Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Thiosulfonylation of alkenes with the insertion of sulfur dioxide under non-metallic conditions

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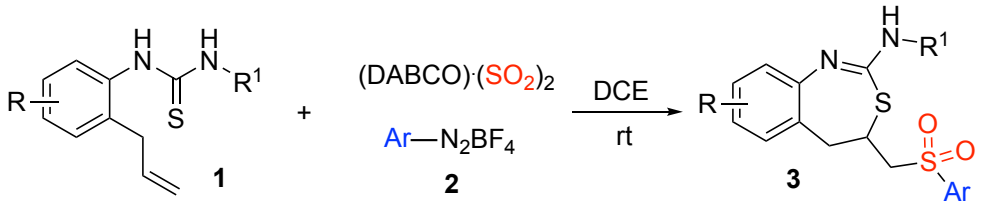
Supporting Information

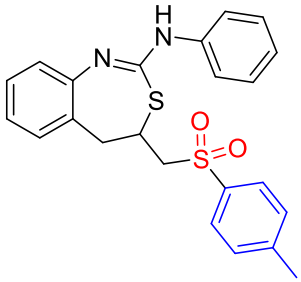
General experimental methods:

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, 32-63 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 reaction of alkenes **1**, (DABCO)·$(SO_2)_2$, and aryldiazonium tetrafluoroborates **2**.*

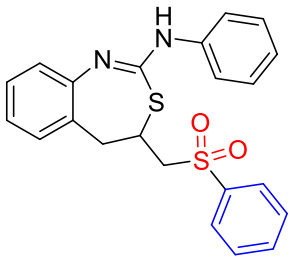


1-(2-Alylaryl)thiourea **1** (0.2 mmol) was added to a mixture of aryldiazonium tetrafluoroborate **2** (0.3 mmol) and DABCO·$(SO_2)_2$ (0.3 mmol) in DCE (2.0 mL) under N_2 atmosphere. The mixture was stirred at room temperature for 12 h. After completion of reaction as indicated by TLC, the solvent was evaporated and the residue was purified directly by flash column chromatography (*n*-hexane/ethyl acetate = 8:1) to give the corresponding product **3**.



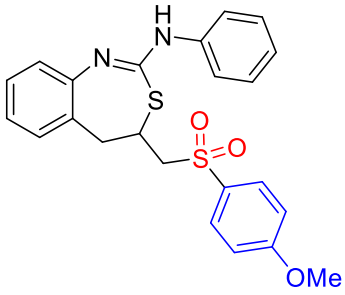
N-phenyl-4-(tosylmethyl)-4,5-dihydrobenzo[*d*][1,3]thiazepin-2-amine (**3a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.26 (m, 3H), 7.20 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.10 – 6.97 (m, 3H), 6.87 (brs, 1H), 4.42 – 4.32 (m, 1H), 3.59 (dd, *J* = 14.3, 7.8 Hz, 1H), 3.37 (dd, *J* = 14.3, 5.5 Hz, 1H), 3.20 (dd, *J* = 13.8, 5.2 Hz, 1H), 2.94 (dd, *J* = 13.8, 8.1 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 145.5, 145.3, 139.9, 136.5, 130.2, 129.7, 129.1, 128.9, 128.2, 128.1, 123.9, 123.5, 123.5, 119.5, 62.1, 49.7, 36.9, 21.7; HRMS (ESI) calcd for $C_{23}H_{23}N_2O_2S_2^+$ ($M+H^+$): 423.1195, found: 423.1179.



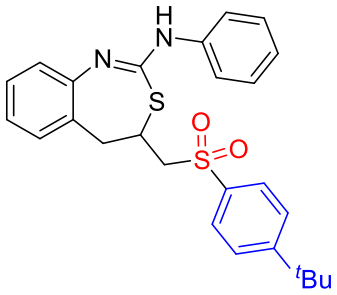
N-phenyl-4-((phenylsulfonyl)methyl)-4,5-dihydrobenzo[*d*][1,3]thiazepin-2-amine (**3b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 2H), 7.72 – 7.64 (m, 3H), 7.59 (dd, *J* = 10.5, 4.7 Hz, 2H), 7.35 – 7.25 (m, 3H), 7.19 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.10 – 6.98 (m, 3H), 6.91 (brs, 1H), 4.44 – 4.34 (m, 1H), 3.61 (dd, *J* = 14.3, 7.8 Hz, 1H), 3.39 (dd, *J* = 14.2, 5.5 Hz, 1H), 3.20 (dd, *J* = 13.8, 5.2 Hz, 1H), 2.94 (dd, *J* = 13.8, 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 145.5, 139.9, 139.4, 134.2, 129.7, 129.6, 129.1, 129.0, 128.2, 128.0, 123.9, 123.6, 123.5, 119.5, 62.0, 49.6, 36.9; HRMS (ESI) calcd for $C_{22}H_{21}N_2O_2S_2^+$ ($M+H^+$): 409.1039, found: 409.1020.



4-(((4-Methoxyphenyl)sulfonyl)methyl)-*N*-phenyl-4,5-dihydrobenzo[*d*][1,3]thiazepin-2-amine (**3c**)

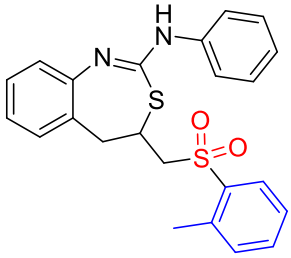
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 2H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.36 – 7.26 (m, 3H), 7.24 – 7.17 (m, 1H), 7.11 – 6.98 (m, 5H), 6.83 (brs, 1H), 4.43 – 4.32 (m, 1H), 3.90 (s, 3H), 3.59 (dd, *J* = 14.3, 7.7 Hz, 1H), 3.37 (dd, *J* = 14.2, 5.5 Hz, 1H), 3.21 (dd, *J* = 13.8, 5.2 Hz, 1H), 2.95 (dd, *J* = 13.8, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 148.2, 145.7, 139.9, 130.8, 130.3, 129.7, 129.2, 129.0, 128.2, 123.9, 123.6, 123.5, 119.5, 114.7, 62.3, 55.8, 49.8, 36.9; HRMS (ESI) calcd for $C_{23}H_{23}N_2O_3S_2^+$ ($M+H^+$): 439.1145, found: 439.1139.



4-(((4-(*tert*-Butyl)phenyl)sulfonyl)methyl)-*N*-phenyl-4,5-dihydrobenzo[*d*][1,3]thiazepin-2-amine (**3d**)

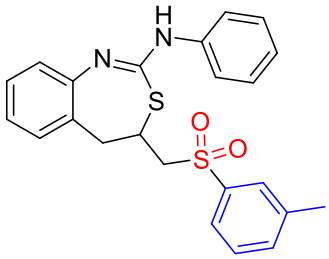
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.6 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.64 – 7.57 (m, 2H), 7.36 – 7.26 (m, 3H), 7.24 – 7.17 (m, 1H), 7.11 – 6.97 (m, 3H), 6.87 (brs, 1H), 4.45 – 4.36 (m, 1H), 3.60 (dd, *J* = 14.2, 8.0 Hz, 1H), 3.38 (dd, *J* = 14.2, 5.3 Hz, 1H), 3.23 (dd, *J* = 13.8, 5.2 Hz, 1H), 2.96 (dd, *J* = 13.8, 8.0 Hz, 1H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 148.2, 145.7, 140.0, 136.4, 129.7, 129.2, 129.0, 128.2,

127.9, 126.6, 123.9, 123.6, 123.5, 119.6, 62.0, 49.7, 36.8, 35.4, 31.1; HRMS (ESI) calcd for $C_{26}H_{29}N_2O_2S_2^+$ ($M+H^+$): 465.1665, found: 465.1662.



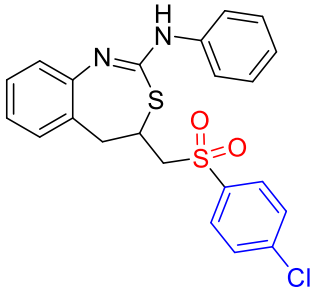
N-phenyl-4-((*o*-tolylsulfonyl)methyl)-4,5-dihydrobenzo[*d*][1,3]thiazepin-2-amine (**3e**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.56 (td, *J* = 7.5, 1.3 Hz, 1H), 7.45 – 7.26 (m, 5H), 7.19 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.12 – 6.97 (m, 3H), 6.81 (brs, 1H), 4.51 – 4.39 (m, 1H), 3.65 (dd, *J* = 14.3, 7.9 Hz, 1H), 3.40 (dd, *J* = 14.3, 5.3 Hz, 1H), 3.20 (dd, *J* = 13.8, 5.2 Hz, 1H), 2.95 (dd, *J* = 13.8, 7.9 Hz, 1H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 145.6, 139.9, 138.0, 137.6, 134.2, 133.0, 130.1, 129.7, 129.1, 129.0, 128.2, 127.0, 123.9, 123.6, 123.5, 119.6, 61.0, 49.6, 36.9, 20.5; HRMS (ESI) calcd for $C_{23}H_{23}N_2O_2S_2^+$ ($M+H^+$): 423.1195, found: 423.1162.



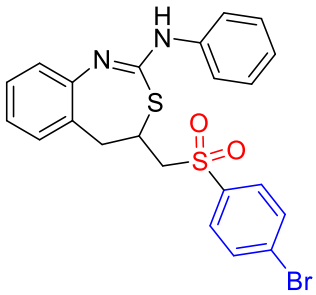
N-phenyl-4-((*m*-tolylsulfonyl)methyl)-4,5-dihydrobenzo[*d*][1,3]thiazepin-2-amine (**3f**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.65 (m, 4H), 7.56 – 7.46 (m, 2H), 7.38 – 7.27 (m, 3H), 7.21 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.13 – 6.98 (m, 3H), 6.83 (brs, 1H), 4.46 – 4.35 (m, 1H), 3.61 (dd, *J* = 14.2, 7.9 Hz, 1H), 3.38 (dd, *J* = 14.2, 5.2 Hz, 1H), 3.22 (dd, *J* = 13.8, 5.2 Hz, 1H), 2.96 (dd, *J* = 13.8, 8.1 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (10 MHz, $CDCl_3$) δ 148.2, 145.5, 140.0 139.9, 139.2, 135.0, 129.7, 129.4, 129.1, 129.0, 128.3, 128.2, 125.1, 123.9, 123.6, 123.5, 119.5, 62.0, 49.6, 36.9, 21.4; HRMS (ESI) calcd for $C_{23}H_{23}N_2O_2S_2^+$ ($M+H^+$): 423.1195, found: 423.1171.



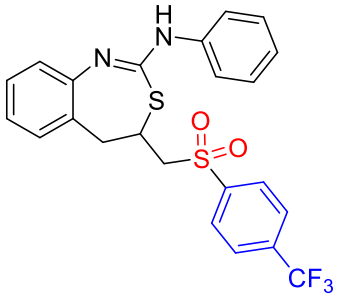
4-(((4-Chlorophenyl)sulfonyl)methyl)-*N*-phenyl-4,5-dihydrobenzo[*d*][1,3]thiazepin-2-amine (**3g**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.83 (m, 2H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.36 – 7.26 (m, 3H), 7.24 – 7.18 (m, 1H), 7.11 – 6.97 (m, 3H), 6.85 (brs, 1H), 4.45 – 4.35 (m, 1H), 3.60 (dd, *J* = 14.2, 7.7 Hz, 1H), 3.38 (dd, *J* = 14.2, 5.6 Hz, 1H), 3.22 (dd, *J* = 13.8, 5.2 Hz, 1H), 2.96 (dd, *J* = 13.8, 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 145.4, 141.1, 139.9, 137.8, 129.9, 129.7, 129.5, 129.0, 128.3, 123.9, 123.7, 123.6, 119.6, 62.1, 49.4, 36.9; HRMS (ESI) calcd for $C_{22}H_{20}ClN_2O_2S_2^+$ ($M+H^+$): 443.0649, found: 443.0629.



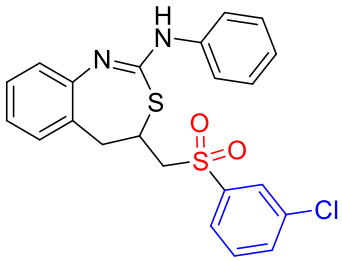
4-(((4-Bromophenyl)sulfonyl)methyl)-*N*-phenyl-4,5-dihydrobenzo[*d*][1,3]thiazepin-2-amine (**3h**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.7 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.38 – 7.26 (m, 3H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.14 – 6.96 (m, 3H), 6.87 (brs, 1H), 4.46 – 4.34 (m, 1H), 3.60 (dd, *J* = 14.3, 7.6 Hz, 1H), 3.38 (dd, *J* = 14.2, 5.6 Hz, 1H), 3.22 (dd, *J* = 13.8, 5.1 Hz, 1H), 2.95 (dd, *J* = 13.8, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 145.4, 139.9, 138.3, 132.9, 129.7, 129.6, 129.0, 128.3, 123.9, 123.7, 123.6, 119.6, 62.1, 49.4, 36.9; HRMS (ESI) calcd for $C_{22}H_{20}BrN_2O_2S_2^+$ ($M+H^+$): 487.0131, found: 487.0136.



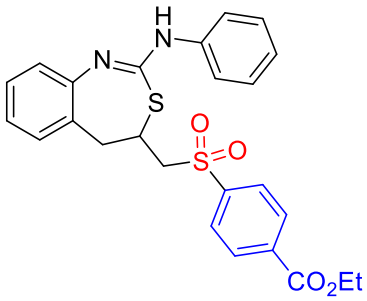
N-phenyl-4-(((4-(trifluoromethyl)phenyl)sulfonyl)methyl)-4,5-dihydrobenzo[*d*][1,3]thiazepin-2-amine (**3i**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.2 Hz, 2H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.38 – 7.27 (m, 3H), 7.23 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.12 – 6.99 (m, 3H), 6.83 (brs, 1H), 4.50 – 4.39 (m, 1H), 3.64 (dd, *J* = 14.2, 7.7 Hz, 1H), 3.41 (dd, *J* = 14.2, 5.6 Hz, 1H), 3.26 (dd, *J* = 13.8, 5.2 Hz, 1H), 2.98 (dd, *J* = 13.9, 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 145.2, 142.9, 139.8, 135.9 (q, *J* = 33.3 Hz), 129.7, 129.0, 128.8, 128.7, 128.4, 126.7 (q, *J* = 3.6 Hz), 124.0, 123.7, 123.6, 123.0 (q, *J* = 273.2 Hz), 119.5, 61.9, 49.3, 37.0; HRMS (ESI) calcd for $C_{23}H_{20}F_3N_2O_2S_2^+$ ($M+H^+$): 477.0913, found: 477.0899.



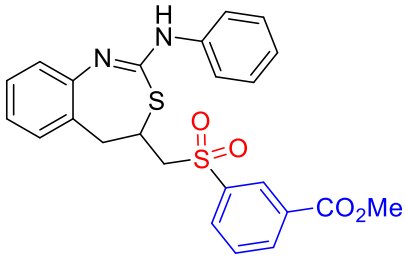
4-(((3-Chlorophenyl)sulfonyl)methyl)-*N*-phenyl-4,5-dihydrobenzo[*d*][1,3]thiazepin-2-amine (**3j**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (t, *J* = 1.8 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.76 – 7.62 (m, 3H), 7.55 (t, *J* = 7.9 Hz, 1H), 7.37 – 7.27 (m, 3H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.12 – 6.98 (m, 3H), 6.86 (brs, 1H), 4.47 – 4.36 (m, 1H), 3.62 (dd, *J* = 14.2, 7.7 Hz, 1H), 3.40 (dd, *J* = 14.2, 5.6 Hz, 1H), 3.23 (dd, *J* = 13.8, 5.1 Hz, 1H), 2.97 (dd, *J* = 13.8, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 145.3, 141.1, 139.9, 135.9, 134.4, 130.9, 129.7, 129.0, 128.9, 128.3, 128.1, 126.2, 123.9, 123.7, 123.6, 119.6, 62.0, 49.4, 36.9; HRMS (ESI) calcd for $C_{22}H_{20}ClN_2O_2S_2^+$ ($M+H^+$): 443.0649, found: 443.0642.



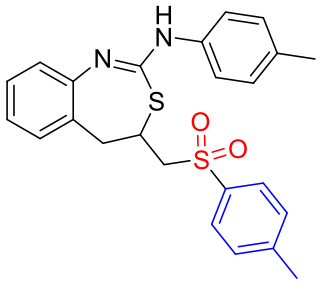
Ethyl 4-(((2-(phenylamino)-4,5-dihydrobenzo[*d*][1,3]thiazepin-4-yl)methyl)sulfonyl) benzoate (**3k**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.21 (m, 2H), 8.05 – 7.98 (m, 2H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.36 – 7.27 (m, 3H), 7.24 – 7.18 (m, 1H), 7.12 – 6.97 (m, 3H), 6.82 (brs, 1H), 4.47 – 4.36 (m, 3H), 3.63 (dd, *J* = 14.3, 7.7 Hz, 1H), 3.41 (dd, *J* = 14.3, 5.6 Hz, 1H), 3.22 (dd, *J* = 13.8, 5.2 Hz, 1H), 2.96 (dd, *J* = 13.8, 8.0 Hz, 1H), 1.43 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 148.0, 145.4, 143.0, 139.9, 135.6, 130.6, 129.7, 129.0, 128.9, 128.3, 128.1, 123.9, 123.6, 123.5, 119.6, 62.0 61.9, 49.4, 36.9, 14.3; HRMS (ESI) calcd for $C_{25}H_{25}N_2O_4S_2^+$ ($M+H^+$): 481.1250, found: 481.1245.



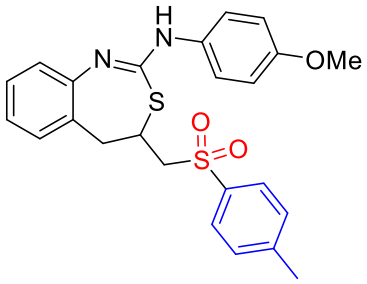
Methyl 3-(((2-(phenylamino)-4,5-dihydrobenzo[*d*][1,3]thiazepin-4-yl)methyl)sulfonyl) benzoate (**3l**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (t, *J* = 1.5 Hz, 1H), 8.38 – 8.33 (m, 1H), 8.16 – 8.11 (m, 1H), 7.74 – 7.63 (m, 3H), 7.36 – 7.26 (m, 3H), 7.23 (d, *J* = 6.6 Hz, 1H), 7.10 – 6.98 (m, 3H), 6.85 (brs, 1H), 4.47 – 4.37 (m, 1H), 3.98 (s, 3H), 3.64 (dd, *J* = 14.2, 7.6 Hz, 1H), 3.43 (dd, *J* = 14.2, 5.6 Hz, 1H), 3.24 (dd, *J* = 13.8, 5.2 Hz, 1H), 2.97 (dd, *J* = 13.8, 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 148.1, 145.4, 140.1, 139.9, 135.0, 132.0, 131.8, 129.9, 129.7, 129.2, 129.0, 128.3, 123.9, 123.6, 123.5, 119.5, 62.0, 52.8, 49.5, 37.0; HRMS (ESI) calcd for $C_{24}H_{23}N_2O_4S_2^+$ ($M+H^+$): 467.1094, found: 467.1079.



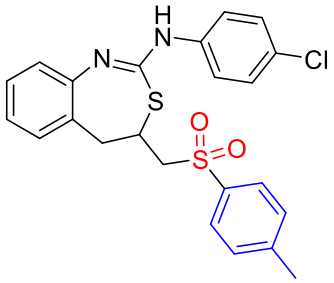
N-(*p*-tolyl)-4-(tosylmethyl)-4,5-dihydrobenzo[*d*][1,3]thiazepin-2-amine (**3m**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.26 (m, 1H), 7.22 – 7.17 (m, 1H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.08 – 6.95 (m, 2H), 6.77 (brs, 1H), 4.42 – 4.30 (m, 1H), 3.59 (dd, *J* = 14.3, 7.9 Hz, 1H), 3.36 (dd, *J* = 14.2, 5.4 Hz, 1H), 3.20 (dd, *J* = 13.8, 5.2 Hz, 1H), 2.94 (dd, *J* = 13.8, 8.0 Hz, 1H), 2.47 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 145.6, 145.3, 137.4, 136.5, 133.1, 130.2, 129.7, 129.4, 129.2, 128.2, 128.1, 123.9, 123.4, 119.7, 62.1, 49.6, 36.9, 21.7, 20.9; HRMS (ESI) calcd for $C_{24}H_{25}N_2O_2S_2^+$ ($M+H^+$): 437.1352, found: 437.1345.



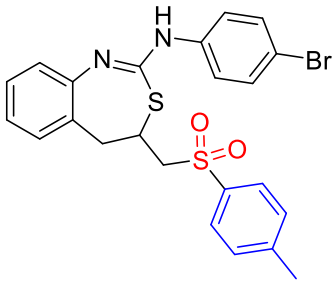
N-(4-methoxyphenyl)-4-(tosylmethyl)-4,5-dihydrobenzo[*d*][1,3]thiazepin-2-amine (**3n**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.9 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.24 (m, 1H), 7.22 – 7.17 (m, 1H), 7.06 – 6.94 (m, 2H), 6.91 – 6.82 (m, 2H), 6.71 (brs, 1H), 4.40 – 4.30 (m, 1H), 3.80 (s, 3H), 3.59 (dd, *J* = 14.3, 7.9 Hz, 1H), 3.36 (dd, *J* = 14.2, 5.4 Hz, 1H), 3.20 (dd, *J* = 13.8, 5.2 Hz, 1H), 2.94 (dd, *J* = 13.8, 8.0 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 148.3, 145.9, 145.3, 136.4, 133.2, 130.2, 129.7, 129.2, 128.2, 128.1, 123.8, 123.4, 121.4, 114.1, 62.1, 55.5, 49.4, 36.9, 21.7; HRMS (ESI) calcd for $C_{24}H_{25}N_2O_3S_2^+$ ($M+H^+$): 453.1301, found: 453.1296.



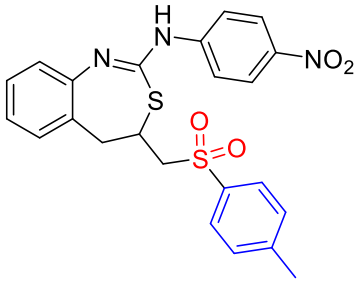
N-(4-chlorophenyl)-4-(tosylmethyl)-4,5-dihydrobenzo[*d*][1,3]thiazepin-2-amine (**3o**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.26 (m, 3H), 7.21 (d, *J* = 6.5 Hz, 1H), 7.05 (td, *J* = 7.4, 1.1 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.87 (brs, 1H), 4.44 – 4.33 (m, 1H), 3.59 (dd, *J* = 14.3, 7.8 Hz, 1H), 3.36 (dd, *J* = 14.2, 5.5 Hz, 1H), 3.20 (dd, *J* = 13.9, 5.2 Hz, 1H), 2.95 (dd, *J* = 13.8, 8.0 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 145.8, 145.4, 138.6, 136.3, 130.2, 129.7, 129.1, 128.9, 128.3, 128.2, 128.0, 123.9, 123.8, 120.8, 62.0, 49.8, 36.8, 21.7; HRMS (ESI) calcd for $C_{23}H_{22}ClN_2O_2S_2^+$ ($M+H^+$): 457.0806, found: 457.0790.



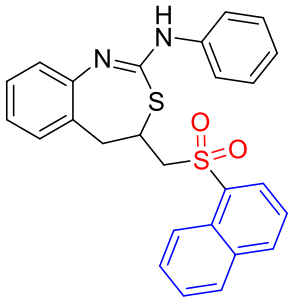
N-(4-bromophenyl)-4-(tosylmethyl)-4,5-dihydrobenzo[*d*][1,3]thiazepin-2-amine (**3p**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.47 – 7.36 (m, 4H), 7.33 – 7.27 (m, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.85 (brs, 1H), 4.45 – 4.33 (m, 1H), 3.59 (dd, *J* = 14.2, 7.8 Hz, 1H), 3.36 (dd, *J* = 14.2, 5.5 Hz, 1H), 3.20 (dd, *J* = 13.9, 5.1 Hz, 1H), 2.95 (dd, *J* = 13.8, 8.0 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 145.7, 145.4, 139.1, 136.3, 131.8, 130.2, 129.7, 129.1, 128.3, 128.0, 123.9, 123.8, 121.2, 115.7, 62.0, 49.8, 36.8, 21.7; HRMS (ESI) calcd for $C_{23}H_{22}BrN_2O_2S_2^+$ ($M+H^+$): 501.0301, found: 501.0301.



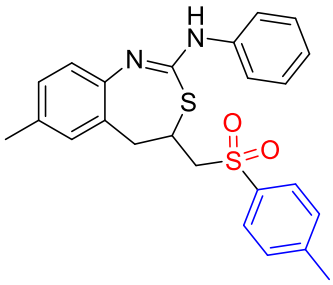
N-(4-nitrophenyl)-4-(tosylmethyl)-4,5-dihydrobenzo[*d*][1,3]thiazepin-2-amine (**3q**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 9.1 Hz, 2H), 7.92 – 7.74 (m, 4H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.33 (td, *J* = 7.7, 1.4 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.10 (td, *J* = 7.4, 0.9 Hz, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 4.53 – 4.40 (m, 1H), 3.60 (dd, *J* = 14.2, 7.5 Hz, 1H), 3.38 (dd, *J* = 14.2, 5.6 Hz, 1H), 3.21 (dd, *J* = 13.9, 5.0 Hz, 1H), 2.98 (dd, *J* = 13.9, 8.0 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 145.9, 145.8, 145.6, 142.4, 136.2, 130.3, 129.8, 129.0, 128.4, 128.0, 125.0, 124.3, 124.0, 118.8, 62.1, 50.5, 36.9, 21.7; HRMS (ESI) calcd for $C_{23}H_{22}N_3O_4S_2^+$ ($M+H^+$): 468.1046, found: 468.1032.



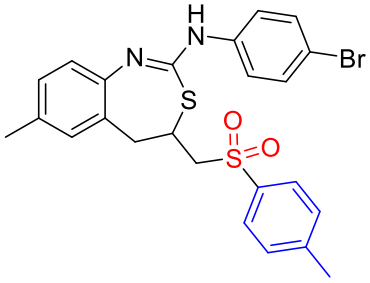
4-((Naphthalen-1-ylsulfonyl)methyl)-*N*-phenyl-4,5-dihydrobenzo[*d*][1,3]thiazepin-2-amine (**3r**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.6 Hz, 1H), 8.34 (dd, *J* = 7.4, 1.2 Hz, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.80 – 7.72 (m, 1H), 7.71 – 7.52 (m, 4H), 7.33 – 7.21 (m, 3H), 7.12 (d, *J* = 6.5 Hz, 1H), 7.07 – 6.92 (m, 3H), 6.55 (brs, 1H), 4.46 – 4.34 (m, 1H), 3.78 (dd, *J* = 14.4, 7.1 Hz, 1H), 3.64 (dd, *J* = 14.4, 5.9 Hz, 1H), 3.14 (dd, *J* = 13.8, 5.3 Hz, 1H), 2.88 (dd, *J* = 13.7, 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 145.5, 139.8, 135.8, 134.4, 134.2, 130.9, 129.6, 129.1, 128.9, 128.9, 128.2, 127.3, 124.7, 123.8, 123.6, 123.5, 119.5, 61.7, 50.1, 37.1; HRMS (ESI) calcd for $C_{26}H_{23}N_2O_2S_2^+$ ($M+H^+$): 459.1195, found: 459.1191.



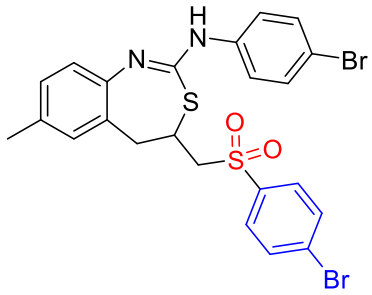
7-Methyl-*N*-phenyl-4-(tosylmethyl)-4,5-dihydrobenzo[*d*][1,3]thiazepin-2-amine (**3s**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.13 – 7.03 (m, 2H), 6.99 (s, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.80 (brs, 1H), 4.40 – 4.30 (m, 1H), 3.60 (dd, *J* = 14.3, 7.9 Hz, 1H), 3.38 (dd, *J* = 14.3, 5.4 Hz, 1H), 3.16 (dd, *J* = 13.8, 5.2 Hz, 1H), 2.89 (dd, *J* = 13.8, 8.2 Hz, 1H), 2.47 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 145.3, 140.0, 136.5, 133.1, 130.3, 130.2, 128.9, 128.9, 128.1, 123.7, 123.4, 119.5, 62.2, 49.7, 36.9, 21.7, 20.9; HRMS (ESI) calcd for $C_{26}H_{23}N_2O_2S_2^+$ ($M+H^+$): 437.1352, found: 437.1338.



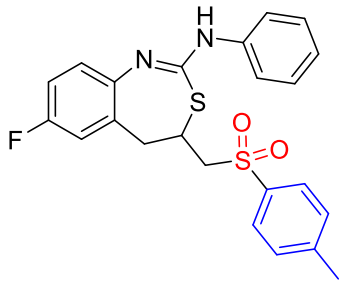
N-(4-bromophenyl)-7-methyl-4-(tosylmethyl)-4,5-dihydrobenzo[*d*][1,3]thiazepin-2-amine (**3t**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.46 – 7.37 (m, 4H), 7.10 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.99 (s, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.80 (brs, 1H), 4.42 – 4.31 (m, 1H), 3.59 (dd, *J* = 14.3, 7.8 Hz, 1H), 3.37 (dd, *J* = 14.3, 5.5 Hz, 1H), 3.15 (dd, *J* = 13.8, 5.2 Hz, 1H), 2.89 (dd, *J* = 13.8, 8.1 Hz, 1H), 2.47 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 145.4, 145.1, 139.2, 136.4, 133.3, 131.8, 130.3, 130.2, 128.9, 128.0, 123.7, 121.2, 115.6, 62.2, 49.8, 36.9, 21.7, 20.9; HRMS (ESI) calcd for $C_{24}H_{24}BrN_2O_2S_2^+$ ($M+H^+$): 515.0457, found: 515.0471.



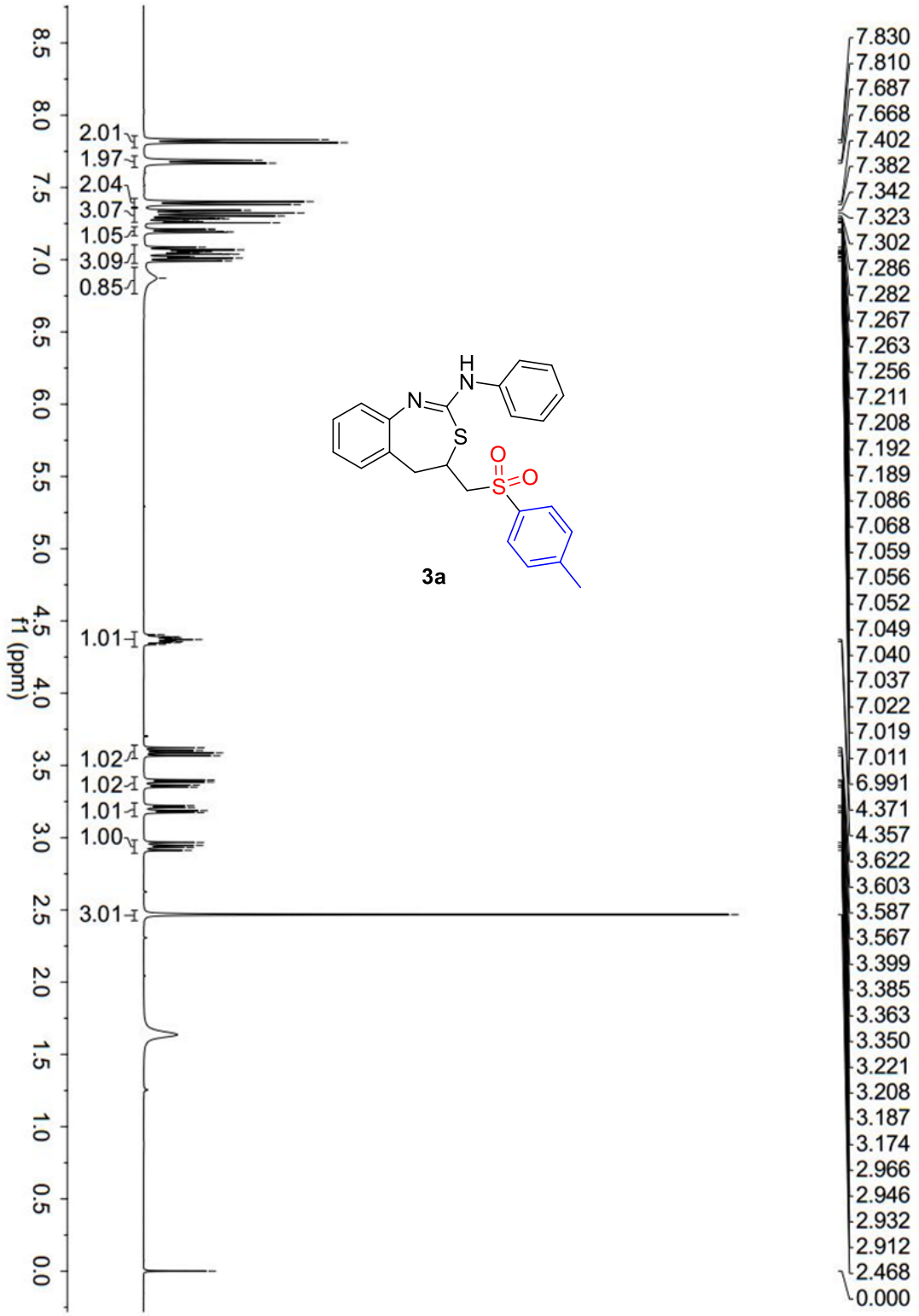
N-(4-bromophenyl)-4-(((4-bromophenyl)sulfonyl)methyl)-7-methyl-4,5-dihydrobenzo[*d*][1,3]thiazepin-2-amine (**3u**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.69 (m, 4H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.9 Hz, 2H), 7.15 – 7.06 (m, 1H), 7.04 – 6.97 (m, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.77 (brs, 1H), 4.44 – 4.33 (m, 1H), 3.60 (dd, *J* = 14.3, 7.6 Hz, 1H), 3.38 (dd, *J* = 14.2, 5.7 Hz, 1H), 3.17 (dd, *J* = 13.8, 5.2 Hz, 1H), 2.90 (dd, *J* = 13.8, 8.0 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 139.1, 138.3, 133.4, 132.9, 131.88, 131.8, 130.3, 129.7, 129.6, 129.0, 128.7, 123.7, 121.1, 115.7, 62.2, 49.6, 37.0, 20.9; HRMS (ESI) calcd for $C_{23}H_{21}Br_2N_2O_2S_2^+$ ($M+H^+$): 578.9406, found: 578.9407.



7-Fluoro-*N*-phenyl-4-(tosylmethyl)-4,5-dihydrobenzo[*d*][1,3]thiazepin-2-amine (**3v**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.01 – 6.91 (m, 3H), 6.83 (brs, 1H), 4.44 – 4.34 (m, 1H), 3.57 (dd, *J* = 14.2, 8.1 Hz, 1H), 3.36 (dd, *J* = 14.2, 5.3 Hz, 1H), 3.18 (dd, *J* = 13.8, 5.2 Hz, 1H), 2.94 (dd, *J* = 13.9, 7.9 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8 (d, *J* = 242.8 Hz), 145.8, 145.5, 144.4 (d, *J* = 2.2 Hz), 139.7, 136.4, 130.6 (d, *J* = 7.8 Hz), 130.2, 129.0, 128.0, 123.6, 125.1 (d, *J* = 8.2 Hz), 119.5, 116.2 (d, *J* = 22.4 Hz), 114.8 (d, *J* = 22.0 Hz), 61.9, 49.2, 36.7, 21.7; HRMS (ESI) calcd for $C_{23}H_{22}FN_2O_2S_2^+$ ($M+H^+$): 441.1101, found: 441.1090.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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)
2.01
1.97
2.04
3.07
1.05
3.09
0.85
1.01
1.02
1.02
1.01
1.00
3.01
H
N
N
S
O
S
O
7.830
7.810
7.687
7.668
7.402
7.382
7.342
7.323
7.302
7.286
7.282
7.267
7.263
7.256
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7.208
7.192
7.189
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7.052
7.049
7.040
7.037
7.022
7.019
7.011
6.991
4.371
4.357
3.622
3.603
3.587
3.567
3.399
3.385
3.363
3.350
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3.174
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2.932
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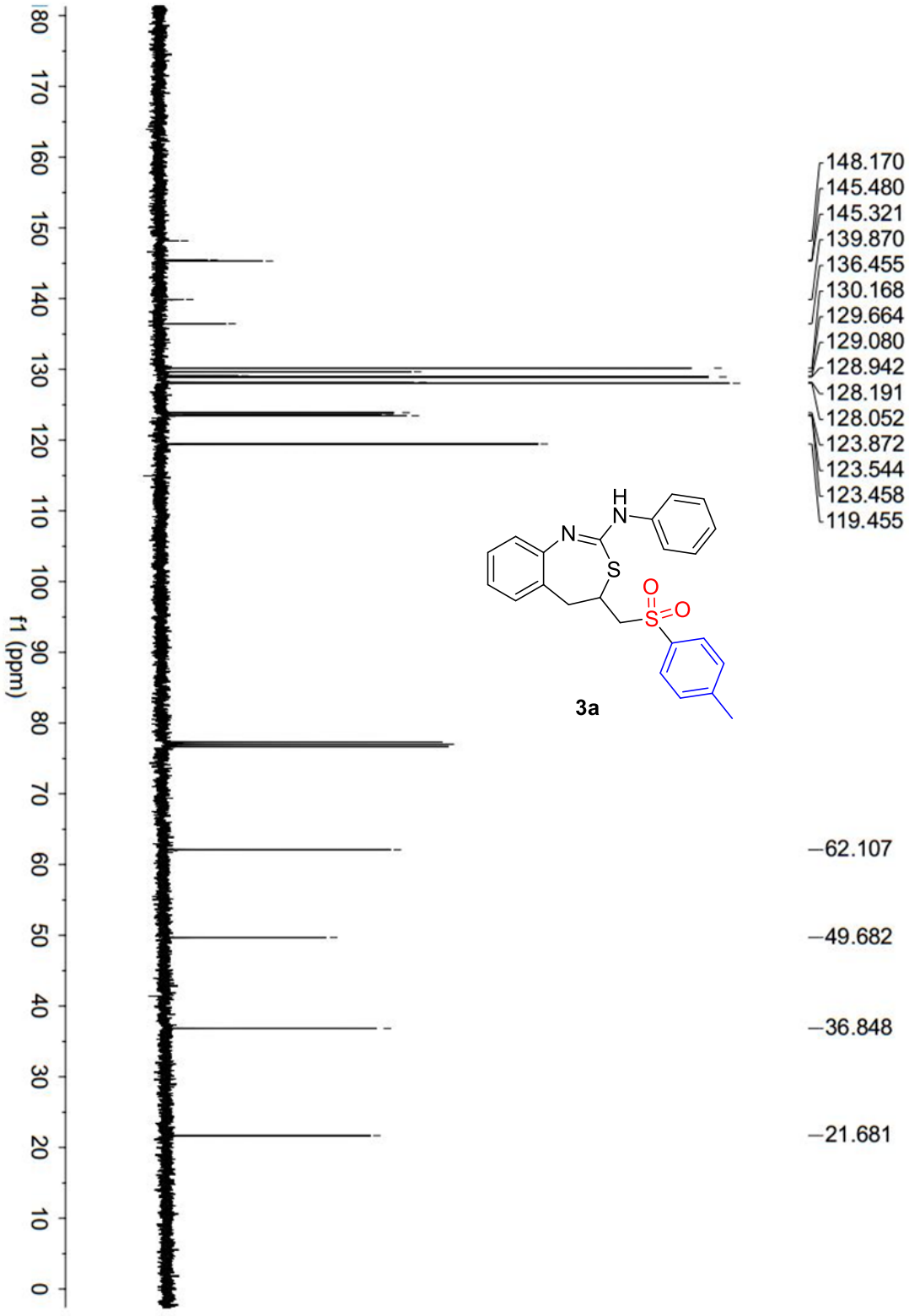
2.468
0.000

3a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145.321
139.870
136.455
130.168
129.664
129.080
128.942
128.191
128.052
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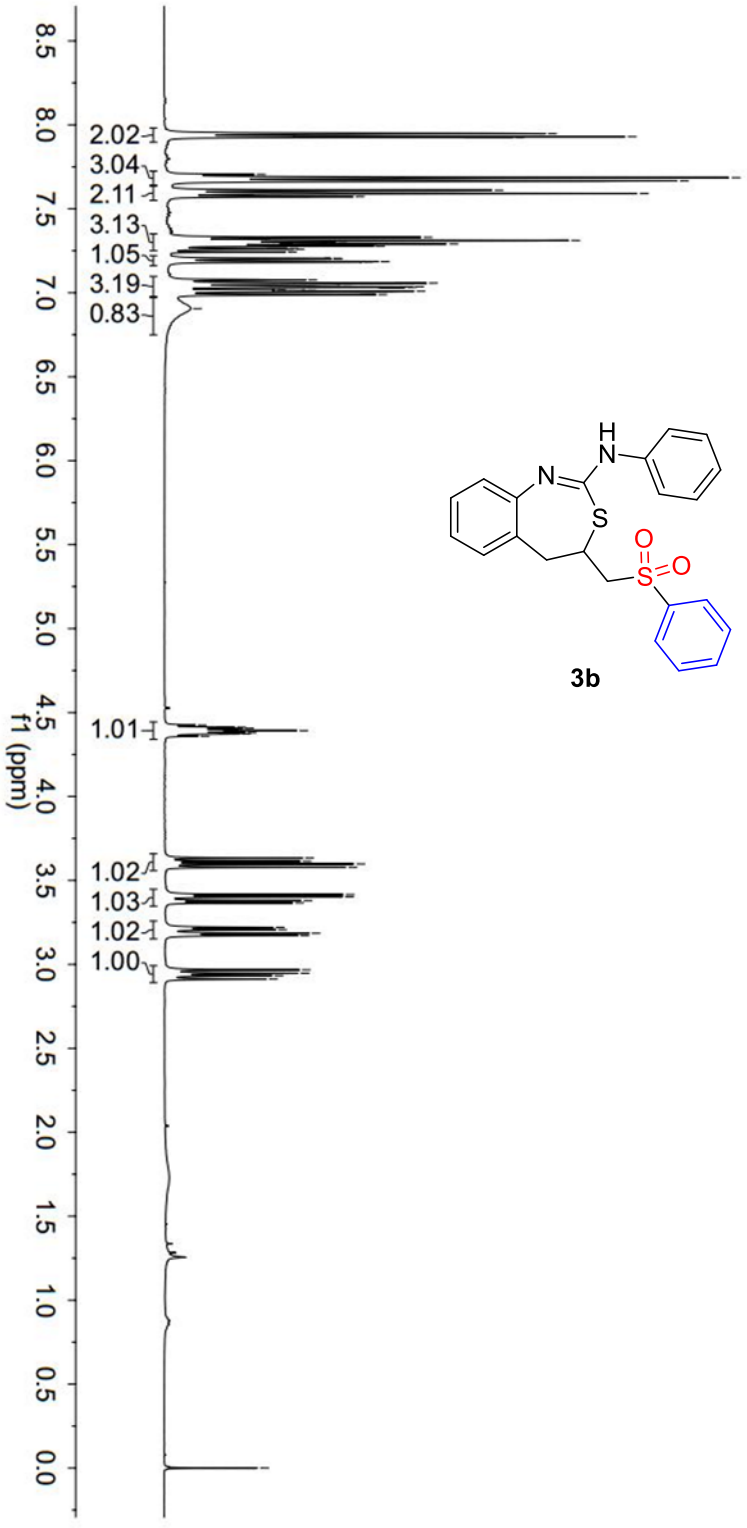
123.544
123.458
119.455
62.107
49.682
36.848
21.681
f1 (ppm)
3a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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
2.02
3.04
2.11
3.13
1.05
3.19
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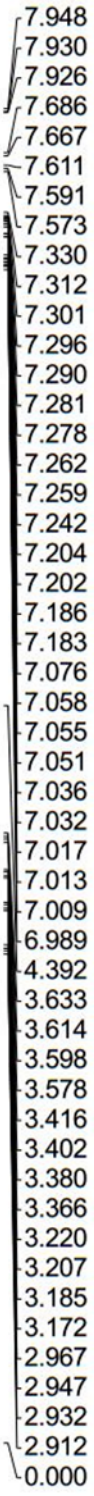
1.01
1.02
1.03
1.02
1.00
H
N
N
S
O
S
O

3b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7.926
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7.667
7.611
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7.573
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7.281
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7.262
7.259
7.242
7.204
7.202
7.186
7.183
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7.055
7.051
7.036
7.032
7.017
7.013
7.009
6.989
4.392
3.633
3.614
3.598
3.578
3.416
3.402
3.380
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3.207
3.185
3.172
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2.947
2.932
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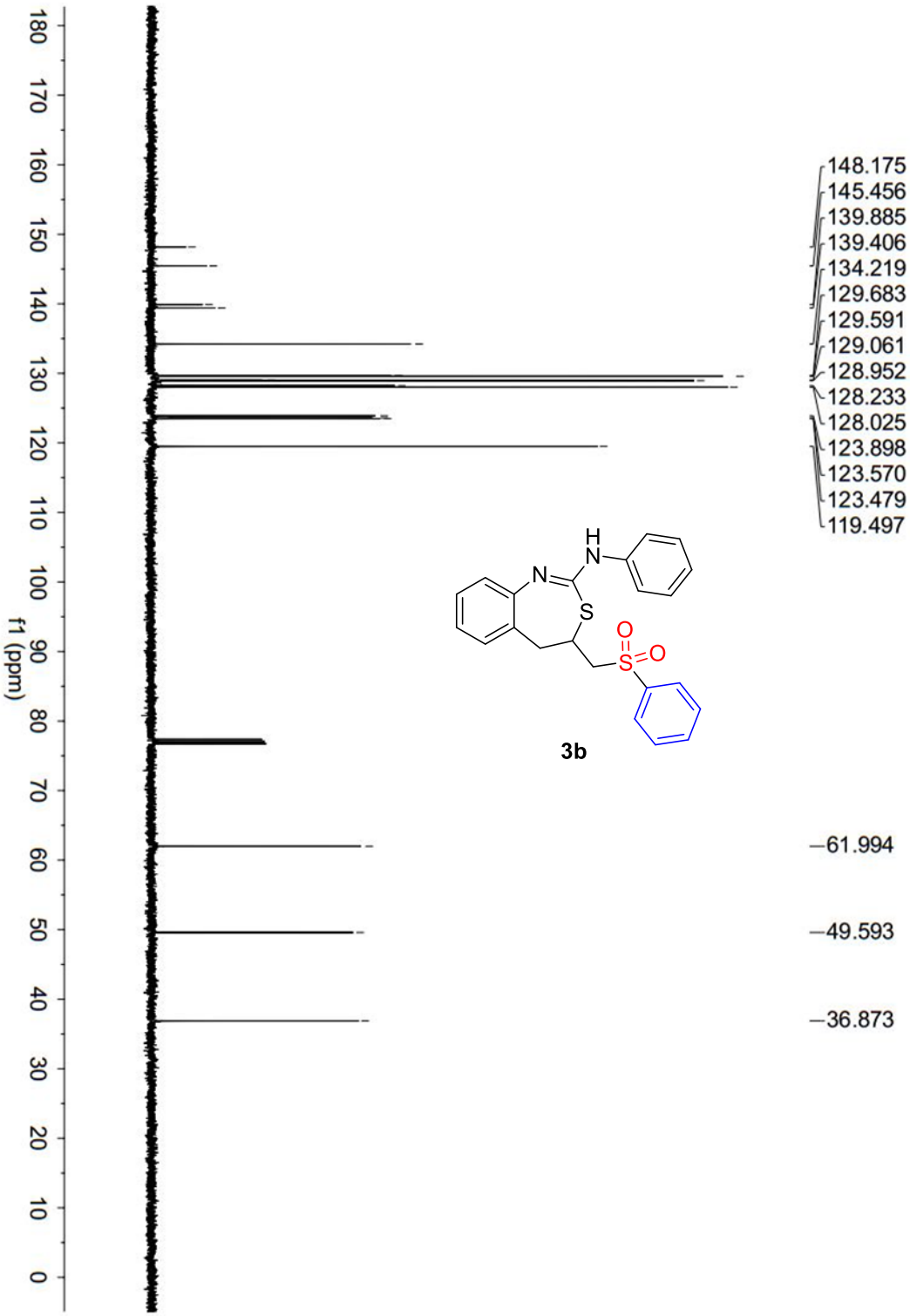
0.000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129.683
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129.061
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128.233
128.025
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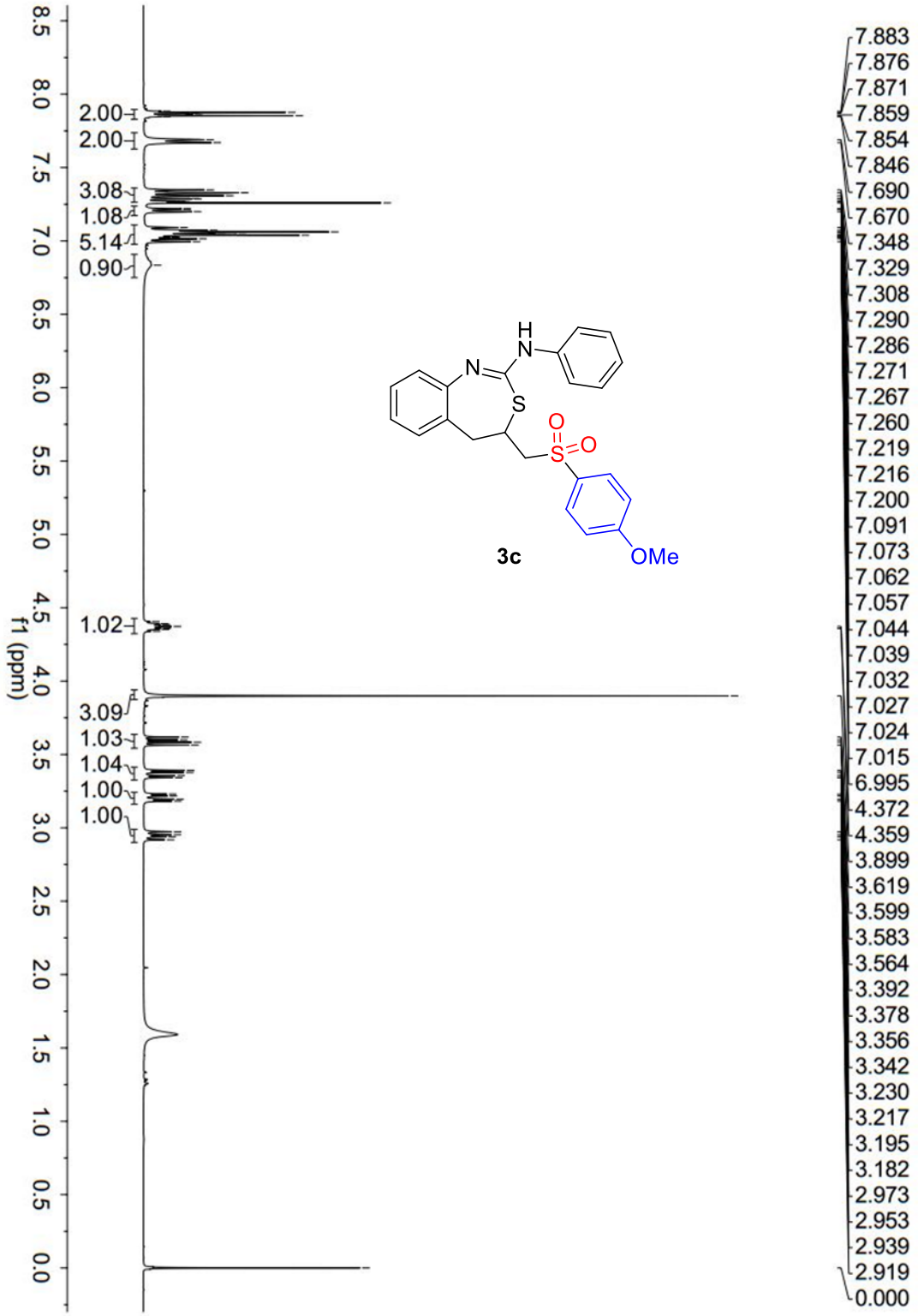
123.570
123.479
119.497
61.994
49.593
36.873
f1 (ppm)
H
N
N
S
O
S
O

3b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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
f1 (ppm)
2.00
2.00
3.08
1.08
5.14
0.90
1.02
3.09
1.03
1.04
1.00
1.00
H
N
N
S
O
S
O
OMe
3c
7.883
7.876
7.871
7.859
7.854
7.846
7.690
7.670
7.348
7.329
7.308
7.290
7.286
7.271
7.267
7.260
7.219
7.216
7.200
7.091
7.073
7.062
7.057
7.044
7.039
7.032
7.027
7.024
7.015
6.995
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3.378
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3.217
3.195
3.182
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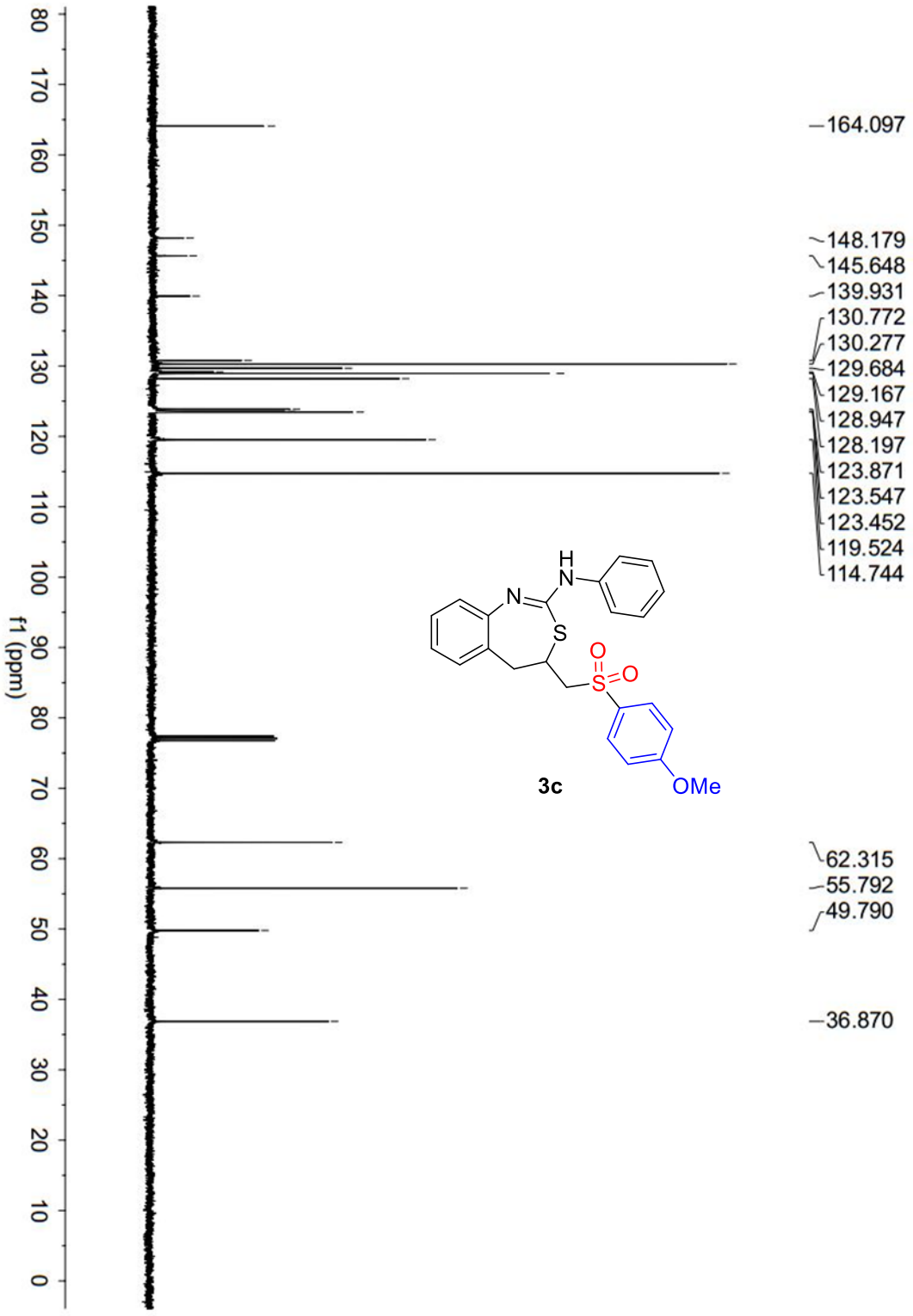
2.953
2.939
2.919
0.000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130.277
129.684
129.167
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128.197
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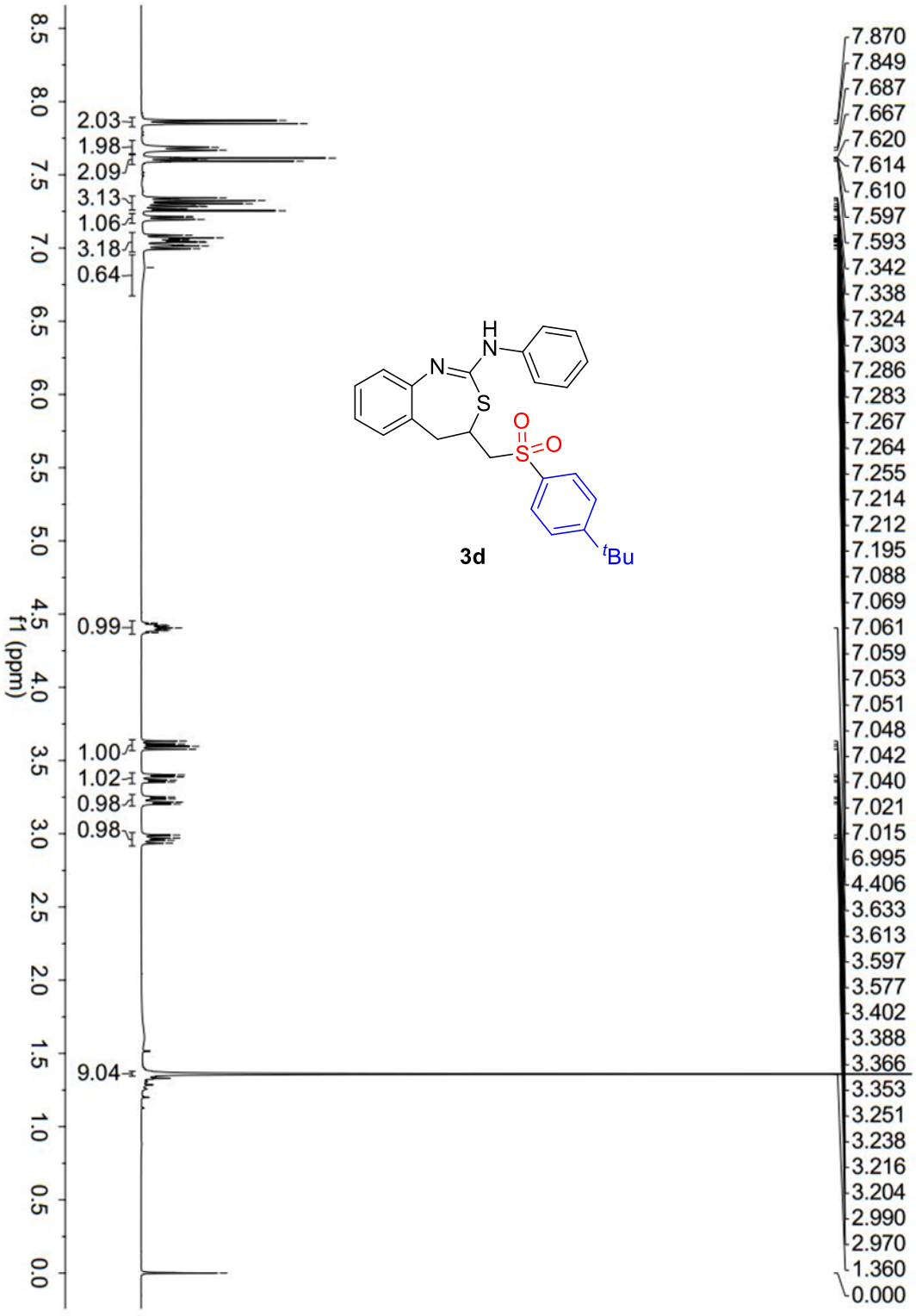
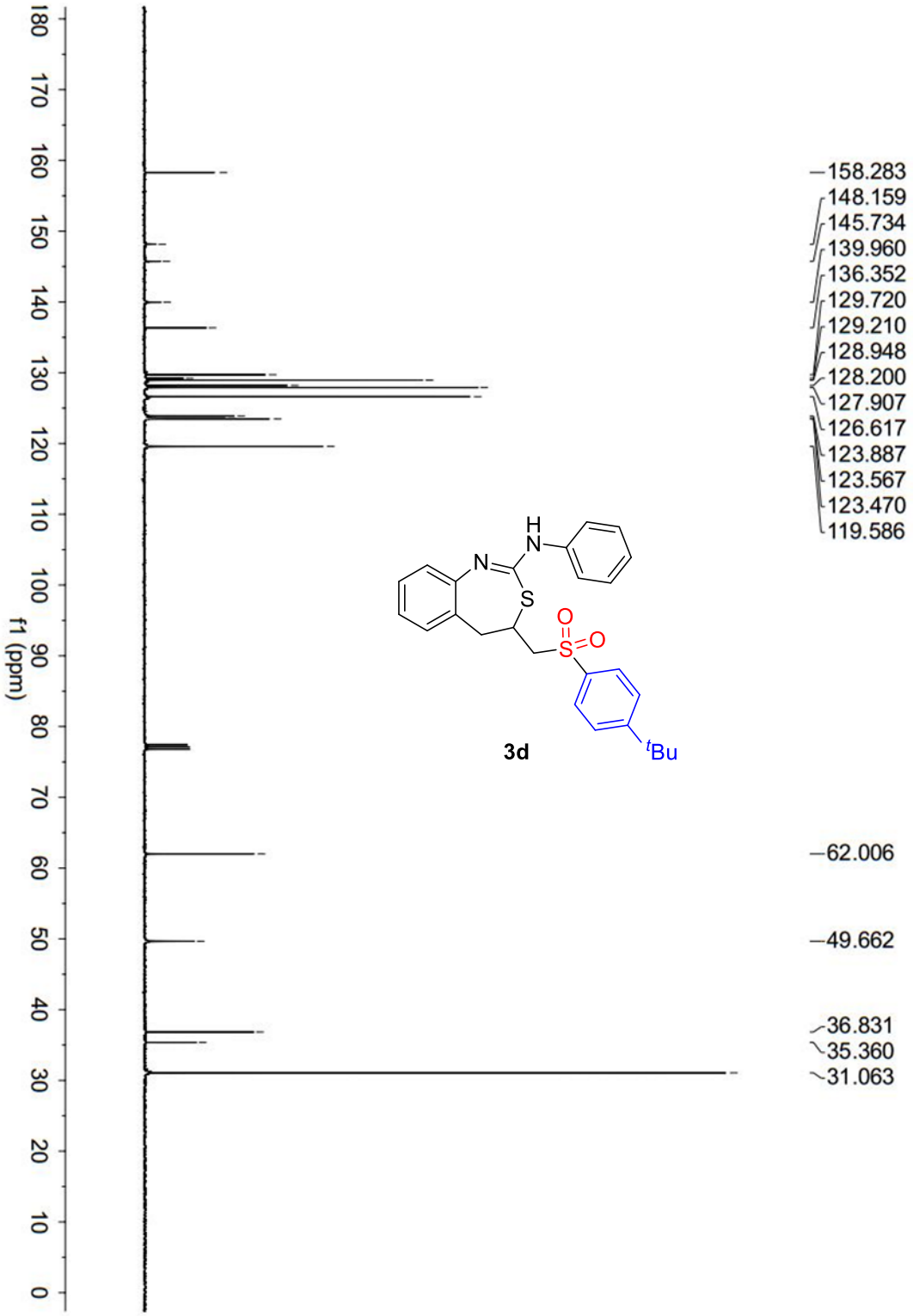
123.547
123.452
119.524
114.744
62.315
55.792
49.790
36.870
f1 (ppm)
3c
OMe


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)
2.03
1.98
2.09
3.13
1.06
3.18
0.64
0.99
1.00
1.02
0.98
0.98
9.04
H
N
N
S
O
S
O
3d
tBu
7.870
7.849
7.687
7.667
7.620
7.614
7.610
7.597
7.593
7.342
7.338
7.324
7.303
7.286
7.283
7.267
7.264
7.255
7.214
7.212
7.195
7.088
7.069
7.061
7.059
7.053
7.051
7.048
7.042
7.040
7.021
7.015
6.995
4.406
3.633
3.613
3.597
3.577
3.402
3.388
3.366
3.353
3.251
3.238
3.216
3.204
2.990
2.970
1.360
0.000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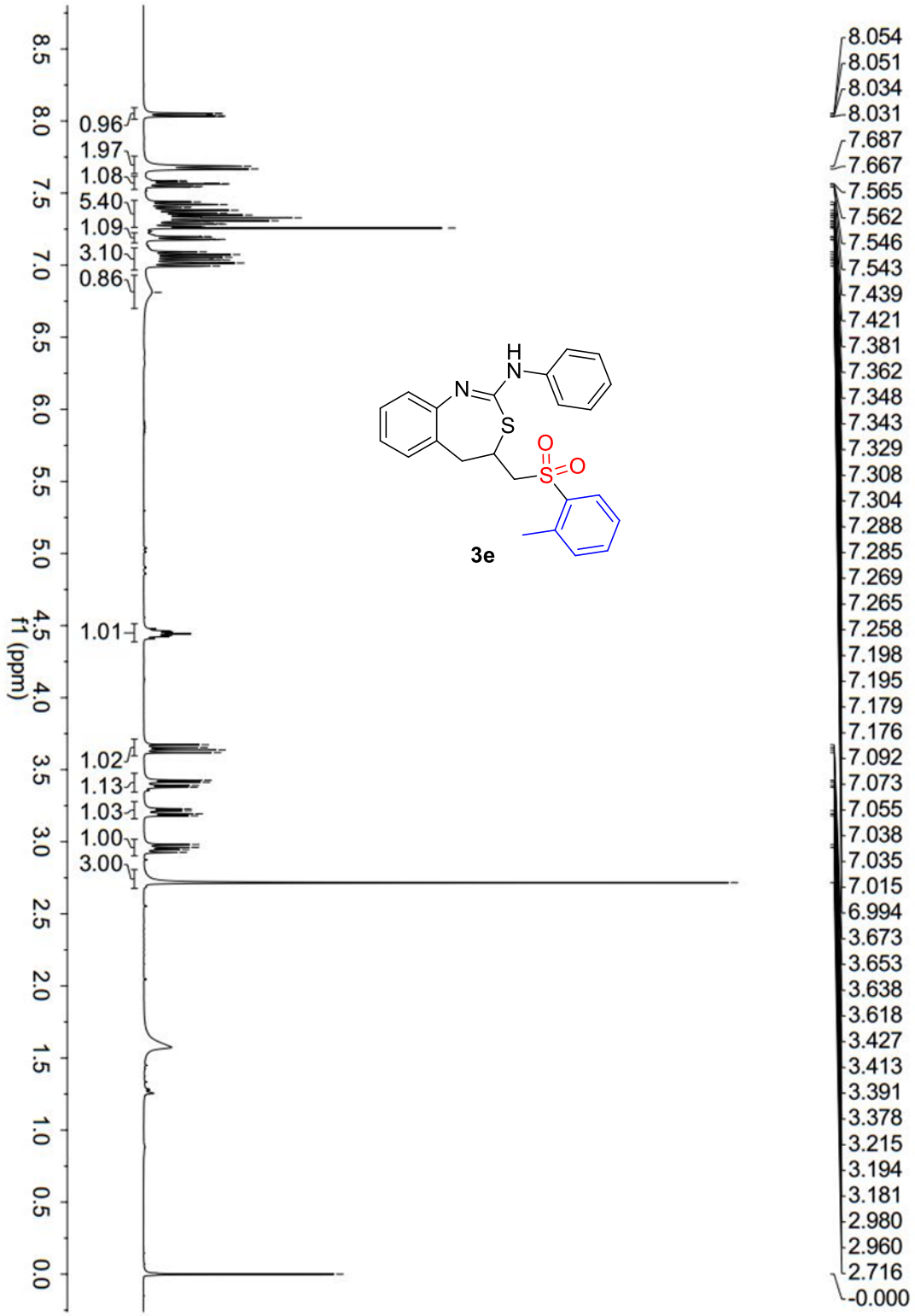
148.159
145.734
139.960
136.352
129.720
129.210
128.948
128.200
127.907
126.617
123.887
123.567
123.470
119.586
62.006
49.662
36.831
35.360
31.063
f1 (ppm)
H
N
N
S
O
S
O
tBu
3d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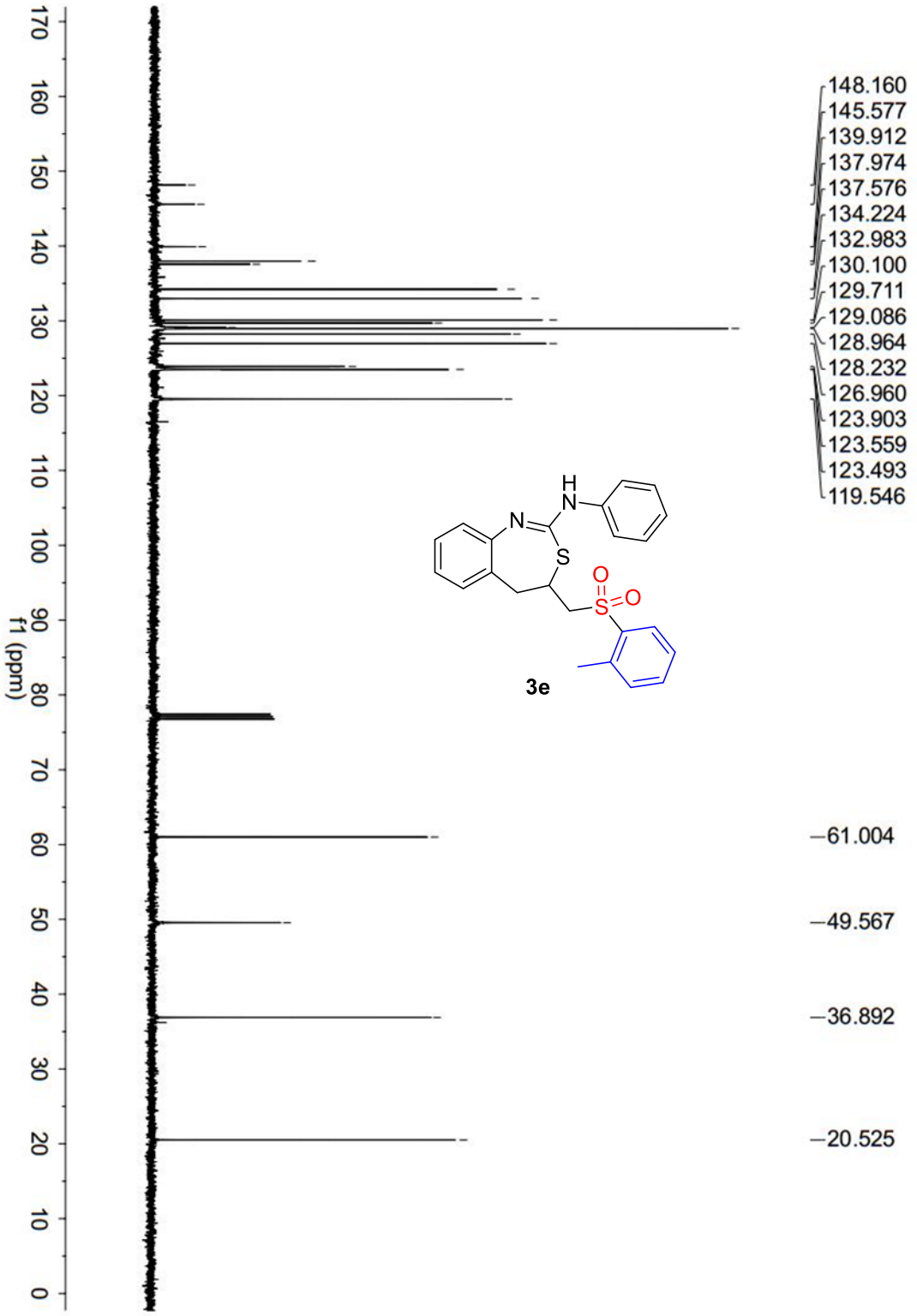
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
0.96
1.97
1.08
5.40
1.09
3.10
0.86
1.01
1.02
1.13
1.03
1.00
3.00
H
N
N
S
O
S
O
3e
8.054
8.051
8.034
8.031
7.687
7.667
7.565
7.562
7.546
7.543
7.439
7.421
7.381
7.362
7.348
7.343
7.329
7.308
7.304
7.288
7.285
7.269
7.265
7.258
7.198
7.195
7.179
7.176
7.092
7.073
7.055
7.038
7.035
7.015
6.994
3.673
3.653
3.638
3.618
3.427
3.413
3.391
3.378
3.215
3.194
3.181
2.980
2.960
2.716
-0.000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145.577
139.912
137.974
137.576
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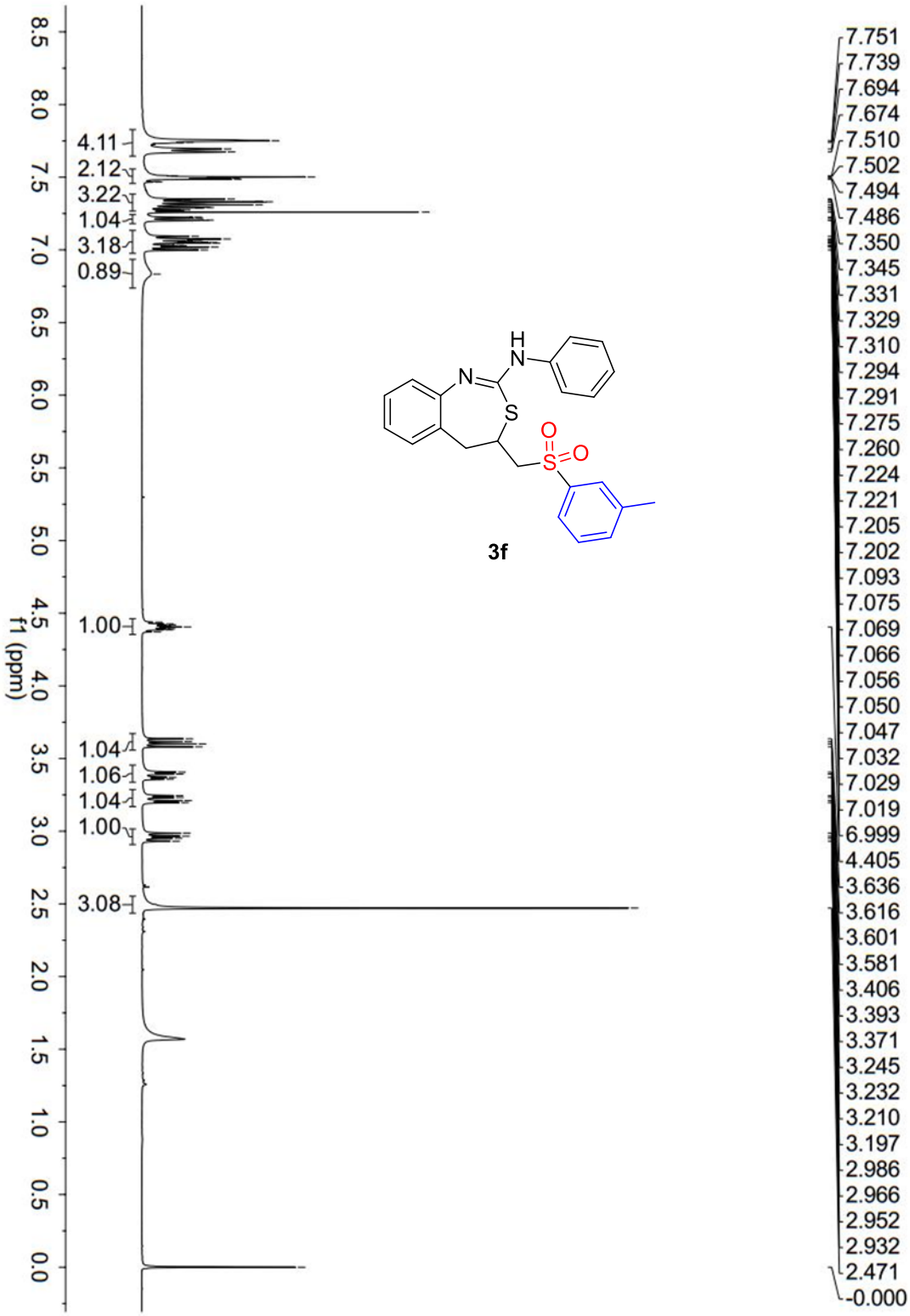
132.983
130.100
129.711
129.086
128.964
128.232
126.960
123.903
123.559
123.493
119.546
61.004
49.567
36.892
20.525
f1 (ppm)
3e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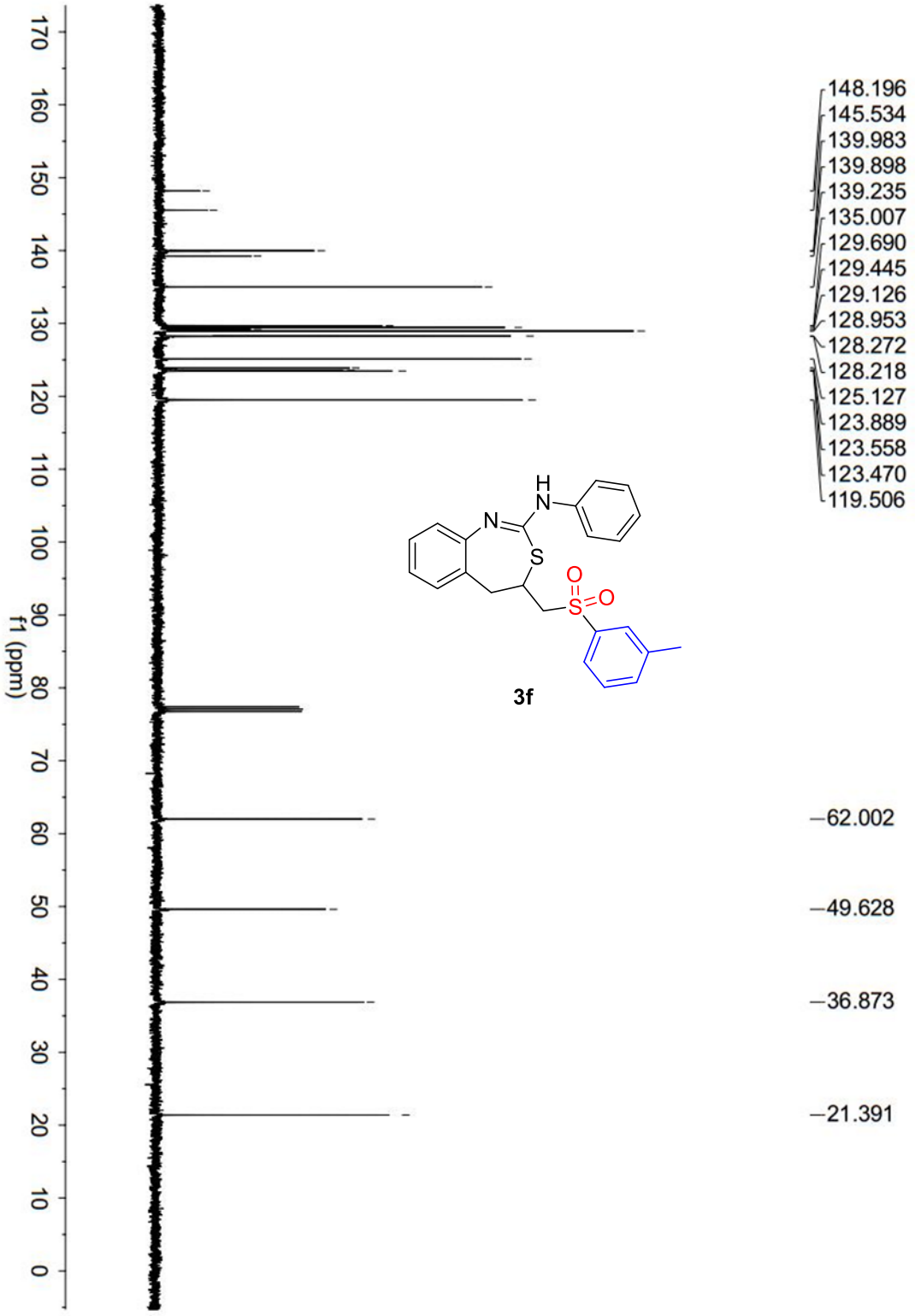
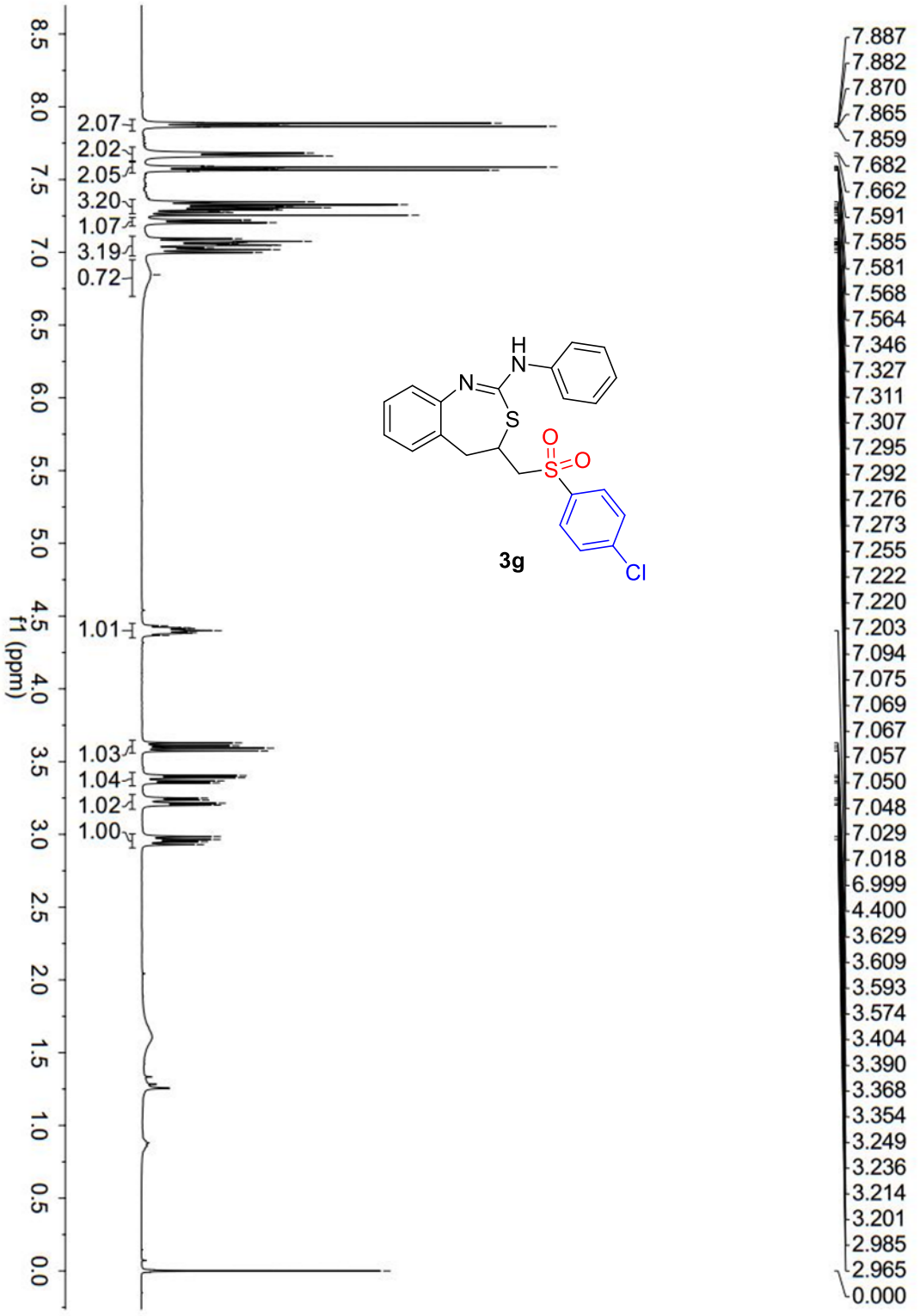
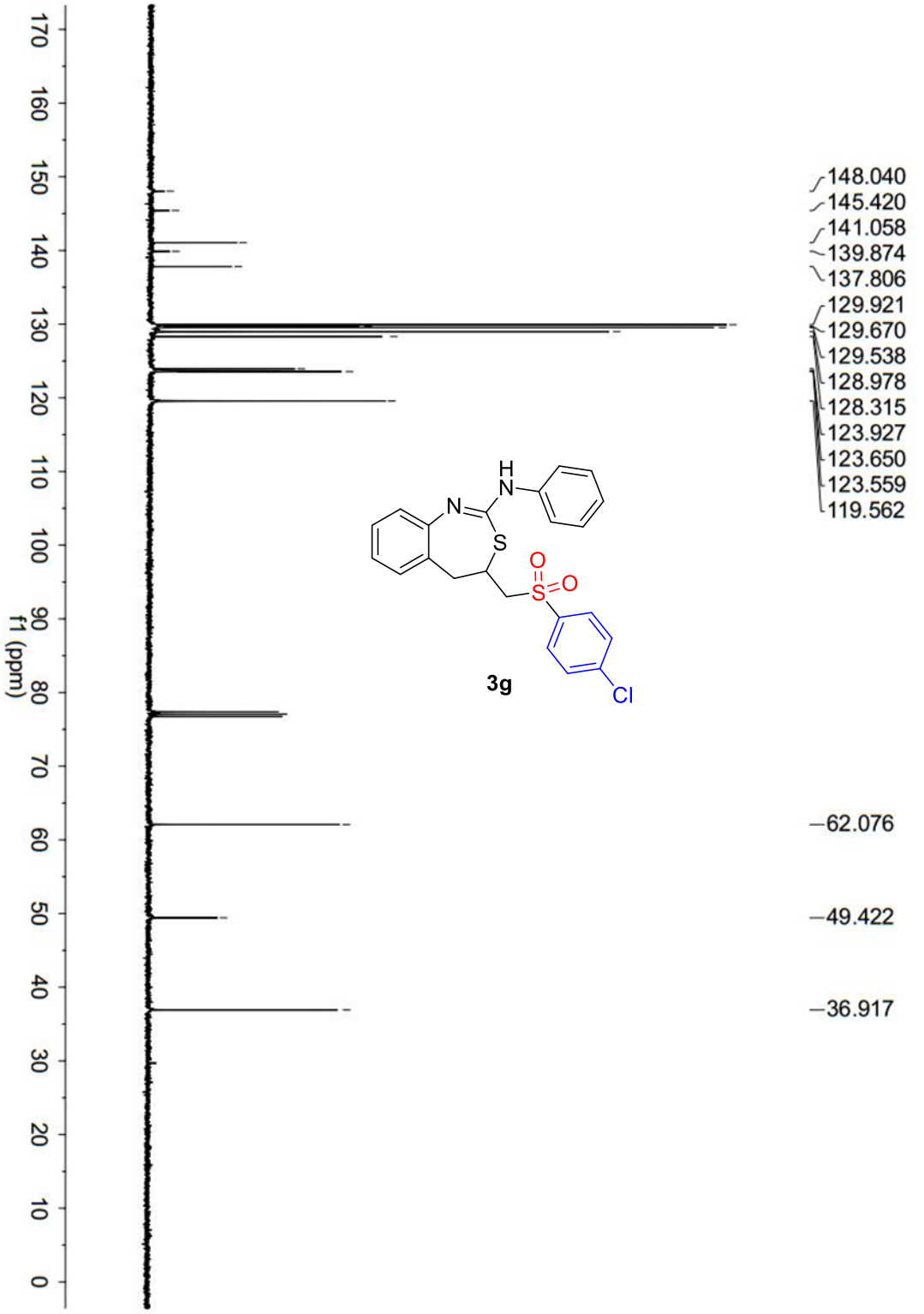
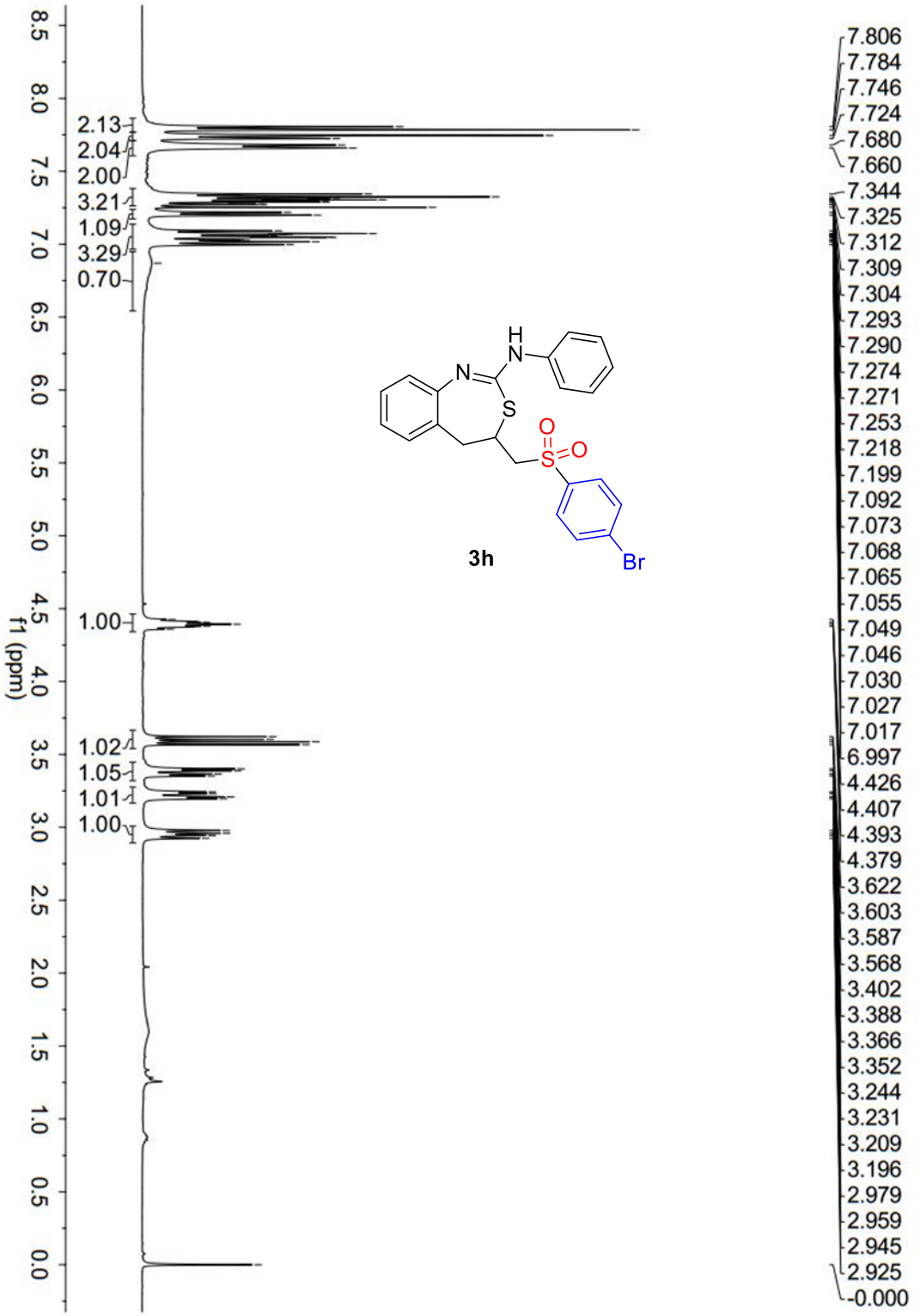
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
4.11
2.12
3.22
1.04
3.18
0.89
1.00
1.04
1.06
1.04
1.00
3.08
H
N
N
S
O
S
O
3f
7.751
7.739
7.694
7.674
7.510
7.502
7.494
7.486
7.350
7.345
7.331
7.329
7.310
7.294
7.291
7.275
7.260
7.224
7.221
7.205
7.202
7.093
7.075
7.069
7.066
7.056
7.050
7.047
7.032
7.029
7.019
6.999
4.405
3.636
3.616
3.601
3.581
3.406
3.393
3.371
3.245
3.232
3.210
3.197
2.986
2.966
2.952
2.932
2.471
-0.000

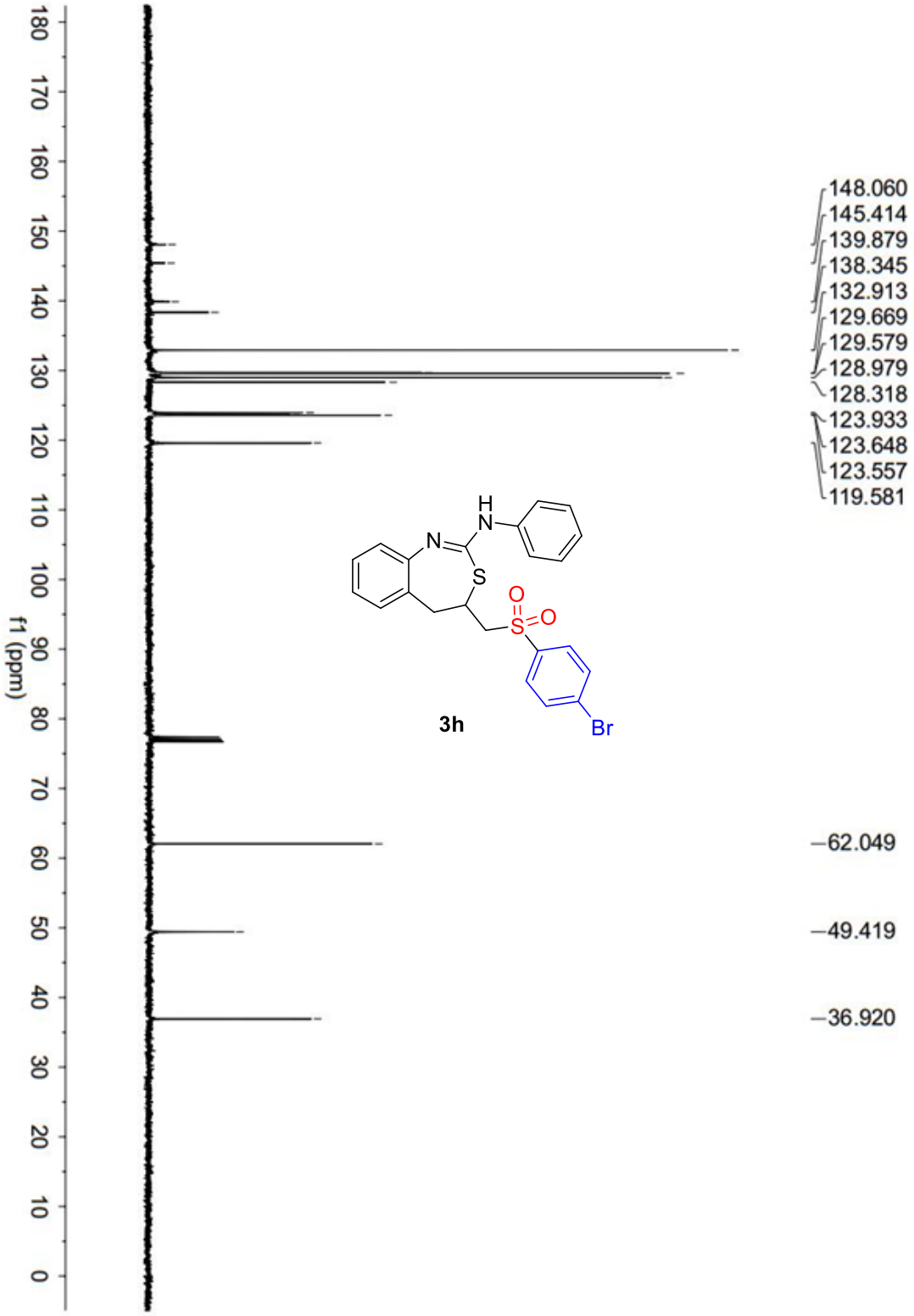

148.196
145.534
139.983
139.898
139.235
135.007
129.690
129.445
129.126
128.953
128.272
128.218
125.127
123.889
123.558
123.470
119.506
62.002
49.628
36.873
21.391
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
H
N
N
S
O
S
O

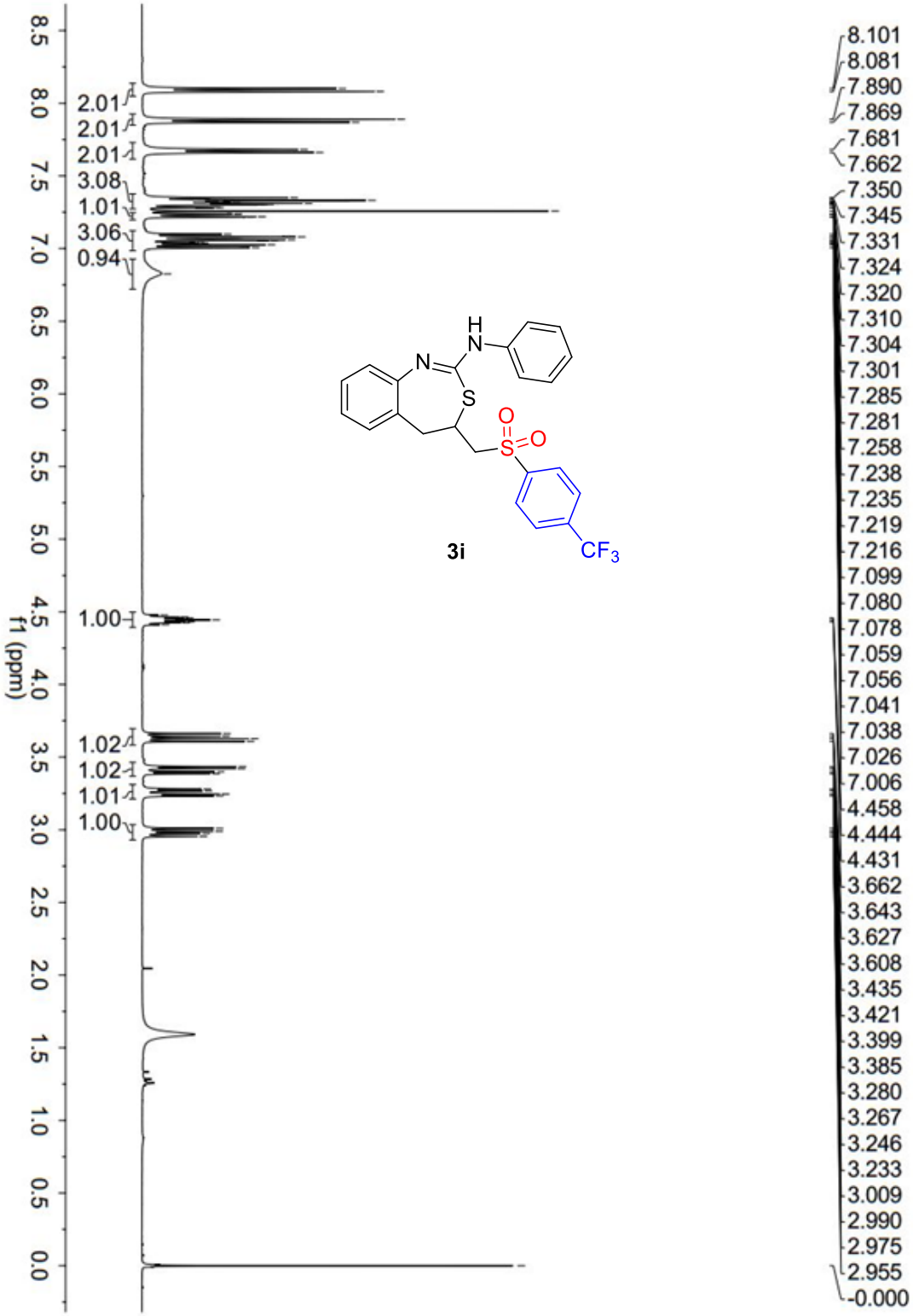
3f

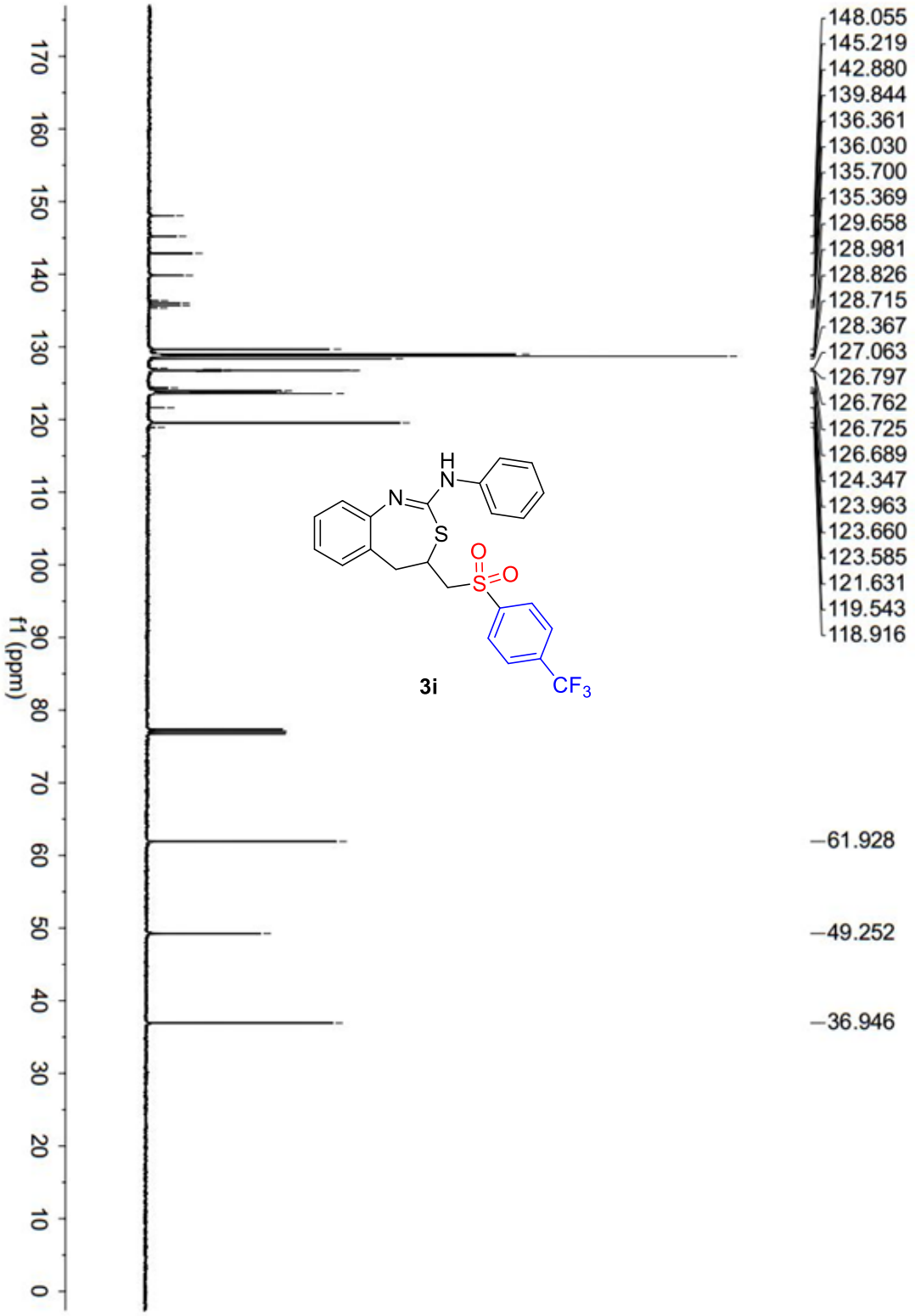

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
2.07
2.02
2.05
3.20
1.07
3.19
0.72
1.01
1.03
1.04
1.02
1.00
H
N
N
S
O
S
O
Cl
3g
7.887
7.882
7.870
7.865
7.859
7.682
7.662
7.591
7.585
7.581
7.568
7.564
7.346
7.327
7.311
7.307
7.295
7.292
7.276
7.273
7.255
7.222
7.220
7.203
7.094
7.075
7.069
7.067
7.057
7.050
7.048
7.029
7.018
6.999
4.400
3.629
3.609
3.593
3.574
3.404
3.390
3.368
3.354
3.249
3.236
3.214
3.201
2.985
2.965
0.000

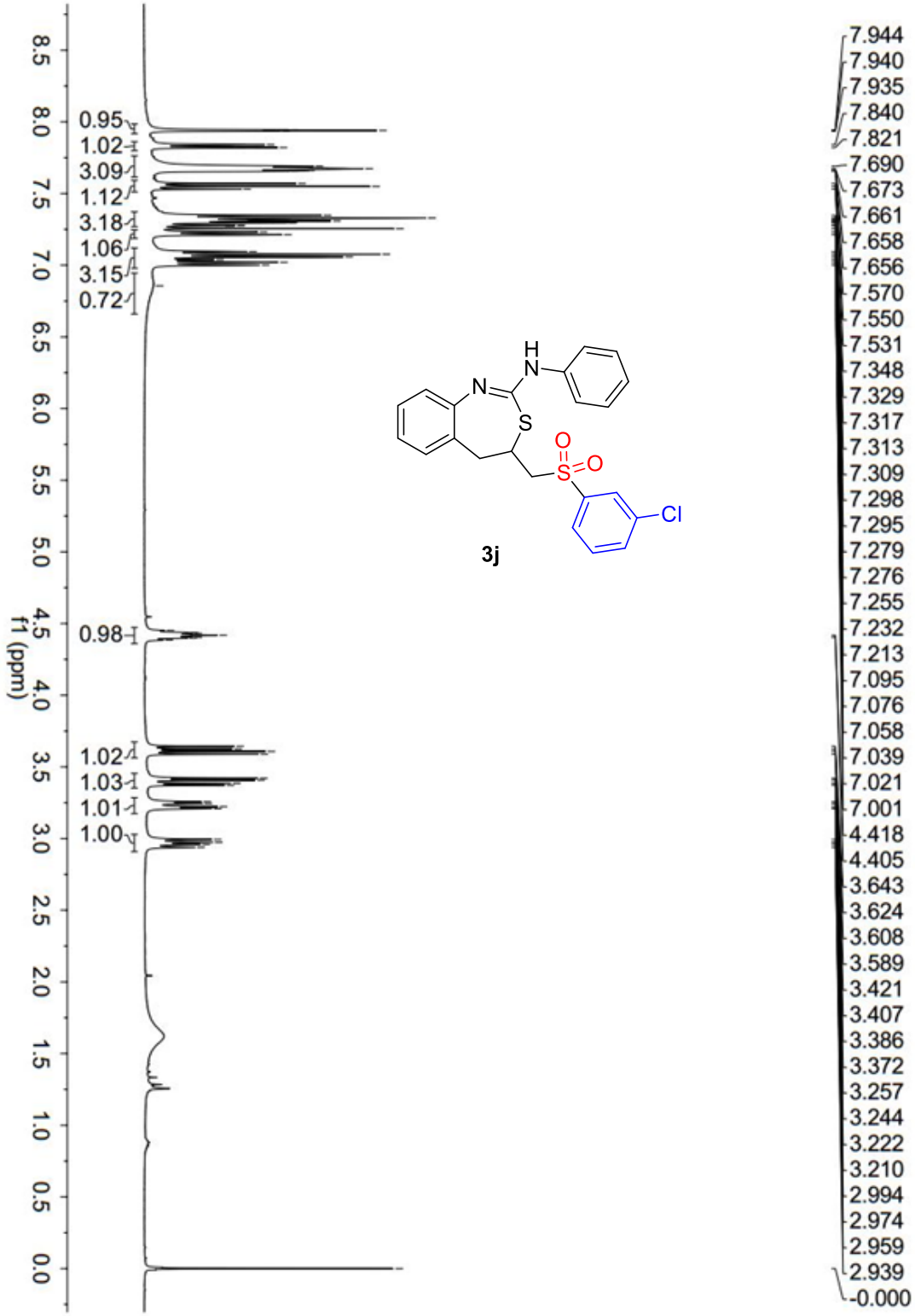

148.040
145.420
141.058
139.874
137.806
129.921
129.670
129.538
128.978
128.315
123.927
123.650
123.559
119.562
62.076
49.422
36.917
f1 (ppm)
3g


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)
2.13
2.04
2.00
3.21
1.09
3.29
0.70
1.00
1.02
1.05
1.01
1.00
H
N
N
S
O
O
S
Br
3h
7.806
7.784
7.746
7.724
7.680
7.660
7.344
7.325
7.312
7.309
7.304
7.293
7.290
7.274
7.271
7.253
7.218
7.199
7.092
7.073
7.068
7.065
7.055
7.049
7.046
7.030
7.027
7.017
6.997
4.426
4.407
4.393
4.379
3.622
3.603
3.587
3.568
3.402
3.388
3.366
3.352
3.244
3.231
3.209
3.196
2.979
2.959
2.945
2.925
-0.000


148.060
145.414
139.879
138.345
132.913
129.669
129.579
128.979
128.318
123.933
123.648
123.557
119.581
62.049
49.419
36.920
f1 (ppm)
3h


8.101
8.081
7.890
7.869
7.681
7.662
7.350
7.345
7.331
7.324
7.320
7.310
7.304
7.301
7.285
7.281
7.258
7.238
7.235
7.219
7.216
7.099
7.080
7.078
7.059
7.056
7.041
7.038
7.026
7.006
4.458
4.444
4.431
3.662
3.643
3.627
3.608
3.435
3.421
3.399
3.385
3.280
3.267
3.246
3.233
3.009
2.990
2.975
2.955
-0.000
2.01
2.01
2.01
3.08
1.01
3.06
0.94
1.00
1.02
1.02
1.01
1.00
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
H
N
N
S
O
S
O
CF3
3i


148.055
145.219
142.880
139.844
136.361
136.030
135.700
135.369
129.658
128.981
128.826
128.715
128.367
127.063
126.797
126.762
126.725
126.689
124.347
123.963
123.660
123.585
121.631
119.543
118.916
61.928
49.252
36.946
f1 (ppm)
3i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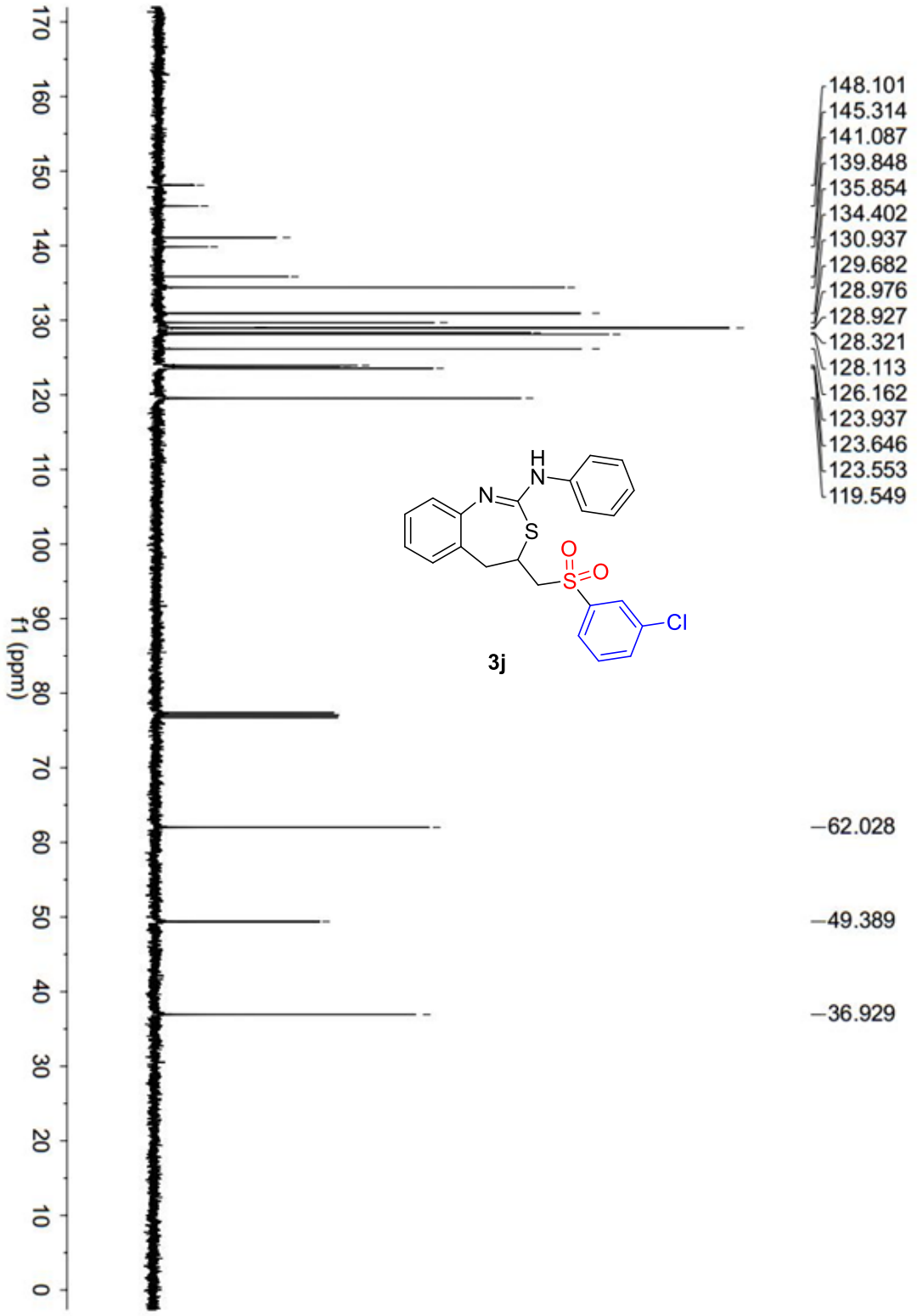
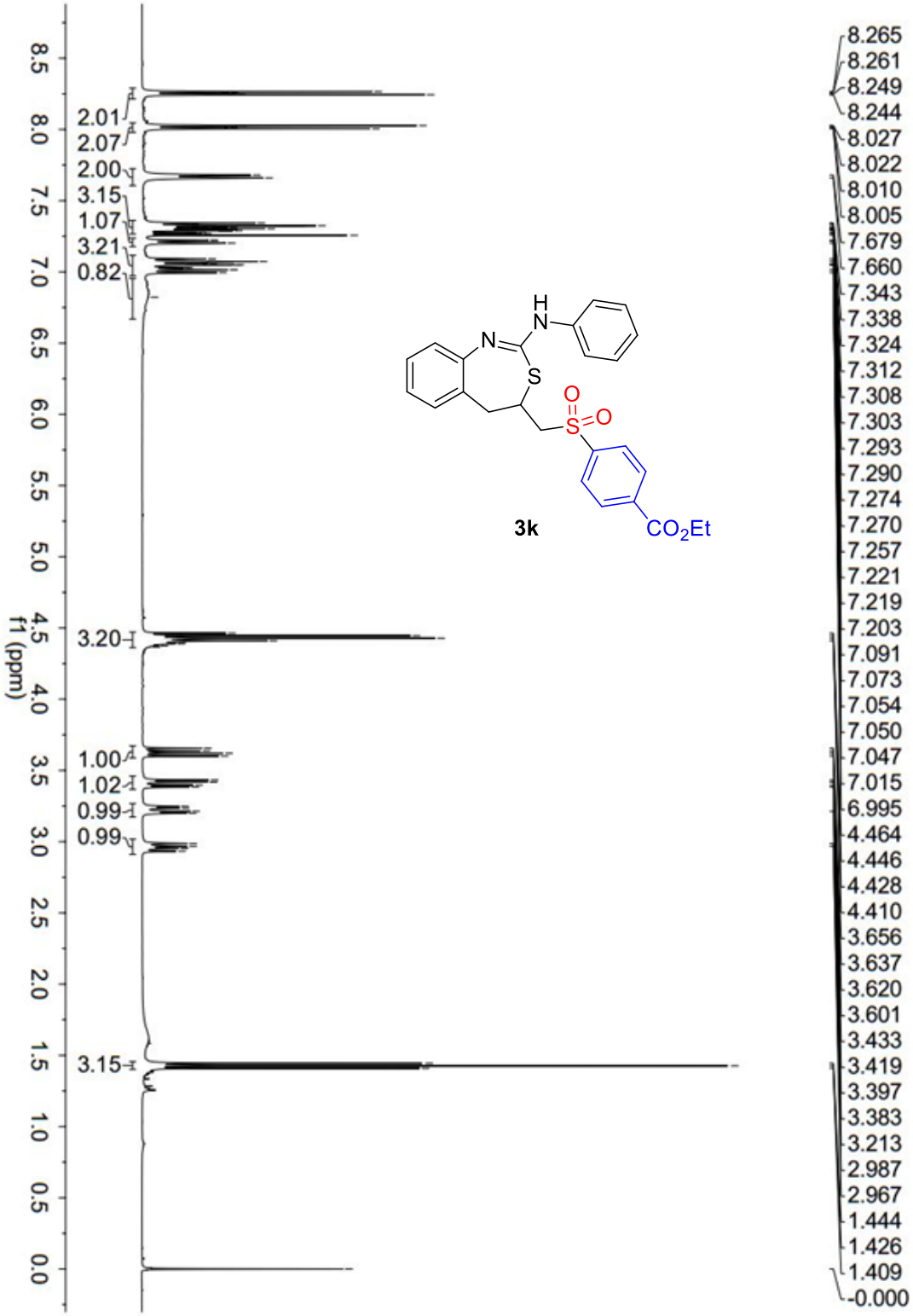
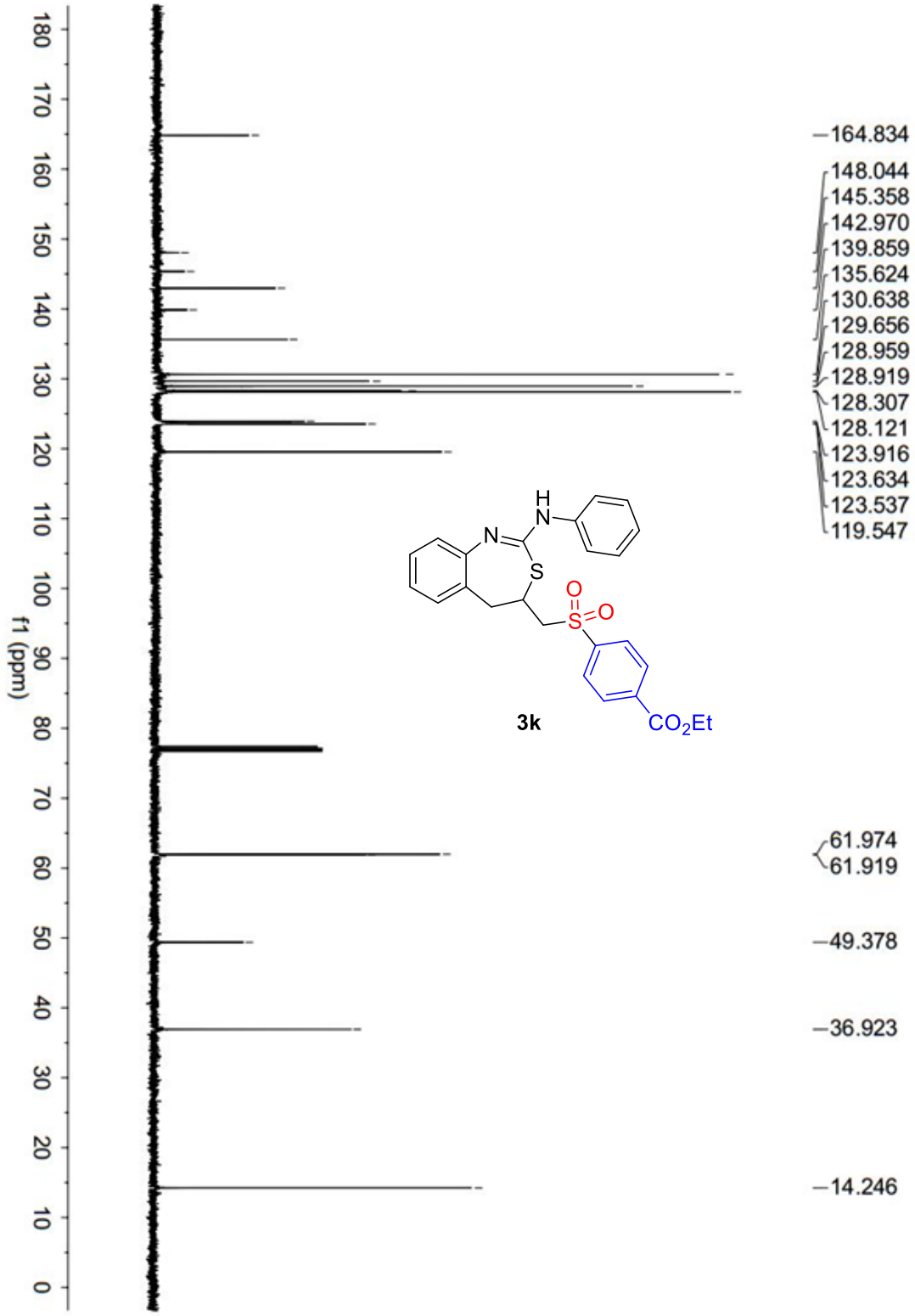
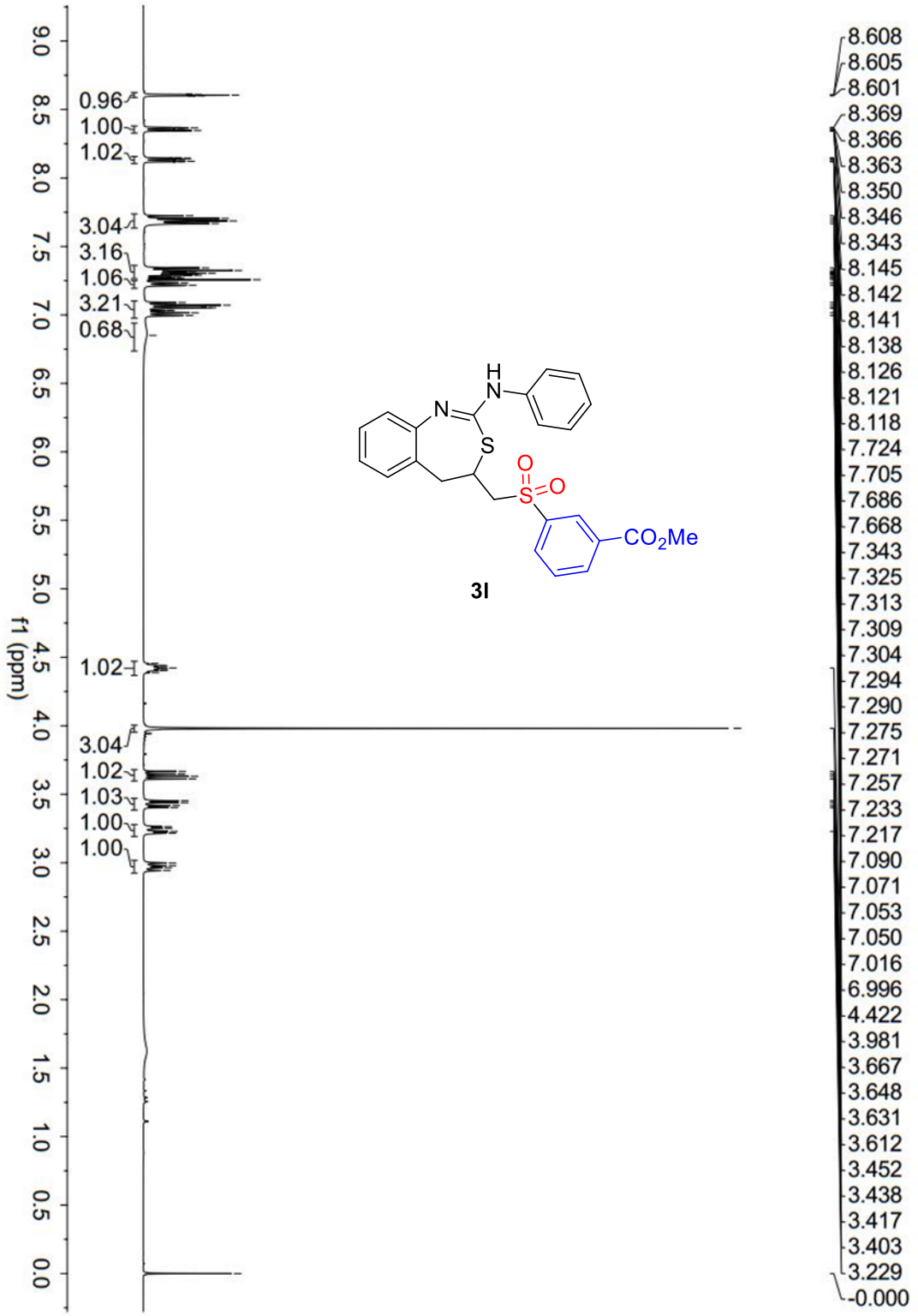
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
0.95
1.02
3.09
1.12
3.18
1.06
3.15
0.72
0.98
1.02
1.03
1.01
1.00
H
N
N
S
O
S
O
Cl
3j
7.944
7.940
7.935
7.840
7.821
7.690
7.673
7.661
7.658
7.656
7.570
7.550
7.531
7.348
7.329
7.317
7.313
7.309
7.298
7.295
7.279
7.276
7.255
7.232
7.213
7.095
7.076
7.058
7.039
7.021
7.001
4.418
4.405
3.643
3.624
3.608
3.589
3.421
3.407
3.386
3.372
3.257
3.244
3.222
3.210
2.994
2.974
2.959
2.939
-0.000


148.101
145.314
141.087
139.848
135.854
134.402
130.937
129.682
128.976
128.927
128.321
128.113
126.162
123.937
123.646
123.553
119.549
62.028
49.389
36.929
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
H
N
N
S
O
S
O
Cl

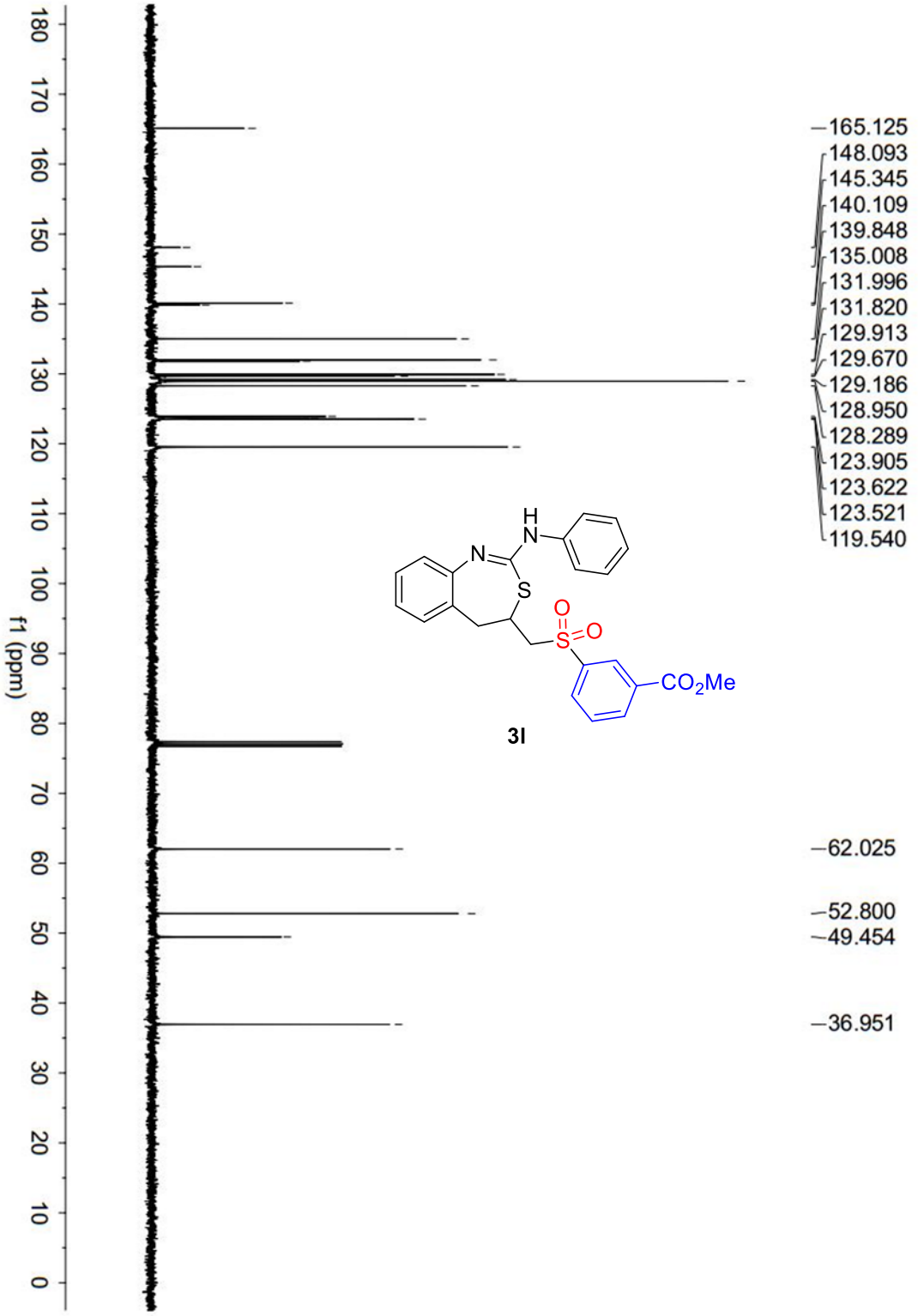
3j


8.265
8.261
8.249
8.244
8.027
8.022
8.010
8.005
7.679
7.660
7.343
7.338
7.324
7.312
7.308
7.303
7.293
7.290
7.274
7.270
7.257
7.221
7.219
7.203
7.091
7.073
7.054
7.050
7.047
7.015
6.995
4.464
4.446
4.428
4.410
3.656
3.637
3.620
3.601
3.433
3.419
3.397
3.383
3.213
2.987
2.967
1.444
1.426
1.409
-0.000
2.01
2.07
2.00
3.15
1.07
3.21
0.82
3.20
1.00
1.02
0.99
0.99
3.15
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
H
N
N
S
O
S
O
CO2Et
3k

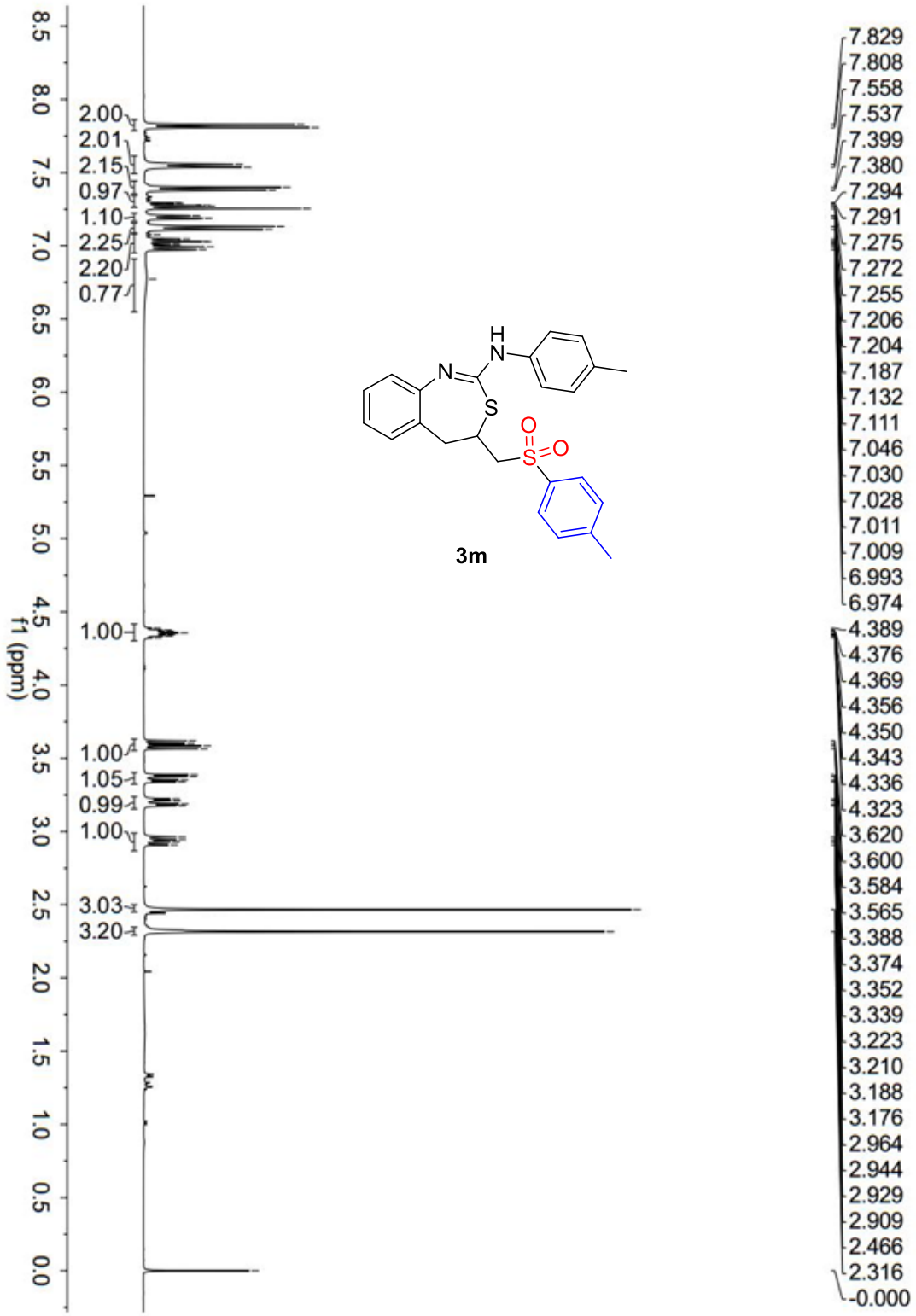

164.834
148.044
145.358
142.970
139.859
135.624
130.638
129.656
128.959
128.919
128.307
128.121
123.916
123.634
123.537
119.547
61.974
61.919
49.378
36.923
14.246
f1 (ppm)
3k

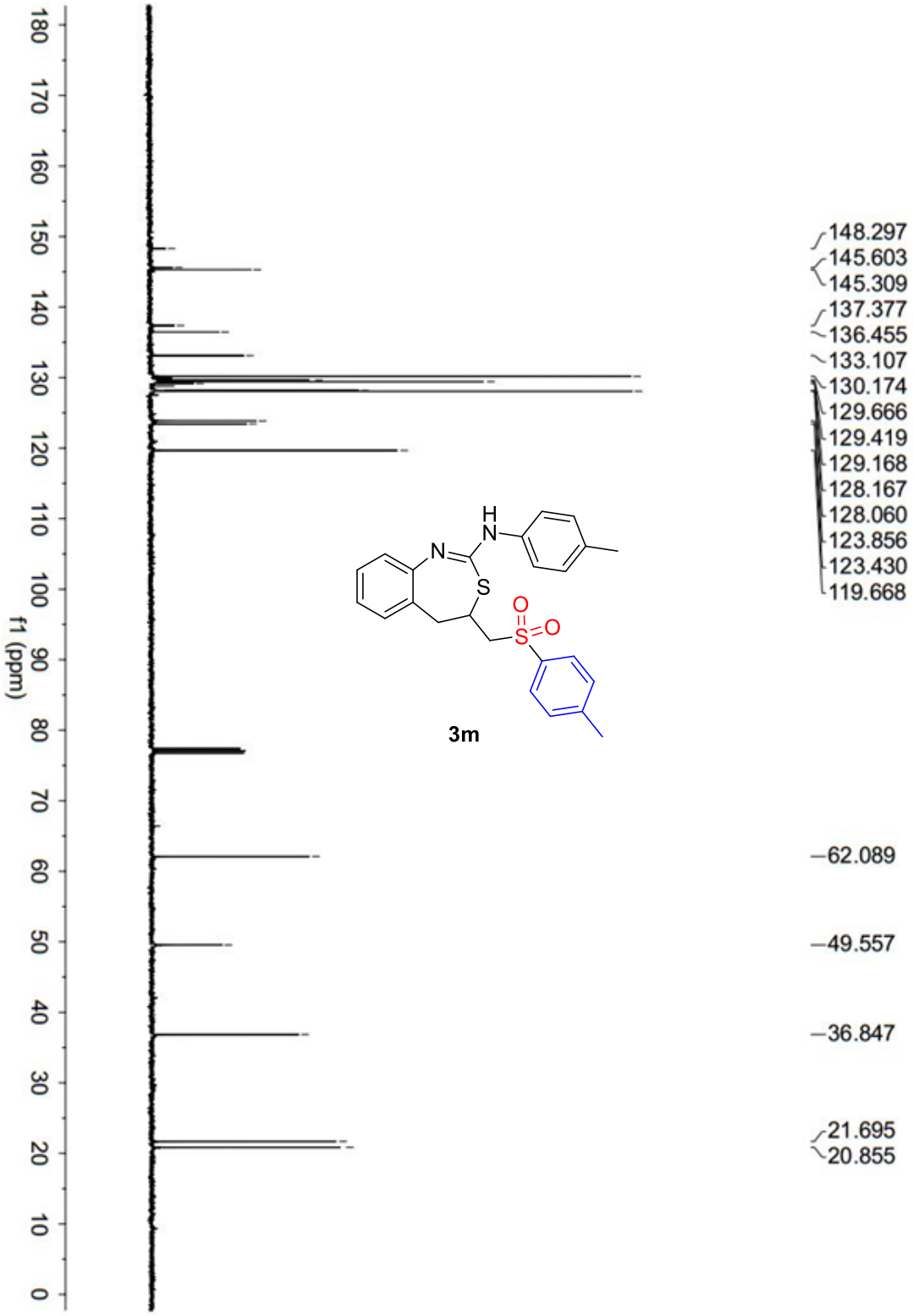

f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.96
1.00
1.02
3.04
3.16
1.06
3.21
0.68
1.02
3.04
1.02
1.03
1.00
1.00
H
N
N
S
O
S
O
CO2Me
8.608
8.605
8.601
8.369
8.366
8.363
8.350
8.346
8.343
8.145
8.142
8.141
8.138
8.126
8.121
8.118
7.724
7.705
7.686
7.668
7.343
7.325
7.313
7.309
7.304
7.294
7.290
7.275
7.271
7.257
7.233
7.217
7.090
7.071
7.053
7.050
7.016
6.996
4.422
3.981
3.667
3.648
3.631
3.612
3.452
3.438
3.417
3.403
3.229
-0.000

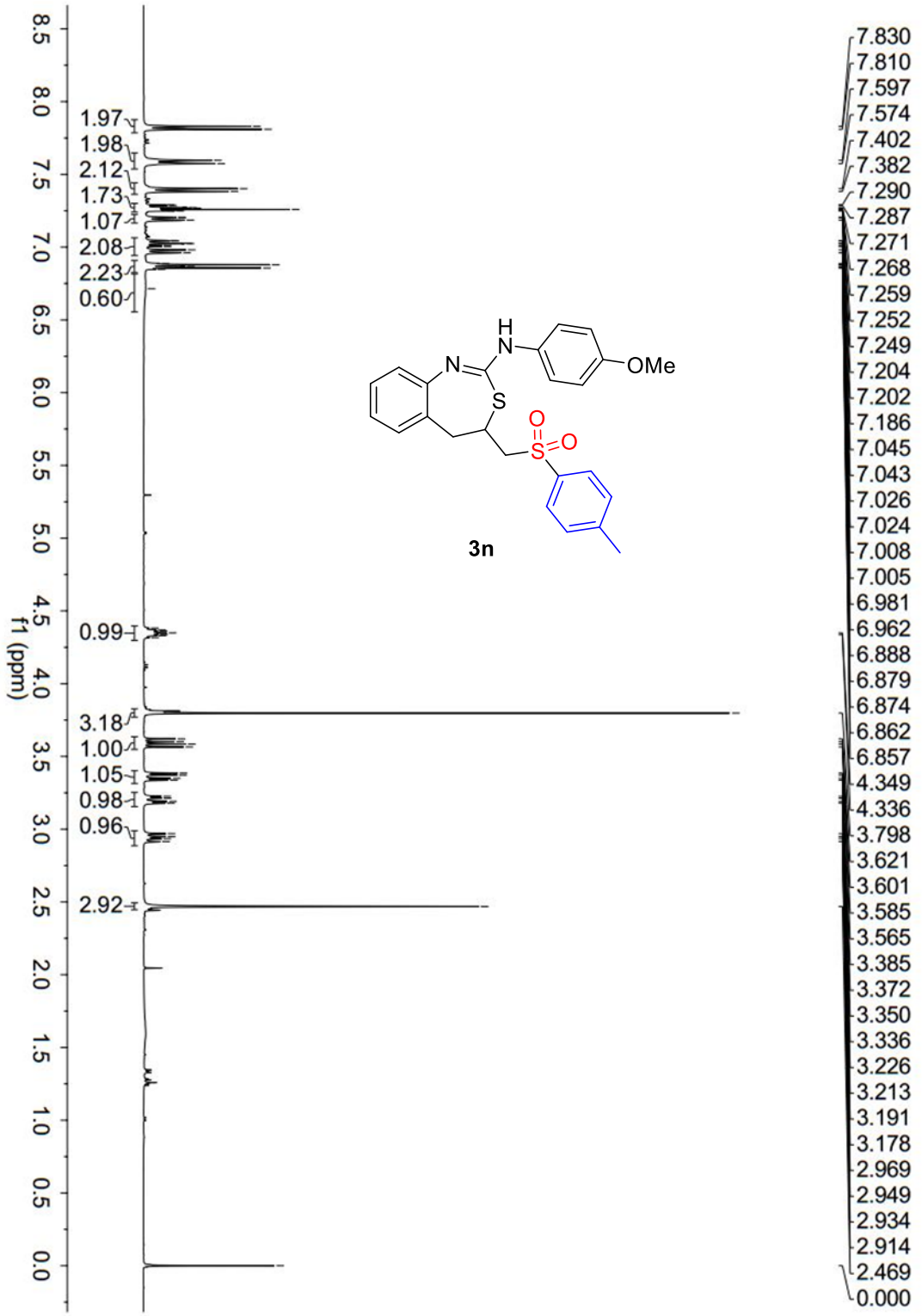
3l

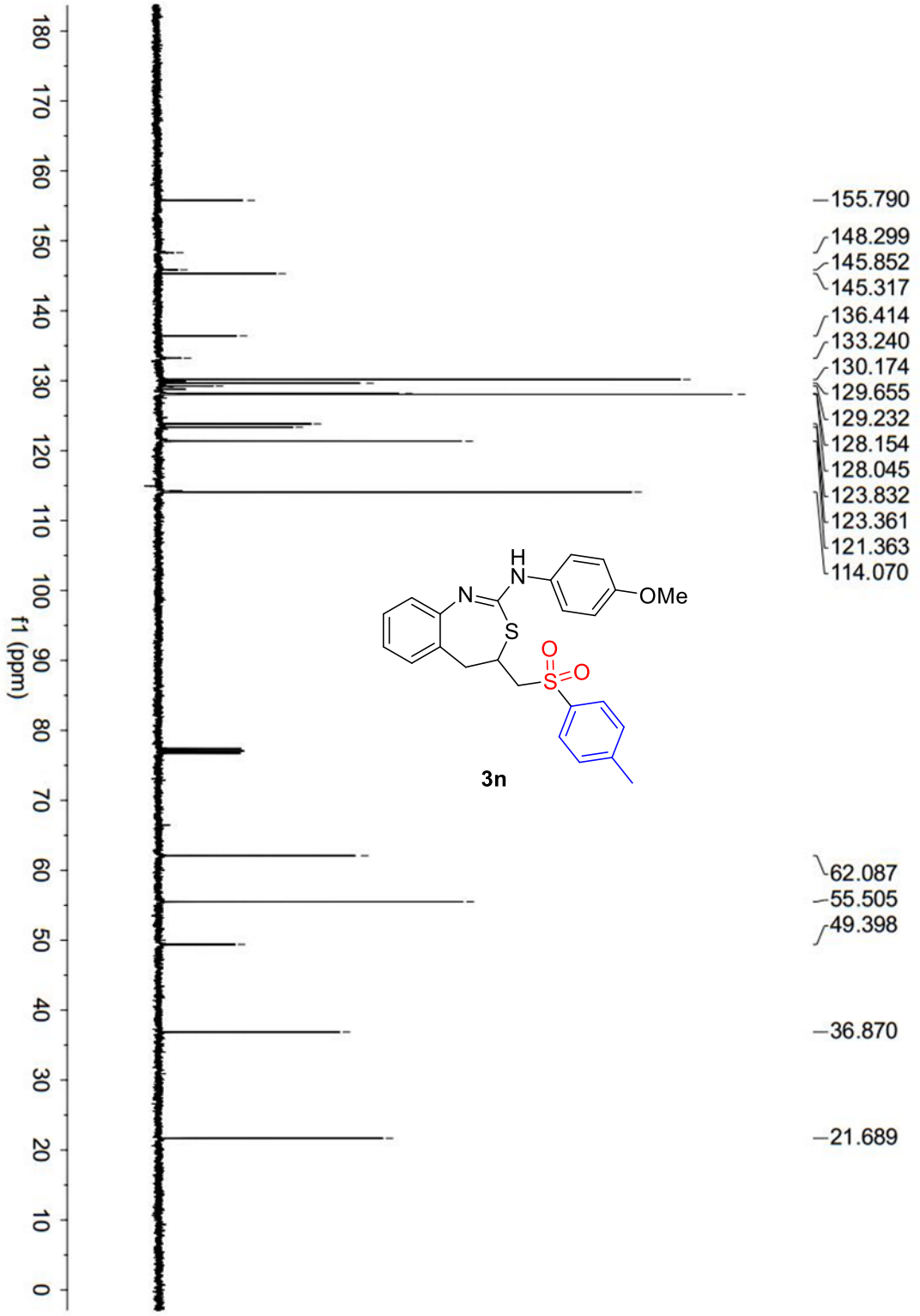

165.125
148.093
145.345
140.109
139.848
135.008
131.996
131.820
129.913
129.670
129.186
128.950
128.289
123.905
123.622
123.521
119.540
62.025
52.800
49.454
36.951
f1 (ppm)
CO2Me

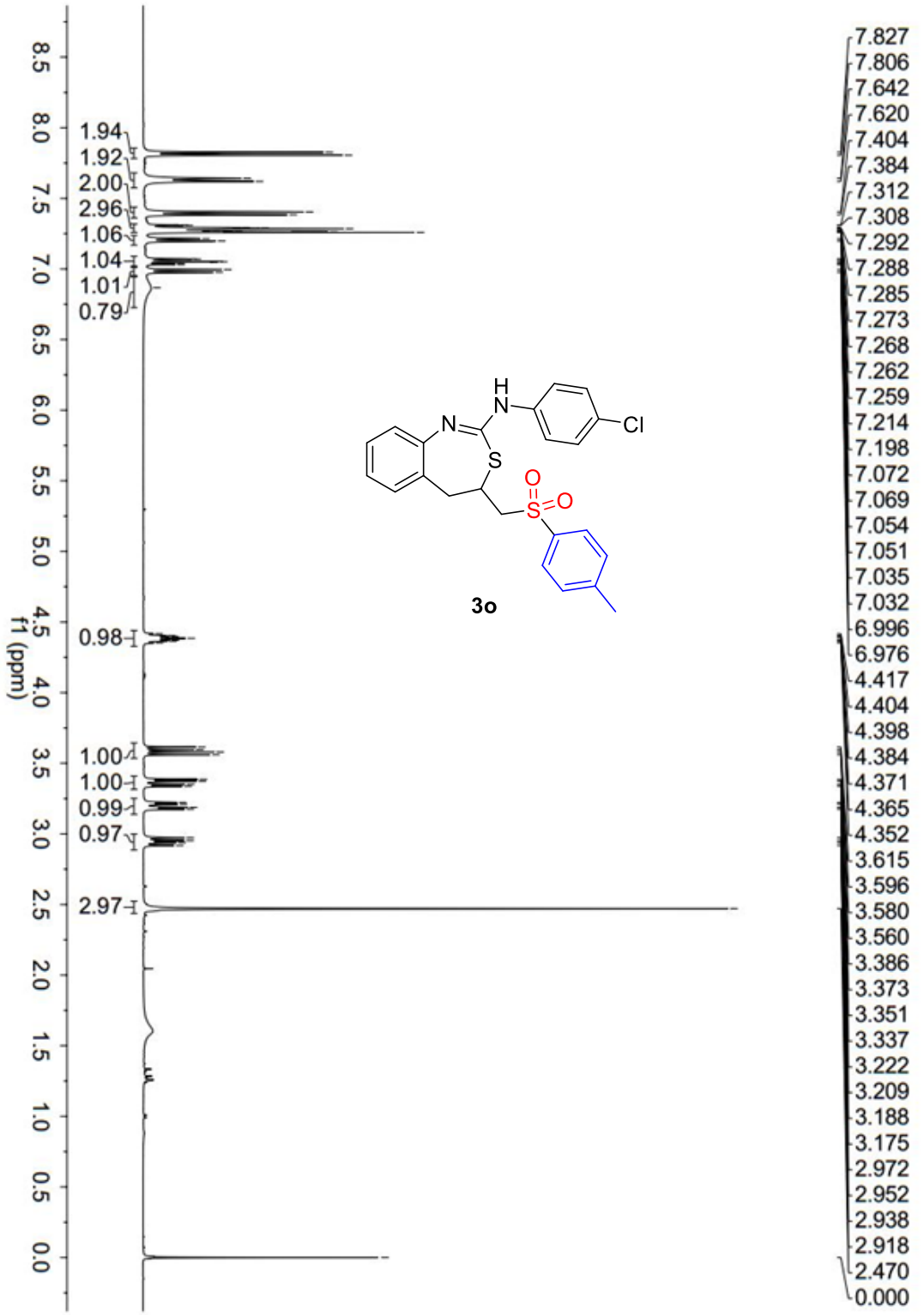
3l


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)
2.00
2.01
2.15
0.97
1.10
2.25
2.20
0.77
1.00
1.00
1.05
0.99
1.00
3.03
3.20
H
N
N
S
O
S
O
3m
7.829
7.808
7.558
7.537
7.399
7.380
7.294
7.291
7.275
7.272
7.255
7.206
7.204
7.187
7.132
7.111
7.046
7.030
7.028
7.011
7.009
6.993
6.974
4.389
4.376
4.369
4.356
4.350
4.343
4.336
4.323
3.620
3.600
3.584
3.565
3.388
3.374
3.352
3.339
3.223
3.210
3.188
3.176
2.964
2.944
2.929
2.909
2.466
2.316
-0.000

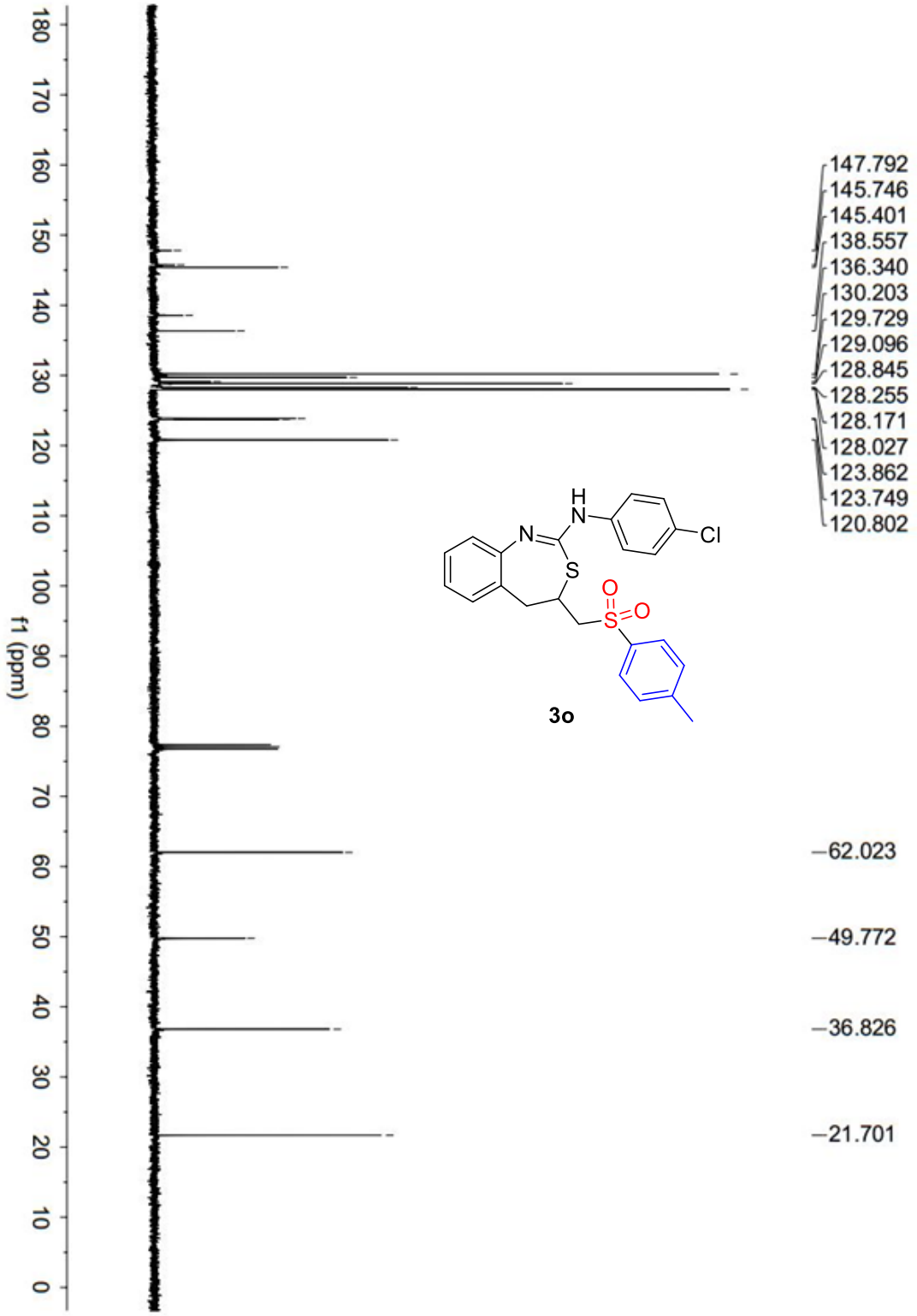

148.297
145.603
145.309
137.377
136.455
133.107
130.174
129.666
129.419
129.168
128.167
128.060
123.856
123.430
119.668
62.089
49.557
36.847
21.695
20.855
f1 (ppm)
3m

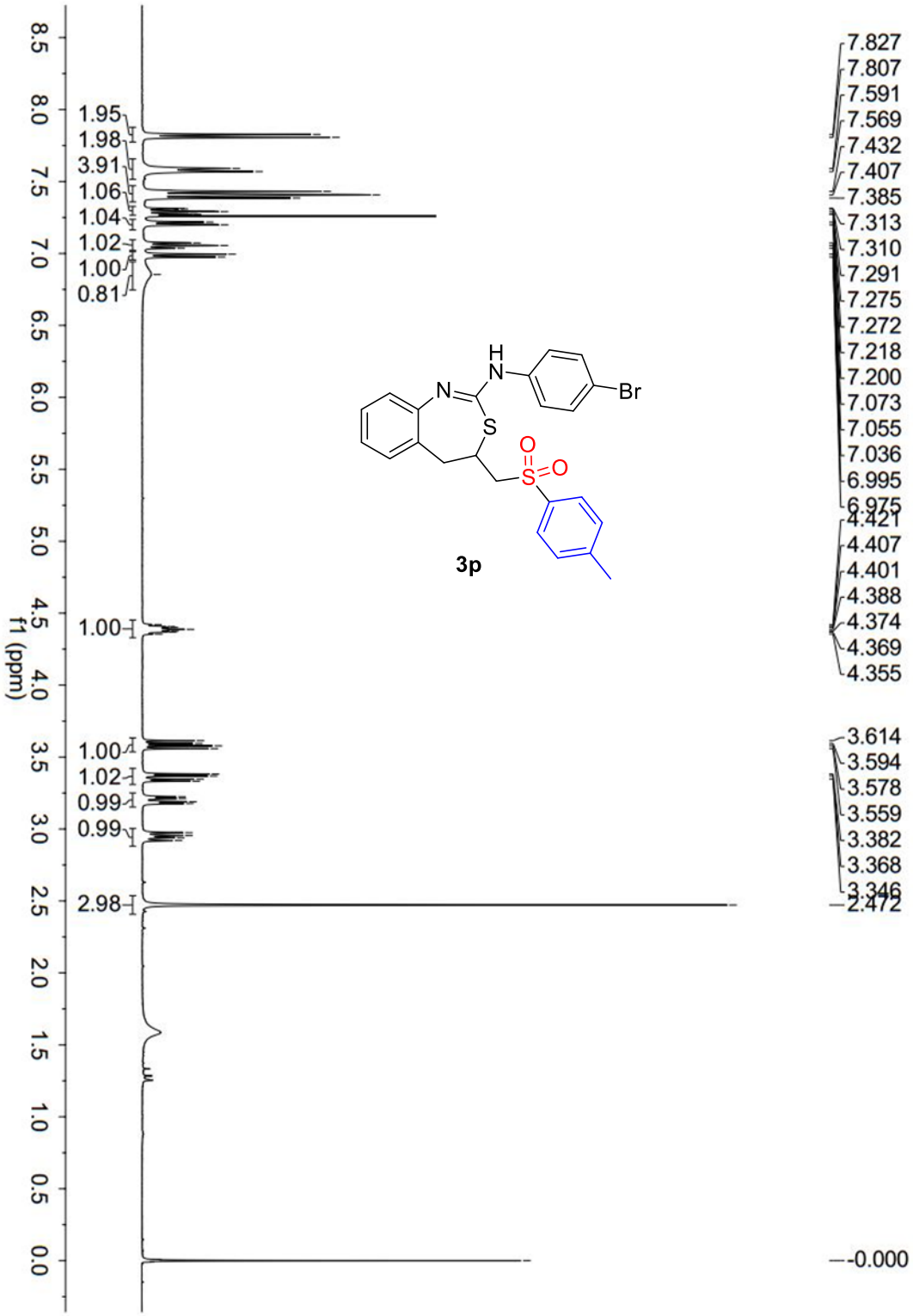

f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.97
1.98
2.12
1.73
1.07
2.08
2.23
0.60
0.99
3.18
1.00
1.05
0.98
0.96
2.92
H
N
N
S
O
S
O
OMe
3n
7.830
7.810
7.597
7.574
7.402
7.382
7.290
7.287
7.271
7.268
7.259
7.252
7.249
7.204
7.202
7.186
7.045
7.043
7.026
7.024
7.008
7.005
6.981
6.962
6.888
6.879
6.874
6.862
6.857
4.349
4.336
3.798
3.621
3.601
3.585
3.565
3.385
3.372
3.350
3.336
3.226
3.213
3.191
3.178
2.969
2.949
2.934
2.914
2.469
0.000

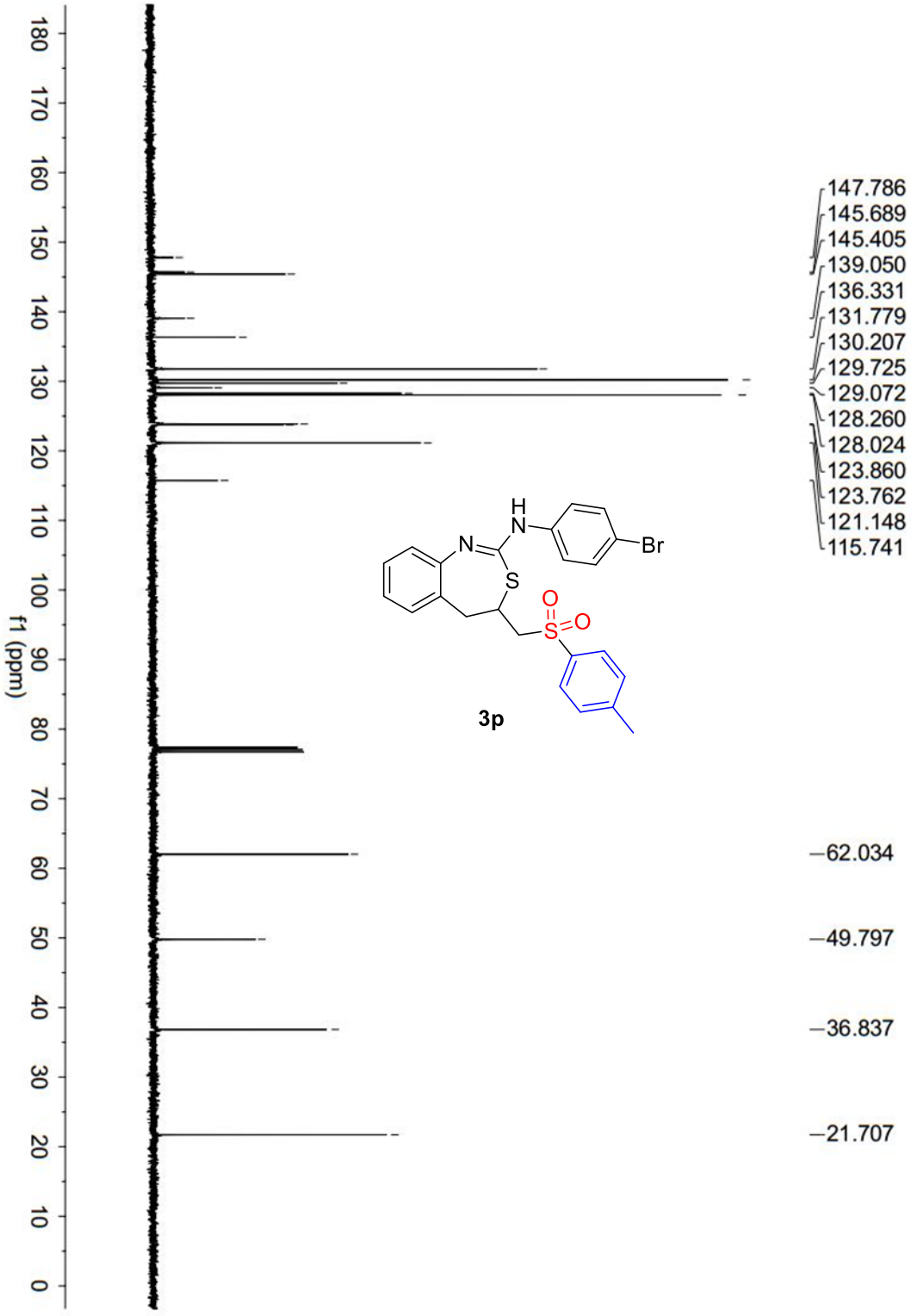

155.790
148.299
145.852
145.317
136.414
133.240
130.174
129.655
129.232
128.154
128.045
123.832
123.361
121.363
114.070
62.087
55.505
49.398
36.870
21.689
f1 (ppm)
H
N
N
S
OMe
O
S
O
3n

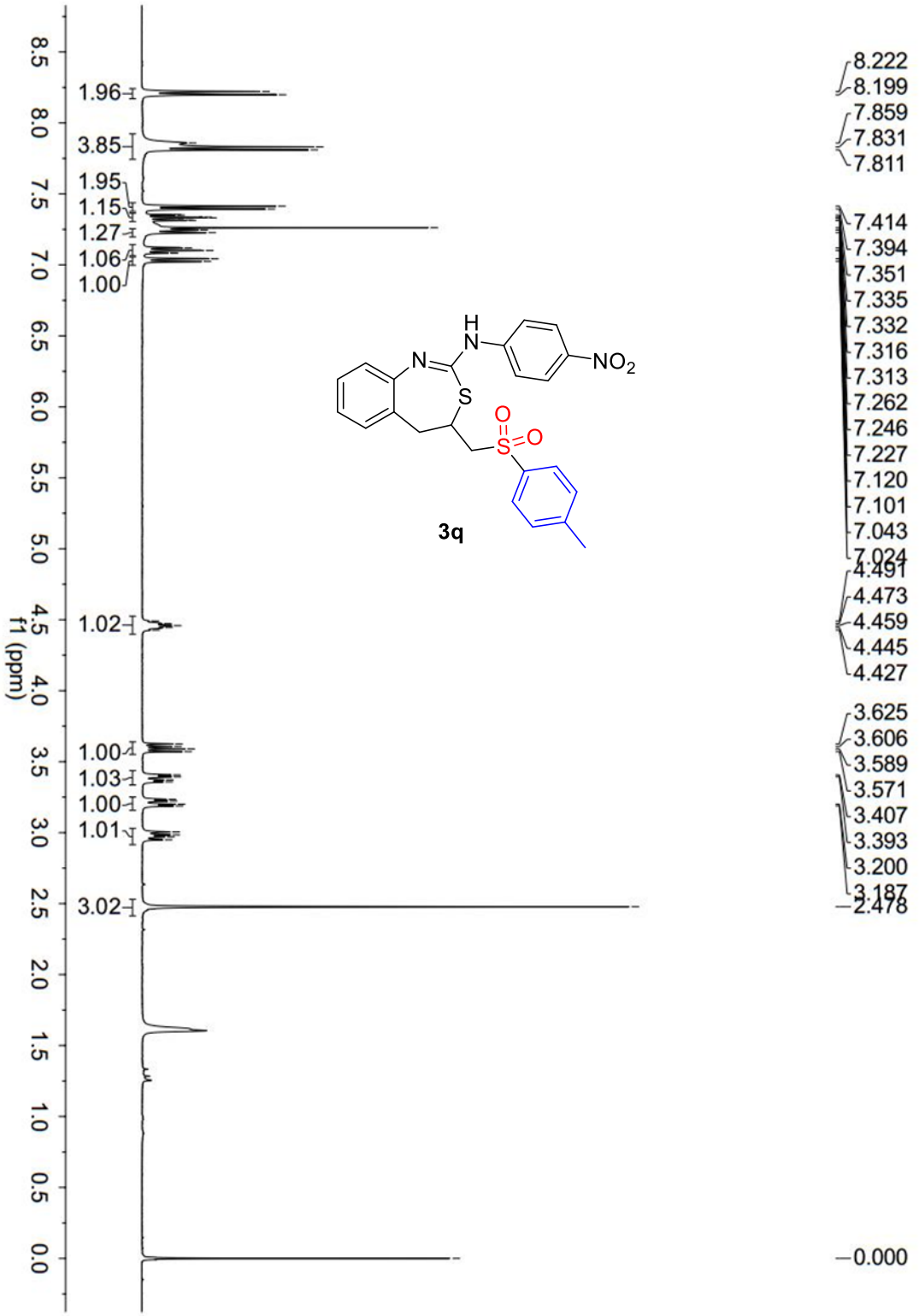

1.94
1.92
2.00
2.96
1.06
1.04
1.01
0.79
0.98
1.00
1.00
0.99
0.97
2.97
f1 (ppm)
7.827
7.806
7.642
7.620
7.404
7.384
7.312
7.308
7.292
7.288
7.285
7.273
7.268
7.262
7.259
7.214
7.198
7.072
7.069
7.054
7.051
7.035
7.032
6.996
6.976
4.417
4.404
4.398
4.384
4.371
4.365
4.352
3.615
3.596
3.580
3.560
3.386
3.373
3.351
3.337
3.222
3.209
3.188
3.175
2.972
2.952
2.938
2.918
2.470
0.000
H
N
N
S
O
S
O
Cl

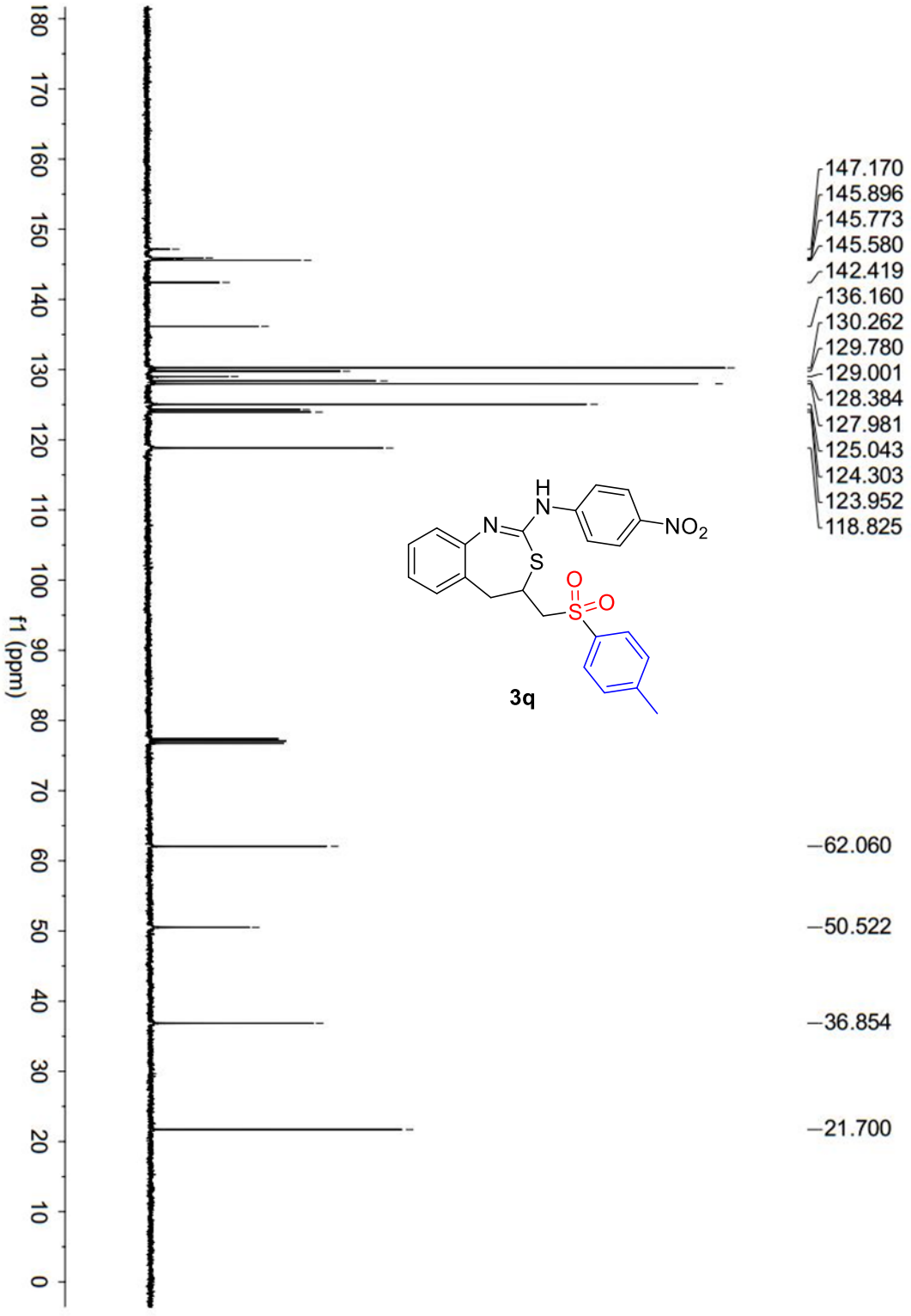
3o

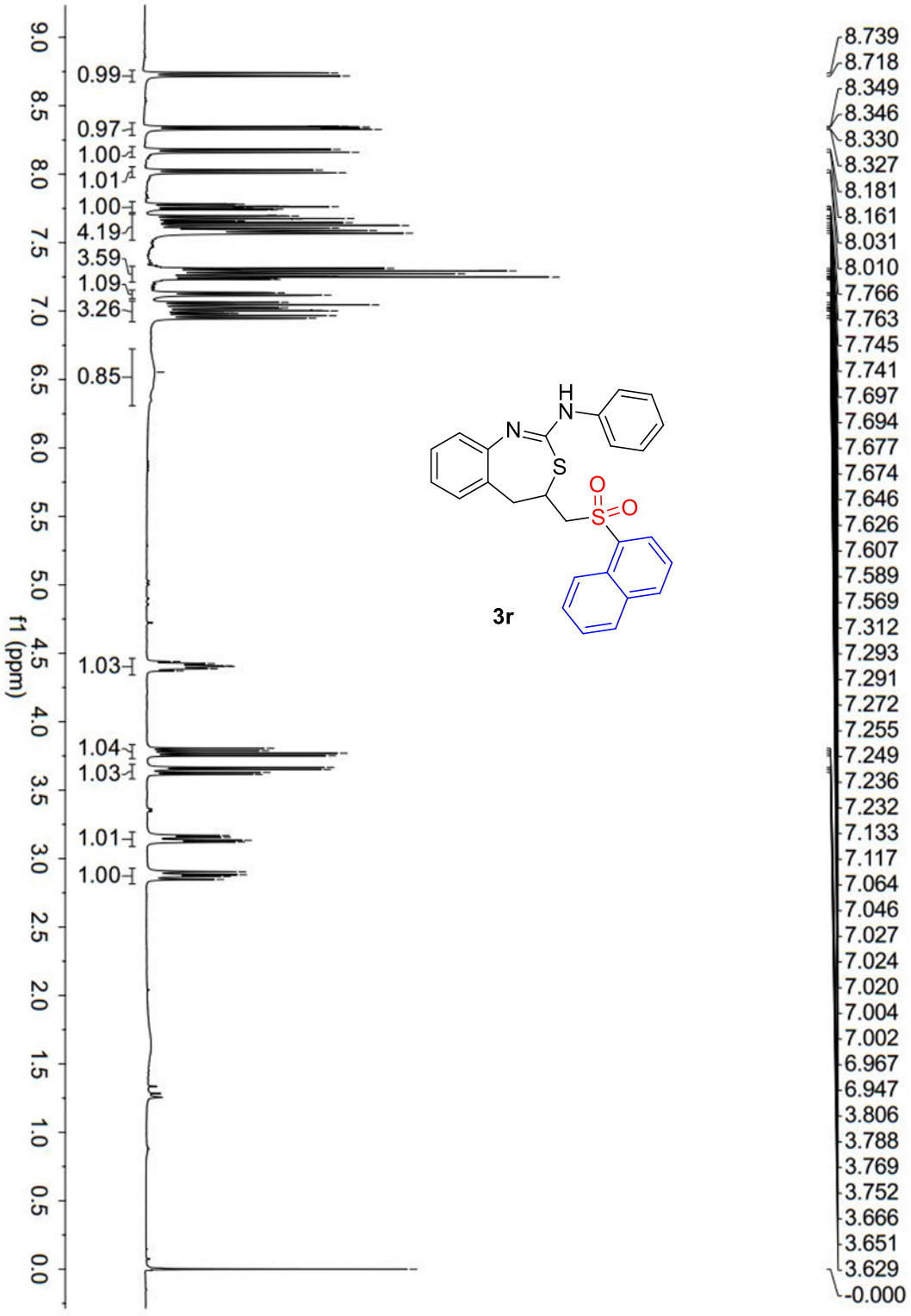

147.792
145.746
145.401
138.557
136.340
130.203
129.729
129.096
128.845
128.255
128.171
128.027
123.862
123.749
120.802
62.023
49.772
36.826
21.701
f1 (ppm)
H
N
N
S
Cl
O
S
O
3o

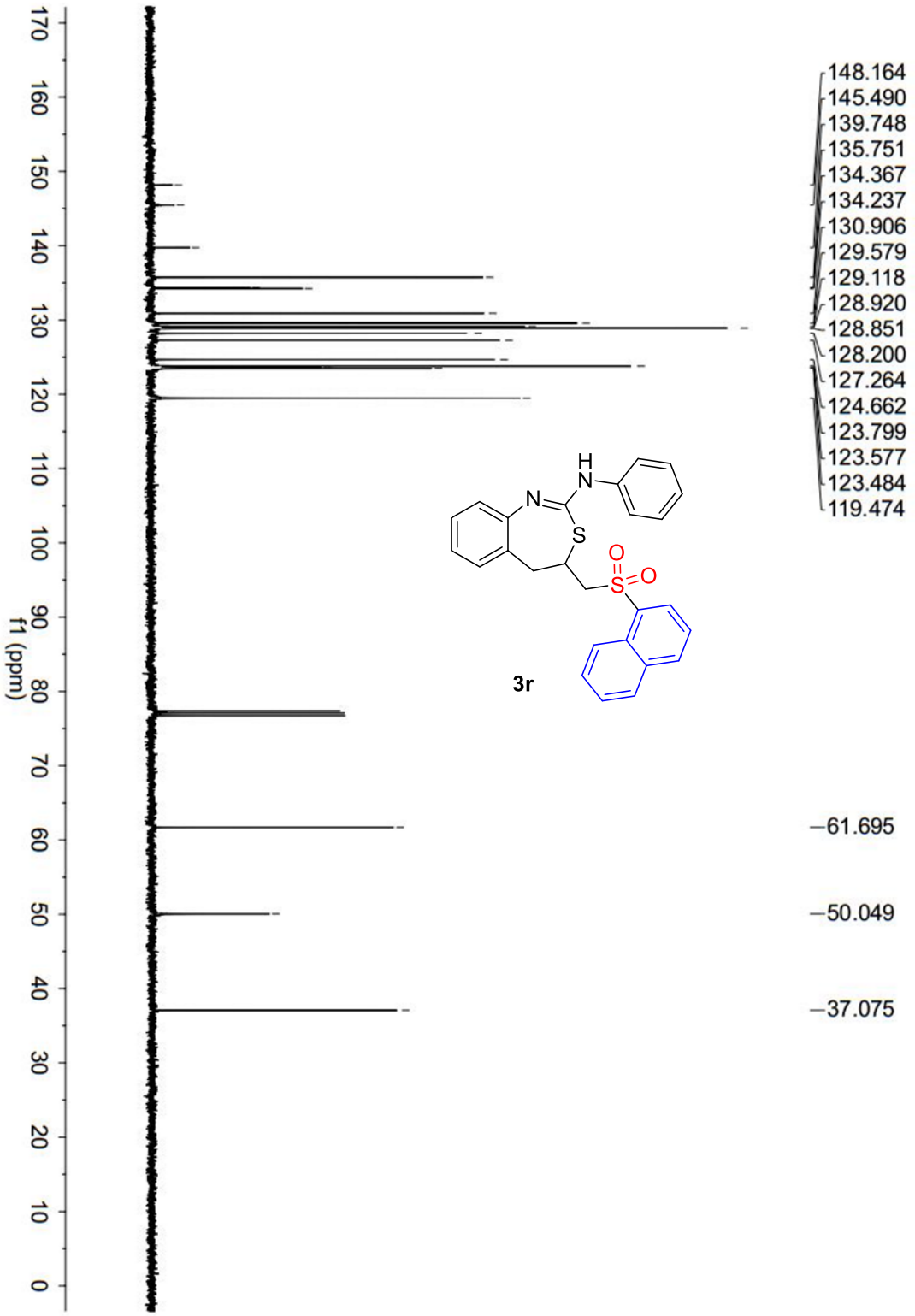

7.827
7.807
7.591
7.569
7.432
7.407
7.385
7.313
7.310
7.291
7.275
7.272
7.218
7.200
7.073
7.055
7.036
6.995
6.975
4.421
4.407
4.401
4.388
4.374
4.369
4.355
3.614
3.594
3.578
3.559
3.382
3.368
3.346
2.472
0.000
1.95
1.98
3.91
1.06
1.04
1.02
1.00
0.81
1.00
1.00
1.02
0.99
0.99
2.98
f1 (ppm)
H
N
N
S
O
S
O
Br
3p

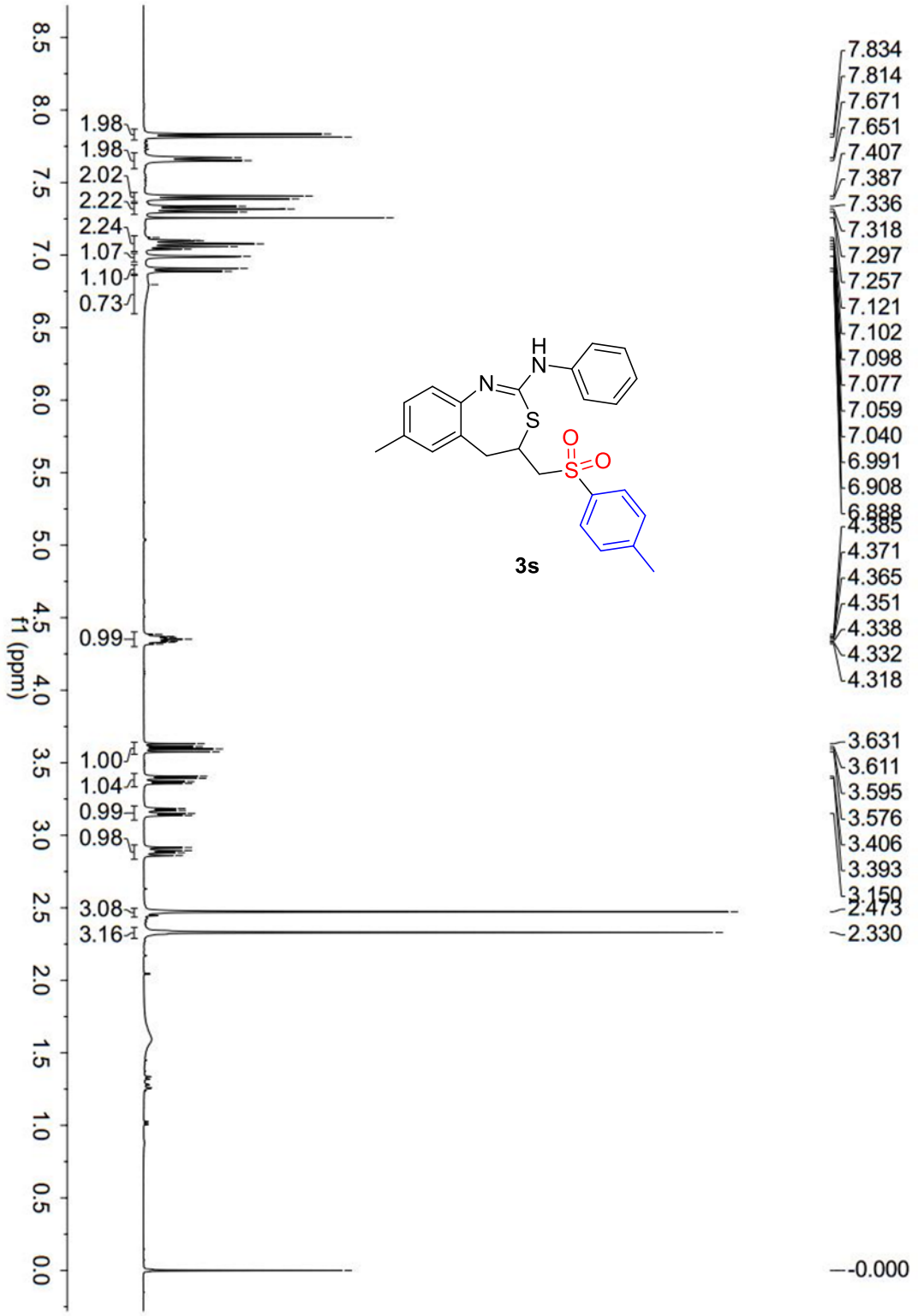

147.786
145.689
145.405
139.050
136.331
131.779
130.207
129.725
129.072
128.260
128.024
123.860
123.762
121.148
115.741
62.034
49.797
36.837
21.707
f1 (ppm)
H
N
N
S
Br
O
S
O
3p

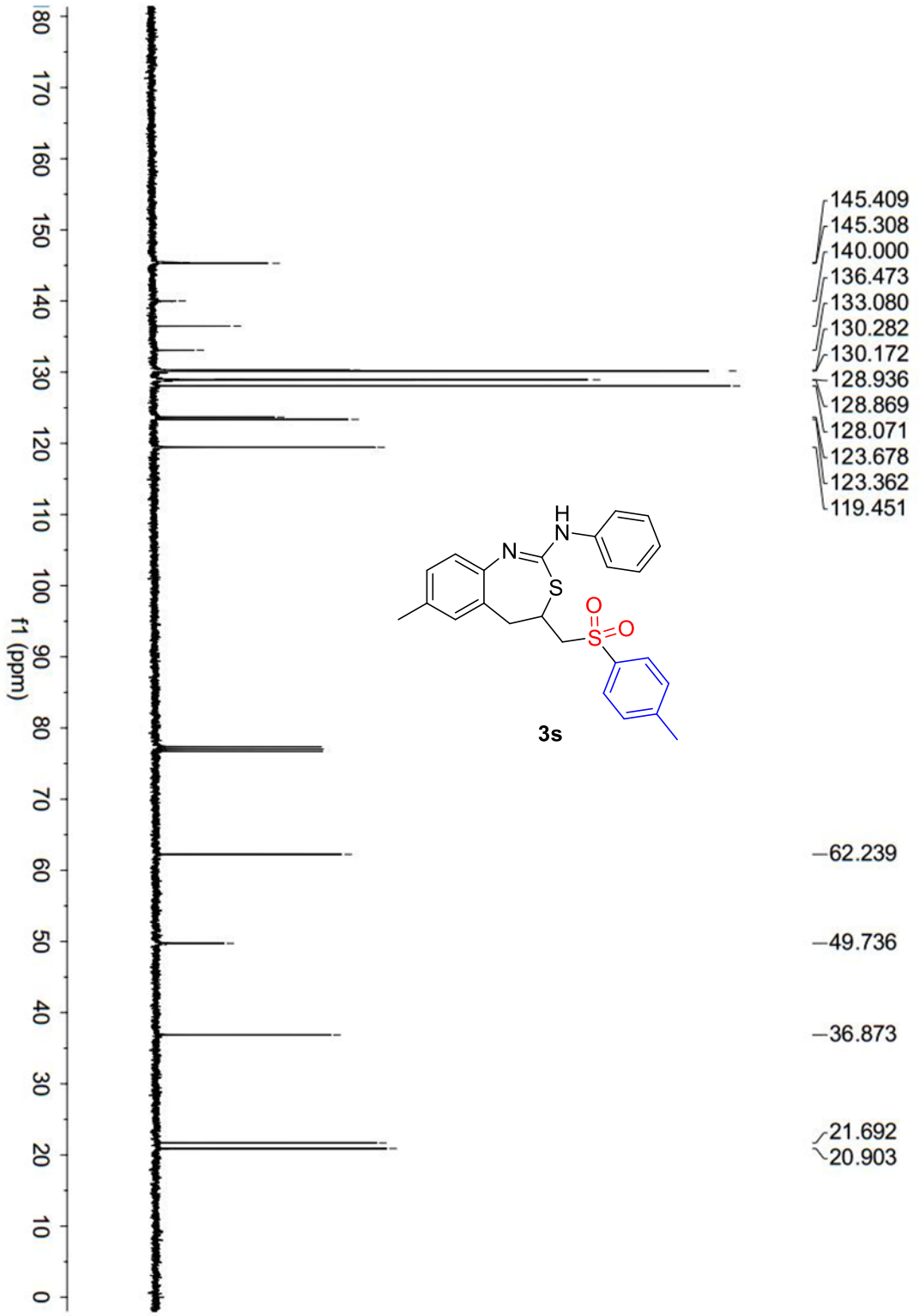

8.222
8.199
7.859
7.831
7.811
7.414
7.394
7.351
7.335
7.332
7.316
7.313
7.262
7.246
7.227
7.120
7.101
7.043
7.024
4.491
4.473
4.459
4.445
4.427
3.625
3.606
3.589
3.571
3.407
3.393
3.200
3.187
2.478
0.000
1.96
3.85
1.95
1.15
1.27
1.06
1.00
1.02
1.00
1.03
1.00
1.01
3.02
f1 (ppm)
H
N
N
S
O
S
O
NO2
3q

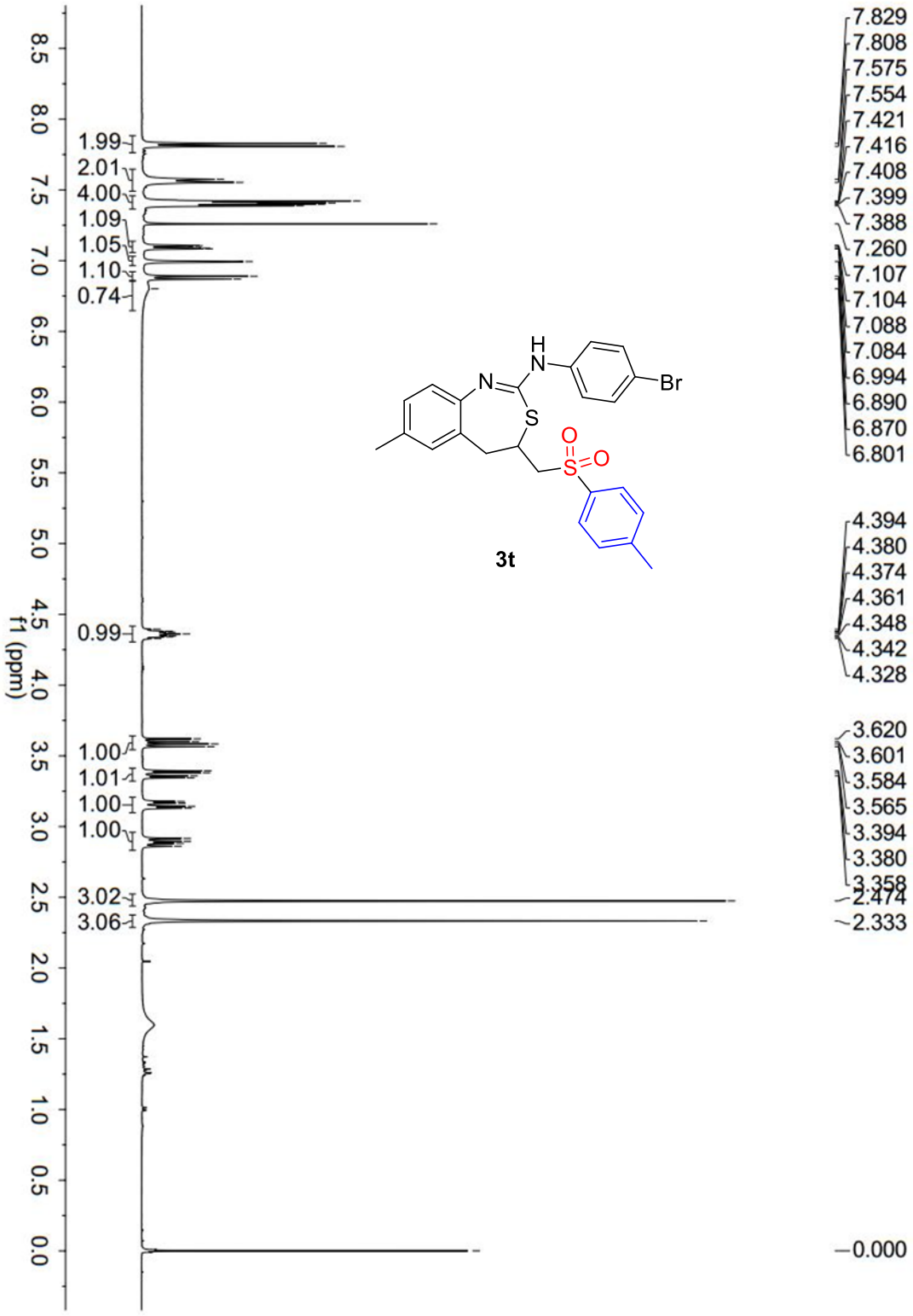

f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
147.170
145.896
145.773
145.580
142.419
136.160
130.262
129.780
129.001
128.384
127.981
125.043
124.303
123.952
118.825
62.060
50.522
36.854
21.700
H
N
N
S
O
S
O
NO2
3q


f1 (ppm)
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
0.99
0.97
1.00
1.01
1.00
4.19
3.59
1.09
3.26
0.85
1.03
1.04
1.03
1.01
1.00
H
N
N
S
O
S
O
3r
8.739
8.718
8.349
8.346
8.330
8.327
8.181
8.161
8.031
8.010
7.766
7.763
7.745
7.741
7.697
7.694
7.677
7.674
7.646
7.626
7.607
7.589
7.569
7.312
7.293
7.291
7.272
7.255
7.249
7.236
7.232
7.133
7.117
7.064
7.046
7.027
7.024
7.020
7.004
7.002
6.967
6.947
3.806
3.788
3.769
3.752
3.666
3.651
3.629
-0.000

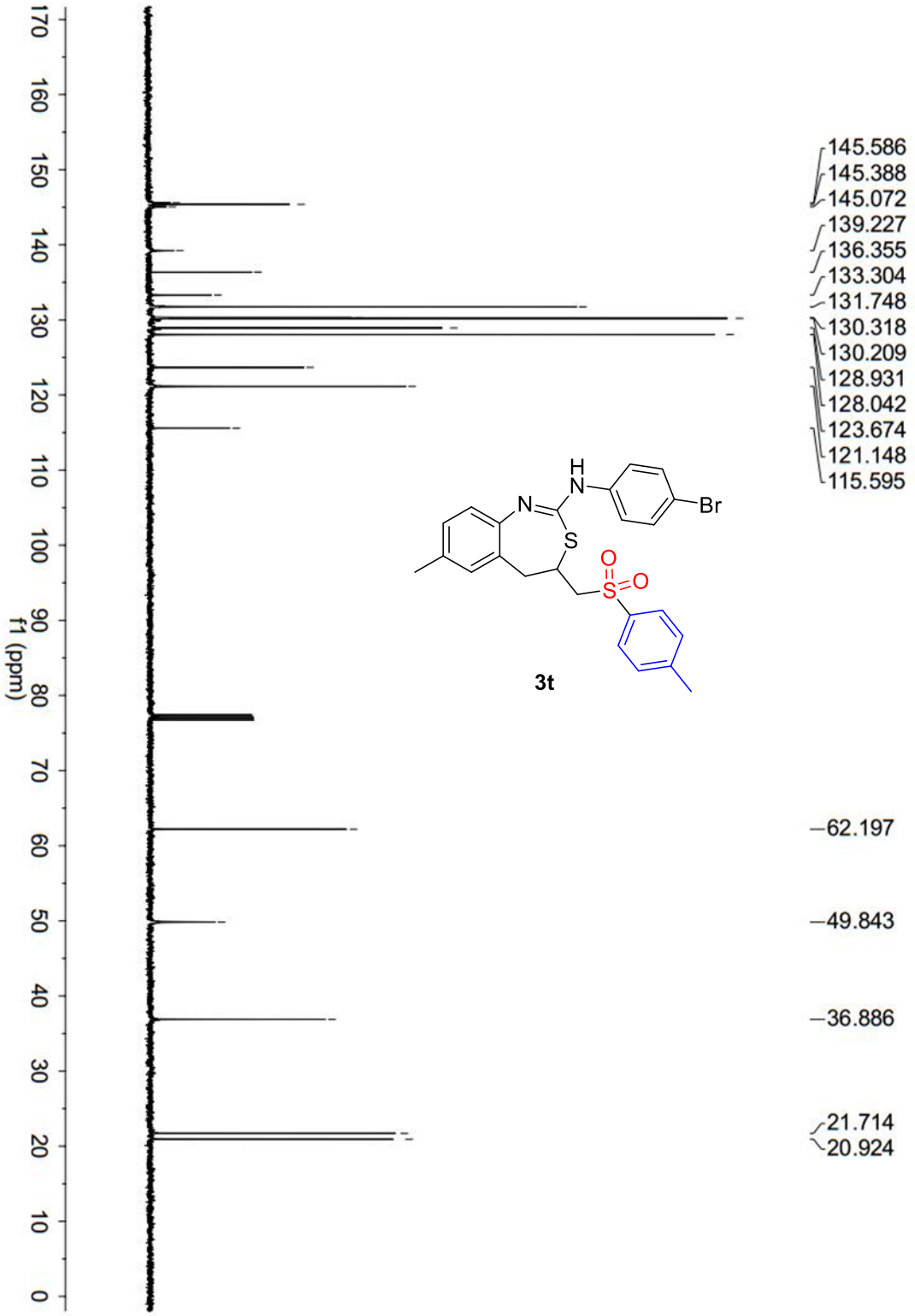

148.164
145.490
139.748
135.751
134.367
134.237
130.906
129.579
129.118
128.920
128.851
128.200
127.264
124.662
123.799
123.577
123.484
119.474
61.695
50.049
37.075
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
H
N
N
S
O
O
S
3r

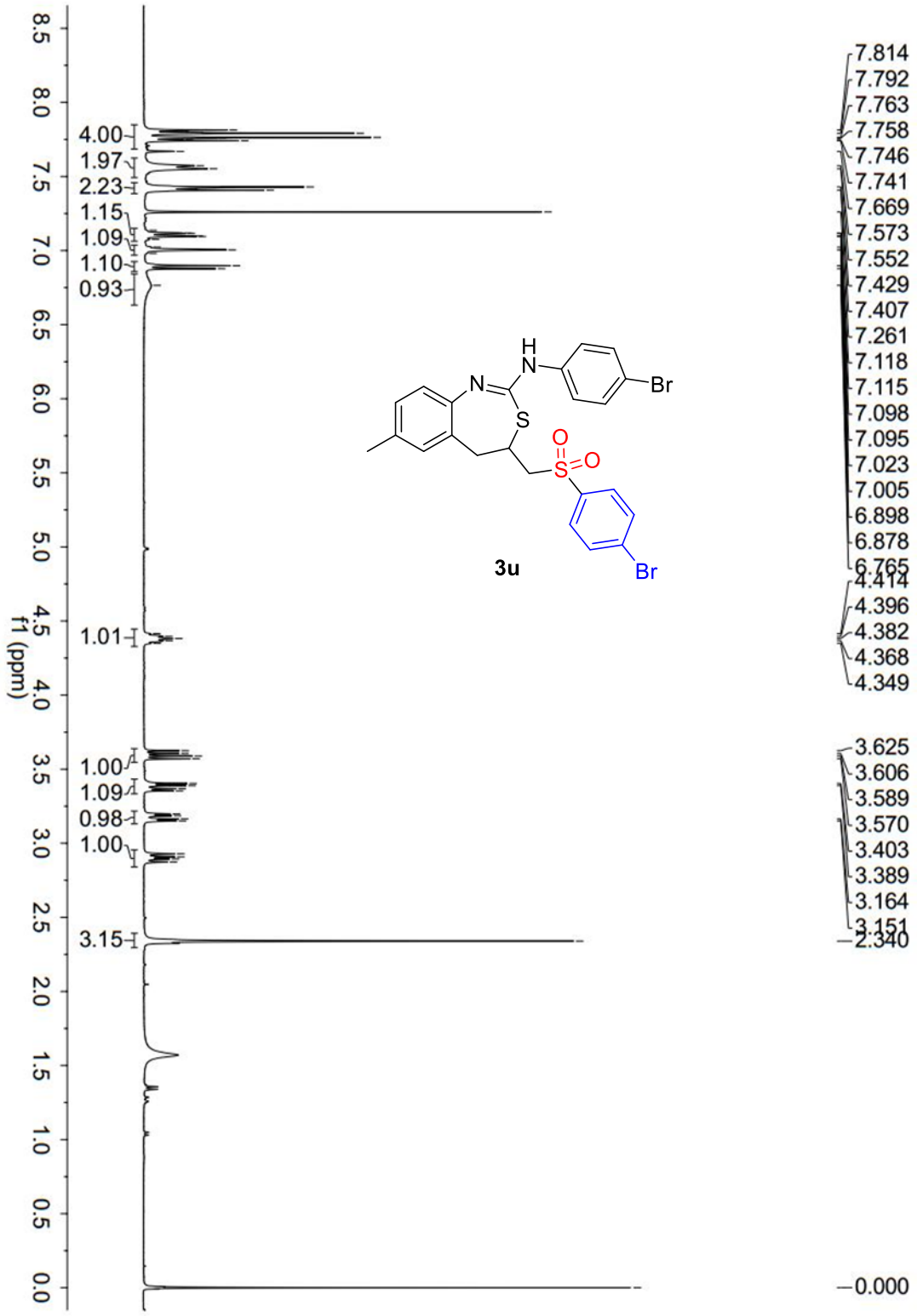

7.834
7.814
7.671
7.651
7.407
7.387
7.336
7.318
7.297
7.257
7.121
7.102
7.098
7.077
7.059
7.040
6.991
6.908
4.385
4.371
4.365
4.351
4.338
4.332
4.318
3.631
3.611
3.595
3.576
3.406
3.393
3.150
2.473
2.330
-0.000
1.98
1.98
2.02
2.22
2.24
1.07
1.10
0.73
0.99
1.00
1.04
0.99
0.98
3.08
3.16
f1 (ppm)
H
N
N
S
O
S
O
3s

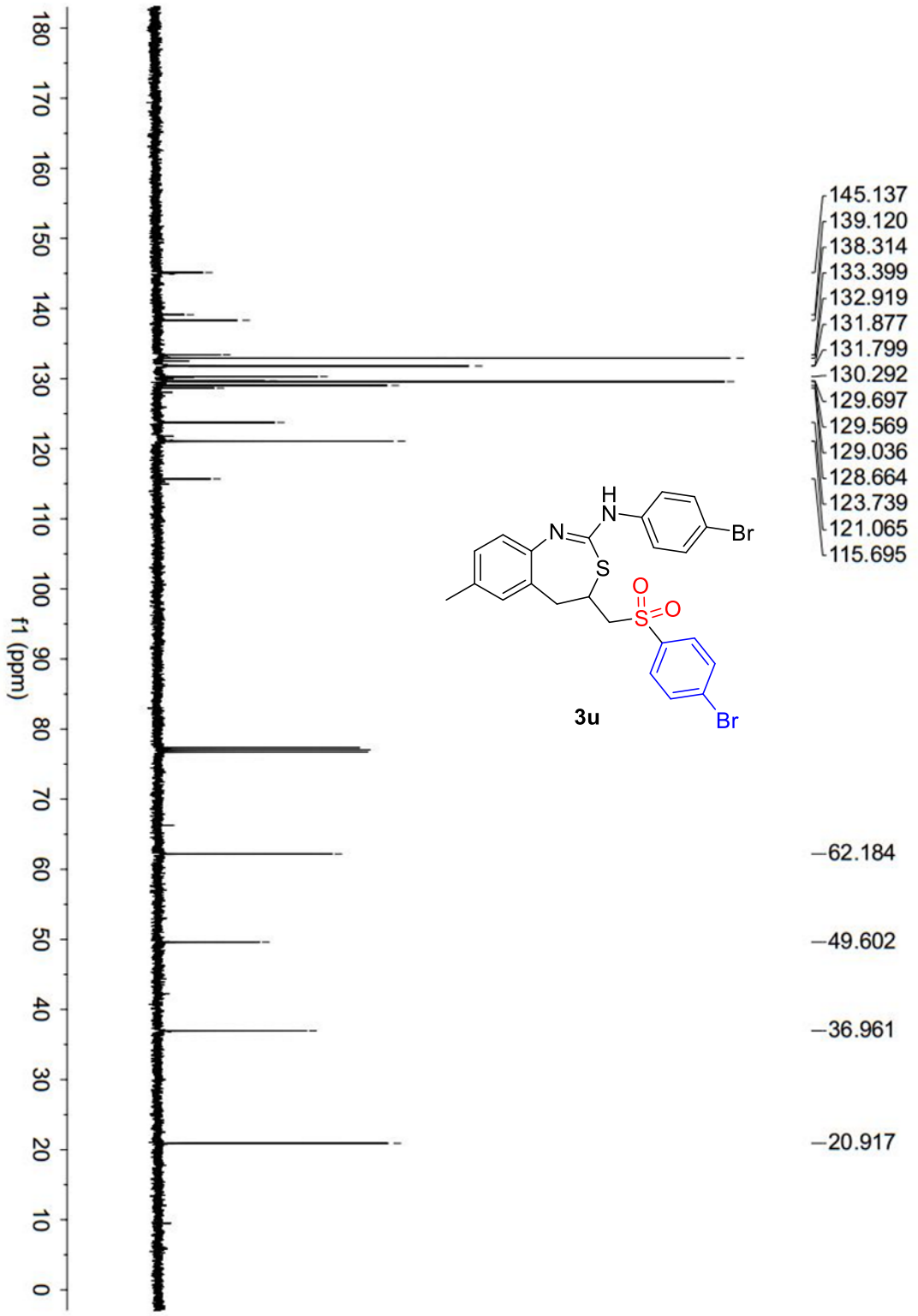

145.409
145.308
140.000
136.473
133.080
130.282
130.172
128.936
128.869
128.071
123.678
123.362
119.451
62.239
49.736
36.873
21.692
20.903
f1 (ppm)
H
N
N
S
O
S
O
3s

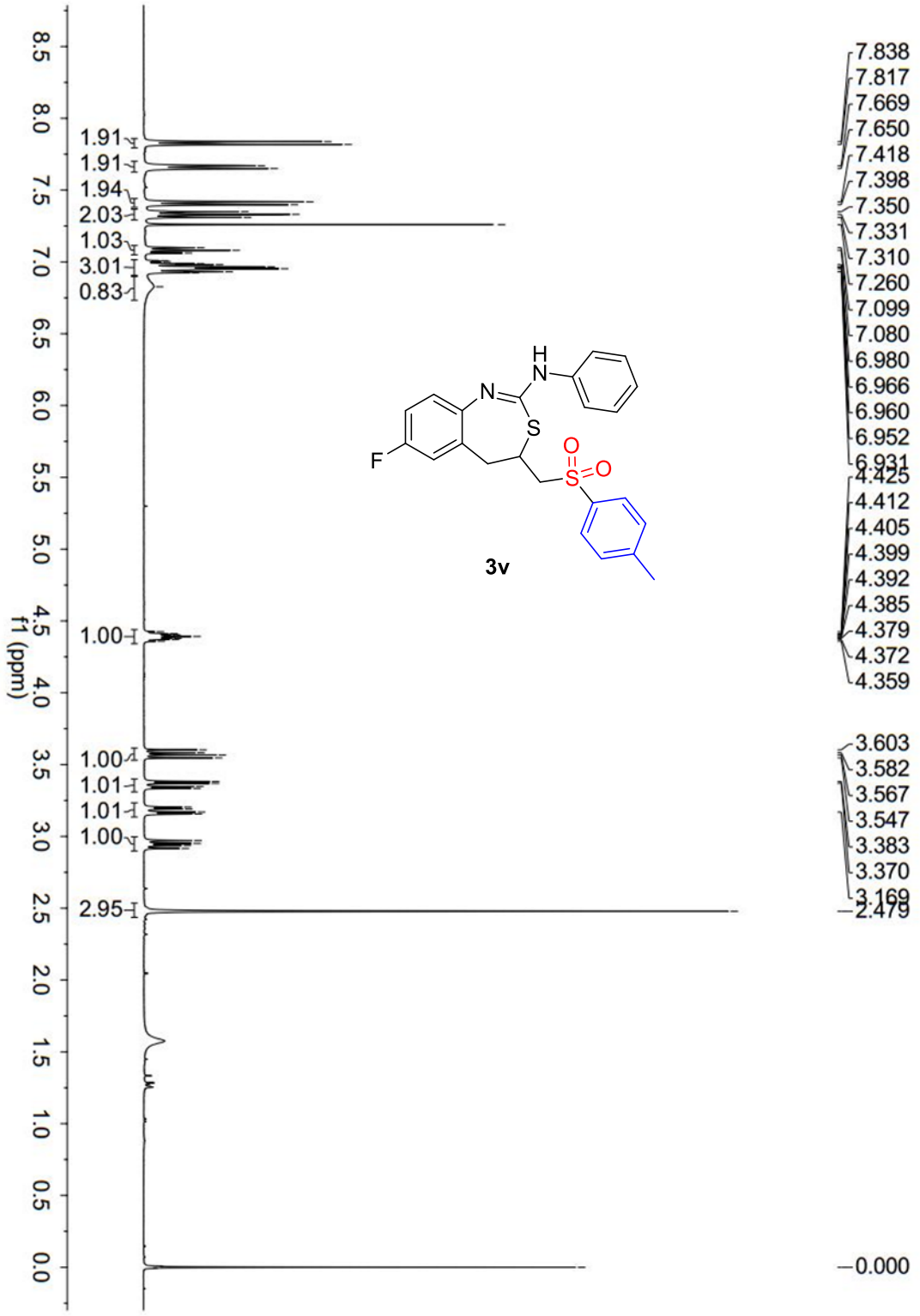

7.829
7.808
7.575
7.554
7.421
7.416
7.408
7.399
7.388
7.260
7.107
7.104
7.088
7.084
6.994
6.890
6.870
6.801
4.394
4.380
4.374
4.361
4.348
4.342
4.328
3.620
3.601
3.584
3.565
3.394
3.380
3.358
2.474
2.333
0.000
1.99
2.01
4.00
1.09
1.05
1.10
0.74
0.99
1.00
1.01
1.00
1.00
3.02
3.06
f1 (ppm)
H
N
N
S
O
S
O
Br

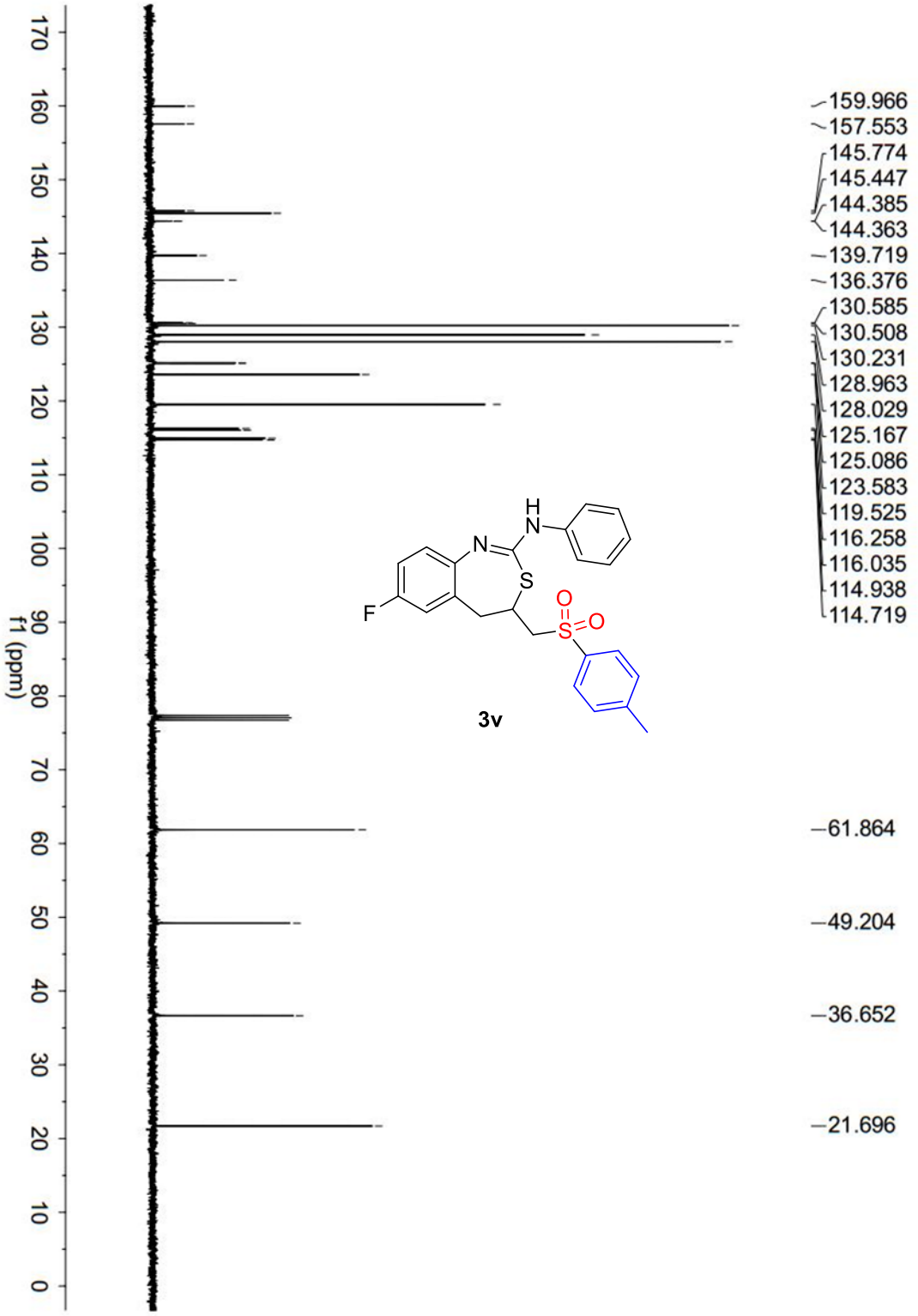
3t


145.586
145.388
145.072
139.227
136.355
133.304
131.748
130.318
130.209
128.931
128.042
123.674
121.148
115.595
62.197
49.843
36.886
21.714
20.924
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
H
N
N
S
Br
O
S
O
3t


7.814
7.792
7.763
7.758
7.746
7.741
7.669
7.573
7.552
7.429
7.407
7.261
7.118
7.115
7.098
7.095
7.023
7.005
6.898
6.878
6.765
4.414
4.396
4.382
4.368
4.349
3.625
3.606
3.589
3.570
3.403
3.389
3.164
3.151
2.340
0.000
4.00
1.97
2.23
1.15
1.09
1.10
0.93
1.01
1.00
1.09
0.98
1.00
3.15
f1 (ppm)
3u


145.137
139.120
138.314
133.399
132.919
131.877
131.799
130.292
129.697
129.569
129.036
128.664
123.739
121.065
115.695
62.184
49.602
36.961
20.917
f1 (ppm)
H
N
N
S
O
S
O
Br
Br
3u


7.838
7.817
7.669
7.650
7.418
7.398
7.350
7.331
7.310
7.260
7.099
7.080
6.980
6.966
6.960
6.952
6.931
4.425
4.412
4.405
4.399
4.392
4.385
4.379
4.372
4.359
3.603
3.582
3.567
3.547
3.383
3.370
3.169
2.479
0.000
1.91
1.91
1.94
2.03
1.03
3.01
0.83
1.00
1.00
1.01
1.01
1.00
2.95
f1 (ppm)
H
N
N
S
F
O
S
O
3v


159.966
157.553
145.774
145.447
144.385
144.363
139.719
136.376
130.585
130.508
130.231
128.963
128.029
125.167
125.086
123.583
119.525
116.258
116.035
114.938
114.719
61.864
49.204
36.652
21.696
f1 (ppm)
3v

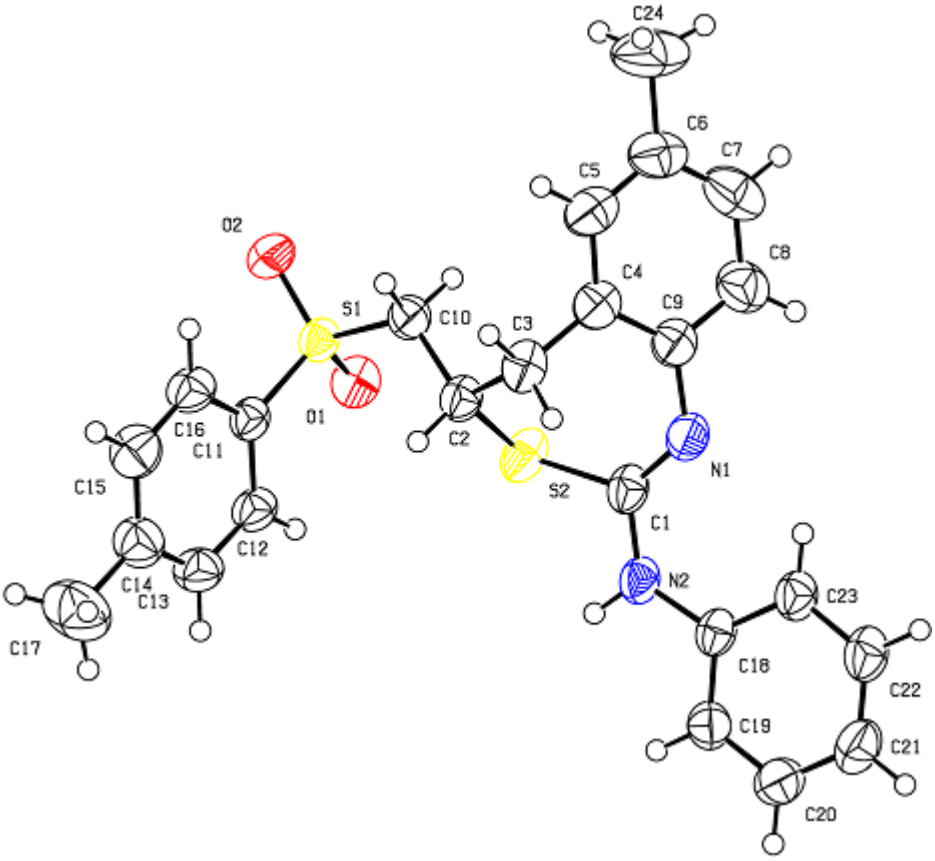


Table 1. Crystal data and structure refinement for **3s** (CCDC 1859862).

Identification code	ga_80710ea_a	
Empirical formula	C24 H24 N2 O2 S2	
Formula weight	436.57	
Temperature	296(2) K	
Wavelength	1.34138 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 18.532(2) Å	a= 90°.
	b = 11.0873(17) Å	b= 90°.
	c = 21.537(4) Å	g = 90°.
Volume	4425.2(11) $Å^3$	
Z	8	

Density (calculated)	1.311 Mg/m^3
Absorption coefficient	1.551 mm^{-1}
F(000)	1840
Crystal size	0.480 x 0.450 x 0.100 mm^3
Theta range for data collection	4.131 to 58.989°.
Index ranges	-21<=h<=23, -11<=k<=14, -27<=l<=27
Reflections collected	26282
Independent reflections	4786 [R(int) = 0.0508]
Completeness to theta = 53.594°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.805 and 0.503
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4786 / 0 / 277
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0549, wR2 = 0.1506
R indices (all data)	R1 = 0.0585, wR2 = 0.1569
Extinction coefficient	n/a
Largest diff. peak and hole	1.155 and -0.477 $e.Å^{-3}$