Electronic Supplementary Material (ESI) for Chemical Communications

ELECTRONIC SUPPORTING INFORMATION

Epoxidation of Bromoallenes Connects Red Algae Metabolites by an Intersecting Bromoallene Oxide - Favorskii Manifold

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Cover Page and Contents

Notes:

‡ See Electronic Supporting Information for details.

§ The use of *m*CPBA as an epoxidising agent did not result in any desired product formation.

¶ At least 50 different side products were observed in this reaction on the basis of ^{13}C NMR analysis. Attempts to use the dioxirane of cyclohexanone (ref. 15b in the main manuscript) to keep any biradicals inherently tethered (and thus recombine), resulted instead in its rearangement to ε-caprolactone. We propose this rearrangement follows a diradical pathway analogous to that known for DMDO (ref. 16b in the main manuscript). The resistance of the bromoallene to necessarily liberated HBr was established by adding conc. HBr (0.5 eq.) to the bromoallene in acetone solution.

¥ Each olefin has two distinct faces and each of **A** and **B** can exist as two diastereomers.

†† We invoke NGP by bromide lone pairs to facilitate this process (*vide infra* the calculations which show significant shortening of the C-Br bonds in this process).

** The Favorskii reaction of α,α- and α,α'-dibromoketones is *Z*-selective for the products, but this is often obscured by base mediated isomerisation to the *E* adduct (see ref. 17 in the main manuscript). Isolated *Z*-**5** was re-subjected to the reaction conditions and was found not to isomerise over the course of 48 h.

‡‡ Attempts to dry DMDO solutions over Na_2SO_4 or 4Å MS and thus observe cyclopropanone **E** still gave acids **5**. Evidently there is still sufficient adventitious water to attack the highly reactive cyclopropanone.

§§ We have also studied the reaction of 1,1-diiodonon-1-ene with LDA, which gives the terminal alkyne non-1-yne in good yield.

¶¶ One referee suggested that such a vinylidene could also arise from 1,1-elimination of *Z*- and *E*-**15**.

¥¥ We attribute the lower level of deuteration in the products to a secondary normal kinetic isotope effect where (1-^{1}H)-bromoallene **4** is epoxidised faster than (1-^{2}H)-bromoallene **4**.

††† The results of this experiment are consistent also with an initial epoxidation to give bromoallene oxide **A**, hydride shift from C_1 to C_2 with concomitant opening of the epoxide by breaking the C_2-O bond. Hydrolysis of the resulting carboxylic acid bromide would give the product. However, the ^{13}C-labeling experiments (*vide infra*) rule out this pathway.

*** In a DMDO epoxidation competition experiment between a 1,3-dialkylallene and bromoallene **4**, only the dialkylallene was consumed. This reveals that bromoallenes are deactivated relative to dialkylallenes. Moreover, in contrast to the epoxidation of bromoallenes, this reaction was very clean suggesting that the necessarily liberated HBr in the Favorskii collapse of the bromocyclopropanone intermediate mediates the decomposition of DMDO. The attempted use of K_2CO_3 (1.5 equiv.) as a base in the DMDO epoxidation of bromoallene **4** did not improve the isolated yield.

‡‡‡However, metabolite **3** is a methyl ester. This could be the result of an isolation artifact since MeOH was used as an extraction solvent (ref. 5 in the main manuscript) (although we found that carboxylic acid (*E*-2-^{13}C)-**5** was not converted into the methyl ester on standing in MeOH at r.t. for 6 days), or by capture of the bromocyclopropanone with MeOH in the algae, or by a biological methylation event of the carboxylic acid. Ethyl esters in an isolation of 3-bromo-2-alkenoic acids from red algae *Bonnemaisonia* were analysed as their esters because the algae was stored in ethanol (ref. 18 in the main manuscript).

General Experimental.

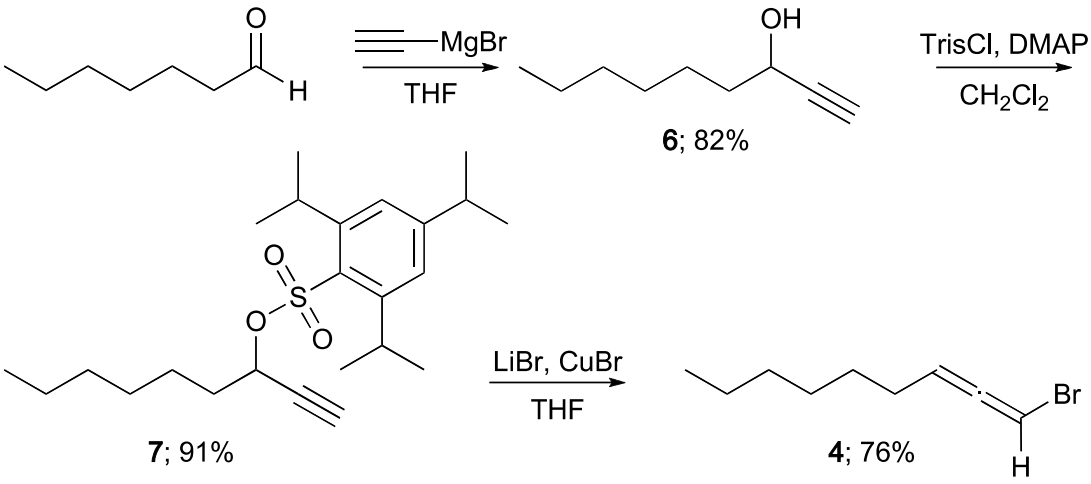
Experimental Techniques: All reactions were carried out in oven-dried glassware. Air-sensitive reactions were performed under a positive pressure of nitrogen. Air and moisture sensitive reagents were transferred by syringe. Reaction temperatures other than room temperature were achieved with a dry-syn and heating mantle, dry ice/acetone bath or dry ice/Et_2O bath. Solvent removal and concentrations were achieved with a rotary evaporator. Column chromatography was performed on Geduran® silica gel, particle size 40-63 μm. Analytical TLC was performed on Kieselgel 60 F254 pre-coated aluminium-backed plates and visualised with either irradiation with UV light (254 or 350 nm) or potassium permanganate/vanillin staining. Brine refers to a saturated aqueous solution of NaCl.

Characterisation: Melting points are uncorrected. Fourier transform infra-red (IR) spectra were recorded neat using an ATR-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker DRX-400 or Bruker AV-400. Chemical shifts (δ) are expressed in parts per million (ppm) relative to the residual solvent peak. ^{1}H NMR spectra were recorded at 400 MHz. ^{13}C NMR spectra were recorded at 101 MHz. ^{31}P NMR spectra were recorded at 162 MHz. Coupling constants (*J*) are quoted in Hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; qu., quintet; sept., septet; m, multiplet. Low resolution MS (ESI, CI) and HRMS were recorded by the Imperial College Department of Chemistry Mass Spectrometry Service.

Reagents: DMDO solutions were distilled under reduced pressure from a flask containing $NaHCO_3$ (2.9 g, 34.5 mmol), oxone (6.0 g, 19.5 mmol), acetone (9.56 mL, 130 mmol) and water (12.7 mL) at 0 °C and collected in a receiver flask at -100 °C as adapted from the reported procedure.[1] Concentrations were determined by iodometric titration or assumed to be 0.1 M. Heptaldehyde, octaldehyde and triethylamine were distilled under nitrogen, and I_2 was sublimed before use. The molarity of *n*BuLi was determined by titration with menthol and 2,2'-bipyridine in THF directly before use.[2] LDA was freshly prepared from *n*BuLi and diisopropylamine in THF at -78 °C under N_2. The yellow solution was warmed to 0 °C, stirred for 30 min and used immediately.[3] All other reagents were obtained from commercial suppliers and used as received.

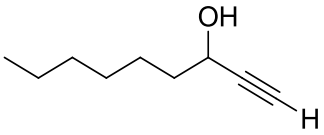
Solvents: All reactions were carried out in anhydrous solvents, unless used in combination with H_2O. HPLC grade CH_2Cl_2, THF, Et_2O and toluene were dried by passing through a column of alumina beads. $CHCl_3$ and MeOH were dried over $MgSO_4$. Extraction solvents and chromatography eluents were used as received. Petroleum ether (40 – 60 °C) and Et_2O were GPR grade. EtOAc and CH_2Cl_2 were GPR or HiPerSolv grade.

Experimental details and characterising data for compounds leading to bromoallene 4



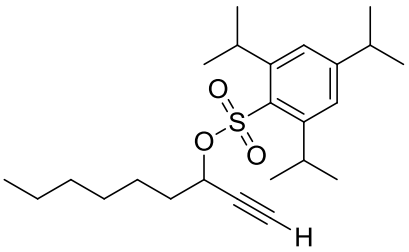
ESI Scheme 1. Synthesis of bromoallene **4**.

Non-1-yn-3-ol (6)



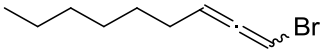
A solution of heptaldehyde (3.00 mL, 21.3 mmol) in THF (43 mL) was added dropwise to a stirred 0.5 M solution of ethynylmagnesium bromide in THF (64 mL, 0.5M, 32.0 mmol) at 0 °C over 20 min. After 1 h, the orange solution was quenched with sat. aq. NH_4Cl solution (8 mL), the solvent removed *in vacuo*, and the residue partitioned between Et_2O (60 mL) and sat. aq. NH_4Cl solution (60 mL). The layers were separated, the organic layer was washed with brine (2 × 60 mL), dried over Na_2SO_4 and the solvent removed *in vacuo* to give a brown oil (3.13g). Column chromatography (petroleum ether : EtOAc 6 : 1) gave the title compound **6** (2.35 g, 17.4 mmol, 82%) as a colourless oil: R_f 0.31 (petroleum ether : EtOAc 6 : 1); IR (neat) 3600-3100, 3310, 1038 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 4.34 (td, J = 6.6, 2.0 Hz, 1H, C*H*OH), 2.43 (d, J = 2.0 Hz, 1H, C≡C*H*), 2.01 (br. s, 1H, O*H*), 1.73 – 1.64 (m, 2H, CH_2), 1.46 – 1.38 (m, 2H, CH_2), 1.31 – 1.23 (m, 6H, 3 × CH_2), 0.86 (t, J = 6.7 Hz, 3H, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 85.1 (*C*≡CH), 72.8 (C≡*C*H), 62.3 (*C*OH), 37.7 (*C*H_2), 31.7 (*C*H_2), 28.9 (*C*H_2), 25.0 (*C*H_2), 22.6 (*C*H_2), 14.1 (*C*H_3); MS (CI^+, NH_3) m/z 158 $(M + NH_4)^+$; HRMS (CI^+, NH_3) m/z calcd for $C_9H_{20}NO$ $(M + NH_4)^+$ 158.1545, found 158.1538.

Non-1-yn-3-yl 2,4,6-tris(propan-2-yl)benzene-1-sulphonate (7)



According to the method of Kim,[4] to a solution of alcohol **6** (1.10 g, 7.86 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added a solution of 2,4,6-triisopropylbenzenesulfonyl chloride (2.38 mg, 7.86 mmol) in CH_2Cl_2 (20 mL) followed by a solution of DMAP (208 mg, 1.70 mmol) in CH_2Cl_2 (20 mL). The colourless solution was warmed to room temperature and stirred for 19 h until TLC (petroleum ether : EtOAc 6 : 1) showed completion of the reaction. The solution was passed through a silica plug with Et_2O and the solvent was removed *in vacuo* to give a light yellow oil (3.02 g). Column chromatography (petroleum ether : EtOAc 50 : 1 to 40 : 1) gave the title compound **7** (2.91 g, 7.16 mmol, 91%) as a colourless oil: R_f 0.78 (petroleum ether : EtOAc 6 : 1); IR (neat) 3312, 1560, 1463, 1350, 1176, 938 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 7.14 (s, 2H, 2 × Ar-*H*), 5.14 (td, *J* = 6.4, 2.0 Hz, 1H, C*H*OTris), 4.13 (sept., *J* = 6.8 Hz, 2H, 2 × *ortho*-C*H*$(CH_3)_2$), 2.88 (sept., *J* = 6.8 Hz, 1H, *para*-C*H*$(CH_3)_2$), 2.26 (d, *J* = 2.0 Hz, 1H, C≡C*H*), 1.85 – 1.78 (m, 2H, CH_2), 1.48 – 1.40 (m, 2H, CH_2), 1.26 – 1.20 (m, 6H, 3 × CH_2), 1.25 (d, *J* = 7.0 Hz, 6H, *ortho*-CH(CH_3)$_2$), 1.24 (d, *J* = 7.0 Hz, 6H, *ortho*-CH(CH_3)$_2$), 1.23 (d, *J* = 7.0 Hz, 6H, *para*-CH(CH_3)$_2$), 0.85 (t, *J* = 6.9 Hz, 3H, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 153.6 (*para*-C), 150.6 (2 × *ortho*-C), 130.8 (*ipso*-C), 123.6 (2 × *meta*-C), 79.2 (*C*≡CH), 75.9 (C≡*C*H), 70.2 (*C*OTris), 35.7 (*C*H_2), 34.3 (*para*-*C*H$(CH_3)_2$), 31.6 (*C*H_2), 29.6 (2 × *ortho*-*C*H$(CH_3)_2$), 28.6 (*C*H_2), 24.7 (2 × *ortho*-CH(*C*H_3)$_2$), 24.7 (2 × *ortho*-CH(*C*H_3)$_2$) 24.6 (*C*H_2), 23.6 (2 × *para*-CH(*C*H_3)$_2$), 22.5 (*C*H_2), 14.0 (*C*H_3); MS (CI^+, NH_3) *m*/*z* 424 $(M + NH_4)^+$; HRMS (CI^+, NH_3) *m*/*z* calcd for $C_{24}H_{42}NO_3S$ $(M + NH_4)^+$ 424.2885, found 424.2887.

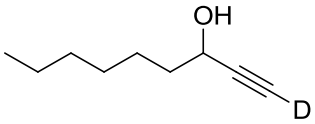
1-Bromonona-1,2-diene (4)



According to the method of Kim,[4] LiBr (896 mg, 10.3 mmol) and CuBr (1.48 g, 10.3 mmol) were dissolved in THF (41 mL) and stirred at room temperature for 30 min. The green solution was transferred to a solution of trisylate **7** (1.40 g, 3.44 mmol) in THF (172 mL) and stirred at reflux for 30 min. The solvent was removed *in vacuo* and the brown residue was passed though a short silica plug eluting with petroleum ether. Column chromatography (hexane) gave the title compound **4** (529 mg, 2.60 mmol, 76%) as a colourless oil: R_f 0.78 (petroleum ether : EtOAc 50 : 1); IR (neat) 3059, 1956, 652 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.91 (dt, *J* = 5.4, 2.4 Hz, 1H, HC=C=C*H*Br), 5.38 (app. q., *J* = 5.4 Hz 1H, *H*C=C=CHBr), 2.13 (qd, *J* = 7.0, 2.4 Hz, 2H, CH_2CH=C), 1.48-1.36 (m, 2H, CH_2), 1.35 – 1.23 (m, 6H, 3 × CH_2), 0.87 (t, *J* = 7.0 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1(C=*C*=C), 101.1 (H*C*=C=CHBr), 72.2 (HC=C=*C*HBr), 31.6 (*C*H_2), 28.7 (*C*H_2), 28.3 (*C*H_2), 28.3 (*C*H_2), 22.6 (*C*H_2), 14.1 (*C*H_3). The molecular ion for this compound could not be observed by electron or chemical ionisation methods.

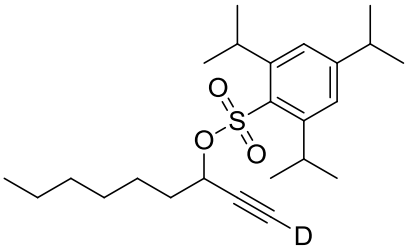
Experimental details and characterising data for compounds leading to bromoallene (1-^{2}H)-4

(1-^{2}H)-Non-1-yn-3-ol [(1-^{2}H)-6]



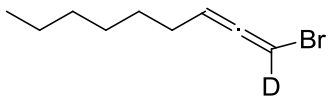
A 0.5 M solution of heptaldehyde (2.50 mL, 17.7 mmol) inTHF (35.5 mL) was added to a stirred solution of 0.5 M ethynylmagnesium bromide (58.7 mL, 26.6 mmol) at 0 °C over 20 min. After 1 h, a solution of *n*-BuLi in hexanes (12 mL, 2.21M, 26.6 mmol) was added dropwise over 5 min. and stirred for an additional 1 h at room temperature. MeOH-d_4 (2.00 mL, 49.2 mmol) was added dropwise to the orange solution before being quenched with sat. aq. NH_4Cl solution (20 mL) and the solvent removed *in vacuo*. The resulting brown residue was triturated with Et_2O (2 × 20 mL), the organic layers were combined and dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give a yellow oil (2.93 g). Column chromatography (petroleum ether : EtOAc 6 : 1) gave the title compound (1-^{2}H)-**6** (2.13 g, 15.1 mmol, 85 %, 70% alkyne deuteration) as a colourless oil [the extent of deuterium incorporation was deduced by inspection of the relative integral (0.30H) for residual non-deuterated alkyne **6** at 2.43 ppm in the ^{1}H NMR spectrum (see ESI p24)]: R_f 0.18 (petroleum ether : EtOAc 6 : 1); IR (neat) 3600-3100, 2593 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 4.34 (t, J = 6.6 Hz, 1H, C*H*OH), 1.92 (br. s, 1H, O*H*), 1.72 – 1.65 (m, 2H, CH_2), 1.47 – 1.38 (m, 2H, CH_2), 1.34 – 1.23 (m, 6H, 3 × CH_2), 0.86 (t, J = 6.7 Hz, 3H, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 84.6 (t, $^2J_{CD}$ = 7.2 Hz, *C*≡CD), 72.6 (t, $^1J_{CD}$ = 38.1 Hz, C≡*C*D), 62.3 (*C*OH), 37.7 (*C*H_2), 31.7 (*C*H_2), 28.9 (*C*H_2), 25.0 (*C*H_2), 22.6 (*C*H_2), 14.1 (*C*H_3); MS (CI$^+$, NH_3) *m/z* 159 (M + NH_4)$^+$; HRMS (CI$^+$, NH_3) *m/z* calcd for $C_9H_{19}{}^2HNO$ (M + NH_4)$^+$ 159.1602, found 159.1604.

(1-^{2}H)-Non-1-yn-3-yl 2,4,6-tris(propan-2-yl)benzene-1-sulphonate [(1-^{2}H)-7]



According to the method of Kim,[4] to a solution of (1-^{2}H)-non-1-yn-3-ol (1-^{2}H)-**6** (1.05 g, 7.42 mmol) in CH_2Cl_2 (18 mL) at 0°C was added a solution of 2,4,6-triisopropylbenzenesulfonyl chloride (2.25 g, 5.55 mmol) in CH_2Cl_2 (10 mL), followed by a solution of DMAP (907 mg, 7.42 mmol) in CH_2Cl_2 (10 mL). The colourless solution was warmed to room temperature and stirred for 19 h until TLC (petroleum ether : EtOAc 6 : 1) showed completion. The solution was passed through a silica plug with Et_2O and the solvent was removed *in vacuo* to give a light yellow oil (2.90 g). Column chromatography (petroleum ether : EtOAc 50 : 1 to 6 : 1) gave the title compound (1-^{2}H)-**7** (2.85 g, 6.98 mmol, 94%, 70% deuteration) as a colourless oil [the deuterium content was deduced by inspection of the integral (0.30H) for residual non-deuterated alkyne **7** at 2.26 ppm in the ^{1}H NMR spectrum (see ESI p25)]: R_f 0.63 (petroleum ether : EtOAc 6 : 1); IR (neat) 2594 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.14 (s, 2H, 2 × Ar-*H*), 5.14 (t, *J* = 6.5 Hz, 1H, C*H*OTris), 4.13 (sept., *J* = 6.8 Hz, 2H, 2 × *ortho*-C*H*$(CH_3)_2$), 2.88 (sept., *J* = 6.8 Hz, 1H, *para*-C*H*$(CH_3)_2$), 1.86 – 1.79 (m, 2H, CH_2), 1.48 – 1.39 (m, 2H, CH_2), 1.31 – 1.23 (m, 6H, 3 × CH_2), 1.30 (d, *J* = 6.8 Hz, 6H, *ortho*-CH(CH_3)$_2$), 1.29 (d, *J* = 6.8 Hz, 6H, *ortho*-CH(CH_3)$_2$), 1.27 (d, *J* = 7.0 Hz, 6H, *para*-CH(CH_3)$_2$), 0.85 (t, *J* = 6.9 Hz, 3H, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 153.6 (*para*-C), 150.6 (2 × *ortho*-C), 130.8 (*ipso*-C), 123.6 (2 × *meta*-C), 78.7 (t, $^2J_{CD}$ = 6.5 Hz, *C*≡CD), 75.9 (t, $^1J_{CD}$ = 38.7 Hz, C≡*C*D), 70.2 (*C*OTris), 35.7 (*C*H_2), 34.3 (*para*-*C*H$(CH_3)_2$), 31.6 (*C*H_2), 29.6 (2 × *ortho*-*C*H$(CH_3)_2$), 28.6 (*C*H_2), 24.7 (2 × *ortho*-CH(*C*H_3)$_2$), 24.7, (2 × *ortho*-CH(*C*H_3)$_2$), 24.6 (*C*H_2), 23.6 (2 × *para*-CH(*C*H_3)$_2$), 22.5 (*C*H_2), 14.0 (*C*H_3); MS (CI$^+$, NH_3) *m/z* 425 (M + NH_4)$^+$; HRMS (CI$^+$, NH_3) *m/z* calcd for $C_{24}H_{41}{}^2HNO_3S$ (M + NH_4)$^+$ 425.2943, found 425.2938.

(1-^{2}H)-1-Bromonona-1,2-diene [(1-^{2}H)-4]

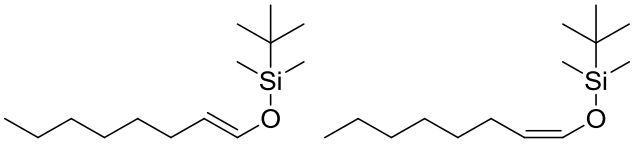


According to the method of Kim,[4] LiBr (895 mg, 10.3 mmol) and CuBr (1.48 g, 10.3 mmol) dissolved in THF (41 mL) and stirred at room temperature for 30 min. The green solution was transferred to a solution of propargylic trisylate (1-^{2}H)-**7** (1.40 g, 3.43 mmol) in THF (172 mL) at stirred at reflux for 30 min. The solvent was removed *in vacuo* and the brown residue was passed though a short silica plug with petroleum ether. The solvent was removed *in vacuo* once more to give a yellow oil (745 mg). Column chromatography (petroleum ether) gave the title compound (1-^{2}H)-**4** (482 mg, 2.36 mmol, 69%, 70% deuteration) as a colourless oil [the deuterium content was deduced by inspection of the integral (0.30H) for the residual non-deuterated allene **4** at 5.91 ppm in the ^{1}H NMR spectrum (see ESI p26)]: R_f 0.63 (petroleum ether : EtOAc 50 : 1); IR (neat) 1940, 653

cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 – 5.35 (m, 1H, *H*C=C=CDBr), 2.13 (q, *J* = 7.0 Hz, 2H, C*H*$_2$CH=C), 1.47 – 1.39 (m, 2H, C*H*$_2$), 1.35 – 1.24 (m, 6H, 3 × C*H*$_2$), 0.87 (t, *J* = 6.8 Hz, 3H, C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0 (HC=*C*=CDBr), 101.2 (H*C*=C=CDBr), 72.2 (t, $^{1}J_{CD}$ = 32.5 Hz, HC=C=*C*DBr), 31.6 (*C*H$_2$), 28.7 (*C*H$_2$), 28.4 (*C*H$_2$), 28.3 (*C*H$_2$), 22.6 (*C*H$_2$), 14.1 (*C*H$_3$); The molecular ion for this compound could not be observed by electron or chemical ionisation methods.

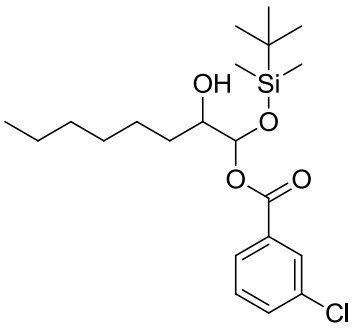
Experimental details and characterising data for compounds leading to bromoallene (1-^{13}C)-4

(*E*)-*tert*-Butyldimethyl(oct-1-enyloxy)silane and (*Z*)-*tert*-butyldimethyl(oct-1-enyloxy)silane (8)



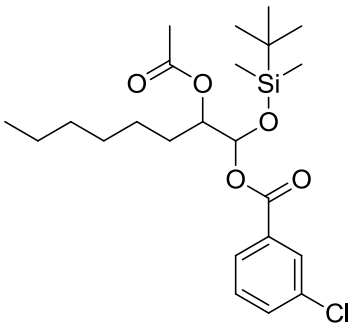
Using a modified procedure of Taniguchi,[5] to a solution of octaldehyde (900 mg, 1.10 mL, 7.0 mmol) in CH_2Cl_2 (9.6 mL) at room temperature was added *tert*-butyldimethylsilyl chloride (1.27 g, 8.45 mmol) followed by DBU (1.72 g, 1.69 mL, 11.3 mmol) and stirred for 1.5 h. Water (xx mL) was added to the yellow solution, the layers were separated, and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with brine (2 × 10 mL), dried over Na_2SO_4 and the solvent removed *in vacuo* to give the crude product as a yellow oil (2.08 g). Column chromatography (petroleum ether : EtOAc 20 : 1) gave the title compounds (*E*)-**8** and (*Z*)-**8** (1.32 g, 5.46 mmol, 78%) as a colourless oil as an inseparable mixture (2 : 1 respectively): R_f 0.75 (petroleum ether : EtOAc 5 : 1); IR (neat) 3034, 1660, 1254, 1163 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) (*E*)-**8**: δ 6.20 (dt, *J* = 11.9, 1.4 Hz, 1H, C*H*OTBS), 4.96 (dt, *J* = 11.9, 7.5 Hz, 1H, CH_2CH), 1.85 (q, *J* = 7.5 Hz, 2H, CH_2CH), 1.34 – 1.20 (m, 8H, 4 × CH_2), 0.90 (s, 9H, $C(CH_3)_3$), 0.86 (t, *J* = 6.8 Hz, 3H, CH_3), 0.10 (s, 6H, $Si(CH_3)_2$); (*Z*)-**8**: 6.14 (dt, *J* = 5.8, 1.4 Hz 1H, C*H*OTBS), 4.42 (dt, *J* = 6.9, 5.8 Hz, 1H, CH_2CH), 2.05 (q, *J* = 6.9 Hz, 2H, CH_2CH), 1.34 – 1.20 (m, 8H, 4 × CH_2), 0.90 (s, 9H, $C(CH_3)_3$), 0.86 (t, *J* = 6.8 Hz, 3H, CH_3), 0.10 (s, 6H, $Si(CH_3)_2$); ^{13}C NMR (101 MHz, $CDCl_3$) (*E*)-**8**: δ 140.0 (*C*HOTBS), 111.8 (CH_2CH), 31.7 (CH_2), 30.4 (CH_2), 28.8 (CH_2), 27.3 (CH_2), 25.8 ($C(CH_3)_3$), 22.7 (CH_2), 18.4 ($C(CH_3)_3$), 14.1 (CH_3), -5.2 ($Si(CH_3)_2$); (*Z*)-**8**: δ 138.4 (*C*HOTBS), 110.9 (CH_2CH), 31.8 (CH_2), 30.4 (CH_2), 29.7 (CH_2), 29.0 (CH_2), 25.7 ($C(CH_3)_3$), 23.6 (CH_2), 18.3 ($C(CH_3)_3$), 14.1 (CH_3), -5.4 ($Si(CH_3)_2$); MS (EI^+) *m/z* 242 $(M)^{+\cdot}$; HRMS (EI^+) *m/z* calcd for $C_{14}H_{30}OSi$ $(M)^{+\cdot}$ 242.2066, found 242.2078.

1-[(*tert*-Butyldimethylsilyl)oxy]-2-hydroxyoctyl 3-chlorobenzoate (9)



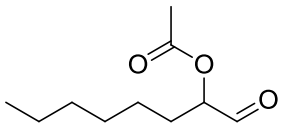
According to the method of Hassner,[6] to a stirred solution of (*E*)- and (*Z*)- silyl enol ethers **8** (600 mg, 2.47 mmol, 7 : 3) in $CHCl_3$ (8.4 mL) was added *m*CPBA (779 mg, 3.48 mmol) at 0 °C. After 1 h, the colourless solution was transferred to a separating funnel and washed with brine (2 × 10 mL). The aqueous layer was extracted with Et_2O (2 × 10mL). The combined organic layers were dried over Na_2SO_4 and the solvent removed *in vacuo* to give the crude product (1.30 g, 56 : 44 d.r.) which could be used directly in the subsequent acetylation. Column chromatography (petroleum ether : EtOAc 15: 1) provided analytically pure **9** (903 mg, 2.17 mmol, 88%, 61 : 39 d.r.) as a colourless oil: R_f 0.51 (petroleum ether : EtOAc 3 : 1); IR (neat) 3600-3300, 1726, 1254, 835, 780 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.99 (m, 1H, ArH), 7.96 – 7.91 (m, 1H, ArH), 7.56 – 7.51 (m, 1H, ArH), 7.38 (t, *J* = 7.9 Hz, 1H, ArH), 6.14 (d, *J* = 4.0 Hz, 0.61H, C*H*OTBS), 6.11 (d, *J* = 3.9 Hz, 0.39H, C*H*OTBS), 3.73 – 3.66 (m, 1H, C*H*OH), 2.03 (br. s, 1H, O*H*), 1.63 – 1.41 (m, 2H, CH_2COH), 1.34 – 1.23 (m, 4H, 2 × CH_2), 0.89 – 0.88 (m, 9H, C(CH_3)$_3$), 0.85 (t, *J* = 6.6 Hz, 3H, CH_3), 0.17 (s, 3H, Si(CH_3)), 0.07 (s, 1.17H, Si(CH_3)), 0.06 (s, 1.83H, Si(CH_3)); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6 & 164.5 (CO_2Ar), 134.7 (*C*-Cl), 133.4 (*ipso*-C), 131.7 (*para*-C), 129.8 (*ortho* & *meta*-C), 127.9 (*ortho*-C), 94.2 & 93.9 (*C*HOTBS), 73.7 & 73.5 (*C*HOH), 31.9, 31.8, 31.3, 29.3 & 29.2 (3 × CH_2), 25.7 (C(CH_3)$_3$), 25.4, 25.3 & 22.6 (2 × CH_2), 18.0 ($C(CH_3)_3$), 14.1 (CH_3), -4.5 & -5.3 (Si(CH_3)$_2$); MS (CI^+, NH_3) *m/z* 301 $(M - TBS)^+$, 276 $(M - O_2CAr + NH_3)^+$, 259 $(M - O_2CAr + H)^+$.

1-[(*tert*-Butyldimethylsilyl)oxy]-1-[(3-chlorophenyl)carbonyloxy-2-yl acetate (10)



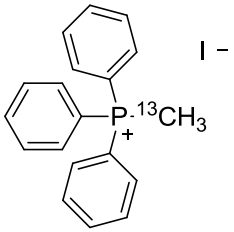
To a stirred solution of alcohol **9** (4.48 g, 10.8 mmol, 0.56 : 0.44 d.r.) in Et_2O (112.5mL) at room temperature was added Ac_2O (2.34 g, 2.16 mL, 22.9 mmol), Et_3N (3.13 g, 4.31mL, 30.9 mmol) and DMAP (35.5 mg, 0.29 mmol). After 4 h, the colourless solution was quenched with MeOH and stirred for a further 10 min. The solution was transferred to a separating funnel and washed successively with sat. aq. $NaHCO_3$ solution (2 × 50 mL), 1M HCl (2 × 50 mL) and brine (2 × 50 mL). The organic layer was dried over Na_2SO_4 and the solvent removed *in vacuo* to give the title compound **10** (4.89 g, 10.7 mmol, 99%, 56 : 44 d.r.) as a colourless oil: R_f 0.68 (petroleum ether : EtOAc 10 : 1); IR (neat) 1729 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 1H, ArH), 7.93 – 7.87 (m, 1H, ArH), 7.54 - 7.49 (m, 1H, ArH), 7.40 – 7.34 (m, 1H, ArH), 6.28 (d, *J* = 3.5 Hz, 0.44H, C*H*OTBS), 6.20 (d, *J* = 5.0 Hz, 0.56H, C*H*OTBS), 5.05 (ddd, *J* = 8.8, 5.0, 3.7 Hz, 0.56H, C*H*OAc), 4.96 (dt, *J* = 9.5, 3.5 Hz, 0.54H, C*H*OAc), 2.02 (s, 1.32H, O_2CCH_3), 1.96 (s, 1.68H, O_2CCH_3), 1.80 – 1.60 (m, 2H, CH_2), 1.40 – 1.20 (m, 8H, 4 × CH_2), 0.87 (s, 9H, $C(CH_3)_3$), 0.85 (t, *J* = 6.6 Hz, 3H, CH_3), 0.15 (m, 3H, $Si(CH_3)$), 0.05 (m, 3H, $Si(CH_3)$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6 & 170.2 (O_2CCH_3), 164.3 (O_2CCH_3), 134.7 & 134.7 (*C*-Cl), 133.3 & 133.3 (*ipso*-C), 131.8 & 131.6 (*para*-C), 129.8 (*ortho* & *meta*-C), 127.9 (*ortho*-C), 92.1 & 91.5 (*C*HOTBS), 74.5 & 74.3 (*C*HOAc), 31.7, 29.1, 29.0, 29.0 & 27.4 (3 × CH_2), 25.6 ($C(CH_3)_3$), 25.3, 24.9 & 22.6 (2 × CH_2), 21.0 & 20.9 (CO_2CH_3), 17.9, ($C(CH_3)_3$), 14.1 (CH_3), -4.5, -4.6 & -5.3 ($Si(CH_3)_2$); MS (ES^+, TOF) *m/z* 479 $(M + Na)^+$; HRMS (ES^+, ToF) *m/z* calcd for $C_{23}H_{37}O_5{}^{35}ClSiNa$ $(M + Na)^+$ 479.1995, found 479.1995.

1-Oxooctan-2-yl acetate (11)



According to a modified method of Fraser-Reid,[7] to a stirred solution of acetate **10** (4.79 g, 10.5 mmol) in THF (144 mL) was added AcOH (5.26 mL, 91.9 mmol) and a solution of TBAF in THF (26.2 mL, 1M, 26.2 mmol). The colourless solution was stirred at room temperature for 90 min before being transferred to a separating funnel and washed successively with sat. aq. $NaHCO_3$ solution (2 × 100 mL) and 1M HCl (2 × 100mL). The aqueous layers were extracted with Et_2O (2 × 50mL). The combined organic layers were washed with brine (2 × 100 mL), dried over Na_2SO_4 and the solvent removed *in vacuo* to give the crude product (2.12 g). Column chromatography (petroleum ether : EtOAc 5: 1) gave the title compound **11** (1.29 g, 6.93 mmol, 66%) as a colourless oil: R_f 0.38 (petroleum ether : EtOAc 5 : 1); IR (neat) 1738, 1231 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H, C*H*O), 4.95 (dd, *J* = 8.6, 4.7 Hz, 1H, C*H*OAc), 2.14 (s, 3H, O_2CCH_3), 1.99 – 1.56 (m, 2H, CH_3), 1.44 – 1.32 (m, 2H, CH_2), 1.33 – 1.21 (m, 6H, 3 × CH_2), 0.85 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4 (*C*HO), 170.6 (O_2CCH_3), 78.4 (*C*HOAc), 31.5 (CH_2), 28.9 (CH_2), 28.6 (CH_2), 24.9 (CH_2), 22.5 (CH_2), 20.6 (O_2CCH_3), 14.0 (CH_3). The molecular ion for this compound could not be observed by electron or electrospray ionisation methods.

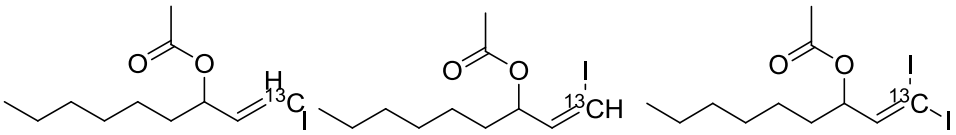
(^{13}C)-Methyltriphenylphosphonium iodide [(^{13}C)-12]



According to a modified method of Sato,[8] to a solution of PPh_3 (1.84 g, 7.00 mmol) in dry THF (10 mL) in a Schlenk tube was added ^{13}MeI (99 atom % ^{13}C, 0.440 mL, 7.00 mmol) dropwise with minimal stirring. A white precipitate formed immediately. After stirring overnight, the solvent was removed via cannula. The white crystals were washed with THF (3 × 5 mL) and the solvent again removed via cannula to give the phosphonium salt (^{13}C)-**12** (99% ^{13}C atom) in quantitative yield [the extent of ^{13}C incorporation was deduced by inspection of the relative integral (0.03H, 3H) for residual non-labeled phosphonium salt **12** at 2.20 ppm in the ^1H NMR spectrum (see ESI p31)]: m.p. 175-176 °C; IR (neat) 3017, 2919, 1586, 1490, 1440, 999, 752, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.50 (m, 15H, 15 × Ar-H), 3.20 (dd, $^1J_{CH}$ = 135.1 Hz, $^2J_{PH}$ = 13.2 Hz, 3H, $^{13}CH_3$]; ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2 (d, *J* = 2.6 Hz, 3 × *para*-C), 133.4 (d, *J* = 10.8 Hz, 6 × *meta*-C), 130.5 (d, *J* = 12.9 Hz, 6 × *ortho*-C), 119.0 (d, *J* = 89.4 Hz, 3 × *ipso*-C), 11.6 (d, *J* = 57.0 Hz, $^{13}CH_3$); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.57 (d, *J* = 56.8 Hz, 1P). MS (ES^+, ToF) *m/z* 278 ($M - I^-$

)$^+$; HRMS (ES$^+$, ToF) *m/z* calcd for $C_{18}{}^{13}CH_{18}{}^{31}P$ $(M - I^-)^+$ 278.1180, found 278.1191.

(*E*-1-^{13}C)-1-Iodonon-1-en-3-yl acetate [(*E*-1-^{13}C)-13], (*Z*-1-^{13}C)-1-Iodonon-1-en-3-yl acetate [(*Z*-1-^{13}C)-13] & (1-^{13}C)-1,1-diiodonon-1-en-3-yl acetate [(1-^{13}C)-14]



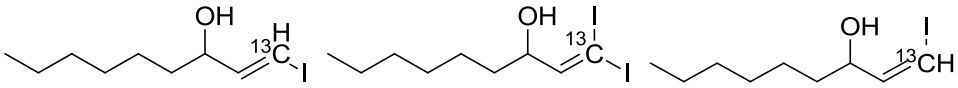
According to an adapted method of Curran,[9] to a stirred suspension of phosponium salt (1-^{13}C)-**12** (2.70 g, 6.63 mmol) in THF (14.2 mL) at 0 °C was added *n*-BuLi in hexanes (3.00 mL, 2.21M, 6.63 mmol). After 10 min, the orange solution was transferred to a stirred solution of I_2 (1.68 g, 6.63 mmol) in THF (21.5 mL) at -78 ˚C over 30 min. The resulting brown suspension was stirred for 30 min at -78 ˚C, and a solution of sodium hexamethyldisilazane in THF (3.6 mL, 1.0 M, 3.6 mmol) was added dropwise over 15 min. The resulting red suspension was stirred at -78 °C for 30 min, then -20 °C for 15 min, re- cooled to -78 °C and a 1 M solution of aldehyde **11** (1.060 g, 5.69 mmol) in THF (5.69 mL) was added dropwise over 30 min. The orange suspension was stirred at -78 °C for 30 min, -20 °C for 1 h and finally room temperature for 1 h. TLC (petroleum ether : EtOAc 5 : 1) of the yellow suspension showed that no aldehyde remained. The reaction mixture was passed through a short silica plug with petroleum ether : EtOAc 5 :1 and the solvent removed *in vacuo* to give the crude product (1.15 g) as a yellow oil. Column chromatography (petroleum ether : EtOAc 50 : 1) gave a 2 : 3 : 5 mixture of iodoalkene acetates (*E*-1-^{13}C)-**13** : (*Z*-1-^{13}C)-**13** : (1-^{13}C)-**14** (705 mg, 1.87 mmol, 33%) as a colourless oil, which could be subsequently deprotected as a mixture. Separation of *E*-**13** and *Z*-**13** geometrical isomers from each other, but not diiodide **14** from either was possible by careful column chromatography. Each compound was formed as 99% 1-^{13}C atom [the extent of ^{13}C incorporation at the 1-position was deduced by inspection of their ^{1}H NMR and ^{13}C NMR spectra (see ESI p33-34)].

Iodide (*E*-1-^{13}C)-**13** (99% 1-^{13}C atom): R_f 0.58 (petroleum ether : EtOAc 10 : 1); IR (neat) 1738, 1590 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (ddd, $^1J_{CH}$ = 190.4 Hz, *J* = 15.6, 0.9 Hz, 1H, ^{13}C*H*I), 6.45 (ddd, $^2J_{CC}$ = 7.0 Hz, *J* = 15.6, 7.0, Hz, 1H, C*H*=^{13}CHI), 5.15 (app. qu., *J* = 6.9 Hz, 1H, C*H*OAc), 2.04 (s, 3H, O_2CCH_3), 1.70 – 1.50 (m, 2H, CH_2), 1.40 – 1.20 (m, 8H, 4 × CH_2), 0.86 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3 (O_2CCH_3), 144.0 (d, $^1J_{CC}$ = 76.1 Hz, *C*H=^{13}CHI), 79.8 (^{13}*C*HI), 75.7 (*C*HOAc), 33.7 (*C*H_2), 31.6 (*C*H_2), 28.9 (*C*H_2), 24.9 (*C*H_2), 22.6 (*C*H_2), 21.2 (O_2C*C*H_3), 14.1 (*C*H_3).

Iodide (*Z*-1-^{13}C)-**13** (99% 1-^{13}C atom): R_f 0.53 (petroleum ether : EtOAc 10 : 1); IR (neat) 1737, 1594 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (ddd, $^1J_{CH}$ = 184.6 Hz, J = 8.0, 0.9 Hz, 1H, ^{13}C*H*I), 6.20 (ddd, $^2J_{CH}$ = 15.5, J = 8.0, 7.8 Hz, 1H, C*H*=^{13}CHI), 5.40 (app. qu., J = 6.6 Hz, 1H, C*H*OAc), 2.03 (s, 3H, O_2CCH_3), 1.75 – 1.55 (m, 2H, CH_2), 1.35 – 1.20 (m, 8H, 4 × CH_2), 0.87 (t, J = 6.9 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1 (O_2CCH_3), 139.8 (d, $^1J_{CC}$ = 76.0 Hz, *C*H=^{13}CHI), 83.6 (^{13}*C*HI), 79.3 (*C*HOAc), 33.4 (*C*H_2), 32.9 (*C*H_2), 31.7 (*C*H_2), 29.1 (*C*H_2), 24.7 (*C*H_2), 21.1 (O_2CCH_3), 14.1 (*C*H_3).

Diiodide (1-^{13}C)-**14** (99% 1-^{13}C atom): R_f 0.56 (petroleum ether : EtOAc 10 : 1); IR (neat) 1738, 1575 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, J = 7.6 Hz, 1H, C*H*=CI_2), 5.11-4.98 (m, 1H, C*H*OAc), 2.03 (s, 3H, O_2CCH_2), 1.75 – 1.55 (m, 2H, CH_2), 1.40 – 1.20 (m, 8H, 4 × CH_2), 0.87 (t, J = 6.9 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0 (O_2CCH_3), 150.7 (d, $^1J_{CC}$ = 75.7 Hz, *C*H=$^{13}CI_2$), 79.3 (*C*HOAc), 33.4 (*C*H_2), 31.6 (*C*H_2), 29.0 (*C*H_2), 24.6 (*C*H_2), 22.6 (*C*H_2), 21.0 (O_2CCH_3), 14.1($^{13}CI_2$ & *C*H_3).

(*E*-1-^{13}C)-1-Iodonon-1-en-3-ol [(*E*-1-^{13}C)-15], (*Z*-1-^{13}C)-1-Iodonon-1-en-3-ol [(*Z*-1-^{13}C)-15] & (1-^{13}C)-1,1-diiodo-non-1-en-3-ol [(1-^{13}C)-16]



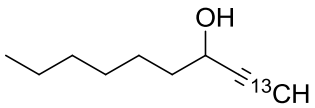
According to a modified procedure of Bakkestuen,[10] to a 2 : 3 : 5 mixture (691 mg, 1.82 mmol) of acetates (*E*-1-^{13}C)-**13** : (*Z*-1-^{13}C)-**13** : (1-^{13}C)-**14** was added a 3% solution of K_2CO_3 in MeOH (27.3 mL, 5.92 mmol) and the cloudy mixture stirred at room temperature for 18 h. The reaction was quenched with sat. aq. NH_4Cl solution (10 mL) and extracted with Et_2O (3 × 30 mL). The organic layers were dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give a colourless oil as a 2 : 3 : 5 mixture of alcohols (*E*-1-^{13}C)-**15** : (*Z*-1-^{13}C)-**15** : (1-^{13}C)-**16** (666 mg, 86% purity, 1.72 mmol, 94%) which could be used directly in the subsequent dehydrohalogenation. Column chromatography of a small quantity of the mixture (petroleum ether : EtOAc 10 : 1) separated iodide (*Z*-1-^{13}C)-**15** from a mixture of iodide (*E*-1-^{13}C)-**15** and diiodide (1-^{13}C)-**16** to give each as colourless oils with 99% 1-^{13}C atom [the ^{13}C content at the 1-position was deduced by inspection of their ^{1}H NMR and ^{13}C NMR spectra (see ESI p35-36)].

Iodide (*E*-1-^{13}C)-**15**: (99% 1-^{13}C atom); R_f 0.36 (petroleum ether : EtOAc 5 : 1); IR (neat) 3600-3100, 1587 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 6.56 (dd, J = 14.6, 6.5 Hz, 1H, C*H*=^{13}CHI), 6.33 (ddd. $^1J_{CH}$ = 194.7, J = 14.6, 1.2 Hz, 1H, CH=^{13}C*H*I), 4.07 (app. qu., J = 6.5 Hz, 1H, C*H*OH), 1.80 – 1.60 (br. s, 1H, OH), 1.61 – 1.48 (m, 2H, CH_2), 1.40 – 1.20 (m, 8H, 4 × CH_2), 0.86 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7 (d, $^1J_{CC}$ = 75.4 Hz, *C*H=^{13}CHI), 77.1 (^{13}*C*HI), 74.7 (*C*HOH), 36.6 (*C*H_2), 31.7 (*C*H_2), 29.1 (*C*H_2), 25.1 (*C*H_2), 22.6 (*C*H_2), 14.1 (*C*H_3).

Iodide (*Z*-1-^{13}C)-**15**: (99% 1-^{13}C atom); R_f 0.30 (petroleum ether : EtOAc 5 : 1); IR (neat) 3600-3100, 1592 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 6.30 (ddd, $^1J_{CH}$ = 193.8, J = 7.6, 0.9 Hz, 1H, CH=^{13}C*H*I), 6.22 (app. q,. J = 7.8 Hz, 1H, C*H*=^{13}CHI), 4.38 (app. qu., J = 6.7 Hz, 1H, C*H*OH), 1.75 – 1.65 (br. s, 1H, OH), 1.64 – 1.51 (m, 2H, CH_2), 1.40 – 1.20 (m, 8H, 4 × CH_2), 0.87 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4 (d, $^1J_{CC}$ = 74.7 Hz, *C*H=^{13}CHI), 82.3 (^{13}*C*HI), 74.4 (*C*HOH), 35.9 (*C*H_2), 31.8 (*C*H_2), 29.2 (*C*H_2), 24.9 (*C*H_2), 22.6 (*C*H_2), 14.1 (*C*H_3).

Diiodide (1-^{13}C)-**16**: (99% 1-^{13}C atom); R_f 0.36 (petroleum ether : EtOAc 5 : 1); IR (neat) 3600-3100, 1566, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.01 (d, J = 7.8 Hz, 1H, C*H*=^{13}CI_2), 4.01 (app. qu., J = 7.4 Hz, 1H, C*H*OH), 1.80 – 1.60 (br. s, 1H, OH), 1.61 – 1.48 (m, 2H, CH_2), 1.40 – 1.20 (m, 8H, 4 × CH_2), 0.87 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7 (d, $^1J_{CC}$ = 75.0 Hz, *C*H=^{13}CHI), 78.0 (*C*HOH), 35.4 (*C*H_2), 31.7 (*C*H_2), 29.2 (*C*H_2), 24.9 (*C*H_2), 22.6 (*C*H_2), 14.1 (*C*H_3), 12.3 (^{13}*C*HI).

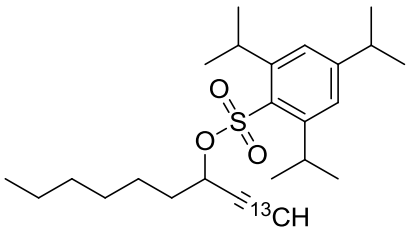
(1-^{13}C)-Non-1-yn-3-ol [(1-^{13}C)-6]



To a 2 : 3 : 5 mixture (533 mg, 1.60 mmol) of alcohols (*E*-1-^{13}C)-**15** : (*Z*-1-^{13}C)-**15** : (1-^{13}C)-**16** in THF (8 mL) at -78 °C was added a solution of LDA in THF (8.7 mL, 0.63 M, 5.48 mmol) and the colourless solution was stirred for 2 h. A further quantity of LDA in THF (0.64, 0.63 M, 0.403 mmol) was added and stirred for 1 h. The reaction was quenched with sat. aq. NH_4Cl (10 mL) and extracted with Et_2O (3 x 10 mL). The organic layers were washed with sat. aq. $Na_2S_2O_3$ solution (20 mL), dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give a yellow oil (506 mg). A smaller scale reaction using 0.23 mmol of the 2 : 3 : 5 mixture of alcohols was also conducted under the same conditions. Column chromatography of the combined crude reaction mixtures (petroleum ether : EtOAc 7 : 1) gave the title compound (1-^{13}C)-**6** (207 mg, 1.47 mmol, 80%, 96% ^{13}C-1, 4%

^{13}C-2 atom) as a colourless oil [the ^{13}C content at the 1- and 2-positions was deduced by inspection of their ^{1}H NMR and ^{13}C NMR spectra (see ESI p37)]: R_f 0.30 (petroleum ether : EtOAc 5 : 1); IR (neat) 3600-3100, 3294, 1036 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 4.38 – 4.31 (m, 1H, C*H*OH), 2.43 (dt, $^{1}J_{CH}$ = 249.9 Hz, J = 1.6 Hz, 1H, C≡^{13}C*H*), 1.93 – 1.81 (br. s, 1H, O*H*), 1.75 – 1.65 (m, 2H, CH_2), 1.48 – 1.39 (m, 2H, CH_2), 1.34 – 1.23 (m, 6H, 3 × CH_2), 0.86 (t, J = 6.7 Hz, 3H, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 85.1 (d, $^{1}J_{CC}$ = 169 Hz, *C*≡^{13}CH), 72.8 (C≡^{13}*C*H), 62.3 (d, $^{2}J_{CC}$ = 11.4 Hz, *C*OH), 37.7 (*C*H_2), 31.7 (*C*H_2), 28.9 (*C*H_2), 25.0 , 22.6 (*C*H_2), 14.1 (*C*H_3).

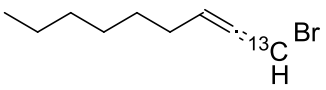
(1-^{13}C)-Non-1-yn-3-yl 2,4,6-tris(propan-2-yl)benzene-1-sulphonate [(1-^{13}C)-7]



According to the method of Kim,[4] to a solution of (1-^{13}C)-alcohol (1-^{13}C)-**6** (207 mg, 1.47 mmol, 96% ^{13}C-1, 4% ^{13}C-2 atom) in CH_2Cl_2 (4 mL) at 0 °C was added a solution of 2,4,6-triisopropylbenzenesulfonyl chloride (444 mg, 1.47 mmol) and DMAP (179 mg, 1.47 mmol) in CH_2Cl_2 (7 mL). The colourless solution was warmed to room temperature and stirred for 24 h until TLC (petroleum ether : EtOAc 6 : 1) showed completion. The solution was passed through a silica plug with Et_2O and the solvent was removed *in vacuo* to give a light yellow oil (553 mg). Column chromatography (petroleum ether : EtOAc 1 : 0 to 50 : 1) gave the title compound (1-^{13}C)-**7** (501 mg, 1.23 mmol, 84%, 96% ^{13}C-1, 4% ^{13}C-2 atom) as a colourless oil [the ^{13}C content at the 1- and 2-positions was deduced by inspection of their ^{1}H NMR and ^{13}C NMR spectra (see ESI p38)]: R_f 0.56 (petroleum ether : EtOAc 6 : 1); IR (neat) 3298, 1600, 1463, 1350, 1177, 937 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.14 (s, 2H, 2 × Ar-*H*), 5.17 – 5.11 (m, 1H, C*H*OTris), 4.13 (sept., J = 6.8 Hz, 2H, 2 × *ortho*-C*H*(CH_3)$_2$), 2.88 (sept., J = 6.8 Hz, 1H, *para*-C*H*(CH_3)$_2$), 2.26 (dd, $^{1}J_{CH}$ = 252.7, J = 2.0 Hz, 1H, C≡^{13}C*H*), 1.86 – 1.78 (m, 2H, CH_2), 1.48 – 1.39 (m, 2H, CH_2), 1.31 – 1.23 (m, 6H, 3 × CH_2), 1.25 (d, J = 7.0 Hz, 6H, *ortho*-CH(CH_3)$_2$), 1.24 (d, J = 7.0 Hz, 6H, *ortho*-CH(CH_3)$_2$), 1.23 (d, J = 7.0 Hz, 6H, *para*-CH(CH_3)$_2$), 0.85 (t, J = 6.7 Hz, 3H, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$) δ 153.6 (*para*-C), 150.6 (2 × *ortho*-C), 130.9 (*ipso*-C), 123.6 (2 × *meta*-C), 79.4 (d, $^{1}J_{CC}$ = 176.1 Hz, *C*≡^{13}CH), 75.9 (C≡^{13}*C*H), 70.2 (d, $^{2}J_{CC}$ = 12.5 Hz, *C*OTris), 35.7 (*C*H_2), 34.3 (*para*-C*H*(CH_3)$_2$), 31.6 (*C*H_2), 29.6 (2 × *ortho*-C*H*(CH_3)$_2$), 28.6 (*C*H_2), 24.7 (2 × *ortho*-CH(*C*H_3)$_2$), 24.7 (2 × *ortho*-

$CH(CH_3)_2$), 24.6 (CH_2), 23.6 (2 × *para*-$CH(CH_3)_2$), 22.5 (CH_2), 14.0 (CH_3); MS (ESI) *m/z* 430 (M + Na)$^+$; HRMS (ESI) *m/z* calcd for $C_{23}(^{13}C)H_{38}O_3NaS$ (M + Na)$^+$ 430.2467, found 430.2468.

(1-^{13}C)-1-Bromonona-1,2-diene [(1-^{13}C)-4]



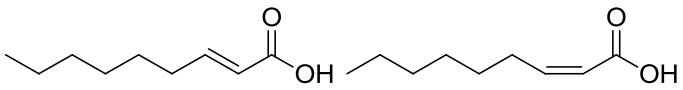
According to the method of Kim,[4] LiBr (319 mg, 3.68 mmol) and CuBr (528 g, 3.68 mmol) were dissolved in THF (14.7 mL) and stirred at room temperature for 30 min. The green solution was transferred to a solution of propargylic trisylate (1-^{13}C)-**7** (500 mg, 1.23 mmol) in THF (62 mL) at stirred at reflux for 30 min. The solvent was removed *in vacuo* and the brown residue was passed though a short silica plug with petroleum ether. The solvent was removed *in vacuo* once more to give a colourless oil (190 mg). Column chromatography (petroleum ether) gave the title compound (1-^{13}C)-**4** (145 mg, 0.710 mmol, 58%, 96% ^{13}C-1, 4% ^{13}C-2 atom) as a colourless oil [the ^{13}C content at the 1- and 2-positions was deduced by inspection of their ^{1}H NMR and ^{13}C NMR spectra (see ESI p39)]: R_f 0.65 (petroleum ether : EtOAc 50 : 1); IR (neat) 1945, 1189, 635 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (ddt, $^1J_{CH}$ = 211.9, *J* = 5.6, 2.3 Hz, 1H, HC=C=^{13}*C*HBr), 5.38 (ddt, *J* = 8.8, 6.8, 5.8 Hz, 1H, *H*C=C=^{13}CHBr), 2.13 (dq, *J* = 7.0, 2.4 Hz, 2H, CH_2CH=^{13}C), 1.47 – 1.39 (m, 2H, CH_2), 1.35 – 1.22 (m, 6H, 3 × CH_2), 0.87 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1 (d, $^1J_{CC}$ = 115.7 Hz, HC=*C*=^{13}CHBr), 101.1 (d, $^2J_{CC}$ = 8.9 Hz, H*C*=C=^{13}CHBr), 72.1 (HC=C=^{13}*C*HBr), 31.6 (CH_2), 28.7 (CH_2), 28.3 (CH_2), 28.3 (CH_2), 22.6 (CH_2), 14.1 (CH_3). The molecular ion for this compound could not be observed by electron, chemical or electrospray ionisation methods.

Experimental details for epoxidation of bromoallenes 4, (1-^{2}H)-4 and (1-^{13}C-4), and characterising data for *E*- and *Z*-5, (*E*-2-^{2}H)- and (*Z*-2-^{2}H)-5, and (*E*-2-^{13}C)- and (*Z*-2-^{13}C)-5

General procedure for the epoxidation of bromoallenes with DMDO solution.

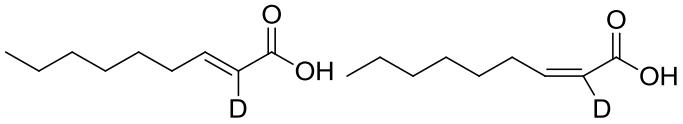
To a stirred solution of either unlabelled, (1-^{2}H)- or (1-^{13}C)-1-bromonona-1,2-diene (**4**, (1-^{2}H)-**4** or (1-^{13}C)-**4**) (100 mg, 0.49 mmol) in acetone (2 mL) at -40 °C was added a 0.10 M solution of DMDO in acetone (3.20 mL, 0.320 mmol). The colourless solution was warmed to room temperature and stirred overnight. The solvent was removed *in vacuo* and the residue extracted with Et_2O (3 × 2 mL) and petroleum ether (3 × 2 mL). The combined organics were evaporated to give a yellow oil. Column chromatography (petroleum ether : EtOAc 4 : 1 to 1 : 2) gave (*E*)- and (*Z*)-**5** in an approximately 1 : 1 ratio and combined yields ranging from 15 – 29%.

(*E*)-Non-2-enoic acid [(*E*)-5] & (*Z*)-non-2-enoic acid [(*Z*)-(5)]



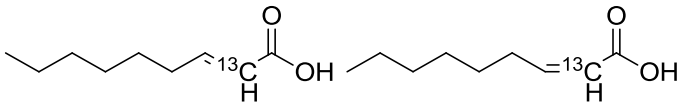
According to the general procedure using bromoallene **4** gave (*E*)-**5** (10 mg, 0.064 mmol, 13%) and (*Z*)-**5** (12 mg, 0.077 mmol, 15%) as colourless oils. (*E*)-**5**: R_f 0.15 (petroleum ether : EtOAc 3 : 1); IR (neat) 3300-2800, 1696, 1650 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (dt, *J* = 15.6, 7.0 Hz, 1H, β-H), 5.80 (dt, *J* = 15.6, 1.5 Hz, 1H, α-H), 2.21 (app. qd, *J* = 7.0, 2.4 Hz, 2H, C*H*$_2$CH=CH), 1.46 – 1.40 (m, 2H, C*H*$_2$), 1.34 – 1.21 (m, 6H, 3 × C*H*$_2$), 0.87 (t, *J* = 7.0 Hz, 3H, C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8 (*C*O_2H), 152.5 (β-*C*), 120.5 (α-*C*), 32.3 (*C*H_2), 31.6 (*C*H_2), 28.8 (*C*H_2), 27.8 (*C*H_2), 22.5 (*C*H_2), 14.0 (*C*H_3); MS (CI$^+$, NH_3) *m/z* 174 (M + NH_4)$^+$; HRMS (CI$^+$, NH_3) *m/z* calcd for $C_9H_{20}NO_2$ (M + NH_4)$^+$ 174.1494, found 174.1494. (*Z*)-(**5**): R_f 0.26 (petroleum ether : EtOAc 3 : 1); IR (neat) 3300-2800, 1696, 1640 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (dt, *J* = 11.5, 7.6 Hz, 1H, β-H), 5.76 (dt, *J* = 11.5, 1.7 Hz, 1H, α-H), 2.64 (app. qd, *J* = 7.6, 1.7 Hz, 2H, C*H*$_2$CH=CH), 1.46 – 1.38 (m, 2H, C*H*$_2$), 1.35 – 1.22 (m, 6H, 3 × C*H*$_2$), 0.86 (t, *J* = 6.9 Hz, 3H, C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8 (*C*O_2H), 153.7 (β-*C*), 118.9 (α-*C*), 31.6 (*C*H_2), 29.3 (*C*H_2), 29.0 (*C*H_2), 28.9 (*C*H_2), 22.6 (*C*H_2), 14.1 (*C*H_3); MS (CI$^+$, NH_3) *m/z* 174 (M + NH_4)$^+$; HRMS (CI$^+$, NH_3) *m/z* calcd for $C_9H_{20}NO_2$ (M + NH_4)$^+$ 174.1494, found 174.1487.

(*E*-2-^{2}H)-Non-2-enoic acid [(*E*-2-^{2}H)]-5 & (*Z*-2-^{2}H)-non-2-enoic acid [(*Z*-2-^{2}H)]-5]



According to the general procedure using bromoallene (1-^{2}H)-**4** gave (*E*-2-^{2}H)-**5** (9 mg, 0.057 mmol, 12%, 65% deuteration) and (*Z*-2-^{2}H)-**5** (3 mg, 0.019 mmol, 4%, 65% deuteration) as colourless oils [the deuterium content was deduced by inspection of the integral (0.35H) for the residual non-deuterated α,β-unsaturated carboxylic acids at 5.80 and 5.76 ppm in the ^{1}H NMR spectrum for *E* and *Z*-**5** respectively (see ESI p42-43)]. (*E*-2-^{2}H)-**5**: R_f 0.17 (petroleum ether : EtOAc 3 : 1); IR (neat) 3300-2800, 1692, 1637cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 – 7.02 (m, β-H), 2.21 (q, *J* = 7.0 Hz, 2H, CH_2CH=CD), 1.49 – 1.40 (m, 2H, CH_2), 1.34 – 1.22 (m, 6H, 3 × CH_2), 0.87 (t, *J* = 7.0 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) 171.2 (*C*O_2H), 152.3 (β-*C*), 120.4 (α-*C*), 32.3 (*C*H_2), 31.6 (*C*H_2), 28.8 (*C*H_2), 27.8 (*C*H_2), 22.5 (*C*H_2), 14.0 (*C*H_3); MS (CI^{+}, NH_3) *m/z* 175 (M + NH_4)$^{+}$; HRMS (CI^{+}, NH_3) *m/z* calcd for $C_9H_{19}{}^{2}HNO_2$ (M + NH_4)$^{+}$ 175.1557, found 175.1554. (*Z*-2-^{2}H)-**5**: R_f 0.26 (petroleum ether : EtOAc 3 : 1); IR (neat) 3300-2800, 1692, 1633 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37 – 6.30 (m, β-H), 2.64 (q, *J* = 7.5 Hz, 2H, CH_2CH=CD), 1.47 – 1.39 (m, 2H, CH_2), 1.35 – 1.25 (m, 6H, 3 × CH_2), 0.87 (t, *J* = 6.9 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) 170.6 (*C*O_2H), 153.4 (β-*C*), 118.7 (α-*C*), 31.6 (*C*H_2), 29.7 (*C*H_2), 29.2 (*C*H_2), 28.9 (*C*H_2), 22.6 (*C*H_2), 14.0 (*C*H_3); MS (CI^{+}, NH_3) *m/z* 175 (M + NH_4)$^{+}$; HRMS (CI^{+}, NH_3) $C_9H_{19}{}^{2}HNO_2$ (M + NH_4)$^{+}$ 175.1557, found 175.1560.

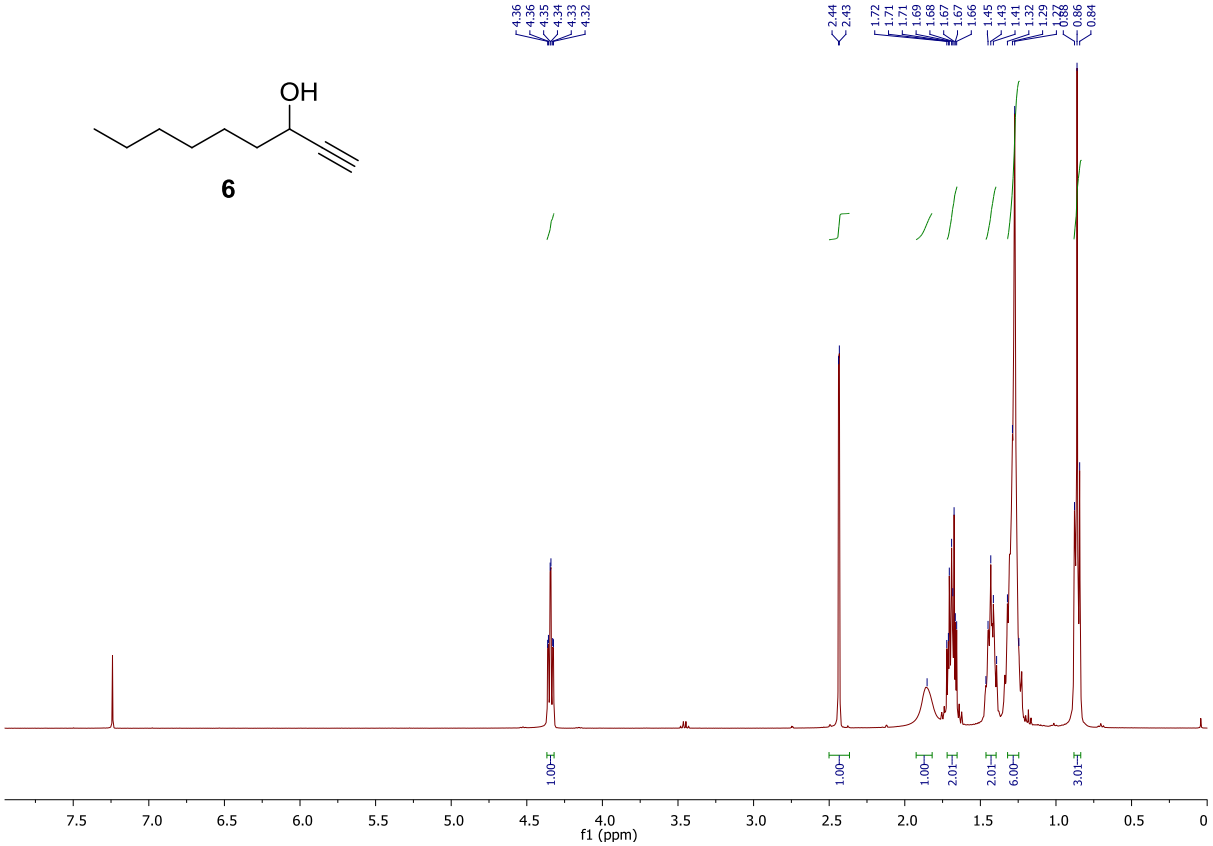
(*E*-2-^{13}C)-Non-2-enoic acid [(*E*-2-^{13}C)-5] & (*Z*-2-^{13}C)-non-2-enoic acid [(Z-2-^{13}C)-5]



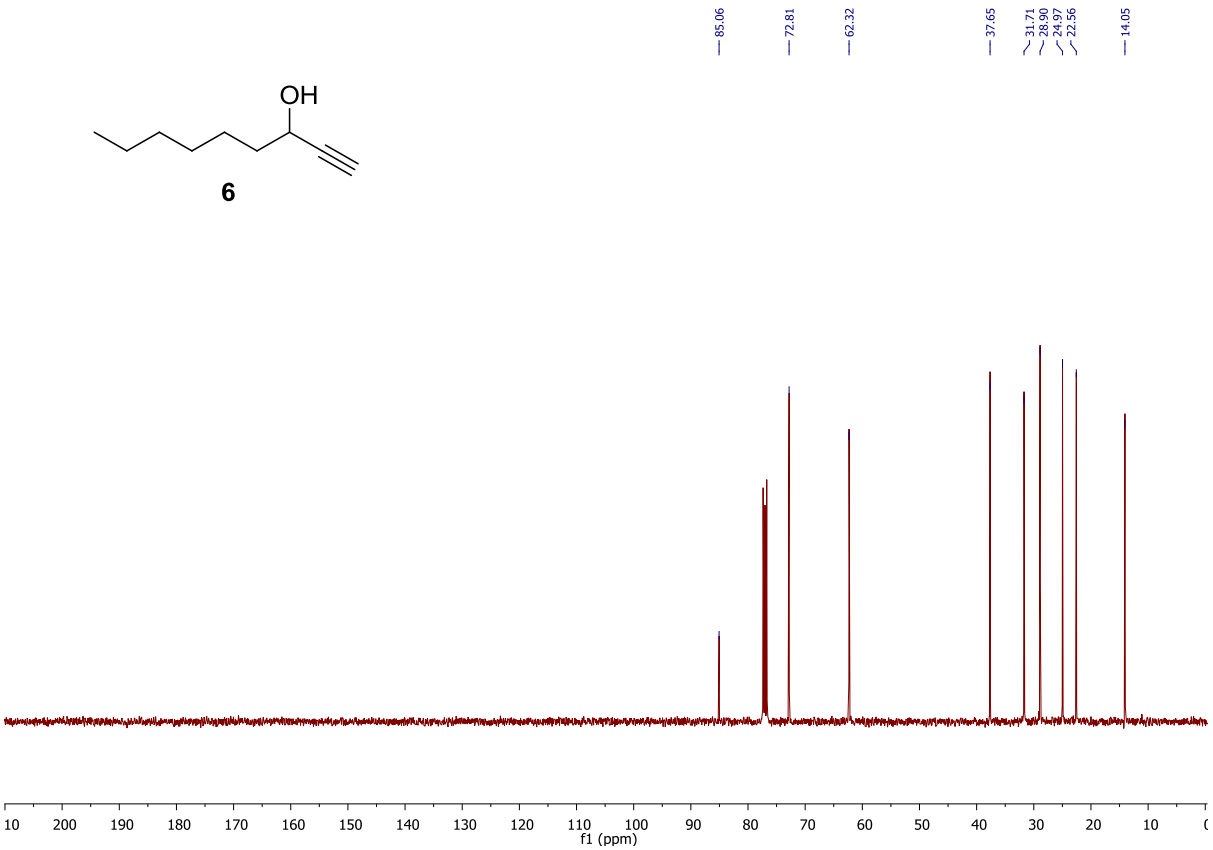
According to the general procedure using bromoallene (1-^{13}C)-**4** gave (*E*-2-^{13}C)-**5** (10 mg, 0.064 mmol, 14%, 96% ^{13}C-2, 4% ^{13}C-1 atom) and (*Z*-2-^{13}C)-**5** 10 mg, 0.064 mmol, 14%, 96% ^{13}C-2, 4% ^{13}C-1 atom) as colourless oils [the ^{13}C content at the 1- and 2-positions were deduced by inspection of their ^{1}H NMR and ^{13}C NMR spectra (see ESI p44-45)]. (*E*-2-^{13}C)-**5**: R_f 0.14 (petroleum ether : EtOAc 6 : 1); IR (neat) 3300-2800, 1692, 1627 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (ddt, *J* = 15.6, 7.0, 1.8 Hz, 1H, β-H), 5.78 (ddt, $^{1}J_{CH}$ = 163, *J* = 15.6, 1.5 Hz, 1H, α-H), 2.21 (ddq, *J* = 6.8, 6.0, 1.5 Hz, 2H, CH_2CH=^{13}CH), 1.48 – 1.40 (m, 2H, CH_2), 1.32 – 1.22 (m, 6H, 3 × CH_2), 0.87 (t, *J*

= 7.0 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8 (d, J = 74.2 Hz, CO_2H), 152.4 (d, $^1J_{CC}$ = 69.7 Hz, β-C), 120.3 (α-^{13}C), 32.3 (CH_2), 31.6 (CH_2), 28.8 (CH_2), 27.8 (CH_2), 22.5 (CH_2), 14.1 (CH_3); MS (CI^+, NH_3) m/z 175 $(M + NH_4)^+$; HRMS (CI^+, NH_3) m/z calcd for $C_8(^{13}C)H_{22}NO_2$ $(M + NH_4)^+$ 175.1527, found 175.1527. (*Z*-2-^{13}C)-**5**: R_f 0.20 (petroleum ether : EtOAc 6 : 1); IR (neat) 3300-2800, 1694, 1615 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.33 (dt, J = 11.4, 7.5 Hz, 1H, β-H), 5.75 (ddt, $^1J_{CH}$ = 163.2, J = 11.5, 1.7 Hz, 1H, α-H), 2.64 (ddq, J = 7.1, 5.6, 1.7 Hz, 2H, CH_2CH=^{13}CH), 1.47 – 1.37 (m, 2H, CH_2), 1.34 – 1.23 (m, 6H, 3 × CH_2), 0.86 (t, J = 6.9 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3 (d, J = 70.8 Hz, CO_2H), 153.5 (d, J = 69.3 Hz, β-C), 118.6 (α-C), 31.6 (CH_2), 29.7 (CH_2), 29.2 (CH_2), 28.9 (CH_2), 22.6 (CH_2), 14.1 (CH_3); MS (CI^+, NH_3) m/z 175 $(M + NH_4)^+$; HRMS (CI^+, NH_3) m/z calcd for $C_8(^{13}C)H_{22}NO_2$ $(M + NH_4)^+$ 175.1527, found 175.1526.

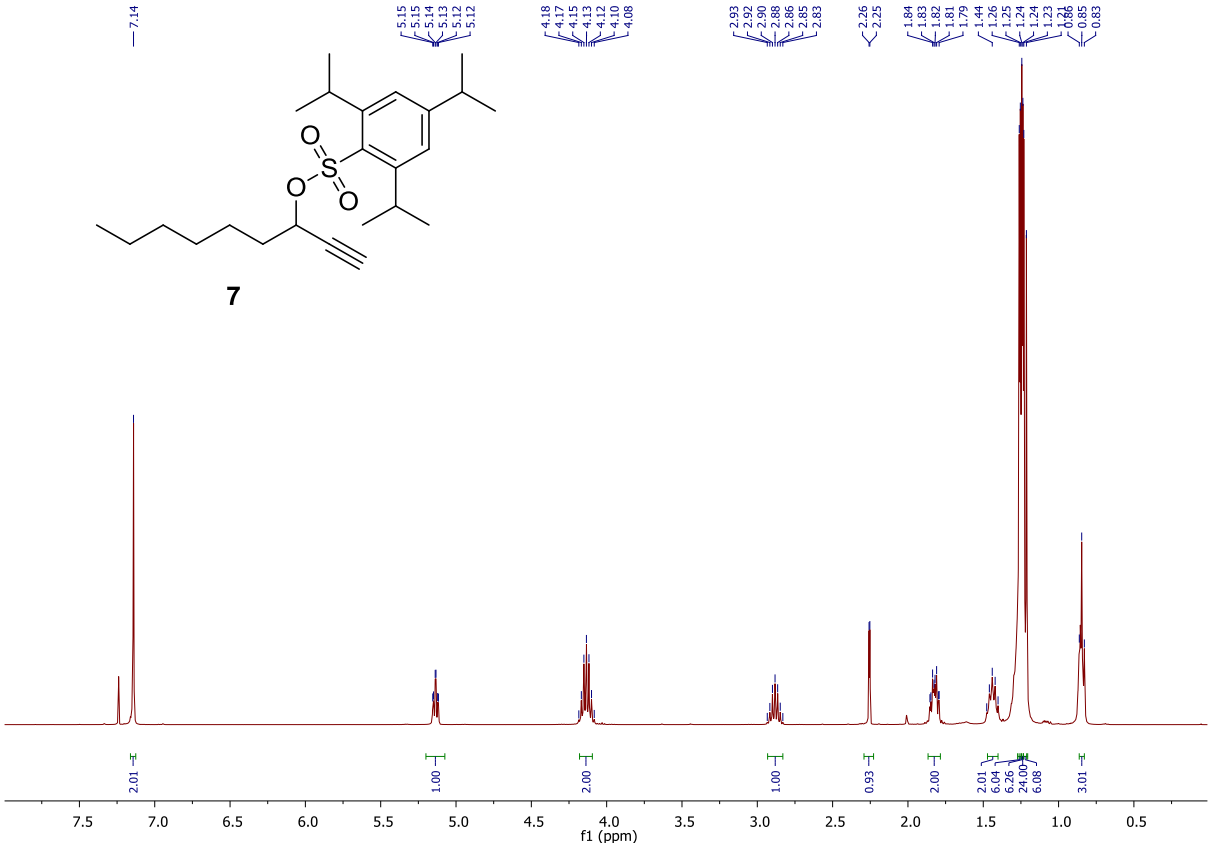
^{1}H NMR spectrum of non-1-yn-3-ol (**6**) (400 MHz, $CDCl_3$)



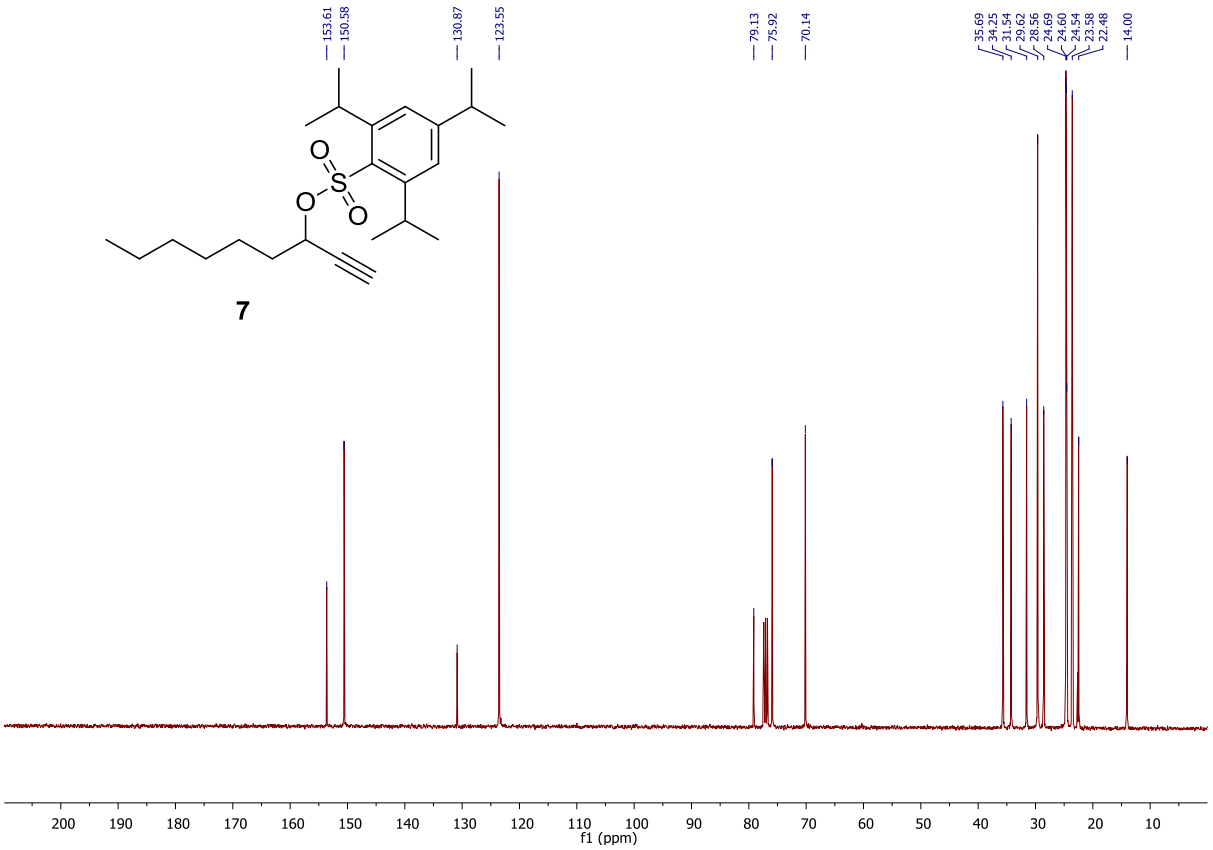
^{13}C NMR spectrum of non-1-yn-3-ol (**6**) (101 MHz, $CDCl_3$)



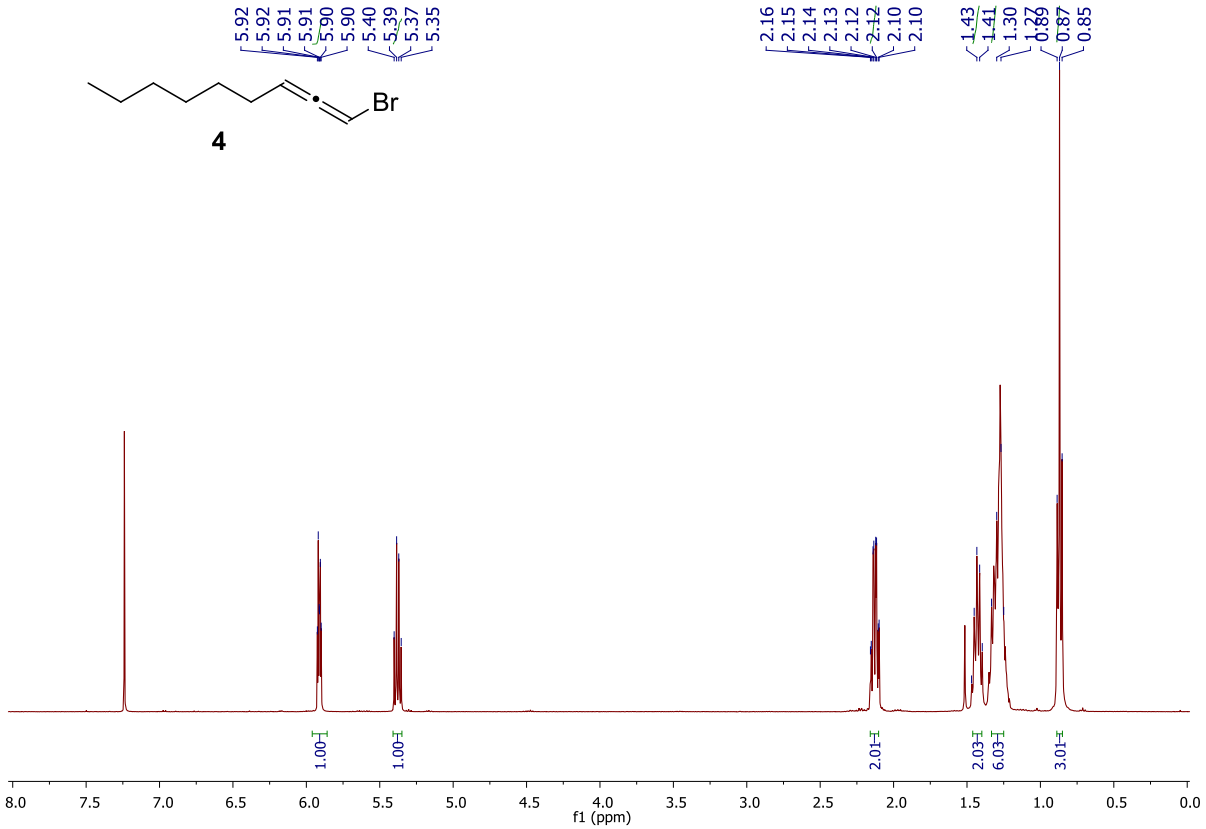
^{1}H NMR spectrum of non-1-yn-3-yl 2,4,6-tris(propan-2-yl)benzene-1-sulphonate (**7**) (400 MHz, $CDCl_3$)



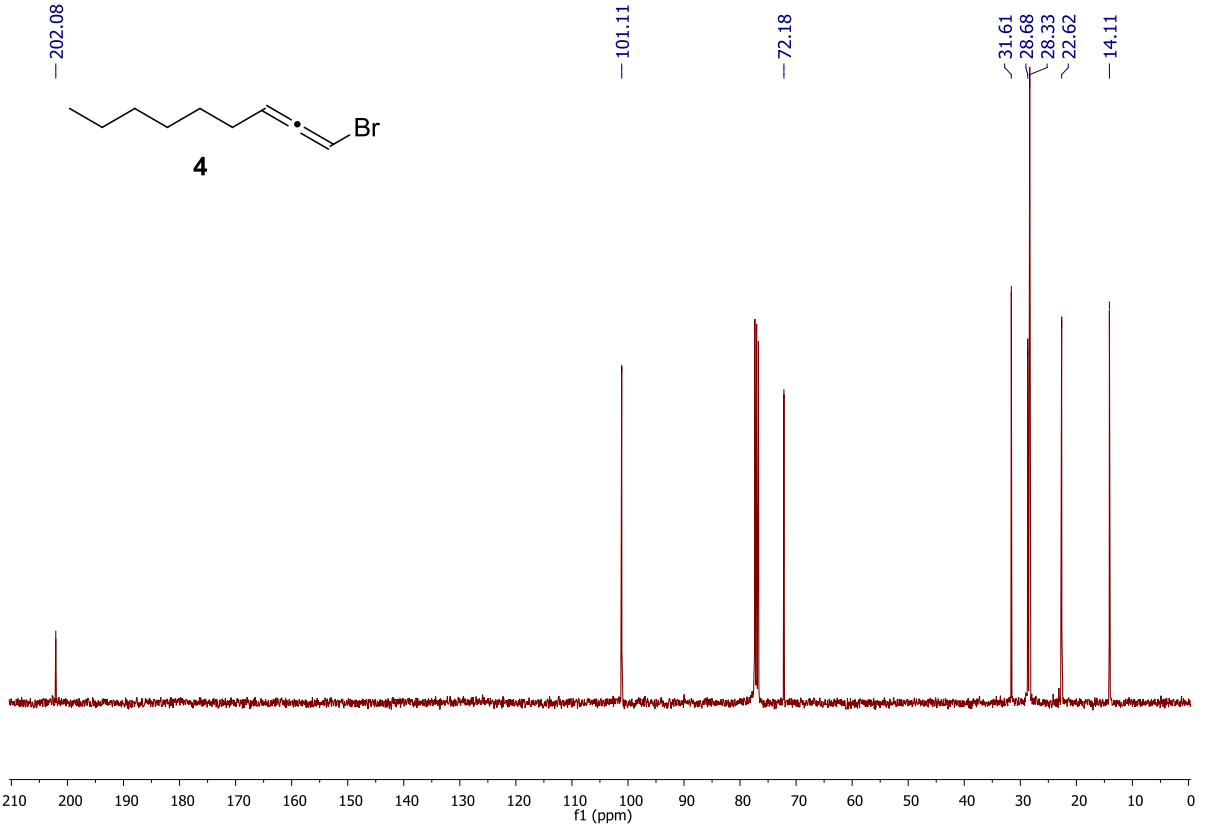
^{13}C NMR spectrum of non-1-yn-3-yl 2,4,6-tris(propan-2-yl)benzene-1-sulphonate (**7**) (101 MHz, $CDCl_3$)



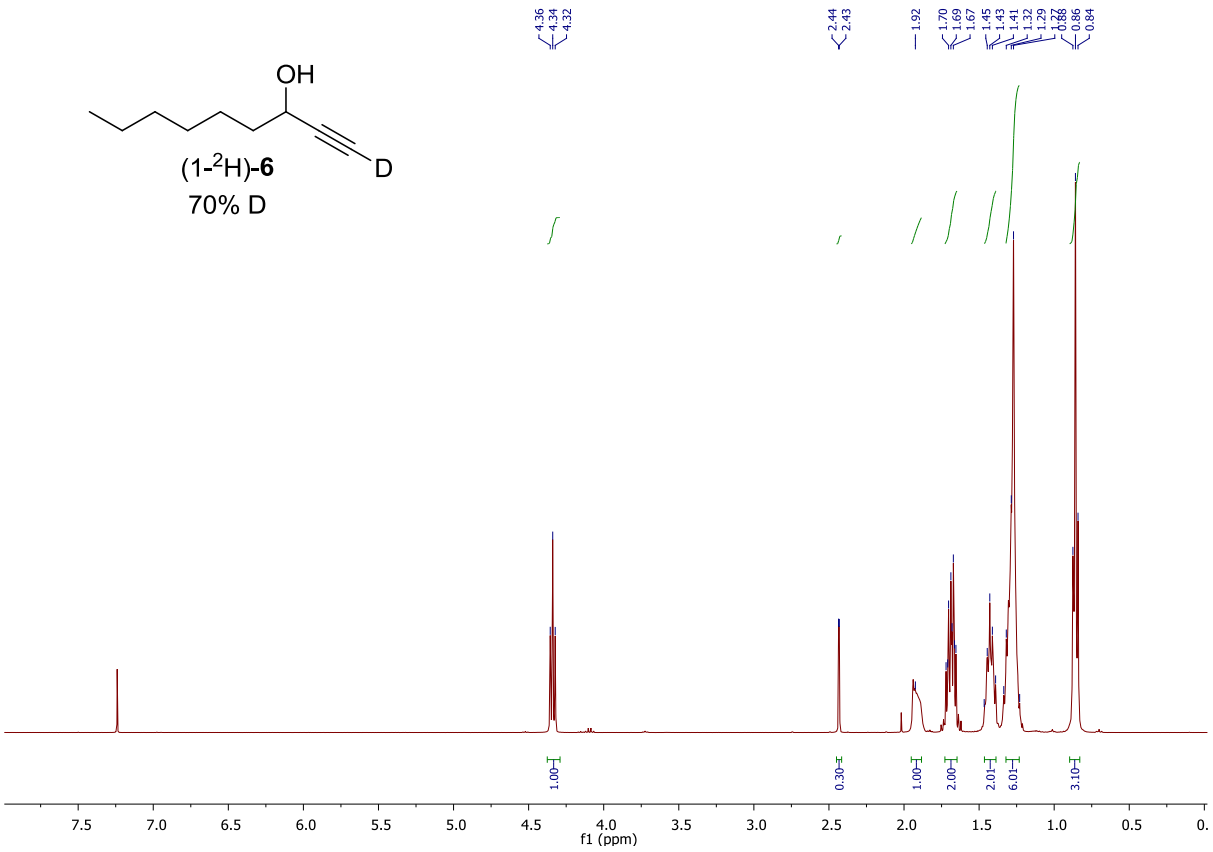
^{1}H NMR spectrum of 1-bromonona-1,2-diene (**4**) (400 MHz, $CDCl_3$)



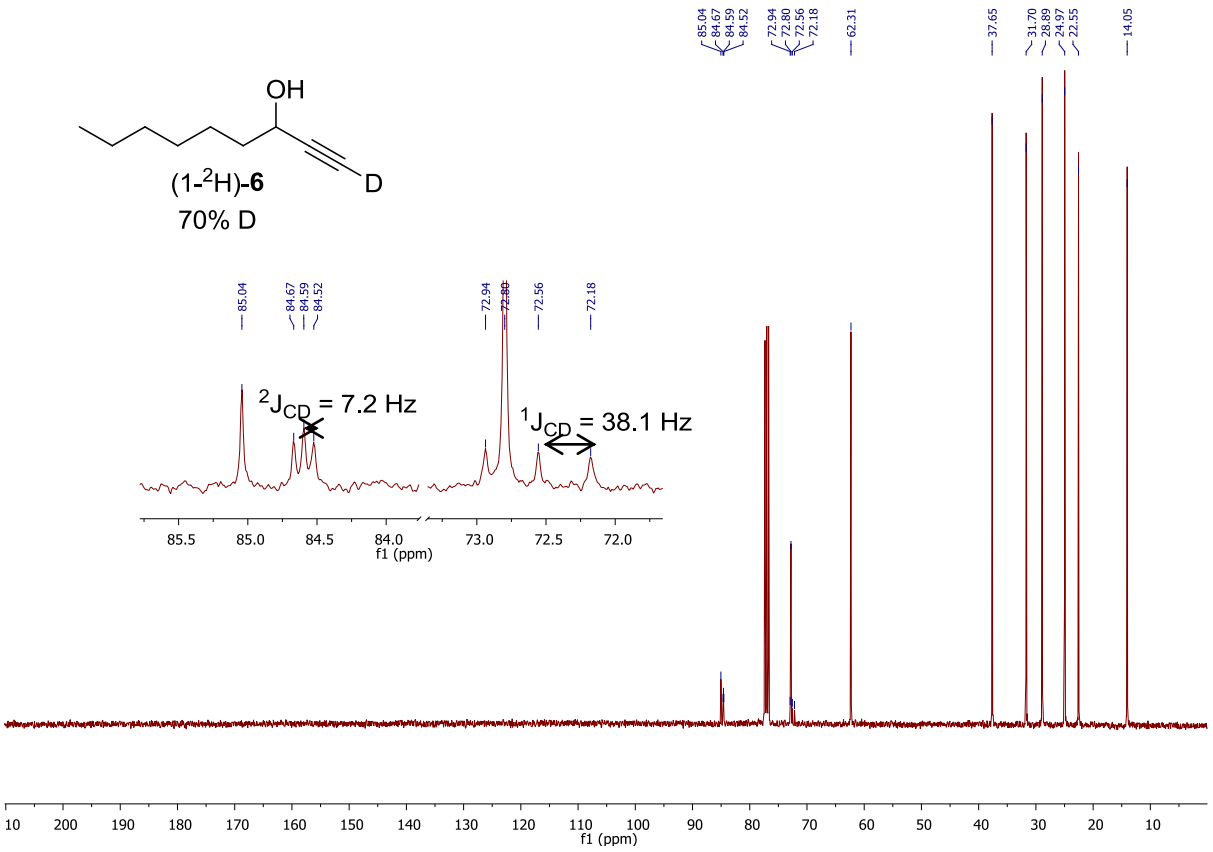
^{13}C NMR spectrum of 1-bromonona-1,2-diene (**4**) (101 MHz, $CDCl_3$)



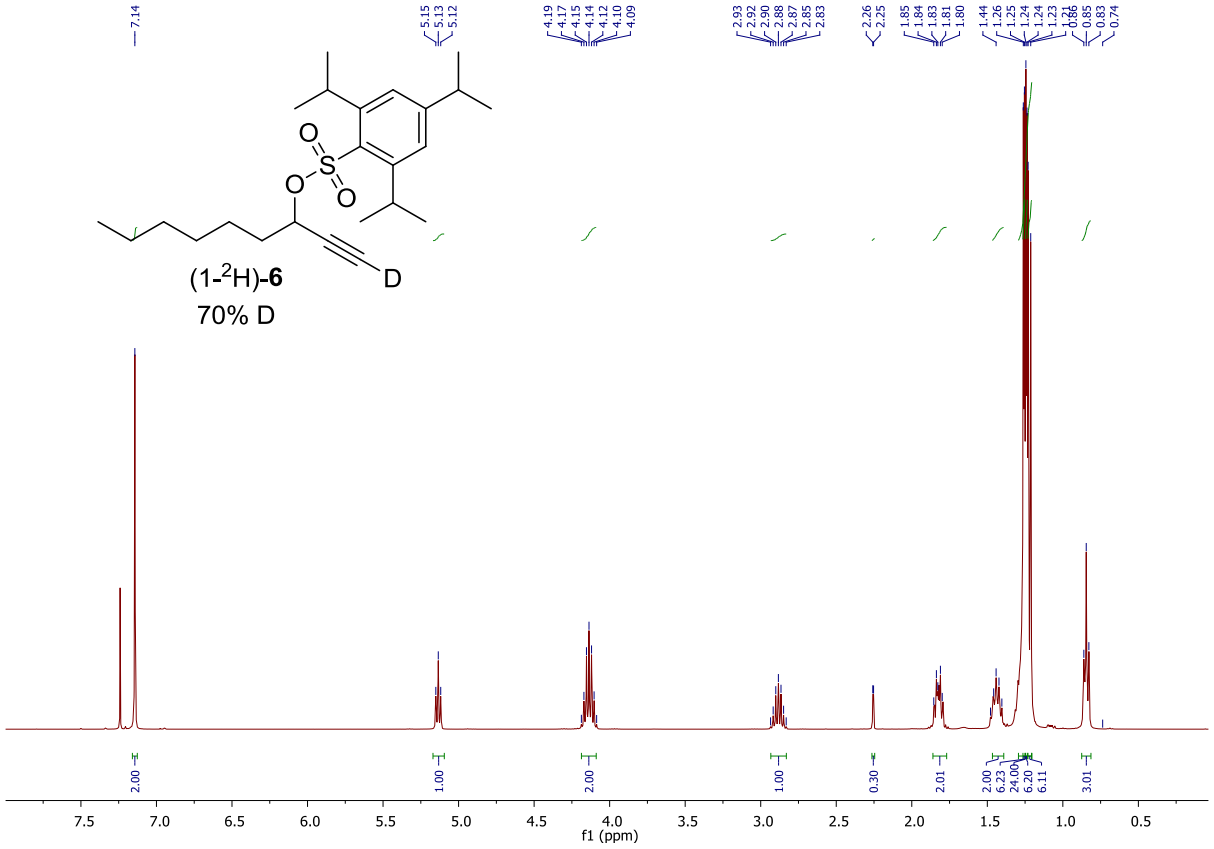
^{1}H NMR spectrum of (1-^{2}H)-non-1-yn-3-ol [(1-^{2}H)-**6**] (400 MHz, $CDCl_3$)



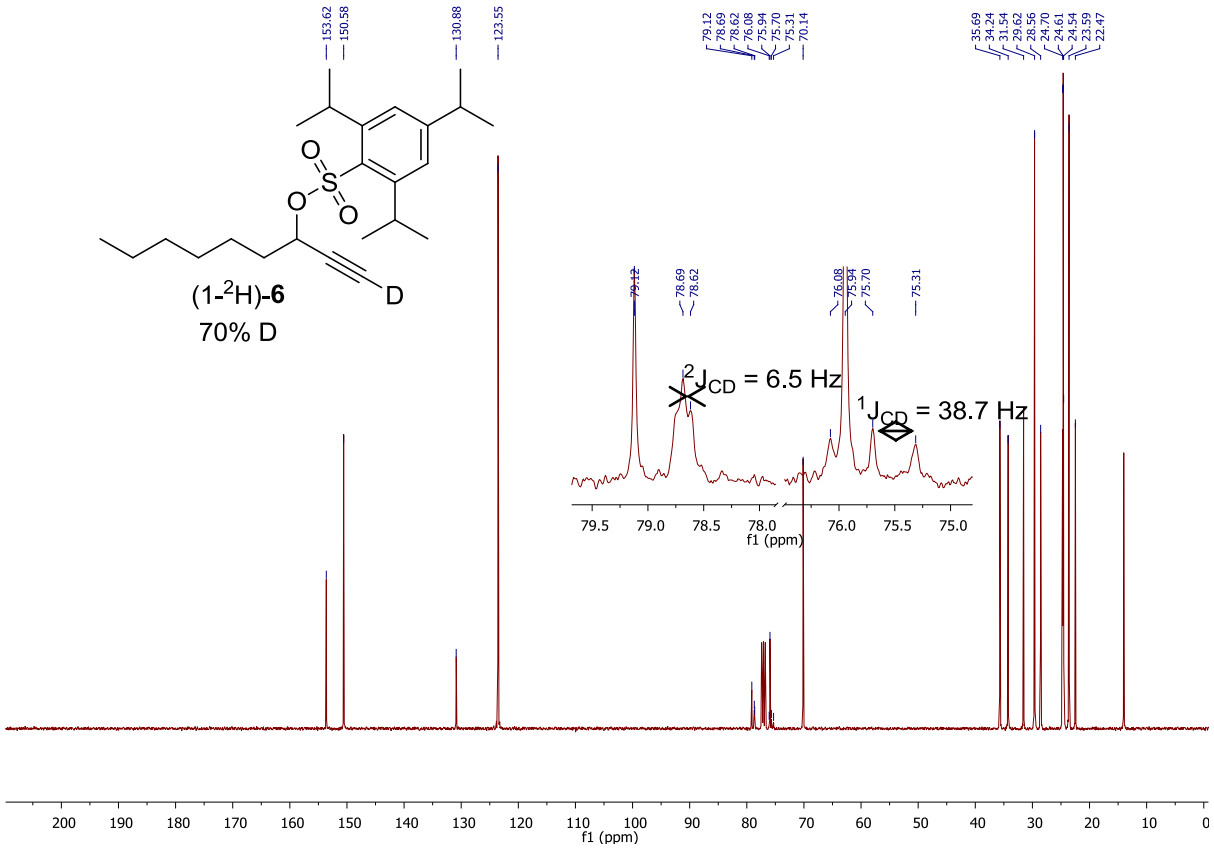
^{13}C NMR spectrum of (1-^{2}H)-non-1-yn-3-ol [(1-^{2}H)-**6**] (101 MHz, $CDCl_3$)



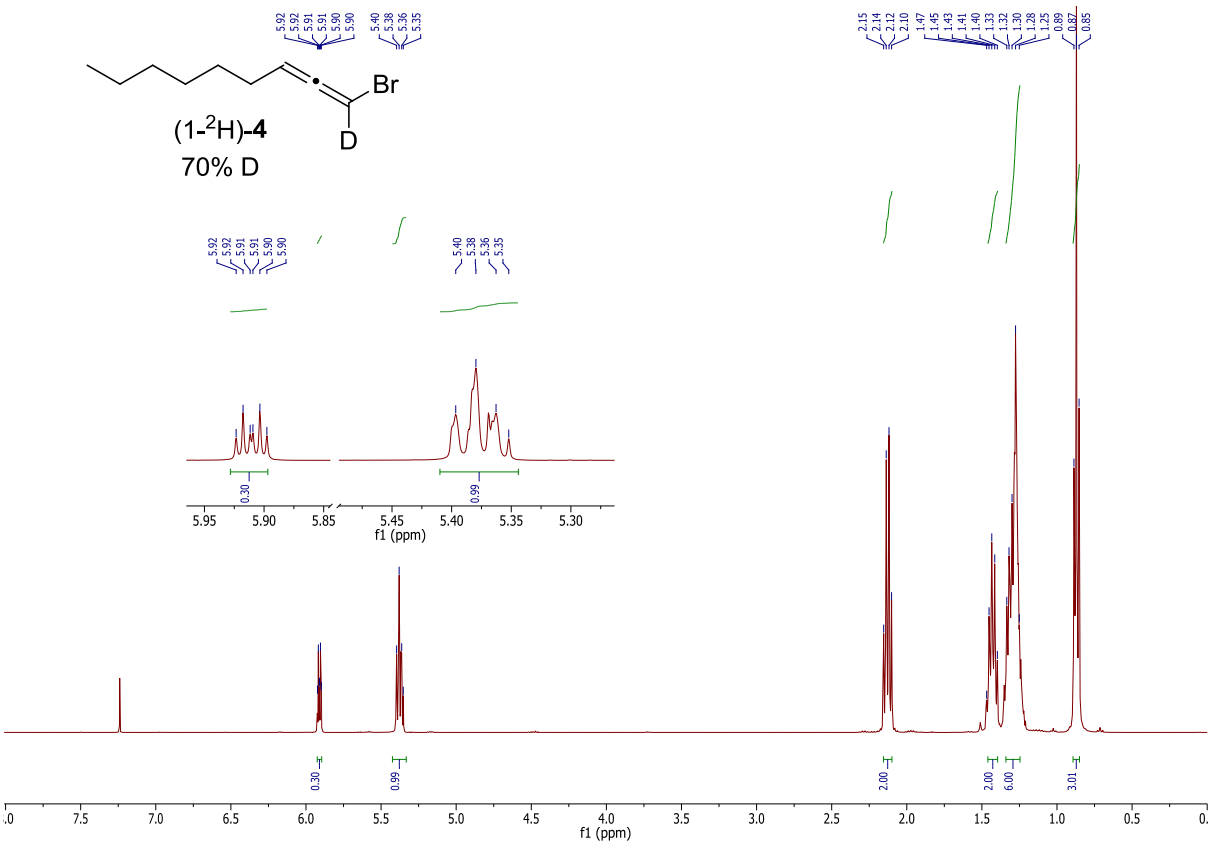
^{1}H NMR spectrum of (1-^{2}H)-non-1-yn-3-yl 2,4,6-tris(propan-2-yl)benzene-1-sulphonate [(1-^{2}H)-**6**] (400 MHz, $CDCl_3$)



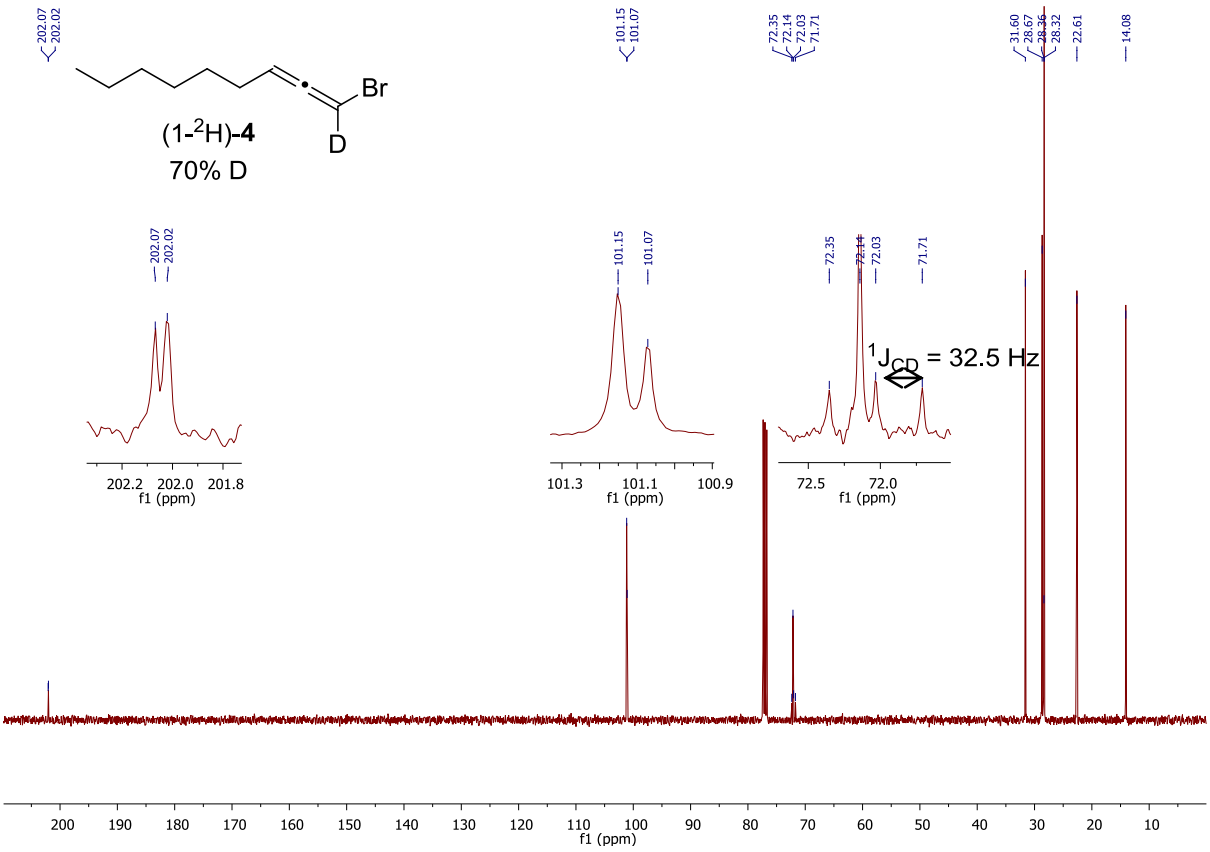
^{13}C NMR spectrum of (1-^{2}H)-non-1-yn-3-yl 2,4,6-tris(propan-2-yl)benzene-1-sulphonate [(1-^{2}H)-**6**] (400 MHz, $CDCl_3$)



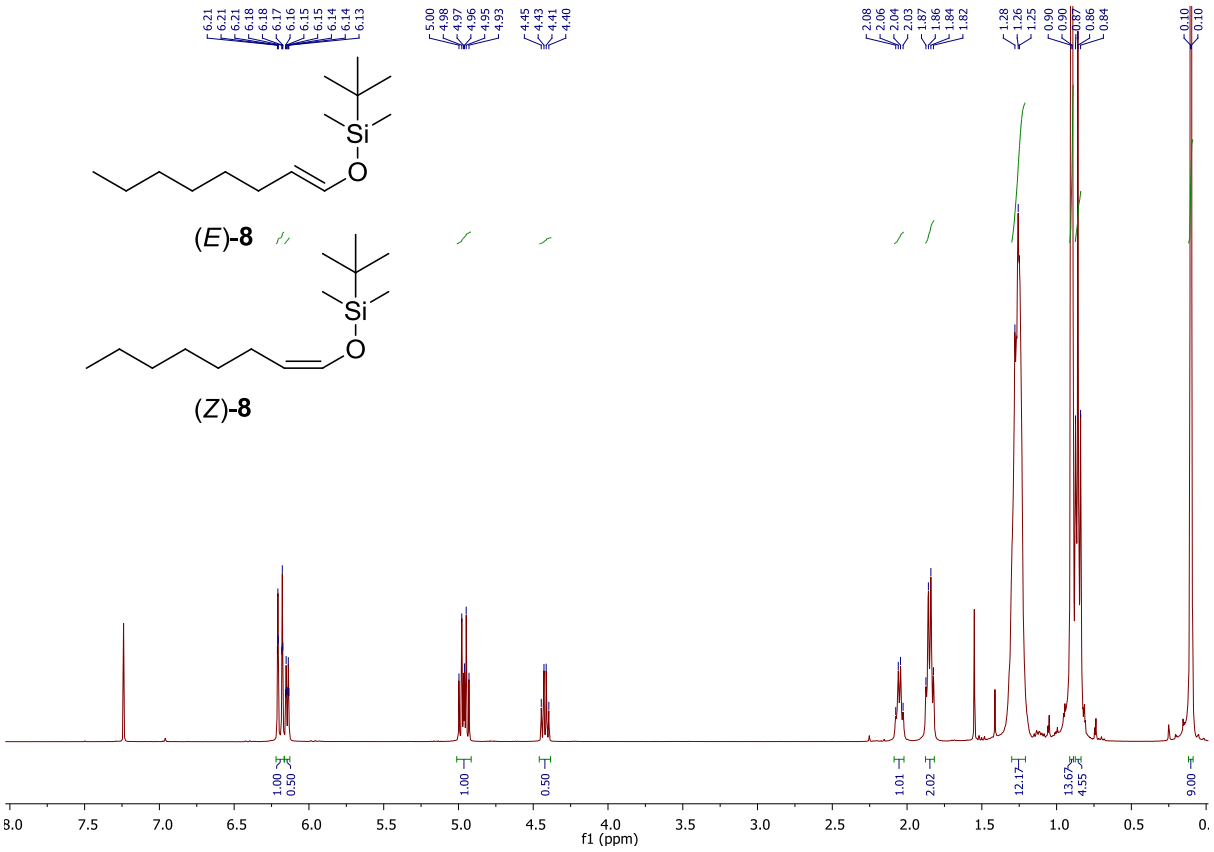
^{1}H NMR spectrum of (1-^{2}H)-1-bromonona-1,2-diene [(1-^{2}H)-**4**] (400 MHz, $CDCl_3$)



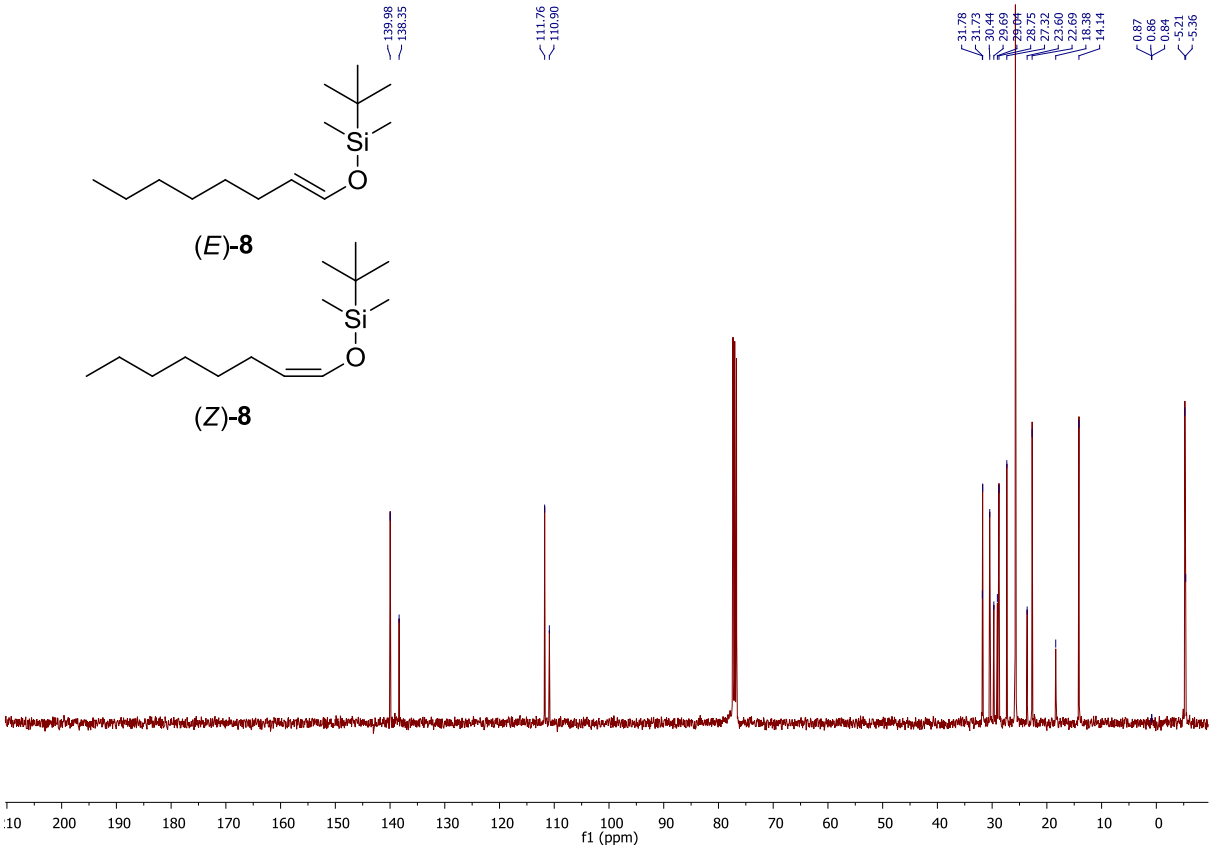
^{13}C NMR spectrum of (1-^{2}H)-1-bromonona-1,2-diene [(1-^{2}H)-**4**] (101 MHz, $CDCl_3$)



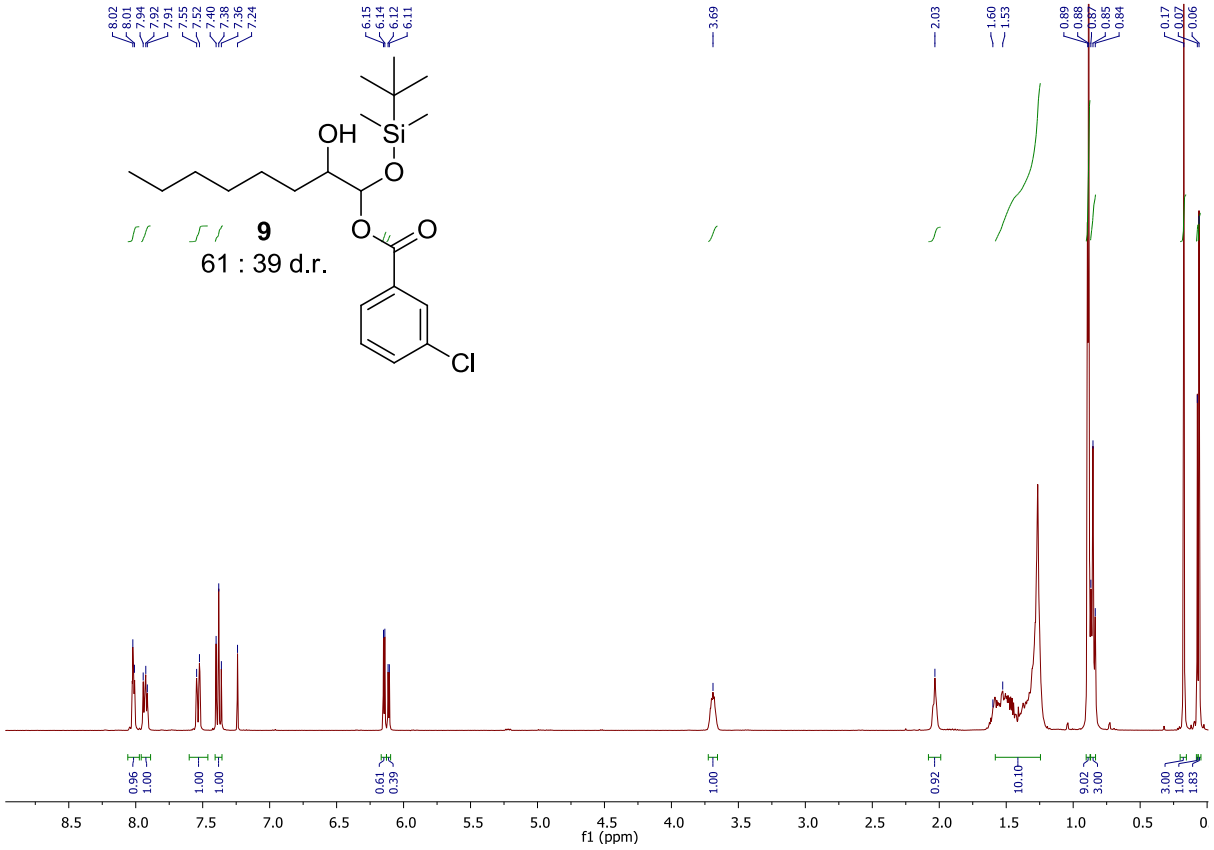
^{1}H NMR spectrum of *tert*-butyldimethyl[(1*E*)-oct-1-en-1-yloxy]silane and *tert*-butyldimethyl[(1*Z*)-oct-1-en-1-yloxy]silane (**8**) (400 MHz, $CDCl_3$)



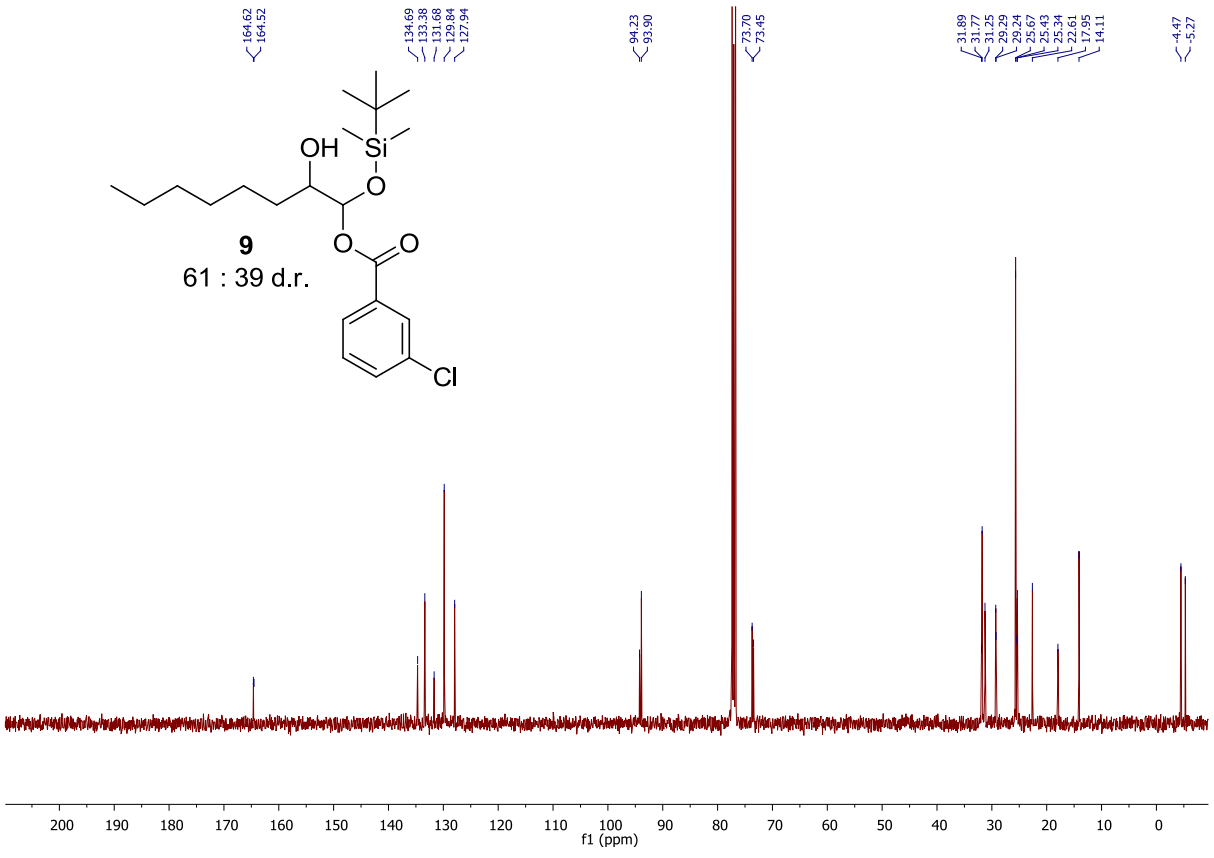
^{13}C NMR spectrum of *tert*-butyldimethyl[(1*E*)-oct-1-en-1-yloxy]silane and *tert*-butyldimethyl[(1*Z*)-oct-1-en-1-yloxy]silane (**8**) (101 MHz, $CDCl_3$)



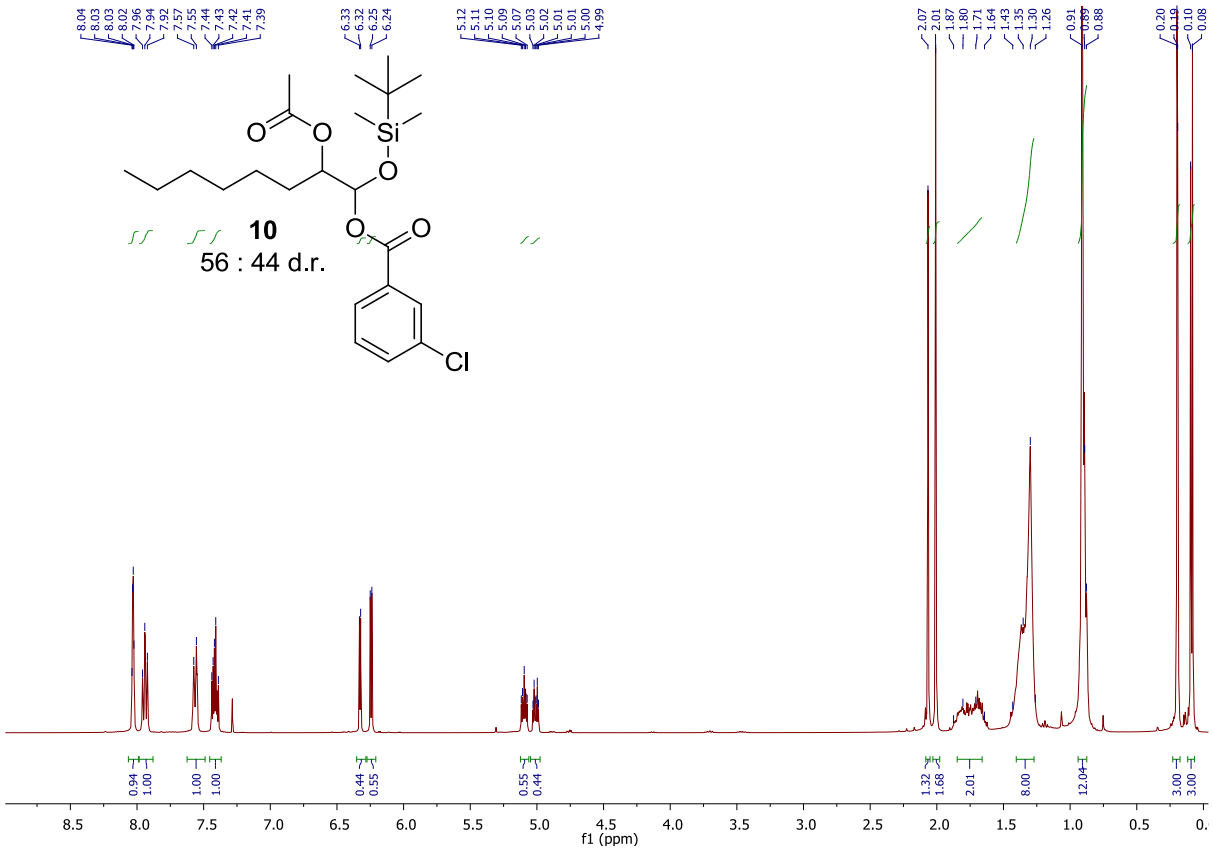
^{1}H NMR spectrum of 1-[(*tert*-butyldimethylsilyl)oxy]-2-hydroxyoctyl 3-chlorobenzoate (**9**) (400 MHz, $CDCl_3$)



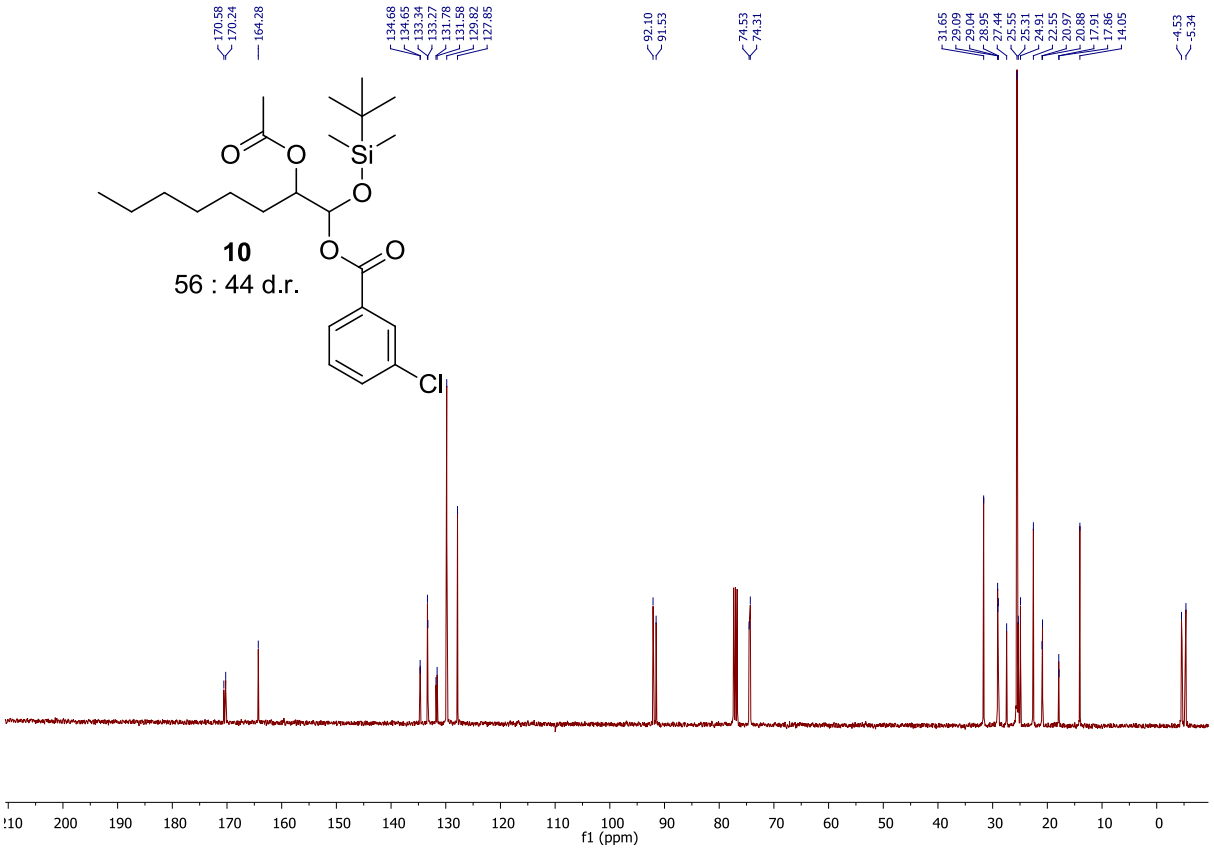
^{13}C NMR spectrum of 1-[(*tert*-butyldimethylsilyl)oxy]-2-hydroxyoctyl 3-chlorobenzoate (**9**) (101 MHz, $CDCl_3$)



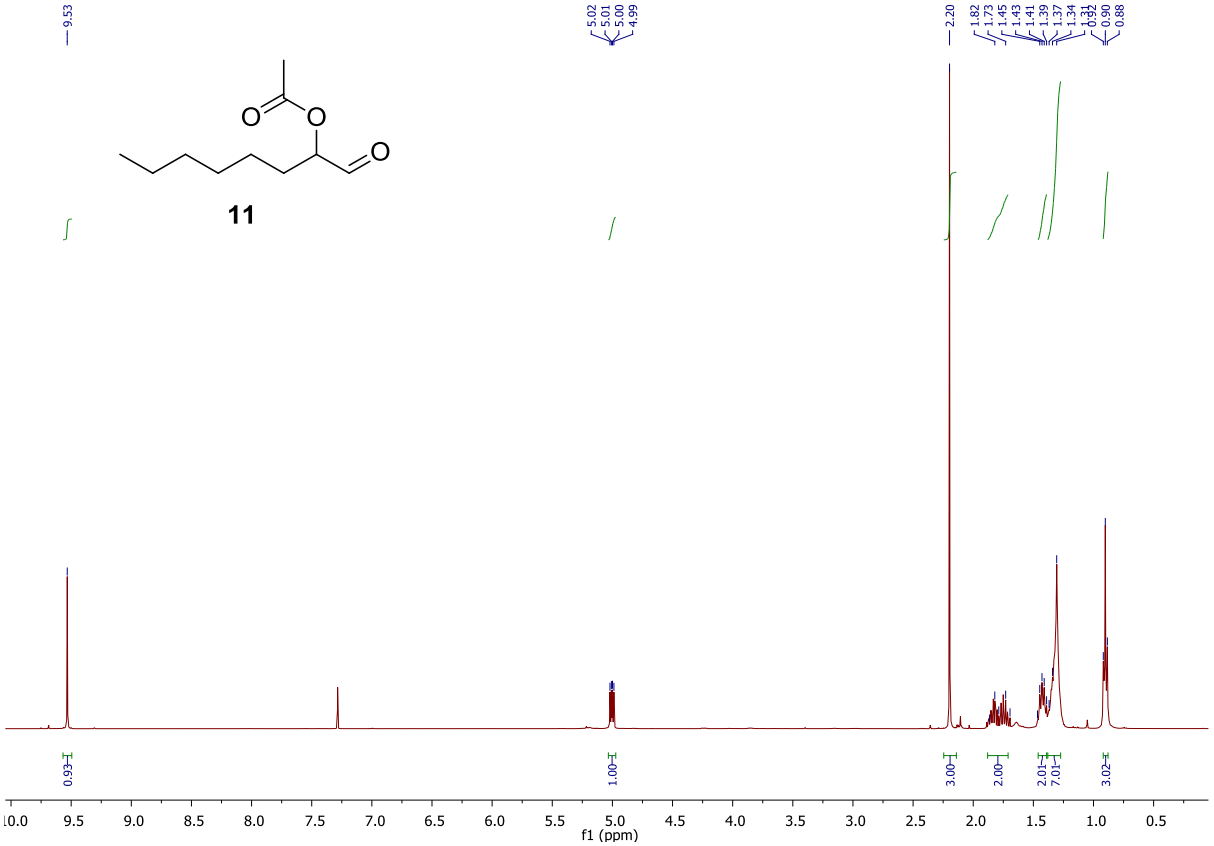
^{1}H NMR spectrum of 1-[(tert-butyldimethylsilyl)oxy]-1-[(3-chlorophenyl)carbonyloxy-2-yl acetate (**10**) (400 MHz, $CDCl_3$)



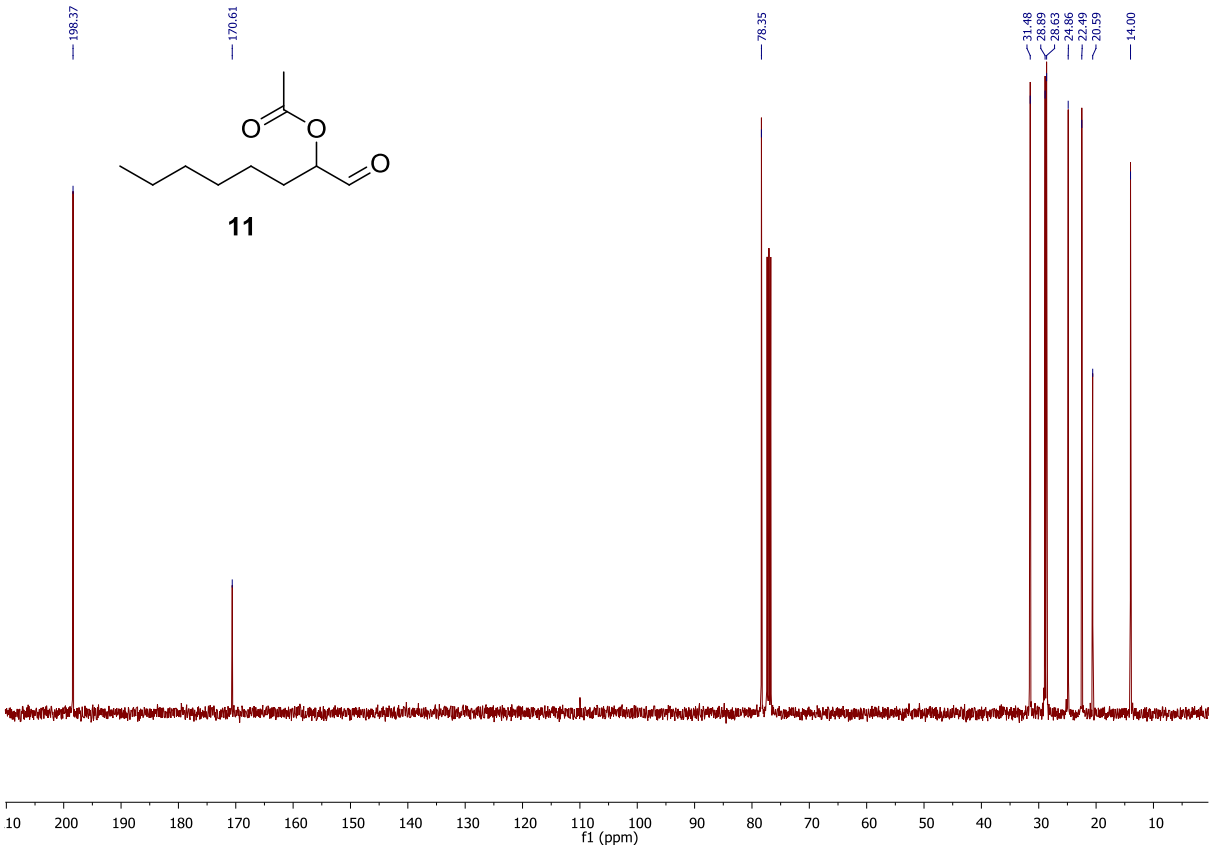
^{13}C NMR spectrum of 1-[(tert-butyldimethylsilyl)oxy]-1-[(3-chlorophenyl)carbonyloxy-2-yl acetate (**10**) (101 MHz, $CDCl_3$)



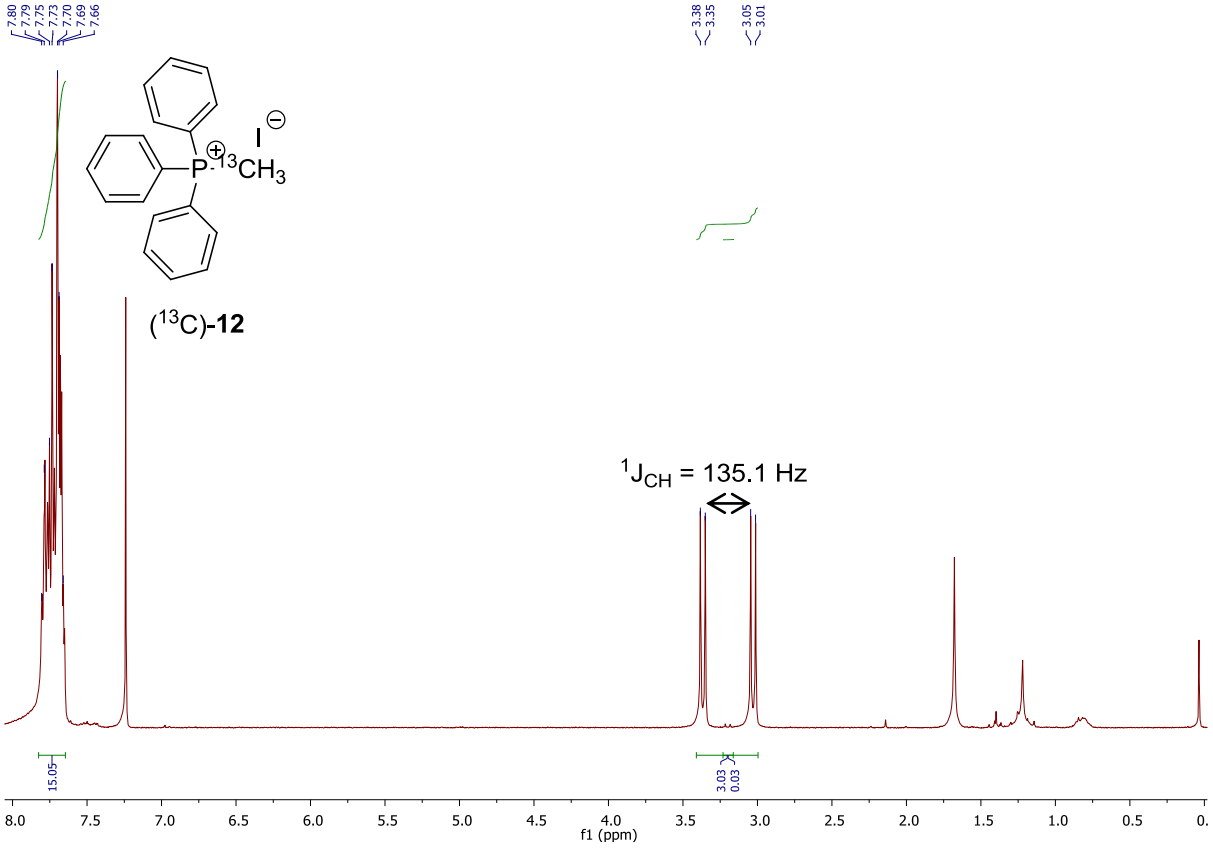
^{1}H NMR spectrum of 1-oxooctan-2-yl acetate (**11**) (400 MHz, $CDCl_3$)



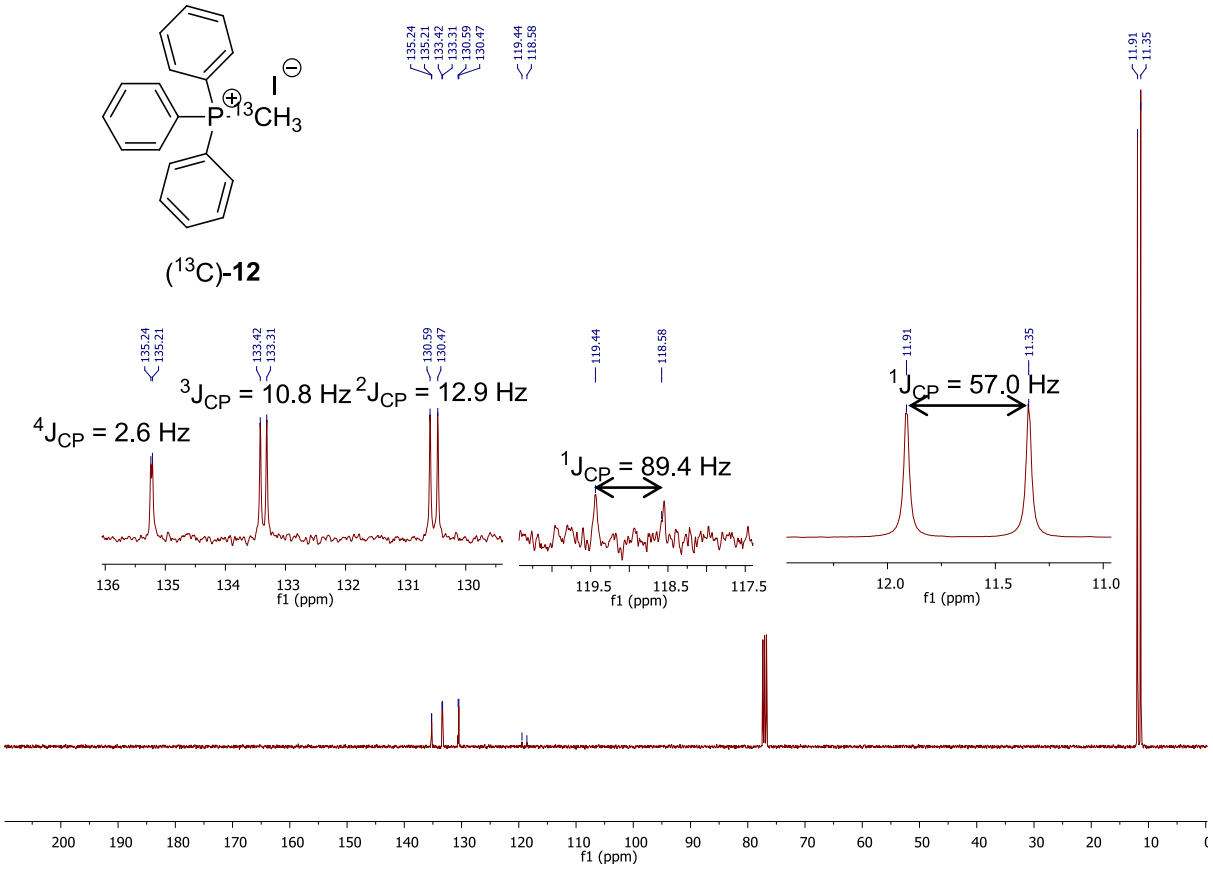
^{13}C NMR spectrum of 1-oxooctan-2-yl acetate (**11**) (101 MHz, $CDCl_3$)



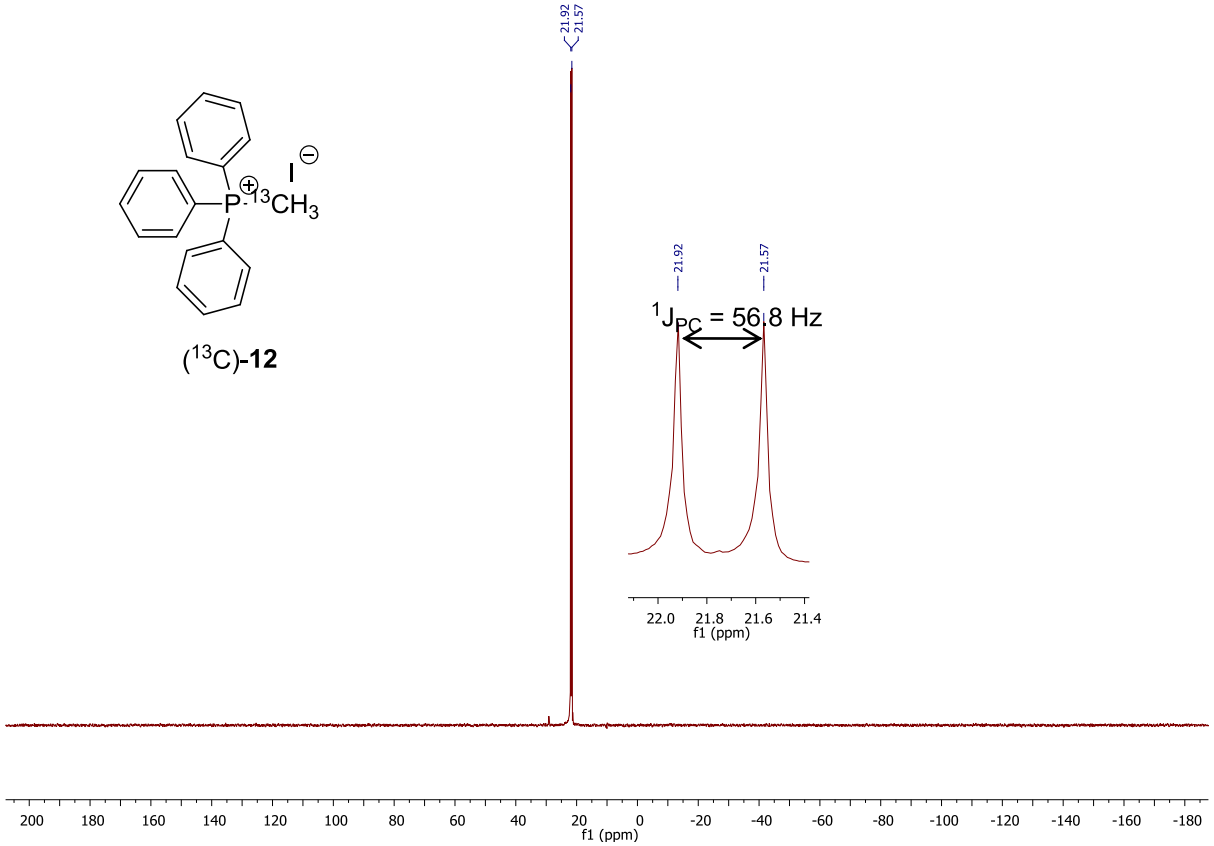
^{1}H NMR spectrum of (^{13}C)-methyltriphenylphosphonium iodide [(^{13}C)-**12**] (400 MHz, $CDCl_3$)



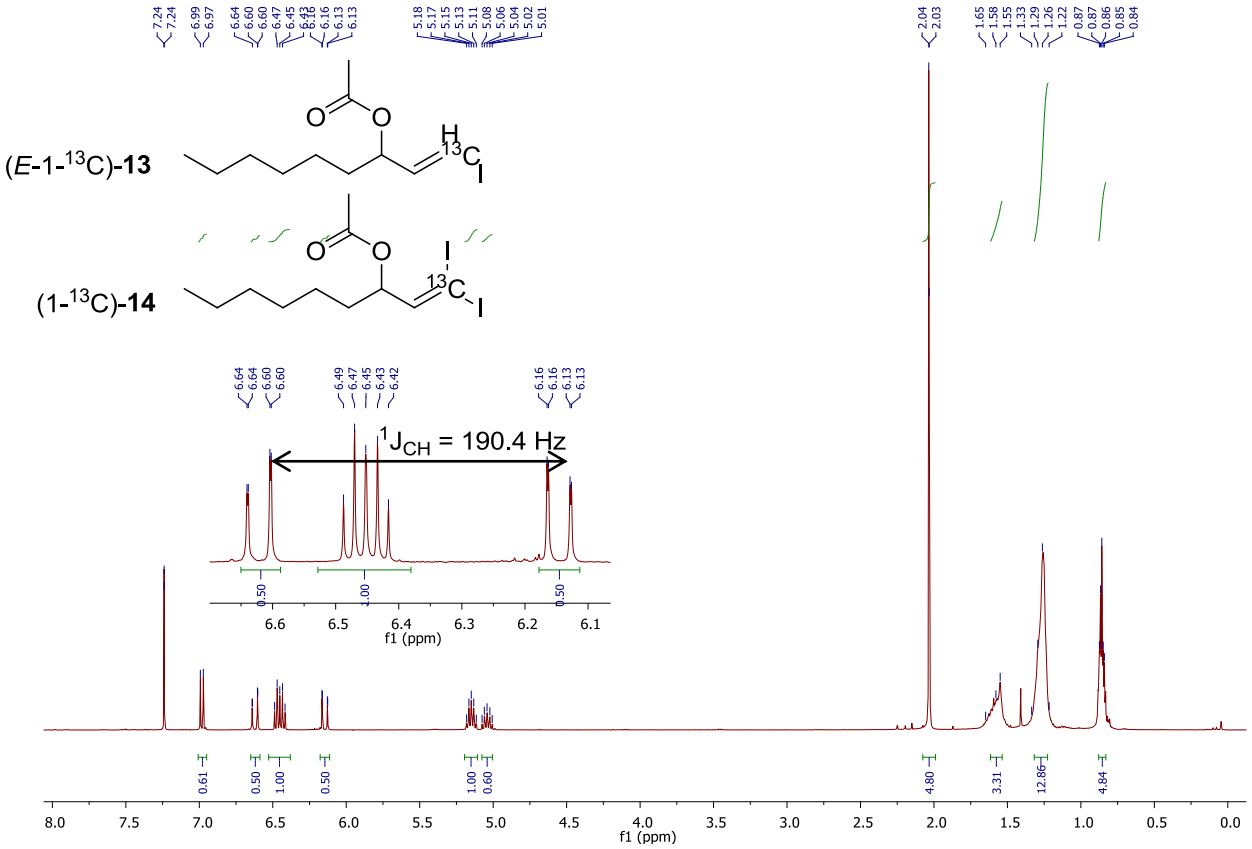
^{13}C NMR spectrum of (^{13}C)-methyltriphenylphosphonium iodide [(^{13}C)-**12**] (101 MHz, $CDCl_3$)



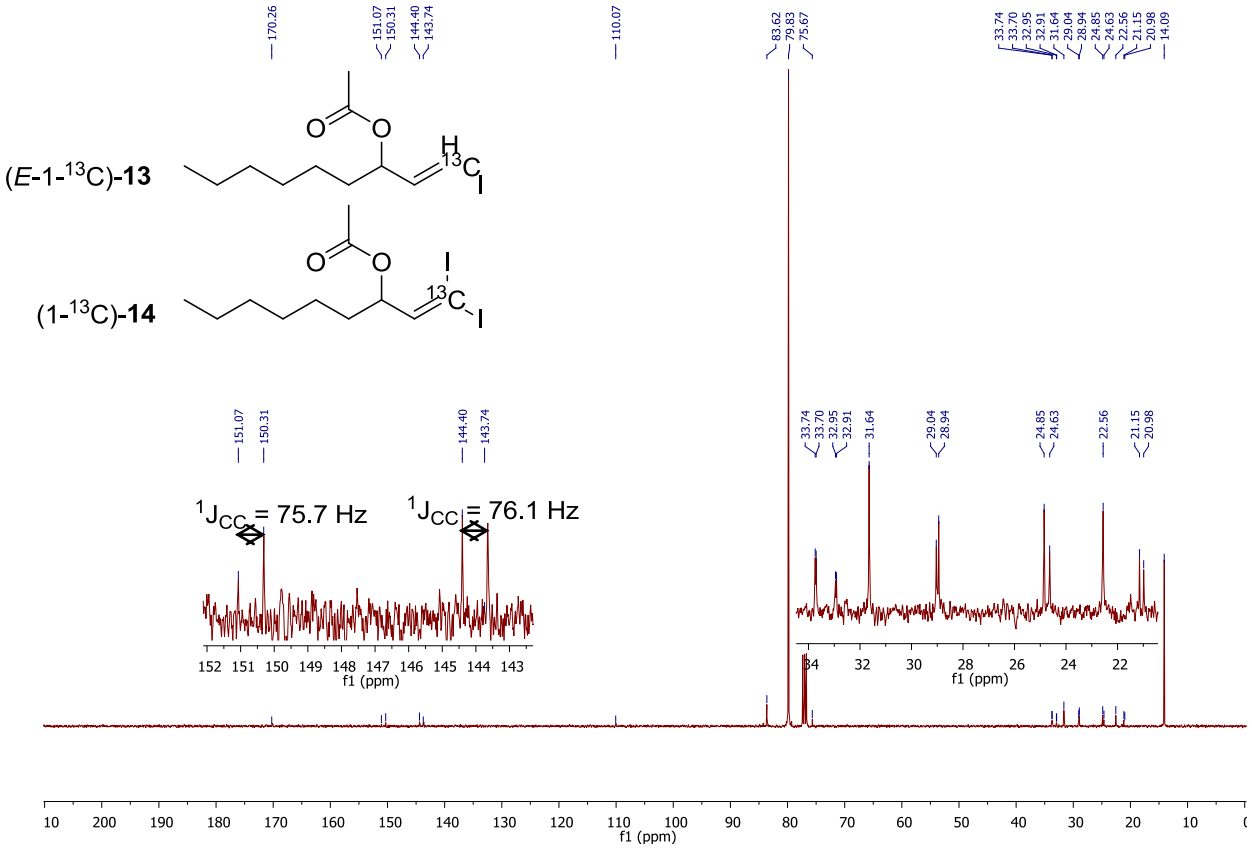
^{31}P NMR spectrum of (^{13}C)-methyltriphenylphosphonium iodide [(^{13}C)-**12**] (162 MHz, $CDCl_3$)



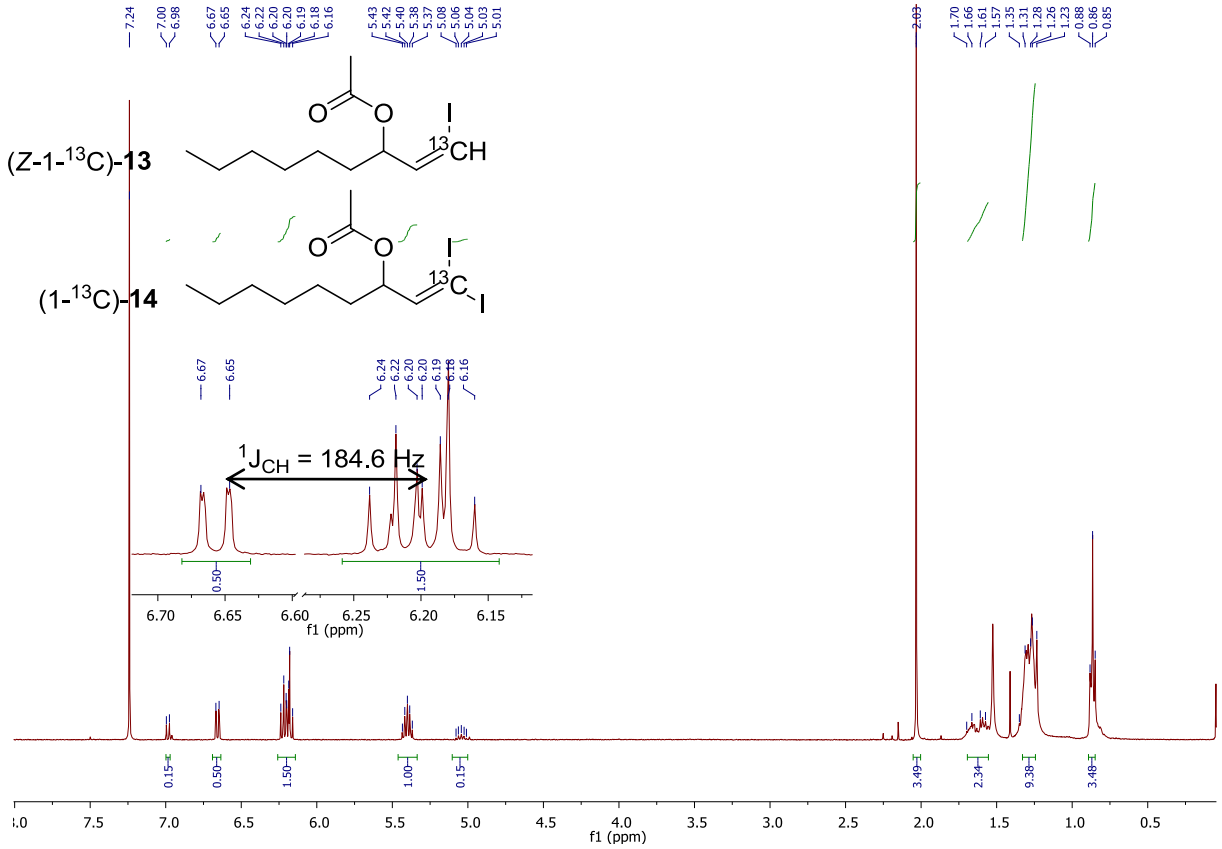
^{1}H NMR spectrum of (*E*-1-^{13}C)-1-iodonon-1-en-3-yl acetate [(*E*-1-^{13}C)-**13**] & (1-^{13}C)-1,1-diiodonon-1-en-3-yl acetate [(1-^{13}C)-**14**] (400 MHz, $CDCl_3$)



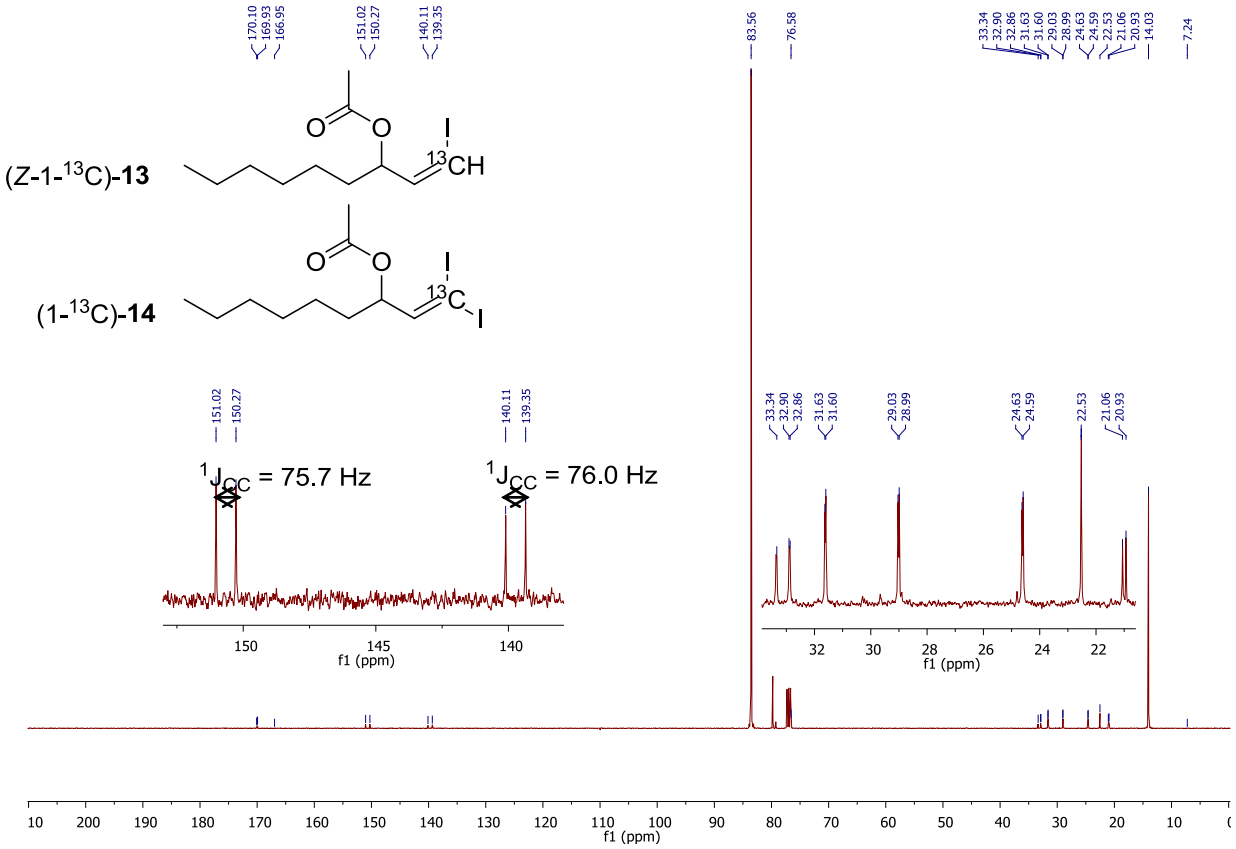
^{13}C NMR spectrum of (1*E*)-1-iodonon-1-en-3-yl acetate [(*E*-1-^{13}C)-**13**] & 1,1-diiodonon-1-en-3-yl acetate [(1-^{13}C)-**14**] (101 MHz, $CDCl_3$)



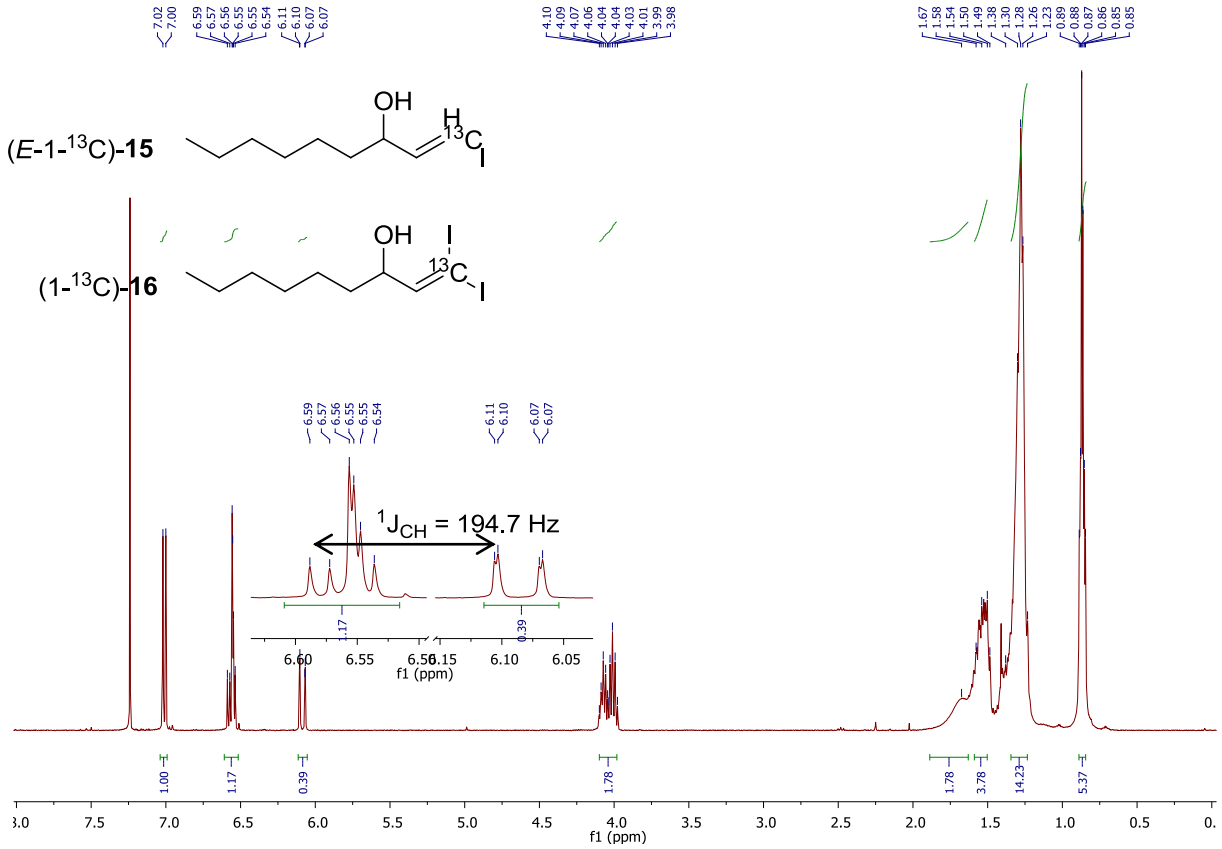
^{1}H NMR spectrum of (*Z*-1-^{13}C)-1-iodonon-1-en-3-yl acetate [(*Z*-1-^{13}C)-**13**] & (1-^{13}C)-1,1-diiodonon-1-en-3-yl acetate [(1-^{13}C)-**14**] (400 MHz, $CDCl_3$)



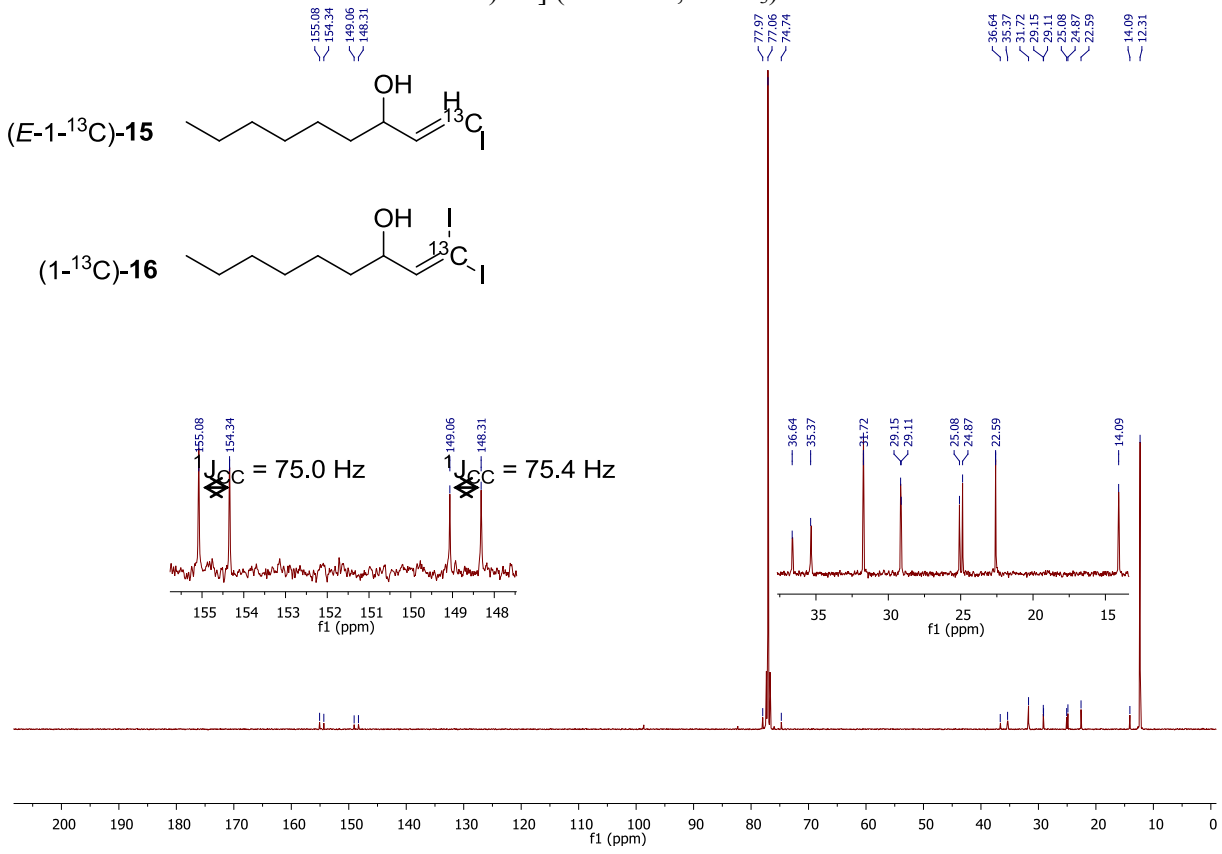
^{13}C NMR spectrum of (*Z*-1-^{13}C)-1-iodonon-1-en-3-yl acetate [(*Z*-1-^{13}C)-**13**] & (1-^{13}C)-1,1-diiodonon-1-en-3-yl acetate [(1-^{13}C)-**14**] (101 MHz, $CDCl_3$)



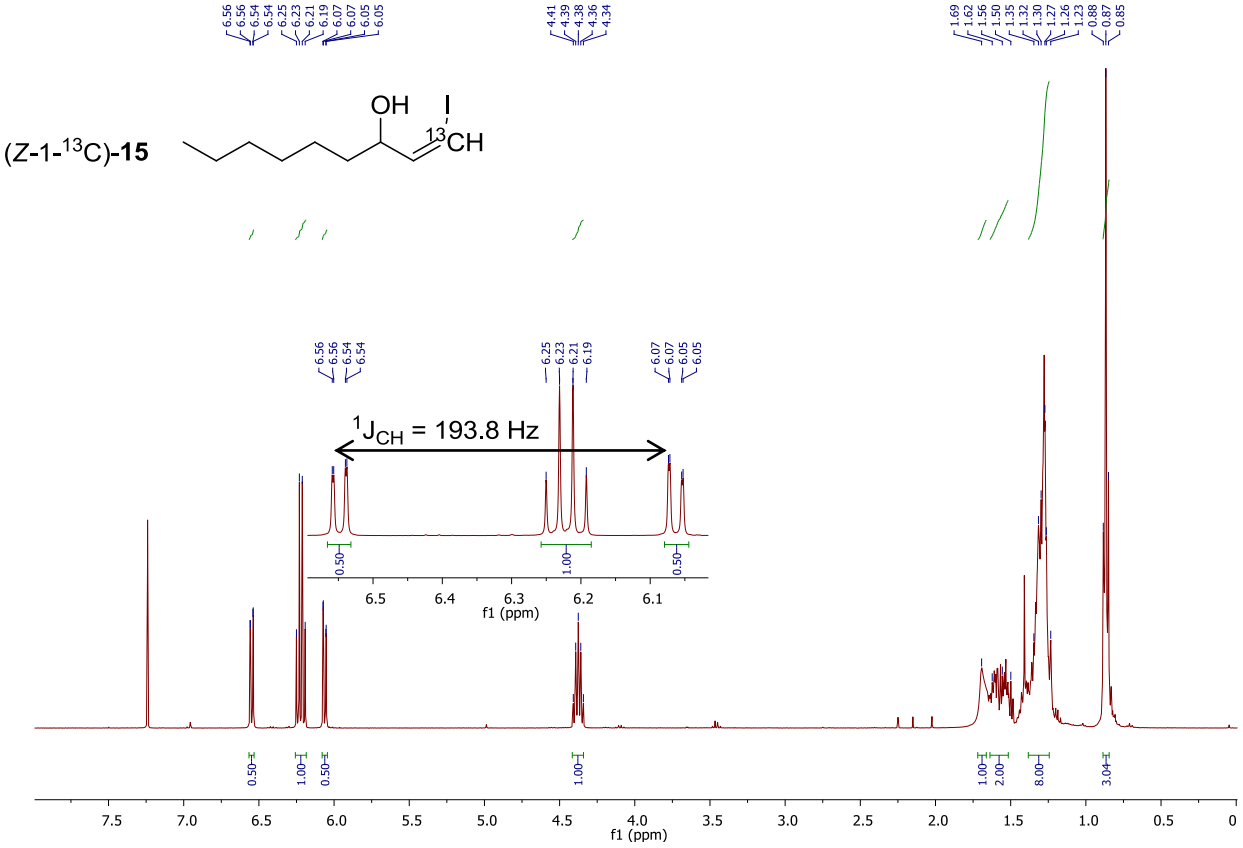
^{1}H NMR spectrum of (*E*-1-^{13}C)-1-iodonon-1-en-3-ol [(*E*-1-^{13}C)-**15**] & (1-^{13}C)-1,1-diiodonon-1-en-3-ol [(1-^{13}C)-**16**] (400 MHz, $CDCl_3$)



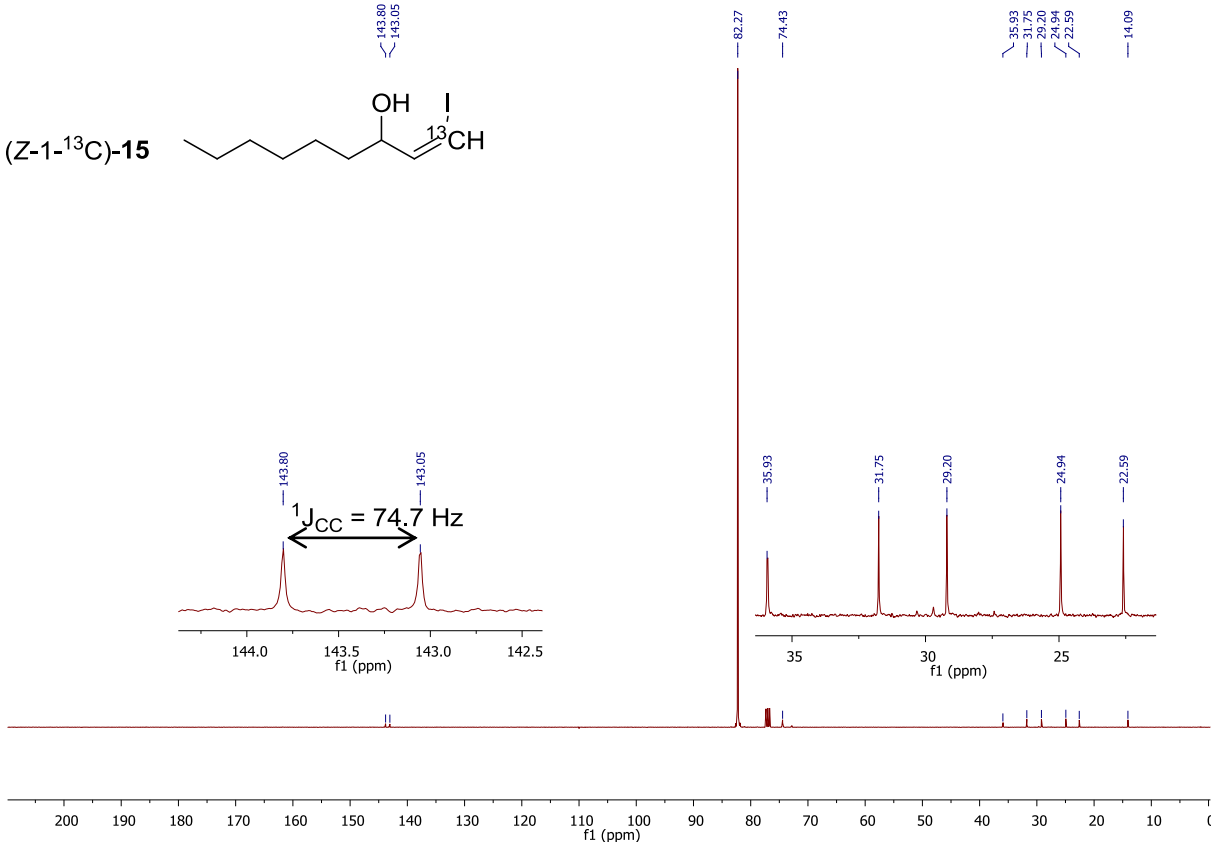
^{13}C NMR spectrum of (*E*-1-^{13}C)-1-iodonon-1-en-3-ol [(*E*-1-^{13}C)-**15**] & (1-^{13}C)-1,1-diiodonon-1-en-3-ol [(1-^{13}C)-**16**] (101 MHz, $CDCl_3$)



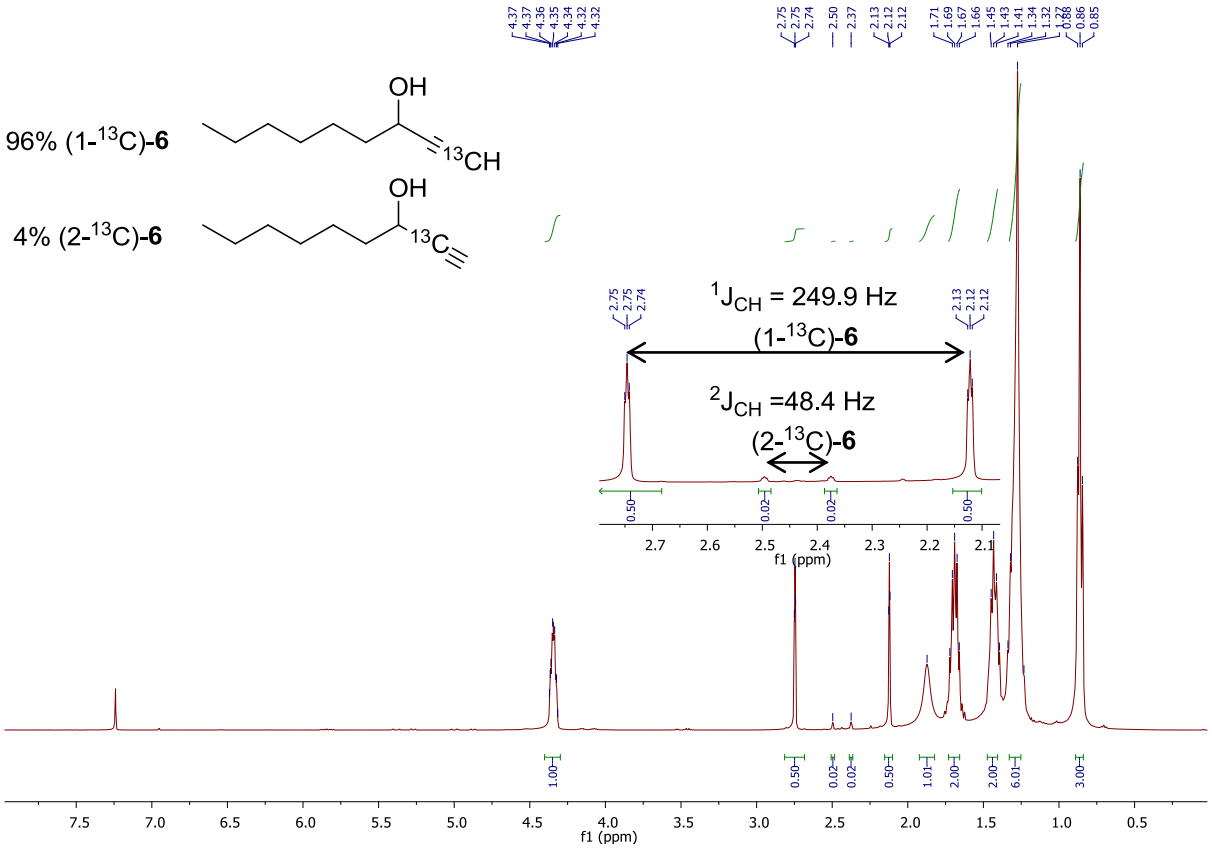
^{1}H NMR spectrum of (*Z*-1-^{13}C)-1-iodonon-1-en-3-ol [(*Z*-1-^{13}C)-**15**] (400 MHz, $CDCl_3$)



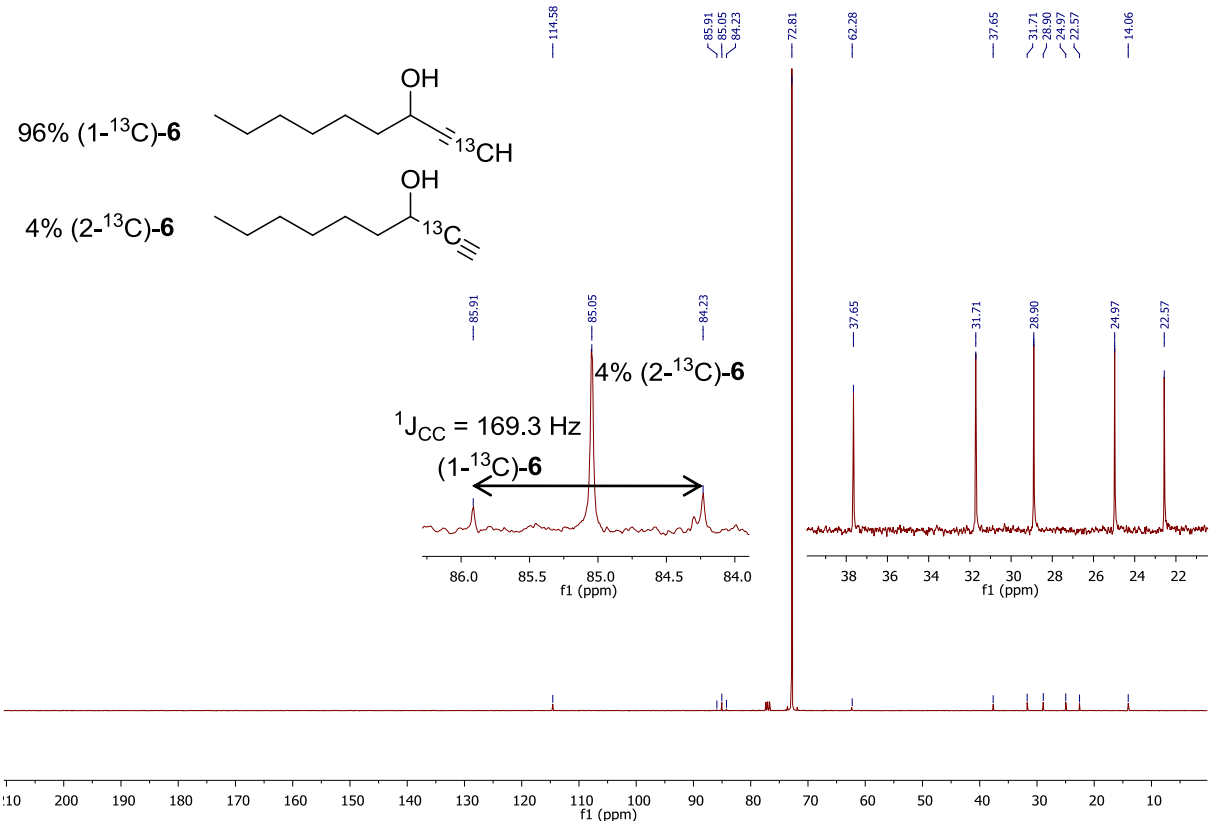
^{13}C NMR spectrum of (*Z*-1-^{13}C)-1-iodonon-1-en-3-ol [(*Z*-1-^{13}C)-**15**] (101 MHz, $CDCl_3$)



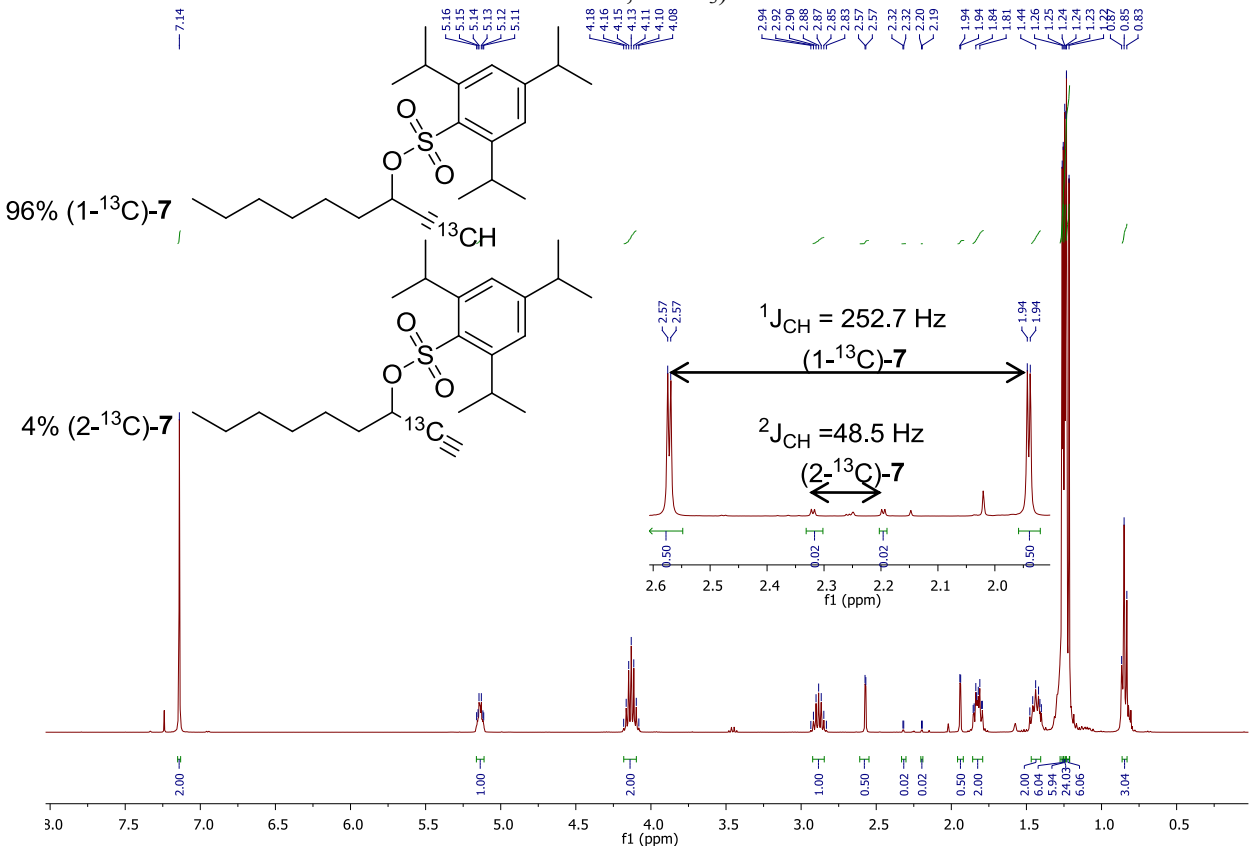
^{1}H NMR spectrum of (1-^{13}C)-non-1-yn-3-ol [(1-^{13}C)-**6**] (400 MHz, $CDCl_3$)



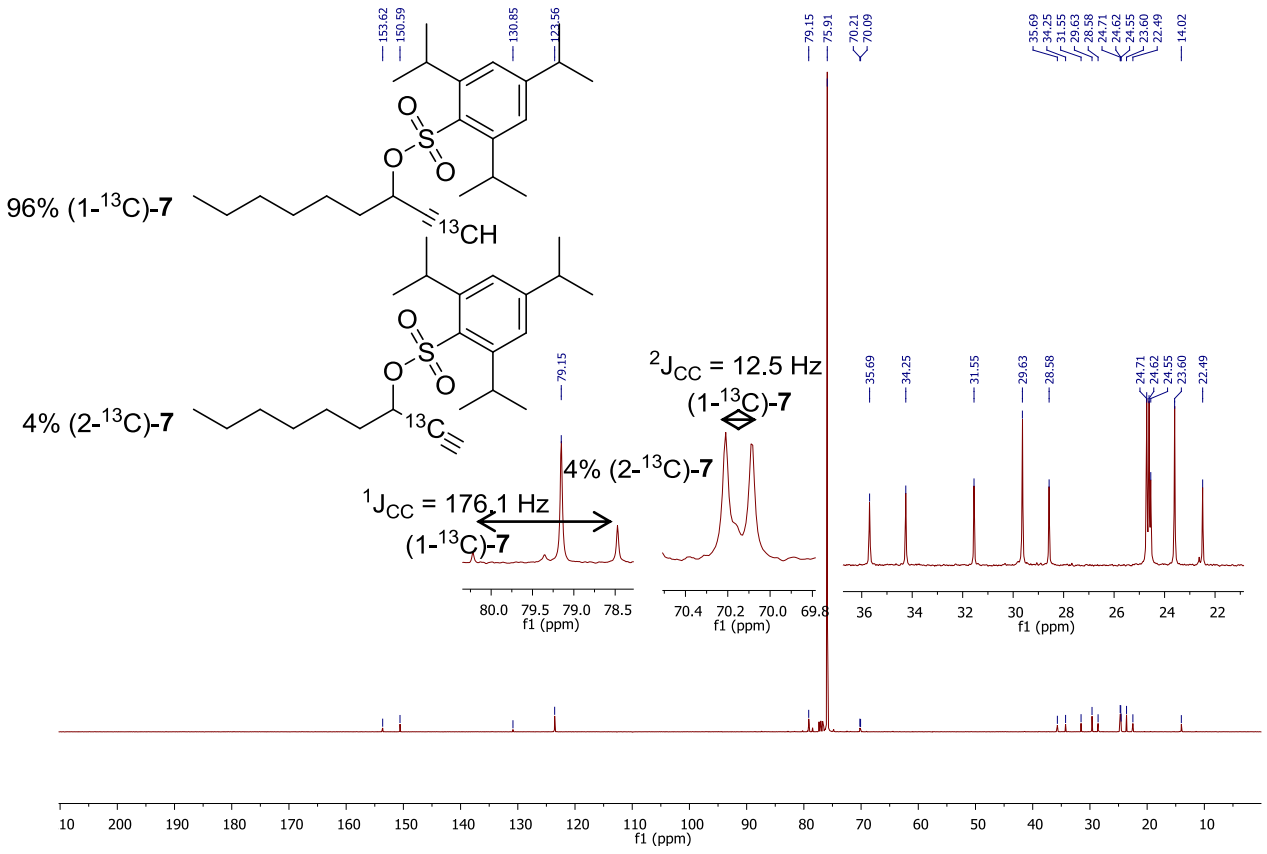
^{13}C NMR spectrum of (1-^{13}C)-non-1-yn-3-ol [(1-^{13}C)-**6**] (101 MHz, $CDCl_3$)



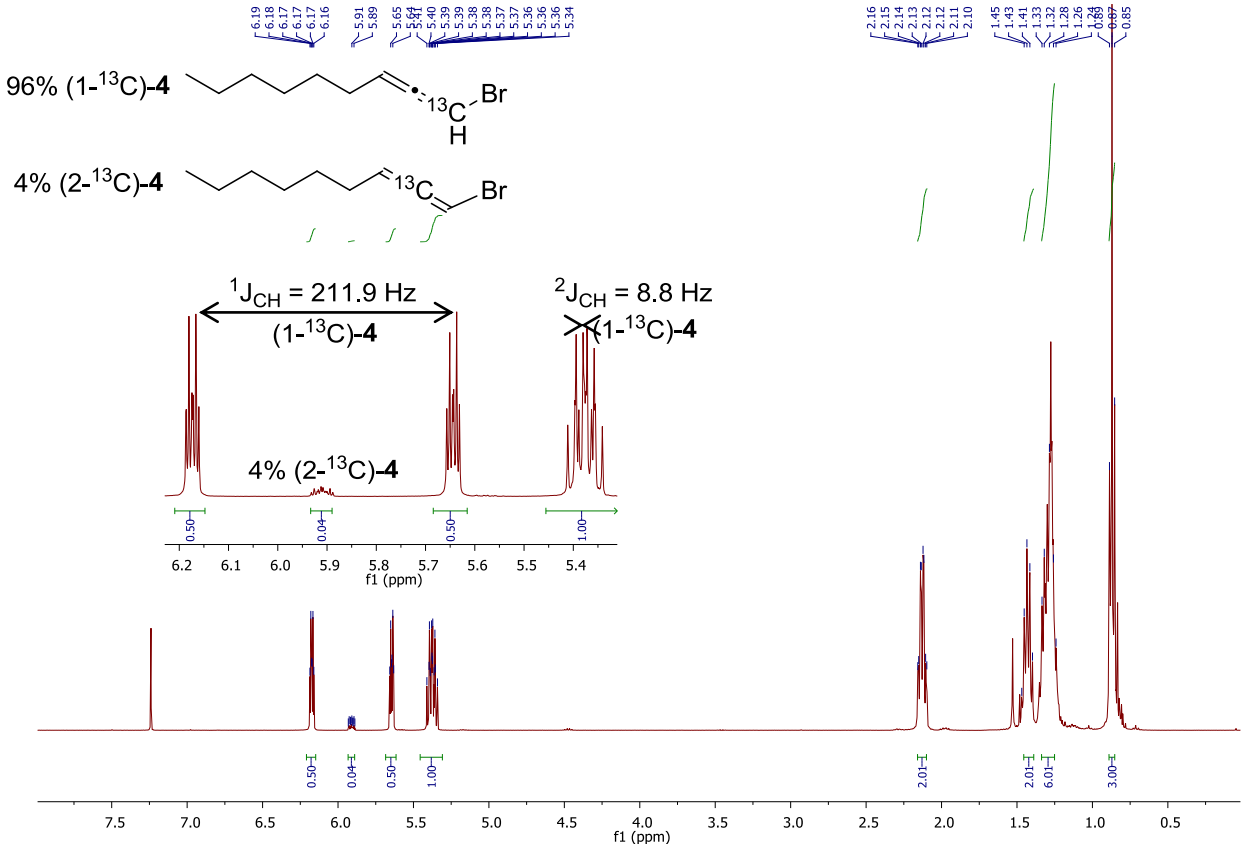
^{1}H NMR spectrum of (1-^{13}C)-non-1-yn-3-yl 2,4,6-tris(propan-2-yl)benzene-1-sulphonate [(1-^{13}C)-**7**] (400 MHz, $CDCl_3$)



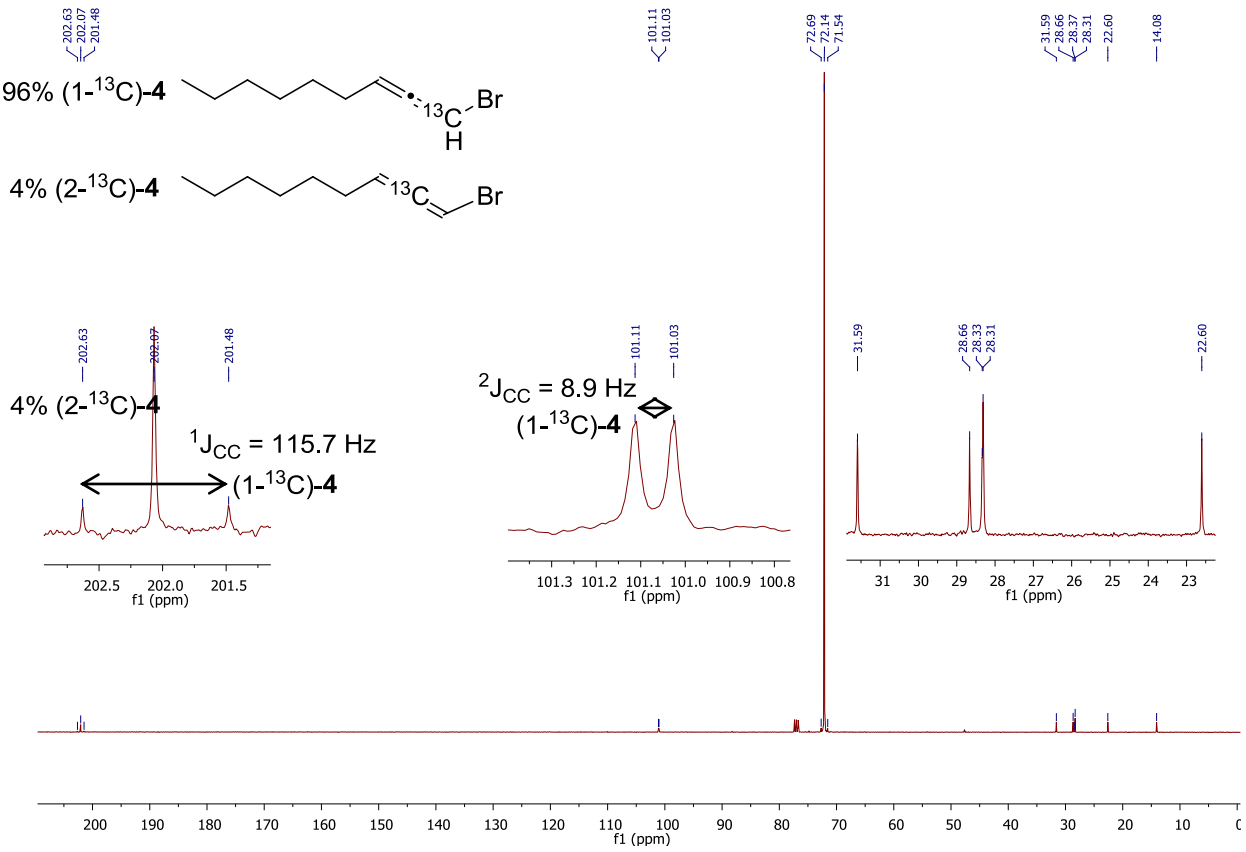
^{13}C NMR spectrum of (1-^{13}C)-Non-1-yn-3-yl 2,4,6-tris(propan-2-yl)benzene-1-sulphonate [(1-^{13}C)-**7**] (101 MHz, $CDCl_3$)



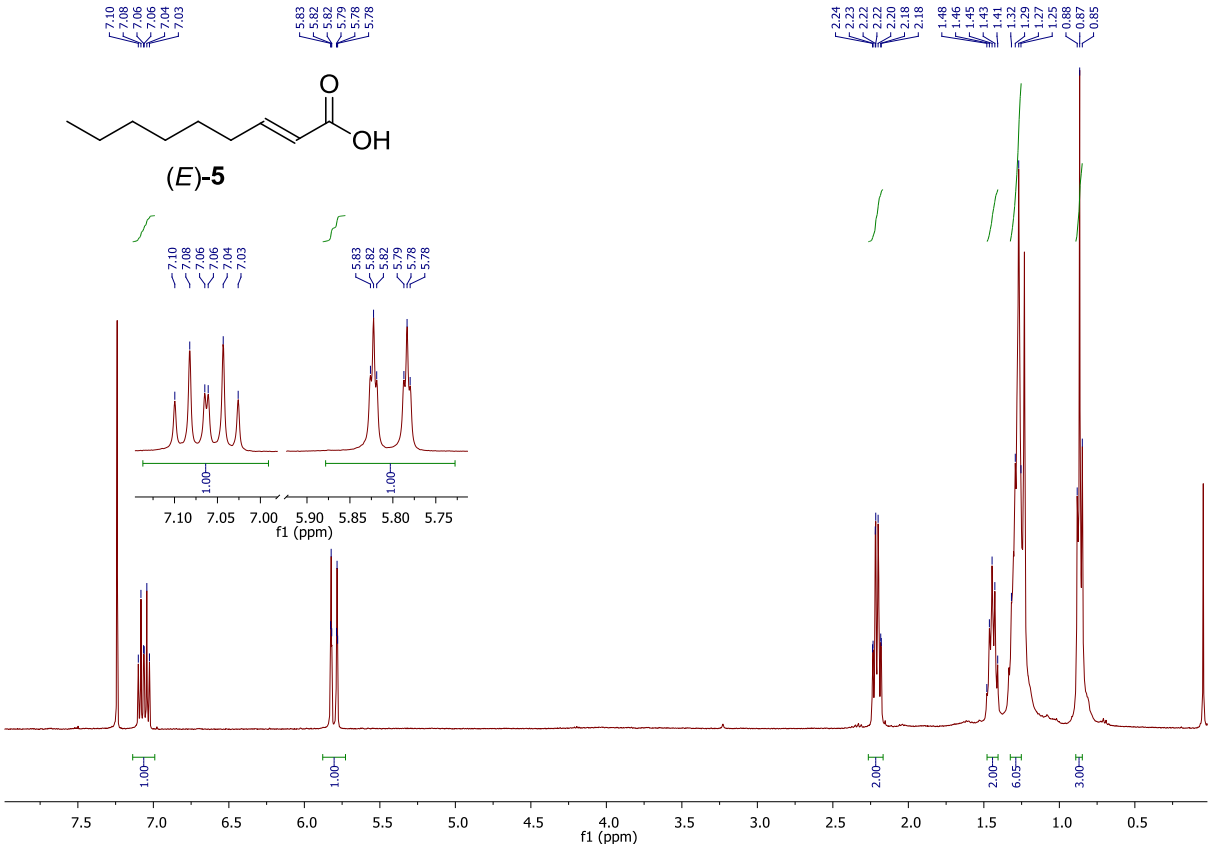
^{1}H NMR spectrum of (1-^{13}C)-1-bromonona-1,2-diene [(1-^{13}C)-**4**] (400 MHz, $CDCl_3$)



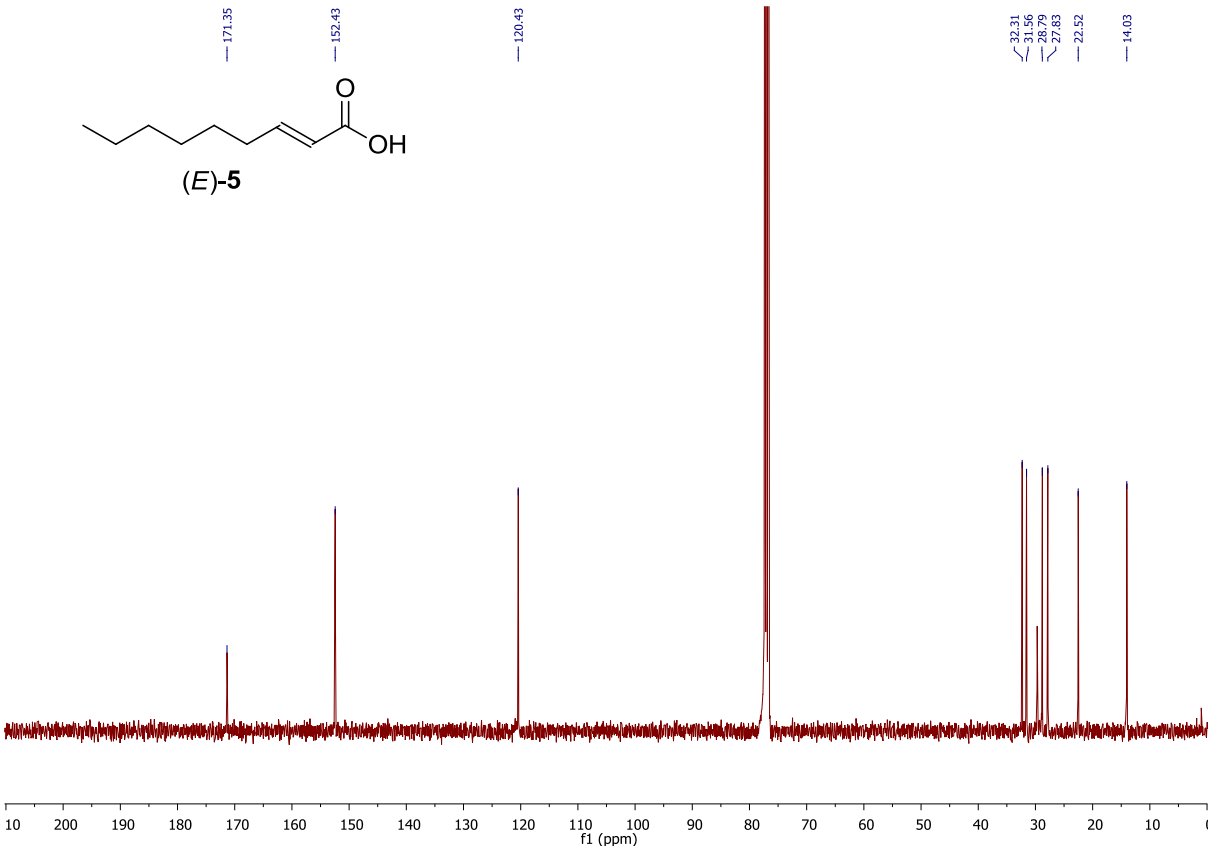
^{13}C NMR spectrum of (1-^{13}C)-1-bromonona-1,2-diene [(1-^{13}C)-**4**] (101 MHz, $CDCl_3$)



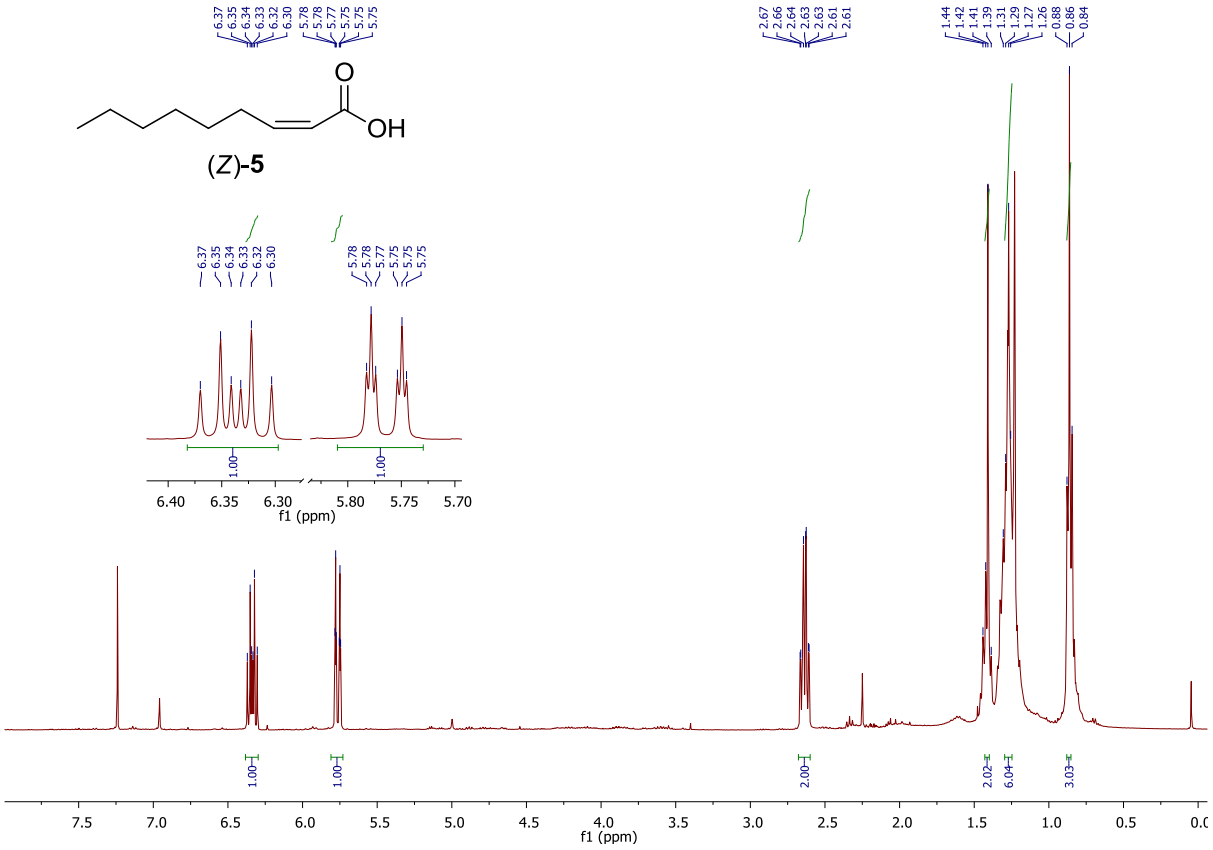
^{1}H NMR spectrum of (2*E*)-non-2-enoic acid (*E*)-**5** (400 MHz, $CDCl_3$)



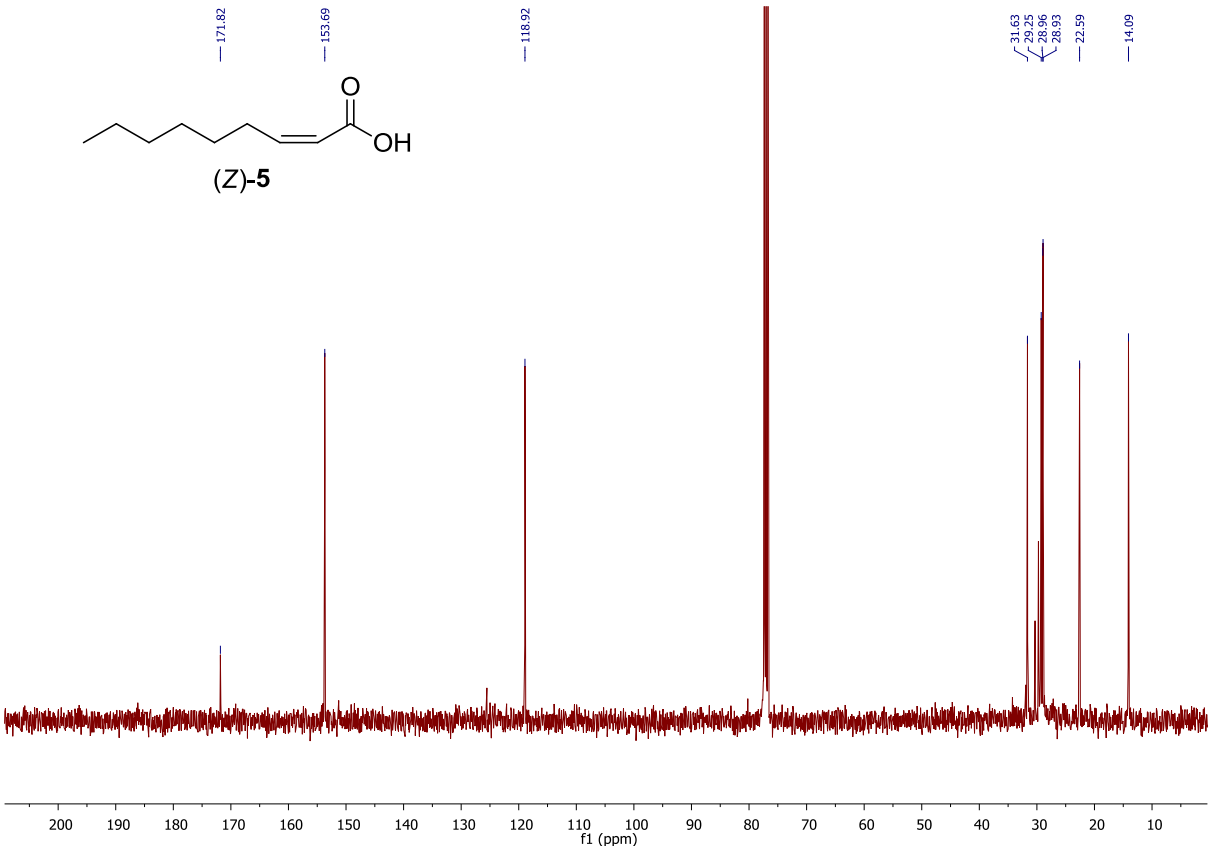
^{13}C NMR spectrum of (2*E*)-non-2-enoic acid (*E*)-**5** (101 MHz, $CDCl_3$)



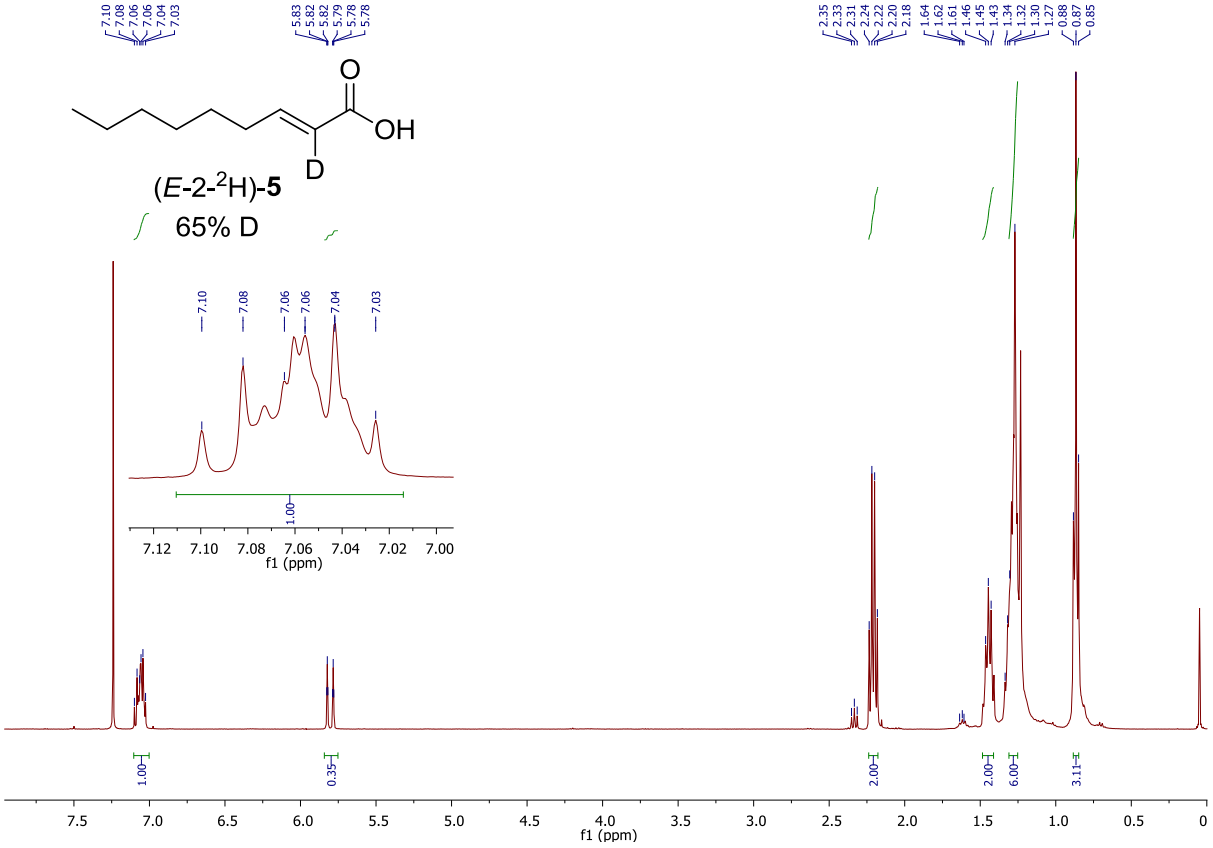
^{1}H NMR spectrum of (2*Z*)-non-2-enoic acid (*Z*)-**5** (400 MHz, $CDCl_3$)



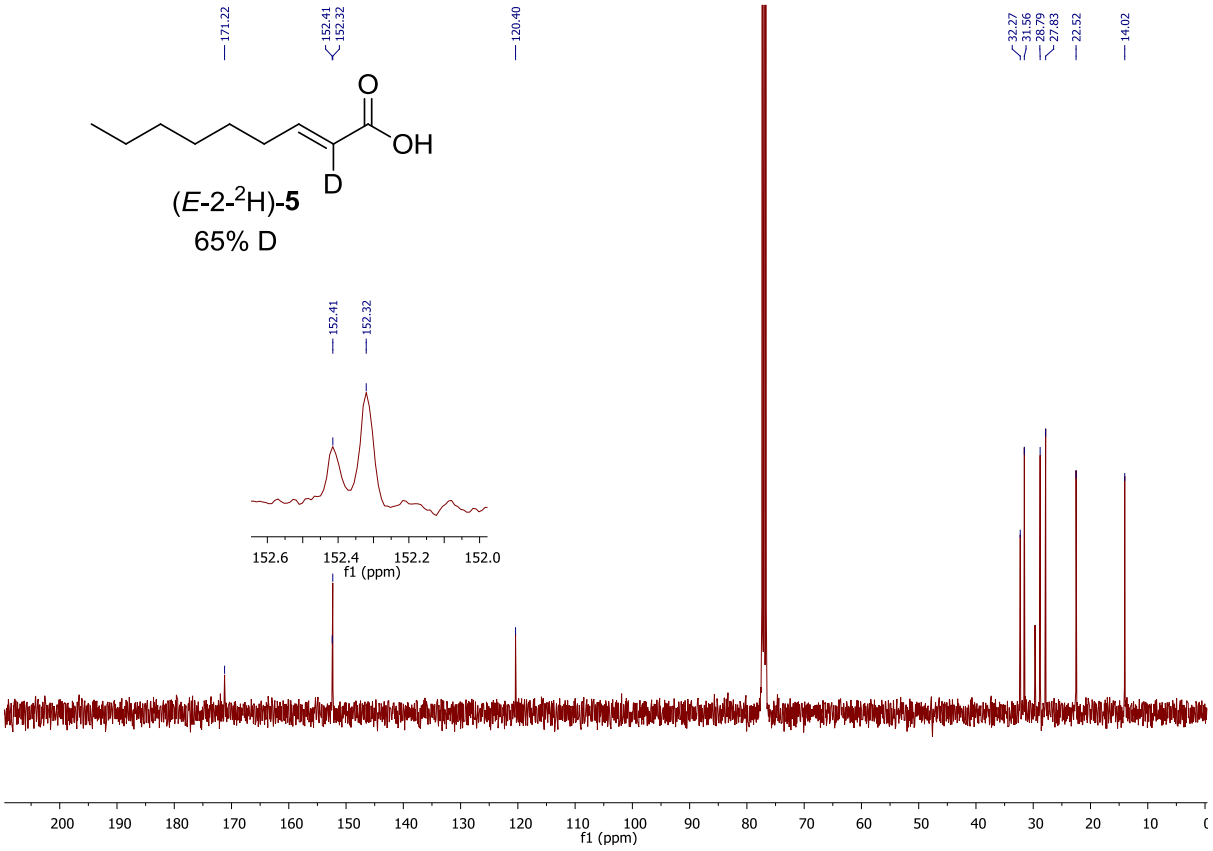
^{13}C NMR spectrum of (2*Z*)-non-2-enoic acid (*Z*)-**5** (101 MHz, $CDCl_3$)



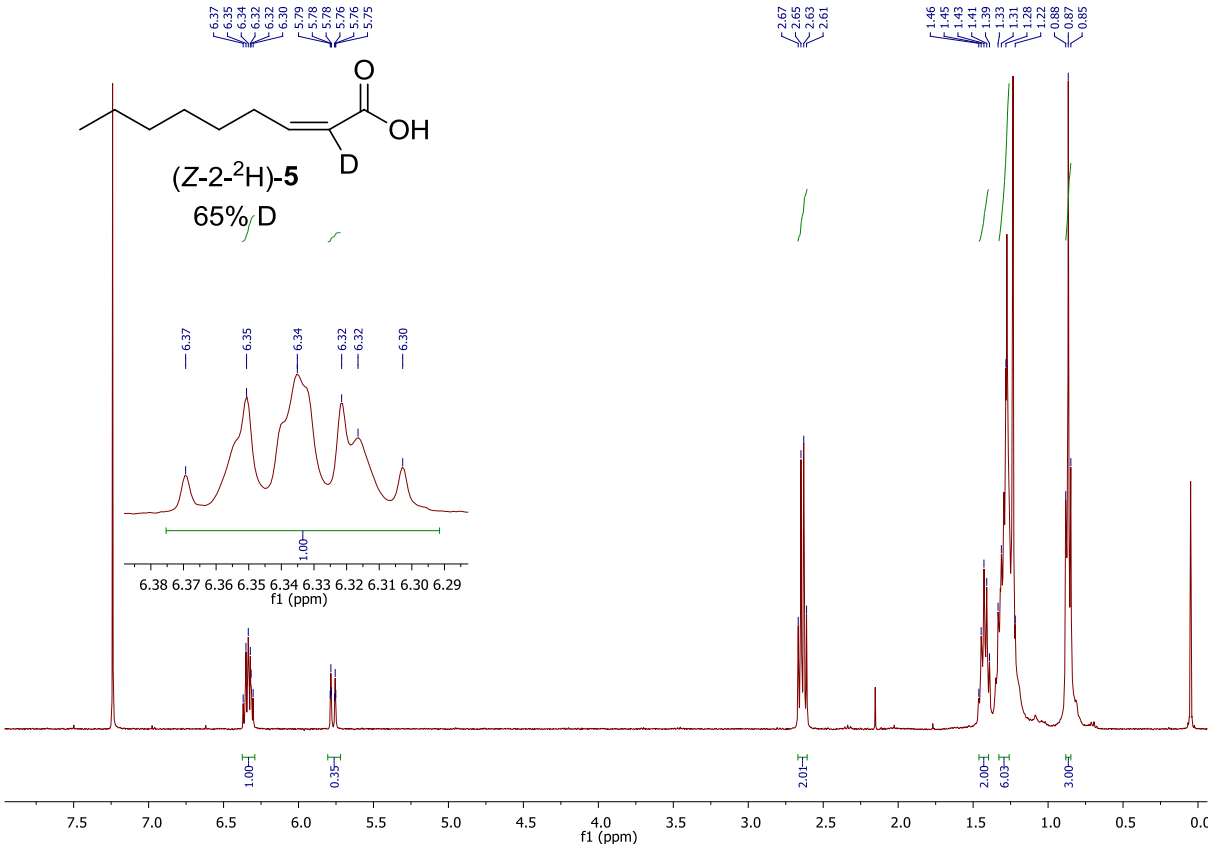
^{1}H NMR spectrum of (*E*-2-^{2}H)-non-2-enoic acid [(*E*-2-^{2}H)-**5**] (400 MHz, $CDCl_3$)



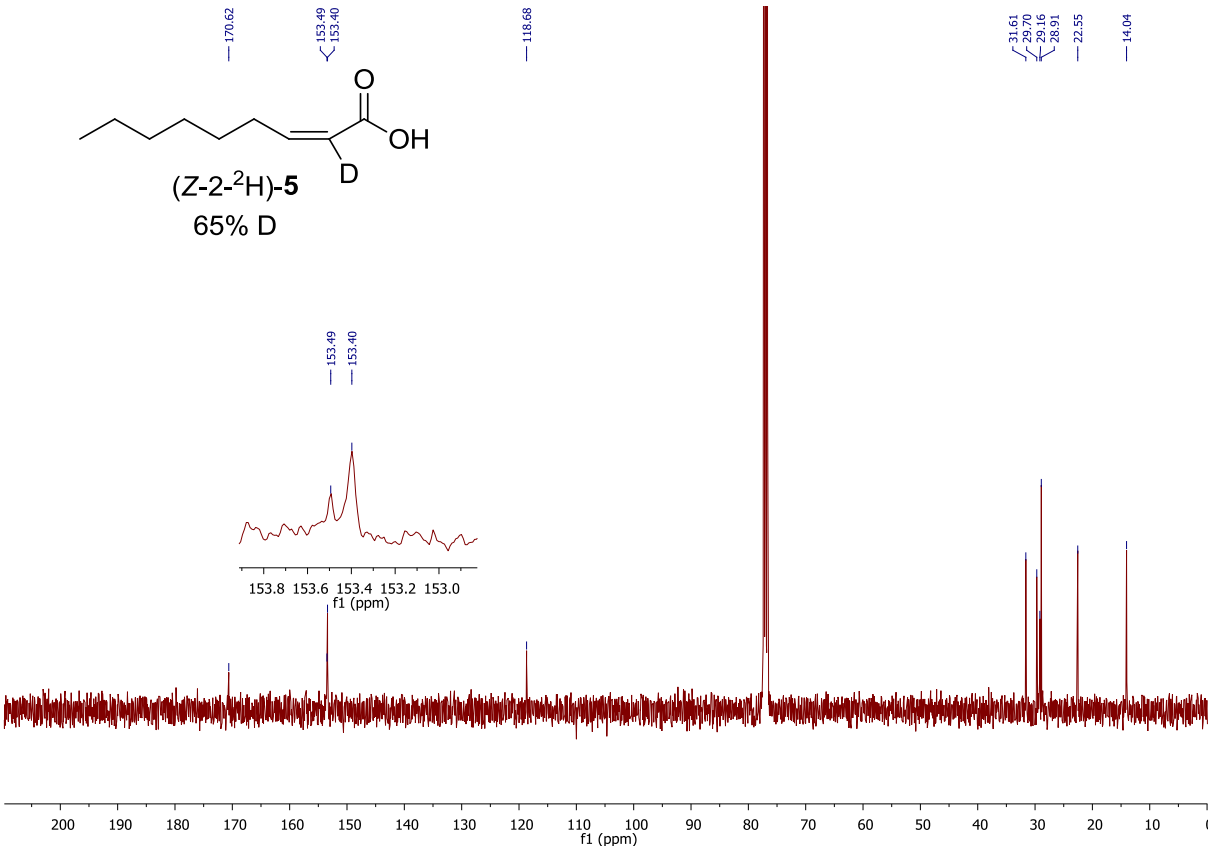
^{13}C NMR spectrum of (*E*-2-^{2}H)-non-2-enoic acid [(*E*-2-^{2}H)-**5**] (101 MHz, $CDCl_3$)



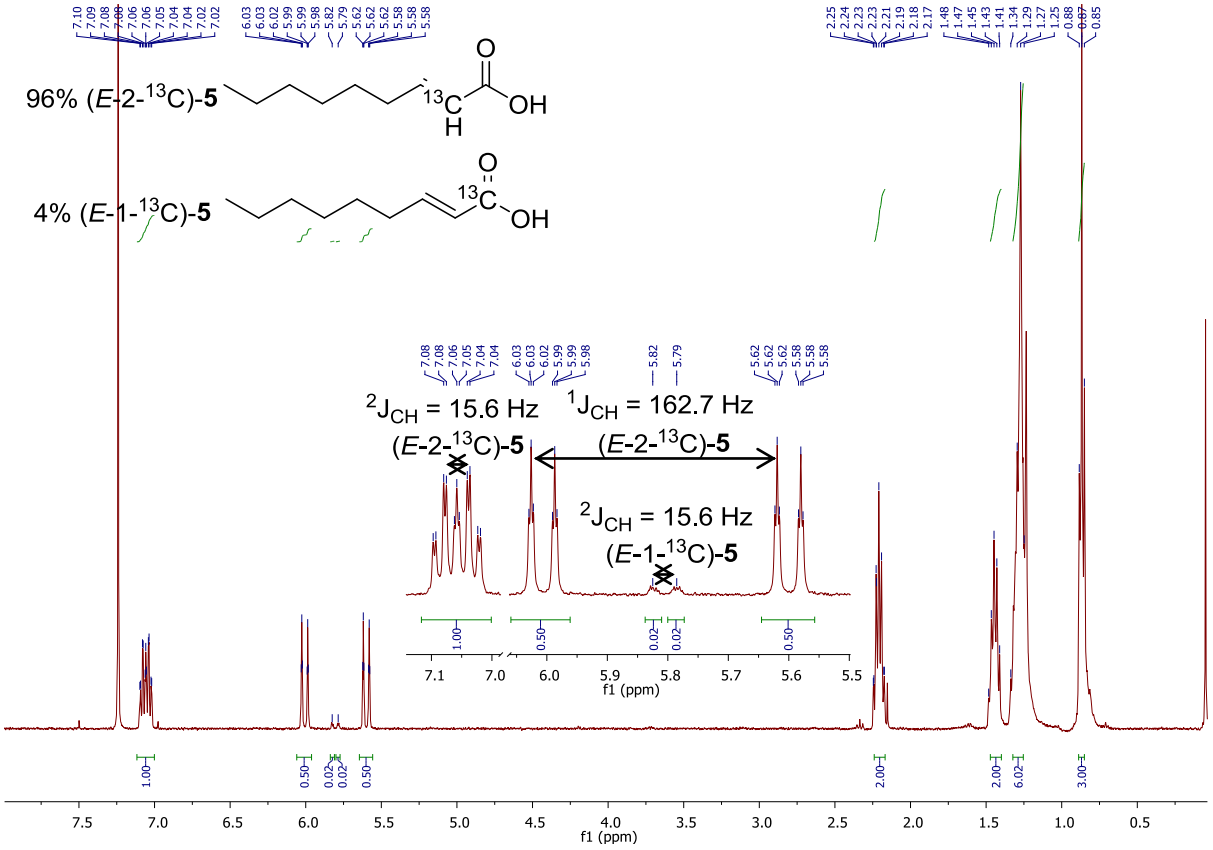
^{1}H NMR spectrum of (*E*-2-^{2}H)-non-2-enoic acid [(*E*-2-^{2}H)-**5**] (400 MHz, $CDCl_3$)



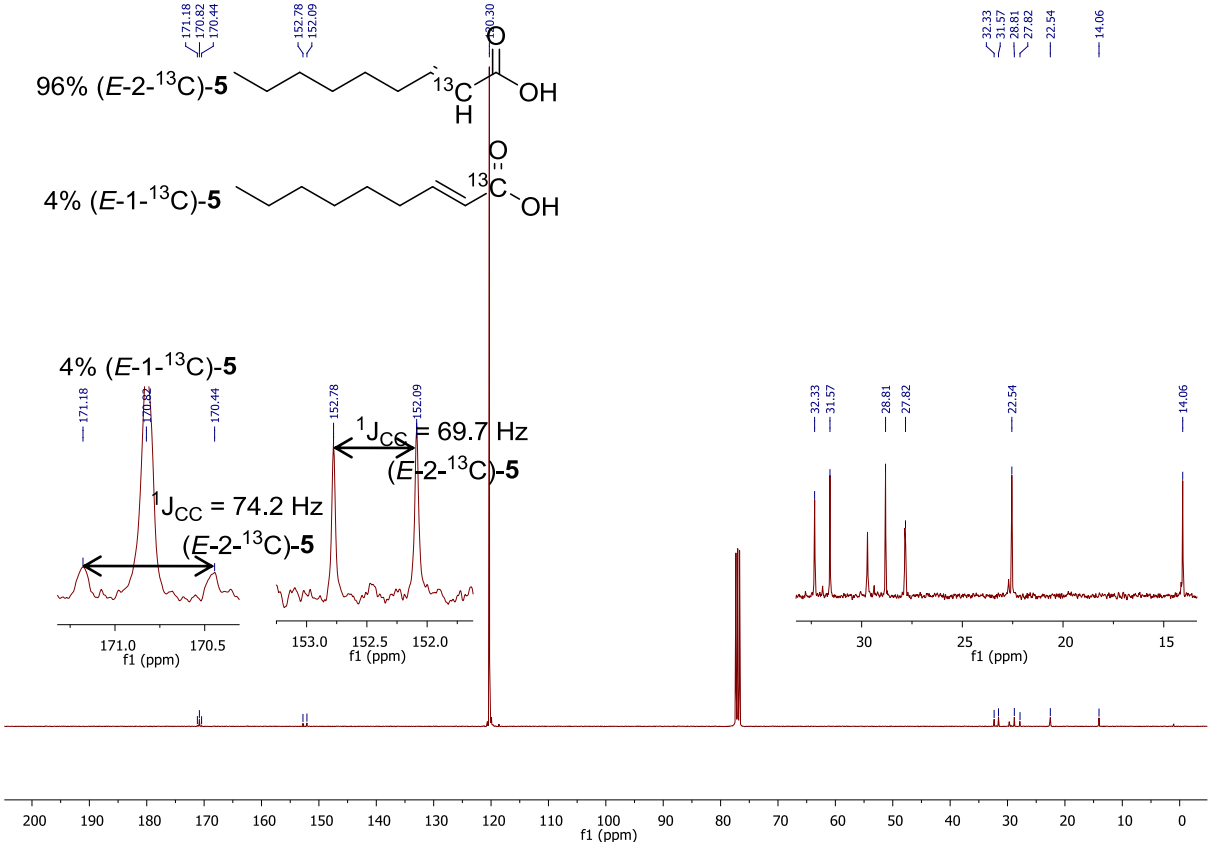
^{13}C NMR spectrum of (*E*-2-^{2}H)-non-2-enoic acid [(*E*-2-^{2}H)-**5**] (101 MHz, $CDCl_3$)



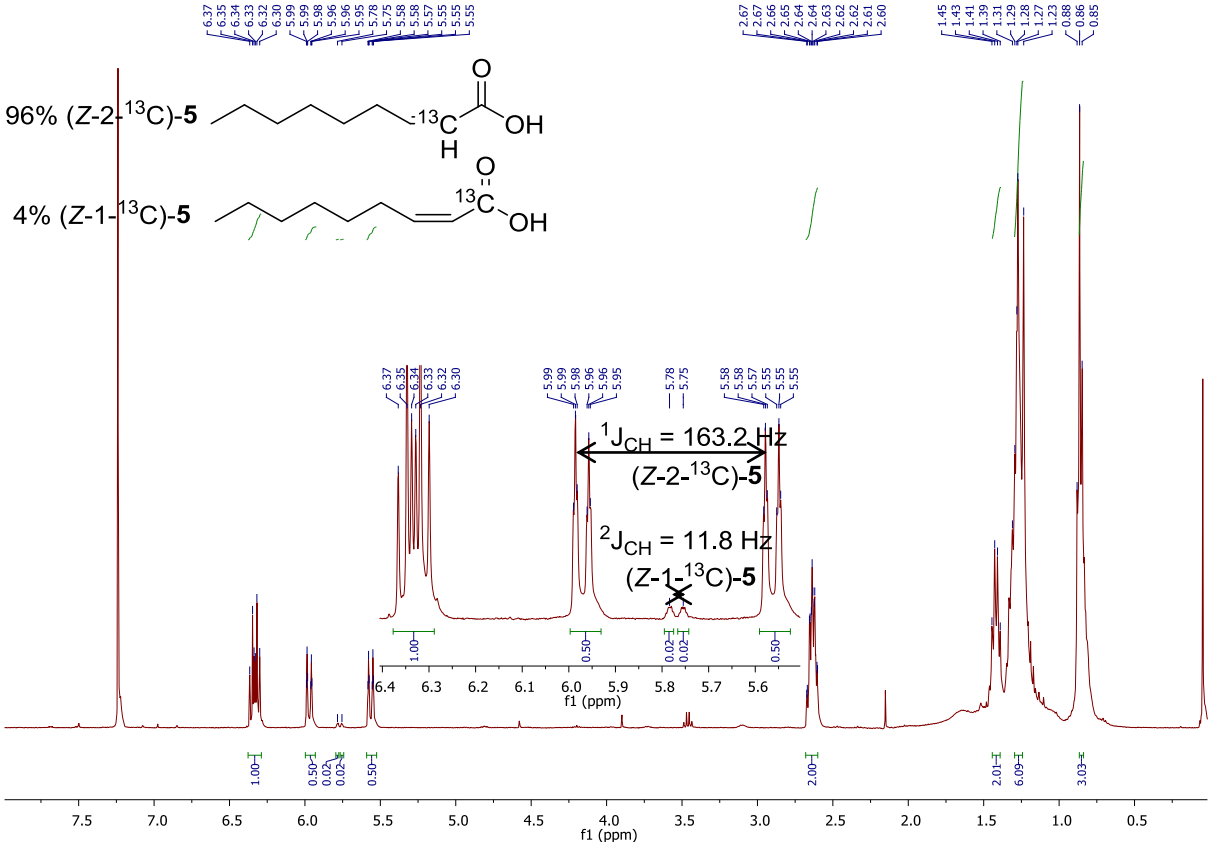
^{1}H NMR spectrum of (*E*-2-^{13}C)-non-2-enoic acid [(*E*-2-^{13}C)-**5**] (400 MHz, $CDCl_3$)



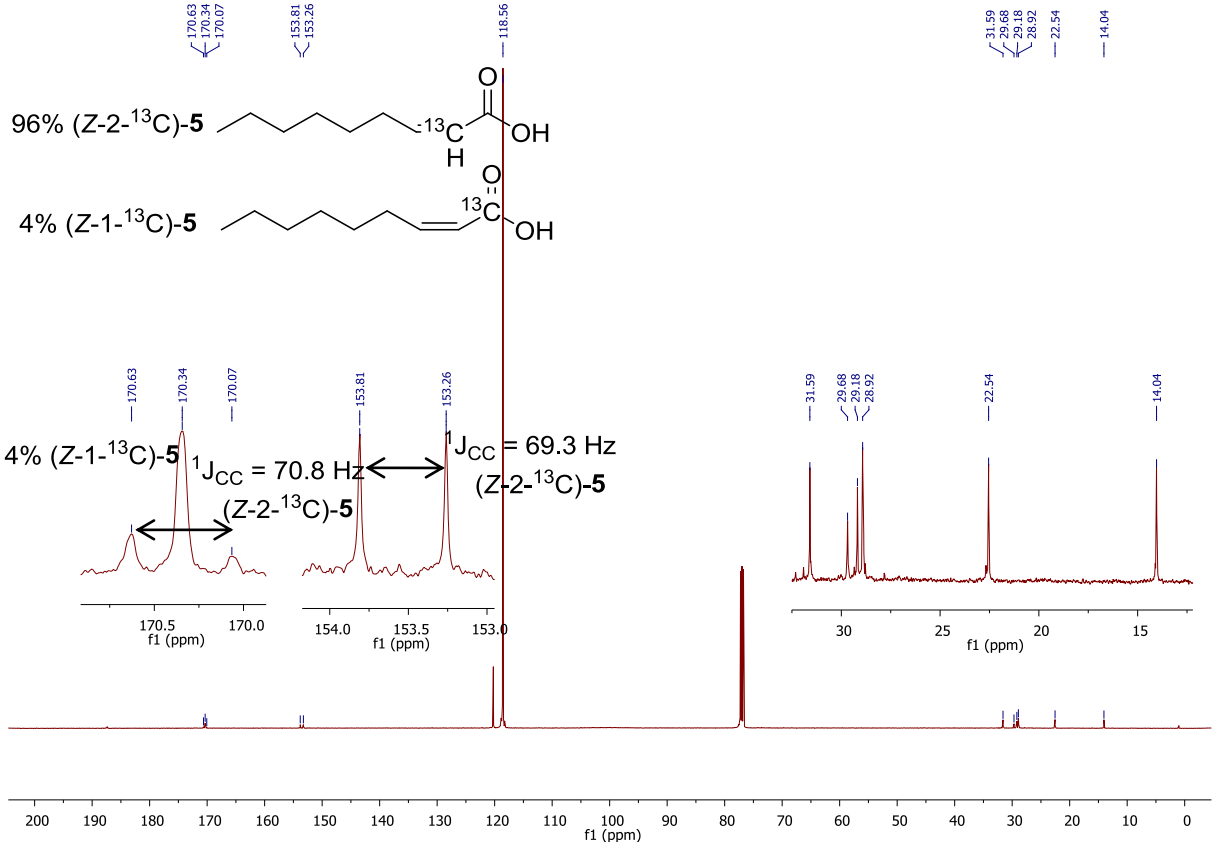
^{13}C NMR spectrum of (*E*-2-^{13}C)-non-2-enoic acid [(*E*-2-^{13}C)-**5**] (101 MHz, $CDCl_3$)



^{1}H NMR spectrum of (*Z*-2-^{13}C)-non-2-enoic acid [(*Z*-2-^{13}C)-**5**] (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of (*Z*-2-^{13}C)-non-2-enoic acid [(*Z*-2-^{13}C)-**5**] (101 MHz, $CDCl_3$)



References:

1. R. W. Murray and R. Jeyaraman, *J*. *Org*. *Chem*., 1985, **50**, 2847-2853.
2. H. S. Lin and L. A. Paquette, *Synth*. *Commun*., 1994, **24**, 2503–2506.
3. Y. Ahn, G. I. Cardenas, J. Yang and D. Romo, *Org*. *Lett*., 2001, **3**, 751 – 754.
4. W. Jeong, M. J. Kim, H. Kim, S. Kim, D. Kim and K. J. Shin, *Angew*. *Chem*. *Int*. *Ed*., 2010, **49**, 752-756.
5. Y. Taniguchi, J. Inanaga and M. Yamaguchi, *Bull*. *Chem*. *Soc*. *Jpn*., 1981, **54**, 3229-3230.
6. A. Hassner, R. H. Reuss and H. W. Pinnick, *J*. *Org*. *Chem*., 1975, **40**, 3427-3429.
7. J. S. Debenham, R. Rodebaugh and B. Fraser-Reid, *J*. *Org*. *Chem*., 1997, **62**, 4591-4600.
8. K. Sato, S. Akai, T. Hiroshima, H. Aoki, M. Sakuma, K. Suzuki, *Tetrahedron*. *Lett*., 2003, **44**, 3513-3516.
9. W. Zhu, M. Jimenez, W.-H. Jung, D. P. Camarco, R. Balachandran, A. Vogt, B. W. Day and D. P. Curran, *J*. *Am*. *Chem*. *Soc*., 2010, **132**, 9175-9187.
10. A. K. Bakkestuen, L.-L. Gundersen, D. Petersen, B. T. Utenova and A. Vik, *Org*. *Biomol*. *Chem*., 2005, **3**, 1025-1033.