Supplementary Material (ESI) for Chemical Communications

Silica gel-mediated rearrangement of allylic acetates and application to the synthesis of 1,3-enynes

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Supplementary Information

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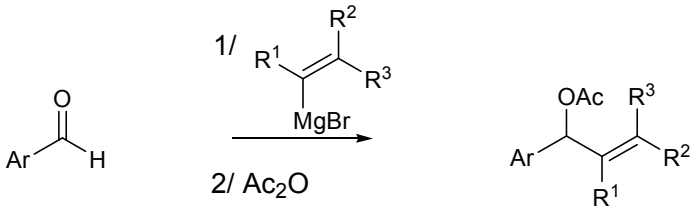
General experimental methods

Infrared (IR) spectra were recorded on a Bruker TENSOR TM 27 (IRFT), wave-numbers are indicated in cm^{-1}. NMR spectra were recorded on a Bruker AVANCE 400. ^1H NMR spectra were recorded at 400 MHz and data are reported as follows: chemical shift in ppm from tetramethylsilane as an internal standard with the residual solvent peak as an internal indicator ($CDCl_3$ δ: 7.26), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of non-equivalent resonances), integration. ^{13}C NMR spectra were recorded at 100 MHz and data are reported as follows: chemical shift in ppm from tetramethylsilane with the solvent as an internal indicator ($CDCl_3$ δ 77.1 ppm), multiplicity with respect to proton (deduced from DEPT experiments, s = quaternary C, d = CH, t = CH_2, q = CH_3). CH_2Cl_2 was distilled from CaH_2. TLC was performed on silica gel plates visualized either with a UV lamp (254 nm), or using solutions of *p*-anisaldehyde/sulfuric/acid–acetic acid in EtOH followed by heating. Silica gel Geduran Si60 (40-63 µm) was purchased from Merck. Mass spectra with electronic impact (MS-EI) were recorded on a GC/MS (70 eV). HRMS were performed at the Laboratoire de Spectrométrie de Masse SM^3E de l'Université Pierre et Marie Curie in Paris. Microwave irradiation experiments were performed using a single-mode Initiator Discover (0-300W, 2.45 GHz) from CEM. When mentioned, silica gel was deactivated by eluting Et_3N. The *E*/*Z* ratio were determined by ^1H NMR and/or GC/MS analysis. PE = petroleum ether.

Experimental section

Synthesis of allylic acetates of type 5



General procedure 1

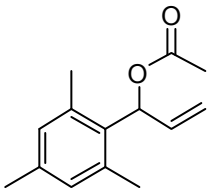
To a solution of benzylic aldehyde in THF (0.2 M) at -78 °C was added a solution of the alkenyl Grignard reagent (1.2 equiv) in THF (0.5-1 M). After 1 h at -78 °C, the reaction mixture was warmed to rt and stirred until full conversion. The reaction mixture was then cooled to 0 °C and acetic anhydride (1.5 equiv) was added. After one night at rt, a saturated aqueous solution of ammonium chloride was added, the two phases were separated and the aqueous phase was extracted with Et_2O. The organic layers were then washed with brine, dried over $MgSO_4$, filtered and the solvents were removed under reduced pressure to afford the expected allylic acetate of type **5**.

General procedure 2

To a solution of benzylic aldehyde in THF (0.2 M) at -78 °C was added a solution of the alkenyl Grignard reagent (1.2 equiv) in THF (0.5-1 M). After 1 h at -78 °C, the reaction media was warmed to rt and stirred until full conversion. The reaction mixture was quenched by addition of a saturated

aqueous solution of ammonium chloride, the two phases were separated and the aqueous phase was extracted with Et_2O. The organic layers were combined, dried over $MgSO_4$, filtered and the solvents were removed under reduced pressure. The residue was dissolved in a 3/1 mixture of CH_2Cl_2/pyridine (0.3 M) and cooled to 0 °C before 4-DMAP (0.05 equiv) and acetic anhydride (1.5 equiv) were added. After one night at rt, the reaction mixture was washed with a 10% copper sulfate aqueous solution and the aqueous phase was extracted with Et_2O. The organic phases were then washed with brine, dried over $MgSO_4$, filtered and the solvents were removed under vacuum to afford the expected allylic acetate of type **5**.

Acetic acid 1-(2,4,6-trimethyl-phenyl)-allyl ester, 5b



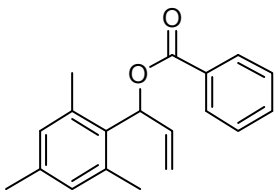
Prepared according to the general procedure 1 using mesitaldehyde and vinylmagnesium bromide (1 M THF) (90% yield).

IR (*neat*) : 2922, 1738, 1612, 1448, 1371, 1235, 1018 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 6.83 (s, 2H), 6.70 (m, 1H), 6.07 (ddd, *J* = 17.3, 10.6, 4.5 Hz, 1H), 5.18 (dd, *J* = 10.6, 2.0 Hz, 1H), 5.09 (dd, *J* = 17.3, 2.0 Hz, 1H), 2.39 (s, 6H), 2.26 (s, 3H), 2.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 170.2 (s), 137.8 (s), 137.3 (2s), 135.6 (d), 131.9 (s), 130.0 (2d), 116.2 (t), 73.1 (d), 21.2 (q), 21.0 (q), 20.6 (2q).

HRMS (ESI) : Calculated for $C_{14}H_{18}NaO_2$ $[M+Na]^+$: 241.1199. Found : 241.1197.



Benzoic acid 1-(2,4,6-trimethyl-phenyl)-allyl ester, 5c

Prepared according to general procedure 1 using mesitaldehyde and vinylmagnesium bromide (1 M in THF). Benzoyl chloride was used instead of acetic anhydride (16% yield).

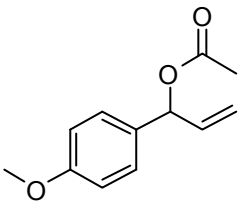
IR (*neat*) : 2920, 1718, 1612, 1451, 1314, 1268, 1108, 1069, 1026 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.09 (d_{app}, *J* = 7.4 Hz, 2H), 7.56 (t_{app}, *J* = 7.4 Hz, 1H), 7.45 (t_{app}, *J* = 7.4 Hz, 2H), 6.96 (m, 1H), 6.86 (s, 2H), 6.20 (m, 1H), 5.19-5.27 (m, 2H), 2.50 (s, 6H), 2.26 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 165.8 (s), 137.8 (s), 137.3 (2s), 135.6 (d), 133.1 (d), 131.8 (s), 130.4 (s), 130.0 (2d), 129.8 (d), 128.5 (2d), 116.3 (2t), 73.6 (d), 21.0 (q), 20.8 (2q).

MS (EI, 70eV) *m/z* : 280 ($[M]^{+\cdot}$, 9), 159 (28), 158 (65), 144 (27), 143 (100), 129 (25), 128 (25), 105 (75), 77 (26).

HRMS (ESI) : Calculated for $C_{19}H_{20}NaO_2$ $[M+Na]^+$: 303.13610. Found : 303.13536.



Acetic acid 1-(4-methoxy-phenyl)-allyl ester, 5d

Prepared according to the general procedure 2 using 4-methoxybenzaldehyde and vinylmagnesium bromide (1 M THF) (quant.).

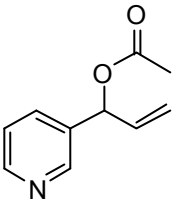
IR (*neat*) : 2937, 2838, 1737, 1612, 1514, 1370, 1233, 1176, 1032 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.29 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.24 (d, *J* = 6.1 Hz, 1H), 6.0 (ddd, *J* = 16.4, 10.3, 6.1 Hz, 1H), 5.22-2.30 (m, 2H), 3.80 (s, 3H,), 2.09 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 170.0 (s), 159.6 (s), 136.5 (d), 131.2 (s), 128.8 (2d), 116.5 (t), 114.0 (2d), 75.9 (d), 55.3 (q), 21.3 (q).

MS (EI, 70eV) *m/z* : 206 ($[M]^{+\cdot}$, 91), 164 (35), 163 ($[M\text{-}Ac]^+$, 80), 147 (99), 146 (32), 135 (80), 132 (25), 131 (71), 121 (57), 117 (20), 116 (15), 115 (51), 108 (63), 105 (30), 104 (26), 103 (100), 91(75), 79 (20), 78 (31), 77 (51), 51 (25).

HRMS (ESI) : Calculated for $C_{12}H_{14}NaO_3$ $[M+Na]^+$: 229.08352. Found : 229.08325.



Acetic acid 1-pyridin-3-yl-allyl ester, 5g

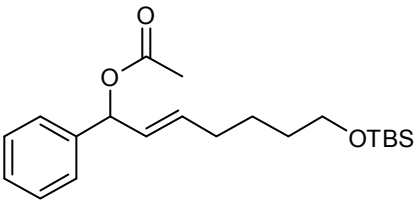
Prepared according to the general procedure 2 using pyridine-2-aldehyde and vinylmagnesium bromide (1 M THF). A flash chromatography on silica gel previously deactivated with Et_3N (EP/AcOEt 6/4 to 5/5) delivered **5f** (95% yield).

IR (*neat*) : 3014, 1738, 1644, 1591, 1573, 1472, 1435, 1371, 1225, 1150, 1117, 1093, 1023 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.61 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.71 (td, *J* = 7.6, 1.8 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.23 (dd, *J* = 7.6, 1.0 Hz, 1H), 6.30 (d, *J* = 6.3 Hz, 1H), 6.11 (ddd, *J* = 17.3, 10.7, 6.3 Hz, 1H), 5.40 (dd, *J* = 17.3, 1.2 Hz, 1H), 5.31 (dd, *J* = 10.7, 1.2 Hz, 1H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 169.8 (s), 158.1 (s), 149.4 (d), 136.8 (d), 135.0 (d), 122.8 (d), 121.2 (d), 117.8 (t), 77.0 (d), 21.1 (q).

MS (EI, 70eV) *m/z* : 134 ($[M\text{-}Ac]^+$, 24), 118 (100), 117 (37), 106 (17), 79 (22), 78 (25).



Acetic acid (*E*)-7-(*tert*-butyl-dimethyl-silanyloxy)-1-phenyl-hept-2-enyl ester, 5h

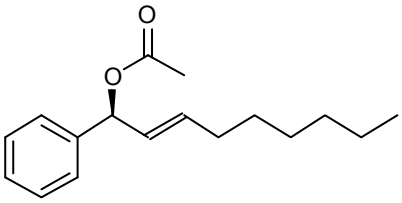
The Grubbs-Hoveyda catalyst (40 mg, 0.06 mmol, 0.025 equiv) was added to a solution of 5-hexenol (303 μl, 2.5 mmol, 1.0 equiv) and allylic acetate **5a** (1.09 g, 5.0 mmol, 2.0 eq.) in CH_2Cl_2 (14 mL). After one night at 40 °C another portion of the Grubbs-Hoveyda catalyst (40 mg, 0.06 mmol, 0.025 equiv) was added. After 24 h at 40 °C, volatiles were removed under reduced pressure and the residue was purified by flash chromatography on silica gel previously deactivated with Et_3N (PE/AcOEt 8/2 to 6/4) to give a colourless oil (332 mg, 53%). TBSCl (47 μl, 0.30 mmol, 1.5 equiv) and imidazole (41 mL, 0.60 mmol, 3.0 equiv) were added to a solution of the obtained oil (50 mg, 0.20

mmol, 1.0 equiv) in CH_2Cl_2 (2.5 mL) at 0 °C. After stirring overnight at rt, saturated aqueous solution of sodium hydrogenocarbonate solution was added and the aqueous phase was extracted with CH_2Cl_2. The organic layers were then dried over $MgSO_4$ and the solvents were removed under reduced pressure. The residue was purified by flash chromatography on silica gel previously deactivated with Et_3N (PE/Et_2O : 100/0 to 95/5) to give **5h** (60 mg, 83%, 44% overall yield) as a mixture of *E*/*Z* diastereoisomers.

IR (*neat*) : 3033, 2929, 2857, 1738, 1495, 1472, 1462, 1370, 1230, 1098, 1017 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.34 (m, 5H), 6.23 (d, *J* = 6.7 Hz, 1H), 6.61-5.77 (m, 2H), 3.59 (m, 2H), 2.09 (s, 3H), 2.06-2.09 (m, 2H), 1.40-1.62 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 170.1 (s), 140.0 (s), 134.7 (d), 128.6 (d), 128.5 (d), 128.0 (d), 127.0 (d), 76.4 (d), 63.1 (t), 32.5 (t), 32.1 (t), 26.1 (3q), 25.3 (t), 21.5 (q), 18.5 (s), - 5.1 (2q).



(*S*)-Acetic acid (*E*)-1-phenyl-non-2-enyl ester, **5i**

To a solution of (*S*)-1-phenyl-2-propen-1-ol (131 µL, 1 mmol, 1 equiv) and 1-octene (1.6 mL, 10 mmol, 10 equiv) in CH_2Cl_2 (10 mL) was added Grubbs II catalyst (42 mg, 0.05 mmol, 0.05 equiv). The reaction mixture was stirred overnight at 40 °C and the volatiles were removed under vacuum. A flash chromatography on silica gel (PE/Et_2O : 95/5 to 5/5) previously deactivated with Et_3N afforded the benzylic allylic alcohol (102 mg, 47%). The alcohol (91 mg, 0.42 mmol) was dissolved in a 3/1 mixture of CH_2Cl_2/pyridine (2 mL/0.8 mL) and cooled to 0 °C before 4-DMAP (2.5 mg, 0.02 mmol, 0.05 equiv) and acetic anhydride (59 µL, 0.63 mmol, 1.5 equiv) were added. After one night at rt, the reaction mixture was washed with a 10% copper sulfate aqueous solution and the aqueous phase was extracted with Et_2O. The organic layers were then washed with brine, dried over $MgSO_4$, filtered and the solvents were removed under vacuum to give **5i** (156 mg, 82%).

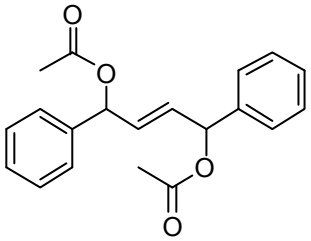
$[\alpha]^{20}_D$: -0.128 (*c* = 0.95, $CHCl_3$).

IR (neat) : 2956, 2926, 2855, 1951, 1737, 1494, 1455, 1369, 1229, 1073, 1017 cm^{-1}.

^{1}H NMR (400 MHZ, $CDCl_3$) *δ* : 7.36-7.27 (m, 5H), 6.23 (d, *J* = 6.8 Hz, 1H), 5.74 (m, 1H), 5.63 (m, 1H), 2.10 (s, 3H), 2.08-2.01 (m, 2H), 1.43-1.22 (m, 8H), 0.91-0.85 (m, 3H).

^{13}C NMR (100 MHZ, $CDCl_3$) *δ* : 170.1 (s), 140.0 (s), 135.0 (d), 128.6 (2d), 128.2 (d), 127.9 (d), 126.9 (2d), 76.4 (d), 32.3 (t), 31.7 (t), 28.9 (2t), 22.7 (t), 21.5 (q), 14.1 (q).

HRMS (ESI) : Calculated for $C_{17}H_{24}O_2Na$ $[M+Na]^+$: 238.1669. Found : 238.1666.



Acetic acid (*E*)-4-acetoxy-1,4-diphenyl-but-2-enyl ester, 5k

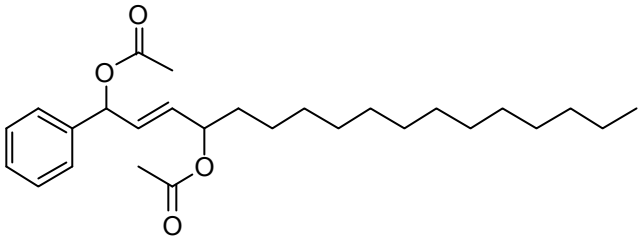
5j was obtained as a side-product during a metathesis reaction.

IR (*neat*) : 2930, 1732, 1603, 1494, 1454, 1369, 1222 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.31-7.38 (m, 10H), 6.26-6.21 (m, 2H), 5.86-5.83 (m, 2H), 2.10 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 169.9 (2s), 138.7 (2s), 130.7 (2d), 128.6 127.2 (4d), 127.2 (4d), 128.3 (2d), 75.0 (2d), 21.3 (2q).

HRMS (ESI) : Calculated for $C_{20}H_{20}NaO_4$ $[M+Na]^+$: 347.12538. Found : 347.12531.



Acetic acid (*E*)-4-acetoxy-1-phenyl-heptadec-2-enyl ester, 5l

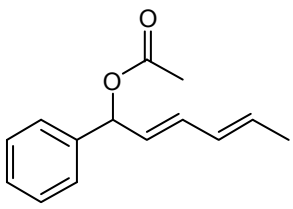
Grubbs-Hoveyda catalyst (78 mg, 0.12 mmol, 0.05 equiv) was added to a solution of acetic acid 1-vinyltetradecyl ester (705 mg, 2.5 mmol, 1.0 equiv) and **5a** (1.32 g, 7.5 mmol, 3.0 equiv) in CH_2Cl_2 (15 mL). After 24 h of stirring at 40 °C, another portion of Grubbs-Hoveyda catalyst (50 mg, 0.08 mmol, 0.03 equiv) was added and the mixture was stirred at 40 °C for 24 h. The volatiles were removed under reduced pressure and the residue was purified by flash chromatography on silica gel previously deactivated with Et_3N (PE/Et_2O : 100/0 to 90/10) to give **5k** (212 mg, 20 %).

IR (*neat*) : 2924, 2855, 1742, 1456, 1370, 1231, 1142, 1019 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.35 (m, 5H), 6.27 (d, *J* = 6.4 Hz, 1H), 5.86 (dd, *J* = 15.5, 6.0 Hz, 1H), 5.67 (dm, *J* = 15.5 Hz, 1H), 5.27 (q, *J* = 6.7 Hz, 1H), 2.10 (s, 3H), 2.04 (m, 3H), 1.60-1.63 (m, 2H), 1.26 (m, 22H), 0.89 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 170.4 (s), 170.0 (s), 139.0 (s), 131.5 (d), 130.5 (d), 128.4 (2d), 128.7 (d), 127.3 (2d), 75.3 (d), 73.8 (d), 34.5 (t), 32.1 (t), 29.9 (t), 29.8 (2t), 29.7 (t), 29.6 (t), 29.5 (t), 29.4 (t), 29.3 (t), 25.2 (t), 22.8 (t), 21.4 (q), 21.3 (q), 14.3 (q).

HRMS (ESI) : Calculated for $C_{27}H_{42}NaO_4$ $[M+Na]^+$: 453.2975. Found : 453.2975.



Acetic acid (2*E*,4*E*)-1-phenyl-hexa-2,4-dienyl ester, 5m

To a solution of (2*E*,4*E*)-*N*-methoxy-*N*-methyl-hexa-2,4-dienamide[1] (500 mg, 3.23 mmol, 1 equiv) in a 1/1 mixture of CH_2Cl_2/hexanes (60 mL) at -78 °C was added dropwise a solution of DIBAL-H (1 M in hexanes). The reaction mixture was stirred for 30 min at -78 °C and then poured into a

[1] Prepared according to reported procedure, see J. Cossy, T. Tsuchiya, L. Ferrié, S. Reymond, T. Kreuzer, F. Colobert, P. Jourdain and I. Marko, *Synlett*, 2007, 2286.

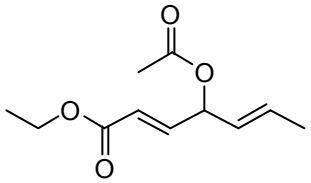
saturated aqueous solution of sodium-potassium tartrate at 0 °C. The mixture was warmed to rt and stirred for 2 h. The two phases were separated, the aqueous phase was extracted with CH_2Cl_2 , the combined organic layers were dried over $MgSO_4$, filtered and the solvents were removed under vacuum. The obtained aldehyde was dissolved in THF (20 mL) and a solution of phenylmagnesium bromide (1 M in THF, 3.4 mL, 3.87 mmol, 1.2 equiv) was added at -78 °C. The reaction mixture was allowed to warm to room temperature and after 2 h cooled to 0 °C. Acetic anhydride (460 µL, 4.84 mmol, 1.5 equiv) was added and after 3 h at rt, a saturated solution of ammonium chloride was added. The two phases were separated, the aqueous phase was extracted with Et_2O, the combined organic layers were dried over $MgSO_4$, filtered and the solvents were removed under reduced pressure. A flash chromatography on silica gel previously with Et_3N (PE/Et_2O : 100/0 to 100/5) afforded **5l** as a colorless oil (279 mg, 40%).

IR (neat) : 2977, 1736, 1692, 1494, 1453, 1371, 1228, 1114, 1021 cm^{-1}.

^{1}H NMR (400 MHZ, $CDCl_3$) δ : 7.41-7.11 (m, 5H), 6.22-6.10 (m, 2H), 5.96 (m, 1H), 5.72-5.59 (m, 2H), 2.02 (s, 3H), 1.67 (dd, *J* = 6.8, 1.5 Hz, 3H).

^{13}C NMR (100 MHZ, $CDCl_3$) δ : 170.1 (s), 139.5 (s), 133.3 (d), 131.6 (d), 130.5 (d), 128.6 (2d), 128.2 (d), 128.1 (d), 127.0 (2d), 76.1 (d), 21.4 (q), 18.2 (q).

HRMS (ESI) : Calculated for $C_{14}H_{16}NaO_2$ $[M+Na]^+$: 239.1043. Found : 239.1036.



(2*E*,5*E*)-4-Acetoxy-hepta-2,5-dienoic acid ethyl ester, 5n

To a solution of diisopropylamine (2.38 mL, 17 mmol, 1.7 equiv) in THF (28 mL) at -78 °C was added a solution of *n*-butyllithium (2.32 M in hexanes, 6.9 mL,16 mmol, 1.6 equiv). The mixture was stirred at -78 °C for 15 min and then 30 min at 0 °C. The mixture was cooled at -78 °C and ethyl propiolate (1.53 mL, 15 mmol, 1.5 equiv) was added. After 30 min, at -78 °C, a solution of crotonaldehyde (828 µl, 10 mmol, 1.0 equiv) in THF (10 mL) was added. After 1.5 h at -78 °C, the reaction mixture was added to a saturated aqueous solution of ammonium chloride at 0 °C. The aqueous phase was extracted with Et_2O, the organic layers were washed with brine, dried over $MgSO_4$ and the solvents were removed under reduced pressure to give an oil (1.7 g, quantitative). A portion of the obtained oil (1.0 g, 5.93 mmol) was dissolved in THF (74 mL), the solution was cooled at 0 °C and $LiAlH_4$ (135 mg, 3.56 mmol, 0.6 equiv) was added. After 1 h of stirring at 0 °C, saturated aqueous solution of ammonium chloride was added. The aqueous phase was extracted with EtOAc, the organic layers were washed with brine, dried over $MgSO_4$ and the solvents were removed under reduced pressure. The crude was purified by flash chromatography on silica gel (PE/AcOEt : 9/1 to 8/2) to give an oil (357 mg, 36%). A part of the obtained oil (162 mg, 0.95 mmol) was diluted in CH_2Cl_2 (1.4 mL) and pyridine (0.7 mL) and cooled at 0 °C. 4-DMAP (6.0 mg, 0.05 mmol, 0.05 equiv) and acetic anhydride (135 µl, 1.43 mmol, 1.5 equiv) were added. After one night at rt the mixture was washed with a 10% copper sulfate aqueous solution and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude was purified by flash

chromatography on silica gel previously neutralized with Et_3N (PE/Et_2O : 9/1) to give **5m** (192 mg, 95%, 34% overall yield).

IR (*neat*) : 2990, 2872, 1740, 1723, 1372, 1307, 1274, 1229, 1179, 1144, 1042 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 6.80 (dd, *J* = 15.9, 5.3 Hz, 1H), 5.92 (dd, *J* = 15.9, 1.8 Hz, 1H), 5.73-5.83 (m, 2H), 5.41 (dd, *J* = 15.4, 7.4 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.04 (s, 3H), 1.68 (dd, *J* = 6.5, 1.0 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 169.7 (s), 166.0 (s), 144.4 (d), 131.7 (d), 126.6 (d), 121.8 (d), 73.0 (d), 60.6 (t), 21.1 (q), 17.8 (q), 14.2 (q).

MS (EI, 70eV) *m/z* : 169 ([M-Ac]$^+$, 7), 141 (33), 125 (100), 124 (48), 123 (29), 113 (28), 97 (62), 96 (24), 95 (57), 80 (27), 79 (92), 77 (44), 69 (23), 67 (35), 55 (22), 54 (23).

HRMS (ESI) : Calculated for $C_{11}H_{16}NaO_4$ [M+Na]$^+$: 235.0941 . Found : 235.0939.

General method for silica gel-promoted rearrangement :

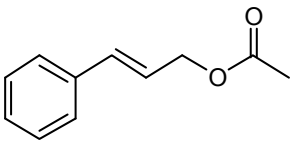
Conditions [A] : To a CH_2Cl_2 solution of **5** (0.2-0.4 M) in a microwave vial was added silica gel (see Table 2 for the nature and the amount of silica). The vial was sealed and the mixture was heated at 80 °C for 15 min. The crude was filtered and the volatiles were removed under reduced pressure to yield the corresponding rearranged allylic acetate **6**.

Conditions [B] : To a CH_2Cl_2 solution of **5** (0.2-0.4 M) in a microwave vial was added silica gel (see Table 2 for the nature and the amount of silica). The vial was sealed and the mixture was heated at 120 °C for 30 min. The crude was filtered and the volatiles were removed under reduced pressure to yield the corresponding rearranged allylic acetate **6**.

Preparation of acidified silica gels S1 and S2 :

To a suspension of commercial silica gel (10 g) in anhydrous Et_2O was added H_2SO_4 95% (**S1** : 0.3 mL, **S2** : 3.3 mL). The mixture was stirred for 15 min at rt and the volatiles were removed under reduced pressure. The obtained solid was dried under vacuum at 110 °C to afford the modified silica gels **S1** and **S2**.

Synthesis of rearranged allylic acetates of type 6



Acetic acid (*E*)-3-phenyl-allyl ester, 6a

Conditions [B] were applied to **5a**[2] (63% yield).

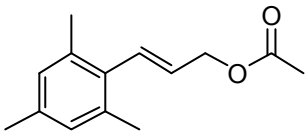
IR (neat) : 3027, 1737, 1495, 1449, 1380, 1363, 1228, 1112, 1069, 1025 cm^{-1}.

^{1}H NMR (400 MHZ, $CDCl_3$) δ : 7.36 (m, 5H), 6.59 (br d, *J* = 15.9 Hz, 1H), 6.22 (dt, *J* = 15.8, 6.4 Hz, 1H), 4.67 (dd, *J* = 6.5, 1.4 Hz, 2H), 2.04 (s, 3H).

^{13}C NMR (100 MHZ, $CDCl_3$) δ : 170.9 (s), 136.2 (s), 134.3 (d), 128.7 (2d), 128.1 (d), 126.7 (2d), 123.2 (d), 65.1 (t), 21.1 (q).

MS (EI) *m/z* : 176 (15, $[M]^{+\cdot}$), 134 (38), 133 (38), 117 (35), 116 (44), 115 (100), 105 (40), 103 (14), 92 (35), 91 (24), 79 (12), 78 (16), 77 (27), 51 (19).

HRMS (ESI) : Calculated for $C_{11}H_{12}NaO_2$ $[M+Na]^+$: 199.0730. Found : 199.0725.



Acetic acid (*E*)-3-(2,4,6-trimethyl-phenyl)-allyl ester, 6b

Conditions [A] were applied to **5b** (98% yield).

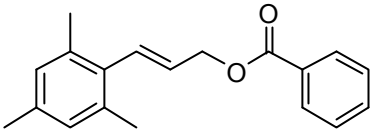
IR (*neat*) : 2919, 1740, 1611, 1444, 1377, 1227, 1026 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 6.87 (s, 2H), 6.62 (br d, *J* = 16.1 Hz, 1H), 5.78 (dt, *J* = 16.1, 6.4 Hz, 1H), 4.74 (dd, *J* = 6.4, 1.5 Hz, 2H), 2.26 (s, 9 H), 2.11 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 170.9 (s), 136.5 (s), 135.9 (2s), 133.0 (s), 132.0 (d), 128.6 (2d), 128.2 (d), 65.5 (t), 21.0 (q), 20.9 (q), 20.8 (2q).

MS (EI, 70eV) *m/z* : 218 ($[M]^{+\cdot}$, 35), 175 ($[M\text{-}Ac]^+$, 6), 158 ($[M\text{-}HOAc]^{+\cdot}$, 27), 143 (100), 128 (46), 120 (37), 115 (21), 91 (14).

HRMS (ESI) : Calculated for $C_{14}H_{18}NaO_2$ $[M+Na]^+$: 241.11990. Found : 241.11974.



Benzoic acid (*E*)-3-(2,4,6-trimethyl-phenyl)-allyl ester, 6c

Conditions [A] were applied to **5c**[2], 25 min of heating were required to reach full conversion (86% yield).

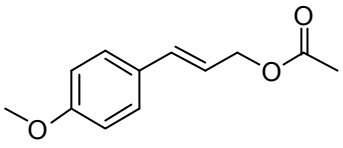
IR (*neat*) : 2947, 1719, 1602, 1452, 1376, 1267, 1111, 1069, 1026 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.10 (d_{app}, *J* = 7.6 Hz, 2H), 7.58 (t_{app}, *J* = 7.6 Hz, 1H), 7.46 (t_{app}, *J* = 7.6 Hz, 2H), 6.88 (s, 2H), 6.74 (br d, *J* = 16.4 Hz, 1H), 5.92 (dt, *J* = 16.4, 6.3 Hz, 1H), 5.01 (dd, *J* = 6.3, 1.2 Hz, 2H), 2.30 (s, 6H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 166.5 (s), 136.7 (s), 136.0 (2s), 133.1 (s), 133.0 (d), 132.3 (d), 130.5 (s), 129.7 (2d), 128.7 (2d), 128.5 (2d), 128.3 (d), 66.0 (t), 21.1 (q), 21.0 (2q).

MS (EI, 70eV) *m/z* : 280 ($[M]^{+\cdot}$, 23), 159 (18), 158 (42), 144 (18), 143 (65), 129 (21), 128 (23), 105 (100), 77 (23).

HRMS (ESI) : Calculated for $C_{19}H_{20}NaO_2$ $[M+Na]^+$: 303.1356. Found : 303.1352.



Acetic acid (*E*)-3-(4-methoxy-phenyl)-allyl ester, 6d

Conditions [A] were applied to **5d** (92% yield).

IR (*neat*) : 2938, 1737, 1655, 1607, 1512, 1463, 1362, 1243, 1176, 1029 cm^{-1}.

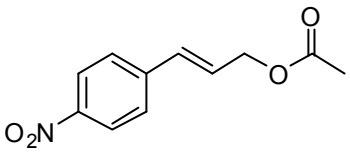
[2] Prepared according to reported procedure, see Marion, N.; Gealageas, R.; Nolan, S. P. *Org. Lett.* **2007**, 9, 2653.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.32 (d_{app}, *J* = 8.9 Hz, 2H), 6.85 (d_{app}, *J* = 8.9 Hz, 2H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.15 (dt, *J* = 16.0, 6.8 Hz, 1H), 4.70 (dd, *J* = 6.8, 1.3 Hz, 2H), 3.81 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 171.0 (s), 159.7 (s), 134.2 (d), 129.1 (s), 128.0 (2d), 121.0 (d), 114.1 (2d), 65.5 (t), 55.4 (q), 21.1 (q).

MS (EI, 70eV) *m/z* : 206 ($[M]^{+\cdot}$, 100), 164 (38), 163 ($[M\text{-}Ac]^+$, 82), 147 (95), 146 (18), 135 (58), 132 (17), 131 (44), 121 (37), 115 (32), 108 (37), 105 (16), 103 (54), 91 (38), 77 (24).

HRMS (ESI) : Calculated for $C_{12}H_{14}NaO_3$ $[M+Na]^+$: 229.08352. Found : 229.08329.



Acetic acid (*E*)-3-(4-nitro-phenyl)-allyl ester, 6e

Conditions [A] were applied to **5e**[2] with silica gel **S1** in a 1/1 weight ratio (54% yield).

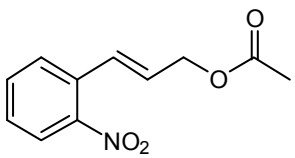
IR (*neat*) : 2941, 2360, 2341, 1739, 1598, 1517, 1343, 1228, 1109, 1028 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.18 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.44 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.77 (dd, *J* = 6.0, 1.4 Hz, 2H), 2.12 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 170.8 (s), 147.4 (s), 142.8 (s), 131.4 (d), 128.4 (d), 127.3 (2d), 124.2 (2d), 64.4 (t), 21.0 (q).

MS (EI, 70eV) *m/z* : 221 ($[M]^{+\cdot}$, 1), 179 ($[M\text{-}Ac]^+$, 80), 162 (21), 150 (31), 116 (39), 115 (100), 103 (23), 89 (21), 77 (24), 63 (17), 51 (17).

HRMS (ESI) : Calculated for $C_{11}H_{11}NNaO_4$ $[M+Na]^+$: 244.0580. Found : 244.0581.



Acetic acid 1-(2-nitro-phenyl)-allyl ester, 6f

Conditions [A] were applied to **5f**[1] with silica gel **S2** in a 1/1 weight ratio (71% yield).

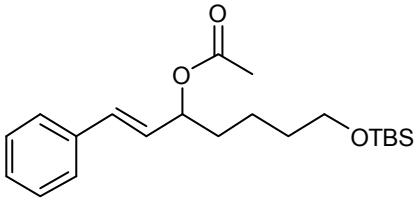
IR (neat) : 2920, 2851, 1739, 1607, 1572, 1524, 1443, 1346, 1228, 1163, 1144, 1082, 1027 cm^{-1}.

^{1}H NMR (400 MHZ, $CDCl_3$) *δ* : 7.95 (m, 1H), 7.62-7.55 (m, 2H), 7.45-7.39 (m, 1H), 7.13 (dt, *J* = 15.6, 1.4 Hz, 1H), 6.26 (dt, *J* = 6.3, 5.8 Hz, 1H), 4.77 (dd, *J* = 6.0, 1.6 Hz, 2H), 2.12 (s, 3H).

^{13}C NMR (100 MHZ, $CDCl_3$) *δ* : 170.8 (s), 147.9 (s), 133.3 (d), 132.1 (s), 128.9 (d), 128.8 (d), 128.7 (d), 128.6 (d), 124.7 (d), 64.4 (t), 21.0 (q).

MS (EI) *m/z* : 189 (4), 132 (33), 130 (44), 129 (100), 128 (19), 120 (52), 117 (17), 116 (32), 115 (29), 105 (16), 104 (57), 103 (33), 102 (41), 92 (35), 91 (18), 90 (18), 89 (26), 78 (30), 77 (60), 76 (26), 75 (20), 65 (28), 64 (13), 63 (29), 51 (42), 50 (22).

HRMS (ESI) : Calculated for $C_{11}H_{11}NNaO_4$ $[M+Na]^+$: 244.0580. Found : 244.0578.



Acetic acid 5-(*tert*-butyldimethylsilyloxy)-1-((*E*)-styryl)-pentyl ester, 6h

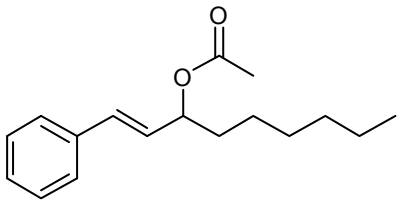
Conditions [A] were applied to **5h** (94% yield).

IR (*neat*) : 2930, 2858, 2360, 1737, 1472, 1371, 1238, 1099, 1018 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.39-7.36 (m, 2H), 7.34-7.29 (m, 2H), 7.27-7.22 (m, 1H), 6.60 (d, *J* = 16.4 Hz, 1H), 6.12 (dd, *J* = 15.9, 7.3 Hz, 1H), 5.41 (q, *J* = 7.1 Hz, 1H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.07 (s, 3H), 1.83-1.63 (m, 2H), 1.61-1.51 (m, 2H), 1.47-1.35 (m, 2H), 0.88 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 170.5 (s), 136.5 (s), 132.6 (d), 128.7 (2d), 128.0 (d), 127.8 (d), 126.7 (2d), 74.9 (d), 63.0 (t), 34.6 (t), 32.7 (t), 26.1 (3q), 21.7 (t), 21.5 (q), 18.5 (s), -5.1 (2q).

HRMS (ESI) : Calculated for $C_{21}H_{34}NaO_3Si$ $[M+Na]^+$: 385.21694. Found : 385.21703.



Acetic acid 1-((E)-styryl)-heptyl ester, 6i

Conditions [A] were applied to **5i** (82% yield, *E*/*Z* = 87/13).

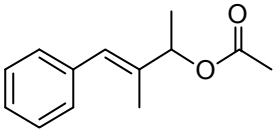
IR (neat) : 3027, 2927, 2857, 1735, 1599, 1579, 1495, 1450, 1370, 1235, 1138, 1018 cm^{-1}.

^{1}H NMR (400 MHZ, $CDCl_3$) *δ* : 7.32 -7.27 (m, 2H), 7.26-7.20 (m, 2H), 7.19-7.13 (m, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.04 (dd, *J* = 16.1, 7.4 Hz, 1H), 5.32 (q, *J* = 7.3 Hz, 1H), 1.99 (s, 3H), 1.71-1.52 (m, 2H), 1.30-1.14 (m, 8H), 0.83-0.77 (m, 3H).

^{13}C NMR (100 MHZ, $CDCl_3$) *δ* : 170.5 (s), 136.4 (s), 132.5 (d), 128.6 (2d), 127.9 (2d), 126.6 (2d), 74.9 (d), 34.6 (t), 31.8 (t), 29.1 (t), 25.2 (t), 22.6 (t), 21.4 (q), 14.1 (q).

MS (EI) *m/z* : 260 ($[M]^{+\cdot}$,6), 217 (28), 148 (23), 143 (19), 134 (11), 133 (100), 131 (17), 130 (67), 129 (58), 128 (30), 117 (24), 115 (43), 113 (31), 105 (21), 104 (33), 103 (11), 96 (23), 95 (16), 94 (12), 91 (44), 77 (15), 55 (27).

HRMS (ESI) : Calculated for $C_{17}H_{24}NaO_2$ $[M+Na]^+$: 283.1669. Found : 283.1666.



Acetic acid (*E*)-1,2-dimethyl-3-phenyl-allyl ester, 6j

Conditions [A] were applied to **5j**[2] (79% yield).

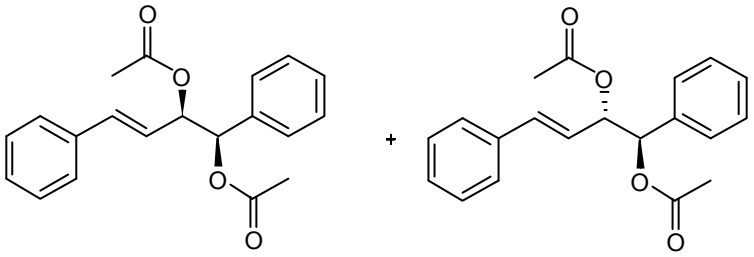
IR (*neat*) : 2982, 1736, 1599, 1444, 1370, 1239, 1068, 1024 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.11-7.26 (m, 5H), 6.44 (s, 1H), 5.33 (q, *J* = 6.7 Hz, 1H), 2.00 (s, 3H), 1.79 (d, *J* = 1.8 Hz, 3H), 1.32 (q, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 170.4 (s), 137.3 (2s), 129.1 (2d), 128.2 (2d), 126.7 (d), 126.5 (d), 75.5 (d), 21.5 (q), 19.4 (q), 13.9 (q).

MS (EI, 70eV) *m/z* : 204 ($[M]^{+\cdot}$, 8), 162 (33), 161 ($[M-Ac]^+$, 17), 147 (17), 145 (17), 144 (25), 130 (15), 129 (100), 128 (29), 115 (23), 91 (23).

HRMS (ESI) : Calculated for $C_{13}H_{16}NaO_2$ $[M+Na]^+$: 227.10425. Found : 227.10389.



Acetic acid (*E*)-2-acetoxy-1,4-diphenyl-but-3-enyl ester, 6k

Conditions [B] were applied to **5k**, (60% yield, *syn*/*anti* = *7/3*).

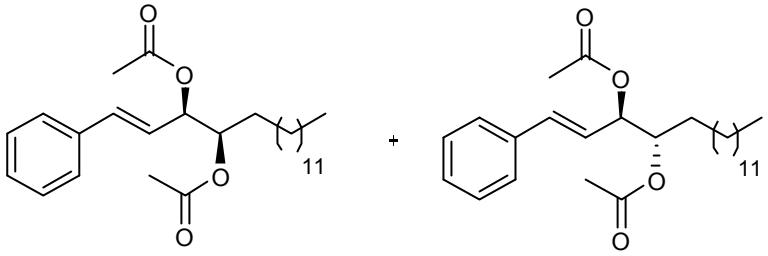
IR (*neat*) : 2970, 1736, 1600, 1495, 1450, 1370, 1218 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.31-7.38 (m, 10H), 6.57 (dd, *J* = 16.0, 1.0 Hz, 0.7H), 6.54 (dd, *J* = 16.0, 1.0 Hz, 0.3H), 6.09 (dd, *J* = 16.0, 8.4 Hz, 0.7H), 6.03 (d, *J* = 4.9 Hz, 0.7H), 5.93 (dd, *J* = 16.0, 7.0 Hz, 0.3H), 5.94 (d, *J* = 7.1 Hz, 0.3H), 5.78 (td, *J* = 7.1, 1.0 Hz, 0.3H), 5.71 (ddd, *J* = 7.9, 4.9, 1.0 Hz, 0.7H), 2.12 (s, 2.1H), 2.11 (s, 0.9H), 2.09 (s, 0.9H), 2.03 (s, 2.1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 169.9 (s), 169.8 (s), 136.4 (s), 136.0 (s),136.2 (s), 136.1 (s), 135.3 (d), 134.5 (d), 128.7 (d), 128.6 (d), 128.55 (d), 128.50 (d), 128.4 (d), 128.3 (d), 128.2 (d), 128.2 (d), 127.5 (d), 127.4 (d), 126.7 (d), 126.6 (d), 123.1 (d), 122.6 (d), 76.3 (d), 75.9 (d), 75.8 (d), 75.2 (d), 21.1 (q), 21.0 (q).

MS (EI, 70eV) *m/z* : 266 (4), 222 (4), 206 (7), 175 (26), 149 (20), 133 (100), 115 (23), 107 (51).

HRMS (ESI) : Calculated for $C_{20}H_{20}NaO_4$ $[M+Na]^+$: 347.12538. Found : 347.12528.



Acetic acid 2-acetoxy-1-((*E*)-styryl)-pentadecyl ester, 6l

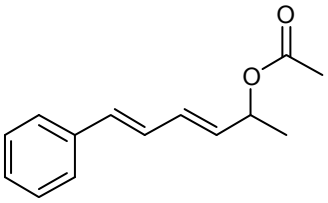
Conditions [B] were applied to **5l** (74% yield, 7/3 mixture of diastereomers). The nature of the major diastereomer (*syn* or *anti*) has not been determined.

IR (*neat*) : 2924, 2854, 1743, 1465, 1370, 1224, 1023 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.19-7.33 (m, 5H), 6.59 (d, *J* = 15.8 Hz, 1H), 6.08 (dd, *J* = 15.8, 7.7 Hz, 0.7H), 6.00 (dd, *J* = 15.8, 7.7 Hz, 0.3H), 5.43 (m, 1H), 5.06 (m, 1H), 2.02 (s, 1.2H), 2.00 (s, 4.8H), 1.50 (m, 2H), 1.17-1.18 (m, 22H), 0.80 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 170.8 (s), 170.2 (s), 170.6 (s), 170.1 (s), 136.3 (s), 136.2 (s), 135.2 (d), 134.7 (d), 128.8 (d), 128.4 (d), 126.9 (d), 126.8 (d), 123.7 (d), 123.1 (d), 75.5 (d), 75.1 (d), 74.2 (d), 74.1 (d), 32.1 (t), 30.7 (t), 30.1 (t), 29.9 (t), 29.8 (t), 29.7 (t), 29.6 (t), 29.5 (t), 29.4 (t), 29.3 (t), 25.6 (t), 25.2 (t), 22.8 (t), 21.7 (t), 21.3 (q), 21.2 (q), 21.4 (q), 14.2 (q).

HRMS (ESI) : Calculated for $C_{27}H_{42}NaO_4$ $[M+Na]^+$: 453.2975. Found : 453.2976.



Acetic acid (2*E*,4*E*)-1-methyl-5-phenyl-penta-2,4-dienyl ester, 6m

Conditions [A] were applied to **5m** (65% yield).

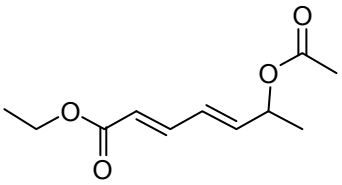
IR (neat) : 3025, 2978, 1730, 1663, 1646, 1597, 1492, 1448, 1369, 1235, 1141, 1072, 1039, 1014 cm^{-1}.

^{1}H NMR (400 MHZ, $CDCl_3$) δ : 7.42 (m, 2H), 7.35-7.29 (m, 2H), 7.26-7.21 (m, 1H), 6.74 (dd, *J* = 16.4, 10.7 Hz, 1H), 6.58 (d, *J* = 15.7 Hz, 1H), 6.41 (dd, *J* = 15.3, 10.3 Hz, 1H), 5.80 (dd, *J* = 15.5, 6.5 Hz, 1H), 5.46 ($quint_{app}$, *J* = 6.7 Hz, 1H), 2.07 (s, 3H), 1.37 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHZ, $CDCl_3$) δ : 170.4 (s), 137.1 (s), 133.6 (d), 132.8 (d), 132.0 (d), 128.7 (2d), 128.0 (d), 127.8 (d), 126.5 (2d), 70.8 (d), 21.4 (q), 20.3 (q)

MS (EI) *m/z* : 216 (10, $[M]^{+\cdot}$), 157 (18, $[M\text{-}OAc]^+$), 156 (82), 155 (36), 153 (16), 152 (10), 142 (10), 141 (59), 131 (14), 129 (39), 128 (60), 127 (18), 116 (10), 115 (68), 102 (11), 91 (100), 89 (10), 78 (32), 77 (30), 76 (13), 65 (13), 63 (15), 60 (12), 51 (24), 50 (11)

HRMS (ESI) : Calculated for $C_{14}H_{16}NaO_2$ $[M+Na]^+$: 239.1040. Found : 239.1043



(2*E*,4*E*)-6-Acetoxy-hepta-2,4-dienoic acid ethyl ester, 6n

Conditions [B] were applied to **5n** (78% yield).

IR (*neat*) : 2982, 1738, 1715, 1649, 1620, 1370, 1235, 1186, 1139, 1039, 1002 cm^{-1}.

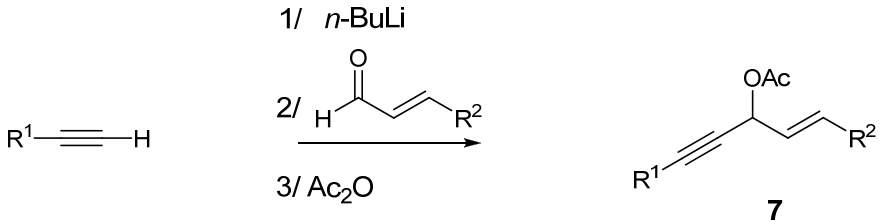
^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.22 (dd, *J* = 15.3, 11.0 Hz, 1H), 6.31 (dd, *J* = 15.3, 11.0 Hz, 1H), 6.03 (dd, *J* = 15.3, 6.2 Hz, 1H), 5.89 (d, *J* = 15.3 Hz, 1H), 5.43 ($quint_{app}$, *J* = 6.4 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 2.05 (s, 3H), 1.33 (d, *J* = 6.7 Hz, 3H), 1.28 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 169.3 (s), 165.8 (s), 142.4 (d), 139.9 (d), 127.7 (d), 121.6 (d), 69.0 (d), 59.5 (t), 20.3 (q), 19.1 (q), 13.4 (q).

MS (EI, 70eV) *m/z* : 169 ($[M\text{-}Ac]^+$, 1), 127 (25), 125 (100), 124 (38), 99 (33), 97 (45), 95 (18), 81 (38), 79 (48), 77 (24), 53 (22).

HRMS (ESI) : Calculated for $C_{11}H_{16}NaO_4$ $[M+Na]^+$: 235.0941. Found : 235.0939.

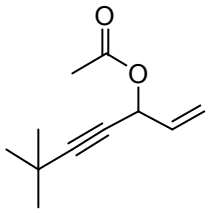
Synthesis of propargylic allylic acetates of type 7



General procedure 3 : preparation of propargylic allylic acetates of type 7 :

To a solution of the alkyne (1.3 equiv) in Et_2O (0.3 M) was added at 0 °C a solution of *n*-butyllithium (2.35M in hexanes, 1.3 equiv). After 1 h at 0 °C, the reaction mixture was cooled to -78 °C and a solution of the aldehyde (1 equiv) in Et_2O (0.3 M) was added. The reaction was allowed to warm to rt

and was stirred until complete conversion was observed. The reaction media was then cooled to 0 °C and acetic anhydride (1.5 equiv) was added. After one night at rt, a saturated aqueous solution of ammonium chloride was added and the aqueous phase was extracted with diethyl ether. The organic layers were then washed with brine, dried over $MgSO_4$ and the solvents were removed under reduced pressure. The crude was purified by flash chromatography on silica gel previously deactivated by Et_3N to give the expected propargylic allylic acetate **7**.



Acetic acid 4,4-dimethyl-1-vinyl-pent-2-ynyl ester, 7a

Prepared according to the general procedure 3 using *tert*-butylacetylene and acrolein (75% yield).

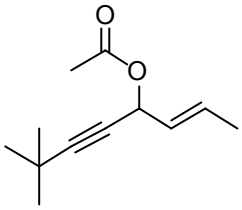
IR (*neat*) : 2971, 2360, 2244, 1745, 1458, 1370, 1227, 1016 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 5.83-5.92 (m, 2H), 5.51 (m, 1H), 5.28 (m, 1H), 2.09 (s, 3H), 1.23 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 169.9 (s), 133.9 (d), 118.5 (t), 96.5 (q), 74.0 (q), 64.9 (d), 31.0 (3q), 27.7 (s), 21.3 (q).

MS (EI, 70eV) *m/z* : 180 ($[M]^{+\cdot}$, 2), 165 ($[M\text{-}Me]^+$, 12), 123 ($[M\text{-}{}^t\!Bu]^+$, 100), 109 (24), 105 (66), 95 (29), 91 (39), 81 (14), 79 (39), 77 (35), 67 (25), 65 (16), 57 (22), 55 (21), 53 (16), 41 (15).

HRMS (ESI) : Calculated for $C_{11}H_{16}NaO_2$ $[M+Na]^+$: 203.1042. Found : 203.1040.



Acetic acid 4,4-dimethyl-1-((*E*)-propenyl)-pent-2-ynyl ester, 7b

Prepared according to the general procedure 3 using *tert*-butylacetylene and crotonaldehyde (95% yield).

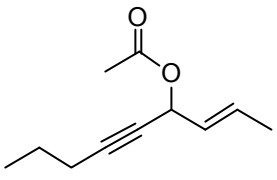
IR (*neat*) : 2970, 2926, 2869, 2360, 1738, 1456, 1368, 1228, 1142, 1013 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 5.98 (dqd, *J* = 15.2, 6.6, 1.2 Hz, 1H), 5.83 (dm, *J* = 6.5 Hz, 1H), 5.53 (ddq, *J* = 15.2, 6.2, 1.6 Hz, 1H), 2.06 (s, 3H), 1.73 (d, *J* = 6.6 Hz, 3H), 1.22 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 170.0 (s), 131.0 (d), 127.1 (d), 95.9 (q), 74.6 (q), 64.8 (d), 31.0 (3q), 27.6 (s), 21.4 (q), 17.7 (q).

MS (EI, 70eV) *m/z* : 194 ($[M]^{+\cdot}$, 23), 179 ($[M\text{-}Me]^+$, 30), 152 (18), 151 ($[M\text{-}Ac]^+$, 24), 137 (100), 135 (18), 134 (24), 123 (43), 122 (15), 119 (58), 109 (35), 107 (32), 105 (42), 96 (18), 95 (55), 93 (26), 91 (87), 71 (28), 79 (33), 77 (43), 67 (21), 65(15), 57 (23), 55 (15).

HRMS (ESI) : Calculated for $C_{12}H_{18}NaO_2$ $[M+Na]^+$: 217.1200. Found : 217.1193.



Acetic acid ((*E*)-1-propenyl)-hex-2-ynyl ester, 7c

Prepared according to the general procedure 3 using 1-pentyne and crotonaldehyde (82% yield).

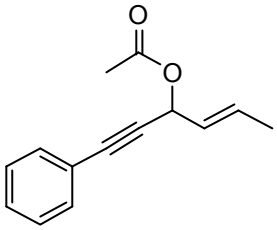
IR (*neat*) : 2967, 2873, 2360, 1740, 1449, 1370, 1228, 1143, 1014 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 5.94 (dqd, *J* = 15.3, 6.7, 1.0 Hz, 1H), 5.77 (m, 1H), 5.55 (ddq, *J* = 15.3, 6.3, 1.6 Hz, 1H), 2.17 (td, *J* = 7.1, 2.0 Hz, 2H), 2.02 (s, 3H), 1.70 (dm, *J* = 6.7 Hz, 3H), 1.50 ($sext_{app}$, *J* = 7.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 169.9 (s), 131.0 (d), 126.9 (d_7), 87.5 (q), 76.3 (q), 64.8 (d), 21.9 (t), 21.2 (q), 20.8 (t), 17.5 (q), 13.5 (q).

MS (EI, 70eV) *m/z* : 180 ($[M]^{+\cdot}$, 9), 151 (37), 138 (26), 137 ($[M\text{-}Ac]^+$, 41), 123 (39), 121 (33), 120 (30), 110 (26), 109 (85), 105 (74), 103 (16), 95 (88), 93 (17), 92 (21), 91 (100), 81 (26), 79 (70), 78 (20), 77 (57), 67 (37), 65 (33), 55 (27), 53 (16), 51 (17).

HRMS (ESI) : Calculated for $C_{11}H_{16}NaO_2$ $[M+Na]^+$: 203.1043. Found : 203.1039.



Acetic acid (*E*)-1-phenylethynyl-but-2-enyl ester, 7d

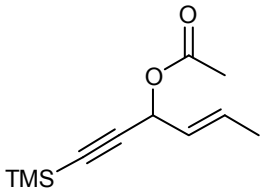
Prepared according to the general procedure 3 using phenylacetylene and crotonaldehyde (91% yield).

IR (*neat*) : 2918, 1742, 1672, 1490, 1370, 1224, 1013 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.48-7.45 (m, 2H), 7.32-7.30 (m, 3H), 6.05-6.13 (m, 2H), 5.66 (dm, *J* = 15.2 Hz, 1H), 2.12 (s, 3H), 1.77 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 169.0 (s), 131.0 (2d), 130.8 (d), 127.8 (d), 127.4 (1s, 1d), 125.3 (d), 121.3 (s), 85.6 (s), 84.2 (s), 63.9 (d), 20.3 (q), 16.7 (q).

HRMS (ESI) : Calculated for $C_{14}H_{14}NaO_2$ $[M+Na]^+$: 237.0886. Found : 237.0885.



Acetic acid (*E*)-1-trimethylsilanylethynyl-but-2-enyl ester, 7e

Prepared according the general procedure 3 using trimethylsilylacetylene and crotonaldehyde (80% yield, *E*/*Z* = 96/4[3]).

IR (neat) : 2964, 2361, 2340, 1748, 1448, 1370, 1339, 1251, 1226, 1148, 1119, 1094, 1062, 1015 cm^{-1}.

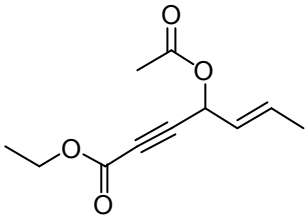
^{1}H NMR (400 MHZ, $CDCl_3$) *δ* : 5.99 ($sext_{app}$, *J* = 7.0 Hz, 1H), 5.83 (d, *J* = 6.6 Hz, 1H), 5.53 (ddd, *J* = 15.4, 6.4, 1.6 Hz, 1H), 2.07 (s, 3H), 1.74 (d, *J* = 6.5 Hz, 3H), 0.18 (s, 9H)

^{13}C NMR (100 MHZ, $CDCl_3$) *δ* : 169.7 (s), 131.7 (d), 126.2 (d), 101.0 (s), 91.7 (s), 64.7 (d), 21.2 (q), 17.7 (q), 0.2 (3q).

MS (EI) *m/z* : 210 (3, $[M]^{+\cdot}$), 168 (11), 167 (48), 136 (10), 135 (51), 117 (27), 109 (14), 107 (14), 97 (20), 95 (22), 83 (18), 78 (17), 77 (11), 75 (80), 74 (10), 73 (100), 69 (11), 61 (12), 59 (30), 58 (12), 55 (10), 53 (15).

HRMS (ESI) : Calculated for $C_{11}H_{18}NaO_2Si$ $[M+Na]^+$: 233.0968. Found : 233.0965.

[3] The *E*/*Z* ratio was determined by GC/MS analysis



(*E*)-4-Acetoxy-hept-5-en-2-ynoic acid ethyl ester, 7f

A solution of *n*-butyllithium (2.32 M in hexanes, 6.9 mL,16 mmol, 1.6 equiv) was added to a solution of diisopropylamine (2.38 mL, 17 mmol, 1.7 equiv) in THF (28 mL) at -78 °C. The mixture was stirred at -78 °C for 15 min and then for 30 min at 0 °C. The mixture was cooled at -78 °C and ethyl propiolate (1.53 mL, 15 mmol, 1.5 equiv) was added. After 30 min at -78 °C, a solution of crotonaldehyde (828 μL, 10 mmol, 1.0 equiv) in THF (10 mL) was added. After 1.5 h of stirring at -78 °C, the reaction mixture was added to a saturated ammonium chloride solution at 0 °C. The aqueous phase was extracted with Et_2O, the organic layers were washed with brine, dried over $MgSO_4$ and the solvents were removed under reduced pressure to give an oil (1.7 g, quant.). A portion of the obtained oil (966 mg, 5.7 mmol, 1.0 equiv) was diluted in CH_2Cl_2 (8 mL) and pyridine (4 mL) and cooled at 0°C. 4-DMAP (35.5 mg, 0.29 mmol, 0.05 equiv) and acetic anhydride (0.85 mL, 8.62 mmol, 1.5 equiv) were added. After one night at rt the mixture was washed with a 10% copper sulfate aqueous solution and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude was purified by flash chromatography on silica gel previously deactivated with Et_3N (PE/Et_2O :100/0 to 90/10) to give **7f** (271 mg, 23%).

IR (*neat*) : 2989, 2245, 1750, 1718, 1450, 1371, 1255, 1220, 1144, 1017 cm^{-1}.

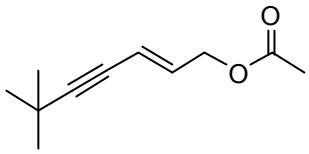
^{1}H NMR (400 MHz, $CDCl_3$) δ : 6.00 (dqd, *J* = 15.2, 6.5, 1.0 Hz, 1H), 5.89 (dm, *J* = 6.8 Hz, 1H), 5.54 (ddq, *J* = 15.2, 6.8, 1.6 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.08 (s, 3H), 1.74 (dm, *J* = 6.5 Hz, 3H), 0.29 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 169.5 (s), 153.1 (s), 133.3 (d), 124.4 (d), 82.6 (s), 77.8 (s), 63.5 (d), 62.4 (t), 21.0 (q), 17.7 (q), 14.1 (q).

MS (EI, 70eV) *m/z* : 210 ($[M]^{+\cdot}$, 1), 140 (47), 123 (61), 122 (100), 121 (18), 106 (15), 95 (28), 94 (26), 93 (25), 79 (27), 78 (36), 477 (48), 66 (19), 53 (19), 51 (24).

HRMS (ESI) : Calculated for $C_{11}H_{14}NaO_4$ $[M+Na]^+$: 233.0784. Found : 233.0782.

Preparation of 1,3-enynes of type 8



Acetic acid 6,6-dimethyl-hept-2-en-4-ynyl ester, 8a

Conditions [A] were applied to **7a** with only 5 min of heating (*E*/*Z* = 9/1, 23% yield,).

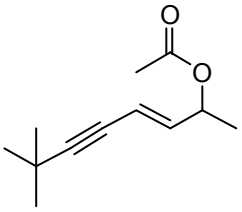
IR (*neat*) : 2969, 2360, 2341, 1745, 1636, 1457, 1362, 1226, 1026 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 6.05 (dt, *J* = 15.7, 6.3 Hz, 1H), 5.73 (dd, *J* = 15.7, 1.6 Hz, 1H), 4.56 (dd, *J* = 6.3, 1.6 Hz, 2H), 2.05 (s, 3H), 1.23 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 170.7 (s), 134.7 (d), 114.6 (d), 100.6 (s), 76.6 (s), 64.3 (t), 31.0 (3q), 28.1 (s), 21.0 (q).

MS (EI, 70eV) *m/z* : 180 ([M]$^{+\cdot}$, 25), 165 ([M-Me]$^{+}$, 24), 138 (35), 135 ([M-Ac]$^{+}$, 82), 124 (34), 120 (100), 109 (21), 105 (60), 95 (60), 93 (29), 91 (56), 81 (47), 79 (44), 77 (55), 67 (27), 65 (34), 57 (20), 55 (18), 53 (16), 51 (18).

HRMS (ESI) : Calculated for $C_{11}H_{16}NaO_2$ [M+Na]$^{+}$: 203.1042. Found : 203.1040.



Acetic acid (*E*)-1,6,6-trimethyl-hept-2-en-4-ynyl ester, 8b

Conditions [A] were applied to **7b** (63% yield).

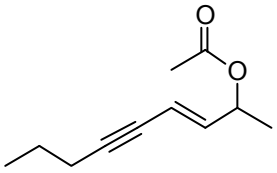
IR (*neat*) : 2971, 2360, 2342, 1743, 1637, 1457, 1371, 1236, 1153, 1044 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 5.97 (dd, *J* = 16.0, 6.6 Hz, 1H), 5.69 (dd, *J* = 16.0, 1.4 Hz, 1H), 5.34 (quint$_{app}$, *J* = 6.6 Hz, 1H), 2.03 (s, 3H), 1.30 (d, *J* = 6.6 Hz, 3H), 1.22 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 170.3 (s), 140.2 (d), 112.2 (d), 100.3 (s), 76.6 (s), 70.4 (d), 31.0 (3q), 28.0 (s), 21.4 (q), 20.1 (d).

MS (EI, 70eV) *m/z* : 194 ([M]$^{+\cdot}$, 16), 179 ([M-Me]$^{+}$, 43), 152 (37), 151 ([M-Ac]$^{+}$, 65), 138 (18), 137 (86), 135 (17), 119 (64), 109 (50), 107 (27), 105 (31), 95 (100), 93 (27), 91 (73), 79 (27), 77 (39), 67 (17), 65 (15).

HRMS (ESI) : Calculated for $C_{12}H_{18}NaO_2$ [M+Na]$^{+}$: 217.1199. Found : 217.1195.



Acetic acid (*E*)-1-methyl-oct-2-en-4-ynyl ester, 8c

Conditions [A] were applied to **7c**, 20 min of heating were necessary to reach full conversion (65% yield).

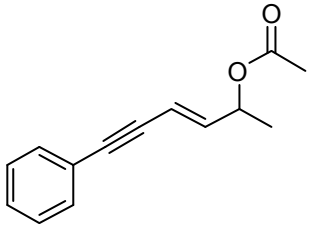
IR (*neat*) : 2966, 2935, 2361, 1740, 1456, 1371, 1236, 1153, 1043 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 5.97 (dd, *J* = 15.9, 6.6 Hz, 1H), 5.68 (dm, *J* = 15.9 Hz, 1H), 5.34 (quint., *J* = 6.6 Hz, 1H), 2.26 (td, J = 7.0, 2.2 Hz, 2H), 2.02 (s, 3H), 1.52 (sext$_{app}$, *J* = 7.2 Hz, 2H), 1.29 (d, *J* = 6.6 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 170.3 (s), 140.5 (d), 112.3 (d), 92.2 (s), 78.2 (s), 70.2 (d), 22.2 (t), 21.5 (t), 21.3 (q), 20.1 (q), 13.6 (q).

MS (EI, 70eV) *m/z* : 180 ([M]$^{+\cdot}$, 15), 151 (39), 138 (31), 137 (84), 123 (26), 121 (26), 109 (68), 105 (48), 95 (100), 92 (17), 91 (70), 81 (29), 79 (48), 77 (40), 65 (24).

HRMS (ESI) : Calculated for $C_{11}H_{16}NaO_2$ [M+Na]$^{+}$: 203.1043. Found : 203.1039.



Acetic acid (*E*)-1-methyl-5-phenyl-pent-2-en-4-ynyl ester, 8d

Conditions [A] were applied to **7d** (10 min of heating) (*E*/*Z* = 9/1, 61% yield).

IR (*neat*) : 2984, 1739, 1492, 1445, 1373, 1238, 1155, 1047 cm^{-1}.

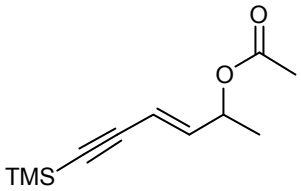
^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.30-7.43 (m, 5H), 6.18 (ddd, *J* = 16.0, 6.2,

2.5 Hz, 1H), 5.92 (d, *J* = 16.0 Hz, 1H), 5.43 ($quint_{app}$, *J* = 6.5 Hz, 1H), 2.07 (d, *J* = 2.5 Hz, 3H), 1.35 (dd, *J* = 6.5, 2.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 170.3 (s), 141.9 (d), 131.7 (2d), 128.5 (3d), 123.2 (s), 111.6 (d), 91.0 (s) , 87.1 (s), 70.3 (d), 21.4 (q), 20.1 (q).

MS (EI, 70eV) *m/z* : 214 ($[M]^{+\cdot}$, 17), 199 ($[M-Me]^+$, 21), 171 ($[M-Ac]^+$, 100), 157 (26), 155 (19), 154 (29), 153 (56), 152 (29), 129 (21), 128 (34), 127 (18), 115 (16), 77 (17).

HRMS (ESI) : Calculated for $C_{14}H_{14}NaO_2$ $[M+Na]^+$: 237.0886. Found : 237.0886.



Acetic acid (*E*)-1-methyl-5-trimethylsilanyl-pent-2-en-4-ynyl ester, 8e

Conditions [B] were applied to **7e** (*E*/*Z* = 85/15, 45% yield).

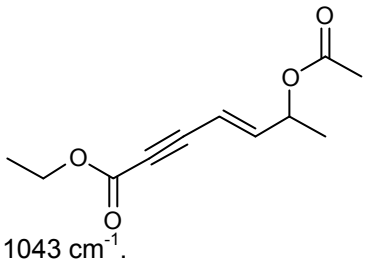
IR (neat) : 2961, 2156, 1739, 1633, 1452, 1372, 1235, 1155, 1088, 1045 cm^{-1}.

^{1}H NMR (400 MHZ, $CDCl_3$) *δ* : 6.13 (dd, *J* = 16.0, 6.3 Hz, $1H_4$), 5.71 (dd, *J* = 16.1, 0.8 Hz, 1H), 5.35 ($quint_{app}$, *J* = 6.3 Hz, 1H), 2.03 (s, 3H), 1.30 (d, *J* = 6.5 Hz, 3H), 0.17 (s, 9H).

^{13}C NMR (100 MHZ, $CDCl_3$) *δ* : 170.1 (s), 143.0 (d), 111.4 (d), 102.6 (s), 96.1 (s), 70.0 (d, C_5), 21.2 (q), 19.9 (q), -0.1 (3q).

MS (EI) *m/z* : 210 (11, $[M]^{+\cdot}$), 168 (13), 167 (37), 135 (42), 117 (46), 109 (13), 107 (13), 97 (12), 95 (66), 83 (19), 77 (11), 75 (100), 73 (91), 61 (14), 59 (22), 53 (11).

HRMS (ESI) : Calculated for $C_{11}H_{18}NaO_2Si$ $[M+Na]^+$: 233.0968. Found : 233.0964.



(*E*)-6-Acetoxy-hept-4-en-2-ynoic acid ethyl ester, 8f

Conditions [A] were applied to **7f** with acidified silica gel **S1** (1/1 weight ratio), 25 min of heating were necessary to reach full conversion (51% yield, *E*/*Z* = 84/16).

IR (*neat*) : 2983, 2214, 1738, 1709, 1448, 1370, 1240, 1138, 1102, 1043 cm^{-1}.

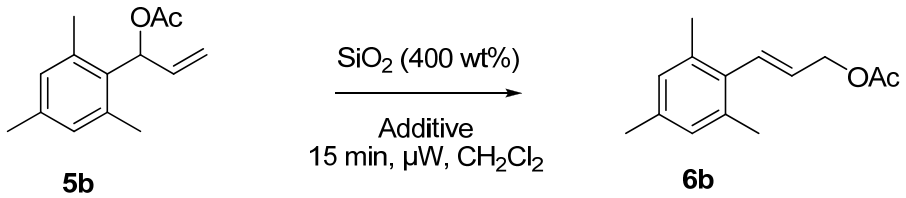
^{1}H NMR (400 MHz, $CDCl_3$) δ : 6.40 (dd, *J* = 16.1, 5.7 Hz, 1H), 5.75 (dd, *J* = 16.1, 1.5 Hz, 1H), 5.40 ($quint_{app}$, *J* = 6.4, 1.6 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.06 (s, 3H), 1.29-1.33 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ : 170.0 (s), 153.9 (s), 148.5 (d, C_7, 108.2 (d), 83.7 (s), 71.7 (s), 69.5 (d), 62.2 (t), 21.2 (q), 19.8 (q), 14.1 (q)

MS (EI, 70eV) *m/z* : 210 ($[M]^{+\cdot}$, 1), 139 (55), 123 (42), 122 (100), 97 (40), 79 (41), 78 (28), 77 (44), 51 (31).

HRMS (ESI) : Calculated for $C_{11}H_{14}NaO_4$ $[M+Na]^+$: 233.0784 . Found : 233.0784.

Additives effect on the outcome of the rearrangement

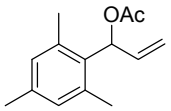


5b **6b**

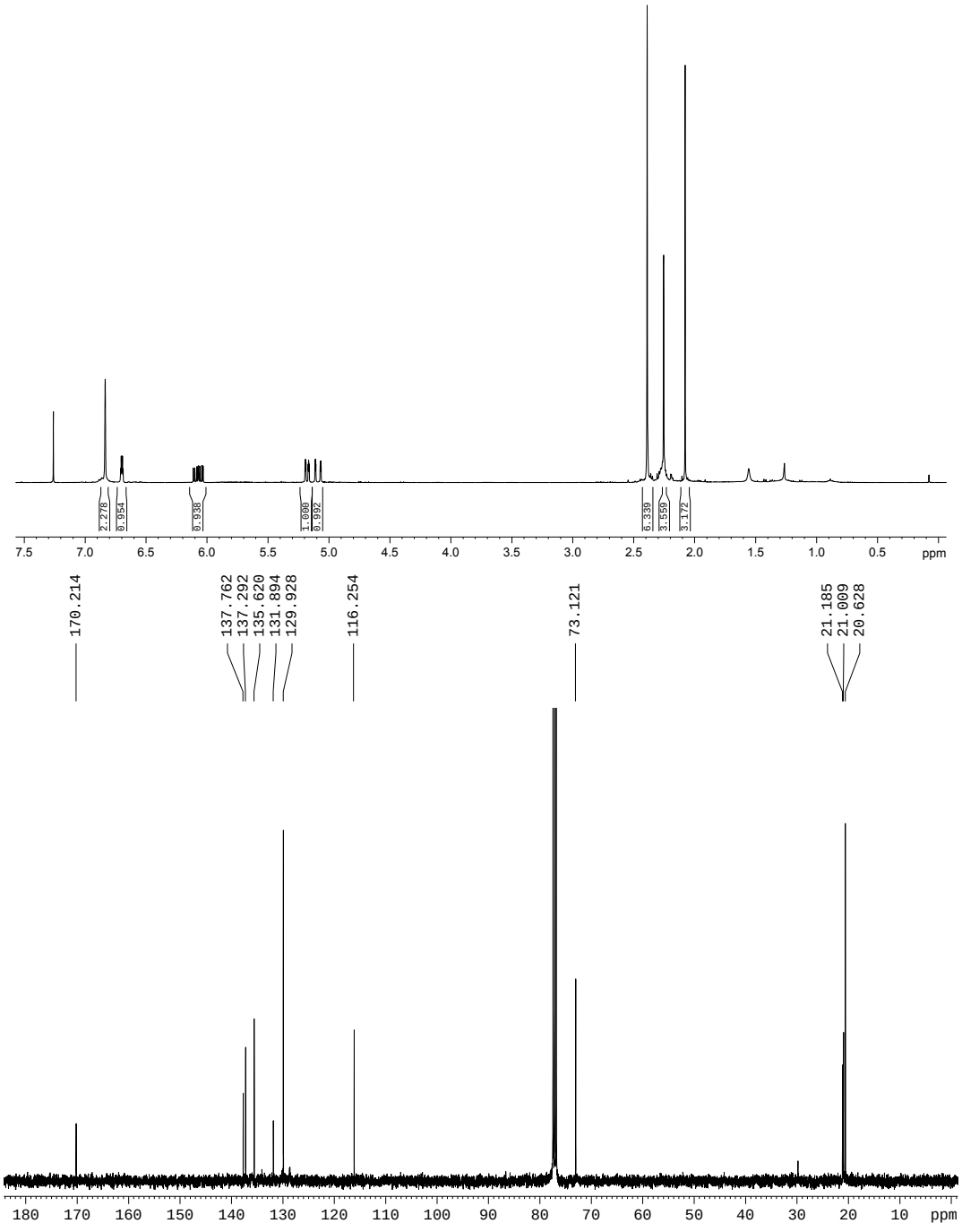
Entry[a]	Additive/SiO_2 wt%	conversion of **5b**
1	H_2O, 10%	84%
2	H_2O, 30%	66%
3	H_2O, 50%	20%
4	Et_3N, 10%	no cv
5[b]	-	55%

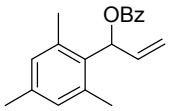
[a] Reactions were performed on 0.2 mmol of **5b** in 1 mL of CH_2Cl_2 [b] The silica-gel was dissolved in acetone, evaporated to dryness and used in the reaction.

The influence of some additives on the rearrangement of **5b** to **6b** was evaluated under conditions [A]. Addition of water to the reaction medium decreased the activity of silica resulting in lower conversions (entries 1-3). In the presence of Et_3N, no reaction occurred (entry 4). Finally, silica-gel was dissolved in acetone (1.7 g in 10 mL), evaporated to dryness and used in the rearrangement reaction leading to a 55% conversion of **5b** (entry 5).

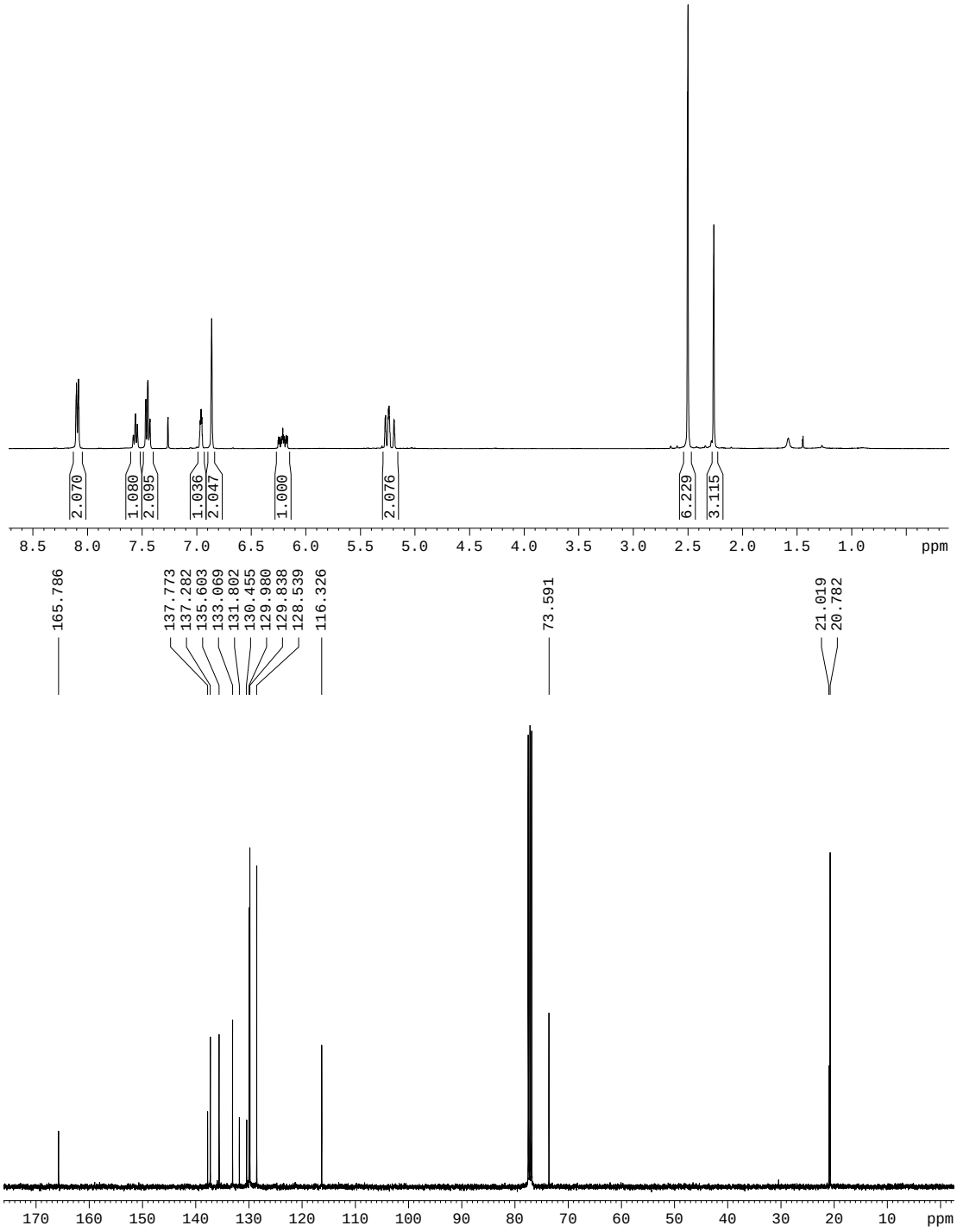

OAc

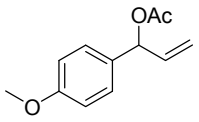
5b


2.278
0.954
0.938
1.000
0.992
6.339
3.559
3.172
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 ppm
170.214
137.762
137.292
135.620
131.894
129.928
116.254
73.121
21.185
21.009
20.628
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

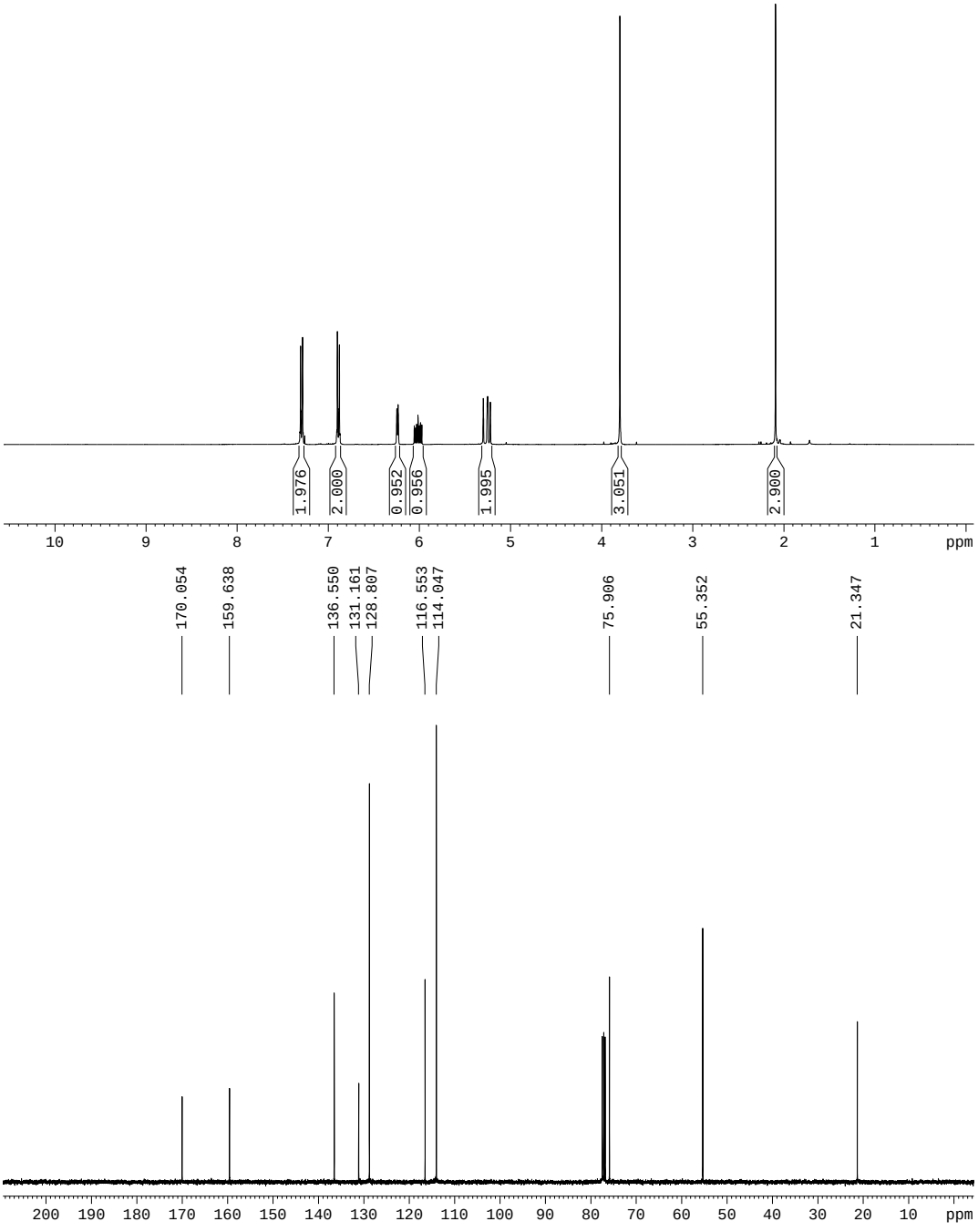

OBz

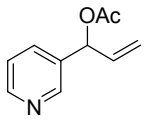
5c


2.070
1.080
2.095
1.036
2.047
1.000
2.076
6.229
3.115
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 ppm
165.786
137.773
137.282
135.603
133.069
131.802
130.455
129.980
129.838
128.539
116.326
73.591
21.019
20.782
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

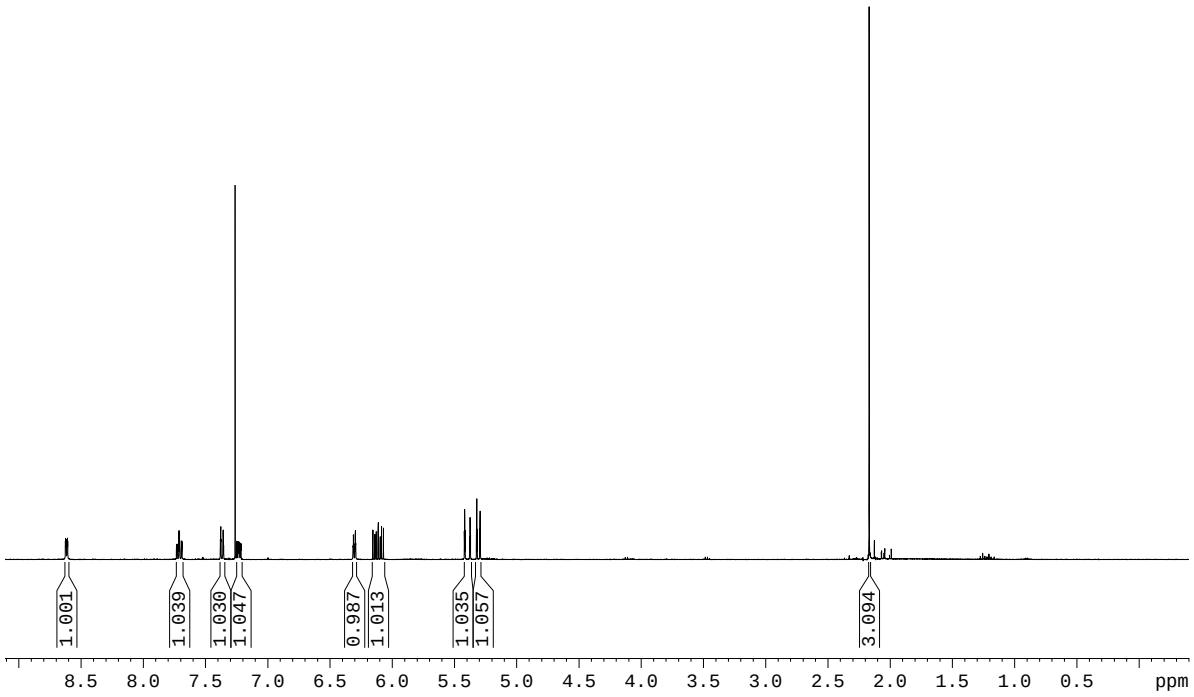

OAc
O

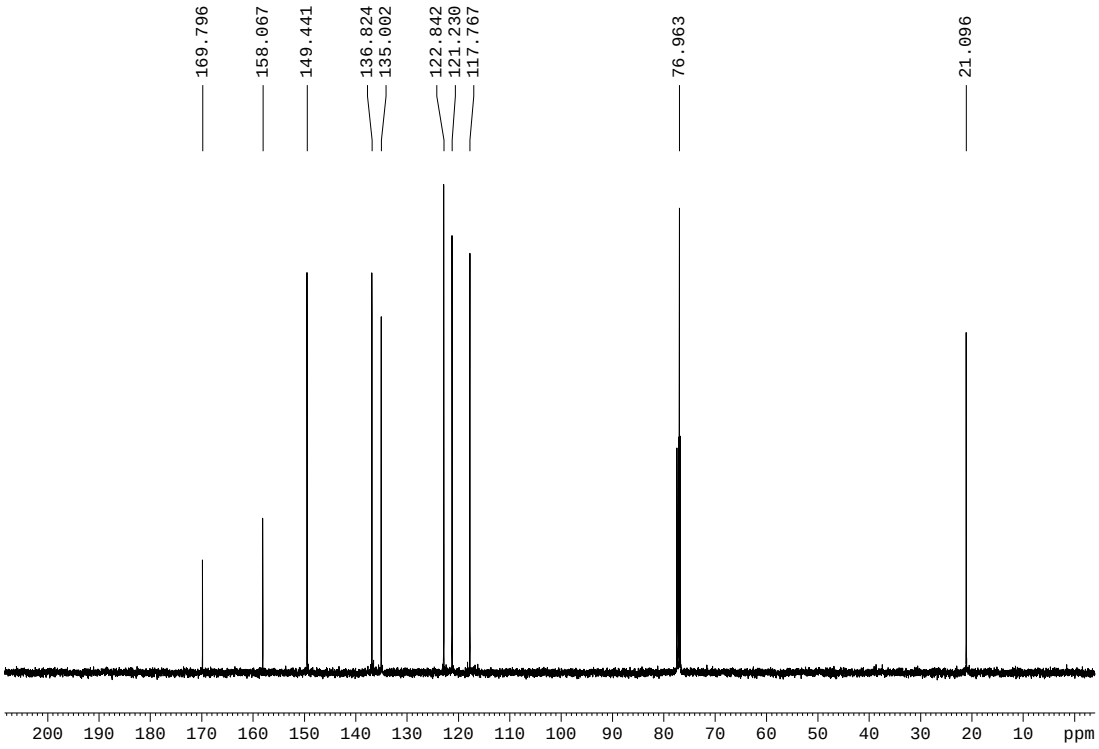
5d

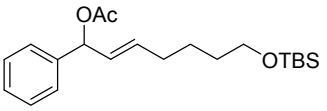

1.976
2.000
0.952
0.956
1.995
3.051
2.900
10 9 8 7 6 5 4 3 2 1 ppm
170.054
159.638
136.550
131.161
128.807
116.553
114.047
75.906
55.352
21.347
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


OAc
N

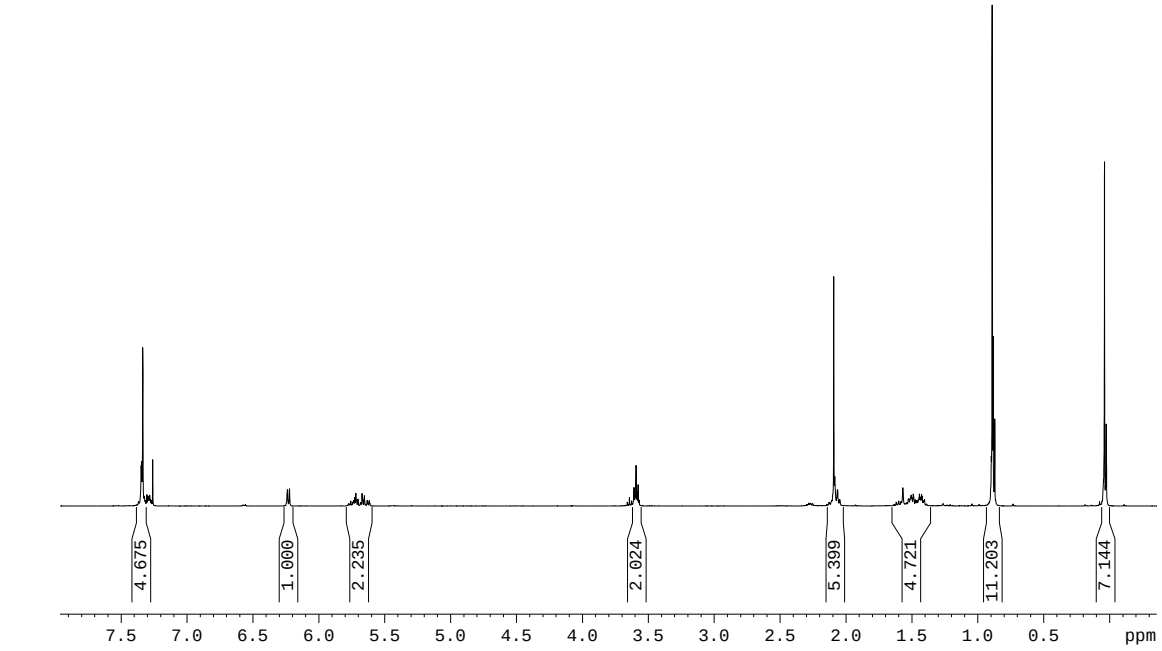
5g

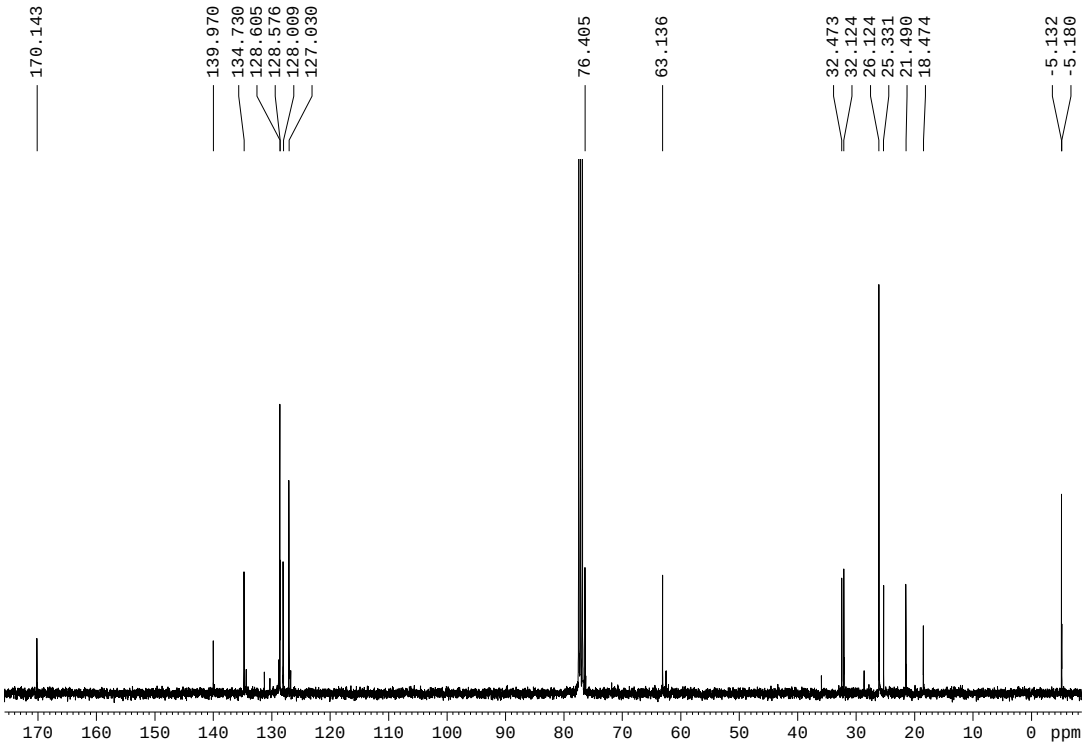

1.001
1.039
1.030
1.047
0.987
1.013
1.035
1.057
3.094
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

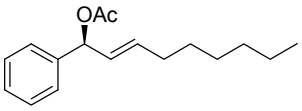

169.796
158.067
149.441
136.824
135.002
122.842
121.230
117.767
76.963
21.096
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


OAc
OTBS

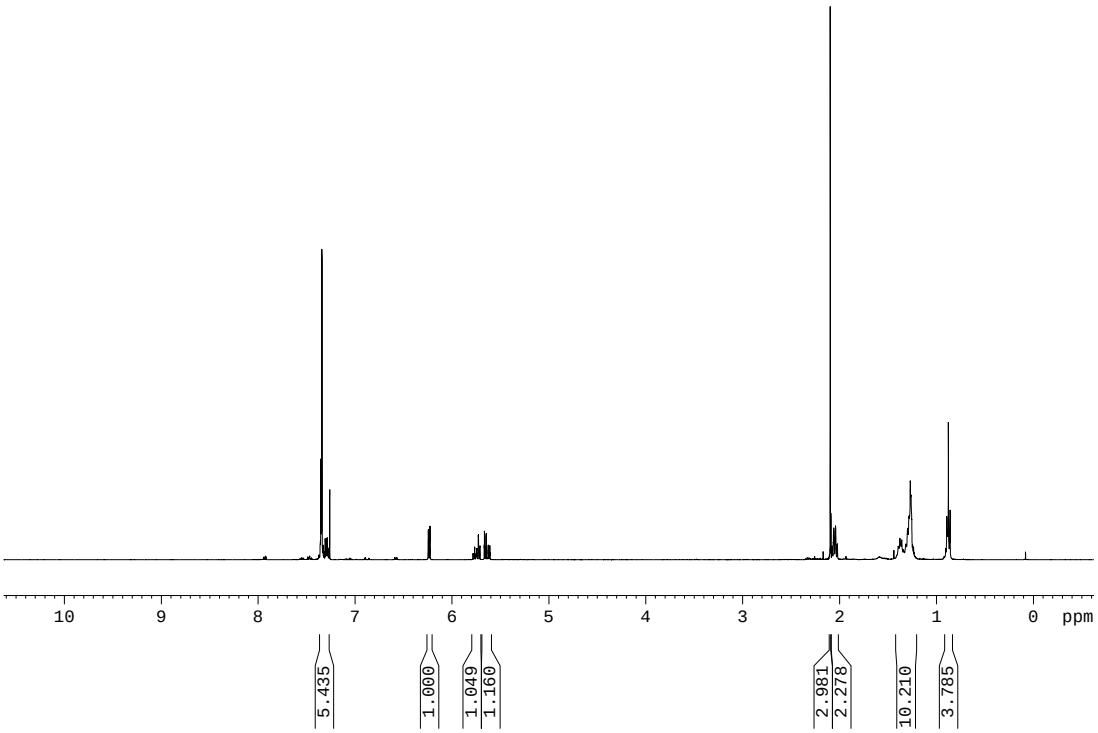
5h

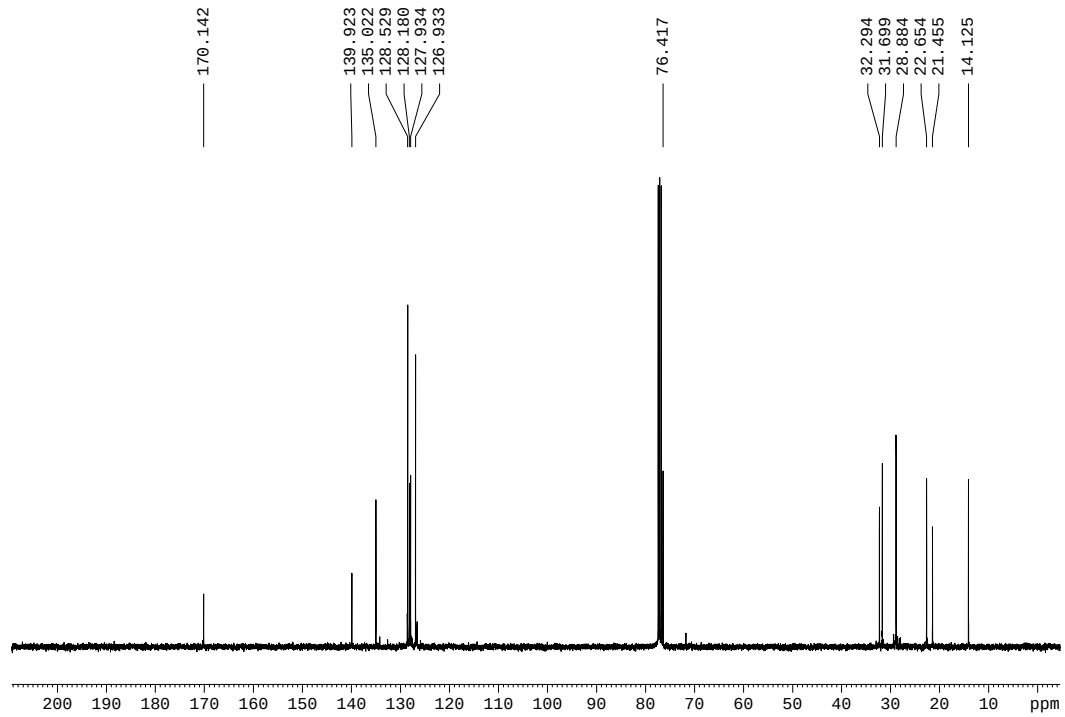

4.675
1.000
2.235
2.024
5.399
4.721
11.203
7.144
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

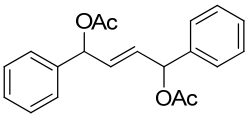

170.143
139.970
134.730
128.605
128.576
128.009
127.030
76.405
63.136
32.473
32.124
26.124
25.331
21.490
18.474
-5.132
-5.180
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OAc

5i

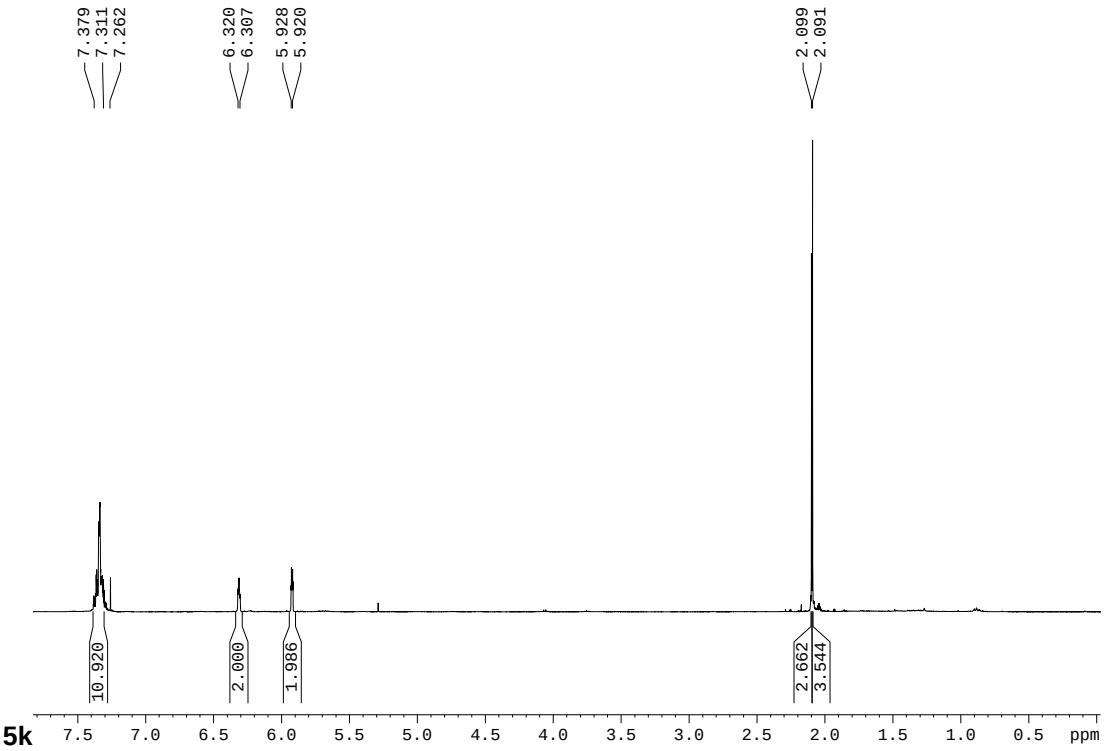

10
9
8
7
6
5
4
3
2
1
0
ppm
5.435
1.000
1.049
1.160
2.981
2.278
10.210
3.785

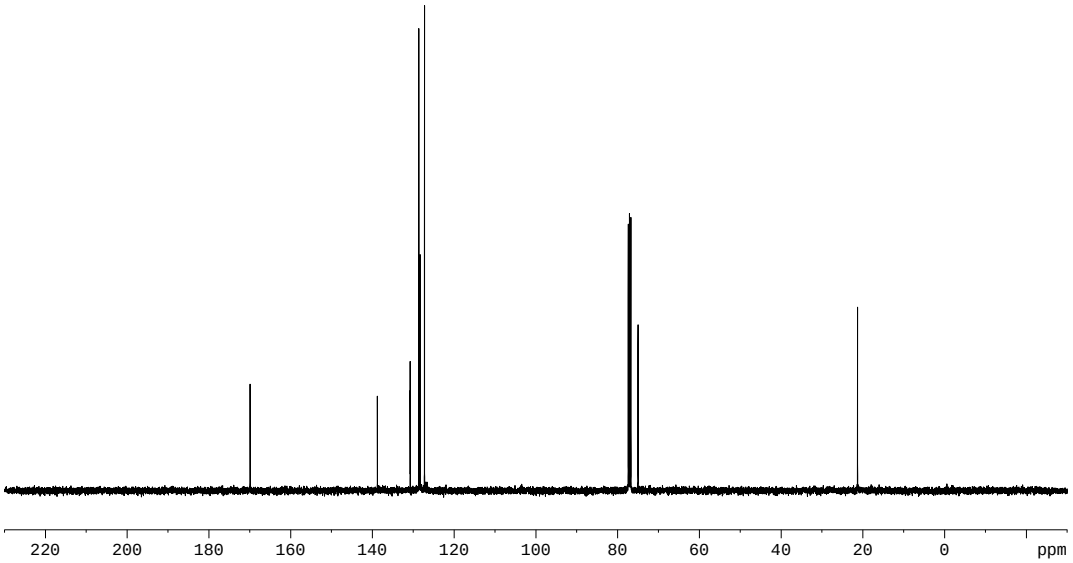

170.142
139.923
135.022
128.529
128.180
127.934
126.933
76.417
32.294
31.699
28.884
22.654
21.455
14.125
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

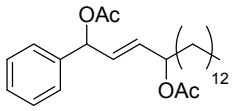

OAc
OAc

5m

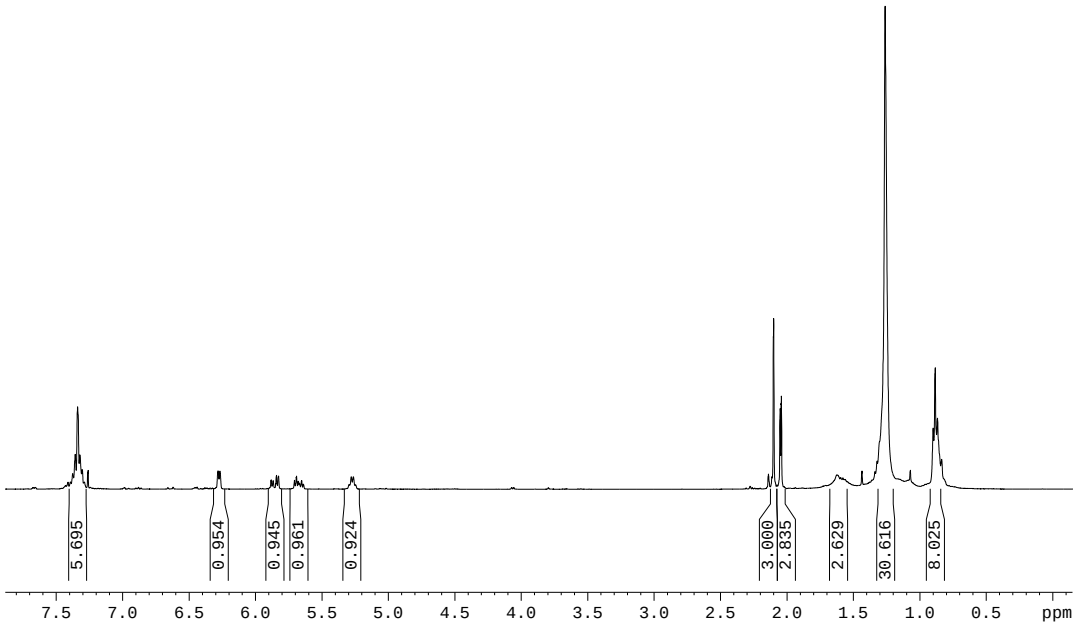
5k

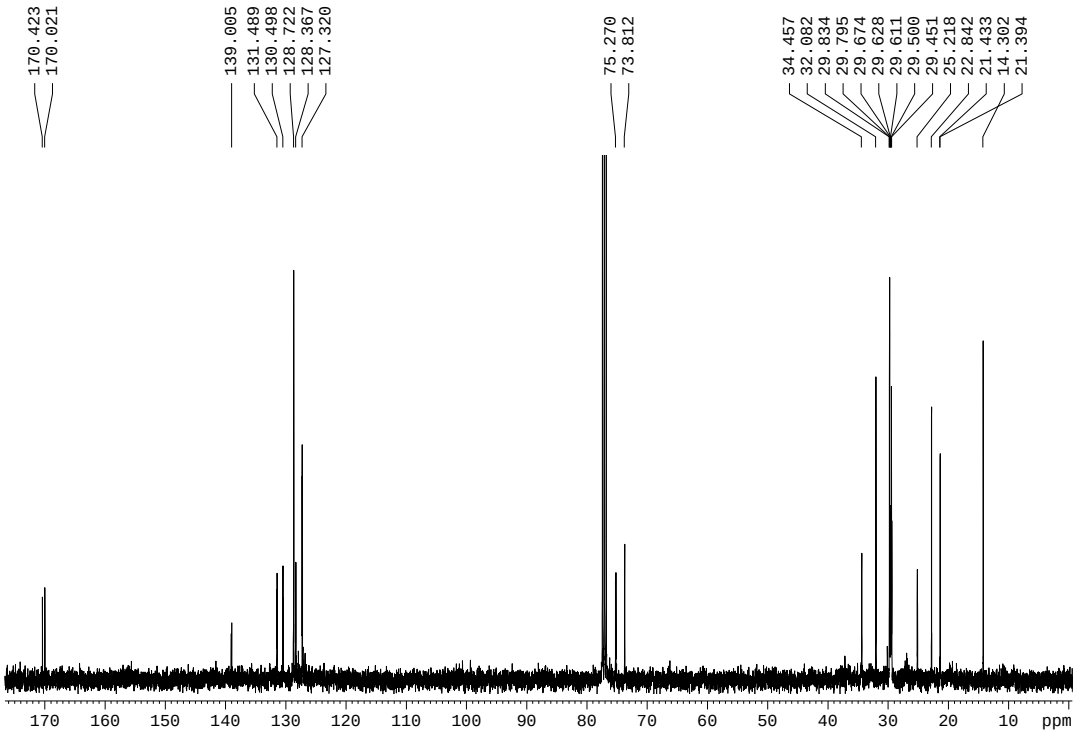

7.379
7.311
7.262
6.320
6.307
5.928
5.920
2.099
2.091
10.920
2.000
1.986
2.662
3.544
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

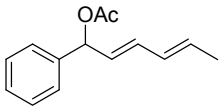

220 200 180 160 140 120 100 80 60 40 20 0 ppm


OAc
OAc
12

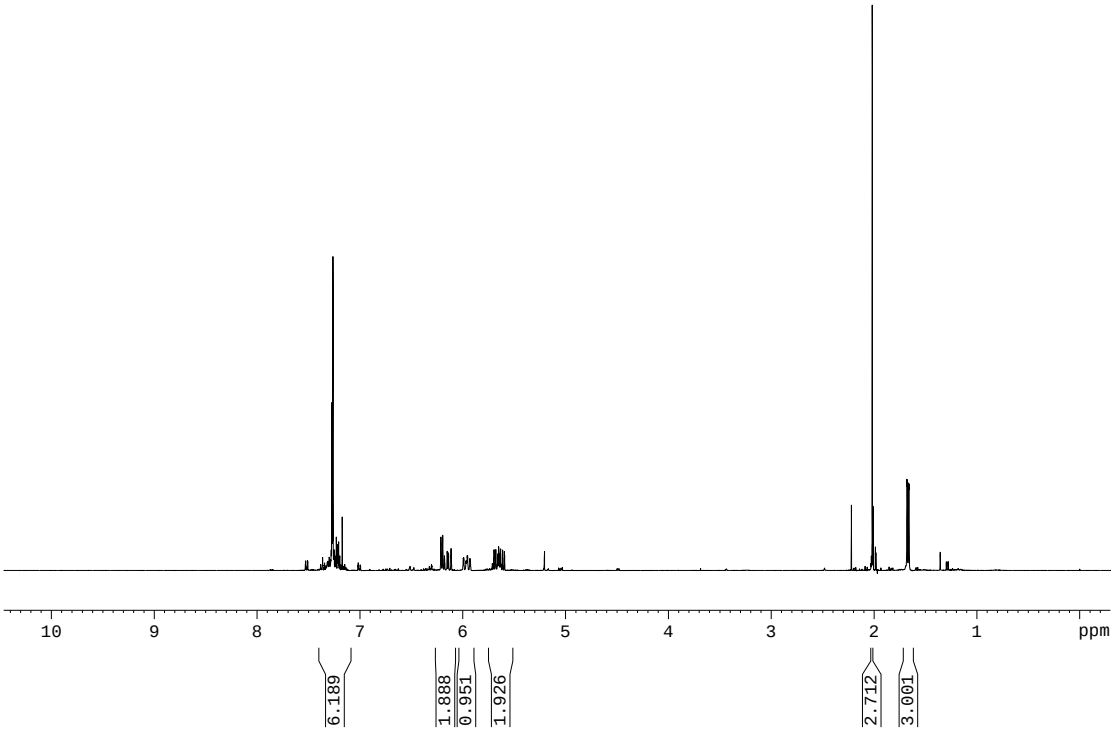
5l

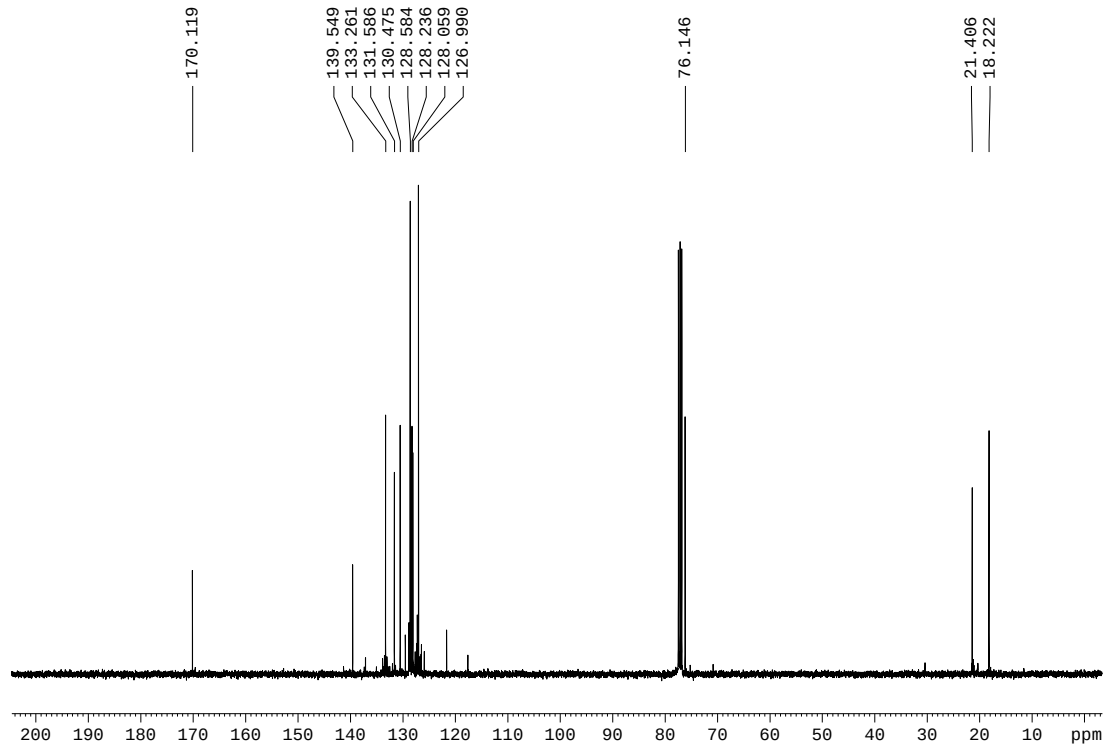

5.695
0.954
0.945
0.961
0.924
3.000
2.835
2.629
30.616
8.025
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

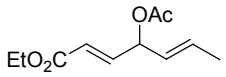

170.423
170.021
139.005
131.489
130.498
128.722
128.367
127.320
75.270
73.812
34.457
32.082
29.834
29.795
29.674
29.628
29.611
29.500
29.451
25.218
22.842
21.433
14.302
21.394
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


OAc

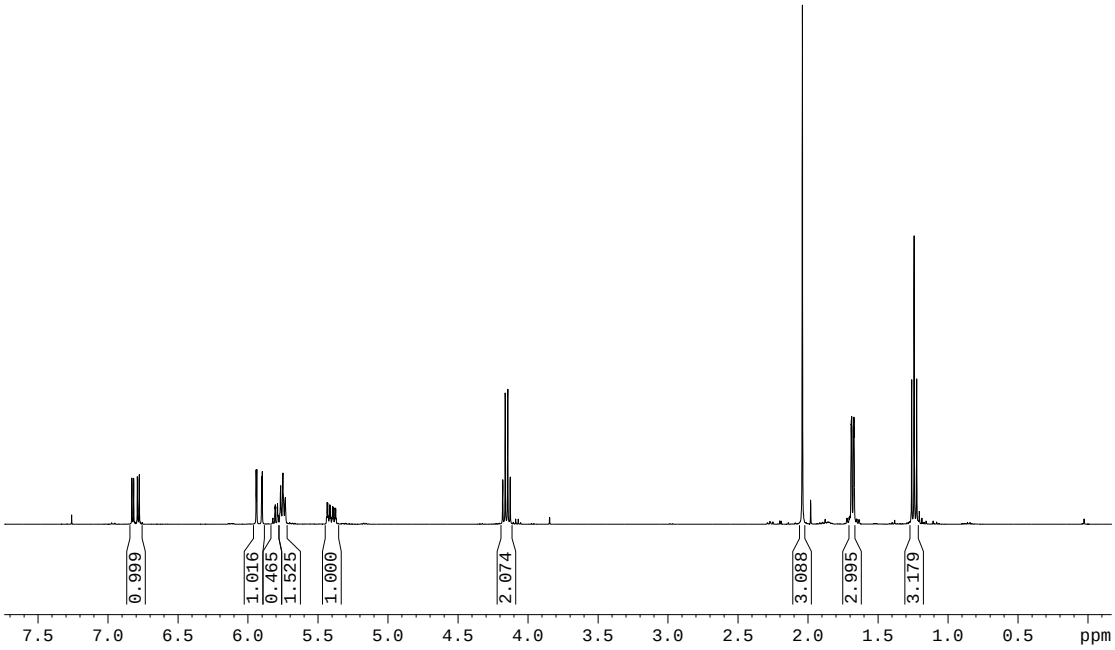
5m

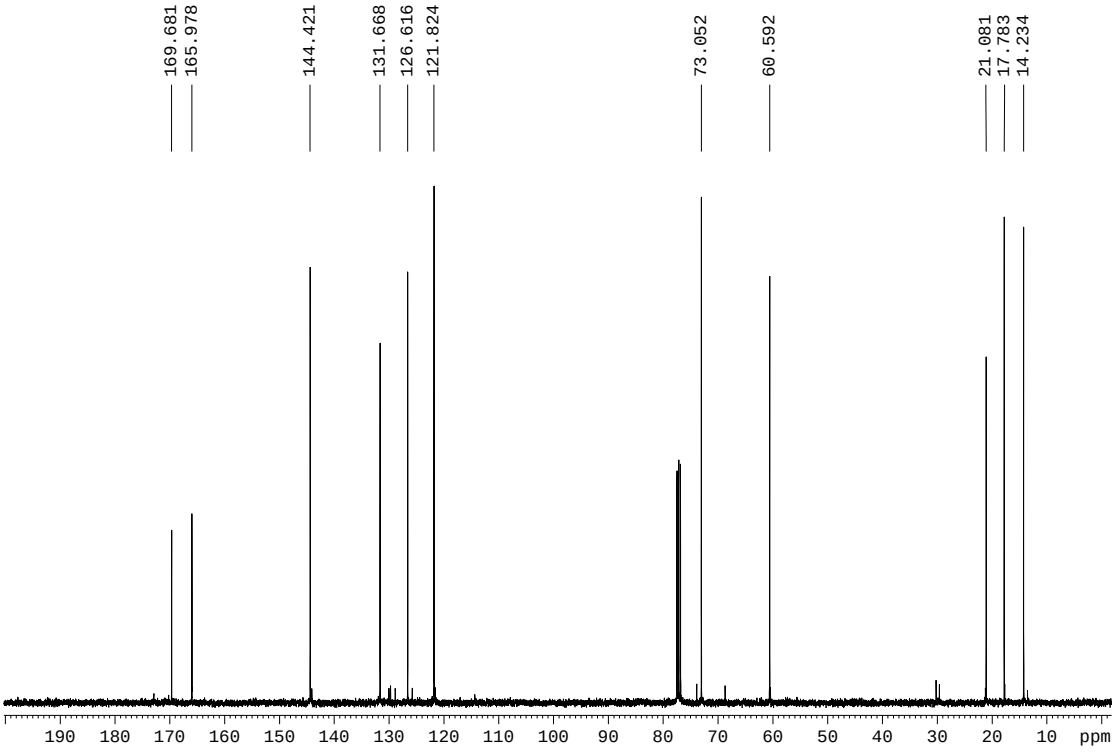

10
9
8
7
6
5
4
3
2
1
ppm
6.189
1.888
0.951
1.926
2.712
3.001

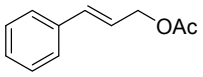

170.119
139.549
133.261
131.586
130.475
128.584
128.236
128.059
126.990
76.146
21.406
18.222
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OAc
EtO2C

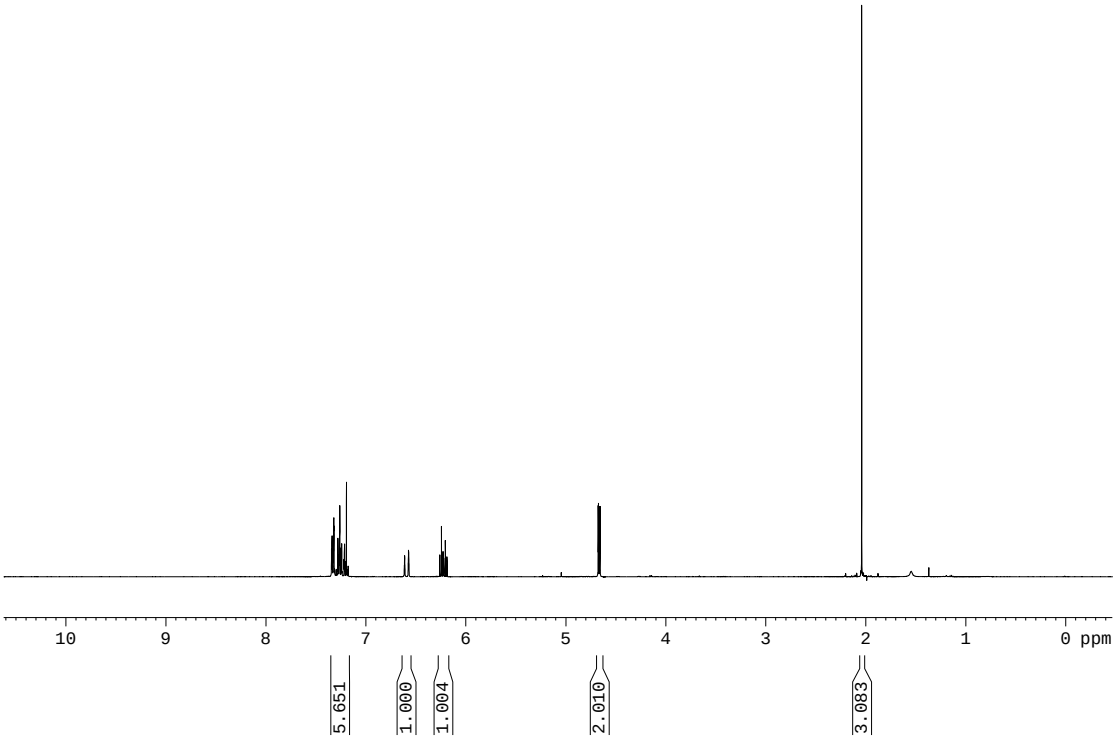
5n

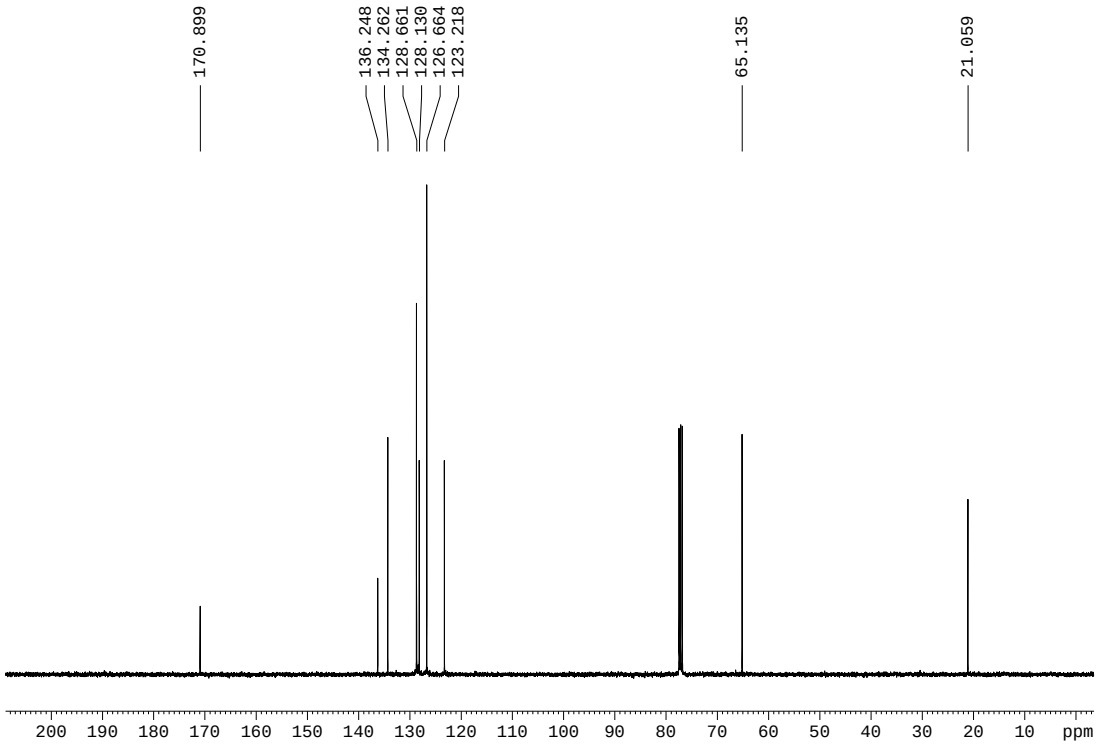

0.999
1.016
0.465
1.525
1.000
2.074
3.088
2.995
3.179
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

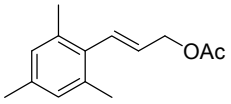

169.681
165.978
144.421
131.668
126.616
121.824
73.052
60.592
21.081
17.783
14.234
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


OAc

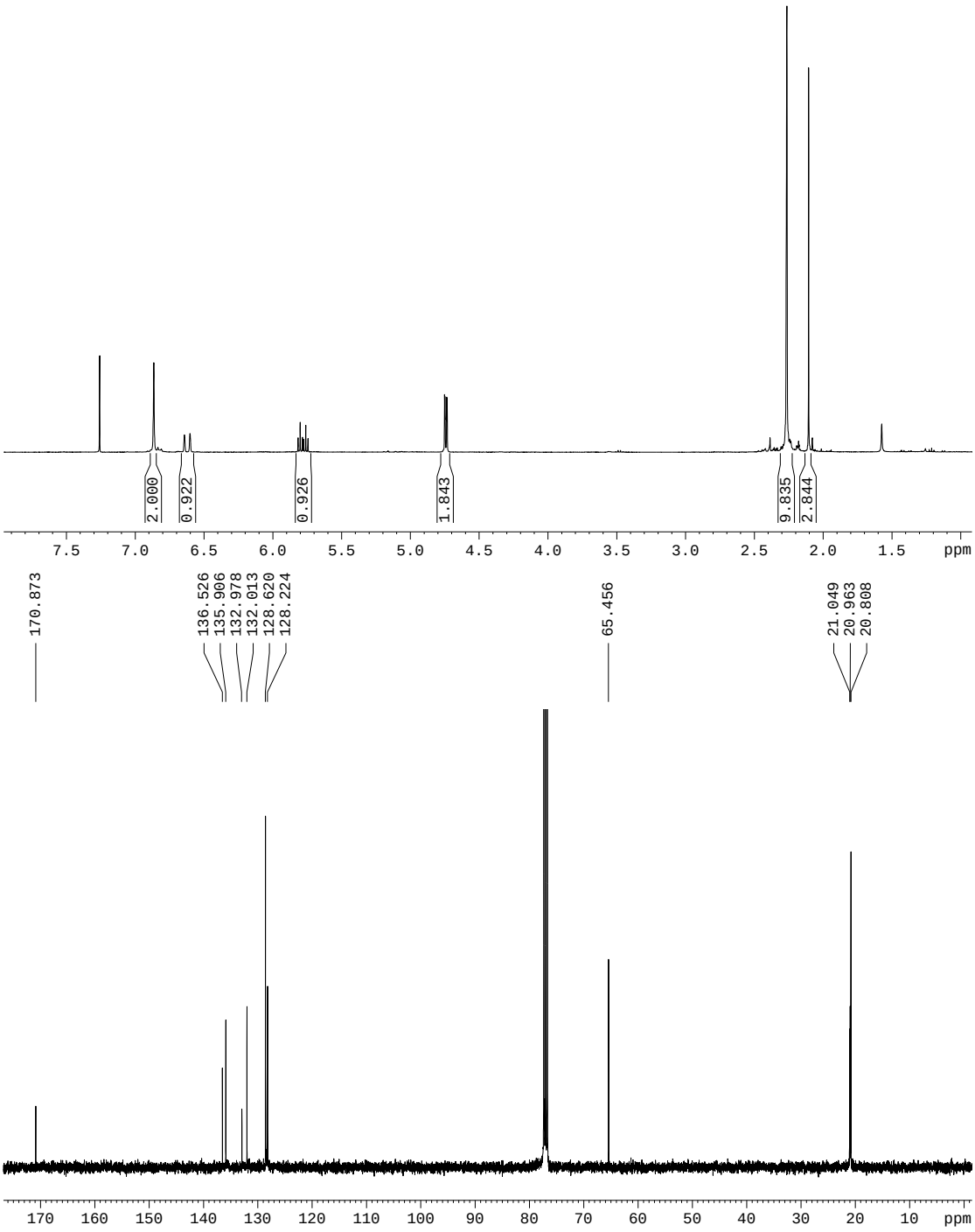
6a

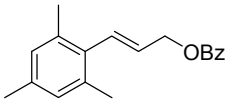

10
9
8
7
6
5
4
3
2
1
0 ppm
5.651
1.000
1.004
2.010
3.083


170.899
136.248
134.262
128.661
128.130
126.664
123.218
65.135
21.059
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

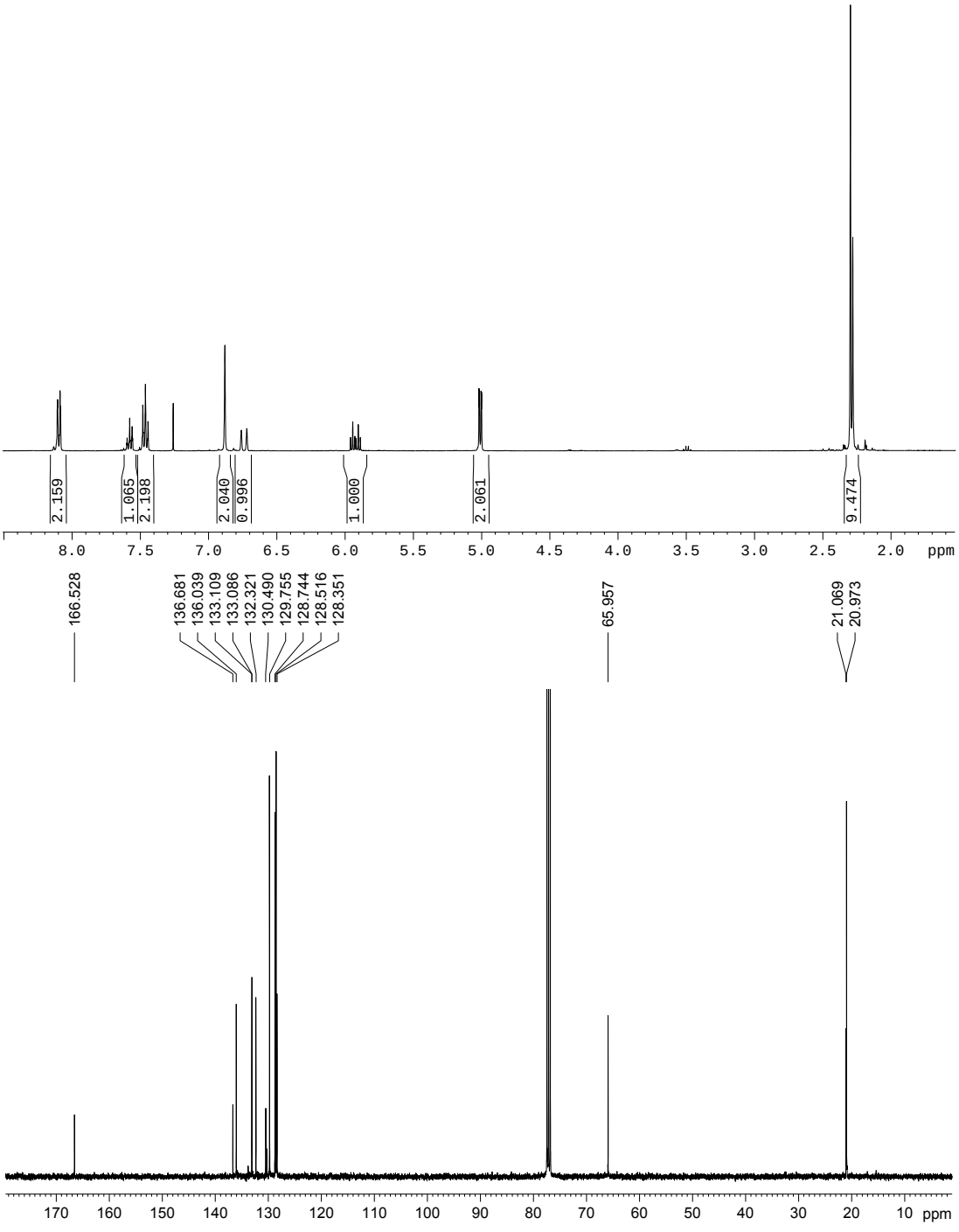

OAc

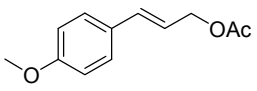
6b


2.000
0.922
0.926
1.843
9.835
2.844
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 ppm
170.873
136.526
135.906
132.978
132.013
128.620
128.224
65.456
21.049
20.963
20.808
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

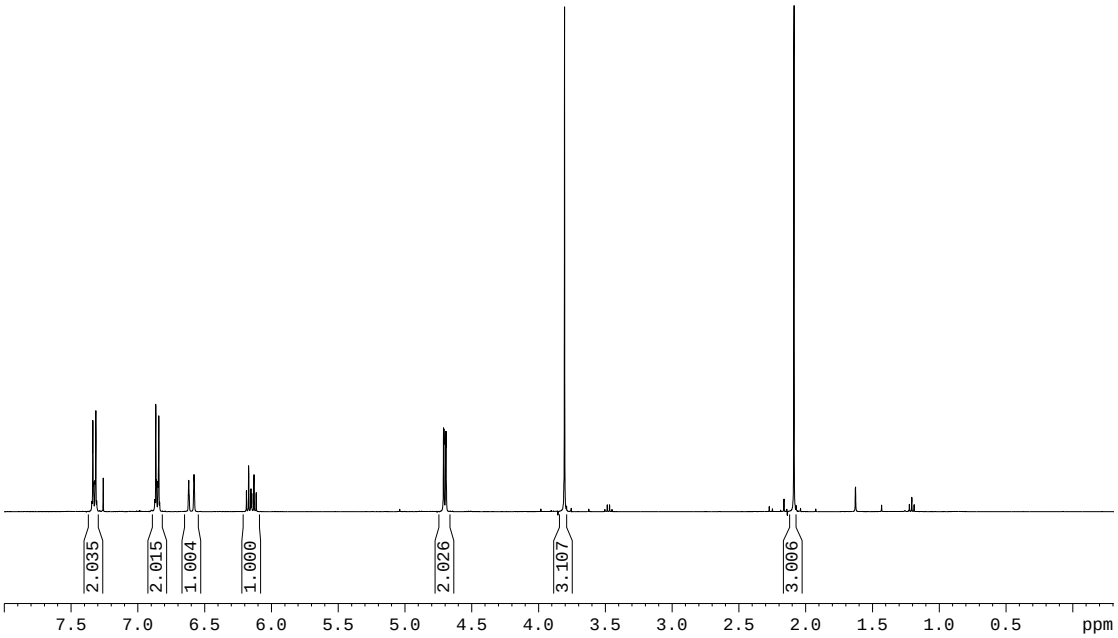

OBz

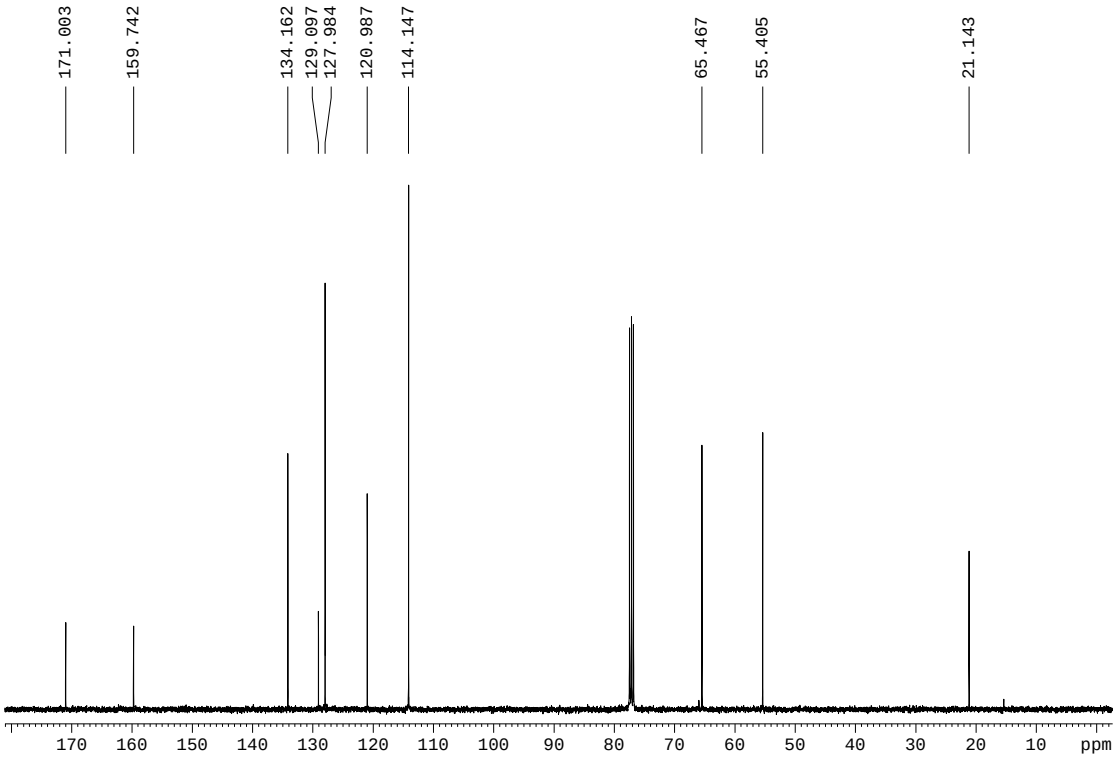
6c

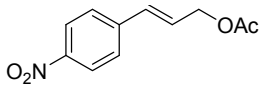

2.159
1.065
2.198
2.040
0.996
1.000
2.061
9.474
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
166.528
136.681
136.039
133.109
133.086
132.321
130.490
129.755
128.744
128.516
128.351
65.957
21.069
20.973
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OAc
O

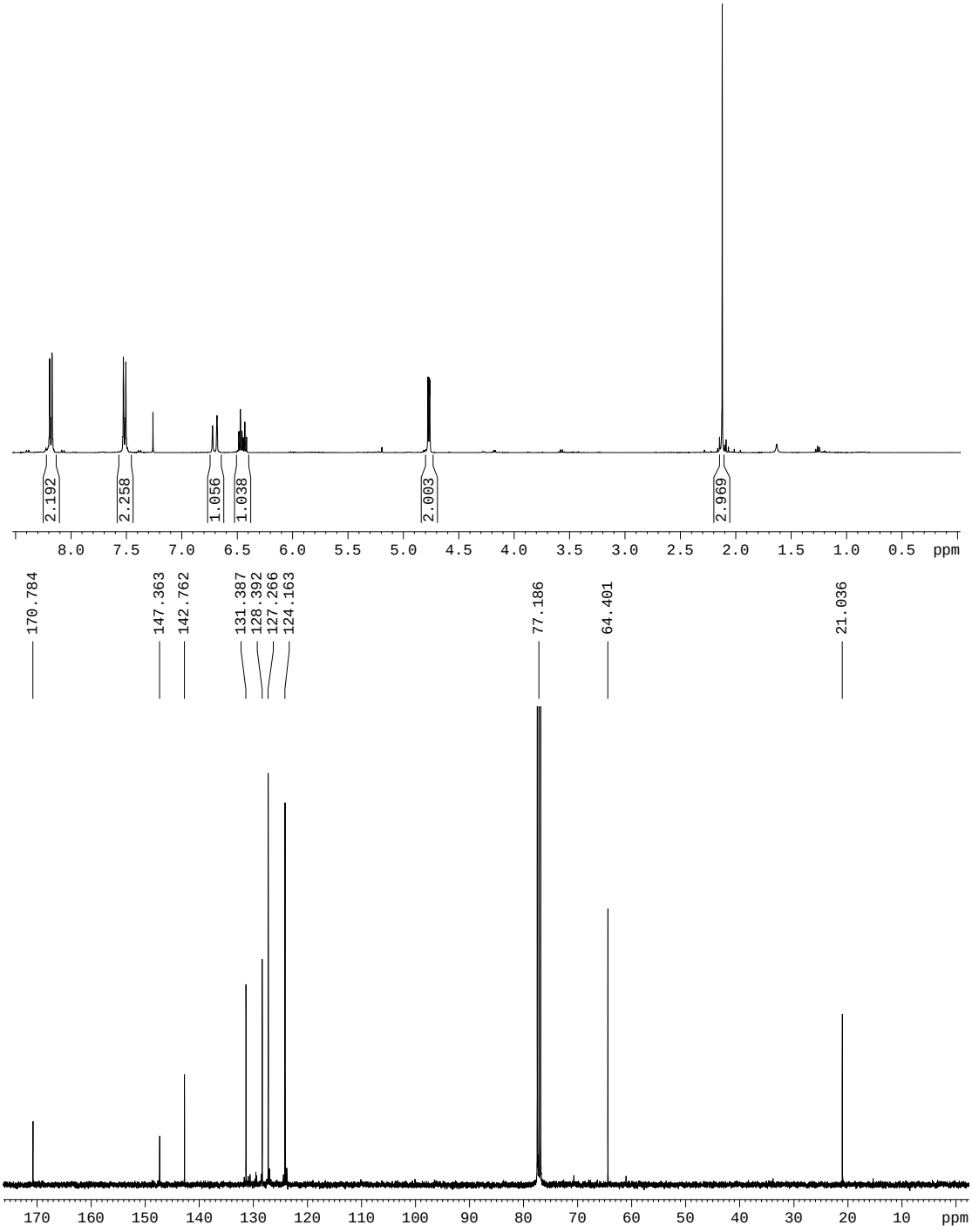
6d

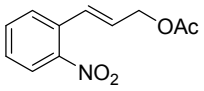

2.035
2.015
1.004
1.000
2.026
3.107
3.006
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


171.003
159.742
134.162
129.097
127.984
120.987
114.147
65.467
55.405
21.143
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

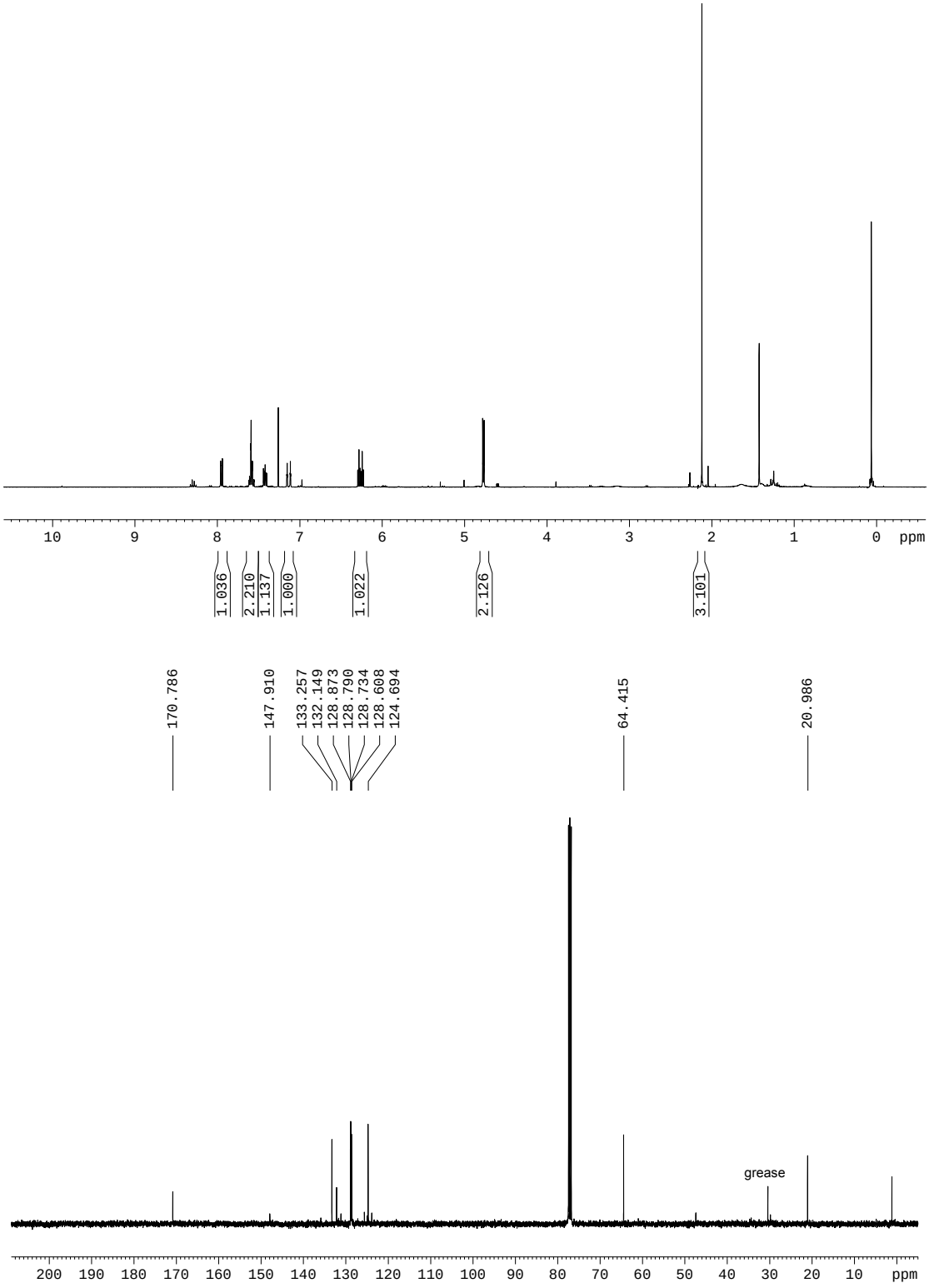

OAc
O2N

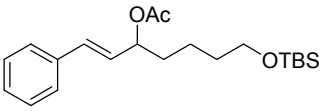
6e


2.192
2.258
1.056
1.038
2.003
2.969
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 ppm
170.784
147.363
142.762
131.387
128.392
127.266
124.163
77.186
64.401
21.036
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

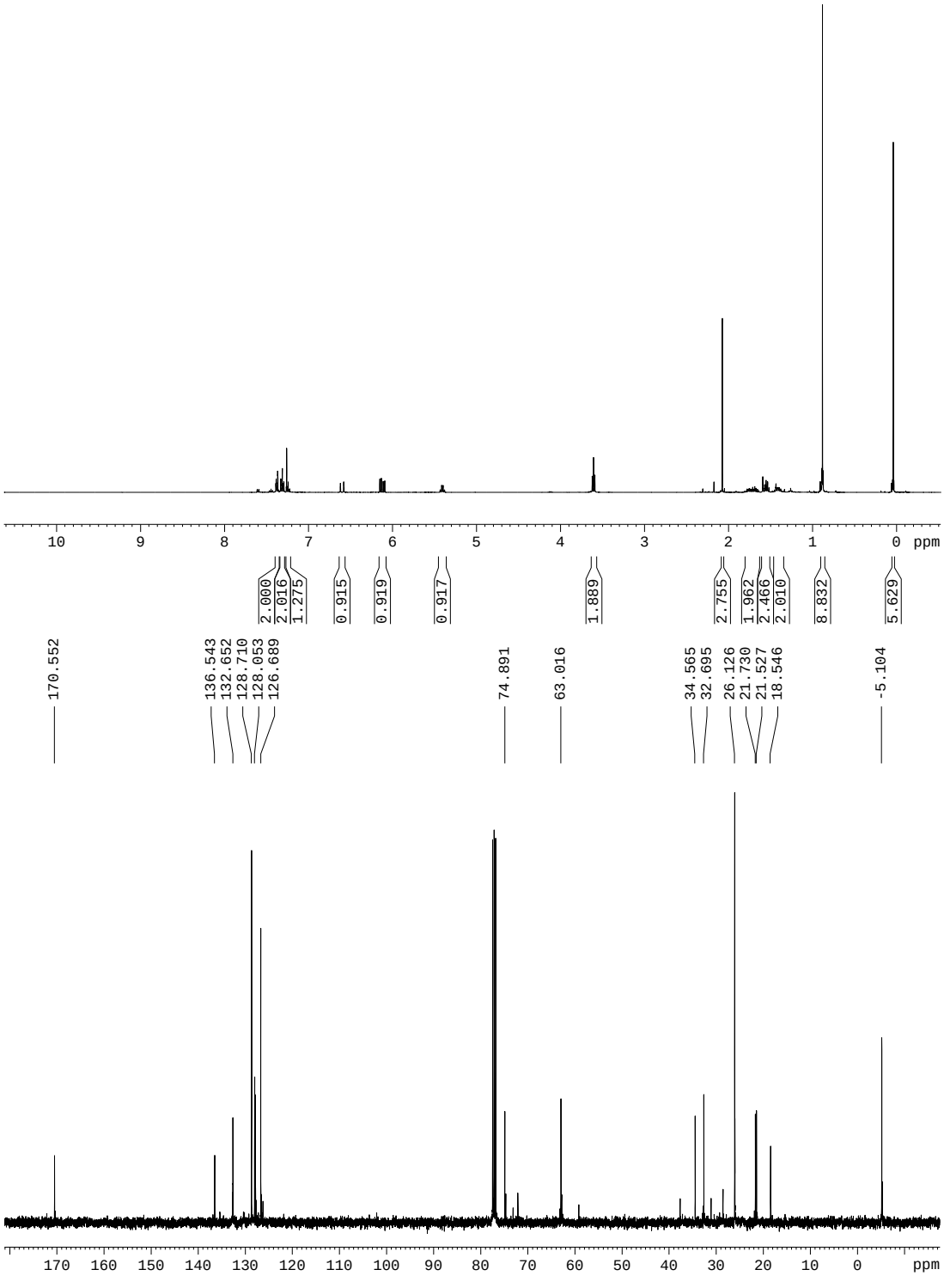

OAc
NO2

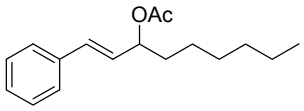
6f


10 9 8 7 6 5 4 3 2 1 0 ppm
1.036
2.210
1.137
1.000
1.022
2.126
3.101
170.786
147.910
133.257
132.149
128.873
128.790
128.734
128.608
124.694
64.415
20.986
grease
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

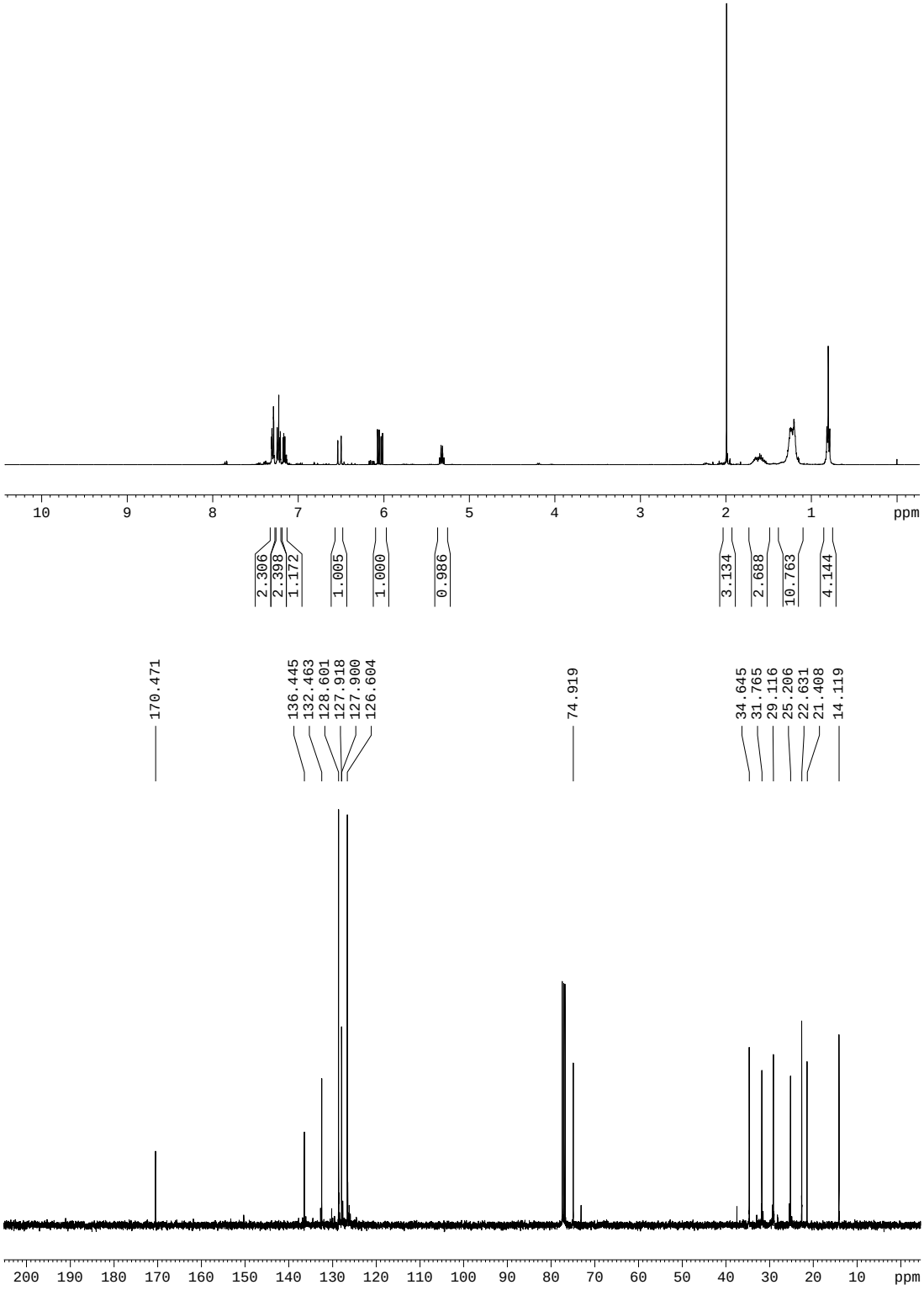

OAc
OTBS

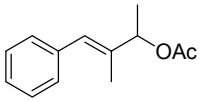
6h


10 9 8 7 6 5 4 3 2 1 0 ppm
2.000 2.016 1.275 0.915 0.919 0.917 1.889 2.755 1.962 2.466 2.010 8.832 5.629
170.552 136.543 132.652 128.710 128.053 126.689 74.891 63.016 34.565 32.695 26.126 21.730 21.527 18.546 -5.104
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

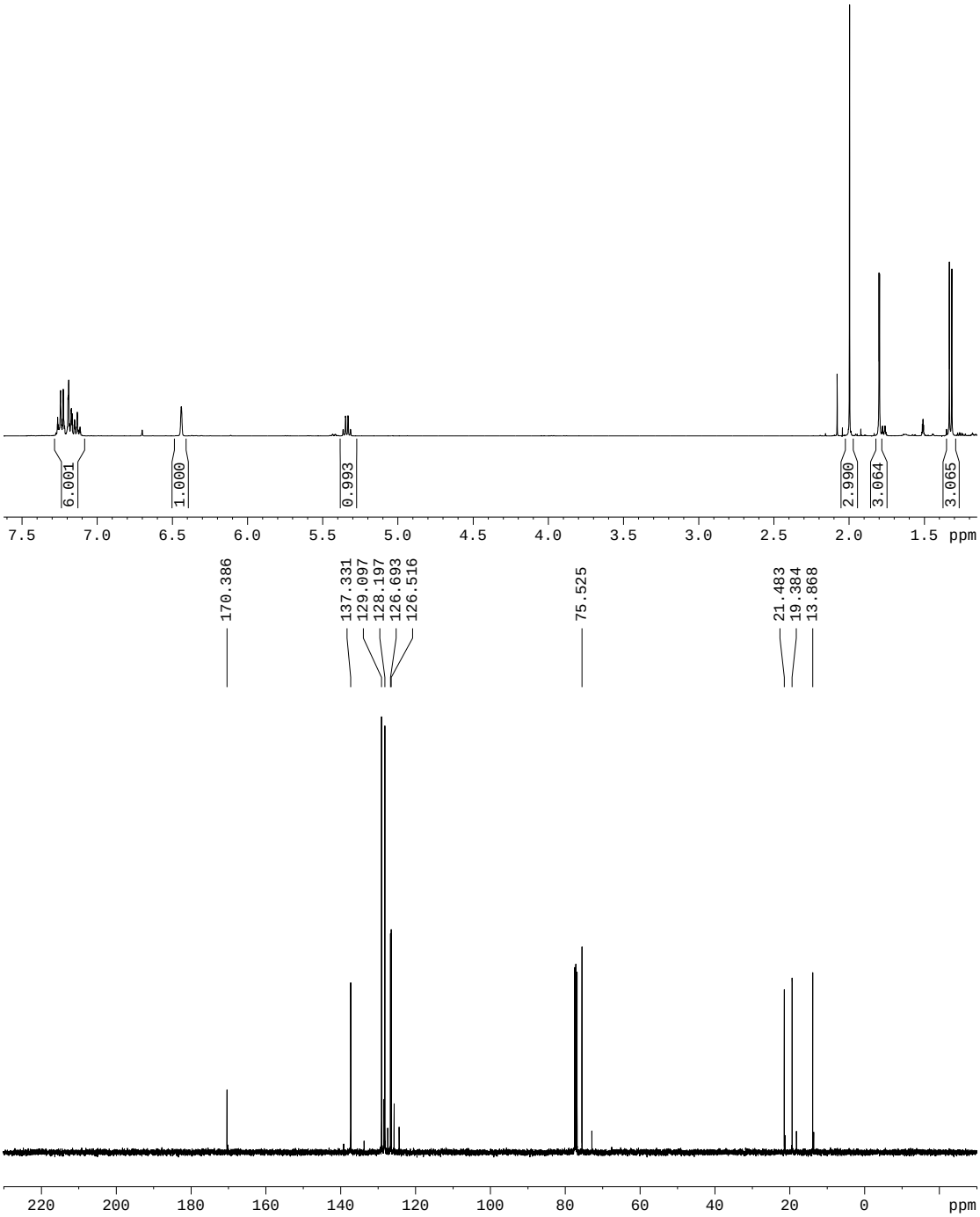

OAc

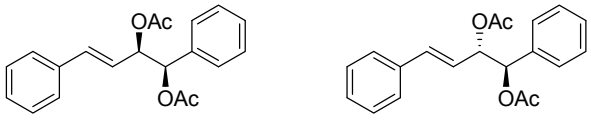
6i


10
9
8
7
6
5
4
3
2
1
ppm
2.306
2.398
1.172
1.005
1.000
0.986
3.134
2.688
10.763
4.144
170.471
136.445
132.463
128.601
127.918
127.900
126.604
74.919
34.645
31.765
29.116
25.206
22.631
21.408
14.119
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

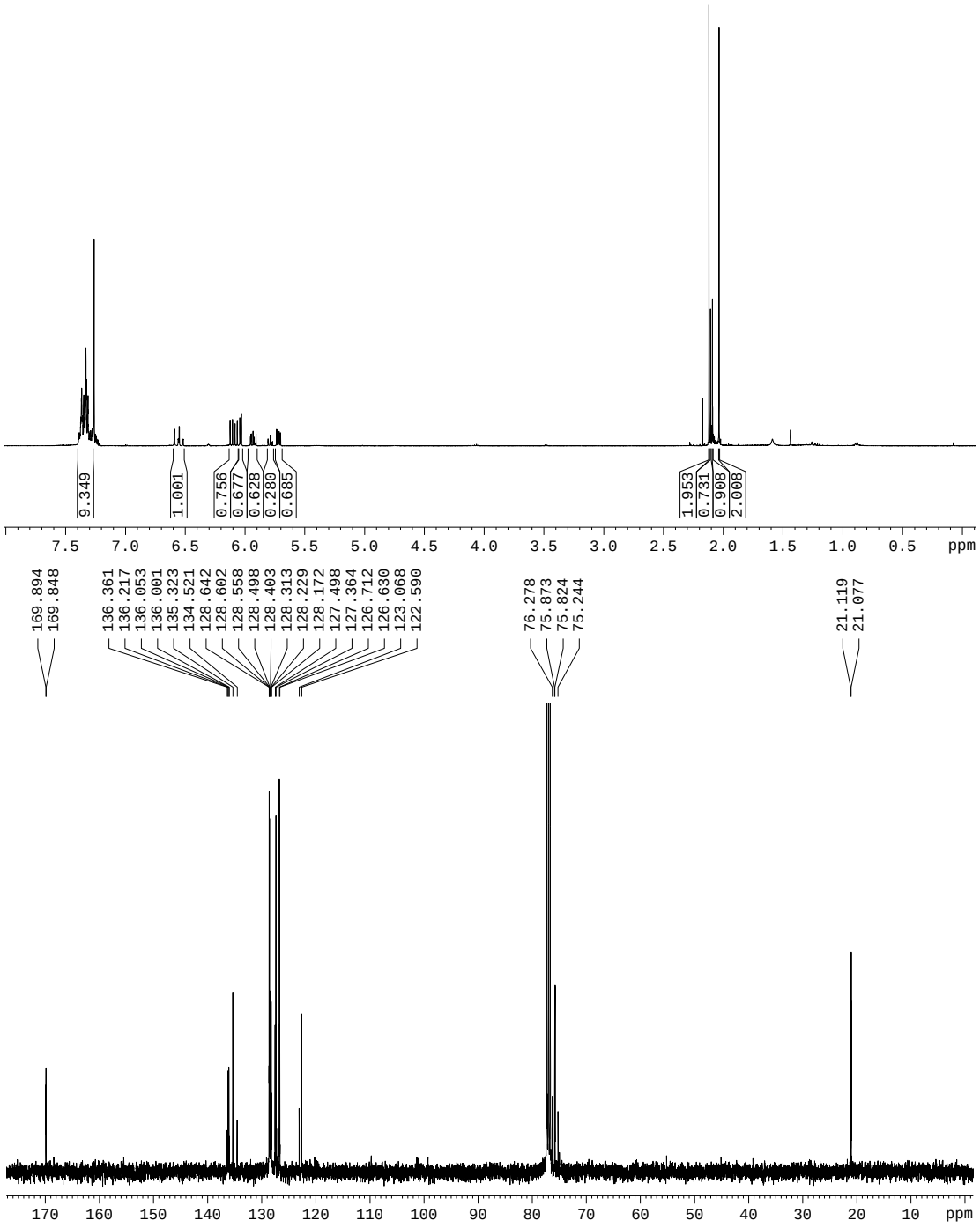

OAc

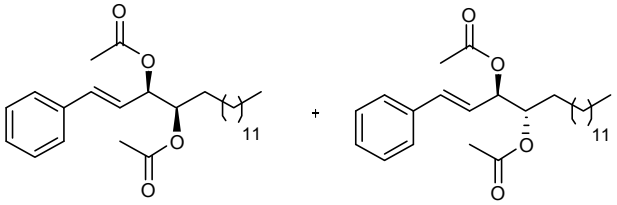
6j


6.001
1.000
0.993
2.990
3.064
3.065
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 ppm
170.386
137.331
129.097
128.197
126.693
126.516
75.525
21.483
19.384
13.868
220
200
180
160
140
120
100
80
60
40
20
0
ppm

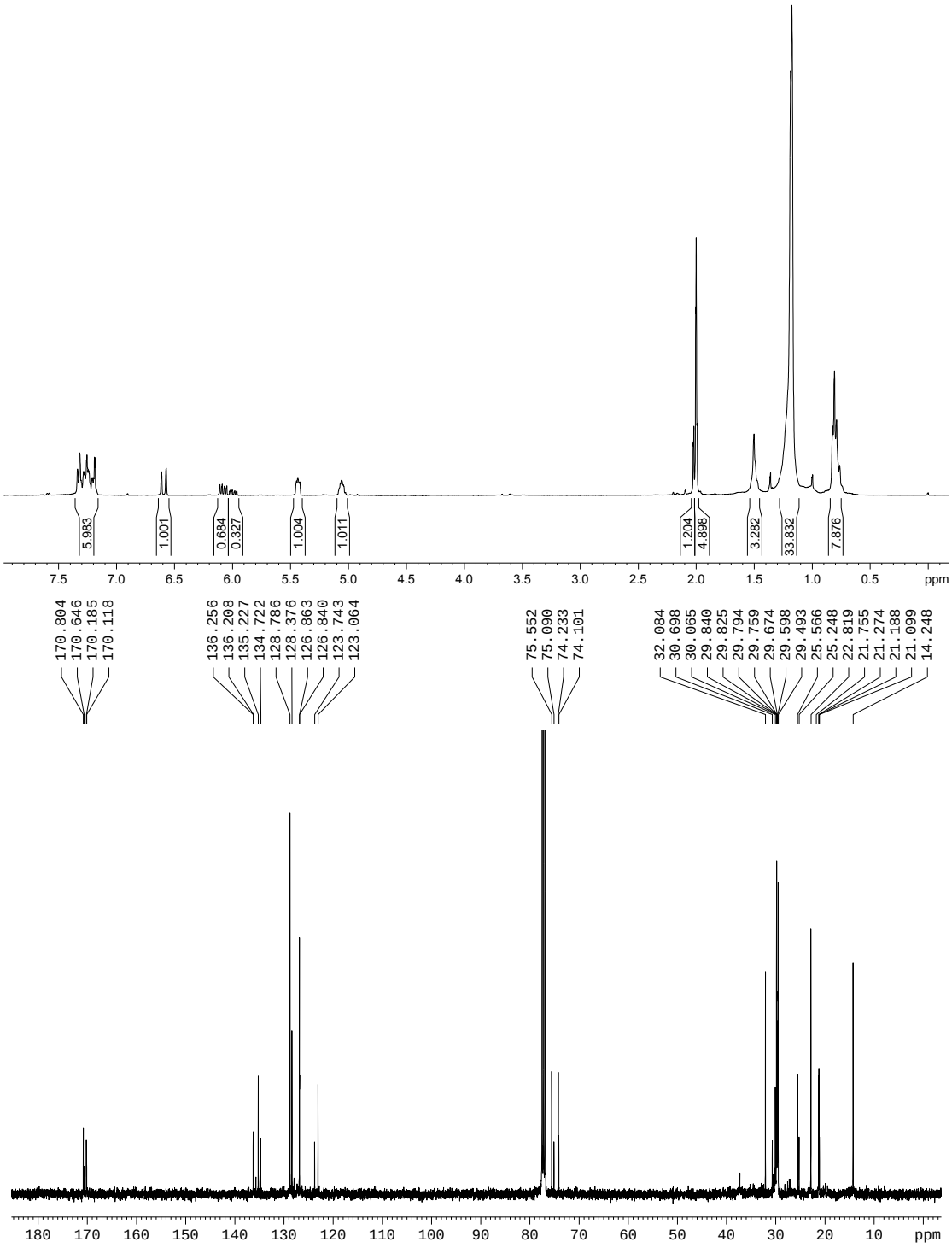

OAc
OAc
OAc
OAc

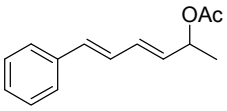
6k


9.349
1.001
0.756
0.677
0.628
0.280
0.685
1.953
0.731
0.908
2.008
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 ppm
169.894
169.848
136.361
136.217
136.053
136.001
135.323
134.521
128.642
128.602
128.558
128.498
128.403
128.313
128.229
128.172
127.498
127.364
126.712
126.630
123.068
122.590
76.278
75.873
75.824
75.244
21.119
21.077
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

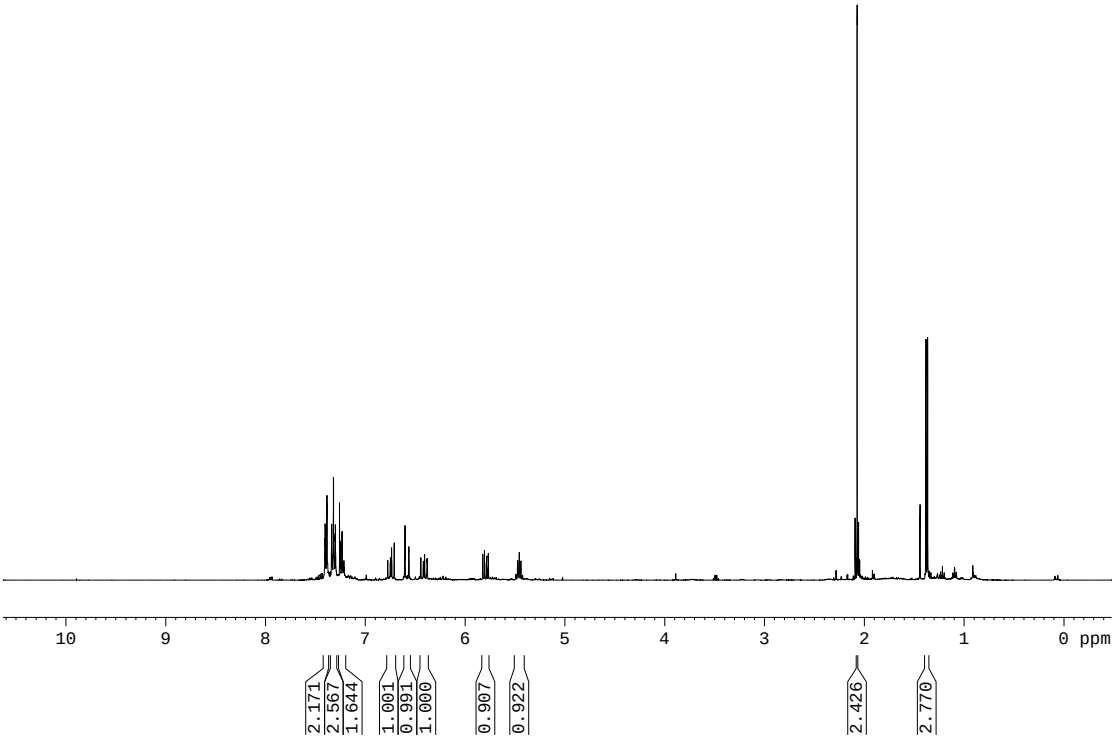


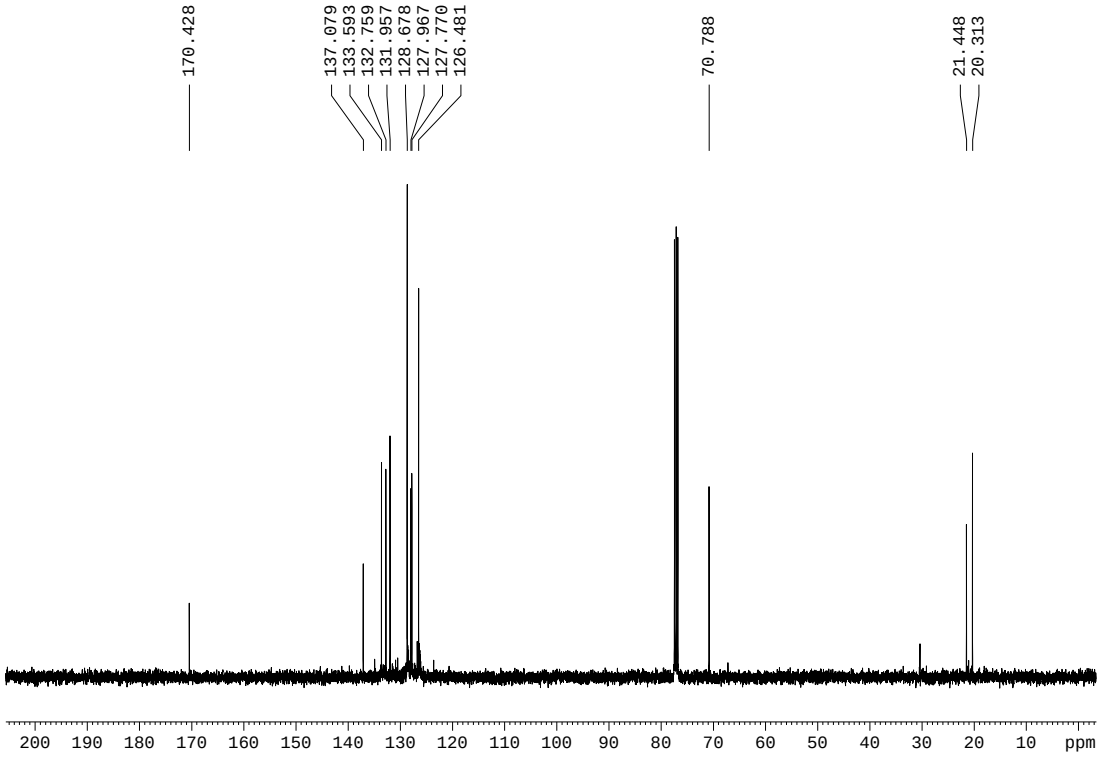
6l

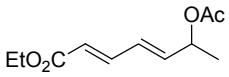

5.983
1.001
0.684
0.327
1.004
1.011
1.204
4.898
3.282
33.832
7.876
ppm
170.804
170.646
170.185
170.118
136.256
136.208
135.227
134.722
128.786
128.376
126.863
126.840
123.743
123.064
75.552
75.090
74.233
74.101
32.084
30.698
30.065
29.840
29.825
29.794
29.759
29.674
29.598
29.493
25.566
25.248
22.819
21.755
21.274
21.188
21.099
14.248
ppm


OAc

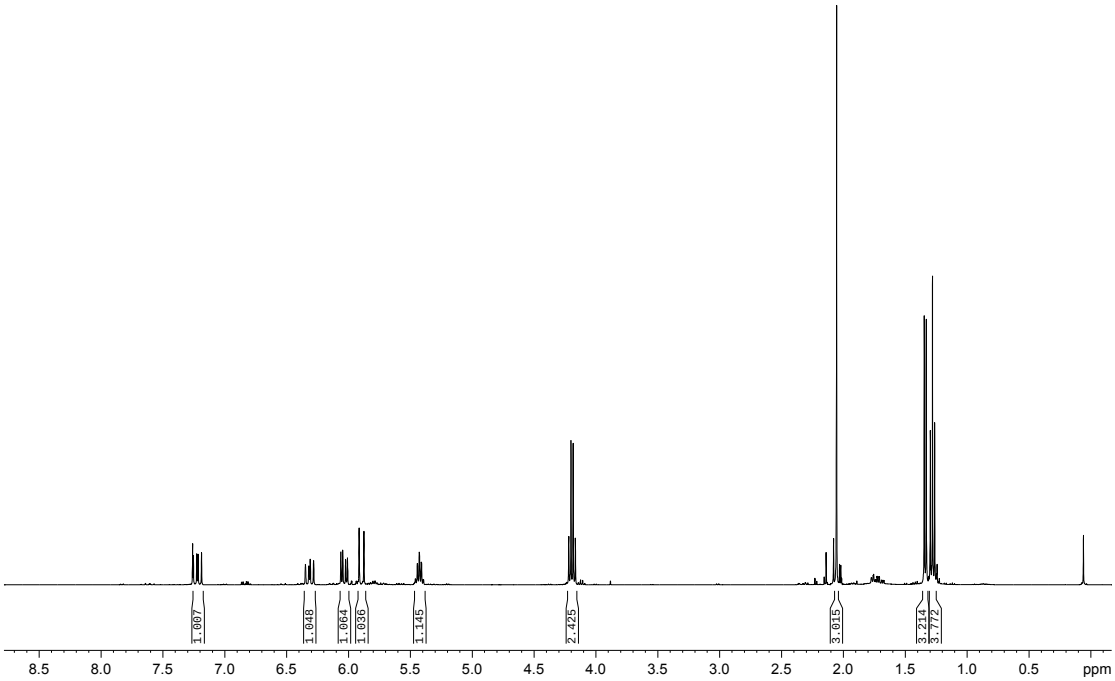
6m

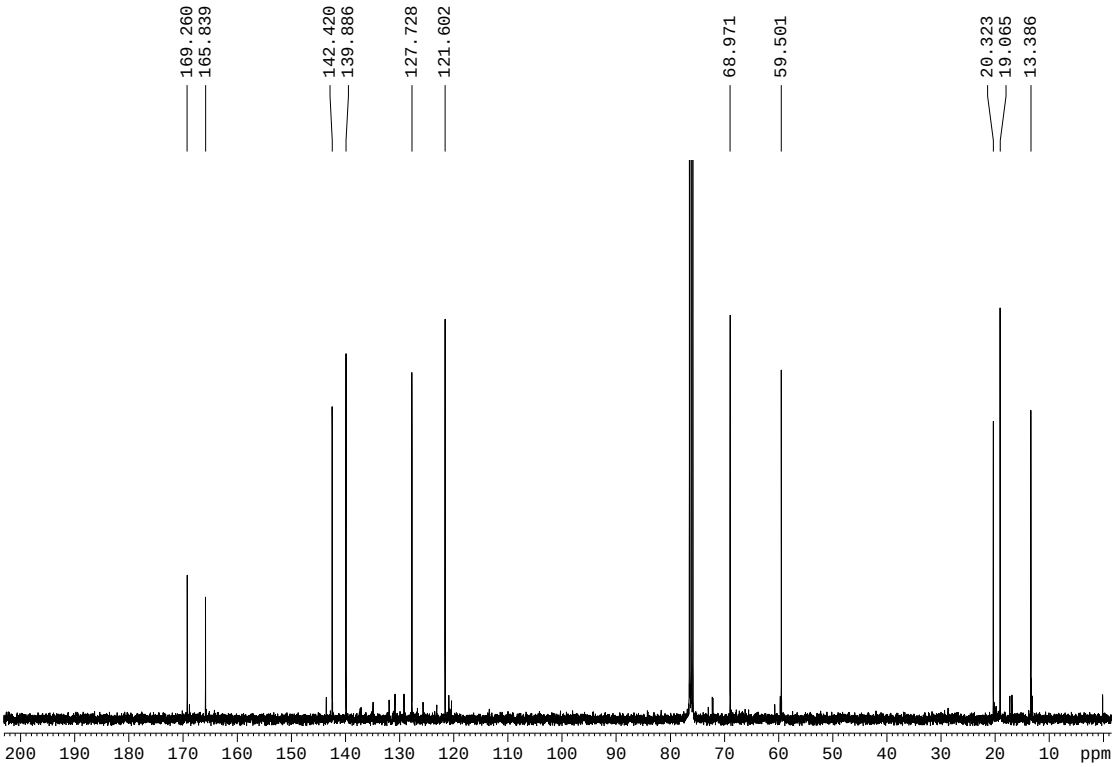

10
9
8
7
6
5
4
3
2
1
0 ppm
2.171
2.567
1.644
1.001
0.991
1.000
0.907
0.922
2.426
2.770

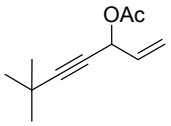

170.428
137.079
133.593
132.759
131.957
128.678
127.967
127.770
126.481
70.788
21.448
20.313
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OAc
EtO2C

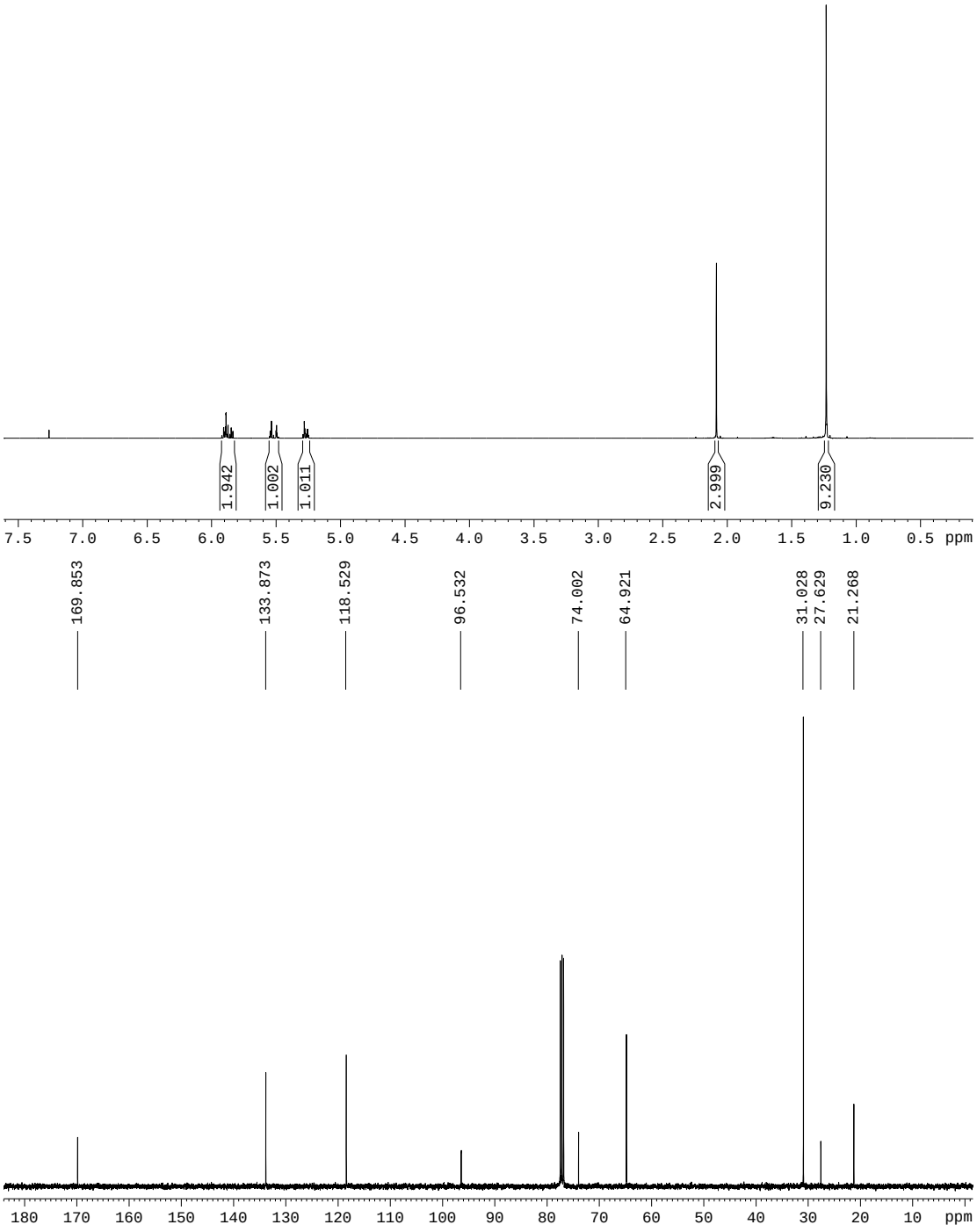
6n

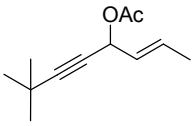

1.007
1.048
1.064
1.036
1.145
2.425
3.015
3.214
3.772
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


169.260
165.839
142.420
139.886
127.728
121.602
68.971
59.501
20.323
19.065
13.386
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

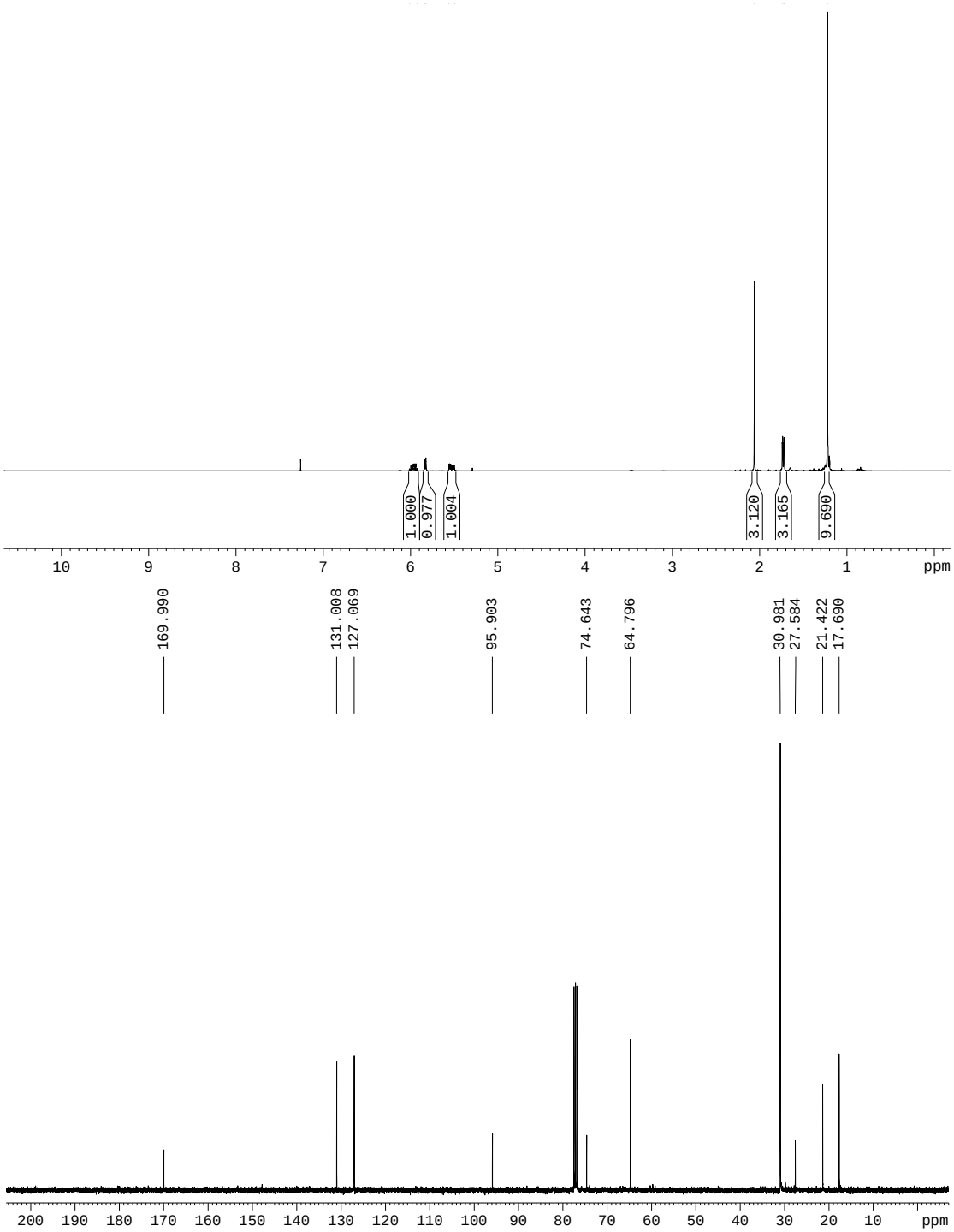

OAc

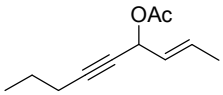
7a


1.942
1.002
1.011
2.999
9.230
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 ppm
169.853
133.873
118.529
96.532
74.002
64.921
31.028
27.629
21.268
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

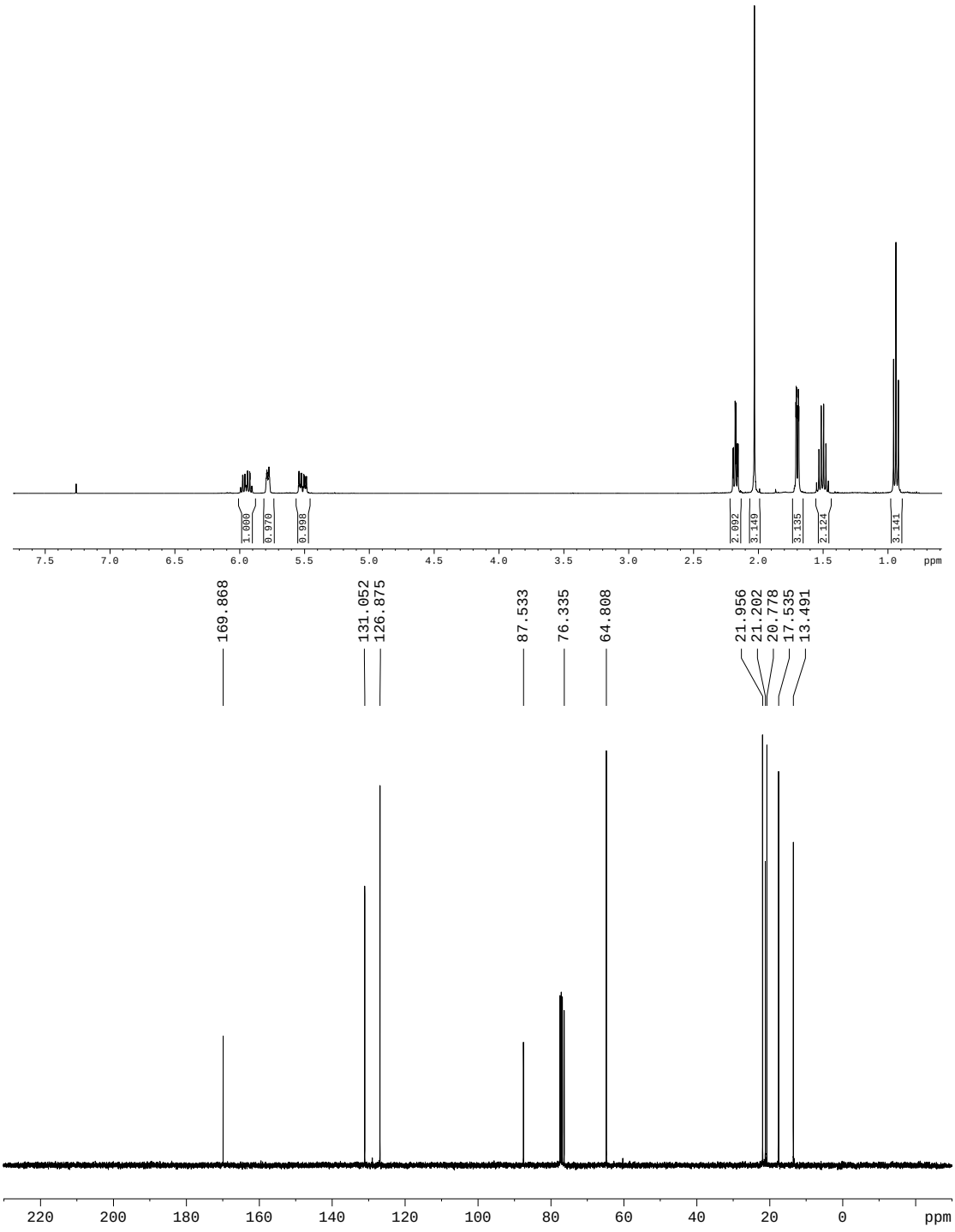

OAc

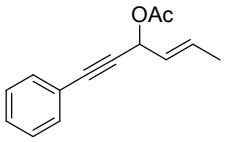
7b


1.000
0.977
1.004
3.120
3.165
9.690
10
9
8
7
6
5
4
3
2
1
ppm
169.990
131.008
127.069
95.903
74.643
64.796
30.981
27.584
21.422
17.690
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

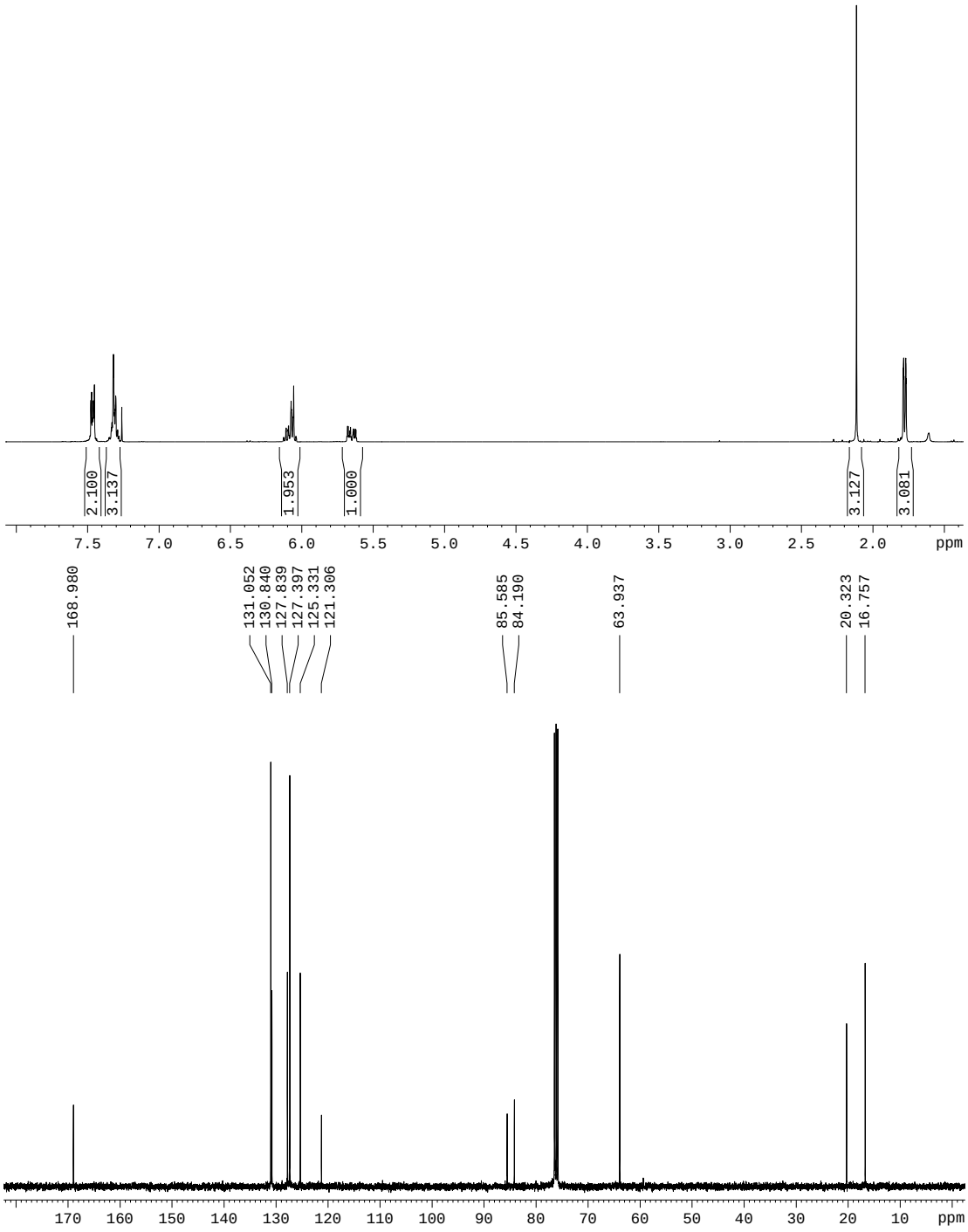

OAc

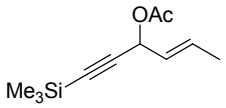
7c


1.000
0.970
0.998
2.092
3.149
3.135
2.124
3.141
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
ppm
169.868
131.052
126.875
87.533
76.335
64.808
21.956
21.202
20.778
17.535
13.491
220
200
180
160
140
120
100
80
60
40
20
0
ppm

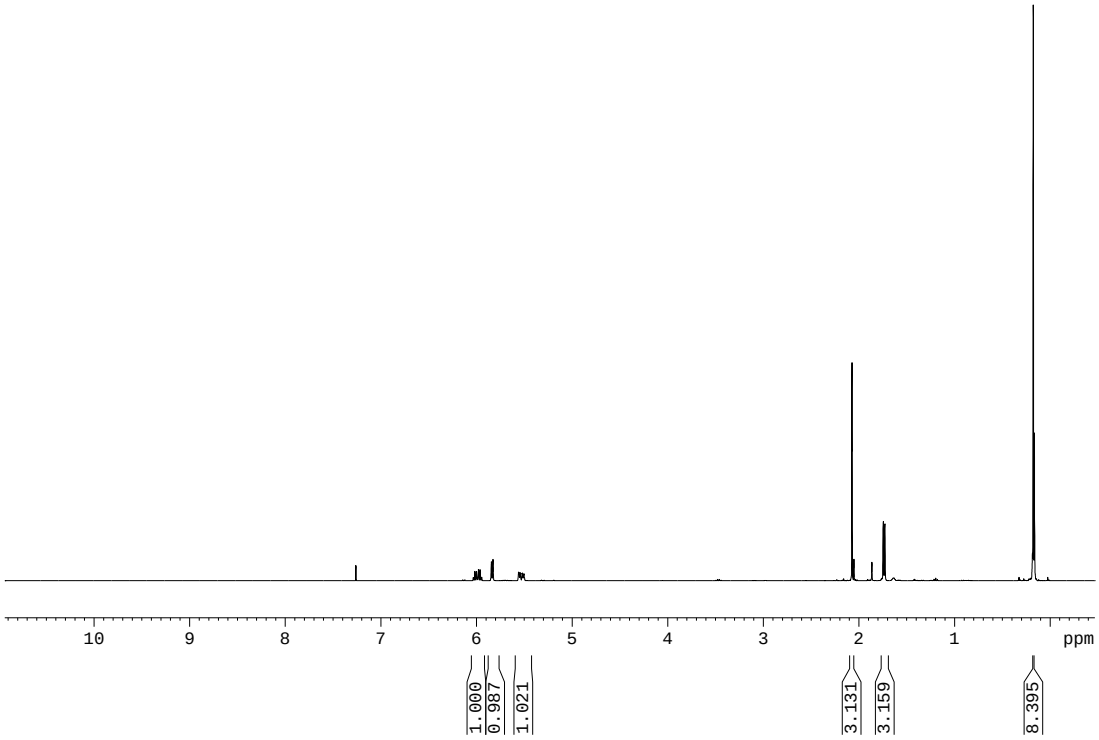

OAc

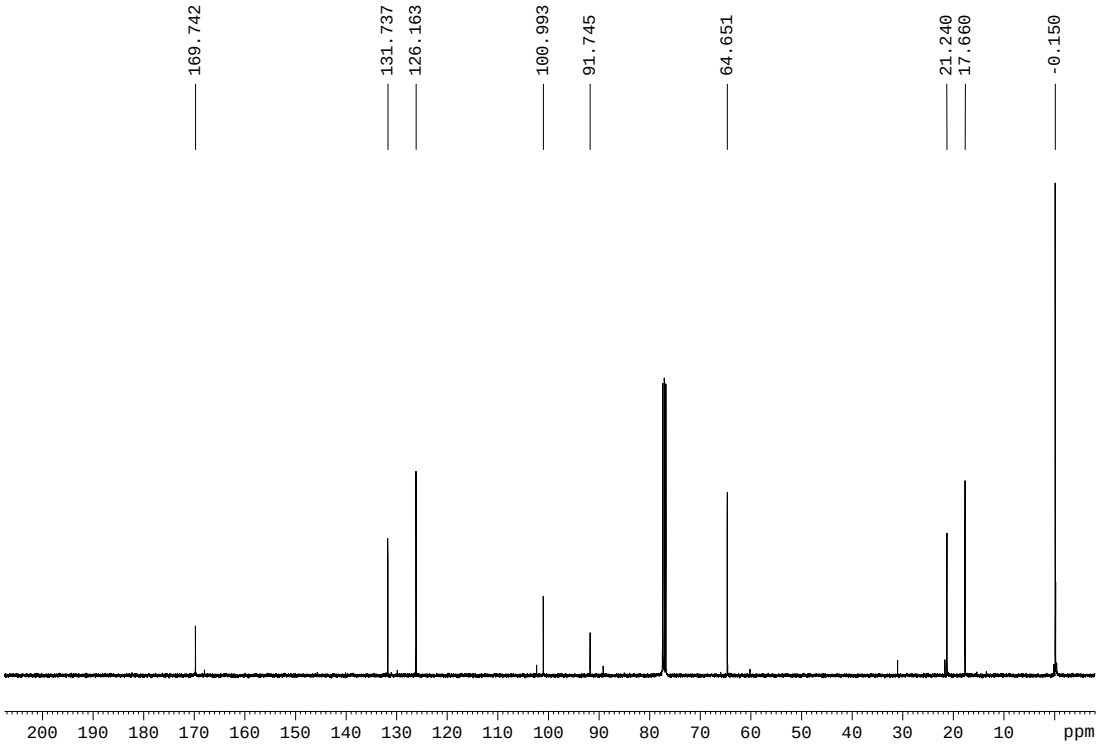
7d

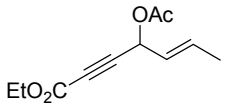

2.100
3.137
1.953
1.000
3.127
3.081
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
168.980
131.052
130.840
127.839
127.397
125.331
121.306
85.585
84.190
63.937
20.323
16.757
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OAc
Me3Si

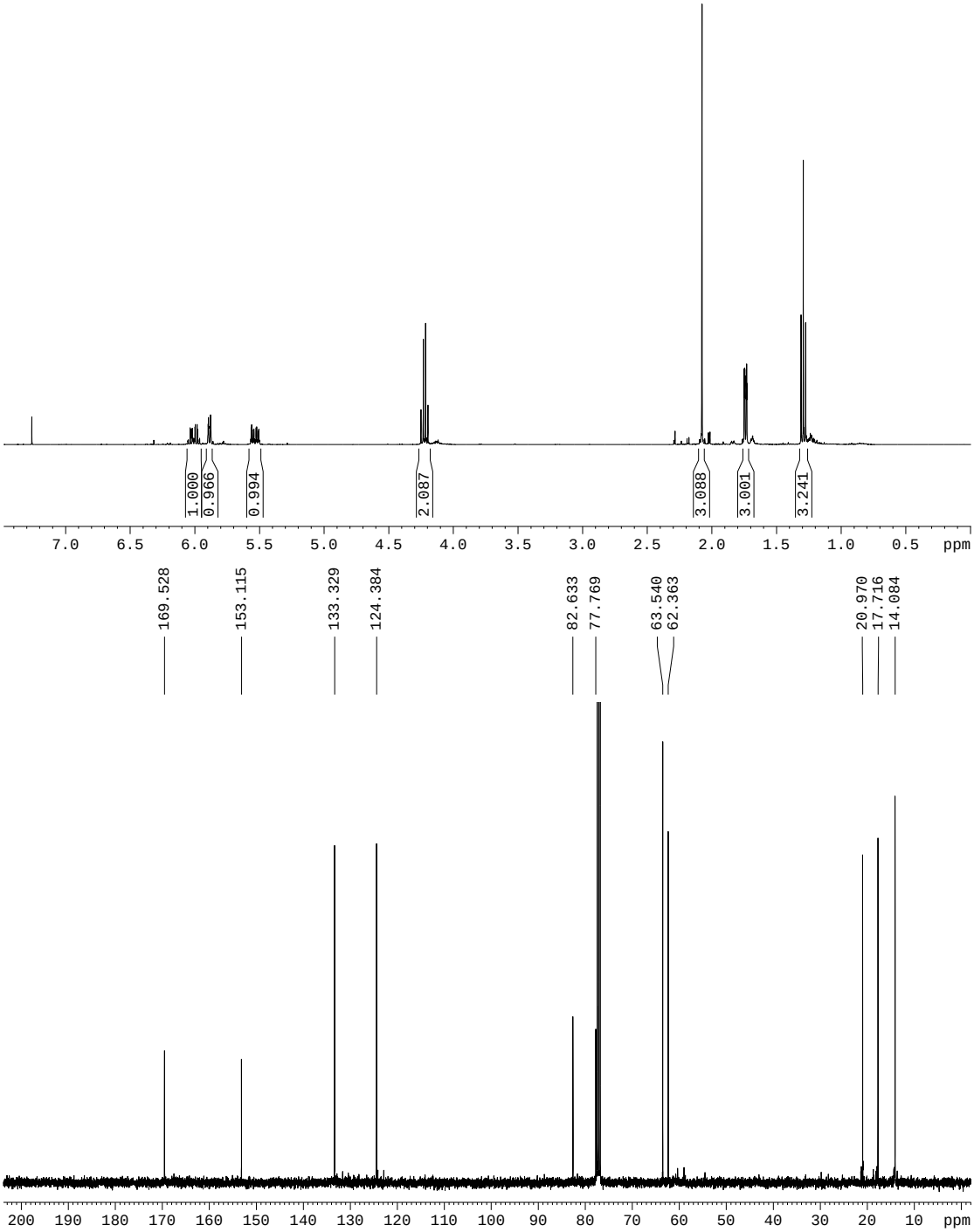
7e

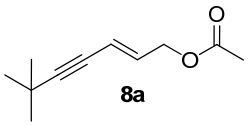

10
9
8
7
6
5
4
3
2
1
ppm
1.000
0.987
1.021
3.131
3.159
8.395


169.742
131.737
126.163
100.993
91.745
64.651
21.240
17.660
-0.150
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

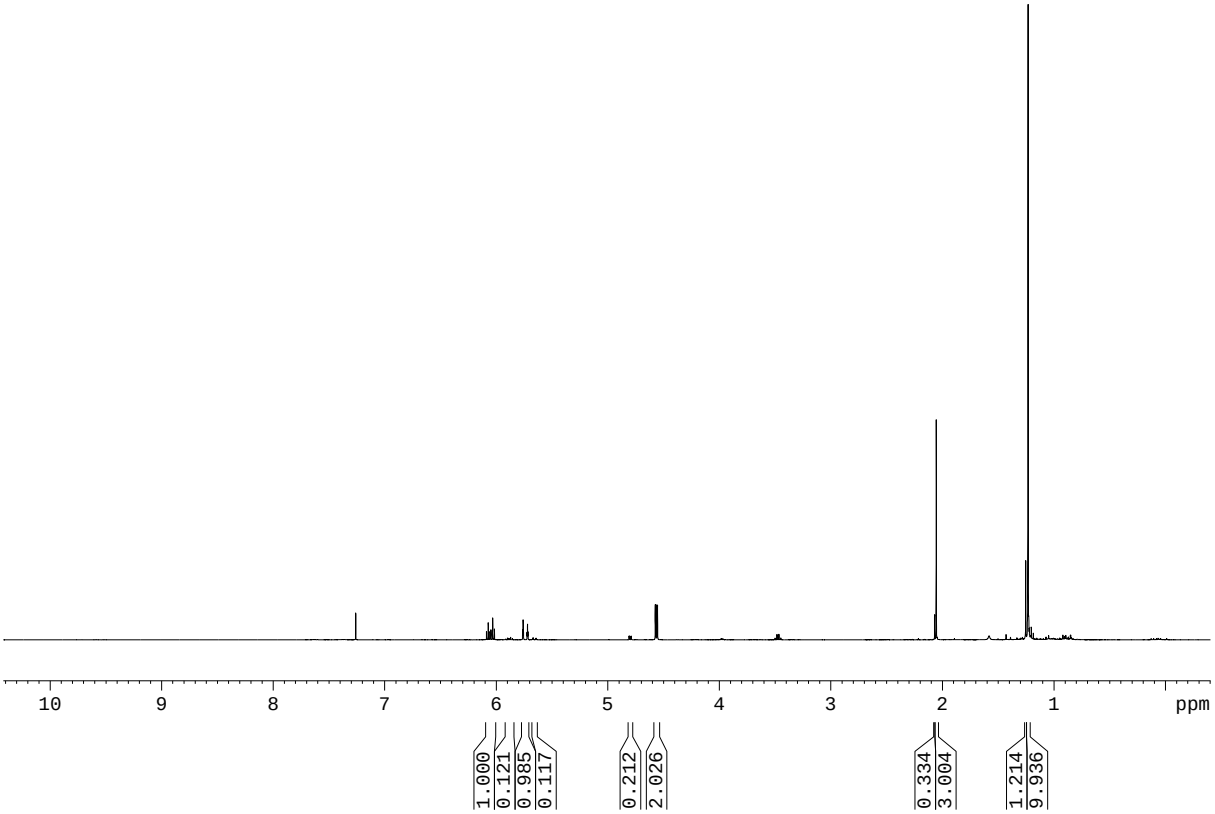

OAc
EtO2C

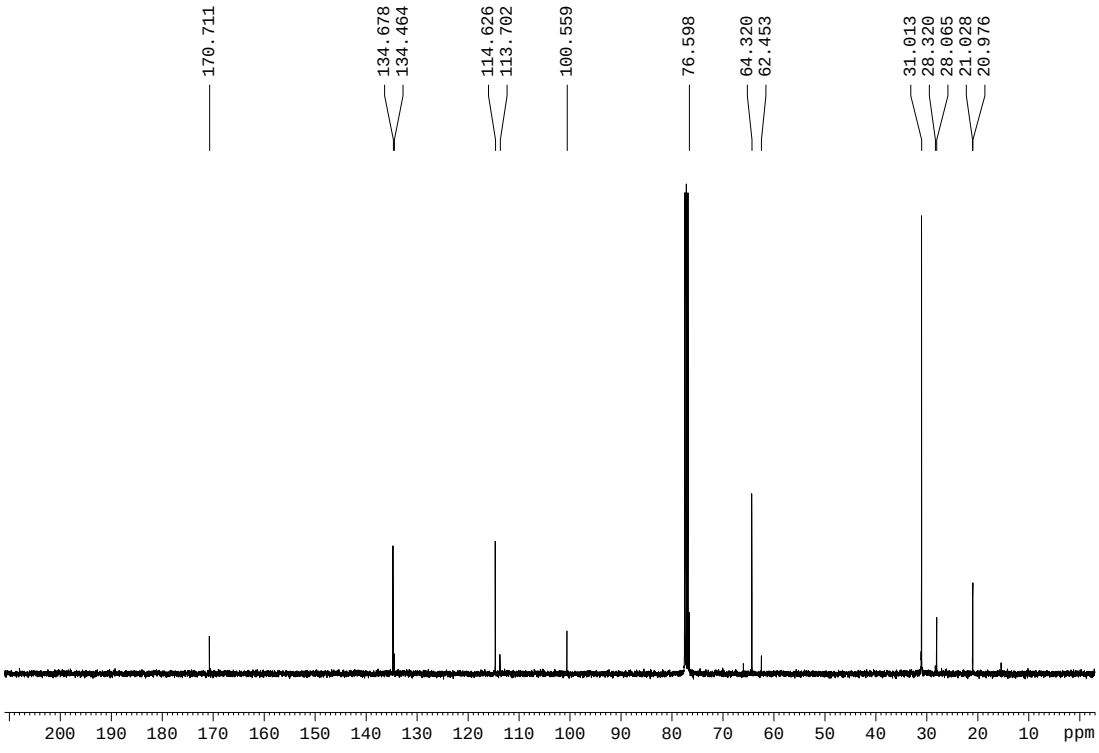
7f

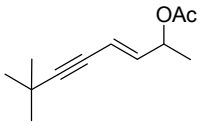

1.000
0.966
0.994
2.087
3.088
3.001
3.241
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
169.528
153.115
133.329
124.384
82.633
77.769
63.540
62.363
20.970
17.716
14.084
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



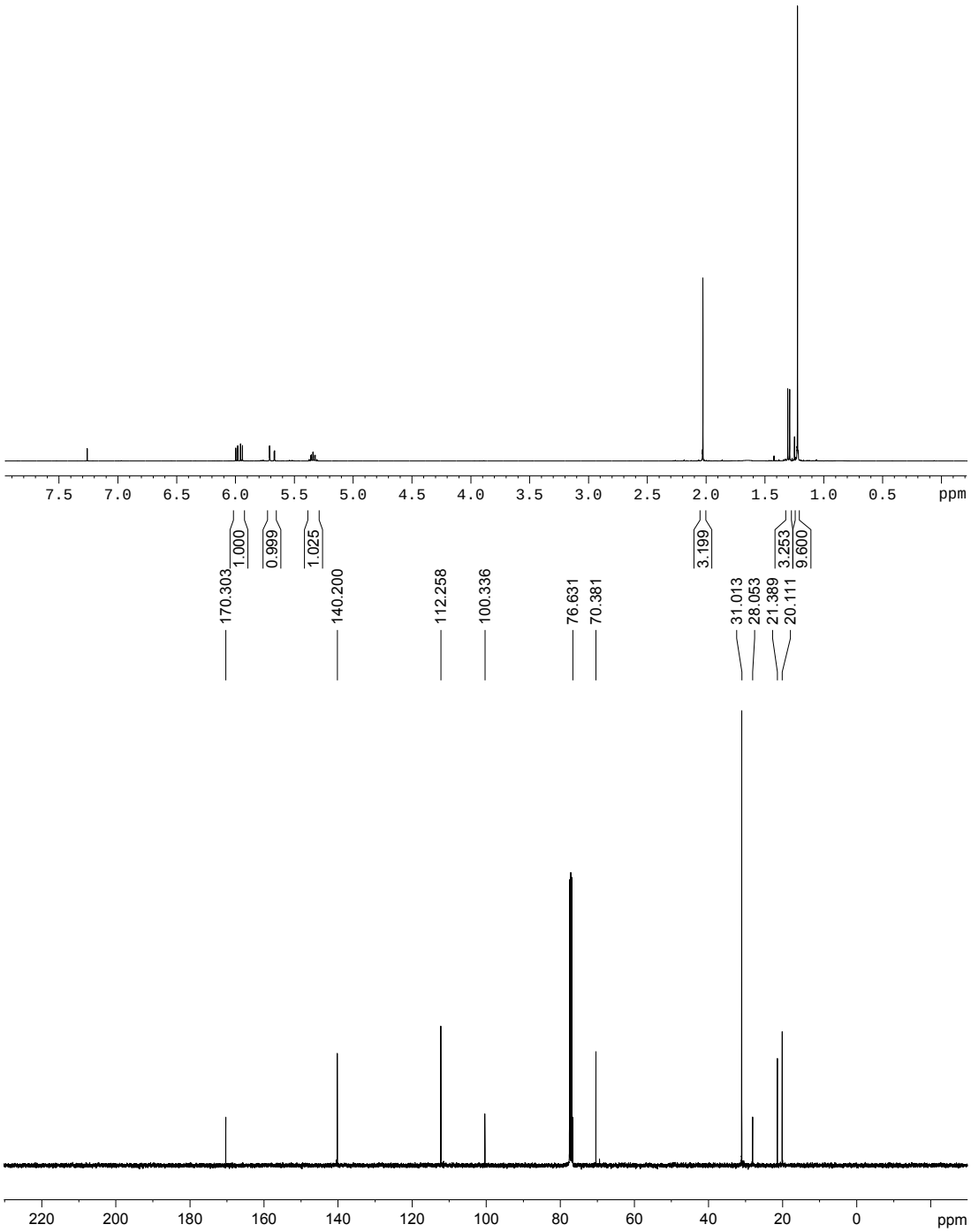
8a

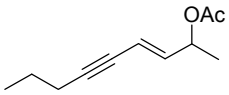

10
9
8
7
6
5
4
3
2
1
ppm
1.000
0.121
0.985
0.117
0.212
2.026
0.334
3.004
1.214
9.936


170.711
134.678
134.464
114.626
113.702
100.559
76.598
64.320
62.453
31.013
28.320
28.065
21.028
20.976
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

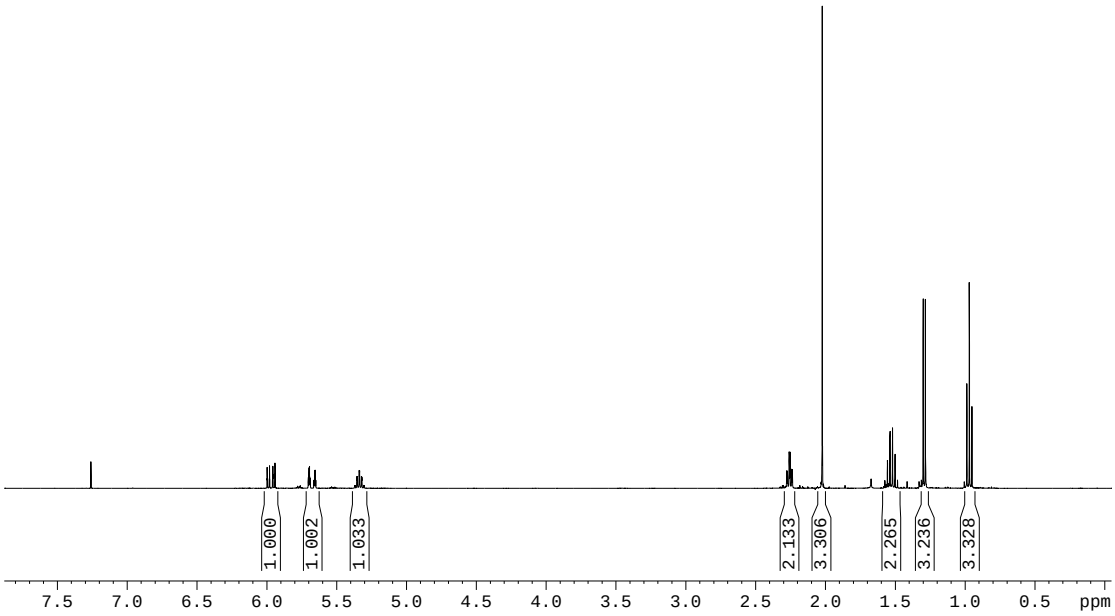

OAc

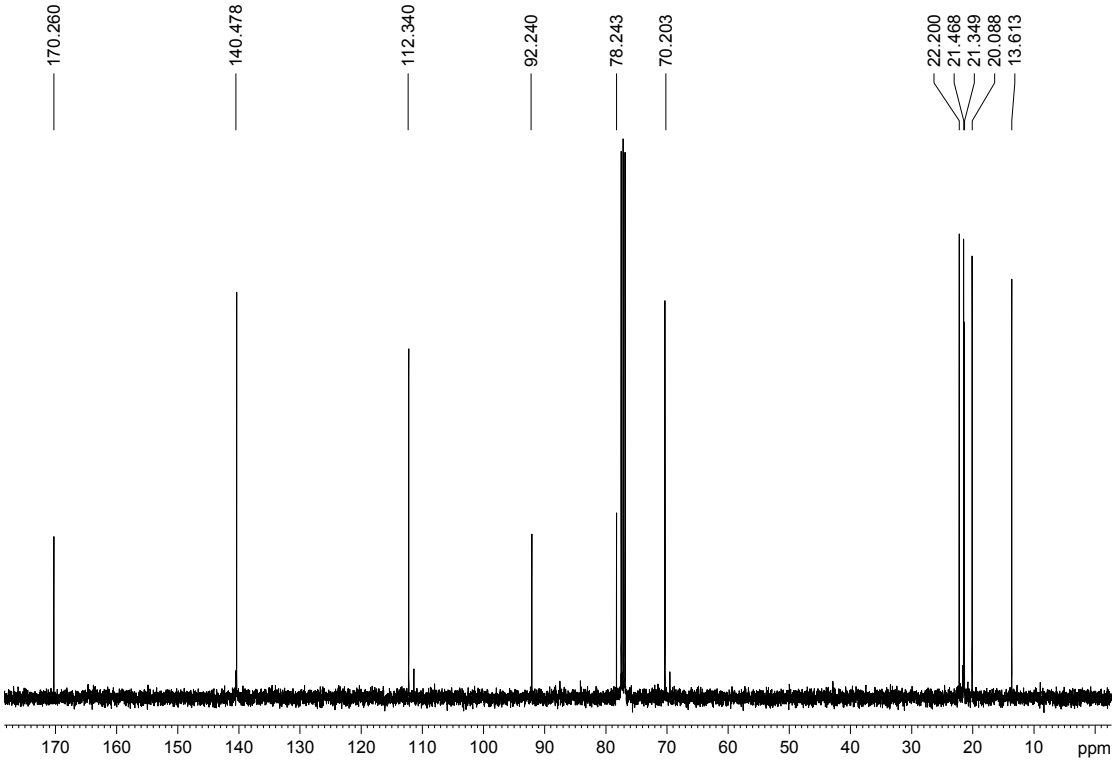
8b

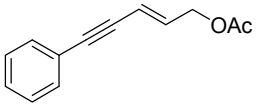

7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
0.999
1.025
3.199
3.253
9.600
170.303
140.200
112.258
100.336
76.631
70.381
31.013
28.053
21.389
20.111
220 200 180 160 140 120 100 80 60 40 20 0 ppm


OAc

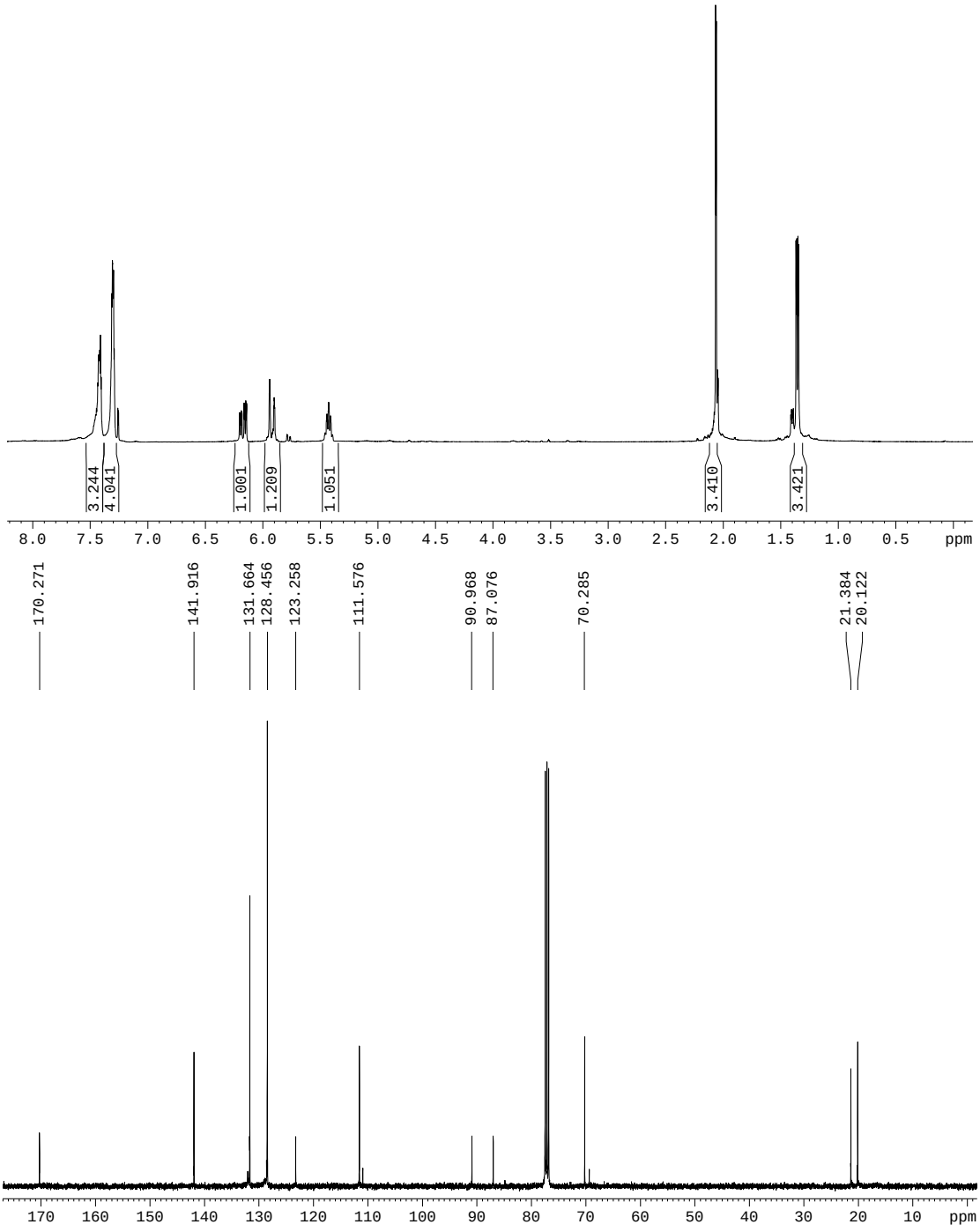
8c

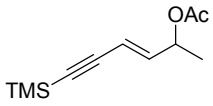

1.000
1.002
1.033
2.133
3.306
2.265
3.236
3.328
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


170.260
140.478
112.340
92.240
78.243
70.203
22.200
21.468
21.349
20.088
13.613
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

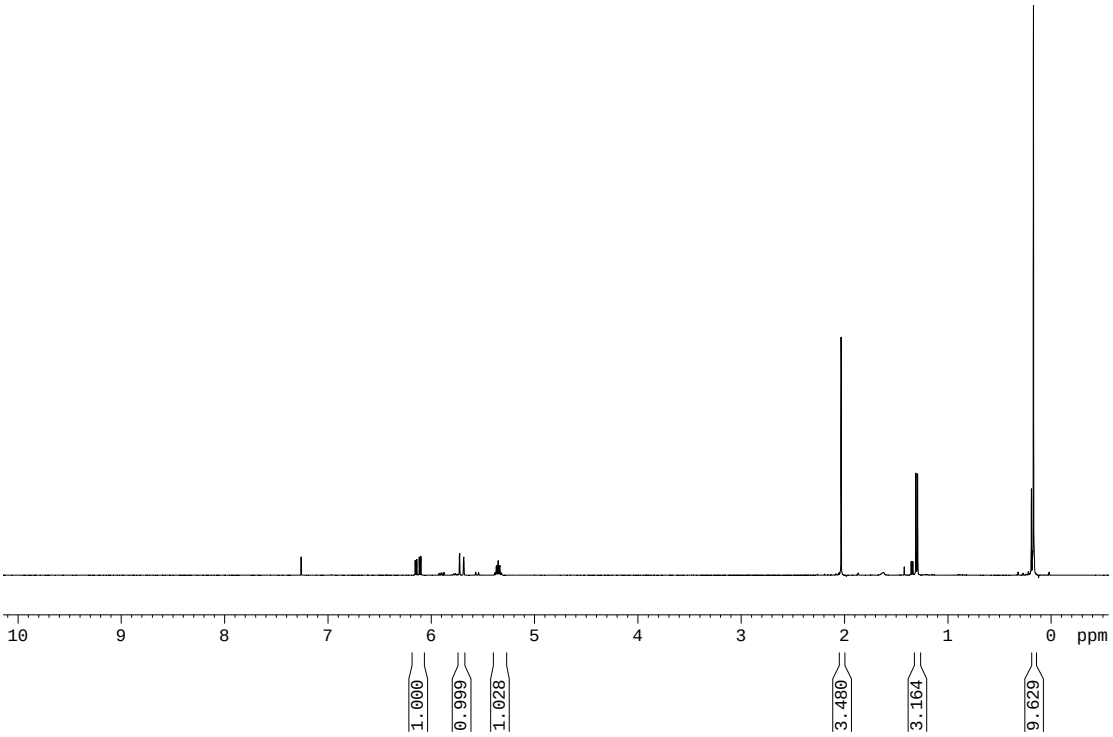

OAc

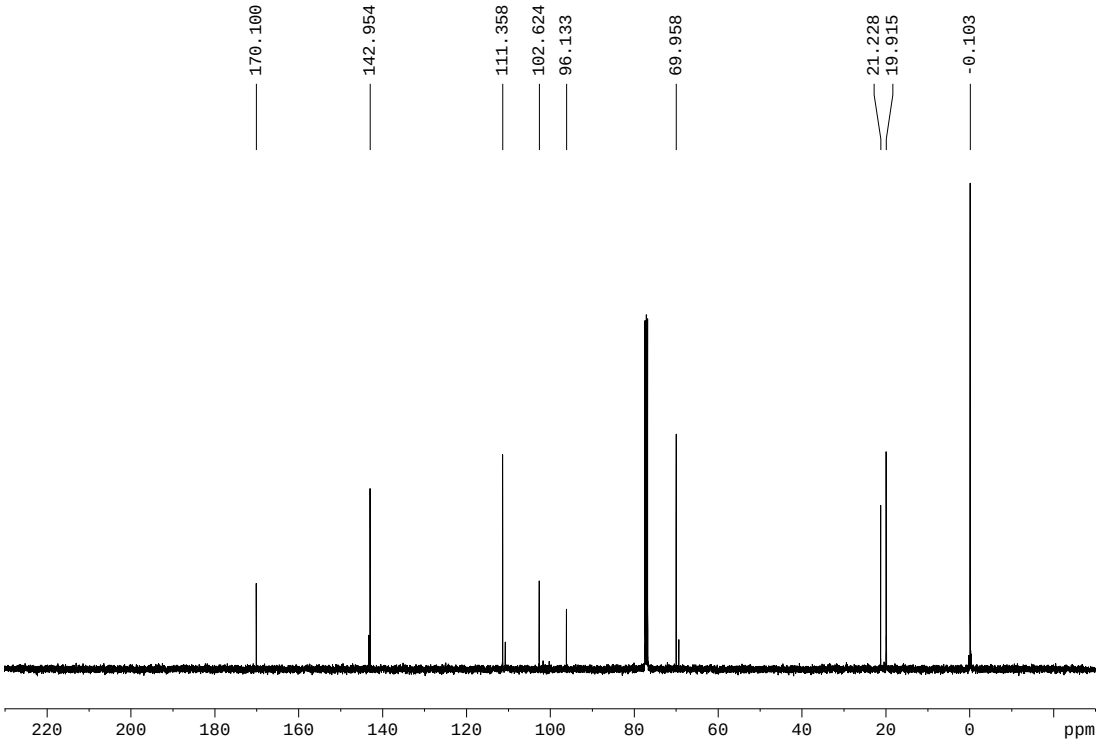
8d

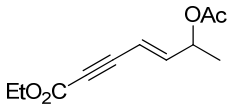

3.244
4.041
1.001
1.209
1.051
3.410
3.421
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
170.271
141.916
131.664
128.456
123.258
111.576
90.968
87.076
70.285
21.384
20.122
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


OAc
TMS

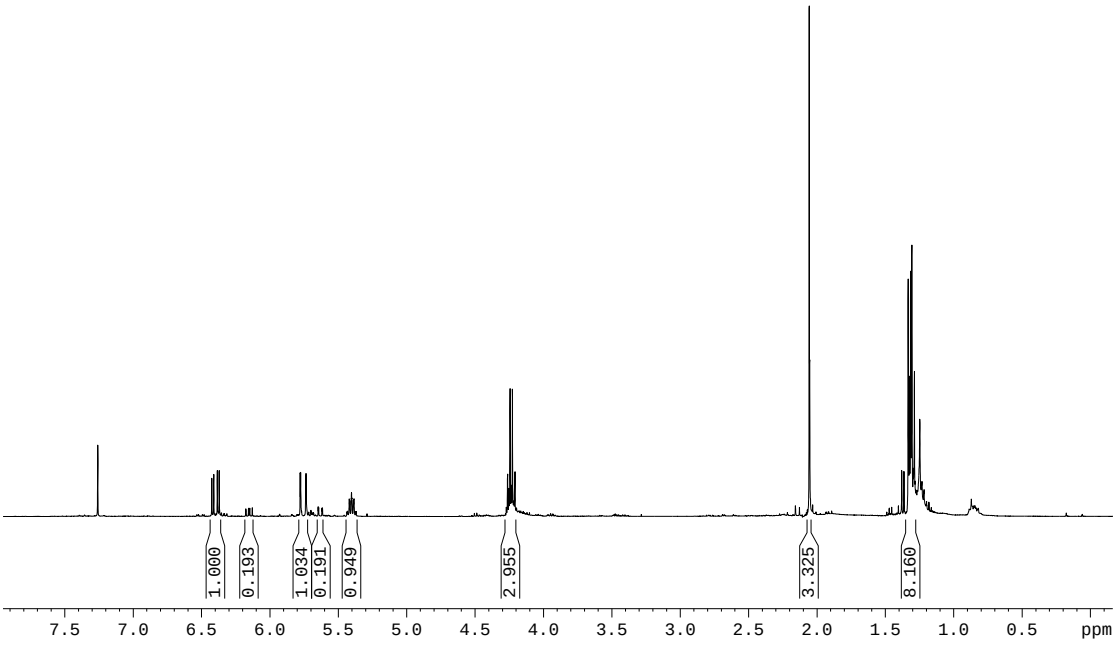
8e

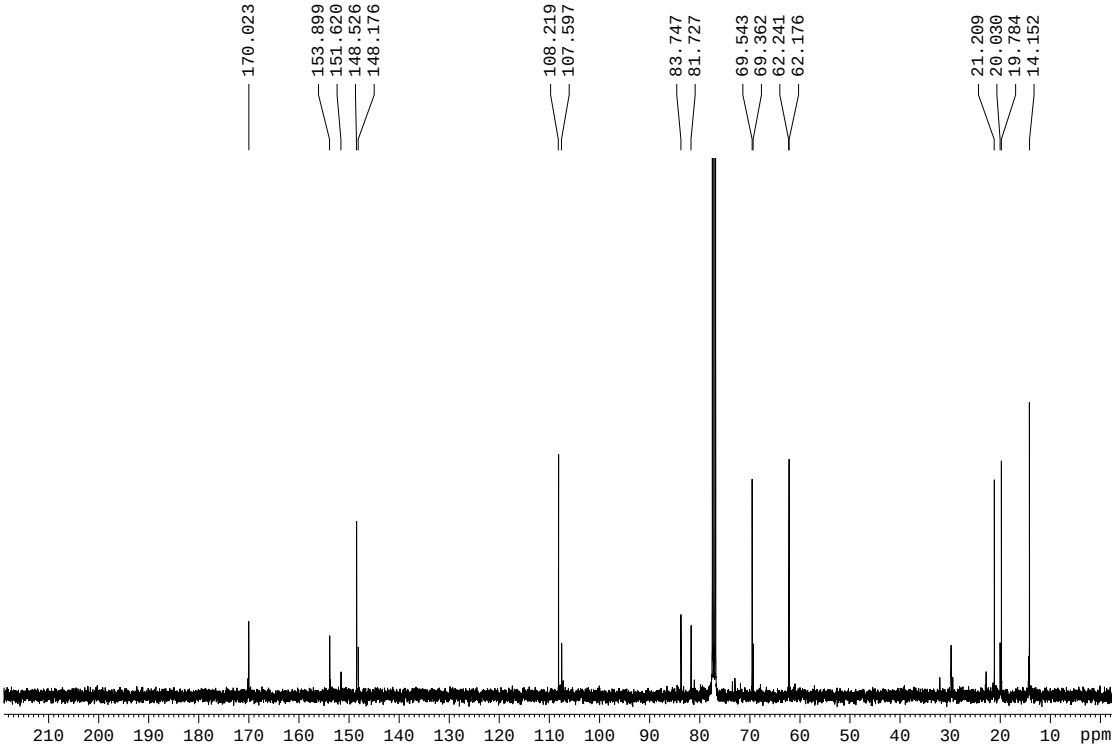

10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
0.999
1.028
3.480
3.164
9.629


170.100
142.954
111.358
102.624
96.133
69.958
21.228
19.915
-0.103
220
200
180
160
140
120
100
80
60
40
20
0
ppm


OAc
EtO2C

8f


1.000
0.193
1.034
0.191
0.949
2.955
3.325
8.160
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 ppm


170.023
153.899
151.620
148.526
148.176
108.219
107.597
83.747
81.727
69.543
69.362
62.241
62.176
21.209
20.030
19.784
14.152
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm