Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Photoinduced synthesis of allylic sulfones using potassium metabisulfite as the source of sulfur dioxide

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Supporting Information

1. General experimental methods (S2).

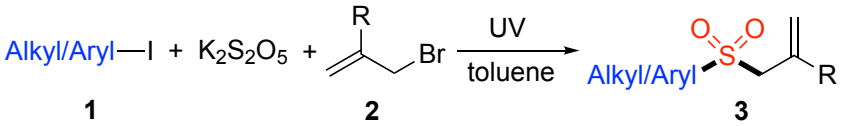
2. General experimental procedure and characterization data (S2-S11).

3. ^{1}H and ^{13}C NMR spectra of compounds **3** and **6** (S11-S64).

General experimental methods:

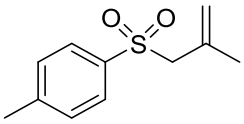
Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63μm, standard grade). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25–35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument.

*General experimental procedure for the reaction of aryl/alkylic halides **1**, sulfur dioxide, and allylic bromides **2**.*



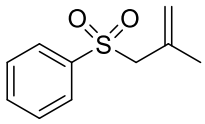
1 **2** **3**

In a quartz tube, aryl/alkyl halide 1 (0.4 mmol) was added to a mixture of $K_2S_2O_5$ (1.2 mmol) and allylic bromide 2 (1.0 mmol) in toluene (4.0 mL) under N_2 atmosphere. The mixture, placed around the mercury lamp (purchased from Yuming, Shanghai) with a distance of 10 centimeters, was stirred under UV irradiation (0.67 W cm^{-1}) at room temperature. After 12 hours, the solvent was evaporated and the residue was purified directly by flash column chromatography (*n*-hexane/ethyl acetate = 16:1-8:1) to give the corresponding product 3.



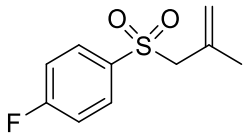
1-Methyl-4-((2-methylallyl)sulfonyl)benzene (**3a**) [1]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.75 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.02 (s, 1H), 4.69 (s, 1H), 3.75 (s, 2H), 2.44 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.5, 135.4, 133.4, 129.5, 128.4, 120.5, 64.4, 22.6, 21.5.



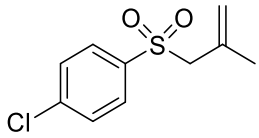
((2-Methylallyl)sulfonyl)benzene (**3b**) [2]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.89 (d, *J* = 7.5 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 5.04-5.03 (m, 1H), 4.69 (s, 1H), 3.78 (s, 2H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 138.3, 133.6, 133.3, 128.9, 128.4, 120.7, 64.3, 22.6.



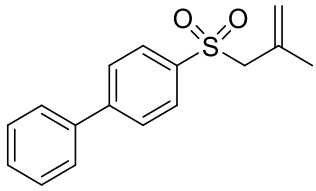
1-Fluoro-4-((2-methylallyl)sulfonyl)benzene (**3c**) [3]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.92 – 7.88 (m, 2H), 7.28 – 7.20 (m, 2H), 5.05-5.04 (m, 1H), 4.68 (s, 1H), 3.77 (s, 2H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.7 (d, $^1J_{CF}$ = 256.2 Hz), 134.2, 133.3, 131.3 (d, $^3J_{CF}$ = 9.6 Hz), 120.9, 116.2 (d, $^3J_{CF}$ = 22.6), 64.5, 22.6. ^{19}F NMR (276 MHz, $CDCl_3$): δ (ppm) 103.89-103.96 (m).



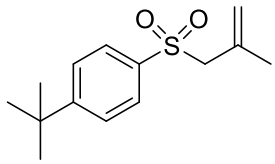
1-Chloro-4-((2-methylallyl)sulfonyl)benzene (**3d**)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.83 – 7.80 (m, 2H), 7.55 – 7.52 (m, 2H), 5.06 – 5.05 (m, 1H), 4.68 (s, 1H), 3.77 (s, 2H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 140.3, 136.6, 133.1, 129.9, 129.2, 121.0, 64.4, 22.6. HRMS (ESI) calcd for $C_{10}H_{15}ClNO_2S^+$: 248.0507 ($M+NH_4^+$), found: 248.0508.



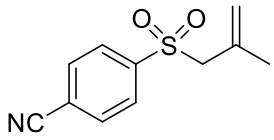
4-((2-Methylallyl)sulfonyl)-1,1'-biphenyl (**3e**)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.64 – 7.61 (m, 2H), 7.51 – 7.47 (m, 2H), 7.45 – 7.41 (m, 1H), 5.13 – 4.97 (m, 1H), 4.74 (s, 1H), 3.81 (s, 2H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 146.5, 139.0, 136.9, 133.4, 129.0, 129.0, 128.6, 127.5, 127.3, 120.8, 64.5, 22.7. HRMS (ESI) calcd for $C_{16}H_{20}NO_2S^+$: 290.1209 ($M+NH_4^+$), found: 290.1229.



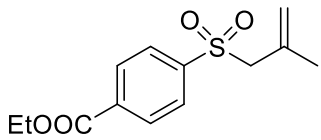
1-(*tert*-Butyl)-4-((2-methylallyl)sulfonyl)benzene (**3f**)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 5.05 (m, 1H), 4.74 (s, 1H), 3.76 (s, 2H), 1.87 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 157.5, 135.5, 133.3, 128.2, 125.9, 120.6, 64.4, 35.2, 31.0, 22.7. HRMS (ESI) calcd for $C_{14}H_{21}O_2S^+$: 253.1257 ($M+H^+$), found: 253.1257.



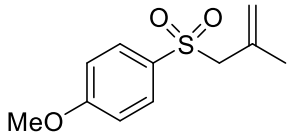
4-((2-Methylallyl)sulfonyl)benzonitrile (**3g**)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.01 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 5.06 (s, 1H), 4.66 (s, 1H), 3.81 (s, 2H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 142.2, 132.8, 132.7, 129.3, 121.5, 117.5, 117.1, 64.3, 22.6. HRMS (ESI) calcd for $C_{11}H_{15}N_2O_2S^+$: 239.0849 ($M+NH_4^+$), found: 239.0817.



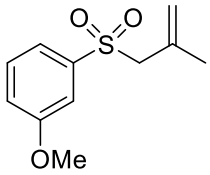
Ethyl 4-((2-methylallyl)sulfonyl)benzoate (**3h**)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.22 – 8.20 (m, 2H), 7.97 – 7.95 (m, 2H), 5.04 – 5.03 (m, 1H), 4.65 (s, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 2H), 1.87 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.0, 141.9, 135.2, 133.1, 130.0, 128.6, 121.1, 64.4, 61.8, 22.6, 14.2. HRMS (ESI) calcd for $C_{13}H_{17}O_4S^+$: 269.0842 ($M+H^+$), found: 269.0844.



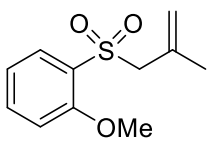
1-Methoxy-4-((2-methylallyl)sulfonyl)benzene (**3i**) [3]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.81-7.79 (m, 2H), 7.01-6.99 (m, 2H), 5.04-5.03 (m, 1H), 4.69 (s, 1H), 3.88 (s, 3H), 3.75 (s, 2H), 1.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 163.6, 133.6, 130.6, 129.9, 120.5, 114.1, 64.6, 55.6, 22.7.



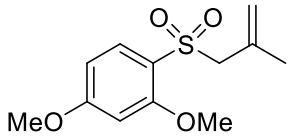
1-Methoxy-3-((2-methylallyl)sulfonyl)benzene (**3j**)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.46-7.38 (m, 2H), 7.38 (s, 1H), 7.17-7.15 (m, 1H), 5.07 (s, 1H), 4.75 (s, 1H), 3.87 (s, 3H), 3.78 (s, 2H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 159.8, 139.6, 133.3, 130.0, 120.7, 120.6, 120.1, 112.9, 64.3, 55.7, 22.7. HRMS (ESI) calcd for $C_{11}H_{15}O_3S^+$: 227.0736 ($M+H^+$), found: 227.0737.



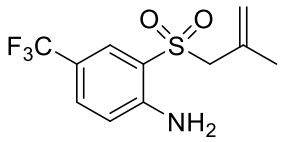
1-Methoxy-2-((2-methylallyl)sulfonyl)benzene (**3k**)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.91 (d, *J* = 7.8 Hz, 1H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 4.98 (s, 1H), 4.80 (s, 1H), 4.05 (s, 2H), 4.00 (s, 3H), 1.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 157.2, 135.5, 133.7, 130.8, 126.3, 120.6, 120.0, 112.0, 62.2, 56.2, 22.6. HRMS (ESI) calcd for $C_{11}H_{15}O_3S^+$: 227.0736 ($M+H^+$), found: 227.0742.



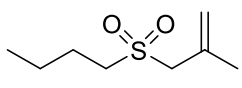
2,4-Dimethoxy-1-((2-methylallyl)sulfonyl)benzene (**3l**)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)7.82 (d, *J* = 8.7 Hz, 1H), 6.56 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.52 (d, *J* = 2.1 Hz, 1H), 4.98 – 4.97 (m, 1H), 4.79 (s, 1H), 4.00 (s, 2H), 3.96 (s, 3H), 3.87 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.4, 158.6, 133.9, 132.4, 119.6, 118.5, 104.5, 99.1, 62.3, 56.1, 55.6, 22.5. HRMS (ESI) calcd for $C_{12}H_{20}NO_4S^+$: 274.1108 ($M+NH_4^+$), found: 274.1136.



2-((2-Methylallyl)sulfonyl)-4-(trifluoromethyl)aniline (**3m**)

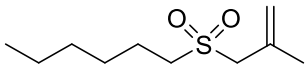
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.88 (s, 1H), 7.54 (dd, *J* = 8.6, 1.5 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 1H), 5.45 (s, 2H), 5.06 (s, 1H), 4.76 (s, 1H), 3.81 (s, 2H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 149.1, 132.8, 131.7 (q, $^3J_{CF}$ = 3.3 Hz), 128.7 (q, $^3J_{CF}$ = 4.1 Hz), 123.7 (d, $^1J_{CF}$ = 271.0 Hz), 121.1, 119.5 (q, $^2J_{CF}$ = 33.9 Hz), 118.9, 117.5, 62.0, 22.8. ^{19}F NMR (276 MHz, $CDCl_3$): δ (ppm) 61.77 (s). HRMS (ESI) calcd for $C_{11}H_{13}F_3NO_2S^+$: 280.0614 ($M+NH_4^+$), found: 280.0638.



1-((2-Methylallyl)sulfonyl)butane (**3n**)

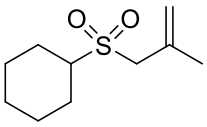
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.23-5.22 (m, 1H), 5.09 (s, 1H), 3.67 (s, 2H), 3.02 – 2.98 (m, 2H), 1.99 (s, 3H), 1.87-1.79 (m, 2H), 1.52-1.43 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 134.2, 120.2, 61.1, 50.9, 23.8, 22.6, 21.7, 13.5. HRMS (ESI) calcd for $C_8H_{17}O_2S^+$: 177.0944 ($M+H^+$), found: 177.0943.



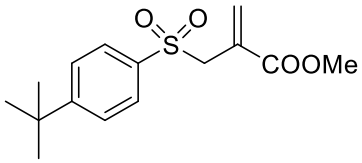
1-((2-Methylallyl)sulfonyl)hexane (**3o**)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.22 (s, 1H), 5.08 (s, 1H), 3.67 (s, 2H), 3.01-2.97 (m, 2H), 1.99 (s, 3H), 1.88-1.80 (m, 2H), 1.47-1.40 (m, 2H), 1.35-1.30 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 134.3, 120.2, 61.1, 51.2, 31.2, 28.1, 22.6, 22.2, 21.8, 13.9. HRMS (ESI) calcd for $C_{10}H_{21}O_2S^+$: 205.1257 ($M+H^+$), found: 205.1258.



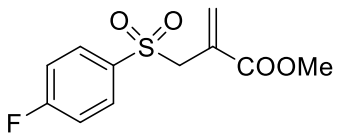
((2-Methylallyl)sulfonyl)cyclohexane (**3p**)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.32-5.17 (m, 1H), 5.08 (s, 1H), 3.64 (s, 2H), 3.02-2.94 (m, 1H), 2.18-2.15 (m, 2H), 1.99 (s, 3H), 1.95-1.92 (m, 2H), 1.72-1.70 (m, 1H), 1.62-1.53 (m, 2H), 1.35-1.20 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 133.9, 120.2, 59.5, 57.8, 25.0, 25.0, 22.9. HRMS (ESI) calcd for $C_{10}H_{19}O_2S^+$: 203.1100 ($M+H^+$), found: 203.1105.



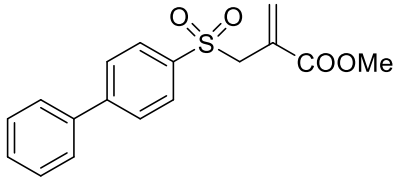
Methyl 2-(((4-(*tert*-butyl)phenyl)sulfonyl)methyl)acrylate (**3q**)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.77 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 6.51 (s, 1H), 5.93 (s, 1H), 4.14 (s, 2H), 3.55 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.2, 157.8, 135.3, 133.5, 128.9, 128.6, 126.0, 57.6, 52.2, 35.2, 31.0. HRMS (ESI) calcd for $C_{15}H_{21}O_4S^+$: 297.1155 ($M+H^+$), found: 297.1178.



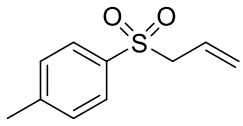
Methyl 2-(((4-fluorophenyl)sulfonyl)methyl)acrylate (**3r**)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.88 (dd, *J* = 8.5, 5.1 Hz, 2H), 7.22 (t, *J* = 8.5 Hz, 2H), 6.52 (s, 1H), 5.94 (s, 1H), 4.16 (s, 2H), 3.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.8 (d, $^{1}J_{CF}$ = 255.2 Hz), 165.1, 134.3, 133.7, 131.6 (d, $^{3}J_{CF}$ = 9.6 Hz), 128.7, 116.3 (d, $^{2}J_{CF}$ = 22.7 Hz), 57.6, 52.4. ^{19}F NMR (276 MHz, $CDCl_3$): δ (ppm) 102.98-103.04 (m). HRMS (ESI) calcd for $C_{11}H_{12}FO_4S^+$: 259.0435 ($M+H^+$), found: 259.0428.



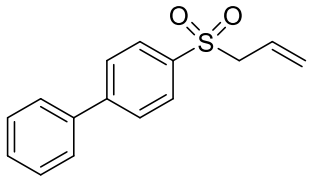
Methyl 2-(([1,1'-biphenyl]-4-ylsulfonyl)methyl)acrylate (**3s**)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 7.2 Hz,2H), 7.53-7.44 (m, 3H), 6.56 (s, 1H), 5.98 (s, 1H), 4.22 (s, 2H), 3.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.2, 146.7, 138.9, 136.7, 133.6, 129.2, 129.0, 128.8, 128.6, 127.5, 127.2, 57.6, 52.3. HRMS (ESI) calcd for $C_{17}H_{17}O_4S^+$: 317.0842 ($M+H^+$), found: 317.0852.



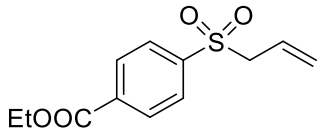
1-(Allylsulfonyl)-4-methylbenzene (**3t**)[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.76 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 5.85-5.75 (m, 1H), 5.34 (d, *J* = 10.1 Hz, 1H), 5.16 (d, *J* = 17.1 Hz, 1H), 3.80 (d, *J* = 7.4 Hz, 2H), 2.46 (s,3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.7, 135.3, 129.6, 128.4, 124.7, 124.5, 60.9, 21.6.



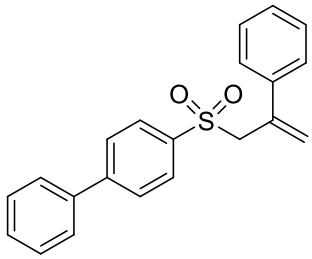
4-(Allylsulfonyl)-1,1'-biphenyl (**3u**)[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.95-1.93 (m, 2H), 7.77-7.74 (m, 2H), 7.63-7.66 (m, 2H), 7.51-7.41 (m, 3H), 5.89-5.79 (m, 1H), 5.37 (dd, *J* = 10.1, 0.7 Hz, 1H), 5.21 (dd, *J* = 17.1, 1.1 Hz, 1H), 3.86 (d, *J* = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 146.7, 139.1, 136.9, 129.1, 129.0, 128.7, 127.6, 127.4, 124.7, 124.7, 61.0.



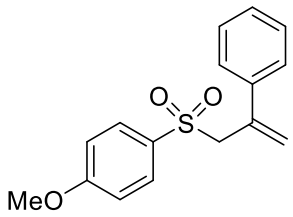
Ethyl 4-(allylsulfonyl)benzoate (**3v**)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.23-8.21 (m, 2H), 7.96-7.94 (m, 2H), 5.85-5.74 (m, 1H), 5.35 (dd, *J* = 10.2, 0.7 Hz, 1H), 5.14 (dd, *J* = 17.1, 1.0 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 3.85 (d, *J* = 7.4 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.0, 141.9, 135.3, 130.1, 128.6, 125.1, 124.3, 61.8, 60.8, 14.2. HRMS (ESI) calcd for $C_{12}H_{15}O_4S^+$: 255.0686 ($M+H^+$), found: 255.0678.



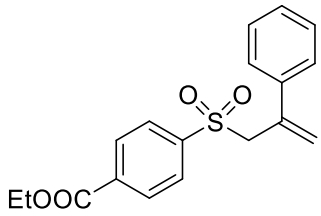
4-((2-Phenylallyl)sulfonyl)-1,1'-biphenyl (**3w**)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.8-7.82 (m, 2H), 7.61-7.55 (m, 4H), 7.52-7.42 (m, 3H), 7.29-7.25 (m, 2H), 7.25 – 7.21 (m, 3H), 5.64 (s, 1H), 5.32 (s, 1H), 4.34 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 146.5, 139.2, 138.8, 137.0, 136.6, 129.2, 129.0, 128.6, 128.4, 127.9, 127.5, 127.3, 126.2, 121.9, 62.3. HRMS (ESI) calcd for $C_{21}H_{19}O_2S^+$: 335.1100 ($M+H^+$), found: 335.1101.



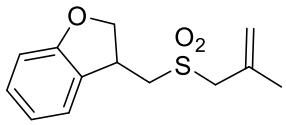
1-Methoxy-4-((2-phenylallyl)sulfonyl)benzene (**3x**)[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.68 (d, *J* = 8.8 Hz, 2H), 7.27-7.23 (m, 5H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.58 (s, 1H), 5.21 (s, 1H), 4.24 (s, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 163.6, 138.8, 136.7, 130.8, 129.9, 128.3, 127.9, 126.2, 121.6, 114.0, 62.2, 55.6.



Ethyl 4-((2-phenylallyl)sulfonyl)benzoate (**3y**)[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.07 (d, *J* = 8.3 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.27-7.22 (m, 5H), 5.59 (s, 1H), 5.21 (s, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 4.31 (s, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 164.9, 141.9, 138.4, 136.2, 135.0, 129.8, 128.7, 128.4, 128.1, 126.1, 122.1, 62.0, 61.7, 14.2.



3-(((2-Methylallyl)sulfonyl)methyl)-2,3-dihydrobenzofuran (**6**)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.18 (t, *J* = 7.7 Hz, 2H), 7.94-6.87 (m, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 5.27-5.24 (m, 1H), 5.10 (s, 1H), 4.81-4.73 (m, 1H), 4.57 (dd, *J* = 9.8, 6.0 Hz, 1H), 4.16-4.04 (m, 1H), 3.74 (q, *J* = 13.9 Hz, 2H), 3.43 (dd, *J* = 13.7, 3.0 Hz, 1H), 3.22 (dd, *J* = 13.7, 10.8 Hz, 1H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 159.7, 133.9, 129.3, 126.9, 124.2, 120.9, 120.9, 110.1, 75.9, 62.4, 54.7, 35.7, 22.5.

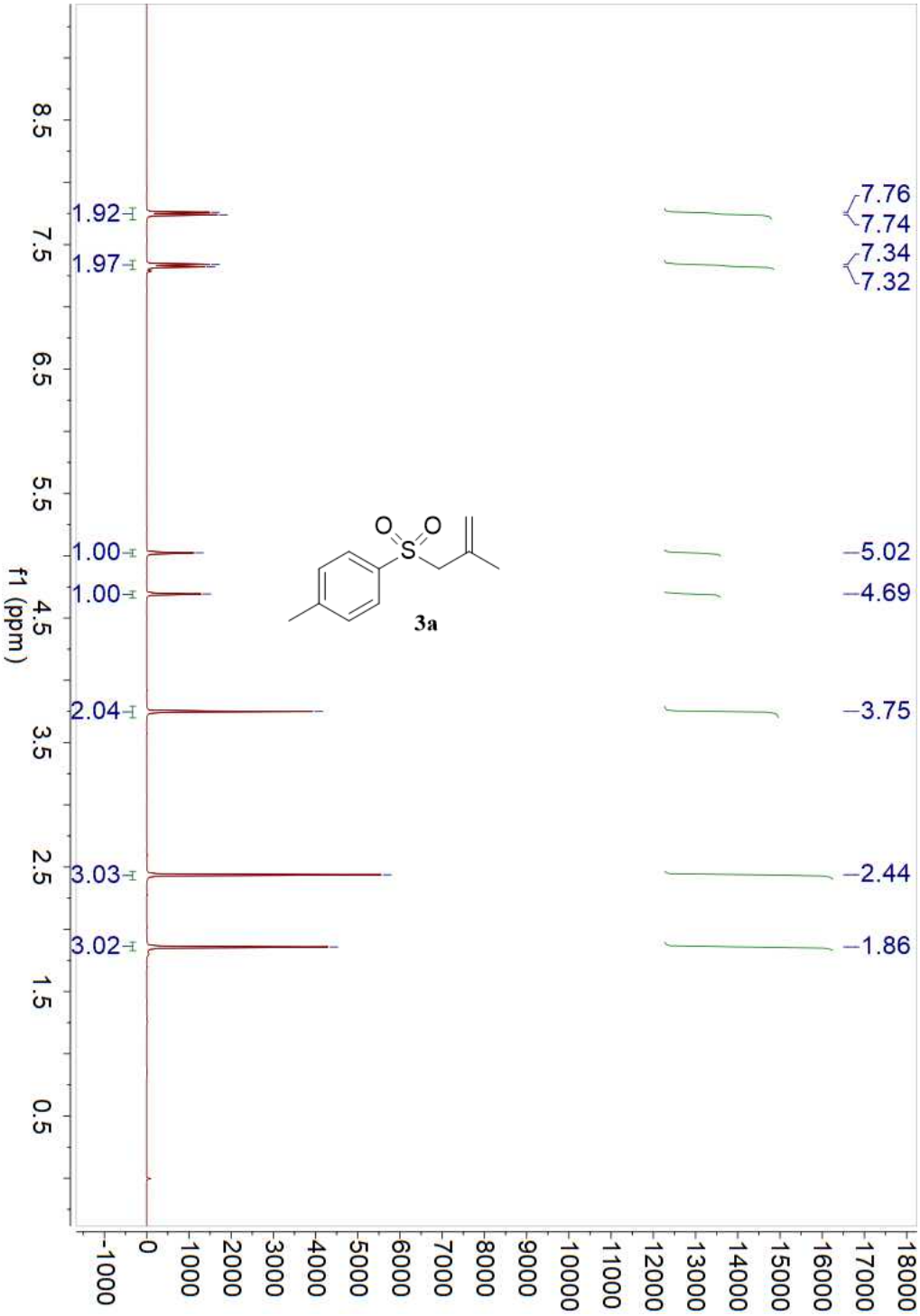
Reference:

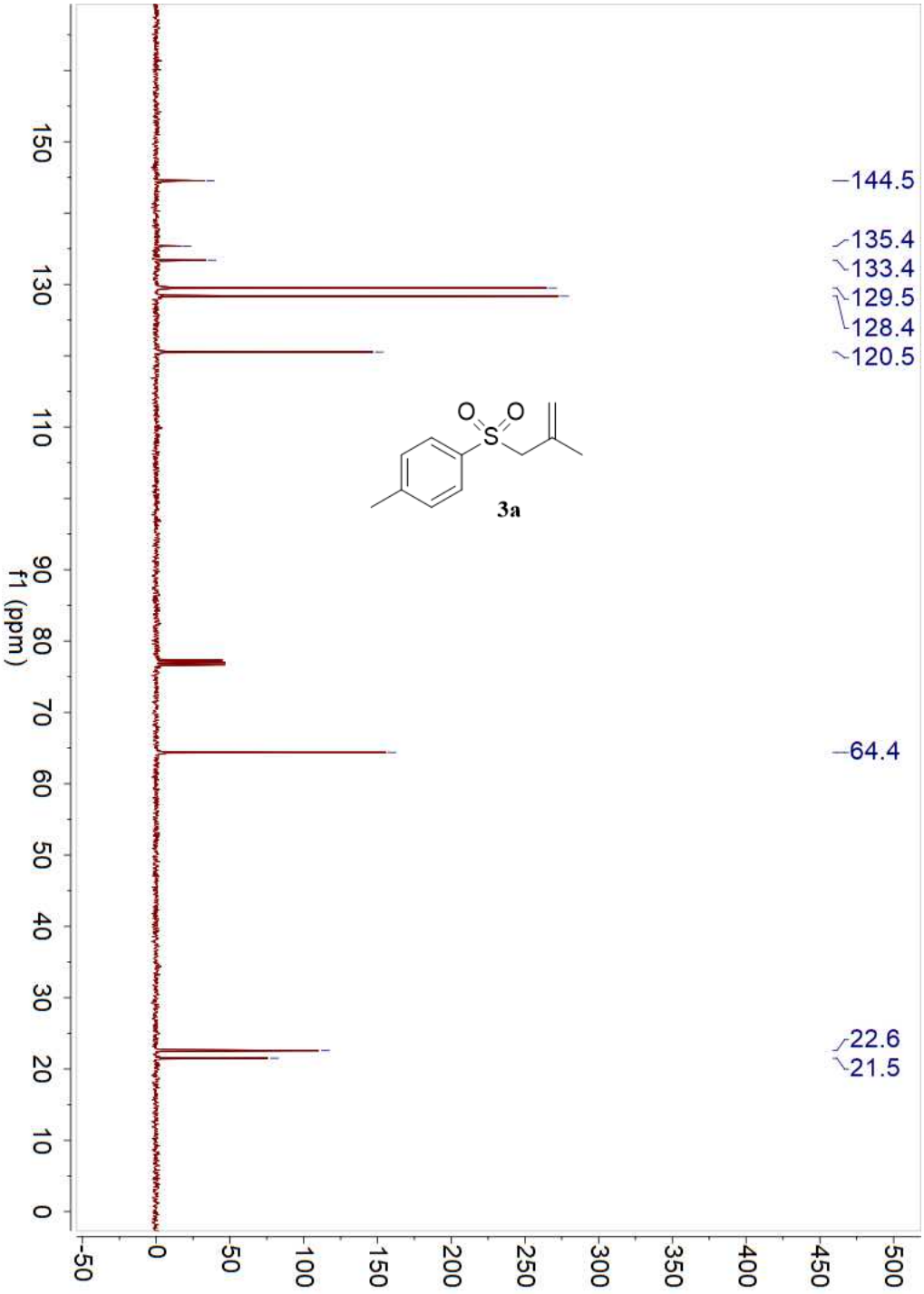
1. M.-H. Larraufie, R. Pellet, L. Fensterbank, J.-P. Goddard, E. Lacte, M. Malacria, C. Ollivier, *Angew. Chem. Int. Ed.* **2011**, *50*, 4463.

2. B. M. Trost, N. R. Schmuff, *J. Am. Chem. Soc.* **1985**, *107*, 396.

3. H. Zhu, Y. Shen, Q. Deng, J. Chen, T. Tu, *ACS Catal.* **2017**, *7*, 4655.

4. G. C. Tusi, M. Lautens, *Angew. Chem. Int. Ed.* **2010**, *49*, 8938.

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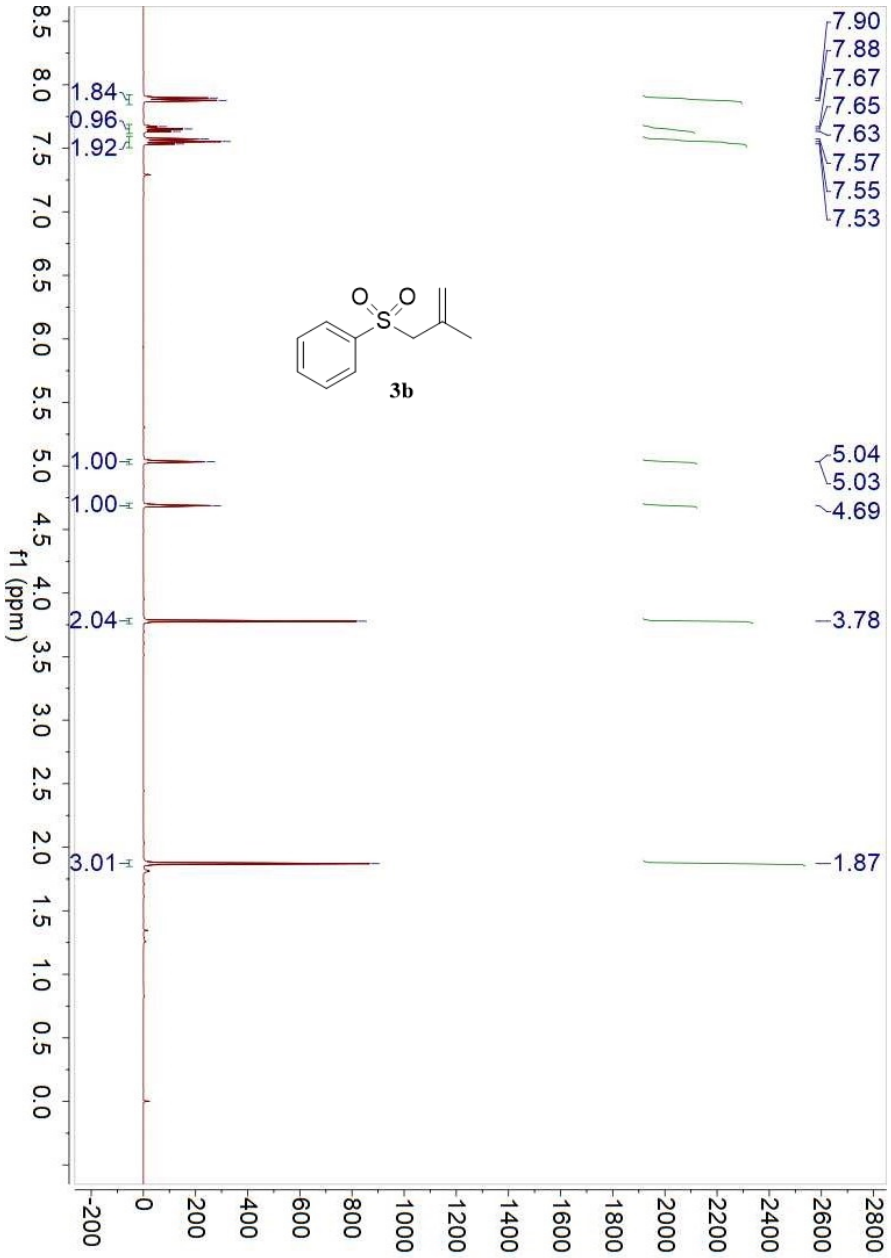
120.5
64.4
22.6
21.5
3a
f1 (ppm)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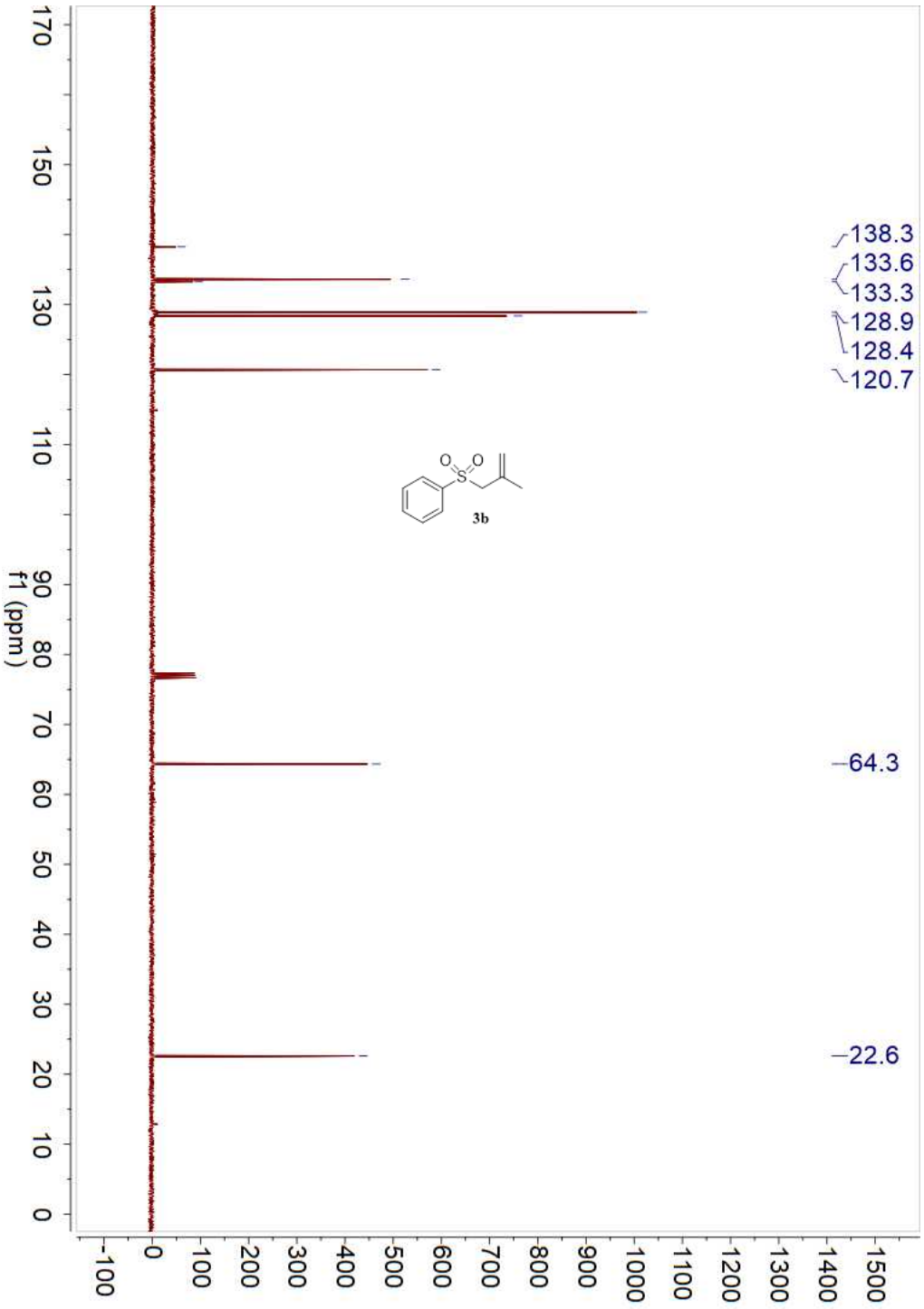
1.87
3b
f1 (ppm)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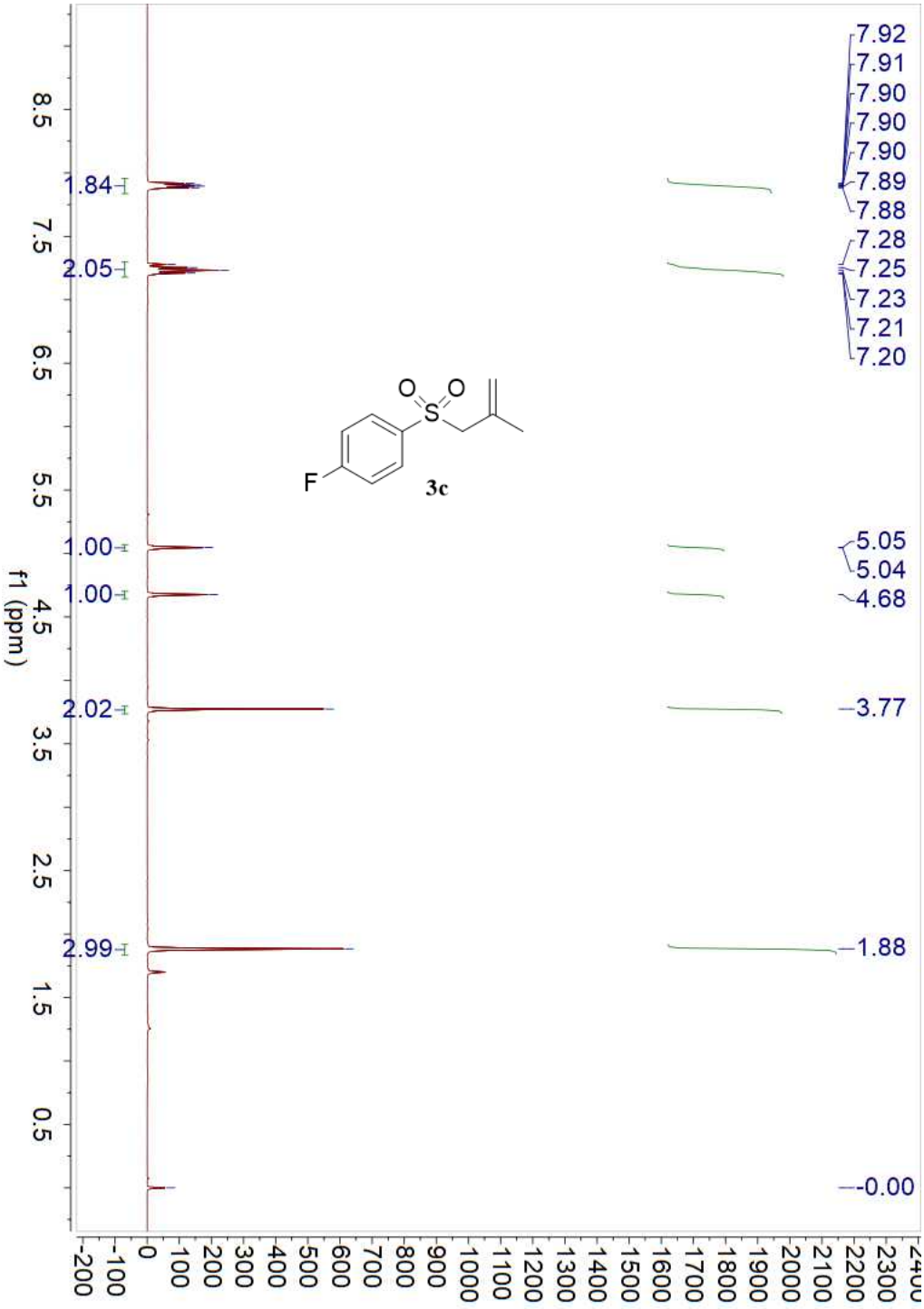
22.6
3b
f1 (ppm)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7.28
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7.20
5.05
5.04
4.68
3.77
1.88
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1.00
1.00
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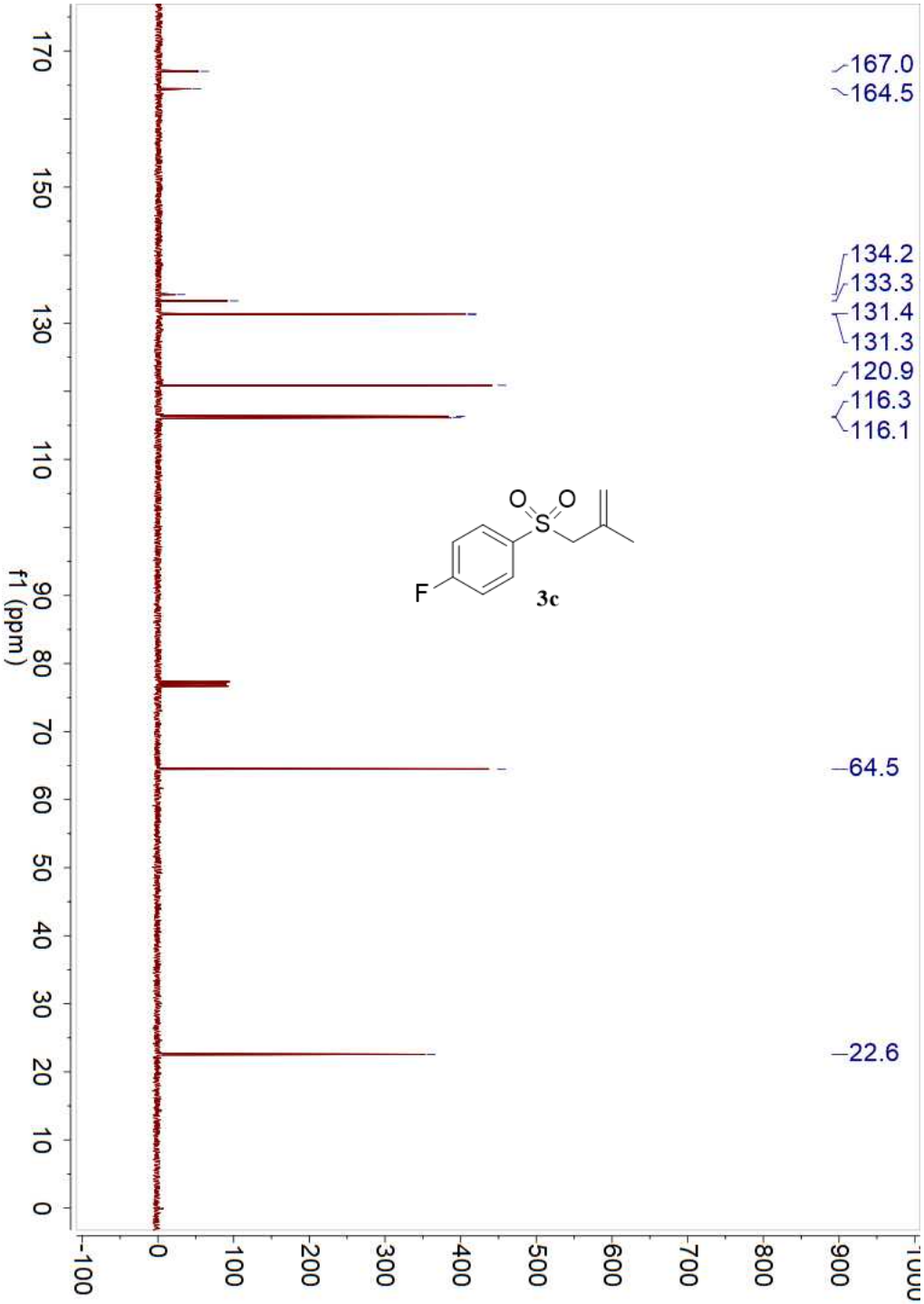
O
O
S
F
3c
f1 (ppm)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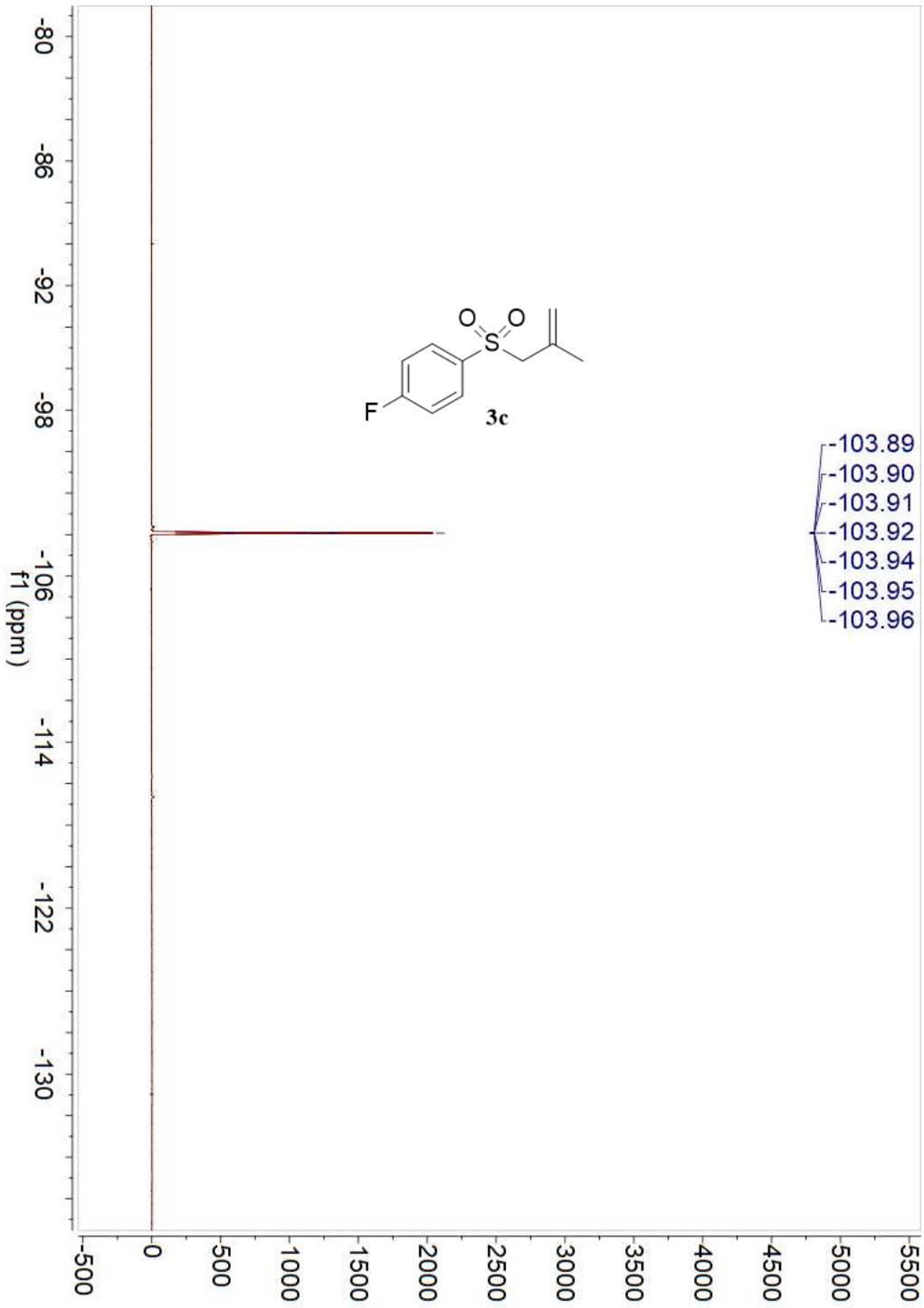
116.3
116.1
64.5
22.6
O
O
S
F
3c
f1 (ppm)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-114
-122
-130
f1 (ppm)
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500
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1500
2000
2500
3000
3500
4000
4500
5000
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O
S
F
3c
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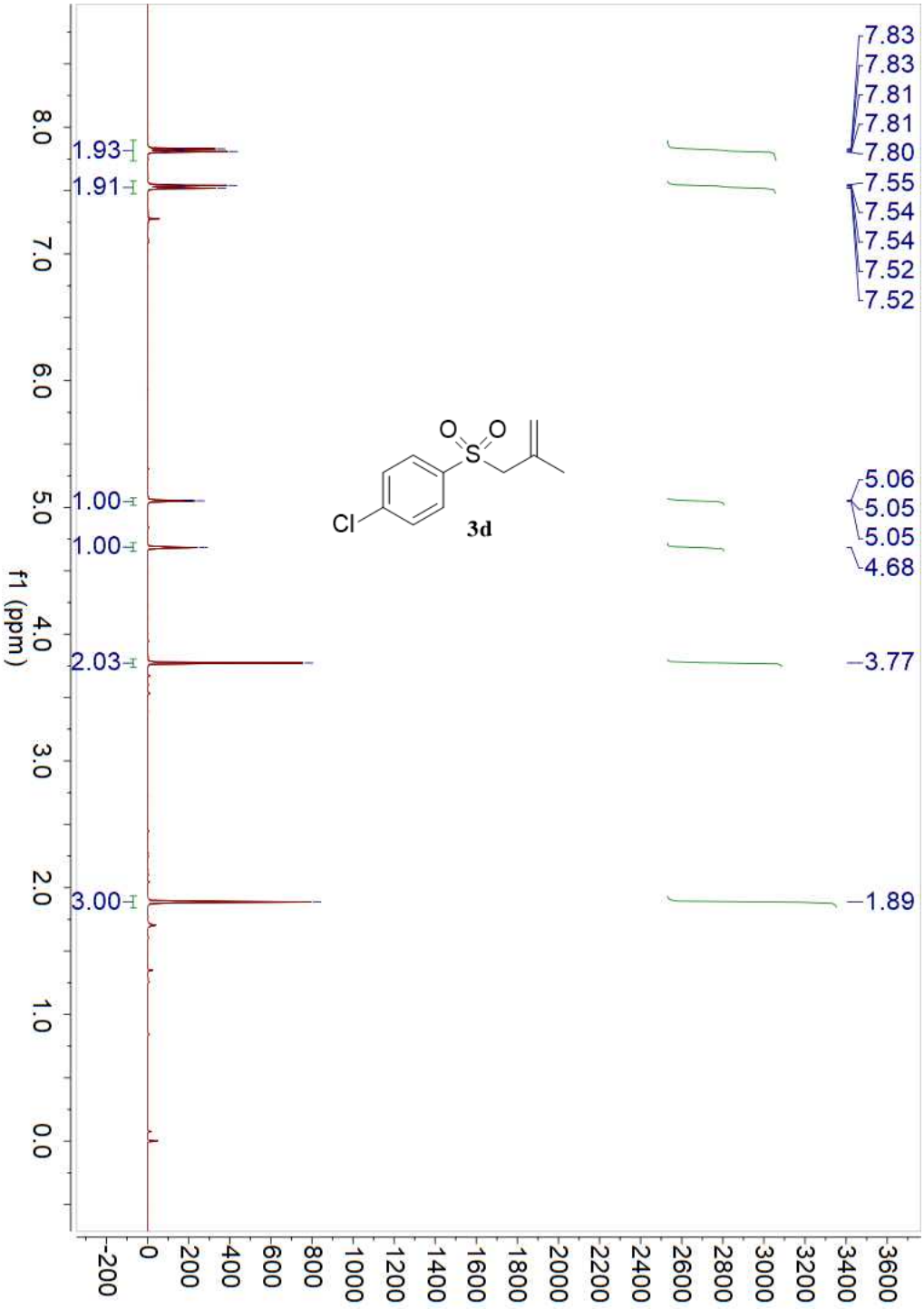
-103.96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5.05
4.68
3.77
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1.00
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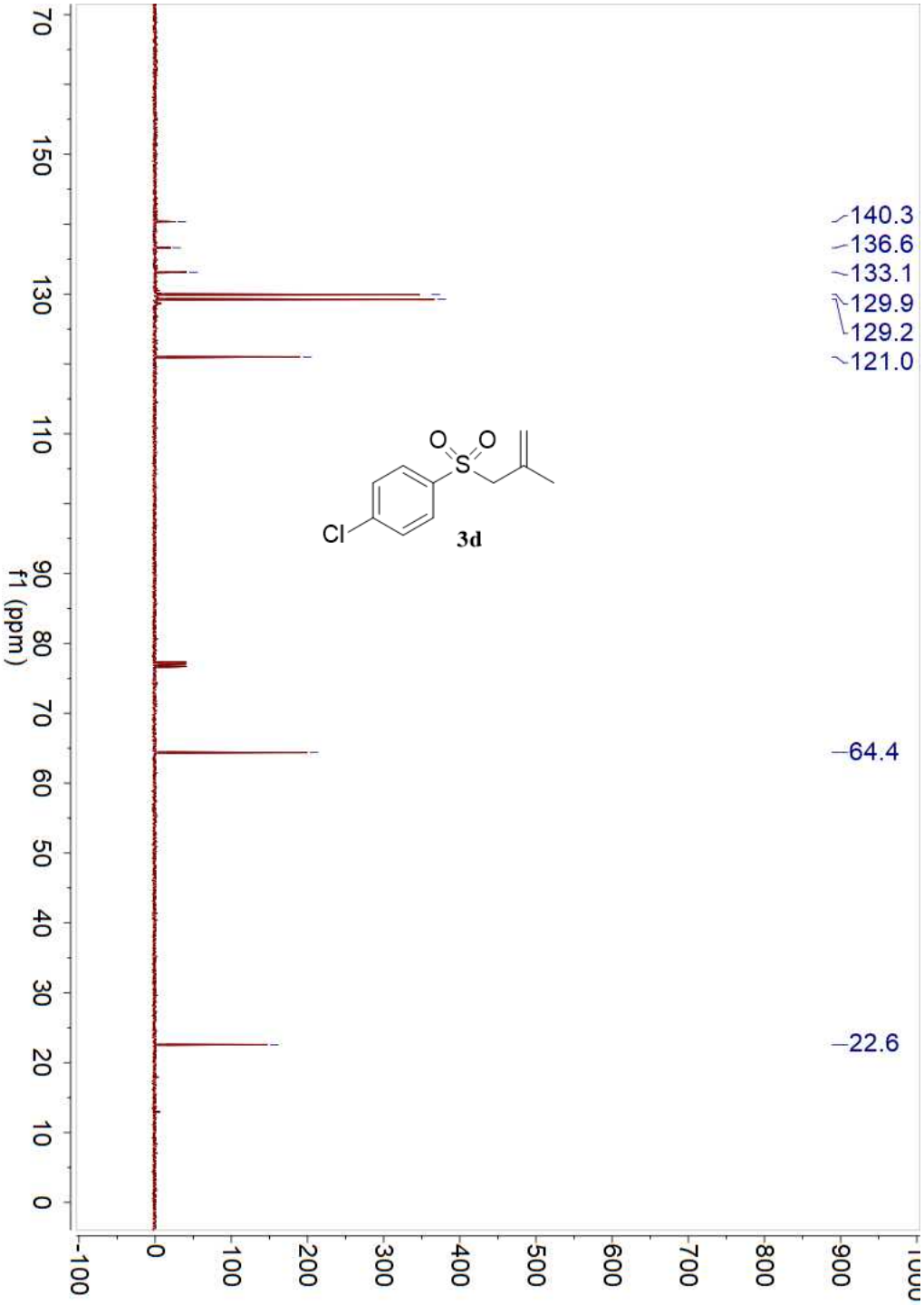
Cl
O
O
S
3d
f1 (ppm)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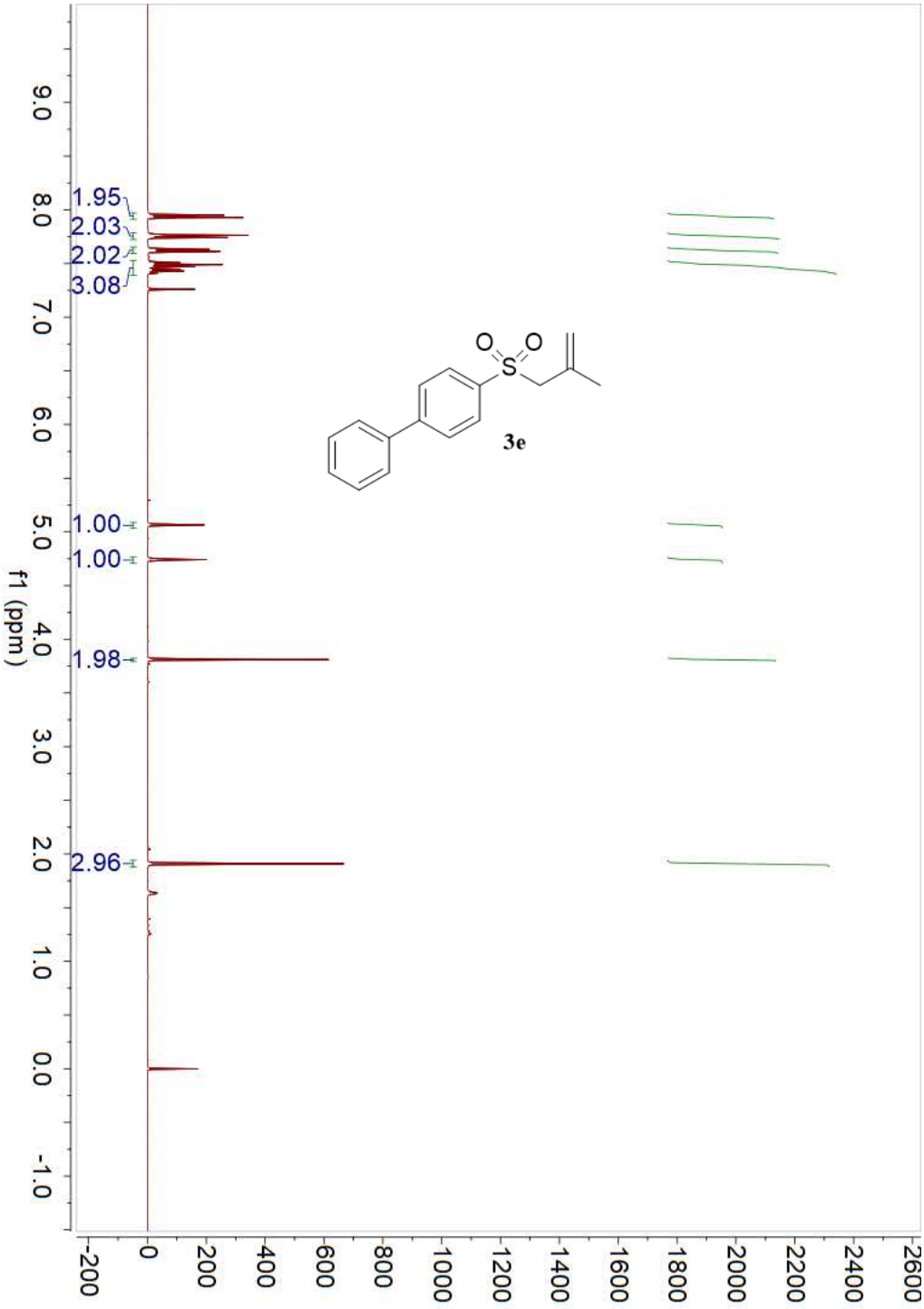
O
S
Cl
3d
f1 (ppm)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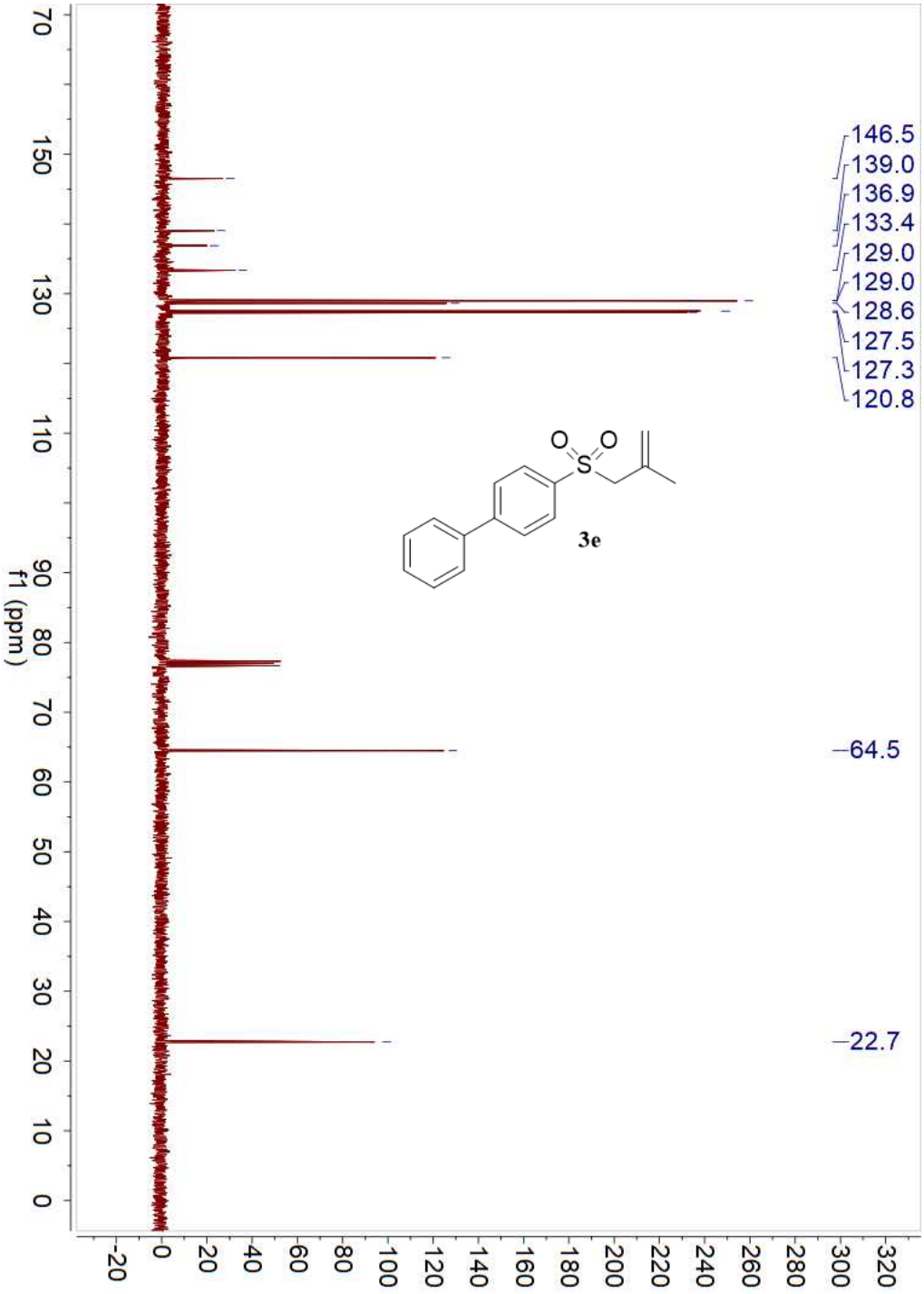
f1 (ppm)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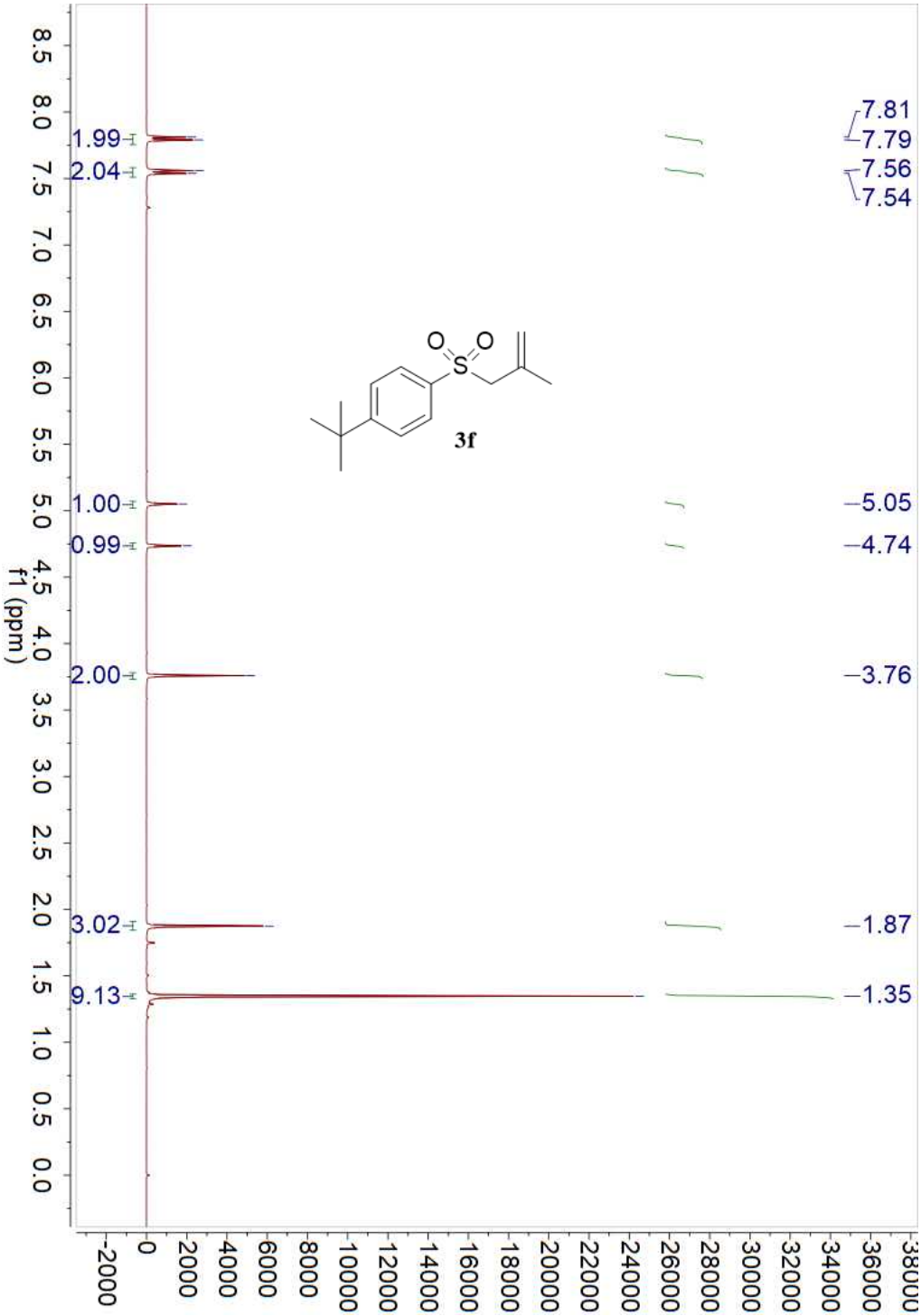
22.7
3e
f1 (ppm)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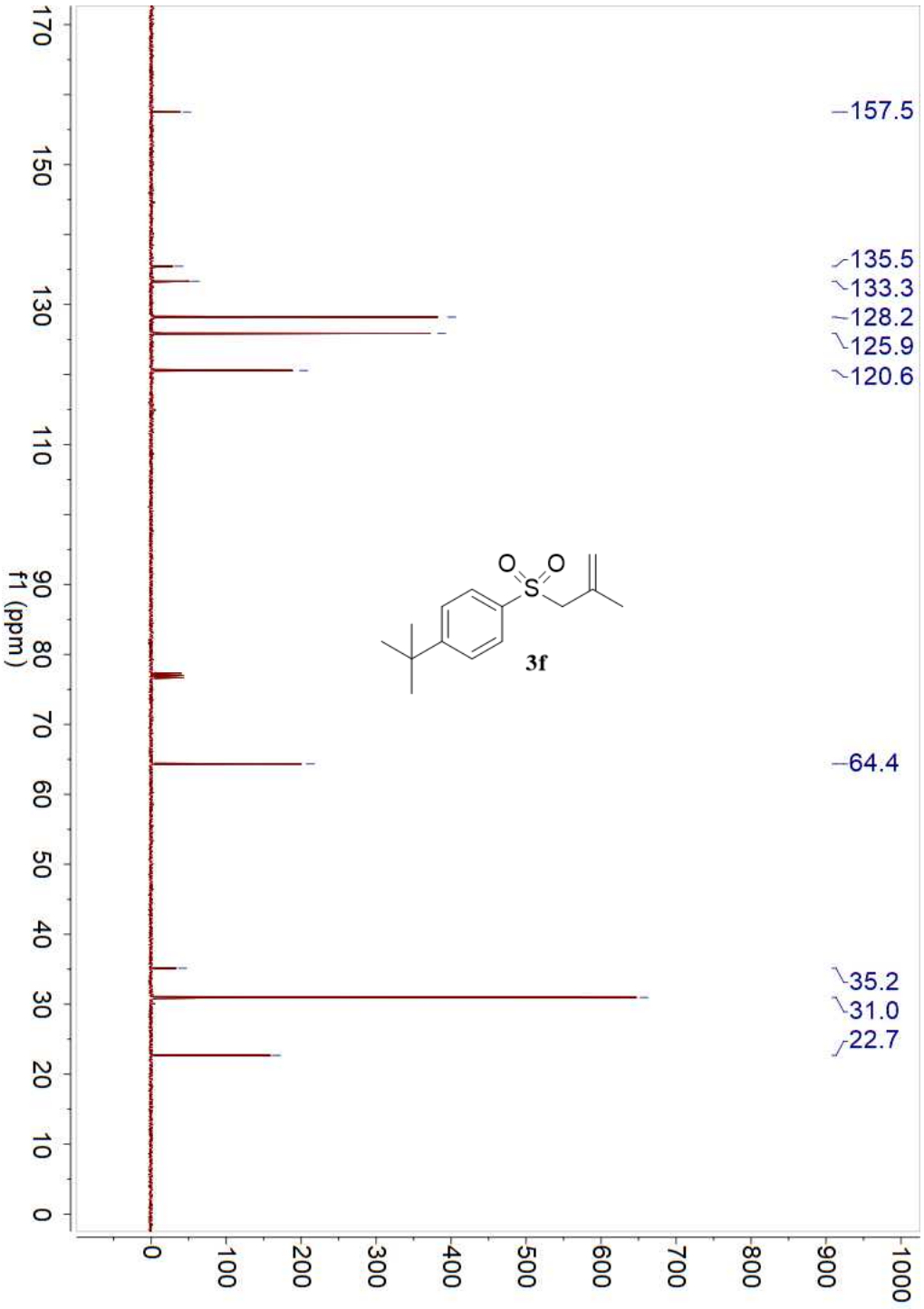
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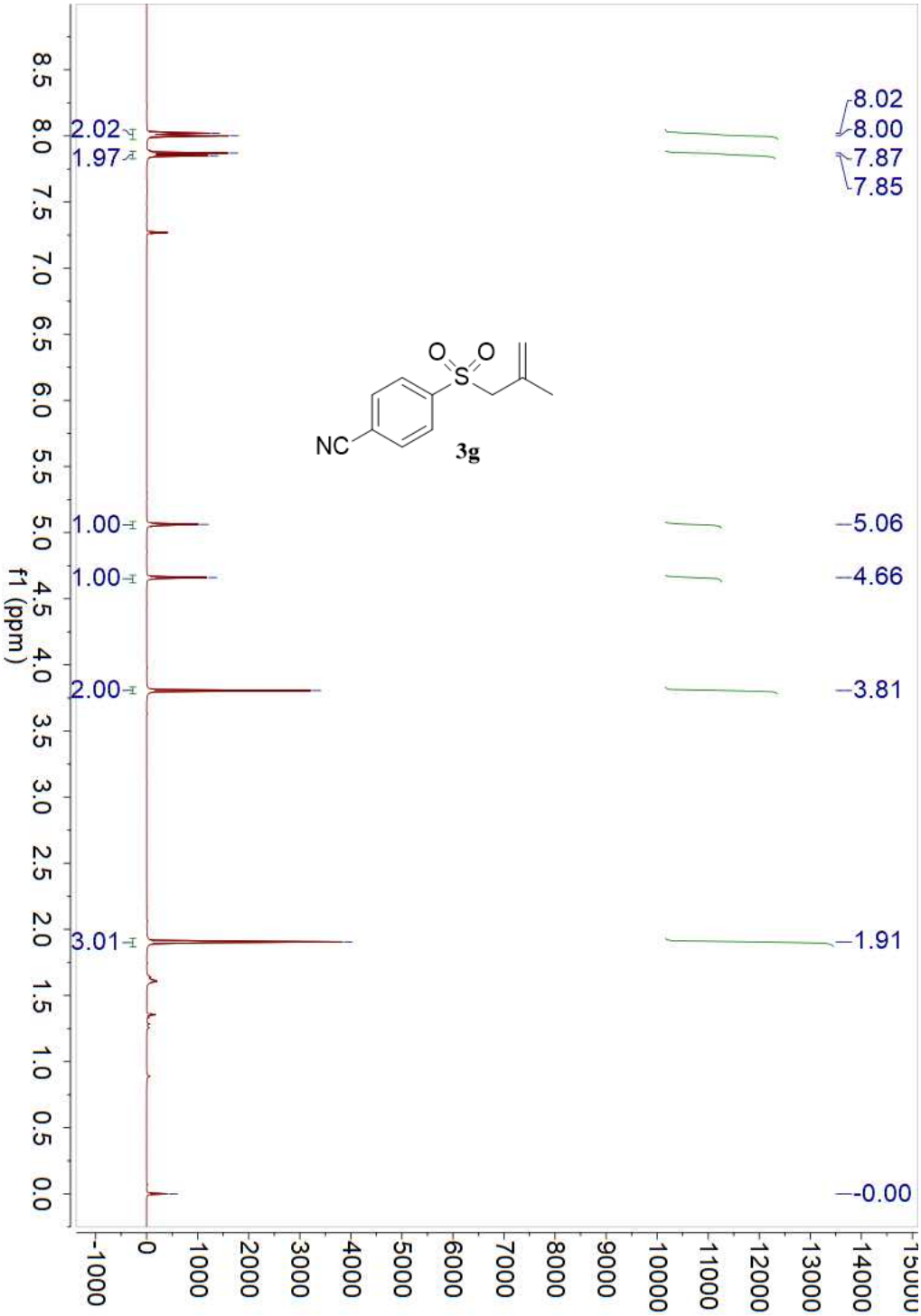
f1 (ppm)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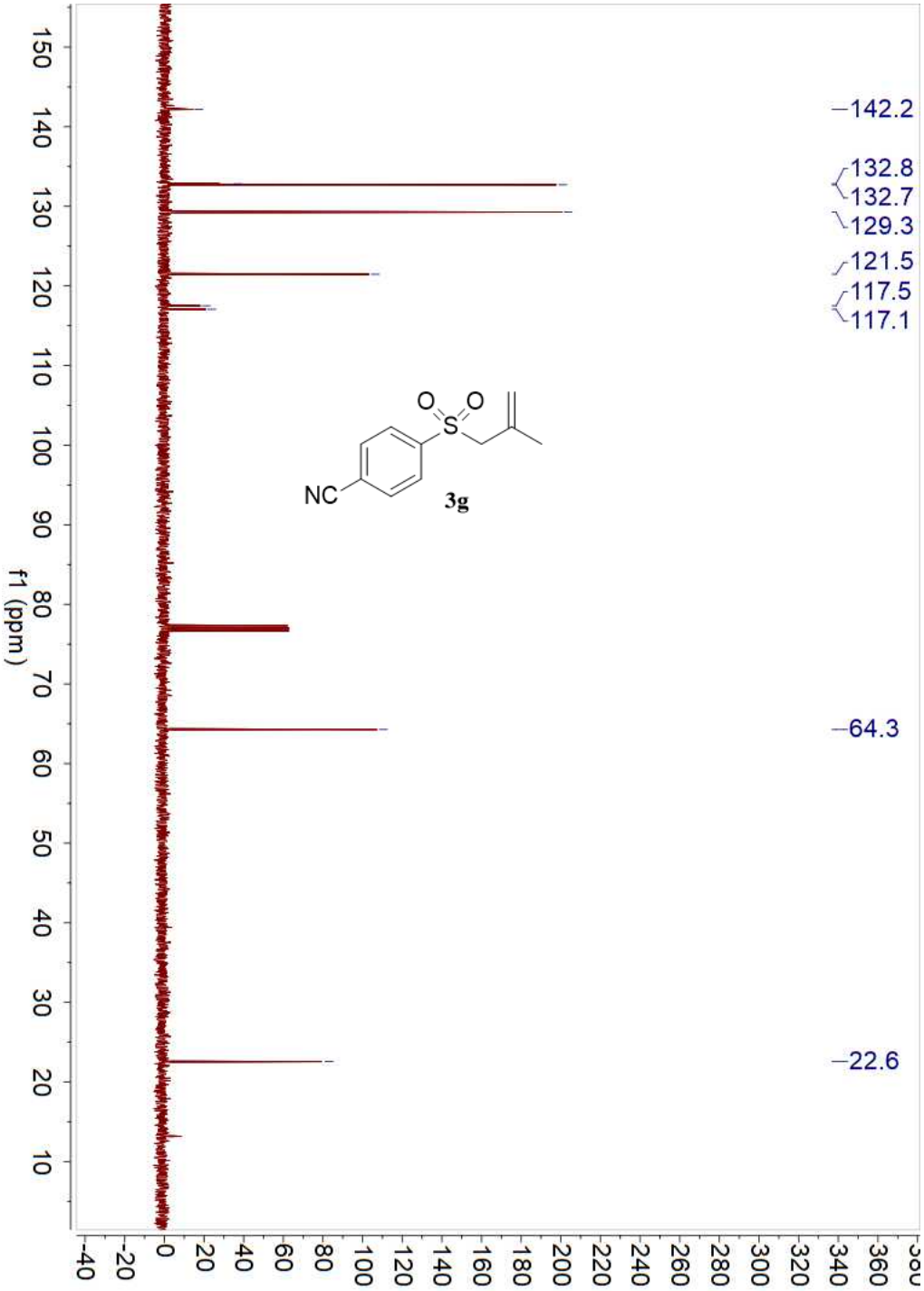
3g
f1 (ppm)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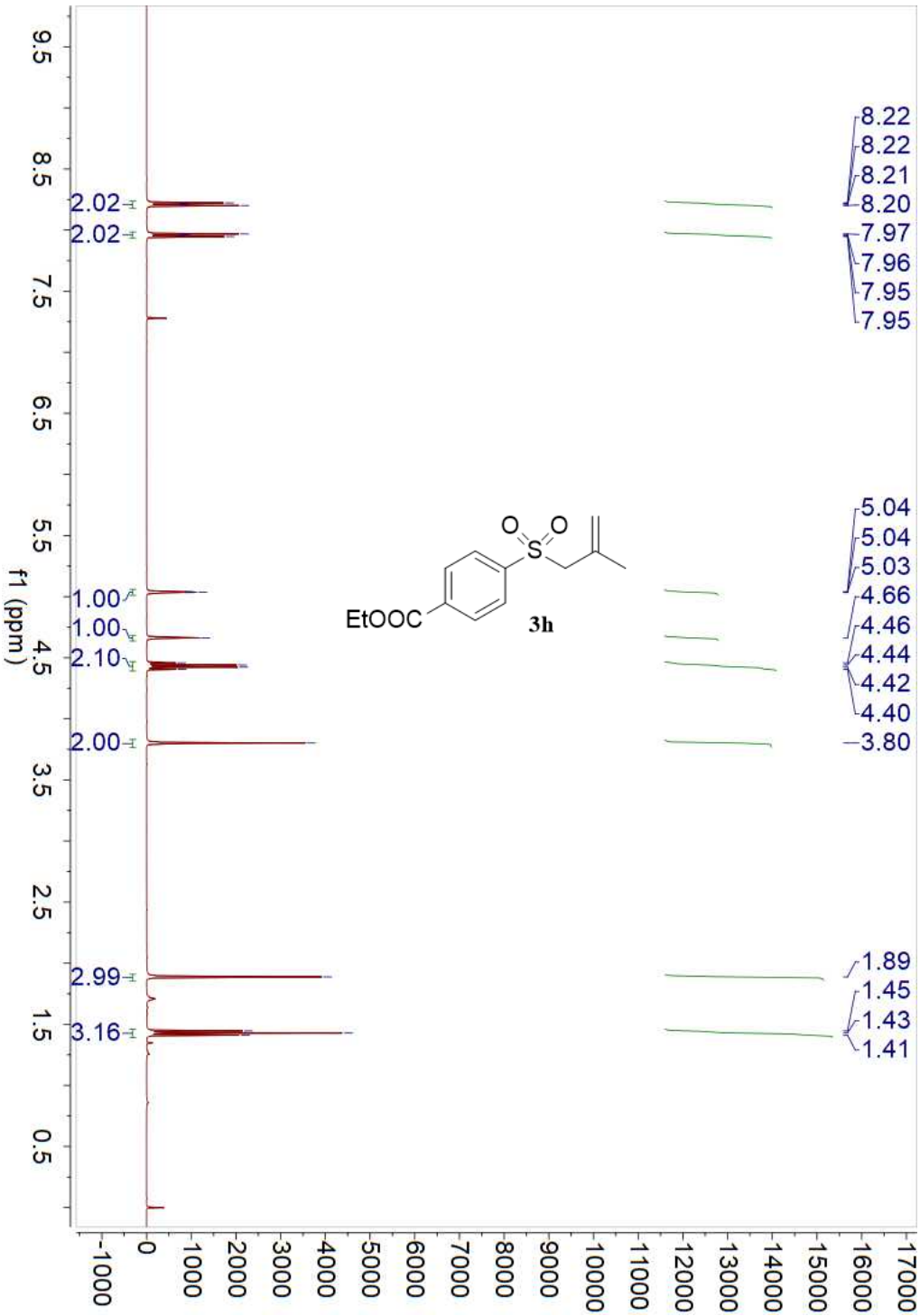
O
O
S
NC
3g
f1 (ppm)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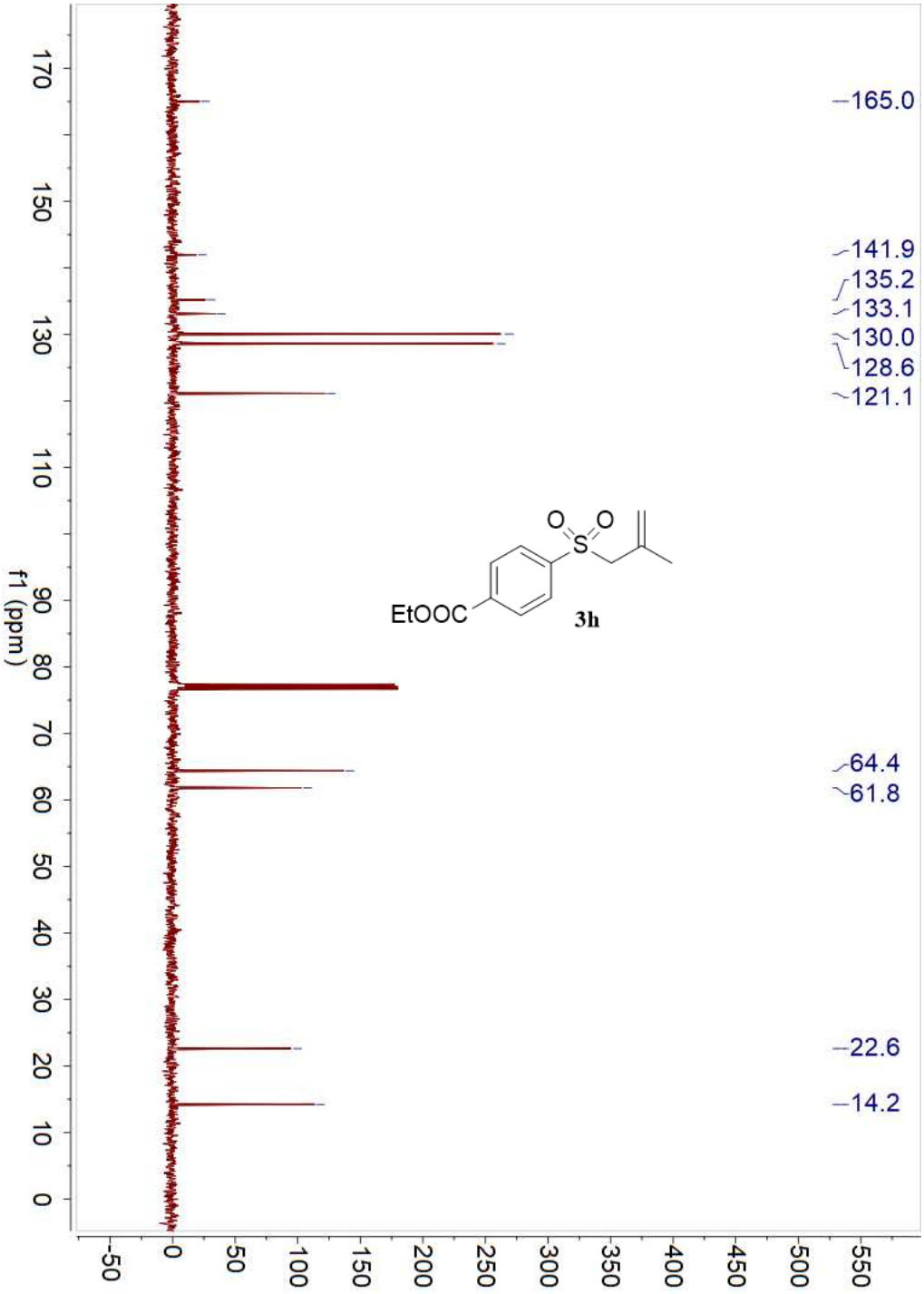
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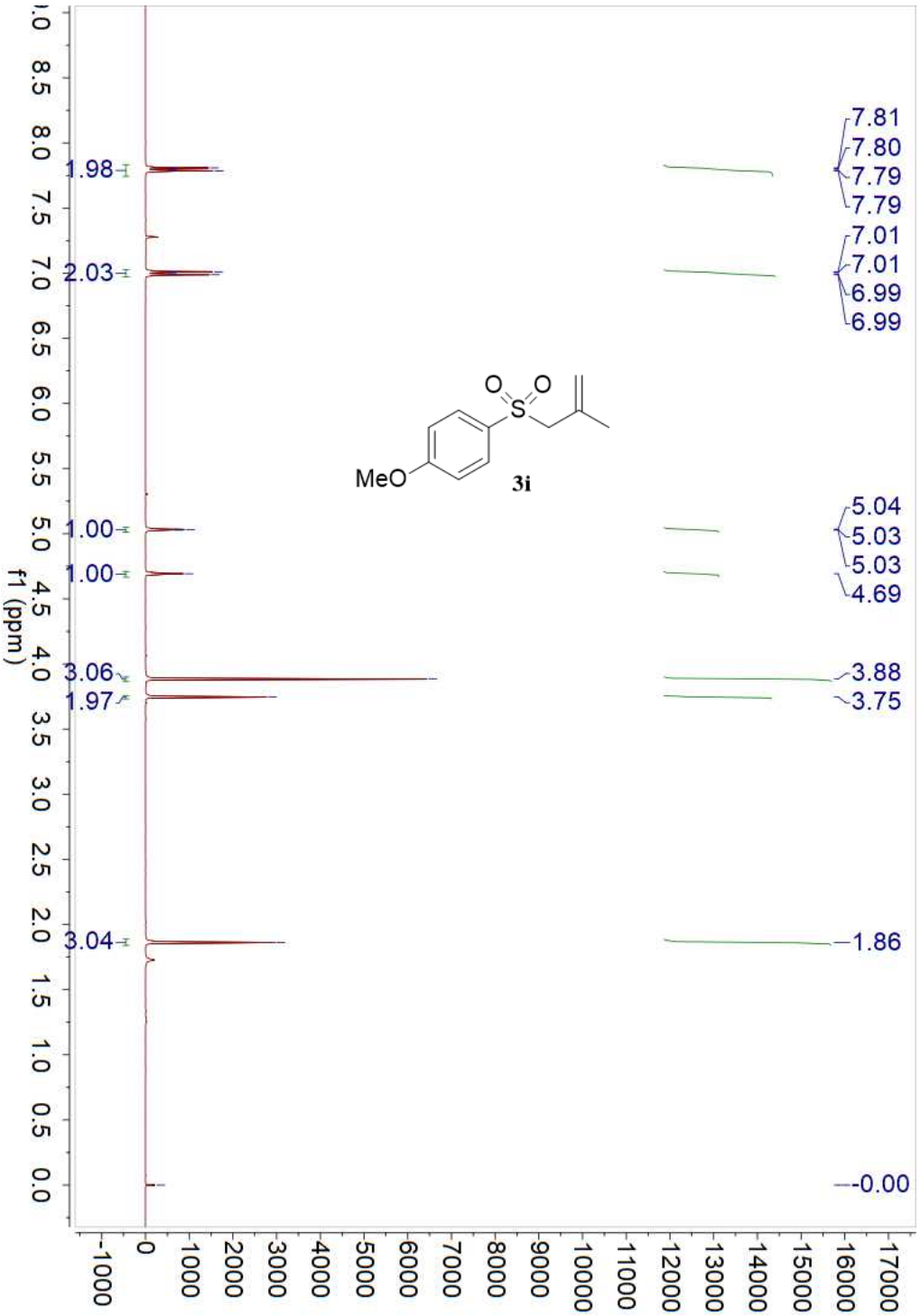
f1 (ppm)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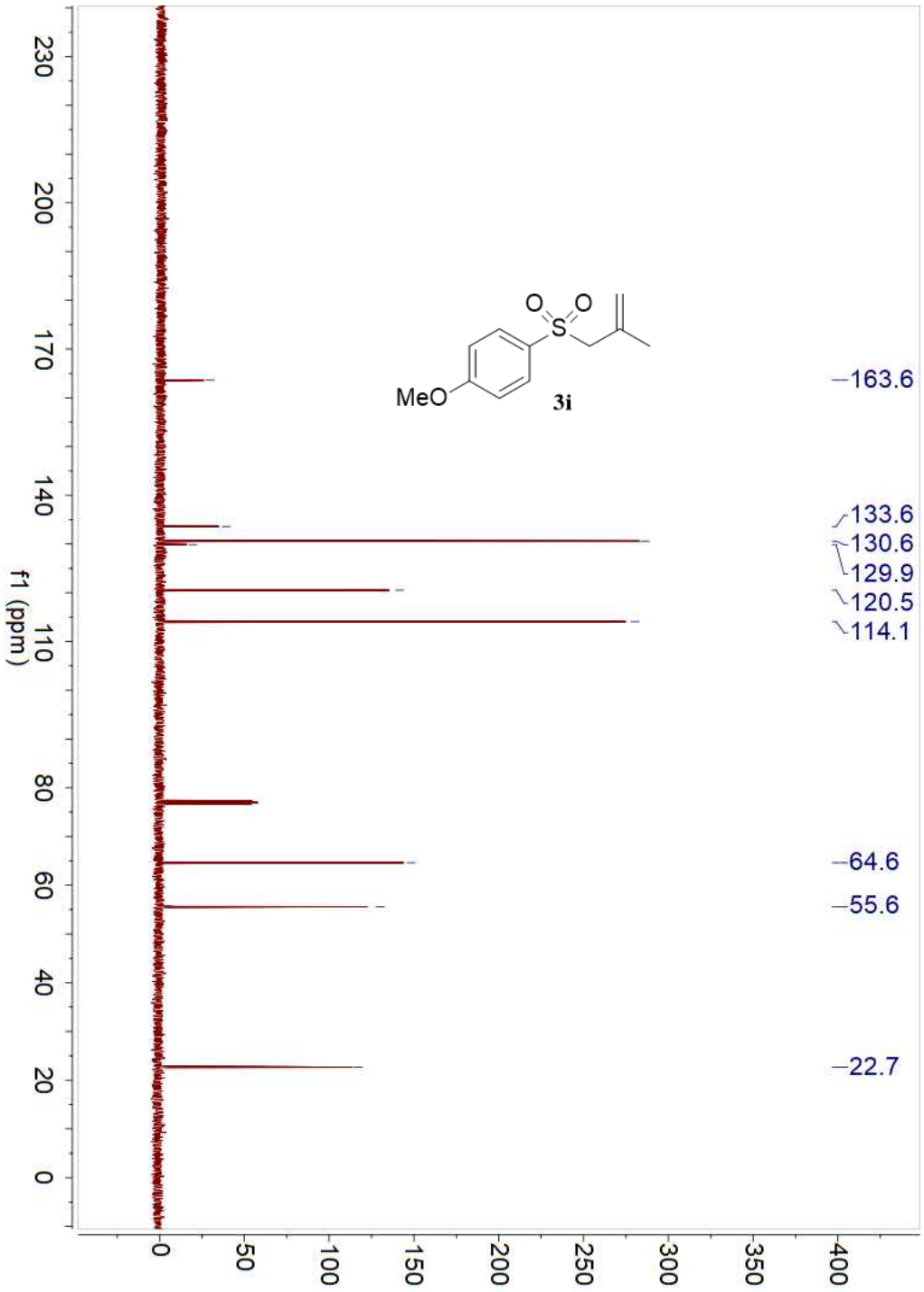
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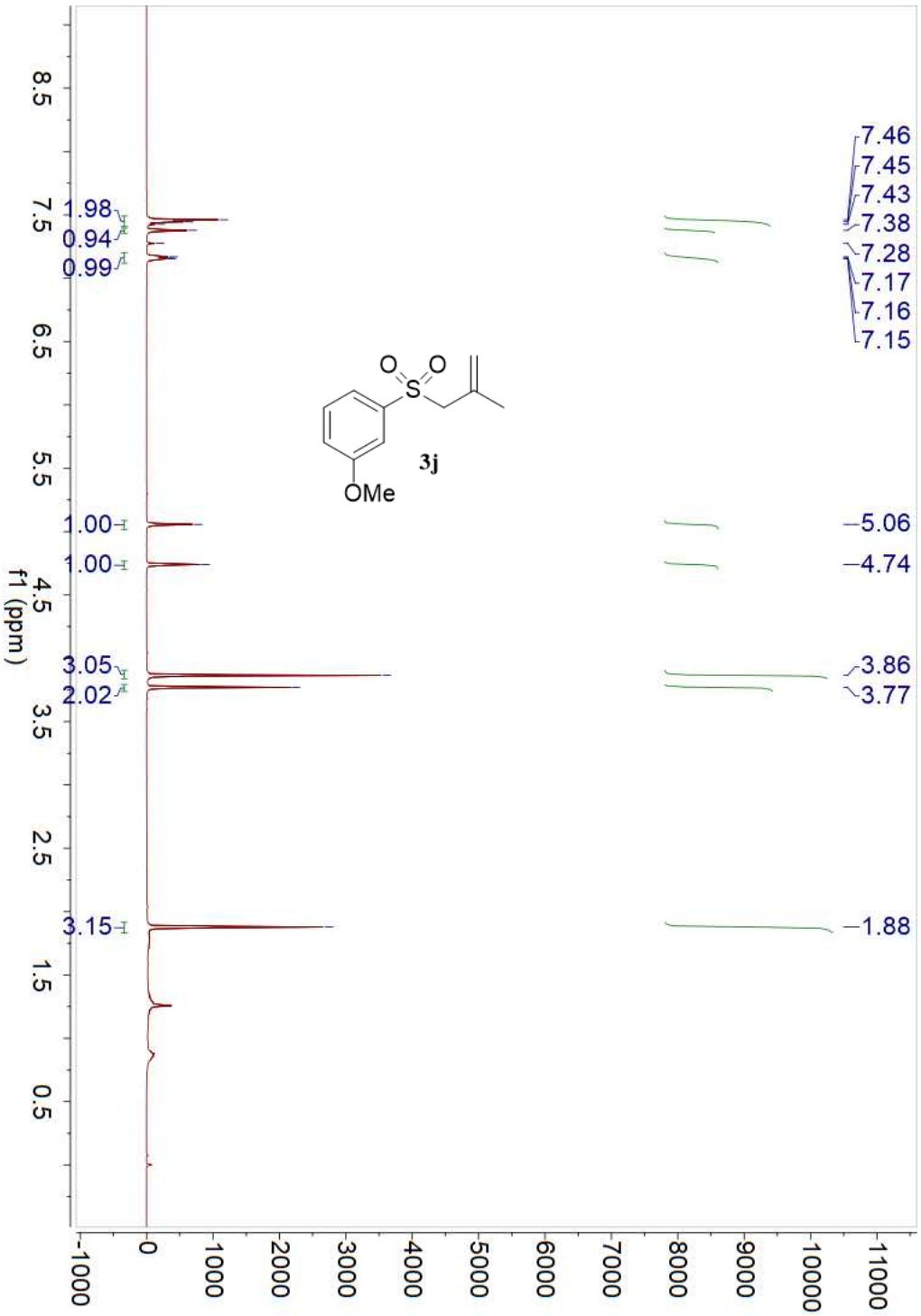
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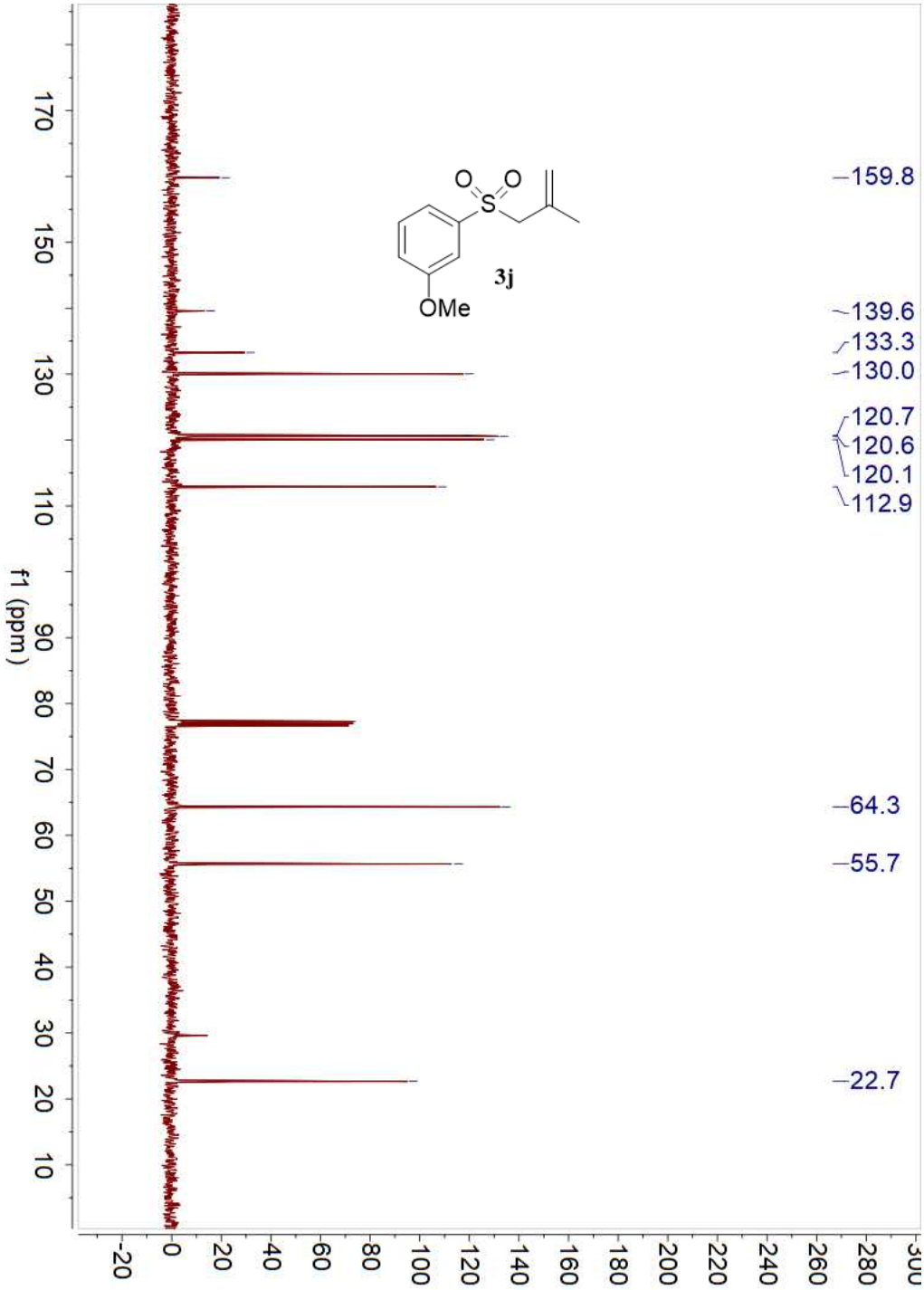
OMe
3j
f1 (ppm)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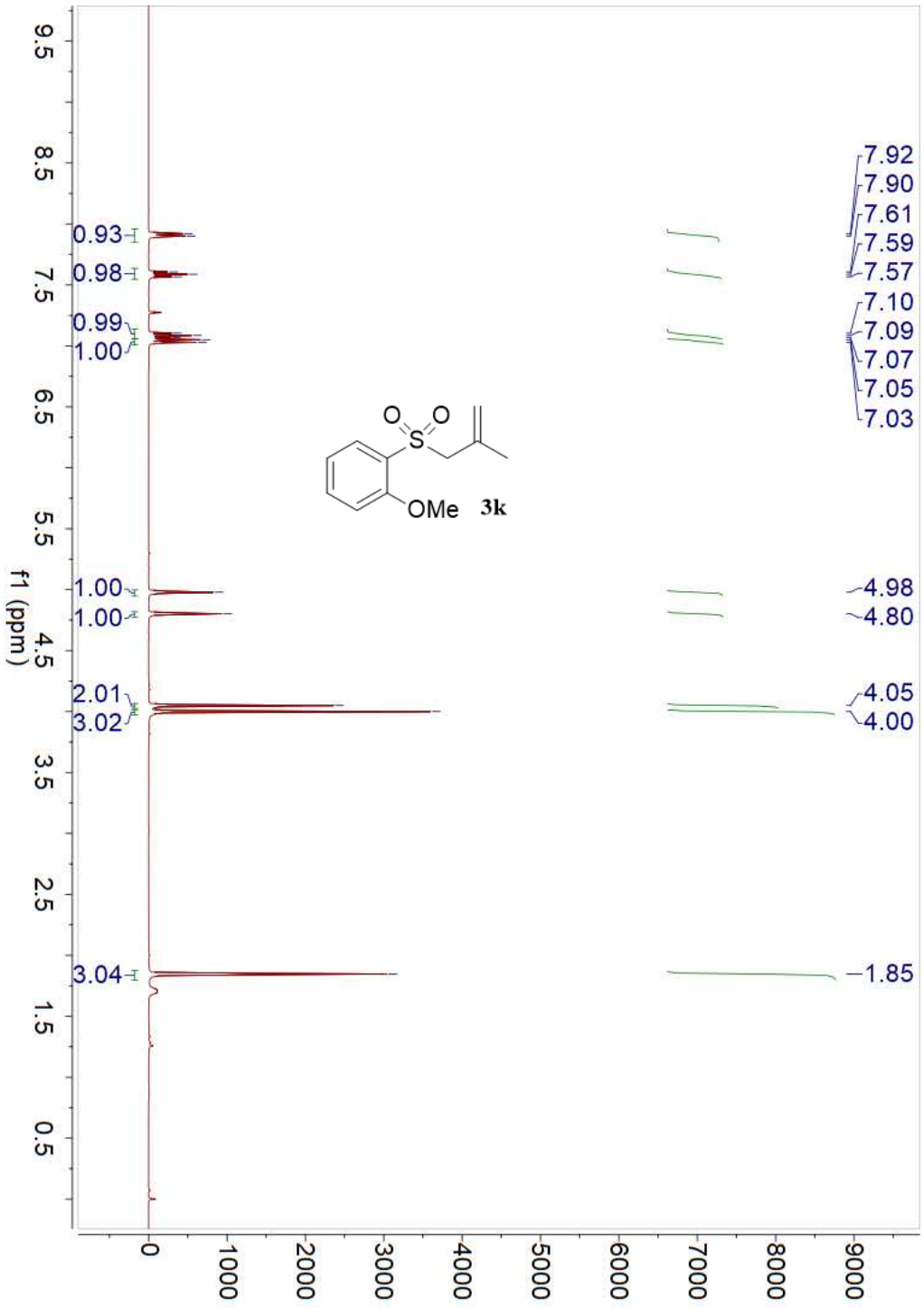
f1 (ppm)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0.99
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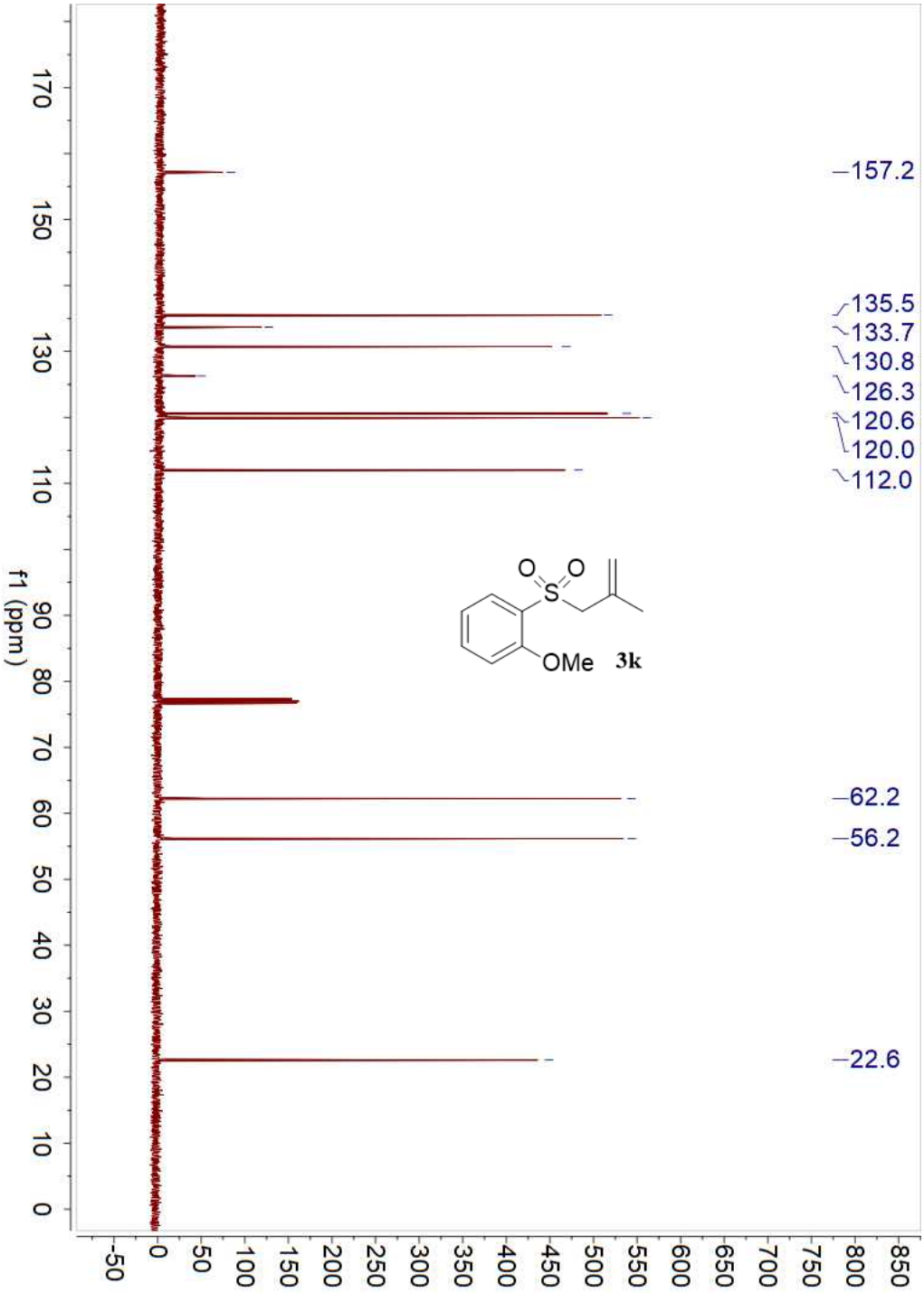
3k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56.2
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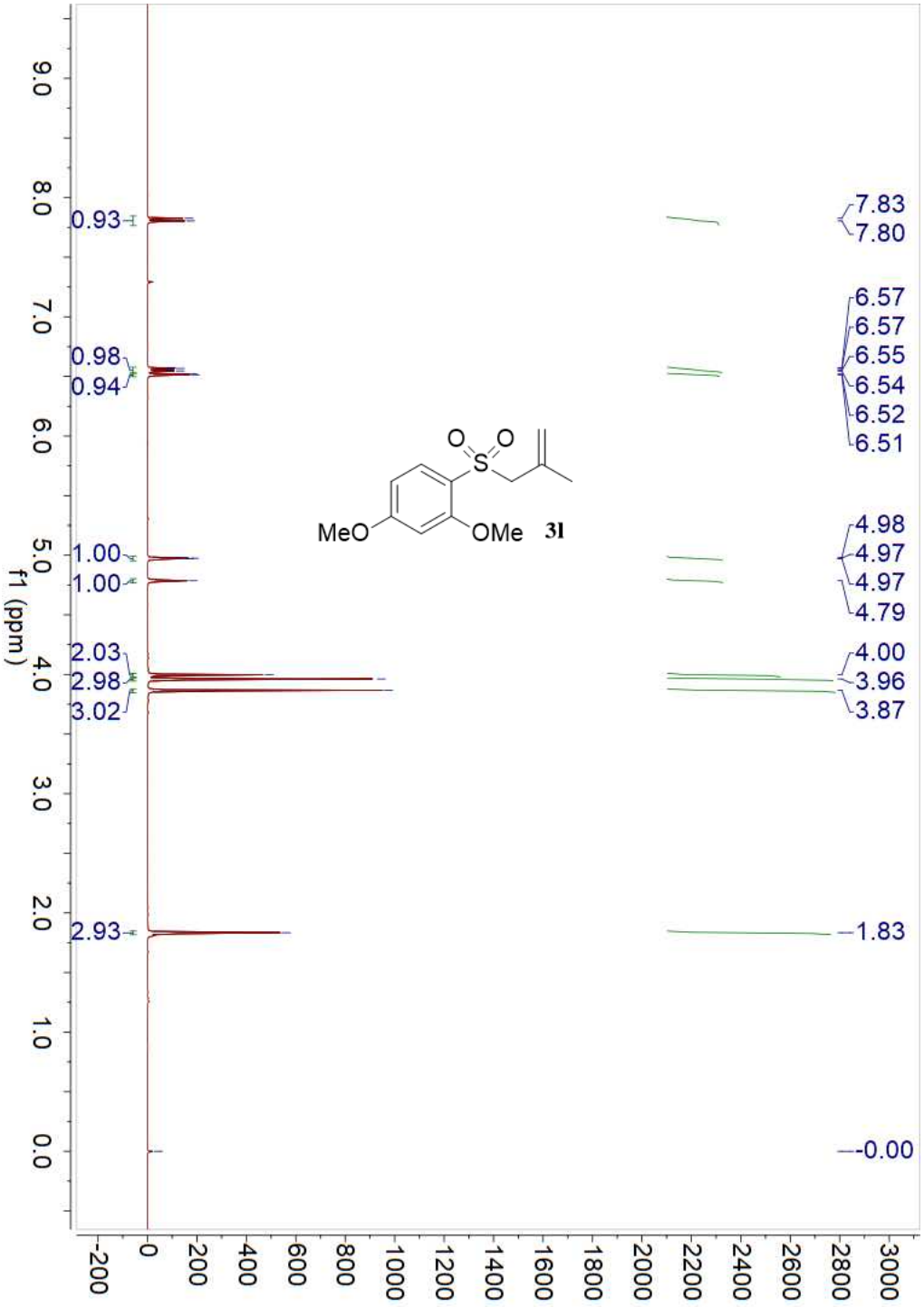
OMe
3k
f1 (ppm)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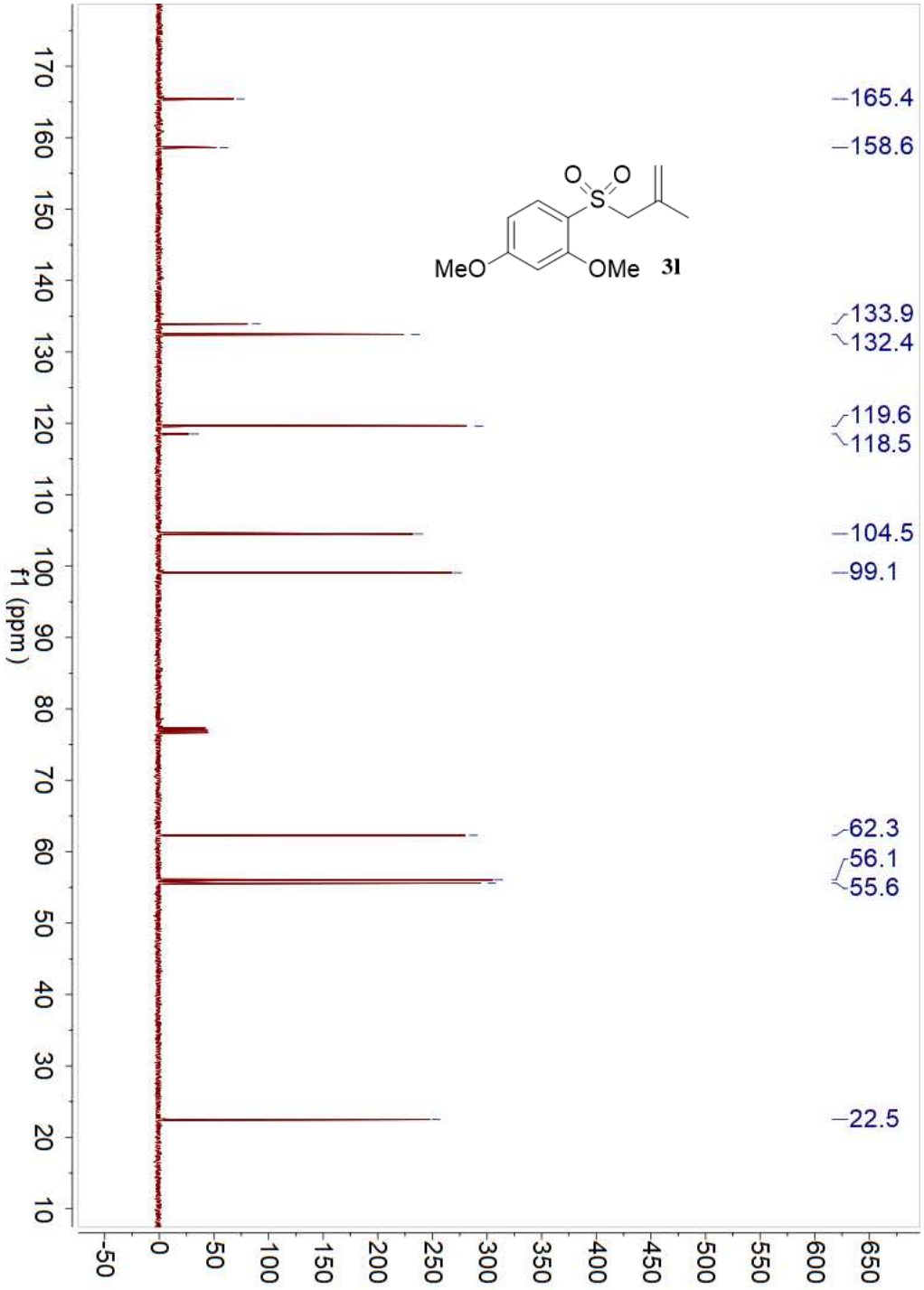
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22.5
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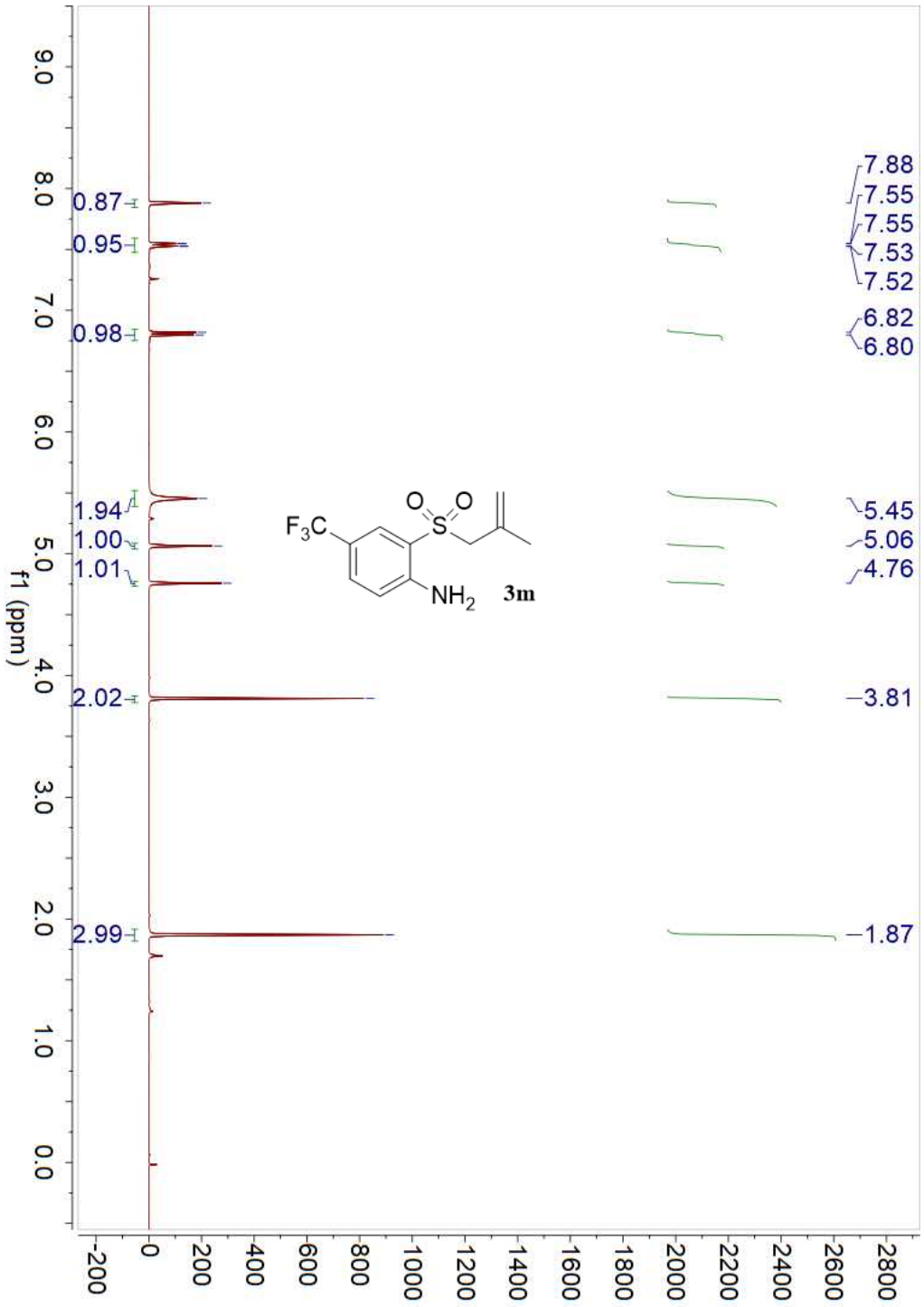
3l
f1 (ppm)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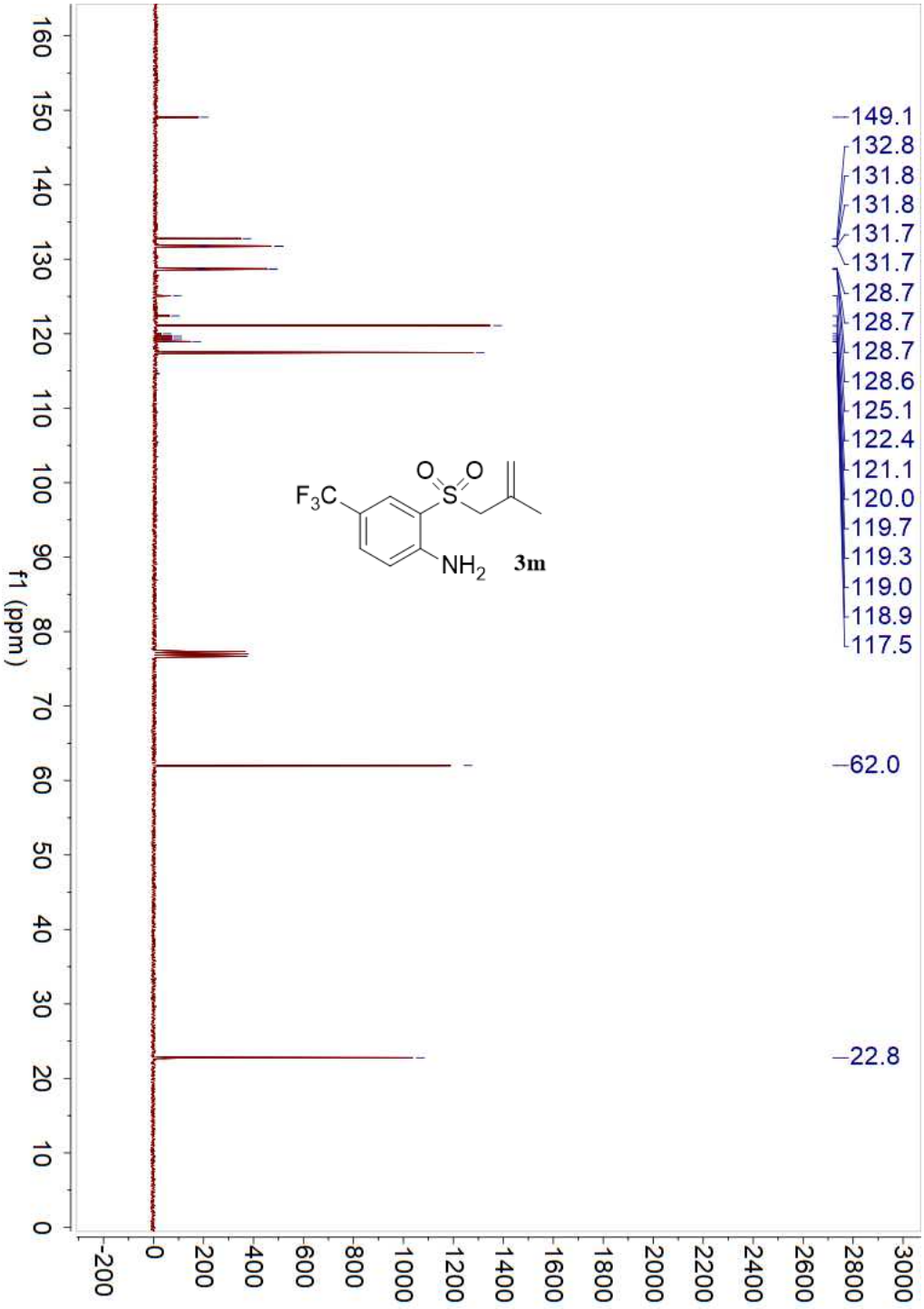
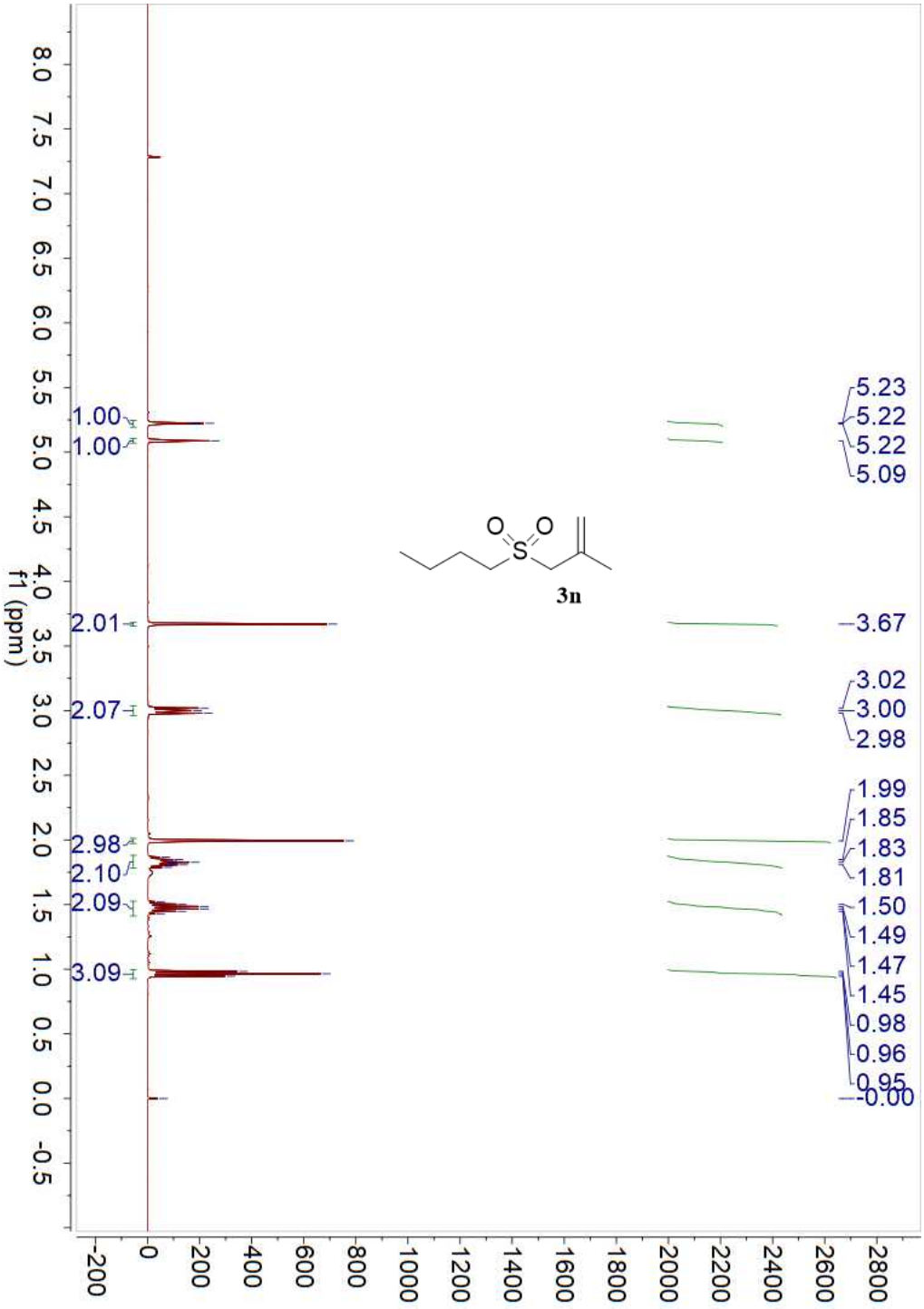
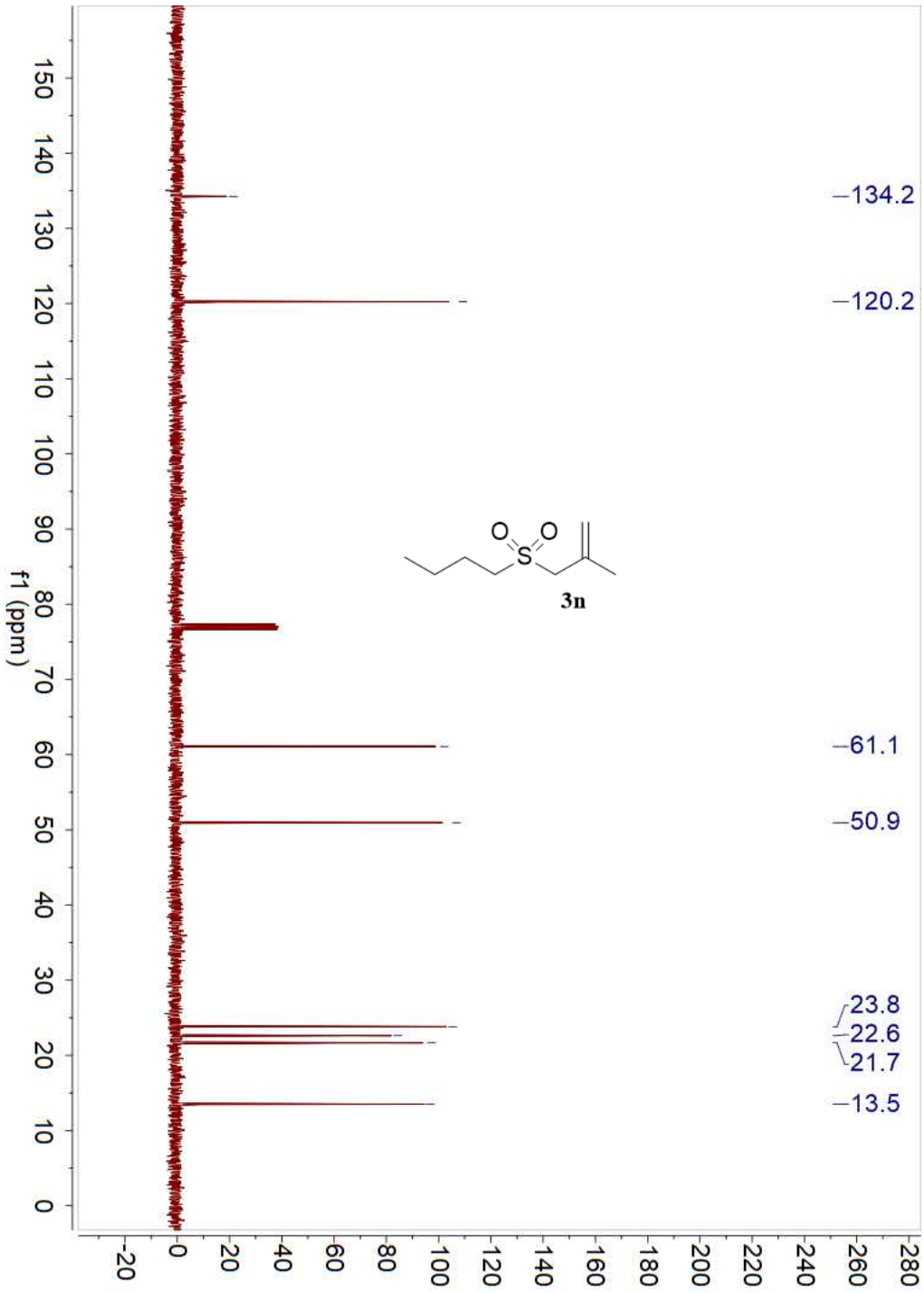
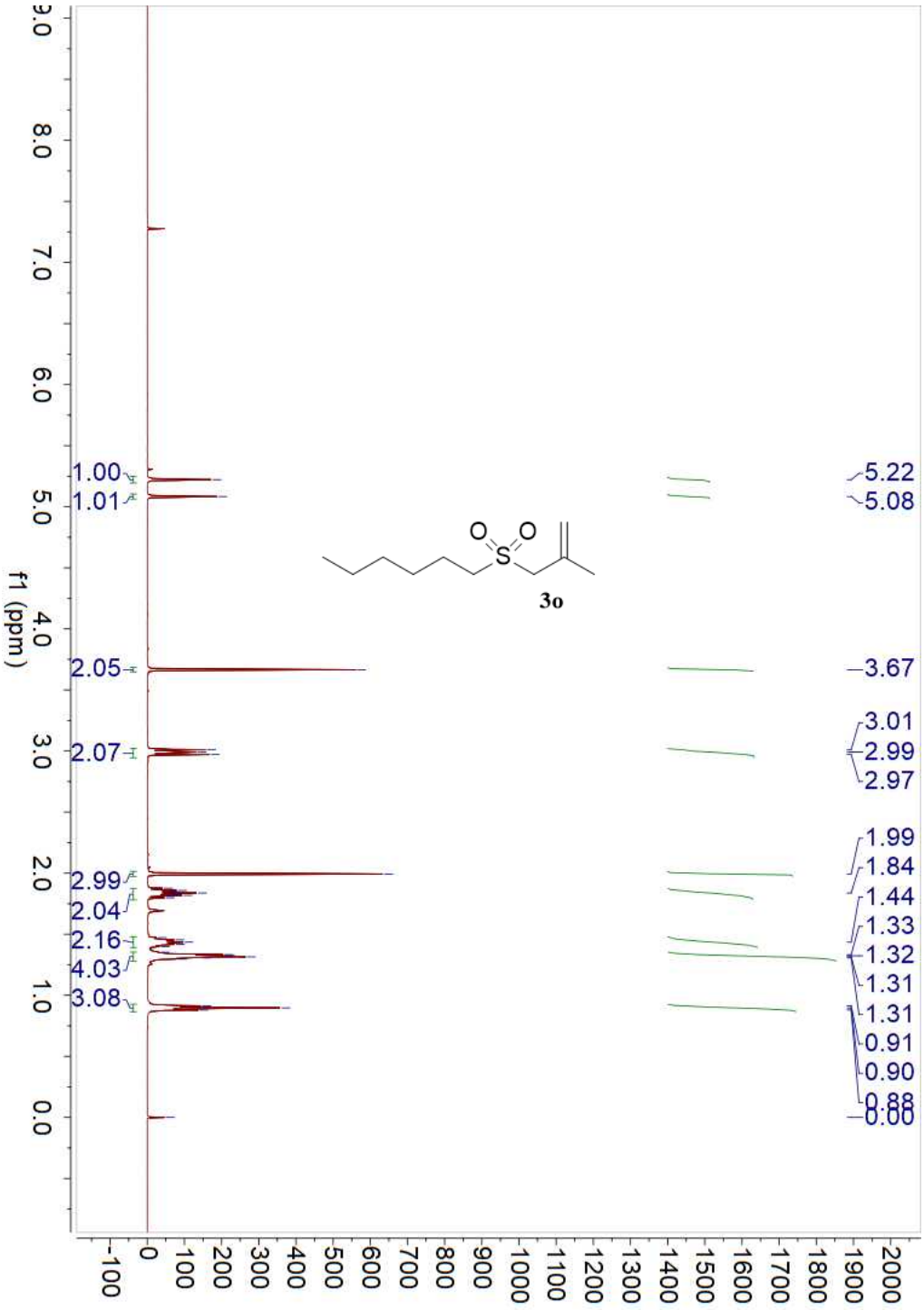
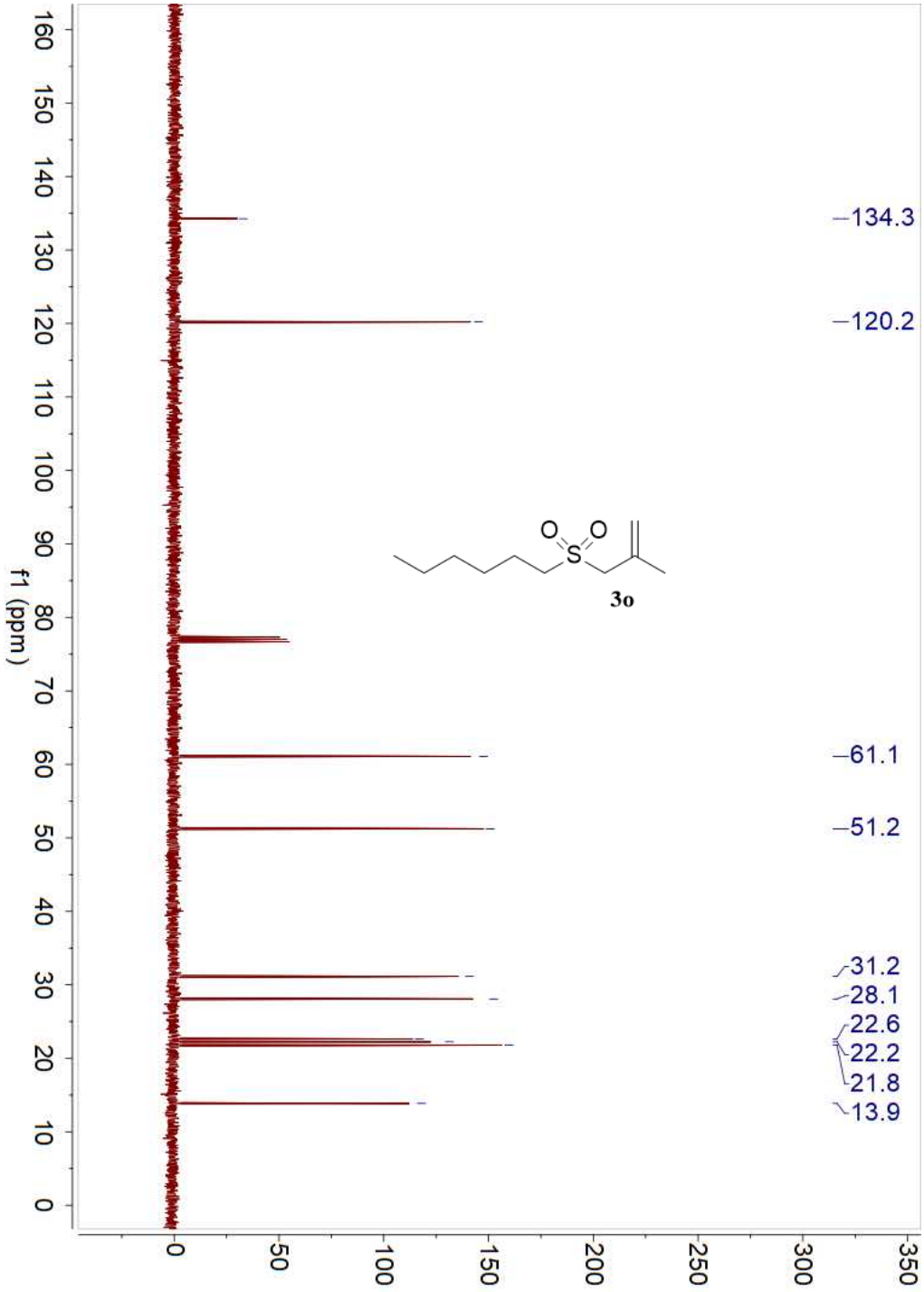
4.76
3.81
1.87
0.87
0.95
0.98
1.94
1.00
1.01
2.02
2.99
F3C
O
O
S
NH2
3m
f1 (ppm)

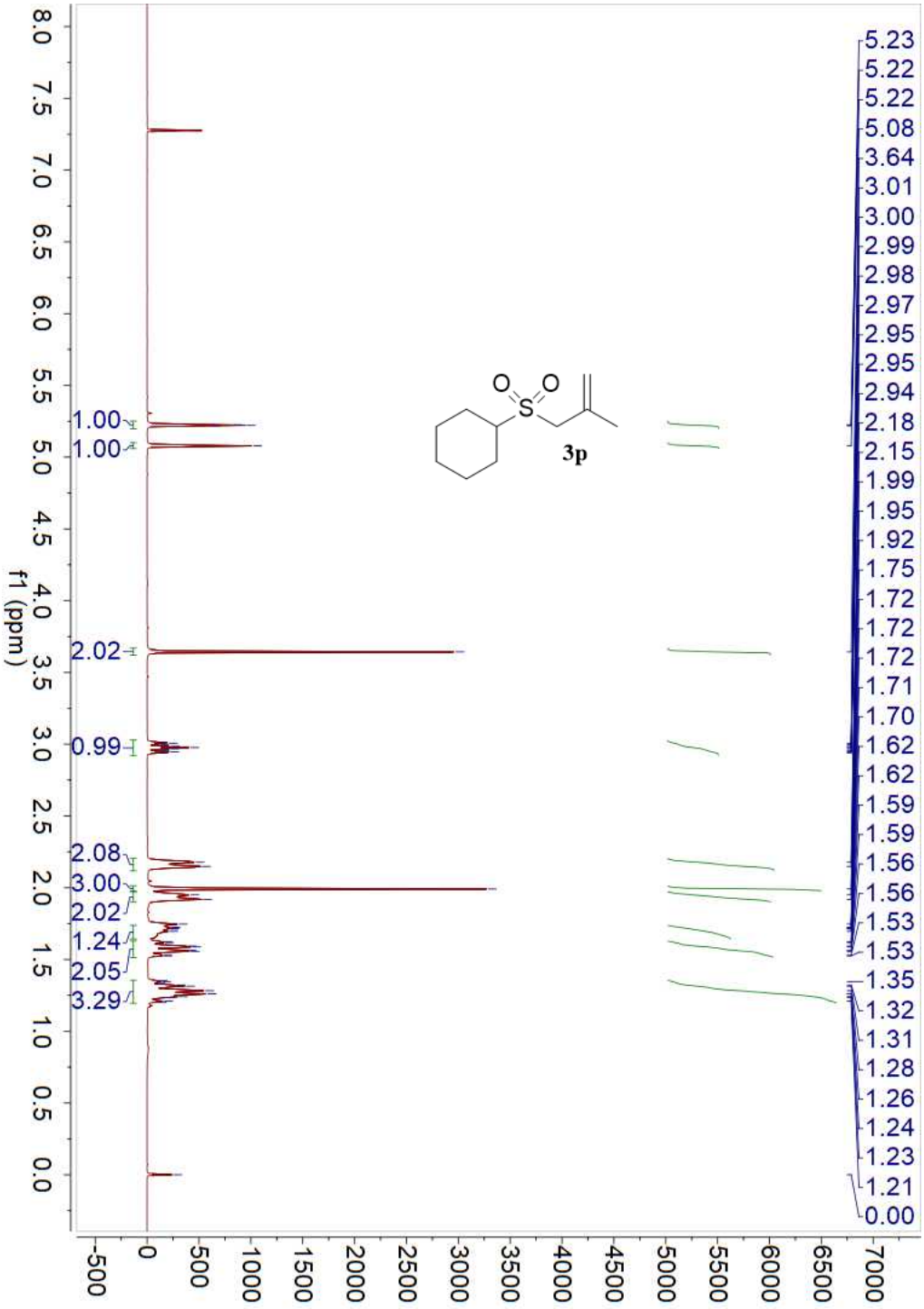

149.1
132.8
131.8
131.8
131.7
131.7
128.7
128.7
128.7
128.6
125.1
122.4
121.1
120.0
119.7
119.3
119.0
118.9
117.5
62.0
22.8
F3C
O
S
O
NH2
3m
f1 (ppm)

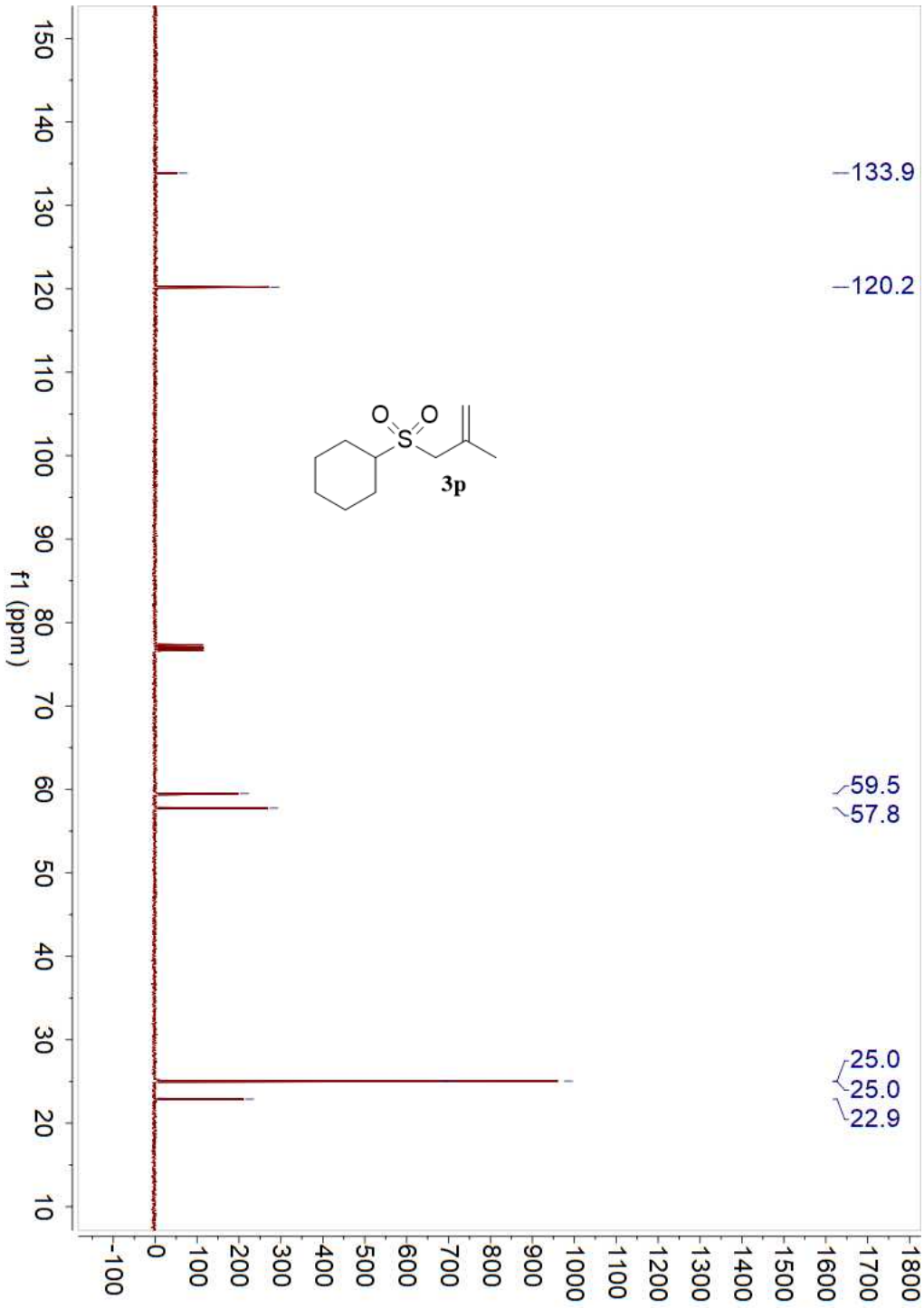

f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
-200 0 200 400 600 800 1000 1200 1400 1600 1800 2000 2200 2400 2600 2800
1.00
1.00
2.01
2.07
2.98
2.10
2.09
3.09
O
O
S
3n
5.23
5.22
5.22
5.09
3.67
3.02
3.00
2.98
1.99
1.85
1.83
1.81
1.50
1.49
1.47
1.45
0.98
0.96
0.95
0.00

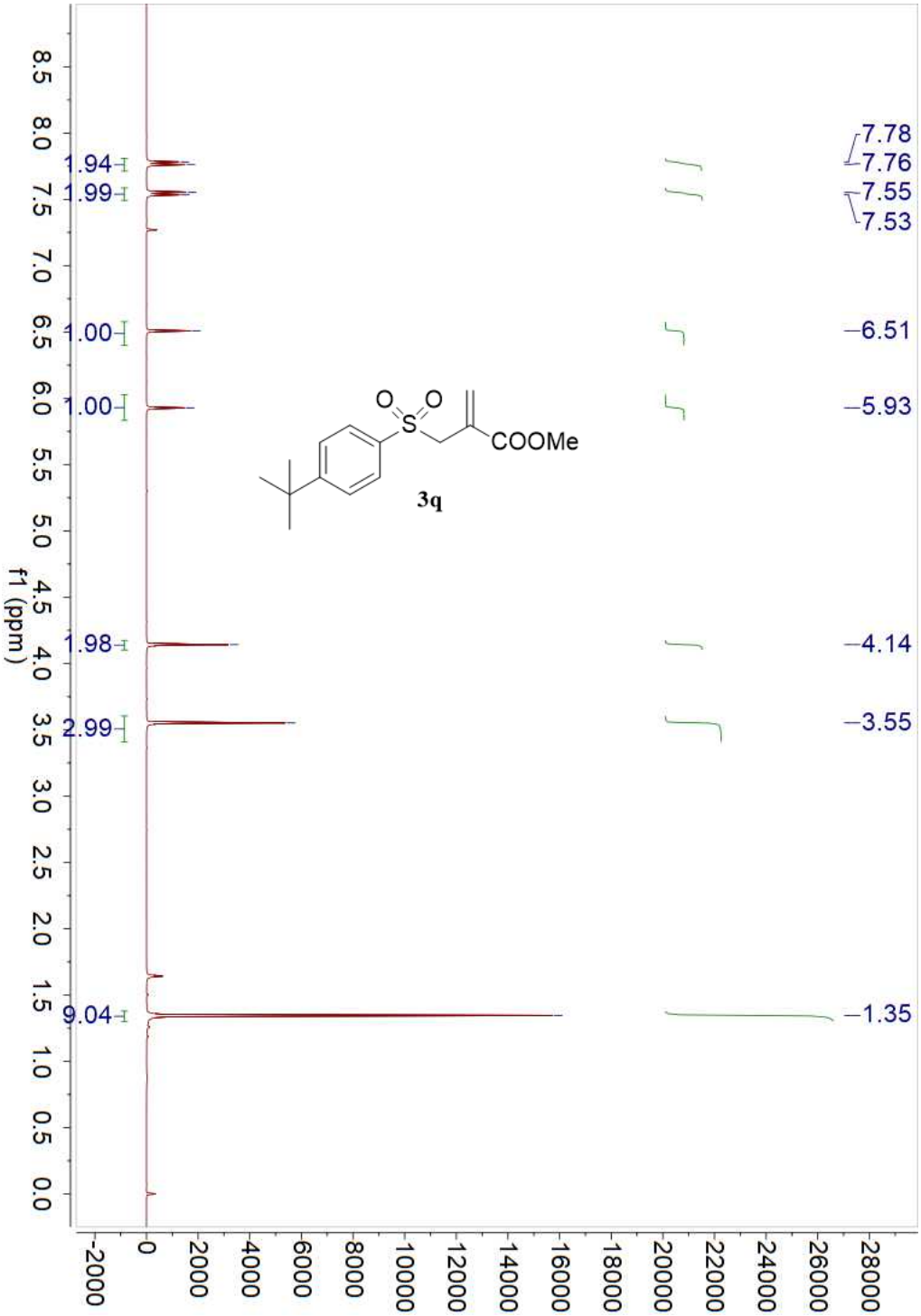

134.2
120.2
61.1
50.9
23.8
22.6
21.7
13.5
3n
f1 (ppm)

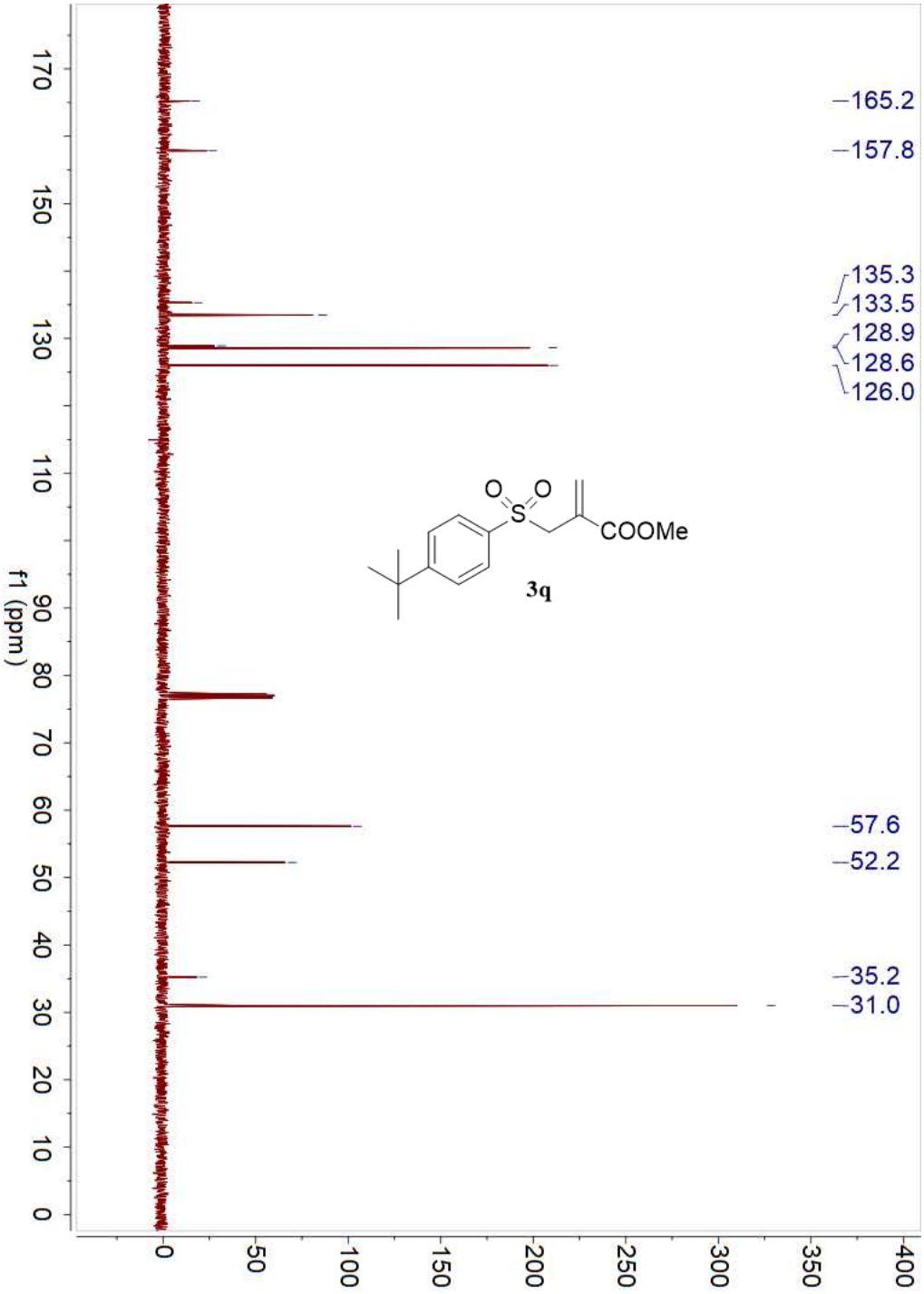

1.00
1.01
2.05
2.07
2.99
2.04
2.16
4.03
3.08
5.22
5.08
3.67
3.01
2.99
2.97
1.99
1.84
1.44
1.33
1.32
1.31
1.31
0.91
0.90
0.88
0.00
O
O
S
3o
f1 (ppm)

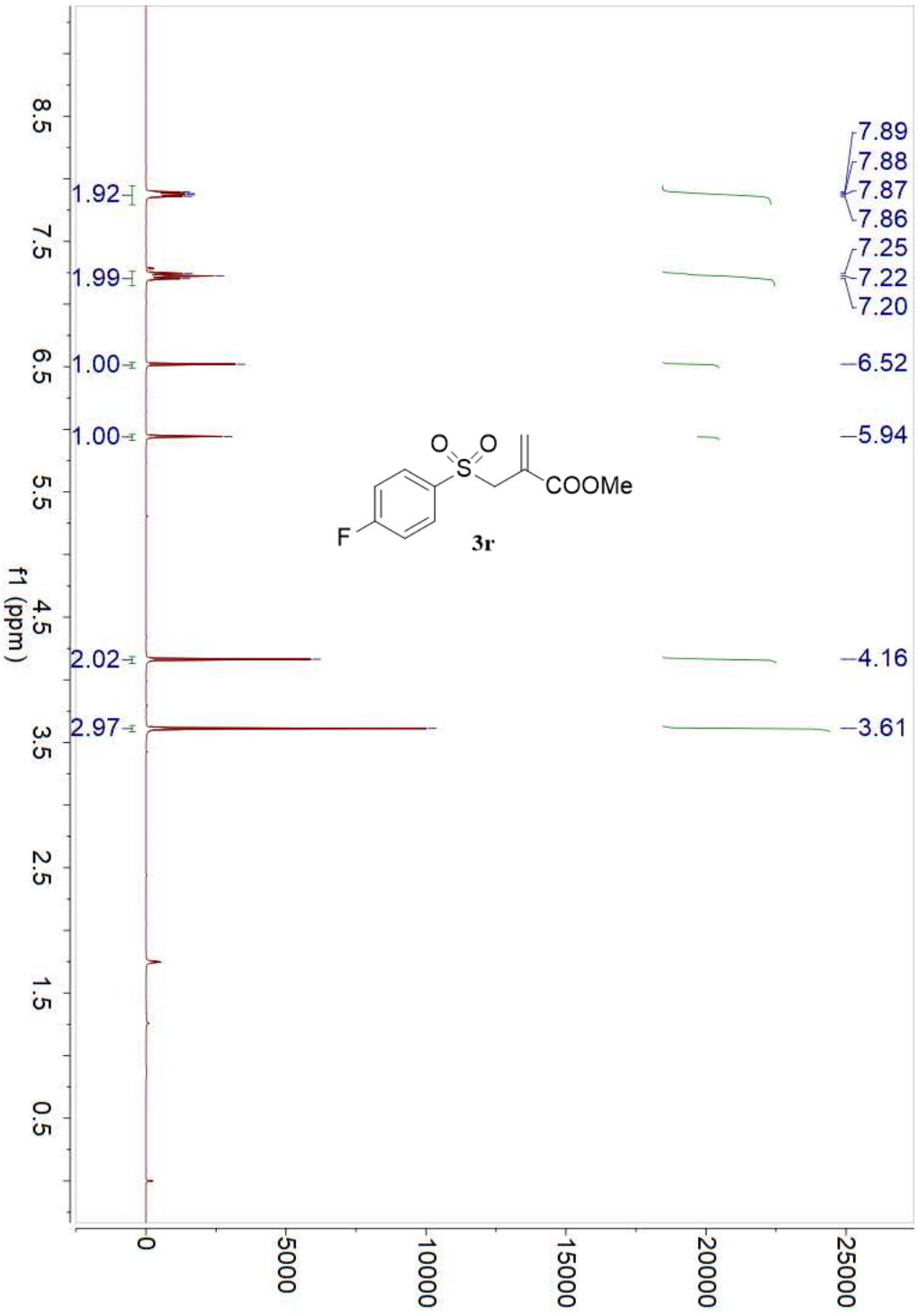

134.3
120.2
61.1
51.2
31.2
28.1
22.6
22.2
21.8
13.9
3o
f1 (ppm)

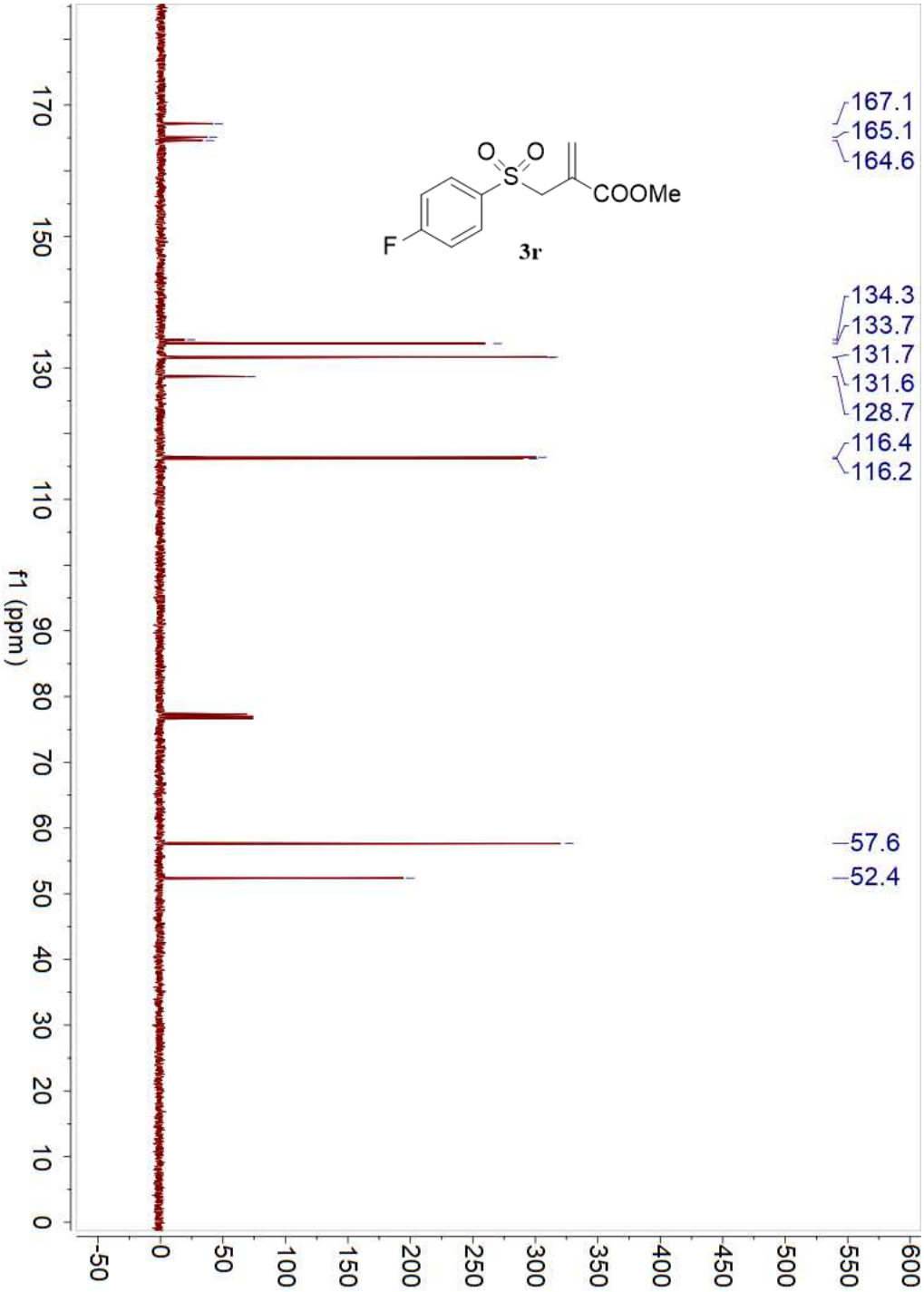

3p
f1 (ppm)
1.00
1.00
2.02
0.99
2.08
3.00
2.02
1.24
2.05
3.29

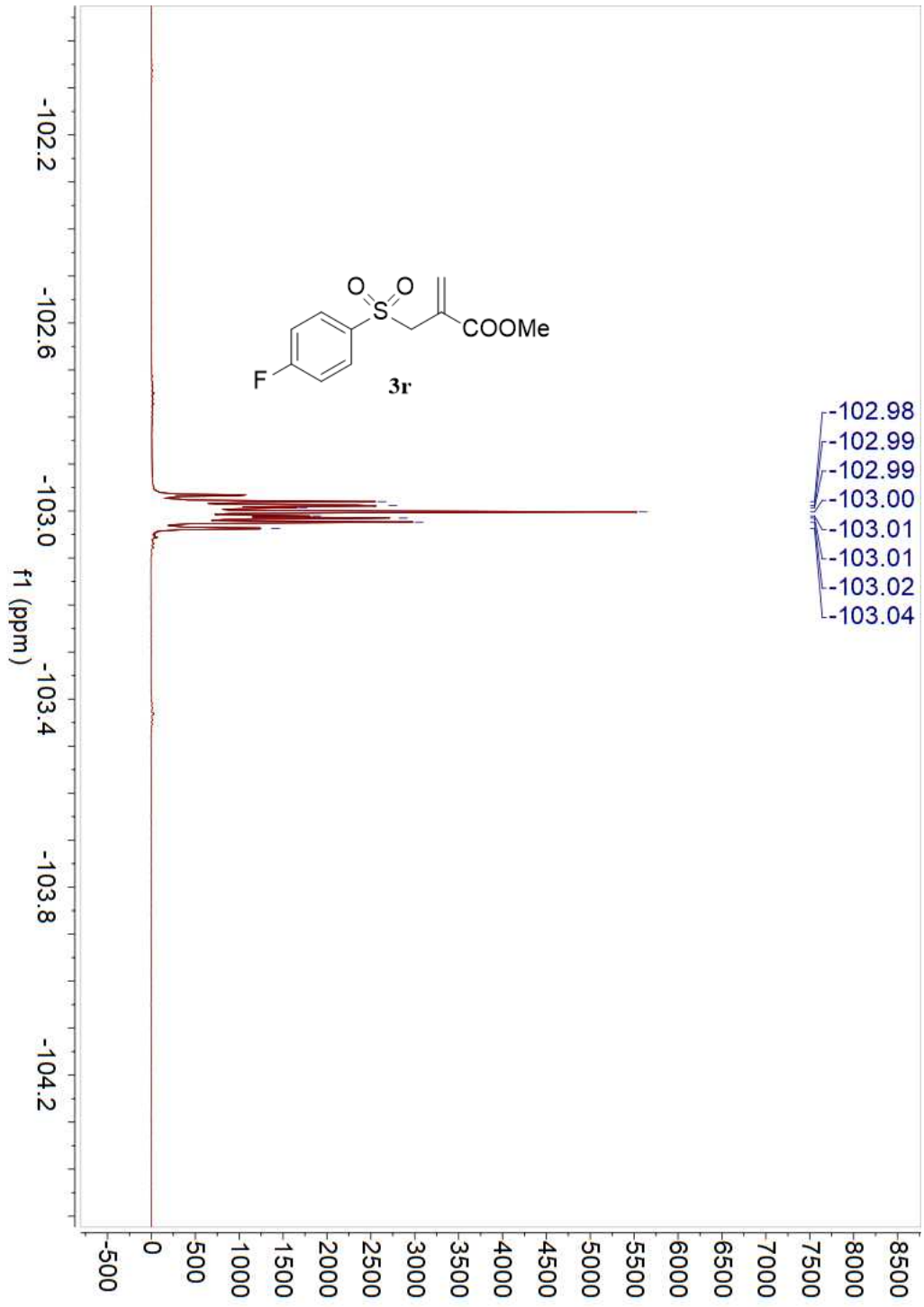

133.9
120.2
59.5
57.8
25.0
25.0
22.9
3p
f1 (ppm)

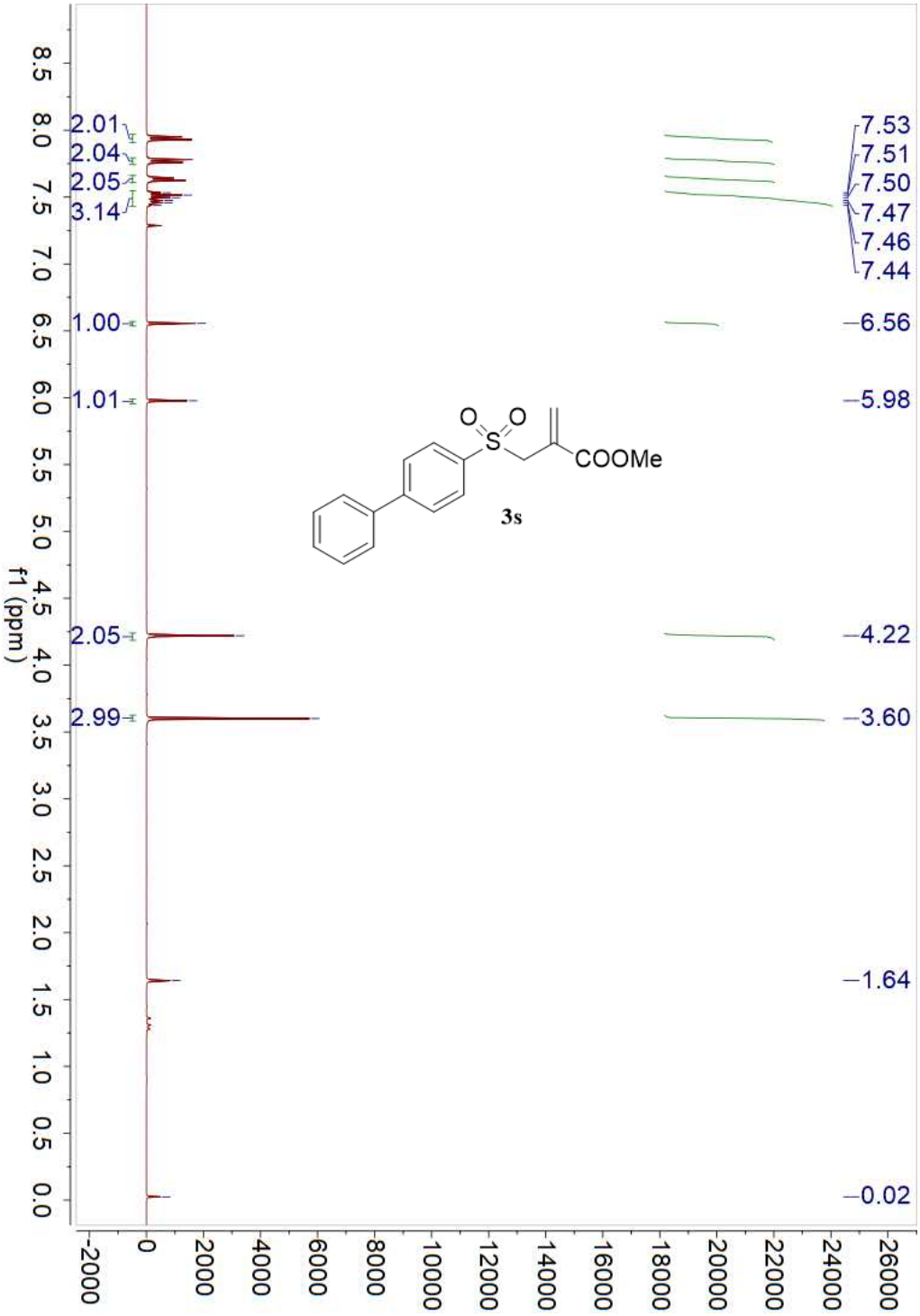

7.78
7.76
7.55
7.53
6.51
5.93
4.14
3.55
1.35
1.94
1.99
1.00
1.00
1.98
2.99
9.04
O
O
S
COOMe
3q
f1 (ppm)

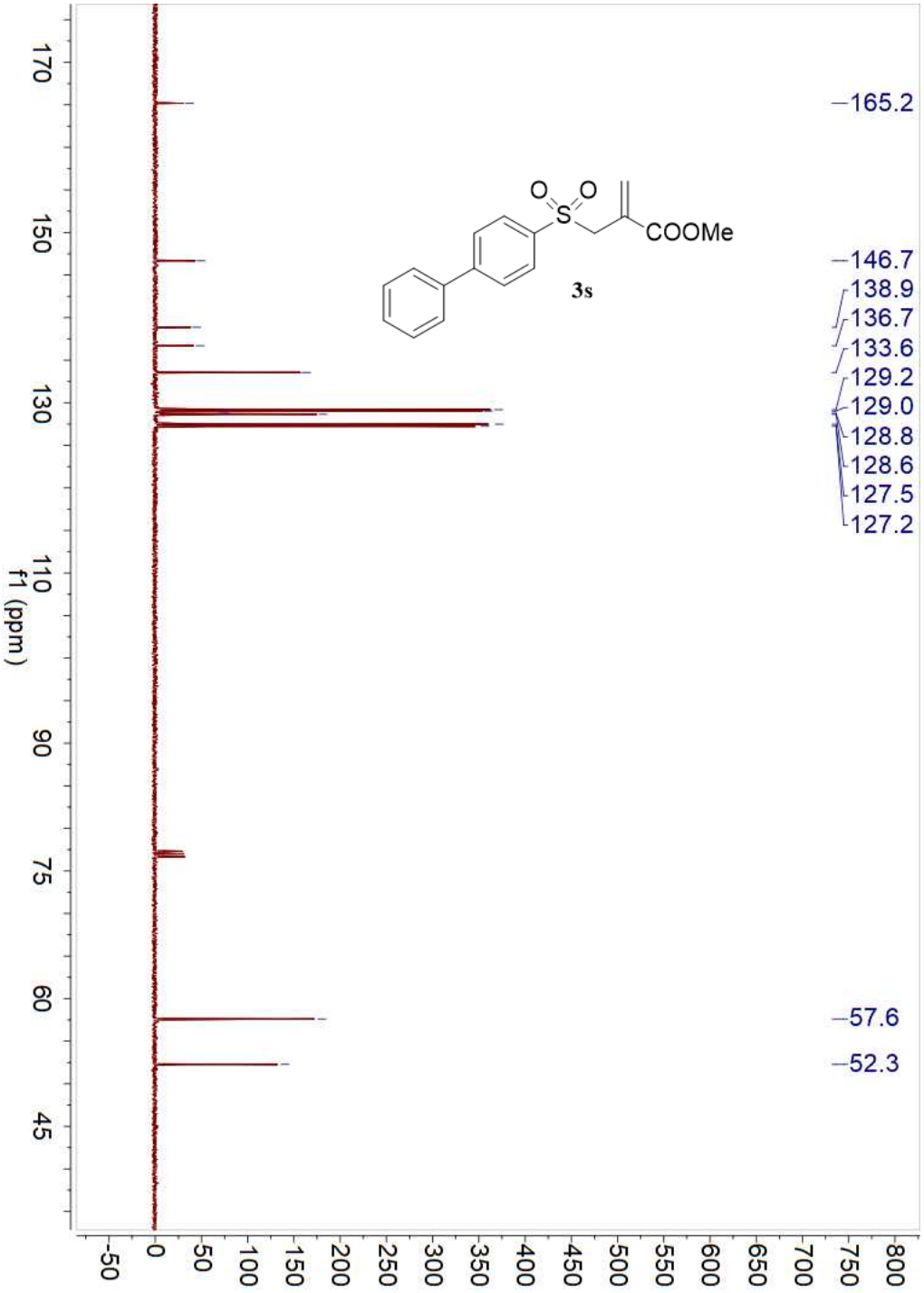

165.2
157.8
135.3
133.5
128.9
128.6
126.0
57.6
52.2
35.2
31.0
COOMe
3q
f1 (ppm)

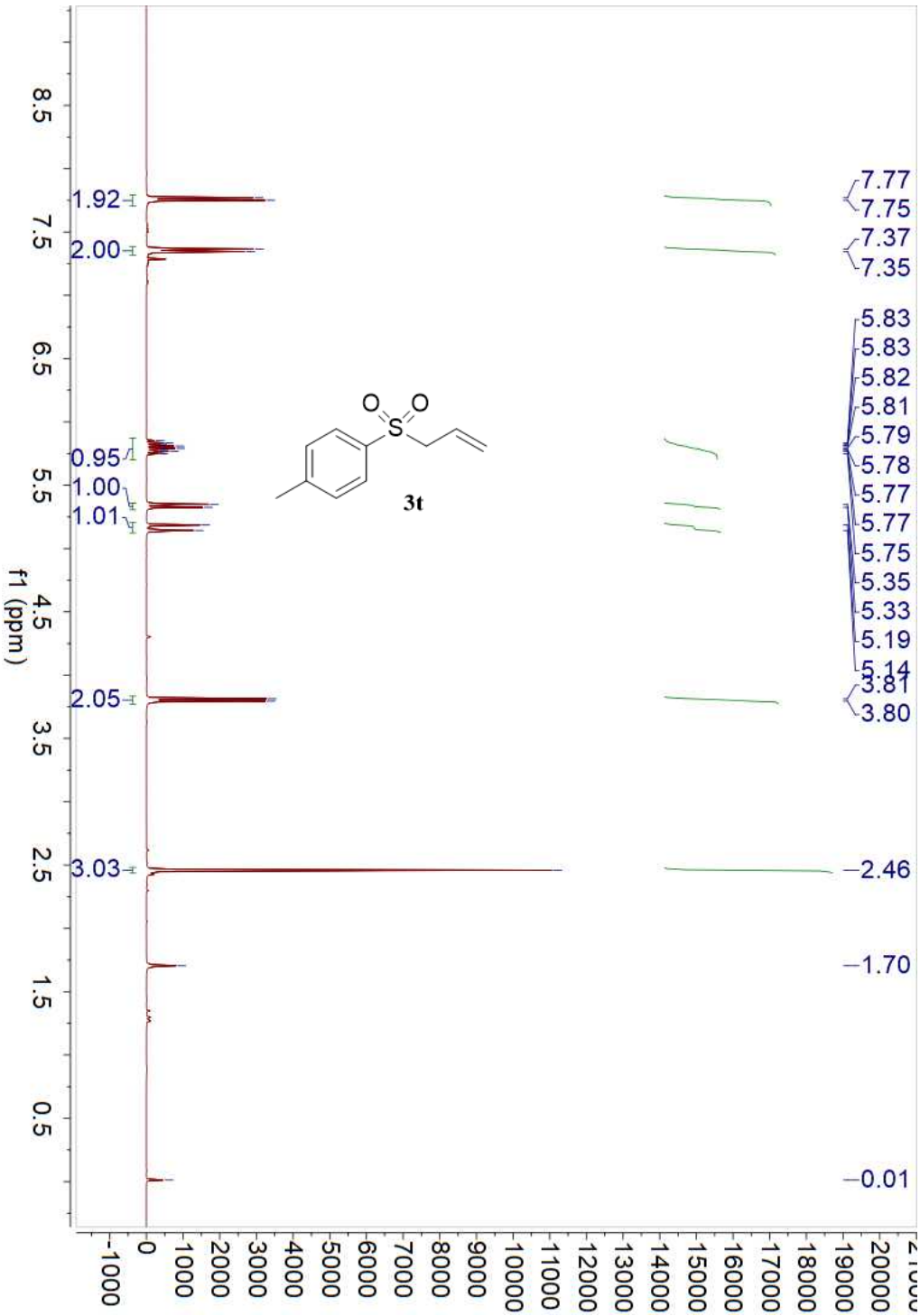

7.89
7.88
7.87
7.86
7.25
7.22
7.20
6.52
5.94
4.16
3.61
1.92
1.99
1.00
1.00
2.02
2.97
O
O
S
COOMe
F
3r
f1 (ppm)
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
0
5000
10000
15000
20000
25000

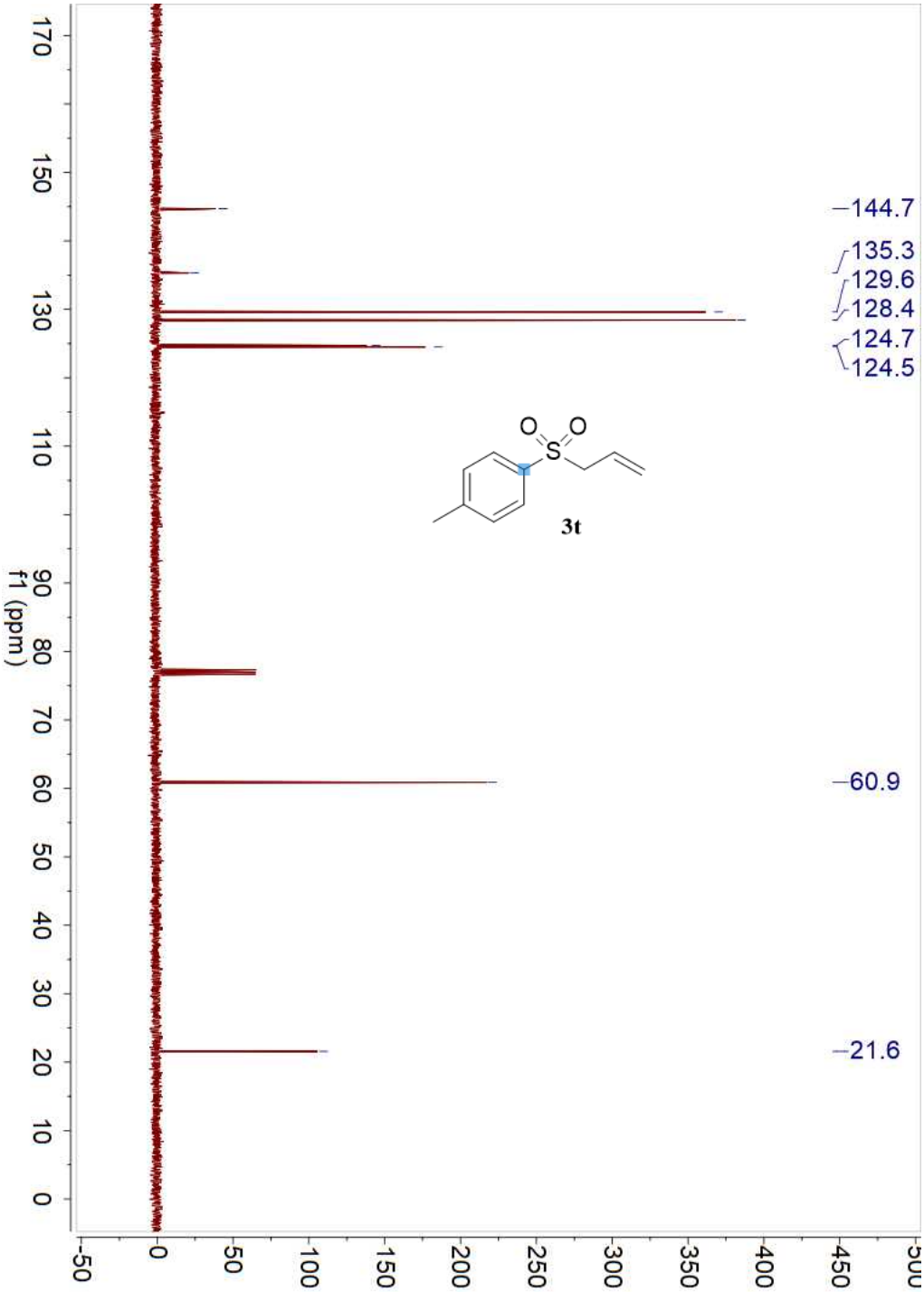

167.1
165.1
164.6
134.3
133.7
131.7
131.6
128.7
116.4
116.2
57.6
52.4
O
O
S
COOMe
F
3r
f1 (ppm)

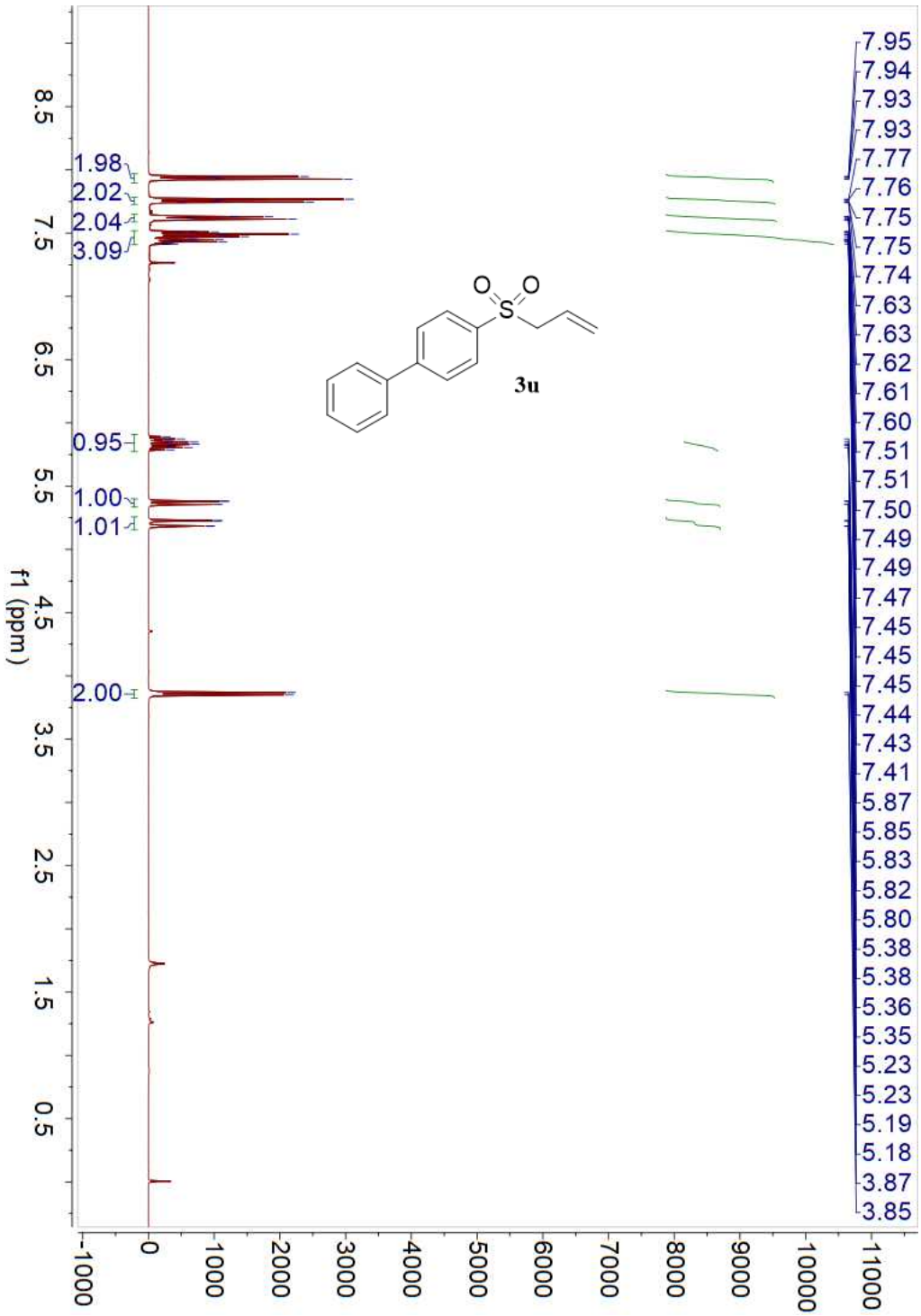

-102.2
-102.6
-103.0
-103.4
-103.8
-104.2
f1 (ppm)
-500
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
7500
8000
8500
-102.98
-102.99
-102.99
-103.00
-103.01
-103.01
-103.02
-103.04
O
O
S
COOMe
F
3r

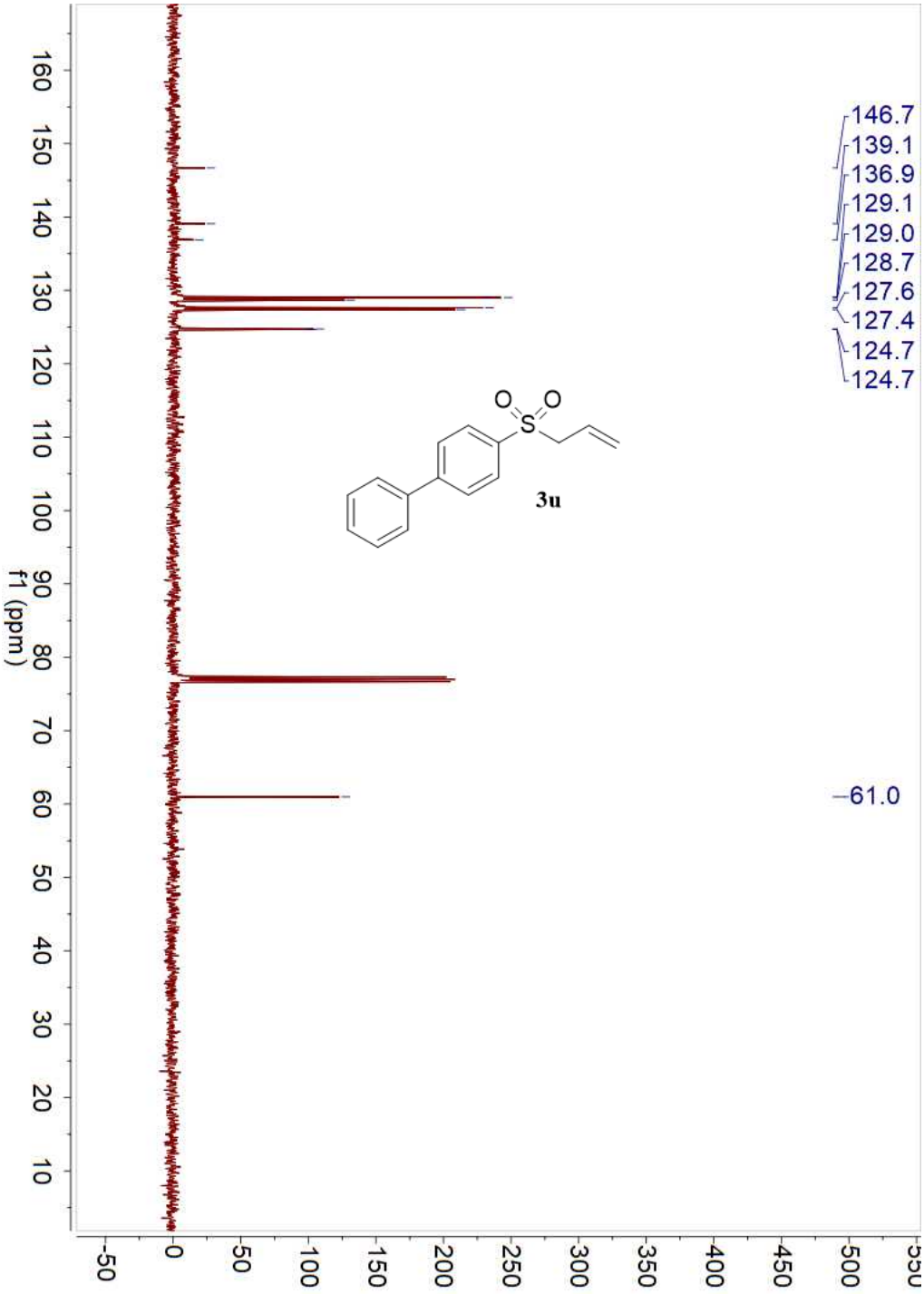

2.01
2.04
2.05
3.14
1.00
1.01
2.05
2.99
7.53
7.51
7.50
7.47
7.46
7.44
6.56
5.98
4.22
3.60
1.64
0.02
O
O
S
COOMe
3s
f1 (ppm)

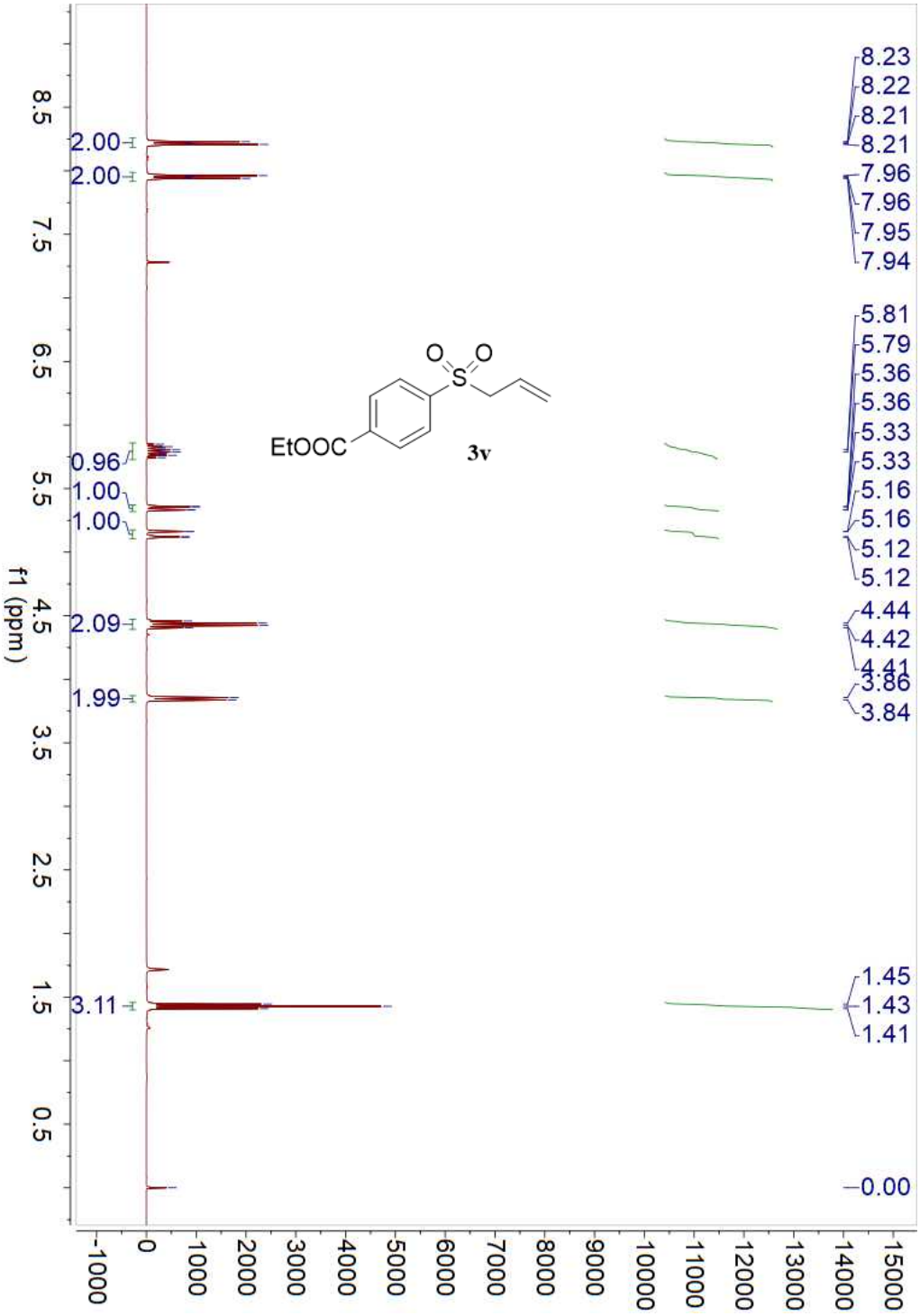

165.2
146.7
138.9
136.7
133.6
129.2
129.0
128.8
128.6
127.5
127.2
57.6
52.3
COOMe
3s
f1 (ppm)

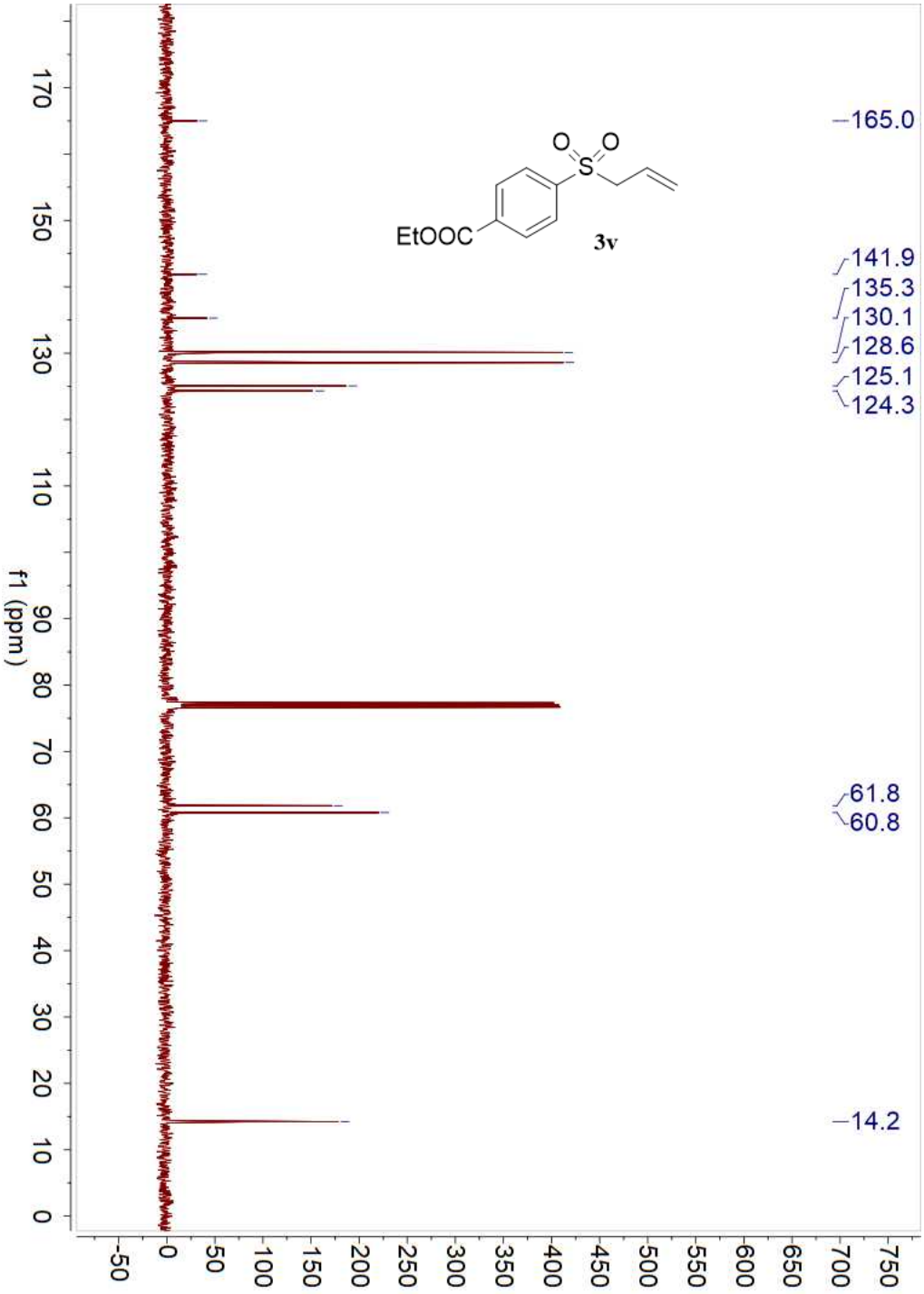

1.92
2.00
0.95
1.00
1.01
2.05
3.03
7.77
7.75
7.37
7.35
5.83
5.83
5.82
5.81
5.79
5.78
5.77
5.77
5.75
5.35
5.33
5.19
5.14
3.81
3.80
2.46
1.70
0.01
3t
f1 (ppm)

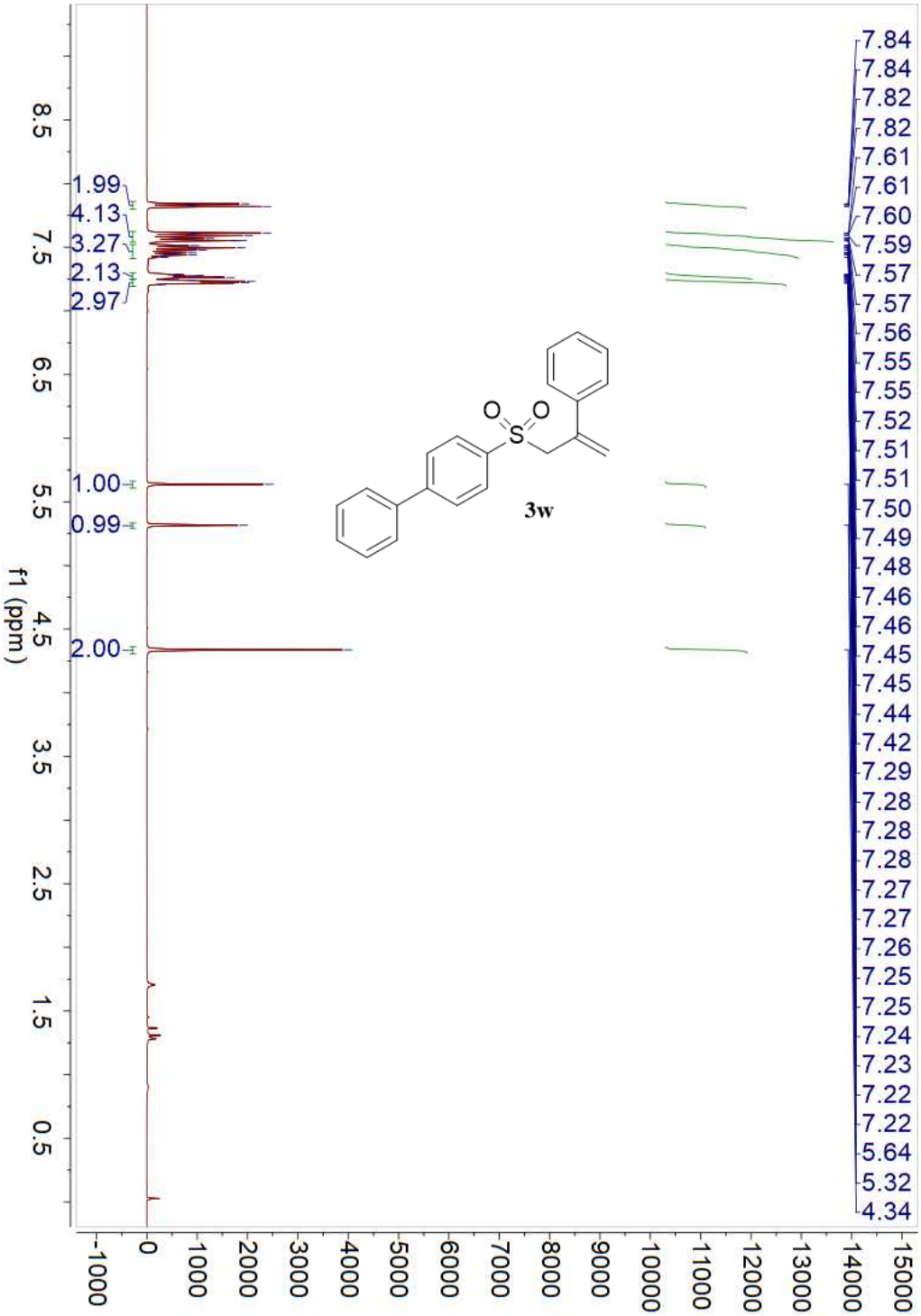

144.7
135.3
129.6
128.4
124.7
124.5
60.9
21.6
3t
f1 (ppm)

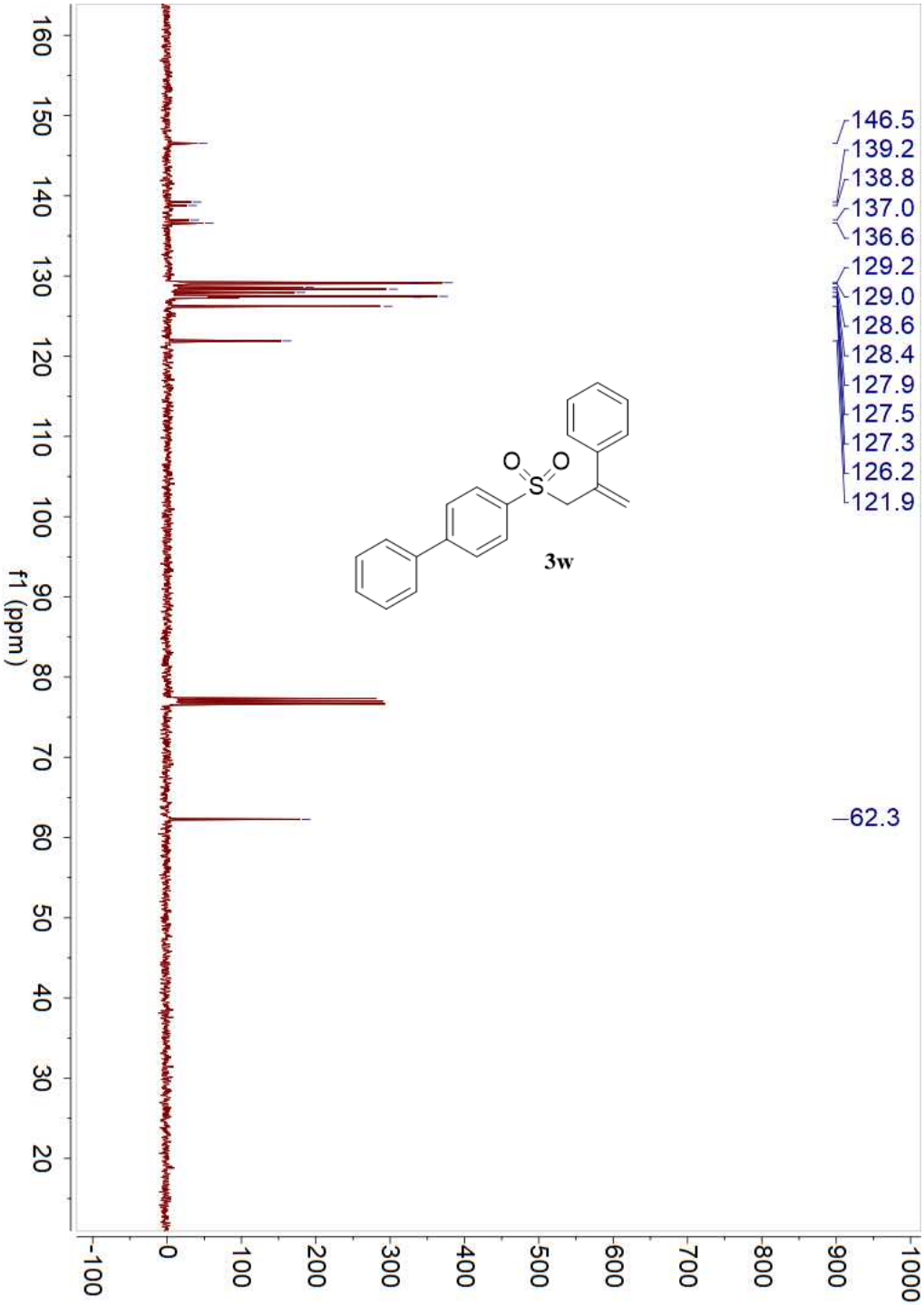

1.98
2.02
2.04
3.09
0.95
1.00
1.01
2.00
3u
f1 (ppm)
7.95
7.94
7.93
7.93
7.77
7.76
7.75
7.75
7.74
7.63
7.63
7.62
7.61
7.60
7.51
7.51
7.50
7.49
7.49
7.47
7.45
7.45
7.45
7.44
7.43
7.41
5.87
5.85
5.83
5.82
5.80
5.38
5.38
5.36
5.35
5.23
5.23
5.19
5.18
3.87
3.85

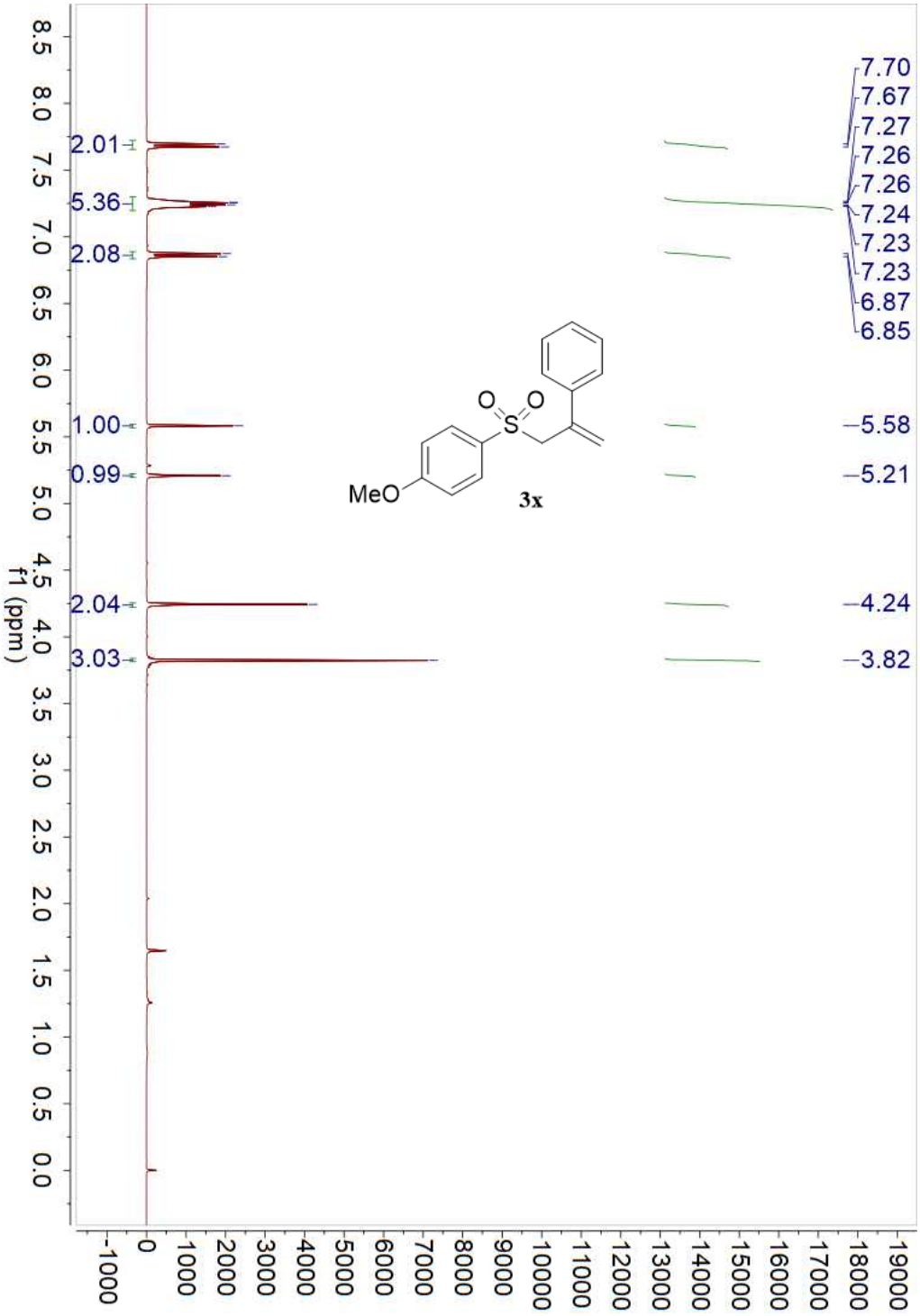

146.7
139.1
136.9
129.1
129.0
128.7
127.6
127.4
124.7
124.7
61.0
O
O
S
3u
f1 (ppm)

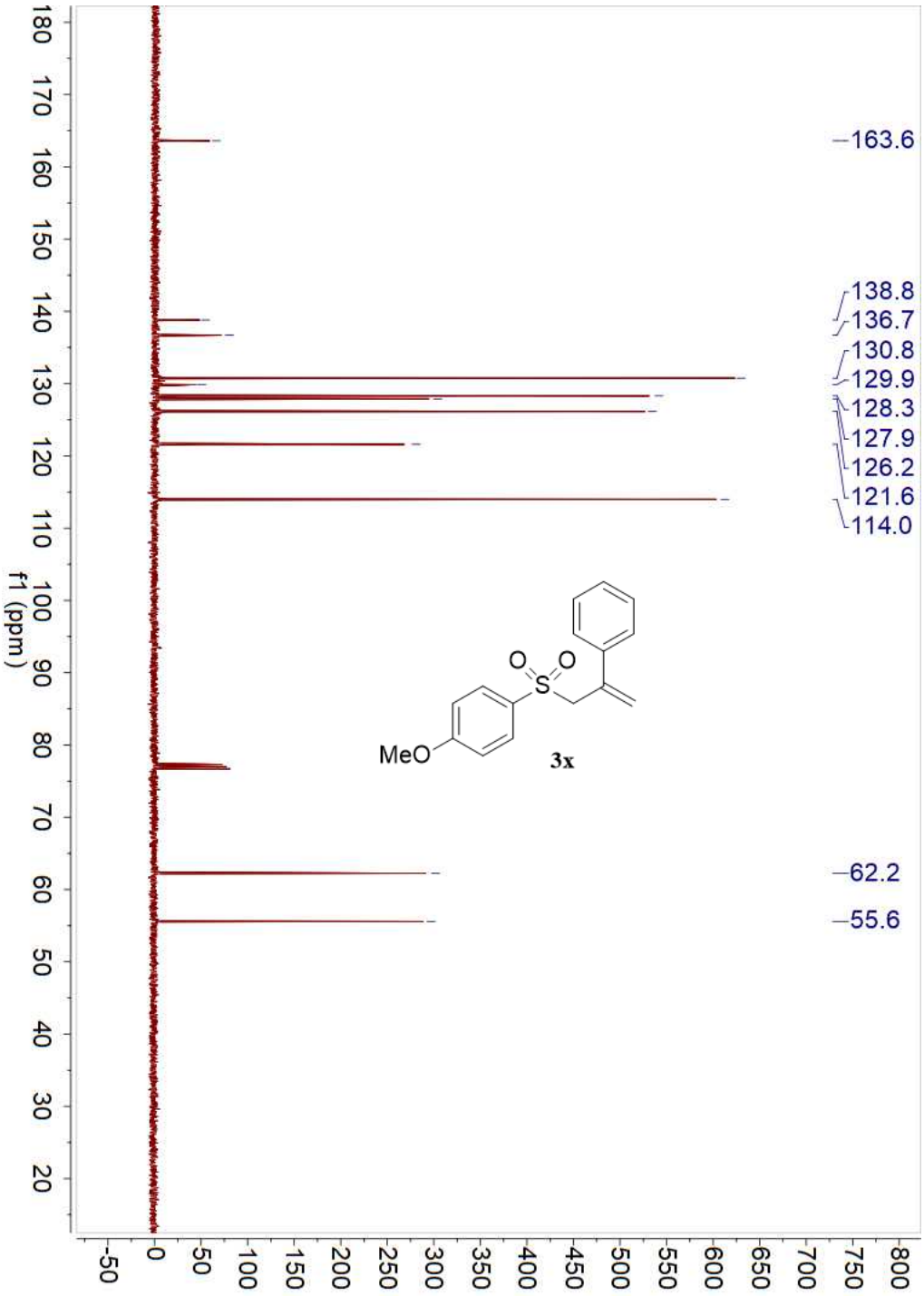

8.23
8.22
8.21
8.21
7.96
7.96
7.95
7.94
5.81
5.79
5.36
5.36
5.33
5.33
5.16
5.16
5.12
5.12
4.44
4.42
4.41
3.86
3.84
1.45
1.43
1.41
0.00
2.00
2.00
0.96
1.00
1.00
2.09
1.99
3.11
O
O
S
EtOOC
3v
f1 (ppm)
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000
15000

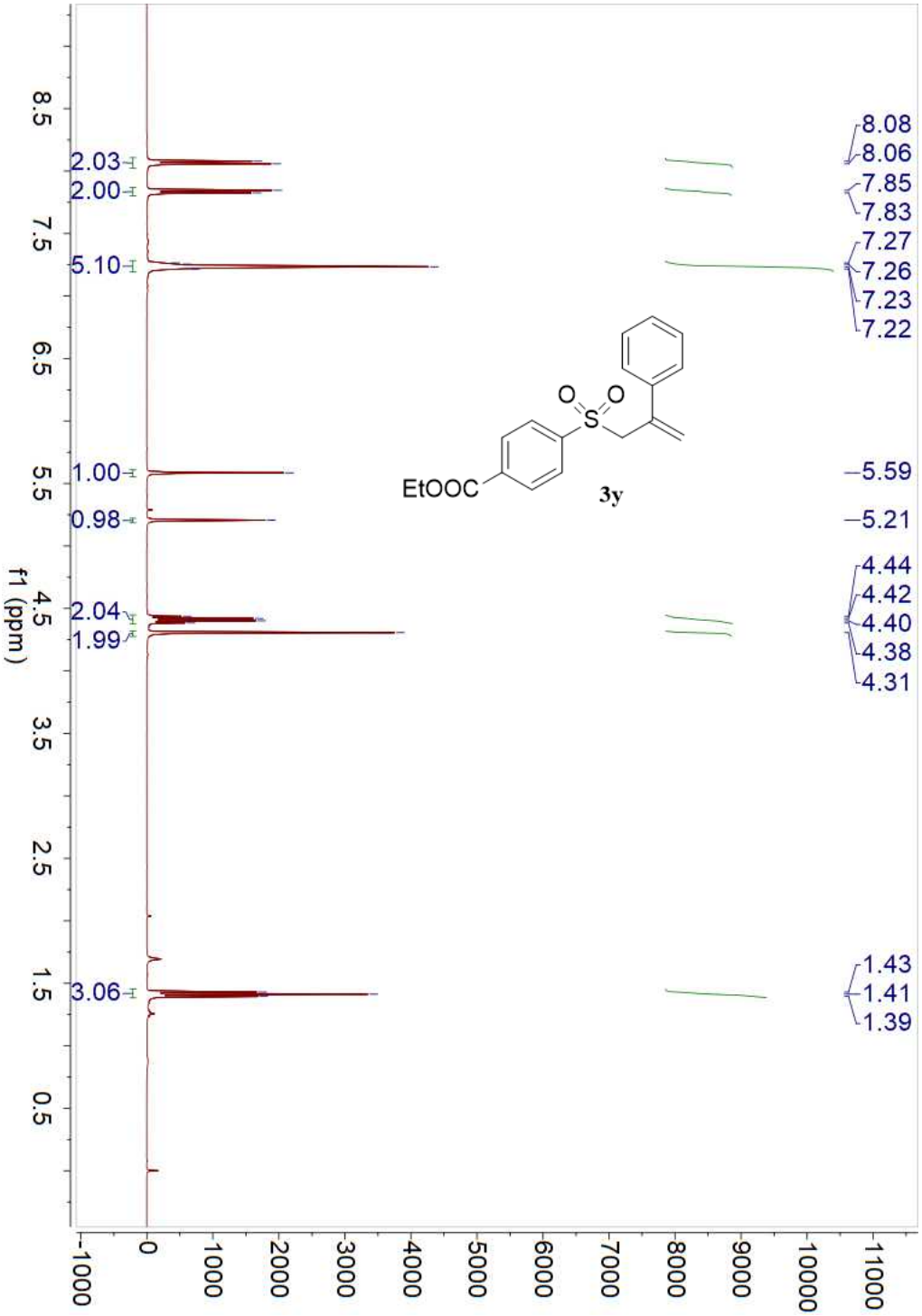

165.0
141.9
135.3
130.1
128.6
125.1
124.3
61.8
60.8
14.2
EtOOC
3v
f1 (ppm)

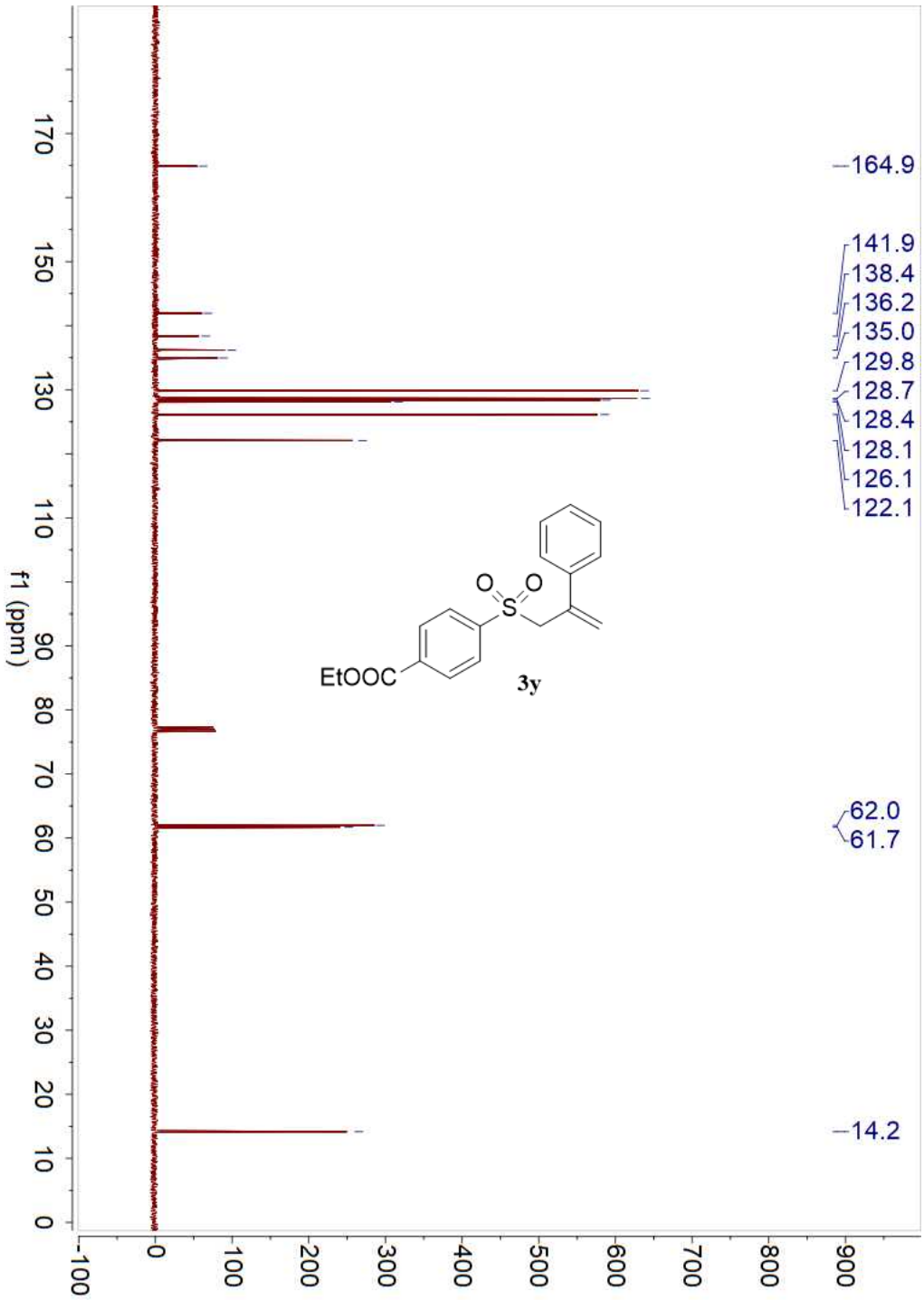

7.84
7.84
7.82
7.82
7.61
7.61
7.60
7.59
7.57
7.57
7.56
7.55
7.55
7.52
7.51
7.51
7.50
7.49
7.48
7.46
7.46
7.45
7.45
7.44
7.42
7.29
7.28
7.28
7.28
7.27
7.27
7.26
7.25
7.25
7.24
7.23
7.22
7.22
5.64
5.32
4.34
1.99
4.13
3.27
2.13
2.97
1.00
0.99
2.00
O
O
S
3w
f1 (ppm)
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000
15000

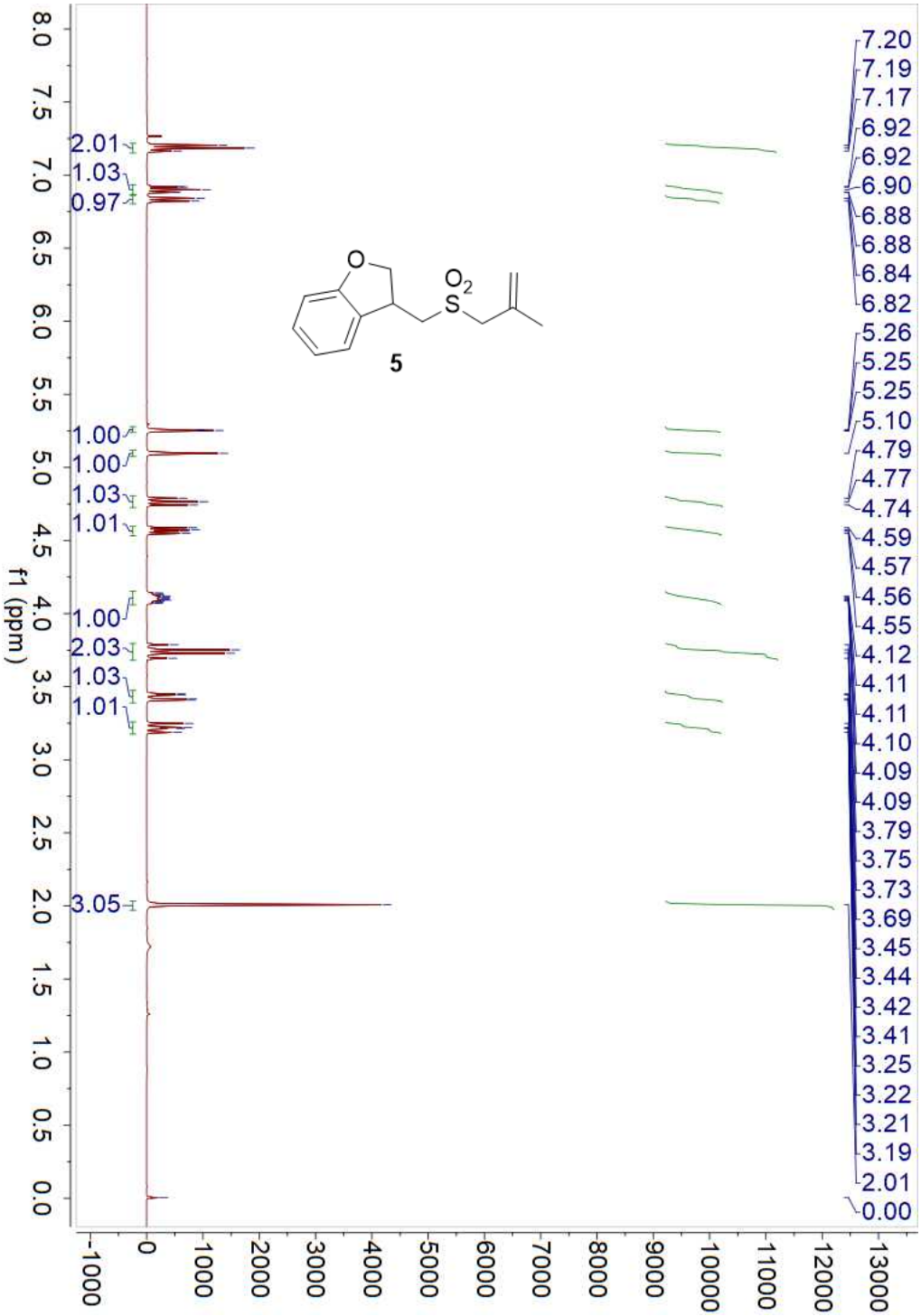

146.5
139.2
138.8
137.0
136.6
129.2
129.0
128.6
128.4
127.9
127.5
127.3
126.2
121.9
62.3
O
O
S
3w
f1 (ppm)

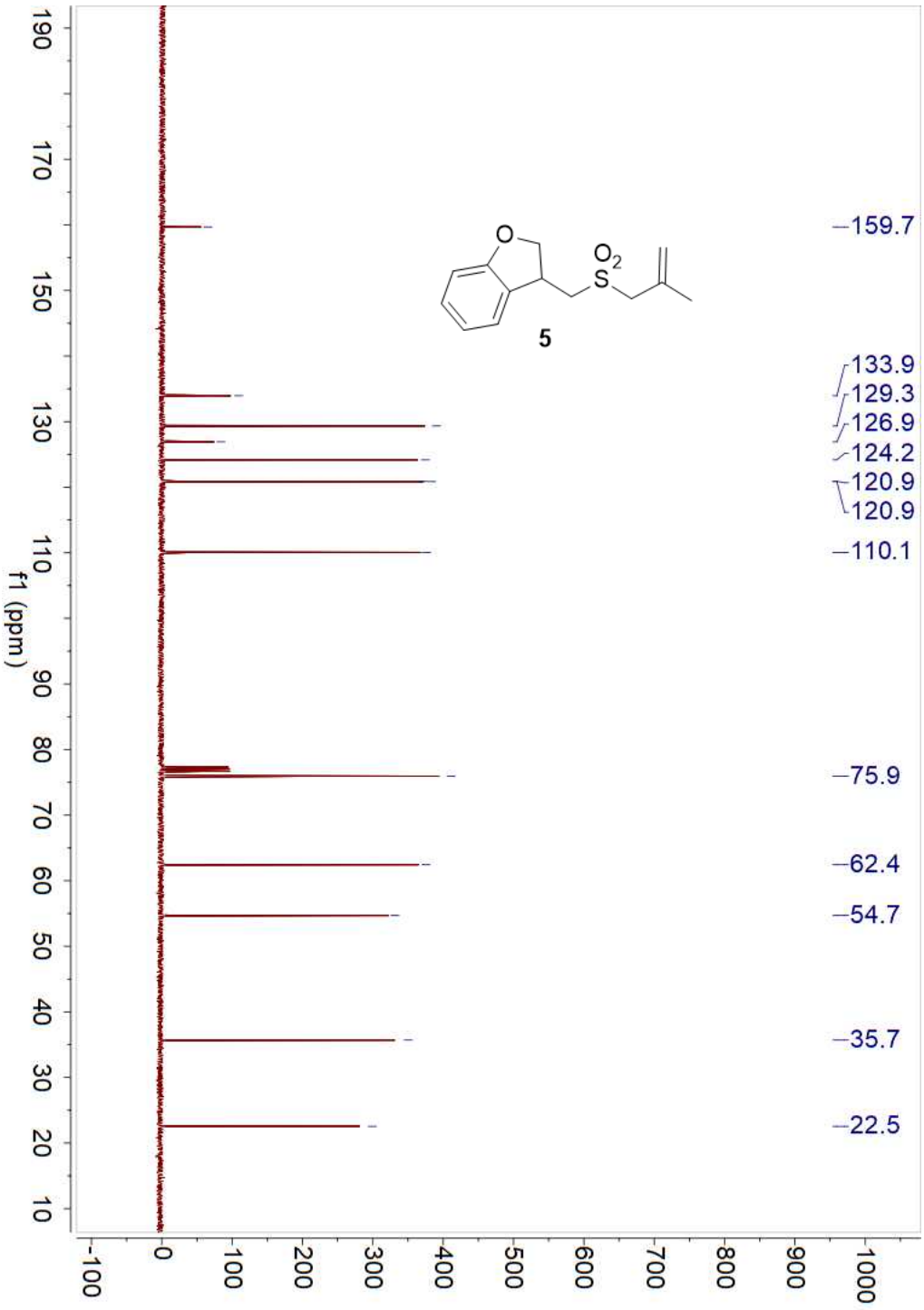

7.70
7.67
7.27
7.26
7.26
7.24
7.23
7.23
6.87
6.85
5.58
5.21
4.24
3.82
2.01
5.36
2.08
1.00
0.99
2.04
3.03
MeO
3x
f1 (ppm)


163.6
138.8
136.7
130.8
129.9
128.3
127.9
126.2
121.6
114.0
62.2
55.6
MeO
3x
f1 (ppm)


8.08
8.06
7.85
7.83
7.27
7.26
7.23
7.22
5.59
5.21
4.44
4.42
4.40
4.38
4.31
1.43
1.41
1.39
2.03
2.00
5.10
1.00
0.98
2.04
1.99
3.06
EtOOC
3y
f1 (ppm)


164.9
141.9
138.4
136.2
135.0
129.8
128.7
128.4
128.1
126.1
122.1
62.0
61.7
14.2
EtOOC
O
O
S
3y
f1 (ppm)


f1 (ppm)
2.01
1.03
0.97
1.00
1.00
1.03
1.01
1.00
2.03
1.03
1.01
3.05
O
O2
S
5
7.20
7.19
7.17
6.92
6.92
6.90
6.88
6.88
6.84
6.82
5.26
5.25
5.25
5.10
4.79
4.77
4.74
4.59
4.57
4.56
4.55
4.12
4.11
4.11
4.10
4.09
4.09
3.79
3.75
3.73
3.69
3.45
3.44
3.42
3.41
3.25
3.22
3.21
3.19
2.01
0.00


159.7
133.9
129.3
126.9
124.2
120.9
120.9
110.1
75.9
62.4
54.7
35.7
22.5
f1 (ppm)
O
O2
S
5