Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

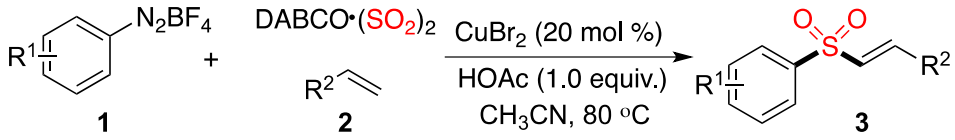
Supporting Information

1. General experimental methods (S2).
2. General experimental procedure and characterization data (S2-S13).
3. ^{1}H and ^{13}C NMR spectra of all products (S14 –S83).

General experimental methods:

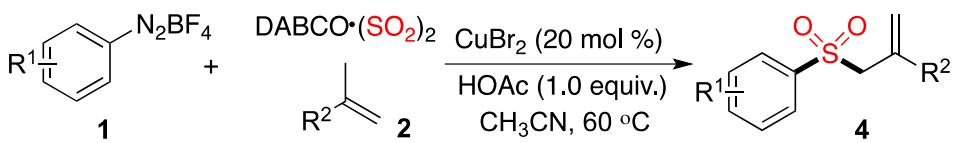
Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63μm, standard grade). Analytical thin–layer chromatography was performed using 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 copper(II)-catalyzed three-component reaction of aryldiazonium tetrafluoroborates, sulfur dioxide, with alkenes



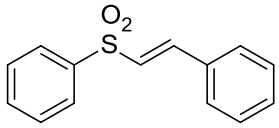
1 **2** **3**

Alkene **2** (0.4 mmol) and acetic acid (0.2 mmol) were added to a solution of $CuBr_2$ (0.04 mmol), aryldiazonium tetrafluoroborate **1** (0.2 mmol) and DABCO•$(SO_2)_2$ (0.5 mmol) in CH_3CN (1.0 mL). The mixture was stirred at 80 °C for about 30 minutes. After the reaction was completed (indicated by TLC), the solvent was evaporated and the residue was purified directly by flash column chromatograph (EtOAc/*n*-hexane, 1:6) to provide the desired product **3**.

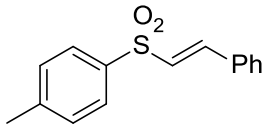


1 **2** **4**

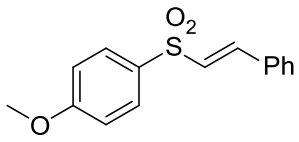
Alkene **2** (0.4 mmol) and acetic acid (0.2 mmol) was added to a solution of $CuBr_2$ (0.04 mmol), aryldiazonium tetrafluoroborate **1** (0.2 mmol) and DABCO•$(SO_2)_2$ (0.5 mmol) in CH_3CN (1.0 mL). The mixture was stirred at 60 °C for about 30 minutes. After the reaction was completed (indicated by TLC), the solvent was evaporated and the residue was purified directly by flash column chromatograph (EtOAc/n-hexane, 1:6) to give the desired product **4**.



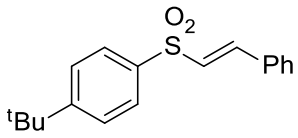
(*E*)-(2-(Phenylsulfonyl)vinyl)benzene **3a**[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 2H), 7.70 (d, *J* = 15.4 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.51 – 7.48 (m, 2H), 7.43 – 7.39 (m, 3H), 6.87 (d, *J* = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 140.7, 133.4, 132.3, 131.2, 129.3, 129.1, 128.6, 127.6, 127.2.



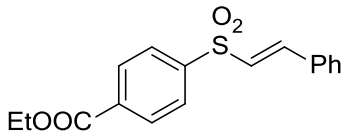
(*E*)-1-Methyl-4-(styrylsulfonyl)benzene **3b**[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 15.4 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.44 – 7.32 (m, 5H), 6.87 (d, *J* = 15.4 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 141.9, 137.7, 132.4, 131.1, 129.9, 129.0, 128.5, 127.7, 127.6, 21.6.



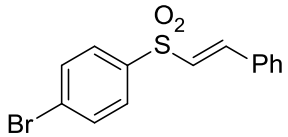
(*E*)-1-Methoxy-4-(styrylsulfonyl)benzene **3c**[2]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 2H), 7.64 (d, *J* = 15.4 Hz, 1H), 7.50 – 7.47 (m, 2H), 7.44 – 7.36 (m, 3H), 7.02 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 15.4 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 141.4, 132.5, 132.2, 131.0, 129.9, 129.0, 128.4, 127.9, 114.5, 55.7.



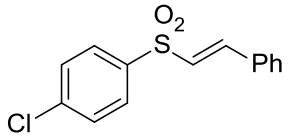
(*E*)-1-(*tert*-Butyl)-4-(styrylsulfonyl)benzene **3d**[3]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 15.4 Hz, 1H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.53 – 7.46 (m, 2H), 7.44 – 7.37 (m, 3H), 6.88 (d, *J* = 15.4 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 141.9, 137.6, 132.4, 131.1, 129.0, 128.5, 127.6, 127.5, 126.3, 35.2, 31.0.



Ethyl (*E*)-4-(styrylsulfonyl)benzoate **3e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.5 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 15.4 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.47 – 7.38 (m, 3H), 6.87 (d, *J* = 15.4 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 144.5, 143.6, 134.8, 132.1, 131.5, 130.4, 129.1, 128.7, 127.6, 126.5, 61.7, 14.2. HRMS (ESI) calcd for $C_{17}H_{17}O_4S^+$: 317.0842 (M + H^+), found: 317.0834.

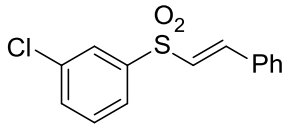


(*E*)-1-Bromo-4-(styrylsulfonyl)benzene **3f**[2]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.6 Hz, 2H), 7.71 (dd, *J* = 11.9, 3.3 Hz, 3H), 7.53 – 7.48 (m, 2H), 7.46 – 7.41 (m, 3H), 6.85 (d, *J* = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 139.8, 132.6, 132.1, 131.4, 129.2, 129.1, 128.6, 126.8.

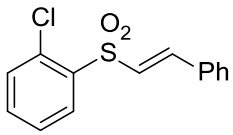


(*E*)-1-Chloro-4-(styrylsulfonyl)benzene **3g**[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.7 Hz, 2H), 7.71 (d, *J* = 15.4 Hz, 1H), 7.58 – 7.48 (m, 4H), 7.45 – 7.41 (m, 3H), 6.85 (d,

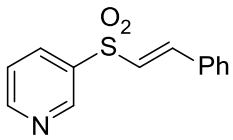
J = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 140.1, 139.2, 132.1, 131.4, 129.6, 129.1, 128.6, 127.3, 126.8.



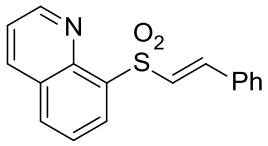
(*E*)-1-Chloro-3-(styrylsulfonyl)benzene **3h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (t, *J* = 1.7 Hz, 1H), 7.89 – 7.81 (m, 1H), 7.73 (d, *J* = 15.4 Hz, 1H), 7.61 – 7. 59 (m, 1H), 7.55 – 7.48 (m, 3H), 7.46 – 7.42 (m, 3H), 6.86 (d, *J* = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 142.5, 135.5, 133.5, 132.1, 131.5, 130.6, 129.1, 128.7, 127.7, 126.5, 125.7. HRMS (ESI) calcd for $C_{14}H_{12}ClO_2S^+$: 279.0241 (M + H^+), found: 279.0253.



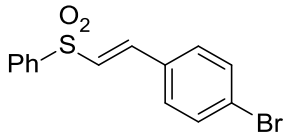
(*E*)-1-Chloro-2-(styrylsulfonyl)benzene **3i**[2]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.79 (d, *J* = 15.4 Hz, 1H), 7.58 – 7.41 (m, 8H), 7.10 (d, *J* = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 143.6, 138.2, 134.5, 132.3, 131.9, 131.4, 130.7, 129.1, 128.7, 127.4, 125.2.



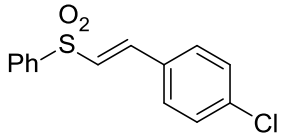
(*E*)-3-(Styrylsulfonyl)pyridine **3j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.86 (d, *J* = 3.1 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 15.4 Hz, 1H), 7.54 – 7.41 (m, 6H), 6.89 (d, *J* = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 150.0, 148.7, 144.1, 135.4, 131.9, 131.7, 129.2, 128.7, 126.5, 123.9. HRMS (ESI) calcd for $C_{13}H_{12}NO_2S^+$: 246.0583 (M + H^+), found: 246.0583.



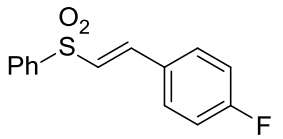
(*E*)-8-(Styrylsulfonyl)quinolone **3k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (dd, *J* = 4.1, 1.4 Hz, 1H), 8.60 (dd, *J* = 7.3, 1.1 Hz, 1H), 8.28 (dd, *J* = 8.3, 1.3 Hz, 1H), 8.10 (d, *J* = 7.2 Hz, 1H), 7.90 (d, *J* = 15.6 Hz, 1H), 7.80 (d, *J* = 15.6 Hz, 1H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.57 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.53 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.42 – 7.35 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 143.2, 138.4, 136.5, 134.1, 132.9, 130.9, 130.5, 128.9, 128.6, 128.3, 125.7, 124.8, 122.2. HRMS (ESI) calcd for $C_{17}H_{14}NO_2S^+$: 296.0740 (M + H^+), found: 296.0741.



(*E*)-1-Bromo-4-(2-(phenylsulfonyl)vinyl)benzene **3l**[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.67 – 7.53 (m, 6H), 7.36 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 140.6, 133.5, 132.3, 131.3, 129.9, 129.4, 128.0, 127.7, 125.6.

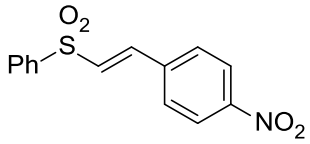


(*E*)-1-Chloro-4-(2-(phenylsulfonyl)vinyl)benzene **3m**[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.69 – 7.61 (m, 2H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 140.4, 137.2, 133.5, 130.8, 129.7, 129.4, 129.2, 127.9, 127.7.

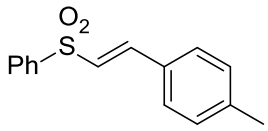


(*E*)-1-Fluoro-4-(2-(phenylsulfonyl)vinyl)benzene **3n**[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01

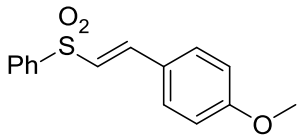
– 7.91 (m, 2H), 7.69 – 7.62 (m, 2H), 7.59 – 7.55 (m, 2H), 7.53 – 7.47 (m, 2H), 7.10 (t, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3 (d, J_{C-F} = 253.5Hz), 141.1, 140.6, 133.4, 130.6 (d, J_{C-F} = 9.1Hz), 129.3, 128.6, 127.6, 127.0, 116.3 (d, J_{C-F} = 22.2Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.7 (m, 1F).



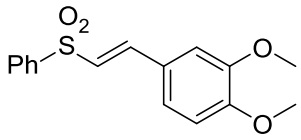
(*E*)-1-Nitro-4-(2-(phenylsulfonyl)vinyl)benzene **3o**[2]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.8 Hz, 2H), 8.03 – 7.93 (m, 2H), 7.74 (d, *J* = 15.5 Hz, 1H), 7.69 – 7.57 (m, 5H), 7.03 (d, *J* = 15.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 139.8, 139.2, 138.4, 134.0, 131.8, 129.6, 129.3, 128.0, 124.3.



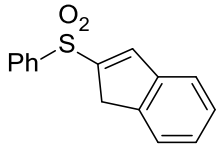
(*E*)-1-Methyl-4-(2-(phenylsulfonyl)vinyl)benzene **3p**[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.91 (m, 2H), 7.70 – 7.60 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.82 (d, *J* = 15.4 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 141.8, 140.9, 133.2, 129.8, 129.6, 129.3, 128.6, 127.6, 126.0, 21.5.



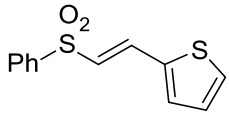
(*E*)-1-Methoxy-4-(2-(phenylsulfonyl)vinyl)benzene **3q**[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.92 (m, 2H), 7.70 – 7.59 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 15.3 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 142.3, 141.1, 133.1, 130.4, 129.2, 127.5, 125.0, 124.4, 114.5, 55.4.



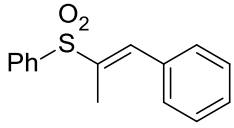
(*E*)-1,2-Dimethoxy-4-(2-(phenylsulfonyl)vinyl)benzene **3r**[4]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.95 (m, 2H), 7.66 –7.54 (m, 4H), 7.11 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.98 (d, *J* = 1.8 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.74 (d, *J* = 15.3 Hz, 1H), 3.91 (d, *J* = 9.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 149.3, 142.6, 141.1, 133.2, 129.3, 127.5, 125.2, 124.6, 123.5, 111.1, 110.0, 56.0, 55.9.



2-(Phenylsulfonyl)-1*H*-indene **3s**[5]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 2H), 7.73 (s, 1H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.58 – 7.54 (m, 3H), 7.48 – 7.44 (m, 1H), 7.37 – 7.35 (m, 2H), 3.66 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 138.7, 137.1, 133.3, 132.6, 129.3, 128.3, 127.7, 127.4, 125.6, 124.3, 124.0, 37.8.

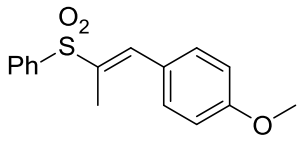


(*E*)-2-(2-(Phenylsulfonyl)vinyl)thiophene **3t**[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.81 (d, *J* = 15.1 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.45 (d, *J* = 5.0 Hz, 1H), 7.33 (d, *J* = 3.4 Hz, 1H), 7.08 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.66 (d, *J* = 15.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 136.9, 135.1, 133.3, 132.4, 130.0, 129.3, 128.3, 127.6, 125.4.

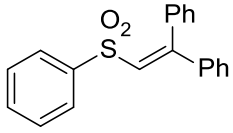


(*E*)-((1-Phenylprop-1-en-2-yl)sulfonyl)benzene **3u**[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.91 (m, 2H), 7.85 (d, *J* = 1.1 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 2H), 7.43 – 7.38 (m, 5H), 2.13 (d, *J* = 1.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 137.2,

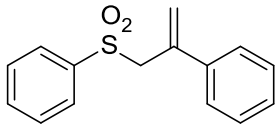
133.8, 133.3, 129.6, 129.3, 129.2, 128.8, 128.7, 128.2, 13.2.



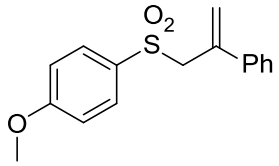
(*E*)-1-Methoxy-4-(2-(phenylsulfonyl)prop-1-en-1-yl)benzene **3v**[6]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.89 (m, 2H), 7.78 (s, 1H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.14 (d, *J* = 1.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 139.4, 137.2, 133.1, 131.5, 129.1, 128.0, 126.3, 114.2, 109.9, 55.3, 13.3.



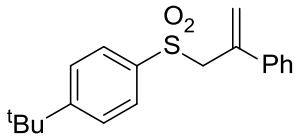
(2-(Phenylsulfonyl)ethene-1,1-diyl)dibenzene **3w**[7]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.39 – 7.28 (m, 8H), 7.25 – 7.21 (m, 2H), 7.12 – 7.07 (m, 2H), 7.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 141.4, 139.1, 135.4, 132.8, 130.3, 129.7, 128.9, 128.7, 128.6, 128.6, 128.2, 127.8, 127.6.



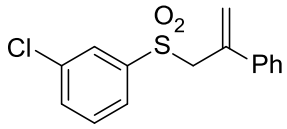
((2-Phenylallyl)sulfonyl)benzene **4a**[8]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.75 (m, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.23 (m, 5H), 5.62 (s, 1H), 5.25 (s, 1H), 4.30 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.5, 136.4, 133.6, 128.8, 128.6, 128.4, 128.0, 126.1, 121.8, 62.0.



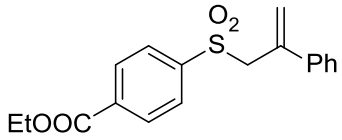
1-Methoxy-4-((2-phenylallyl)sulfonyl)benzene **4b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.9 Hz, 2H), 7.30 – 7.28 (m, 2H), 7.26 – 7.21 (m, 3H), 6.87 (d, *J* = 8.9 Hz, 2H), 5.59 (s, 1H), 5.21 (s, 1H), 4.25 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 138.8, 136.7, 130.8, 129.9, 128.4, 127.9, 126.2, 121.7, 114.0, 62.3, 55.6. HRMS (ESI) calcd for $C_{16}H_{17}O_3S^+$: 289.0893 (M + H^+), found: 289.0899.



1-(*tert*-Butyl)-4-((2-phenylallyl)sulfonyl)benzene **4c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.24 – 7.17 (m, 5H), 5.62 (s, 1H), 5.33 (s, 1H), 4.28 (s, 2H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 138.8, 136.5, 135.4, 128.4, 128.3, 127.9, 126.1, 125.8, 121.8, 62.0, 35.1, 31.0. HRMS (ESI) calcd for $C_{19}H_{23}O_2S^+$: 315.1413 (M + H^+), found: 315.1414.

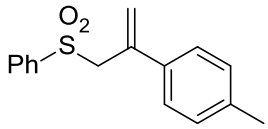


1-Chloro-3-((2-phenylallyl)sulfonyl)benzene **4d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.49 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.26 – 7.20 (m, 5H), 5.63 (s, 1H), 5.29 (s, 1H), 4.30 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 138.4, 136.3, 135.1, 133.7, 130.1, 128.8, 128.4, 128.2, 126.7, 126.1, 122.3, 62.1. HRMS (ESI) calcd for $C_{15}H_{14}ClO_2S^+$: 293.0398 (M + H^+), found: 293.0388.

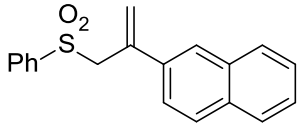


Ethyl 4-((2-phenylallyl)sulfonyl)benzoate **4e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.23-7.25 (m, 5H), 5.61 (s, 1H), 5.22 (s, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 4.32 (s, 2H), 1.43 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 142.0, 138.4, 136.2, 135.0, 129.9, 128.7, 128.4, 128.2, 126.2, 122.1, 62.1, 61.7,

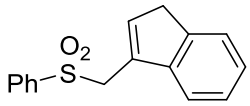
14.2. HRMS (ESI) calcd for $C_{18}H_{19}O_4S^+$: 331.0999 (M + H^+), found: 331.0998.



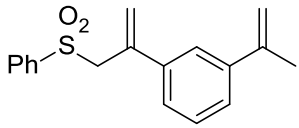
1-Methyl-4-(3-(phenylsulfonyl)prop-1-en-2-yl)benzene **4f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 5.57 (s, 1H), 5.15 (s, 1H), 4.27 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 137.9, 136.3, 135.8, 133.5, 129.1, 128.8, 128.6, 126.0, 120.9, 62.1, 21.0. HRMS (ESI) calcd for $C_{16}H_{17}O_2S^+$: 273.0944 (M + H^+), found: 273.0946.



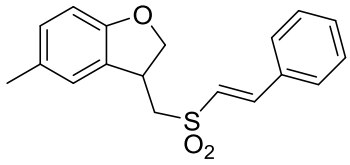
2-(3-(Phenylsulfonyl)prop-1-en-2-yl)naphthalene **4g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.69 (m, 5H), 7.65 (d, *J* = 1.1 Hz, 1H), 7.50 – 7.34 (m, 6H), 5.75 (s, 1H), 5.33 (s, 1H), 4.40 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 136.3, 135.8, 133.6, 133.0, 132.8, 128.8, 128.6, 128.2, 128.1, 127.4, 126.3, 125.4, 124.0, 122.2, 117.5, 62.1. HRMS (ESI) calcd for $C_{19}H_{17}O_2S^+$: 309.0944 (M + H^+), found: 309.0933.



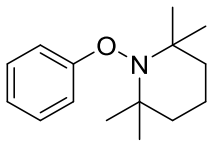
3-((Phenylsulfonyl)methyl)-1*H*-indene **4h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.4 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.53 (m, 3H), 7.26 – 7.16 (m, 3H), 6.37 (s, 1H), 4.39 (s, 2H), 3.35 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 143.0, 138.3, 137.4, 133.7, 131.8, 128.9, 128.5, 126.2, 125.2, 123.7, 119.4, 55.7, 38.3. HRMS (ESI) calcd for $C_{16}H_{15}O_2S^+$: 271.0787 (M + H^+), found: 271.0782.



1-(3-(Phenylsulfonyl)prop-1-en-2-yl)-3-(prop-1-en-2-yl)benzene **4i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.33 – 7.30 (m, 2H), 7.24 – 7.15 (m, 2H), 5.62 (s, 1H), 5.30 (d, *J* = 7.9 Hz, 2H), 5.10 (s, 1H), 4.31 (s, 2H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 141.4, 138.7, 138.4, 136.6, 133.6, 128.8, 128.6, 128.2, 125.2, 123.5, 121.9, 112.9, 62.1, 21.8. HRMS (ESI) calcd for $C_{18}H_{19}O_2S^+$: 299.1100 ($M + H^+$), found: 299.1100.



(*E*)-5-Methyl-3-((styrylsulfonyl)methyl)-2,3-dihydrobenzofuran **6**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 15.5 Hz, 1H), 7.56 – 7.53 (m, 2H), 7.49 – 7.46(m, 3H), 7.02 – 6.96 (m, 2H), 6.88 (d, *J* = 15.5 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 4.78 (t, *J* = 9.2 Hz, 1H), 4.60 (dd, *J* = 9.6, 6.4 Hz, 1H), 4.08 (dd, *J* = 9.5, 2.6 Hz, 1H), 3.48 (dd, *J* = 14.1, 2.9 Hz, 1H), 3.32 (dd, *J* = 14.1, 10.6 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 131.9, 131.7, 130.3, 129.7, 129.5, 129.2, 128.7, 126.9, 124.7, 124.6, 109.6, 76.0, 59.2, 36.7, 20.7. HRMS (ESI) calcd for $C_{18}H_{19}O_3S^+$: 315.1049 ($M + H^+$), found: 315.1065.



2,2,6,6-Tetramethyl-1-phenoxypiperidine **7**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 4H), 6.86 (t, *J* = 6.5 Hz, 1H), 1.67 – 1.57 (m, 5H), 1.46 – 1.41 (m, 1H), 1.26 (s, 6H), 1.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 128.6, 119.8, 113.9, 60.3, 39.7, 32.6, 20.4, 17.0.

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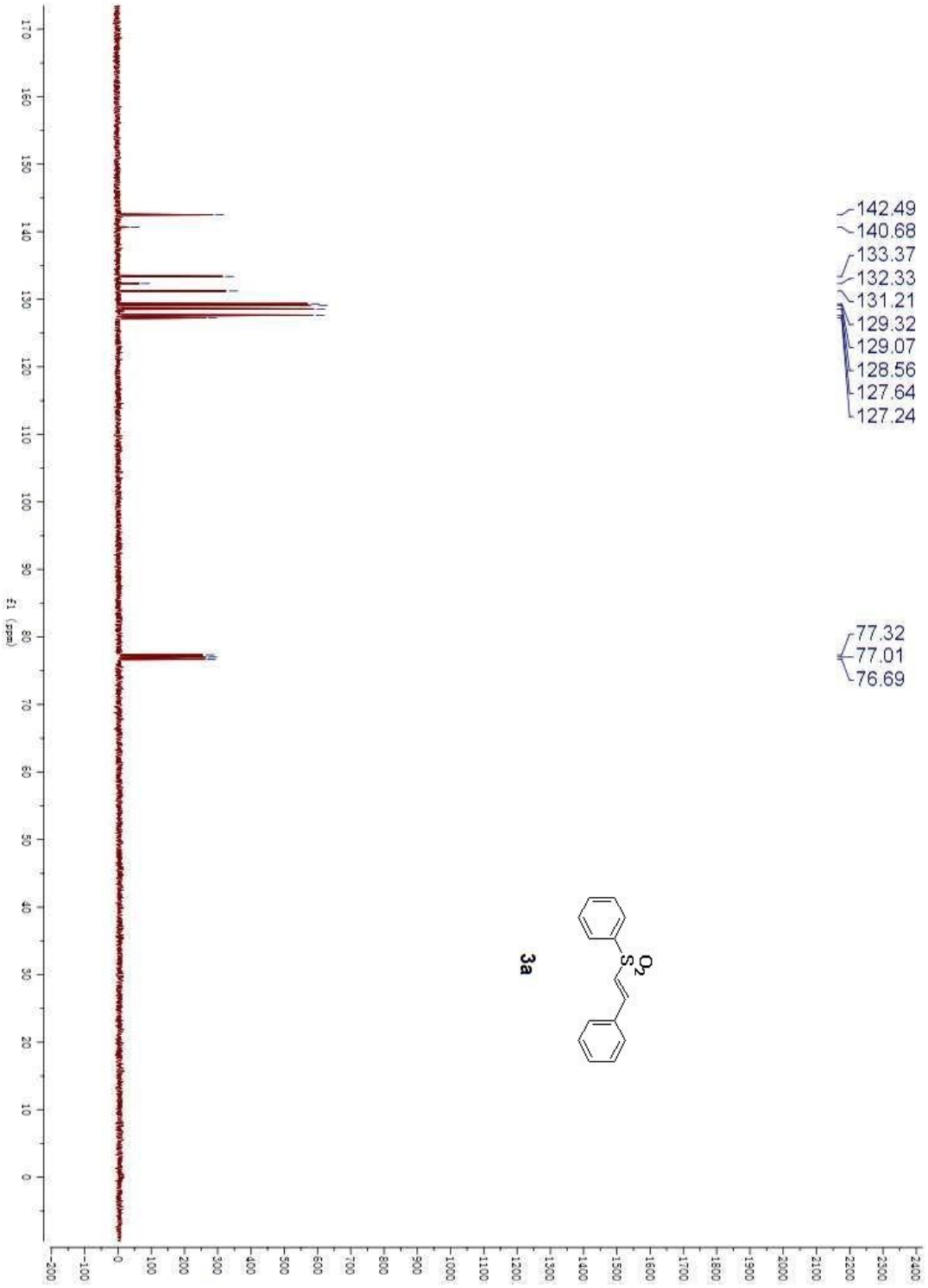
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127.24
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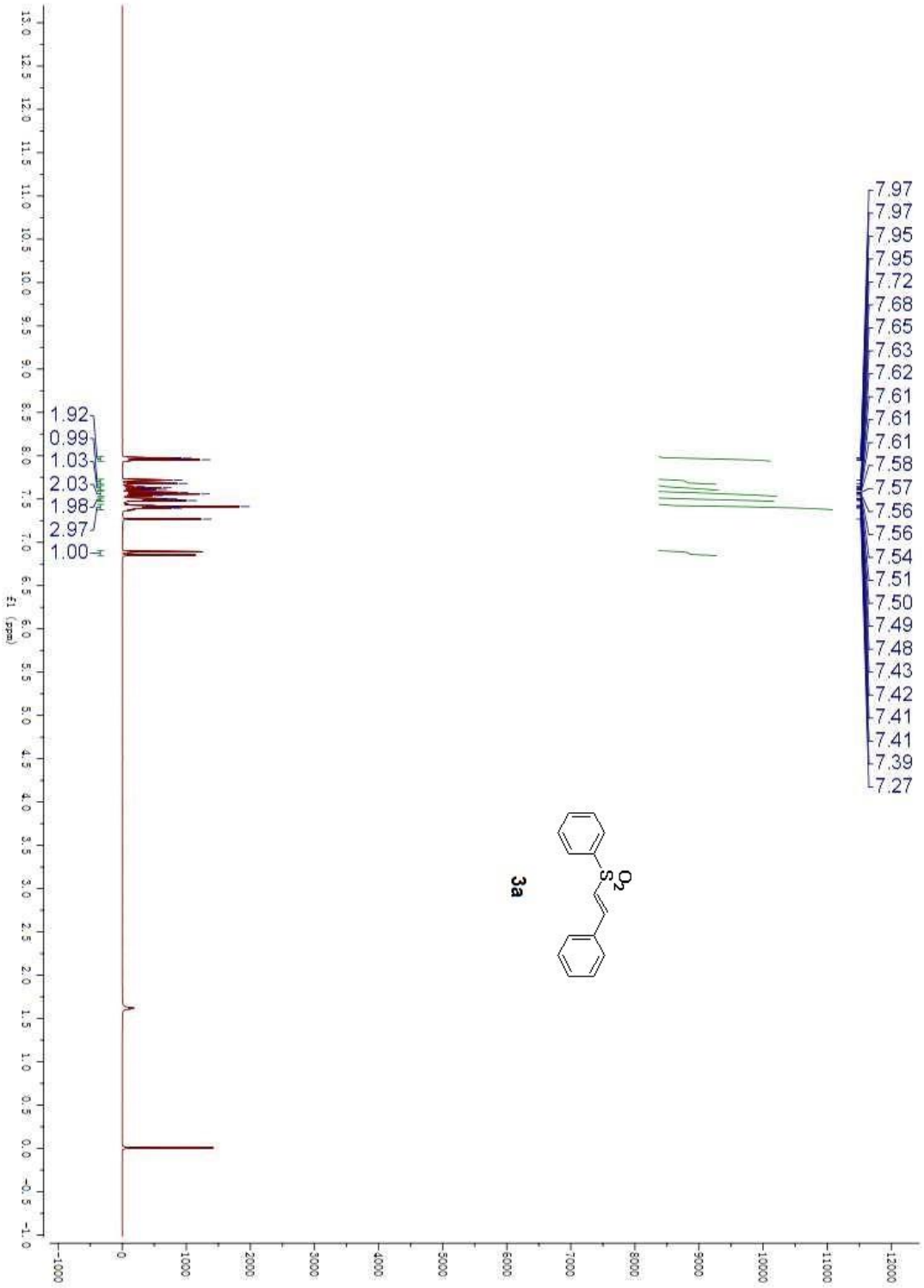
77.01
76.69
f1 (ppm)
3a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7.50
7.49
7.48
7.43
7.42
7.41
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1.98
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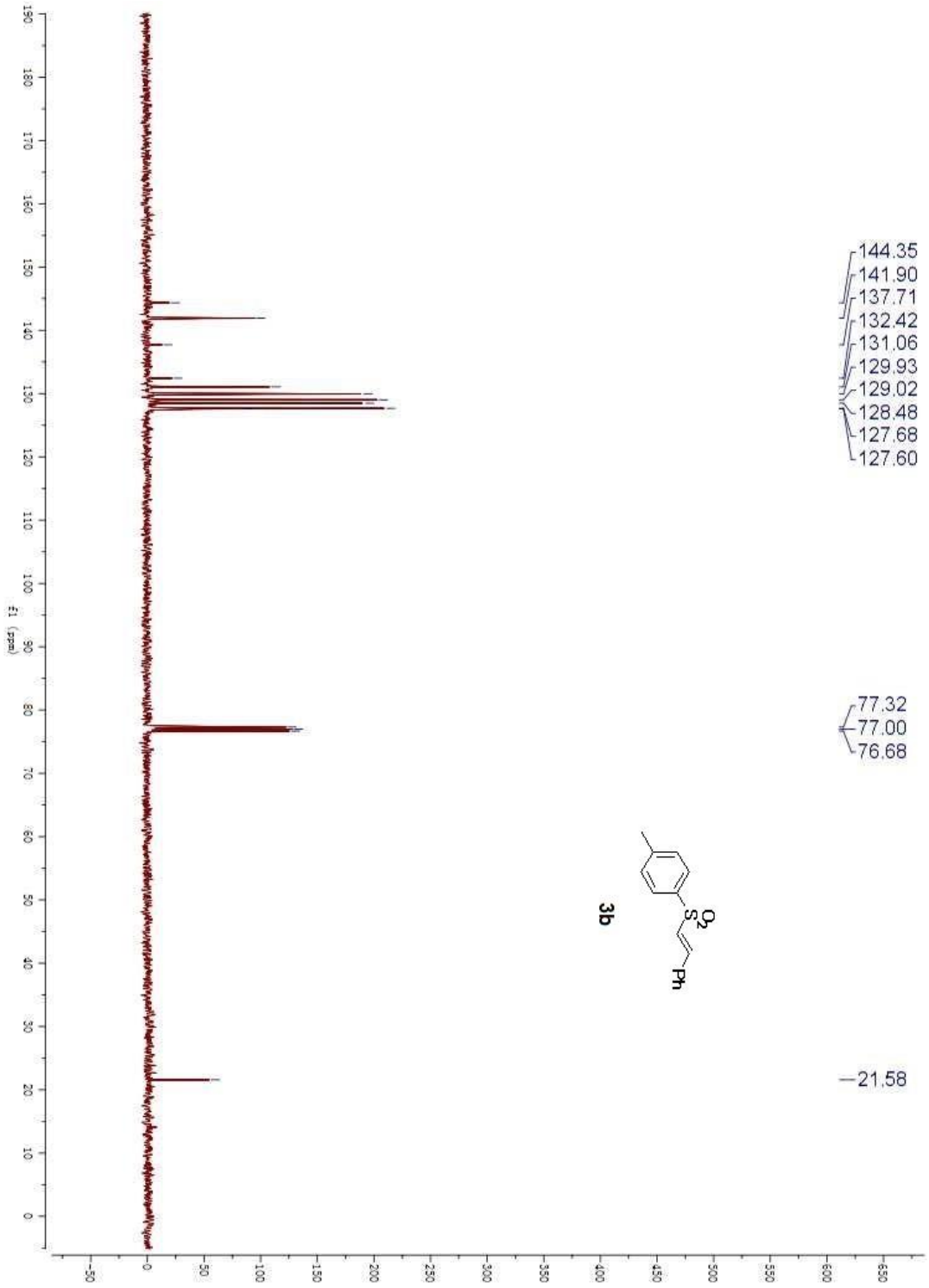
O2
S
3a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3b
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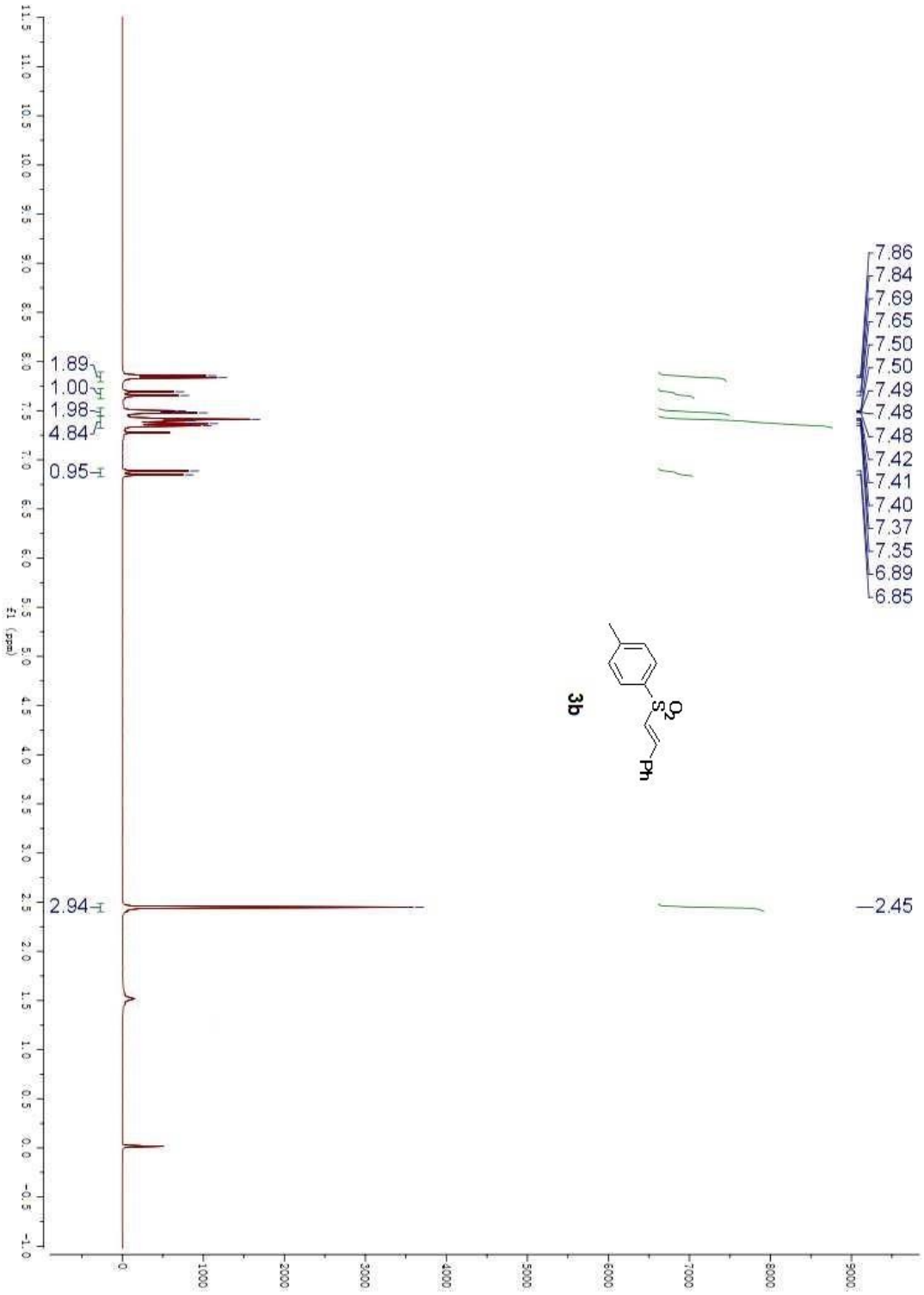
S
Ph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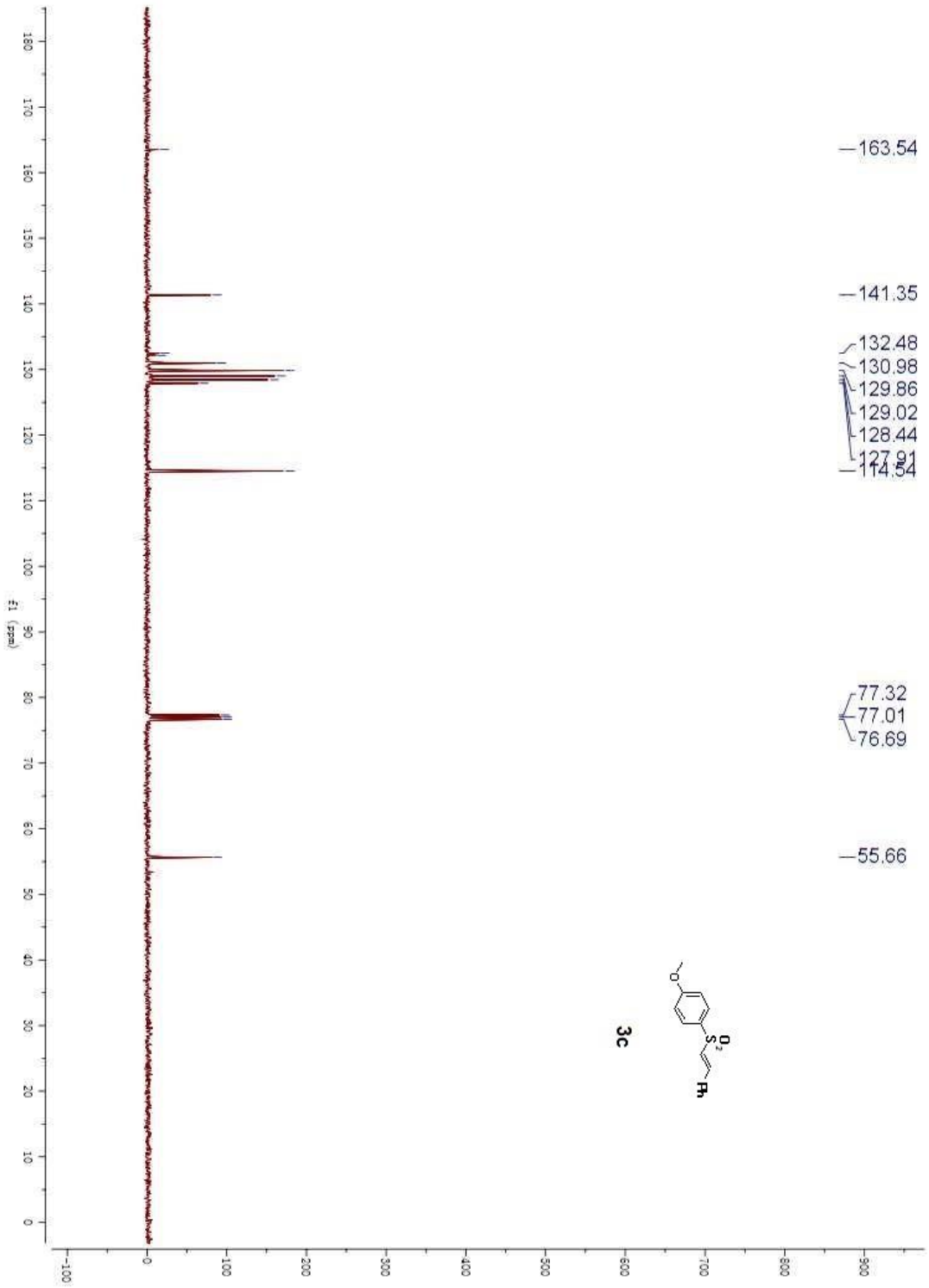
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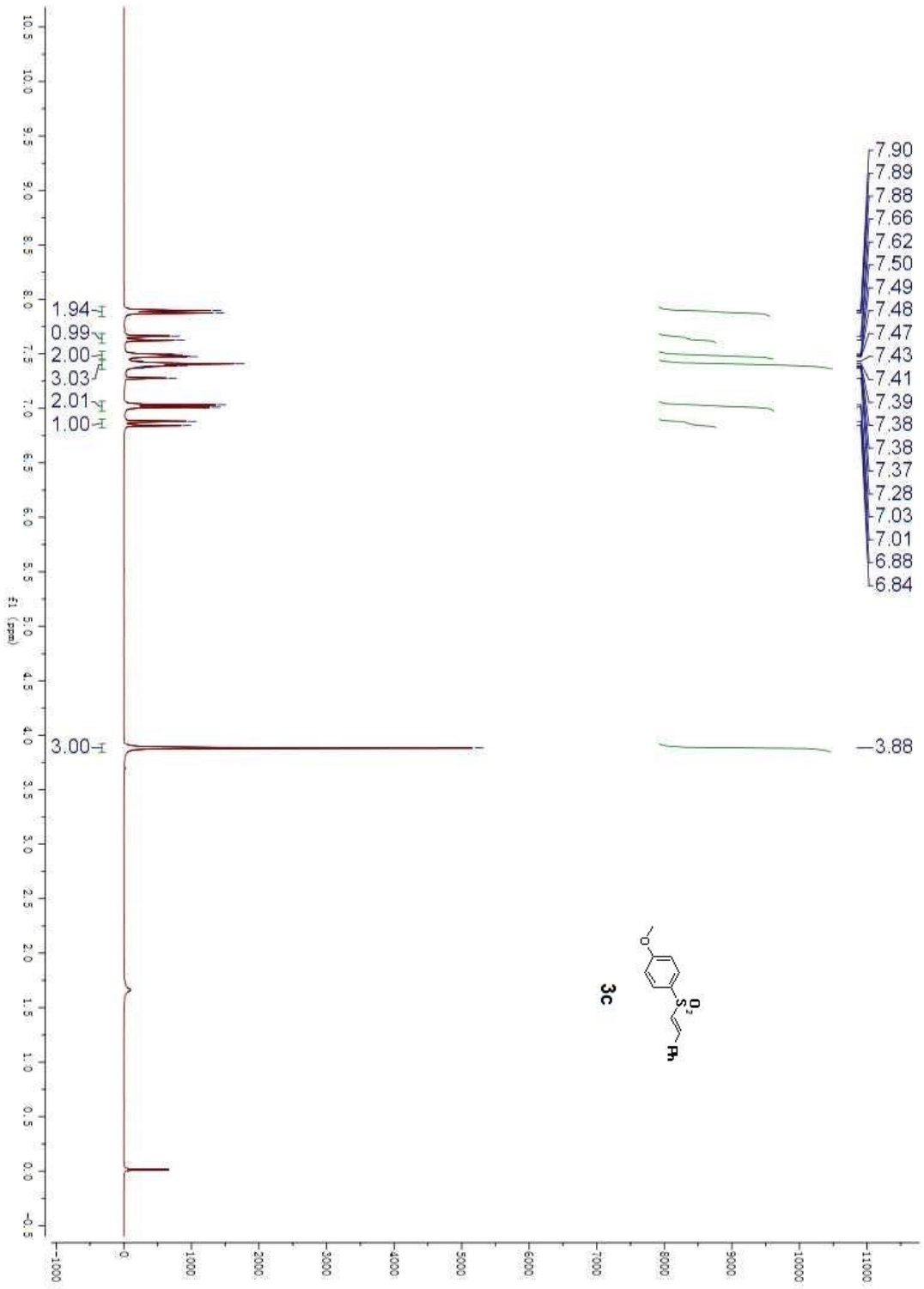
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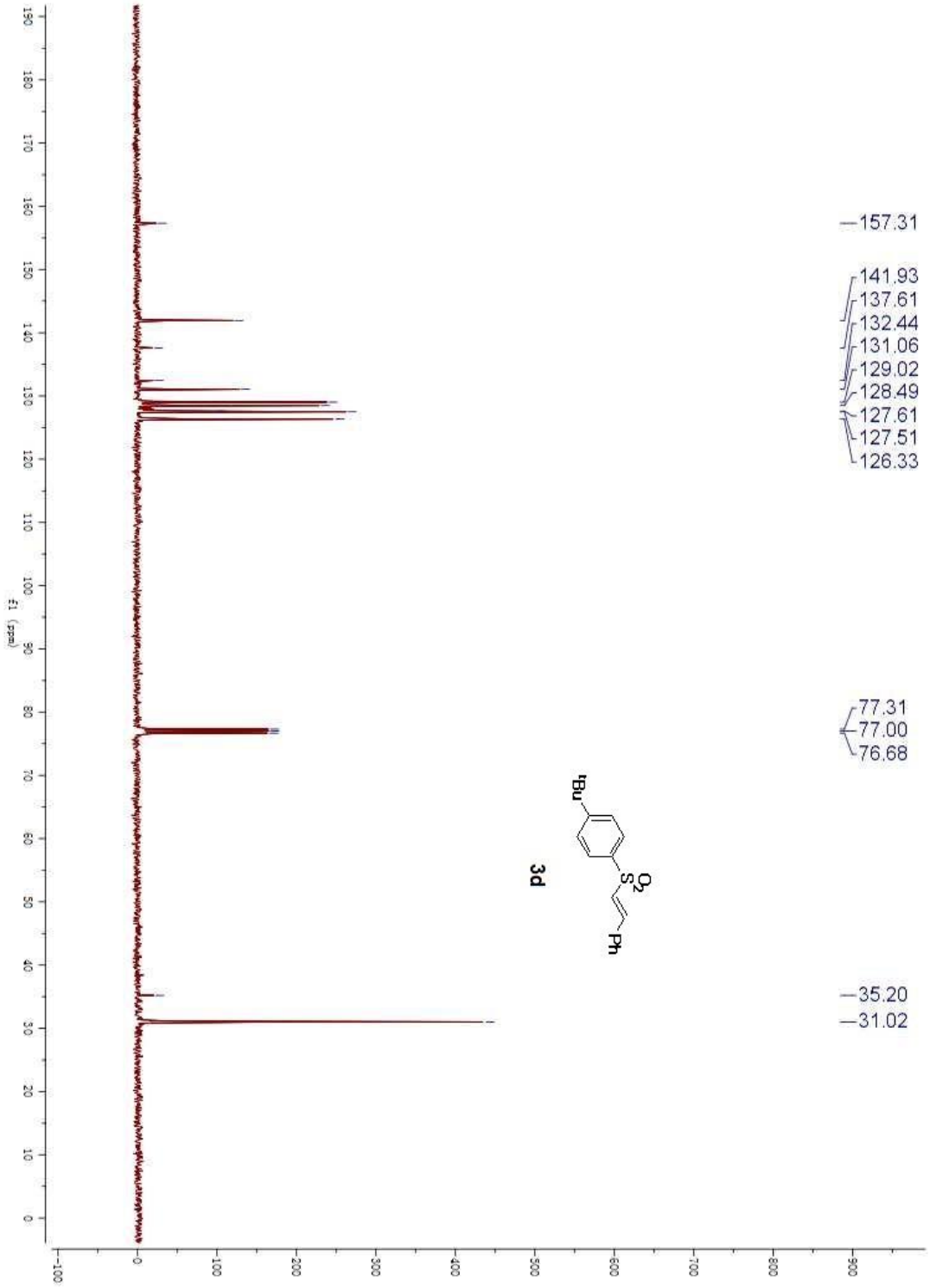
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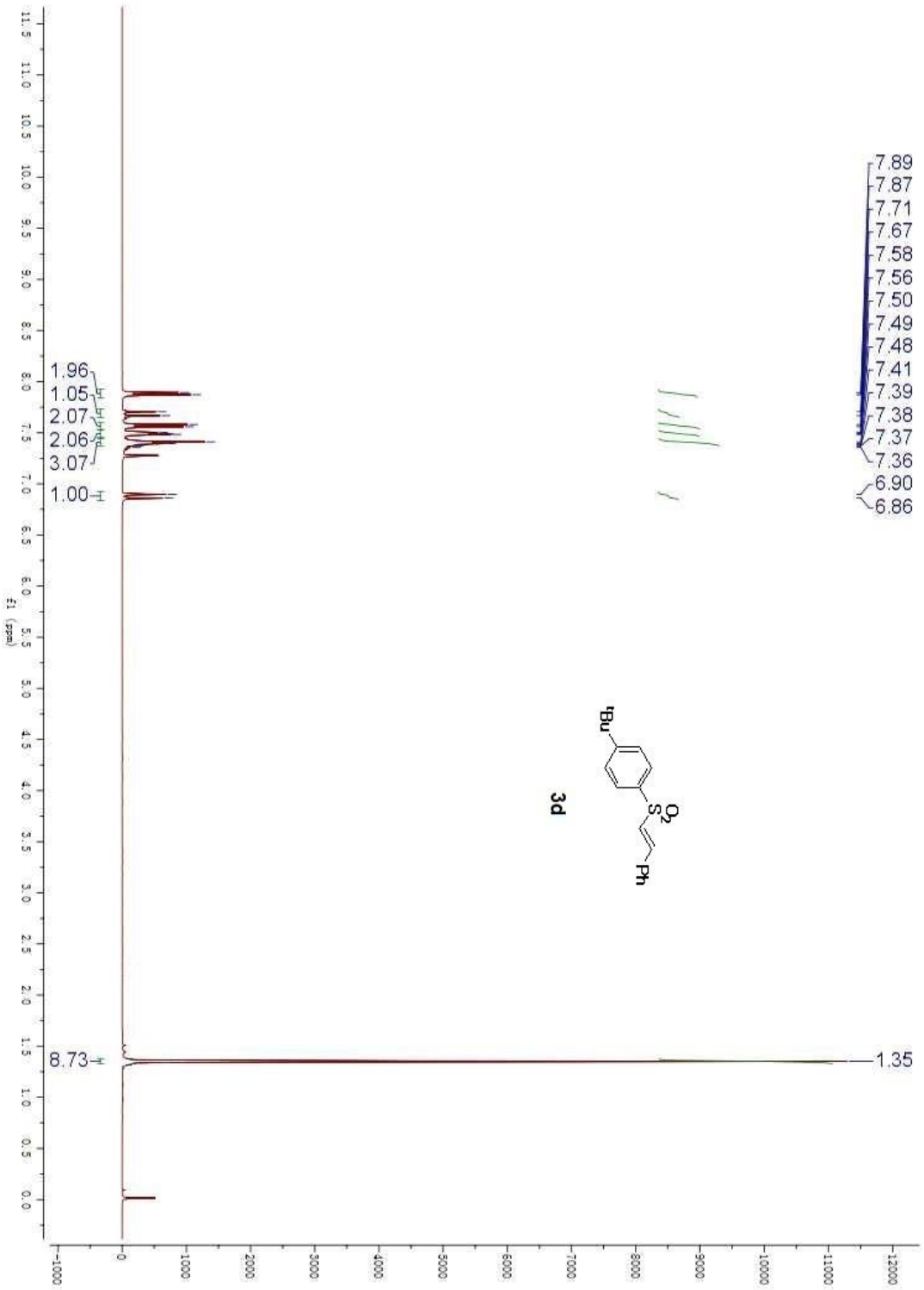
f1 (ppm)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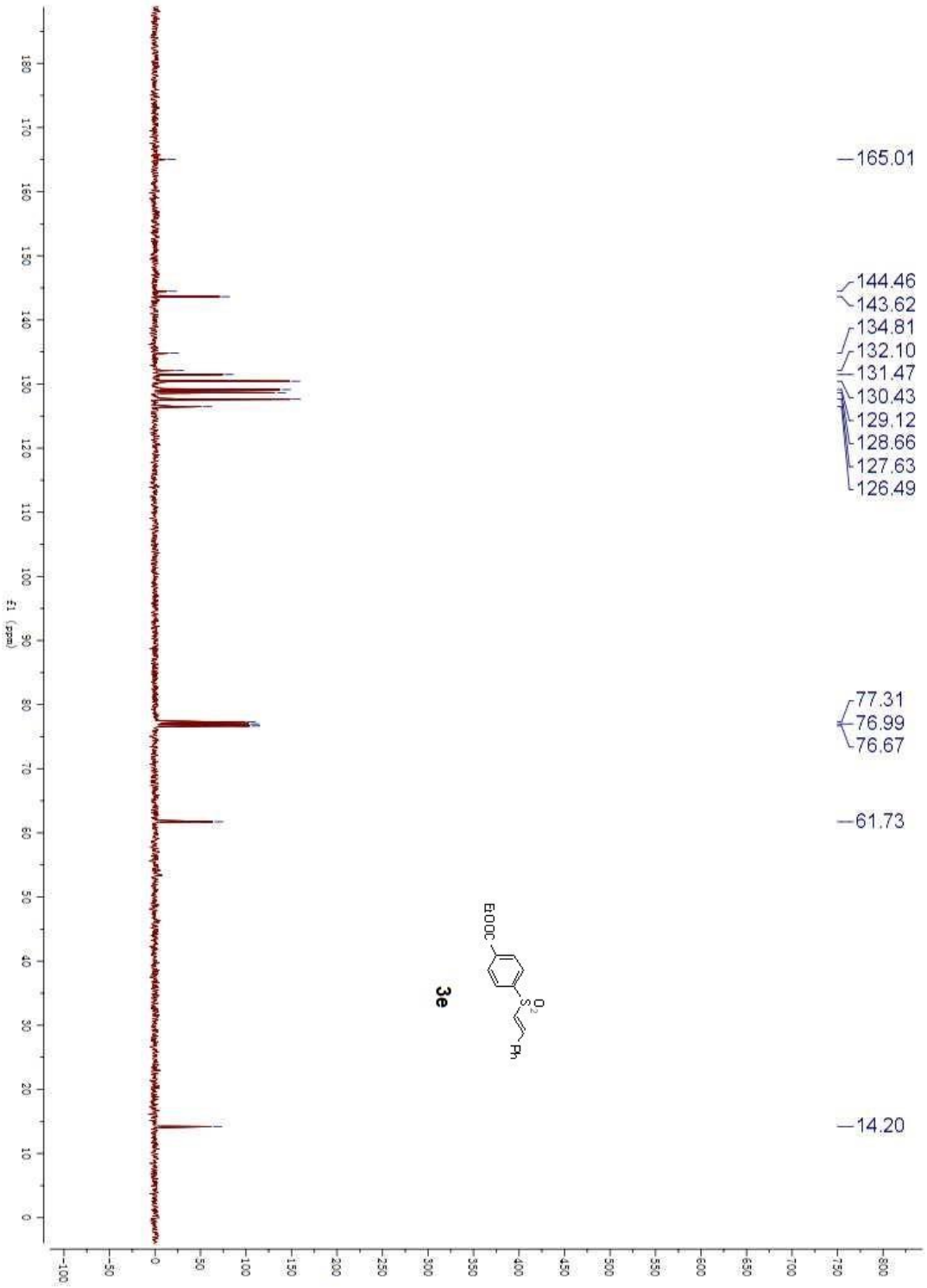
S
Ph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3e
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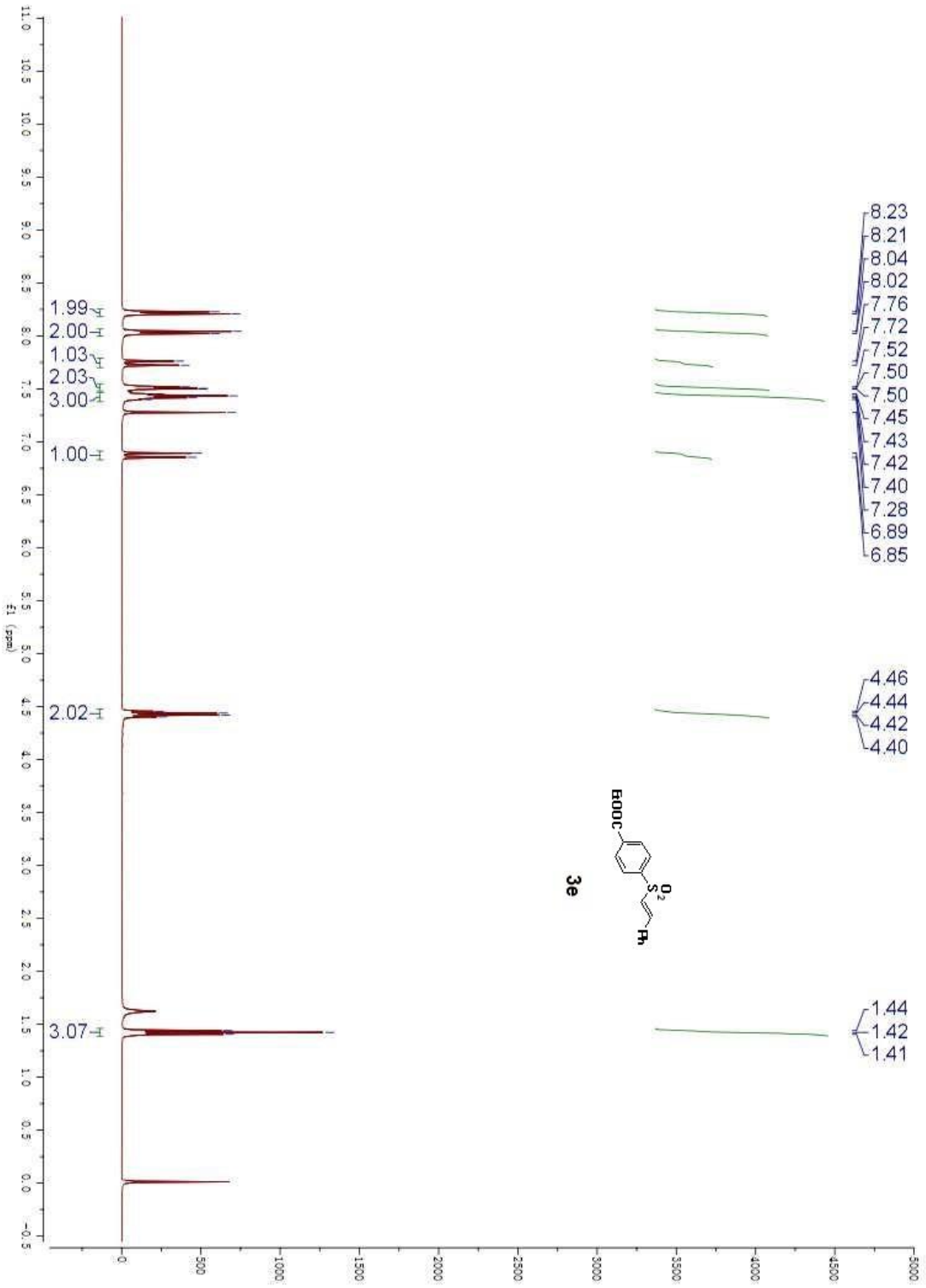
S
Ph
f1 (ppm)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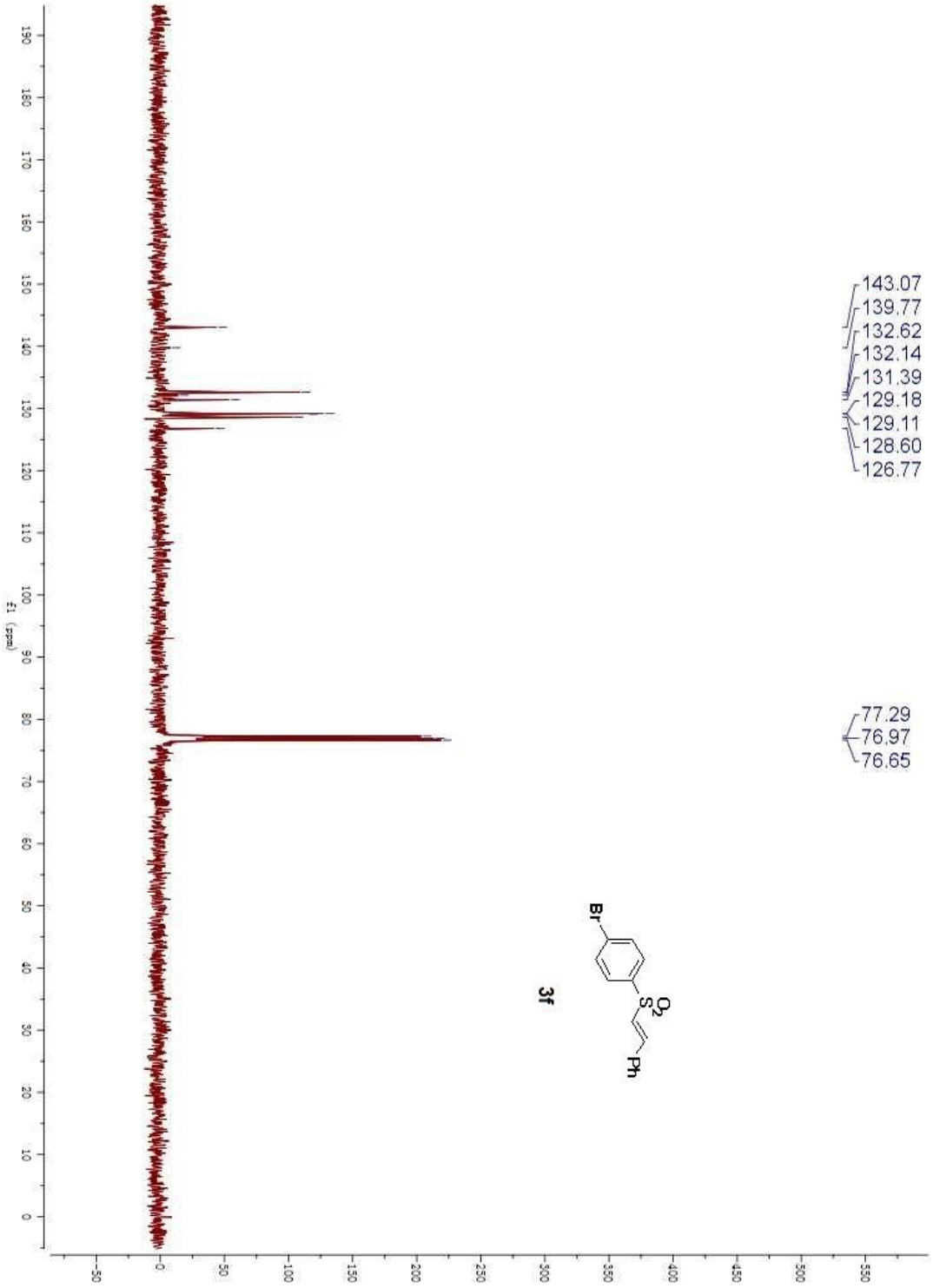
3e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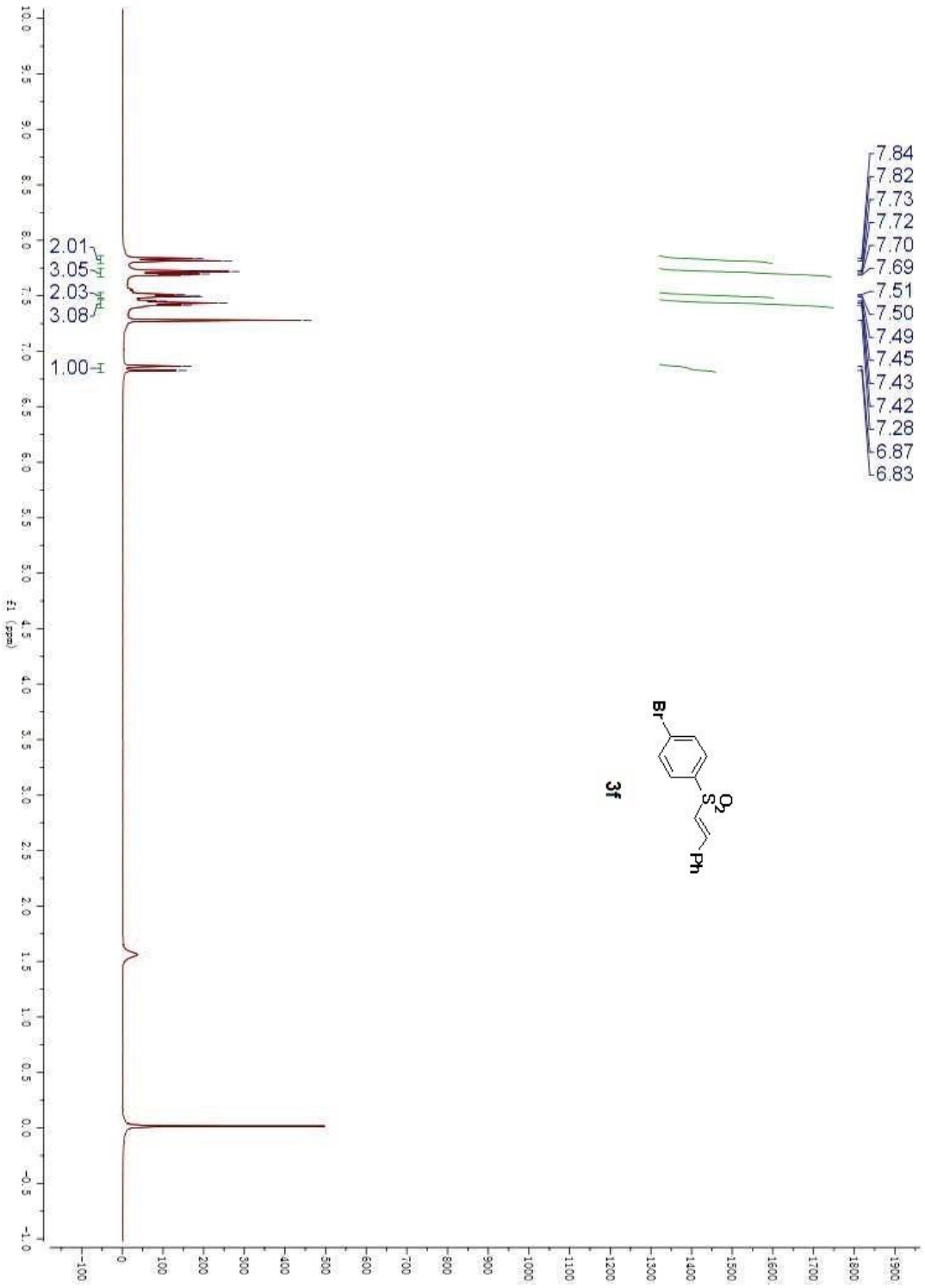
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7.45
7.43
7.42
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6.83
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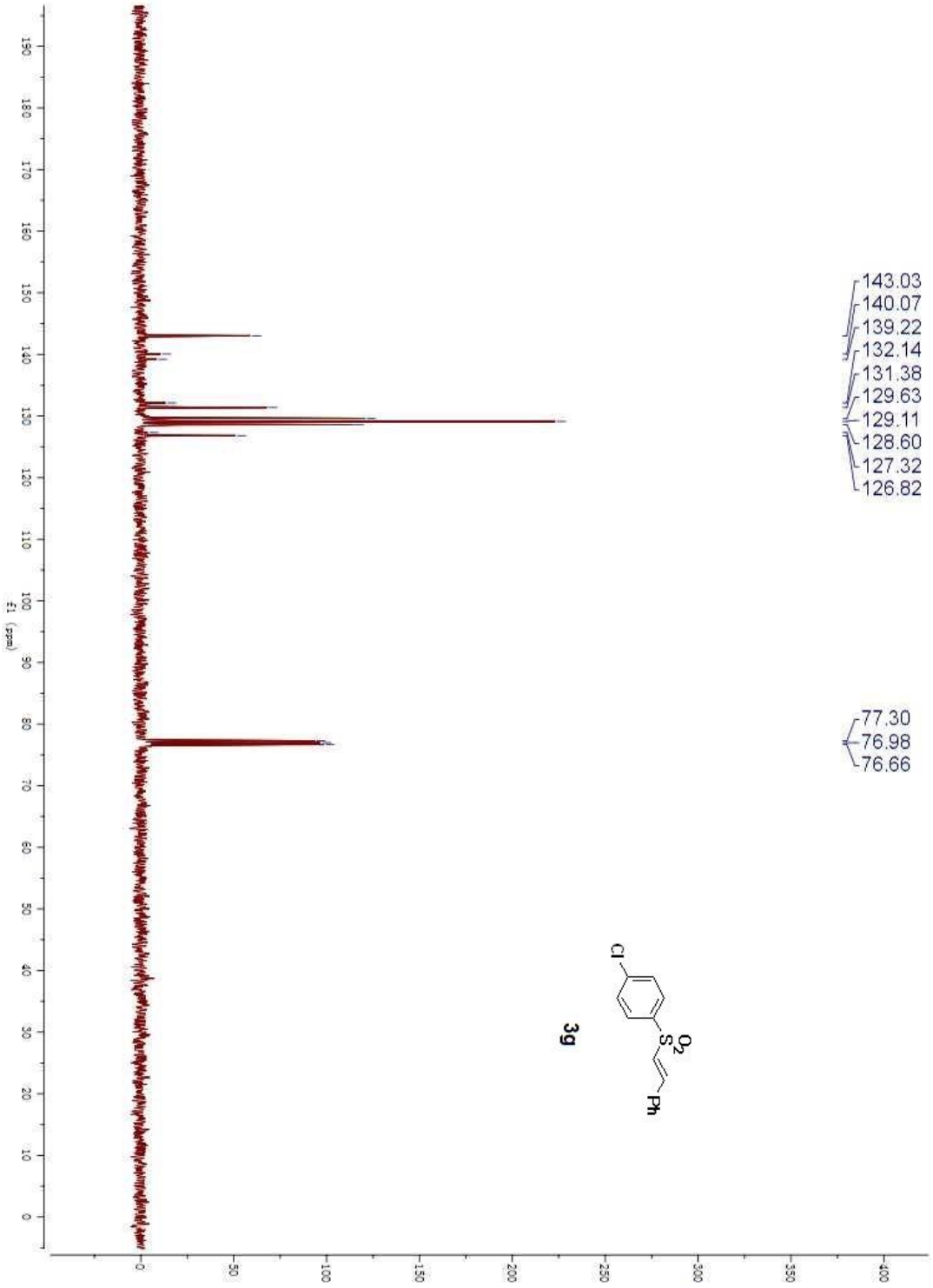
3.05
2.03
3.08
1.00
Br
S
O
O
Ph
3f


143.03
140.07
139.22
132.14
131.38
129.63
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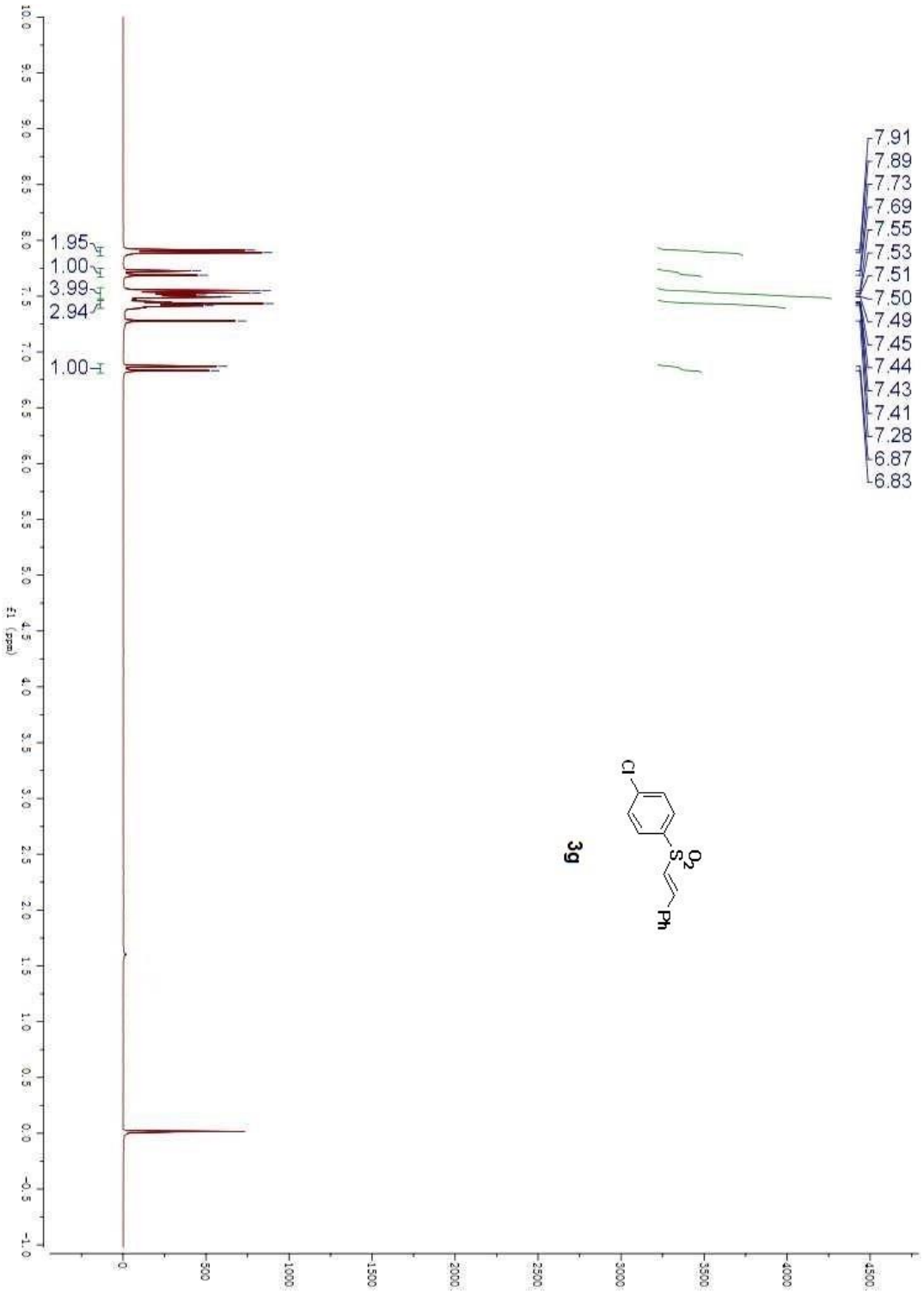
127.32
126.82
77.30
76.98
76.66
3g
Cl
S
O2
Ph
f1 (ppm)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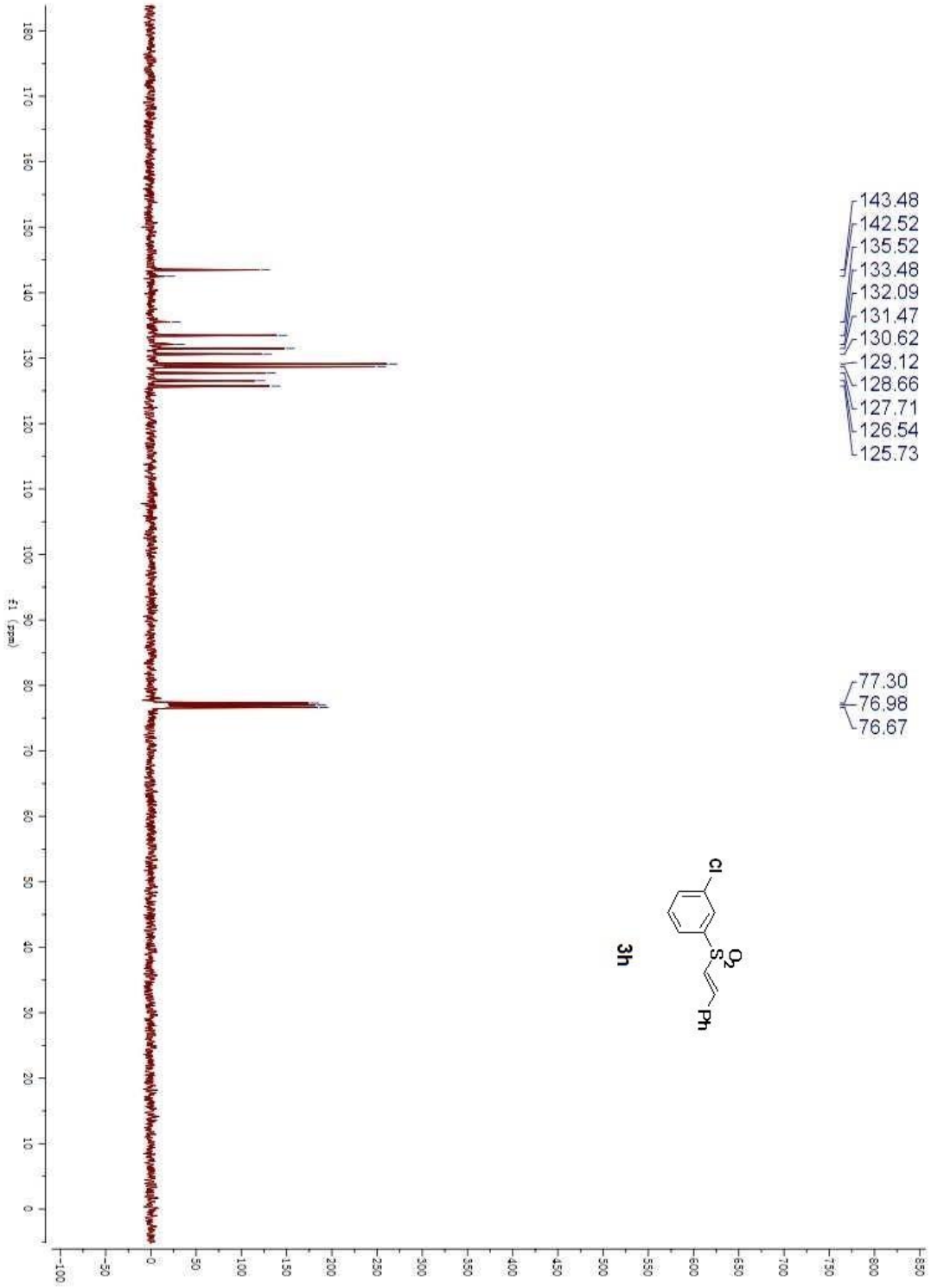
7.89
7.73
7.69
7.55
7.53
7.51
7.50
7.49
7.45
7.44
7.43
7.41
7.28
6.87
6.83
1.95
1.00
3.99
2.94
1.00
f1 (ppm)
Cl
O2
S
Ph
3g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135.52
133.48
132.09
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130.62
129.12
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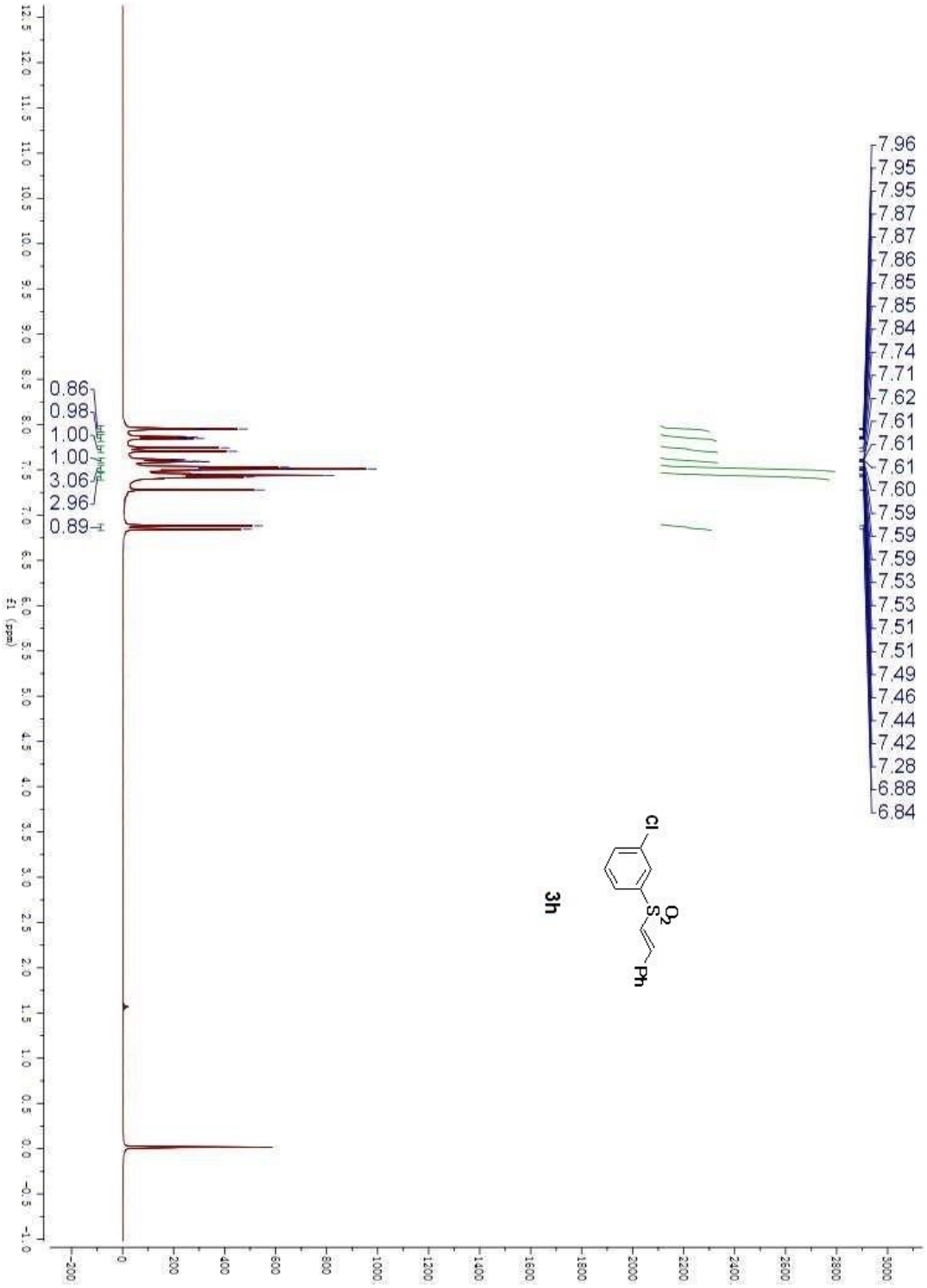
126.54
125.73
77.30
76.98
76.67
3h
Cl
O2
S
Ph
f1 (ppm)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1.00
1.00
3.06
2.96
0.89
7.96
7.95
7.95
7.87
7.87
7.86
7.85
7.85
7.84
7.74
7.71
7.62
7.61
7.61
7.61
7.60
7.59
7.59
7.59
7.53
7.53
7.51
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7.46
7.44
7.42
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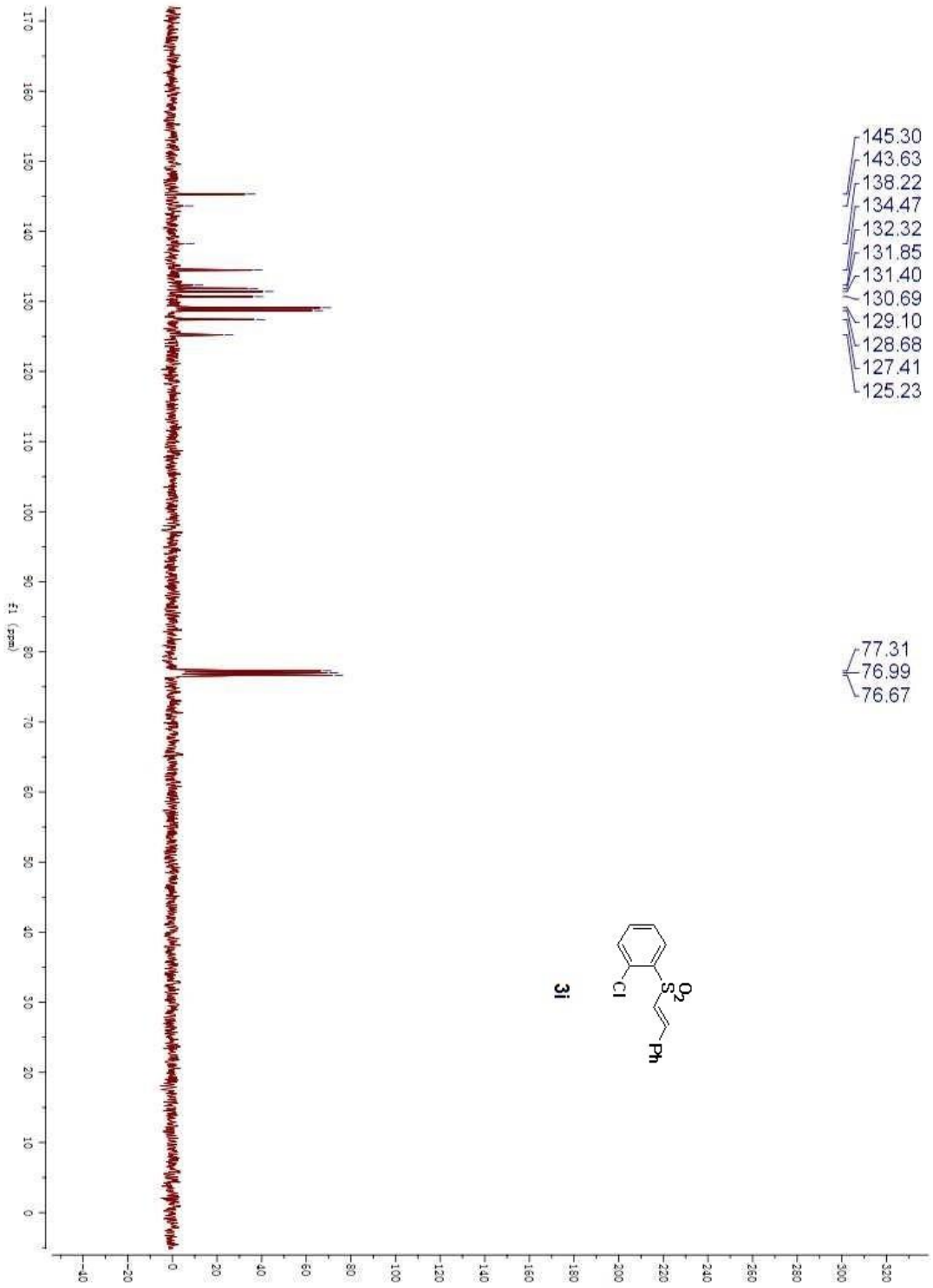
6.88
6.84
Cl
O2
S
Ph
3h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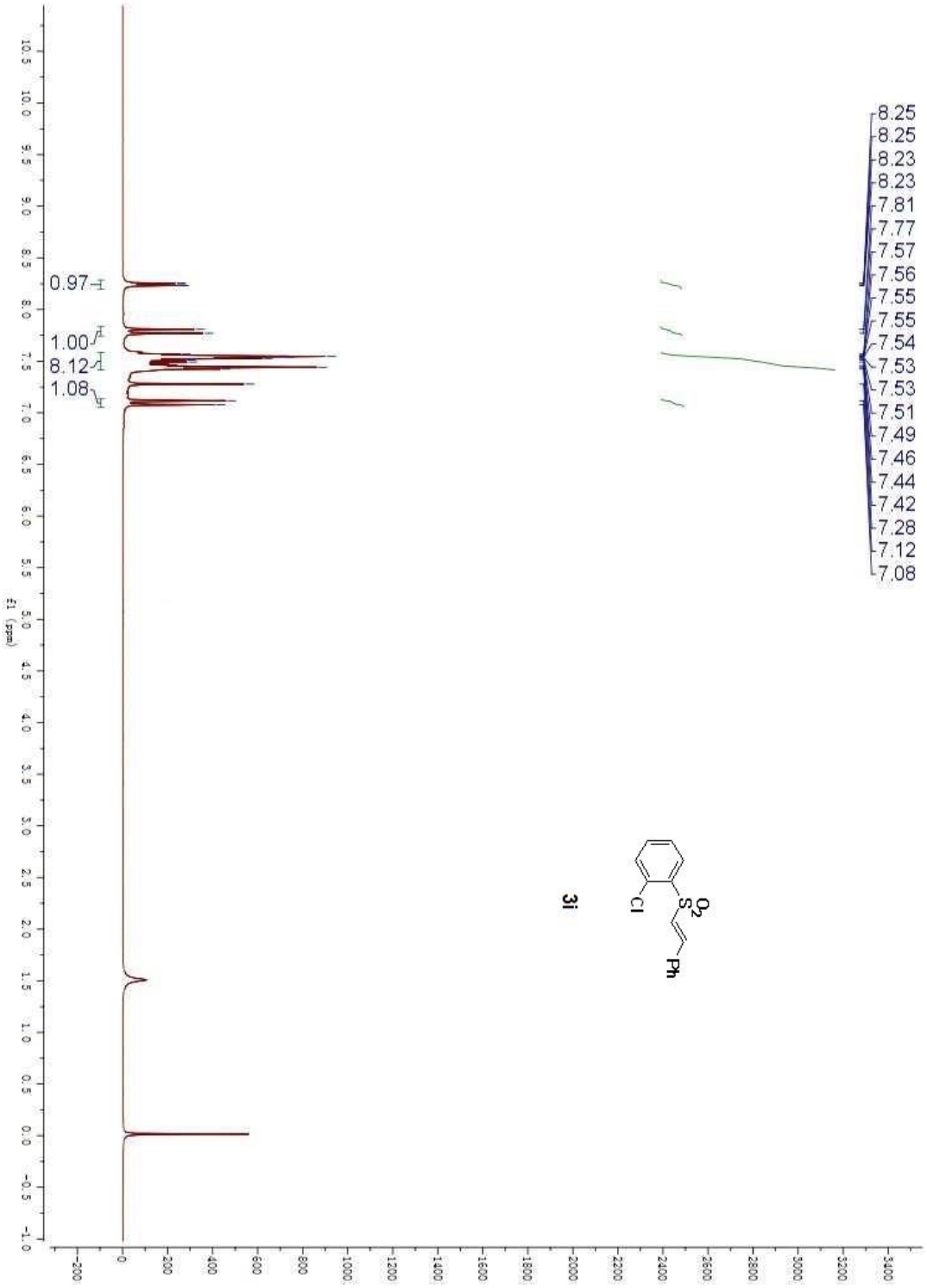
134.47
132.32
131.85
131.40
130.69
129.10
128.68
127.41
125.23
77.31
76.99
76.67
f1 (ppm)
3i
Cl
S
O2
Ph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1.00
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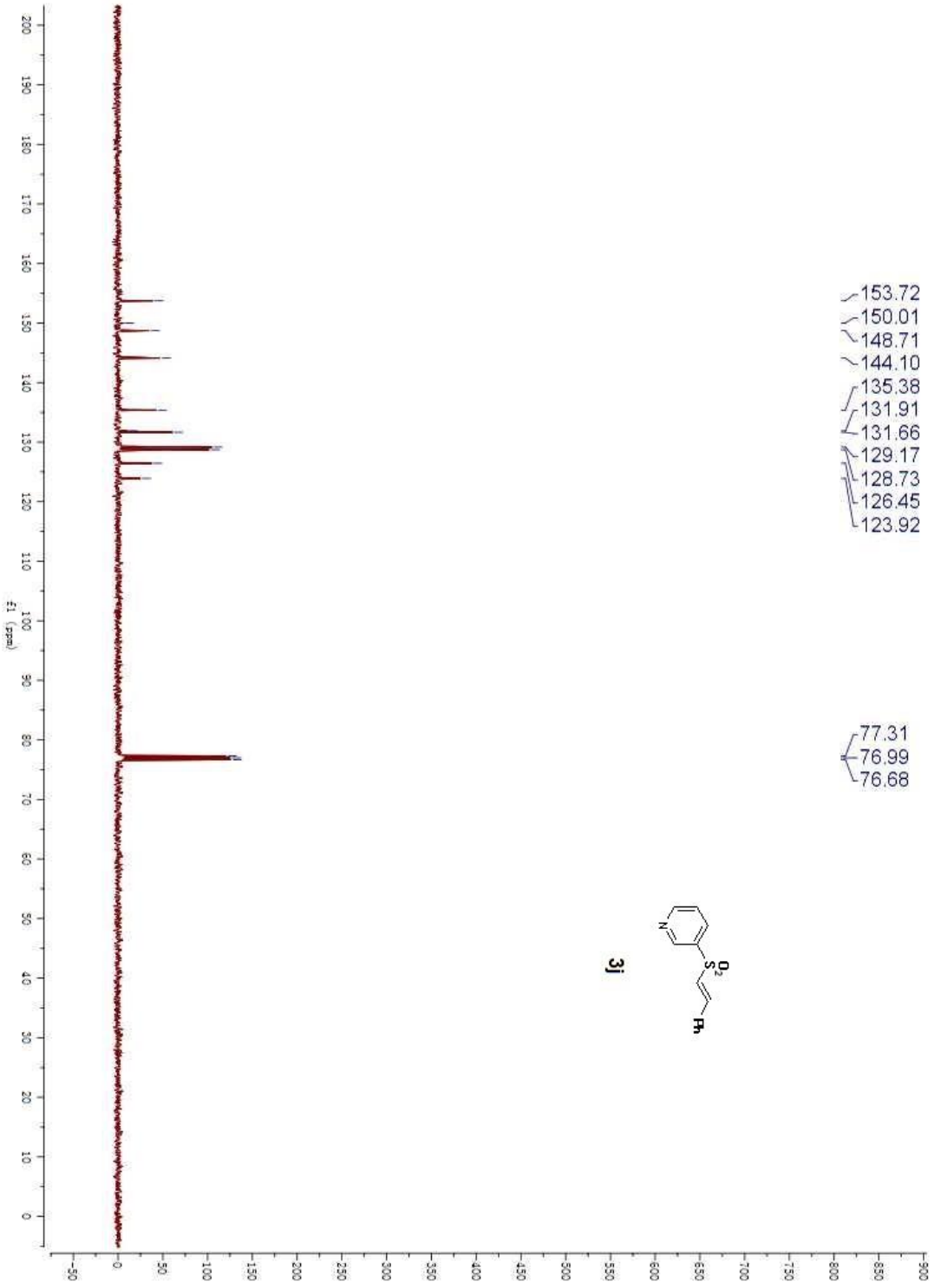
1.08
8.25
8.25
8.23
8.23
7.81
7.77
7.57
7.56
7.55
7.55
7.54
7.53
7.53
7.51
7.49
7.46
7.44
7.42
7.28
7.12
7.08
3i
Cl
S
O
O
Ph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150.01
148.71
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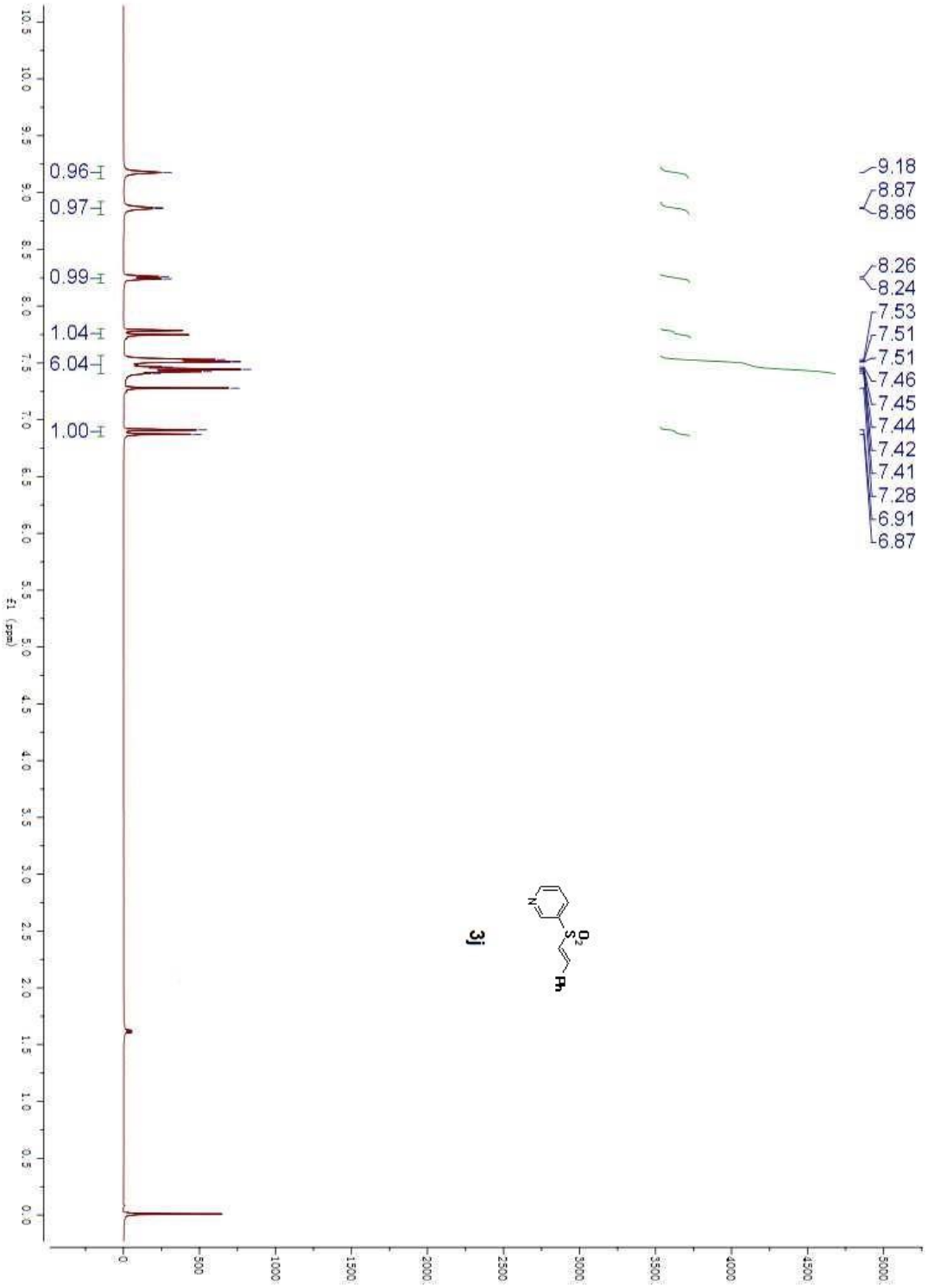
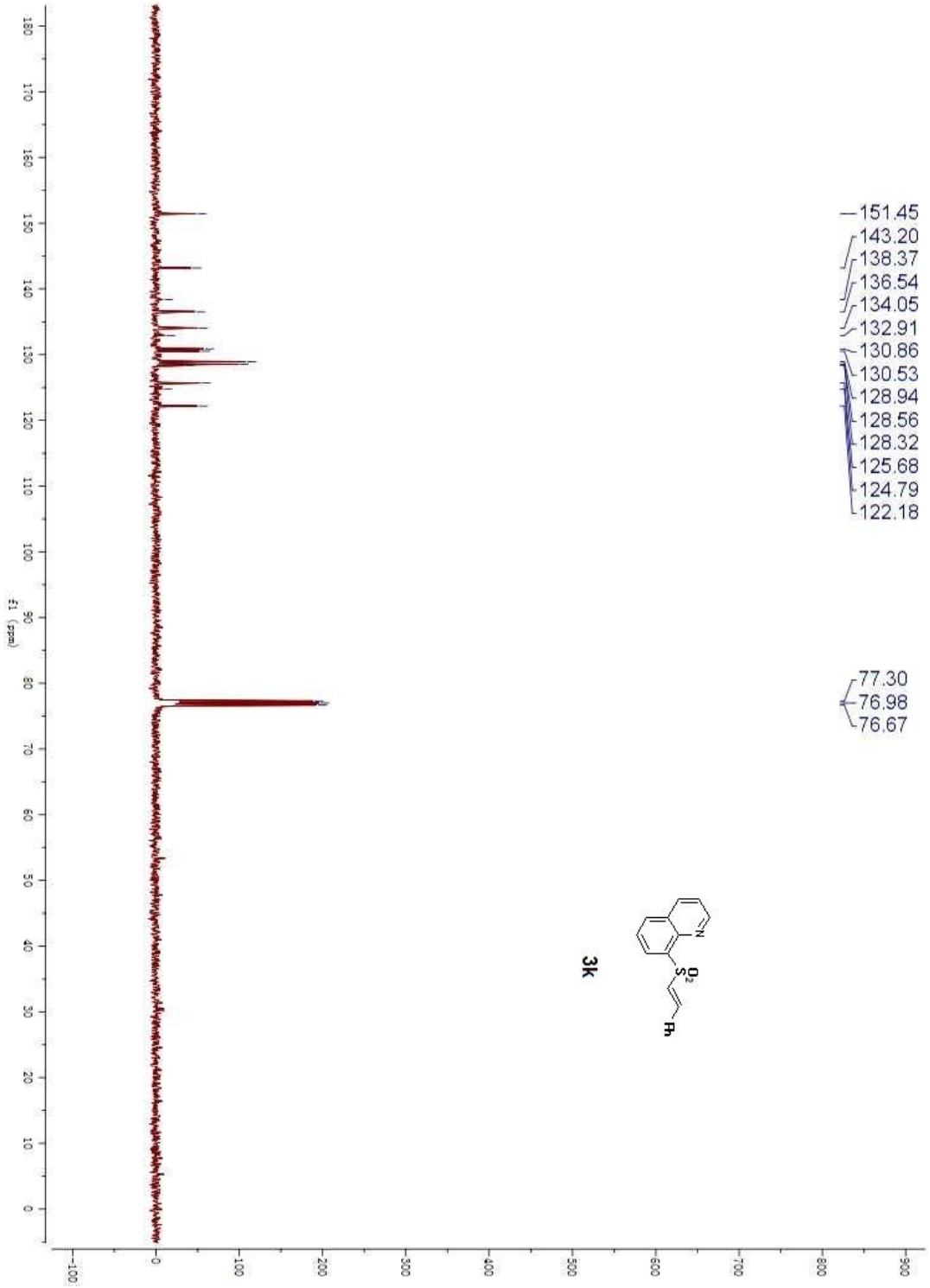
131.91
131.66
129.17
128.73
126.45
123.92
77.31
76.99
76.68
3j


0.96
0.97
0.99
1.04
6.04
1.00
9.18
8.87
8.86
8.26
8.24
7.53
7.51
7.51
7.46
7.45
7.44
7.42
7.41
7.28
6.91
6.87
3j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143.20
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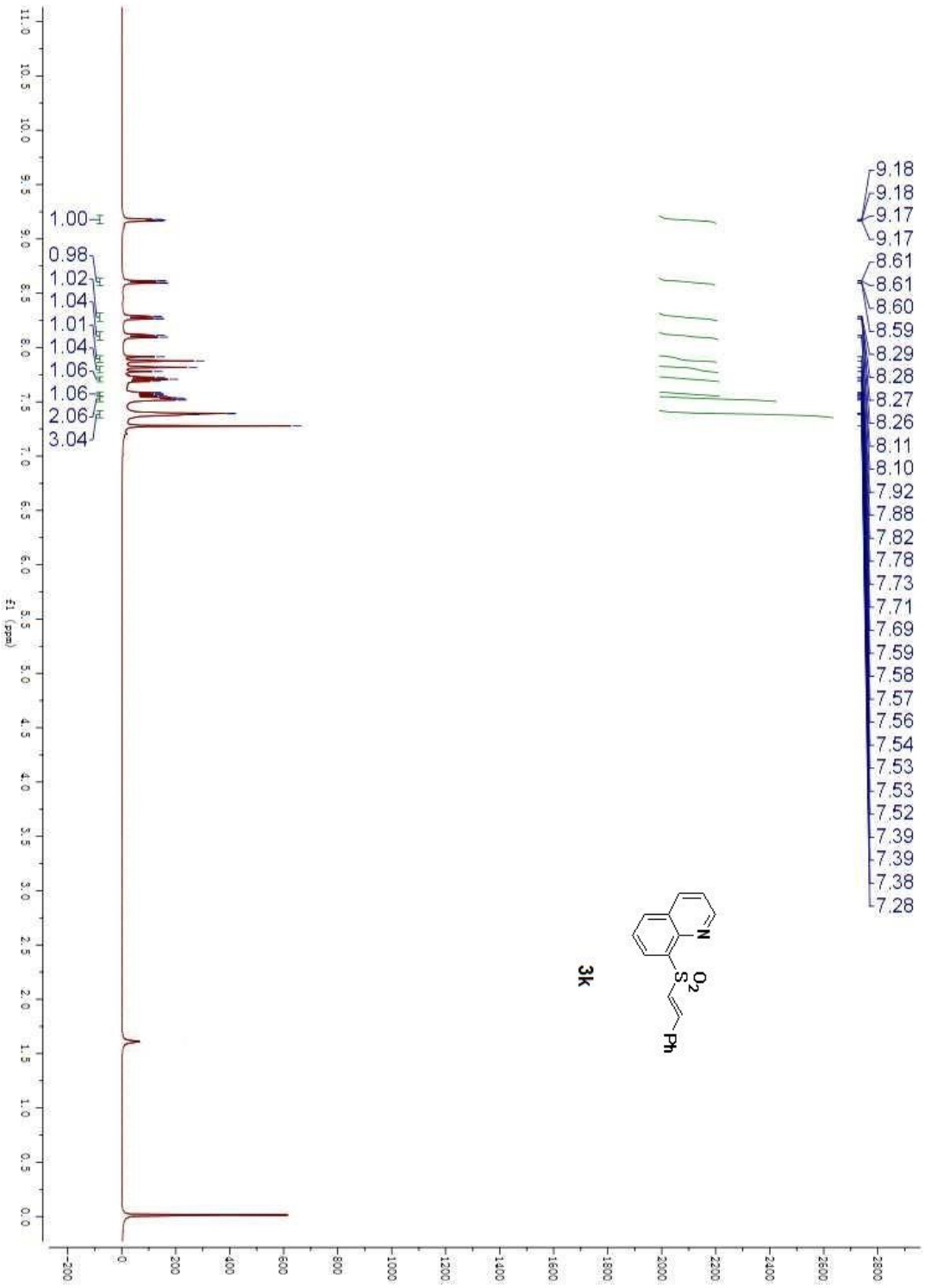
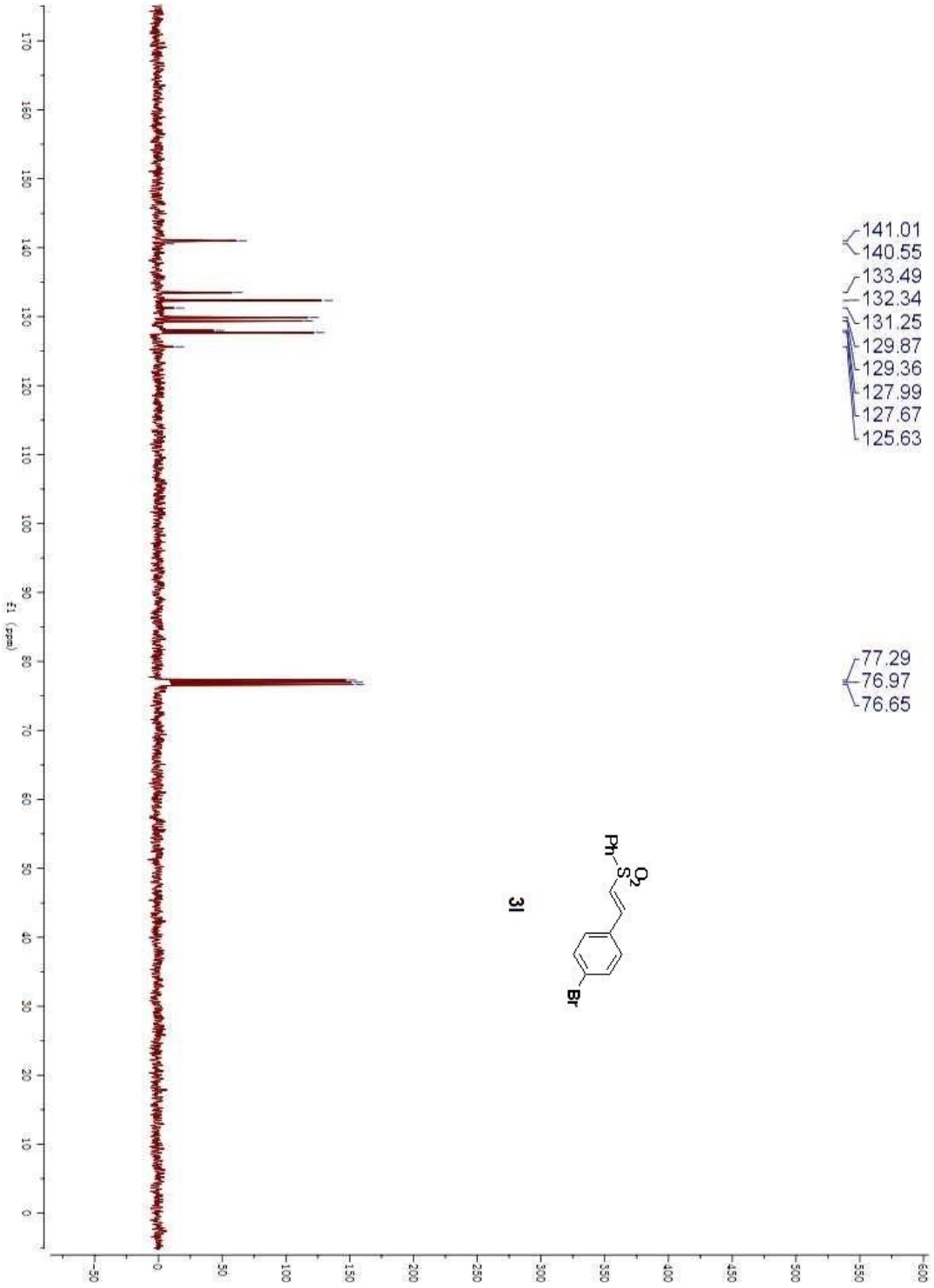
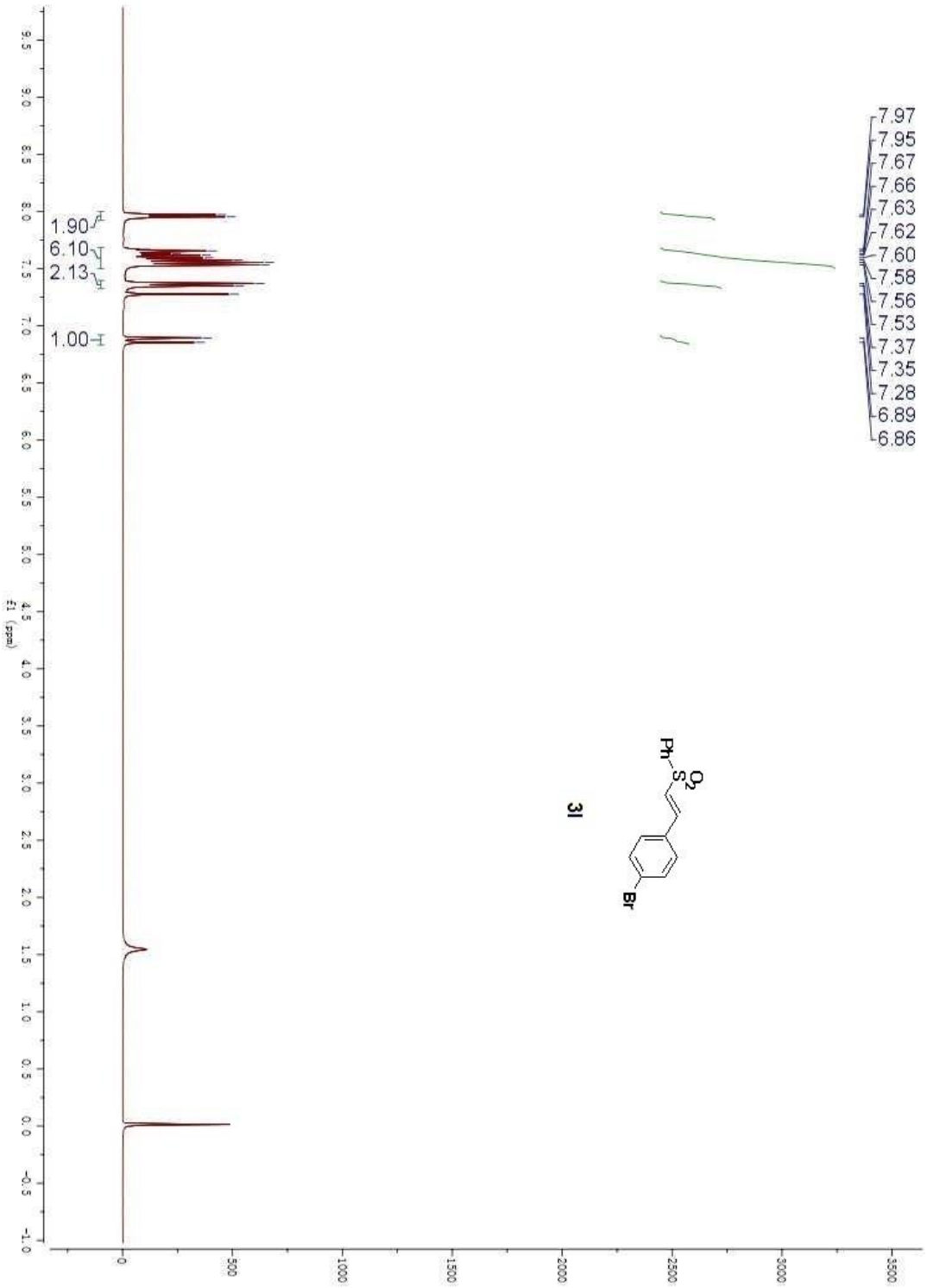
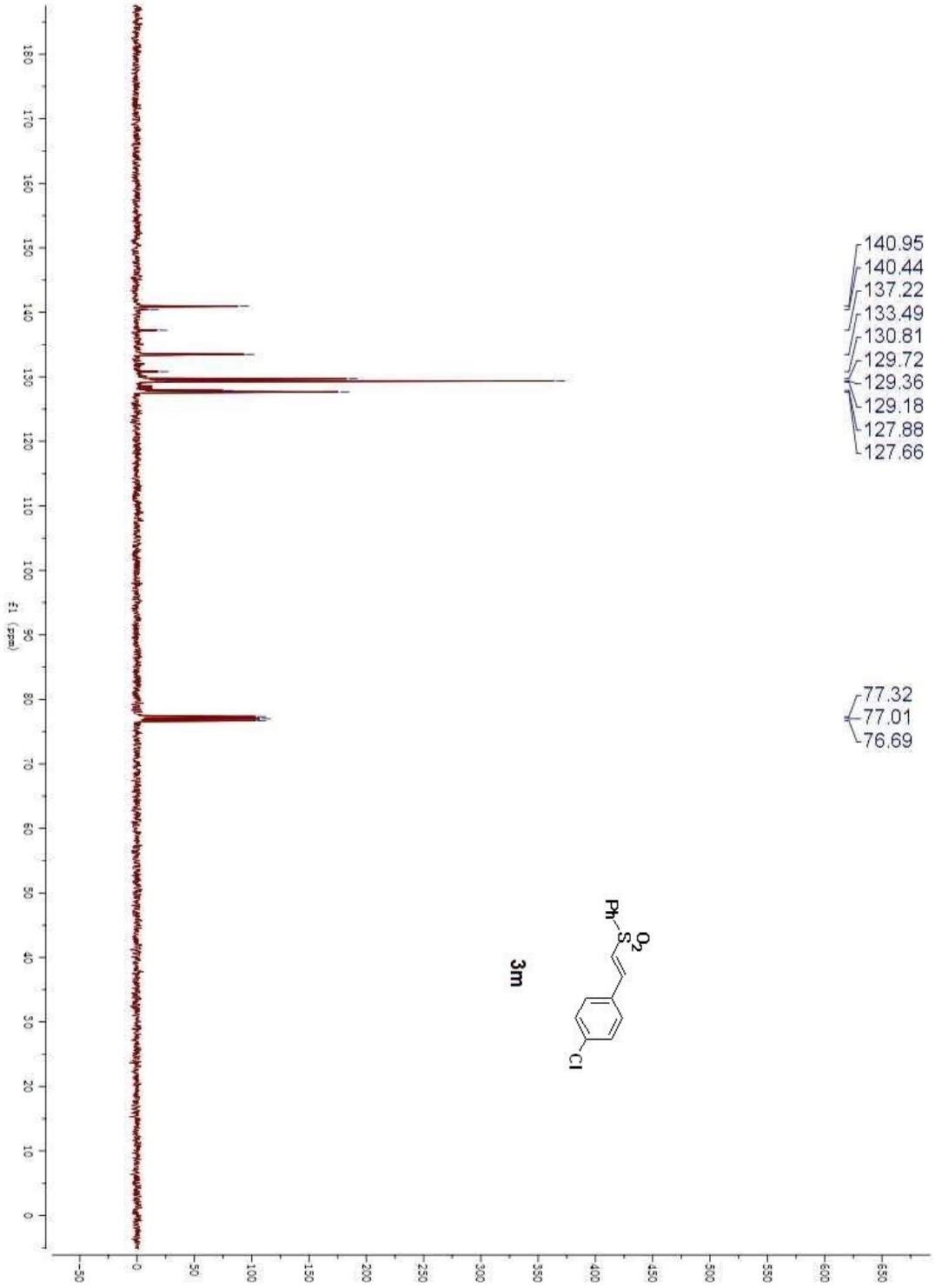
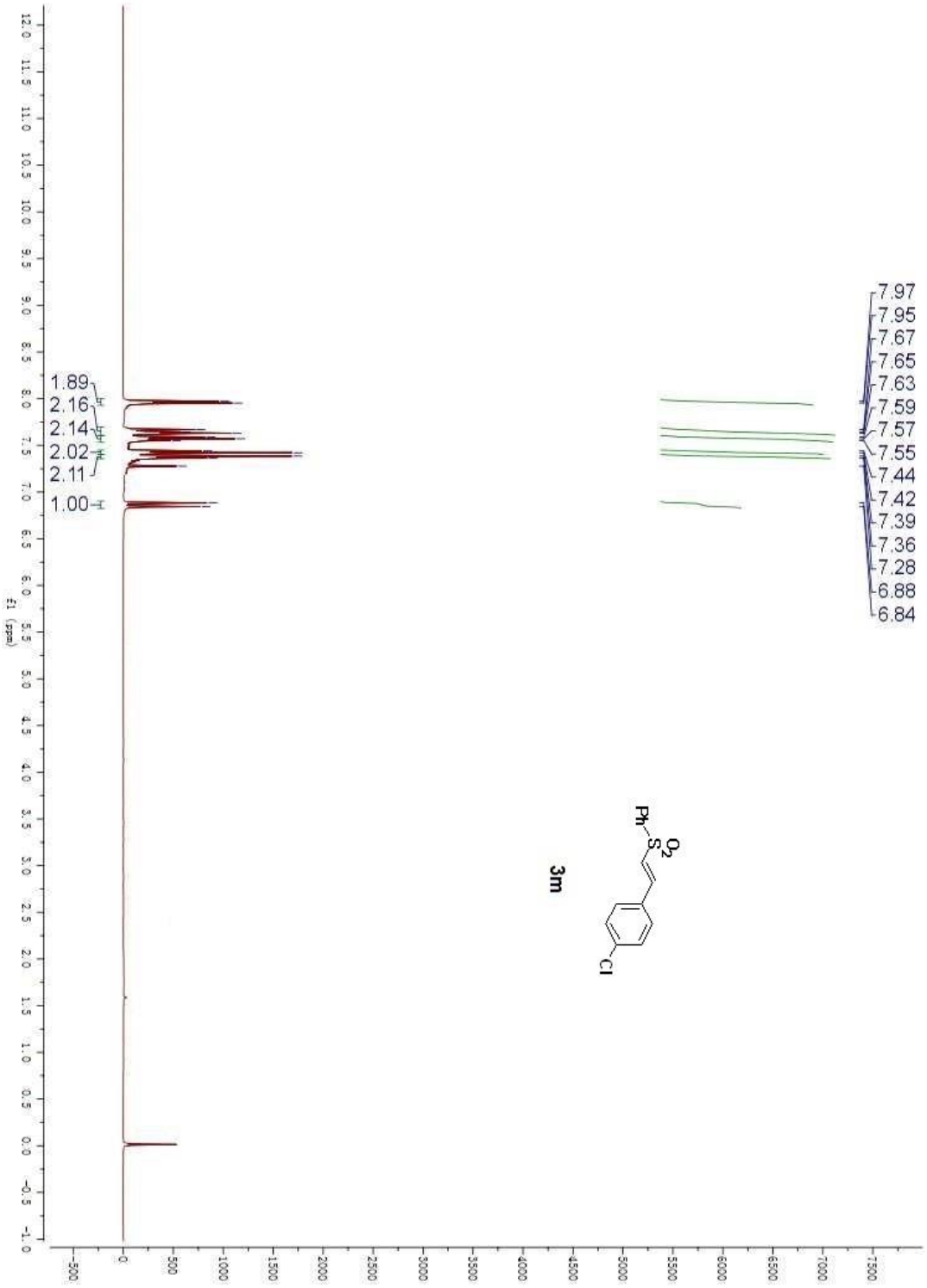
136.54
134.05
132.91
130.86
130.53
128.94
128.56
128.32
125.68
124.79
122.18
77.30
76.98
76.67
3k
f1 (ppm)

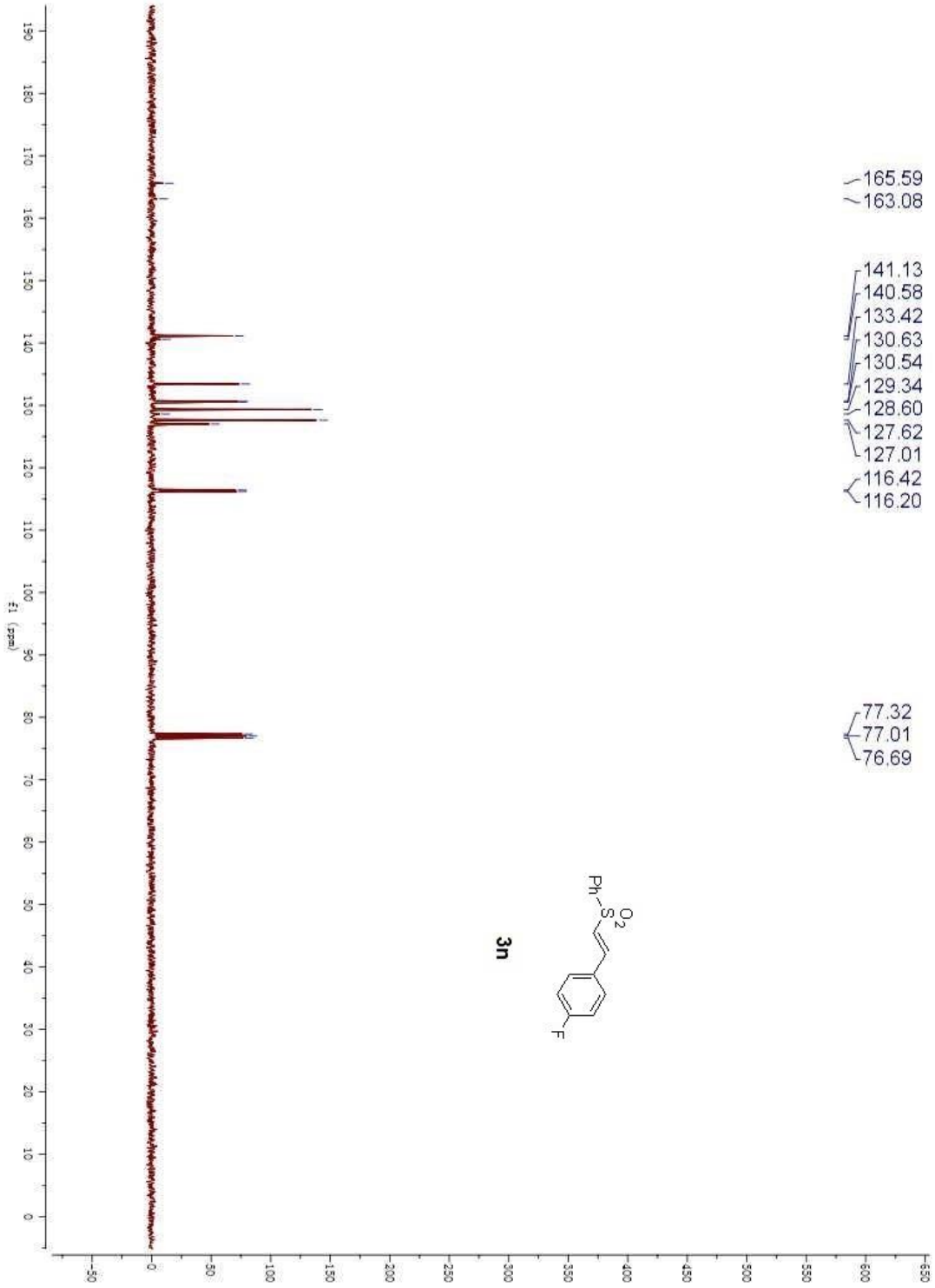

1.00
0.98
1.02
1.04
1.01
1.04
1.06
1.06
2.06
3.04
9.18
9.18
9.17
9.17
8.61
8.61
8.60
8.59
8.29
8.28
8.27
8.26
8.11
8.10
7.92
7.88
7.82
7.78
7.73
7.71
7.69
7.59
7.58
7.57
7.56
7.54
7.53
7.53
7.52
7.39
7.39
7.38
7.28
f1 (ppm)
3k
N
O2
S
Ph

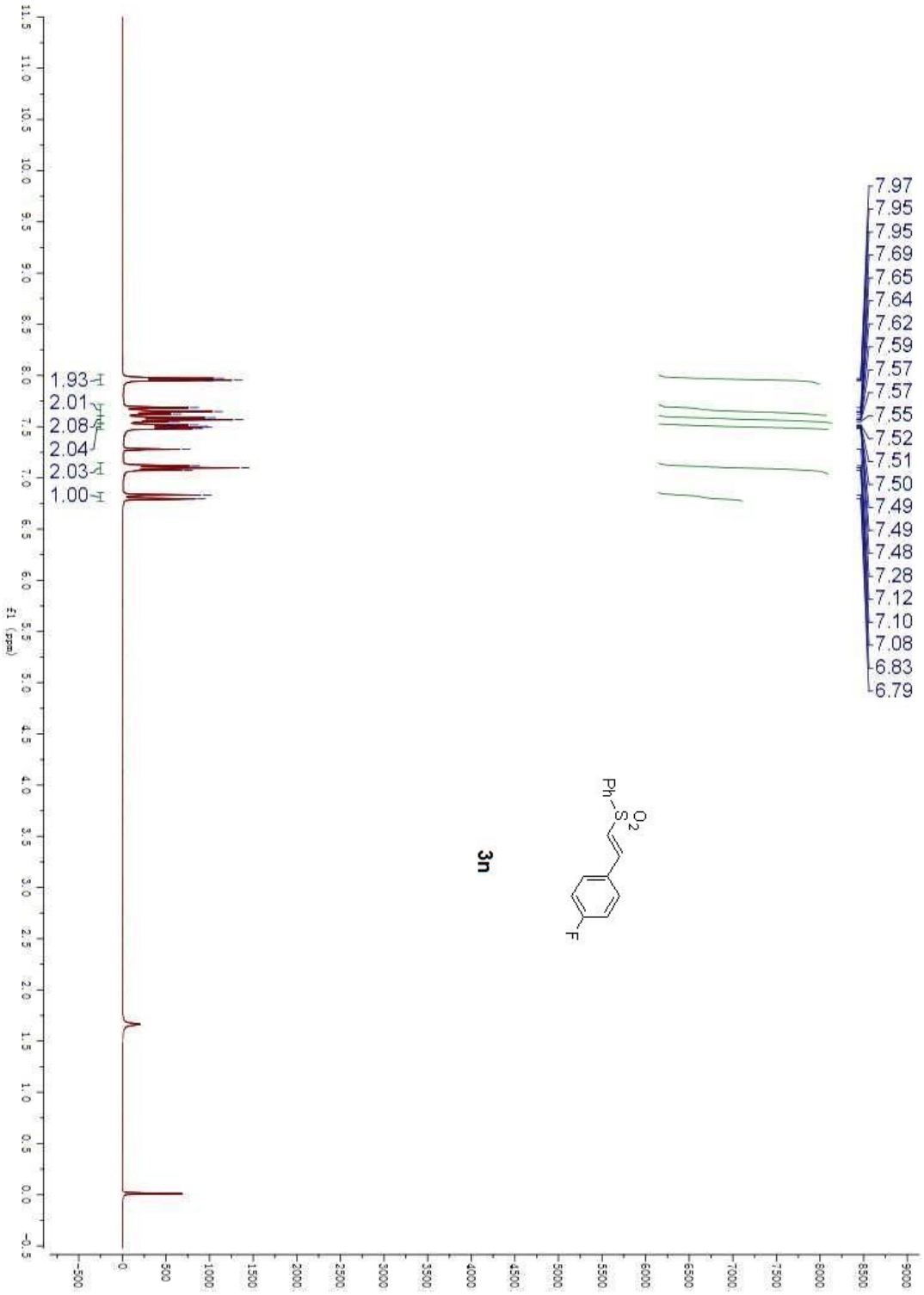

141.01
140.55
133.49
132.34
131.25
129.87
129.36
127.99
127.67
125.63
77.29
76.97
76.65
3l
Ph
S
O2
Br
f1 (ppm)

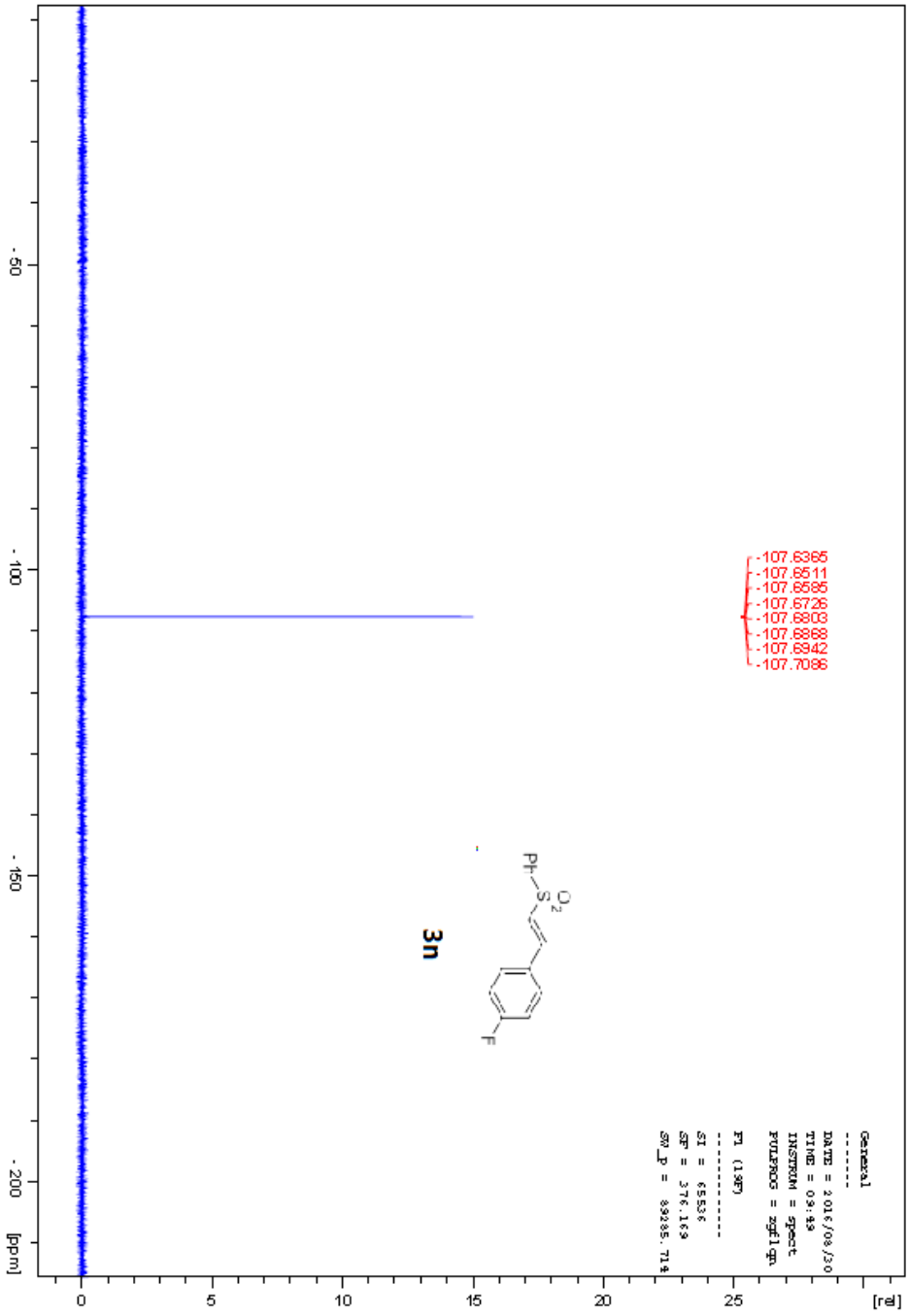

7.97
7.95
7.67
7.66
7.63
7.62
7.60
7.58
7.56
7.53
7.37
7.35
7.28
6.89
6.86
1.90
6.10
2.13
1.00
3l
Ph
S
O2
Br


140.95
140.44
137.22
133.49
130.81
129.72
129.36
129.18
127.88
127.66
77.32
77.01
76.69
3m
Ph
S
O2
Cl
f1 (ppm)


1.89
2.16
2.14
2.02
2.11
1.00
7.97
7.95
7.67
7.65
7.63
7.59
7.57
7.55
7.44
7.42
7.39
7.36
7.28
6.88
6.84
f1 (ppm)
3m
Ph
S
O2
Cl


165.59
163.08
141.13
140.58
133.42
130.63
130.54
129.34
128.60
127.62
127.01
116.42
116.20
77.32
77.01
76.69
3n
Ph
S
O2
F


7.97
7.95
7.95
7.69
7.65
7.64
7.62
7.59
7.57
7.57
7.55
7.52
7.51
7.50
7.49
7.49
7.48
7.28
7.12
7.10
7.08
6.83
6.79
1.93
2.01
2.08
2.04
2.03
1.00
f1 (ppm)
3n
Ph
S
O2
F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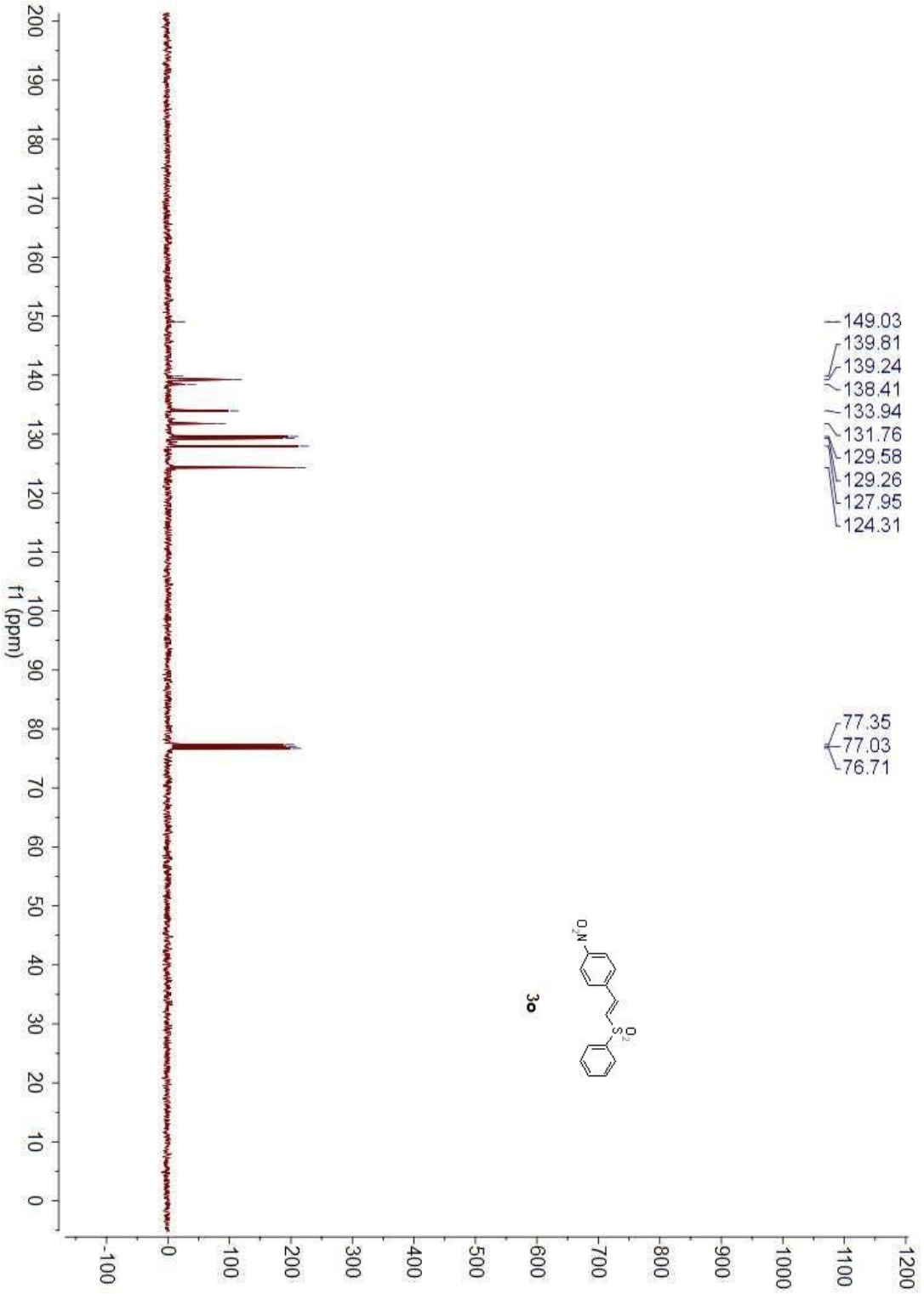
-107.6585
-107.6726
-107.6803
-107.6868
-107.6942
-107.7086
3n
Ph
S
O2
F
General
DATE = 2016/08/30
TIME = 09:49
INSTRUM = spect
PULPROG = zgflqn
F1 (19F)
SI = 65536
SF = 376.169
SW_p = 89285.714
[ppm]
[rel]


149.03
139.81
139.24
138.41
133.94
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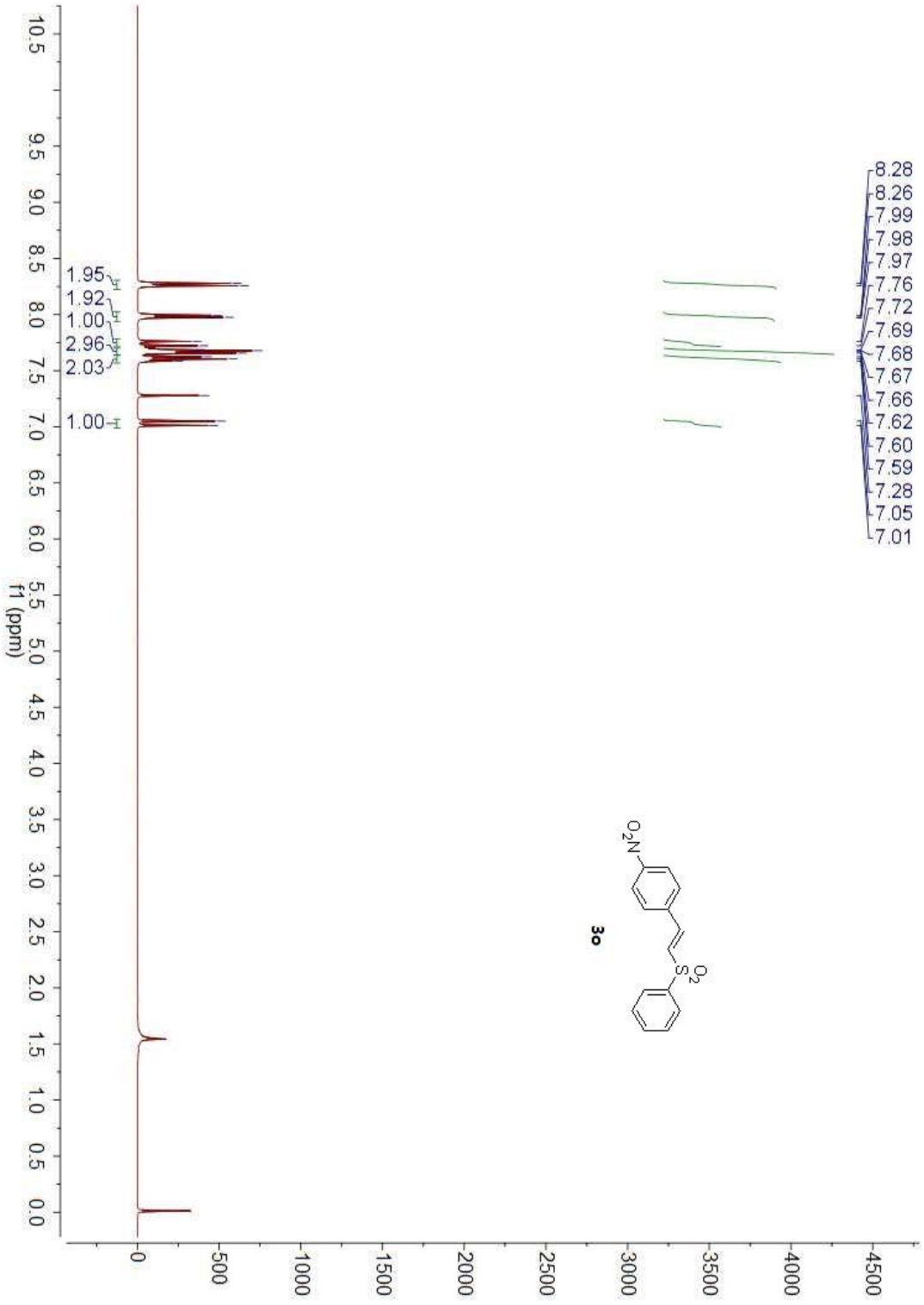
129.58
129.26
127.95
124.31
77.35
77.03
76.71
f1 (ppm)
3o


8.28
8.26
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7.97
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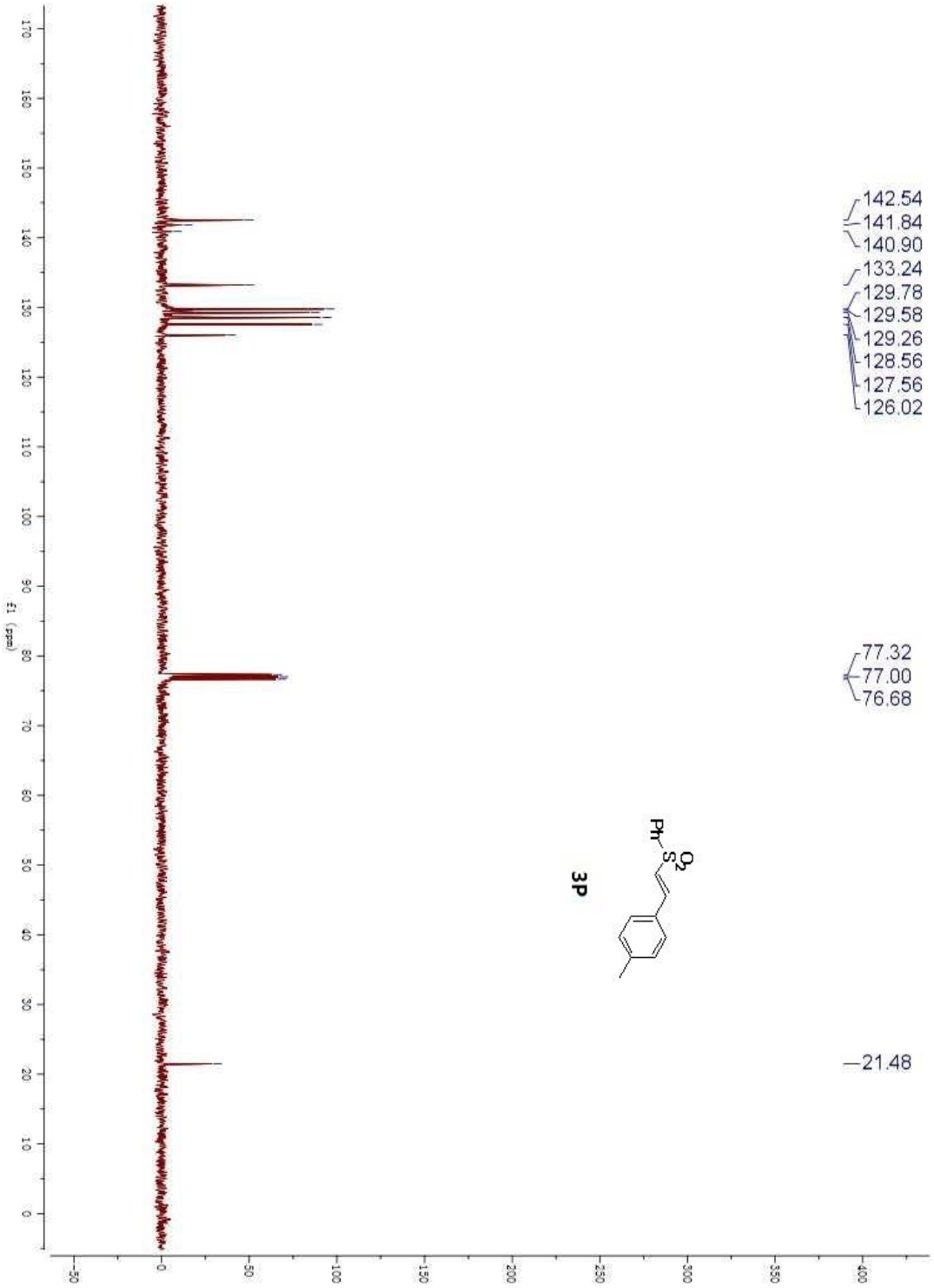
7.69
7.68
7.67
7.66
7.62
7.60
7.59
7.28
7.05
7.01
1.95
1.92
1.00
2.96
2.03
1.00
f1 (ppm)
3o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141.84
140.90
133.24
129.78
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128.56
127.56
126.02
77.32
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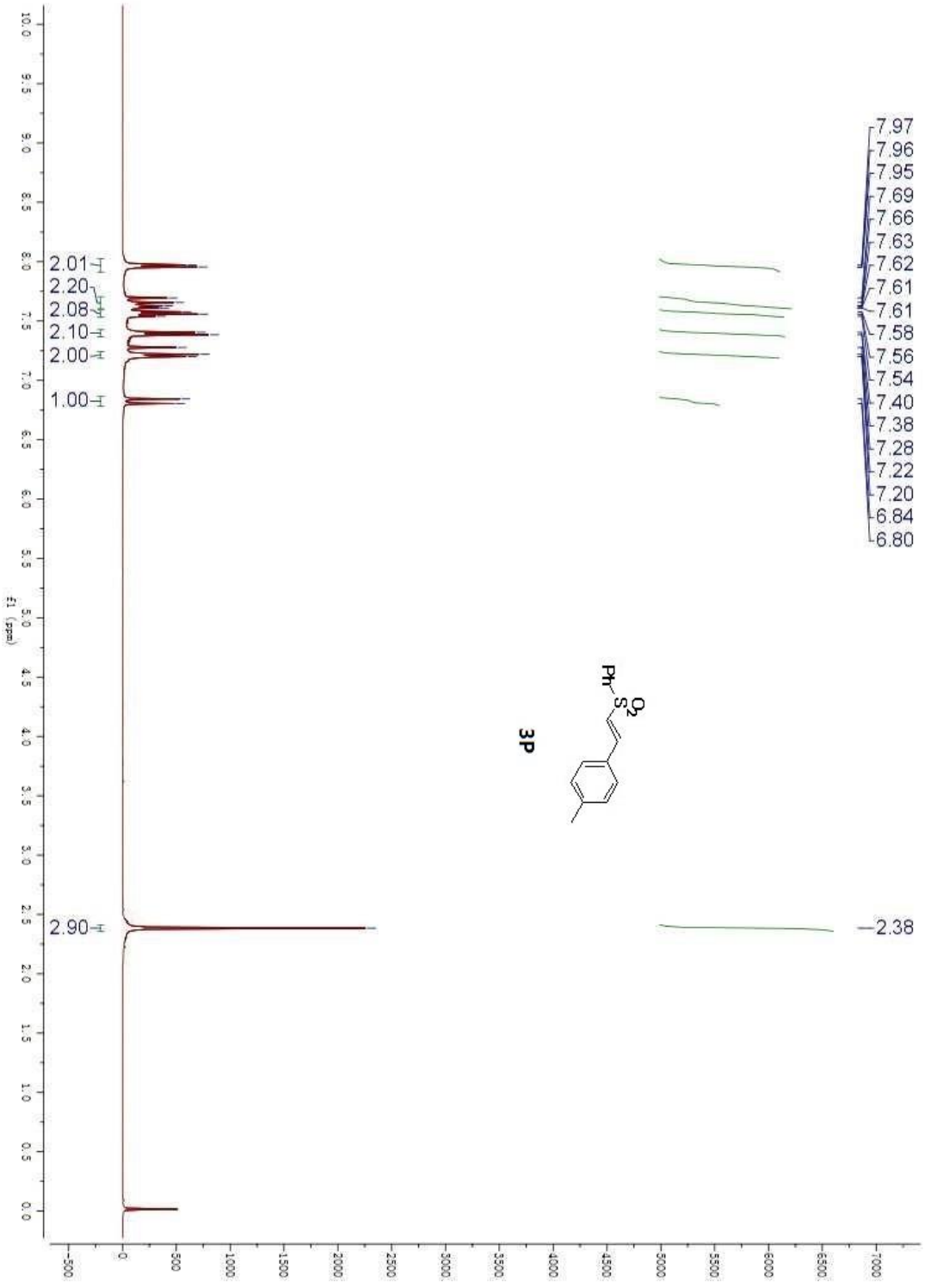
76.68
21.48
3P
Ph
S
O2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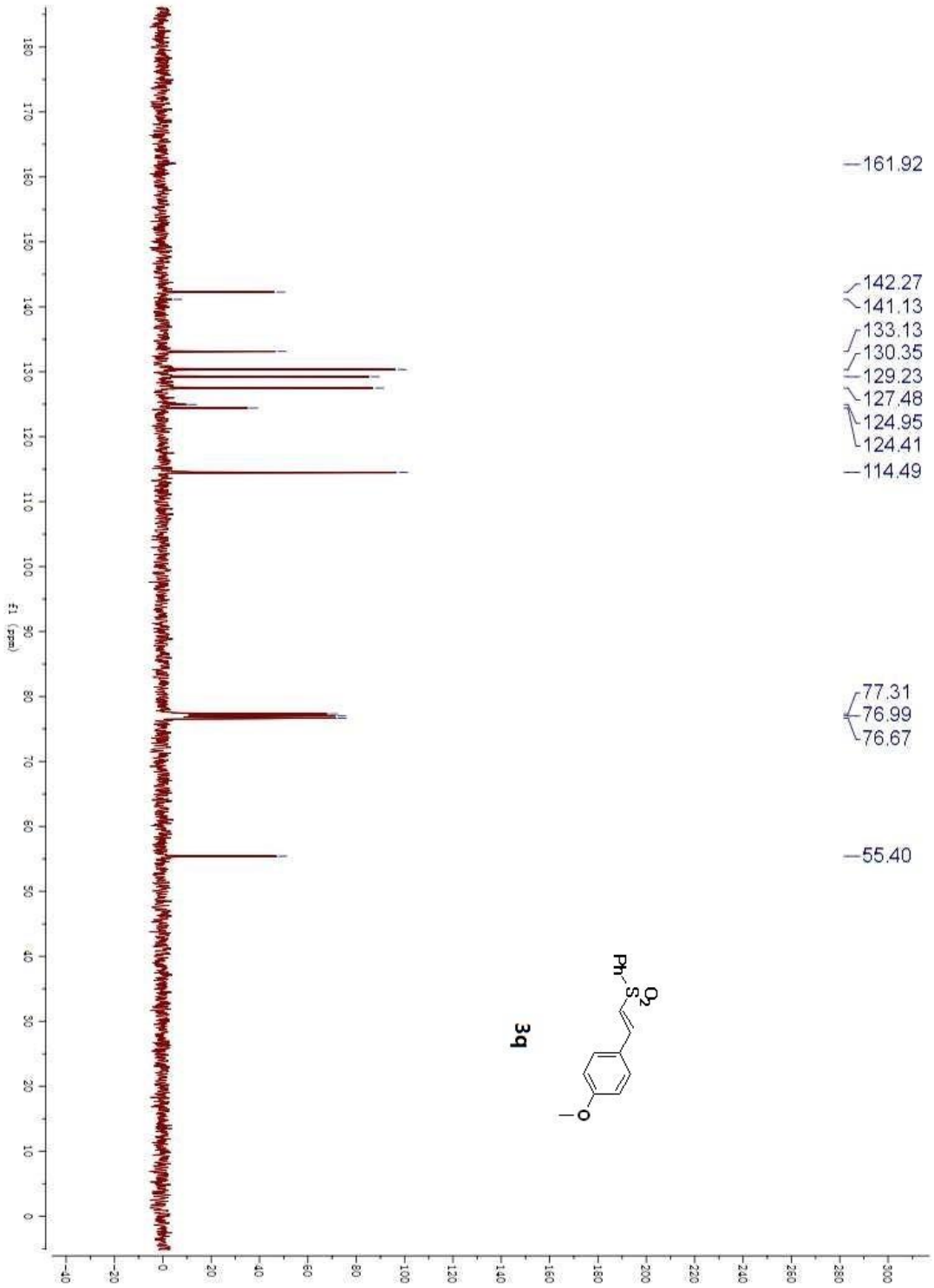
7.96
7.95
7.69
7.66
7.63
7.62
7.61
7.61
7.58
7.56
7.54
7.40
7.38
7.28
7.22
7.20
6.84
6.80
2.01
2.20
2.08
2.10
2.00
1.00
2.90
2.38
3P
f1 (ppm)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127.48
124.95
124.41
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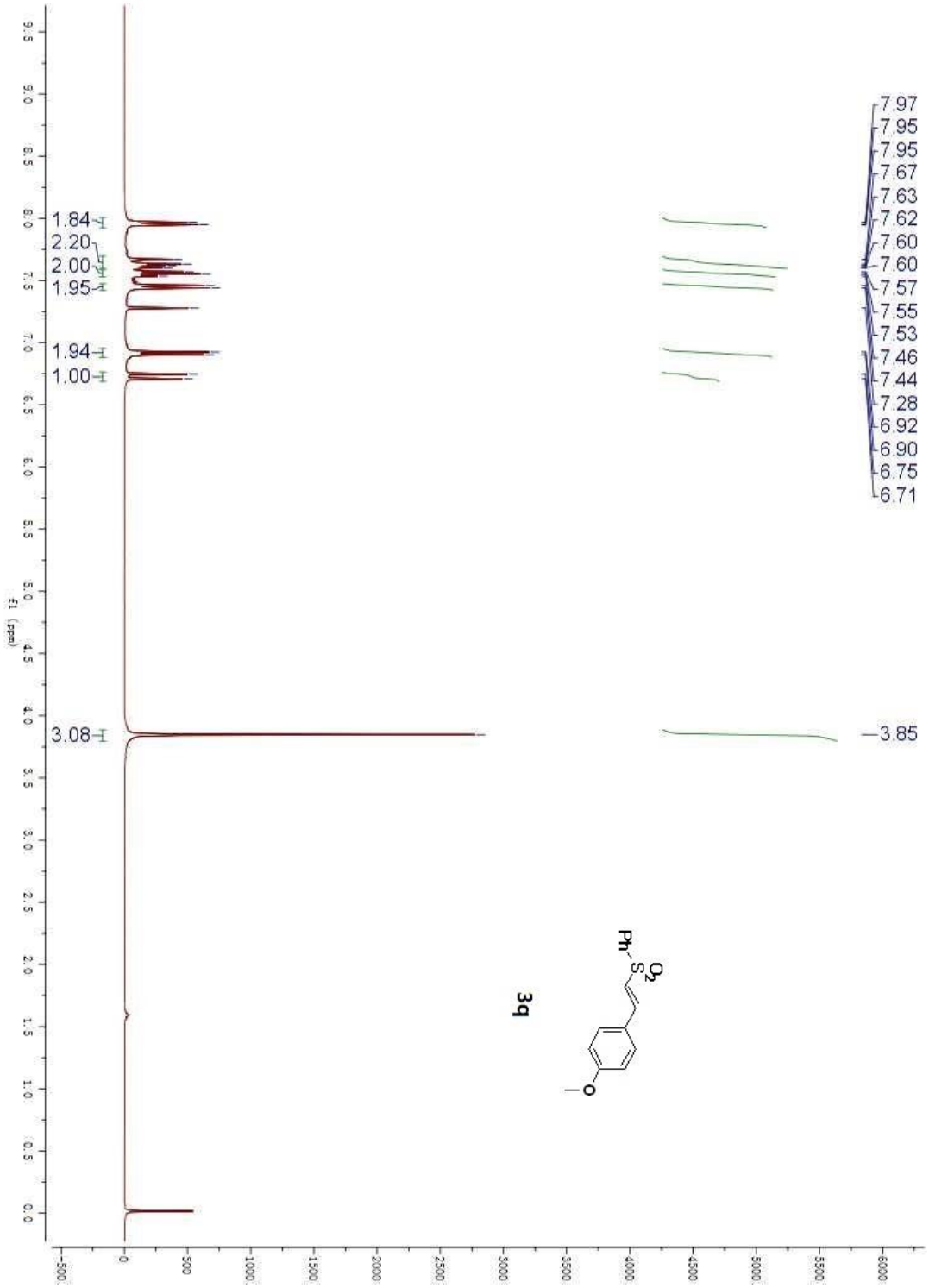
77.31
76.99
76.67
55.40
3q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7.95
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7.67
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7.62
7.60
7.60
7.57
7.55
7.53
7.46
7.44
7.28
6.92
6.90
6.75
6.71
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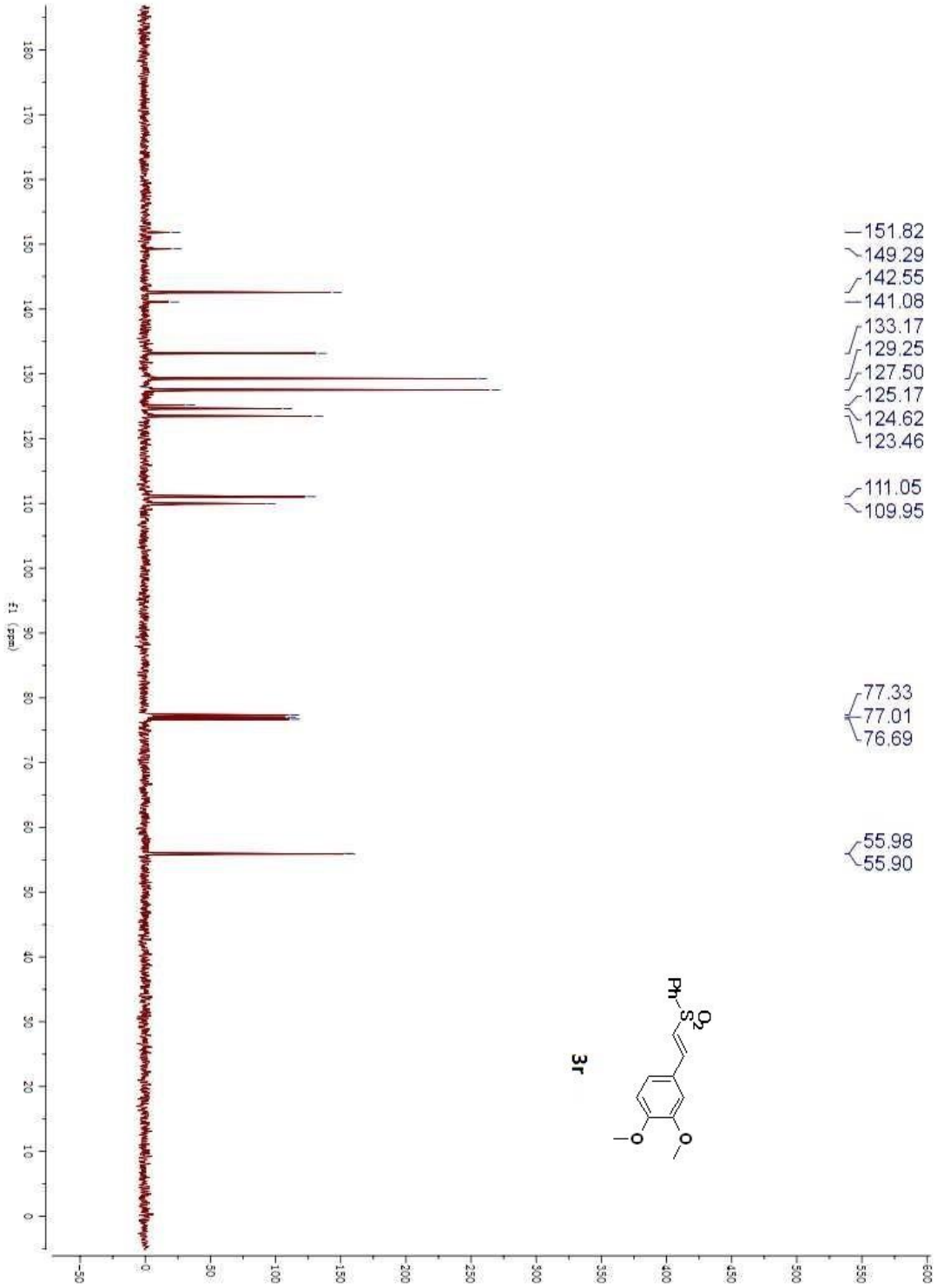
2.00
1.95
1.94
1.00
3.08
3.85
3q
Ph
S
O2
O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111.05
109.95
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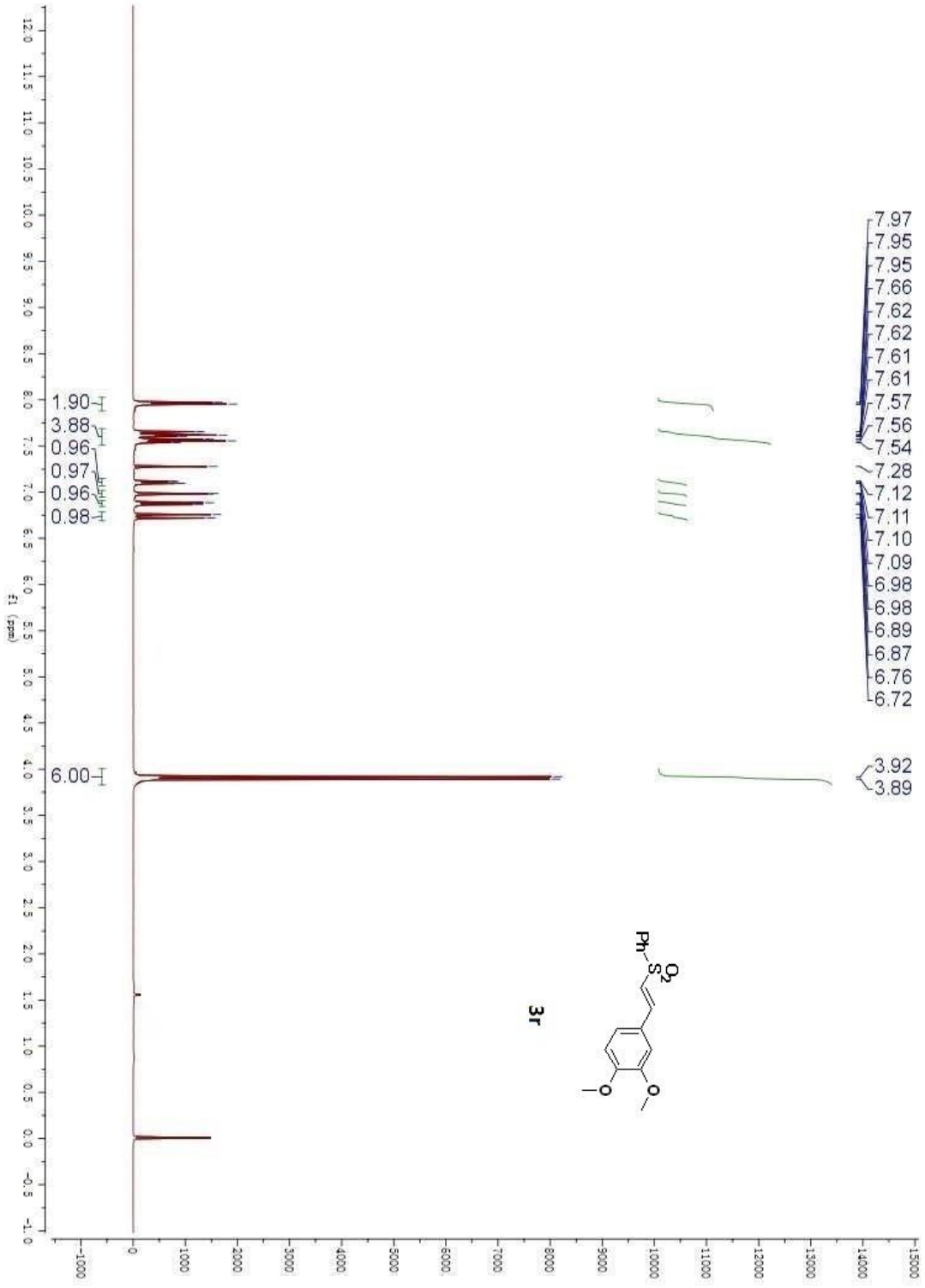
77.01
76.69
55.98
55.90
3r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7.95
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7.62
7.62
7.61
7.61
7.57
7.56
7.54
7.28
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7.11
7.10
7.09
6.98
6.98
6.89
6.87
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3.92
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1.90
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0.97
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0.98
6.00
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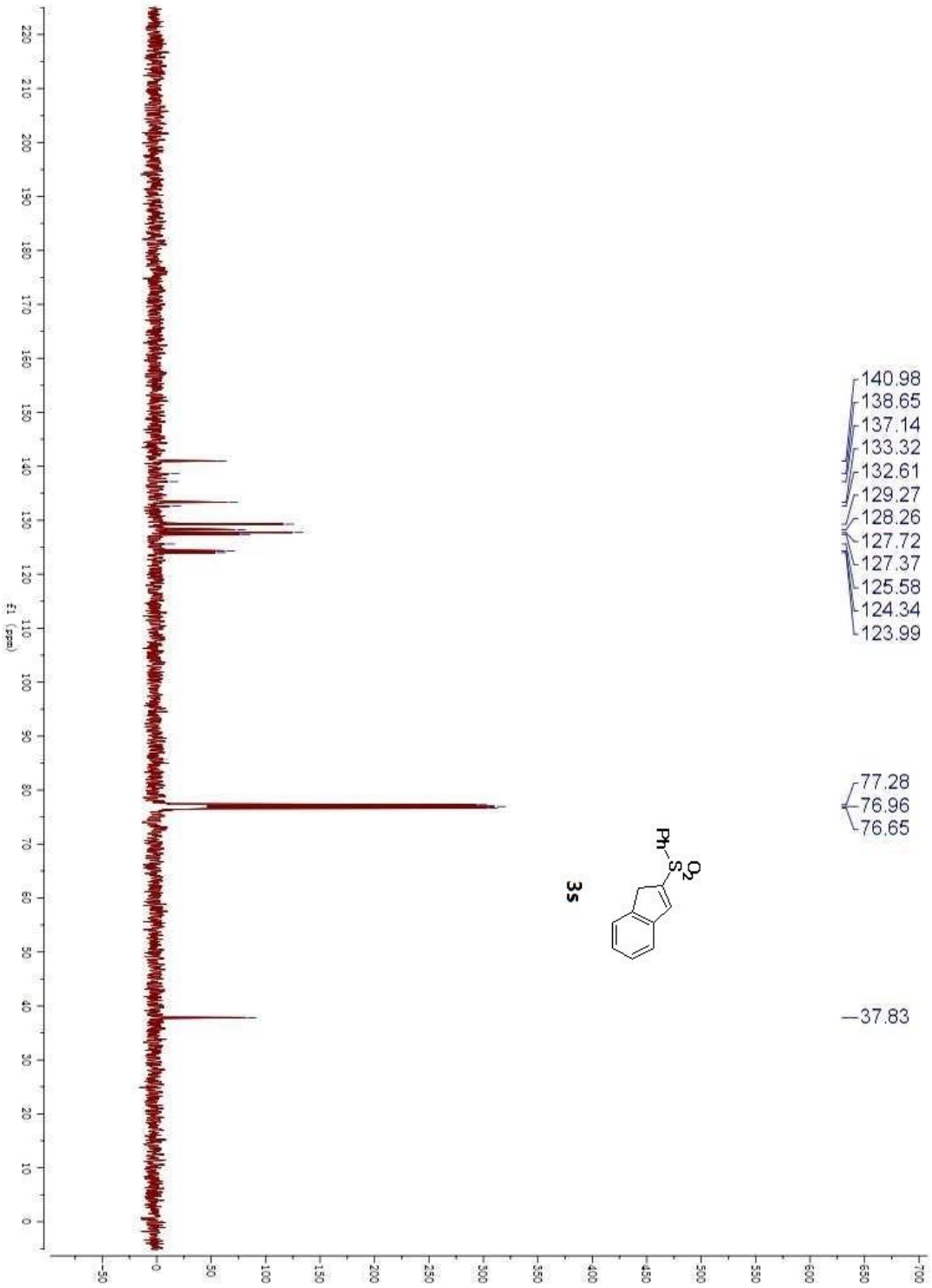
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128.26
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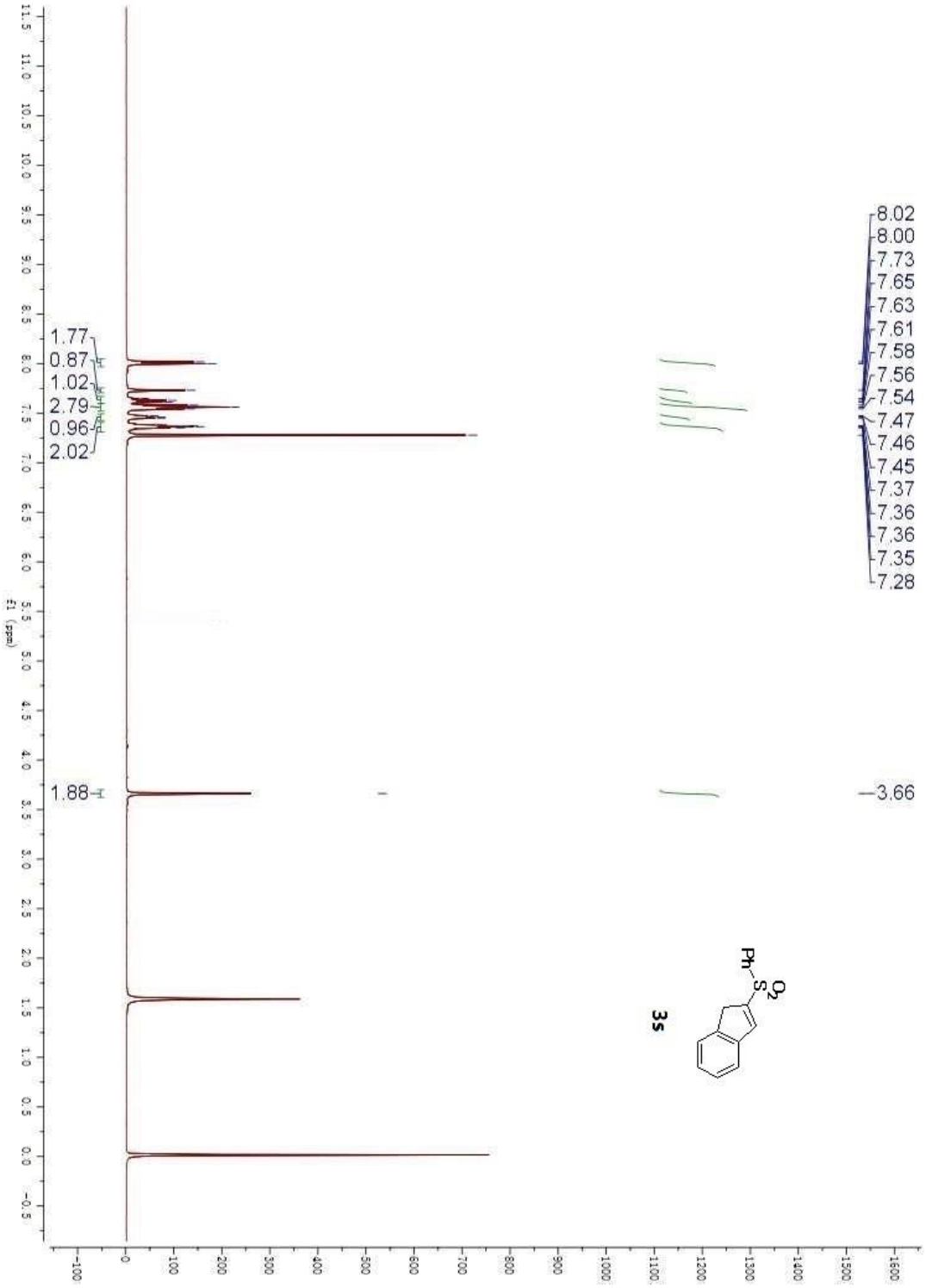
124.34
123.99
77.28
76.96
76.65
37.83
3s
Ph
S
O2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7.58
7.56
7.54
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7.46
7.45
7.37
7.36
7.36
7.35
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1.02
2.79
0.96
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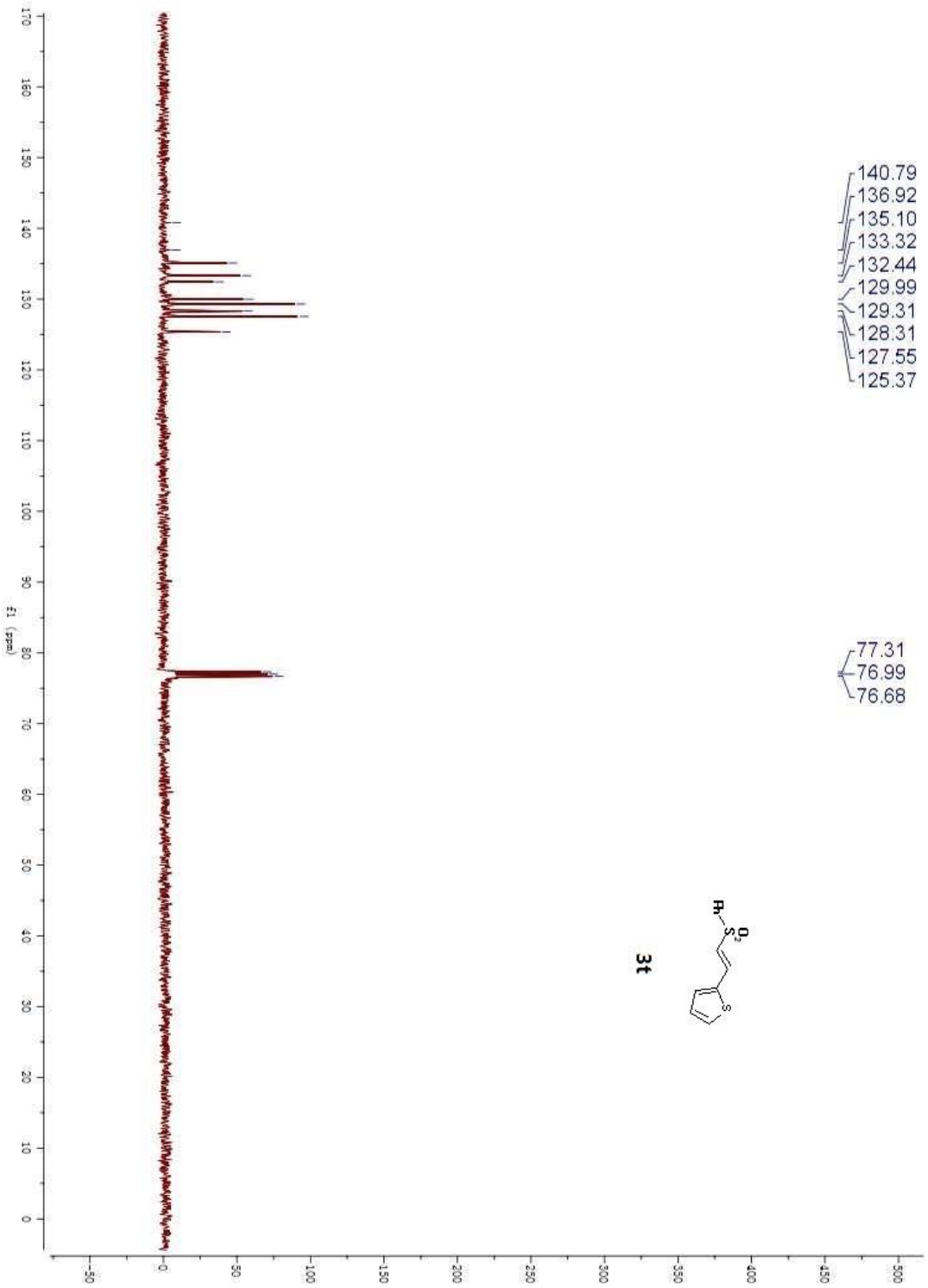
1.88
3.66
3s
Ph
S
O2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136.92
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128.31
127.55
125.37
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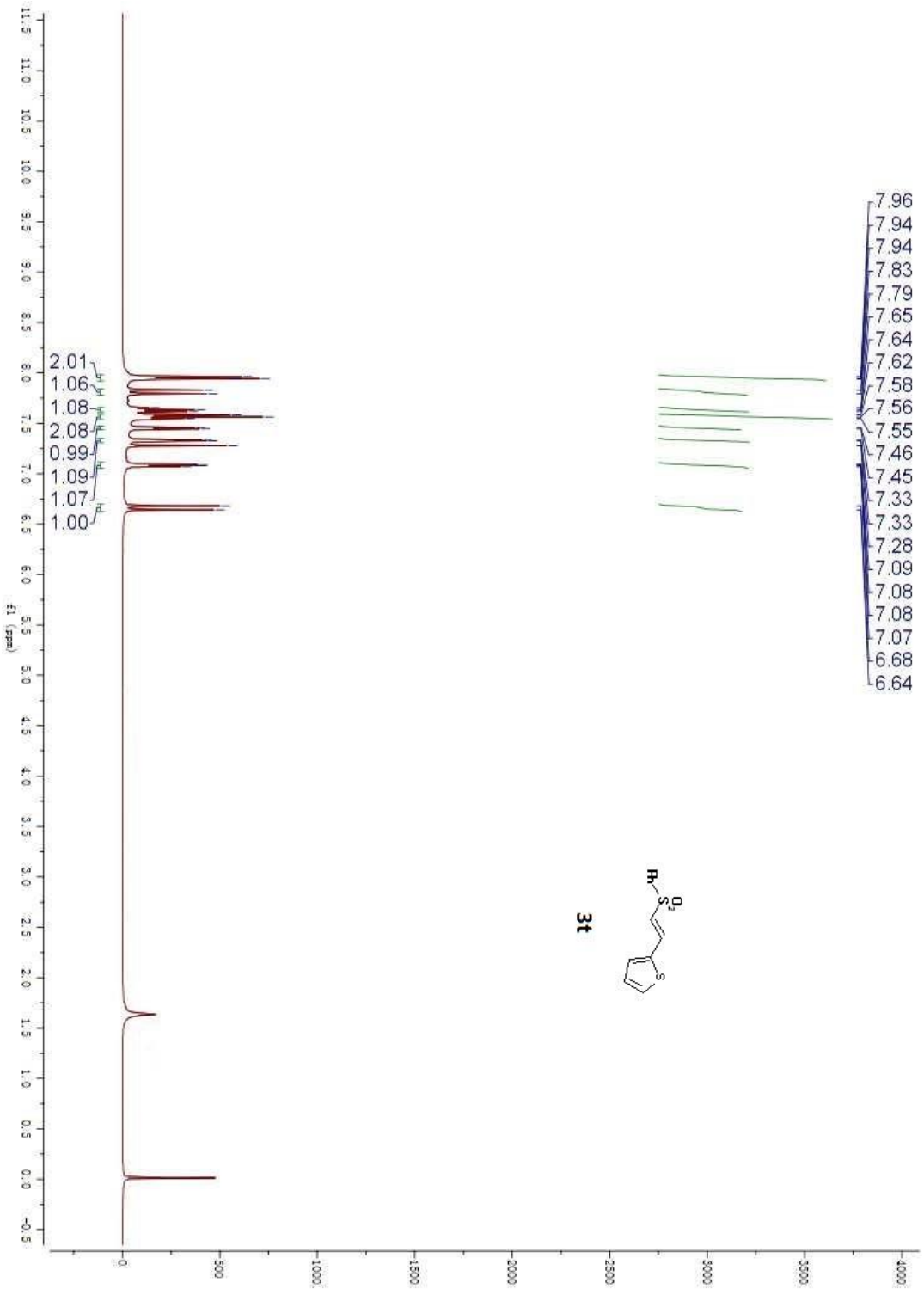
76.99
76.68
3t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7.94
7.94
7.83
7.79
7.65
7.64
7.62
7.58
7.56
7.55
7.46
7.45
7.33
7.33
7.28
7.09
7.08
7.08
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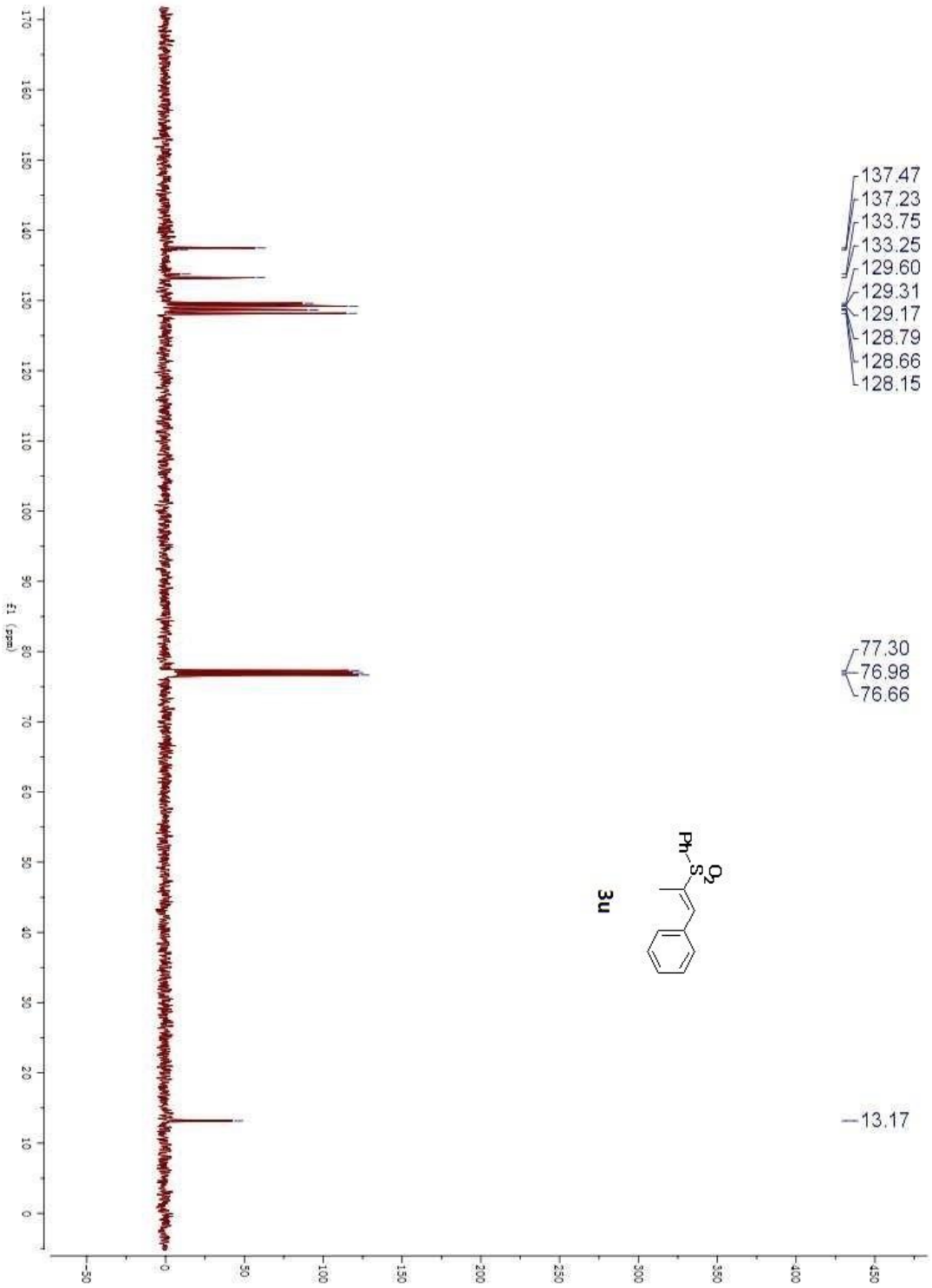
1.06
1.08
2.08
0.99
1.09
1.07
1.00
3t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129.17
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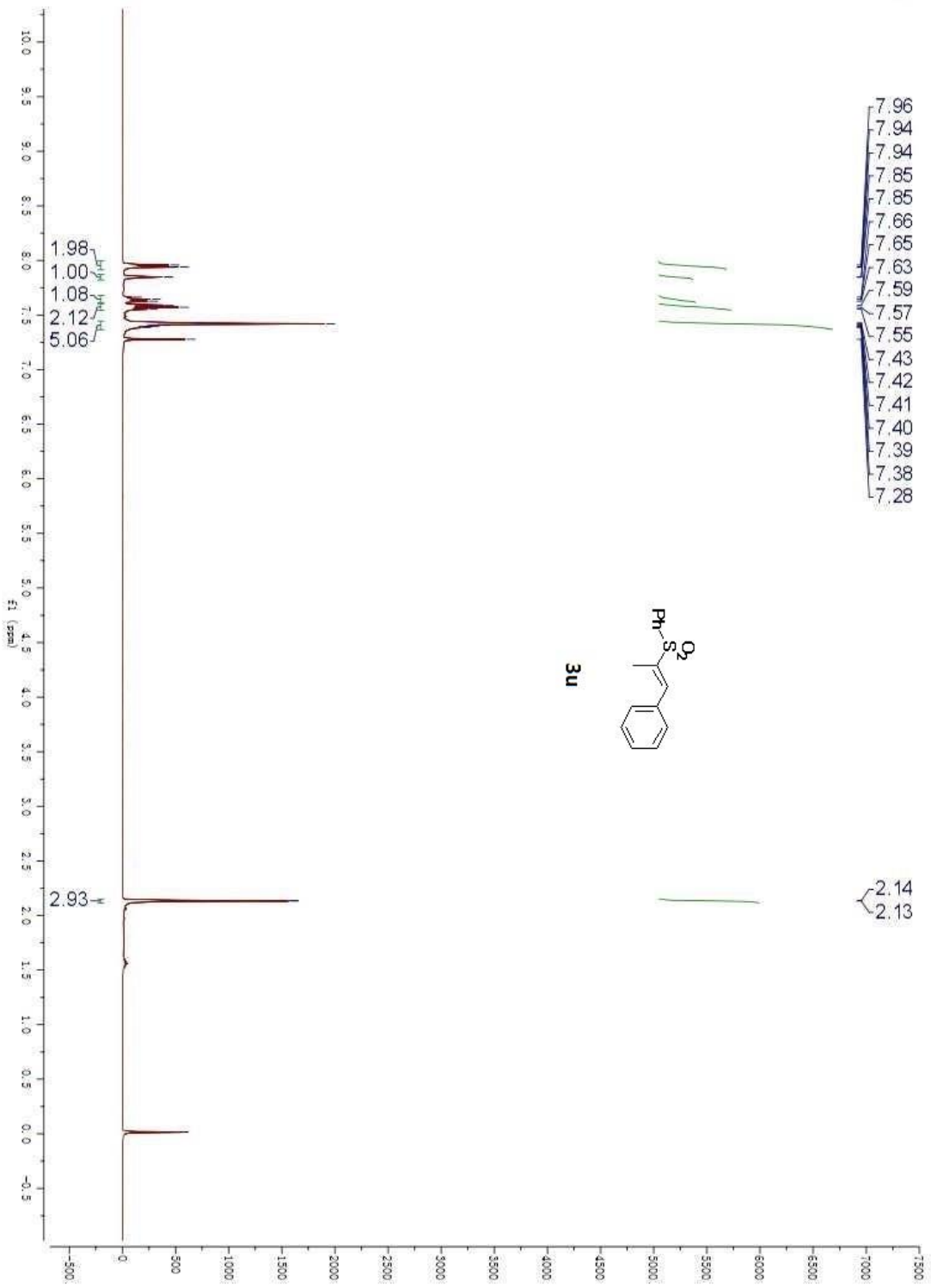
76.66
13.17
3u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7.94
7.94
7.85
7.85
7.66
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7.63
7.59
7.57
7.55
7.43
7.42
7.41
7.40
7.39
7.38
7.28
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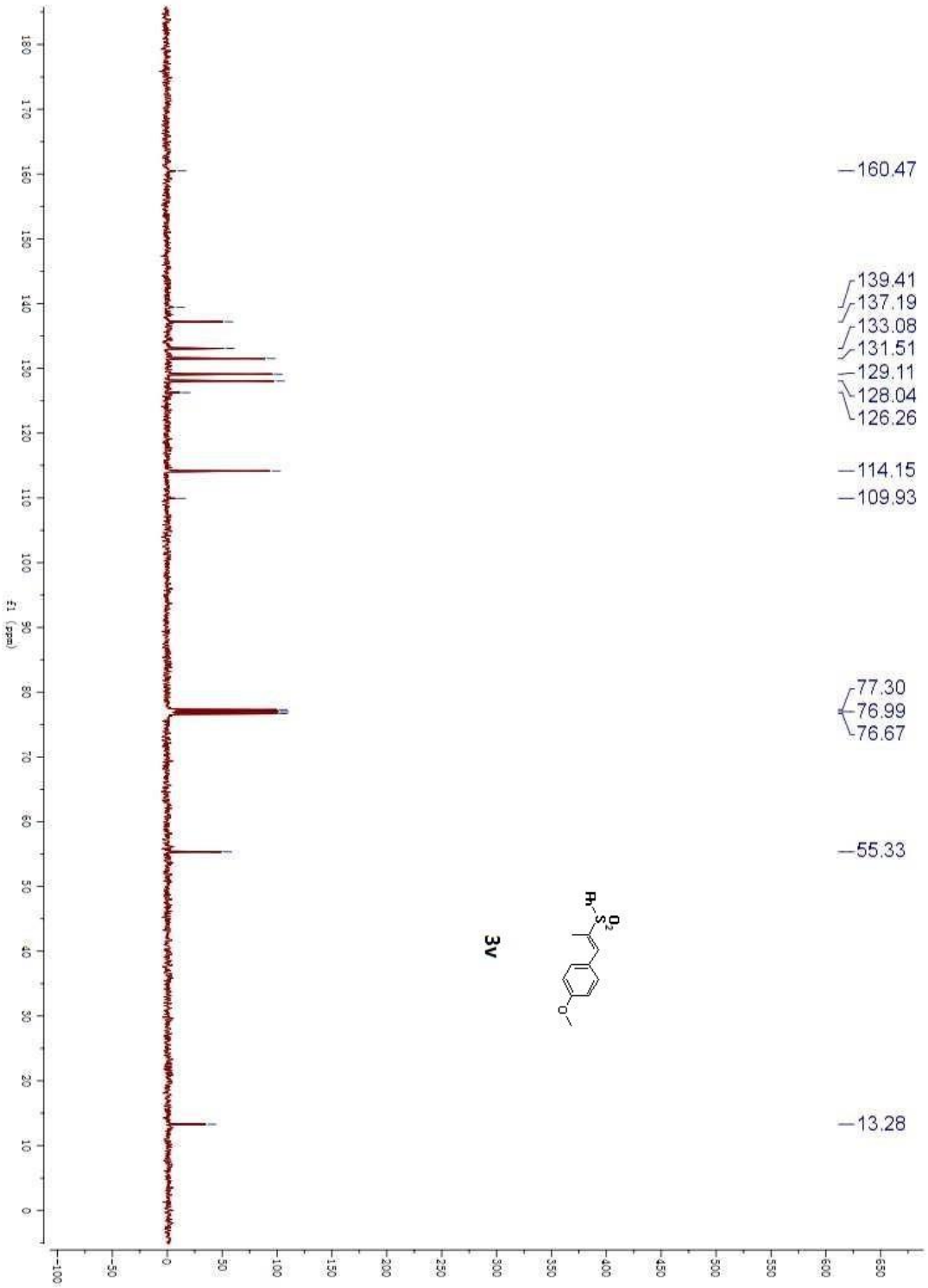
1.00
1.08
2.12
5.06
2.93
2.14
2.13
3u
Ph
S
O2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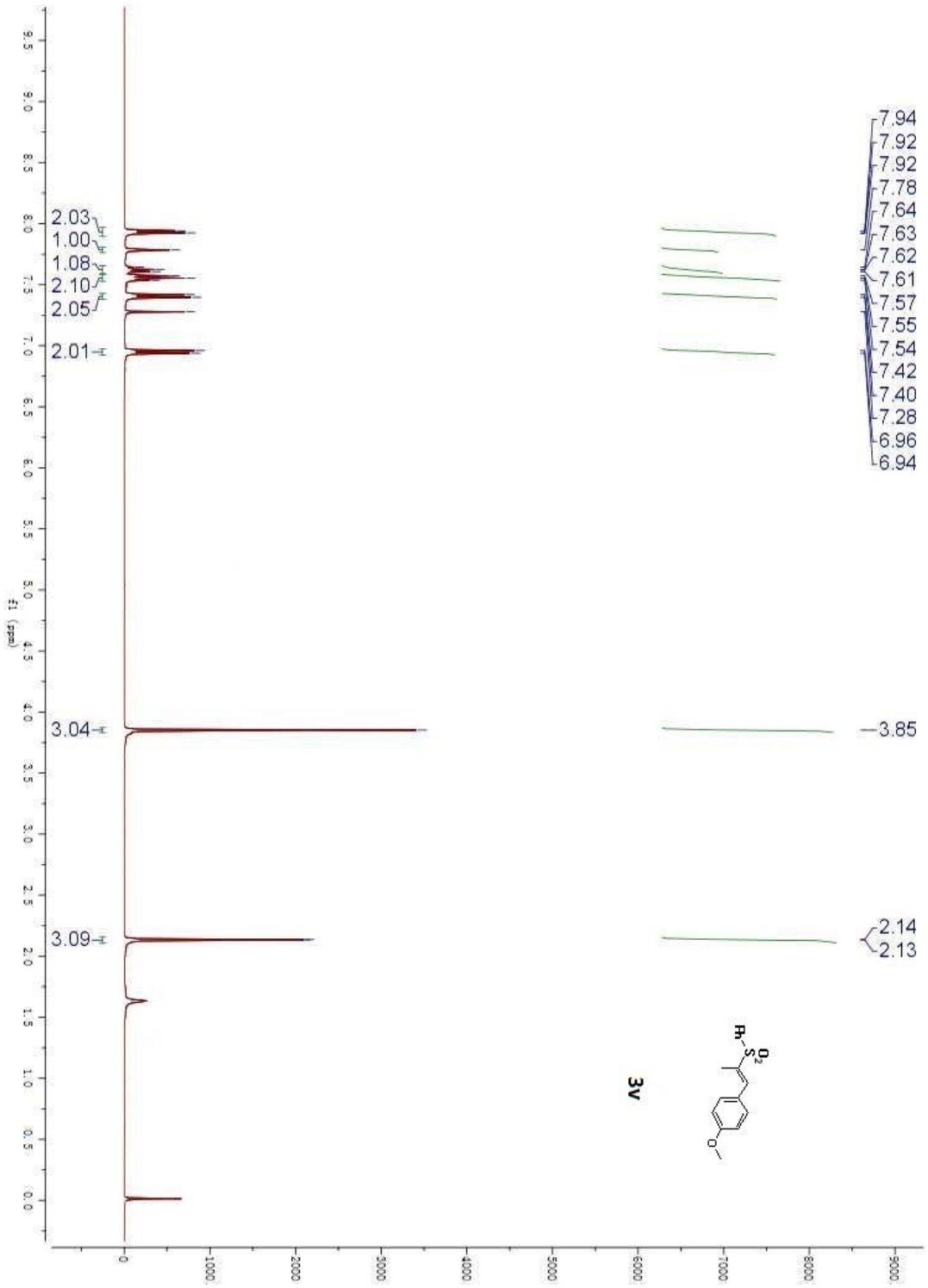
109.93
77.30
76.99
76.67
55.33
13.28
3v
f1 (ppm)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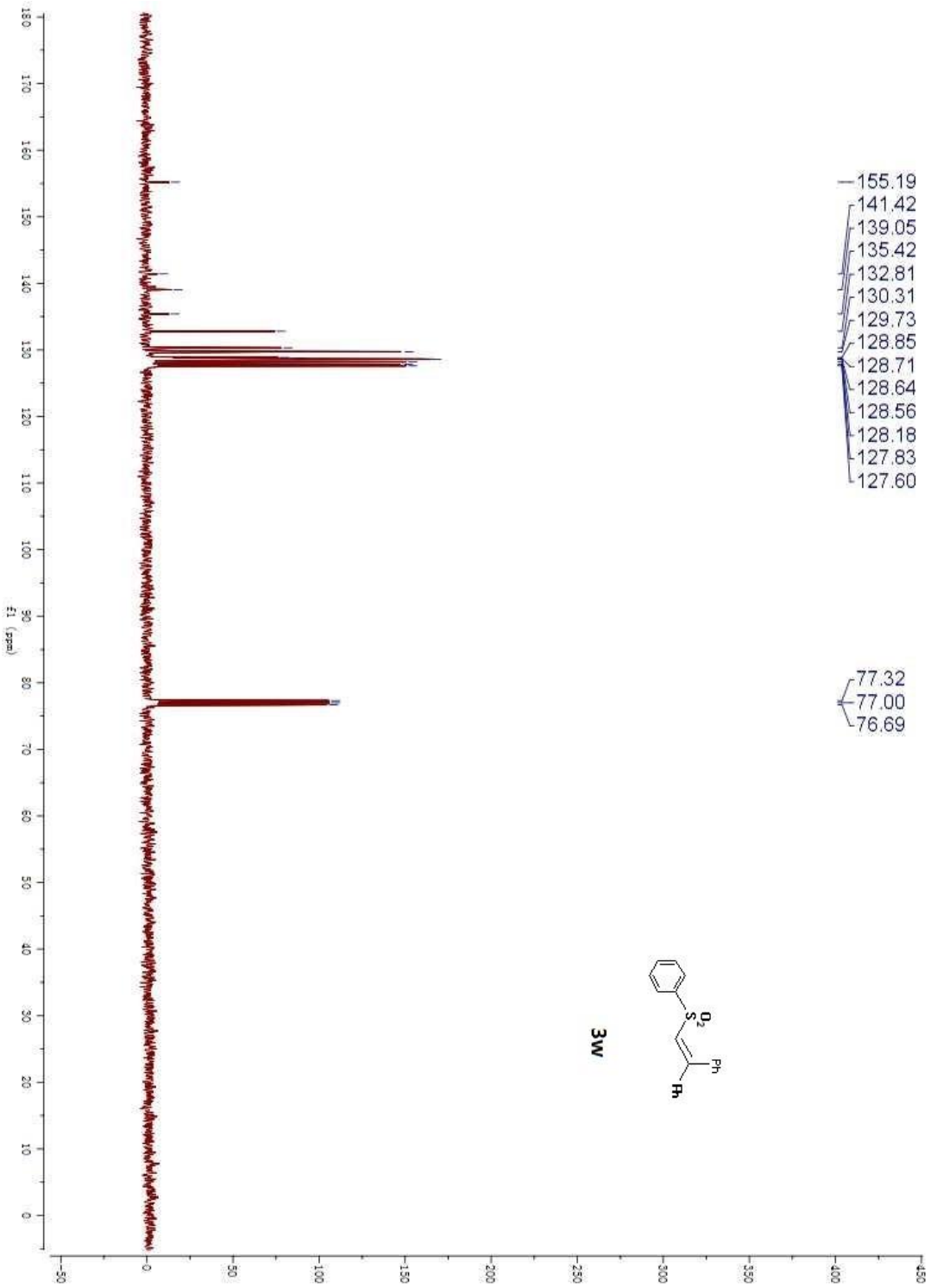
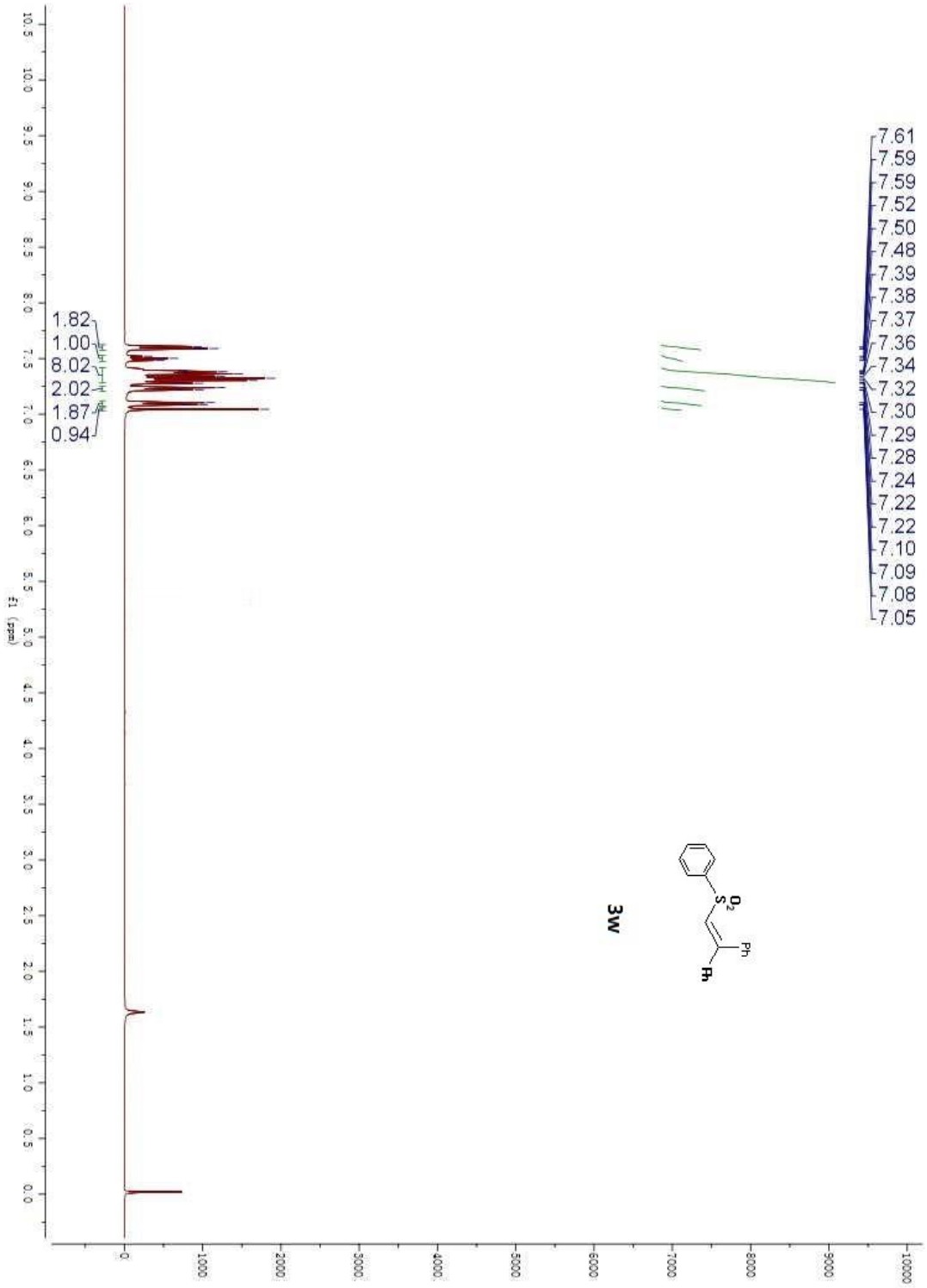
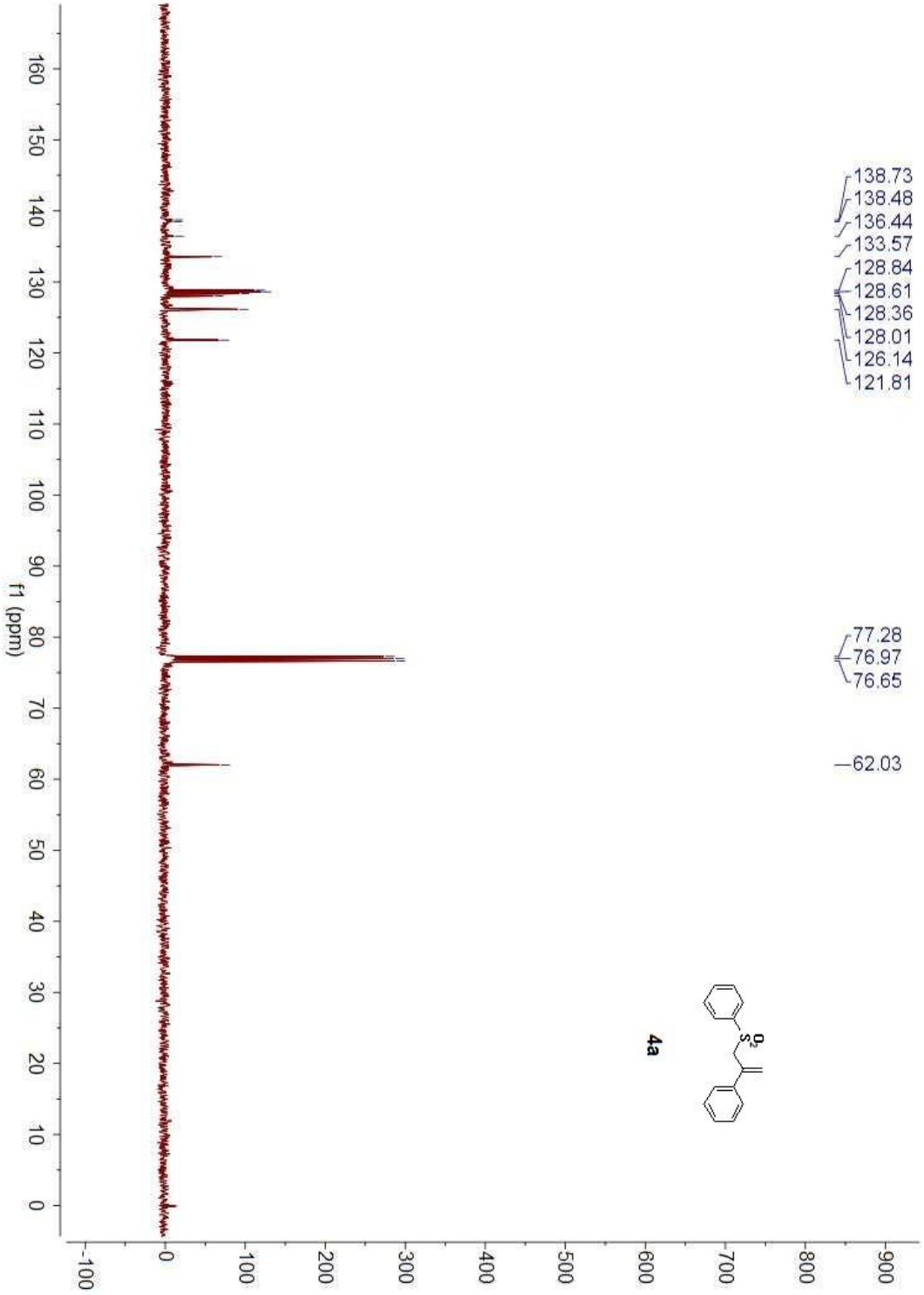
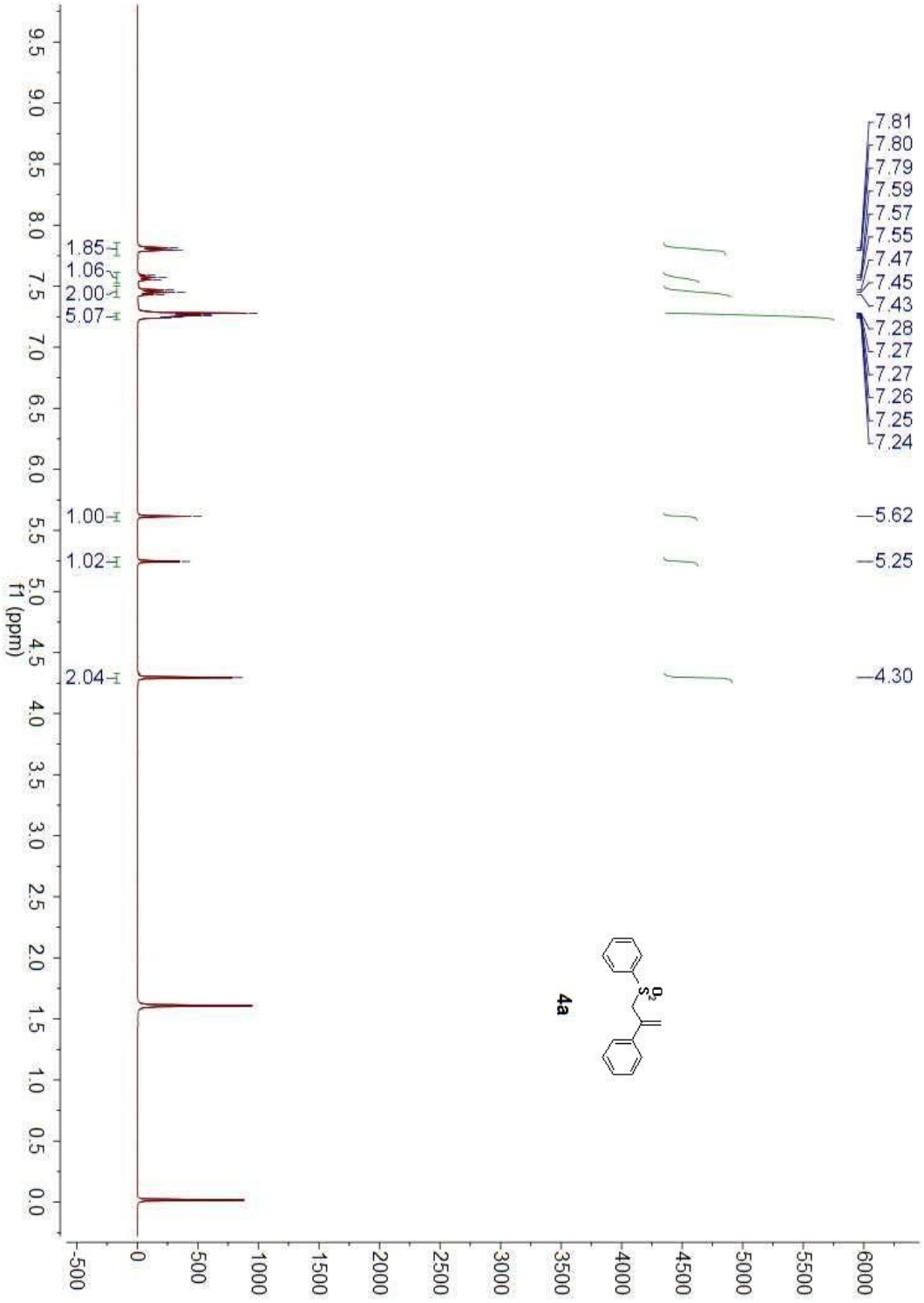
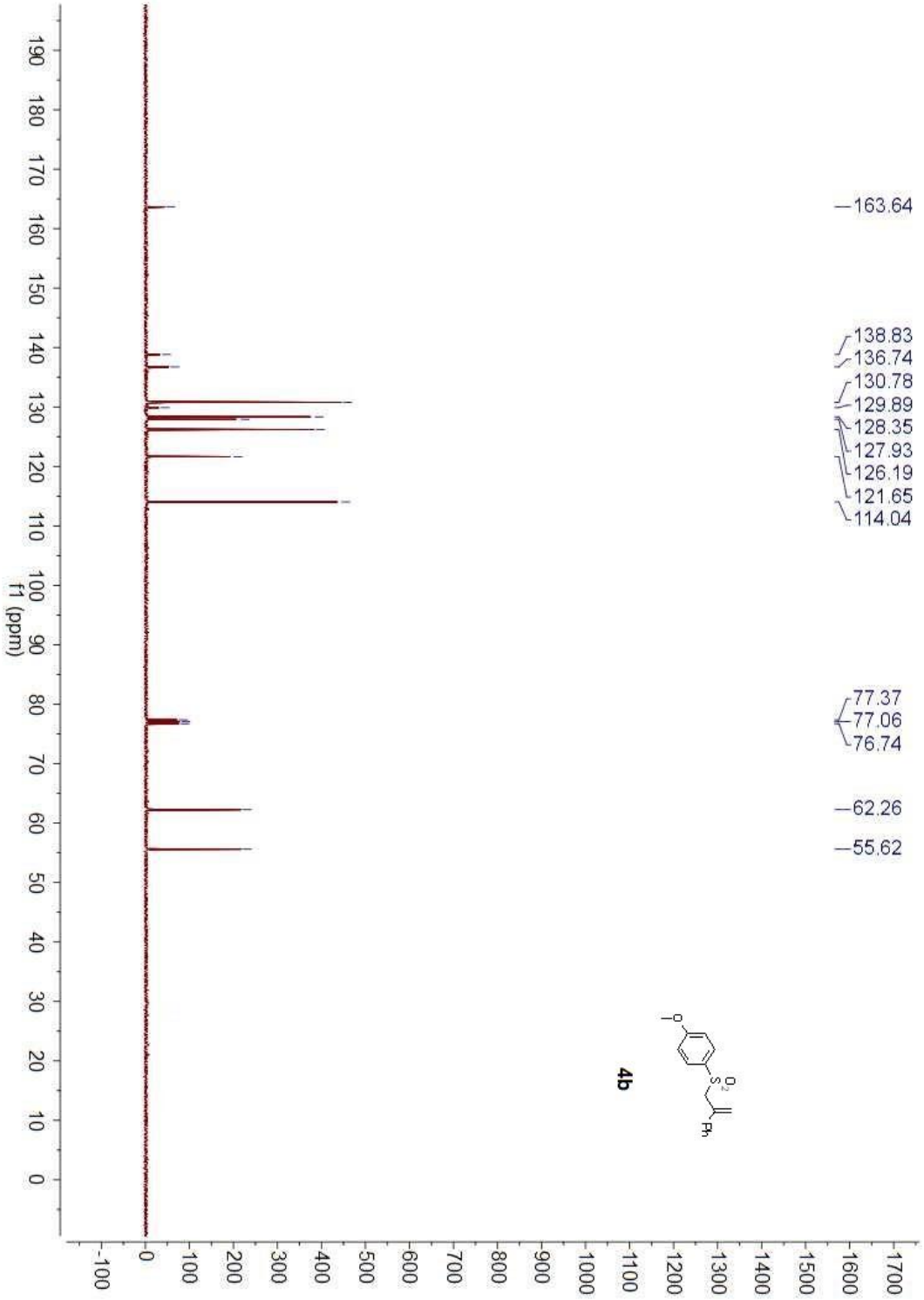
7.63
7.62
7.61
7.57
7.55
7.54
7.42
7.40
7.28
6.96
6.94
2.03
1.00
1.08
2.10
2.05
2.01
3.04
3.09
3.85
2.14
2.13
3v
f1 (ppm)

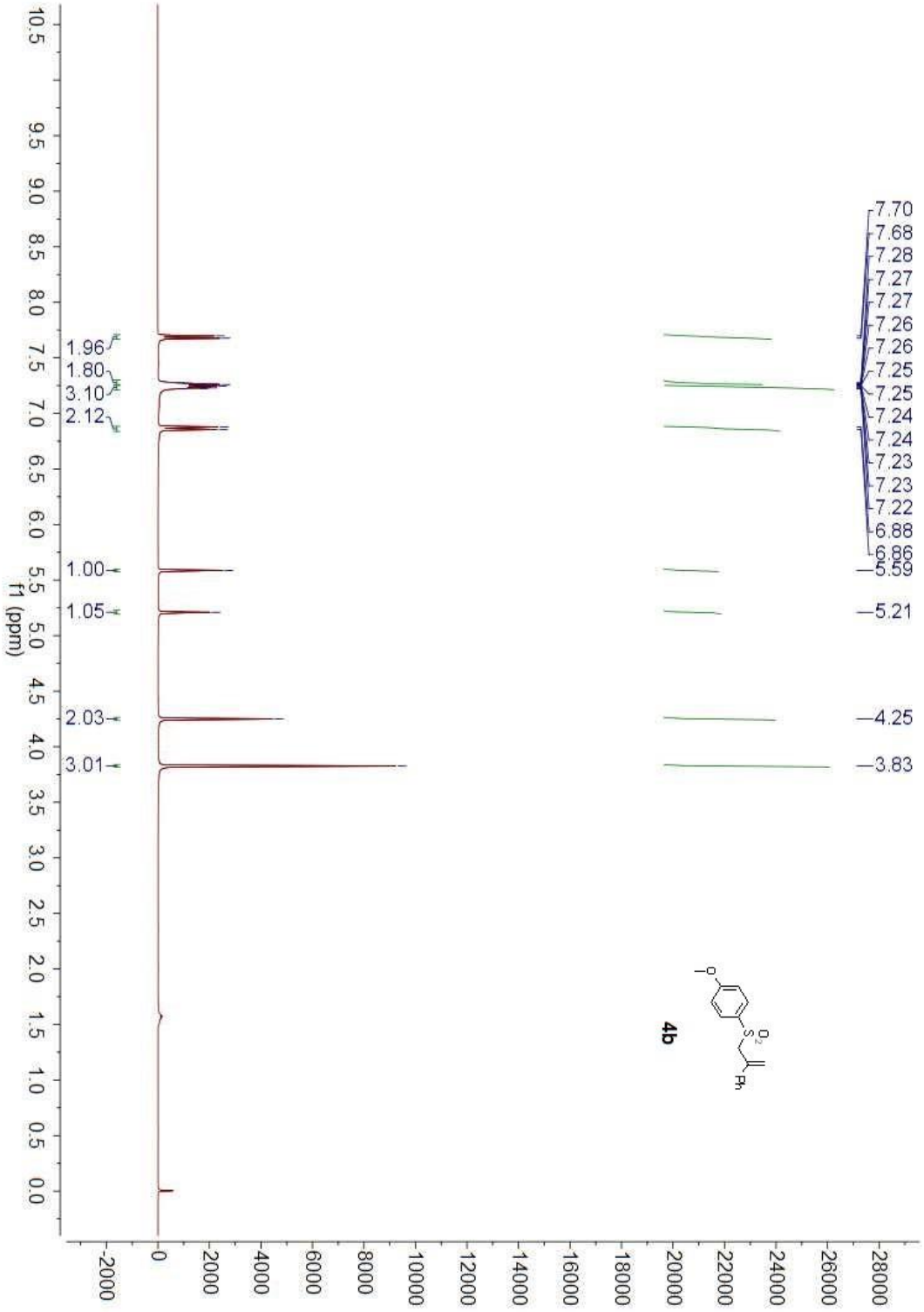

155.19
141.42
139.05
135.42
132.81
130.31
129.73
128.85
128.71
128.64
128.56
128.18
127.83
127.60
77.32
77.00
76.69
f1 (ppm)
3w

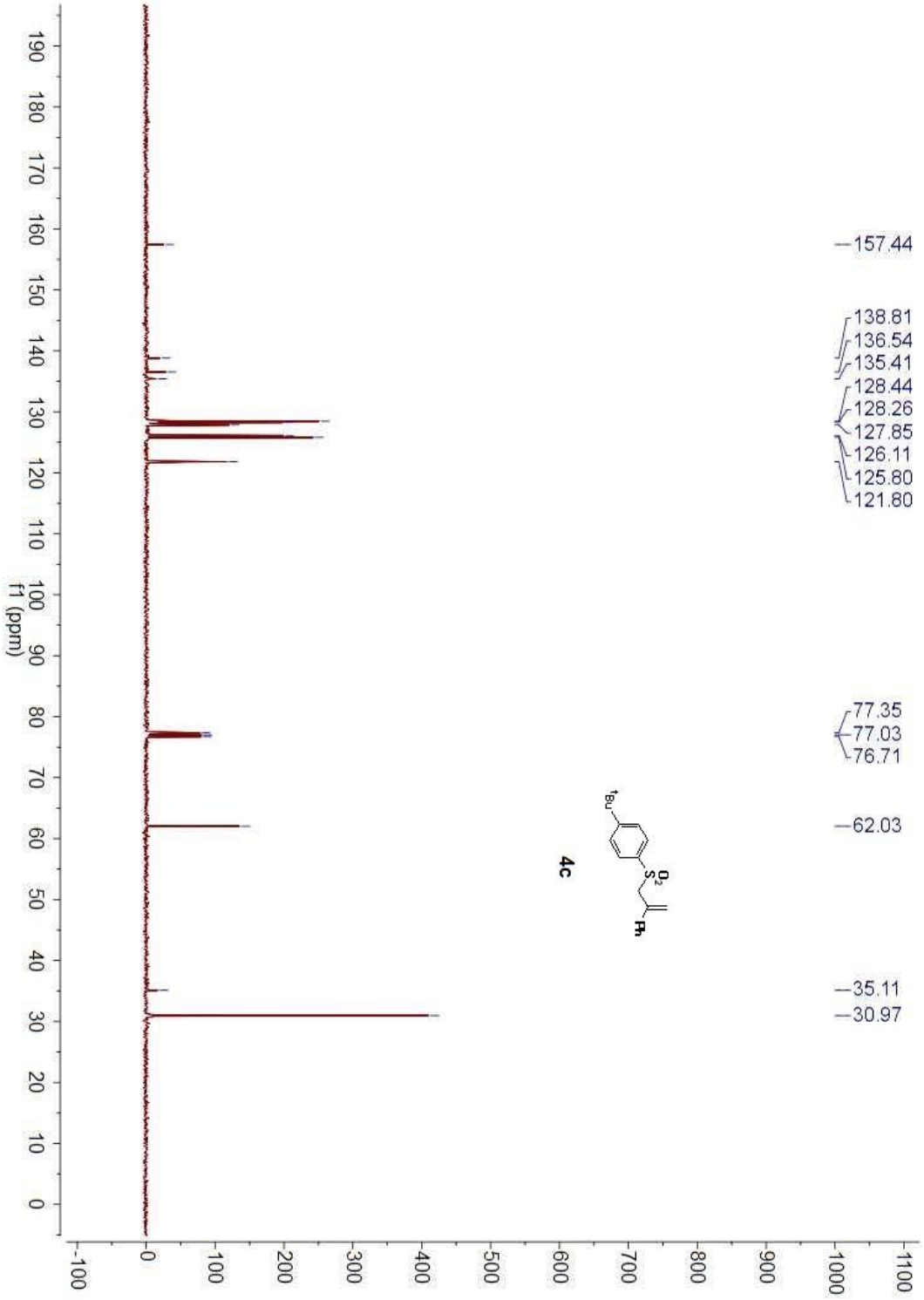

1.82
1.00
8.02
2.02
1.87
0.94
7.61
7.59
7.59
7.52
7.50
7.48
7.39
7.38
7.37
7.36
7.34
7.32
7.30
7.29
7.28
7.24
7.22
7.22
7.10
7.09
7.08
7.05
3w
Ph
Ph

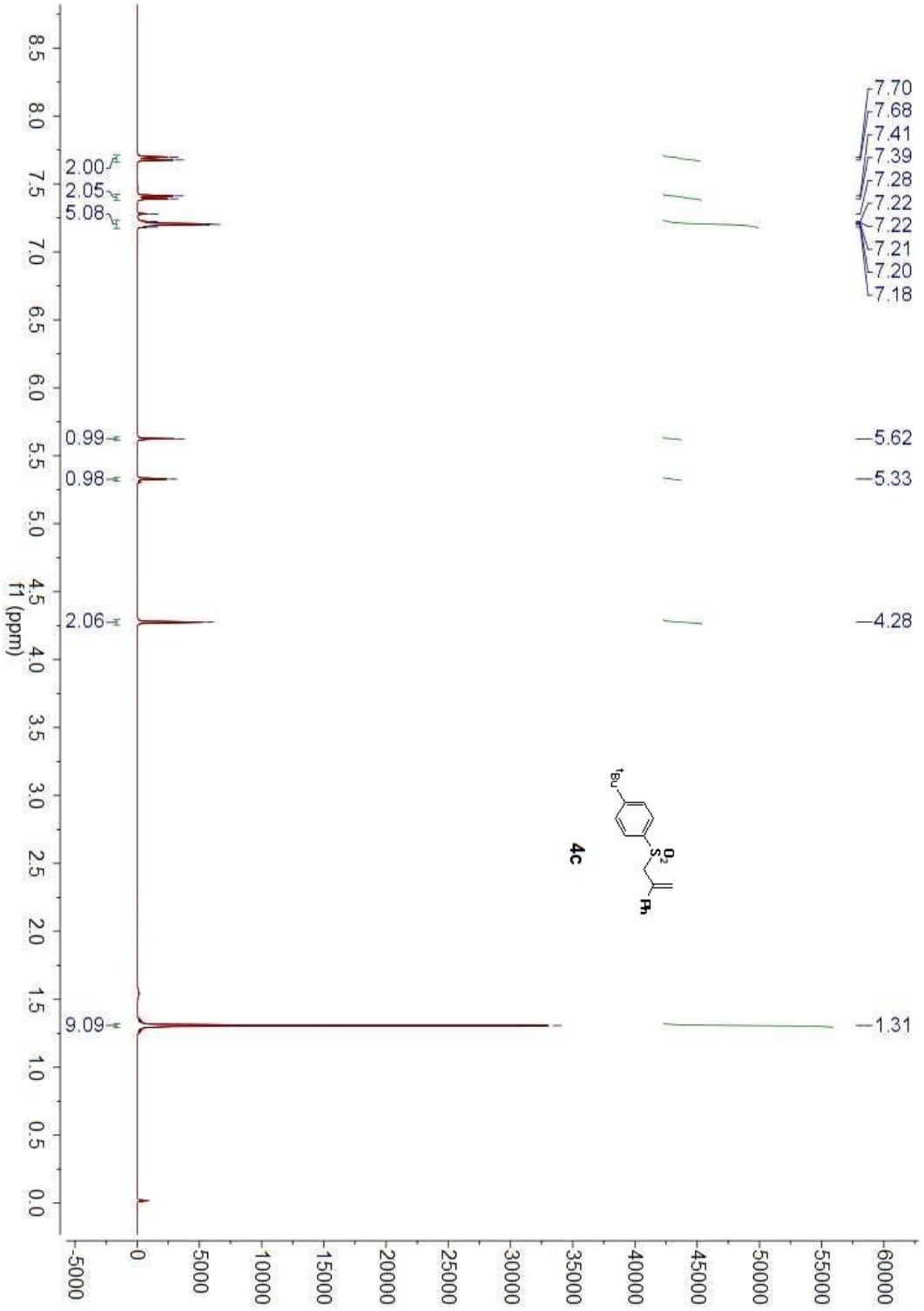

138.73
138.48
136.44
133.57
128.84
128.61
128.36
128.01
126.14
121.81
77.28
76.97
76.65
62.03
4a
f1 (ppm)

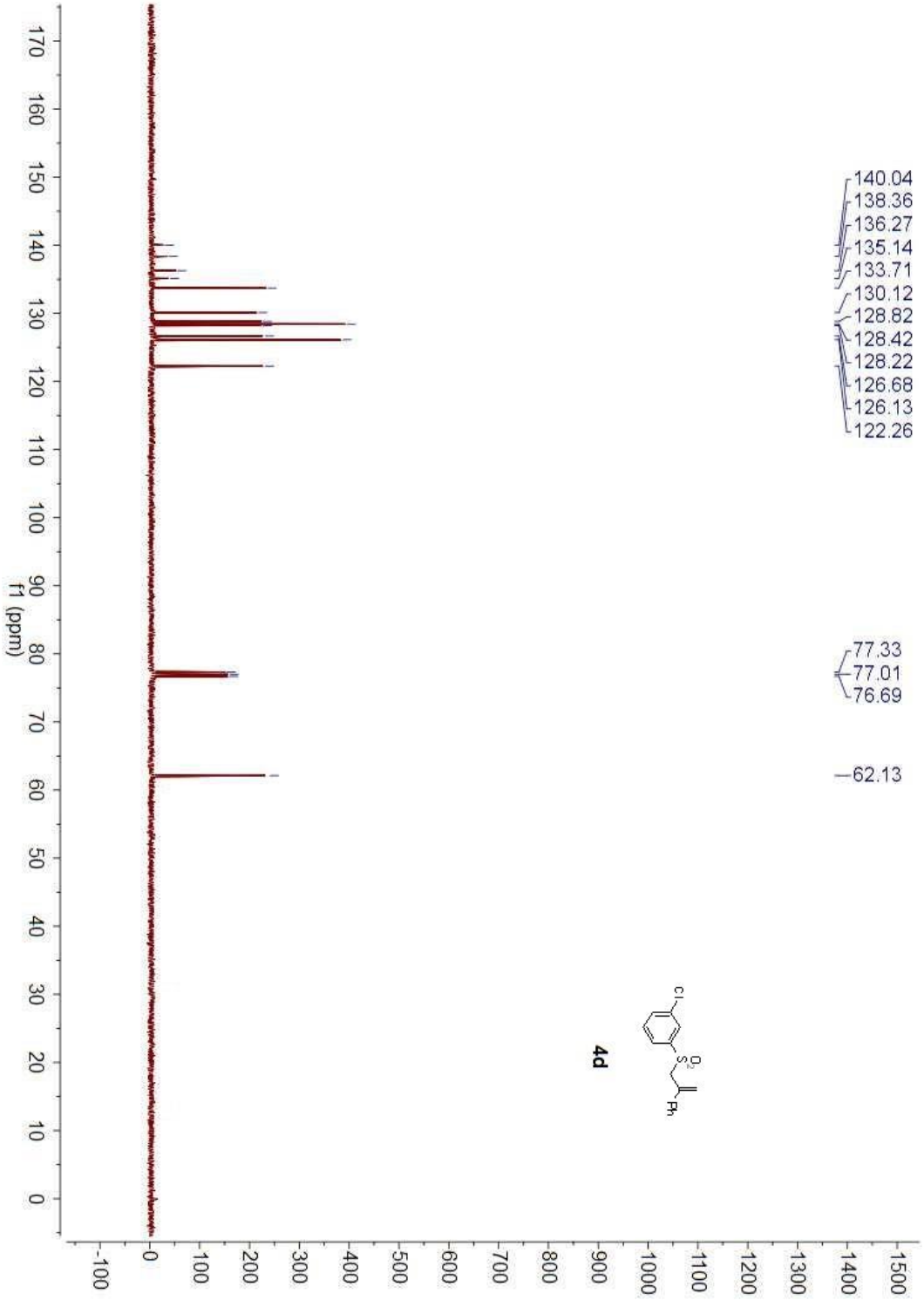

7.81
7.80
7.79
7.59
7.57
7.55
7.47
7.45
7.43
7.28
7.27
7.27
7.26
7.25
7.24
1.85
1.06
2.00
5.07
1.00
1.02
2.04
5.62
5.25
4.30
f1 (ppm)
4a

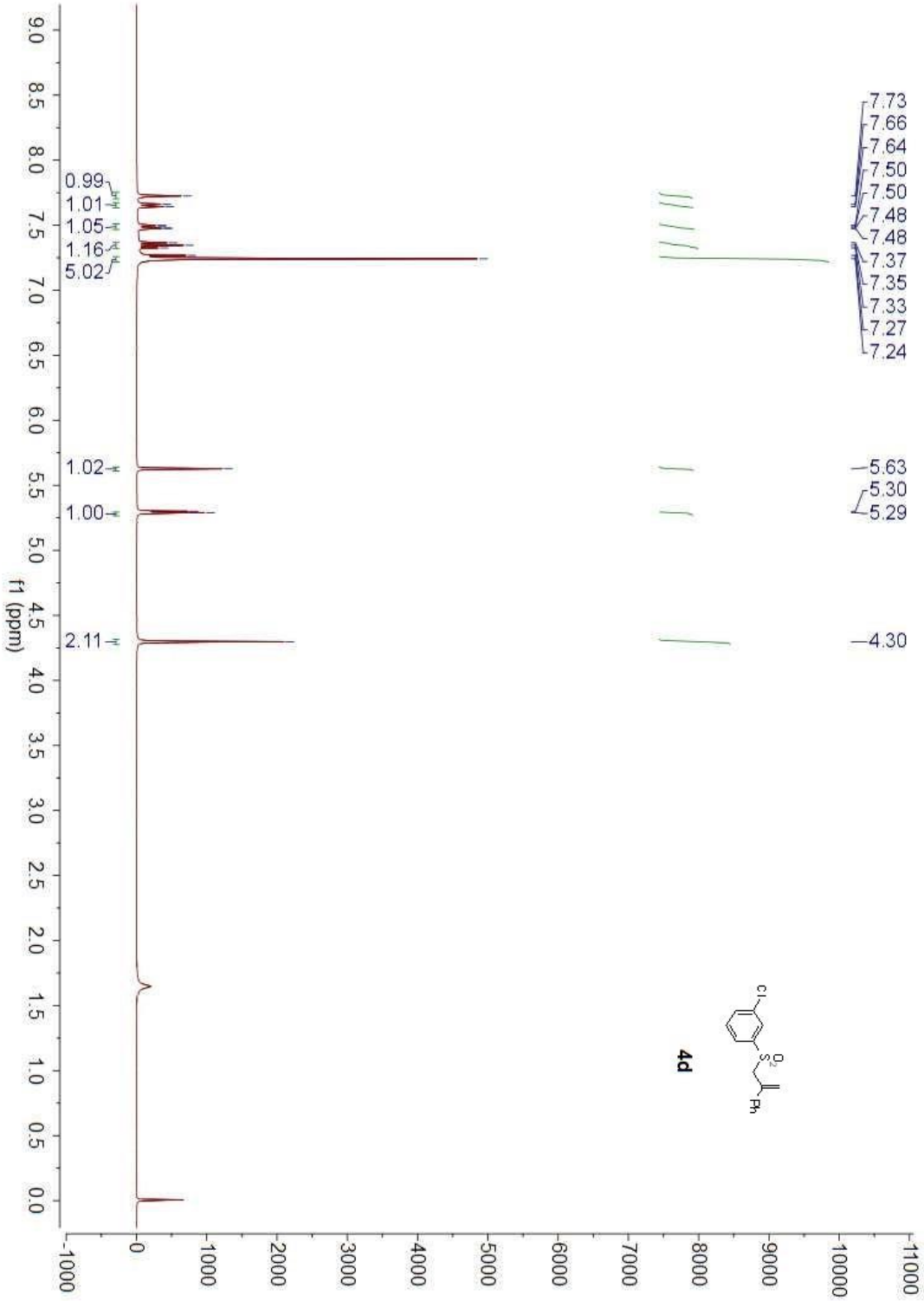

163.64
138.83
136.74
130.78
129.89
128.35
127.93
126.19
121.65
114.04
77.37
77.06
76.74
62.26
55.62
4b
f1 (ppm)

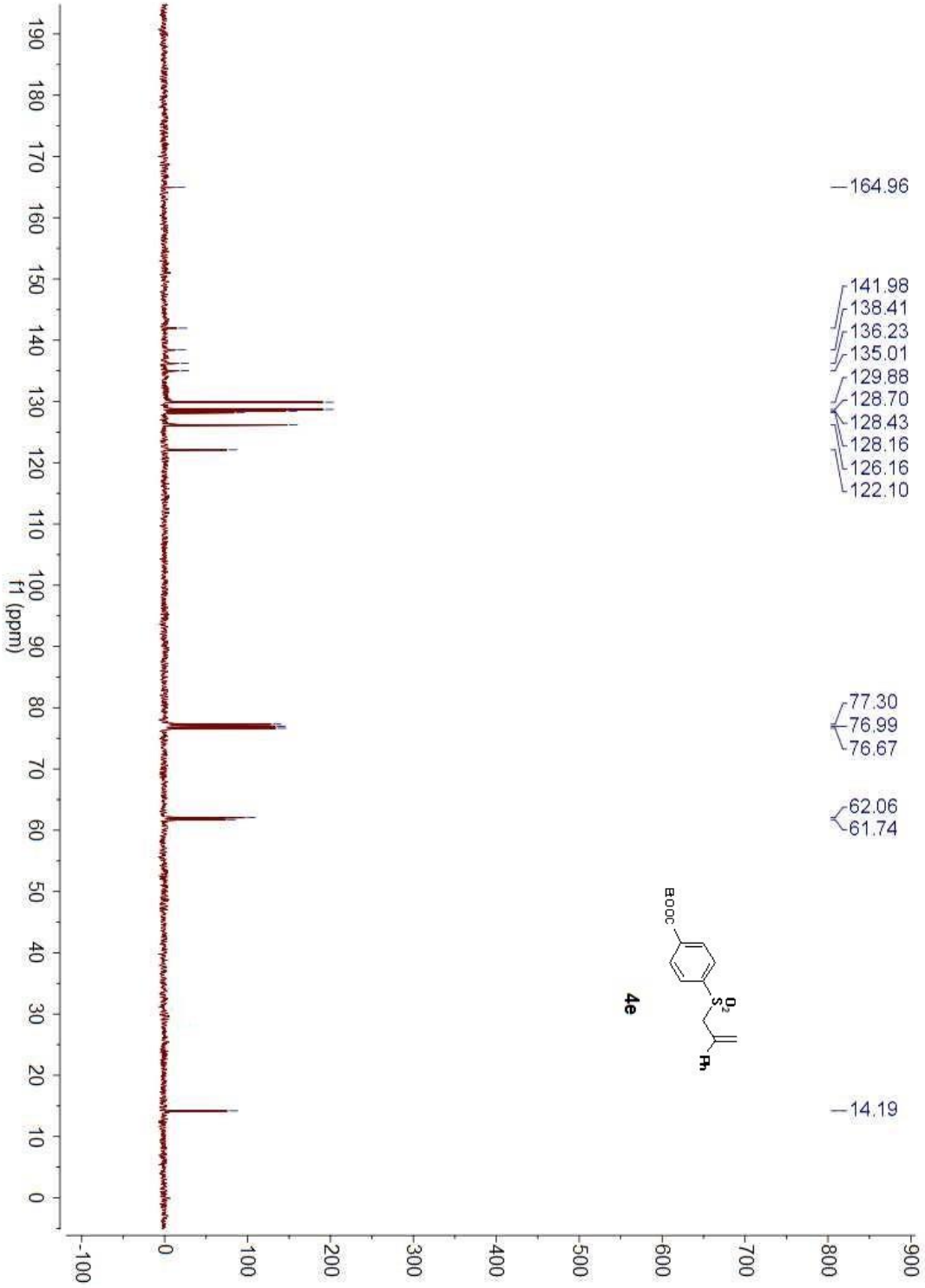

f1 (ppm)
1.96
1.80
3.10
2.12
1.00
1.05
2.03
3.01
7.70
7.68
7.28
7.27
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.22
6.88
6.86
5.59
5.21
4.25
3.83
4b

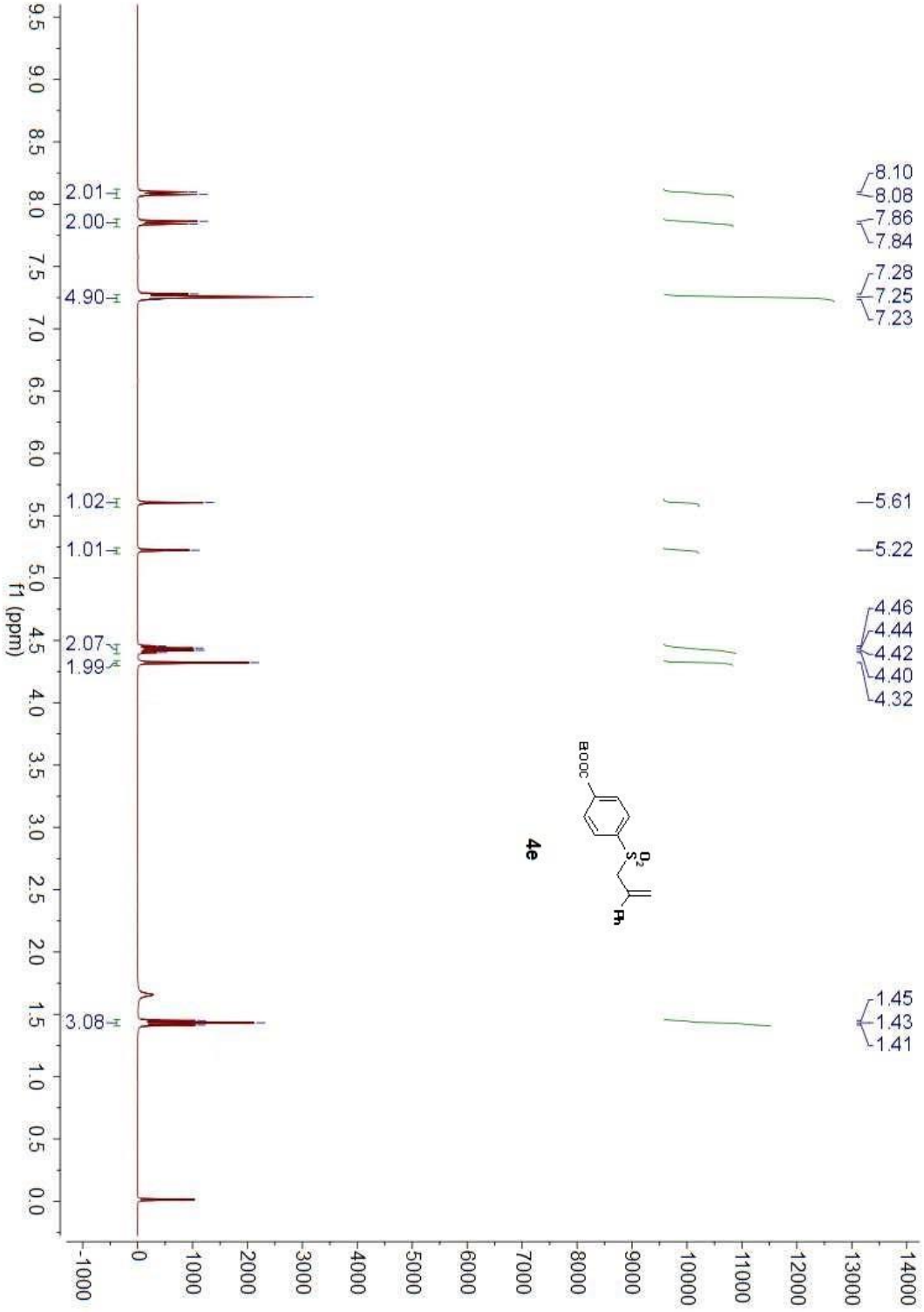

157.44
138.81
136.54
135.41
128.44
128.26
127.85
126.11
125.80
121.80
77.35
77.03
76.71
62.03
35.11
30.97
4c
f1 (ppm)

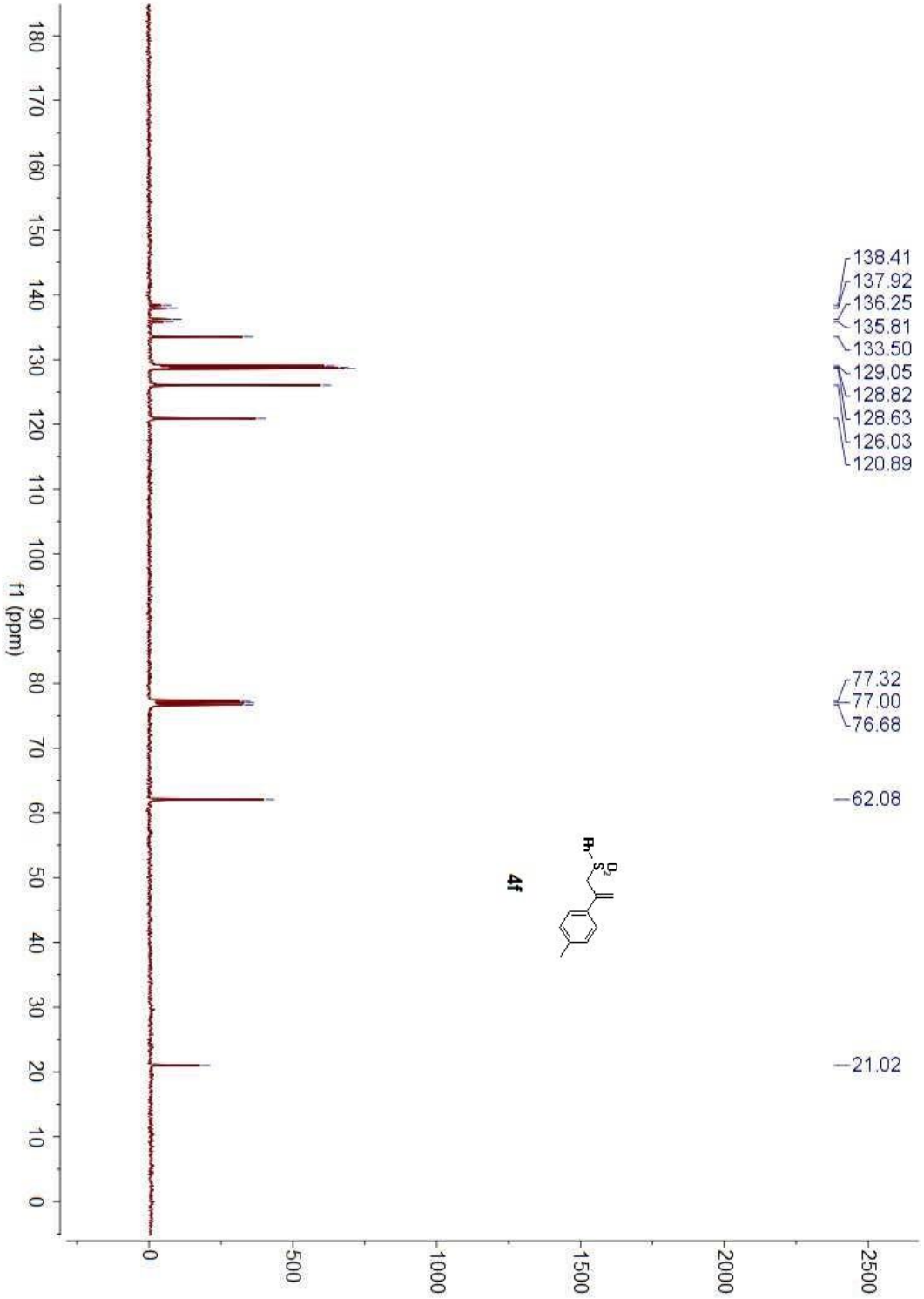

7.70
7.68
7.41
7.39
7.28
7.22
7.22
7.21
7.20
7.18
2.00
2.05
5.08
0.99
0.98
2.06
9.09
5.62
5.33
4.28
1.31
4c
f1 (ppm)

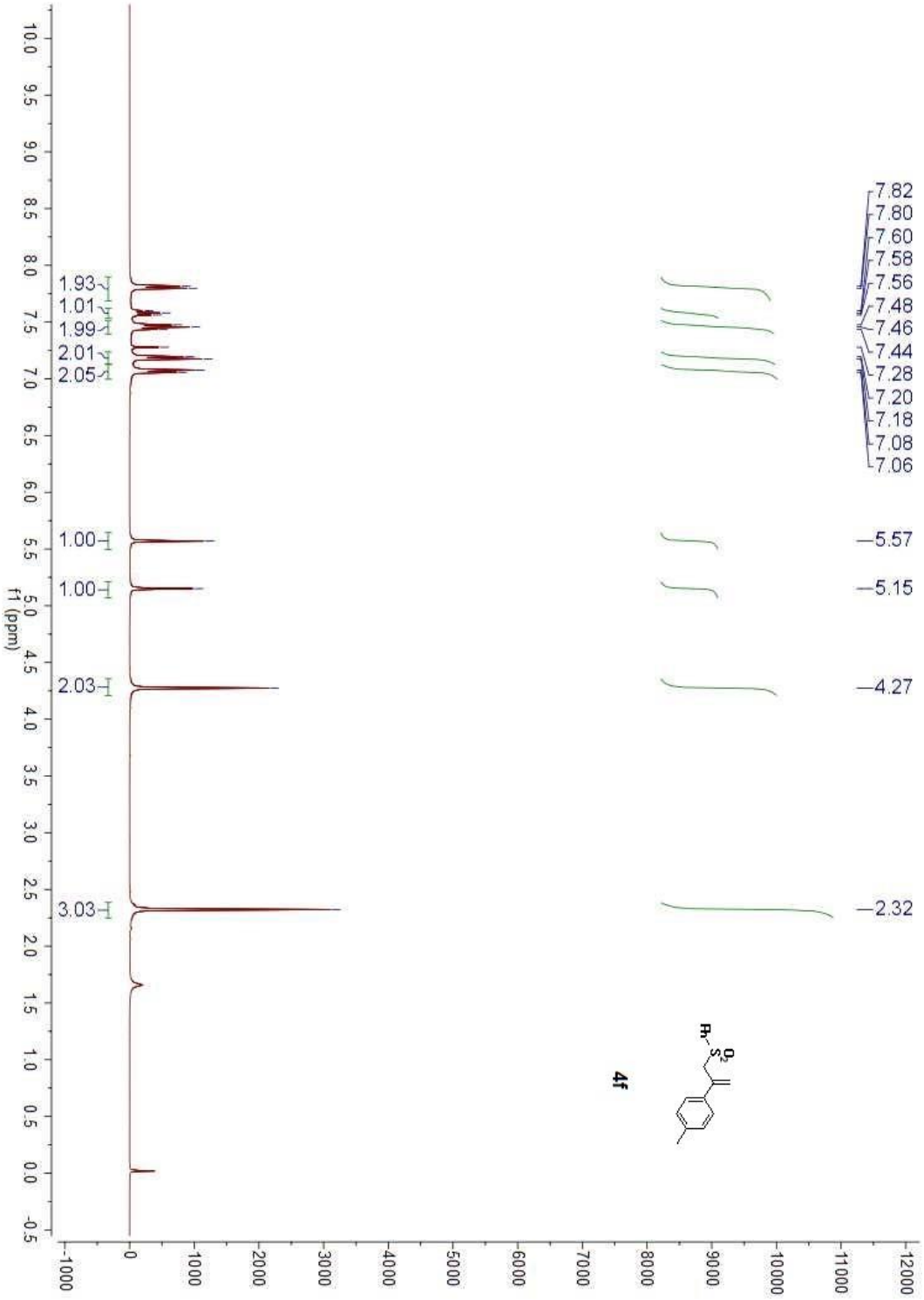

140.04
138.36
136.27
135.14
133.71
130.12
128.82
128.42
128.22
126.68
126.13
122.26
77.33
77.01
76.69
62.13
f1 (ppm)
4d

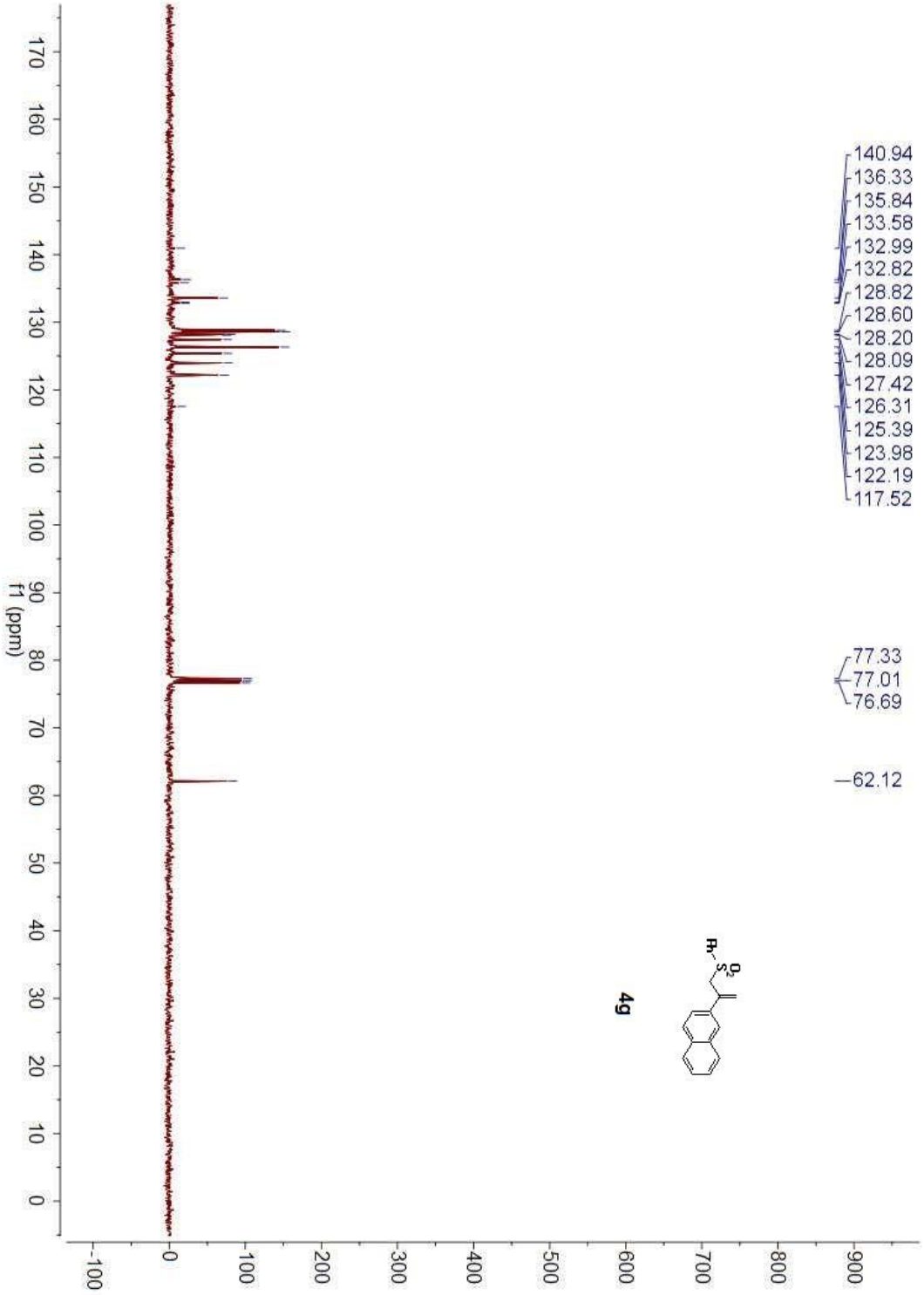

0.99
1.01
1.05
1.16
5.02
1.02
1.00
2.11
7.73
7.66
7.64
7.50
7.50
7.48
7.48
7.37
7.35
7.33
7.27
7.24
5.63
5.30
5.29
4.30
f1 (ppm)
4d
Cl
O
S
O
Ph


164.96
141.98
138.41
136.23
135.01
129.88
128.70
128.43
128.16
126.16
122.10
77.30
76.99
76.67
62.06
61.74
14.19
4e
f1 (ppm)


8.10
8.08
7.86
7.84
7.28
7.25
7.23
5.61
5.22
4.46
4.44
4.42
4.40
4.32
1.45
1.43
1.41
2.01
2.00
4.90
1.02
1.01
2.07
1.99
3.08
f1 (ppm)
4e


138.41
137.92
136.25
135.81
133.50
129.05
128.82
128.63
126.03
120.89
77.32
77.00
76.68
62.08
21.02
4f
f1 (ppm)


7.82
7.80
7.60
7.58
7.56
7.48
7.46
7.44
7.28
7.20
7.18
7.08
7.06
5.57
5.15
4.27
2.32
1.93
1.01
1.99
2.01
2.05
1.00
1.00
2.03
3.03
f1 (ppm)
4f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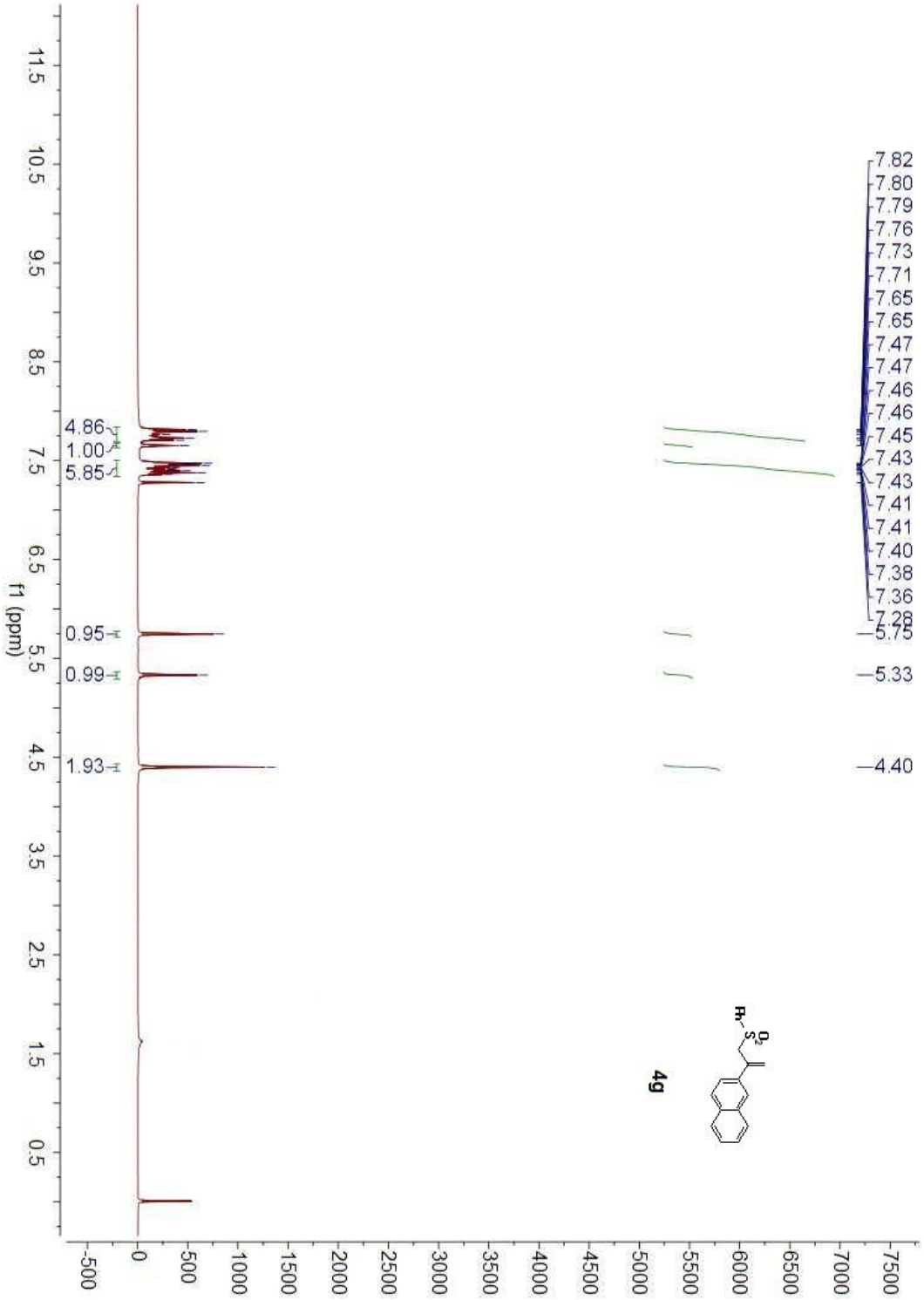
136.33
135.84
133.58
132.99
132.82
128.82
128.60
128.20
128.09
127.42
126.31
125.39
123.98
122.19
117.52
77.33
77.01
76.69
62.12
4g
f1 (ppm)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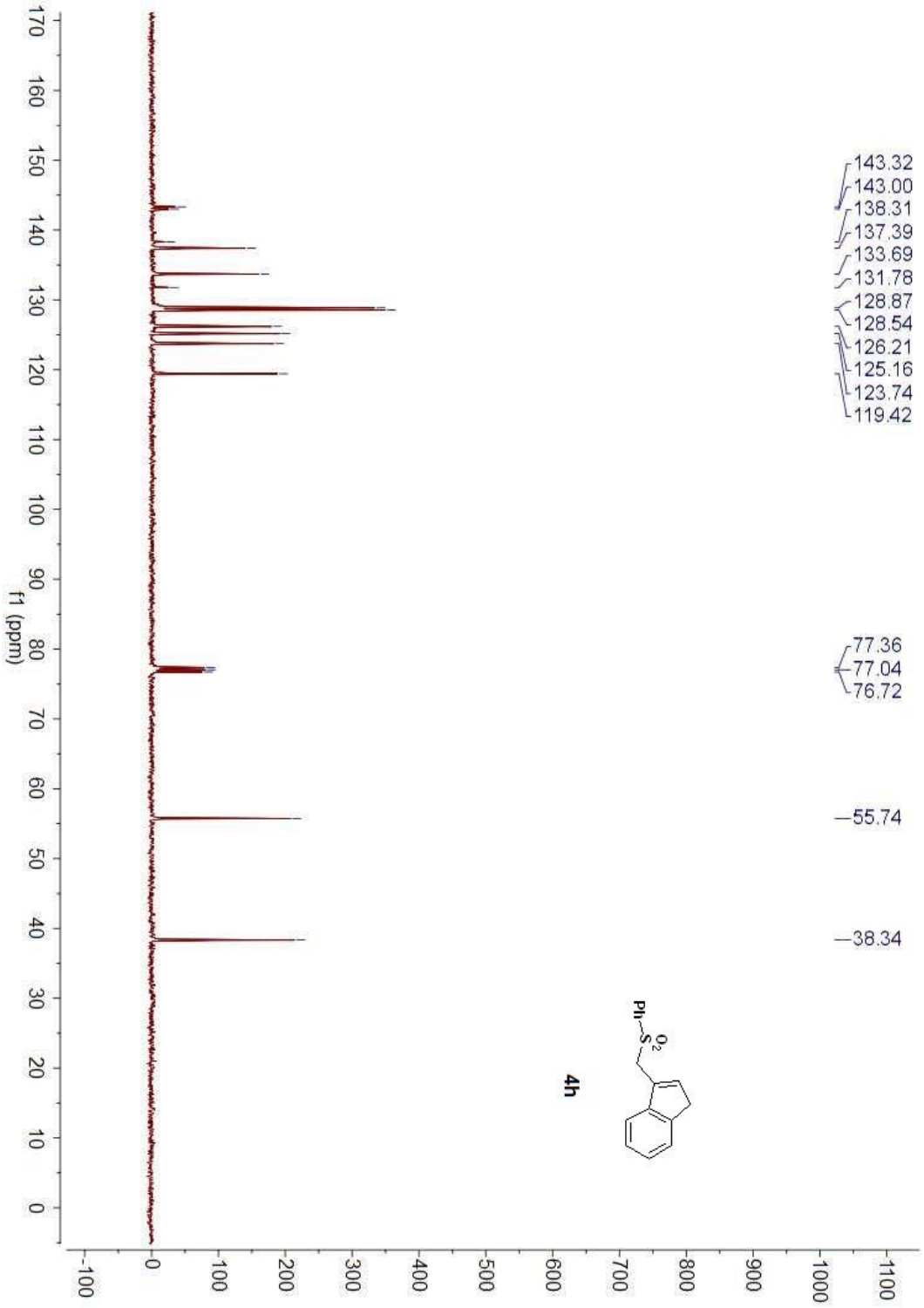
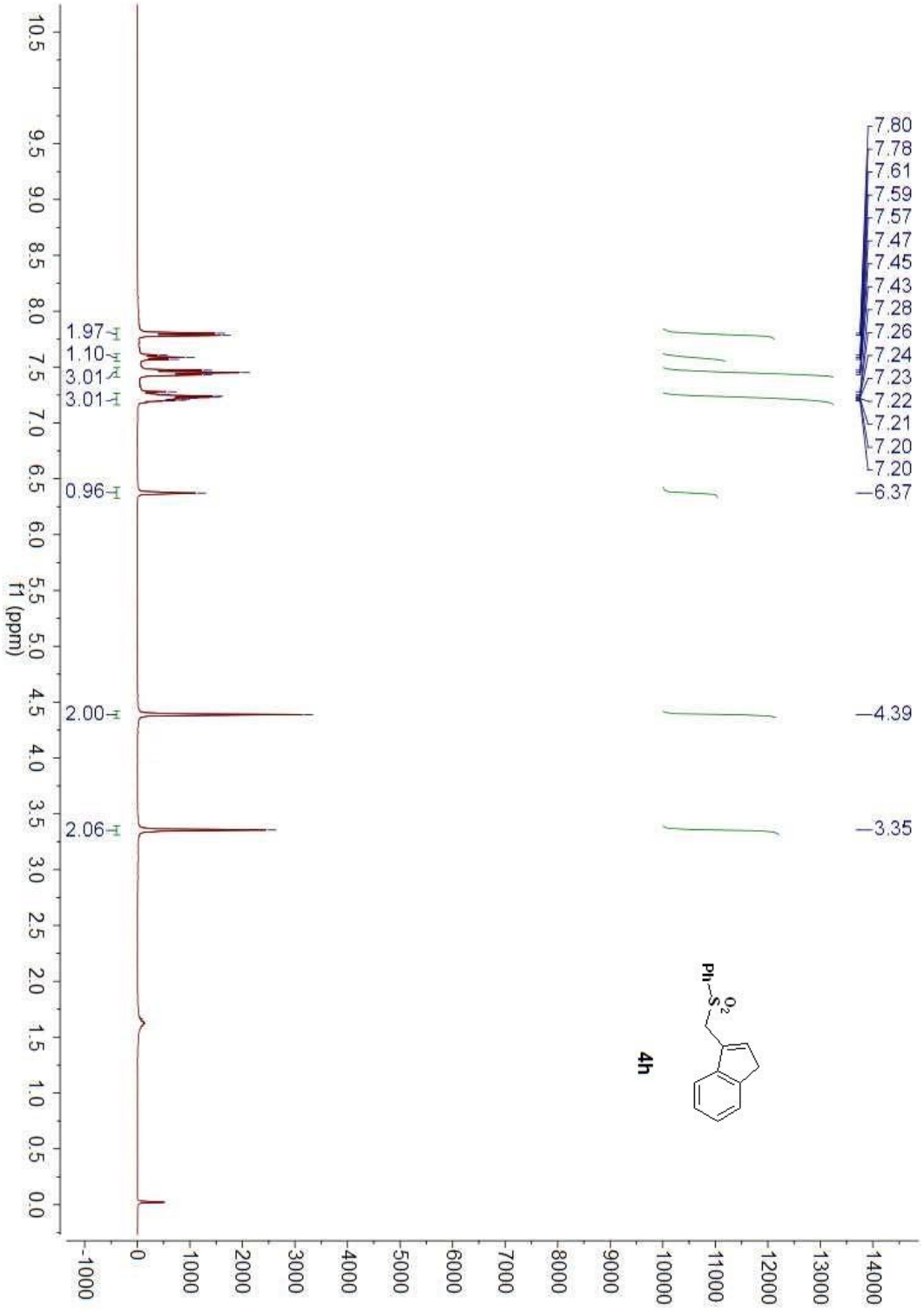
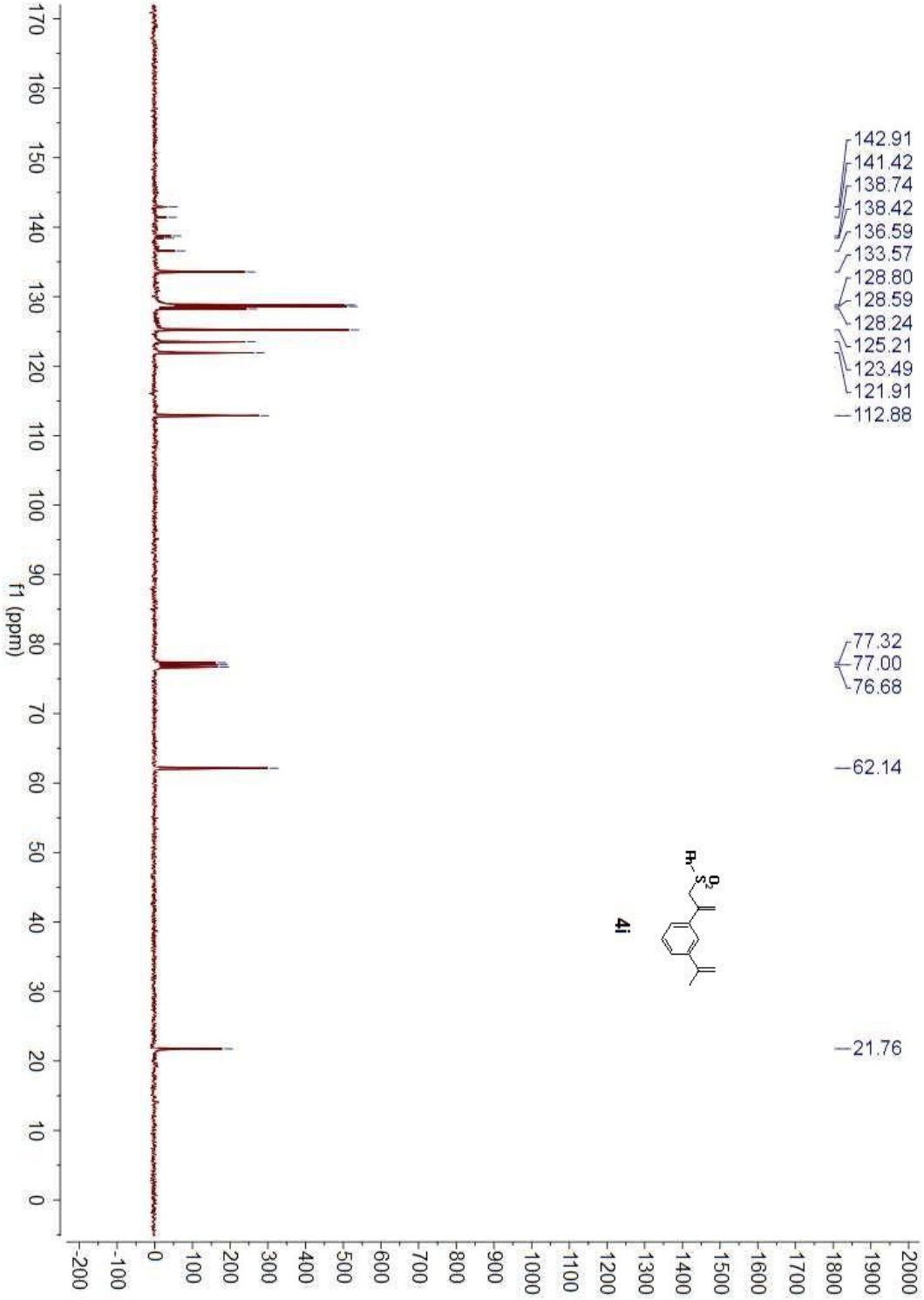
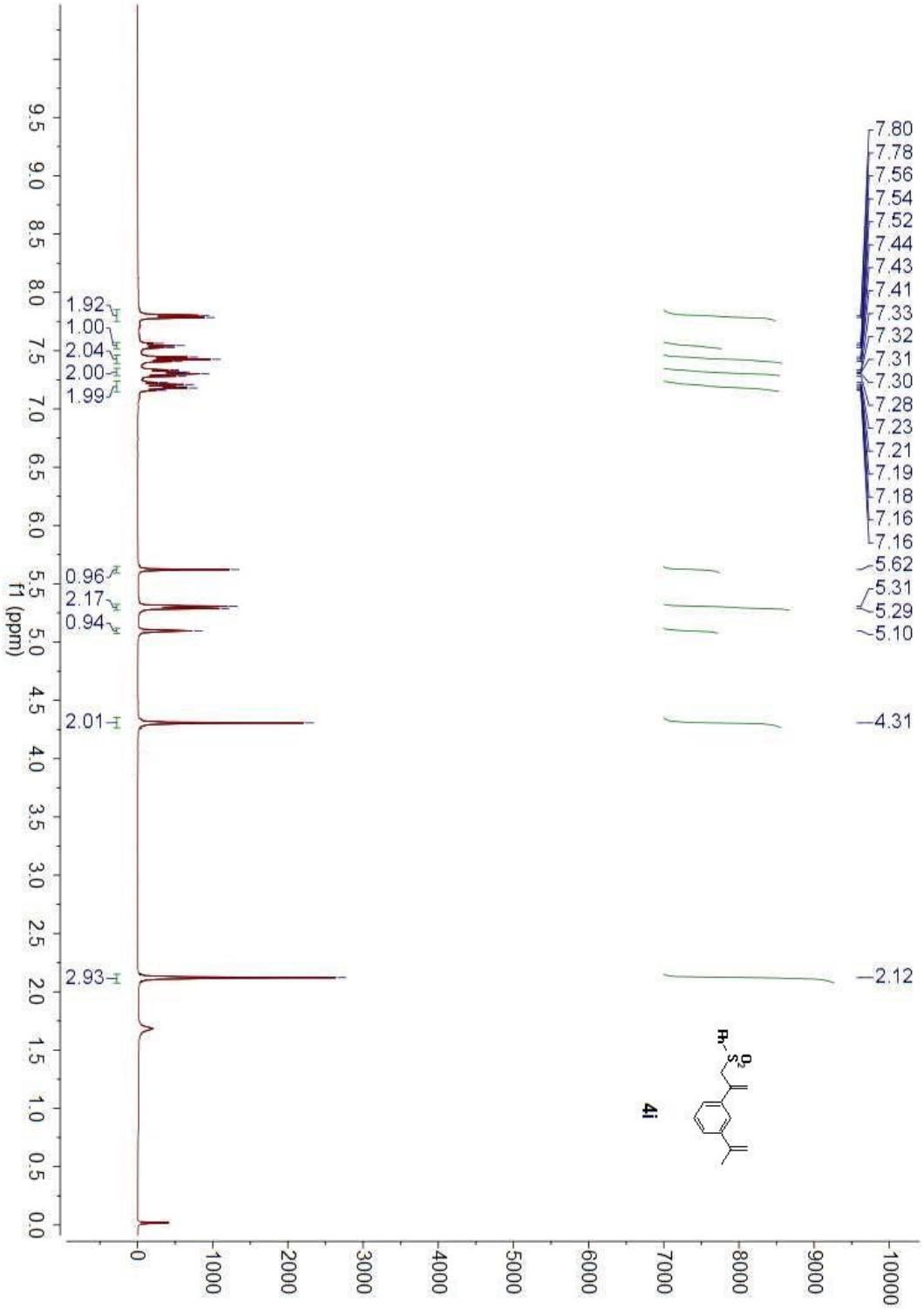
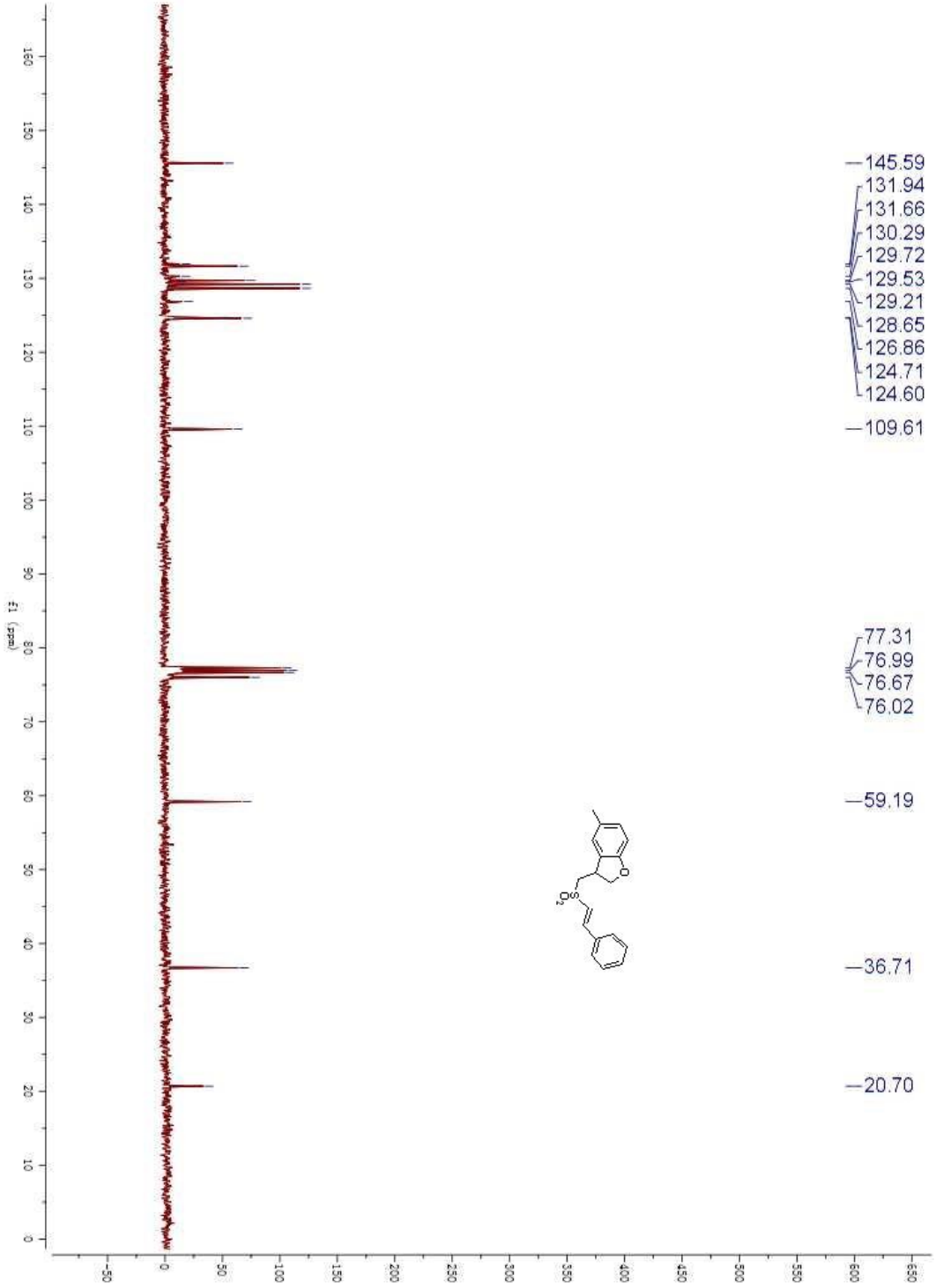
1.00
5.85
0.95
0.99
1.93
7.82
7.80
7.79
7.76
7.73
7.71
7.65
7.65
7.47
7.47
7.46
7.46
7.45
7.43
7.43
7.41
7.41
7.40
7.38
7.36
7.28
5.75
5.33
4.40
f1 (ppm)
4g

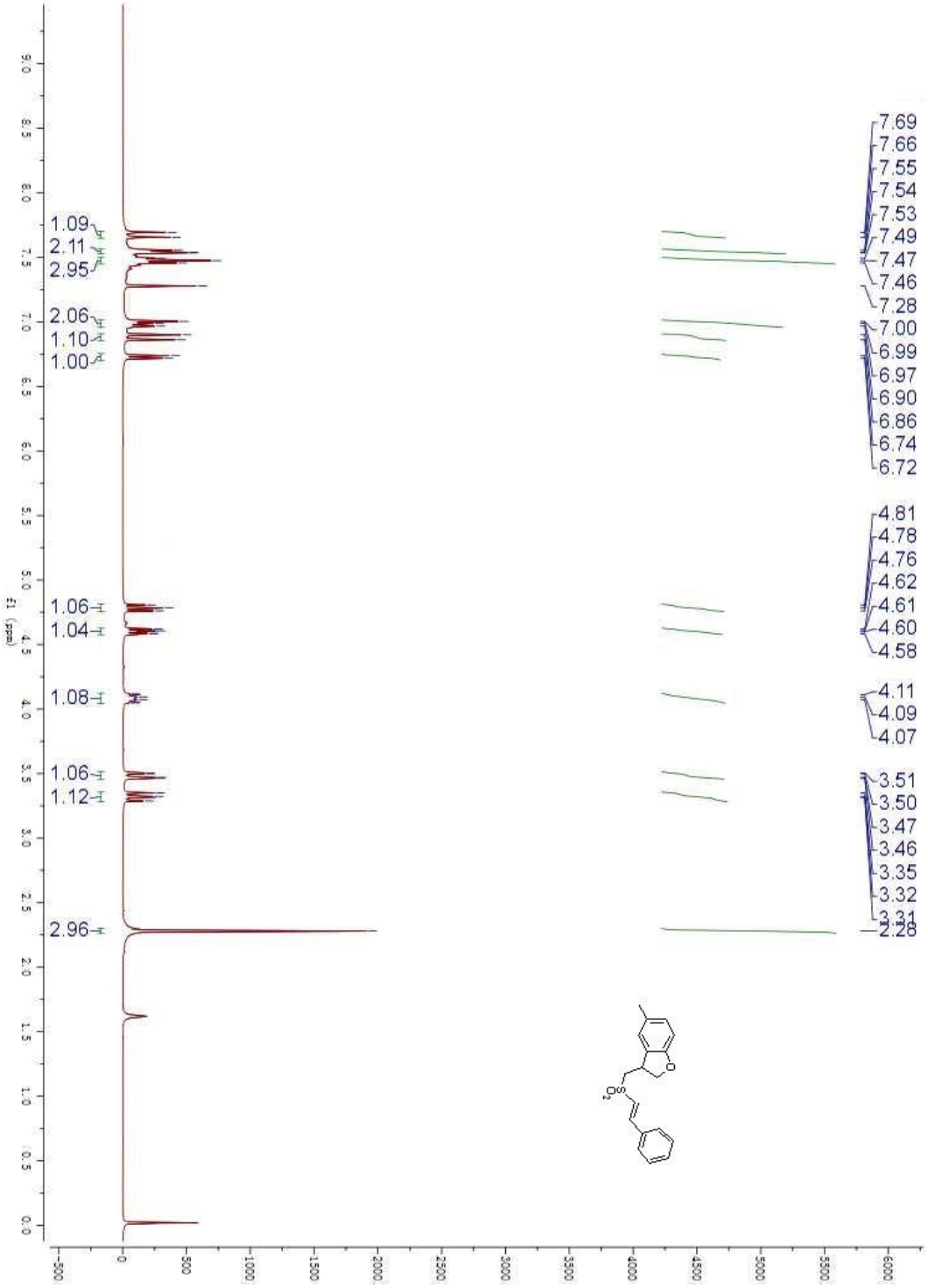

143.32
143.00
138.31
137.39
133.69
131.78
128.87
128.54
126.21
125.16
123.74
119.42
77.36
77.04
76.72
55.74
38.34
4h
f1 (ppm)


7.80
7.78
7.61
7.59
7.57
7.47
7.45
7.43
7.28
7.26
7.24
7.23
7.22
7.21
7.20
7.20
6.37
4.39
3.35
1.97
1.10
3.01
3.01
0.96
2.00
2.06
f1 (ppm)
4h


142.91
141.42
138.74
138.42
136.59
133.57
128.80
128.59
128.24
125.21
123.49
121.91
112.88
77.32
77.00
76.68
62.14
21.76
f1 (ppm)
4i


7.80
7.78
7.56
7.54
7.52
7.44
7.43
7.41
7.33
7.32
7.31
7.30
7.28
7.23
7.21
7.19
7.18
7.16
7.16
5.62
5.31
5.29
5.10
4.31
2.12
1.92
1.00
2.04
2.00
1.99
0.96
2.17
0.94
2.01
2.93
f1 (ppm)
4i


145.59
131.94
131.66
130.29
129.72
129.53
129.21
128.65
126.86
124.71
124.60
109.61
77.31
76.99
76.67
76.02
59.19
36.71
20.70
f1 (ppm)


1.09
2.11
2.95
2.06
1.10
1.00
1.06
1.04
1.08
1.06
1.12
2.96
7.69
7.66
7.55
7.54
7.53
7.49
7.47
7.46
7.28
7.00
6.99
6.97
6.90
6.86
6.74
6.72
4.81
4.78
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4.61
4.60
4.58
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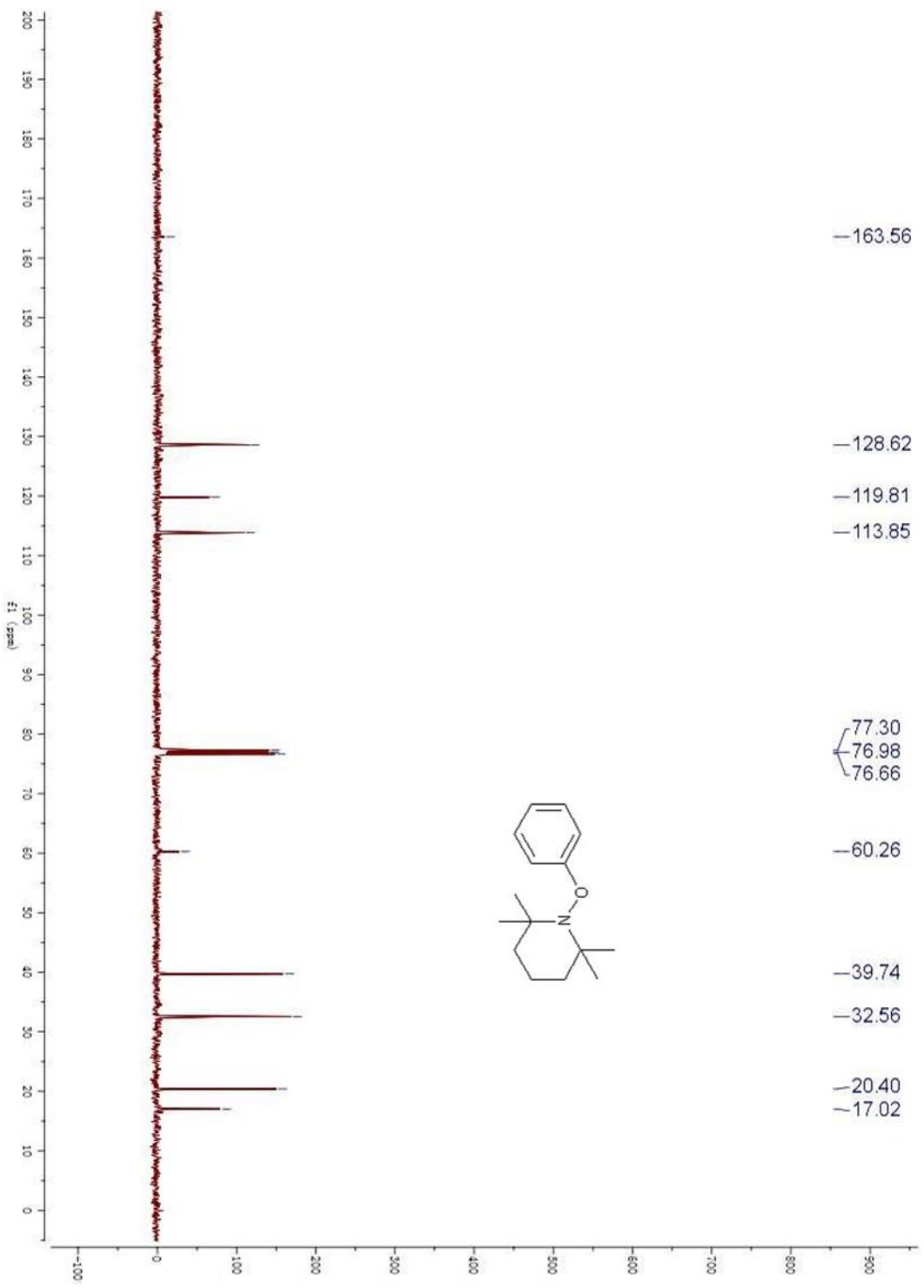
3.35
3.32
3.31
2.28
f1 (ppm)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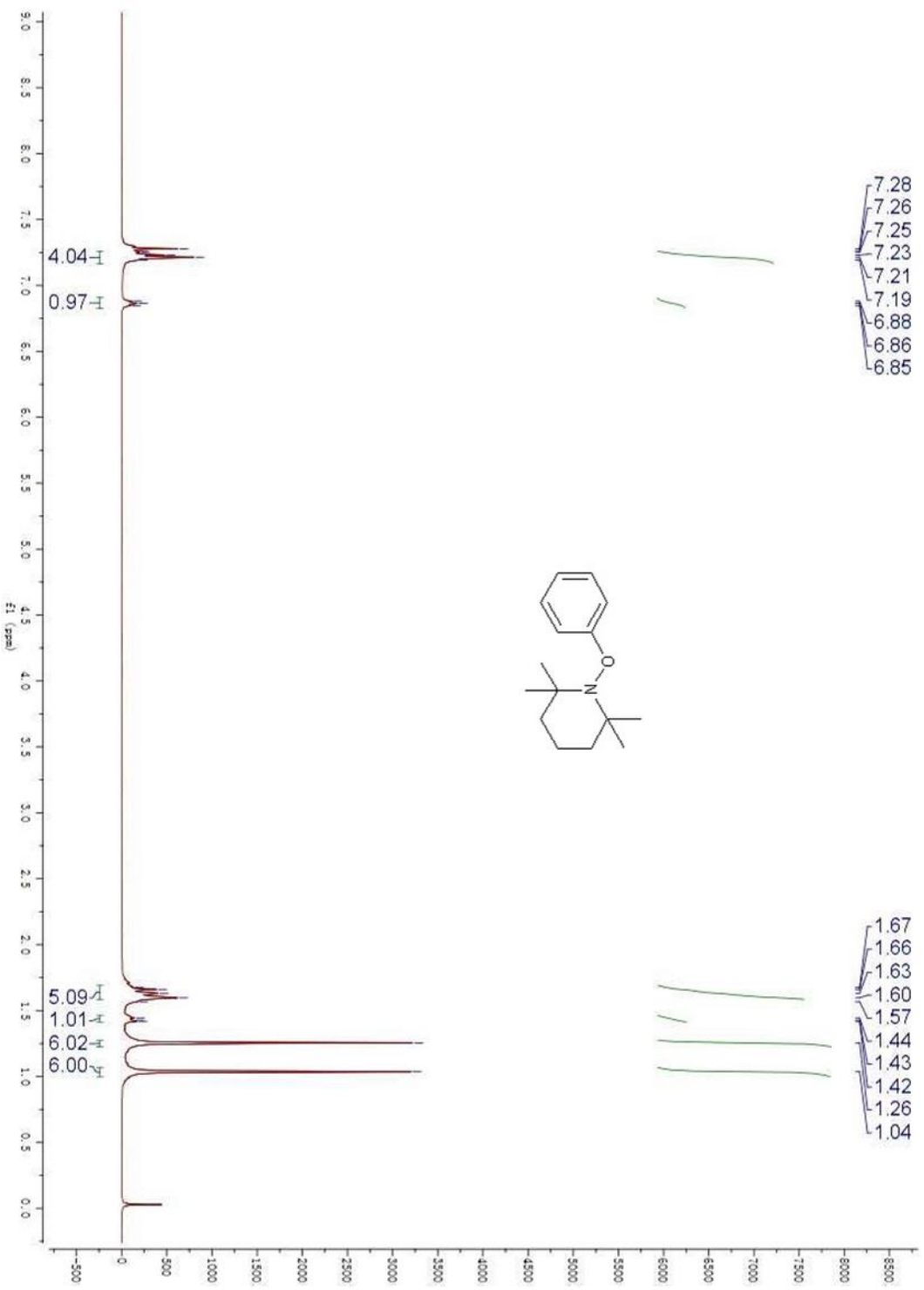
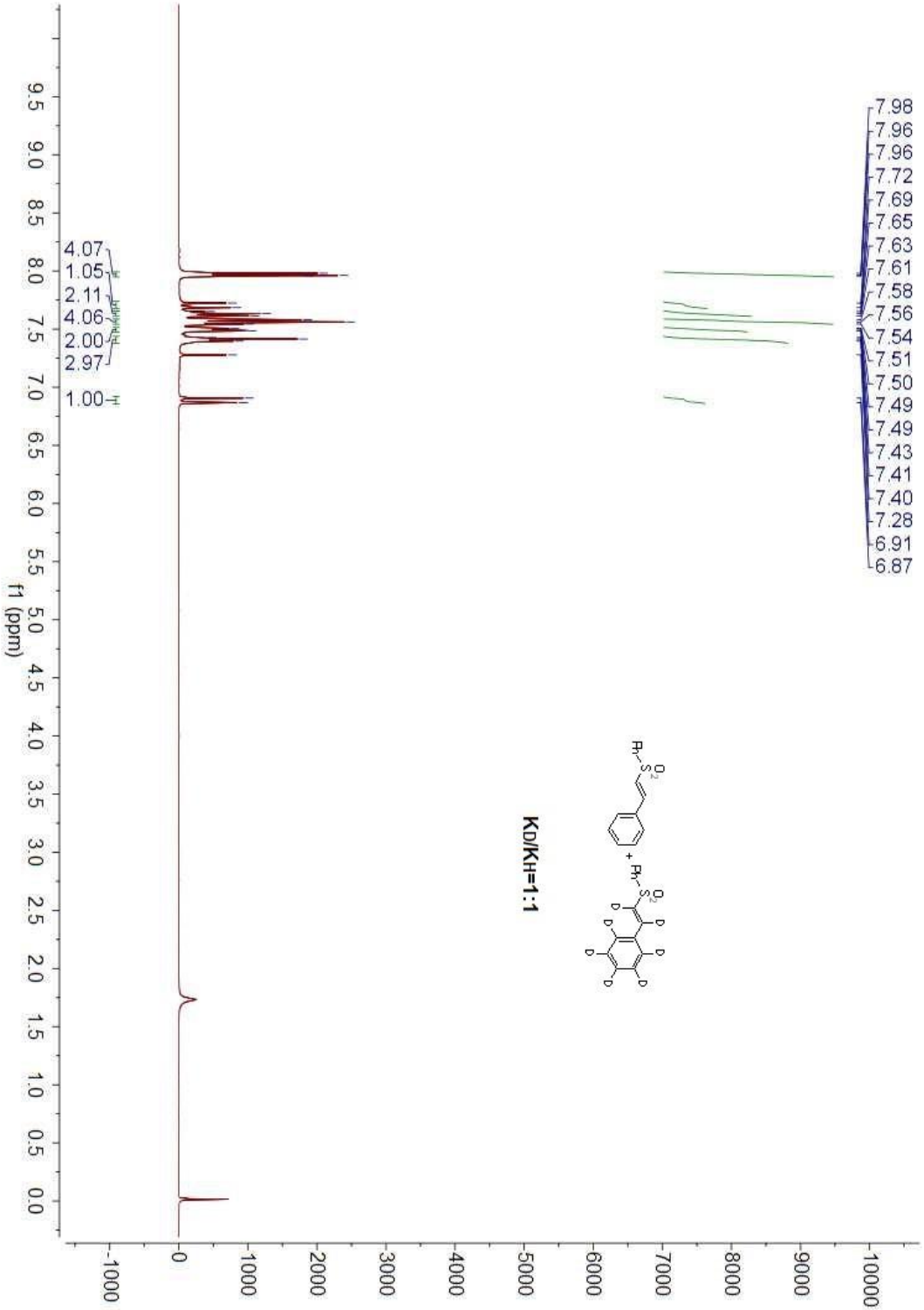
76.66
60.26
39.74
32.56
20.40
17.02
O
N


7.28
7.26
7.25
7.23
7.21
7.19
6.88
6.86
6.85
4.04
0.97
5.09
1.01
6.02
6.00
1.67
1.66
1.63
1.60
1.57
1.44
1.43
1.42
1.26
1.04
O
N
f1 (ppm)


7.98
7.96
7.96
7.72
7.69
7.65
7.63
7.61
7.58
7.56
7.54
7.51
7.50
7.49
7.49
7.43
7.41
7.40
7.28
6.91
6.87
4.07
1.05
2.11
4.06
2.00
2.97
1.00
f1 (ppm)
KD/KH=1:1