Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Iminyl radical initiated sulfonylation of alkenes with rongalite under photoredox conditions

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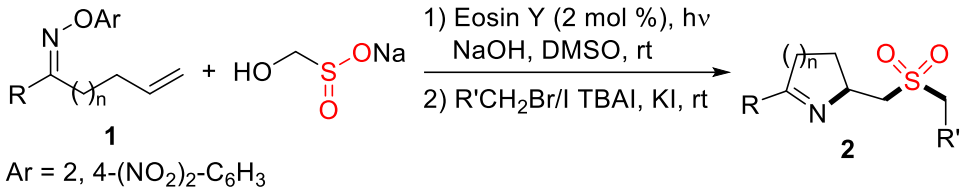
Supporting Information

General experimental methods:

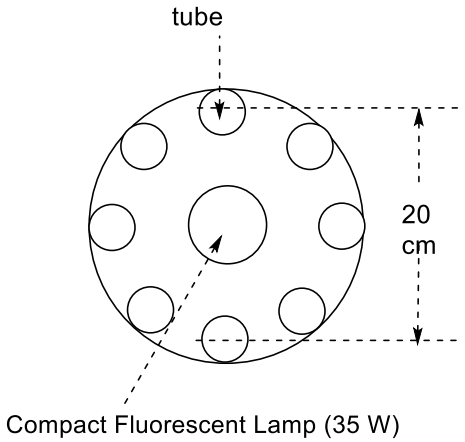
Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32-63μm, standard grade). Analytical thin-layer chromatography was performed using 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 NMR 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 visible-light-induced sulfonylation of O-(2,4-dinitrophenyl) oxime **1**, rongalite and alkyl iodides/bromides **2**.*

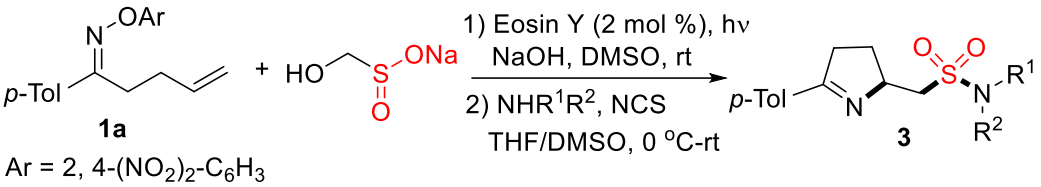


Ar = 2, 4-$(NO_2)_2$-C_6H_3

A dry tube was charged with oxime (**1**, 0.2 mmol), rongalite (0.3 mmol), NaOH (0.4 mmol) and Eosin Y (2 mol %), sealed with a rubber stopper, evacuated and backfilled with argon for four times before the addition of DMSO (3.0 mL) *via* a syringe. The mixture was stirred and irradiated with a commercially available 35 W CFL for 24 h. Subsequently, TBAI (0.02 mmol, 7.4 mg), KI (0.24 mmol, 40.0 mg) and alkyl iodide/bromide (0.4 mmol) were added to the reaction before the tube was evacuated and backfilled with argon three times and stirred at room temperature for another 12 h. After completion of the reaction as indicated by TLC, the mixture was quenched with saturated brine. The mixture was extracted with ethyl acetate (20 mL x 3). The organic phases were combined and dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo*, and purified by flash column chromatography (EtOAc/*n*-hexane, 1:3) to give the desired product **2**.



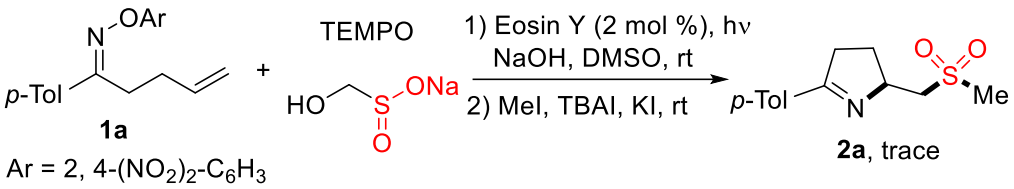
*General experimental procedure for the aminosulfonylation of 1-(p-tolyl)pent-4-en-1-one O-(2,4-dinitrophenyl) oxime **1a** with rongalite and amines **3**.*



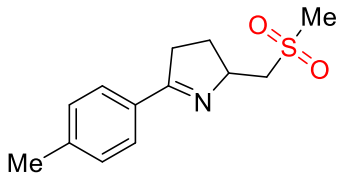
Ar = 2, 4-$(NO_2)_2$-C_6H_3

A dry tube was charged with (*E*)-1-(*p*-tolyl)pent-4-en-1-one *O*-(2,4-dinitrophenyl) oxime **1a** (0.2 mmol), rongalite (0.3 mmol), NaOH (0.4 mmol), Eosin Y (2 mol %), sealed with a rubber stopper, evacuated and backfilled with argon for four times before the addition of DMSO (3.0 mL) *via* a syringe. The mixture was stirred and irradiated with a commercially available 35 W CFL for 24 h. Subsequently, THF (8 mL), triethylamine (0.4 mmol) and amine (0.4 mmol) were added to the mixture *via* a syringe, followed by dropwise addition of *N*-chlorosuccinimide (0.3 mmol, dissolved in THF) at 0 °C in 30 minutes. The reaction mixture was warmed to room temperature and stirred for 2 hours. After completion of the reaction as indicated by TLC, the mixture was quenched with saturated brine. The mixture was extracted with ethyl acetate (20 mL x 3). The organic phases were combined and dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo*, and purified by flash column chromatography (EtOAc/*n*-hexane, 1:4) to give the desired product **3**.

Radical trapping experiment

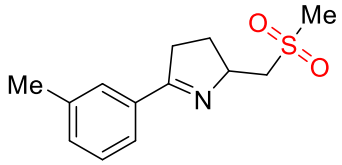


A dry tube was charged with 1-(*p*-tolyl)pent-4-en-1-one *O*-(2,4-dinitrophenyl) oxime **1a** (0.2 mmol), rongalite (0.3 mmol), NaOH (0.4 mmol), Eosin Y (2 mol %) and TEMPO (0.4 mmol), sealed with a rubber stopper, evacuated and backfilled with argon for four times before the addition of DMSO (3.0 mL) *via* a syringe. The mixture was stirred and irradiated with a commercially available 35 W CFL for 24 h. Subsequently, TBAI (0.02 mmol, 7.4 mg), KI (0.24 mmol, 40.0 mg) and iodomethane (0.4 mmol) were added to the reaction before the tube was evacuated and backfilled with argon three times and stirred at room temperature for another 12 h. As indicated by TLC, only a trace amount of product **2a** was detected.



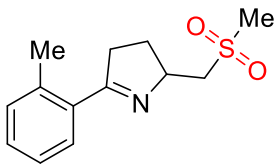
2-((Methylsulfonyl)methyl)-5-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrole (**2a**)

White solid, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.72 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 4.71 – 4.63 (m, 1H), 3.35 (dd, *J* = 14.3, 8.6 Hz, 1H), 3.23 (d, *J* = 4.9 Hz, 1H), 3.20 (s, 3H), 3.15 – 3.06 (m, 1H), 2.97 – 2.87 (m, 1H), 2.48 – 2.41 (m, 1H), 2.40 (s, 3H), 1.83 – 1.73 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 174.1, 141.4, 131.0, 129.2, 127.8, 67.4, 60.6, 42.9, 34.9, 28.9, 21.5. HRMS calcd for $C_{13}H_{18}NO_2S^+$ ($M+H^+$): 252.1053, found: 252.1058.



2-((Methylsulfonyl)methyl)-5-(*m*-tolyl)-3,4-dihydro-2*H*-pyrrole (**2b**)

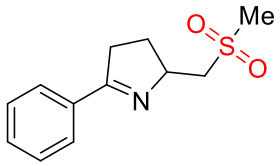
White solid, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.65 (s, 1H), 7.61 (d, *J* = 7.1 Hz, 1H), 7.34 – 7.26 (m, 2H), 4.70 – 4.65 (m, 1H), 3.38 (dd, *J* = 14.5, 8.4 Hz, 1H), 3.25 – 3.19 (m, 4H), 3.17 – 3.08 (m, 1H), 2.99 – 2.88 (m, 1H), 2.49 – 2.41 (m, 1H), 2.40 (s, 3H), 1.85 – 1.75 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 138.3, 133.6, 131.9, 128.5, 128.3, 125.0, 67.5, 60.6, 42.8, 35.1, 28.9, 21.4. HRMS calcd for $C_{13}H_{18}NO_2S^+$ ($M+H^+$): 252.1053, found: 252.1053.



2-((Methylsulfonyl)methyl)-5-(*o*-tolyl)-3,4-dihydro-2*H*-pyrrole (**2c**)

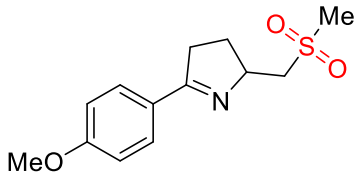
White solid, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.47 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.24 (d, *J* = 7.4 Hz, 2H), 4.74 – 4.66 (m, 1H), 3.39 (dd, *J* = 14.5, 9.0 Hz, 1H), 3.25 – 3.19 (m, 1H), 3.17 (d, *J* = 0.9 Hz, 3H), 3.13 – 3.04 (m, 1H), 3.01 – 2.91 (m, 1H), 2.53 (s, 3H), 2.46 – 2.36 (m, 1H), 1.75 – 1.64 (m, 1H); ^{13}C NMR (101 MHz,

$CDCl_3$) δ (ppm) 175.9, 137.6, 133.5, 131.6, 129.7, 129.3, 125.8, 68.2, 60.9, 42.5, 38.1, 29.1, 22.3; HRMS calcd for $C_{13}H_{18}NO_2S^+$ ($M+H^+$): 252.1053, found: 252.1060.



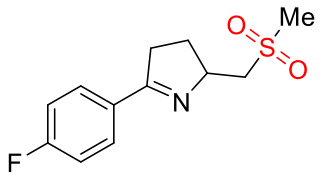
(2-((Methylsulfonyl)methyl)-5-phenyl-3,4-dihydro-2*H*-pyrrole (**2d**)

White solid, 73% yield; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.83 (d, *J* = 6.8 Hz, 2H), 7.49 – 7.40 (m, 3H), 4.74 – 4.65 (m, 1H), 3.37 (dd, *J* = 14.5, 8.6 Hz, 1H), 3.24 (d, *J* = 4.8 Hz, 1H), 3.21 (s, 3H), 3.18 – 3.09 (m, 1H), 3.01 – 2.90 (m, 1H), 2.50 – 2.41 (m, 1H), 1.85 – 1.74 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 174.3, 133.6, 131.1, 128.6, 127.8, 67.5, 60.6, 42.9, 35.0, 28.9; HRMS calcd for $C_{12}H_{16}NO_2S^+$ ($M+H^+$): 238.0896, found: 238.0906.



5-(4-Methoxyphenyl)-2-((methylsulfonyl)methyl)-3,4-dihydro-2*H*-pyrrole (**2e**)

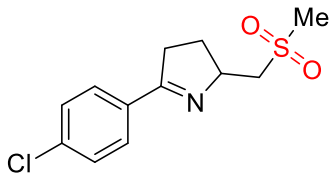
White solid, 86% yield; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.79 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.70 – 4.62 (m, 1H), 3.86 (s, 3H), 3.37 (dd, *J* = 14.4, 8.5 Hz, 1H), 3.23 (d, *J* = 4.9 Hz, 1H), 3.20 (s, 3H), 3.14 – 3.04 (m, 1H), 2.96 – 2.87 (m, 1H), 2.48 – 2.39 (m, 1H), 1.83 – 1.72 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 173.8, 162.1, 129.7, 126.1, 113.9, 67.1, 60.5, 55.4, 42.9, 34.8, 28.9; HRMS calcd for $C_{13}H_{18}NO_3S^+$ ($M+H^+$): 268.1002, found: 268.1008.



(5-(4-Fluorophenyl)-2-((methylsulfonyl)methyl)-3,4-dihydro-2*H*-pyrrole (**2f**)

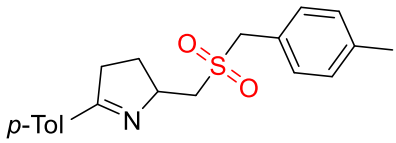
White solid, 60% yield; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86 – 7.80 (m, 2H), 7.13 – 7.07 (m, 2H), 4.72 – 4.62 (m, 1H), 3.36 (dd, *J* = 14.6, 8.9 Hz, 1H), 3.24 (dd, *J* = 4.9, 0.9 Hz, 1H), 3.20 (s, 3H), 3.15 – 3.06 (m, 1H), 2.97 – 2.87 (m, 1H), 2.50 – 2.41 (m, 1H),

1.85 – 1.74 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 164.4 (d, *J* = 251.6 Hz), 123.0 (d, *J* = 3.1 Hz), 129.9 (d, *J* = 8.7 Hz), 115.6 (d, *J* = 21.8 Hz), 67.5, 60.5, 42.8, 35.0, 29.0; HRMS calcd for $C_{12}H_{15}FNO_2S^+$ ($M+H^+$): 256.0802, found: 256.0808.



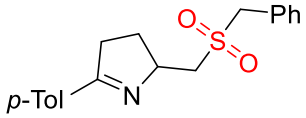
5-(4-Chlorophenyl)-2-((methylsulfonyl)methyl)-3,4-dihydro-2*H*-pyrrole (**2g**)

White solid, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.78 – 7.74 (m, 2H), 7.41 – 7.38 (m, 2H), 4.73 – 4.64 (m, 1H), 3.36 (dd, *J* = 14.3, 8.5 Hz, 1H), 3.25 – 3.19 (m, 1H), 3.19 (s, 3H), 3.14 – 3.05 (m, 1H), 2.97 – 2.86 (m, 1H), 2.51 – 2.41 (m, 1H), 1.85 – 1.74 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 173.2, 137.2, 132.1, 129.1, 128.8, 67.6, 60.5, 42.8, 35.0, 29.0; HRMS calcd for $C_{12}H_{15}ClNO_2S^+$ ($M+H^+$): 272.0507, found: 272.0515.



2-(((4-Methylbenzyl)sulfonyl)methyl)-5-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrole (**2i**)

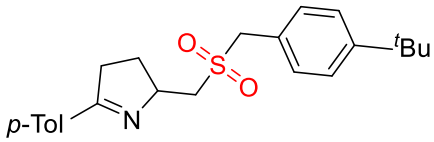
White solid, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.78 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 4.76 (d, *J* = 13.9 Hz, 1H), 4.73 – 4.67 (m, 1H), 4.41 (d, *J* = 13.9 Hz, 1H), 3.31 (dd, *J* = 14.5, 8.2 Hz, 1H), 3.16 – 3.07 (m, 2H), 3.01 – 2.87 (m, 1H), 2.46 – 2.37 (m, 4H), 2.33 (s, 3H), 1.81 – 1.70 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 174.2, 141.5, 138.7, 131.0, 130.8, 129.6, 129.3, 127.9, 125.5, 67.3, 60.3, 56.3, 35.0, 28.9, 21.5, 21.2; HRMS calcd for $C_{20}H_{24}NO_2S^+$ ($M+H^+$): 342.1522, found: 342.1535.



2-((Benzylsulfonyl)methyl)-5-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrole (**2j**)

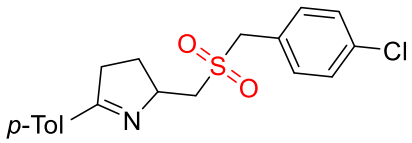
White solid, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77 (d, *J* = 8.1 Hz, 2H), 7.48 – 7.45 (m, 2H), 7.36 – 7.32 (m, 3H), 7.24 (d, *J* = 7.9 Hz, 2H), 4.81 (d, *J* = 13.8 Hz, 1H), 4.75 – 4.67 (m, 1H), 4.46 (d, *J* = 13.8 Hz, 1H), 3.30 (dd, *J* = 14.5, 8.4 Hz, 1H), 3.15

– 3.07 (m, 1H), 3.02 – 2.86 (m, 2H), 2.46 – 2.36 (m, 4H), 1.80 – 1.70 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 174.2, 141.4, 131.1, 131.0, 129.3, 128.9, 128.8, 128.6, 127.8, 67.4, 60.6, 56.5, 35.0, 29.0, 21.5; HRMS calcd for $C_{19}H_{22}NO_2S^+$ ($M+H^+$): 328.1366, found: 328.1373.



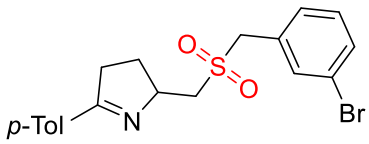
2-(((4-(*tert*-Butyl)benzyl)sulfonyl)methyl)-5-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrole (**2k**)

White solid, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 4.79 (d, *J* = 13.9 Hz, 1H), 4.75 – 4.66 (m, 1H), 4.42 (d, *J* = 13.9 Hz, 1H), 3.33 (dd, *J* = 14.5, 8.3 Hz, 1H), 3.16 – 3.07 (m, 1H), 3.01 – 2.87 (m, 2H), 2.47 – 2.37 (m, 4H), 1.81 – 1.70 (m, 1H), 1.30 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 174.1, 151.8, 141.4, 131.1, 130.7, 129.3, 127.8, 125.9, 125.5, 67.4, 60.2, 56.4, 35.0, 34.6, 31.2, 29.0, 21.5; HRMS calcd for $C_{23}H_{30}NO_2S^+$ ($M+H^+$): 384.1992, found: 384.1998.



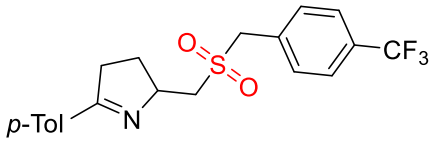
2-(((4-Chlorobenzyl)sulfonyl)methyl)-5-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrole (**2l**)

White solid, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.82 (d, *J* = 13.9 Hz, 1H), 4.75 – 4.66 (m, 1H), 4.44 (d, *J* = 13.8 Hz, 1H), 3.22 (dd, *J* = 14.6, 8.9 Hz, 1H), 3.17 – 3.08 (m, 1H), 3.01 (ddd, *J* = 14.6, 4.5, 1.0 Hz, 1H), 2.95 – 2.86 (m, 1H), 2.45 – 2.36 (m, 4H), 1.78 – 1.67 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 141.5, 135.0, 132.3, 131.0, 129.4, 129.0, 127.8, 127.1, 67.5, 59.8, 56.7, 34.9, 28.9, 21.5; HRMS calcd for $C_{19}H_{21}ClNO_2S^+$ ($M+H^+$): 362.0976, found: 362.0983.



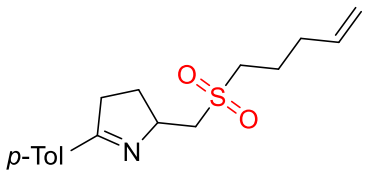
2-(((3-Bromobenzyl)sulfonyl)methyl)-5-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrole (**2m**)

White solid, 62% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77 (d, *J* = 8.1 Hz, 2H), 7.65 (s, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 9.4 Hz, 2H), 7.20 (t, *J* = 7.9 Hz, 1H), 4.79 (d, *J* = 13.8 Hz, 1H), 4.76 – 4.69 (m, 1H), 4.44 (d, *J* = 13.8 Hz, 1H), 3.25 (dd, *J* = 14.6, 8.9 Hz, 1H), 3.17 – 3.09 (m, 1H), 3.04 (ddd, *J* = 14.6, 4.4, 1.1 Hz, 1H), 2.96 – 2.87 (m, 1H), 2.47 – 2.37 (m, 4H), 1.80 – 1.65 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 174.3, 141.5, 134.0, 131.9, 131.0, 130.8, 130.3, 129.6, 129.4, 127.8, 122.7, 67.5, 59.8, 57.0, 35.0, 29.0, 21.5; HRMS calcd for $C_{19}H_{21}BrNO_2S^+$ ($M+H^+$): 406.0471, found: 406.0483.



5-(*p*-Tolyl)-2-(((4-(trifluoromethyl)benzyl)sulfonyl)methyl)-3,4-dihydro-2*H*-pyrrole (**2n**)

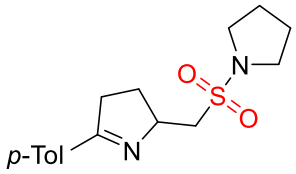
White solid, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.78 (d, *J* = 8.1 Hz, 2H), 7.63 – 7.57 (m, 4H), 7.25 (d, *J* = 7.2 Hz, 2H), 4.94 (d, *J* = 13.7 Hz, 1H), 4.76 – 4.69 (m, 1H), 4.55 (d, *J* = 13.7 Hz, 1H), 3.22 (dd, *J* = 14.7, 9.1 Hz, 1H), 3.18 – 3.10 (m, 1H), 3.09 – 3.03 (m, 1H), 2.97 – 2.87 (m, 1H), 2.47 – 2.38 (m, 4H), 1.79 – 1.68 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 174.4, 141.7, 132.7 (d, *J* = 1.0 Hz), 131.5, 131.1, 130.9, 129.5, 127.9, 125.8 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 272.3 Hz), 67.5, 60.0, 57.1, 35.0, 28.9, 21.5; HRMS calcd for $C_{20}H_{21}F_3NO2S^+$ ($M+H^+$): 396.1240, found: 396.1248.



2-((Pent-4-en-1-ylsulfonyl)methyl)-5-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrole (**2o**)

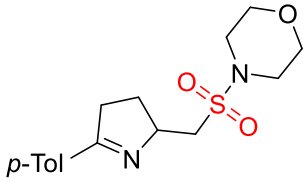
White solid, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.71 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 5.84 – 5.73 (m, 1H), 5.07 (t, *J* = 12.4 Hz, 2H), 4.70 – 4.61 (m, 1H), 3.42 – 3.26 (m, 3H), 3.15 – 3.06 (m, 2H), 2.96 – 2.86 (m, 1H), 2.48 – 2.41 (m, 1H), 2.40 (s, 3H), 2.28 – 2.20 (m, 2H), 2.08 – 1.92 (m, 2H), 1.83 – 1.72 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 174.1, 141.4, 136.6, 131.0, 129.2, 127.8, 116.4, 67.3, 58.6,

53.9, 35.0, 32.4, 29.1, 21.5, 21.3; HRMS calcd for $C_{17}H_{24}NO_2S^+$ ($M+H^+$): 306.1522, found: 306.1533.



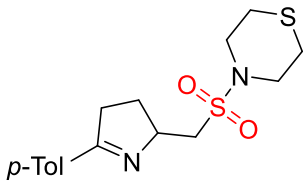
2-((Pyrrolidin-1-ylsulfonyl)methyl)-5-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrole (**3a**)

Reddish solid, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.71 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 4.64 (s, 1H), 3.66 (dd, *J* = 13.8, 4.7 Hz, 1H), 3.50 – 3.37 (m, 4H), 3.16 – 3.07 (m, 1H), 3.04 – 2.89 (m, 2H), 2.51 – 2.43 (m, 1H), 2.39 (s, 3H), 1.97 – 1.94 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 174.3, 141.3, 131.1, 129.3, 127.8, 67.8, 54.4, 47.8, 35.4, 29.0, 25.9, 21.6; HRMS calcd for $C_{16}H_{23}N_2O_2S^+$ ($M+H^+$): 307.1475, found: 307.1483.



4-(((5-(*p*-Tolyl)-3,4-dihydro-2*H*-pyrrol-2-yl)methyl)sulfonyl)morpholine (**3b**)

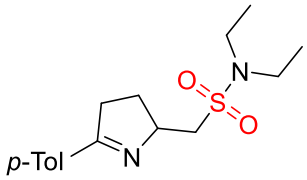
Reddish solid, 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.73 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 4.66 – 4.57 (m, 1H), 3.78 (t, *J* = 4.7 Hz, 4H), 3.56 (dd, *J* = 13.9, 5.4 Hz, 1H), 3.44 – 3.32 (m, 4H), 3.16 – 3.07 (m, 1H), 3.03 – 2.89 (m, 2H), 2.51 – 2.41 (m, 1H), 2.39 (s, 3H), 1.94 – 1.83 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 174.3, 141.3, 131.1, 129.3, 127.8, 67.5, 66.7, 54.6, 45.7, 35.4, 29.1, 21.5; HRMS calcd for $C_{16}H_{23}N_2O_3S^+$ ($M+H^+$): 323.1424, found: 323.1430.



4-(((5-(*p*-Tolyl)-3,4-dihydro-2*H*-pyrrol-2-yl)methyl)sulfonyl)thiomorpholine (**3c**)

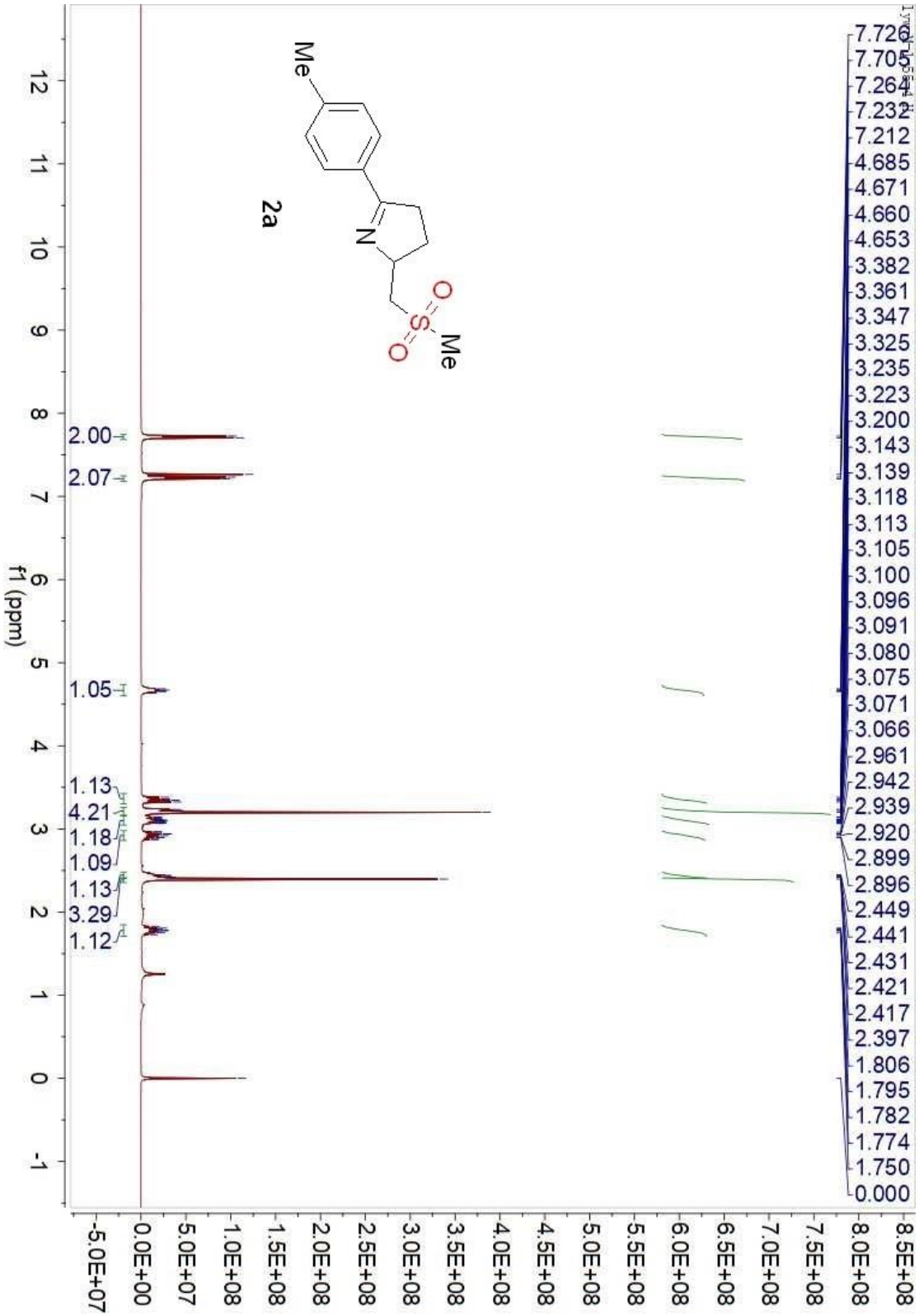
Reddish solid, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.74 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.61 – 4.53 (m, 1H), 3.73 – 3.61 (m, 4H), 3.50 (dd, *J* = 13.9, 5.7 Hz, 1H), 3.16 – 3.06 (m, 1H), 3.01 (dd, *J* = 14.0, 7.7 Hz, 2H), 2.97 – 2.88 (m, 4H), 2.48 –

2.41 (m, 1H), 2.40 (s, 3H), 1.90 – 1.79 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 174.2, 141.3, 131.1, 129.3, 127.8, 67.5, 55.9, 47.6, 35.3, 29.1, 27.7, 21.5; HRMS calcd for $C_{16}H_{23}N_2O_2S_2^+$ ($M+H^+$): 339.1195, found: 339.1204.



N,N-Diethyl-1-(5-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrol-2-yl)methanesulfonamide (**3d**)

Reddish oil, 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.71 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 4.65 – 4.57 (m, 1H), 3.64 (dd, *J* = 13.7, 4.2 Hz, 1H), 3.43 – 3.26 (m, 4H), 3.21 – 3.05 (m, 1H), 2.98 – 2.88 (m, 2H), 2.49 – 2.41 (m, 1H), 2.39 (s, 3H), 2.01 – 1.91 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 174.1, 141.1, 131.2, 129.2, 127.7, 68.0, 57.3, 41.9, 35.4, 28.9, 21.4, 14.6; HRMS calcd for $C_{16}H_{25}N_2O_2S^+$ ($M+H^+$): 309.1631, found: 309.1642.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N
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S
O
Me
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1.13
4.21
1.18
1.09
1.13
3.29
1.12
f1 (ppm)
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7.232
7.212
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4.671
4.660
4.653
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3.361
3.347
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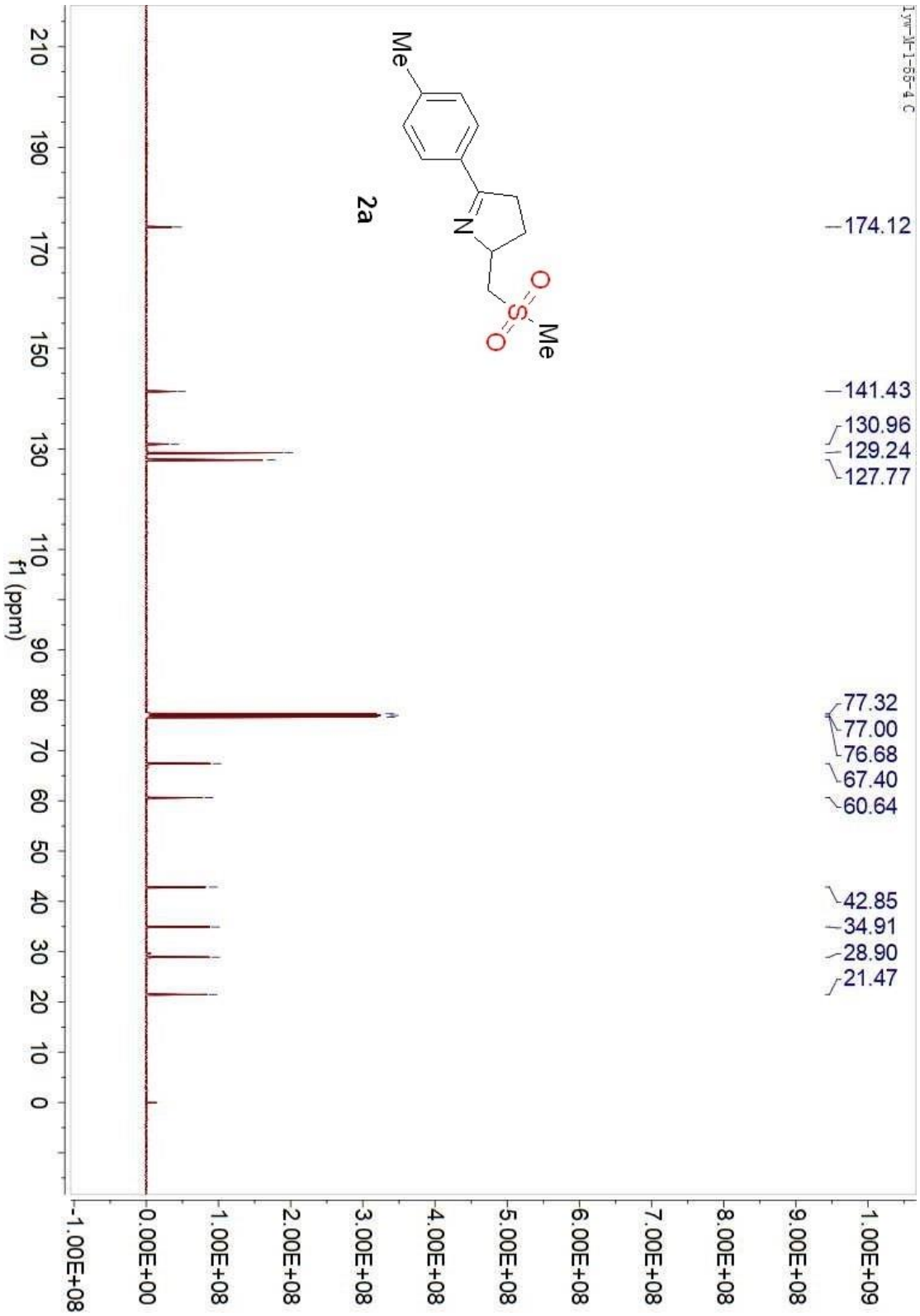
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S
O
Me
2a
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67.40
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34.91
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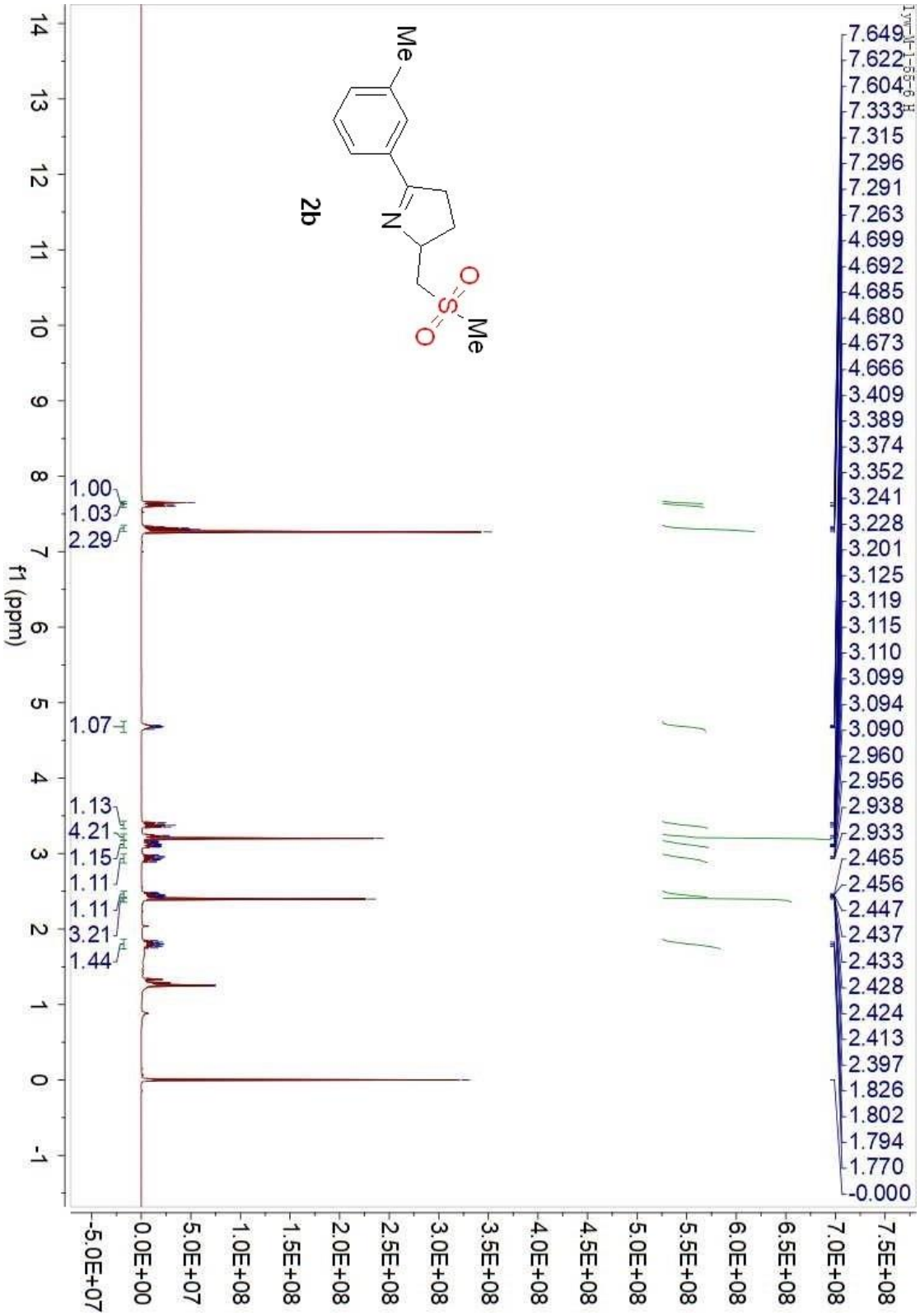
21.47
f1 (ppm)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O
S
O
Me
2b
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1.07
1.13
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1.11
1.11
3.21
1.44
f1 (ppm)
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7.604
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7.296
7.291
7.263
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3.119
3.115
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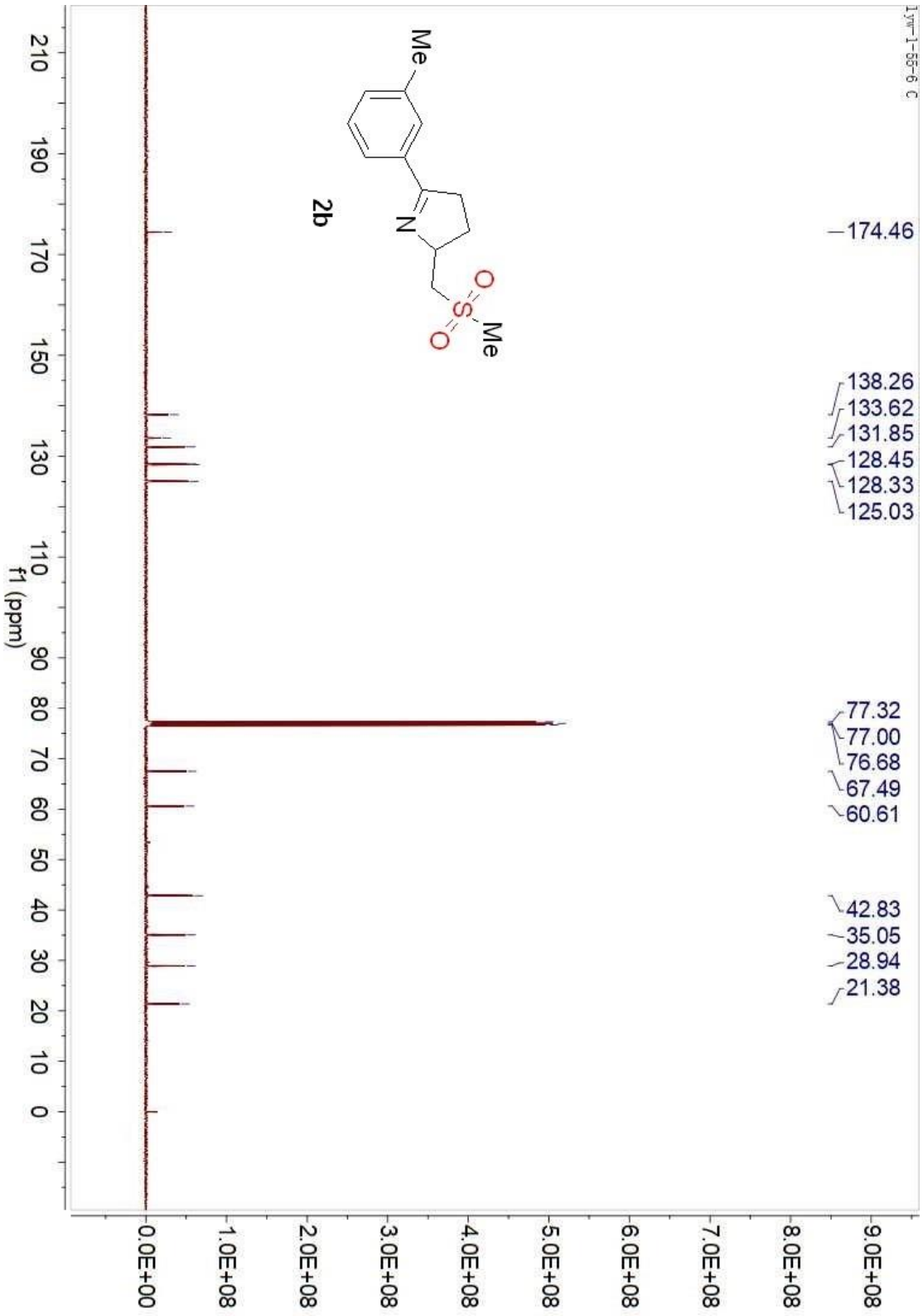
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O
S
O
Me
2b
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128.33
125.03
77.32
77.00
76.68
67.49
60.61
42.83
35.05
28.94
21.38
f1 (ppm)
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1.0E+08
2.0E+08
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4.0E+08
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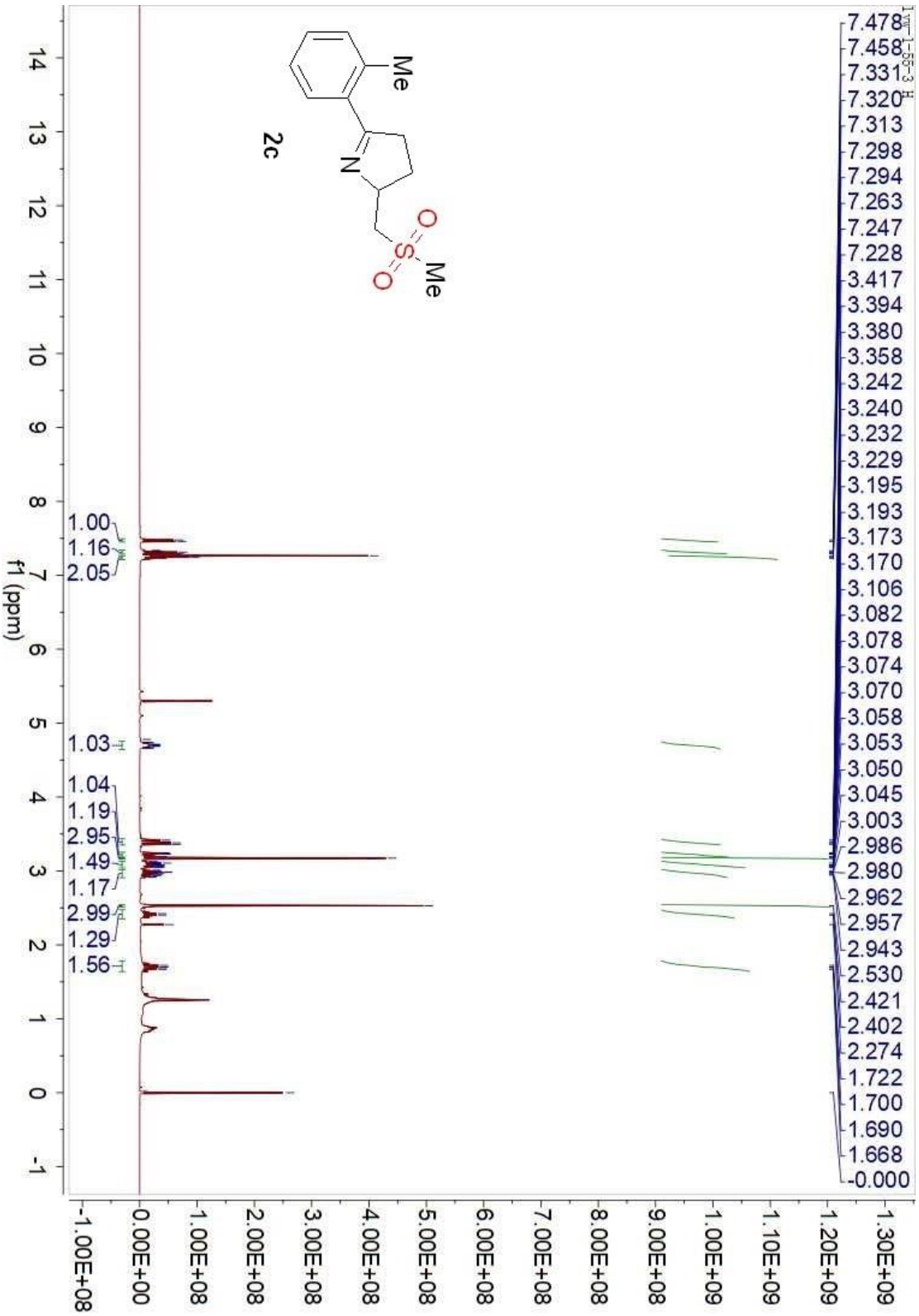
6.0E+08
7.0E+08
8.0E+08
9.0E+08


Me
N
O
S
O
Me
2c
f1 (ppm)
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2.05
1.03
1.04
1.19
2.95
1.49
1.17
2.99
1.29
1.56
7.478
7.458
7.331
7.320
7.313
7.298
7.294
7.263
7.247
7.228
3.417
3.394
3.380
3.358
3.242
3.240
3.232
3.229
3.195
3.193
3.173
3.170
3.106
3.082
3.078
3.074
3.070
3.058
3.053
3.050
3.045
3.003
2.986
2.980
2.962
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2.402
2.274
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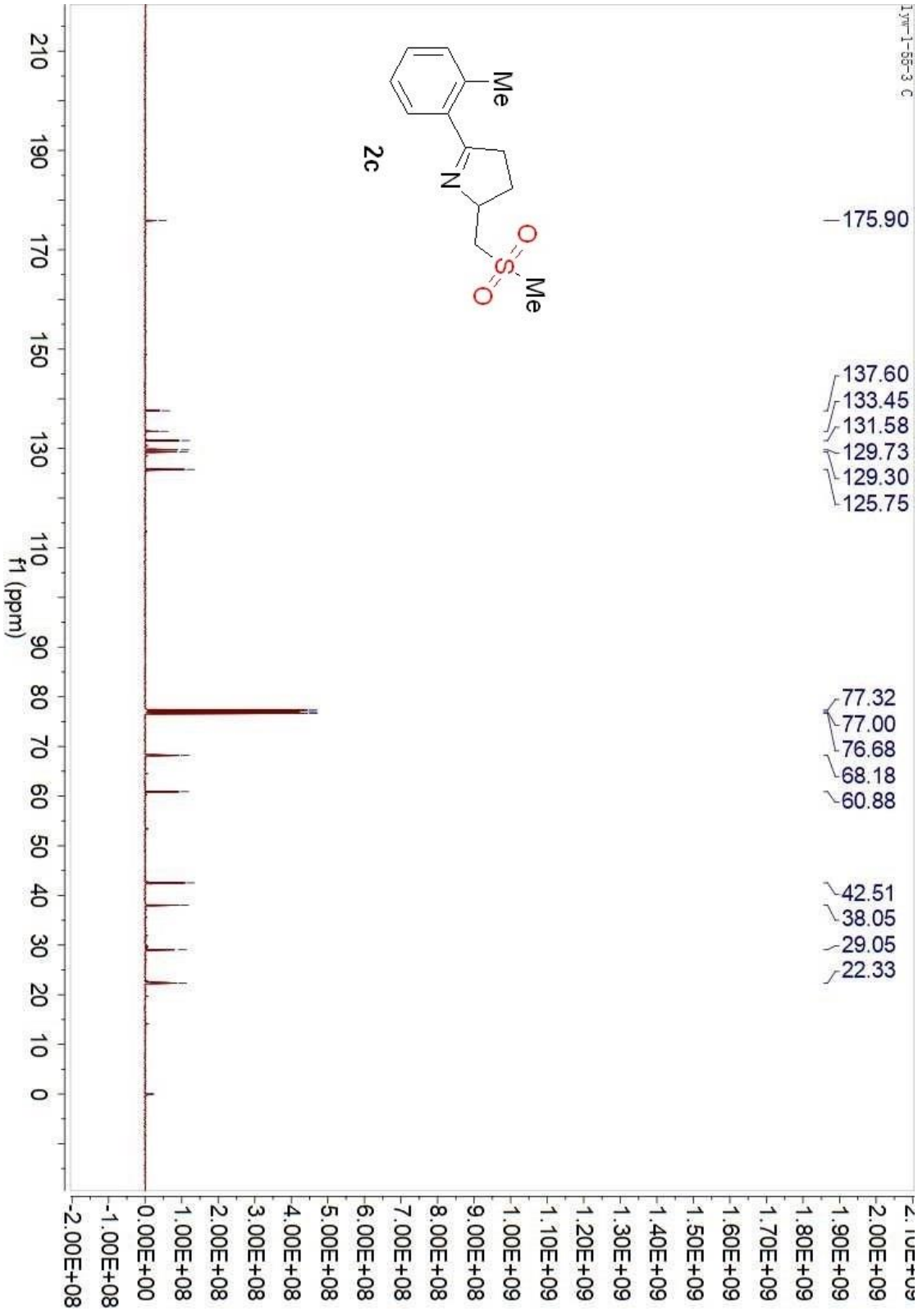
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O
S
O
Me
2c
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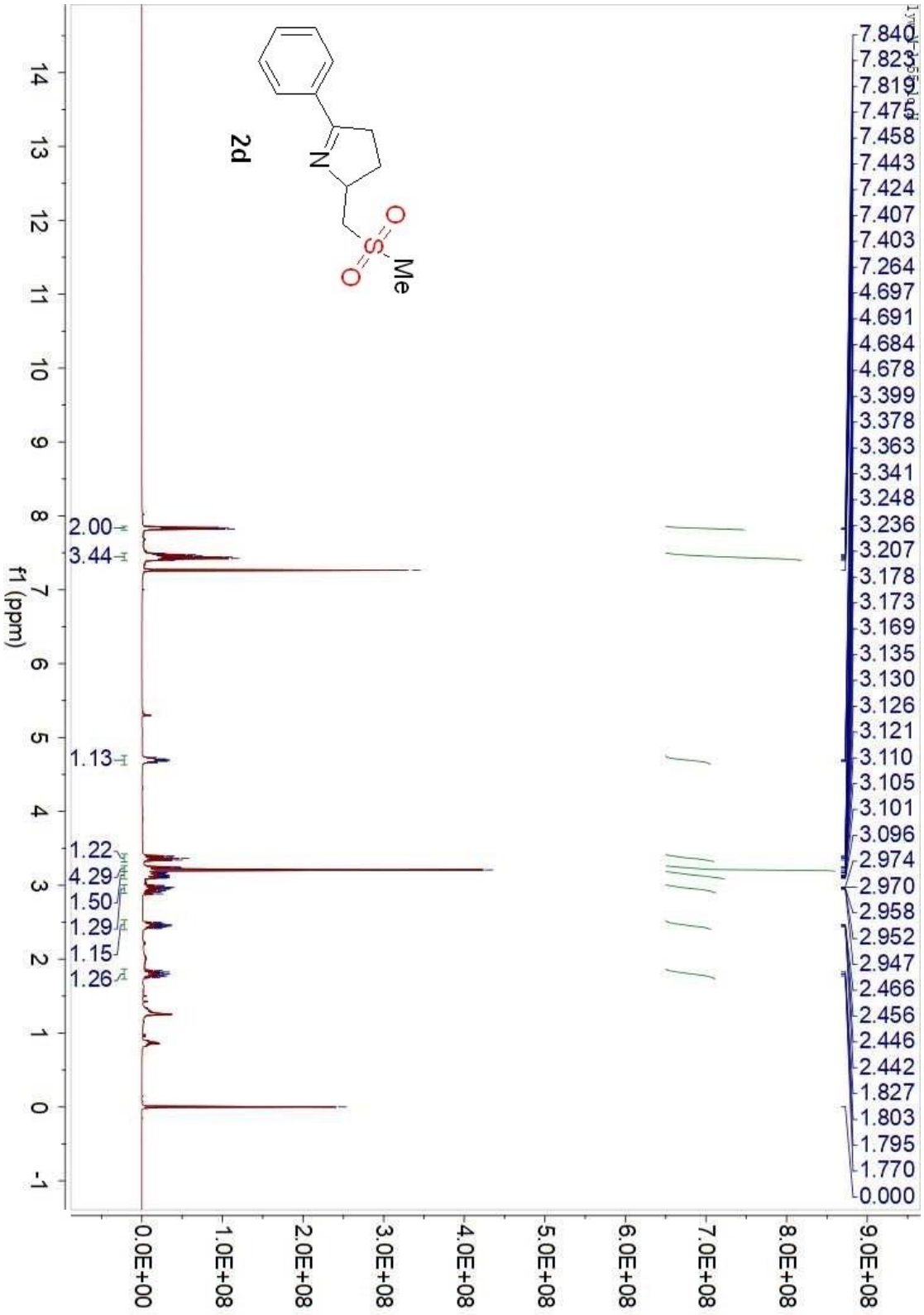
38.05
29.05
22.33
f1 (ppm)


2d
N
O
S
O
Me
f1 (ppm)
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1.29
1.15
1.26
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7.823
7.819
7.475
7.458
7.443
7.424
7.407
7.403
7.264
4.697
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4.684
4.678
3.399
3.378
3.363
3.341
3.248
3.236
3.207
3.178
3.173
3.169
3.135
3.130
3.126
3.121
3.110
3.105
3.101
3.096
2.974
2.970
2.958
2.952
2.947
2.466
2.456
2.446
2.442
1.827
1.803
1.795
1.770
0.000
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1.0E+08
2.0E+08
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7.0E+08
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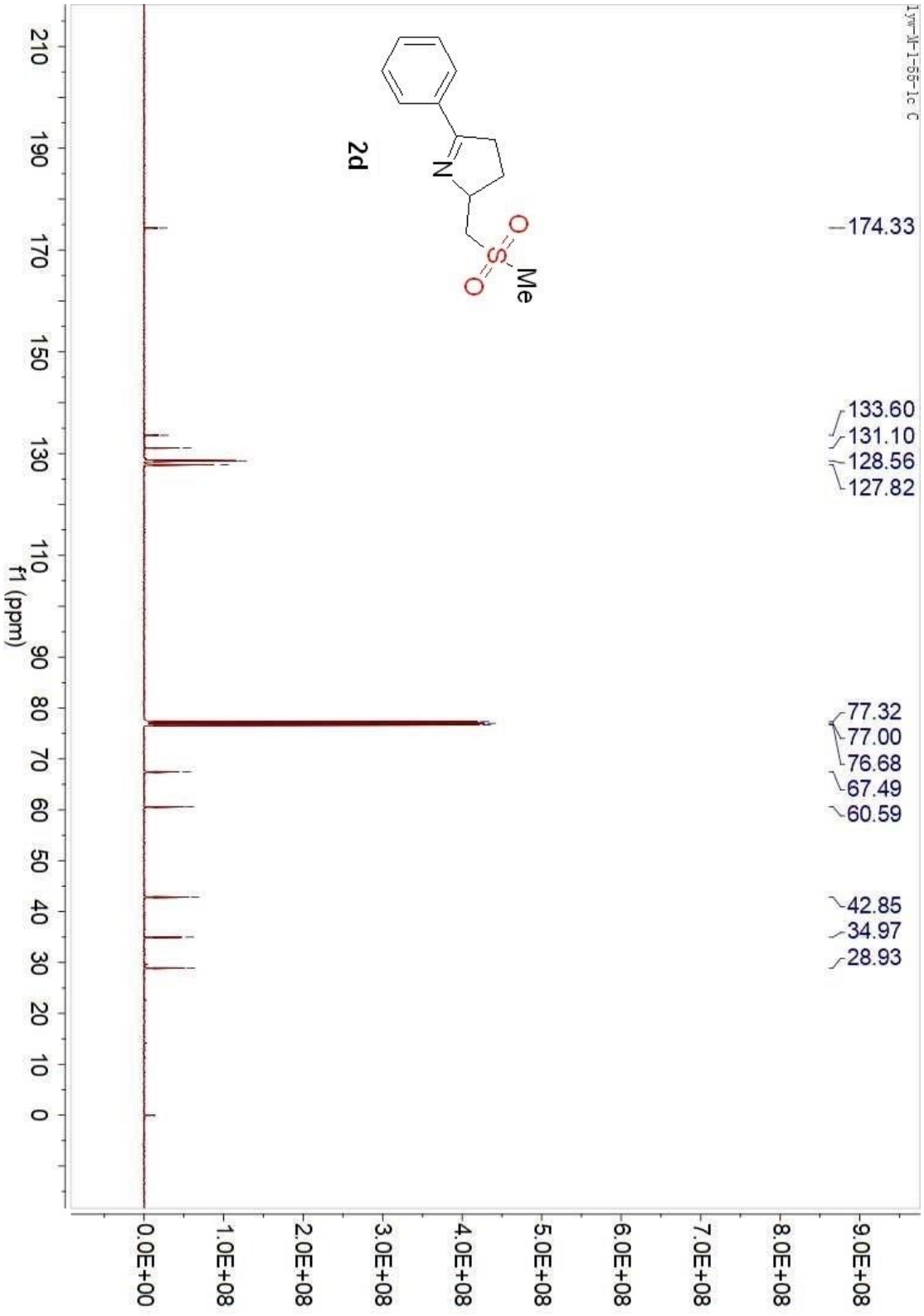
9.0E+08


2d
N
S
O
O
Me
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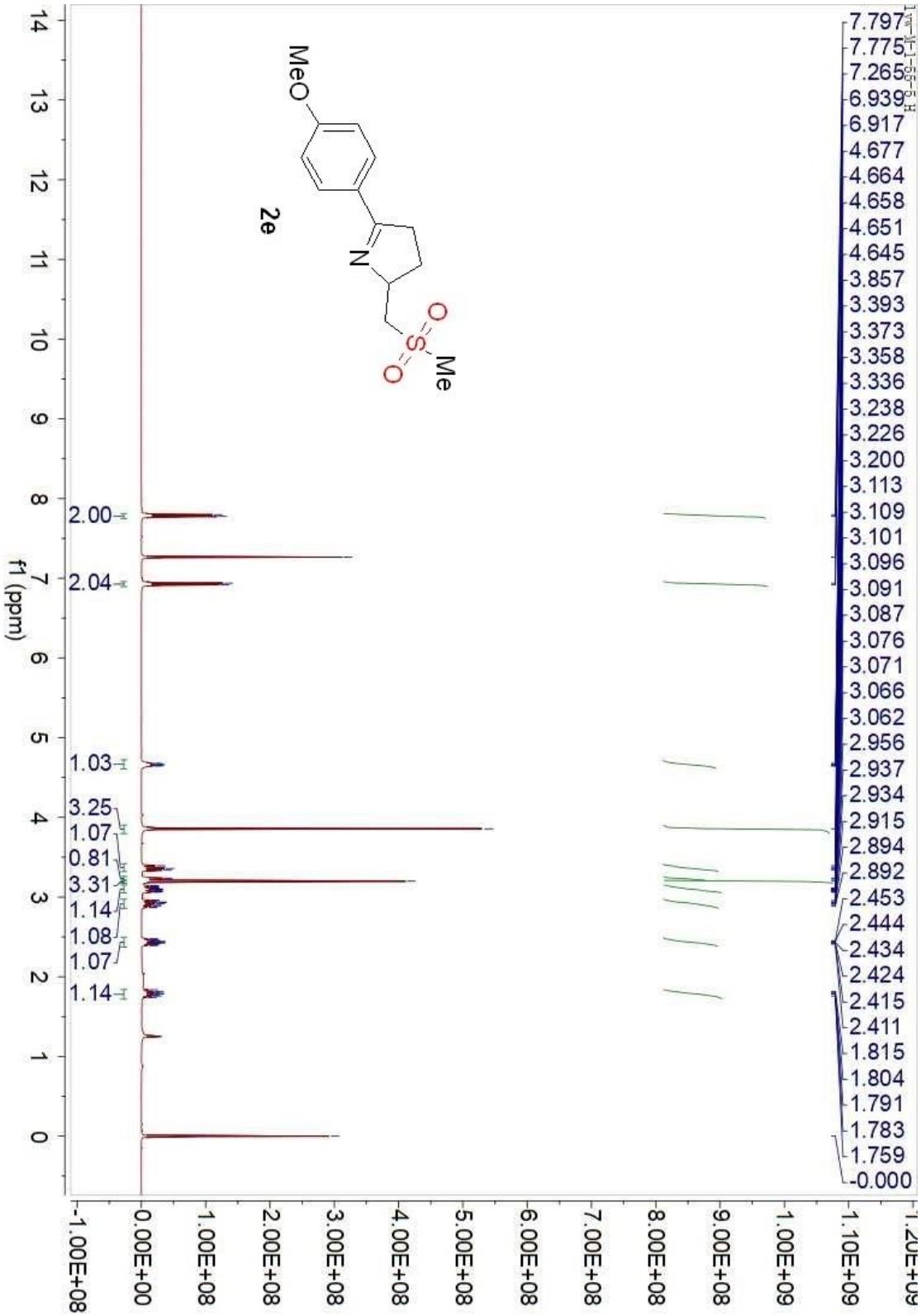
28.93
f1 (ppm)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O
S
O
Me
2e
f1 (ppm)
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1.14
1.08
1.07
1.14
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7.775
7.265
6.939
6.917
4.677
4.664
4.658
4.651
4.645
3.857
3.393
3.373
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3.336
3.238
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3.087
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3.071
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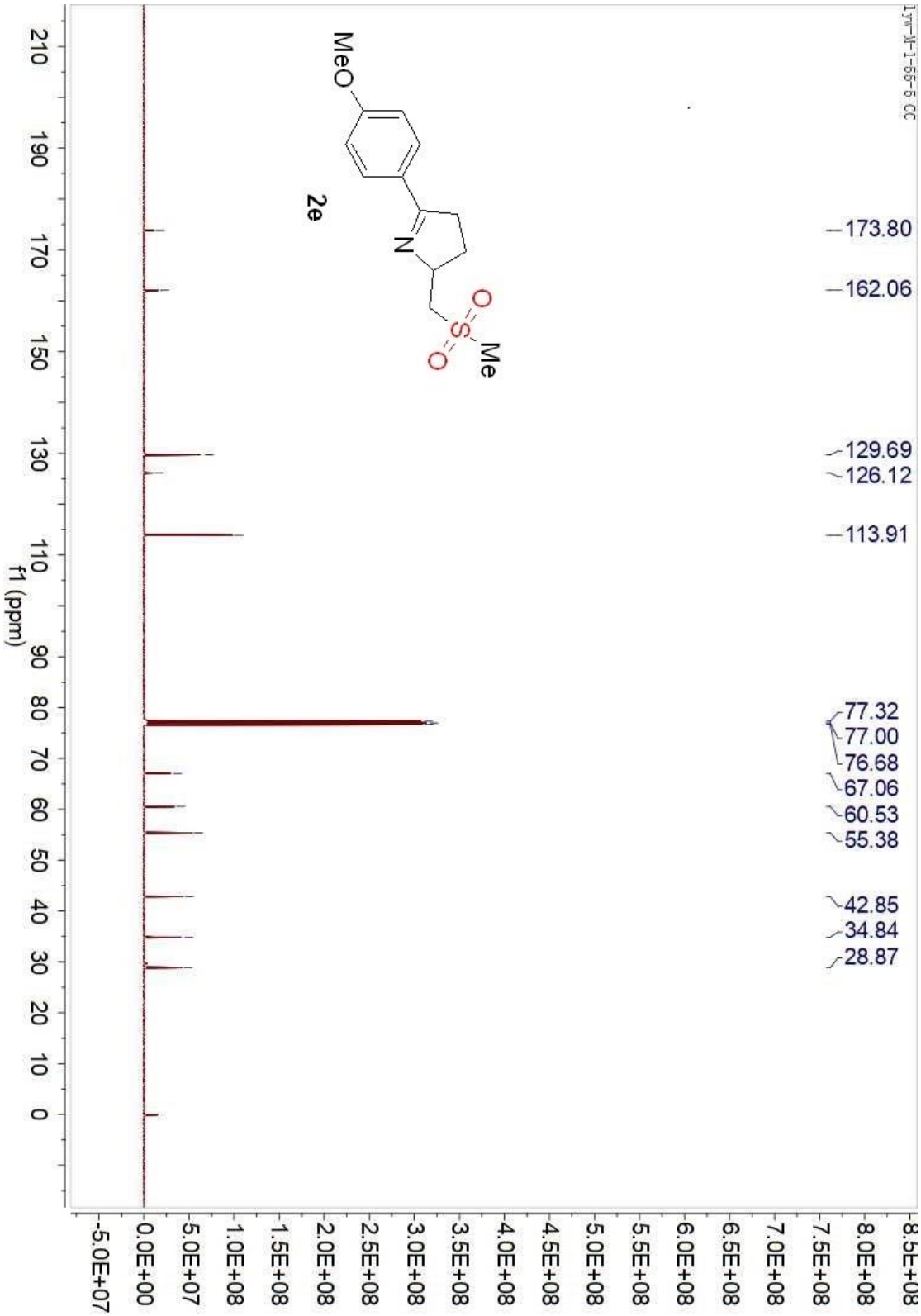
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N
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O
Me
2e
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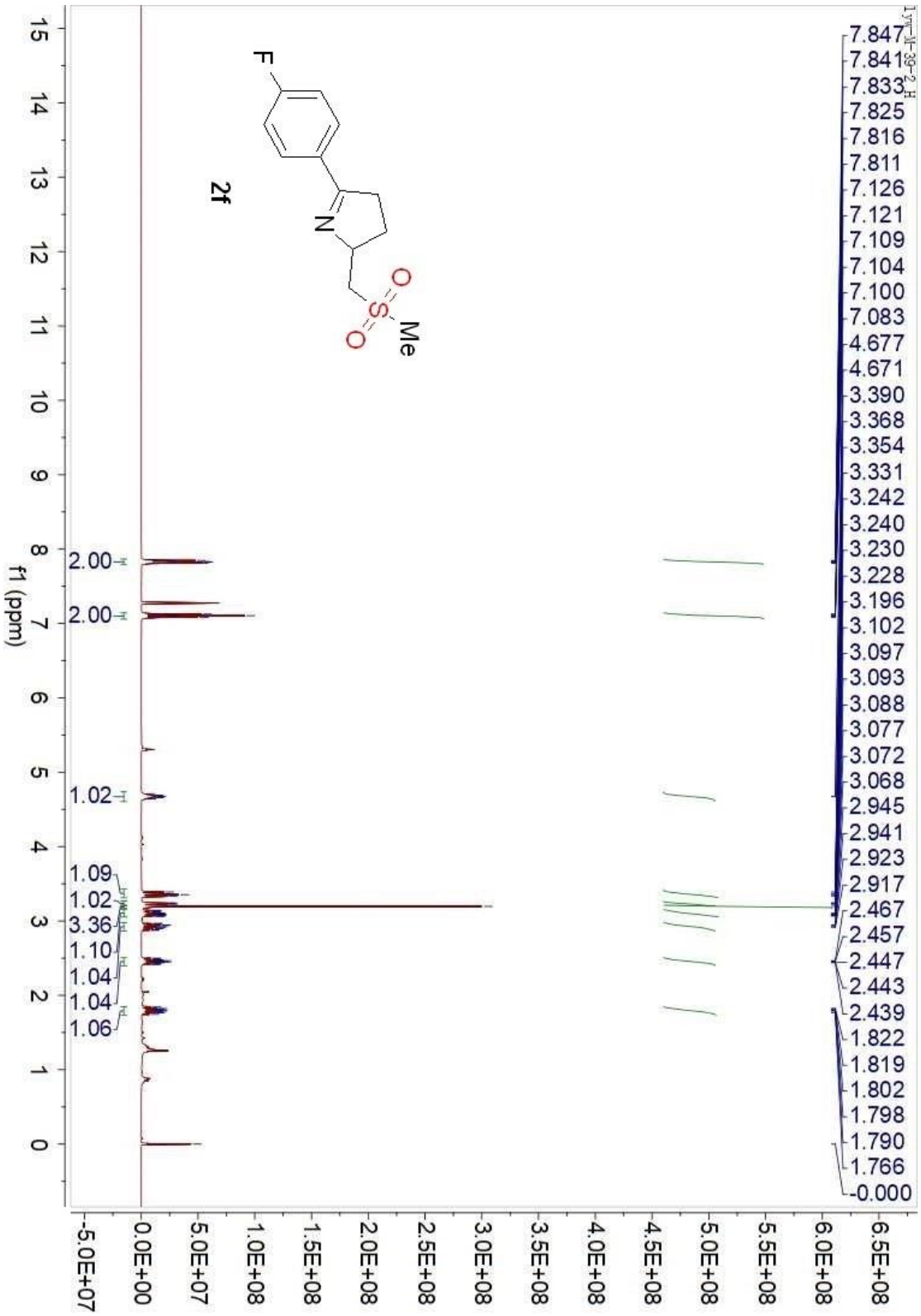
28.87
f1 (ppm)


2f
F
N
O
S
O
Me
f1 (ppm)
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1.02
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3.228
3.196
3.102
3.097
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3.088
3.077
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2.941
2.923
2.917
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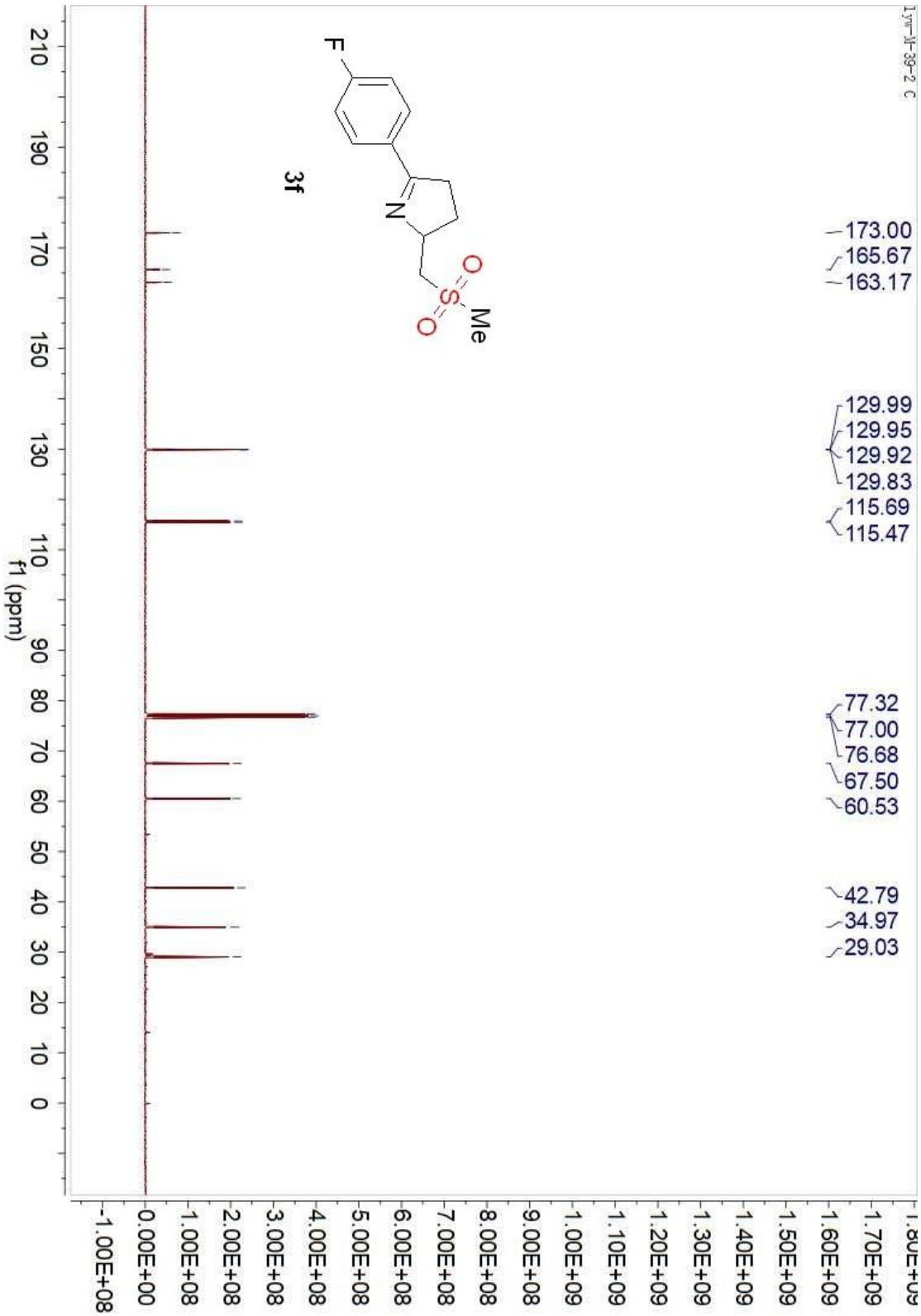
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F
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O
S
O
Me
3f
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129.95
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42.79
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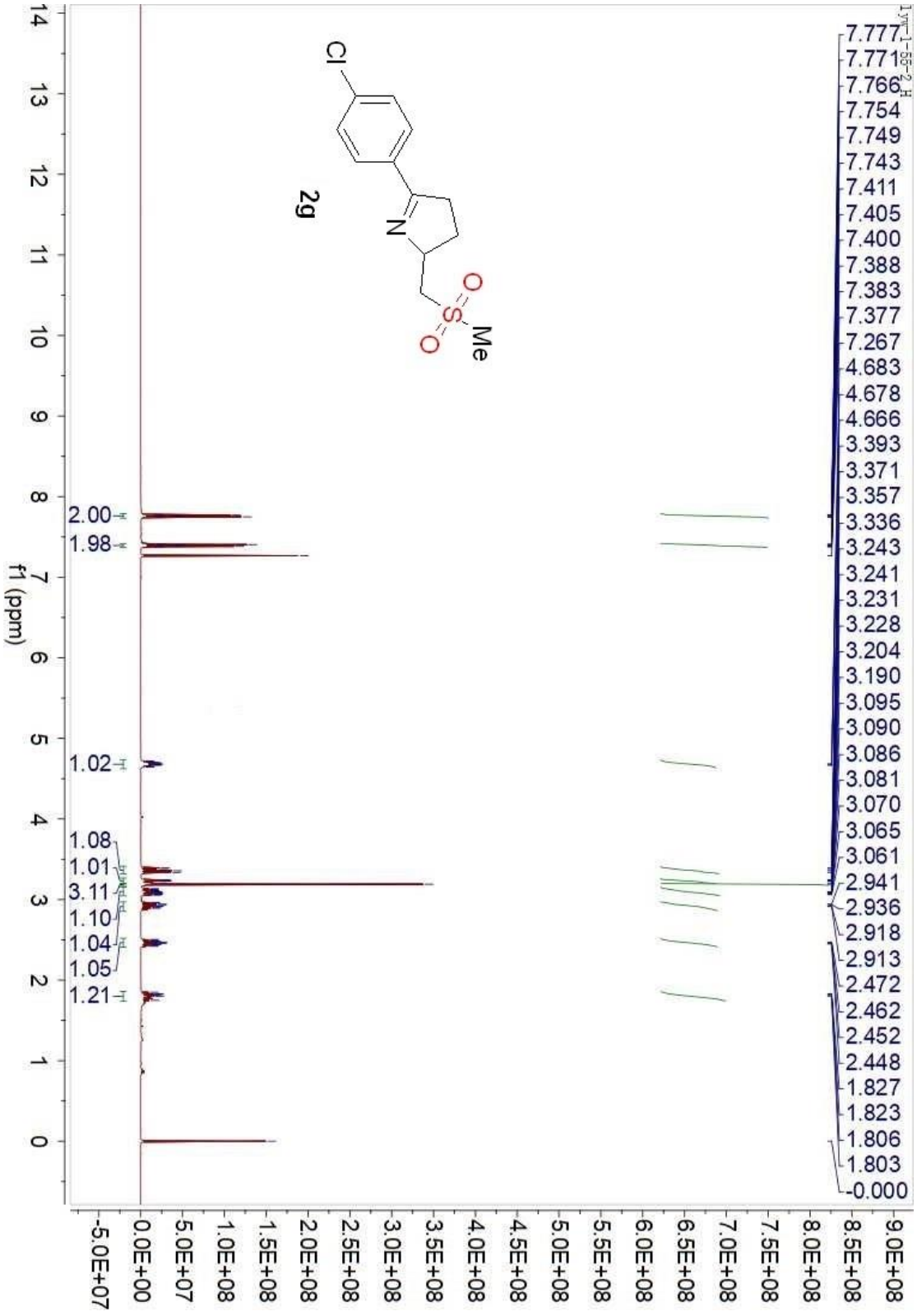
29.03
f1 (ppm)


Cl
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O
S
O
Me
2g
f1 (ppm)
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1.08
1.01
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7.383
7.377
7.267
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4.678
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3.357
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3.241
3.231
3.228
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3.090
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3.065
3.061
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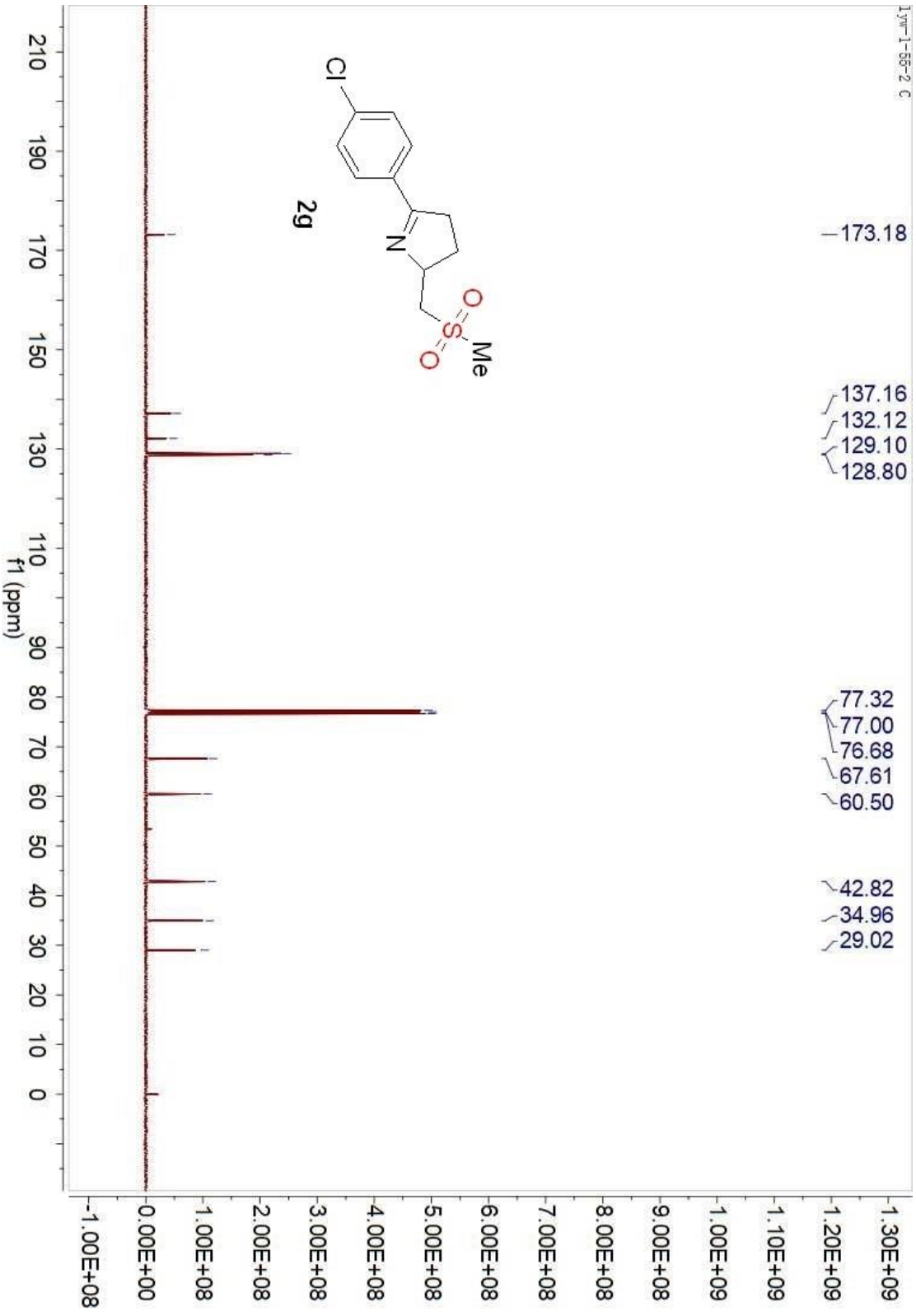
lyw-1-55-2 C
Cl
N
O
S
O
Me
2g
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132.12
129.10
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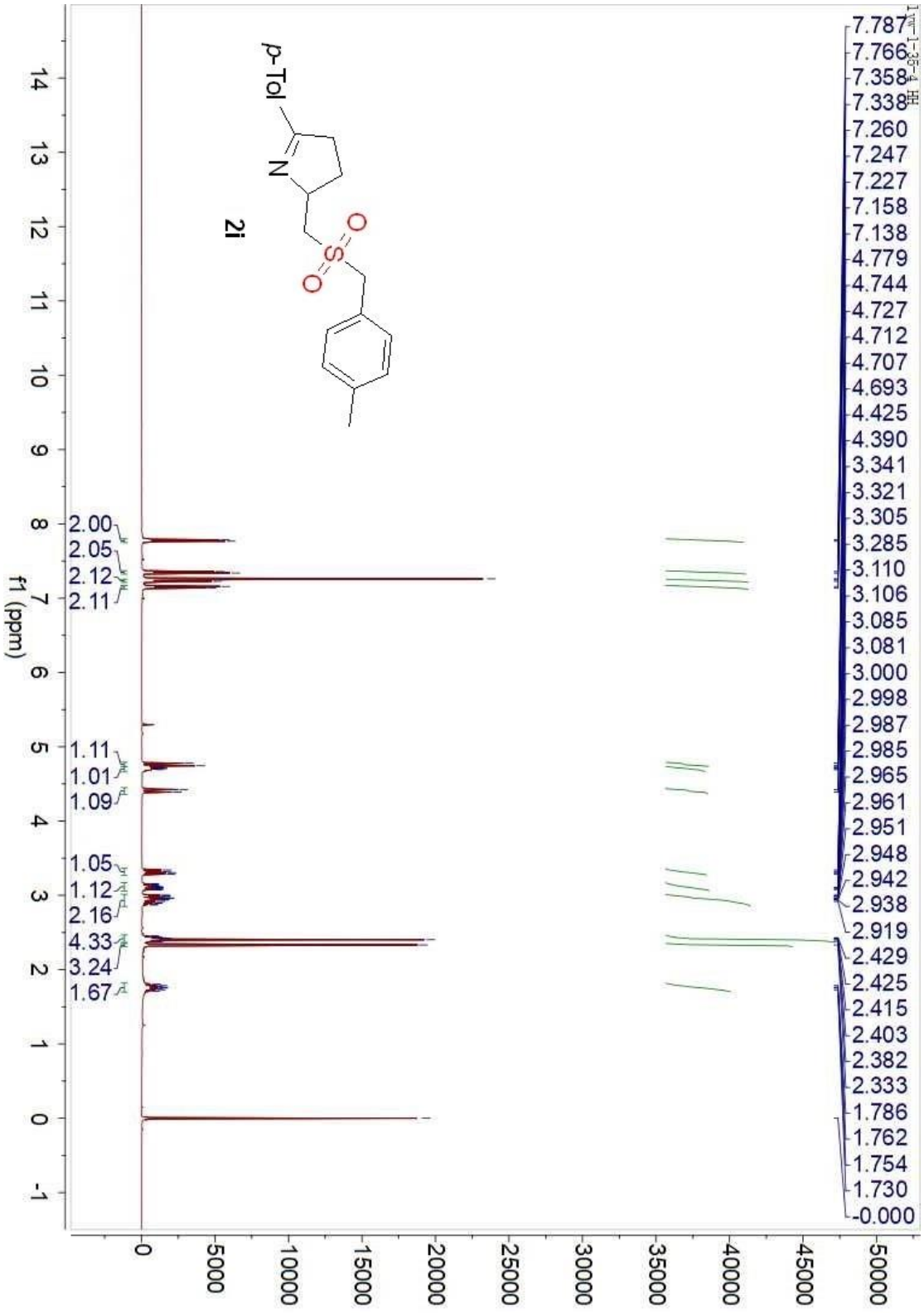
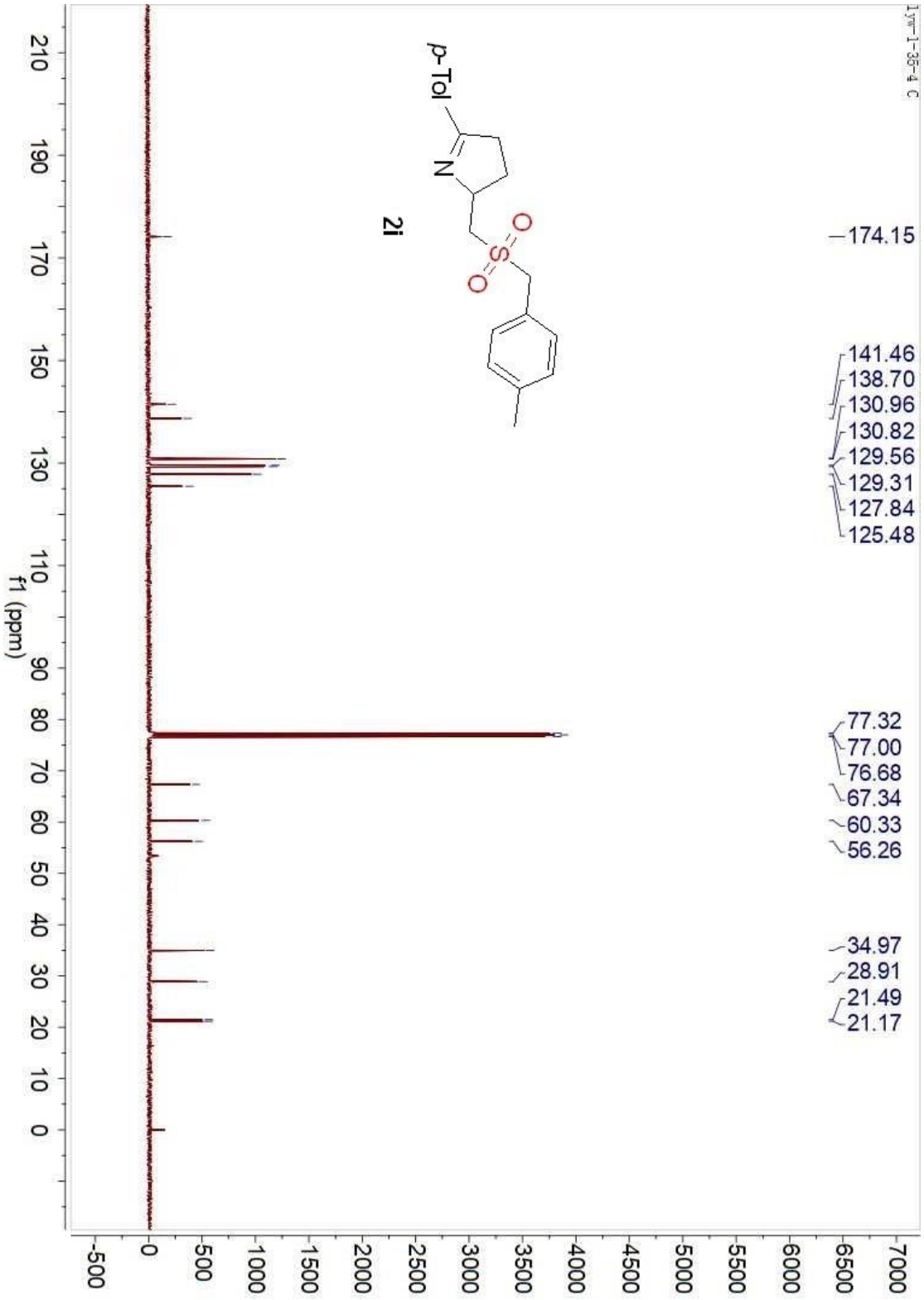
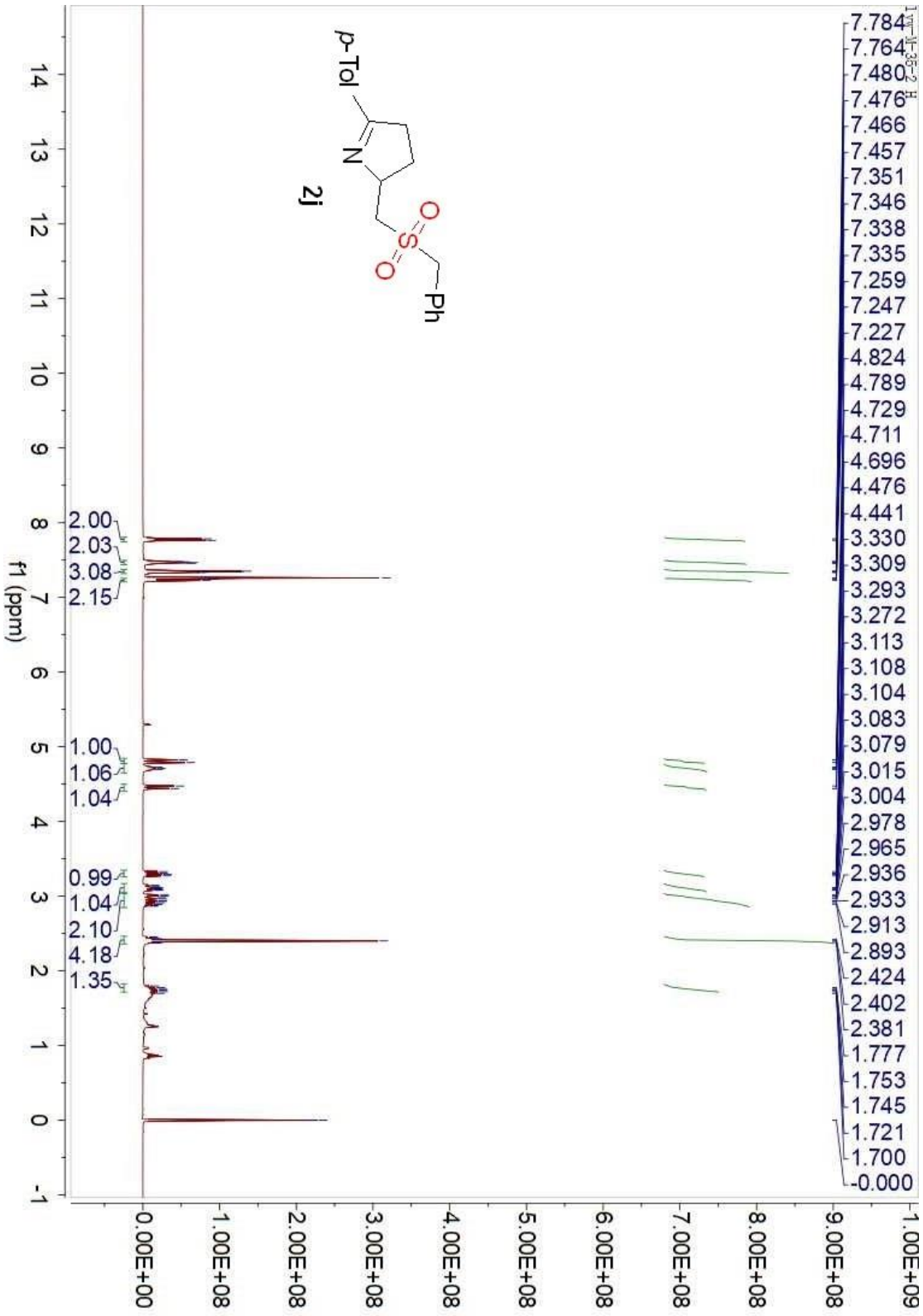
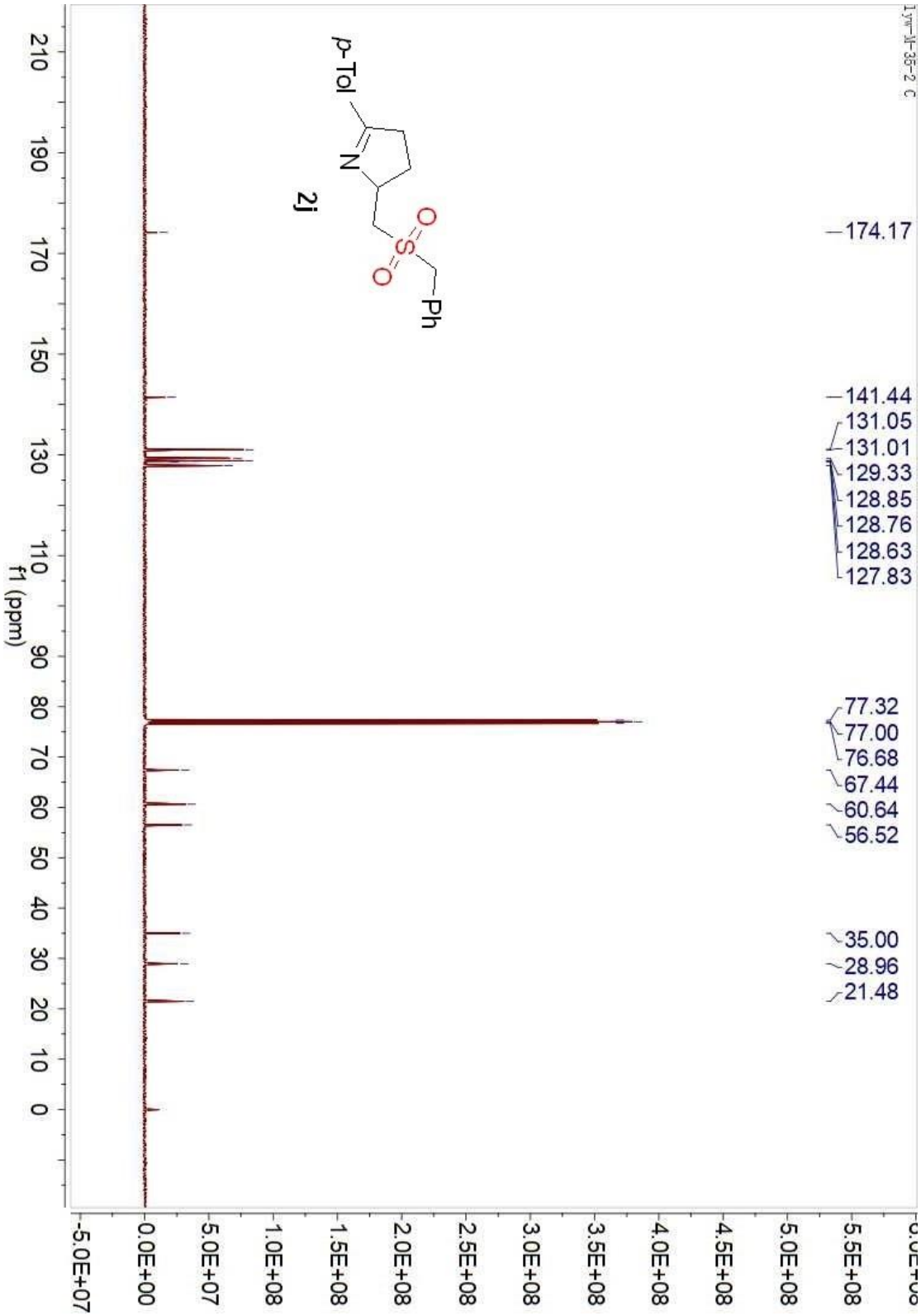
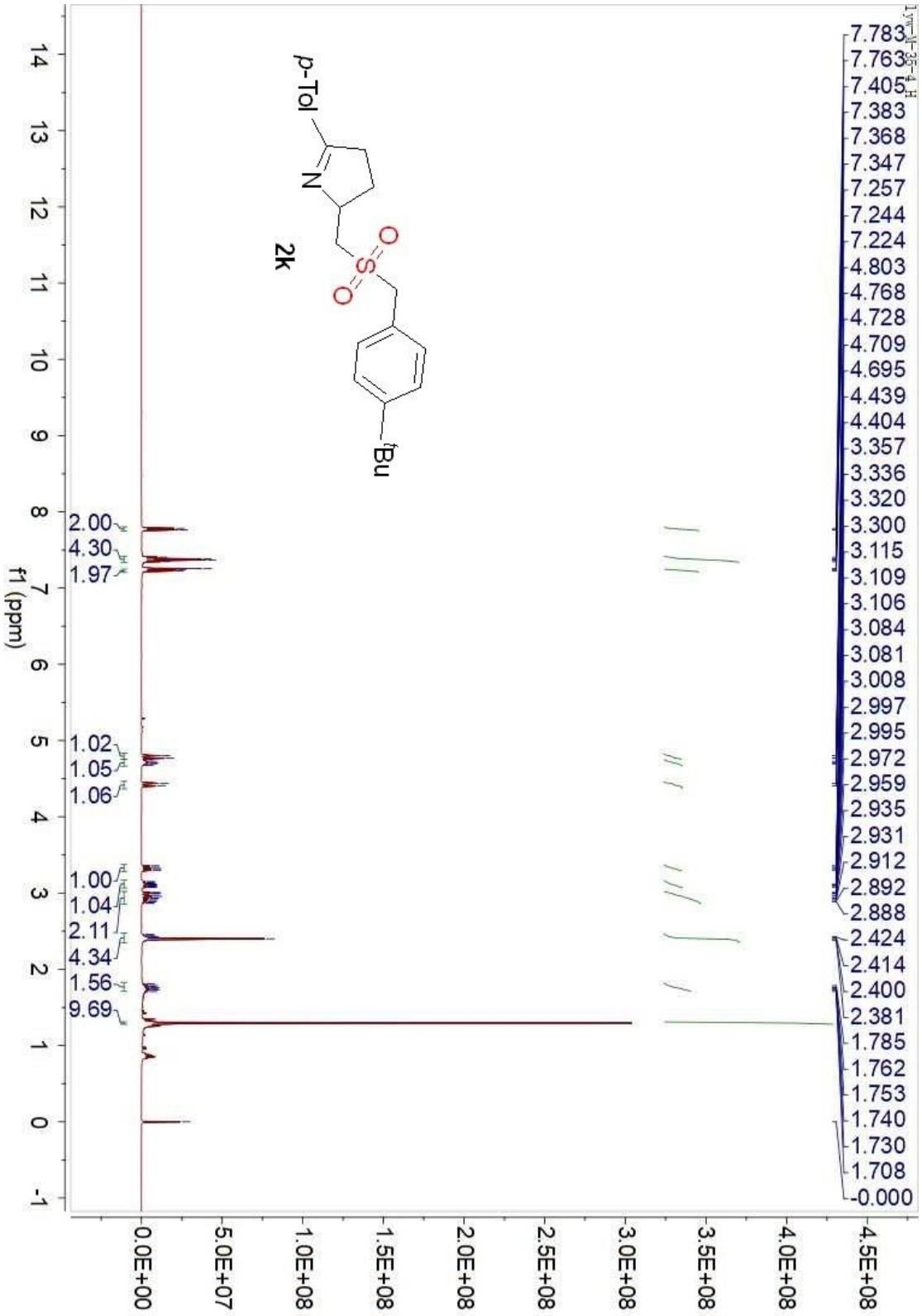
77.00
76.68
67.61
60.50
42.82
34.96
29.02
f1 (ppm)

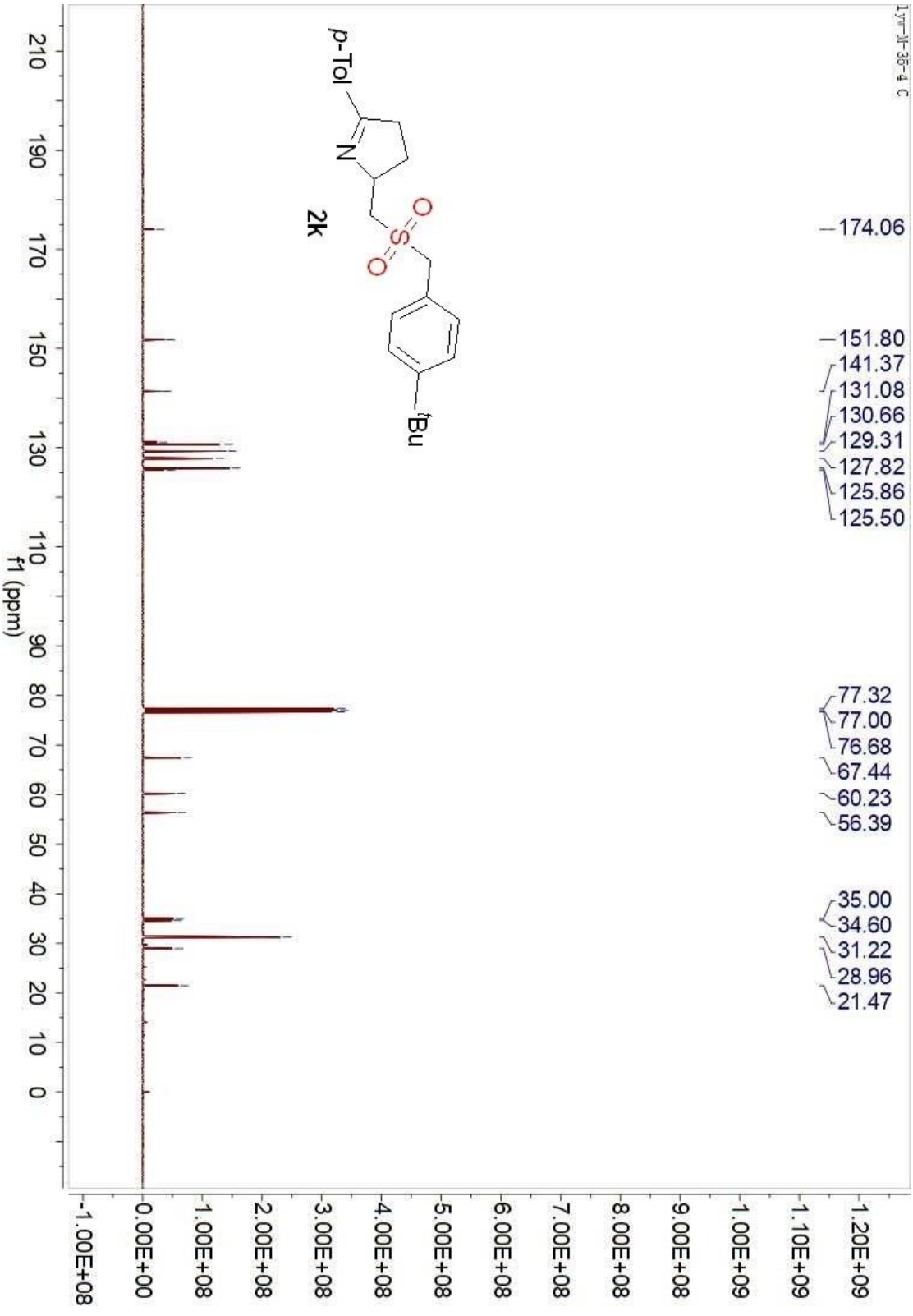

p-Tol
N
O
S
O
2i
f1 (ppm)
2.00
2.05
2.12
2.11
1.11
1.01
1.09
1.05
1.12
2.16
4.33
3.24
1.67
7.787
7.766
7.358
7.338
7.260
7.247
7.227
7.158
7.138
4.779
4.744
4.727
4.712
4.707
4.693
4.425
4.390
3.341
3.321
3.305
3.285
3.110
3.106
3.085
3.081
3.000
2.998
2.987
2.985
2.965
2.961
2.951
2.948
2.942
2.938
2.919
2.429
2.425
2.415
2.403
2.382
2.333
1.786
1.762
1.754
1.730
-0.000

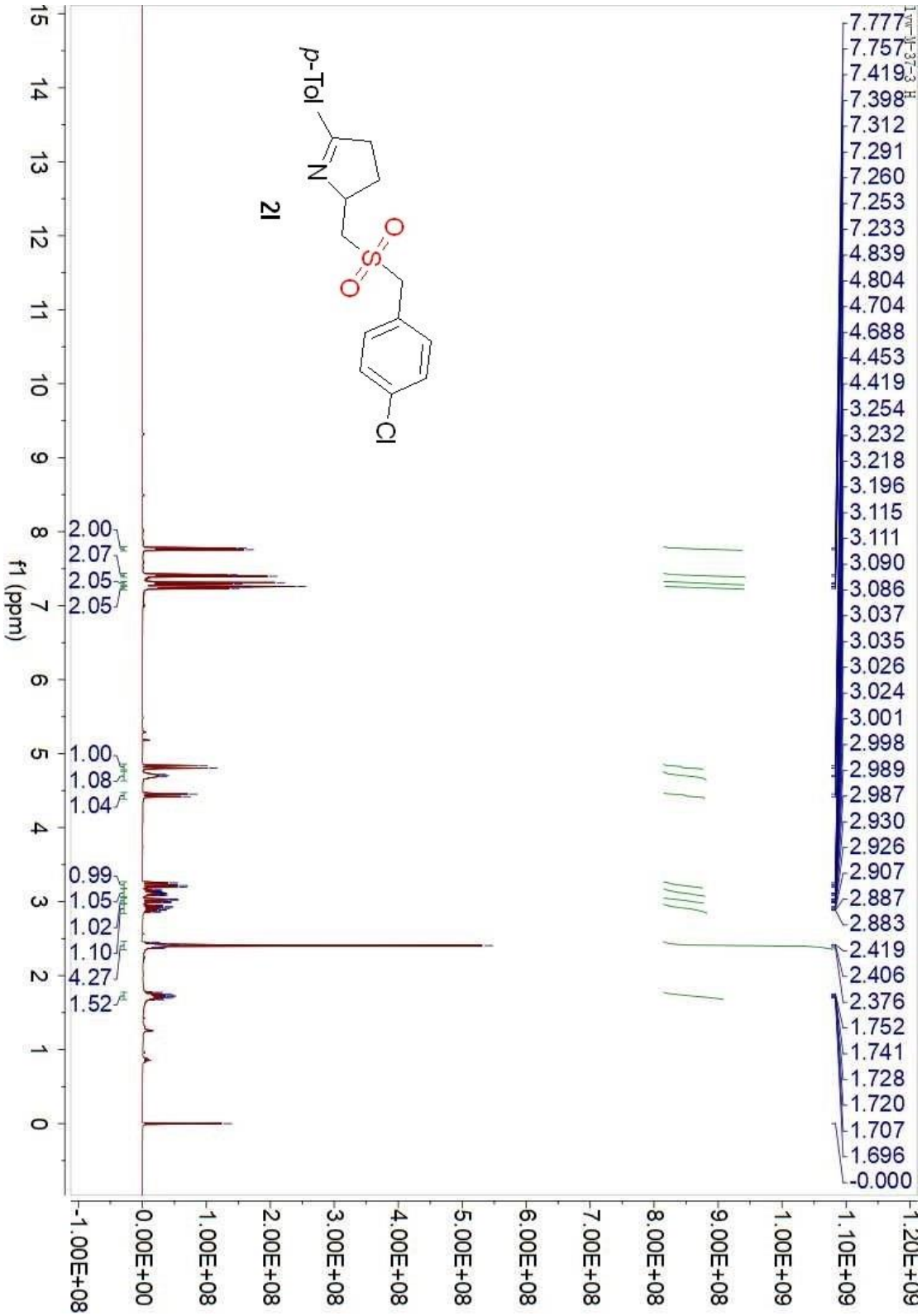

1yw-1-35-4 C
p-Tol
N
O
S
O
2i
174.15
141.46
138.70
130.96
130.82
129.56
129.31
127.84
125.48
77.32
77.00
76.68
67.34
60.33
56.26
34.97
28.91
21.49
21.17
f1 (ppm)

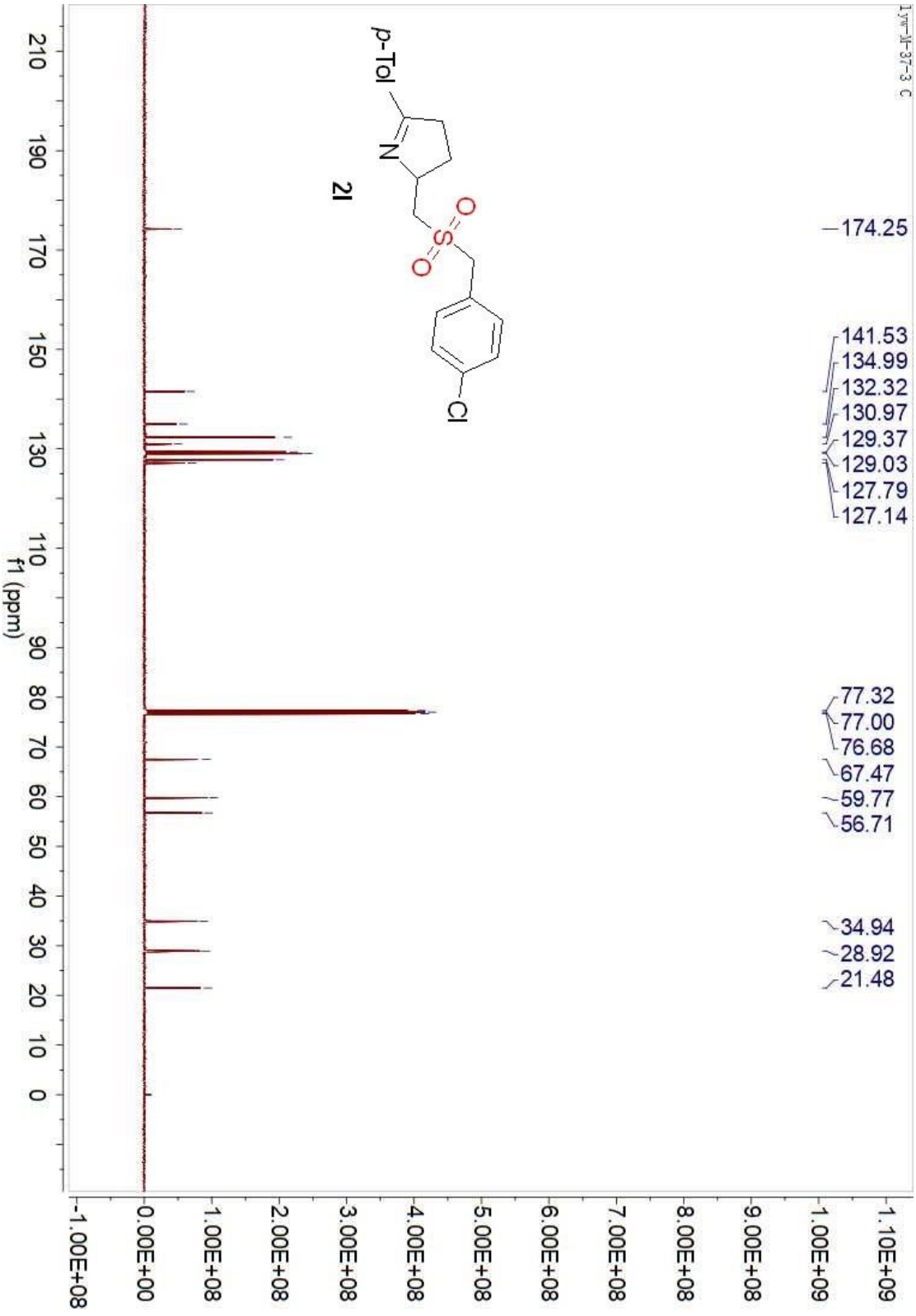

p-Tol
N
O
S
O
Ph
2j
f1 (ppm)
2.00
2.03
3.08
2.15
1.00
1.06
1.04
0.99
1.04
2.10
4.18
1.35
7.784
7.764
7.480
7.476
7.466
7.457
7.351
7.346
7.338
7.335
7.259
7.247
7.227
4.824
4.789
4.729
4.711
4.696
4.476
4.441
3.330
3.309
3.293
3.272
3.113
3.108
3.104
3.083
3.079
3.015
3.004
2.978
2.965
2.936
2.933
2.913
2.893
2.424
2.402
2.381
1.777
1.753
1.745
1.721
1.700
-0.000

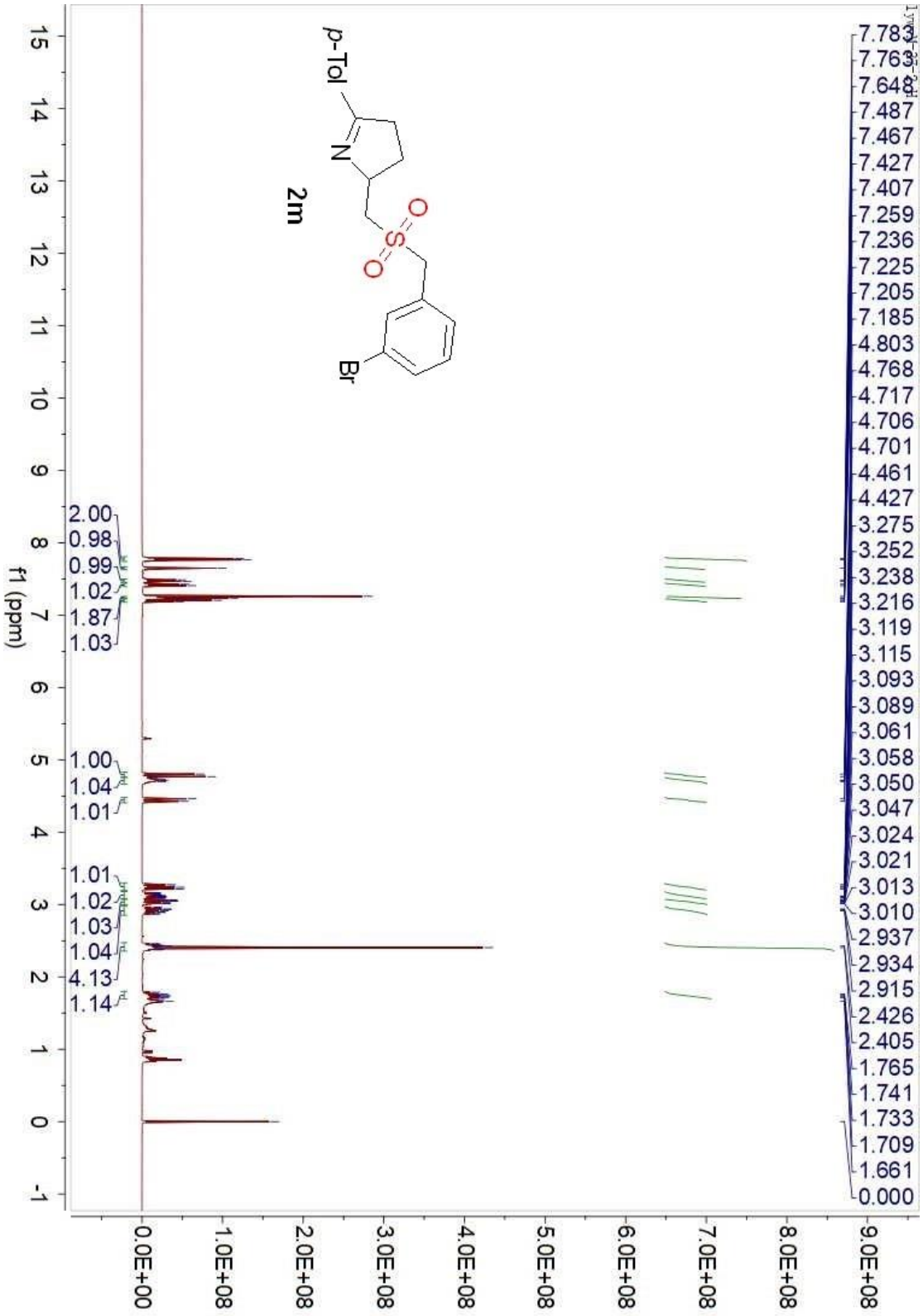

1;yw-3l-35-2 C
p-Tol
N
O
O
S
Ph
2j
174.17
141.44
131.05
131.01
129.33
128.85
128.76
128.63
127.83
77.32
77.00
76.68
67.44
60.64
56.52
35.00
28.96
21.48
f1 (ppm)

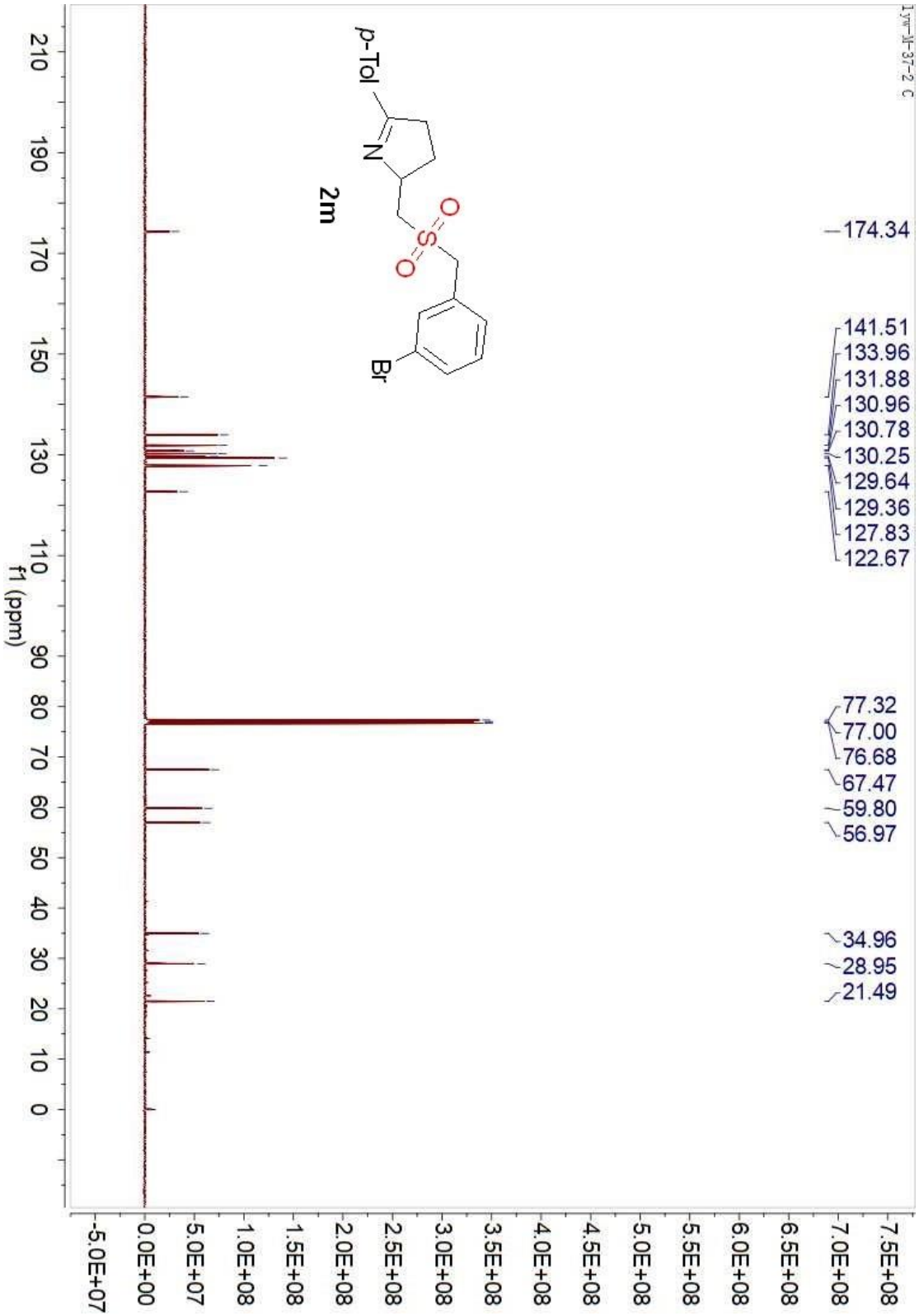

p-Tol
N
O
S
O
tBu
2k
f1 (ppm)
2.00
4.30
1.97
1.02
1.05
1.06
1.00
1.04
2.11
4.34
1.56
9.69
7.783
7.763
7.405
7.383
7.368
7.347
7.257
7.244
7.224
4.803
4.768
4.728
4.709
4.695
4.439
4.404
3.357
3.336
3.320
3.300
3.115
3.109
3.106
3.084
3.081
3.008
2.997
2.995
2.972
2.959
2.935
2.931
2.912
2.892
2.888
2.424
2.414
2.400
2.381
1.785
1.762
1.753
1.740
1.730
1.708
-0.000

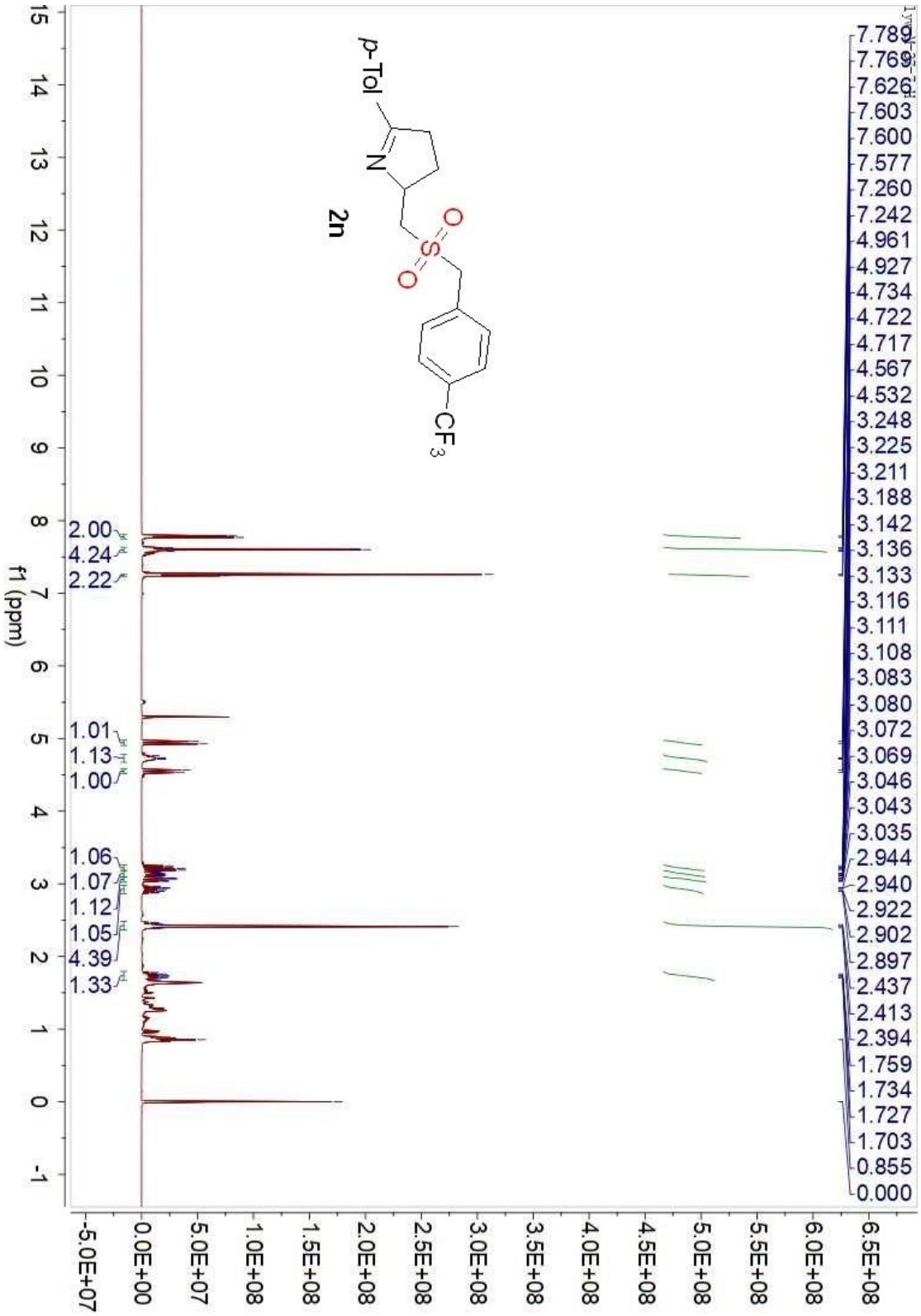

1:yw-3J-35-4 C
174.06
151.80
141.37
131.08
130.66
129.31
127.82
125.86
125.50
77.32
77.00
76.68
67.44
60.23
56.39
35.00
34.60
31.22
28.96
21.47
p-Tol
N
O
S
O
tBu
2k
f1 (ppm)

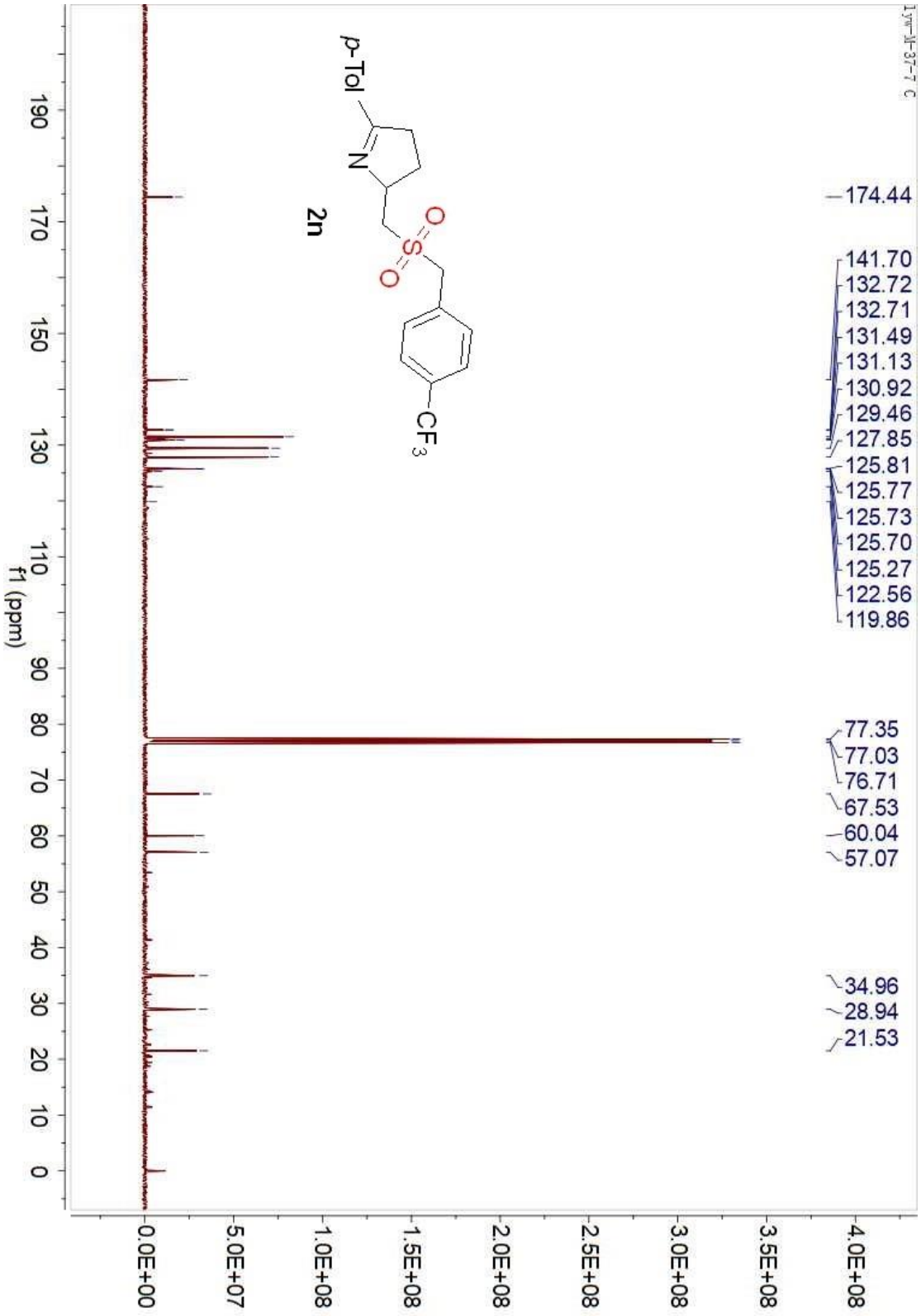

p-Tol
N
O
O
S
Cl
2l
f1 (ppm)
2.00
2.07
2.05
2.05
1.00
1.08
1.04
0.99
1.05
1.02
1.10
4.27
1.52
7.777
7.757
7.419
7.398
7.312
7.291
7.260
7.253
7.233
4.839
4.804
4.704
4.688
4.453
4.419
3.254
3.232
3.218
3.196
3.115
3.111
3.090
3.086
3.037
3.035
3.026
3.024
3.001
2.998
2.989
2.987
2.930
2.926
2.907
2.887
2.883
2.419
2.406
2.376
1.752
1.741
1.728
1.720
1.707
1.696
-0.000

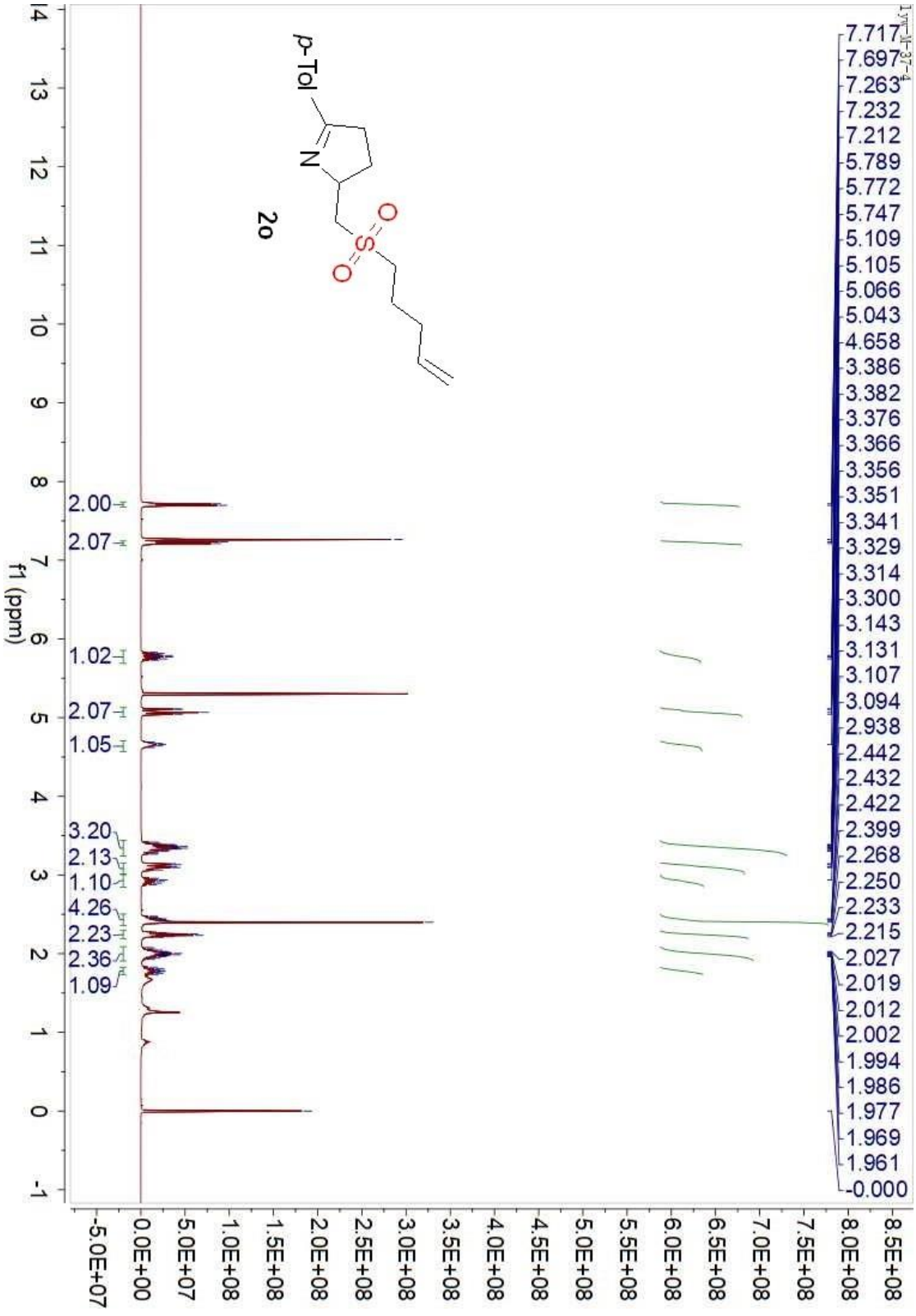

1;yw-3l-37-3 C
p-Tol
N
O
S
O
Cl
2l
174.25
141.53
134.99
132.32
130.97
129.37
129.03
127.79
127.14
77.32
77.00
76.68
67.47
59.77
56.71
34.94
28.92
21.48
f1 (ppm)

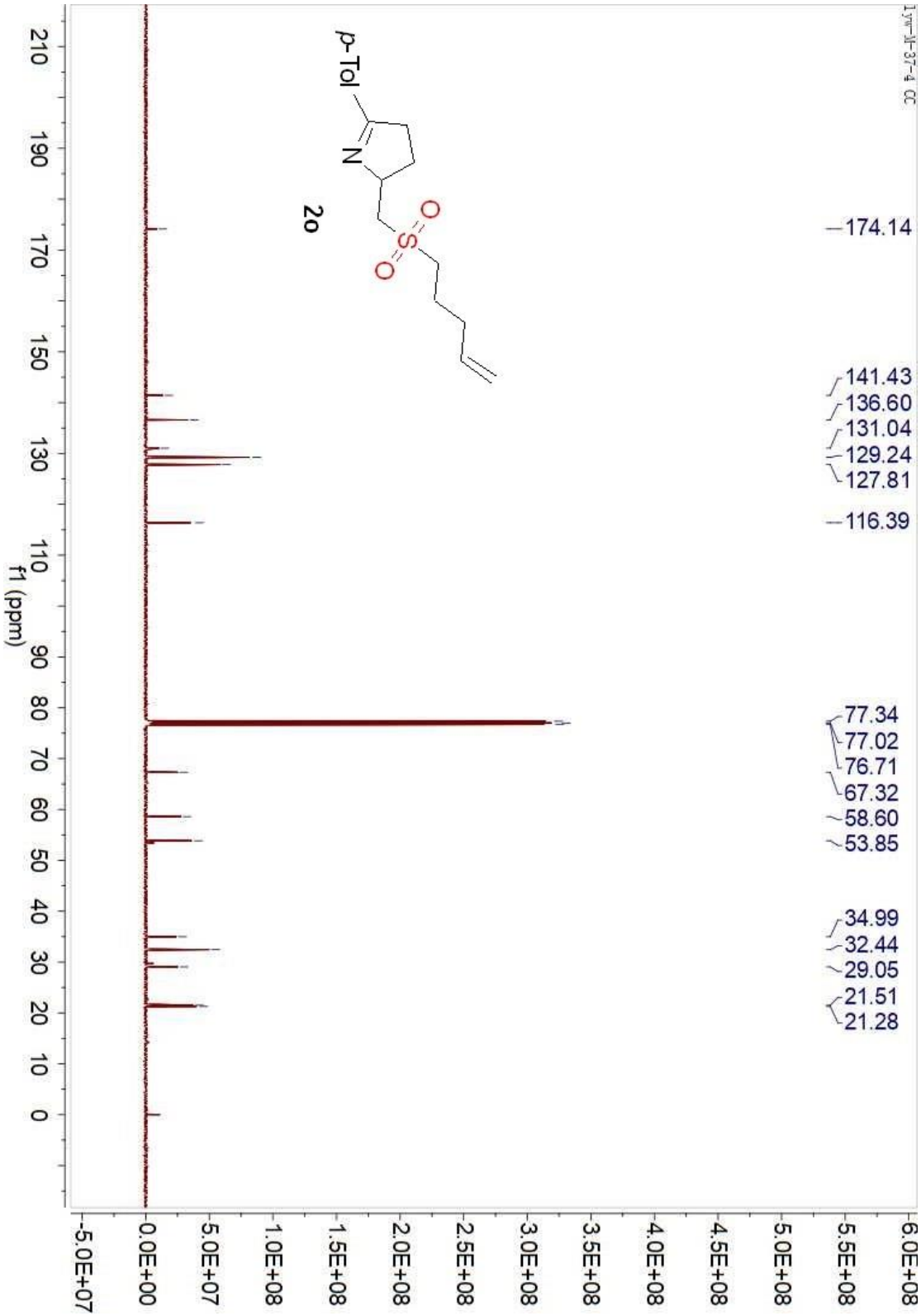

p-Tol
N
O
O
S
Br
2m
f1 (ppm)
2.00
0.98
0.99
1.02
1.87
1.03
1.00
1.04
1.01
1.01
1.02
1.03
1.04
4.13
1.14
7.783
7.763
7.640
7.487
7.467
7.427
7.407
7.259
7.236
7.225
7.205
7.185
4.803
4.768
4.717
4.706
4.701
4.461
4.427
3.275
3.252
3.238
3.216
3.119
3.115
3.093
3.089
3.061
3.058
3.050
3.047
3.024
3.021
3.013
3.010
2.937
2.934
2.915
2.426
2.405
1.765
1.741
1.733
1.709
1.661
0.000

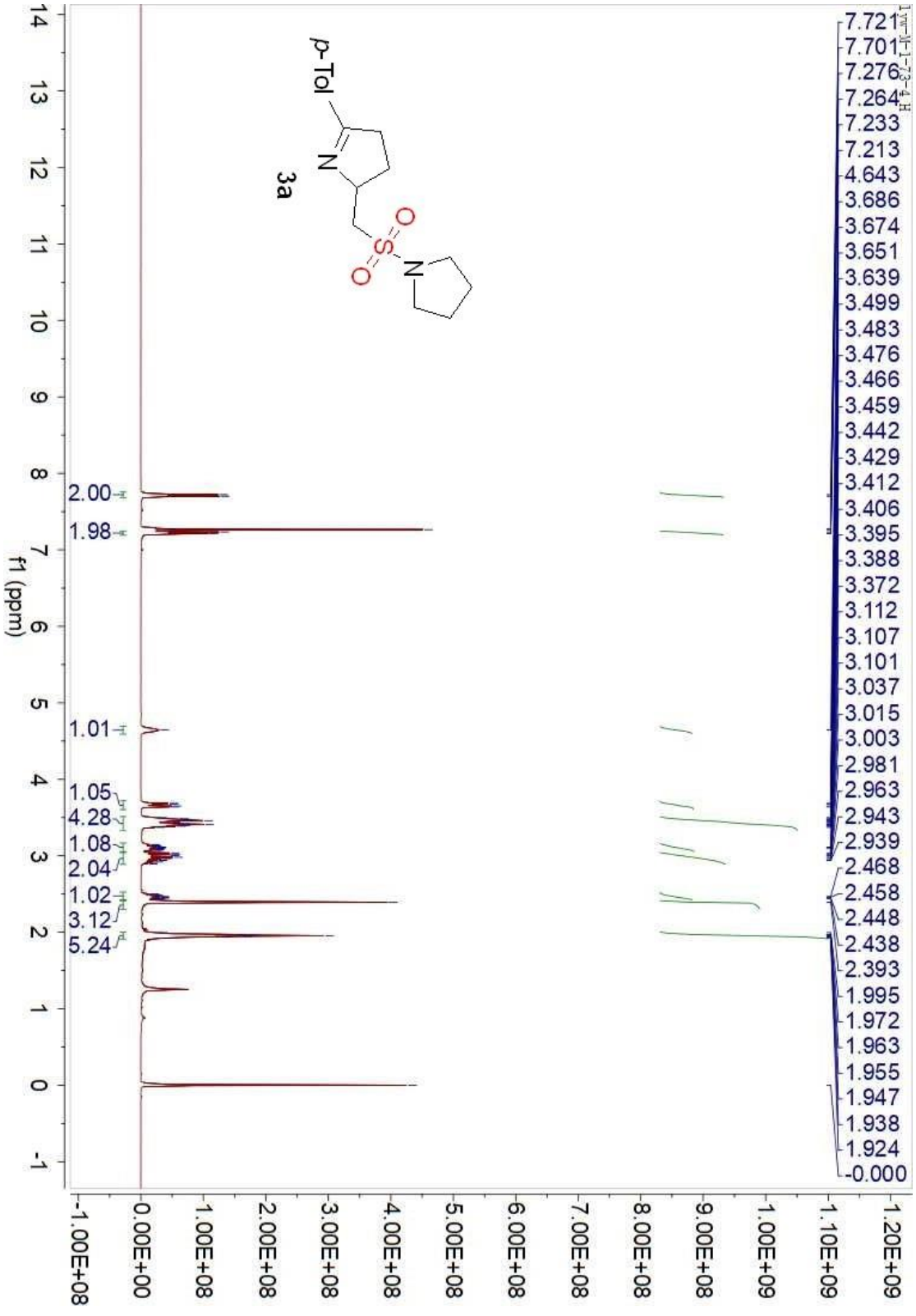

p-Tol
N
O
S
O
Br
2m
174.34
141.51
133.96
131.88
130.96
130.78
130.25
129.64
129.36
127.83
122.67
77.32
77.00
76.68
67.47
59.80
56.97
34.96
28.95
21.49
f1 (ppm)

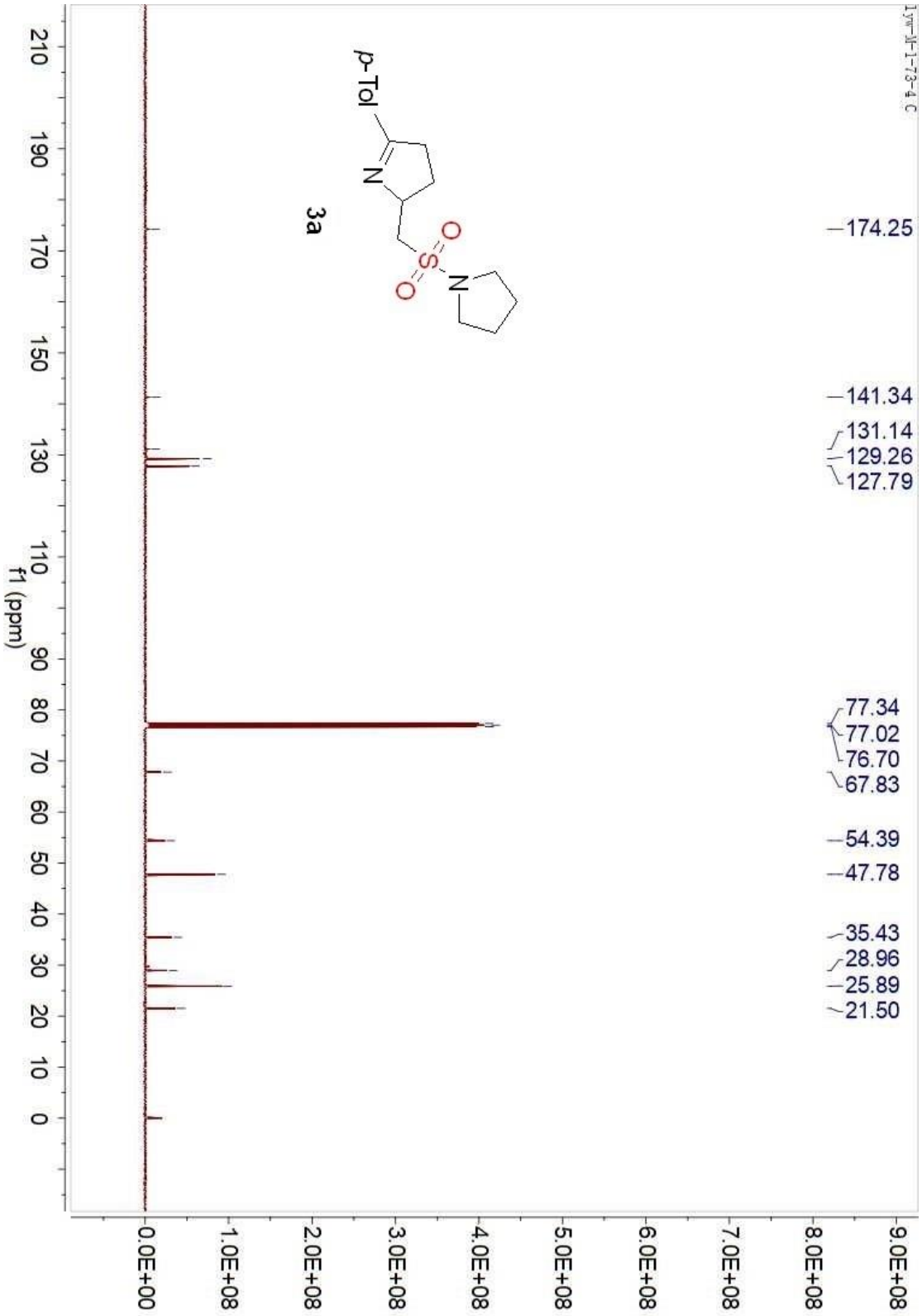

p-Tol
N
O
O
S
CF3
2n
f1 (ppm)
2.00
4.24
2.22
1.01
1.13
1.00
1.06
1.07
1.12
1.05
4.39
1.33
7.789
7.769
7.626
7.603
7.600
7.577
7.260
7.242
4.961
4.927
4.734
4.722
4.717
4.567
4.532
3.248
3.225
3.211
3.188
3.142
3.136
3.133
3.116
3.111
3.108
3.083
3.080
3.072
3.069
3.046
3.043
3.035
2.944
2.940
2.922
2.902
2.897
2.437
2.413
2.394
1.759
1.734
1.727
1.703
0.855
0.000

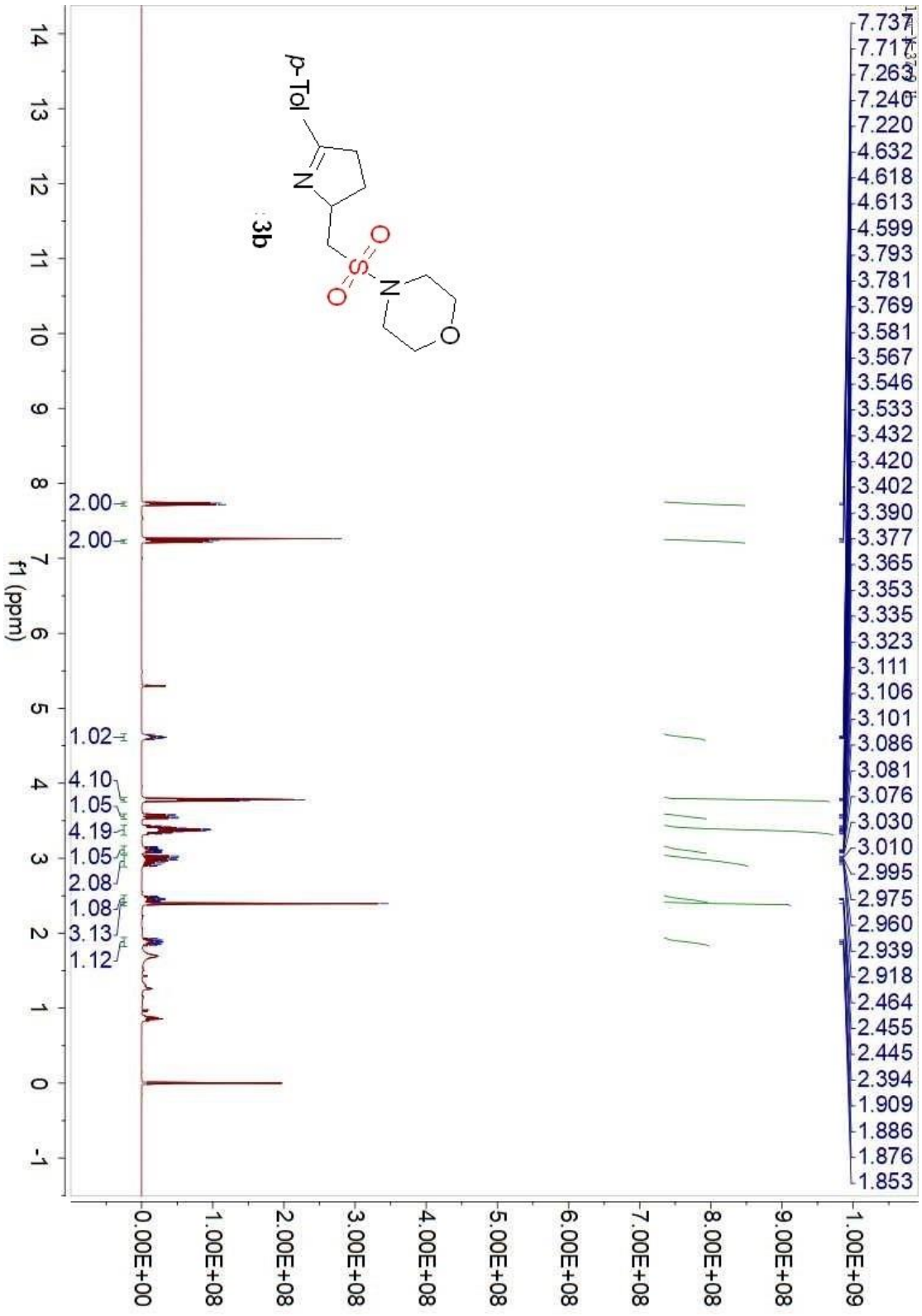

p-Tol
N
O
S
O
CF3
2n
174.44
141.70
132.72
132.71
131.49
131.13
130.92
129.46
127.85
125.81
125.77
125.73
125.70
125.27
122.56
119.86
77.35
77.03
76.71
67.53
60.04
57.07
34.96
28.94
21.53
f1 (ppm)

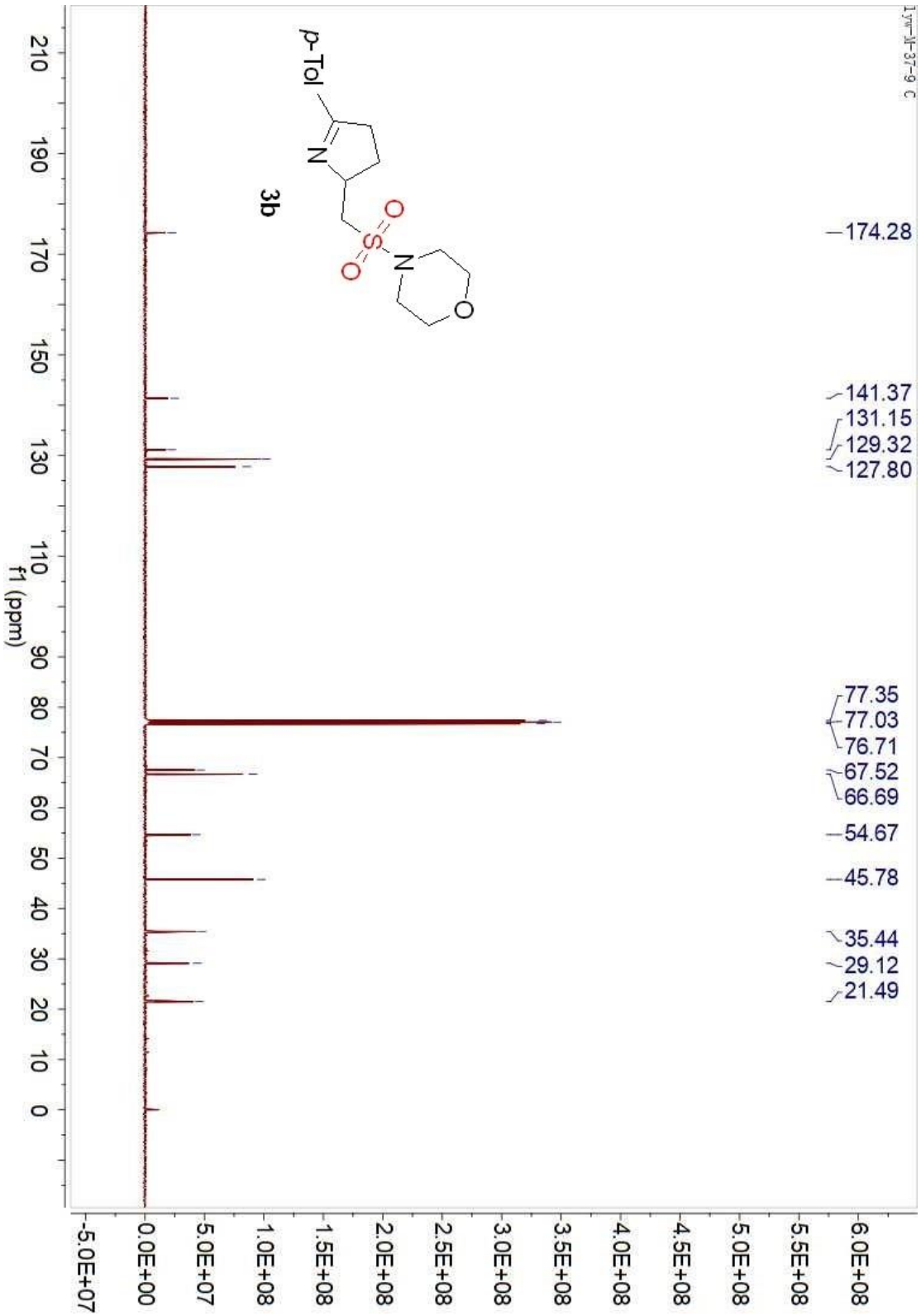

p-Tol
N
O
S
O
2o
f1 (ppm)
2.00
2.07
1.02
2.07
1.05
3.20
2.13
1.10
4.26
2.23
2.36
1.09
7.717
7.697
7.263
7.232
7.212
5.789
5.772
5.747
5.109
5.105
5.066
5.043
4.658
3.386
3.382
3.376
3.366
3.356
3.351
3.341
3.329
3.314
3.300
3.143
3.131
3.107
3.094
2.938
2.442
2.432
2.422
2.399
2.268
2.250
2.233
2.215
2.027
2.019
2.012
2.002
1.994
1.986
1.977
1.969
1.961
-0.000

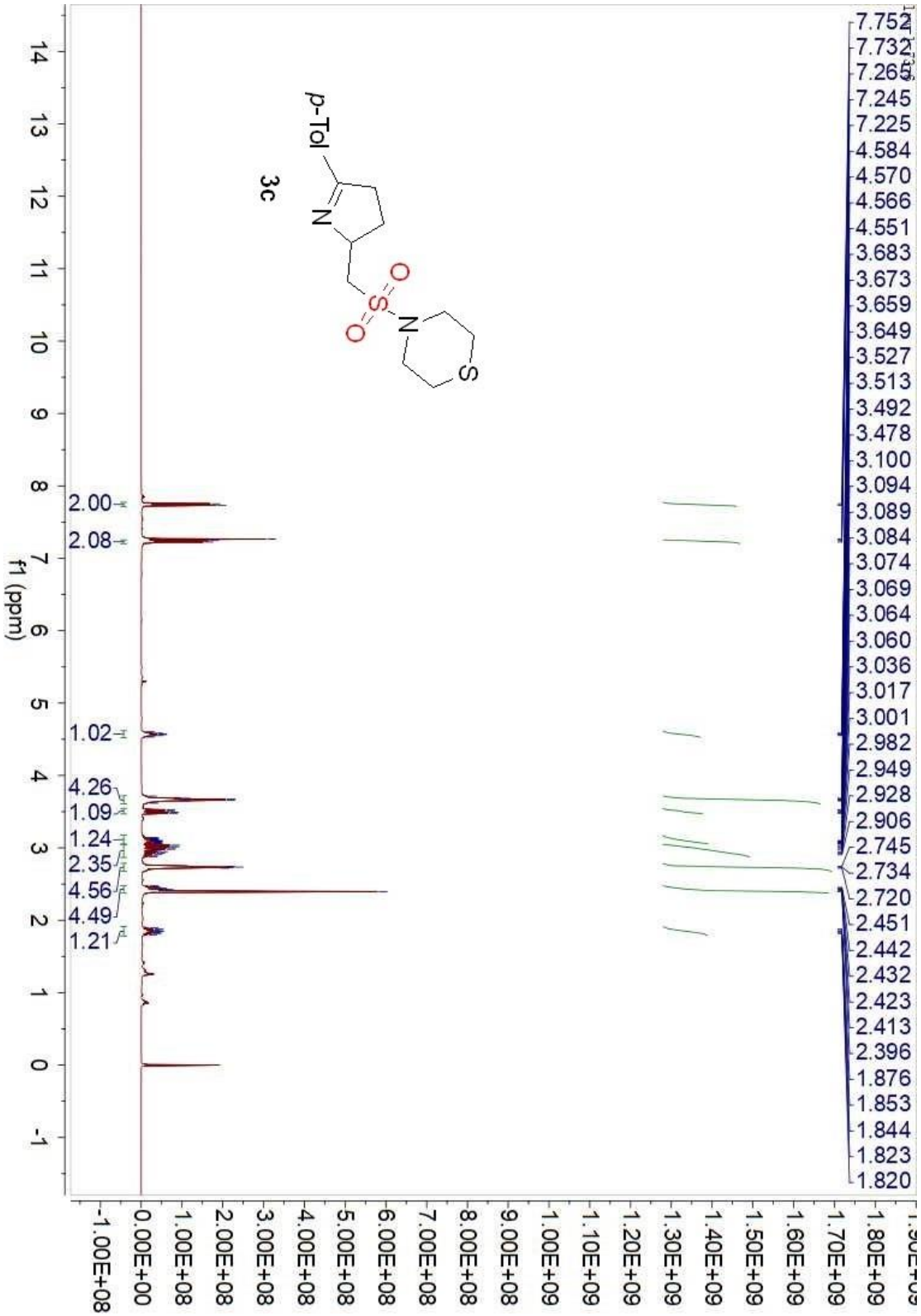

1;ywm-3H-37-4 CC
p-Tol
N
O
O
S
O
2o
174.14
141.43
136.60
131.04
129.24
127.81
116.39
77.34
77.02
76.71
67.32
58.60
53.85
34.99
32.44
29.05
21.51
21.28
f1 (ppm)

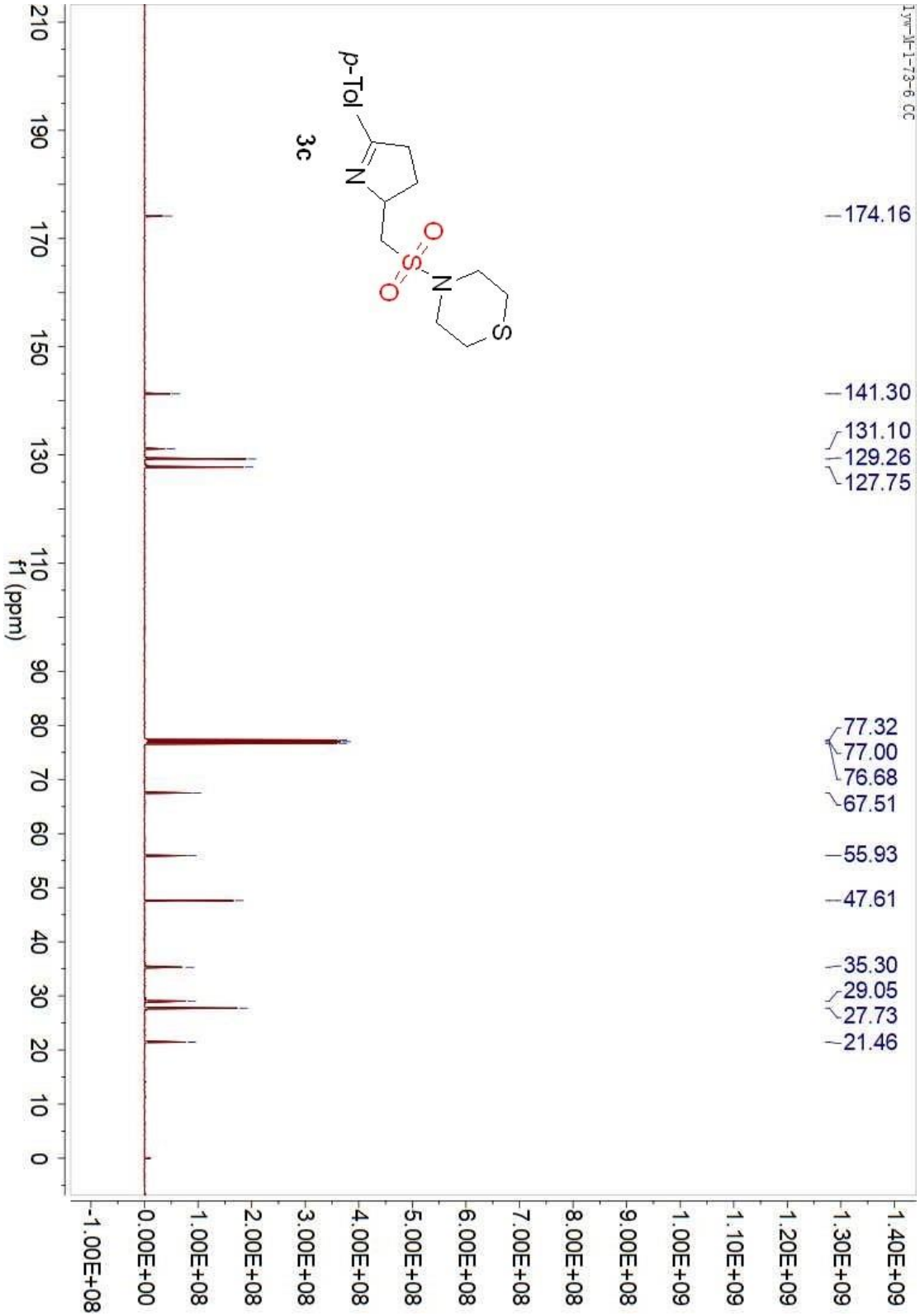

p-Tol
N
O
S
O
N
3a
2.00
1.98
1.01
1.05
4.28
1.08
2.04
1.02
3.12
5.24
f1 (ppm)
7.721
7.701
7.276
7.264
7.233
7.213
4.643
3.686
3.674
3.651
3.639
3.499
3.483
3.476
3.466
3.459
3.442
3.429
3.412
3.406
3.395
3.388
3.372
3.112
3.107
3.101
3.037
3.015
3.003
2.981
2.963
2.943
2.939
2.468
2.458
2.448
2.438
2.393
1.995
1.972
1.963
1.955
1.947
1.938
1.924
-0.000

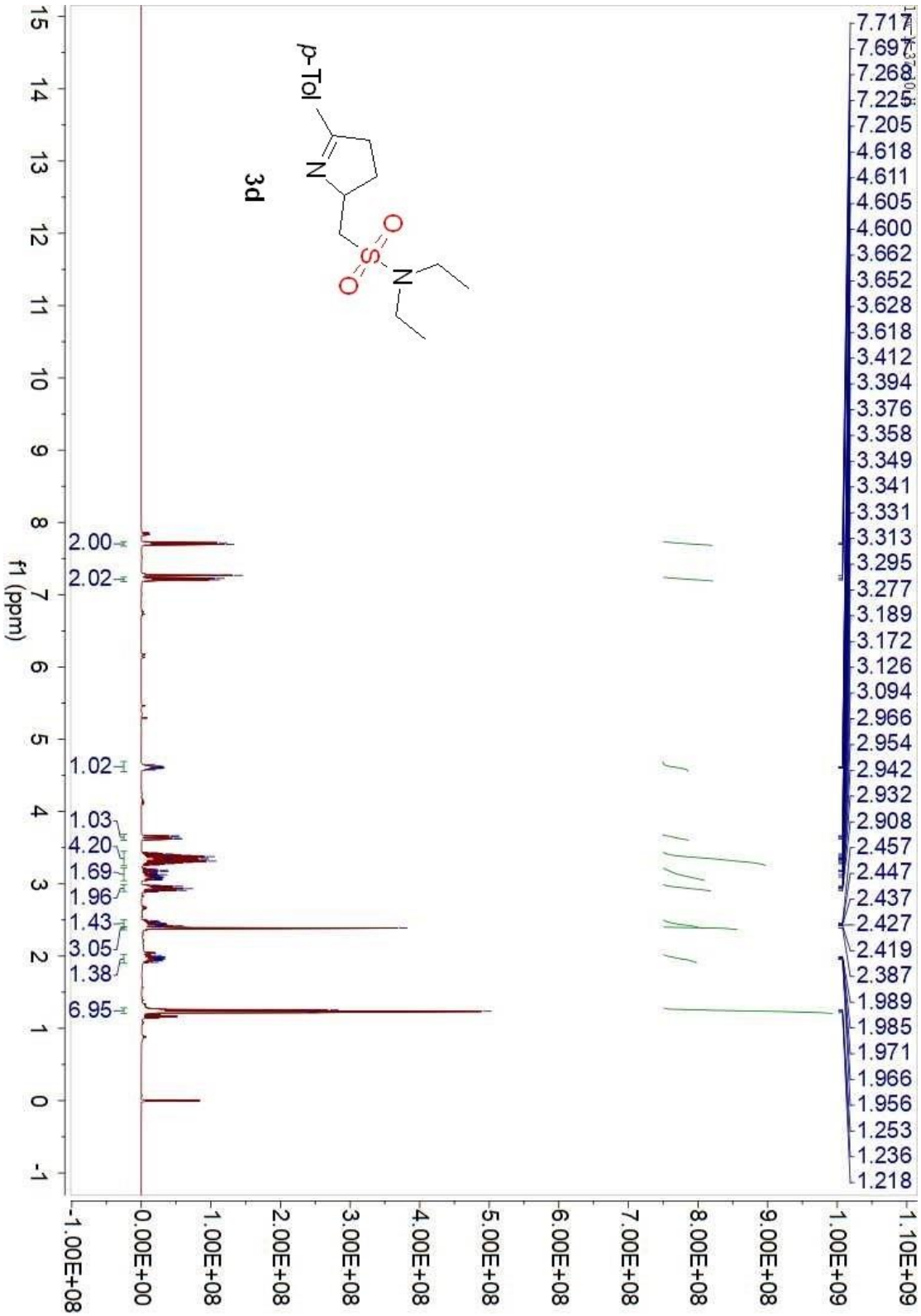

p-Tol
N
O
S
O
N
3a
174.25
141.34
131.14
129.26
127.79
77.34
77.02
76.70
67.83
54.39
47.78
35.43
28.96
25.89
21.50
f1 (ppm)

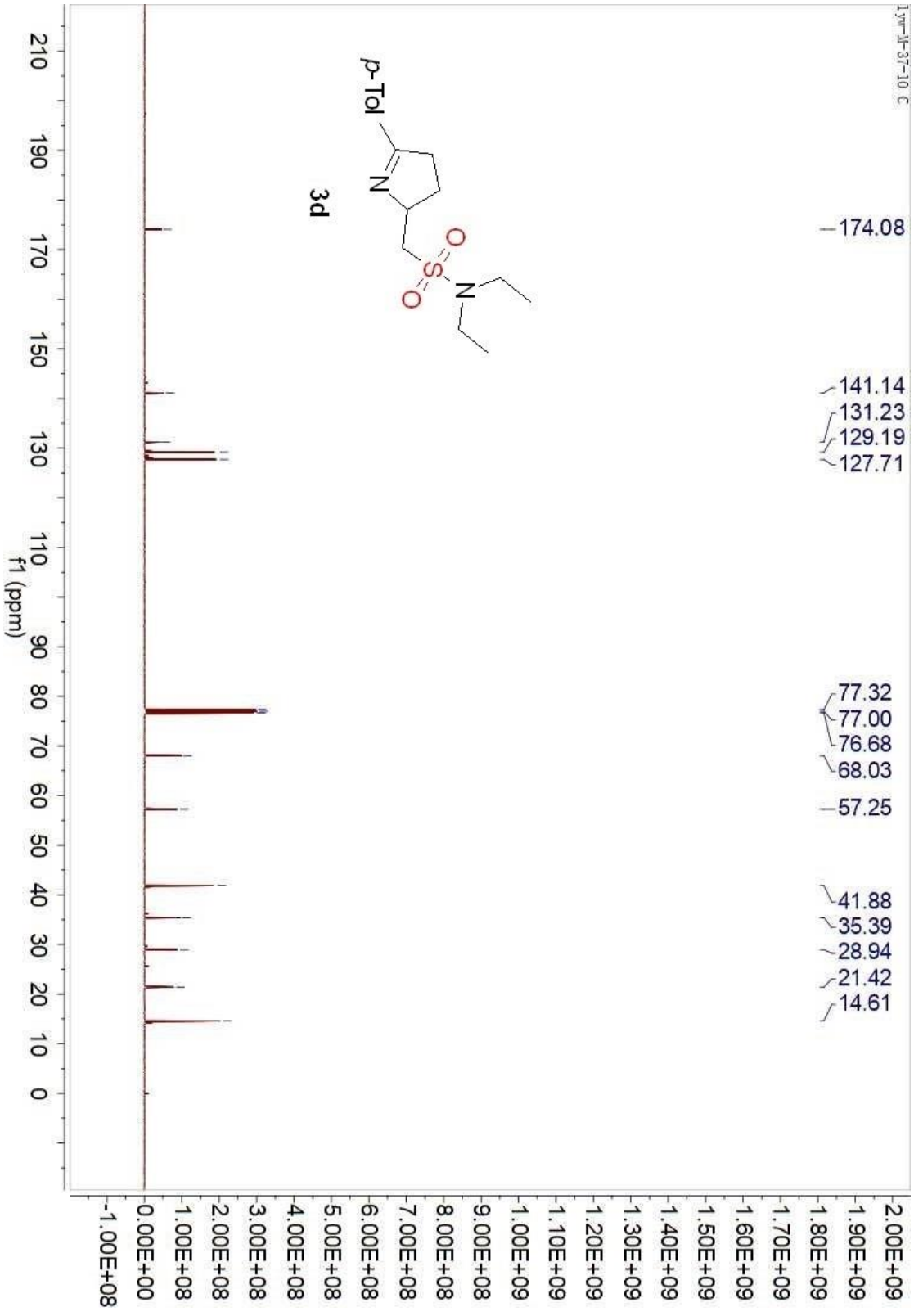

p-Tol
N
O
S
O
N
O
3b
f1 (ppm)
2.00
2.00
1.02
4.10
1.05
4.19
1.05
2.08
1.08
3.13
1.12
7.737
7.717
7.263
7.240
7.220
4.632
4.618
4.613
4.599
3.793
3.781
3.769
3.581
3.567
3.546
3.533
3.432
3.420
3.402
3.390
3.377
3.365
3.353
3.335
3.323
3.111
3.106
3.101
3.086
3.081
3.076
3.030
3.010
2.995
2.975
2.960
2.939
2.918
2.464
2.455
2.445
2.394
1.909
1.886
1.876
1.853
0.00E+00
1.00E+08
2.00E+08
3.00E+08
4.00E+08
5.00E+08
6.00E+08
7.00E+08
8.00E+08
9.00E+08
1.00E+09


p-Tol
N
O
S
O
N
O
3b
174.28
141.37
131.15
129.32
127.80
77.35
77.03
76.71
67.52
66.69
54.67
45.78
35.44
29.12
21.49
f1 (ppm)


p-Tol
N
O
S
O
N
S
3c
f1 (ppm)
2.00
2.08
1.02
4.26
1.09
1.24
2.35
4.56
4.49
1.21
7.752
7.732
7.265
7.245
7.225
4.584
4.570
4.566
4.551
3.683
3.673
3.659
3.649
3.527
3.513
3.492
3.478
3.100
3.094
3.089
3.084
3.074
3.069
3.064
3.060
3.036
3.017
3.001
2.982
2.949
2.928
2.906
2.745
2.734
2.720
2.451
2.442
2.432
2.423
2.413
2.396
1.876
1.853
1.844
1.823
1.820


p-Tol
3c
174.16
141.30
131.10
129.26
127.75
77.32
77.00
76.68
67.51
55.93
47.61
35.30
29.05
27.73
21.46
f1 (ppm)


p-Tol
N
O
S
O
N
3d
f1 (ppm)
2.00
2.02
1.02
1.03
4.20
1.69
1.96
1.43
3.05
1.38
6.95
7.717
7.697
7.268
7.225
7.205
4.618
4.611
4.605
4.600
3.662
3.652
3.628
3.618
3.412
3.394
3.376
3.358
3.349
3.341
3.331
3.313
3.295
3.277
3.189
3.172
3.126
3.094
2.966
2.954
2.942
2.932
2.908
2.457
2.447
2.437
2.427
2.419
2.387
1.989
1.985
1.971
1.966
1.956
1.253
1.236
1.218


1yw-M-37-10 C
p-Tol
N
O
S
O
N
3d
174.08
141.14
131.23
129.19
127.71
77.32
77.00
76.68
68.03
57.25
41.88
35.39
28.94
21.42
14.61
f1 (ppm)