Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Intramolecular oxysulfonylation of alkenes with the insertion of sulfur dioxide under photocatalysis

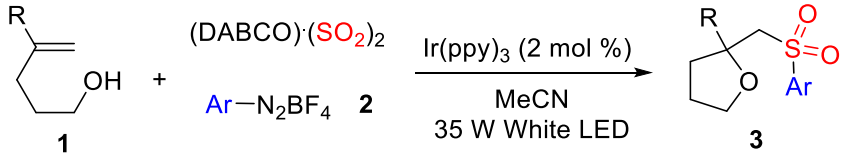
Fu-Sheng He,[a] Xufeng Cen,[a] Shuying Yang,[a] Jun Zhang,[b] Hongguang Xia,*[a] and Jie Wu*[b,c]

Supporting Information

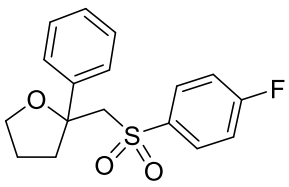
General experimental methods:

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 and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument.

*General experimental procedure for the reaction of alkenols **1**, (DABCO)·$(SO_2)_2$, and aryldiazonium tetrafluoroborates **2**.*

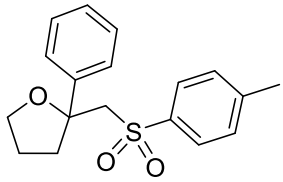


Alkenol **1** (0.2 mmol) was added to a mixture of aryldiazonium tetrafluoroborate **2** (0.3 mmol), DABCO·$(SO_2)_2$ (0.4 mmol) and $Ir(ppy)_3$ (2 mol %) in acetonitrile (2.5 mL) under N_2 atmosphere. The mixture was stirred under white LED irradiation (35 W) for 12 h. After completion of reaction as indicated by TLC, the solvent was evaporated and the residue was purified directly by flash column chromatography (*n*-hexane/ethyl acetate = 8:1) to give the corresponding product **3**.



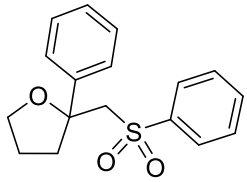
2-(((4-Fluorophenyl)sulfonyl)methyl)-2-phenyltetrahydrofuran (**3a**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.70 (m, 2H), 7.32-7.16 (m, 5H), 7.11-7.05 (m, 2H), 3.98-3.90 (m, 1H), 3.85 (td, *J* = 8.1, 5.7 Hz, 1H), 3.75-3.64 (m, 2H), 2.72 (dt, *J* = 12.5, 8.2 Hz, 1H), 2.29 (ddd, *J* = 12.6, 7.7, 5.0 Hz, 1H), 2.10-1.99 (m, 1H), 1.84-1.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4 (d, $^1J_{CF}$ = 255.4 Hz), 144.0, 137.2, 130.7 (d, $^3J_{CF}$ = 9.5 Hz), 128.3, 127.3, 125.1, 115.9 (d, $^2J_{CF}$ = 22.6 Hz), 83.8, 68.1, 65.5, 37.4, 25.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -104.5-104.6 (m, 1F); HRMS (ESI) calcd for $C_{17}H_{18}FO_3S^+$ ($M+H^+$): 321.0955, found: 321.0957.



2-Phenyl-2-(tosylmethyl)tetrahydrofuran (**3b**)

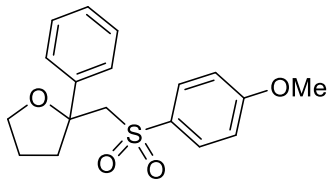
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.33-7.14 (m, 7H), 3.95 (dd, *J* = 15.0, 7.5 Hz, 1H), 3.84 (td, *J* = 8.0, 5.5 Hz, 1H), 3.69-3.59 (m, 2H), 2.80 (dt, *J* = 12.6, 8.2 Hz, 1H), 2.40 (s, 3H), 2.30 (ddd, *J* = 12.5, 7.7, 4.9 Hz, 1H), 2.10-1.99 (m, 1H), 1.83-1.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 144.0, 138.5, 129.4, 128.3, 127.8, 127.2, 125.2, 84.0, 68.1, 65.5, 36.9, 25.2, 21.6; HRMS (ESI) calcd for $C_{18}H_{21}O_3S^+$ ($M+H^+$): 317.1206, found: 317.1209.



2-Phenyl-2-((phenylsulfonyl)methyl)tetrahydrofuran (**3c**)

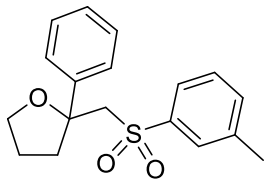
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-7.72 (m, 2H), 7.55 (td, *J* = 7.2, 1.1 Hz, 1H), 7.43 (td, *J* = 8.0, 1.4 Hz, 2H), 7.34-7.15 (m, 4H), 3.98-3.91 (m, 1H), 3.87-3.80 (m, 1H), 3.74 - 3.63 (m, 2H), 2.85-2.74 (m, 1H), 2.34-2.27 (m, 1H), 2.12-1.99 (m, 1H), 1.84-1.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 141.3, 133.1, 128.8, 128.3, 127.8, 127.3,

125.2, 83.9, 68.1, 65.4, 37.0, 25.2; HRMS (ESI) calcd for $C_{17}H_{19}O_3S^+$ ($M+H^+$): 303.1049, found: 303.1057.



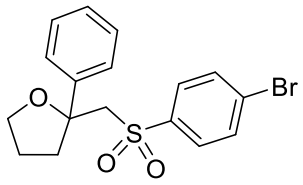
2-(((4-Methoxyphenyl)sulfonyl)methyl)-2-phenyltetrahydrofuran (**3d**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.8 Hz, 2H), 7.32-7.22 (m, 4H), 7.21-7.18 (m, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.00-3.93 (m, 1H), 3.89-3.80 (m, 4H), 3.70-3.60 (m, 2H), 2.78 (dt, *J* = 12.5, 8.2 Hz, 1H), 2.29 (ddd, *J* = 12.6, 7.7, 4.9 Hz, 1H), 2.11-1.99 (m, 1H), 1.83-1.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 144.5, 133.0, 130.0, 128.3, 127.2, 125.2, 114.0, 84.0, 68.1, 65.6, 55.6, 37.0, 25.2; HRMS (ESI) calcd for $C_{18}H_{21}O_4S^+$ ($M+H^+$): 333.1155, found: 333.1165.



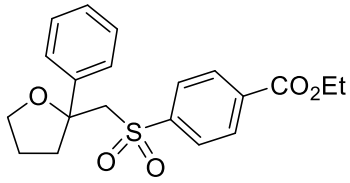
2-Phenyl-2-((*m*-tolylsulfonyl)methyl)tetrahydrofuran (**3e**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.52 (m, 1H), 7.49 (s, 1H), 7.37-7.13 (m, 7H), 3.98 (dd, *J* = 15.0, 7.5 Hz, 1H), 3.85 (td, *J* = 8.1, 5.5 Hz, 1H), 3.72-3.61 (m, 2H), 2.78 (dt, *J* = 12.6, 8.2 Hz, 1H), 2.35 (s, 3H), 2.34-2.26 (m, 1H), 2.12-2.00 (m, 1H), 1.84-1.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 141.1, 139.0, 133.9, 128.7, 128.2, 128.2, 127.3, 125.2, 124.9, 84.0, 68.1, 65.5, 37.0, 25.2, 21.2; HRMS (ESI) calcd for $C_{18}H_{21}O_3S^+$ ($M+H^+$): 317.1206, found: 317.1221.



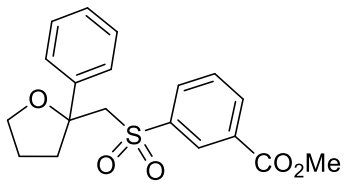
2-(((4-Bromophenyl)sulfonyl)methyl)-2-phenyltetrahydrofuran (**3f**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.51 (m, 4H), 7.30-7.17 (m, 5H), 3.94 (dd, *J* = 15.2, 7.4 Hz, 1H), 3.85 (td, *J* = 8.1, 5.5 Hz, 1H), 3.74-3.64 (m, 2H), 2.71 (dt, *J* = 12.5, 8.2 Hz, 1H), 2.28 (ddd, *J* = 12.6, 7.7, 4.9 Hz, 1H), 2.09-1.98 (m, 1H), 1.84-1.70 (m, 1H).^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 140.2, 132.0, 129.5, 128.3, 127.3, 125.1, 83.8, 68.2, 65.5, 37.5, 25.1; HRMS (ESI) calcd for $C_{17}H_{18}BrO_3S^+$ ($M+H^+$): 381.0155, found: 381.0154.



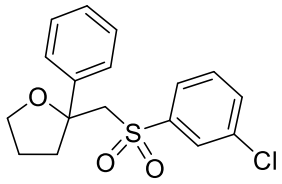
Ethyl 4-(((2-phenyltetrahydrofuran-2-yl)methyl)sulfonyl)benzoate (**3g**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.5 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.26-7.17 (m, 5H), 4.42 (q, *J* = 7.1 Hz, 2H), 3.90 (dd, *J* = 15.2, 7.4 Hz, 1H), 3.82 (td, *J* = 8.1, 5.5 Hz, 1H), 3.77-3.67 (m, 2H), 2.75 (dt, *J* = 12.5, 8.2 Hz, 1H), 2.30 (ddd, *J* = 12.5, 7.7, 4.8 Hz, 1H), 2.09-1.98 (m, 1H), 1.83-1.70 (m, 1H), 1.42 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 145.0, 144.1, 134.5, 129.8, 128.3, 127.9, 127.4, 125.1, 83.8, 68.2, 65.3, 61.7, 37.3, 25.1, 14.3; HRMS (ESI) calcd for $C_{20}H_{23}O_5S^+$ ($M+H^+$): 375.1261, found: 375.1267.



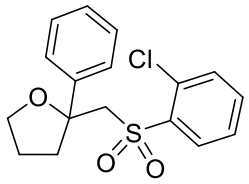
Methyl 3-(((2-phenyltetrahydrofuran-2-yl)methyl)sulfonyl)benzoate (**3h**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39-8.34 (m, 1H), 8.23-8.17 (m, 1H), 7.94-7.87 (m, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.28-7.12 (m, 5H), 4.01-3.88 (m, 4H), 3.83 (td, *J* = 8.1, 5.6 Hz, 1H), 3.78-3.68 (m, 2H), 2.74 (dt, *J* = 12.5, 8.2 Hz, 1H), 2.30 (ddd, *J* = 12.6, 7.7, 4.9 Hz, 1H), 2.11-2.00 (m, 1H), 1.83-1.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 143.9, 141.8, 133.9, 131.9, 131.0, 129.2, 129.0, 128.3, 127.3, 125.1, 83.8, 68.2, 65.4, 52.5, 37.4, 25.1; HRMS (ESI) calcd for $C_{19}H_{21}O_5S^+$ ($M+H^+$): 361.1104, found: 361.1118.



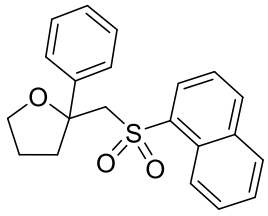
2-(((3-Chlorophenyl)sulfonyl)methyl)-2-phenyltetrahydrofuran (**3i**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.60 (m, 2H), 7.51-7.47 (m, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.28-7.17 (m, 5H), 3.96 (dd, *J* = 15.1, 7.4 Hz, 1H), 3.86 (td, *J* = 8.1, 5.6 Hz, 1H), 3.76-3.65 (m, 2H), 2.70 (dt, *J* = 12.4, 8.2 Hz, 1H), 2.31 (ddd, *J* = 12.6, 7.7, 5.0 Hz, 1H), 2.11-1.99 (m, 1H), 1.85-1.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 142.8, 134.9, 133.2, 130.1, 128.3, 128.1, 127.5, 126.0, 125.2, 83.8, 68.2, 65.6, 37.5, 25.1; HRMS (ESI) calcd for $C_{17}H_{18}ClO_3S^+$ ($M+H^+$): 337.0660, found: 337.0665.



2-(((2-Chlorophenyl)sulfonyl)methyl)-2-phenyltetrahydrofuran (**3j**)

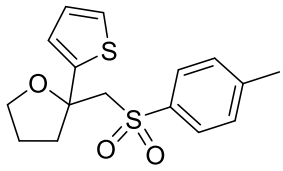
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.84 (m, 1H), 7.47-7.39 (m, 2H), 7.33-7.24 (m, 3H), 7.20 (t, *J* = 7.4 Hz, 2H), 7.16-7.11 (m, 1H), 4.08 (d, *J* = 14.9 Hz, 1H), 3.93 (d, *J* = 14.9 Hz, 1H), 3.86-3.74 (m, 2H), 2.70 (dt, *J* = 12.5, 8.1 Hz, 1H), 2.31 (ddd, *J* = 12.7, 7.7, 5.2 Hz, 1H), 2.08-1.95 (m, 1H), 1.82-1.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143. 7, 138.4, 134.1, 132.3, 131.4, 131.2, 128.2, 127.4, 127.0, 125.2, 83.7, 68.1, 63.3, 37.4, 25.1; HRMS (ESI) calcd for $C_{17}H_{18}ClO_3S^+$ ($M+H^+$): 337.0660, found: 337.0669.



2-((Naphthalen-1-ylsulfonyl)methyl)-2-phenyltetrahydrofuran (**3k**)

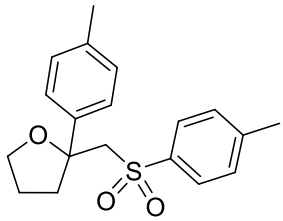
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, *J* = 8.6 Hz, 1H), 8.08 (d, *J* = 7.4 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H),

7.45 (t, *J* = 7.8 Hz, 1H), 7.24-7.18 (m, 2H), 7.17-7.07 (m, 3H), 4.00-3.78 (m, 4H), 2.78 (dt, *J* = 12.5, 8.1 Hz, 1H), 2.34 (ddd, *J* = 12.6, 7.7, 5.1 Hz, 1H), 2.12-2.01 (m, 1H), 1.85 - 1.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 136.0, 134.7, 134.0, 130.2, 129.2, 128.6, 128.5, 128.0, 127.2, 126.7, 125.2, 124.3, 124.0, 84.1, 68.1, 65.0, 37.3, 25.2; HRMS (ESI) calcd for $C_{21}H_{21}O_3S^+$ ($M+H^+$): 353.1206, found: 353.1218.



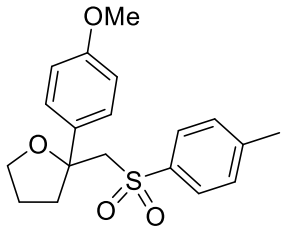
2-(Thiophen-2-yl)-2-(tosylmethyl)tetrahydrofuran (**3l**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.28-7.21 (m, 2H), 7.13 (dd, *J* = 4.7, 1.4 Hz, 1H), 6.87-6.83 (m, 2H), 3.95-3.84 (m, 2H), 3.77-3.68 (m, 2H), 2.81 (dt, *J* = 12.7, 8.6 Hz, 1H), 2.47-2.42 (m, 1H), 2.41 (s, 3H), 2.14-2.03 (m, 1H), 2.00-1.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 144.1, 138.2, 129.5, 127.8, 126.9, 124.9, 123.7, 82.4, 68.2, 65.7, 37.4, 25.6, 21.6; HRMS (ESI) calcd for $C_{16}H_{19}O_3S_2^+$ ($M+H^+$): 323.0770, found: 323.0787.



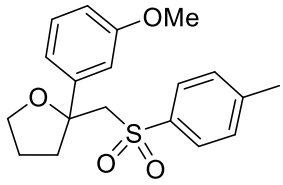
2-(*p*-Tolyl)-2-(tosylmethyl)tetrahydrofuran (**3m**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.27-7.15 (m, 4H), 7.04 (d, *J* = 7.2 Hz, 2H), 3.97-3.90 (m, 1H), 3.85-3.79 (m, 1H), 3.69-3.59 (m, 2H), 2.82-2.69 (m, 1H), 2.40 (s, 3H), 2.38-2.20 (m, 4H), 2.10-1.98 (m, 1H), 1.83-1.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 141.4, 138.5, 136.9, 129.4, 128.9, 127.8, 125.2, 83.9, 68.0, 65.6, 36.8, 25.2, 21.6, 21.0; HRMS (ESI) calcd for $C_{19}H_{23}O_3S^+$ ($M+H^+$): 331.1362, found: 331.1360.



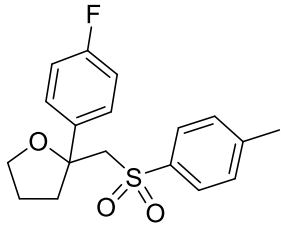
2-(4-Methoxyphenyl)-2-(tosylmethyl)tetrahydrofuran (**3n**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 4H), 6.75 (d, *J* = 8.7 Hz, 2H), 3.96-3.89 (m, 1H), 3.81 (td, *J* = 8.1, 5.5 Hz, 1H), 3.77 (s, 3H), 3.67-3.58 (m, 2H), 2.73 (dt, *J* = 12.5, 8.3 Hz, 1H), 2.40 (s, 3H), 2.30 (ddd, *J* = 12.5, 7.7, 4.8 Hz, 1H), 2.09-1.99 (m, 1H), 1.83-1.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 143.9, 138.4, 136.2, 129.4, 127.8, 126.5, 113.5, 83.7, 67.9, 65.7, 55.2, 36.8, 25.2, 21.5; HRMS (ESI) calcd for $C_{19}H_{23}O_4S^+$ ($M+H^+$): 347.1312, found: 347.1316.



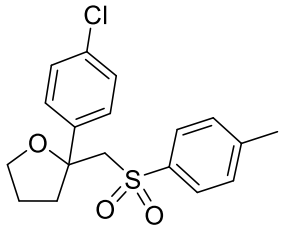
2-(3-Methoxyphenyl)-2-(tosylmethyl)tetrahydrofuran (**3o**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.16 (t, *J* = 7.9 Hz, 1H), 6.84 (t, *J* = 4.9 Hz, 2H), 6.72 (dd, *J* = 8.0, 1.9 Hz, 1H), 4.00-3.92 (m, 1H), 3.85 (td, *J* = 8.0, 5.6 Hz, 1H), 3.75 (s, 3H), 3.69-3.59 (m, 2H), 2.79 (dt, *J* = 12.5, 8.2 Hz, 1H), 2.40 (s, 3H), 2.28 (ddd, *J* = 12.5, 7.7, 4.9 Hz, 1H), 2.11-2.00 (m, 1H), 1.83- 1.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 146.3, 144.0, 138.4, 129.4, 129.3, 127.9, 117.5, 112.5, 111.1, 83.9, 68.2, 65.3, 55.2, 37.0, 25.2, 21.6; HRMS (ESI) calcd for $C_{19}H_{23}O_4S^+$ ($M+H^+$): 347.1312, found: 347.1326.



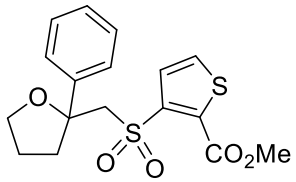
2-(4-Fluorophenyl)-2-(tosylmethyl)tetrahydrofuran (**3p**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.30-7.17 (m, 4H), 6.94-6.87 (m, 2H), 3.94 (dd, *J* = 14.9, 7.6 Hz, 1H), 3.83 (td, *J* = 8.1, 5.6 Hz, 1H), 3.67-3.56 (m, 2H), 2.72 (dt, *J* = 12.6, 8.2 Hz, 1H), 2.41 (s, 3H), 2.28 (ddd, *J* = 12.6, 7.7, 5.0 Hz, 1H), 2.11-1.98 (m, 1H), 1.83-1.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0 (d, $^1J_{CF}$ = 245.9 Hz), 144.1, 139.9, 138.3, 129.5, 127.8, 127.1 (d, $^3J_{CF}$ = 8.1 Hz), 115.0 (d, $^2J_{CF}$ = 21.4 Hz); 83.6, 68.0, 65.6, 37.2, 25.2, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.6 (s, 1F); HRMS (ESI) calcd for $C_{18}H_{20}FO_3S^+$ ($M+H^+$): 335.1112, found: 335.1128.



2-(4-Chlorophenyl)-2-(tosylmethyl)tetrahydrofuran (**3q**)

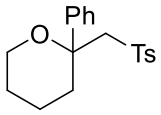
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.28-7.14 (m, 6H), 3.98-3.91 (m, 1H), 3.87-3.79 (m, 1H), 3.69-3.58 (m, 2H), 2.68 (dt, *J* = 12.6, 8.1 Hz, 1H), 2.41 (s, 3H), 2.26 (ddd, *J* = 12.6, 7.6, 5.2 Hz, 1H), 2.10-1.99 (m, 1H), 1.83-1.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 142.5, 138.1, 133.2, 129.4, 128.3, 127.8, 126.8, 83.5, 68.1, 65.4, 37.3, 25.1, 21.6; HRMS (ESI) calcd for $C_{18}H_{20}ClO_3S^+$ ($M+H^+$): 351.0816, found: 351.0818.



Methyl 3-(((2-phenyltetrahydrofuran-2-yl)methyl)sulfonyl)thiophene-2-carboxylate (**3r**)

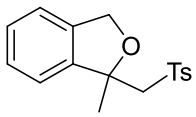
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.30 (m, 2H), 7.29-7.24 (m, 2H), 7.22-7.11 (m, 3H), 4.39 (d, *J* = 14.9 Hz, 1H), 4.13 (d, *J* = 14.9 Hz, 1H), 3.96-3.81 (m, 5H), 2.68 (dt, *J* = 12.5, 8.0 Hz, 1H), 2.29 (ddd, *J* = 12.8, 7.7, 5.3 Hz, 1H), 2.09-1.97 (m, 1H), 1.83-1.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 145.1, 143.7, 133.3, 131.4, 129.0, 128.0, 127.2,

125.2, 83.7, 68.2, 63.9, 52.9, 37.9, 25.0; HRMS (ESI) calcd for $C_{17}H_{19}O_5S_2^+$ ($M+H^+$): 367.0676, found: 367.0673.



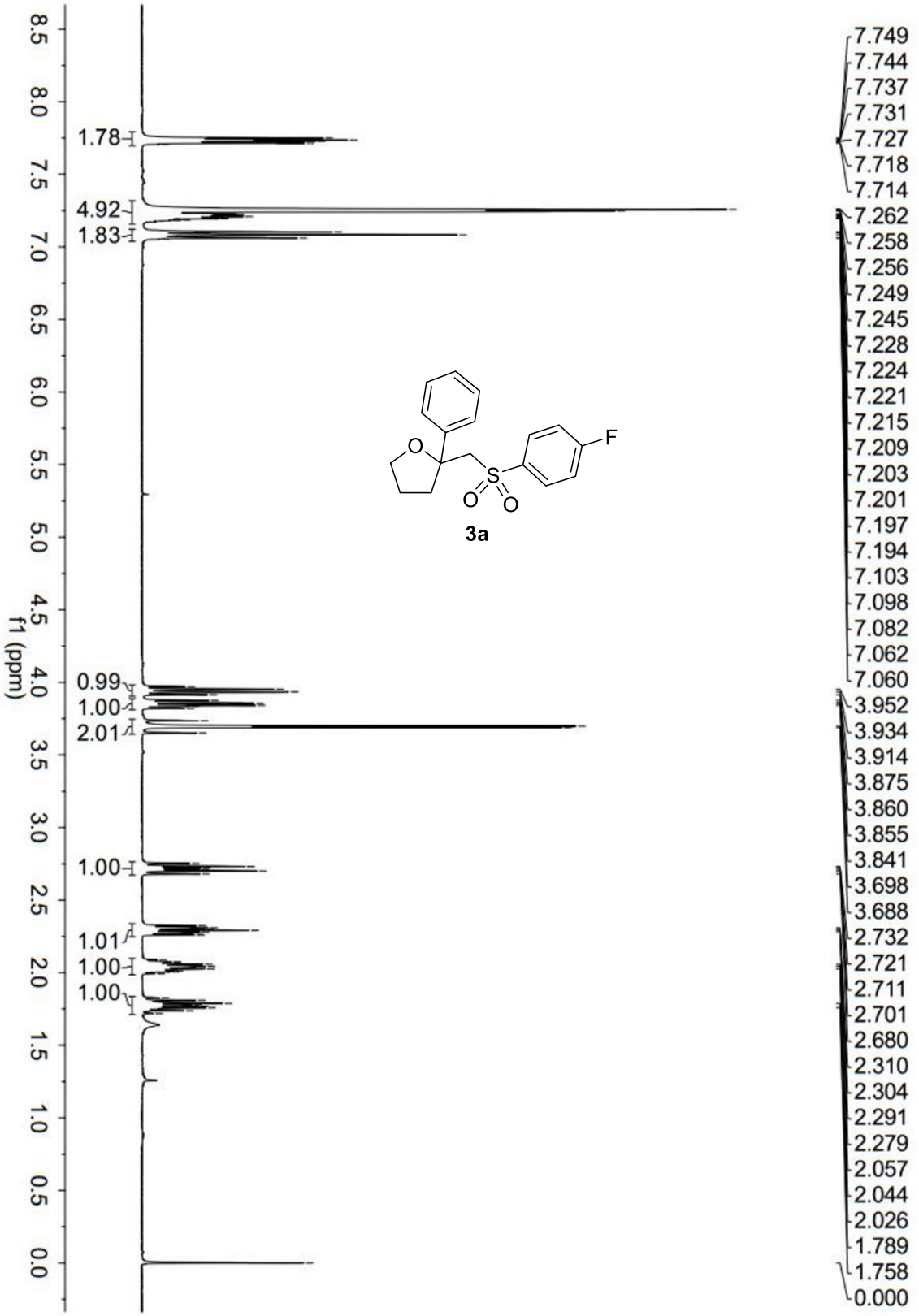
2-Phenyl-2-(tosylmethyl)tetrahydro-2*H*-pyran (**5**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.34-7.25 (m, 4H), 7.24-7.15 (m, 3H), 3.63-3.56 (m, 1H), 3.55-3.41 (m, 2H), 3.36 (td, *J* = 11.6, 2.7 Hz, 1H), 2.58 (dt, *J* = 14.0, 3.4 Hz, 1H), 2.48-2.40 (m, 1H), 2.39 (s, 3H), 1.76-1.59 (m, 2H), 1.54-1.41 (m, 1H), 1.40-1.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 140.6, 138.6, 129.3, 128.6, 127.9, 127.5, 127.0, 76.7, 68.3, 62.6, 31.2, 25.4, 21.5, 19.5; HRMS (ESI) calcd for $C_{19}H_{23}O_3S^+$ ($M+H^+$): 331.1362, found: 331.1372.



1-Methyl-1-(tosylmethyl)-1,3-dihydroisobenzofuran (**7**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.30-7.19 (m, 4H), 7.14 (dd, *J* = 14.3, 7.4 Hz, 2H), 4.97 (d, *J* = 12.4 Hz, 1H), 4.80 (d, *J* = 12.4 Hz, 1H), 3.62 (d, *J* = 14.7 Hz, 1H), 3.56 (d, *J* = 14.7 Hz, 1H), 2.42 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 143.0, 138.5, 138.2, 129.5, 128.2, 128.0, 127.6, 121.4, 121.1, 85.4, 71.8, 65.0, 27.5, 21.6; HRMS (ESI) calcd for $C_{17}H_{19}O_3S^+$ ($M+H^+$): 303.1049, found: 303.1058.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6.0
5.5
5.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
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4.92
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0.99
1.00
2.01
1.00
1.01
1.00
1.00
O
S
O
O
F
3a
7.749
7.744
7.737
7.731
7.727
7.718
7.714
7.262
7.258
7.256
7.249
7.245
7.228
7.224
7.221
7.215
7.209
7.203
7.201
7.197
7.194
7.103
7.098
7.082
7.062
7.060
3.952
3.934
3.914
3.875
3.860
3.855
3.841
3.698
3.688
2.732
2.721
2.711
2.701
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2.304
2.291
2.279
2.057
2.044
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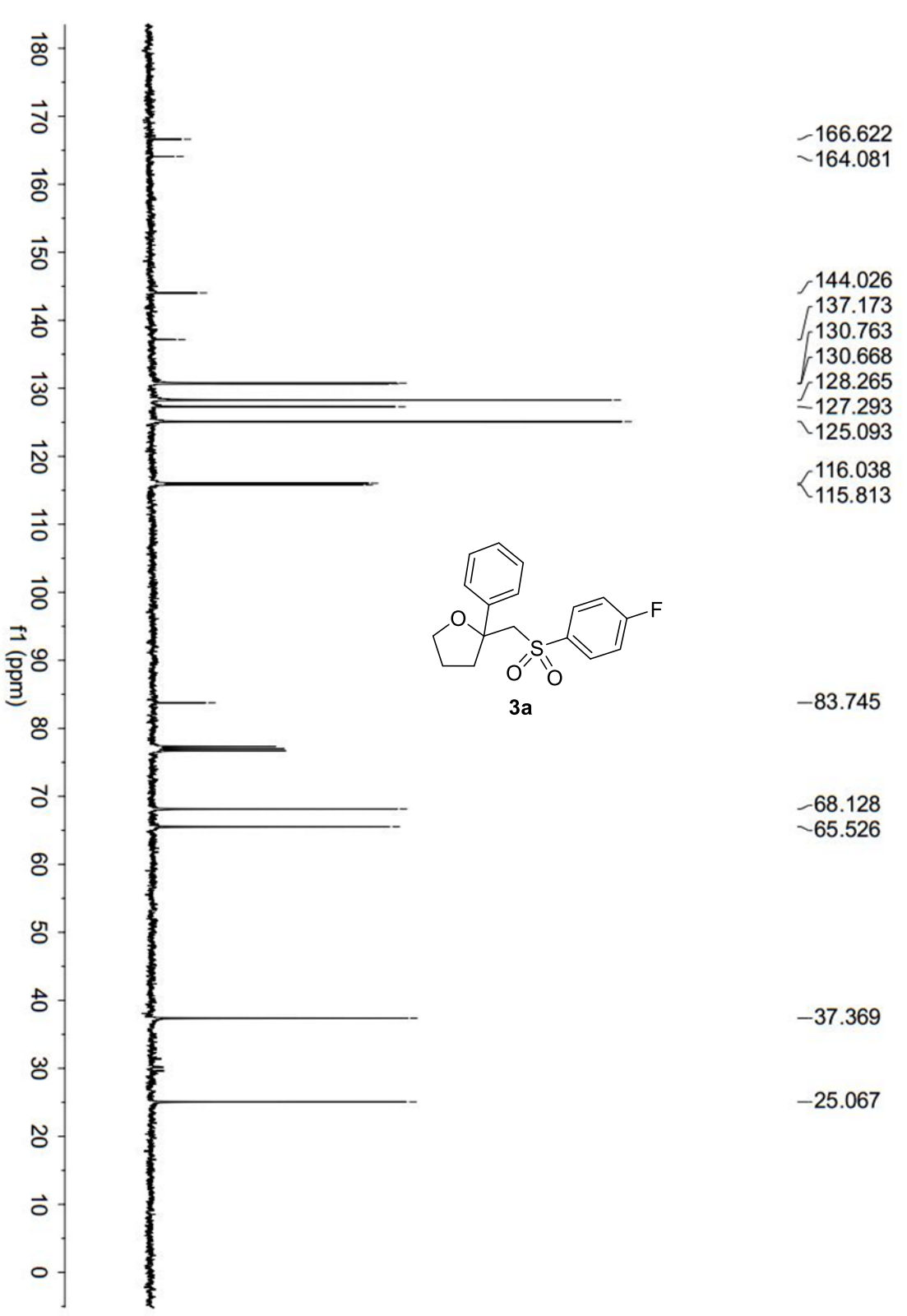
1.758
0.000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164.081
144.026
137.173
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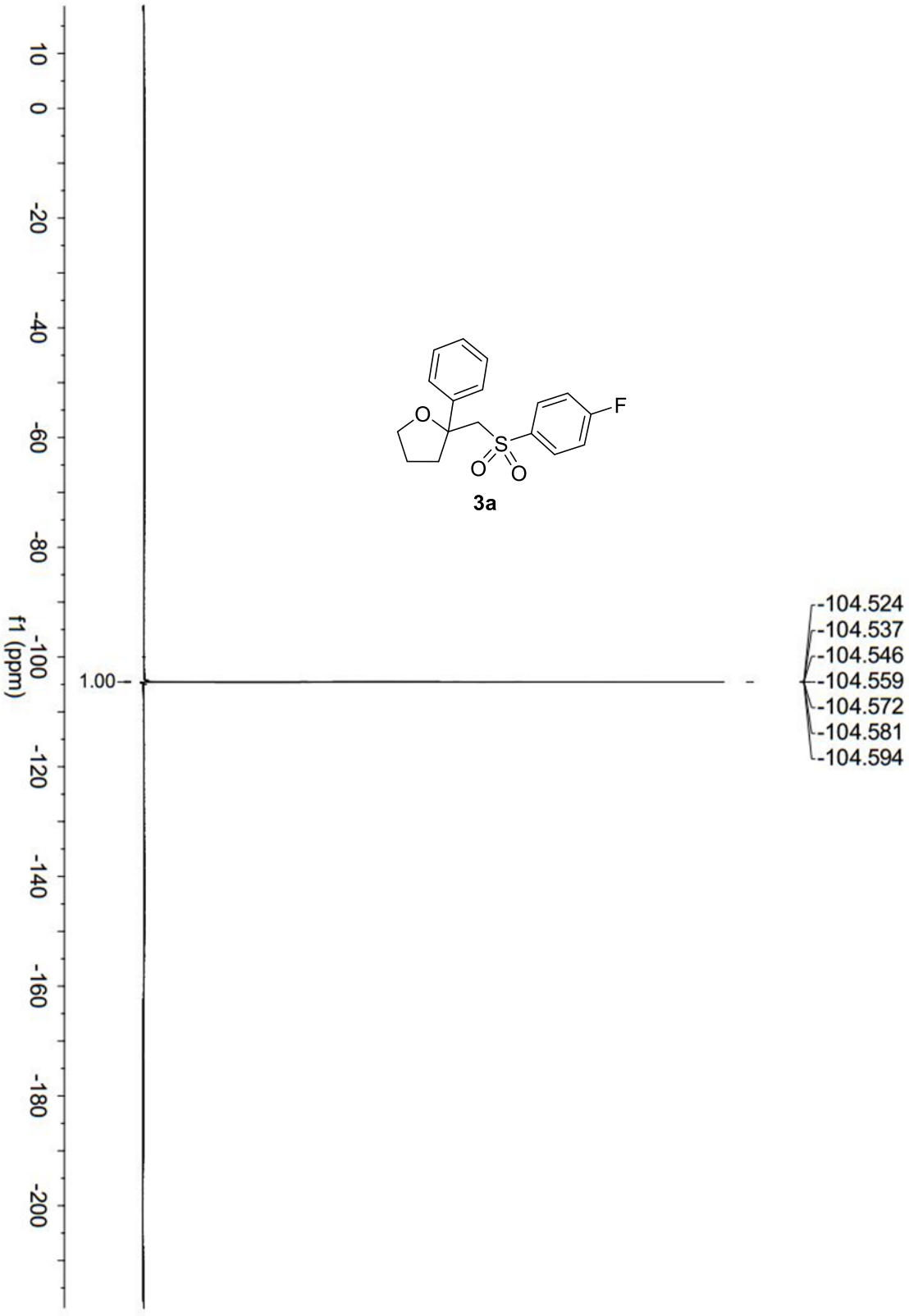
128.265
127.293
125.093
116.038
115.813
83.745
68.128
65.526
37.369
25.067
f1 (ppm)
O
S
O
O
F
3a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-40
-60
-80
-100
-120
-140
-160
-180
-200
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S
O
O
F
3a
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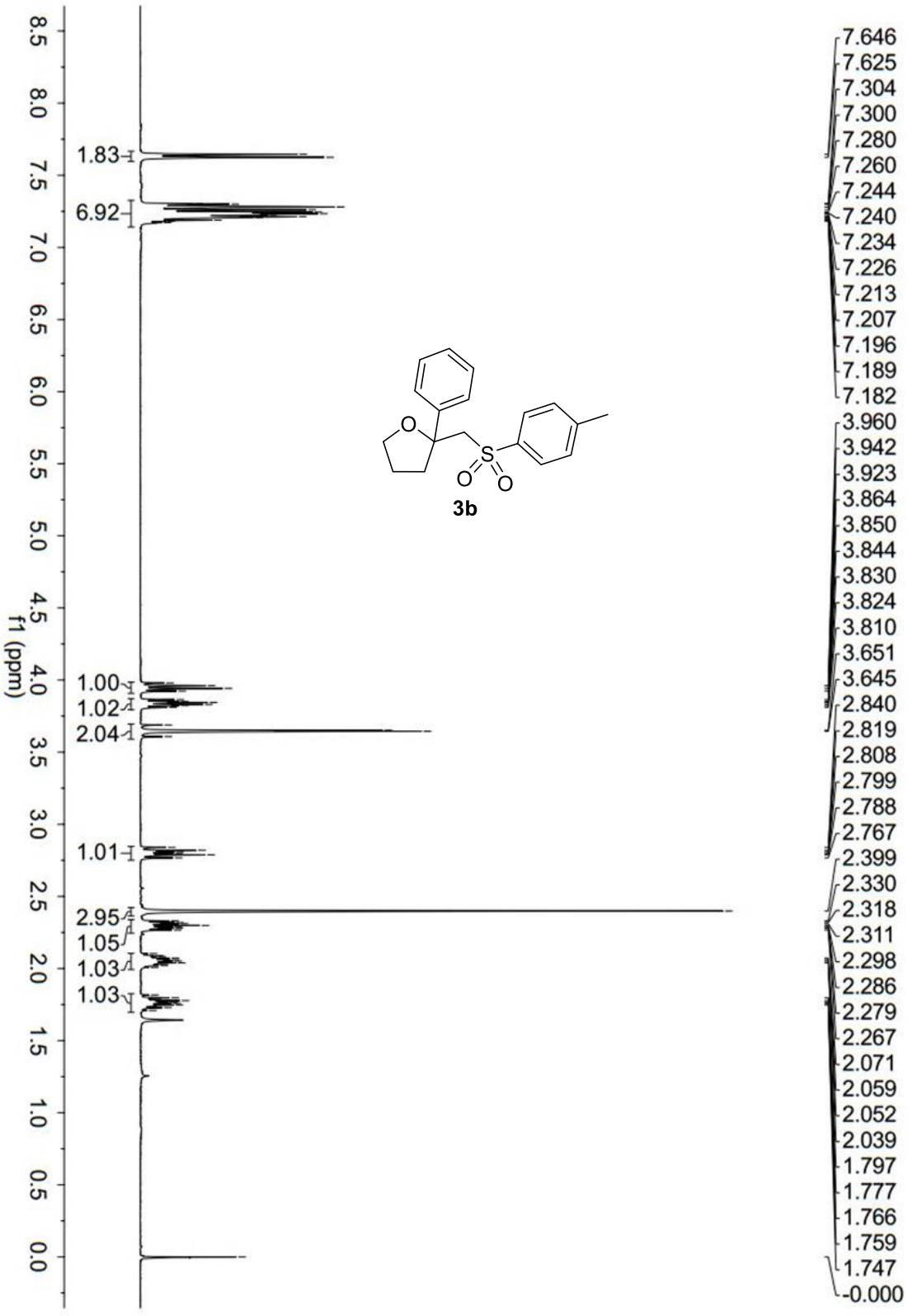
-104.559
-104.572
-104.581
-104.594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4.5
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3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.83
6.92
1.00
1.02
2.04
1.01
2.95
1.05
1.03
1.03
O
S
O
O
3b
7.646
7.625
7.304
7.300
7.280
7.260
7.244
7.240
7.234
7.226
7.213
7.207
7.196
7.189
7.182
3.960
3.942
3.923
3.864
3.850
3.844
3.830
3.824
3.810
3.651
3.645
2.840
2.819
2.808
2.799
2.788
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2.318
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2.286
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1.747
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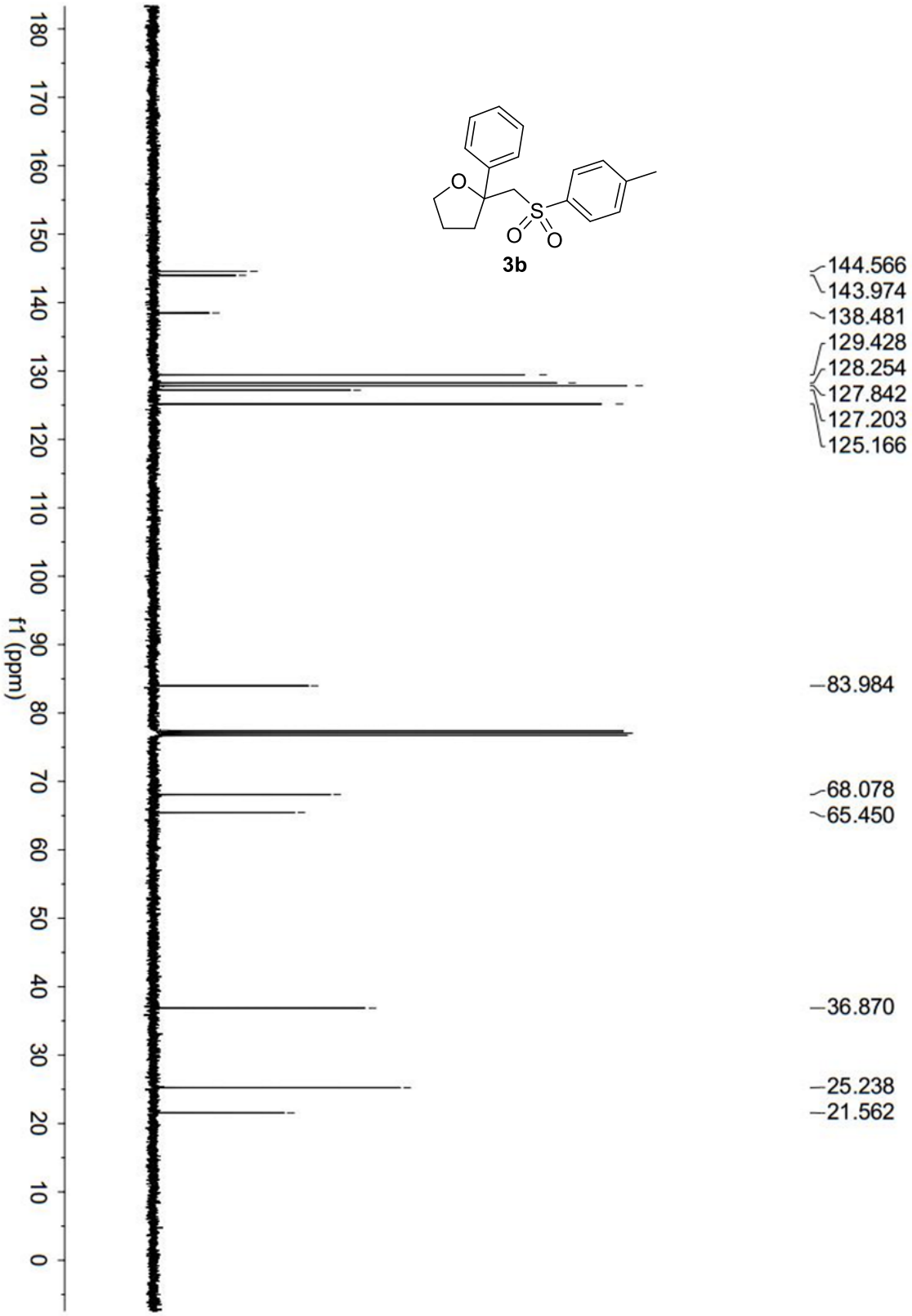
3b
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127.203
125.166
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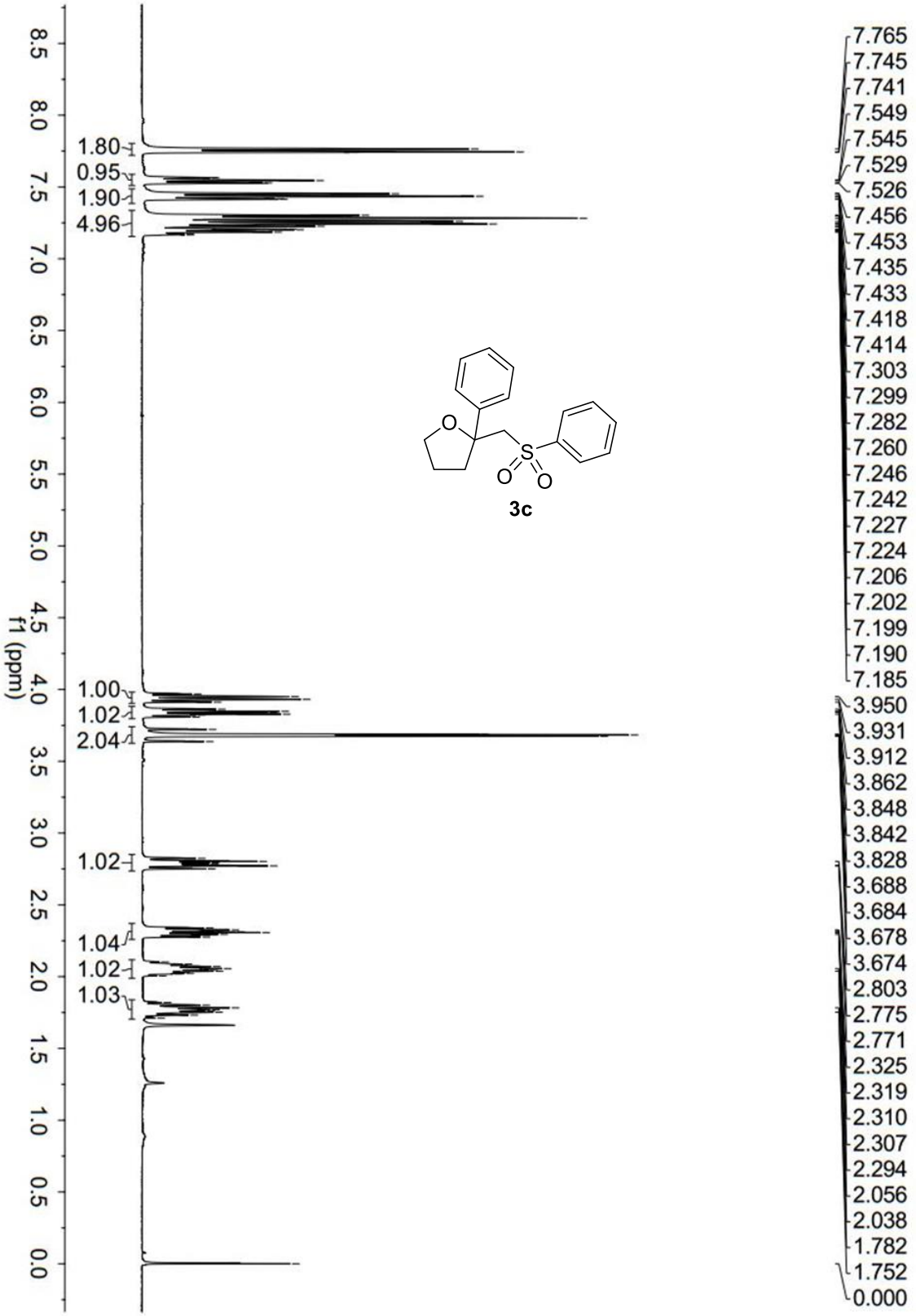
25.238
21.562
f1 (ppm)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5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
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0.95
1.90
4.96
1.00
1.02
2.04
1.02
1.04
1.02
1.03
O
S
O
O
3c
7.765
7.745
7.741
7.549
7.545
7.529
7.526
7.456
7.453
7.435
7.433
7.418
7.414
7.303
7.299
7.282
7.260
7.246
7.242
7.227
7.224
7.206
7.202
7.199
7.190
7.185
3.950
3.931
3.912
3.862
3.848
3.842
3.828
3.688
3.684
3.678
3.674
2.803
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2.319
2.310
2.307
2.294
2.056
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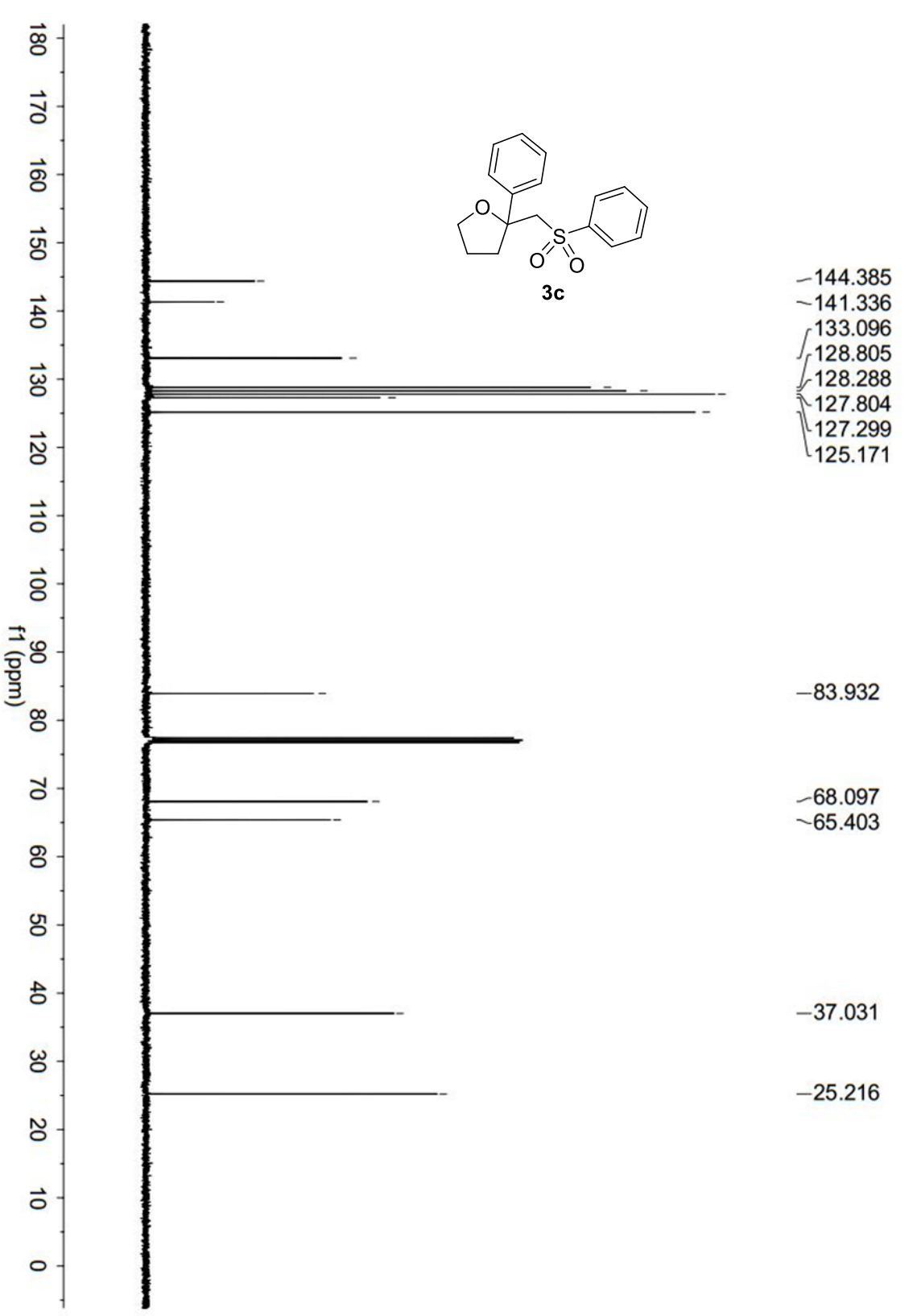
1.752
0.000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133.096
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127.804
127.299
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65.403
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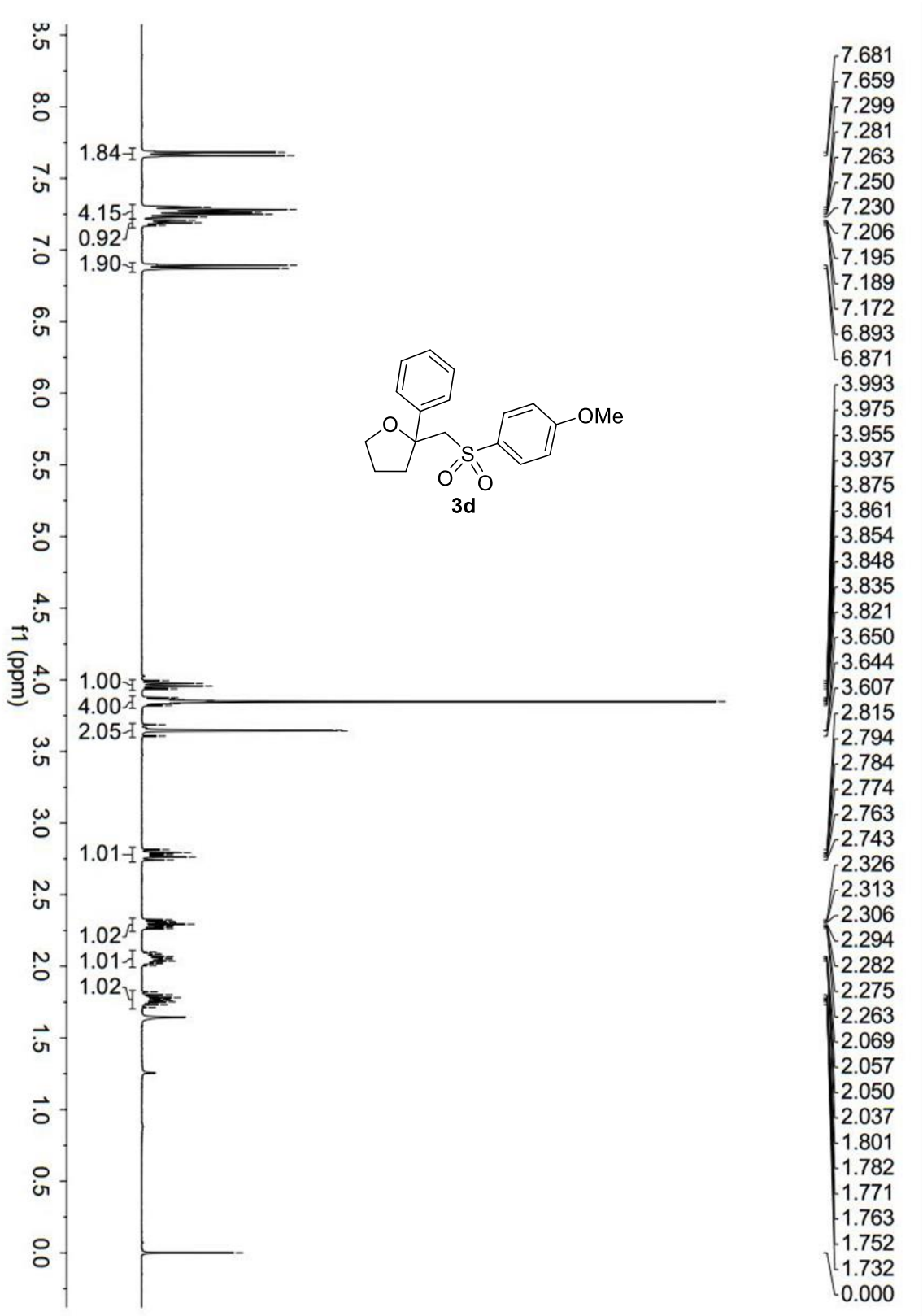
25.216
f1 (ppm)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1.90
1.00
4.00
2.05
1.01
1.02
1.01
1.02
OMe
O
S
O
O
3d
7.681
7.659
7.299
7.281
7.263
7.250
7.230
7.206
7.195
7.189
7.172
6.893
6.871
3.993
3.975
3.955
3.937
3.875
3.861
3.854
3.848
3.835
3.821
3.650
3.644
3.607
2.815
2.794
2.784
2.774
2.763
2.743
2.326
2.313
2.306
2.294
2.282
2.275
2.263
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2.050
2.037
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1.771
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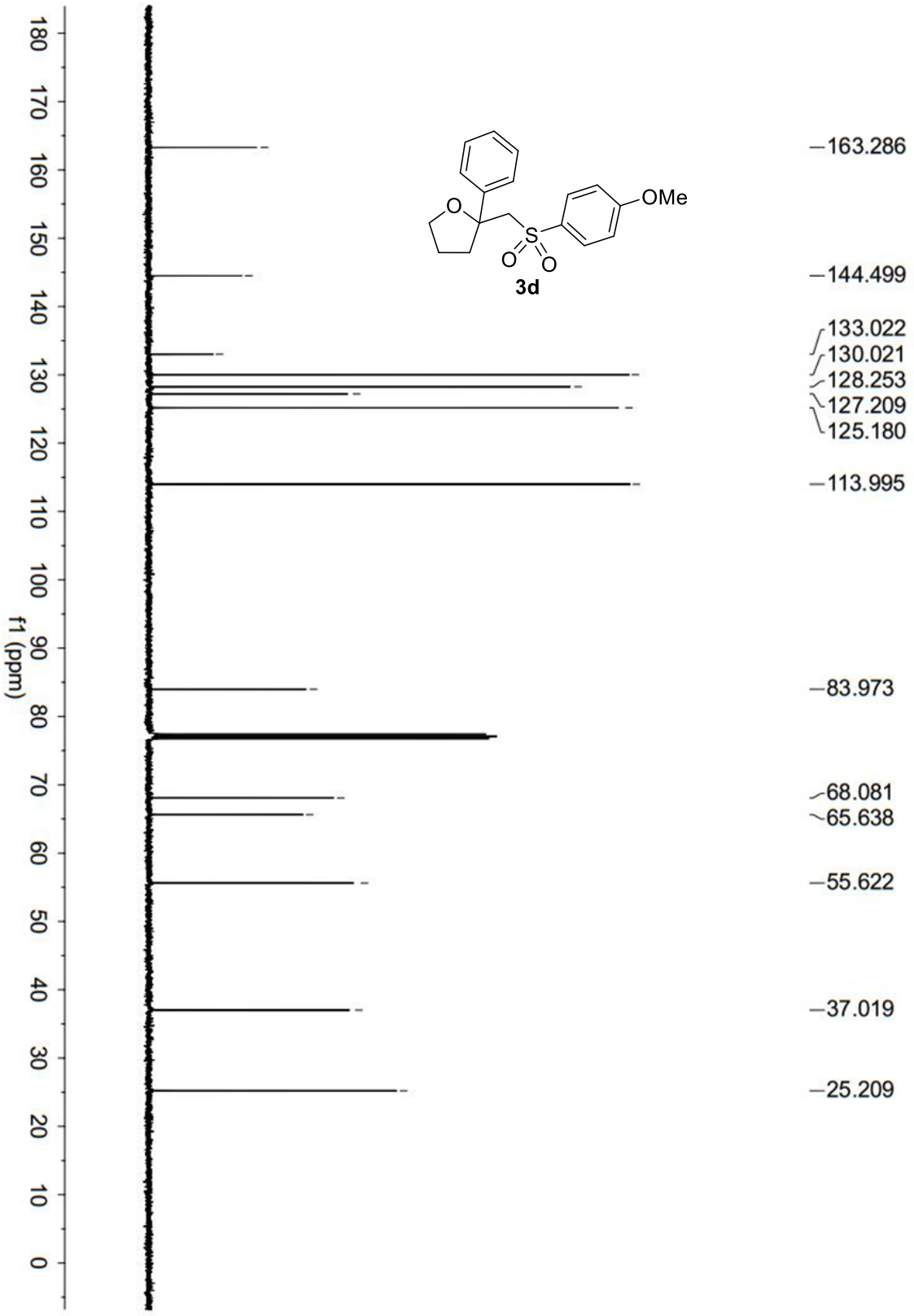
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150
140
130
120
110
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90
80
70
60
50
40
30
20
10
0
O
S
O
O
OMe
3d
163.286
144.499
133.022
130.021
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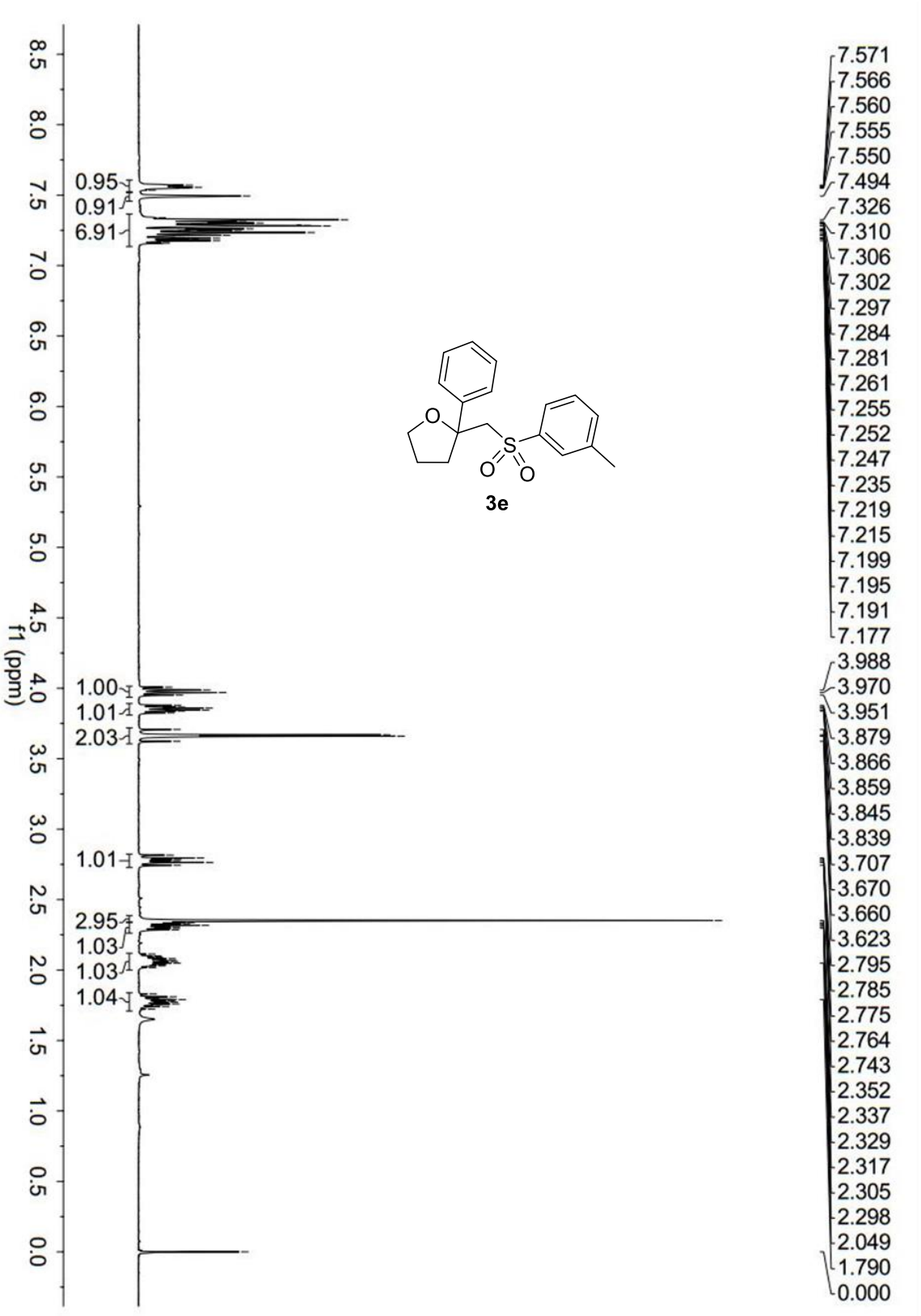
127.209
125.180
113.995
83.973
68.081
65.638
55.622
37.019
25.209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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
0.95
0.91
6.91
1.00
1.01
2.03
1.01
2.95
1.03
1.03
1.04
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7.302
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7.199
7.195
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3.859
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3.660
3.623
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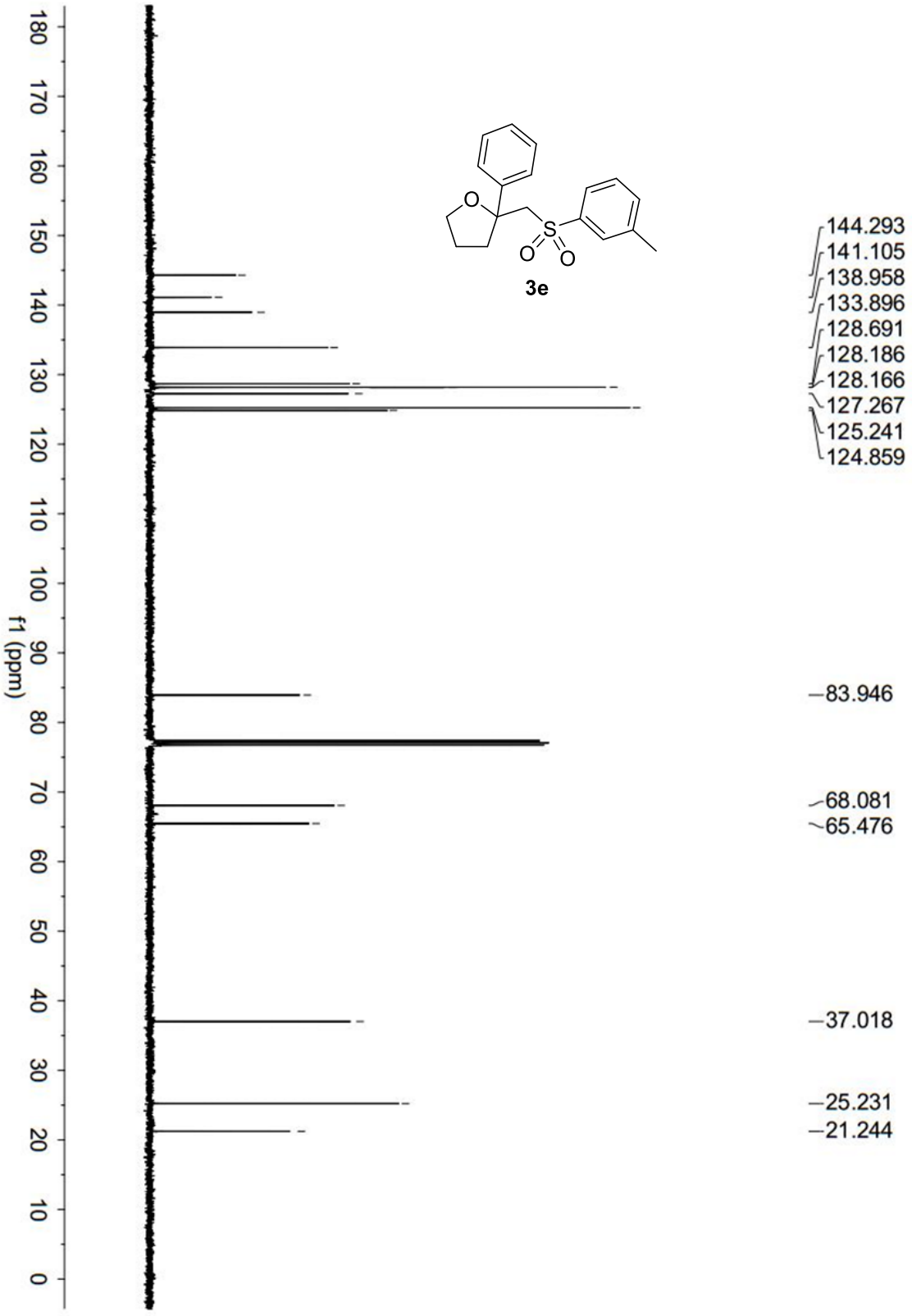
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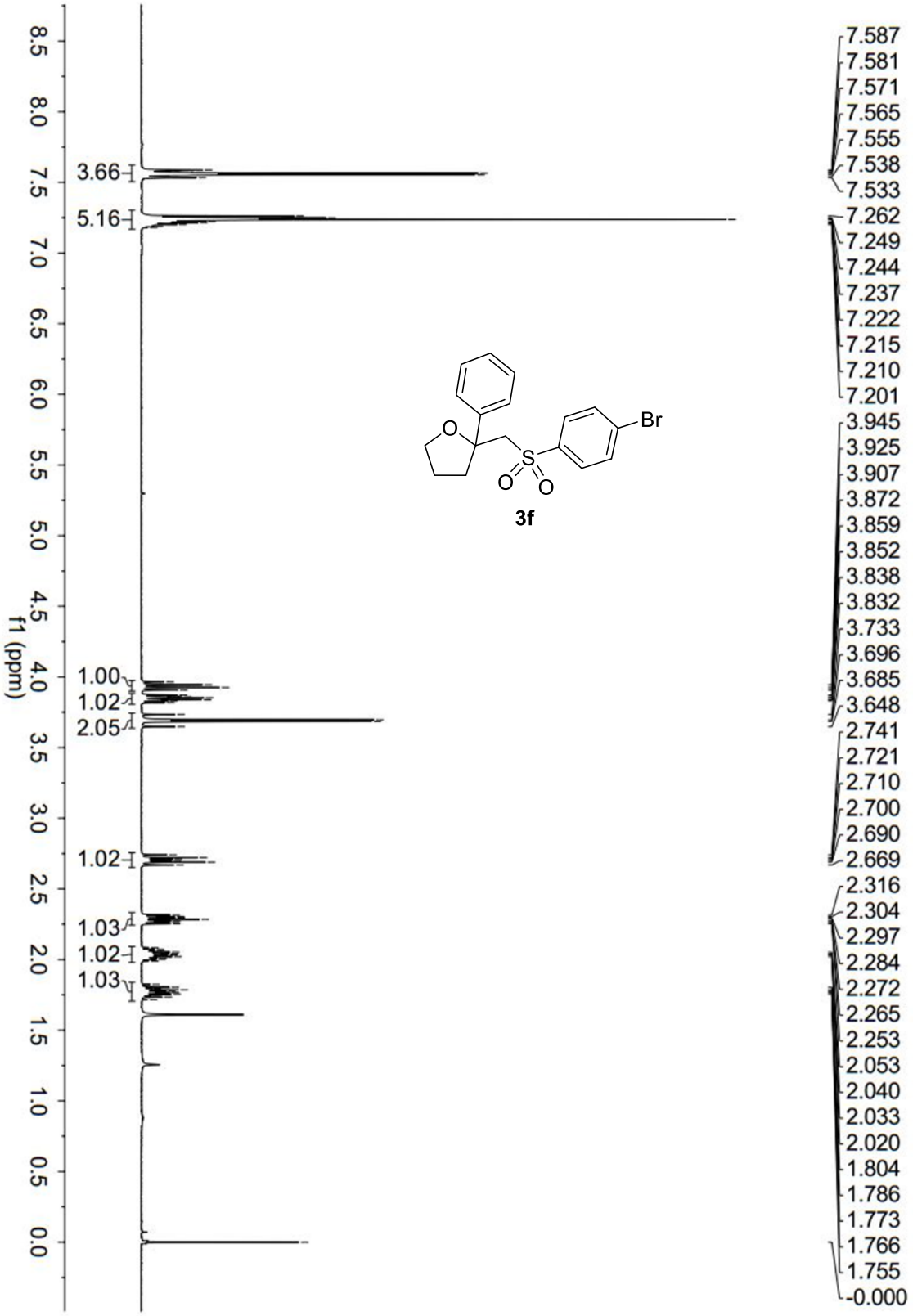
21.244
f1 (ppm)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5.0
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2.5
2.0
1.5
1.0
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0.0
f1 (ppm)
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2.05
1.02
1.03
1.02
1.03
O
S
O
O
Br
3f
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7.565
7.555
7.538
7.533
7.262
7.249
7.244
7.237
7.222
7.215
7.210
7.201
3.945
3.925
3.907
3.872
3.859
3.852
3.838
3.832
3.733
3.696
3.685
3.648
2.741
2.721
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2.700
2.690
2.669
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2.304
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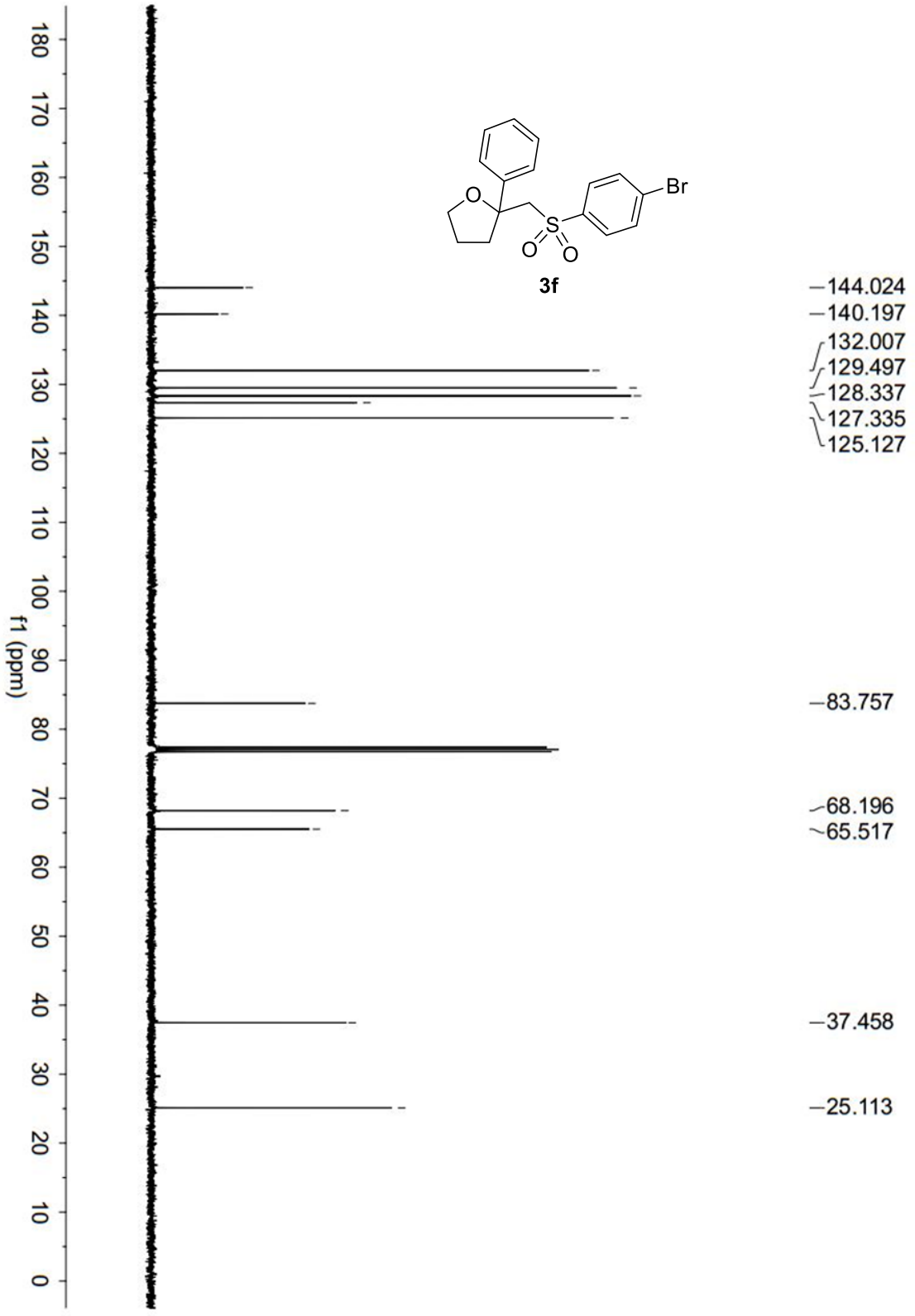
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65.517
37.458
25.113
f1 (ppm)
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150
140
130
120
110
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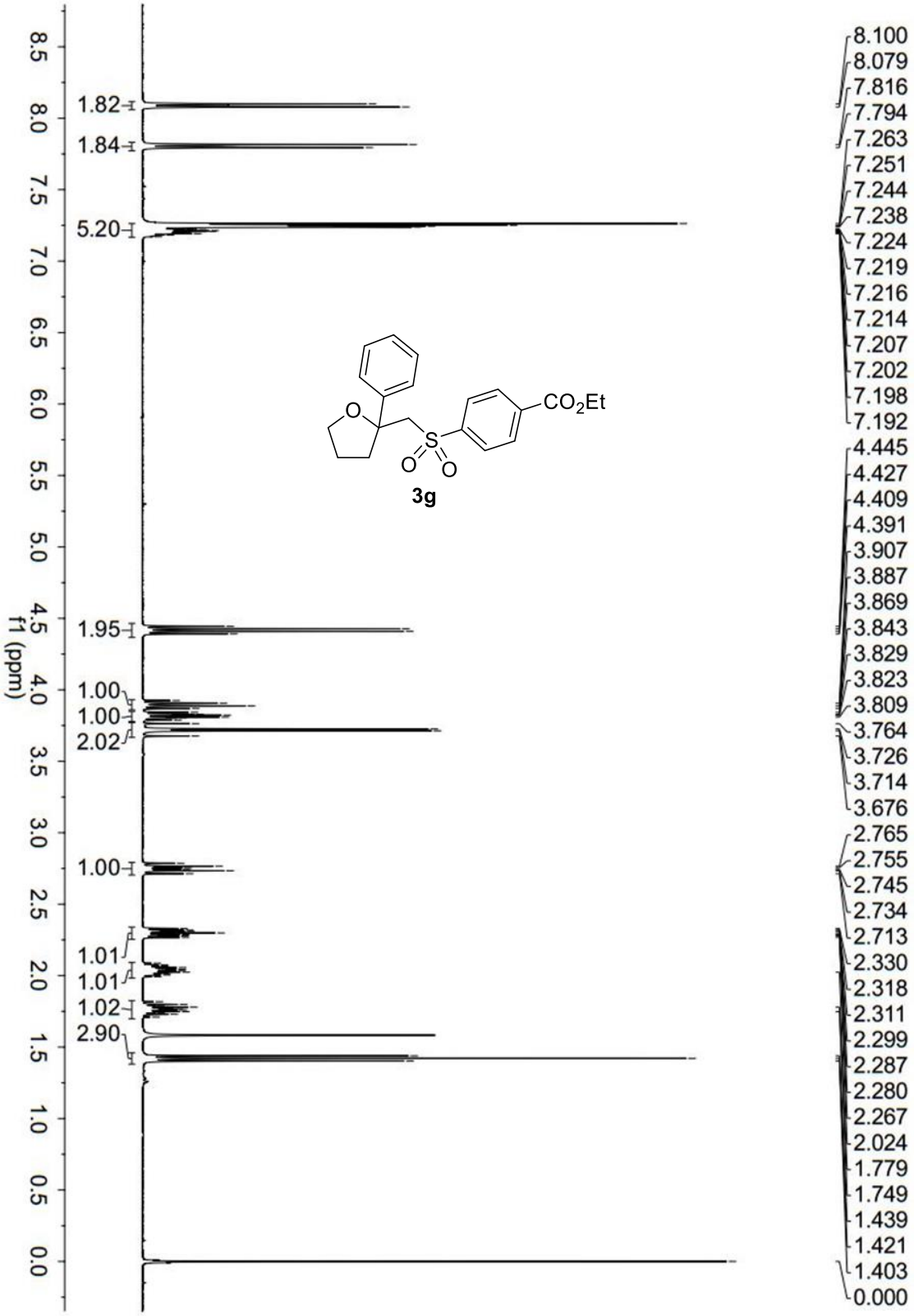
70
60
50
40
30
20
10
0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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.82
1.84
5.20
1.95
1.00
1.00
2.02
1.00
1.01
1.01
1.02
2.90
O
S
O
O
CO2Et
3g
8.100
8.079
7.816
7.794
7.263
7.251
7.244
7.238
7.224
7.219
7.216
7.214
7.207
7.202
7.198
7.192
4.445
4.427
4.409
4.391
3.907
3.887
3.869
3.843
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3.764
3.726
3.714
3.676
2.765
2.755
2.745
2.734
2.713
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2.318
2.311
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2.267
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1.749
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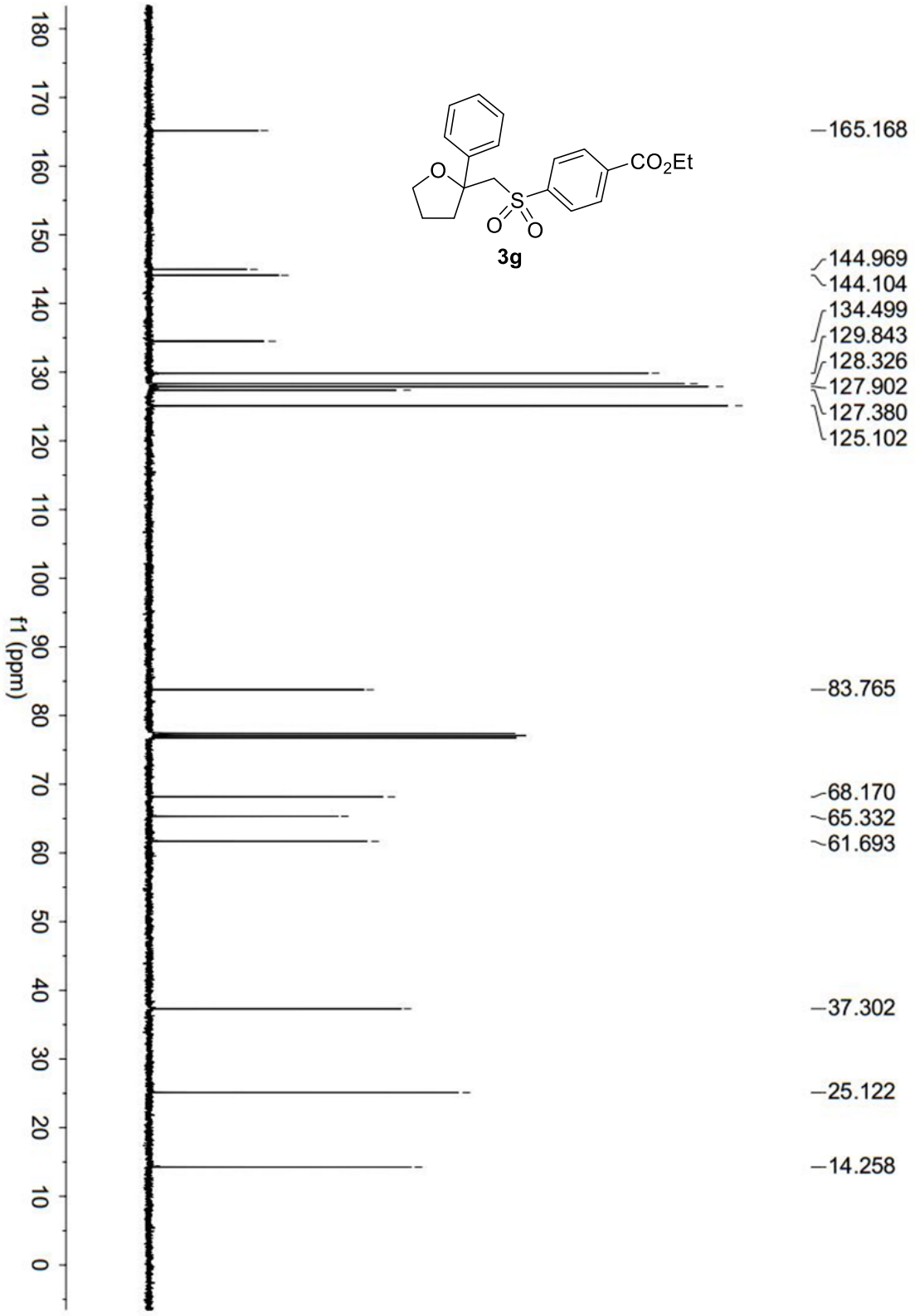
1.403
0.000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S
O
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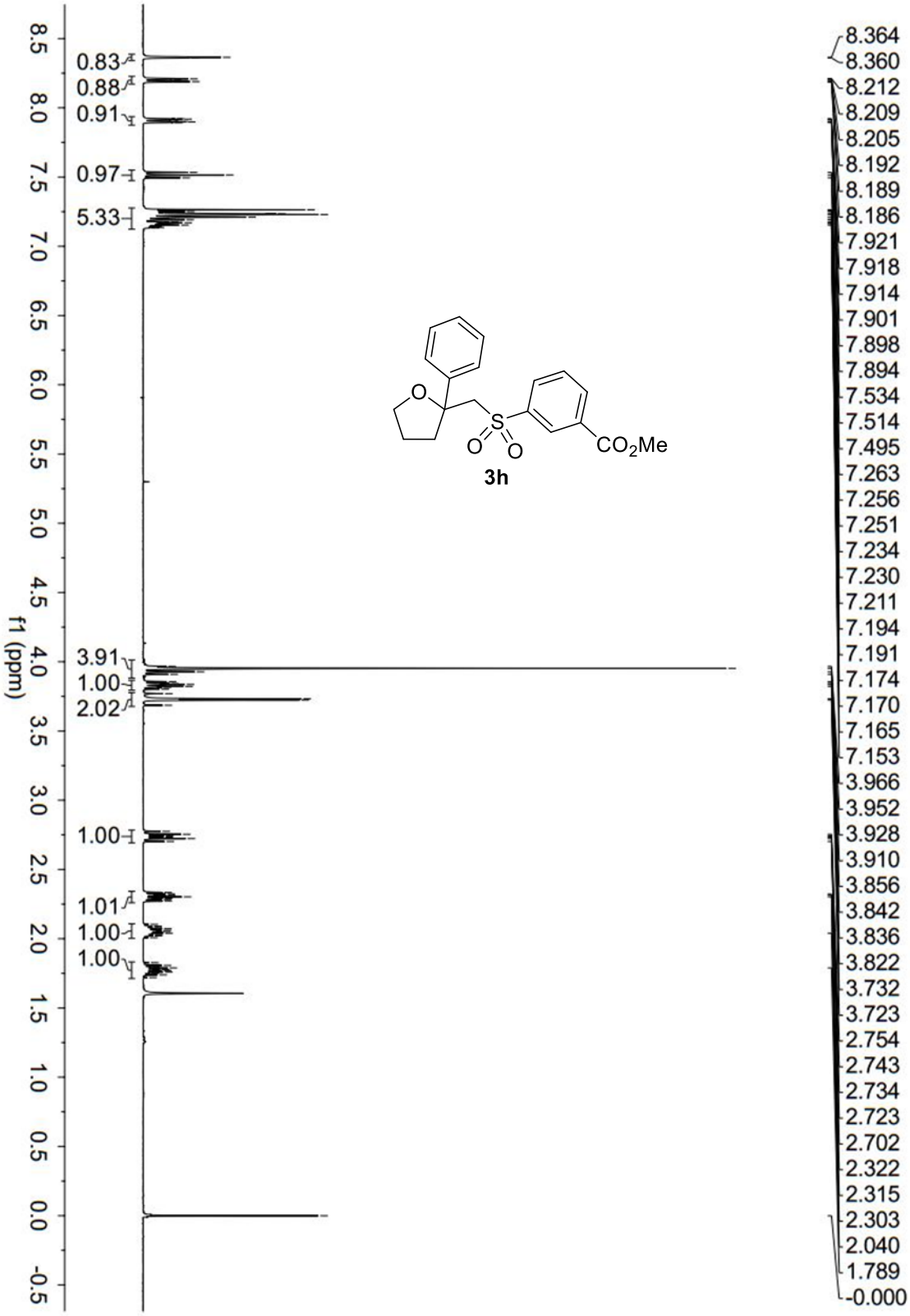
83.765
68.170
65.332
61.693
37.302
25.122
14.258
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


f1 (ppm)
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
0.83
0.88
0.91
0.97
5.33
3.91
1.00
2.02
1.00
1.01
1.00
1.00
O
S
O
O
CO2Me
3h
8.364
8.360
8.212
8.209
8.205
8.192
8.189
8.186
7.921
7.918
7.914
7.901
7.898
7.894
7.534
7.514
7.495
7.263
7.256
7.251
7.234
7.230
7.211
7.194
7.191
7.174
7.170
7.165
7.153
3.966
3.952
3.928
3.910
3.856
3.842
3.836
3.822
3.732
3.723
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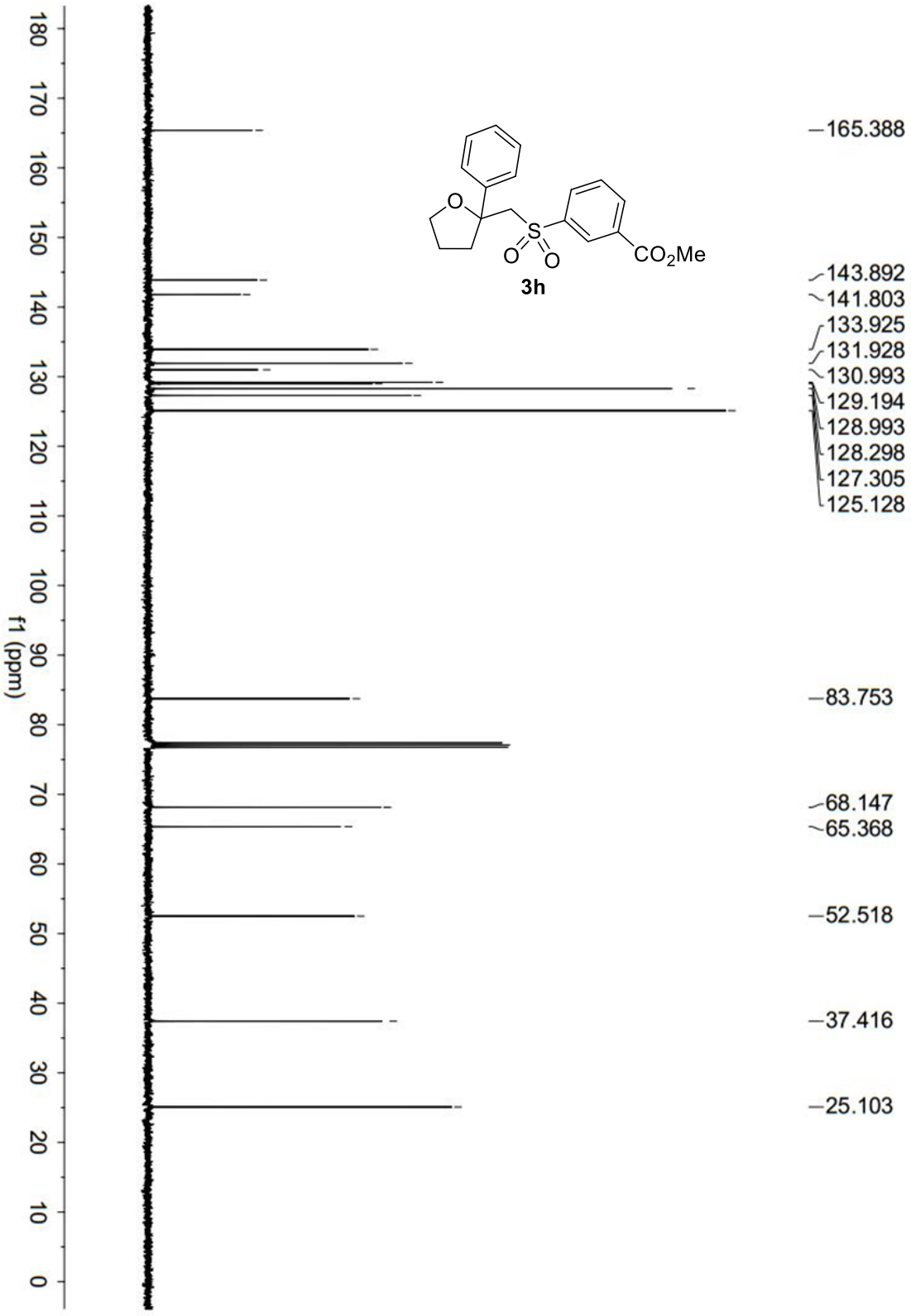
2.734
2.723
2.702
2.322
2.315
2.303
2.040
1.789
-0.000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143.892
141.803
133.925
131.928
130.993
129.194
128.993
128.298
127.305
125.128
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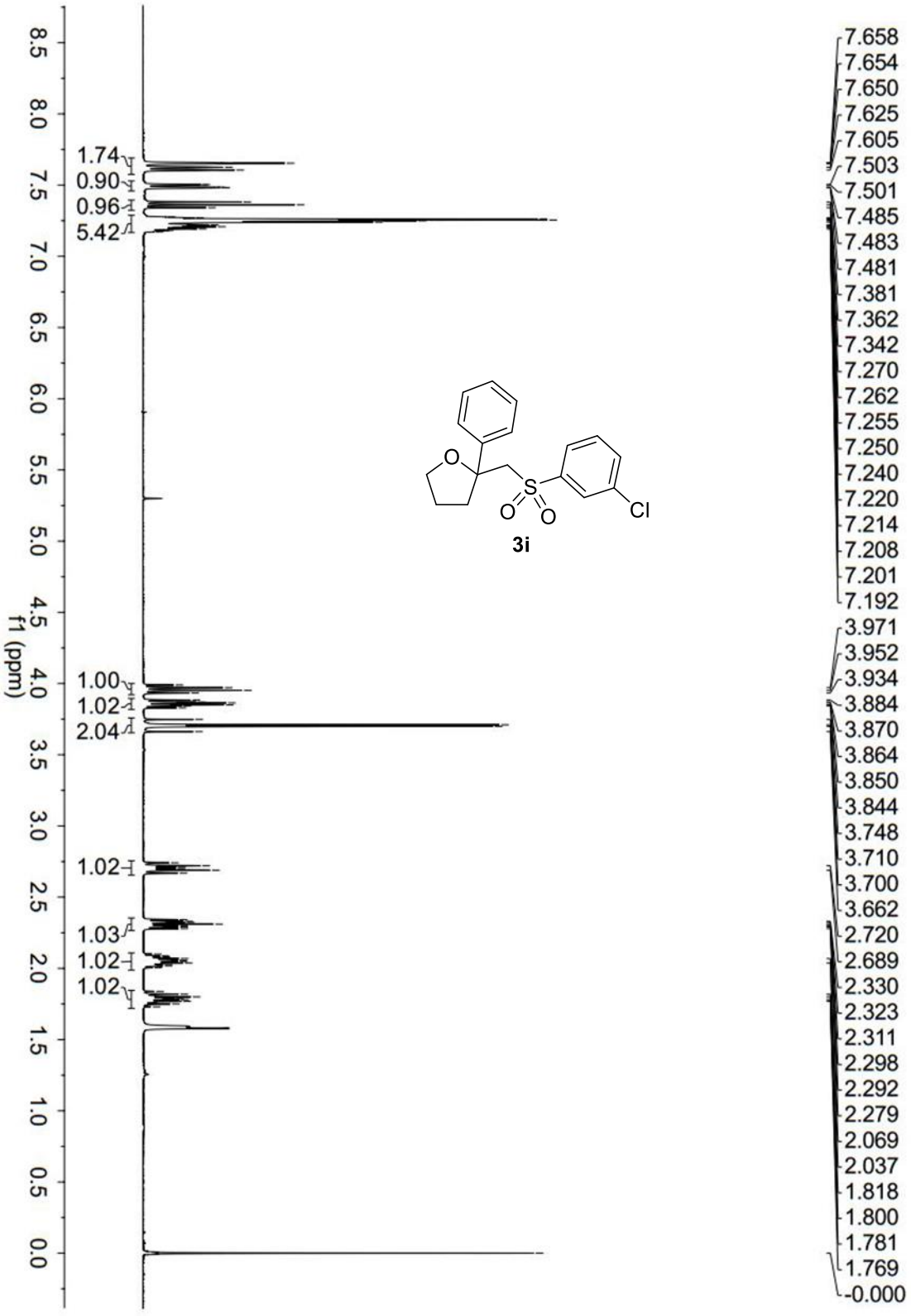
68.147
65.368
52.518
37.416
25.103
f1 (ppm)
O
S
O
O
CO2Me
3h


f1 (ppm)
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.74
0.90
0.96
5.42
1.00
1.02
2.04
1.02
1.03
1.02
1.02
O
S
O
O
Cl
3i
7.658
7.654
7.650
7.625
7.605
7.503
7.501
7.485
7.483
7.481
7.381
7.362
7.342
7.270
7.262
7.255
7.250
7.240
7.220
7.214
7.208
7.201
7.192
3.971
3.952
3.934
3.884
3.870
3.864
3.850
3.844
3.748
3.710
3.700
3.662
2.720
2.689
2.330
2.323
2.311
2.298
2.292
2.279
2.069
2.037
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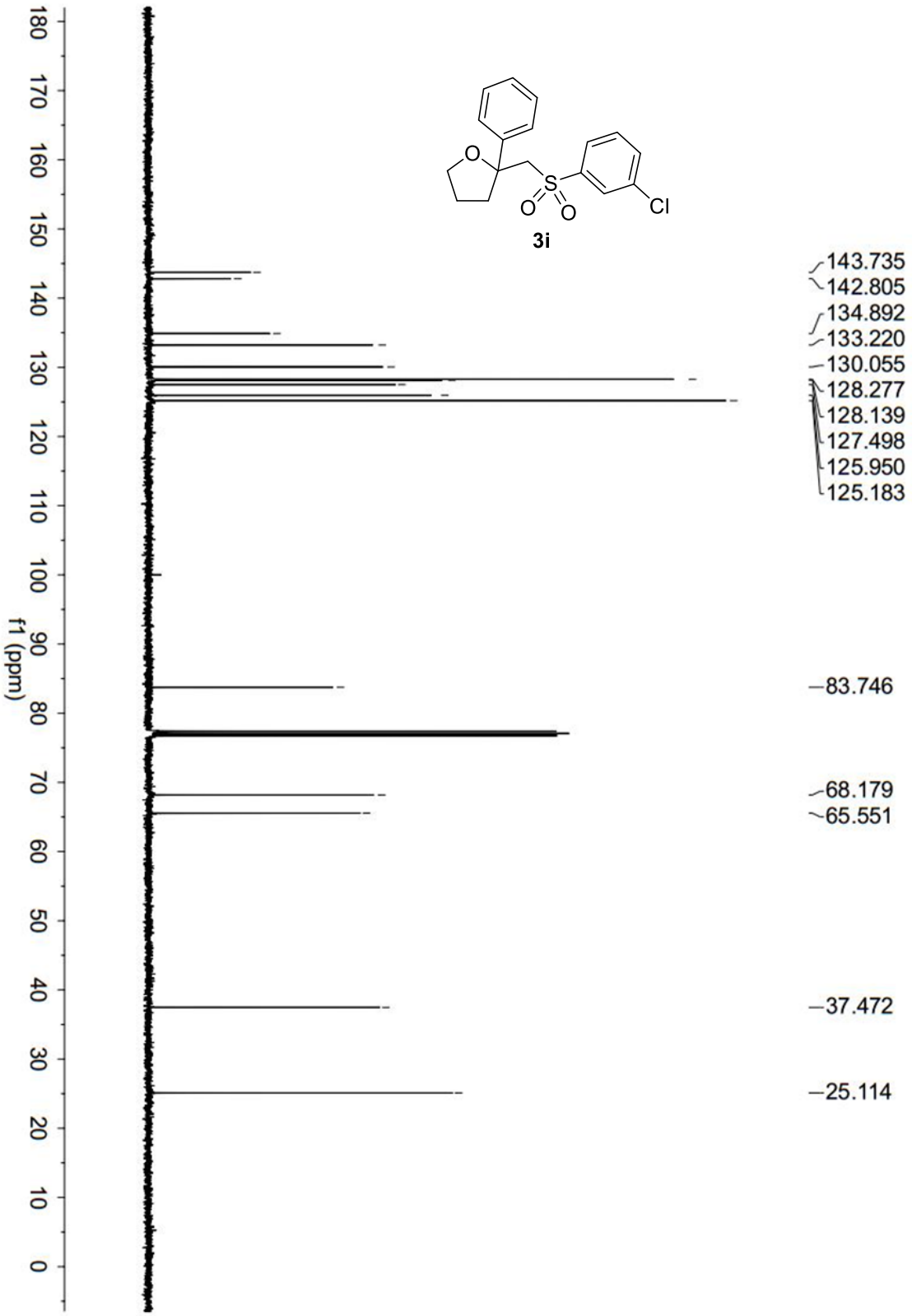
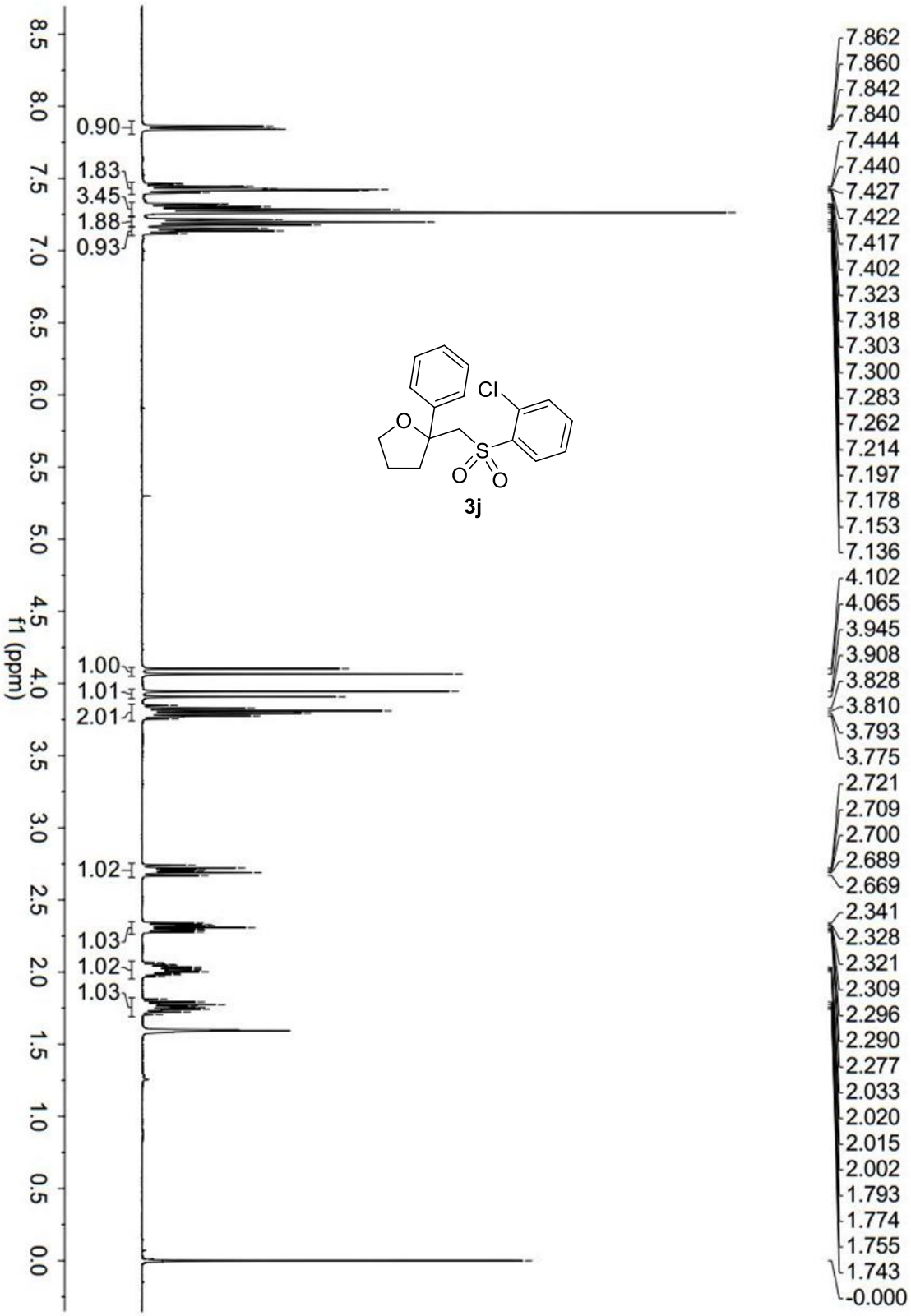
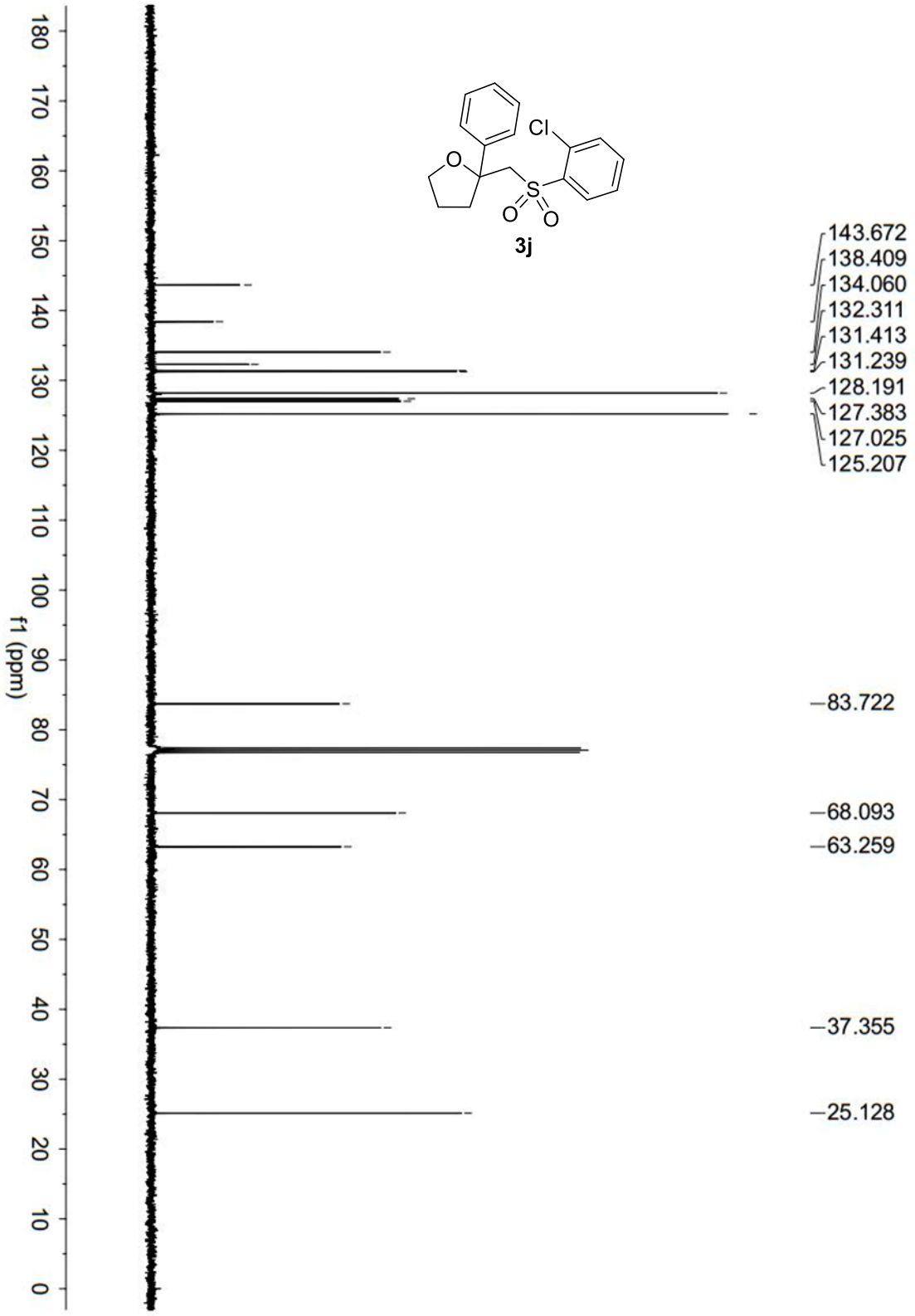
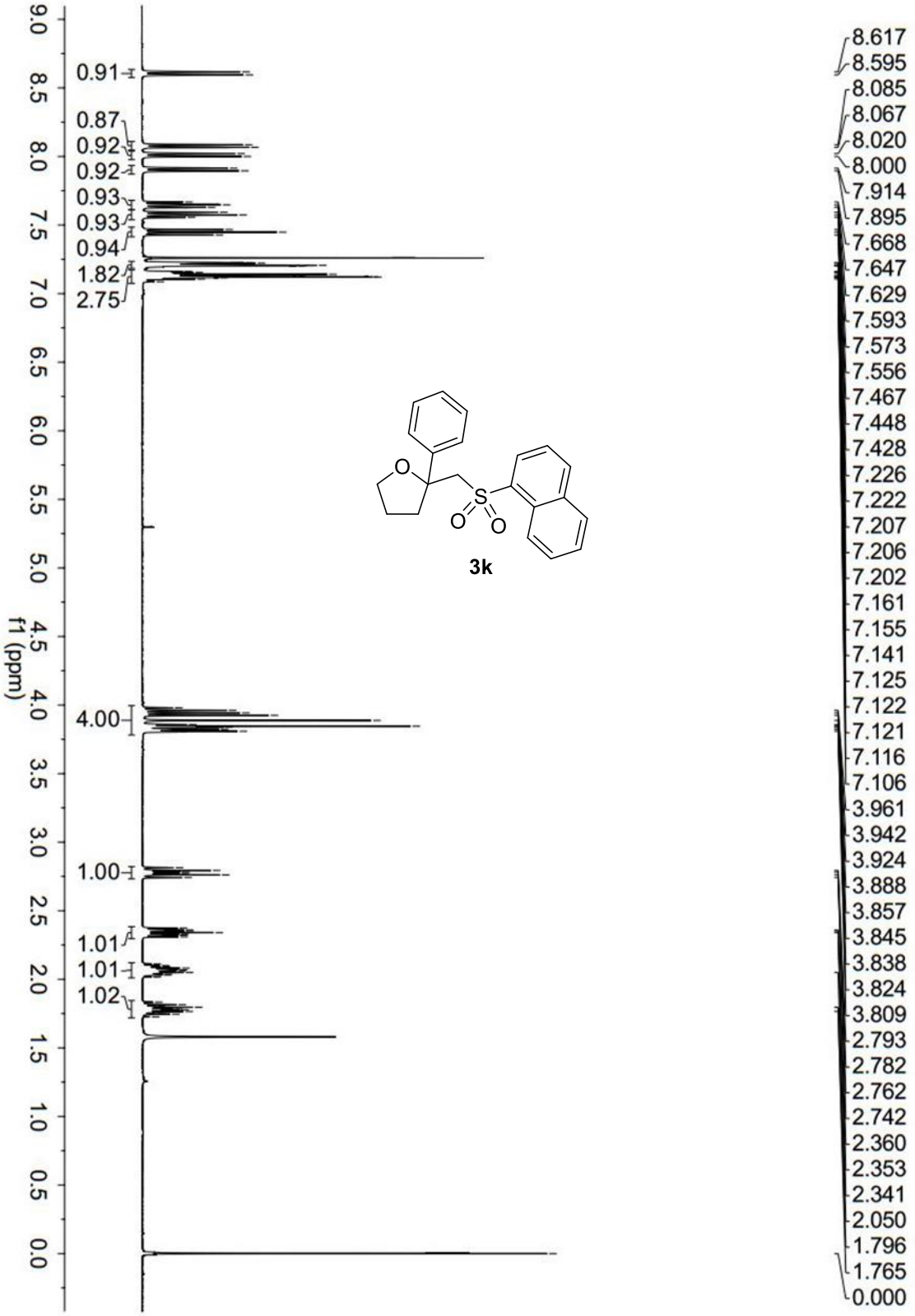
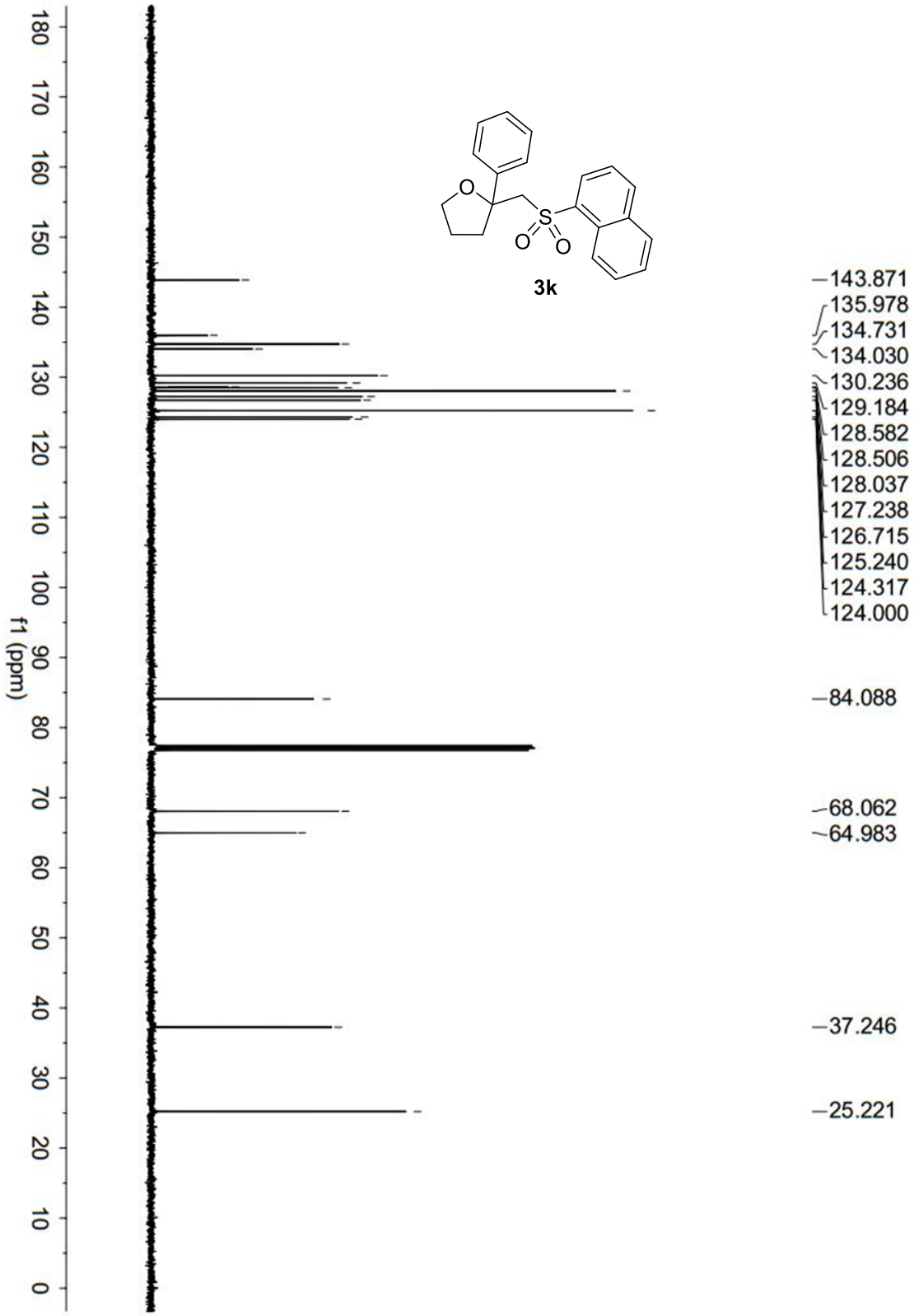
1.800
1.781
1.769
-0.000

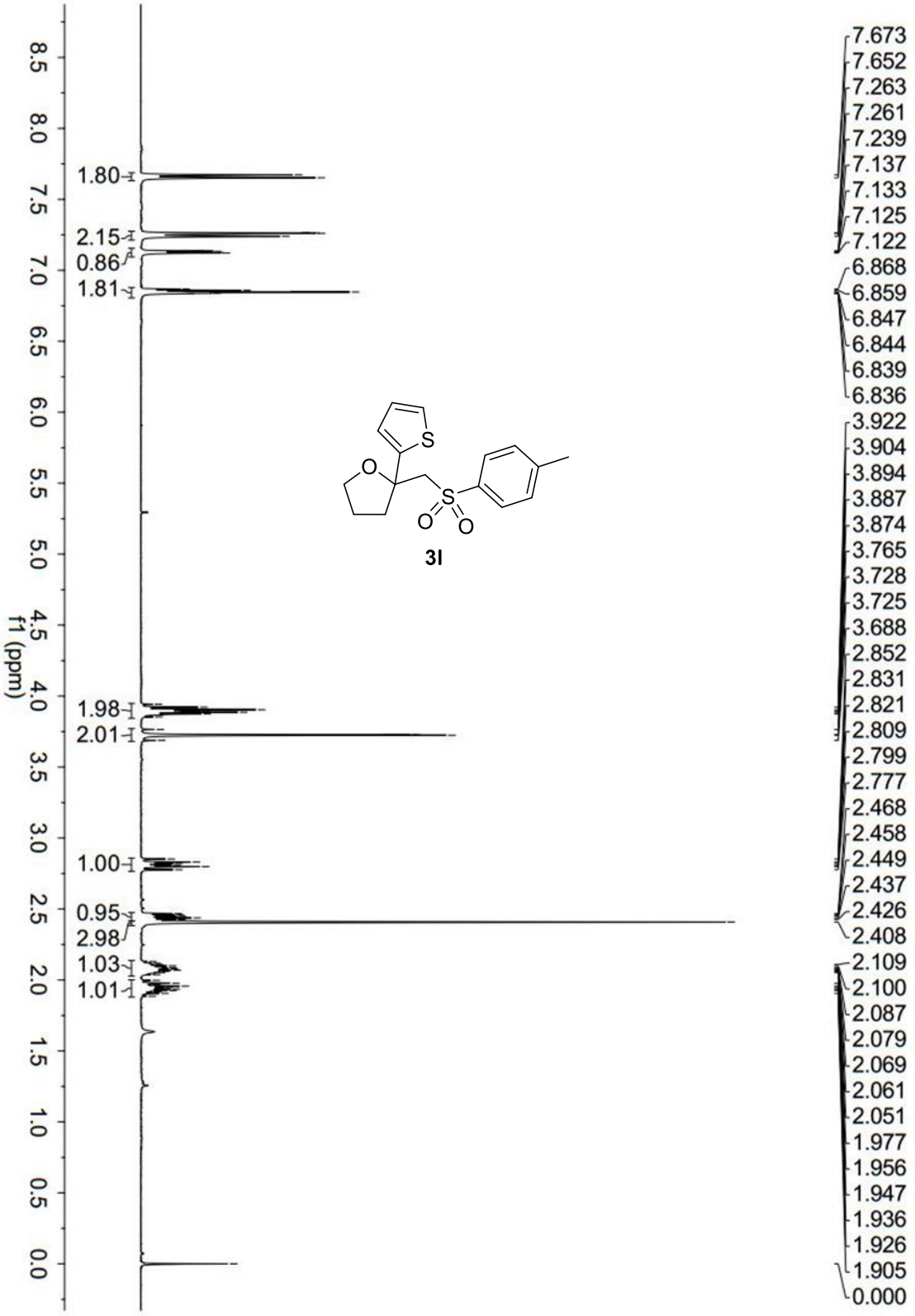

3i
143.735
142.805
134.892
133.220
130.055
128.277
128.139
127.498
125.950
125.183
83.746
68.179
65.551
37.472
25.114
f1 (ppm)

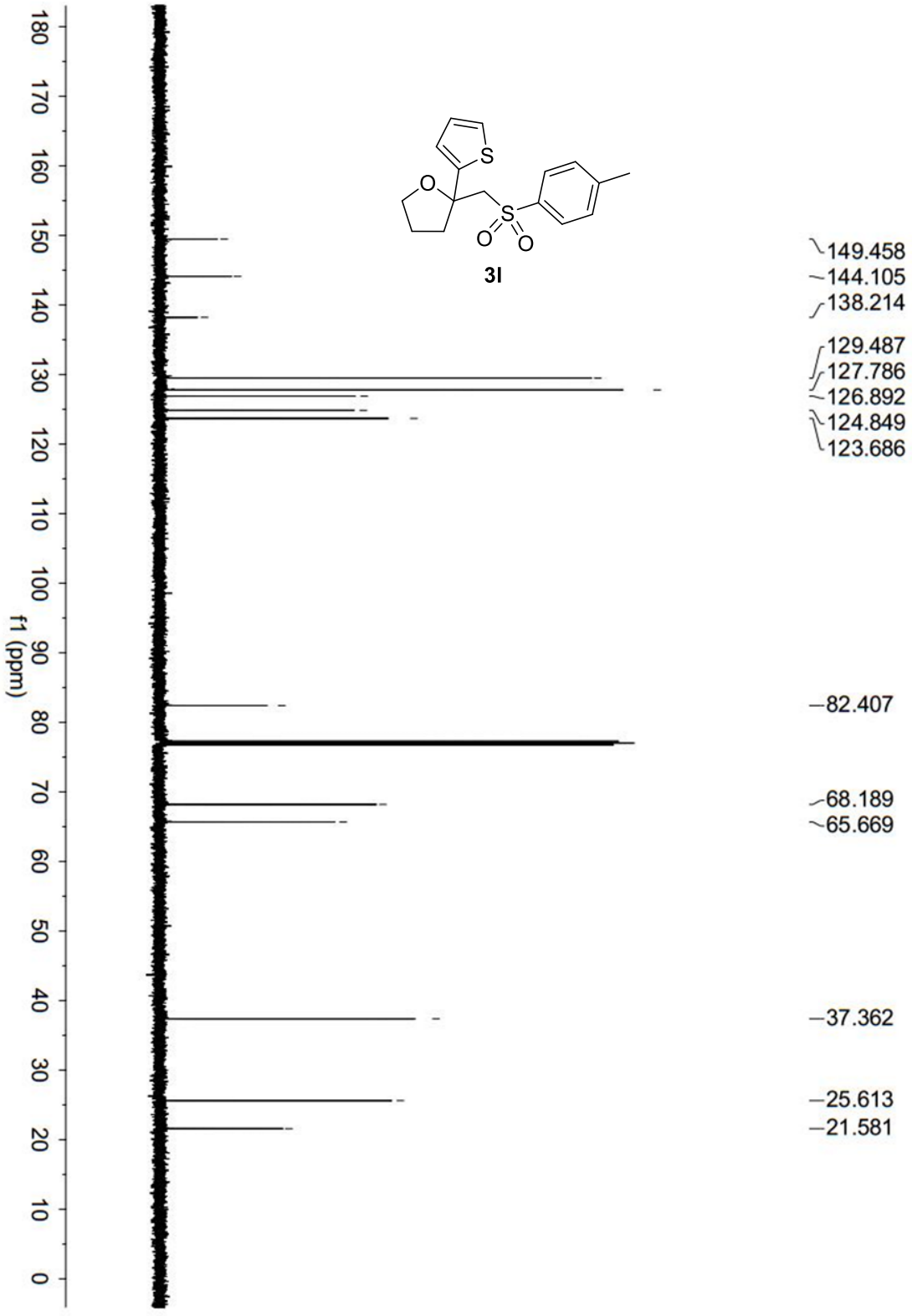

f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.90
1.83
3.45
1.88
0.93
1.00
1.01
2.01
1.02
1.03
1.02
1.03
Cl
O
S
O
O
3j
7.862
7.860
7.842
7.840
7.444
7.440
7.427
7.422
7.417
7.402
7.323
7.318
7.303
7.300
7.283
7.262
7.214
7.197
7.178
7.153
7.136
4.102
4.065
3.945
3.908
3.828
3.810
3.793
3.775
2.721
2.709
2.700
2.689
2.669
2.341
2.328
2.321
2.309
2.296
2.290
2.277
2.033
2.020
2.015
2.002
1.793
1.774
1.755
1.743
-0.000

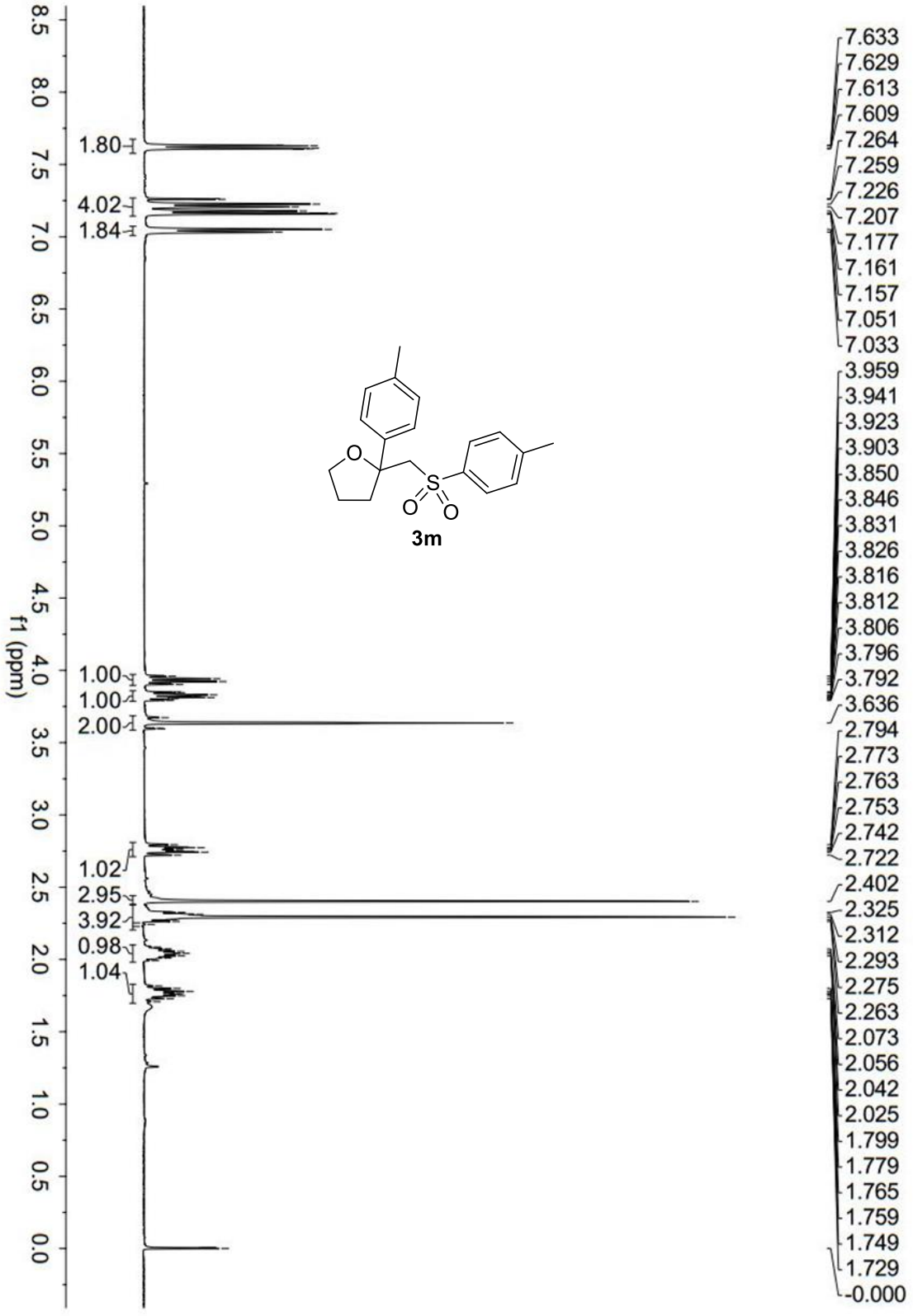

Cl
O
S
O
O
3j
143.672
138.409
134.060
132.311
131.413
131.239
128.191
127.383
127.025
125.207
83.722
68.093
63.259
37.355
25.128
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

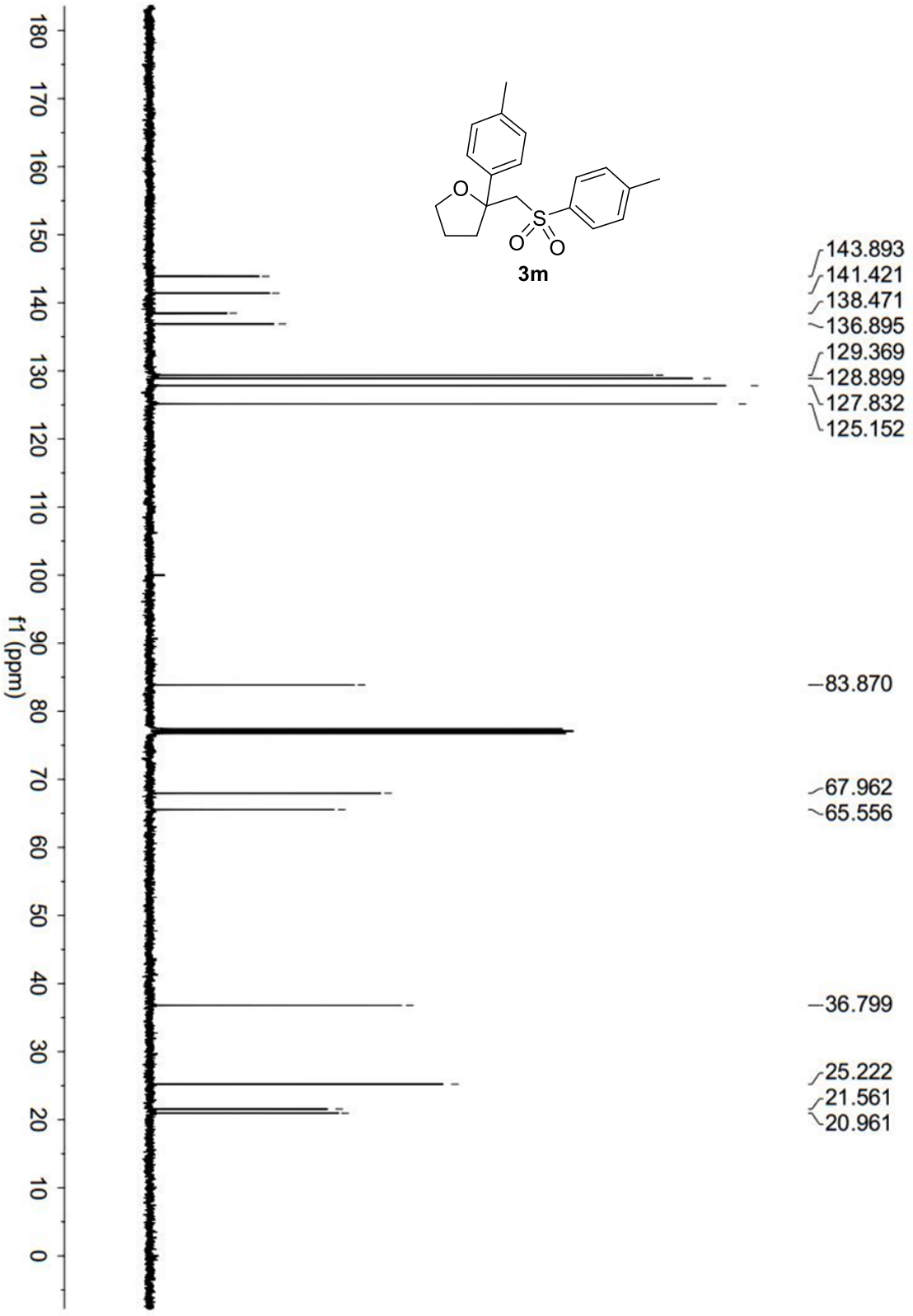

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
0.91
0.87
0.92
0.92
0.93
0.93
0.94
1.82
2.75
4.00
1.00
1.01
1.01
1.02
O
S
O
O
3k
8.617
8.595
8.085
8.067
8.020
8.000
7.914
7.895
7.668
7.647
7.629
7.593
7.573
7.556
7.467
7.448
7.428
7.226
7.222
7.207
7.206
7.202
7.161
7.155
7.141
7.125
7.122
7.121
7.116
7.106
3.961
3.942
3.924
3.888
3.857
3.845
3.838
3.824
3.809
2.793
2.782
2.762
2.742
2.360
2.353
2.341
2.050
1.796
1.765
0.000

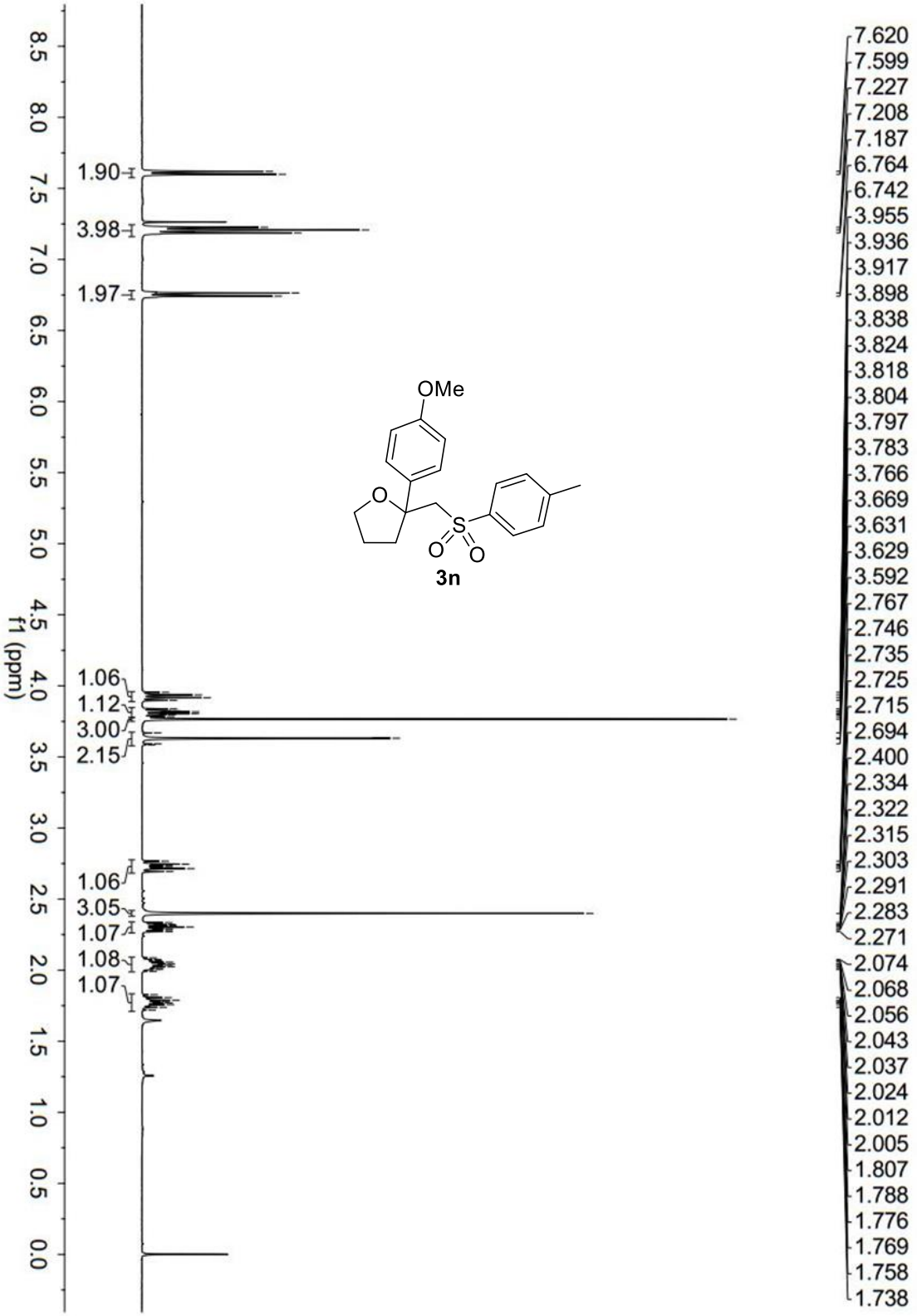

3k
143.871
135.978
134.731
134.030
130.236
129.184
128.582
128.506
128.037
127.238
126.715
125.240
124.317
124.000
84.088
68.062
64.983
37.246
25.221
f1 (ppm)

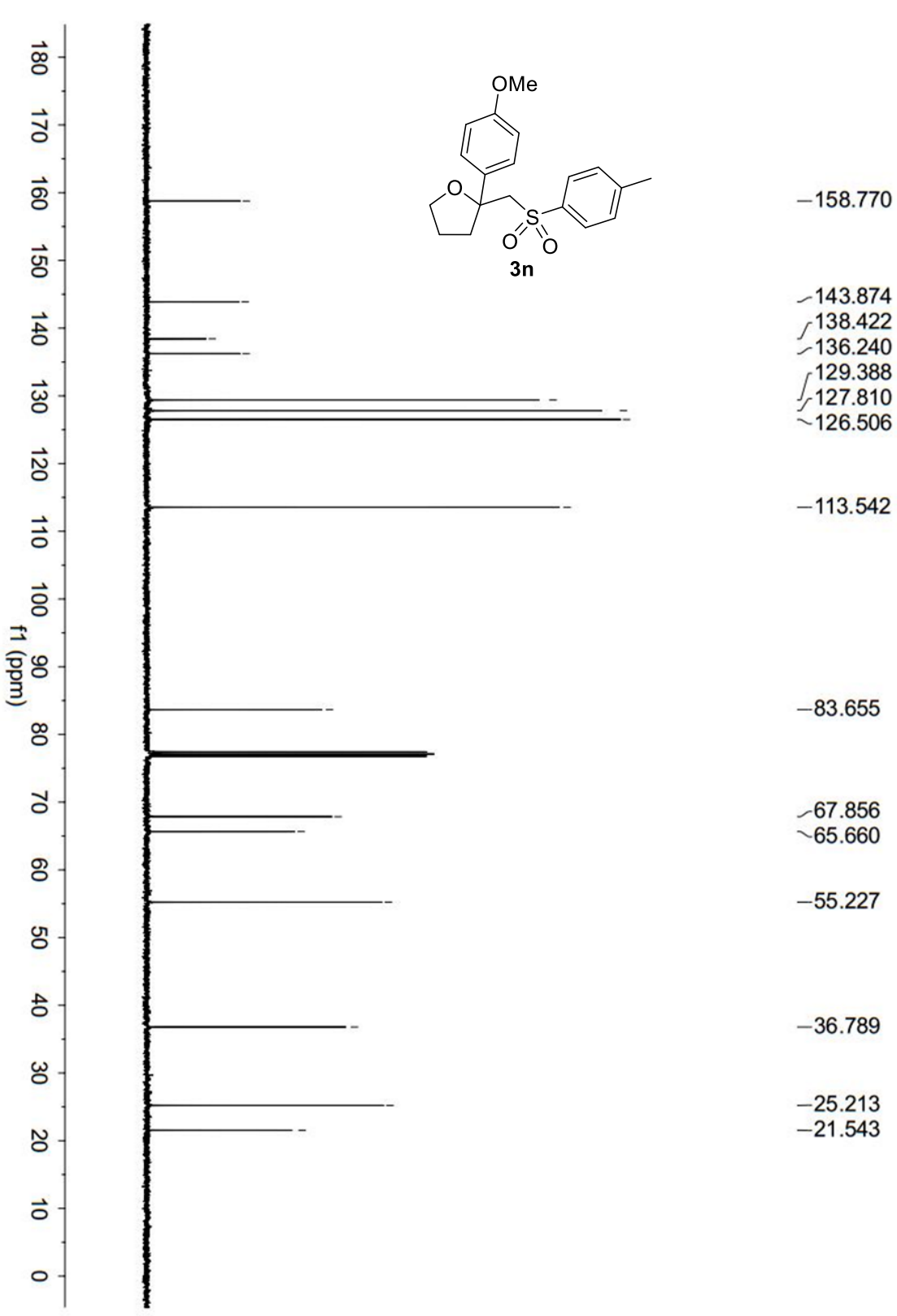

f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.80
2.15
0.86
1.81
1.98
2.01
1.00
0.95
2.98
1.03
1.01
S
O
S
O
O
3l
7.673
7.652
7.263
7.261
7.239
7.137
7.133
7.125
7.122
6.868
6.859
6.847
6.844
6.839
6.836
3.922
3.904
3.894
3.887
3.874
3.765
3.728
3.725
3.688
2.852
2.831
2.821
2.809
2.799
2.777
2.468
2.458
2.449
2.437
2.426
2.408
2.109
2.100
2.087
2.079
2.069
2.061
2.051
1.977
1.956
1.947
1.936
1.926
1.905
0.000

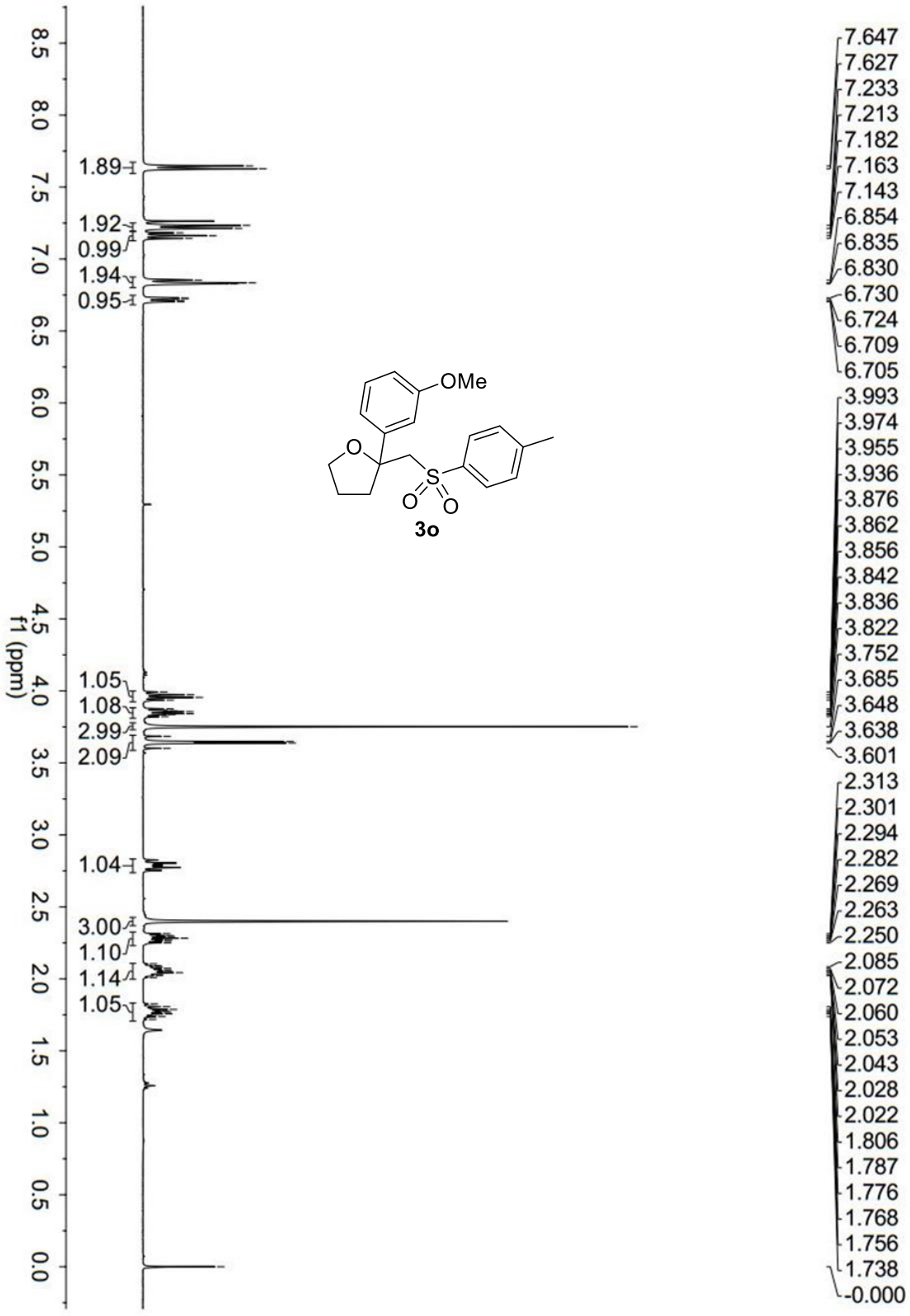

3l
149.458
144.105
138.214
129.487
127.786
126.892
124.849
123.686
82.407
68.189
65.669
37.362
25.613
21.581
f1 (ppm)


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.80
4.02
1.84
1.00
1.00
2.00
1.02
2.95
3.92
0.98
1.04
O
S
O
O
3m
7.633
7.629
7.613
7.609
7.264
7.259
7.226
7.207
7.177
7.161
7.157
7.051
7.033
3.959
3.941
3.923
3.903
3.850
3.846
3.831
3.826
3.816
3.812
3.806
3.796
3.792
3.636
2.794
2.773
2.763
2.753
2.742
2.722
2.402
2.325
2.312
2.293
2.275
2.263
2.073
2.056
2.042
2.025
1.799
1.779
1.765
1.759
1.749
1.729
-0.000


3m
143.893
141.421
138.471
136.895
129.369
128.899
127.832
125.152
83.870
67.962
65.556
36.799
25.222
21.561
20.961
f1 (ppm)


f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.90
3.98
1.97
1.06
1.12
3.00
2.15
1.06
3.05
1.07
1.08
1.07
OMe
O
S
O
O
3n
7.620
7.599
7.227
7.208
7.187
6.764
6.742
3.955
3.936
3.917
3.898
3.838
3.824
3.818
3.804
3.797
3.783
3.766
3.669
3.631
3.629
3.592
2.767
2.746
2.735
2.725
2.715
2.694
2.400
2.334
2.322
2.315
2.303
2.291
2.283
2.271
2.074
2.068
2.056
2.043
2.037
2.024
2.012
2.005
1.807
1.788
1.776
1.769
1.758
1.738


OMe
O
S
O
O
3n
158.770
143.874
138.422
136.240
129.388
127.810
126.506
113.542
83.655
67.856
65.660
55.227
36.789
25.213
21.543
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.89
1.92
0.99
1.94
0.95
1.05
1.08
2.99
2.09
1.04
3.00
1.10
1.14
1.05
OMe
O
S
O
O
3o
7.647
7.627
7.233
7.213
7.182
7.163
7.143
6.854
6.835
6.830
6.730
6.724
6.709
6.705
3.993
3.974
3.955
3.936
3.876
3.862
3.856
3.842
3.836
3.822
3.752
3.685
3.648
3.638
3.601
2.313
2.301
2.294
2.282
2.269
2.263
2.250
2.085
2.072
2.060
2.053
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2.022
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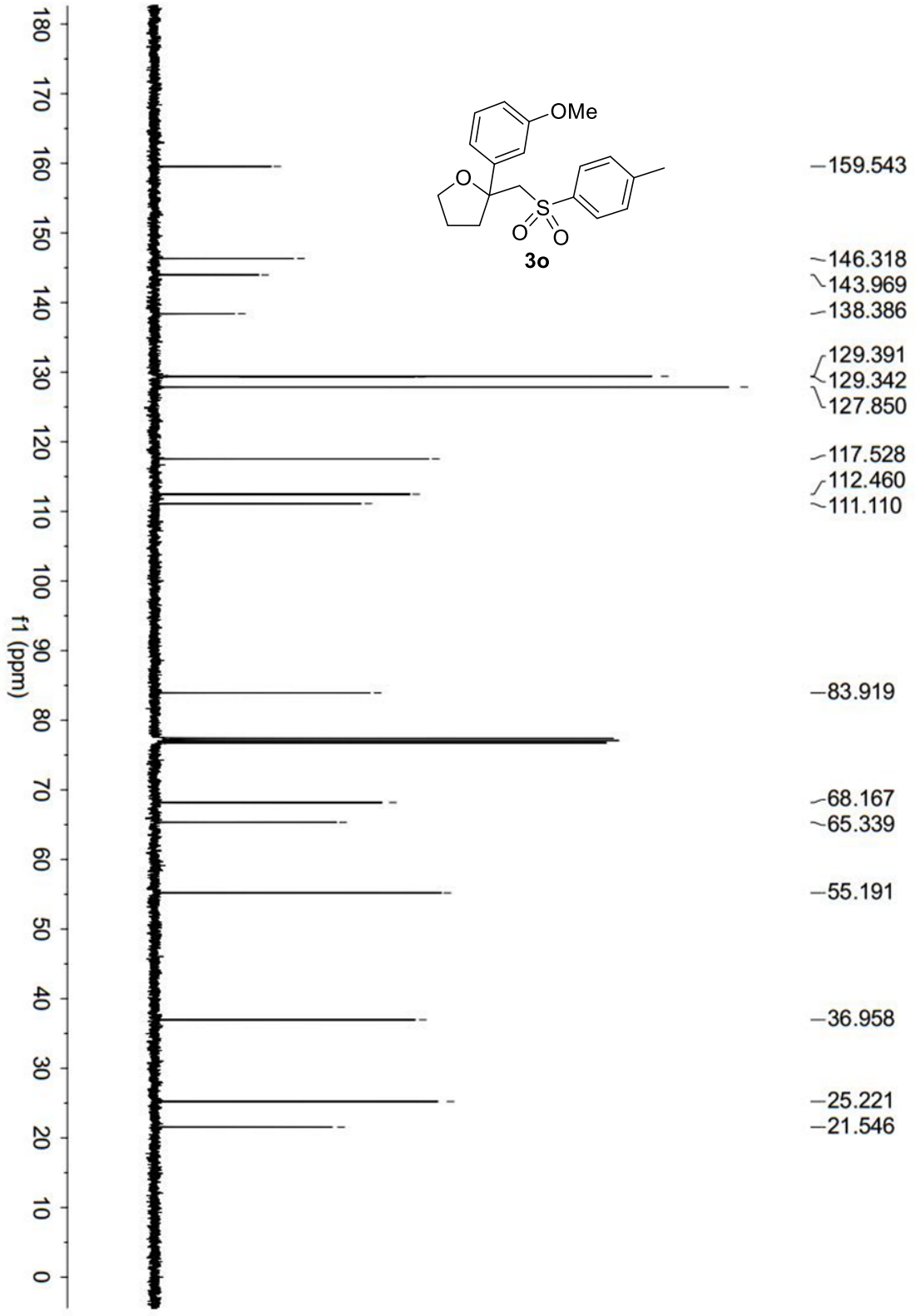
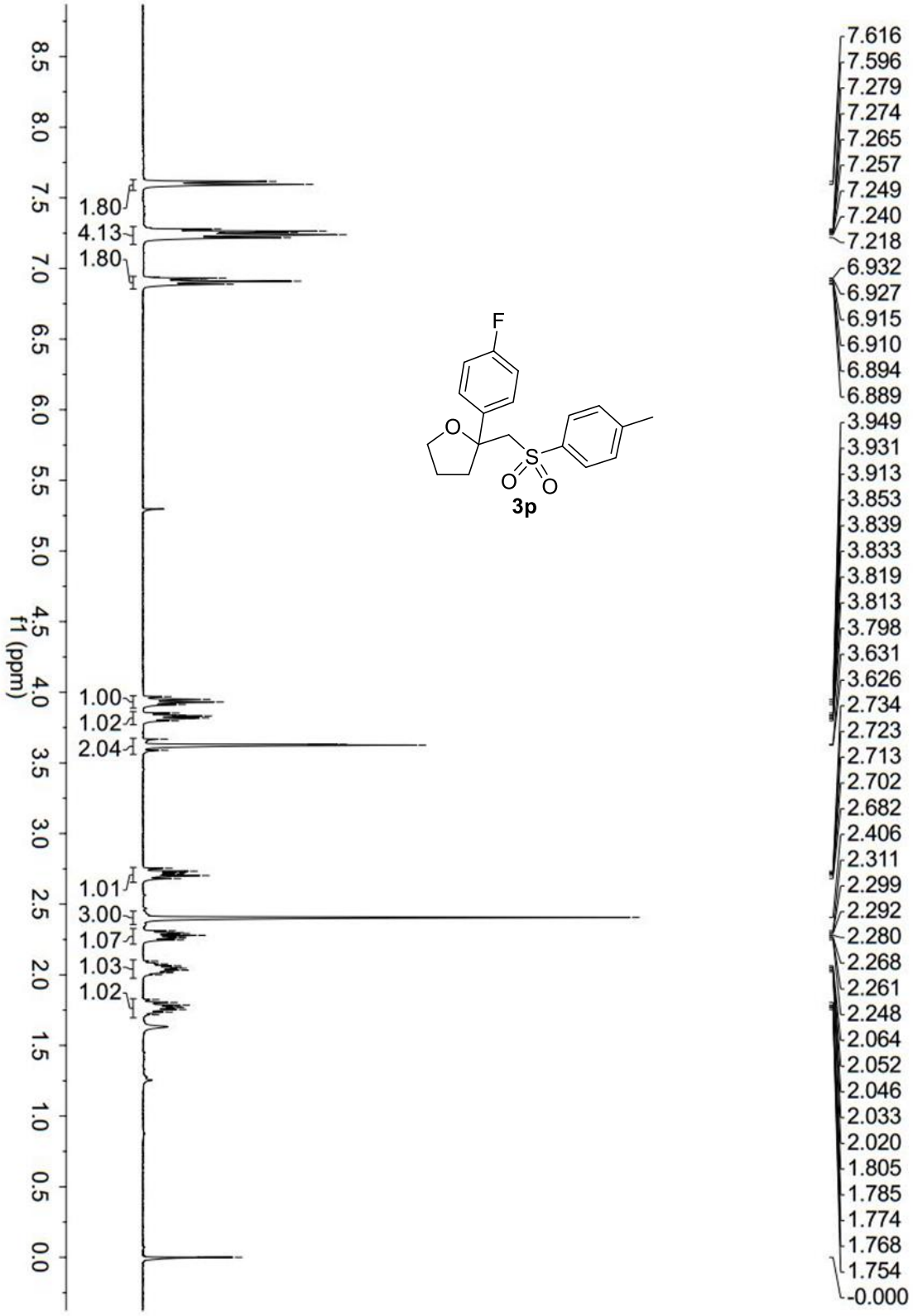
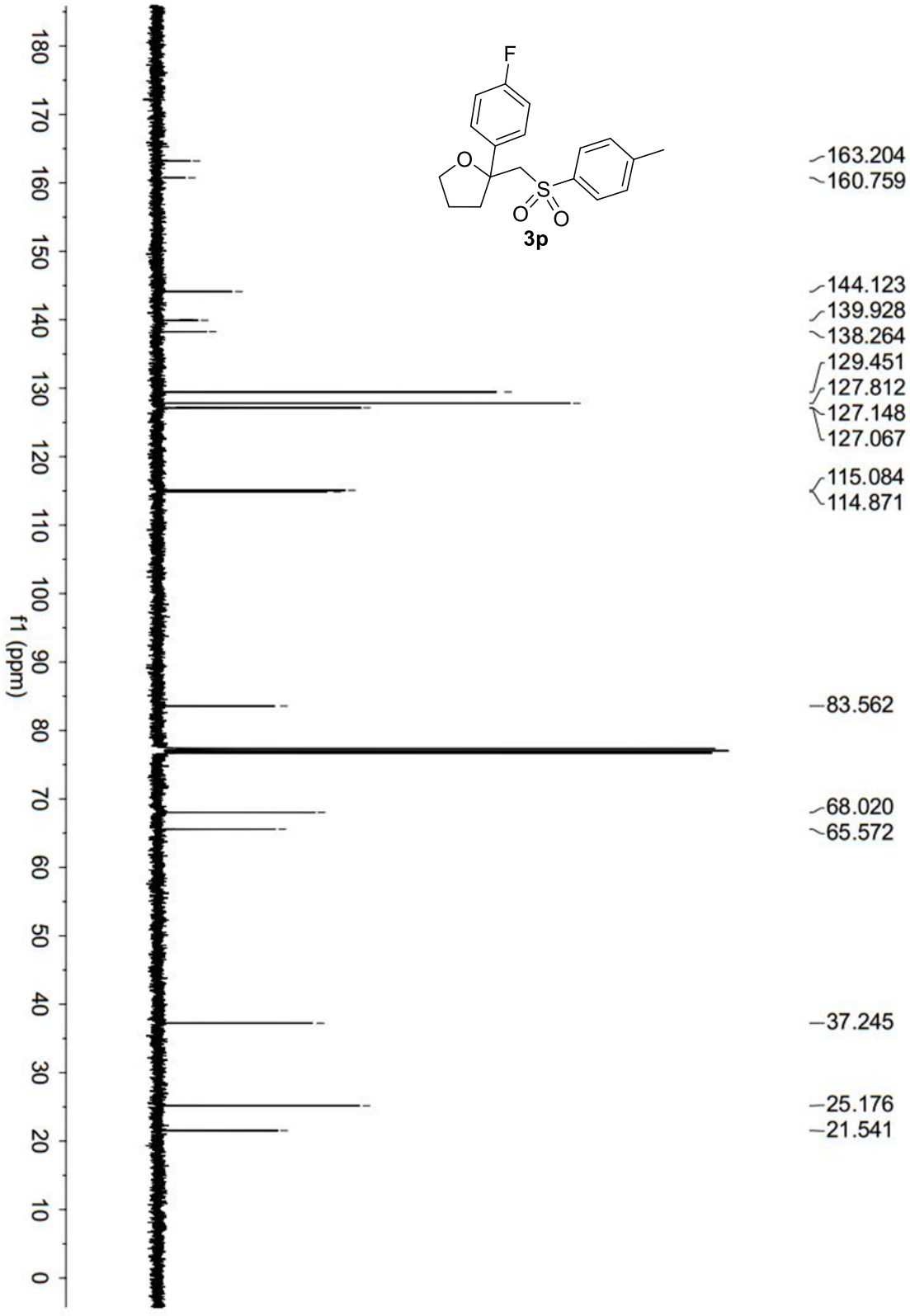
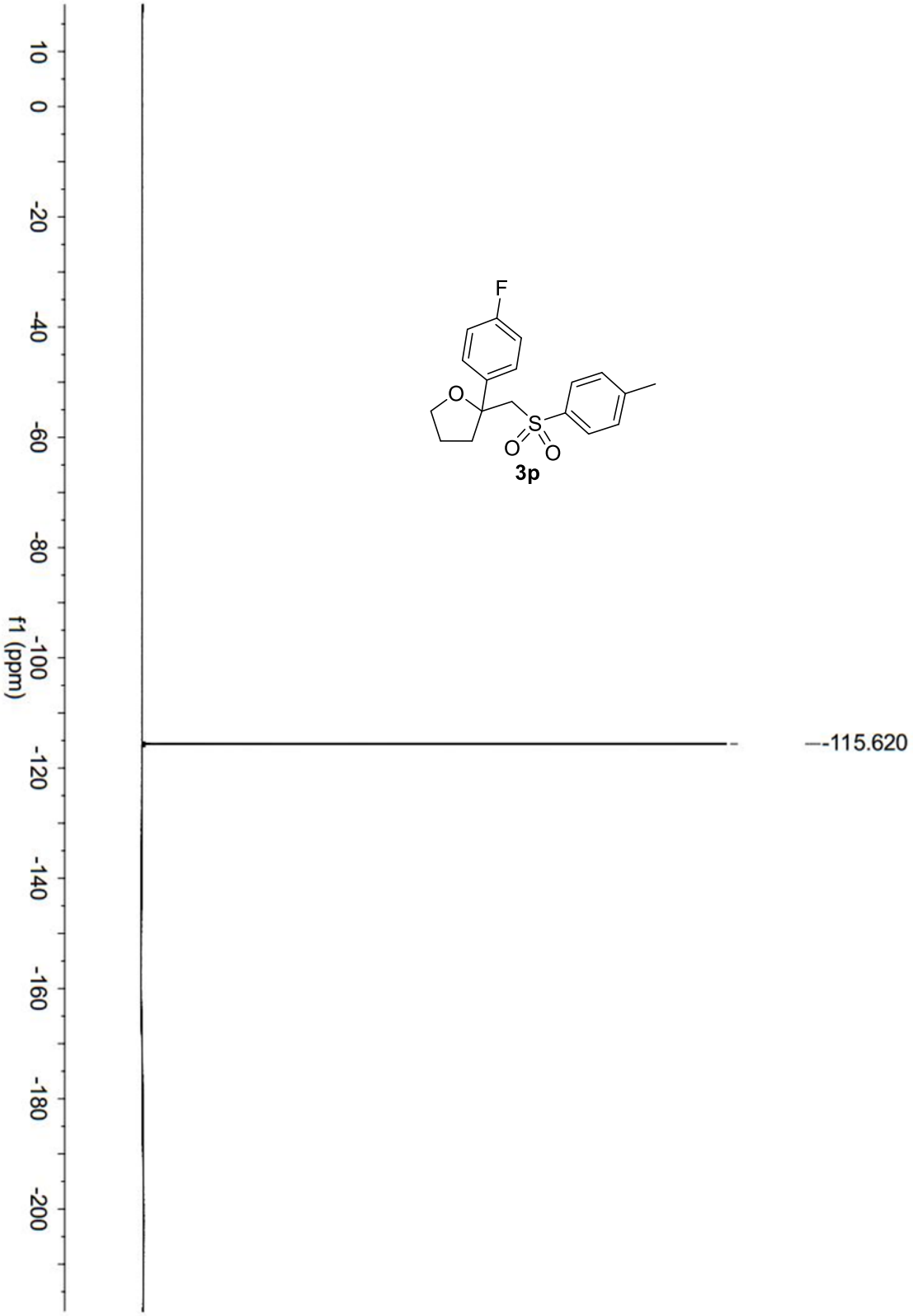
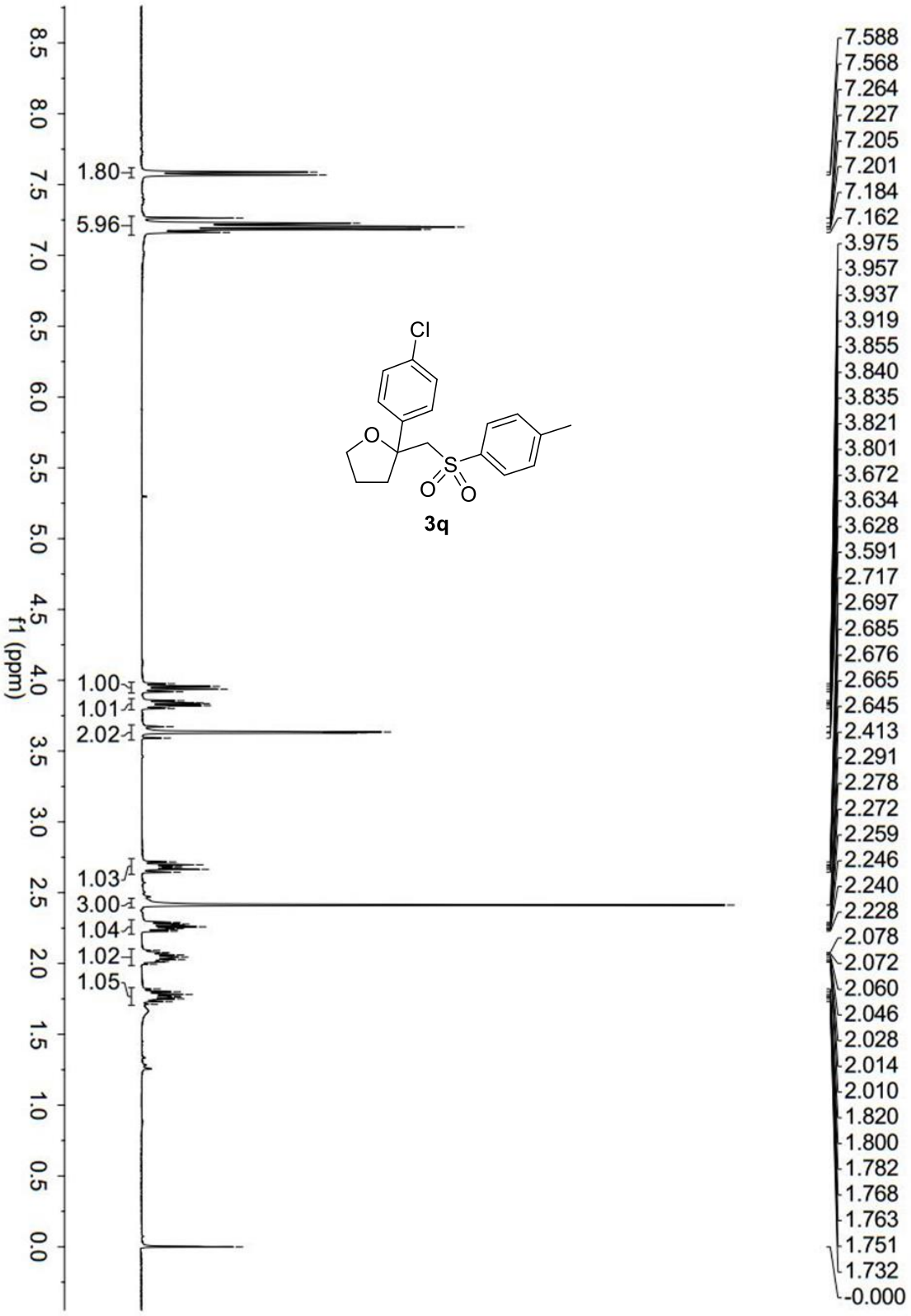
1.768
1.756
1.738
-0.000

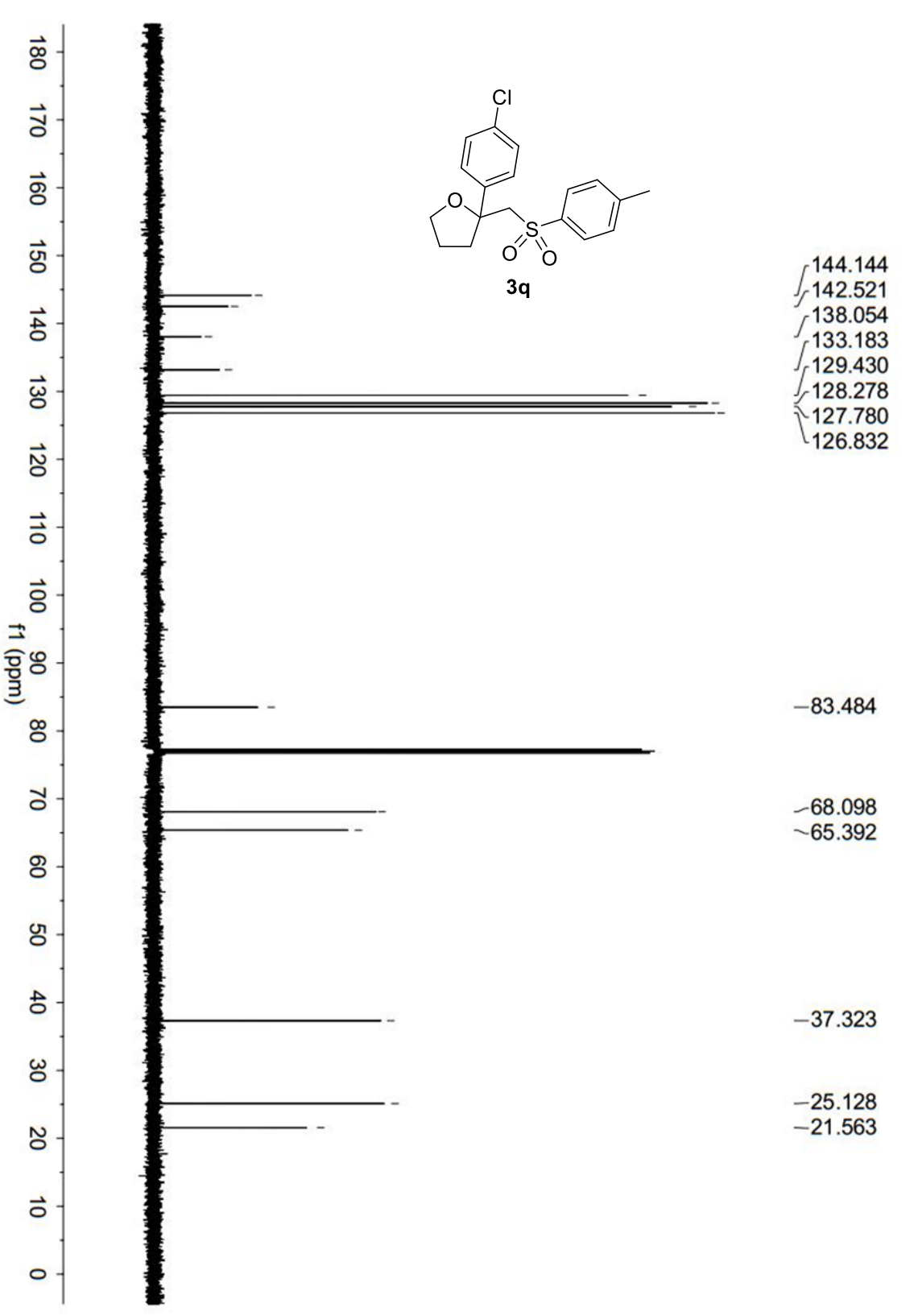

OMe
O
S
O
O
3o
159.543
146.318
143.969
138.386
129.391
129.342
127.850
117.528
112.460
111.110
83.919
68.167
65.339
55.191
36.958
25.221
21.546
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

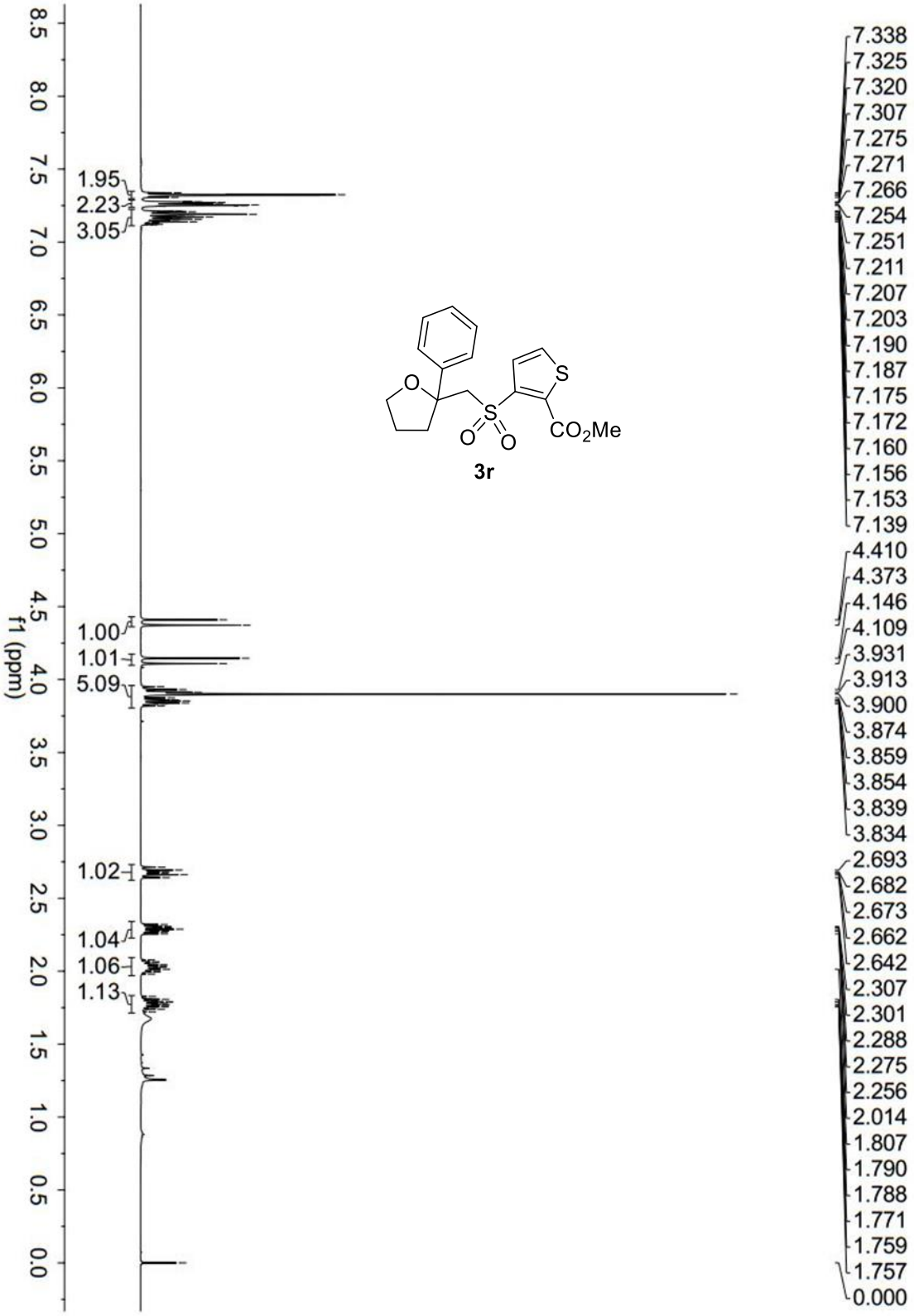

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.80
4.13
1.80
1.00
1.02
2.04
1.01
3.00
1.07
1.03
1.02
F
O
S
O
O
3p
7.616
7.596
7.279
7.274
7.265
7.257
7.249
7.240
7.218
6.932
6.927
6.915
6.910
6.894
6.889
3.949
3.931
3.913
3.853
3.839
3.833
3.819
3.813
3.798
3.631
3.626
2.734
2.723
2.713
2.702
2.682
2.406
2.311
2.299
2.292
2.280
2.268
2.261
2.248
2.064
2.052
2.046
2.033
2.020
1.805
1.785
1.774
1.768
1.754
-0.000

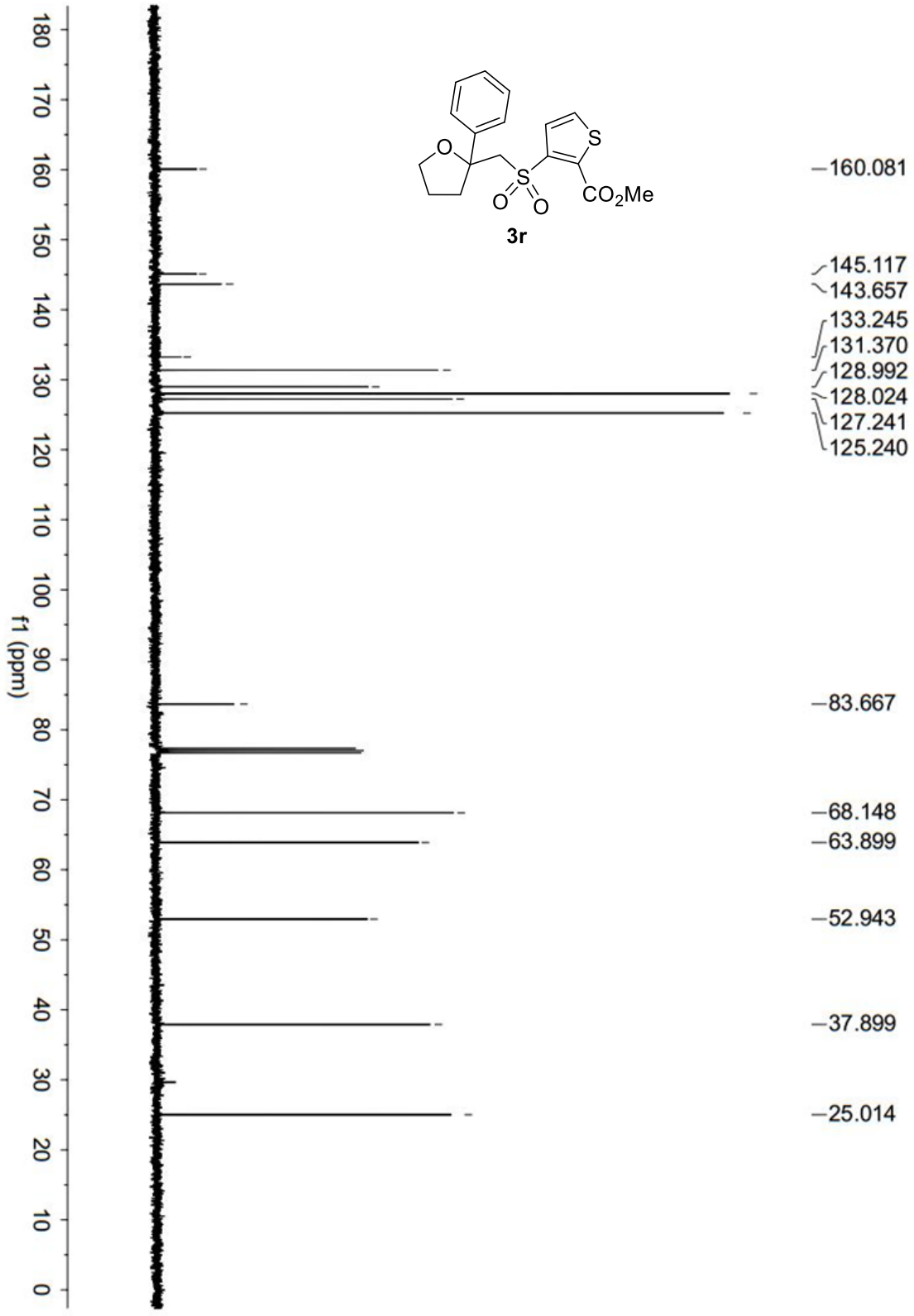

F
O
S
O
O
3p
163.204
160.759
144.123
139.928
138.264
129.451
127.812
127.148
127.067
115.084
114.871
83.562
68.020
65.572
37.245
25.176
21.541
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

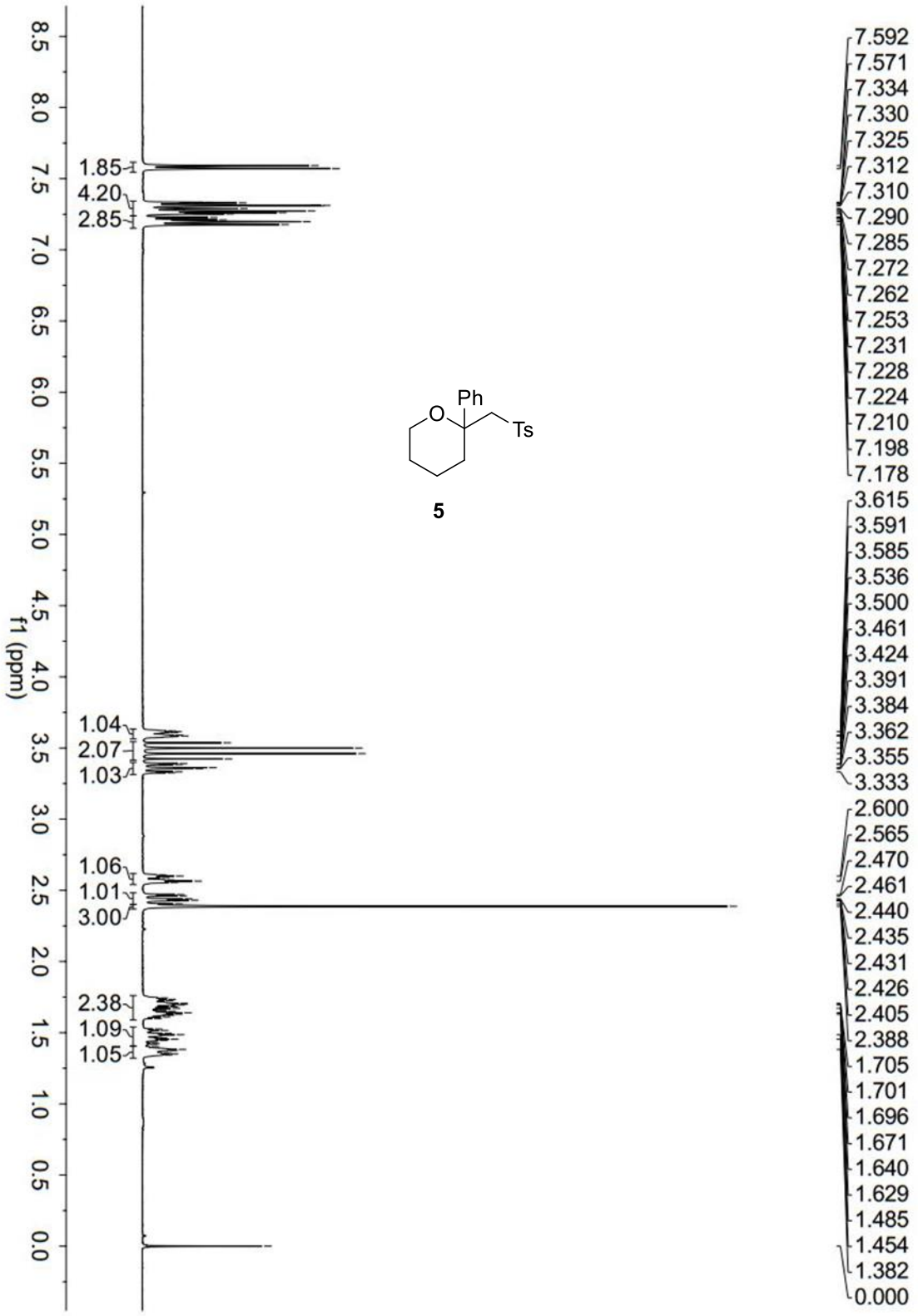

F
O
S
O
O
3p
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)
-115.620

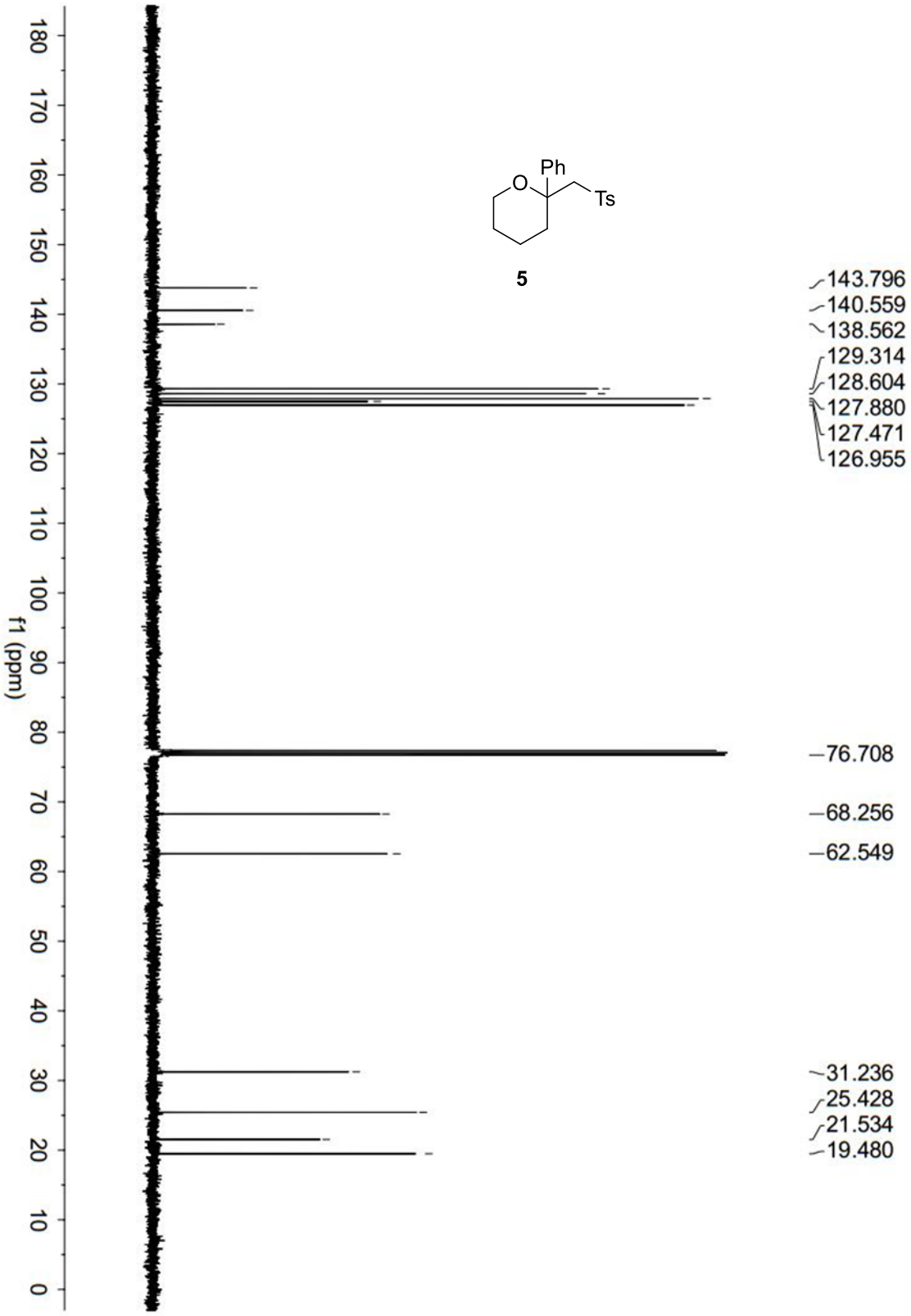

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.80
5.96
1.00
1.01
2.02
1.03
3.00
1.04
1.02
1.05
Cl
O
S
O
O
3q
7.588
7.568
7.264
7.227
7.205
7.201
7.184
7.162
3.975
3.957
3.937
3.919
3.855
3.840
3.835
3.821
3.801
3.672
3.634
3.628
3.591
2.717
2.697
2.685
2.676
2.665
2.645
2.413
2.291
2.278
2.272
2.259
2.246
2.240
2.228
2.078
2.072
2.060
2.046
2.028
2.014
2.010
1.820
1.800
1.782
1.768
1.763
1.751
1.732
-0.000

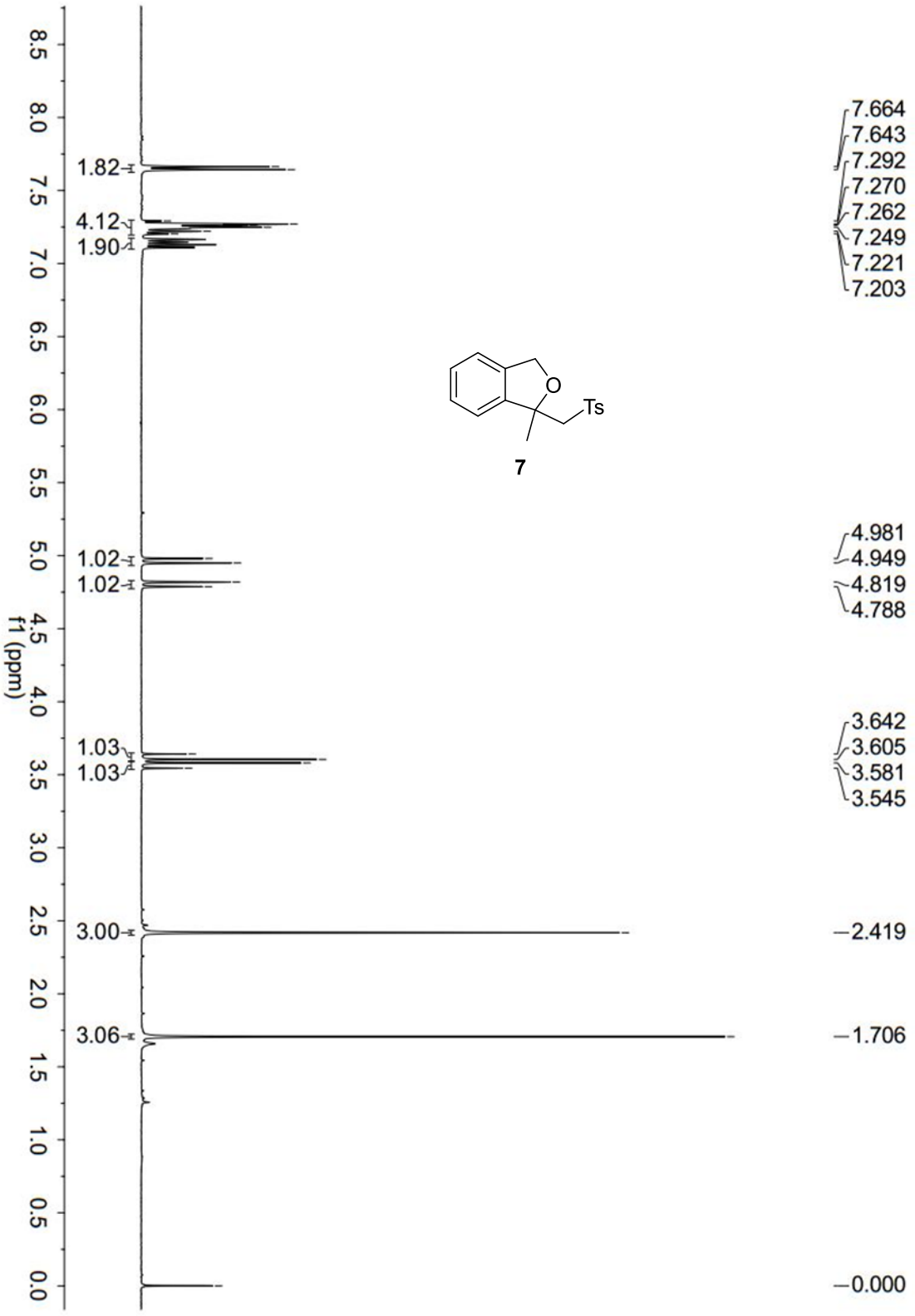

Cl
O
S
O
O
3q
144.144
142.521
138.054
133.183
129.430
128.278
127.780
126.832
83.484
68.098
65.392
37.323
25.128
21.563
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

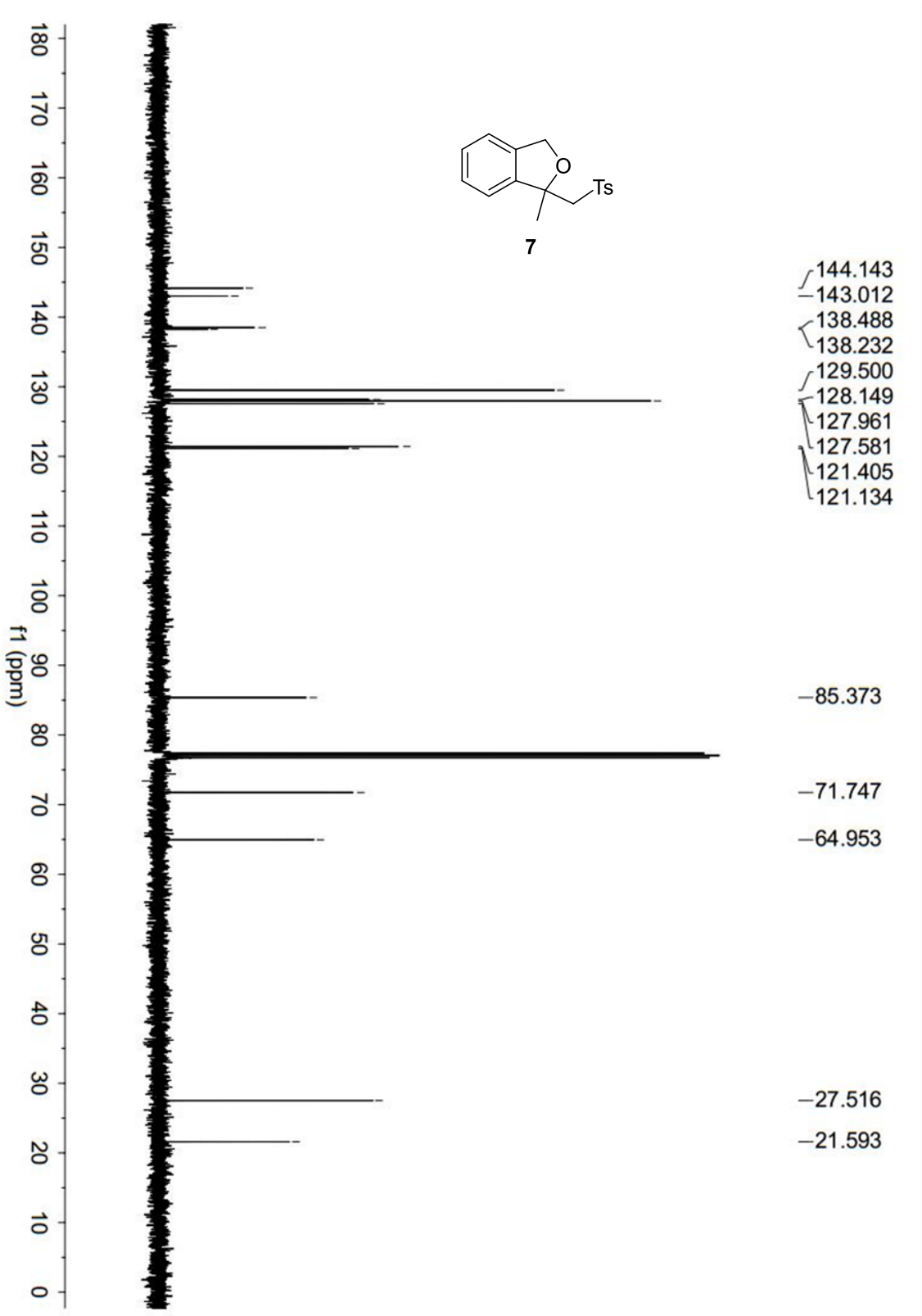

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.95
2.23
3.05
1.00
1.01
5.09
1.02
1.04
1.06
1.13
O
S
O
O
S
CO2Me
3r
7.338
7.325
7.320
7.307
7.275
7.271
7.266
7.254
7.251
7.211
7.207
7.203
7.190
7.187
7.175
7.172
7.160
7.156
7.153
7.139
4.410
4.373
4.146
4.109
3.931
3.913
3.900
3.874
3.859
3.854
3.839
3.834
2.693
2.682
2.673
2.662
2.642
2.307
2.301
2.288
2.275
2.256
2.014
1.807
1.790
1.788
1.771
1.759
1.757
0.000


160.081
145.117
143.657
133.245
131.370
128.992
128.024
127.241
125.240
83.667
68.148
63.899
52.943
37.899
25.014
f1 (ppm)
3r


f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.85
4.20
2.85
1.04
2.07
1.03
1.06
1.01
3.00
2.38
1.09
1.05
Ph
O
Ts
5
7.592
7.571
7.334
7.330
7.325
7.312
7.310
7.290
7.285
7.272
7.262
7.253
7.231
7.228
7.224
7.210
7.198
7.178
3.615
3.591
3.585
3.536
3.500
3.461
3.424
3.391
3.384
3.362
3.355
3.333
2.600
2.565
2.470
2.461
2.440
2.435
2.431
2.426
2.405
2.388
1.705
1.701
1.696
1.671
1.640
1.629
1.485
1.454
1.382
0.000


Ph
O
Ts
5
143.796
140.559
138.562
129.314
128.604
127.880
127.471
126.955
76.708
68.256
62.549
31.236
25.428
21.534
19.480
f1 (ppm)


f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.82
4.12
1.90
1.02
1.02
1.03
1.03
3.00
3.06
7.664
7.643
7.292
7.270
7.262
7.249
7.221
7.203
4.981
4.949
4.819
4.788
3.642
3.605
3.581
3.545
2.419
1.706
0.000
O
Ts
7


O
Ts
7
144.143
143.012
138.488
138.232
129.500
128.149
127.961
127.581
121.405
121.134
85.373
71.747
64.953
27.516
21.593
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0