Supporting Information

Synthesis of Acetylenic Alcohols with Calcium Carbide as the Acetylene Source

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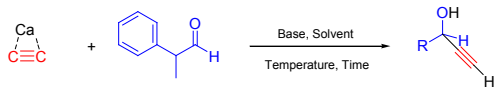
Experimental Section

All solvents were purchased from Aldrich or J.T. Baker. All starting materials are commercially available and were used as received, unless otherwise indicated. Calcium carbide was purchased from Aldrich (purity: 80%). The course of the reactions were monitored by thin layer chromatography using 0.25-mm E. Merck silica gel coated glass plates (60F-254) with UV light. Chemical yields refer to the pure isolated substances. Gas chromatography-mass spectrometry (GC-MS) was performed with a Shimadzu GC-2010 coupled with GCMS-QP2010. ^{1}H and ^{13}C NMR spectra were obtained using a Brucker AV-400 (400 MHz) spectrometer. Chemical shifts are reported in ppm with reference to tetramethylsilane with the solvent resonance as the internal standard. Data are reported in the following order: chemical shift in ppm (); multiplicity is indicated by br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (J, Hz); integration; assignment.

General Procedure for the Coupling Reaction to Synthesize *ter*-Propargyl Alcohols

To a vial was added 0.163 g Cs_2CO_3 (0.5mmol), 0.200 g CaC_2 (2.5mmol), 0.134g 2-phenylpropanal and 3mL (DMSO/H_2O 50:1). The mixture was bubbled with argon for 10 minutes and the reaction was stirred at 60 °C for 8 hours. The reaction was extracted with 50mL ethyl acetate and washed with 3 × 10 mL brine. The organic layer was dried over Na_2SO_4, concentrated in vacuo and the crude product was purified by column chromatography (hexane / ethyl acetate: 5 / 1). All products gave satisfactory spectroscopic data. The NMR spectra data of compounds **2d**, **2g**, **4a**, **4h**, **4i**, **4j** and **4l** are available in the literature and are referenced accordingly.

STable 1. Effect of base on the Synthesis of Propargyl Alcohols.



Entry	Base	Yield[a]
1	Et_3N	28%
2	DBU	21%
3	Cs_2CO_3	61%
4[b]	Cs_2CO_3	63%
5	K_2CO_3	43%
6	Na_2CO_3	No reaction
7	KOAc	56%
8	NaOAc	46%

Reaction conditions: 2-phenylpropropanal (1 mmol), CaC_2 (2.5 mmol), base (0.2 mmol), 3 mL (DMSO/H_2O) 50:1, 70 °C, 8 h
a) Determined by ^{1}H NMR spectroscopy
b) 0.5 mmol base

2-Phenyl-4-pentyn-3-ol (2a)

(Mixture of isomers) ^{1}H NMR (400MHz, $CDCl_3$) δ 7.24 – 7.37 (m, 5H, *Ph*), 4.48 (ddd, 1H, C*H*(OH)C≡CH), 3.00 – 3.12 (m, 1H, C*H*(CH_3)Ph), 2.46, 2.51 (d, 1H, C≡C*H*), 1.76 – 1.78 (m, 1H, O*H*), 1.42 (d, 3H, CH_3); ^{13}C NMR (400MHz, $CDCl_3$) δ 141.2, 140.9, 128.2, 128.1, 128.0, 127.7, 82.9, 82.8, 74.2, 74.0, 67.1, 66.6, 45.8, 45.1, 16.5, 15.6; HRMS (EI) *m/z* calcd.for $C_{11}H_{11}O_1$ 159.0810 found 159.0803

4-methylhept-1-yn-3-ol (2b)

(Mixture of isomers) ^{1}H NMR (400MHz, $CDCl_3$) δ 4.24 – 4.28 (m, 1H, C*H*(OH)C≡CH), 2.45 (dd, 1H, C≡C*H*), 1.68 – 1.81 (m, 1H, C*H*CH_3), 1.14 – 1.59 (m, 4H, CH_2C$H_2$$CH_3$), 1.00 (dd, 3H, CHC$H_3$), 0.91 (dt, 3H, CH_2CH_3); ^{13}C NMR (400MHz, $CDCl_3$) δ 83.6, 83.0, 73.4, 73.1, 66.3, 66.1, 38.5, 38.3, 34.3, 33.6, 19.8, 19.7, 14.4, 13.9, 13.8; HRMS (EI) *m/z* calcd.for $C_8H_{13}O_1$ 125.0966 found 125.0966

4-Ethyl-1-octyn-3-ol (2c)

(Mixture of isomers) ^{1}H NMR (400MHz, $CDCl_3$) δ 4.41 (m, 1H, C*H*(OH)C≡CH), 2.44 (d, 1H, C≡C*H*), 1.27 – 1.65 (m, 10H), 0.89 – 0.96 (m, 6H, 2 CH_3); ^{13}C NMR (400MHz, $CDCl_3$) δ 83.5, 73.18, 73.15, 64.3, 64.2, 45.09, 45.07, 29.0, 28.9, 28.5, 28.2, 22.61, 22.57, 22.0, 21.7, 13.64, 13.61, 11.2, 11.0; HRMS (EI) *m/z* calcd.for $C_{10}H_{18}O_1$ 154.1358 found 154.1351

1-Cyclohexylprop-2-yn-1-ol (2d)[1]

^{1}H NMR (400MHz, $CDCl_3$) δ 4.14 – 4.16 (m, 1H, C*H*(OH)C≡CH), 2.46 (d, 1H, C≡C*H*), 1.76 – 1.88 (m, 4H), 1.66 – 1.70 (m, 1H), 1.52 – 1.61 (m, 1H), 1.02 – 1.31 (m, 5H); ^{13}C NMR (400MHz, $CDCl_3$) δ 83.5, 73.2, 66.5, 43.4, 27.9, 27.5, 25.9, 25.40, 25.36

4-ethyl-1-hexyn-3-ol (2e)
^{1}H NMR (400MHz, $CDCl_3$) δ 4.41 (m, 1H, C*H*(OH)C≡CH), 2.44 (d, 1H, C≡C*H*), 1.33 – 1.66 (m, 5H), 0.91 – 0.96 (m, 6H, 2 CH_3); ^{13}C NMR (400MHz, $CDCl_3$) δ 83.6, 73.2, 64.0, 46.7, 21.4, 21.2, 11.2, 11.0; HRMS (EI) *m/z* calcd.for $C_8H_{13}O_1$ 125.0966 found 125.0965

α-ethynyl-5-norbornene-2-methanol (2f)
(Mixture of isomers) ^{1}H NMR (400MHz, $CDCl_3$) δ 5.95 – 6.21 (m, 2H, *H*C=C*H*), 4.07 – 4.17 (m, 0.5H, C*H*(OH)C≡CH),

3.64 – 3.70 (m, 0.5H, C*H*(OH)C≡CH), 2.80 – 3.02 (m, 2H), 2.45 – 2.53 (m, 0.5H, C≡C*H*), 2.30 – 2.40 (m, 0.8H), 2.02 – 2.22 (m, 0.2H), 1.84 – 1.92 (m, 0.5H), 1.62 – 1.69 (m, 0.5H), 1.26 – 1.51 (m, 3H), 0.67 – 0.95 (m, 0.5H) ^{13}C NMR (400MHz, $CDCl_3$) δ 138.0, 137.8, 137.0, 136.9, 136.2, 135.9, 131.8, 131.5, 84.8, 84.4, 73.2, 72.9, 72.7, 71.6, 66.4, 66.0, 65.2, 49.1, 48.8, 46.8, 46.2, 46.09, 46.06, 45.2, 44.8, 44.5, 44.3, 43.1, 42.7, 42.4, 41.74, 41.72, 41.2, 29.6, 29.5, 29.3, 28.8; HRMS (EI) *m/z* calcd.for $C_{10}H_{12}O_1$ 148.0888 found 148.0885

4,4-dimethyl-1-pentyn-3-ol (2g)[2]
^{1}H NMR (400MHz, $CDCl_3$) δ 4.02 (dd, 1H, C*H*(OH)C≡CH), 2.45 (d, 1H, C≡C*H*), 1.77 (d,, 1H O*H*), 1.01(s, 9H, CH_3); ^{13}C NMR (400MHz, $CDCl_3$) δ 83.5, 73.8, 71.2, 35.6, 25.1

1-Ethynyl-1-cyclohexanol (4a)[3]

^{1}H NMR (400MHz, $CDCl_3$) δ 2.48 (s, 1H, C≡C*H*), 1.86 – 1.93 (m, 2H), 1.67 – 1.73 (m, 2H), 1.51 – 1.61 (m, 5H), 1.20 – 1.29 (m, 1H); ^{13}C NMR (400MHz, $CDCl_3$) δ 87.2, 71.7, 68.0, 39.3, 24.6, 22.7

1-ethynyl-2-methylcyclohexanol (4b)
(Major isomer) ^{1}H NMR (400MHz, $CDCl_3$) δ 2.48 (s, 1H, C≡C*H*), 1.98 – 2.05 (m, 1H), 1.43 – 1.75 (m, 6H), 1.19 – 1.32 (m, 2H), 1.05 (d, 3H, CH_3); ^{13}C NMR (400mHz, $CDCl_3$) δ 84.8, 74.1, 73.0, 42.4, 40.6, 32.1, 25.5, 24.1, 15.9; HRMS (EI) *m/z* calcd.for $C_9H_{14}O_1$ 138.1045 found 138.1048

1-ethynyl-3-methylcyclohexanol (4c)

(Major isomer) ^{1}H NMR (400MHz, $CDCl_3$) δ 2.48 (s, 1H, C≡C*H*), 1.94 – 2.01, (m, 2H), 1.53 – 1.79 (m, 4H), 1.36 – 1.43 (m, 1H), 1.15 (t, 1H), 0.93 (d, 3H, CH_3), 0.75 – 0.89 (1H, m); ^{13}C NMR (400MHz, $CDCl_3$) δ 87.0, 72.2, 69.0, 47.9, 39.2, 33.5, 30.0, 23.1, 21.6; HRMS (EI) *m/z* calcd.for $C_9H_{14}O_1$ 138.1045 found 138.1041

1-ethynyl-4-methylcyclohexanol (4d)

(Major isomer) ^{1}H NMR (400MHz, $CDCl_3$) δ 2.49 (s, 1H, C≡C*H*), 1.95 – 2.00 (m, 2H), 1.66 – 1.70 (m, 2H), 1.50 – 1.58 (m, 2H), 1.19 – 1.42 (m, 3H), 0.92 (3H, m, CH_3); ^{13}C NMR (400MHz, $CDCl_3$) δ 86.8, 72.4, 68.8, 39.4, 31.9, 31.8, 31.3, 21.4; HRMS (EI) *m/z* calcd.for $C_9H_{14}O_1$ 138.1045 found 138.1040

1,4-diethynyl-1,4-Cyclohexanediol (4f)

(Mixture of isomers) ^{1}H NMR (400MHz, $CDCl_3$) δ 2.49, 2.51 (s, 2H, C≡C*H*), 1.91 – 2.04 (m, 8H), 1.97 (s, 2H, O*H*); ^{13}C NMR (400MHz, $CDCl_3$) δ 86.8, 72.0, 66.3, 35.5; HRMS (EI) *m/z* calcd.for $C_{10}H_{11}O_2$ 163.0759 found 163.0753

2-Ethynyl-2-adamantanol (4g)

^{1}H NMR (400MHz, $CDCl_3$) δ 2.53 (s, 1H, C≡C*H*), 2.12 – 2.18 (m, 4H), 1.96 (m, 2H), 1.77 – 1.83 (m, 4H), 1.70 (m, 2H), 1.55 – 1.69 (m, 2H); ^{13}C NMR (400MHz, $CDCl_3$) δ 88.0, 72.3, 71.9, 38.2, 37.1, 34.9, 31.1, 26.4, 26.3; HRMS (EI) *m/z* calcd.for $C_{12}H_{16}O_1$ 176.1201 found 176.1197

3,3-diisopropyl-1-propyn-3-ol (4h)[4]
^{1}H NMR (400MHz, $CDCl_3$) δ 2.41 (1H, s, C≡C*H*), 1.95 (2H, septet, [$(CH_3)_2$C*H*]), 1.74 (s, 1H, O*H*), 1.01 (12H, dd, CH_3); ^{13}C NMR (400MHz, $CDCl_3$) δ 85.0, 73.4, 34.1, 17.9, 16.1

3-Methyl-5-phenyl-1-pentyn-3-ol (4i)[5]

^{1}H NMR (400MHz, $CDCl_3$) δ 7.18 – 7.31 (5H, m, *Ph*), 2.81 – 2.92 (m, 2H, CH_2CH_2Ph), 2.52 (1H, s, C≡C*H*), 1.98 (s, 1H, O*H*), 1.93 – 2.05 (2H, m, CH_2CH_2Ph), 1.56 (3H, s, CH_3); ^{13}C NMR (400mHz, $CDCl_3$) δ 141.7, 128.5, 128.4, 126.0, 87.3, 71.9, 68.0, 45.2, 31.1, 30.0

3-butyn-2-cyclohexyl-2-ol (4j)[6]
^{1}H NMR (400MHz, $CDCl_3$) δ 2.43 (s, 1H, C≡C*H*), 1.94 – 1.99 (m, 1H), 1.92 (s, 1H, O*H*), 1.78 – 1.88 (m, 3H), 1.66 – 1.70 (m, 1H), 1.46 (s, 3H, CH_3), 1.41 – 1.48 (m, 1H), 1.08 – 1.30 (m, 5H); ^{13}C NMR (400mHz, $CDCl_3$) δ 87.2, 71.9, 71.0, 48.5, 27.6, 27.3, 27.1, 26.3, 26.20, 26.15

2-ethynyl-2-hexanol (4k)
^{1}H NMR (400MHz, $CDCl_3$) δ 2.43 (s, 1H, C≡C*H*), 1.95 (s, 1H, O*H*), 1.64 – 1.72 (m, 2H), 1.49 (s, 3H, (OH)(HC≡C)CC*H*$_3$), 1.44 – 1.52 (m, 2H), 1.31 – 1.40 (m, 2H), 0.93 (t, 3H, CH_2CH_3); ^{13}C NMR (400mHz, $CDCl_3$) δ 87.8, 71.2, 68.1, 43.2, 29.7, 26.7, 22.8, 14.0; HRMS (EI) *m/z* calcd.for $C_8H_{14}O_1$ 126.1045 found 126.1045

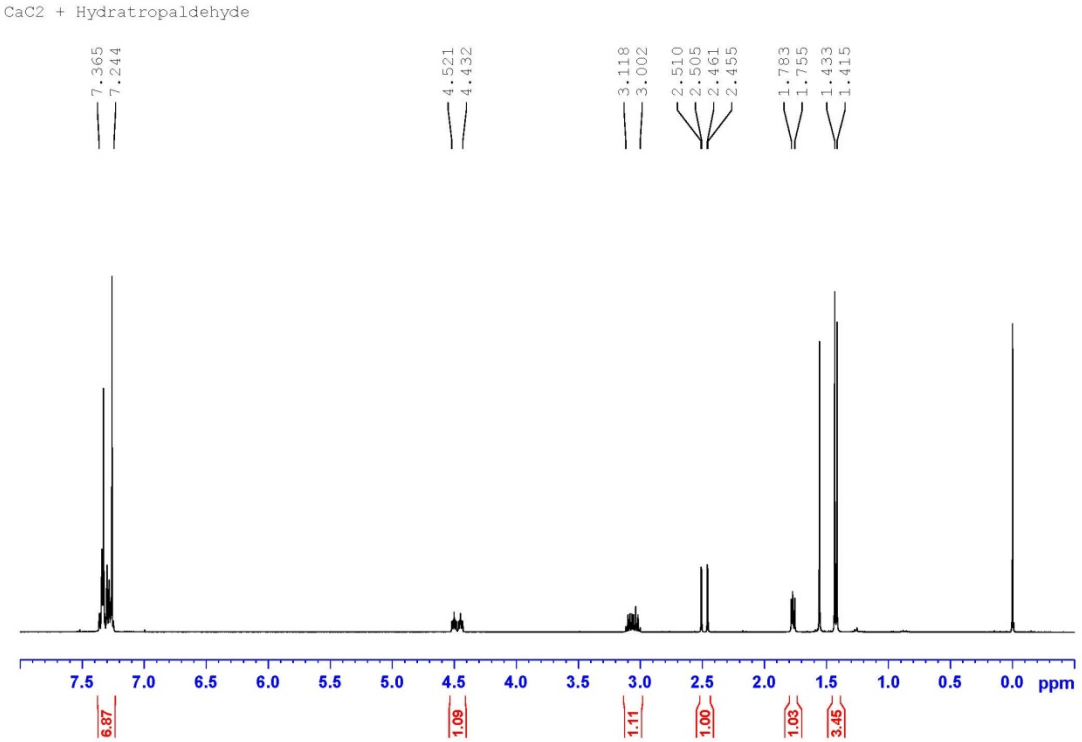
3-methyl-6-hepten-1-yn-3-ol (4l)[7]

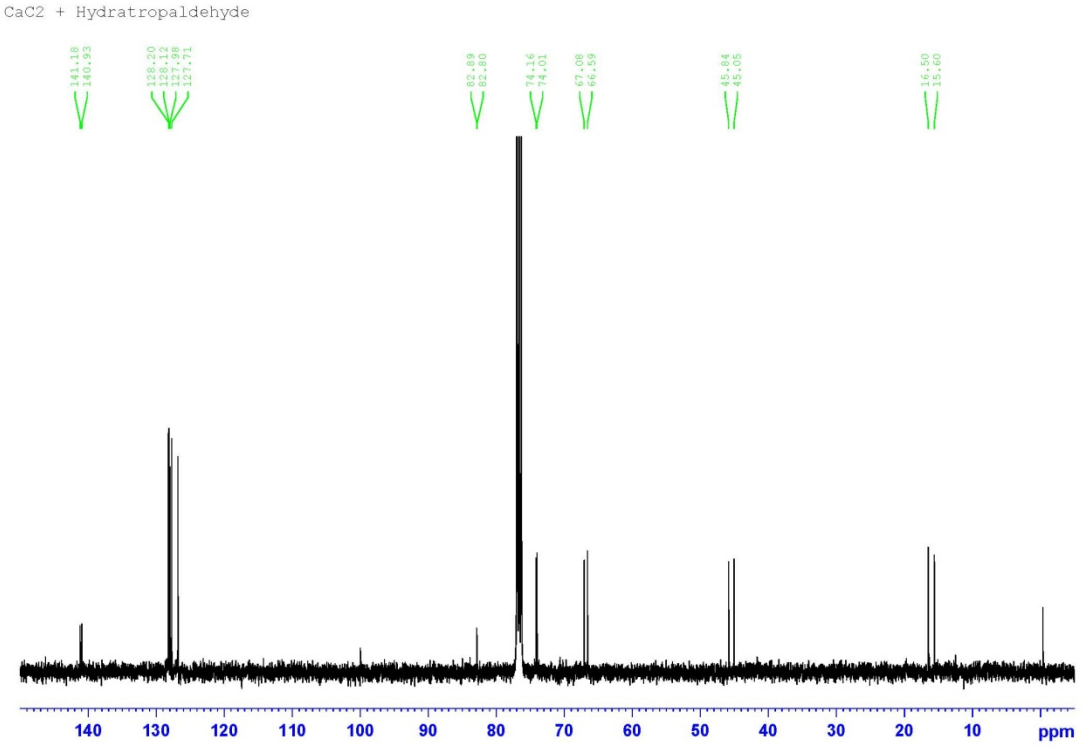
^{1}H NMR (400MHz, $CDCl_3$) δ 5.82 – 5.93 (m, 1H), 4.97 – 5.11 (m, 2H), 2.46 (s, 1H, C≡C*H*), 2.23 – 2.39 (m, 2H), 1.71 – 1.83 (m, 2H), 1.51 (s, 3H, C*H*$_3$); ^{13}C NMR (400mHz, $CDCl_3$) δ 137.8, 114.6, 86.8, 71.2, 67.4, 41.8, 29.4, 28.6

4-ethyl-1-phenyl-1-hexyn-3-ol (5a)

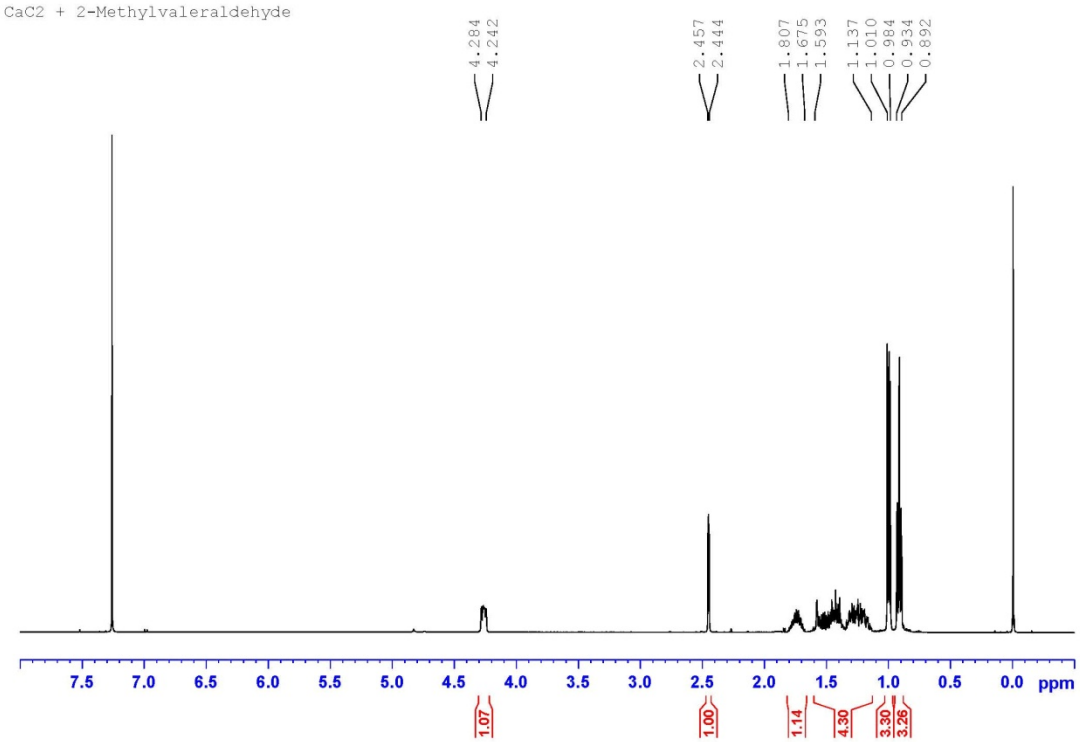
^{1}H NMR (400MHz, $CDCl_3$) δ 7.40 – 7.45 (m, 2H, *Ph*), 7.29-7.33 (m, 3H, *Ph*), 4.63 (d, 1H, C*H*(OH)C≡CPh), 1.40 – 1.72 (m, 5H), 0.95 – 1.00 (m, 6H); ^{13}C NMR (400mHz, $CDCl_3$) δ 131.2, 127.85, 127.82, 122.3, 99.9, 88.8, 85.1, 64.6, 47.1, 21.6, 11.2

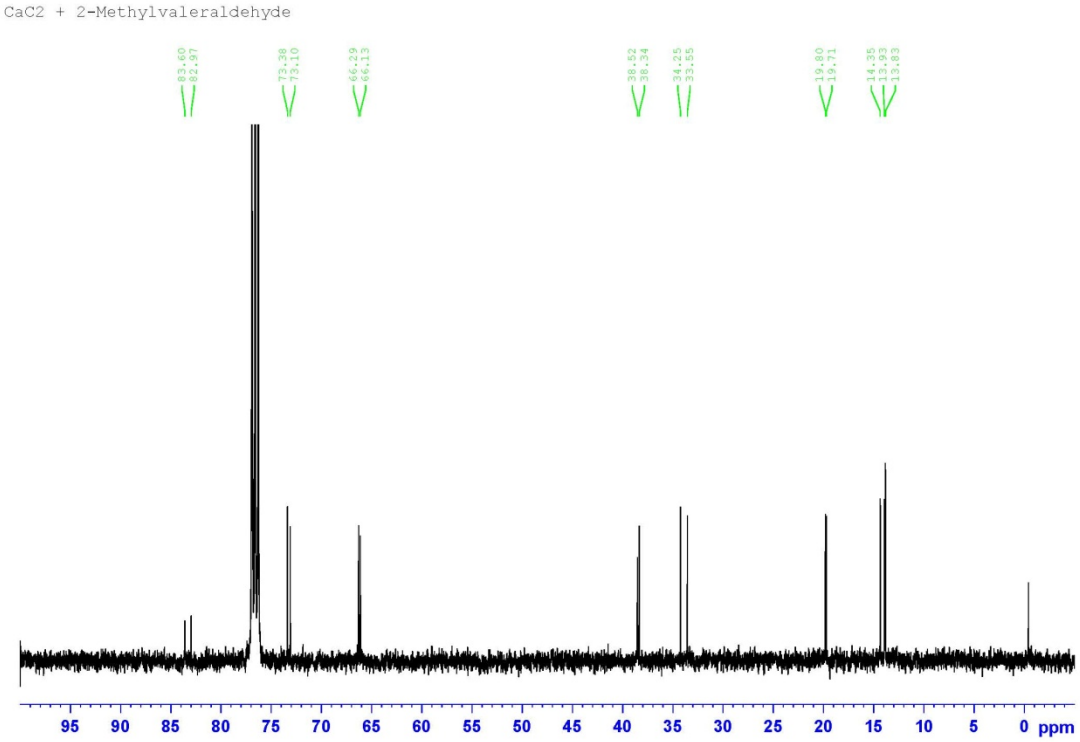
2-Phenyl-4-pentyn-3-ol (2a)



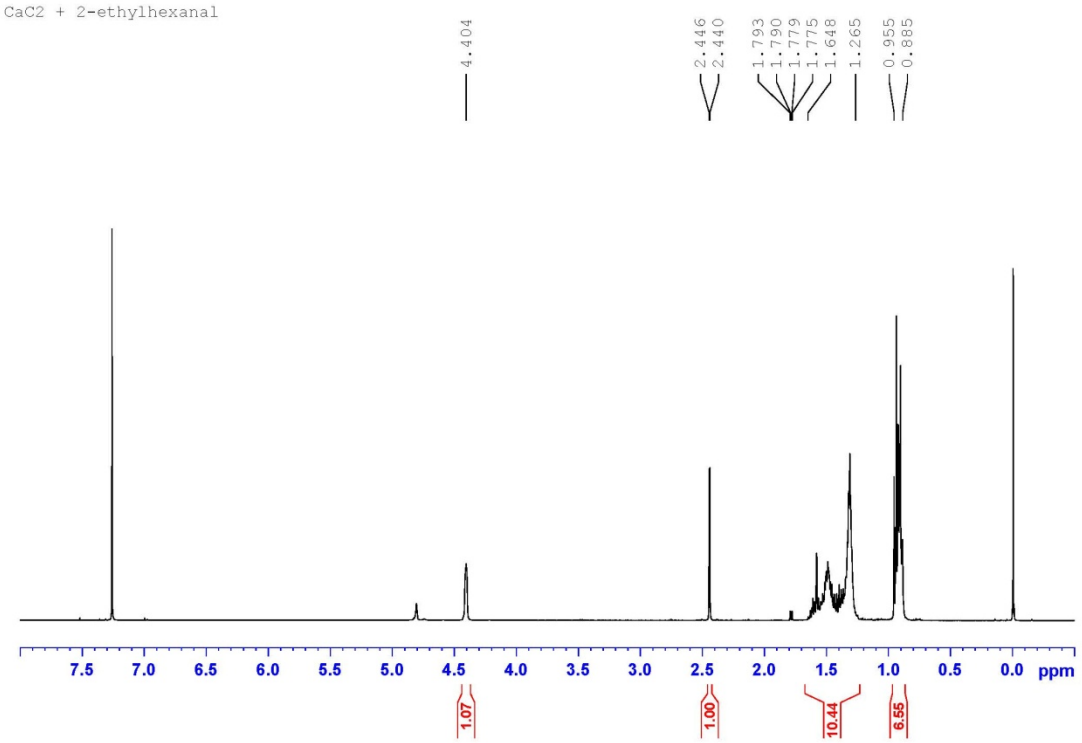


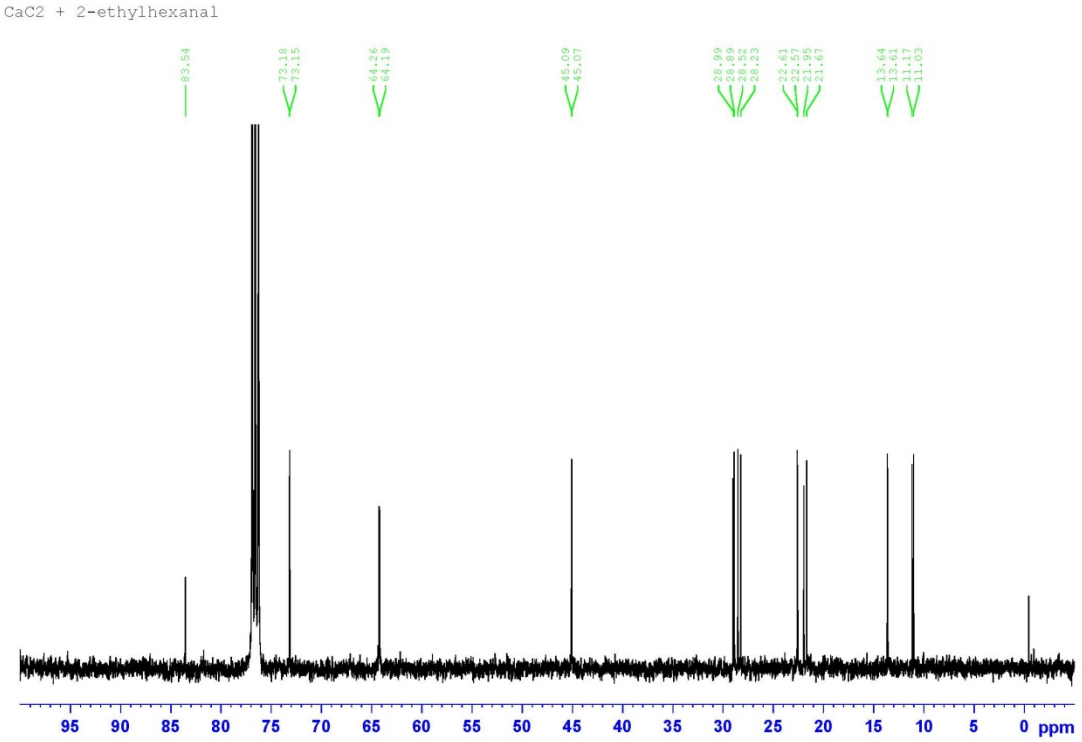
4-methylhept-1-yn-3-ol (2b)



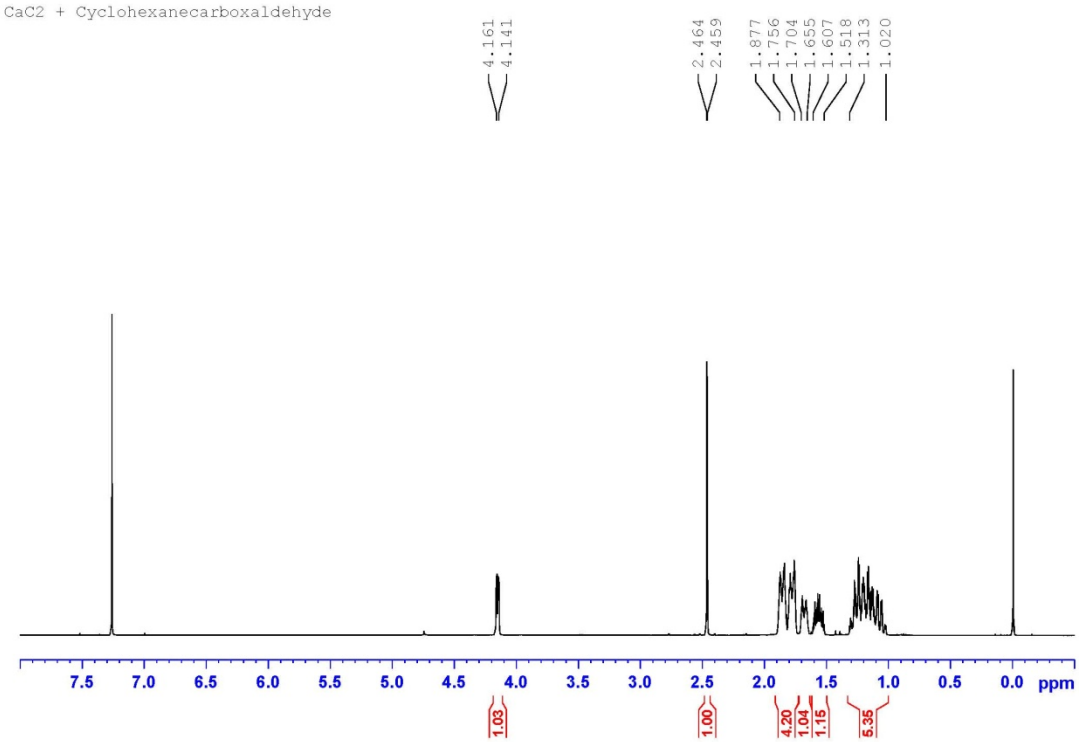


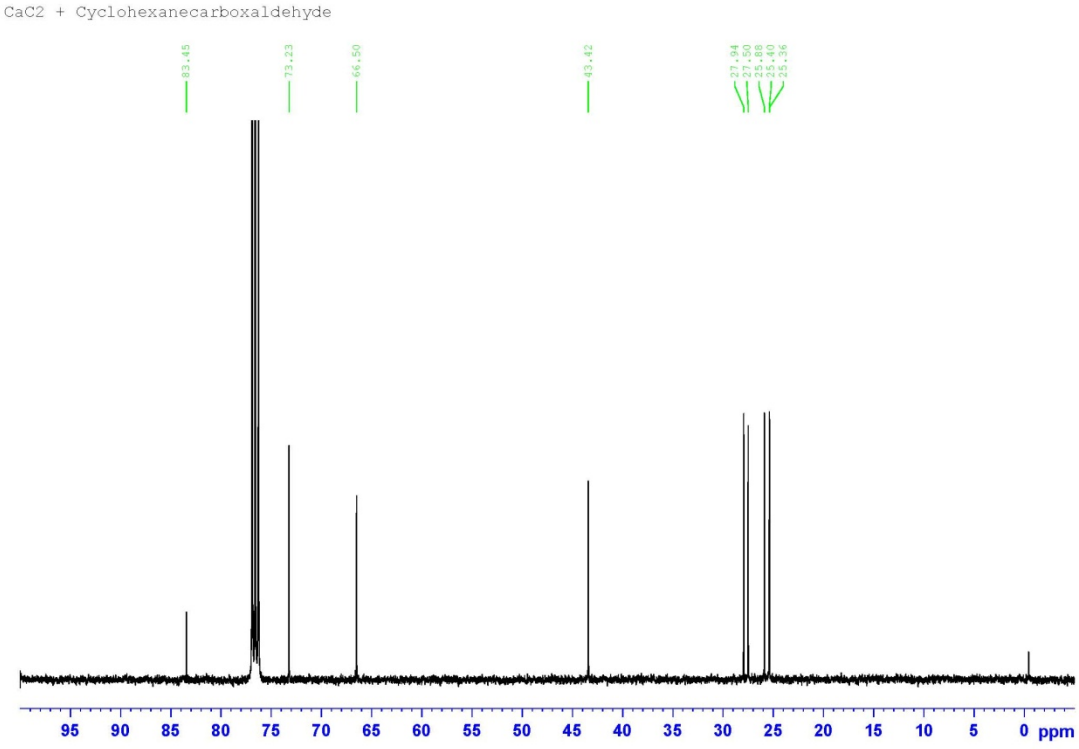
4-ethyl-1-Octyn-3-ol (2c)



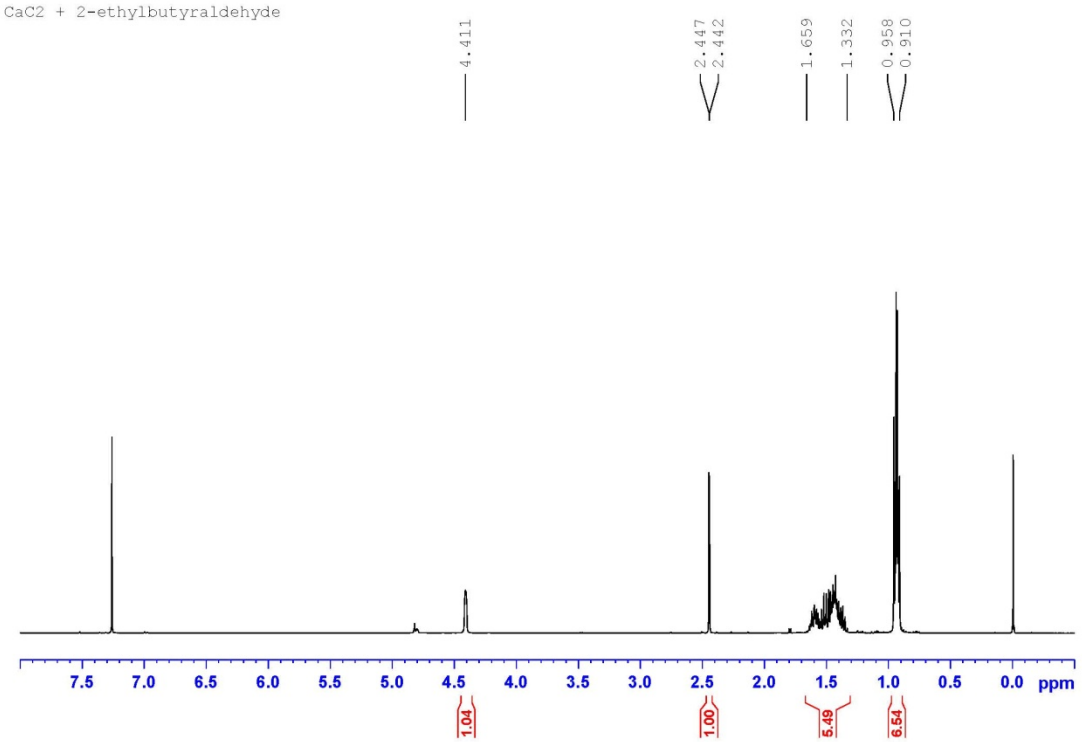


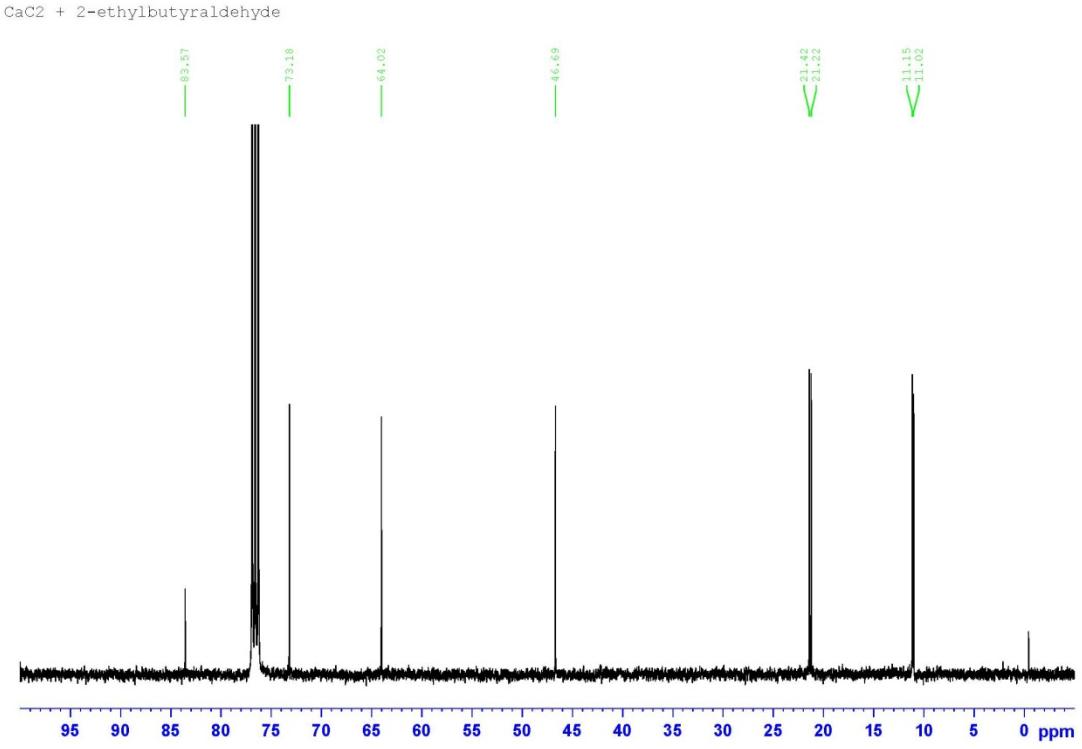
1-Cyclohexylprop-2-yn-1-ol (2d)



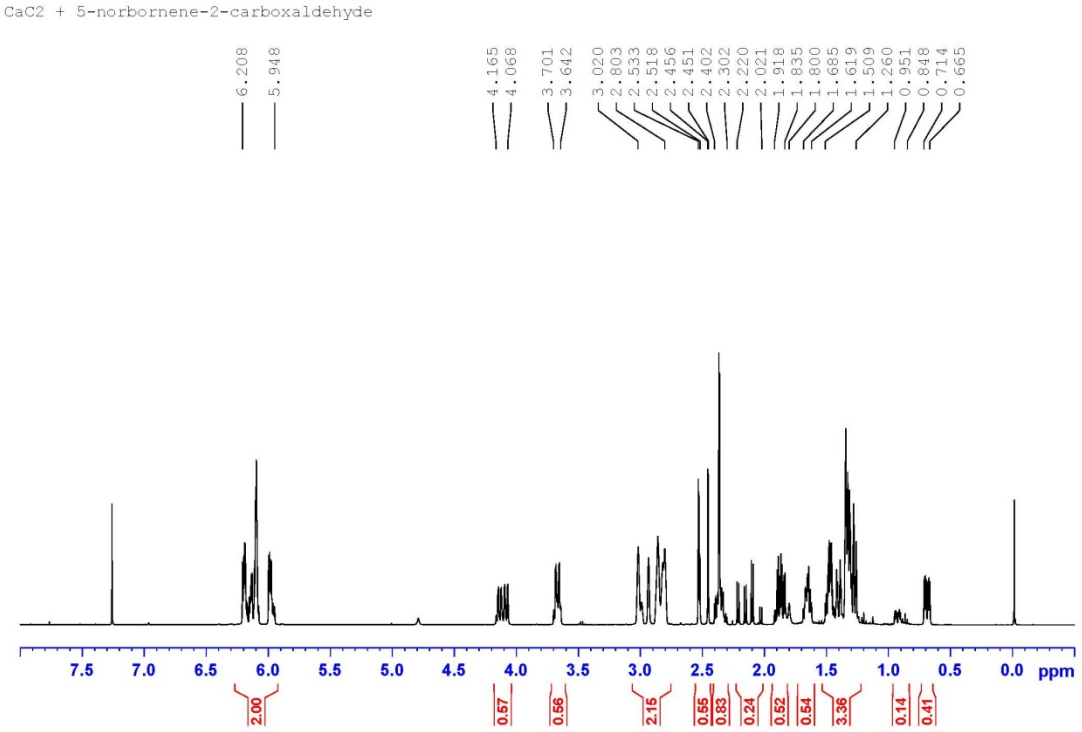


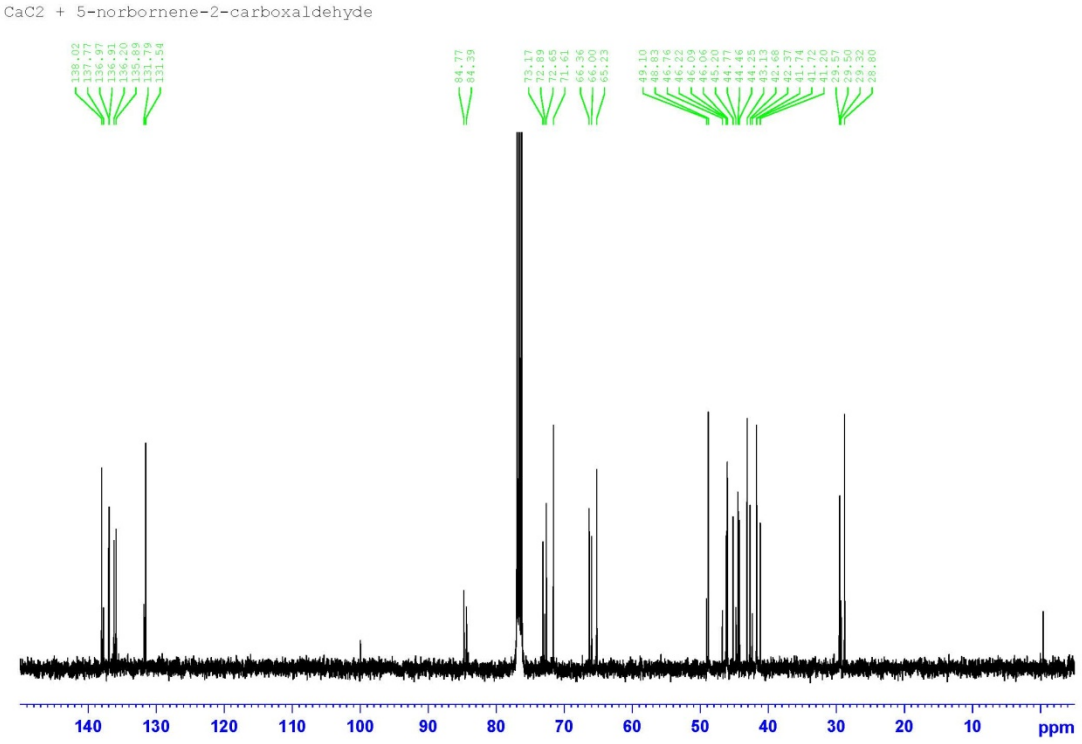
4-ethyl-1-Hexyn-3-ol (2e)



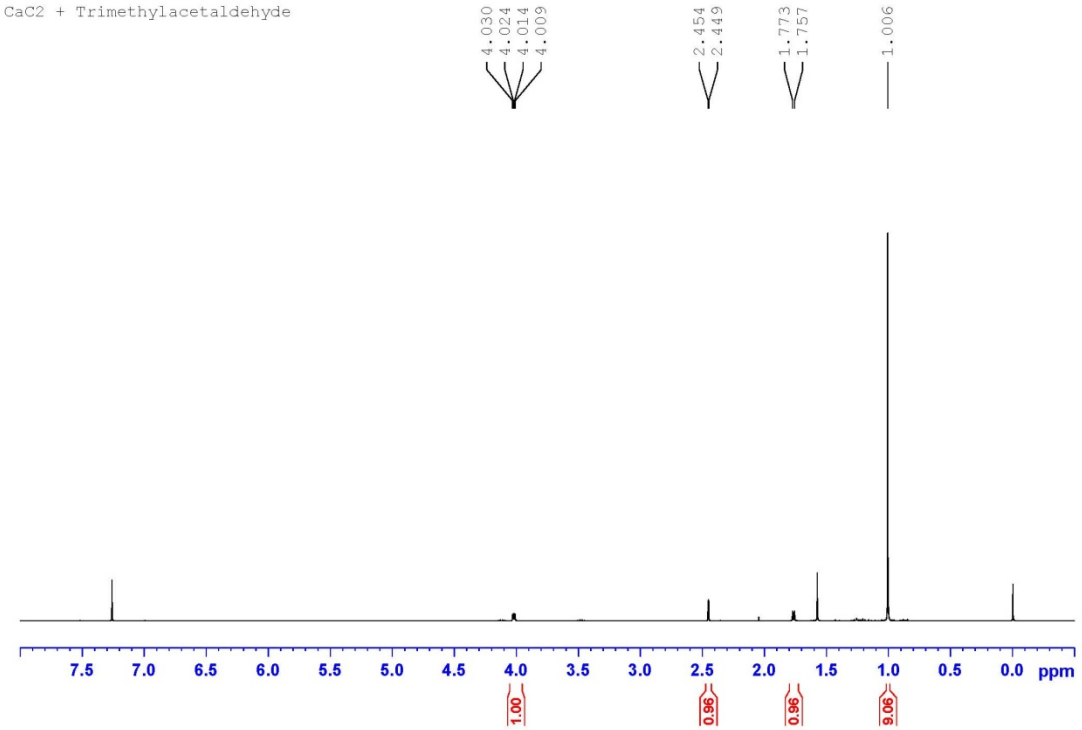


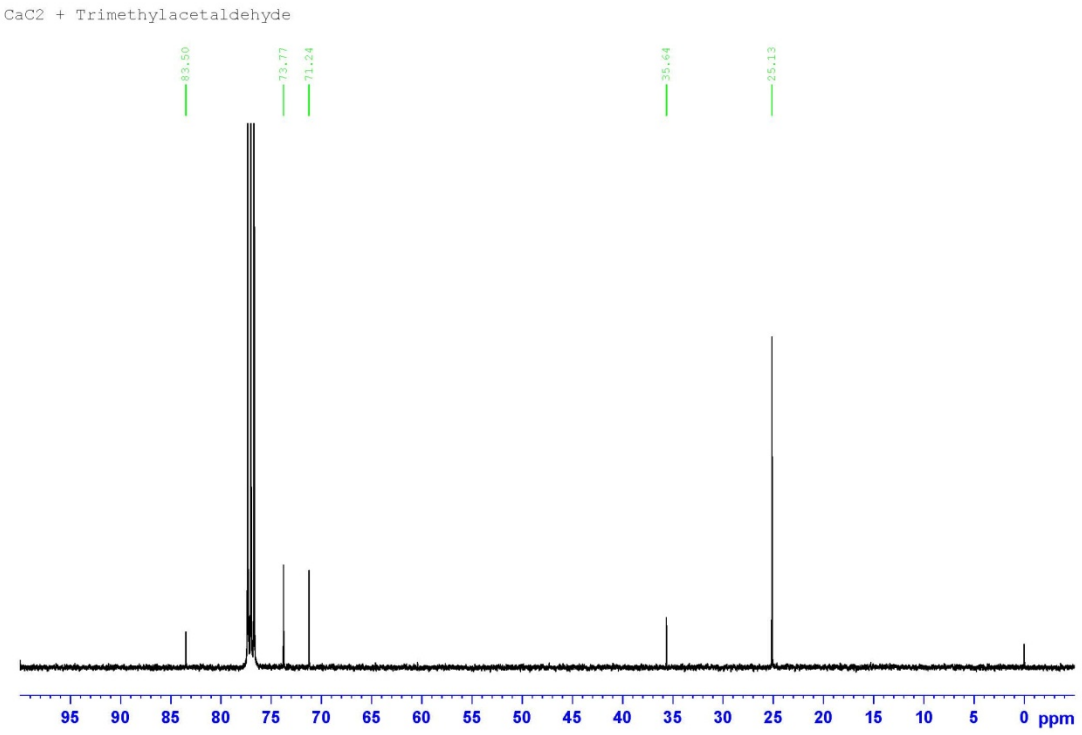
α-ethynyl-5-Norbornene-2-methanol (2f)



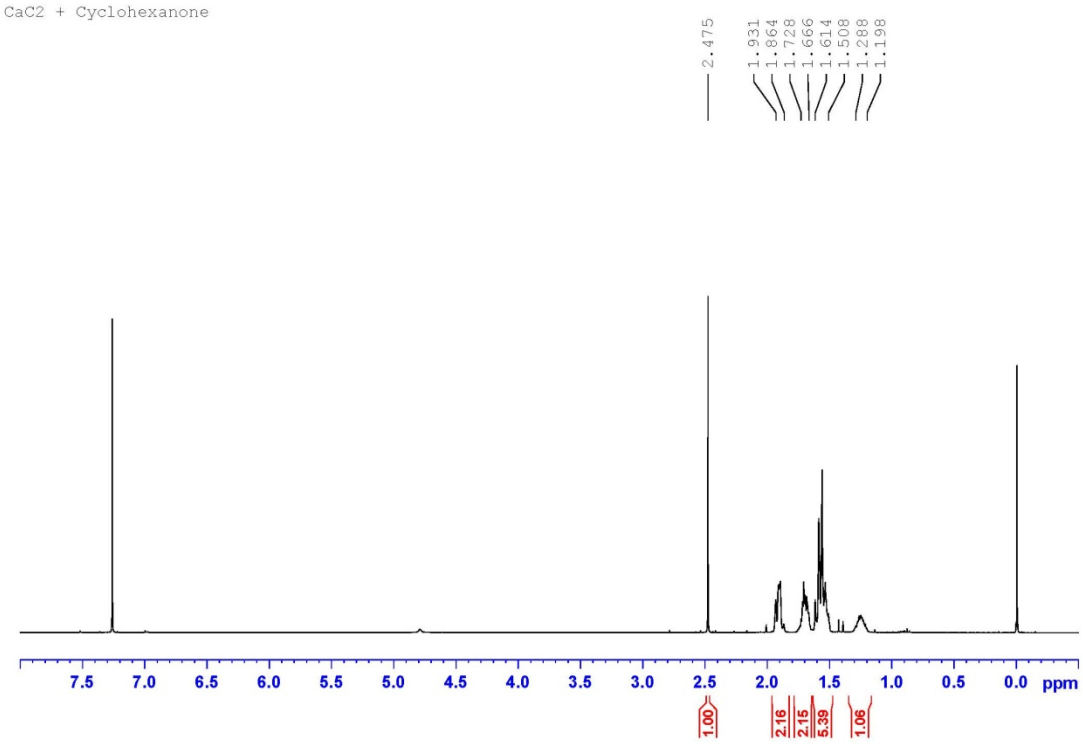


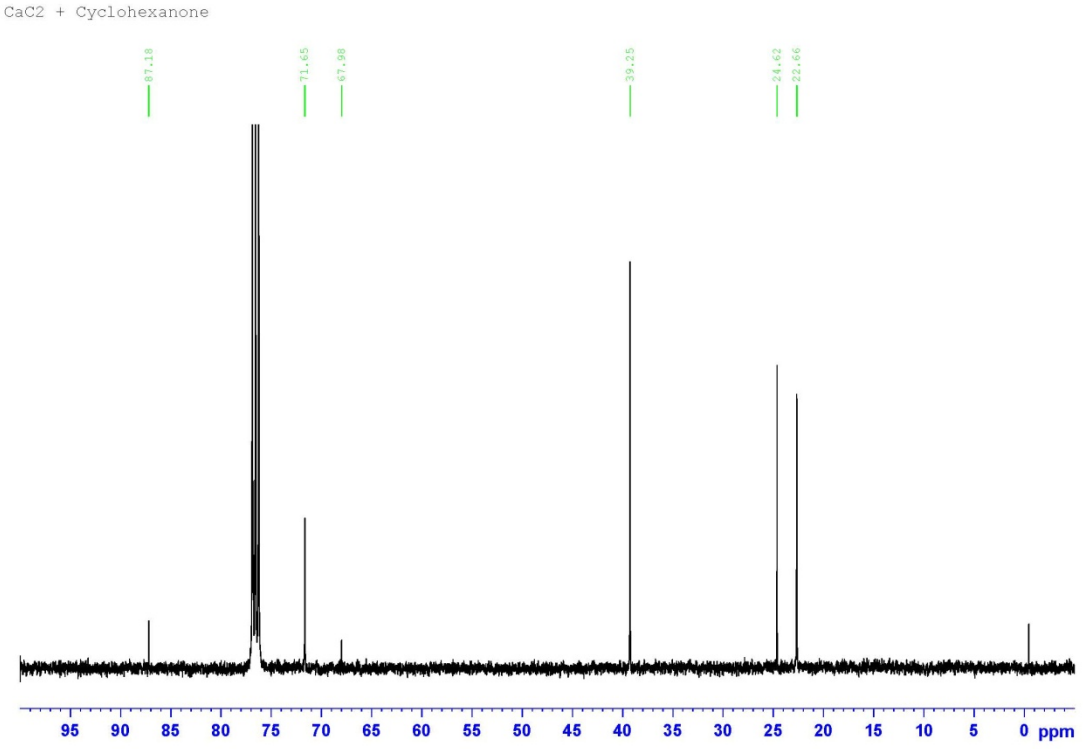
4,4-dimethyl-1-pentyn-3-ol (2g)



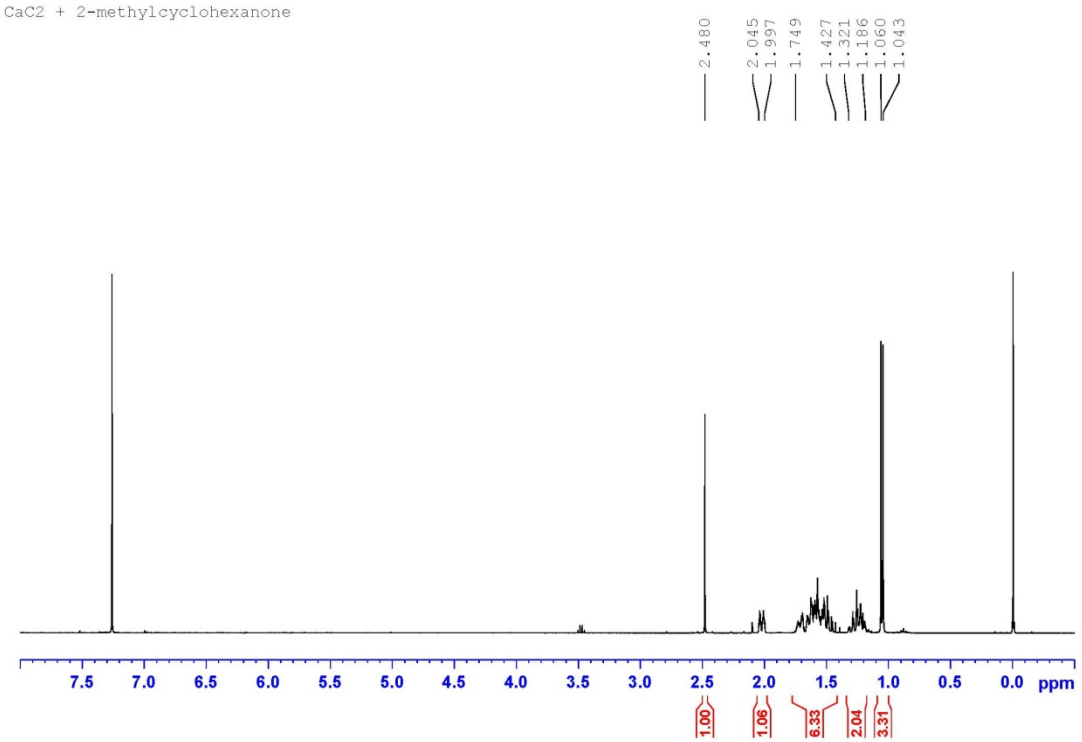


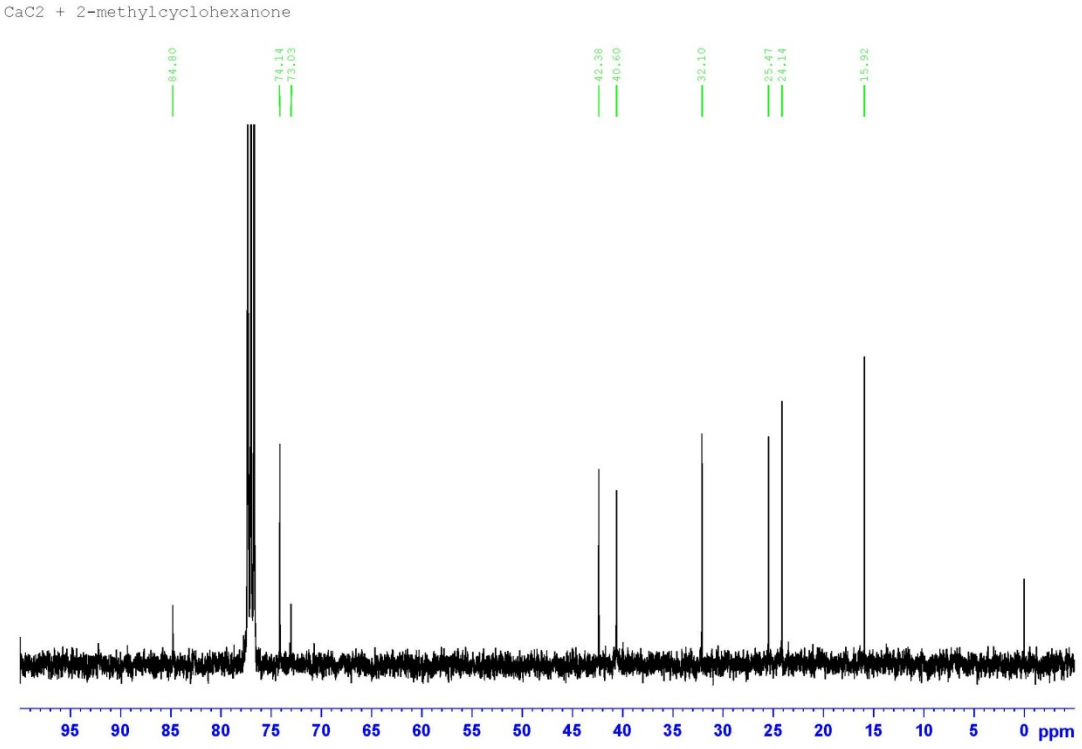
1-Ethynyl-1-cyclohexanol (4a)



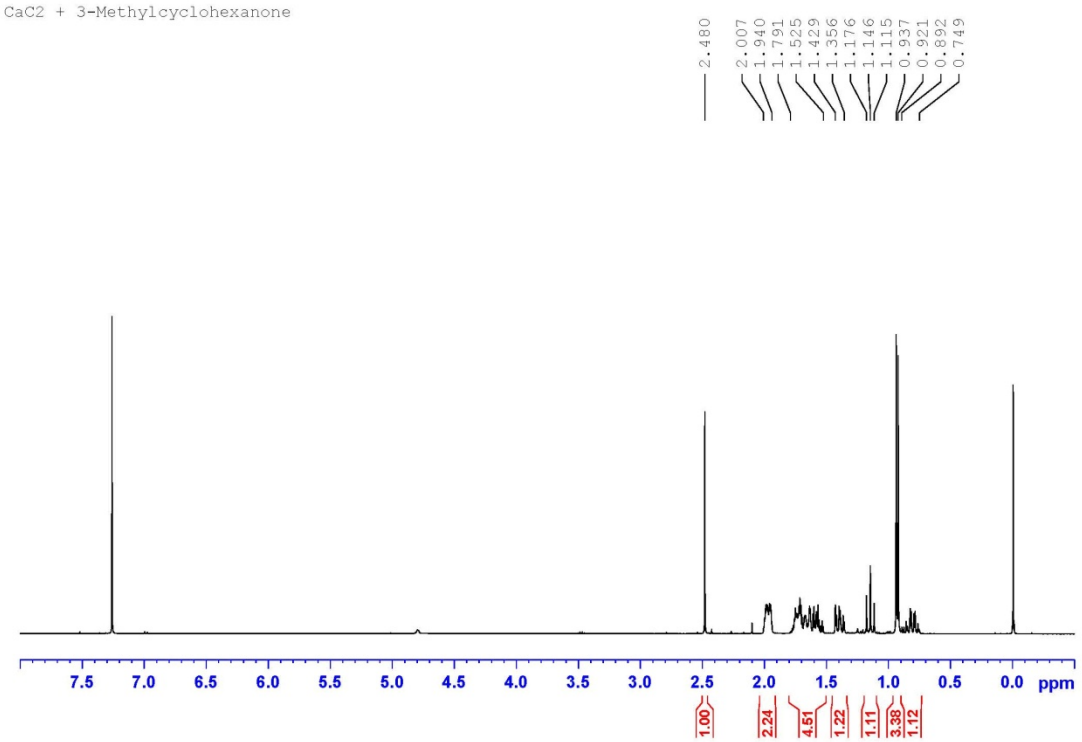


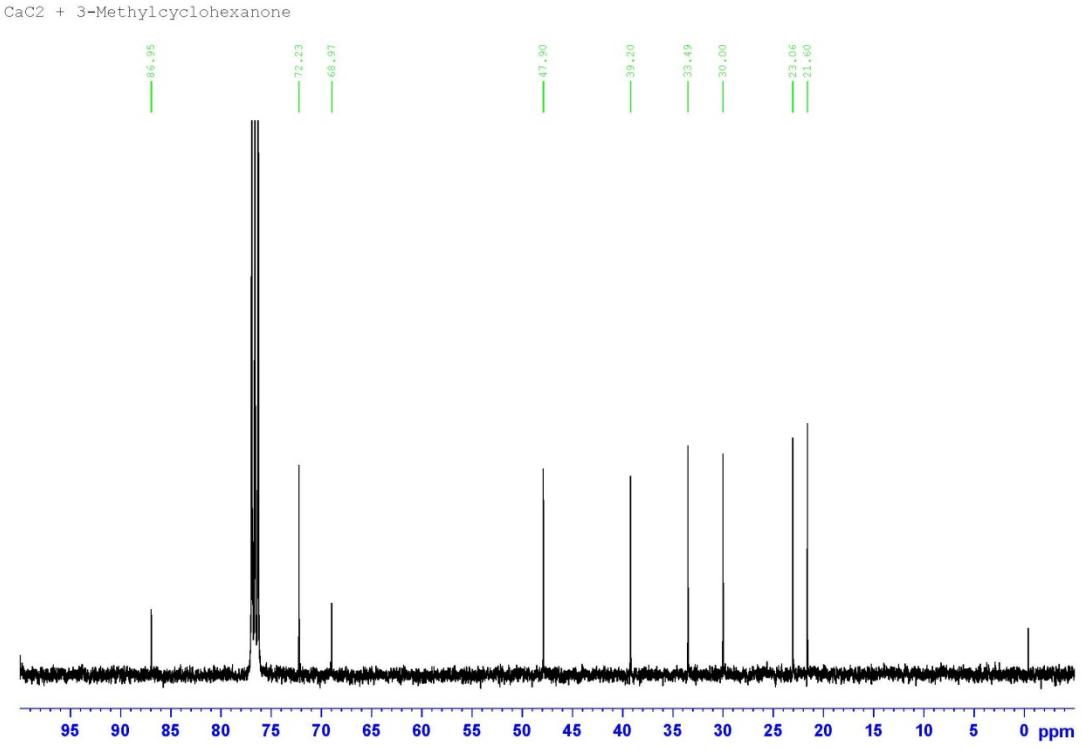
1-ethynyl-2-methylcyclohexanol (4b)



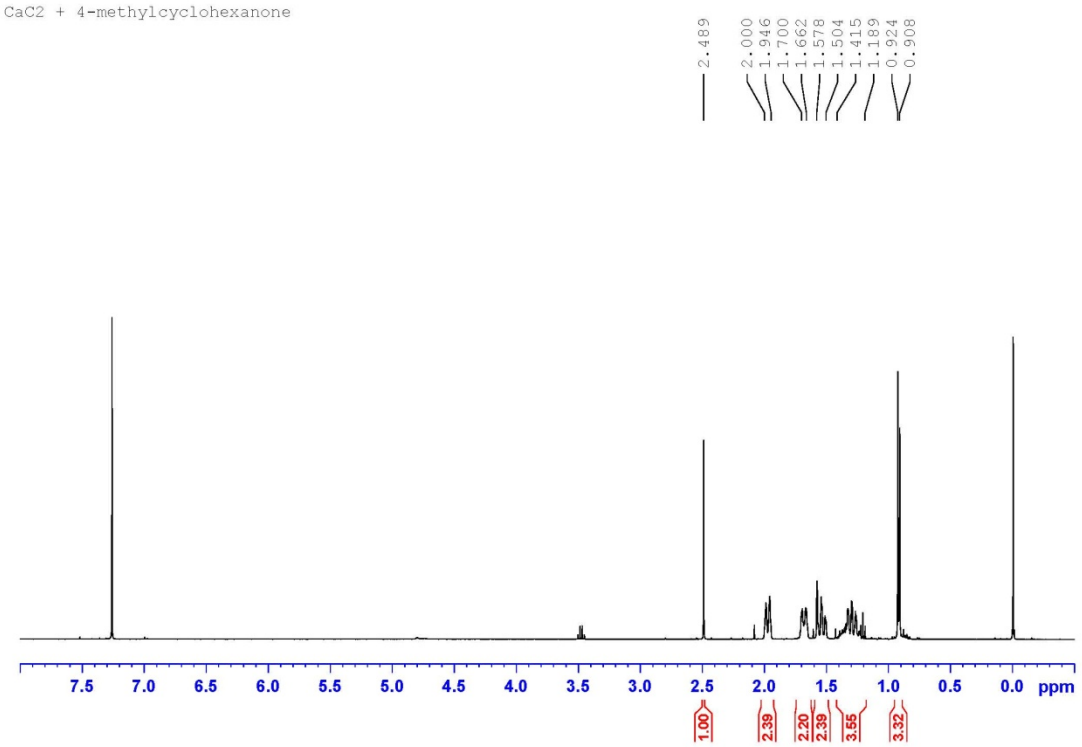


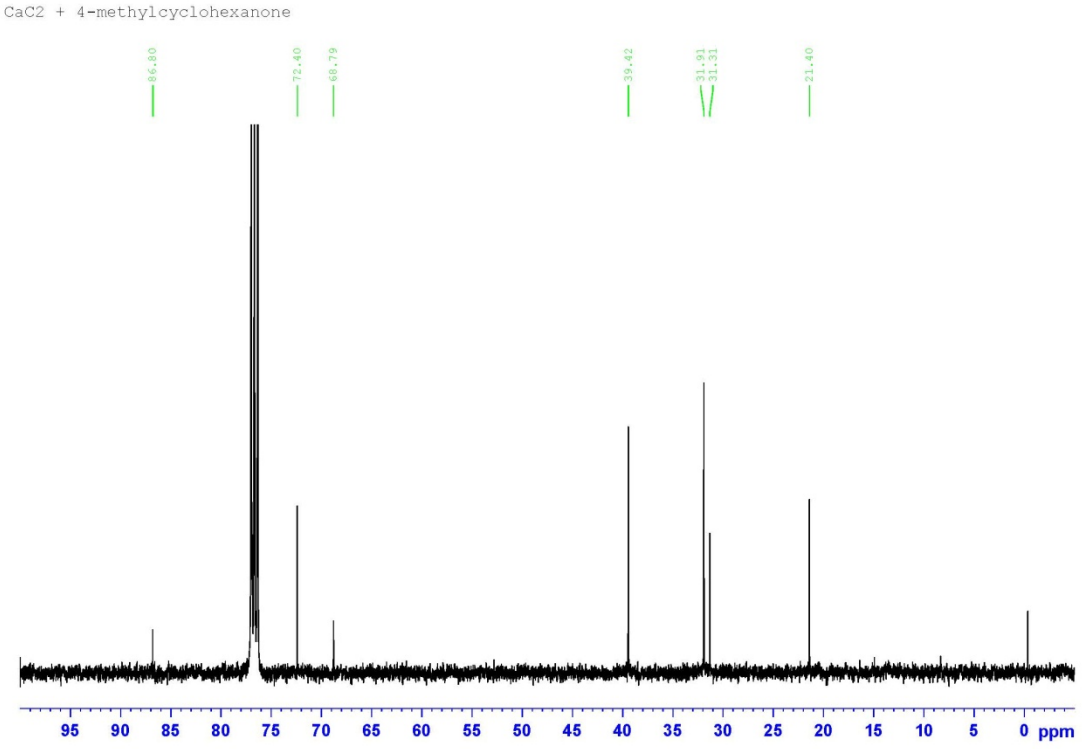
1-ethynyl-3-methylcyclohexanol (4c)



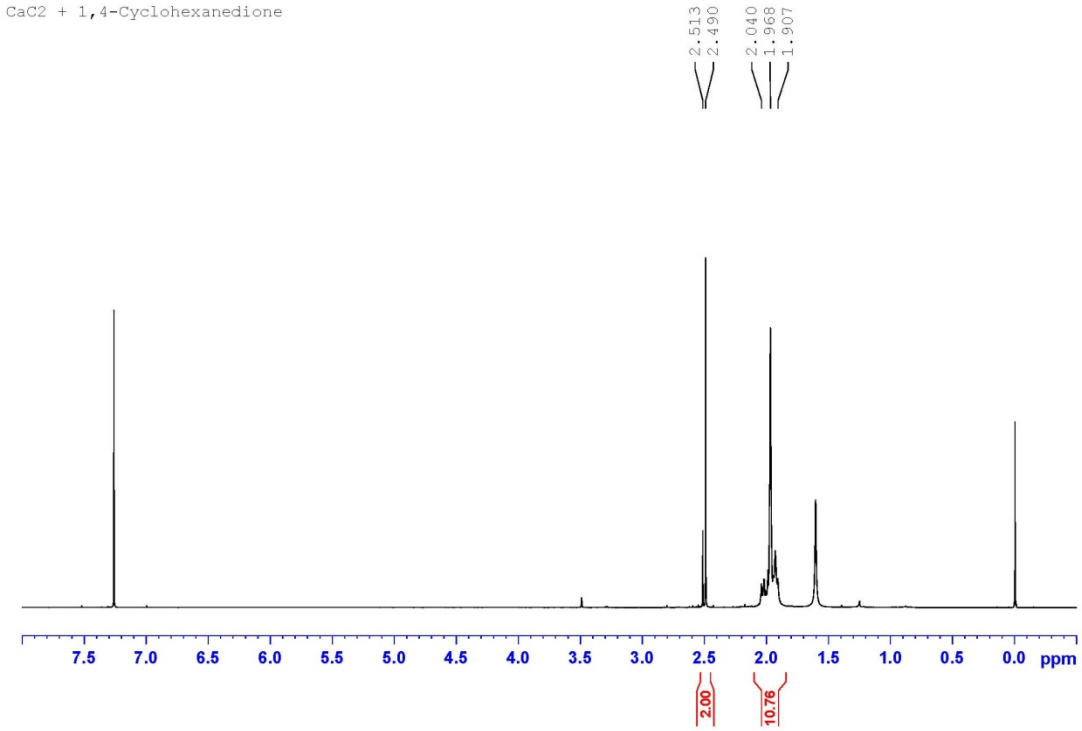


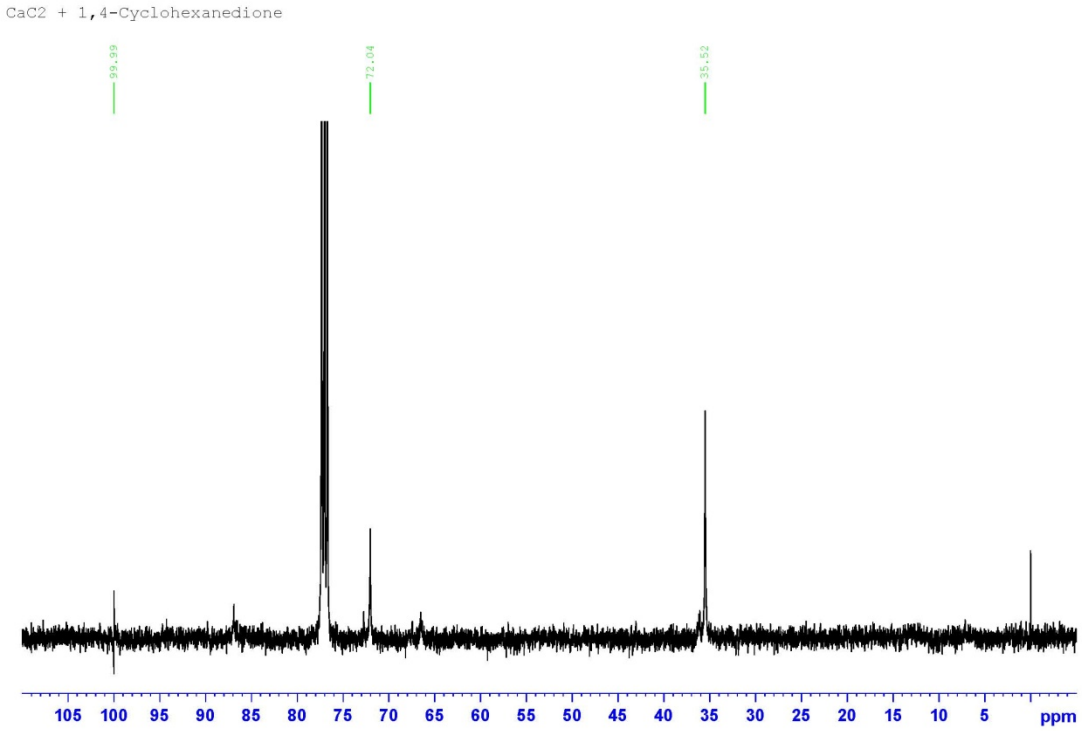
1-ethynyl-4-methylcyclohexanol (4d)



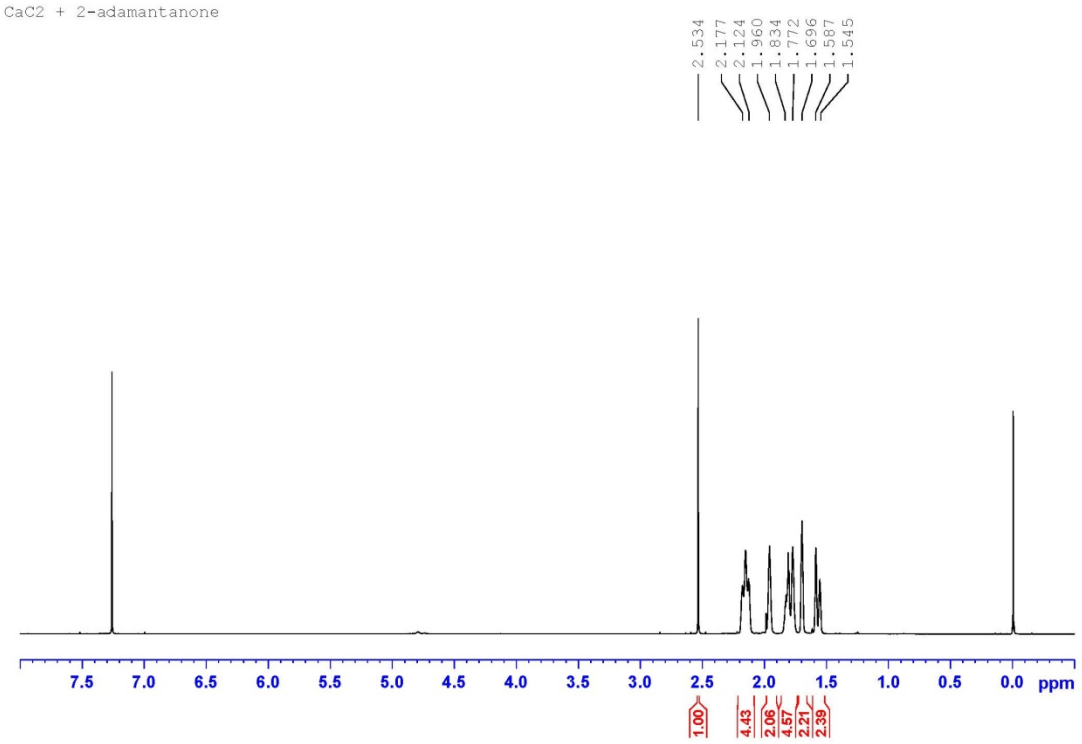


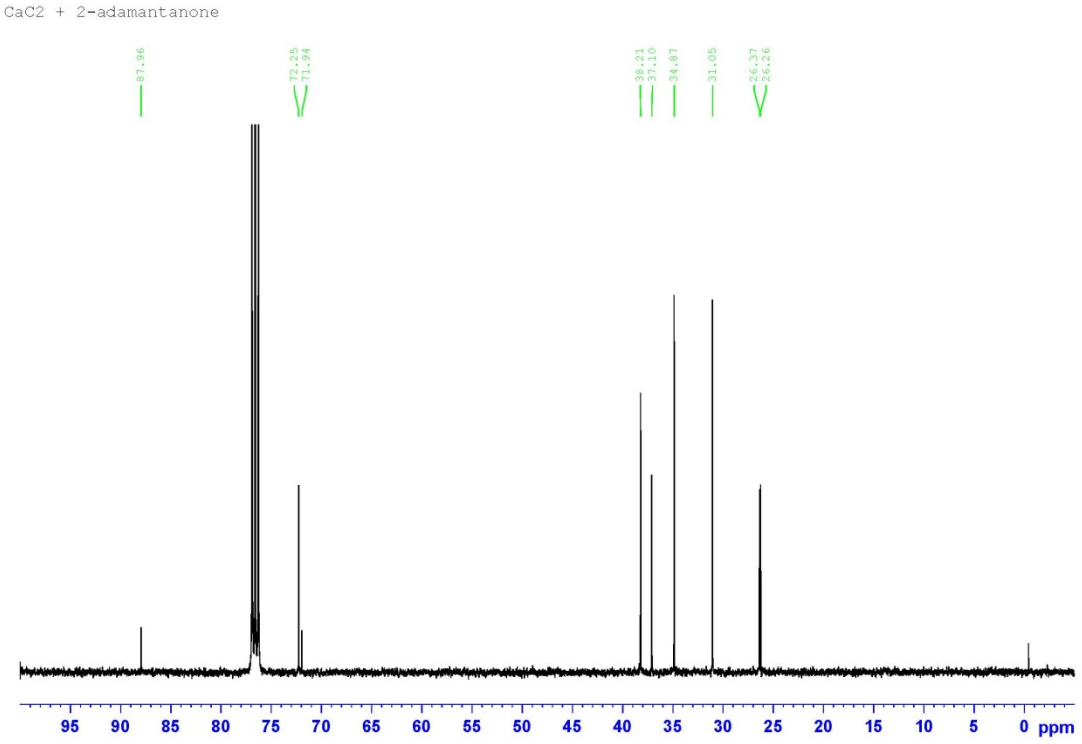
1,4-Diethynyl-1,4-cyclohexanediol (4f)



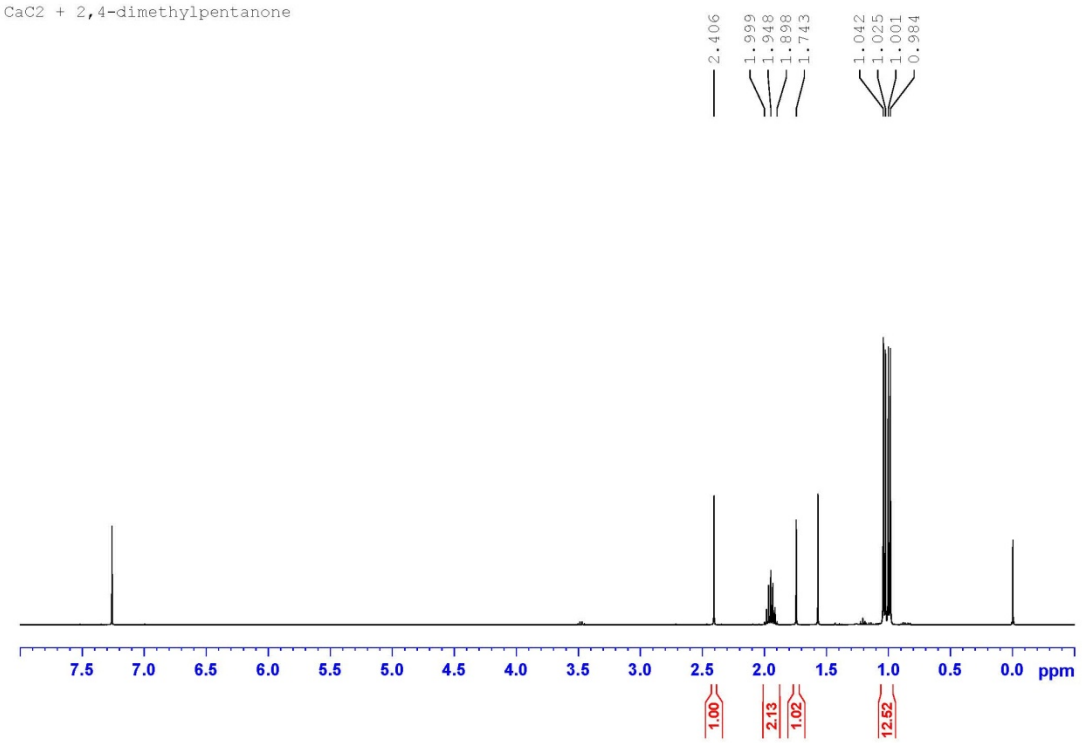


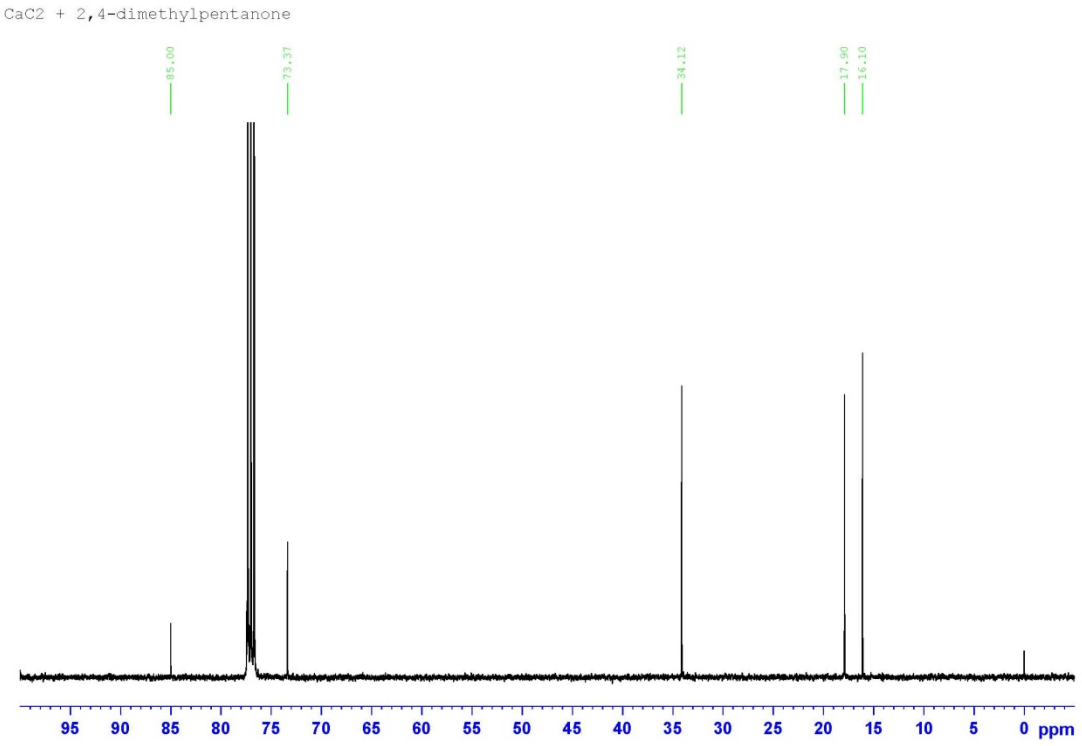
2-Ethynyl-2-adamantanol (4g)



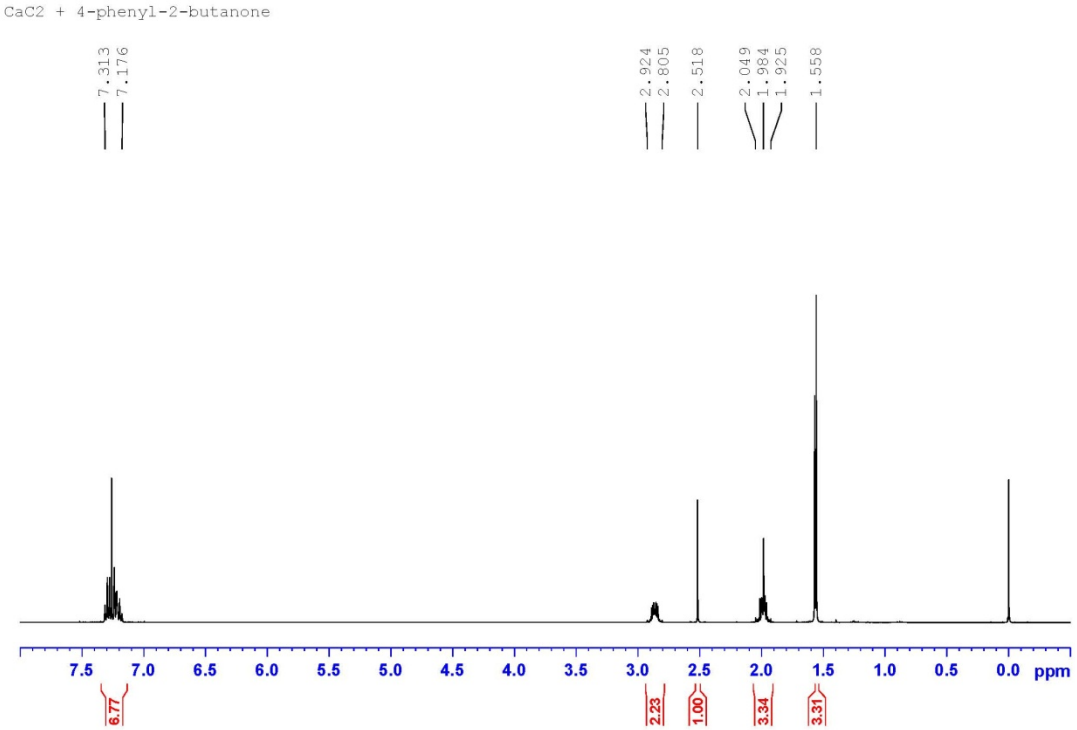


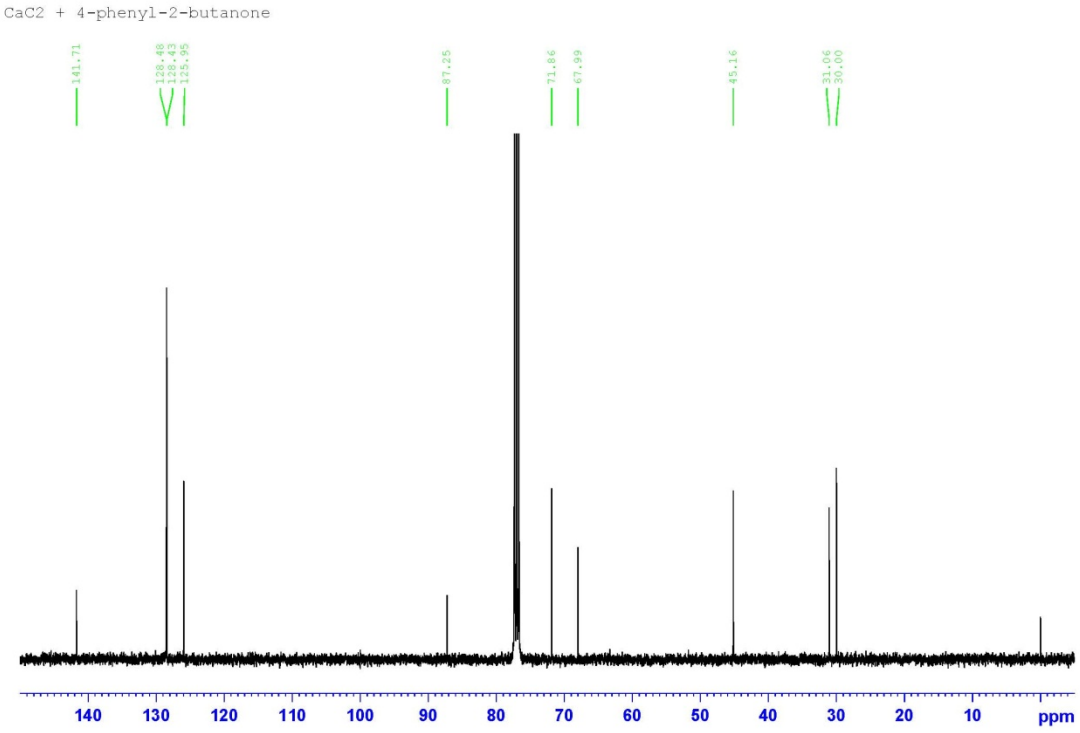
3,3-diisopropyl-1-propyn-3-ol (4h)



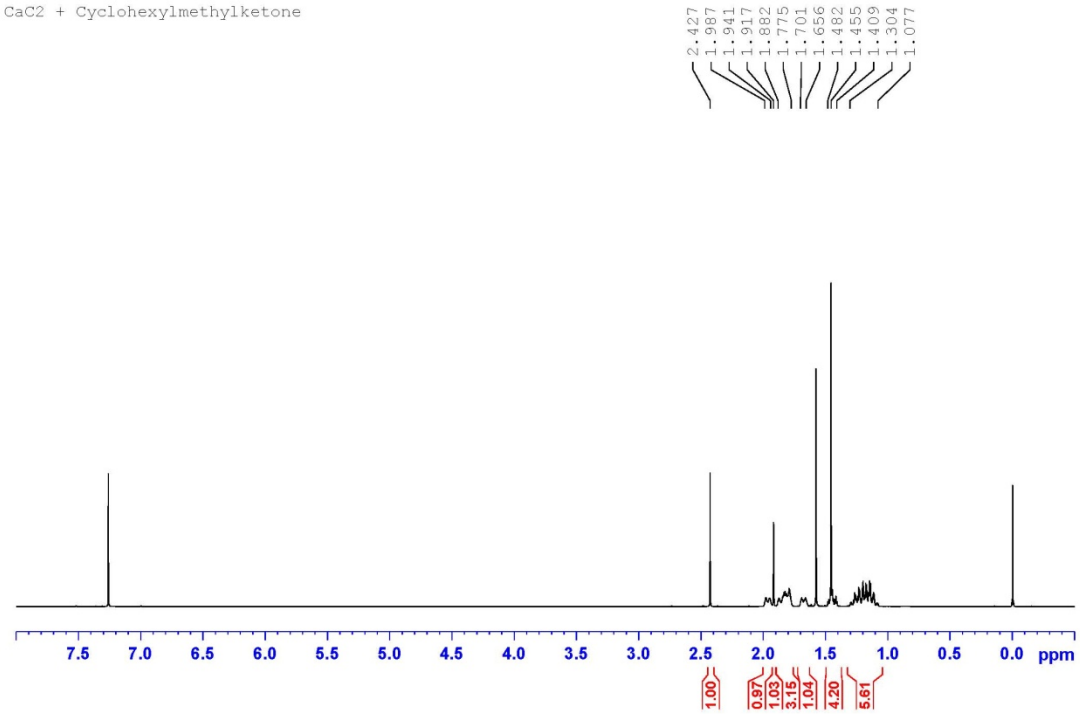


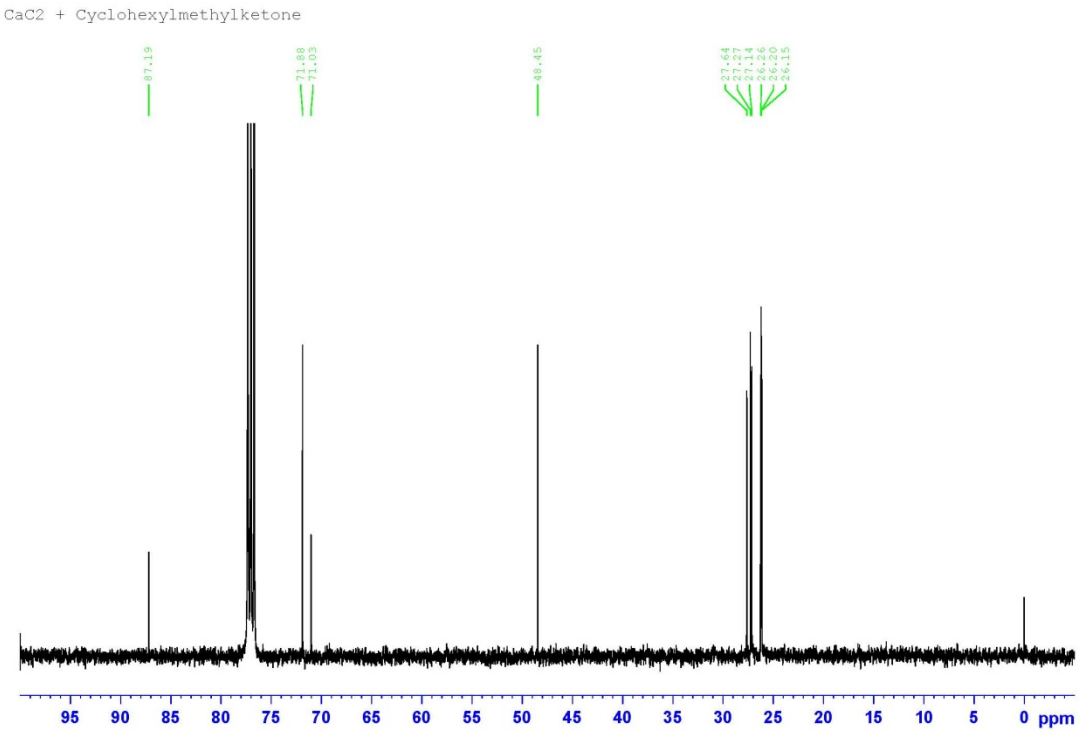
3-Methyl-5-phenyl-1-pentyn-3-ol (4i)



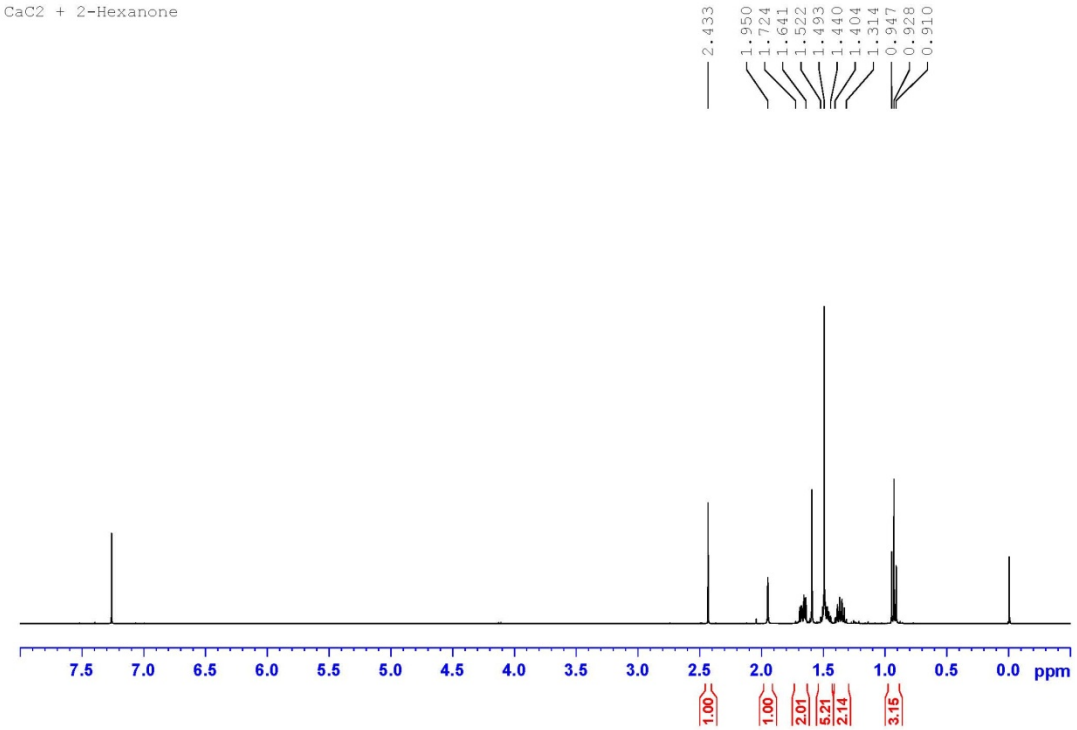


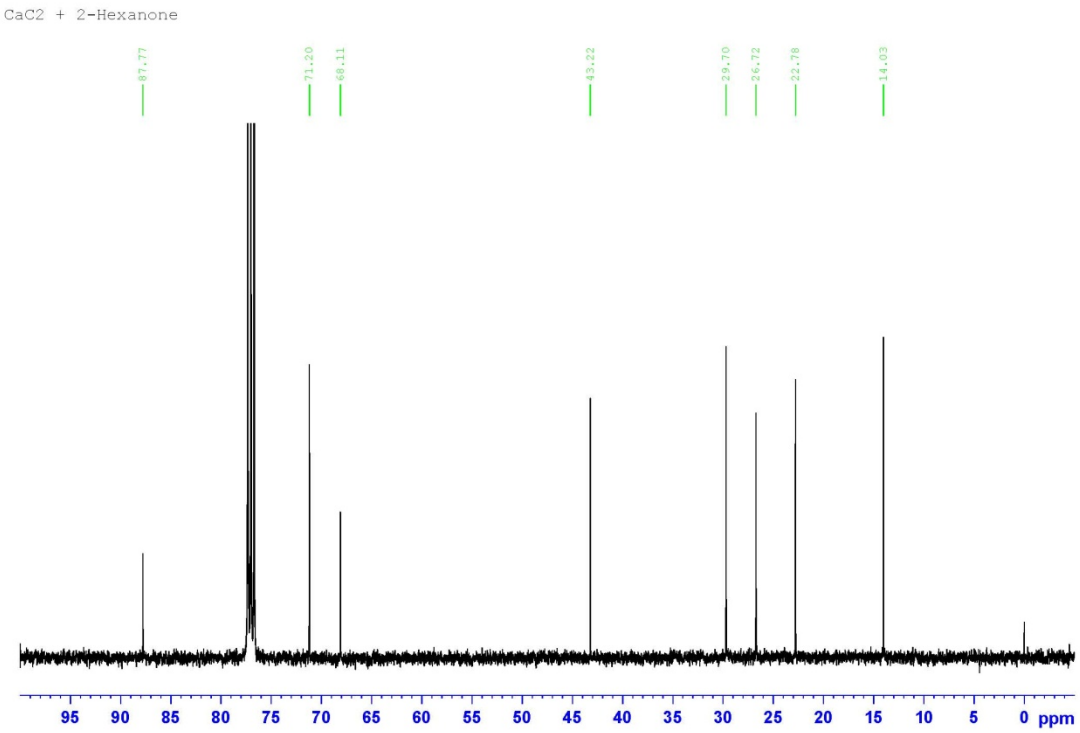
3-butyn-2-cyclohexyl-2-ol (4j)



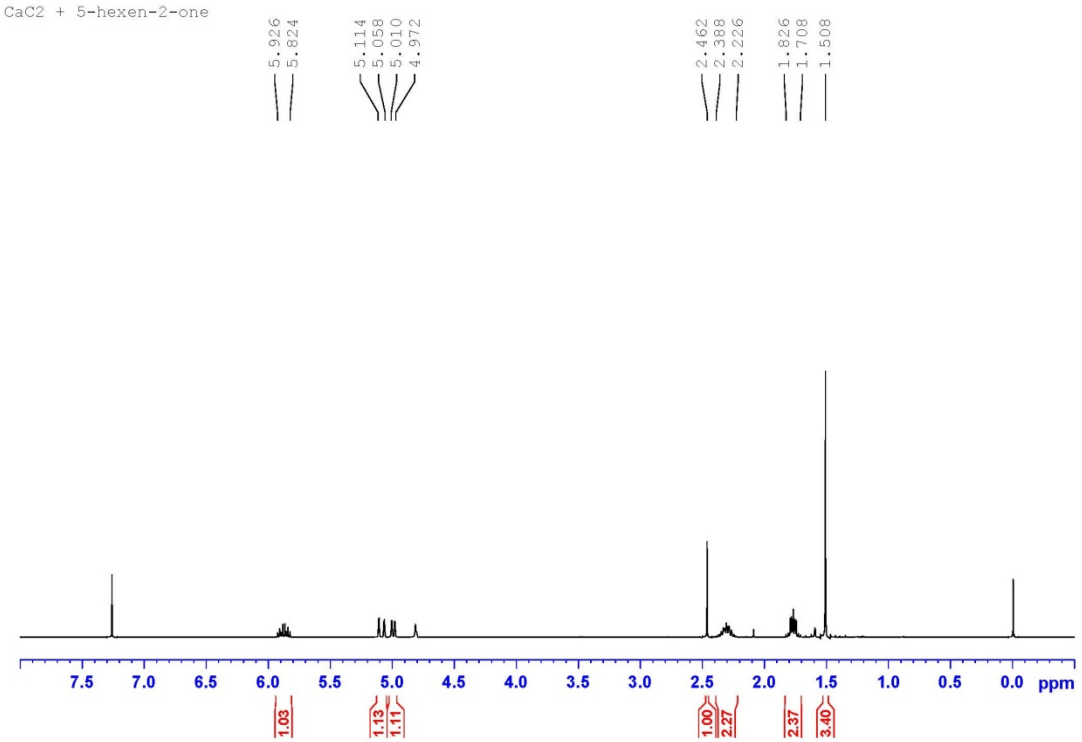


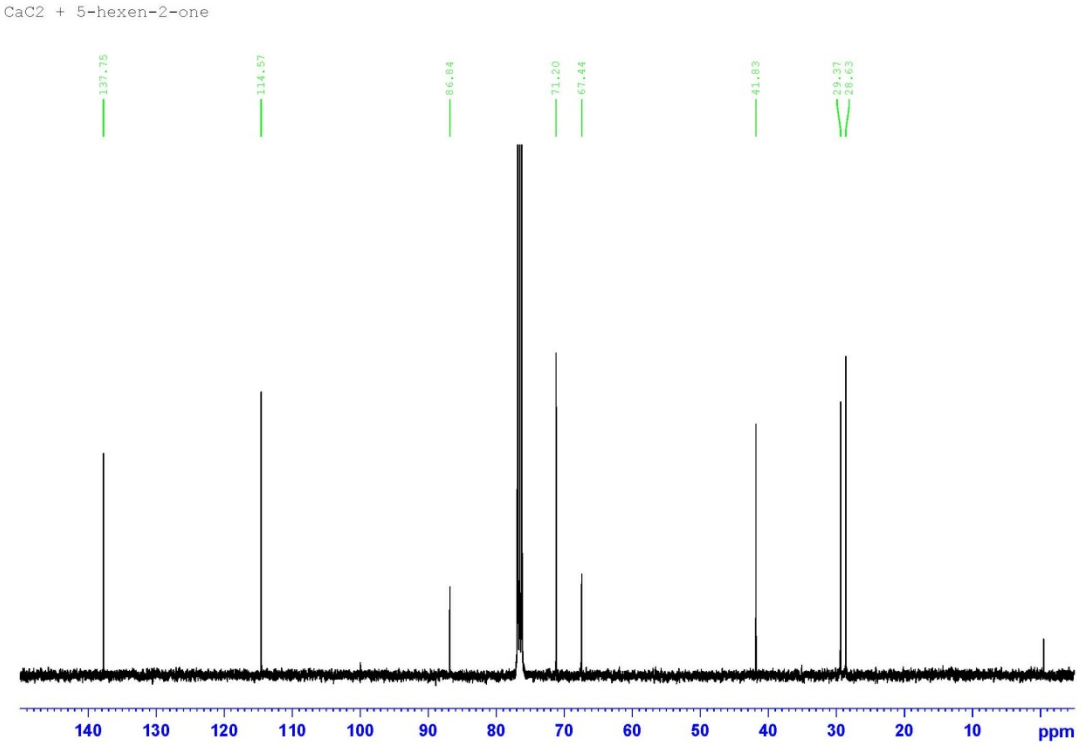
2-ethynyl-2-hexanol (4k)



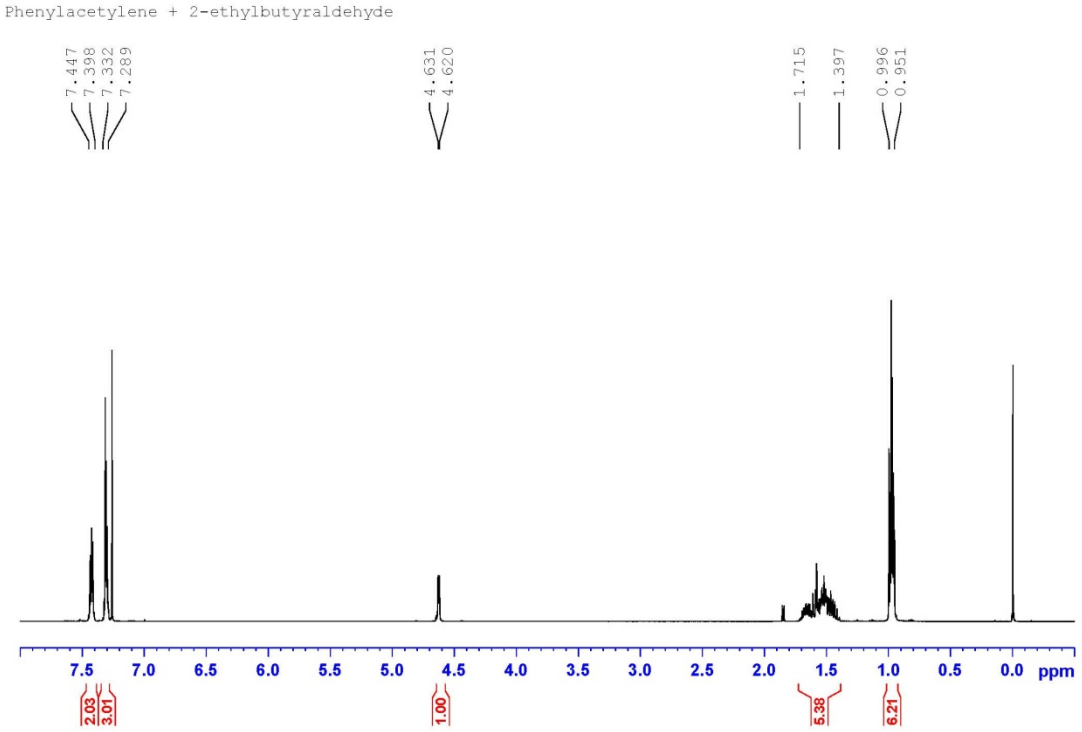


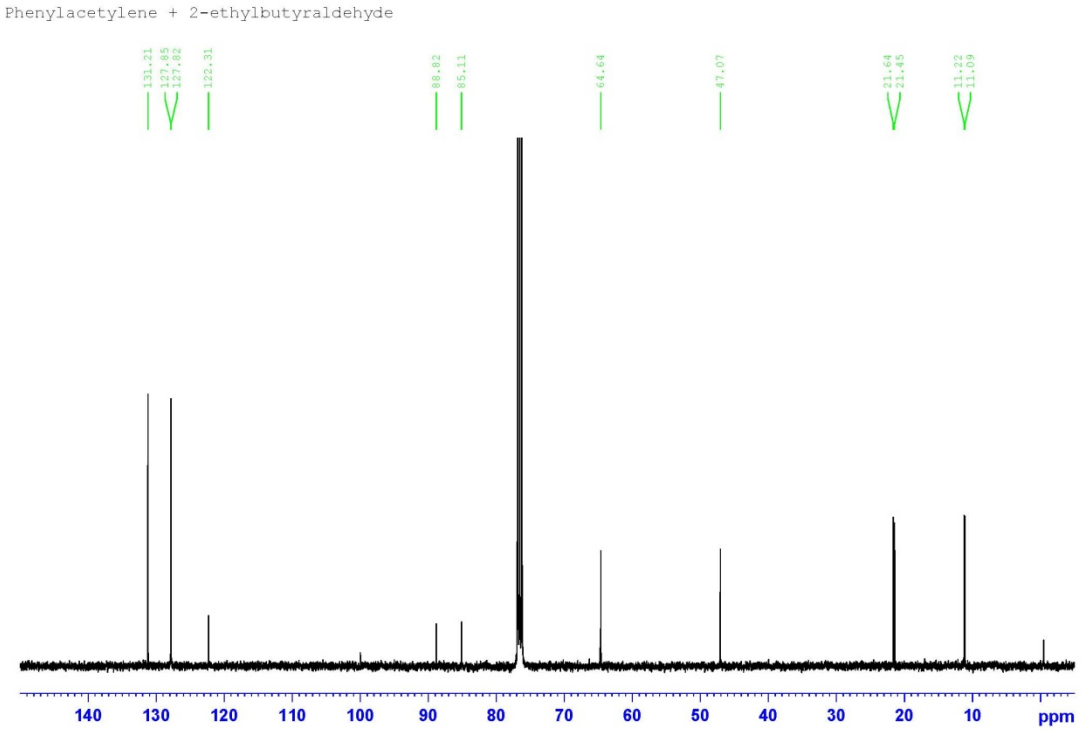
3-methyl-6-hepten-1-yn-3-ol (4l)





4-ethyl-1-phenyl-hexyn-3-ol (5a)





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