-2-yl)octanoic acid (hydrolyzed 28) ($C_{18}H_{26}O_4$)



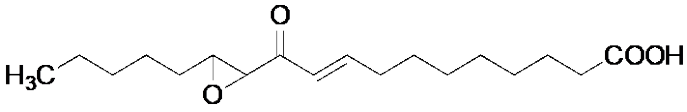
Following the general procedure for PPL hydrolysis of methyl (*E*)-8-(3-(oct-2-en-7-ynoyl)oxiran-2-yl)octanoate **28** afforded 139 mg (91%) of product as yellow oil. Identity and purity of the product were confirmed by ^{1}H, ^{13}C NMR and HRMS. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22-1.88 (m, 12H), 1.70 (quintet, 2H, J = 7.0 Hz), 1.98 (t, 1H, J = 2.5 Hz), 2.17-2.29 (m, 4H,), 2.30-240 (m, 2H), 3.05 (t, 1H, J = 5.0 Hz), 3.33 (bs, 1H), 6.27 (d, 1H, J = 15.5 Hz), 7.06 (1H, dt, J = 15.5, 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_{18}H_{25}O_4^-$ $(M-H)^-$ 305.395, found 305.1758.

Methyl (*E*)-8-(3-(oct-2-enoyl-4,4,5,5,6,6,7,7,8,8,8-$^2H_{11}$)oxiran-2-yl)octanoate (hydrolyzed 29) ($C_{18}H_{19}{}^2H_{11}O_4$)



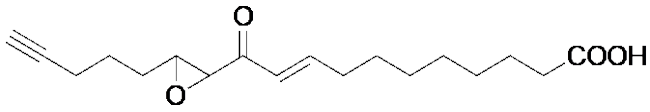
Following the general procedure for PPL hydrolysis of methyl *(E)*-8-(3-(oct-2-enoyl- 4,4,5,5,6,6,7,7,8,8,8-$^2H_{11}$)oxiran-2-yl)octanoate **23** afforded 150 mg (93%) of product as yellow oil. Identity and purity of the product were confirmed by ^{1}H, ^{13}C NMR and HRMS. ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C 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 $C_{18}H_{18}{}^2H_{11}O_4^-$ $(M-H)^-$ 320.493, found 320.2762.

(*E*)-11-oxo-11-(3-pentyloxiran-2-yl)undec-9-enoic acid(*trans*-EKODE-(*E*)-IIb) (2) ($C_{18}H_{30}O_4$)



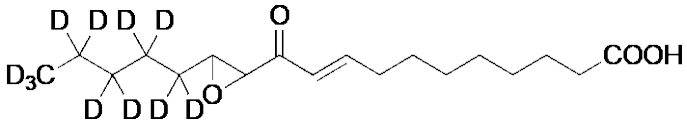
Following the general procedure for PPL hydrolysis of methyl (*E*)-11-oxo-11-(3-pentyloxiran-2-yl)undec-9-enoate **20** afforded 143mg (92%) of product as yellow oil. Identity and purity of the product were confirmed by ^{1}H, ^{13}C NMR and HRMS. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 3H, J = 7.2 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, $CDCl_3$) δ 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 $C_{18}H_{29}O_4^-$ $(M-H)^-$ 309.427, found 309.2072.

(*E*)-11-oxo-11-(3-(pent-4-yn-1-yl)oxiran-2-yl)undec-9-enoic acid (hydrolyzed 30) ($C_{18}H_{26}O_4$)



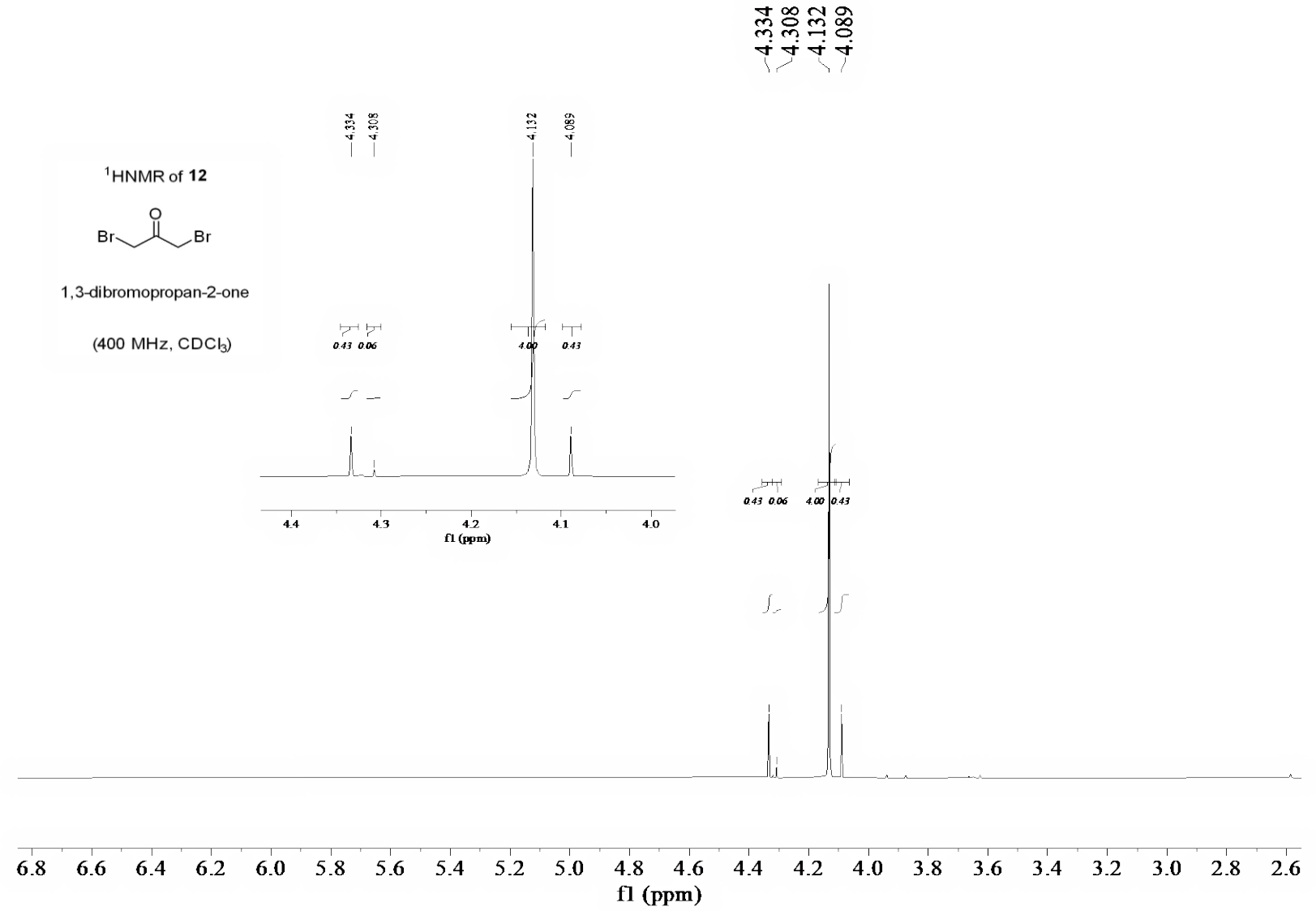
Following the general procedure for PPL hydrolysis of methyl (*E*)-11-oxo-11-(3-(pent-4- yn-1-yl)oxiran-2-yl)undec-9-enoate **30** afforded 144mg (94%) of product as yellow oil. Identity and purity of the product were confirmed by ^{1}H, ^{13}C NMR and HRMS. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22-1.88 (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, $CDCl_3$) δ 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 $C_{18}H_{25}O_4^-$ $(M-H)^-$ 305.395, found 305.1758.

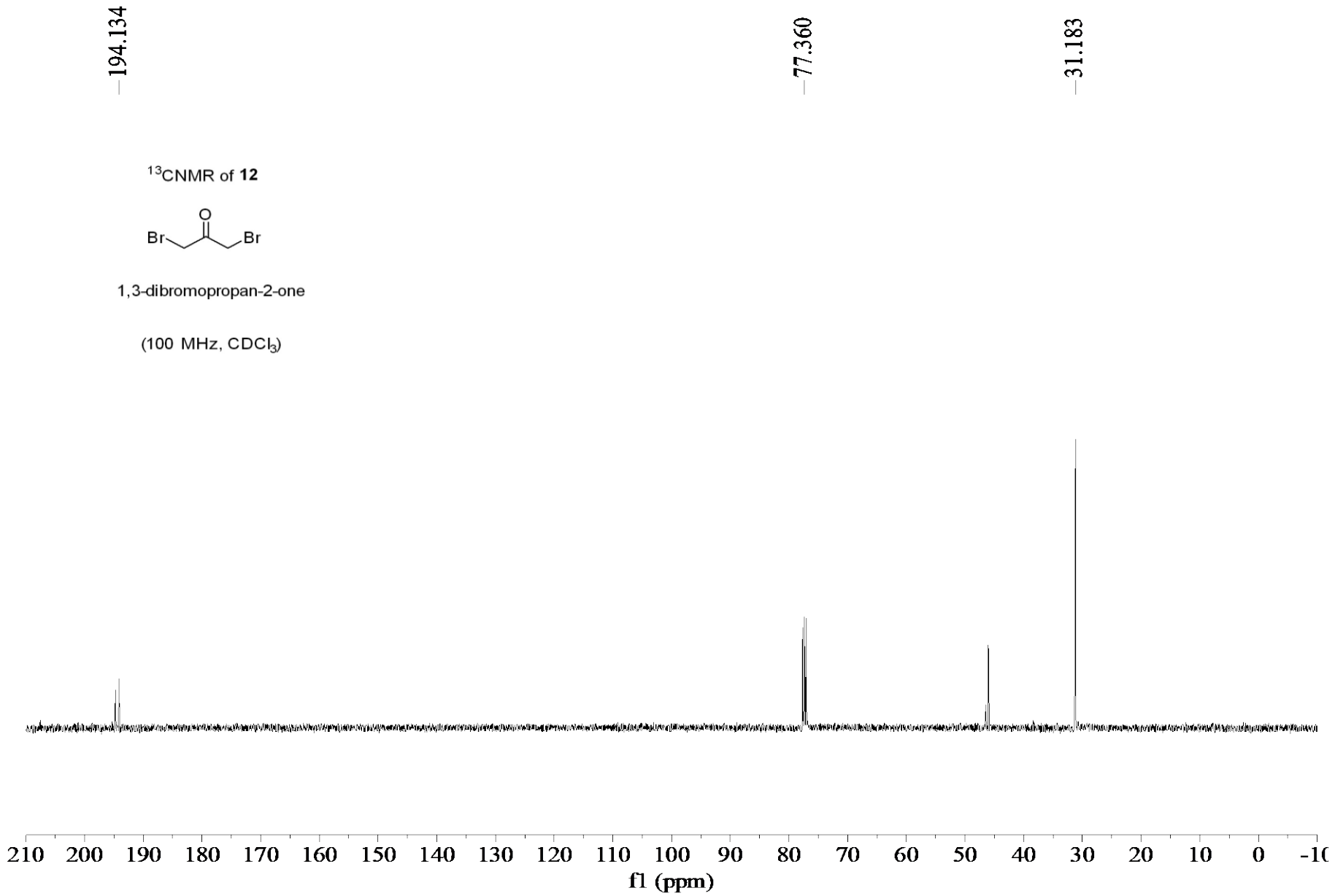
(*E*)-11-oxo-11-(3-(pentyl-$^{2}H_{11}$)oxiran-2-yl)undec-9-enoic acid (hydrolyzed 31) ($C_{18}H_{19}{}^{2}H_{11}O_4$)

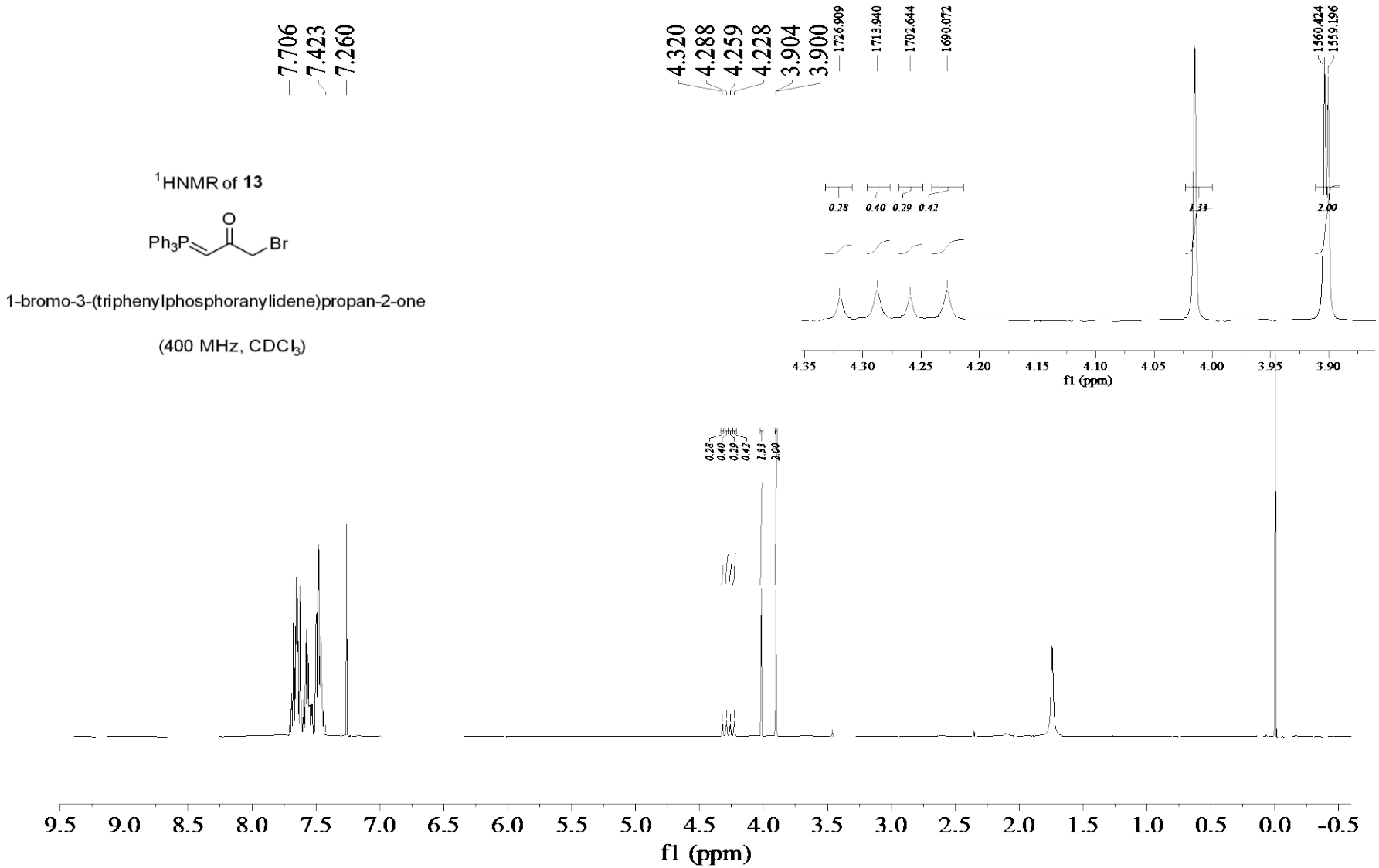


Following the general procedure for PPL hydrolysis of methyl (*E*)-11-oxo-11-(3-(pentyl-$^{2}H_{11}$)oxiran-2-yl)undec-9-enoate **31** afforded 144 mg (94%) of product as yellow oil. Identity and purity of the product were confirmed by ^{1}H, ^{13}C NMR and HRMS. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20-1.71 (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, $CDCl_3$) δ 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 $C_{18}H_{18}{}^{2}H_{11}O_4^-$ $(M-H)^-$ 320.493, found 320.2762

^{1}H and ^{13}C NMR Spectra



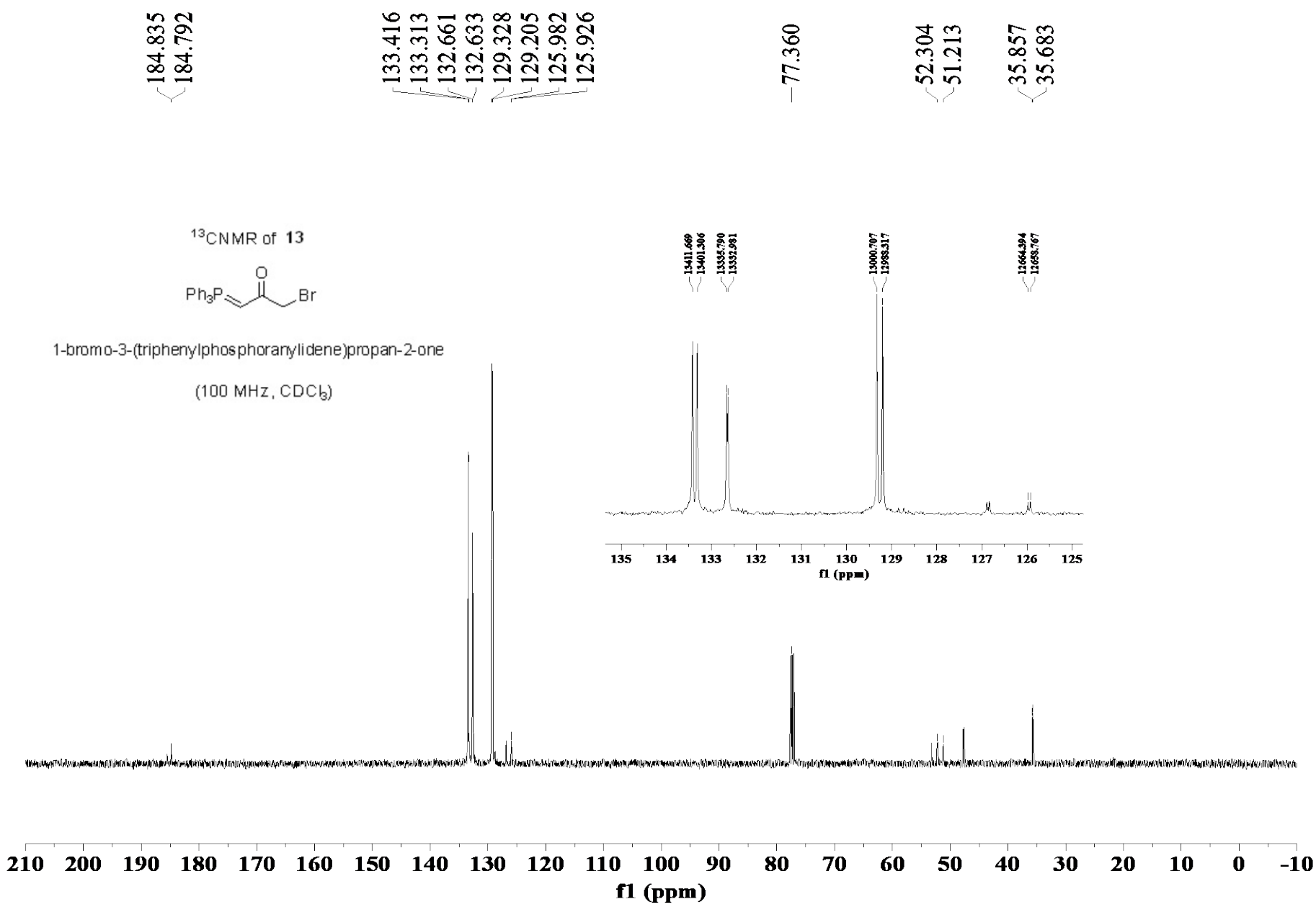

194.134
77.360
31.183
13CNMR of 12
Br
O
Br
1,3-dibromopropan-2-one
(100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



^{1}HNMR of **13**

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

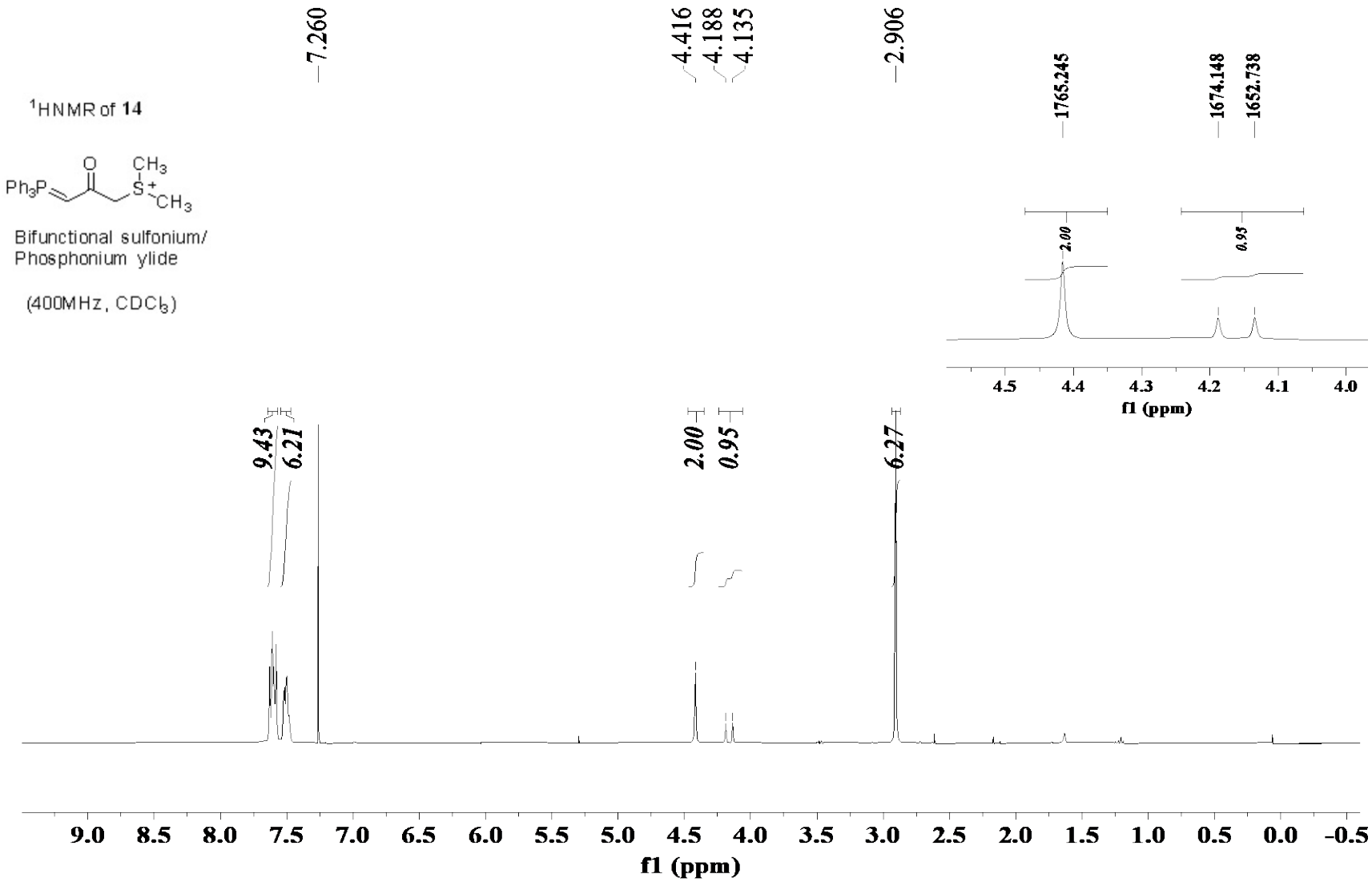
(400 MHz, $CDCl_3$)

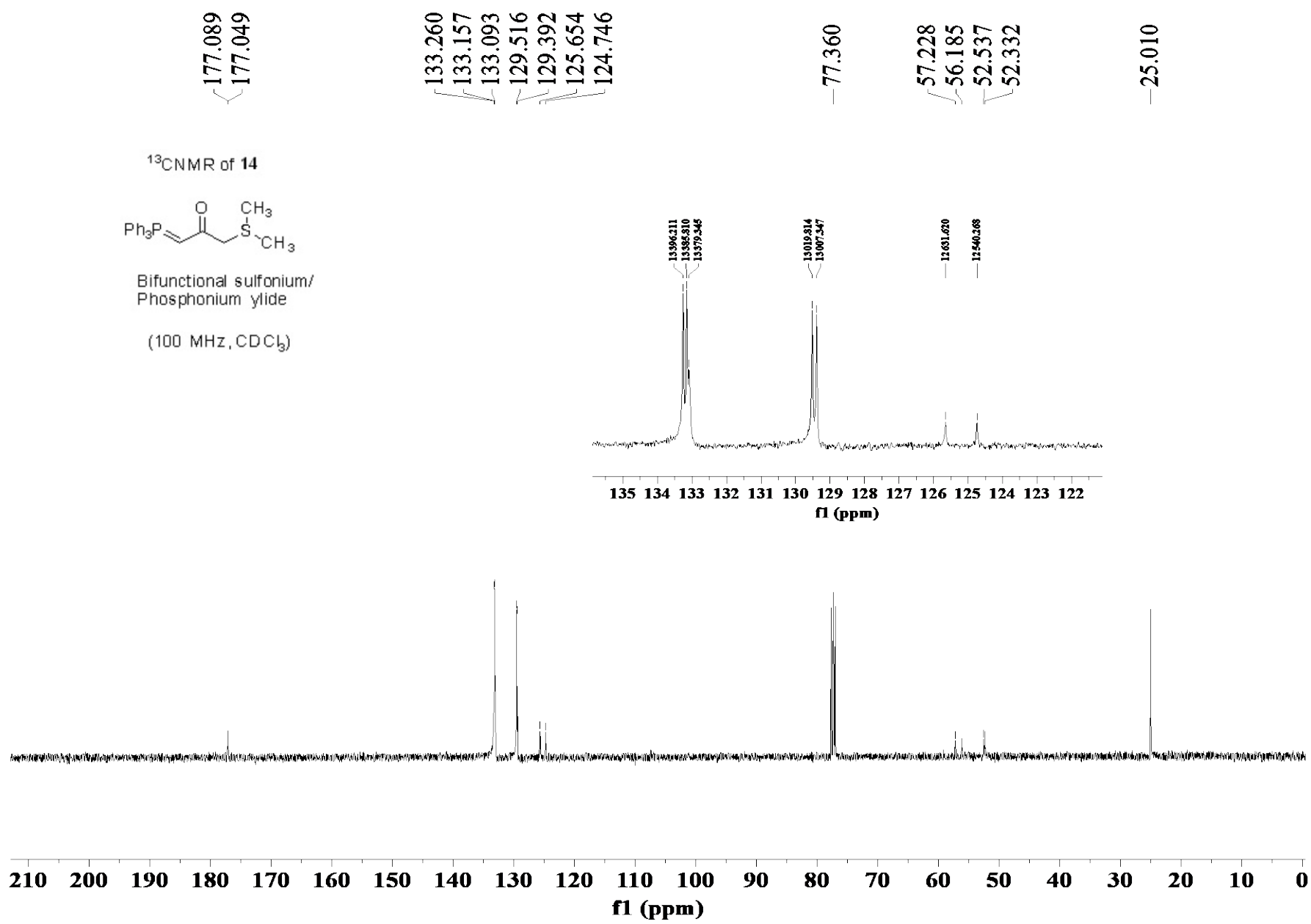


^{13}CNMR of **13**

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

(100 MHz, $CDCl_3$)

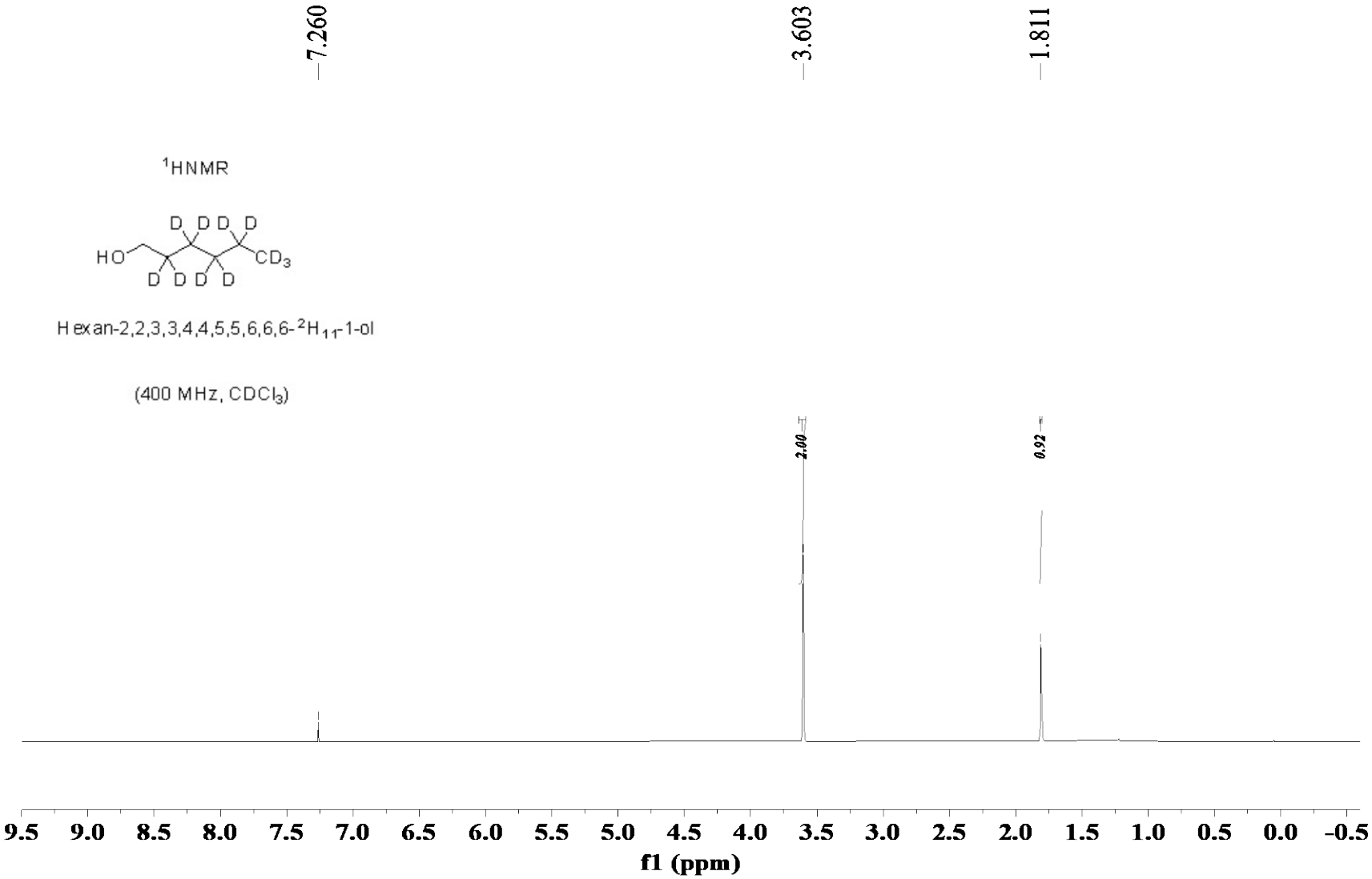

1HNMR of 14
Bifunctional sulfonium/
Phosphonium ylide
(400MHz, CDCl3)
7.260
4.416
4.188
4.135
2.906
1765.245
1674.148
1652.738
9.43
6.21
2.00
0.95
6.27
f1 (ppm)

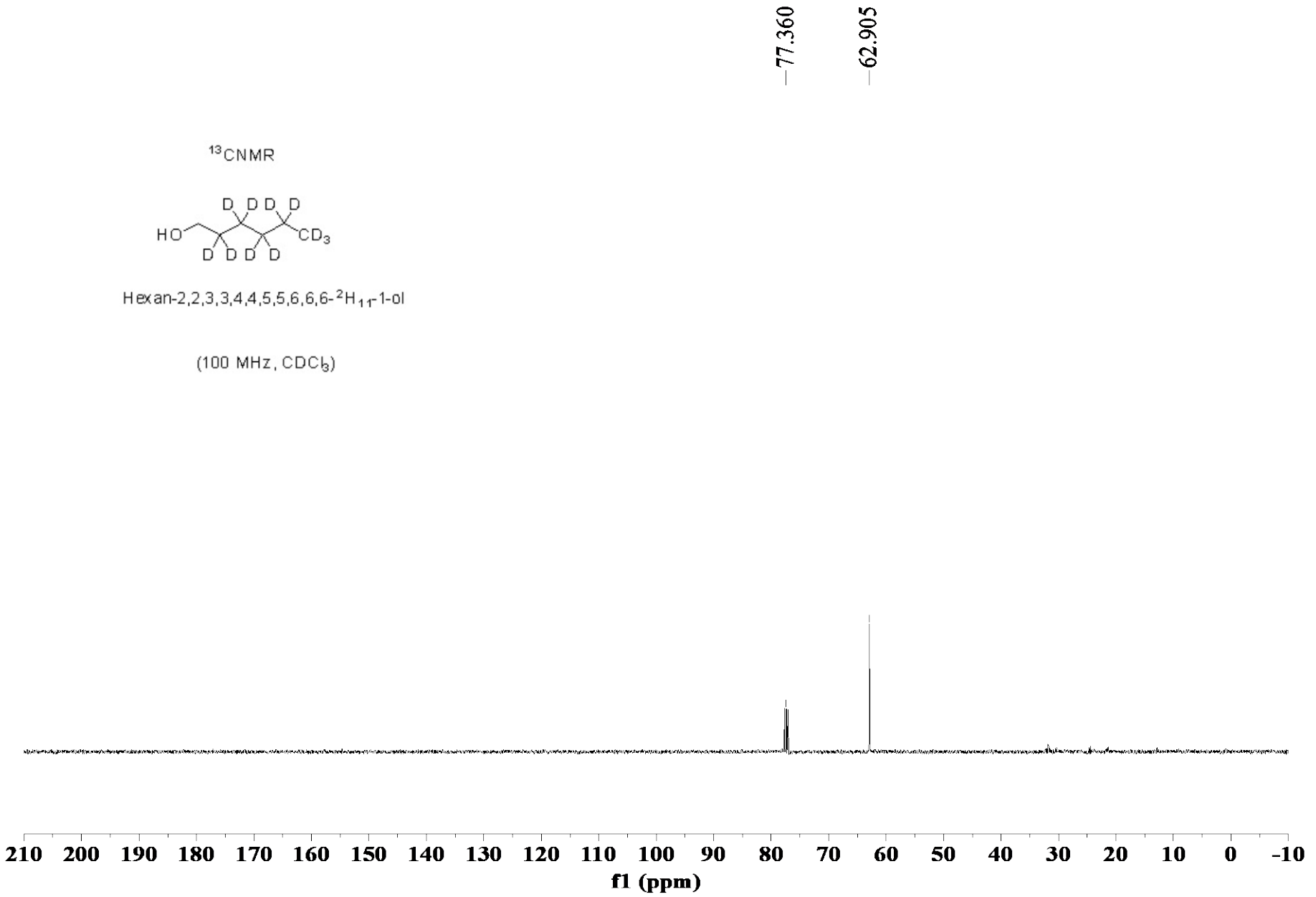


^{13}CNMR of **14**

Bifunctional sulfonium/
Phosphonium ylide

(100 MHz, $CDCl_3$)

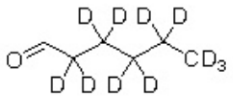

7.260
3.603
1.811
^{1}HNMR
HO
D D D D
D D D D
CD_3
Hexan-2,2,3,3,4,4,5,5,6,6,6-$^2H_{11}$-1-ol
(400 MHz, $CDCl_3$)
2.00
0.92
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


77.360
62.905
13CNMR
HO
D D D D
D D D D
CD3
Hexan-2,2,3,3,4,4,5,5,6,6,6-2H11-1-ol
(100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

9.739

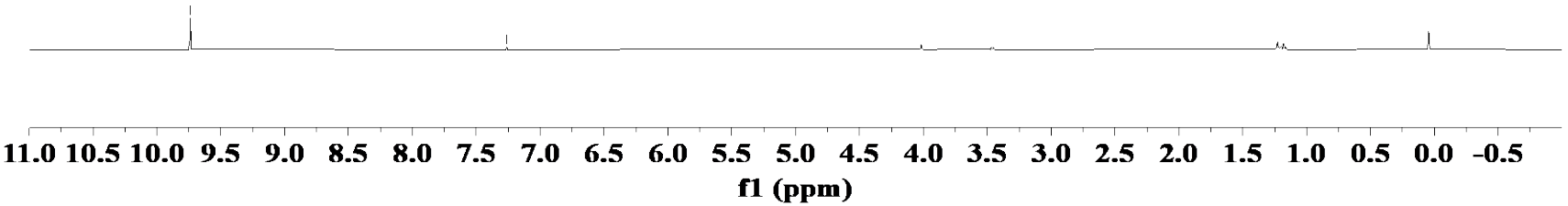
7.260

^{1}HNMR of **23**



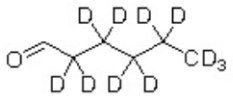
Hexanal-2,2,3,3,4,4,5,5,6,6,6- $^{2}H_{11}$

(400 MHz, $CDCl_3$)



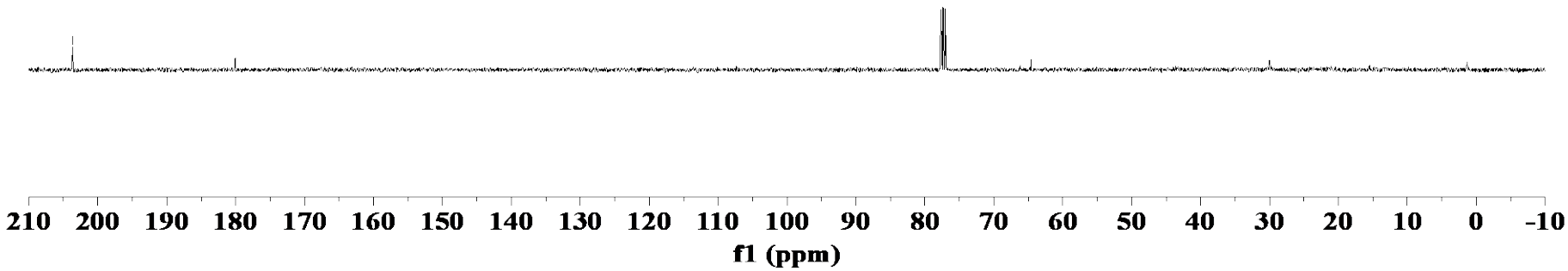
203.659

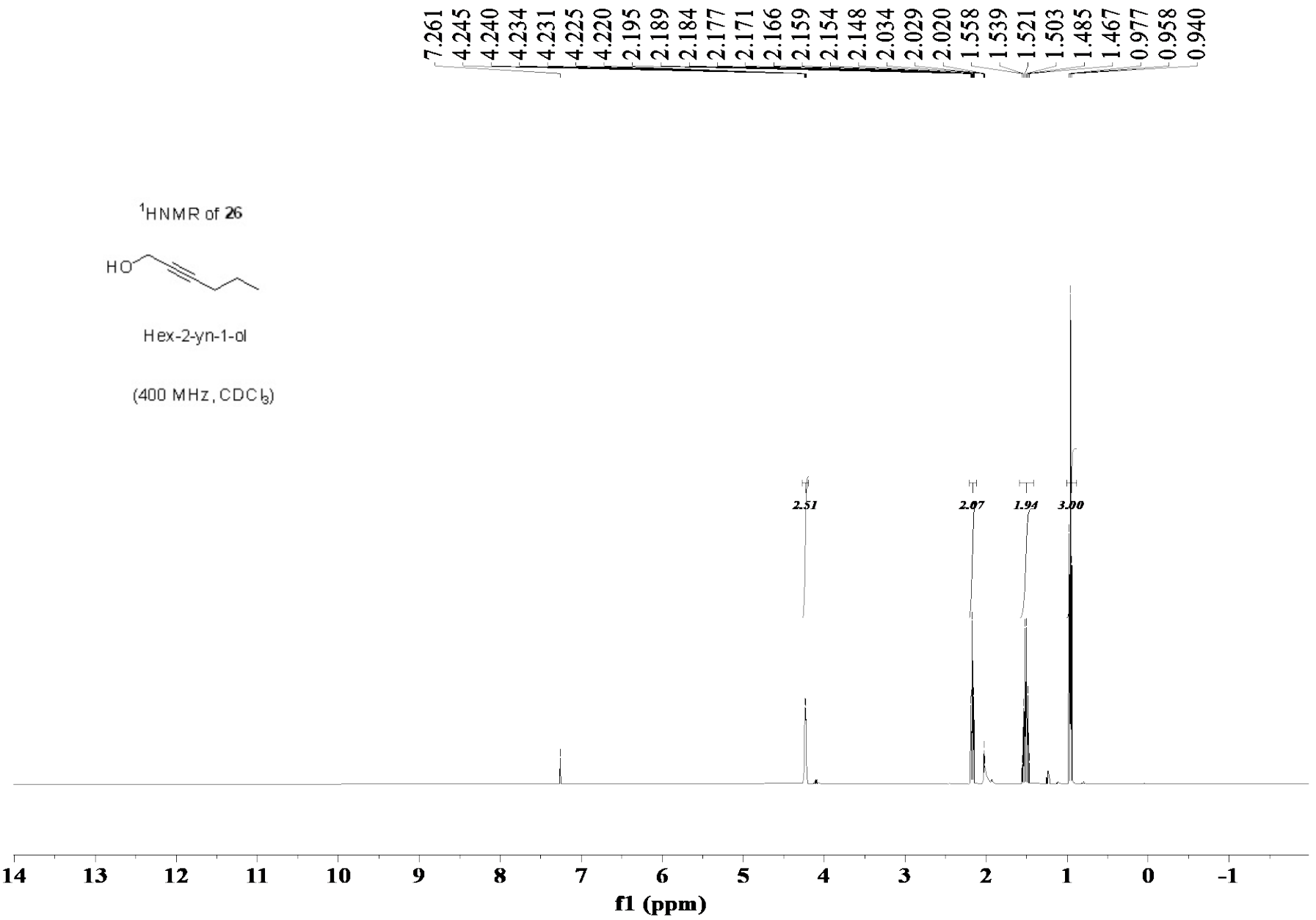
^{13}CNMR of **23**

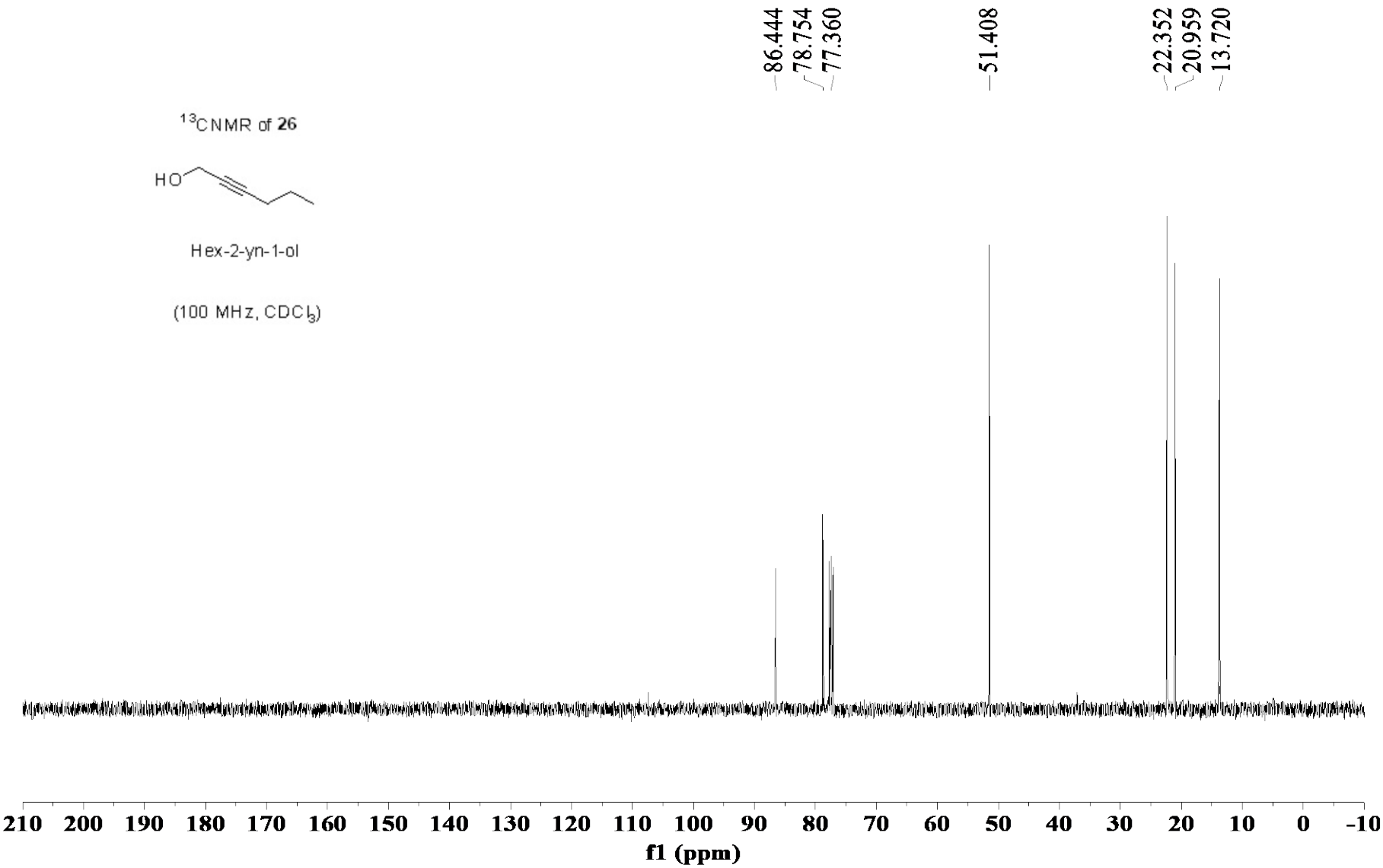


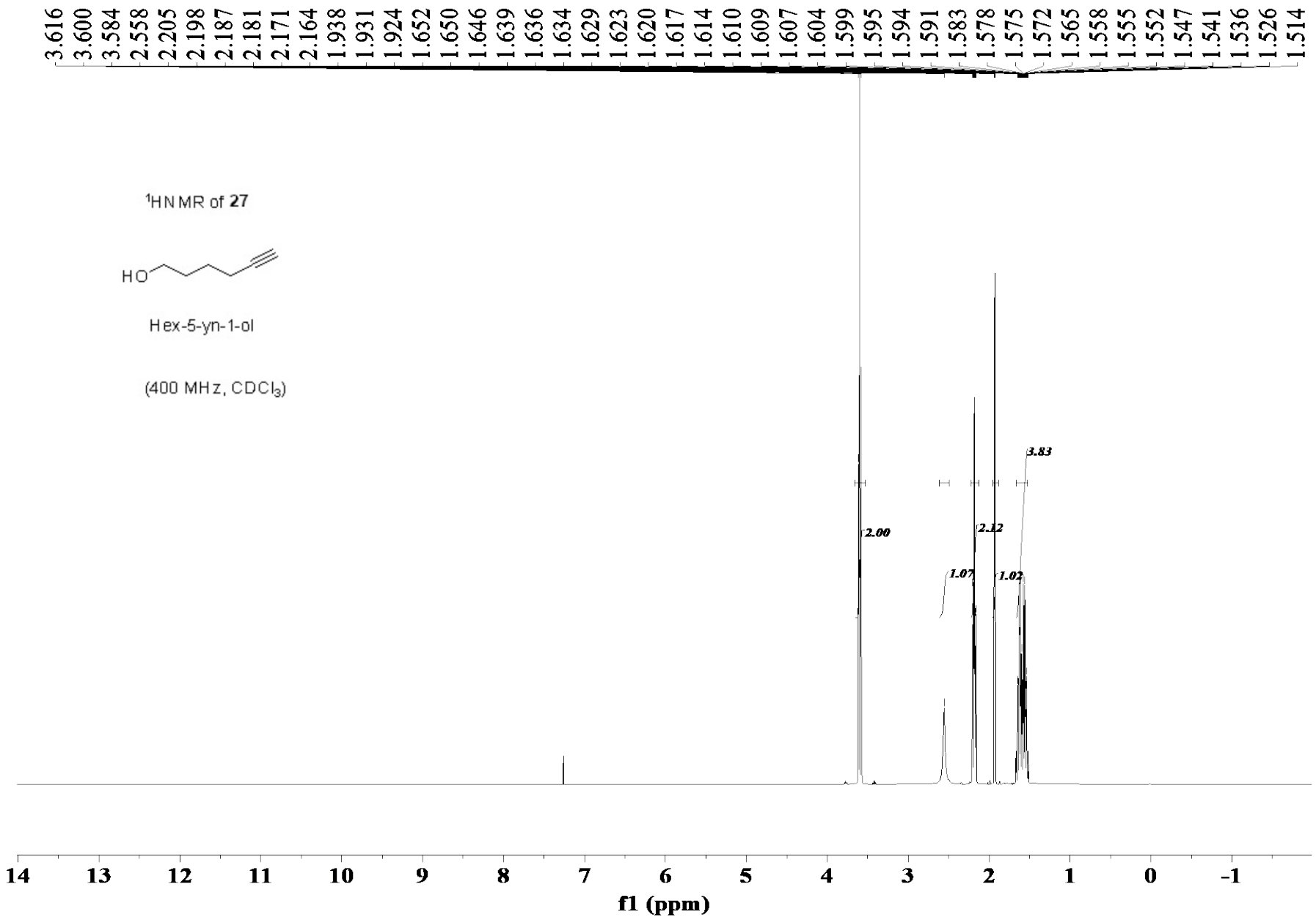
Hexanal-2,2,3,3,4,4,5,5,6,6,6-$^{2}H_{11}$

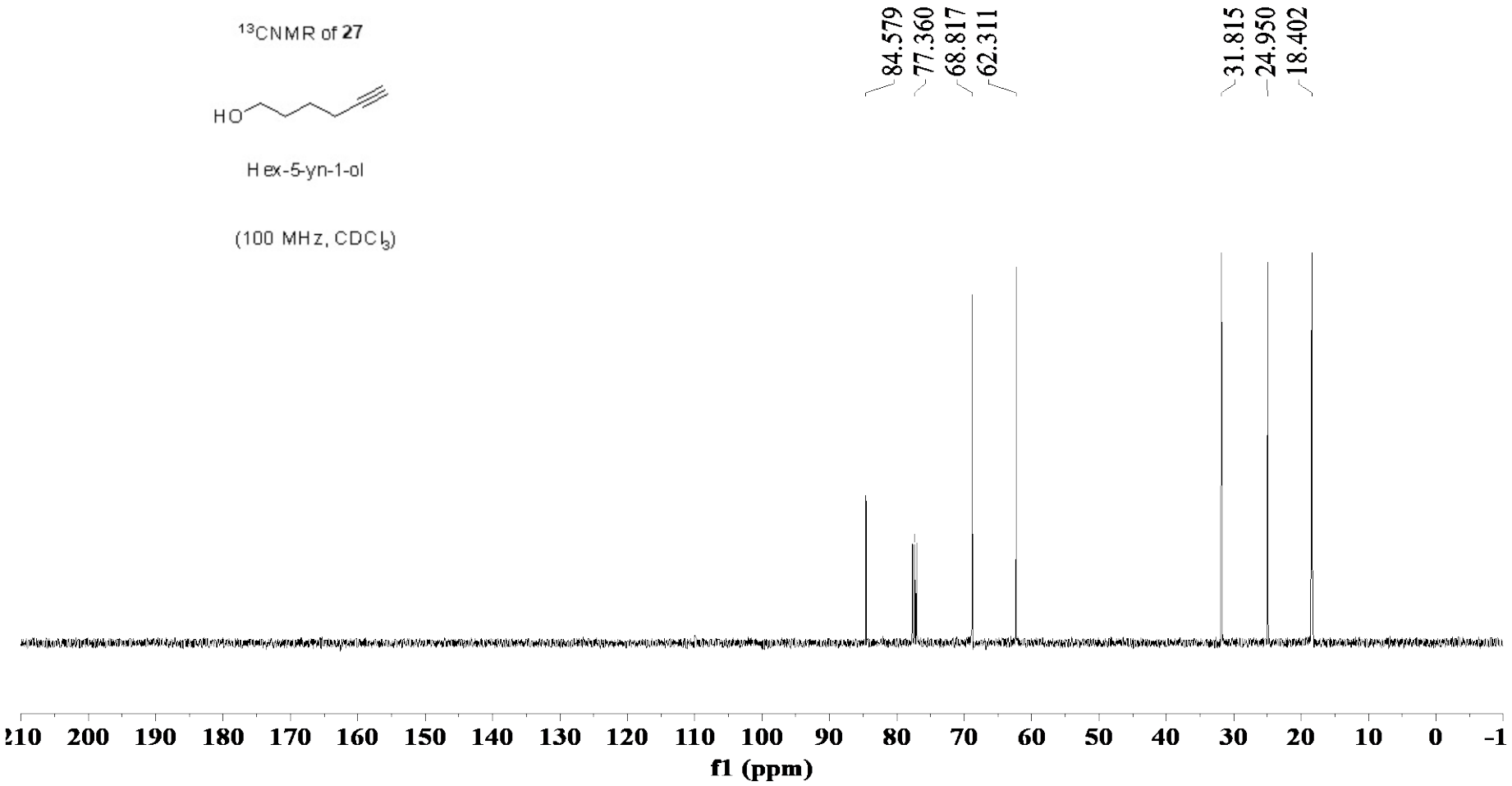
(100 MHz, $CDCl_3$)

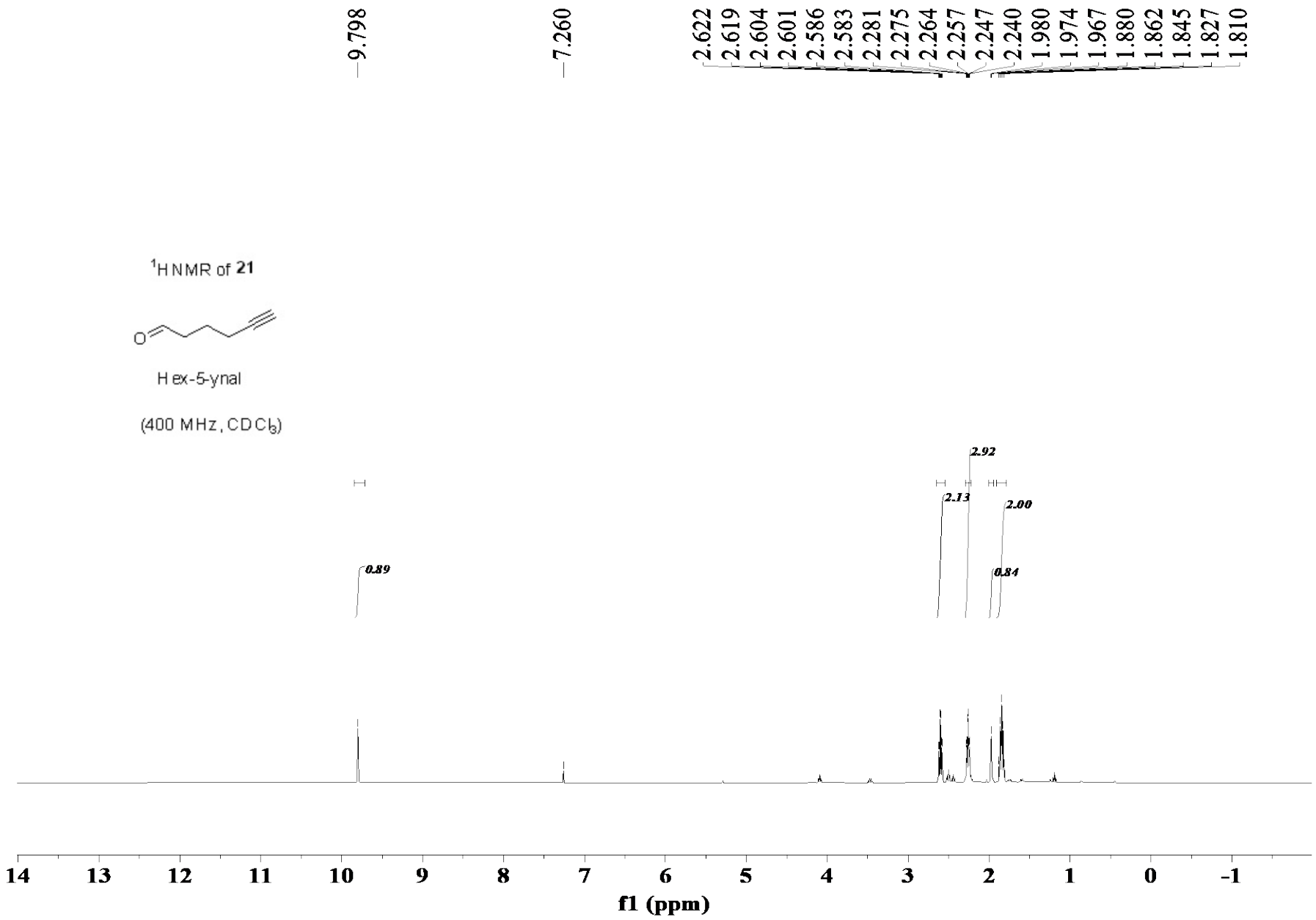


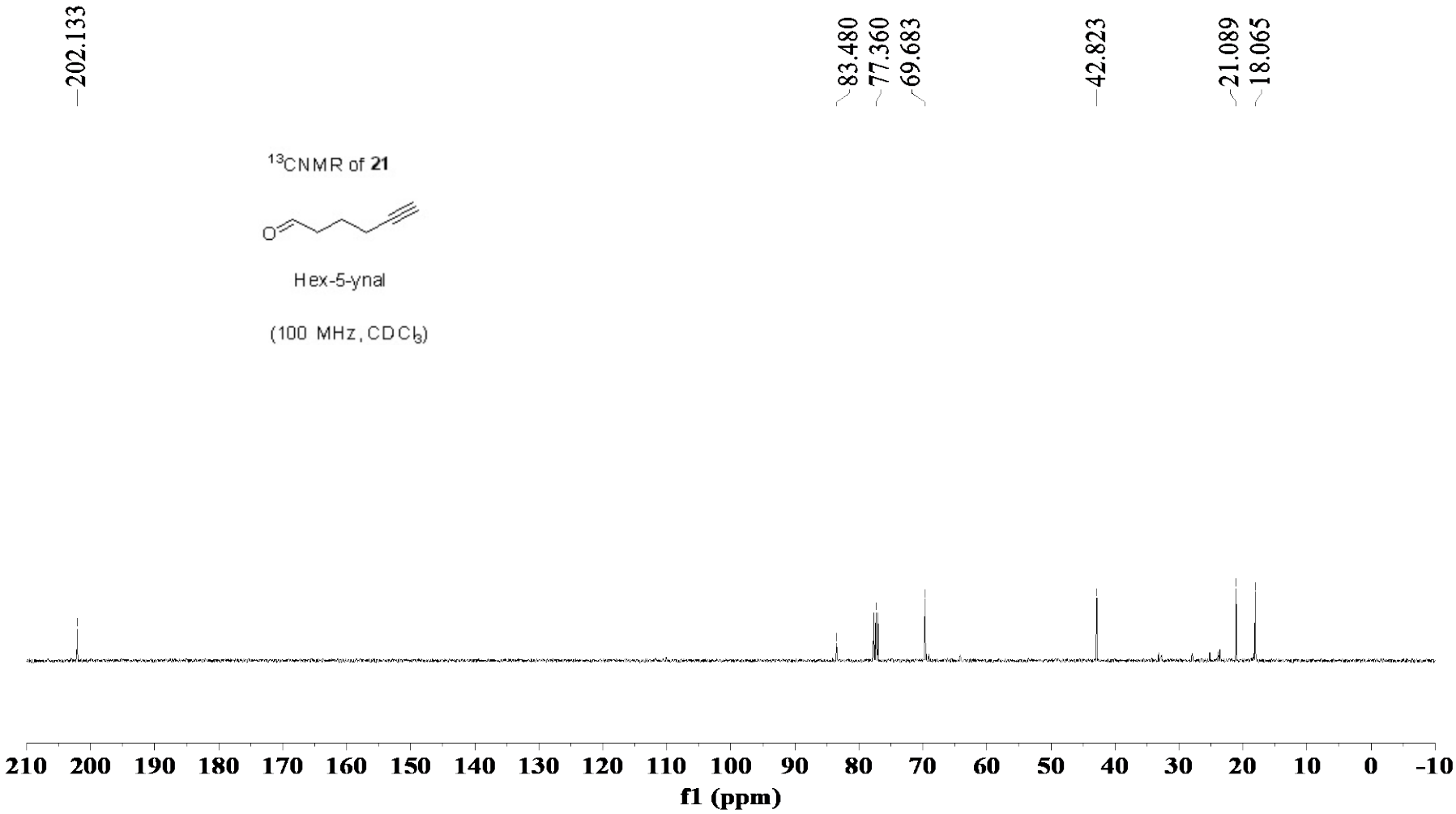

7.261
4.245
4.240
4.234
4.231
4.225
4.220
2.195
2.189
2.184
2.177
2.171
2.166
2.159
2.154
2.148
2.034
2.029
2.020
1.558
1.539
1.521
1.503
1.485
1.467
0.977
0.958
0.940
1HNMR of 26
HO
Hex-2-yn-1-ol
(400 MHz, CDCl3)
2.51
2.07
1.94
3.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


86.444
78.754
77.360
51.408
22.352
20.959
13.720
^{13}CNMR of **26**
HO
Hex-2-yn-1-ol
(100 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

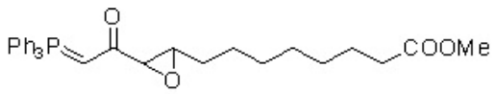

3.616
3.600
3.584
2.558
2.205
2.198
2.187
2.181
2.171
2.164
1.938
1.931
1.924
1.652
1.650
1.646
1.639
1.636
1.634
1.629
1.623
1.620
1.617
1.614
1.610
1.609
1.607
1.604
1.599
1.595
1.594
1.591
1.583
1.578
1.575
1.572
1.565
1.558
1.555
1.552
1.547
1.541
1.536
1.526
1.514
1HNMR of 27
HO
Hex-5-yn-1-ol
(400 MHz, CDCl3)
3.83
2.00
2.12
1.07
1.02
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


13CNMR of 27
HO
Hex-5-yn-1-ol
(100 MHz, CDCl3)
84.579
77.360
68.817
62.311
31.815
24.950
18.402
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


9.798
7.260
2.622
2.619
2.604
2.601
2.586
2.583
2.281
2.275
2.264
2.257
2.247
2.240
1.980
1.974
1.967
1.880
1.862
1.845
1.827
1.810
1HNMR of 21
O
Hex-5-ynal
(400 MHz, CDCl3)
2.92
2.13
2.00
0.89
0.84
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

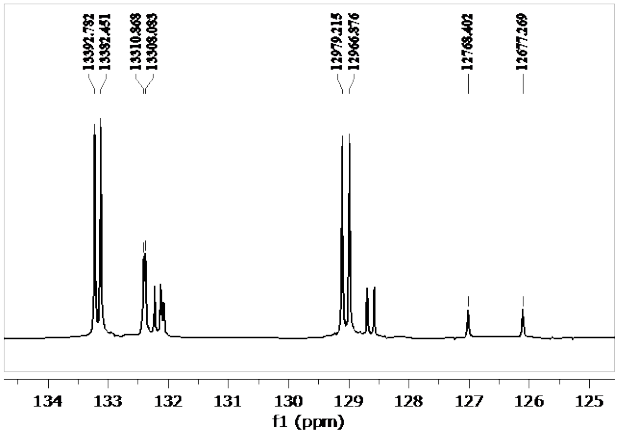

202.133
83.480
77.360
69.683
42.823
21.089
18.065
13CNMR of 21
O
Hex-5-ynal
(100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

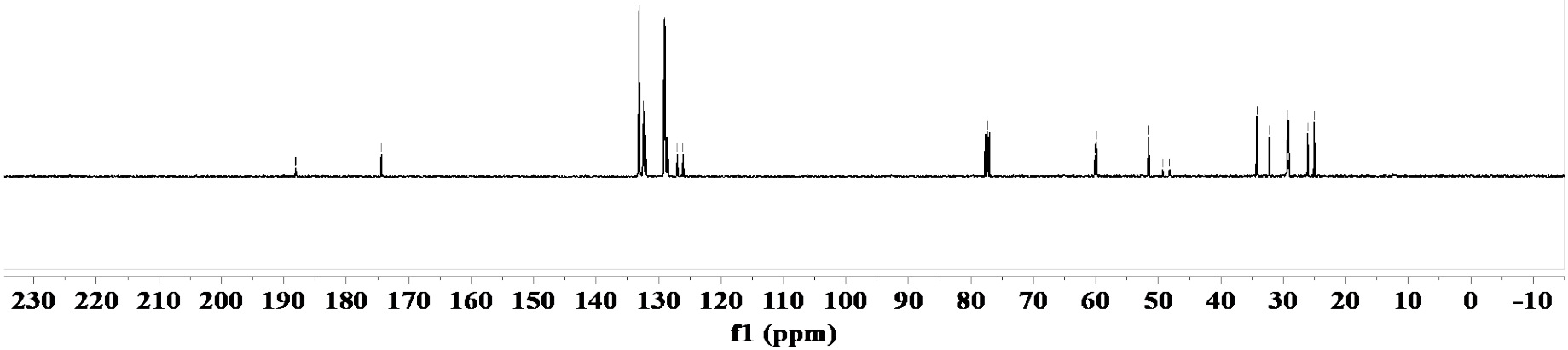
^{13}CNMR of **16**

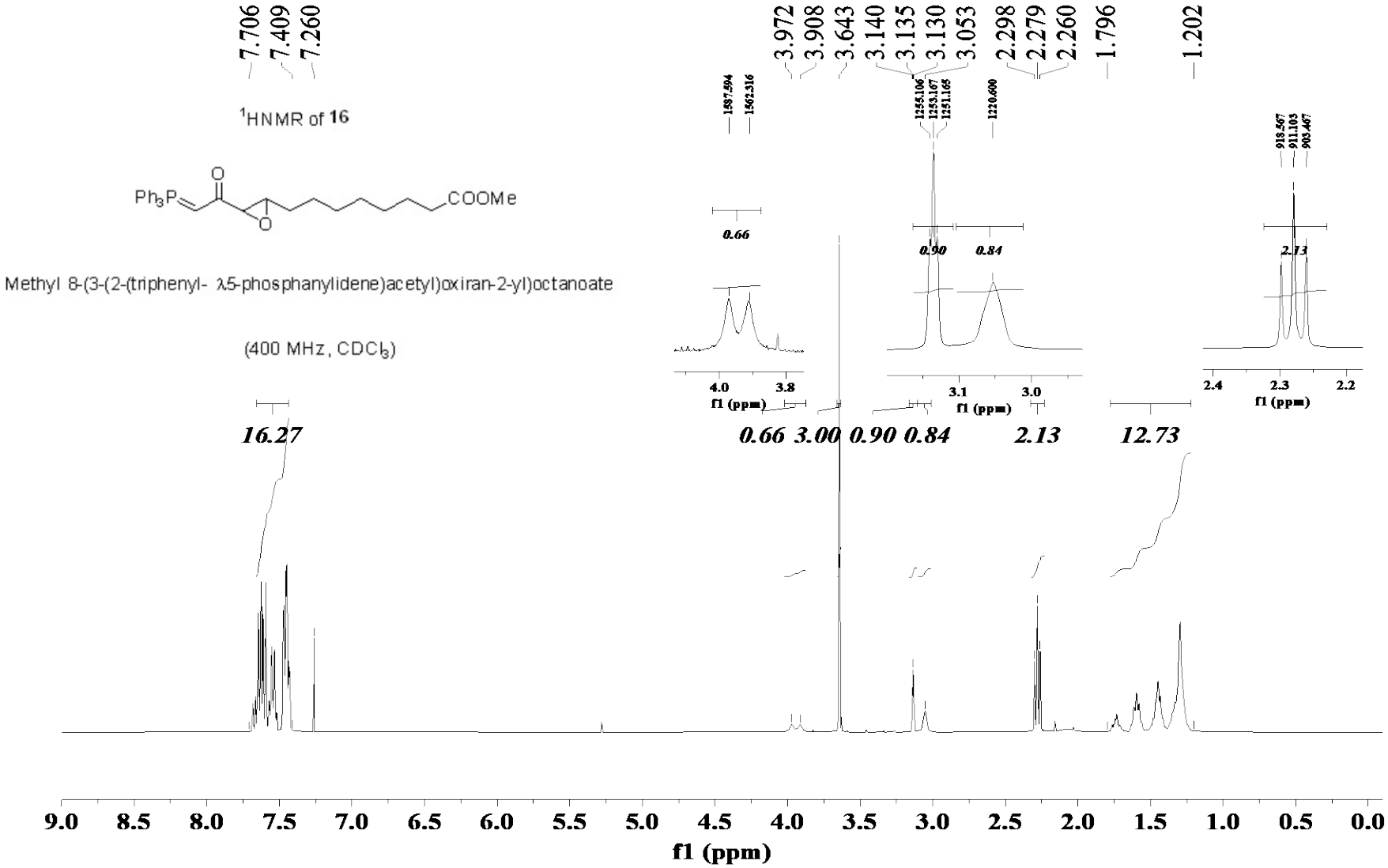


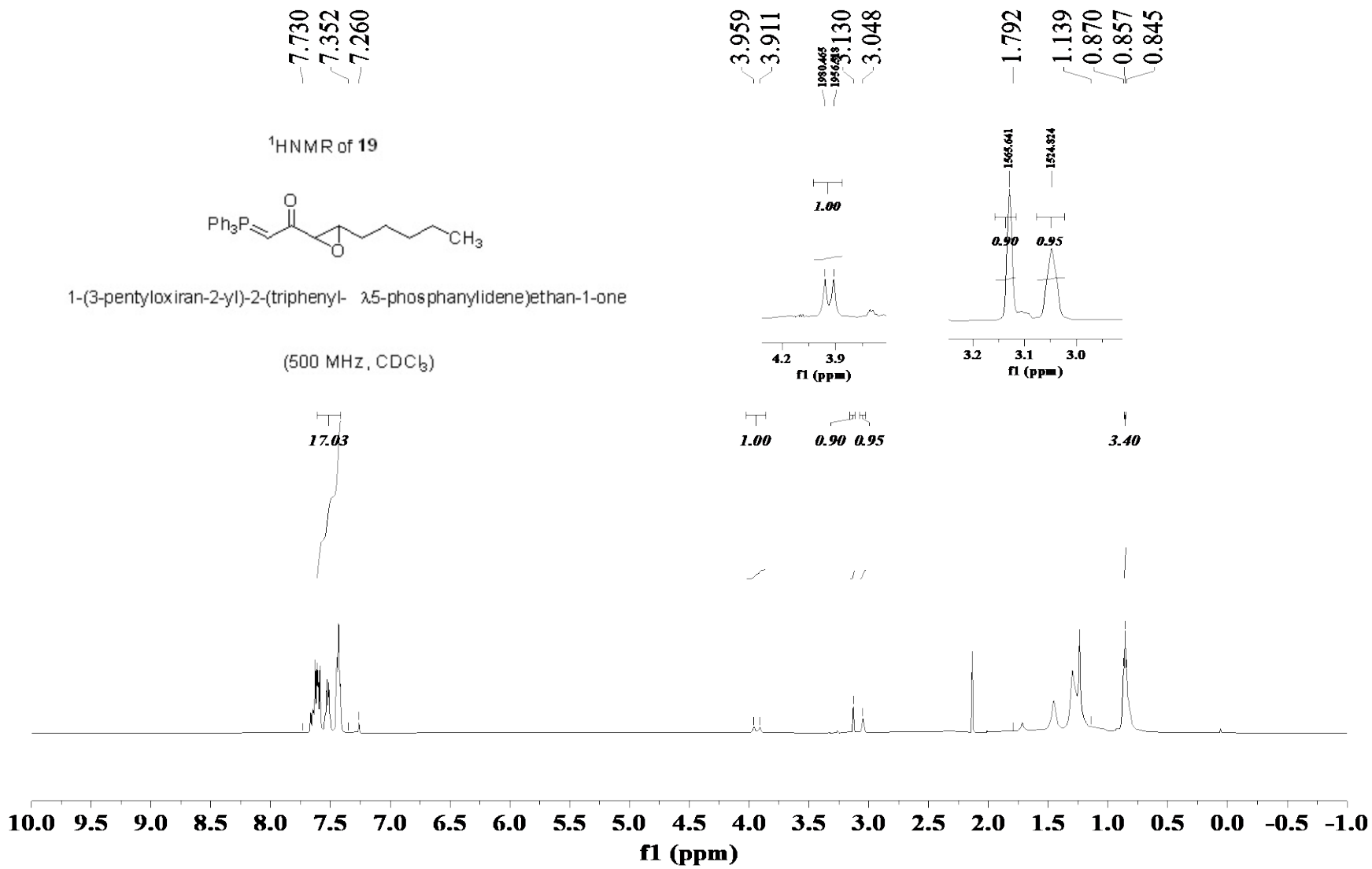
Methyl 8-(3-(2-(triphenyl- λ 5-phosphanylidene)acetyl)oxiran-2-yl)octanoate

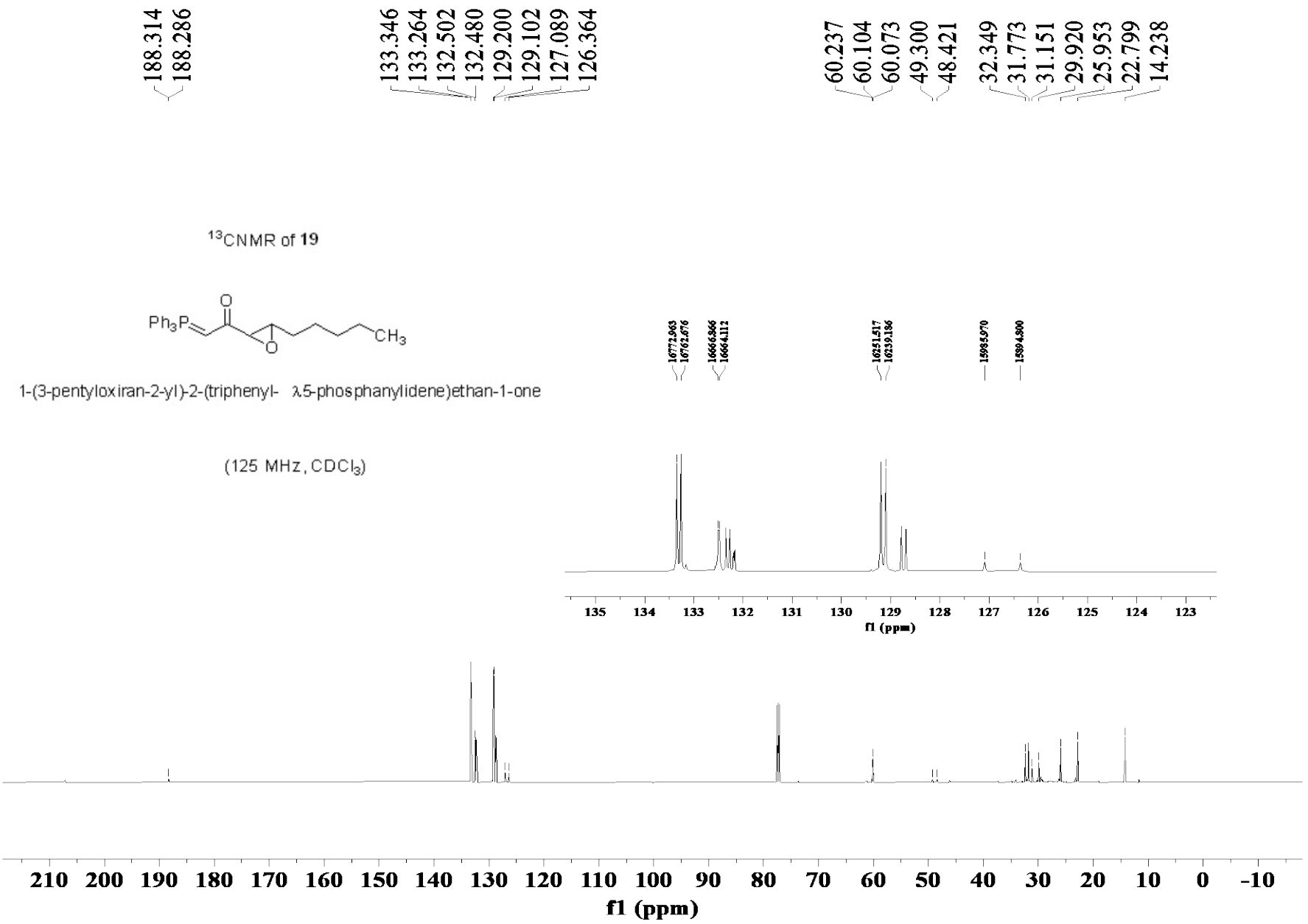
(100 MHz, $CDCl_3$)



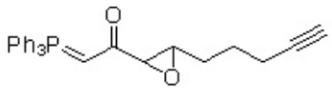



7.706
7.409
7.260
3.972
3.908
3.643
3.140
3.135
3.130
3.053
2.298
2.279
2.260
1.796
1.202
1HNMR of 16
Ph3P
O
O
COOMe
Methyl 8-(3-(2-(triphenyl- λ5-phosphanylidene)acetyl)oxiran-2-yl)octanoate
(400 MHz, CDCl3)
16.27
0.66
3.00
0.90
0.84
2.13
12.73
f1 (ppm)


7.730
7.352
7.260
3.959
3.911
3.130
3.048
1.792
1.139
0.870
0.857
0.845
1H NMR of 19
Ph3P
O
O
CH3
1-(3-pentyloxiran-2-yl)-2-(triphenyl- λ5-phosphanylidene)ethan-1-one
(500 MHz, CDCl3)
1.00
0.90
0.95
17.03
1.00
0.90
0.95
3.40
f1 (ppm)

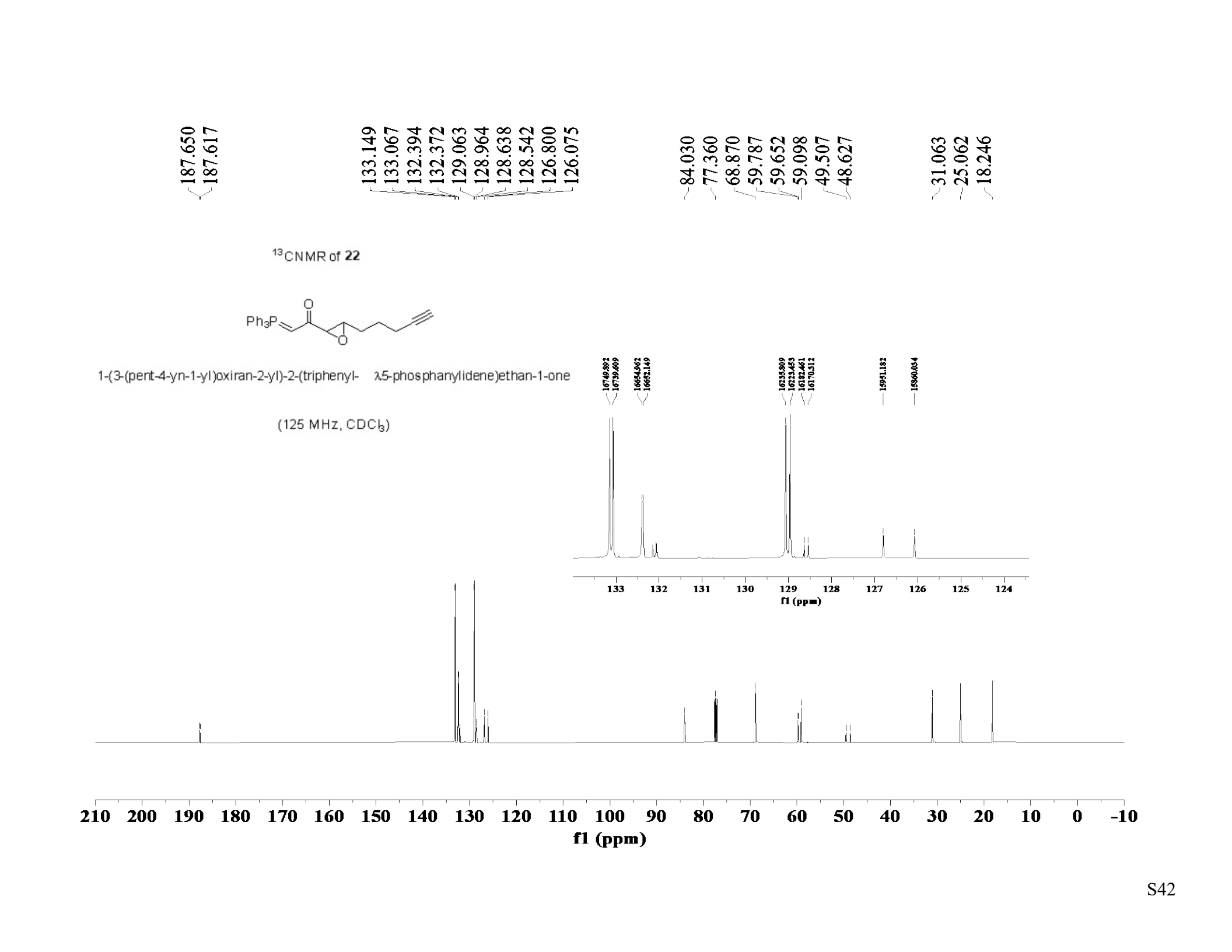

188.314
188.286
133.346
133.264
132.502
132.480
129.200
129.102
127.089
126.364
60.237
60.104
60.073
49.300
48.421
32.349
31.773
31.151
29.920
25.953
22.799
14.238
13CNMR of 19
Ph3P
O
O
CH3
1-(3-pentyloxiran-2-yl)-2-(triphenyl- λ5-phosphanylidene)ethan-1-one
(125 MHz, CDCl3)
16772.963
16762.676
16666.866
16664.112
16251.517
16239.186
15985.970
15894.800
135 134 133 132 131 130 129 128 127 126 125 124 123
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

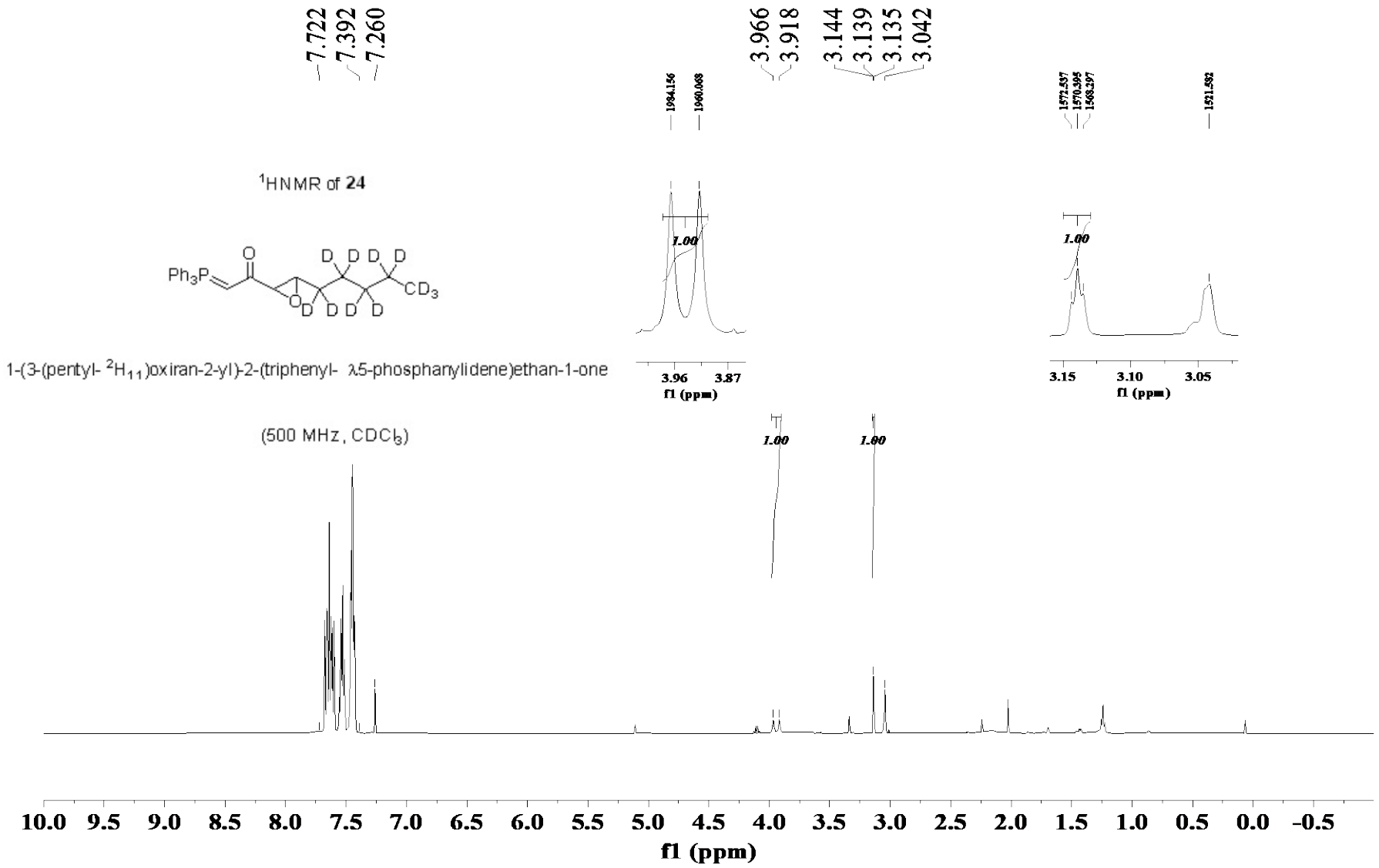
^{1}HNMR of **22**

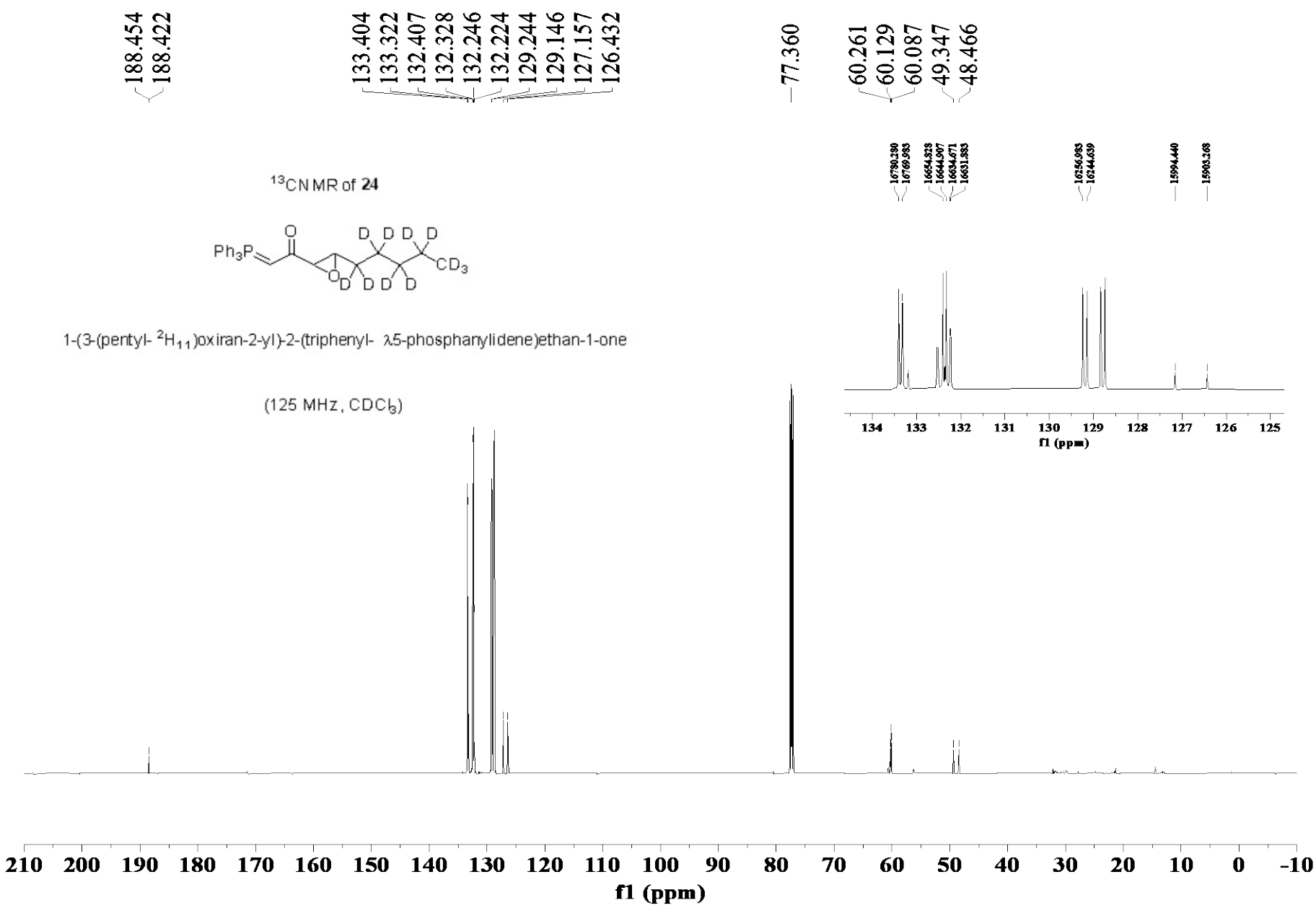


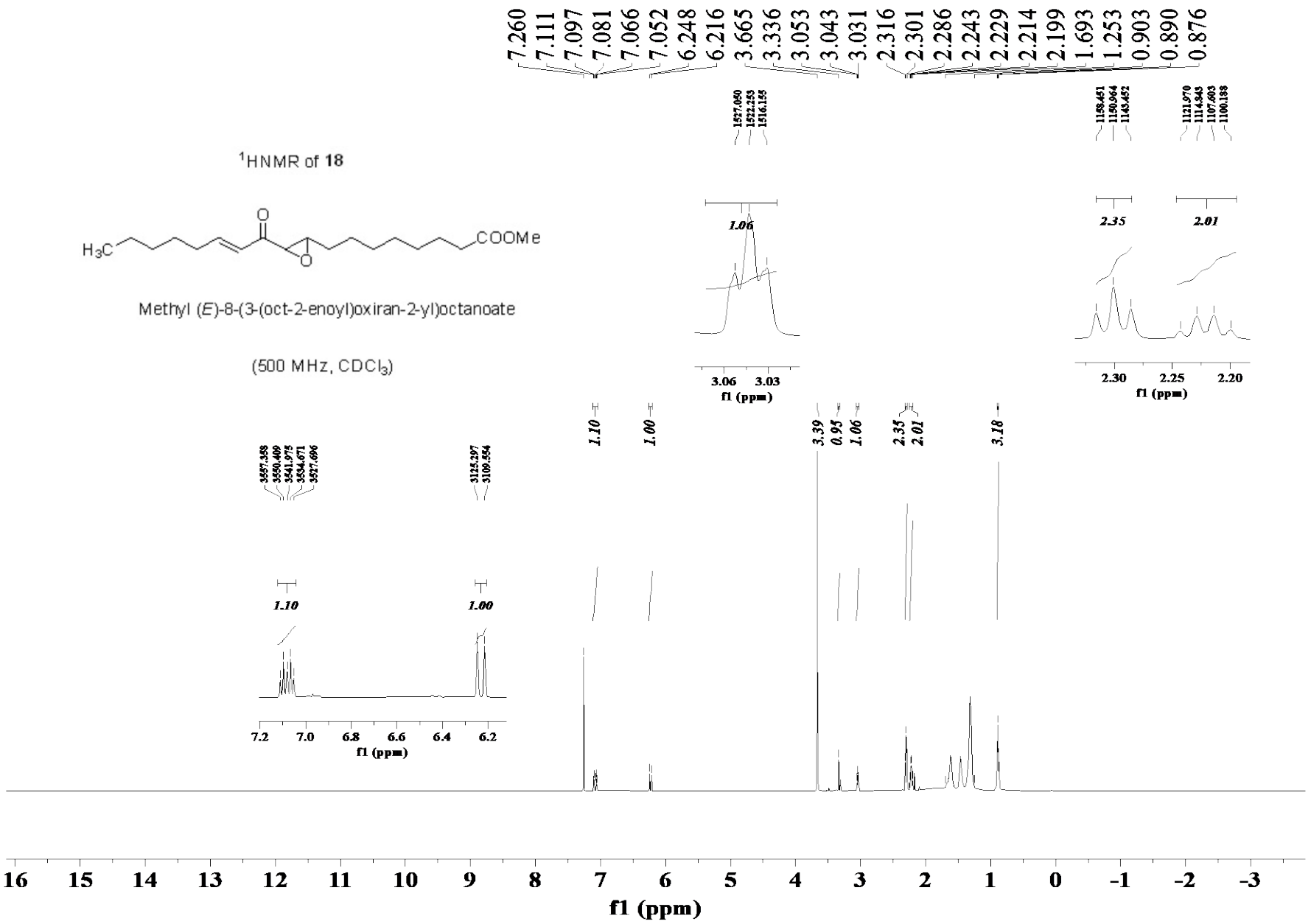
1-(3-(pent-4-yn-1-yl)oxiran-2-yl)-2-(triphenyl- λ5-phosphanylidene)ethan-1-one

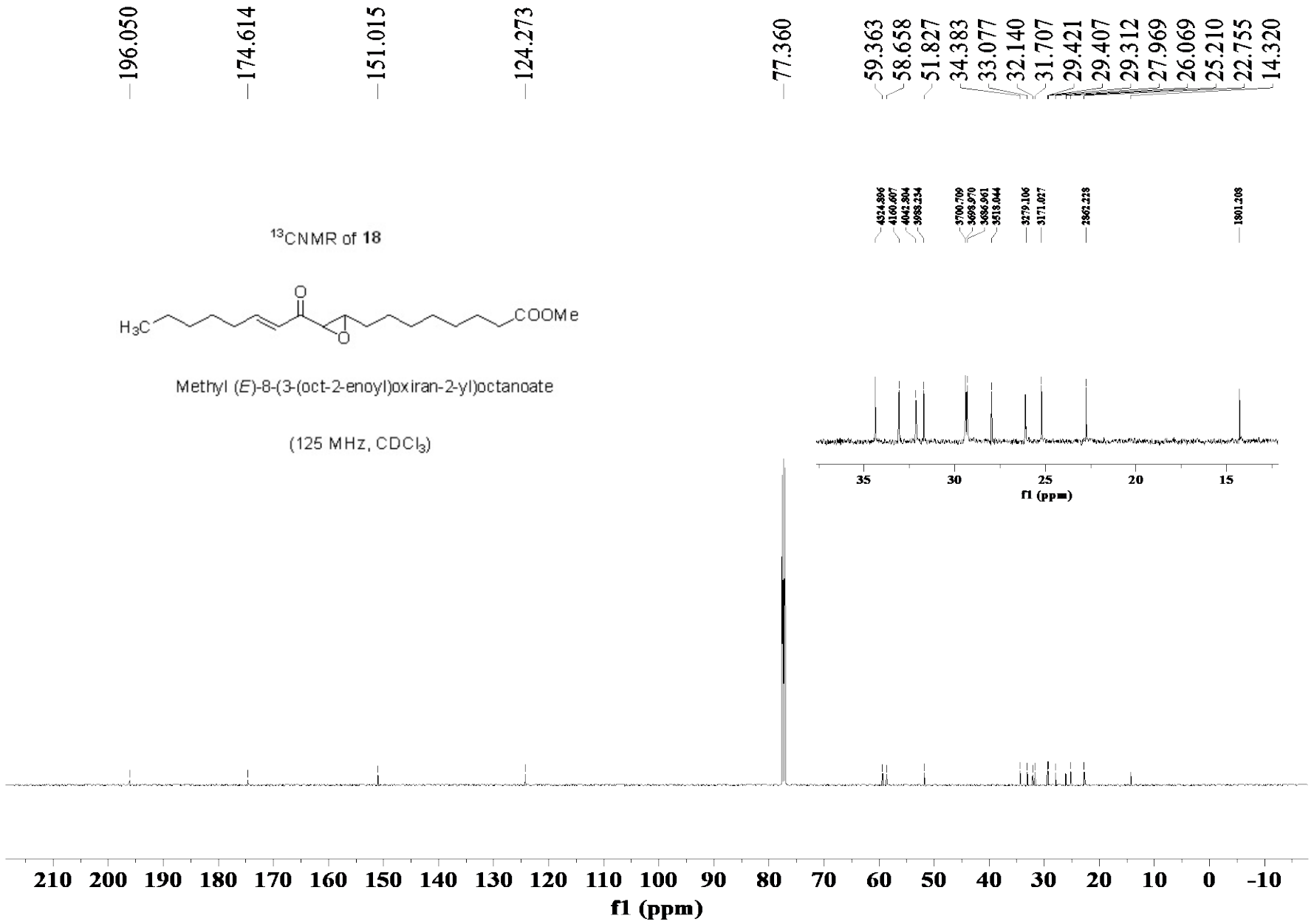
(500 MHz, $CDCl_3$)

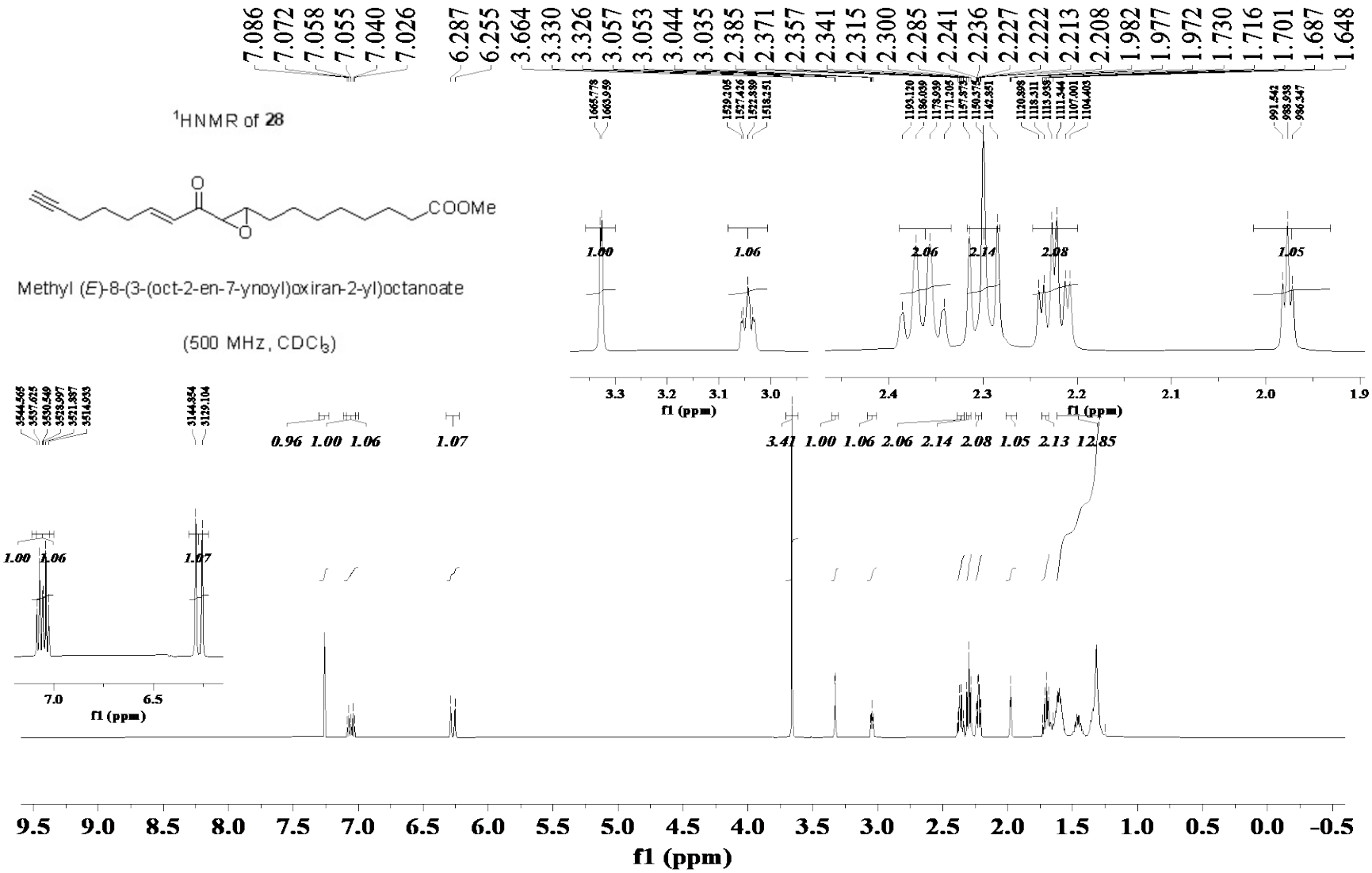

187.650
187.617
133.149
133.067
132.394
132.372
129.063
128.964
128.638
128.542
126.800
126.075
84.030
77.360
68.870
59.787
59.652
59.098
49.507
48.627
31.063
25.062
18.246
13CNMR of 22
Ph3P
O
O
1-(3-(pent-4-yn-1-yl)oxiran-2-yl)-2-(triphenyl- λ5-phosphanylidene)ethan-1-one
(125 MHz, CDCl3)
f1 (ppm)

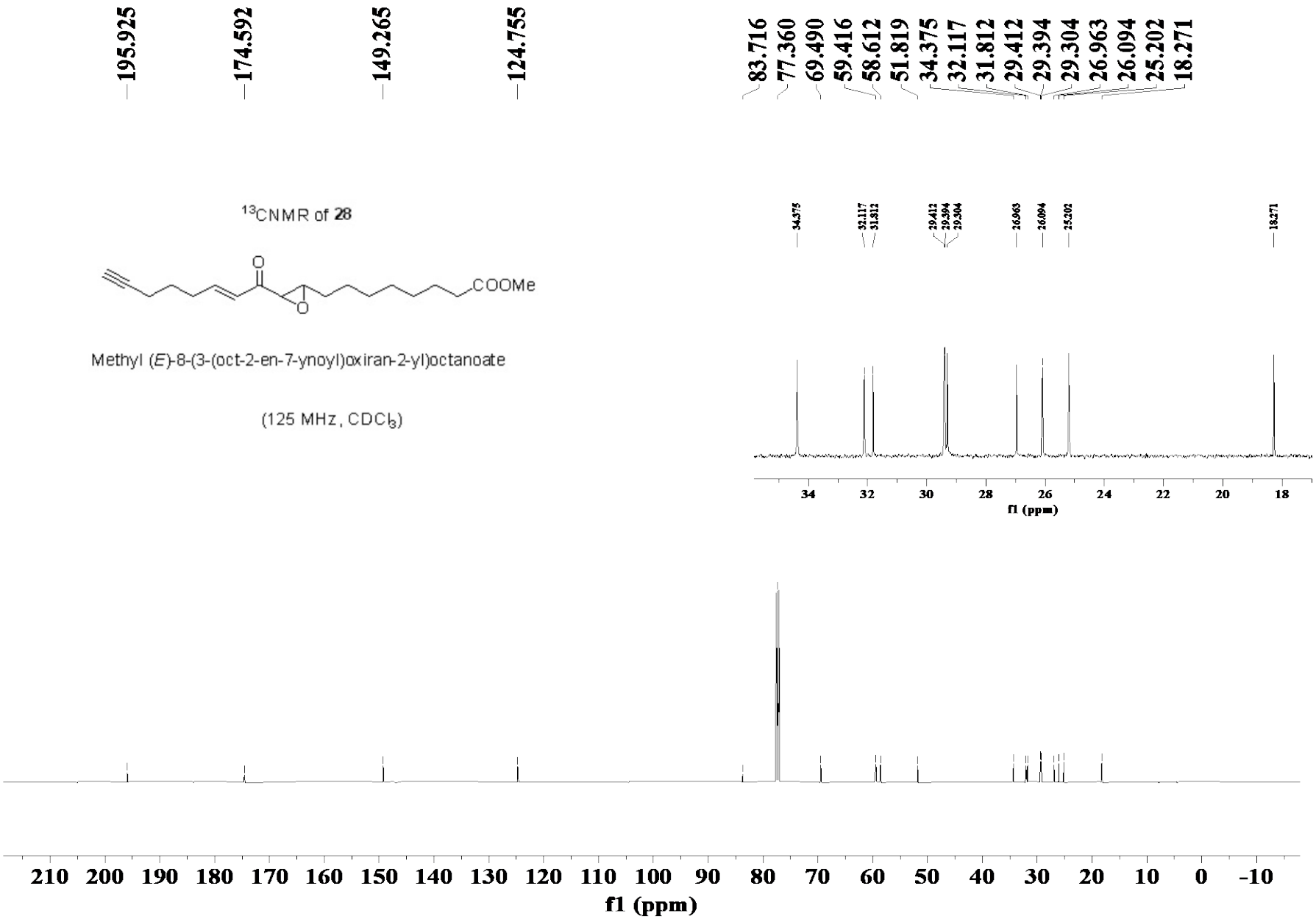

7.722
7.392
7.260
3.966
3.918
3.144
3.139
3.135
3.042
1994.156
1960.068
1572.537
1570.395
1568.297
1521.592
1HNMR of 24
Ph3P
O
D D D D D
CD3
O
D D D D
1-(3-(pentyl- 2H11)oxiran-2-yl)-2-(triphenyl- λ5-phosphanylidene)ethan-1-one
(500 MHz, CDCl3)
1.00
1.00
1.00
3.96 3.87
f1 (ppm)
3.15 3.10 3.05
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

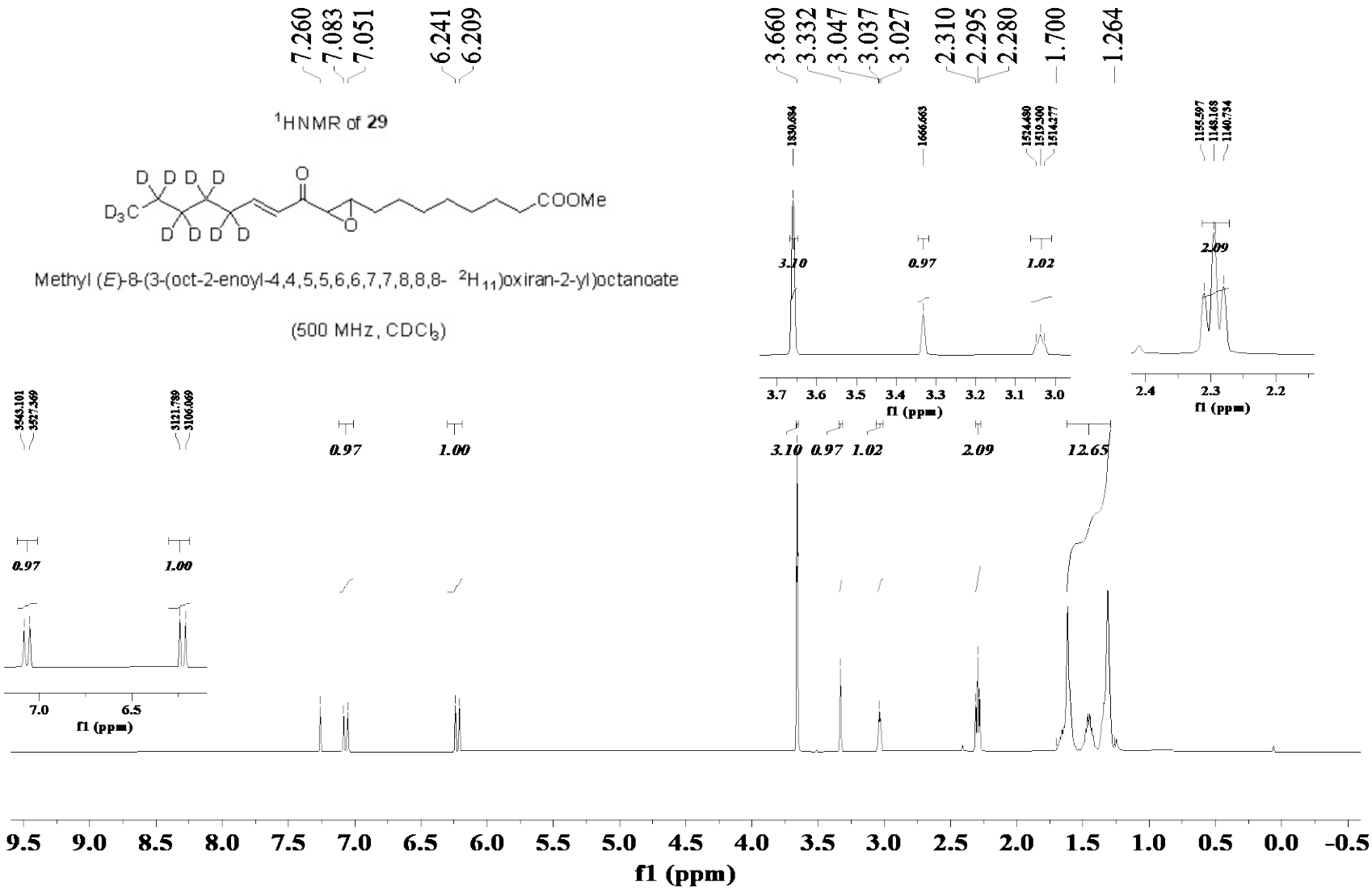

188.454
188.422
133.404
133.322
132.407
132.328
132.246
132.224
129.244
129.146
127.157
126.432
77.360
60.261
60.129
60.087
49.347
48.466
16790.290
16769.983
16654.823
16644.507
16634.671
16631.883
16256.983
16244.639
15994.440
15903.268
^{13}CNMR of **24**
Ph_3P
O
D D D D
D D D D
CD_3
1-(3-(pentyl- $^{2}H_{11}$)oxiran-2-yl)-2-(triphenyl- λ5-phosphanylidene)ethan-1-one
(125 MHz, $CDCl_3$)
f1 (ppm)

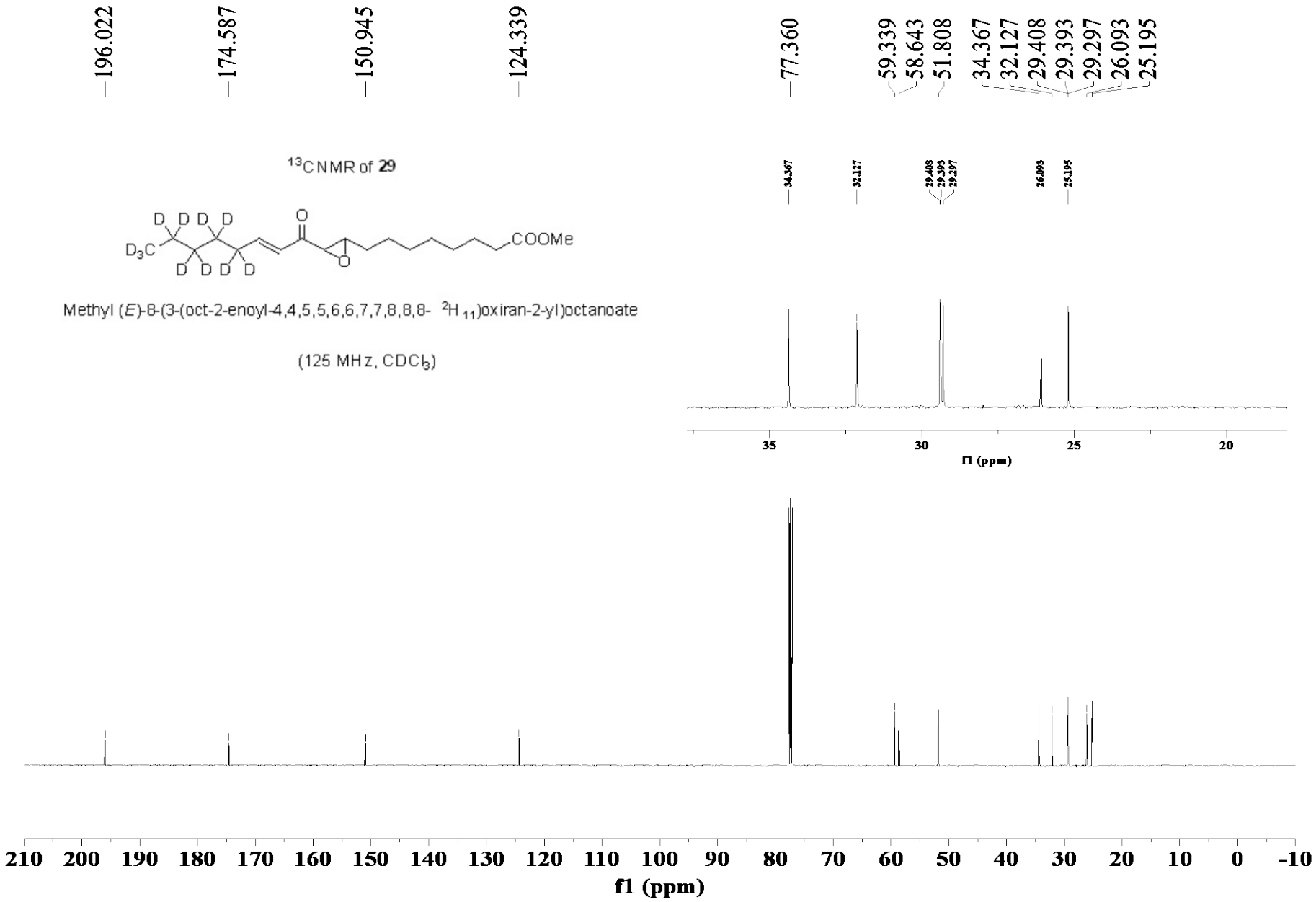

7.260
7.111
7.097
7.081
7.066
7.052
6.248
6.216
3.665
3.336
3.053
3.043
3.031
2.316
2.301
2.286
2.243
2.229
2.214
2.199
1.693
1.253
0.903
0.890
0.876
1HNMR of 18
O
H3C
COOMe
O
Methyl (E)-8-(3-(oct-2-enoyl)oxiran-2-yl)octanoate
(500 MHz, CDCl3)
1.06
3.06
3.03
f1 (ppm)
2.35
2.01
2.30
2.25
2.20
f1 (ppm)
1.10
1.00
3.39
0.95
1.06
2.35
2.01
3.18
1.10
1.00
7.2
7.0
6.8
6.6
6.4
6.2
f1 (ppm)
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

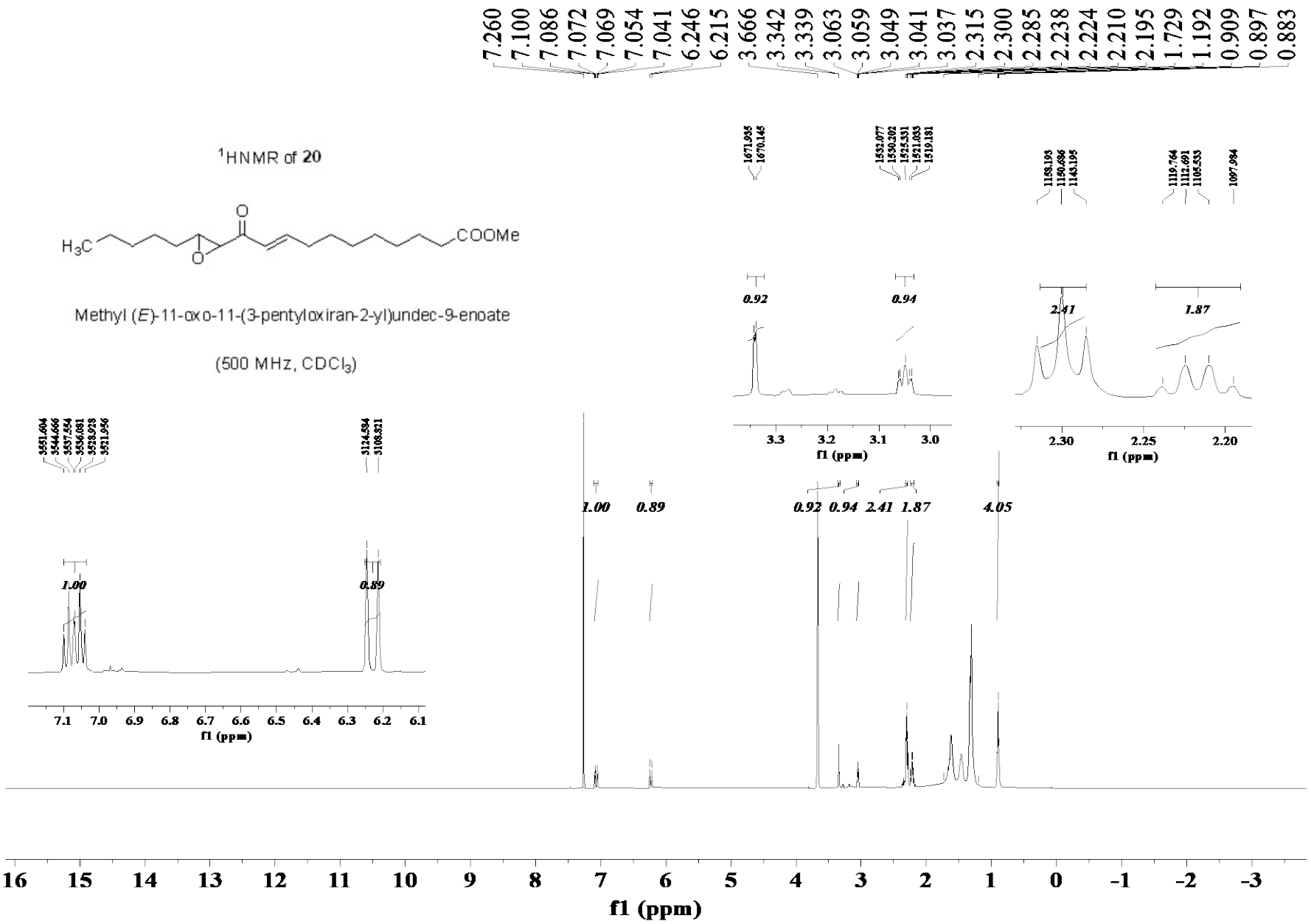

196.050
174.614
151.015
124.273
77.360
59.363
58.658
51.827
34.383
33.077
32.140
31.707
29.421
29.407
29.312
27.969
26.069
25.210
22.755
14.320
4524.896
4160.607
4042.804
3988.234
3700.709
3699.870
3686.661
3513.044
3279.106
3171.027
2862.223
1801.208
13CNMR of 18
H3C
O
O
COOMe
Methyl (E)-8-(3-(oct-2-enoyl)oxiran-2-yl)octanoate
(125 MHz, CDCl3)
35
30
25
20
15
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

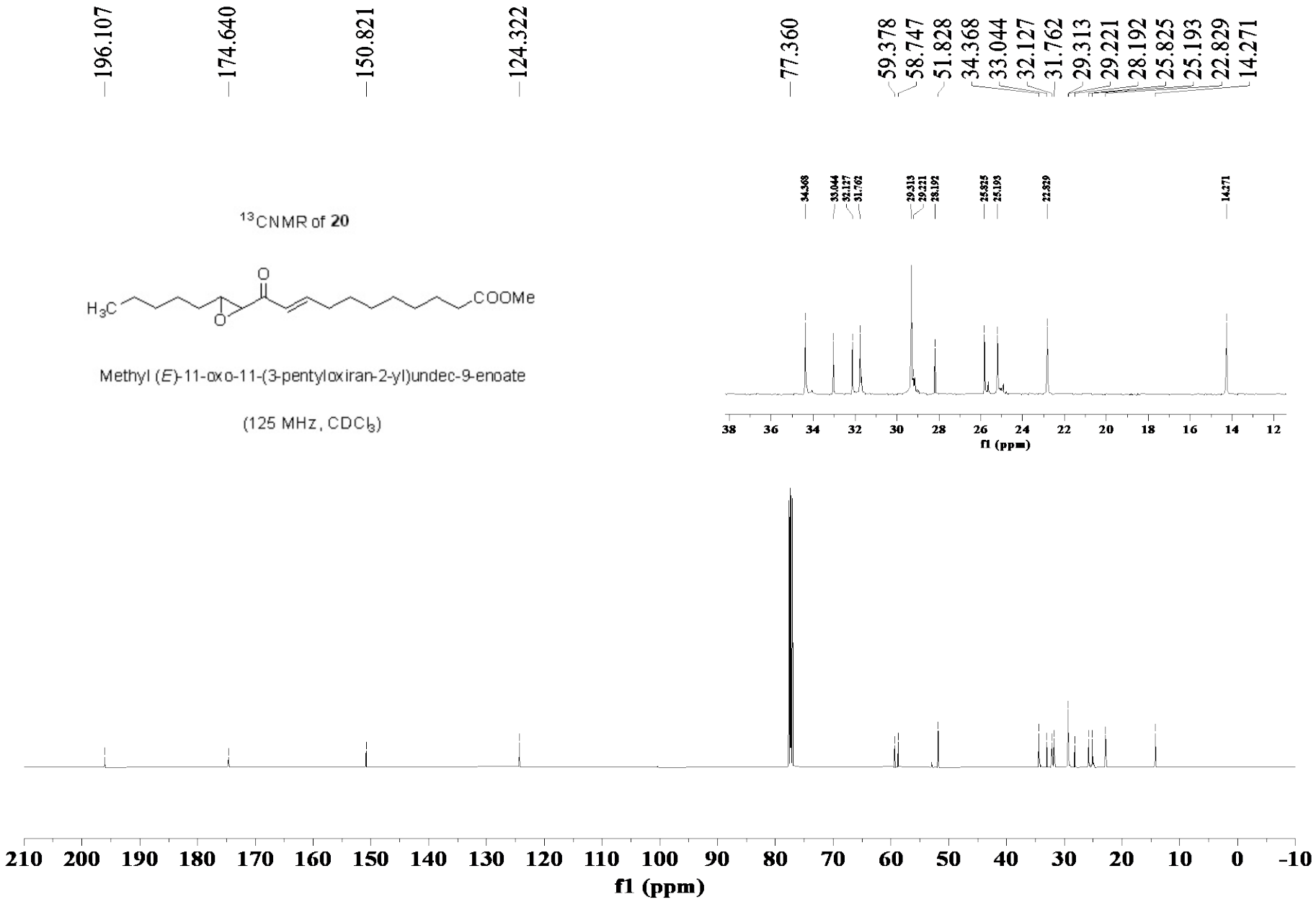

7.086 7.072 7.058 7.055 7.040 7.026 6.287 6.255 3.664 3.330 3.326 3.057 3.053 3.044 3.035 2.385 2.371 2.357 2.341 2.315 2.300 2.285 2.241 2.236 2.227 2.222 2.213 2.208 1.982 1.977 1.972 1.730 1.716 1.701 1.687 1.648
1665.778 1663.959 1529.205 1527.426 1522.589 1518.251 1199.120 1196.039 1178.939 1171.205 1157.875 1150.375 1142.851 1120.898 1118.311 1113.935 1111.344 1107.001 1104.403 991.542 988.938 986.547
1HNMR of 28
O
O
COOMe
Methyl (E)-8-(3-(oct-2-en-7-ynoyl)oxiran-2-yl)octanoate
(500 MHz, CDCl3)
1.00 1.06 2.06 2.14 2.08 1.05
3.3 3.2 3.1 3.0 2.4 2.3 2.2 2.1 2.0 1.9
f1 (ppm)
3544.565 3537.625 3530.549 3528.997 3521.887 3514.933 3144.854 3129.104
0.96 1.00 1.06 1.07
3.41 1.00 1.06 2.06 2.14 2.08 1.05 2.13 12.85
1.00 1.06 1.07
7.0 6.5
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

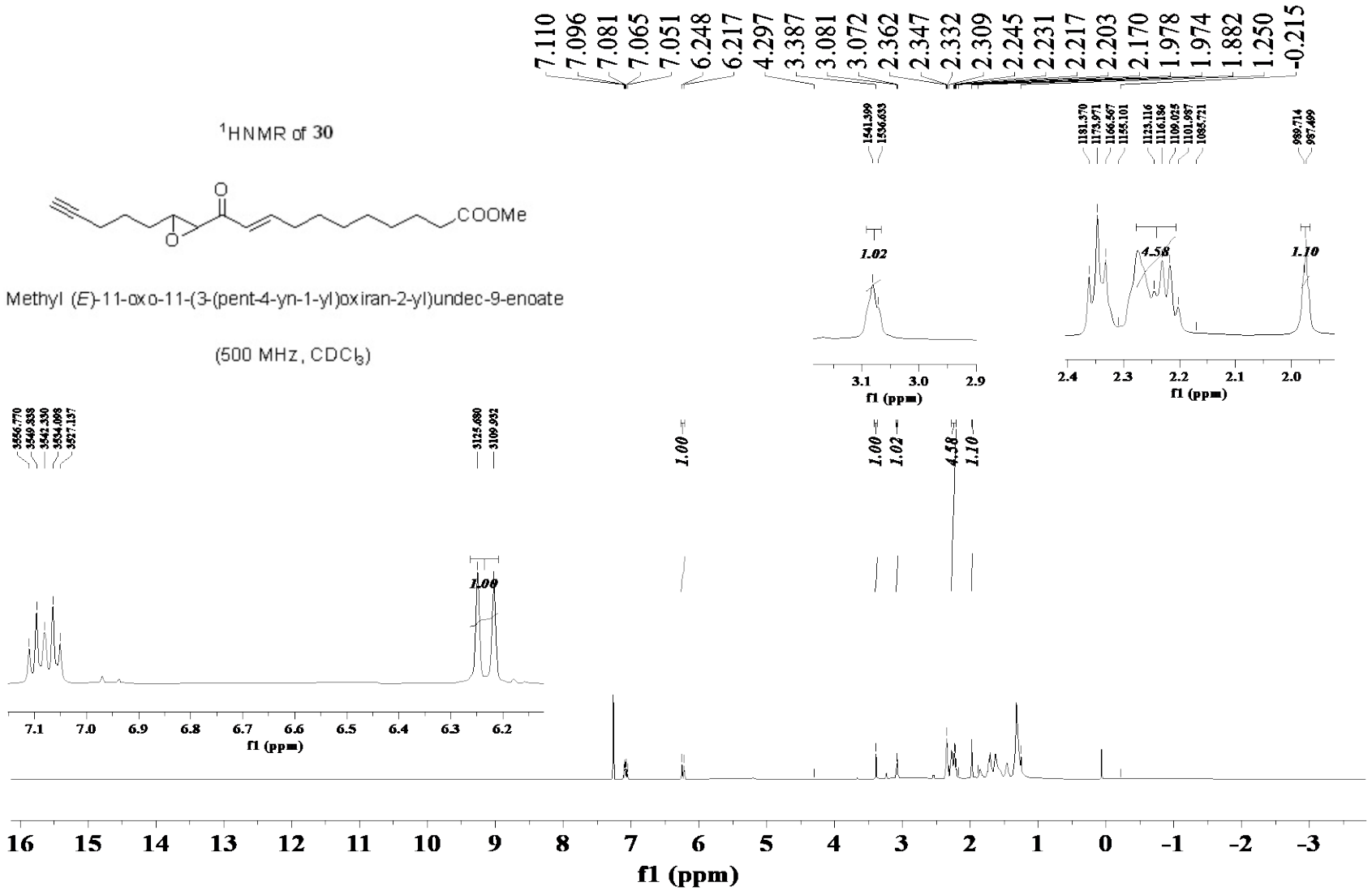

195.925
174.592
149.265
124.755
83.716
77.360
69.490
59.416
58.612
51.819
34.375
32.117
31.812
29.412
29.394
29.304
26.963
26.094
25.202
18.271
13CNMR of 28
O
O
COOMe
Methyl (E)-8-(3-(oct-2-en-7-ynoyl)oxiran-2-yl)octanoate
(125 MHz, CDCl3)
f1 (ppm)

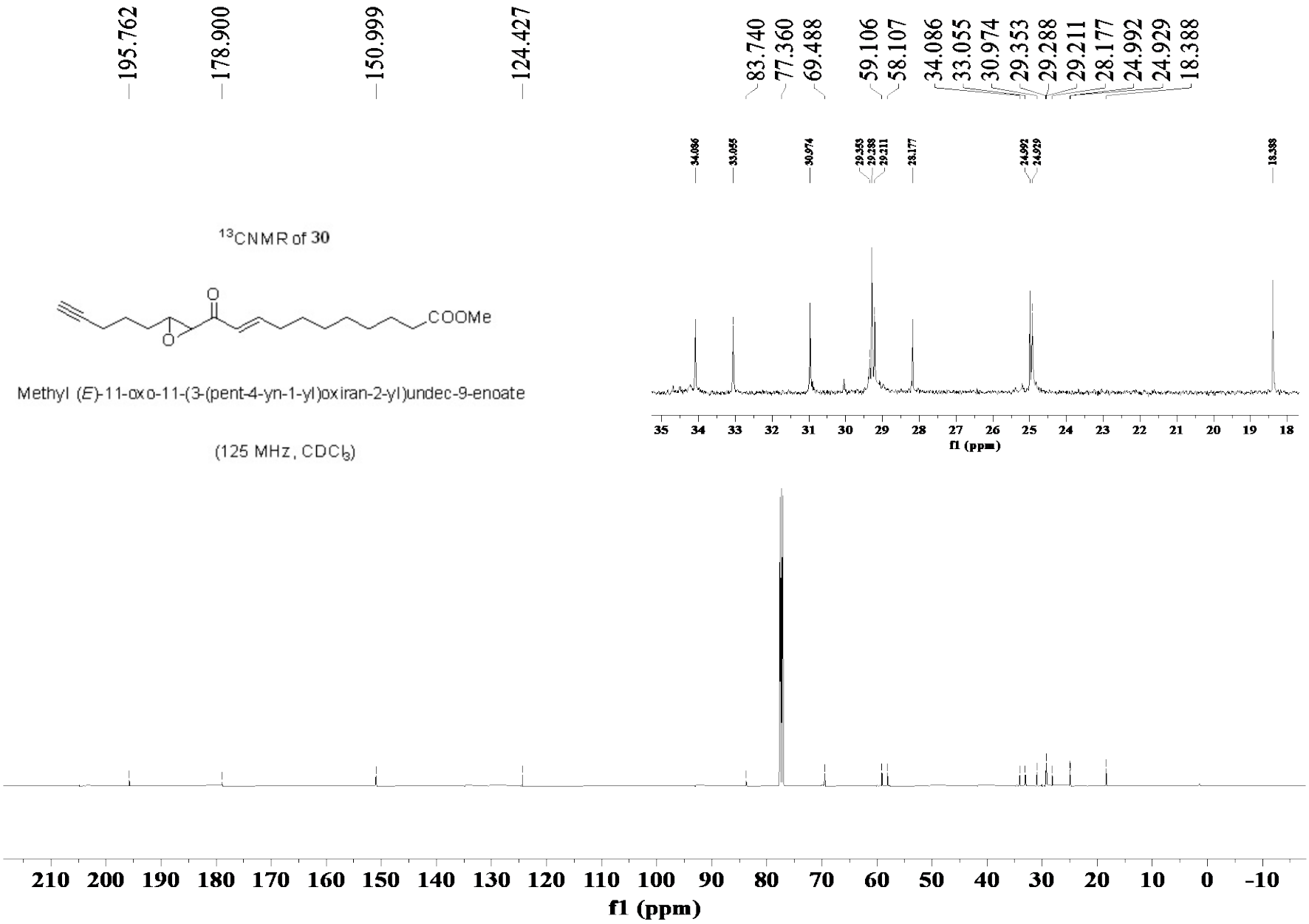

7.260
7.083
7.051
6.241
6.209
3.660
3.332
3.047
3.037
3.027
2.310
2.295
2.280
1.700
1.264
^{1}HNMR of **29**
COOMe
Methyl (*E*)-8-(3-(oct-2-enoyl-4,4,5,5,6,6,7,7,8,8,8- $^2H_{11}$)oxiran-2-yl)octanoate
(500 MHz, $CDCl_3$)
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

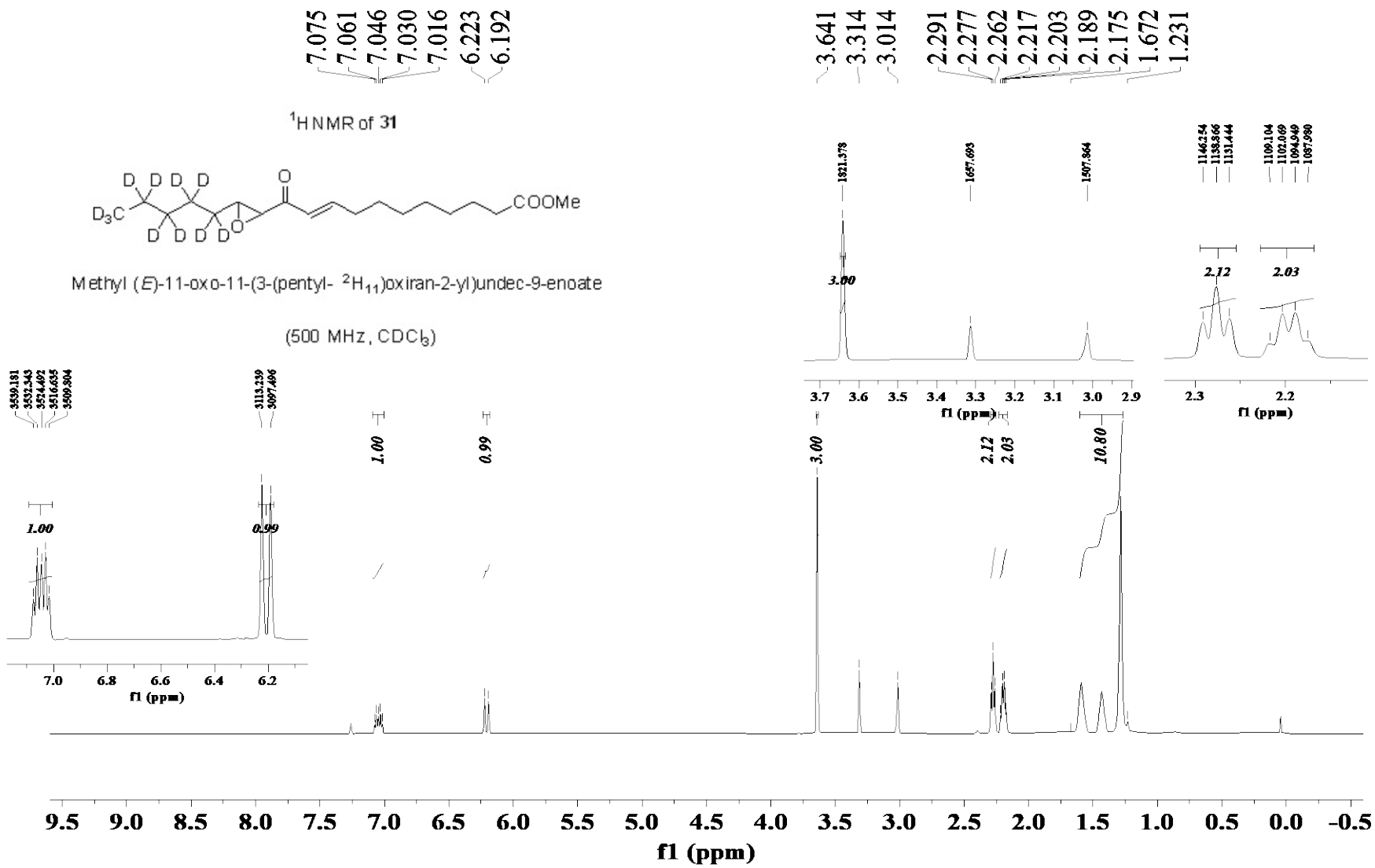

196.022
174.587
150.945
124.339
77.360
59.339
58.643
51.808
34.367
32.127
29.408
29.393
29.297
26.093
25.195
13CNMR of 29
D D D D
O
D3C
COOMe
D D D D
O
Methyl (E)-8-(3-(oct-2-enoyl-4,4,5,5,6,6,7,7,8,8,8- 2H 11)oxiran-2-yl)octanoate
(125 MHz, CDCl3)
34.367
32.127
29.408
29.393
29.297
26.093
25.195
35
30
25
20
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

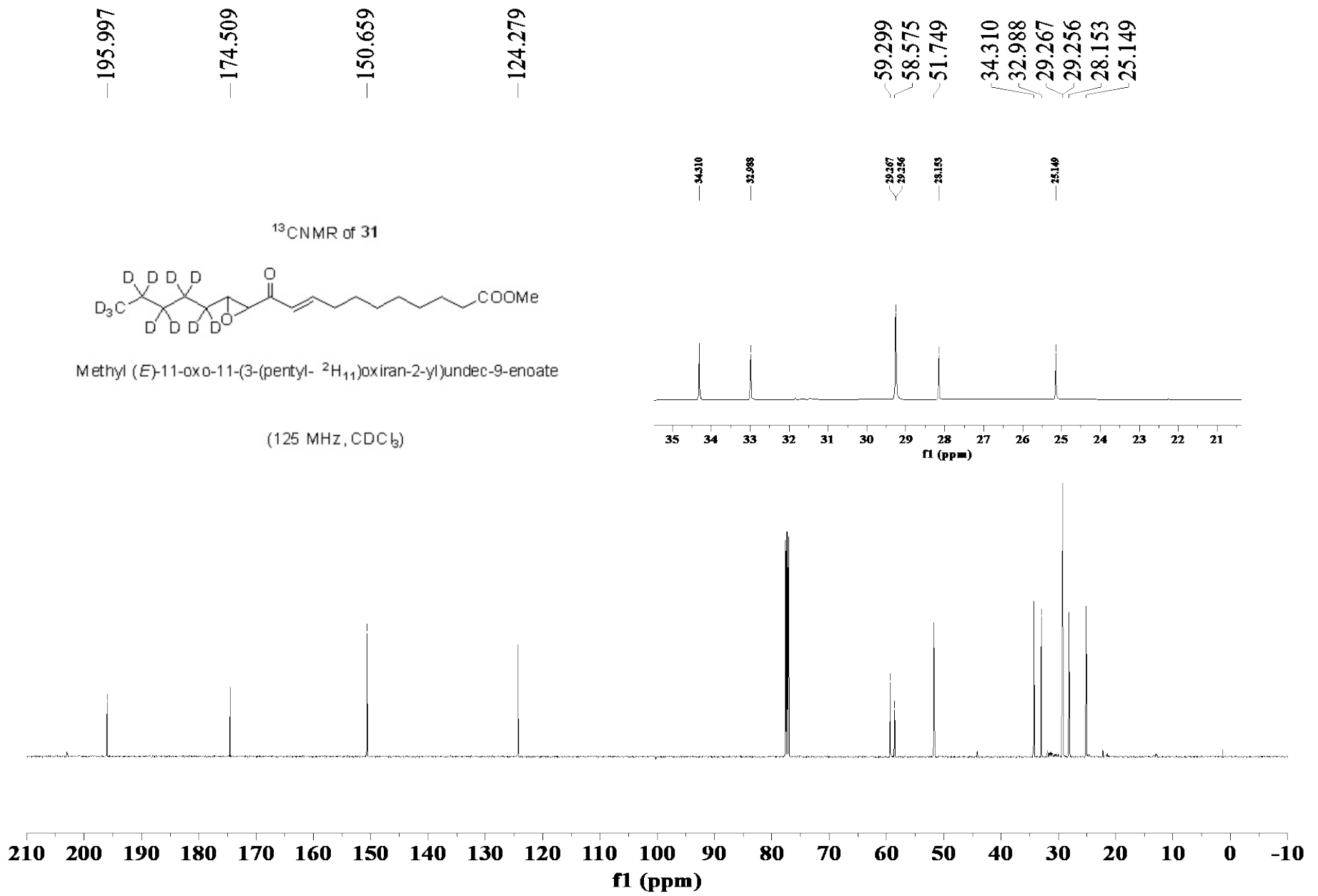

7.260
7.100
7.086
7.072
7.069
7.054
7.041
6.246
6.215
3.666
3.342
3.339
3.063
3.059
3.049
3.041
3.037
2.315
2.300
2.285
2.238
2.224
2.210
2.195
1.729
1.192
0.909
0.897
0.883
1HNMR of 20
O
H3C
O
COOMe
Methyl (E)-11-oxo-11-(3-pentyloxiran-2-yl)undec-9-enoate
(500 MHz, CDCl3)
1671.935
1670.145
1532.077
1530.202
1524.331
1521.033
1519.181
1158.193
1150.686
1143.195
1119.764
1112.691
1105.533
1097.984
0.92
0.94
2.41
1.87
3.3
3.2
3.1
3.0
f1 (ppm)
2.30
2.25
2.20
f1 (ppm)
3551.604
3544.666
3537.554
3536.081
3528.928
3521.956
3124.584
3108.821
1.00
0.89
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
f1 (ppm)
1.00
0.89
0.92
0.94
2.41
1.87
4.05
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

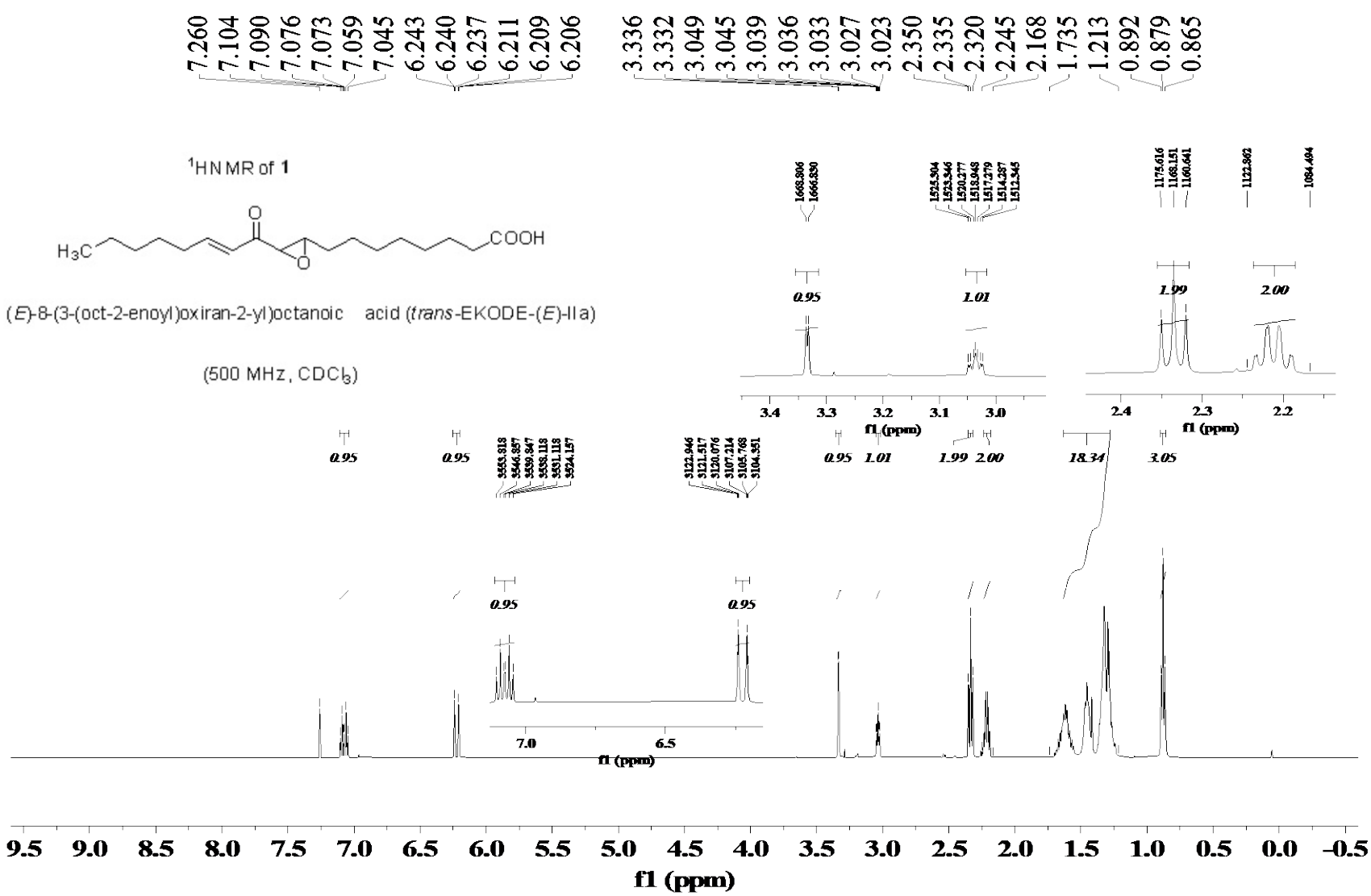

196.107
174.640
150.821
124.322
77.360
59.378
58.747
51.828
34.368
33.044
32.127
31.762
29.313
29.221
28.192
25.825
25.193
22.829
14.271
13CNMR of 20
O
H3C
O
COOMe
Methyl (E)-11-oxo-11-(3-pentyloxiran-2-yl)undec-9-enoate
(125 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

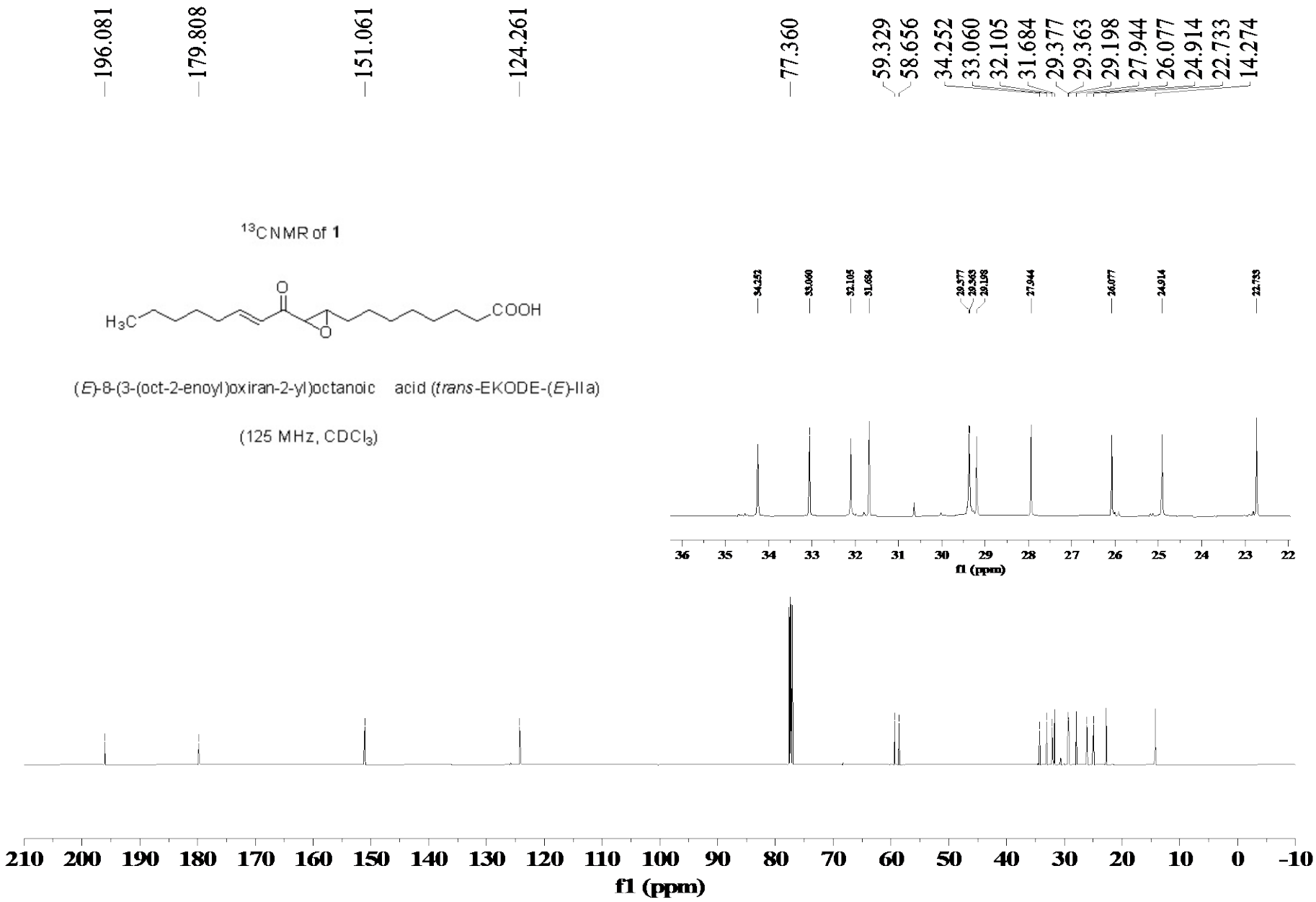

7.110
7.096
7.081
7.065
7.051
6.248
6.217
4.297
3.387
3.081
3.072
2.362
2.347
2.332
2.309
2.245
2.231
2.217
2.203
2.170
1.978
1.974
1.882
1.250
-0.215
^{1}HNMR of **30**
COOMe
Methyl (*E*)-11-oxo-11-(3-(pent-4-yn-1-yl)oxiran-2-yl)undec-9-enoate
(500 MHz, $CDCl_3$)
f1 (ppm)

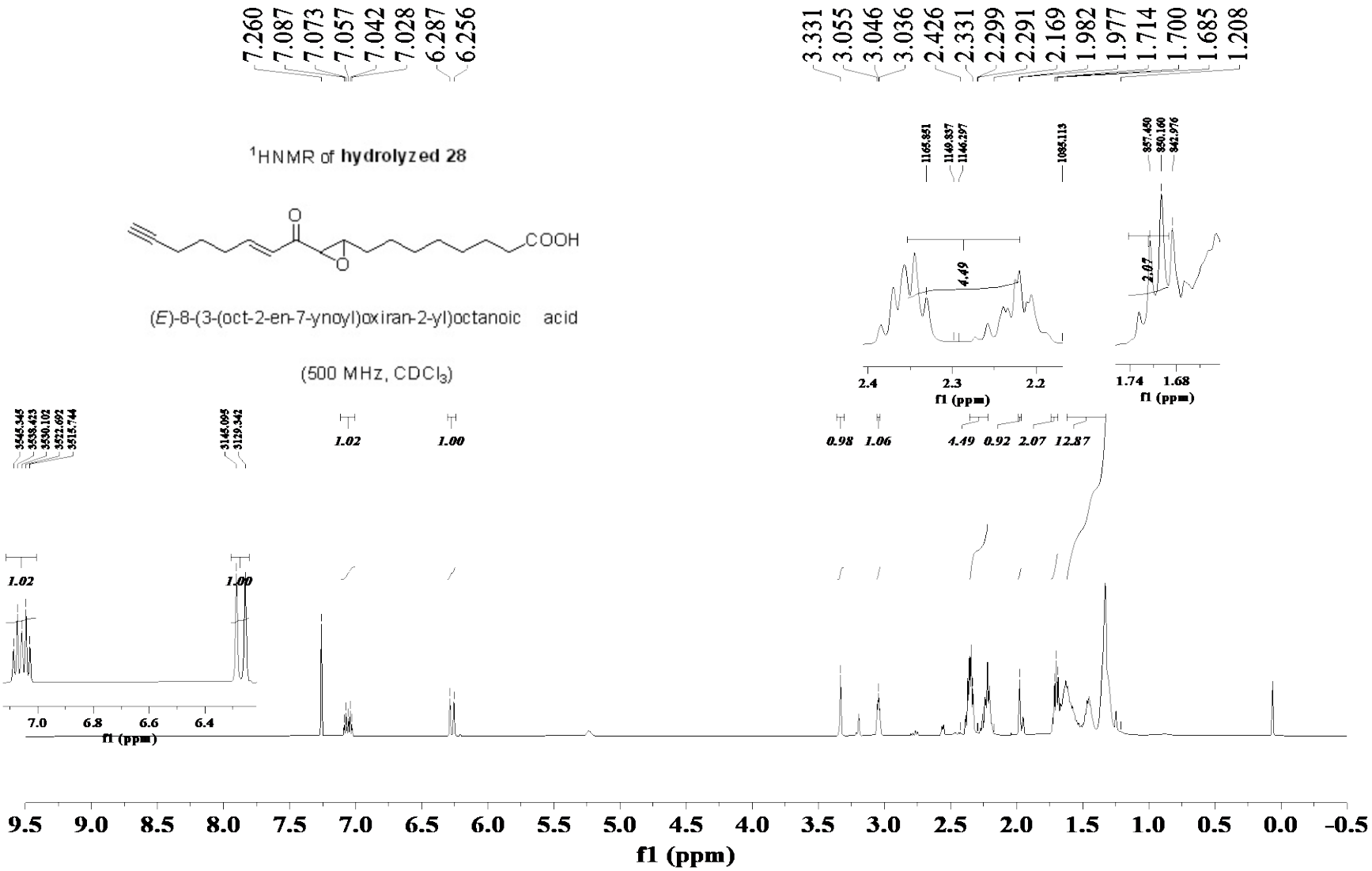

195.762
178.900
150.999
124.427
83.740
77.360
69.488
59.106
58.107
34.086
33.055
30.974
29.353
29.288
29.211
28.177
24.992
24.929
18.388
^{13}CNMR of **30**
COOMe
Methyl (*E*)-11-oxo-11-(3-(pent-4-yn-1-yl)oxiran-2-yl)undec-9-enoate
(125 MHz, $CDCl_3$)
f1 (ppm)

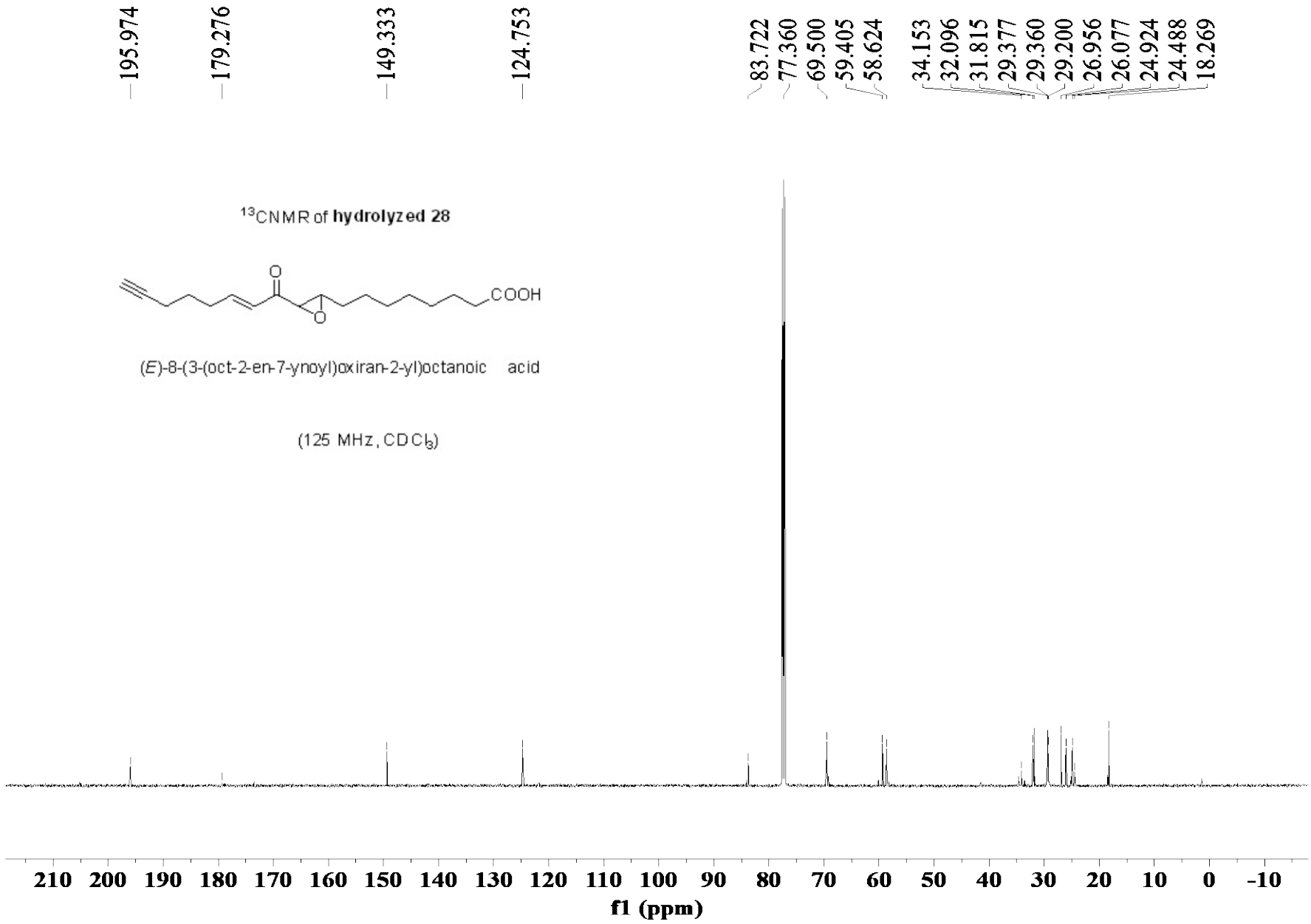

7.075
7.061
7.046
7.030
7.016
6.223
6.192
3.641
3.314
3.014
2.291
2.277
2.262
2.217
2.203
2.189
2.175
1.672
1.231
^{1}H NMR of 31
D D D D
D$_3$C
O
COOMe
D D D D
O
Methyl (E)-11-oxo-11-(3-(pentyl- $^2H_{11}$)oxiran-2-yl)undec-9-enoate
(500 MHz, CDCl$_3$)
1.00
0.99
3.00
2.12
2.03
10.80
f1 (ppm)

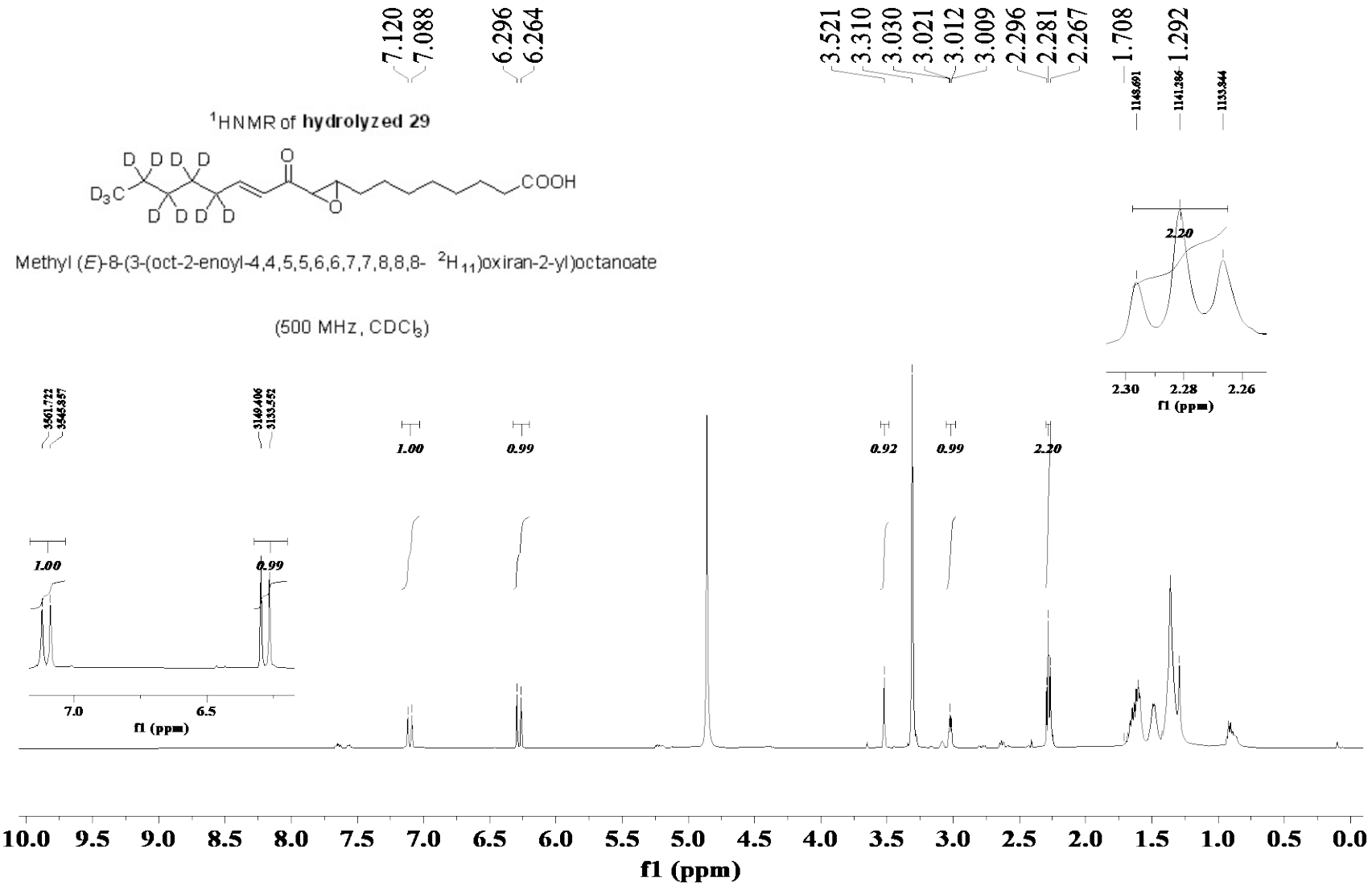

195.997
174.509
150.659
124.279
59.299
58.575
51.749
34.310
32.988
29.267
29.256
28.153
25.149
13CNMR of 31
COOMe
Methyl (E)-11-oxo-11-(3-(pentyl- 2H11)oxiran-2-yl)undec-9-enoate
(125 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

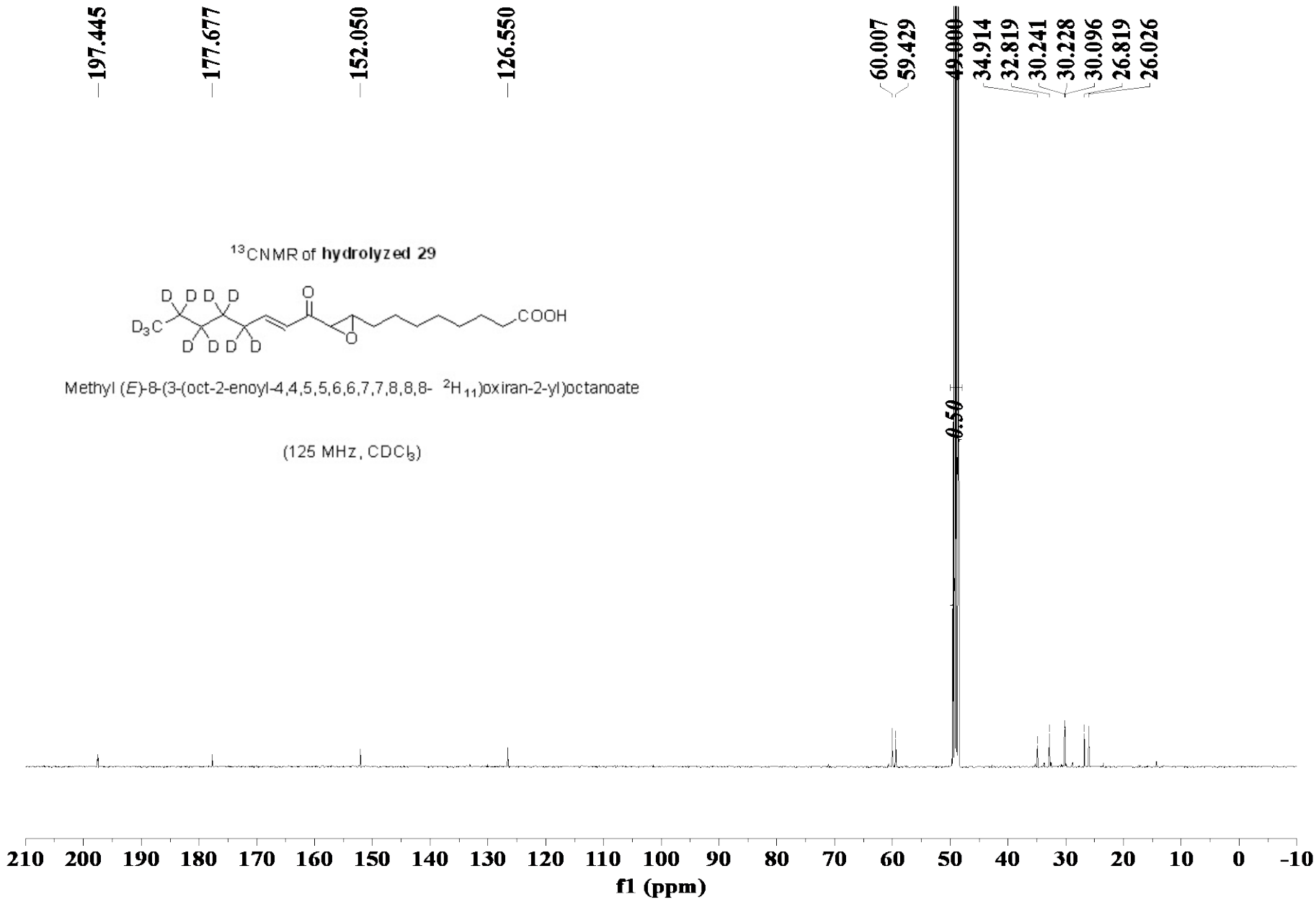

7.260
7.104
7.090
7.076
7.073
7.059
7.045
6.243
6.240
6.237
6.211
6.209
6.206
3.336
3.332
3.049
3.045
3.039
3.036
3.033
3.027
3.023
2.350
2.335
2.320
2.245
2.168
1.735
1.213
0.892
0.879
0.865
1HNMR of 1
H3C
COOH
O
O
(E)-8-(3-(oct-2-enoyl)oxiran-2-yl)octanoic acid (trans-EKODE-(E)-IIa)
(500 MHz, CDCl3)
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

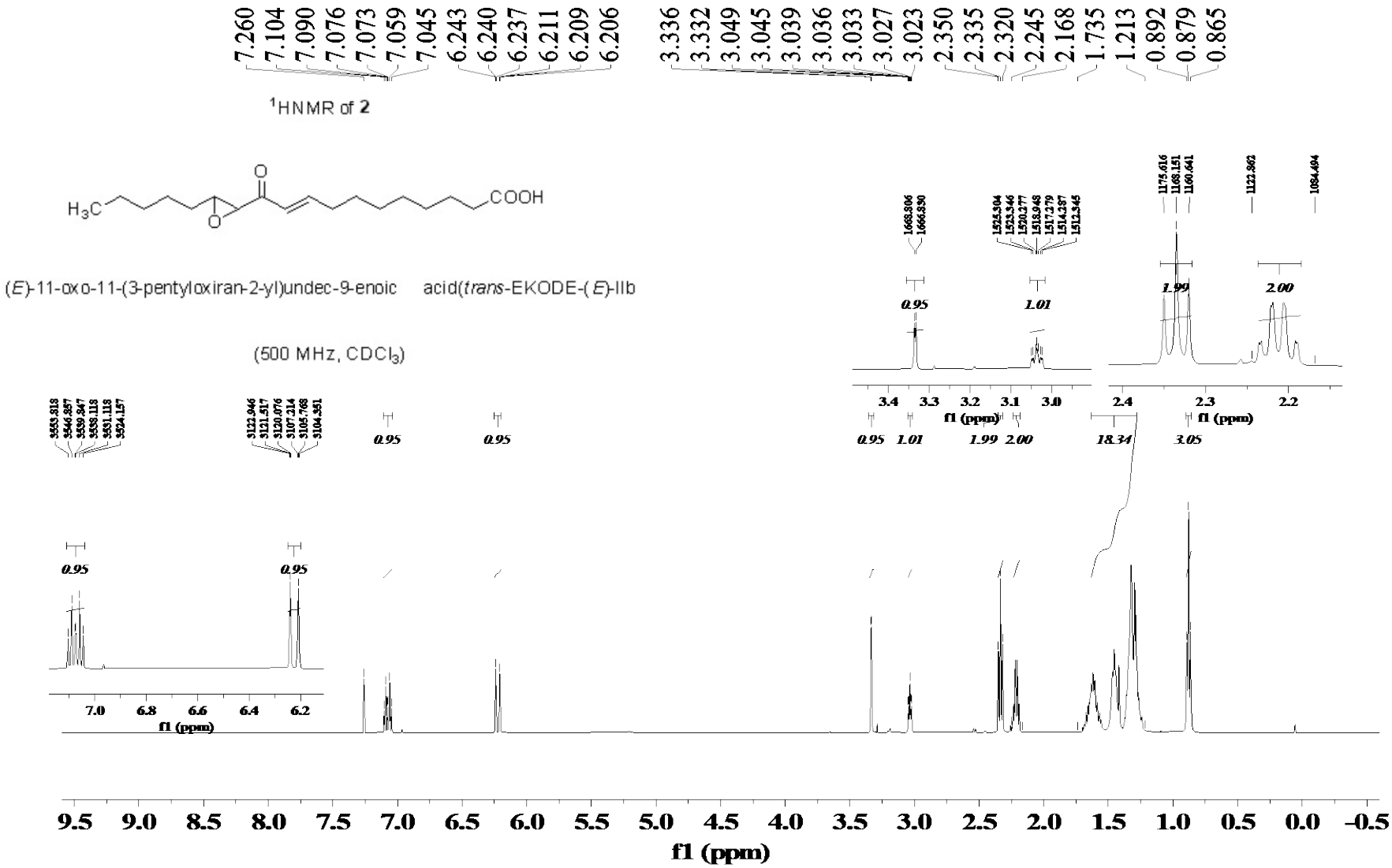

196.081
179.808
151.061
124.261
77.360
59.329
58.656
34.252
33.060
32.105
31.684
29.377
29.363
29.198
27.944
26.077
24.914
22.733
14.274
13CNMR of 1
H3C
O
O
COOH
(E)-8-(3-(oct-2-enoyl)oxiran-2-yl)octanoic acid (trans-EKODE-(E)-IIa)
(125 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

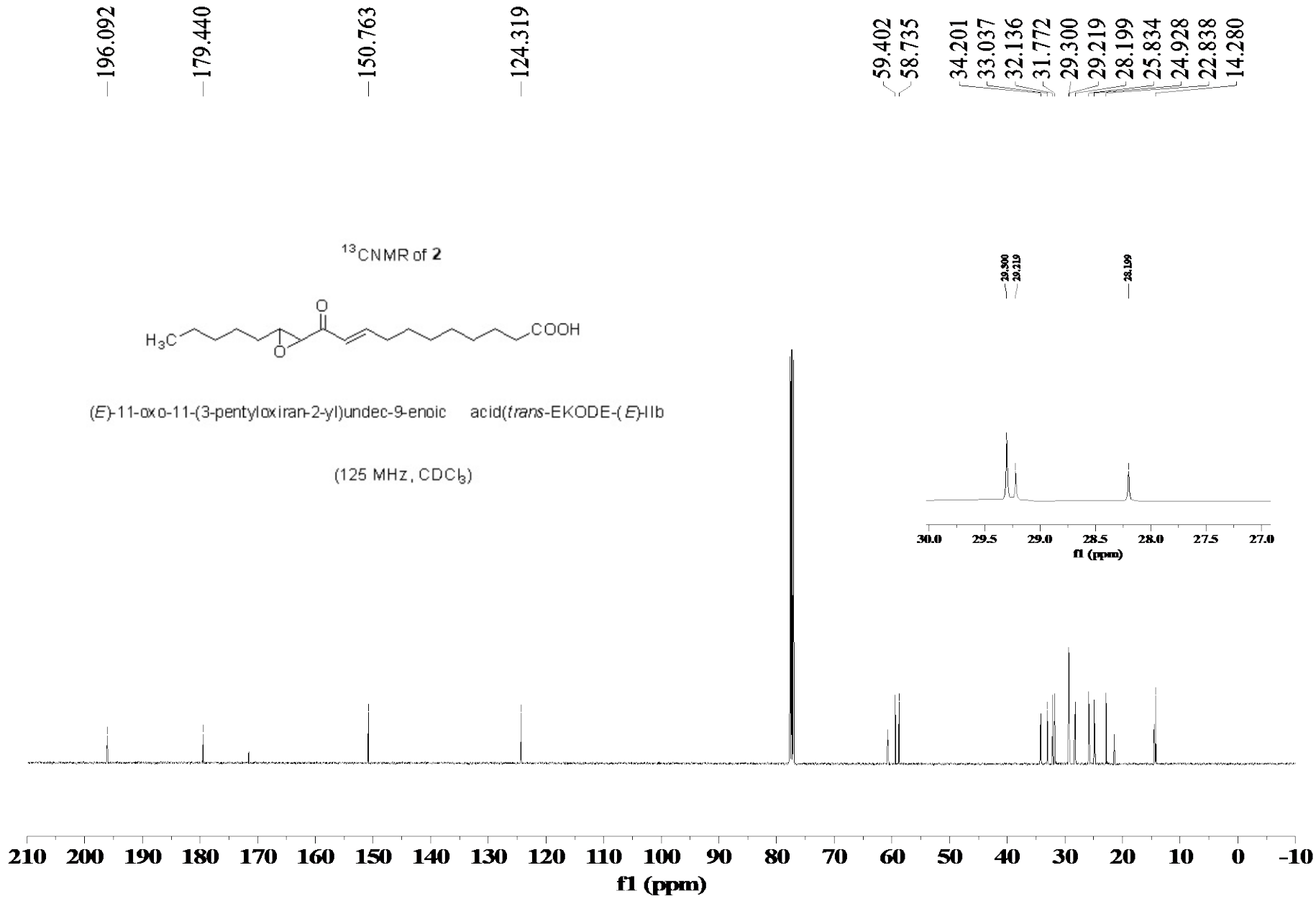

7.260
7.087
7.073
7.057
7.042
7.028
6.287
6.256
3.331
3.055
3.046
3.036
2.426
2.331
2.299
2.291
2.169
1.982
1.977
1.714
1.700
1.685
1.208
1H NMR of hydrolyzed 28
O
O
COOH
(E)-8-(3-(oct-2-en-7-ynoyl)oxiran-2-yl)octanoic acid
(500 MHz, CDCl3)
1165.851
1149.337
1146.297
1085.113
857.450
850.160
842.976
4.49
2.07
2.4
2.3
2.2
f1 (ppm)
1.74
1.68
f1 (ppm)
3545.345
3538.423
3530.102
3522.692
3515.744
3145.095
3129.342
1.02
1.00
0.98
1.06
4.49
0.92
2.07
12.87
1.02
1.00
7.0
6.8
6.6
6.4
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

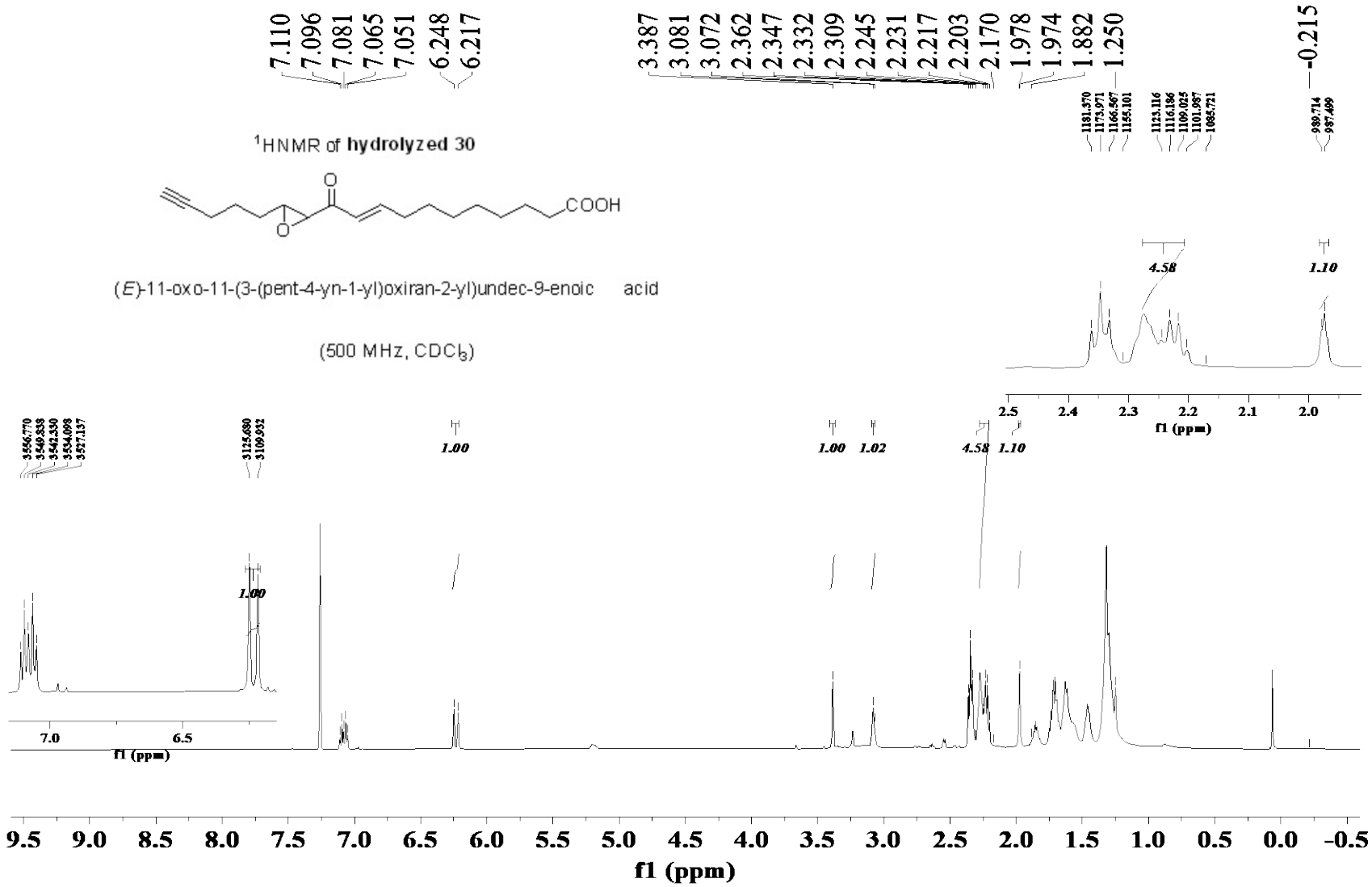

195.974
179.276
149.333
124.753
83.722
77.360
69.500
59.405
58.624
34.153
32.096
31.815
29.377
29.360
29.200
26.956
26.077
24.924
24.488
18.269
13CNMR of hydrolyzed 28
O
COOH
O
(E)-8-(3-(oct-2-en-7-ynoyl)oxiran-2-yl)octanoic acid
(125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

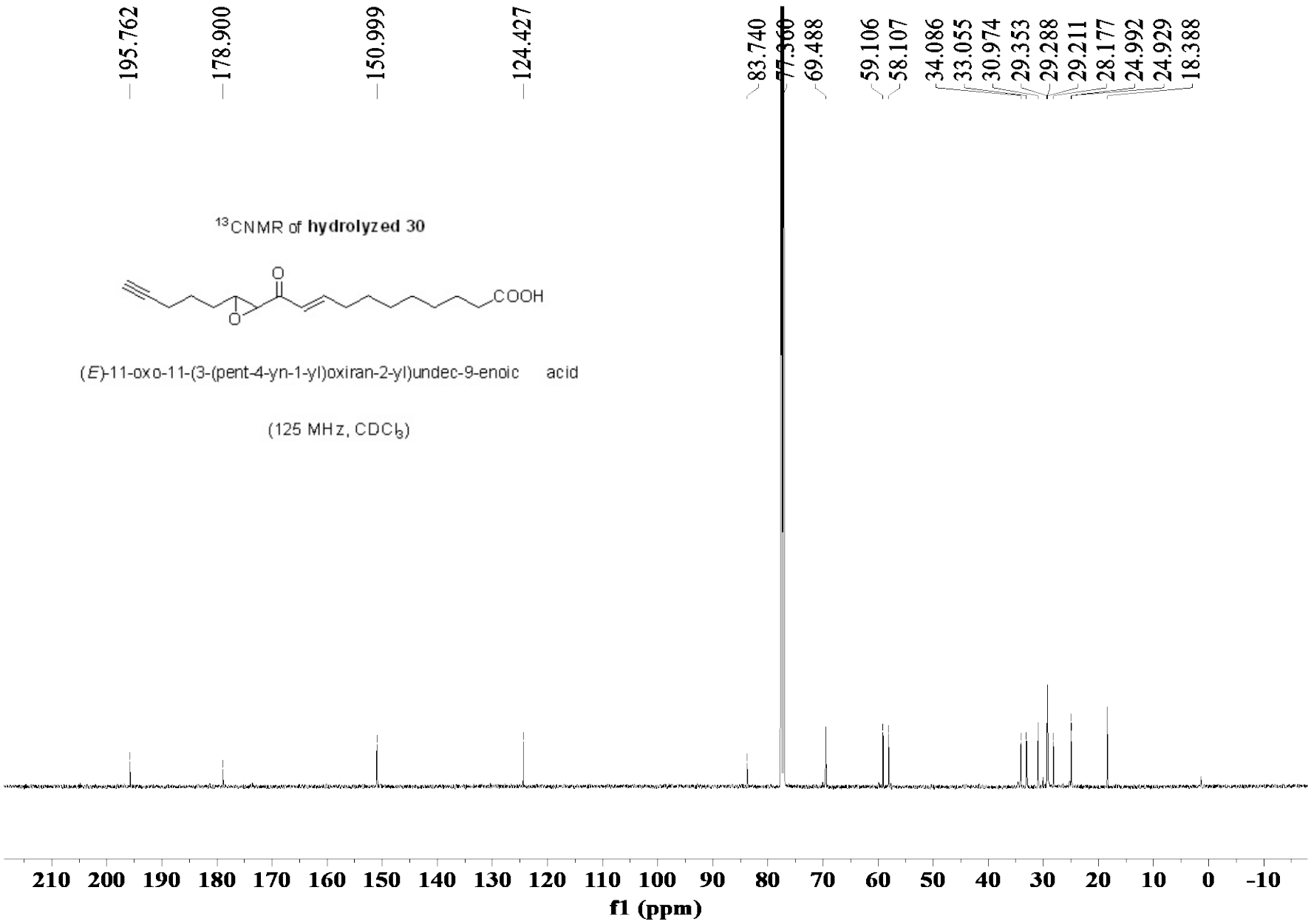

7.120
7.088
6.296
6.264
3.521
3.310
3.030
3.021
3.012
3.009
2.296
2.281
2.267
1.708
1.292
1148.691
1141.286
1133.844
^{1}HNMR of **hydrolyzed 29**
COOH
Methyl (*E*)-8-(3-(oct-2-enoyl-4,4,5,5,6,6,7,7,8,8,8- $^2H_{11}$)oxiran-2-yl)octanoate
(500 MHz, $CDCl_3$)
2.20
2.30
2.28
2.26
f1 (ppm)
3561.722
3545.857
3140.406
3133.552
1.00
0.99
0.92
0.99
2.20
1.00
0.99
7.0
6.5
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

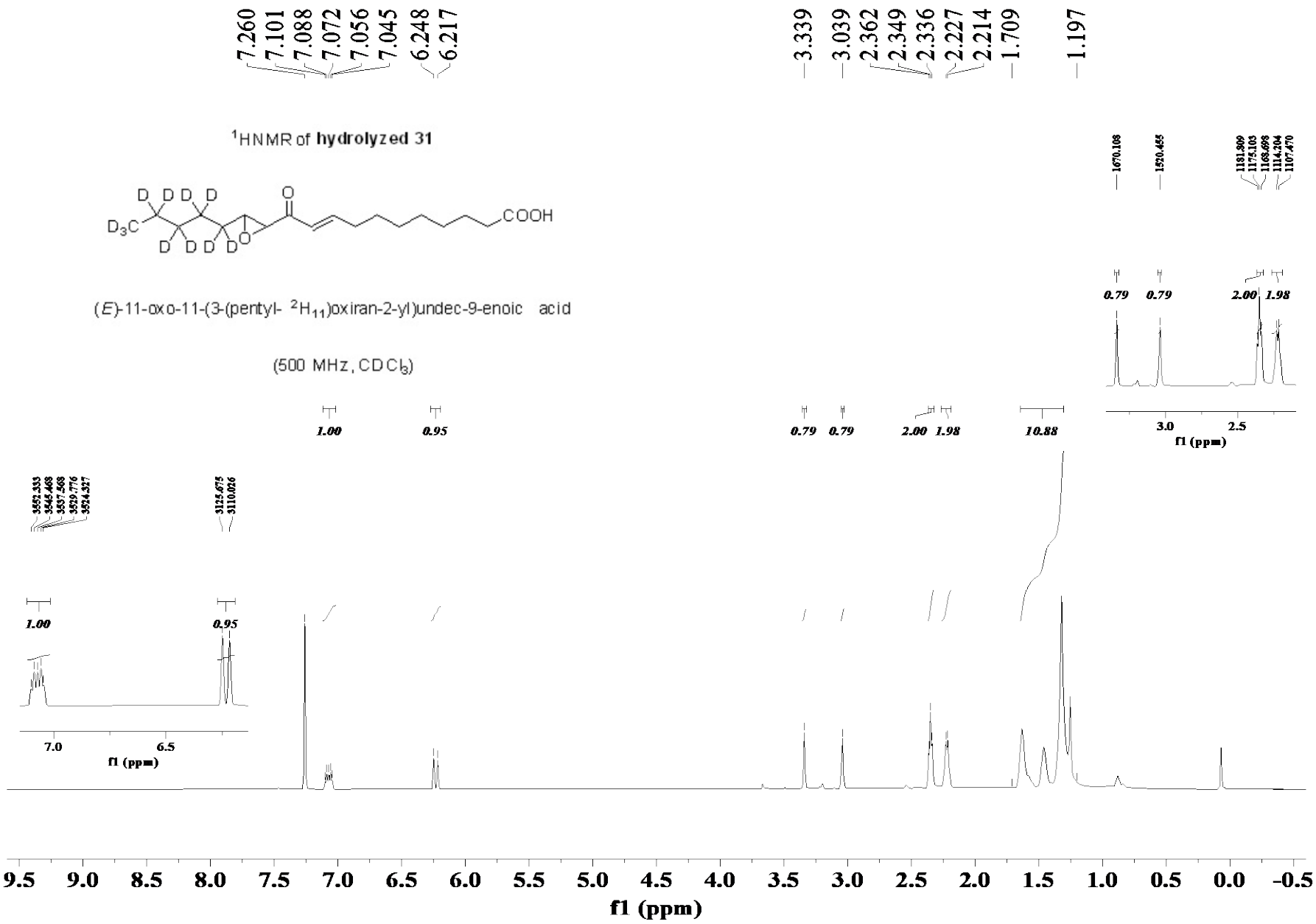

197.445
177.677
152.050
126.550
60.007
59.429
49.000
34.914
32.819
30.241
30.228
30.096
26.819
26.026
0.50
13CNMR of hydrolyzed 29
D D D D
D3C
O
COOH
D D D D
O
Methyl (E)-8-(3-(oct-2-enoyl-4,4,5,5,6,6,7,7,8,8,8- 2H11)oxiran-2-yl)octanoate
(125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

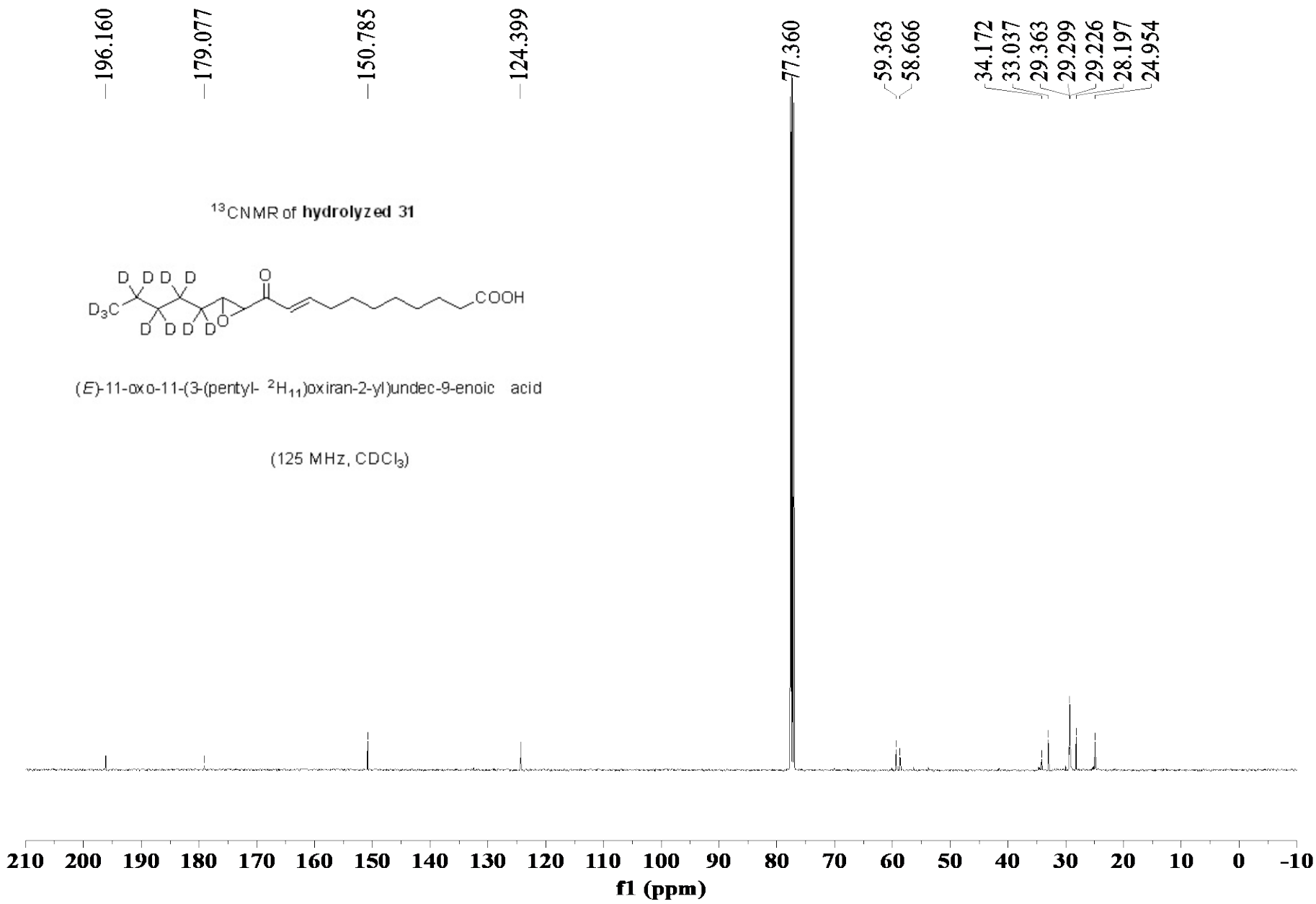

7.260
7.104
7.090
7.076
7.073
7.059
7.045
6.243
6.240
6.237
6.211
6.209
6.206
3.336
3.332
3.049
3.045
3.039
3.036
3.033
3.027
3.023
2.350
2.335
2.320
2.245
2.168
1.735
1.213
0.892
0.879
0.865
1HNMR of 2
H3C
O
O
COOH
(E)-11-oxo-11-(3-pentyloxiran-2-yl)undec-9-enoic acid(trans-EKODE-(E)-IIb
(500 MHz, CDCl3)
0.95
1.01
1.99
2.00
18.34
3.05
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


196.092
179.440
150.763
124.319
59.402
58.735
34.201
33.037
32.136
31.772
29.300
29.219
28.199
25.834
24.928
22.838
14.280
13CNMR of 2
O
H3C
O
COOH
(E)-11-oxo-11-(3-pentyloxiran-2-yl)undec-9-enoic acid(trans-EKODE-(E)-IIb
(125 MHz, CDCl3)
29.300
29.219
28.199
30.0
29.5
29.0
28.5
28.0
27.5
27.0
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.110
7.096
7.081
7.065
7.051
6.248
6.217
3.387
3.081
3.072
2.362
2.347
2.332
2.309
2.245
2.231
2.217
2.203
2.170
1.978
1.974
1.882
1.250
-0.215
1181.370
1173.971
1166.567
1155.101
1123.116
1116.186
1109.025
1101.987
1085.721
989.714
987.499
1H NMR of hydrolyzed 30
O
O
COOH
(E)-11-oxo-11-(3-(pent-4-yn-1-yl)oxiran-2-yl)undec-9-enoic acid
(500 MHz, CDCl3)
4.58
1.10
2.5
2.4
2.3
2.2
2.1
2.0
f1 (ppm)
3556.770
3540.838
3542.330
3534.098
3527.157
3125.690
3109.952
1.00
1.00
1.02
4.58
1.10
1.00
7.0
6.5
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


195.762
178.900
150.999
124.427
83.740
77.360
69.488
59.106
58.107
34.086
33.055
30.974
29.353
29.288
29.211
28.177
24.992
24.929
18.388
13CNMR of hydrolyzed 30
O
O
COOH
(E)-11-oxo-11-(3-(pent-4-yn-1-yl)oxiran-2-yl)undec-9-enoic acid
(125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.260
7.101
7.088
7.072
7.056
7.045
6.248
6.217
3.339
3.039
2.362
2.349
2.336
2.227
2.214
1.709
1.197
1H NMR of hydrolyzed 31
D D D D
D3C
D D D D
O
O
COOH
(E)-11-oxo-11-(3-(pentyl- 2H11)oxiran-2-yl)undec-9-enoic acid
(500 MHz, CDCl3)
1.00
0.95
0.79
0.79
2.00
1.98
10.88
3552.333
3545.468
3537.568
3529.776
3514.327
3125.675
3110.026
1670.108
1520.455
1181.909
1175.103
1168.698
1114.204
1107.470
f1 (ppm)


196.160
179.077
150.785
124.399
77.360
59.363
58.666
34.172
33.037
29.363
29.299
29.226
28.197
24.954
^{13}CNMR of **hydrolyzed 31**
(*E*)-11-oxo-11-(3-(pentyl-$^{2}H_{11}$)oxiran-2-yl)undec-9-enoic acid
(125 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)