Electronic Supplementary Information

Borenium ionic liquids as catalysts for Diels-Alder reaction: tuneable Lewis superacids for catalytic applications

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1. General procedure for catalysts preparation: Boron trichloride adducts were prepared using an argon Schlenk line, by dropwise addition of a base (0.9 eq.) to a vigorously stirred mixture of boron trichloride (1 M solution in heptane, 1.0 eq.) and DCM at -78 °C. After the reaction (-78 °C, 30 min, 600 rpm), excess reactants and solvents were removed under reduced pressure, and the adduct was dried under high vacuum (60 °C, 10^{-2} bar, overnight). Complexes of 4-picoline were recrystallized from a mixture of dry dichloromethane and hexane. Borenium ionic liquids were synthesized in a nitrogen-filled glovebox. Metal(III) chloride (M = Al or Ga) was added slowly to the boron trichloride adduct (1 eq.) and left to react until a homogenous mixture was obtained or no further change was observed (30-50 °C, 10 min - 24 h, 600 rpm).

2. General procedure for Diels-Alder reaction: The dienophile (16 mmol) and the borenium ionic liquid (0.1 mol% per dienophile) were placed in a two-necked round- bottomed flask equipped with septum, the balloon with argon, ice-bath and stirring bar. Then the diene (24 mmol) was added dropwise to the vigorously stirred (1500 rpm) reaction mixture. The reaction was carried out for 5 – 15 min. After this time few drops of water (to quench the reaction), 2 ml of dichloromethane and internal standard (decane) were added. The conversion of ethyl acrylate and selectivity was measured using gas chromatography. Isolation procedure**:** obtained products were purified using column chromatography with silica gel and 100% of chloroform as an eluent.

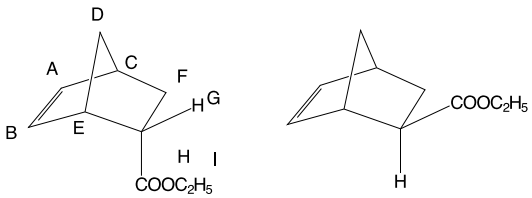
3. Analysis of Diels-Alder cycloadducts

^{1}H and ^{13}C NMR spectra of Diels-Alder cycloadducts were recorded at 599.829 and 150.827 MHz, respectively, using Varian spectrometer with TMS as internal standard.

Gas chromatography was performed using a Perkin Elmer Clarus 500 gas chromatograph equipped with an SPB™-5 column (30 m x 0.2 mm x 0.2 µm) with *n*-decane as internal standard. GC method: temperature program: start 40 °C, hold 2 min then 15 °C/min to 250 °C and hold 2 min. Injector and FID detector temperature – 250 °C. Retention times (RT) of products are given with NMR data.

High resolution mass spectrometry analyses were performed on a Waters Xevo G2 Q-TOF mass spectrometer (Waters Corporation) equipped with an ESI source operating in positive and negative ion modes. Full-scan MS data were collected from 100 to 1000 Da in both ion modes with scan time of 0.1 s. To ensure accurate mass measurements, data were collected in centroid mode and mass was corrected during acquisition using leucine enkephalin solution as an external reference (Lock-Spray TM), which generated reference ion at m/z 556.2771 Da ($[M^{+}H]^{+}$) in positive ESI mode. The accurate mass and composition for the molecular ion adducts were calculated using the MassLynx software (Waters) incorporated with the instrument.

GC–MS analysis was performed using an Agilent gas chromatograph 7890C (HP-5 MS capillary column, 30 m x 0.25 mm x 0.25 μm, helium 1 mL/min) conjugated with an Agilent mass spectrometer 5975C with EI ionization (70 eV). Products were identified using the NIST/EPA/NIH Mass Spectral Library.



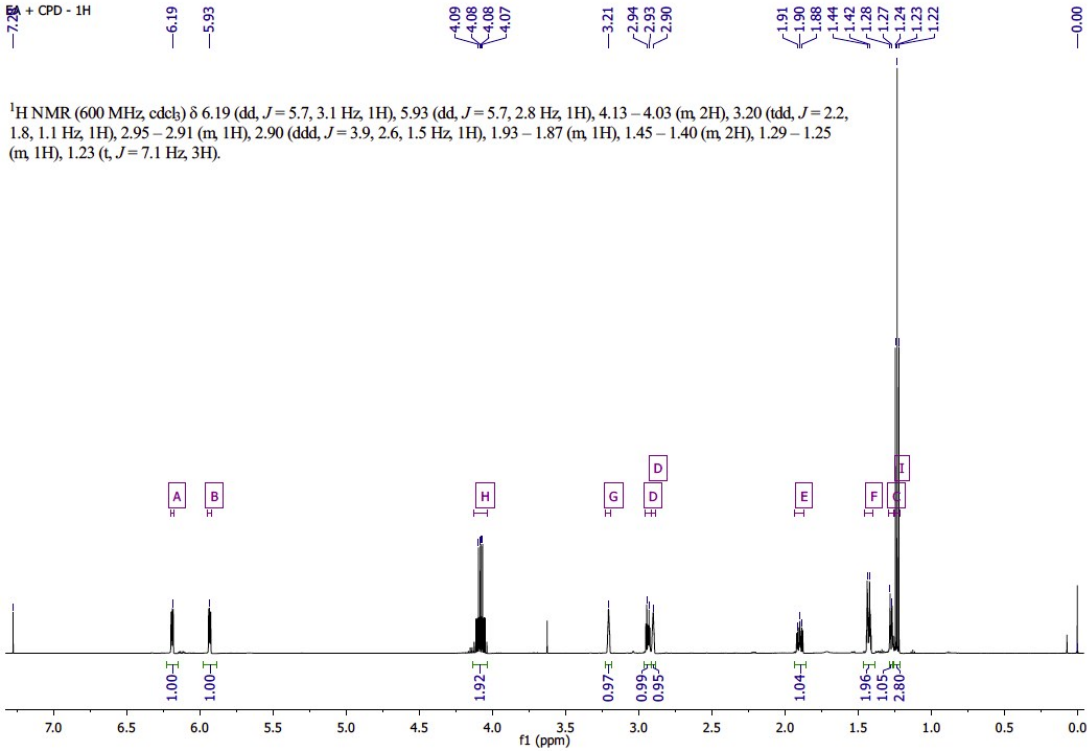
Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid, ethyl ester:

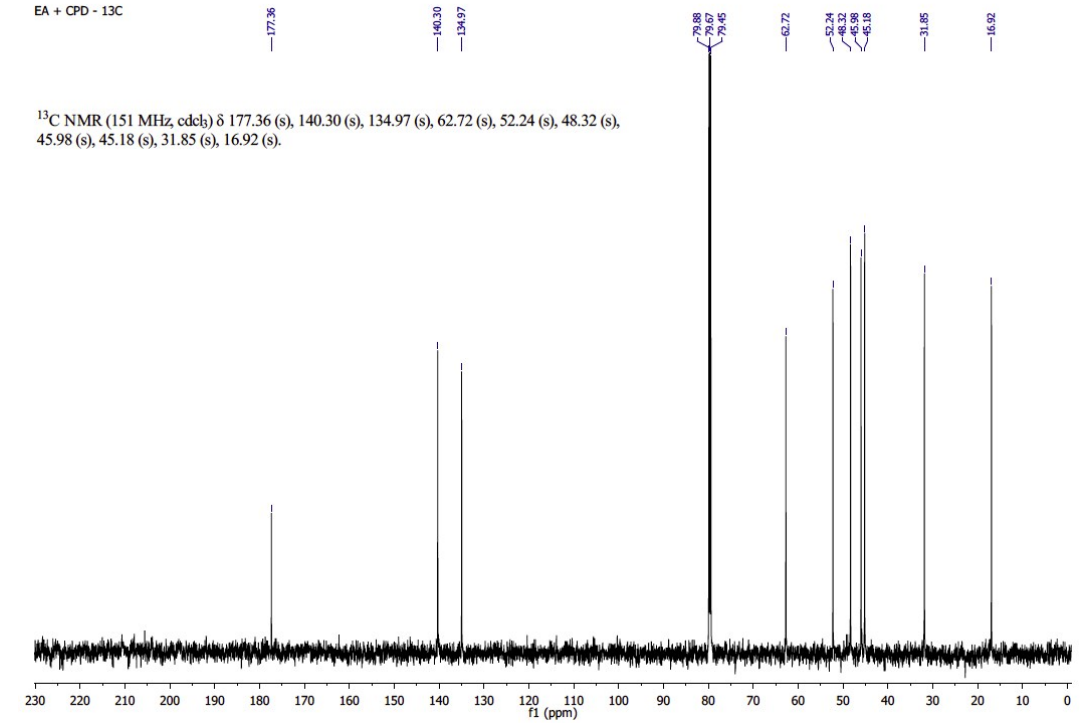
Isolated yield: 96 % by column chromatography with silica gel and 100% of chloroform as an eluent.

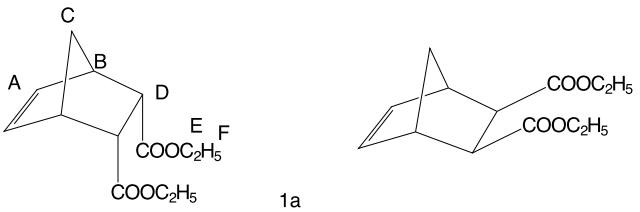
MS (EI) m/z (%) 166 (5, $M^{+\cdot}$), 121 (7) 101 (17), 93 (7), 91 (10), 77 (7), 73 (8), 66 (100), 65 (10), 55 (15), 39 (13).

MS [M + H]$^+$ calcd: 167.1072, found: 167.1069

GC-FID RT = 6.693, 6.799

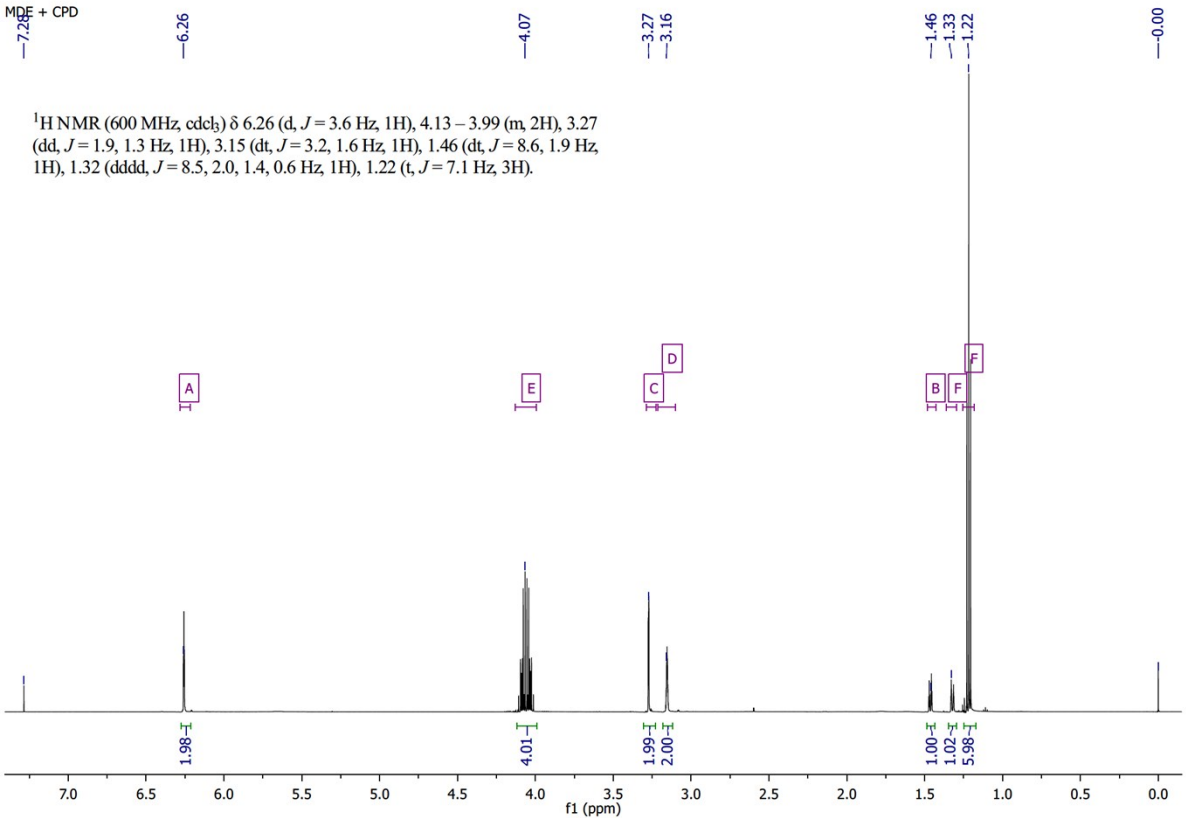




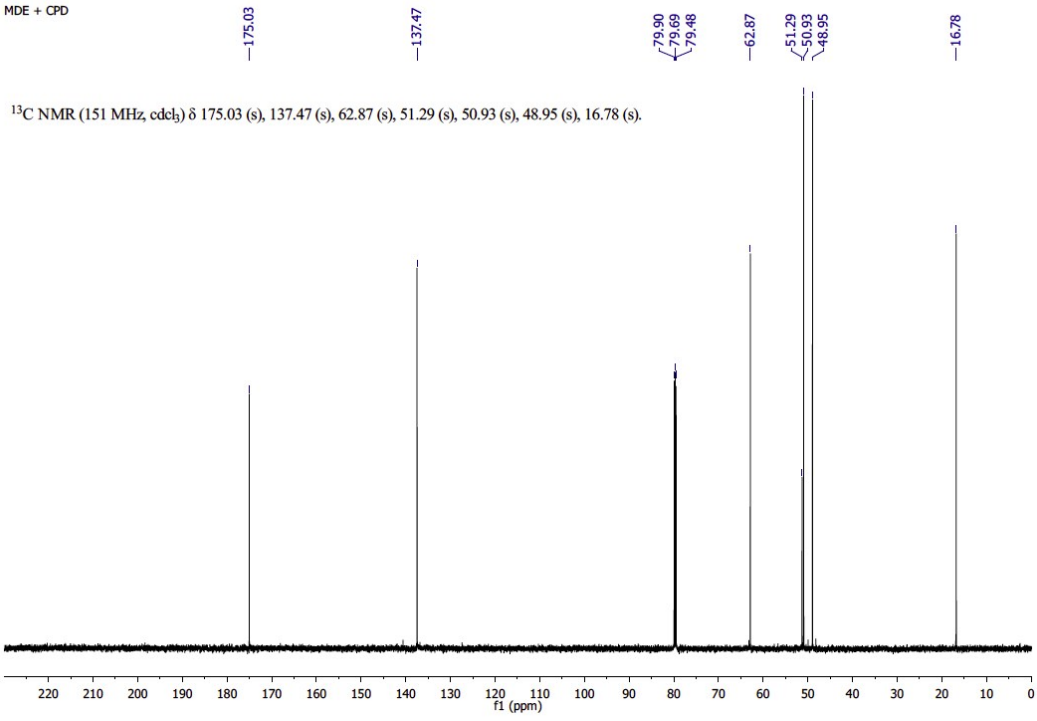


1a

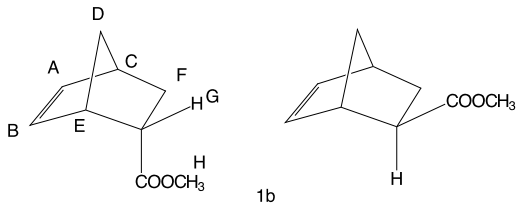
Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, 2,3-diethyl ester (1a):
Isolated yield: 92 % by column chromatography with silica gel and 100% of chloroform as an eluent.
MS (EI) m/z (%) 238 (3, $M^{+\cdot}$), 193 (9), 173 (17), 165 (13), 145 (4), 128 (3), 127 (37), 119 (23), 100 (2), 99 (35), 91 (23), 77 (6), 67 (7), 66 (100), 65 (15), 53 (4), 39 (13).
MS [M + H]$^+$ calcd: 239.1283, found: 239.1288
GC-FID RT = 10.692, 10.847



^{1}H NMR (600 MHz, cdcl$_3$) δ 6.26 (d, *J* = 3.6 Hz, 1H), 4.13 – 3.99 (m, 2H), 3.27 (dd, *J* = 1.9, 1.3 Hz, 1H), 3.15 (dt, *J* = 3.2, 1.6 Hz, 1H), 1.46 (dt, *J* = 8.6, 1.9 Hz, 1H), 1.32 (dddd, *J* = 8.5, 2.0, 1.4, 0.6 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H).

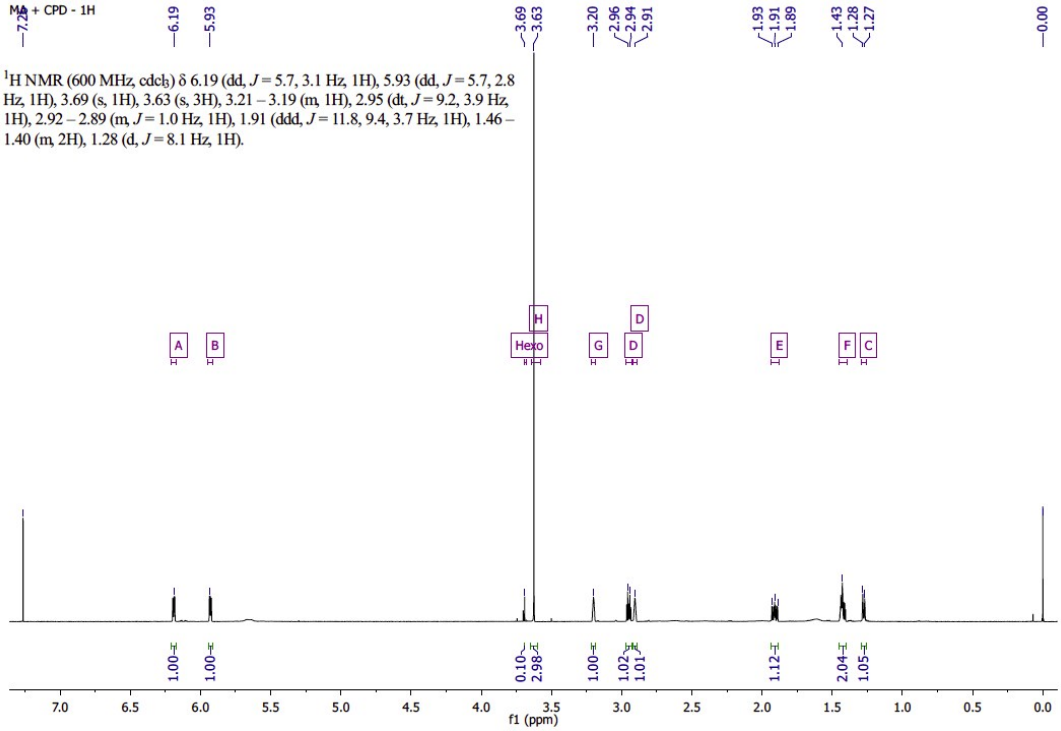


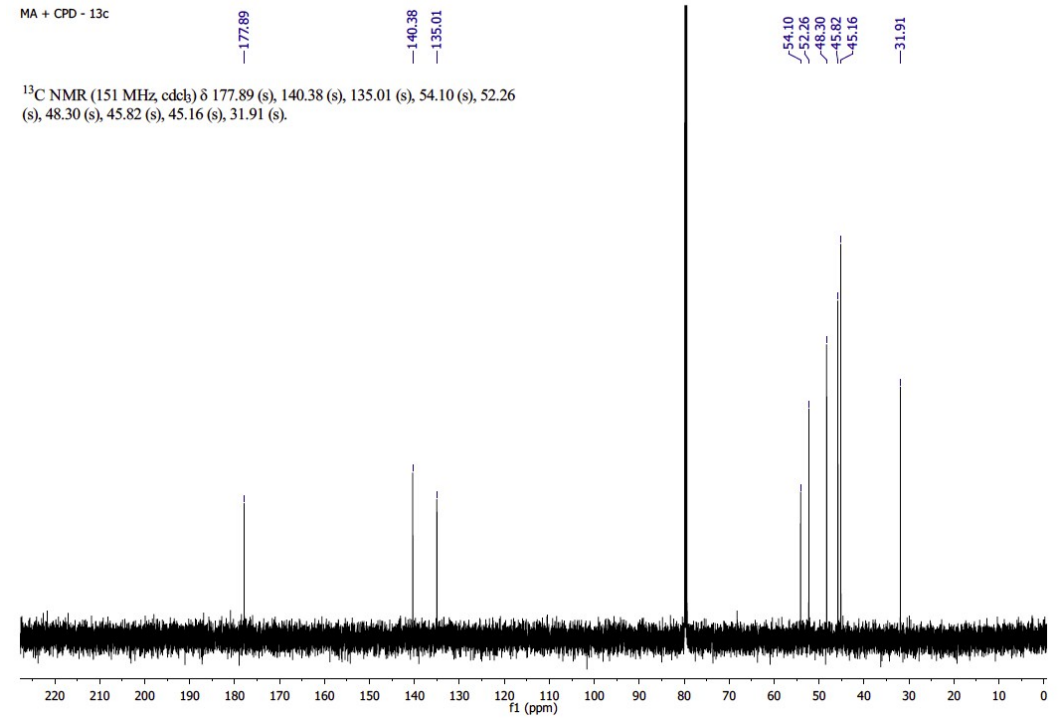
^{13}C NMR (151 MHz, cdcl$_3$) δ 175.03 (s), 137.47 (s), 62.87 (s), 51.29 (s), 50.93 (s), 48.95 (s), 16.78 (s).

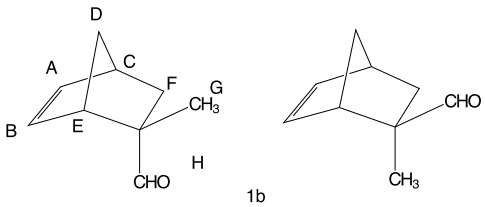


1b

5-(Methoxycarbonyl)bicyclo[2.2.1]hept-2-ene (1b):
Isolated yield: 93 % by column chromatography with silica gel and 100% of chloroform as an eluent.
MS (EI) m/z (%) 152 (21, $M^{+\cdot}$), 95 (49), 94 (100), 93 (19), 79 (73), 77 (23), 67 (36), 55 (25), 41 (25), 39 (33).
MS [M + H]$^+$ calcd: 153.0916, found: 153.0928
GC-FID RT = 6.693, 6.799

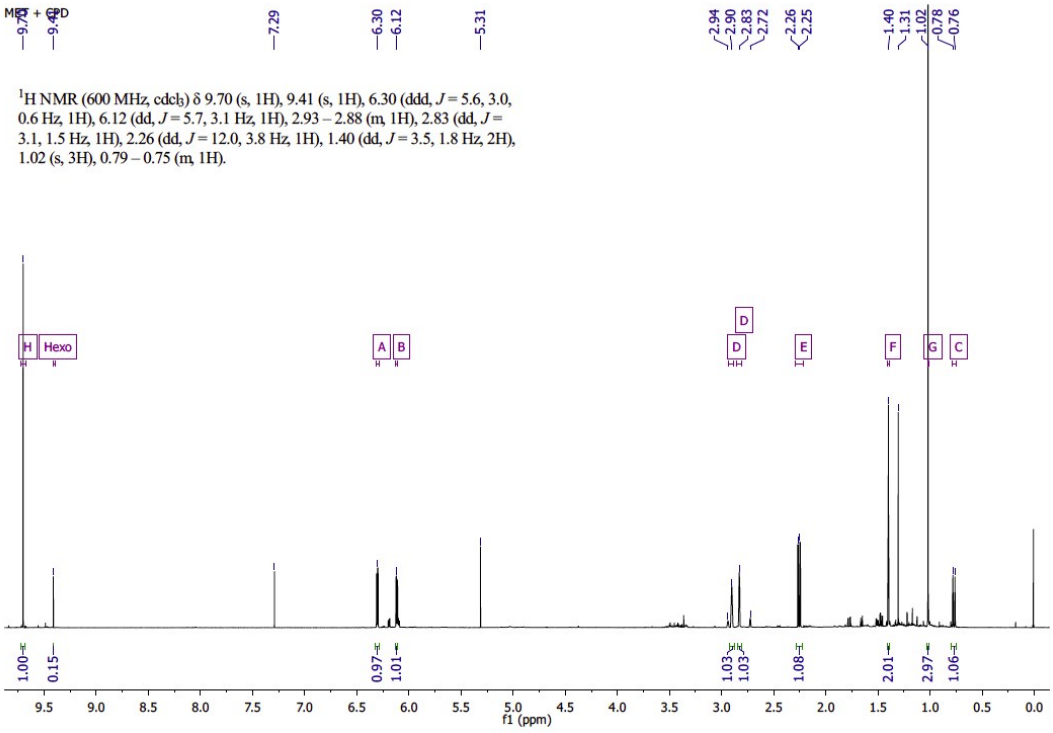


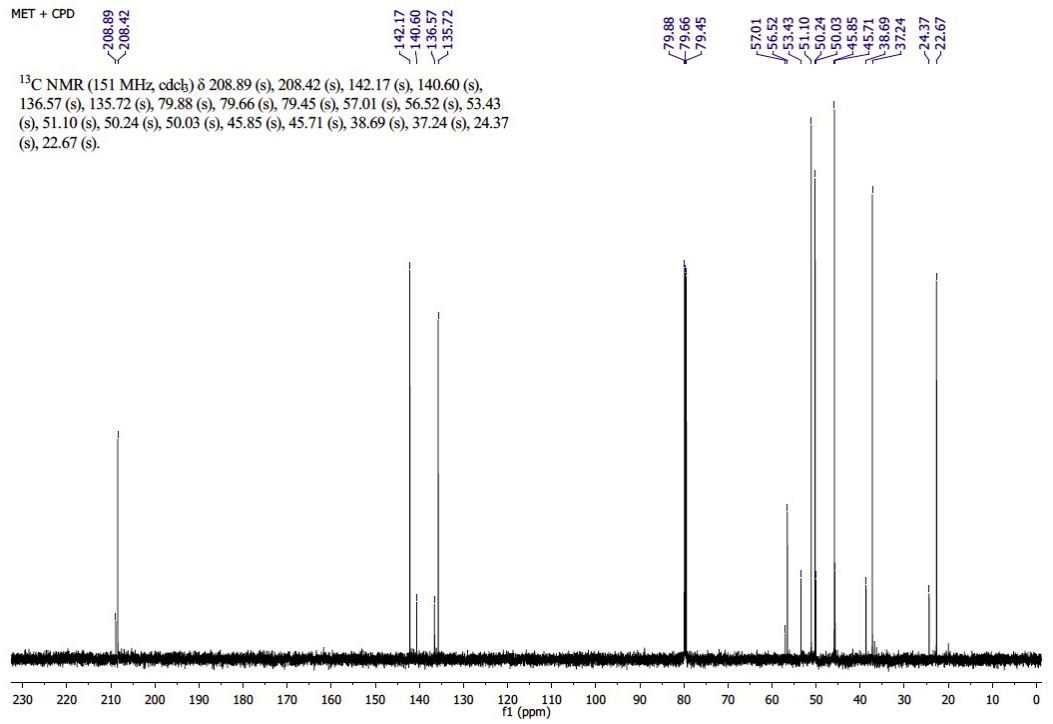


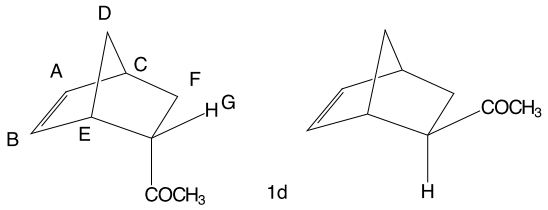


1b

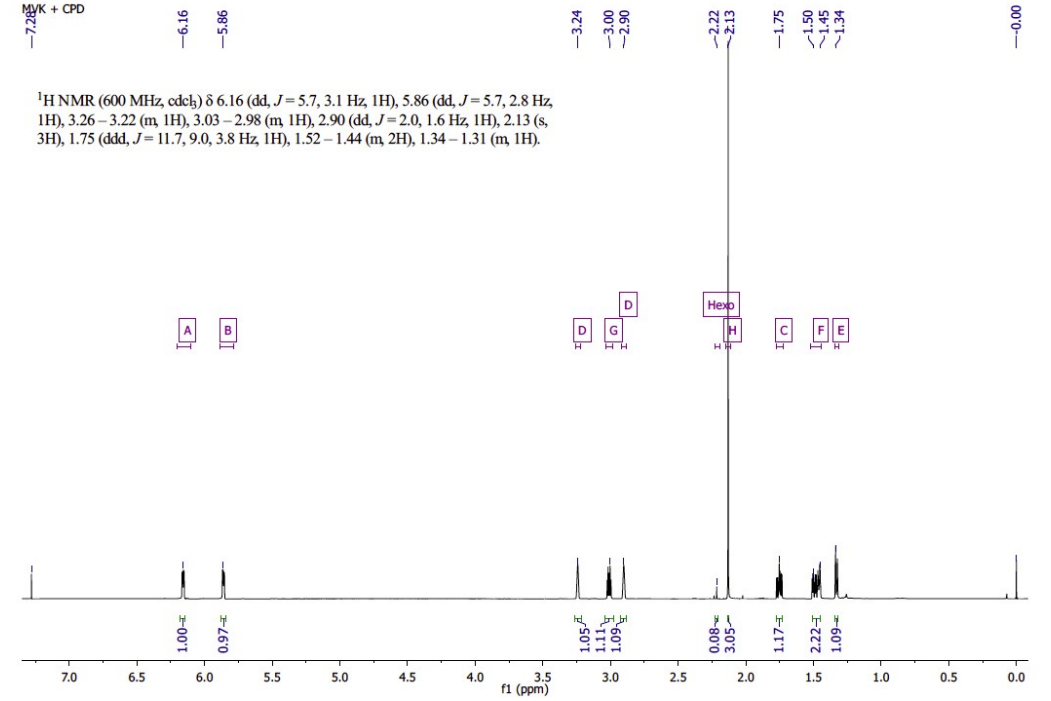
Bicyclo[2.2.1]hept-5-ene-2-methyl-2-carboxaldehyde (1c):
Isolated yield: 91 % by column chromatography with silica gel and 100% of chloroform as an eluent.
MS (EI) m/z (%) 136 (4, $M^{+\cdot}$), 107 (2), 92 (1), 91 (7), 80 (1), 79 (9), 78 (2), 67 (7), 66 (100), 65 (12), 63 (3), 51 (5), 43 (3), 41 (12), 40 (7), 39 (25), 37 (1).
GC-FID RT = 6.782, 6.955

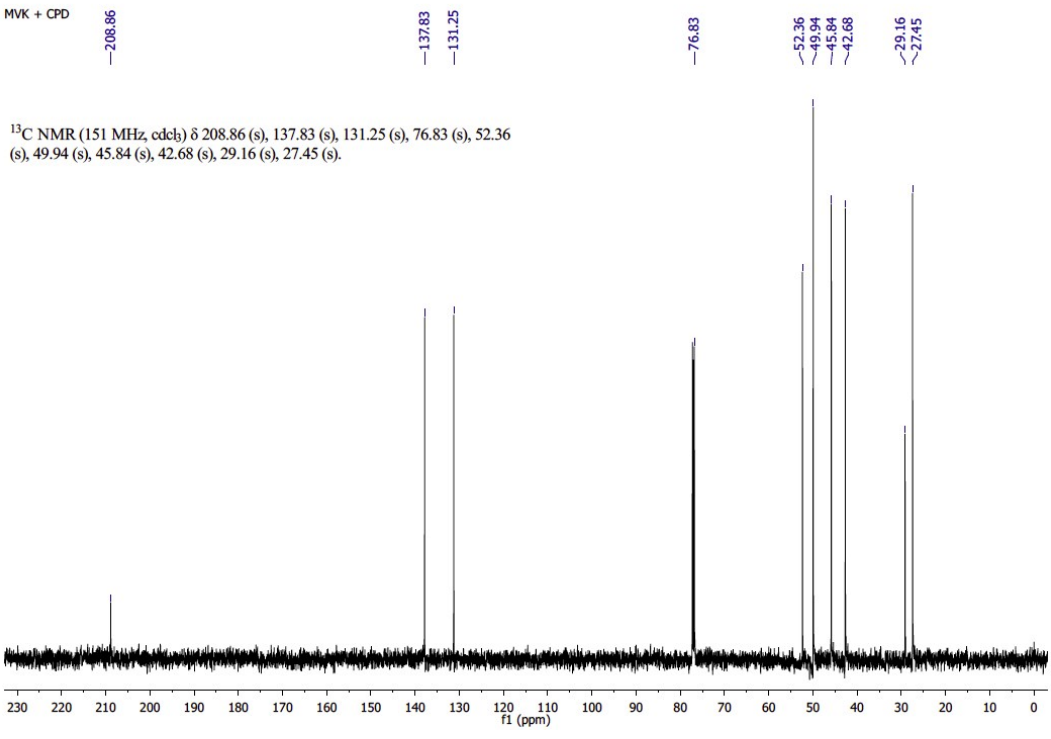


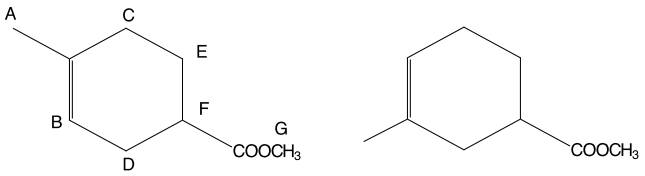




1-(Bicyclo[2.2.1]hept-5-en-2-yl)ethanone (1d):
Isolated yield: 92 % by column chromatography with silica gel and 100% of chloroform as an eluent.
MS (EI) m/z (%) 136 (6, $M^{+\cdot}$), 117 (1), 94 (1), 92 (2), 91 (10), 79 (2), 77 (11), 72 (1), 71 (14), 67 (6), 66 (100), 65 (12), 63 (3), 58 (8), 51 (5), 43 (31), 41 (6), 39 (21).
MS [M + H]$^+$ calcd: 137.0966, found: 137.0977
GC-FID RT = 5.362, 5.682

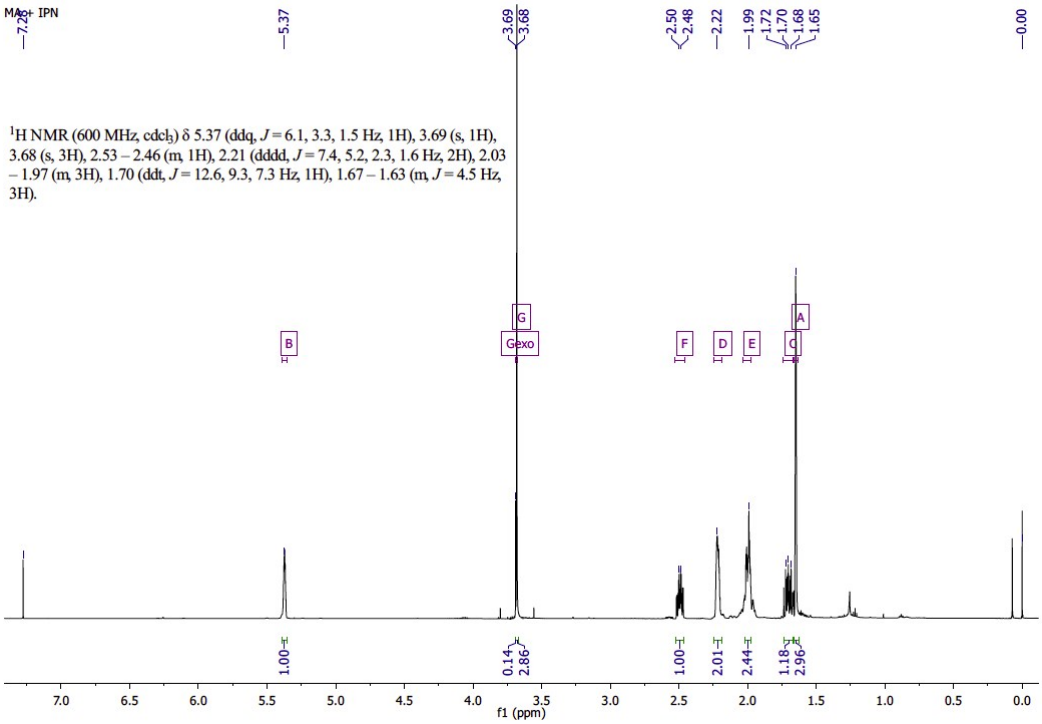


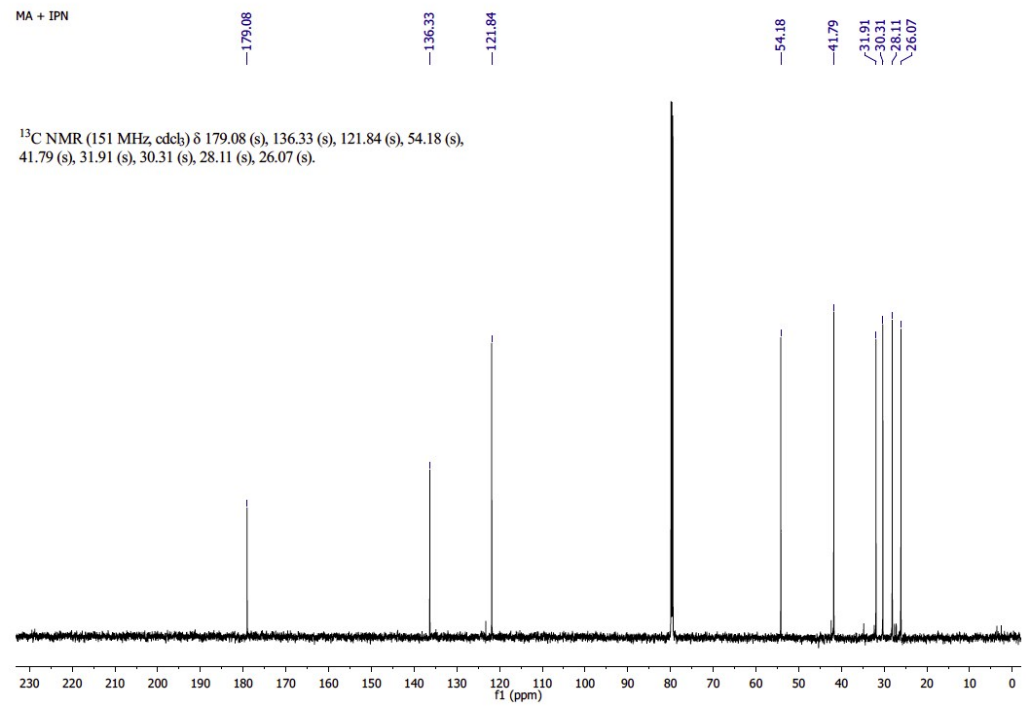


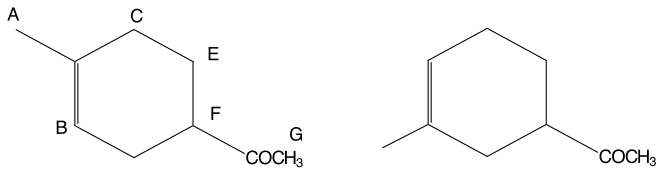


2b

4-Methoxycarbonyl-1-methylcyclohexene (2b):
Isolated yield: 91 % by column chromatography with silica gel and 100% of chloroform as an eluent.
MS (EI) m/z (%) 155 (34, $M^{+\cdot}$), 153 (13), 139 (6), 123 (27), 121 (12), 96 (11), 95 (100), 94 (40), 81 (11), 79 (21), 77 (7), 67 (31), 55 (19), 41 (25), 40 (6).
MS [M + H]$^+$ calcd: 155.0708, found: 155.0729.
GC-FID RT = 8.317, 8.372







2d

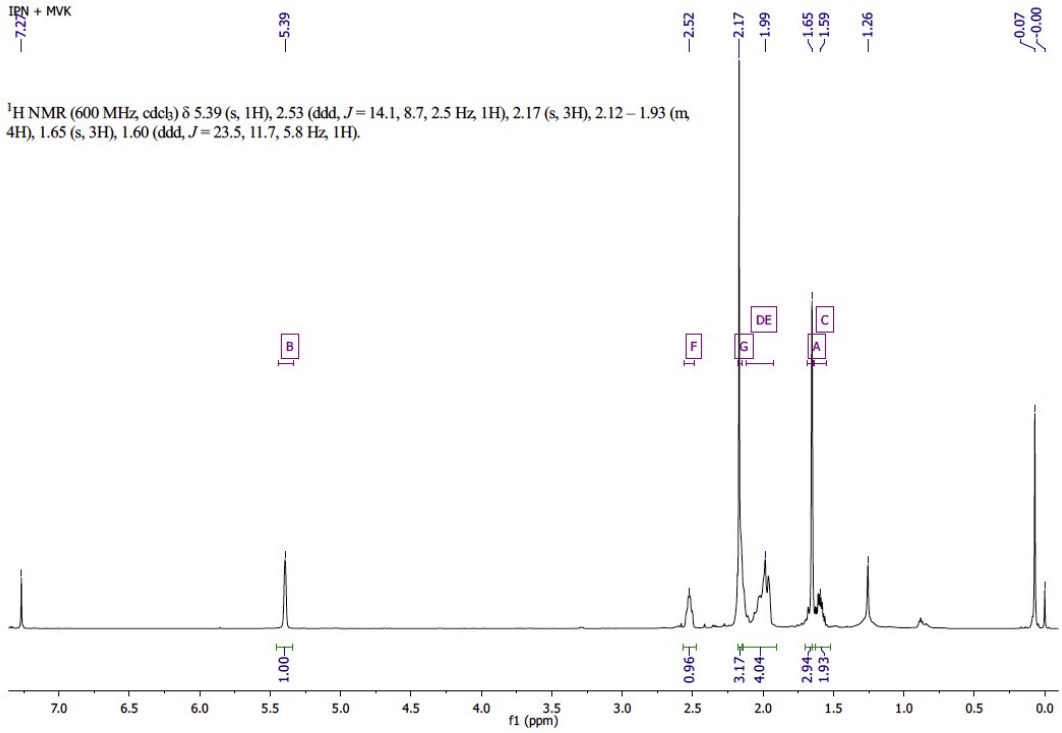
4-Acetyl-1-methylcyclohexene (2d):

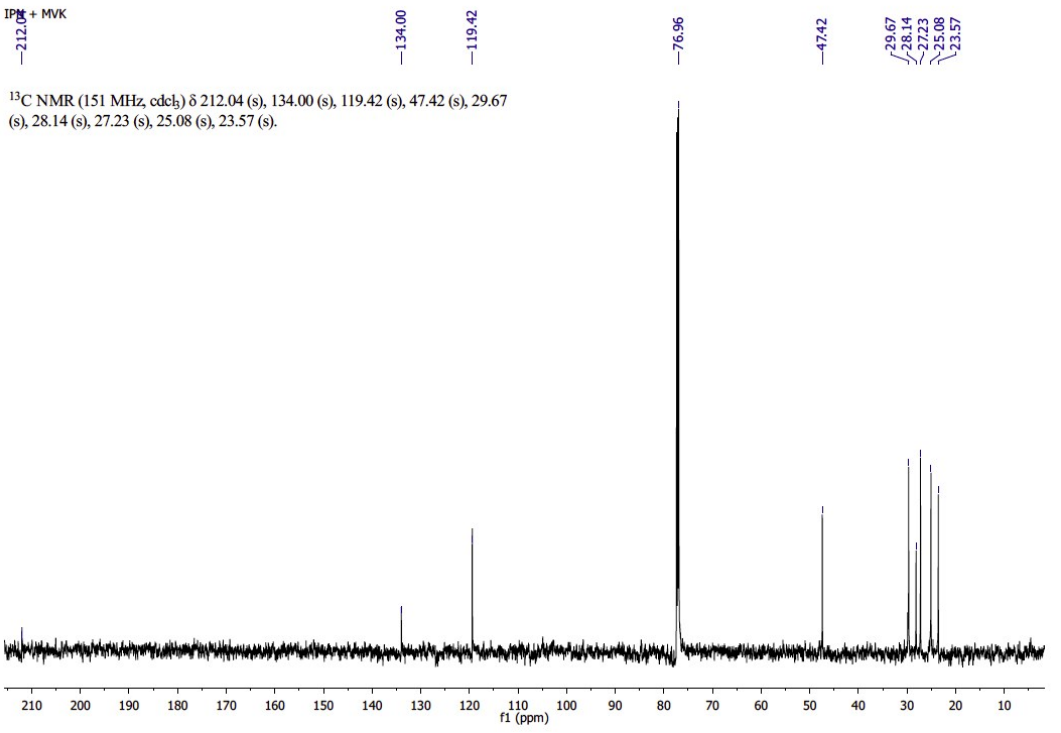
Isolated yield: 90 % by column chromatography with silica gel and 100% of chloroform as an eluent.

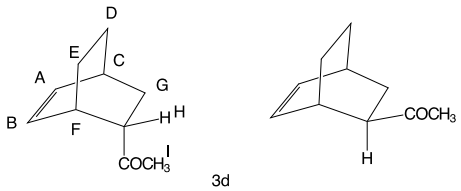
MS (EI) m/z (%) 138 (58 $M^{+\cdot}$), 123(35), 105 (33), 95 (73), 93 (33), 79 (33), 77 (25), 67 (54), 55 (27), 43 (100), 41 (25), 39 (32)

MS [M + H]$^+$ calcd: 139.1123, found: 139.1132

GC-FID RT = 7.568, 7.622







3d

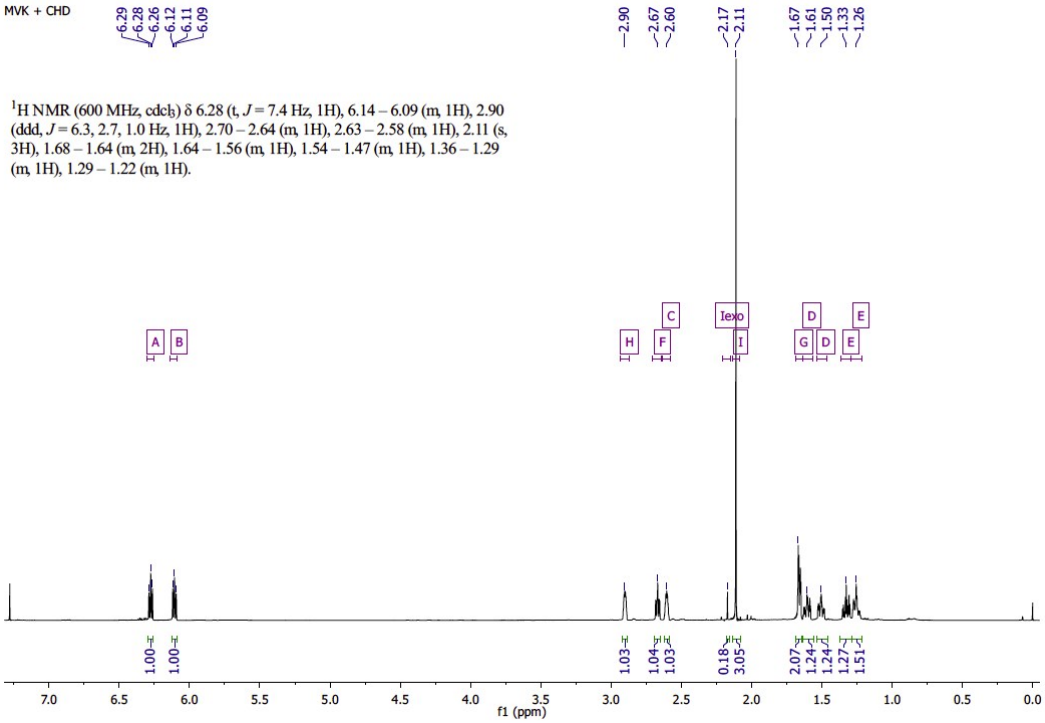
1-(Bicyclo[2.2.2]oct-5-en-2-yl)ethanone (3d):

Isolated yield: 90 % by column chromatography with silica gel and 100% of chloroform as an eluent.

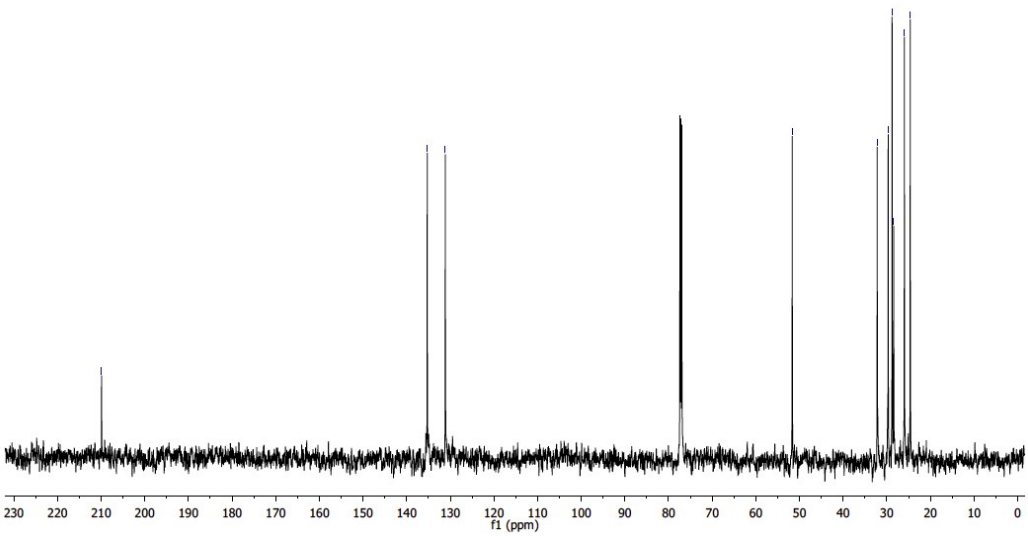
MS (EI) m/z (%) 150 (19 $M^{+\cdot}$), 132 (5), 107 (8), 92 (11), 80 (64), 79 (100), 78 (20), 77 (31), 51 (10), 43 (36).

MS [M + H]$^+$ calcd: 151,1123, obs. 151,1125

GC-FID RT = 8.207, 8.443



^{1}H NMR (600 MHz, cdcl$_3$) δ 6.28 (t, J = 7.4 Hz, 1H), 6.14 – 6.09 (m, 1H), 2.90 (ddd, J = 6.3, 2.7, 1.0 Hz, 1H), 2.70 – 2.64 (m, 1H), 2.63 – 2.58 (m, 1H), 2.11 (s, 3H), 1.68 – 1.64 (m, 2H), 1.64 – 1.56 (m, 1H), 1.54 – 1.47 (m, 1H), 1.36 – 1.29 (m, 1H), 1.29 – 1.22 (m, 1H).



^{13}C NMR (151 MHz, cdcl$_3$) δ 209.90 (s), 135.28 (s), 131.15 (s), 51.66 (s), 32.20 (s), 29.68 (s), 28.78 (s), 28.41 (s), 25.97 (s), 24.62 (s).