Pd-catalyzed regioselective allylation of mono- and disubstituted hydrazines

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Supporting information

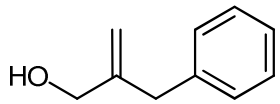
General remarks

DCM was distilled from calcium hydride and stored in dry Schlenk tube under argon. Toluene was distilled from Na / benzophenone and stored in dry Schlenk tube under argon. PhNHNHBoc,[1] EtNHNHBoc,[1] FmocNHNHi-Pr,[2] $BocNHNH_2$,[1] $CbzNHNH_2$,[3] $FmocNHNH_2$,[2] $PhthNNH_2$[4] were prepared by known methods. Allyl alcohols were prepared according to the literature procedures.[5] All other reagents were obtained from commercial sources and used without further purification. TLC was performed using Macherey-Nagel silica gel, TLC plates Alugram® SIL G / UV 254". Spots were visualized by UV light at 254 nm or by ~ 1% ethanolic solution of phosphomolybdic acid with subsequent heating. Column chromatography was carried out on a Merck Kieselgel 70-230 mesh. ^{1}H and ^{13}C NMR spectra were recorded at 200 MHz and 50 MHz respectively on a AVANCE II 200 spectrometer (Spektrospin AG, Switzerland). Deuteroform was used as a solvent. The chemical shifts are reported in ppm scale relative to the singlet (7.26 for ^{1}H) and triplet (77.0 for ^{13}C). Coupling constants are reported in Hz. IR spectra were measured on a Perkin-Elmer Spectrum BXII FTIR spectrometer using ATR technique with ZnSe. Melting points were determined on a Gallenkamp melting point apparatus. HRMS spectra were measured on a Thermo Electron LTQ Orbitrap ESI spectrometer.

The typical procedure for allylation of hydrazines.

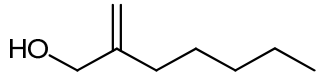
The dried Schlenk tube was charged with $Pd(dba)_2$ (0.078 mmol, 45 mg, 5%), $P(OPh)_3$ (0.16 mmol, 48 mg) and dppf (0.078 mmol, 43 mg), evacuated and backfilled with argon three times. Then dry DCM (1 ml) was added and the obtained mixture was degassed by three freeze-pump-thaw cycles. The resulted solution was stirred for 20 minutes at room temperature under argon and then volatiles were removed in vacuo. $BocNHNH_2$ (2.2 mmol, 302 mg) and 2-(4-methoxyphenyl)prop-2-en-1-ol (1.52 mmol, 250 mg) were added and the flask was evacuated and backfilled with argon. Then dry toluene (1 ml) was added. The resulting mixture was degassed by three freeze-pump-thaw cycles and the reaction was run at 55 ^{o}C under argon. When allyl alcohol was fully consumed (analyzed by TLC) reaction was cooled down to room temperature and purified by column chromatography on silica gel (eluent petroleum ether / ethyl acetate 5:1) yielding to 330 mg (78%) of the monoallylated hydrazine as slightly yellowish solid.

2-benzylprop-2-en-1-ol



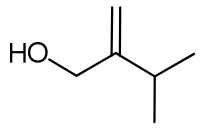
Colorless oil. R_f = 0.52 (petroleum ether / ethyl acetate 5:1)..^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.46–7.16 (m, 5H), 5.21–7.13 (m, 1H), 4.98–4.93 (m, 1H), 4.07 (s, 1H), 3.45 (s, 1H), 2.23–2.08 (broad m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 148.2, 139.0, 128.9, 128.3, 126.2, 111.3, 65.2, 39.8. FTIR (neat) cm^{-1}: 3336, 3087, 3060, 3026, 2911, 2870, 1654, 1494, 1452, 1432, 1054, 1028, 900, 740. HRMS-EI+: Calcd for $C_{10}H_{13}O$ [M+H]: 149.0966; Found: 149.0961.

2-methyleneheptan-1-ol



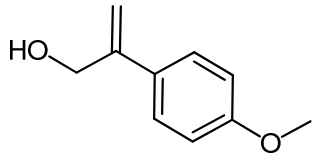
Colorless liquid. R_f = 0.25 (petroleum ether / ethyl acetate 5:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 5.01–4.98 (m, 1H), 4.88–4.82 (m, 1H), 4.06 (s, 1H), 2.04 (t, J = 3.0 Hz, 2H), 1.71 (s, 1H), 1.53–1.18 (m, 6H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 149.3, 109.0, 65.9, 33.0, 31.6, 27.5, 22.5, 14.0. FTIR (neat) cm^{-1}: 3333, 2956, 2927, 2858, 1654, 1457, 1378, 1043, 1026, 894, 727. HRMS-EI+: Calcd for $C_8H_{16}O$ [M+H]: 129.1279; Found: 129.1274.

3-methyl-2-methylenebutan-1-ol



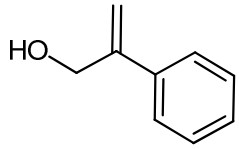
Colorless liquid. R_f = 0.49 (petroleum ether / ethyl acetate 5:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 5.02–4.97 (m, 1H), 4.91–4.87 (m, 1H), 4.12 (d, J = 1.1 Hz, 2H), 2.32 (sept, J = 6.9 Hz, 1H), 1.62 (s, 1H), 1.06 (d, J = 6.9 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 155.3, 107.0, 65.0, 31.1, 21.8. FTIR (neat) cm^{-1}:3326, 2961, 2932, 2873, 1650, 1463, 14420, 1404, 1364, 1095, 1029, 894. HRMS-EI+: Calcd for $C_6H_{12}O$ Na [M+Na]: 123.0786; Found: 123.0780.

2-(4-methoxyphenyl)prop-2-en-1-ol[6]



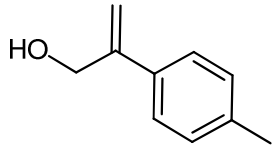
White solid. mp = 67–69 °C. R_f = 0.63(petroleum ether / ethyl acetate 1:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.48 – 7.32 (m, 2H), 6.94 – 6.81 (m, 2H), 5.39 (s, 1H), 5.29 – 5.23 (m, 1H), 4.50 (s, 2H), 3.81 (s, 3H), 1.93 (broad s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 159.5, 146.7, 131.0, 127.2, 113.9, 111.0, 65.1, 55.3. FTIR (neat) cm^{-1}: 3328, 2957, 2936, 2839, 1607, 1512, 1468, 1301, 1246, 1185, 1107, 1050, 1026, 897, 836, 826.

2-phenylprop-2-en-1-ol[6]



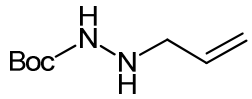
Colorless oil. R_f = 0.71 (petroleum ether / ethyl acetate 3:2). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.52–7.15 (m, 5H), 5.48–5.41 (m, 1H) 5.36–5.30 (m, 1H), 4.53–4.48 (m, 2H), 1.93 (broad s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 147.4, 138.6, 128.5, 127.9, 126.1, 112.5, 65.0. FTIR (neat) cm^{-1}: 3337, 3087, 3056, 3021, 2923, 2862, 1632, 1495, 1444, 1112, 1046, 1024, 902, 778.

2-(p-tolyl)prop-2-en-1-ol[7]



White solid. mp = 46–47 °C. R_f = 0.74 (petroleum ether / ethyl acetate 1:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.40 – 7.31 (m, 2H), 7.22 – 7.11 (m, 2H), 5.45 (s, 1H), 5.33 – 5.29 (m, 1H), 4.57 – 4.50 (m, 2H), 2.36 (s, 3H), 1.76 (broad s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 147.2, 137.7, 135.6, 129.2, 126.0, 111.7, 65.1, 21.1. FTIR (neat) cm^{-1}: 3304, 3032, 2917, 2861, 1516, 1476, 1466, 1382, 1106, 1040, 1014, 894, 824, 740.

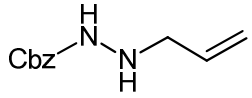
***tert*-butyl 2-allylhydrazinecarboxylate (1a)[8]**



Reaction was run starting from $BocNHNH_2$ (6 mmol, 792 mg), allyl alcohol (3 mmol, 204 uL) in toluene (2 mL) using $Pd(dba)_2$ (0.06 mmol, 34 mg, 2%), $P(OPh)_3$ (0.11mmol, 36 mg) and dppf (0.06 mmol, 33 mg) and the title compound was isolated as colorless solid (366 mg, 71%).

mp = 32–33 ^oC. R_f = 0.49 (petroleum ether / ethyl acetate 5:1). ^1H NMR (200 MHz, $CDCl_3$) δ = 6.60 (broad s, 1H), 5.94 – 5.66 (m, 1H), 5.35 – 4.89 (m, 2H), 4.03 (broad s, 1H), 3.41 (d, *J* = 6.3 Hz, 2H), 1.41 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 156.6, 134.2, 117.7, 80.1, 54.3, 28.2. FTIR (neat) cm^{-1}: 3310, 2978, 2932, 1698, 1480, 1455, 1392, 1366, 1281, 1251, 1156, 1018, 993, 919, 732.

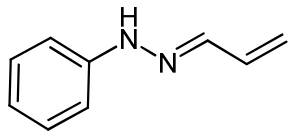
benzyl 2-allylhydrazinecarboxylate (2)



Reaction was run starting from $CbzNHNH_2$ (4 mmol, 664 mg), allyl alcohol (2 mmol, 136 uL) in toluene (1.5 mL) using $Pd(dba)_2$ (0.04 mmol, 23 mg, 2%), $P(OPh)_3$ (0.08 mmol, 25 mg) and dppf (0.04 mmol, 22 mg) and the title compound was isolated as colorless solid (266 mg, 64%).

mp = 39 ^oC. R_f = 0.20 (petroleum ether / ethyl acetate 5:1). ^1H NMR (200 MHz, $CDCl_3$) δ = 7.47 – 7.21 (m, 5H), 6.08 – 5.71 (m, 1H), 5.41 – 4.99 (m, 4H), 5.60 – 4.48 (broad s, 1H), 3.51 (d, *J* = 6.2 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 157.1, 136.1, 133.7, 128.5, 128.2, 128.1, 118.5, 67.1, 54.4. FTIR (neat) cm^{-1}: 3299, 3068, 3033, 2975, 2951, 1705, 1644, 1519, 1497, 1454, 1418, 1332, 1263, 1156, 1142, 1041, 1028, 993, 921, 736. HRMS-EI+: Calcd for $C_{11}H_{15}N_2O_2$ [M+H]: 207.1134; Found: 207.1128.

1-allylidene-2-phenylhydrazine (3)

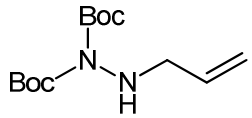


Reaction was run starting from $PhNHNH_2$ (4 mmol, 432 mg), allyl alcohol (2 mmol, 136 uL) in toluene (1.5 mL) using $Pd(dba)_2$ (0.04 mmol, 23 mg, 2%), $P(OPh)_3$ (0.08 mmol, 25 mg) and dppf

(0.04 mmol, 22 mg). The title compound was formed upon oxidation of reaction product on air and isolated as yellow oil (157 mg, 53%).

R_f = 0.63 (petroleum ether / ethyl acetate 5:1). ^{1}H NMR (200 MHz, THF) δ = 9.12 (broad s, 1H), 7.41 (d, *J* = 9.2 Hz, 1H), 7.27 – 7.03 (m, 2H), 7.02 – 6.88 (m, 2H), 6.78 – 6.66 (m, 1H), 6.64 – 6.40 (m, 1H), 5.37 – 5.17 (m, 2H). ^{13}C NMR (50 MHz, THF) δ = 143.5, 136.9, 133.4, 126.8, 117.1, 114.6, 110.3. FTIR (neat) cm^{-1}: 3311, 3087, 3050, 3032, 1598, 1565, 1513, 1494, 1449, 1293, 1256, 1191, 1169, 1132, 1070, 991, 919, 749. HRMS-EI+: Calcd for $C_9H_{11}N_2$ [M+H]: 147.0922; Found: 147.0917.

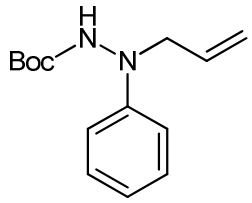
di-*tert*-butyl 2-allylhydrazine-1,1-dicarboxylate (4)



Reaction was run starting from Boc_2NNH_2 (1 mmol, 231 mg), allyl alcohol (0.5 mmol, 34 uL) in toluene (0.8 mL) using $Pd(dba)_2$ (0.02 mmol, 11 mg, 2%), $P(OPh)_3$ (0.04 mmol, 12 mg) and dppf (0.02 mmol, 11 mg) and the title compound was isolated as colorless oil (97 mg, 71%).

R_f = 0.61 (petroleum ether / ethyl acetate 5:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 6.02 – 5.78 (m, 1H), 5.31 – 5.01 (m, 2H), 4.38 (s, 1H), 3.43 (d, *J* = 6.6 Hz, 2H), 1.40 (s, 18H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 152.3, 133.6, 118.6, 83.1, 54.0, 28.0. FTIR (neat) cm^{-1}: 3318, 3076, 2980, 2936, 1746, 1708, 1479, 1457, 1367, 1352, 1274, 1233, 1146, 1136, 1110, 855, 762. HRMS-EI+: Calcd for $C_{13}H_{25}N_2O_4$ [M+H]: 273.1814; Found: 273.1809.

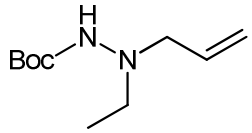
***tert*-butyl 2-allyl-2-phenylhydrazinecarboxylate (5)[9]**



Reaction was run starting from BocNHNHPh (2 mmol, 416 mg), allyl alcohol (2.2 mmol, 150 uL) in toluene (1.5 mL) using $Pd(dba)_2$ (0.04 mmol, 23 mg, 2%) and $P(OPh)_3$ (0.16 mmol, 50 mg) and the title compound was isolated as colorless oil (493 mg, 99%).

R_f = 0.63 (petroleum ether / ethyl acetate 5:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.21 – 7.05 (m, 2H), 6.79 – 6.68 (m, 3H), 6.31 (broad s, 1H), 6.00 – 5.68 (m, 1H), 5.33 – 4.95 (m, 2H), 4.14 – 3.84 (m, 2H), 1.38 (s,9H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 155.1, 149.0, 132.9, 129.0, 119.4, 118.2, 113.0, 80.8, 55.7, 28.3. FTIR (neat) cm^{-1}: 3079, 2979, 2929, 1702, 1599, 1499, 1367, 1241, 1145, 921, 748, 693.

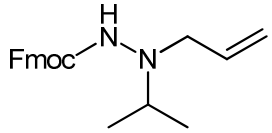
tert-butyl 2-allyl-2-ethylhydrazinecarboxylate (6)[1]



Reaction was run starting from BocNHNHEt (2 mmol, 320 mg), allyl alcohol (2.2 mmol, 150 uL) in toluene (1.5 mL) using $Pd(dba)_2$ (0.04 mmol, 23 mg, 2%) and $P(OPh)_3$ (0.16 mmol, 50 mg) and the title compound was isolated as colorless solid (307 mg, 77%).

mp = 44 °C. R_f = 0.48 (petroleum ether / ethyl acetate 5:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 6.00 – 5.75 (m, 1H), 5.43 (broad s, 1H), 5.29 – 5.07 (m, 2H), 3.38 (d, *J* = 6.3 Hz, 2H), 2.75 (q, *J* = 7.0 Hz, 2H), 1.42 (s, 9H), 1.08 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 155.2, 133.5, 118.8, 79.8, 60.8, 51.2, 28.3, 12.0. FTIR (neat) cm^{-1}: 3273, 2977, 2936, 2878, 2823, 1710, 1518, 1490, 1456, 1390, 1365, 1245, 1170, 1158, 1088, 990, 918, 761.

(9H-fluoren-9-yl)methyl 2-allyl-2-isopropylhydrazinecarboxylate (7)

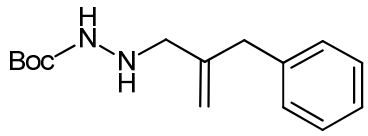


Reaction was run starting from FmocNHNH*i*-Pr (1 mmol, 310 mg), allyl alcohol (1.1 mmol, 75 uL) in toluene (0.8 mL) using $Pd(dba)_2$ (0.02 mmol, 11 mg, 2%) and $P(OPh)_3$ (0.08 mmol, 24 mg) and the title compound was isolated as white solid (95 mg, 27%).

mp = 105–106 °C. R_f = 0.39 (petroleum ether / ethyl acetate 5:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 7.4 Hz, 2H), 7.67 – 7.48 (m, 2H), 7.50 – 7.20 (m, 4H), 6.03 – 5.70 (m, 1H), 5.51 (broad s, 1H), 5.27 – 5.06 (m, 2H), 4.46 (d, *J* = 6.7 Hz, 2H), 4.30 – 4.15 (m, 1H), 3.42 – 3.24 (m, 2H), 3.14 – 2.94 (m, 1H), 1.07 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 156.4, 143.9/143.2, 141.3, 134.8/133.8, 128.9/127.6, 128.3/126.9, 125.5/125.1, 119.9, 118.7, 66.6, 58.4,

55.2, 47.3, 18.3. FTIR (neat) cm^{-1}: 3257, 3042, 2975, 2938, 2884, 1712, 1534, 1448, 1249, 1173, 1164, 1120, 1034, 988, 919, 759, 739. HRMS-EI+: Calcd for $C_{21}H_{25}N_2O_2$ [M+H]: 337.1916; Found: 337.1911.

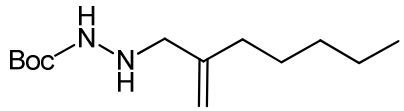
***tert*-butyl 2-(2-benzylallyl)hydrazinecarboxylate (1b)**



Reaction was run starting from $BocNHNH_2$ (4 mmol, 528 mg), 2-benzylprop-2-en-1-ol (2 mmol, 329 mg, 90% in DCM) in toluene (1.5 mL) using $Pd(dba)_2$ (0.04 mmol, 23 mg, 2%), $P(OPh)_3$ (0.08 mmol, 25 mg) and dppf (0.04 mmol, 22 mg) and the title compound was isolated as white solid (370 mg, 71%).

mp = 42–43 °C. R_f = 0.21 (petroleum ether / ethyl acetate 5:1). ^1H NMR (200 MHz, $CDCl_3$) δ = 7.41 – 7.14 (m, 5H), 7.19 (broad s, 1H), 5.09 (s, 1H), 4.94 (s, 1H), 4.45 (broad s, 1H), 3.44/3.41 (s/s, 4H), 1.46 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 156.5, 139.2, 129.0, 128.30 126.13 114.4, 80.5, 55.8, 41.1, 28.3. FTIR (neat) cm^{-1}: 3332, 3282, 3069, 3029, 3006, 2979, 2930, 1692, 1540, 1494, 1485, 1451, 1364, 1268, 1243, 1152, 1028, 992, 941, 907, 858, 730. HRMS-EI+: Calcd for $C_{15}H_{23}N_2O_2$ [M+H]: 263.1760; Found: 263.1754.

***tert*-butyl 2-(2-methyleneheptyl)hydrazinecarboxylate (1c)**

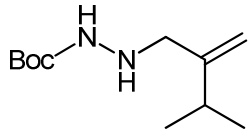


Reaction was run starting from $BocNHNH_2$ (4 mmol, 528 mg), 2-methyleneheptan-1-ol (2 mmol, 256 mg) in toluene (1.5 mL) using $Pd(dba)_2$ (0.04 mmol, 23 mg, 2%), $P(OPh)_3$ (0.08 mmol, 25 mg) and dppf (0.04 mmol, 22 mg) and the title compound was isolated as slightly yellowish oil (350bmg, 72%).

R_f = 0.27 (petroleum ether / ethyl acetate 5:1). ^1H NMR (200 MHz, $CDCl_3$) δ = 6.19 (broad s, 1H), 4.94 (s, 1H), 4.88 (s, 1H), 4.51 (s, 1H), 3.40 (s, 2H), 2.05 (t, *J* = 7.4 Hz, 2H), 1.63 – 1.14 (m, 15H), 0.87 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 156.6, 145.8, 111.9, 34.4, 31.5, 28.3, 27.4, 22.5, 14.0. FTIR (neat) cm^{-1}: 3323, 2958, 2928, 2859, 1705, 1455, 1392, 1355, 1279, 1252, 1150,

1047, 1021, 898, 873, 898, 779. HRMS-EI+: Calcd for $C_{26}H_{53}N_4O_4$ [2M+H]: 485.4067; Found: 485.4061.

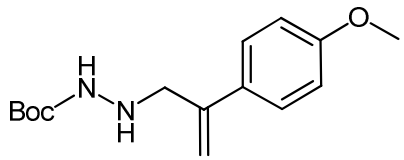
***tert*-butyl 2-(3-methyl-2-methylenebutyl)hydrazinecarboxylate (1d)**



Reaction was run starting from $BocNHNH_2$ (4 mmol, 528 mg), 3-methyl-2-methylenebutan-1-ol (2 mmol, 200 mg) in toluene (1.5 mL) using $Pd(dba)_2$ (0.04 mmol, 23 mg, 2%), $P(OPh)_3$ (0.08 mmol, 25 mg) and dppf (0.04 mmol, 22 mg) and the title compound was isolated as slightly yellowish oil (298 mg, 70%).

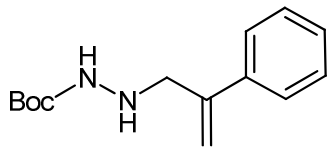
R_f = 0.26 (petroleum ether / ethyl acetate 5:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 6.16 (broad s, 1H), 4.90 (d, *J* = 6.0 Hz, 2H), 4.00 (broad s, 1H), 3.42 (s, 2H), 2.31 (sept, J = 6.9 Hz, 1H), 1.44 (s, 9H), 1.02 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 156.6, 151.7, 109.6, 80.4, 55.2, 32.2, 28.3, 21.6. FTIR (neat) cm^{-1}: 3326, 2963, 2928, 2870, 1704, 1456, 1392, 1366,1280, 1251, 1157, 1047, 1019, 901. HRMS-EI+: Calcd for $C_{11}H_{23}N_2O_2$ [M+H]: 215.1760; Found: 215.1755.

***tert*-butyl 2-(2-(4-methoxyphenyl)allyl)hydrazinecarboxylate (1e)**



mp = 61–62 °C. R_f = 0.27 (petroleum ether / ethyl acetate 5:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.46 – 7.34 (m, 2H), 6.91 – 6.81 (m, 2H), 6.34 (broad s, 1H), 5.40 (d, *J* = 1.0 Hz, 1H), 5.19 (s, 1H), 4.35 (broad s, 1H), 3.87 (s, 2H), 3.78 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 159.3, 156.5, 143.0, 131.7, 127.2, 113.9, 113.8, 81.2/80.5, 55.5, 55.2, 28.3/ 28.1. FTIR (neat) cm^{-1}: 3328, 3248, 3091, 2981, 2930, 2834, 1702, 1605, 1544, 1514, 1366, 1285, 1270, 1250, 1183, 1150, 1042, 854, 835. HRMS-EI+: Calcd for $C_{20}H_{45}N_4O_6$ [2M+H]: 557.3339; Found: 557.3337.

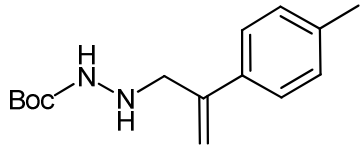
***tert*-butyl 2-(2-phenylallyl)hydrazinecarboxylate (1f)**



Reaction was run starting from $BocNHNH_2$ (2.2 mmol, 302 mg), 2-phenylprop-2-en-1-ol (1.5 mmol, 203 mg) in toluene (1 mL) using $Pd(dba)_2$ (0.078 mmol, 45 mg, 5%), $P(OPh)_3$ (0.15 mmol, 48 mg) and dppf (0.078 mmol, 43 mg) and the title compound was isolated as white solid (190 mg, 51%).

mp = 55–56 ^{o}C. R_f = 0.84 (petroleum ether / ethyl acetate 5:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.43 – 7.32 (m, 2H), 7.31 – 7.08 (m, 3H), 5.99 (broad s, 1H), 5.37 (d, *J* = 1.2 Hz, 1H), 5.18 (d, *J* = 1.1 Hz, 1H), 3.96 (broad s, 1H), 3.79 (s, 2H), 1.36 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 156.5, 144.0, 139.4, 128.3, 127.7, 126.1, 115.4, 80.4, 55.5, 28.3. FTIR (neat) cm^{-1}:3301, 2978, 2932, 1705, 1598, 1498, 1454, 1366, 1269, 1248, 1156, 990, 920, 872, 746. HRMS-EI+: Calcd for $C_{28}H_{41}N_4O_4$ [2M+H]: 497.3128; Found: 497.3122.

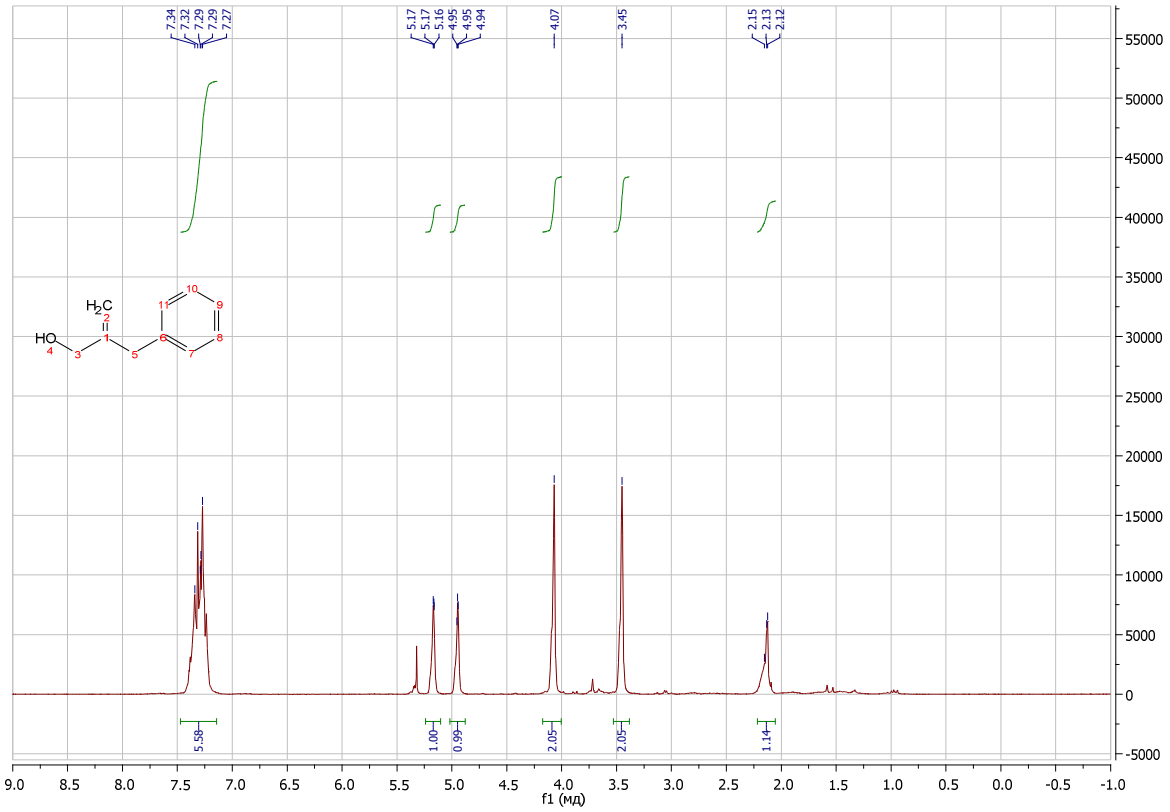
***tert*-butyl 2-(2-(p-tolyl)allyl)hydrazinecarboxylate (1g)**

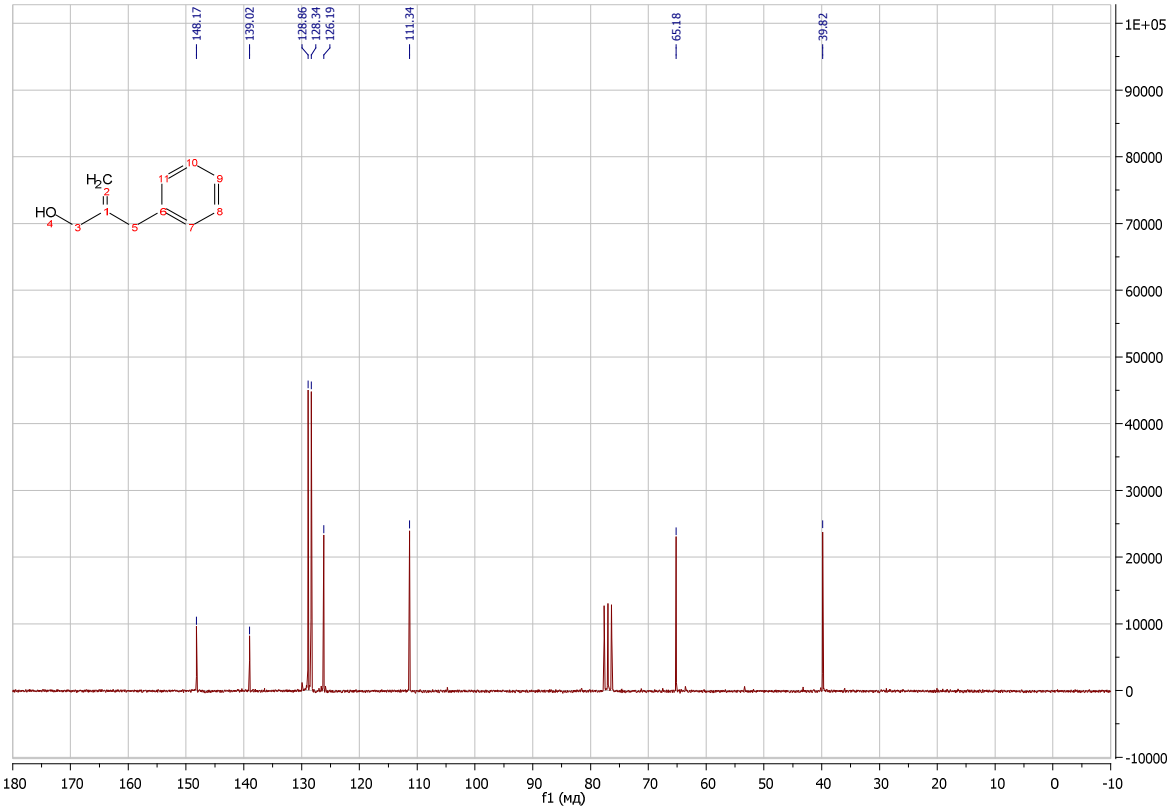


Reaction was run starting from $BocNHNH_2$ (2.2 mmol, 302 mg), 2-(*p*-tolyl)prop-2-en-1-ol (1.5 mmol, 224 mg) in toluene (1 mL) using $Pd(dba)_2$ (0.078 mmol, 45 mg, 5%), $P(OPh)_3$ (0.15 mmol, 48 mg) and dppf (0.078 mmol, 43 mg) and the title compound was isolated as white solid (234 mg, 60%).

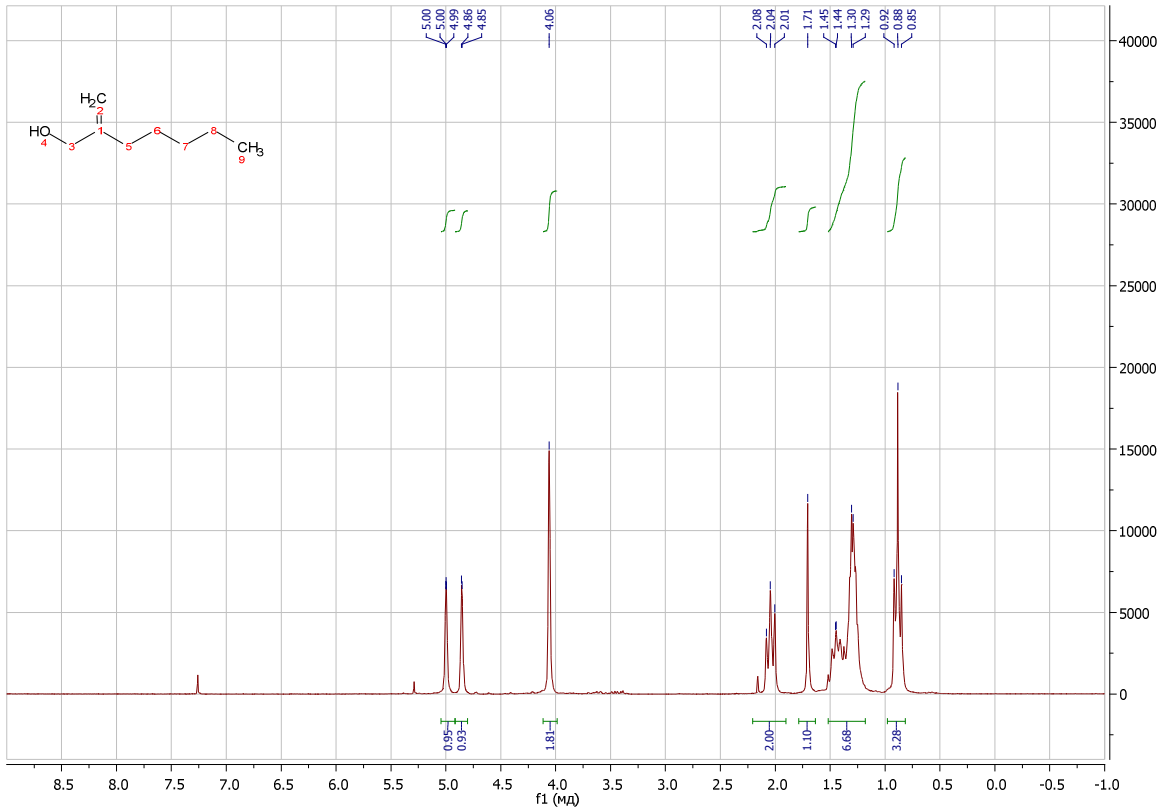
mp = 86 ^{o}C. R_f = 0.52 (petroleum ether / ethyl acetate 5:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.45 – 7.34 (m, 2H), 7.21 – 7.11 (m, 1H), 6.34 (broad s, 1H), 5.46 (d, *J* = 1.1 Hz, 1H), 5.25 (d, *J* = 0.9 Hz, 1H), 4.01 (broad s, 1H), 3.89 (s, 2H), 2.35 (s, 3H), 1.48 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) δ = 156.5, 143.8, 137.4, 136.4, 129.0, 125.9, 114.4, 80.3, 55.4, 28.3, 21.0. FTIR (neat) cm^{-1}: 3319, 1249, 2978, 2935, 2878, 1702, 1547, 1514, 1366, 1272, 1241, 1173, 1150, 1106, 940, 890, 856, 820. HRMS-EI+: Calcd for $C_{20}H_{45}N_4O_4$ [2M+H]: 525.3441; Found: 525.3440.

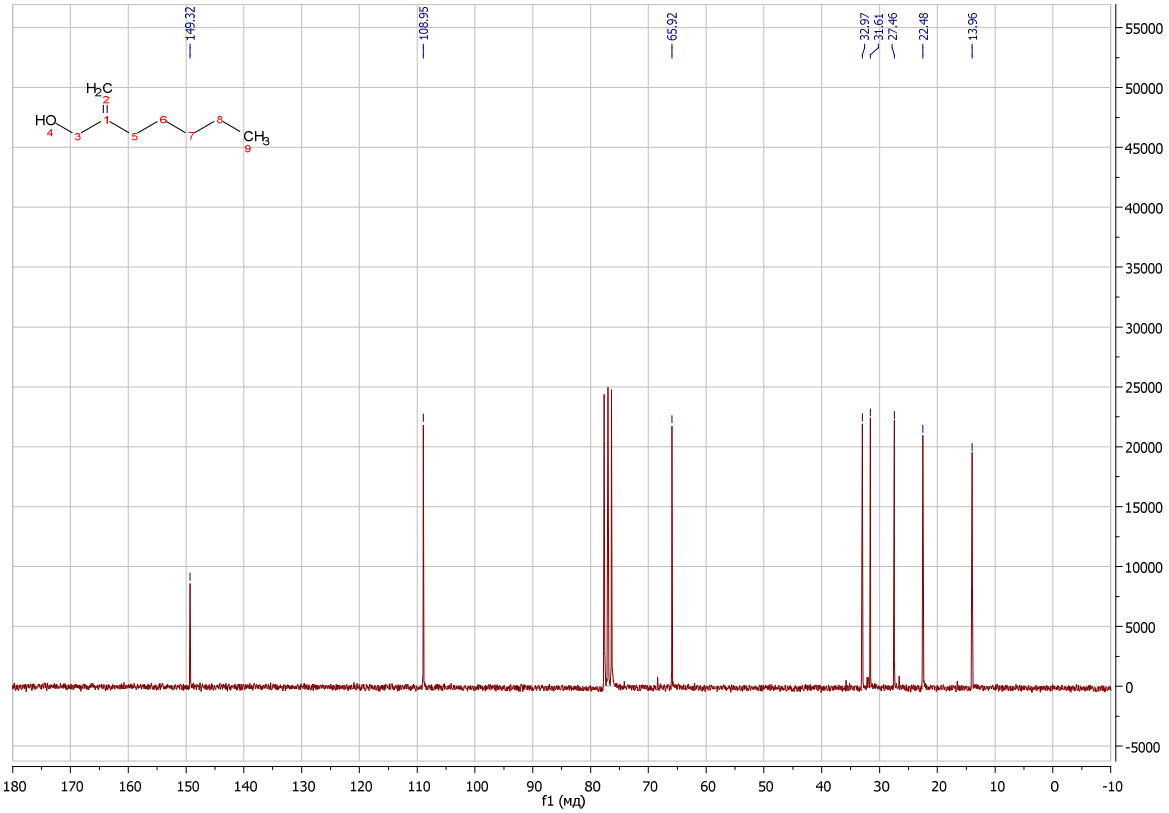
2-benzylprop-2-en-1-ol



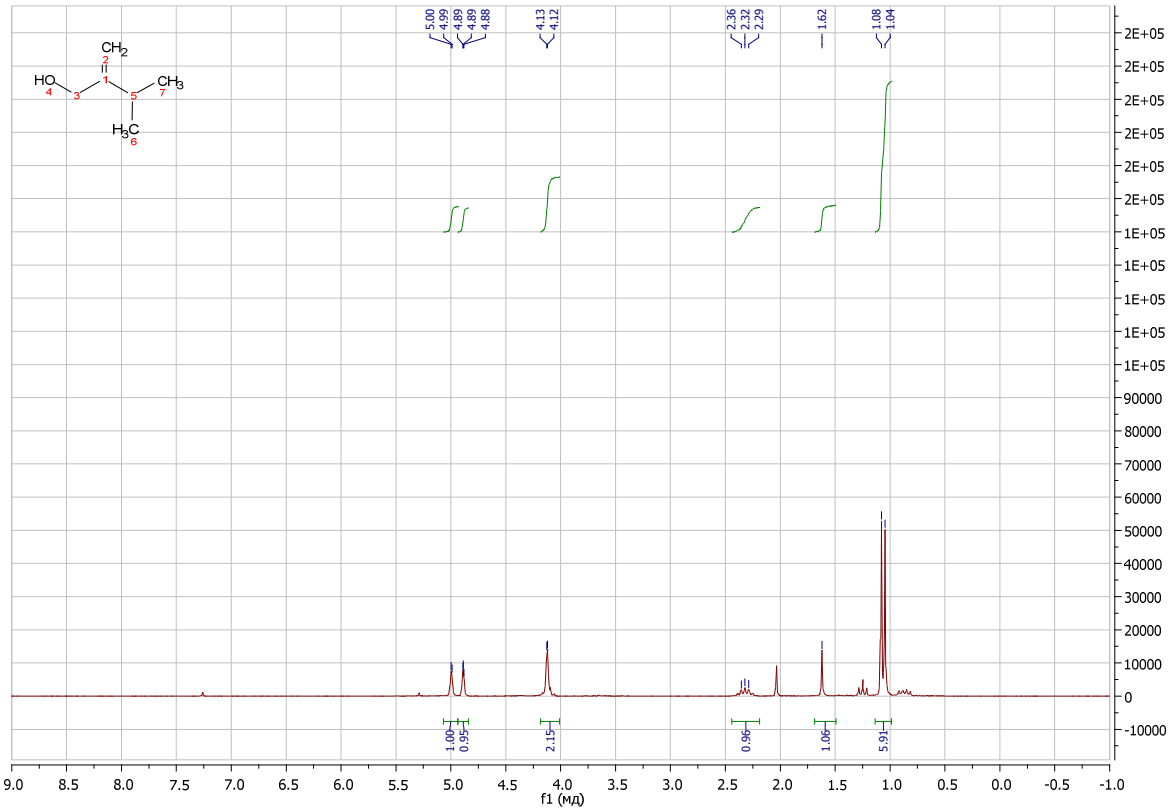


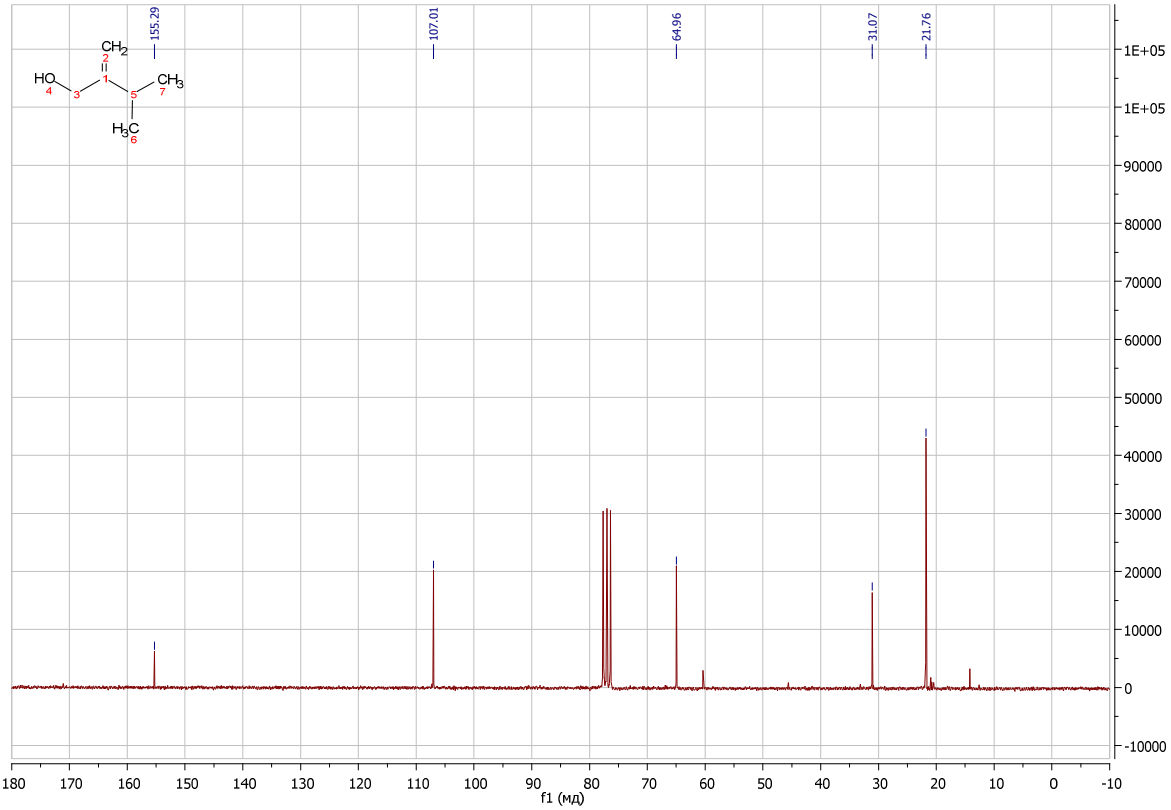
2-methyleneheptan-1-ol



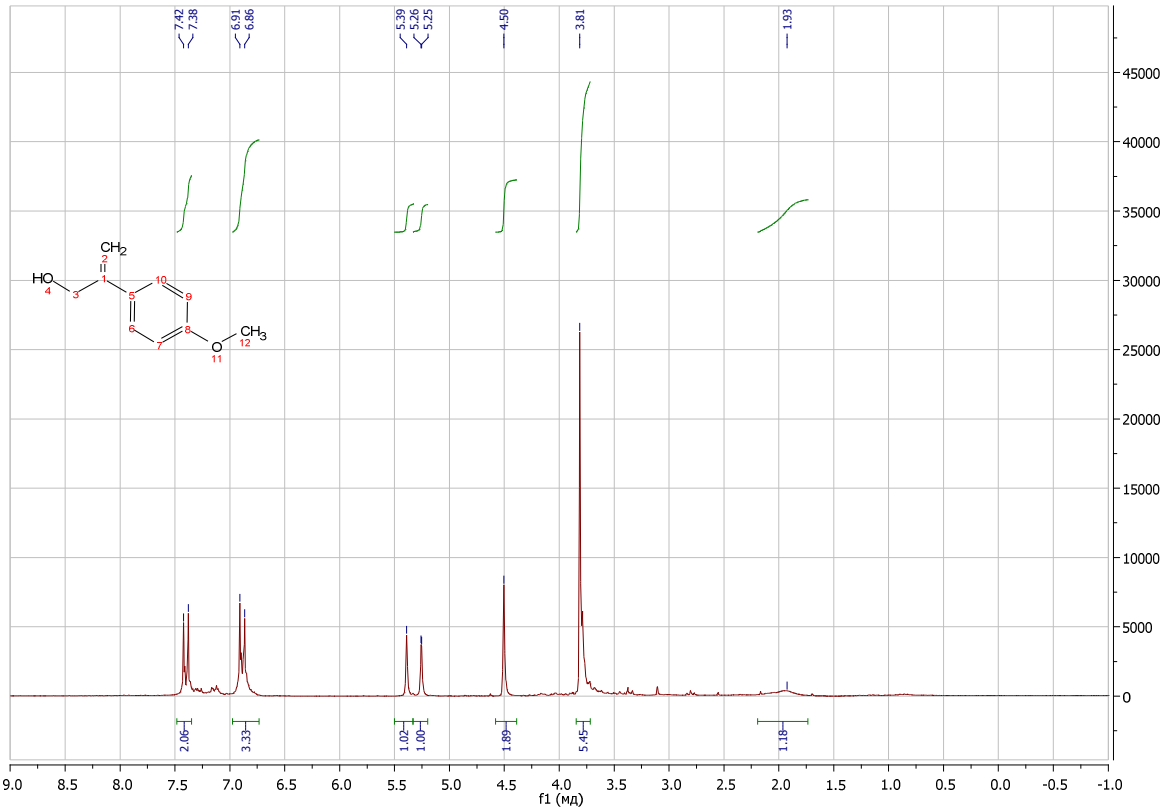


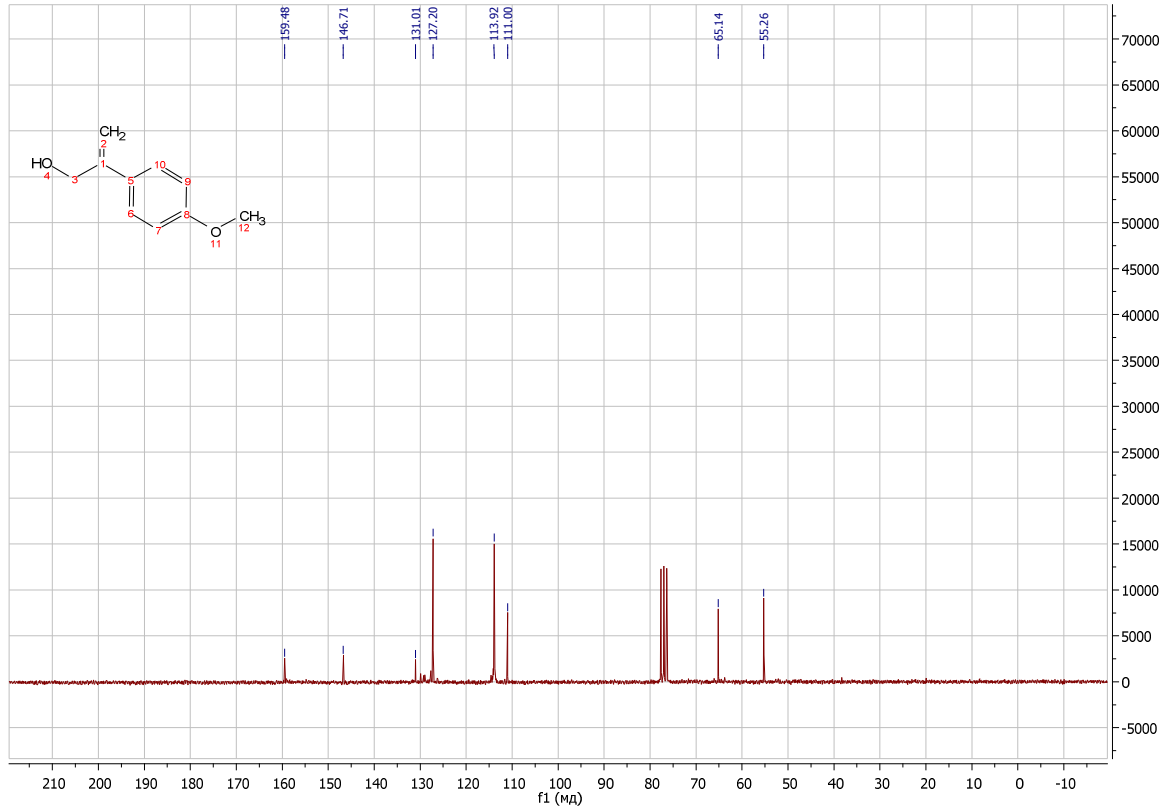
3-methyl-2-methylenebutan-1-ol



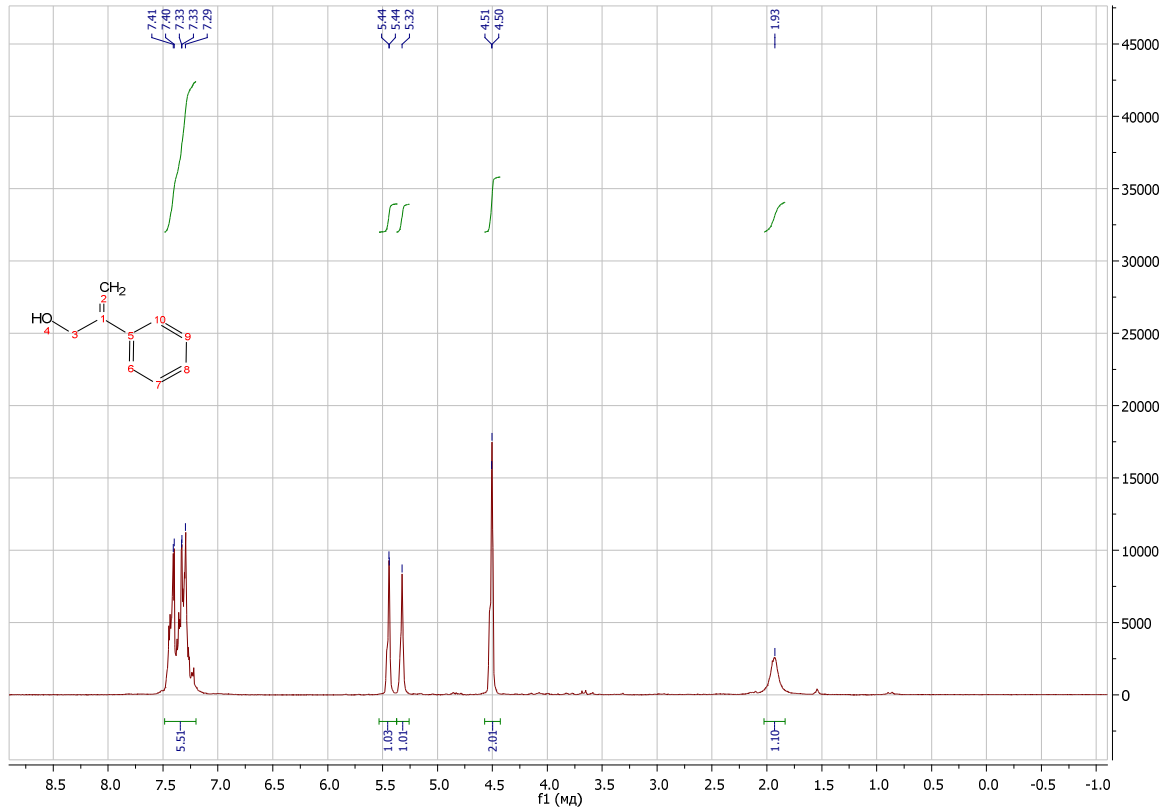


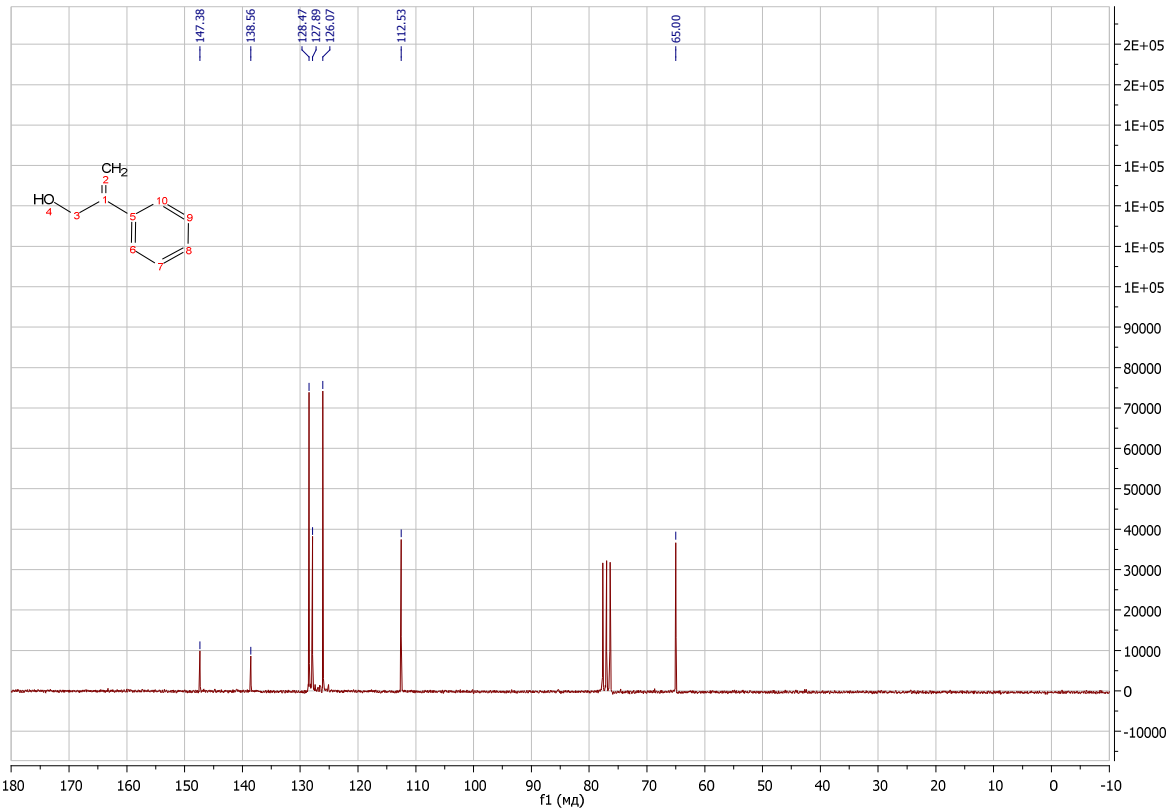
2-(4-methoxyphenyl)prop-2-en-1-ol



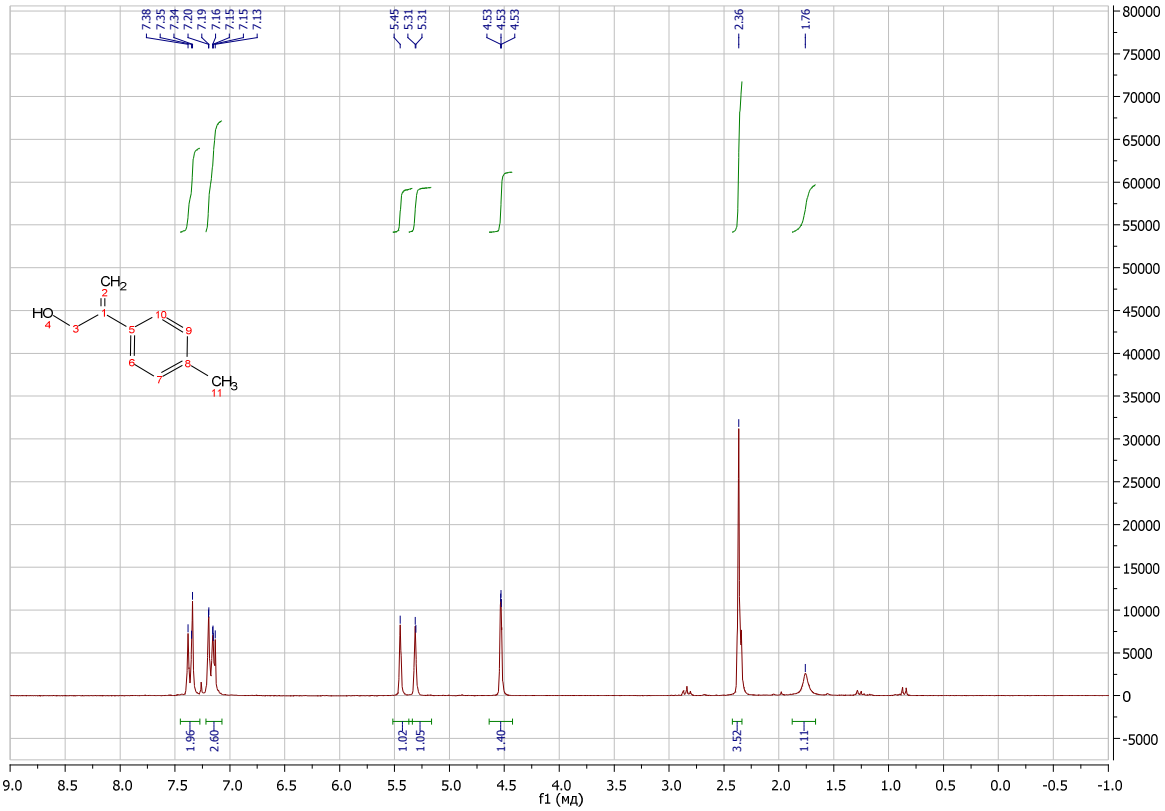


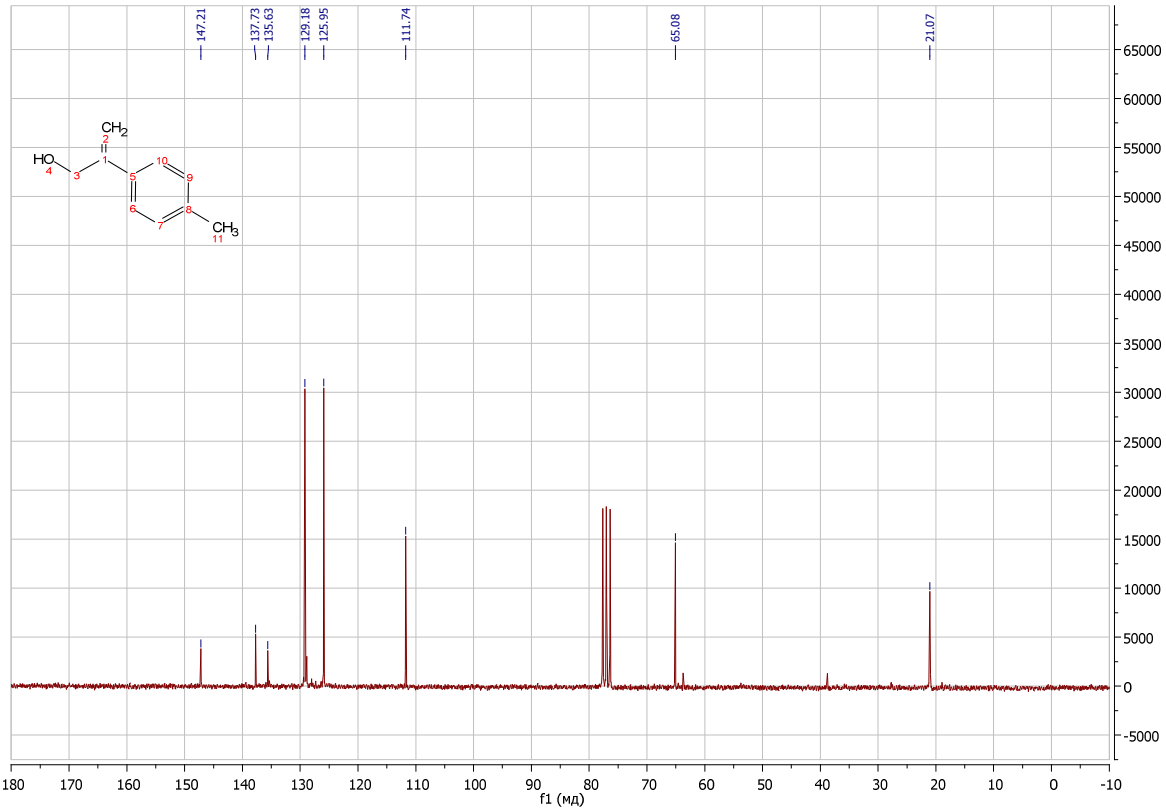
2-phenylprop-2-en-1-ol



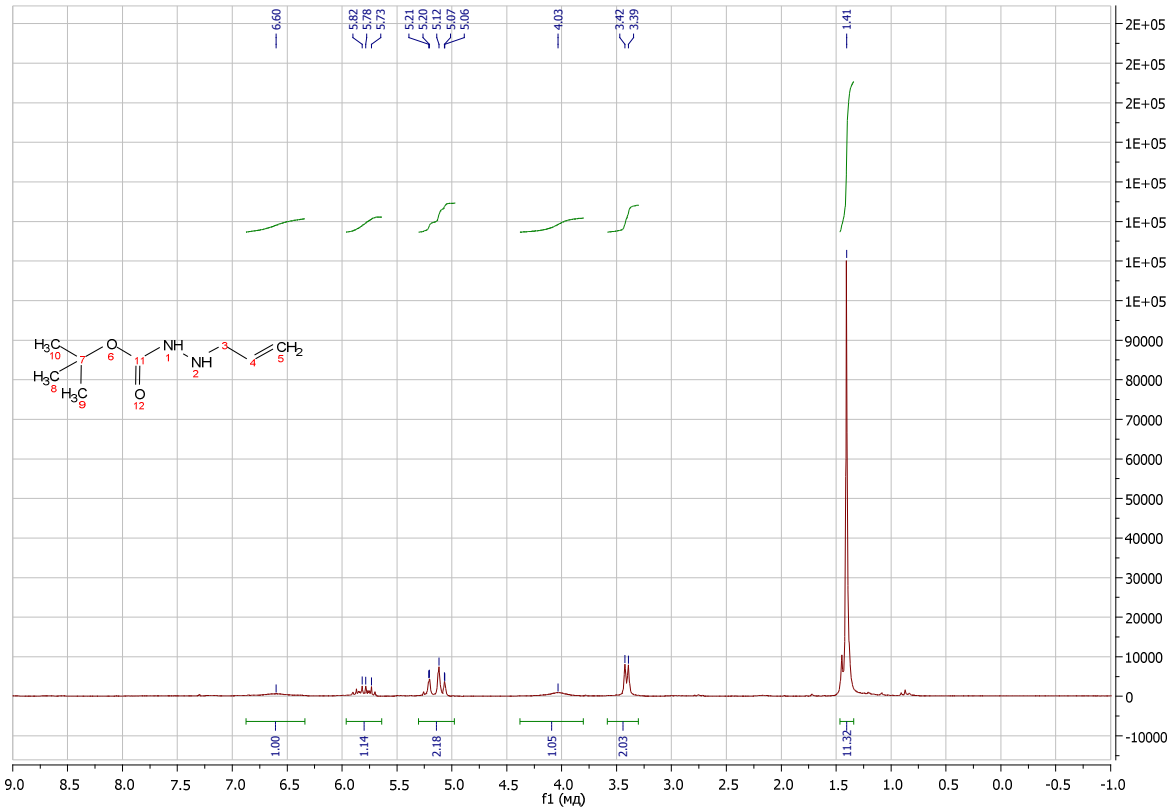


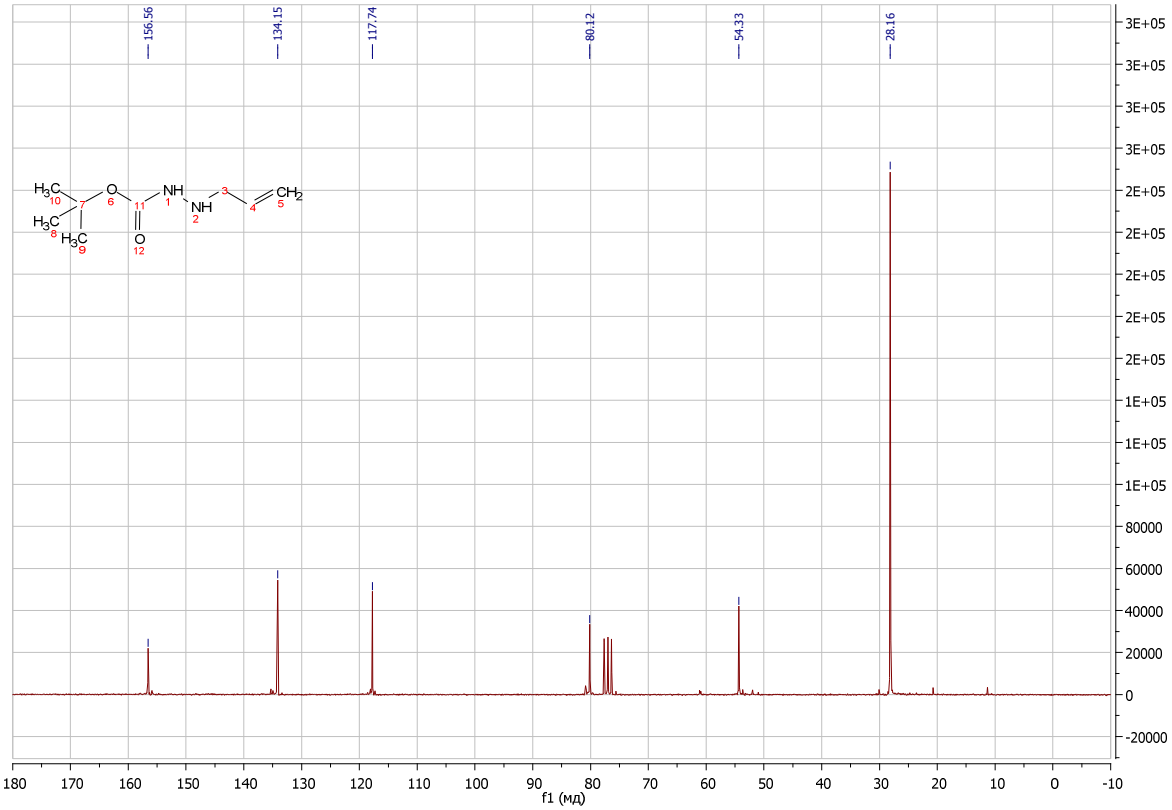
2-(*p*-tolyl)prop-2-en-1-ol


7.38
7.35
7.34
7.20
7.19
7.16
7.15
7.15
7.13
5.45
5.31
5.31
4.53
4.53
4.53
2.36
1.76
1.96
2.60
1.02
1.05
1.40
3.52
1.11
f1 (мд)

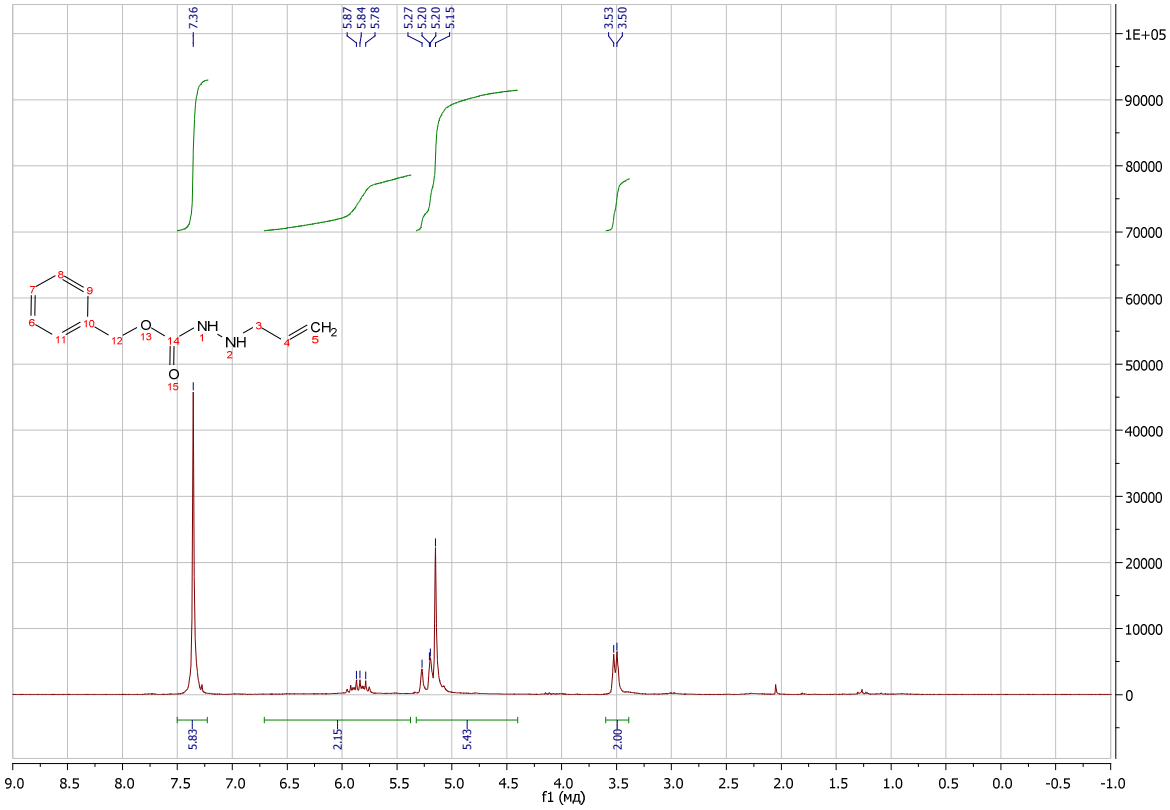

147.21
137.73
135.63
129.18
125.95
111.74
65.08
21.07
f1 (мд)

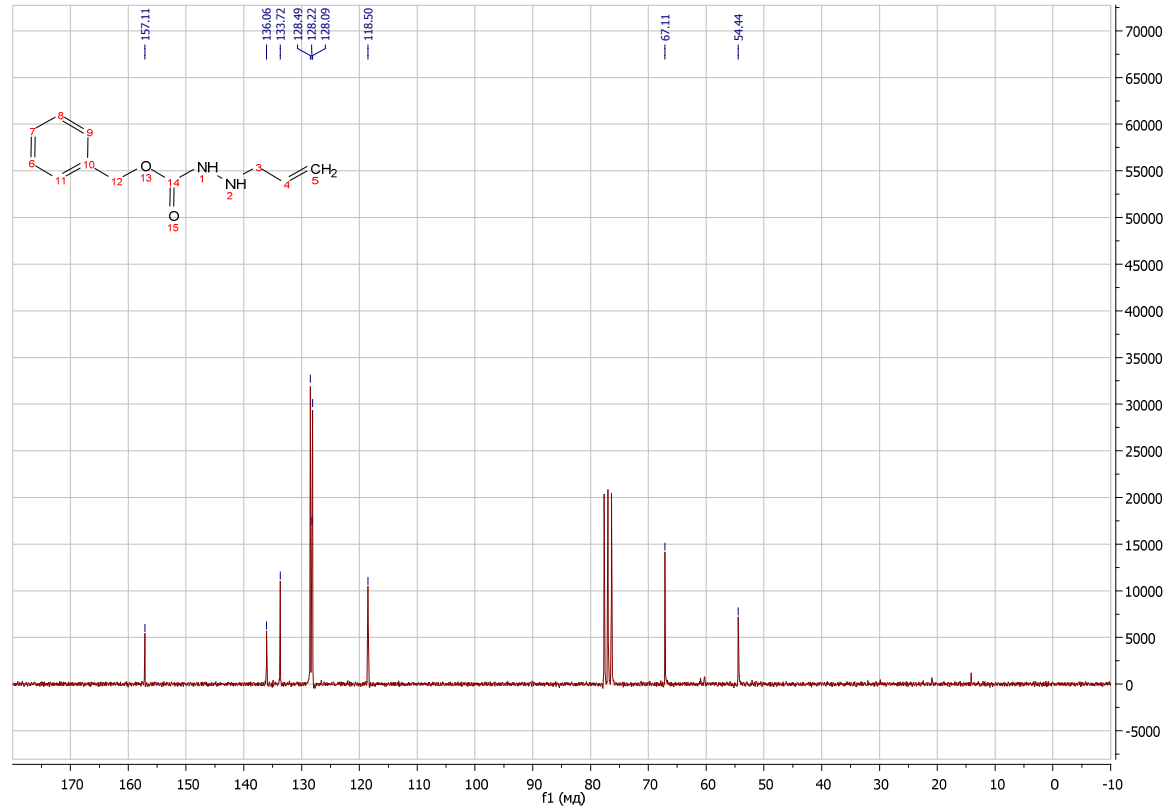
tert-butyl 2-allylhydrazinecarboxylate (1a)



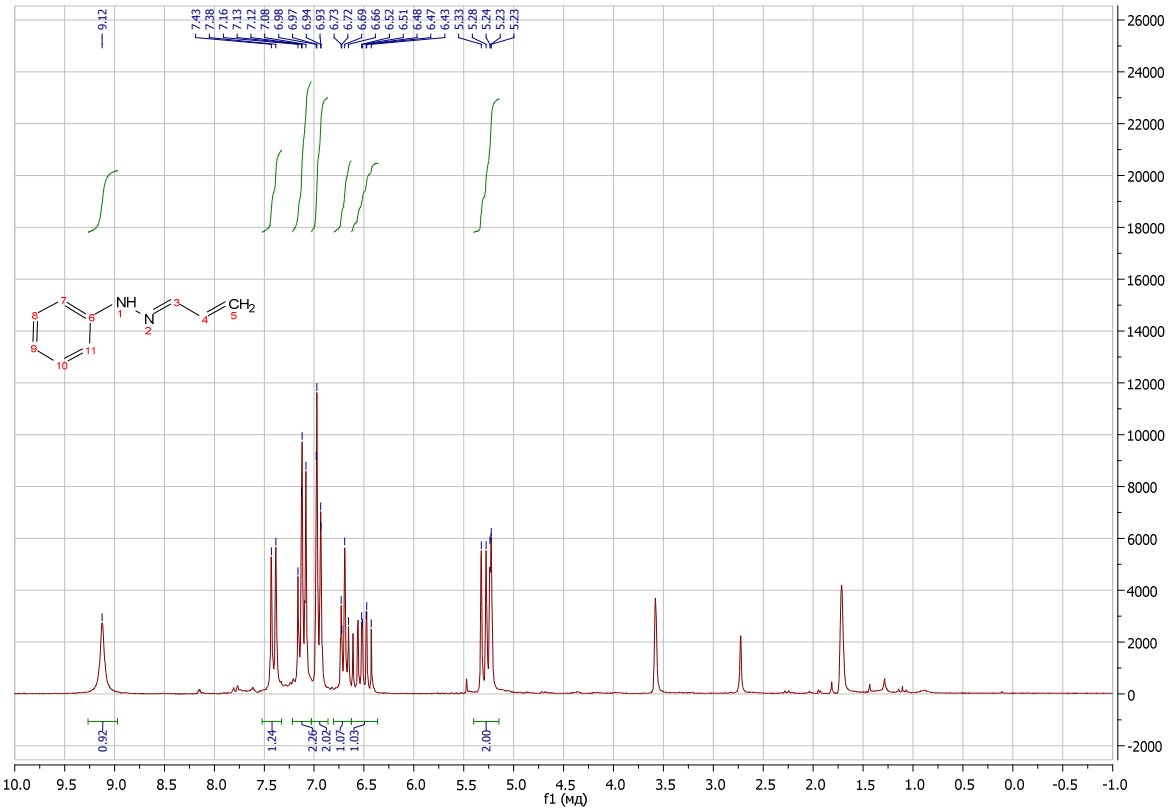


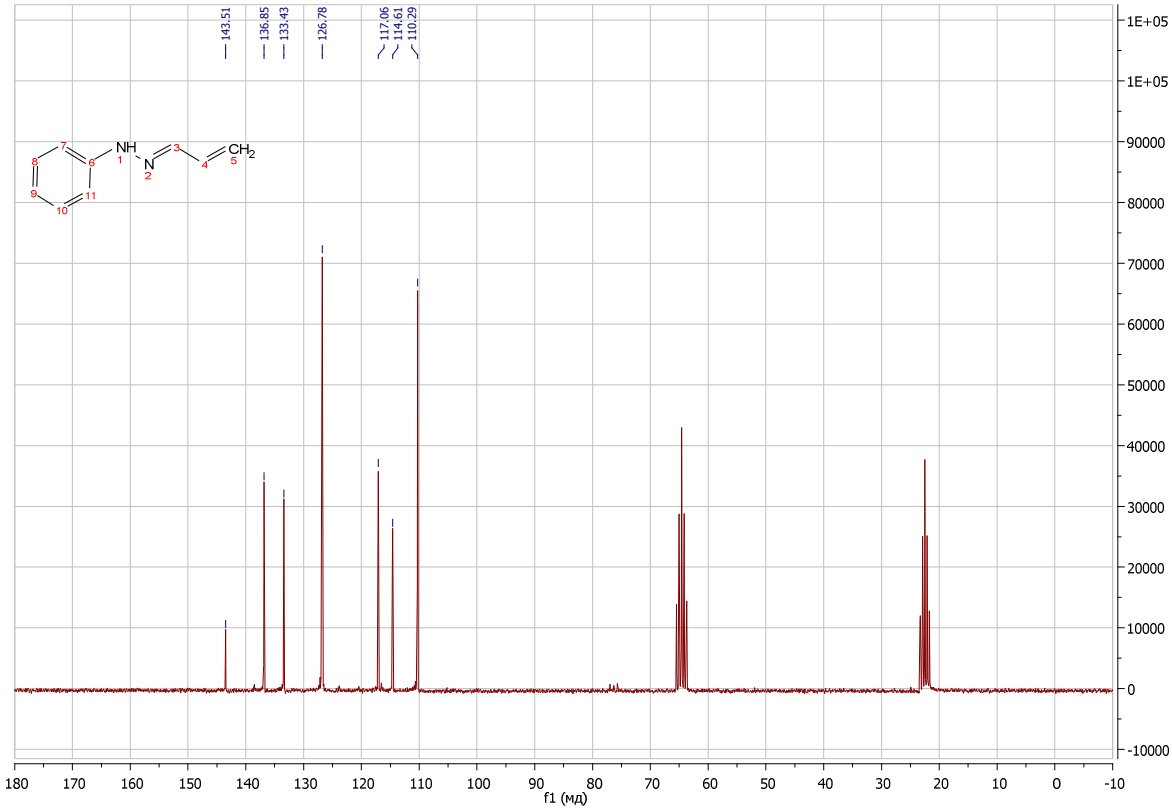
benzyl 2-allylhydrazinecarboxylate (2)



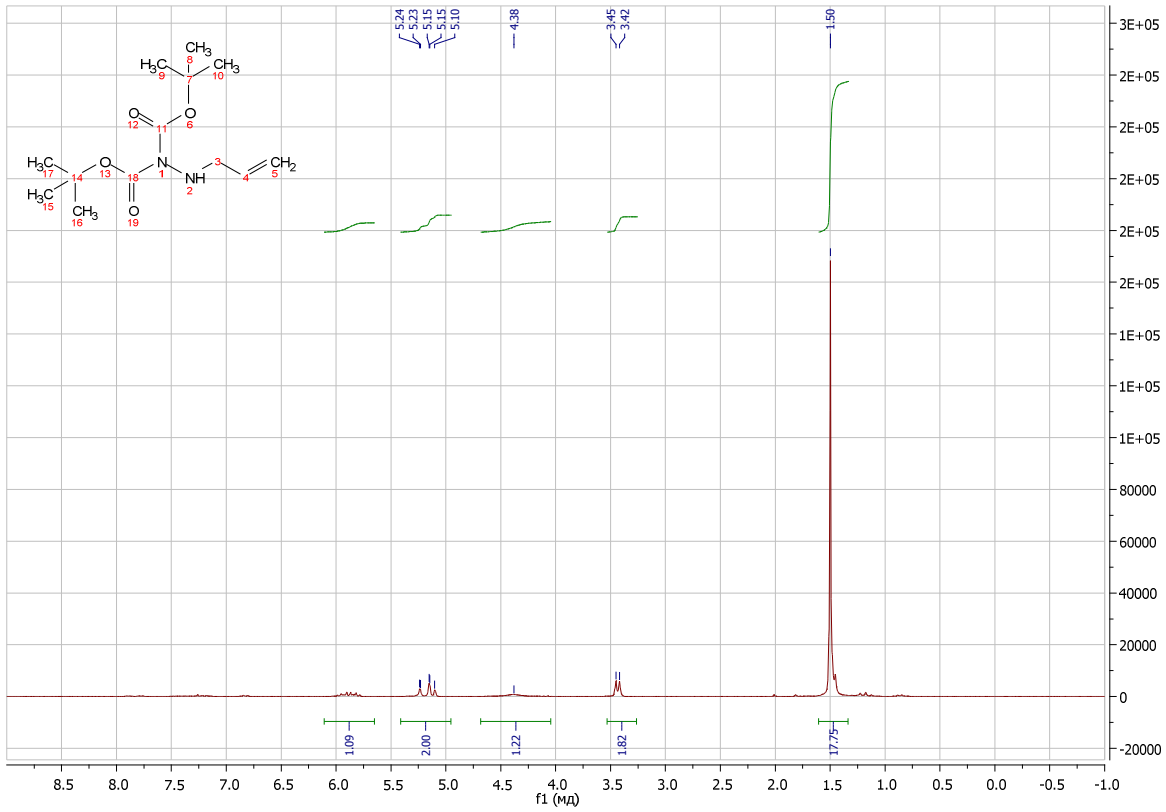


1-allylidene-2-phenylhydrazine (3)

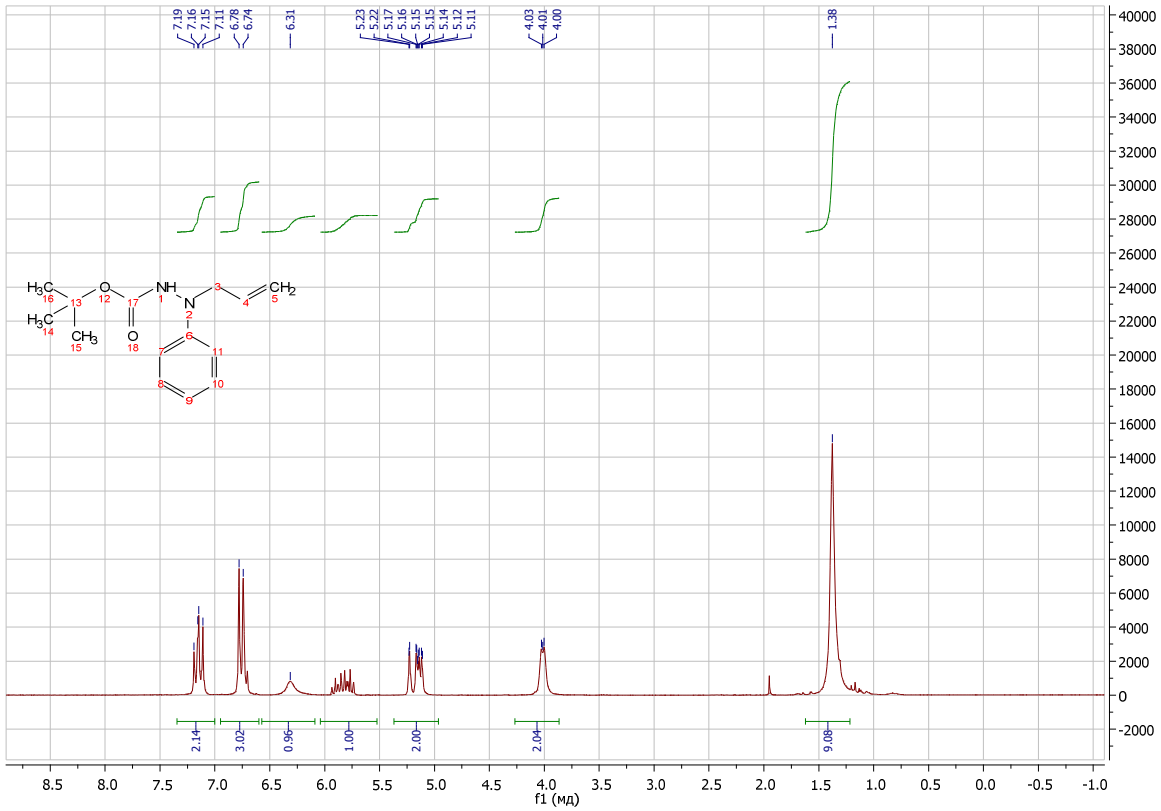


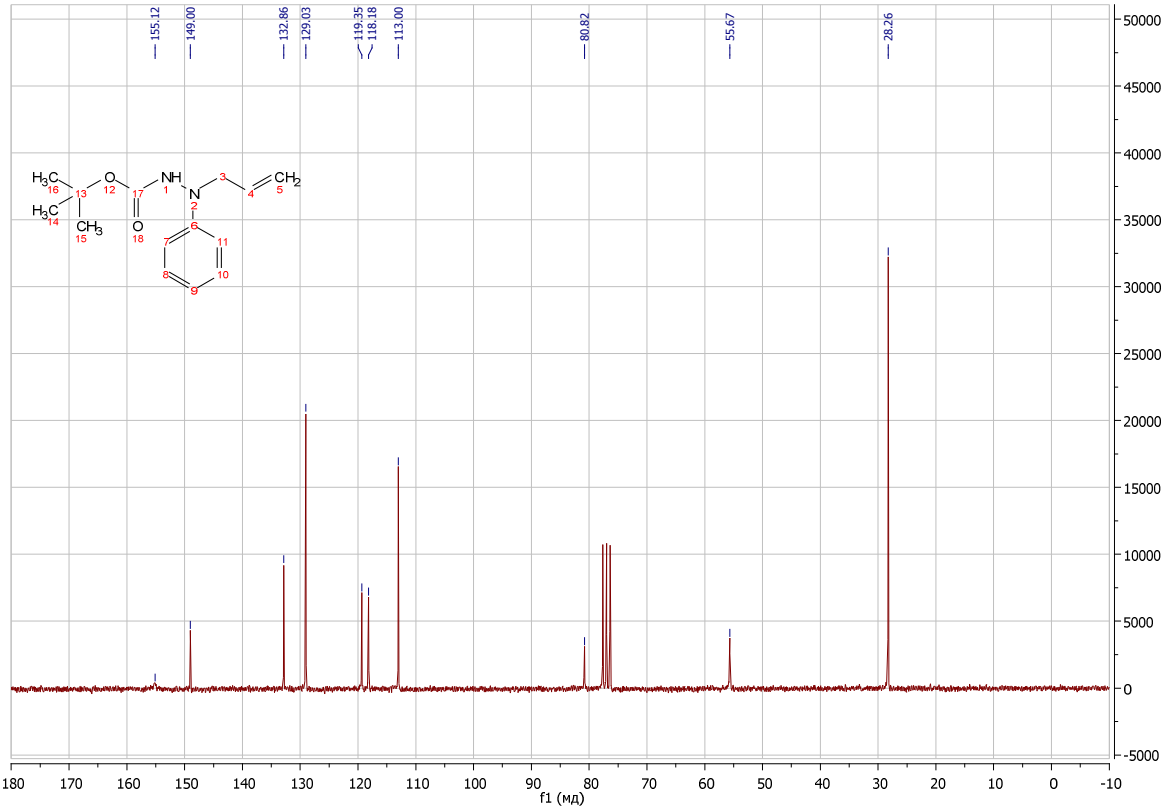


di-*tert*-butyl 2-allylhydrazine-1,1-dicarboxylate (4)

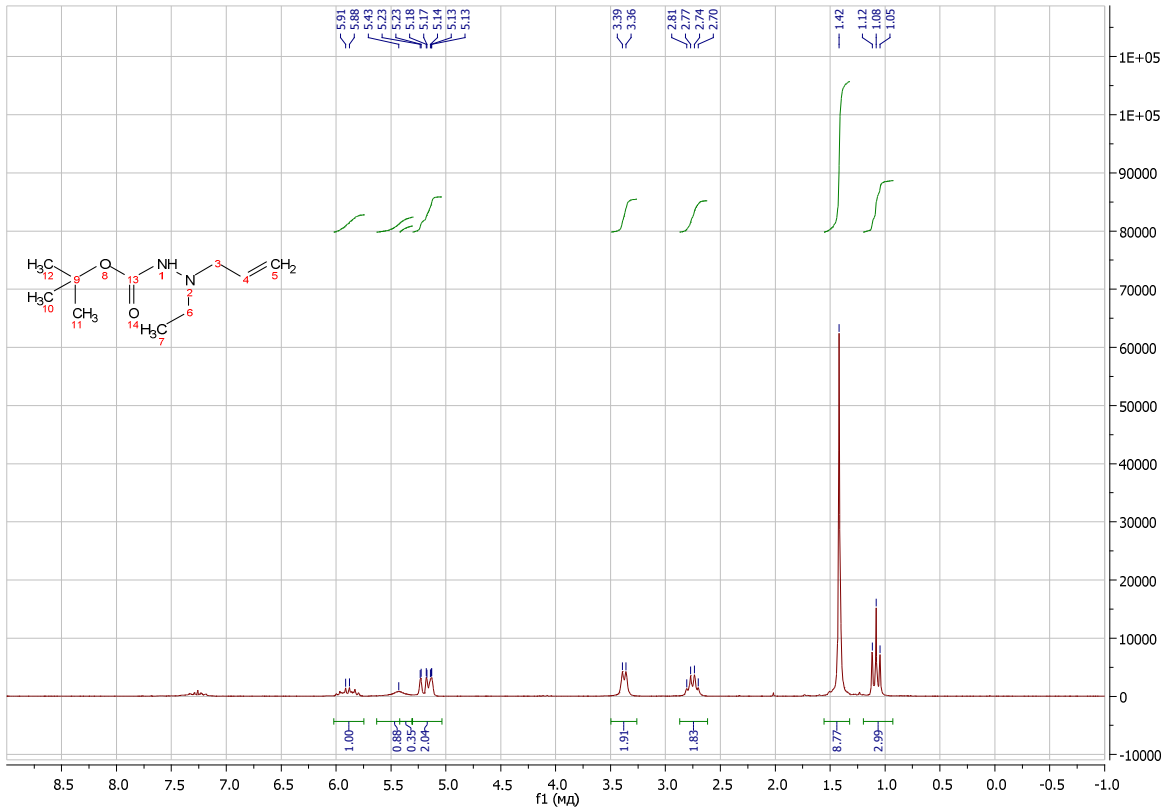


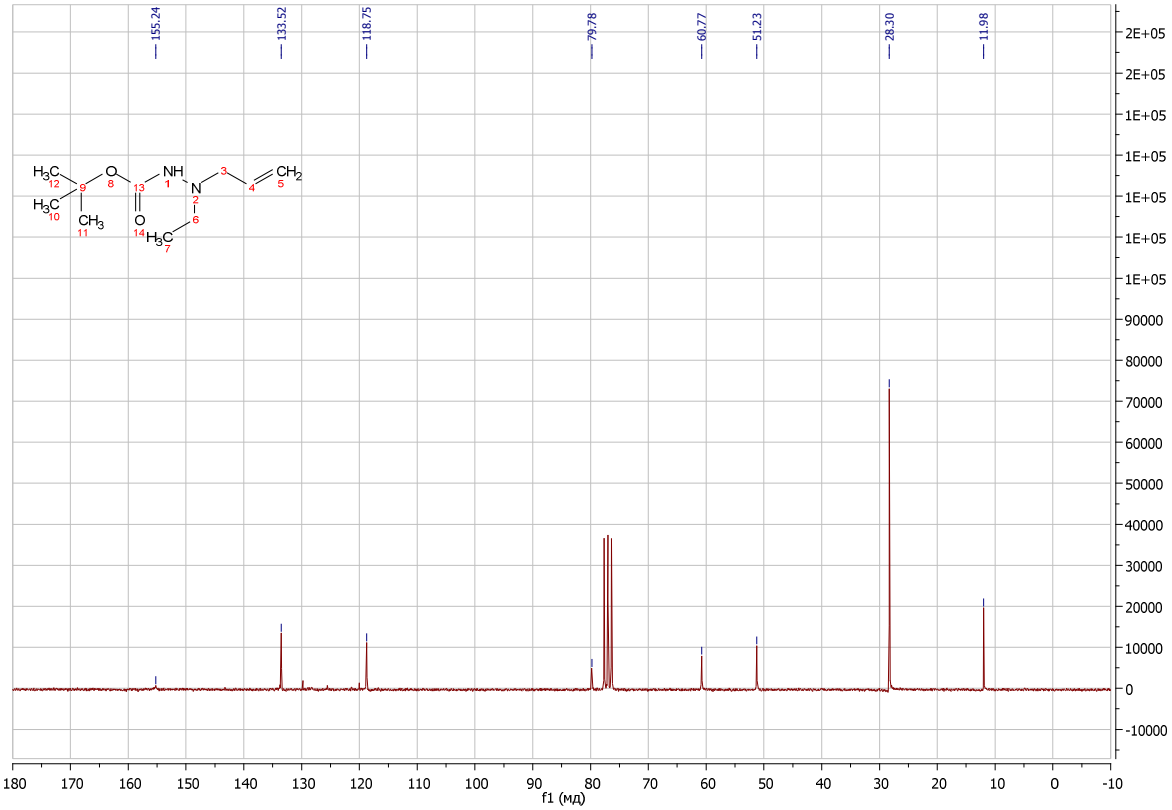
tert-butyl 2-allyl-2-phenylhydrazinecarboxylate (5)



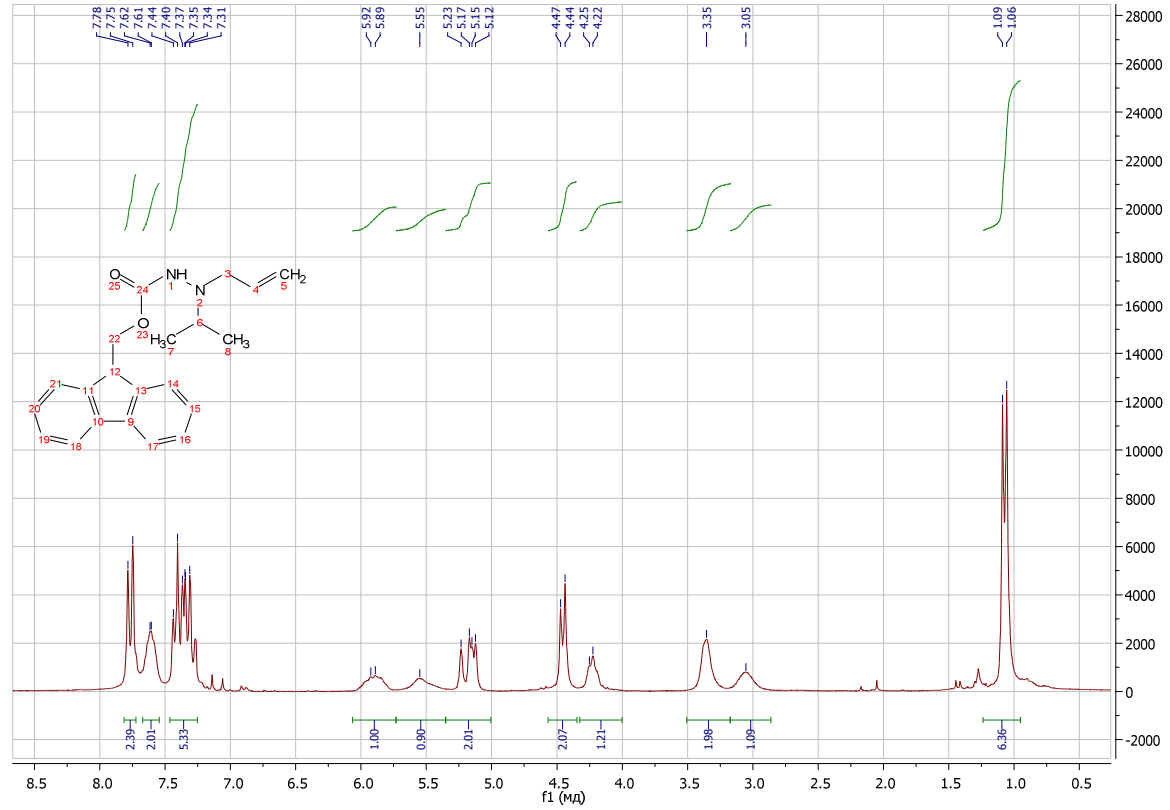


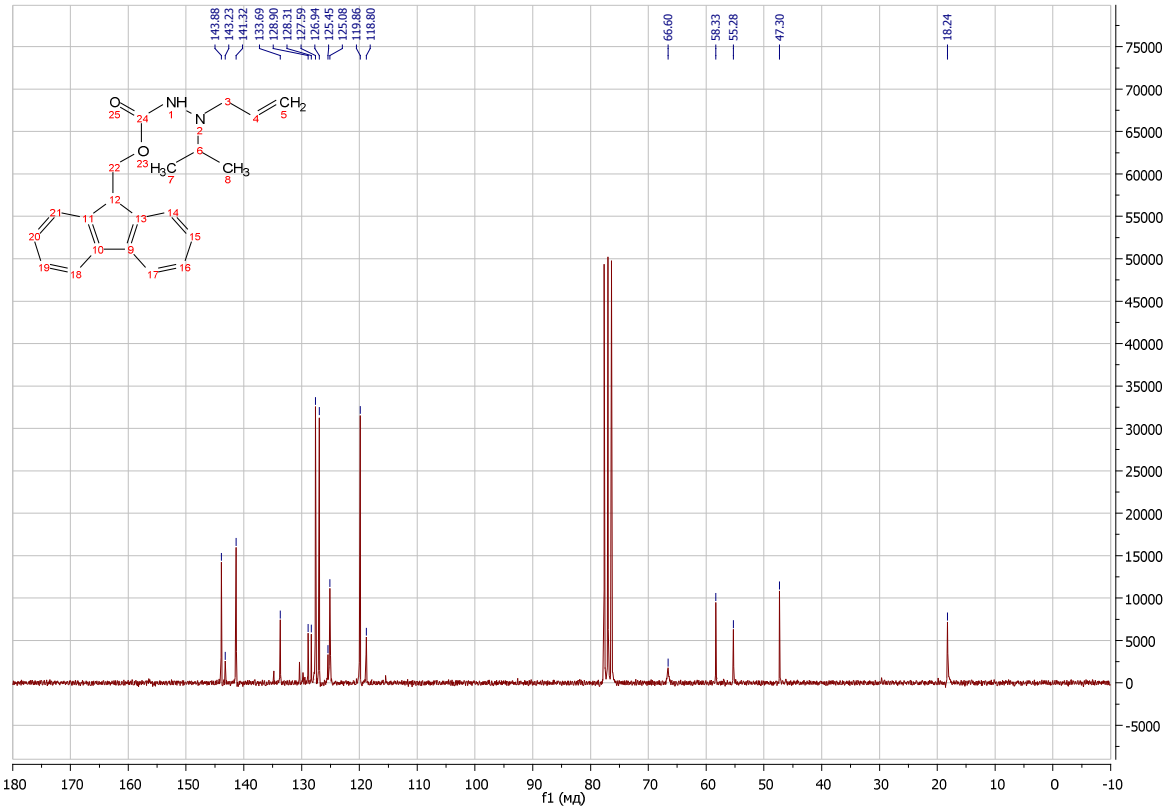
tert-butyl 2-allyl-2-ethylhydrazinecarboxylate (6)



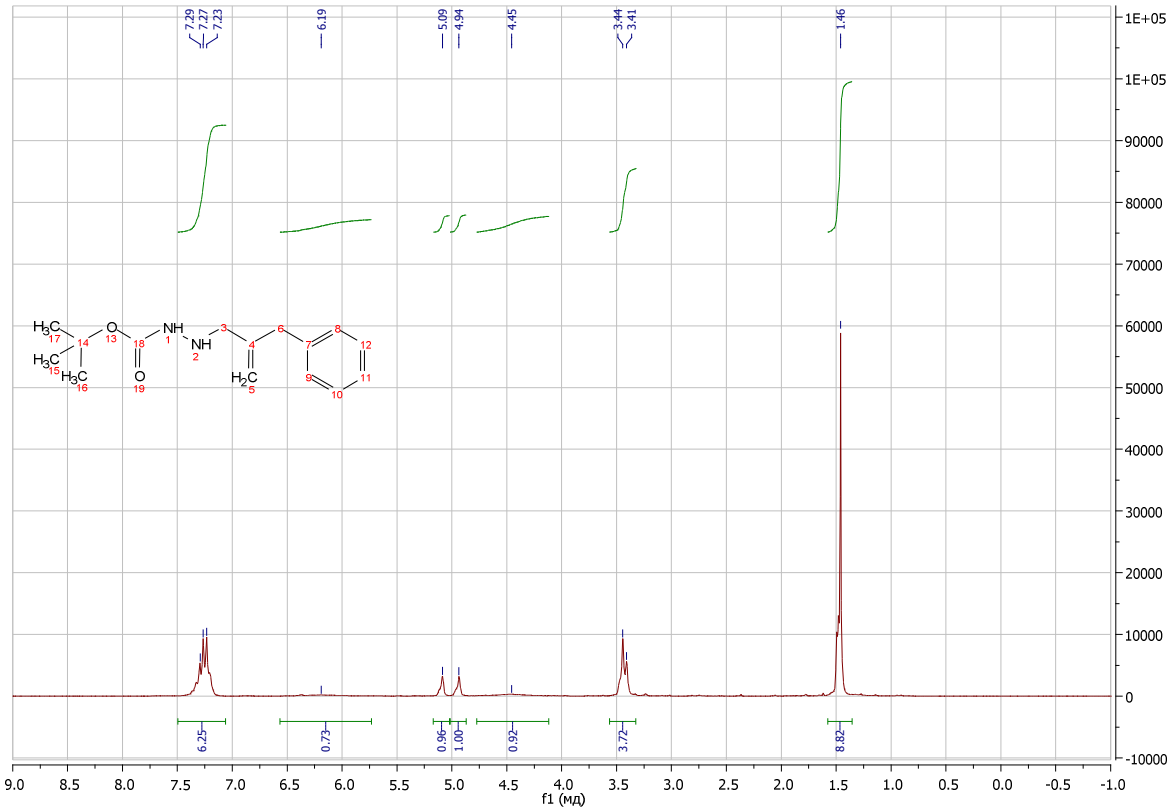


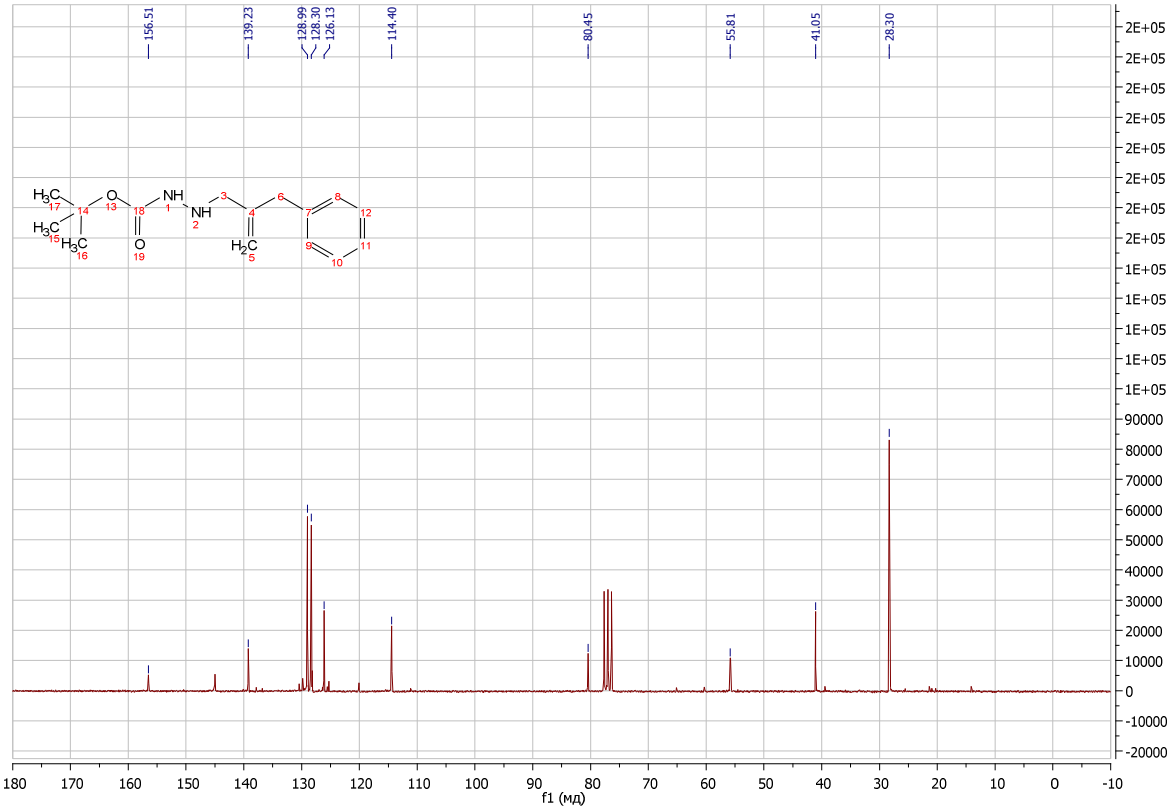
(9H-fluoren-9-yl)methyl 2-allyl-2-isopropylhydrazinecarboxylate (7)



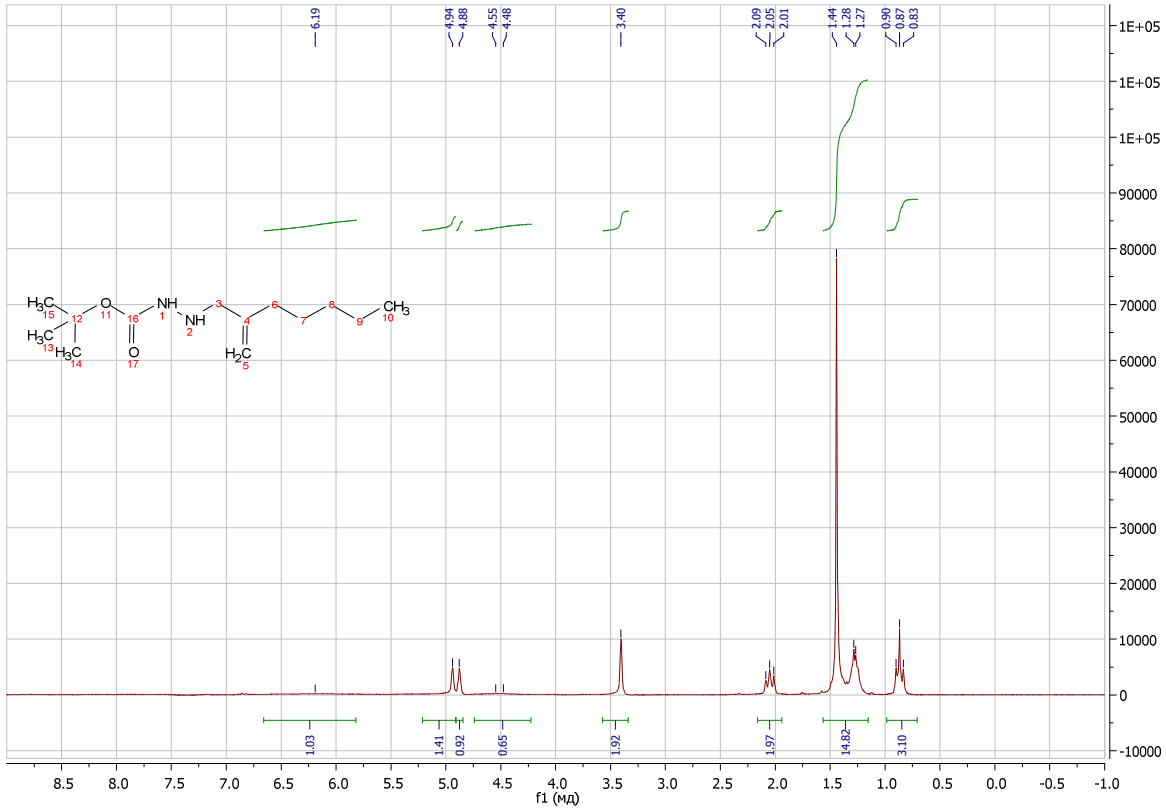


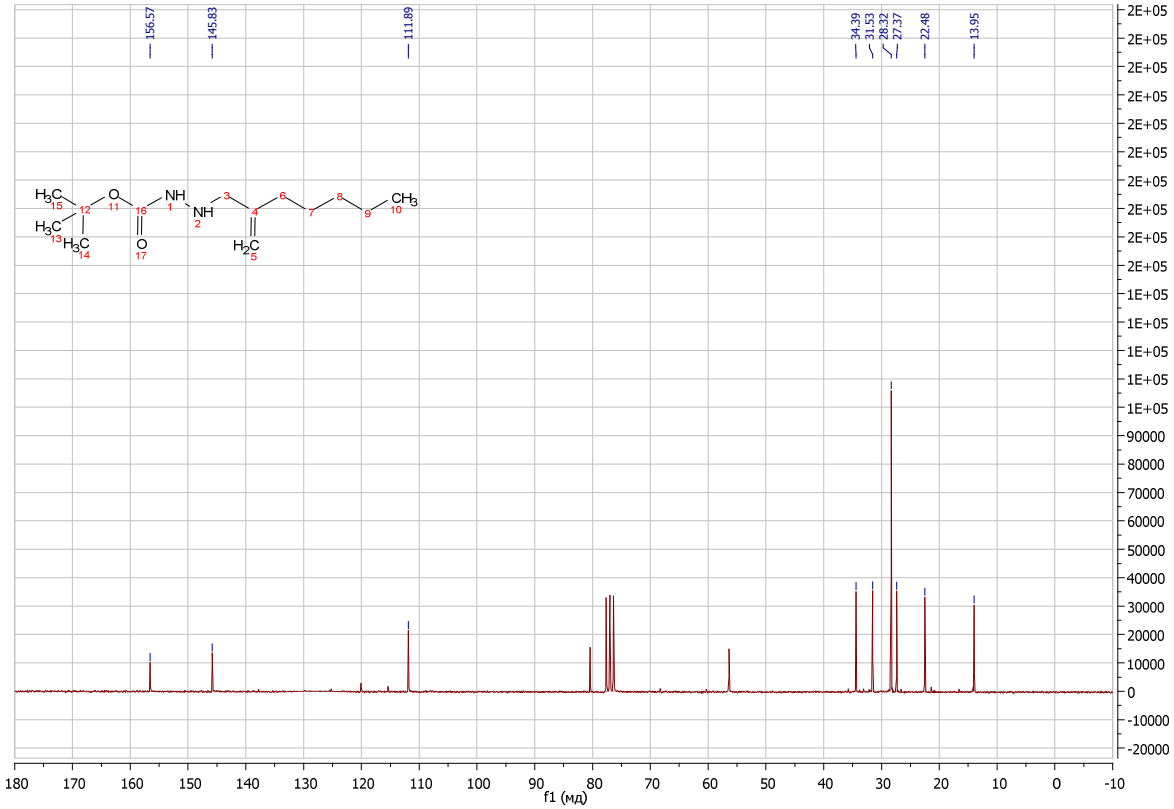
tert-butyl 2-(2-benzylallyl)hydrazinecarboxylate (1b)



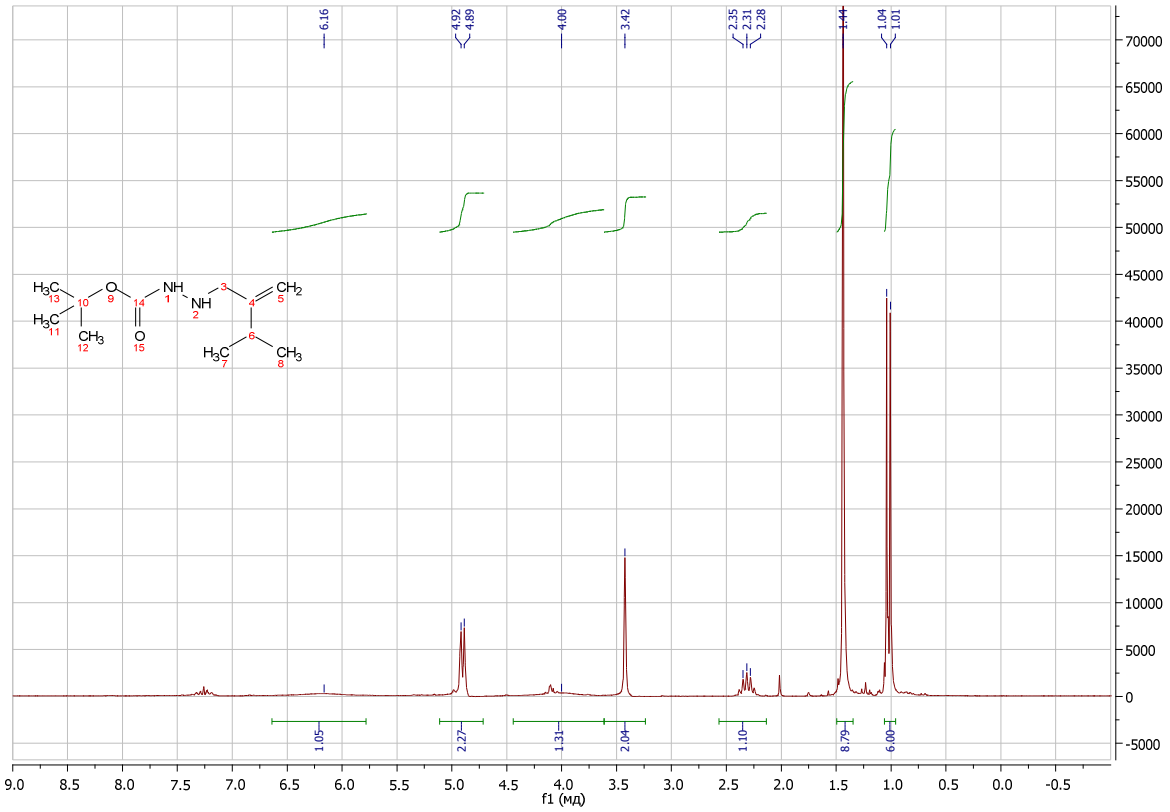


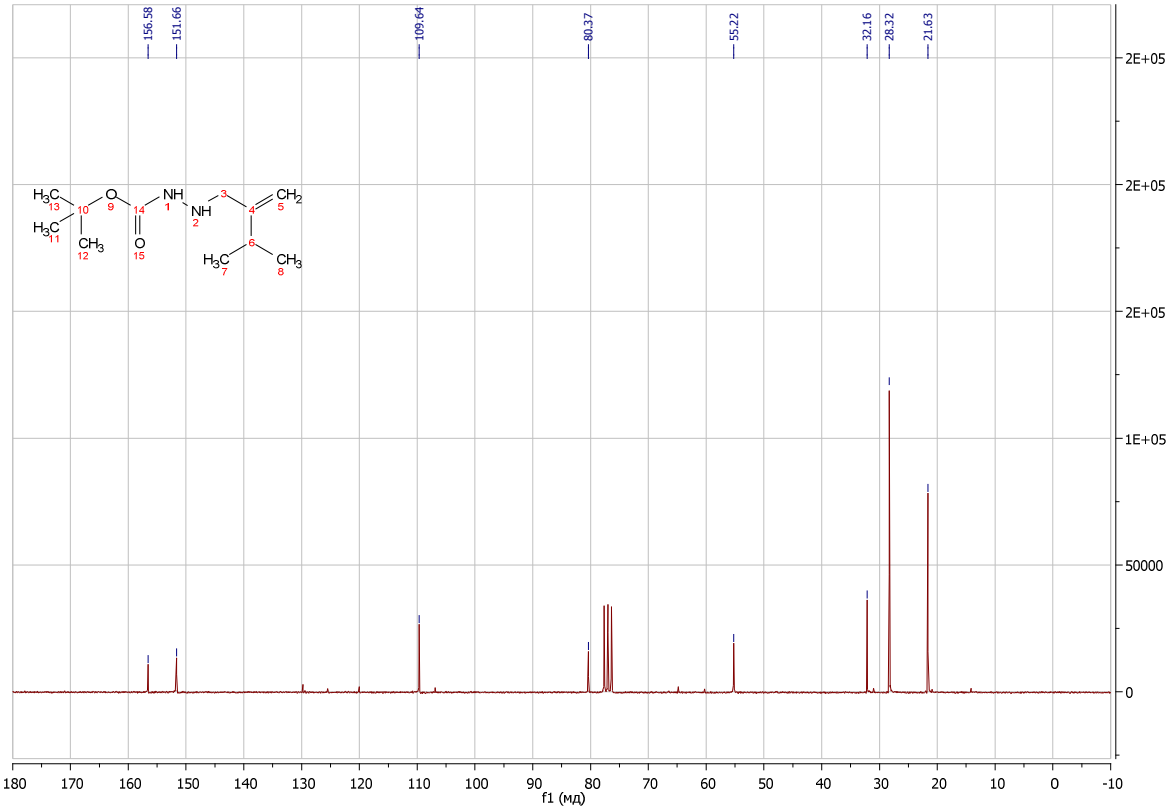
tert-butyl 2-(2-methyleneheptyl)hydrazinecarboxylate (1c)



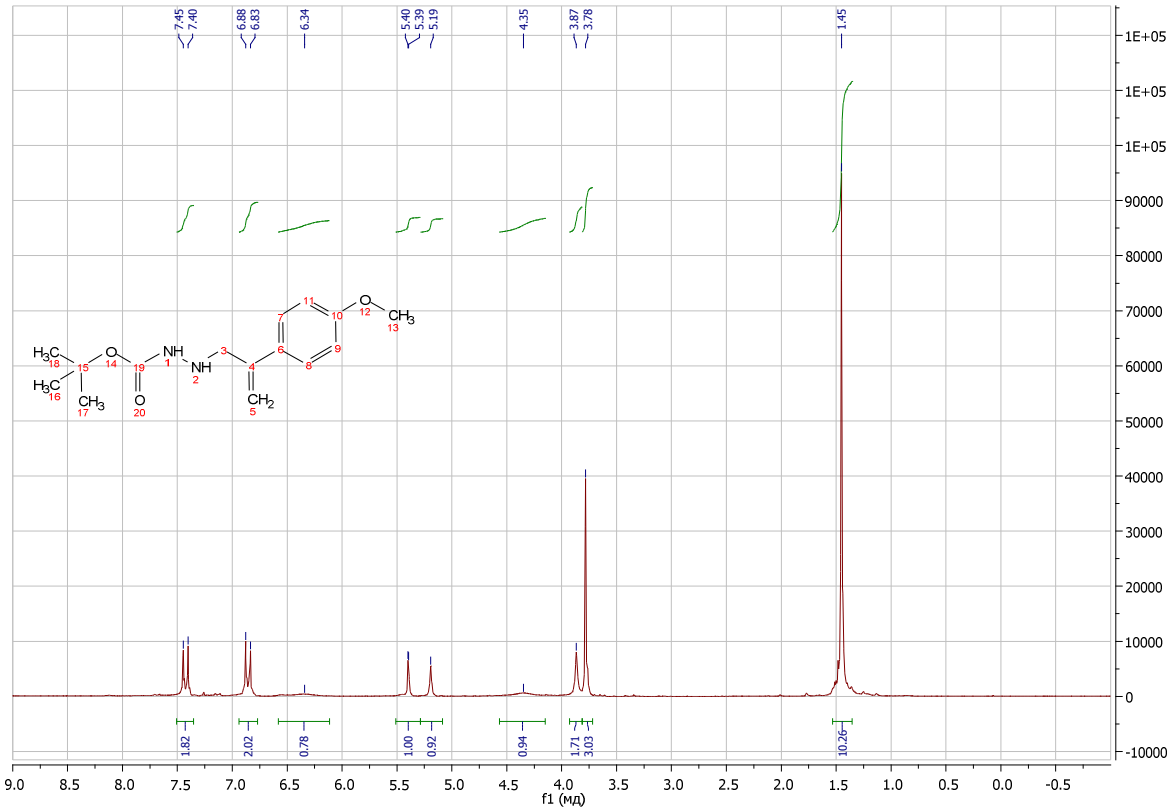


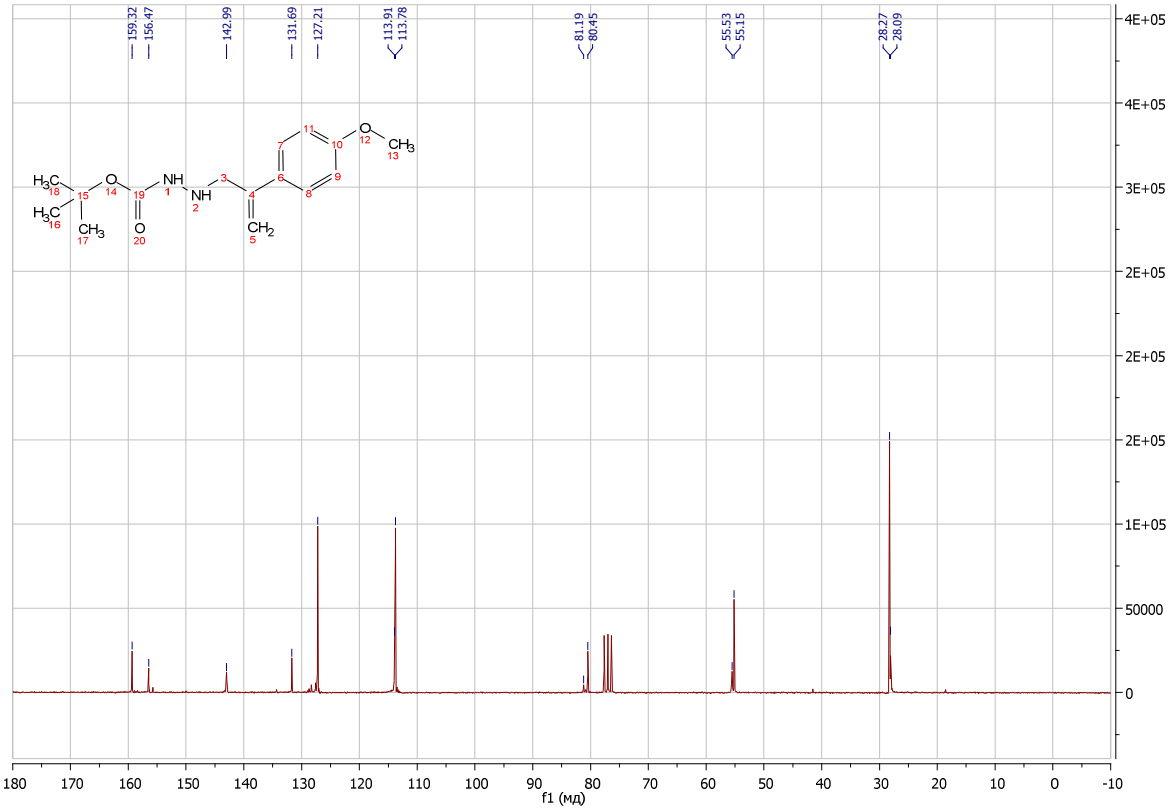
tert-butyl 2-(3-methyl-2-methylenebutyl)hydrazinecarboxylate (1d)



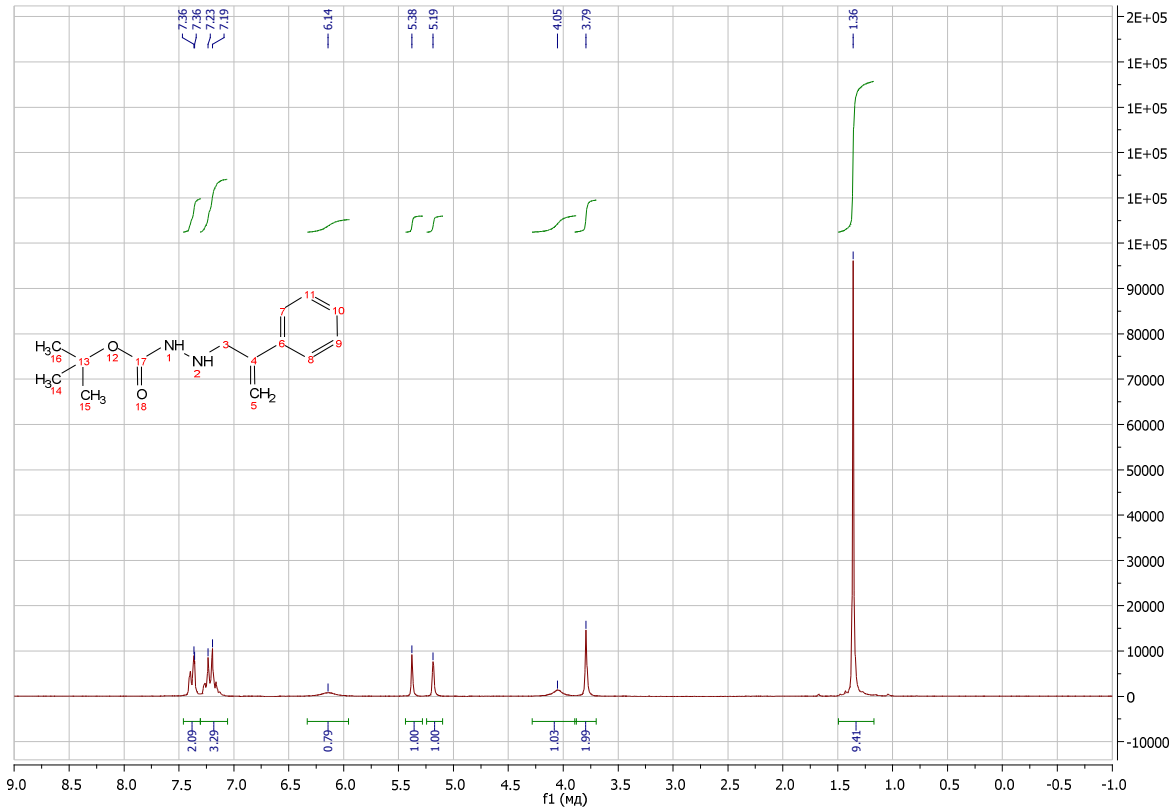


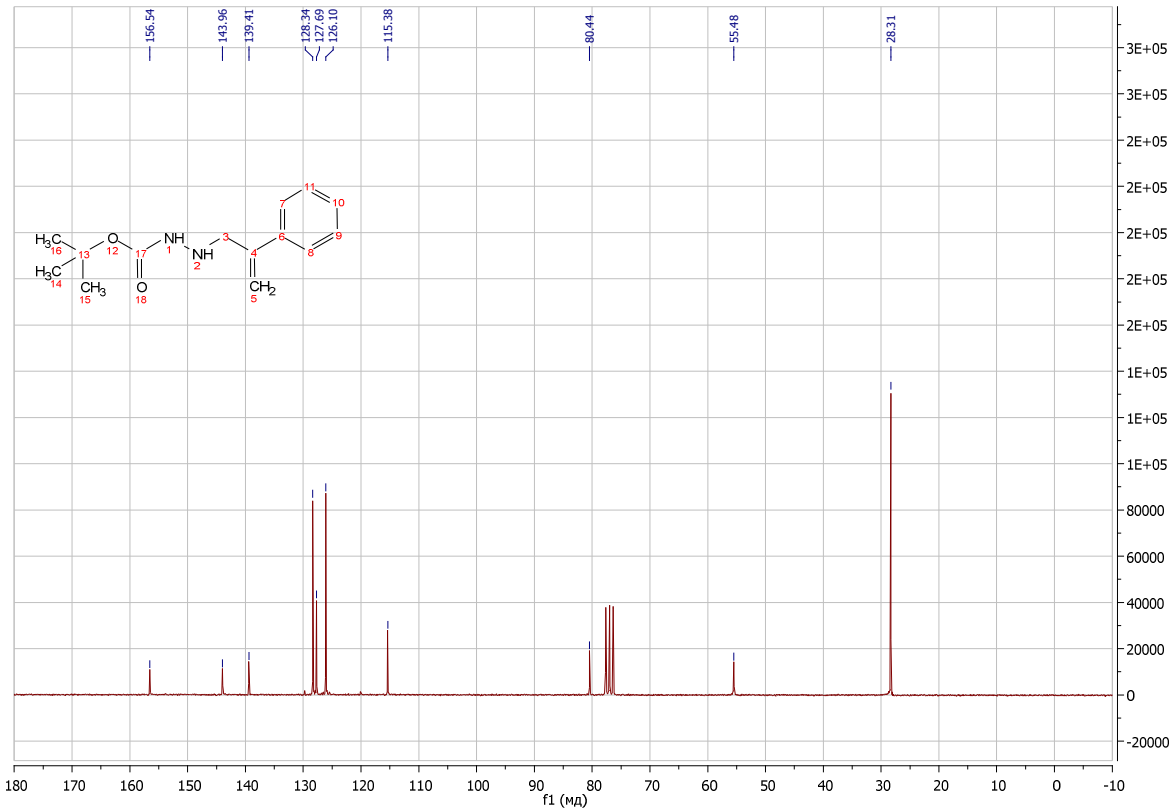
tert-butyl 2-(2-(4-methoxyphenyl)allyl)hydrazinecarboxylate (1e)



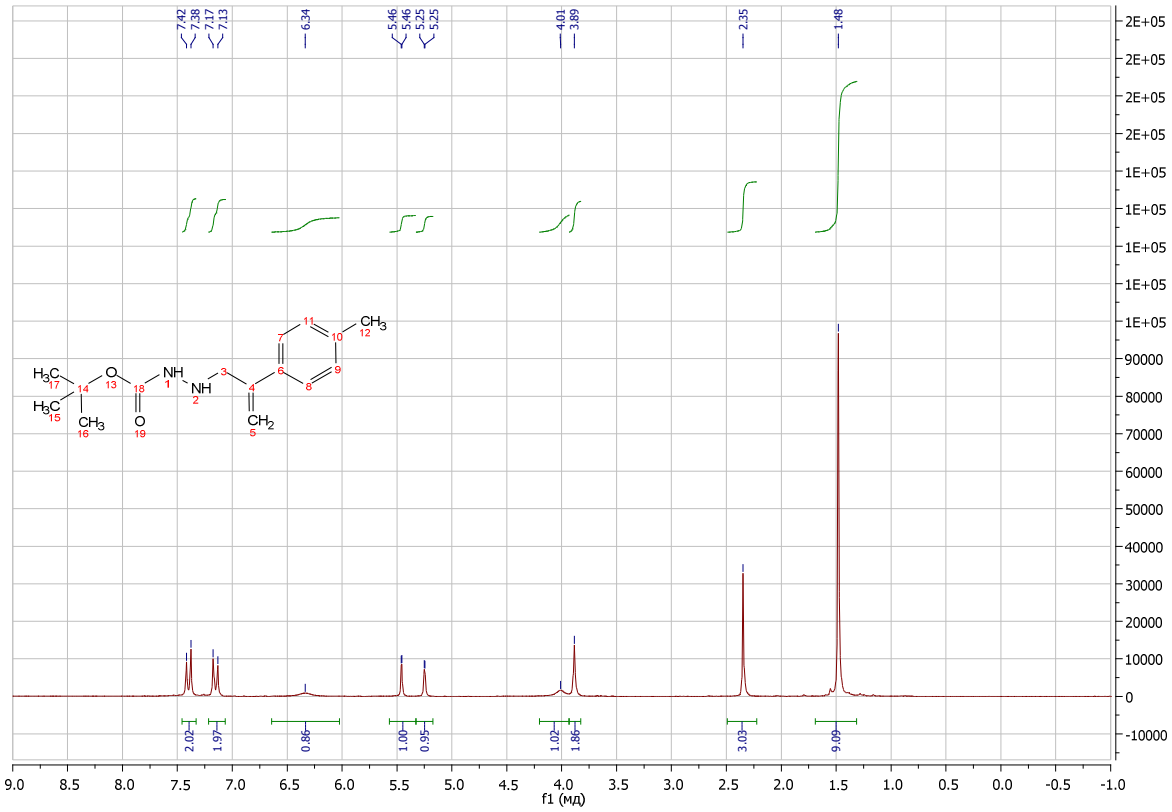


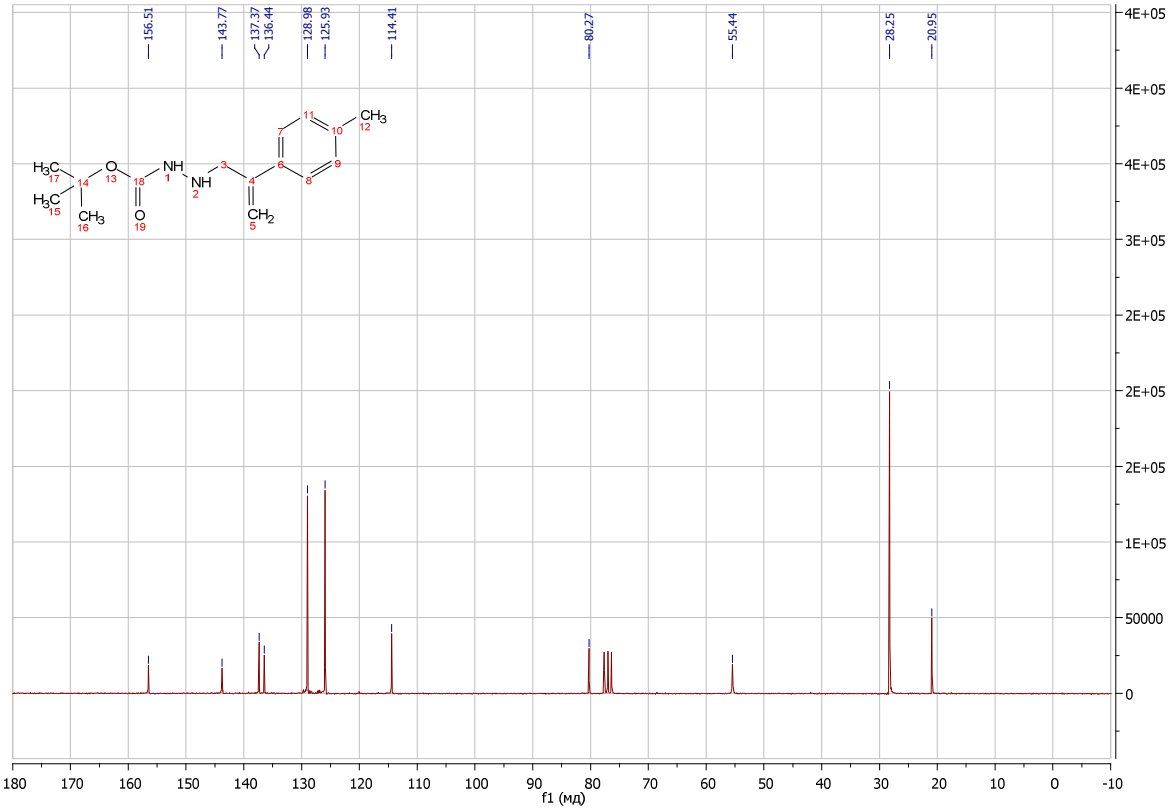
tert-butyl 2-(2-phenylallyl)hydrazinecarboxylate (1f)





tert-butyl 2-(2-(*p*-tolyl)allyl)hydrazinecarboxylate (1g)





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[2] Boeglin, D.; Lebell, W. D. *J. Comb. Chem. 2005*, *7*, 864 – 878.

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