# Ruthenium – catalyzed selective *N,N*-diallylation- and *N,N,O*-triallylation of free amino acids

Basker Sundararaju, Mathieu Achard, G. V. M. Sharma, Christian Bruneau*

e-mail: christian.bruneau@univ-rennes1.fr

*UMR 6226 : CNRS - Université de Rennes 1, Sciences Chimiques-Catalyse et Organométalliques, Campus de Beaulieu-35042 Rennes Cedex, France*

## SUPPORTING INFORMATION

Experimental details for compounds **3-4** and NMR spectra are available free of charge via internet

at: http://

All reactions were carried out under argon atmosphere. Dichloromethane was distilled after drying according to conventional methods and HPLC grade methanol was used as received and stored under a nitrogen atmosphere. $^{1}H$ NMR spectra were recorded on a Bruker GPX (200.131 MHz) spectrometer. $^{1}H$ NMR assignment abbreviations are the following: singlet (s), doublet (d), triplet (t), quartet (q), broad singlet (bs), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). $^{13}C$ NMR spectra were recorded at 50.32, 75.0 MHz spectrometer and reported in ppm from $CDCl_3$, $CD_3OD$, dmso-$d_6$, as an internal standard (77.0, 49.0, 39.4 ppm for $^{13}C$). Infra red spectra were obtained as nujol mulls with a Bruker IFS28 FT-IR infrared spectrophotometer (4000-400 $cm^{-1}$). Melting points were determined on a Kofler Bank and HRMS were recorded on Varian MAT 311 mass spectrometer with EI source or on ZAB Spec TOF with ESI source.

**General procedure for the preparation of diallylated compounds**

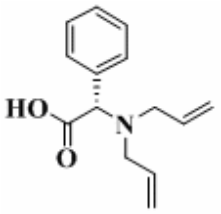
$[Ru(Cp^*)(CH_3CN)_3][PF_6]$ ($5.0 \times 10^{-3}$ mmol, 5 mol %) complex **I** was added to the mixture of amino acid **1** (0.1 mmol) in MeOH (4 mL) under inert atmosphere and the resulting solution was stirred at room temperature for two min. Then potassium carbonate (0.12 mmol), allyl chloride **2a** (0.22 mmol) were successively added and the resulting mixture was stirred at room temperature for 16 h. The crude mixture obtained after filtration and concentration in vacuo was acidified with 1 N HCl (pH~2) and then extracted with EtOAc (5 x 3ml) to afford compound **3** after drying over $Na_2SO_4$ and evaporation.

**General procedure for the preparation of triallylated compounds**

$[Ru(Cp^*)(CH_3CN)_3][PF_6]$ ($5.0 \times 10^{-3}$ mmol, 5 mol %) complex **I** was added to the mixture of amino acid **1** (0.1 mmol) in $CH_2Cl_2$ (6 mL) under inert atmosphere and the resulting solution was stirred at room temperature for two minutes. Then cesium carbonate (0.3 mmol), allyl chloride **2a** (0.33 mmol) were successively added and the resulting mixture was stirred at room temperature for 16 h. The crude mixture obtained after filtration on a short pad of silica using dichloromethane as eluent and concentration in vacuo was purified by flash chromatography (silica gel) to afford **4**.

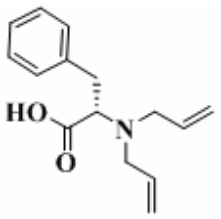
**Double allylation of free amino acids**

(2*S*)-(diprop-2-en-1-ylamino)phenylethanoic acid **3a**



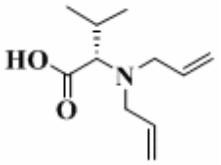

Compound **3a** was obtained as a pale yellow powder, 114.7 mg, yield = 75%, $[\alpha]^{20}{}_{D}$ + 123.7, (*c* = 0.4, $CH_2Cl_2$) $^1$H NMR (200 MHz, DMSO - $d_6$) δ 7.45 – 7.27 (m, 5H), 5.89 – 5.69 (m, 2H), 5.20 – 5.09 (m, 4H), 4.42 (s, 1H), 3.26 – 3.04 (m, 4H); $^{13}$C NMR (75 MHz, $D_2O$) δ 172.7, 137.2, 135.2, 128.5, 128.2, 127.6, 117.7, 67.8, 52.5; HRMS calculated for $C_{14}H_{18}NO_2^+$ $[M+H]^+$: 232.1338, found 232.1336.

(2*S*)-2-(diprop-2-en-1-ylamino)-3-phenylpropanoic acid **3b**



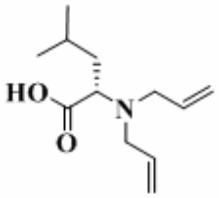

Compound **3b** was obtained as a pale yellow powder, 130.2 mg, yield = 88% , $[\alpha]^{20}{}_{D}$ -5.71, (*c* = 0.47, $CH_2Cl_2$), $^1$H NMR (200 MHz, DMSO – $d_6$) δ 7.33 – 7.09 (m, 5H), 5.33 – 5.49 (m, 2H), 5.19 – 4.98 ( m, 4H), 3.51 (t, *J*= 6.9 Hz, 1H), 3.39 – 3.22 (dd, *J*= 4.3, 14.2 Hz, 2H), 3.18 - 2.72 (m, 4H); $^{13}$C NMR (75 MHz, DMSO – $d_6$) δ 173.6, 138.9, 136.5, 129.1, 127.8, 125.8, 116.7, 63.3, 52.8, 34.8; HRMS calculated for $C_{15}H_{20}NO_2^+$ $[M+H]^+$: 246.1498, found 245.1496.

(2*S*)-2-(diprop-2-en-1-ylamino)-3-methylbutanoic acid **3c**



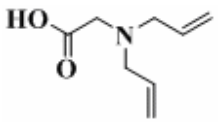
Compound **3c** was obtained as a pale yellow powder, 67.8 mg, yield = 40%, $[\alpha]^{20}_{D}$ -35.33, (*c* = 0.6, $CH_2Cl_2$), $^1$H NMR (200 MHz, DMSO – $d_6$) δ 5.88 – 5.61 ( m, 2H), 5.25 – 5.04 ( m, 4H), 3.40 – 3.24 (m, 2H), 3.04 (dd, *J*= 7.6, 15.0 Hz, 3H), 2.0 – 1.82 (m, 1H), 0.90 (d, *J*= 6.5, Hz, 3H), 0.82 (d, *J*= 6.2 Hz, 3H); $^{13}$C NMR (75 MHz, $D_2O$) δ 171.2, 127.3, 125.4, 65.3, 50.0, 29.5, 18.4, 17.2; HRMS calculated for $C_{11}H_{20}NO_2^+$ $[M+H]^+$: 198.1494, found 198.1497.

(2*S*)-2-(diprop-2-en-1-ylamino)-4-methylpentanoic acid **3d**



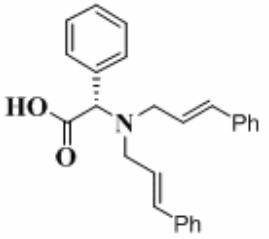
Compound **3d** was obtained as a pale white powder, 96.6 mg, yield = 60%, $[\alpha]^{20}_{D}$ -17.68, (*c* = 1.4, $CH_2Cl_2$),$^1$H NMR (200 MHz, DMSO – $d_6$) δ 5.84 – 5.64 ( m, 2H), 5.25 – 5.03 (m, 4H), 3.39 – 3.22 (m, 3H), 3.11 – 2.97 (dd, *J*=7.6, 15.0 Hz, 2H), 1.77 – 1.32 (m, 3H), 0.85 (t, *J*= 5.8 Hz, 6H); $^{13}$C NMR (75 MHz, DMSO – $d_6$) δ 174.2, 136.7, 116.6, 59.2, 52.8, 37.9, 24.0, 22.7, 21.6; mp = 167°C, HRMS calculated for $C_{12}H_{22}NO_2^+$ $[M+H]^+$: 212.1650, found 212.1646.

(2*S*)- (diprop-2-en-1-ylamino)acetic acid **3e**



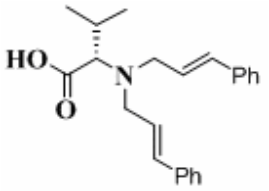

Compound **3e** was obtained as a pale yellow powder, 190 mg, yield = 92%, $^{1}$H NMR (200 MHz, $CD_3OD$) δ 6.12 - 5.91 (m, 2H), 5.67 – 5.54 (m, 4H), 3.84 (d, *J*= 6.9 Hz, 4H), 3.65 (s, 2H); $^{13}$C NMR (75 MHz, $CD_3OD$) δ 170.6, 128.9, 125.8, 57.5, 55.5; HRMS calculated for $C_8H_{14}NO_2^+$ $[M+H]^+$: 156.1025, found 156.1023.

(2*S*){di[(2*E*)-3-phenylprop-2-en-1-yl]amino} phenyl ethanoic acid **3f**



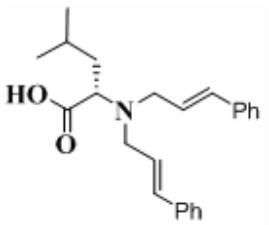

Compound **3f** was obtained as a pale yellow powder, 205.4 mg, yield = 88%, $[\alpha]^{20}_{D}$ +121.4, (*c* = 0.42, $CH_2Cl_2$), $^{1}$H NMR (200 MHz, $CD_3OD$) δ 7.74 –7.24 (m, 15H), 6.81 (d, *J*= 15.7 Hz, 2H), 6.48 – 6.26 (m, 2H), 5.20 (s, 1H), 4.18 – 3.67 (m, 4H); $^{13}$C NMR (75 MHz, $CD_3OD$) δ 178.0, 141.8, 140.1, 136.6, 131.9, 131.4, 130.1, 129.8, 128.1, 118.9, 117.3, 70.6, 55.6; HRMS calculated for $C_{26}H_{26}NO_2^+$ $[M+H]^+$: 384.1964, found 384.1966.

(2*S*)-2-{di[(E,E)-3-phenylprop-2-en-1-yl]amino}-3-methyl butanoic acid **3g**




Compound **3g** was obtained as a pale white powder, 199.8 mg, yield = 67%, $[\alpha]^{20}_{D}$ -33.6, (*c* = 0.5, $CH_2Cl_2$), $^1$H NMR (200 MHz, $CDCl_3$) δ 9.05 (bs, 1H), 7.48 – 7.16 (10H, m), 6.64 (d, *J*= 15.7 Hz, 2H), 6.36 – 6.17 (m, 2H), 3.75 (dd, *J*= 4.7, 14.2 Hz, 2H), 3.55 – 3.34 (m, 3H), 2.32 – 2.13 (m,1H), 1.17 (d, *J*= 6.2 Hz, 3H), 1.04 (d, *J*= 6.2 Hz, 3H); $^{13}$C NMR (75 MHz, $CD_3OD$) δ 180.2, 138.9, 132.5, 130.6, 129.4, 128.0, 127.2, 75.2, 54.4, 28.9, 20.8, 20.7; HRMS calculated for $C_{23}H_{28}NO_2^+$ $[M+H]^+$: 350.2120, found 350.2124.

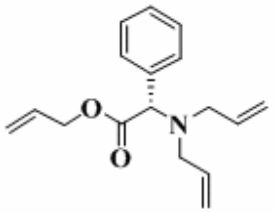
(2*S*)-2-{di[(2E)-3-phenylprop-2-en-1-yl]amino}-4-methyl pentanoic acid **3h**




Compound **3h** was obtained as a pale white powder, 218.9 mg, yield = 79%, $[\alpha]^{20}_{D}$ -46.7, (*c* = 0.4, $CH_2Cl_2$), $^1$H NMR (200 MHz, DMSO – $d_6$) δ 7.41 (d, *J*= 6.9 Hz, 4H), 7.36 – 7.16 (m, 6H), 6.55 (d, *J*= 16.1 Hz, 2H), 6.33 – 6.17 (m, 2H), 3.57 – 3.23 (m, 5H), 1.86 - 1.37 (m, 3H), 0.854 (t, *J*= 6.9 Hz, 6H); $^{13}$C NMR (75 MHz, DMSO – $d_6$) δ 174.5, 136.7, 131.2, 128.5, 128.4, 127.1, 126.0, 59.6, 52.4, 38.1, 24.0, 22.8, 21.5; mp = 174° C. HRMS calculated for $C_{24}H_{30}NO_2^+$ $[M+H]^+$: 364.2277, found 364.2274.

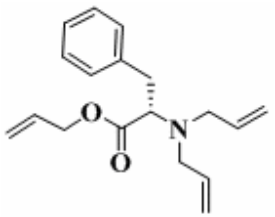
**Triple allylation of amino acids**

(2*S*)- Prop-2-en-1-yl (diprop-2-en-1-ylamino)phenyl ethanoate **4a**



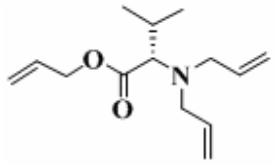
Compound **4a** was obtained after purification through Chromatography (silica gel, petroleum ether/ethyl acetate : 95/5) as a colorless oil, 226.1 mg, yield = 63%, $[\alpha]^{20}_{D}$ +17.6, (*c* = 1, $CH_2Cl_2$), $^1$H NMR (200 MHz, $CDCl_3$) δ 7.49 – 7.25 (d, *J*= 7.6 Hz, 5H), 6.01 – 5.70 (m, 3H), 5.37 – 5.08 (m, 6H), 4.67 ( s, 3H), 3.25 ( d, *J*= 5.9 Hz, 4H) ; $^{13}$C NMR (75 MHz, $CDCl_3$) δ 171.7, 136.5, 135.5, 131.9, 128.6, 128.3, 127.8, 118.4, 117.5, 67.5, 65.0, 53.1; IR (nujol) $cm^{-1}$ : 3081, 2980, 1740, 1642. HRMS calculated for $C_{17}H_{21}NNaO_2^+$ $[M+ Na]^+$: 294.1470, found 294.1471.

(2*S*)-prop-2-en-1-yl 2-(diprop-2-en-1-ylamino)-3-phenylpropanoate **4b**



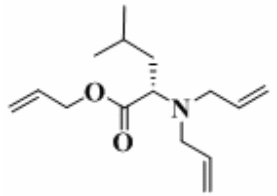
Compound **4b** was obtained after purification through Chromatography (silica gel, petroleum ether/ethyl acetate : 95/5) as a colorless oil, 269.5 mg, yield = 78%, $[\alpha]^{20}_{D}$ -29.8, (*c* = 0.92, $CH_2Cl_2$), $^1$H NMR (200 MHz, $CDCl_3$) δ 7.34 – 7.15 (m, 5H), 5.96 – 5.61 (m, 3H), 5.33 – 5.06 (m, 6H), 4.57 (d, *J*= 5.5 Hz, 2H), 3.76 (t, *J*=7.6 Hz, 1H), 3.50 – 3.36 (dd, *J*= 5.1, 14.7 Hz, 2H), 3.21 – 3.03 (m, 3H), 3.0 – 2.88 (dd, *J*= 6.9, 13.5 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 171.8, 138.2, 136.1, 131.9, 129.1, 127.9, 126.0, 118.0, 116.9, 64.5, 63.6, 53.3, 35.7; IR (nujol) $cm^{-1}$ : 3075, 2958, 1731, 1642. HRMS calculated for $C_{18}H_{24}NO_2^+$ $[M+ H]^+$: 286.1807, found 286.1827.

(2*S*)-prop-2-en-1-yl 2-(diprop-2-en-1-ylamino)-3-methylbutanoate **4c**



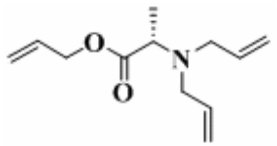
Compound **4c** was obtained after purification through Chromatography (silica gel, petroleum ether/ethyl acetate : 95/5) as a colorless oil, 259.3 mg, yield = 64%, $[\alpha]^{20}_{D}$ -88.7, (*c* = 4.0, $CH_2Cl_2$); $^1$H NMR (200 MHz, $CDCl_3$) δ 6.04 – 5.65 (m, 3H), 5.41 – 5.05 (m, 6H), 4.61 (d, *J*= 5.8 Hz, 2H), 3.48 – 3.35 (d, *J*= 14.7 Hz, 2H), 3.03 – 2.78 (m, 3H), 2.14 – 1.95 (m, 1H), 0.96 (d, *J*= 6.5Hz,3H), 0.86 (d, *J*= 6.5Hz,3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 171.8, 136.4, 132.2, 118.1, 116.6, 68.6, 64.2, 53.1, 27.4, 19.7, 19.3; HRMS calculated for $C_{14}H_{24}NO_2^+$[M+ H]$^+$: 238.1807, found 238.1807.

(2*S*)-prop-2-en-1-yl 2-(diprop-2-en-1-ylamino)-4-methylpentanoate **4d**



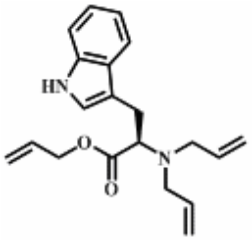
Compound **4d** was obtained after purification through Chromatography (silica gel, petroleum ether/ethyl acetate : 95/5) as a colorless oil, 295.1 mg, yield = 77%, $[\alpha]^{20}_{D}$ -57.7, (c 1.2, $CH_2Cl_2$); $^1$H NMR (200 MHz, $CDCl_3$) δ 6.03 – 5.67 (m, 3H), 5.39 – 5.04 (m, 6H), 4.59 (d, *J*= 5.5 Hz, 2H), 3.58 – 3.50 (t, *J*= 7.6 Hz, 1H), 3.44 – 3.28 (dd, *J*= 4.7, 14.6 Hz, 2H), 3.04 (dd, *J*= 7.6, 14.6 Hz, 2H), 1.63 (m, 3H), 0.98 (t, *J*= 6.2 Hz, 6H) ; $^{13}$C NMR (75 MHz, $CDCl_3$) δ 172.9, 136.6, 132.2, 117.9, 116.6, 64.3, 59.6, 53.2, 38.5, 24.4, 22.8, 21.7; IR (nujol) cm$^{-1}$ : 3080, 1734, 1641. HRMS calculated for $C_{15}H_{26}NO_2^+$ [M+H]$^+$: 252.1963, found 252.1963.

(2*S*)-prop-2-en-1-yl 2-(diprop-2-en-1-ylamino)propanoate **4e**



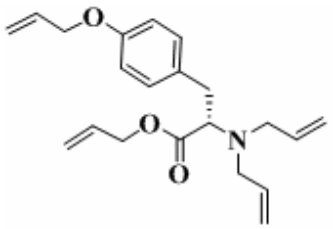
Compound **4e** was obtained after purification through Chromatography (silica gel, petroleum ether/ethyl acetate : 95/5) as a colorless oil,272.4 mg, yield = 58%, $[\alpha]^{20}_{D}$ -59.62, (c = 2.7, $CH_2Cl_2$); $^1$H NMR (200 MHz, $CDCl_3$) δ 6.06 – 5.72 (ddt, *J*= 6.1, 10.0, 16.8 Hz, 3H), 5.40 – 5.10 (m, 6H), 4.62 (d, *J= 5.7 Hz*, 2H), 3.67 – 3.57 (q, *J=6.9, 14.2 Hz*, 1H), 3.35 – 3.08 (m, 4H), 1.31 (d, *J*= 7.1 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 173.0, 136.3, 132.0, 117.7, 116.6, 64.4, 56.9, 53.2, 14.6; IR (nujol) $cm^{-1}$ : 3081, 2982, 2839, 1732, 1643. HRMS calculated for $C_{12}H_{20}NO_2^+$ $[M+H]^+$: 210.1494, found 210.1497.

(2R)-Prop-2-en-1-yl 2-(diprop-2-en-1-ylamino)-3-(1*H*-indol-3-yl)propanoate **4f**



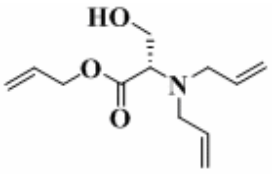
Compound **4f** was obtained after purification through Chromatography (silica gel, petroleum ether/ethyl acetate: 85/15) as a colorless oil,241.4 mg, yield = 76%, $[\alpha]^{20}_{D}$ +0.6, (*c* = 1.5, $CH_2Cl_2$); $^1$H NMR (200 MHz, $CDCl_3$) δ 8.16 (bs, 1H), 7.67 (d, *J*= 7.3 Hz, 1H), 7.37 (d, *J*= 8.4 Hz, 1H), 7.30 -7.12 (m, 2H), 7.05 (s, 1H), 5.98 – 5.77 (m, 3H), 5.33 – 5.12 (m, 6H), 4.58 (t, *J*= 5.12 Hz, 2H), 3.97 (dd, *J*= 5.8, 9.1 Hz, 1H), 3.55 (dd, *J*= 5.1, 14.6 Hz, 2H), 3.46 – 3.05 (m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 172.4, 136.3, 136.0, 132.0, 127.4, 122.7, 121.7, 119.1, 118.6, 118.0, 117.1, 112.0, 111.0, 64.6, 62.9, 53.5, 25.5; HRMS calculated for $C_{20}H_{25}N_2O_2^+$ $[M+H]^+$: 325.1916, found 325.1911.

(2*S*)-Prop-2-en-1-yl 2-(diprop-2-en-1-ylamino)-3-[4-(prop-2-en-1-yloxy)phenyl]propanoate **4g**



Compound **4g** was obtained after purification through Chromatography (silica gel, petroleum ether/ethyl acetate : 90/10) as a colorless oil,248.7 mg, yield = 66%, $[\alpha]^{20}_{D}$ -14.6, (c 1.1, $CH_2Cl_2$), $^1$H NMR (200 MHz, $CDCl_3$) δ 7.08 ( d, *J*= 8.4 Hz, 2H), 6.82 (d, *J*= 8.4 Hz, 2H), 6.14 – 5.60 (m, 4H), 5.44 – 5.06 (m, 8H), 4.68 – 4.47 (m, 4H), 3.68 (t, *J*= *7.3 Hz*, 1H), 3.39 (dd, *J*= 4.75, 14.27 Hz, 2H), 3.17 – 2.75 (m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 172.1, 157.0, 136.2, 133.3, 132.0, 130.5, 130.1, 118.1, 117.3, 117.0, 114.3, 68.7, 64.6, 63.9, 53.4, 34.9; IR (nujol) $cm^{-1}$ : 3079, 1729, 1644, 1611. HRMS calculated for $C_{21}H_{28}NO_3^+[M+H]^+$: 342.2069, found 342.2066.

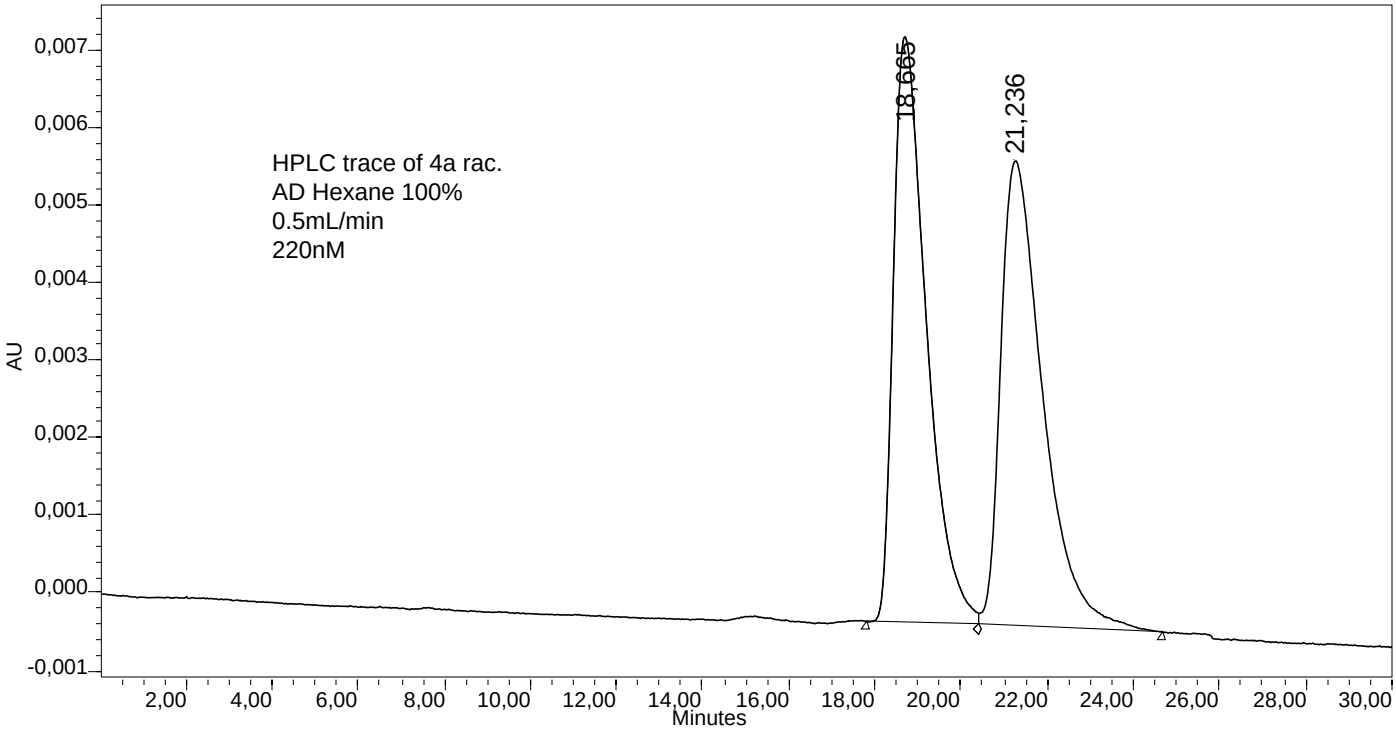
(2*S*)-prop-2-en-1-yl 2-(diprop-2-en-1-ylamino)-3-hydroxypropanoate **4h**



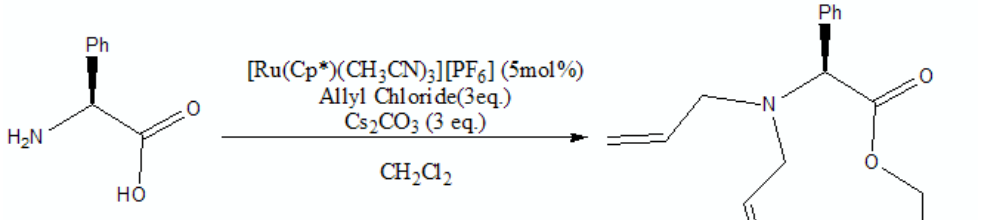
Compound **4h** was obtained as a colorless oil, 300.1 mg, yield = 70%, $[\alpha]^{20}_{D}$ -3.29, (c 0.05, $CH_2Cl_2$), $^1$H NMR (200 MHz, $CDCl_3$) δ 6.01 – 5.64 (m, 3H), 5.36 – 5.07 (m, 6H), 4.59 (d, *J*= 5.4 Hz, 2H), 3.80 – 3.48 (m, 4H), 3.36 (dd, *J*= 4.7, 14.2 Hz, 2H), 3.23 -3.09 (dd, *J*= 8.5, 14.2 Hz, 2H), 2.75 (bs, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 172.8, 135.7, 131.7, 118.5, 117.8, 64.9, 62.4, 58.9, 53.5; HRMS calculated for $C_{12}H_{20}NO_3^+[M+H]^+$: 226.1443, found 225.1441.

# SAMPLE INFORMATION

| | | | |
|---|---|---|---|
| Sample Name: | RacPGtriallAD0,5mL100H1507 | Acquired By: | System |
| Sample Type: | Unknown | Date Acquired: | 15/07/09 14:48:22 |
| Vial: | 999 | Acq. Method: | MathieBaskeraminoacids |
| Injection #: | 1 | Date Processed: | 15/07/09 15:20:01 |
| Injection Volume: | 10,00 ul | Channel Name: | 2487Channel 1 |
| Run Time: | 35,00 Minutes | Sample Set Name: | |




| | RT (min) | Area (µV*sec) | % Area | Height (µV) | % Height |
|---|---|---|---|---|---|
| 1 | 18,665 | 404276 | 49,69 | 7553 | 55,70 |
| 2 | 21,236 | 409295 | 50,31 | 6007 | 44,30 |

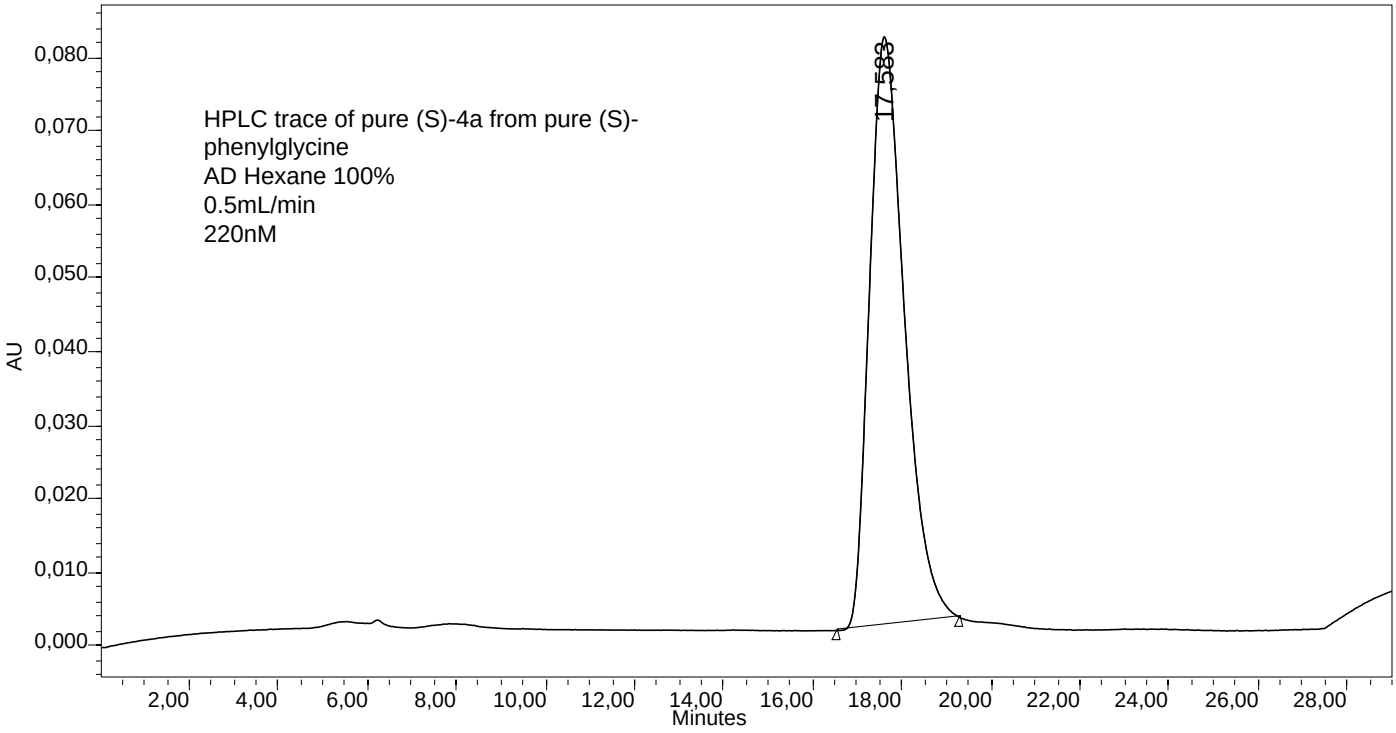



phenylglycine *rac.*

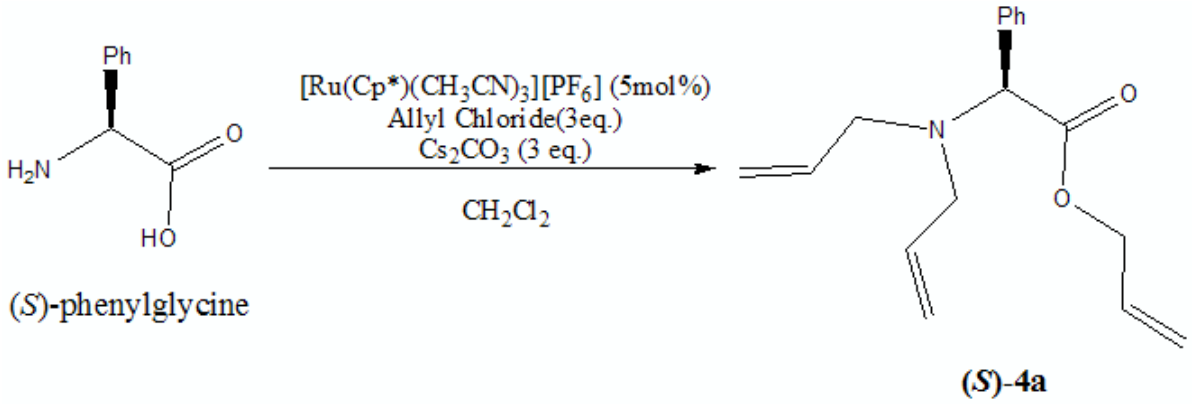
**4a** *rac.*

## SAMPLE INFORMATION

| | | | |
|---|---|---|---|
| Sample Name: | LPGtridirectAD0,5mL100H1507 | Acquired By: | System |
| Sample Type: | Unknown | Date Acquired: | 15/07/09 17:17:35 |
| Vial: | 999 | Acq. Method: | MathieBaskeraminoacids |
| Injection #: | 1 | Date Processed: | 15/07/09 17:47:56 |
| Injection Volume: | 10,00 ul | Channel Name: | 2487Channel 2 |
| Run Time: | 30,00 Minutes | Sample Set Name: | |




| | RT (min) | Area (µV*sec) | % Area | Height (µV) | % Height |
|---|---|---|---|---|---|
| 1 | 17,583 | 4373832 | 100,00 | 79974 | 100,00 |

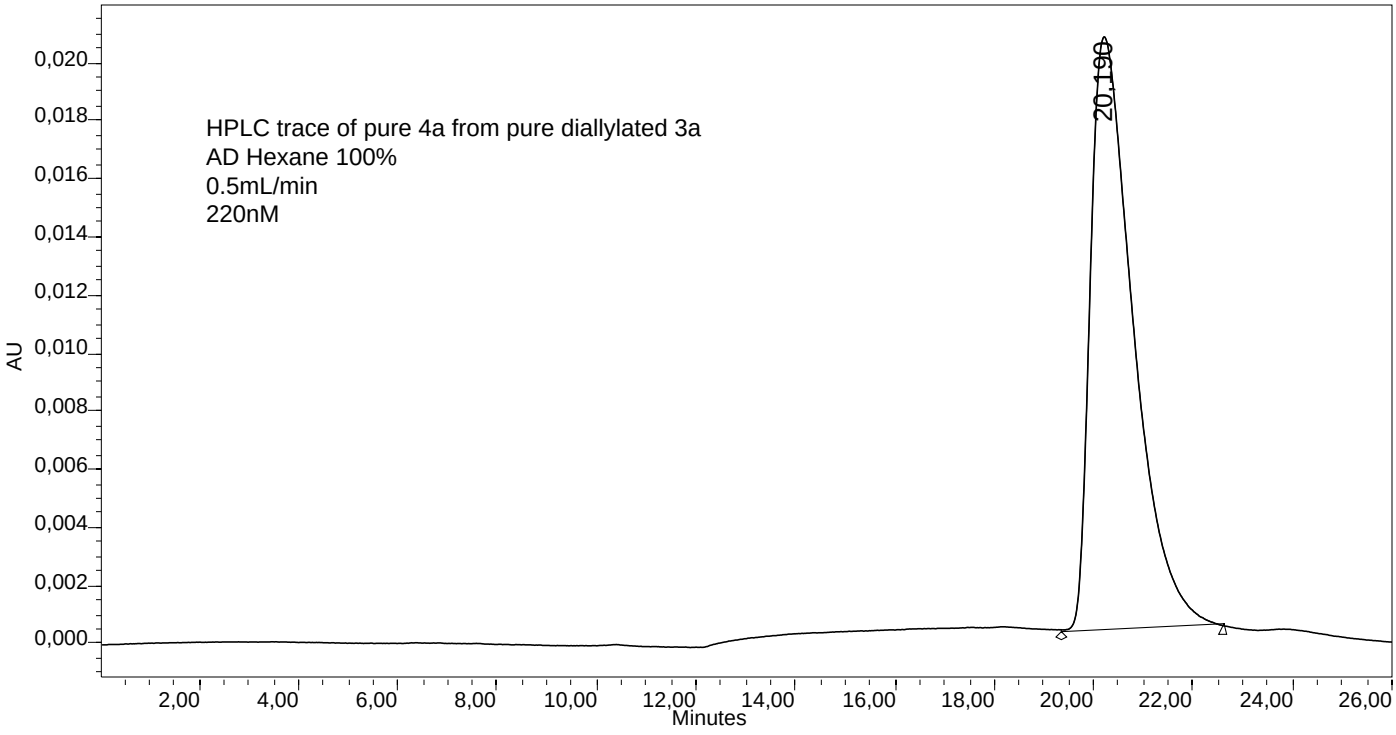



(*S*)-phenylglycine

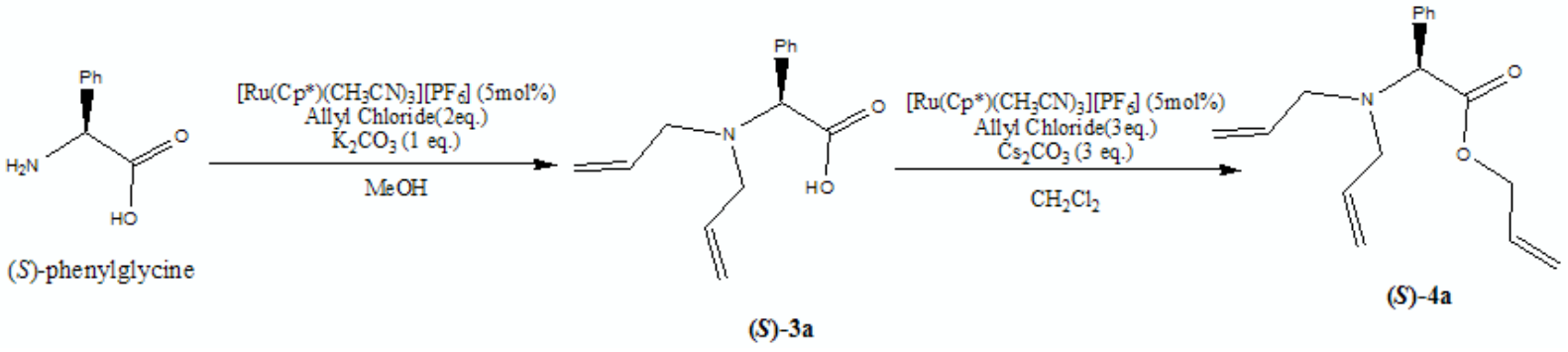
**(*S*)-4a**

# SAMPLE INFORMATION

| | | | |
|---|---|---|---|
| Sample Name: | LPGDitoTriAD0,5mL100Hdilue16 | Acquired By: | System |
| Sample Type: | Unknown | Date Acquired: | 16/07/09 10:51:52 |
| Vial: | 999 | Acq. Method: | MathieBaskeraminoacids |
| Injection #: | 3 | Date Processed: | 16/07/09 16:39:01 |
| Injection Volume: | 10,00 ul | Channel Name: | 2487Channel 1 |
| Run Time: | 26,00 Minutes | Sample Set Name: | |

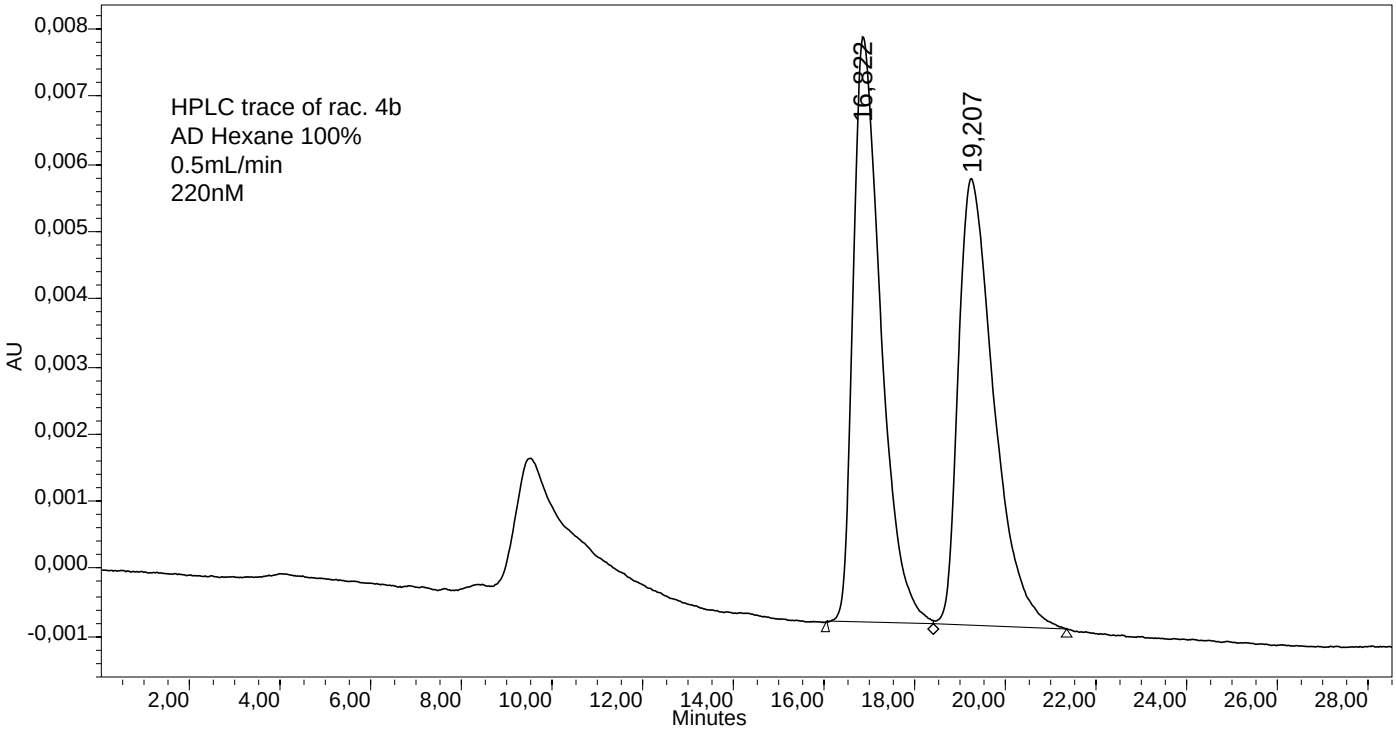



| | RT (min) | Area (µV*sec) | % Area | Height (µV) | % Height |
|---|---|---|---|---|---|
| 1 | 20,190 | 1233241 | 100,00 | 20444 | 100,00 |

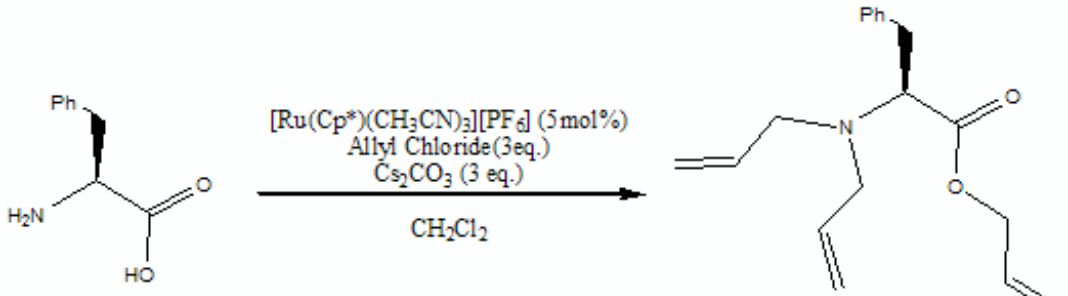


## SAMPLE INFORMATION

| | | | |
|---|---|---|---|
| Sample Name: | RacPAtriallAD0,5mL100Hdilue | Acquired By: | System |
| Sample Type: | Unknown | Date Acquired: | 16/07/09 14:40:20 |
| Vial: | 999 | Acq. Method: | MathieBaskeraminoacids |
| Injection #: | 5 | Date Processed: | 16/07/09 16:40:35 |
| Injection Volume: | 10,00 ul | Channel Name: | 2487Channel 1 |
| Run Time: | 30,00 Minutes | Sample Set Name: | |




| | RT (min) | Area (µV*sec) | % Area | Height (µV) | % Height |
|---|---|---|---|---|---|
| 1 | 16,822 | 372421 | 50,59 | 8698 | 56,71 |
| 2 | 19,207 | 363737 | 49,41 | 6640 | 43,29 |

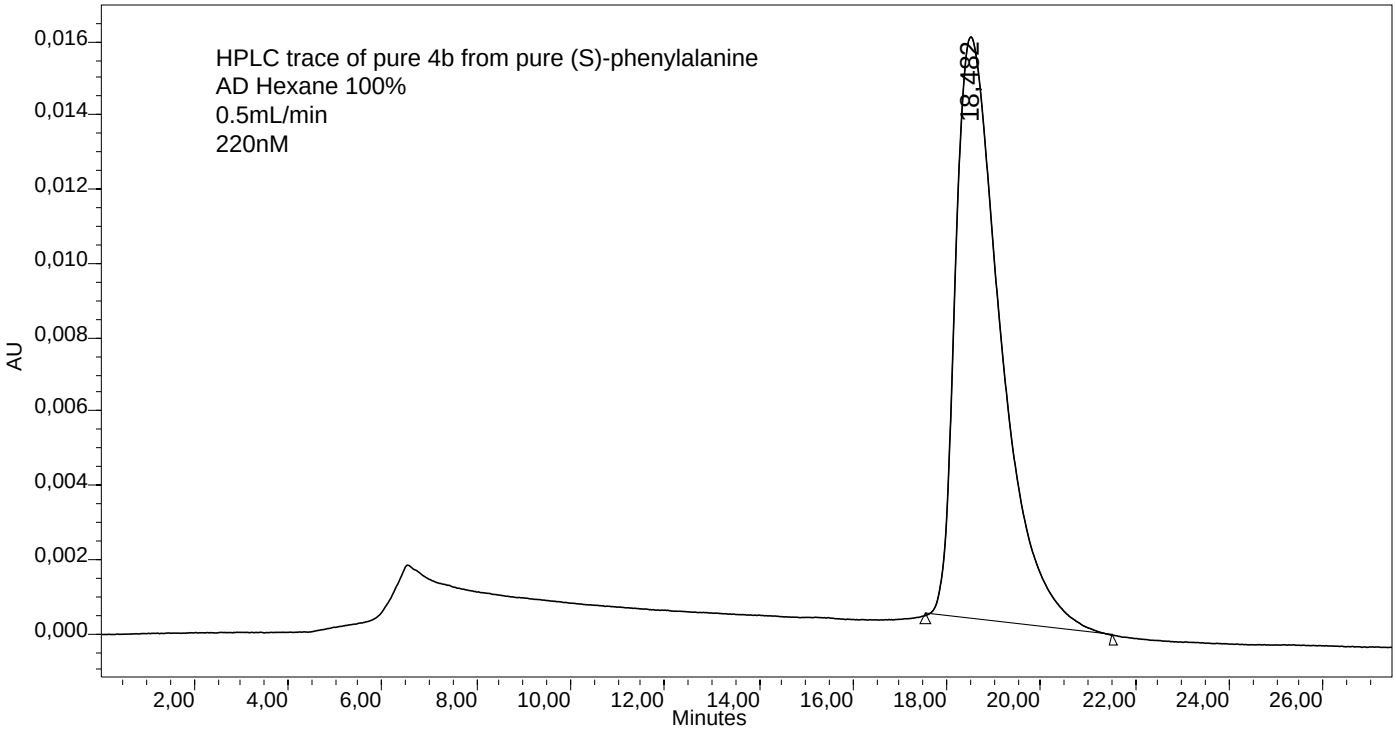



phenylalanine *rac.*

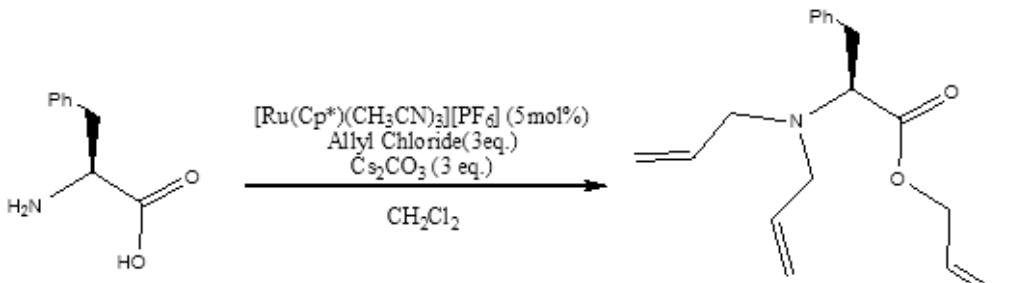
**4b** *rac.*

# SAMPLE INFORMATION

| | | | |
|---|---|---|---|
| Sample Name: | LPAtridirectAD0,5mL100H | Acquired By: | System |
| Sample Type: | Unknown | Date Acquired: | 16/07/09 15:50:42 |
| Vial: | 999 | Acq. Method: | MathieBaskeraminoacids |
| Injection #: | 7 | Date Processed: | 16/07/09 16:42:12 |
| Injection Volume: | 10,00 ul | Channel Name: | 2487Channel 1 |
| Run Time: | 30,00 Minutes | Sample Set Name: | |




| | RT (min) | Area (µV*sec) | % Area | Height (µV) | % Height |
|---|---|---|---|---|---|
| 1 | 18,482 | 1054440 | 100,00 | 15750 | 100,00 |

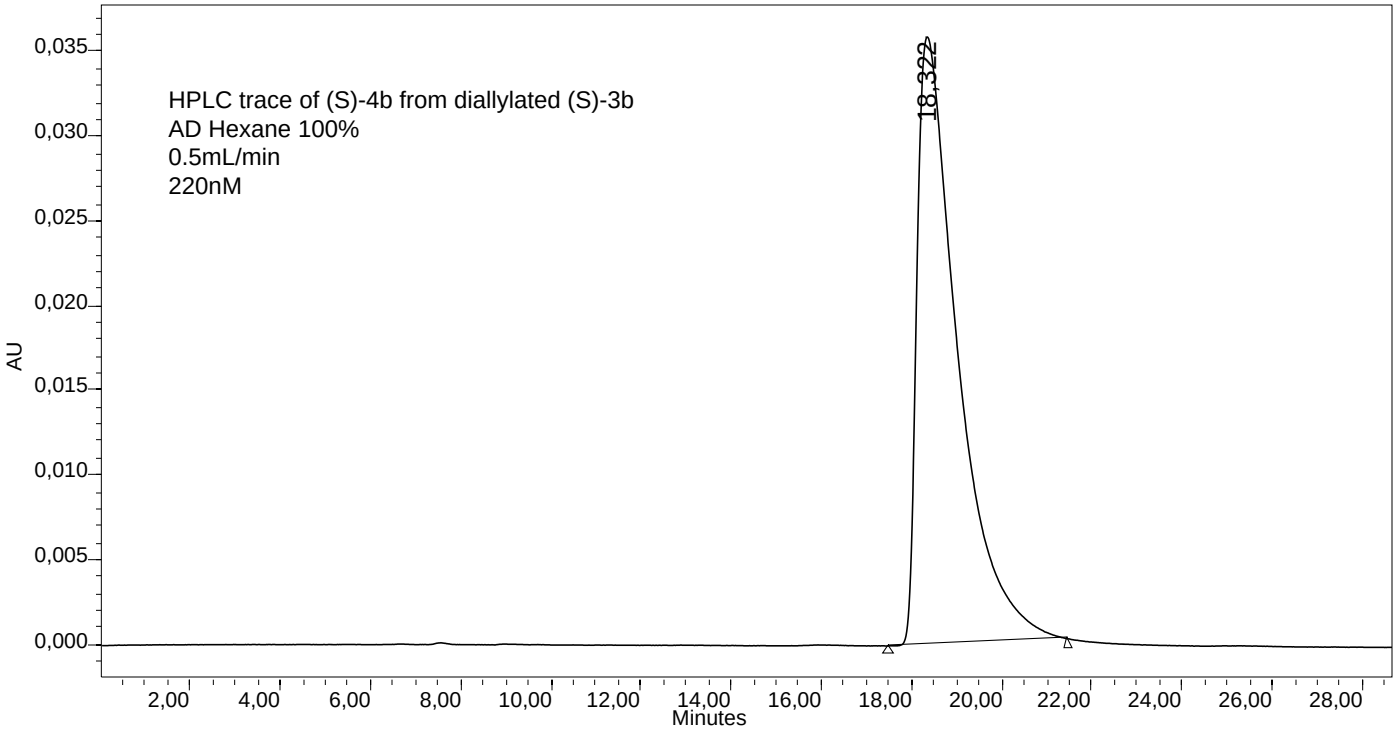



(S)-phenylalanine

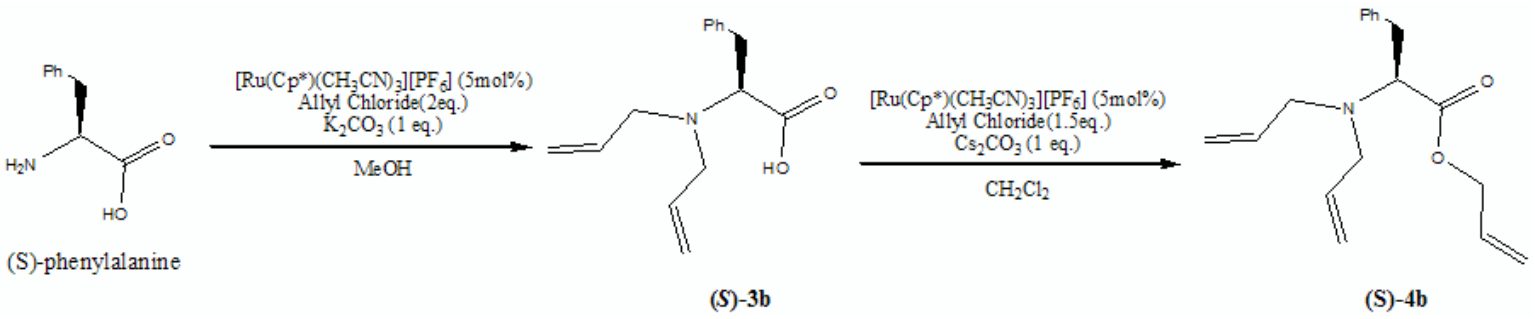
**4b**

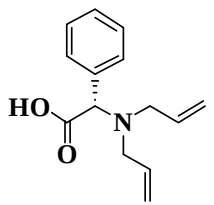
# SAMPLE INFORMATION

| | | | |
|---|---|---|---|
| Sample Name: | LPAditotriAD0,5mL100Hdilue | Acquired By: | System |
| Sample Type: | Unknown | Date Acquired: | 16/07/09 17:16:29 |
| Vial: | 999 | Acq. Method: | MathieBaskeraminoacids |
| Injection #: | 10 | Date Processed: | 16/07/09 17:45:50 |
| Injection Volume: | 10,00 ul | Channel Name: | 2487Channel 1 |
| Run Time: | 30,00 Minutes | Sample Set Name: | |



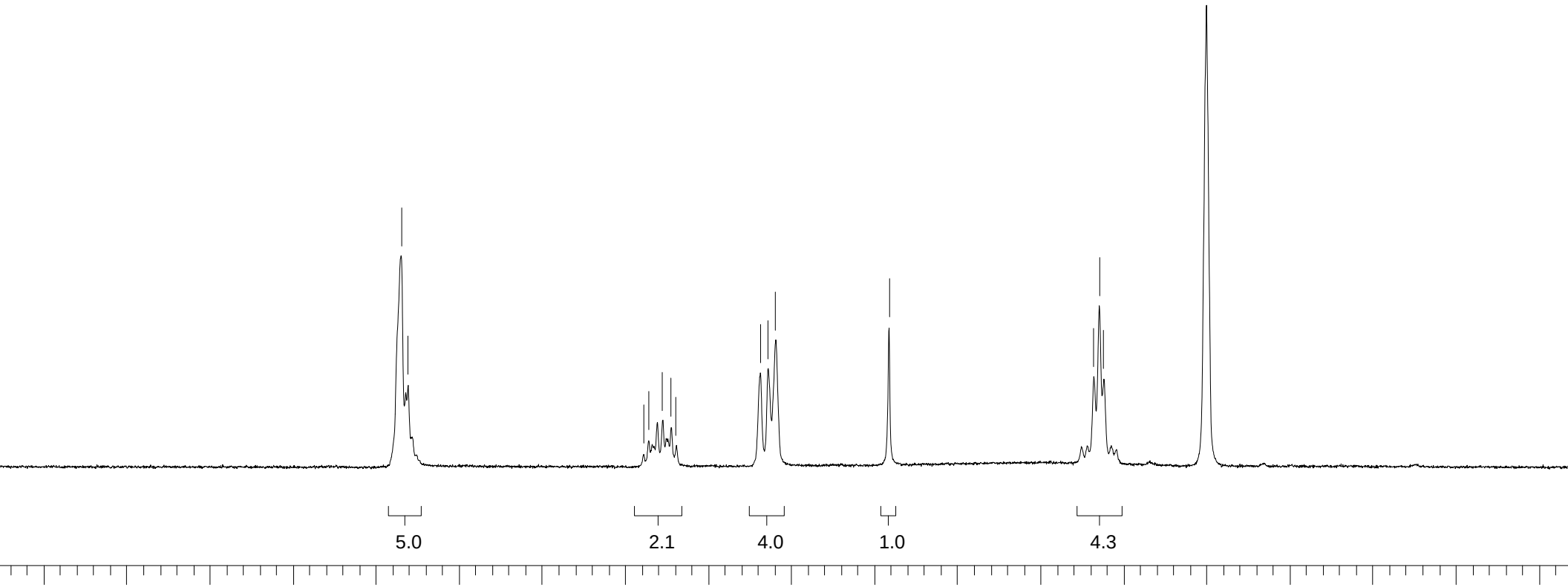

| | RT (min) | Area (µV*sec) | % Area | Height (µV) | % Height |
|---|---|---|---|---|---|
| 1 | 18,322 | 2252298 | 100,00 | 35880 | 100,00 |

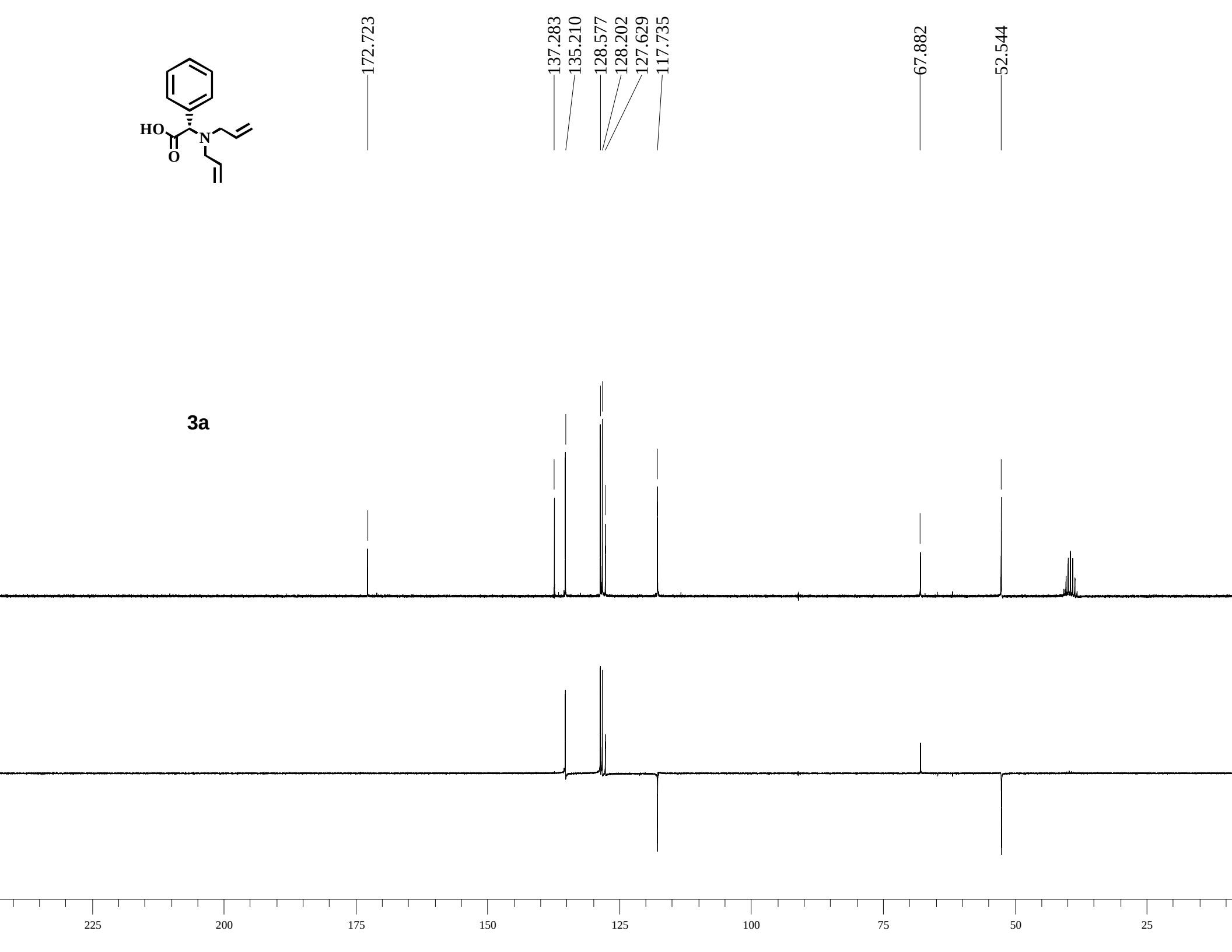


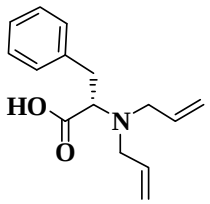



7.346
7.304
5.887
5.856
5.772
5.721
5.690
5.185
5.138
5.092
4.409
3.177
3.145
3.117

**3a**




HO
O
N
172.723
137.283
135.210
128.577
128.202
127.629
117.735
67.882
52.544
3a
225
200
175
150
125
100
75
50
25

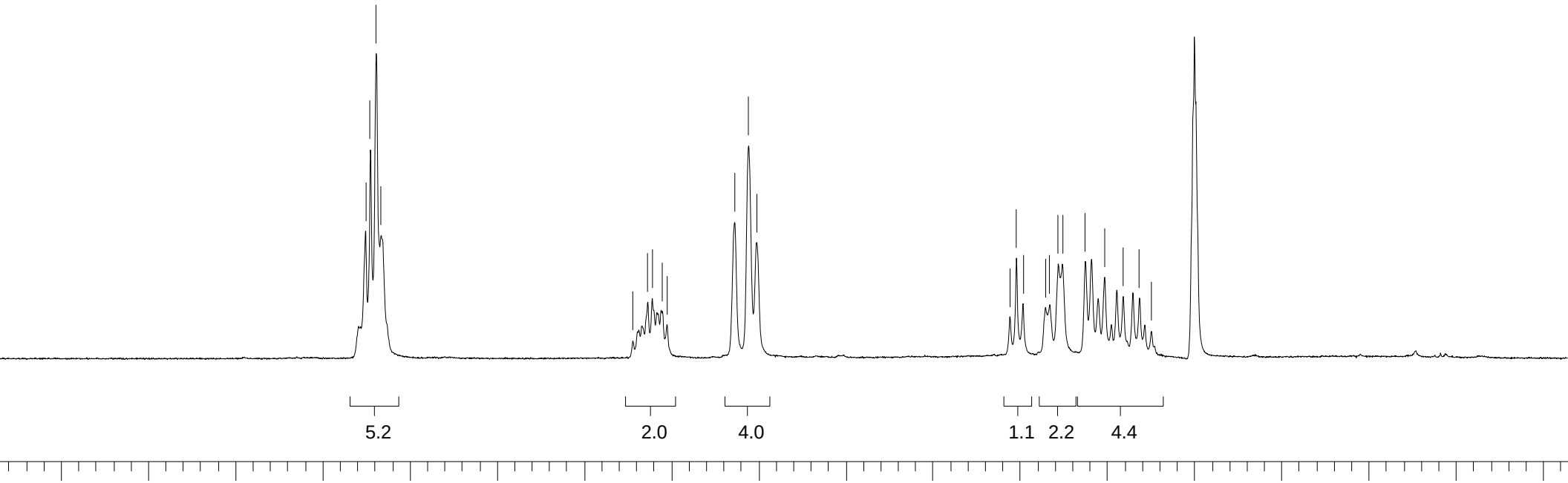


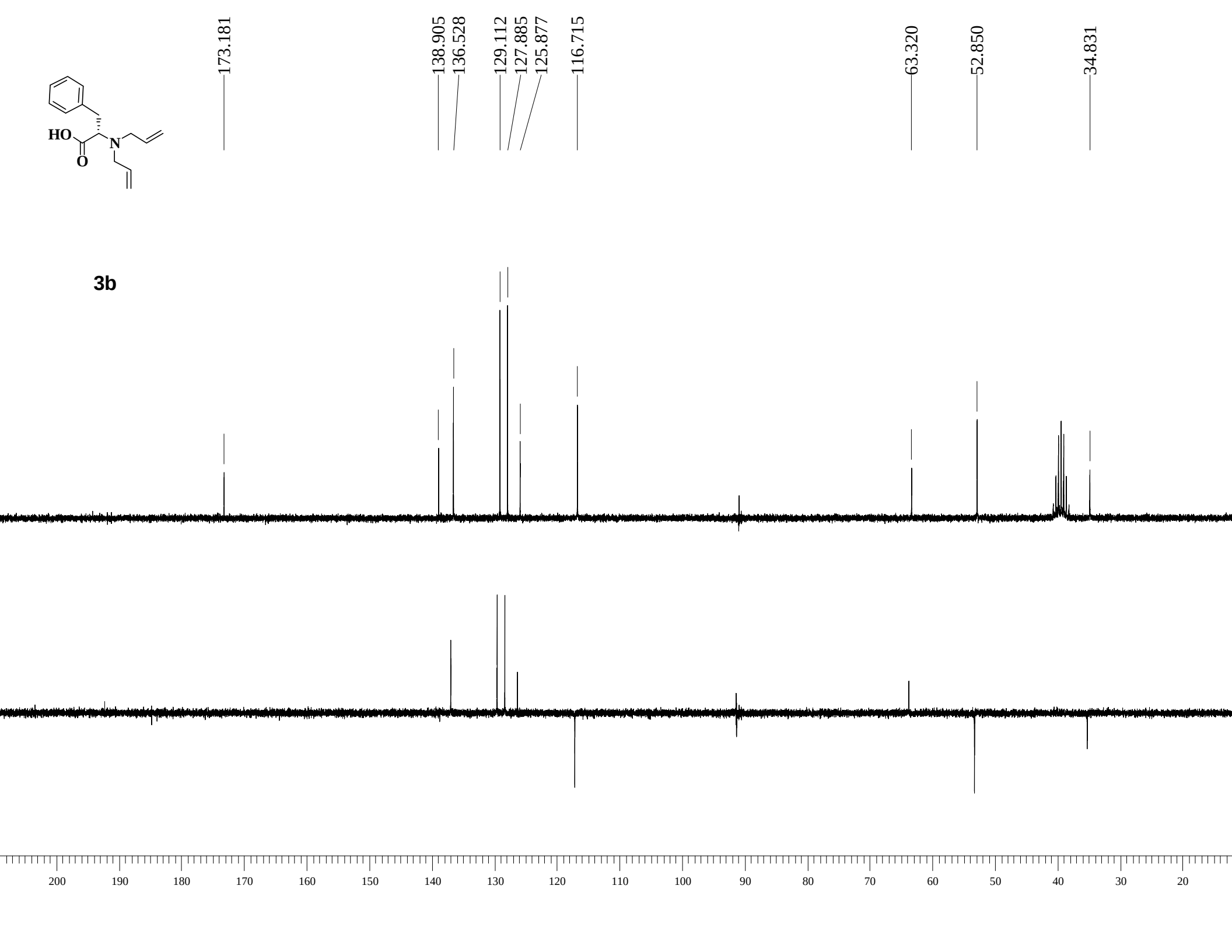

7.251 7.224 7.191 7.161

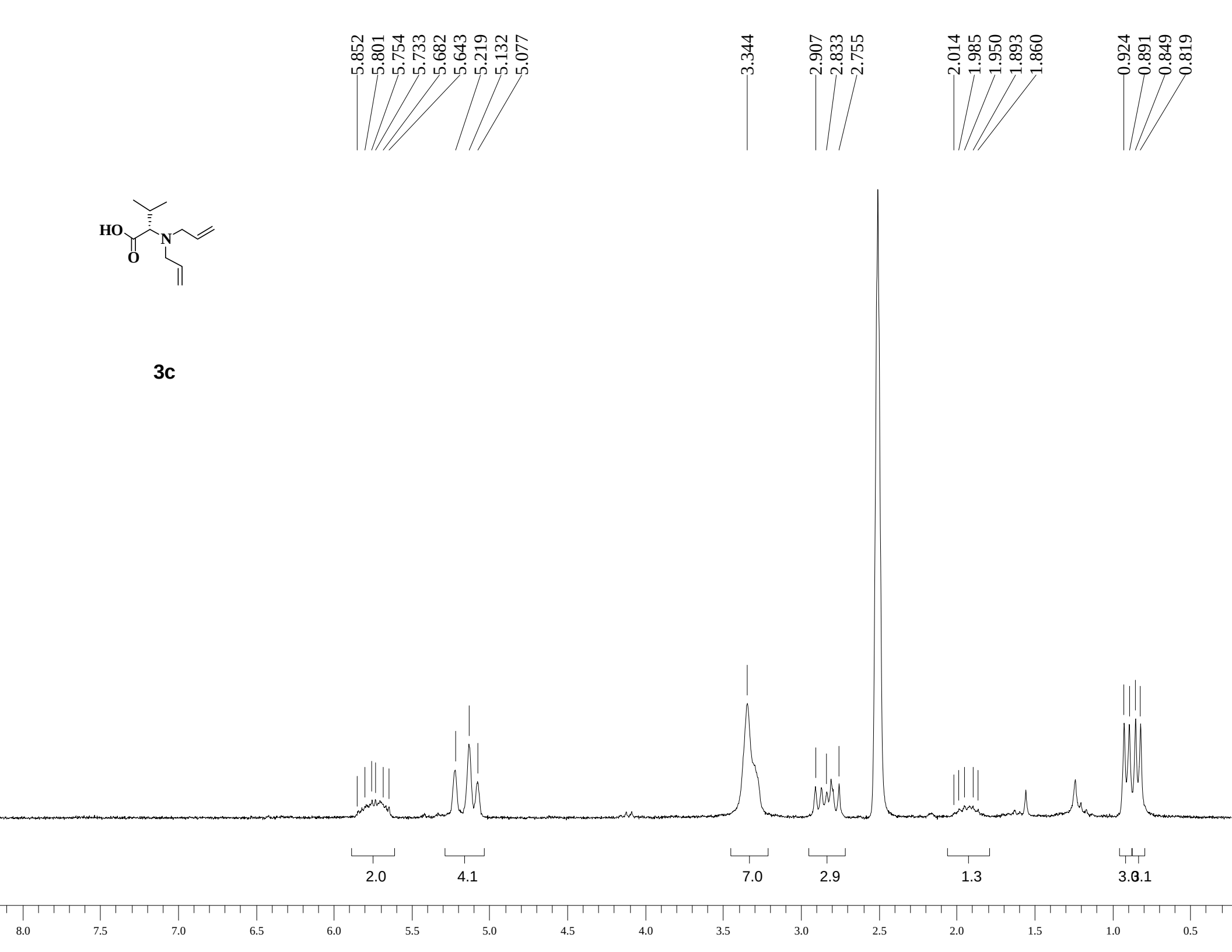
5.719 5.633 5.607 5.549 5.523 5.136 5.055 5.009

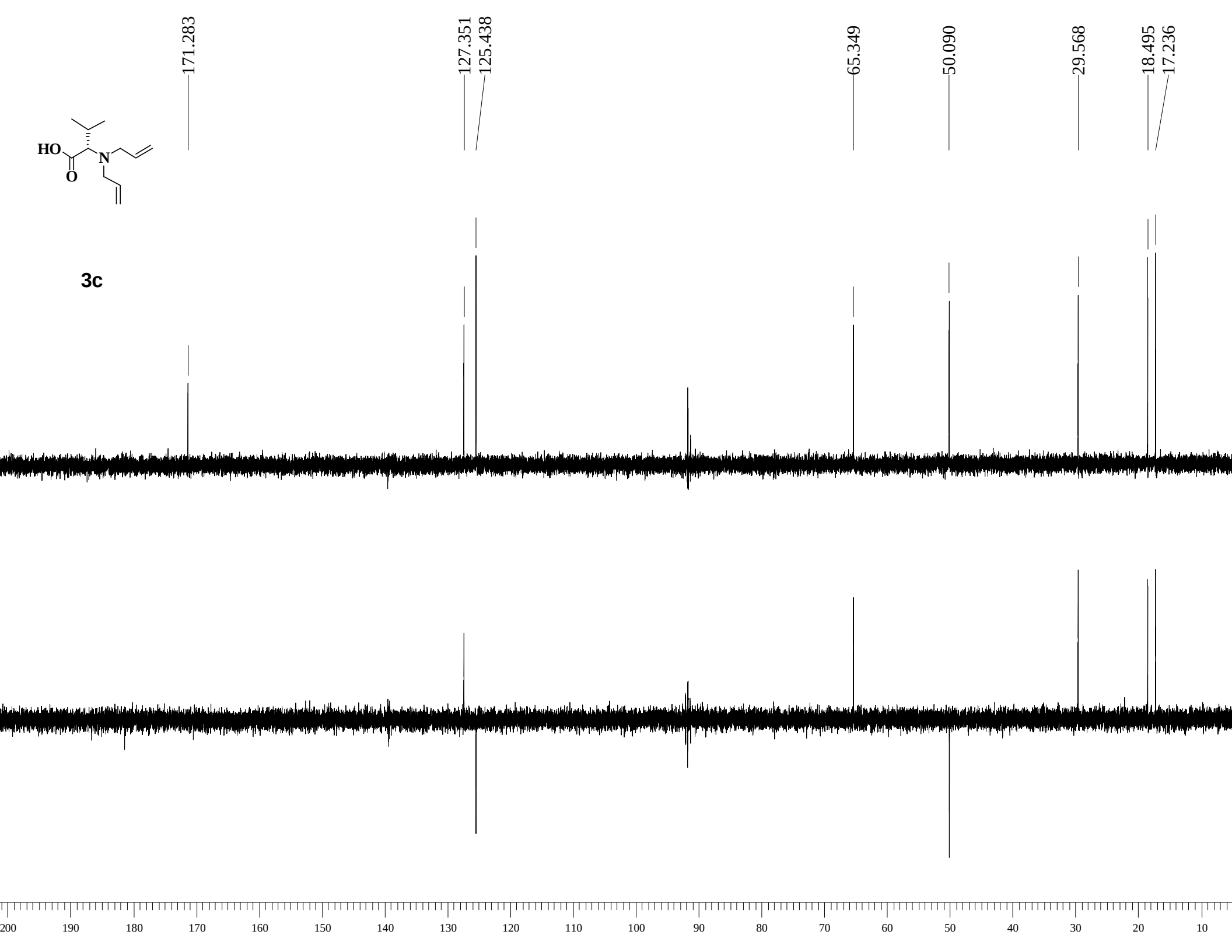
3.556 3.519 3.481 3.353 3.327 3.279 3.256 3.124 3.013 2.907 2.813 2.744

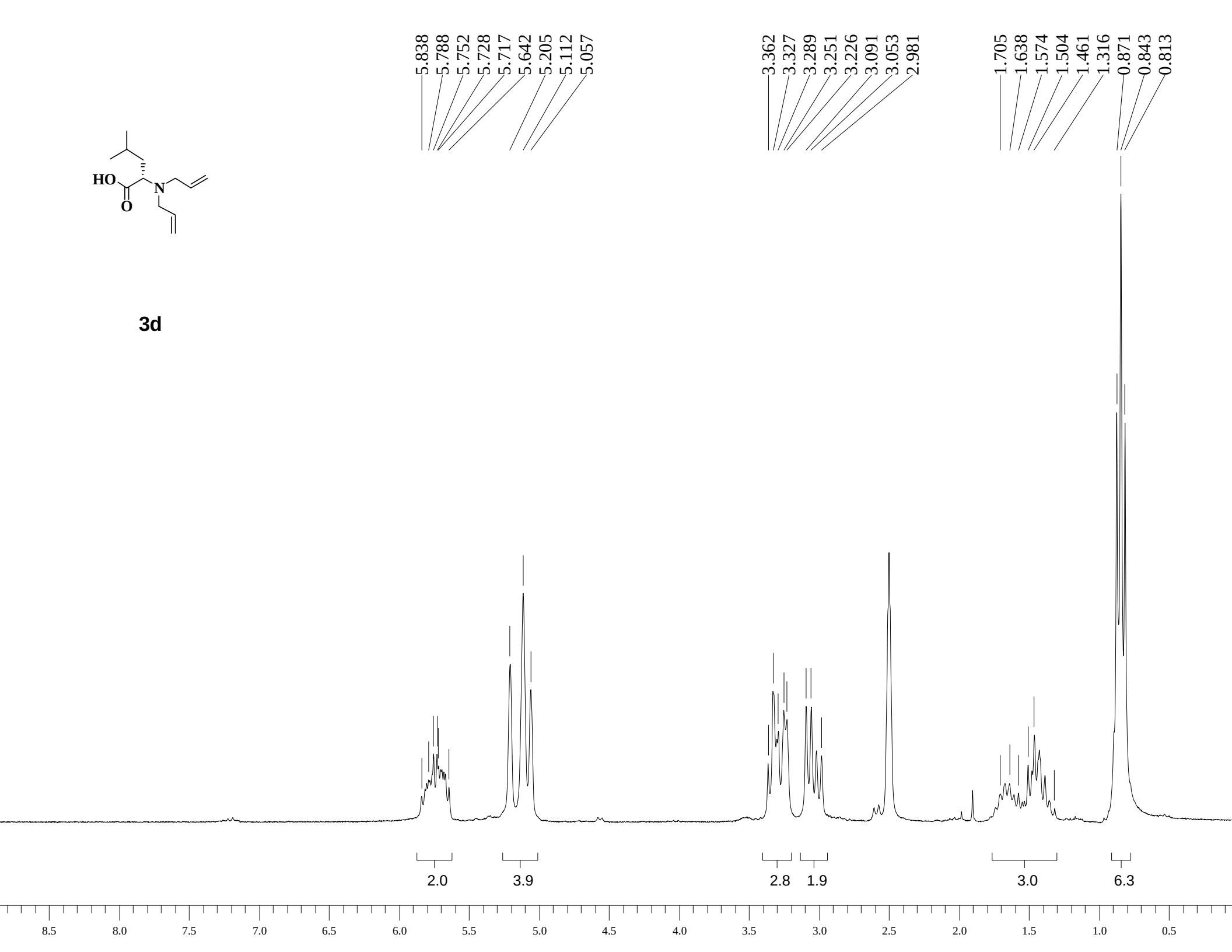
**3b**

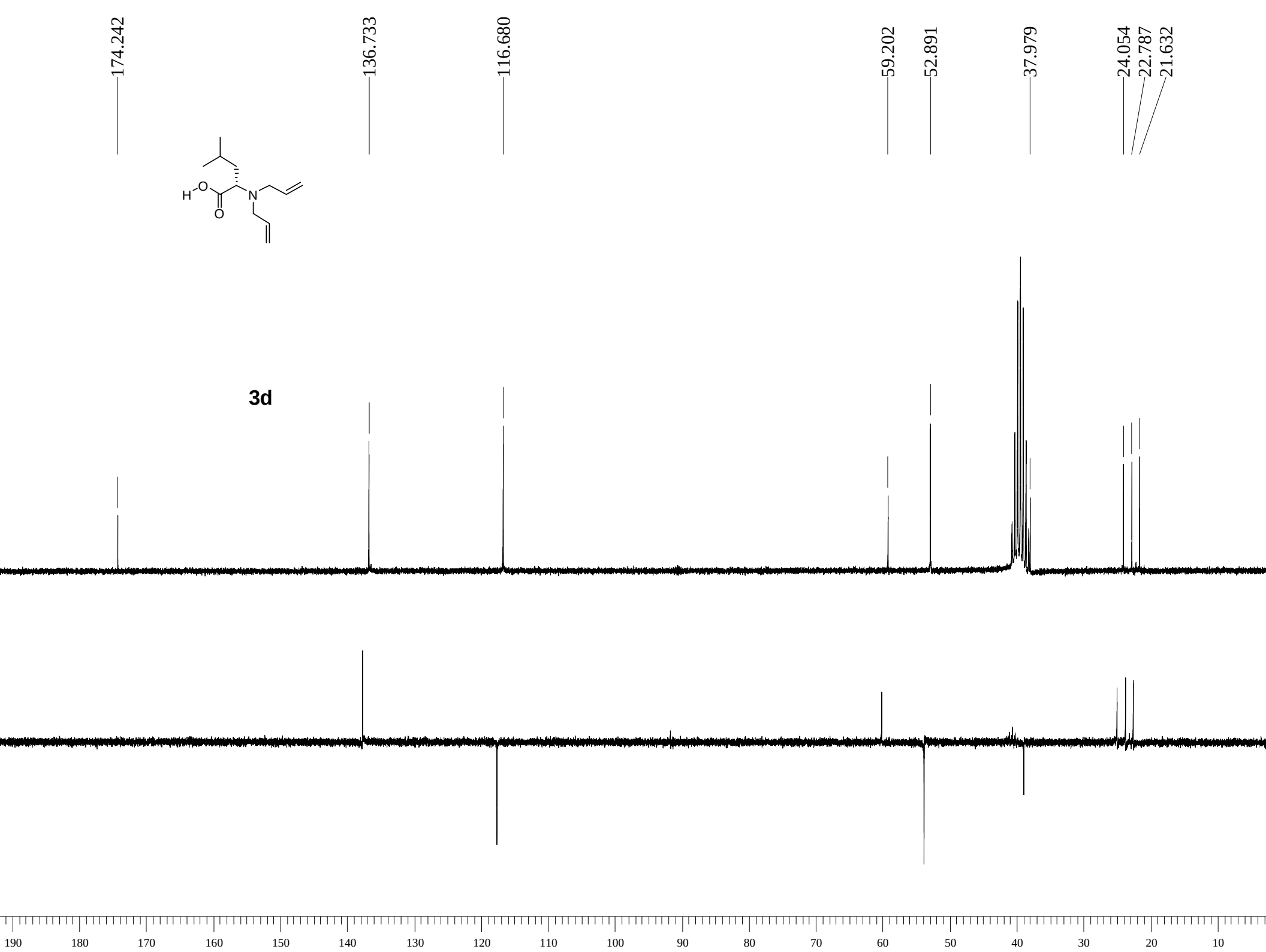


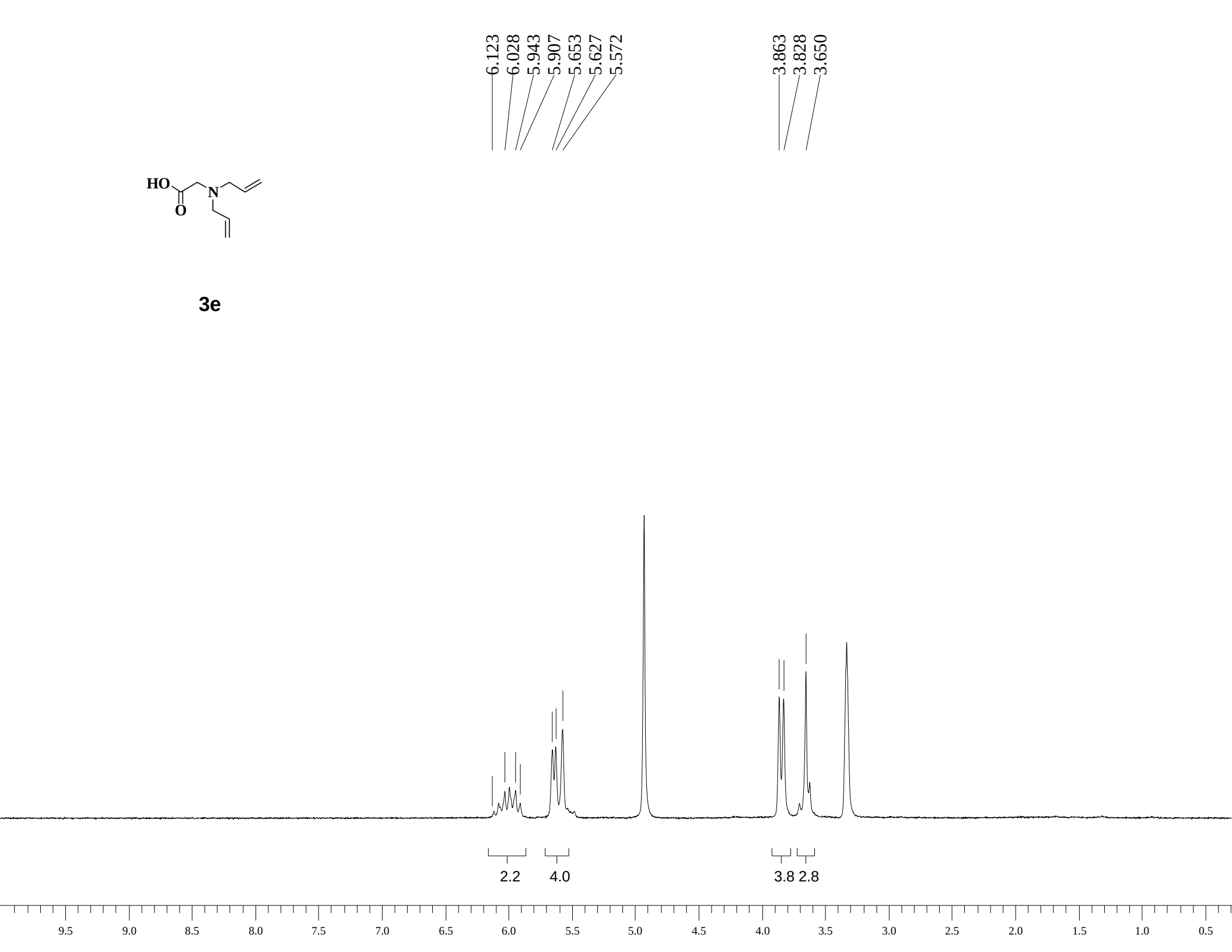

173.181
138.905
136.528
129.112
127.885
125.877
116.715
63.320
52.850
34.831
HO
O
N
3b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20


5.852
5.801
5.754
5.733
5.682
5.643
5.219
5.132
5.077
3.344
2.907
2.833
2.755
2.014
1.985
1.950
1.893
1.860
0.924
0.891
0.849
0.819
HO
O
N
3c
2.0
4.1
7.0
2.9
1.3
3.0
3.1
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

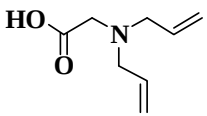

171.283
127.351
125.438
65.349
50.090
29.568
18.495
17.236
HO
O
N
3c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


5.838
5.788
5.752
5.728
5.717
5.642
5.205
5.112
5.057
3.362
3.327
3.289
3.251
3.226
3.091
3.053
2.981
1.705
1.638
1.574
1.504
1.461
1.316
0.871
0.843
0.813
HO
O
N
3d
2.0
3.9
2.8
1.9
3.0
6.3
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


174.242
136.733
116.680
59.202
52.891
37.979
24.054
22.787
21.632
3d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


6.123
6.028
5.943
5.907
5.653
5.627
5.572
3.863
3.828
3.650
HO
O
N
2.2
4.0
3.8
2.8
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

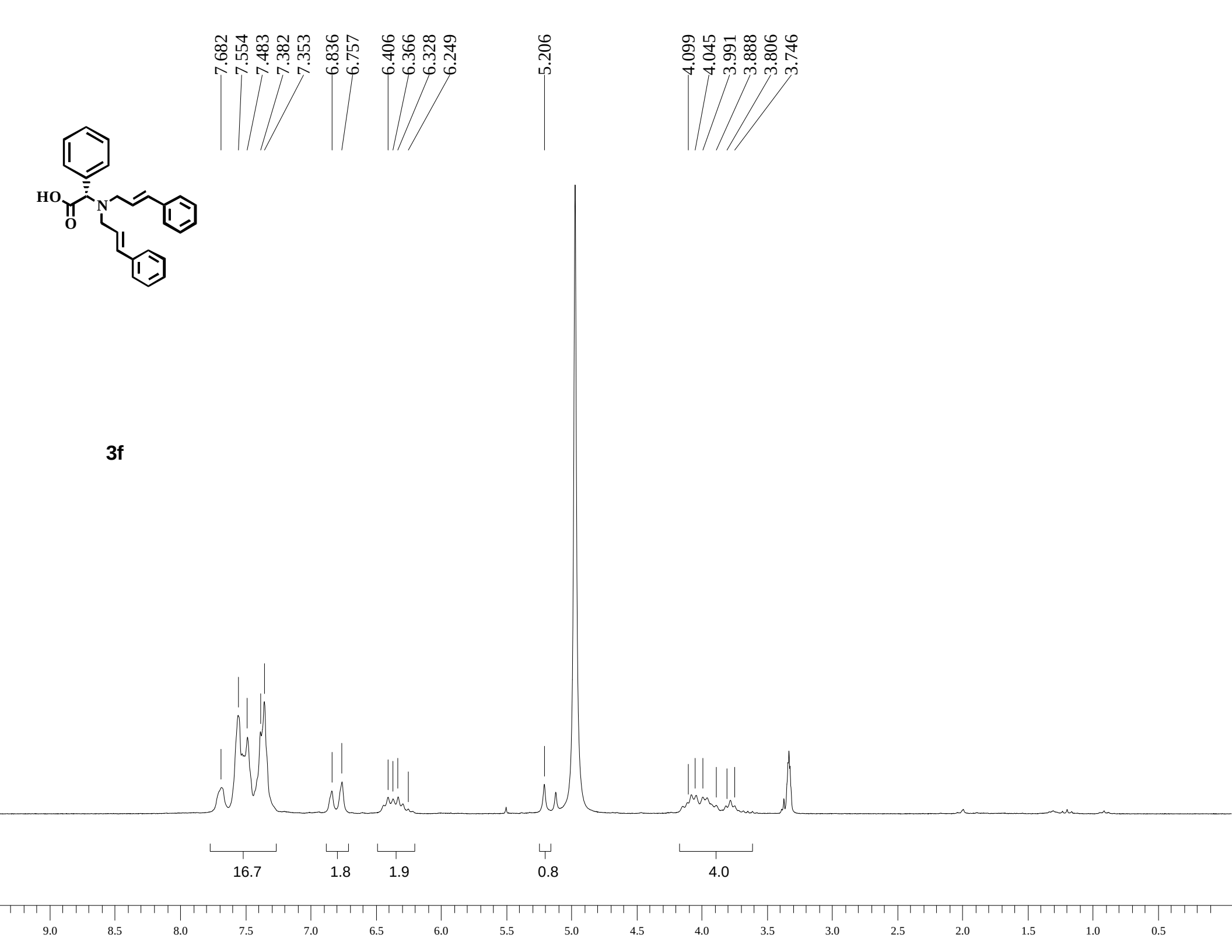
**3e**

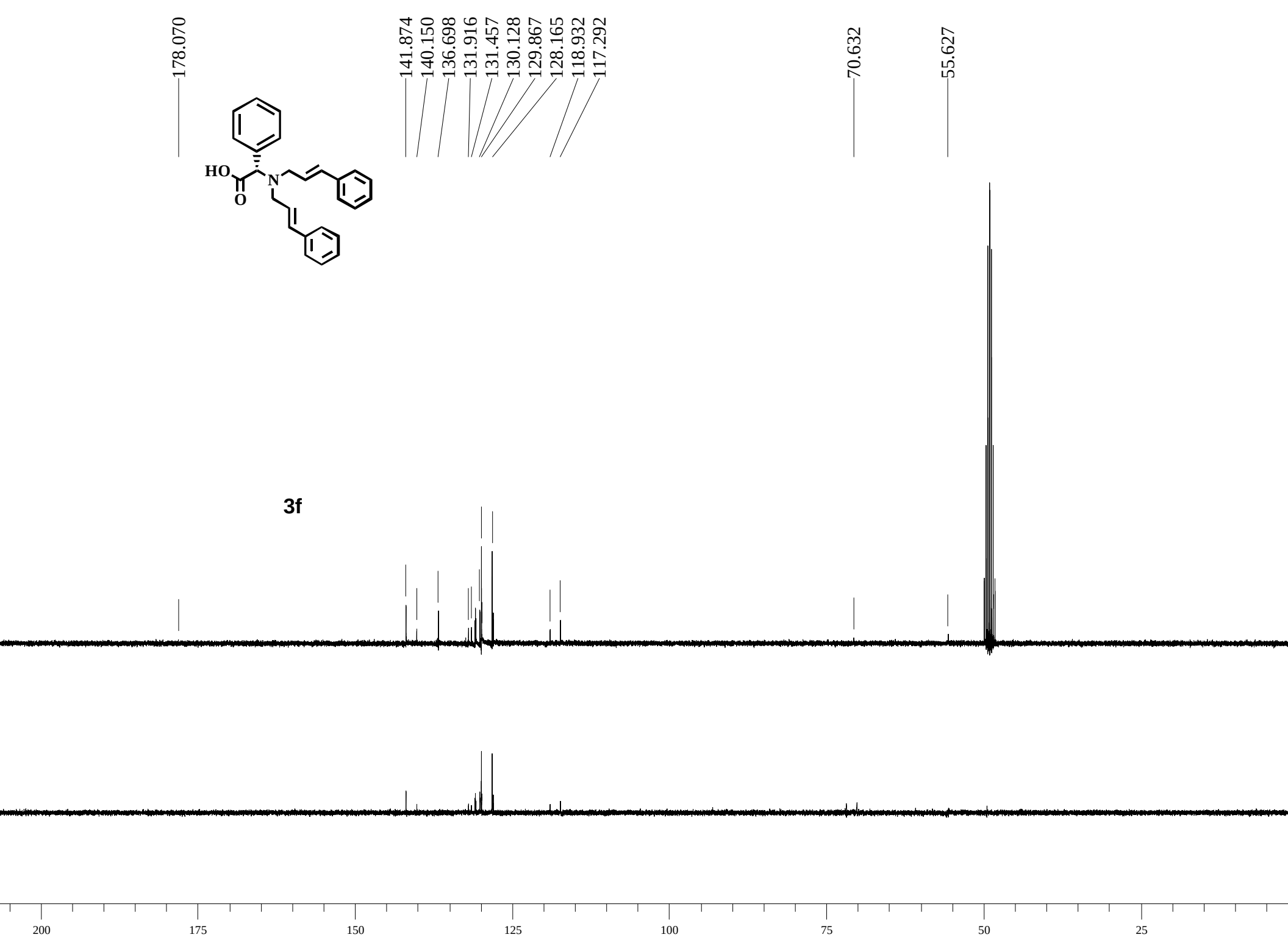


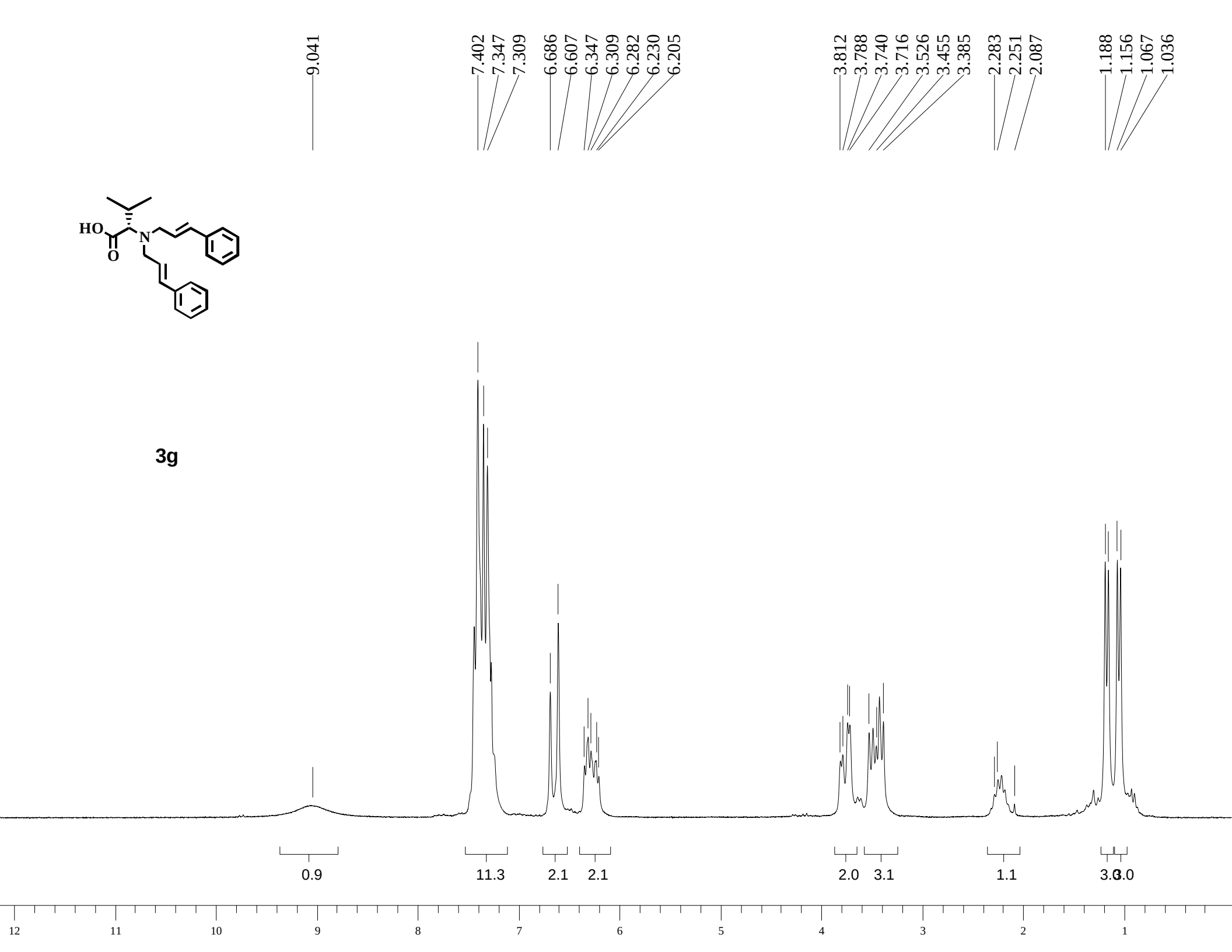

**3e**

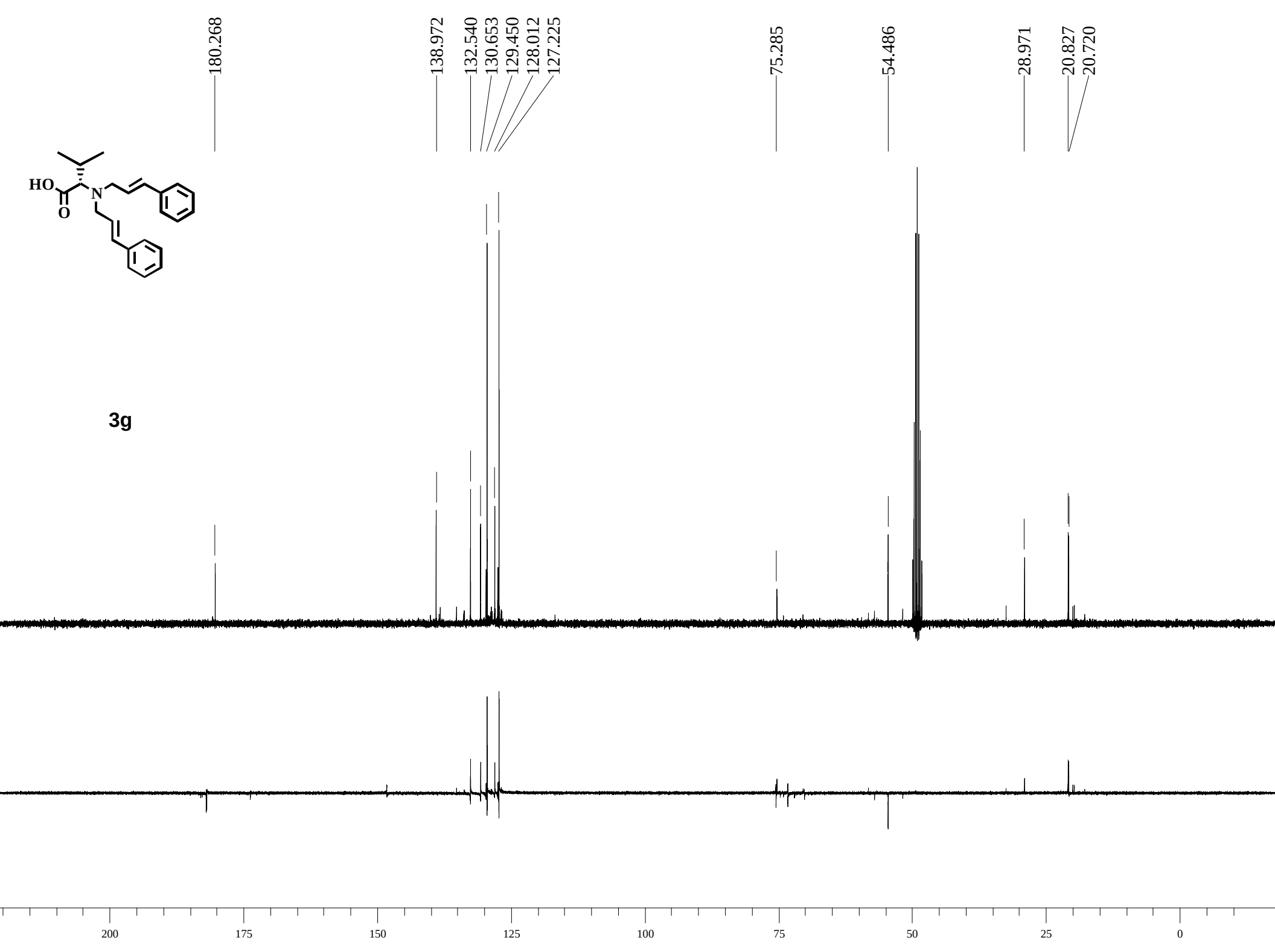
170.690
128.931
125.832
57.563
55.548

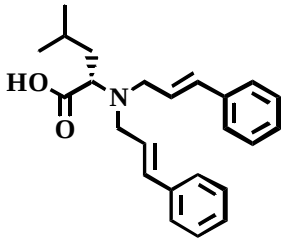
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


7.682
7.554
7.483
7.382
7.353
6.836
6.757
6.406
6.366
6.328
6.249
5.206
4.099
4.045
3.991
3.888
3.806
3.746
HO
O
N
3f
16.7
1.8
1.9
0.8
4.0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


178.070
141.874
140.150
136.698
131.916
131.457
130.128
129.867
128.165
118.932
117.292
70.632
55.627
HO
O
N
3f
200
175
150
125
100
75
50
25


9.041
7.402
7.347
7.309
6.686
6.607
6.347
6.309
6.282
6.230
6.205
3.812
3.788
3.740
3.716
3.526
3.455
3.385
2.283
2.251
2.087
1.188
1.156
1.067
1.036
HO
O
N
3g
0.9
11.3
2.1
2.1
2.0
3.1
1.1
3.0
12
11
10
9
8
7
6
5
4
3
2
1


180.268
138.972
132.540
130.653
129.450
128.012
127.225
75.285
54.486
28.971
20.827
20.720
HO
O
N
3g
200
175
150
125
100
75
50
25
0



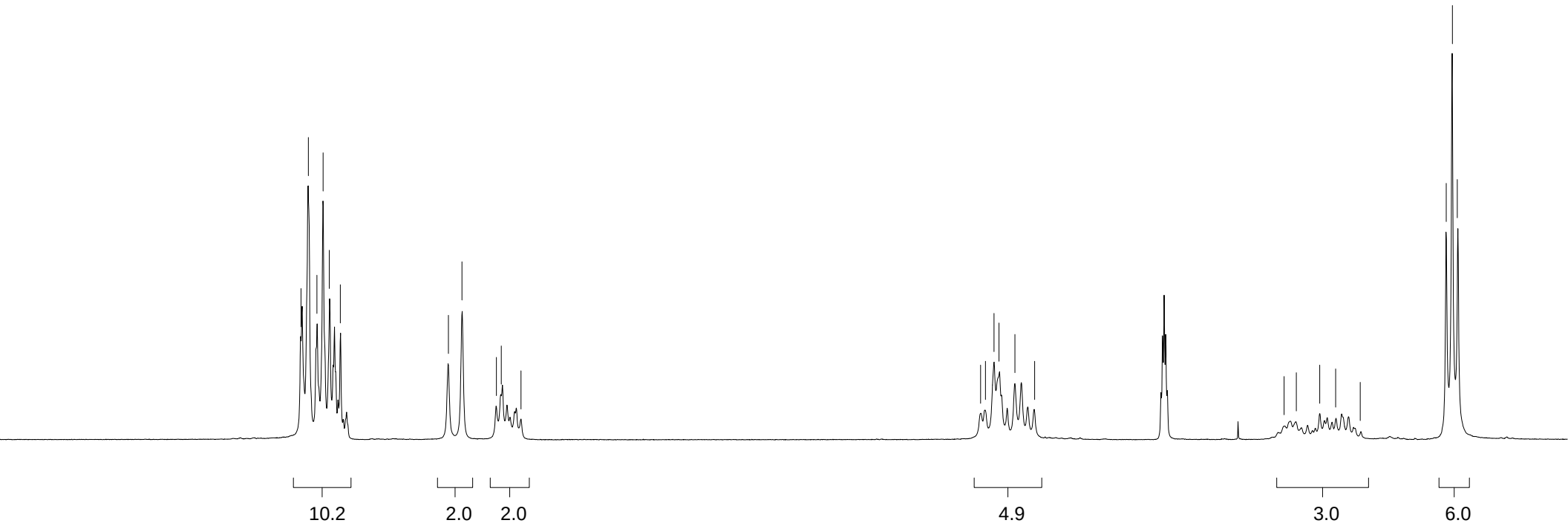

7.422 7.379 7.328 7.295 7.257 7.194 6.580 6.500 6.306 6.278 6.163

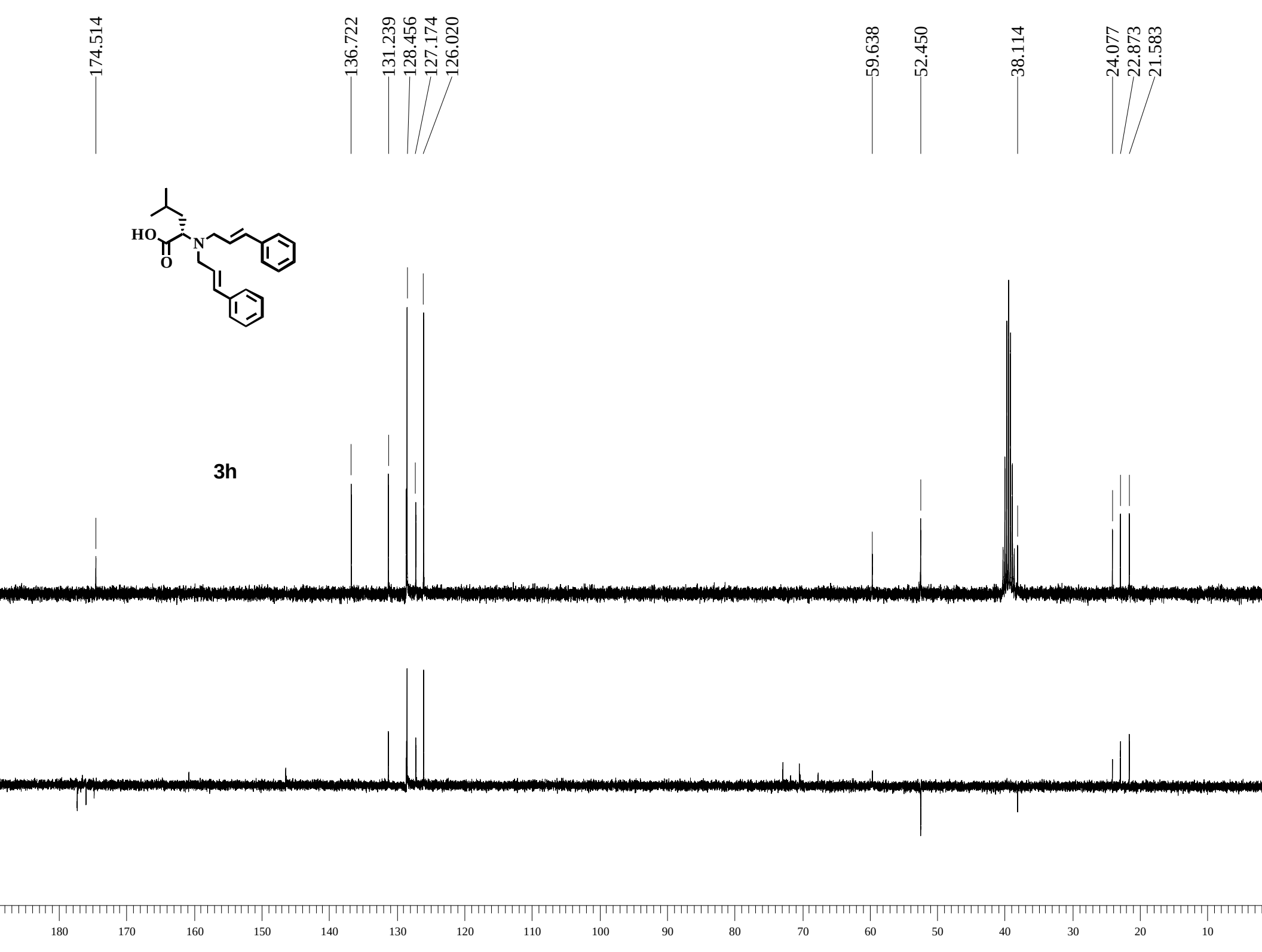
3.537 3.512 3.461 3.430 3.342 3.232

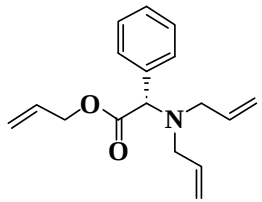
1.801 1.736 1.601 1.508 1.366

0.879 0.845 0.812

**3h**

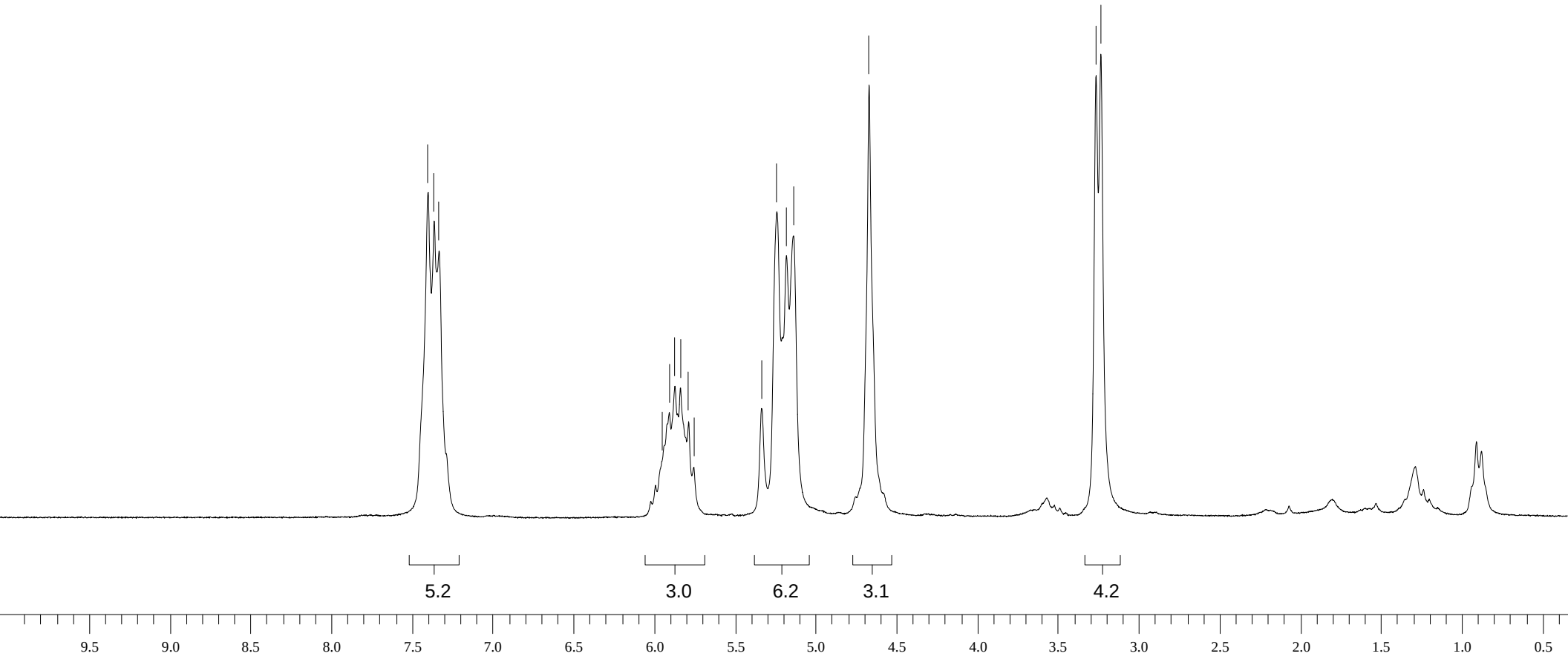


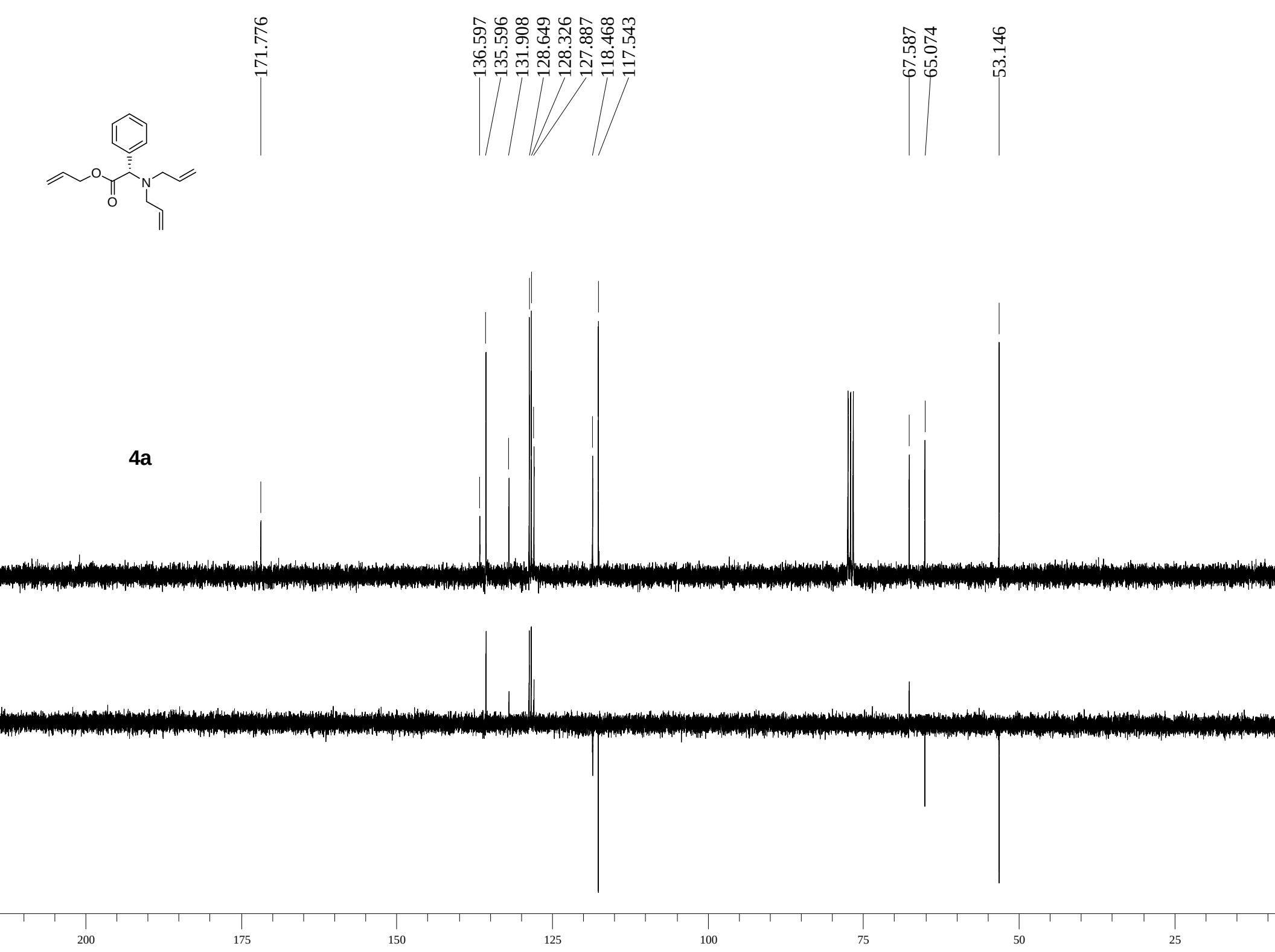

174.514
136.722
131.239
128.456
127.174
126.020
59.638
52.450
38.114
24.077
22.873
21.583
HO
O
N
3h
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

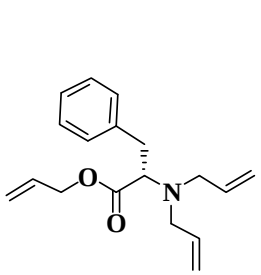



7.399
7.362
7.331
5.952
5.905
5.870
5.835
5.786
5.753
5.334
5.240
5.181
5.137
4.669
3.263
3.234

**4a**

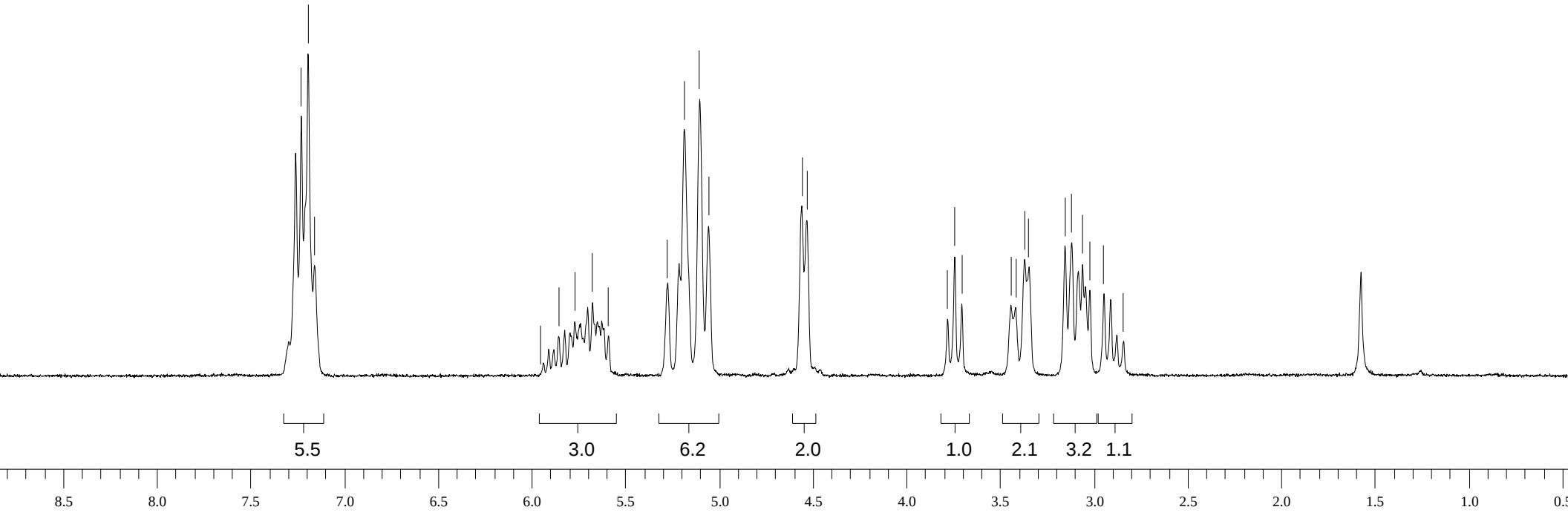


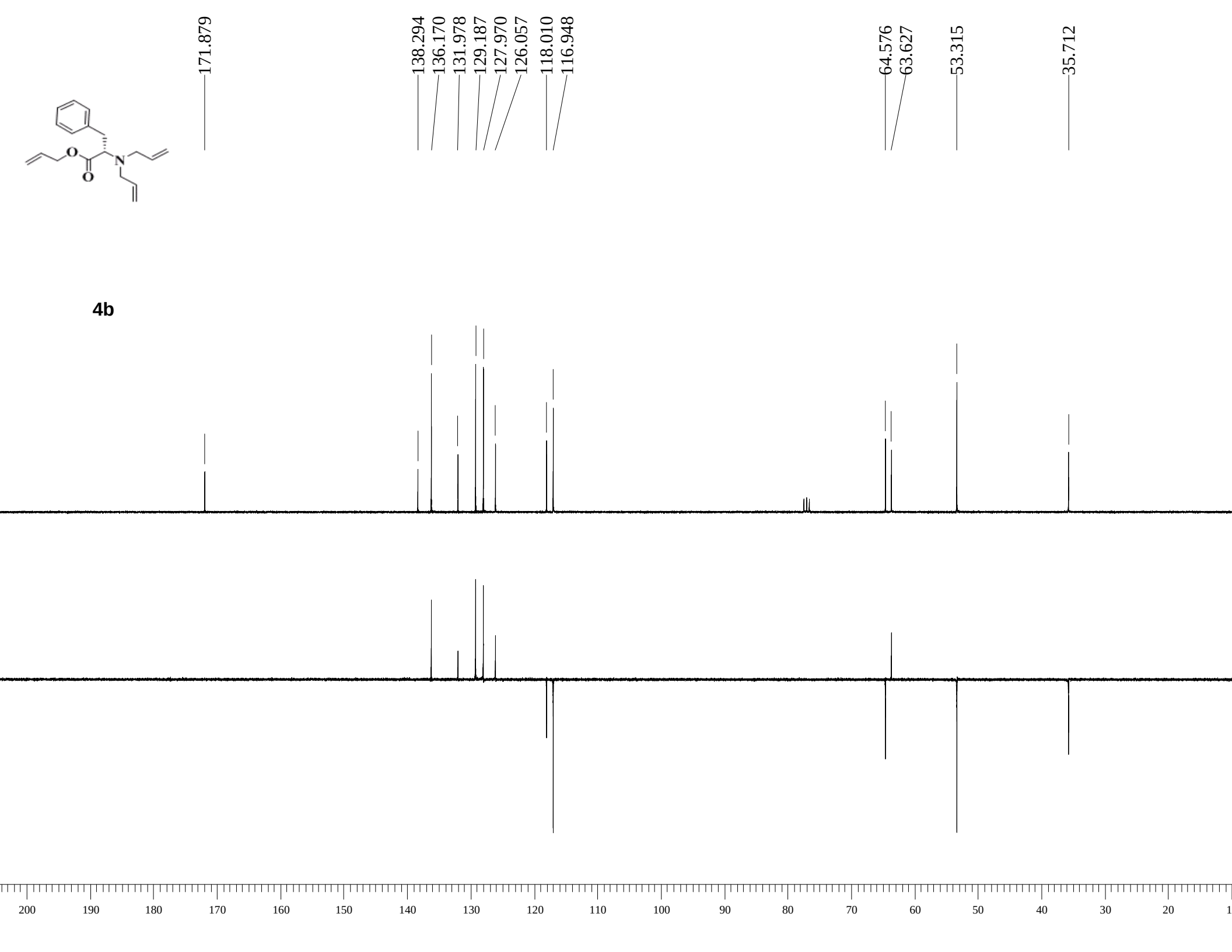

171.776
136.597
135.596
131.908
128.649
128.326
127.887
118.468
117.543
67.587
65.074
53.146
4a
O
O
N
200
175
150
125
100
75
50
25




7.229 7.192 7.158 5.953 5.856 5.770 5.675 5.589 5.278 5.185 5.103 5.055 4.558 4.530 3.780 3.742 3.704 3.442 3.417 3.369 3.345 3.153 3.117 3.060 3.020 2.945 2.841

**4b**




171.879
138.294
136.170
131.978
129.187
127.970
126.057
118.010
116.948
64.576
63.627
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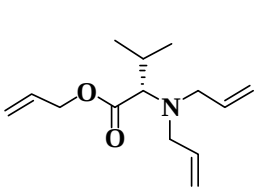
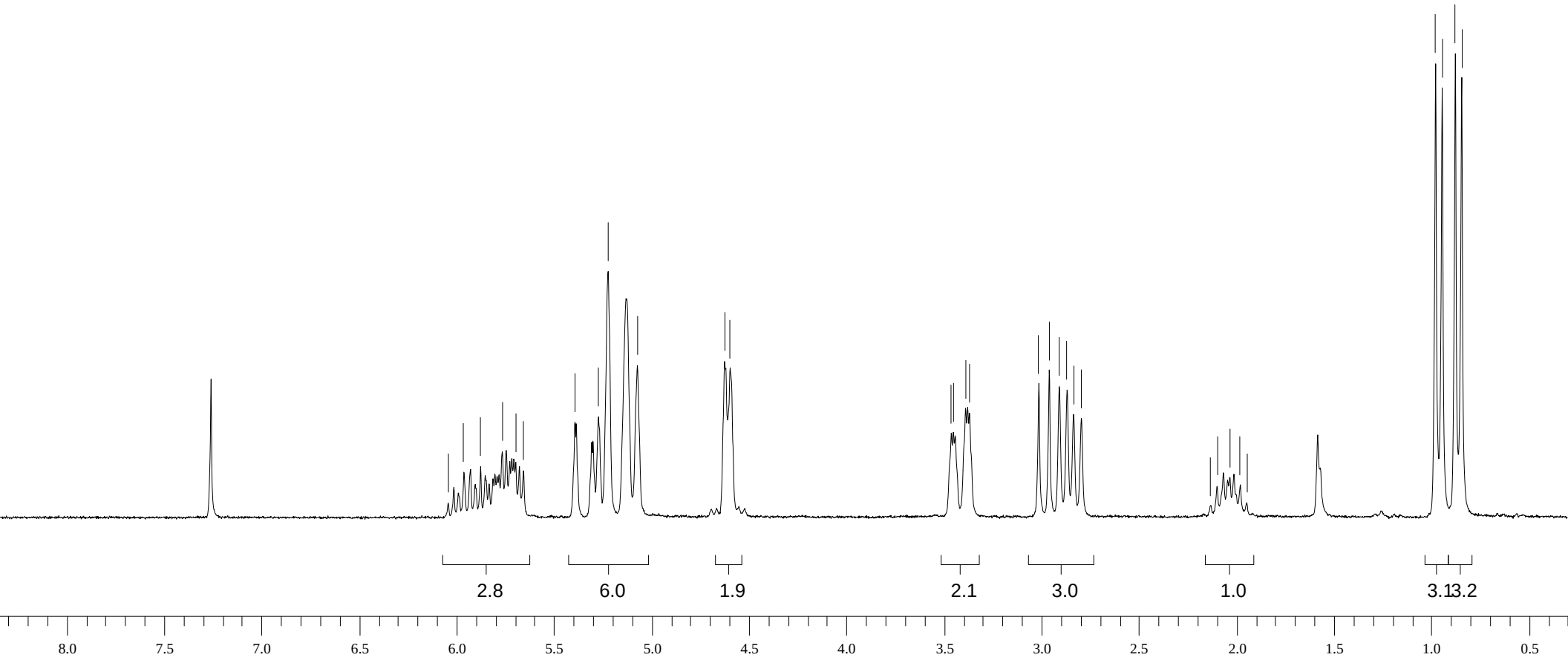
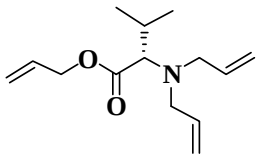
35.712
4b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20




6.043 5.962 5.876 5.764 5.695 5.656 5.391 5.271 5.221 5.072 4.625 4.596 3.463 3.452 3.389 3.369 3.013 2.960 2.908 2.868 2.835 2.795 2.131 2.098 2.032 1.980 1.947 0.978 0.945 0.877 0.844

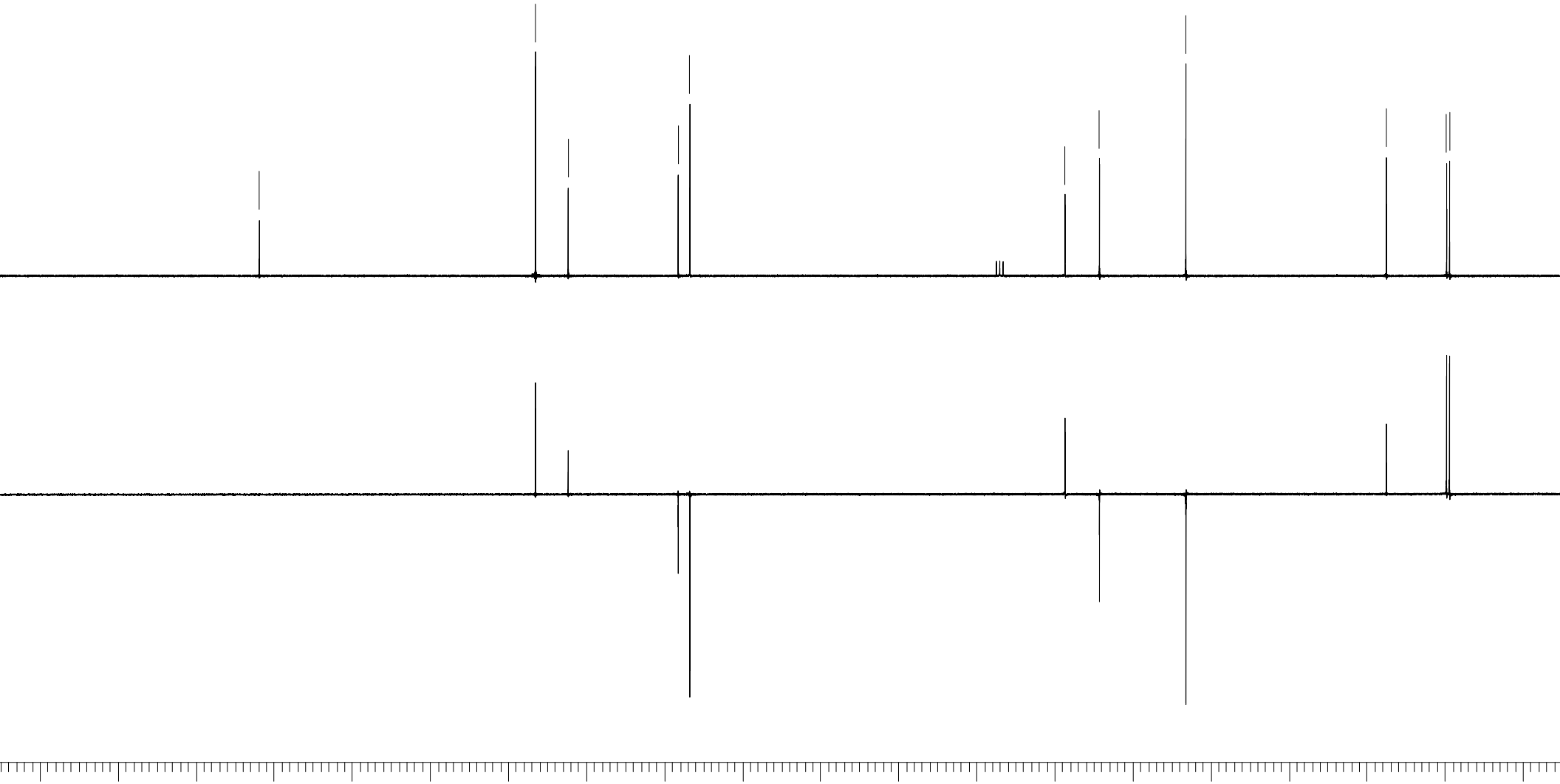
**4c**



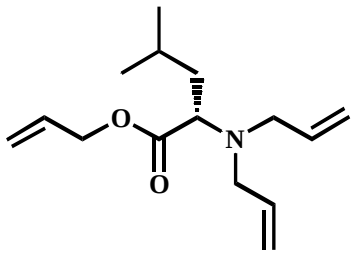



171.850
136.473
132.281
118.186
116.694
68.636
64.228
53.155
27.472
19.751
19.374

**4c**



200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10




6.001 5.914 5.832 5.783 5.671 5.375 5.282 5.214 5.125 5.068 4.604 4.576

3.574 3.536 3.497 3.410 3.393 3.336 3.315 3.090

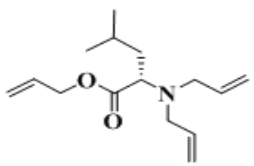
1.780 1.716 1.649 1.565 1.528

0.917 0.886 0.855

**4d**

3.0 6.2 2.0 1.1 2.1 2.1 3.7 6.5

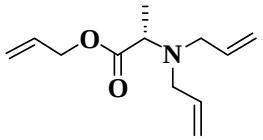
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0



172.996
136.606
132.228
117.945
116.653
64.380
59.669
53.249
38.542
24.420
22.853
21.753

**4d**

200
175
150
125
100
75
50
25
0



6.024 5.944 5.859 5.789 5.737 5.705 5.364 5.224 5.130 5.076 4.609 4.582

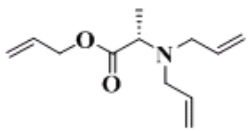
3.679 3.644 3.607 3.572 3.333 3.260 3.189 3.082

1.298 1.263

**4e**

2.9 6.0 2.0 1.0 4.1 3.1

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0



173.032
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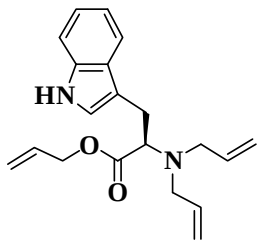
132.033
117.794
116.598
64.415
56.906
53.194
14.694

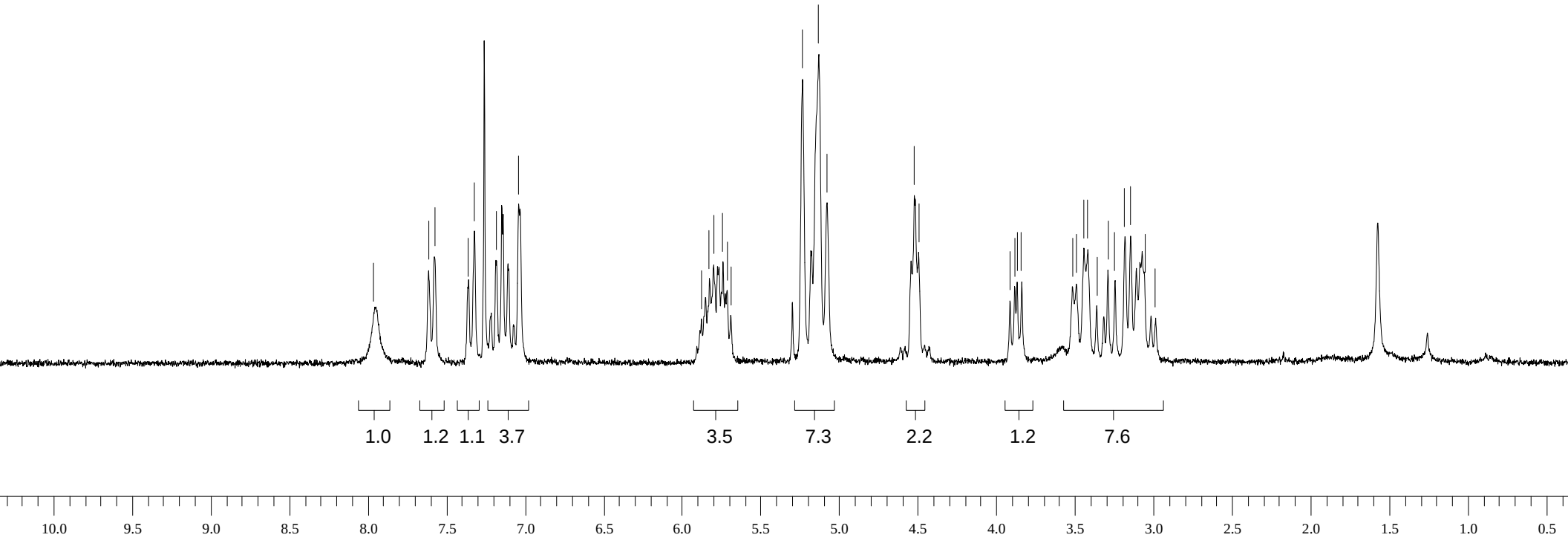
**4e**

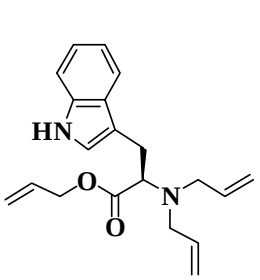
200
175
150
125
100
75
50
25
0




7.960 7.611 7.575 7.362 7.321 7.183 7.039 5.876 5.825 5.797 5.739 5.711 5.689 5.233 5.128 5.077 4.521 4.494 3.912 3.883 3.867 3.838 3.515 3.490 3.442 3.417 3.361 3.289 3.243 3.181 3.145 3.058 2.986

**4f**



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122.741
121.715
119.124
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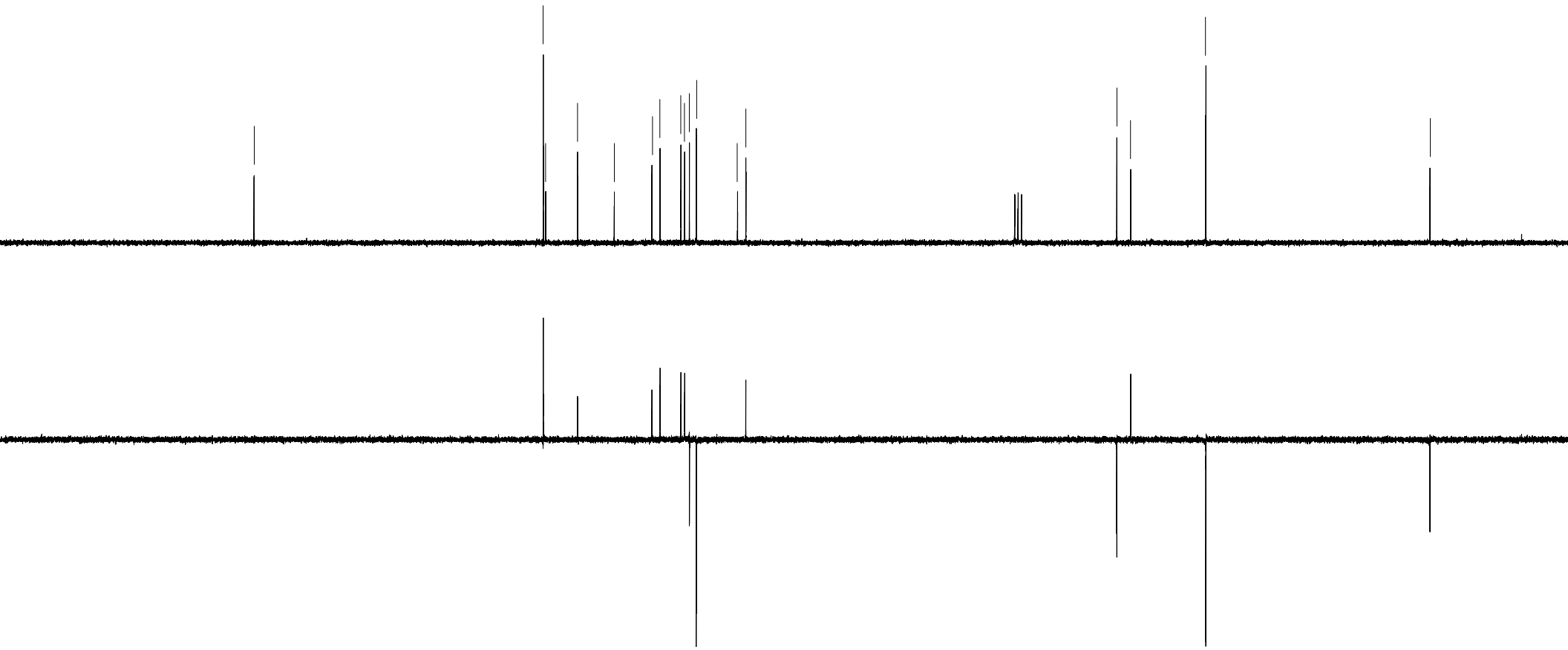
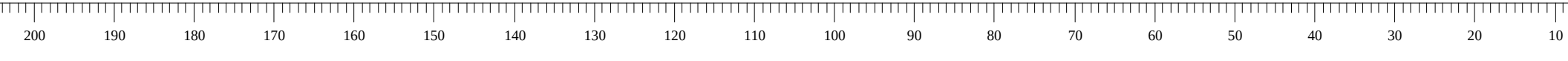
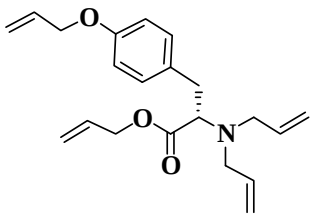
118.058
117.192
112.047
111.005
64.667
62.941
53.545
25.560

**4f**

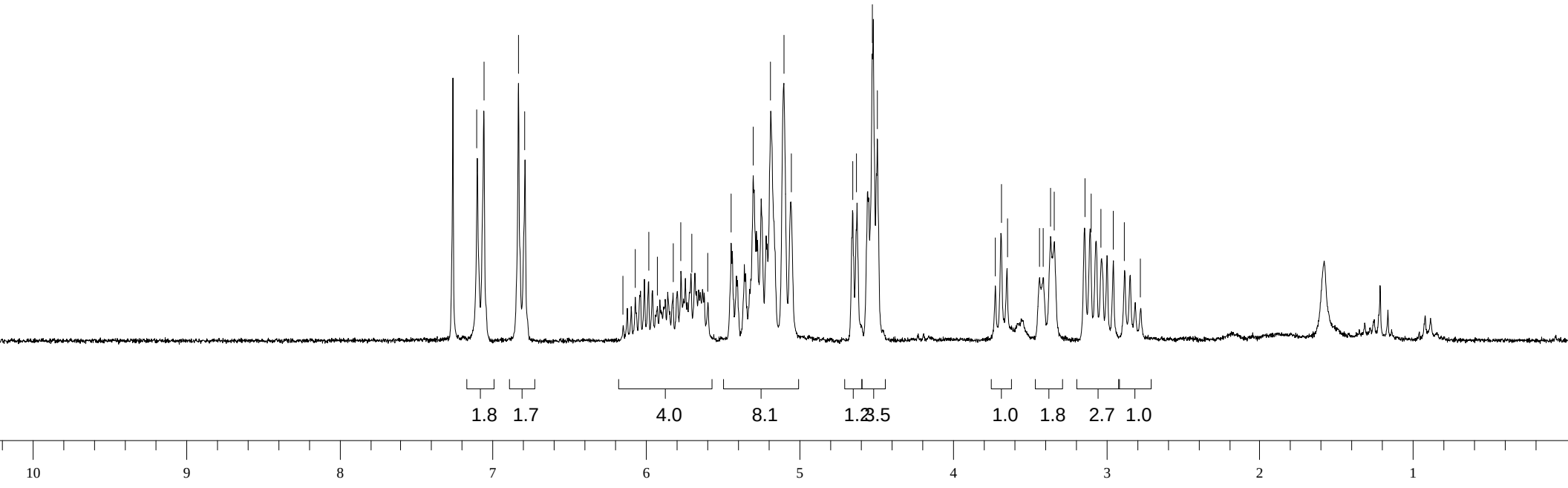


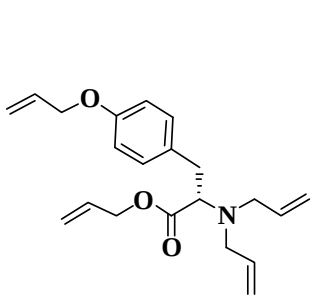




7.100 7.057 6.830 6.789 6.148 6.070 5.982 5.926 5.823 5.772 5.706 5.596 5.445 5.300 5.186 5.101 5.055 4.653 4.624 4.525 4.492 3.722 3.686 3.645 3.433 3.410 3.362 3.336 3.141 3.104 3.029 2.952 2.879 2.773

**4g**





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157.039
136.257
133.373
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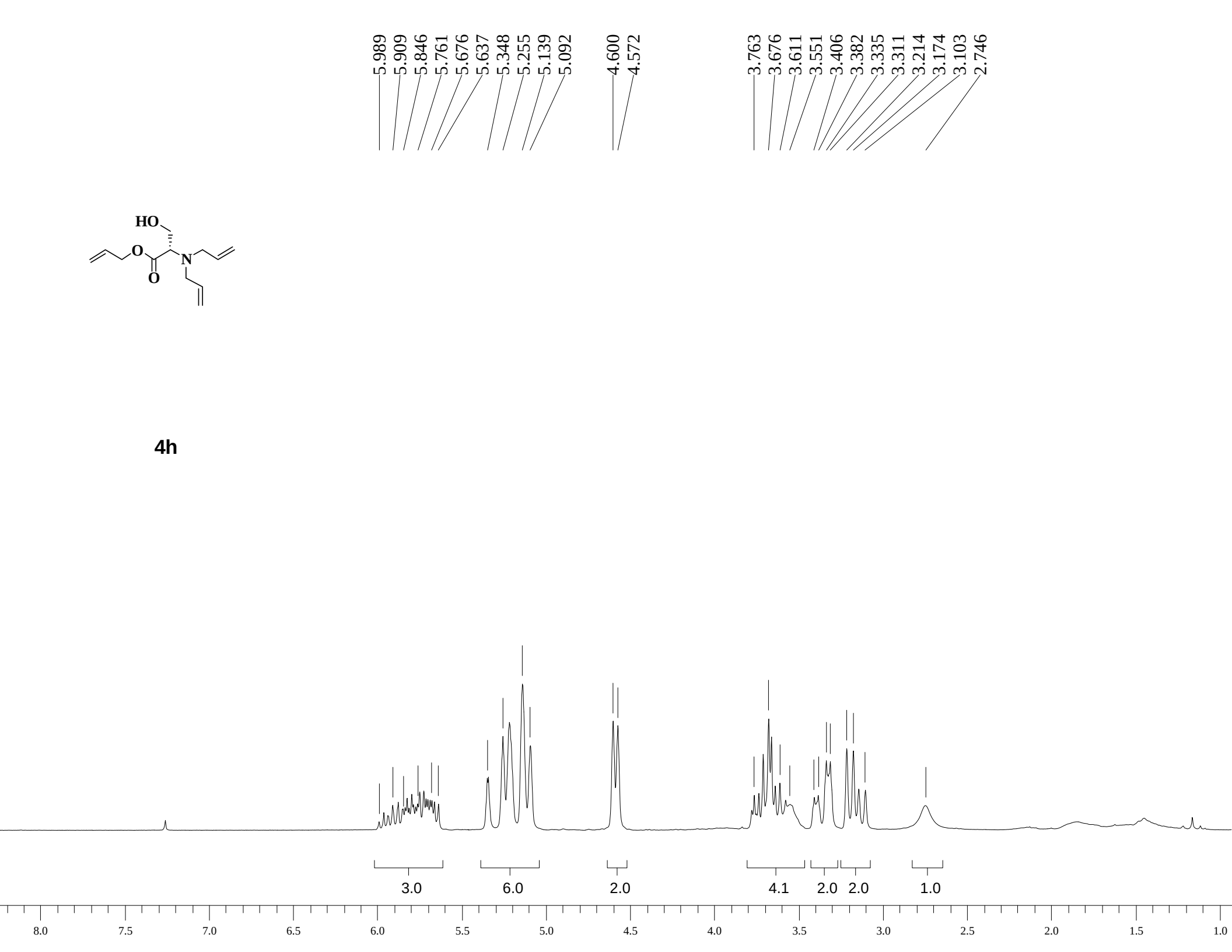
130.198
118.139
117.397
117.058
114.371
68.704
64.684
63.950
53.411
34.934

**4g**

200
175
150
125
100
75
50
25
0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3.763
3.676
3.611
3.551
3.406
3.382
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3.311
3.214
3.174
3.103
2.746
HO
O
O
N
4h
3.0
6.0
2.0
4.1
2.0
2.0
1.0
8.0
7.5
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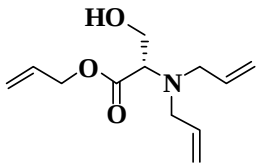
1.5
1.0


HO
O
O
N

**4h**


170.803
135.725
131.720
118.549
117.828
64.960
62.458
58.935
53.559
200
175
150
125
100
75
50
25
0