Supporting Information

Visible-Light Photoredox Catalysis: Debromination of *vic*-Dibromides and Dehalogenation of α-halocarbonyl Compounds

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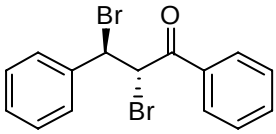
1. General Information:

All reactions were performed using common dry, inert atmosphere techniques. Reactions were monitored by TLC and visualized by a dual short/long wave UV lamp and stained with an ethanolic solution of vanillin. Column flash chromatography was performed using 230-400 mesh silica gel. NMR spectra were recorded on 300 MHz spectrometer. Chemical shifts for ^{1}H NMR were reported as δ, parts per million, relative to the signal of $CDCl_3$ at 7.26 ppm. Chemical shifts for ^{13}C NMR were reported as δ, parts per million, relative to the center line signal of the $CDCl_3$ triplet at 77 ppm. Proton and carbon assignments were established using spectral data of similar compounds. The abbreviations s, d, dd, t, q and m stand for the resonance multiplicity singlet, doublet, doublet of doublets, triplet, quartet and multiplet respectively.

2. General procedure for preparation of vicinal dibromides:[1]

To a solution or suspension of the corresponding chalcone (1.53 mmol) in 8.0 mL of $CHCl_3$ was added dropwise 3.0 mL of bromine solution (0.56 M in chloroform) at 0 °C. The mixture was stirred at room temperature until the reaction was completed (monitored by TLC). After completion of the reaction a saturated solution of $Na_2S_2O_3$ was added to quench the unreacted bromine and stirring continued for another 30 min. The reaction mixture was extracted with $CHCl_3$ (2x 8.0 mL) and the combined organic layers were washed with brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Depending upon the substrate the desired compound was obtained by crystallization (EA/PE) or by column chromatography.

(*2S, 3R*)-2, 3-dibromo-1,3-diphenylpropan-1-one (1a)[2]

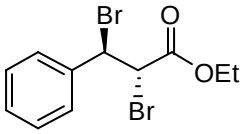


According to the general procedure, (*E*)-1,3-diphenylprop-2-en-1-one (0.32 g, 1.53 mmol) and 3.10 mL of bromine solution (0.56 M in chloroform) afforded **1a** (0.46 g, 1.12 mmol, 82%) as white solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.46

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.65 (d, *J* = 11.4 Hz, 1H), 5.83 (d, *J* = 11.4 Hz, 1H), 7.34-7.49 (m, 3H), 7.51-7.61 (m, 4H), 7.63-7.71 (m, 1H), 8.10 (d, *J* = 8.4 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 46.8, 49.8, 128.4, 128.9, 128.9, 129.0, 129.3, 134.2, 134.4, 138.2, 191.2.

(*2S, 3R*)-ethyl 2,3-dibromo-3-phenylpropanoate (1b)[3]



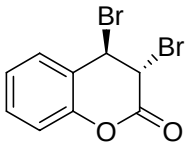
According to the general procedure, ethyl cinnamate (1.99 g, 11.31 mmol) and 22.30 mL of bromine solution (0.56 M in chloroform) afforded **1b** (3.35 g, 9.97 mmol, 88%) as white crystalline solid after crystallization from EA/PE mixture. R_f (EtOAc/hexane 1:9): 0.59

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.38 (t, *J* = 7.13 Hz, 3H), 4.36 (q, *J* = 7.13 Hz, 2H), 4.83 (d, *J* = 11.8 Hz, 1H), 5.35 (d, *J* = 11.8 Hz, 1H), 7.30-7.65 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 47.0, 50.7, 62.7, 128.1, 128.9, 129.4, 137.7, 167.8.

MS (EI, 70 eV): m/z = 77.1 (42.09), 103.1 (100), 183.0 (29.65), 225 (59.95), 335.8 (2.26) [M+].

3,4-Dibromochroman-2-one (1d)[4]



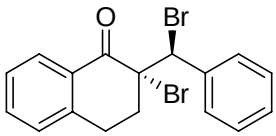
According to the general procedure, 2H-chromen-2-one (0.51 g, 3.49 mmol) and 6.70 mL of bromine solution (0.56 M in chloroform) afforded **1d** (0.96 g, 3.15 mmol, 92 %) as light yellow solid after crystallization from EA/PE mixture. R_f (EtOAc/hexane 1:9): 0.33.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.96 (d, *J* = 2.74 Hz, 1H), 5.35 (d, *J* = 2.74 Hz, 1H), 7.14-7.29 (m, 2H), 7.36- 7.52 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.3, 43.7, 117.7, 119.9, 125.6, 128.7, 131.6, 150.4, 160.7.

MS (EI, 70 eV): m/z = 118.0 (100), 146.0 (76.33), 225.0 (35.64), 303.8 (6.25) [M+].

(*R*)-2-bromo-2-((*S*)-bromo(phenyl)methyl)-3,4-dihydronaphthalen-1(2H)-one (1e) [5]



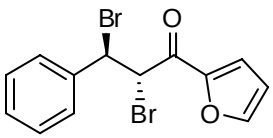
According to the general procedure, (*E*)-2-benzylidene-3,4-dihydro naphthalen-1(2H)-one (0.39 g, 1.66 mmol) and 3.40 mL of bromine solution (0.56 M in chloroform) afforded **1e** (0.52 g, 1.33 mmol, 78 %) as light pink solid (mp 152-154 ^{o}C; lit. 153-154 ^{o}C) after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.48.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.42-2.52 (m, 1H), 2.93-3.27 (m, 3H), 6.2 (s, 1H), 7.25-7.65 (m, 8H), 8.25 (d, *J* = 7.68 Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ = 26.2, 30.7, 55.4, 68.8, 127.3, 127.8, 128.7, 128.9, 129.4, 129.8, 131.1, 134.3, 136.2, 142.5, 188.6.

MS (EI, 70 eV): m/z = 233.1 (100), 313.0 (4.16), 393.9 (0.15) [M+].

(*2S,3R*)-2,3-dibromo-1-(furan-2-yl)-3-phenylpropan-1-one (1f)[6]



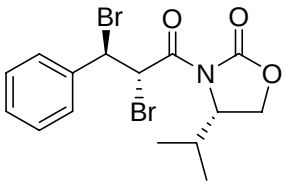
According to the general procedure, (*E*)-1-(furan-2-yl)-3-phenylprop-2-en-1-one (0.81 g, 4.09 mmol) and 8.05 mL of bromine solution (0.56 M in chloroform) afforded **1f** (1.21 g, 3.35 mmol, 82 %) as light yellow solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.34.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.57 (d, *J* = 11.80 Hz, 1H), 5.74 (d, *J* = 11.80 Hz, 1H), 6.64-6.72 (m, 1H), 7.35-7.60 (m, 6H), 7.70-7.79 (m, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ = 47.1, 49.1, 113.3, 119.8, 128.3, 128.9, 129.3, 138.1, 147.6, 150.3, 180.1.

MS (EI, 70 eV): m/z = 95.0 (100), 197.1 (86.18), 277.0 (9.71), 357.9 (0.15) [M+].

(*S*)-3-((*2S, 3R*)-2,3-dibromo-3-phenylpropanoyl)-4-isopropyloxazolidin-2-one (1g)[7]



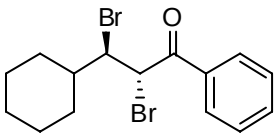
According to the general procedure, (*S*)-3-cinnamoyl-4-isopropyloxazolidin-2-one (1.19 g, 4.63 mmol) and 9.10 mL of bromine solution (0.56 M in chloroform) afforded **1g** (1.72 g, 4.07 mmol, 88 %) as light yellow solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.27.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88-1.02 (m, 6H), 2.40-2.60 (m, 1H), 4.20-4.47 (m, 2H), 4.50-4.65 (m, 1H), 5.51 (d, *J* = 11.52 Hz, 1H), 6.58 (d, *J* = 11.52 Hz, 1H), 7.26-7.60 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.8, 17.8, 28.0, 43.4, 50.2, 58.6, 63.5, 128.4, 128.9, 129.4, 137.5, 153.2, 167.2.

MS (EI, 70 eV): m/z = 260.2 (35.79), 277.1 (100), 279.2 (75.78), 437.0 (6.60) [MNH_4^+].

(*2R,3S*)-2,3-dibromo-3-cyclohexyl-1-phenylpropan-1-one (1h)



According to the general procedure, (*E*)-3-cyclohexyl-1-phenylprop-2-en-1-one (0.54 g, 2.52 mmol) and 4.90 mL of bromine solution (0.56 M in chloroform) afforded **1h** (0.83 g, 2.22 mmol, 88 %) as white solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.63.

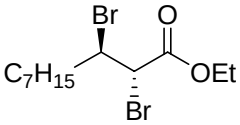
^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11-1.95 (m, 10H), 2.00-2. 22 (m, 1H), 4.72 (dd, *J* = 2.19, 11.25 Hz, 1H), 5.52 (d, *J* = 11.25 Hz, 1H), 7.46-7.55 (m, 2H), 7.59-7.66 (m, 1H), 7.95-8.08(m, 2H).

^{13}C NMR (75MHz, $CDCl_3$): δ = 25.5, 26.0, 26.07, 26.13, 32.0, 39.6, 45.4, 59.1, 128.8, 128.9, 133.9, 134.6, 191.3.

MS (EI, 70 eV): m/z = 105.0 (100), 213.1 (1.99), 292.1 [M-HBr].

Elemental Analysis: Anal. Calcd for $C_{15}H_{18}Br_2O$: C, 48.16; H, 4.85. Found: C, 48.59; H, 4.94.

Ethyl 2,3-dibromodecanoate (1i)



According to the general procedure, (*E*)-ethyl dec-2-enoate (0.78 g, 4.02 mmol) and 7.90 mL of bromine solution (0.56 M in chloroform) afforded **1i** (1.18 g, 3.31 mmol, 82 %) as gummy oil after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.70.

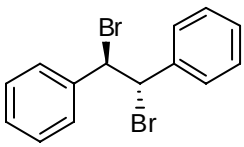
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.72 Hz, 3H), 1.21-1.67 (m, 13H), 1.74-1.88 (m, 1H), 2.15-2.30 (m, 1H), 4.28 (q, *J* = 7.13 Hz, 2H), 4.36-4.40 (m, 2H).

^{13}C NMR (75MHz, $CDCl_3$): δ = 13.8, 14.1, 22.6, 26.2, 28.7, 29.0, 31.7, 35.1, 48.1, 52.9, 62.3, 167.9.

MS (EI, 70 eV): m/z = 216.3 (100), 233.3 (11.01), 374.0 (41.02) [MNH_4^+].

HRMS (EI, 70 eV): Calcd for $C_{12}H_{22}Br_2O_2$ $[M+H]^+$: 357.0065, found: 357.0029.

(*1R,2S*)-1,2-dibromo-1,2-diphenylethane (1j)[2]

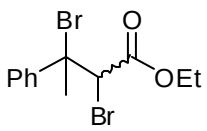


According to the general procedure, (*E*)-1,2-diphenylethene (2.11 g, 11.72 mmol) and 21.80 mL of bromine solution (0.56 M in chloroform) afforded **1j** (3.62 g, 10.66 mmol, 96 %) as white solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.69.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.52 (s, 2H), 7.12-7.32 (m, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 59.1, 128.2, 128.6, 137.8.

Ethyl 2,3-dibromo-3-phenylbutanoate (*erythro*:*threo* = 67:33) (1k)



According to the the general procedure, (*E*)-ethyl 3-phenylbut-2-enoate (1.01 g, 5.31 mmol) and 10.40 mL of bromine solution (0.56 M in chloroform) afforded **1k** (1.25 g, 3.57 mmol, 68 %) as colorless oil after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.60.

^{1}H NMR (*erythro* compound) (300 MHz, $CDCl_3$): δ = 1.37 (t, *J* = 7.13 Hz, 3H), 2.55 (s, 3H), 4.30-4.37 (m, 2H), 5.08 (s, 1H), 7.30-7.40 (m, 3H), 7.57-7.67 (m, 2H).

^{13}C NMR (75MHz, $CDCl_3$): δ = 13.8, 25.4, 54.0, 62.3, 65.7, 126.6, 128.4, 142.5, 167.5.

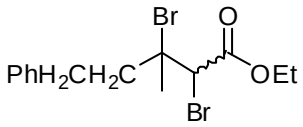
^{1}H NMR (*threo* compound) (300 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.13 Hz, 3H), 2.55 (s, 3H), 3.86 (q, *J* = 7.04 Hz, 2H), 5.11 (s, 1H), 7.30-7.40 (m, 3H), 7.57-7.67 (m, 2H).

^{13}C NMR (75MHz, $CDCl_3$): δ = 13.5, 27.8, 57.8, 61.8, 68.9, 127.1, 128.9, 140.5, 166.5.

MS (EI, 70 eV): m/z = 191.2 (41.45), 208.2 (100), 286.1 (2.85) [M-HBr], 368.0 (10.02) [MNH_4^+].

HRMS (EI, 70 eV): Calcd for $C_{12}H_{14}Br_2O_2$ $[M-H]^+$: 346.9283, found: 346.9284

Ethyl 2,3-dibromo-3-methyl-5-phenylpentanoate (*erythro*:*threo* = 80:20) (1l)



According to the the general procedure, ethyl 3-methyl-5-phenylpent-2-enoate (0.49 g, 2.24 mmol) and 4.50 mL of bromine solution (0.56 M in chloroform) afforded **1l** (0.67 g, 1.78 mmol, 78 %) as colorless oil after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.66.

^{1}H NMR (*erythro* compound) (300 MHz, $CDCl_3$): δ = 1.35 (t, *J* = 7.13 Hz, 3H), 2.10 (s, 3H), 2.20-2.30 (m, 2H), 2.80-2.90 (m, 2H), 4.24-4.32 (m, 2H), 4.70 (s, 1H), 7.17-7.36 (m, 5H).

^{13}C NMR (75MHz, $CDCl_3$): δ = 13.9, 26.7, 31.7, 46.0, 51.9, 62.2, 66.8, 126.2, 128.5, 140.6, 167.5.

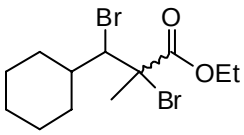
^{1}H NMR (*threo* compound) (300 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.13 Hz, 3H), 2.00 (s, 3H), 2.20-2.30 (m, 2H), 2.80-2.90 (m, 2H), 4.24-4.32 (m, 2H), 4.74 (s, 1H), 7.17-7.36 (m, 5H).

^{13}C NMR (75MHz, $CDCl_3$): δ = 13.9, 29.8, 32.5, 41.3, 55.5, 62.2, 67.6, 126.2, 128.5, 141.0, 167.4.

MS (EI, 70 eV): m/z = 91.1 (100), 131.1 (28.72), 217.2 (15.40), 299.1 (5.21), 376.0 (1.20) [M^+].

HRMS (EI, 70 eV): Calcd for $C_{14}H_{18}Br_2O_2$, [M^+]: 375.9674, found: 375.9667.

(*2S,3R*)-ethyl 2,3-dibromo-3-cyclohexyl-2-methylpropanoate (*erythro*:*threo*= 52:48) (1m)



According to the general procedure, (*E*)-ethyl 3-cyclohexyl-2-methylacrylate (0.74 g, 3.77 mmol) and 7.40 mL of bromine solution (0.56 M in chloroform) afforded **1m** (1.02 g, 2.80 mmol, 75 %) as colorless oil after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.81.

^{1}H NMR (*erythro* compound) (300 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.13 Hz, 3H), 1.00-2.20 (m, 11H), 1.99 (s, 3H), 4.20-4.32 (m, 2H), 4.54 (d, *J* = 3.63 Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ = 13.8, 23.6, 25.8, 26.1, 31.9, 33.7, 39.4, 42.8, 62.5, 64.9, 68.9, 169.2.

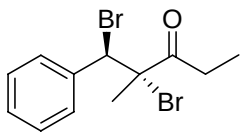
^{1}H NMR (*threo* compound) (300 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.13 Hz, 3H), 1.00-2.20 (m, 11H), 2.02 (s, 3H), 4.20-4.32 (m, 2H), 4.59 (d, *J* = 1.64 Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ = 13.8, 23.6, 25.8, 26.1, 31.9, 33.7, 39.4, 42.8, 62.5, 64.9, 68.9, 169.3.

MS (EI, 70 eV): m/z = 197.3 (16.27), 214.2 (100), 231.2 (5.99), 374.1 (20.84) [MNH_4+].

Elemental Analysis: Anal. Calcd for $C_{12}H_{20}Br_2O_2$: C, 40.47; H, 5.66. Found: C, 40.69; H, 5.73.

(*1R,2S*)-1,2-dibromo-2-methyl-1-phenylpentan-3-one (1n)



According to the general procedure, (*E*)-2-methyl-1-phenylpent-1-en-3-one (0.61 g, 3.50 mmol) and 6.80 mL of bromine solution (0.56 M in chloroform) afforded **1n** (0.79 g, 2.39 mmol, 70 %) as colorless oil after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.57.

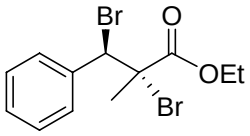
^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (t, *J* = 7.13 Hz, 3H), 2.01 (s, 3H), 2.75-3.10 (m, 2H), 5.68 (s, 1H), 7.30-7.40 (m, 3H), 7.47-7.59 (m, 2H).

^{13}C NMR (75MHz, $CDCl_3$): δ = 8.7, 21.6, 29.4, 56.5, 68.8, 127.9, 129.0, 130.9, 135.5, 202.6.

MS (EI, 70 eV): m/z = 175.1 (100), 192.2 (98.01), 349.9 (21.43) [MNH_4^+].

HRMS (EI, 70 eV): Calcd for $C_{12}H_{14}Br_2O$, [M^+]: 331.9412, found: 331.9410.

(*2S,3R*)-ethyl 2,3-dibromo-2-methyl-3-phenylpropanoate (1o)



According to the general procedure, ethyl 2-methyl-3-phenylacrylate (0.81 g, 4.26 mmol) and 8.30 mL of bromine solution (0.56 M in chloroform) afforded **1o** (0.82 g, 2.43 mmol, 72 %) as colorless oil after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.40.

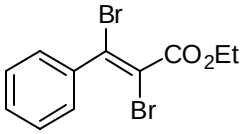
^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.39 (t, *J* = 7.13 Hz, 3H), 2.06 (s, 3H), 4.30-4.40 (m, 2H), 5.77 (s, 1H), 7.32-7.40 (m, 3H), 7.50-7.58 (m, 2H).

^{13}C NMR (75MHz, $CDCl_3$): δ = 13.9, 22.1, 57.3, 61.8, 62.8, 127.7, 129.0, 130.9, 135.5, 169.3.

MS (EI, 70 eV): m/z = 191.2 (21.78), 208.2 (100), 286.1 (3.19) [M-HBr], 366 (96.9) [MNH_4+].

HRMS (EI, 70 eV): Calcd for $C_{12}H_{14}Br_2O_2$, [M^+]: 347.9361, found: 347.9355.

(*E*)-ethyl 2,3-dibromo-3-phenylacrylate (1p)[2]



According to the general procedure, ethyl 3-phenylpropiolate (1.22 g, 7.01 mmol) and 13.70 mL of bromine solution (0.56 M in chloroform) afforded **1p** (0.74 g, 2.24 mmol, 32 %) as gummy oil after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.58.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.41 (t, *J* = 7.13 Hz, 3H), 4.39 (q, *J* = 7.13 Hz, 2H), 7.35-7.49 (m, 5H).

^{13}C NMR (75MHz, $CDCl_3$): δ = 13.4, 62.8, 107.6, 121.5, 128.1, 128.3, 128.4, 128.7, 129.7, 138.2, 164.0.

MS (EI, 70 eV): m/z = 102.1 (100), 182.0 (47.31), 227 (67.10), 253.0 (68.31), 288.9 (38.81), 331.9 (38.64) [M+].

General Procedure for the preparation of α-bromo/α,α'-dibromo carbonyl compounds:

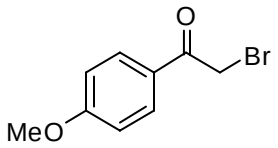
General Procedure A[8] (GP-A):

To a stirred solution of the corresponding ketone (1 mmol) in $CHCl_3$ (3.0 mL) was added dropwise 2.0 mL (4.0 mL for dibromination) of bromine solution (0.55 M in chloroform) at 0 °C and after complete addition the reaction mixture brought into room temperature. The stirring was continued at room temperature for another 1h and then gently heated at 65 °C. Completion of the reaction was determined by checking TLC. After completion of the reaction, reaction mixture brought to room temperature and a saturated solution of $Na_2S_2O_3$ was added to quench the unreacted bromine and stirring continued for another 30 min. The reaction mixture was extracted with $CHCl_3$ (2 x 5.0 mL) and the combined organic layers washed with brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Depending upon the substrate the desire compound was obtained by crystallization (EA/PE) or by column chromatography.

General Procedure B[9] (GP-B):

Ketone (1 mmol) N-halosuccinimide (NBS/ NCS, 1 mmol) were triturated together with p-toluenesulfonic acid (PTSA, 0.1 mmol) in a porcelain mortar for 20 min. The reaction mixture was then heated to 80 °C for 2 h, turning into a dense paste. Water was then added (5.0 mL) followed by extraction with diethyl ether (20.0 mL). The organic phase was washed with water (10.0 mL), dried over Na_2SO_4 and solvent evaporated under reduced pressure. Depending upon the substrate the desire compound was obtained by crystallization (EA/PE) or by column chromatography.

2-Bromo-1-(4-methoxyphenyl)ethanone (3a) (GP-A)[10]



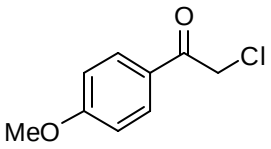
According to the general procedure (GP-A), 1-(4-methoxyphenyl) ethanone (0.16 g, 1.01 mmol) and 2.05 mL of bromine solution (0.55 M in chloroform) afforded **3a** (0.17 g, 0.75 mmol, 75 %) as crystalline solid after crystallization from EA/PE. R_f (EtOAc/hexane 1:9): 0.24.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 3.91 (s, 3H), 4.45 (s, 3H), 6.95 (d, *J* = 9.05 Hz, 2H), 7.97 (d, *J*

= 8.78 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 30.7, 55.6, 114.1, 126.9, 131.4, 164.1, 189.9.

2-Chloro-1-(4-methoxyphenyl)ethanone (3b) (GP-B)[11]

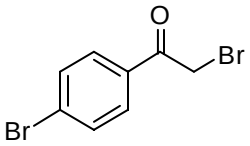


According to the general procedure (GP-B), 1-(4-methoxyphenyl) ethanone (0.52 g, 3.46 mmol) and NCS (0.44 g, 3.33 mmol) afforded **3b** (0.45 g, 2.49 mmol, 75 %) as crystalline solid after crystallization from EA/PE. R_f (EtOAc/hexane 1:9): 0.30.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 3.89 (s, 3H), 4.66 (s, 2H), 6.95 (d, *J* = 9.05 Hz, 2H), 7.93 (d, *J* = 9.05 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 45.7, 55.6, 114.1, 127.2, 130.9, 164.1, 189.6.

2-Bromo-1(4-bromophenyl)ethanone (3c) (GP-A)[12]

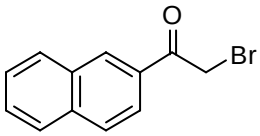


According to the general procedure (GP-A), 1-(4-bromophenyl) ethanone (0.48 g, 2.41 mmol) and 5.10 mL of bromine solution (0.55 M in chloroform) afforded **3c** (0.57 g, 2.06 mmol, 82 %) as crystalline solid after crystallization from EA/PE. R_f (EtOAc/hexane 1:9): 0.47.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 4.4 (s, 2H), 7.65 (d, *J* = 8.78 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 30.3, 129.3, 130.4, 132.2, 133.3, 190.4.

2-Bromo-1-(naphthalen-2-yl)ethanone (3e) (GP-A)[13]

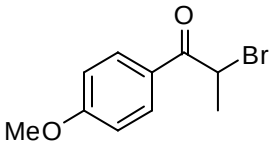


According to the general procedure (GP-A), 1-(naphthalen-2-yl)-ethanone (1.01 g, 5.94 mmol) and 11.80 mL of bromine solution (0.55 M in chloroform) afforded **3e** (1.03 g, 4.17 mmol, 71 %) as crystalline solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.43.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 4.59 (s, 2H), 7.53-7.69 (m, 2H), 7.84-8.08 (m, 4H), 8.52 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 30.9, 124.2, 127.1, 127.9, 128.8, 129.0, 129.7, 131.0, 131.3, 135.9, 191.3.

2-Bromo-1-(4-methoxyphenyl)propan-1-one (3f) (GP-A)[14]

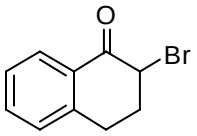


According to the general procedure (GP-A), 1-(4-methoxyphenyl)-propan-1-one (0.59 g, 3.59 mmol) and 7.30 mL of bromine solution (0.55 M in chloroform) afforded **3f** (0.64 g, 2.67 mmol, 73 %) as white solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.42.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 1.89 (d, *J* = 6.8 Hz, 3H); 3.88 (s, 3H); 5.27 (q, *J* = 6.8 Hz, 1H); 6.96 (dd, 2.4, 8.8 Hz, 2H); 8.02 (dd, *J* = 2.4, 8.8 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 20.2, 41.4, 55.5, 113.9, 126.8, 131.3, 163.9, 192.0.

2-Bromo-3,4-dihydronaphthalen-1(2H)-one (3g) (GP-B)[15]

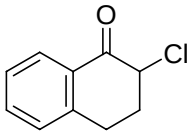


According to the general procedure (GP-B), 3,4-dihydronaphthalene-1(2H)-one (0.49 g, 3.35 mmol) and NBS (0.61 g, 3.44 mmol) afforded **3g** (0.44 g, 1.95 mmol, 57 %) as gummy oil after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.39.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 2.35-2.58 (m, 2H), 2.83- 2.95 (m, 1H), 3.22-3.49 (m, 1H), 4.71 (t, *J* = 4.39 Hz, 1H), 7.21-7.37 (m, 2H), 7.45-7.55 (m, 1H), 8.11 (dd, *J* = 1.37, 7.95 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 26.1, 31.9, 50.6, 127.1, 128.6, 128.8, 129.9, 134.2, 143.0, 190.5.

2-Chloro-3,4-dihydronaphthalen-1(2H)-one (3h) (GP-B)[16]



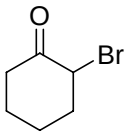
According to the general procedure (GP-B), 3,4-dihydronaphthalene-1(2H)-one (0.98 g, 6.71 mmol) and NCS (0.91 g, 6.84 mmol) afforded **3h** (0.79 g, 4.45 mmol, 65 %) as yellowish oil after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.41.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 2.36-2.67 (m, 2H), 2.90- 3.06 (m, 1H), 3.18-3.33 (m, 1H), 4.57-4.67 (m, 1H), 7.22-7.38 (m, 2H), 7.45-7.58 (m, 1H), 8.08 (d, *J* = 7.95 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 26.3, 32.4, 59.8, 127.1, 128.5, 128.7, 130.4, 134.1, 143.1, 190.8.

MS (EI, 70 eV): m/z = 90.1 (37.22), 118.0 (100), 145.1 (11.00), 180.5 (39.40) [M+].

2-Bromocyclohexanone (3i) (GP-B)[16]



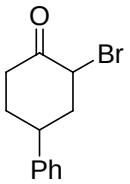
According to the general procedure (GP-B), cyclohexanone (1.99 g, 20.31 mmol) and NBS (3.63 g, 20.41 mmol) afforded **3i** (2.34 g, 13.26 mmol, 65 %) as brown oil after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.66.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 1.61-2.11 (m, 4H), 2.12-2.41 (m, 3H), 2.90-3.33 (m, 1H), 4.39-4.49 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 22.1, 27.6, 36.7, 37.9, 53.4, 203.5.

MS (EI, 70 eV): m/z = 97.1(100), 132.0(15.49), 176.0(29.52) [M+].

2-Bromo, 4-phenylcyclohexanone (3j) (GP-B)[17]



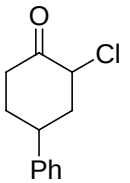
According to the general procedure (GP-B), 4-phenylcyclohexanone (0.51 g, 2.93 mmol) and NBS (0.51 g, 2.87 mmol) upon refluxation in CCl_4 (12 h) afforded **3j** (0.54 g, 2.15 mmol, 75 %) as white crystalline solid (mp 112-116 ^{o}C; lit. 115-116 ^{o}C) after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.47.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 1.85-2.05 (m, 1H), 2.17-2.30 (m, 1H), 2.35-2.50 (m, 3H), 3.25-3.41 (m, 1H), 3.45-3.60 (m, 1H), 4.40-4.47 (m, 1H), 7.20-7.40 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 33.6, 35.6, 37.2, 41.9, 50.8, 126.9, 128.8, 143.3, 203.9.

MS (EI, 70 eV): m/z =117.1 (100), 173.1 (32.79), 252.0 (68.19) [M+].

2-Chloro, 4-phenylcyclohexanone (3k) (GP-B)



According to the general procedure (GP-B), 4-phenylcyclohexanone (0.49 g, 2.81 mmol) and NCS (0.38 g, 2.87 mmol) upon refluxation in CCl_4 (12 h) afforded **3k** (0.20 g, 1.02 mmol, 35 %) as white crystalline solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.46.

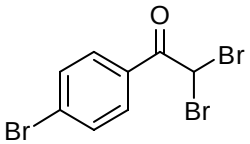
^{1}H NMR (300 MHz, $CDCl_3$), δ = 1.85-2.07 (m, 1H), 2.13-2.51 (m, 4H), 3.09-3.28 (m, 1H), 3.42-3.62 (m, 1H), 4.29-4.34 (m, 1H), 7.20-7.39 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 33.7, 35.9, 36.6, 40.5, 59.9, 126.9, 128.8, 143.2, 204.3.

MS (EI, 70 eV): m/z =104.1(100), 153.1(43.06), 208.1(49.82) [M+].

HRMS (EI, 70 eV): Calcd for $C_{12}H_{13}ClO$ $[M]^+$: 208.0655, found: 208.0658.

2,2-Dibromo-1-(4-bromophenyl)ethanone (3l) (GP-A)[18]

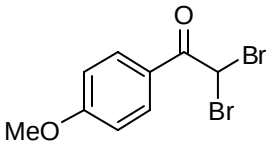


According to the general procedure (GP-A), 1-(4-bromophenyl)-ethanone (0.52 g, 2.61 mmol) 9.20 mL of bromine solution (0.55 M in chloroform) afforded **3l** (0.76 g, 2.11 mmol, 84 %) as crystalline solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.62.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 6.6 (s, 1H), 7.65 (d, *J* = 8.78 Hz, 2H), 7.98 (d, *J* = 8.50 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 39.2, 129.5, 129.9, 131.2, 132.3, 185.1.

2,2-Dibromo-1-(4-methoxyphenyl)ethanone (3m) (GP-A)[19]

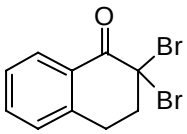


According to the general procedure (GP-A), 1-(4-methoxyphenyl)-ethanone (0.42 g, 2.80 mmol) and 10.20 mL of bromine solution (0.55 M in chloroform) afforded **3m** (0.62 g, 2.01 mmol, 72 %) as crystalline solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.30.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 3.90 (s, 3H), 6.66 (s, 1H), 6.97 (d, *J* = 8.78 Hz, 2H), 8.08 (d, *J* = 9.05 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 39.8, 55.6, 114.2, 123.3, 132.2, 164.5.

2,2-Dibromo-3,4-dihydronaphthalen-1(2H)-one (3n) (GP-B)[18]



According to the general procedure (GP-B), 3, 4-dihydronaphthalene-1(2H)-one (0.48 g, 3.28 mmol) and NBS (1.21 g, 6.84 mmol) afforded **3n** (0.47 g, 1.54 mmol, 45 %) as colorless gummy oil after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.48.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 2.95-3.18 (m, 4H), 7.20-7.43 (m, 2H), 7.46-7.60 (m, 1H), 8.11-8.24 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 29.3, 45.8, 67.3, 127.3, 127.6, 128.6, 129.4, 130.1, 134.4, 142.1, 184.2.

3. General procedure for the Photoredox catalyzed reduction of halides:

An oven dried 10 mL vial equipped with a plastic septum and magnetic stir bar was charged with tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), the corresponding halide (0.173 mmol, 1.0 equiv), 1,5-dimethoxynaphthalene (0.087 mmol, 0.5 equiv) and ascorbic acid (0.348 mmol, 2 equiv). The flask was purged with a stream of nitrogen and 1.0 mL of solvent (MeOH: H_2O = 10:1) was added. The resultant mixture was degassed for 10 min by nitrogen sparging and placed at a distance of ~ 0.5 -1.0 cm from a blue LED lamp.[20] After the reaction was completed (as judged by TLC analysis), the mixture was diluted with 3.0 mL of methanol and directly concentrated in vacuo. The residue was purified by chromatography on silica gel, using PE/ EA as the solvent system. 1,5-Dimethoxynaphthalene (DMN) was re-isolated during the column purification [R_f (EtOAc/hexane 1:9): 0.63].

Determination of Quantum Yield:

Quantum yield was determined by the laboratory apparatus reported by Riedle et.al.[21] In a typical experimental setup, light from a blue LED was passed through a reference cuvette containing 2.0 mL of solvent (MeOH:H_2O = 10:1) and the transmitted radient power P_{ref} was noted by a solar cell. Then the reference cuvette was exchanged with the sample cuvette containing **1a** (0.271 mmol, 1 equiv), tris(2,2́-bipyridyl) ruthenium (II) chloride hexahydrate (0.004 g, 2 mol%), 1,5-dimethoxynaphthalene (0.025 g, 0.135 mmol, 0.5 equiv) and ascorbic acid (0.093 g, 0.542 mmol, 2 eqiv) in 2.0 mL of solvent (MeOH:H_2O = 10:1) and the timer was started. After 30 min, transmitted power, P_{sample} was noted in the same solar cell and the sample was taken to the chemical analysis to measure the final product concentration. Conversion to the product **2a** was determined by the crude NMR of the sample and the quantum yield was determined by the following equation:

$$Q.Y. = \frac{N_{prod}}{N_{ph,\ abs}}$$

$$= \frac{C_{prod}.V.N_A.h.c}{P_{abs}\ .t.\lambda}$$

Here, N_{prod} and C_{prod} are the number of molecules and the according concentration of product species. $N_{ph,\ abs}$ is the number of photons absorbed. V is the sample volume, N_A, h and c are natural constants, P_{abs} is the absorbed optical power, t is the illumination time and λ is the wavelength of the blue LED.

Therefore,

C_{prod} = 18 mmol/l (13% conversion)

V = 2.0 mL

$N_A = 6.022 \times 10^{23}\ mol^{-1}$

$P_{abs} = (P_{ref} - P_{sample}) = 371$ mW

$h = 6.626 \times 10^{-34}$ Js

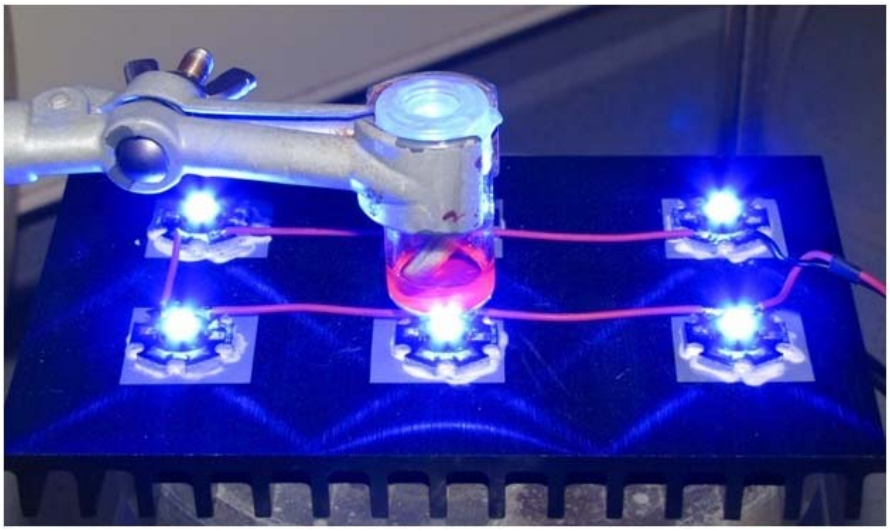
$c = 2.998 \times 10^{8}$ m/s

t = 30 min = 1800 s

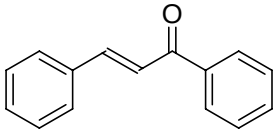
λ = 460 nm

Quantum yield = 0.014

Reaction Apparatus



(*E*)-1,3-diphenylprop-2-en-1-one (2a)[22]

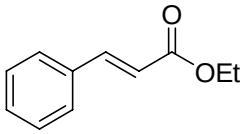


According to the general procedure, **1a** (0.064 g, 0.17 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxy naphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **2a** (0.033 g, 0.16 mmol, 92 %) as pale yellow solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.41.

^{1}H NMR (300 MHz; $CDCl_3$), δ = 7.36-7.70 (m, 9H), 7.84 (d, *J* = 15.6 Hz, 1H), 7.98-8.10 (m, 2H).

^{13}C NMR (75 MHz; $CDCl_3$), δ = 122.1, 128.5, 128.5, 128.6, 128.9, 130.5, 132.8, 134.9, 138.2, 144.8, 190.6.

Ethyl (*E*)-cinnamate (2b)[22]

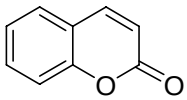


According to the general procedure, **1b** (0.11 g, 0.29 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxy naphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **2b** (0.046 g, 0.26 mmol, 88 %) as gummy oil after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.51.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 1.33 (t, *J* = 7.2 Hz, 3H), 4.26 (q, *J* = 7.2, 2H), 6.43 (d, *J* = 16 Hz, 1H), 7.34-7.39 (m, 3H), 7.46-7.53 (m, 2H), 7.68 (d, *J* = 16 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 14.3, 60.5, 118.3, 128.0, 128.9, 130.2, 134.4, 144.6, 167.0.

2H-chromen-2-one (2d)[23]

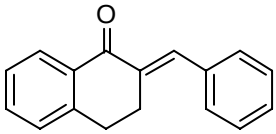


According to the general procedure, **1d** (0.10 g, 0.33 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxy naphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **2d** (0.044 g, 0.30 mmol, 92 %) as yellow solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.16.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.42 (d, *J* = 9.87 Hz, 1H), 7.21-7.35 (m, 2H), 7.46- 7.56 (m, 2H), 7.72 (d, *J* = 9.87, 1H)

^{13}C NMR (75 MHz, $CDCl_3$): δ = 116.7, 116.9, 118.8, 124.4, 127.8, 131.8, 143.4, 154.0, 160.8.

(*E*)-2-benzylidene-3,4-dihydronaphthalen-1(2H)-one (2e)[24]



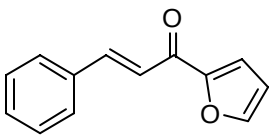
According to the general procedure, **1e** (0.20 g, 0.50 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxy naphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **2e** (0.089 g, 0.38 mmol, 75 %) as white solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.41.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.95 (t, *J* = 6.27 Hz, 2H), 3.14 (t, *J* = 6.27 Hz, 2H), 7.23-7.52 (m, 8H), 7.89(s, 1H), 8.14 (d, *J* = 7.68, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 120.0, 121.3, 129.1, 129.8, 130.7, 135.3, 135.4, 159.3, 162.8.

MS (EI, 70 eV): m/z = 233.1 (100), 234.1 (55.48) [M+].

(*E*)-1-(furan-2-yl)-3-phenylprop-2-en-1-one (2f)[25]



According to the general procedure, **1f** (0.071 g, 0.20 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxy naphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **2f** (0.01 g, 0.052 mmol, 26 %) as white solid after column purification on silica gel.

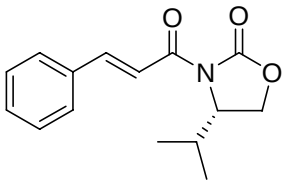
R_f (EtOAc/hexane 1:9): 0.22.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.59-6.61 (m, 1H), 7.32-7.49 (m, 5H), 7.62-7.70 (m, 3H), 7.88 (d, *J* = 15.64 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 112.5, 117.5, 121.1, 128.5, 128.9, 130.6, 134.7, 144.0, 146.5, 153.7, 178.0.

MS (EI, 70 eV): m/z = 77.1 (27.63), 103.1 (27.39), 141.0 (35.24), 197.1 (100), 198.1 (72.91) [M+].

(*S*)-3-cinnamoyl-4-isopropyloxazolidin-2-one (2g)[26]



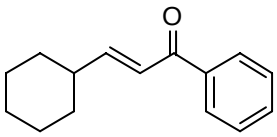
According to the general procedure, **1g** (0.06 g, 0.14 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxy naphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **2g** (0.033 g, 0.13 mmol, 89 %) as white solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.12.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (d, *J* = 7.12 Hz, 3H), 0.96 (d, *J* = 7.12 Hz, 3H), 2.38-2.52 (m, 1H), 4.11-4.37 (m, 2H), 4.51-4.60 (m, 1H), 7.32-7.50 (m, 3H), 7.53-7.70 (m, 2H), 7.83 (d, *J* = 15.7 Hz, 1H), 7.96 (d, *J* = 15.7 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.7, 18.0, 28.5, 58.6, 63.4, 117.1, 128.6, 128.9, 130.6, 134.6, 146.2, 154.2, 165.2.

MS (EI, 70 eV): m/z = 147.1 (15.45), 260.2 (31.55) [MH^+], 277.1 (100) [MNH_4^+].

(*E*)-3-cyclohexyl-1-phenylprop-2-en-1-one (2h)[25]



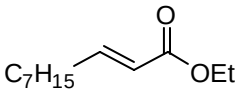
According to the general procedure, **1h** (0.049 g, 0.13 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxy naphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **2h** (0.008 g, 0.04 mmol, 28 %) as yellow oil after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.53.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12-1.42 (m, 5H), 1.61-1.91 (m, 5H), 2.17-2.33 (m, 1H), 6.82 (d, *J* = 15.6 Hz, 1H), 7.01 (dd, *J* = 15.6, 6.6 Hz, 1H), 7.40-7.58 (m, 3H), 7.92 (d, *J* = 6.9 Hz, 2H).

^{13}C NMR (75MHz, $CDCl_3$): δ = 25.7, 25.9, 31.8, 41.0, 123.4, 128.4, 128.5, 132.5, 138.2, 154.9, 191.4.

MS (EI, 70 eV): m/z = 77.0 (28.75), 105.0 (100), 157.1 (6.07), 214.1 (28.58) [M+].

(*E*)-ethyl dec-2-enoate (2i)[27]



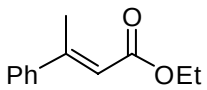
According to the general procedure, **1i** (0.112 g, 0.31 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxy naphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **2i** (0.016 g, 0.08 mmol, 26 %) as gummy colorless oil after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.56.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.72 Hz, 3H), 1.13-1.65 (m, 13H), 2.11-2.25 (m, 2H), 4.17 (q, *J* = 7.13 Hz, 2H), 5.80 (d, *J* = 15.64 Hz, 1H), 6.90-7.03 (m, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ = 14.0, 14.2, 22.6, 28.0, 29.0, 29.1, 31.7, 32.2, 60.1, 121.2, 149.5, 166.8.

MS (EI, 70 eV): m/z = 55.1 (100), 101.1 (90.63), 153.2 (61.84), 198.2 (2.95) [M+].

(*E*)-ethyl 3-phenylbut-2-enoate (2k)[28]



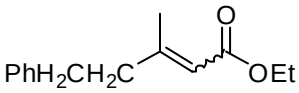
According to the general procedure, **1k** (0.094 g, 0.27 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxy naphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **2k** (0.036 g, 0.19 mmol, 70 %) as yellow oil after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.48.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.13 Hz, 3H), 2.58 (s, 3H), 4.22 (q, *J* = 7.13 Hz, 2H), 6.14 (s, 1H), 7.32-7.55 (m, 5H).

^{13}C NMR (75MHz, $CDCl_3$): δ = 14.3, 17.9, 59.8, 117.2, 126.3, 128.4, 128.9, 142.2, 155.6, 166.9.

MS (EI, 70 eV): m/z = 191.2 (44.35) [MH+], 208.1 (100) [MNH_4+].

Ethyl 3-methyl-5-phenylpent-2-enoate (*E*:*Z* = 84:16) (2l)[29]



According to the general procedure, **1l** (0.088 g, 0.23 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxy naphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **2l** (0.033 g, 0.15 mmol, 65 %) as yellow oil (*E/Z* mixture) after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.46.

^{1}H NMR (*E*-isomer) (300 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.13 Hz, 3H), 2.21 (s, 3H), 2.40-2.48 (m, 2H), 2.74-2.84 (m, 2H), 4.15 (q, *J* = 7.13 Hz, 2H), 5.69 (s, 1H), 7.13-7.35 (m, 5H).

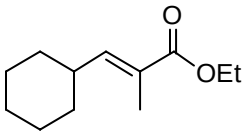
^{13}C NMR (75MHz, $CDCl_3$): δ = 14.3, 18.9, 33.9, 42.7, 59.5, 116.0, 126.1, 128.2, 128.4, 141.1, 158.9, 166.8.

^{1}H NMR (*Z*-isomer) (300 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.13 Hz, 3H), 1.88 (s, 3H), 2.40-2.48 (m, 2H), 2.74-2.84 (m, 2H), 4.15 (q, *J* = 7.13 Hz, 2H), 5.69 (s, 1H), 7.13-7.35 (m, 5H).

^{13}C NMR (75MHz, $CDCl_3$): δ = 14.3, 18.9, 33.9, 42.7, 59.5, 116.0, 126.1, 128.2, 128.4, 141.1, 158.9, 166.8.

MS (EI, 70 eV): m/z = 91.1 (100), 144.2 (22.65), 173.1 (9.47), 218.2 (1.87) [M+].

(*E*)-ethyl 3-cyclohexyl-2-methylacrylate (2m)[28]



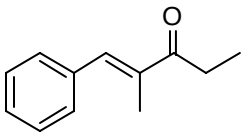
According to the general procedure, **1m** (0.13 g, 0.34 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxy naphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **2m** (0.019 g, 0.09 mmol, 27 %) as gummy oil after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.76.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11-1.78 (m, 10H), 1.28 (t, *J* = 7.13 Hz, 3H), 1.84 (s, 3H), 2.23-2.39 (m, 1H), 4.18 (q, *J* = 7.13 Hz, 2H), 6.58 (d, *J* = 8.23 Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ =12.4, 14.3, 25.6, 25.9, 31.9, 37.7, 60.4, 147.3, 168.2.

MS (EI, 70 eV): m/z = 197.2 (25.78) [MH+], 214.3 (100) [MNH_4+].

(*E*)-2-methyl-1-phenylpent-1-en-3-one (2n)[24]



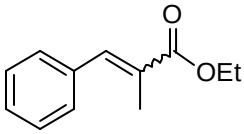
According to the general procedure, **1n** (0.08 g, 0.24 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxy naphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **2n** (0.032 g, 0.18 mmol, 75 %) as colorless oil after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.42.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (t, *J* = 7.27 Hz, 3H), 2.09 (s, 3H), 2.84 (q, *J* = 7.27 Hz, 2H), 7.30-7.45 (m, 5H), 7.53 (s, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ = 8.8, 13.2, 30.8, 128.5, 129.7, 136.0, 137.2, 138.2. 203.0.

MS (EI, 70 eV): m/z = 145.1 (5.11), 175.1 (100) [MH+], 192.2 (90.75) [MNH_4+].

Ethyl 2-methyl-3-phenylacrylate (*E*:*Z* = 75:25) ((2o)[28]



According to the general procedure, **1o** (0.064 g, 0.19 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxy naphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **2o** (0.023 g, 0.12 mmol, 65 %) as colorless oil (*E/Z* mixture) after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.34.

^{1}H NMR (*E*-isomer) (300 MHz, $CDCl_3$): δ = 1.35 (t, *J* = 7.13 Hz, 3H), 2.12 (s, 3H), 4.28 (q, *J* = 7.13 Hz, 2H), 7.29-7.43 (m, 5H), 7.70 (s, 1H).

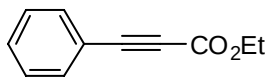
^{13}C NMR (75MHz, $CDCl_3$): δ = 14.0, 14.3, 128.2, 128.3, 128.6, 129.6, 135.9, 138.6, 168.7.

^{1}H NMR (*Z*-isomer) (300 MHz, $CDCl_3$): δ = 1.15 (t, *J* = 7.13 Hz, 3H), 2.12 (s, 3H), 4.18 (q, *J* = 7.13 Hz, 2H), 6.71 (s, 3H), 7.29-7.43 (m, 5H).

^{13}C NMR (75MHz, $CDCl_3$): δ = 13.6, 21.3, 60.5, 127.4, 127.9, 128.0, 134.2, 168.7.

MS (EI, 70 eV): m/z = 191.2 (43.49) [MH+], 208.1 (100) [MNH_4+].

Ethyl 3-phenylpropiolate (2p)[30]



According to the general procedure, **1p** (0.08 g, 0.24 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxy naphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **2p** (0.03 g,

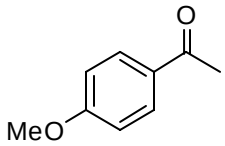
0.17 mmol, 72 %) as gummy colorless oil after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.50.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.35 (t, *J* = 7.13 Hz, 3H), 4.30 (q, *J* = 7.13 Hz, 2H), 7.30-7.50 (m, 3H), 7.55 - 7.65 (m, 2H).

^{13}C NMR (75MHz, $CDCl_3$): δ = 14.1, 62.1, 80.7, 86.0, 119.6, 128.5, 130.6, 133.0, 154.1.

MS (EI, 70 eV): m/z = 102.1 (65.32), 129.0 (100), 174.0 (16.37) [M+].

1-(4-methoxyphenyl) ethanone (4a)[31]

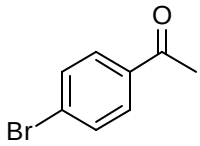


According to the general procedure, **3a** (0.102 g, 0.44 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxy naphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **4a** (0.06 g, 0.41 mmol, 93 %) as white solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.25.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 2.52 (s, 3H), 3.83 (s, 3H), 6.91 (d, *J* = 9.05 Hz, 2H), 7.91 (d, *J* = 9.05 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 26.3, 55.4, 113.6, 130.3, 130.8, 163.4, 196.8.

1-(4-bromophenyl) ethanone (4c)[31]

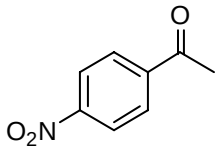


According to the general procedure, **3c** (0.101 g, 0.36 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxy naphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **4c** (0.064 g, 0.32 mmol, 89 %) as white solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.38.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 2.59 (s, 3H), 7.61 (d, *J* = 8.78 Hz, 2H), 7.82 (d, *J* = 8.78 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 26.5, 128.3, 129.8, 131.9, 135.8, 197.0.

1-(4-nitrophenyl)ethanone (4d)[31]

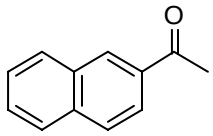


According to the general procedure, **3d** (0.148 g, 0.61 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxy naphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **4d** (0.073 g, 0.44 mmol, 72 %) as white solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.31.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 2.69 (s, 3H), 8.08-8.15 (d, *J* = 8.78 Hz, 2H), 8.29-8.35 (d, *J* = 9.05 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 27.0, 123.9, 129.3, 141.3, 196.3.

1-(naphthalen-2-yl)ethanone (4e)[31]

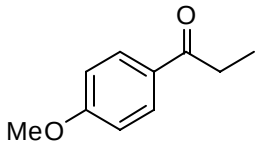


According to the general procedure, **3e** (0.152 g, 0.60 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxy naphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **4e** (0.086 g, 0.51 mmol, 84 %) as white solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.35.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 2.79 (s, 3H), 7.51-7.70 (m, 2H), 7.83-8.12 (m, 4H), 8.48 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 26.7, 123.9, 126.8, 127.8, 128.4, 128.5, 129.5, 130.2, 197.7.

1-(4-methoxyphenyl)propan-1-one (4f)[31]

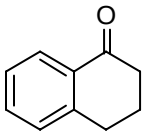


According to the general procedure, **3f** (0.098 g, 0.41 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxy naphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **4f** (0.037 g, 0.22 mmol, 54 %) as white solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.32.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 1.21 (t, *J* = 7.40 Hz, 3H), 2.95 (q, *J* = 7.31 Hz, 2H), 3.86 (s, 3H), 6.93 (d, *J* = 9.05 Hz, 2H), 7.95 (d, *J* = 9.05 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 8.4, 31.4, 55.4, 113.6, 130.0, 130.2, 163.3, 199.5.

3,4-Dihydronaphthalen-1(2H)-one (4g)[32]

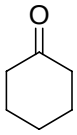


According to the general procedure, **3g** (0.079 g, 0.36 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxynaphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **4g** (0.037 g, 0.25 mmol, 71 %) as gummy oil after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.33.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 2.07-2.21 (m, 2H), 2.66 (t, *J* = 6.99 Hz, 2H), 2.97 (t, *J* = 6.17 Hz, 2H), 7.21-7.35 (m, 2H), 7.41-7.52 (m, 1H), 8.03 (dd, *J* = 1.09 Hz, 7.68 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 23.3, 29.7, 39.2, 126.2, 126.6, 127.5, 132.6, 133.4, 144.5, 198.4.

Cyclohexanone (4i) [33]

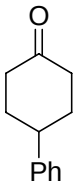


According to the general procedure, **3i** (0.101 g, 0.56 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxynaphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **4i** (0.028 g, 0.28 mmol, 50 %) as yellowish oil after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.36.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 1.59-1.71 (m, 2H), 1.72-1.87 (m, 4H), 2.21-2.32 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 24.7, 26.9, 42.1, 212.0.

4-Phenylcyclohexanone (4j) [34]



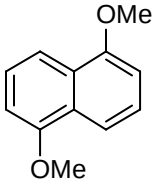
According to the general procedure, **3j** (0.075 g, 0.29 mmol), tris(2,2´-bipyridyl)ruthenium(II)chloride hexahydrate (2 mol%), 1,5-dimethoxynaphthalene (0.5 equiv) and ascorbic acid (2 equiv) afforded **4j** (0.039 g, 0.22 mmol, 75 %) as white solid after column purification on silica gel. R_f (EtOAc/hexane 1:9): 0.28.

^{1}H NMR (300 MHz, $CDCl_3$), δ = 1.85-2.05 (m, 2H), 2.15-2.30 (m, 2H), 2.45-2.57 (m, 4H), 2.95-3.10 (m, 1H), 7.15-7.40 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$), δ = 33.9, 41.4, 42.8, 126.6, 128.6, 144.8, 211.2.

MS (EI, 70 eV): m/z =104.1 (89.14), 119.1 (63.97), 174.1 (100) [M+].

1, 5-Dimethoxynaphthalene (Isolated after reaction)



^{1}H NMR (300 MHz; $CDCl_3$), δ = 3.98 (s, 6H); 6.85 (d, *J* = 7.47 Hz, 2H), 7.36 (t, *J* = 8.09 Hz, 2H), 7.84 (d, *J* = 8.72 Hz, 2H).

^{13}C NMR (75 MHz; $CDCl_3$), δ = 55.5, 104.5, 114.1, 125.1, 126.6, 155.2.

R_f (EtOAc/hexane 1:9): 0.63

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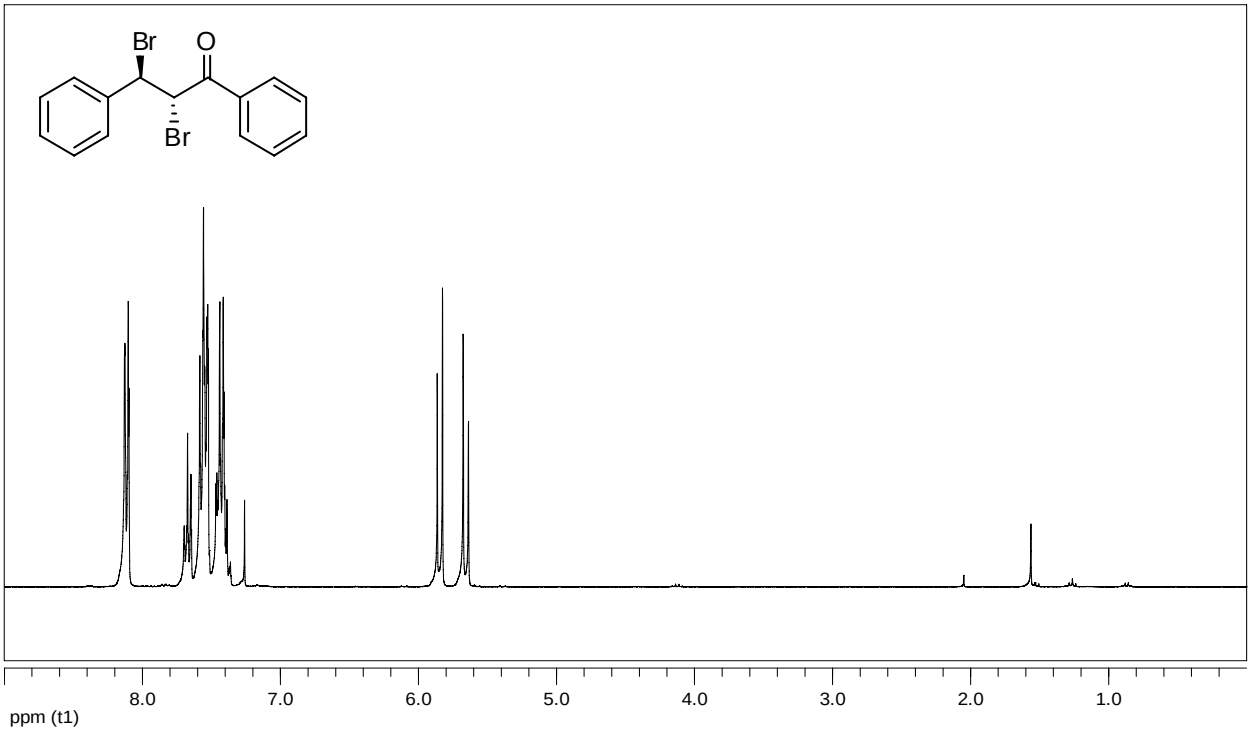
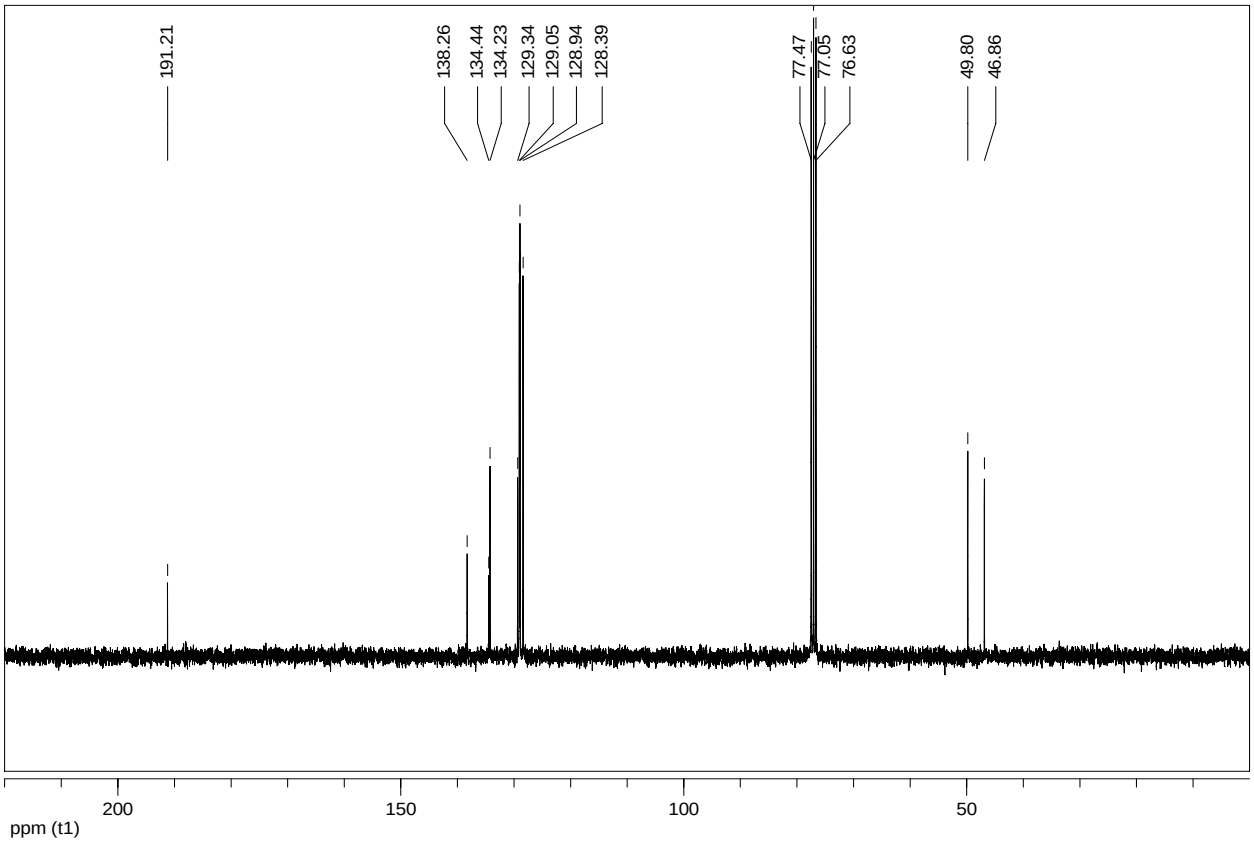
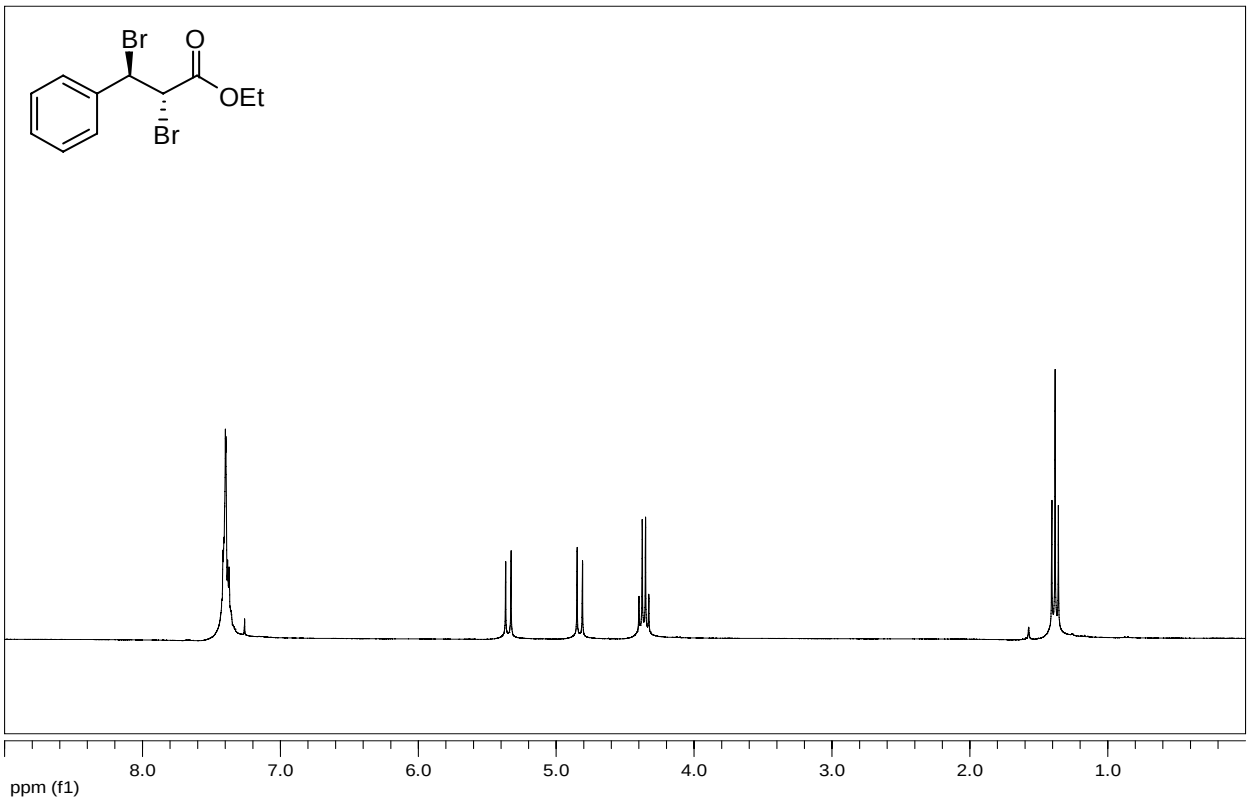
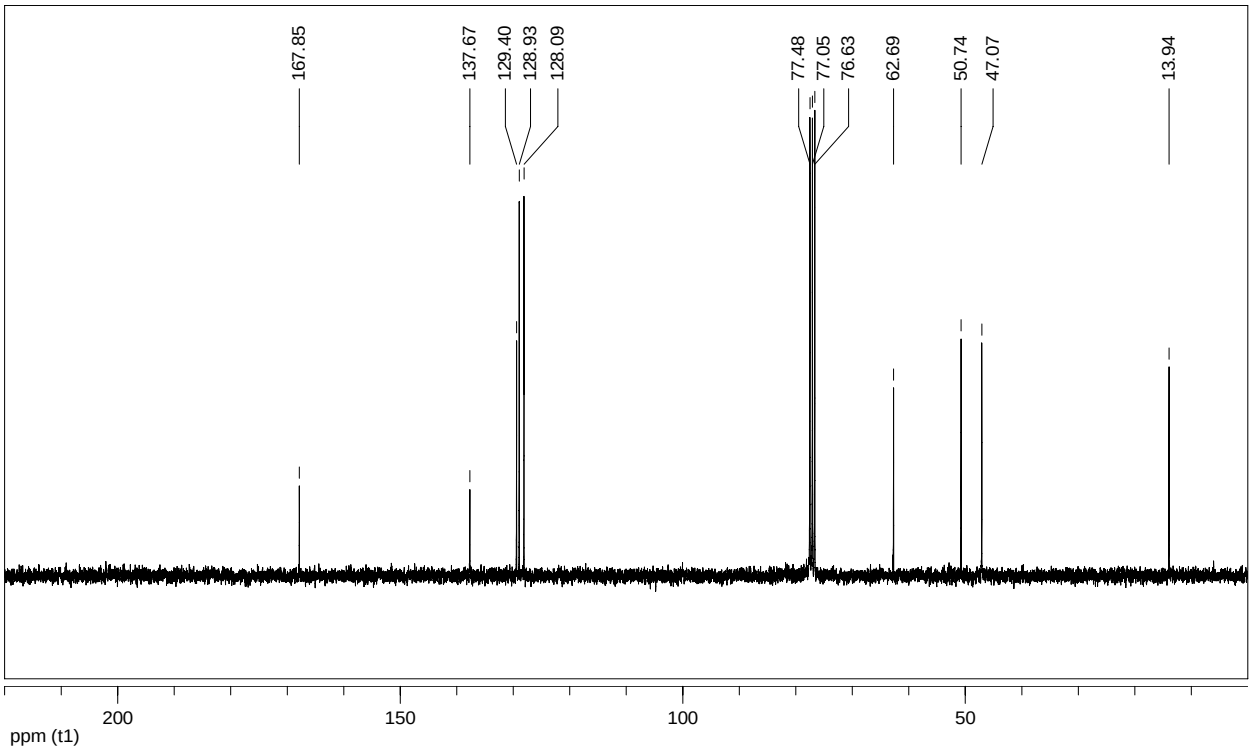
(*2S, 3R*)-2,3-dibromo-1,3-diphenylpropan-1-one (1a)



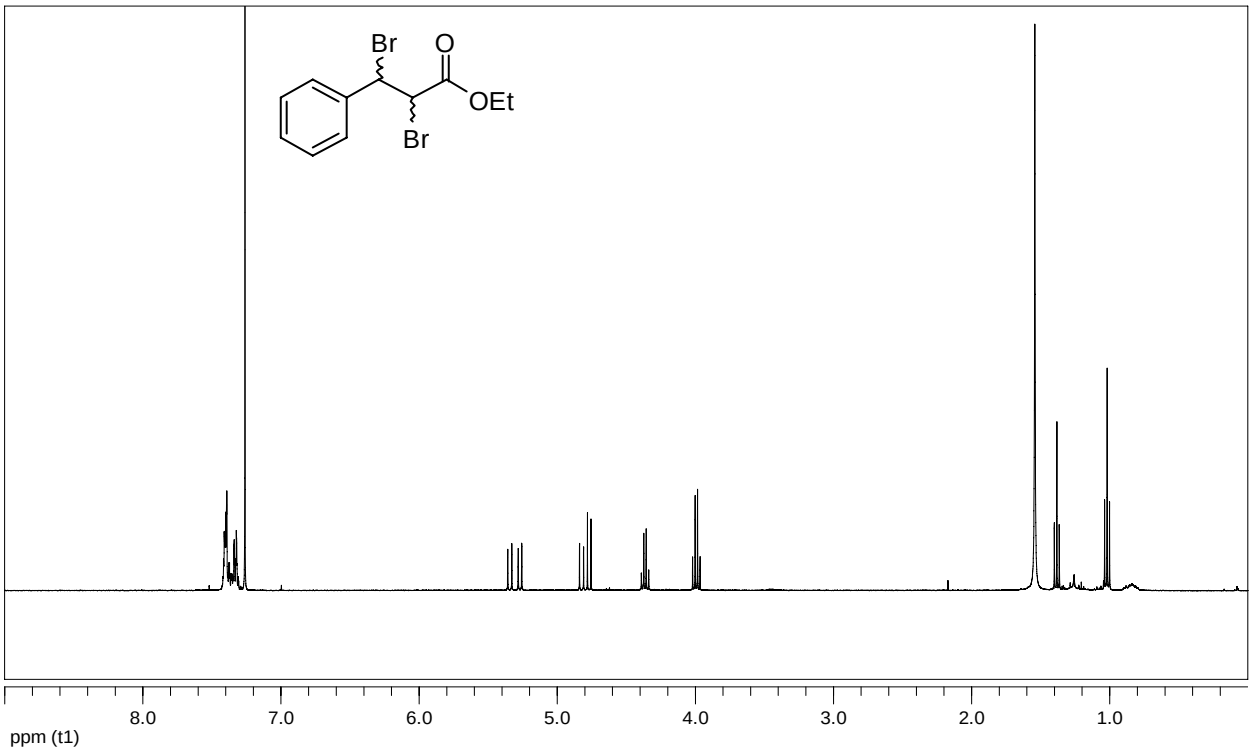


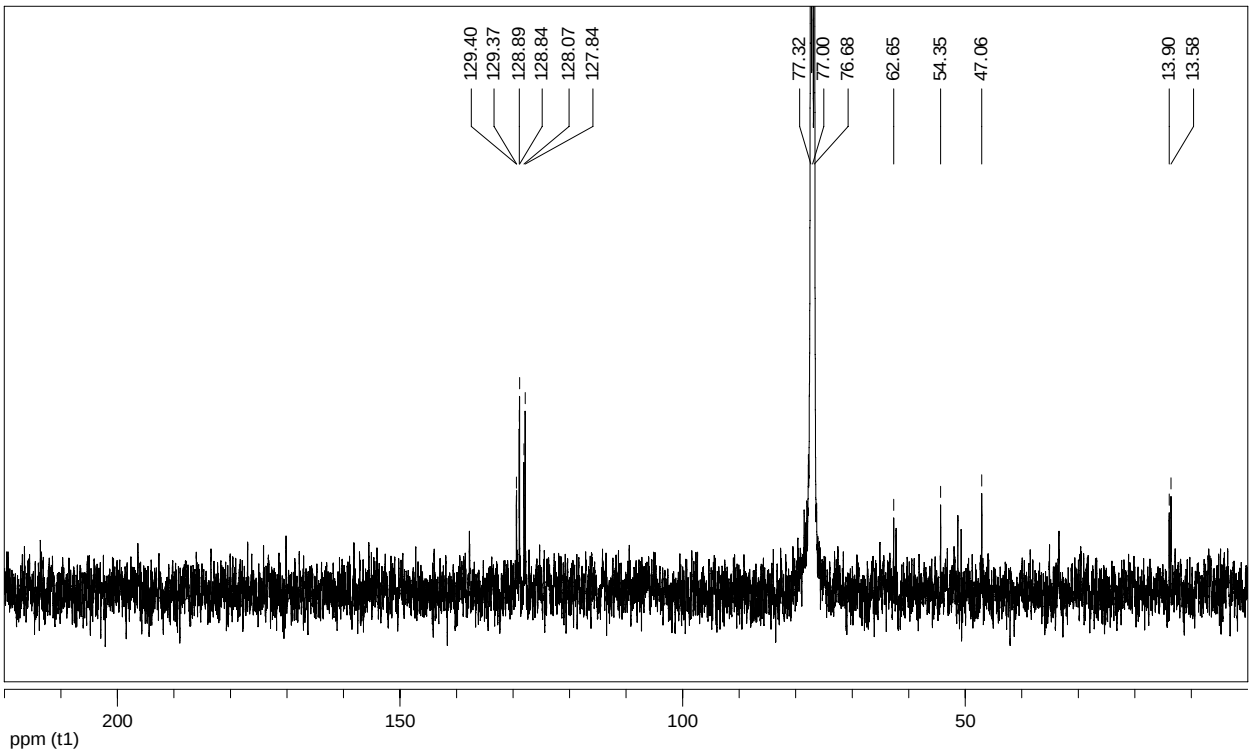
(*2S,3R*)-ethyl 2,3-dibromo-3-phenylpropanoate (1b)



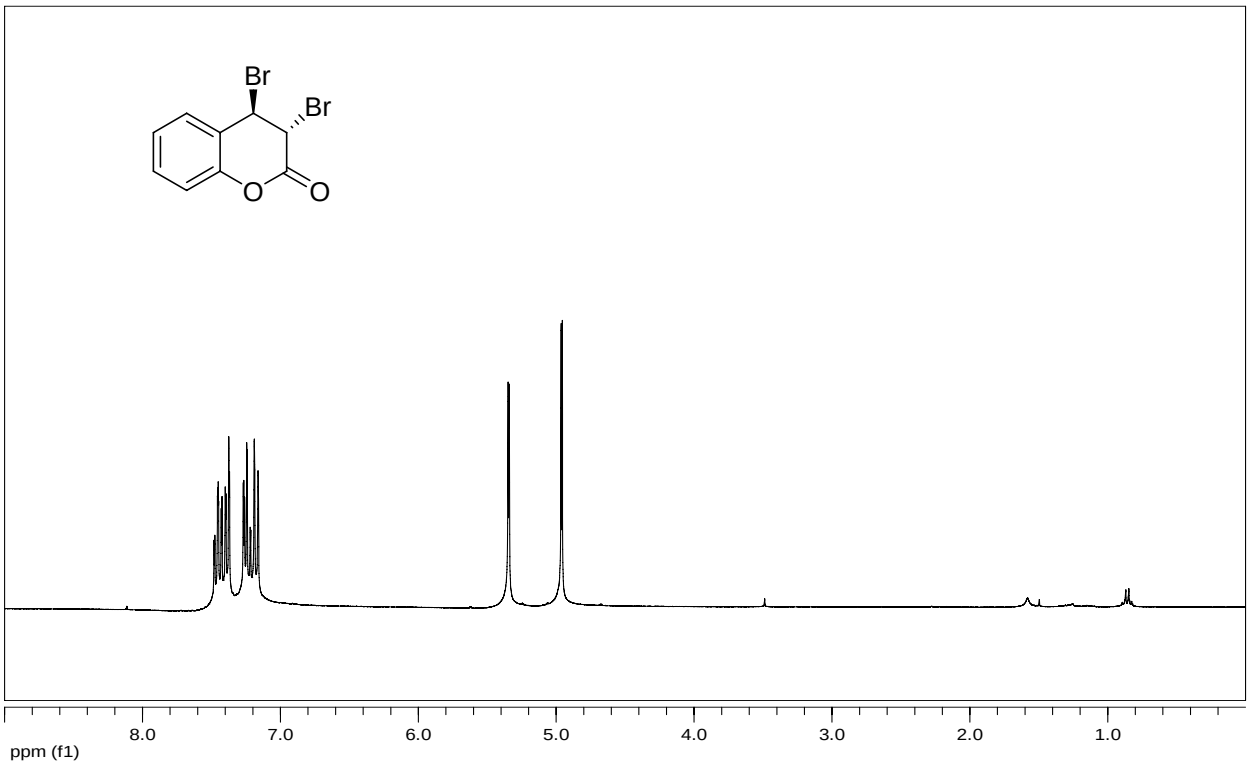


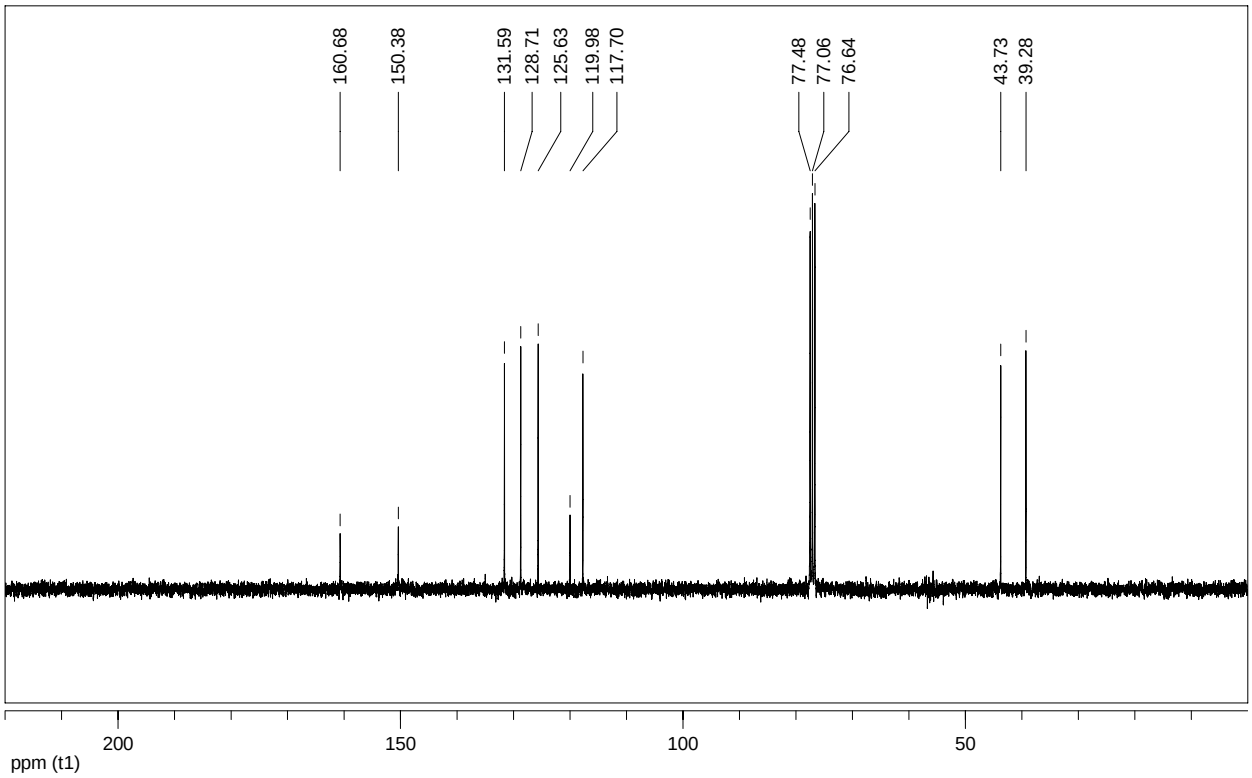
Ethyl 2,3-dibromo-3-phenylpropanoate (*erythro: threo* = 43: 57)(1c)



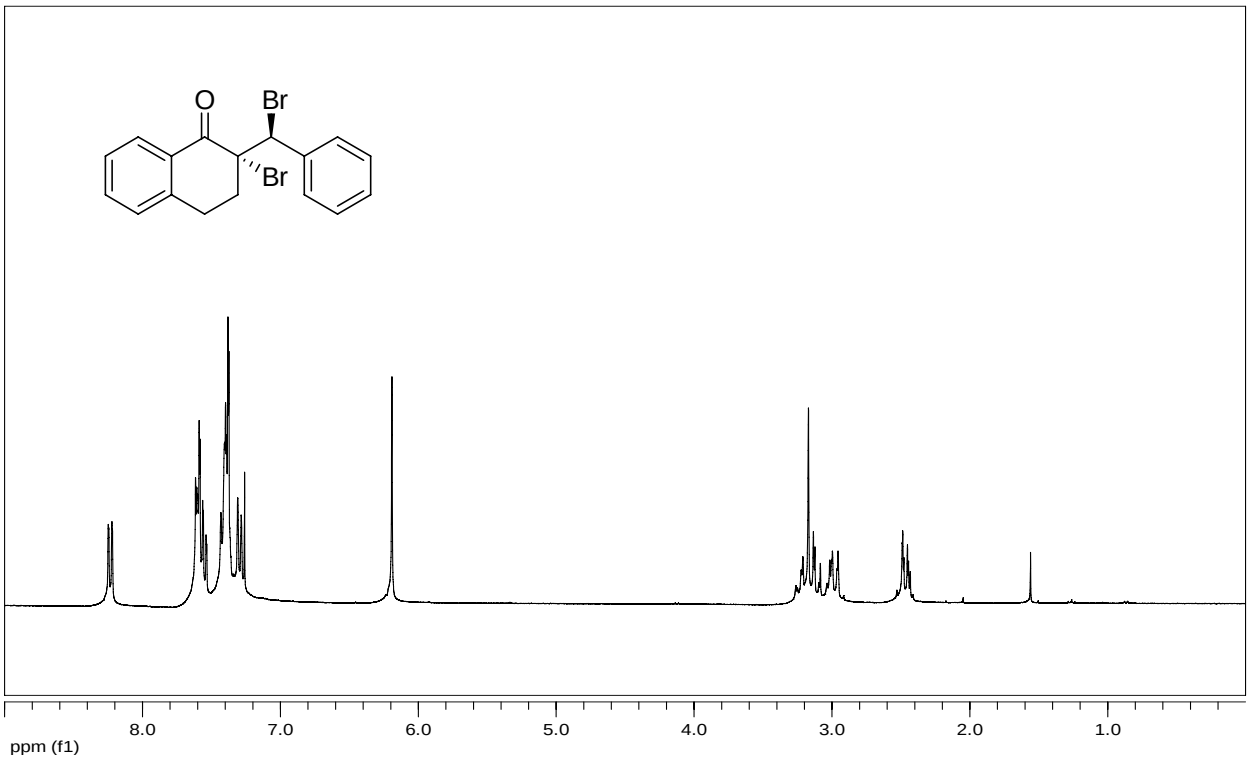


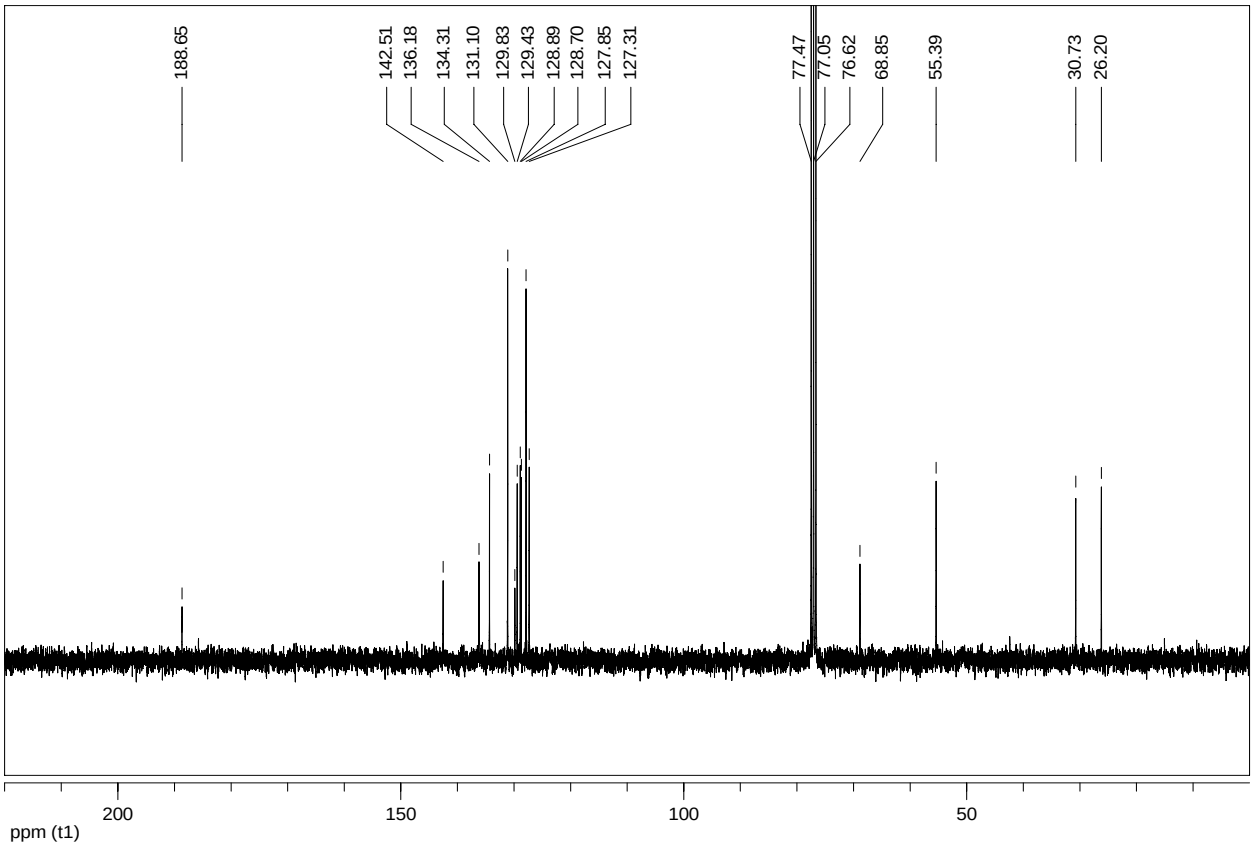
3,4-Dibromochroman-2-one (1d)



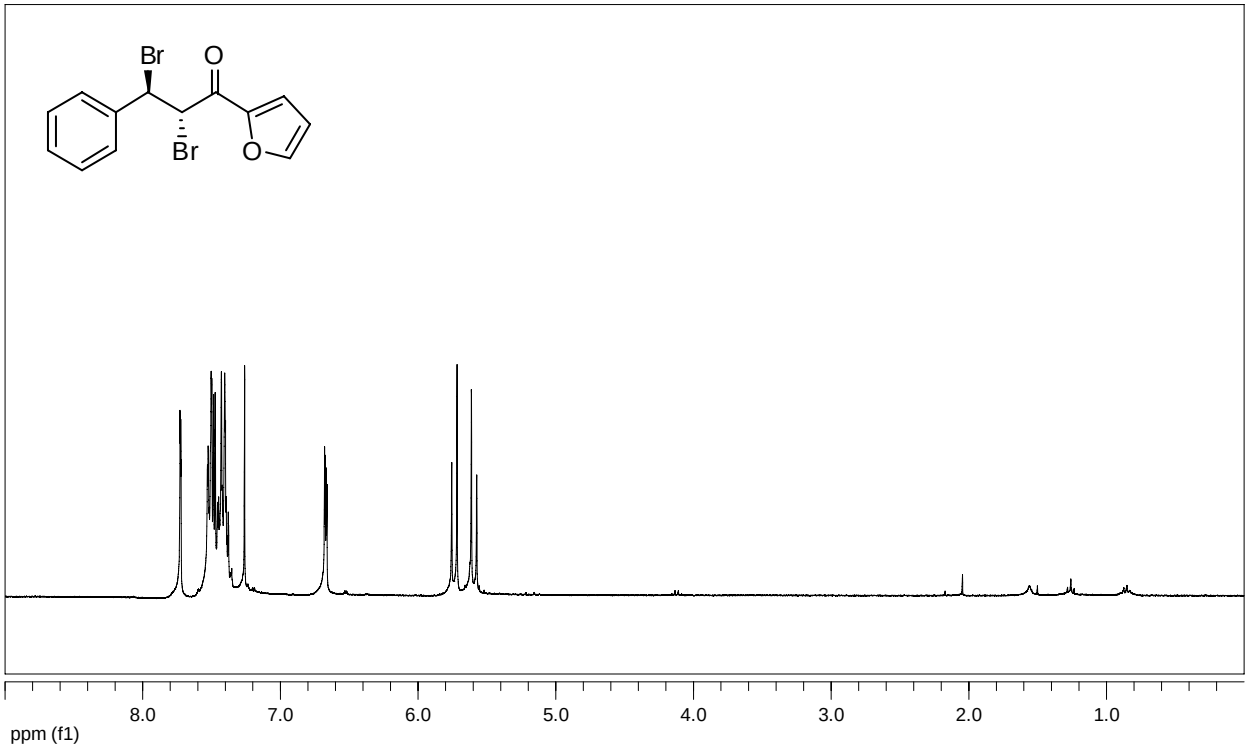


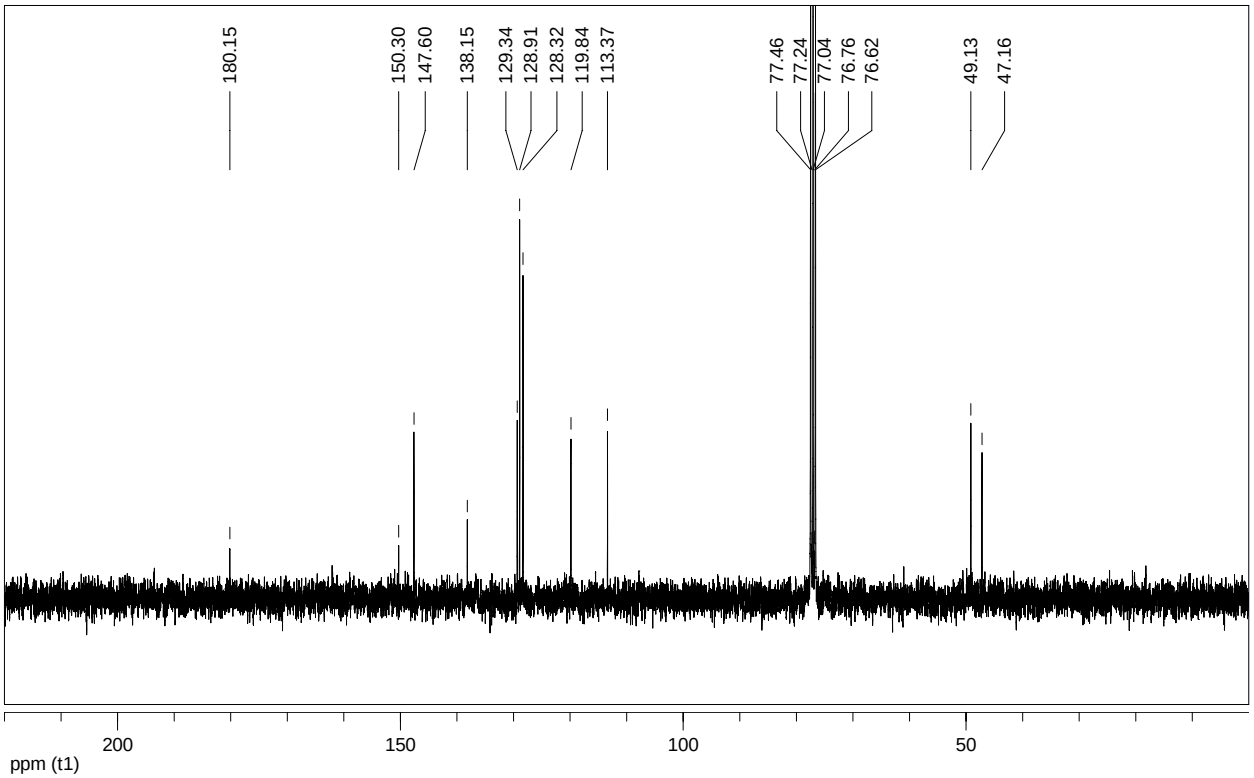
(*R*)-2-bromo-2-((*S*)-bromo(phenyl)methyl)-3,4-dihydronaphthalen-1(2H)-one (1e)



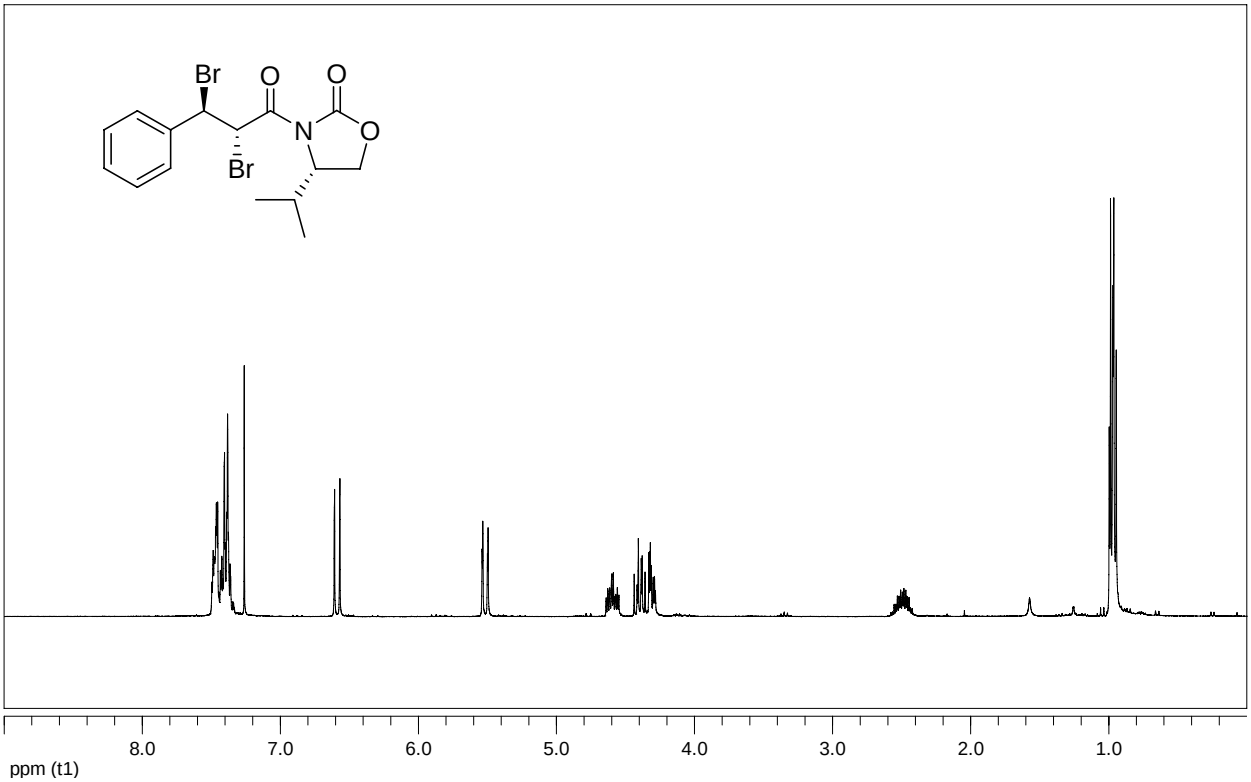


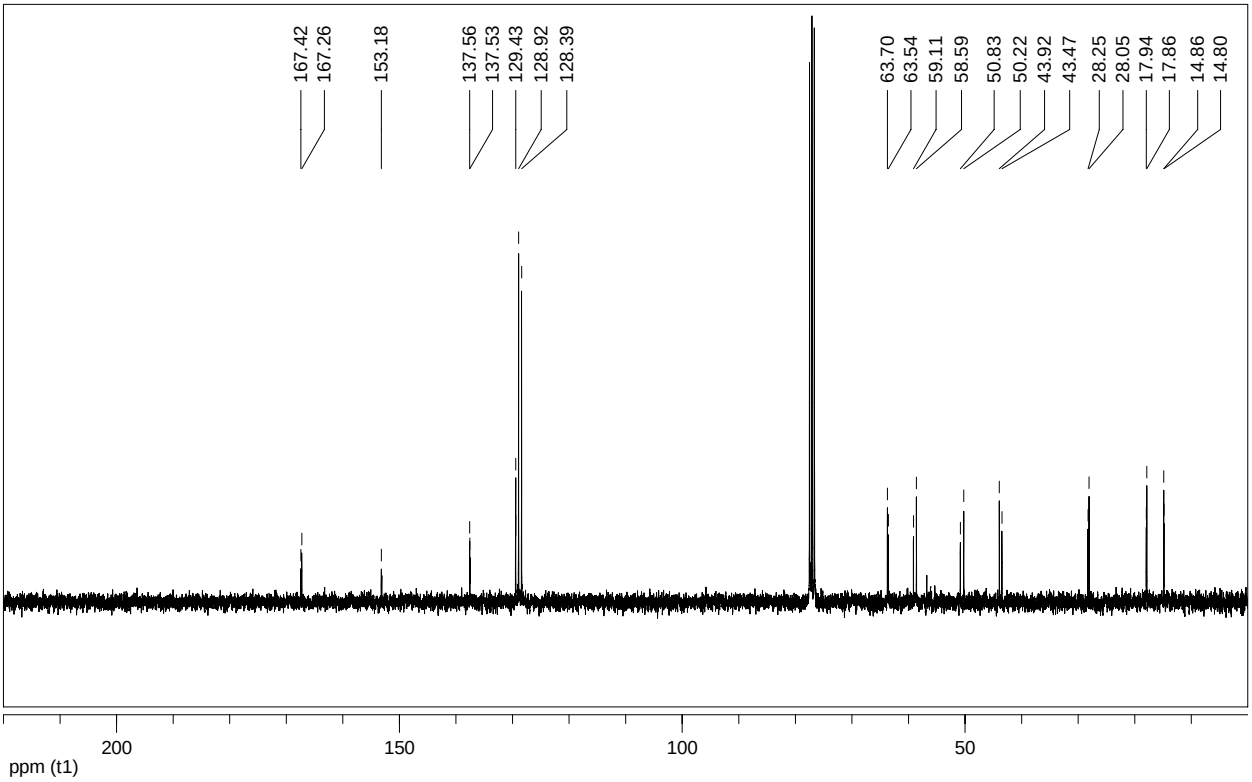
(*2S,3R*)-2,3-dibromo-1-(furan-2-yl)-3-phenylpropan-1-one (1f)



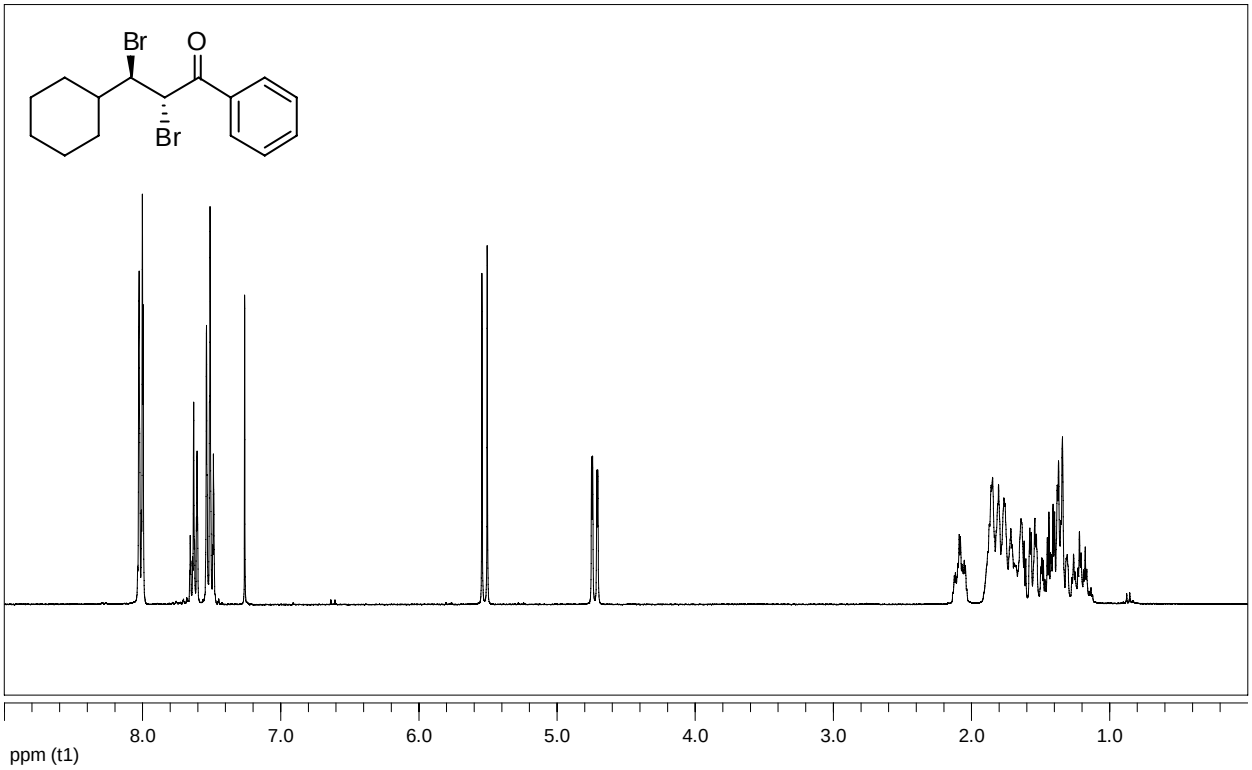


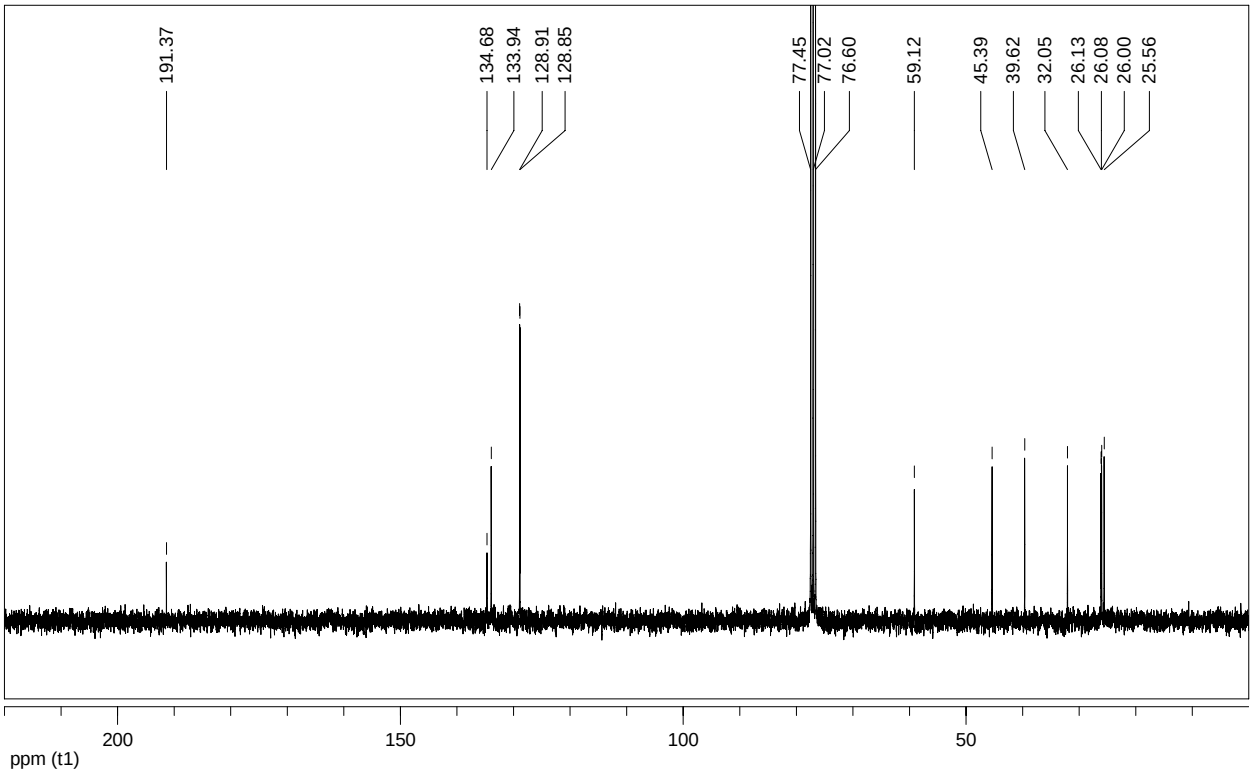
(*S*)-3-((*2S,3R*)-2,3-dibromo-3-phenylpropanoyl)-4-isopropyloxazolidin-2-one (1g)



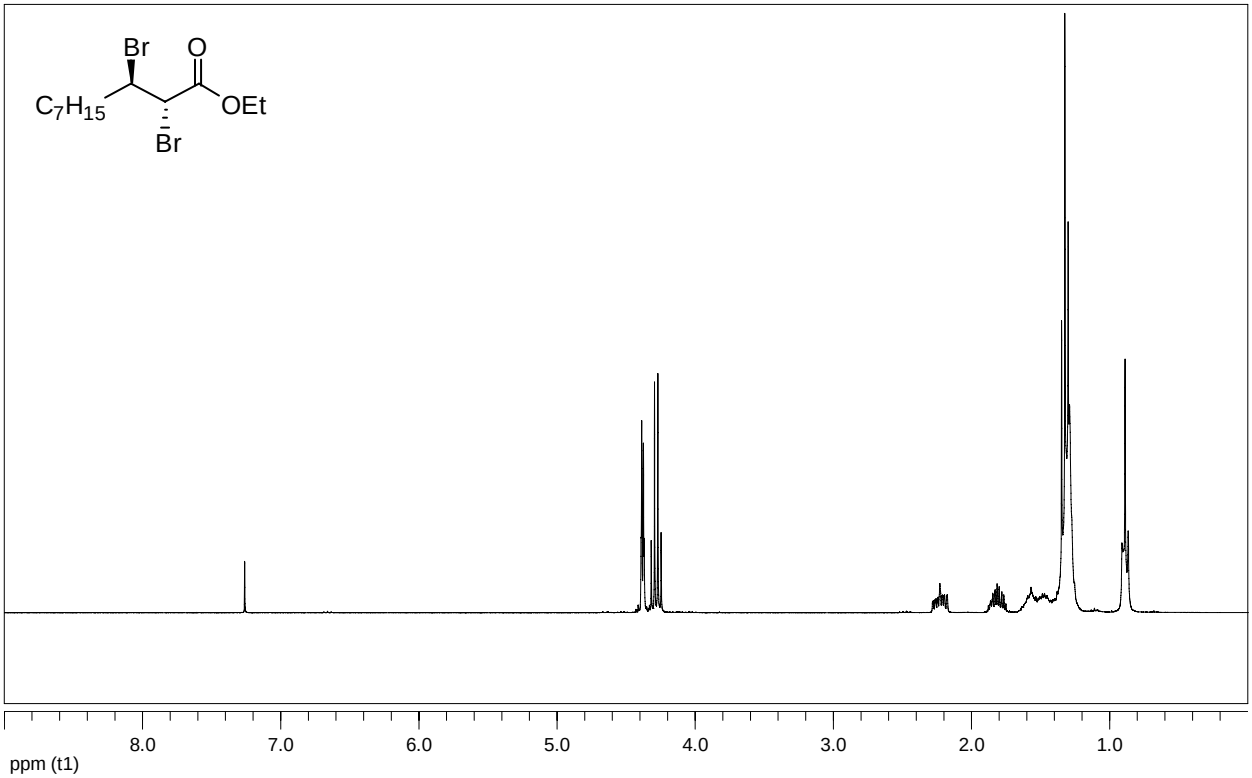


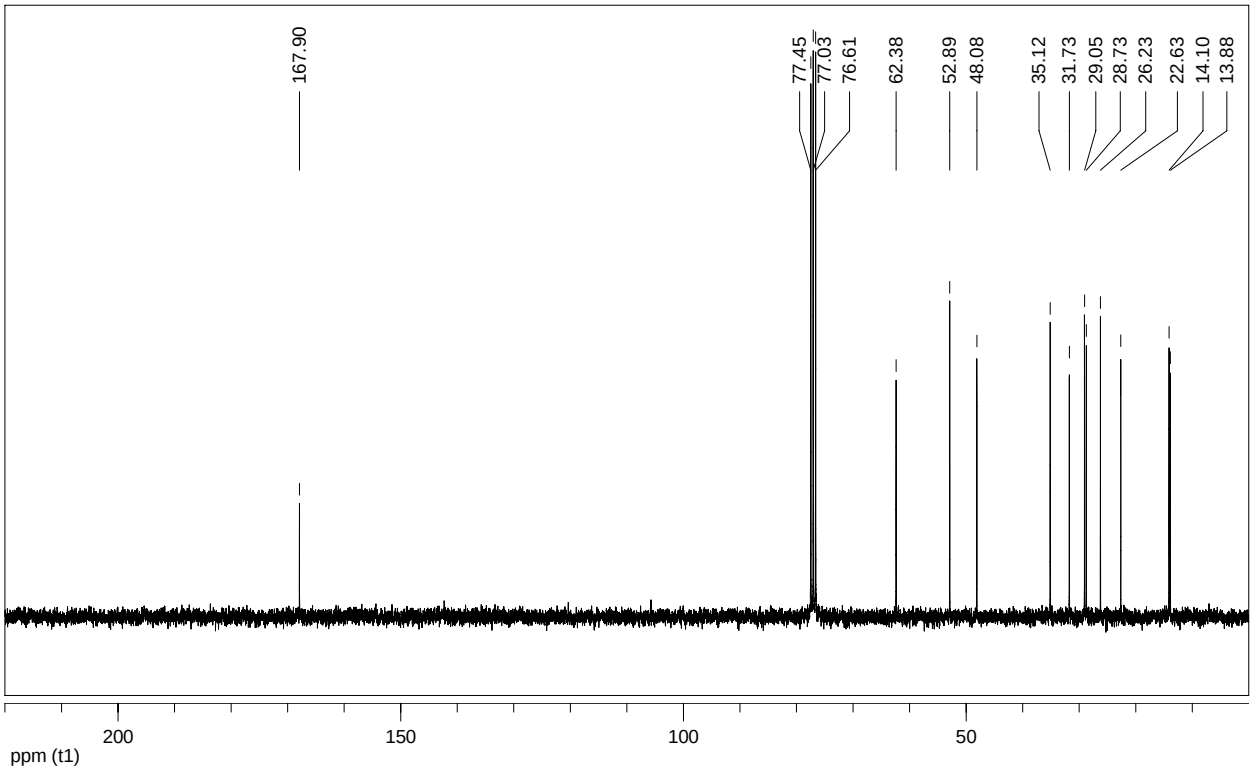
(*2R,3S*)-2,3-dibromo-3-cyclohexyl-1-phenylpropan-1-one (1h)



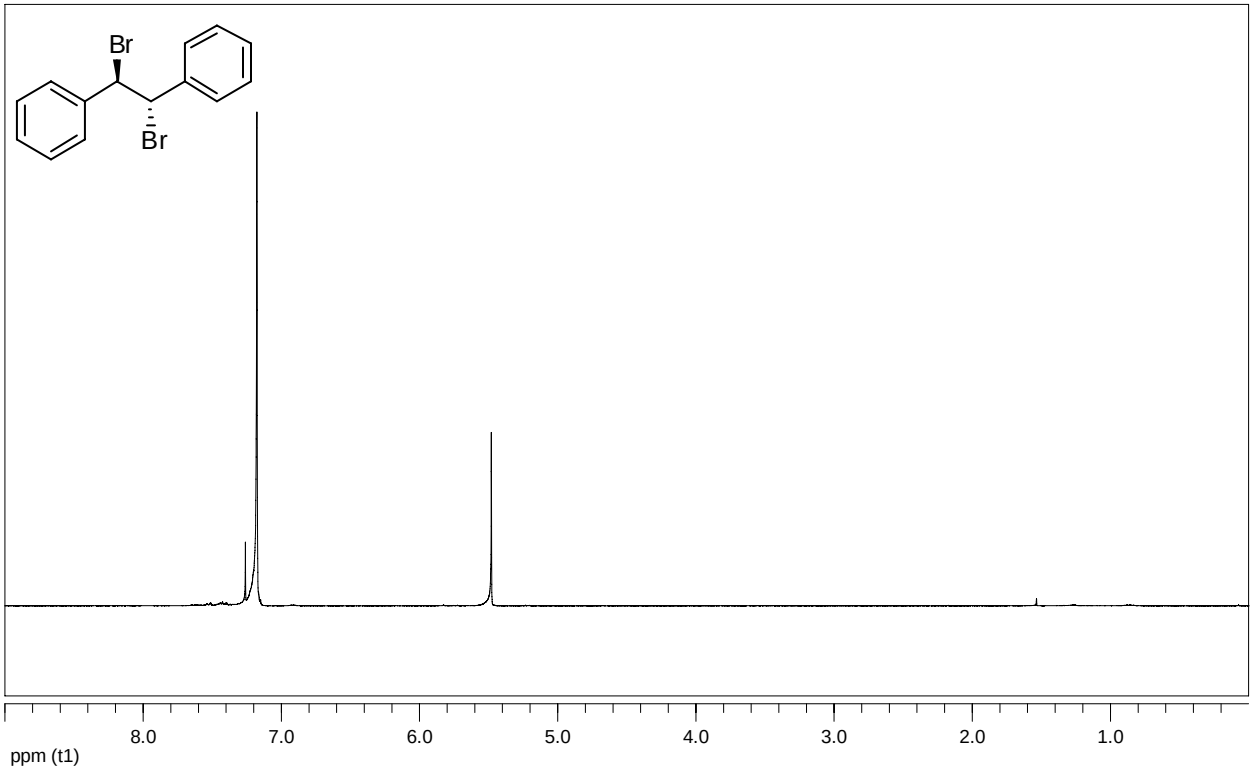


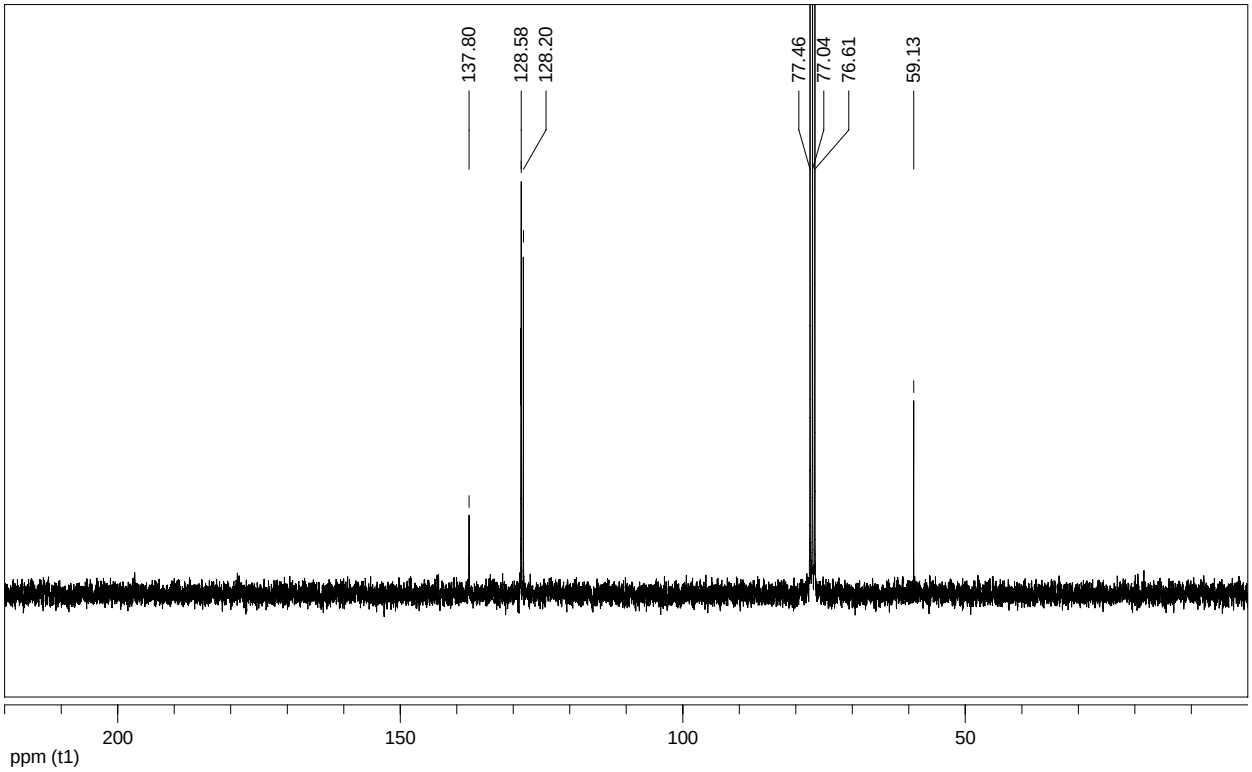
Ethyl 2,3-dibromodecanoate(1i)



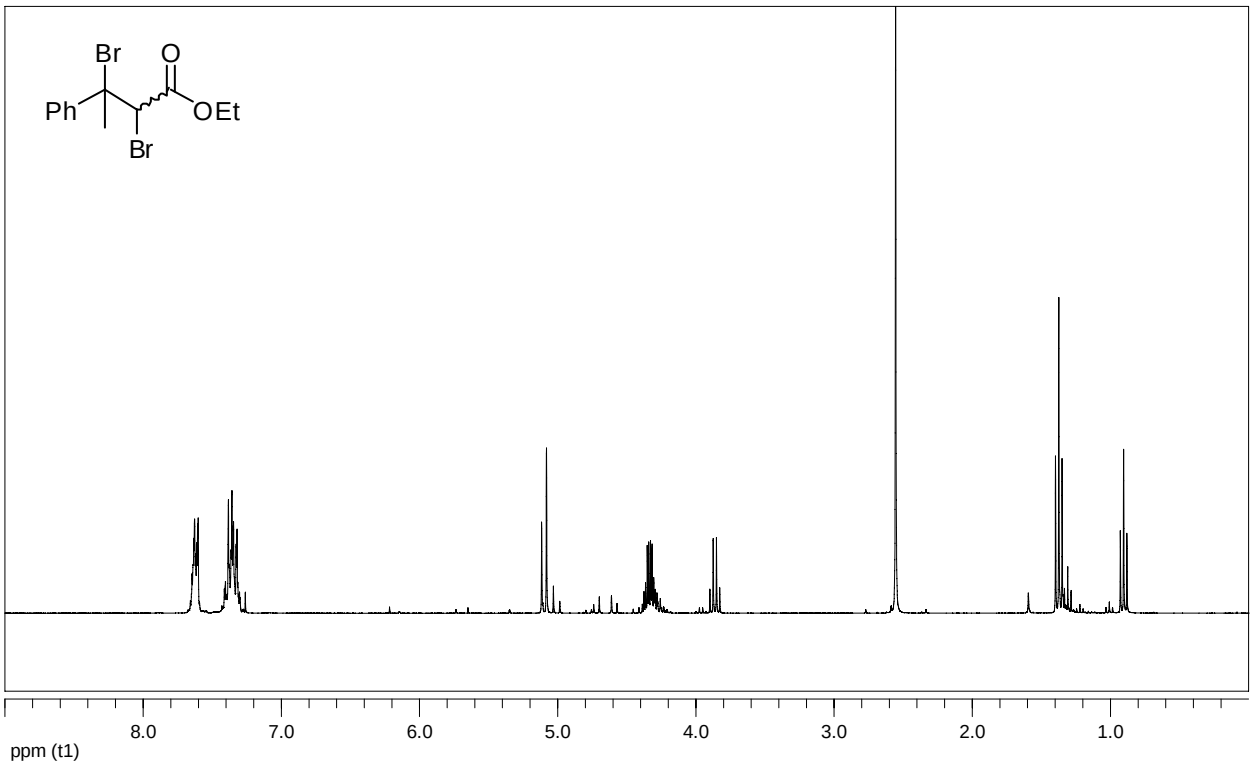


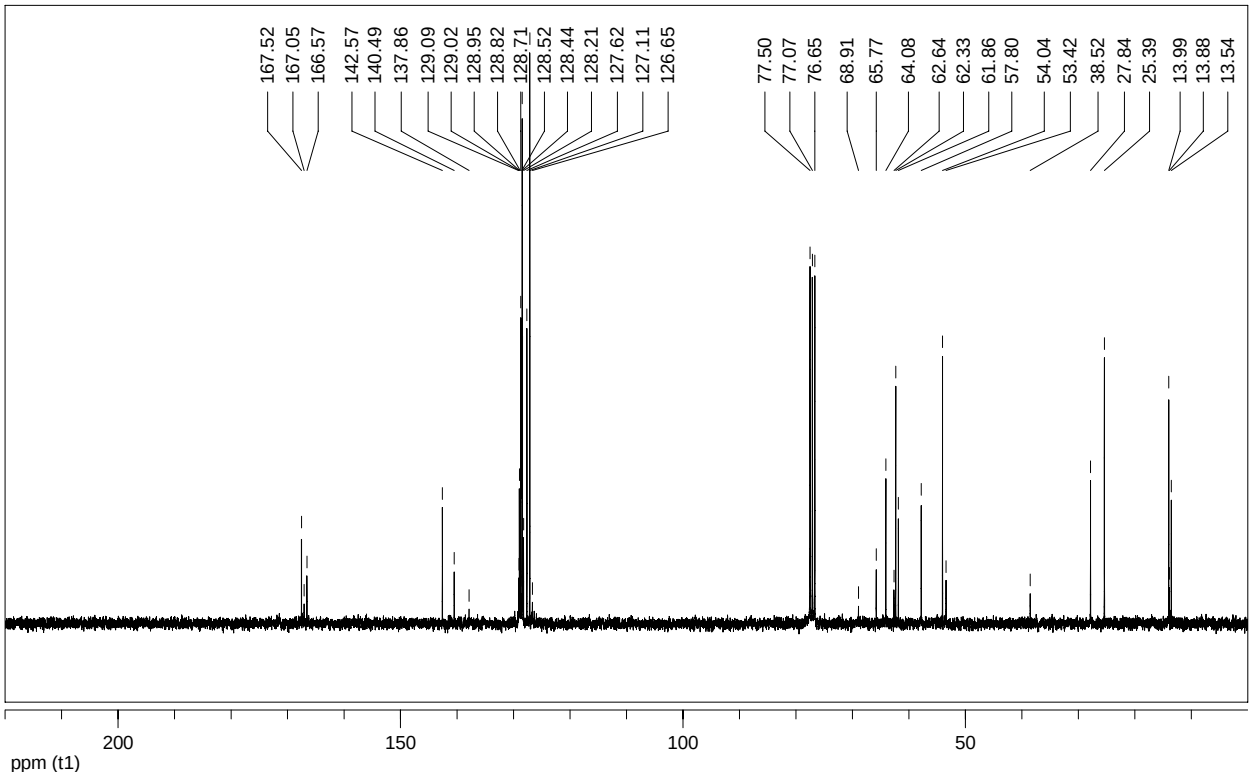
(*1R,2S*)-1,2-dibromo-1,2-diphenylethane (1j)



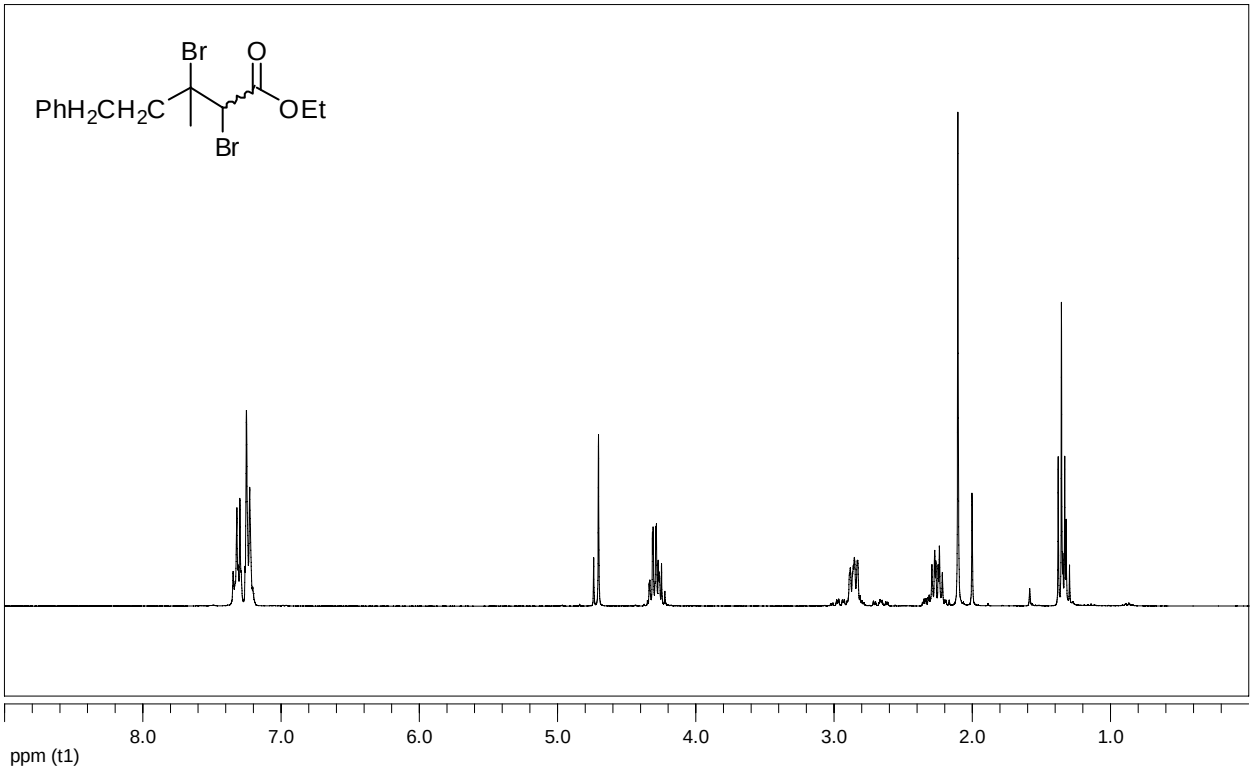


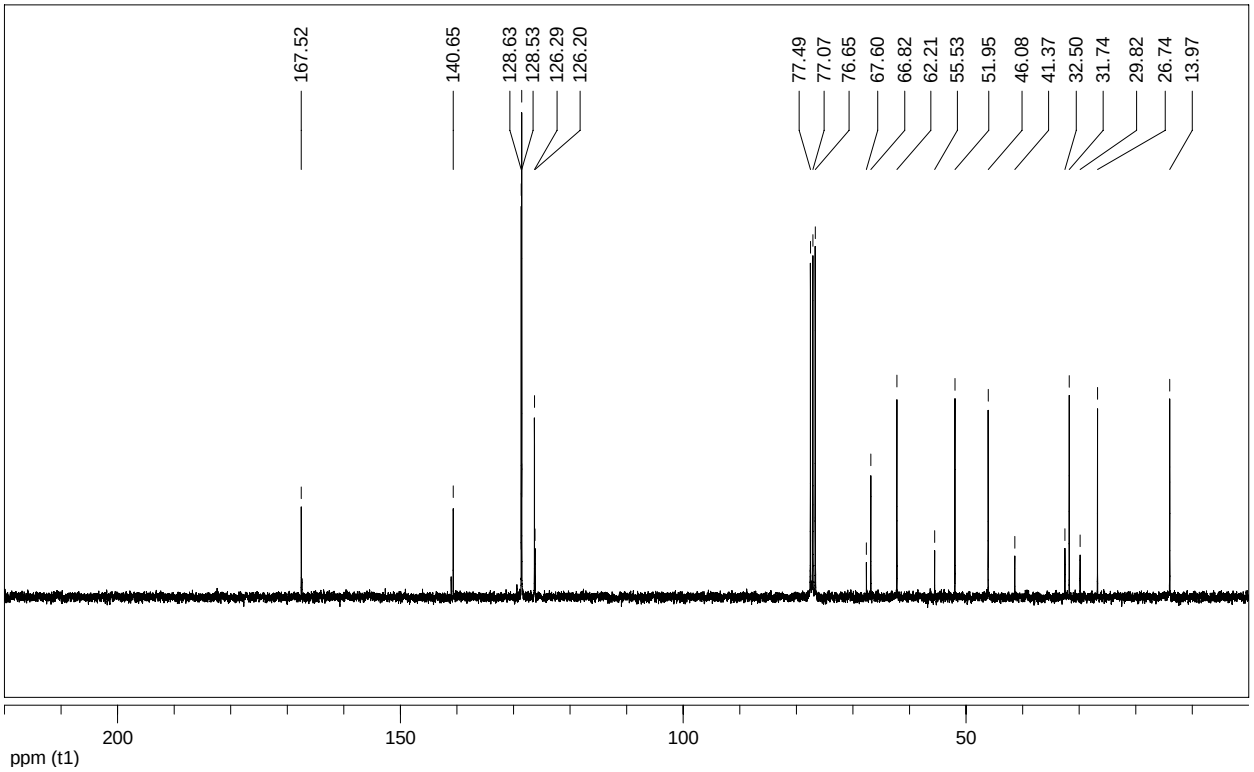
Ethyl 2,3-dibromo-3-phenylbutanoate (*erythro:threo* = 67:33) (1k)



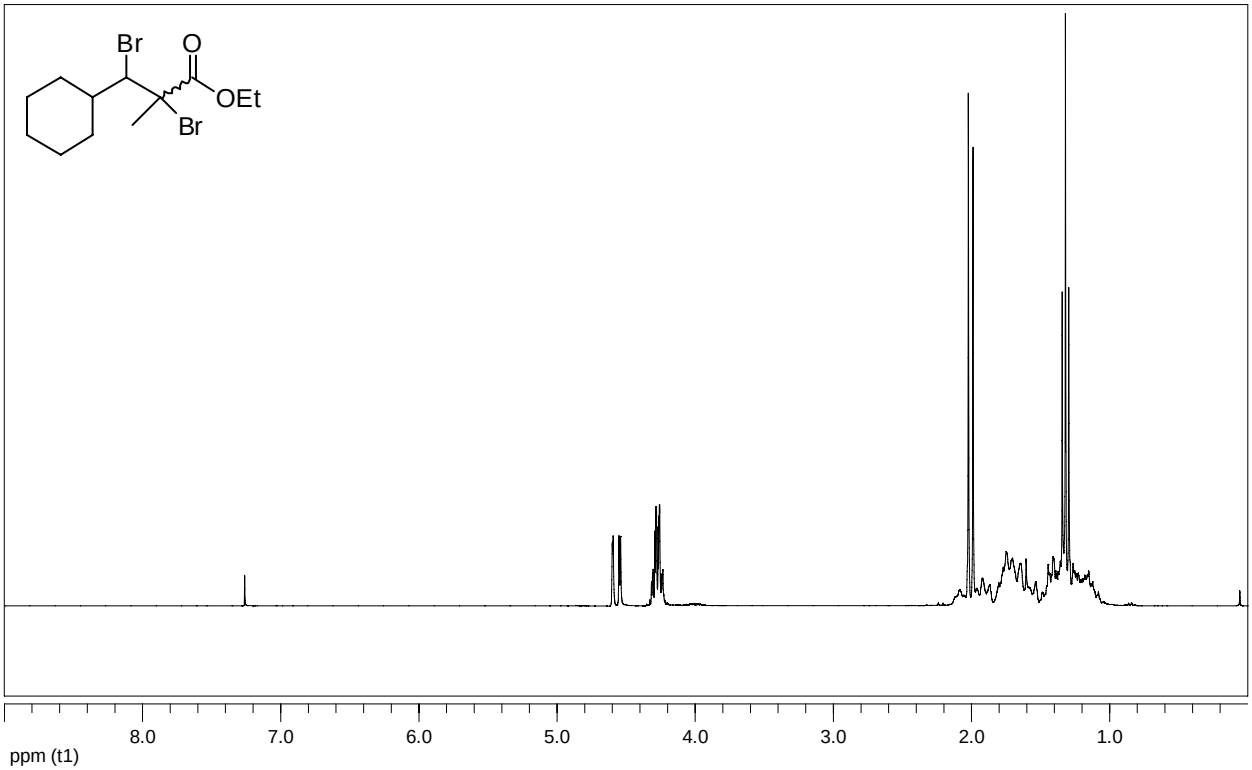


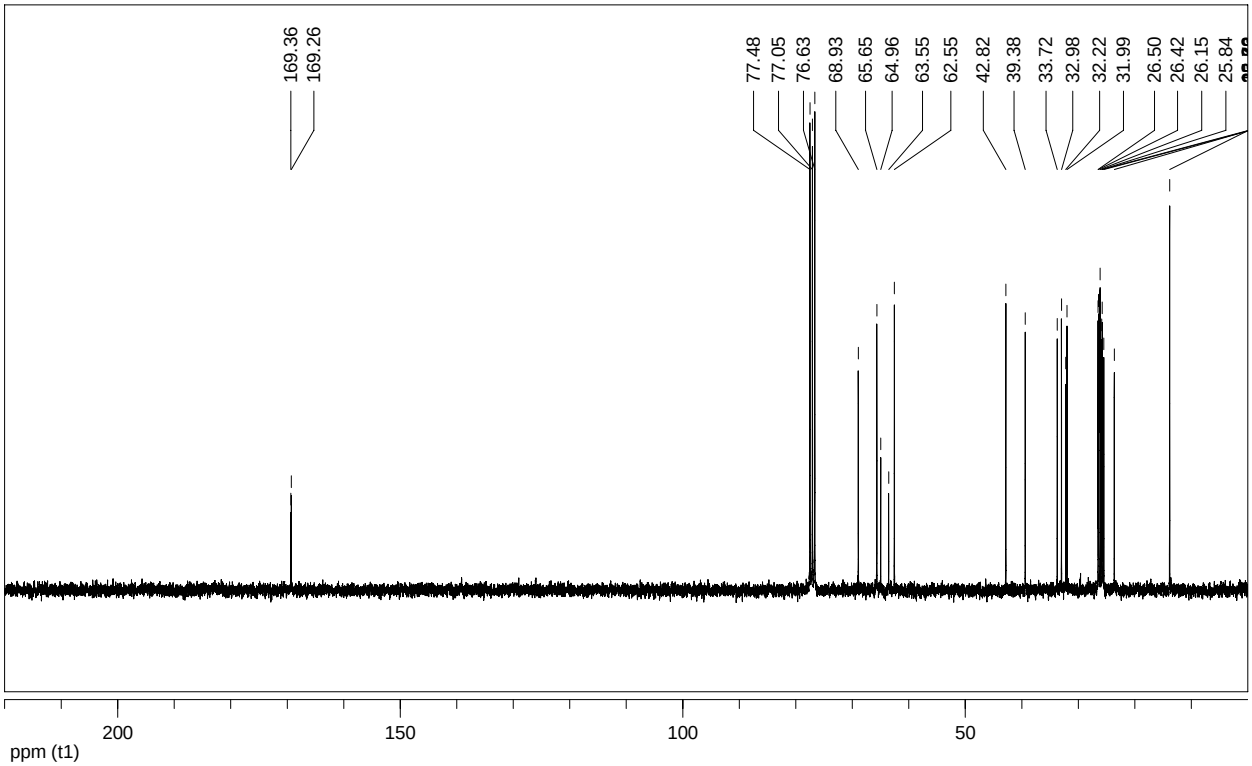
Ethyl 2,3-dibromo-3-methyl-5-phenylpentanoate (*erythro:threo* = 80:20) (1l)



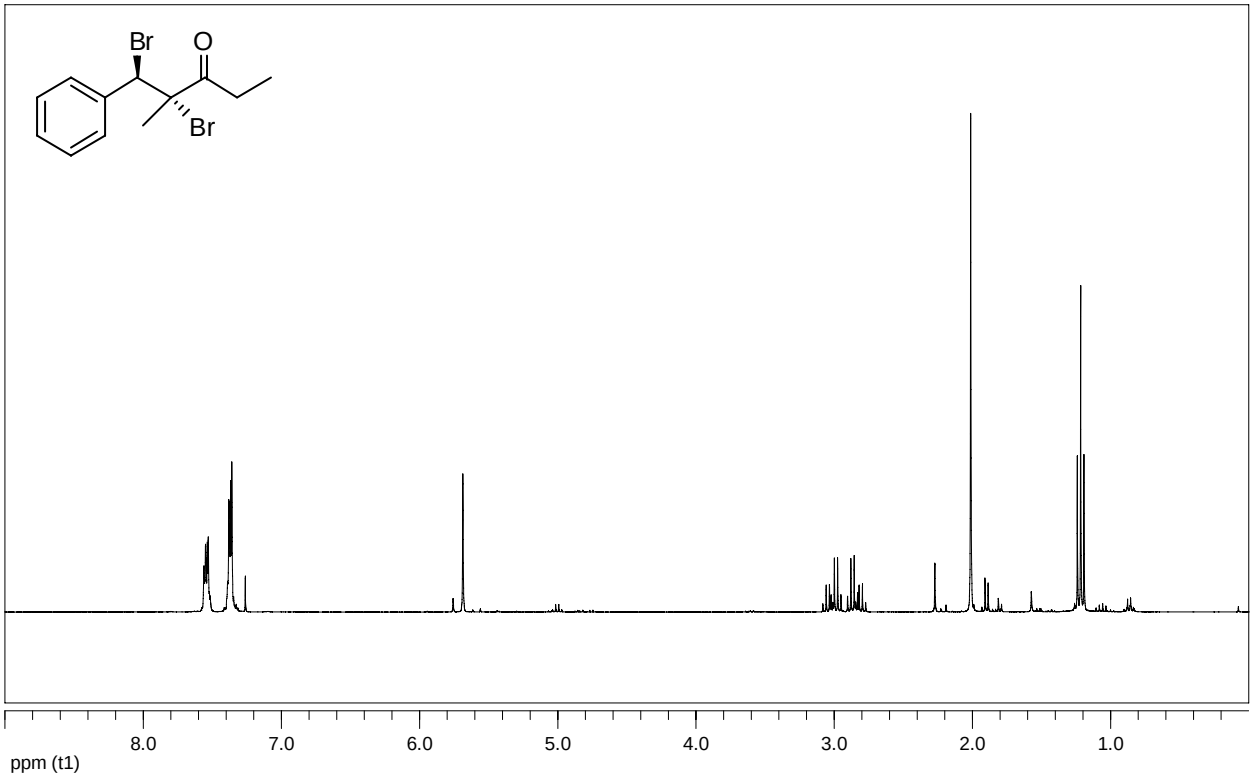


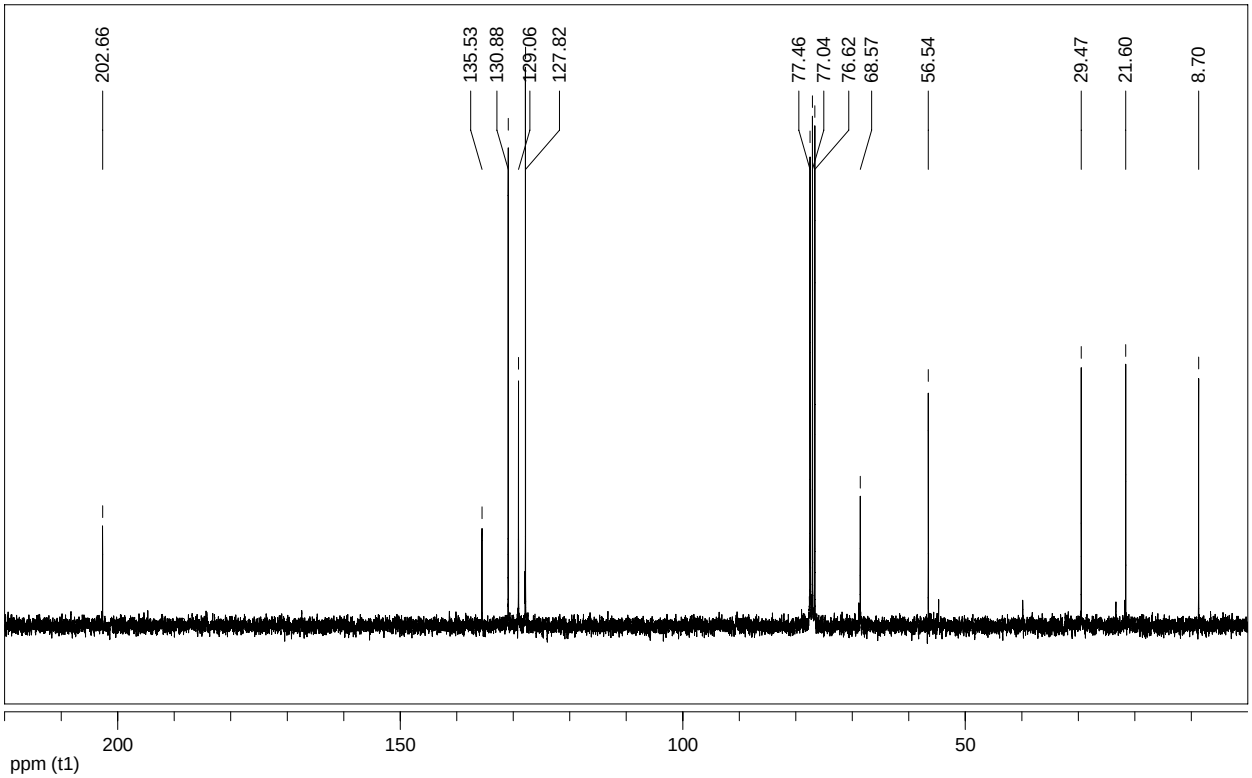
Ethyl 2,3-dibromo-3-cyclohexyl-2-methylpropanoate (*erythro:threo* = 52:48) (1m)



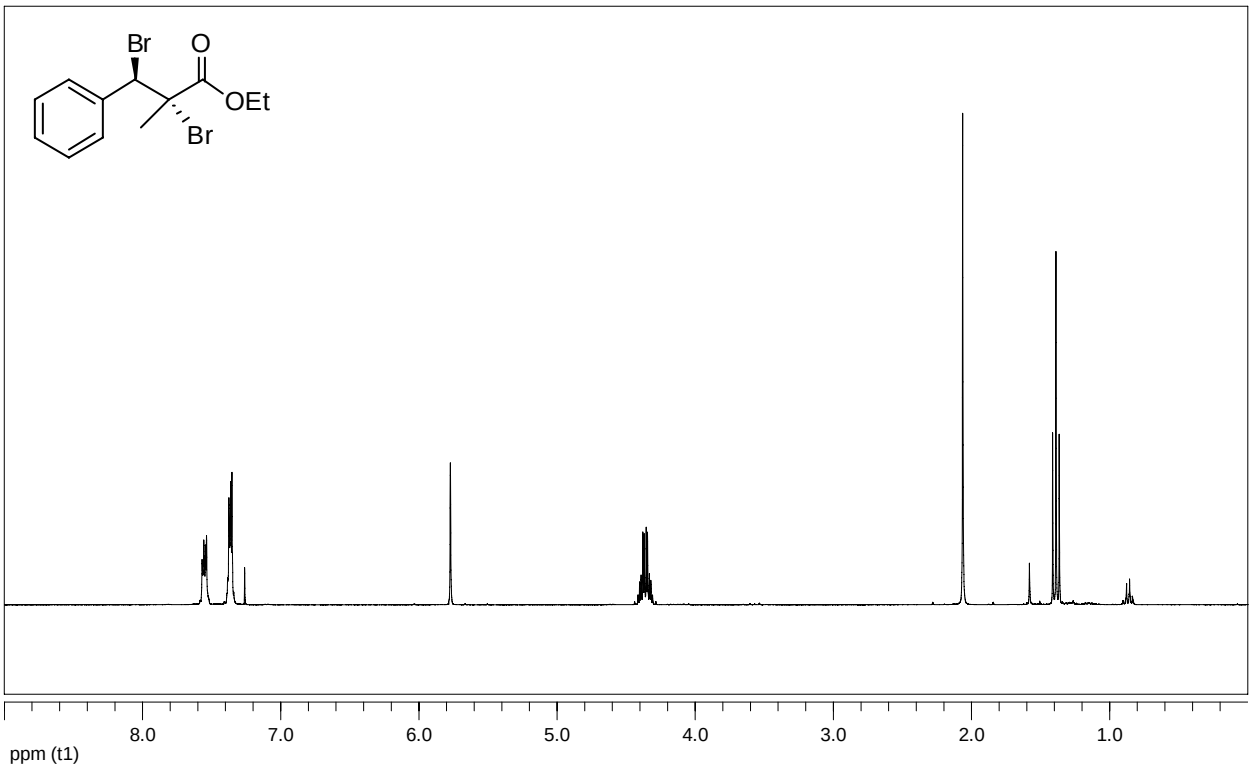


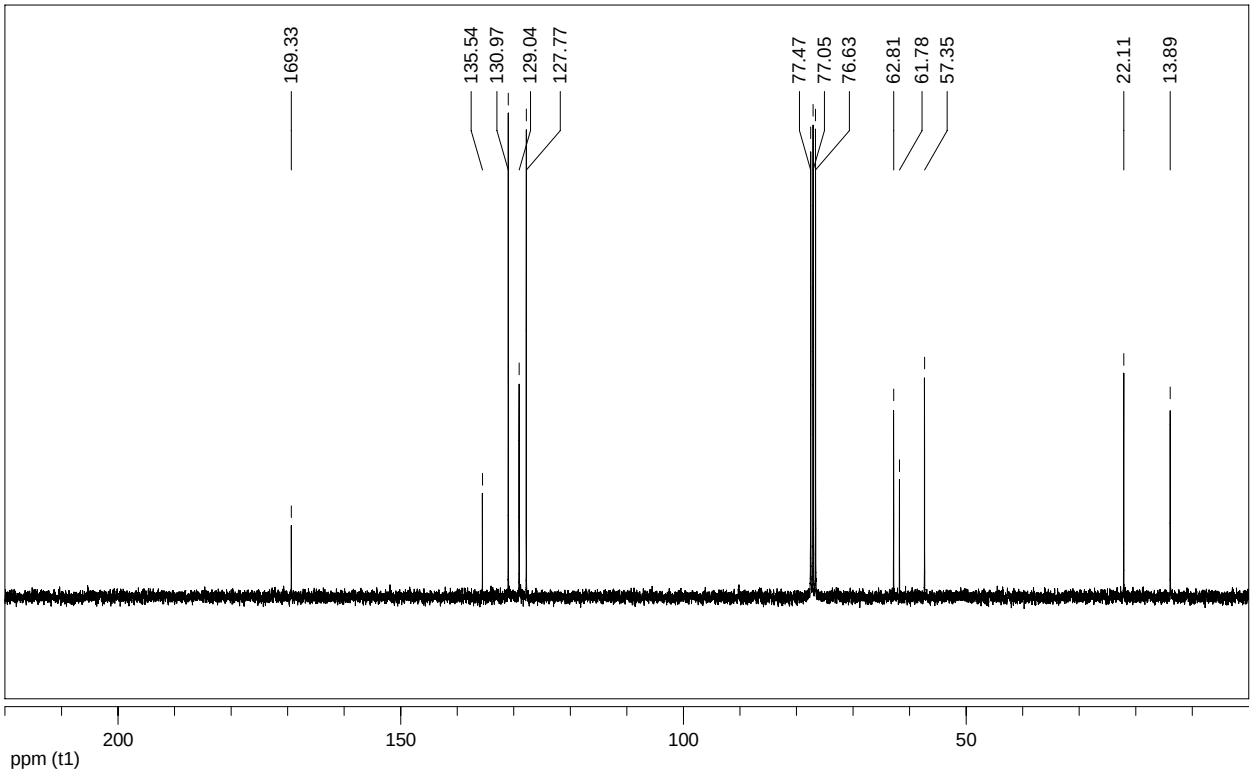
(*1R,2S*)-1,2-dibromo-2-methyl-1-phenylpentan-3-one (1n)



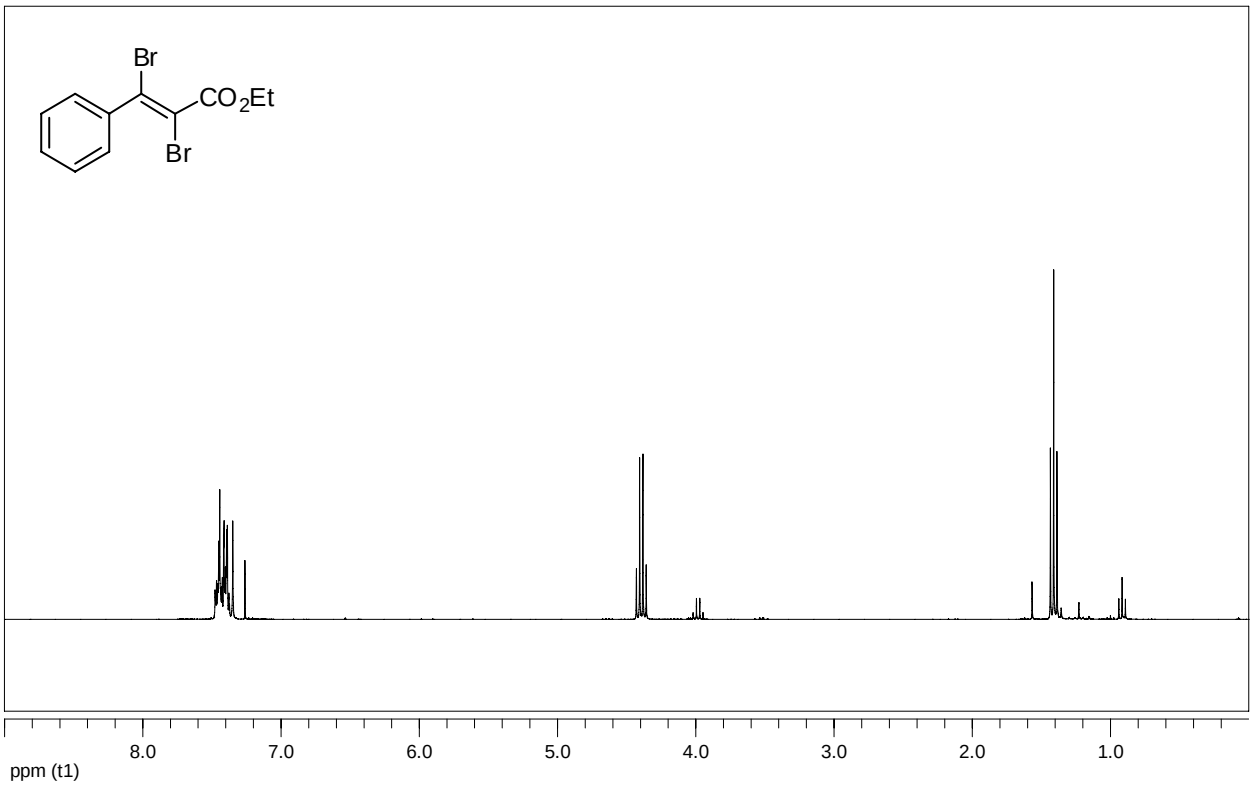


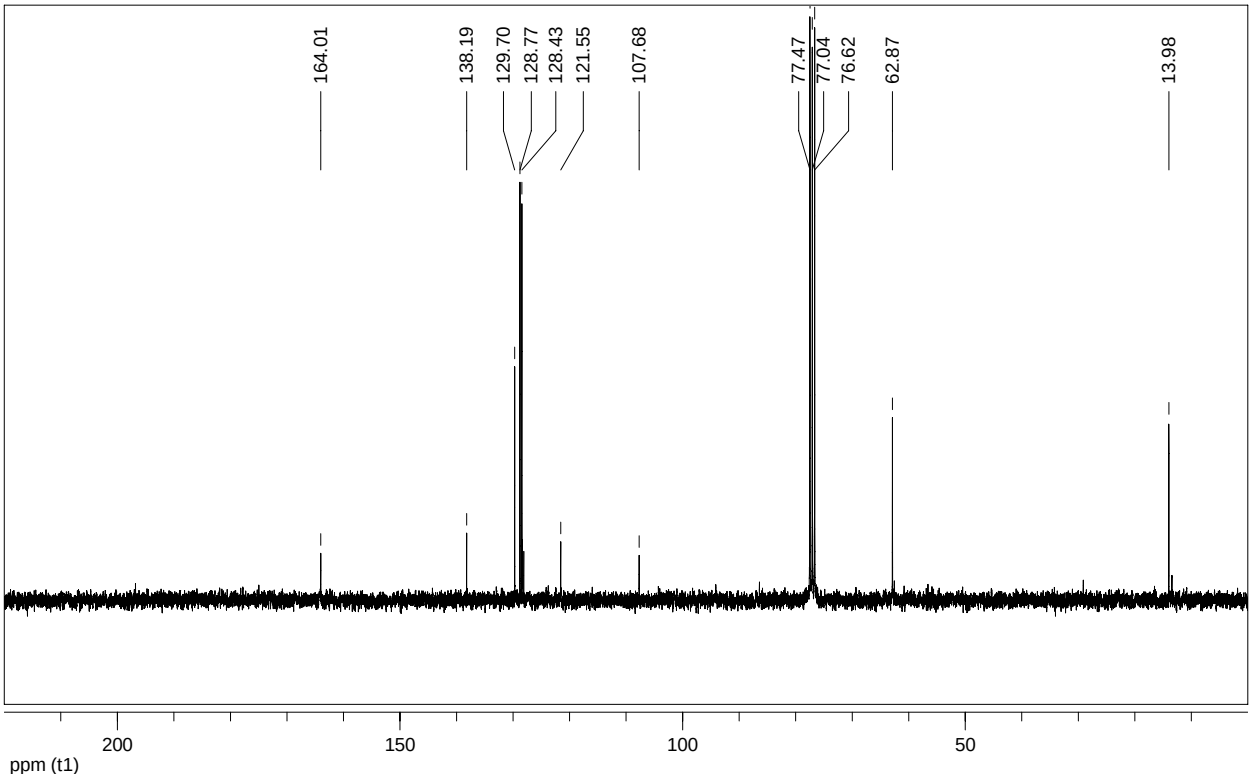
(*2S,3R*)-ethyl 2,3-dibromo-2-methyl-3-phenylpropanoate (1o)



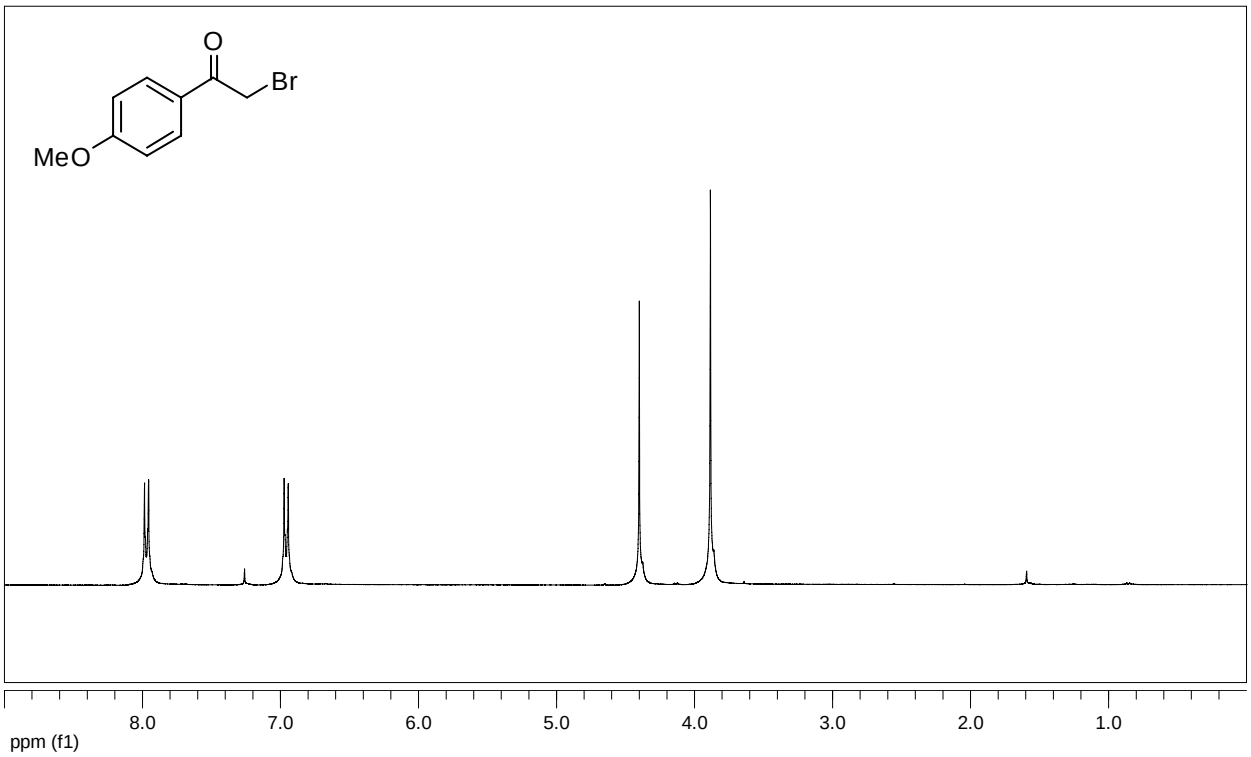


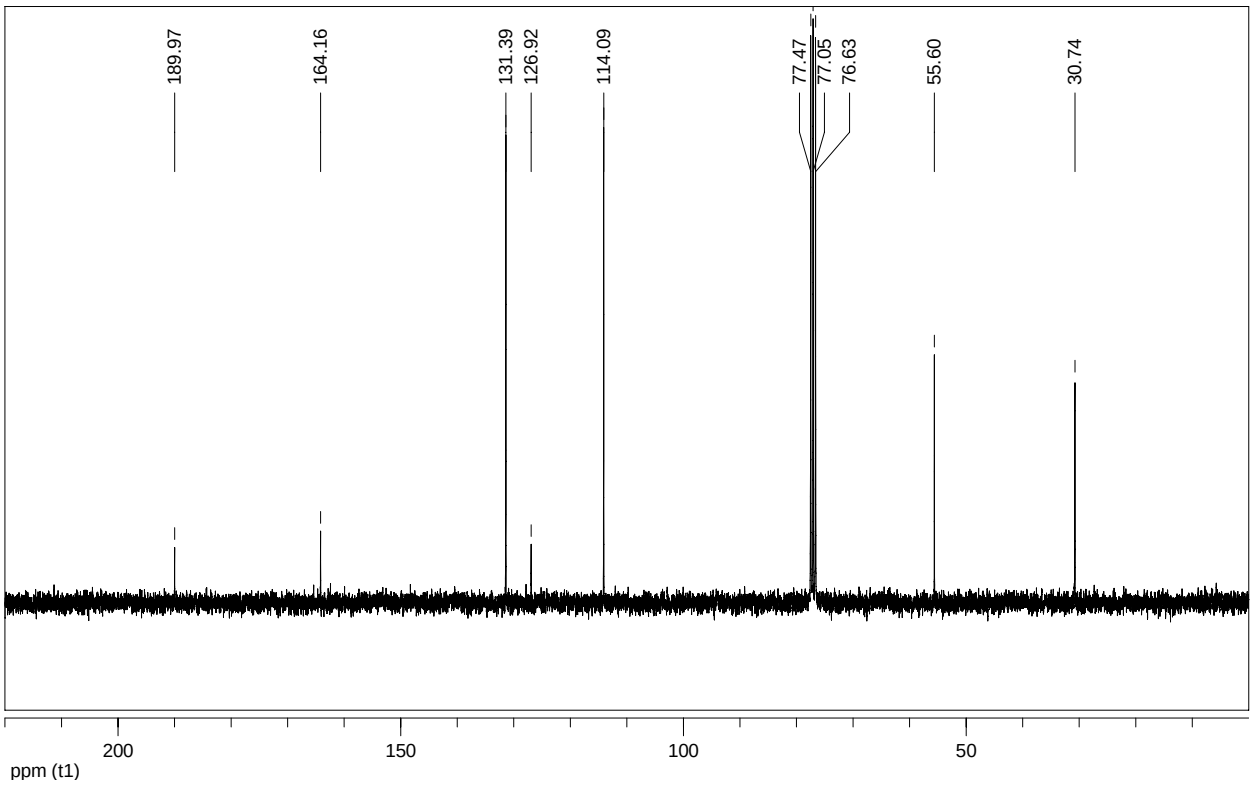
(*E*)-ethyl 2,3-dibromo-3-phenylacrylate (1p)



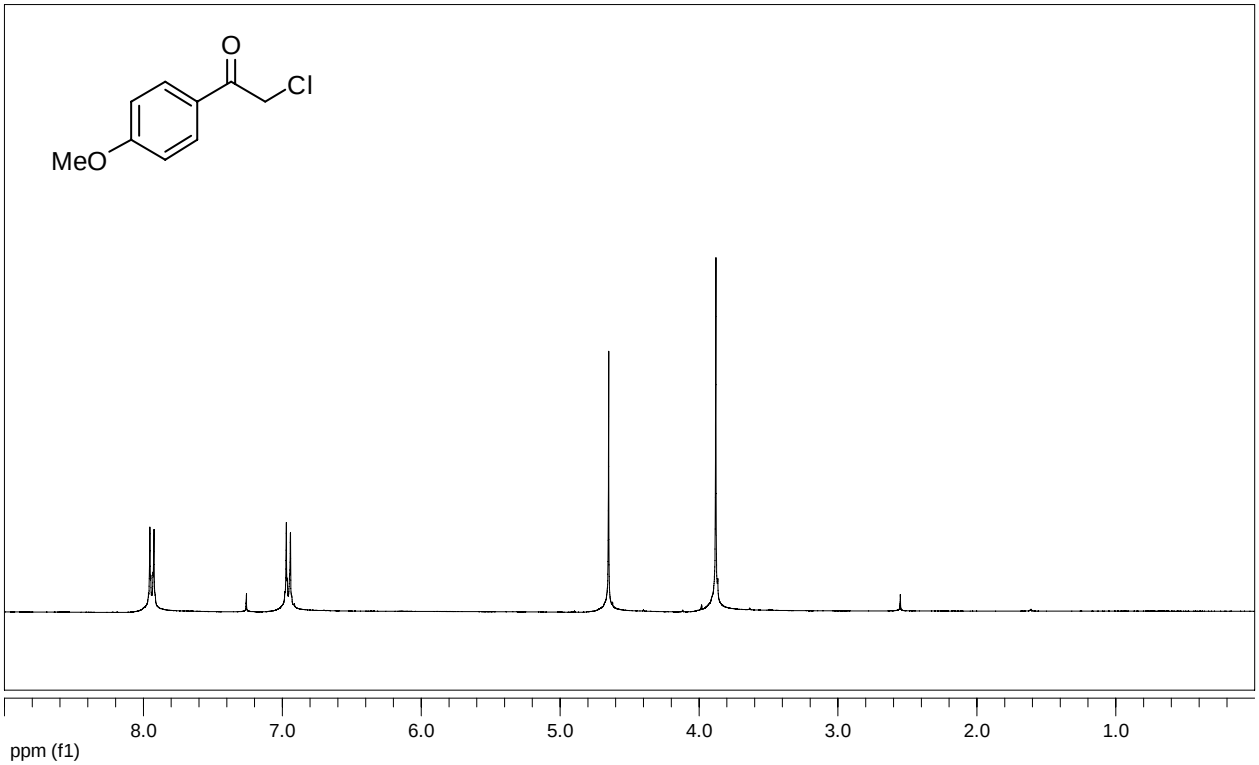


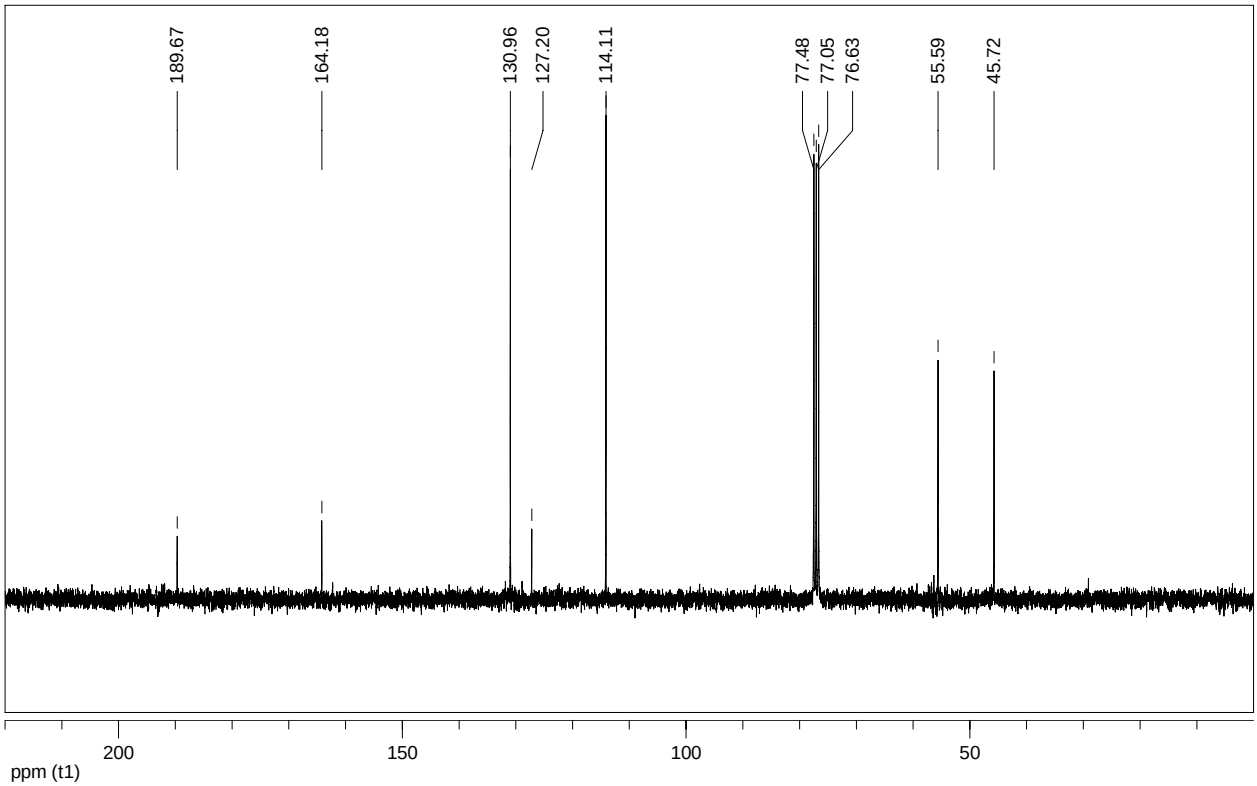
2-Bromo-1-(4-methoxyphenyl)ethanone (3a)



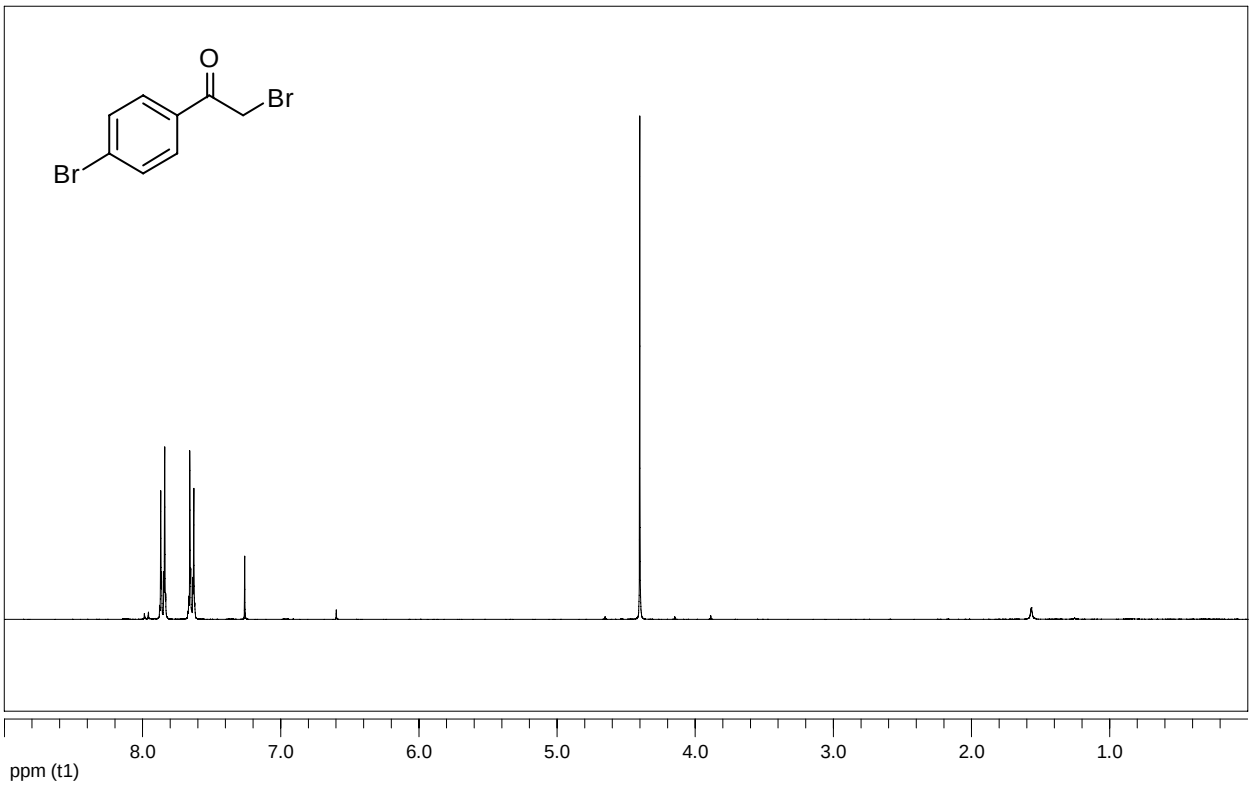


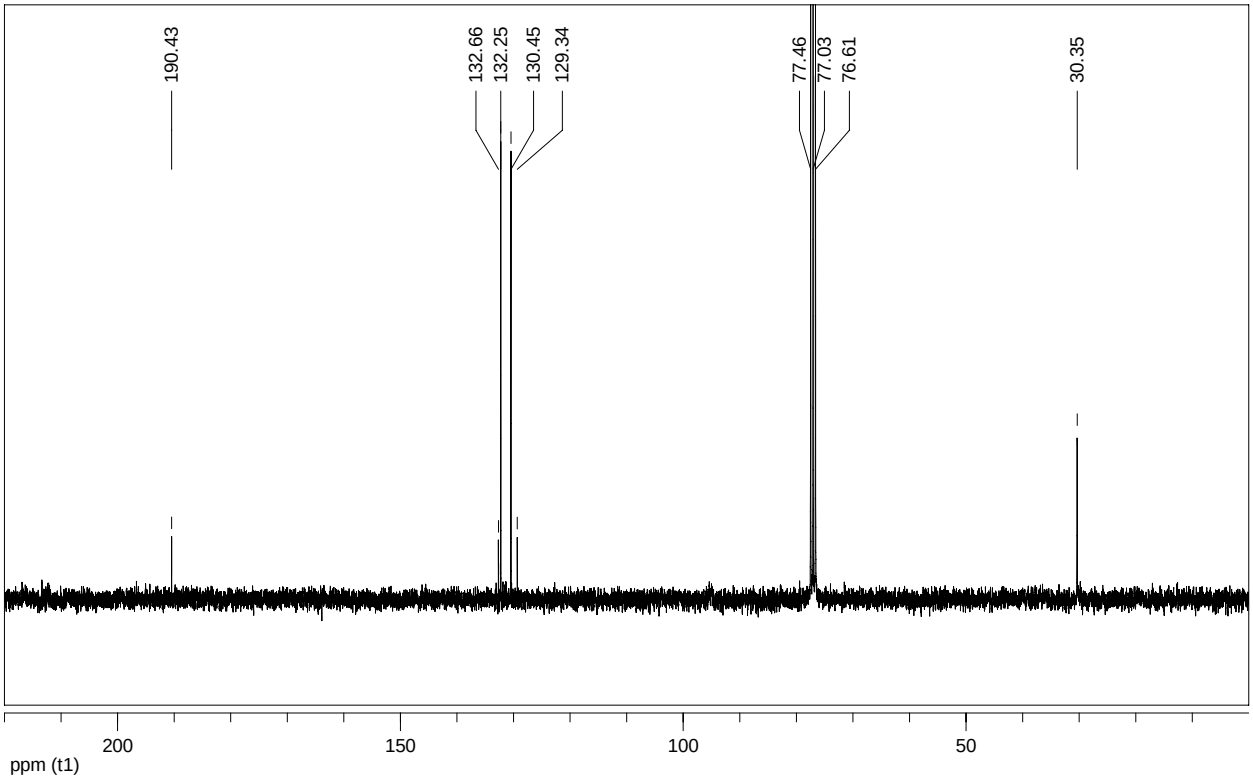
2-Chloro-1-(4-methoxyphenyl)ethanone (3b)



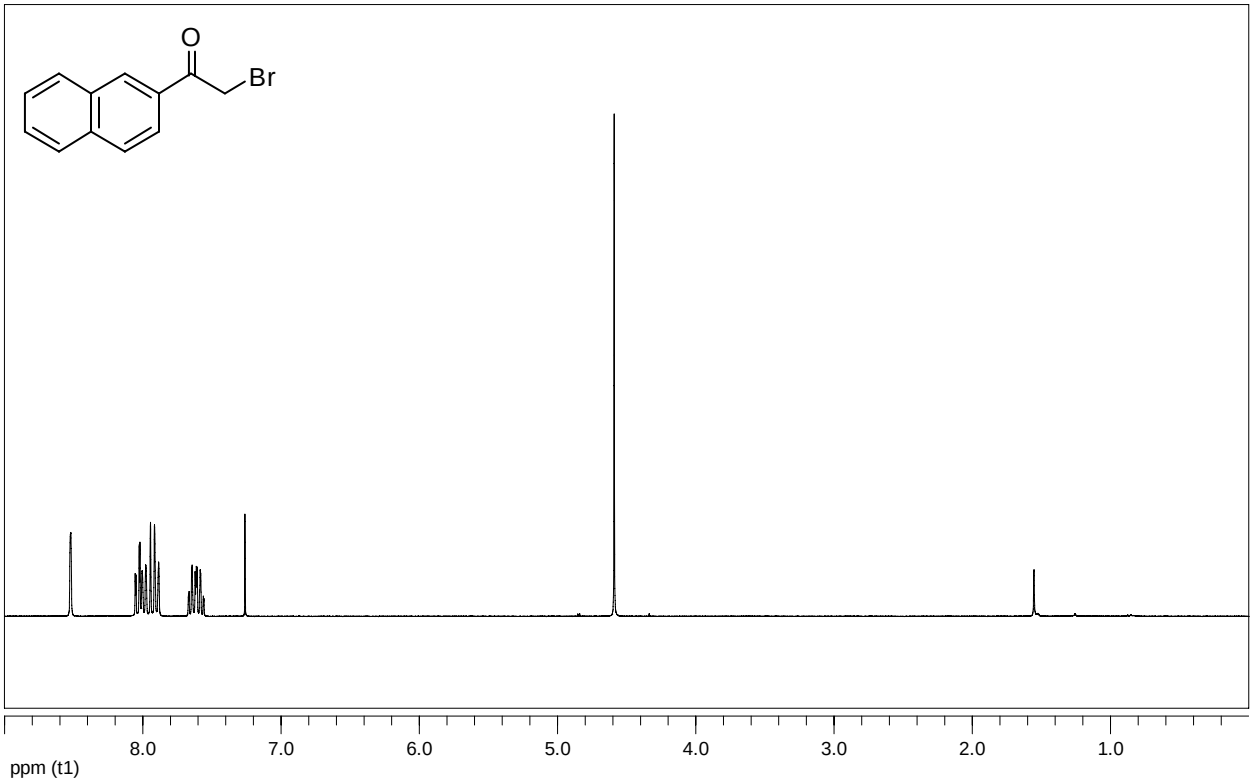


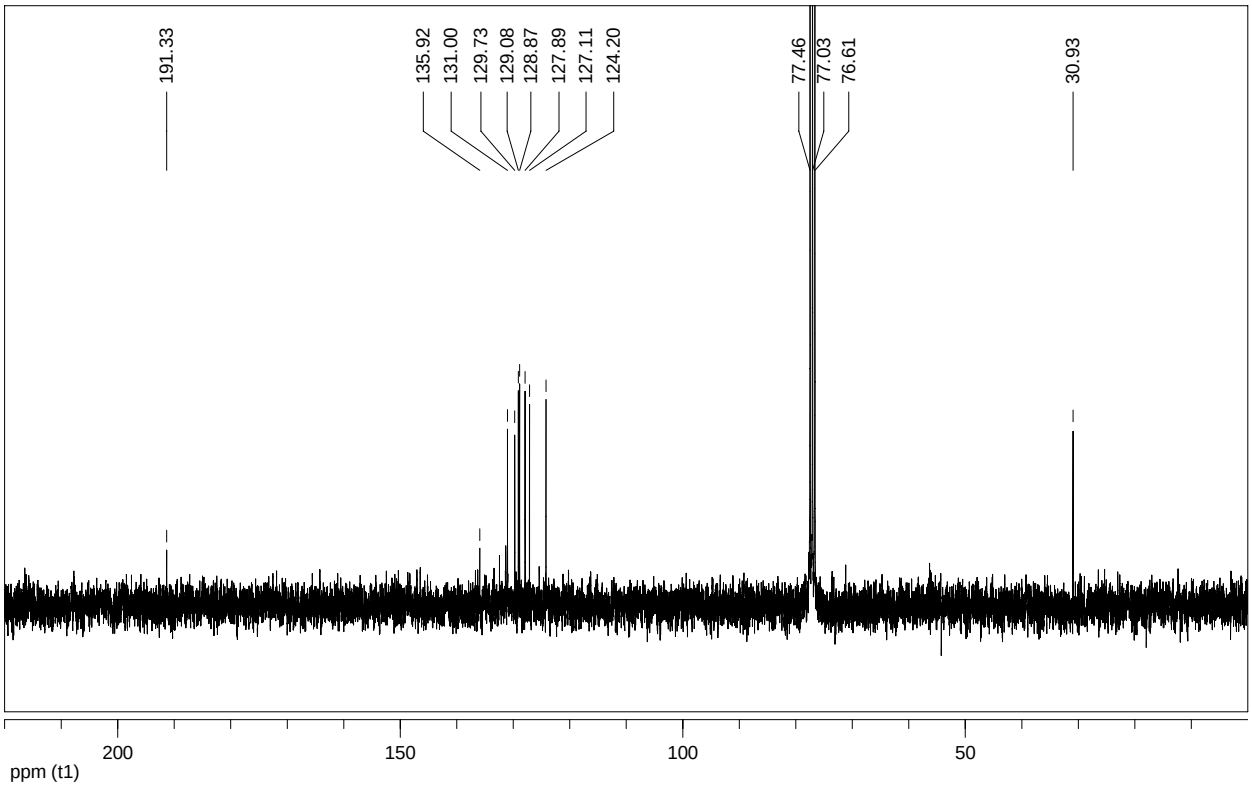
2-Bromo-1(4-bromophenyl)ethanone (3c)



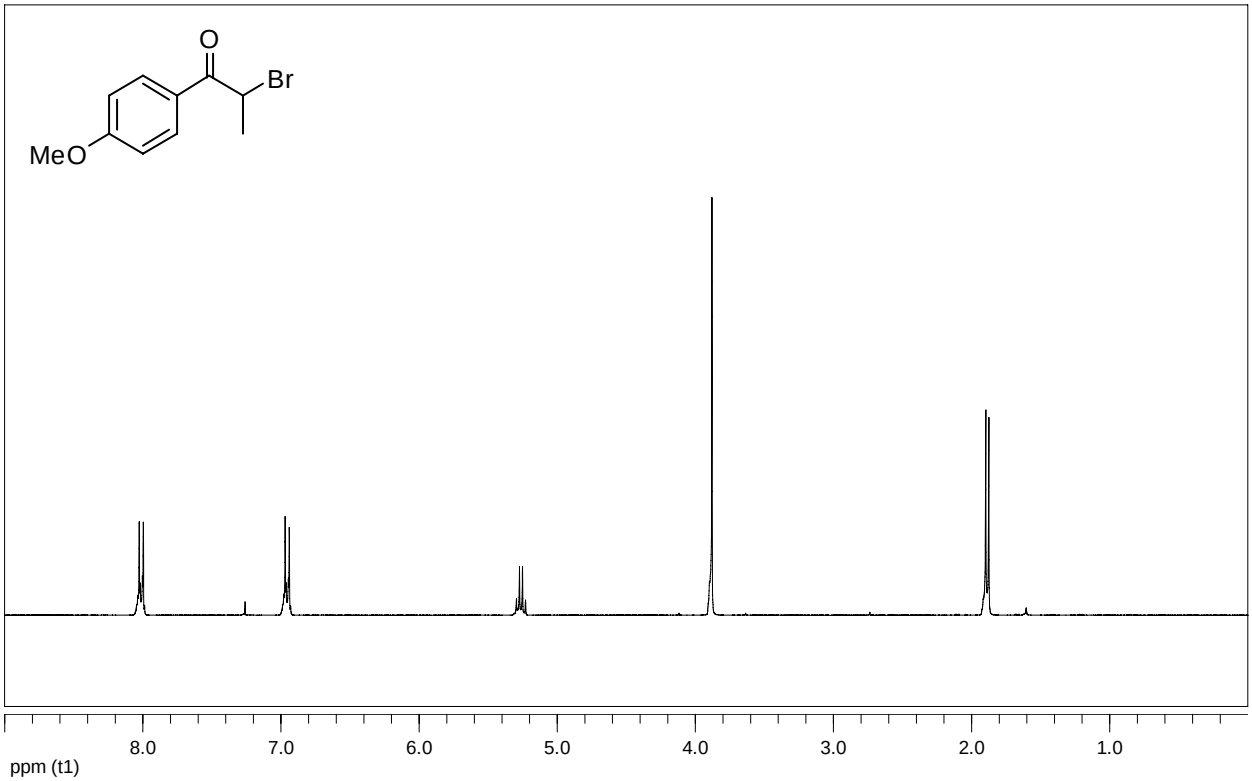


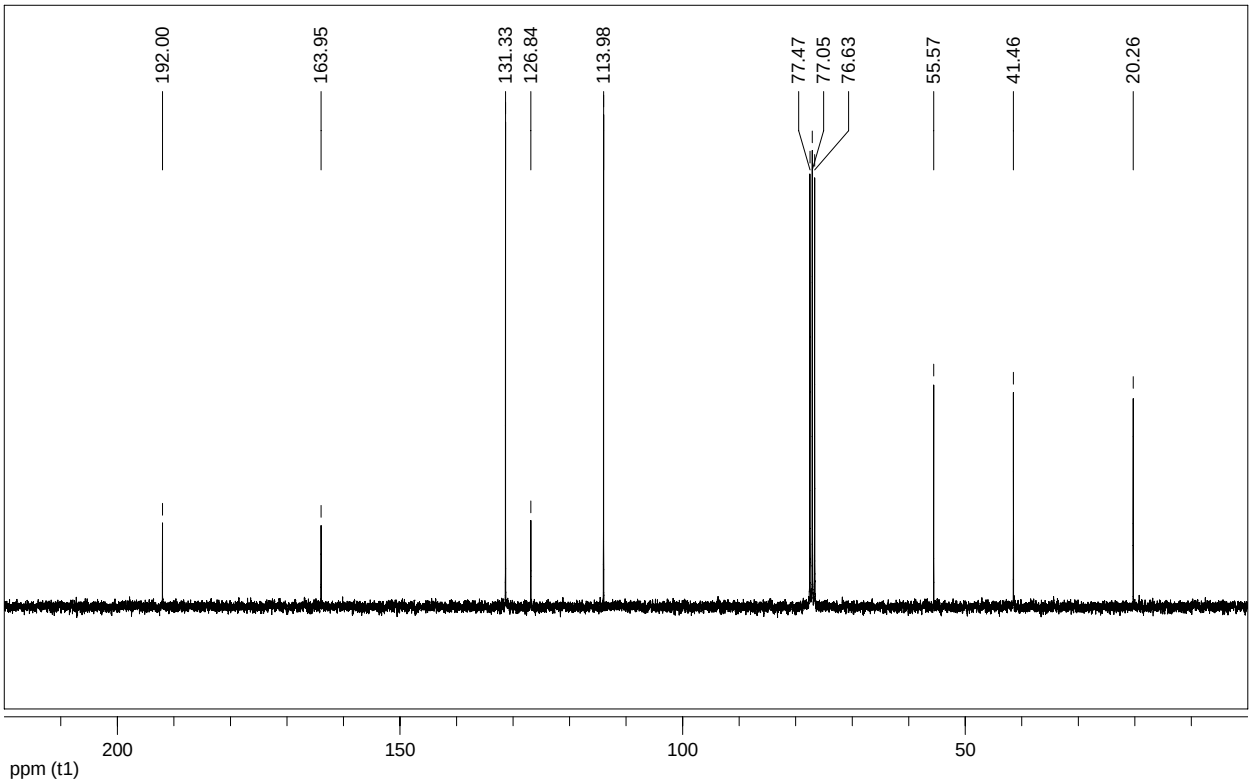
2-Bromo-1-(naphthalen-2-yl)ethanone (3e)



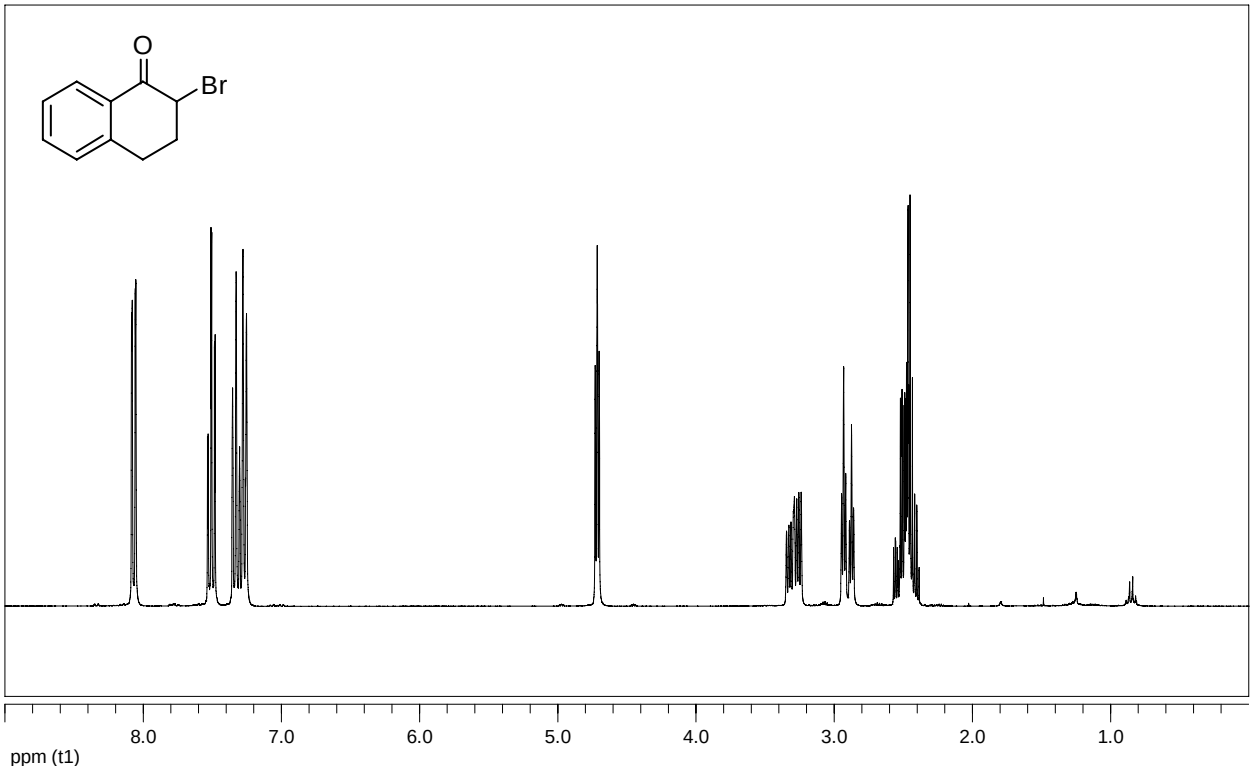


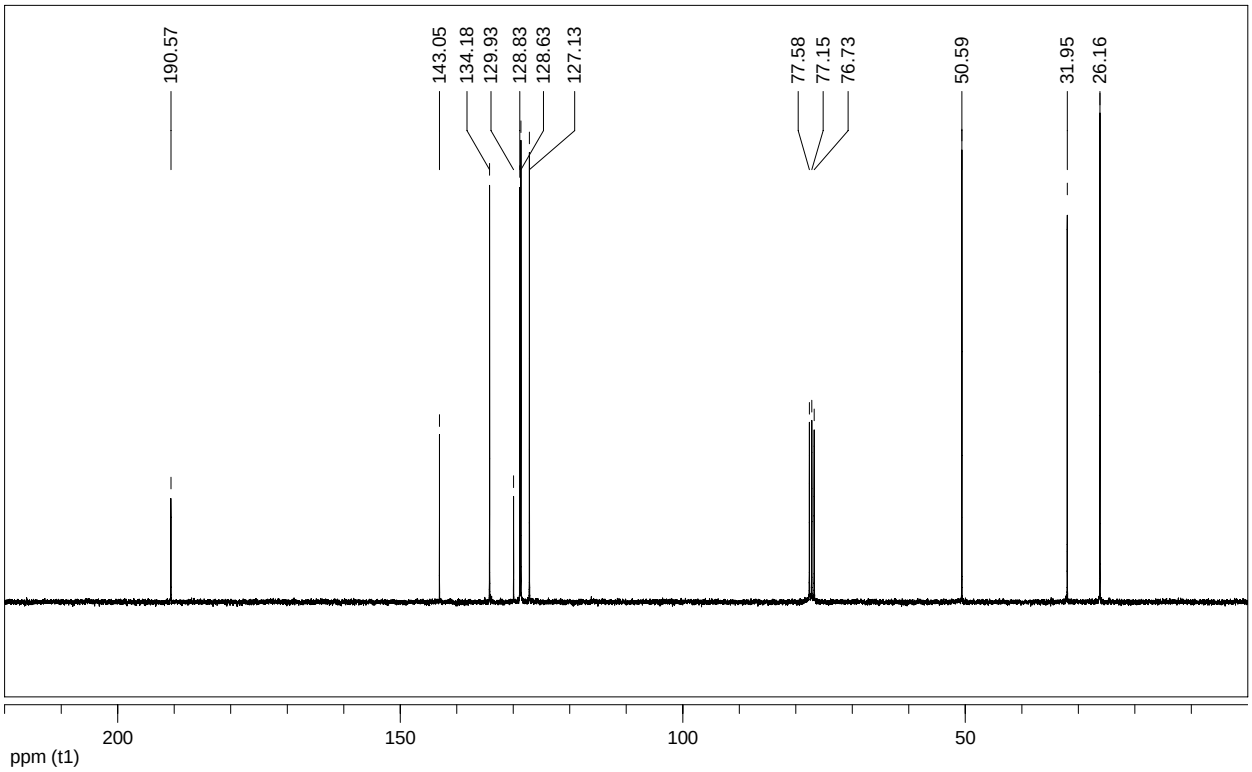
2-Bromo-1-(4-methoxyphenyl)propan-1-one (3f)



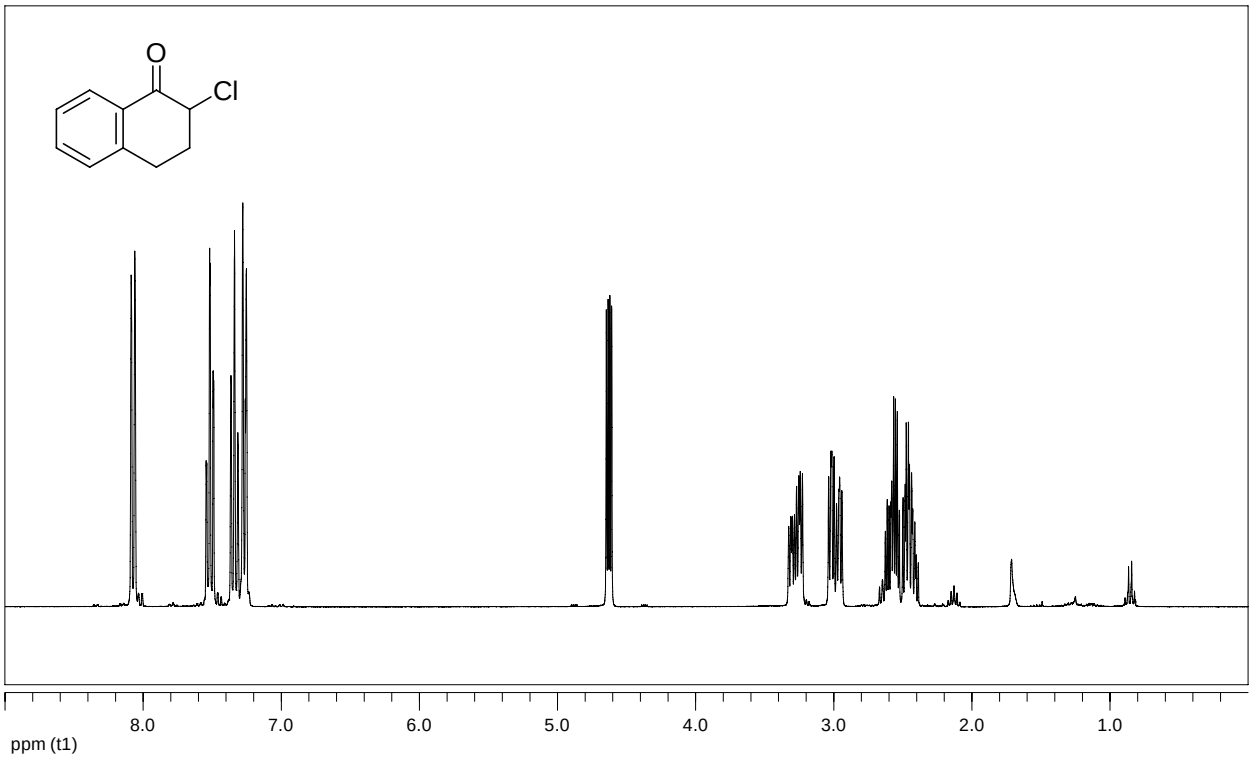


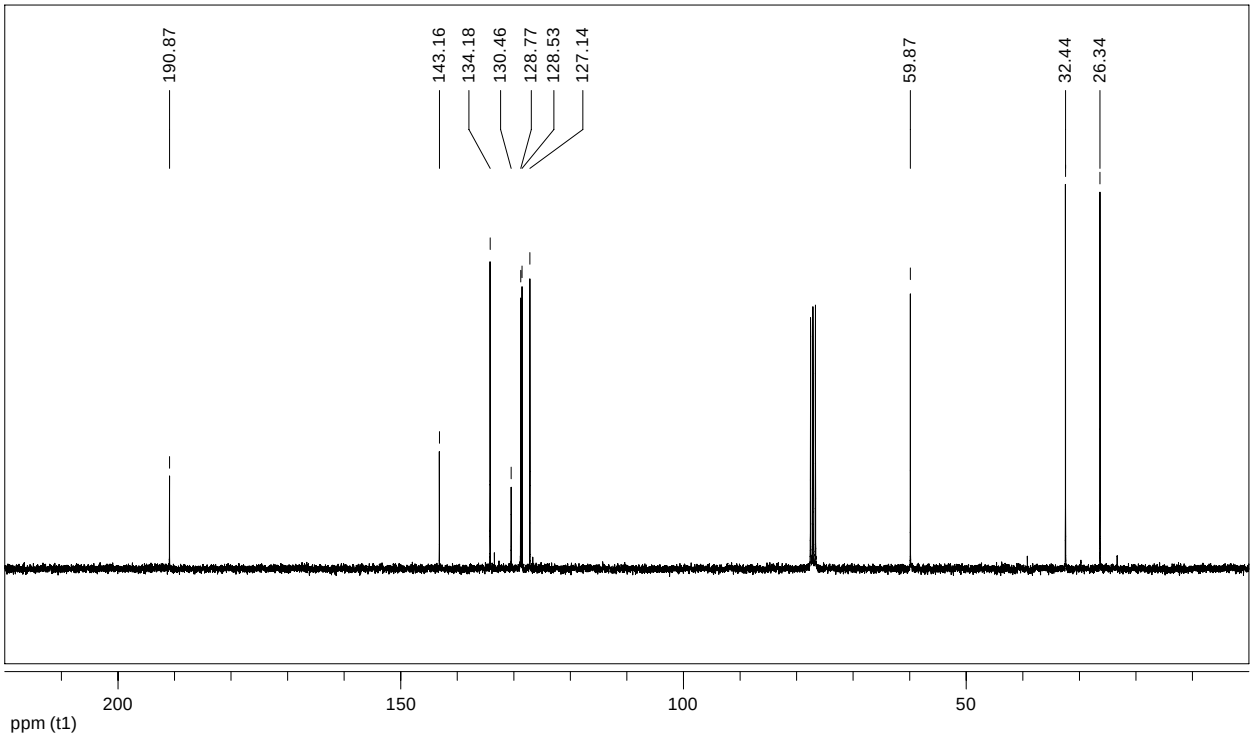
2-Bromo-3,4-dihydronaphthalen-1(2H)-one (3g)



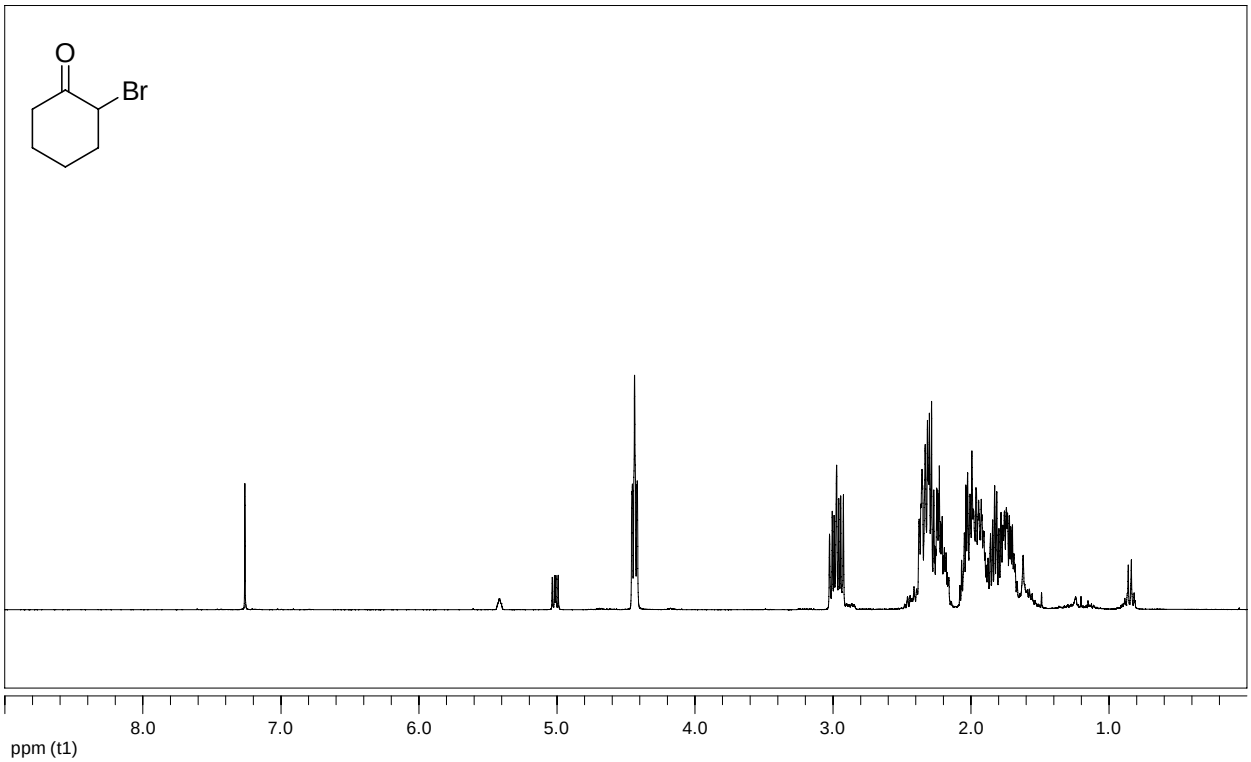


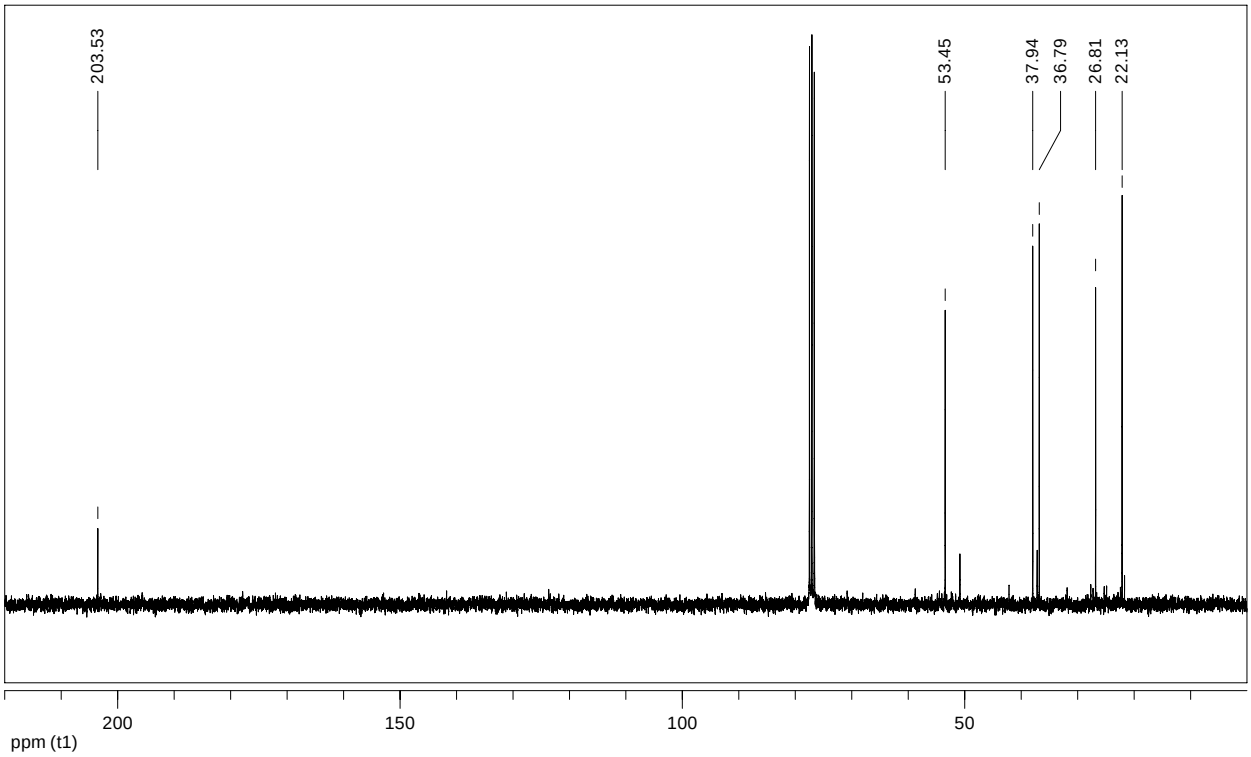
2-Chloro-3,4-dihydronaphthalen-1(2H)-one (3h)



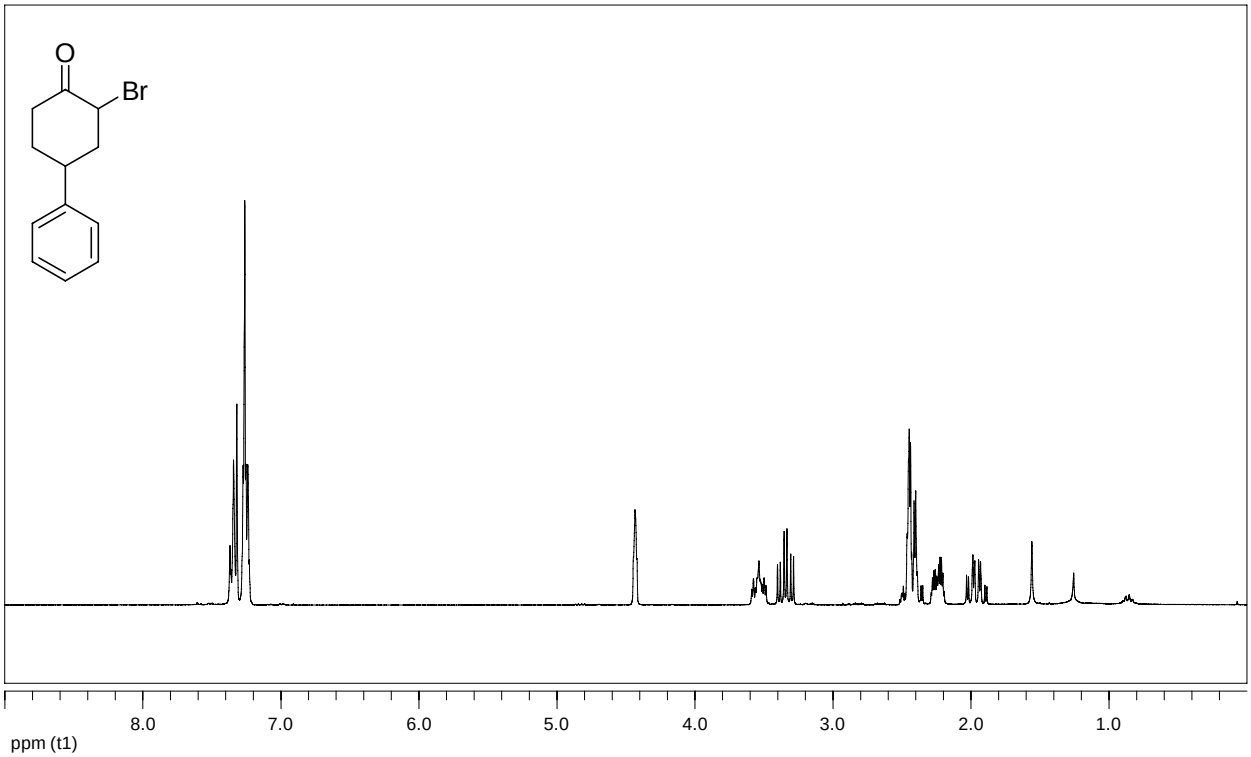


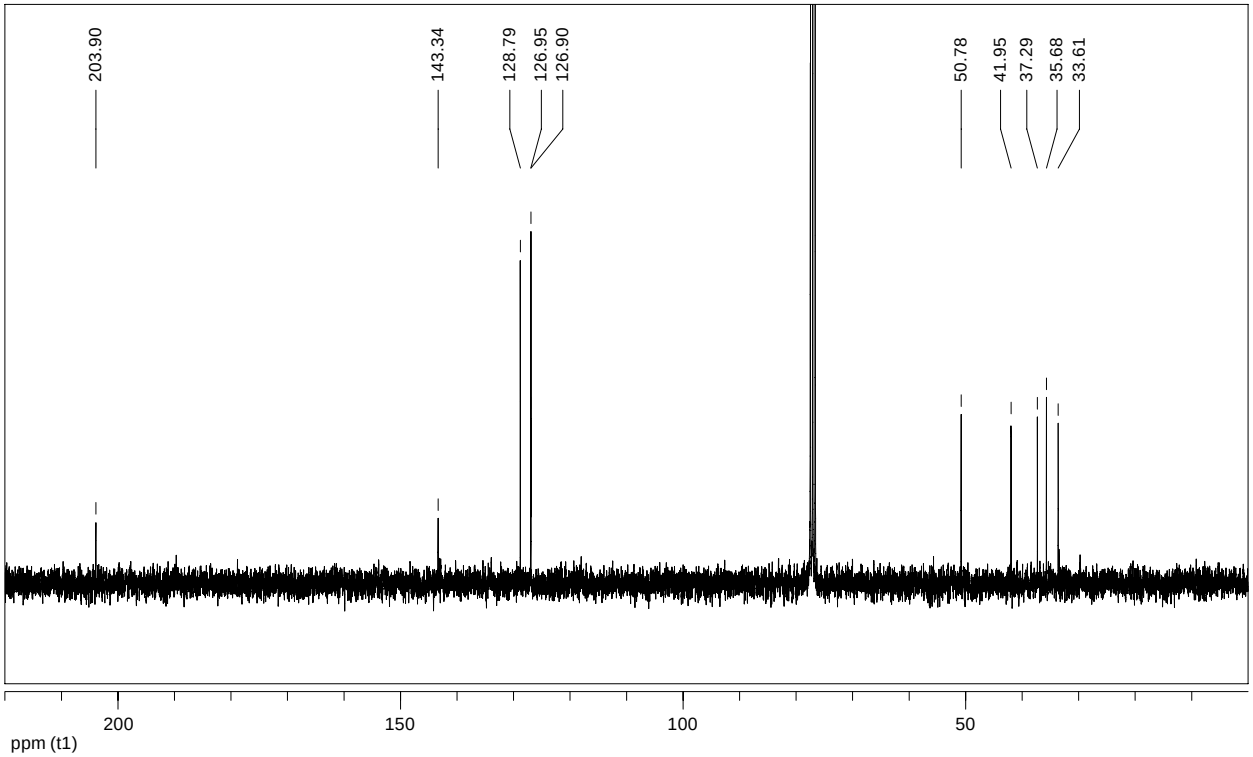
2-Bromocyclohexanone (3i)



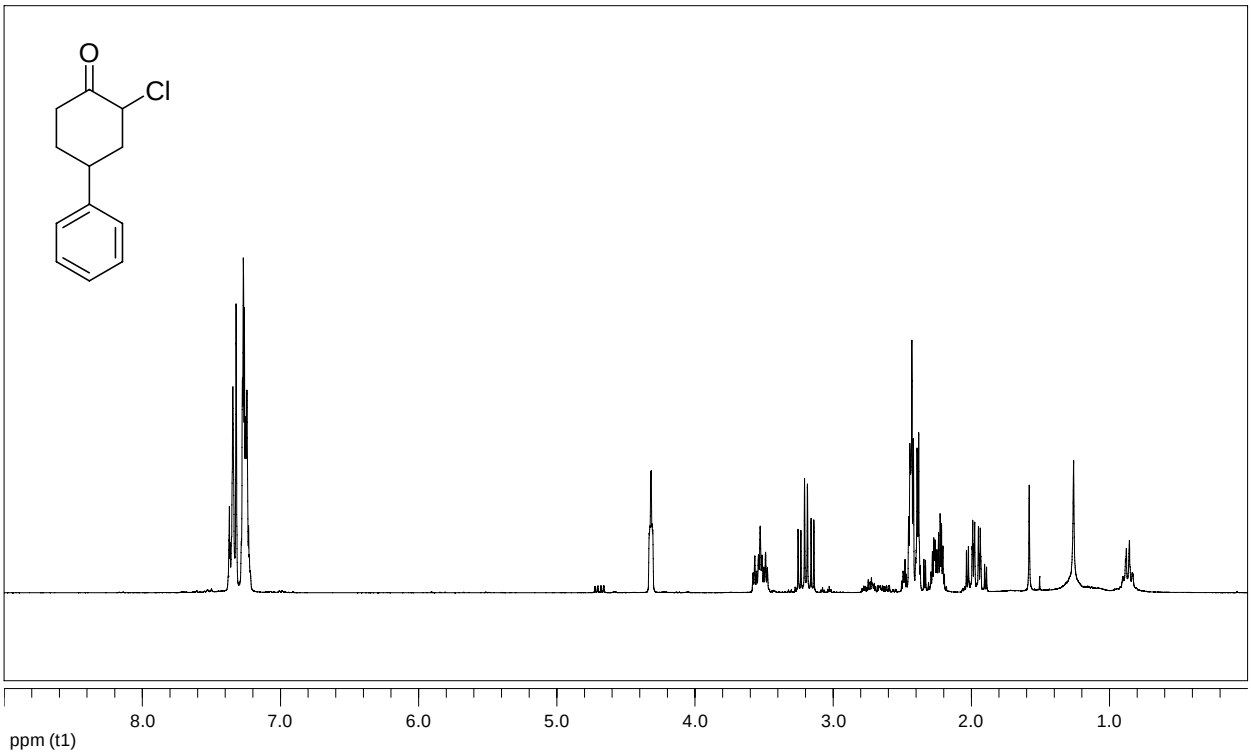


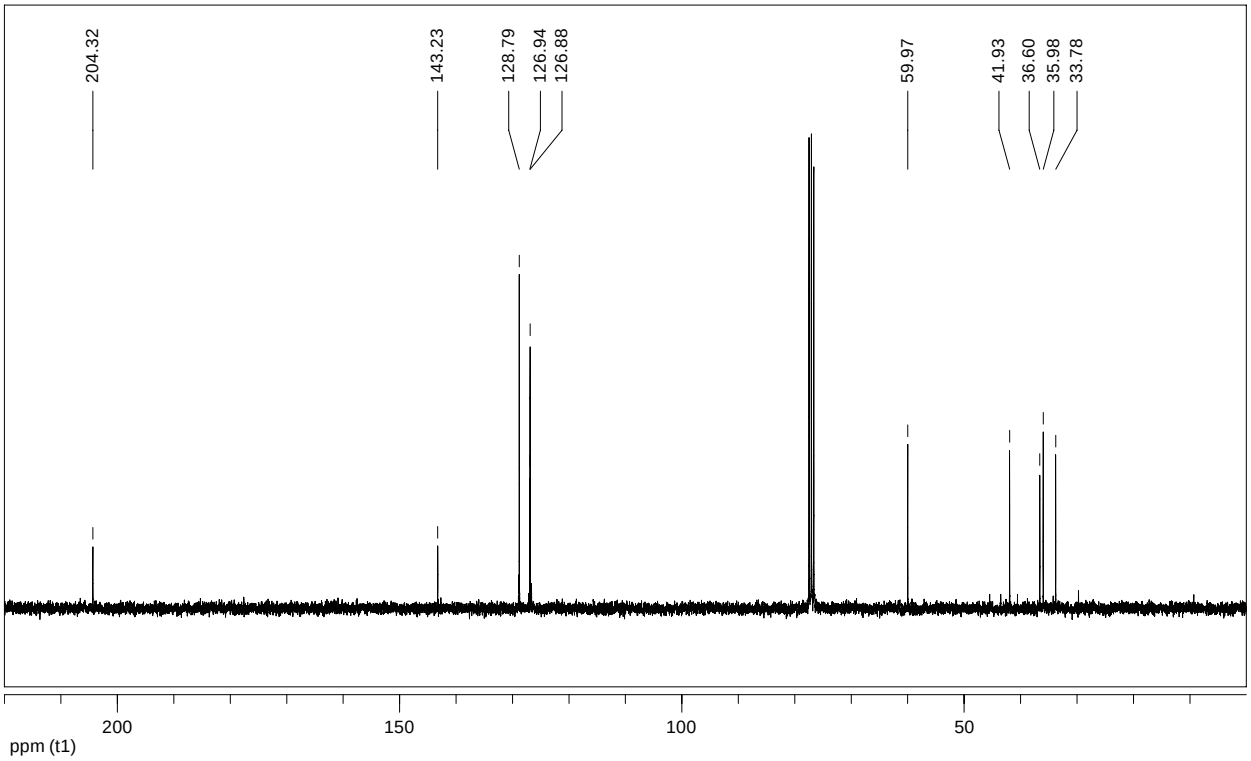
2-Bromo, 4-phenylcyclohexanone (3j)



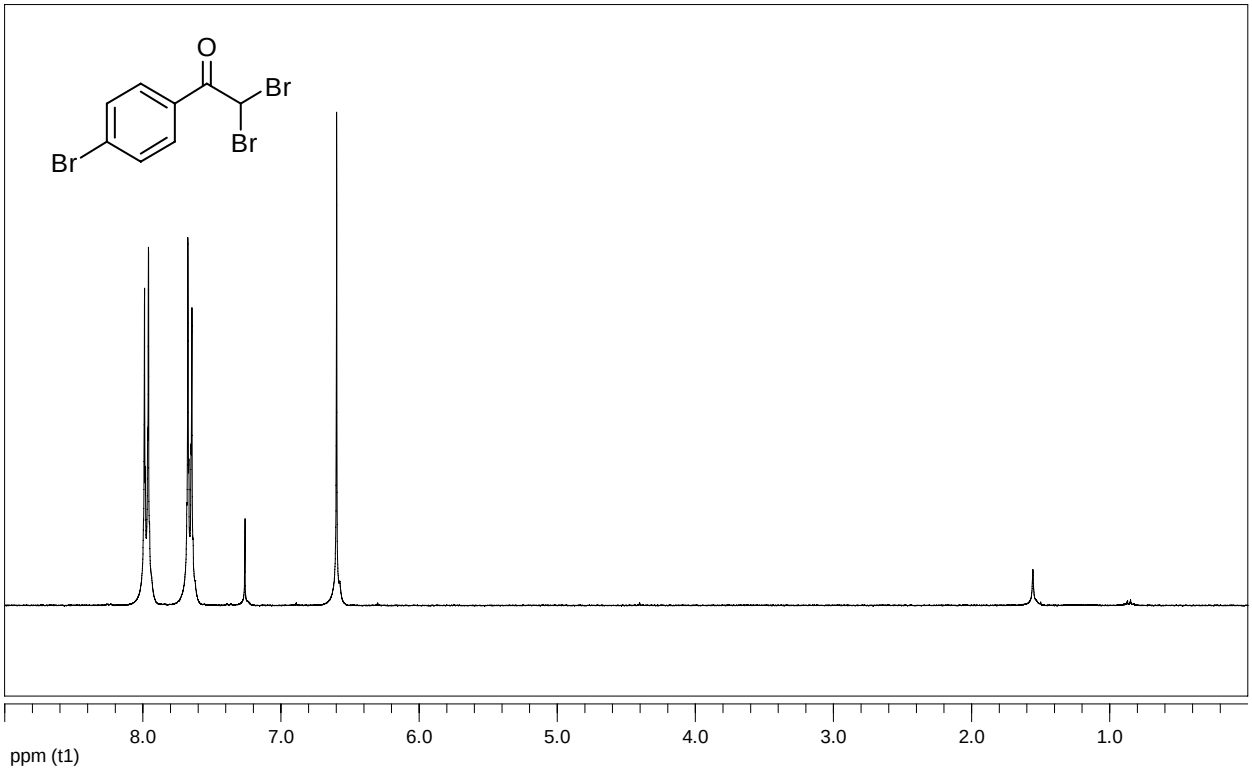


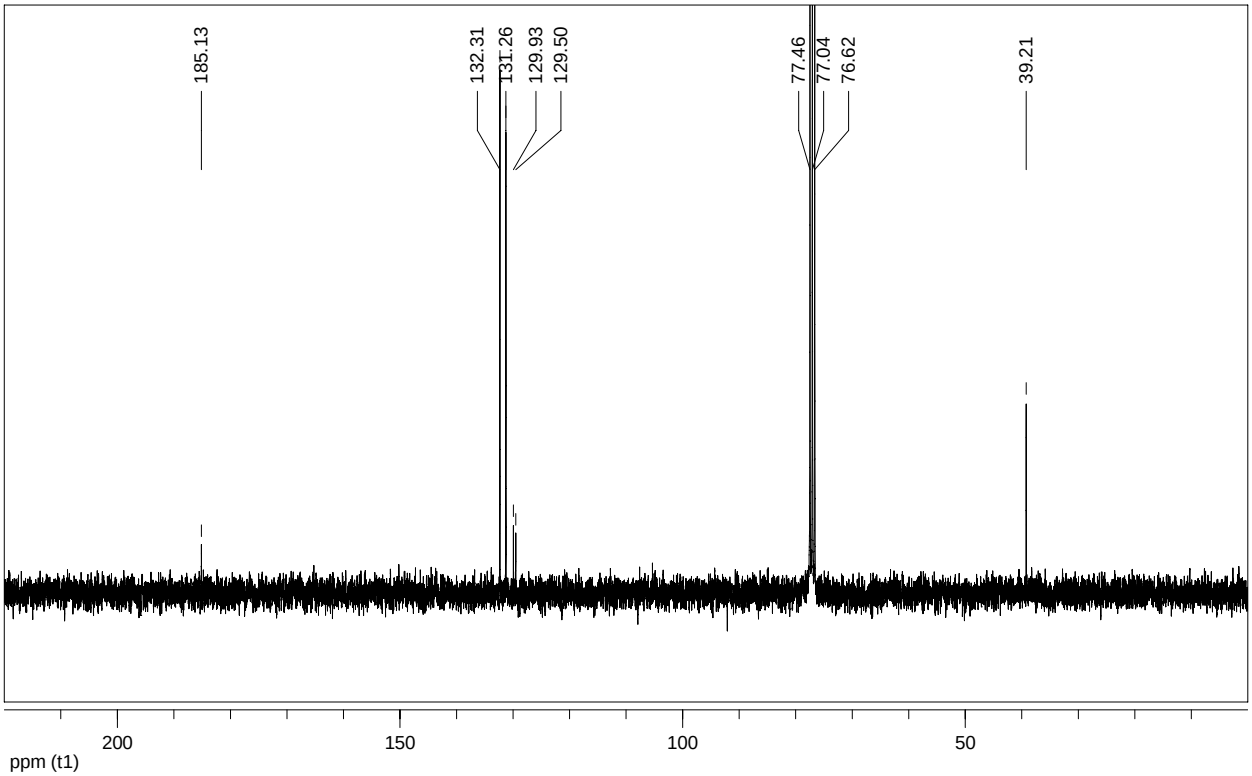
2-Chloro, 4-phenylcyclohexanone (3k)



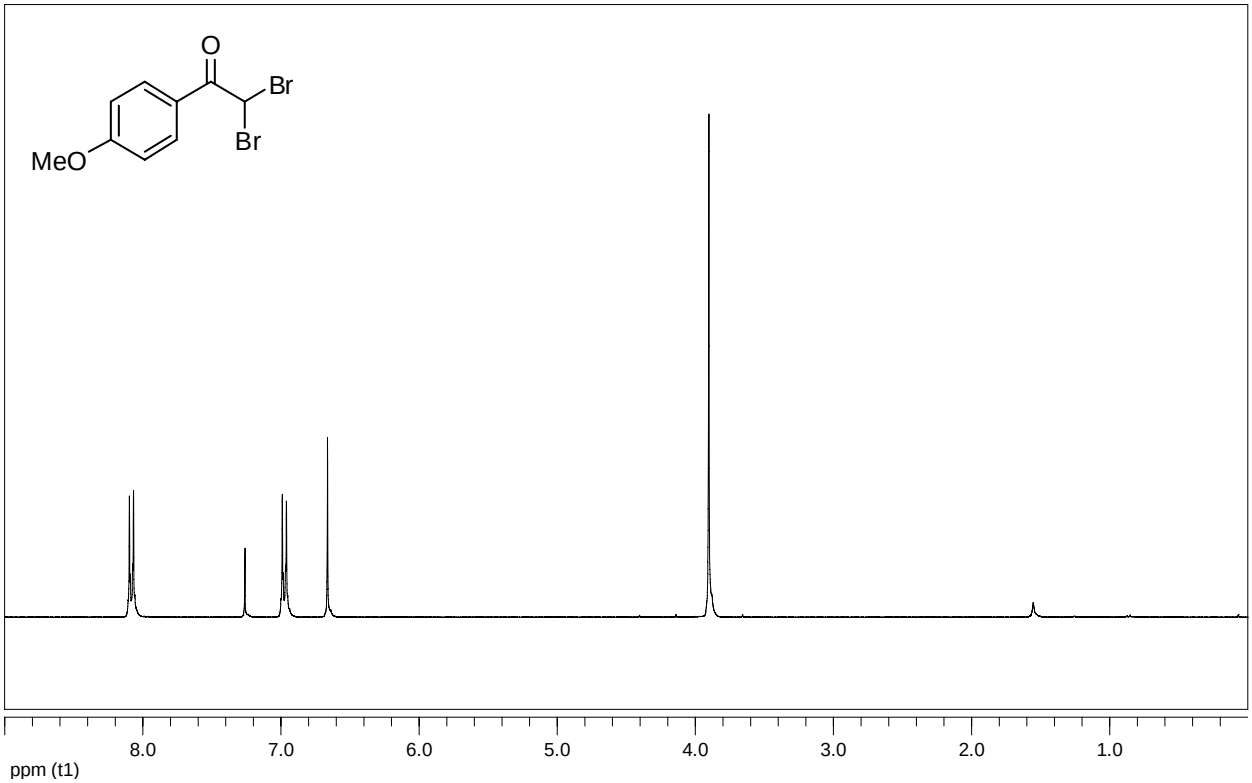


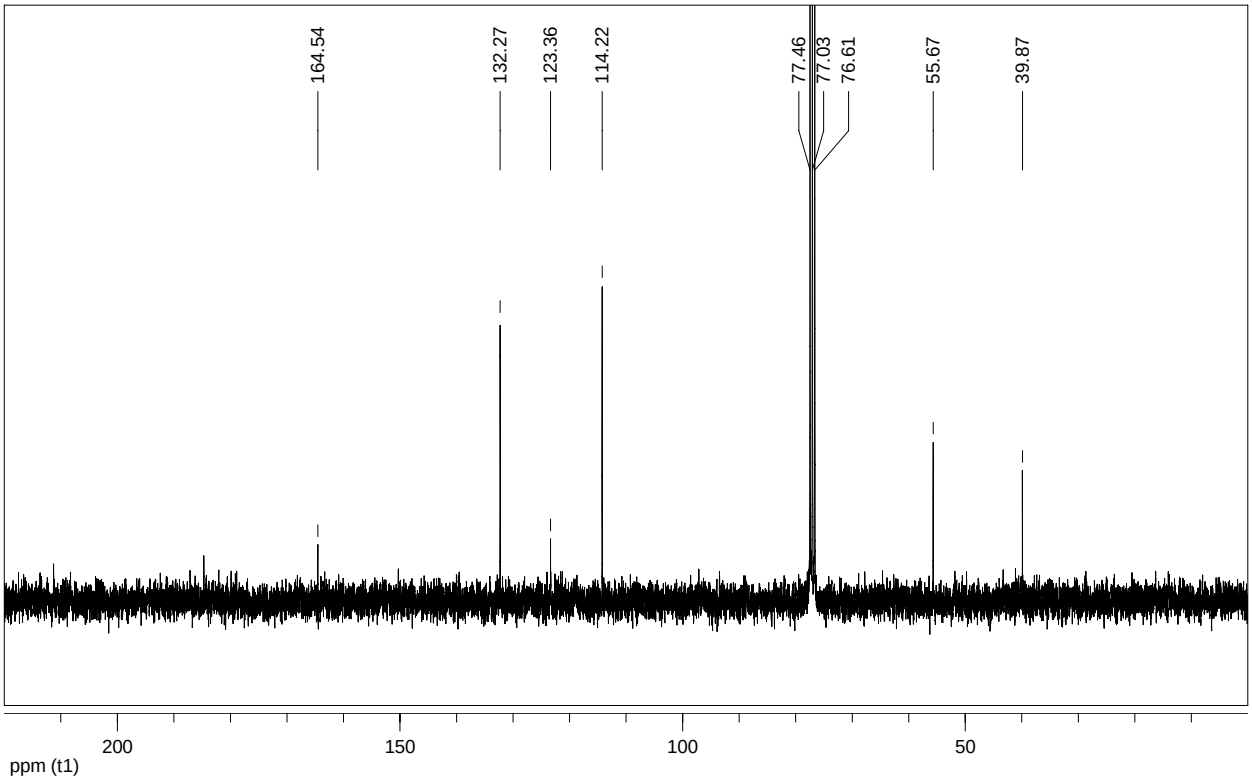
2,2-Dibromo-1-(4-bromophenyl)ethanone (3l)



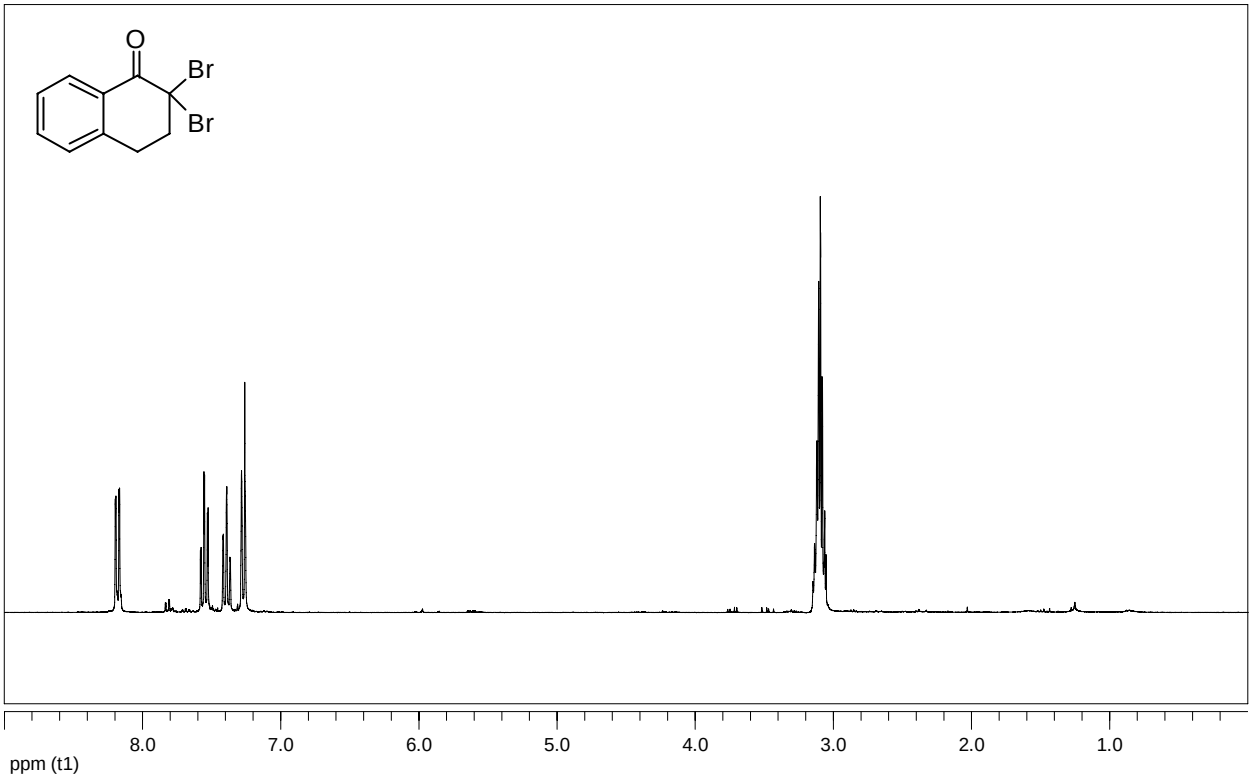


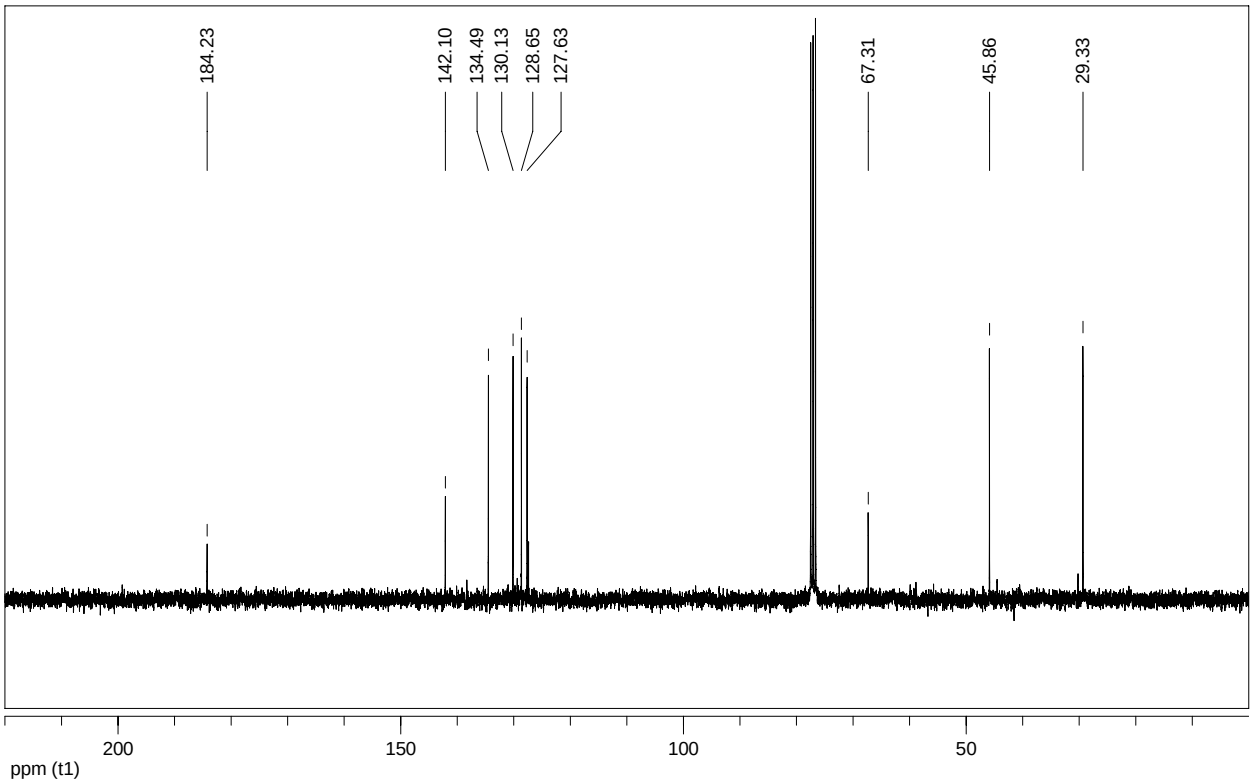
2,2-Dibromo-1-(4-methoxyphenyl)ethanone (3m)



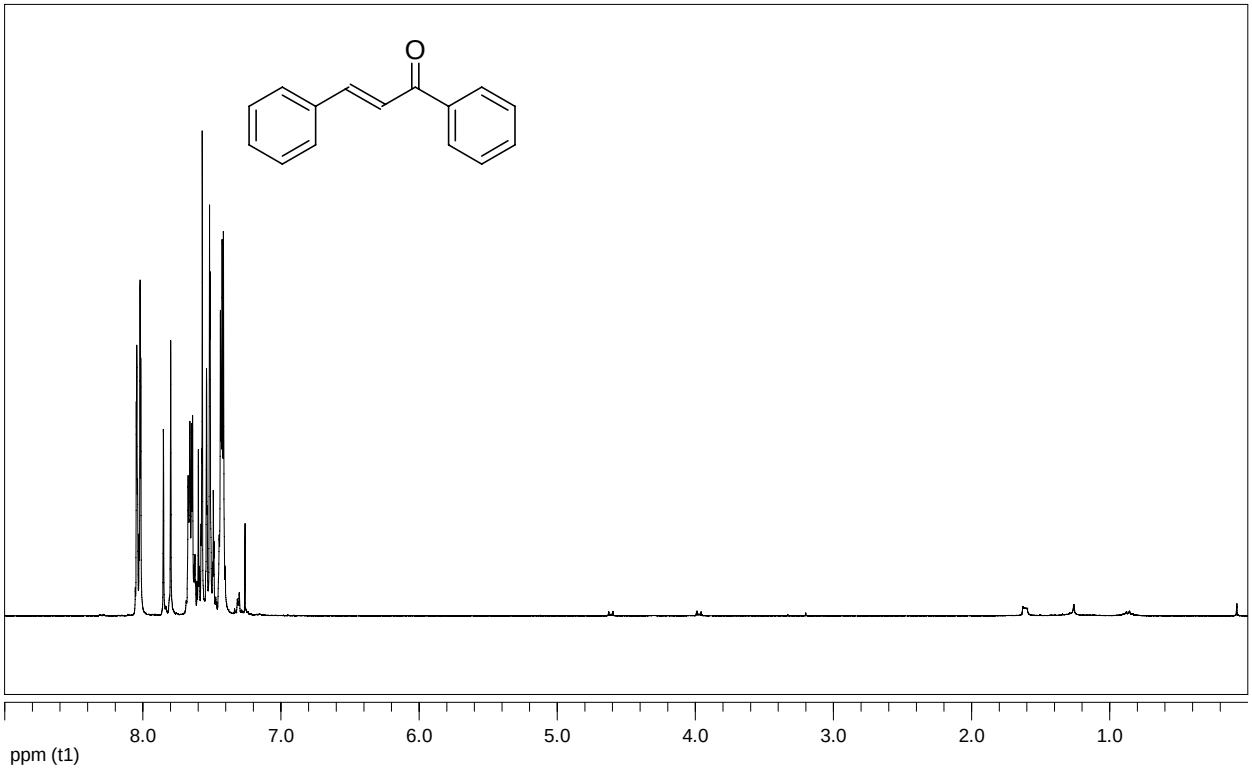


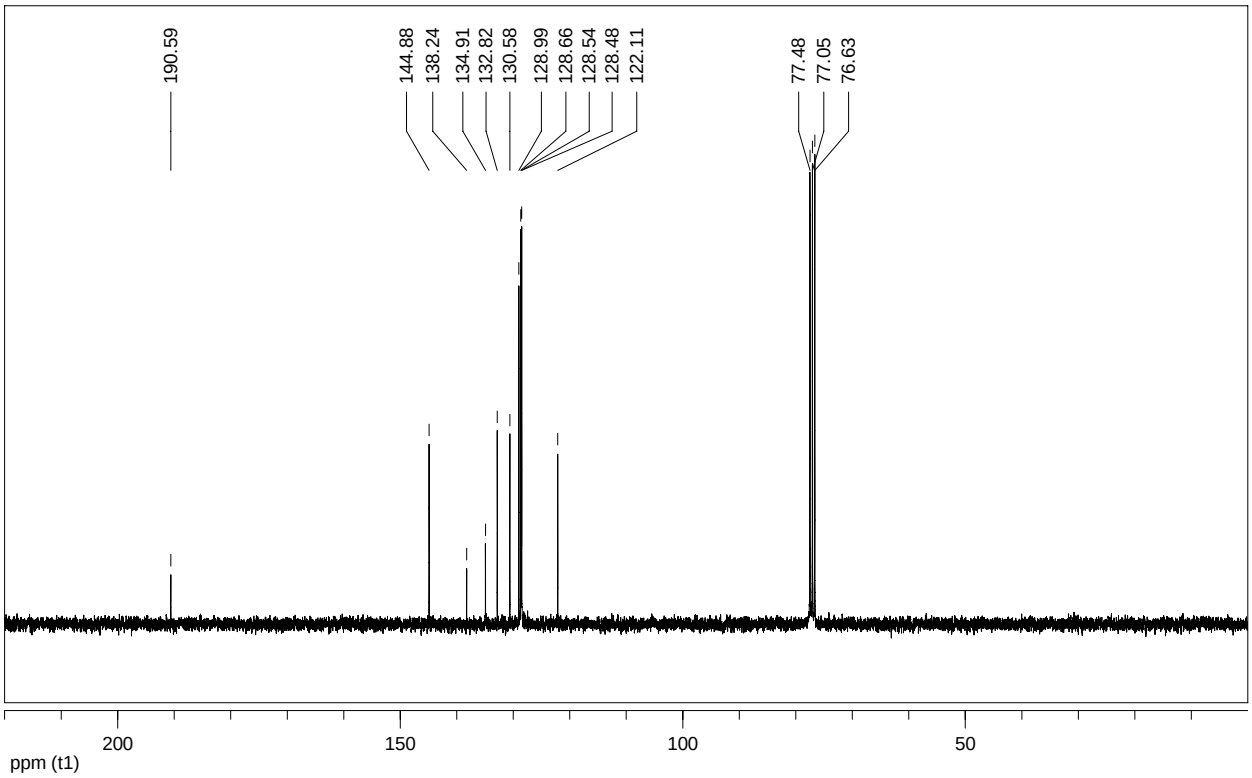
2,2-Dibromo-3,4-dihydronaphthalen-1(2H)-one (3n)



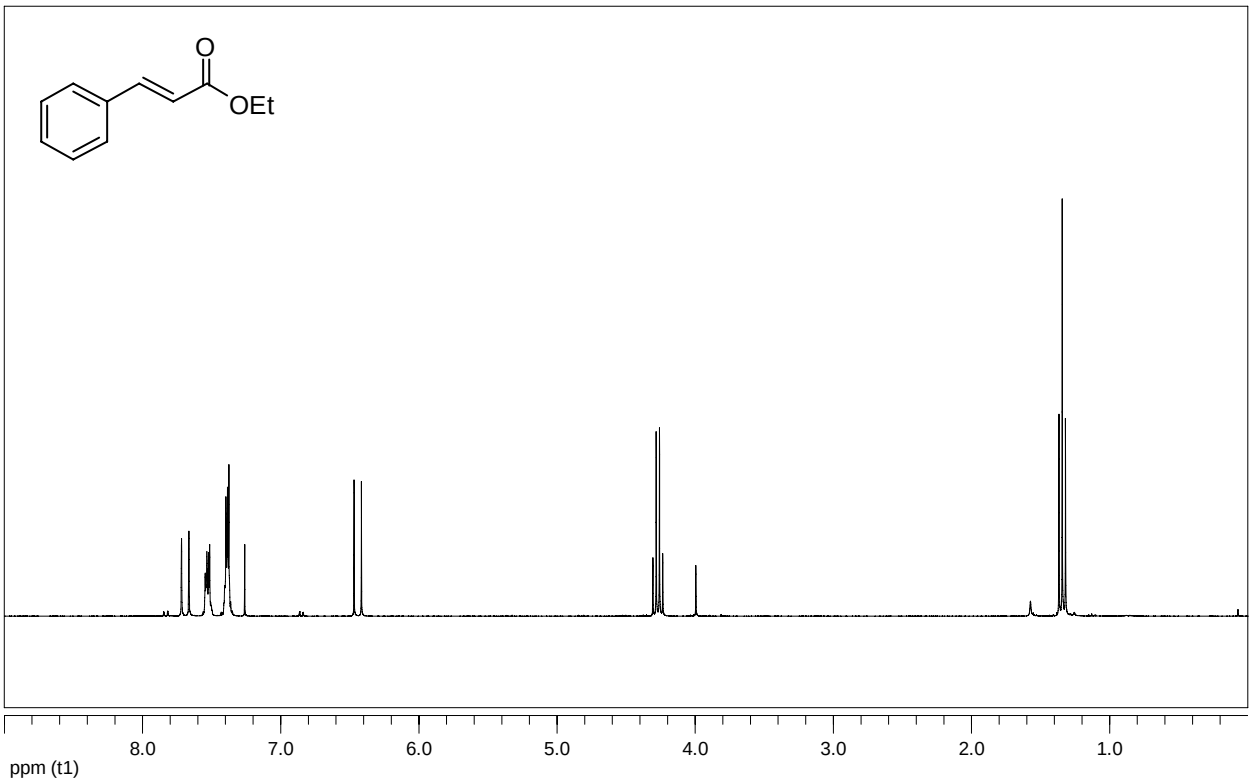


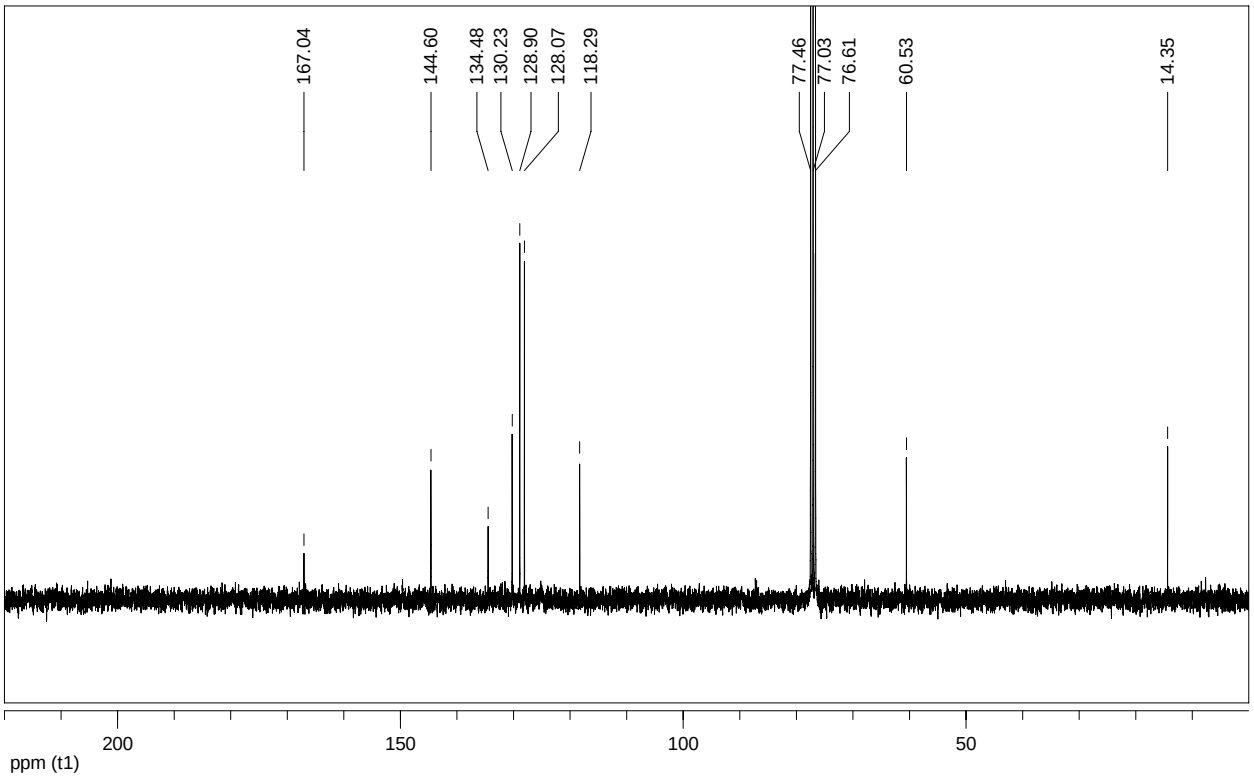
(*E*)-1,3-diphenylprop-2-en-1-one (2a)



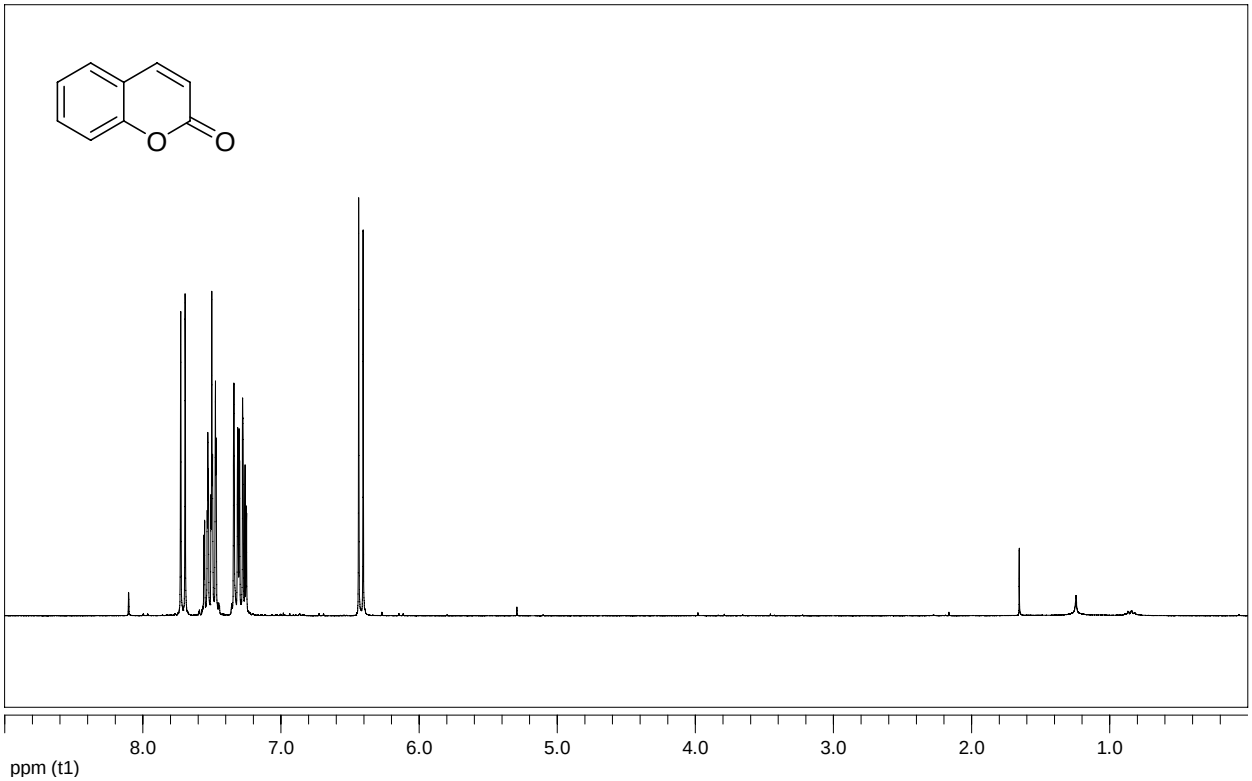


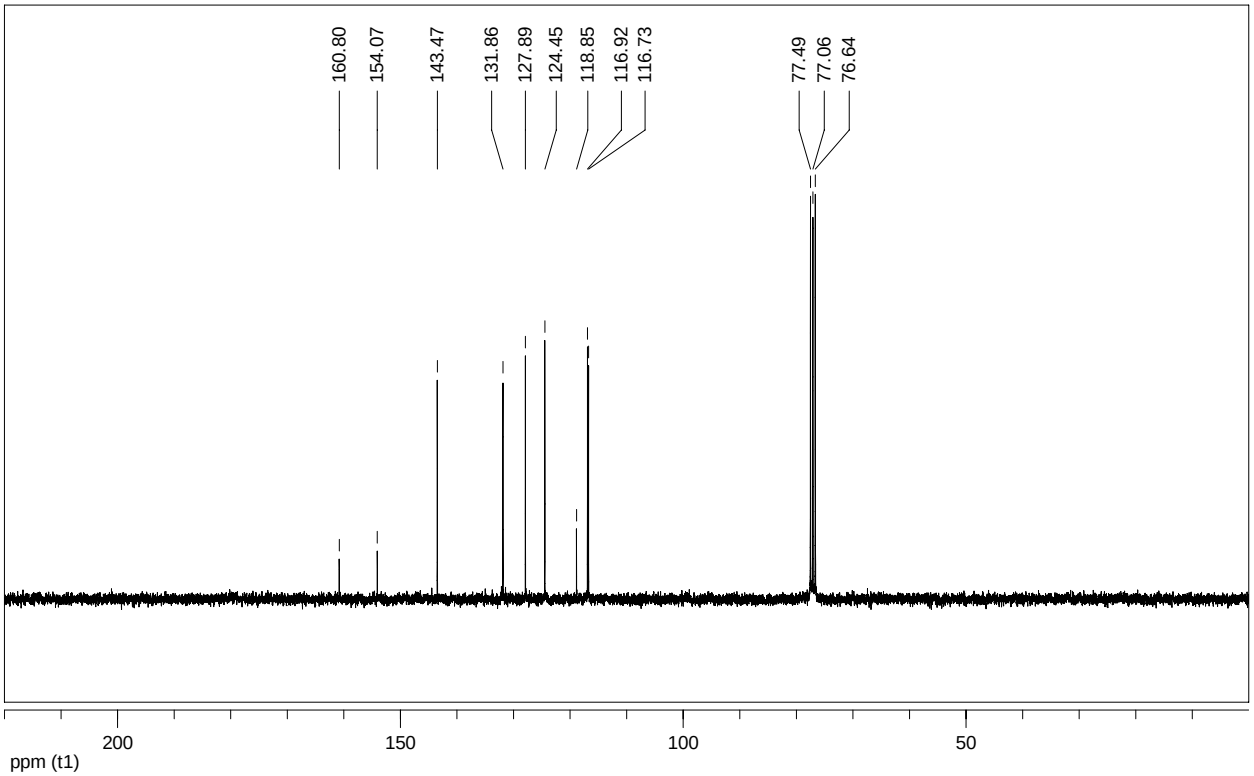
Ethyl (*E*)-cinnamate (2b)



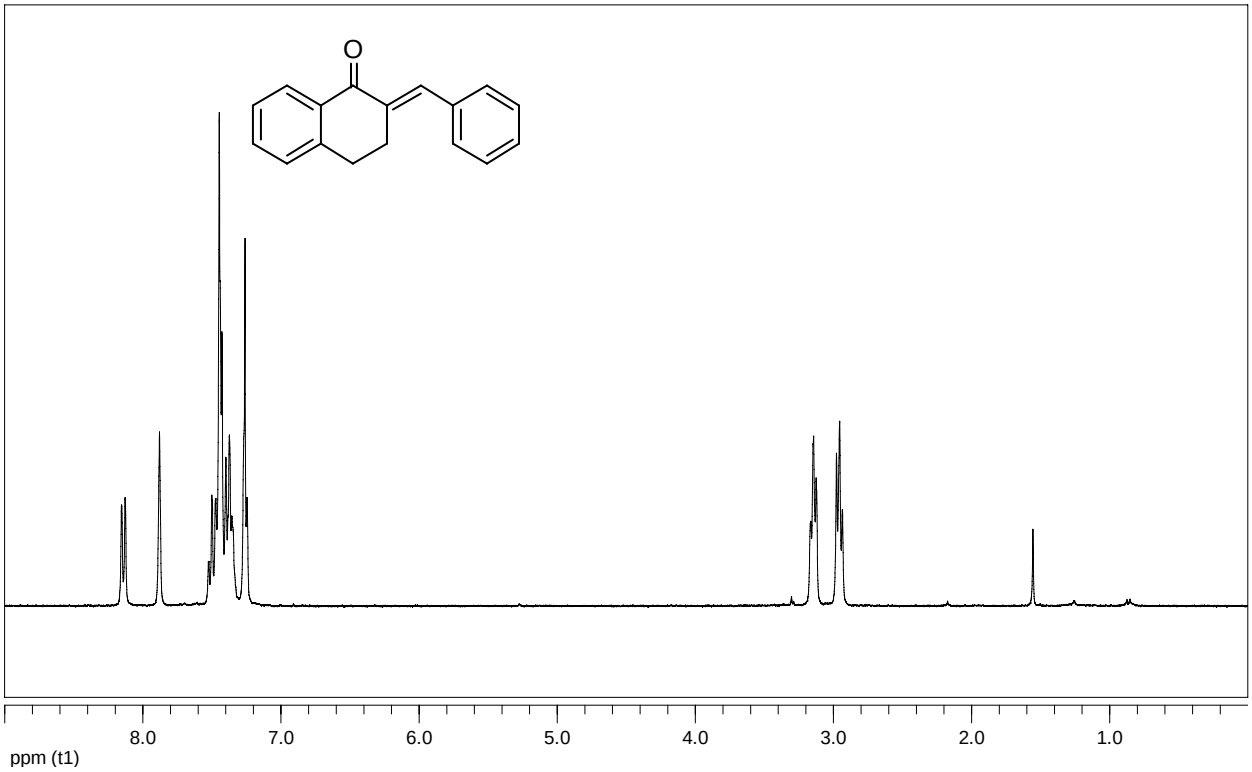


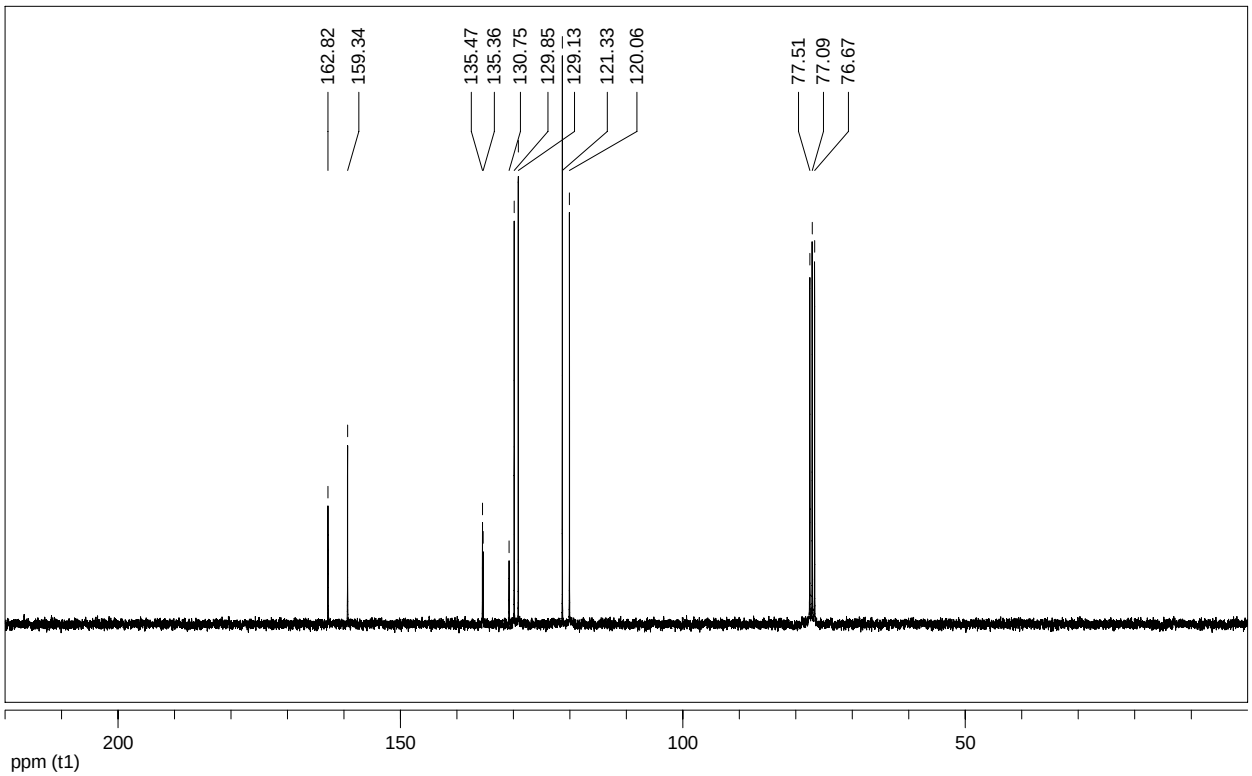
2H-chromen-2-one (2d)



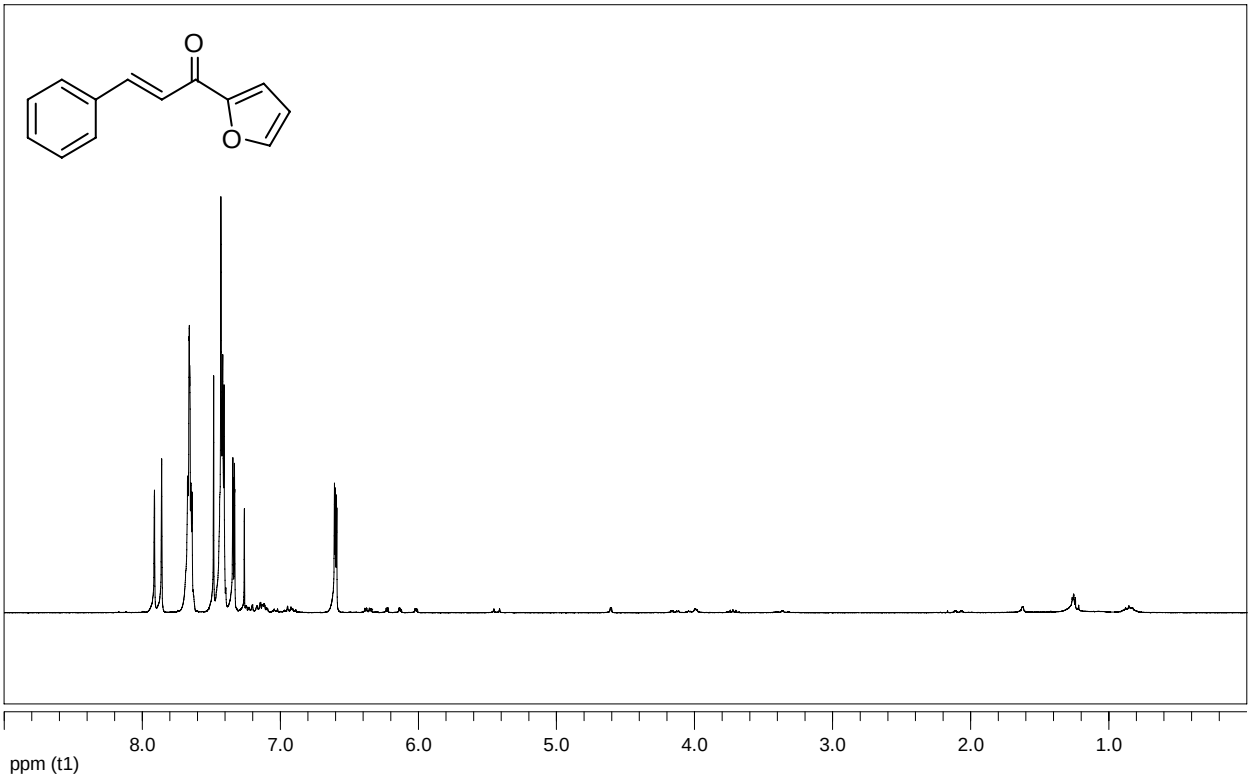


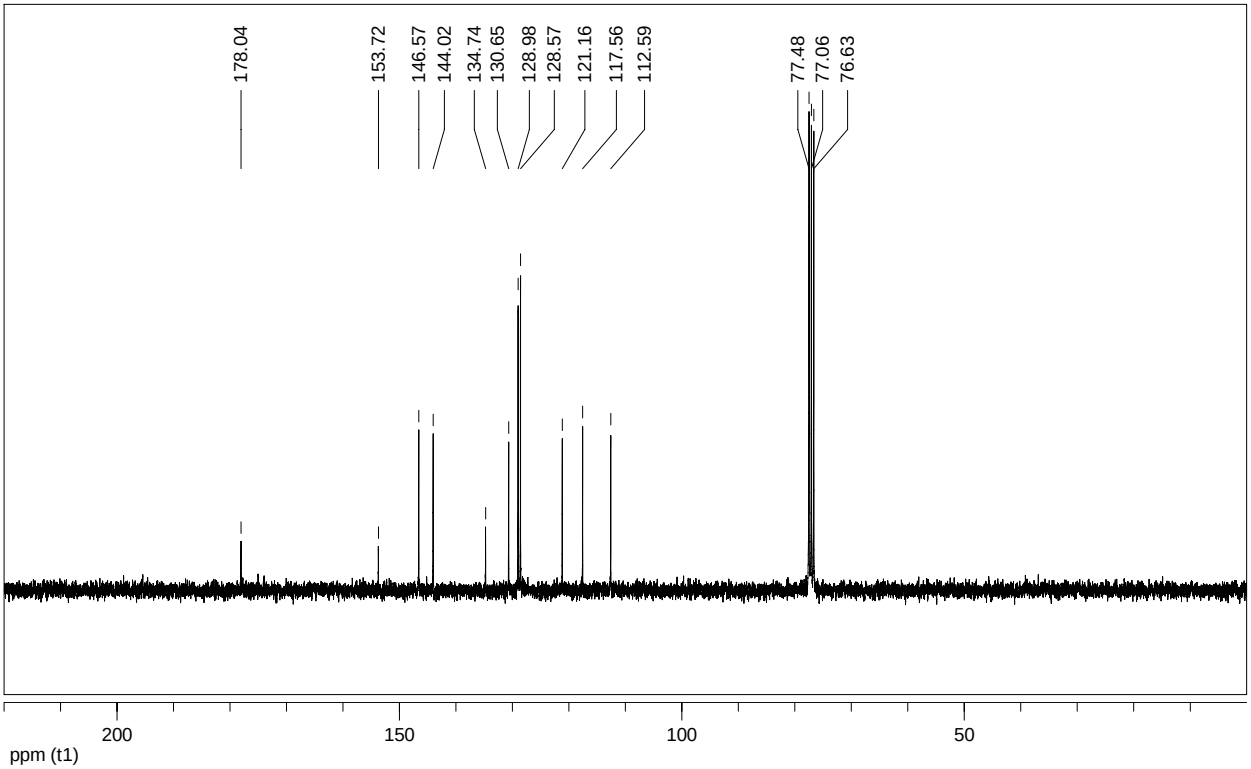
(*E*)-2-benzylidene-3,4-dihydronaphthalen-1(2H)-one (2e)



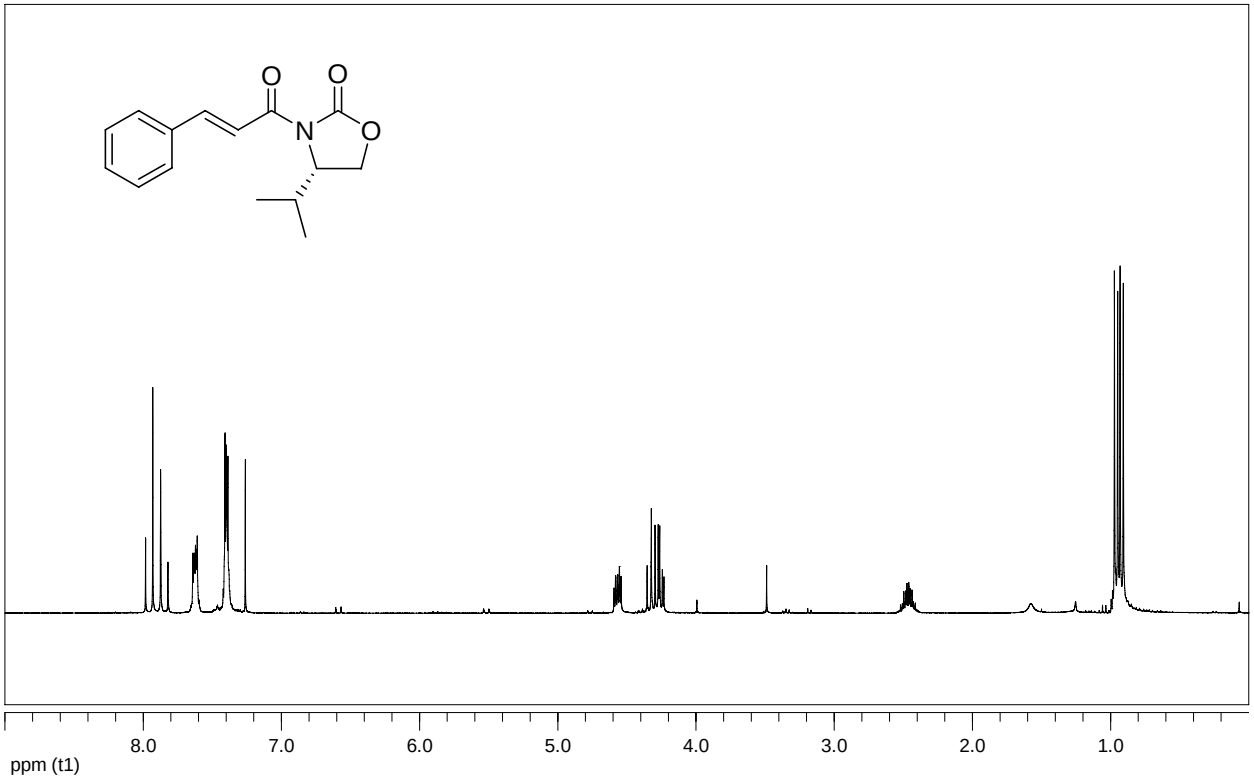


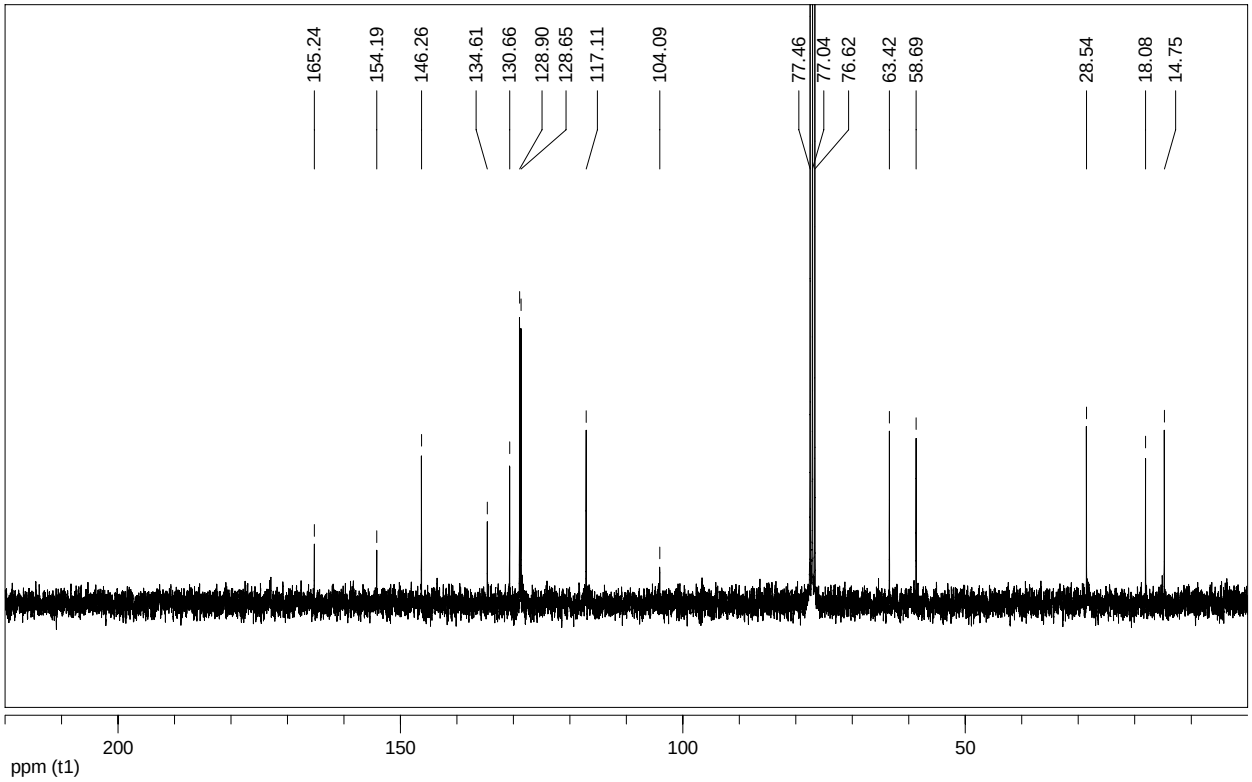
(*E*)-1-(furan-2-yl)-3-phenylprop-2-en-1-one (2f)



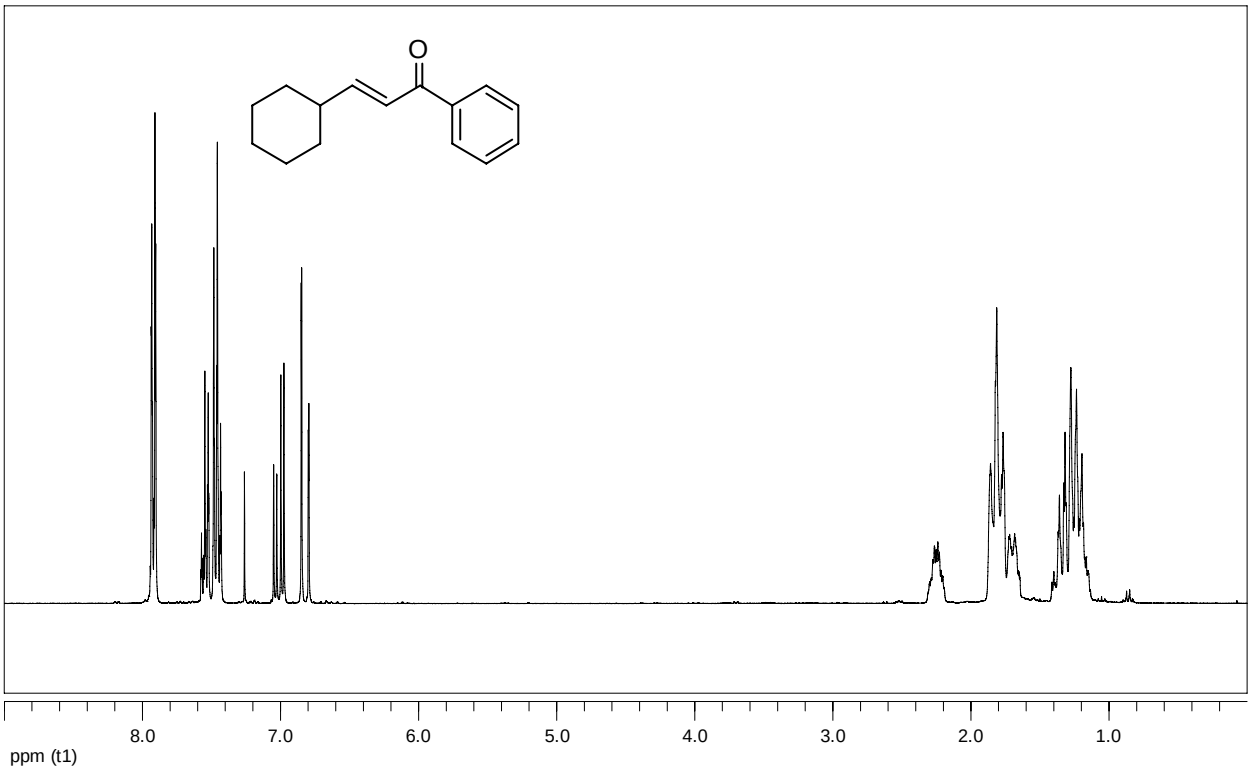


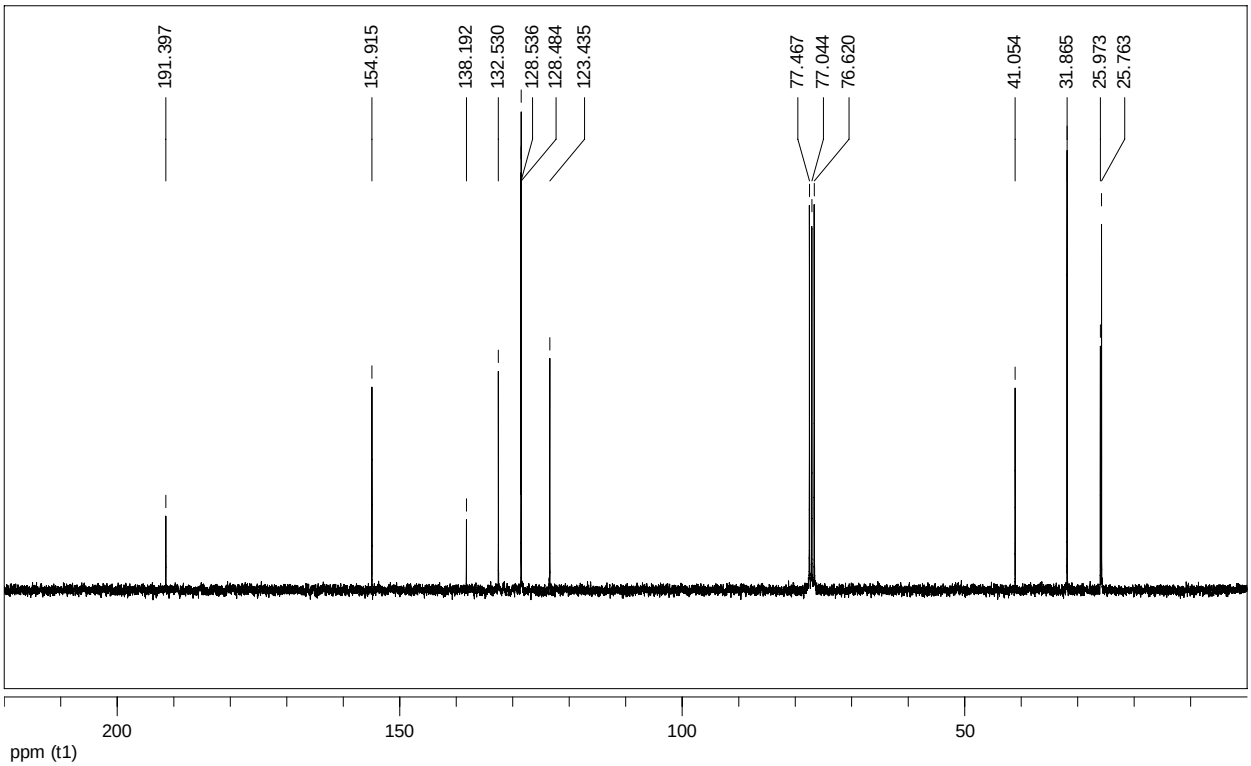
(*S*)-3-cinnamoyl-4-isopropyloxazolidin-2-one (2g)



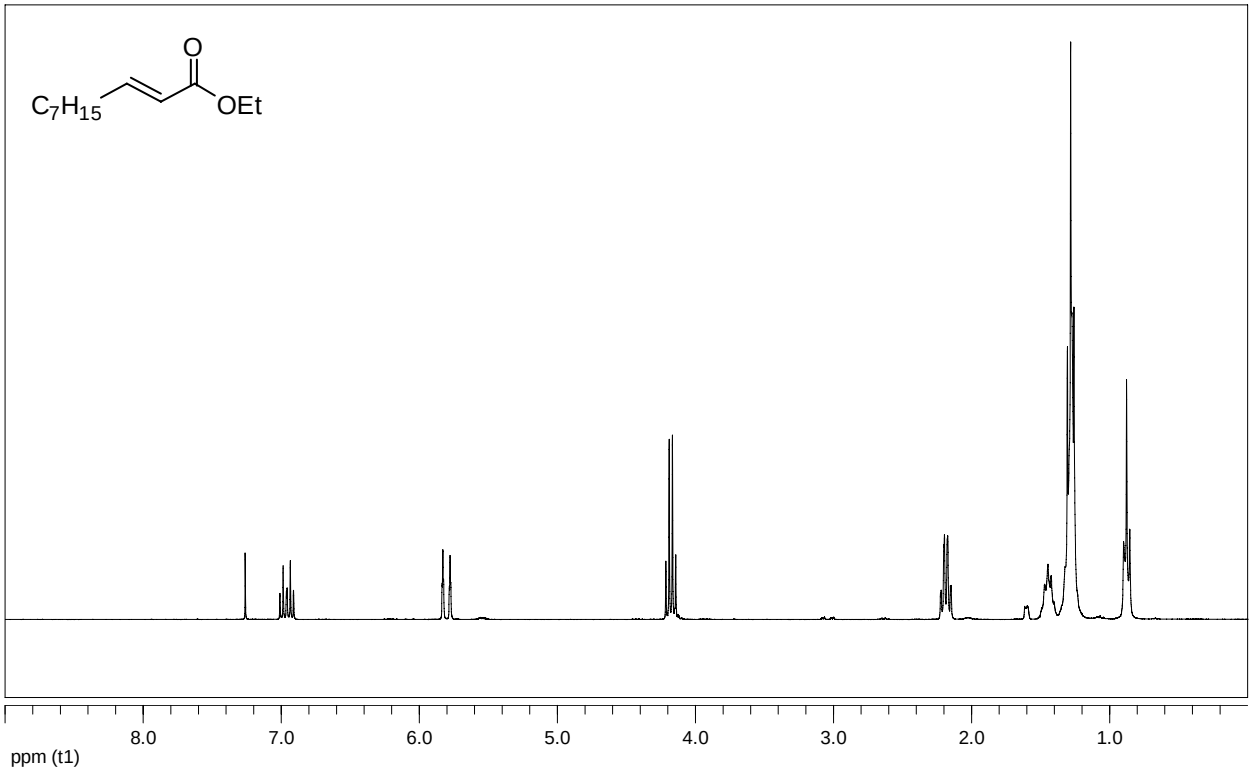


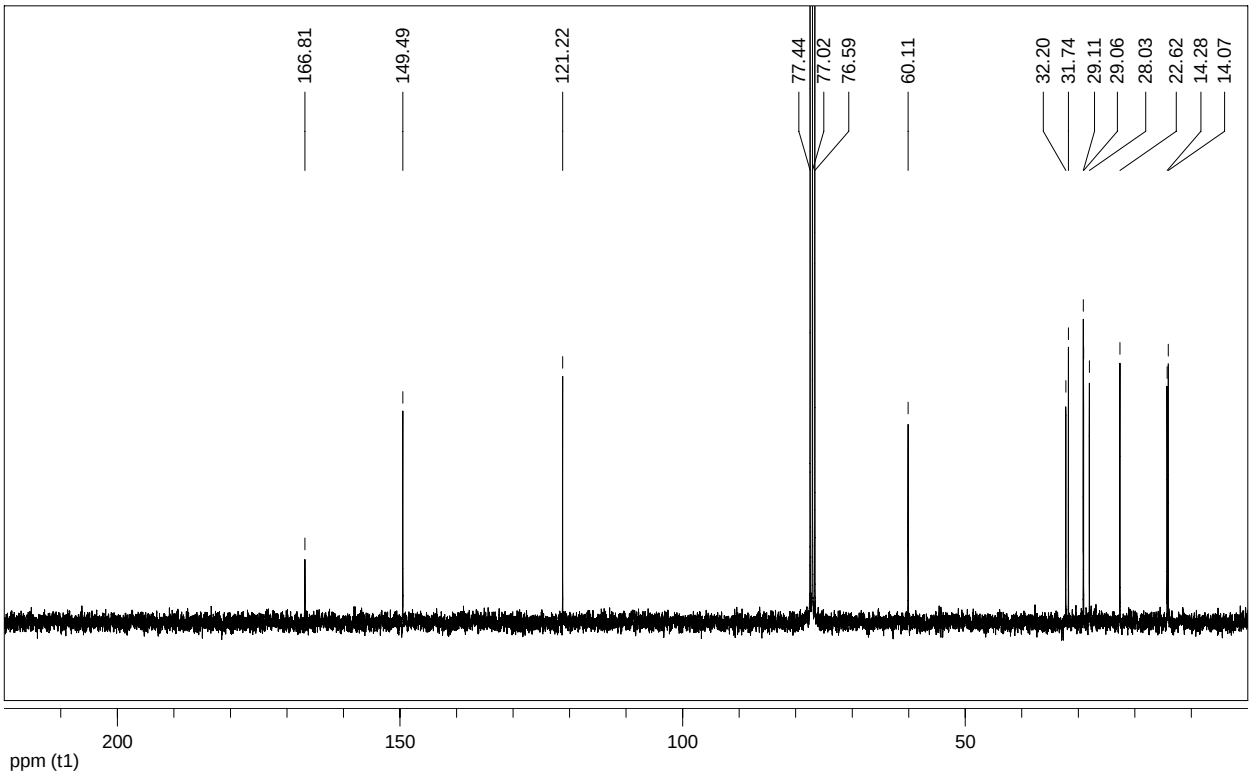
(*E*)-3-cyclohexyl-1-phenylprop-2-en-1-one (2h)



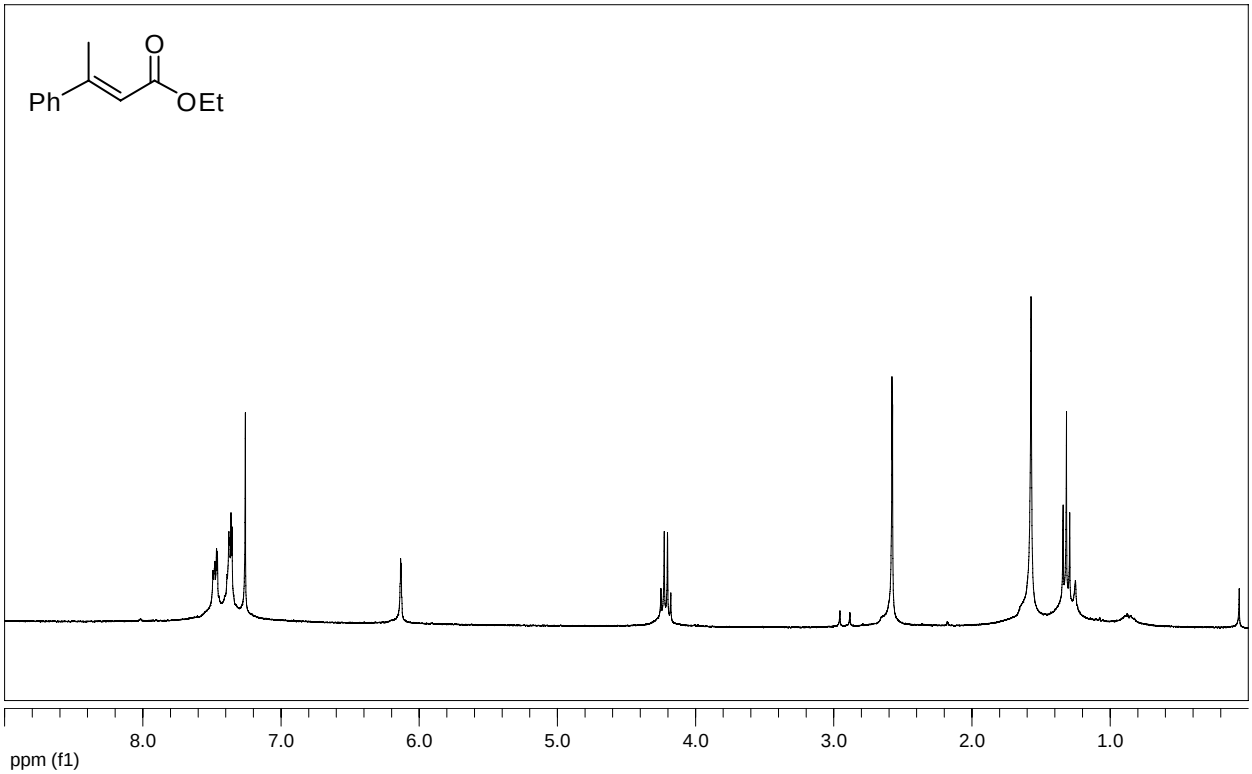


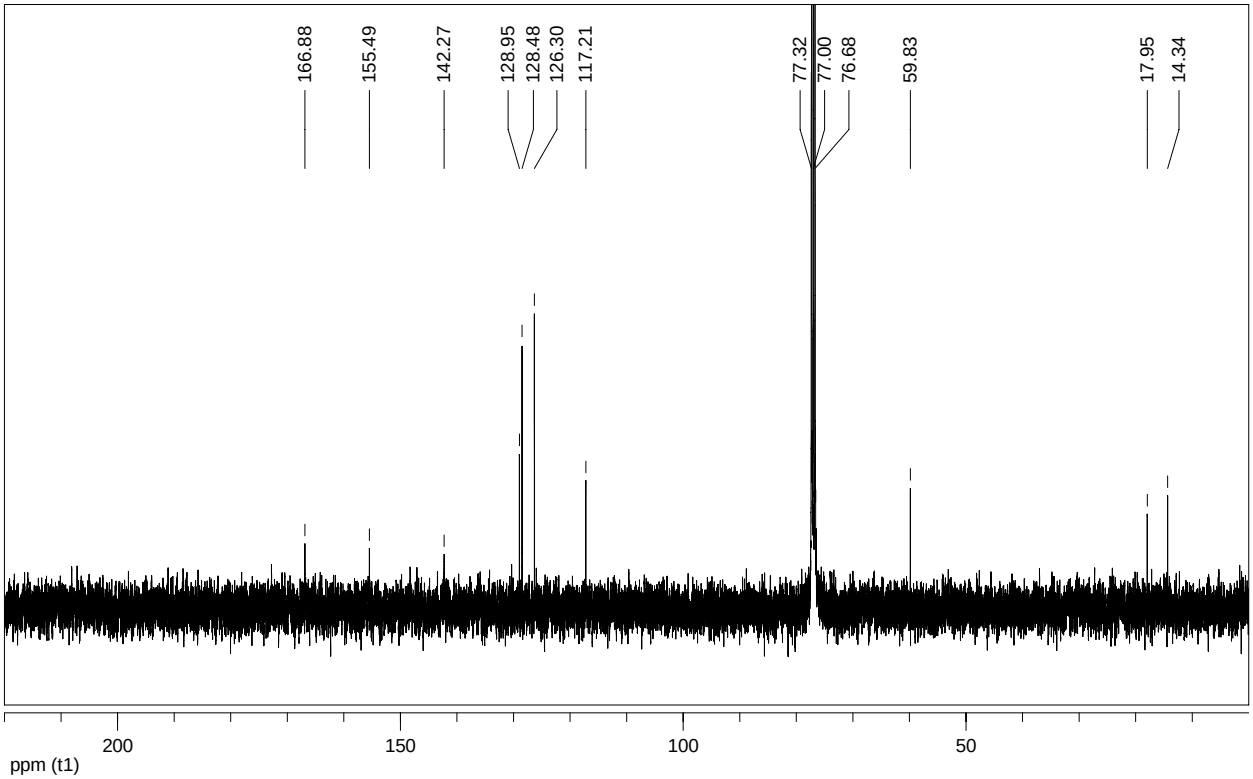
(*E*)-ethyl dec-2-enoate (2i)



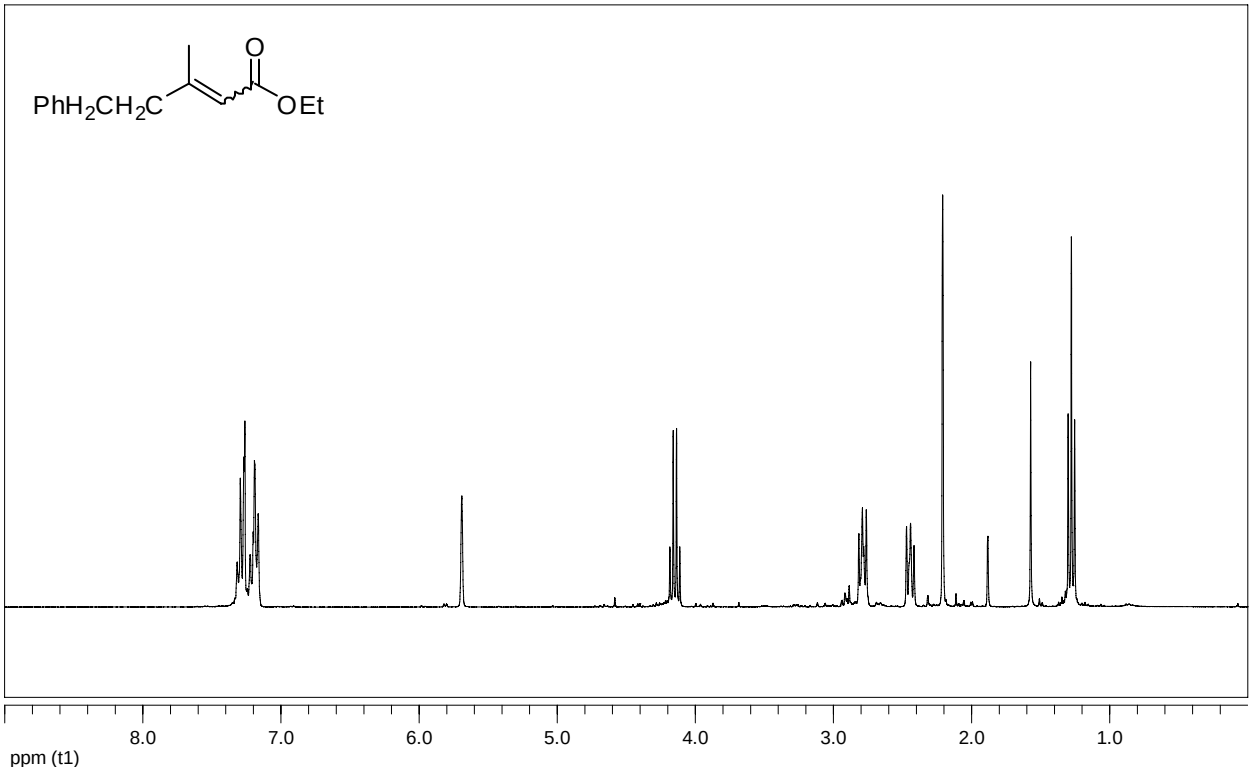


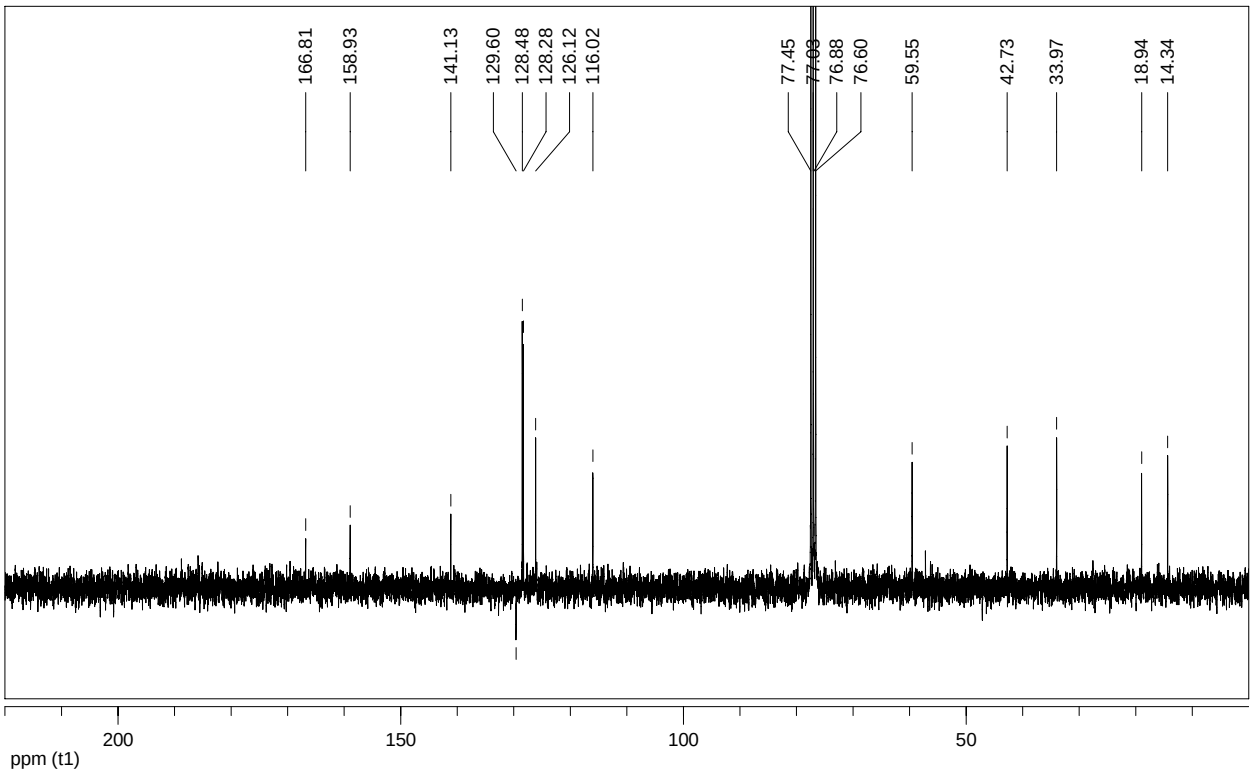
(*E*)-ethyl 3-phenylbut-2-enoate (2k)



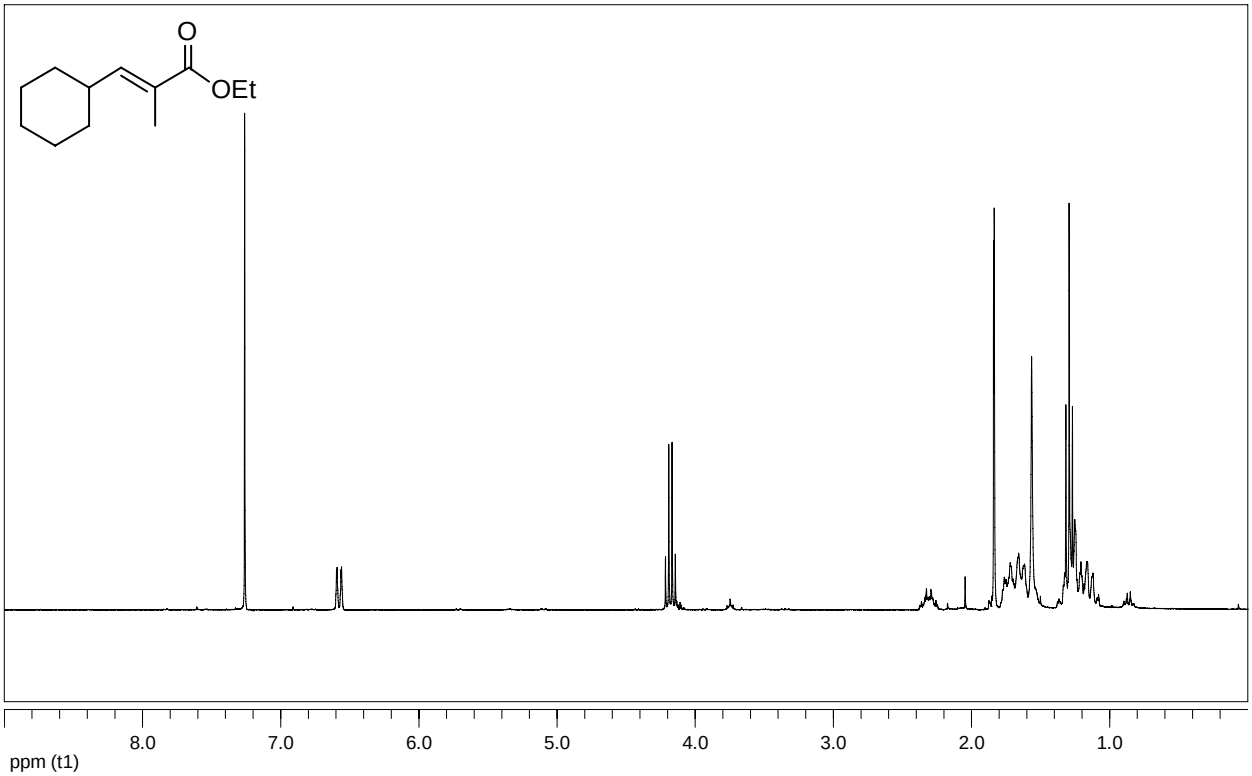


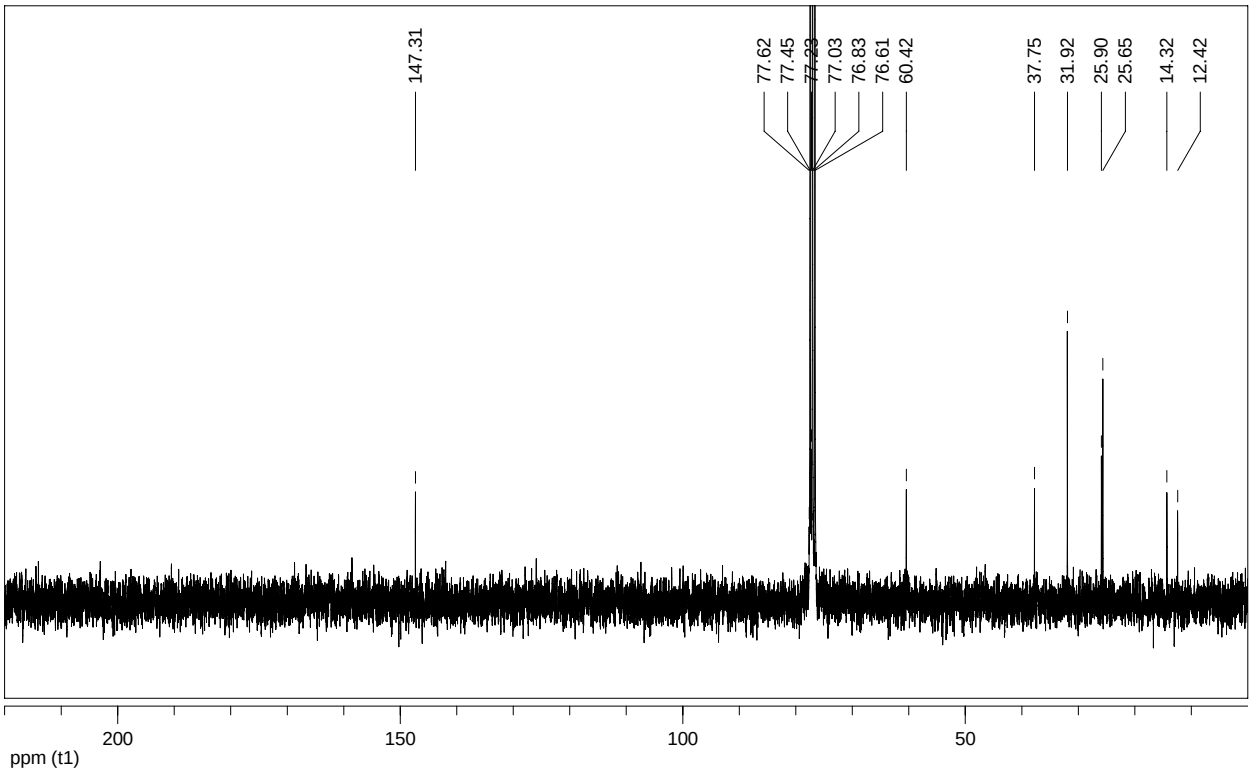
Ethyl 3-methyl-5-phenylpent-2-enoate (*E*:*Z*= 84:16) (2l)



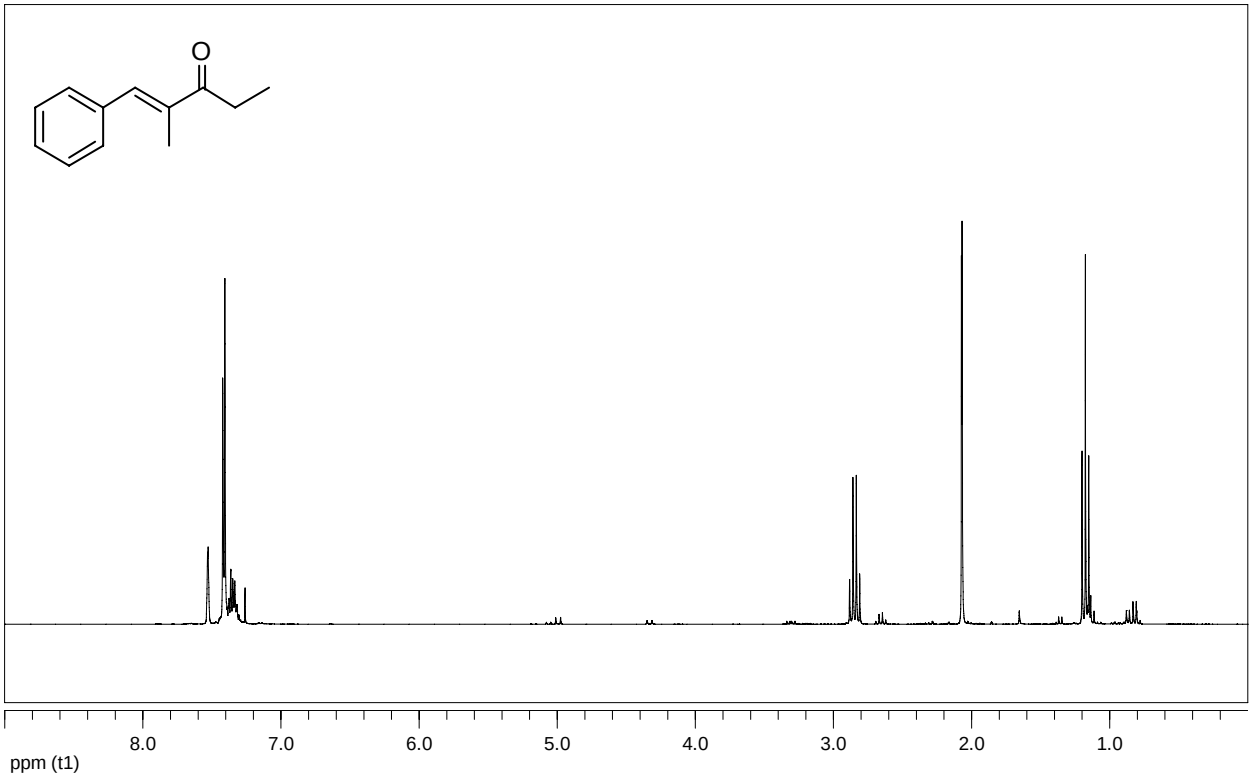


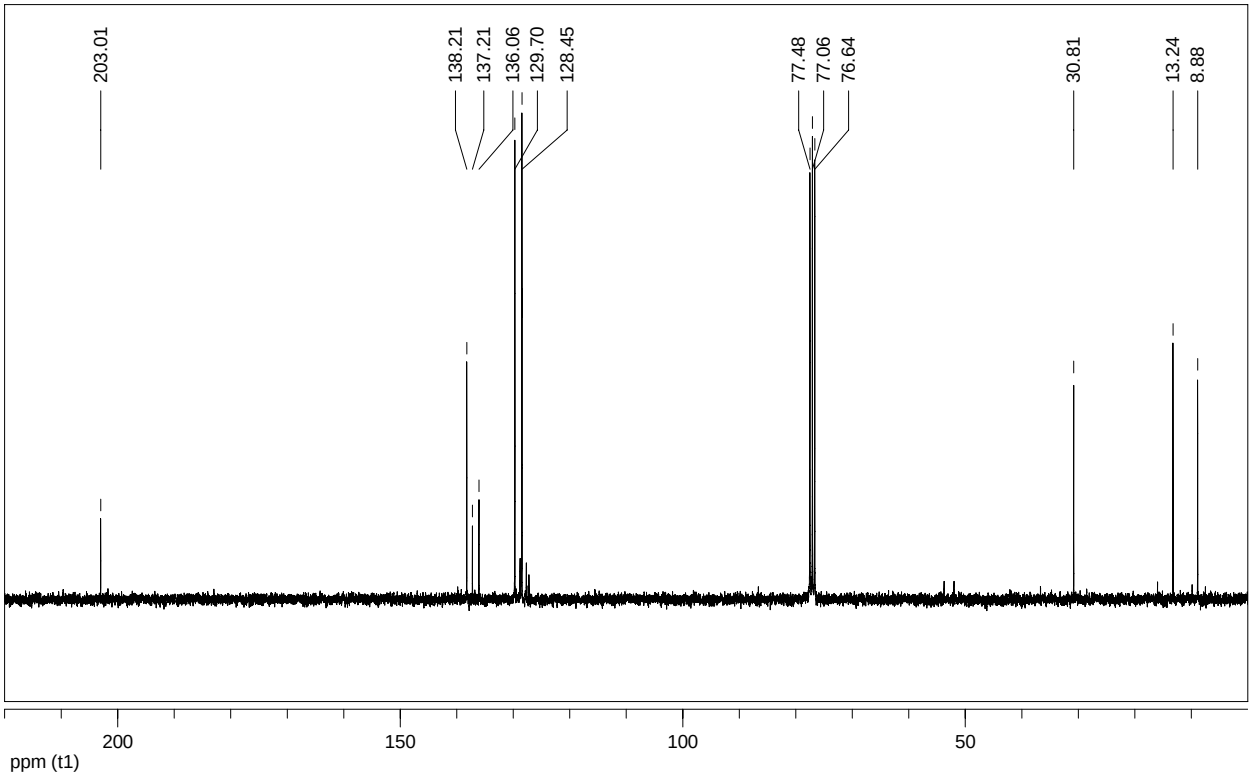
(*E*)-ethyl 3-cyclohexyl-2-methylacrylate (2m)



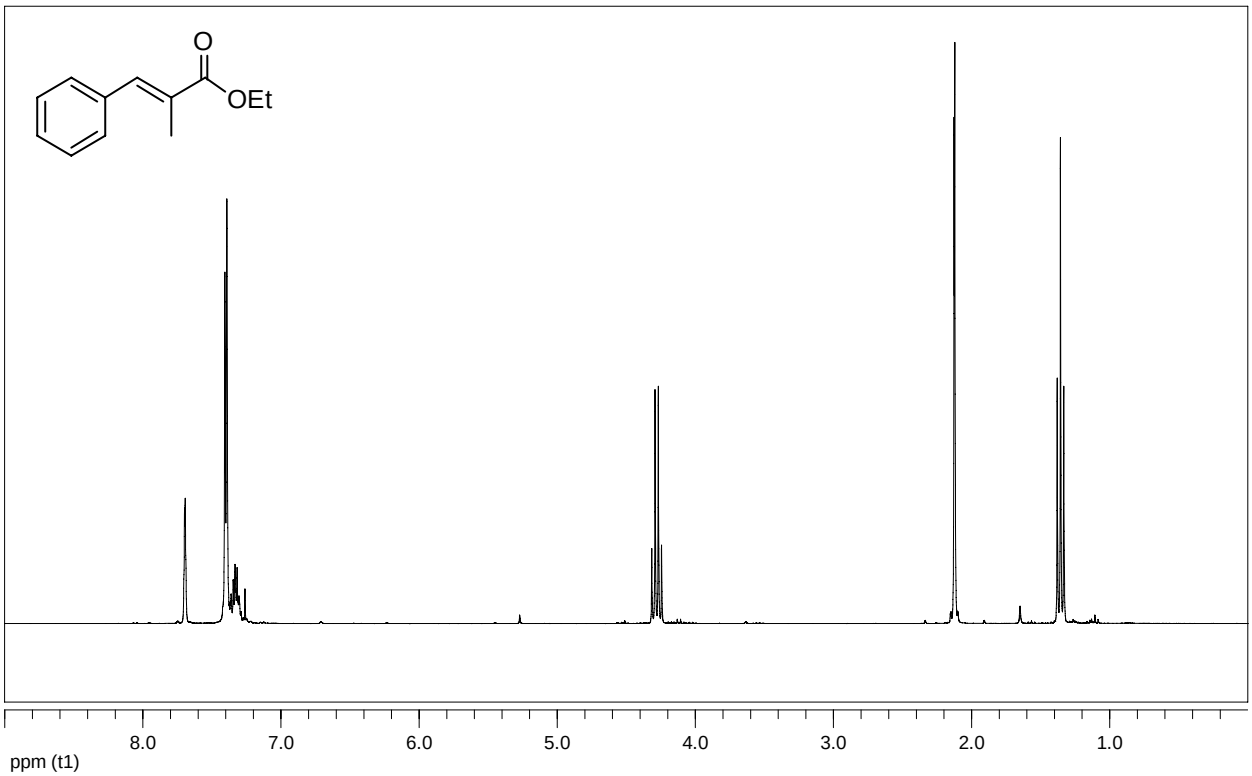


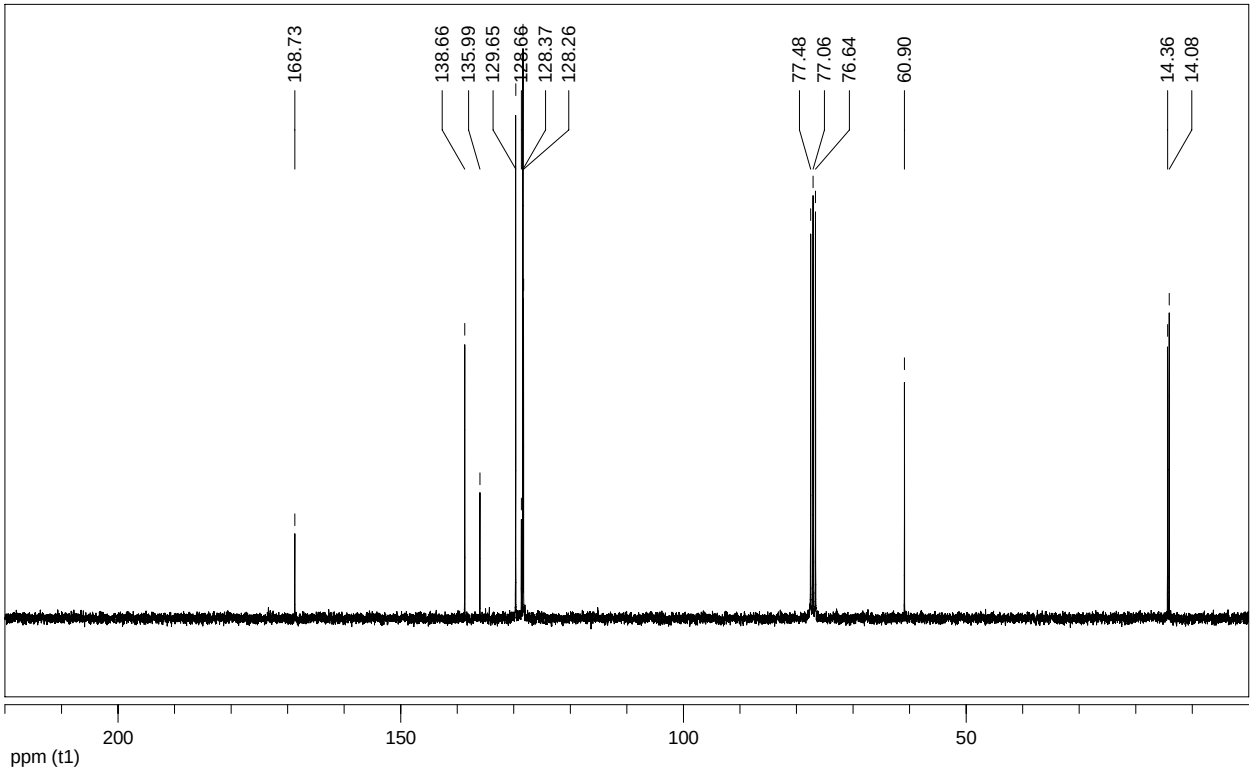
(*E*)-2-methyl-1-phenylpent-1-en-3-one (2n)



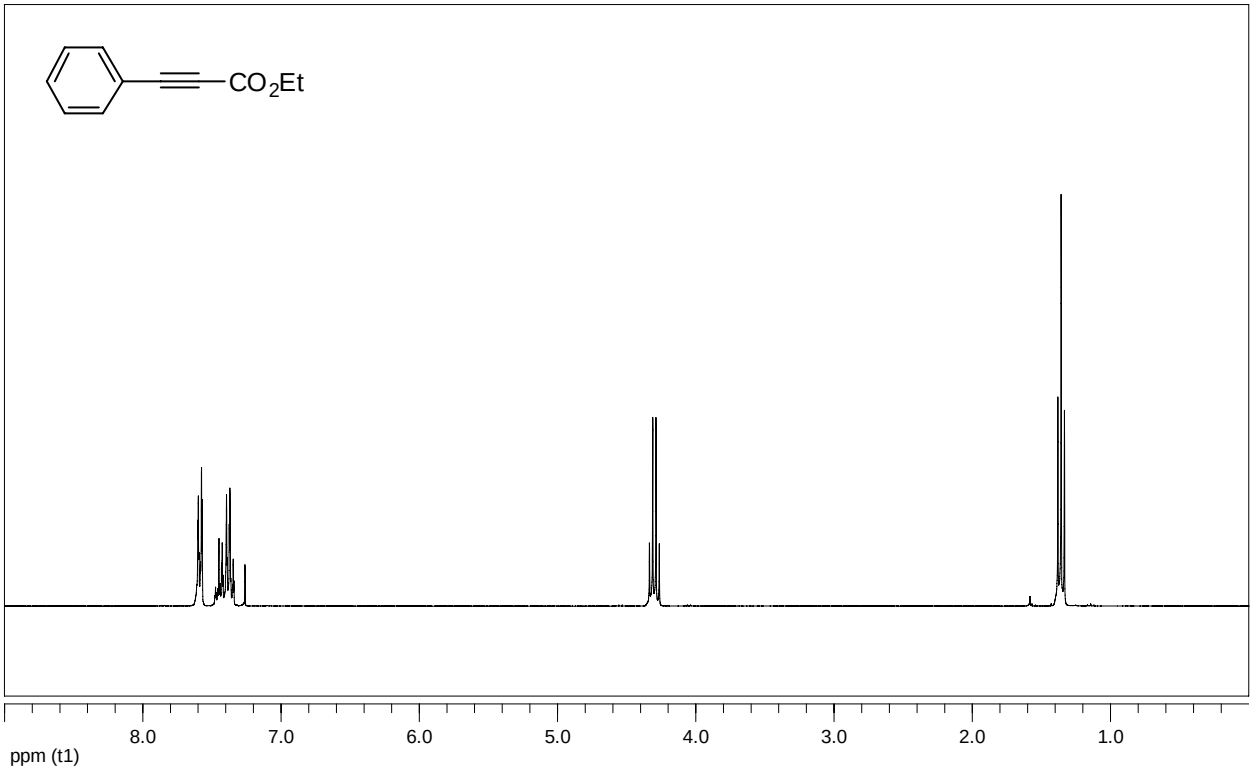


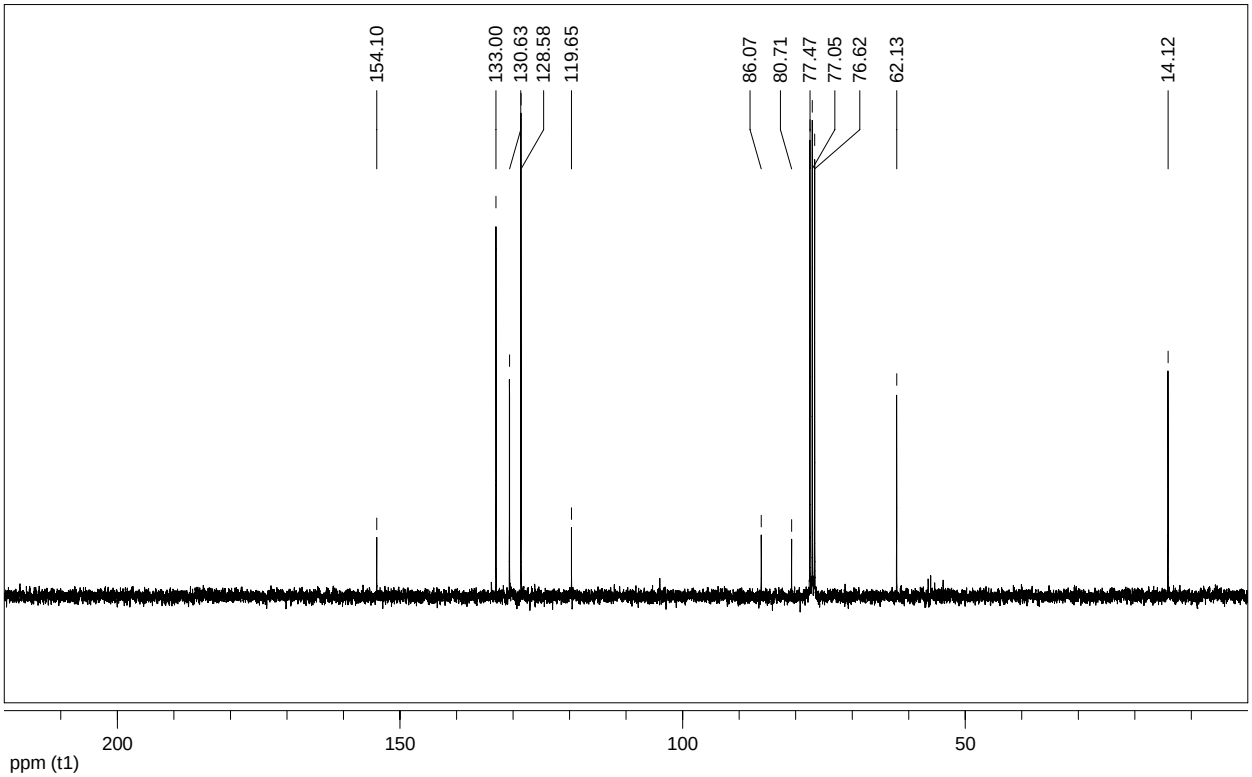
Ethyl 2-methyl-3-phenylacrylate (2o)



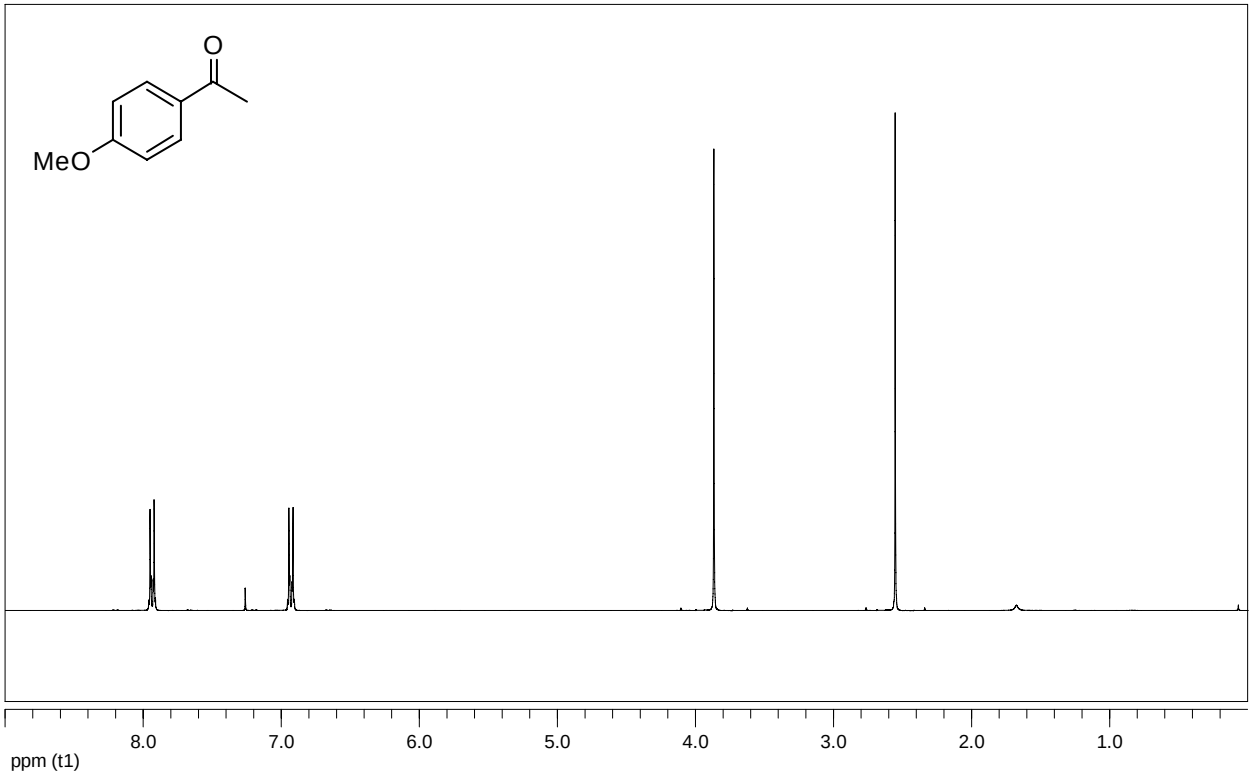


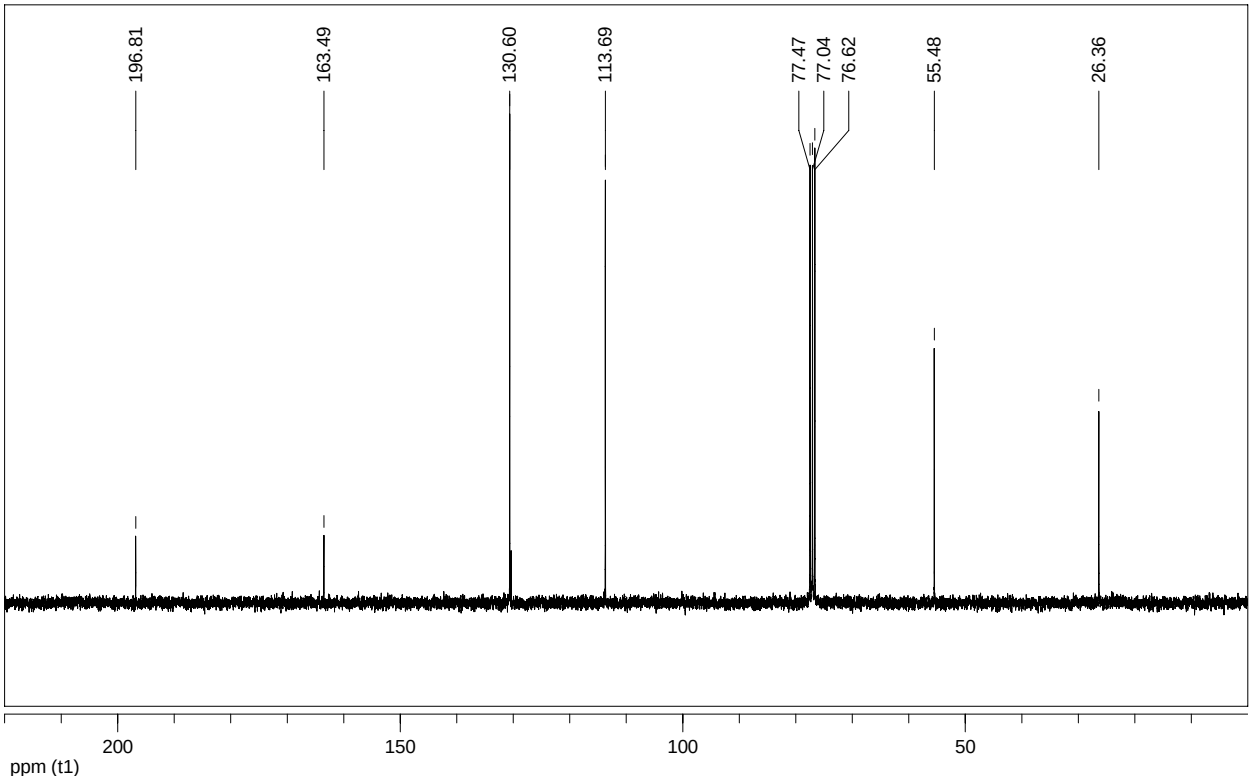
Ethyl 3-phenylpropiolate (2p)



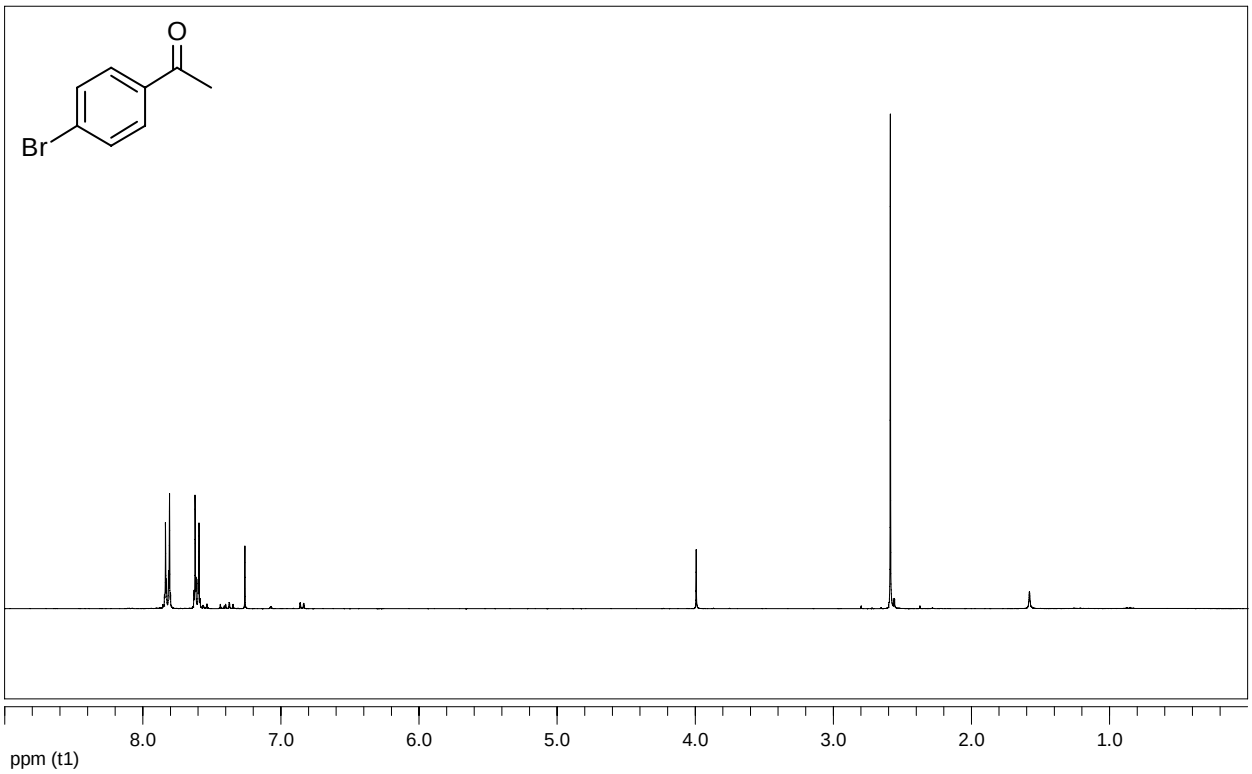


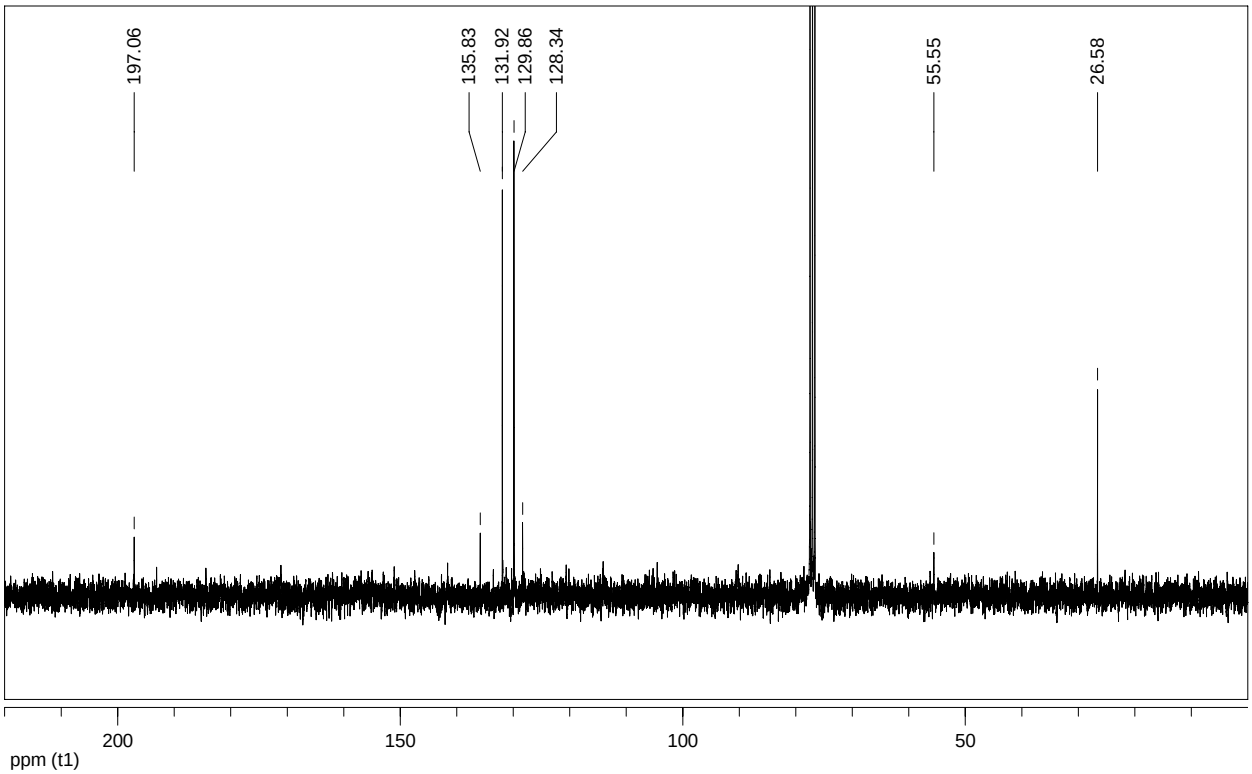
1-(4-methoxyphenyl) ethanone (4a)



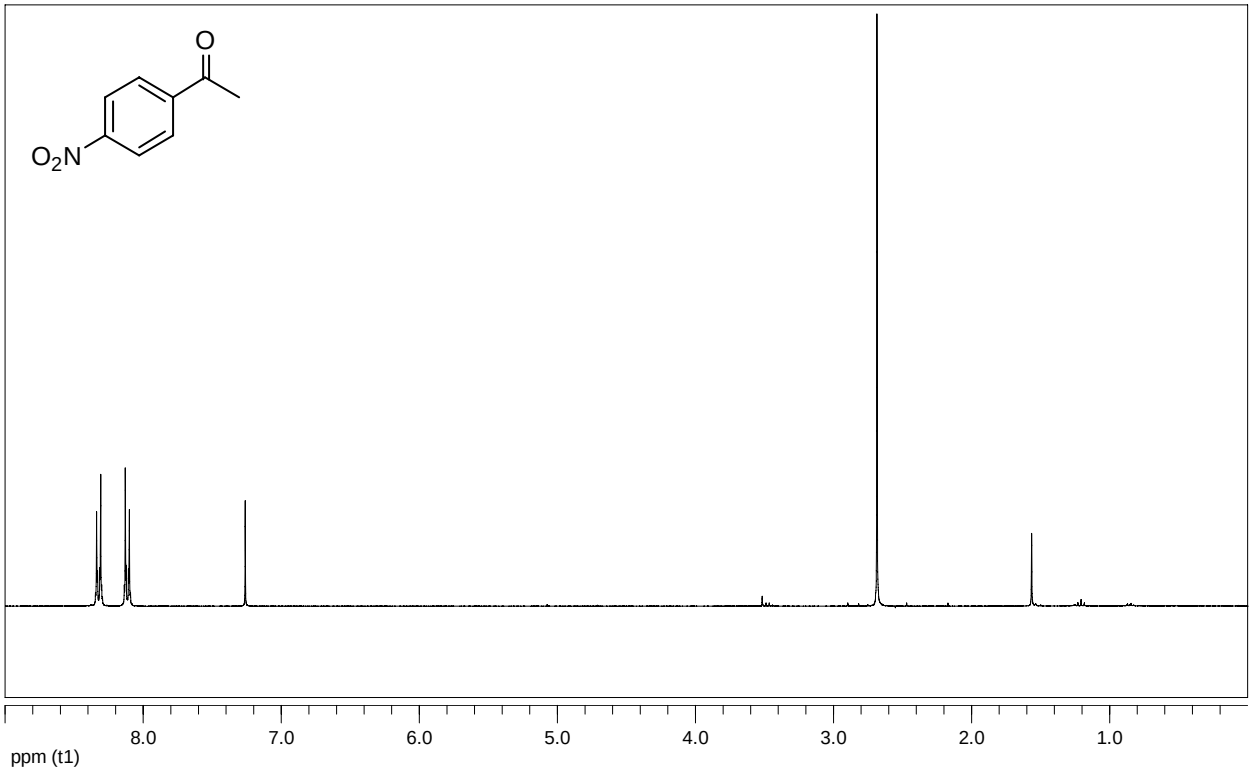


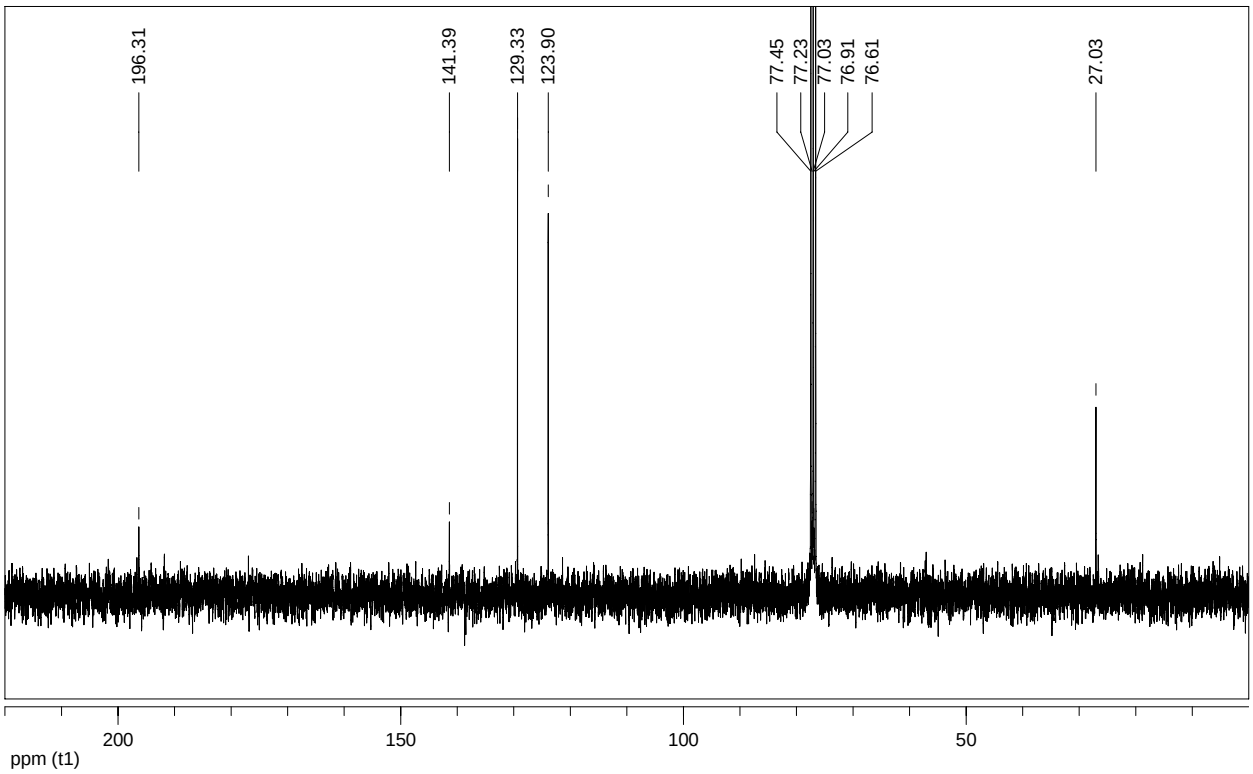
1-(4-bromophenyl) ethanone (4c)



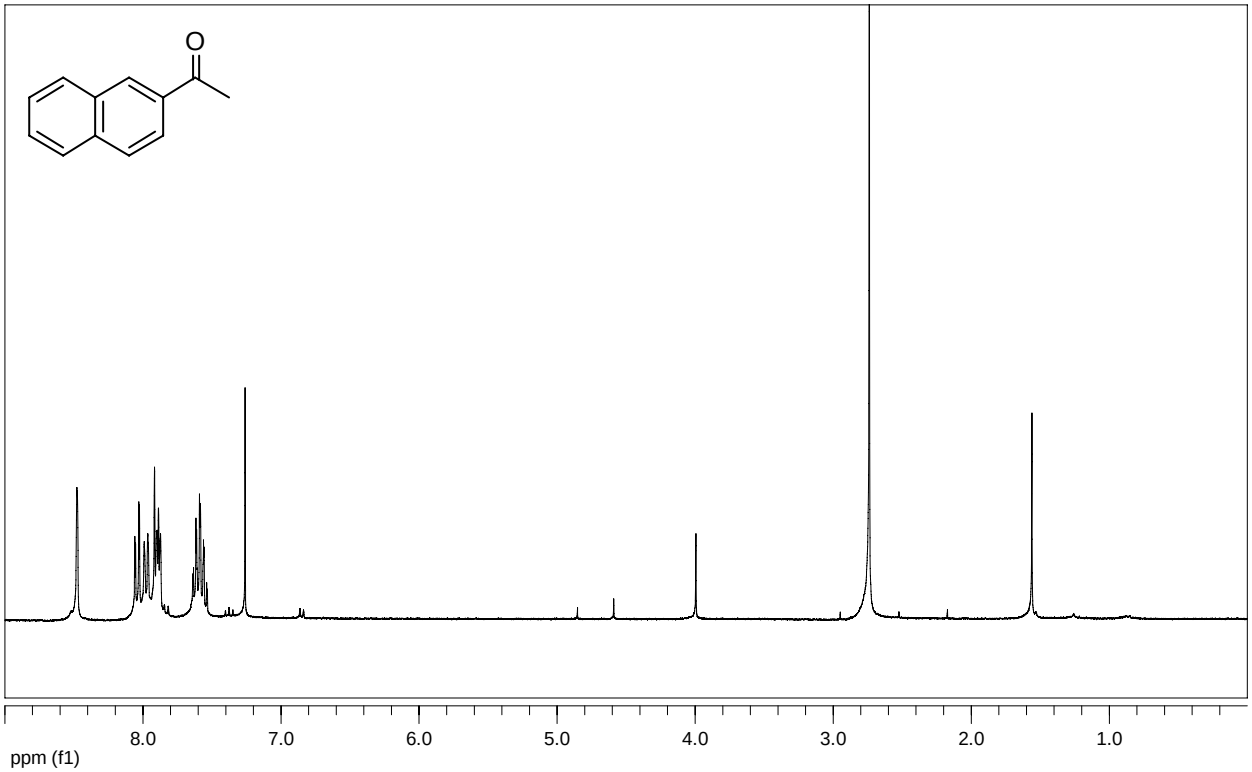


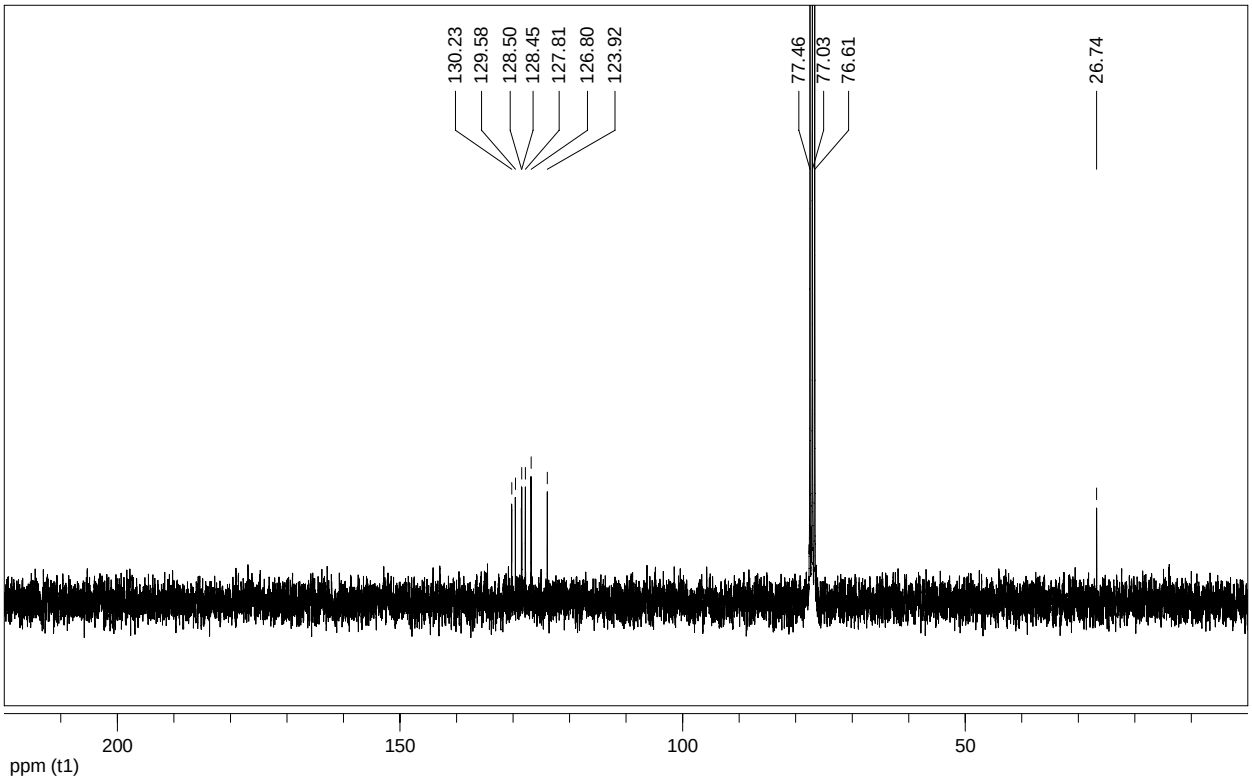
1-(4-nitrophenyl)ethanone (4d)



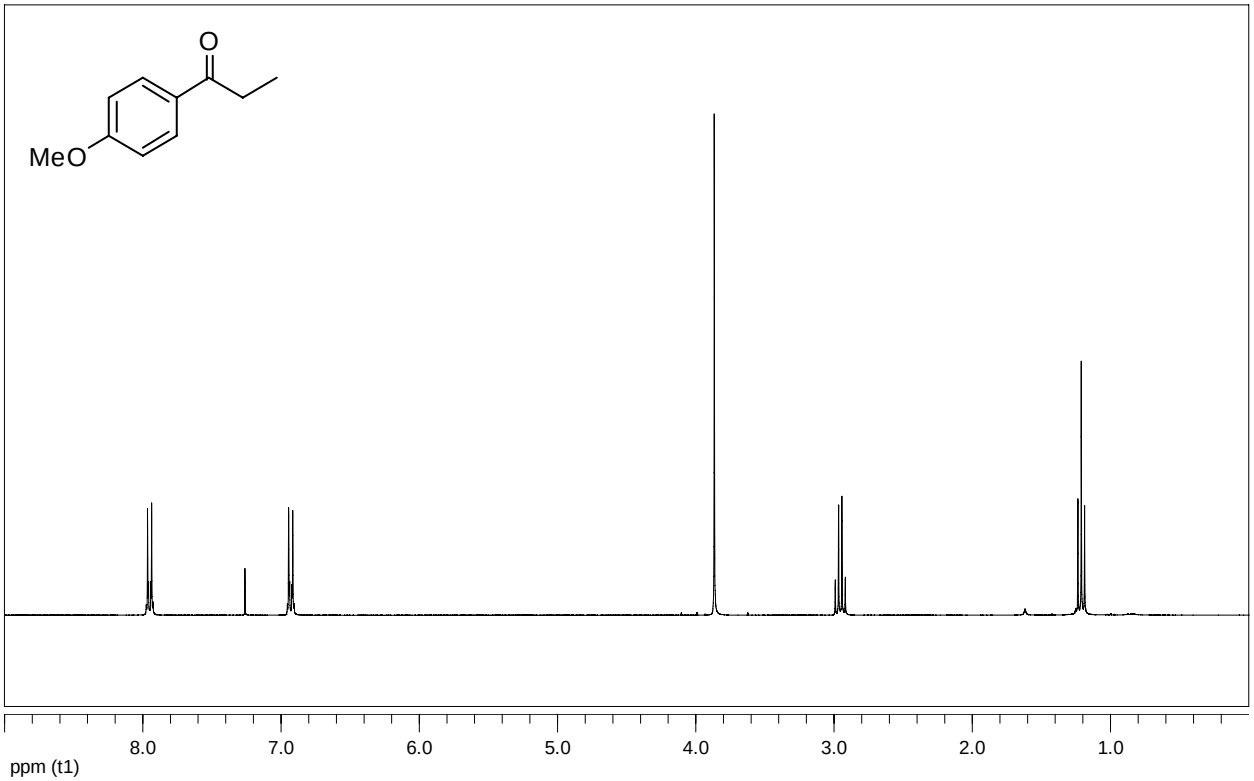


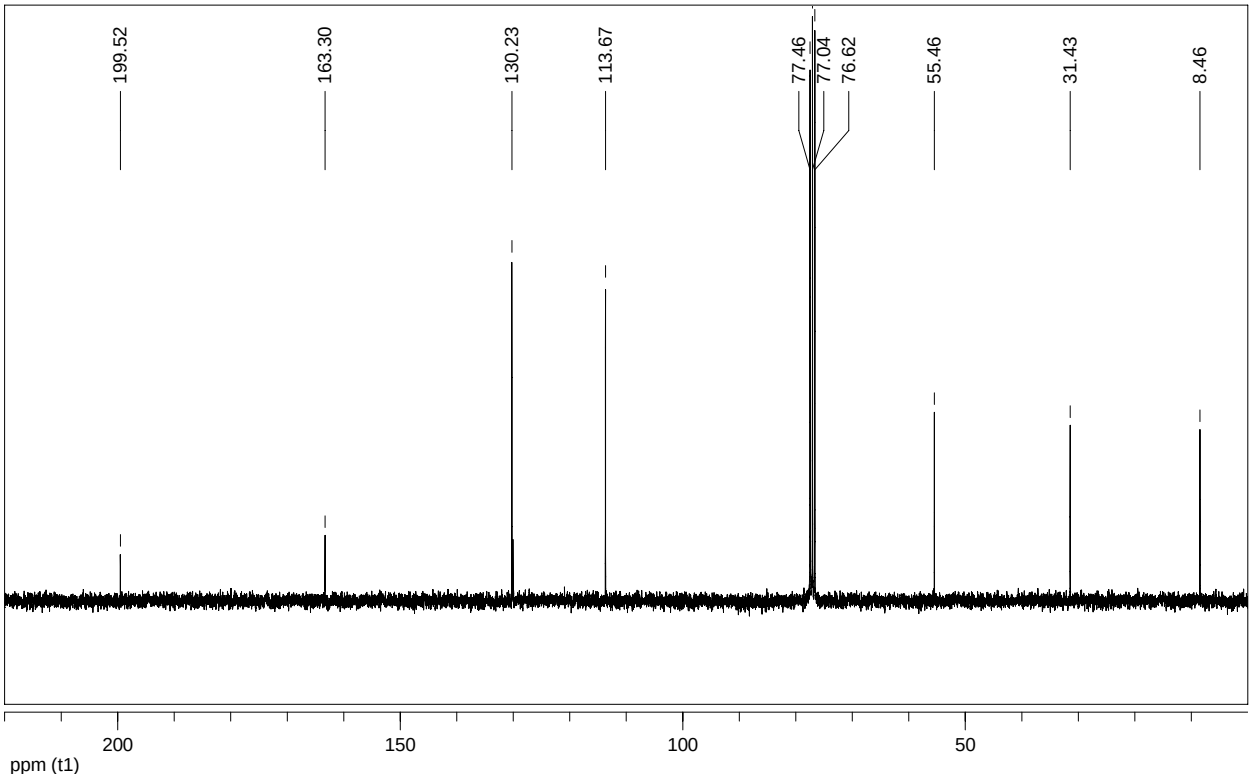
1-(naphthalen-2-yl)ethanone (4e)



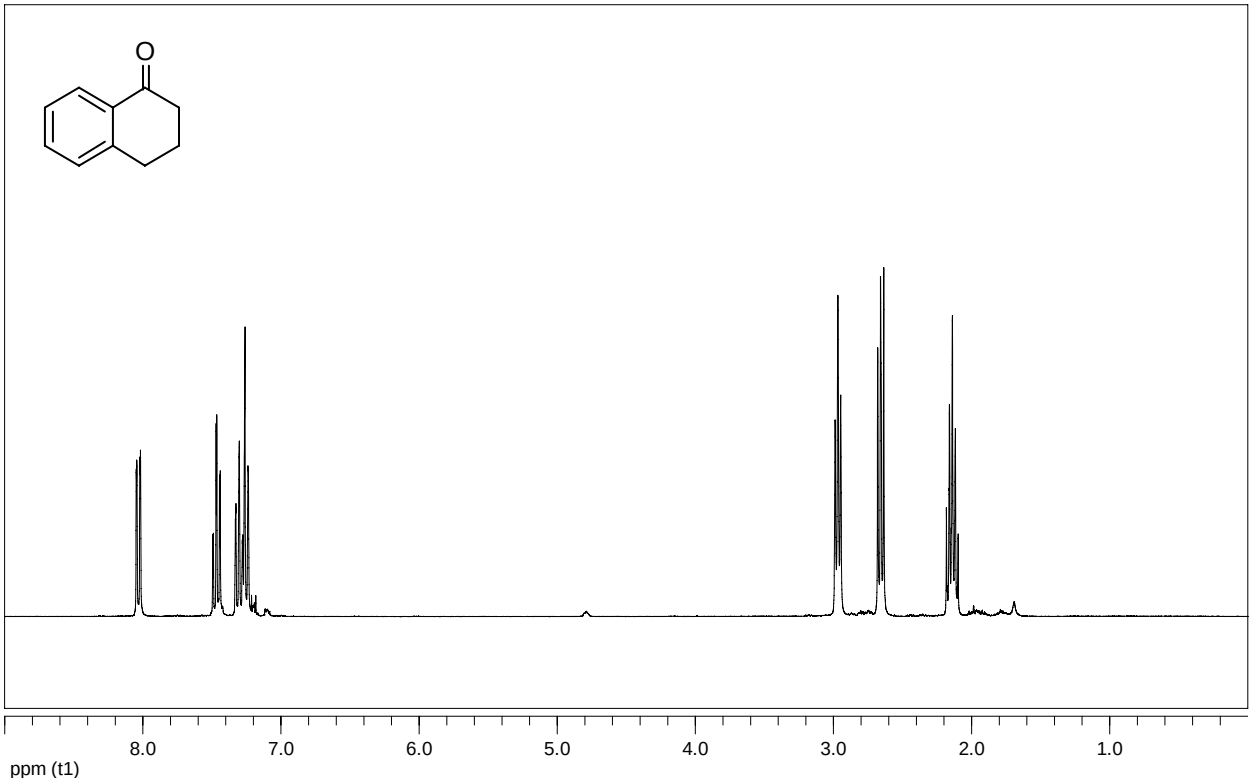


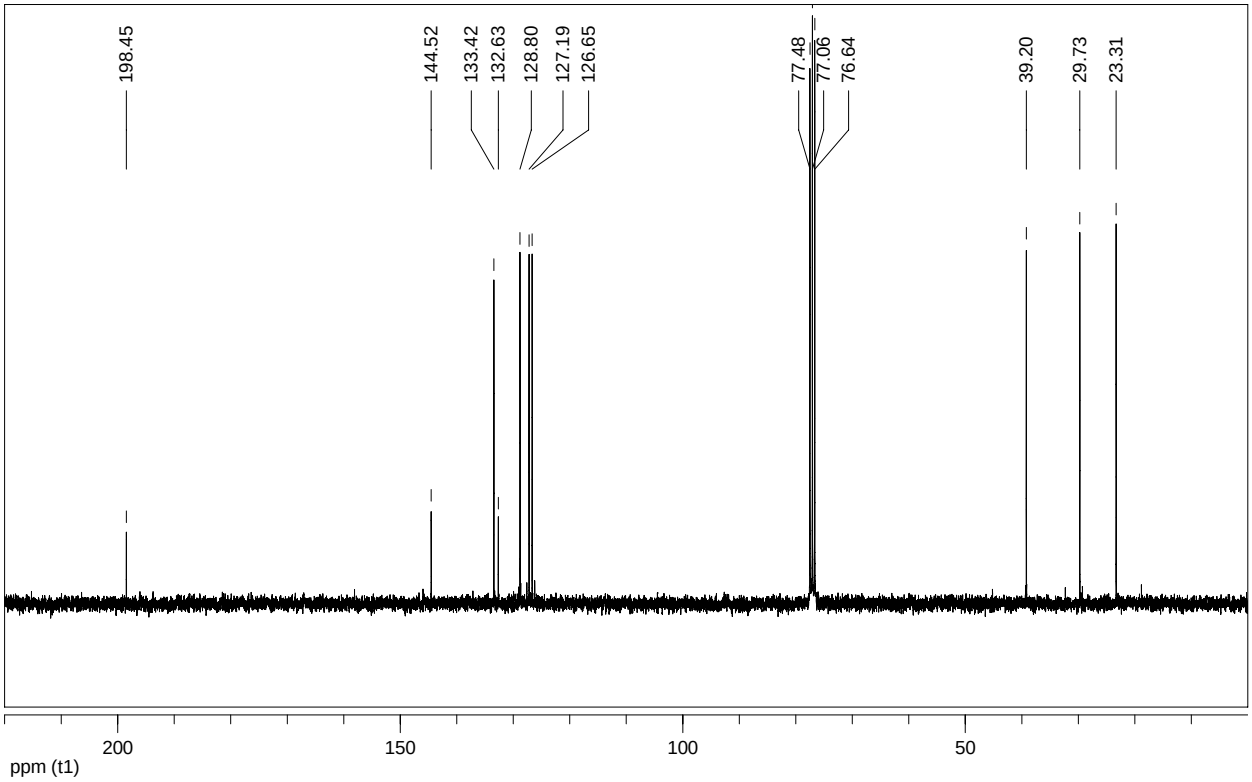
1-(4-methoxyphenyl)propan-1-one (4f)



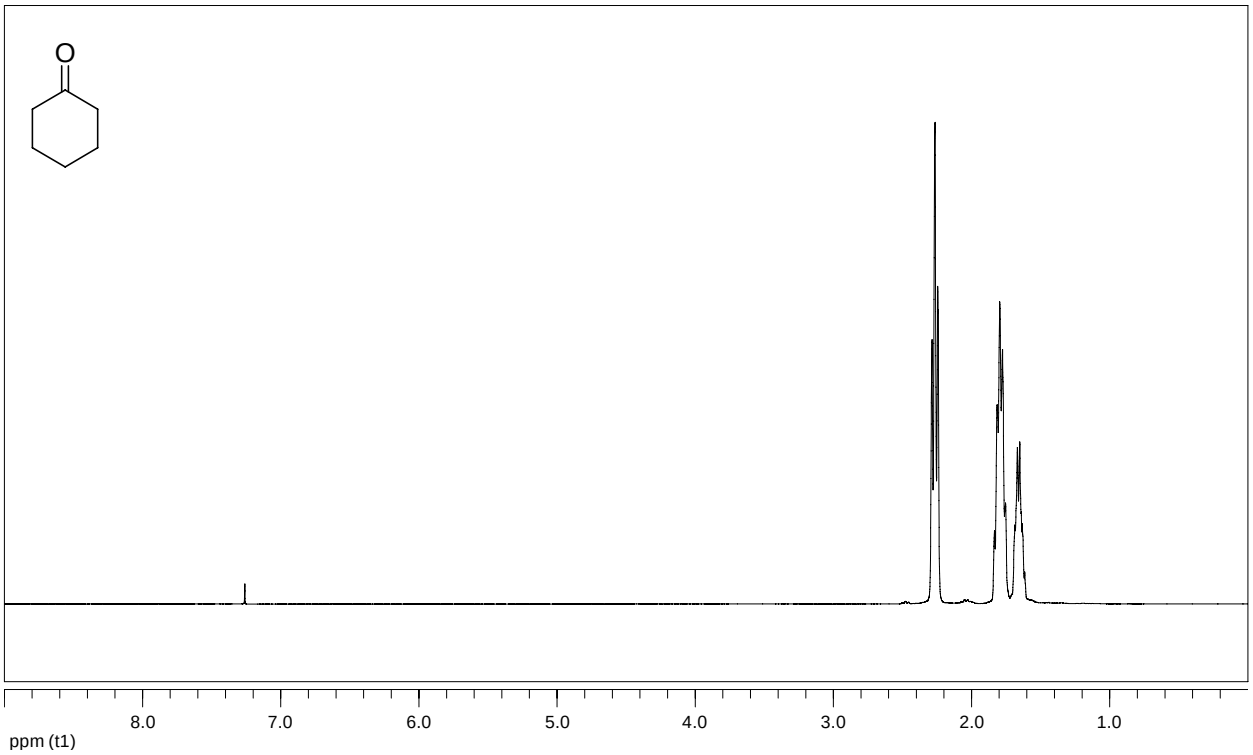


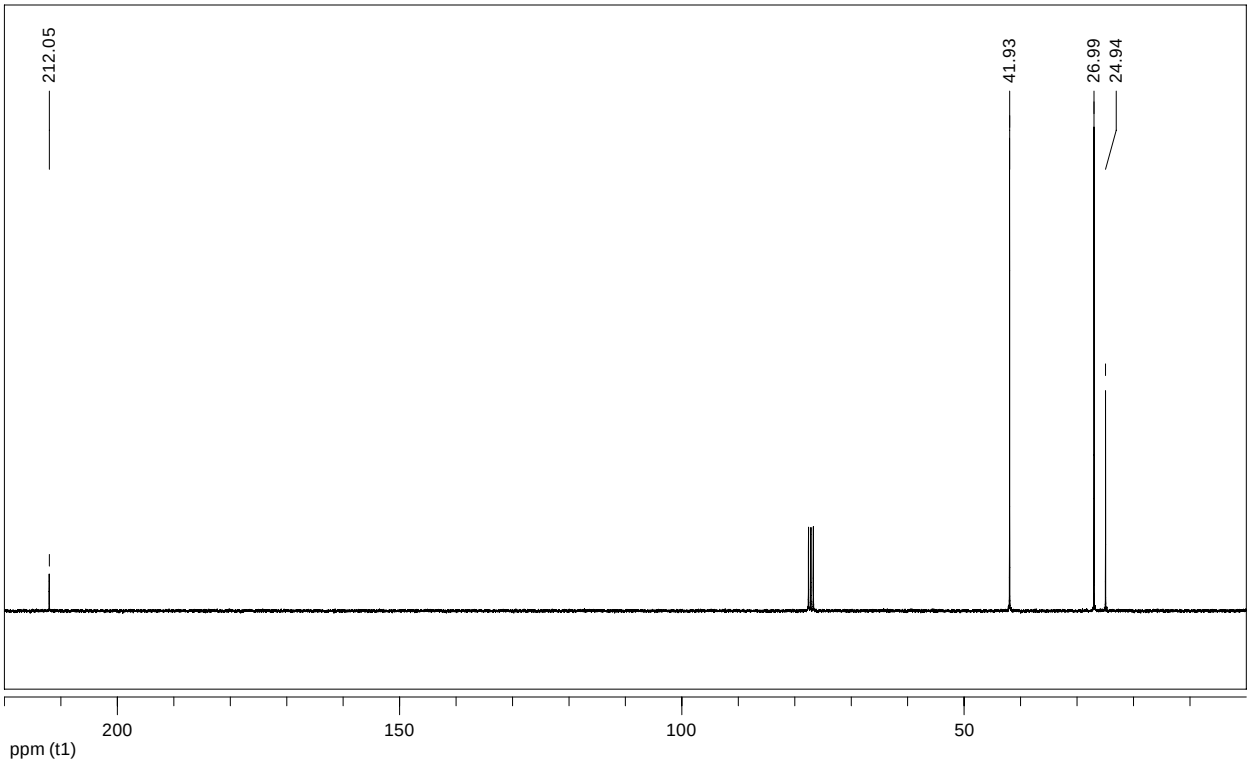
3,4-Dihydronaphthalen-1(2H)-one (4g)



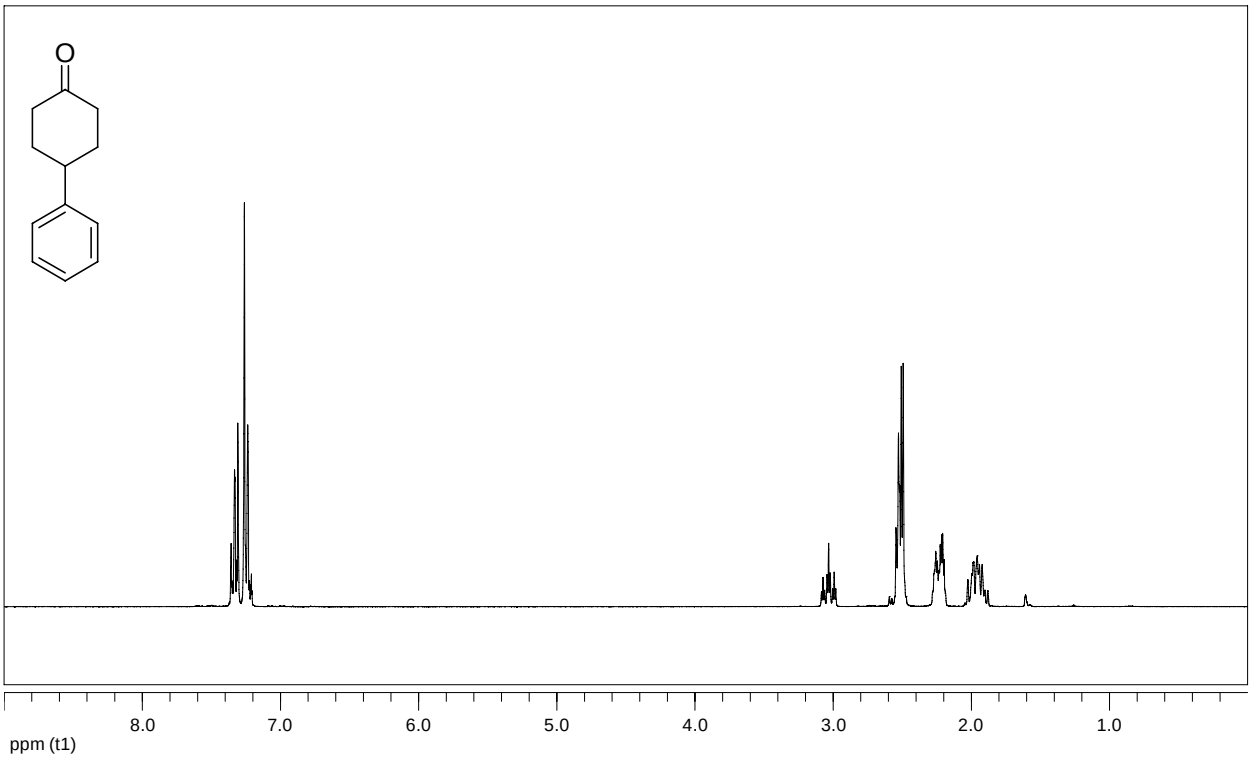


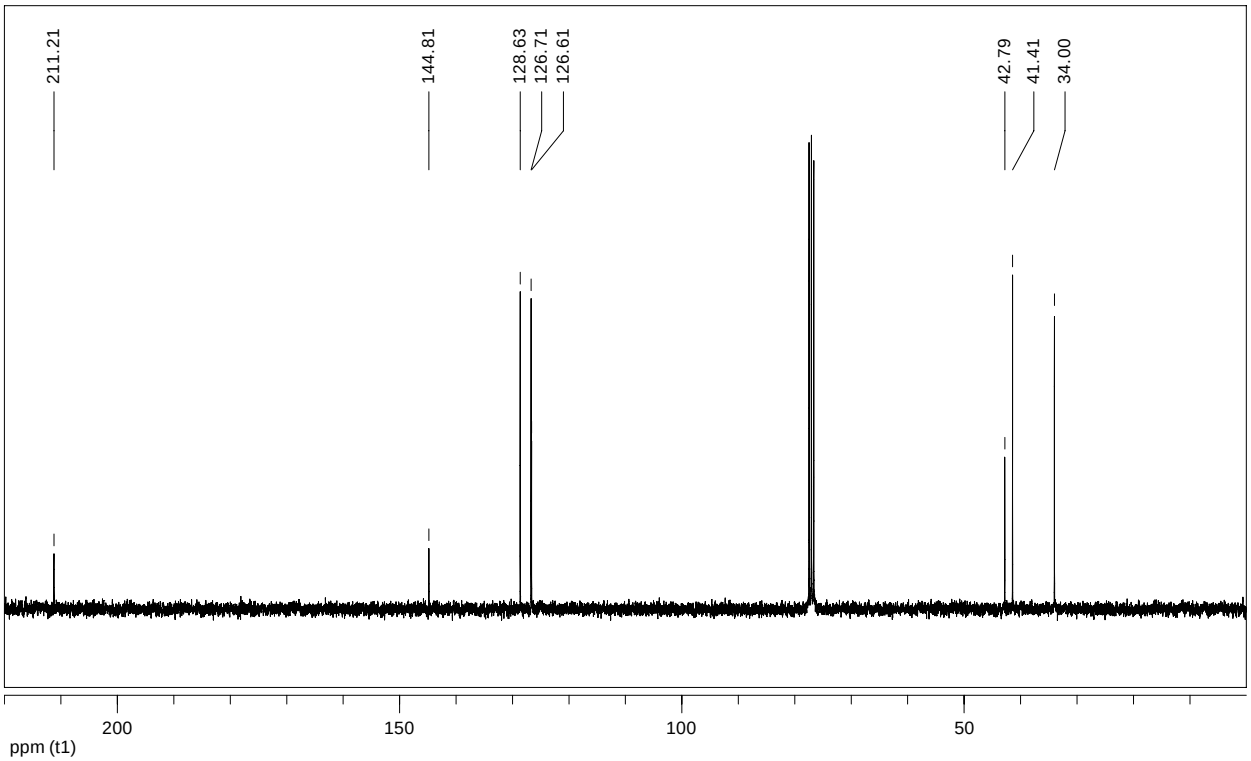
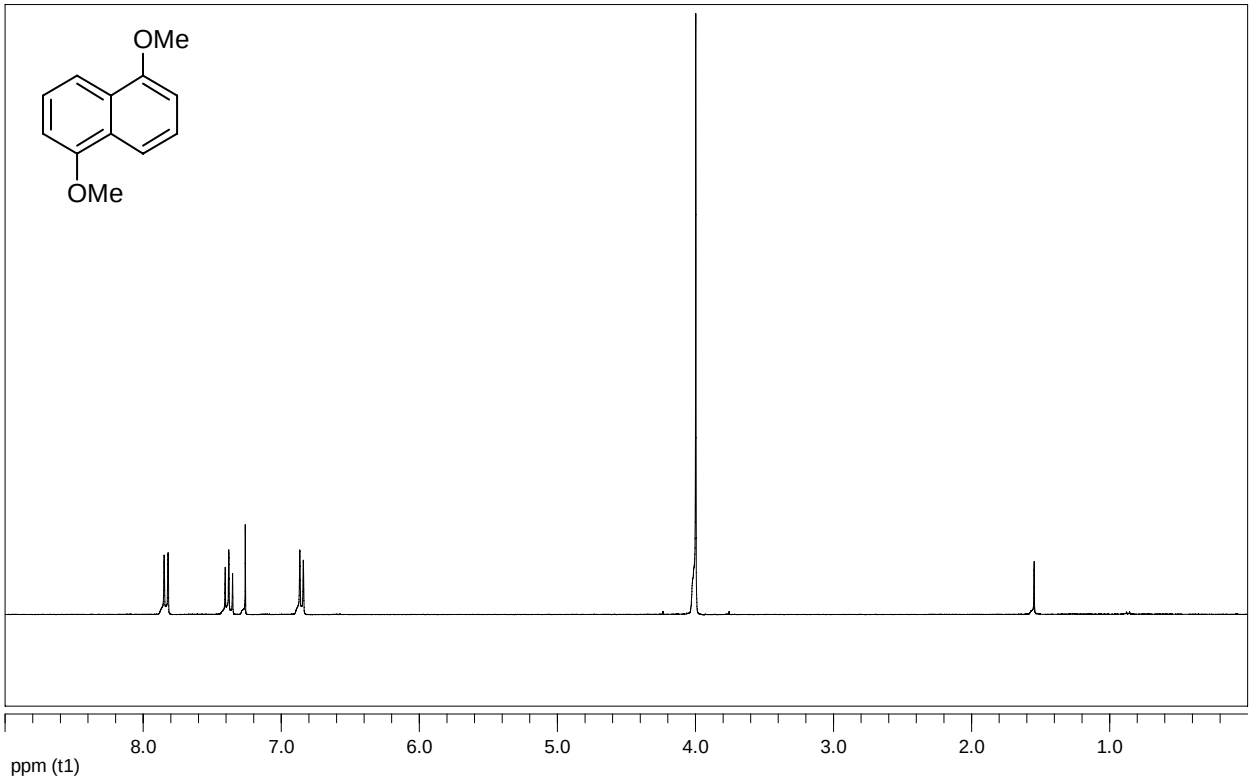
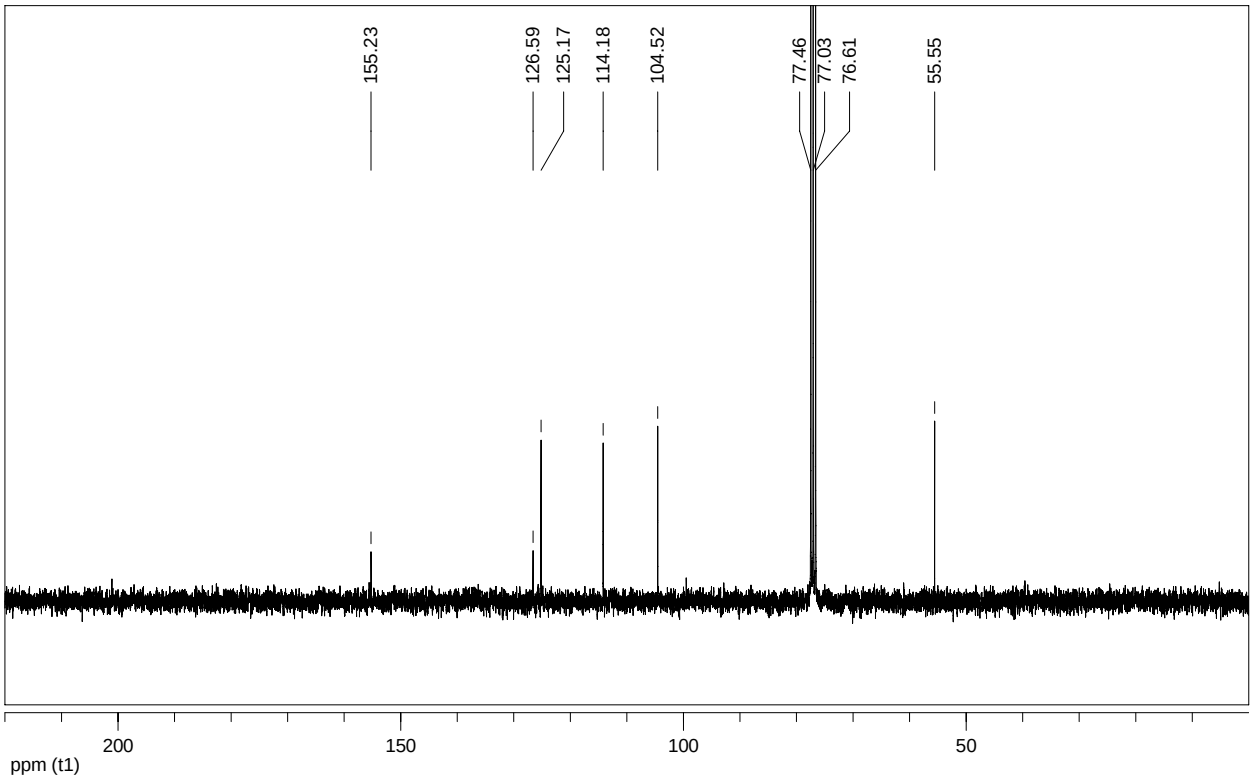
Cyclohexanone (4i)





4-Phenylcyclohexanone (4j)





1, 5-Dimethoxy naphthalene