Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Photoredox-catalyzed sulfonylation of alkenylcyclobutanols with the insertion of sulfur dioxide through semipinacol rearrangement

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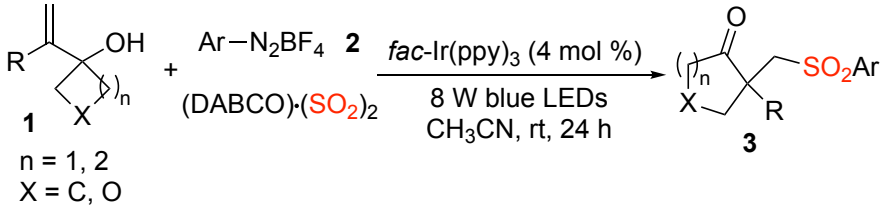
Supporting Information

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, 32-63 μm, 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.

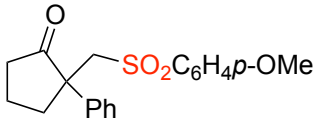
General experimental procedure for the photoredox-catalyzed sulfonylation of alkenylcyclobutanols with the insertion of sulfur dioxide



Cyclobutanol **1** (0.2 mmol) was added to a mixture of $Ir(ppy)_3$ (4 mol %), aryldiazonium tetrafluoroborate **2** (0.3 mmol) and DABCO·$(SO_2)_2$ (0.3 mmol) in DCE (2.0 mL) under N_2 atmosphere. The mixture was stirred under blue LED irradiation (8 W) for 24 hours. 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**.

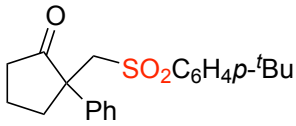
2-Phenyl-2-(tosylmethyl)cyclopentan-1-one (**3a**)

Yellow solid, 55.9 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.26 – 7.16 (m, 5H), 3.72 (d, *J* = 14.6 Hz, 1H), 3.62 (d, *J* = 14.6 Hz, 1H), 3.04 (dd, *J* = 13.8, 6.0 Hz, 1H), 2.73 – 2.61 (m, 1H), 2.45 – 2.25 (m, 5H), 2.14 – 2.02 (m, 1H), 1.85 – 1.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.8, 144.2, 137.8, 135.5, 129.6, 128.8, 127.6, 127.5, 126.9, 63.9, 54.6, 35.8, 32.4, 21.5, 18.5; HRMS (ESI) calcd for $C_{19}H_{21}O_3S$ $[M+H]^+$: 329.1206, found: 329.1214.



2-(((4-Methoxyphenyl)sulfonyl)methyl)-2-phenylcyclopentan-1-one (**3b**)

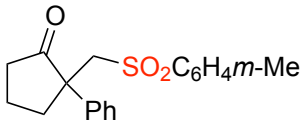
Yellow solid, 62.5 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 2H), 7.33 – 7.27 (m, 2H), 7.27 – 7.17 (m, 3H), 6.89 – 6.82 (m, 2H), 3.83 (s, 3H), 3.72 (d, *J* = 14.6 Hz, 1H), 3.61 (d, *J* = 14.6 Hz, 1H), 3.04 (dd, *J* = 13.9, 6.3 Hz, 1H), 2.67 (ddd, *J* = 13.8, 12.5, 6.9 Hz, 1H), 2.43 – 2.25 (m, 2H), 2.12 – 2.02 (m, 1H), 1.85 – 1.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.9, 163.5, 135.7, 132.6, 129.8, 128.9, 127.7, 127.1, 114.3, 64.2, 55.7, 54.7, 35.9, 32.5, 18.6; HRMS (ESI) calcd for $C_{19}H_{20}O_4SNa$ $[M+Na]^+$: 367.0975, found: 367.0965.



2-(((4-(*tert*-Butyl)phenyl)sulfonyl)methyl)-2-phenylcyclopentan-1-one (**3c**)

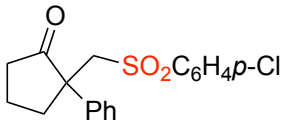
Yellow solid, 63.1 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.9 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.24 – 7.13 (m, 3H), 3.77 (d, *J* = 14.6 Hz, 1H), 3.60 (d, *J* = 14.6 Hz, 1H), 3.09 (dd, *J* = 13.9, 6.0 Hz, 1H), 2.66 (td, *J* = 13.1, 6.9 Hz, 1H), 2.45 – 2.26 (m, 2H), 2.14 – 2.02 (m, 1H), 1.86 – 1.71 (m, 1H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.8, 157.0, 137.6, 135.2, 128.8, 127.6, 127.3, 127.0, 125.9, 63.8,

54.5, 35.7, 35.0, 32.4, 30.9, 18.5; HRMS (ESI) calcd for $C_{22}H_{27}O_4S$ $[M+H]^+$: 371.1675, found: 371.1663.



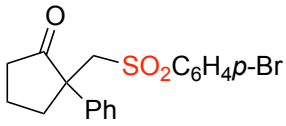
2-Phenyl-2-((*m*-tolylsulfonyl)methyl)cyclopentan-1-one (**3d**)

Yellow solid, 37.0 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 6.8 Hz, 1H), 7.43 (s, 1H), 7.36 – 7.27 (m, 4H), 7.26 – 7.14 (m, 3H), 3.77 (d, *J* = 14.6 Hz, 1H), 3.60 (d, *J* = 14.6 Hz, 1H), 3.09 (dd, *J* = 13.8, 6.0 Hz, 1H), 2.65 (td, *J* = 13.1, 6.8 Hz, 1H), 2.45 – 2.25 (m, 5H), 2.15 – 2.02 (m, 1H), 1.88 – 1.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.8, 140.7, 139.3, 135.4, 134.1, 128.9, 128.8, 127.9, 127.8, 127.1, 124.6, 64.0, 54.7, 35.9, 32.6, 21.2, 18.6; HRMS (ESI) calcd for $C_{19}H_{21}O_3S$ $[M+H]^+$: 329.1206, found: 329.1204.



2-(((4-Chlorophenyl)sulfonyl)methyl)-2-phenylcyclopentan-1-one (**3e**)

Yellow solid, 56.4 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.30 – 7.16 (m, 5H), 3.82 (d, *J* = 14.7 Hz, 1H), 3.58 (d, *J* = 14.7 Hz, 1H), 3.10 (dd, *J* = 13.9, 6.0 Hz, 1H), 2.58 (td, *J* = 13.1, 6.9 Hz, 1H), 2.44 – 2.25 (m, 2H), 2.15 – 2.01 (m, 1H), 1.87 – 1.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.6, 139.9, 139.0, 134.7, 129.2, 128.9, 128.9, 127.8, 127.0, 64.0, 54.5, 35.6, 32.5, 18.5; HRMS (ESI) calcd for $C_{18}H_{17}ClO_3SNa$ $[M+Na]^+$: 371.0479, found: 371.0461.



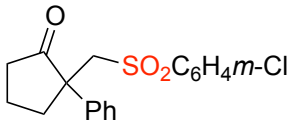
2-(((4-Bromophenyl)sulfonyl)methyl)-2-phenylcyclopentan-1-one (**3f**)

Yellow solid, 65.7 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.45 (m, 4H), 7.31 – 7.17 (m, 5H), 3.82 (d, *J* = 14.7 Hz, 1H), 3.57 (d, *J* = 14.8 Hz, 1H), 3.10 (dd, *J* = 13.9, 6.0 Hz, 1H), 2.57 (td, *J* = 13.1, 6.9 Hz, 1H), 2.43 – 2.25 (m, 2H), 2.14 – 2.03 (m, 1H), 1.87 – 1.70 (m,

1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.5, 139.5, 134.6, 132.2, 129.0, 128.9, 128.5, 127.8, 127.0, 64.0, 54.5, 35.6, 32.5, 18.5; HRMS (ESI) calcd for $C_{18}H_{18}BrO_3S$ $[M+H]^+$: 393.0155, found: 393.0131.

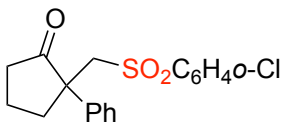
2-Phenyl-2-(((4-(trifluoromethyl)phenyl)sulfonyl)methyl)cyclopentan-1-one (**3g**)

Yellow solid, 56.5 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.21 (m, 2H), 7.20 – 7.11 (m, 3H), 3.92 (d, *J* = 14.9 Hz, 1H), 3.57 (d, *J* = 14.9 Hz, 1H), 3.16 (dd, *J* = 13.9, 6.0 Hz, 1H), 2.53 (td, *J* = 13.1, 7.0 Hz, 1H), 2.39 – 2.25 (m, 2H), 2.16 – 2.02 (m, 1H), 1.91 – 1.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.4, 144.0, 134.7 (q, *J* = 33.1 Hz), 134.2, 128.9, 128.1, 128.0, 127.1, 126.0 (q, *J* = 3.7 Hz), 121.7 (q, *J* = 273.0 Hz), 64.1, 54.4, 35.6, 32.6, 18.5; HRMS (ESI) calcd for $C_{19}H_{17}F_3O_3SNa$ $[M+Na]^+$: 405.0726, found: 405.0743.



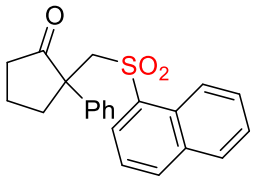
2-(((3-Chlorophenyl)sulfonyl)methyl)-2-phenylcyclopentan-1-one (**3h**)

Yellow solid, 44.5 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.50 (m, 2H), 7.49 – 7.43 (m, 1H), 7.37 – 7.31 (m, 1H), 7.30 – 7.25 (m, 2H), 7.25 – 7.15 (m, 3H), 3.87 (d, *J* = 14.8 Hz, 1H), 3.56 (d, *J* = 14.8 Hz, 1H), 3.14 (dd, *J* = 13.9, 6.2 Hz, 1H), 2.61 – 2.47 (m, 1H), 2.38 – 2.28 (m, 2H), 2.14 – 2.02 (m, 1H), 1.88 – 1.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.5, 142.4, 135.2, 134.5, 133.4, 130.3, 128.9, 128.1, 127.8, 127.1, 125.6, 64.2, 54.6, 35.7, 32.7, 18.5; HRMS (ESI) calcd for $C_{18}H_{17}ClO_3SNa$ $[M+Na]^+$: 371.0479, found: 371.0460.



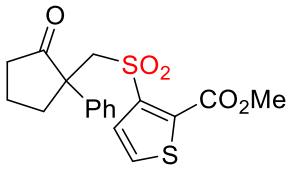
2-(((2-Chlorophenyl)sulfonyl)methyl)-2-phenylcyclopentan-1-one (**3i**)

Yellow solid, 45.3 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.43 – 7.33 (m, 2H), 7.33 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 7.18 – 7.06 (m, 3H), 4.37 (d, *J* = 15.0 Hz, 1H), 3.62 (d, *J* = 15.0 Hz, 1H), 3.15 (dd, *J* = 14.0, 6.2 Hz, 1H), 2.54 – 2.42 (m, 1H), 2.36 – 2.23 (m, 2H), 2.12 – 2.00 (m, 1H), 1.88 – 1.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.3, 138.1, 134.2, 134.1, 132.3, 131.5, 131.1, 128.8, 127.9, 127.1, 62.0, 54.3, 35.6, 32.9, 18.5; HRMS (ESI) calcd for $C_{18}H_{17}ClO_3SNa$ $[M+Na]^+$: 371.0479, found: 371.0473.



2-((Naphthalen-1-ylsulfonyl)methyl)-2-phenylcyclopentan-1-one (**3j**)

Yellow oil, 64.1 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.7 Hz, 1H), 8.06 – 7.94 (m, 2H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.75 – 7.67 (m, 1H), 7.63 – 7.54 (m, 1H), 7.45 – 7.38 (m, 1H), 7.25 – 7.18 (m, 2H), 7.15 – 7.04 (m, 3H), 3.93 (d, *J* = 14.6 Hz, 1H), 3.81 (d, *J* = 14.6 Hz, 1H), 3.12 (dd, *J* = 13.9, 6.2 Hz, 1H), 2.80 – 2.67 (m, 1H), 2.48 – 2.25 (m, 2H), 2.15 – 2.05 (m, 1H), 1.87 – 1.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.8, 135.5, 135.2, 135.0, 134.0, 130.2, 129.1, 128.8, 128.7, 128.5, 127.7, 126.9, 124.3, 124.1, 63.1, 54.6, 36.0, 32.6, 18.7; HRMS (ESI) calcd for $C_{22}H_{20}O_3SNa$ $[M+Na]^+$: 387.1025, found: 387.1012.



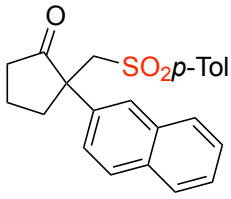
Methyl 3-(((2-oxo-1-phenylcyclopentyl)methyl)sulfonyl)thiophene-2-carboxylate (**3k**)

Yellow solid, 60.5 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 3H), 7.23 – 7.11 (m, 4H), 4.72 (d, *J* = 15.0 Hz, 1H), 3.91 (s, 3H), 3.71 (d, *J* = 15.0 Hz, 1H), 3.14 (dd, *J* = 14.1, 6.1 Hz, 1H), 2.55 – 2.44 (m, 1H), 2.33 – 2.24 (m, 2H), 2.11 – 2.01 (m, 1H), 1.88 – 1.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.4, 159.9, 144.7, 134.4, 133.8, 131.0, 129.4,

128.7, 127.8, 127.2, 62.8, 54.3, 53.1, 35.7, 32.8, 18.6; HRMS (ESI) calcd for $C_{18}H_{18}O_5S_2Na$ $[M+Na]^+$: 401.0488, found: 401.0471.

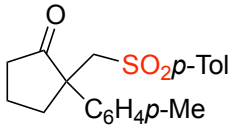
2-(((4-Methoxyphenyl)sulfonyl)methyl)-2-(*p*-tolyl)cyclopentan-1-one (**3l**)

Yellow solid, 55.9 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 2H), 7.20 – 7.14 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.88 – 6.82 (m, 2H), 3.84 (s, 3H), 3.73 (d, *J* = 14.6 Hz, 1H), 3.57 (d, *J* = 14.6 Hz, 1H), 3.04 (dd, *J* = 13.8, 6.2 Hz, 1H), 2.66 – 2.55 (m, 1H), 2.36 – 2.29 (m, 2H), 2.27 (s, 3H), 2.12 – 2.00 (m, 1H), 1.84 – 1.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.0, 163.3, 137.5, 132.5, 132.2, 129.7, 129.6, 127.0, 114.1, 64.2, 55.6, 54.3, 35.8, 32.5, 20.9, 18.6; HRMS (ESI) calcd for $C_{20}H_{22}O_4SNa$ $[M+Na]^+$: 382.1131, found: 382.1127.



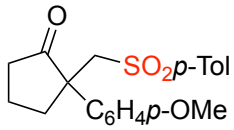
2-(Naphthalen-2-yl)-2-(tosylmethyl)cyclopentan-1-one (**3m**)

Yellow solid, 46.0 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.57 (m, 4H), 7.49 – 7.33 (m, 5H), 6.94 (d, *J* = 8.2 Hz, 2H), 3.93 (d, *J* = 14.8 Hz, 1H), 3.62 (d, *J* = 14.8 Hz, 1H), 3.23 (dd, *J* = 14.0, 6.2 Hz, 1H), 2.72 – 2.59 (m, 1H), 2.45 – 2.27 (m, 2H), 2.19 (s, 3H), 2.16 – 2.06 (m, 1H), 1.91 – 1.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.7, 144.1, 137.5, 133.0, 132.5, 131.9, 129.3, 128.8, 128.0, 127.4, 127.3, 126.7, 126.5, 126.4, 124.4, 63.8, 54.7, 35.8, 32.6, 21.4, 18.6; HRMS (ESI) calcd for $C_{23}H_{22}O_3SNa$ $[M+Na]^+$: 401.1182, found: 401.1173.



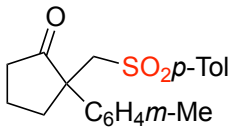
2-(*p*-Tolyl)-2-(tosylmethyl)cyclopentan-1-one (**3n**)

Yellow solid, 55.4 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.13 (m, 4H), 7.02 (d, *J* = 8.3 Hz, 2H), 3.73 (d, *J* = 14.6 Hz, 1H), 3.57 (d, *J* = 14.6 Hz, 1H), 3.04 (dd, *J* = 13.8, 6.2 Hz, 1H), 2.67 – 2.56 (m, 1H), 2.39 (s, 3H), 2.33 (dd, *J* = 10.5, 7.7 Hz, 2H), 2.27 (s, 3H), 2.12 – 2.01 (m, 1H), 1.84 – 1.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.9, 144.2, 137.9, 137.6, 132.2, 129.5, 127.6, 126.9, 64.0, 54.3, 35.8, 32.5, 21.6, 20.9, 18.6; HRMS (ESI) calcd for $C_{20}H_{22}O_3SNa$ $[M+Na]^+$: 365.1182 , found: 365.1170.



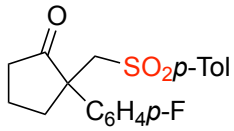
2-(4-Methoxyphenyl)-2-(tosylmethyl)cyclopentan-1-one (**3o**)

Light yellow solid, 53.0 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.23 – 7.15 (m, 4H), 6.77 – 6.70 (m, 2H), 3.79 – 3.70 (m, 4H), 3.55 (d, *J* = 14.6 Hz, 1H), 3.04 (dd, *J* = 13.9, 6.2 Hz, 1H), 2.64 – 2.52 (m, 1H), 2.39 (s, 3H), 2.36 – 2.28 (m, 2H), 2.10 – 2.01 (m, 1H), 1.84 – 1.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.8, 159.0, 144.1, 137.9, 129.6, 128.3, 127.5, 126.7, 114.2, 64.1, 55.2, 53.9, 35.7, 32.6, 21.5, 18.5; HRMS (ESI) calcd for $C_{20}H_{22}O_4SNa$ $[M+Na]^+$: 381.1131, found: 381.1114.



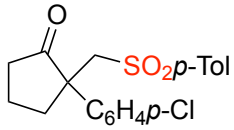
2-(*m*-Tolyl)-2-(tosylmethyl)cyclopentan-1-one (**3p**)

Yellow solid, 45.8 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.23 – 7.08 (m, 4H), 7.05 – 6.94 (m, 2H), 3.74 (d, *J* = 14.6 Hz, 1H), 3.60 (d, *J* = 14.6 Hz, 1H), 3.04 (dd, *J* = 13.8, 5.8 Hz, 1H), 2.72 – 2.59 (m, 1H), 2.43 – 2.29 (m, 5H), 2.22 (s, 3H), 2.12 – 2.01 (m, 1H), 1.86 – 1.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.0, 144.1, 138.5, 137.9, 135.3, 129.5, 128.8, 128.4, 127.8, 127.5, 124.0, 63.9, 54.6, 35.9, 32.5, 21.5, 21.4, 18.6; HRMS (ESI) calcd for $C_{20}H_{22}O_3S$ $[M+Na]^+$: 365.1182, found: 365.1173.



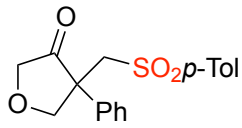
2-(4-Fluorophenyl)-2-(tosylmethyl)cyclopentan-1-one (**3q**)

Yellow solid, 41.5 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.30 – 7.24 (m, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.94 – 6.86 (m, 2H), 3.75 (d, *J* = 14.7 Hz, 1H), 3.52 (d, *J* = 14.6 Hz, 1H), 3.10 – 3.01 (m, 1H), 2.65 – 2.54 (m, 1H), 2.40 (s, 3H), 2.37 – 2.25 (m, 2H), 2.14 – 2.03 (m, 1H), 1.84 – 1.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.7, 162.2 (d, *J* = 248.0 Hz), 144.4, 137.8, 130.7 (d, *J* = 3.3 Hz), 129.6, 129.0 (d, *J* = 8.2 Hz), 127.5, 115.7 (d, *J* = 21.4 Hz), 64.0, 54.0, 35.7, 32.7, 21.5, 18.6; HRMS (ESI) calcd for $C_{19}H_{19}FO_3SNa$ $[M+Na]^+$: 369.0931, found: 369.0934.



2-(4-Chlorophenyl)-2-(tosylmethyl)cyclopentan-1-one (**3r**)

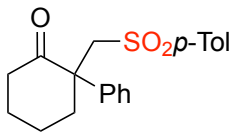
Yellow solid, 52.1 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.45 (m, 2H), 7.24 – 7.12 (m, 6H), 3.79 (d, *J* = 14.7 Hz, 1H), 3.49 (d, *J* = 14.7 Hz, 1H), 3.12 – 3.03 (m, 1H), 2.62 – 2.50 (m, 1H), 2.40 (s, 3H), 2.37 – 2.29 (m, 2H), 2.14 – 2.03 (m, 1H), 1.84 – 1.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.4, 144.4, 137.6, 134.0, 133.3, 129.6, 128.9, 128.6, 127.5, 63.9, 54.0, 35.7, 32.5, 21.6, 18.6; HRMS (ESI) calcd for $C_{19}H_{19}ClO_3SNa$ $[M+Na]^+$: 385.0636, found: 385.0625.



4-Phenyl-4-(tosylmethyl)dihydrofuran-3(2*H*)-one (**3s**)

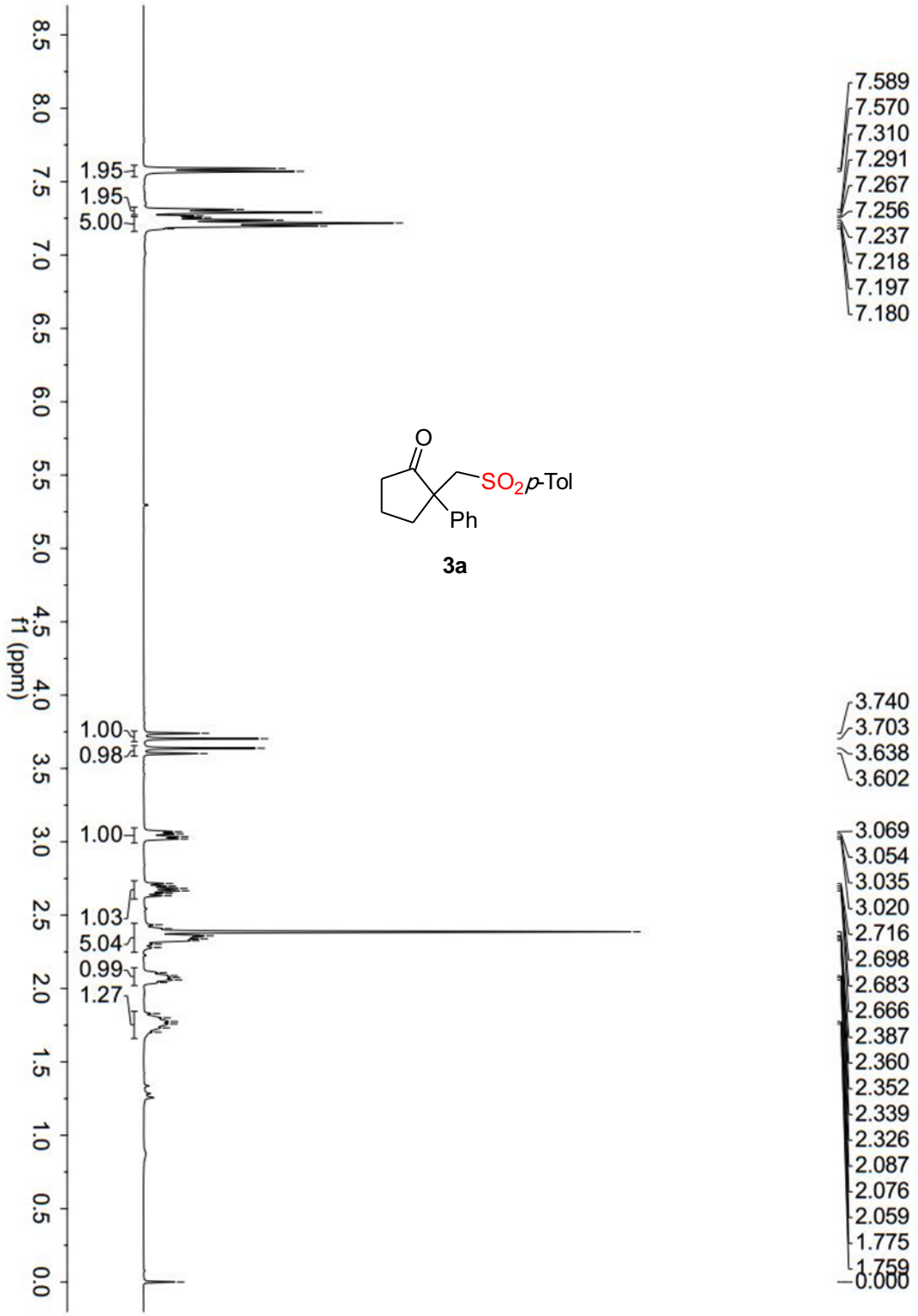
Yellow solid, 37.0 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H), 7.35 – 7.29 (m, 2H), 7.24 – 7.18 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.22 (d, *J* = 10.9 Hz, 1H), 4.63 (d, *J* = 10.9 Hz, 1H), 4.09 (d, *J* = 17.4 Hz, 1H), 4.03 – 3.93 (m, 2H), 3.59 (d, *J* = 14.9 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.2, 144.6, 137.1, 133.1, 129.7, 128.9,

128.0, 127.7, 126.8, 73.9, 69.5, 60.9, 53.2, 21.6; HRMS (ESI) calcd for $C_{18}H_{18}O_4SNa$ $[M+Na]^+$: 353.0818, found: 353.0810.



2-Phenyl-2-(tosylmethyl)cyclohexan-1-one (**3t**)

Yellow solid, 34.9 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.30 – 7.21 (m, 3H), 7.21 – 7.15 (m, 4H), 3.73 (d, *J* = 14.8 Hz, 1H), 3.63 (d, *J* = 14.8 Hz, 1H), 3.43 – 3.35 (m, 1H), 2.38 (s, 3H), 2.37 – 2.21 (m, 3H), 1.99 – 1.90 (m, 1H), 1.87 – 1.74 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 143.9, 138.6, 136.8, 129.5, 129.1, 127.6, 127.4, 127.2, 65.0, 56.1, 39.2, 34.0, 27.4, 21.5, 21.3; HRMS (ESI) calcd for $C_{20}H_{22}O_3SNa$ $[M+Na]^+$: 365.1182, found: 365.1175.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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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1.95
5.00
1.00
0.98
1.00
1.03
5.04
0.99
1.27
7.589
7.570
7.310
7.291
7.267
7.256
7.237
7.218
7.197
7.180
3.740
3.703
3.638
3.602
3.069
3.054
3.035
3.020
2.716
2.698
2.683
2.666
2.387
2.360
2.352
2.339
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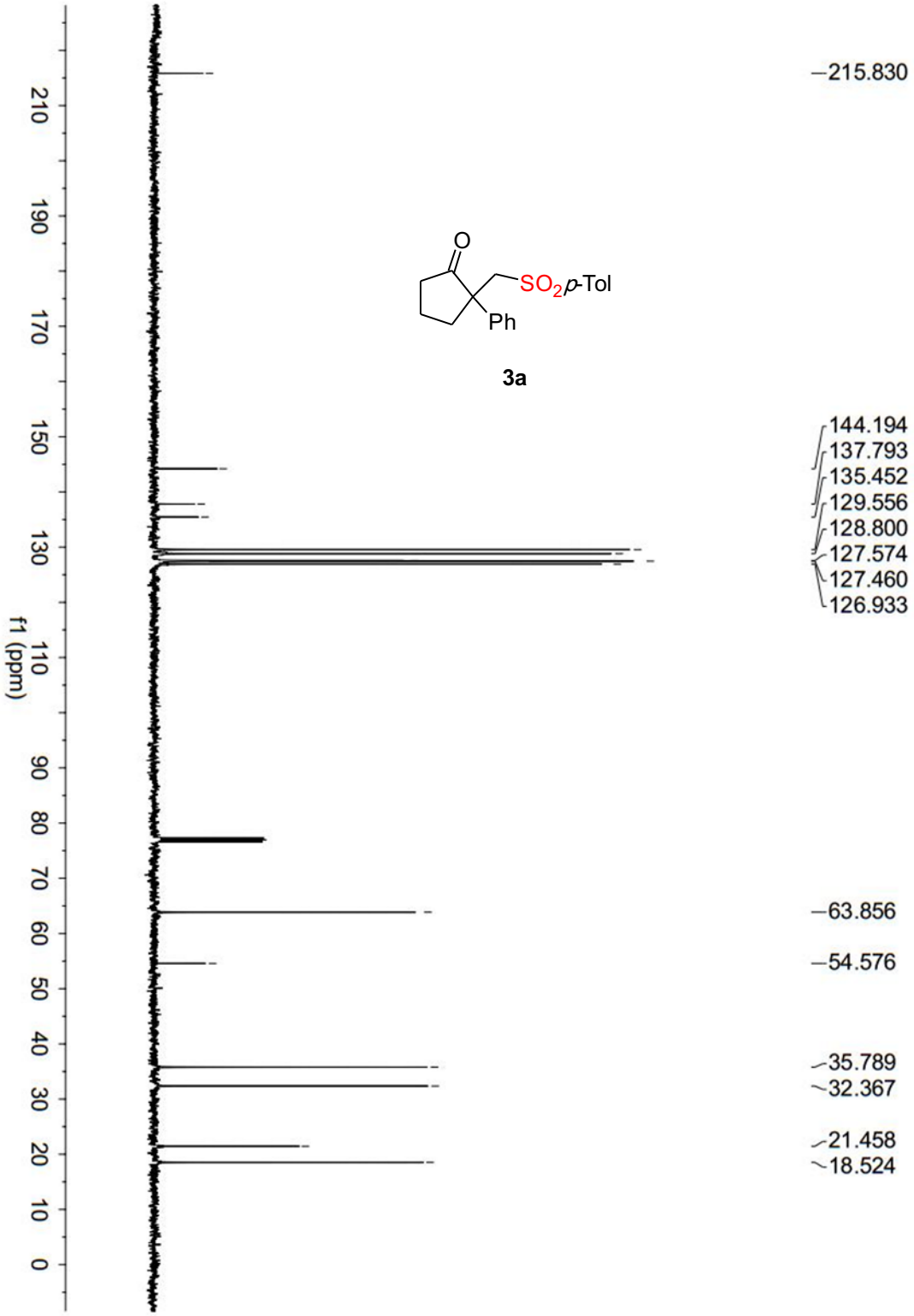
2.076
2.059
1.775
1.759
0.000
O
SO2p-Tol
Ph

3a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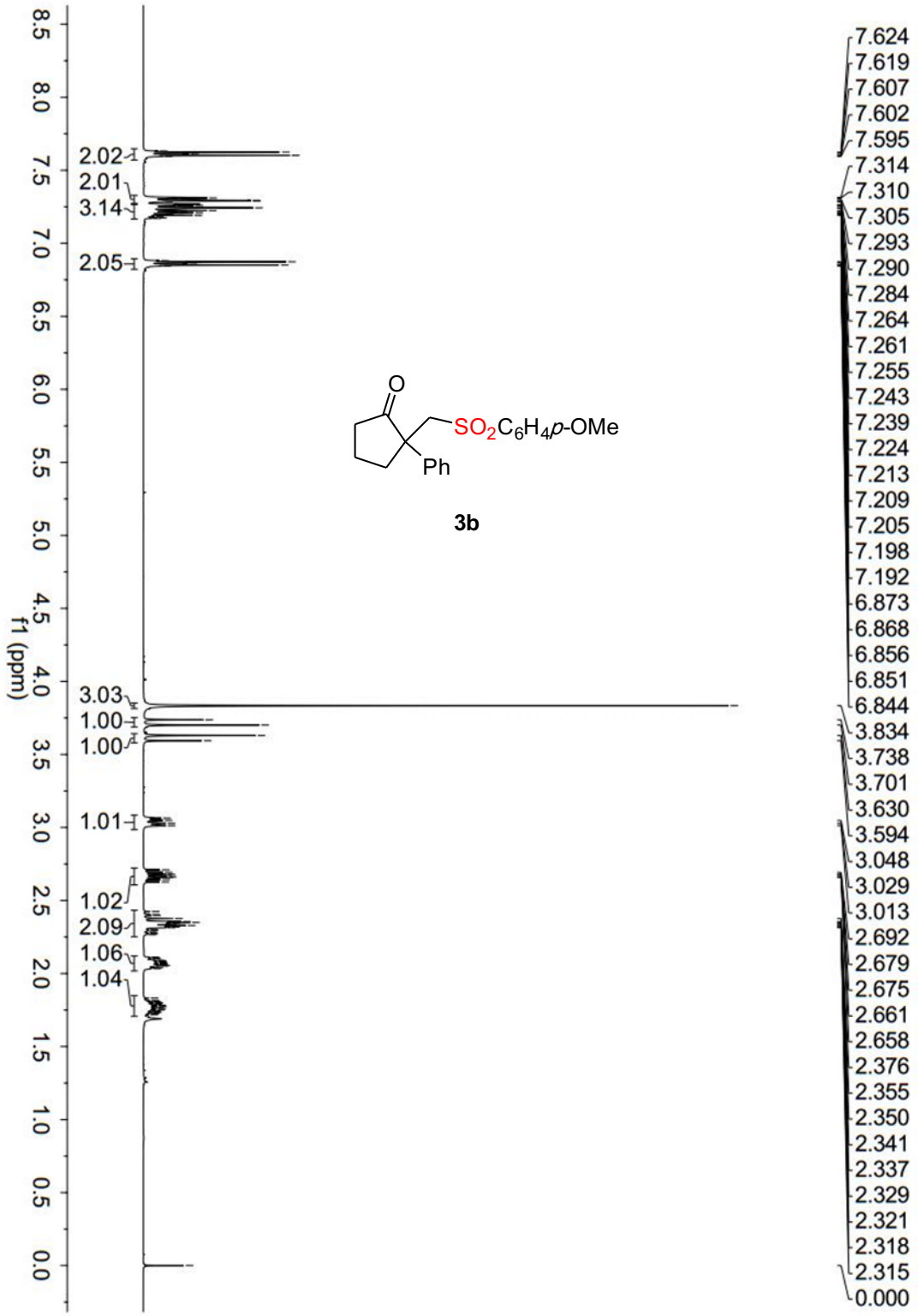
144.194
137.793
135.452
129.556
128.800
127.574
127.460
126.933
63.856
54.576
35.789
32.367
21.458
18.524
f1 (ppm)
O
SO2p-Tol
Ph

3a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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)
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2.01
3.14
2.05
3.03
1.00
1.00
1.01
1.02
2.09
1.06
1.04
O
SO2C6H4p-OMe
Ph
7.624
7.619
7.607
7.602
7.595
7.314
7.310
7.305
7.293
7.290
7.284
7.264
7.261
7.255
7.243
7.239
7.224
7.213
7.209
7.205
7.198
7.192
6.873
6.868
6.856
6.851
6.844
3.834
3.738
3.701
3.630
3.594
3.048
3.029
3.013
2.692
2.679
2.675
2.661
2.658
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2.355
2.350
2.341
2.337
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2.321
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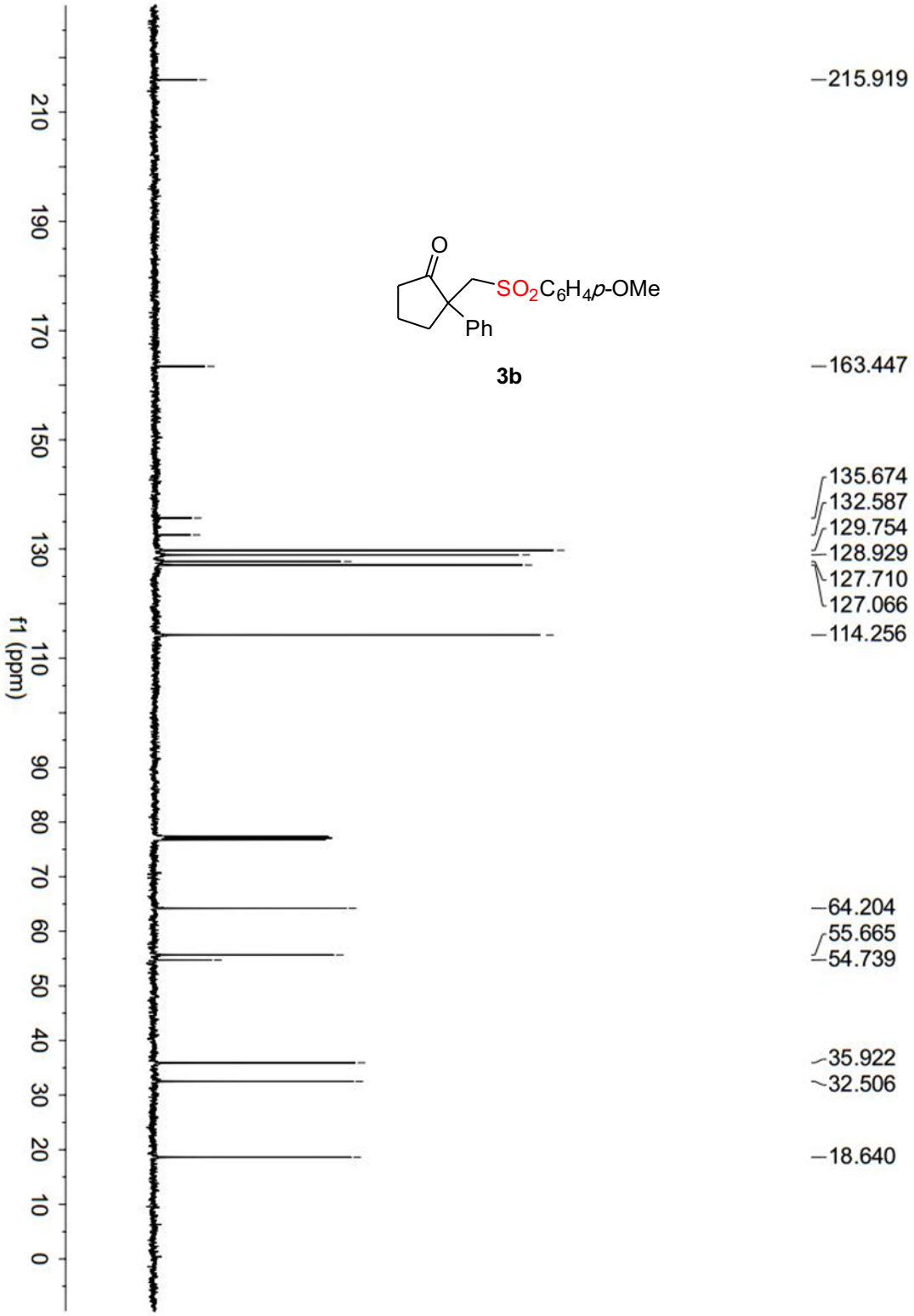
2.315
0.000

3b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163.447
135.674
132.587
129.754
128.929
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127.066
114.256
64.204
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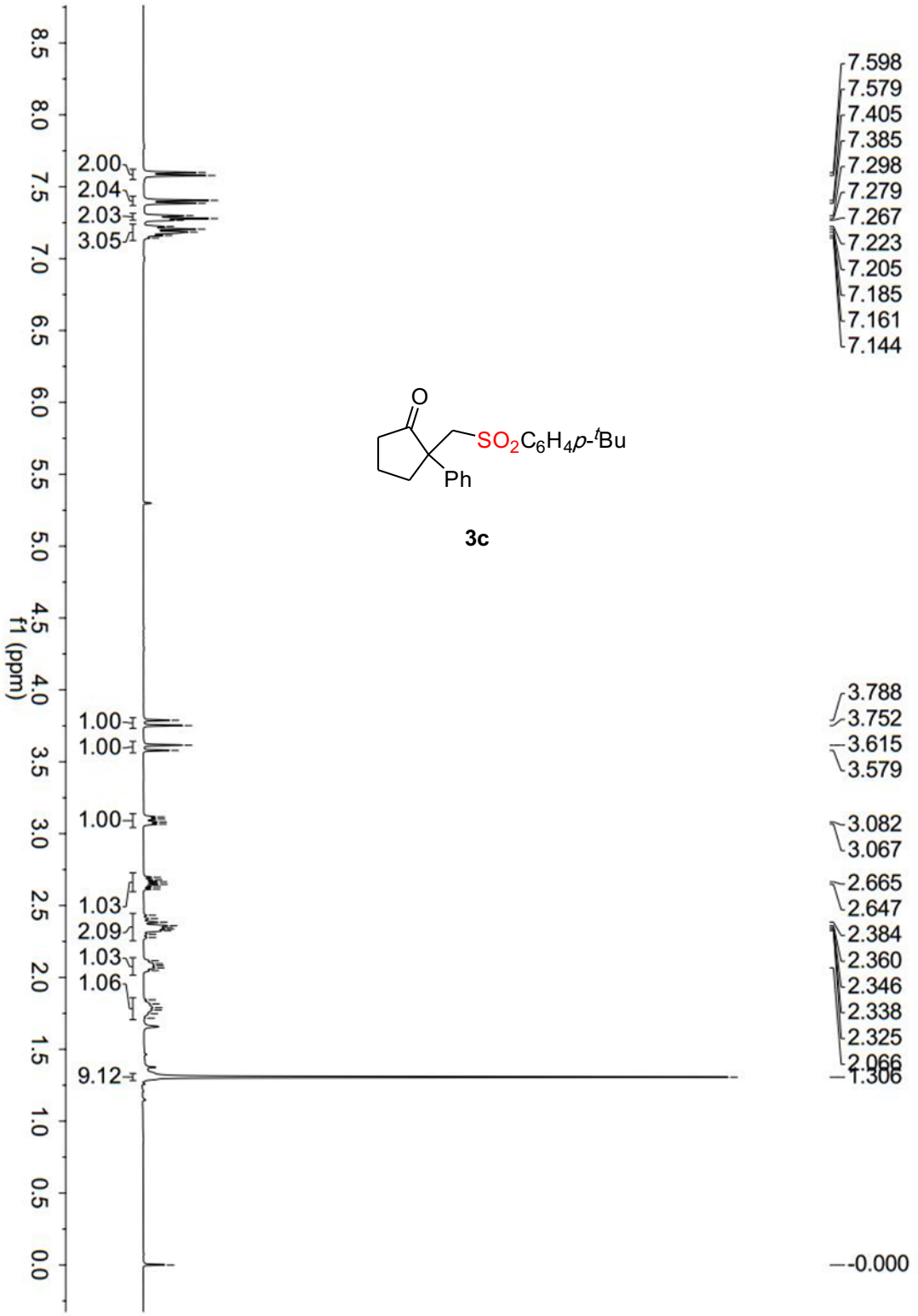
54.739
35.922
32.506
18.640
f1 (ppm)
O
SO2C6H4p-OMe
Ph
3b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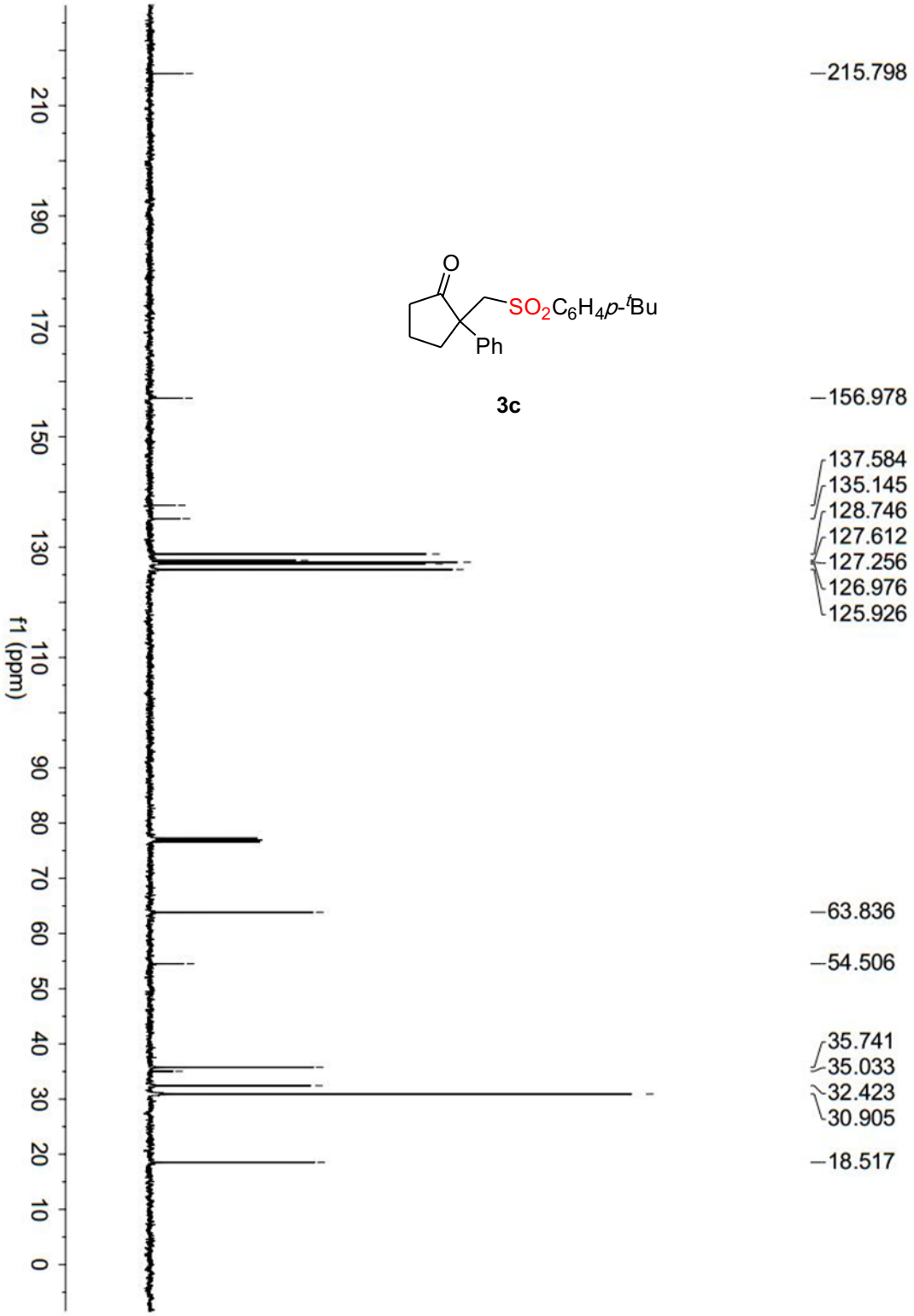
7.385
7.298
7.279
7.267
7.223
7.205
7.185
7.161
7.144
3.788
3.752
3.615
3.579
3.082
3.067
2.665
2.647
2.384
2.360
2.346
2.338
2.325
2.066
1.306
-0.000
2.00
2.04
2.03
3.05
1.00
1.00
1.00
1.03
2.09
1.03
1.06
9.12
f1 (ppm)
O
SO2C6H4p-tBu
Ph

3c


O
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Ph
3c
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135.145
128.746
127.612
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63.836
54.506
35.741
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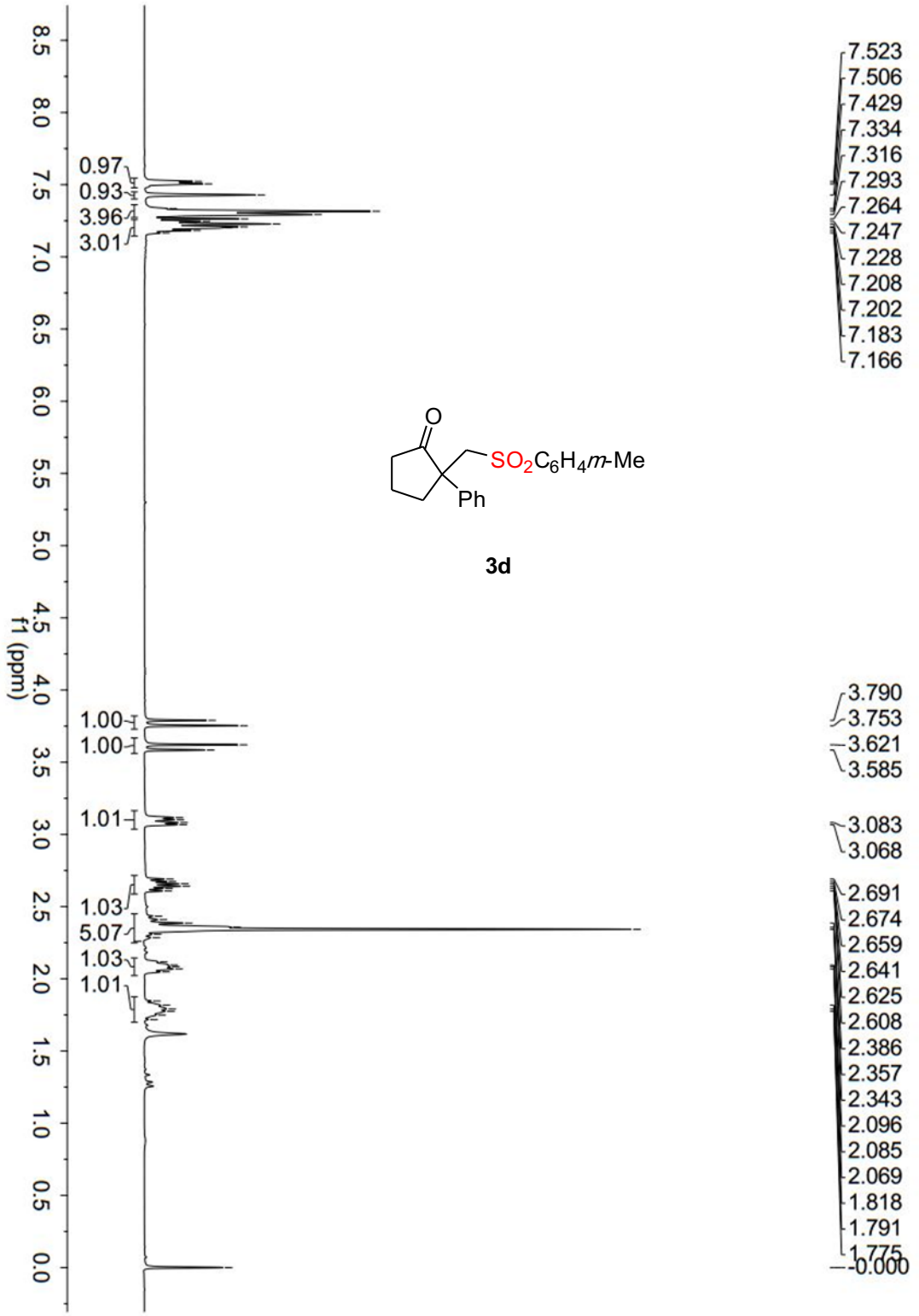
32.423
30.905
18.517
f1 (ppm)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7.429
7.334
7.316
7.293
7.264
7.247
7.228
7.208
7.202
7.183
7.166
O
SO2C6H4m-Me
Ph
3d
3.790
3.753
3.621
3.585
3.083
3.068
2.691
2.674
2.659
2.641
2.625
2.608
2.386
2.357
2.343
2.096
2.085
2.069
1.818
1.791
1.775
0.000
0.97
0.93
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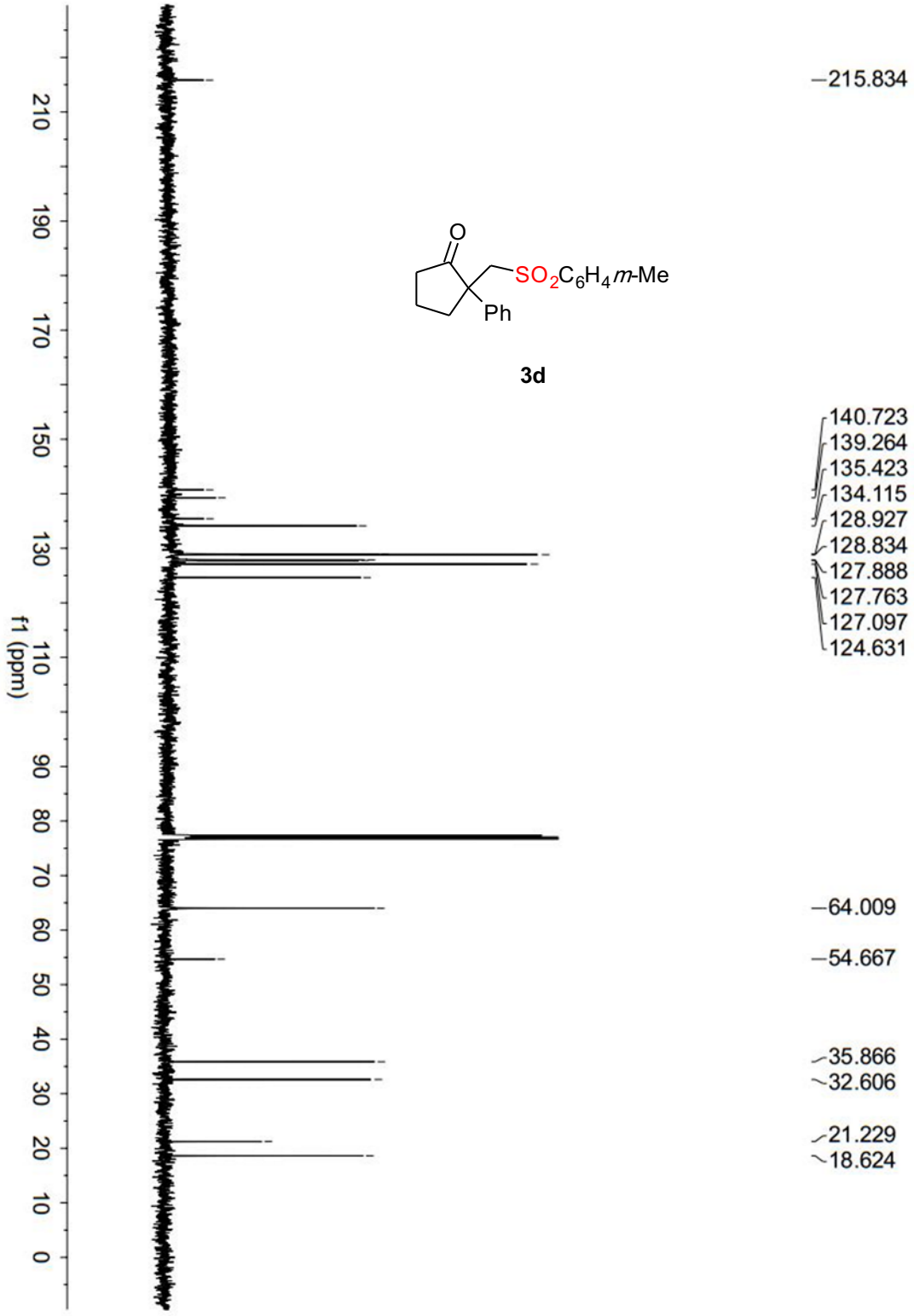
1.00
1.00
1.01
1.03
5.07
1.03
1.01
f1 (ppm)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Ph
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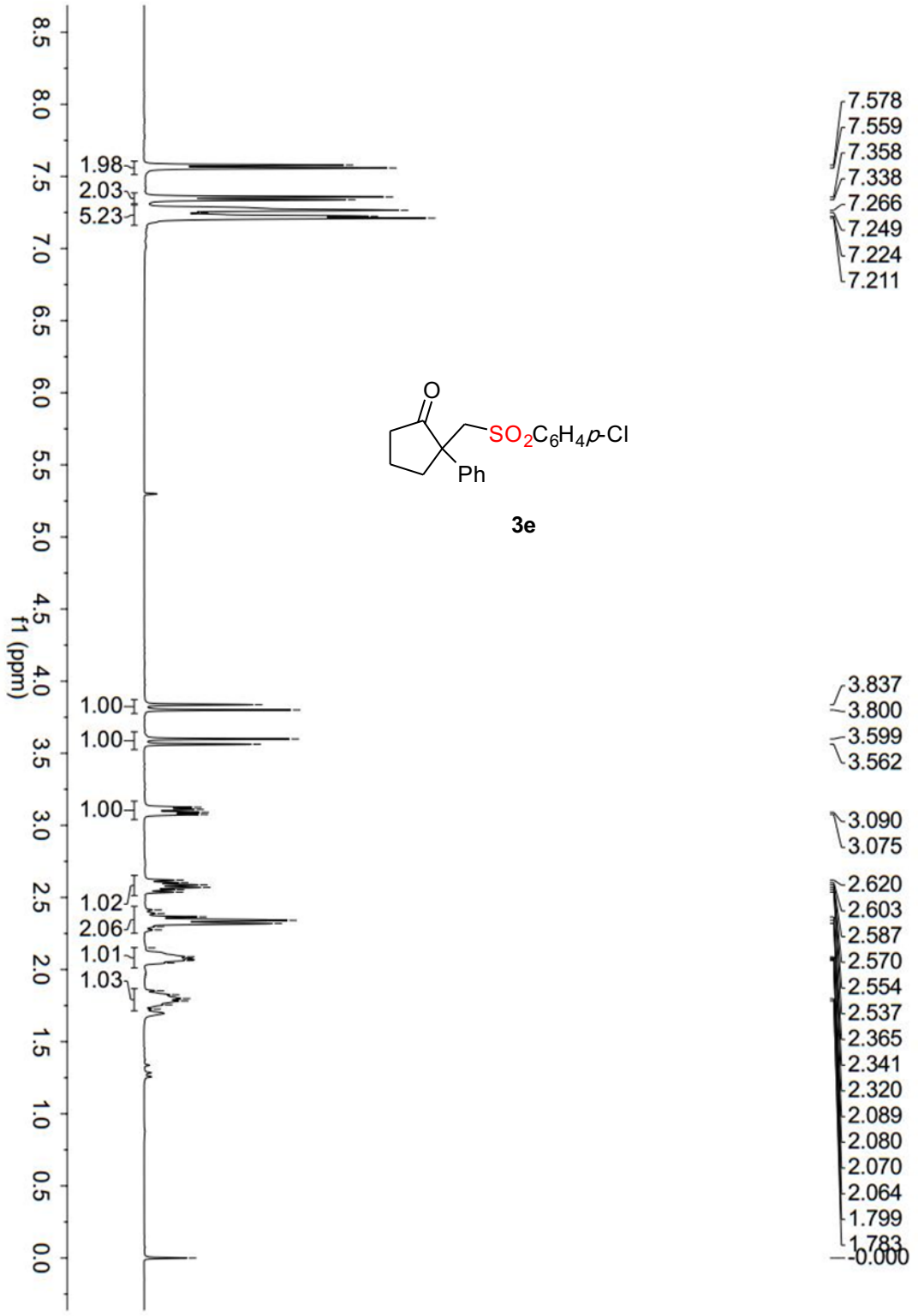
135.423
134.115
128.927
128.834
127.888
127.763
127.097
124.631
64.009
54.667
35.866
32.606
21.229
18.624
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.98
2.03
5.23
1.00
1.00
1.00
1.02
2.06
1.01
1.03
7.578
7.559
7.358
7.338
7.266
7.249
7.224
7.211
3.837
3.800
3.599
3.562
3.090
3.075
2.620
2.603
2.587
2.570
2.554
2.537
2.365
2.341
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2.089
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2.070
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0.000
O
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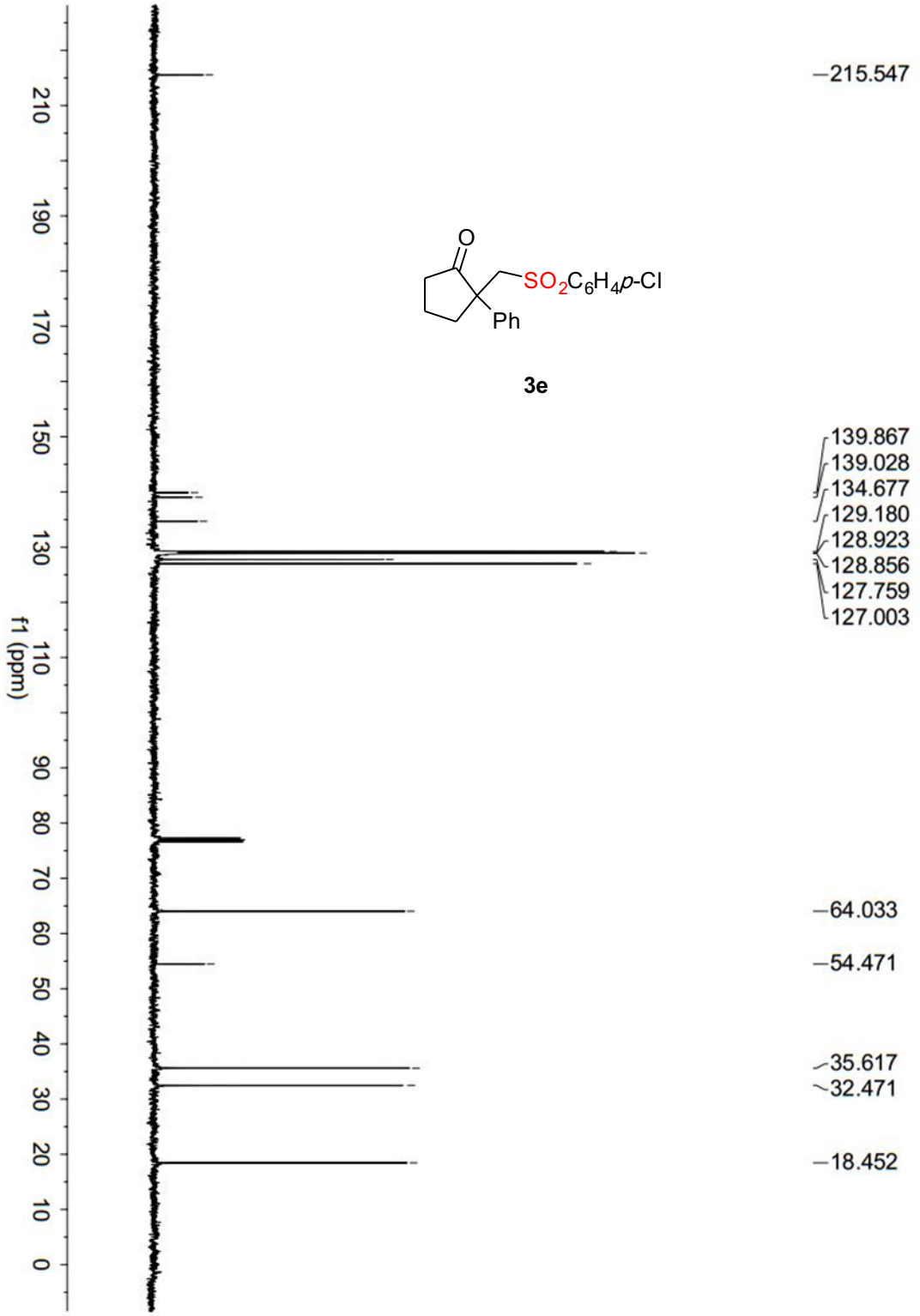
Ph

3e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127.759
127.003
64.033
54.471
35.617
32.471
18.452
f1 (ppm)
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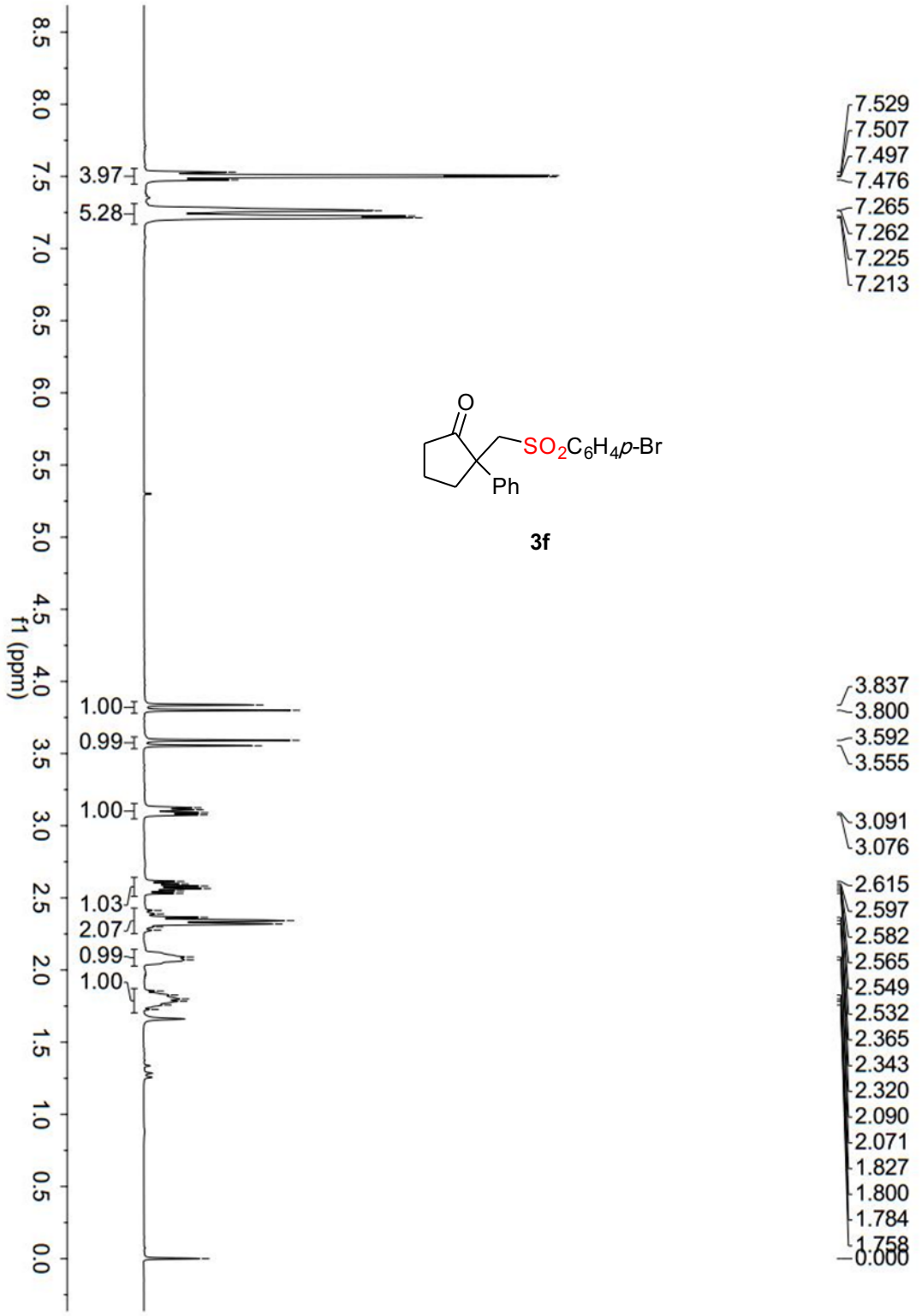
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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7.262
7.225
7.213
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5.28
O
SO2C6H4p-Br
Ph
3f
3.837
3.800
3.592
3.555
3.091
3.076
2.615
2.597
2.582
2.565
2.549
2.532
2.365
2.343
2.320
2.090
2.071
1.827
1.800
1.784
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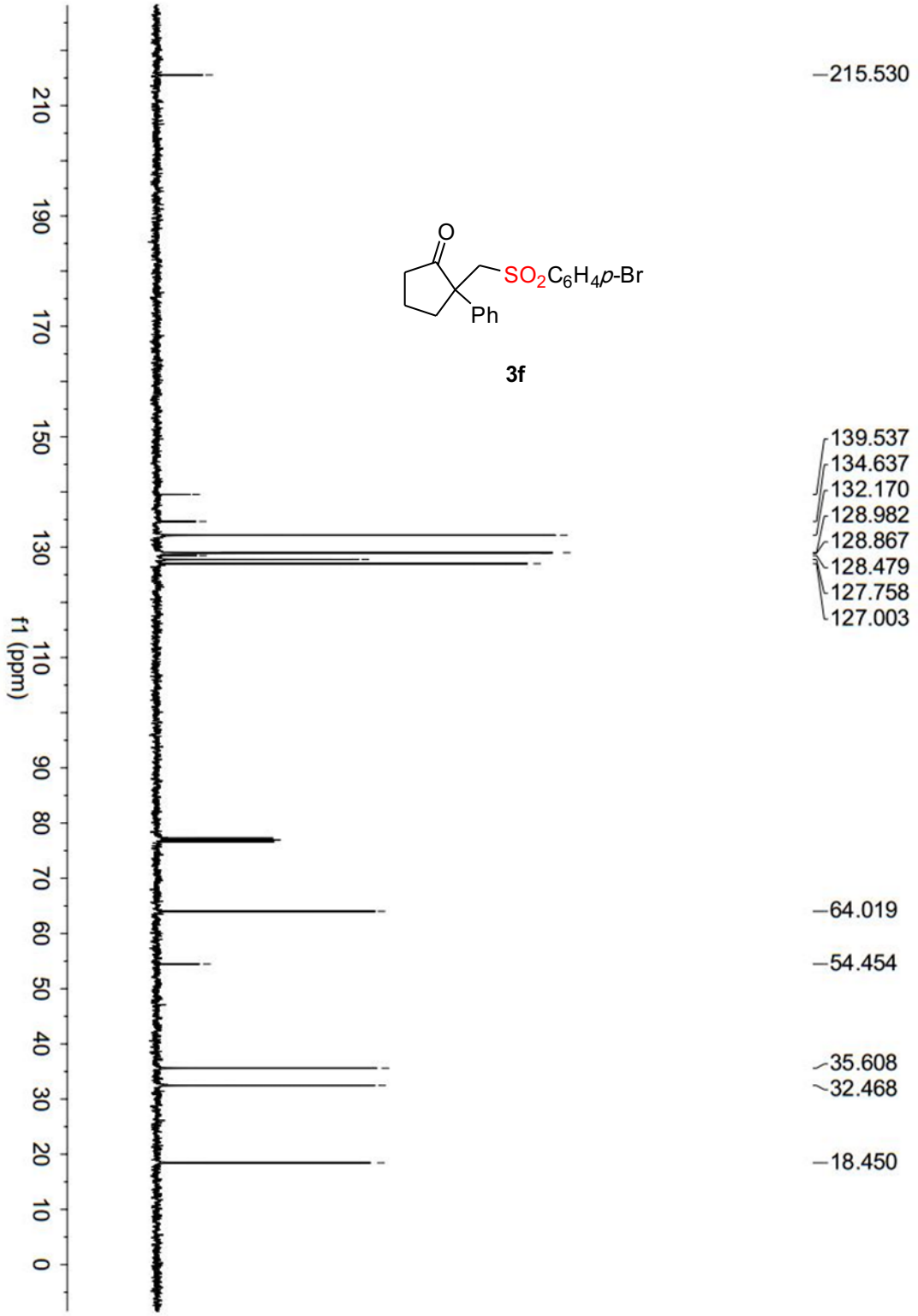
0.000
1.00
0.99
1.00
1.03
2.07
0.99
1.00
f1 (ppm)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Ph
3f
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134.637
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128.867
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127.758
127.003
64.019
54.454
35.608
32.468
18.450
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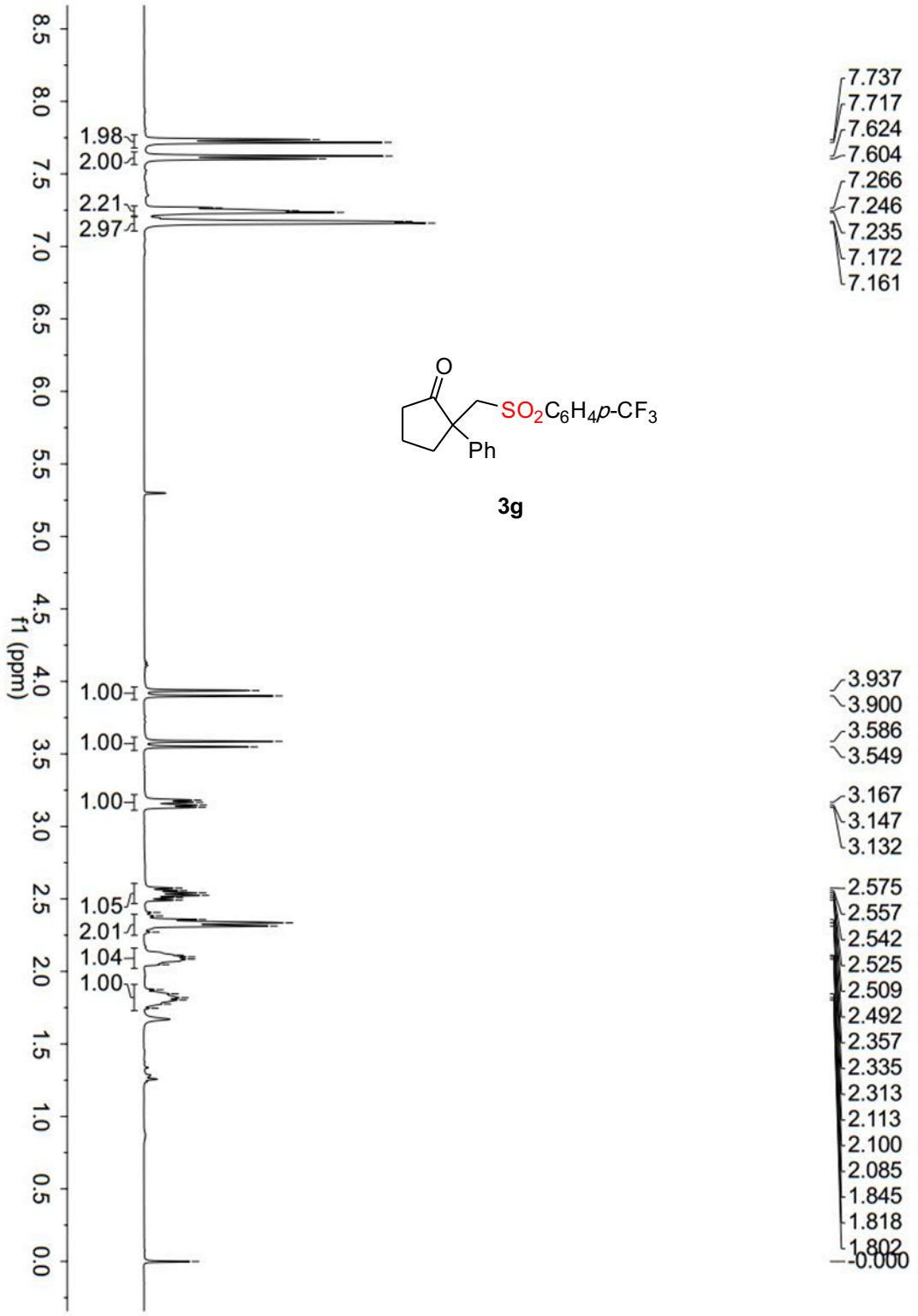
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.98
2.00
2.21
2.97
1.00
1.00
1.00
1.05
2.01
1.04
1.00
7.737
7.717
7.624
7.604
7.266
7.246
7.235
7.172
7.161
3.937
3.900
3.586
3.549
3.167
3.147
3.132
2.575
2.557
2.542
2.525
2.509
2.492
2.357
2.335
2.313
2.113
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2.085
1.845
1.818
1.802
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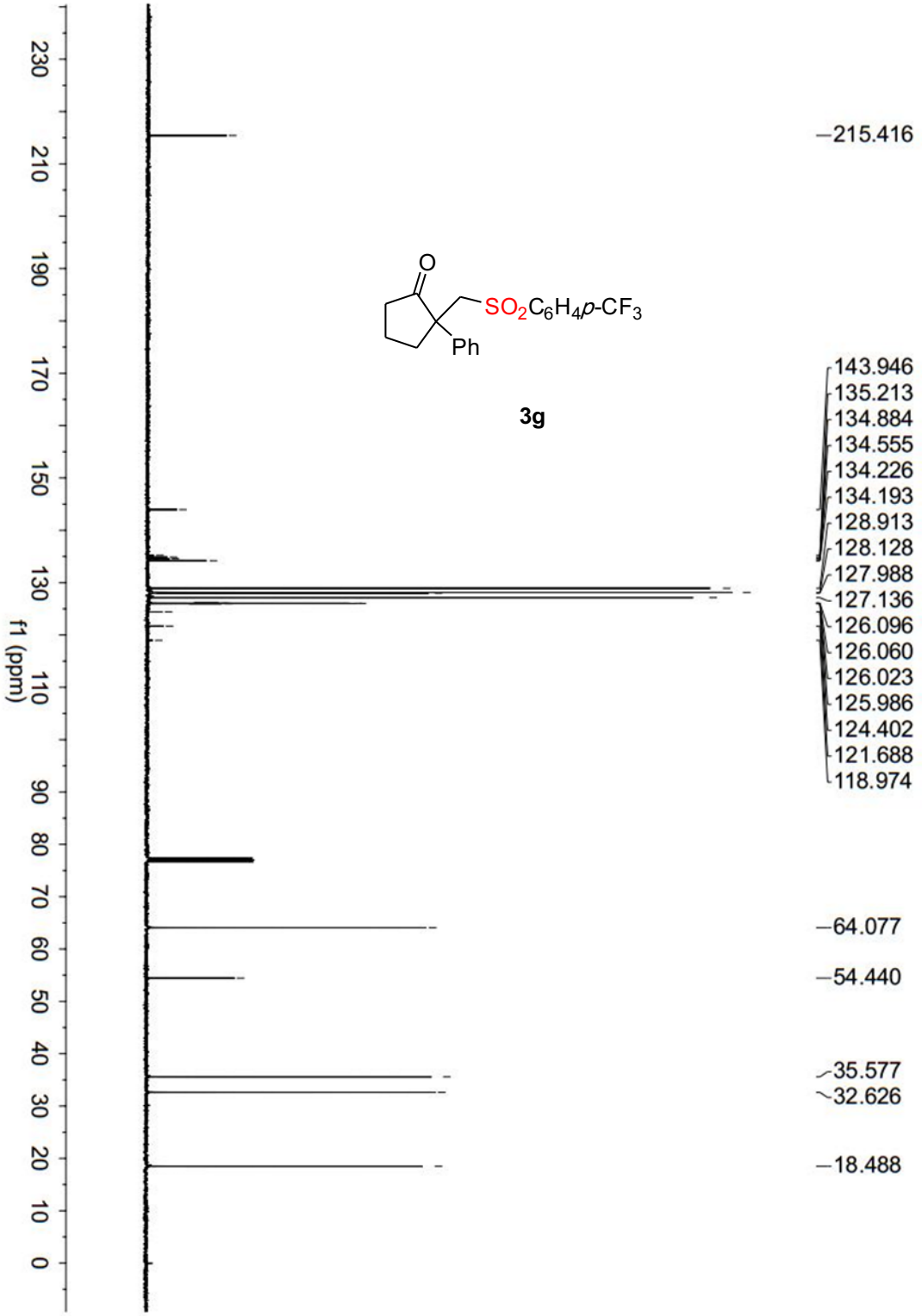
O
SO2C6H4p-CF3
Ph

3g


O
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Ph
3g
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134.226
134.193
128.913
128.128
127.988
127.136
126.096
126.060
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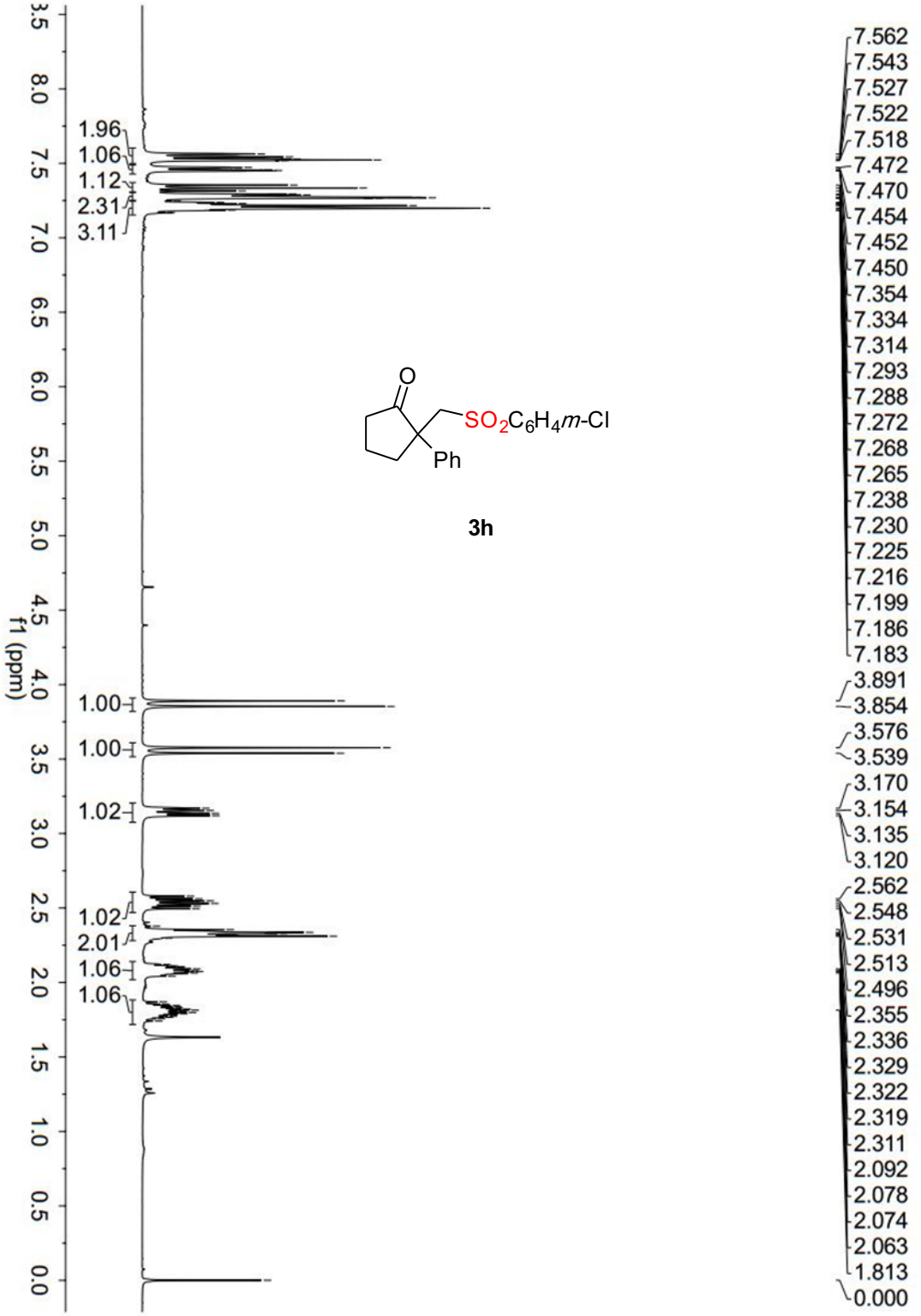
124.402
121.688
118.974
64.077
54.440
35.577
32.626
18.488
f1 (ppm)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3.11
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1.00
1.02
1.02
2.01
1.06
1.06
O
SO2C6H4m-Cl
Ph
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7.543
7.527
7.522
7.518
7.472
7.470
7.454
7.452
7.450
7.354
7.334
7.314
7.293
7.288
7.272
7.268
7.265
7.238
7.230
7.225
7.216
7.199
7.186
7.183
3.891
3.854
3.576
3.539
3.170
3.154
3.135
3.120
2.562
2.548
2.531
2.513
2.496
2.355
2.336
2.329
2.322
2.319
2.311
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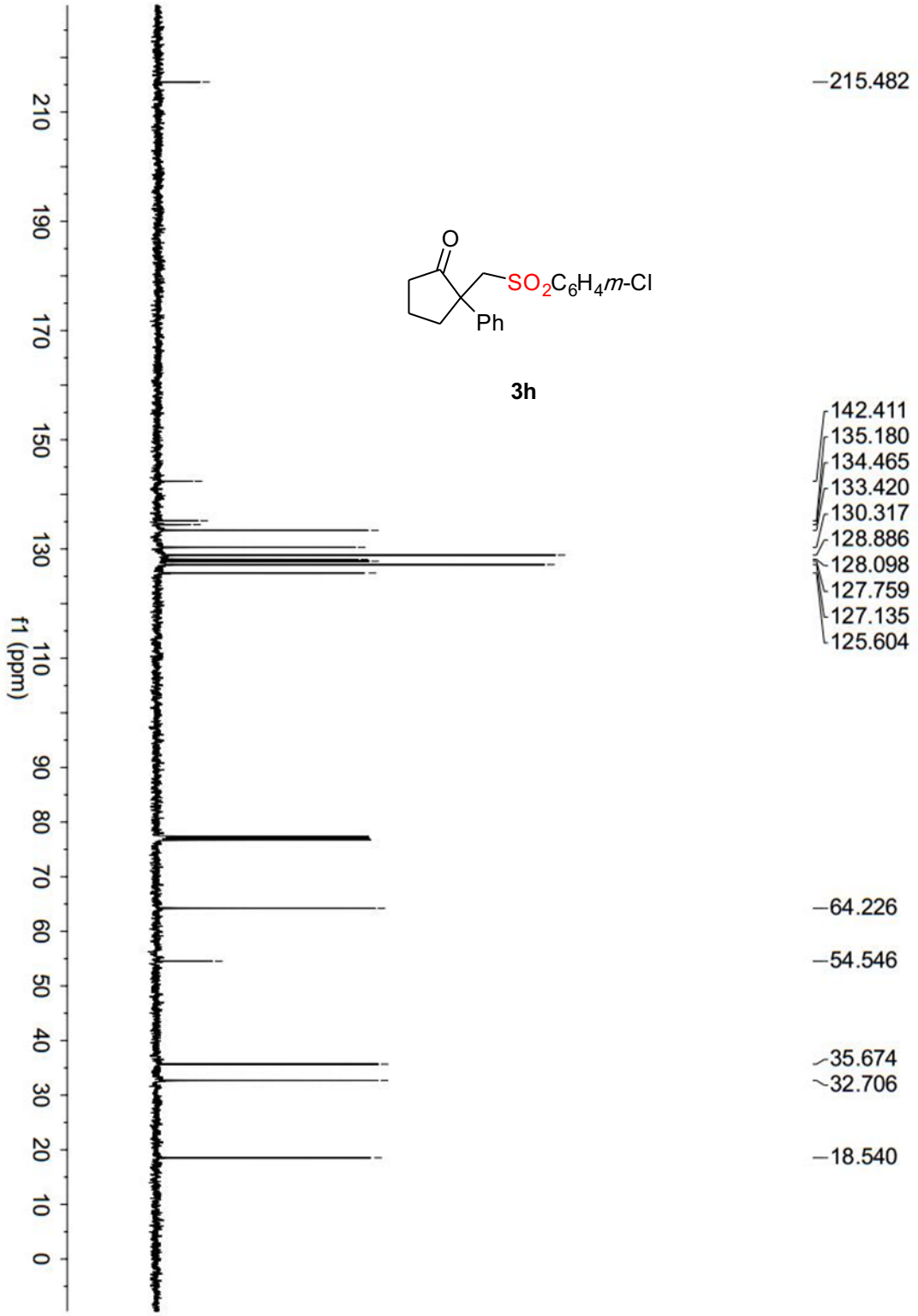
2.074
2.063
1.813
0.000

3h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130.317
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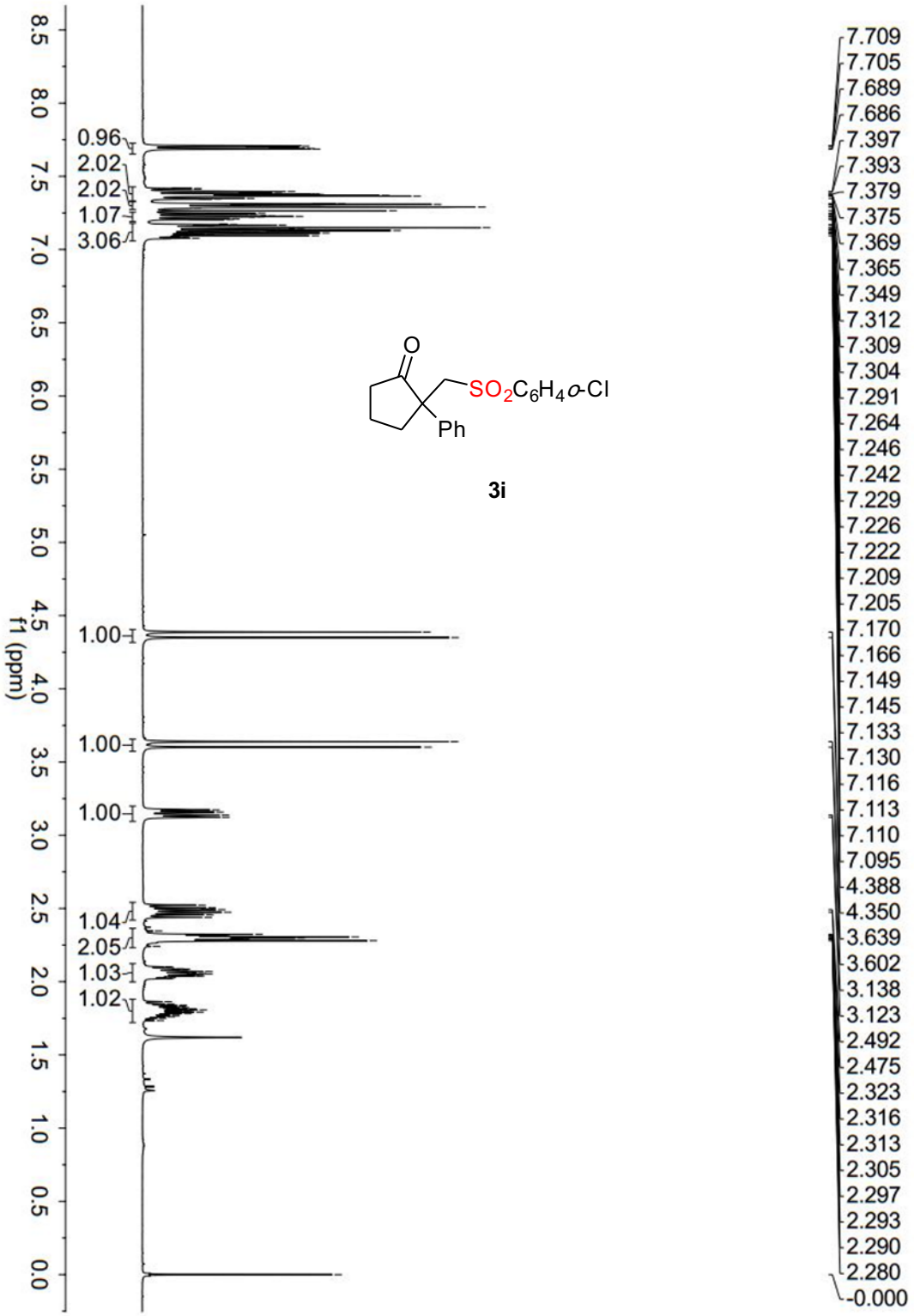
128.098
127.759
127.135
125.604
64.226
54.546
35.674
32.706
18.540
f1 (ppm)
O
SO2C6H4m-Cl
Ph

3h


f1 (ppm)
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2.02
1.07
3.06
1.00
1.00
1.00
1.04
2.05
1.03
1.02
O
SO2C6H4o-Cl
Ph
7.709
7.705
7.689
7.686
7.397
7.393
7.379
7.375
7.369
7.365
7.349
7.312
7.309
7.304
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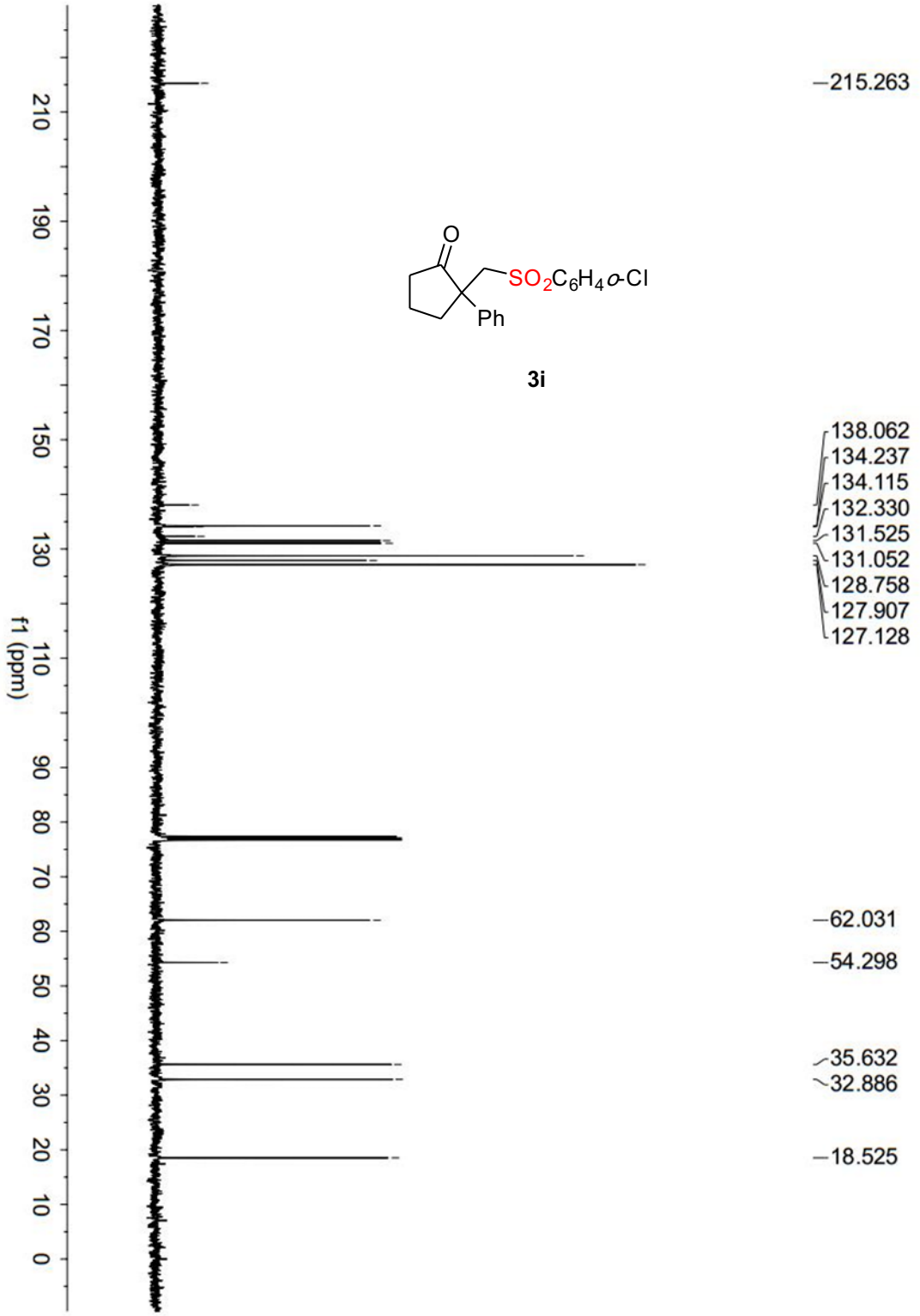
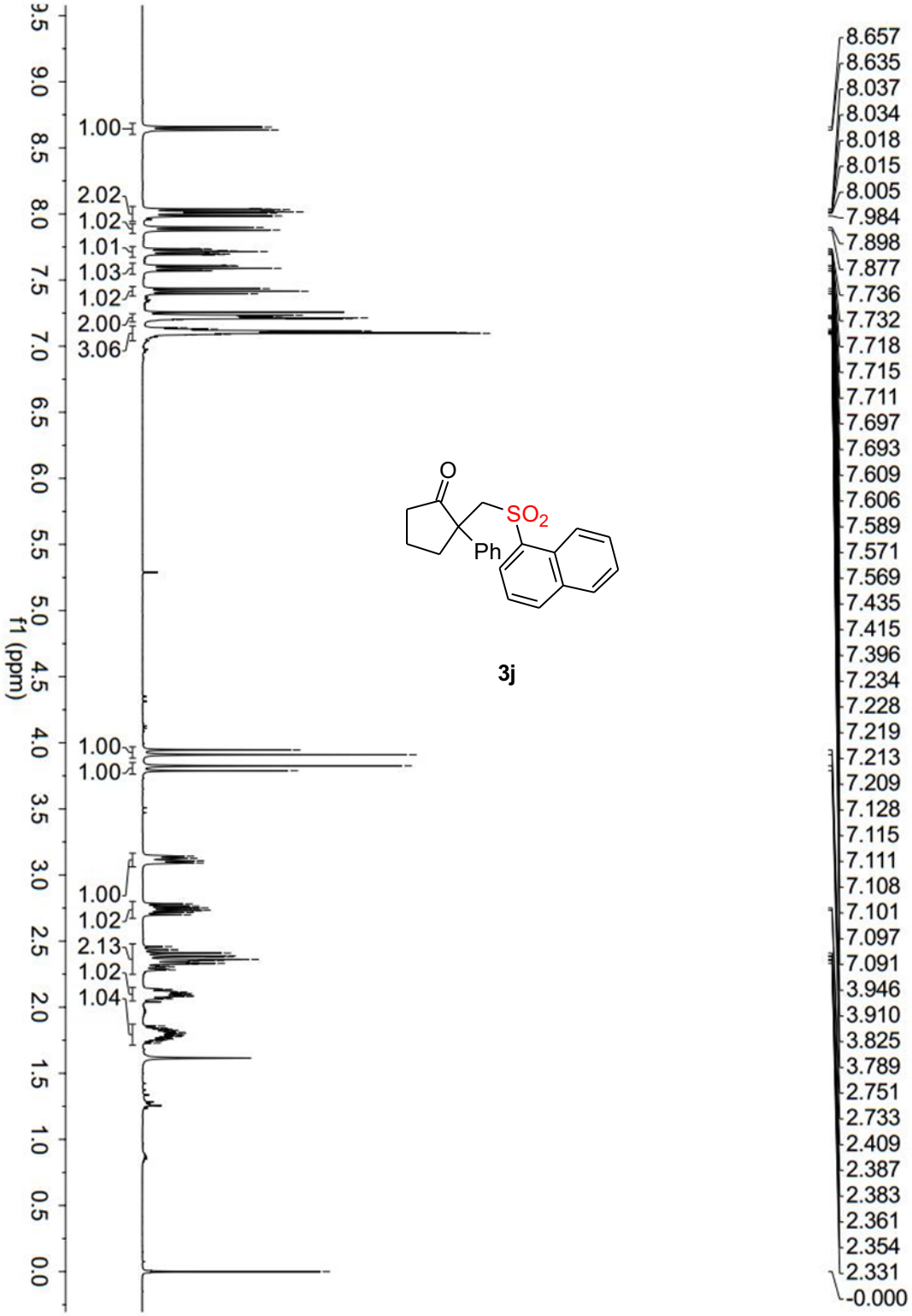
7.264
7.246
7.242
7.229
7.226
7.222
7.209
7.205
7.170
7.166
7.149
7.145
7.133
7.130
7.116
7.113
7.110
7.095
4.388
4.350
3.639
3.602
3.138
3.123
2.492
2.475
2.323
2.316
2.313
2.305
2.297
2.293
2.290
2.280
-0.000

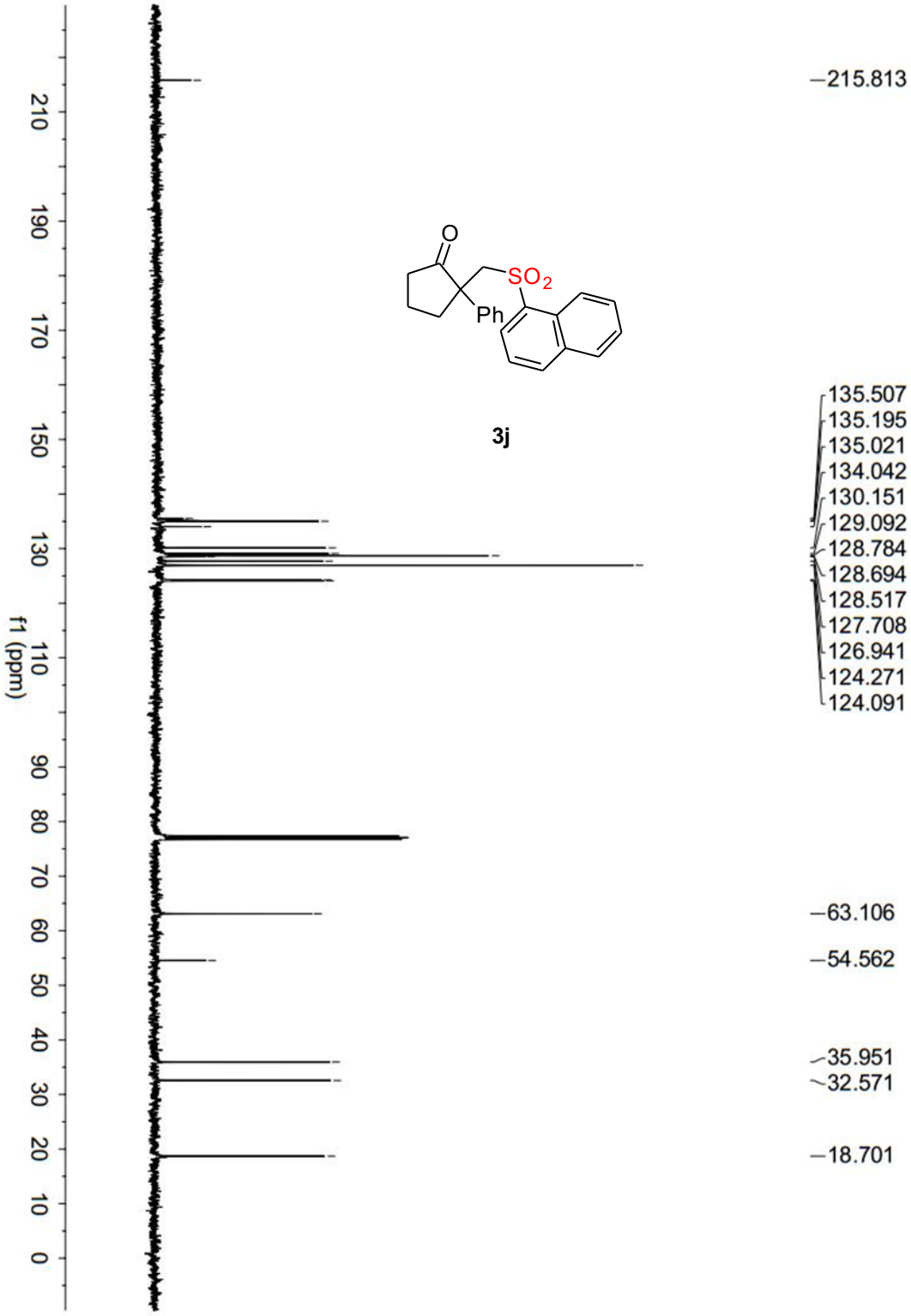
3i

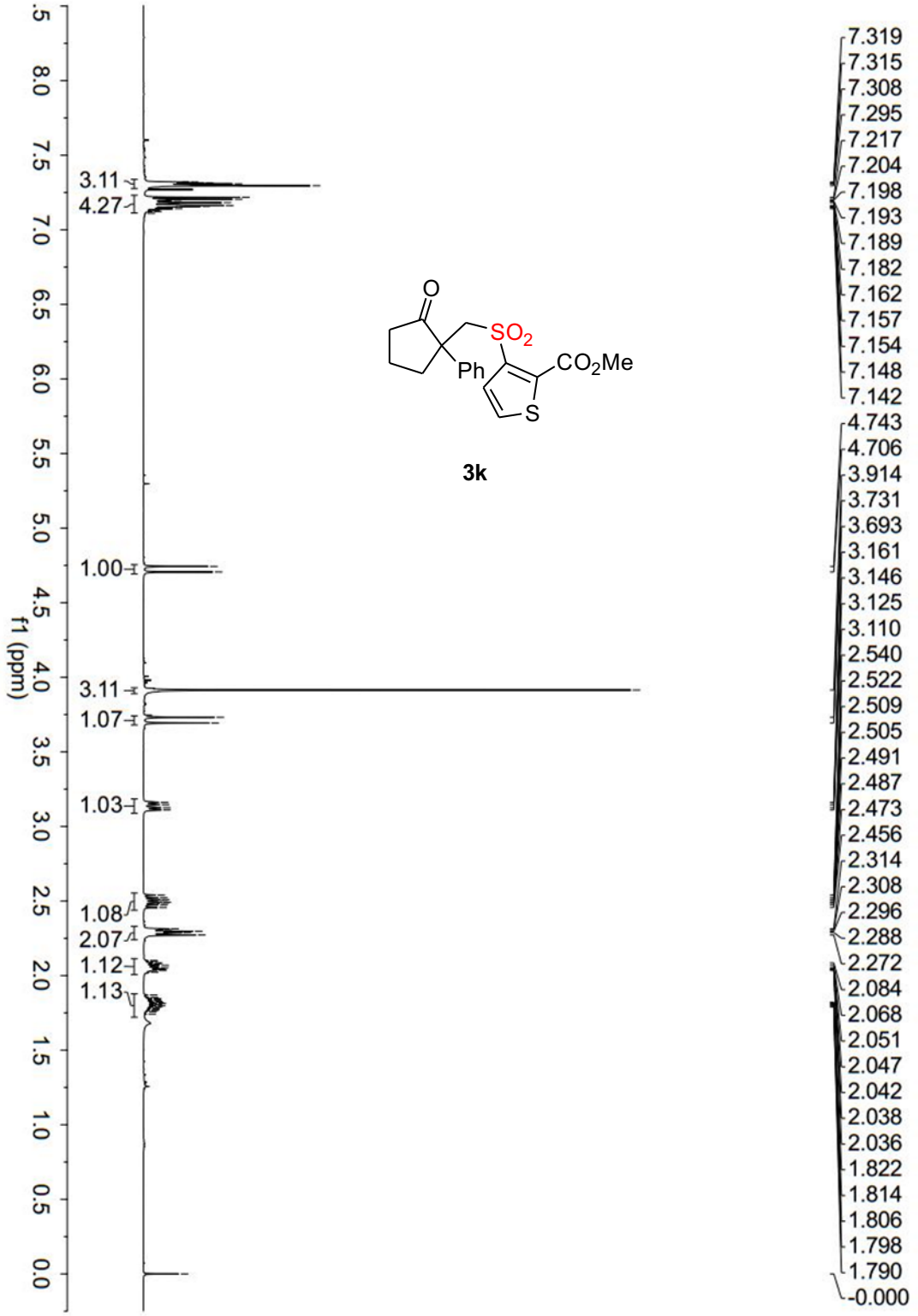

215.263
138.062
134.237
134.115
132.330
131.525
131.052
128.758
127.907
127.128
62.031
54.298
35.632
32.886
18.525
f1 (ppm)
O
SO2C6H4o-Cl
Ph

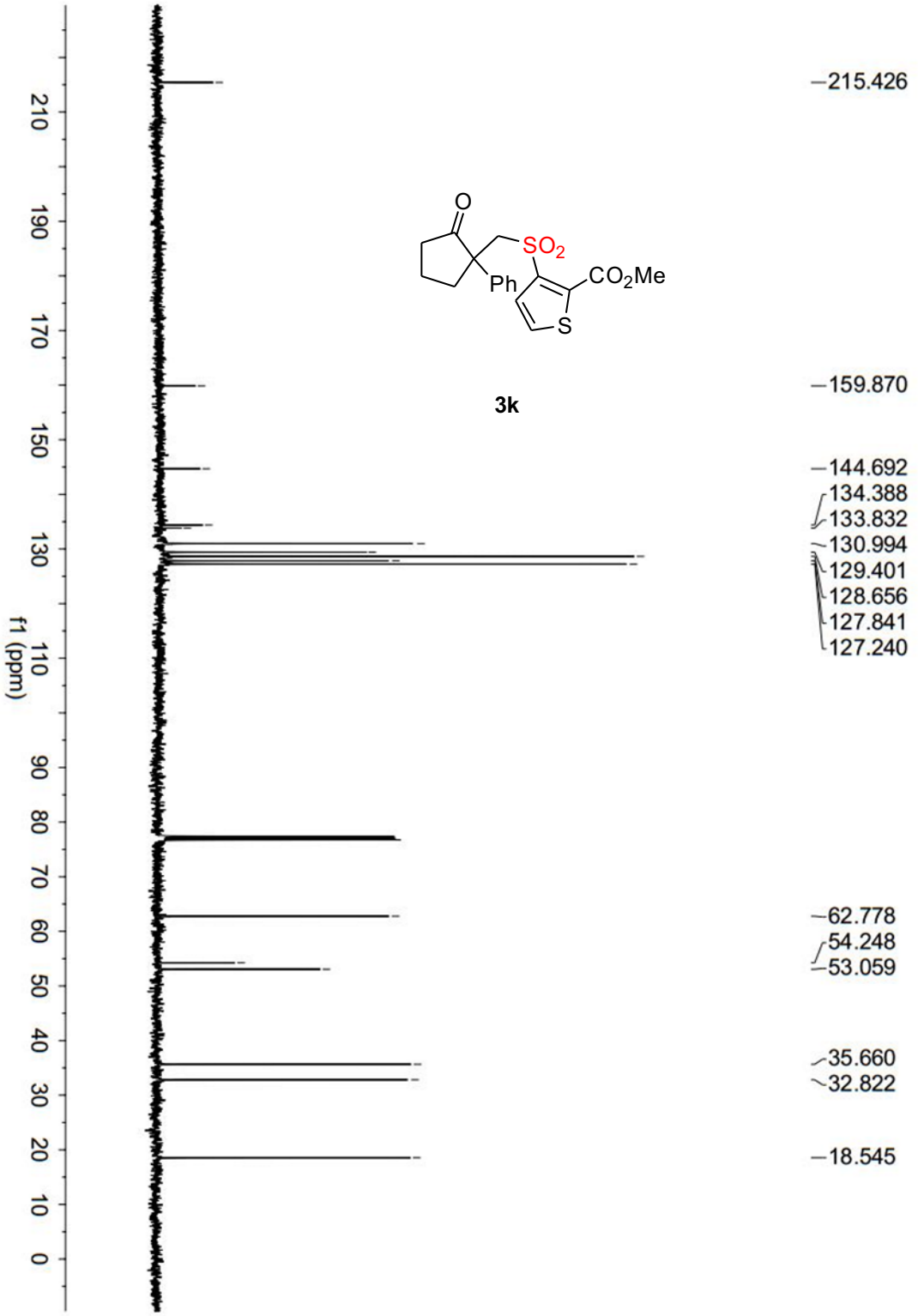
3i


f1 (ppm)
1.00
2.02
1.02
1.01
1.03
1.02
2.00
3.06
1.00
1.00
1.00
1.02
2.13
1.02
1.04
O
SO2
Ph
8.657
8.635
8.037
8.034
8.018
8.015
8.005
7.984
7.898
7.877
7.736
7.732
7.718
7.715
7.711
7.697
7.693
7.609
7.606
7.589
7.571
7.569
7.435
7.415
7.396
7.234
7.228
7.219
7.213
7.209
7.128
7.115
7.111
7.108
7.101
7.097
7.091
3.946
3.910
3.825
3.789
2.751
2.733
2.409
2.387
2.383
2.361
2.354
2.331
-0.000

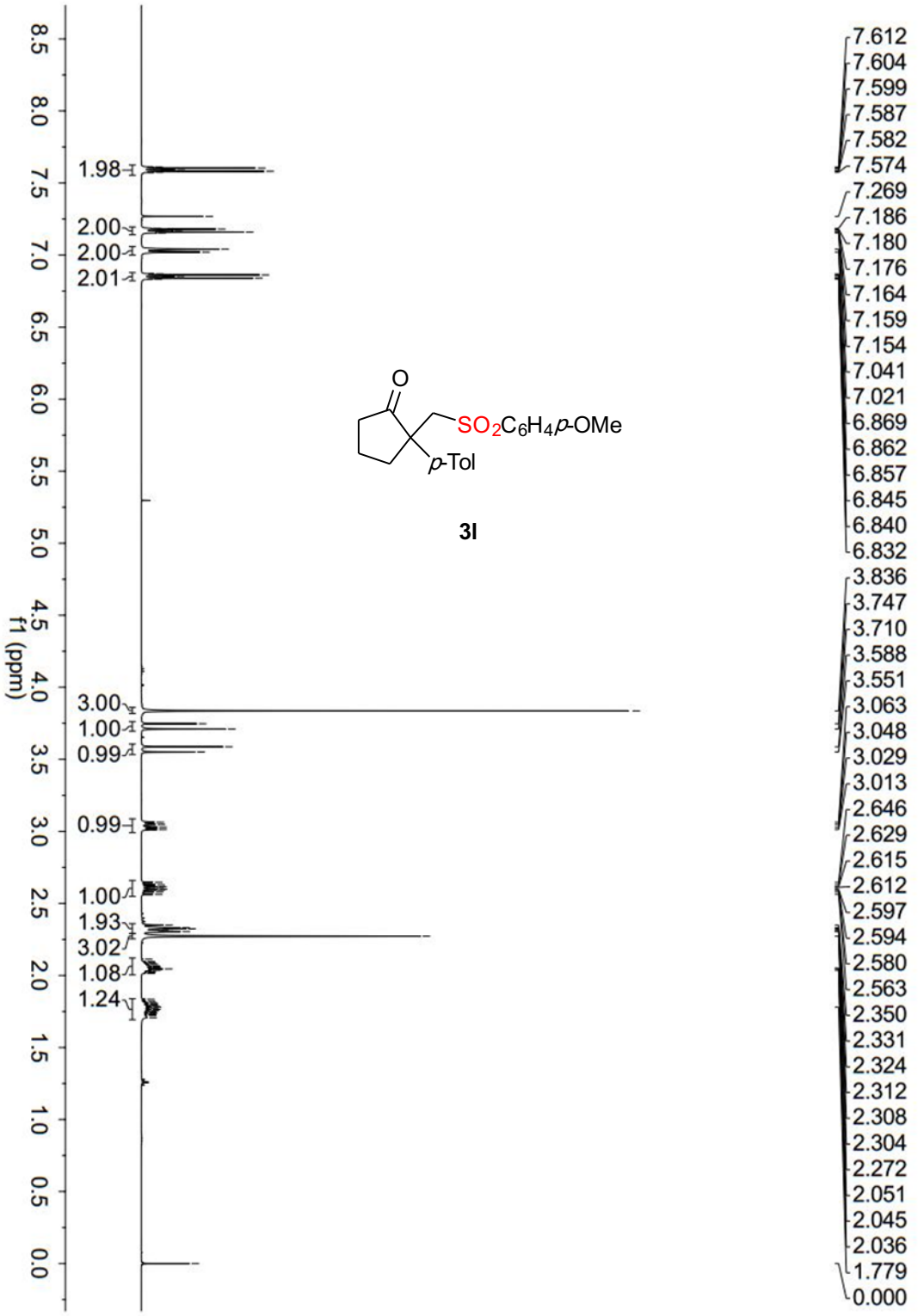
3j

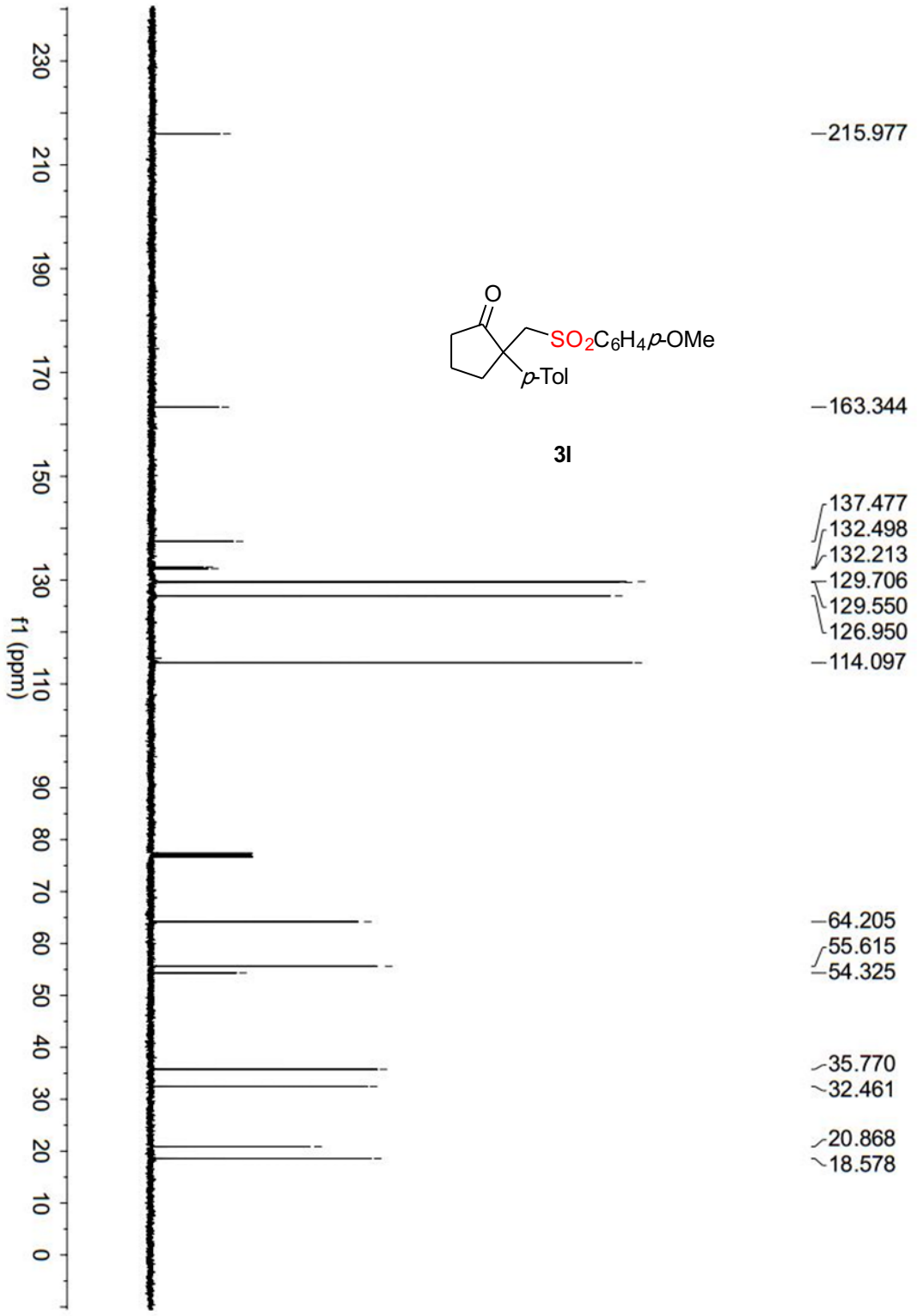

215.813
135.507
135.195
135.021
134.042
130.151
129.092
128.784
128.694
128.517
127.708
126.941
124.271
124.091
63.106
54.562
35.951
32.571
18.701
f1 (ppm)
O
SO2
Ph
3j

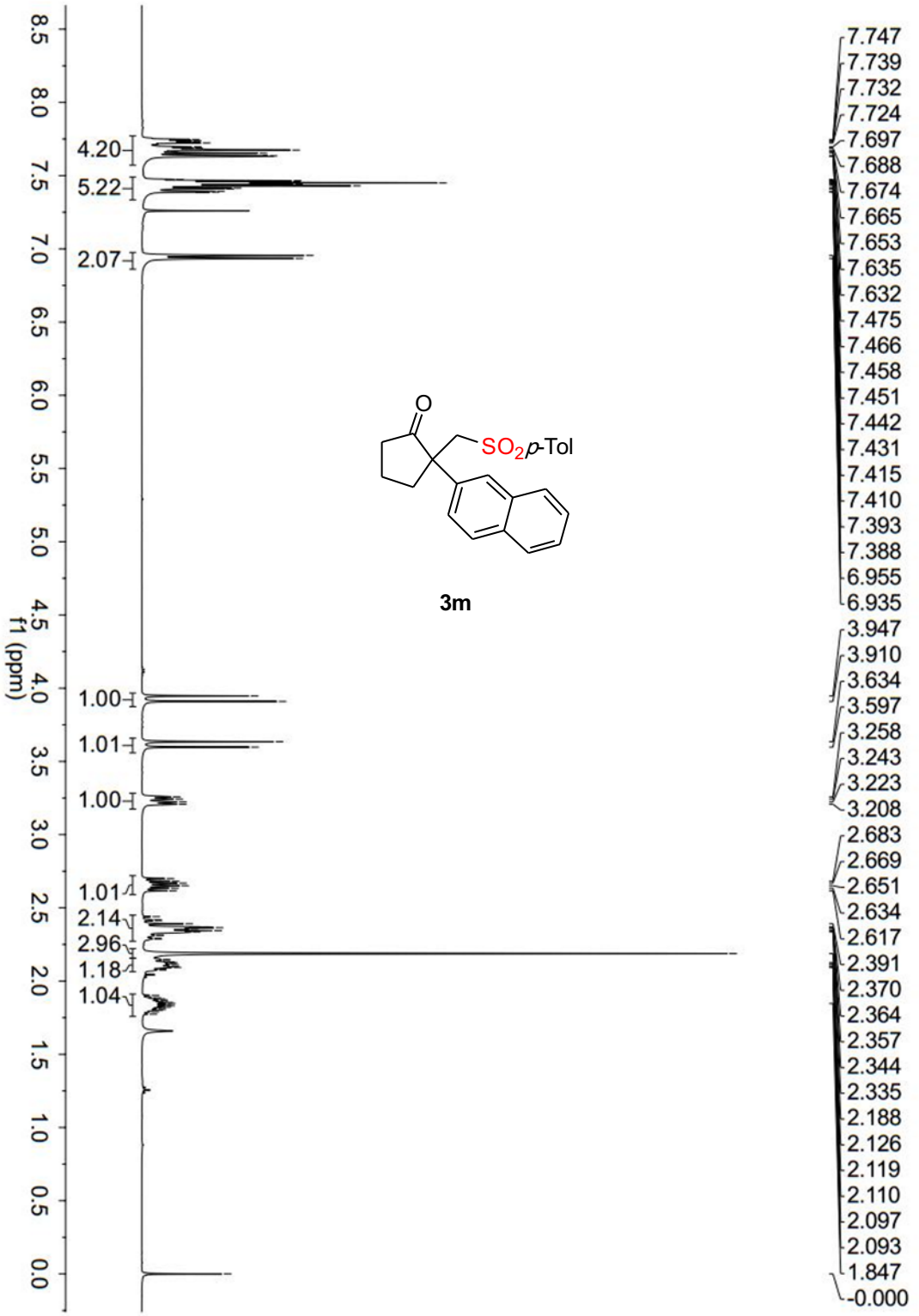

f1 (ppm)
3.11
4.27
1.00
3.11
1.07
1.03
1.08
2.07
1.12
1.13
O
SO2
Ph
CO2Me
S
3k
7.319
7.315
7.308
7.295
7.217
7.204
7.198
7.193
7.189
7.182
7.162
7.157
7.154
7.148
7.142
4.743
4.706
3.914
3.731
3.693
3.161
3.146
3.125
3.110
2.540
2.522
2.509
2.505
2.491
2.487
2.473
2.456
2.314
2.308
2.296
2.288
2.272
2.084
2.068
2.051
2.047
2.042
2.038
2.036
1.822
1.814
1.806
1.798
1.790
-0.000

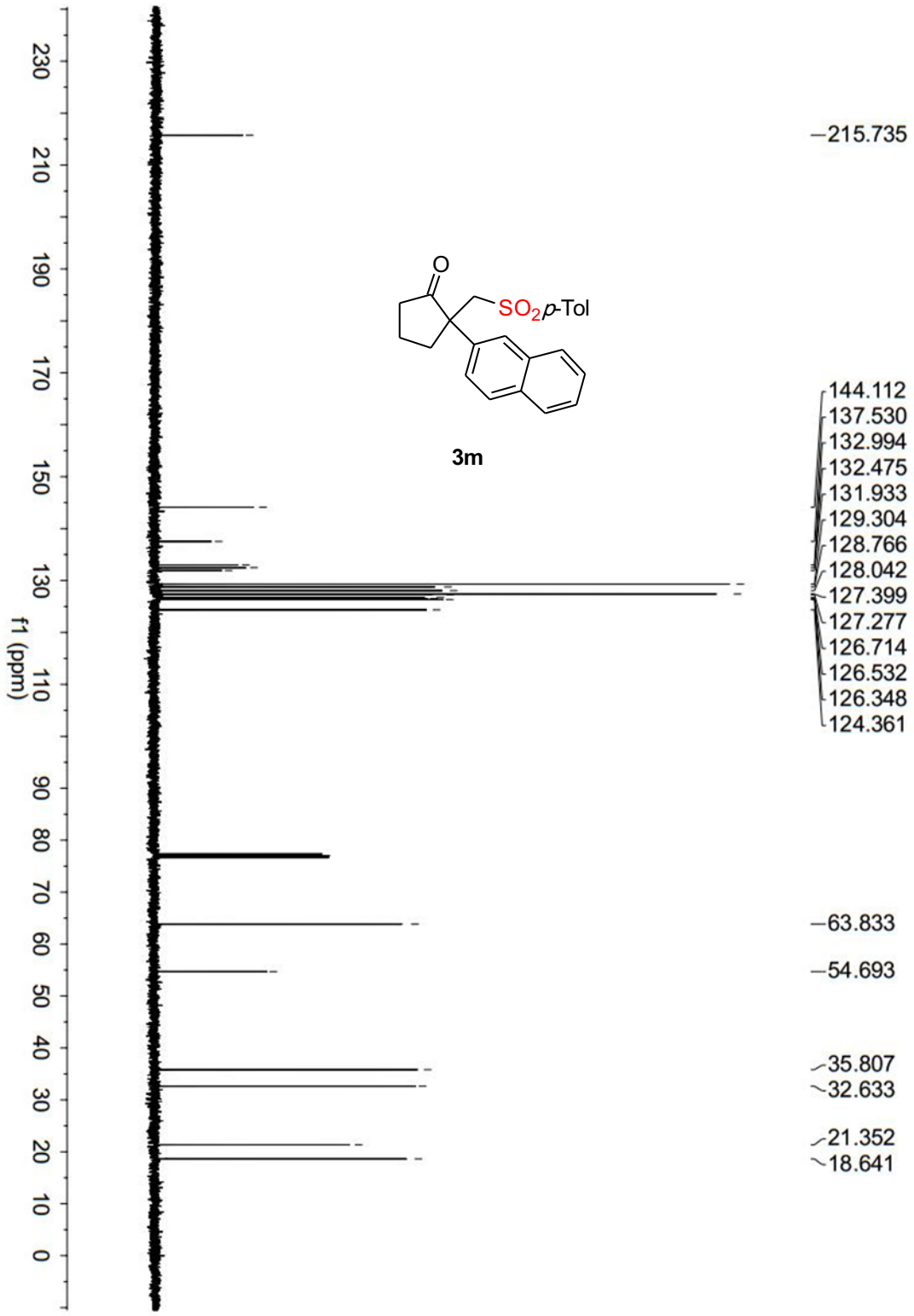

215.426
159.870
144.692
134.388
133.832
130.994
129.401
128.656
127.841
127.240
62.778
54.248
53.059
35.660
32.822
18.545
f1 (ppm)
O
SO2
Ph
CO2Me
S

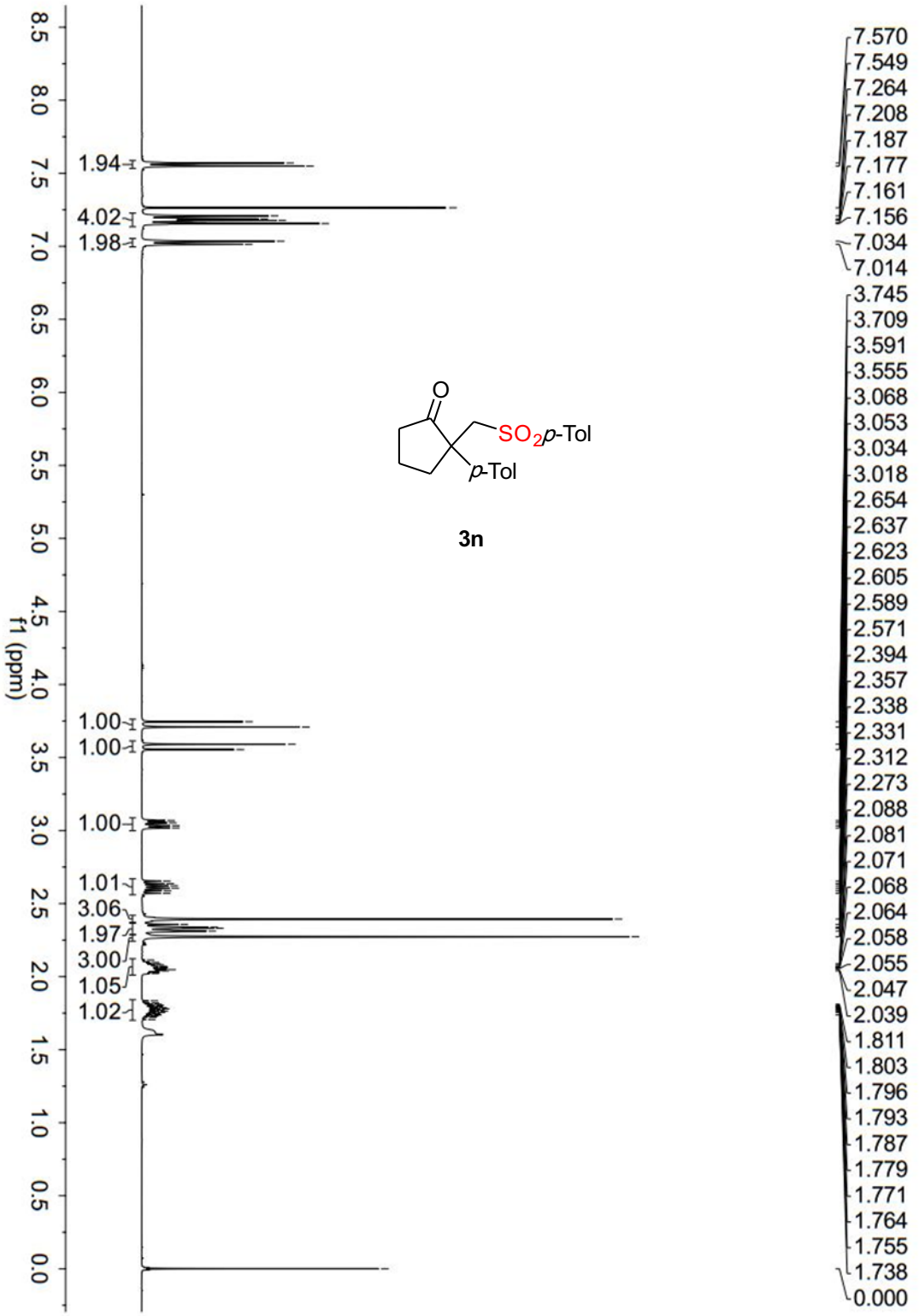
3k

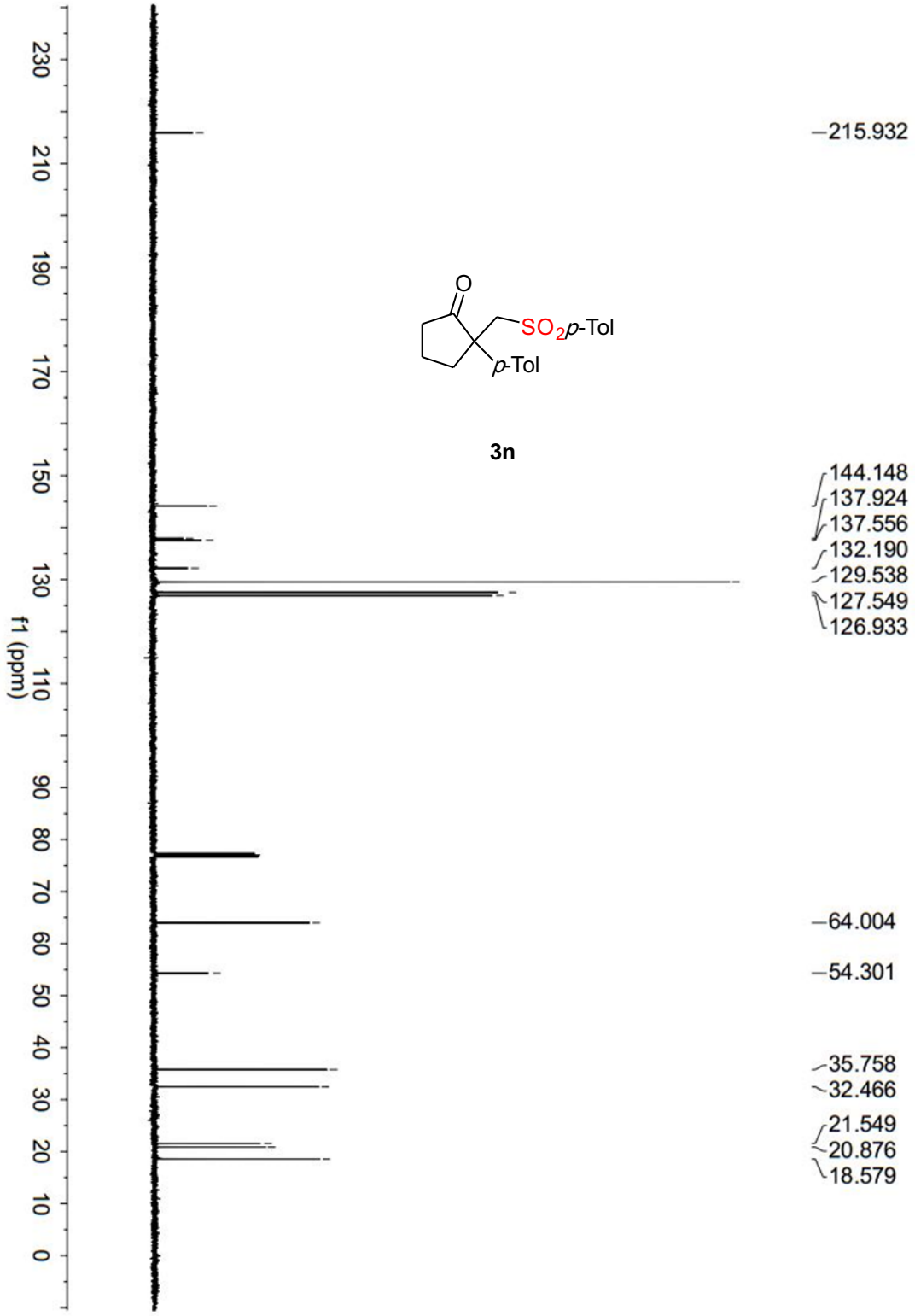

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.98
2.00
2.00
2.01
3.00
1.00
0.99
0.99
1.00
1.93
3.02
1.08
1.24
O
SO2C6H4p-OMe
p-Tol
3l
7.612
7.604
7.599
7.587
7.582
7.574
7.269
7.186
7.180
7.176
7.164
7.159
7.154
7.041
7.021
6.869
6.862
6.857
6.845
6.840
6.832
3.836
3.747
3.710
3.588
3.551
3.063
3.048
3.029
3.013
2.646
2.629
2.615
2.612
2.597
2.594
2.580
2.563
2.350
2.331
2.324
2.312
2.308
2.304
2.272
2.051
2.045
2.036
1.779
0.000


215.977
163.344
137.477
132.498
132.213
129.706
129.550
126.950
114.097
64.205
55.615
54.325
35.770
32.461
20.868
18.578
f1 (ppm)
O
SO2C6H4p-OMe
p-Tol
3l

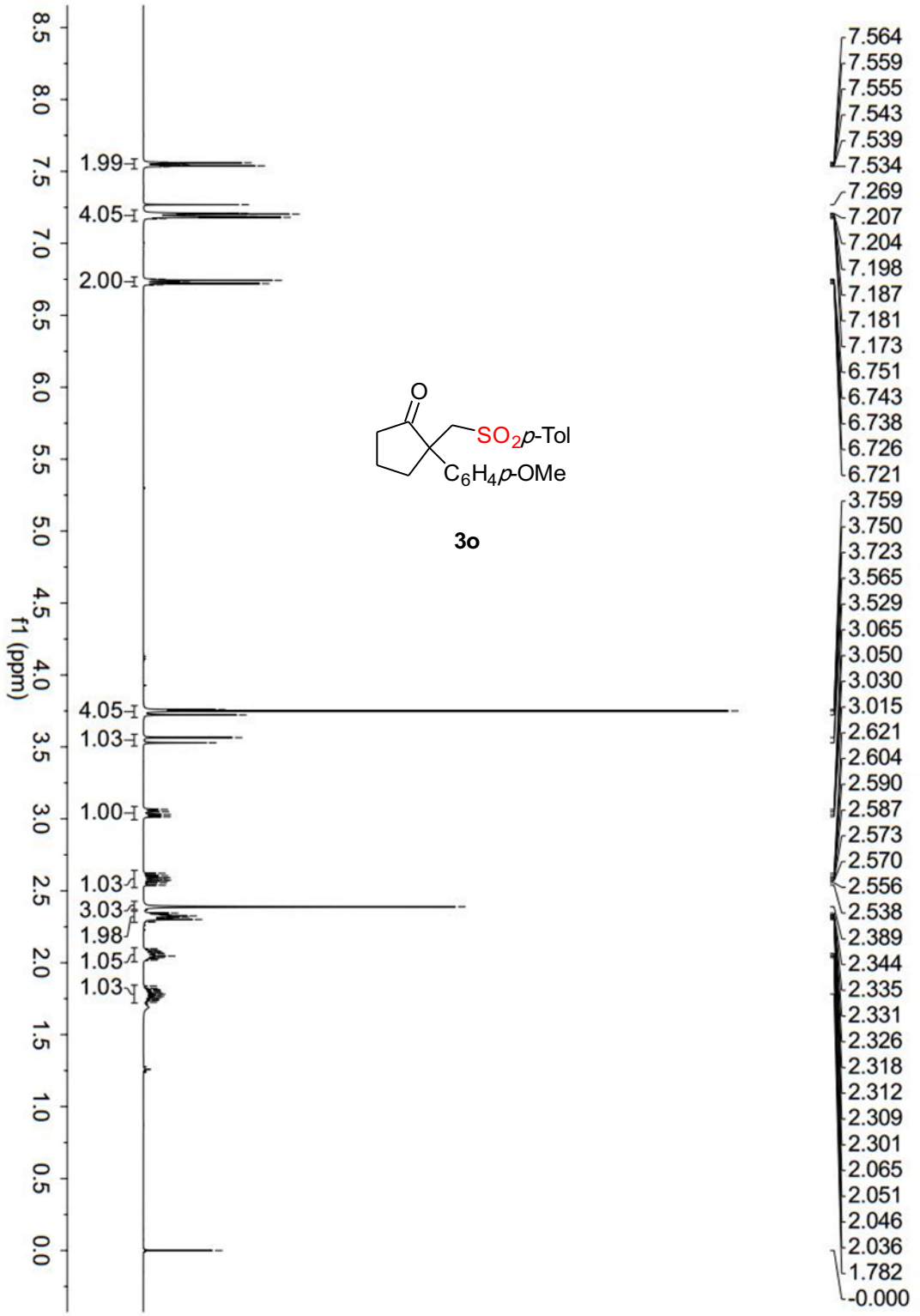

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
4.20
5.22
2.07
1.00
1.01
1.00
1.01
2.14
2.96
1.18
1.04
O
SO2p-Tol
3m
7.747
7.739
7.732
7.724
7.697
7.688
7.674
7.665
7.653
7.635
7.632
7.475
7.466
7.458
7.451
7.442
7.431
7.415
7.410
7.393
7.388
6.955
6.935
3.947
3.910
3.634
3.597
3.258
3.243
3.223
3.208
2.683
2.669
2.651
2.634
2.617
2.391
2.370
2.364
2.357
2.344
2.335
2.188
2.126
2.119
2.110
2.097
2.093
1.847
-0.000


215.735
144.112
137.530
132.994
132.475
131.933
129.304
128.766
128.042
127.399
127.277
126.714
126.532
126.348
124.361
63.833
54.693
35.807
32.633
21.352
18.641
f1 (ppm)
O
SO2p-Tol
3m

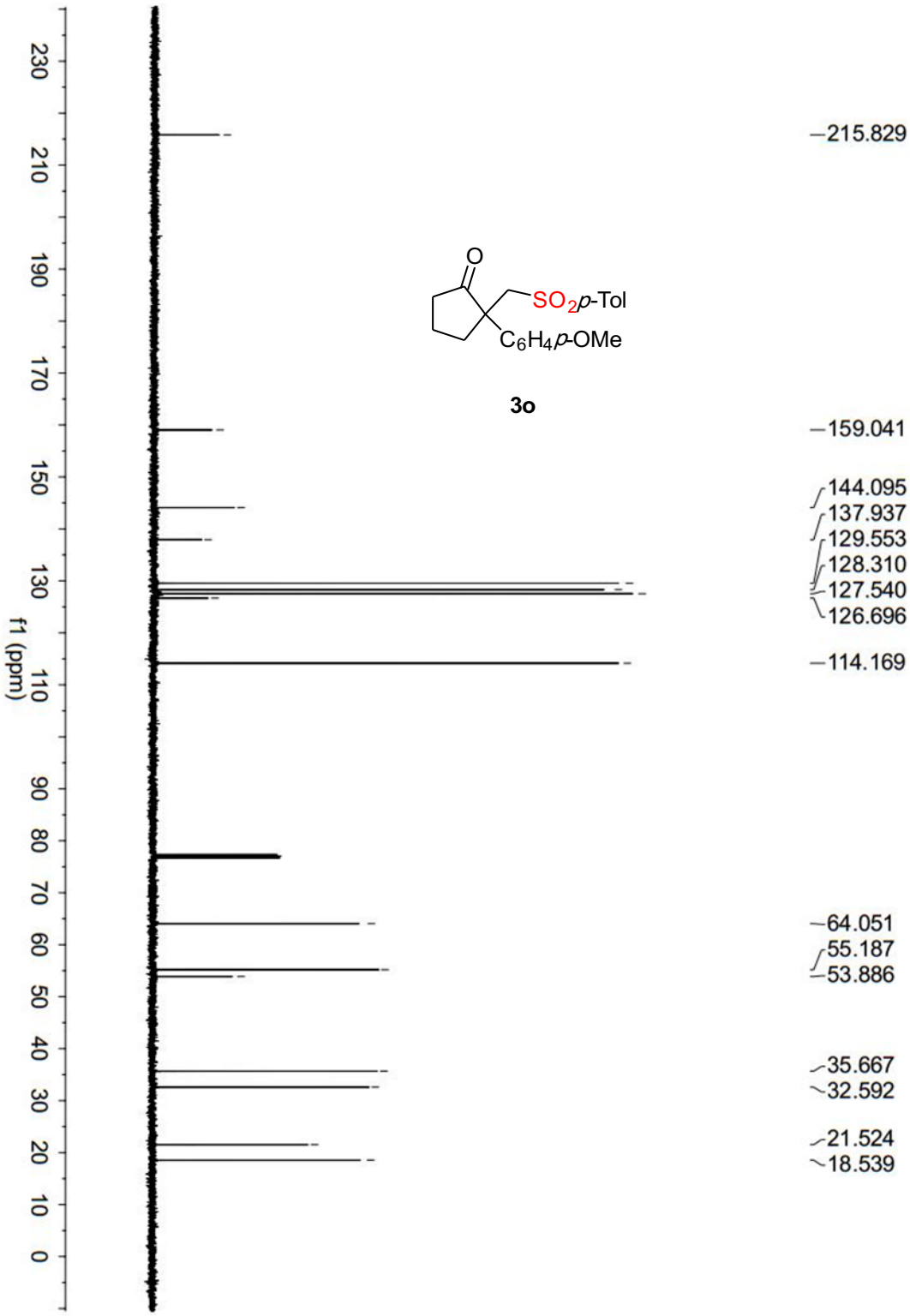

f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.94
4.02
1.98
1.00
1.00
1.00
1.01
3.06
1.97
3.00
1.05
1.02
O
SO2p-Tol
p-Tol
3n
7.570
7.549
7.264
7.208
7.187
7.177
7.161
7.156
7.034
7.014
3.745
3.709
3.591
3.555
3.068
3.053
3.034
3.018
2.654
2.637
2.623
2.605
2.589
2.571
2.394
2.357
2.338
2.331
2.312
2.273
2.088
2.081
2.071
2.068
2.064
2.058
2.055
2.047
2.039
1.811
1.803
1.796
1.793
1.787
1.779
1.771
1.764
1.755
1.738
0.000

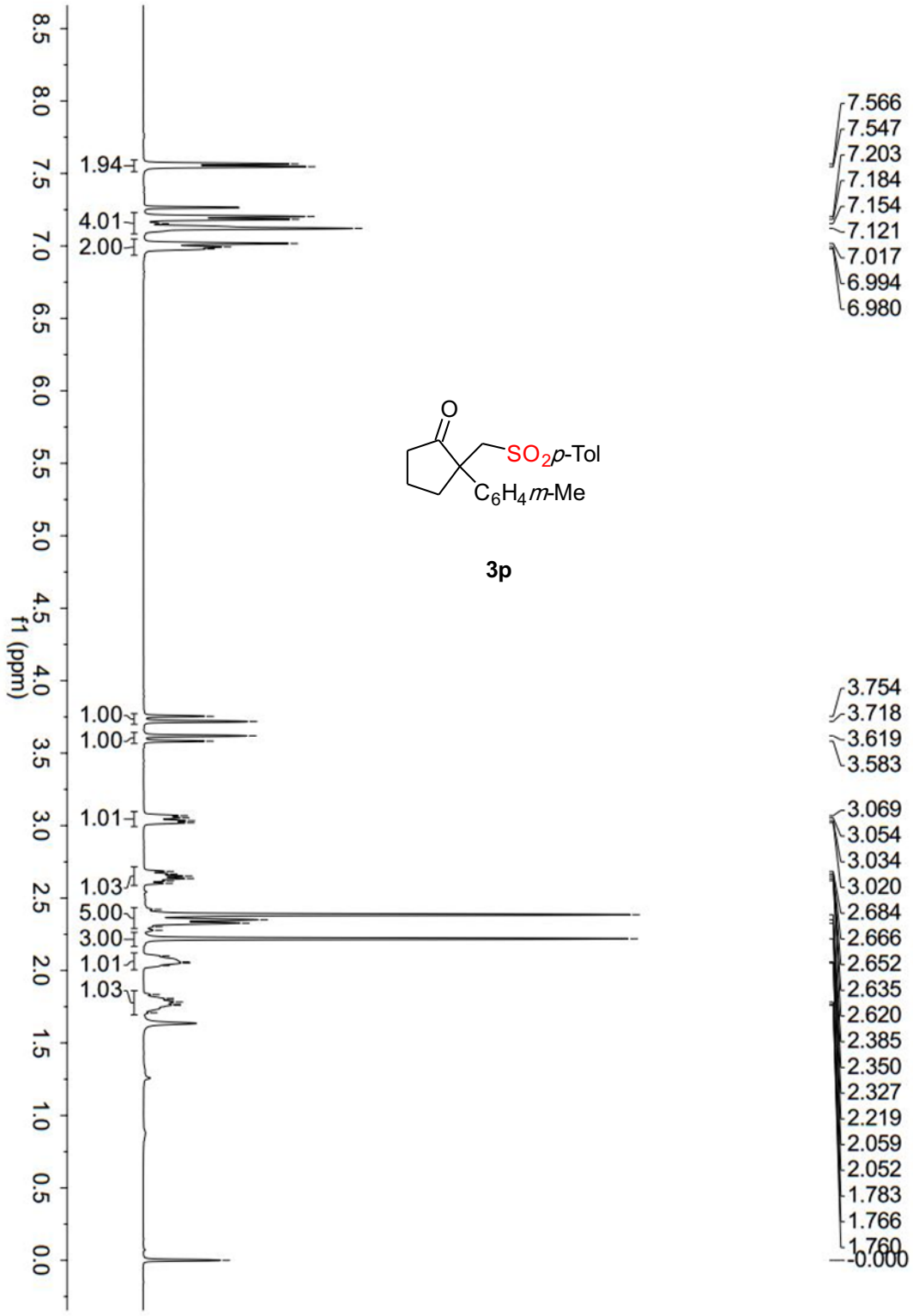

215.932
144.148
137.924
137.556
132.190
129.538
127.549
126.933
64.004
54.301
35.758
32.466
21.549
20.876
18.579
f1 (ppm)
O
SO2p-Tol
p-Tol

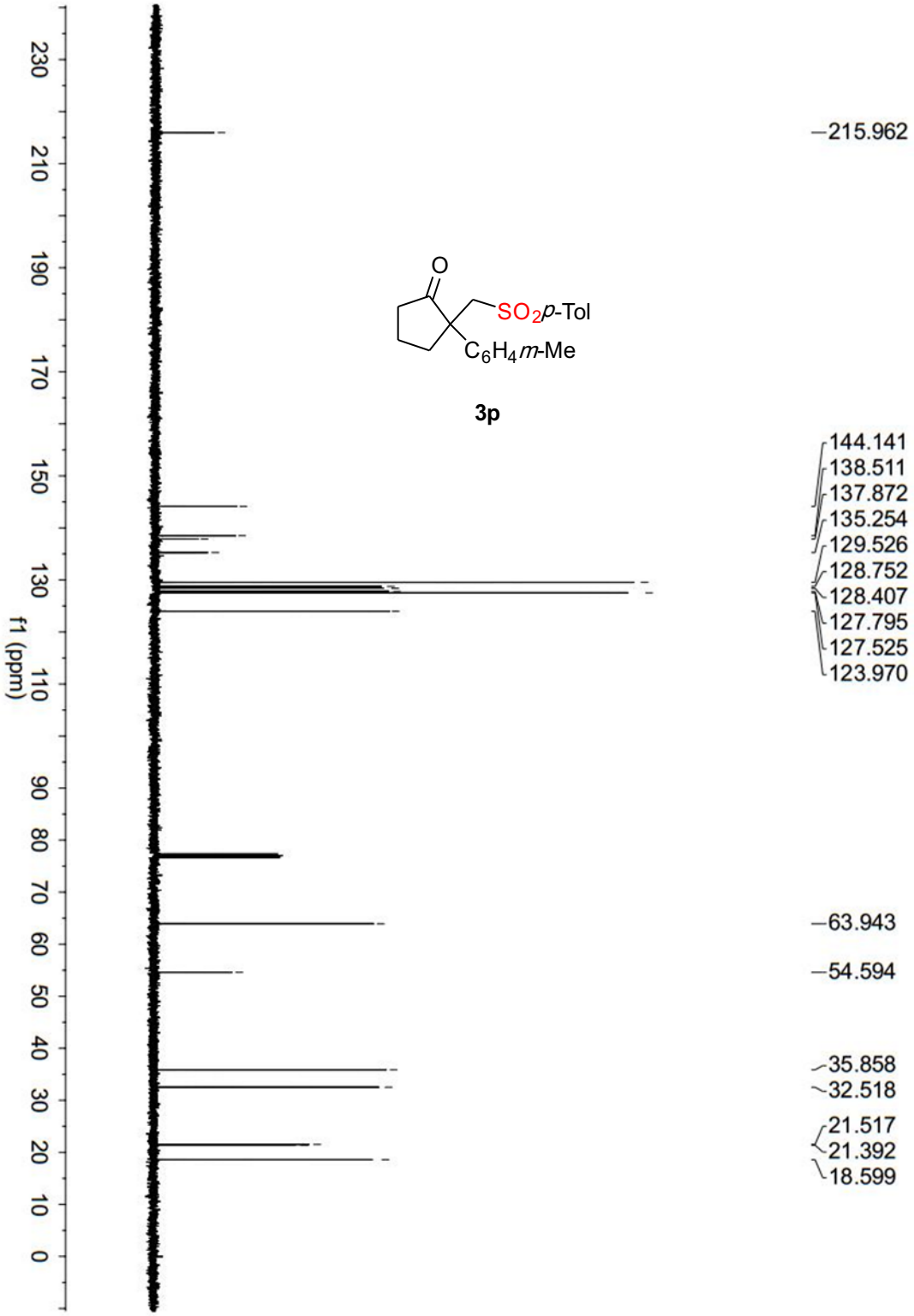
3n

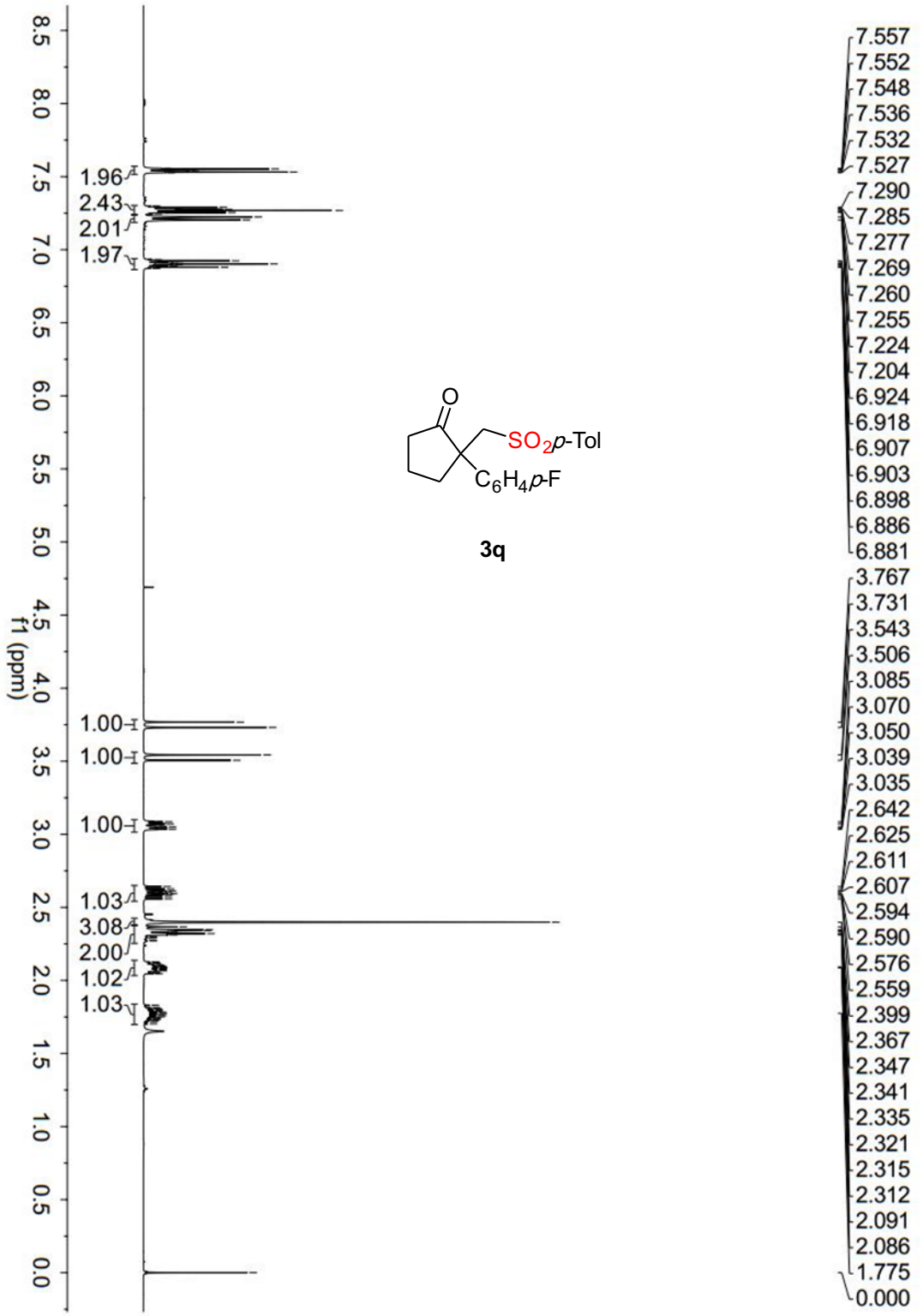

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.99
4.05
2.00
4.05
1.03
1.00
1.03
3.03
1.98
1.05
1.03
O
SO2p-Tol
C6H4p-OMe
7.564
7.559
7.555
7.543
7.539
7.534
7.269
7.207
7.204
7.198
7.187
7.181
7.173
6.751
6.743
6.738
6.726
6.721
3.759
3.750
3.723
3.565
3.529
3.065
3.050
3.030
3.015
2.621
2.604
2.590
2.587
2.573
2.570
2.556
2.538
2.389
2.344
2.335
2.331
2.326
2.318
2.312
2.309
2.301
2.065
2.051
2.046
2.036
1.782
-0.000

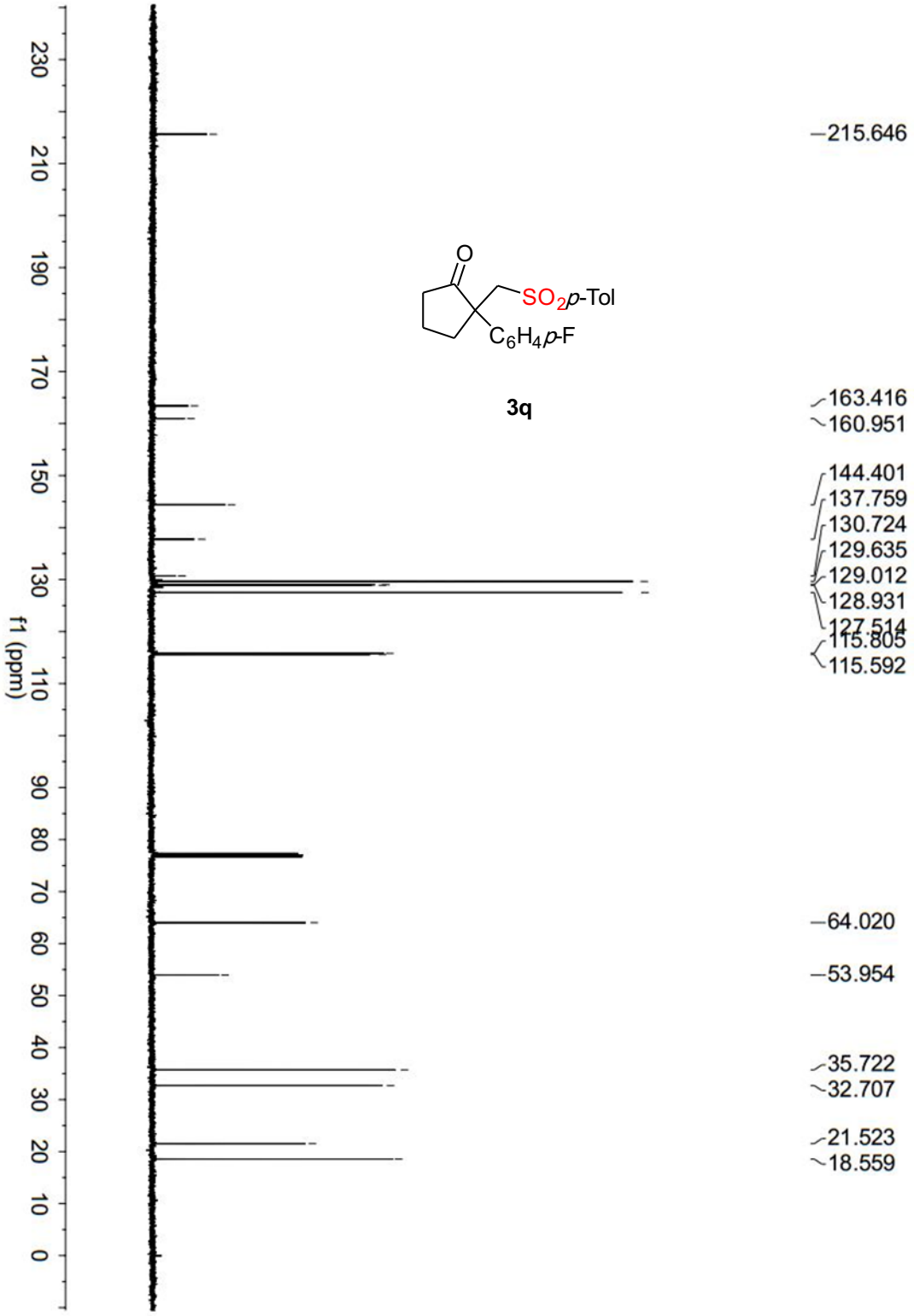
3o

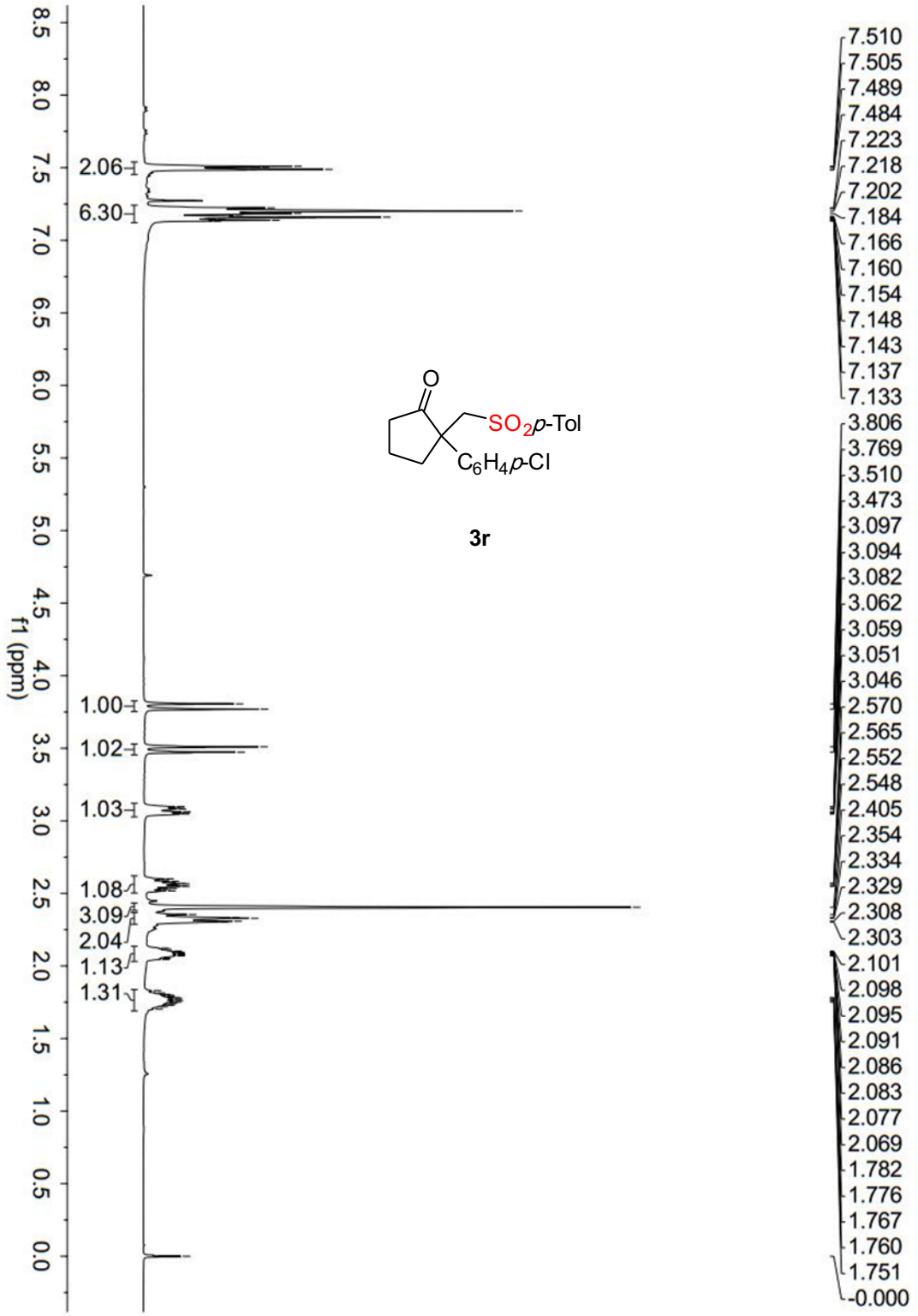

O
SO2p-Tol
C6H4p-OMe
3o
215.829
159.041
144.095
137.937
129.553
128.310
127.540
126.696
114.169
64.051
55.187
53.886
35.667
32.592
21.524
18.539
f1 (ppm)

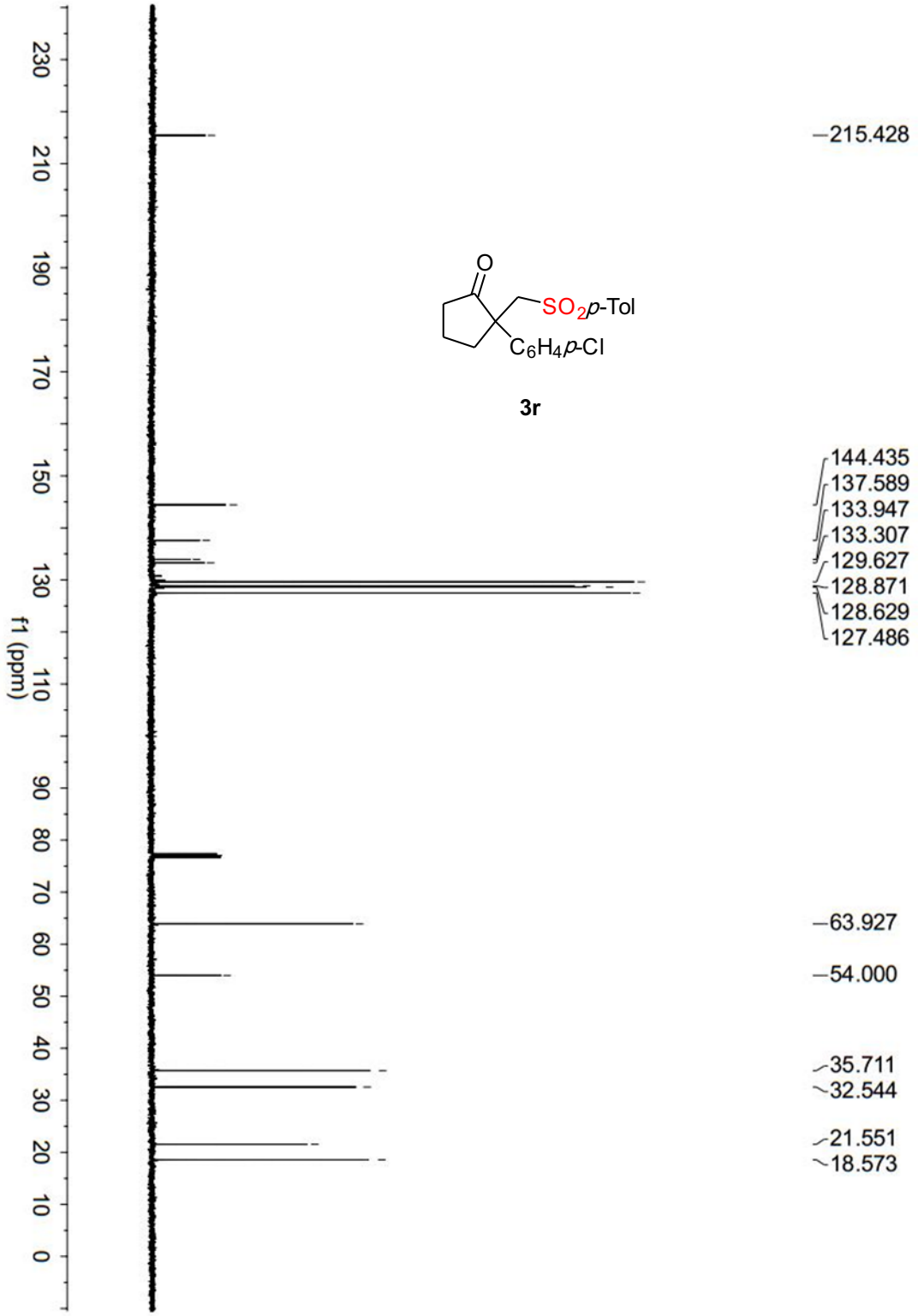

7.566
7.547
7.203
7.184
7.154
7.121
7.017
6.994
6.980
O
SO2p-Tol
C6H4m-Me
3p
3.754
3.718
3.619
3.583
3.069
3.054
3.034
3.020
2.684
2.666
2.652
2.635
2.620
2.385
2.350
2.327
2.219
2.059
2.052
1.783
1.766
1.760
-0.000
1.94
4.01
2.00
1.00
1.00
1.01
1.03
5.00
3.00
1.01
1.03
f1 (ppm)

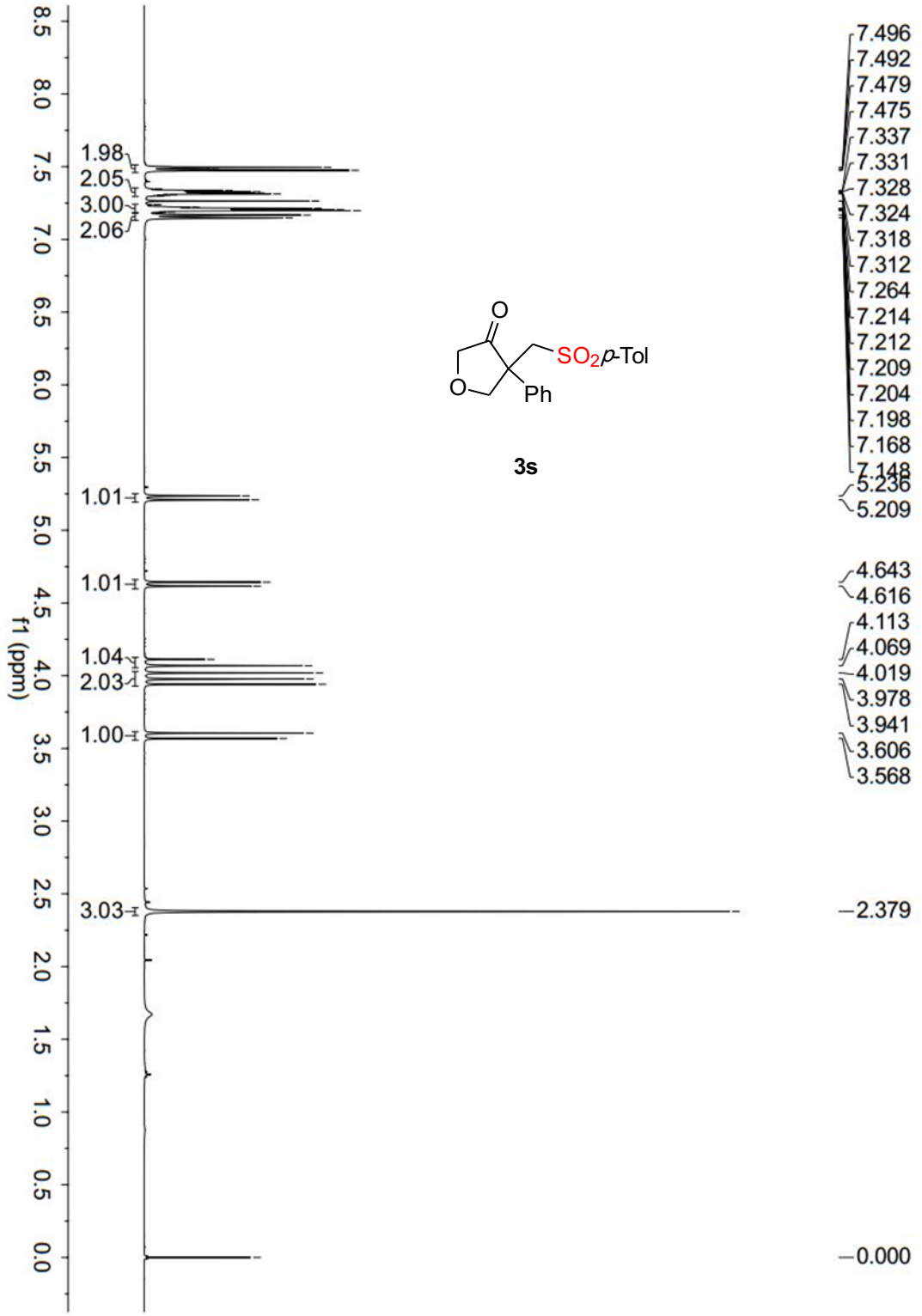

215.962
144.141
138.511
137.872
135.254
129.526
128.752
128.407
127.795
127.525
123.970
63.943
54.594
35.858
32.518
21.517
21.392
18.599
f1 (ppm)
O
SO2p-Tol
C6H4m-Me
3p


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)
1.96
2.43
2.01
1.97
1.00
1.00
1.00
1.03
3.08
2.00
1.02
1.03
O
SO2p-Tol
C6H4p-F
3q
7.557
7.552
7.548
7.536
7.532
7.527
7.290
7.285
7.277
7.269
7.260
7.255
7.224
7.204
6.924
6.918
6.907
6.903
6.898
6.886
6.881
3.767
3.731
3.543
3.506
3.085
3.070
3.050
3.039
3.035
2.642
2.625
2.611
2.607
2.594
2.590
2.576
2.559
2.399
2.367
2.347
2.341
2.335
2.321
2.315
2.312
2.091
2.086
1.775
0.000

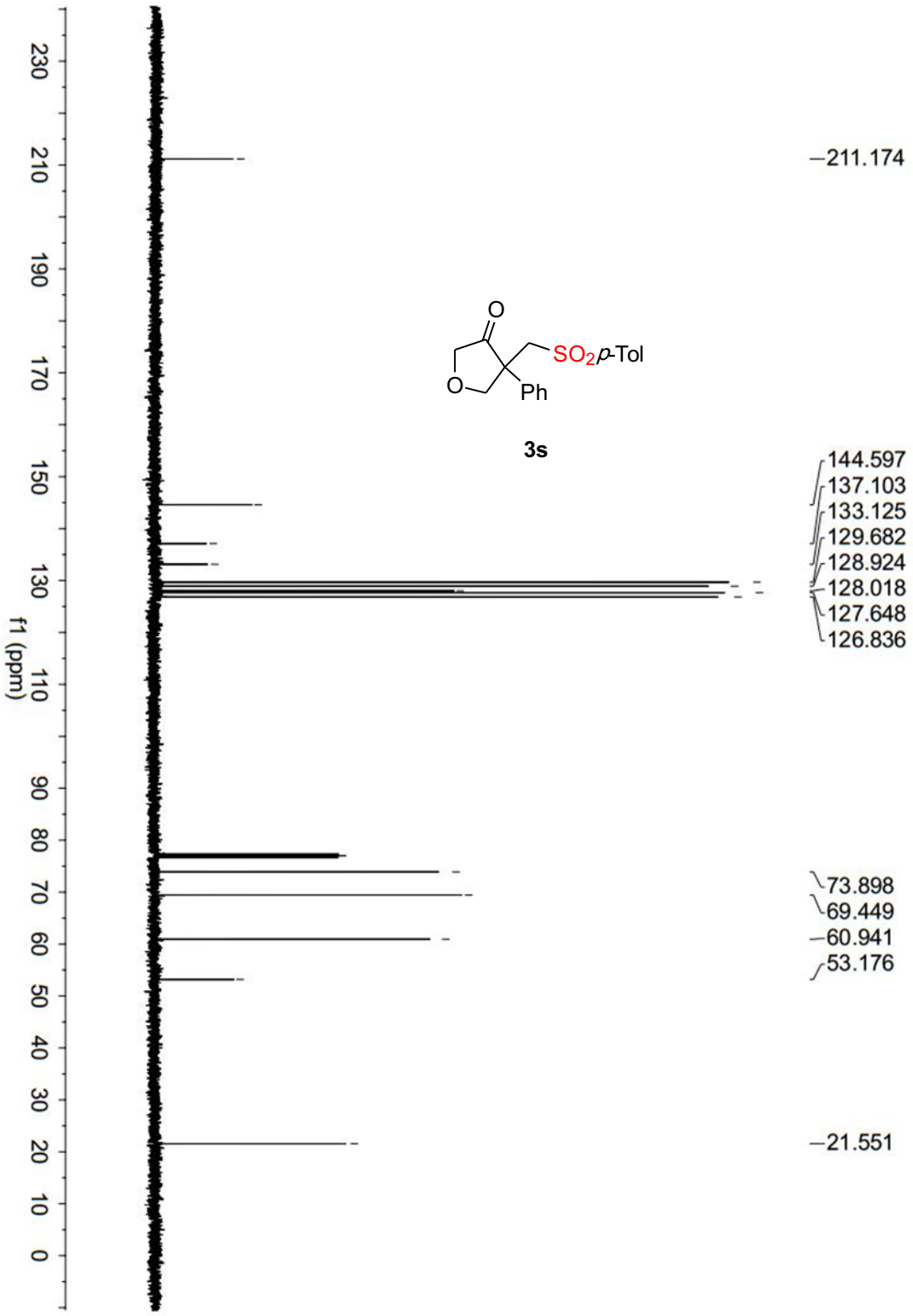

215.646
163.416
160.951
144.401
137.759
130.724
129.635
129.012
128.931
127.514
115.805
115.592
64.020
53.954
35.722
32.707
21.523
18.559
f1 (ppm)
O
SO2p-Tol
C6H4p-F
3q


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)
2.06
6.30
1.00
1.02
1.03
1.08
3.09
2.04
1.13
1.31
O
SO2p-Tol
C6H4p-Cl
3r
7.510
7.505
7.489
7.484
7.223
7.218
7.202
7.184
7.166
7.160
7.154
7.148
7.143
7.137
7.133
3.806
3.769
3.510
3.473
3.097
3.094
3.082
3.062
3.059
3.051
3.046
2.570
2.565
2.552
2.548
2.405
2.354
2.334
2.329
2.308
2.303
2.101
2.098
2.095
2.091
2.086
2.083
2.077
2.069
1.782
1.776
1.767
1.760
1.751
-0.000

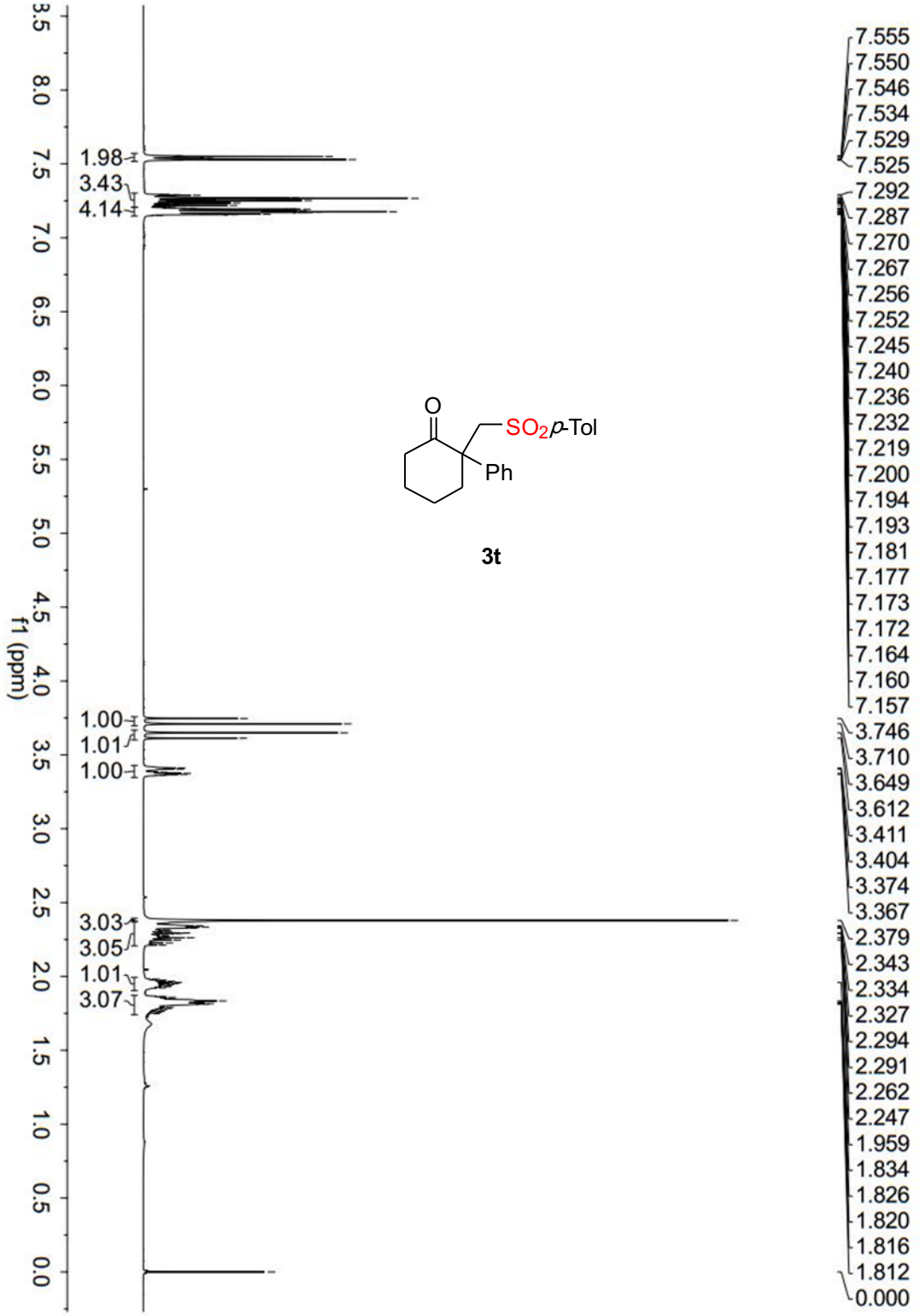

215.428
144.435
137.589
133.947
133.307
129.627
128.871
128.629
127.486
63.927
54.000
35.711
32.544
21.551
18.573
f1 (ppm)
SO2p-Tol
C6H4p-Cl
3r


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
1.98
2.05
3.00
2.06
1.01
1.01
1.04
2.03
1.00
3.03
O
O
SO2p-Tol
Ph
7.496
7.492
7.479
7.475
7.337
7.331
7.328
7.324
7.318
7.312
7.264
7.214
7.212
7.209
7.204
7.198
7.168
7.148
5.236
5.209
4.643
4.616
4.113
4.069
4.019
3.978
3.941
3.606
3.568
2.379
0.000

3s


211.174
144.597
137.103
133.125
129.682
128.924
128.018
127.648
126.836
73.898
69.449
60.941
53.176
21.551
f1 (ppm)
O
O
SO2p-Tol
Ph

3s


f1 (ppm)
1.98
3.43
4.14
1.00
1.01
1.00
3.03
3.05
1.01
3.07
O
SO2p-Tol
Ph
3t
7.555
7.550
7.546
7.534
7.529
7.525
7.292
7.287
7.270
7.267
7.256
7.252
7.245
7.240
7.236
7.232
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7.193
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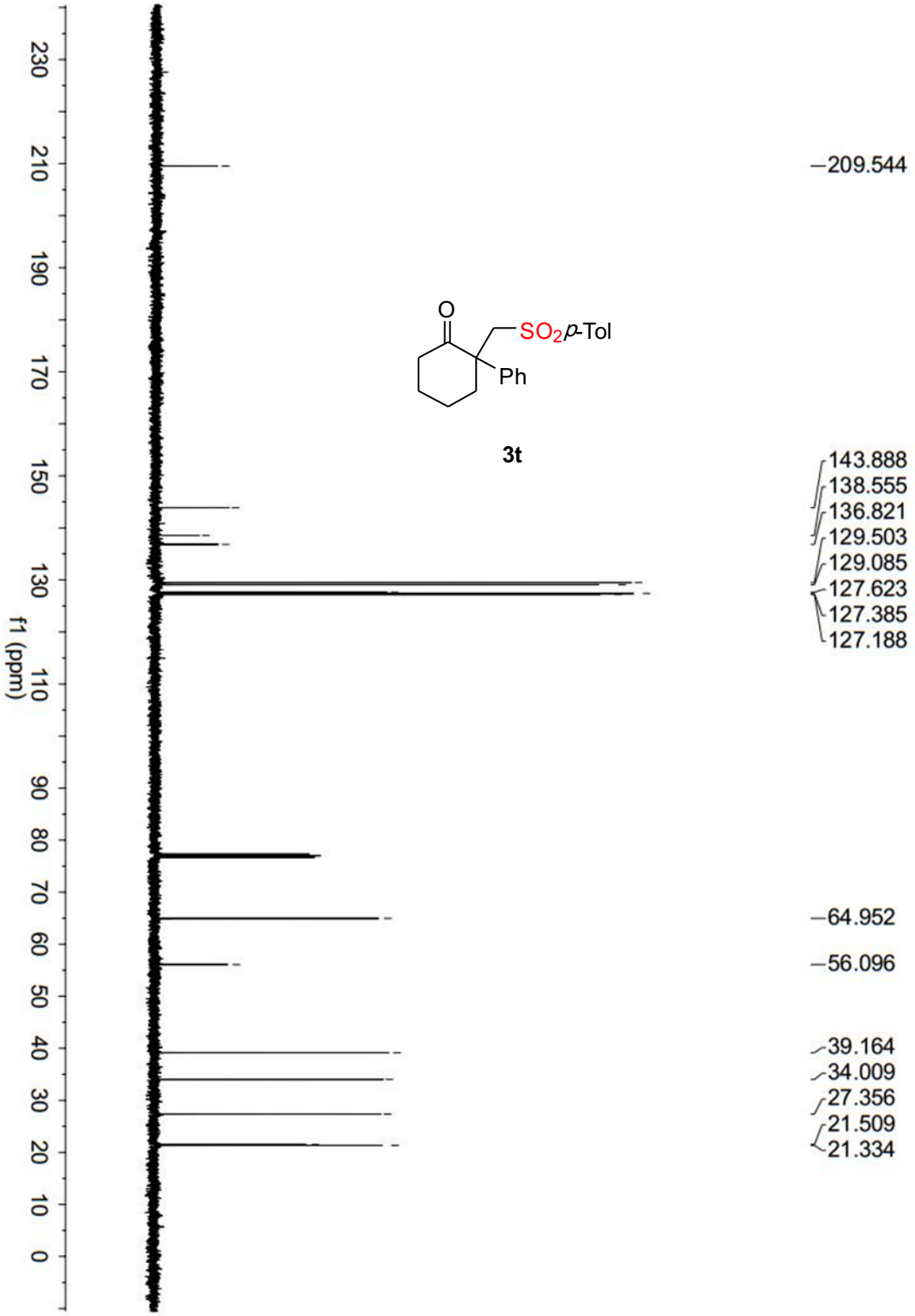
0.000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143.888
138.555
136.821
129.503
129.085
127.623
127.385
127.188
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39.164
34.009
27.356
21.509
21.334
O
SO2p-Tol
Ph
3t
f1 (ppm)

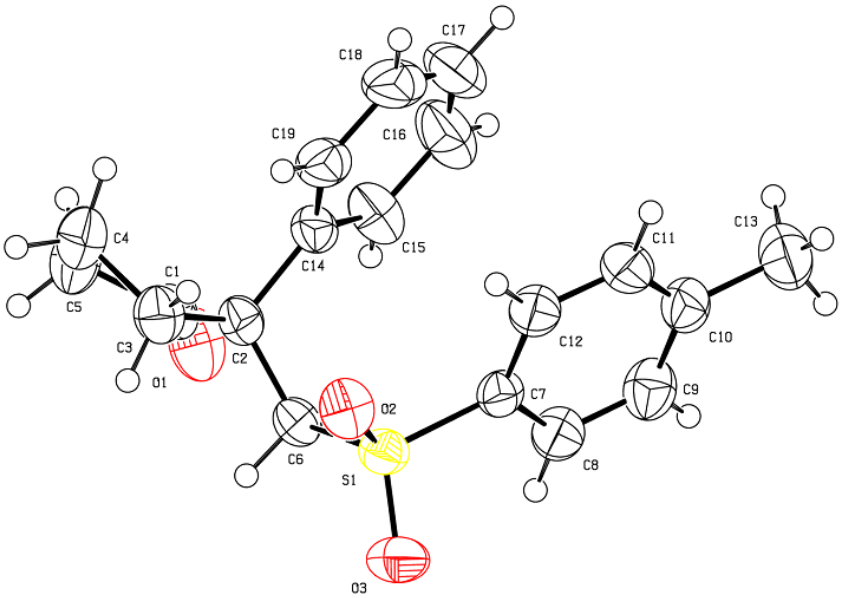

Table 1. Crystal data and structure refinement for **3a**.

Identification code	ga_81211c_a	
Empirical formula	C19 H20 O3 S	
Formula weight	328.41	
Temperature	296(2) K	
Wavelength	1.34138 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.9512(2) Å	a= 102.3370(10)°.
	b = 8.6039(3) Å	b= 92.4660(10)°.
	c = 15.1128(4) Å	g= 108.0020(10)°.
Volume	833.95(4) $Å^3$	
Z	2	
Density (calculated)	1.308 Mg/m^3	
Absorption coefficient	1.192 mm^{-1}	
F(000)	348	
Crystal size	0.310 x 0.240 x 0.160 mm^3	
Theta range for data collection	4.926 to 57.489°.	
Index ranges	-8<=h<=8, -10<=k<=10, -18<=l<=18	
Reflections collected	23271	

Independent reflections	3458 [R(int) = 0.0558]
Completeness to theta = 53.594°	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.864 and 0.692
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3458 / 0 / 210
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0415, wR2 = 0.1121
R indices (all data)	R1 = 0.0440, wR2 = 0.1148
Extinction coefficient	0.044(5)
Largest diff. peak and hole	0.495 and -0.253 e.$Å^{-3}$