Electronic Supplementary Material (ESI) for ChemComm.

Photoinduced intramolecular carbosulfonylation of alkynes: access to sulfone-containing dibenzazepines from sulfur dioxide

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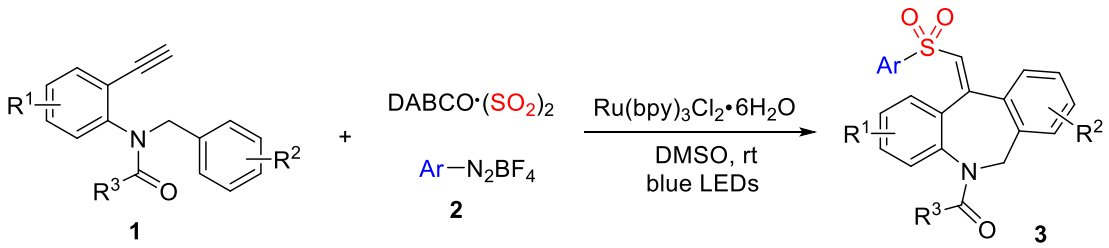
Supporting Information

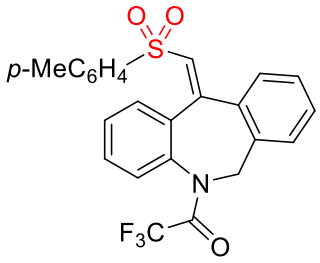
General experimental methods:

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 alkynes **1**, (DABCO)·$(SO_2)_2$, and aryldiazonium tetrafluoroborates **2**.*

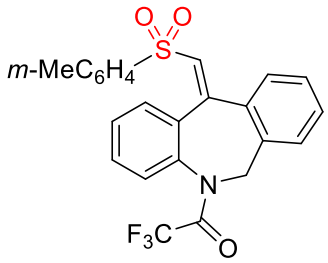


Alkynes **1** (0.2 mmol) was added to a mixture of aryldiazonium tetrafluoroborate **2** (0.3 mmol), DABCO·$(SO_2)_2$ (0.2 mmol), $Ru(bpy)_3Cl_2·6H_20$ (2 mol%) in DMSO (2.0 mL) under N_2 atmosphere. The mixture was placed around a blue LED (30 W) and stirred under blue light irradiation for 24 h at room temperature. After completion of reaction as indicated by TLC, the reaction mixture was diluted with water (30 mL) then extracted with EtOAc (10 mL × 3). The organic phases were combined and washed with brine before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified directly by flash column chromatography (*n*-hexane/ethyl acetate = 4:1) to give the corresponding product **3**.



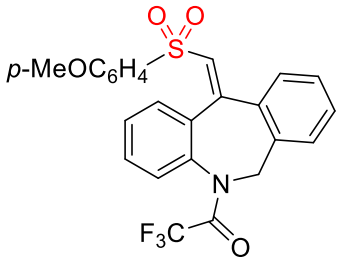
(*Z*)-2,2,2-Trifluoro-1-(11-(tosylmethylene)-6,11-dihydro-*5H*-dibenzo[*b*,*e*]azepin-5-yl)ethan-1-one (**3a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.72 – 7.68 (m, 1H), 7.52 – 7.48 (m, 2H), 7.41 – 7.31 (m, 6H), 7.13 (d, *J* = 7.8 Hz, 1H), 6.71 (s, 1H), 5.94 (d, *J* = 13.3 Hz, 1H), 4.33 (d, *J* = 12.4 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9 (q, *J* = 36.6 Hz), 149.0, 144.8, 138.0, 135.5, 134. 7, 134.3, 134.1, 131.8, 130.8, 130.5, 130.2, 130.0, 129.5, 128.8, 128.2, 127.9, 127.7, 126.2, 116.1 (q, *J* = 288.4 Hz), 50.7, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.0; IR (KBr, cm^{-1}): 3034, 1699, 1319, 1211, 1147; HRMS (ESI) calcd for $C_{24}H_{18}NO_3NaSF_3^+$ ($M+Na^+$): 480.0857, found: 480.0866.



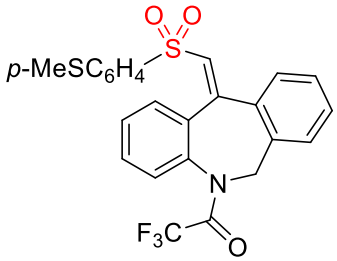
(*Z*)-2,2,2-Trifluoro-1-(11-((*m*-tolylsulfonyl)methylene)-6,11-dihydro-*5H*-dibenzo[*b*,*e*]azepin-5-yl)ethan-1-one (**3b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 3H), 7.52 – 7.48 (m, 2H), 7.42 – 7.40 (m, 2H), 7.37 (d, *J* = 9.0 Hz, 1H), 7.32 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.71 (s, 1H), 5.95 (d, *J* = 16.0 Hz, 1H), 4.34 (d, *J* = 15.9 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9 (q, *J* = 36.7 Hz), 149.4, 140.8, 139.8, 135.6, 134.7, 134.5, 134.3, 134.2, 131.7, 130.8, 130.6, 130.3, 129.6, 129.3, 128.9, 128.3, 128.0, 126.3, 124.7, 116.2 (q, *J* = 288.4 Hz), 50.7, 21.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.0; IR (KBr, cm^{-1}): 3034, 1695, 1318, 1265, 1148; HRMS (ESI) calcd for $C_{24}H_{18}NO_3NaSF_3^+$ ($M+Na^+$): 480.0857, found: 480.0861.



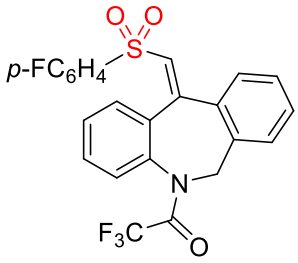
(*Z*)-2,2,2-Trifluoro-1-(11-(((4-methoxyphenyl)sulfonyl)methylene)-6,11-dihydro-*5H*-dibenzo[*b*,*e*]azepin-5-yl)ethan-1-one (**3c**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.9 Hz, 2H), 7.71 – 7.67 (m, 1H), 7.52 – 7.47 (m, 2H), 7.41 – 7.27 (m, 4H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.9 Hz, 2H), 6.70 (s, 1H), 5.94 (d, *J* = 16.3 Hz, 1H), 4.33 (d, *J* = 16.0 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 156.9 (q, *J* = 36.7 Hz), 148.4, 135.5, 134.7, 134.3, 134.1, 132.5, 132.1, 130.8, 130.5, 130.2, 129.9, 129.5, 128.8, 128.2, 127.9, 126.2, 116.1 (q, *J* = 288.4 Hz), 114.6, 55.7, 50.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.0; IR (KBr, cm^{-1}): 3034, 1693, 1318, 1210, 1143, 1088; HRMS (ESI) calcd for $C_{24}H_{18}NO_4F_3NaS^+$ ($M+Na^+$): 496.0806, found: 496.0807.



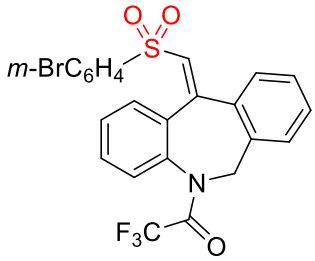
(*Z*)-2,2,2-Trifluoro-1-(11-(((4-(methylthio)phenyl)sulfonyl)methylene)-6,11-dihydro-*5H*-dibenzo[*b*,*e*]azepin-5-yl)ethan-1-one (**3d**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.6 Hz, 2H), 7.70 – 7.66 (m, 1H), 7.52 – 7.47 (m, 2H), 7.40 – 7.36 (m, 2H), 7.35 – 7.27 (m, 4H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.70 (s, 1H), 5.94 (d, *J* = 16.4 Hz, 1H), 4.34 (d, *J* = 16.6 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8 (q, *J* = 36.7 Hz), 149.1, 147.4, 136.5, 135.5, 134.7, 134.2, 134.1, 131.7, 130.7, 130.6, 130.3, 129.5, 128.9, 128.2, 127.9, 127.9, 126.2, 125.6, 116.1 (q, *J* = 288.5 Hz), 50.7, 14.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.0; IR (KBr, cm^{-1}): 3032, 2923, 1702, 1577, 1319, 1152; HRMS (ESI) calcd for $C_{24}H_{18}NO_3F_3NaS_2^+$ ($M+Na^+$): 512.0578, found: 512.0579.



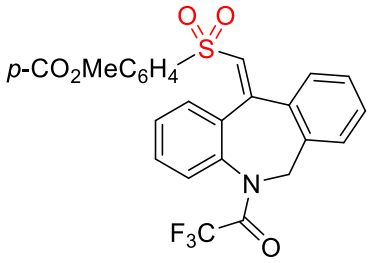
(*Z*)-2,2,2-Trifluoro-1-(11-(((4-fluorophenyl)sulfonyl)methylene)-6,11-dihydro-*5H*-dibenzo[*b*,*e*]azepin-5-yl)ethan-1-one (**3e**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.86 (m, 2H), 7.69 (dd, *J* = 7.0, 1.8 Hz, 2H), 7.55 – 7.47 (m, 2H), 7.43 – 7.33 (m, 3H), 7.30 – 7.25 (m, 1H), 7.24 – 7.09 (m, 3H), 6.71 (s, 1H), 5.95 (d, *J* = 16.3 Hz, 1H), 4.34 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8 (d, *J* = 256.4 Hz), 156.8 (q, *J* = 36.7 Hz), 149.9, 137.0 (d, *J* = 3.1 Hz), 135.5, 134.5, 134.2, 134.1, 131.3, 130.7 (d, *J* = 3.0 Hz), 130.6, 130.5, 130.4, 129.5, 128.9, 128.3, 128.0, 126.3, 116.7 (d, *J* = 22.7 Hz), 116.2 (q, *J* = 288.4 Hz), 50.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.0, -103.3; IR (KBr, cm^{-1}): 3016, 1707, 1485, 1319, 1144; HRMS (ESI) calcd for $C_{23}H_{15}NO_3F_4NaS^+$ ($M+Na^+$): 484.0606, found: 484.0612.



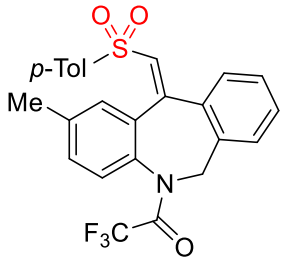
(*Z*)-1-(11-(((3-Bromophenyl)sulfonyl)methylene)-6,11-dihydro-*5H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (**3f**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.67 (dd, *J* = 7.2, 1.7 Hz, 1H), 7.50 (td, *J* = 6.6, 1.5 Hz, 2H), 7.40 (m, 3H), 7.34 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 6.71 (s, 1H), 5.95 (d, *J* = 16.2 Hz, 1H), 4.34 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8 (q, *J* = 36.7 Hz), 150.7, 142.8, 136.8, 135.5, 134.4, 134.3, 134.0, 131.0, 130.8, 130.7, 130.6, 130.5, 129.6, 128.9, 128.4, 128.1, 126.4, 126.2, 123.4, 116.2 (q, *J* = 288.4 Hz), 50.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.0; IR (KBr, cm^{-1}): 3020, 1690, 1327, 1208, 1147; HRMS (ESI) calcd for $C_{23}H_{15}NO_3F_3NaSBr^+$ ($M+Na^+$): 543.9806, found: 543.9810.



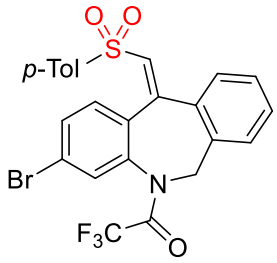
Methyl-(*Z*)-4-(((5-(2,2,2-trifluoroacetyl)-5,6-dihydro-*11H*-dibenzo[*b*,*e*]azepin-11-ylidene)methyl)sulfonyl)benzoate (**3g**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.3 Hz, 2H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.71 – 7.66 (m, 1H), 7.57 – 7.47 (m, 2H), 7.43 – 7.33 (m, 3H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.72 (s, 1H), 5.95 (d, *J* = 16.0 Hz, 1H), 4.35 (d, *J* = 16.1 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5 (q, *J* = 36.4 Hz), 150.9, 144.8, 135.5, 134.8, 134.5, 134.3, 134.1, 130.8, 130.7, 130.6, 130.5, 129.5, 128.9, 128.3, 128.0, 127.7, 126.3, 116.1 (q, *J* = 288.3 Hz), 52.7, 50.9, 29.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.0; IR (KBr, cm^{-1}): 3030, 1750, 1696, 1318, 1201, 1181; HRMS (ESI) calcd for $C_{25}H_{18}NO_5F_3NaS^+$ ($M+Na^+$): 524.0755, found: 524.0758.



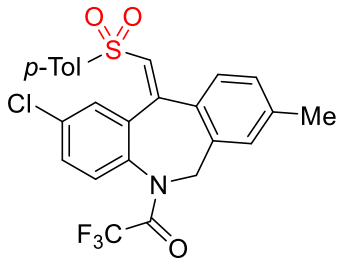
(*Z*)-2,2,2-Trifluoro-1-(2-methyl-11-(tosylmethylene)-6,11-dihydro-*5H*-dibenzo[*b*,*e*]azepin-5-yl)ethan-1-one (**3h**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.45 (s, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.27 (s, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.70 (s, 1H), 5.93 (d, *J* = 16.4 Hz, 1H), 4.31 (d, *J* = 16.0 Hz, 1H), 2.42 (d, *J* = 2.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0 (q, *J* = 36.6 Hz), 149.4, 144.7, 139.1, 138.3, 134.5, 134.5, 134.2, 132.9, 131.6, 131.2, 131.1, 130.2, 130.0, 129.5, 128.3, 127.9, 127.7, 126.0, 116.2 (q, *J* = 288.4 Hz), 50.8, 21.6, 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.0; IR (KBr, cm^{-1}): 3031, 2918, 1696, 1496, 1319, 1213, 1147; HRMS (ESI) calcd for $C_{25}H_{20}NO_3F_3NaS^+$ ($M+Na^+$): 494.1014, found: 494.1021.



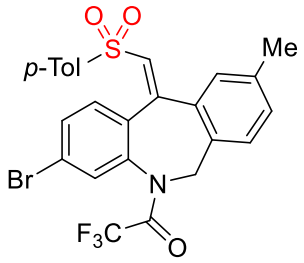
(*Z*)-1-(3-Bromo-11-(tosylmethylene)-6,11-dihydro-*5H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (**3i**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.62 – 7.54 (m, 3H), 7.39 – 7.31 (m, 4H), 7.28 (s, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.73 (s, 1H), 5.92 (d, *J* = 15.1 Hz, 1H), 4.33 (d, *J* = 14.8 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (q, *J* = 36.8 Hz), 147.8, 145.0, 137.8, 136.5, 133.9, 133.8, 132.2, 132.1, 132.1, 130.4, 130.1, 129.6, 129.5, 128.3, 128.1, 127.7, 123.5, 116.0 (q, *J* = 288.5 Hz), 50.6, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.0; IR (KBr, cm^{-1}): 3081, 3029, 1702, 1319, 1205, 1149; HRMS (ESI) calcd for $C_{24}H_{17}NO_3F_3NaSBr^+$ (M+Na^+): 557.9962, found: 557.9962.



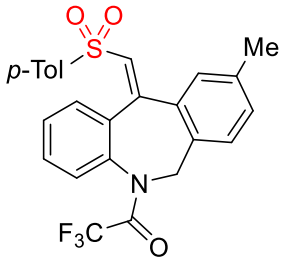
(*Z*)-1-(2-Chloro-8-methyl-11-(tosylmethylene)-6,11-dihydro-*5H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (**3j**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 2.0 Hz, 1H), 7.44 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.16 (d, *J* = 5.8 Hz, 2H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.73 (s, 1H), 5.88 (d, *J* = 15.8 Hz, 1H), 4.26 (d, *J* = 15.6 Hz, 1H), 2.43 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8 (q, *J* = 37.0 Hz), 147.8, 144.9, 138.0, 137.9, 136.4, 134.8, 134.0, 133.5, 132.0, 131.3, 130.8, 130.6, 130.4, 130.1, 129.9, 128.2, 127.7, 127.6, 116.0 (q, *J* = 288.0 Hz), 50.4, 21.6, 20.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.0; IR (KBr, cm^{-1}): 3023, 2923, 1699, 1480, 1222, 1144; HRMS (ESI) calcd for $C_{25}H_{19}NO_3F_3NaSCl^+$ (M+Na^+): 528.0624, found: 528.0627.



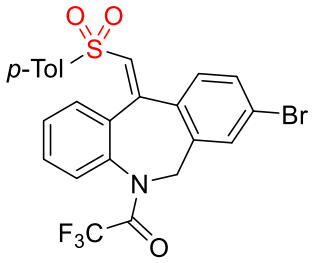
(*Z*)-1-(3-Bromo-9-methyl-11-(tosylmethylene)-6,11-dihydro-*5H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (**3k**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.65 – 7.51 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.13 (m, 2H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.72 (s, 1H), 5.87 (d, *J* = 14.6 Hz, 1H), 4.29 (d, *J* = 15.0 Hz, 1H), 2.42 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6 (q, *J* = 37.0 Hz), 148.1, 144.9, 138.0, 137.8, 136.5, 133.9, 133.6, 132.1, 132.0, 131.9, 131.3, 130.8, 130.1, 130.0, 129.5, 128.2, 127.7, 123.4, 116.0 (q, *J* = 286.1 Hz), 50.4, 21.6, 20.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.0; IR (KBr, cm^{-1}): 3037, 2923, 1713, 1316, 1152, 1093; HRMS (ESI) calcd for $C_{25}H_{19}NO_3F_3NaSBr^+$ ($M+Na^+$): 572.0119, found: 572.0124.



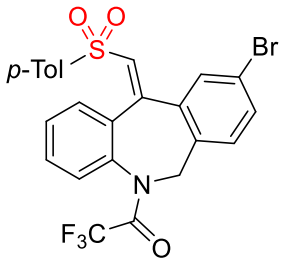
(*Z*)-2,2,2-Trifluoro-1-(9-methyl-11-(tosylmethylene)-6,11-dihydro-*5H*-dibenzo[*b*,*e*]azepin-5-yl)ethan-1-one (**3l**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.72 – 7.65 (m, 1H), 7.52 – 7.44 (m, 2H), 7.38 – 7.30 (m, 3H), 7.20 (s, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.71 (s, 1H), 5.90 (d, *J* = 16.4 Hz, 1H), 4.29 (d, *J* = 16.1 Hz, 1H), 2.41 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8 (q, *J* = 36.7 Hz), 149.3, 144.7, 138.1, 137.8, 135.5, 134.8, 134.1, 131.5, 131.1, 130.8, 130.5, 130.0, 130.0, 128.8, 128.2, 127.7, 126.3, 116.2 (q, *J* = 288.4 Hz), 50.5, 21.6, 20.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.0; IR (KBr, cm^{-1}): 3040, 2926, 1699, 1316, 1144, 1083; HRMS (ESI) calcd for $C_{25}H_{20}NO_3F_3NaS^+$ ($M+Na^+$): 494.1014, found: 494.1017.



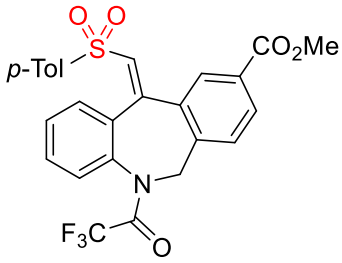
(*Z*)-1-(8-Bromo-11-(tosylmethylene)-6,11-dihydro-*5H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (**3m**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.71 – 7.66 (m, 1H), 7.54 – 7.48 (m, 2H), 7.42 – 7.34 (m, 3H), 7.32 – 7.27 (m, 3H), 6.69 (s, 1H), 5.89 (d, *J* = 16.5 Hz, 1H), 4.29 (d, *J* = 19.2 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9 (q, *J* = 37.0 Hz), 147.7, 144.9, 137.8, 136.2, 135.4, 134.2, 133.3, 132.3, 131.1, 131.0, 130.9, 130.8, 130.1, 129.0, 127.7, 126.3, 124.3, 116.0 (q, *J* = 288.5 Hz), 50.3, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.1; IR (KBr, cm^{-1}): 3039, 2923, 1702, 1319, 1152, 1088; HRMS (ESI) calcd for $C_{24}H_{17}NO_3F_3NaSBr^+$ ($M+Na^+$): 557.9962, found: 557.9968.



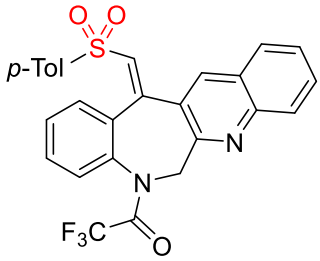
(*Z*)-1-(9-Bromo-11-(tosylmethylene)-6,11-dihydro-*5H*-dibenzo[*b*,*e*]azepin-5-yl)-2,2,2-trifluoroethan-1-one (**3n**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.72 – 7.66 (m, 1H), 7.56 – 7.49 (m, 3H), 7.44 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.35 (t, *J* = 8.5 Hz, 3H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.71 (s, 1H), 5.88 (d, *J* = 16.5 Hz, 1H), 4.25 (d, *J* = 16.7 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9 (q, *J* = 36.9 Hz), 147.3, 145.0, 137.7, 136.0, 135.4, 134.1, 133.2, 133.0, 132.8, 132.0, 130.9, 130.8, 130.1, 129.9, 129.0, 127.8, 126.3, 121.3, 116.1 (q, *J* = 288.4 Hz), 50.3, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.0; IR (KBr, cm^{-1}): 3031, 2923, 1707, 1324, 1155, 1083; HRMS (ESI) calcd for $C_{24}H_{17}NO_3F_3NaSBr^+$ ($M+Na^+$): 557.9962, found: 557.9971.



Methyl-(*Z*)-11-(tosylmethylene)-5-(2,2,2-trifluoroacetyl)-6,11-dihydro-*5H*-dibenzo[*b*,*e*]azepine-9-carboxylate (**3o**)

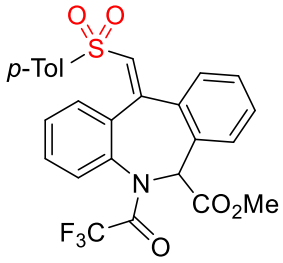
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 1.2 Hz, 1H), 7.96 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.71 (dd, *J* = 6.9, 2.1 Hz, 1H), 7.58 – 7.46 (m, 2H), 7.38 (d, *J* = 7.0 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 1H), 6.79 (s, 1H), 6.00 (d, *J* = 17.5 Hz, 1H), 4.37 (d, *J* = 17.3 Hz, 1H), 3.94 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 157.0 (q, J = 36.9 Hz), 147.8, 145.0, 139.2, 137.7, 135.4, 134.6, 134.4, 132.8, 130.9, 130.8, 130.7, 130.1, 129.9, 129.1, 128.6, 127.8, 126.3, 116.1 (q, J = 288.5 Hz), 52.5, 50.7, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.0; IR (KBr, cm^{-1}): 3037, 2959, 1707, 1319, 1152; HRMS (ESI) calcd for $C_{26}H_{20}NO_5F_3NaS^+$ ($M+Na^+$): 538.0912, found: 538.0910.



(*Z*)-2,2,2-Trifluoro-1-(13-(tosylmethylene)-7,13-dihydro-*8H*-benzo[6,7]azepino[3,4-*c*]quinolin-8-yl)ethan-1-one (**3p**)

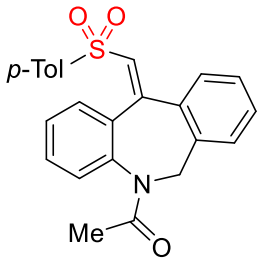
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.82 – 7.77 (m, 2H), 7.76 – 7.66 (m, 2H), 7.60 – 7.50 (m, 3H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.86 (s, 1H), 6.24 (d, *J* = 17.9 Hz, 1H), 4.55 (d, *J* = 17.9 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2 (q, *J* = 37.4 Hz), 153.3, 147.8, 146.7, 145.1, 137.6, 137.3, 135.7, 134.0, 132.5, 131.4, 131.1, 131.0, 130.1, 129.9, 129.2, 128.3, 127.9, 127.8, 127.5, 126.7, 126.6, 116.2 (q, *J* = 281.0 Hz), 54.1, 21.6; ^{19}F NMR

(376 MHz, $CDCl_3$) δ -67.1; IR (KBr, cm^{-1}): 3062, 2923, 1699, 1485, 1324, 1147, 1083; HRMS (ESI) calcd for $C_{27}H_{19}N_2O_3F_3NaS^+$ ($M+Na^+$): 531.0966, found: 531.0967.



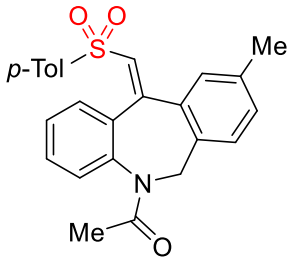
Methyl-(*Z*)-11-(tosylmethylene)-5-(2,2,2-trifluoroacetyl)-6,11-dihydro-*5H*-dibenzo[*b*,*e*]azepine-6-carboxylate (**3q**)

^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.72 – 7.67 (m, 1H), 7.52 – 7.43 (m, 3H), 7.40 – 7.29 (m, 5H), 7.20 (d, *J* = 7.4 Hz, 1H), 6.81 (s, 1H), 6.70 (s, 1H), 3.66 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 157.4 (q, *J* = 36.9 Hz), 148.5, 144.8, 138.0, 134.7, 134.3, 132.5, 131.3, 131.0, 130.0, 130.0, 129.8, 129.4, 129.0, 127.8, 127.7, 116.1 (q, *J* = 288.3 Hz), 60.8, 53.1, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.5; IR (KBr, cm^{-1}): 3042, 2953, 1757, 1696, 1316, 1172; HRMS (ESI) calcd for $C_{26}H_{20}NO_5F_3NaS^+$ ($M+Na^+$): 538.0912, found: 538.0909.



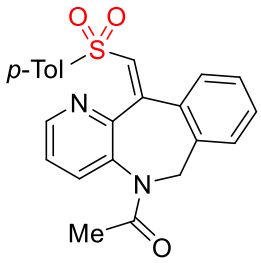
(*Z*)-1-(11-(Tosylmethylene)-6,11-dihydro-*5H*-dibenzo[*b*,*e*]azepin-5-yl)ethan-1-one (**3r**)

^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.52 – 7.41 (m, 2H), 7.36 – 7.27 (m, 5H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.72 (s, 1H), 6.07 (d, *J* = 15.9 Hz, 1H), 4.16 (d, *J* = 16.5 Hz, 1H), 2.43 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 152.1, 144.7, 138.5, 138.5, 136.3, 136.2, 134.7, 131.5, 130.7, 130.0, 129.9, 129.8, 128.8, 128.3, 128.3, 127.6, 127.2, 126.9, 48.1, 22.1, 21.6; IR (KBr, cm^{-1}): 3017, 1657, 1305, 1144; HRMS (ESI) calcd for $C_{24}H_{21}NO_3NaS^+$ ($M+Na^+$): 426.1140, found: 426.1138.



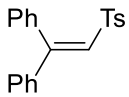
(*Z*)-1-(9-Methyl-11-(tosylmethylene)-6,11-dihydro-*5H*-dibenzo[*b*,*e*]azepin-5-yl)ethan-1-one (**3s**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.59 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.45 – 7.41 (m, 1H), 7.36 – 7.28 (m, 3H), 7.11 (d, *J* = 6.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.70 (s, 1H), 6.02 (d, *J* = 17.1 Hz, 1H), 4.11 (d, *J* = 15.8 Hz, 1H), 2.43 (s, 3H), 2.30 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 152.3, 144.7, 138.5, 138.5, 137.0, 136.4, 134.5, 133.1, 131.1, 130.7, 130.7, 130.0, 129.8, 129.2, 128.3, 128.2, 127.6, 126.9, 47.9, 22.1, 21.6, 20.8; IR (KBr, cm^{-1}): 3051, 2918, 1674, 1591, 1316, 1149, 1088; HRMS (ESI) calcd for $C_{25}H_{23}NO_3NaS^+$ ($M+Na^+$): 440.1296, found: 440.1290.



(*Z*)-1-(11-(Tosylmethylene)-6,11-dihydro-*5H*-benzo[*e*]pyrido[3,2-*b*]azepin-5-yl)ethan-1-one (**3t**)

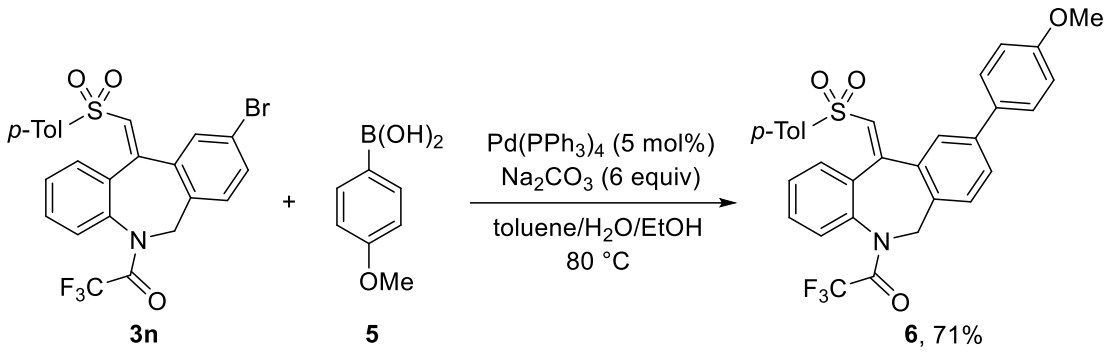
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.3 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.26 (m, 2H), 7.22 – 7.12 (m, 2H), 6.74 (s, 1H), 5.12 (s, 2H), 2.45 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 154.8, 152.2, 149.2, 144.6, 138.1, 135.9, 135.5, 135.0, 132.7, 132.2, 130.2, 129.9, 129.0, 128.2, 128.2, 127.5, 125.1, 47.9, 22.2, 21.7; IR (KBr, cm^{-1}): 3031, 1671, 1310, 1147, 1088; HRMS (ESI) calcd for $C_{23}H_{20}N_2O_3NaS^+$ ($M+Na^+$): 427.1092, found: 427.1096.



(2-Tosylethene-1,1-diyl)dibenzene (**4**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.9 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.32 – 7.26 (m, 3H), 7.25 – 7.22 (m, 1H), 7.21 – 7.16 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.99 (d, *J* = 0.9 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 143.9, 139.3, 138.7, 135.7, 130.4, 129.9, 129.5, 129.1, 129.0, 128.7, 128.3, 127.9, 127.8, 21.7; HRMS (ESI) calcd for $C_{21}H_{18}O_2NaS^+$ ($M+Na^+$): 357.0925, found: 357.0927.

*General experimental procedure for the Suzuki coupling with **3n***



The sulfonated dibenzazepine **3n** (0.1 mmol, 1 equiv), 4-methoxyphenylboronic acid **5** (0.12 mmol, 1.2 equiv), Na_2CO_3 (0.6 mmol, 6 equiv) and $Pd(PPh_3)_4$ (0.005 mmol, 5 mol%) were suspended in a degassed solvent mixture of toluene/H_2O/EtOH (5:3:1 v/v/v, 4.5 mL) in a sealed tube under N_2 atmosphere. The reaction mixture was stirred at 80 °C for 20 h. After completion of reaction as indicated by TLC, the reaction mixture was extracted with EtOAc (10 mL × 3). The organic phases were combined and washed with brine before dried with anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified by preparative TLC (*n*-hexane/ethyl acetate = 3:1) to give the desired product **6** in 71% yield.

(*Z*)-2,2,2-trifluoro-1-(9-(4-methoxyphenyl)-11-(tosylmethylene)-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepin-5-yl)ethan-1-one (**6**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 3H), 7.57 – 7.45 (m, 6H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.77 (s, 1H), 5.97 (d, *J* = 17.1 Hz, 1H), 4.36 (d, *J* = 16.9 Hz, 1H), 3.86 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 156.9 (q, *J* = 36.4 Hz), 149.1, 144.8, 140.8, 137.9, 135.5, 134.6, 132.2, 131.9, 131.9, 131.0, 130.6, 130.0, 128.9, 128.8, 128.5, 128.2, 127.7,

127.6, 126.3, 116.2 (q, J = 288.2 Hz), 114.4, 55.4, 50.5, 21.6; IR (KBr, cm^{-1}): 3021, 2926, 1707, 1607, 1488, 1247, 1149; HRMS (ESI) calcd for $C_{31}H_{24}NO_4F_3NaS^+$ ($M+Na^+$): 586.1276, found: 586.1273.

UV/Vis Absorption Spectra

The UV/Vis absorption spectra of DMSO solutions of **1a** (0.0.25 M), DABSO (0.0.25 M), and **2a** (0.0.25 M) are shown in Figure S1.

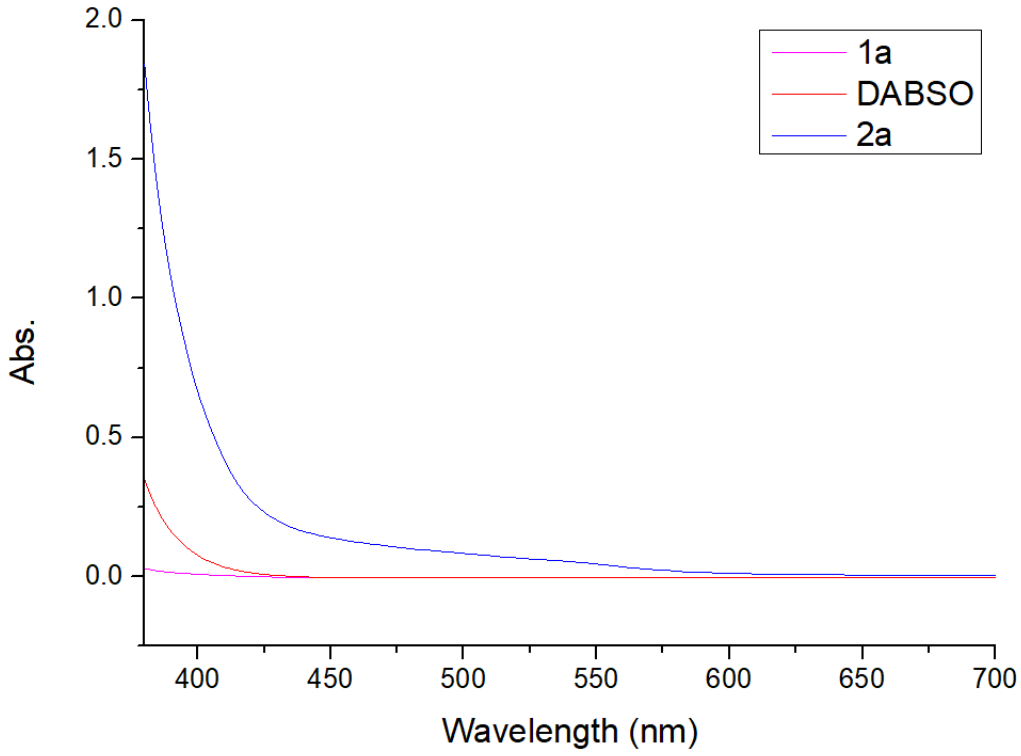
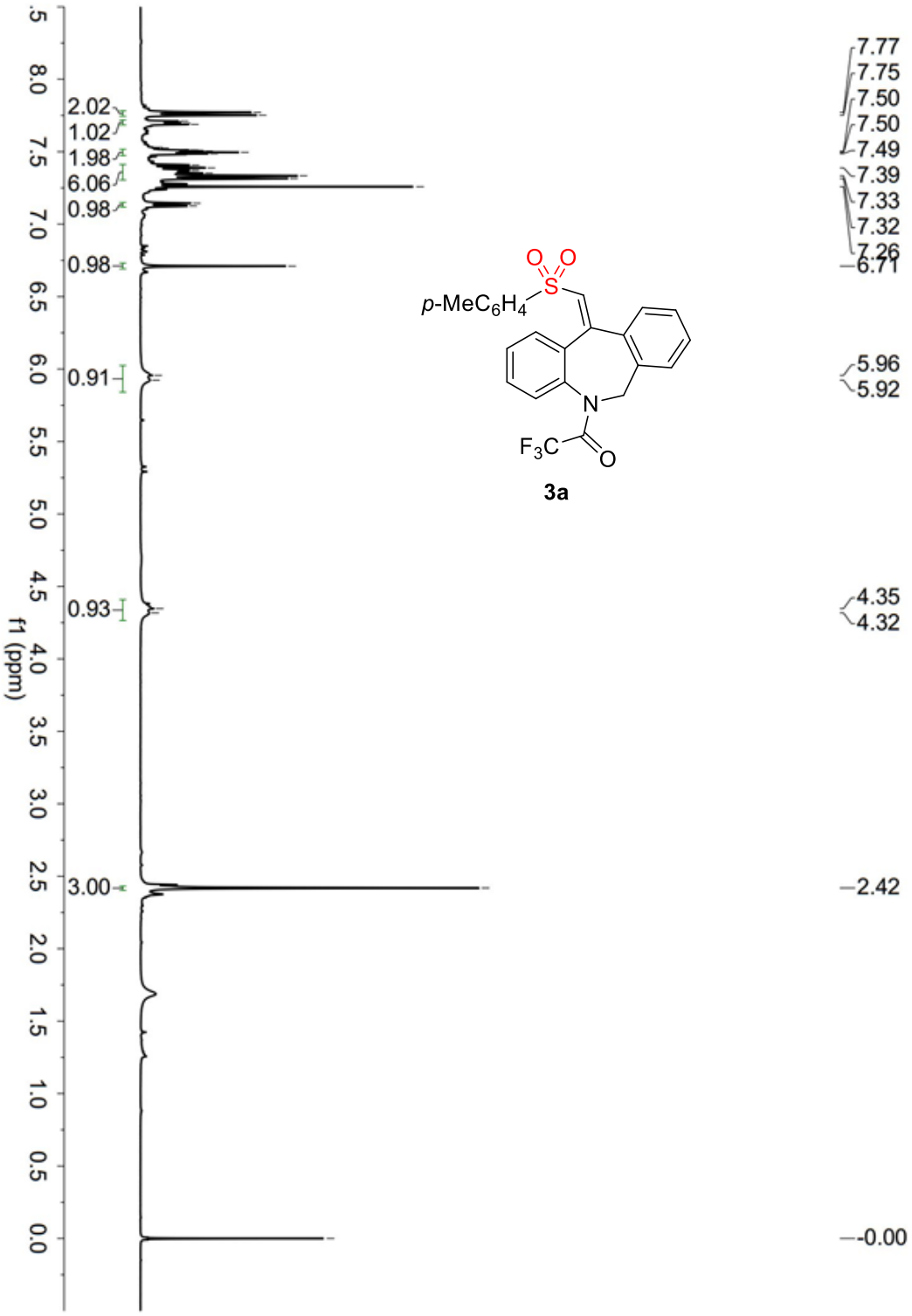


Figure S1. UV/Vis absorption spectra for **1a**, DABSO and **2a** in DMSO.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1.02
1.98
6.06
0.98
0.98
0.91
0.93
3.00
f1 (ppm)
7.77
7.75
7.50
7.50
7.49
7.39
7.33
7.32
7.26
6.71
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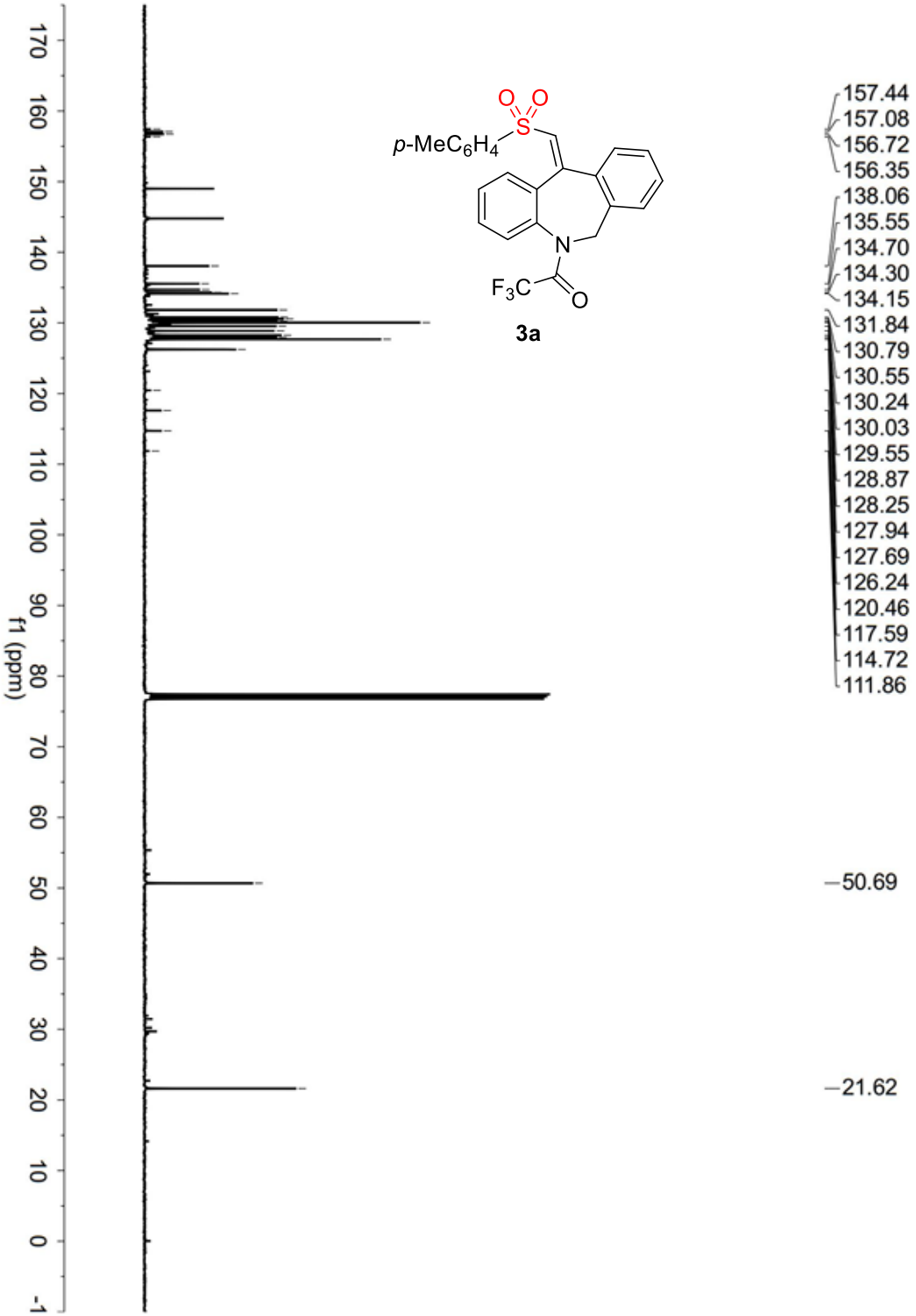
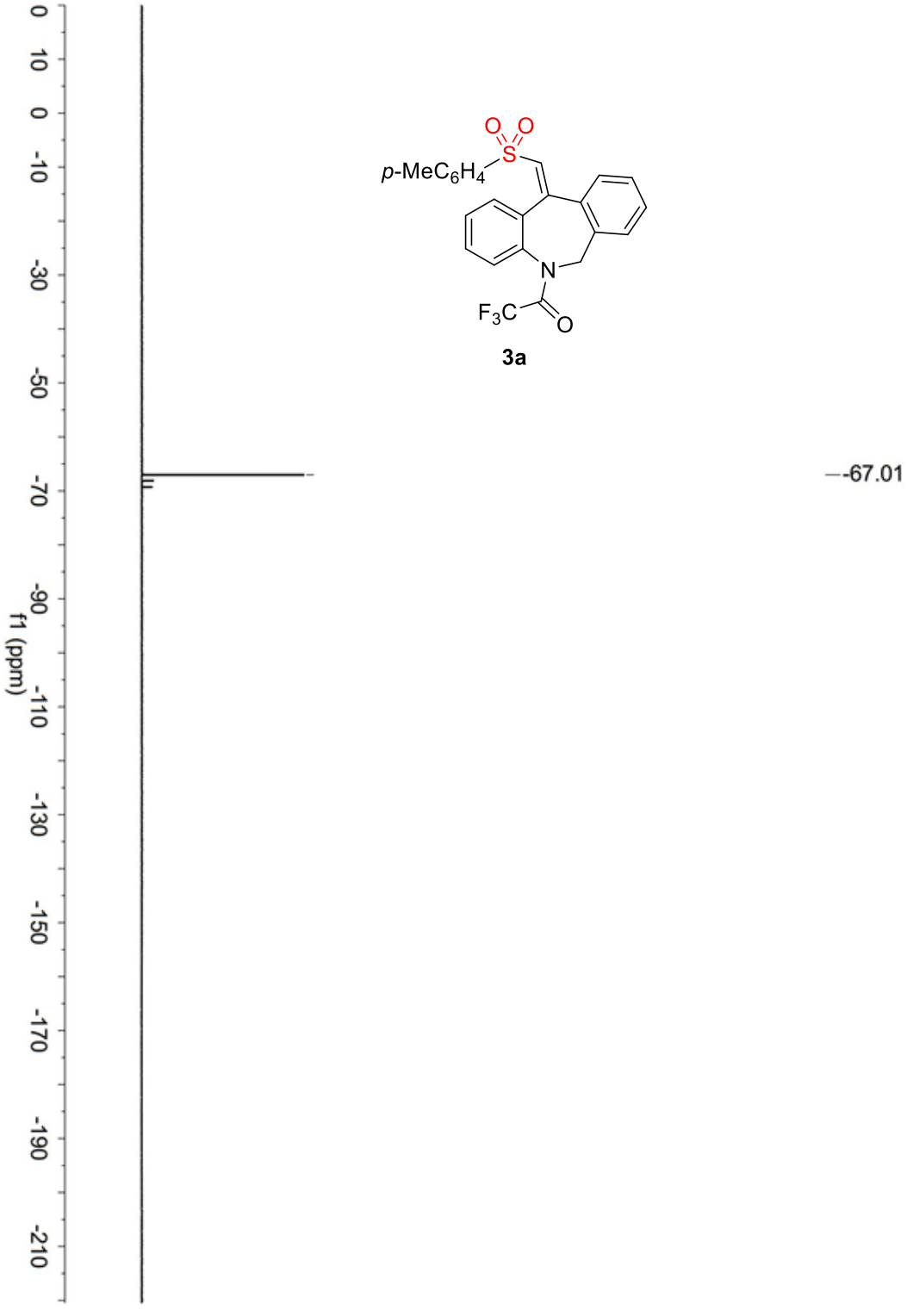
2.42
-0.00
p-MeC6H4
F3C
3a


157.44
157.08
156.72
156.35
138.06
135.55
134.70
134.30
134.15
131.84
130.79
130.55
130.24
130.03
129.55
128.87
128.25
127.94
127.69
126.24
120.46
117.59
114.72
111.86
50.69
21.62
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
p-MeC6H4
O
O
S
N
F3C
O

3a


f1 (ppm)
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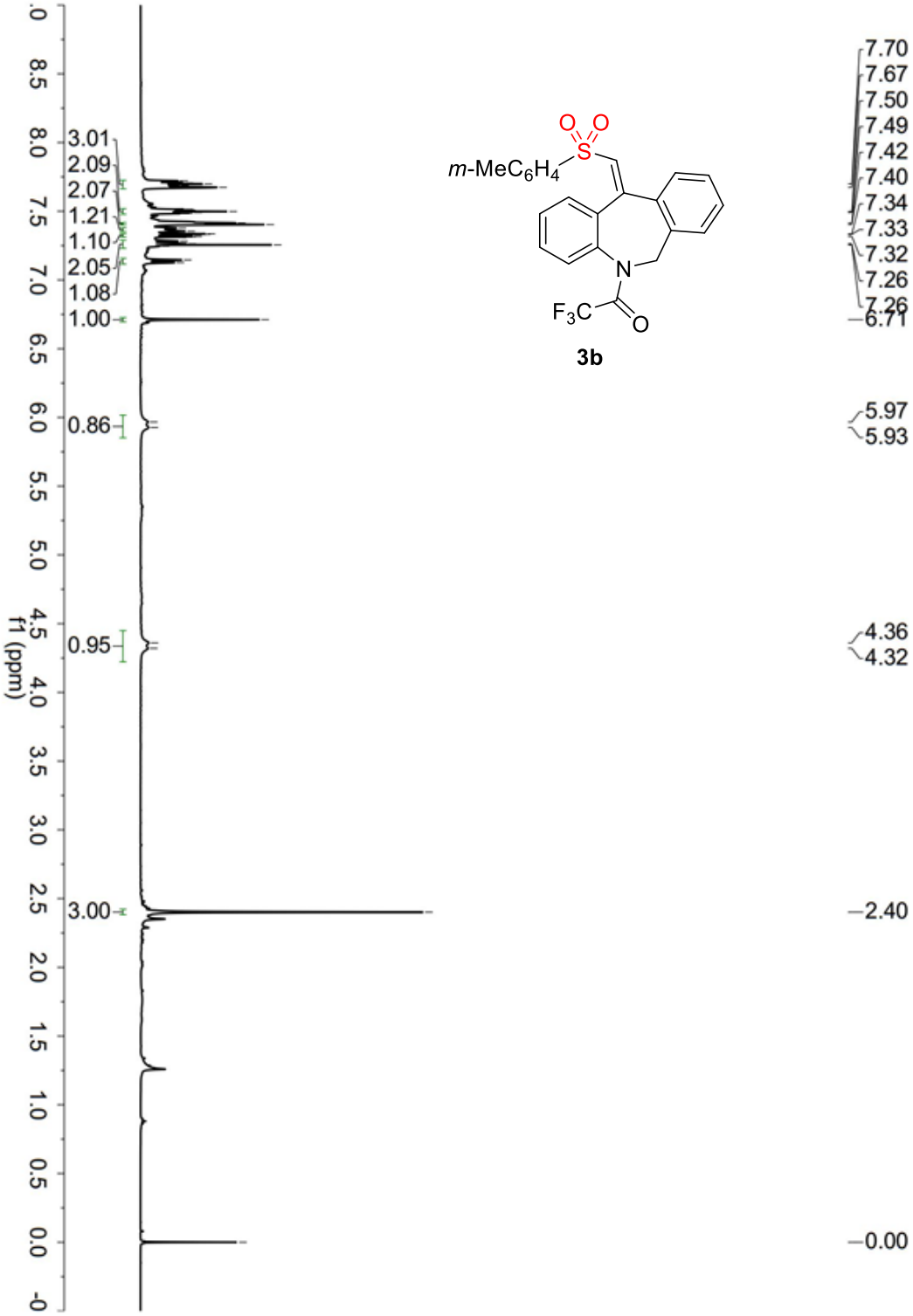
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-67.01
O
O
S
p-MeC6H4
N
F3C
O

3a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2.09
2.07
1.21
1.10
2.05
1.08
1.00
0.86
0.95
3.00
f1 (ppm)
m-MeC6H4
F3C
N
O
S
3b
7.70
7.67
7.50
7.49
7.42
7.40
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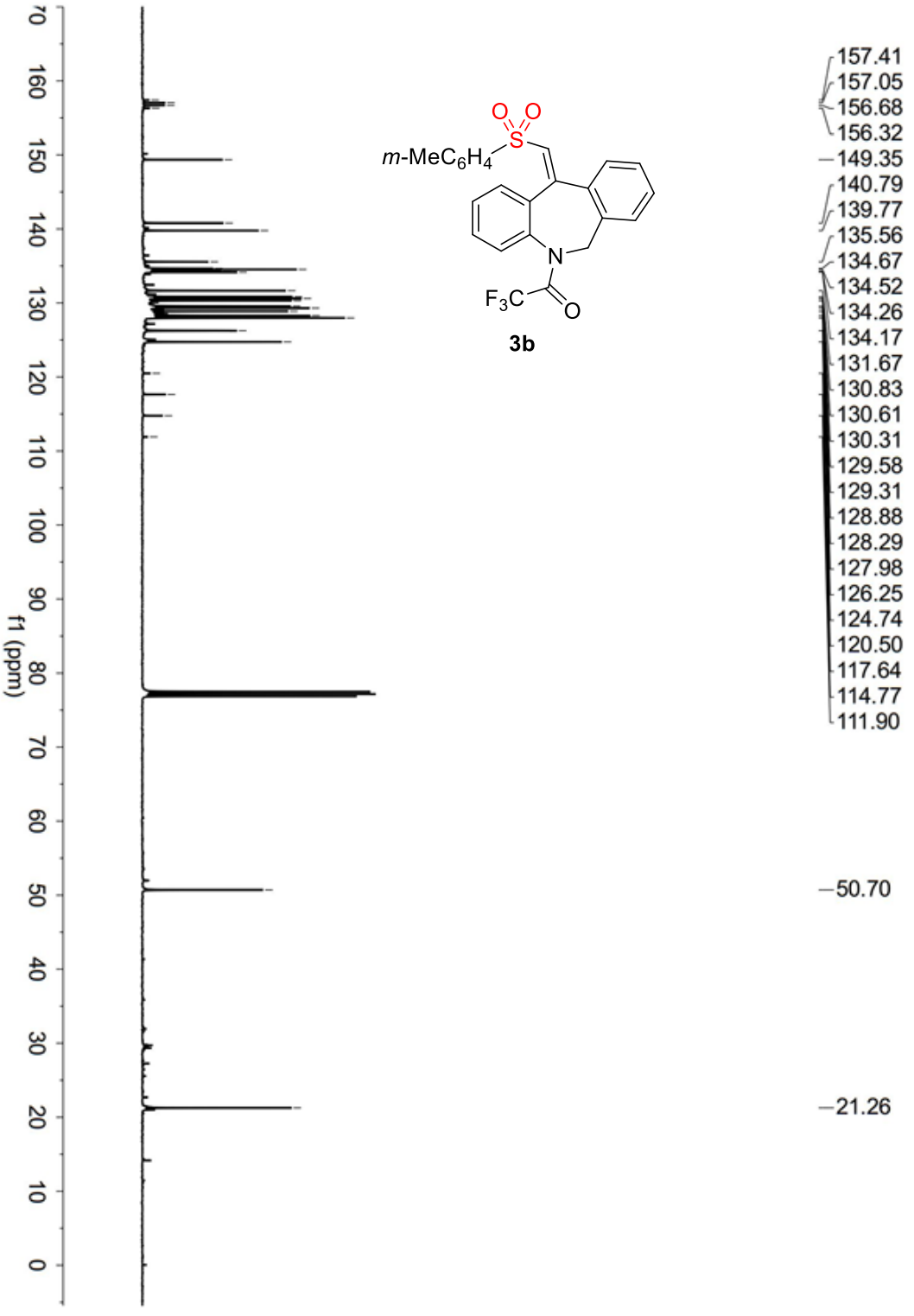
5.97
5.93
4.36
4.32
2.40
0.00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157.05
156.68
156.32
149.35
140.79
139.77
135.56
134.67
134.52
134.26
134.17
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130.83
130.61
130.31
129.58
129.31
128.88
128.29
127.98
126.25
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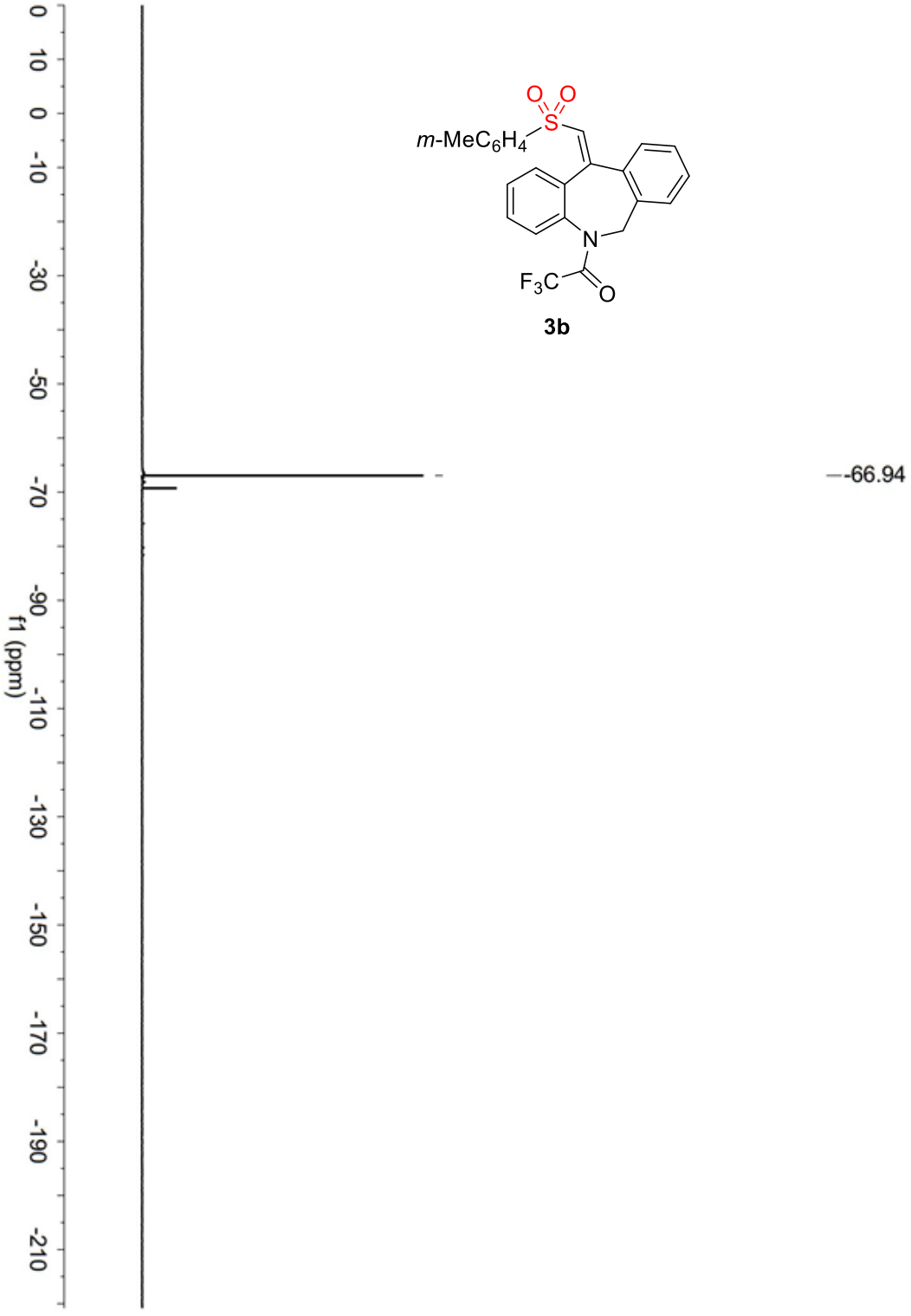
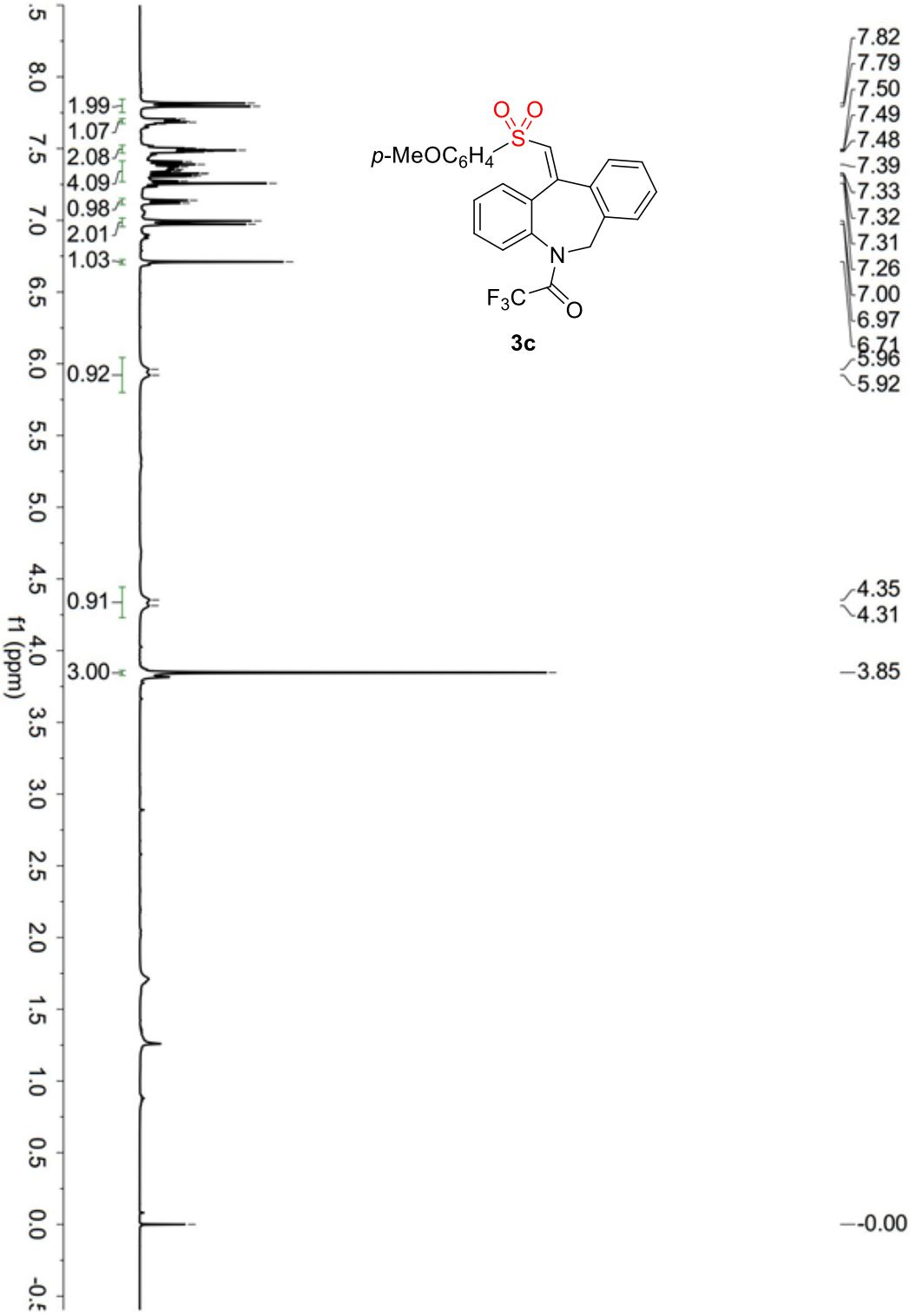
21.26
f1 (ppm)
m-MeC6H4
F3C
3b


O
O
S
m-MeC6H4
N
F3C
O
3b
-66.94
f1 (ppm)
0
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210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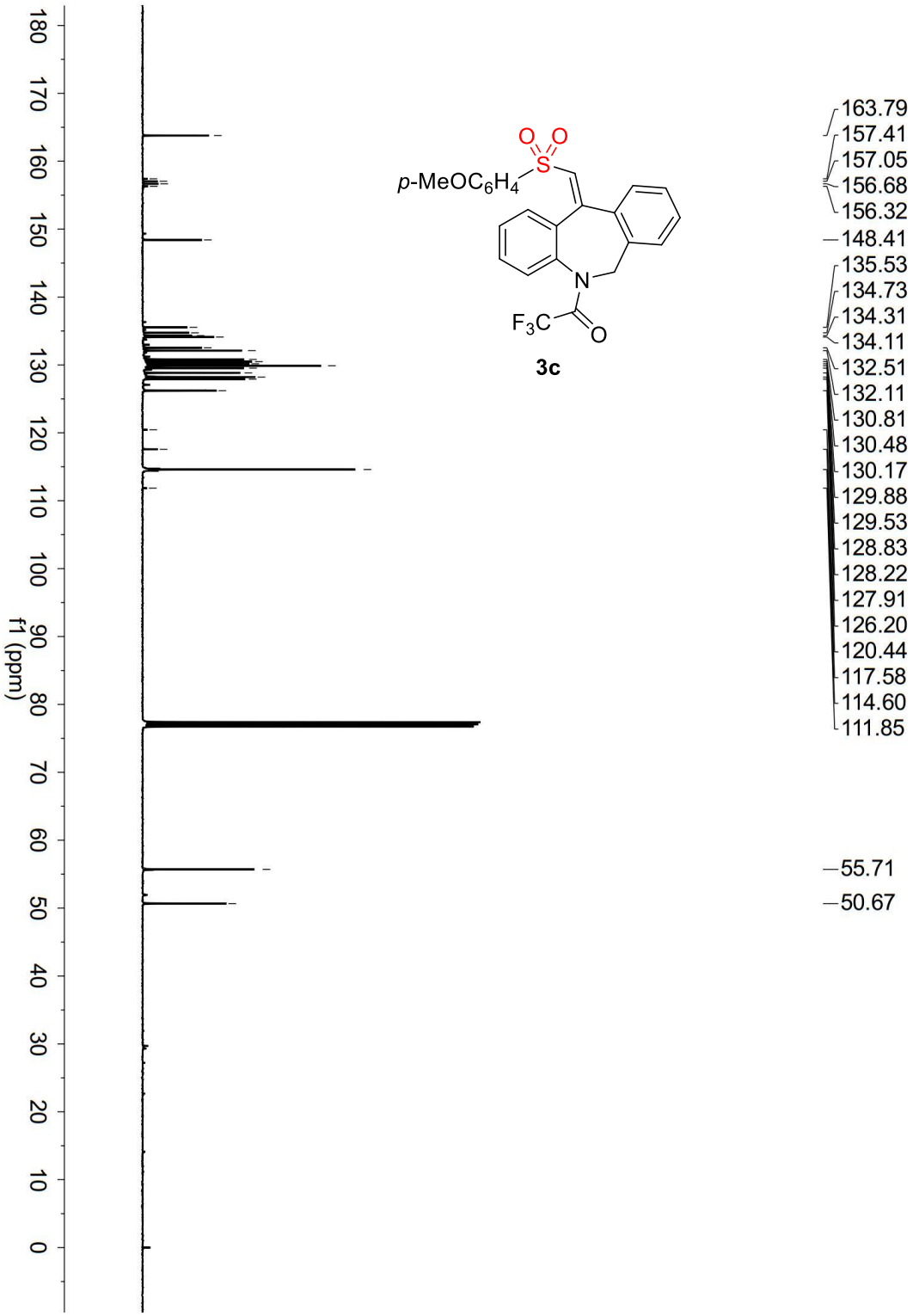
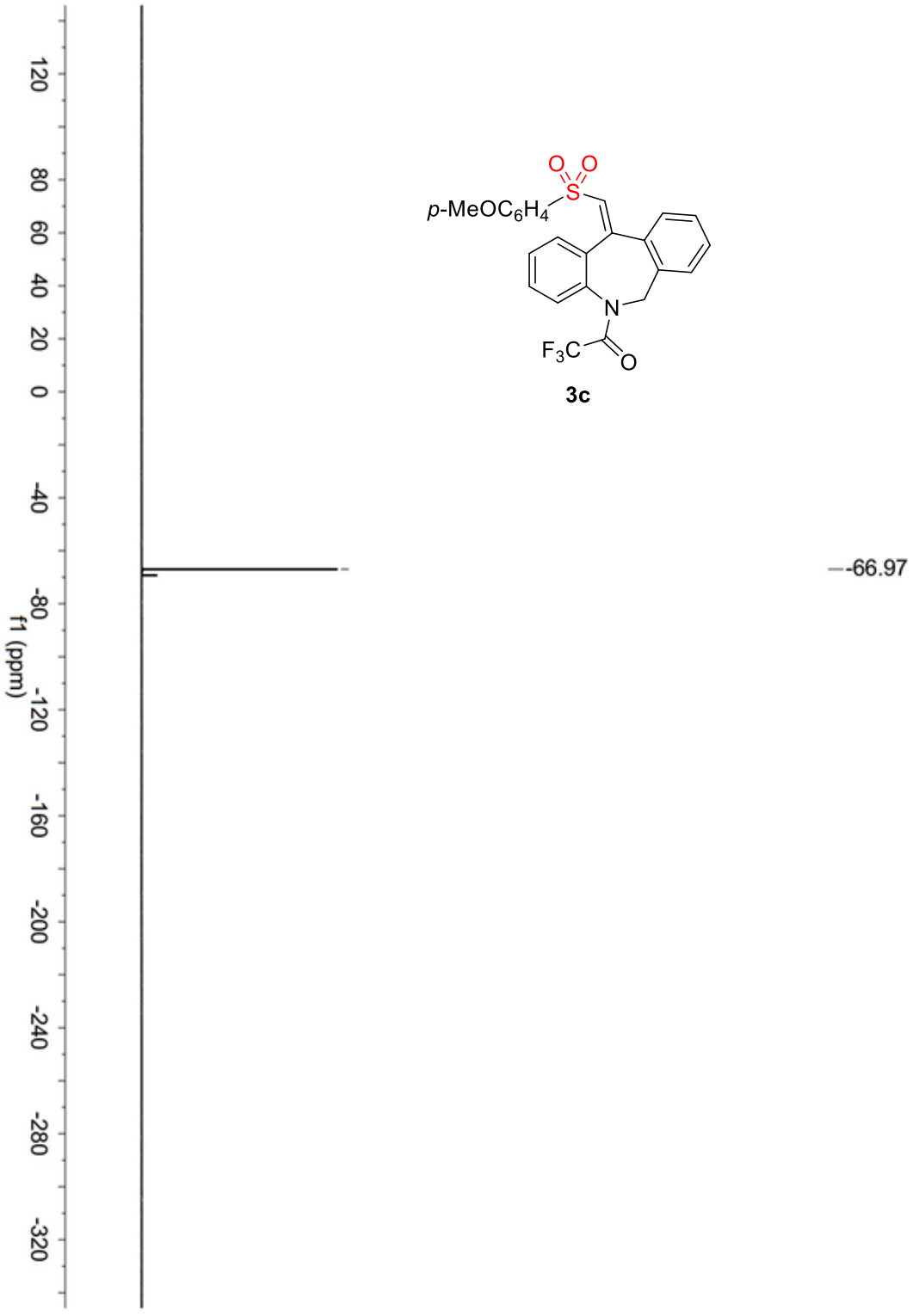
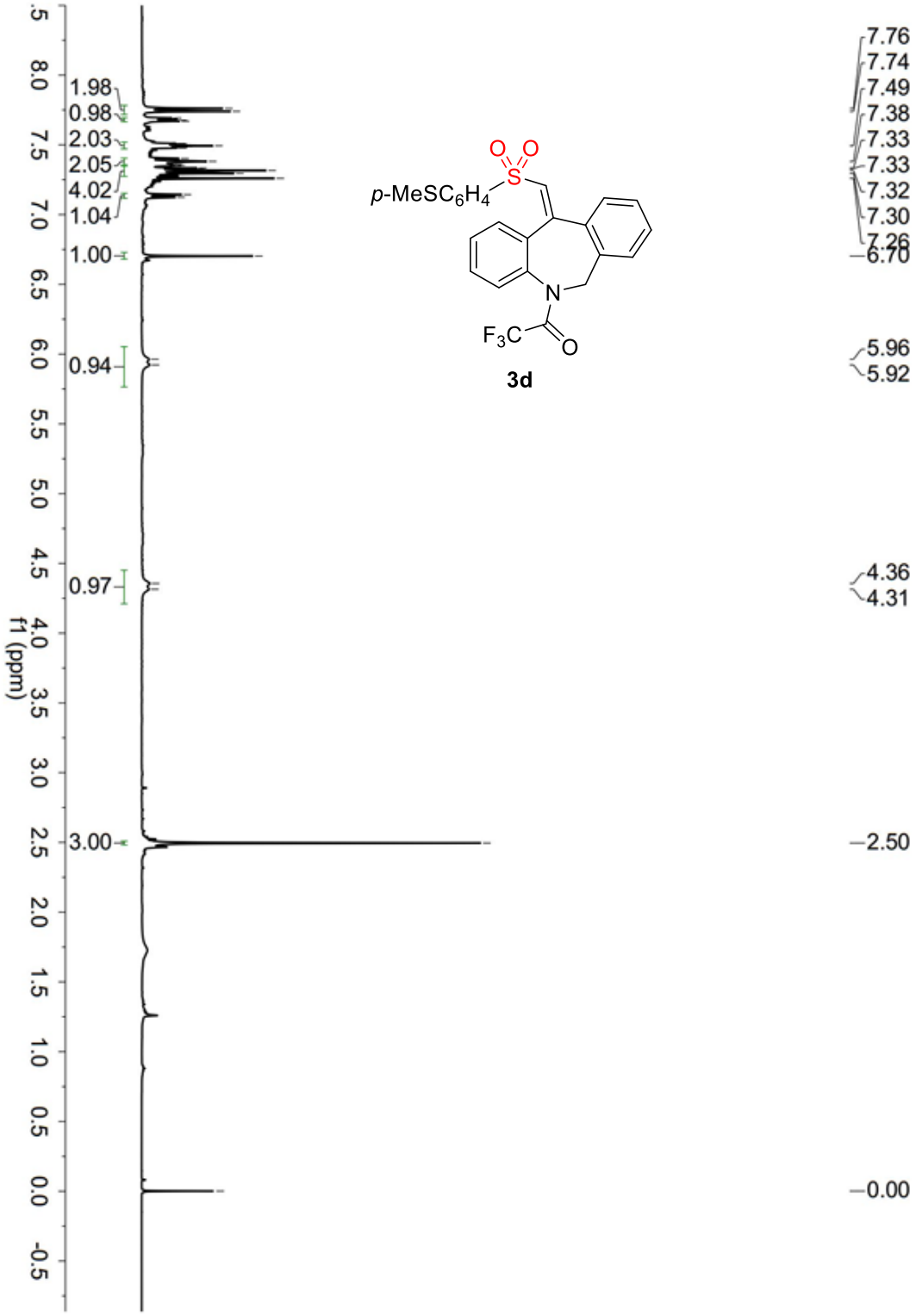
2.08
4.09
0.98
2.01
1.03
0.92
0.91
3.00
f1 (ppm)
p-MeOC6H4
F3C
3c
7.82
7.79
7.50
7.49
7.48
7.39
7.33
7.32
7.31
7.26
7.00
6.97
6.71
5.96
5.92
4.35
4.31
3.85
-0.00

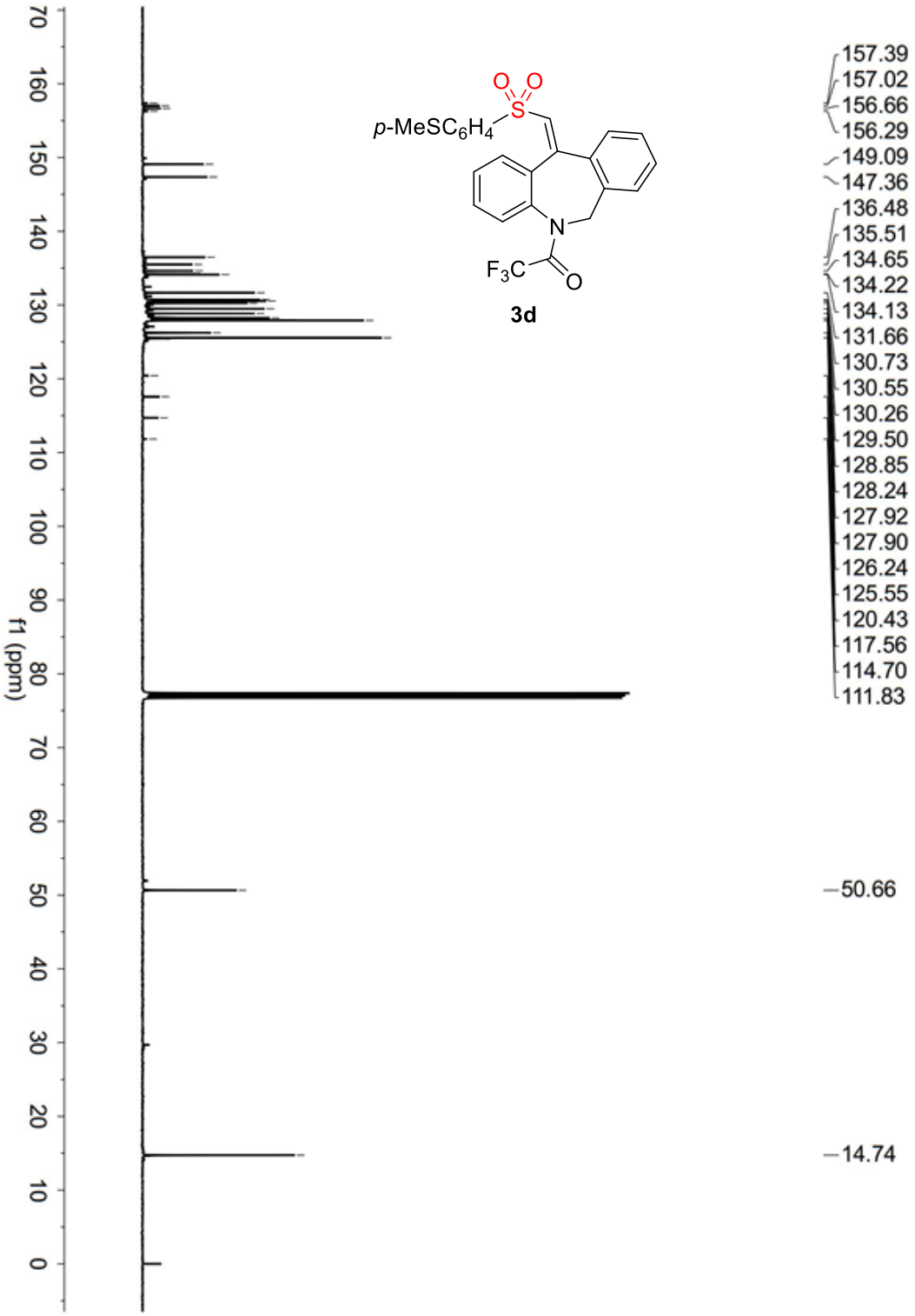

f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
p-MeOC6H4
S
O
O
N
F3C
O
3c
163.79
157.41
157.05
156.68
156.32
148.41
135.53
134.73
134.31
134.11
132.51
132.11
130.81
130.48
130.17
129.88
129.53
128.83
128.22
127.91
126.20
120.44
117.58
114.60
111.85
55.71
50.67

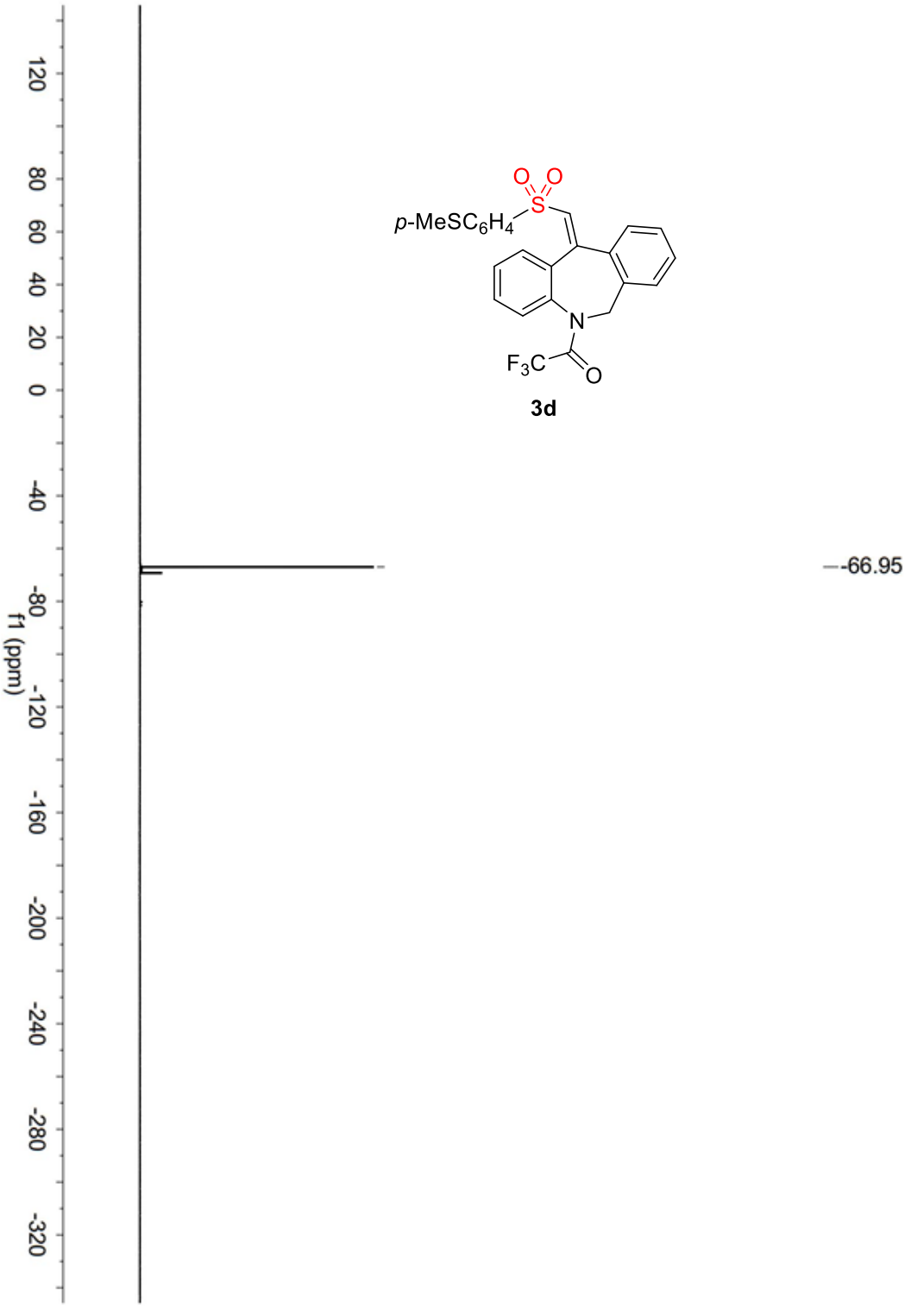

120
80
60
40
20
0
-40
-80
-120
-160
-200
-240
-280
-320
f1 (ppm)
-66.97
O
O
S
p-MeOC6H4
N
F3C
O

3c

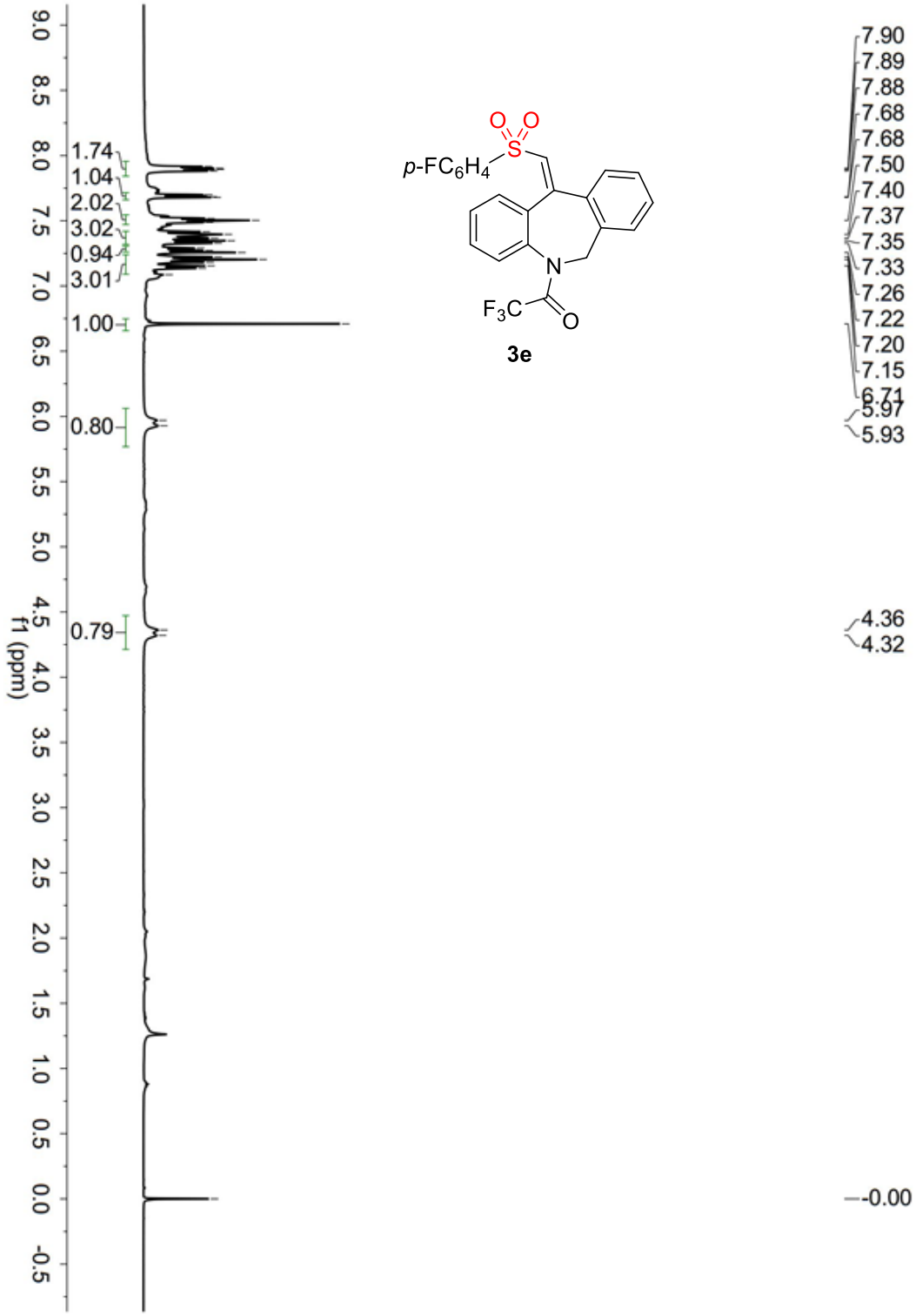

1.98
0.98
2.03
2.05
4.02
1.04
1.00
0.94
0.97
3.00
f1 (ppm)
7.76
7.74
7.49
7.38
7.33
7.33
7.32
7.30
7.26
6.70
5.96
5.92
4.36
4.31
2.50
0.00
p-MeSC6H4
O
O
S
N
F3C
O

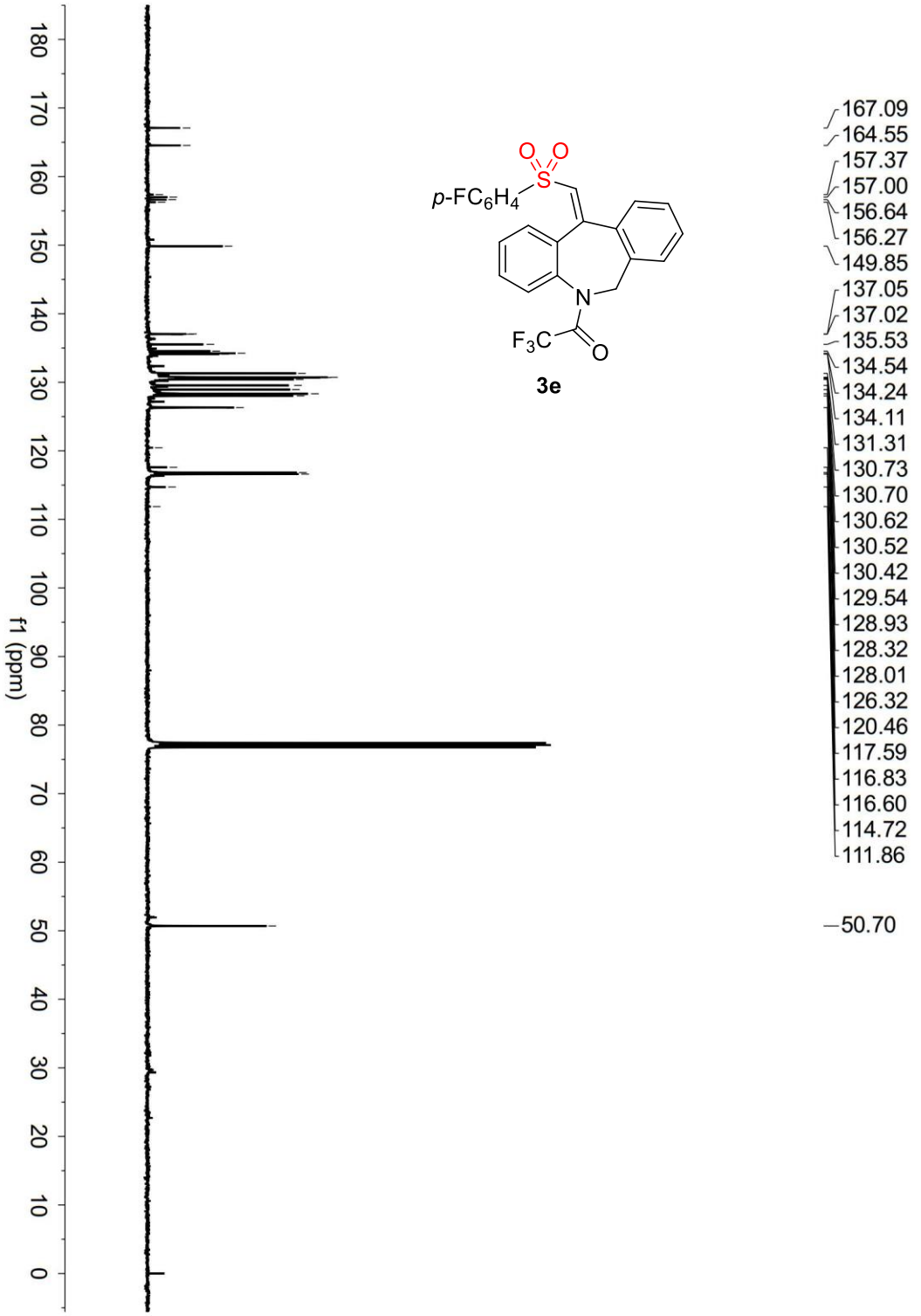
3d

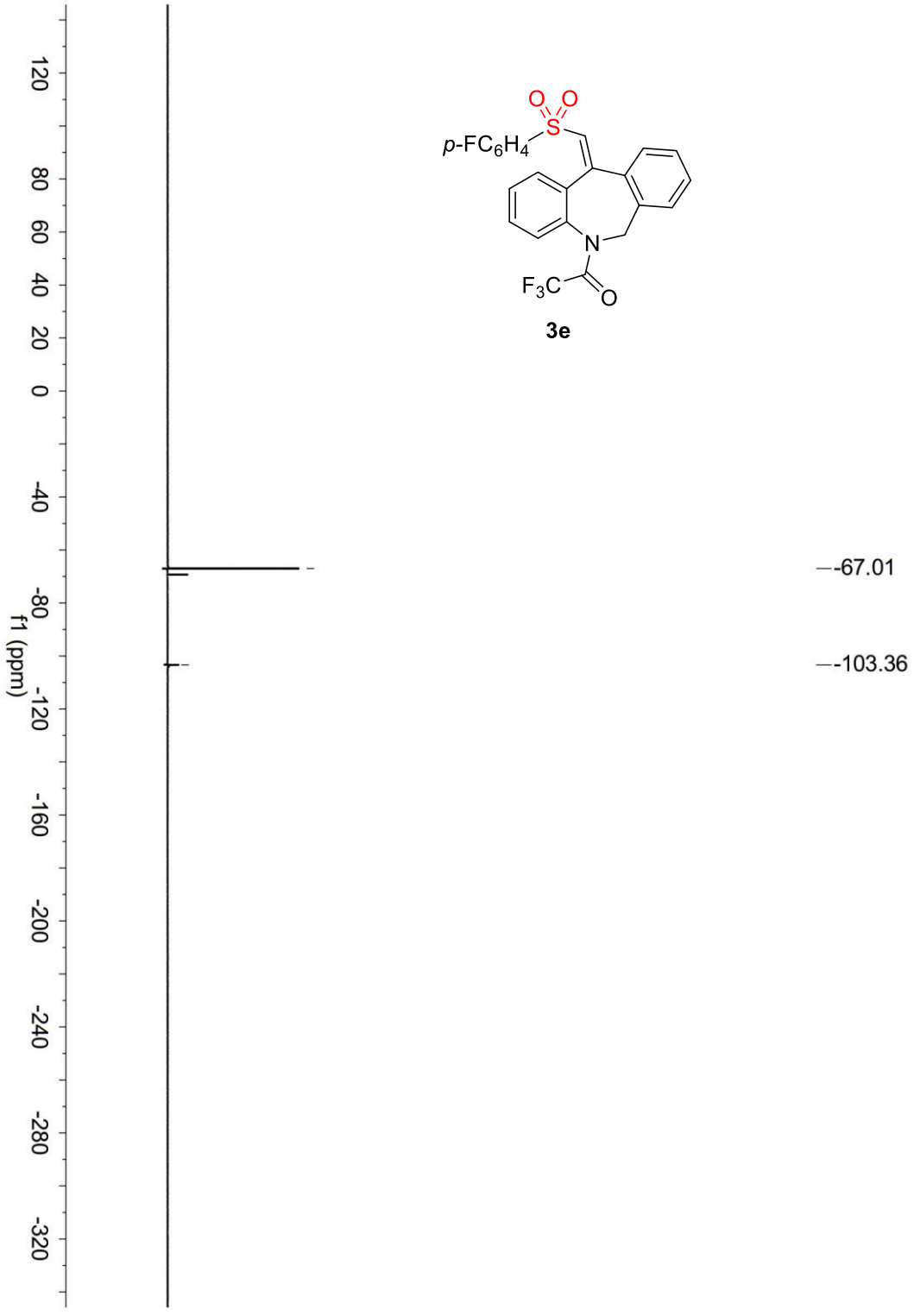

157.39
157.02
156.66
156.29
149.09
147.36
136.48
135.51
134.65
134.22
134.13
131.66
130.73
130.55
130.26
129.50
128.85
128.24
127.92
127.90
126.24
125.55
120.43
117.56
114.70
111.83
50.66
14.74
f1 (ppm)
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
p-MeSC6H4
S
O
O
N
F3C
O
3d


120
80
60
40
20
0
-40
-80
-120
-160
-200
-240
-280
-320
f1 (ppm)
-66.95
O
O
S
p-MeSC6H4
N
F3C
O

3d

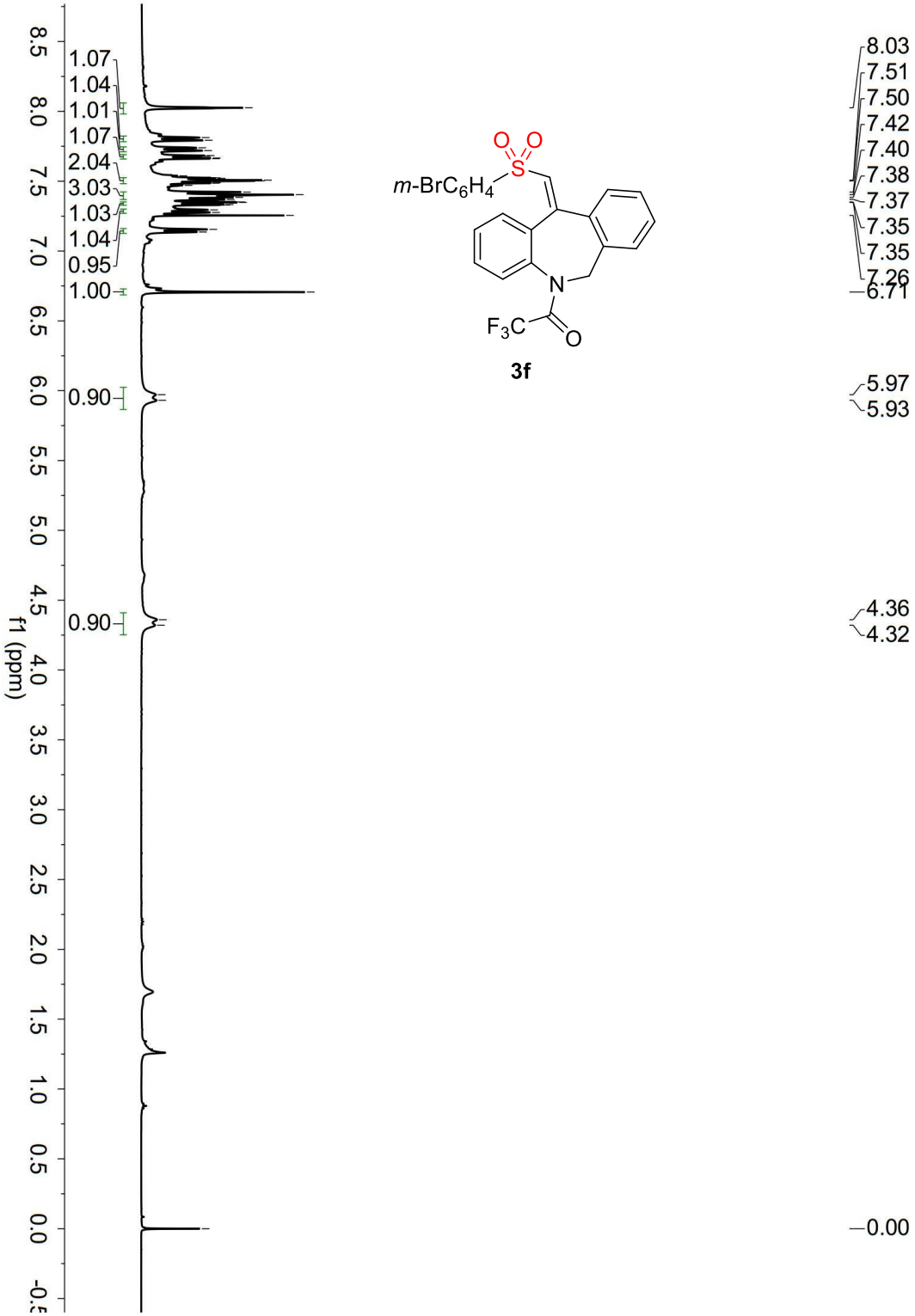

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
1.74
1.04
2.02
3.02
0.94
3.01
1.00
0.80
0.79
p-FC6H4
O
O
S
N
F3C
O
3e
7.90
7.89
7.88
7.68
7.68
7.50
7.40
7.37
7.35
7.33
7.26
7.22
7.20
7.15
6.71
5.97
5.93
4.36
4.32
-0.00

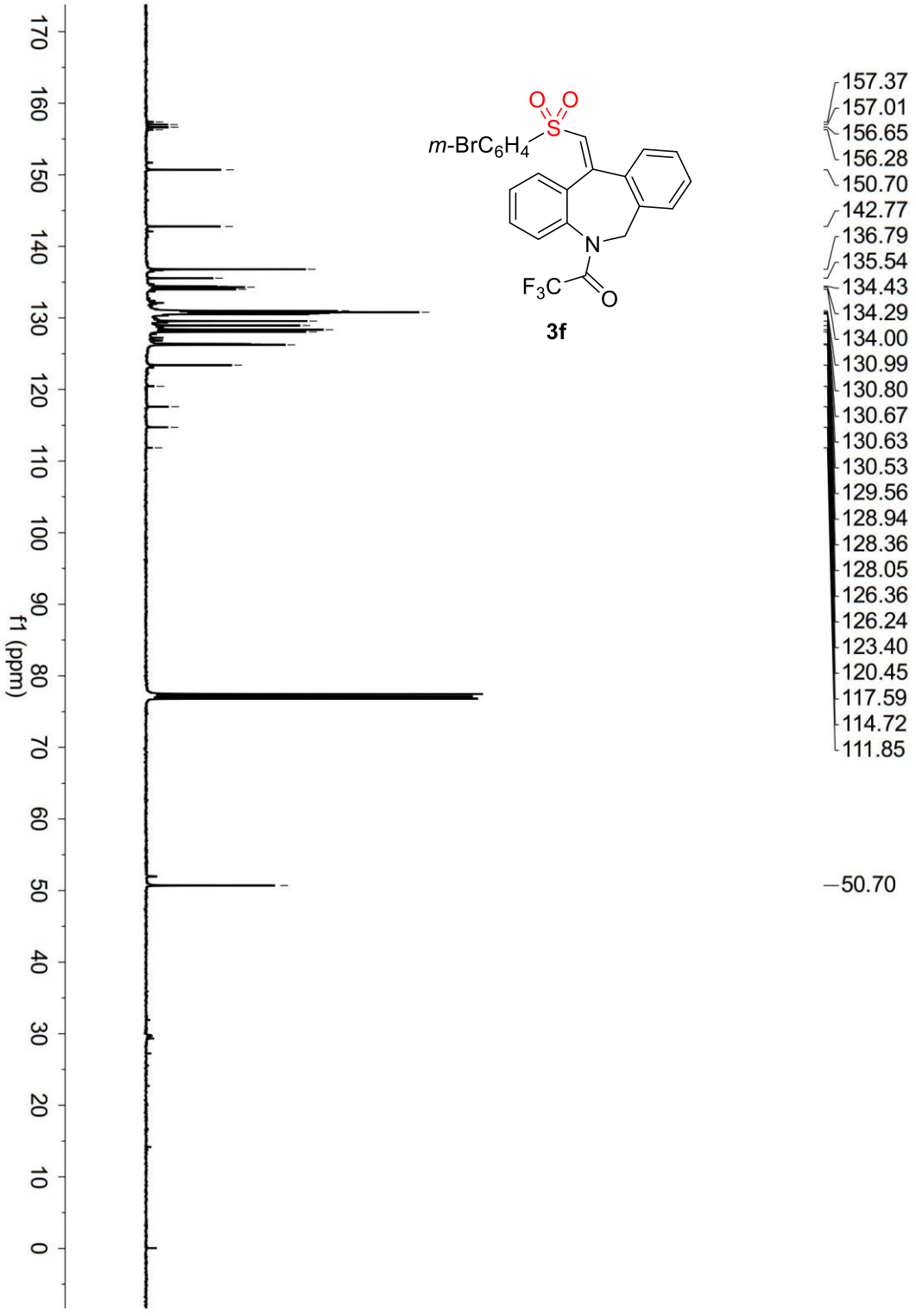

f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
p-FC6H4
O
O
S
N
F3C
O
3e
167.09
164.55
157.37
157.00
156.64
156.27
149.85
137.05
137.02
135.53
134.54
134.24
134.11
131.31
130.73
130.70
130.62
130.52
130.42
129.54
128.93
128.32
128.01
126.32
120.46
117.59
116.83
116.60
114.72
111.86
50.70

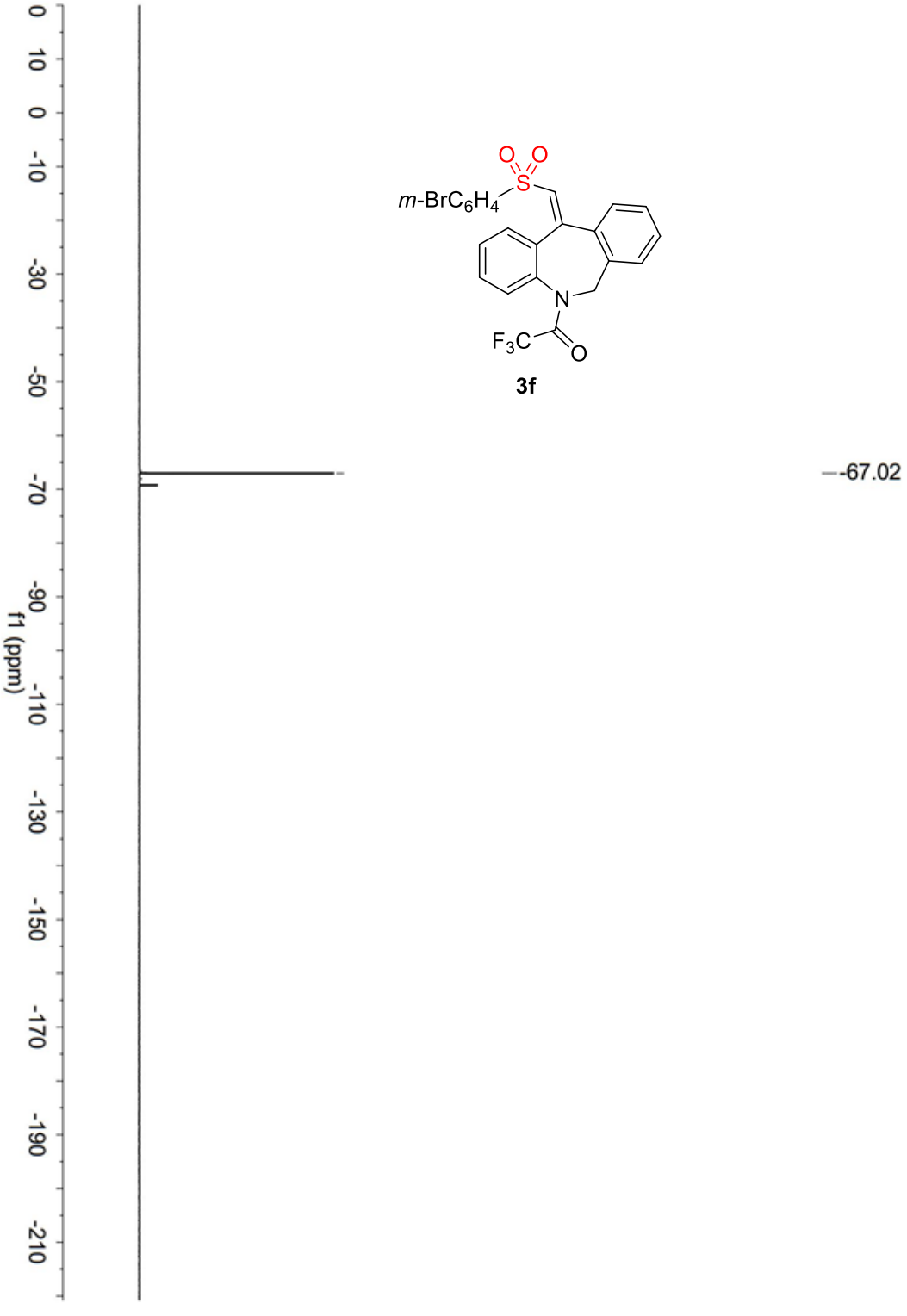

120
80
60
40
20
0
-40
-80
-120
-160
-200
-240
-280
-320
f1 (ppm)
-67.01
-103.36

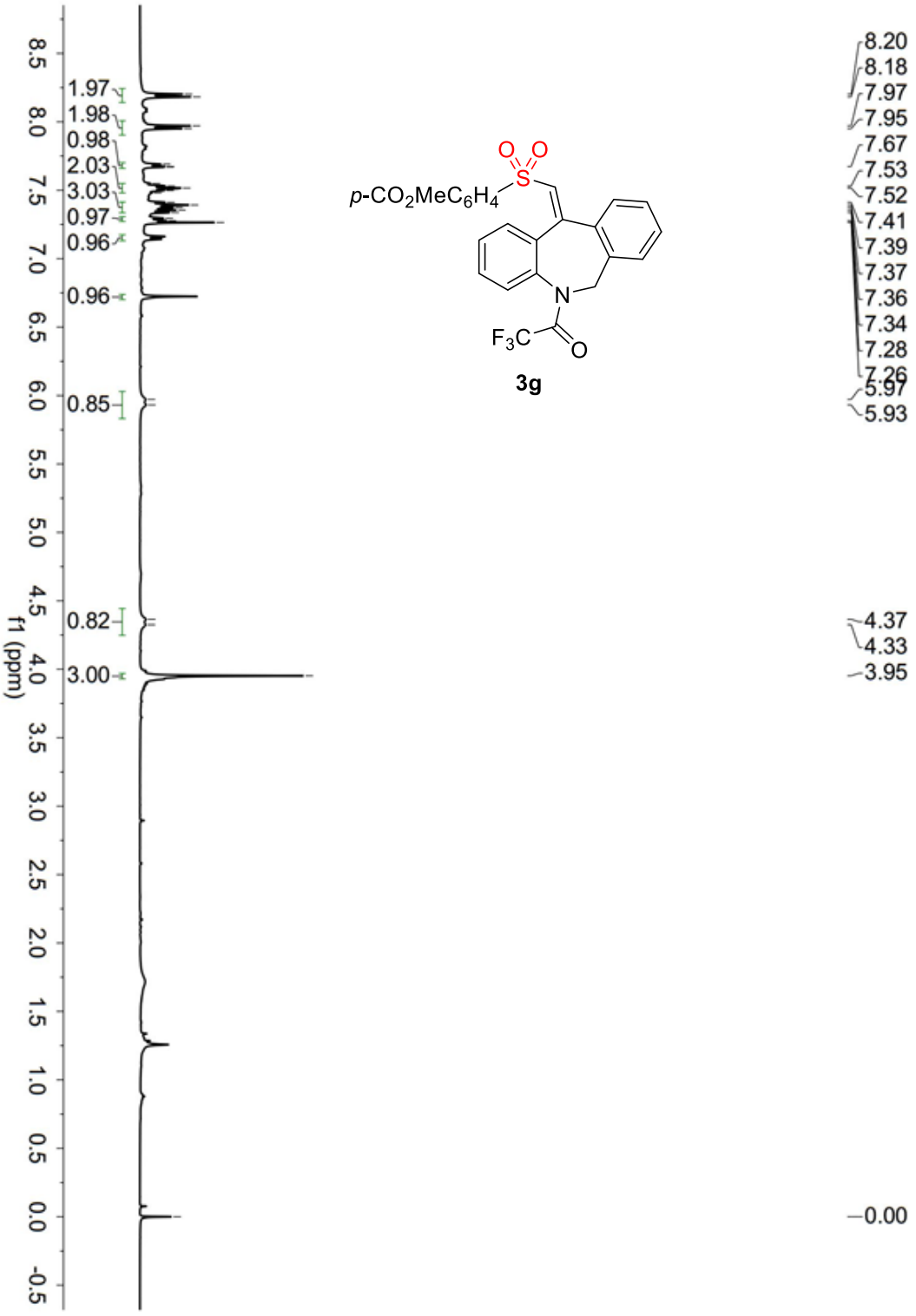
O
O
S
p-FC6H4
N
F3C
O

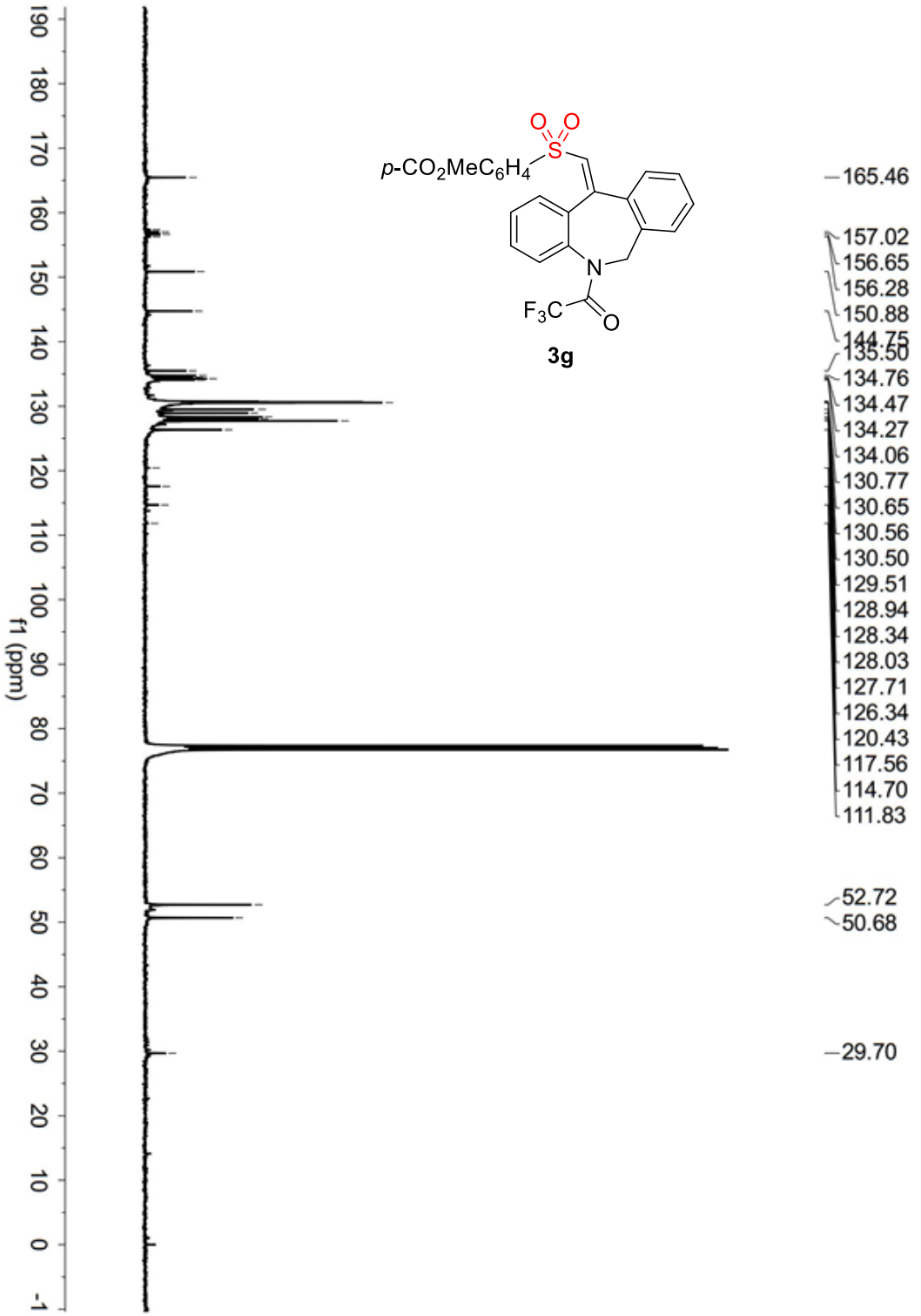
3e

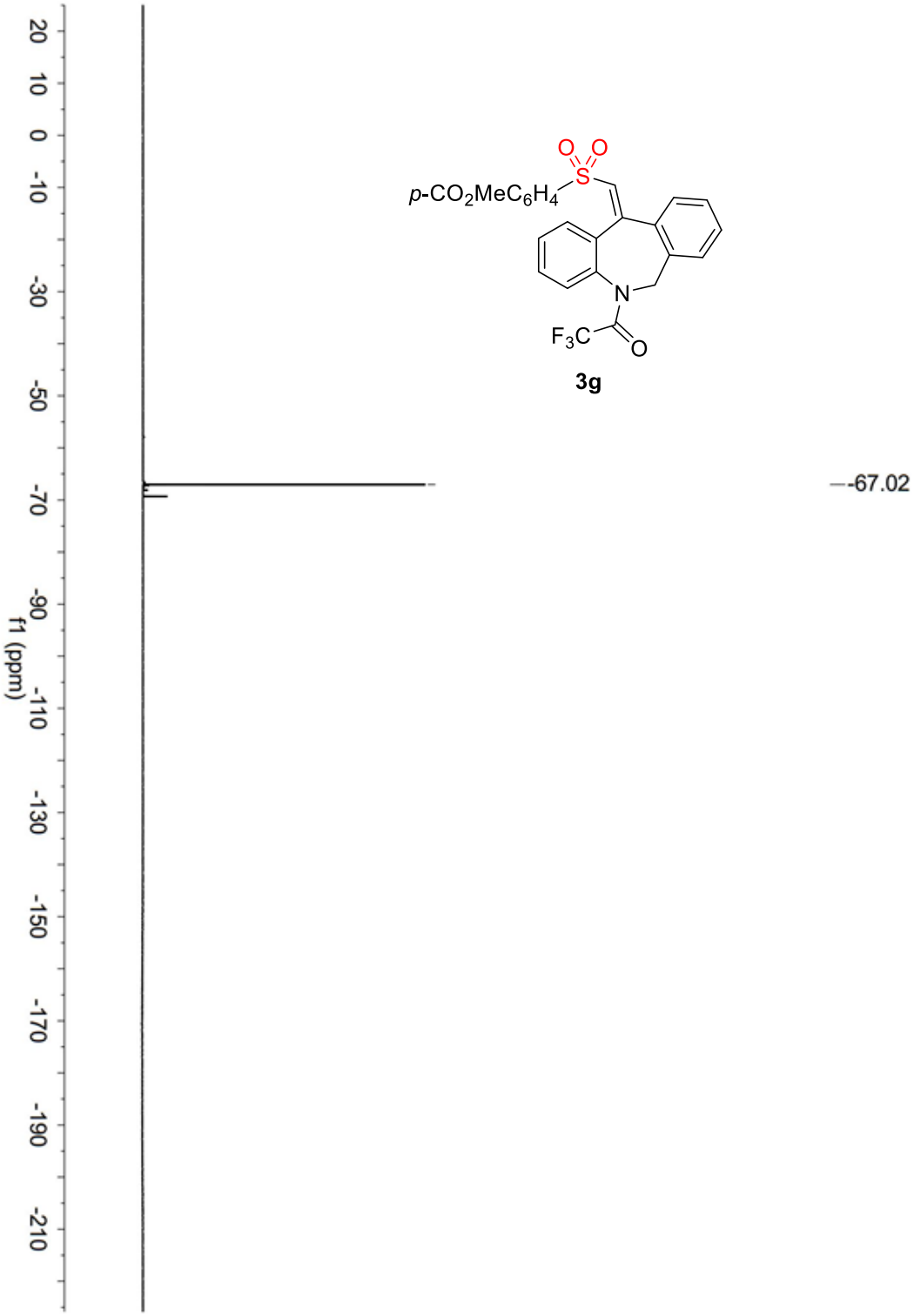

8.03
7.51
7.50
7.42
7.40
7.38
7.37
7.35
7.35
7.26
6.71
5.97
5.93
4.36
4.32
0.00
1.07
1.04
1.01
1.07
2.04
3.03
1.03
1.04
0.95
1.00
0.90
0.90
f1 (ppm)
m-BrC6H4
F3C
N
O
S
3f


f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
m-BrC6H4
S
O
O
N
F3C
O
3f
157.37
157.01
156.65
156.28
150.70
142.77
136.79
135.54
134.43
134.29
134.00
130.99
130.80
130.67
130.63
130.53
129.56
128.94
128.36
128.05
126.36
126.24
123.40
120.45
117.59
114.72
111.85
50.70

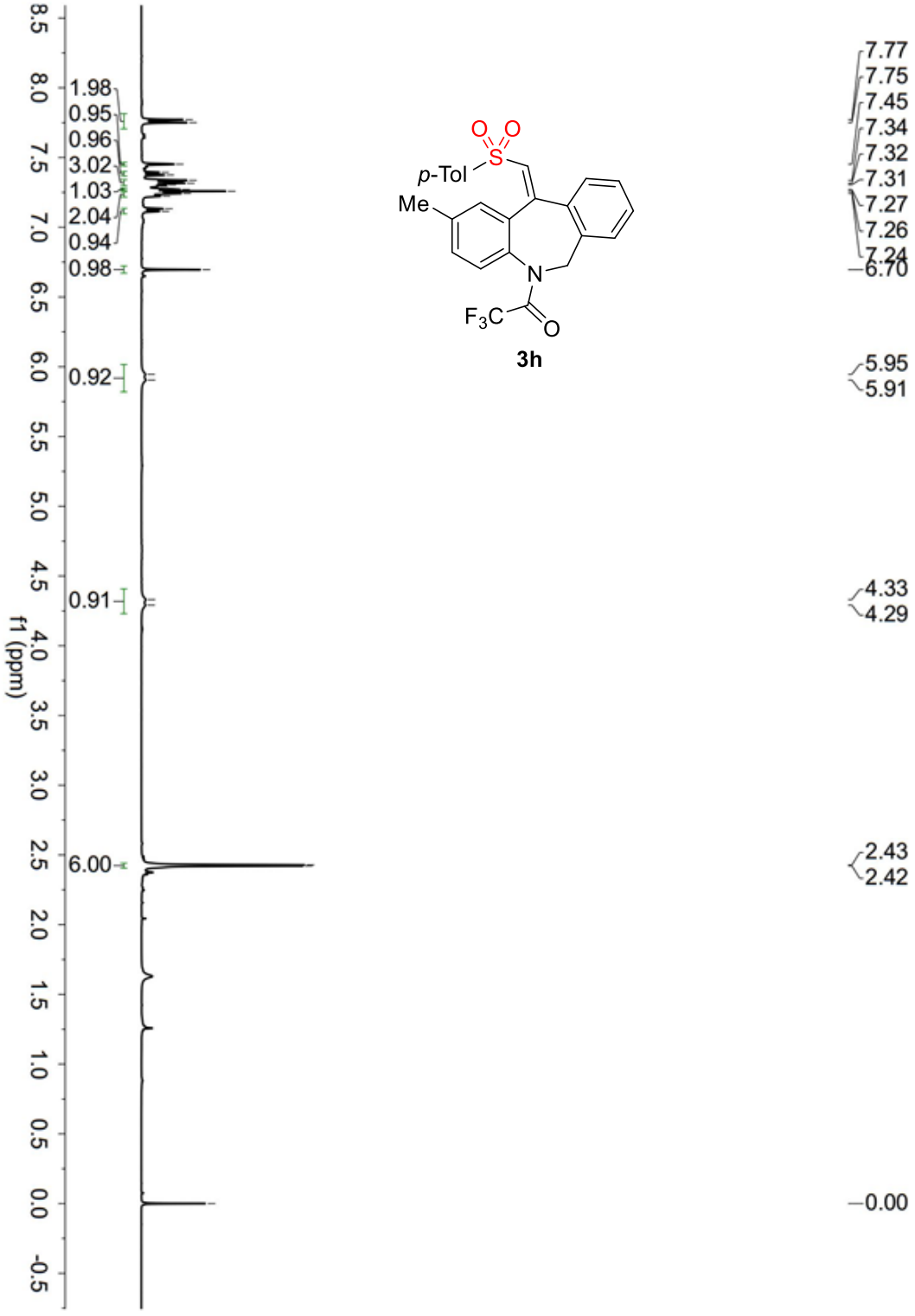

O
O
S
m-BrC6H4
N
F3C
O
3f
-67.02
0
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

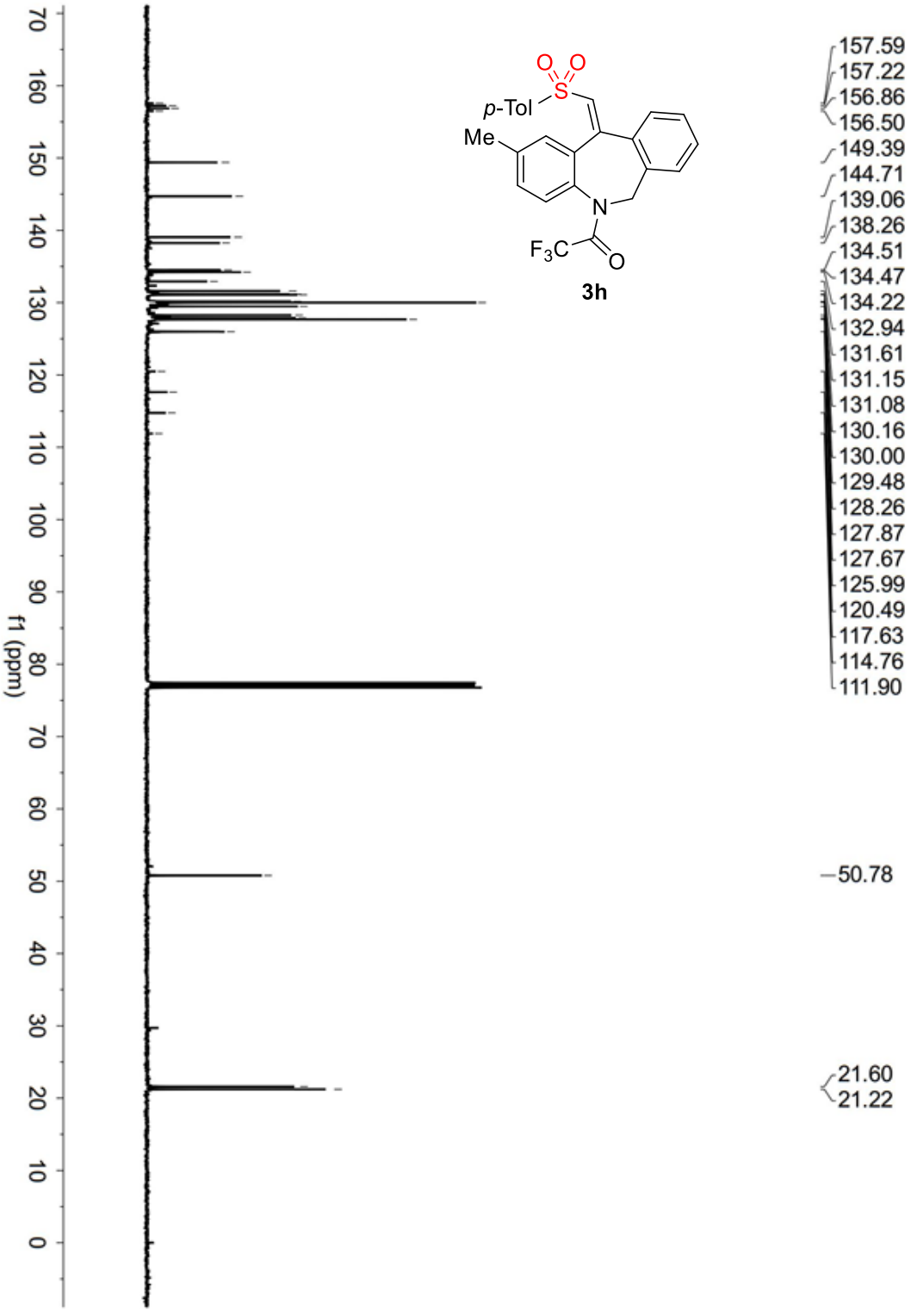

8.20
8.18
7.97
7.95
7.67
7.53
7.52
7.41
7.39
7.37
7.36
7.34
7.28
7.26
5.97
5.93
4.37
4.33
3.95
0.00
1.97
1.98
0.98
2.03
3.03
0.97
0.96
0.96
0.85
0.82
3.00
f1 (ppm)
p-CO2MeC6H4
F3C
3g

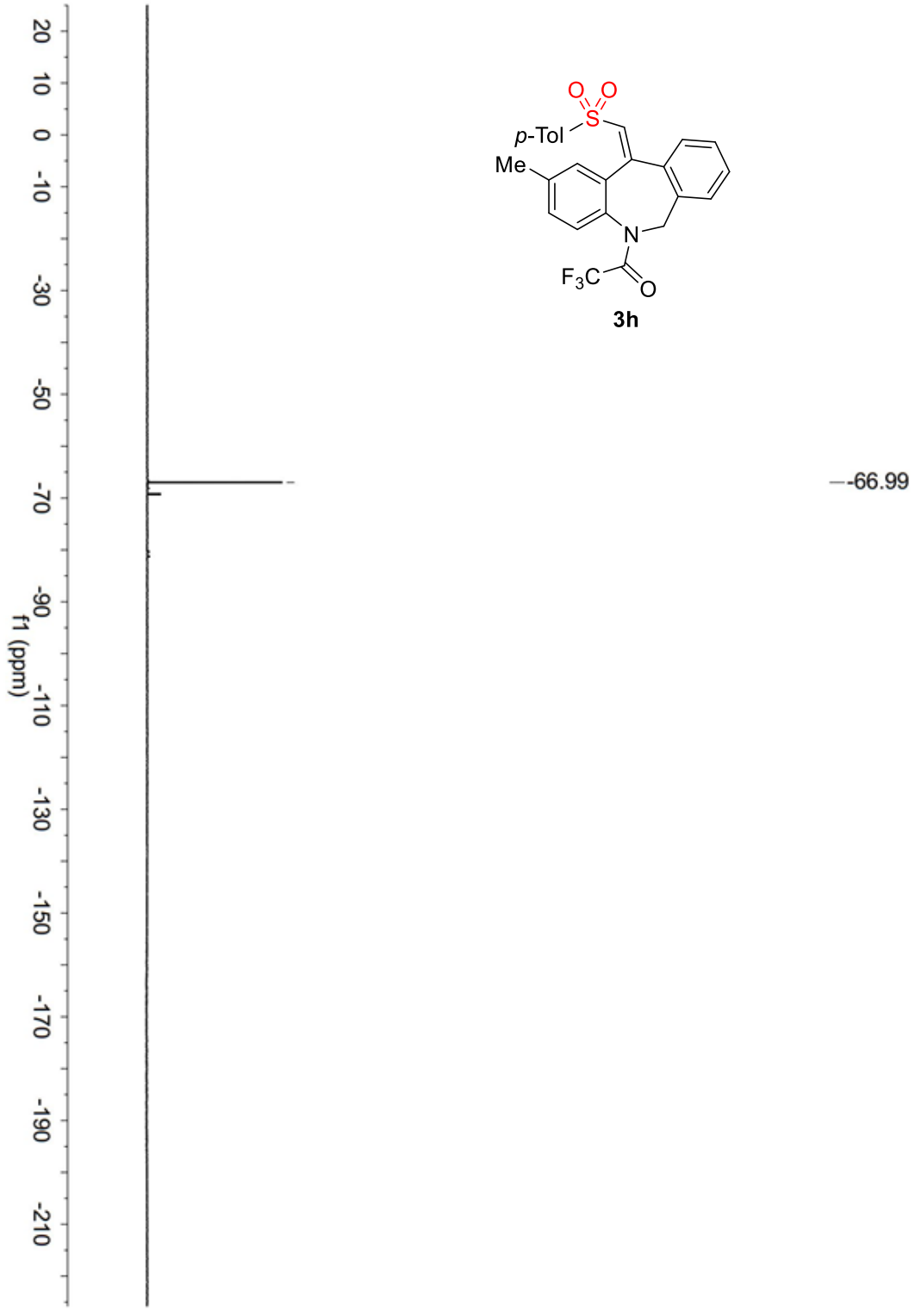

f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
p-CO2MeC6H4
S
O
O
N
F3C
O
3g
165.46
157.02
156.65
156.28
150.88
144.75
135.50
134.76
134.47
134.27
134.06
130.77
130.65
130.56
130.50
129.51
128.94
128.34
128.03
127.71
126.34
120.43
117.56
114.70
111.83
52.72
50.68
29.70


20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)
-67.02
O
O
S
p-CO2MeC6H4
N
F3C
O

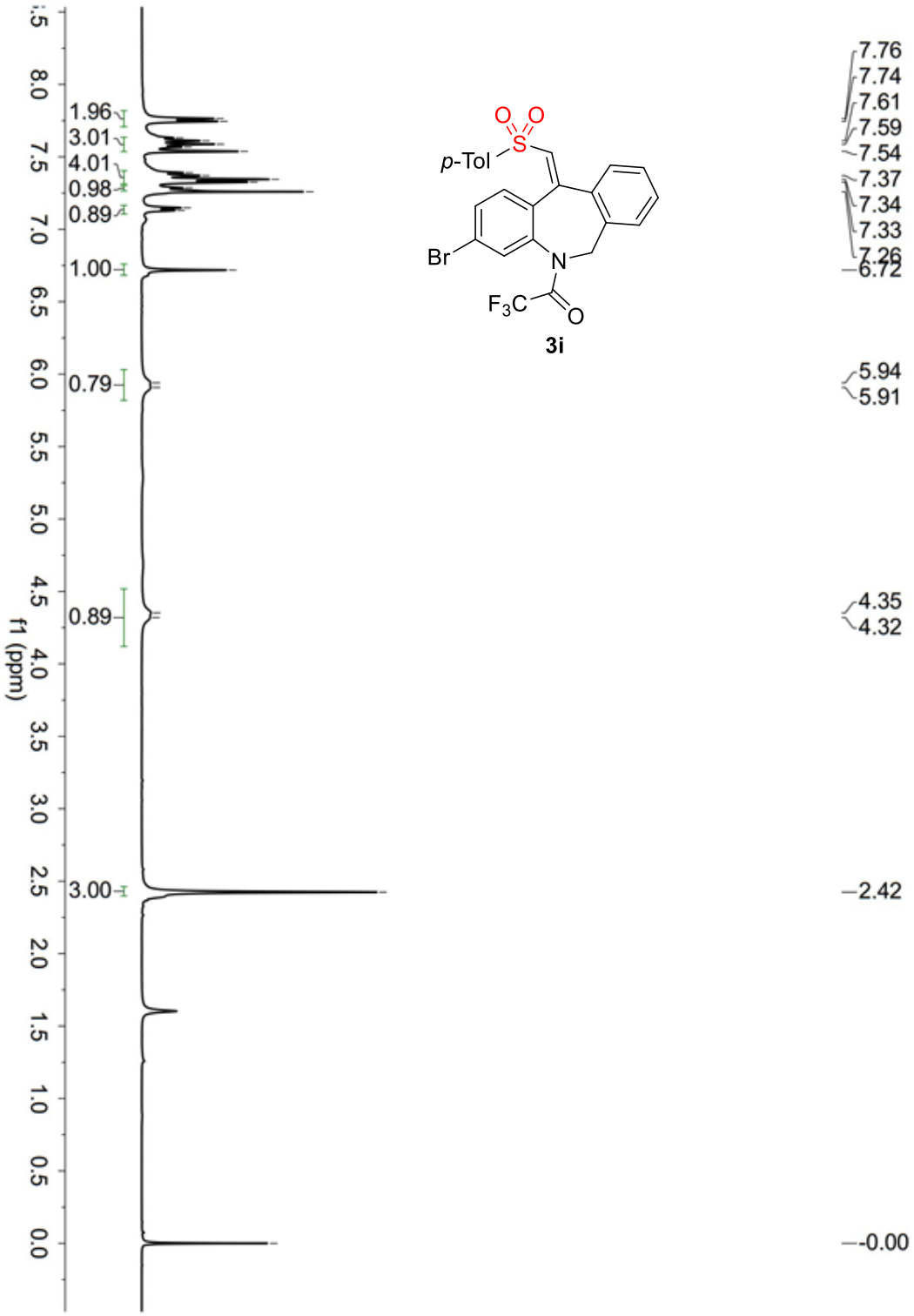
3g

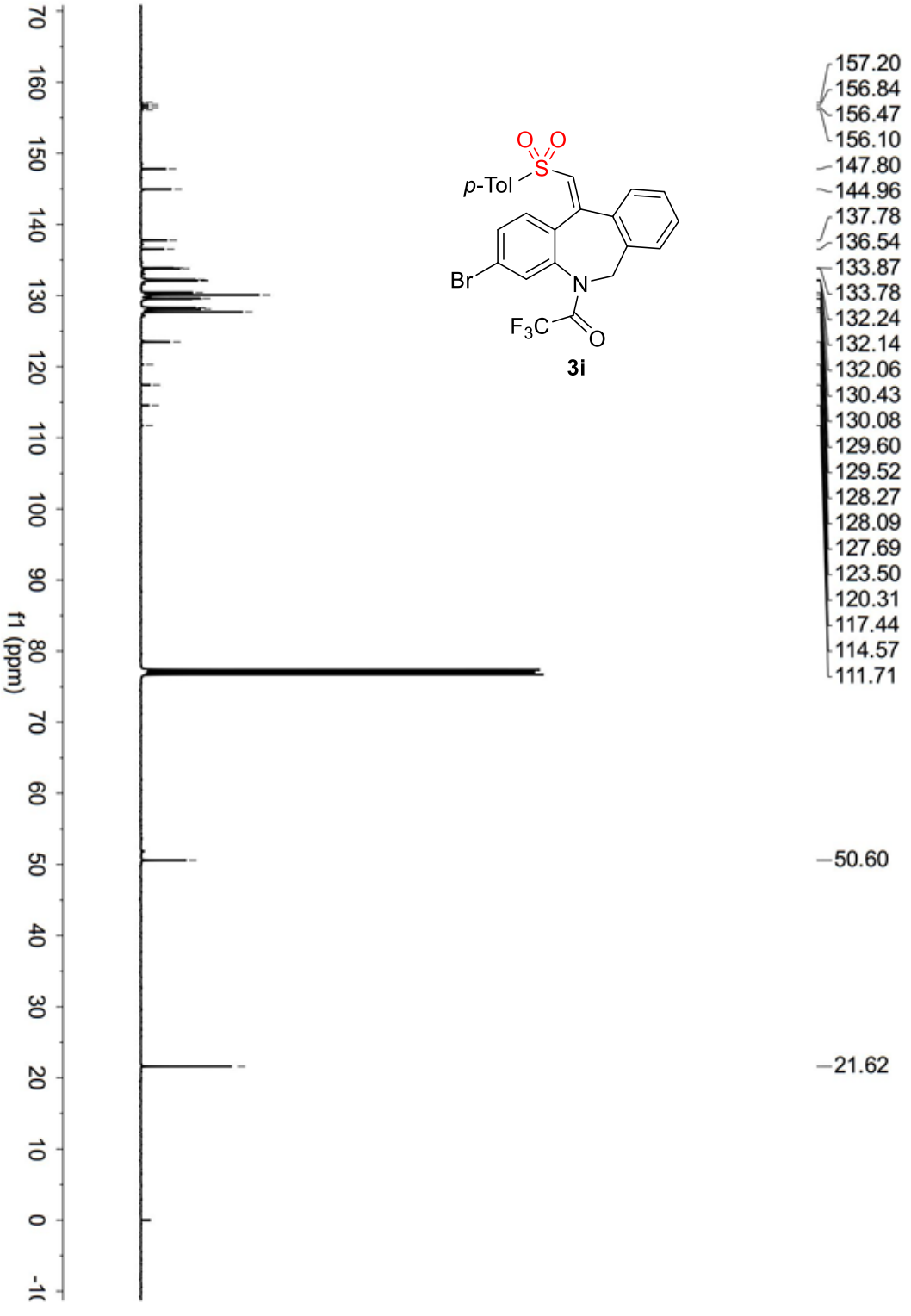

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
1.98
0.95
0.96
3.02
1.03
2.04
0.94
0.98
0.92
0.91
6.00
O
O
S
p-Tol
Me
N
F3C
O
3h
7.77
7.75
7.45
7.34
7.32
7.31
7.27
7.26
7.24
6.70
5.95
5.91
4.33
4.29
2.43
2.42
0.00

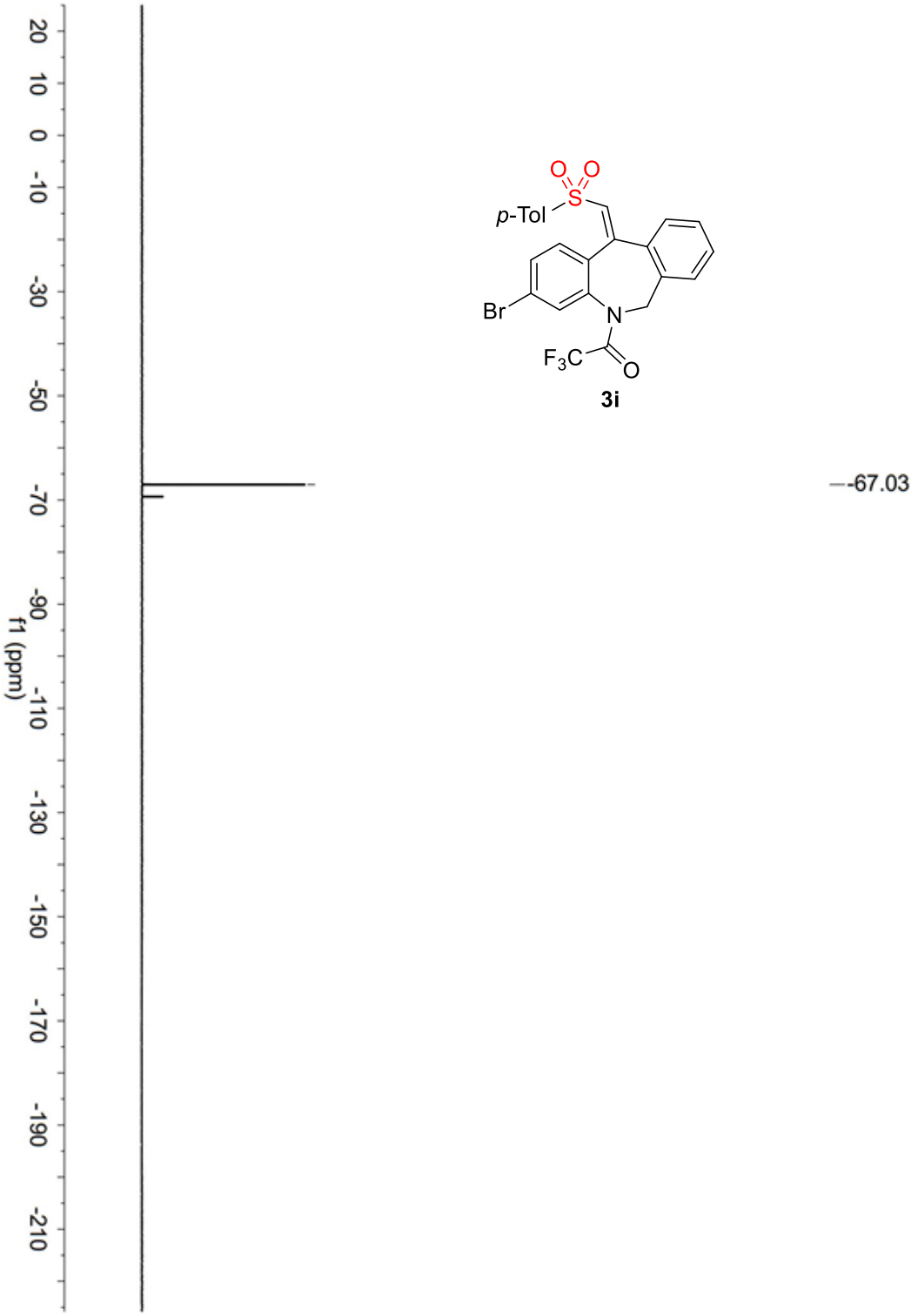

157.59
157.22
156.86
156.50
149.39
144.71
139.06
138.26
134.51
134.47
134.22
132.94
131.61
131.15
131.08
130.16
130.00
129.48
128.26
127.87
127.67
125.99
120.49
117.63
114.76
111.90
50.78
21.60
21.22
f1 (ppm)
p-Tol
Me
N
F3C
O
O
O
S
3h

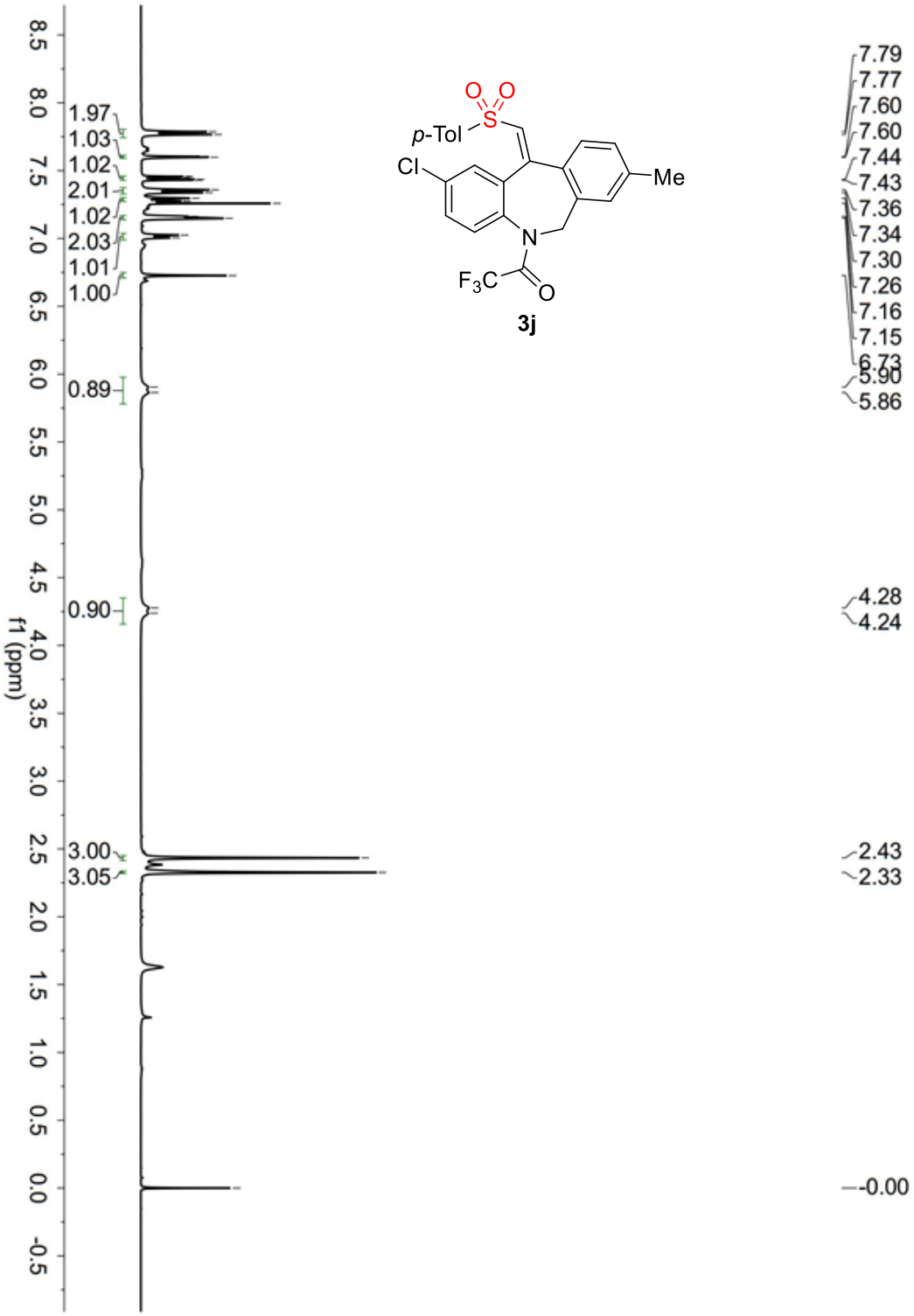

20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)
-66.99
O
O
S
p-Tol
Me
N
F3C
O

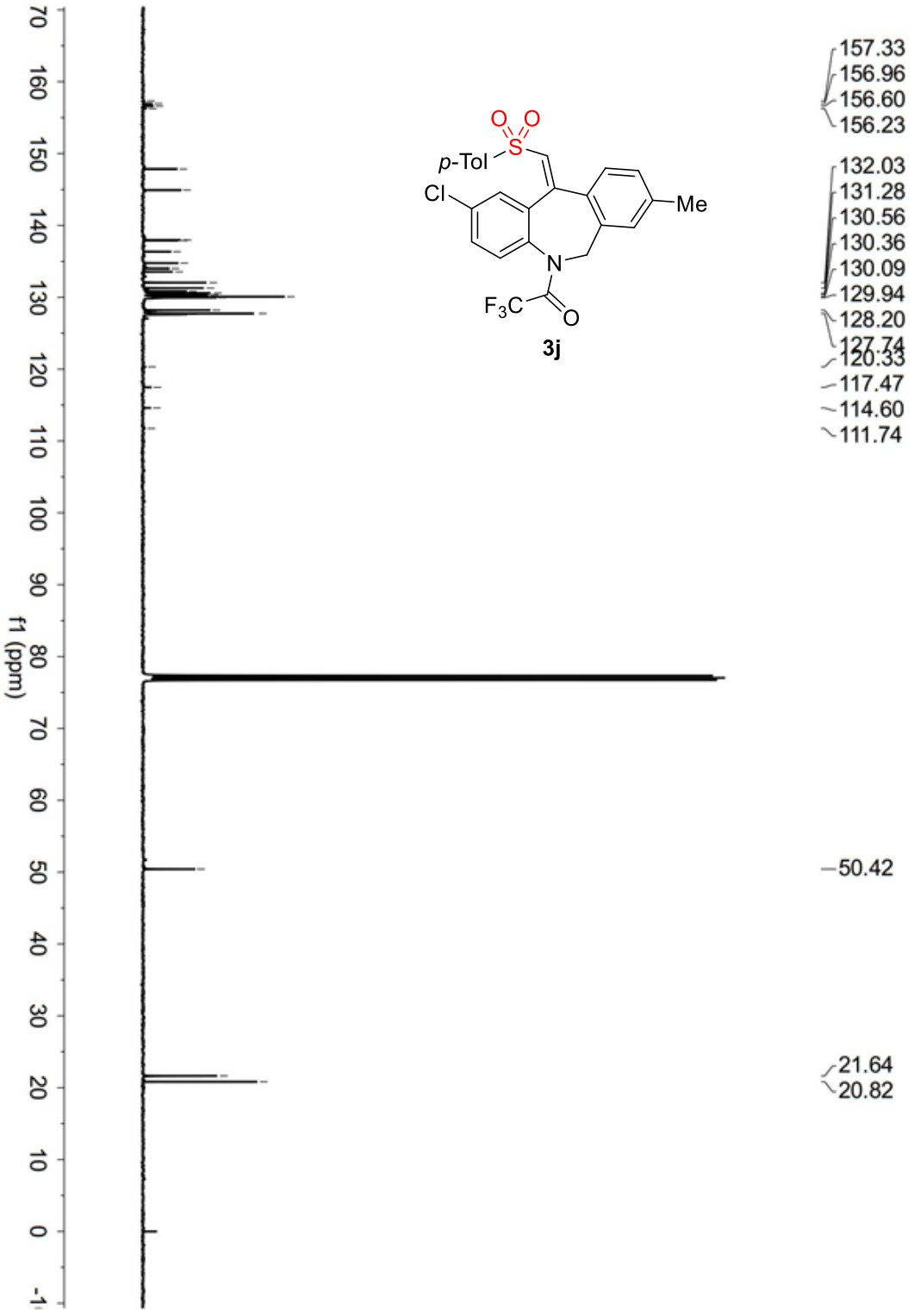
3h

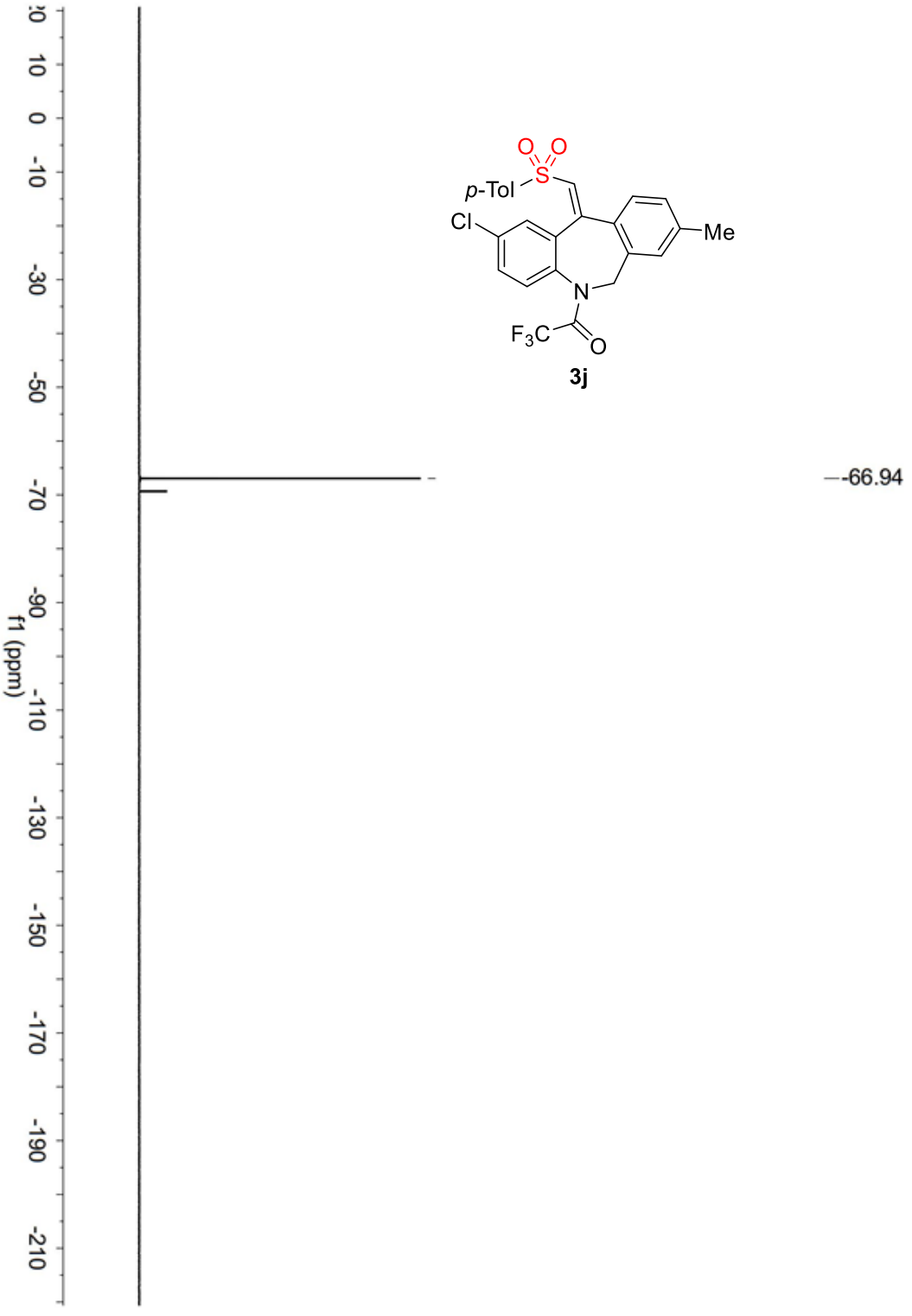

1.96
3.01
4.01
0.98
0.89
1.00
0.79
0.89
3.00
f1 (ppm)
p-Tol
Br
N
F3C
O
O
S
O
3i
7.76
7.74
7.61
7.59
7.54
7.37
7.34
7.33
7.26
6.72
5.94
5.91
4.35
4.32
2.42
0.00


157.20
156.84
156.47
156.10
147.80
144.96
137.78
136.54
133.87
133.78
132.24
132.14
132.06
130.43
130.08
129.60
129.52
128.27
128.09
127.69
123.50
120.31
117.44
114.57
111.71
50.60
21.62
f1 (ppm)
p-Tol
Br
N
F3C
O
3i

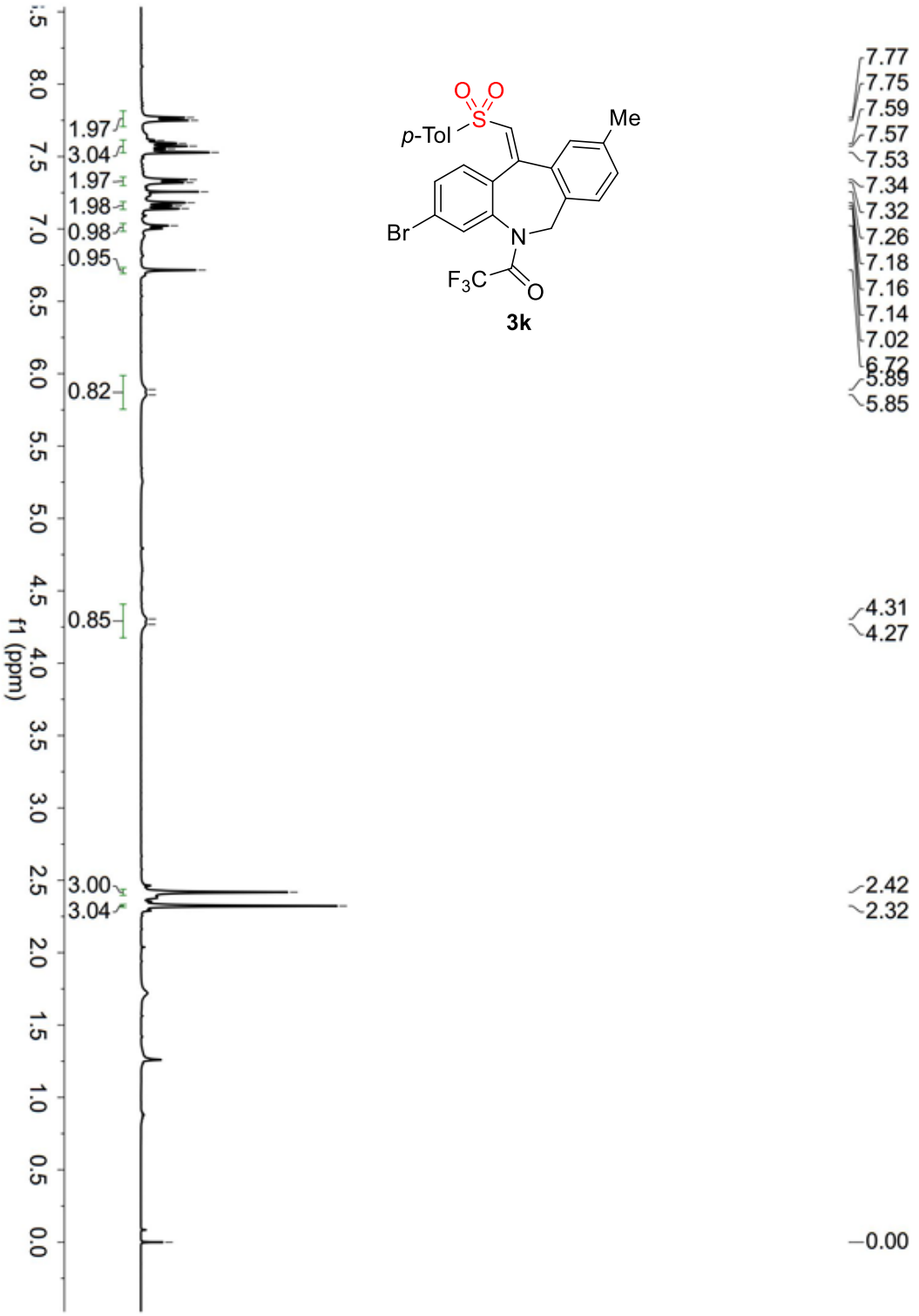

20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)
-67.03
O
O
S
p-Tol
Br
N
F3C
O
3i

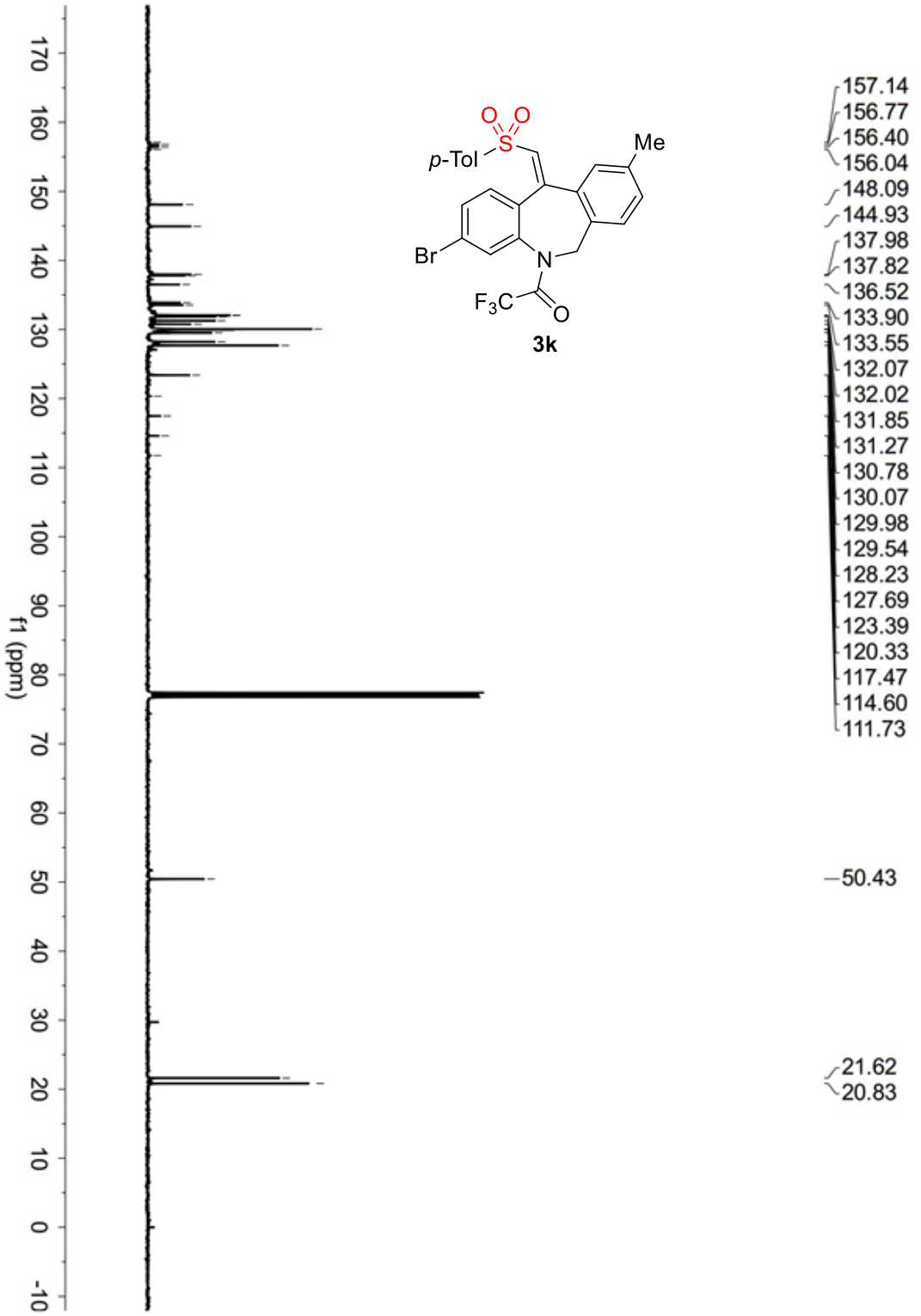

f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1.97
1.03
1.02
2.01
1.02
2.03
1.01
1.00
0.89
0.90
3.00
3.05
p-Tol
Cl
Me
N
F3C
O
3j
7.79
7.77
7.60
7.60
7.44
7.43
7.36
7.34
7.30
7.26
7.16
7.15
6.73
5.90
5.86
4.28
4.24
2.43
2.33
-0.00

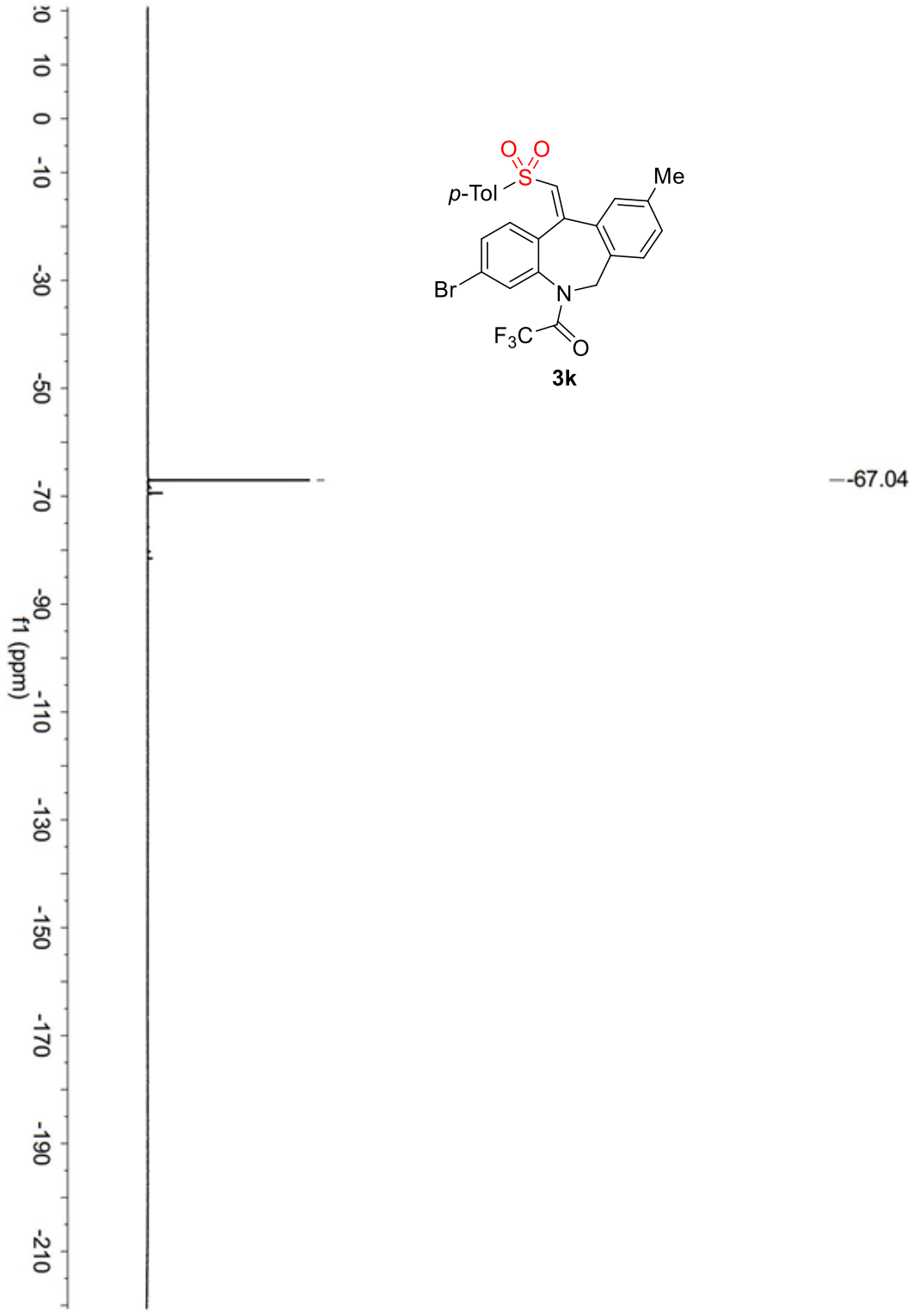

157.33
156.96
156.60
156.23
132.03
131.28
130.56
130.36
130.09
129.94
128.20
127.74
120.33
117.47
114.60
111.74
50.42
21.64
20.82
f1 (ppm)
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
O
O
S
p-Tol
Cl
Me
N
F3C
O
3j


-66.94
f1 (ppm)
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
O
O
S
p-Tol
Cl
Me
N
F3C
O

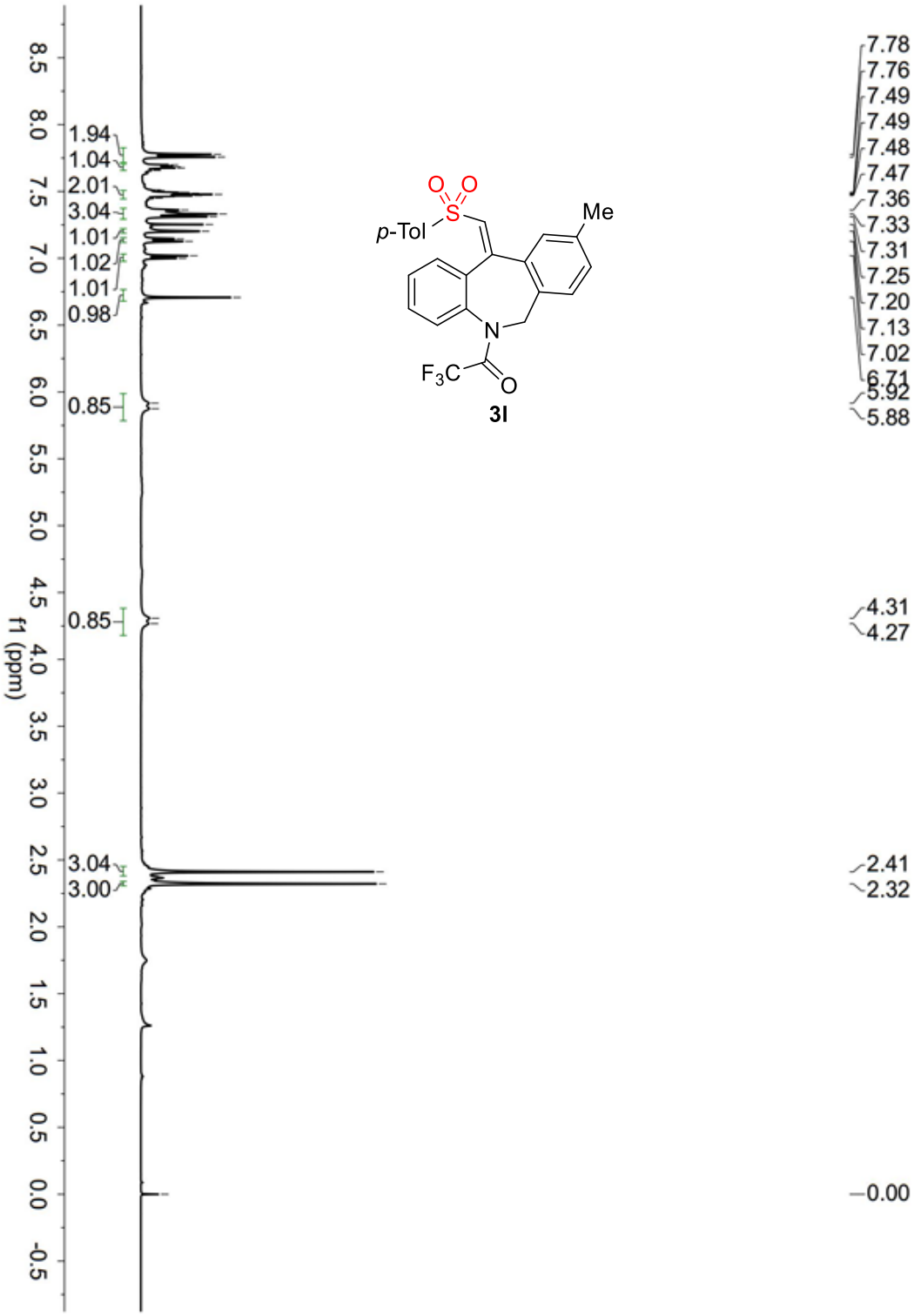
3j

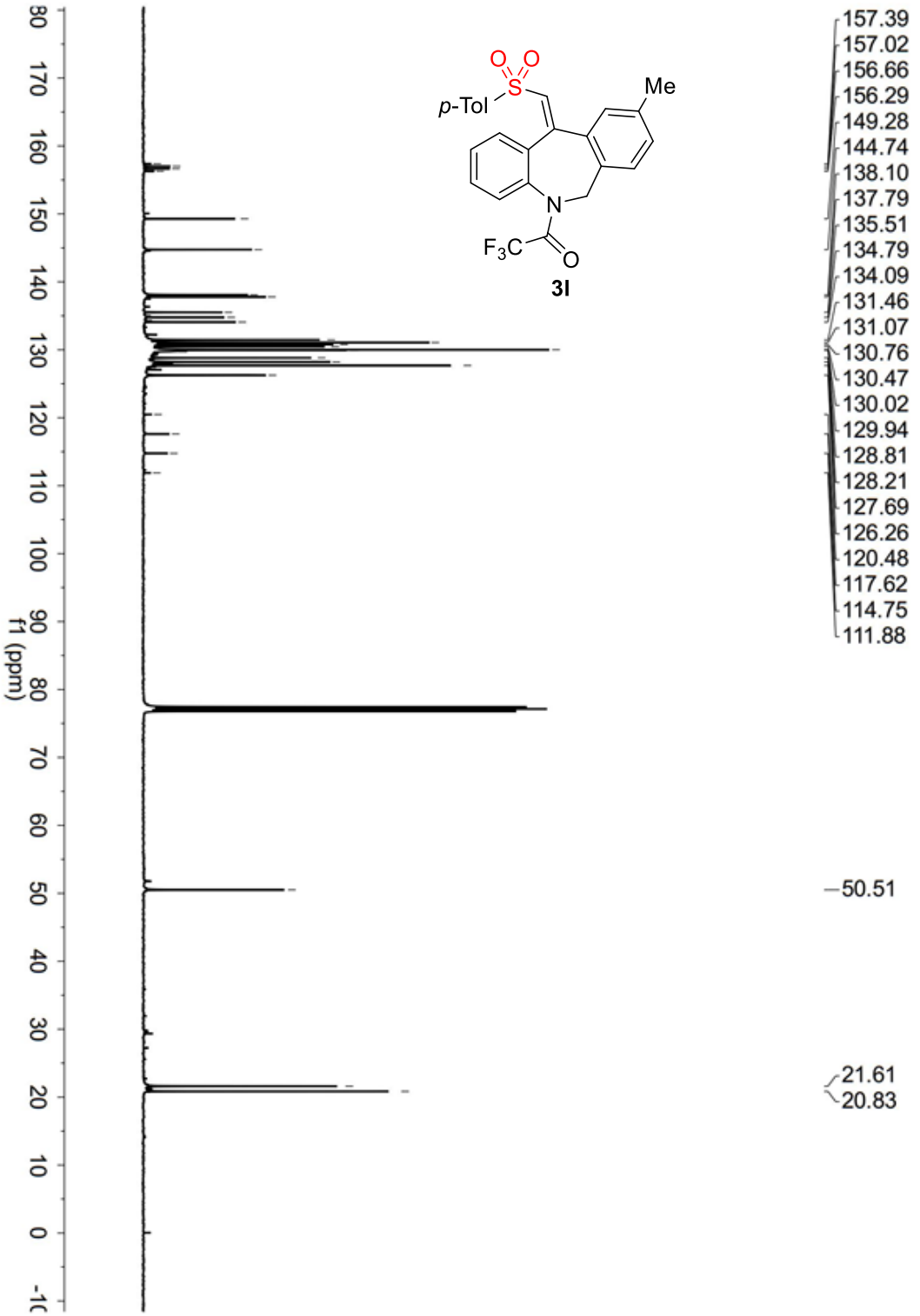

1.97
3.04
1.97
1.98
0.98
0.95
0.82
0.85
3.00
3.04
f1 (ppm)
p-Tol
Me
Br
N
F3C
O
3k
7.77
7.75
7.59
7.57
7.53
7.34
7.32
7.26
7.18
7.16
7.14
7.02
6.72
5.89
5.85
4.31
4.27
2.42
2.32
0.00

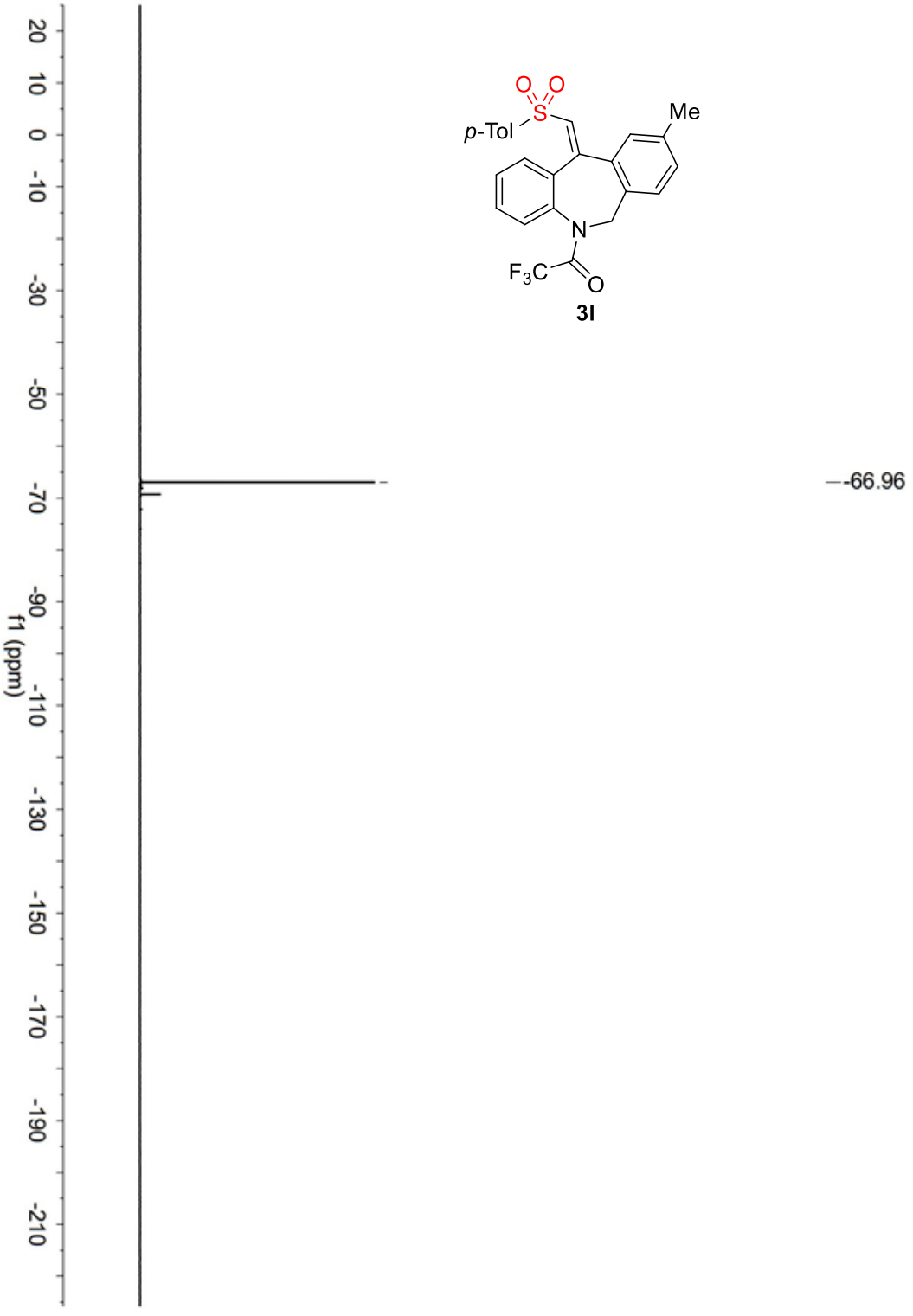

f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
O
O
S
p-Tol
Me
Br
N
F3C
O
3k
157.14
156.77
156.40
156.04
148.09
144.93
137.98
137.82
136.52
133.90
133.55
132.07
132.02
131.85
131.27
130.78
130.07
129.98
129.54
128.23
127.69
123.39
120.33
117.47
114.60
111.73
50.43
21.62
20.83


-67.04
f1 (ppm)
20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
O O
S
p-Tol
Me
Br
N
F3C
O

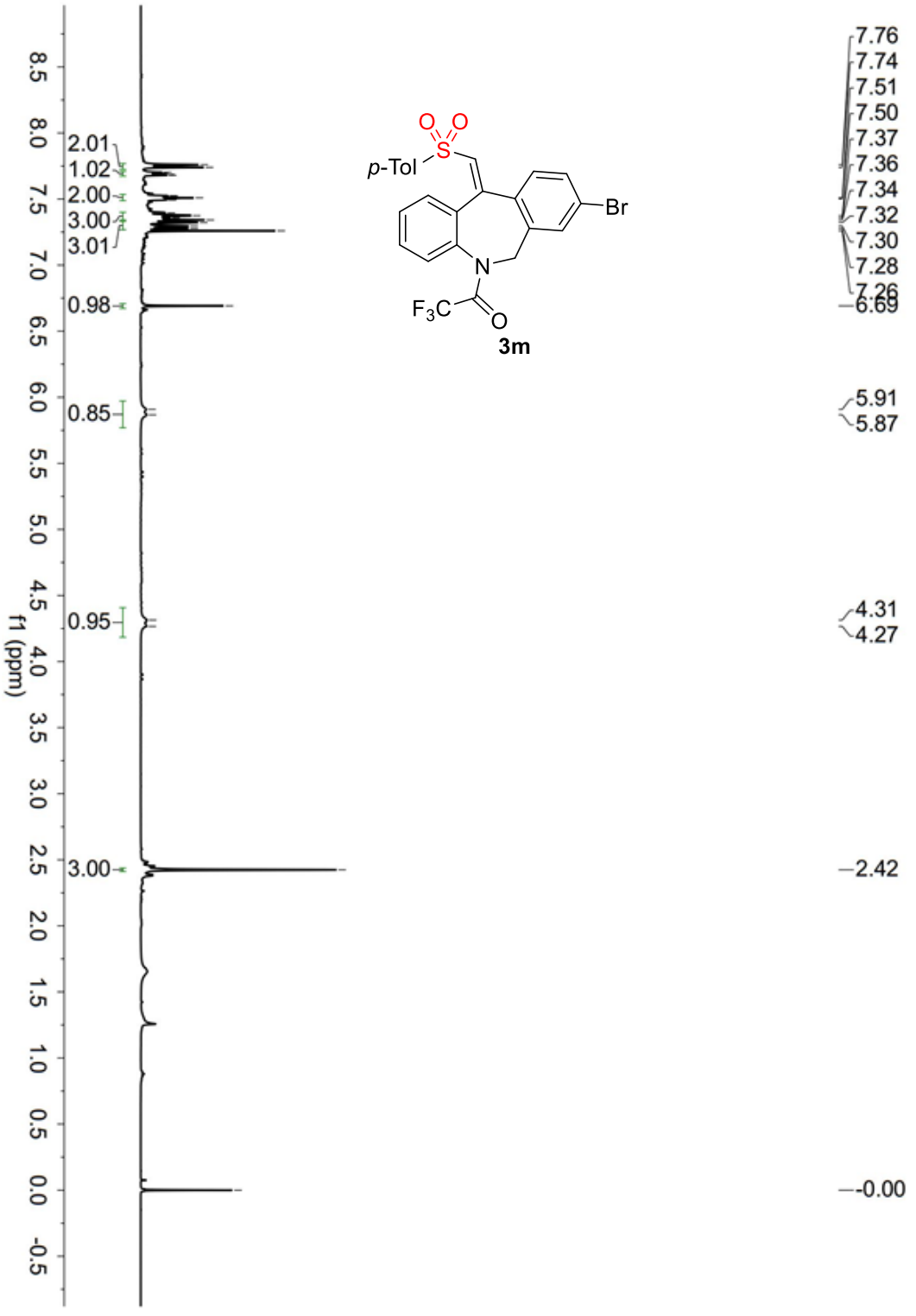
3k

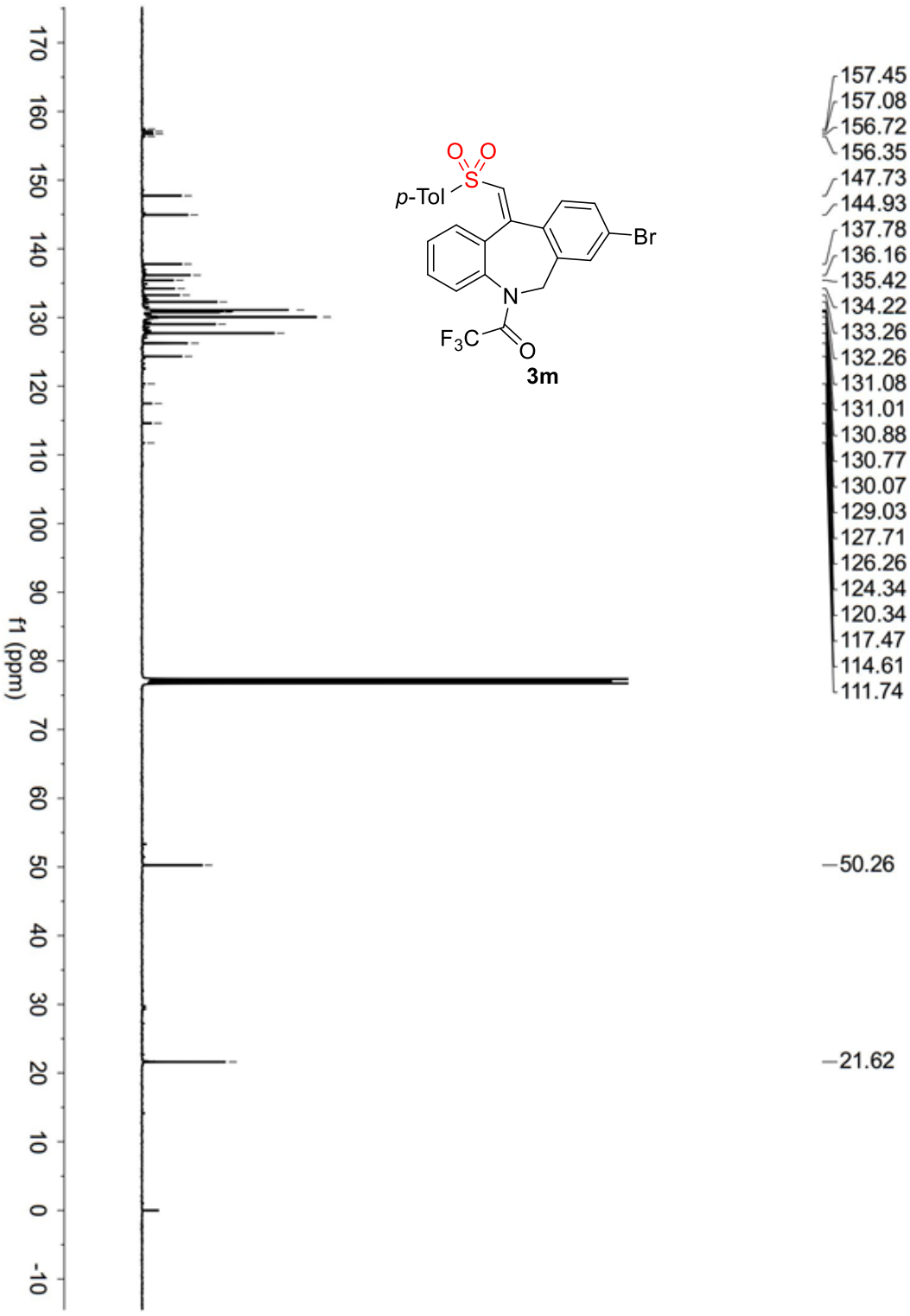

7.78
7.76
7.49
7.49
7.48
7.47
7.36
7.33
7.31
7.25
7.20
7.13
7.02
6.71
5.92
5.88
4.31
4.27
2.41
2.32
0.00
1.94
1.04
2.01
3.04
1.01
1.02
1.01
0.98
0.85
0.85
3.04
3.00
f1 (ppm)
p-Tol
Me
F3C
3l

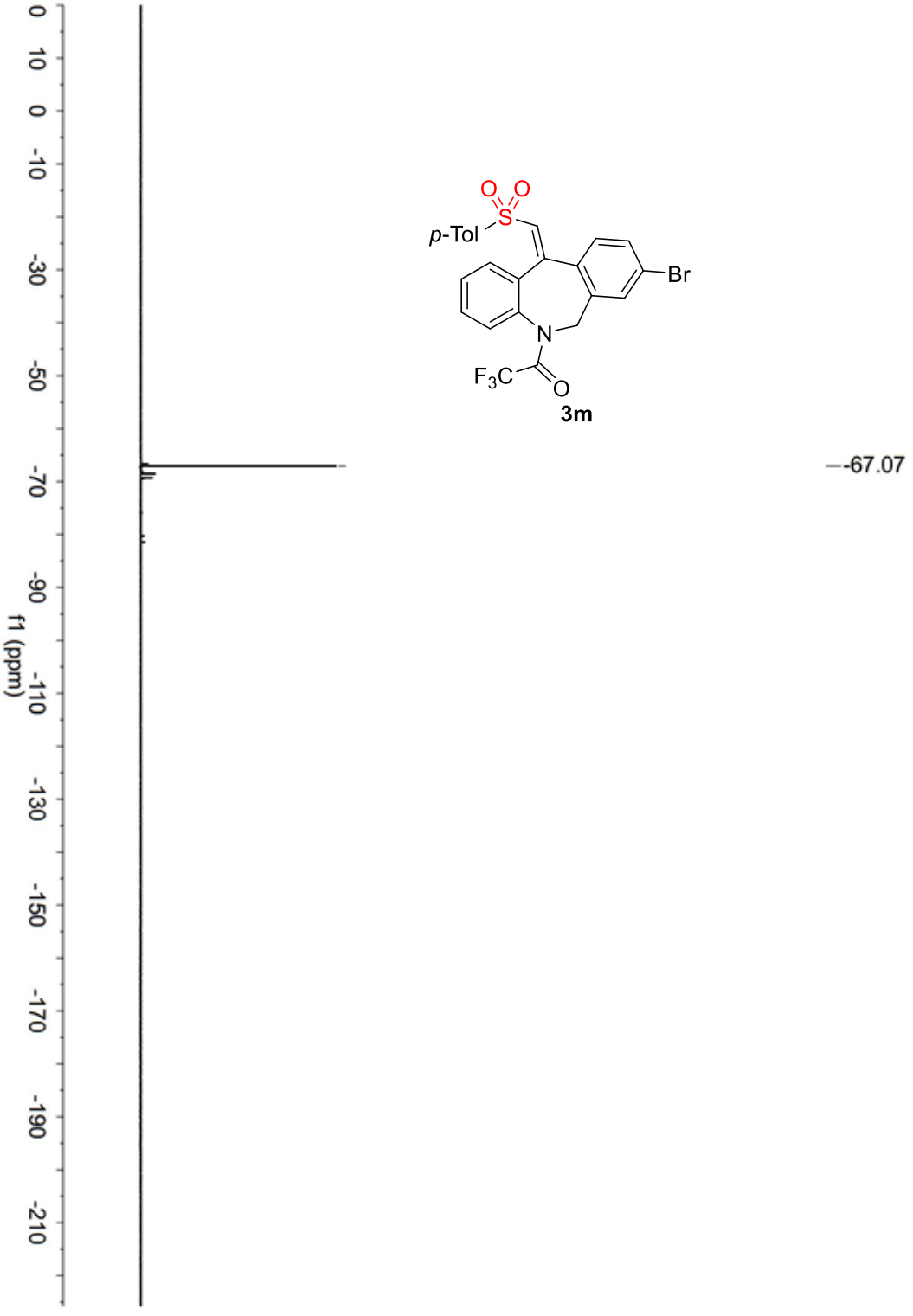

157.39
157.02
156.66
156.29
149.28
144.74
138.10
137.79
135.51
134.79
134.09
131.46
131.07
130.76
130.47
130.02
129.94
128.81
128.21
127.69
126.26
120.48
117.62
114.75
111.88
50.51
21.61
20.83
f1 (ppm)
p-Tol
Me
F3C
3l

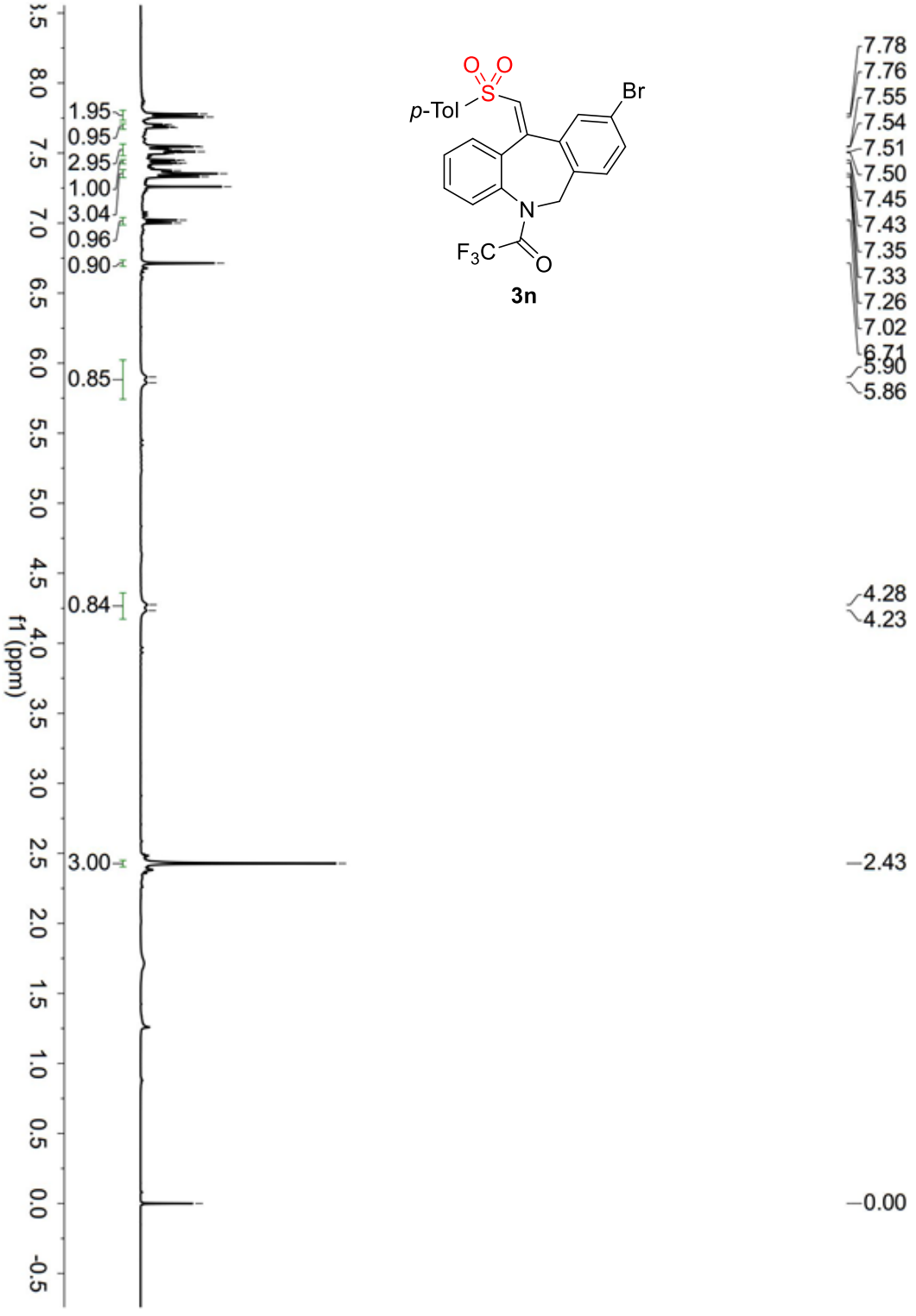

20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)
-66.96
O
O
S
p-Tol
Me
N
F3C
O

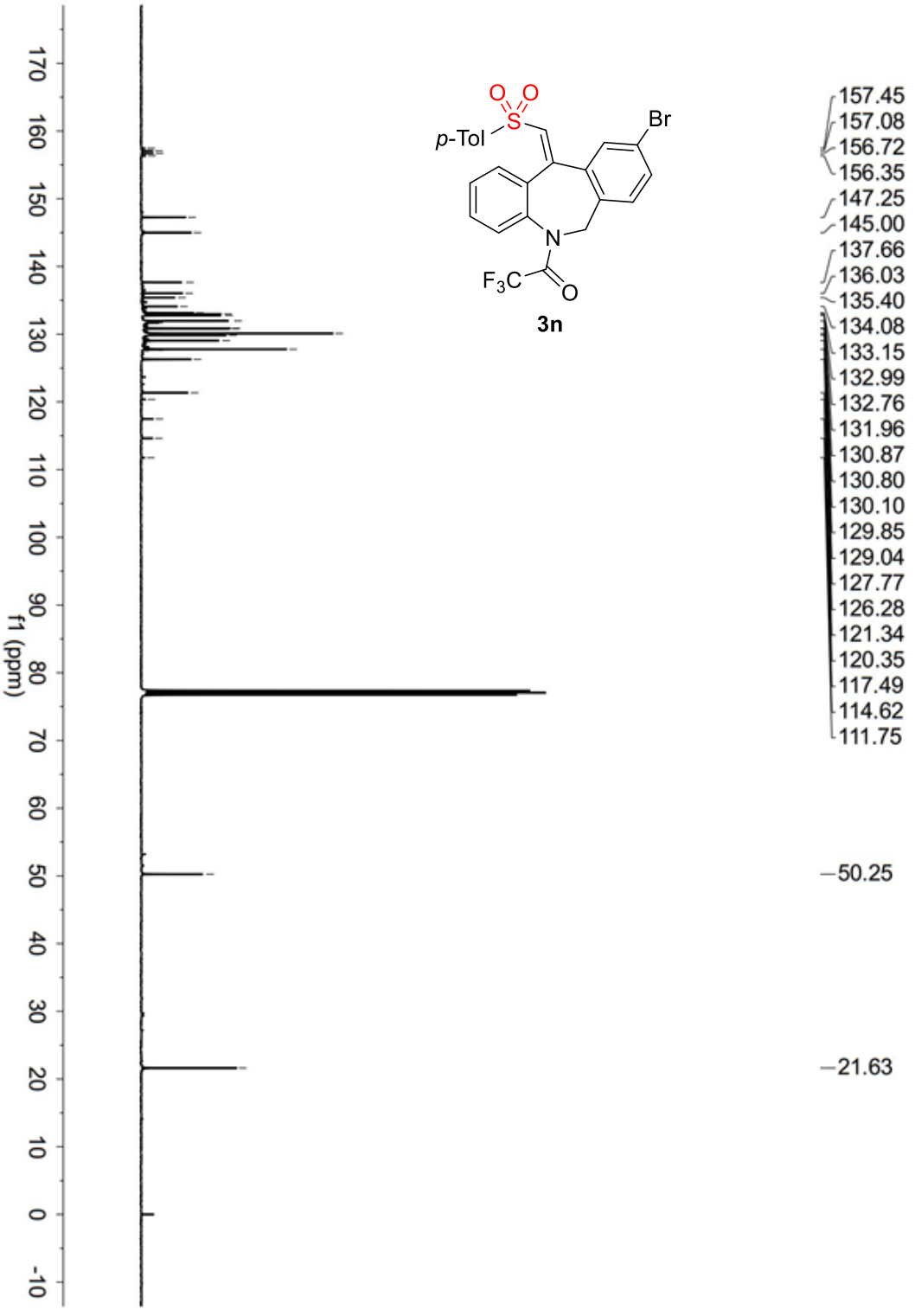
3l

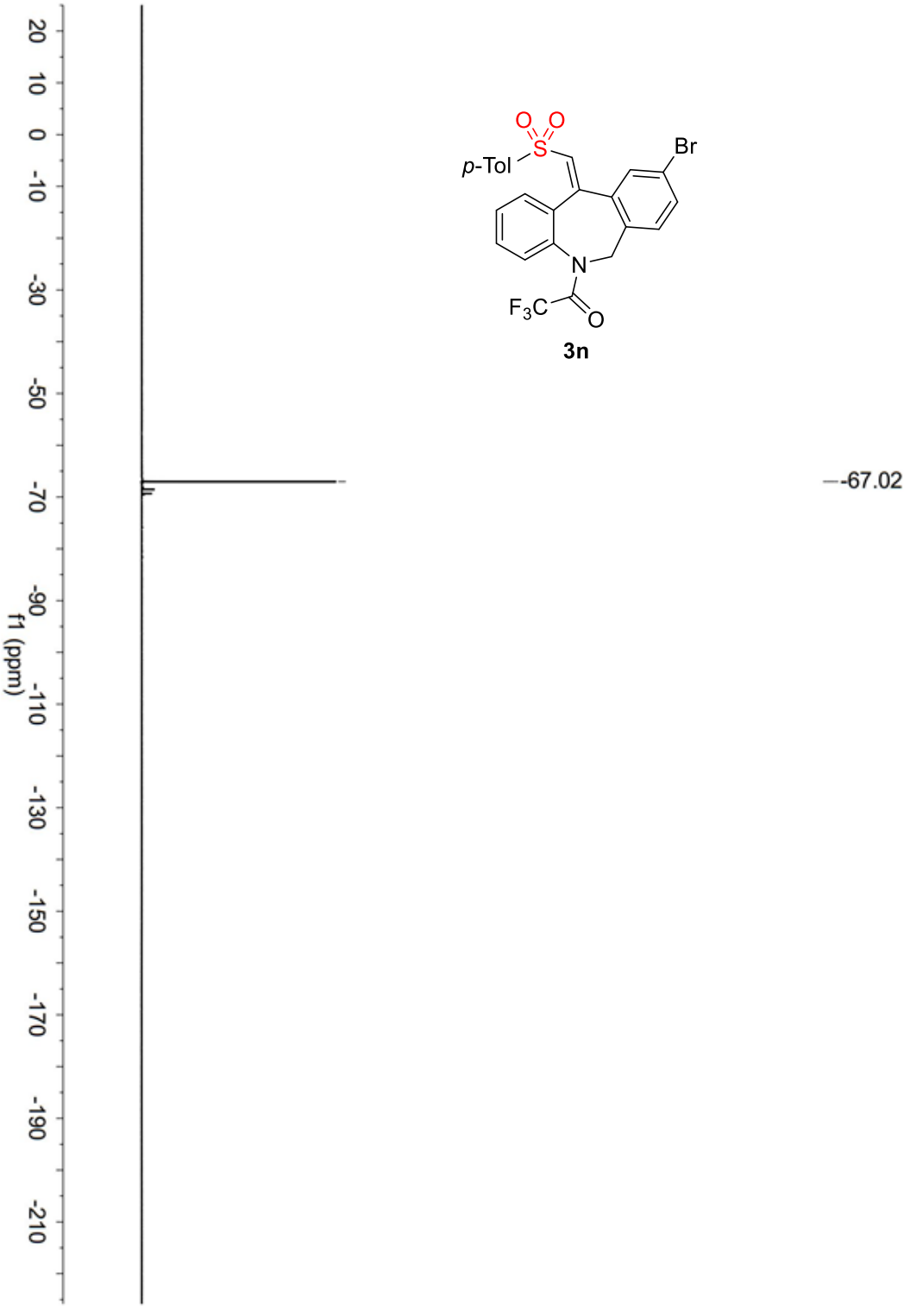

7.76
7.74
7.51
7.50
7.37
7.36
7.34
7.32
7.30
7.28
7.26
6.69
5.91
5.87
4.31
4.27
2.42
-0.00
2.01
1.02
2.00
3.00
3.01
0.98
0.85
0.95
3.00
f1 (ppm)
p-Tol
Br
N
F3C
O
3m


157.45
157.08
156.72
156.35
147.73
144.93
137.78
136.16
135.42
134.22
133.26
132.26
131.08
131.01
130.88
130.77
130.07
129.03
127.71
126.26
124.34
120.34
117.47
114.61
111.74
50.26
21.62
f1 (ppm)
p-Tol
Br
F3C
3m

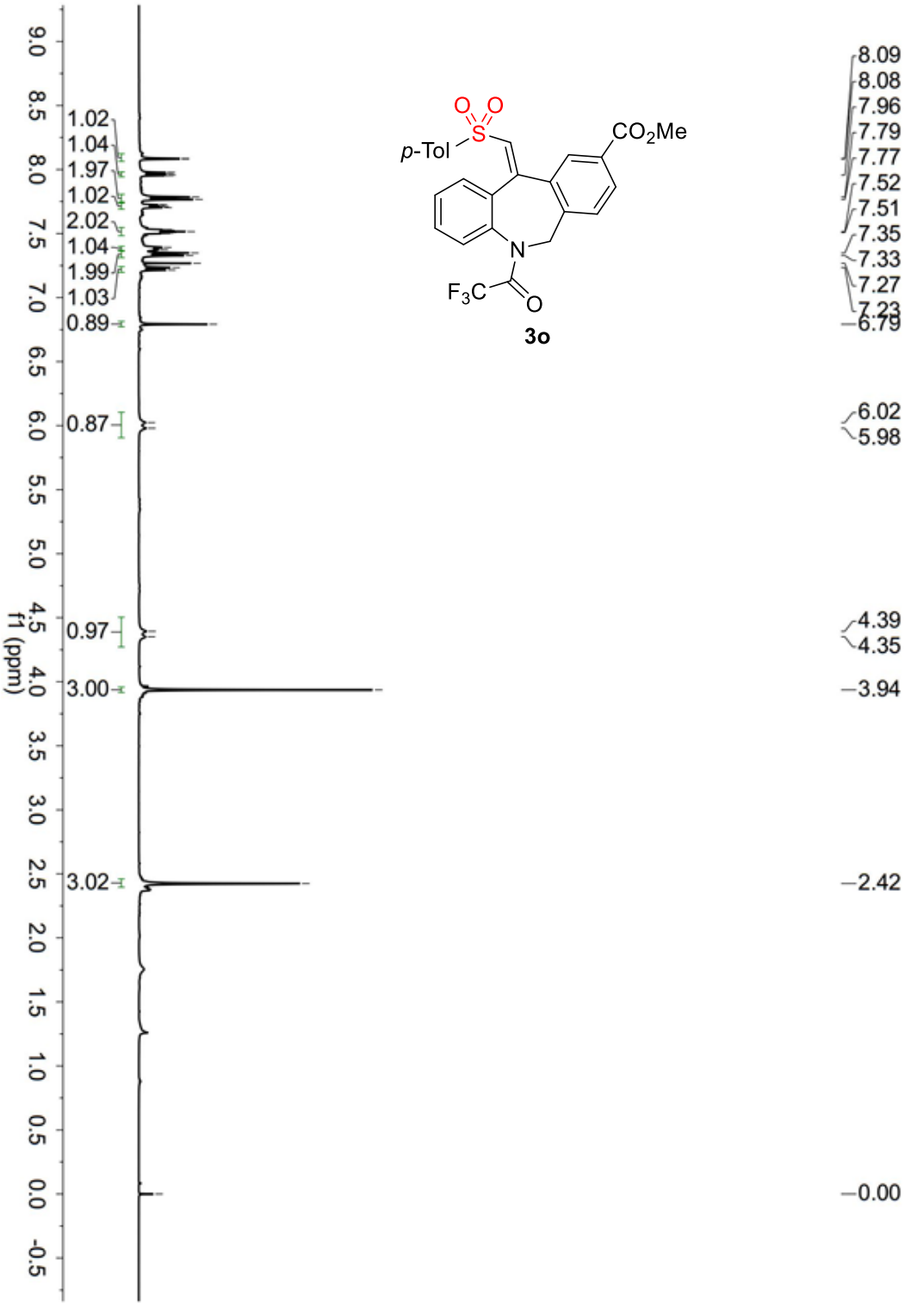

O
O
S
p-Tol
Br
N
F3C
O
3m
-67.07
0
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

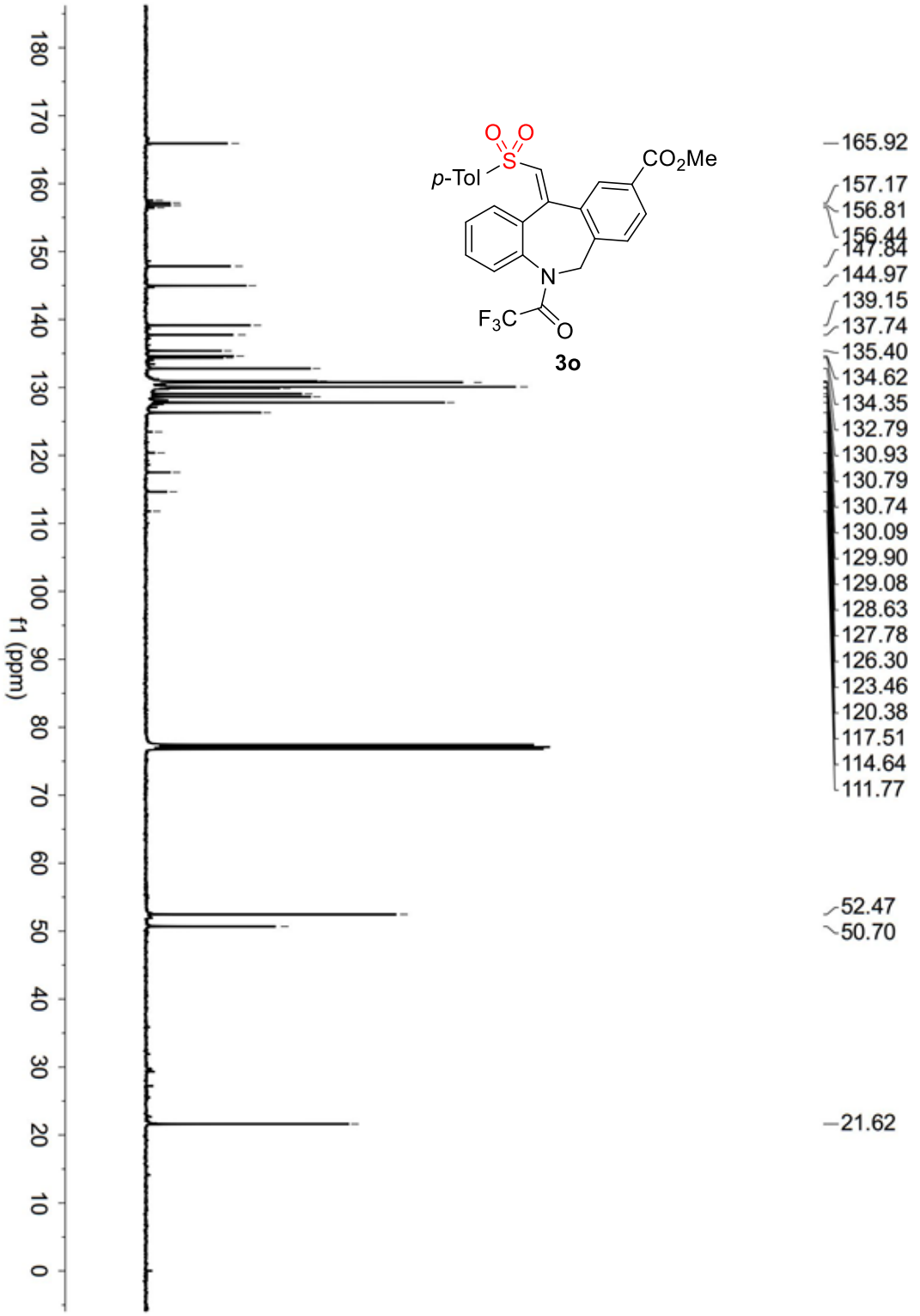

1.95
0.95
2.95
1.00
3.04
0.96
0.90
0.85
0.84
3.00
f1 (ppm)
p-Tol
Br
N
F3C
O
3n
7.78
7.76
7.55
7.54
7.51
7.50
7.45
7.43
7.35
7.33
7.26
7.02
6.71
5.90
5.86
4.28
4.23
2.43
0.00

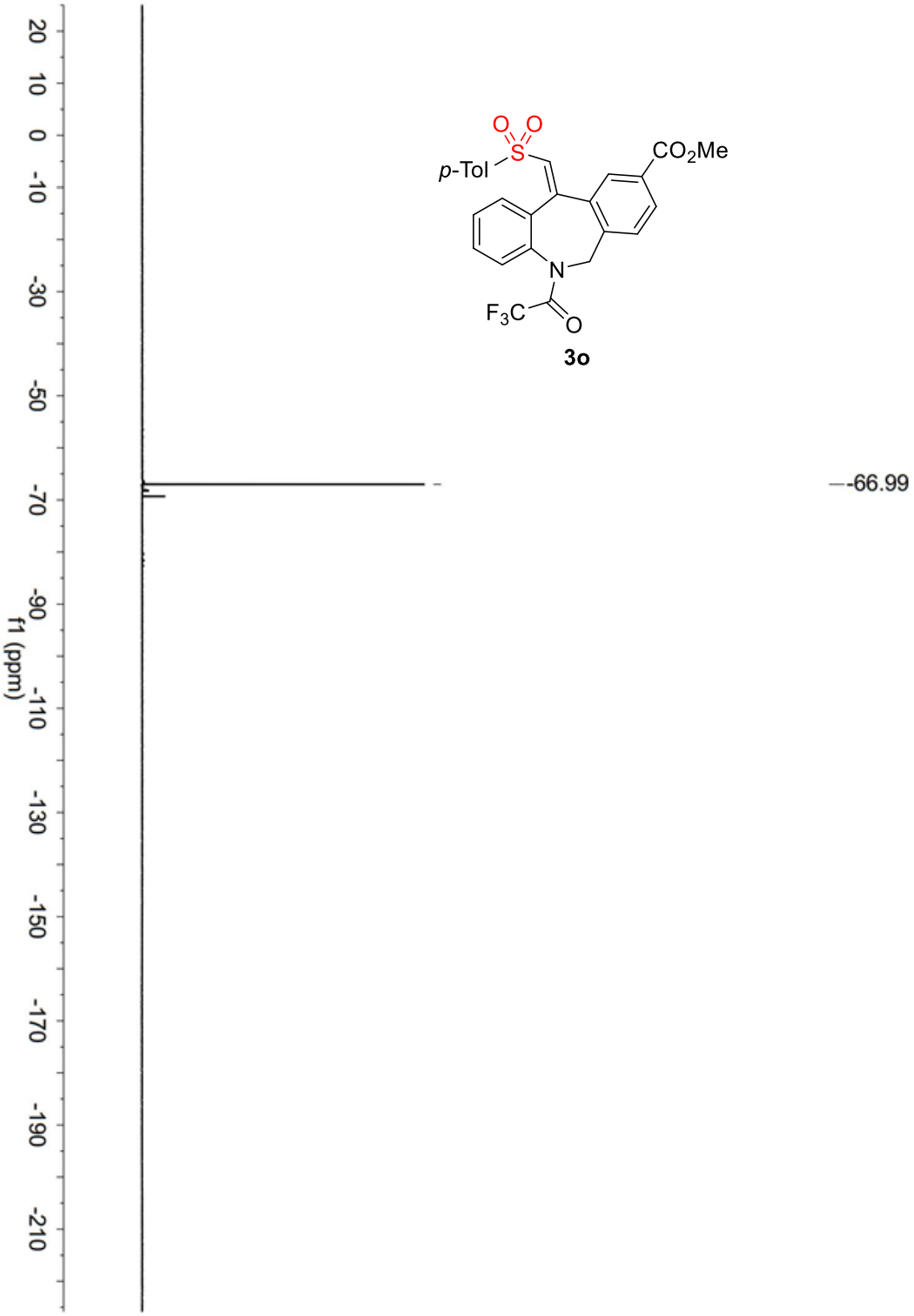

f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
p-Tol
Br
N
F3C
O
3n
157.45
157.08
156.72
156.35
147.25
145.00
137.66
136.03
135.40
134.08
133.15
132.99
132.76
131.96
130.87
130.80
130.10
129.85
129.04
127.77
126.28
121.34
120.35
117.49
114.62
111.75
50.25
21.63


20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)
-67.02
p-Tol
Br
N
F3C
O
O
O
S

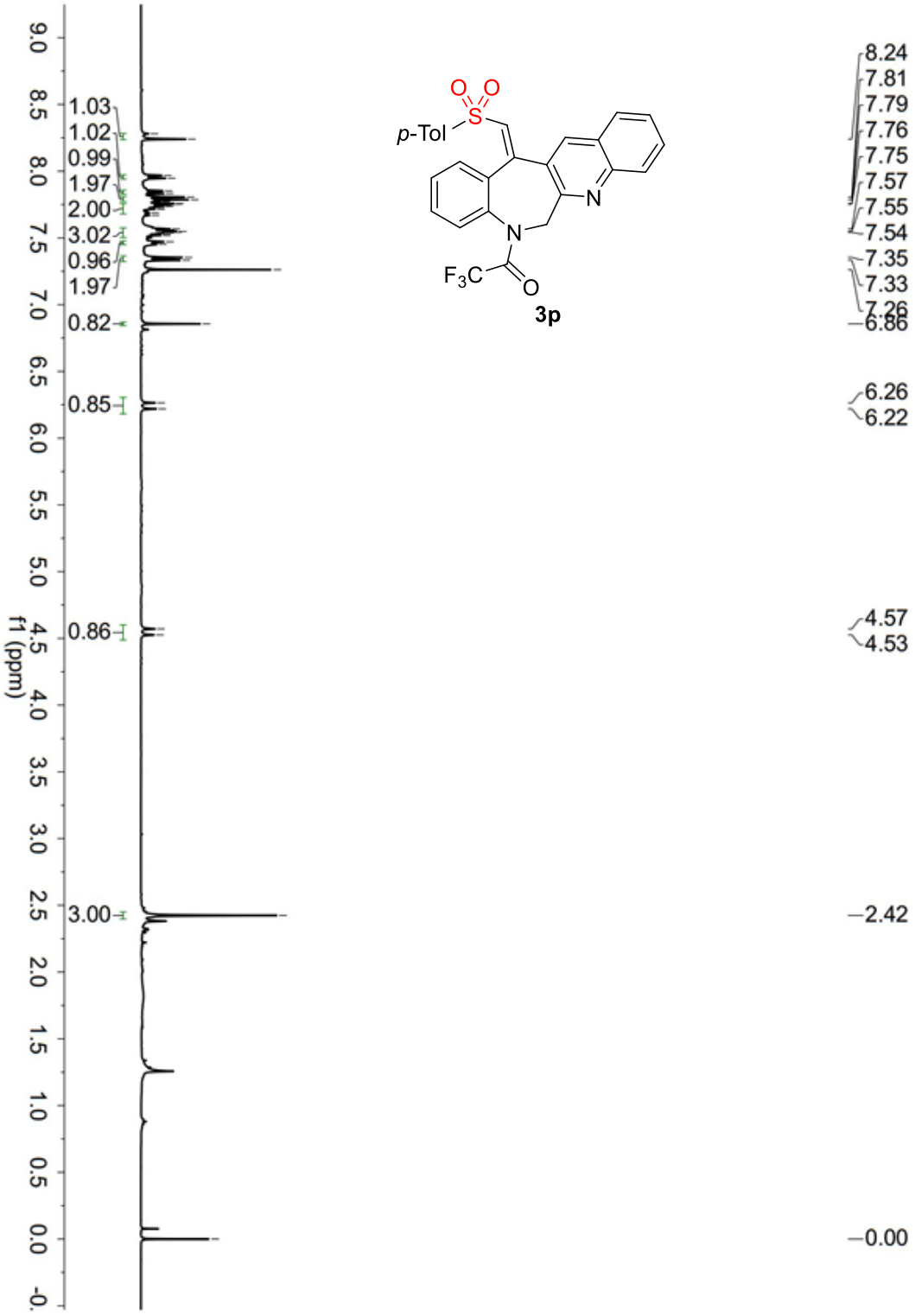
3n

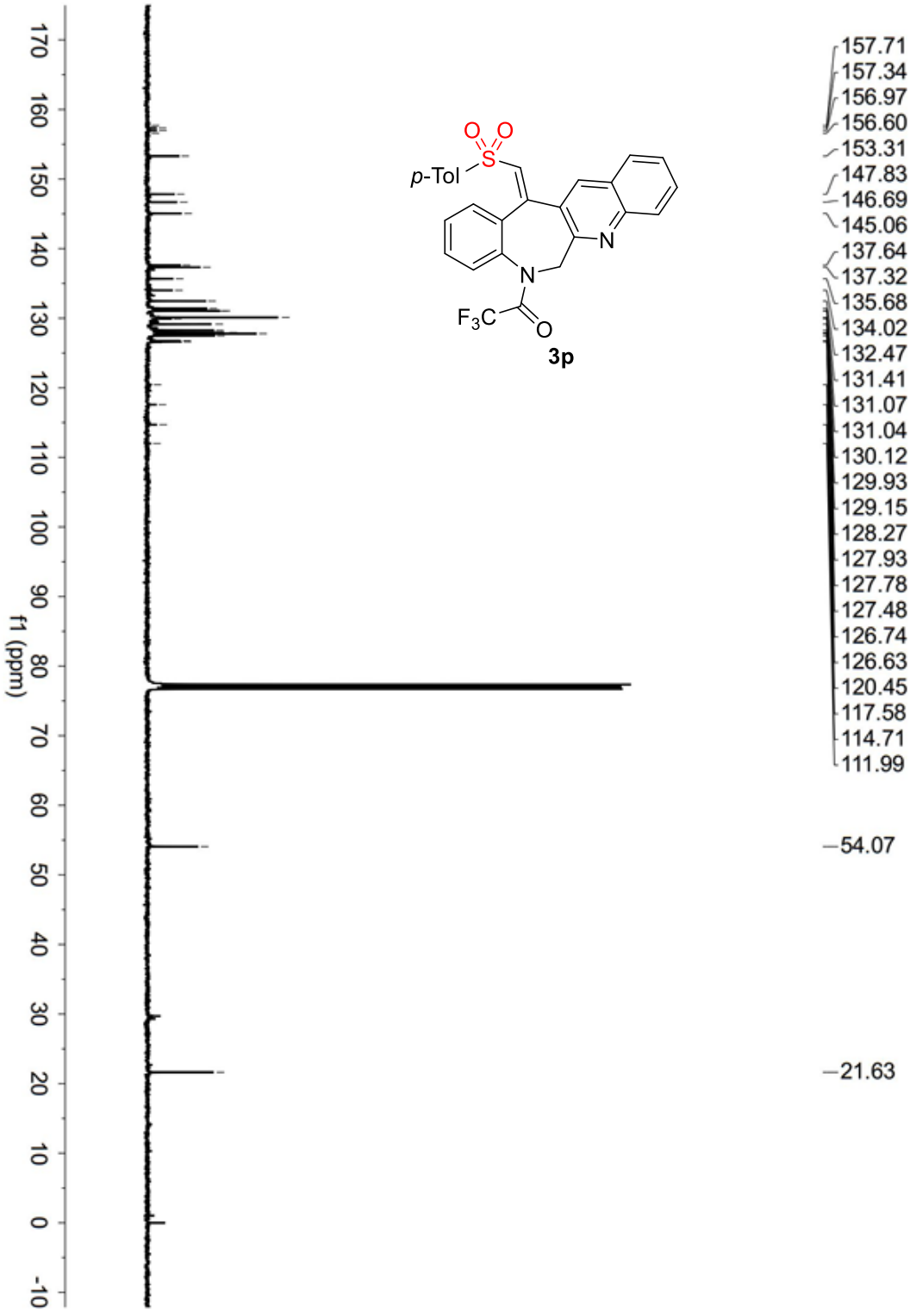

f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1.02
1.04
1.97
1.02
2.02
1.04
1.99
1.03
0.89
0.87
0.97
3.00
3.02
p-Tol
O
O
S
CO2Me
N
F3C
O
3o
8.09
8.08
7.96
7.79
7.77
7.52
7.51
7.35
7.33
7.27
7.23
6.79
6.02
5.98
4.39
4.35
3.94
2.42
0.00

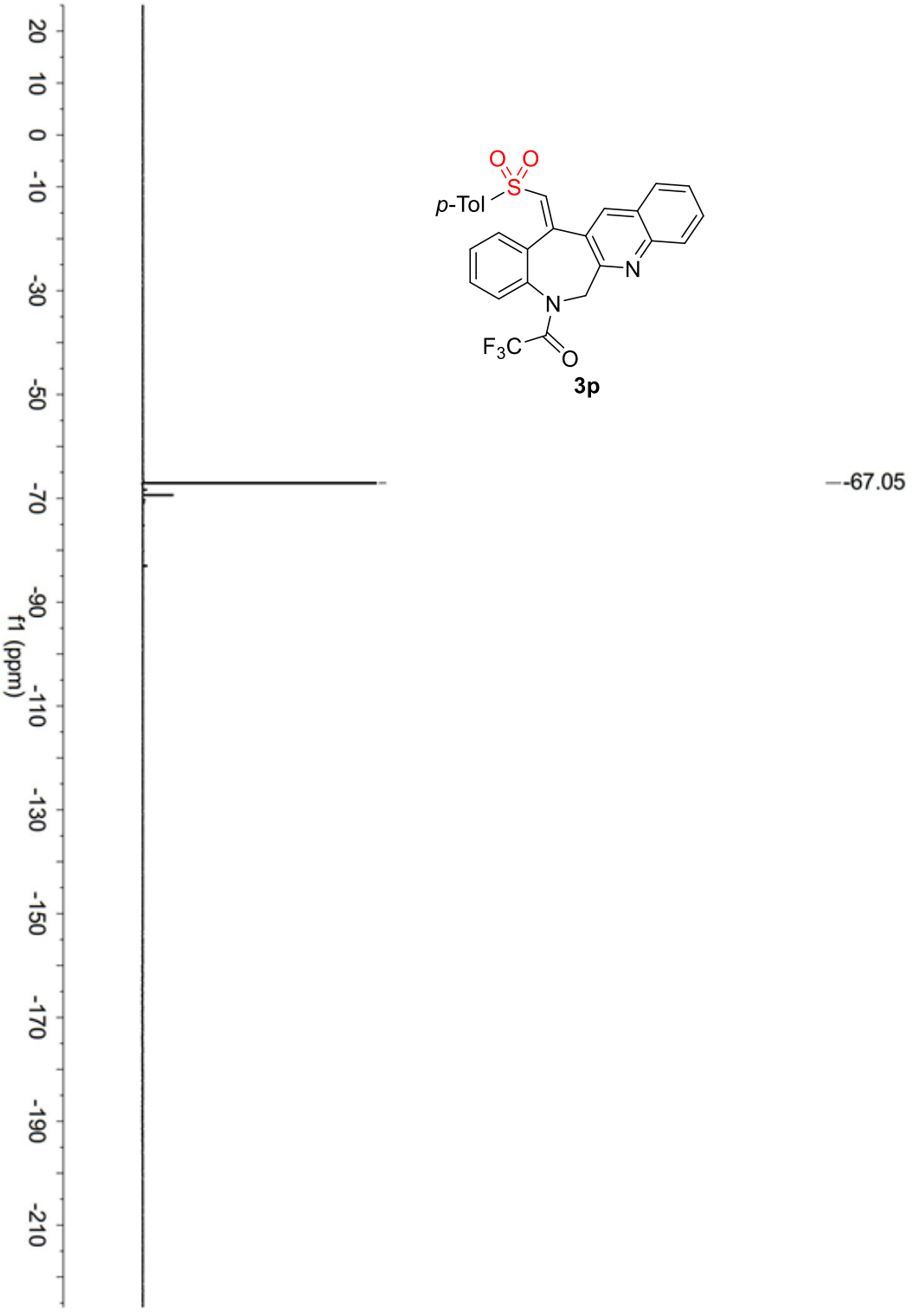

f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
O
S
p-Tol
CO2Me
N
F3C
O
3o
165.92
157.17
156.81
156.44
147.84
144.97
139.15
137.74
135.40
134.62
134.35
132.79
130.93
130.79
130.74
130.09
129.90
129.08
128.63
127.78
126.30
123.46
120.38
117.51
114.64
111.77
52.47
50.70
21.62

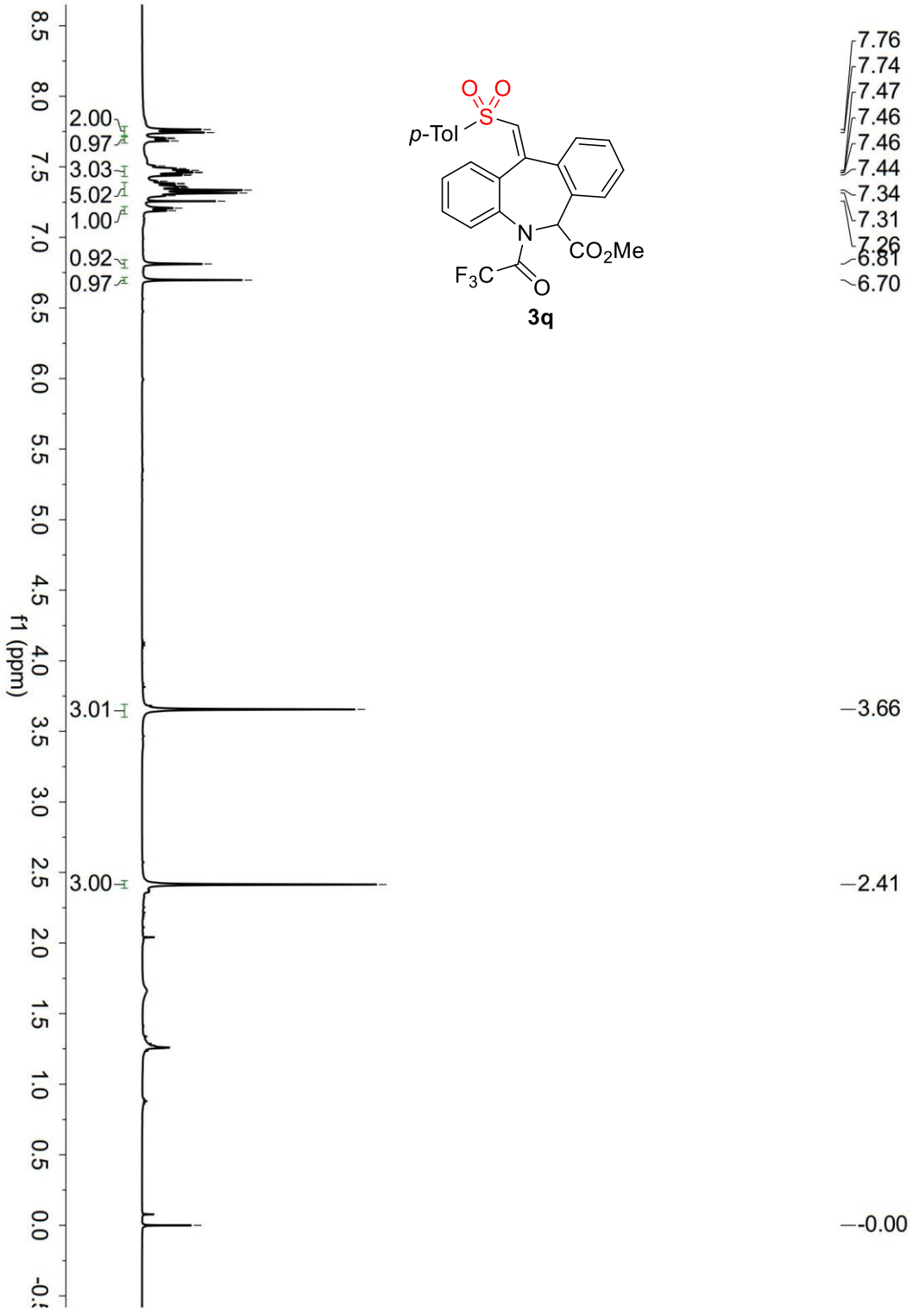

20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)
-66.99
O
O
S
p-Tol
CO2Me
N
F3C
O

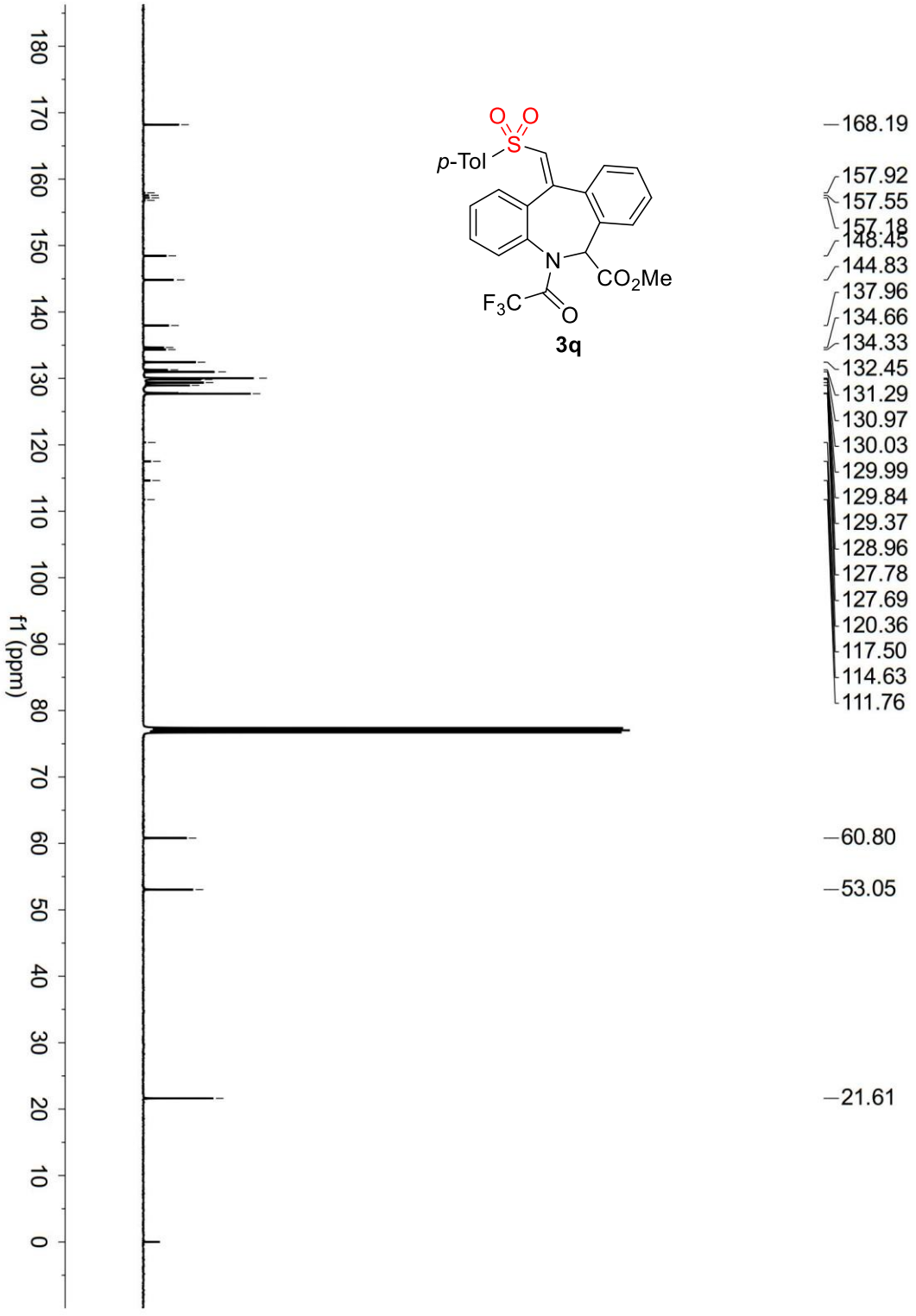
3o

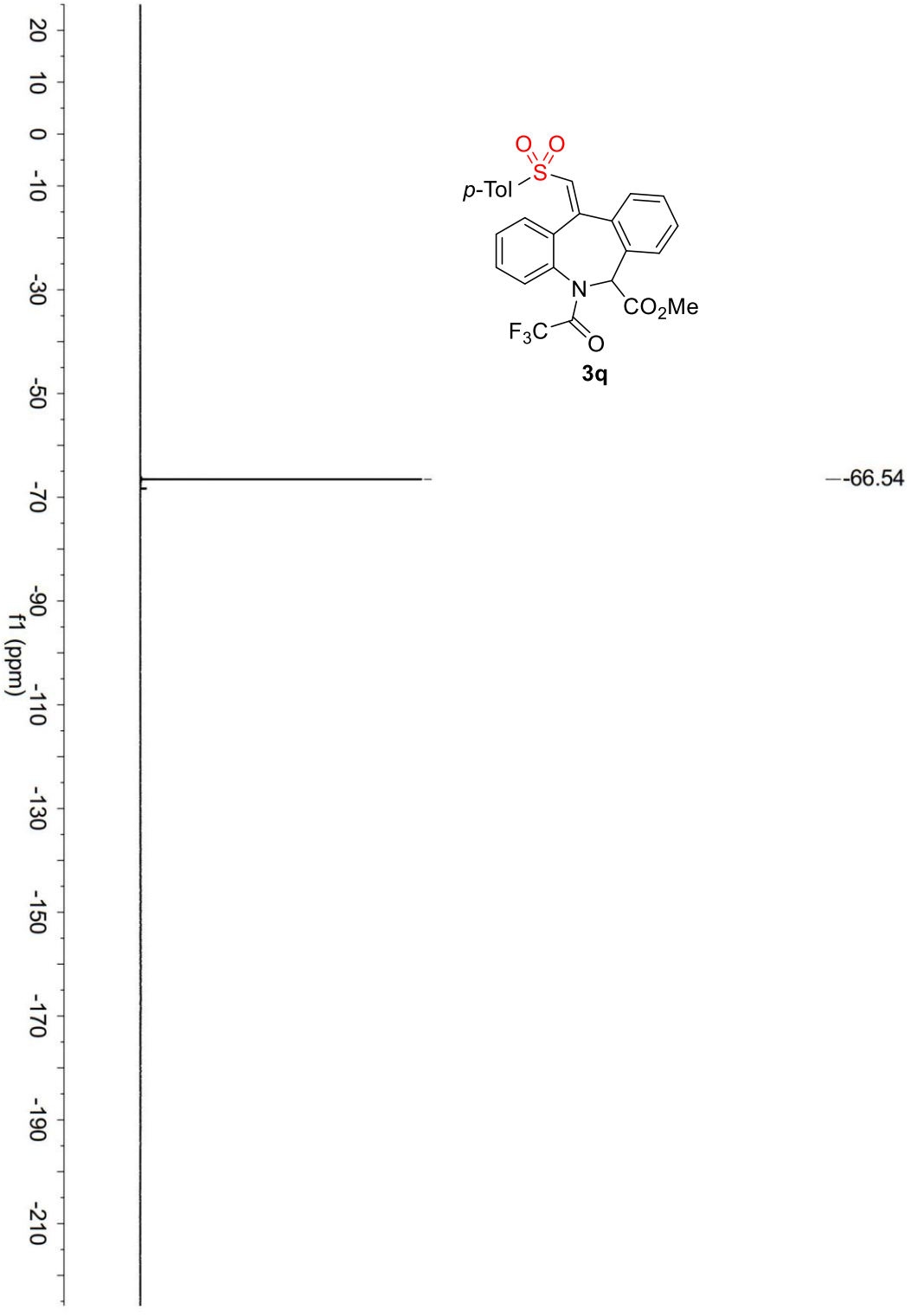

1.03
1.02
0.99
1.97
2.00
3.02
0.96
1.97
0.82
0.85
0.86
3.00
f1 (ppm)
p-Tol
F3C
3p
8.24
7.81
7.79
7.76
7.75
7.57
7.55
7.54
7.35
7.33
7.26
6.86
6.26
6.22
4.57
4.53
2.42
0.00

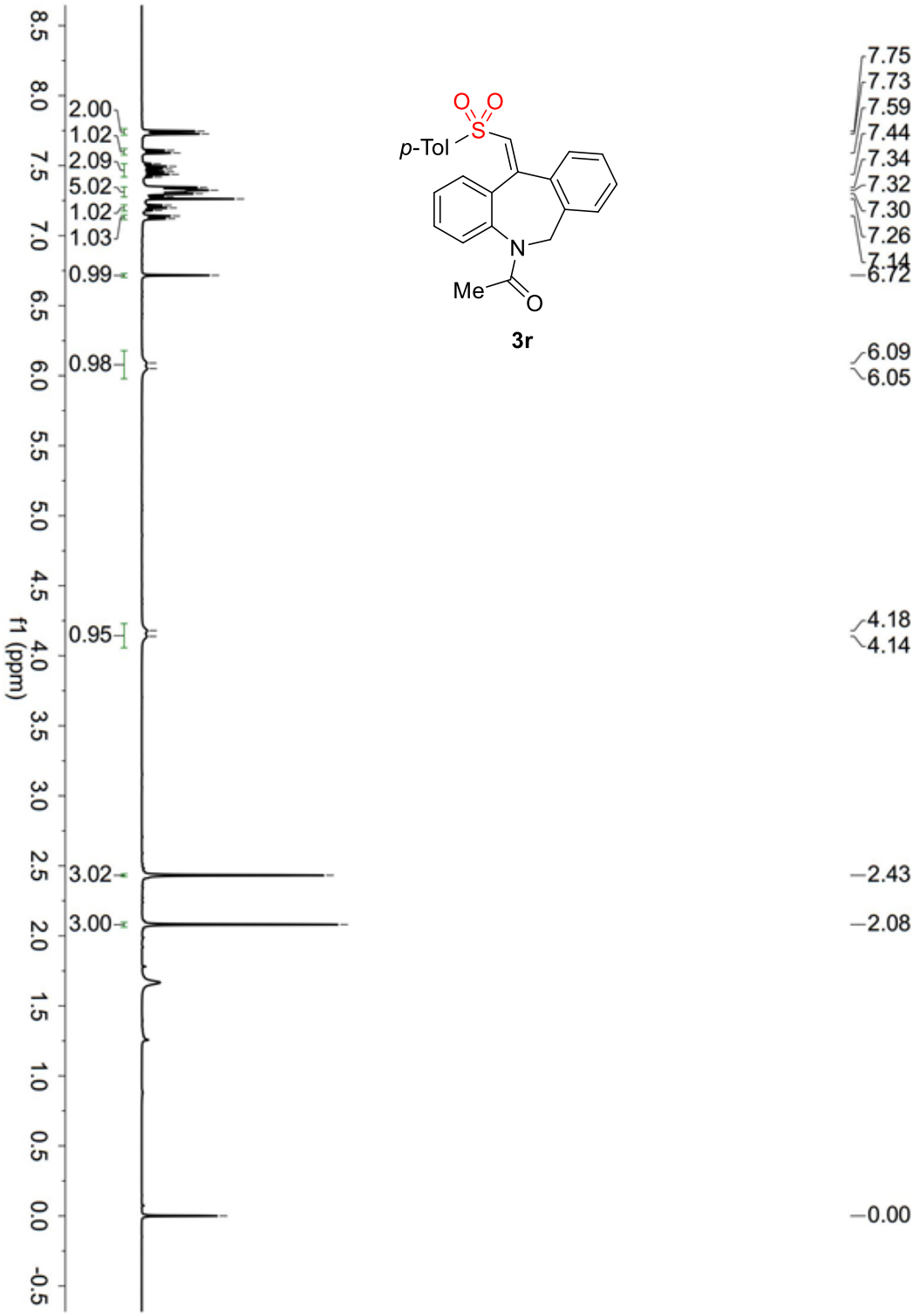

f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
p-Tol
O
O
S
N
N
F3C
O
3p
157.71
157.34
156.97
156.60
153.31
147.83
146.69
145.06
137.64
137.32
135.68
134.02
132.47
131.41
131.07
131.04
130.12
129.93
129.15
128.27
127.93
127.78
127.48
126.74
126.63
120.45
117.58
114.71
111.99
54.07
21.63

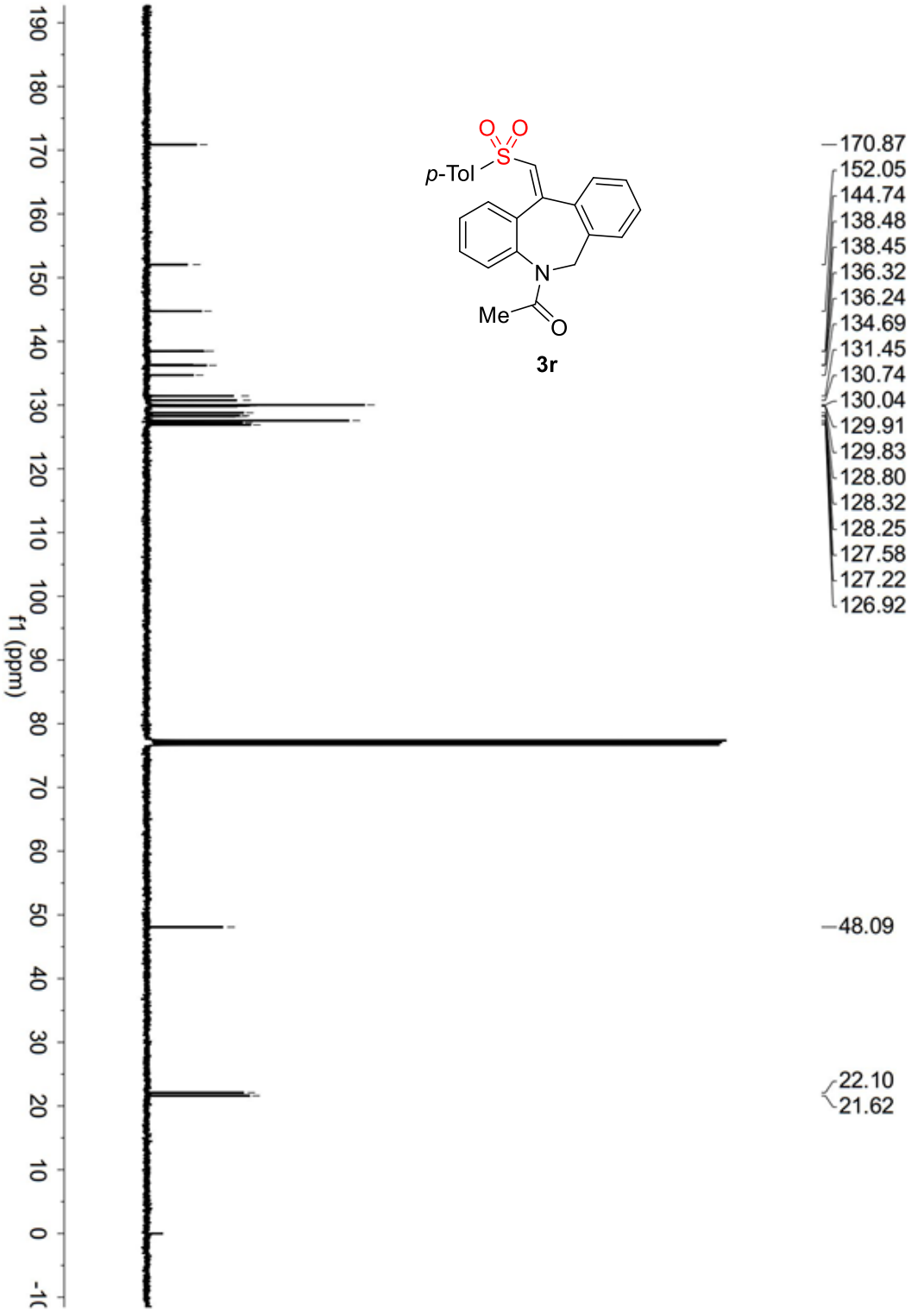

20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)
-67.05
p-Tol
O
O
S
N
N
F3C
O
3p

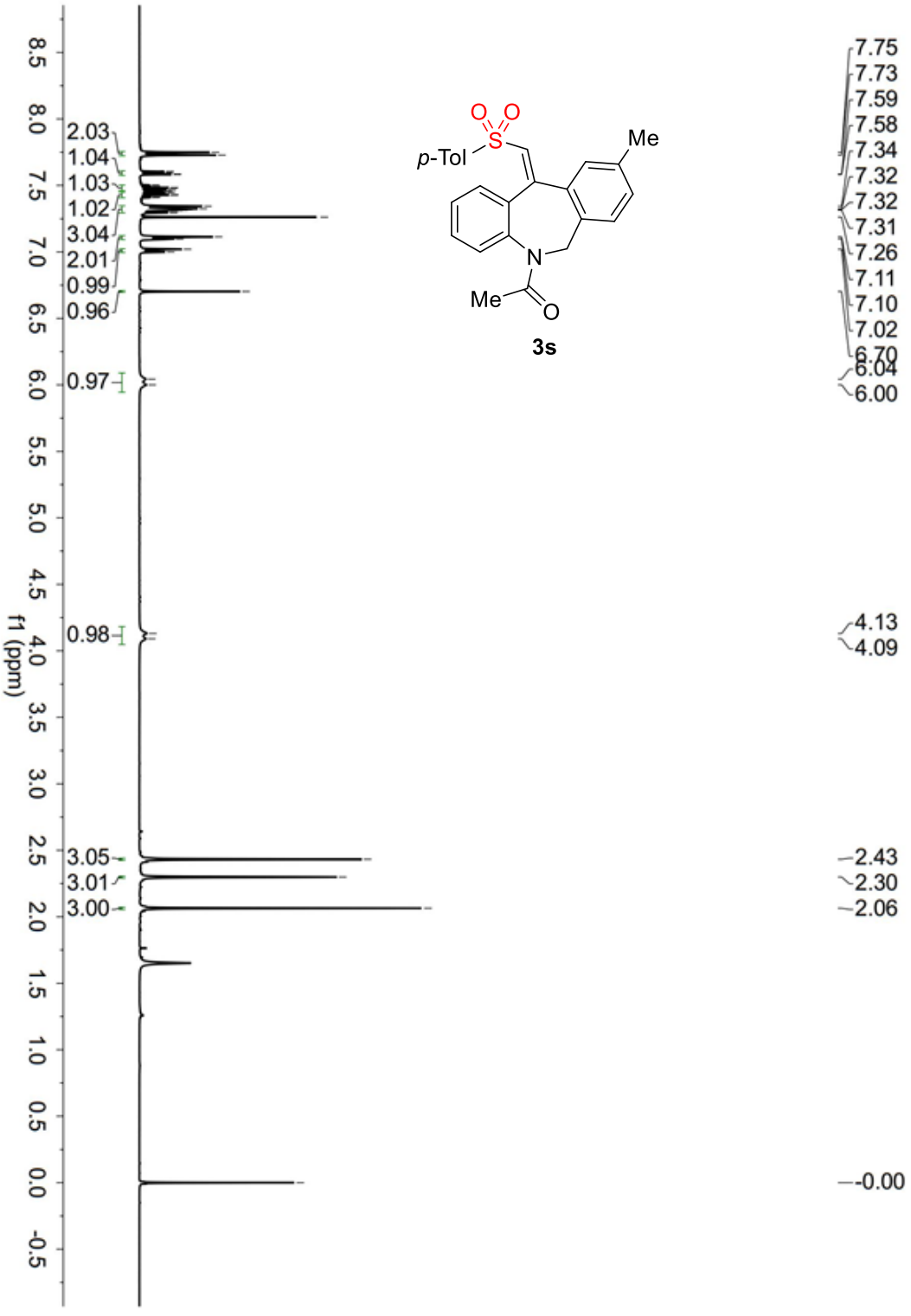

7.76
7.74
7.47
7.46
7.46
7.44
7.34
7.31
7.26
6.81
6.70
2.00
0.97
3.03
5.02
1.00
0.92
0.97
3.01
3.00
3.66
2.41
0.00
f1 (ppm)
p-Tol
CO2Me
F3C
3q

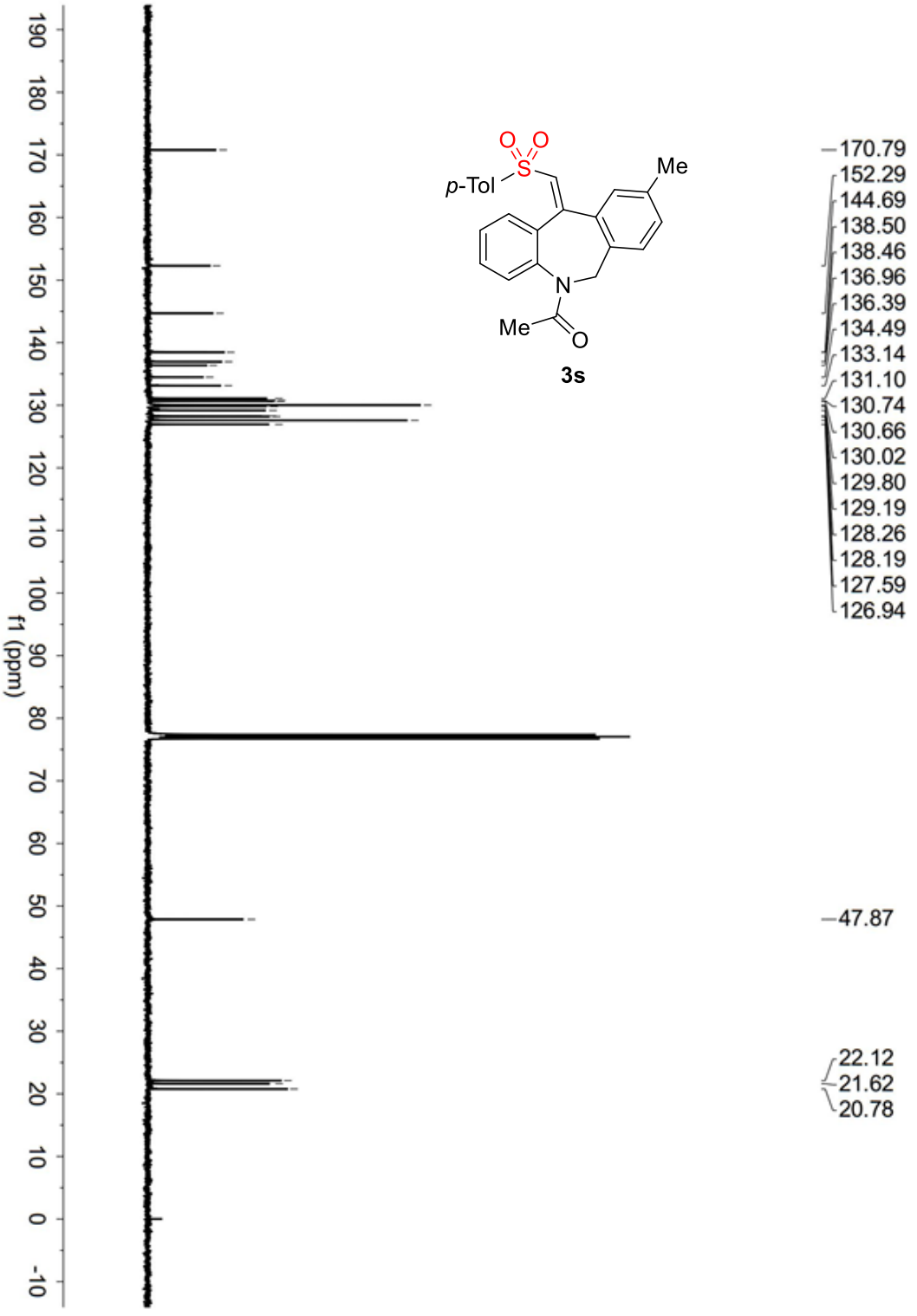

f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
p-Tol
O
O
S
N
CO2Me
F3C
O
3q
168.19
157.92
157.55
157.18
148.45
144.83
137.96
134.66
134.33
132.45
131.29
130.97
130.03
129.99
129.84
129.37
128.96
127.78
127.69
120.36
117.50
114.63
111.76
60.80
53.05
21.61

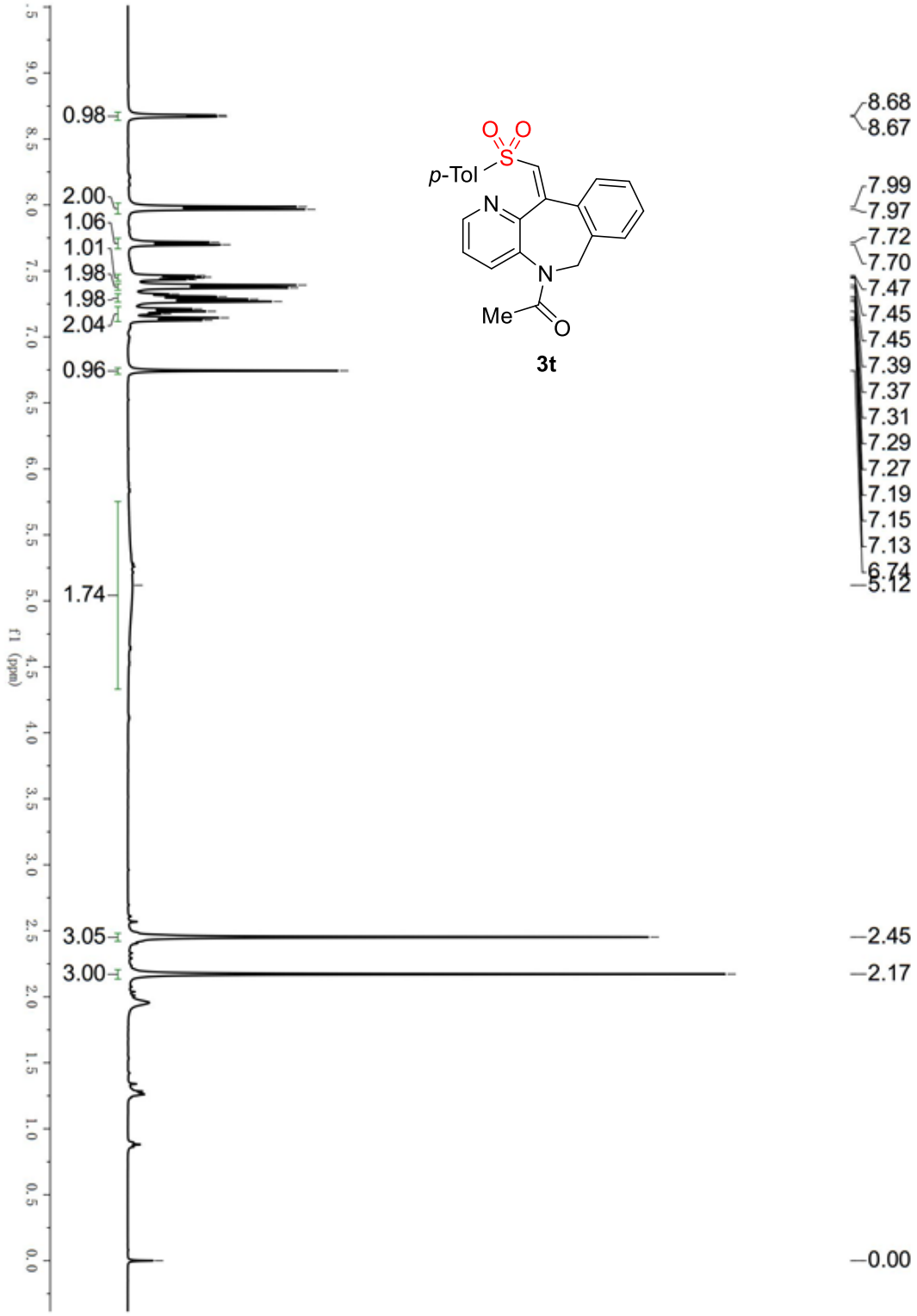

20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)
-66.54
p-Tol
O
O
S
N
CO2Me
F3C
O
3q


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
-0.5
f1 (ppm)
2.00
1.02
2.09
5.02
1.02
1.03
0.99
0.98
0.95
3.02
3.00
p-Tol
O
O
S
N
Me
O
3r
7.75
7.73
7.59
7.44
7.34
7.32
7.30
7.26
7.14
6.72
6.09
6.05
4.18
4.14
2.43
2.08
0.00

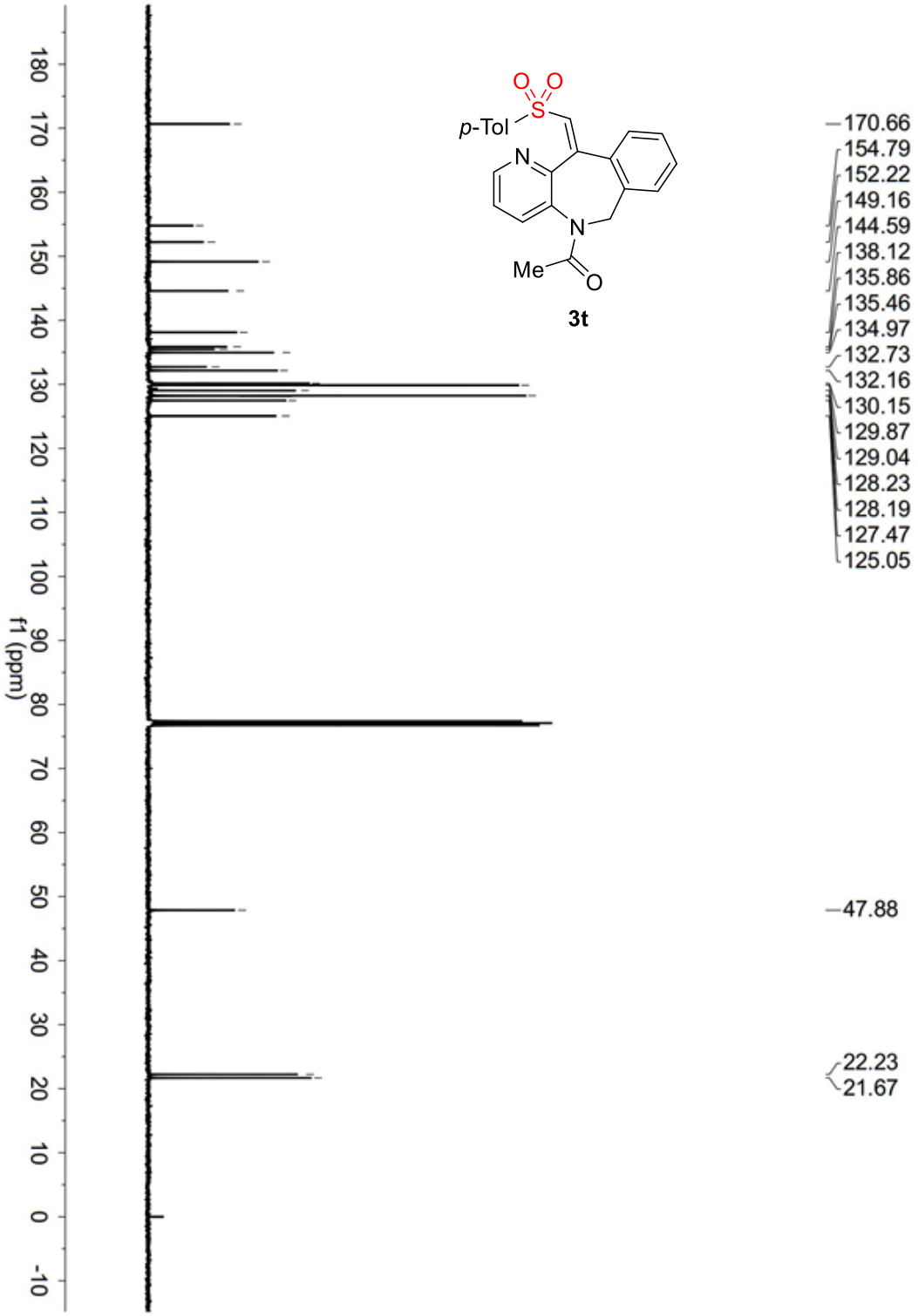

170.87
152.05
144.74
138.48
138.45
136.32
136.24
134.69
131.45
130.74
130.04
129.91
129.83
128.80
128.32
128.25
127.58
127.22
126.92
48.09
22.10
21.62
f1 (ppm)
p-Tol
Me
3r

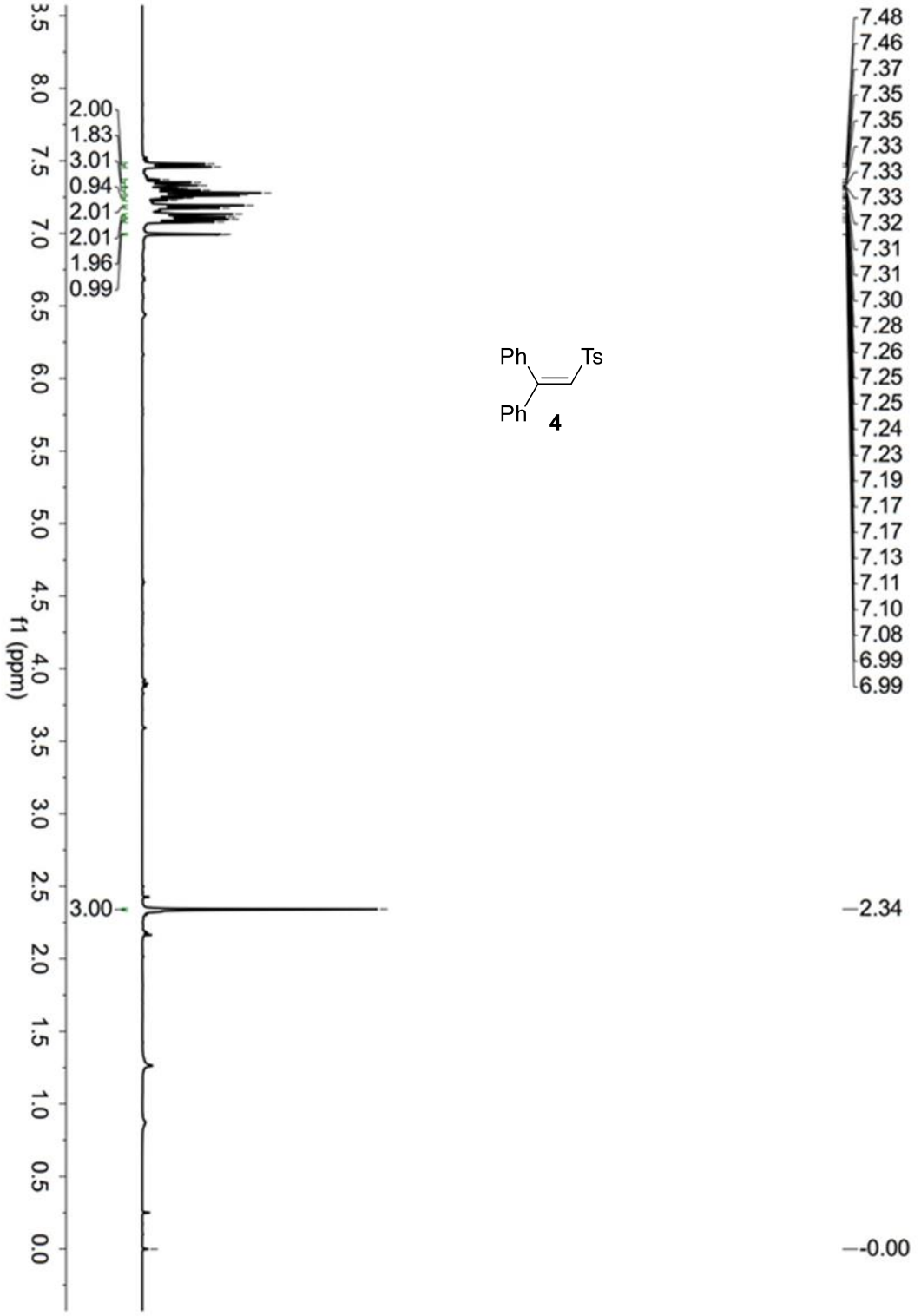

f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
2.03
1.04
1.03
1.02
3.04
2.01
0.99
0.96
0.97
0.98
3.05
3.01
3.00
O
O
S
p-Tol
Me
N
Me
O
3s
7.75
7.73
7.59
7.58
7.34
7.32
7.32
7.31
7.26
7.11
7.10
7.02
6.70
6.04
6.00
4.13
4.09
2.43
2.30
2.06
-0.00

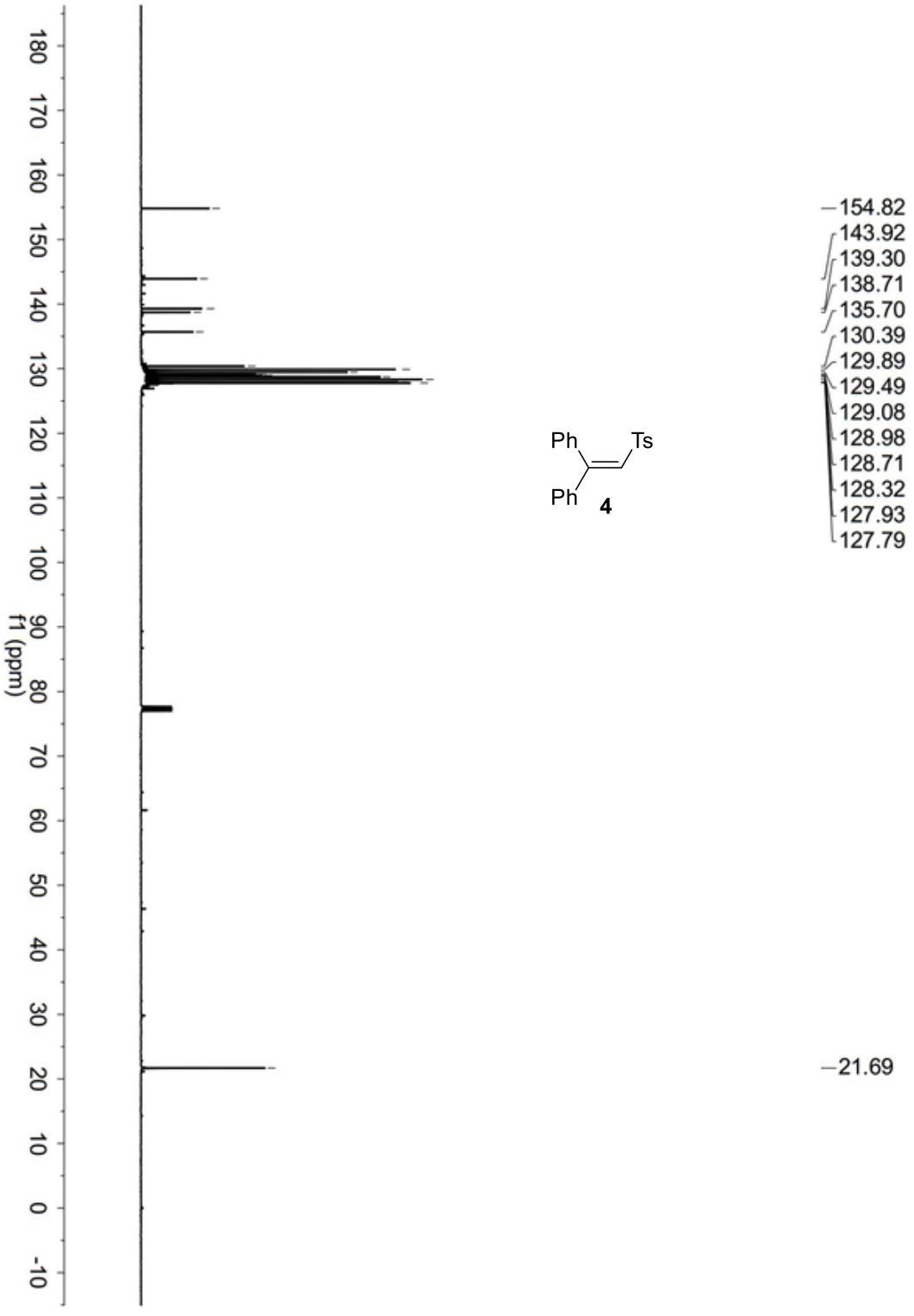

f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
O
O
S
p-Tol
Me
N
Me
O
3s
170.79
152.29
144.69
138.50
138.46
136.96
136.39
134.49
133.14
131.10
130.74
130.66
130.02
129.80
129.19
128.26
128.19
127.59
126.94
47.87
22.12
21.62
20.78

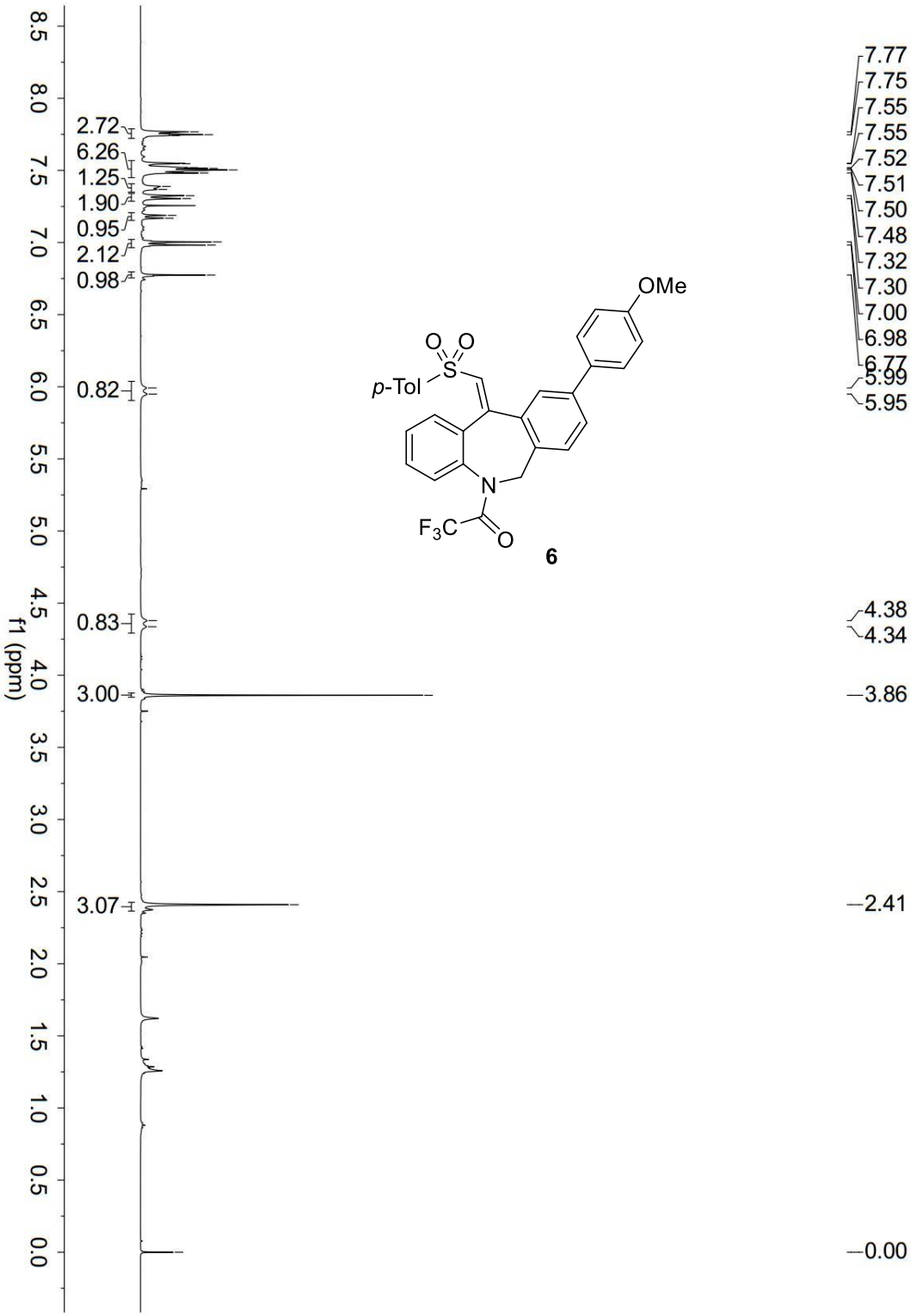

0.98
2.00
1.06
1.01
1.98
1.98
2.04
0.96
1.74
3.05
3.00
f1 (ppm)
p-Tol
N
N
Me
O
O
O
S
8.68
8.67
7.99
7.97
7.72
7.70
7.47
7.45
7.45
7.39
7.37
7.31
7.29
7.27
7.19
7.15
7.13
6.74
5.12
2.45
2.17
0.00

3t


f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
p-Tol
O
O
S
N
N
Me
O
3t
170.66
154.79
152.22
149.16
144.59
138.12
135.86
135.46
134.97
132.73
132.16
130.15
129.87
129.04
128.23
128.19
127.47
125.05
47.88
22.23
21.67


2.00
1.83
3.01
0.94
2.01
2.01
1.96
0.99
3.00
f1 (ppm)
Ph
Ts
Ph
4
7.48
7.46
7.37
7.35
7.35
7.33
7.33
7.33
7.32
7.31
7.31
7.30
7.28
7.26
7.25
7.25
7.24
7.23
7.19
7.17
7.17
7.13
7.11
7.10
7.08
6.99
6.99
2.34
-0.00


154.82
143.92
139.30
138.71
135.70
130.39
129.89
129.49
129.08
128.98
128.71
128.32
127.93
127.79
21.69
Ph
Ts
Ph
4
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


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
2.72
6.26
1.25
1.90
0.95
2.12
0.98
0.82
0.83
3.00
3.07
OMe
O
O
S
p-Tol
N
F3C
O
6
7.77
7.75
7.55
7.55
7.52
7.51
7.50
7.48
7.32
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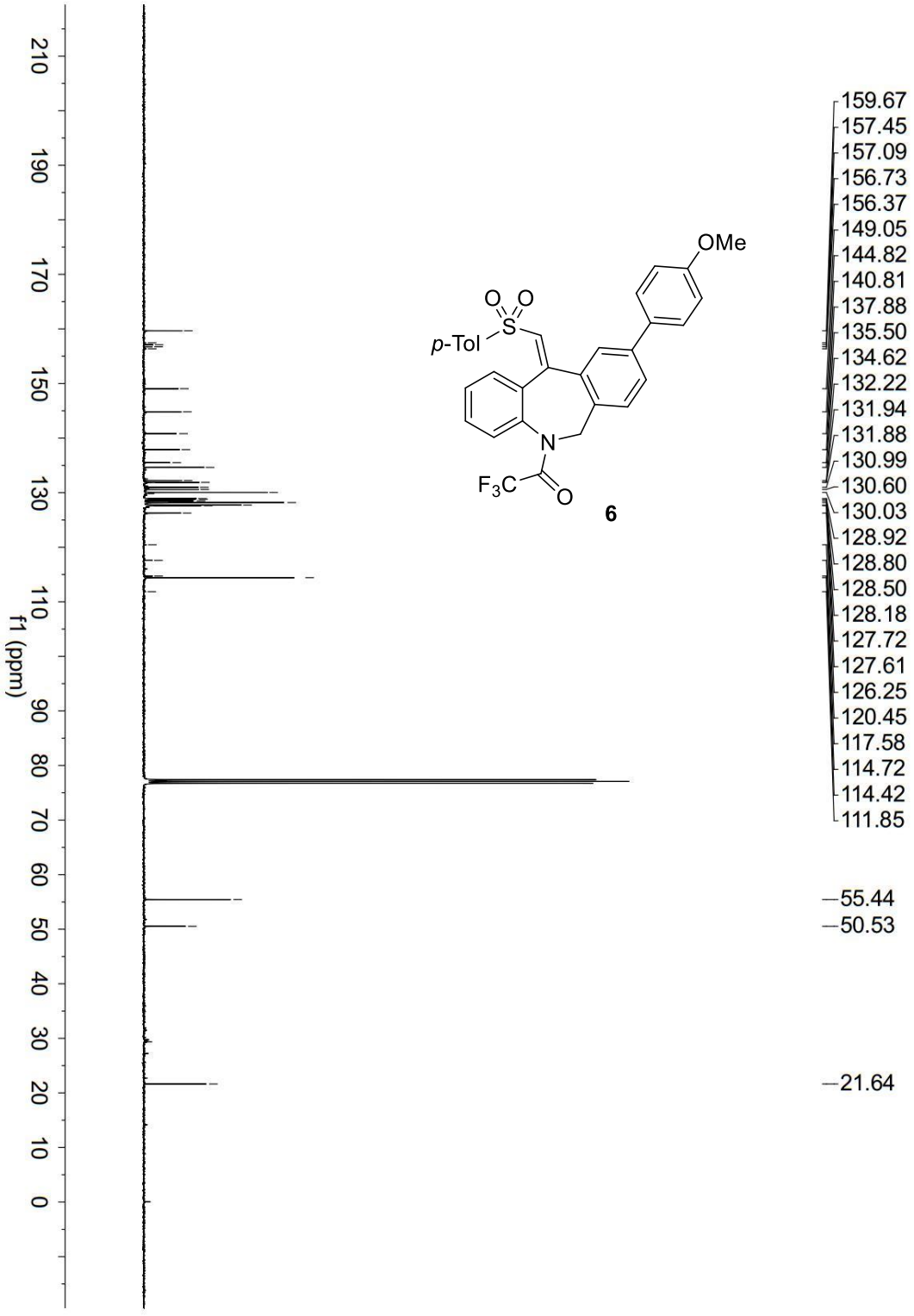
7.00
6.98
6.77
5.99
5.95
4.38
4.34
3.86
2.41
0.00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170
150
130
110
90
80
70
60
50
40
30
20
10
0
OMe
O
O
S
p-Tol
N
F3C
O
6
159.67
157.45
157.09
156.73
156.37
149.05
144.82
140.81
137.88
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132.22
131.94
131.88
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130.60
130.03
128.92
128.80
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114.42
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50.53
21.64

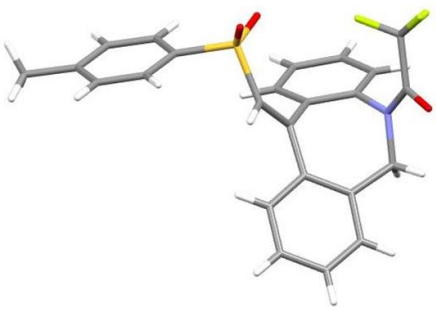

Table 1. Crystal data and structure refinement for **3a**.

Identification code	ga_200108e_a	
Empirical formula	C24 H18 F3 N O3 S	
Formula weight	457.45	
Temperature	293(2) K	
Wavelength	1.34138 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.1482(9) Å	α = 98.241(3)°.
	b = 12.6677(13) Å	β = 97.455(3)°.
	c = 19.356(2) Å	γ = 99.310(3)°.
Volume	2163.7(4) $Å^3$	
Z	4	
Density (calculated)	1.404 Mg/m^3	
Absorption coefficient	1.168 mm^{-1}	
F(000)	944	
Crystal size	0.400 x 0.350 x 0.220 mm^3	
Theta range for data collection	4.065 to 58.498°.	
Index ranges	-11<=h<=11, -16<=k<=16, -24<=l<=24	
Reflections collected	80905	
Independent reflections	9246 [R(int) = 0.0495]	
Completeness to theta = 53.594°	99.1 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.752 and 0.668
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9246 / 39 / 607
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0575, wR2 = 0.1786
R indices (all data)	R1 = 0.0598, wR2 = 0.1815
Extinction coefficient	n/a
Largest diff. peak and hole	0.630 and -0.469 e.$Å^{-3}$