Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Copper(I)-Amine Metallo-Organocatalyzed Synthesis of Carbo- and Heterocyclic Systems

Supporting Information

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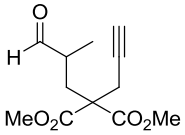
A. General information

DCE and cyclohexylamine were distilled on CaH_2. All manipulations were carried out under argon atmosphere. All signals were expressed as ppm (δ) and internally referenced to residual protio solvent signals. Coupling constants (J) are reported in Hz and refer to apparent peak multiplicities. High resolution mass spectra were performed at the University Pierre and Marie Curie (Paris). IR spectra were recorded on a JASCO FT/IR 6300. Melting points (m.p.) were determined on a Kofler block and were uncorrected.

B. Formyl alkynes substrates

All formyl alkynes substrates were prepared according to procedures already described in the literature.[1]

dimethyl 2-(2-methyl-3-oxopropyl)-2-(prop-2-ynyl)malonate (1) :

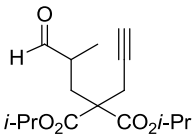


^{1}H NMR (CDCl$_3$, 300 MHz) δ 9.52 (d, *J* = 2.0 Hz, 1H), 3.71 (s, 6H), 2.85 (d, *J* = 2.7 Hz, 2H), 2.64-2.57 (dd, 1H), 2.55-2.48 (m, 1H), 2.04 (t, *J* = 2.7 Hz, 1H), 2.04-1.99 (m, 1H), 1.12 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (CDCl$_3$, 75 MHz) δ 203.1, 170.3, 78.4, 72.0, 56.0, 52.9, 42.4, 32.9, 23.9, 15.4.

The ^{1}H and ^{13}C NMR data obtained were in agreement with that reported in the literature.[1a]

di*iso*propyl 2-(2-methyl-3-oxopropyl)-2-(prop-2-ynyl)malonate (3) :



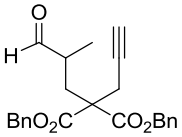
^{1}H NMR (300 MHz, C) δ 9.33 (d, *J* = 1.9 Hz, 1H), 4.99 (m, 2H), 2.95 (d, *J* = 2.7 Hz, 2H), 2.81 (dd, *J* = 14.8, 7.4 Hz, 1H), 2.49 – 2.24 (m, 1H), 2.11 (dd, *J* = 14.8, 4.2 Hz, 1H), 1.68 (dd, *J* = 3.2, 2.2 Hz, 1H), 1.05 – 0.97 (m, 9H), 0.95 (d, *J* = 6.3 Hz, 3H), 0.82 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, C$_6$D$_6$) δ 202.1, 169.5, 79.1, 72.1, 69.3, 69.3, 69.2, 56.3, 56.3, 42.5, 35.9, 35.7, 33.0, 24.0, 23.9, 21.3, 19.5, 15.4.

HRMS calculated for $C_{16}H_{24}O_6Na$: 335.14651 ; found : 335.14668.

IR (neat, cm^{-1}) 3295, 2978, 1725, 1276, 1197, 1102.

dibenzyl 2-(2-methyl-3-oxopropyl)-2-(prop-2-ynyl)malonate (5) :



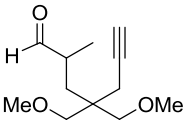
^{1}H NMR (300 MHz, C$_6$D$_6$) δ 8,99 (d, *J* = 1.9 Hz, 1H), 6.99 – 6.76 (m, 18H), 4.72 (d, *J* = 12.4 Hz, 4H), 2.73 (d, *J* = 2.7 Hz, 2H), 2.63 – 2.49 (m, 1H), 2.19 – 2.05 (m, 1H), 1.98 – 1.85 (m, 1H), 1.48 – 1.40 (m, 1H), 0.50 (d, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 199.6, 170.9, 170.8, 149.4, 135.3, 135.2, 128.5, 128.4, 128.3, 128.1, 110.8, 67.6, 67.5, 58.2, 56.7, 41.0, 40.2, 21.6.

HRMS calculated for $C_{24}H_{24}O_5Na$: 415.15160 ; found : 415.15207.

IR (neat, cm^{-1}) 3297, 2980, 1725, 1289, 1202.

4,4-bis(methoxymethyl)-2-methylhept-6-ynal (7) :



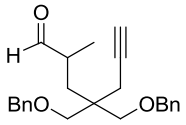
^{1}H NMR (CDCl$_3$, 300 MHz) δ 9.43 (d, *J* = 3,6 Hz, 1H), 3.27-3.17 (m, 10H), 2.58-2.45 (m, 1H), 2.27-2.25 (d, *J* = 2.7 Hz, 2H), 1.99 (m,1H), 2.00-1.92 (m, 1H), 1.42-1.36 (dd, *J* = 14.6 Hz, *J* = 2.8 Hz, 1H), 1.07 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (CDCl$_3$, 75 MHz) δ 204.7, 80.7, 74.6, 74.0, 70.5, 59.0, 58.9, 41.9, 40.4, 33.8, 22.8, 16.7.

[1] (a) J. T. Binder, B. Crone, T. T. Haug, H. Menz, S. F. Kirsch, Org. Lett., 2008, **10**, 1025; (b) B. Montaignac, M. R. Vitale, V. Michelet, V. Ratovelomanana-Vidal, *Org. Lett.*, 2010**, 12**, 2582; (c) B. Montaignac, M. R. Vitale, V. Ratovelomanana-Vidal, V. Michelet, *J. Org. Chem.*, 2010, **75**, 8322; (d) B. Montaignac, M. R. Vitale, V. Ratovelomanana-Vidal, V. Michelet, *Eur. J. Org. Chem.*, **2011**, 3723

The ^{1}H and ^{13}C NMR data obtained were in agreement with that reported in the literature.[1a]

4,4-bis(benzyloxymethyl)-2-methylhept-6-ynal (9) :

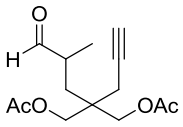


^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.42 (d, *J* = 3.5 Hz, 1H), 7.36-7.26 (m, 10H), 4.49-4.39 (m, 4H), 3.43-3.33 (m, 4H), 2.56-2.49 (m, 1H), 2.34 (d, *J* = 2.7 Hz, 2H), 2.03 (dd, *J* = 14.5 Hz, *J* = 9.0 Hz, 1H), 1.96 (t, *J* = 2.7 Hz, 1H), 1.45 (dd, *J* = 14.5 Hz, *J* = 2.9 Hz, 1H), 1.06 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 204.7, 138.3, 128.3, 127.1, 80.9, 73.1, 72.0, 71.6, 70.7, 41.9, 41.8, 33.6, 22.9, 16.7.

The ^{1}H and ^{13}C NMR data obtained were in agreement with that reported in the literature.[1a]

2-(2-methyl-3-oxopropyl)-2-(prop-2-ynyl)propane-1,3-diyl diacetate (11) :



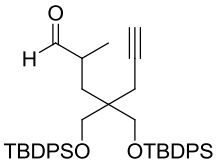
^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.56 (d, *J* = 2.6 Hz, 1H), 4.09 – 3.90 (m, 4H), 2.61 – 2.43 (m, 1H), 2.29 (d, *J* = 2.7 Hz, 2H), 2.13 (dd, *J* = 14.9, 7.8 Hz, 1H), 2.09 – 2.03 (m, 7H), 1.40 (dd, *J* = 14.9, 3.7 Hz, 1H), 1.15 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 203.5, 170.5(2C), 78.9, 72.0, 65.5, 65.4, 41.6, 39.8, 32.4, 22.7, 20.8(2C), 16.4.

HRMS calculated for $C_{14}H_{20}O_5Na$: 291.12029 ; found : 291.12030.

IR (neat, cm^{-1}) 3296, 1741, 1226, 1040.

4,4-bis((*tert*-butyldiphenylsilyloxy)methyl)-2-methylhept-6-ynal (13) :



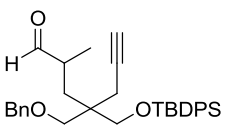
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.38 (d, *J* = 2.8 Hz, 1H), 7.72 – 7.42 (m, 8H), 7.38 – 7.20 (m, 12H), 3.63 – 3.36 (m, 4H), 2.40 – 2.11 (m, 1H), 2.21 (dd, *J* = 7.9, 2.7 Hz, 2H), 1.93 (dd, *J* = 14.6, 7.7 Hz, 1H), 1.78 (t, *J* = 2.6 Hz, 1H), 1.34 (dd, *J* = 14.7, 4.1 Hz, 1H), 0.97 (s, 18H), 0.92 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 204.7, 135.7(8C), 133.1(4C), 129.7(4C), 127.6(8C), 81.1, 70.1, 65.3, 65.2, 43.7(2C), 41.7, 32.4, 26.9(6C), 22.0, 19.3, 16.3.

HRMS calculated for $C_{42}H_{52}O_3NaSi_2$: 683.33472 ; found : 683.33441.

IR (neat, cm^{-1}) 3300, 2929, 1725, 1426, 1110, 1089.

4-(benzyloxymethyl)-4-((tert-butyldiphenylsilyloxy)methyl)-2-methylhept-6-ynal (15) mixture of two diastereoisomers (d.r. = 1.2:1) :



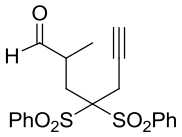
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.46 (d, *J* = 3.3 Hz, 1H), 9.43 (d, *J* = 3.5 Hz, 1H), 7.68 (m, 8H), 7.54 – 7.07 (m, 22H), 5.32 (s, 2H), 4.57 – 4.27 (m, 4H), 3.79 – 3.17 (m, 2H), 3.49 (d, *J* = 9.0 Hz, 2H), 3.31 (d, *J* = 9.0 Hz, 2H), 2.59 – 2.43 (m, 2H), 2.46 – 2.25 (m, 4H), 2.14 – 1.86 (m, 4H), 1.53 – 1.34 (m, 2H), 1.07 (m, 24H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 204.8, 138.2, 135.7, 133.2, 129.6, 128.3, 127.6, 127.5, 80.9, 80.8, 72.9, 71.2, 70.8, 65.2, 64.6, 53.4, 42.8, 41.9, 41.8, 32.9, 32.5, 26.8, 23.0, 21.5, 19.3, 16.5, 16.4.

HRMS calculated for $C_{33}H_{40}O_3SiNa$, CH_3OH : 567.29011 ; found : 567.28996.

IR (neat, cm^{-1}) 3299, 1721, 1272, 1260, 1114, 1090.

2-methyl-4,4-bis(phenylsulfonyl)hept-6-ynal (17) :



^{1}H NMR (300 MHz, $CDCl_3$) δ 9.69 (d, *J* = 1.4 Hz, 1H), 8.26 – 7.91 (m, 4H), 7.79 – 7.65 (m, 2H), 7.61-7.55 (m, 4H), 3.58 – 3.29 (m, 1H), 3.25 – 2.96 (m, 3H), 2.24 – 2.08 (m, 1H), 2.01 – 1.90 (m, 1H), 1.26 (d, *J* = 7.5 Hz, 3H).

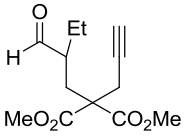
^{13}C NMR (75 MHz, $CDCl_3$) δ 202.1, 136.5, 135.0, 131.6, 131.4, 128.9, 128.8, 88.4, 75.6, 74.7, 41.5, 29.9, 22.3, 16.8.

HRMS calculated for $C_{18}H_{20}O_5Na$: 427.06444 ; found : 427.06431.

IR (neat, cm^{-1}) 3289, 1721, 1330, 1314, 1148.

mp 108-109°C

Dimethyl 2-(2-formylbutyl)-2-(prop-2-ynyl)malonate (19) :



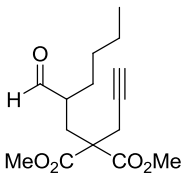
^{1}H NMR (300 MHz, C_6D_6) δ 9.25 (d, *J* = 2.5 Hz, 1H), 3.33 (s, 3H), 3.31 (s, 3H) 3.04 – 2.79 (m, 2H), 2.66 (dd, *J* = 14.6, 9.1 Hz, 1H), 2.36 – 2.24 (m, 1H), 2.21 (dd, *J* = 14.6, 2.2 Hz, 1H), 1.74 (t, *J* = 2.7 Hz, 1H), 1.43 – 1.24 (m, 1H), 1.24 – 1.05 (m, 1H), 0.68 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, C_6D_6) δ 202.2, 170.3, 170.3, 78.9, 72.3, 56.3, 52.4, 49.1, 31.1, 24.2, 23.6, 11.0.

HRMS calculated for $C_{13}H_{18}O_5Na$: 277.10464 ; found : 277.10488.

IR (neat, cm^{-1}) 3289, 2962, 1737, 1434, 1280, 1260.

dimethyl 2-(2-formylhexyl)-2-(prop-2-ynyl)malonate (21) :



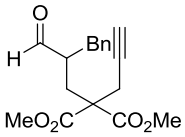
^{1}H NMR (300 MHz, C_6D_6) δ 9.29 (d, *J* = 2.7 Hz, 1H), 3.34 (s, 3H), 3.32 (s, 3H), 2.94 (dd, *J* = 5.1, 2.7 Hz, 2H), 2.69 (dd, *J* = 14.6, 9.3 Hz, 1H), 2.49 – 2.32 (m, 1H), 2.25 (d, *J* = 14.7 Hz, 1H), 1.43 – 1.22 (m, 2H), 1.24 – 0.97 (m, 5H), 0.83 – 0.63 (m, 3H).

^{13}C NMR (75 MHz, C_6D_6) δ 200.4, 168.4, 168.4, 77.0, 70.4, 54.4, 50.5, 45.9, 29.7, 28.5, 27.0, 22.3, 20.9, 12.0.

HRMS calculated for $C_{15}H_{22}O_5Na$: 305.13594 ; found : 305.13568.

IR (neat, cm^{-1}) 3299, 2958, 2929, 1734, 1437, 1276, 1261, 1203.

Dimethyl 2-(2-benzyl-3-oxopropyl)-2-(prop-2-ynyl)malonate (23) :



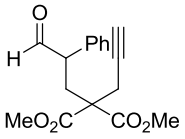
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.48 (d, *J* = 2.4 Hz, 1H), 7.32 – 6.90 (m, 5H), 3.56 (d, *J* = 12.8 Hz, 6H), 2.84 (dd, *J* = 12.2, 6.0 Hz, 1H), 2.76 – 2.56 (m, 4H), 2.47 (dd, *J* = 14.8, 8.9 Hz, 1H), 2.06 (dd, *J* = 14.9, 1.8 Hz, 1H), 1.84 (t, *J* = 2.7 Hz, 1H).

^{13}C NMR (75 MHz, C_6D_6) δ 202.1, 170.4, 170.2, 138.2, 129.6 (2C), 128.8(2C), 126.8, 78.6, 72.3, 56.4, 52.5, 49.5, 37.1, 31.3, 24.2.

HRMS calculated for $C_{18}H_{20}O_5Na$: 339.12029 ; found : 339.12009.

IR (neat, cm^{-1}) 3291, , 1732, 1437, 1274, 1261, 1203.

dimethyl 2-(3-oxo-2-phenylpropyl)-2-(prop-2-ynyl)malonate (25) :



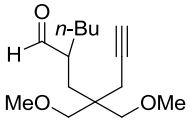
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.59 (d, *J* = 1.3 Hz, 1H), 7.54 – 7.09 (m, 5H), 3.89 – 3.74 (m, 1H), 3.68 (s, 3H), 3.51 (s, 3H), 3.03 (dd, *J* = 14.8, 6.2 Hz, 1H), 2.87 (dd, *J* = 2.7, 1.0 Hz, 2H), 2.47 (dd, *J* = 14.8, 6.5 Hz, 1H), 2.04 (t, *J* = 2.7 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 198.4, 170.2, 170.0, 135.4, 129.2 (2C), 129.1 (2C), 127.9, 78.3, 72.1, 55.7, 54.8, 52.9, 52.7, 31.9, 24.0.

HRMS calculated for $C_{17}H_{18}O_5Na$: 325.10464 ; found : 325.10458.

IR (neat, cm^{-1}) 3300, 2960, 1734, 1435, 1273, 1261, 1203.

2-butyl-4,4-bis(methoxymethyl)hept-6-ynal (27) :



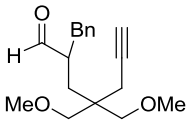
^{1}H NMR (300 MHz, C_6D_6) δ 9.35 (d, *J* = 4.1 Hz, 1H), 3.25 – 3.07 (m, 4H), 3.04 (s, 3H), 3.02 (s, 3H), 2.40 – 2.24 (m, 3H), 1.92 (dd, *J* = 14.4, 9.9 Hz, 1H), 1.78 (t, *J* = 2.7 Hz, 1H), 1.43 (dd, *J* = 14.4, 1.8 Hz, 1H), 1.38 – 1.26 (m, 1H), 1.24 – 1.04 (m, 5H), 0.88 – 0.68 (m, 3H).

^{13}C NMR (75 MHz, C_6D_6) δ 203.0, 81.1, 74.4, 73.8, 70.7, 58.5, 58.4, 47.3, 41.6, 32.1, 31.2, 29.0, 23.0, 22.8, 13.9.

HRMS calculated for $C_{15}H_{26}O_3Na$: 277.17742 ; found : 277.17780.

IR (neat, cm^{-1}) 3289, 2929, 2870, 1709, 1447, 1107.

2-benzyl-4,4-bis(methoxymethyl)hept-6-ynal (29) :



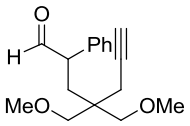
^{1}H NMR (300 MHz, C_6D_6) δ 9.43 (d, *J* = 3.3 Hz, 1H), 7.34 – 6.78 (m, 5H), 3.20 – 3.02 (m, 4H), 2.98 (s, 3H), 2.93 (s, 3H), 2.84 – 2.60 (m, 2H), 2.38 (dd, *J* = 13.0, 7.0 Hz, 1H), 2.31 – 2.12 (m, 2H), 2.04 – 1.88 (m, 1H), 1.68 (t, *J* = 2.7 Hz, 1H), 1.48 (dd, *J* = 14.5, 1.6 Hz, 1H).

^{13}C NMR (75 MHz, C_6D_6) δ 202.5, 138.8, 129.4, 128.5, 126.5, 80.9, 74.6, 73.9, 70.7, 58.4, 58.4, 48.9, 41.5, 37.8, 31.7, 23.0.

HRMS calculated for $C_{18}H_{24}O_3Na$: 311.16177 ; found : 311.16183.

IR (neat, cm^{-1}) 3282, 2883, 1721, 1447, 1102.

4,4-bis(methoxymethyl)-2-phenylhept-6-ynal (31) :



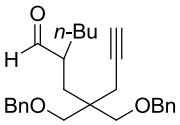
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.64 (d, *J* = 2.6 Hz, 1H), 7.41 – 7.11 (m, 5H), 3.93 (ddd, *J* = 8.3, 4.5, 2.6 Hz, 1H), 3.34 (m, 4H), 3.23 – 2.97 (m, 6H), 2.72 (ddd, *J* = 14.4, 8.3, 1.3 Hz, 1H), 2.50 (d, *J* = 2.6 Hz, 2H), 2.07 (dd, *J* = 14.3, 4.5 Hz, 1H), 1.97 – 1.78 (m, 1H).

^{13}C NMR (75 MHz, C_6D_6) δ 198.3, 138.5, 129.2 (2C), 129.1 (2C), 127.5, 81.1, 74.9, 74.3, 71.1, 58.6, 54.8, 41.9, 33.2, 23.2.

HRMS calculated for $C_{17}H_{22}O_3Na$: 297.14612 ; found : 297.14582.

IR (neat, cm^{-1}) 3286, 2883, 1725, 1451, 1102.

4,4-bis(benzyloxymethyl)-2-butylhept-6-ynal (33) :



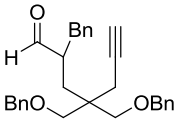
^{1}H NMR (300 MHz, C_6D_6) δ 9.31 (d, *J* = 4.2 Hz, 1H), 7.42 – 6.95 (m, 10H), 4.37 – 4.16 (m, 4H), 3.47 – 3.17 (m, 4H), 2.45 – 2.19 (m, 3H), 1.92 (dd, *J* = 14.4, 9.9 Hz, 1H), 1.78 (t, *J* = 2.6 Hz, 1H), 1.44 (dd, *J* = 14.4, 1.8 Hz, 1H), 1.36 – 1.21 (m, 1H), 1.19 – 1.03 (m, 5H), 0.78 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (75 MHz, C_6D_6) δ 203.5, 138.9, 138.8, 128.6, 127.9, 81.2, 73.3, 73.2, 72.2, 71.7, 71.1, 47.5, 42.0, 32.0, 31.3, 29.2, 23.2, 23.0, 14.1.

HRMS calculated for $C_{27}H_{34}O_3Na$: 429.24002 ; found : 429.23937.

IR (neat, cm^{-1}) 2933, 2862, 1725, 1455, 1098.

2-benzyl-4,4-bis(benzyloxymethyl)hept-6-ynal (35) :



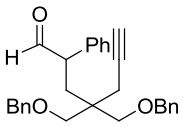
^{1}H NMR (400 MHz, C_6D_6) δ 9.39 (d, *J* = 3.6 Hz, 1H), 7.27 – 7.12 (m, 8H), 7.13 – 7.03 (m, 4H), 7.00 (ddd, *J* = 7.3, 3.8, 1.4 Hz, 1H), 6.95 (dd, *J* = 5.2, 3.1 Hz, 2H), 4.29 – 4.06 (m, 4H), 3.35 – 3.12 (m, 4H), 2.80 – 2.69 (m, 1H), 2.62 (dd, *J* = 13.7, 7.2 Hz, 1H), 2.34 (dd, *J* = 13.7, 7.4 Hz, 1H), 2.28 (dd, *J* = 16.8, 2.7 Hz, 1H), 2.22 (dd, *J* = 16.8, 2.7 Hz, 1H), 1.94 (dd, *J* = 14.5, 9.7 Hz, 1H), 1.67 (t, *J* = 2.7 Hz, 1H), 1.49 (dd, *J* = 14.5, 2.0 Hz, 1H).

^{13}C NMR (75 MHz, C_6D_6) δ 202.9, 138.8, 129.6, 128.7, 128.6, 127.9, 126.6, 81.0, 73.3, 72.4, 71.9, 71.1, 49.2, 41.9, 37.7, 31.7, 23.2.

HRMS calculated for $C_{30}H_{32}O_3Na$: 463.22437 ; found : 463.22351.

IR (neat, cm^{-1}) 3298, 2854, 1721, 1451, 1089.

4,4-bis(benzyloxymethyl)-2-phenylhept-6-ynal (37) :



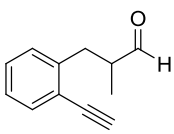
^{1}H NMR (300 MHz, C_6D_6) δ 9.38 (d, *J* = 2.5 Hz, 1H), 7.42 – 6.73 (m, 15H), 4.17 (s, 4H), 3.69 (ddd, *J* = 7.7, 4.8, 2.5 Hz, 1H), 3.42 – 3.11 (m, 4H), 2.50 (dd, *J* = 14.4, 7.9 Hz, 1H), 2.33 (d, *J* = 2.6 Hz, 2H), 1.90 (dd, *J* = 14.4, 4.9 Hz, 1H), 1.70 (t, *J* = 2.6 Hz, 1H).

^{13}C NMR (75 MHz, C_6D_6) δ 198.5, 138.9, 138.3, 129.2, 129.1, 128.6, 127.7, 127.5, 81.1, 73.3, 72.4, 72.0, 71.2, 54.8, 42.1, 32.9, 23.34.

HRMS calculated for $C_{29}H_{30}O_3Na$: 449.20872 ; found : 449.20815.

IR (neat, cm^{-1}) 3294, 3029, 1721, 1455, 1090.

3-(2-ethynylphenyl)-2-methylpropanal (39) :

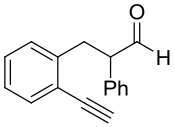


^{1}H NMR (300 MHz, C_6D_6) δ 9.36 (d, *J* = 1.2 Hz, 1H), 7.55 – 7.25 (m, 1H), 6.97 – 6.86 (m, 1H), 6.84 – 6.76 (m, 2H), 3.19 – 2.99 (m, 1H), 2.88 (s, 1H), 2.59 – 2.31 (m, 2H), 0.77 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 202.4, 142.0, 133.1, 129.8, 128.7, 126.3, 122.1, 82.1, 81.8, 47.0, 34.9, 12.8.

The ^{1}H and ^{13}C NMR data obtained were in agreement with that reported in the literature.[1a]

3-(2-ethynylphenyl)-2-phenylpropanal (40) :



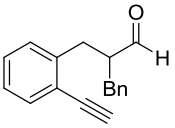
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.68 (d, *J* = 1.4 Hz, 1H), 7.47 – 7.33 (m, 1H), 7.33 – 7.13 (m, 3H), 7.14 – 7.00 (m, 4H), 6.94 – 6.90 (m, 1H), 3.98 (td, *J* = 7.5, 1.2 Hz, 1H), 3.59 (dd, *J* = 13.7, 7.1 Hz, 1H), 3.22 (s, 1H), 3.00 (dd, *J* = 13.7, 7.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.8, 141.4, 135.7, 132.9, 130.0, 129.0, 128.9, 128.7, 127.6, 126.3, 121.6, 82.11, 81.6, 59.4, 35.0.

HRMS calculated for $C_{17}H_{14}ONa$: 257.09369 ; found : 257.09392.

IR (neat, cm^{-1}) 3248, 1716, 765, 700.

2-benzyl-3-(2-ethynylphenyl)propanal (41) :



^{1}H NMR (400 MHz, C_6D_6) δ 9.49 (d, *J* = 1.8 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.14 – 6.97 (m, 7H), 6.93 – 6.88 (m, 1H), 3.04 (dd, *J* = 20.8, 8.1 Hz, 1H), 3.05 – 2.92 (m, 1H), 2.87 (s, 1H), 2.88 – 2.80 (m, 2H), 2.55 (dd, *J* = 13.7, 6.2 Hz, 1H).

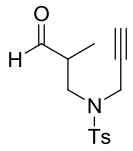
^{13}C NMR (100MHz, C_6D_6) δ 202.9, 142.4, 138.4, 133.5, 130.5, 129.8, 128.9, 126.9, 126.8, 122.6, 82.5, 82.4, 54.5, 35.7, 34.1.

HRMS calculated for $C_{18}H_{16}ONa$: 271.10934 ; found : 271.10981.

IR (neat, cm^{-1}) 3252, 3029, 1712, 1442, 762, 695.

mp 51-52°C

4-methyl-N-(2-methyl-3-oxopropyl)-N-(prop-2-ynyl)benzenesulfonamide (45) :



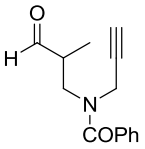
^{1}H NMR (300 MHz ,$CDCl_3$) δ 9.70 (d, *J* = 1.7 Hz, 1H), 7.63-7.71 (m, 2H), 7.32-7.30 (m, 2H), 4.13 (d, *J* = 2.5 Hz, 2H), 3.50 (dd, *J* = 14.3 Hz, *J* = 7.6 Hz, 1H), 3.21 (dd, *J* = 14.3 Hz, *J* = 6.8 Hz, 1H), 2.90-2.77 (m, 1H), 2.43 (s, 3H), 2.04 (t, *J* = 2.5 Hz, 1H), 1.19 (d, *J* = 7.3 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 202.9, 143.9, 135.2, 129.6 (2C), 127.8 (2C), 76.3, 74.2, 47.0, 45.4, 37.7, 21.6, 11.9.

HRMS calculated for $C_{14}H_{17}O_3NNaS$: 302.08214 ; found : 302.08221.

IR (neat, cm^{-1}) 3277, 2924, 1721, 1343, 1165.

N-(2-methyl-3-oxopropyl)-N-(prop-2-ynyl)benzamide (47) :



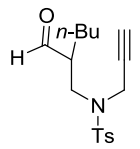
^{1}H NMR (400 MHz, C_6D_6, T = 60°C) δ 9.42 (s, 1H), 7.43 – 7.30 (m, 2H), 7.11 – 6.98 (m, 3H), 3.87 – 3.76 (m, 2H), 3.72 (dd, *J* = 14.0, 8.0 Hz, 1H), 3.41 (dd, *J* = 14.0, 5.9 Hz, 1H), 2.70 – 2.37 (m, 1H), 1.86 (t, *J* = 2.5 Hz, 1H), 0.79 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, C_6D_6, T = 60°C) δ 201.9, 171.5, 136.6, 129.9, 128.7, 127.4, 79.5, 73.4, 47.3, 45.6, 39.1, 11.9.

HRMS calculated for $C_{17}H_{14}ONa$: 230.11756 ; found : 230.11760.

IR (neat, cm^{-1}) 3269, 1725, 1629,1455, 1422, 1260.

***N*-(2-formylhexyl)-4-methyl-N-(prop-2-ynyl)benzenesulfonamide (49)** :



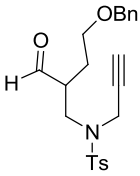
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.66 (d, *J* = 2.7 Hz, 1H), 7.82 – 7.65 (m, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 4.28 – 3.97 (m, 2H), 3.51 (dd, *J* = 14.1, 8.7 Hz, 1H), 3.21 (dd, *J* = 14.1, 5.8 Hz, 1H), 2.79 – 2.66 (m, 1H), 2.42 (s, 3H), 2.02 (t, *J* = 2.5 Hz, 1H), 1.77 – 1.44 (m, 2H), 1.44 – 1.18 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 203.3, 143.9, 135.1, 129.6, 127.8, 76.2, 74.2, 50.5, 45.5, 37.4, 28.8, 26.8, 22.7, 21.5, 13.8.

HRMS calculated for $C_{17}H_{23}O_3NSNa$: 344.12909 ; found : 344.12947.

IR (neat, cm^{-1}) 3277, 2924, 1721, 1451, 1347, 1160, 1094.

N-(4-(benzyloxy)-2-formylbutyl)-4-methyl-N-(prop-2-ynyl)benzenesulfonamide (51) :

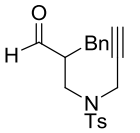


^{1}H NMR (300 MHz, C_6D_6) δ 9.50 (d, *J* = 1.4 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.34 – 6.98 (m, 5H), 6.76 (d, *J* = 8.0 Hz, 2H), 4.21 (s, 2H), 4.00 (dd, *J* = 18.6, 2.3 Hz, 1H), 3.82 (dd, *J* = 18.6, 2.5 Hz, 1H), 3.52 – 3.38 (m, 2H), 3.38 – 3.27 (m, 1H), 3.27 – 3.15 (m, 1H), 2.70 – 2.44 (m, 1H), 1.89 (s, 3H), 1.79 – 1.53 (m, 2H), 1.47 (t, *J* = 2.5 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 202.7, 144.0, 138.1, 135.2, 129.7, 128.5, 127.9, 127.8 (2C), 76.3, 74.4, 73.2, 67.3, 48.1, 45.4, 37.4, 27.6, 21.7.

HRMS calculated for $C_{22}H_{25}O_4NSNa$: 422.13965 ; found : 422.14006.

N-(2-benzyl-3-oxopropyl)-4-methyl-N-(prop-2-ynyl)benzenesulfonamide (53) :



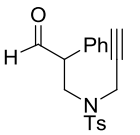
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.76 (d, *J* = 1.6 Hz, 1H), 7.79 – 7.46 (m, 2H), 7.46 – 6.99 (m, 7H), 4.10 (d, *J* = 2.4 Hz, 2H), 3.57 – 3.34 (m, 1H), 3.32 – 3.11 (m, 2H), 3.04 (dd, *J* = 14.2, 7.0 Hz, 1H), 2.79 (dd, *J* = 14.2, 7.1 Hz, 1H), 2.41 (s, 3H), 1.99 (t, *J* = 2.5 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 202.7, 143.8, 137.5, 134.6, 129.5, 128.9, 128.7, 128.5, 127.8, 126.7, 76.3, 74.2, 52.2, 45.5, 38.1, 33.4, 21.5.

HRMS calculated for $C_{20}H_{21}O_3NSNa$: 378.11344 ; found : 378.11385.

IR (neat, cm^{-1}) 3306, 2920, 1721, 1351, 1327, 1168.

4-methyl-N-(3-oxo-2-phenylpropyl)-N-(prop-2-ynyl)benzenesulfonamide (55) :



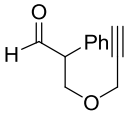
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.63 (d, *J* = 1.1 Hz, 1H), 7.70 – 7.57 (m, 2H), 7.37 – 7.24 (m, 3H), 7.24 – 7.14 (m, 4H), 4.12 – 4.04 (m, 2H), 3.77 (dd, *J* = 14.7, 7.6 Hz, 1H), 3.68 (dd, *J* = 18.6, 2.4 Hz, 1H), 3.36 (dd, *J* = 14.7, 7.2 Hz, 1H), 2.32 (s, 3H), 1.90 (t, *J* = 2.5 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.0, 143.9, 135.2, 133.4, 129.6, 129.5, 129.2, 128.4, 127.9, 76.7, 74.1, 58.9, 46.9, 38.3, 21.6.

HRMS calculated for $C_{19}H_{19}O_3NSNa$: 364.09779 ; found : 364.09809.

IR (neat, cm^{-1}) 3303, 2918, 1719, 1348, 1327, 1167.

2-phenyl-3-(prop-2-ynyloxy)propanal (57) :



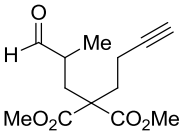
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.76 (m, 1H), 7.51 – 7.13 (m, 5H), 4.23 – 4.13 (m, 3H), 3.95 – 3.83 (m, 2H), 2.44 (t, *J* = 2.4 Hz, 1H).

^{13}C NMR (75 MHz, C_6D_6) δ 198.0, 134.4, 129.1, 129.0, 79.6, 74.8, 69.0, 58.7, 58.2.

HRMS calculated for $C_{12}H_{12}O_2Na$: 211.07295 ; found : 211.07281.*

IR (neat, cm^{-1}) 3293, 1723, 1267, 1095, 735, 699.

dimethyl 2-(but-3-yn-1-yl)-2-(2-methyl-3-oxopropyl)malonate (59) :



^{1}H NMR (200 MHz, $CDCl_3$) δ 9.50 (d, *J* = 1.7 Hz, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 2.61 – 2.38 (m, 2H), 2.30 – 2.01 (m, 4H), 1.95 (s, 1H), 1.89 – 1.72 (m, 1H), 1.09 (d, *J* = 7.0 Hz, 3H).

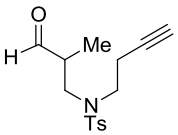
^{13}C NMR (50 MHz, C_6D_6) δ 202.9, 171.3, 171.2, 83.0, 69.1, 56.4, 52.7, 42.6, 33.7, 32.9, 15.6, 14.2.

HRMS calculated for $C_{13}H_{18}O_5Na$: 277.10464 ; found : 277.10514.

IR (neat, cm^{-1}) 3286, 2953, 1728, 1435, 1202.

mp 38-40°C

N-(but-3-yn-1-yl)-4-methyl-N-(2-methyl-3-oxopropyl)benzenesulfonamide (61) :



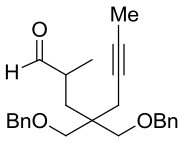
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.69 (d, *J* = 1.6 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = **8.0 Hz, 2H), 3.48 (dd, *J* = 14.5, 7.4 Hz, 1H), 3.33 – 3.23 (m, 2H), 3.17 (dd, *J* = 14.5, 6.9 Hz,** 1H), 2.95 – 2.77 (m, 1H), 2.49 – 2.38 (m, 5H), 1.98 (t, *J* = 2.7 Hz, 1H), 1.18 (d, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 203.2, 143.9, 135.7, 130.0, 127.3, 80.9, 70.6, 49.7, 48.4, 46.1, 21.6, 19.3, 12.1.

HRMS calculated for $C_{15}H_{19}O_3NSNa$: 316.09779 ; found : 316.09657.

IR (neat, cm^{-1}) 3286, 2933, 1721, 1334, 1156, 978, 812.

4,4-bis(benzyloxymethyl)-2-methyloct-6-ynal (63) :



^{1}H NMR (300 MHz, $CDCl_3$) δ 9.36 (d, *J* = 3.3 Hz, 1H), 7.38 – 6.92 (m, 10H), 4.46 – 4.14 (m, 4H), 3.51 – 3.16 (m, 4H), 2.55 – 2.24 (m, 3H), 2.01 (dd, *J* = 14.4, 8.8 Hz, 1H), 1.52 (t, *J* = 2.6 Hz, 3H), 1.36 (dd, *J* = 14.4, 2.9 Hz, 1H), 0.82 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, C_6D_6) δ 203.3, 139.0, 128.5, 127.8, 77.8, 76.0, 73.2, 72.5, 72.0, 42.2, 42.0, 33.9, 23.6, 16.5, 3.3.

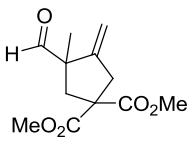
HRMS calculated for $C_{25}H_{30}O_3Na$: 401.20872 ; found : 401.20935.

C. Carbocyclization Reactions

General procedure for the carbocyclization reactions

In a sealed vial under argon atmosphere were successively introduced triphenylphosphine (0.08 mmol, 0,2 eq.), copper(II) trifloromethanesulfonate (0.02 mmol, 0.05 eq.) and 0.4 mL of DCE. The resulting mixture was stirred 20 minutes at room temperature before freshly purified formyl-alkyne (0.4 mmol, 1eq.) in 0.4 mL of a freshly prepared 0,2 M solution of amine in DCE (0.08 mmol, 0.2 eq.) was added. After introduction of additional 0.2 mL of DCE, the reaction mixture was stirred at room temperature until GC or TLC analysis indicated complete conversion. The reaction mixture was then treated with 1 mL of an aqueous solution of AcOH (1/1 v/v) and then vigorously stirred 15 min at room temperature before extraction of the aqueous layer with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure and the resulting crude material purified by silica gel flash chromatography to afford the desired carbocyclized aldehyde.

4,4-bis-(carbomethoxy)-1-methyl-2-methylene-cyclopentanecarbaldehyde (2) :

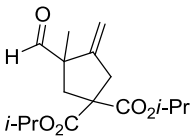


^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.29 (s, 1H), 5.23 (t, *J* = 2.1 Hz, 1H), 4.95 (t, *J* = 2.0 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.07-2.92 (m, 2H), 2.95 (d, *J* = 14.4 Hz, 1H), 2.27 (d, *J* = 14.0 Hz, 1H), 1.27 (s, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 199.6, 171.7, 171.5, 149.3, 110.7, 58.0, 56.7, 53.0, 52.9, 41.0, 40.3, 21.7.

The ^{1}H and ^{13}C NMR data obtained were in agreement with that reported in the literature.[1a]

di*iso*propyl 3-formyl-3-methyl-4-methylenecyclopentane-1,1-dicarboxylate (4) :



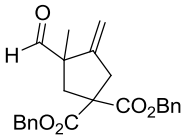
^{1}H NMR (300 MHz, C_6D_6) δ 9.16 (s, 1H), 4.99 (m, 2H), 4.92 (t, *J* = 1.9 Hz, 1H), 4.66 (t, *J* = 2.2 Hz, 1H), 3.23 – 3.03 (m, 2H), 2.92 (d, *J* = 16.5 Hz, 1H), 2.35 (d, *J* = 14.0 Hz, 1H), 1.07 (d, *J* = 6.3 Hz, 3H), 1.04 – 0.90 (m, 12H).

^{13}C NMR (75 MHz, C_6D_6) δ 198.9, 170.8, 170.6, 150.6, 110.0, 69.1, 68.9, 58.5, 57.0, 41.4, 40.6, 21.7, 21.5.

HRMS calculated for $C_{16}H_{24}O_5Na$: 319.15160 ; found : 319.15176.

IR (neat, cm^{-1}) 2983, 1727, 1650, 1261, 1106.

dibenzyl 3-formyl-3-methyl-4-methylenecyclopentane-1,1-dicarboxylate (6) :



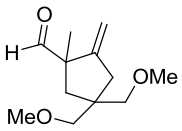
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.37 – 6.99 (m, 10H), 5.12 (t, *J* = 2.0 Hz, 1H), 5.03 (s, 4H), 4.85 (t, *J* = 2.2 Hz, 1H), 3.04 – 2.81 (m, 3H), 2.21 (d, *J* = 14.1 Hz, 1H), 1.15 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.6, 170.9, 170.8, 149.4, 135.3, 135.2, 128.5, 128.4, 128.3, 128.1, 110.8, 67.6, 67.5, 58.2, 56.7, 41.0, 40.2, 21.6.

HRMS calculated for $C_{24}H_{24}O_5Na$: 415.15160 ; found : 415.15200.

IR (neat, cm^{-1}) 2962, 1730, 1654, 1455, 1261, 1227, 1172, 1060.

4,4-bis(methoxymethyl)-1-methyl-2-methylenecyclopentanecarbaldehyde (8) :

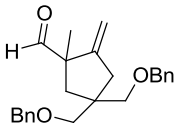


^{1}H NMR (CDCl$_3$, 300 MHz) δ 9.32 (s, 1H), 5.12 (t, *J* = 2.0 Hz, 1H), 4.88 (t, *J* = 2.1 Hz, 1H), 3.33 (s, 3H), 3.32 (s, 3H), 3.27-3.19 (m, 4H), 2.37 (dt, *J* = 16.1 Hz, *J* = 1.5 Hz, 1H), 2.30 (d, *J* = 14.1 Hz, 1H), 2.22 (dt, *J* = 16.0 Hz, *J* = 2.3 Hz, 1H), 1.47 (d, *J* = 14.2 Hz, 1H), 1.25 (s, 3H).

^{13}C NMR (CDCl$_3$, 75 MHz) δ 200.8, 152.5, 109.8, 76.0, 75.9, 59.2, 56.7, 45.9, 40.2, 38.8, 22.3.

The ^{1}H and ^{13}C NMR data obtained were in agreement with that reported in the literature.[1a]

4,4-bis(benzyloxymethyl)-1-methyl-2-methylenecyclopentanecarbaldehyde (10) :

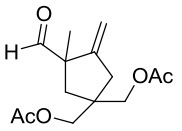


^{1}H NMR (CDCl$_3$, 300 MHz) δ 9.24 (s, 1H), 7,31-7.22 (m, 10H) 5.05 (t, *J* = 1.9 Hz, 1H), 4.80 (t, *J* = 2.0 Hz, 1H), 4.46 (s, 2H), 4.45 (s, 4H), 3.38-3.31 (m, 4H), 2.42-2.32 (m, 2H), 2.32 (d, *J* = 14.2 Hz, 1H), 1.48 (d, *J* = 14.1 Hz, 1H), 1.17 (s, 3H).

^{13}C NMR (CDCl$_3$, 75 MHz) δ 200.8, 152.6, 138.7, 128.4, 127.5, 109.8, 73.2, 73.5, 56.8, 46.3, 40.5, 39.0, 22.4.

The ^{1}H and ^{13}C NMR data obtained were in agreement with that reported in the literature.[1a]

(3-formyl-3-methyl-4-methylenecyclopentane-1,1-diyl)bis(methylene) diacetate (12) :



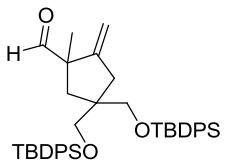
^{1}H NMR (CDCl$_3$, 300 MHz) δ 9.29 (s, 1H), 5.18 (t, *J* = 1.9 Hz, 1H), 4.97 (dd, *J* = 2.3, 1.7 Hz, 1H), 4.12 – 3.80 (m, 4H), 2.55 – 2.16 (m, 3H), 2.06 (d, *J* = 1.4 Hz, 6H), 1.43 (d, *J* = 14.3 Hz, 1H), 1.29 (s, 3H).

^{13}C NMR (CDCl$_3$, 75 MHz,) δ 199.7, 171.0, 170.9, 150.4, 110.9, 66.7, 66.6, 56.6, 43.8, 39.9, 38.1, 22.0, 20.8 (2C).

HRMS calculated for $C_{14}H_{20}O_5Na$: 291.12029 ; found : 291.12015.

IR (neat, cm^{-1}) 2949, 1739, 1724, 1654, 1225, 1036.

4,4-bis((tert-butyldiphenylsilyloxy)methyl)-1-methyl-2-methylenecyclopentanecarbaldehyde (14) :



^{1}H NMR (300 MHz, CDCl$_3$) δ 9.16 (s, 1H), 7.67-7.62 (m, 8H), 7.52 – 7.28 (m, 12H), 5.02 (t, *J* = 1.7 Hz, 1H), 4.76 (t, *J* = 1.9 Hz, 1H), 3.72 – 3.47 (m, 4H), 2.43 (d, *J* = 15.8 Hz, 1H), 2.30-2.23 (m, 2H), 1.46 (d, *J* = 14.6 Hz, 1H), 1.11 (s, 3H), 1.05 (d, *J* = 1.1 Hz, 18H).

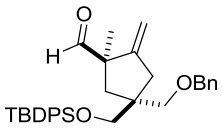
^{13}C NMR (75 MHz, CDCl$_3$) δ 200.5, 152.5, 135.7, 133.5, 129.6, 127.6, 109.8, 66.1, 66.0, 56.6, 48.8, 38.9, 37.9, 26.9, 22.1, 19.3.

HRMS calculated for $C_{42}H_{52}O_3NaSi_2$: 683.33472 ; found : 683.33442.

IR (neat, cm^{-1}) 2937, 2854, 1722, 1652, 1470, 1428, 1109, 1082, 822, 700.

4-(benzyloxymethyl)-4-((tert-butyldiphenylsilyloxy)methyl)-1-methyl-2-methylenecyclopentane carbaldehyde (16) :

Major diastereoisomer :



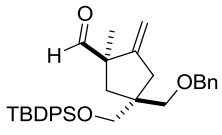
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.22 (s, 1H), 7.78 – 7.53 (m, 4H), 7.47 – 7.27 (m, 11H), 5.09 (t, *J* = 1.9 Hz, 1H), 4.83 (t, *J* = 2.0 Hz, 1H), 4.52 (s, 2H), 3.60 (s, 2H), 3.46 (d, *J* = 8.7 Hz, 1H), 3.43 (d, *J* = 8.7 Hz, 1H), 2.50 – 2.23 (m, 3H), 1.53 (d, *J* = 14.2 Hz, 1H), 1.23 (s, 3H), 1.14 – 0.95 (m, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 200.5, 152.5, 138.6, 135.6, 133.5, 129.6, 128.3, 127.6, 127.4, 127.3, 109.9, 73.1, 73.0, 66.3, 56.6, 47.5, 40.0, 38.4, 26.8, 22.3, 19.4.

HRMS calculated for $C_{33}H_{40}O_3SiNa$: 535.26389 ; found : 535.26381.

IR (neat, cm^{-1}) 2933, 2854, 1722, 1651, 1109, 1088, 701.

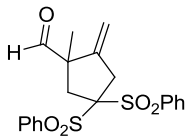
Minor diastereoisomer :



^{1}H NMR (300 MHz, $CDCl_3$) δ 9.29 (s, 1H), 7.70 – 7.60 (m, 4H), 7.46 – 7.27 (m, 11H), 5.08 (t, *J* = 1.9 Hz, 1H), 4.84 (t, *J* = 2.0 Hz, 1H), 4.52 (s, 2H), 3.59 (d, *J* = 2.9 Hz, 2H), 3.47 (d, *J* = 8.7 Hz, 1H), 3.42 (d, *J* = 8.7 Hz, 1H), 2.55 – 2.14 (m, 3H), 1.49 (d, *J* = 14.2 Hz, 1H), 1.16 (s, 3H), 1.05 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 200.8, 152.4, 138.6, 135.6, 133.5, 129.6, 128.3, 127.6, 127.4, 109.9, 73.2, 66.1, 56.7, 47.3, 39.9, 38.5, 26.8, 22.2, 19.4.

1-methyl-2-methylene-4,4-bis(phenylsulfonyl)cyclopentanecarbaldehyde (18) :



^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.36 (s, 1H), 8.21 – 7.93 (m, 4H), 7.73 (m, 2H), 7.62 (m, 4H), 5.17 (s, 1H), 5.00 (t, *J* = 1.8 Hz, 1H), 3.40 (d, *J* = 16.1 Hz, 1H), 3.32 – 3.24 (m, 2H), 2.52 (d, *J* = 16.2 Hz, 1H), 1.33 (s, 3H).

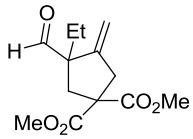
^{13}C NMR ($CDCl_3$, 75 MHz) δ 199.0, 147.8, 135.9, 135.8, 134.8, 131.5, 131.3, 128.8, 128.8, 110.2, 91.0, 57.4, 38.9, 37.3, 22.1.

HRMS calculated for $C_{20}H_{20}O_5NaS_2$: 427.06444 ; found : 427.06411.

IR (neat, cm^{-1}) 1725, 1642, 1447, 1327, 1309, 1143, 1077.

mp 132-133°C

dimethyl 3-ethyl-3-formyl-4-methylenecyclopentane-1,1-dicarboxylate (20) :



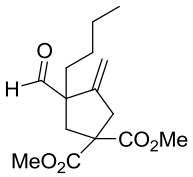
^{1}H NMR (300 MHz, C_6D_6) δ 9.04 (s, 1H), 4.97 (t, *J* = 2.0 Hz, 1H), 4.69 (t, *J* = 2.2 Hz, 1H), 3.39 (s, 3H), 3.30 (s, 3H), 3.20 – 3.07 (m, 2H), 2.67 (dt, *J* = 16.4, 2.3 Hz, 1H), 2.43 (d, *J* = 14.2 Hz, 1H), 1.59 – 1.21 (m, 2H), 0.58 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (75 MHz, C_6D_6) δ 199.0, 171.5, 171.3, 148.9, 110.0, 61.3, 57.9, 52.4, 52.2, 41.2, 36.7, 28.3, 8.6.

HRMS calculated for $C_{13}H_{18}O_5Na$: 277.10464 ; found : 277.10484.

IR (neat, cm^{-1}) 2962, 1734, 1651, 1434, 1278, 1255, 1230, 1203, 1175, 1068, 900.

dimethyl 3-butyl-3-formyl-4-methylenecyclopentane-1,1-dicarboxylate (22) :

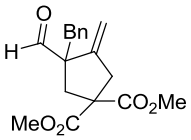


^{1}H NMR (300 MHz, $CDCl_3$) δ 9.08 (s, 1H), 4.97 (d, *J* = 1.8 Hz, 1H), 4.72 (t, *J* = 2.1 Hz, 1H), 3.41 (s, 3H), 3.29 (s, 3H), 3.26 – 3.09 (m, 2H), 2.78 – 2.60 (m, 1H), 2.50 (d, *J* = 14.0 Hz, 1H), 1.51 (ddd, *J* = 13.7, 11.2, 4.9 Hz, 1H), 1.41 – 1.21 (m, 1H), 1.16 – 0.82 (m, 4H), 0.73 (t, *J* = 6.9 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1, 171.7, 171.5, 149.3, 110.1, 61.1, 58.1, 52.6, 52.4, 41.3, 37.5, 35.7, 26.9, 23.3, 14.0.

HRMS calculated for $C_{15}H_{22}O_5Na$: 305.13594 ; found : 305.13554.

IR (neat, cm^{-1}) 2956, 2933, 1861, 1735, 1650, 1434, 1258, 1255, 1203, 1068, 893.

dimethyl 3-benzyl-3-formyl-4-methylenecyclopentane-1,1-dicarboxylate (24) :

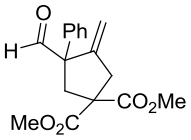


^{1}H NMR (C_6D_6, 300 MHz) δ 9.29 (s, 1H), 7.10 – 6.93 (m, 5H), 5.00 (t, *J* = 2.0 Hz, 1H), 4.78 (t, *J* = 2.2 Hz, 1H), 3.26 (d, *J* = 14.1 Hz, 6H), 3.15 (dd, *J* = 16.4, 1.0 Hz, 1H), 2.96 (dd, *J* = 14.2, 8.2 Hz, 2H), 2.76 – 2.60 (m, 3H).
^{13}C NMR (75 MHz, C_6D_6) δ 198.4, 171.7, 171.3, 148.8, 137.1, 130.3, 128.7, 127.1, 111.1, 62.1, 58.2, 52.5, 52.4, 41.7, 37.0.

HRMS calculated for $C_{18}H_{20}O_5Na$: 339.12029 ; found : 339.11985.

IR (neat, cm^{-1}) 2958, 1731, 1649, 1435, 1258, 1265, 1200, 1068.

dimethyl 3-formyl-4-methylene-3-phenylcyclopentane-1,1-dicarboxylate (26) :

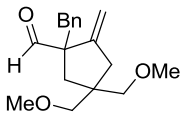


^{1}H NMR (300 MHz, C_6D_6) δ 9.23 (d, *J* = 1.0 Hz, 1H), 7.24 – 6.82 (m, 5H), 5.19 (t, *J* = 2.1 Hz, 1H), 4.72 (t, *J* = 2.3 Hz, 1H), 3.65 (dd, *J* = 13.9, 1.0 Hz, 1H), 3.37 (d, *J* = 1.6 Hz, 3H), 3.19 – 3.08 (m, 4H), 2.92-2.85 (m, 1H), 2.71 (d, *J* = 13.9 Hz, 1H).
^{13}C NMR (75 MHz, C_6D_6) δ 195.7, 171.2, 171.1, 147.0, 140.3, 129.2, 128.4, 128.0, 127.9, 127.7, 127.6, 114.2, 66.3, 58.3, 52.7, 52.3, 42.8, 41.7.

HRMS calculated for $C_{17}H_{18}O_5Na$: 325.10464 ; found : 325.10431.

IR (neat, cm^{-1}) 2958, 1737, 1646, 1435, 1260, 1206, 1069.

1-benzyl-4,4-bis(methoxymethyl)-2-methylenecyclopentanecarbaldehyde (30) :



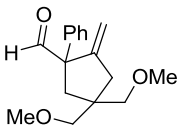
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.40 (s, 1H), 7.23 – 6.98 (m, 5H), 5.17 (t, *J* = 1.9 Hz, 1H), 4.96 (t, *J* = 2.1 Hz, 1H), 3.22 (s, 3H), 3.21 (s, 3H), 3.15 – 3.03 (m, 3H), 3.02 (s, 2H), 2.78 (d, *J* = 13.8 Hz, 1H), 2.09 (t, *J* = 2.0 Hz, 2H), 2.05 (d, *J* = 14.4 Hz, 1H), 1.62 (d, *J* = 14.4 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 200.5, 151.2, 137.2, 130.2, 128.2, 126.6, 110.6, 76.0, 75.7, 61.7, 59.2, 59.1, 46.0, 42.0, 40.6, 35.2.

HRMS calculated for $C_{18}H_{24}O_3Na$: 311.16177 ; found : 311.16163.

IR (neat, cm^{-1}) 2883, 1721, 1639, 1457, 1200, 1115, 1095.

mp 40-42°C

4,4-bis(methoxymethyl)-2-methylene-1-phenylcyclopentanecarbaldehyde (32) :



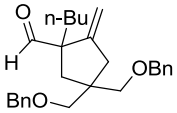
^{1}H NMR (300 MHz, C_6D_6) δ 9.39 (d, *J* = 0.7 Hz, 1H), 7.32 – 6.86 (m, 5H), 5.21 (t, *J* = 2.0 Hz, 1H), 4.80 (t, *J* = 2.2 Hz, 1H), 3.24 – 2.98 (m, 8H), 2.95 (s, 3H), 2.42 (dt, *J* = 3.9, 2.1 Hz, 2H), 1.91 (d, *J* = 13.9 Hz, 1H).

^{13}C NMR (75 MHz, C_6D_6) δ 196.8, 150.2, 142.1, 129.2, 128.9, 128.0, 127.3, 113.1, 76.1, 75.4, 66.4, 58.9, 58.8, 46.7, 41.2, 41.0.

HRMS calculated for $C_{17}H_{22}O_3Na$: 297.14612 ; found : 297.14572.

IR (neat, cm^{-1}) 2883, 1723, 1646, 1445, 1200, 1107, 1095, 963, 903.

4,4-bis(benzyloxymethyl)-1-butyl-2-methylenecyclopentanecarbaldehyde (34) :



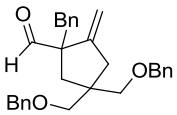
^{1}H NMR (300 MHz, C_6D_6) δ 9.21 (s, 1H), 7.35 – 7.03 (m, 10H), 4.98 (t, *J* = 1.8 Hz, 1H), 4.76 (t, *J* = 2.0 Hz, 1H), 4.45 – 4.18 (m, 4H), 3.34 (s, 4H), 2.54 (d, *J* = 14.0 Hz, 1H), 2.38 (dt, *J* = 15.9, 1.8 Hz, 1H), 2.24 (d, *J* = 15.0 Hz, 1H), 1.69 – 1.52 (m, 1H), 1.60 (d, *J* = 15,0 Hz, 1H), 1.42 – 1.27 (m, 1H), 1.21 – 0.93 (m, 4H), 0.77 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (75 MHz, C_6D_6) δ 200.1, 152.2, 139.3, 139.3, 128.5, 127.7, 109.4, 73.8, 73.6, 73.4, 73.4, 61.1, 46.3, 40.7, 36.4, 35.6, 27.2, 23.5, 14.1.

HRMS calculated for $C_{27}H_{34}O_3Na$: 429.24002 ; found : 429.23960.

IR (neat, cm^{-1}) 2929, 2858, 1721, 1648, 1453, 1361, 1203, 1115, 1097, 734, 697.

1-benzyl-4,4-bis(benzyloxymethyl)-2-methylenecyclopentanecarbaldehyde (36) :



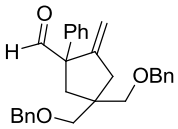
^{1}H NMR (300 MHz, C_6D_6) δ 9.32 (s, 1H), 7.25 – 6.89 (m, 15H), 4.98 (t, *J* = 2.0 Hz, 1H), 4.78 (t, *J* = 2.0 Hz, 1H), 4.21 (s, 4H), 3.23 (s, 2H), 3.17 (s, 2H), 2.97 (d, *J* = 13.8 Hz, 1H), 2.67 (d, *J* = 13.8 Hz, 1H), 2.27 (d, *J* = 14.3 Hz, 1H), 2.21 – 2.13 (m, 2H), 1.78 (d, *J* = 14.3 Hz, 1H).

^{13}C NMR (75 MHz, C_6D_6) δ 199.6, 152.0, 139.3, 139.2, 137.8, 130.6, 128.5, 128.5, 126.8, 110.3, 73.7, 73.4, 73.3, 73.3, 62.0, 46.6, 42.3, 41.1, 35.4.

HRMS calculated for $C_{30}H_{32}O_3Na$: 463.22437 ; found : 463.22372.

IR (neat, cm^{-1}) 2921, 2854, 1720, 1648, 1494, 1451, 1096, 903, 737, 699.

4,4-bis(benzyloxymethyl)-2-methylene-1-phenylcyclopentanecarbaldehyde (38) :



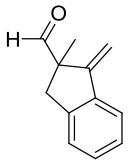
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.44 – 6.92 (m, 15H), 5.22 (t, *J* = 2.0 Hz, 1H), 4.81 (t, *J* = 2.1 Hz, 1H), 4.38-4.28 (m, 2H), 4.19 (d, *J* = 1.6 Hz, 2H), 3.37 (s, 2H), 3.32-3.22 (m, 2H), 3.13 (d, *J* = 13.9 Hz, 1H), 2.57 – 2.31 (m, 2H), 1.95 (d, *J* = 13.9 Hz, 1H).

^{13}C NMR (75 MHz, C_6D_6) δ 196.7, 150.0, 142.1, 139.4, 139.2, 129.2, 128.5, 127.9, 127.6, 127.3, 113.3, 73.7, 73.4, 73.2, 73.1, 66.5, 46.8, 41.4, 41.2.

HRMS calculated for $C_{29}H_{30}O_3Na$: 449.20872 ; found : 449.20828.

IR (neat, cm^{-1}) 2853, 1721, 1650, 1452, 1452, 1362, 1096, 1076, 737, 698.

2-methyl-1-methylene-2,3-dihydro-1H-indene-2-carbaldehyde (42) :

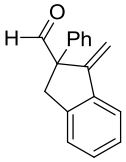


^{1}H NMR (300 MHz, C_6D_6) δ 8.94 (s, 1H), 7.05 – 6.92 (m, 2H), 6.88 – 6.70 (m, 2H), 5.23 (s, 1H), 4.58 (s, 1H), 3.01 (d, *J* = 16.8 Hz, 1H), 2.13 (d, *J* = 16.8 Hz, 1H), 0.92 (s, 3H).

^{13}C NMR (75 MHz, C_6D_6) δ 198.7, 152.3, 144.1, 139.9, 129.8, 127.6, 125.9, 121.7, 106.0, 57.8, 39.1, 21.3.

The ^{1}H and ^{13}C NMR data obtained were in agreement with that reported in the literature.[1a]

1-methylene-2-phenyl-2,3-dihydro-1H-indene-2-carbaldehyde (43) :



^{1}H NMR (300 MHz, C_6D_6) δ 9.47 (s, 1H), 7.29 – 7.22 (m, 1H), 7.17 – 6.84 (m, 9H), 5.64 (s, 1H), 4.77 (s, 1H), 4.09 (d, *J* = 16.8, 1H), 2.70 (d, *J* = 16.8 Hz, 1H).

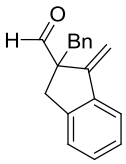
^{13}C NMR (75 MHz, C_6D_6) δ 194.7, 149.0, 143.1, 141.7, 138.6, 129.4, 128.8, 126.9, 126.7, 125.1, 120.8, 108.6, 66.9, 40.3.

HRMS calculated for $C_{14}H_{17}O_3NNaS$: 257.09369 ; found : 257.09390.

IR (neat, cm^{-1}) 2920, 1718, 1634, 904.

mp 108-109°C

2-benzyl-1-methylene-2,3-dihydro-1H-indene-2-carbaldehyde (44) :



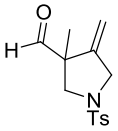
^{1}H NMR (300 MHz, C_6D_6) δ 9.28 (s, 1H), 7.26 – 7.17 (m, 1H), 7.11 – 6.81 (m, 8H), 5.53 (s, 1H), 4.87 (s, 1H), 3.21 (d, *J* = 14.0 Hz, 1H), 3.11 (d, *J* = 17.0 Hz, 1H), 2.73 (d, *J* = 14.0 Hz, 1H), 2.70 (d, *J* = 17.0 Hz, 1H).

^{13}C NMR (75 MHz, C_6D_6) δ 198.3, 150.7, 144.1, 139.4, 137.6, 130.4, 129.6, 128.6, 127.2, 126.9, 125.6, 121.4, 106.7, 62.9, 40.8, 35.7.

HRMS calculated for $C_{18}H_{16}ONa$: 271.10934 ; found : 271.10975.

IR (neat, cm^{-1}) 3027, 2921, 1721, 1629, 884.

3-methyl-4-methylene-1-tosylpyrrolidine-3-carbaldehyde (46) :



^{1}H NMR ($CDCl_3$, 200 MHz) δ 9.29 (s, 1H), 7,31-7.22 (m, 2H), 7.38-7.34 (m, 2H), 5.21 (t, *J* = 1.8 Hz, 1H), 5.01 (t, *J* = 2.3 Hz, 1H), 3.88-3.84 (m, 2H), 3.80 (d, *J* = 9.9 Hz, 1H), 3.03 (d, *J* = 10.0 Hz, 1H), 2.04 (s, 3H), 1.24 (s, 3H).

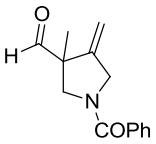
^{13}C NMR ($CDCl_3$, 75 MHz) δ 197.8, 145.7, 144.5, 132.7, 130.2 (2C), 128.3 (2C), 111.1, 57.2, 54.4, 52.5, 21.9, 19.0.

HRMS calculated for $C_{14}H_{17}O_3NNaS$: 302.08214 ; found : 302.08223.

IR (neat, cm^{-1}) 2925, 1727, 1658, 1339, 1161, 1093, 1042.

mp 82-83°C

1-benzoyl-3-methyl-4-methylenepyrrolidine-3-carbaldehyde (48) :



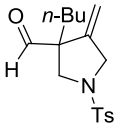
^{1}H NMR (400 MHz, C_6D_6, 60°C) δ 8.99 (s, 1H), 7.46 (s, 2H), 7.28 – 6.98 (m, 5H), 4.73 (s, 1H), 4.62 (s, 1H), 4.26 – 3.80 (m, 3H), 3.02 (d, *J* = 9.7 Hz, 1H), 0.82 (s, 3H).

^{13}C NMR (101 MHz, C_6D_6, 60°C) δ 197.0, 169.3, 146.9, 137.4, 129.9, 128.4, 127.8, 109.2, 56.9, 54.1, 51.6, 17.5.

HRMS calculated for $C_{14}H_{15}O_2NNa$: 252.09950 ; found : 252.09970.

IR (neat, cm^{-1}) 2929, 1729, 1626, 1572, 1447, 1417, 1248, 907.

3-butyl-4-methylene-1-tosylpyrrolidine-3-carbaldehyde (50) :



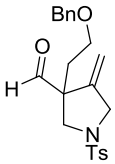
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.22 (s, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.22 (s, 1H), 5.03 (t, *J* = 1.8 Hz, 1H), 3.95 – 3.67 (m, 3H), 3.09 (d, *J* = 10.0 Hz, 1H), 2.44 (s, 3H), 1.88 – 1.69 (m, 1H), 1.59 – 1.43 (m, 1H), 1.37 – 1.16 (m, 2H), 1.16 – 0.99 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.6, 144.3, 144.0, 132.3, 129.7, 127.9, 110.7, 60.7, 52.2, 51.3, 33.2, 26.6, 22.9, 21.5, 13.7.

HRMS calculated for $C_{17}H_{23}O_3NSNa$: 344.12909 ; found : 344.12930.

IR (neat, cm^{-1}) 2931, 1726, 1658, 1346, 1163, 1093.

3-(2-(benzyloxy)ethyl)-4-methylene-1-tosylpyrrolidine-3-carbaldehyde (52) :



^{1}H NMR (300 MHz, $CDCl_3$) δ 9.14 (s, 2H), 7.55 (d, *J* = 8.3 Hz, 4H), 7.33 – 6.93 (m, 17H), 5.05 (s, 2H), 4.90 (s, 2H), 4.22 (s, 4H), 3.78 – 3.49 (m, 6H), 3.41 – 3.27 (m, 2H), 3.27 – 3.13 (m, 2H), 3.05 (d, *J* = 10.1 Hz, 2H), 2.28 (s, 6H), 2.23 – 2.05 (m, 2H), 1.74 – 1.54 (m, 2H).

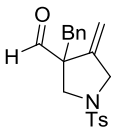
^{13}C NMR (75 MHz, $CDCl_3$) δ 196.9, 144.3, 144.0, 137.7, 132.2, 129.7, 128.4, 128.0, 127.8, 127.7, 110.9, 73.2, 66.2, 59.1, 51.9, 51.7, 34.3, 21.6.

HRMS calculated for $C_{22}H_{25}O_4NSNa$: 422.13965 ; found : 422.13984.

IR (neat, cm^{-1}) 2854, 1731, 1652, 1337, 1163, 1109, 1094, 920.

mp 94-95°C

3-benzyl-4-methylene-1-tosylpyrrolidine-3-carbaldehyde (54) :



^{1}H NMR (300 MHz, $CDCl_3$) δ 9.30 (s, 1H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.04 (m, 5H), 7.01 – 6.87 (m, 2H), 5.21 (s, 1H), 5.04 (s, 1H), 3.79 – 3.57 (m, 2H), 3.46 (d, *J* = 10.2 Hz, 1H), 3.17 (d, *J* = 10.2 Hz, 1H), 3.15 (d, *J* = 14.0 Hz, 1H), 2.76 (d, *J* = 14.0 Hz, 1H), 2.36 (s, 3H).

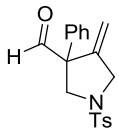
^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 144.1, 144.0, 135.6, 131.9, 129.8, 129.7, 128.5, 127.9, 127.0, 111.4, 61.33, 52.3, 51.3, 39.3, 21.5.

HRMS calculated for $C_{20}H_{21}O_3NSNa$: 378.11344 ; found : 378.11393.

IR (neat, cm^{-1}) 1725, 1660, 1334, 1161, 1095, 1045, 916.

mp 116-117°C

4-methylene-3-phenyl-1-tosylpyrrolidine-3-carbaldehyde (56) :



^{1}H NMR (300 MHz, $CDCl_3$) δ 9.37 (s, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.17 (m, 5H), 7.11 – 7.02 (m, 2H), 5.46 (s, 1H), 5.18 – 4.91 (m, 1H), 4.15 (d, *J* = 9.9 Hz, 1H), 4.03 – 3.73 (m, 2H), 3.21 (d, *J* = 9.9 Hz, 1H), 2.37 (s, 3H).

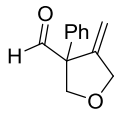
^{13}C NMR (75 MHz, $CDCl_3$) δ 194.3, 144.0, 143.0, 136.6, 132.3, 129.8, 129.3, 128.2, 128.0, 127.5, 113.9, 65.9, 54.8, 52.7, 21.6.

HRMS calculated for $C_{19}H_{19}O_3NSNa$: 364.09779 ; found : 364.09811.

IR (neat, cm^{-1}) 3053, 2920, 1718, 1657, 1339, 1167, 1094, 1036, 906.

mp 117-118°C

4-methylene-3-phenyltetrahydrofuran-3-carbaldehyde (58) :



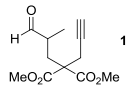
^{1}H NMR (300 MHz, C_6D_6) δ 9.27 (d, *J* = 1.1 Hz, 1H), 7.11 – 6.93 (m, 6H), 4.90 (t, *J* = 1.9 Hz, 1H), 4.79 (d, *J* = 8.9 Hz, 1H), 4.70 (t, *J* = 2.3 Hz, 1H), 4.18 (dt, *J* = 13.2, 1.9 Hz, 1H), 4.06 (dt, *J* = 13.2, 2.2 Hz, 1H), 3.58 (d, *J* = 8.9 Hz, 1H).

^{13}C NMR (75 MHz, C_6D_6) δ 194.5, 147.6, 137.6, 129.1, 129.0, 127.7, 110.1, 75.2, 72.3, 67.2.

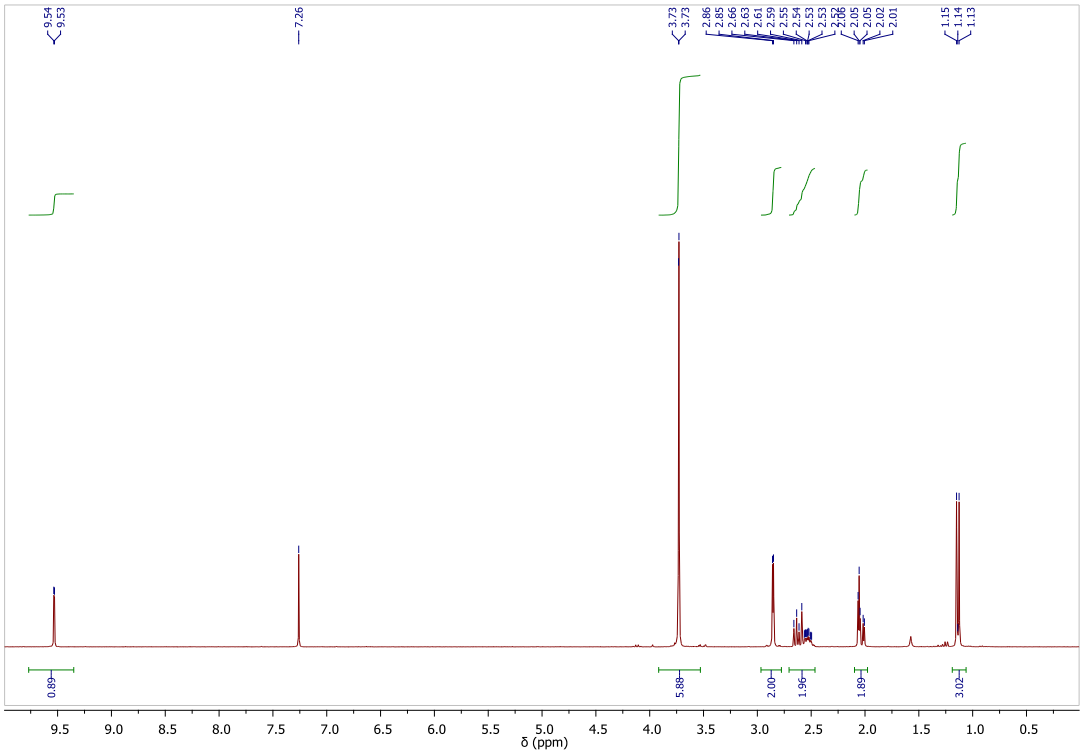
HRMS calculated for $C_{12}H_{12}O_2Na$: 211.07295 ; found : 211.07291.

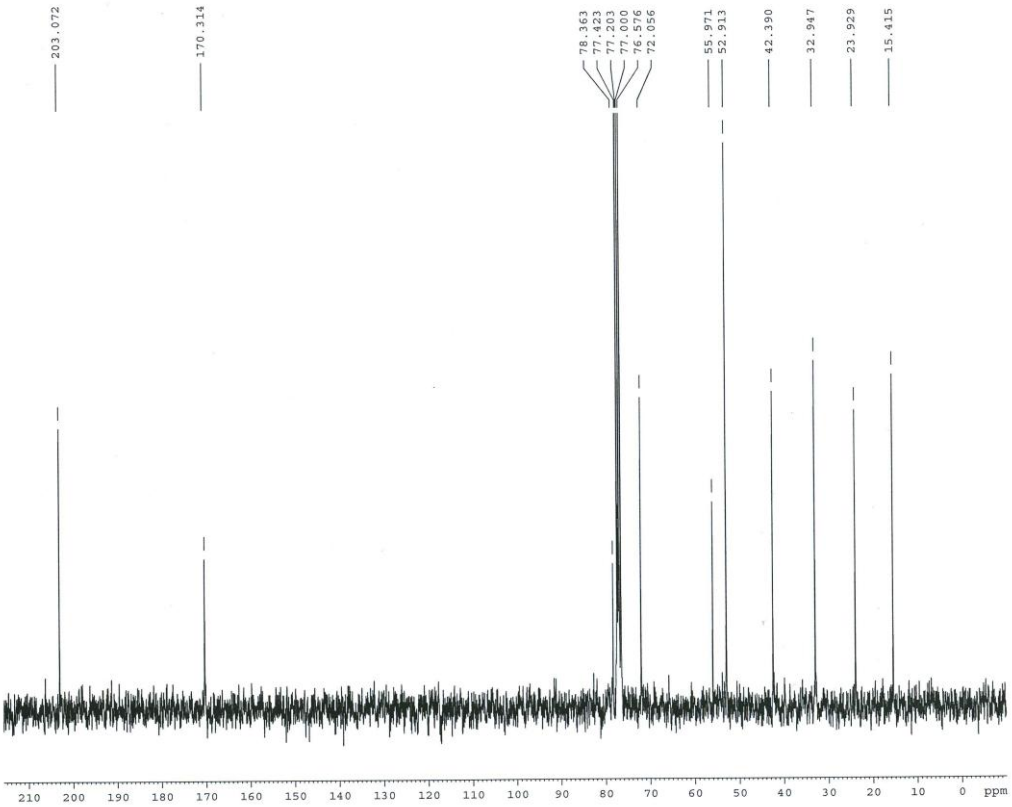
IR (neat, cm^{-1}) 2858, 1724, 1658, 1264, 1069, 924.

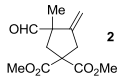
D. Copies of ^{1}H and ^{13}C NMR Spectra



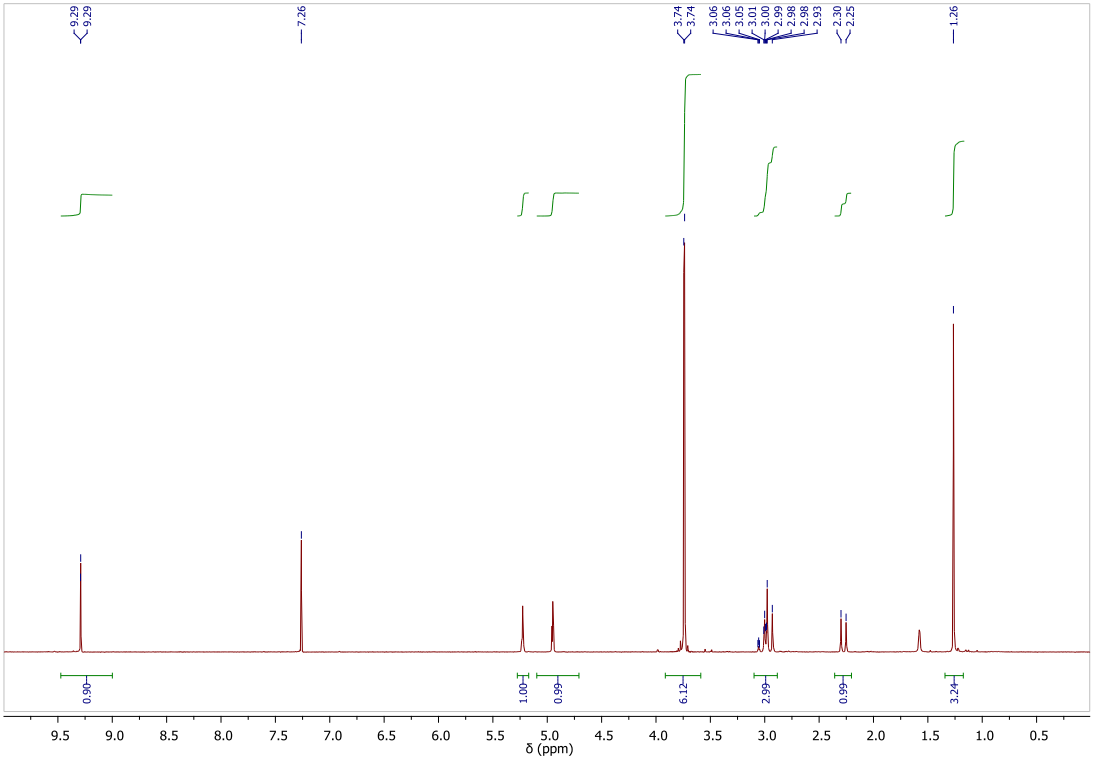
Chemical Formula: $C_{12}H_{16}O_5$
Molecular Weight: 240,25244

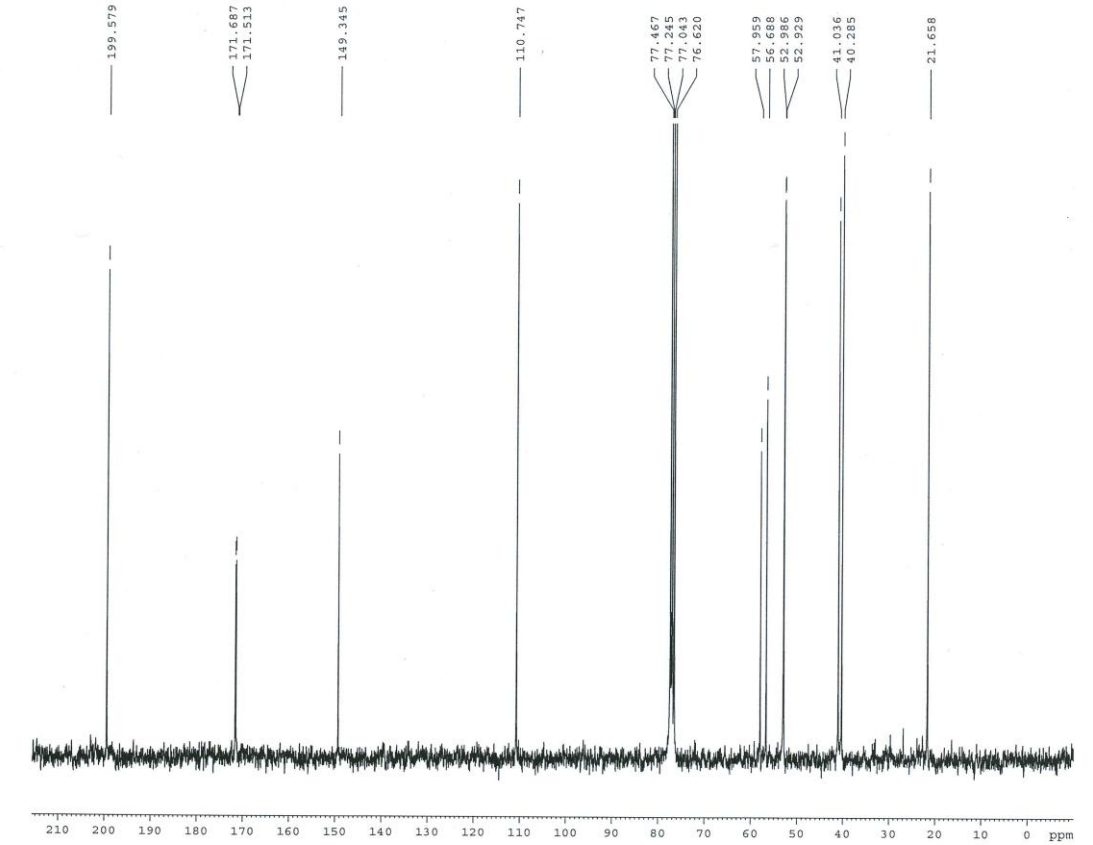


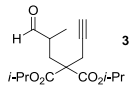




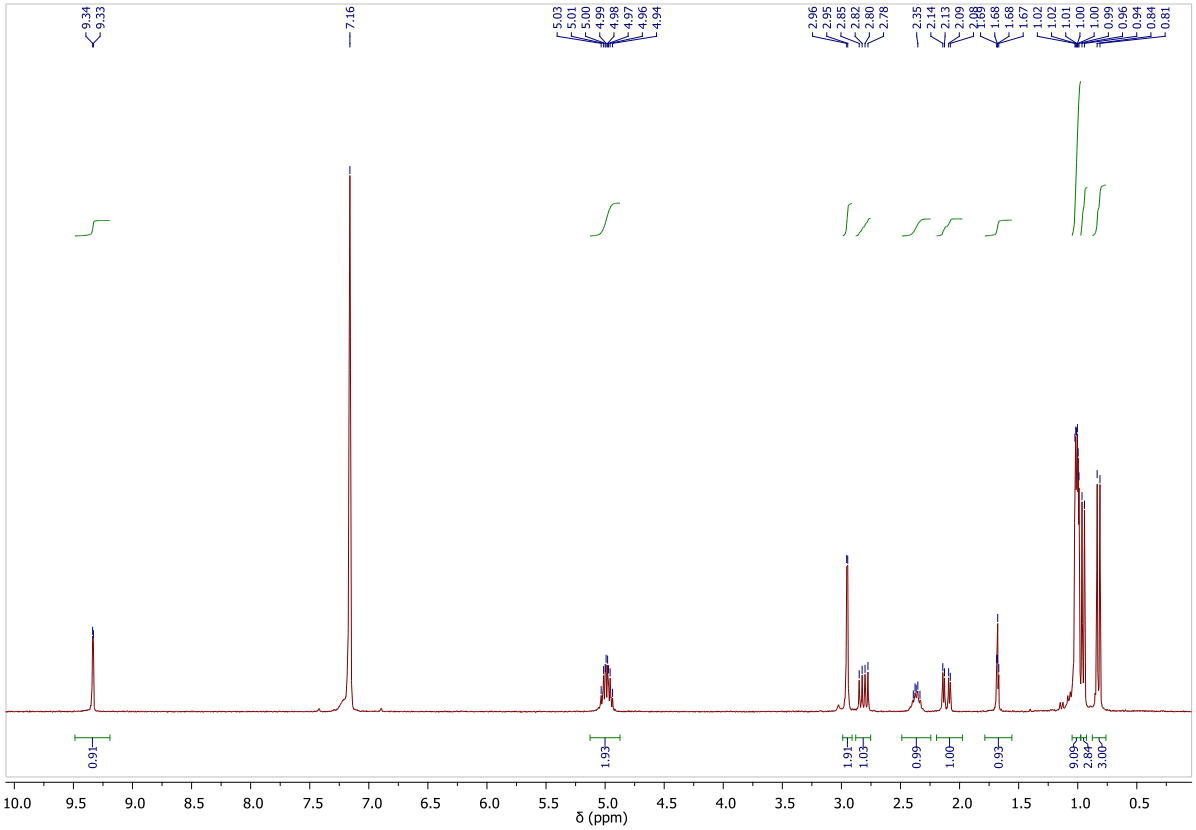
Chemical Formula: $C_{12}H_{16}O_5$
Molecular Weight: 240,25244

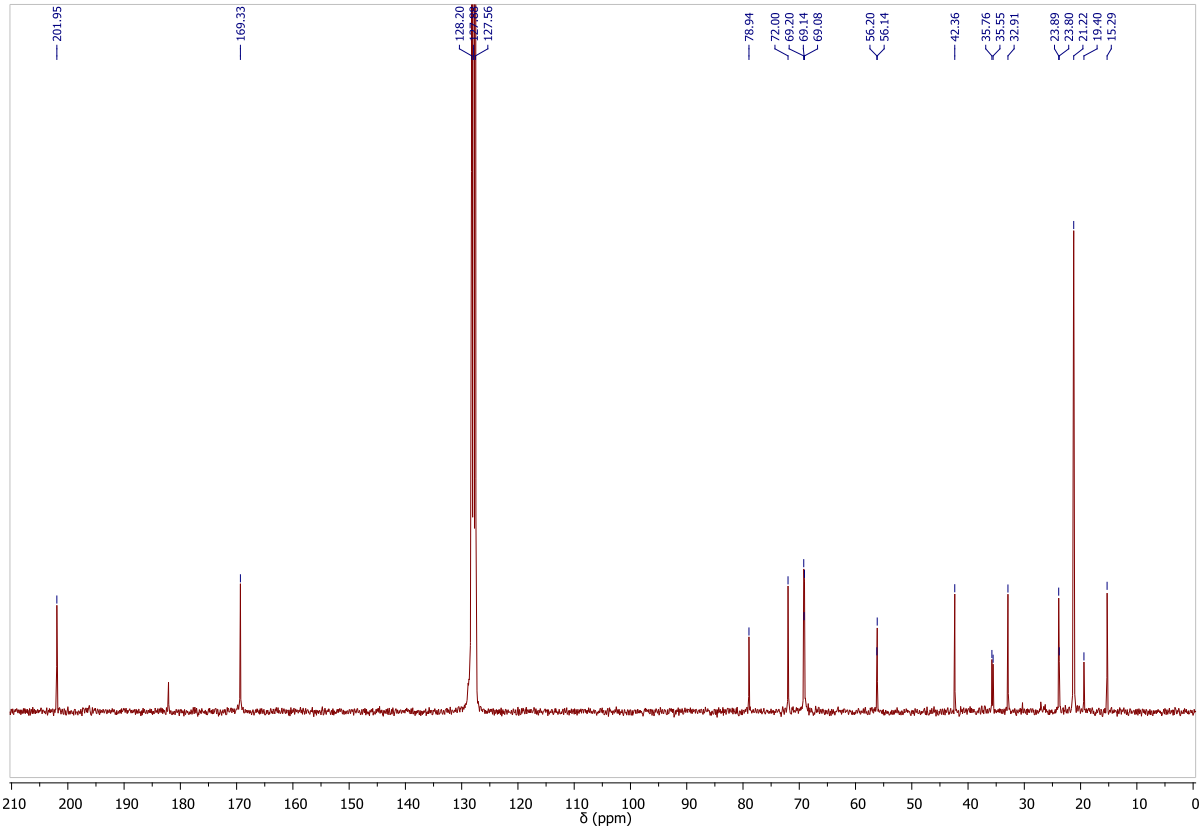


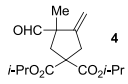




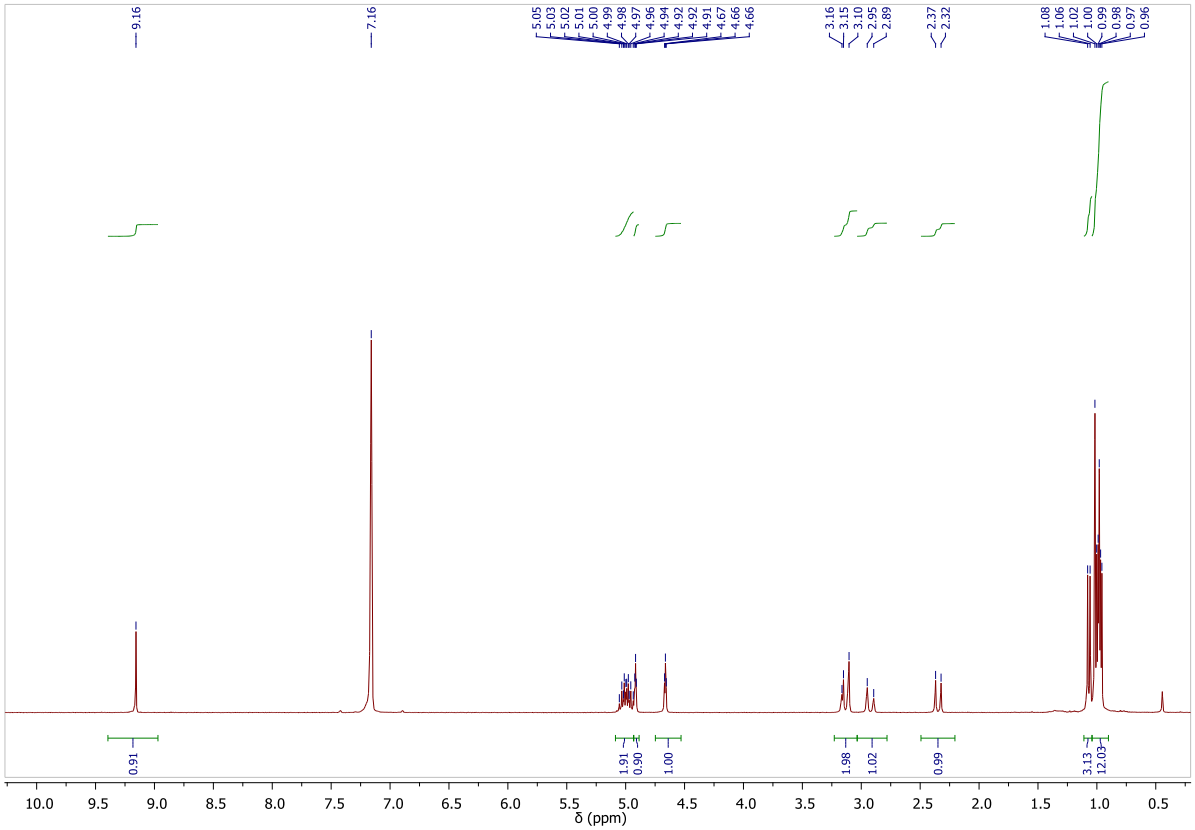
Chemical Formula: $C_{16}H_{24}O_5$
Molecular Weight: 296,35876

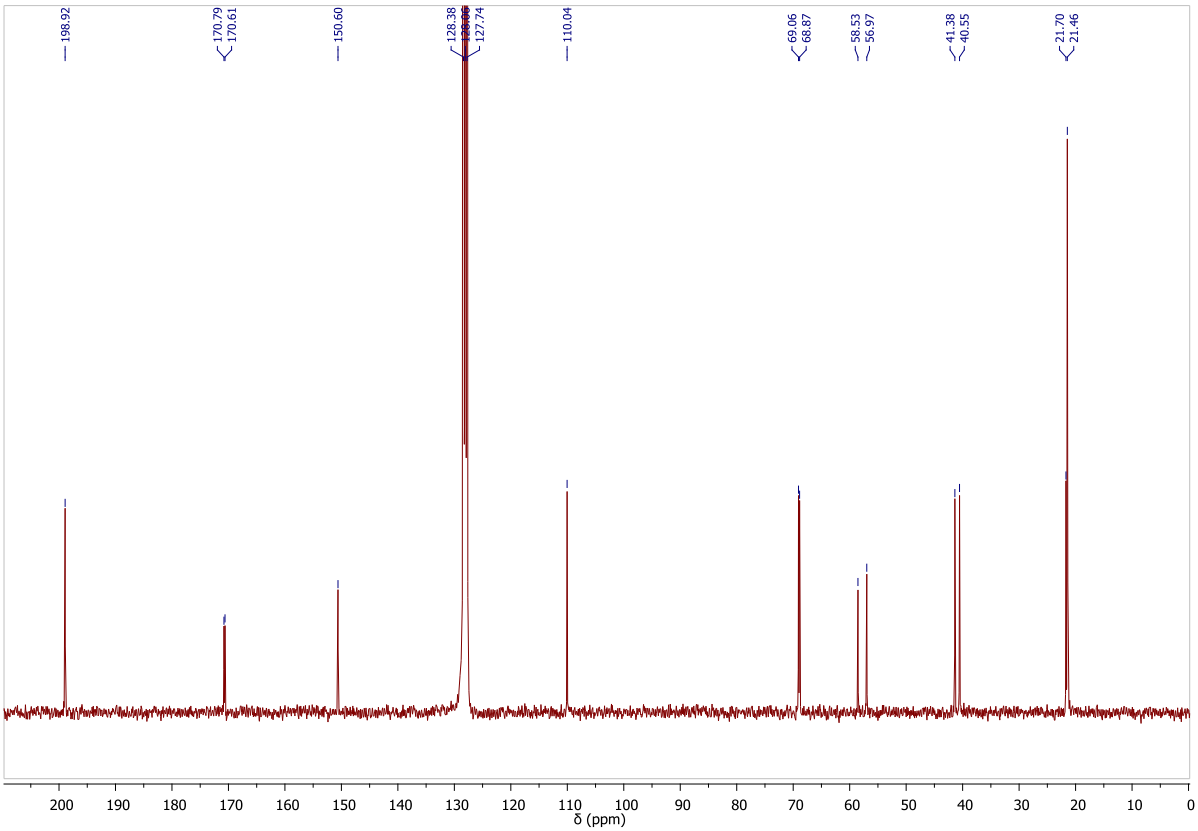


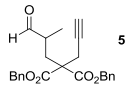




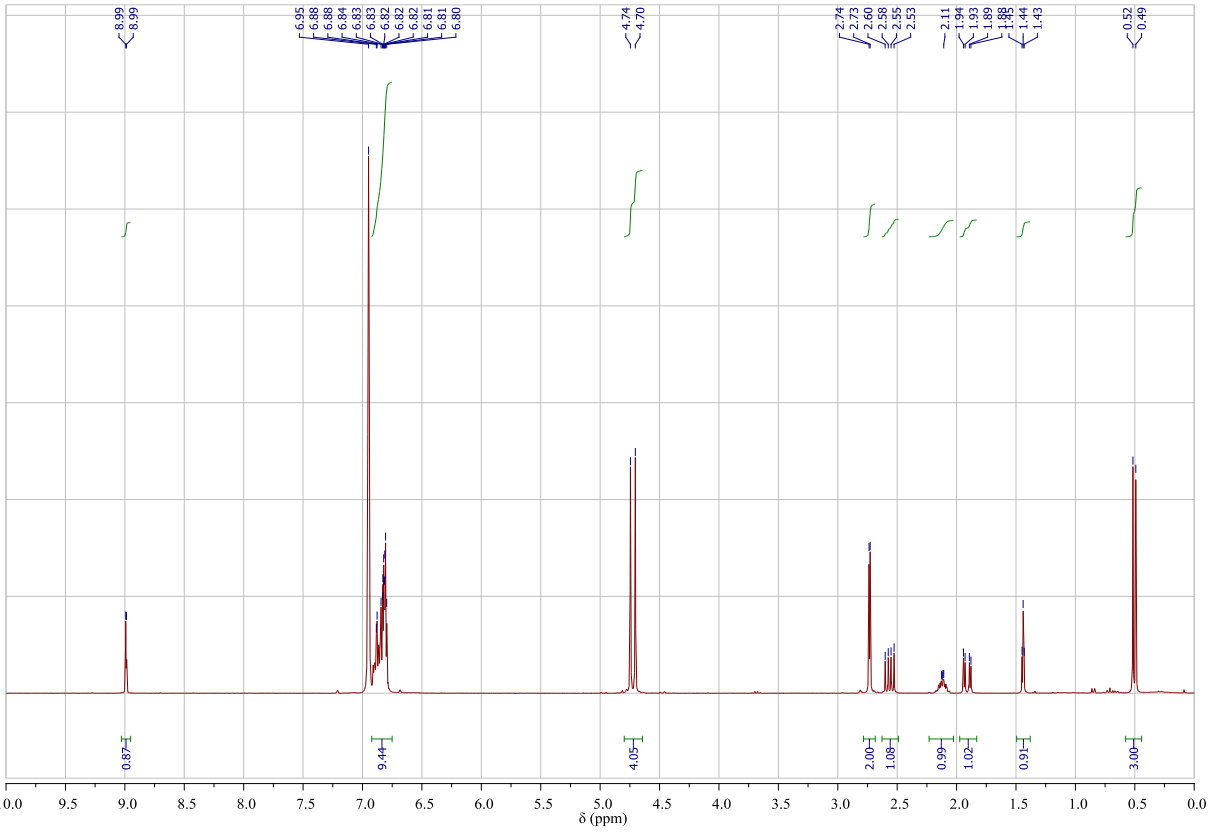
Chemical Formula: $C_{16}H_{24}O_5$
Molecular Weight: 296,35876

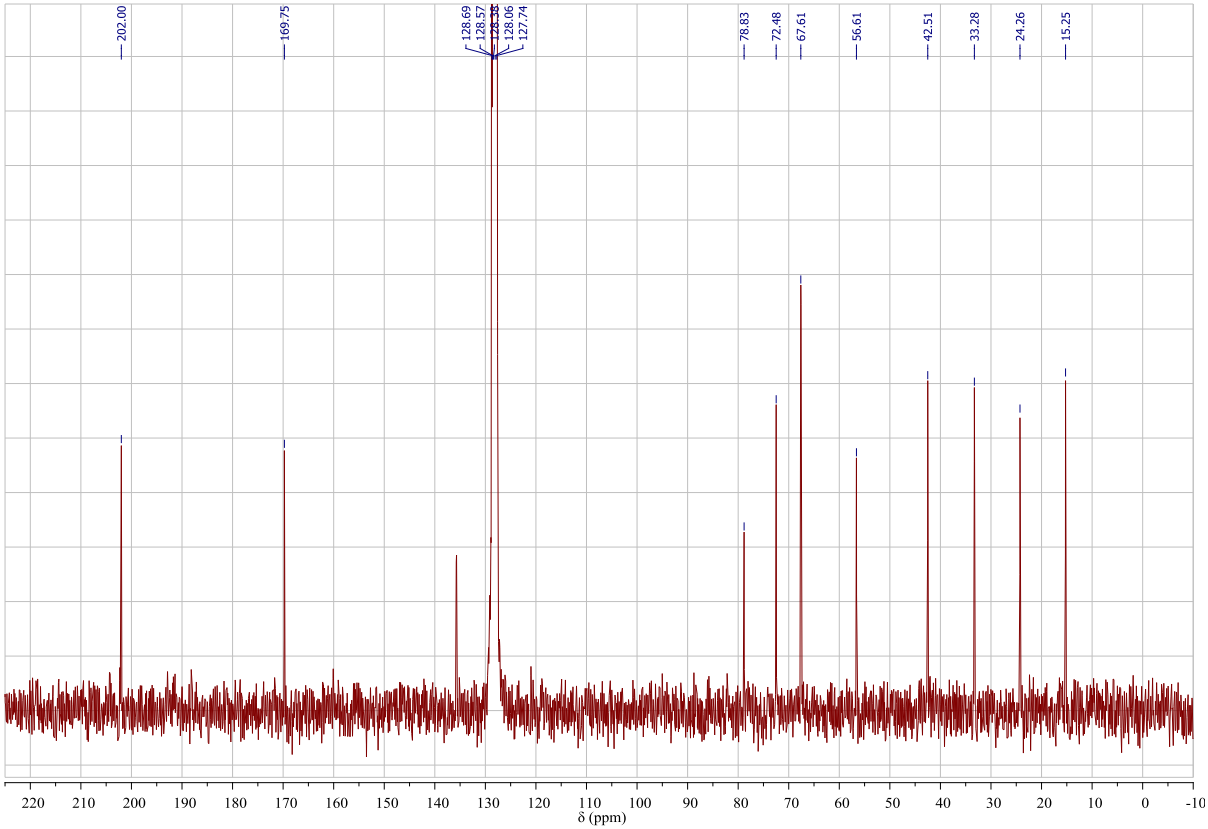


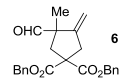




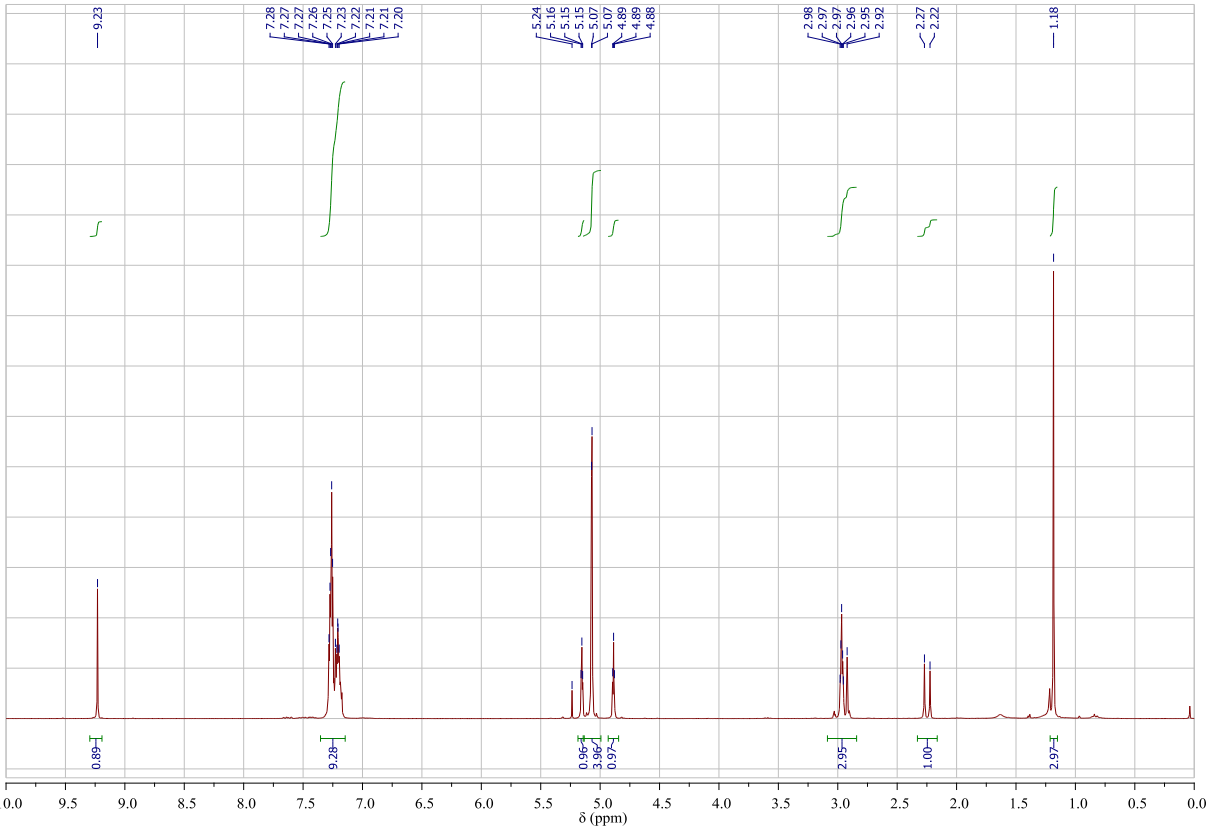
Chemical Formula: $C_{24}H_{24}O_5$
Molecular Weight: 392,44436

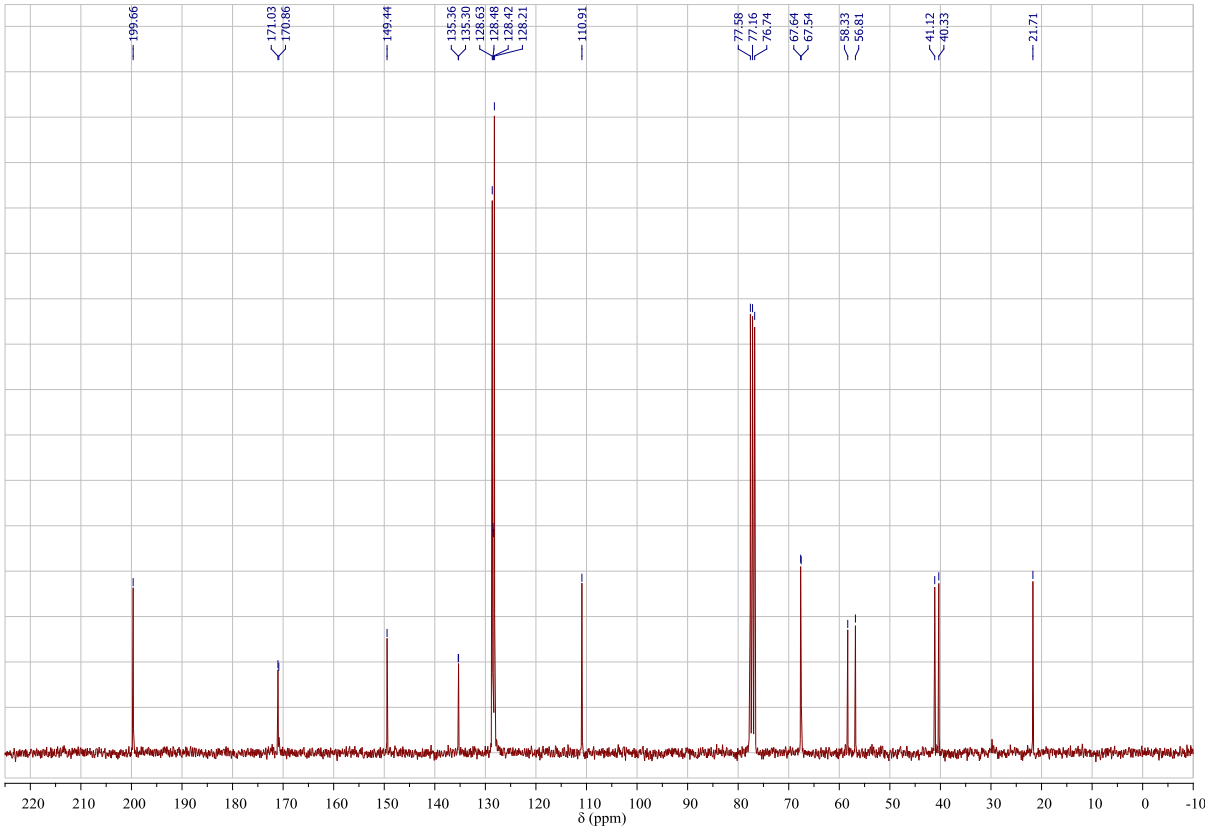


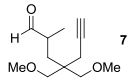




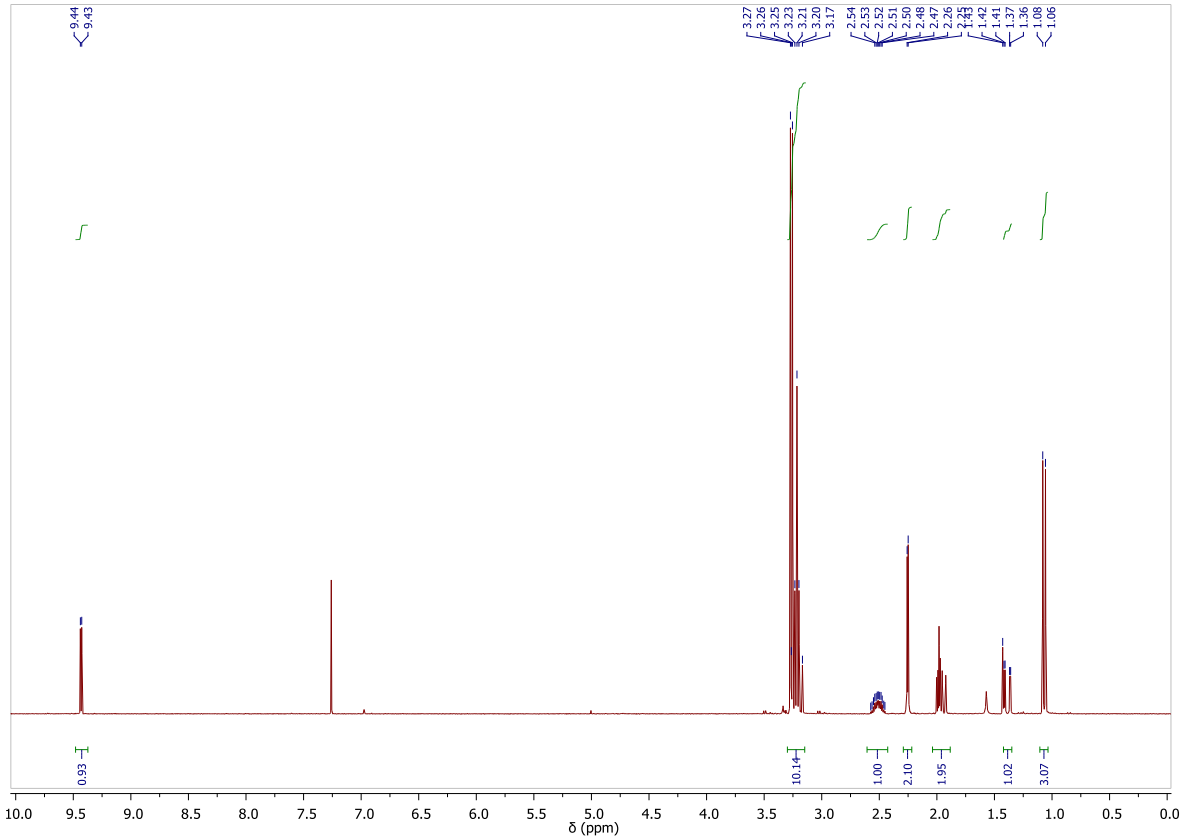
Chemical Formula: $C_{24}H_{24}O_5$
Molecular Weight: 392,44436

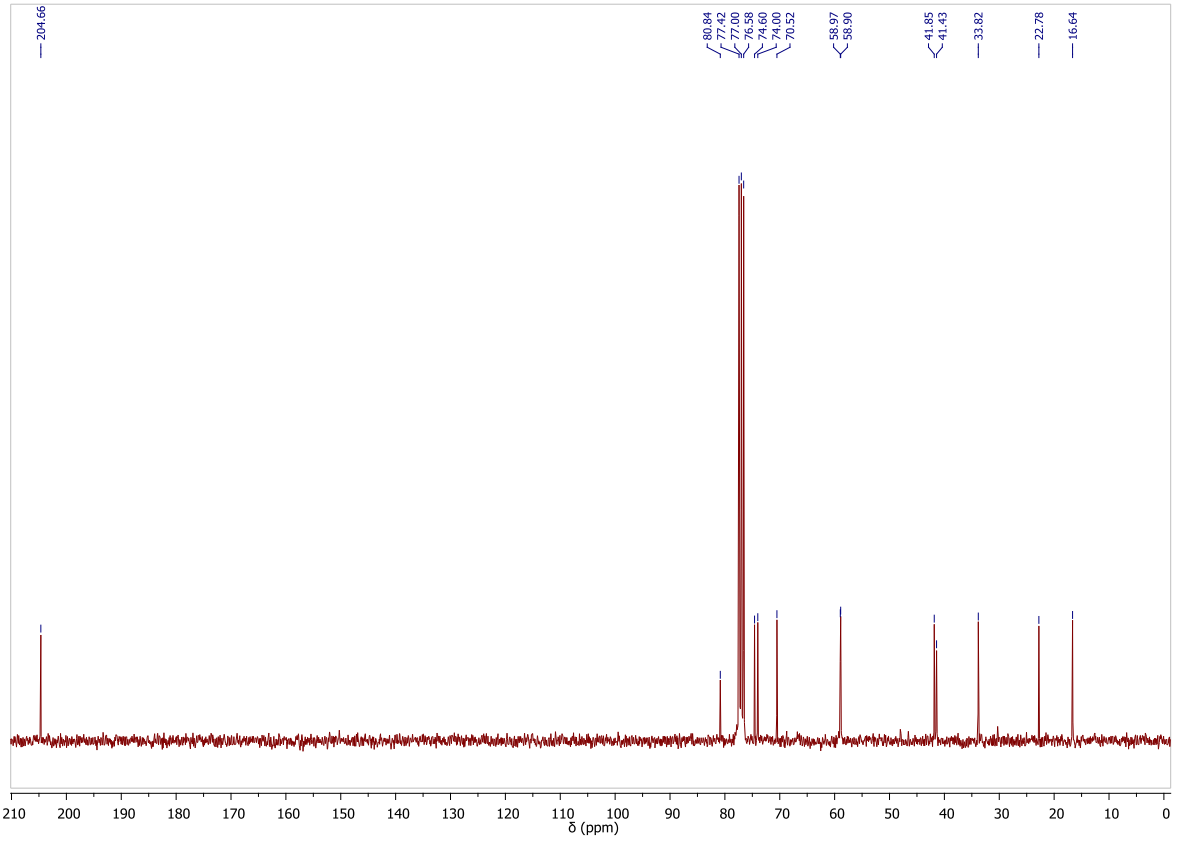


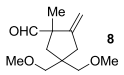




Chemical Formula: $C_{12}H_{20}O_3$
Molecular Weight: 212,28540







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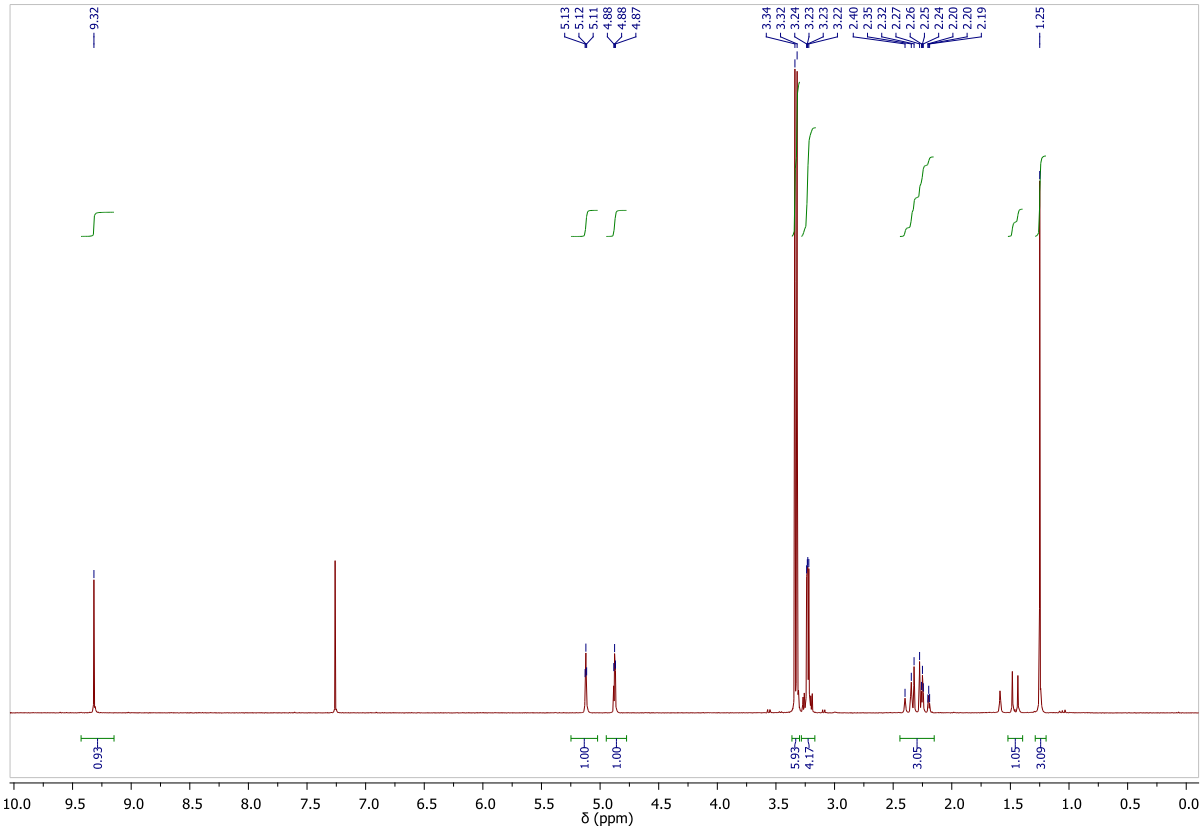
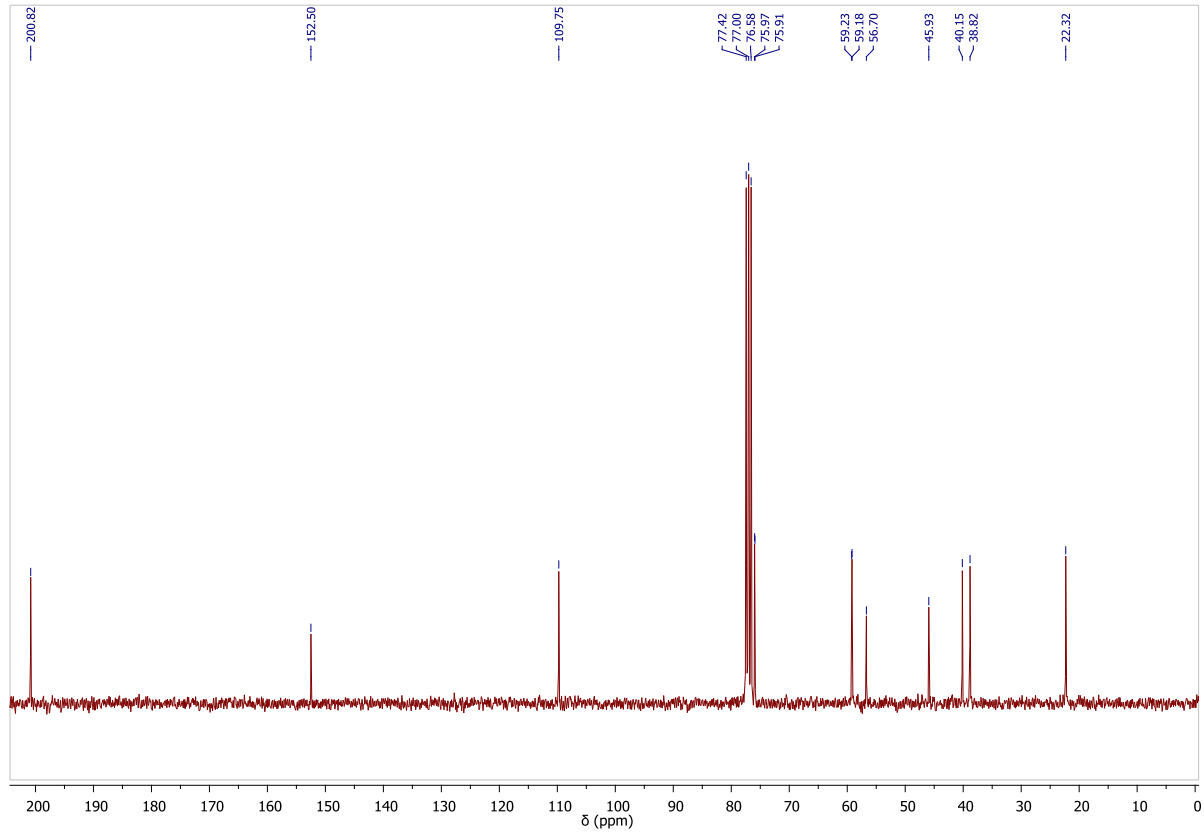
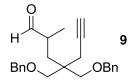
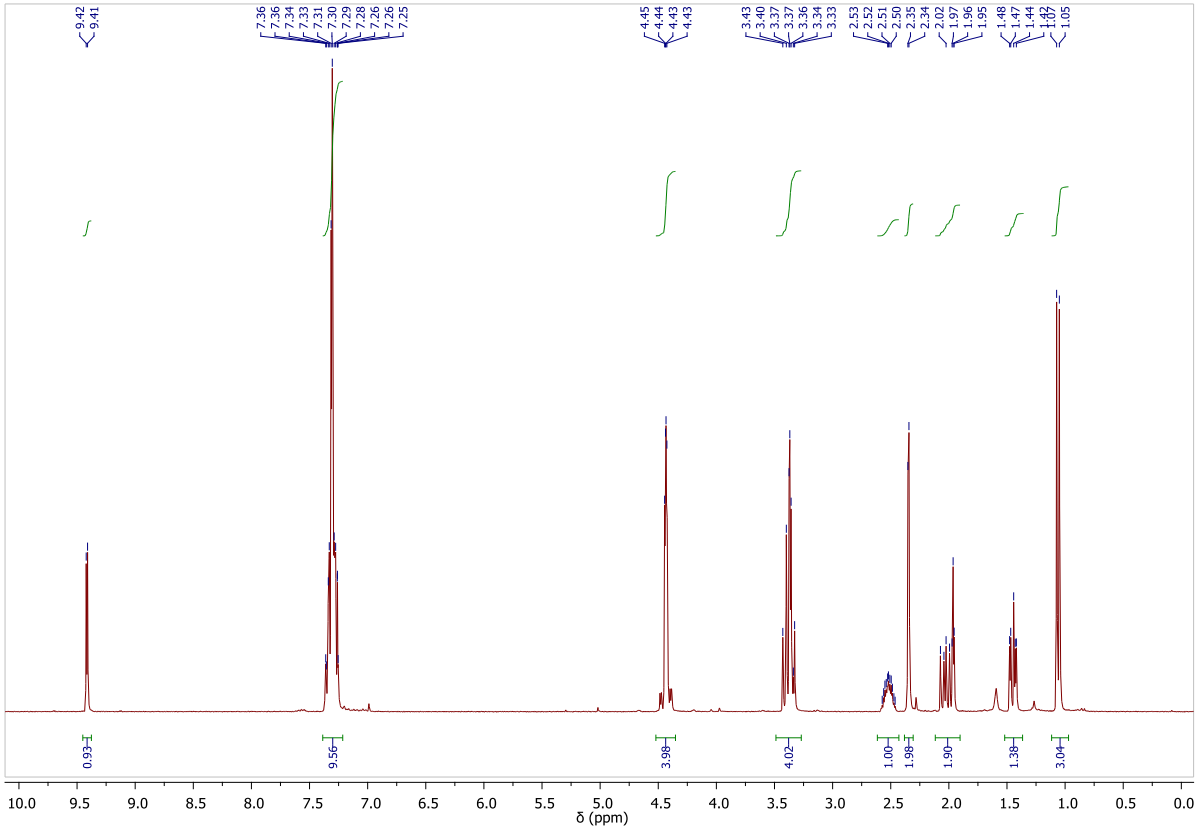
Chemical Formula: $C_{12}H_{20}O_3$
Molecular Weight: 212,28540

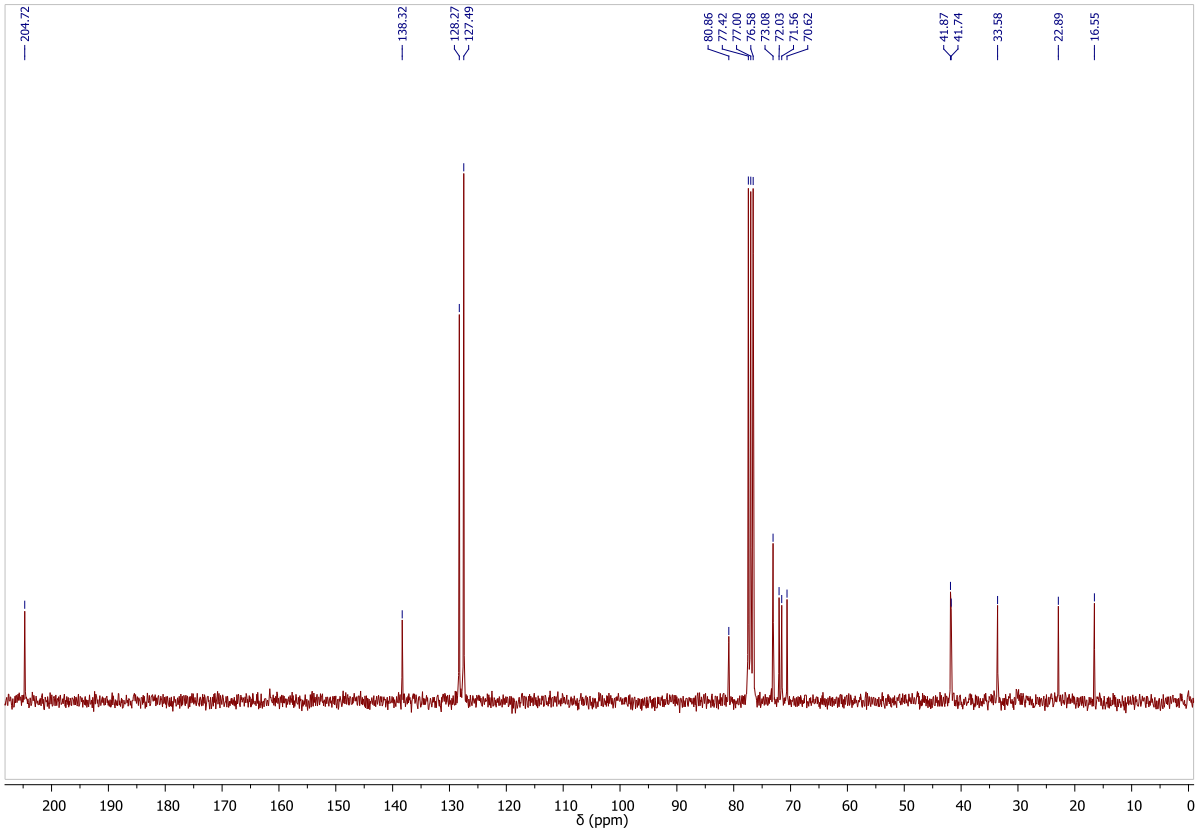


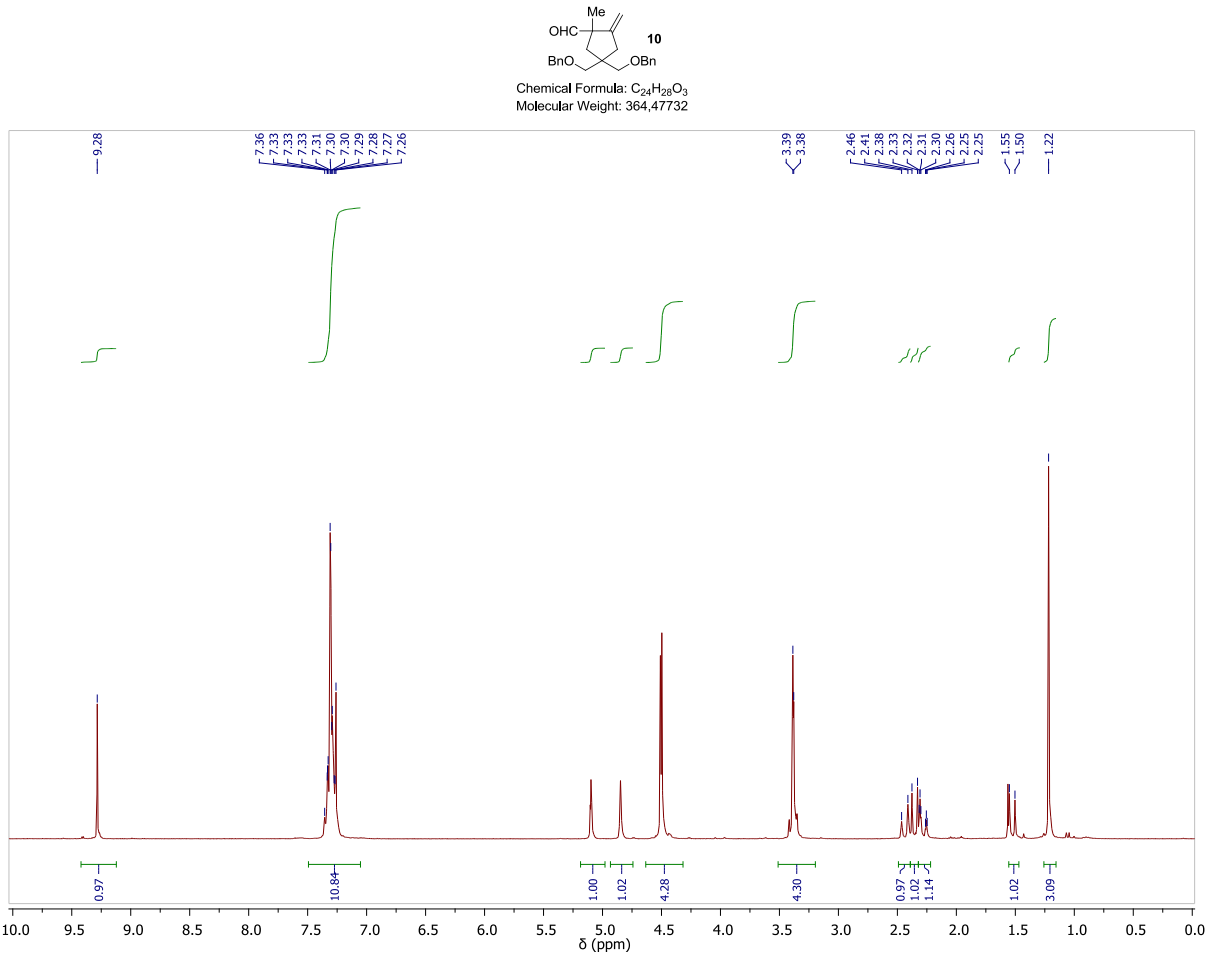




Chemical Formula: $C_{24}H_{28}O_3$
Molecular Weight: 364,47732






Me
OHC
10
BnO
OBn
Chemical Formula: C24H28O3
Molecular Weight: 364,47732
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7.36
7.33
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7.31
7.30
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7.28
7.27
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2.33
2.32
2.31
2.30
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2.25
2.25
1.55
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1.22
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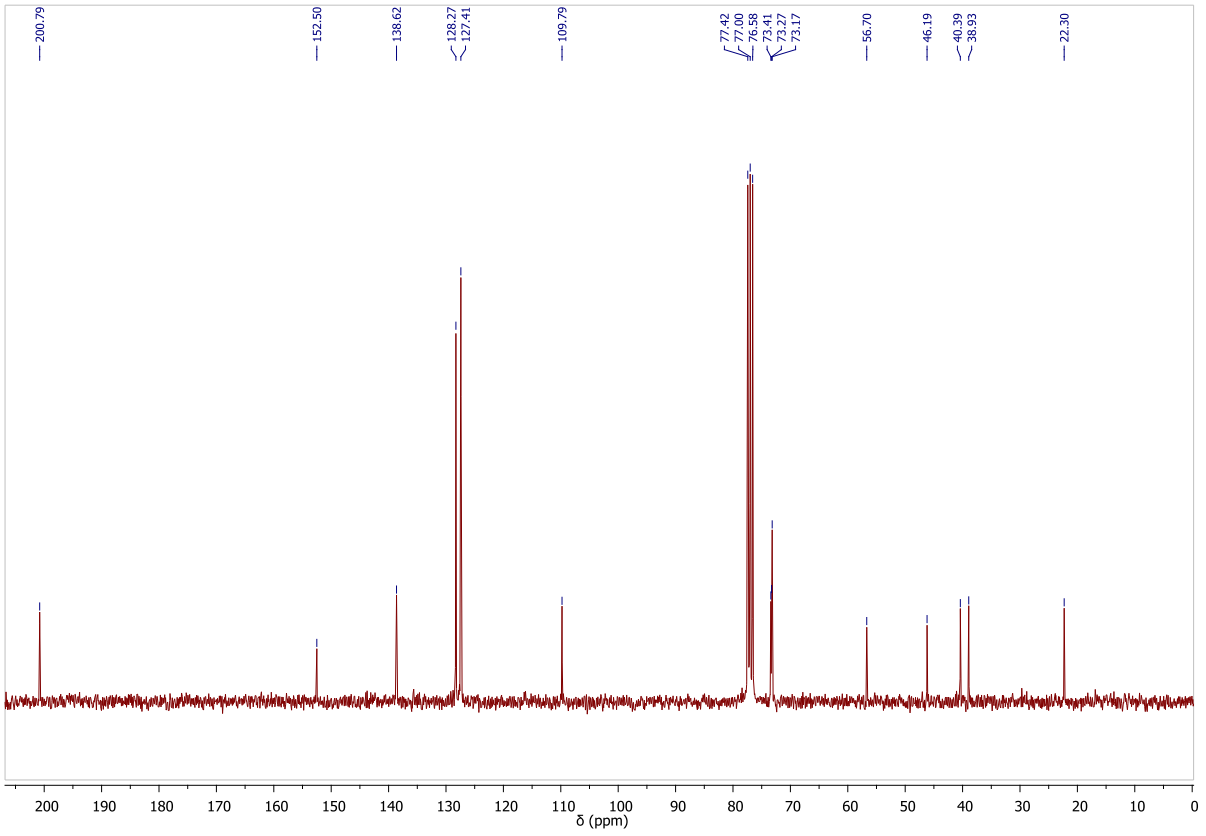
4.30
0.97
1.02
1.14
1.02
3.09
δ (ppm)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40.39
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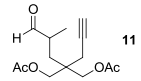
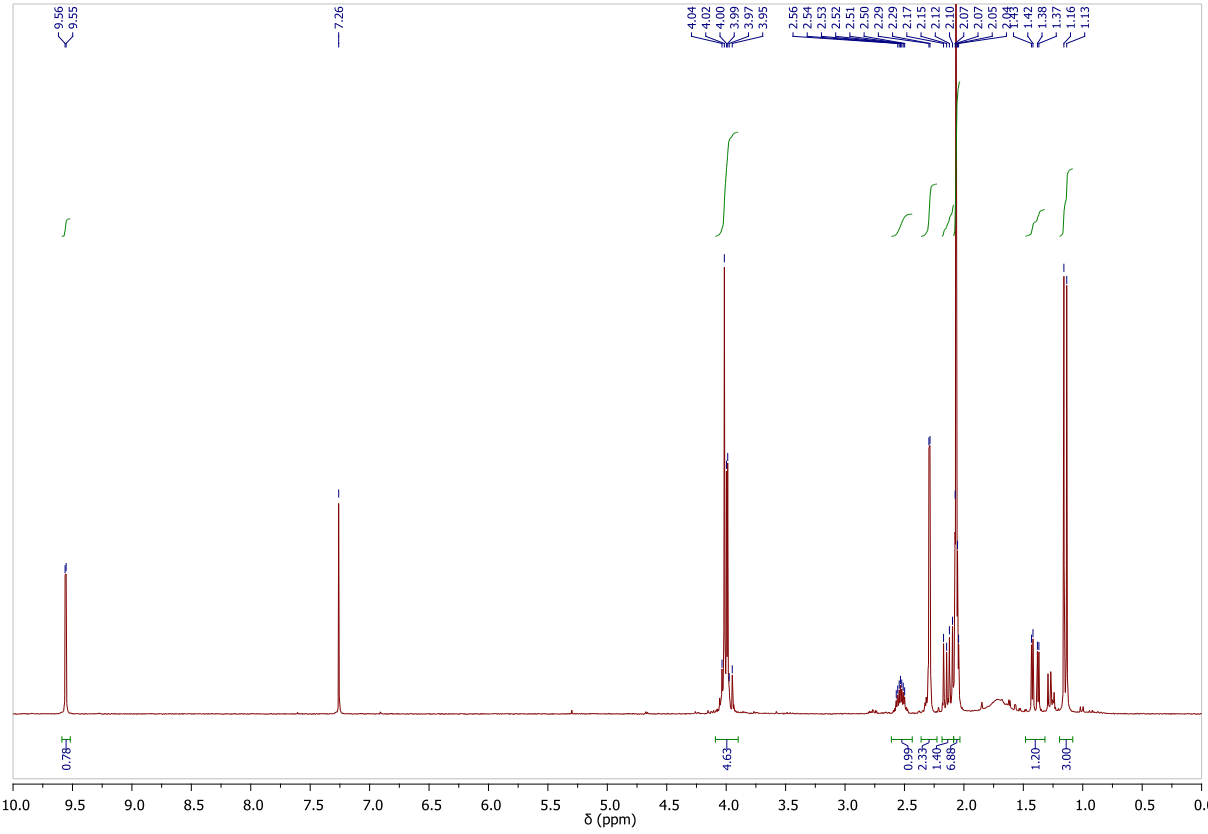
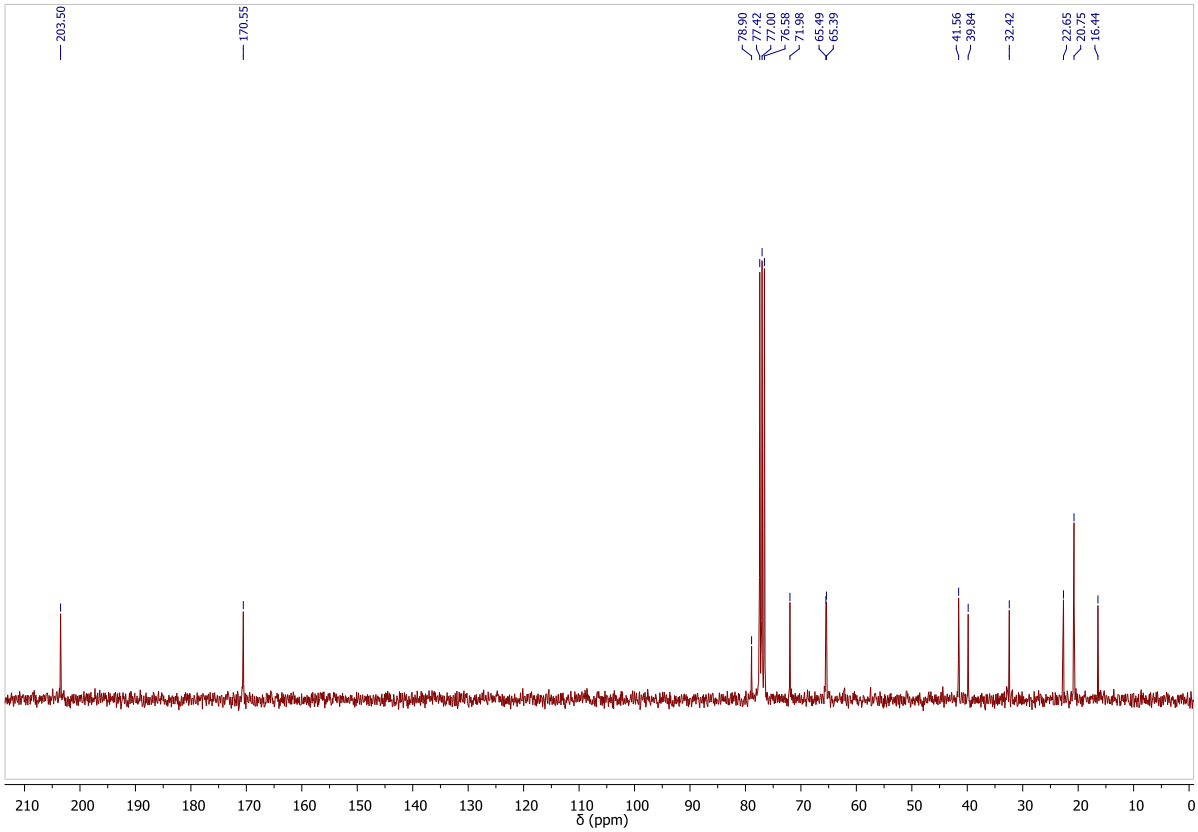
22.30
δ (ppm)

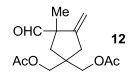


11

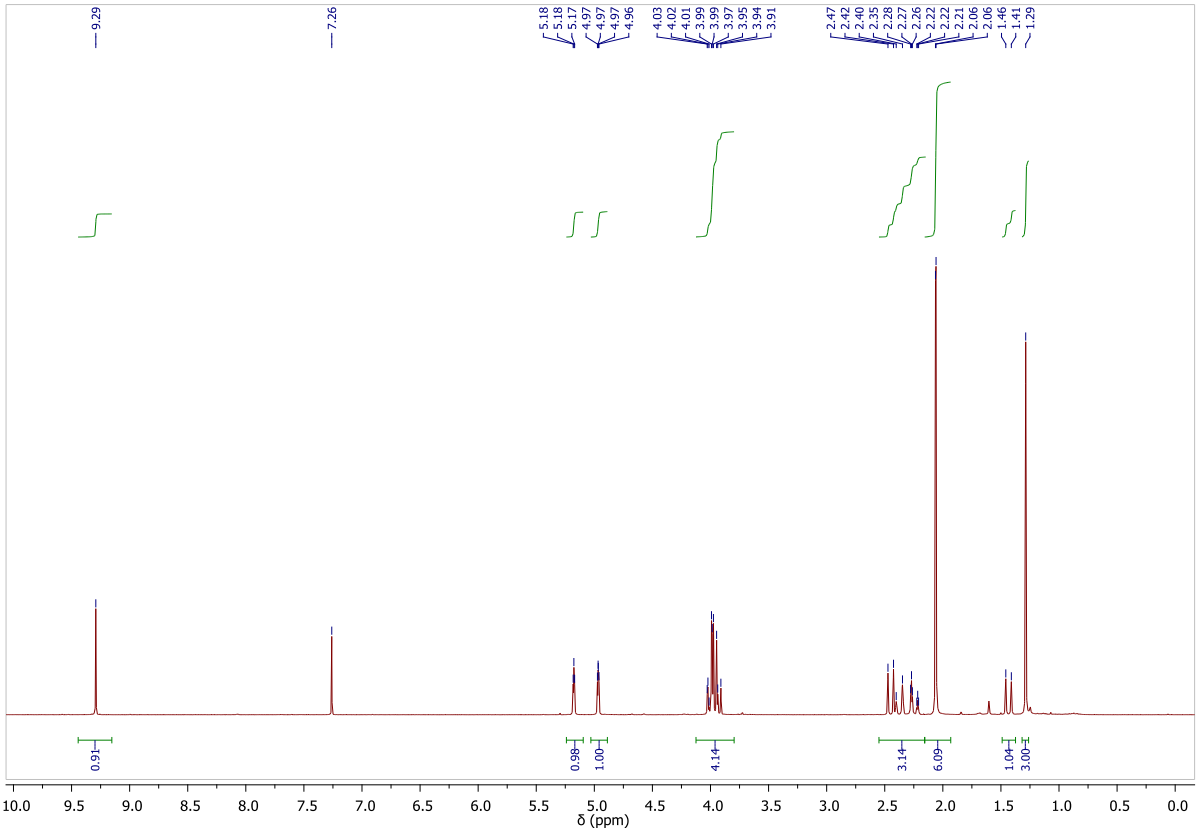
Chemical Formula: $C_{14}H_{20}O_5$
Molecular Weight: 268,30560

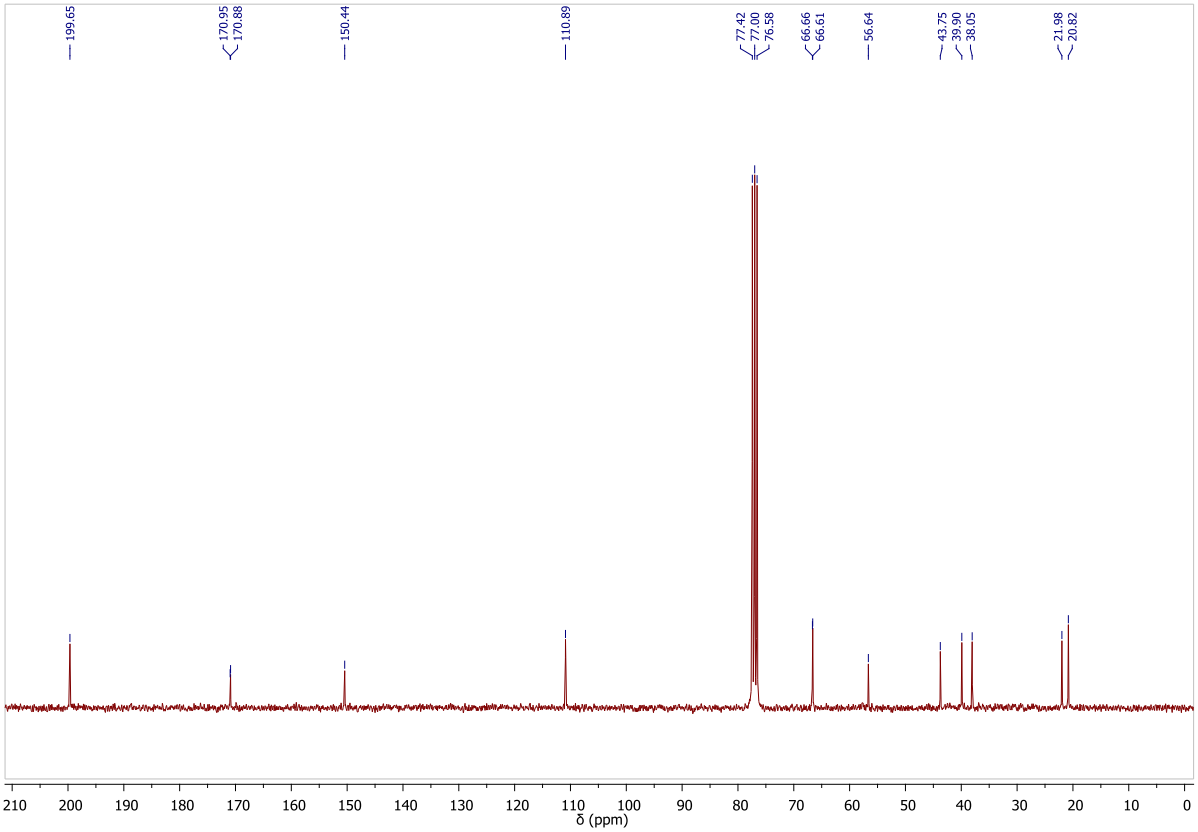


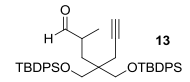




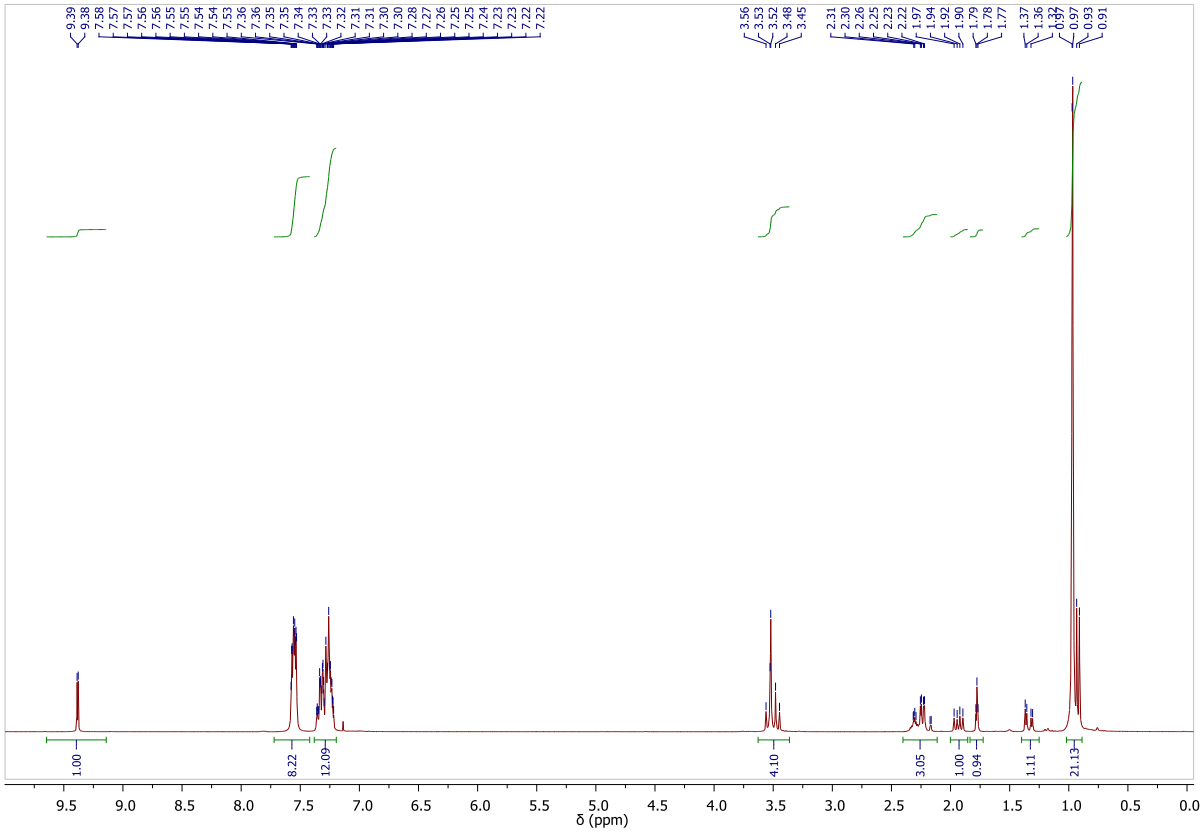
Chemical Formula: $C_{14}H_{20}O_5$
Molecular Weight: 268,30560

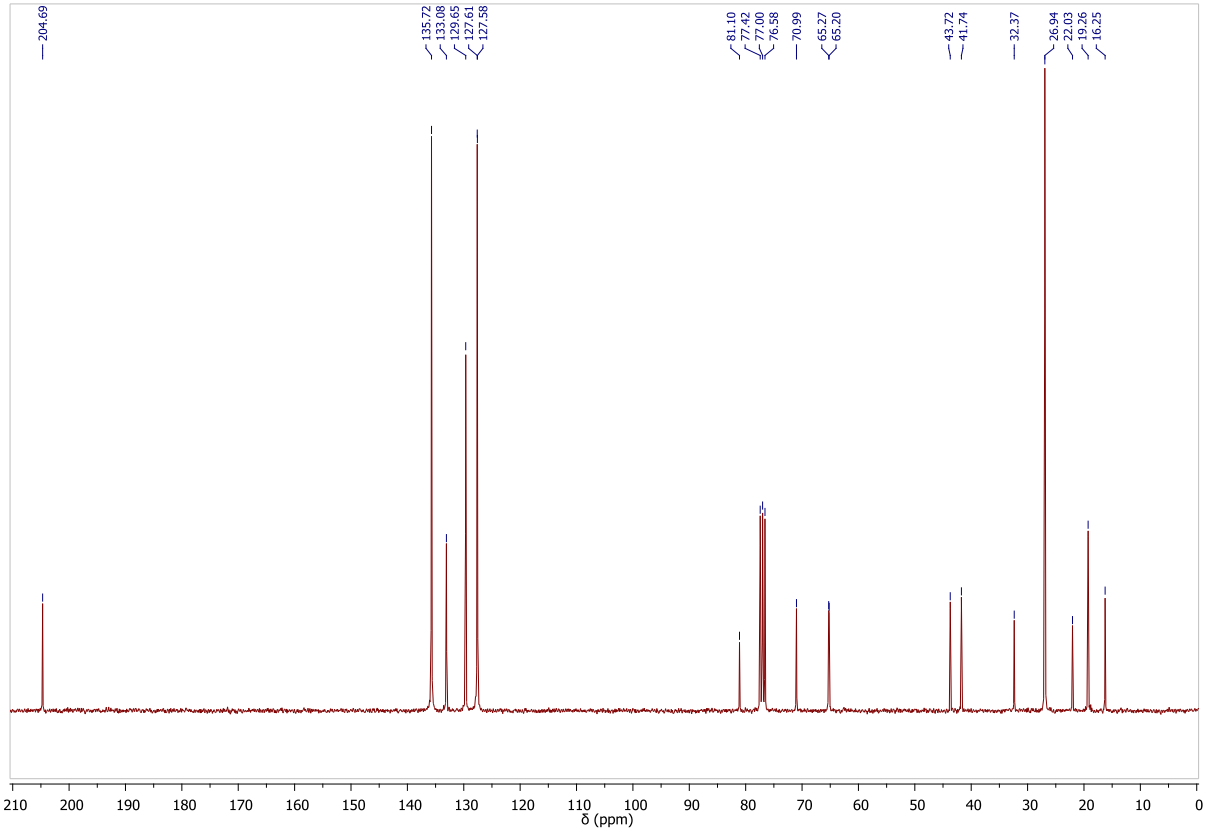


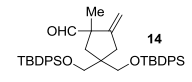




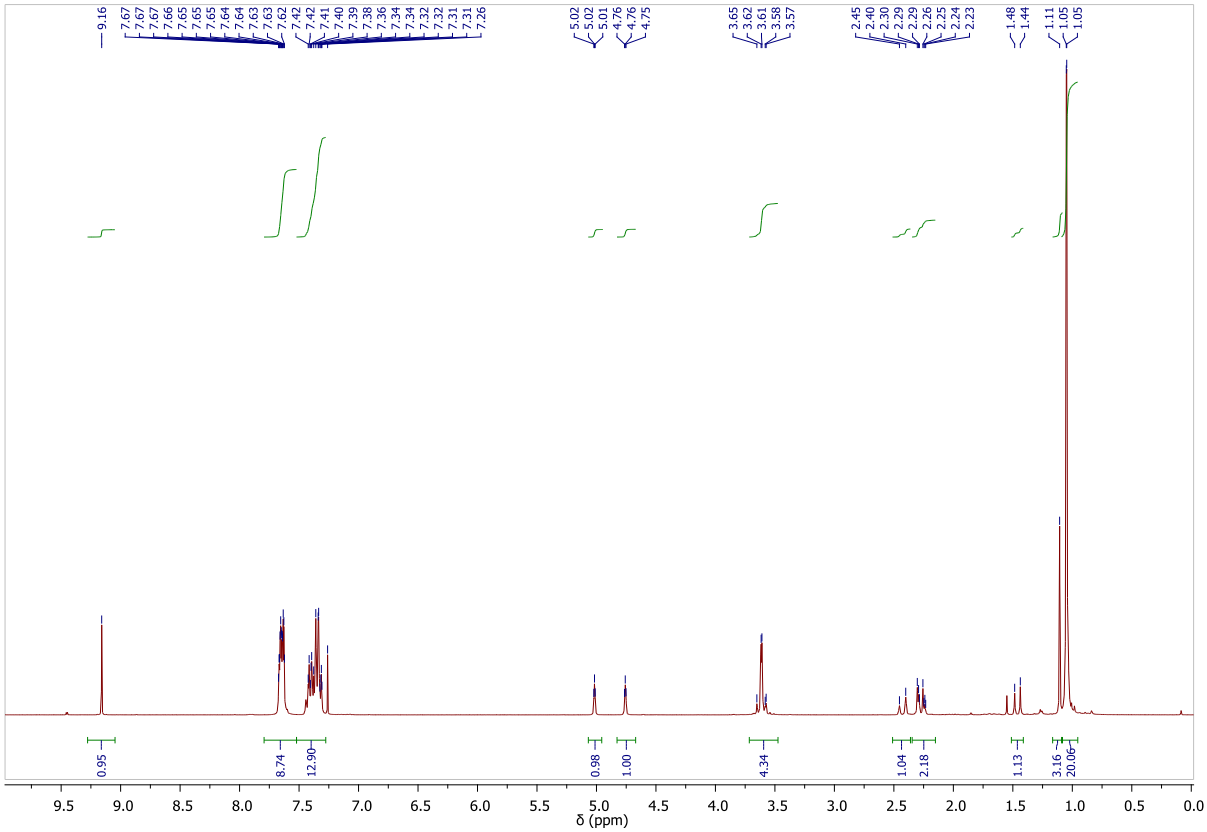
Chemical Formula: $C_{42}H_{52}O_3Si_2$
Molecular Weight: 661,03148

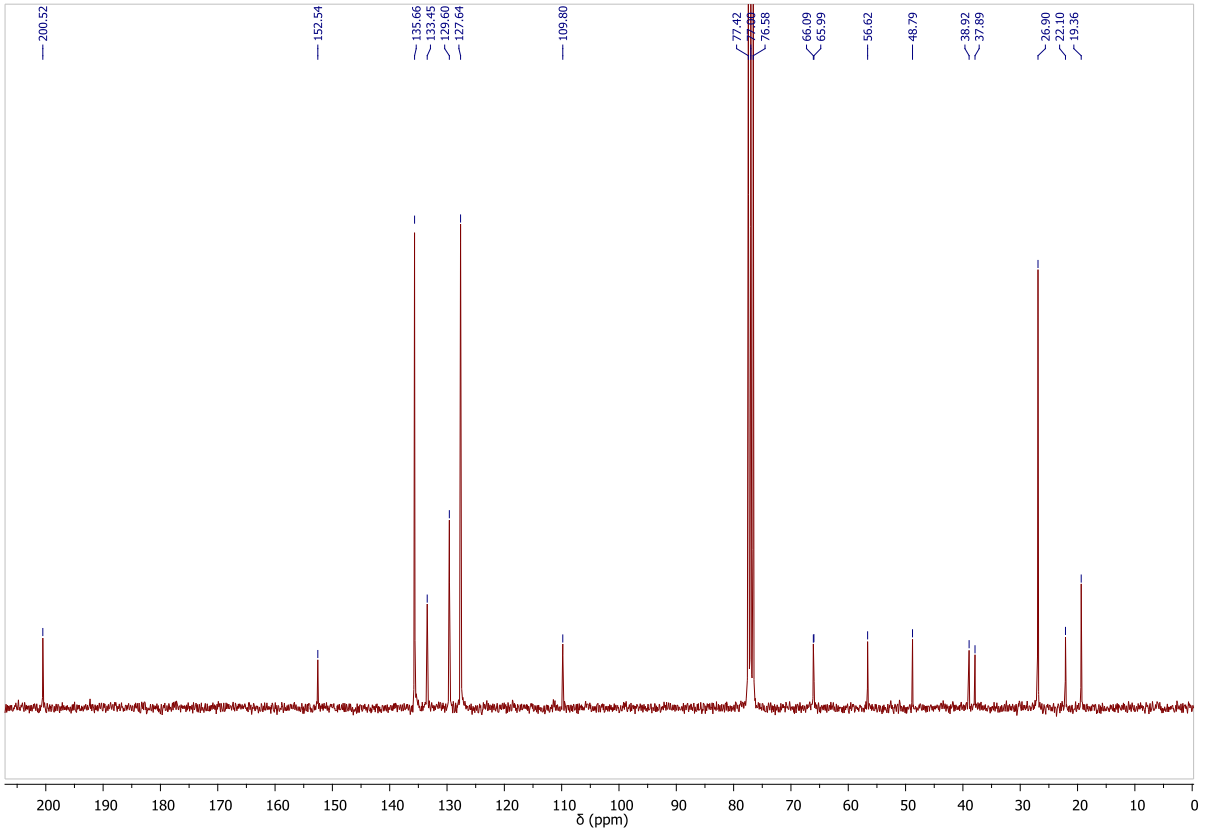


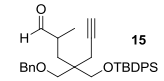




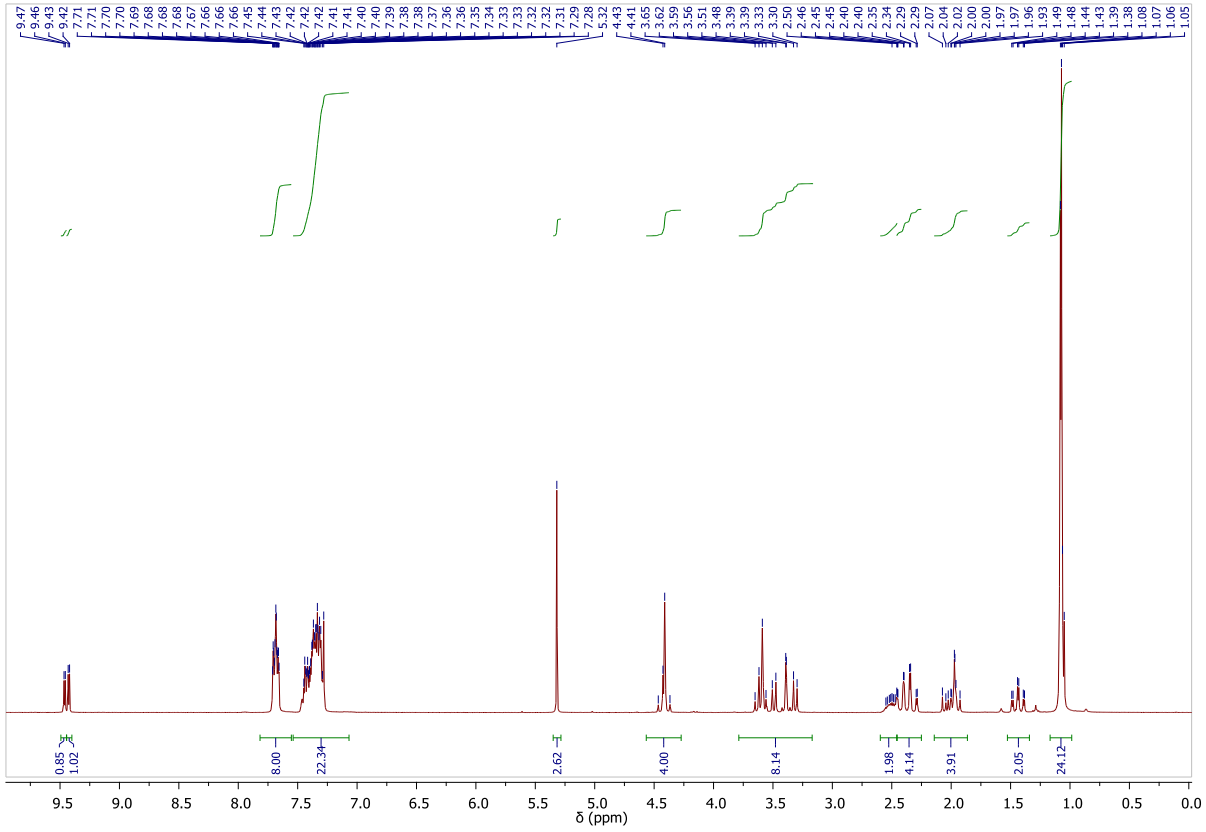
Chemical Formula: $C_{42}H_{52}O_3Si_2$
Molecular Weight: 661,03148

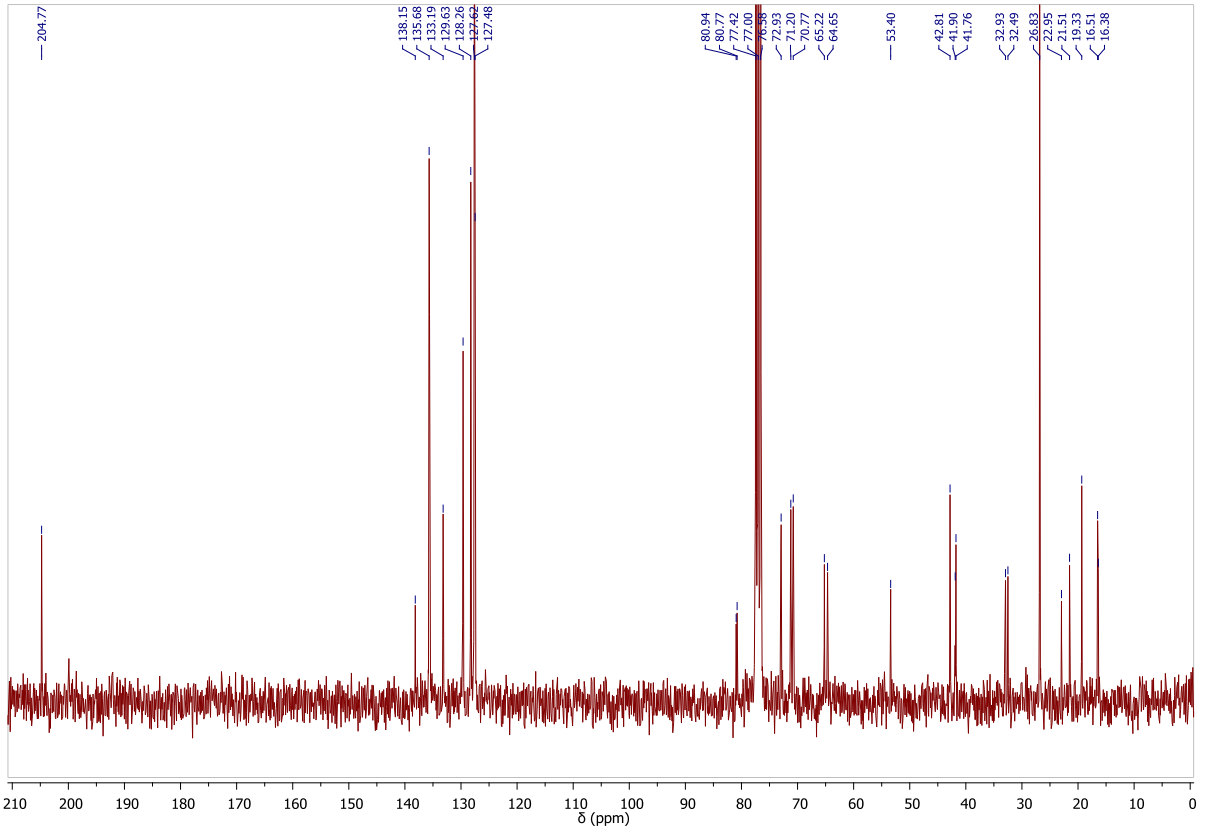


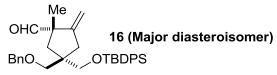




Chemical Formula: $C_{33}H_{40}O_3Si$
Molecular Weight: 512,75440

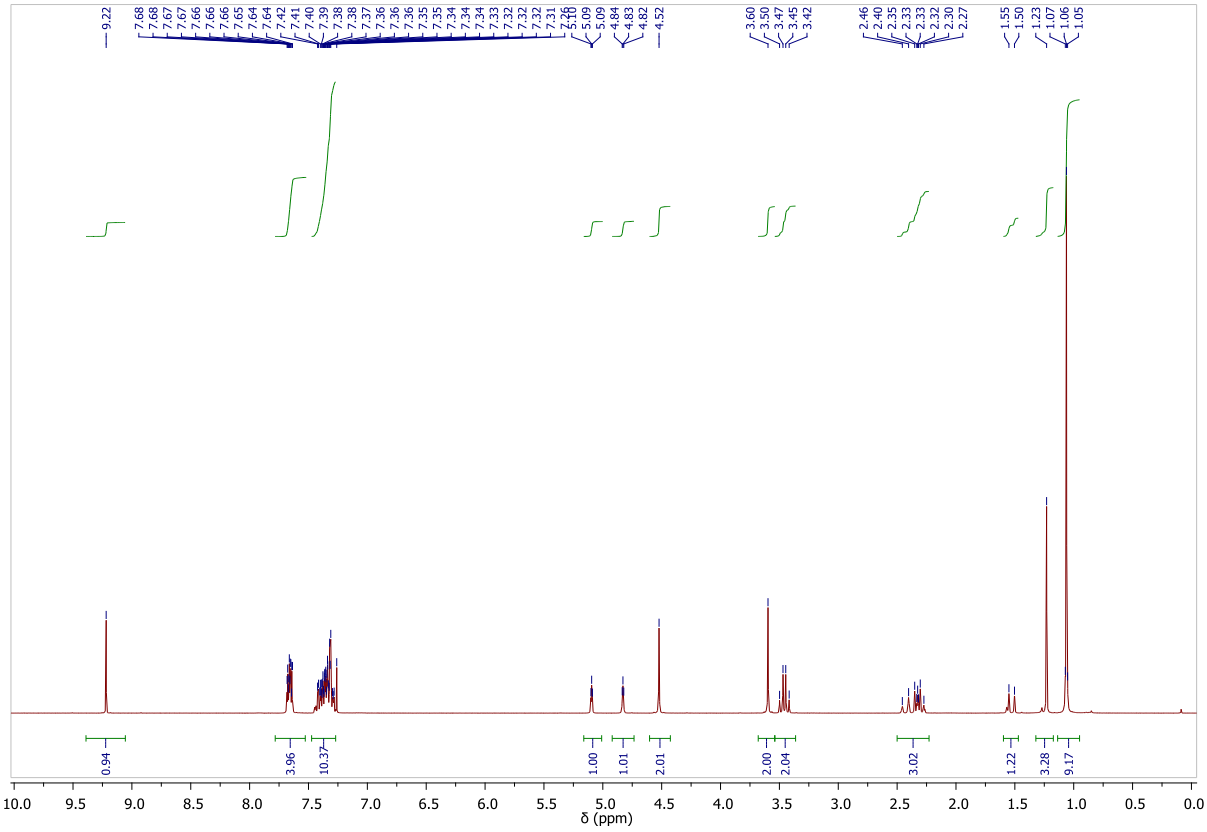


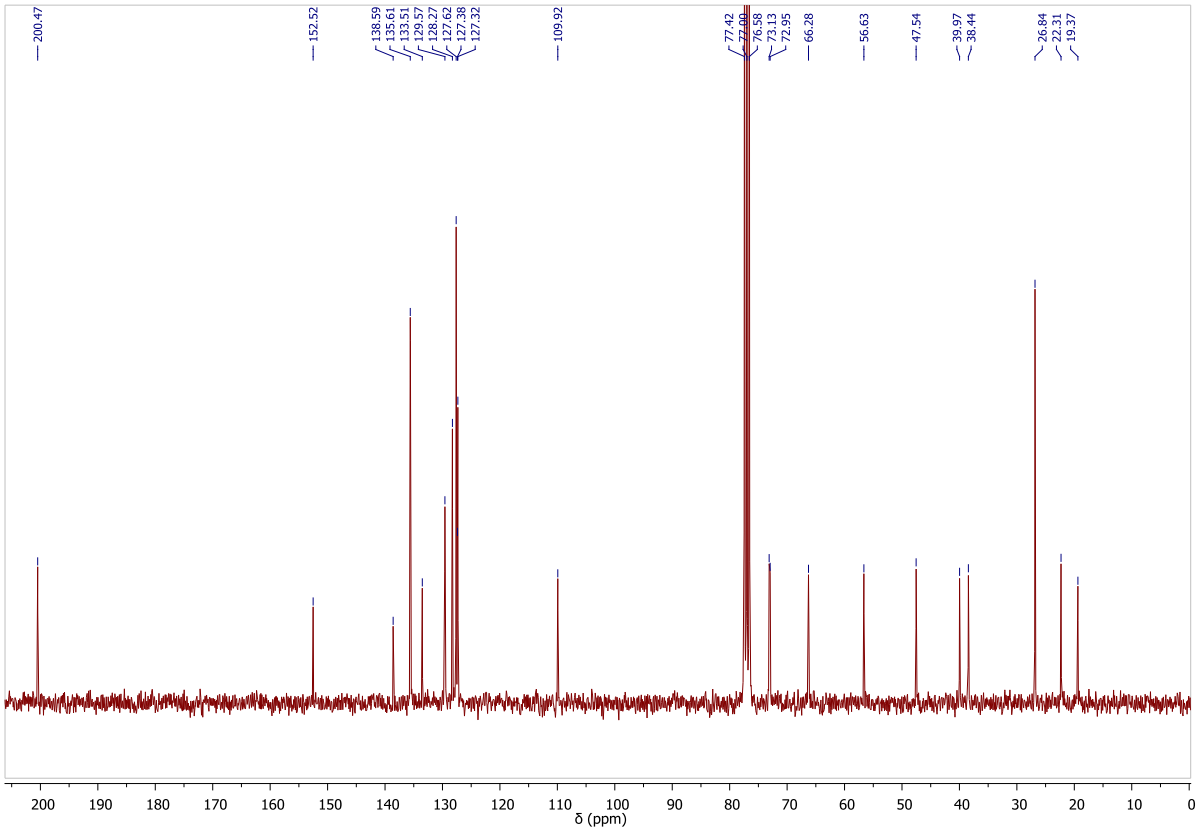




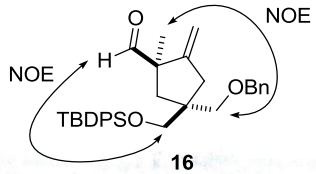
16 (Major diasteroisomer)

Chemical Formula: $C_{33}H_{40}O_3Si$
Molecular Weight: 512,75440

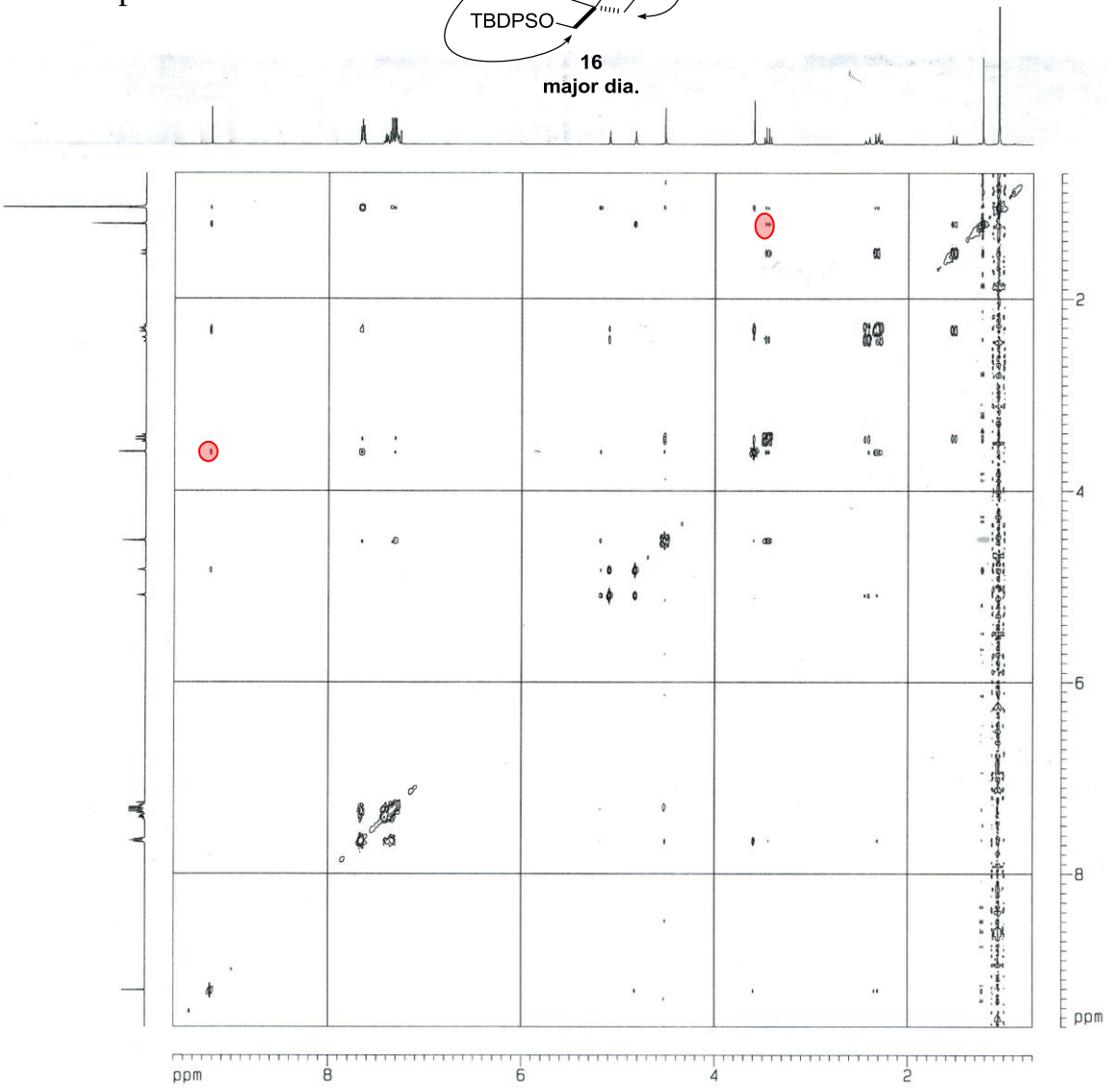




NOESY spectrum

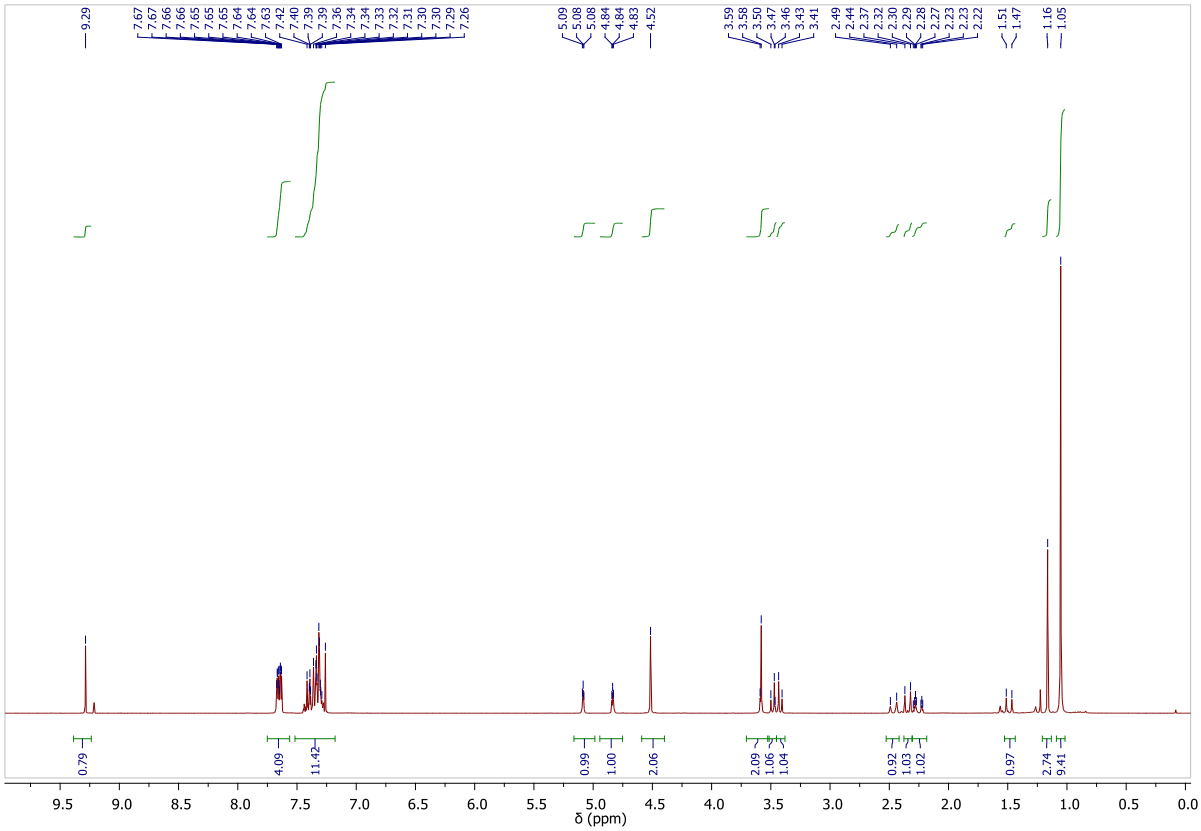


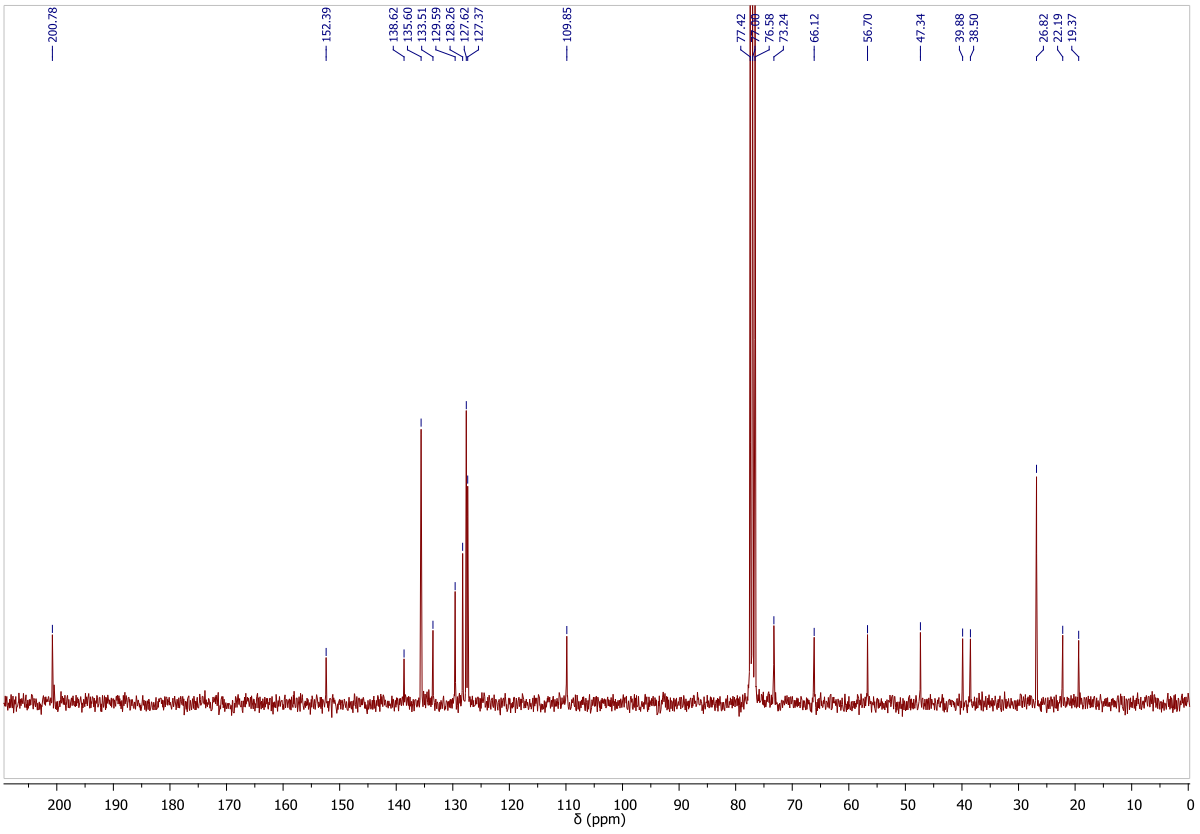
16
major dia.

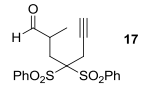


16' (Minor diasteroisomer)

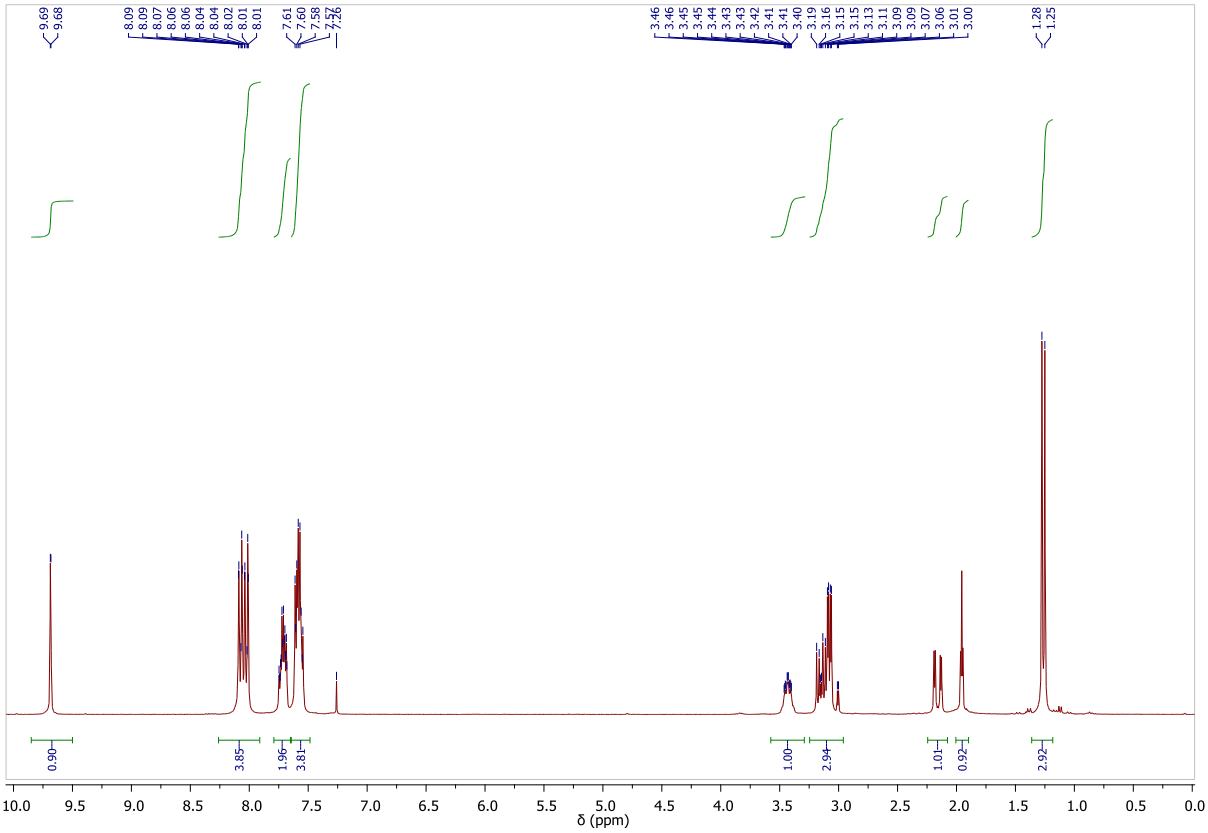
Chemical Formula: $C_{33}H_{40}O_3Si$
Molecular Weight: 512,75440

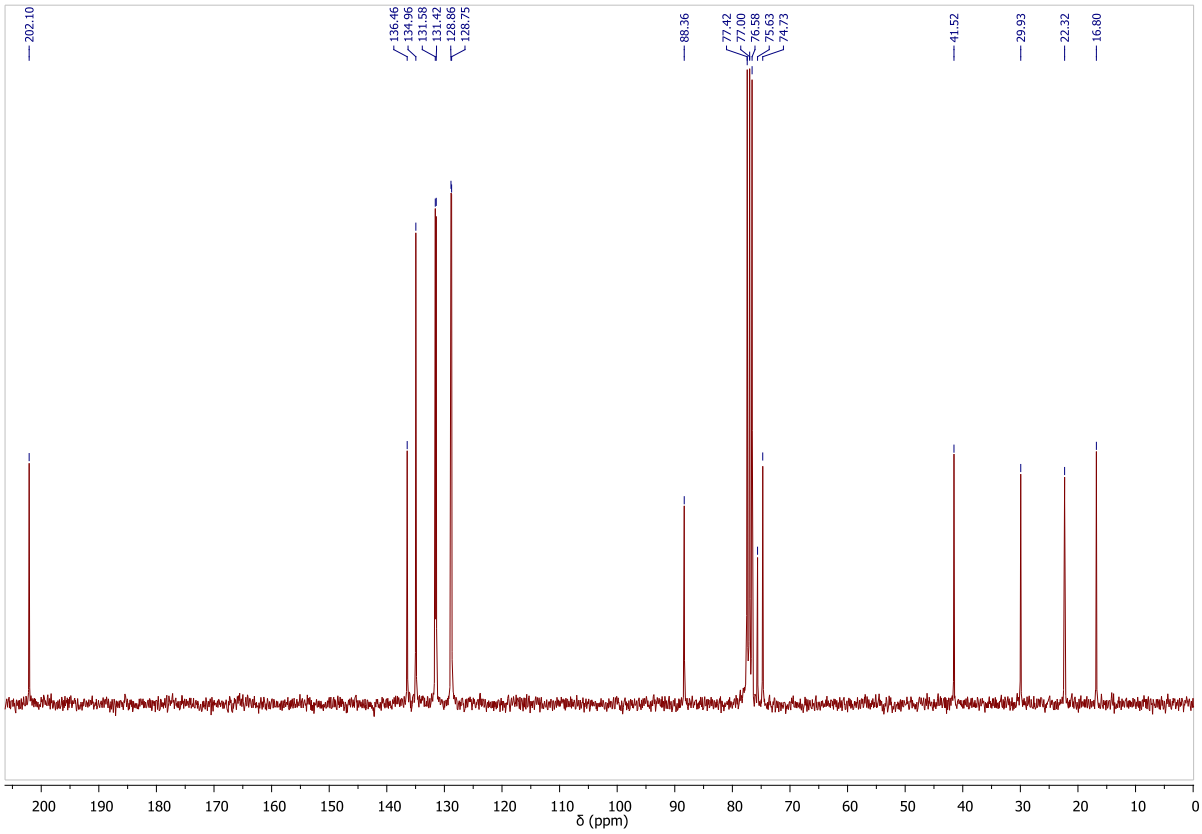


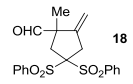




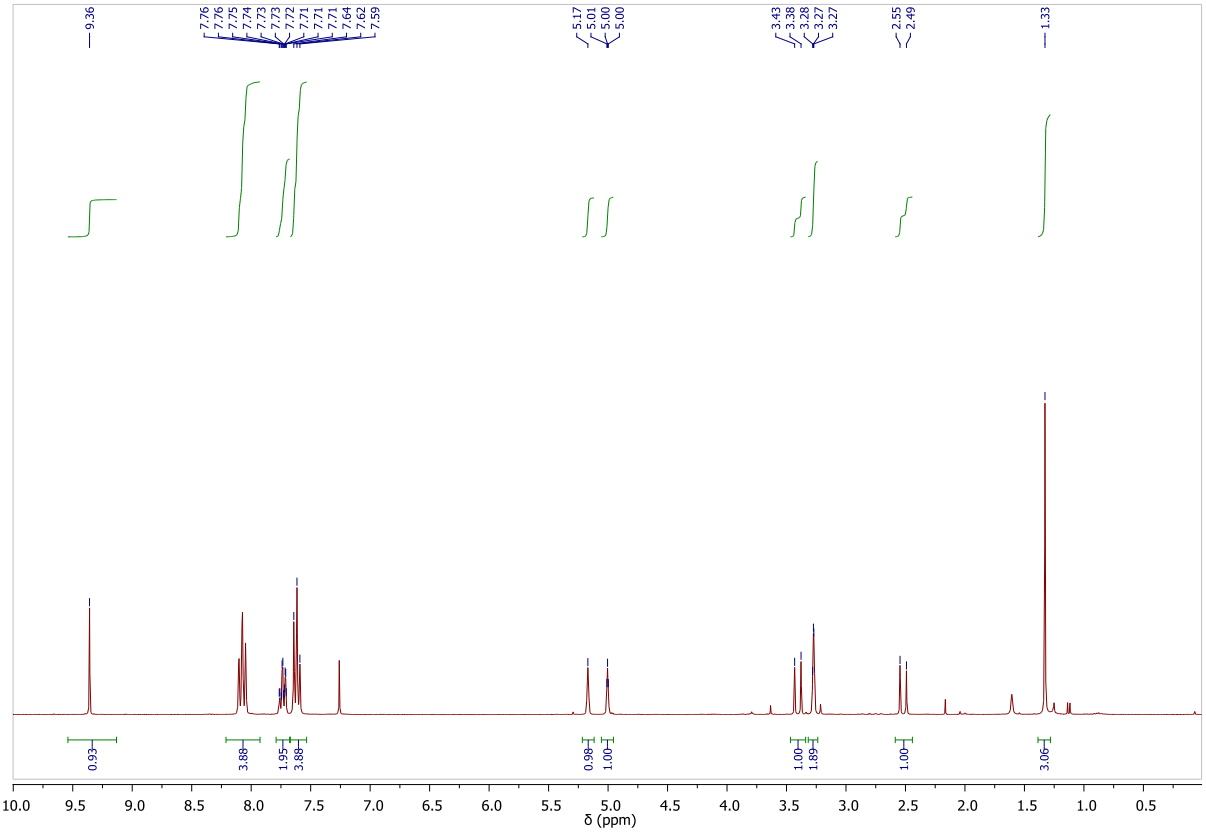
Chemical Formula: $C_{20}H_{20}O_5S_2$
Molecular Weight: 404,49980

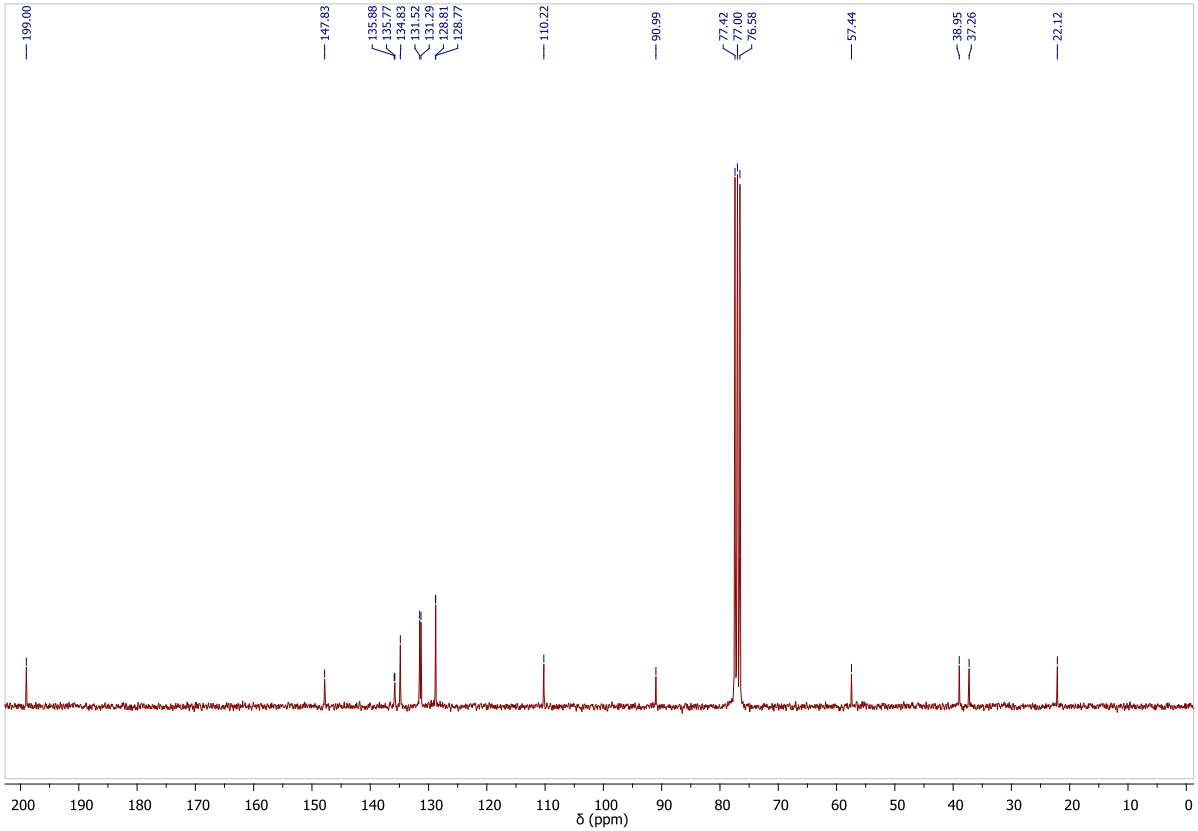


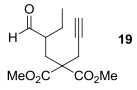




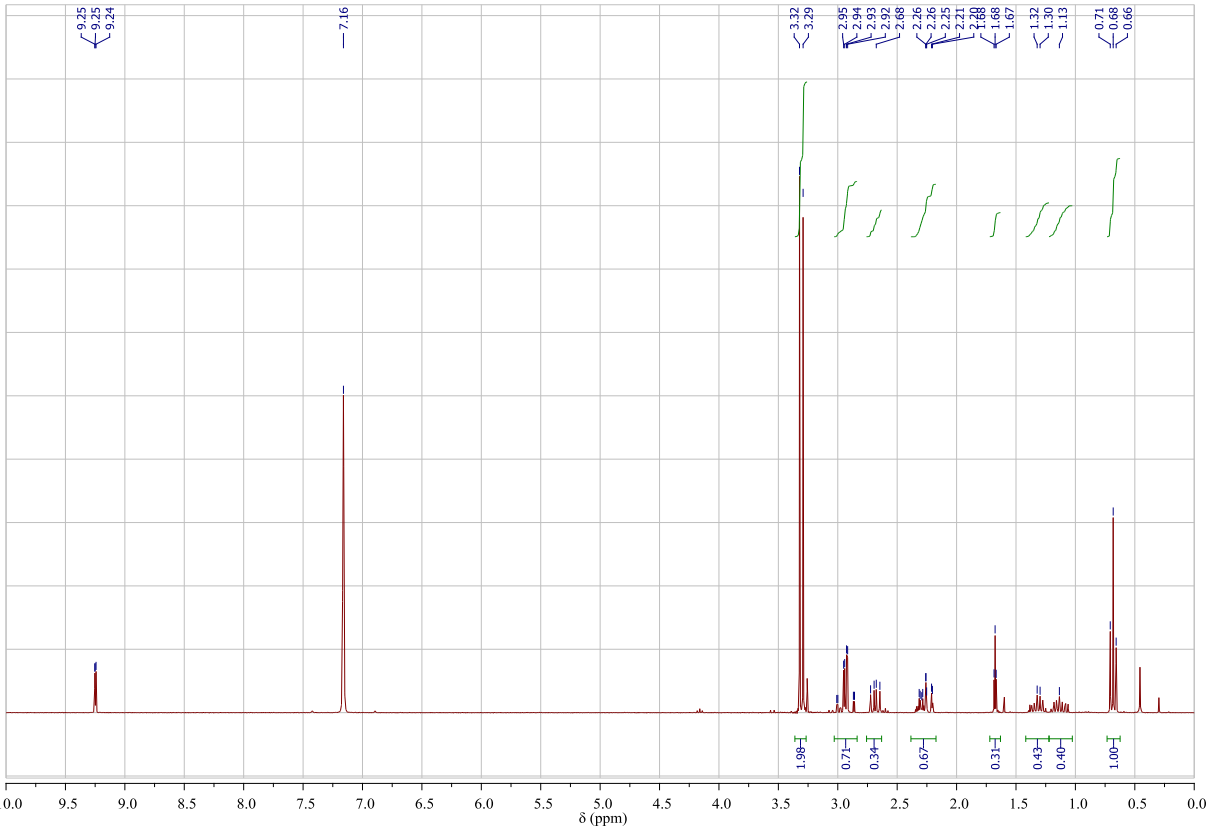
Chemical Formula: $C_{20}H_{20}O_5S_2$
Molecular Weight: 404,49980

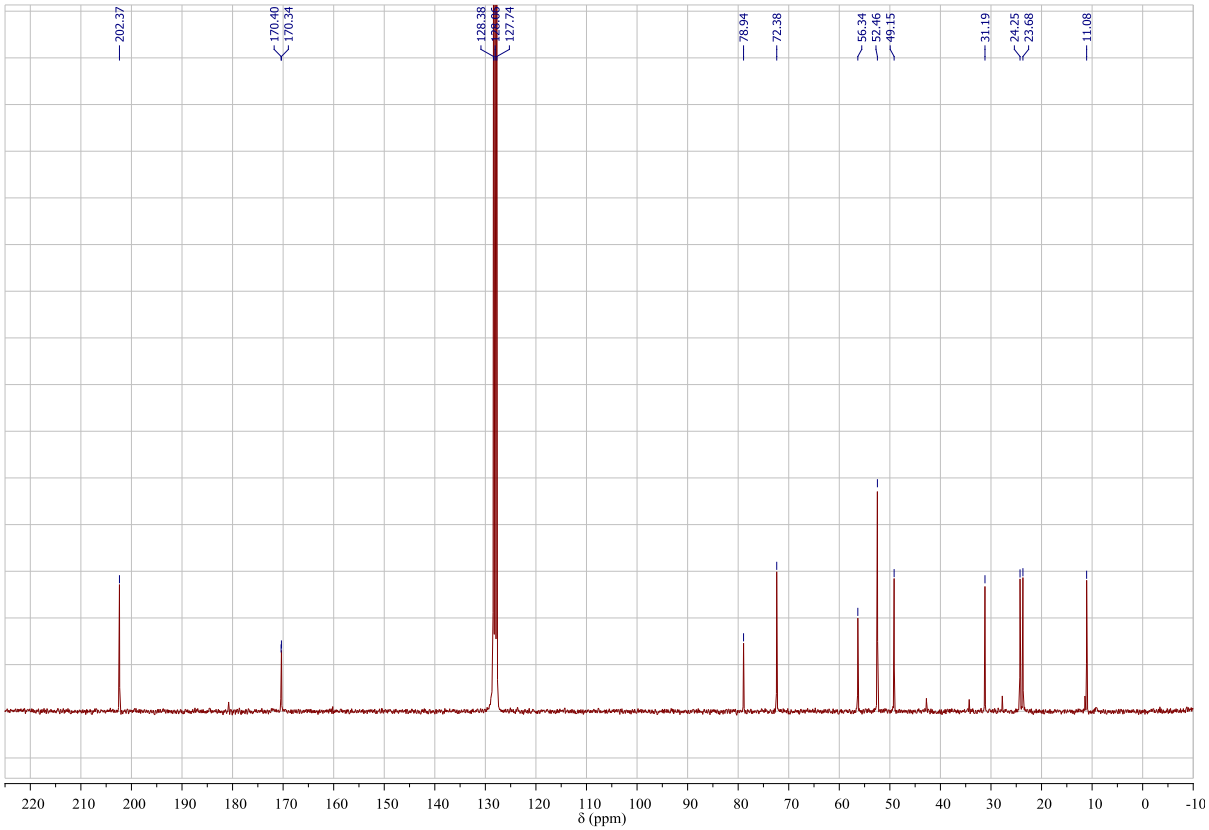


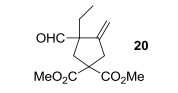




Chemical Formula: $C_{13}H_{18}O_5$
Molecular Weight: 254,27902

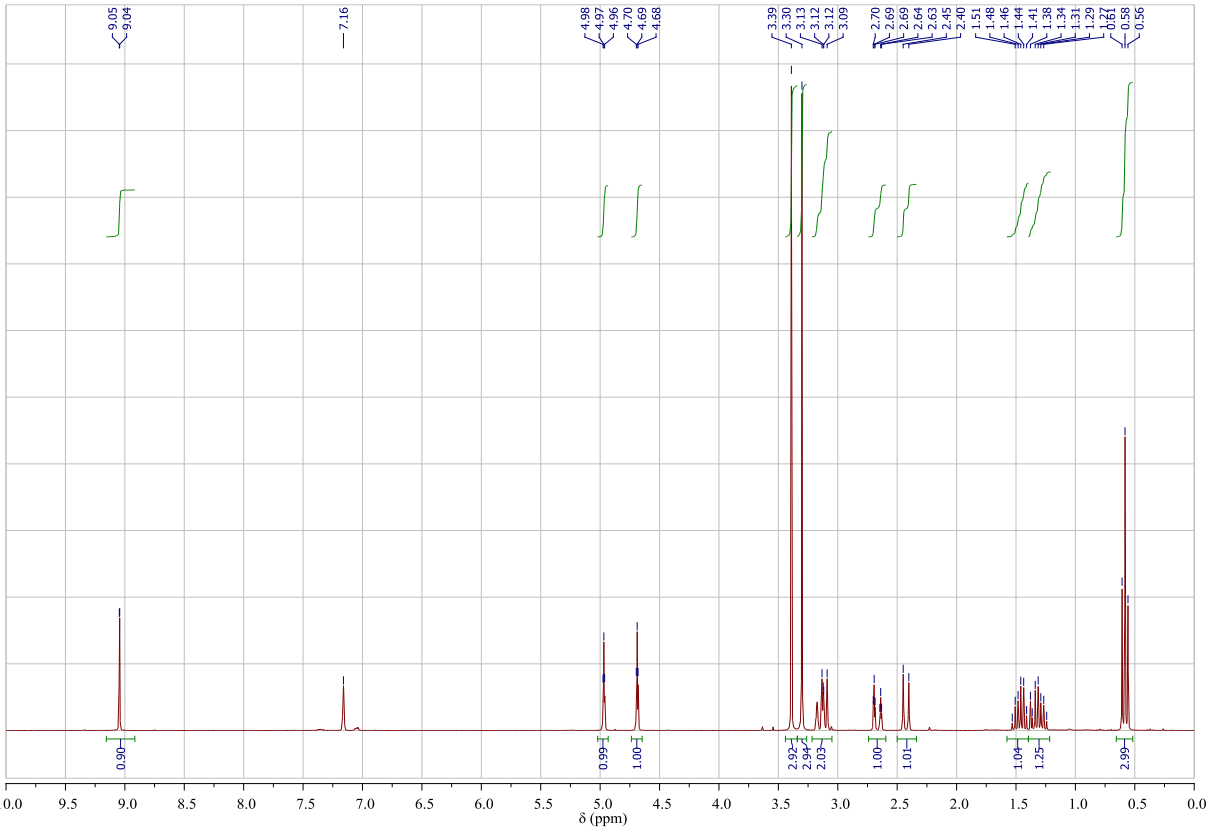


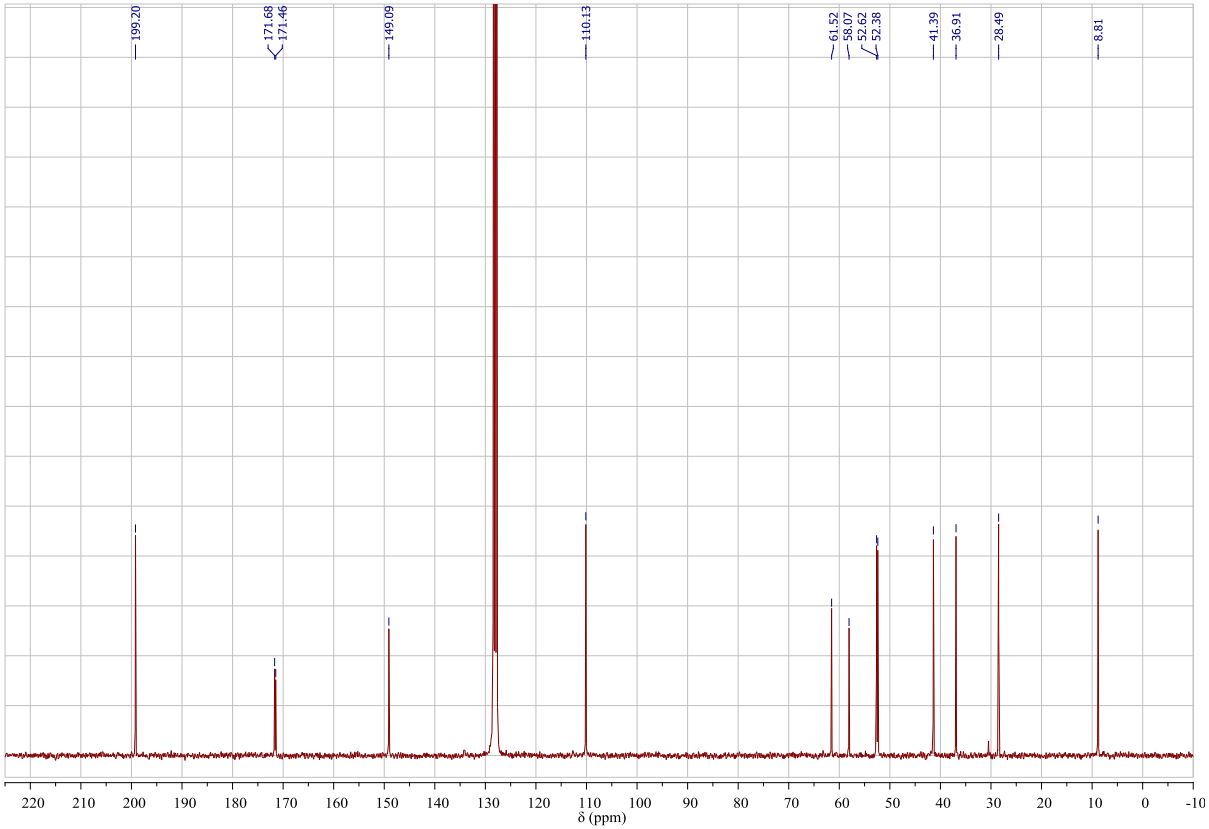


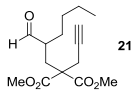


20

Chemical Formula: $C_{13}H_{18}O_5$
Molecular Weight: 254,27902

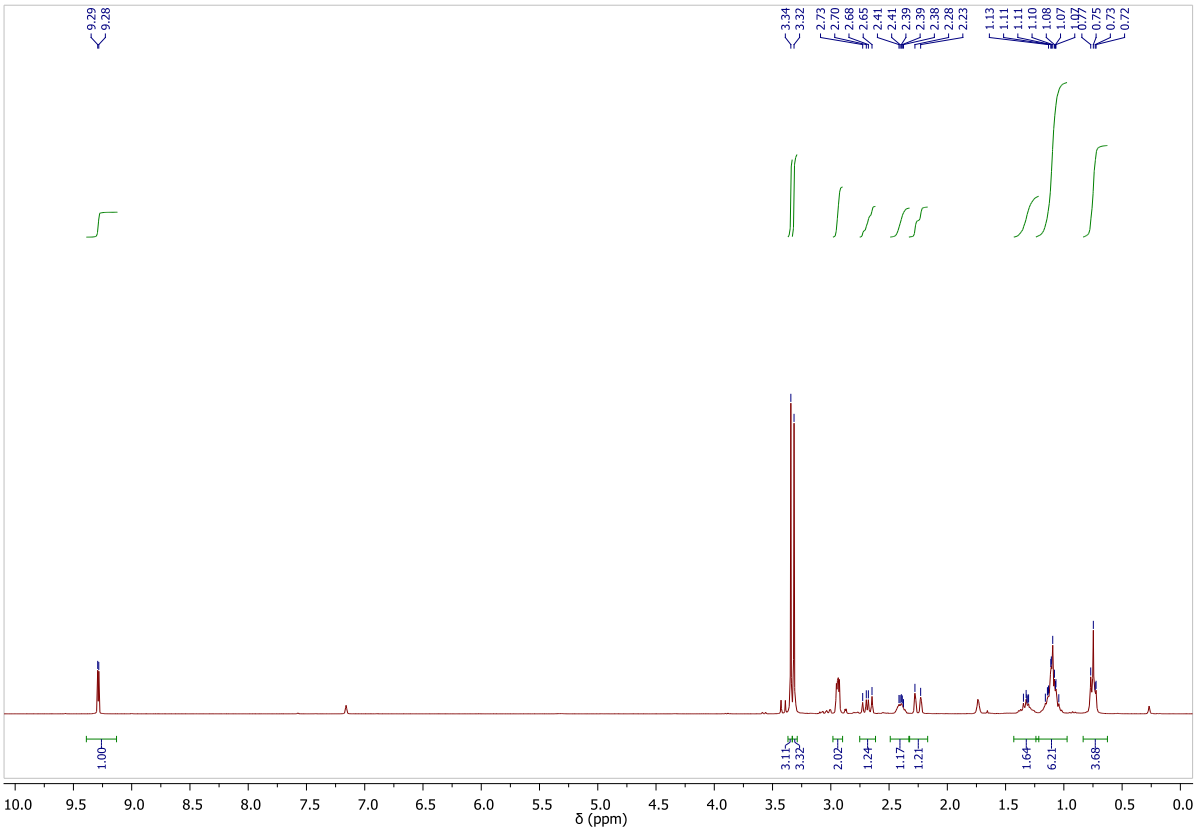


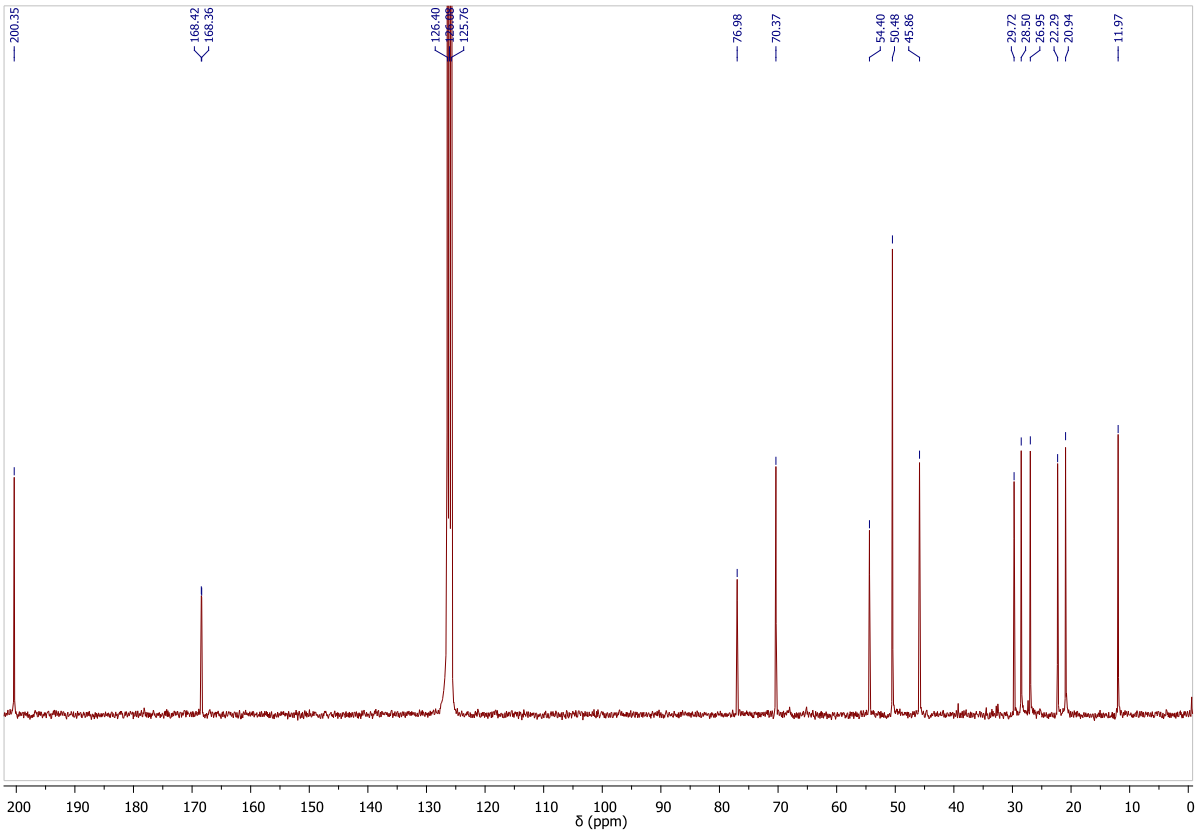


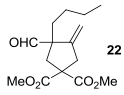


21

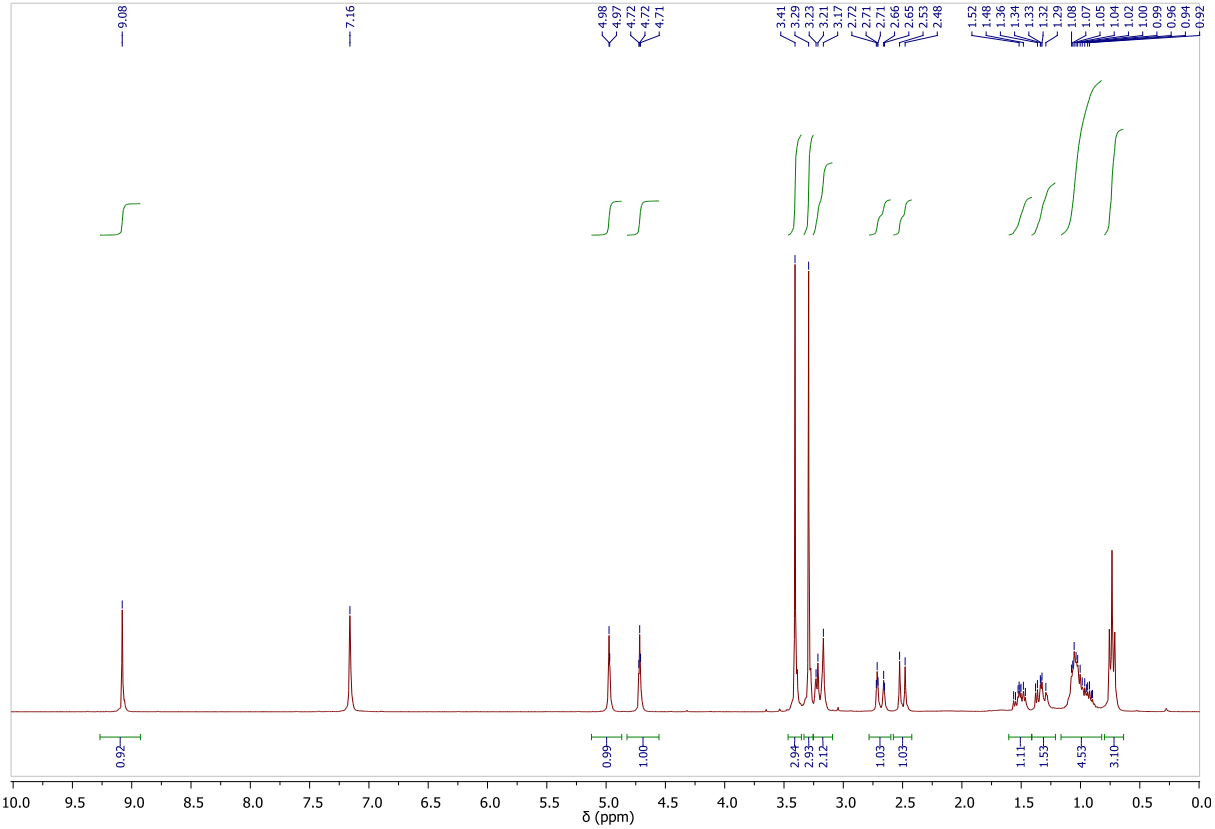
Chemical Formula: $C_{15}H_{22}O_5$
Molecular Weight: 282,33218

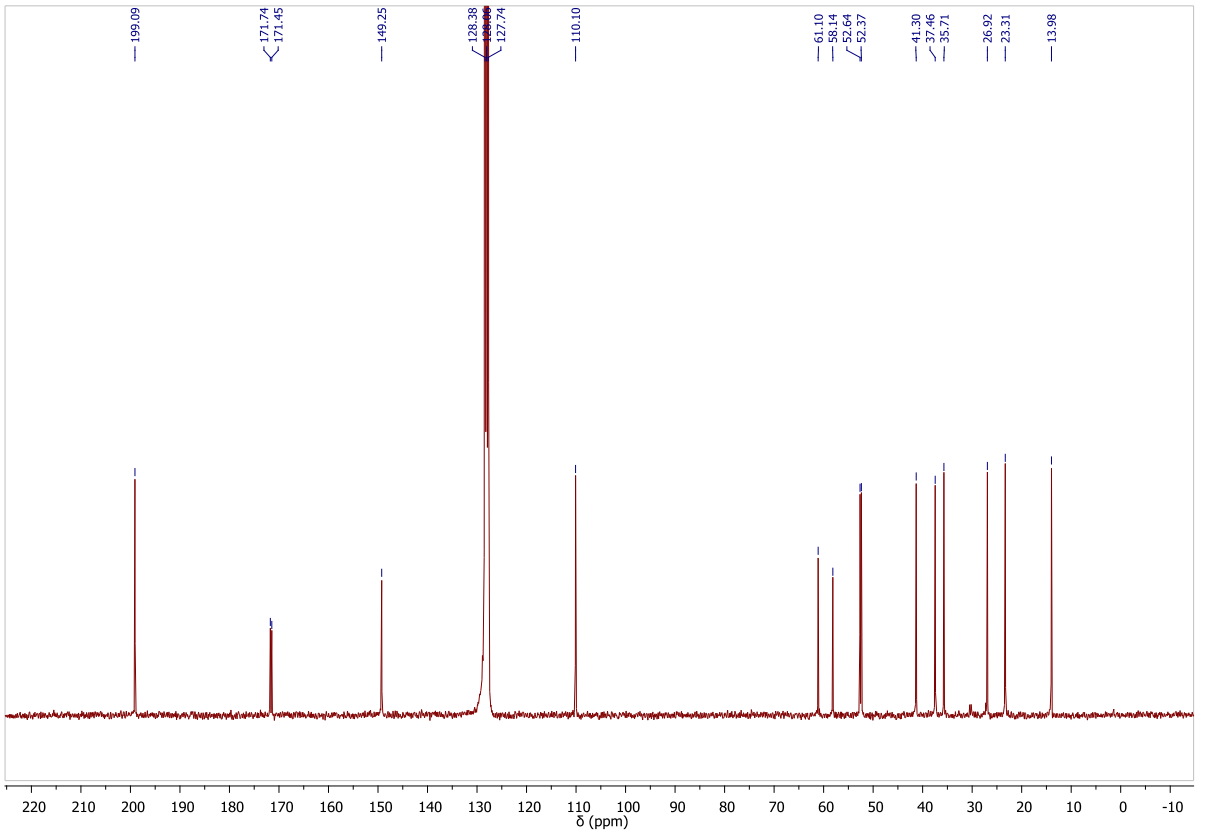


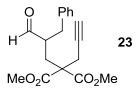




Chemical Formula: $C_{15}H_{22}O_5$
Molecular Weight: 282,33218

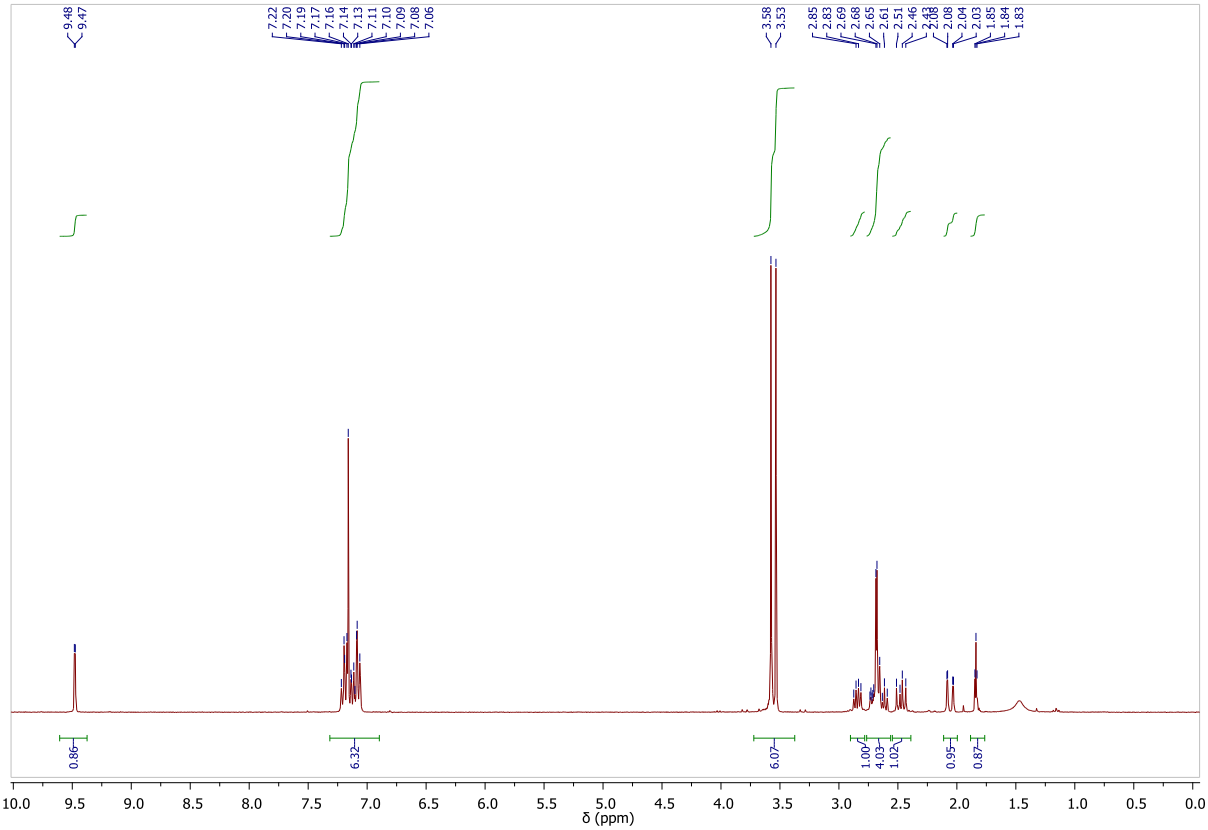


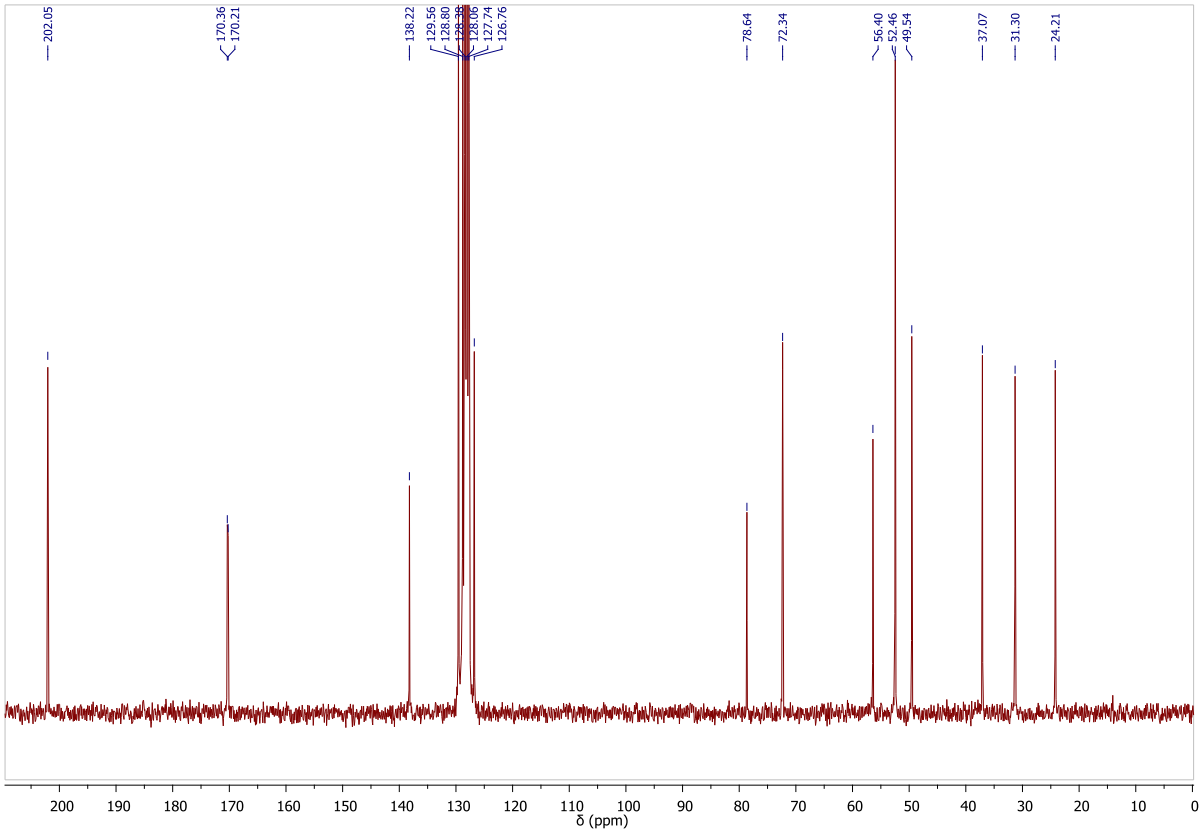


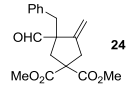


23

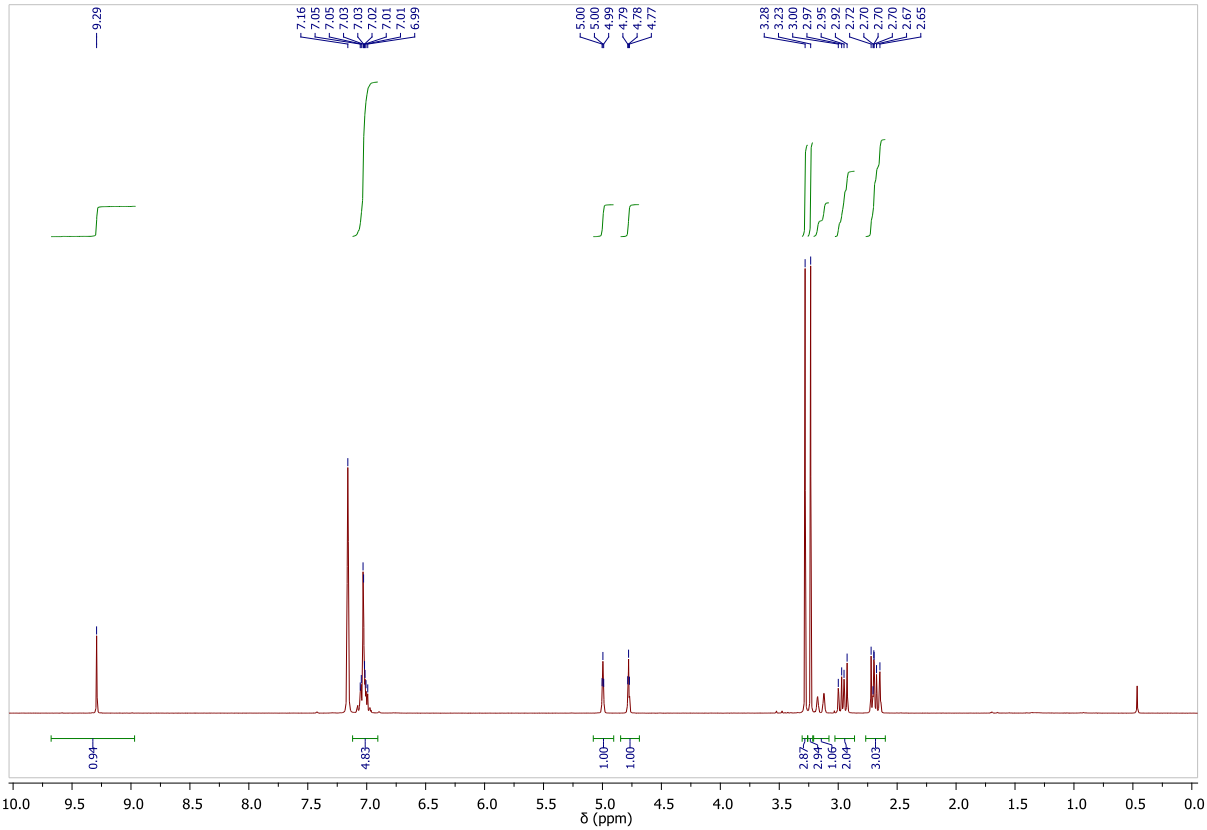
Chemical Formula: $C_{18}H_{20}O_5$
Molecular Weight: 316,34840

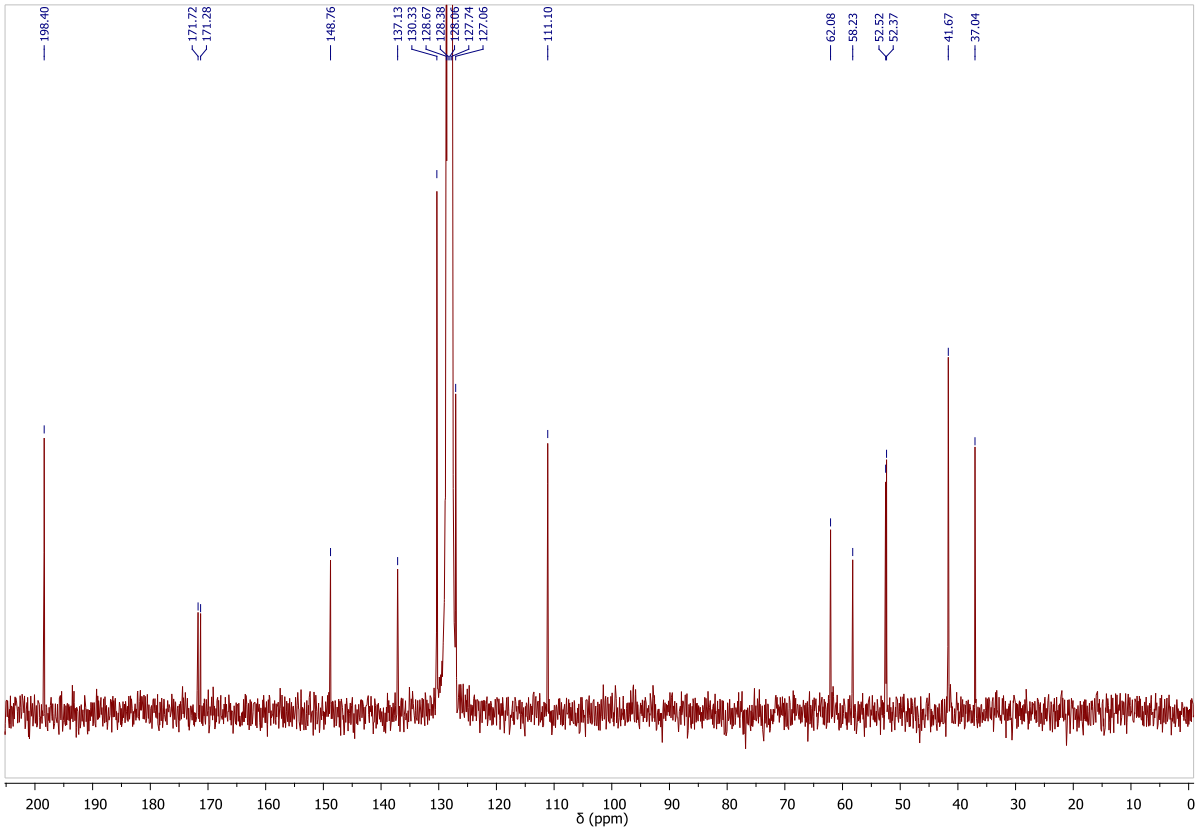


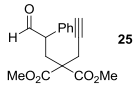




Chemical Formula: $C_{18}H_{20}O_5$
Molecular Weight: 316,34840

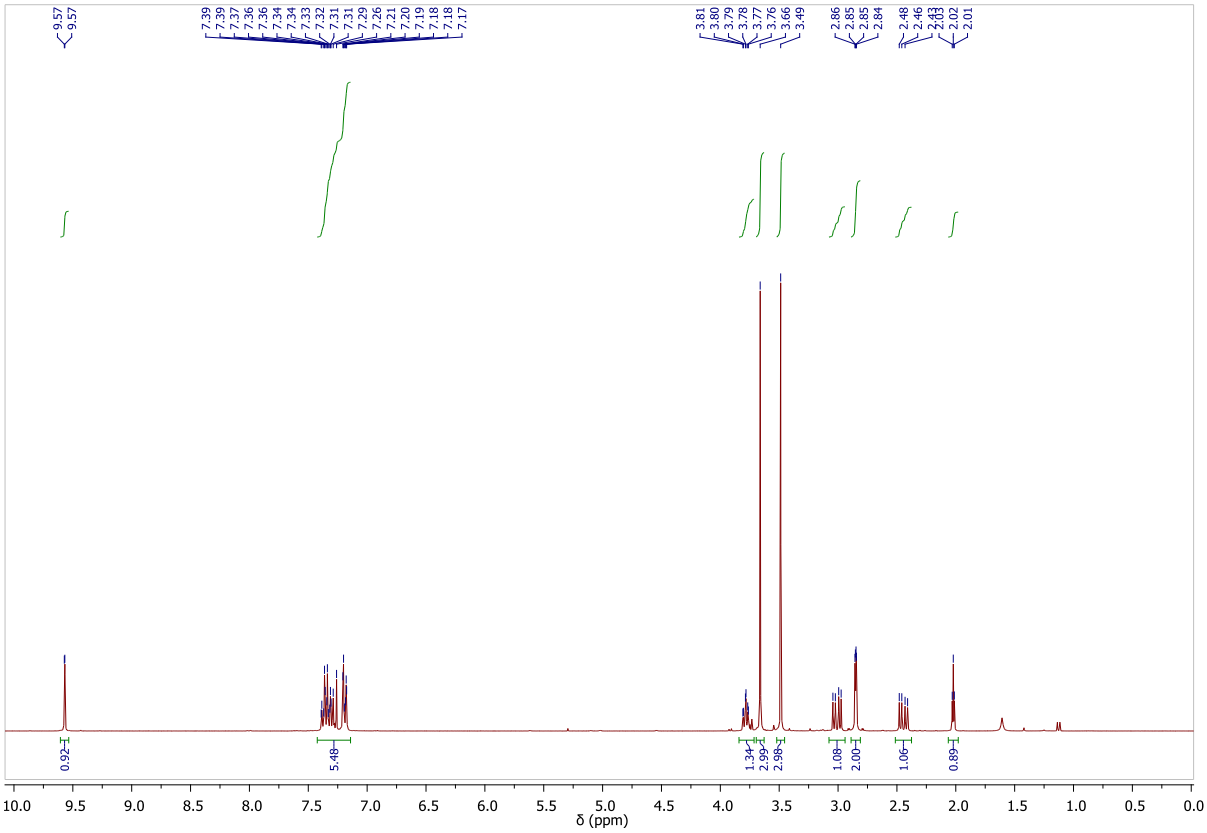


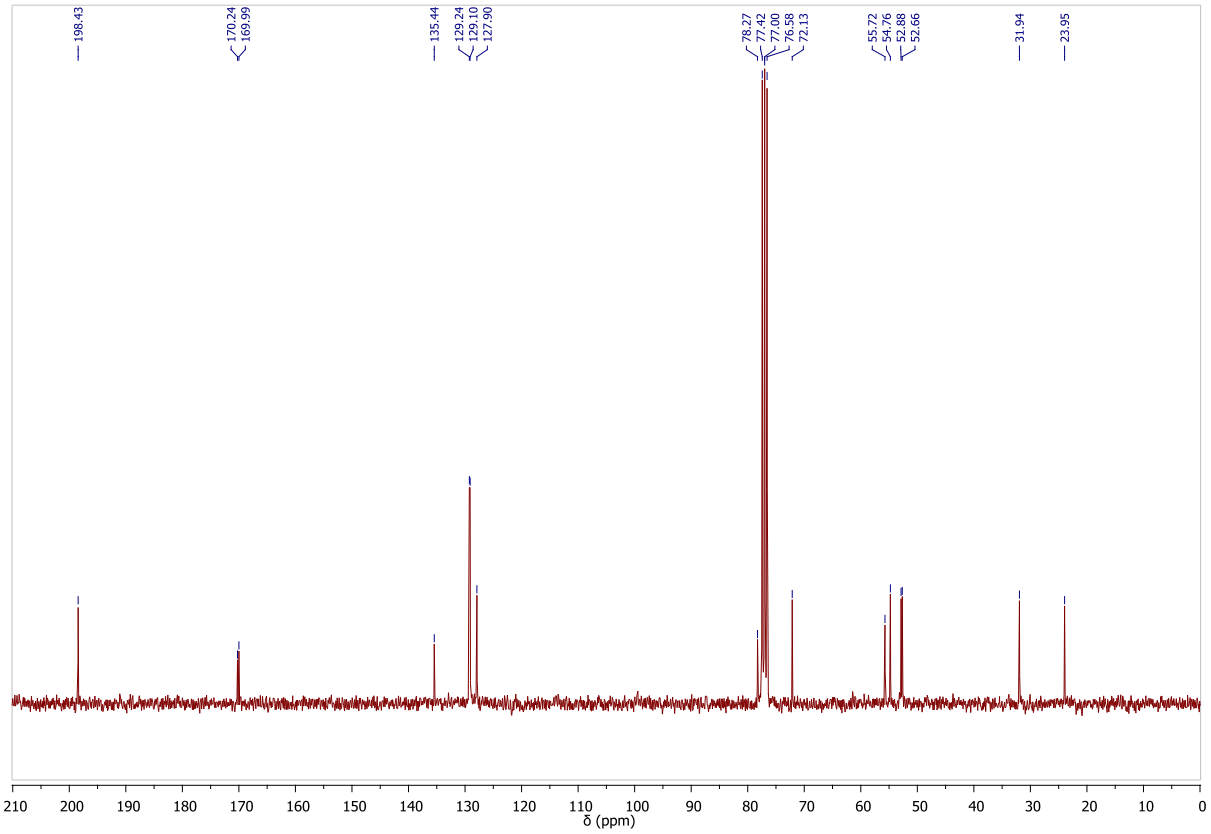


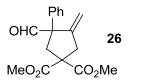


25

Chemical Formula: $C_{17}H_{18}O_5$
Molecular Weight: 302,32182

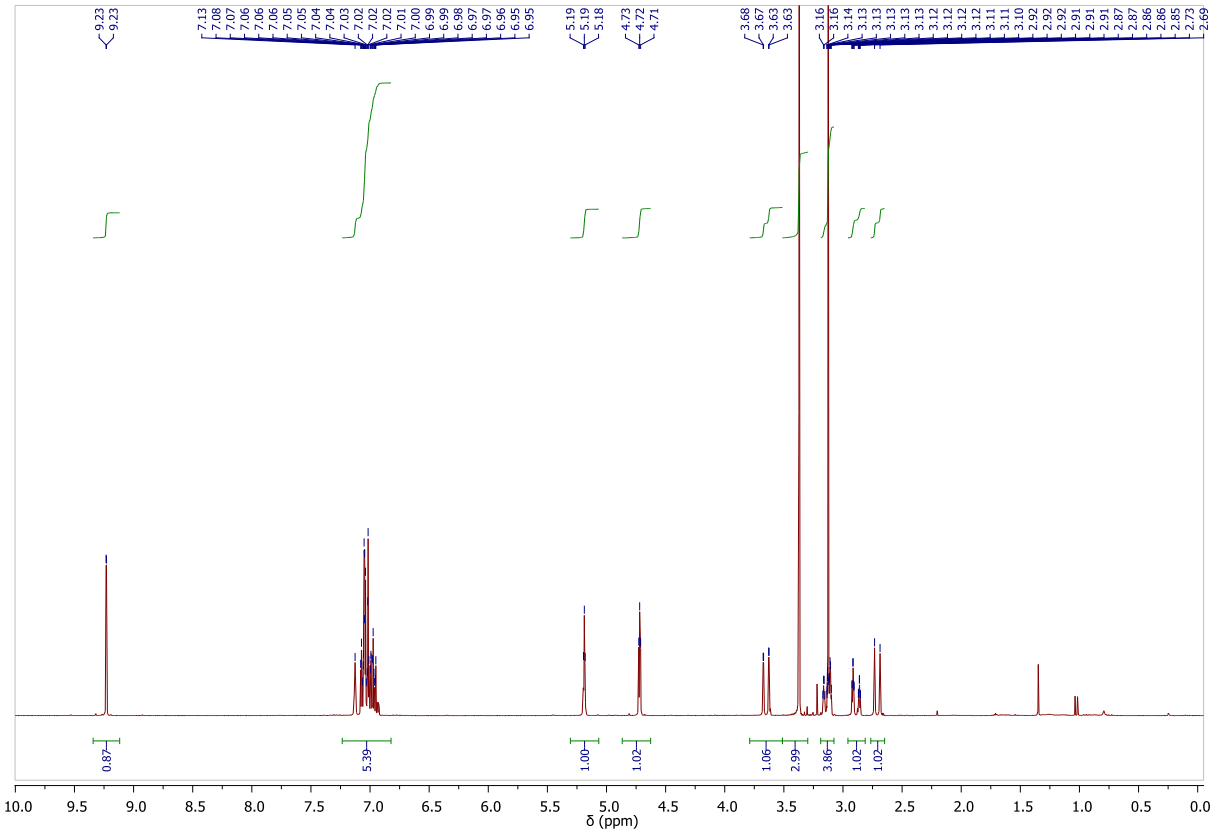


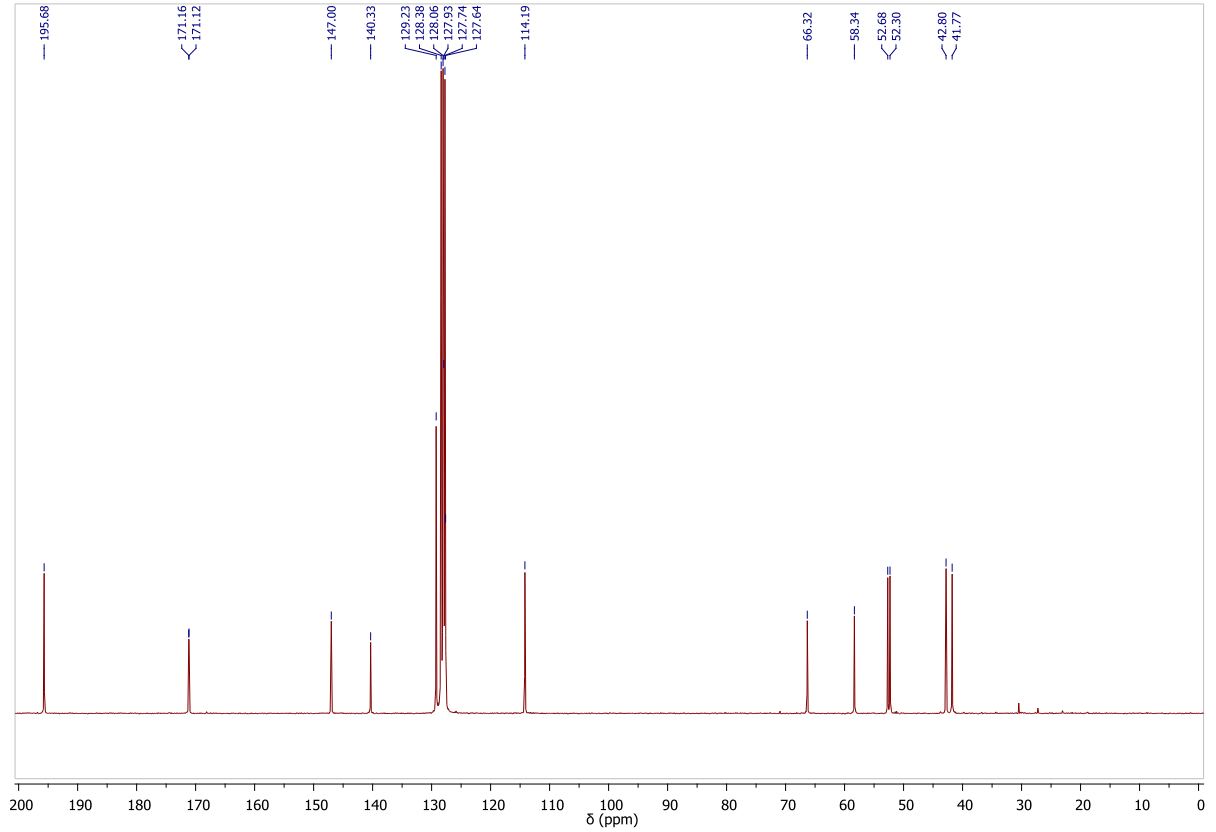


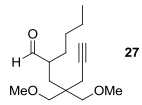


26

Chemical Formula: $C_{17}H_{18}O_5$
Molecular Weight: 302,32182

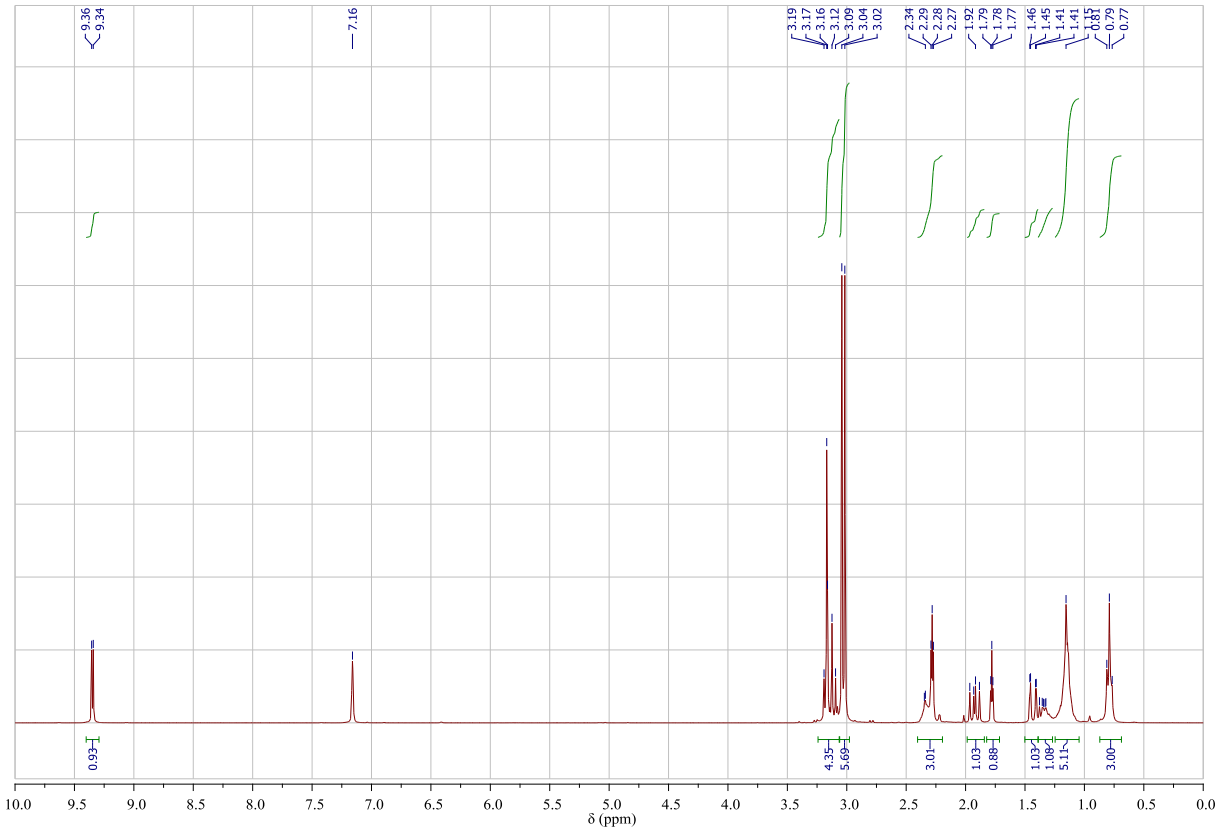


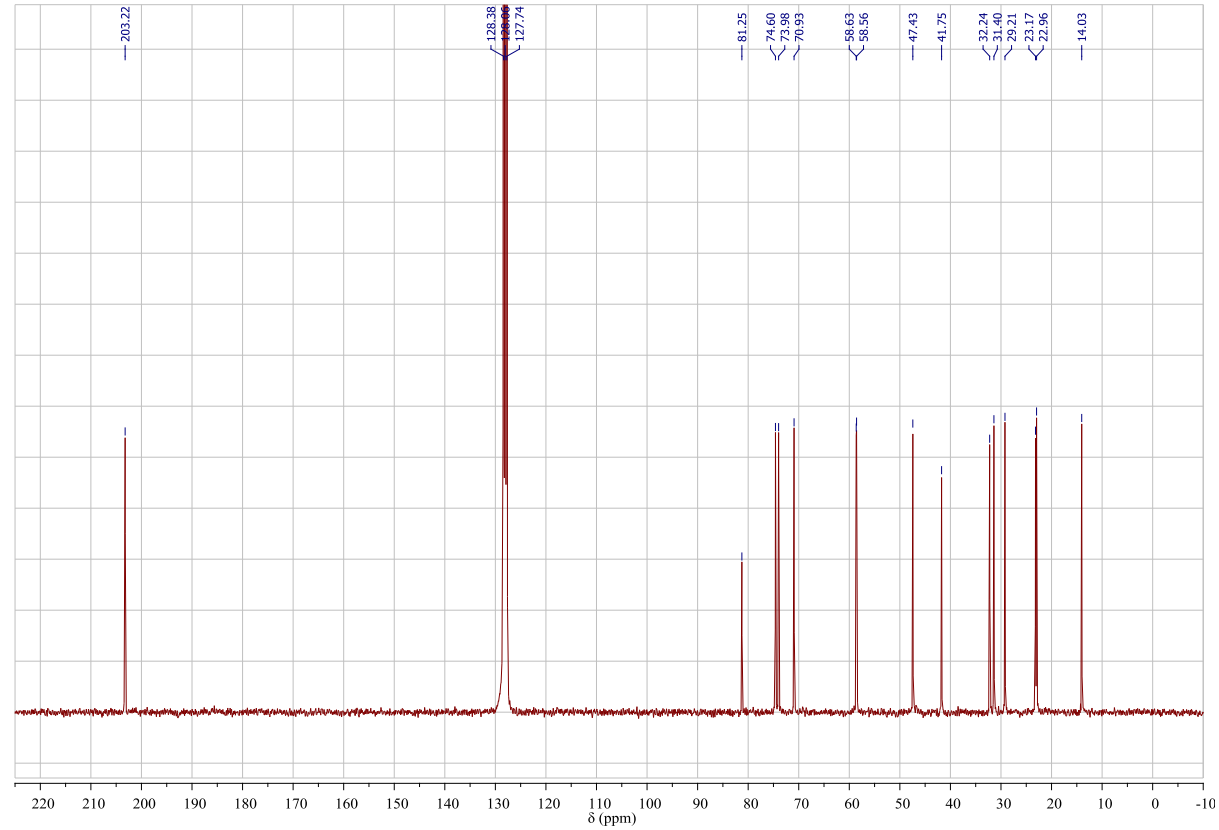


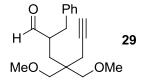


27

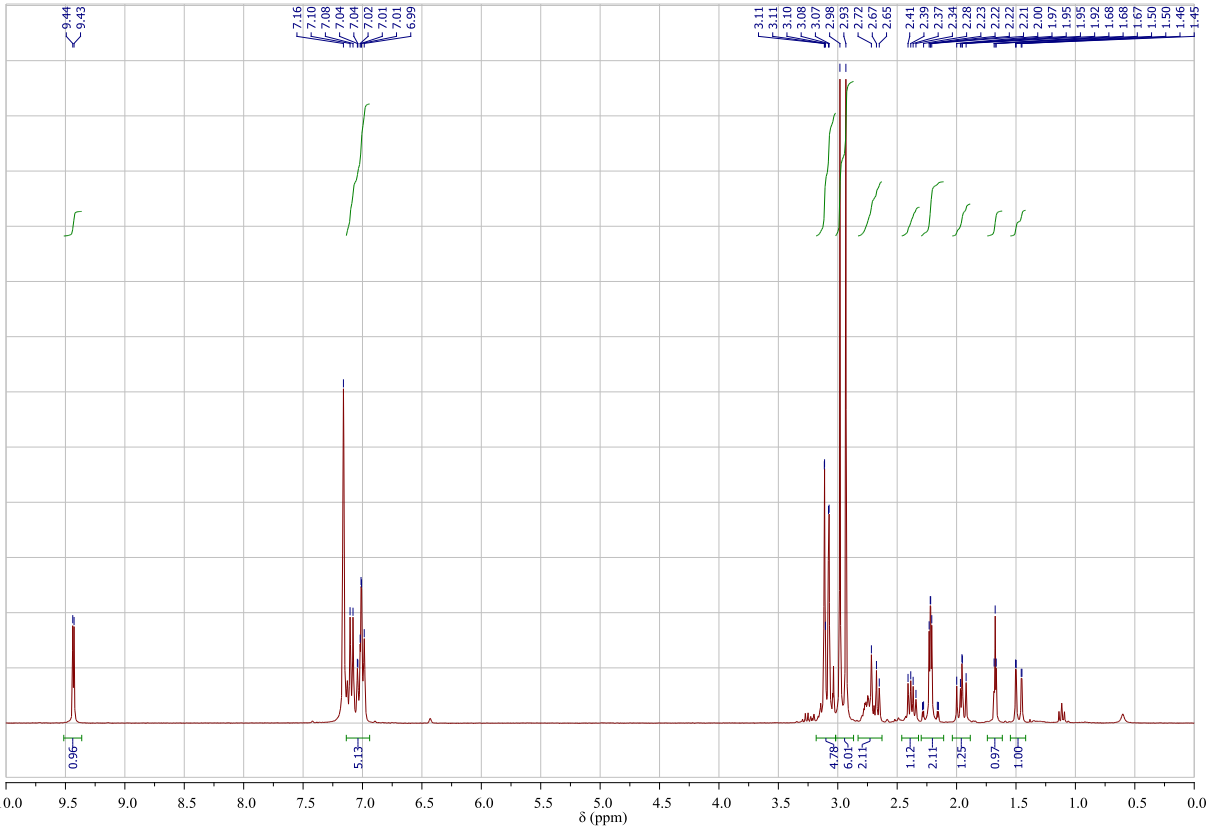
Chemical Formula: $C_{15}H_{26}O_3$
Molecular Weight: 254,36514

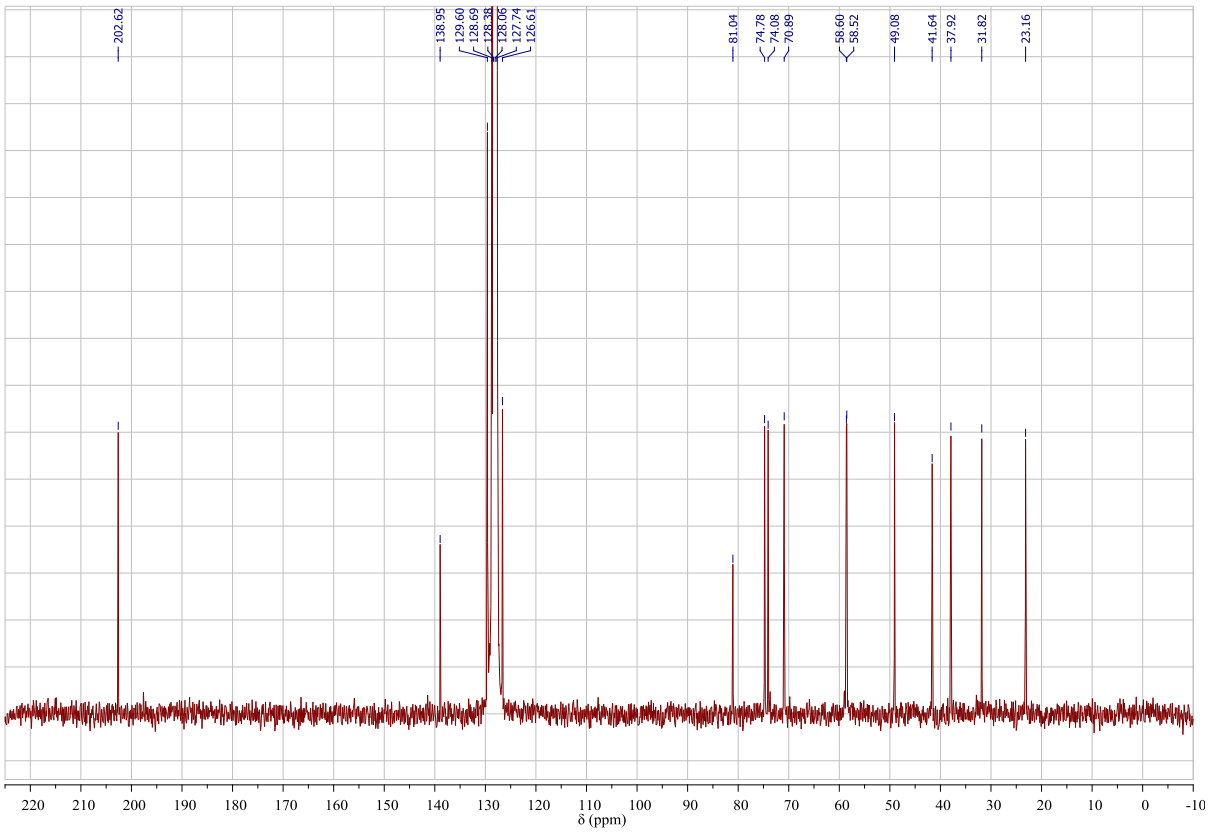


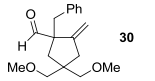




Chemical Formula: $C_{18}H_{24}O_3$
Molecular Weight: 288,38136

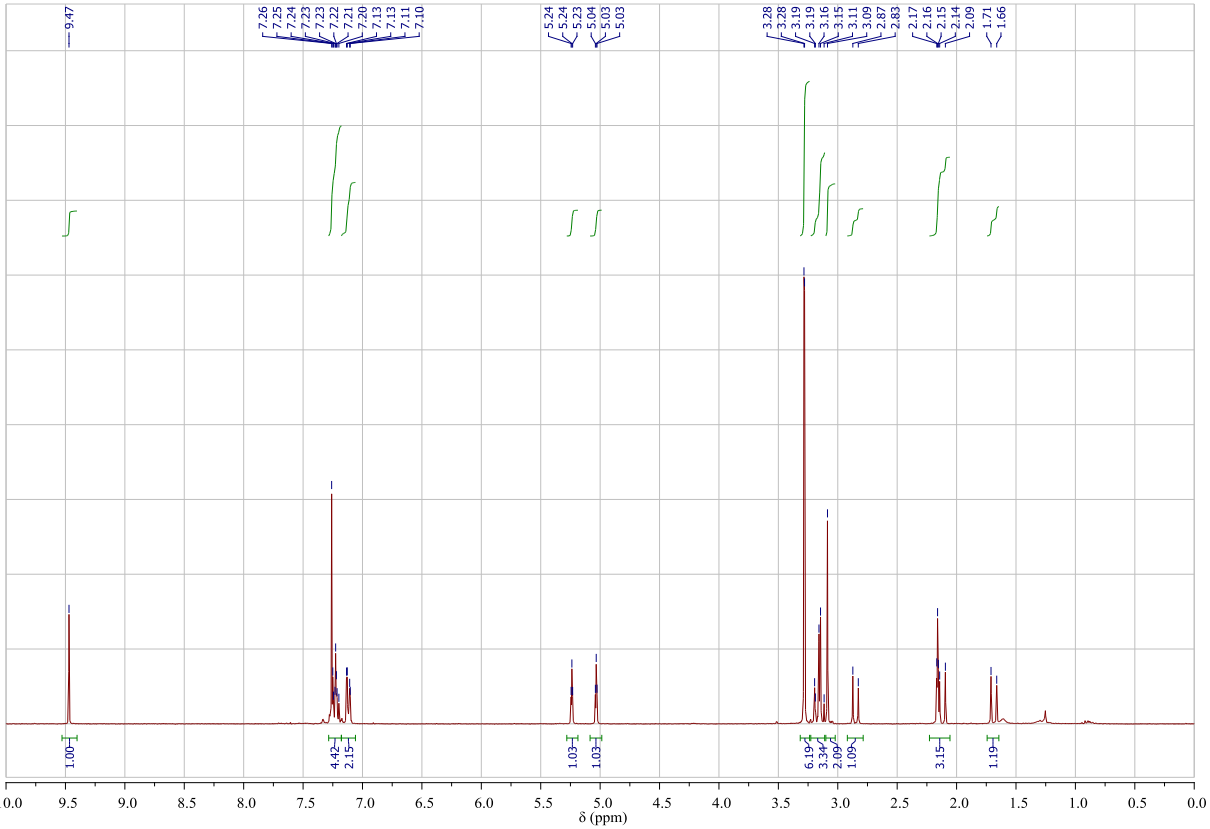


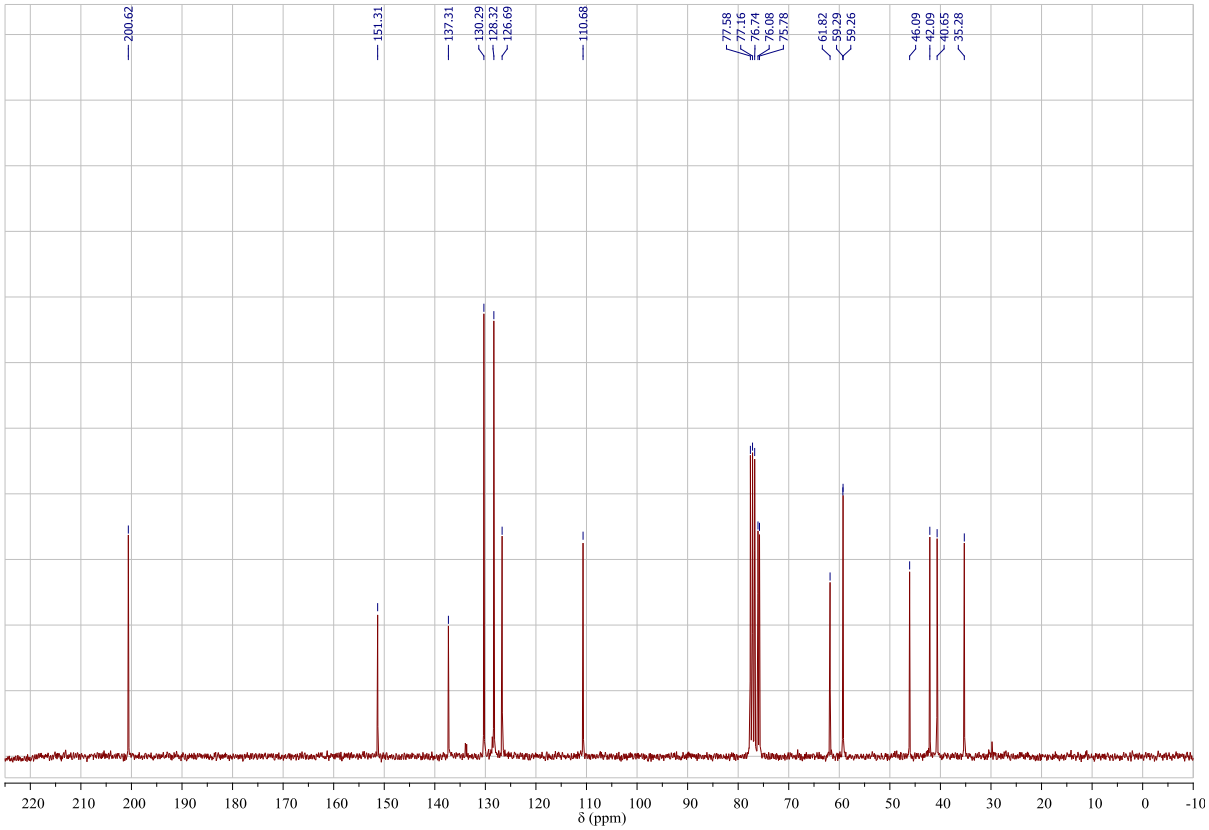


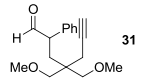


30

Chemical Formula: $C_{18}H_{24}O_3$
Molecular Weight: 288,38136

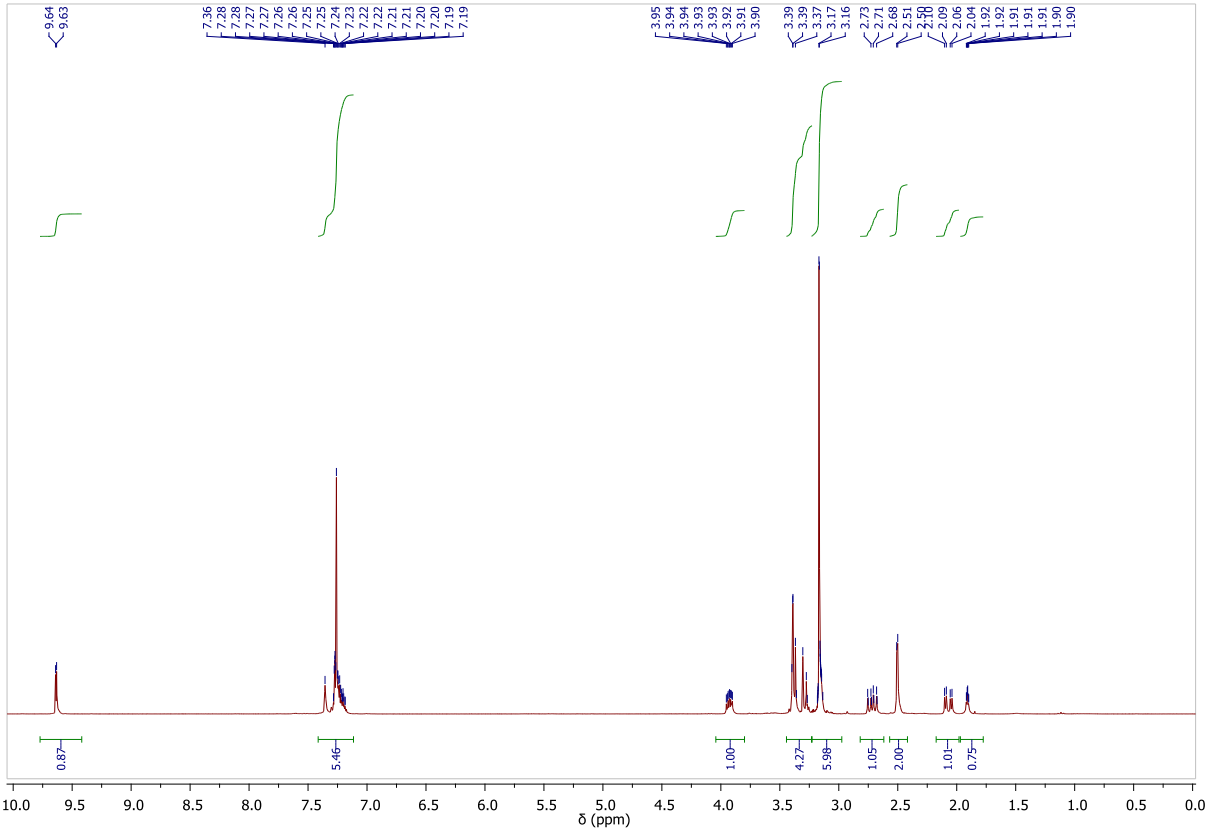


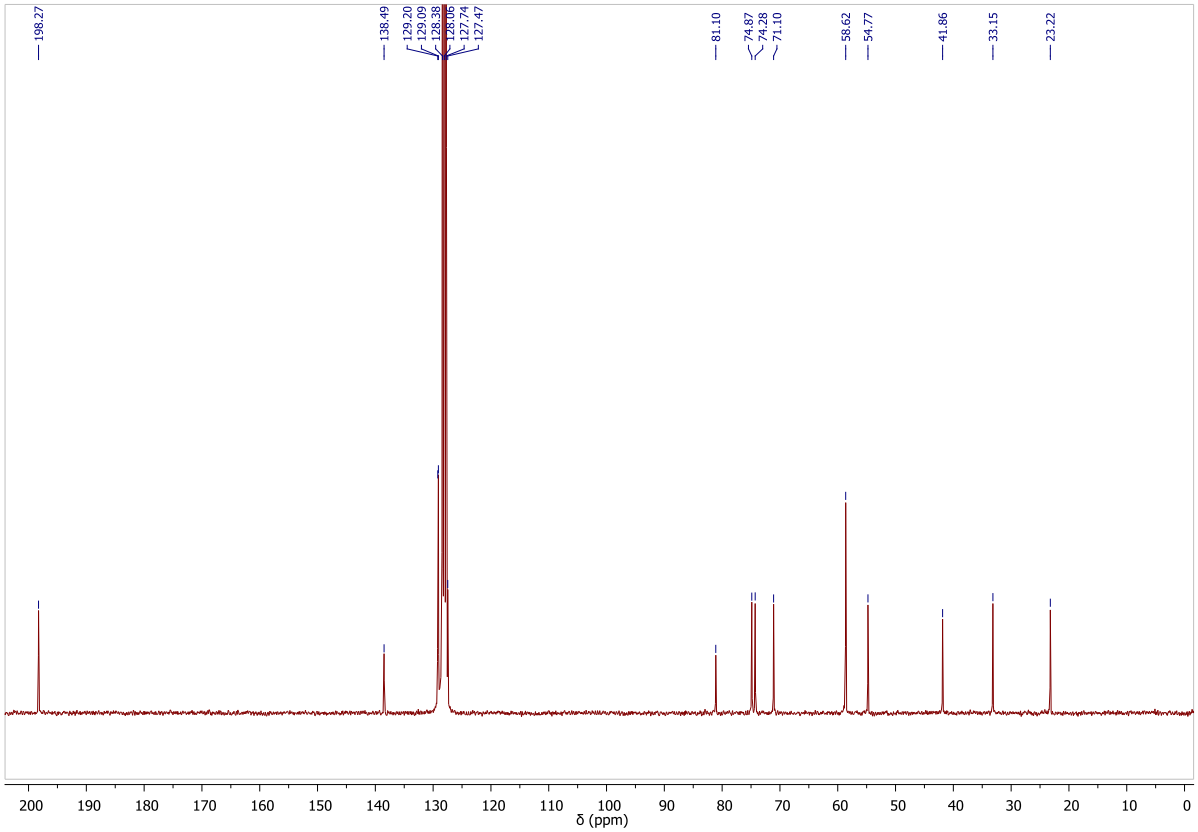


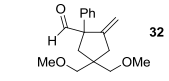


31

Chemical Formula: $C_{17}H_{22}O_3$
Molecular Weight: 274,35478

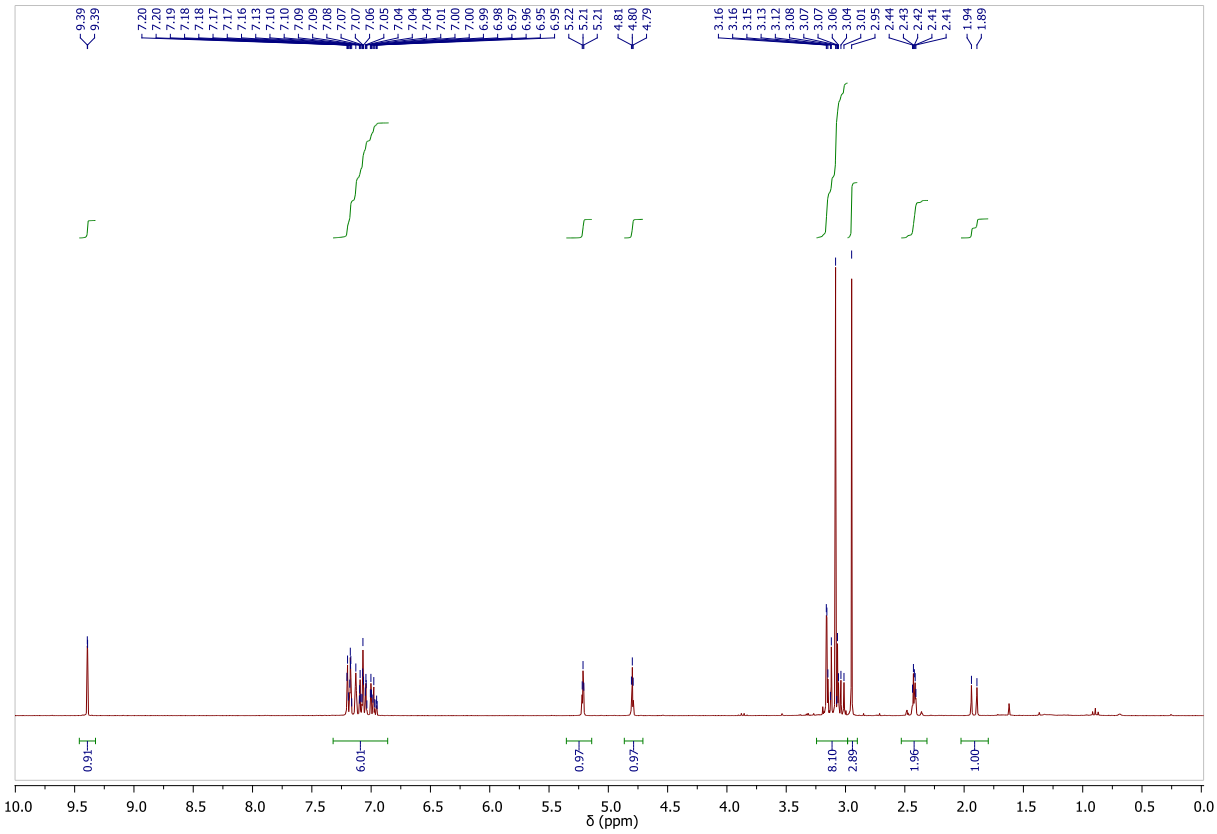


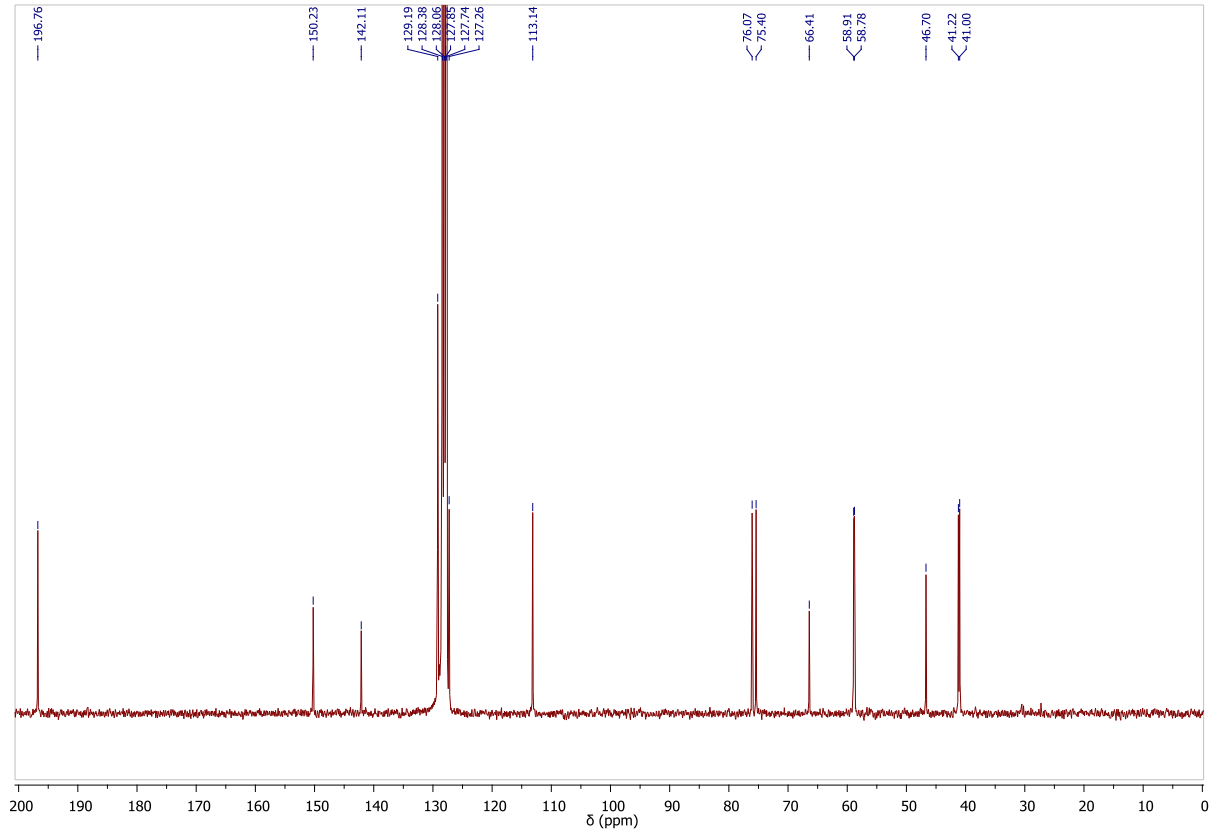


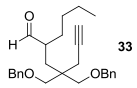


32

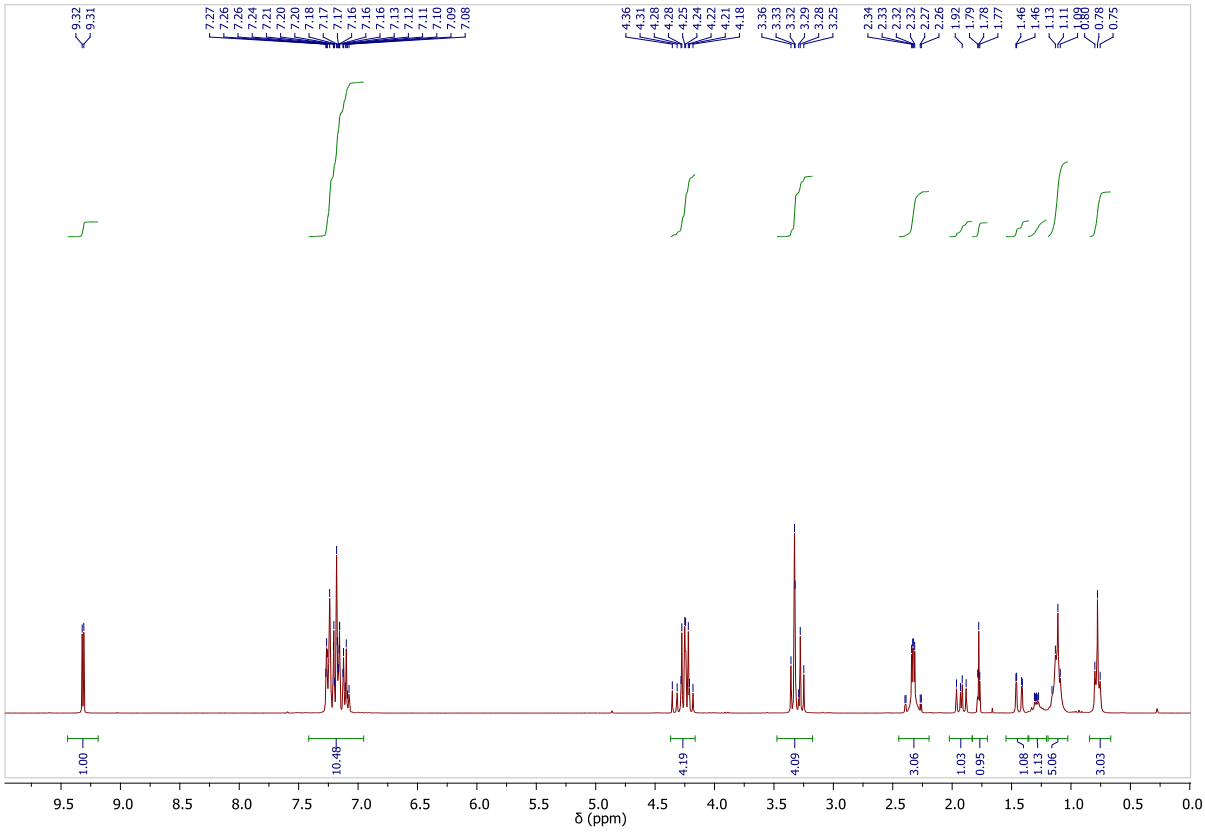
Chemical Formula: $C_{17}H_{22}O_3$
Molecular Weight: 274,35478

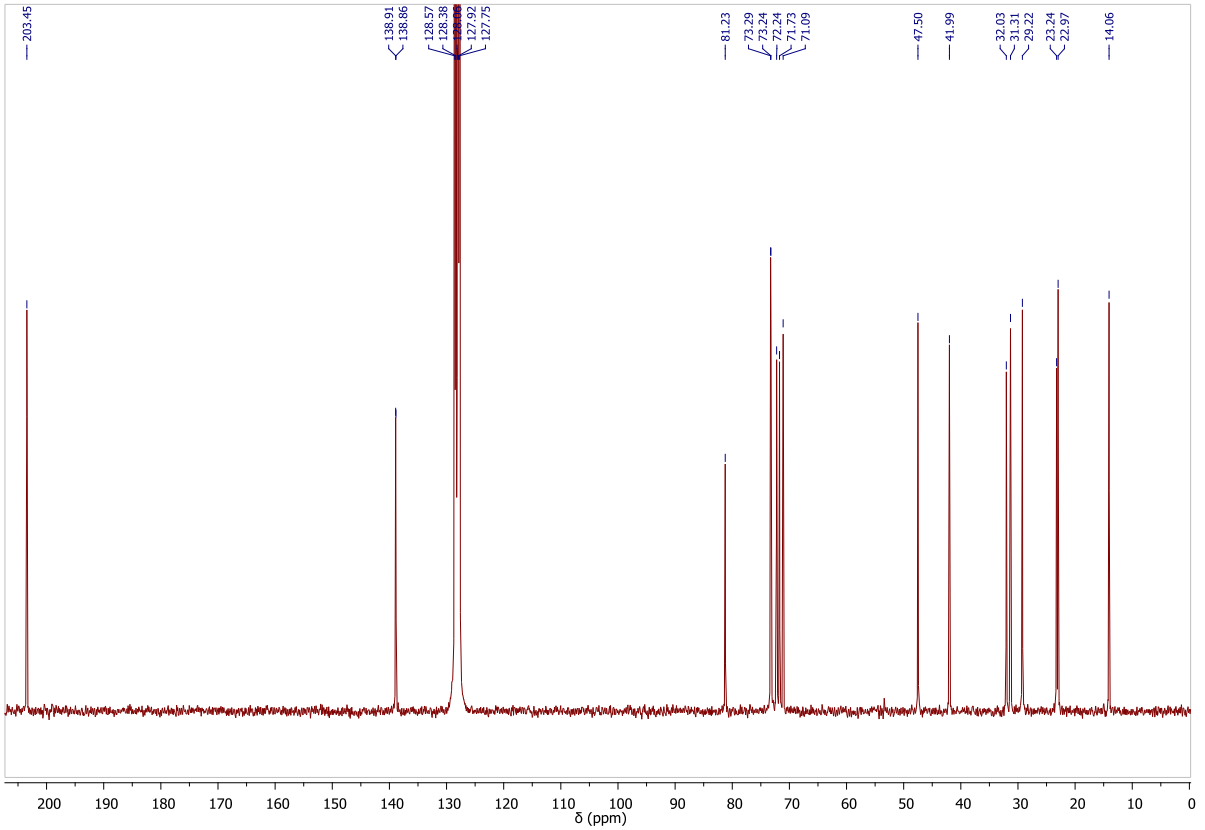


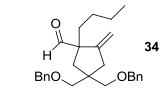




Chemical Formula: $C_{27}H_{34}O_3$
Molecular Weight: 406,55706

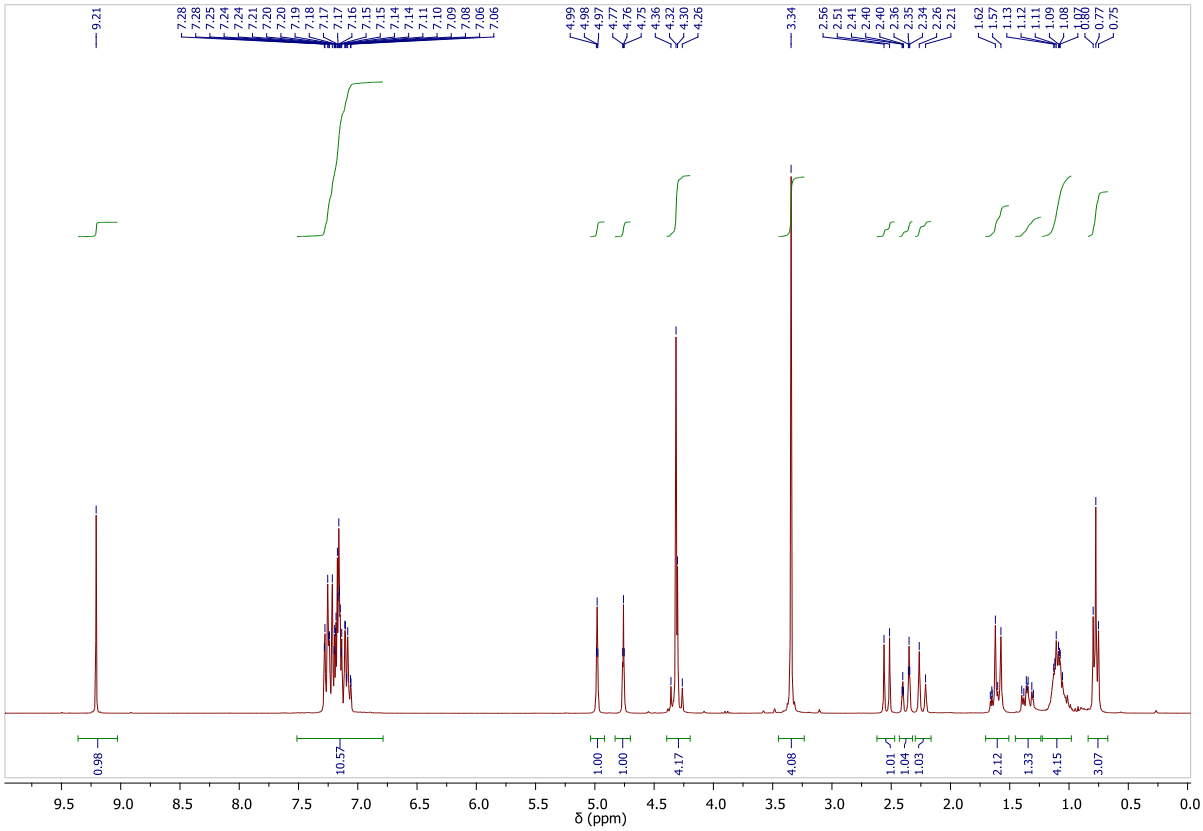


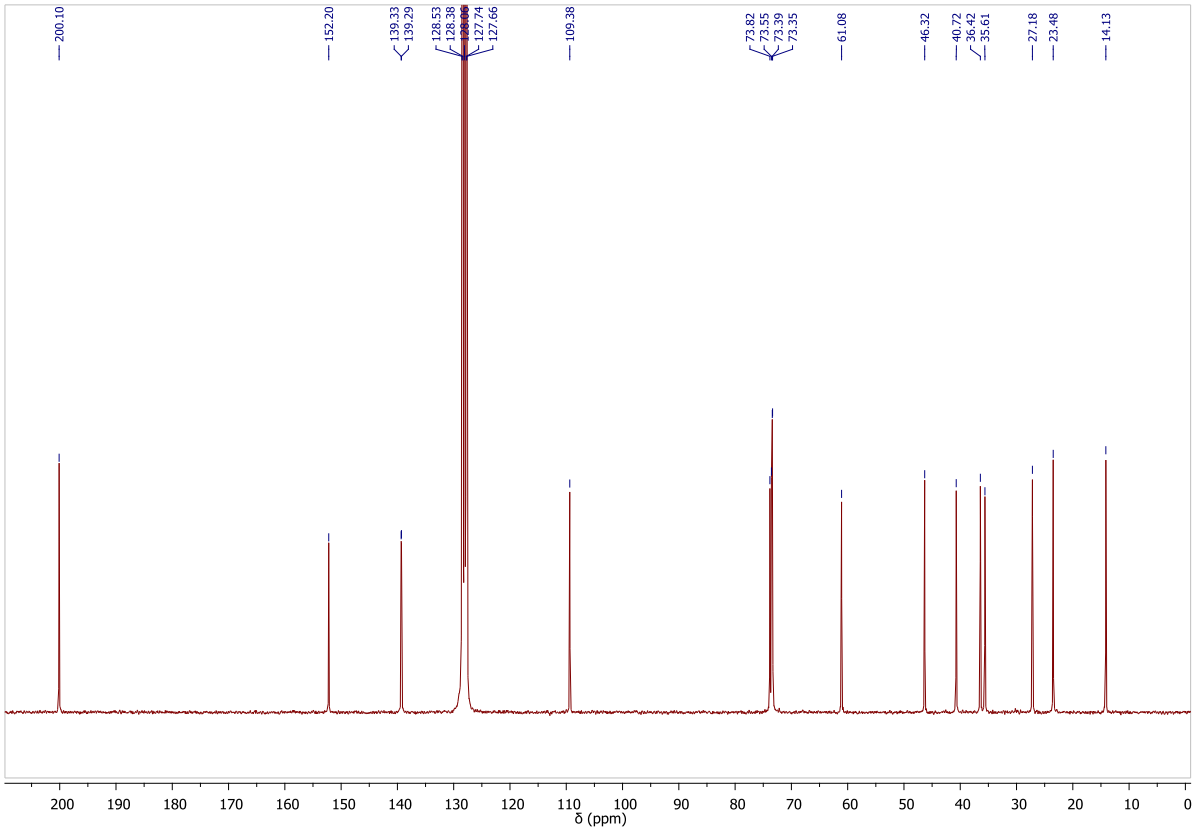


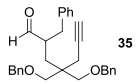


34

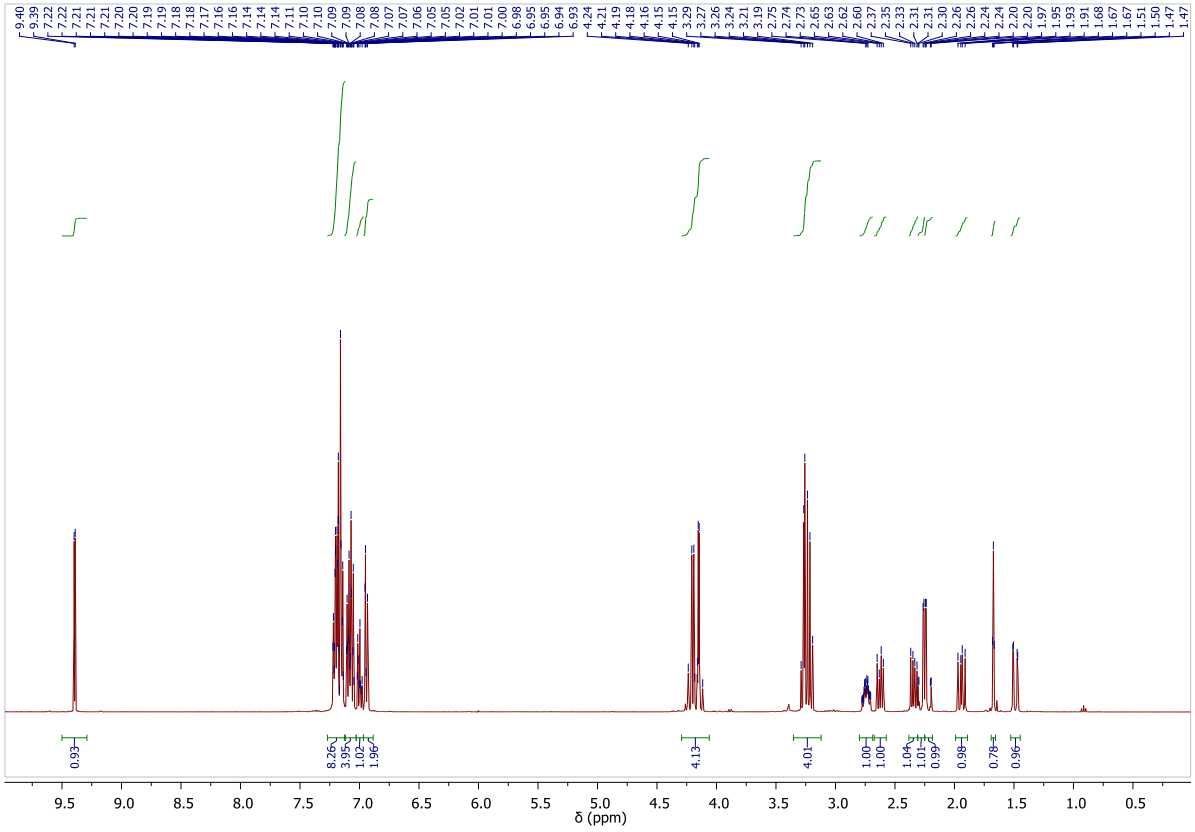
Chemical Formula: $C_{27}H_{34}O_3$
Molecular Weight: 406,55706

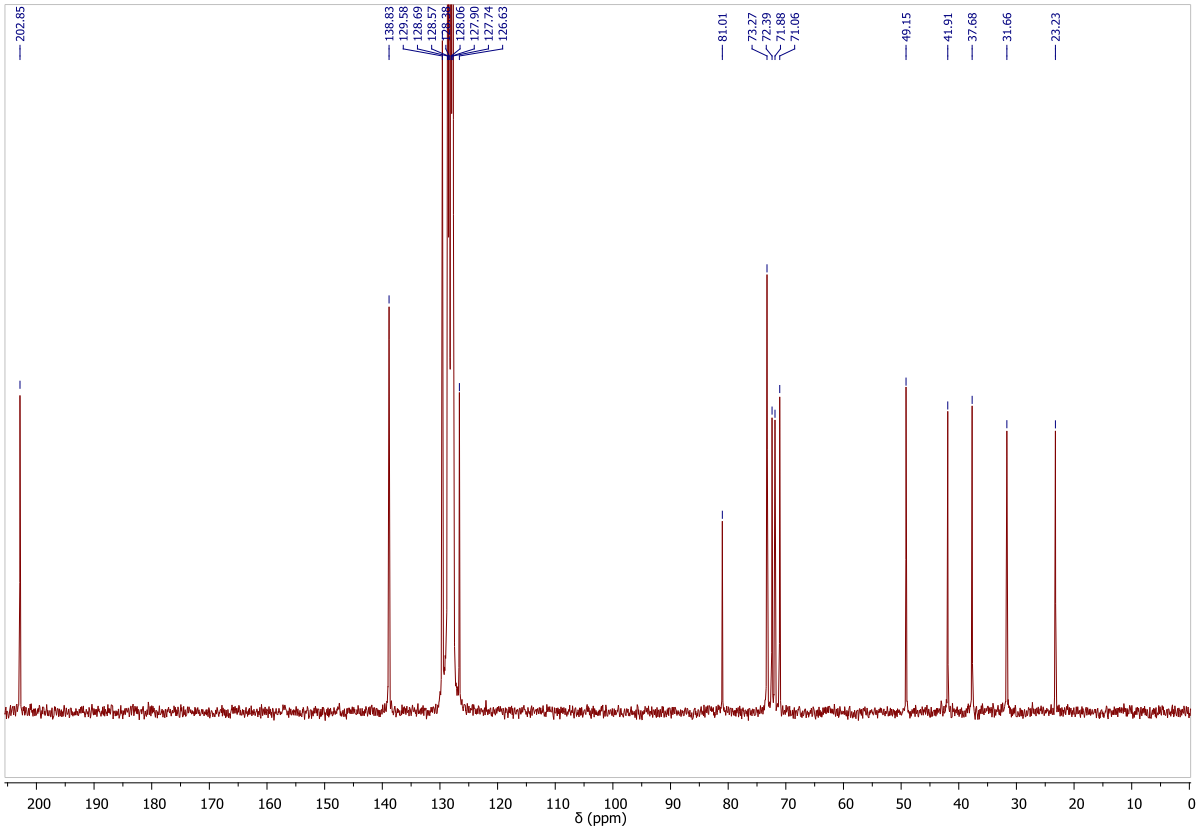


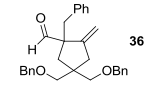




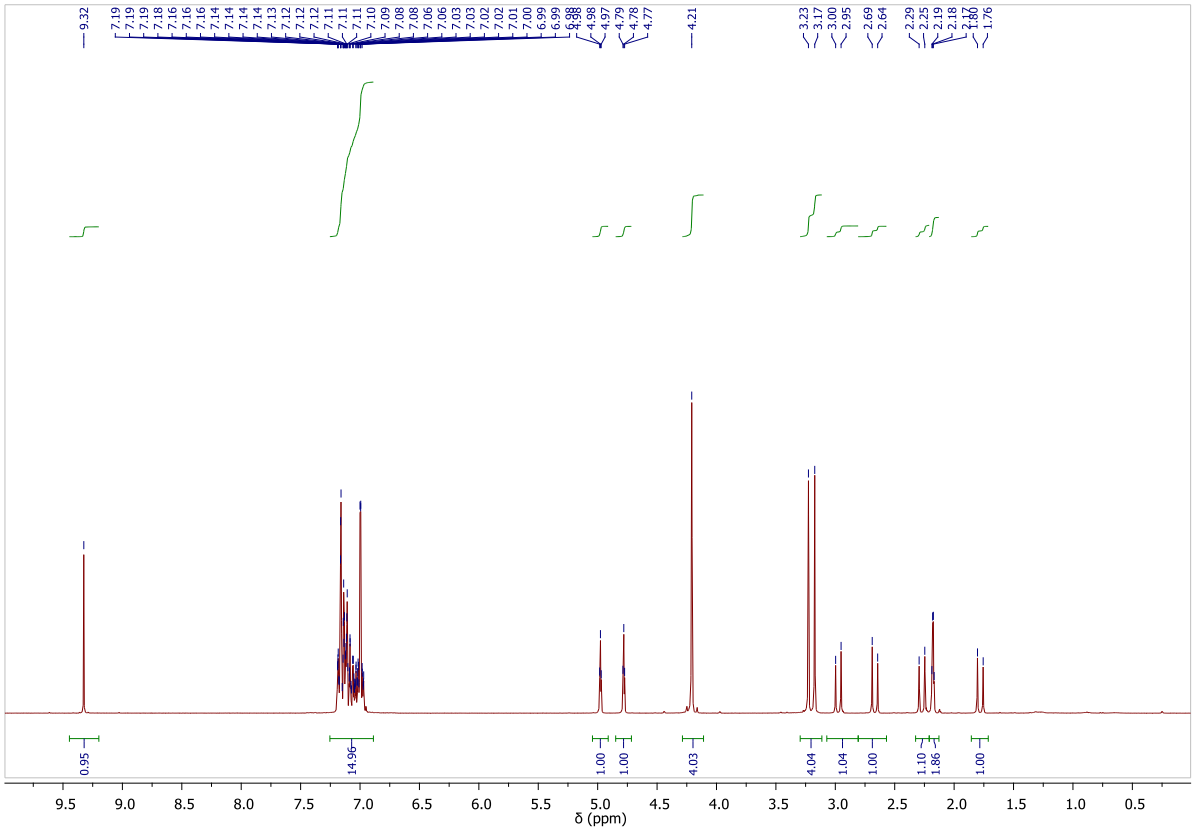
Chemical Formula: $C_{30}H_{32}O_3$
Molecular Weight: 440,57328

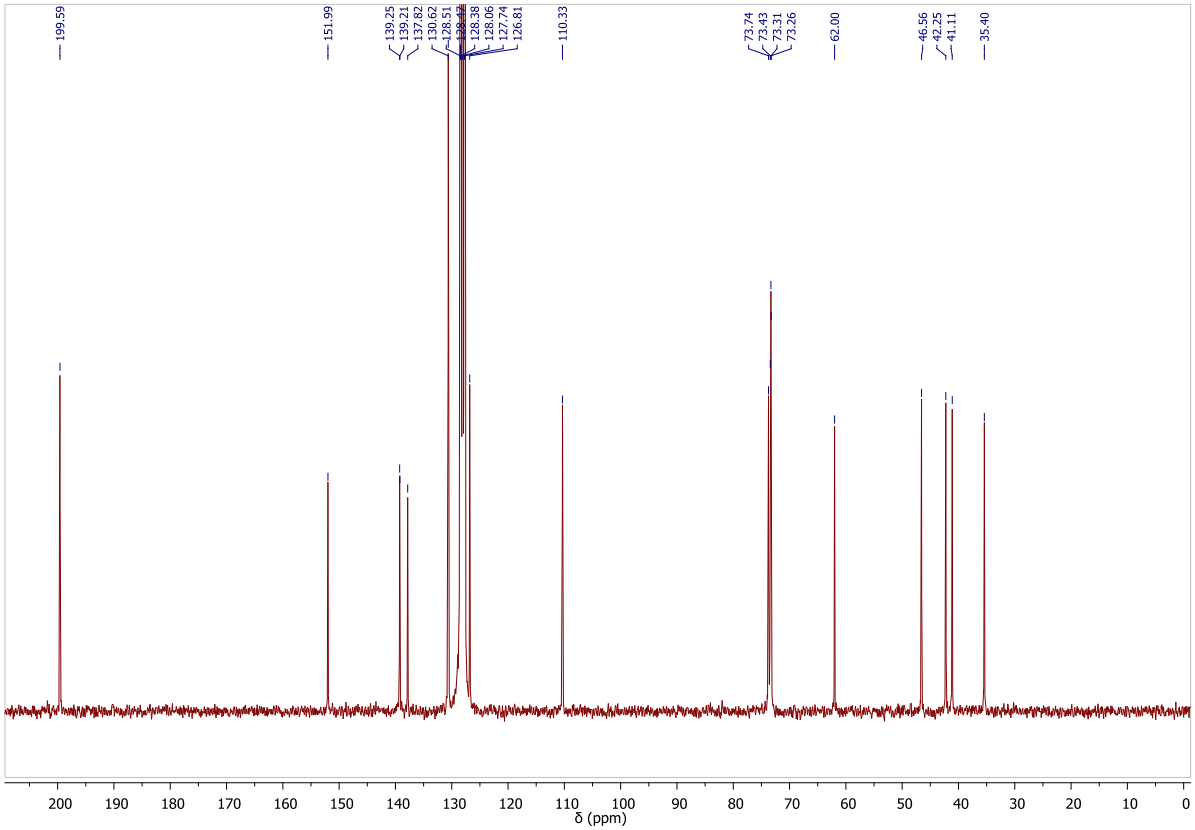


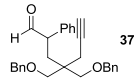




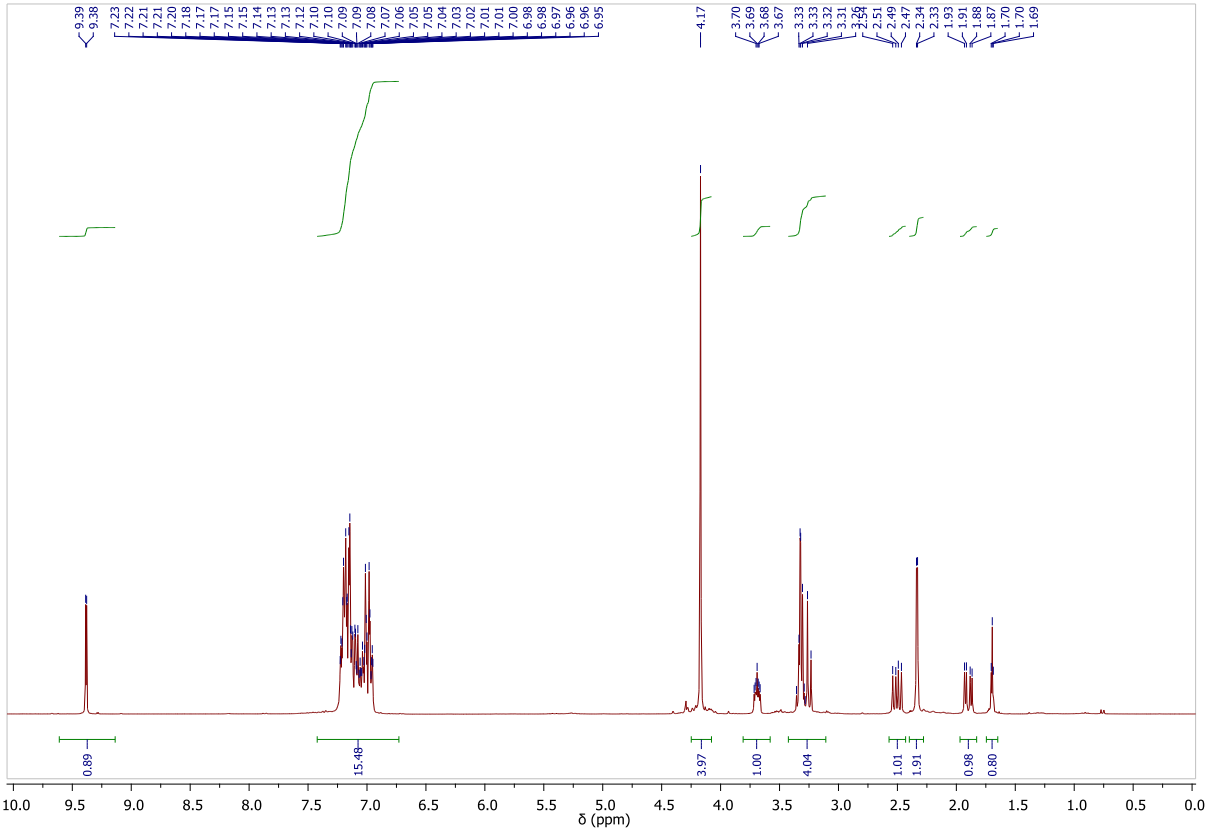
Chemical Formula: $C_{30}H_{32}O_3$
Molecular Weight: 440,57328

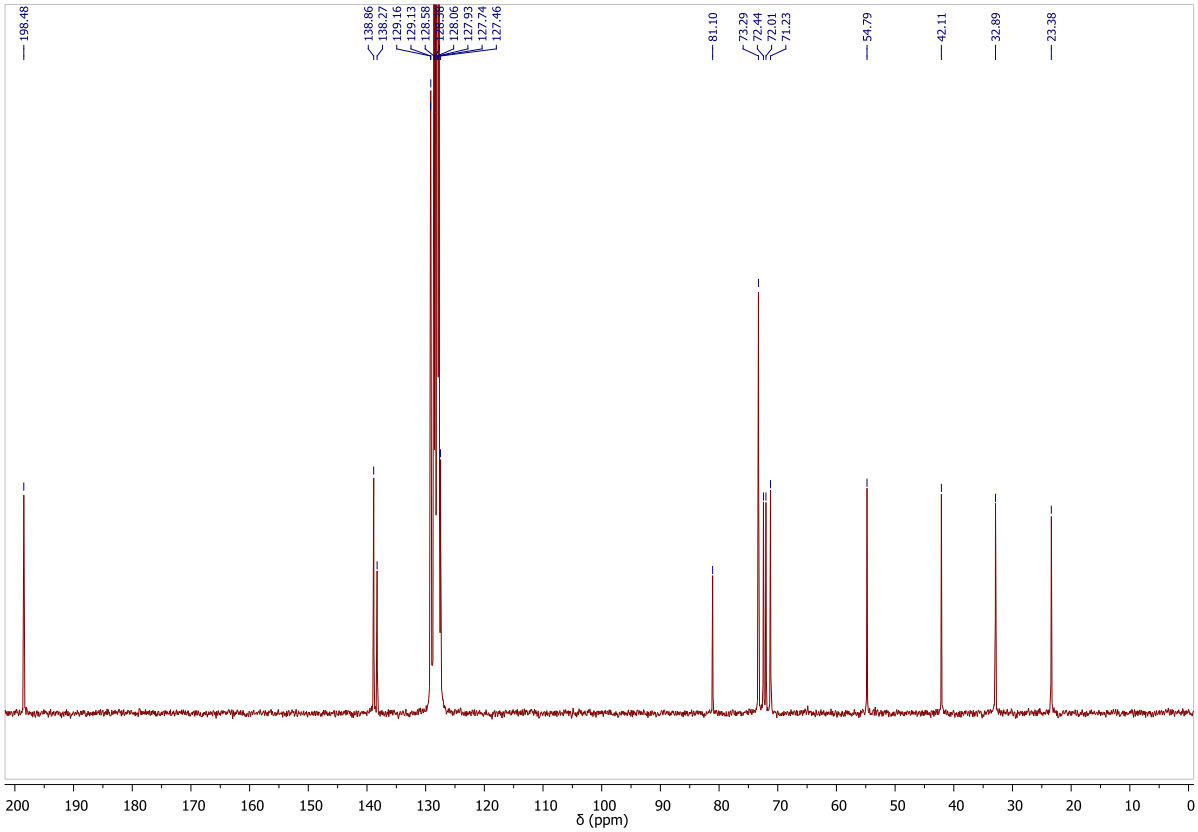


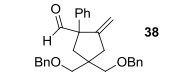




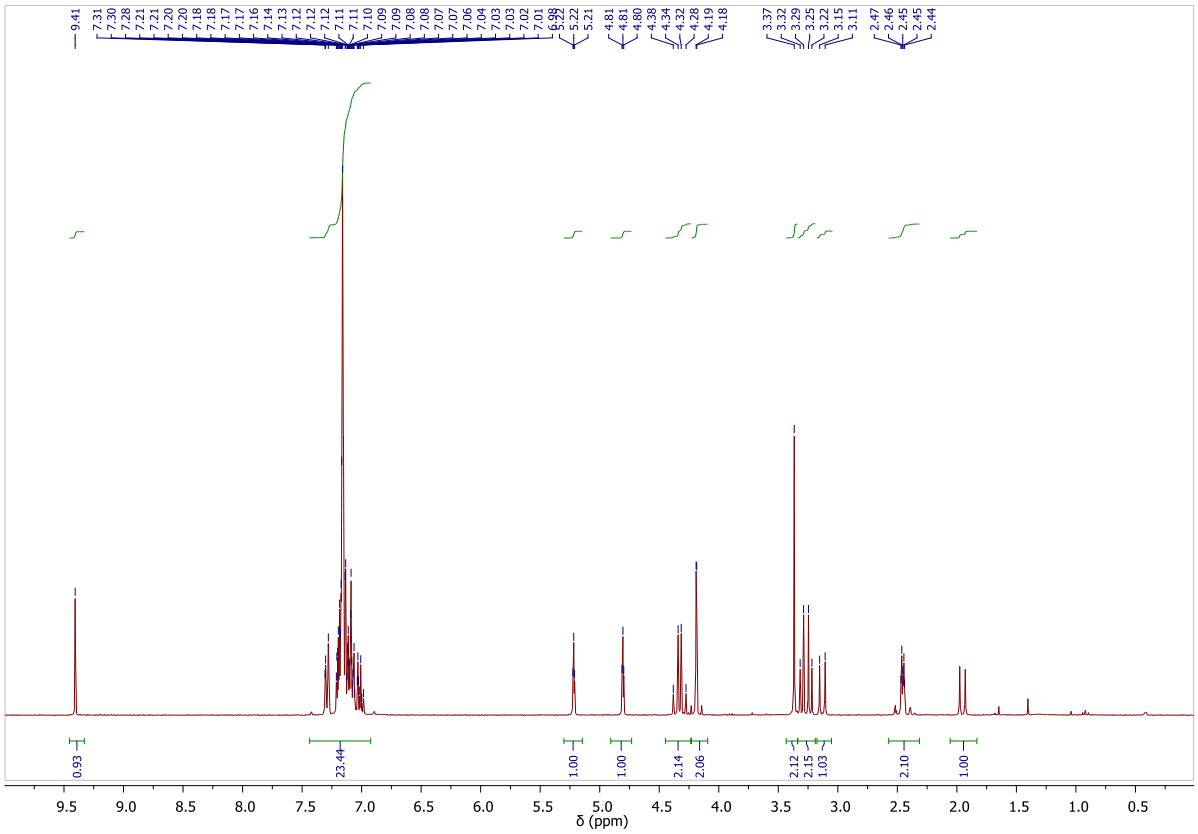
Chemical Formula: $C_{29}H_{30}O_3$
Molecular Weight: 426,54670

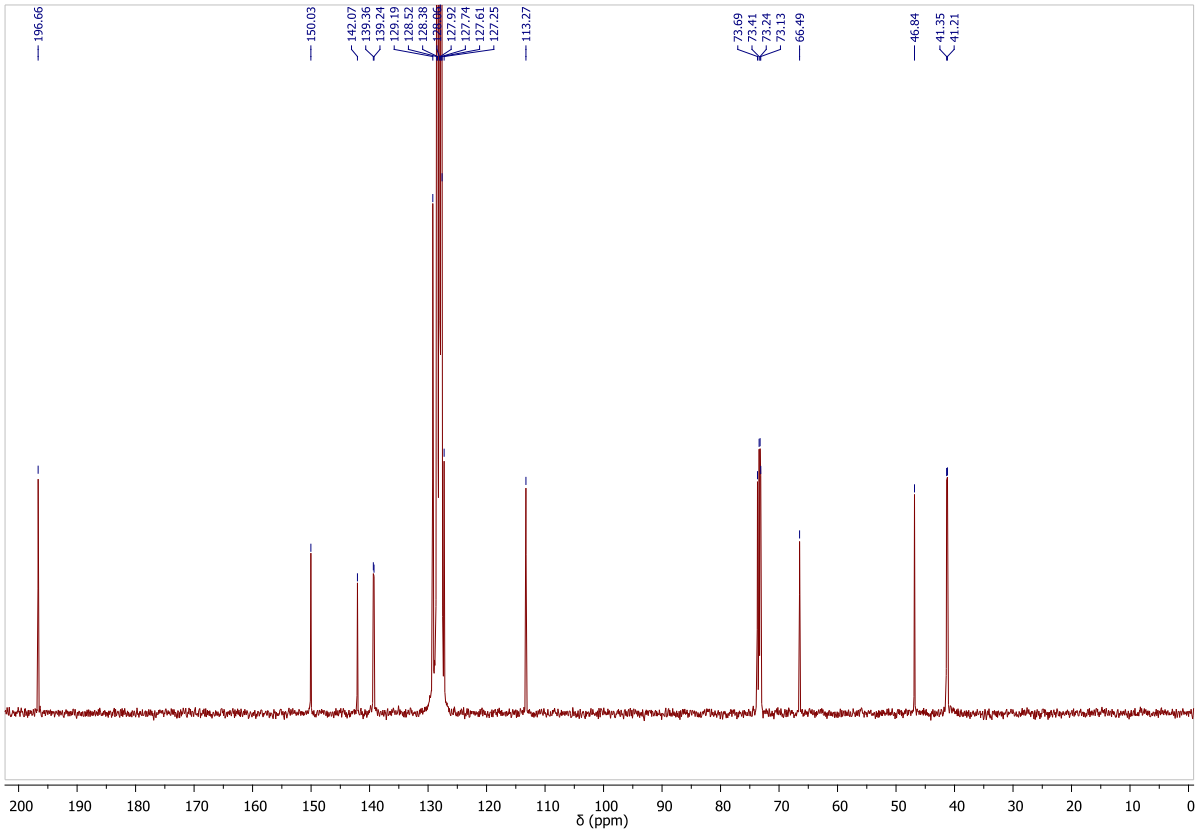


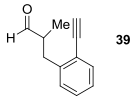




Chemical Formula: $C_{29}H_{30}O_3$
Molecular Weight: 426,54670







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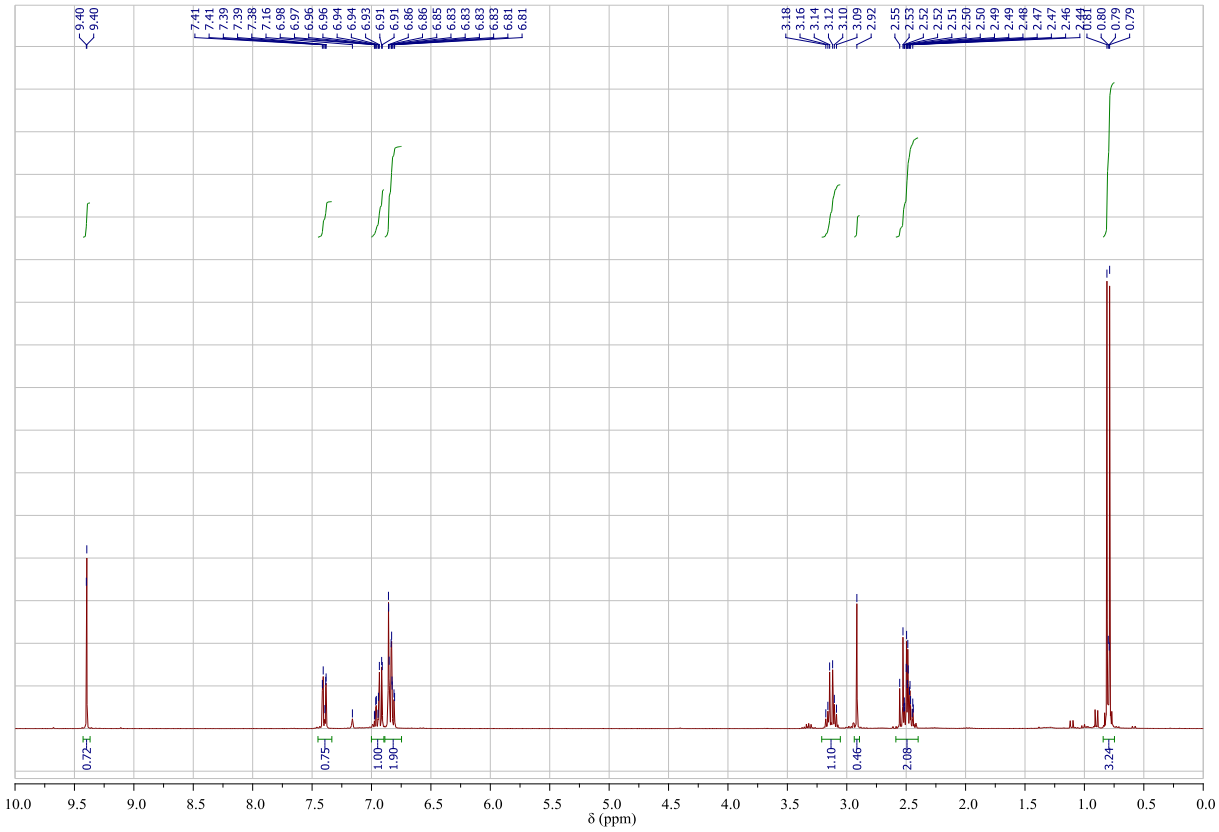
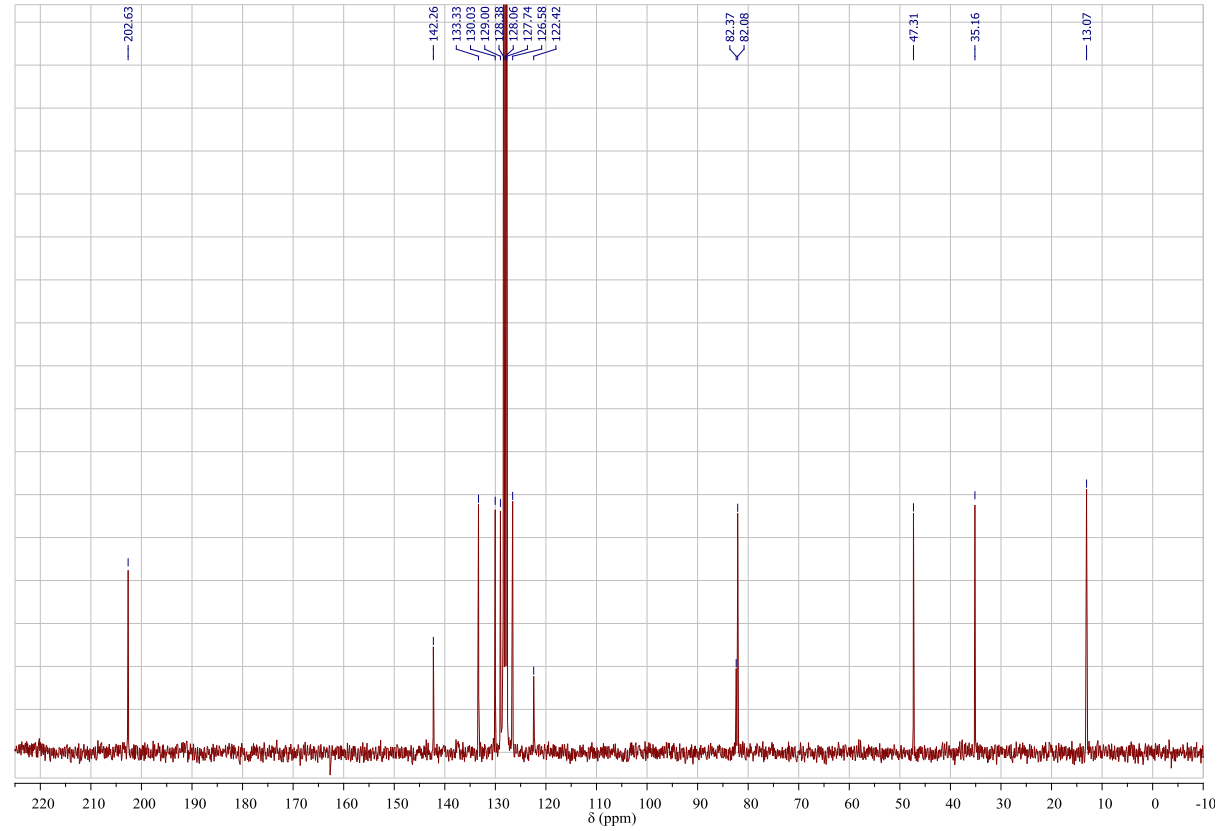
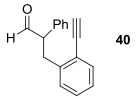
Chemical Formula: $C_{12}H_{12}O$
Molecular Weight: 172,22308

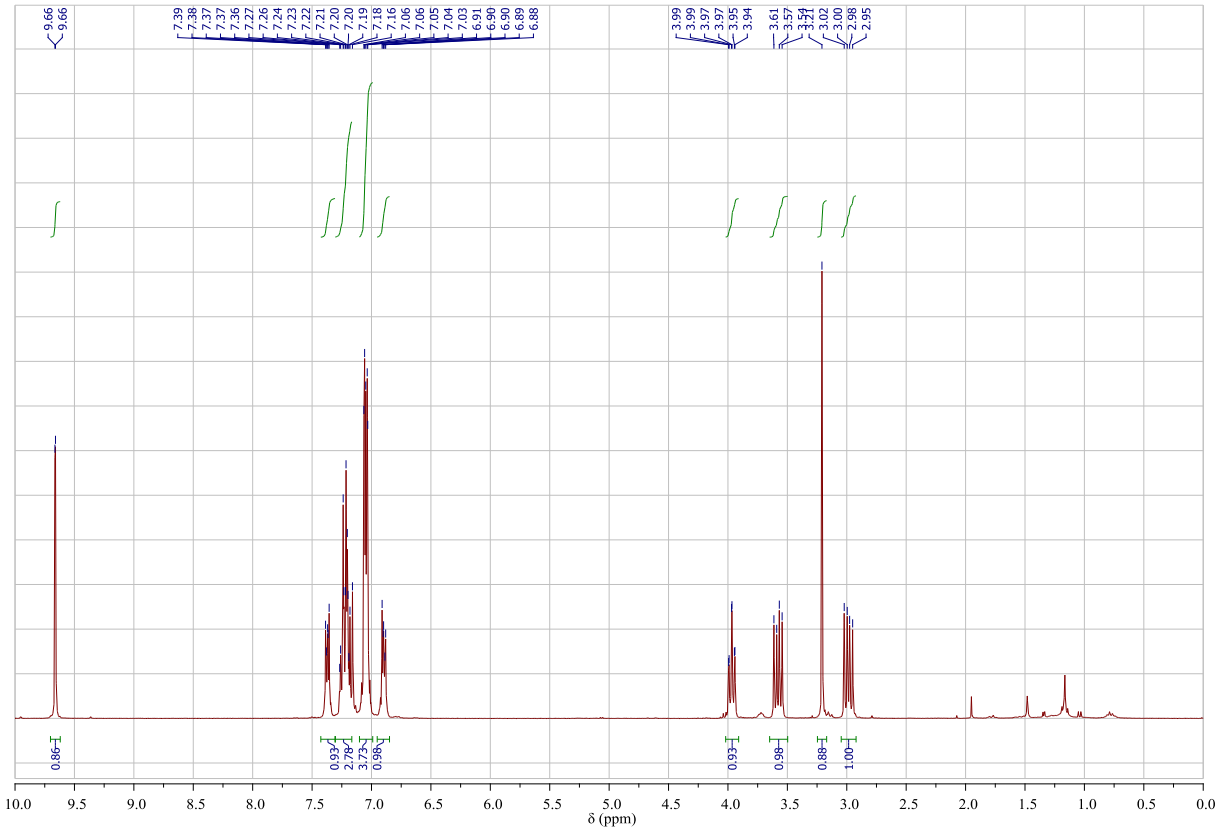


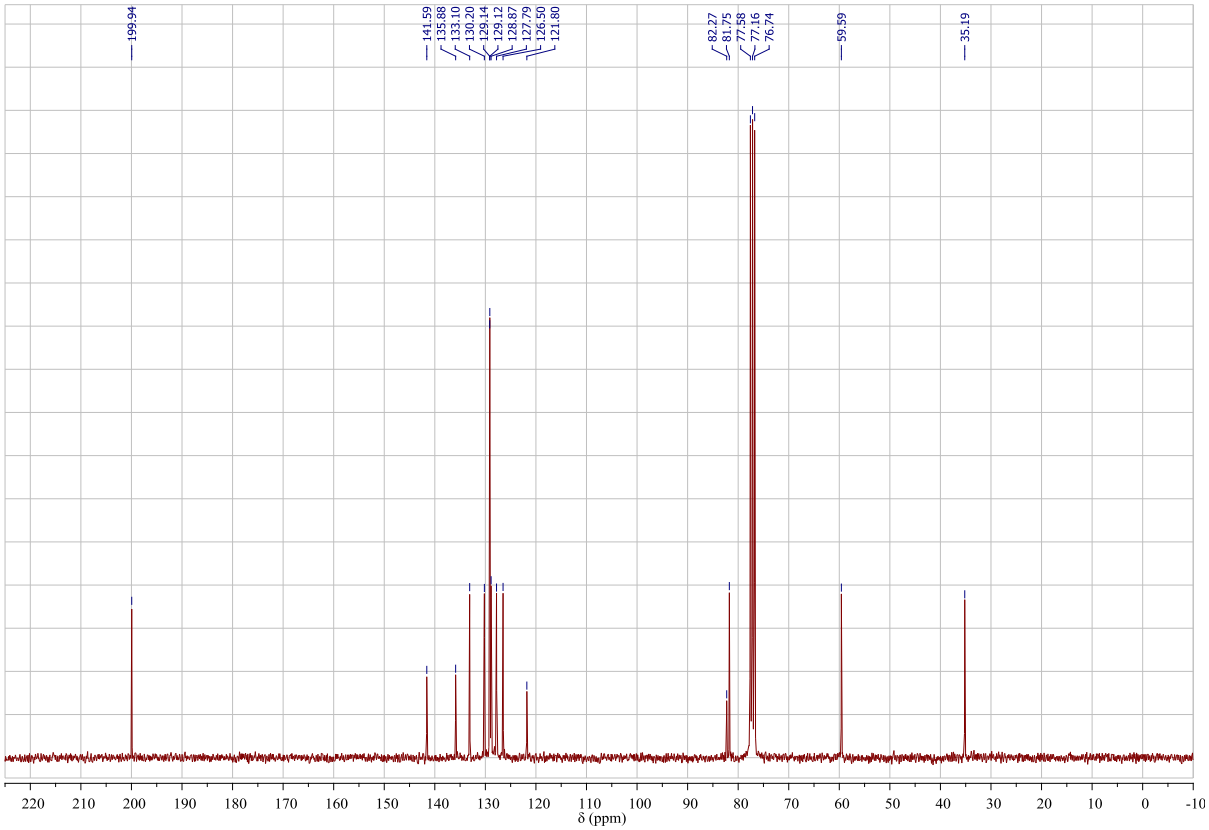


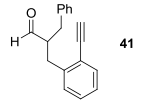


40

Chemical Formula: $C_{17}H_{14}O$
Molecular Weight: 234,29246

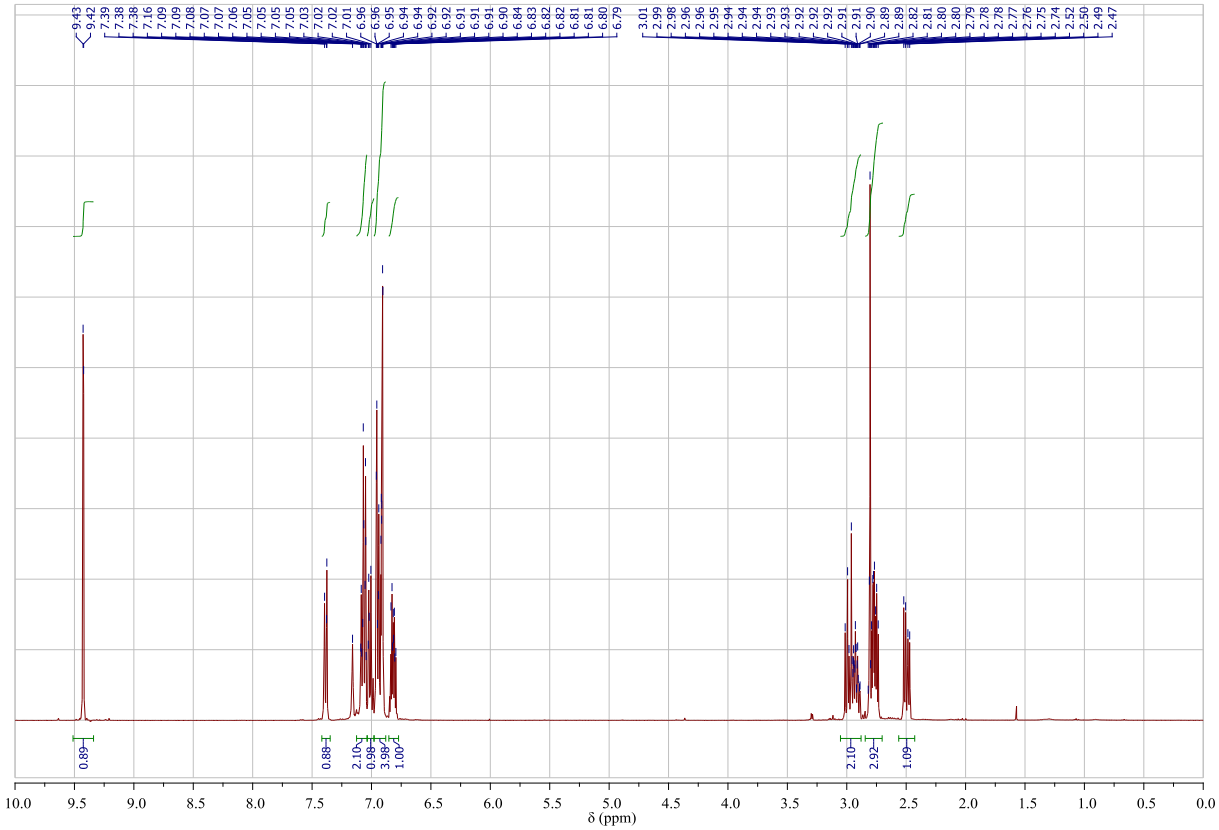


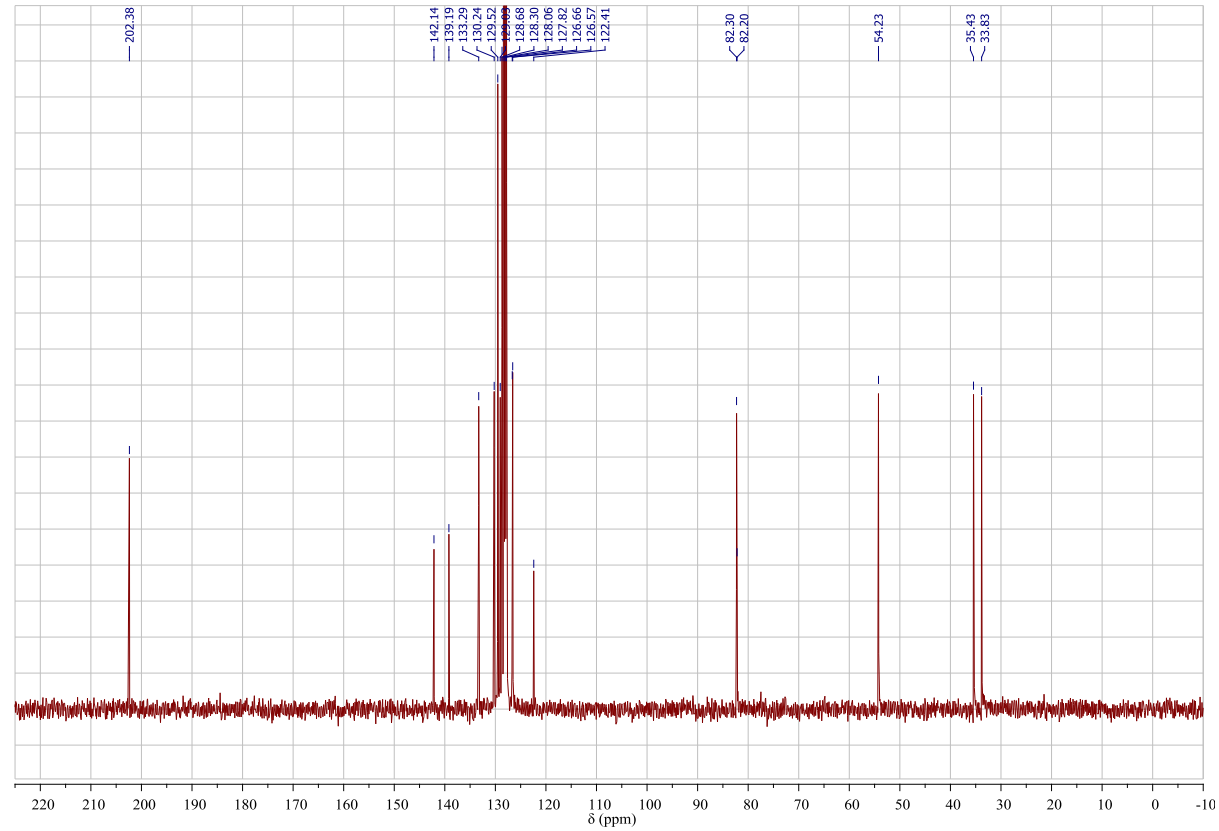


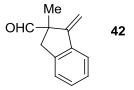


41

Chemical Formula: $C_{18}H_{16}O$
Molecular Weight: 248,31904

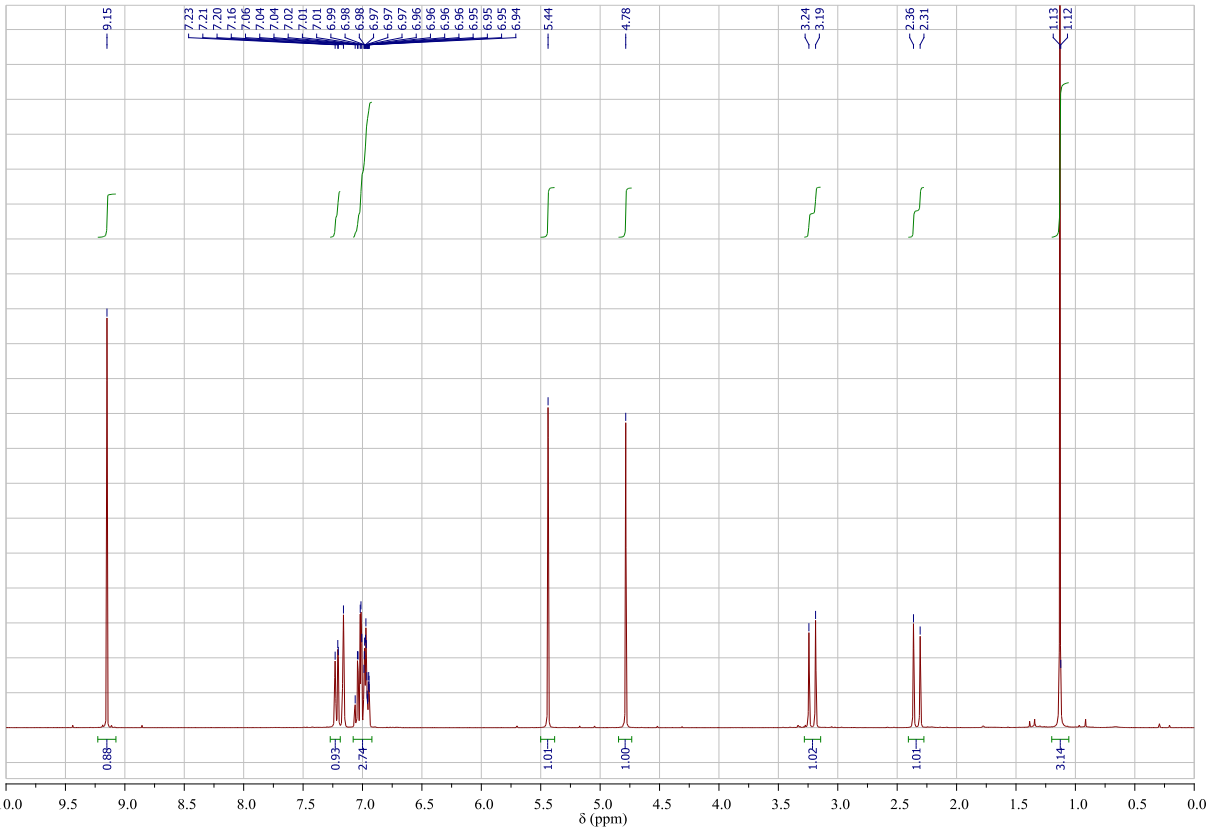


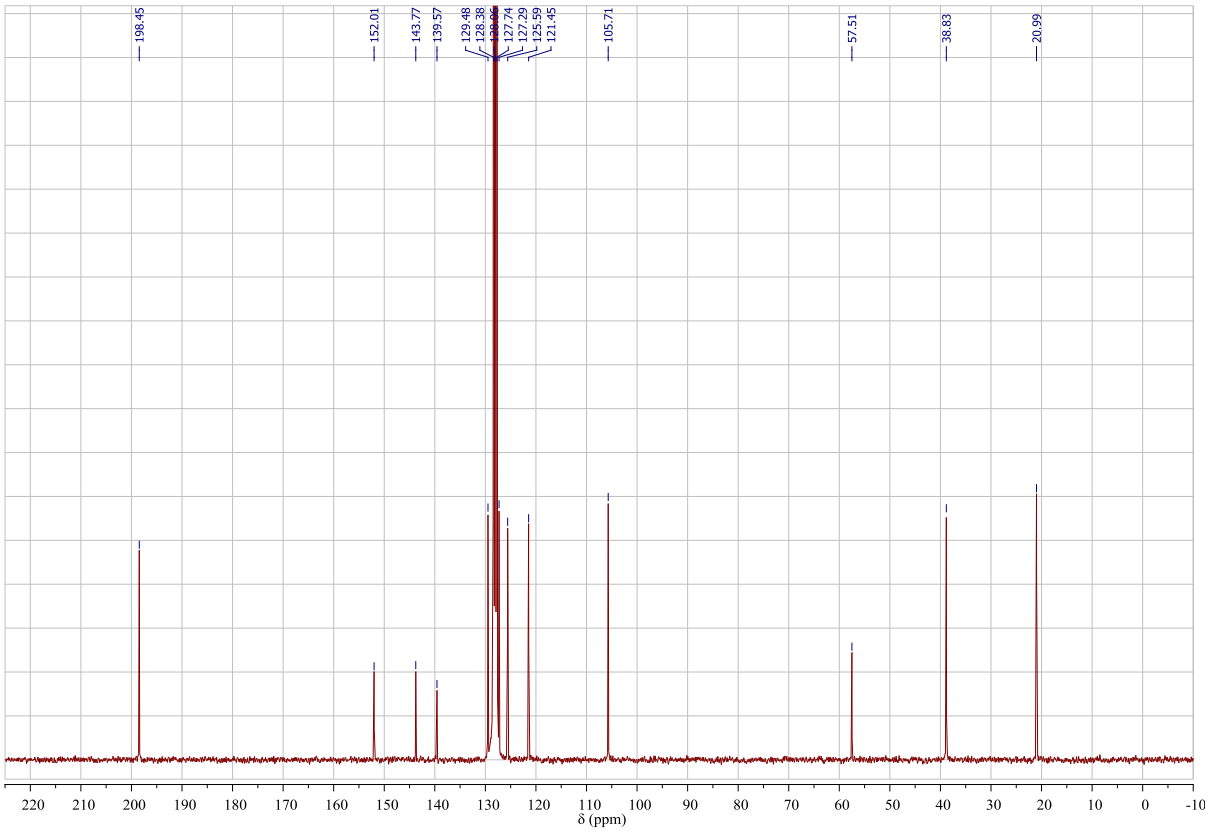


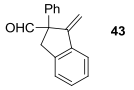


42

Chemical Formula: $C_{12}H_{12}O$
Molecular Weight: 172,22308

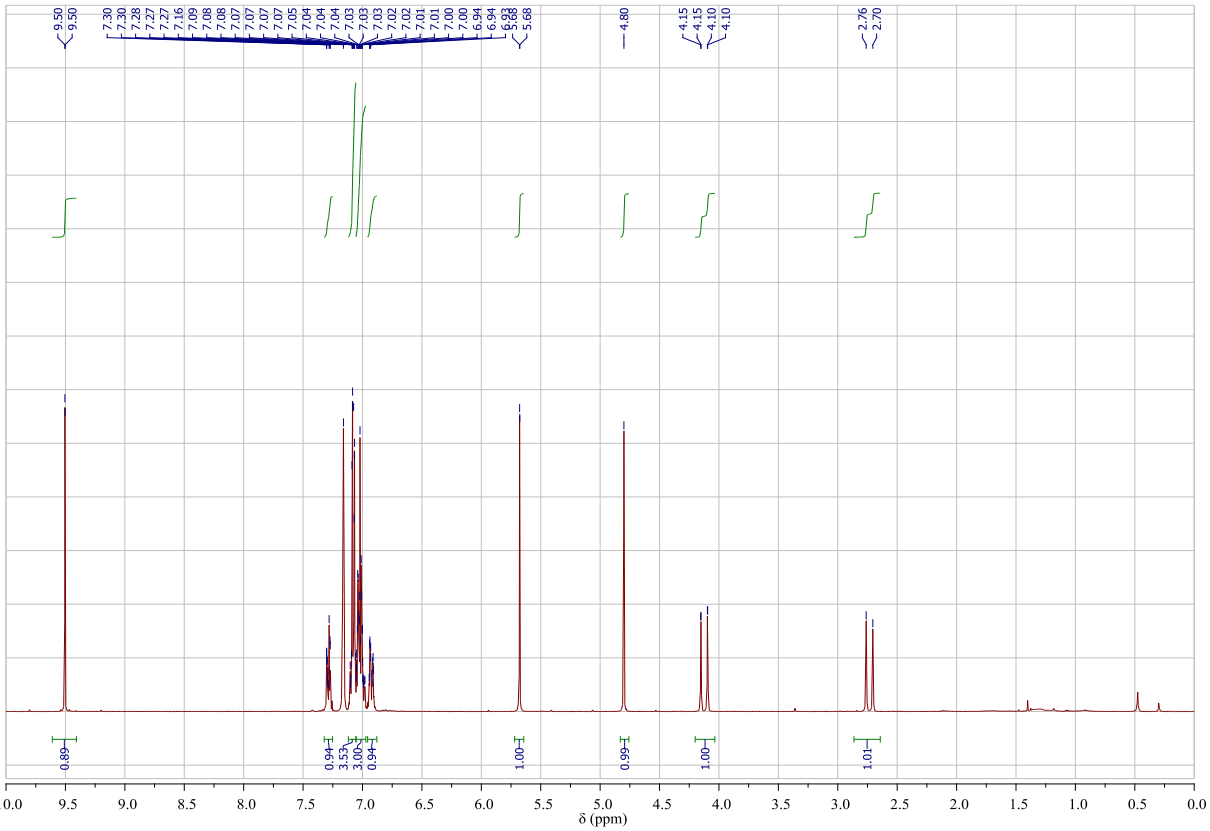


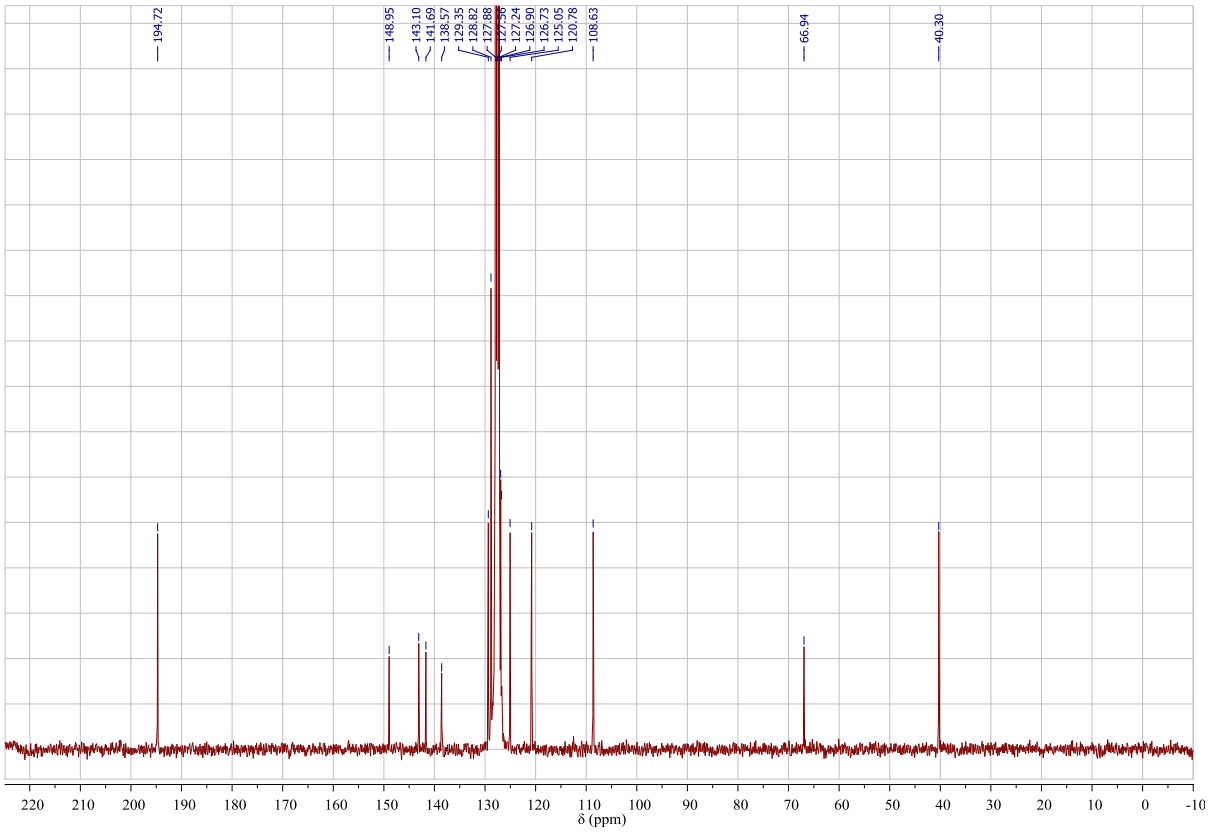


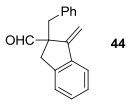


43

Chemical Formula: $C_{17}H_{14}O$
Molecular Weight: 234,29246

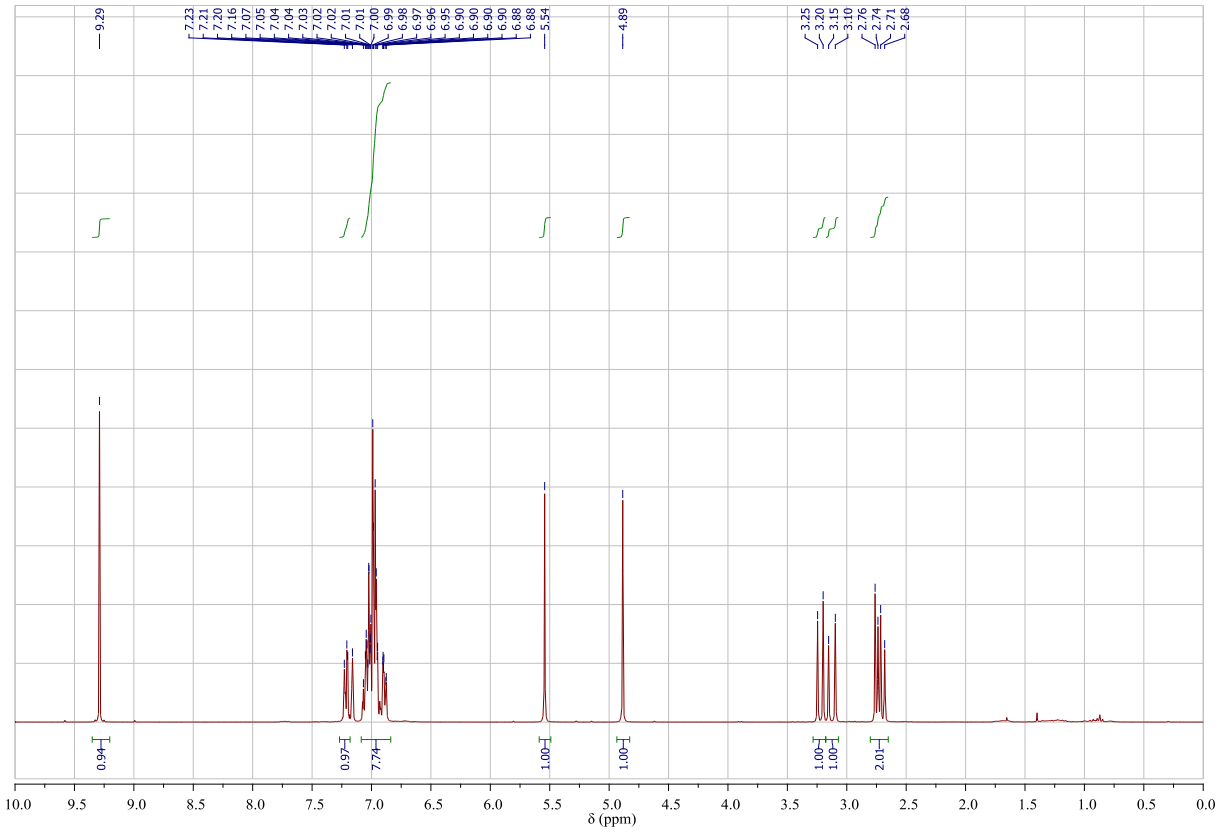


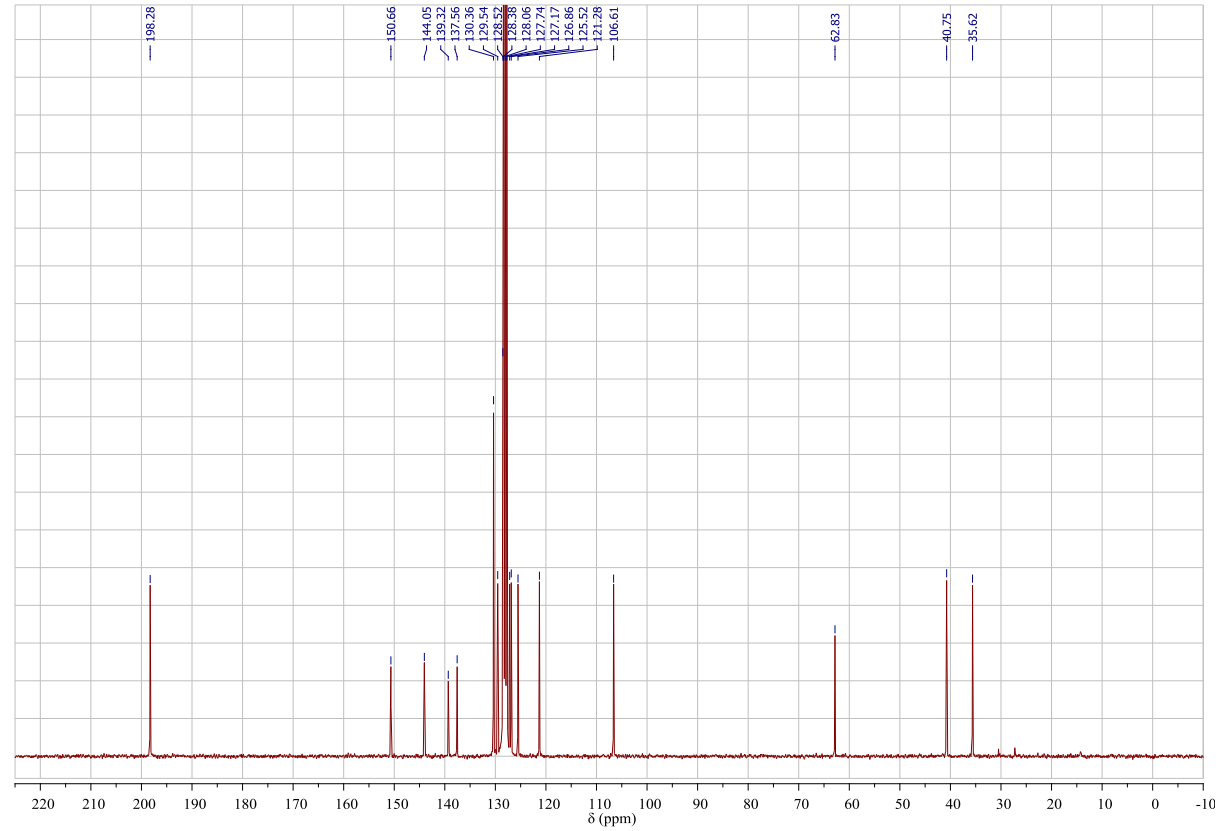




44

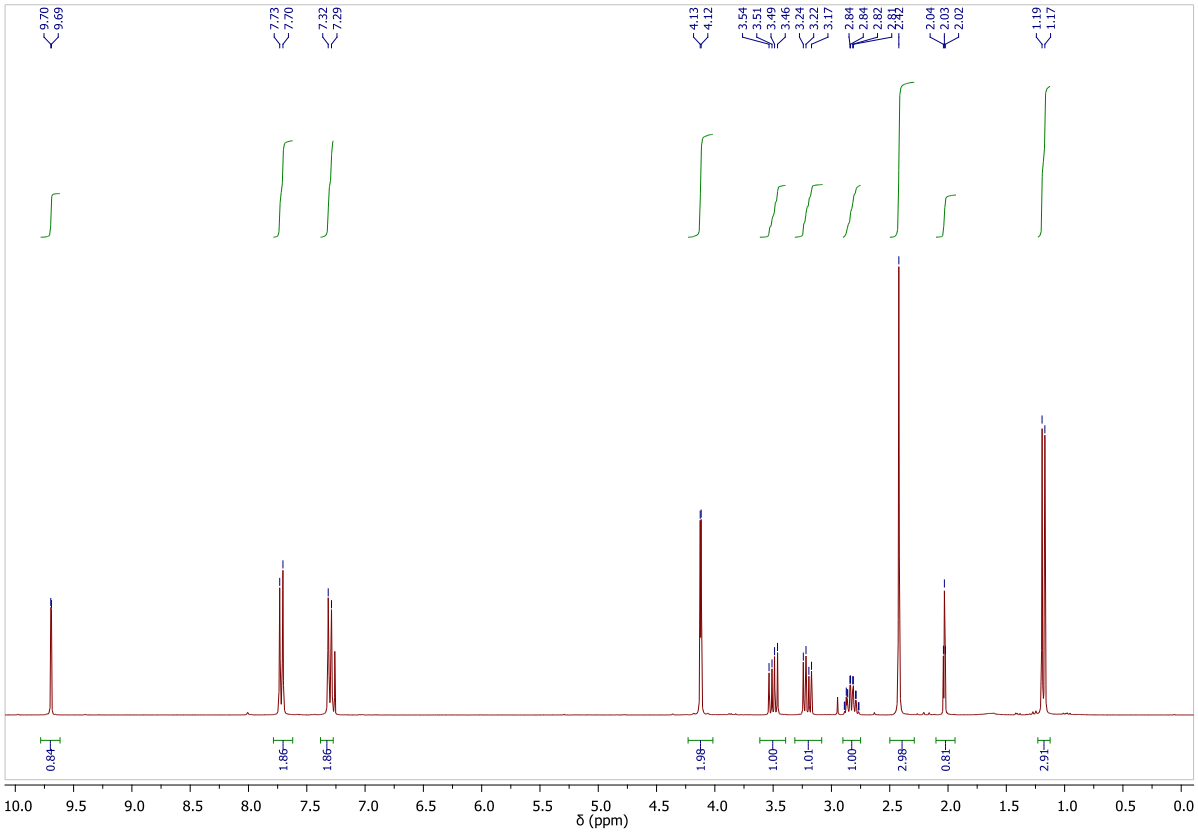
Chemical Formula: $C_{18}H_{16}O$
Molecular Weight: 248,31904

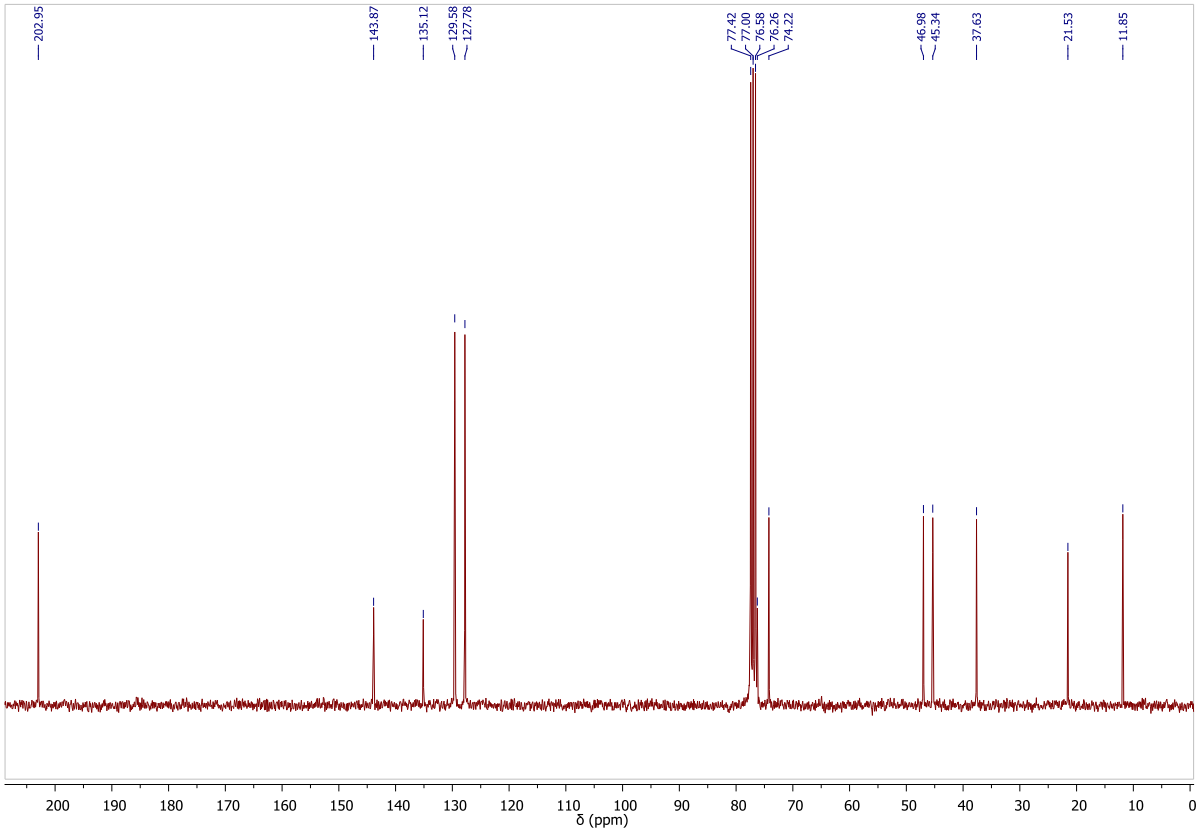


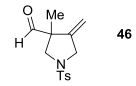


45

Chemical Formula: $C_{14}H_{17}NO_3S$
Molecular Weight: 279,35468

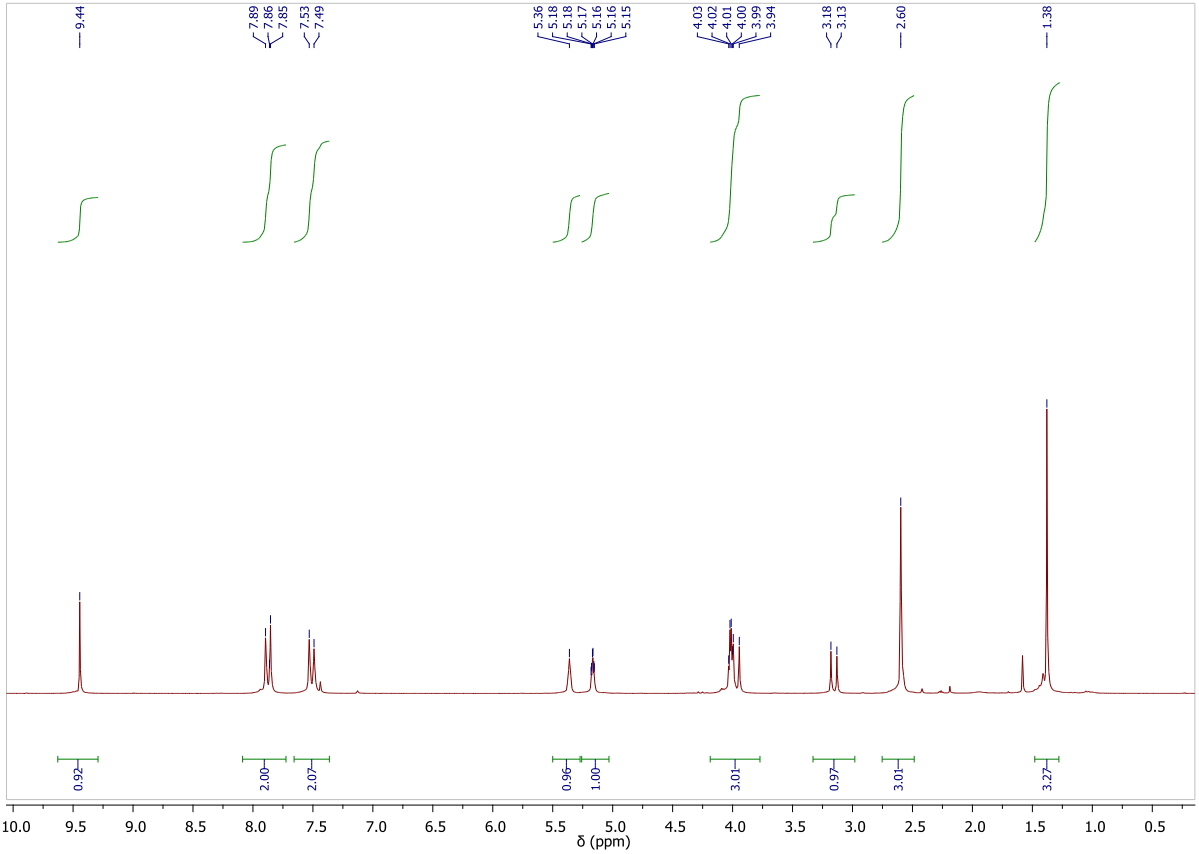


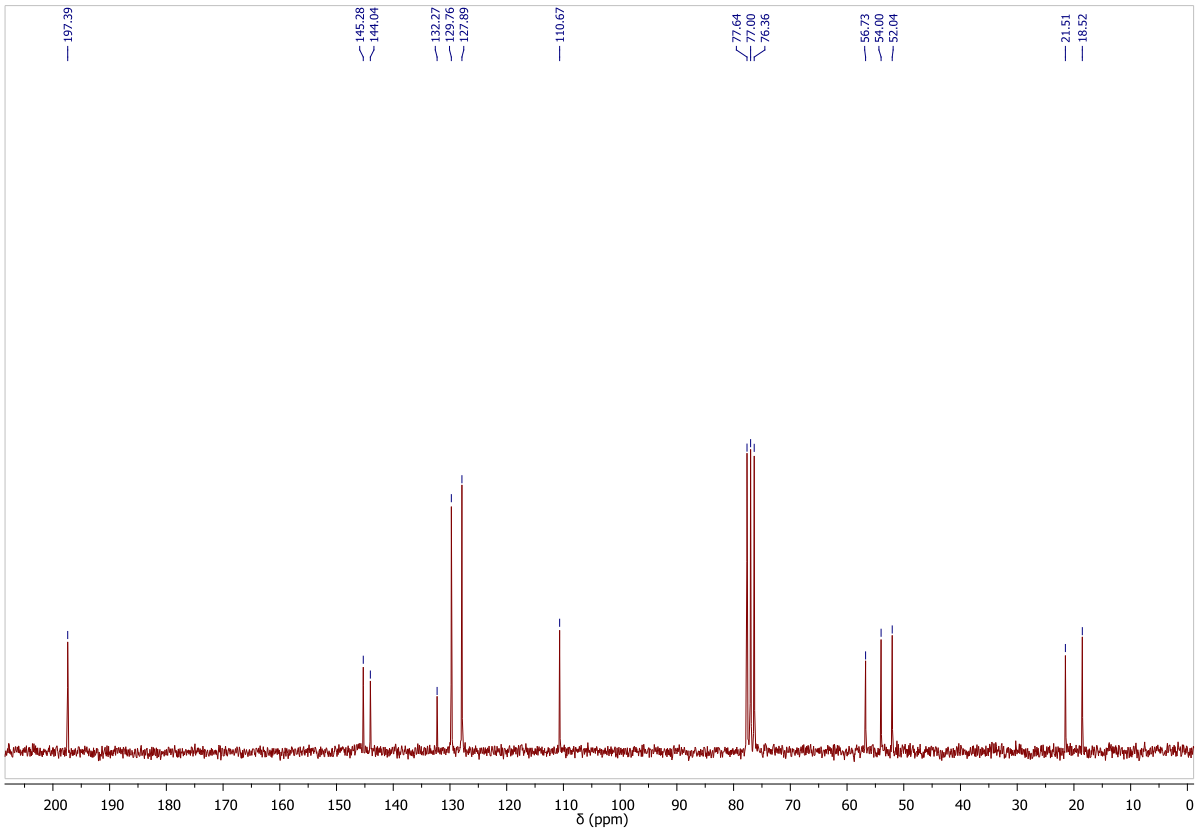


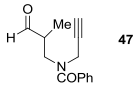


46

Chemical Formula: $C_{14}H_{17}NO_3S$
Molecular Weight: 279,35468

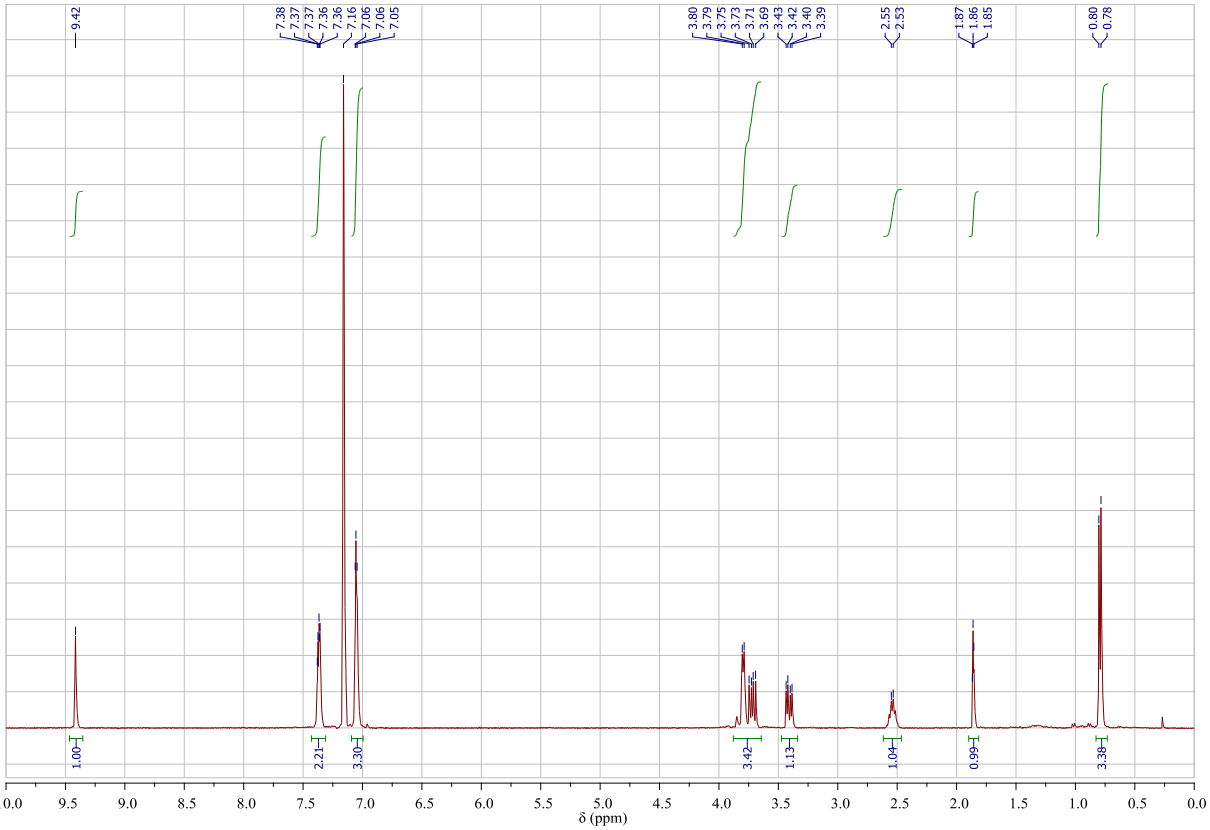


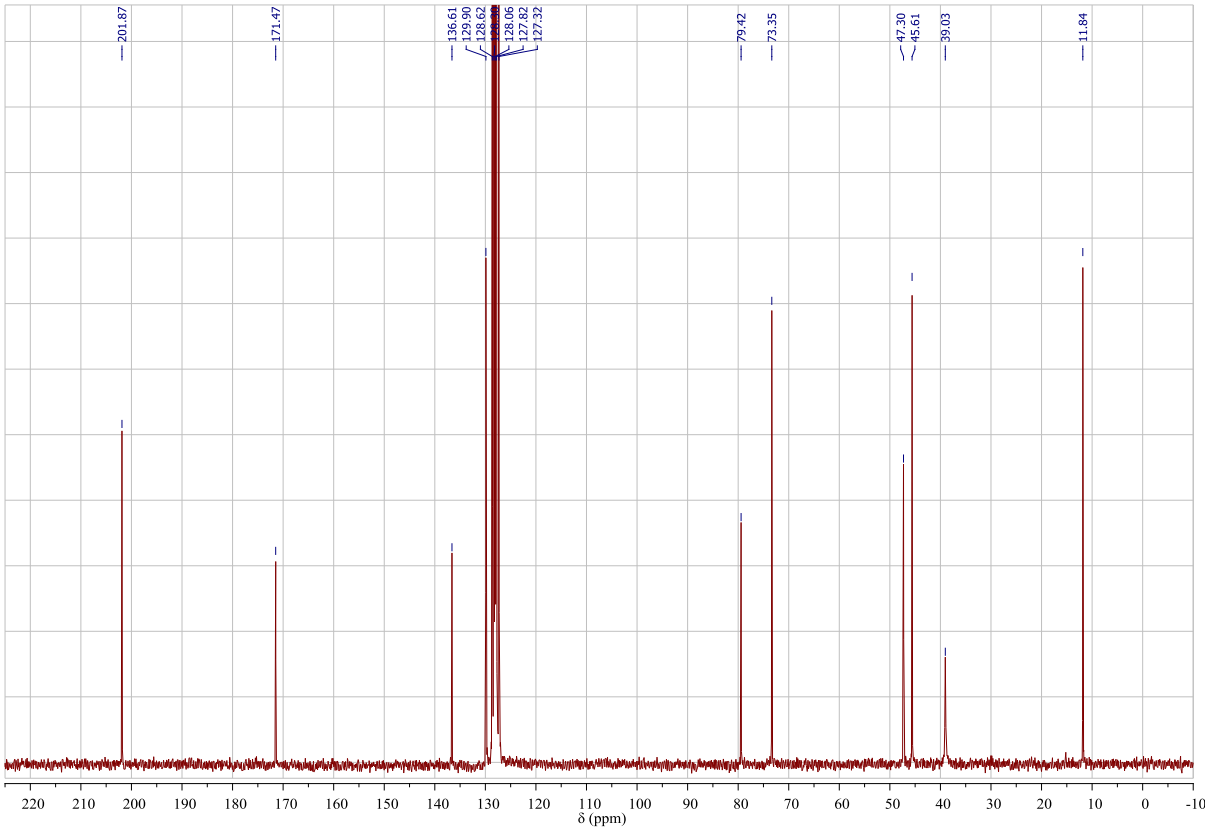


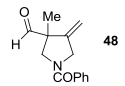


47

Chemical Formula: $C_{14H15NO2}$
Molecular Weight: 229,27440

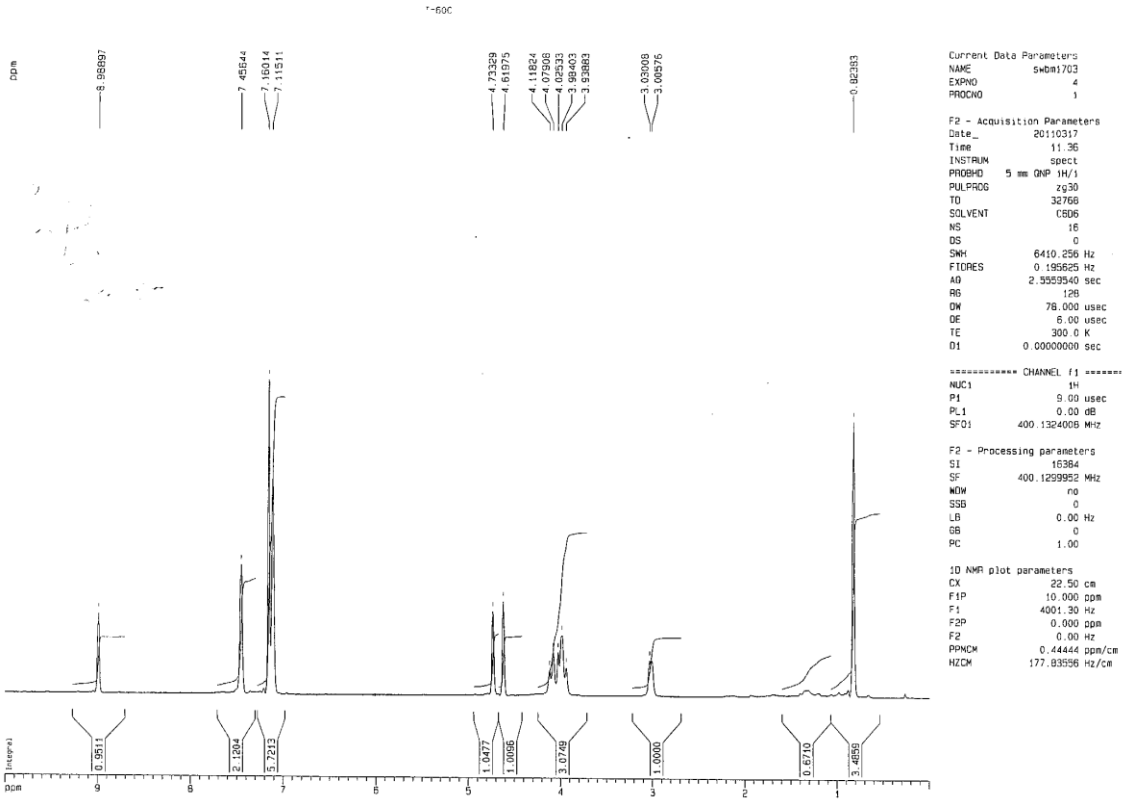


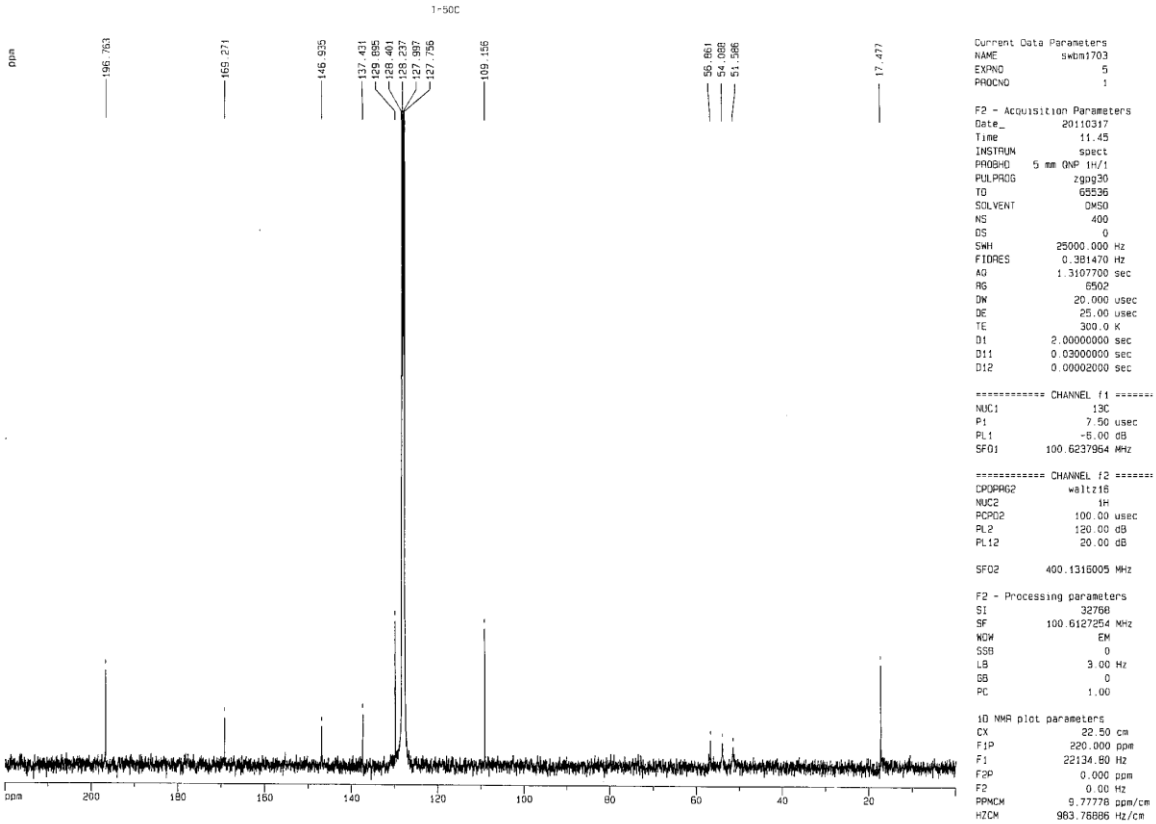




48

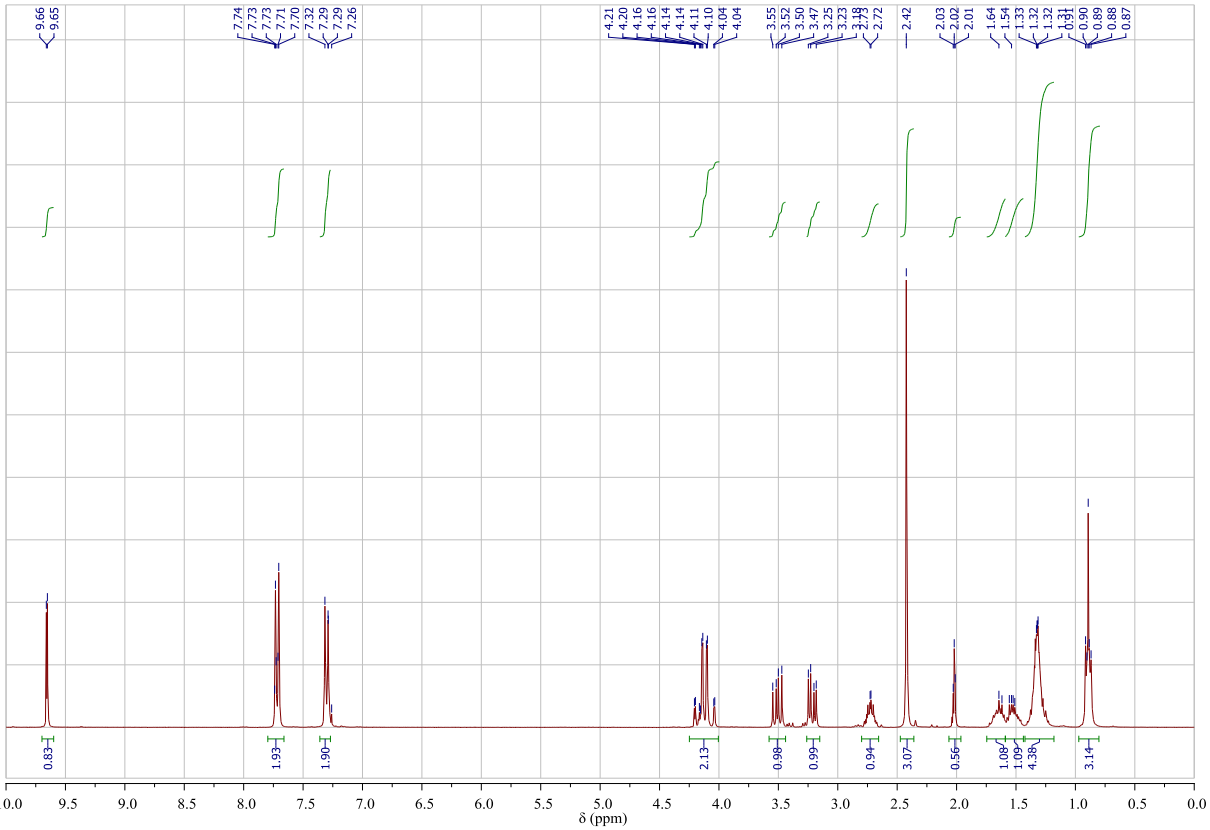
Chemical Formula: $C_{14H15NO2}$
Molecular Weight: 229,27440

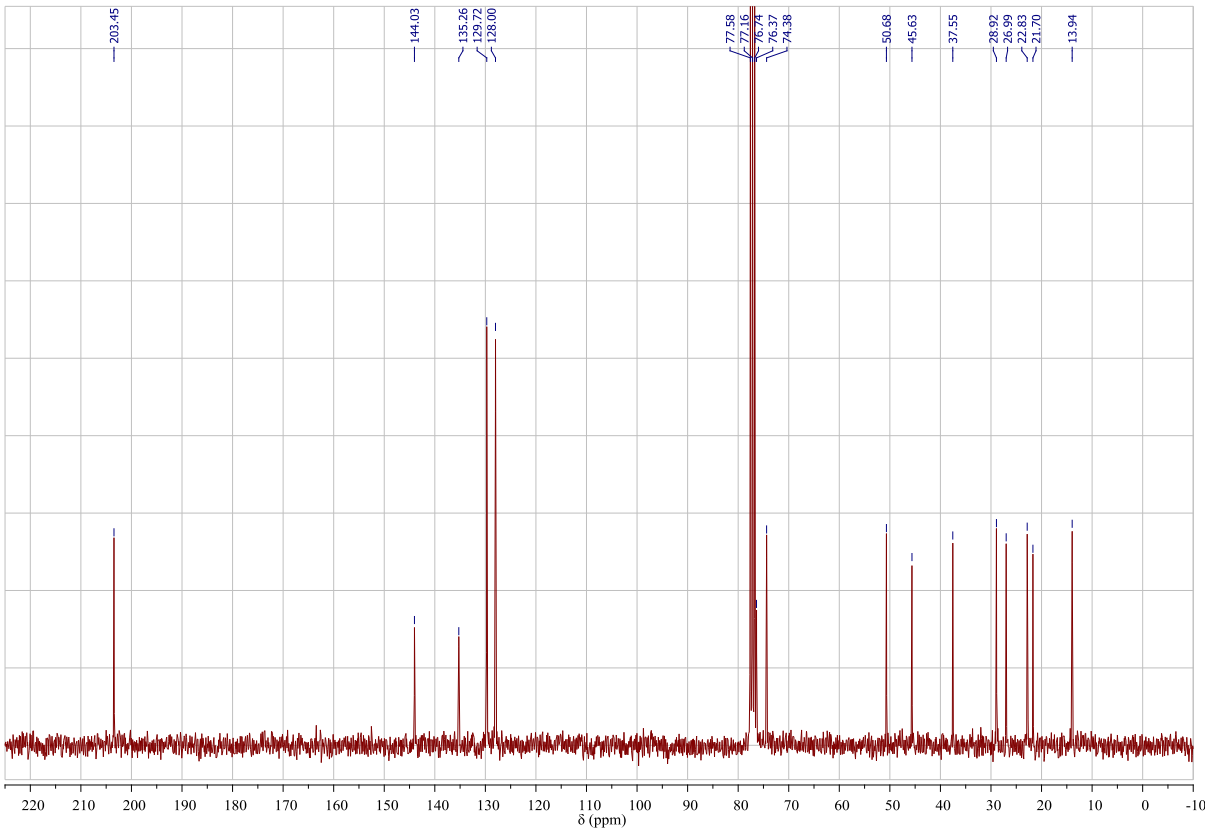


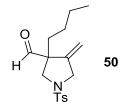


49

Chemical Formula: $C_{17}H_{23}NO_3S$
Molecular Weight: 321,43442

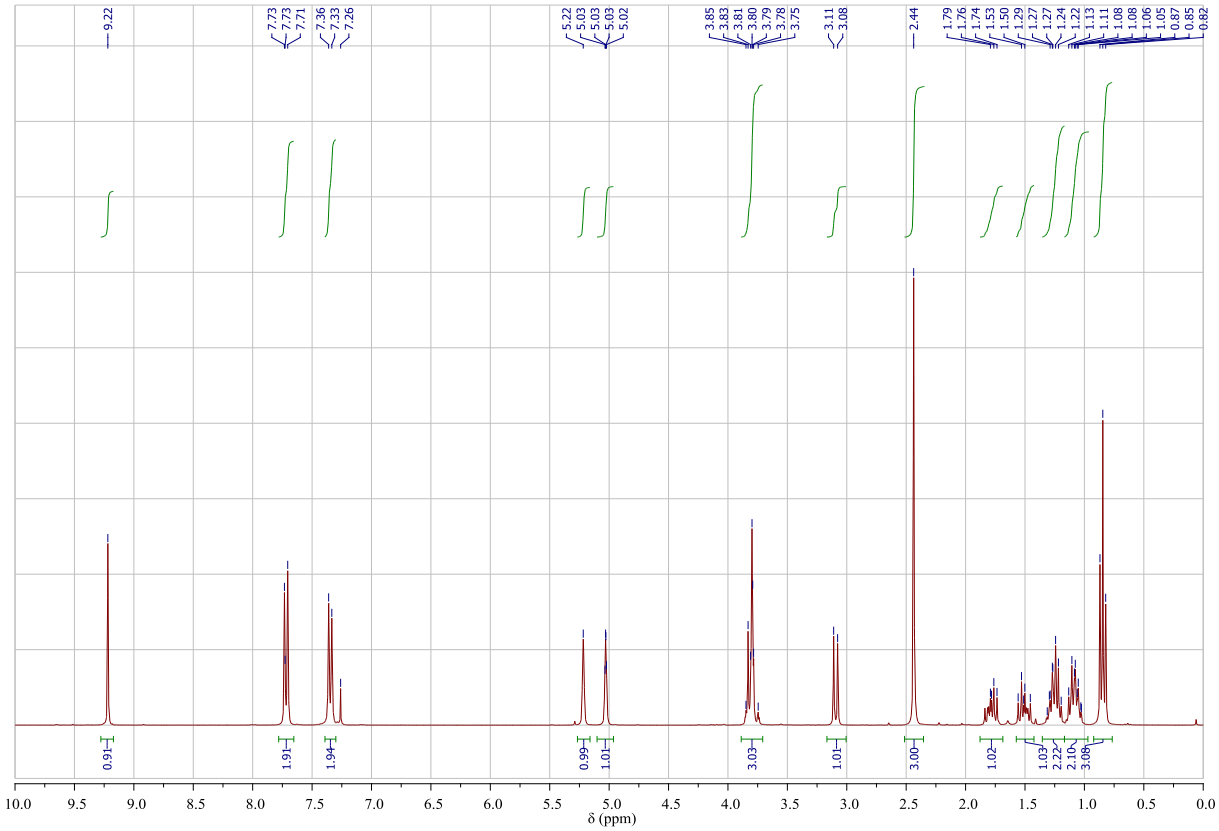


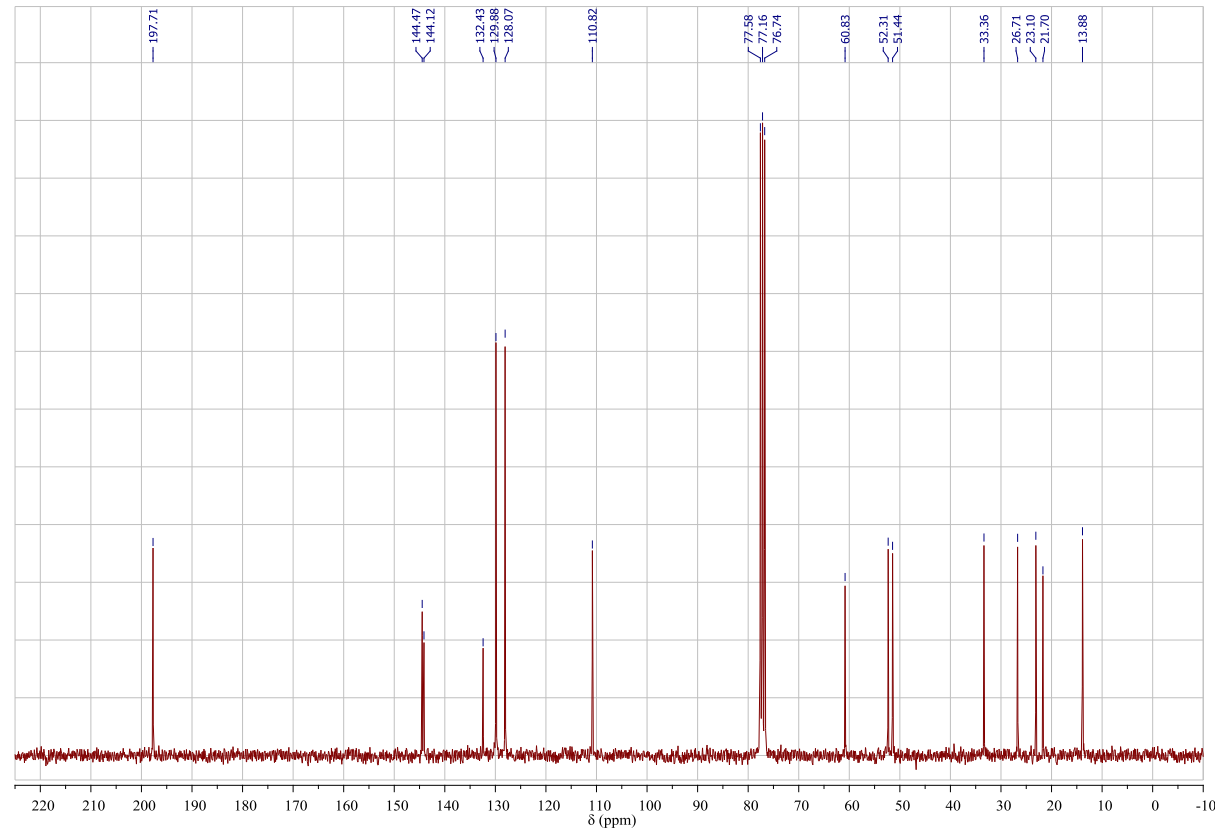


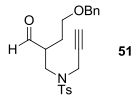


50

Chemical Formula: $C_{17}H_{23}NO_3S$
Molecular Weight: 321,43442

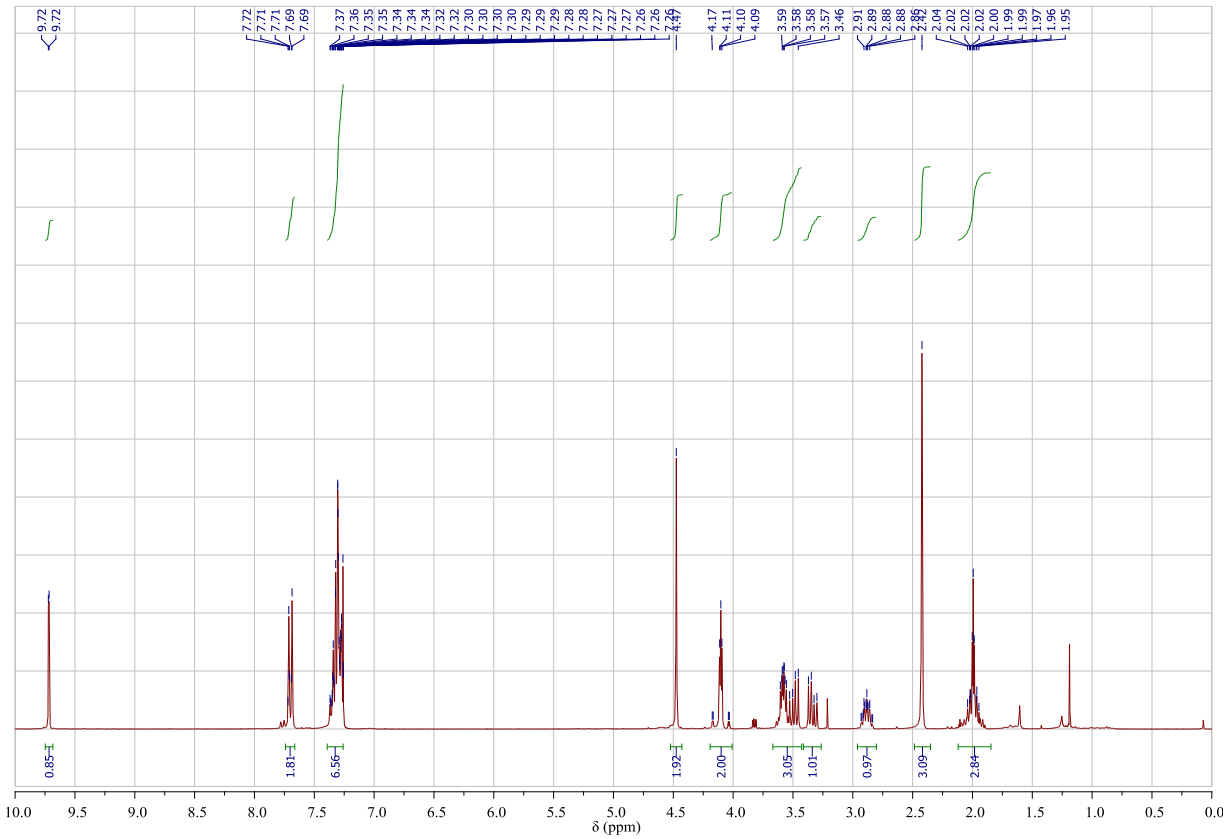


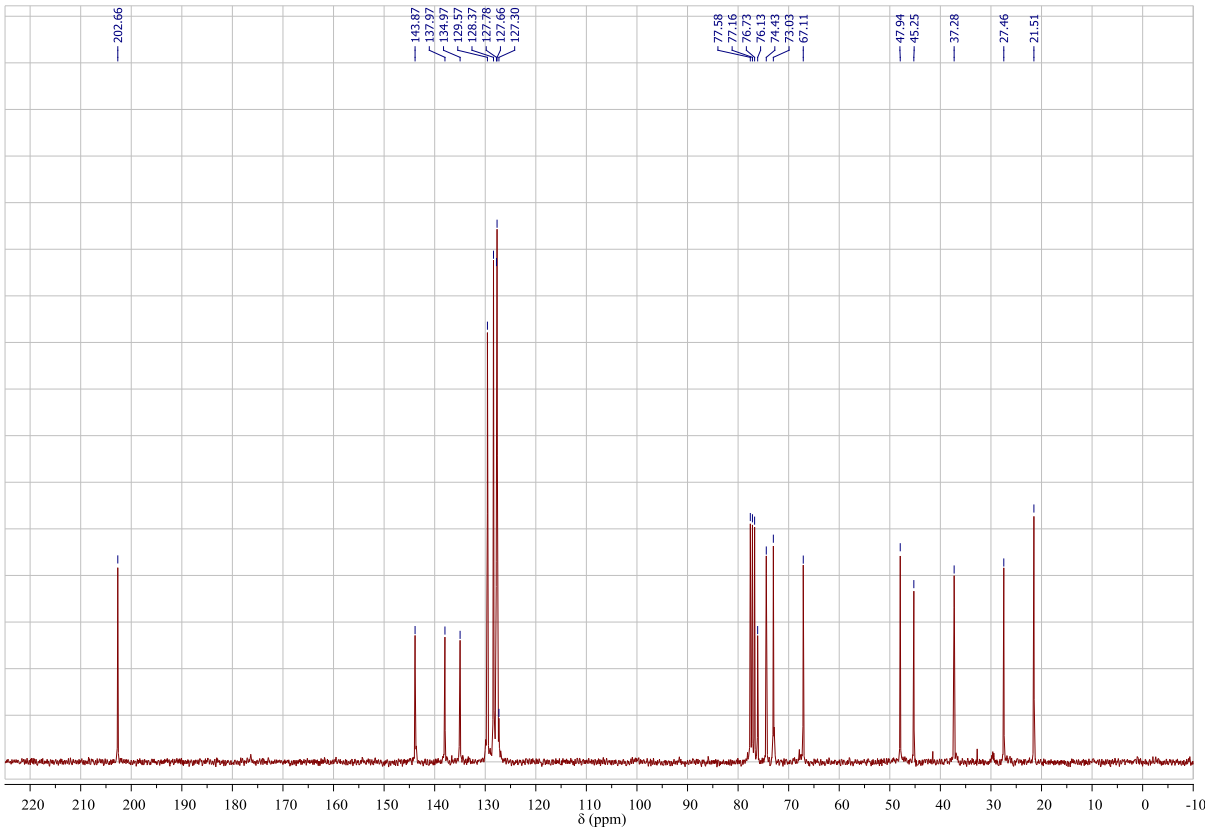


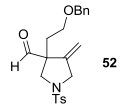


51

Chemical Formula: $C_{22}H_{25}NO_4S$
Molecular Weight: 399,50320

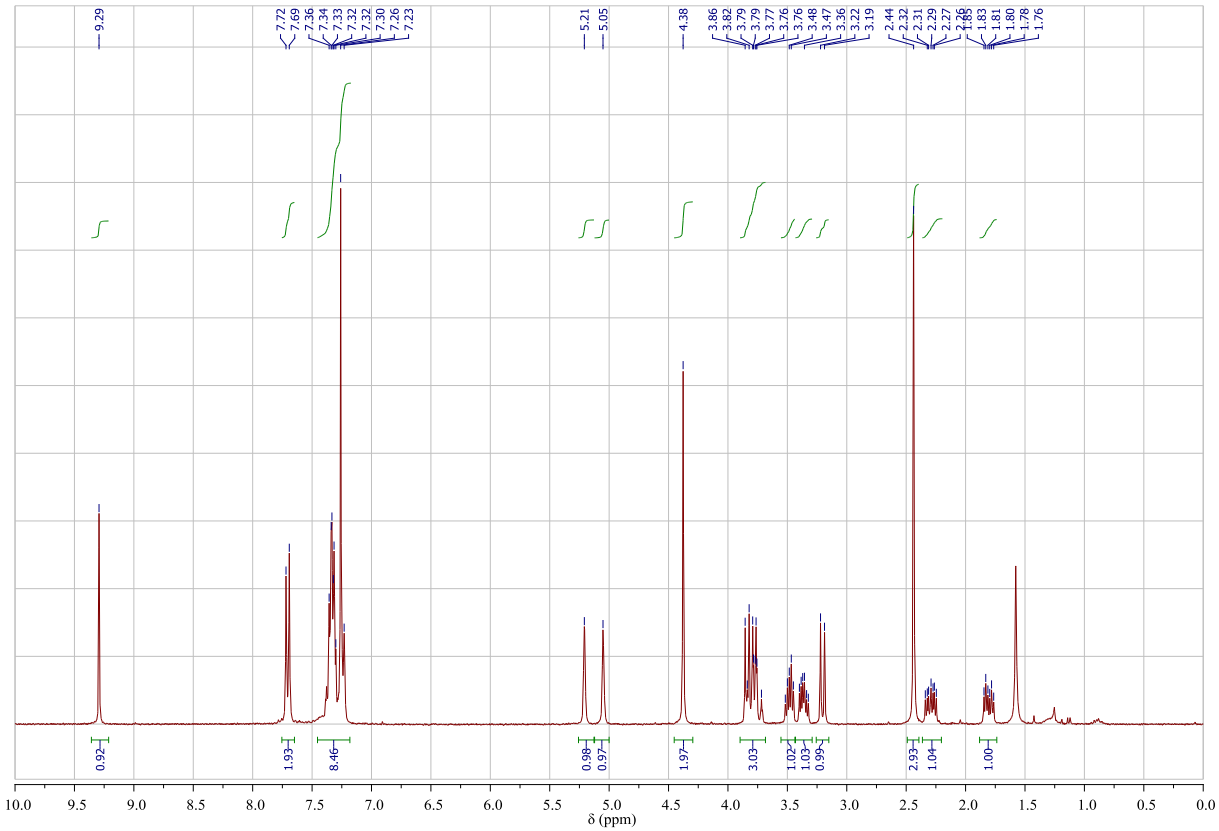


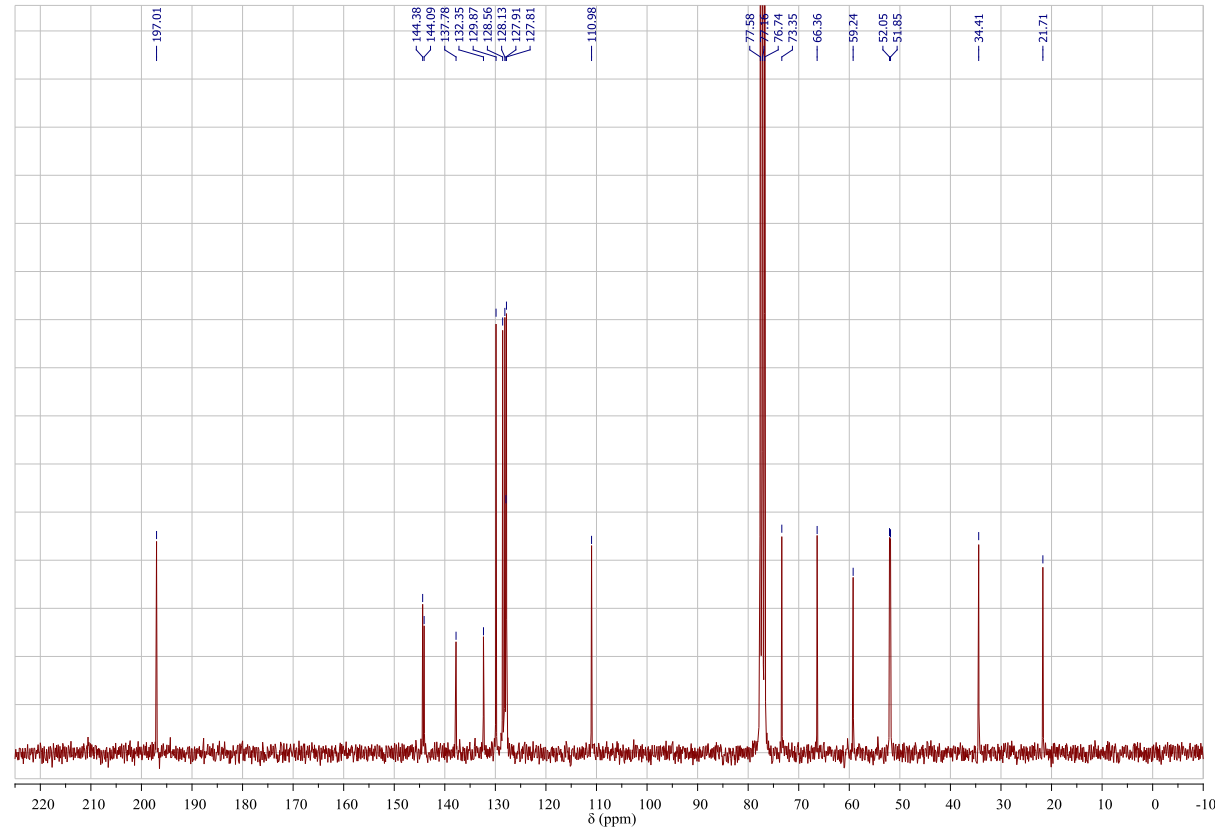


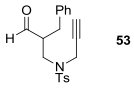


52

Chemical Formula: $C_{22}H_{25}NO_4S$
Molecular Weight: 399,50320

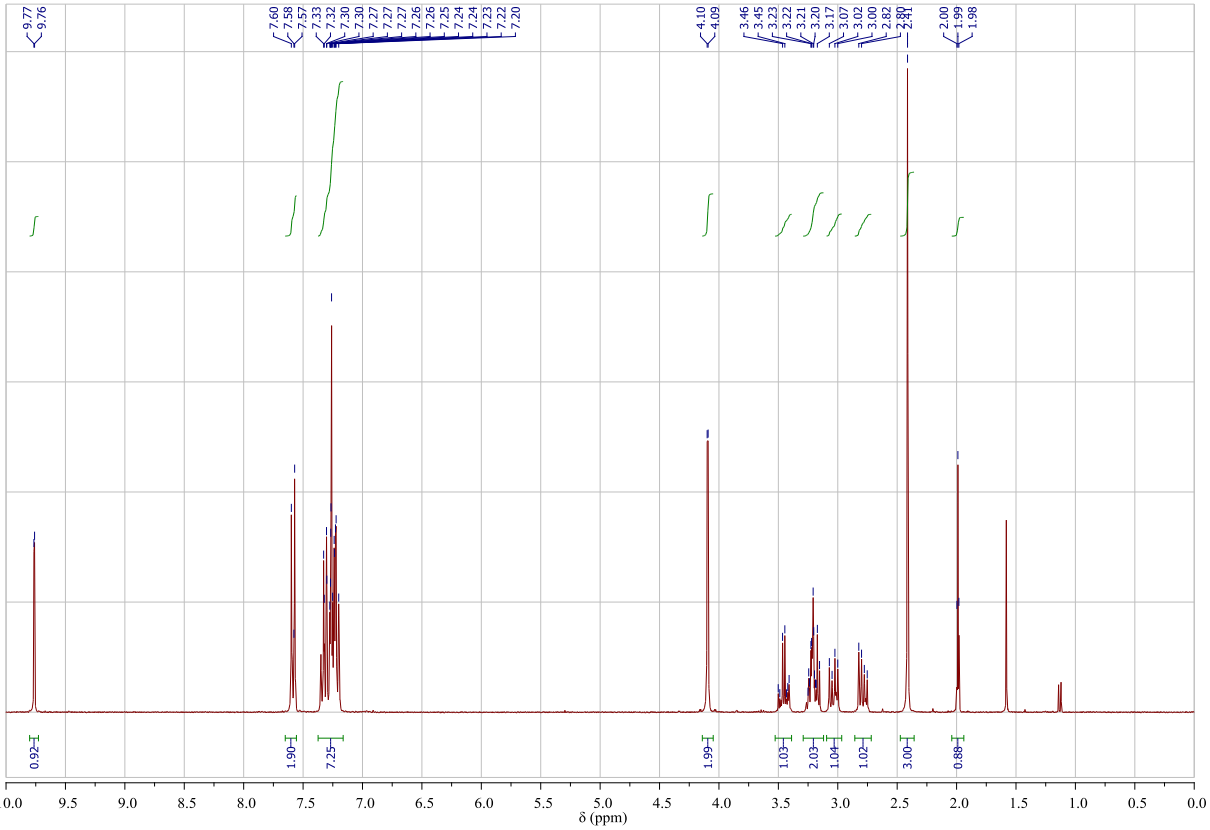


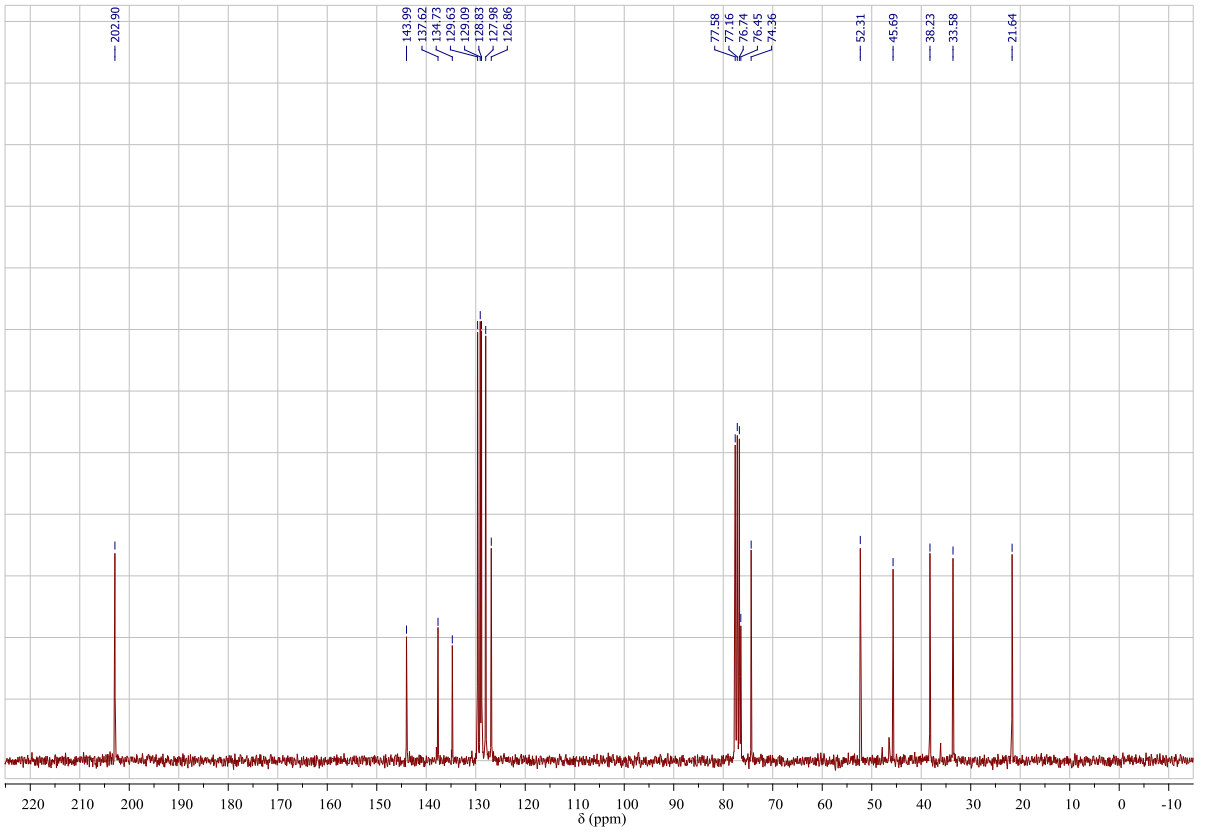


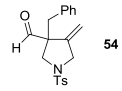


53

Chemical Formula: $C_{20}H_{21}NO_3S$
Molecular Weight: 355.45064

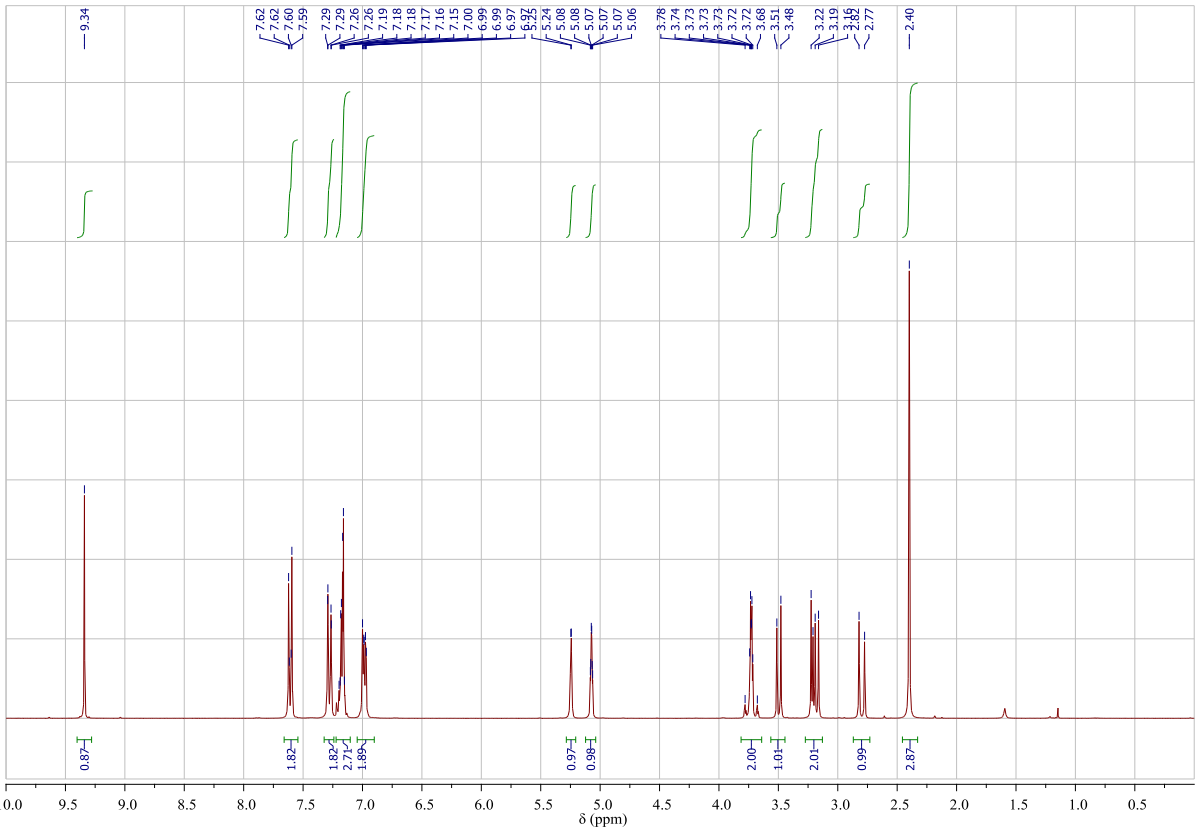


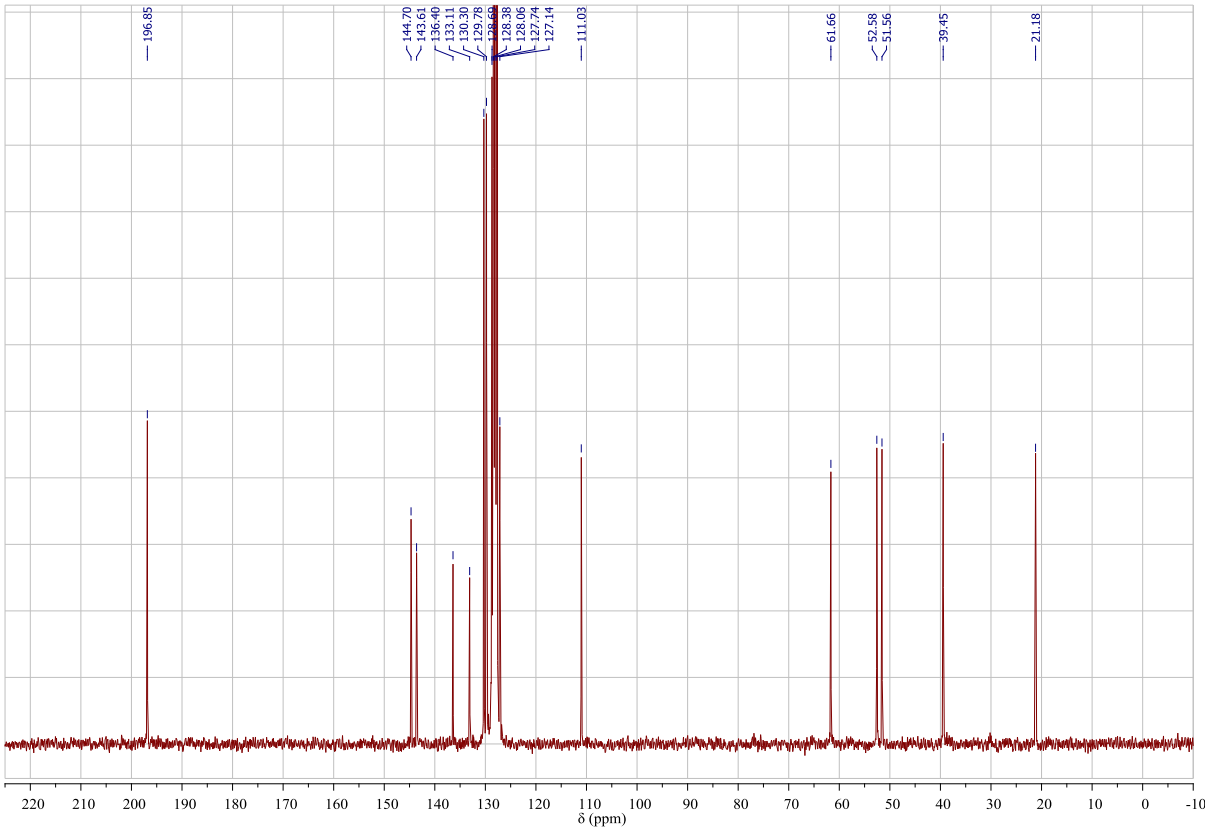


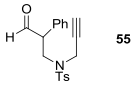


54

Chemical Formula: $C_{20}H_{21}NO_3S$
Molecular Weight: 355,45064

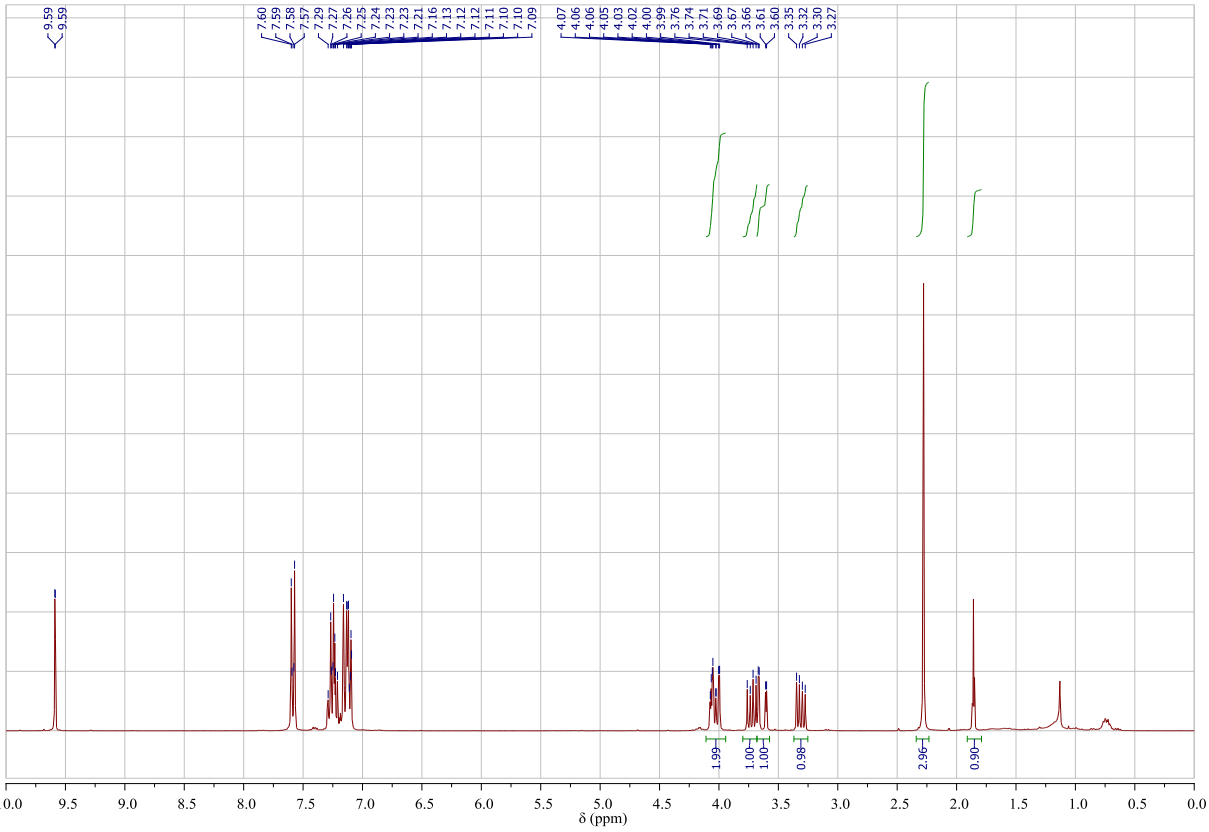


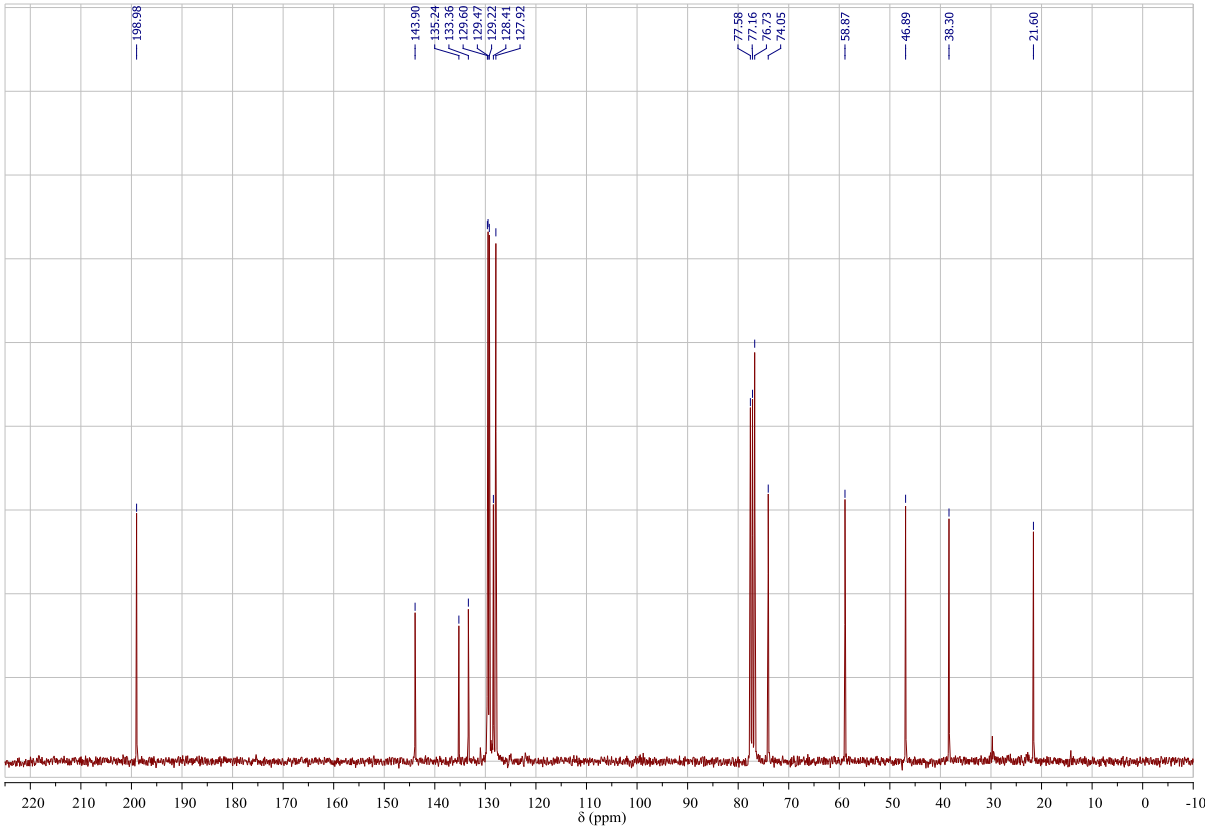


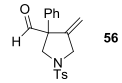


55

Chemical Formula: $C_{19}H_{19}NO_3S$
Molecular Weight: 341,42406

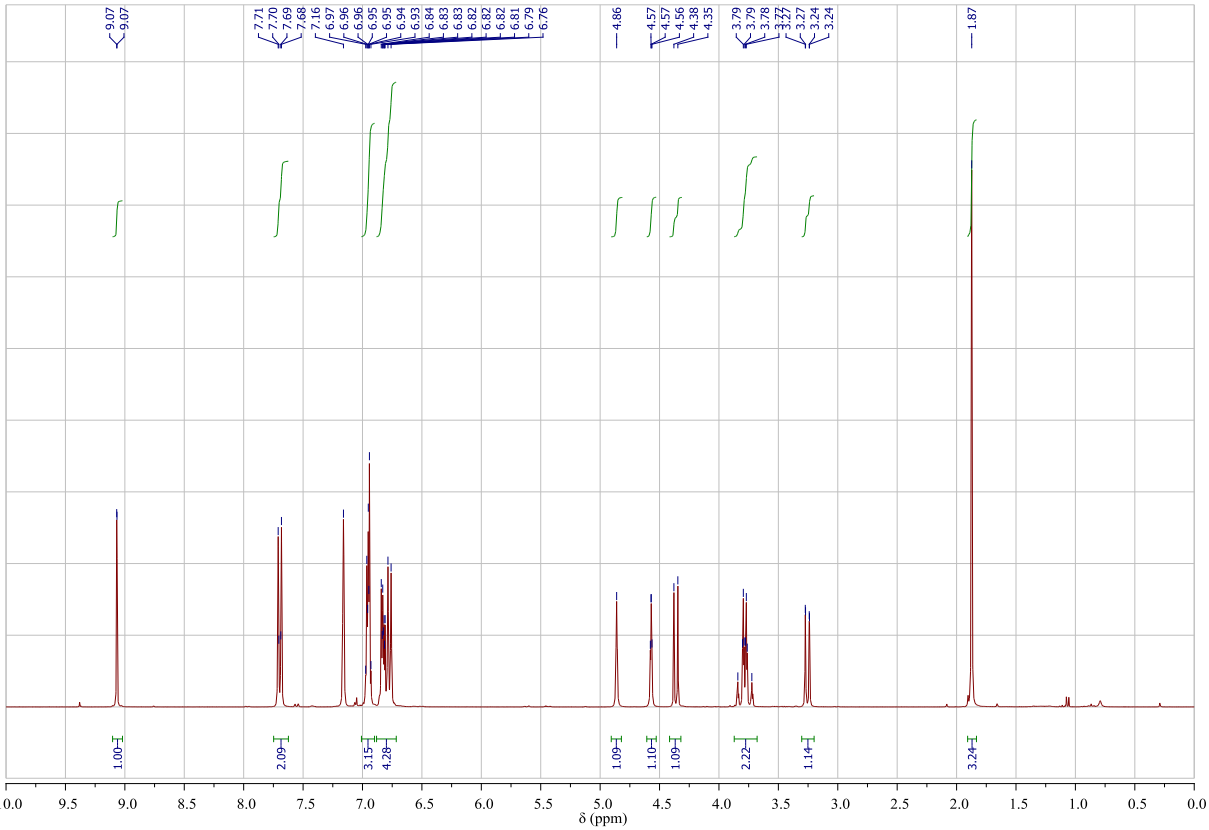


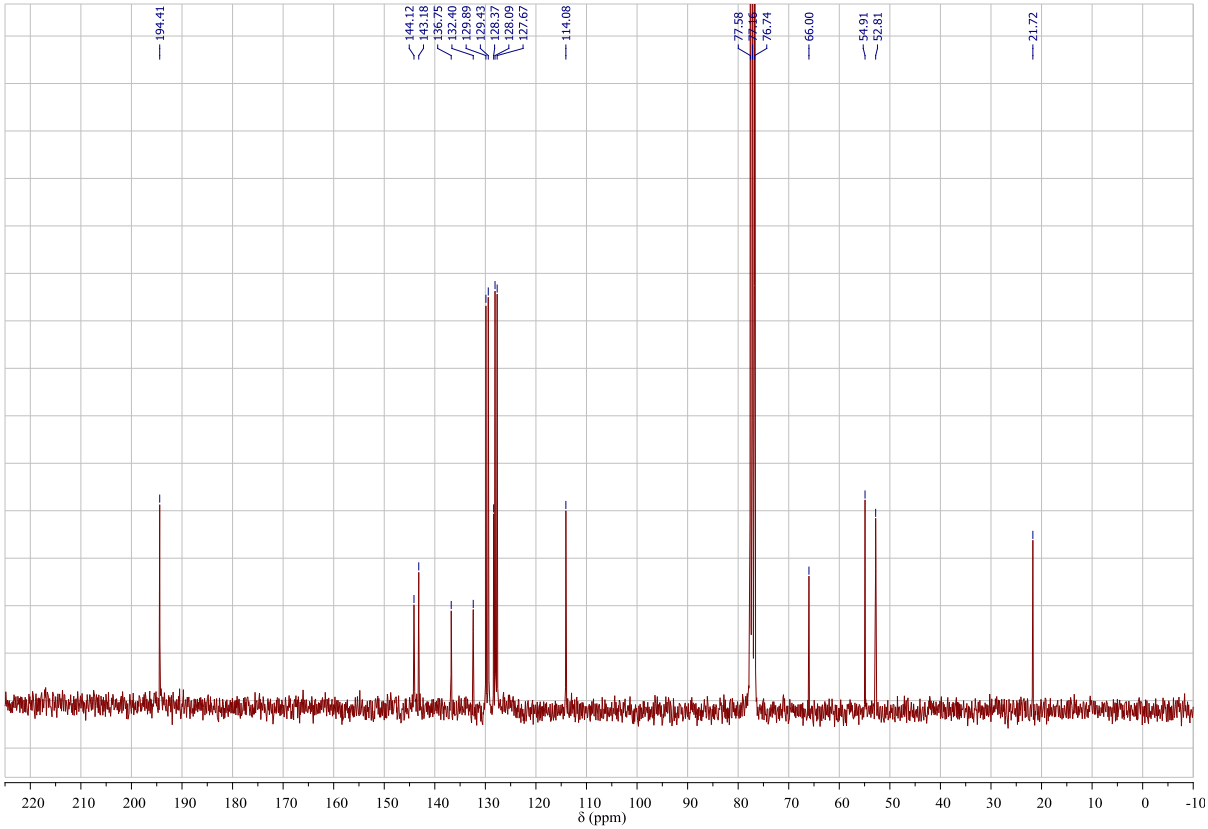


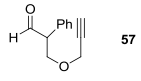


56

Chemical Formula: $C_{19}H_{19}NO_3S$
Molecular Weight: 341,42406

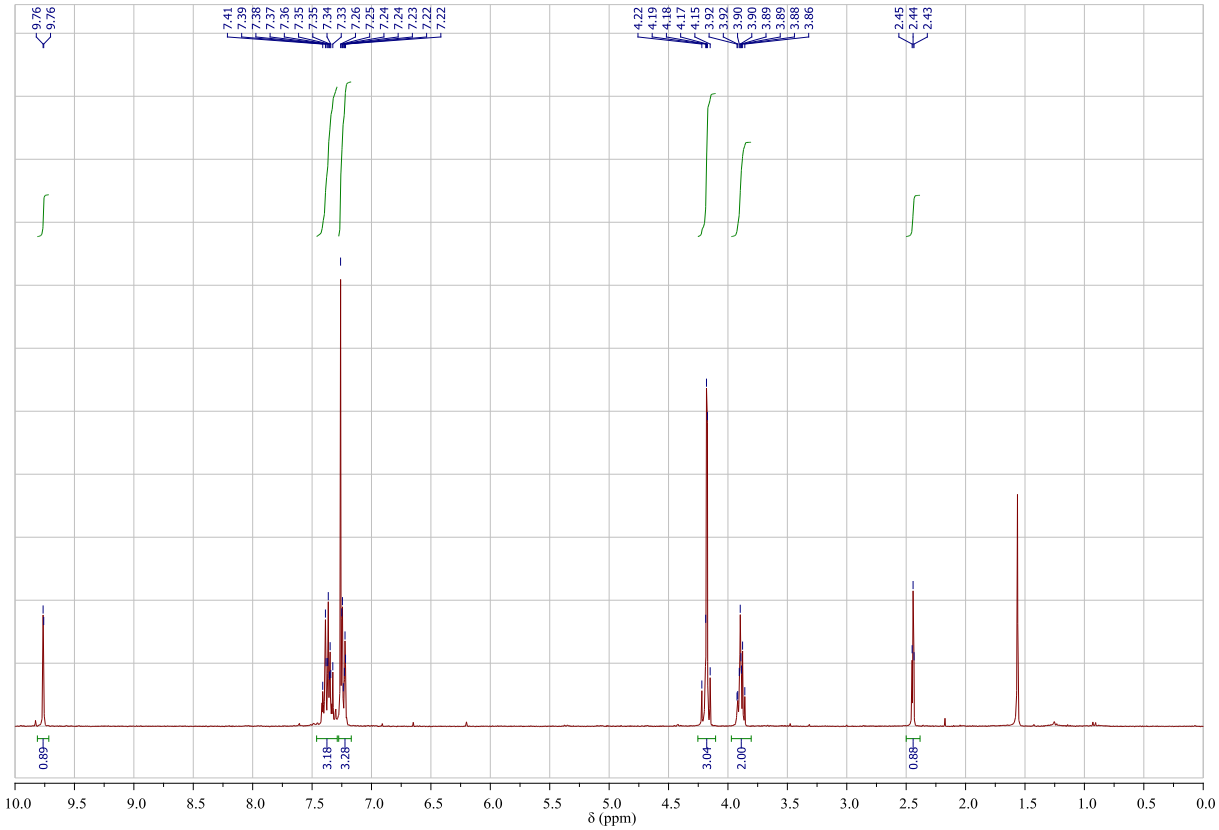


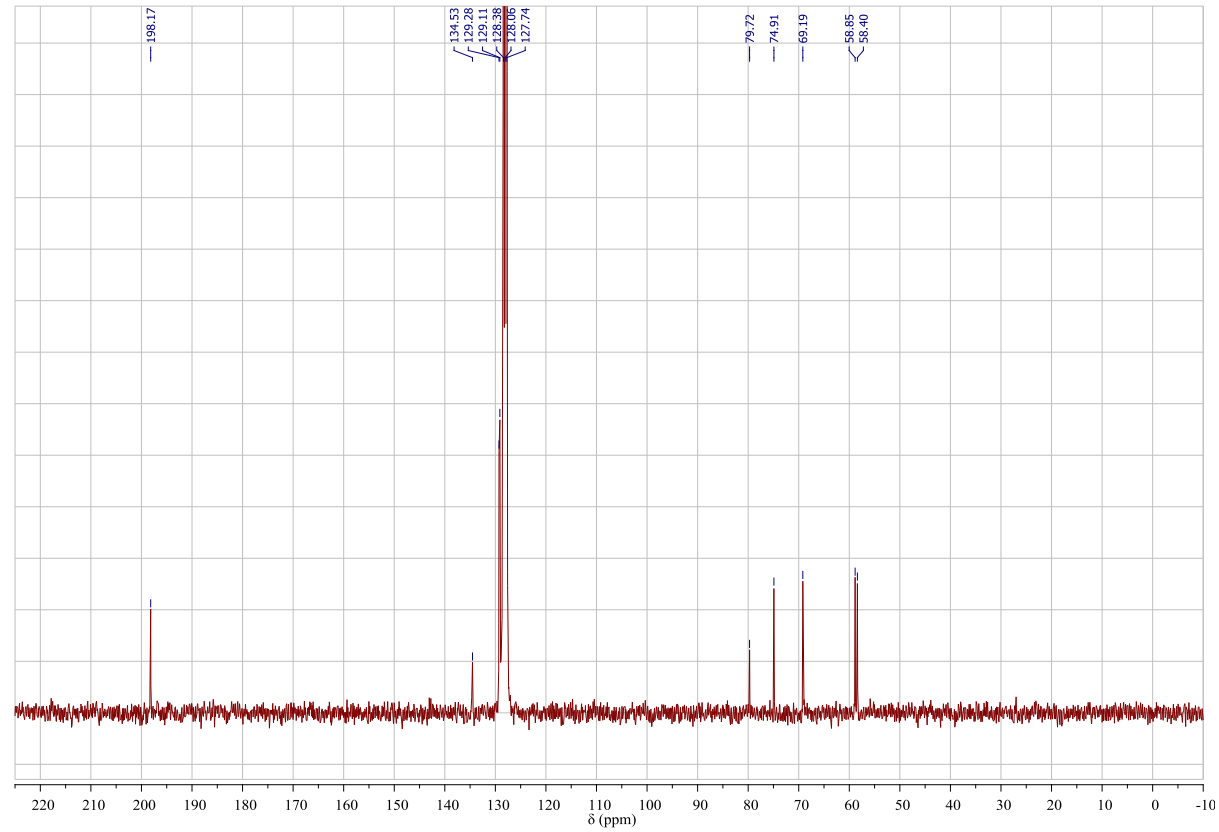


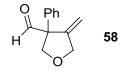


57

Chemical Formula: $C_{12}H_{12}O_2$
Molecular Weight: 188,22248

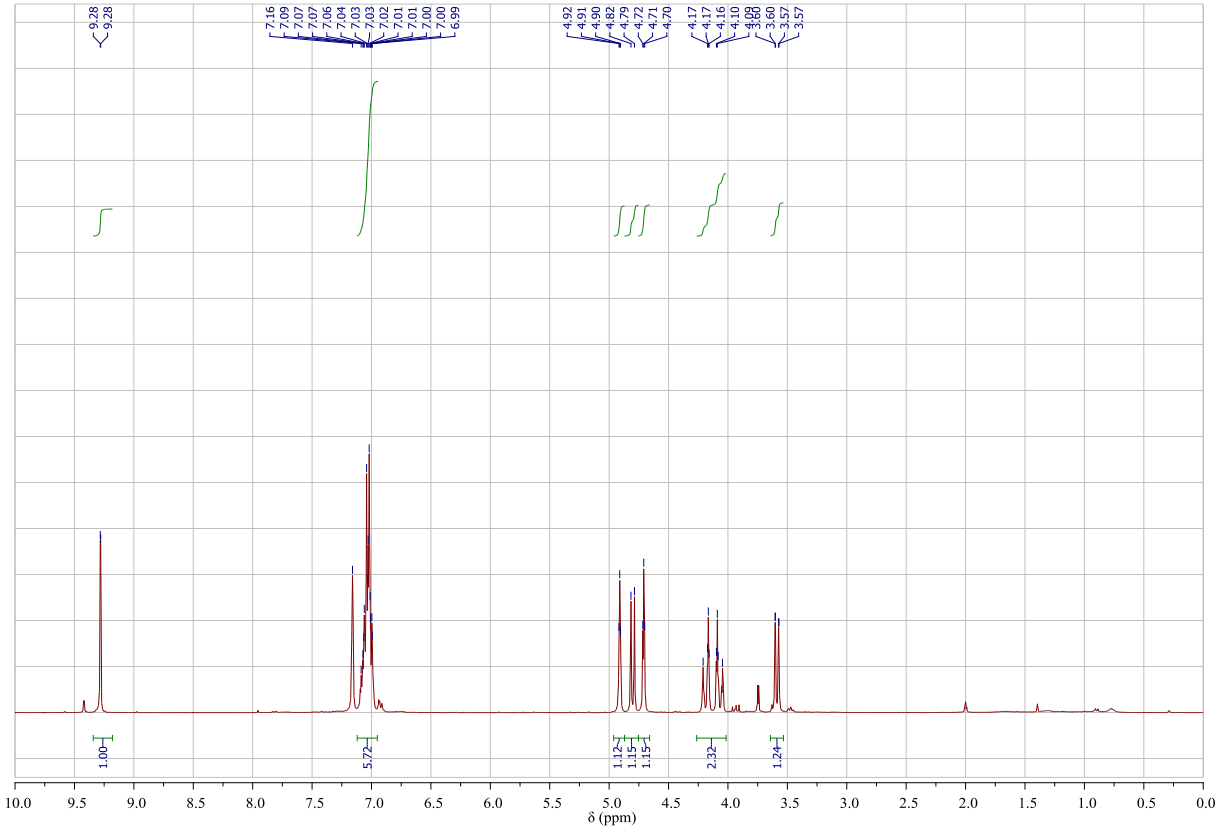


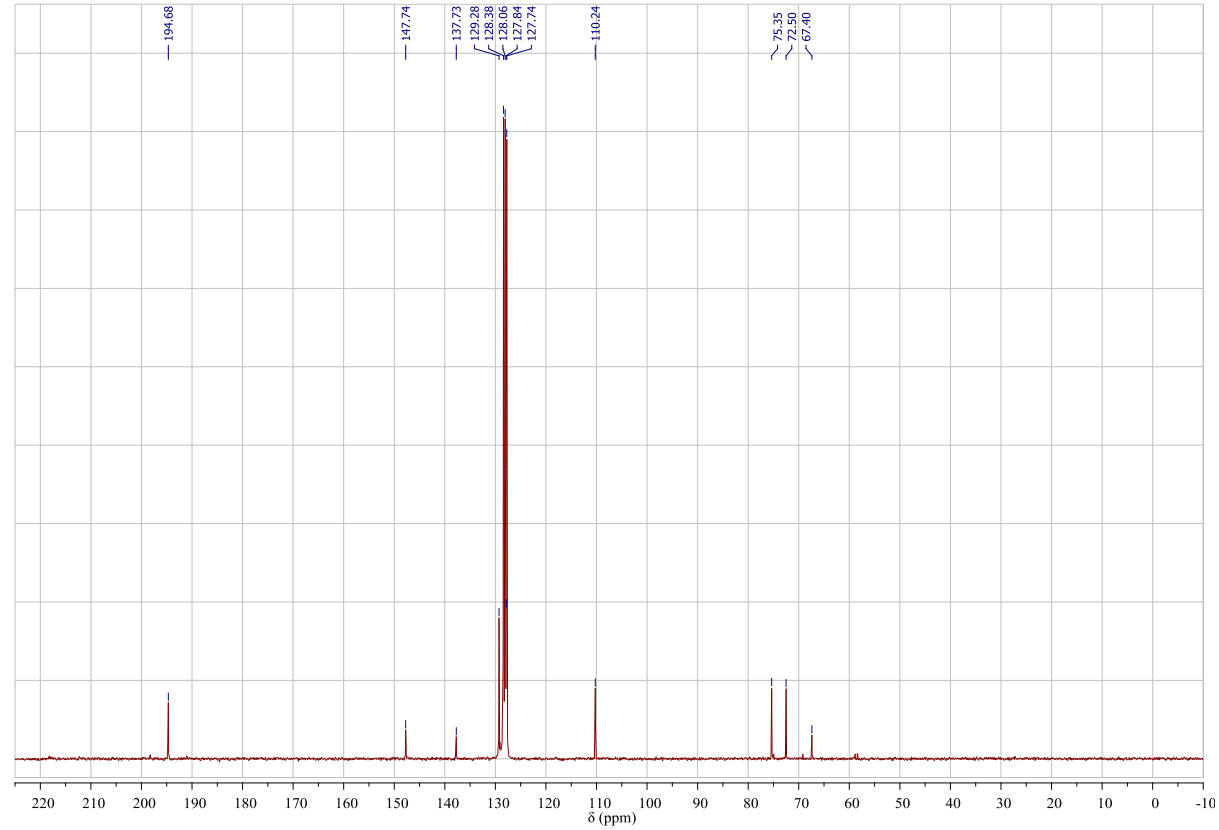


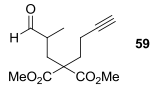


58

Chemical Formula: $C_{12}H_{12}O_2$
Molecular Weight: 188,22248

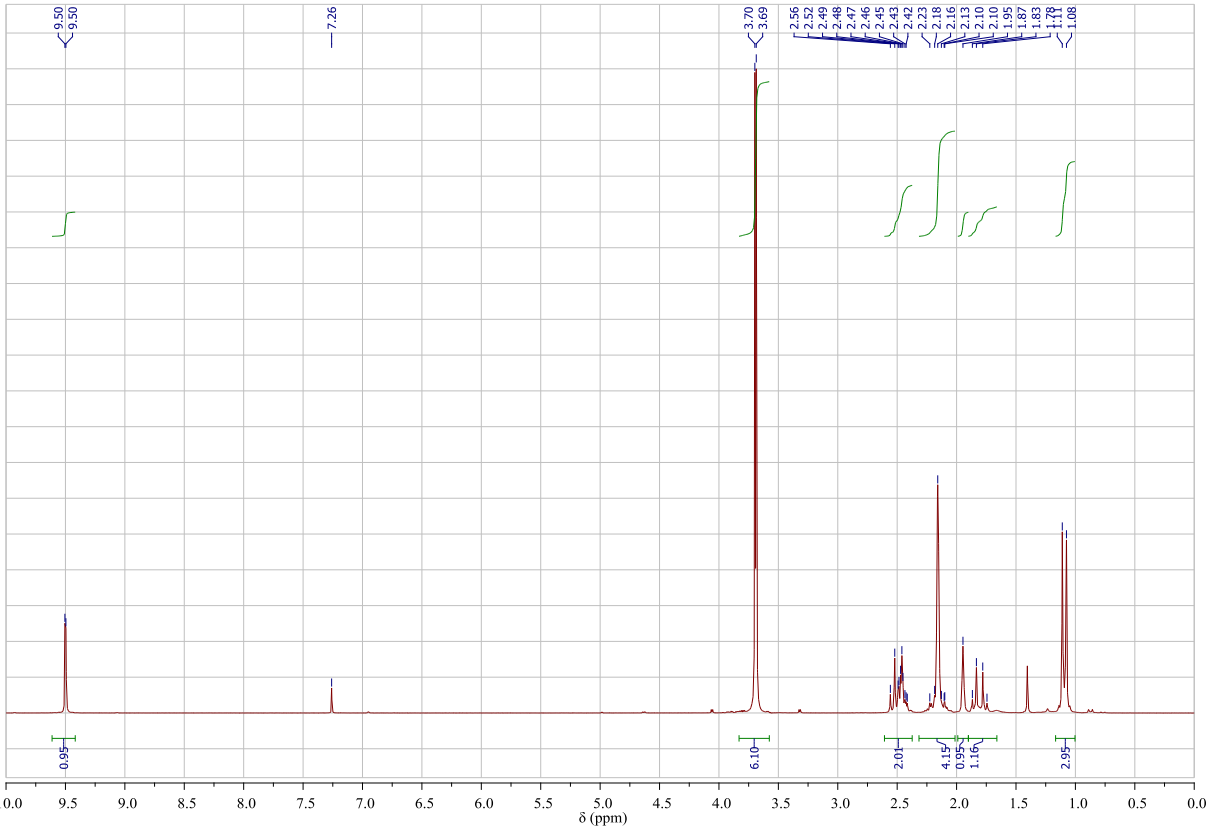


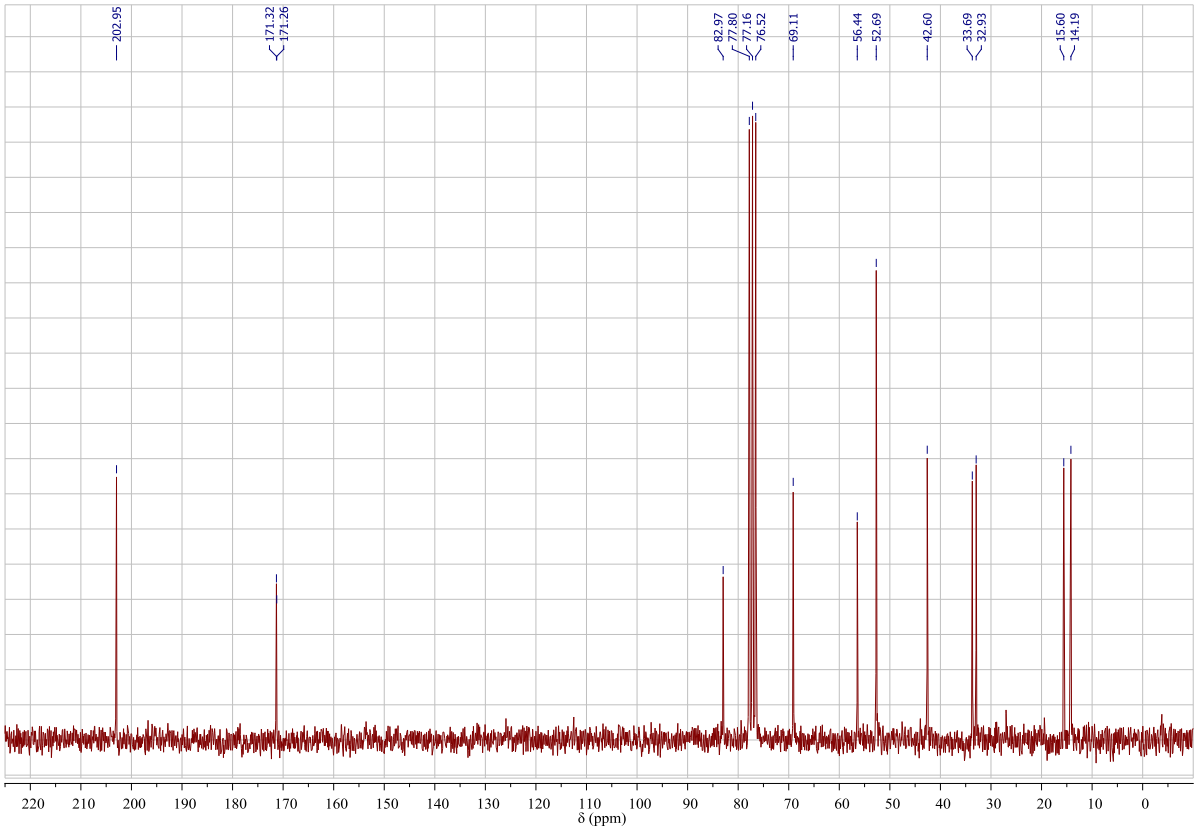


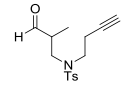


59

Chemical Formula: $C_{13}H_{18}O_5$
Molecular Weight: 254,27902

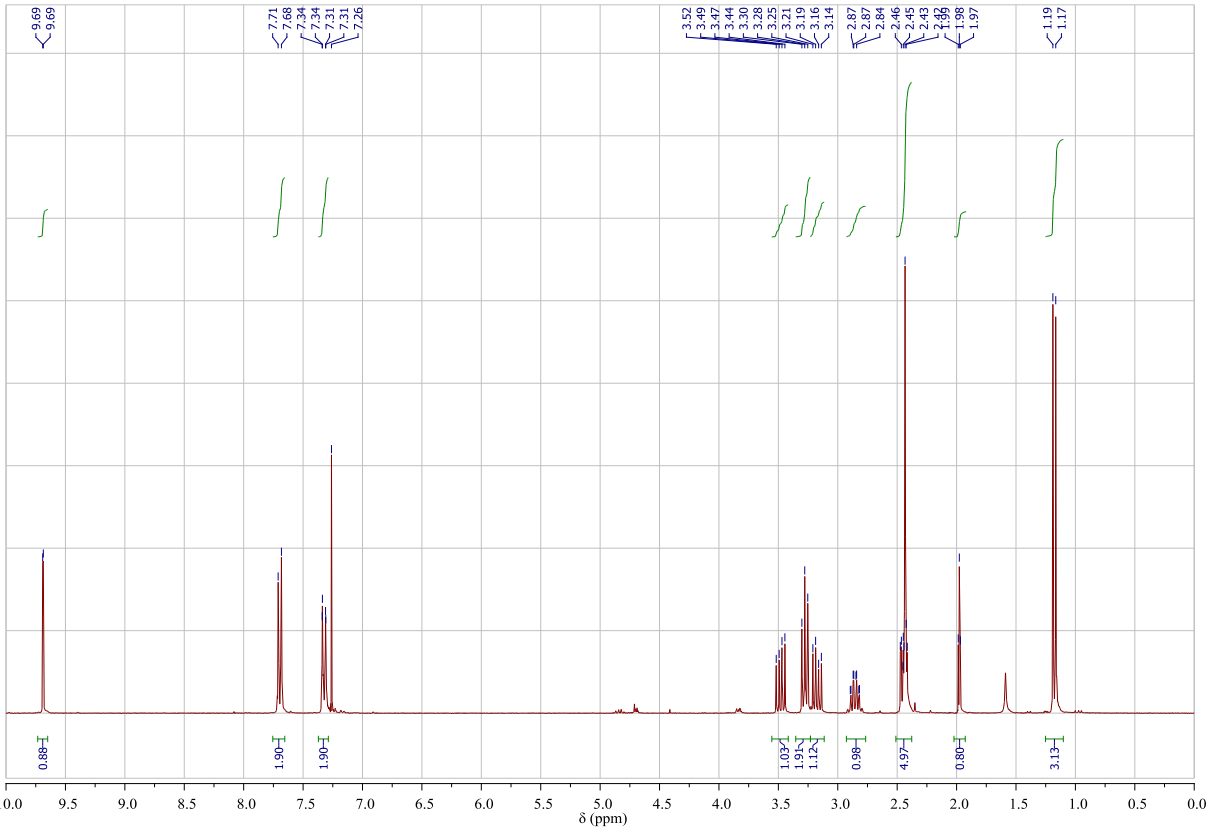


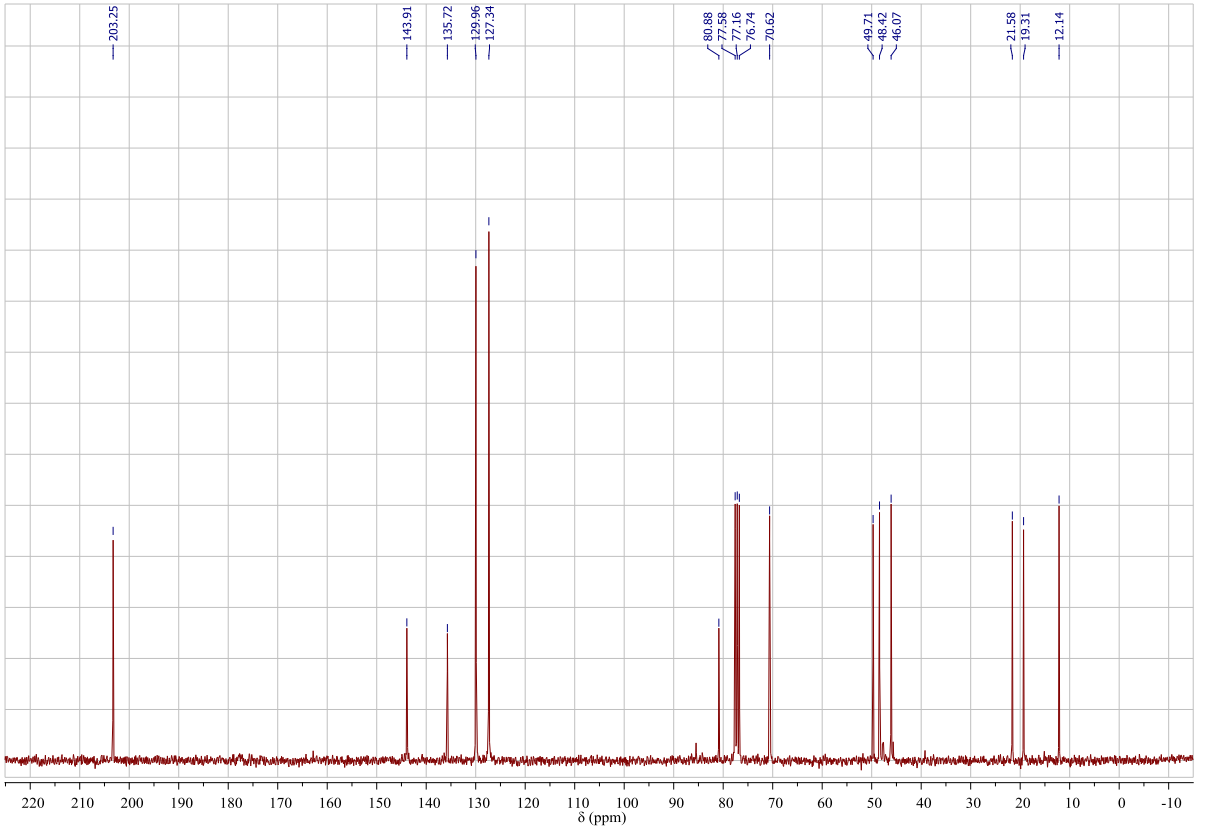


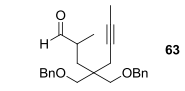


61

Chemical Formula: $C_{15}H_{19}NO_3S$
Molecular Weight: 293,38126







63

Chemical Formula: $C_{25}H_{30}O_3$
Molecular Weight: 378,50390