Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Direct vicinal difunctionalization of alkynes through trifluoromethylation and aminosulfonylation via insertion of sulfur dioxide under catalyst-free conditions

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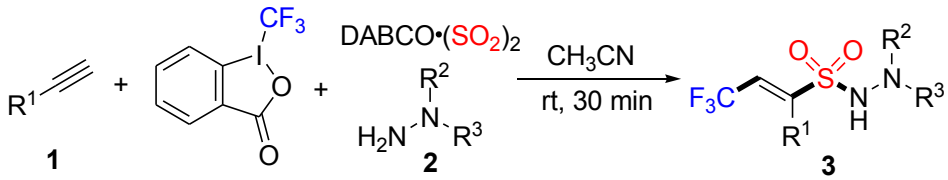
Supporting Information

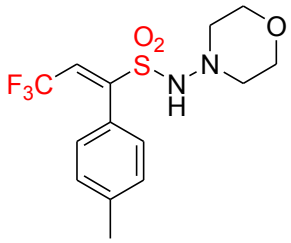
General experimental methods:

Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32-63μm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25-35 °C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX - 400 spectromete operating at 400 MHz, 376 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 four-component reaction of Togni's reagent, alkynes, sulfur dioxide, and hydrazines:

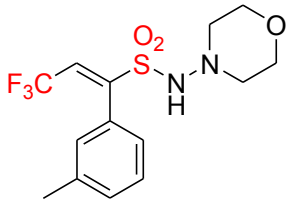


Alkyne **1** (0.2 mmol) was combined with Togni reagent (0.3mmol) and DABSO (0.16 mmol) in a tube. The tube was evacuated and backfilled with N_2 three times before the addition of CH_3CN (4.0 mL). Subsequently, hydrazine **2** (1.5 equiv.) was added dropwisely to the solution. After completion of reaction as indicated by TLC, the mixture was washed with saturated sodium bicarbonate and brine. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate three times. The combined organic phases were dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuo, and the residue was purified by flash column chromatograph (EtOAc/*n*-hexane, 1:4) to give the desired product **3**.



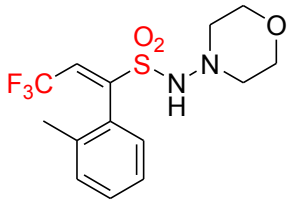
(Z)-3,3,3-trifluoro-N-morpholino-1-p-tolylprop-1-ene-1-sulfonamide (**3a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.99 (q, *J* = 7.4 Hz, 1H), 5.29 (s, 1H), 3.68 (t, *J* = 4.8 Hz, 4H), 2.74 (t, *J* = 4.4 Hz, 4H), 2.39 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.99 (d, *J* = 7.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9 (d, *J* = 5.1 Hz), 140.7, 129.5 (d, *J* = 1.4 Hz), 129.0, 126.8 (q, *J* = 35.7 Hz), 125.3, 121.5 (q, *J* = 273.0 Hz), 66.5, 57.2, 21.4 ; HRMS calcd for $C_{14}H_{17}F_3N_2O_3S$ Na ($M+Na^+$): 373.0804, found: 373.0801.



(Z)-3,3,3-trifluoro-N-morpholino-1-m-tolylprop-1-ene-1-sulfonamide (**3b**)

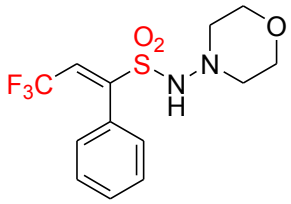
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 2H), 7.23 (s, 1H), 7.18 (d, *J* = 6.7 Hz, 1H), 6.98 (q, *J* = 7.3 Hz, 1H), 5.51 (s, 1H), 3.66 (t, *J* = 4.6 Hz, 4H), 2.72 (t, *J* = 4.4 Hz, 4H), 2.38 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.05 (d, *J* = 7.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0 (d, *J* = 5.2 Hz), 138.0, 131.1, 130.0 (d, *J* = 1.3 Hz), 128.3, 128.1, 126.8 (d, *J* = 1.5 Hz)126.5 (q, *J* = 35.7 Hz) 121.4 (q, *J* = 273.1 Hz), 66.4, 57.1, 21.3; HRMS calcd for $C_{14}H_{18}F_3N_2O_3S$ ($M+H^+$): 351.0985, found: 351.0988.



(Z)-3,3,3-trifluoro-N-morpholino-1-o-tolylprop-1-ene-1-sulfonamide (**3c**)

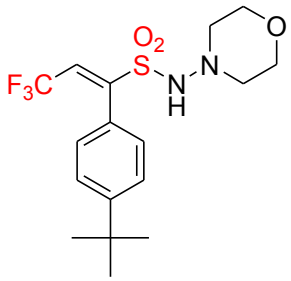
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (td, *J* = 7.6, 1.1 Hz, 1H), 7.27 (d, *J* = 6.0 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.0 Hz, 1H), 7.02 (q, *J* = 7.1 Hz, 1H), 5.62 (s, 1H), 3.75 –

3.64 (m, 4H), 2.84 – 2.74 (m, 4H), 2.34 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.25 (d, *J* = 7.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1 (d, *J* = 5.1 Hz), 138.0, 130.4, 130.1, 129.2, 128.0, 127.4 (q, *J* = 35.5 Hz), 125.3, 121.3 (q, *J* = 273.1 Hz), 66.5, 57.3, 20.0; HRMS calcd for $C_{14}H_{18}F_3N_2O_3S$ ($M+H^+$): 351.0985, found: 351.0997.



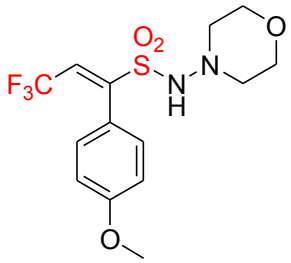
(Z)-3,3,3-trifluoro-N-morpholino-1-phenylprop-1-ene-1-sulfonamide (**3d**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 1H), 7.42 (d, *J* = 4.5 Hz, 4H), 7.01 (q, *J* = 7.3 Hz, 1H), 5.43 (s, 1H), 3.66 (t, *J* = 4.6 Hz, 4H), 2.73 (t, *J* = 4.6 Hz, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.03 (d, *J* = 7.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8 (d, *J* = 5.2 Hz), 130.3, 129.6 (d, *J* = 1.5 Hz), 128.4 , 128.2, 126.9 (q, *J* = 35.8 Hz), 121.4 (q, *J* = 273.2 Hz), 66.5, 57.2; HRMS calcd for $C_{13}H_{16}F_3N_2O_3S$ ($M+H^+$): 337.0828, found: 337.0819.



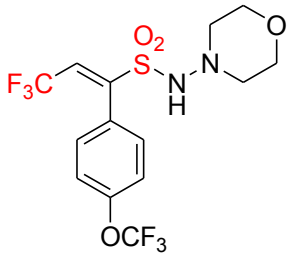
(Z)-1-(4-tert-butylphenyl)-3,3,3-trifluoro-N-morpholinoprop-1-ene-1-sulfonamide (**3e**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 6.99 (q, *J* = 7.4 Hz, 1H), 5.30 (s, 1H), 3.66 (t, *J* = 4.6 Hz, 4H), 2.72 (t, *J* = 4.6 Hz, 4H), 1.33 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.94 (d, *J* = 7.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 149.9 (d, *J* = 5.1 Hz), 129.5 (d, *J* = 1.4 Hz), 126.5 (q, *J* = 35.7 Hz), 125.2, 121.5 (q, *J* = 273.0 Hz), 66.5, 57.2, 34.8, 31.2; HRMS calcd for $C_{17}H_{24}F_3N_2O_3S$ ($M+H^+$): 393.1454, found: 393.1458.



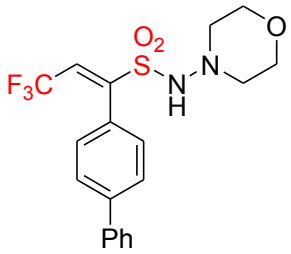
(Z)-3,3,3-trifluoro-1-(4-methoxyphenyl)-N-morpholinoprop-1-ene-1-sulfonamide (**3f**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.7 Hz, 2H), 6.97 (q, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.34 (s, 1H), 3.84 (s, 3H), 3.68 (t, *J* = 4.6 Hz, 4H), 2.73 (s, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.96 (d, *J* = 7.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 149.6 (d, *J* = 4.9 Hz), 131.2 (d, *J* = 1.4 Hz), 126.5 (q, *J* = 35.7 Hz), 121.5 (q, *J* = 272.0 Hz); 120.2, 113.8, 66.5, 57.2, 55.3; HRMS calcd for $C_{14}H_{18}F_3N_2O_4S$ ($M+H^+$): 367.0934, found: 367.0935.



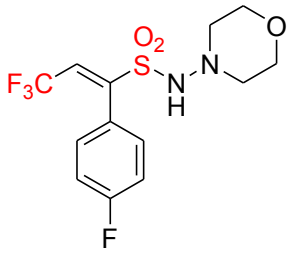
(Z)-3,3,3-trifluoro-N-morpholino-1-(4-(trifluoromethoxy)phenyl)prop-1-ene-1-sulfon amide (**3g**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.04 (q, *J* = 7.3 Hz, 1H), 5.26 (s, 1H), 3.67 (t, *J* = 4.6 Hz, 4H), 2.75 (t, *J* = 4.6 Hz, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.74 (s, 3F), -58.05 (d, *J* = 7.2 Hz, 3F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 148.6 (d, *J* = 5.1 Hz), 131.5, 130.9, 128.8, 127.6 (q, *J* = 35.9 Hz), 126.9, 121.3 (q, *J* = 271.0 Hz), 120.4, 66.4, 57.3; HRMS calcd for $C_{14}H_{15}F_6N_2O_4S$ ($M+H^+$): 421.0651, found: 421.0655.



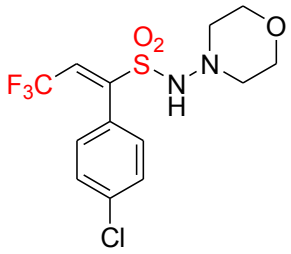
(E)-1-([1,1'-biphenyl]-4-yl)-3,3,3-trifluoro-N-morpholinoprop-1-ene-1-sulfonamide (**3h**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 7.1 Hz, 2H), 7.51 – 7.45 (m, 4H), 7.42 – 7.37 (m, 1H), 7.04 (q, *J* = 7.3 Hz, 1H), 5.35 (s, 1H), 3.68 (t, *J* = 4.6 Hz, 4H), 2.76 (t, *J* = 4.4 Hz, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.89 (d, *J* = 7.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6 (d, *J* = 5.0 Hz), 143.2, 139.7, 130.15, 128.9, 128.1, 127.1, 126.9, 126.5 (q, *J* = 35.7 Hz), 121.5 (q, *J* = 273.2 Hz), 66.5, 57.3; HRMS calcd for $C_{19}H_{20}F_3N_2O_3S$ ($M+H^+$): 413.1141, found: 413.1144.



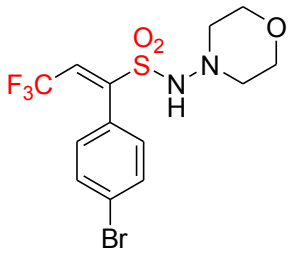
(Z)-3,3,3-trifluoro-1-(4-fluorophenyl)-N-morpholinoprop-1-ene-1-sulfonamide (**3i**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 2H), 7.12 (t, *J* = 8.6 Hz, 2H), 7.01 (q, *J* = 7.3 Hz, 1H), 5.57 (s, 1H), 3.67 (t, *J* = 4.6 Hz, 4H), 2.74 (t, *J* = 4.4 Hz, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.07 (d, *J* = 7.3 Hz, 3F), -109.33 – 109.40 (m, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8 (d, *J* = 251.6 Hz), 148.9 (d, *J* = 5.2 Hz), 131.8 (d, *J* = 7.2 Hz), 127.4 (q, *J* = 35.7 Hz), 124.3 (d, *J* = 3.4 Hz), 121.3 (q, *J* = 273.2 Hz), 115.6 (d, *J* = 22.0 Hz), 66.4, 57.2; HRMS calcd for $C_{13}H_{15}F_4N_2O_3S$ ($M+H^+$): 355.0734, found: 355.0727.



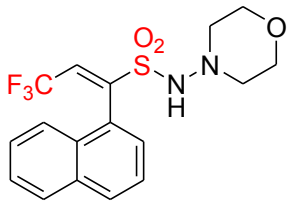
(Z)-1-(4-chlorophenyl)-3,3,3-trifluoro-N-morpholinoprop-1-ene-1-sulfonamide (**3j**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.03 (q, *J* = 7.3 Hz, 1H), 5.31 (s, 1H), 3.69 (t, *J* = 4.6 Hz, 4H), 2.75 (t, *J* = 4.6 Hz, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.03 (d, *J* = 7.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8 (d, *J* = 5.0 Hz), 136.8, 131.0 (d, *J* = 1.5 Hz), 128.6, 127.5 (q, *J* = 35.9 Hz), 126.8, 121.3 (q, *J* = 273.3 Hz), 66.5, 57.3; HRMS calcd for $C_{13}H_{15}F_4N_2O_3S$ ($M+H^+$): 355.0734, found: 355.0727.



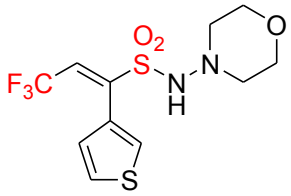
(Z)-1-(4-bromophenyl)-3,3,3-trifluoro-N-morpholinoprop-1-ene-1-sulfonamide (**3k**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.01 (q, *J* = 7.3 Hz, 1H), 5.60 (s, 1H), 3.67 (t, *J* = 4.4 Hz, 4H), 2.73 (s, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.02 (d, *J* = 7.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8 (d, *J* = 5.1 Hz), 131.6, 131.1 (d, *J* = 1.4 Hz), 127.4 (q, *J* = 35.9 Hz), 127.3, 125.0, 121.2 (q, *J* = 273.3 Hz), 66.4, 57.1; HRMS calcd for $C_{13}H_{15}BrF_3N_2O_3S$ ($M+H^+$): 414.9933, found: 414.9924.



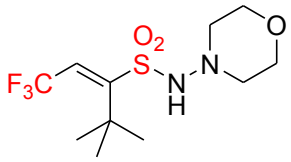
(Z)-3,3,3-trifluoro-N-morpholino-1-(naphthalen-1-yl)prop-1-ene-1-sulfonamide (**3l**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.94 (m, 1H), 7.89 – 7.86 (m, 2H), 7.56 – 7.52 (m, 2H), 7.50 – 7.49 (m, 2H), 7.27 (q, *J* = 7.1 Hz, 1H), 5.24 (s, 1H), 3.65 – 3.55 (m, 4H), 2.59 (s, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.17 (d, *J* = 7.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0 (d, *J* = 4.9 Hz), 133.2, 131.6, 130.7, 128.6 (q, *J* = 35.8 Hz), 128.4, 127.8, 126.9, 126.5, 125.8, 125.3, 124.6, 121.2 (q, *J* = 273.3 Hz), 66.4, 57.3; HRMS calcd for $C_{17}H_{18}F_3N_2O_3S$ ($M+H^+$): 387.0985, found: 387.0977.



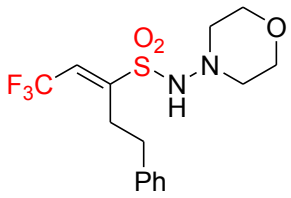
(Z)-3,3,3-trifluoro-N-morpholino-1-(thiophen-3-yl)prop-1-ene-1-sulfonamide (**3m**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.65 (m, 1H), 7.39 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.23 (d, *J* = 4.9 Hz, 1H), 6.98 (q, *J* = 7.5 Hz, 1H), 5.60 (s, 1H), 3.66 (t, *J* = 4.6 Hz, 4H), 2.69 (t, *J* = 4.4 Hz, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.11 (d, *J* = 7.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2 (d, *J* = 5.4 Hz), 128.7, 127.5, 126.4 (q, *J* = 36.1 Hz), 125.9, 121.5 (q, *J* = 272.8 Hz), 66.5, 57.1; HRMS calcd for $C_{11}H_{14}F_3N_2O_3S_2$ ($M+H^+$): 343.0392, found: 343.0393.



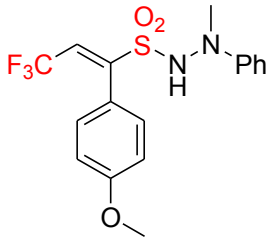
(Z)-1,1,1-trifluoro-4,4-dimethyl-N-morpholinopent-2-ene-3-sulfonamide (**3n**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (q, *J* = 9.3 Hz, 1H), 5.69 (s, 1H), 3.72 (t, *J* = 4.6 Hz, 4H), 2.85 (t, *J* = 4.4, 4H), 1.41 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -55.44 (d, *J* = 9.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (d, *J* = 5.7 Hz), 123.8 (q, *J* = 38.3 Hz), 121.2 (q, *J* = 272.0 Hz), 66.5, 56.9, 39.0, 30.0; HRMS calcd for $C_{11}H_{20}F_3N_2O_3S$ ($M+H^+$): 317.1141, found: 317.1148.



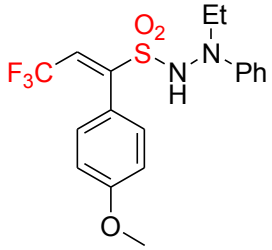
(Z)-1,1,1-trifluoro-N-morpholino-5-phenylpent-2-ene-3-sulfonamide (**3o**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.25 – 7.22 (m, 3H), 6.82 (q, *J* = 8.0 Hz, 1H), 5.53 (s, 1H), 3.82 – 3.59 (m, 4H), 3.00 – 2.95 (m, 2H), 2.86 – 2.80 (m, 6H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.56 (d, *J* = 7.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9 (d, *J* = 5.2 Hz), 140.19, 128.7, 128.3, 127.2 (q, *J* = 35.9 Hz), 126.6, 122.0 (q, *J* = 273.1 Hz), 66.5, 57.3, 35.9, 30.4; HRMS calcd for $C_{15}H_{20}F_3N_2O_3S$ ($M+H^+$): 365.1141, found: 365.1139.



(Z)-3,3,3-trifluoro-1-(4-methoxyphenyl)-N'-methyl-N'-phenylprop-1-ene-1-sulfonohydrazide (**3p**)

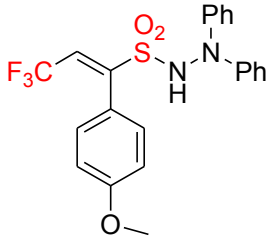
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.8 Hz, 2H), 7.27 – 7.23 (m, 2H), 6.99 – 6.94 (m, 2H), 6.92 – 6.86 (m, 4H), 5.99 (s, 1H), 3.83 (s, 3H), 3.12 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.03 (d, *J* = 7.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 150.1 (d, *J* = 5.2 Hz), 149.6, 131.5 (d, *J* = 1.5 Hz), 129.1, 126.6 (q, *J* = 35.7 Hz), 121.9, 126.4 (q, *J* = 271.0 Hz), 119.7, 115.4, 113.7, 55.3, 44.5; HRMS calcd for $C_{17}H_{18}F_3N_2O_3S$ ($M+H^+$): 387.0985, found: 387.0975.



(Z)-N'-ethyl-3,3,3-trifluoro-1-(4-methoxyphenyl)-N'-phenylprop-1-ene-1-sulfonohydr

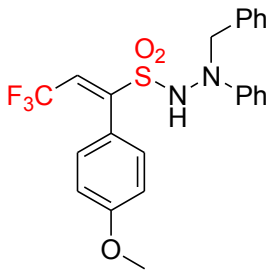
azide (**3q**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 7.00 (t, *J* = 7.3 Hz, 1H), 6.96 – 6.88 (m, 3H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.20 (s, 1H), 3.82 (s, 3H), 3.51 (q, *J* = 7.1 Hz, 2H), 1.01 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.12 (d, *J* = 7.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 150.0 (d, *J* = 5.4 Hz), 147.8, 131.5 (d, *J* = 1.4 Hz), 129.1, 126.5 (q, *J* = 35.6 Hz), 122.4, 121.4 (q, *J* = 271.0 Hz), 119.7, 117.2, 113.6, 55.3, 51.0, 9.7; HRMS calcd for $C_{18}H_{20}F_3N_2O_3S$ ($M+H^+$): 401.1141, found: 401.1140.



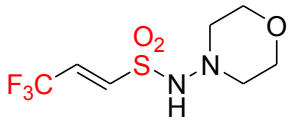
(Z)-3,3,3-trifluoro-1-(4-methoxyphenyl)-N',N'-diphenylprop-1-ene-1-sulfonohydrazide (**3r**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 4H), 7.20 – 7.16 (m, 2H), 7.07 – 7.04 (m, 4H), 6.89 (q, *J* = 7.3 Hz, 1H), 6.71 – 6.63 (m, 5H), 3.78 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.49 (d, *J* = 7.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 149.9 (d, *J* = 5.1 Hz), 146.7, 131.3 (d, *J* = 1.4 Hz), 129.5, 126.8 (q, *J* = 35.7 Hz), 124.8, 121.4, 121.1 (q, *J* = 272.0 Hz), 119.2, 113.4, 55.2; HRMS calcd for $C_{22}H_{20}F_3N_2O_3S$ ($M+H^+$): 449.1141, found: 449.1140.



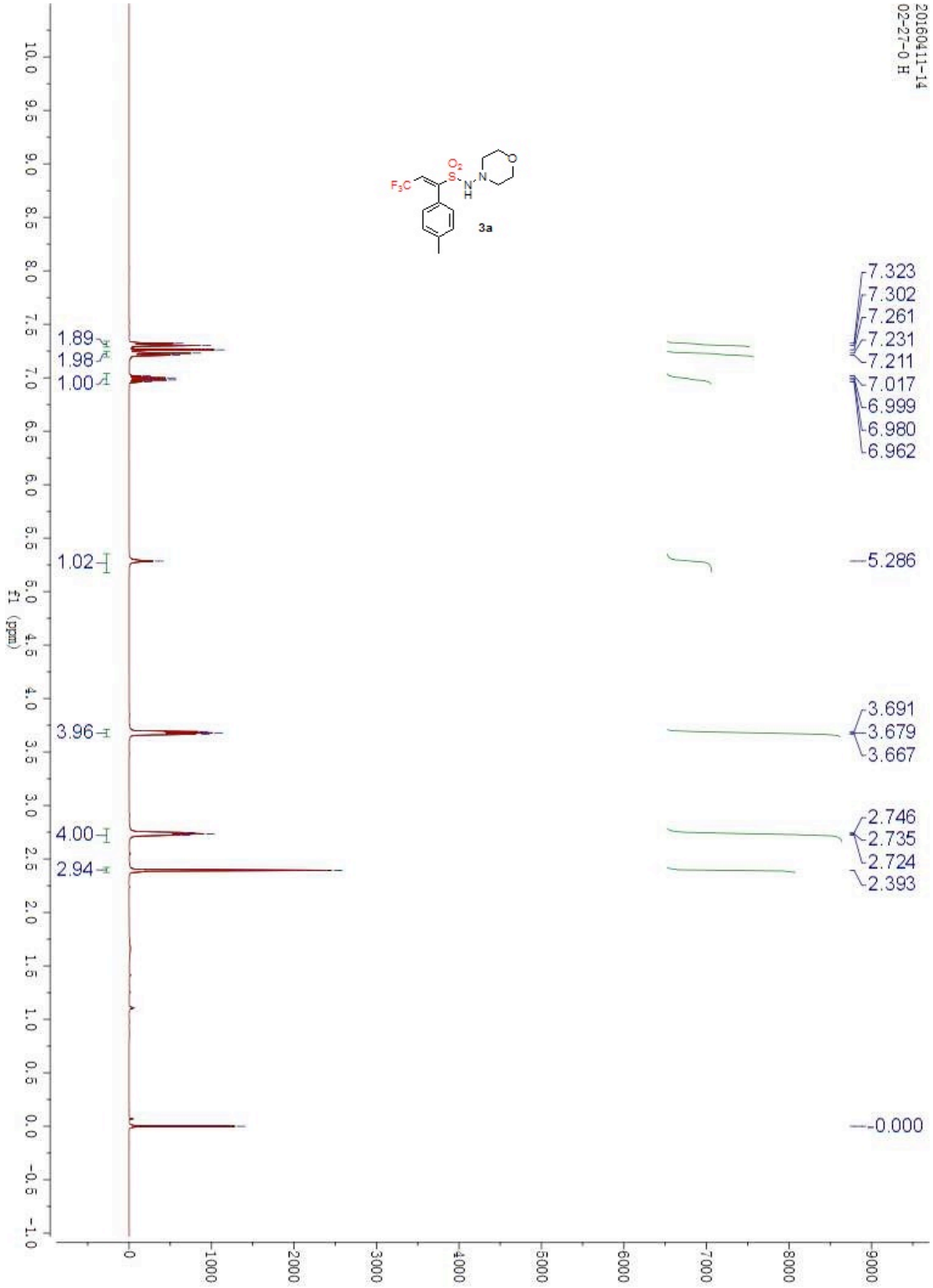
(Z)-N'-benzyl-3,3,3-trifluoro-1-(4-methoxyphenyl)-N'-phenylprop-1-ene-1-sulfonohydrazide (**3s**)

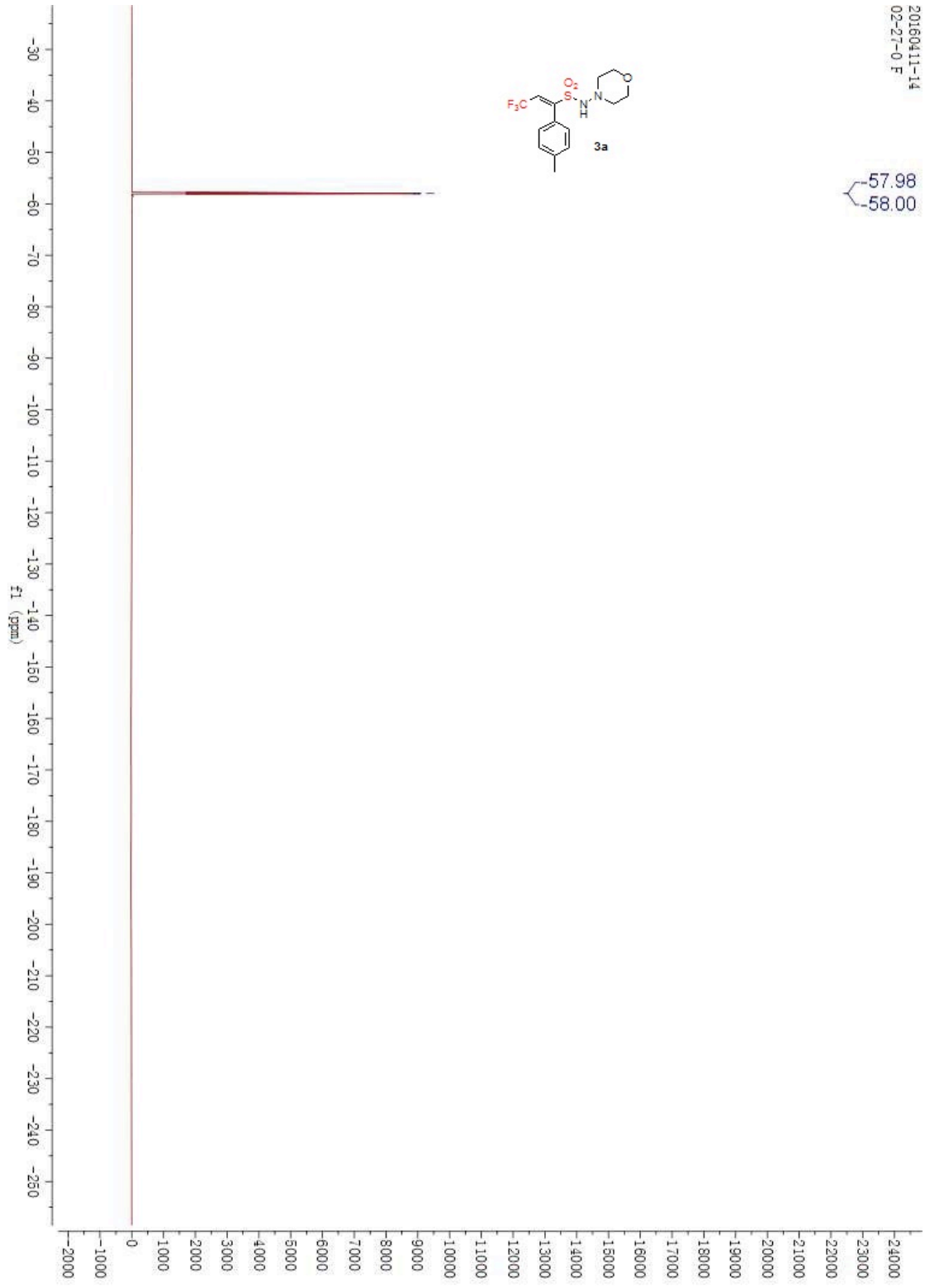
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 5H), 7.11 (d, *J* = 8.7 Hz, 2H), 7.06 – 7.02 (m, 2H), 6.99 (t, *J* = 7.3 Hz, 1H), 6.91 (q, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 5.97 (s, 1H), 4.63 (s, 2H), 3.79 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.13 (d, *J* = 7.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 145.0 (d, *J* = 4.7 Hz), 148.6, 133.9, 131.4 (d, *J* = 1.4 Hz), 129.0, 128.8, 128.6, 128.2, 126.6 (q, *J* = 35.7 Hz), 124.4 (q, *J* = 272.0 Hz), 122.3, 119.7, 117.2 (d, *J* = 16.3 Hz), 113.5, 60.9, 55.2; HRMS calcd for $C_{23}H_{22}F_3N_2O_3S$ ($M+H^+$): 463.1298, found: 463.1298.

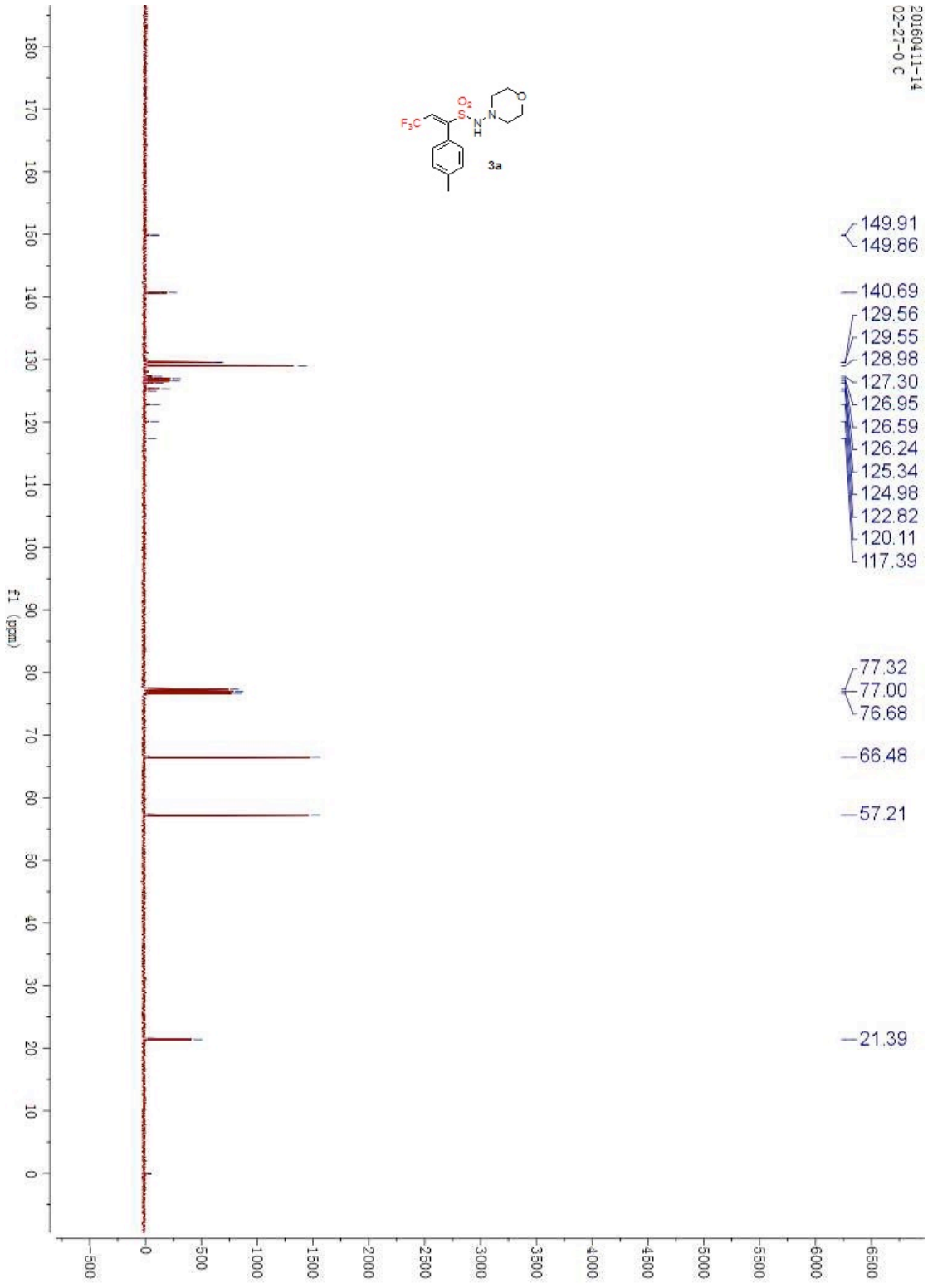


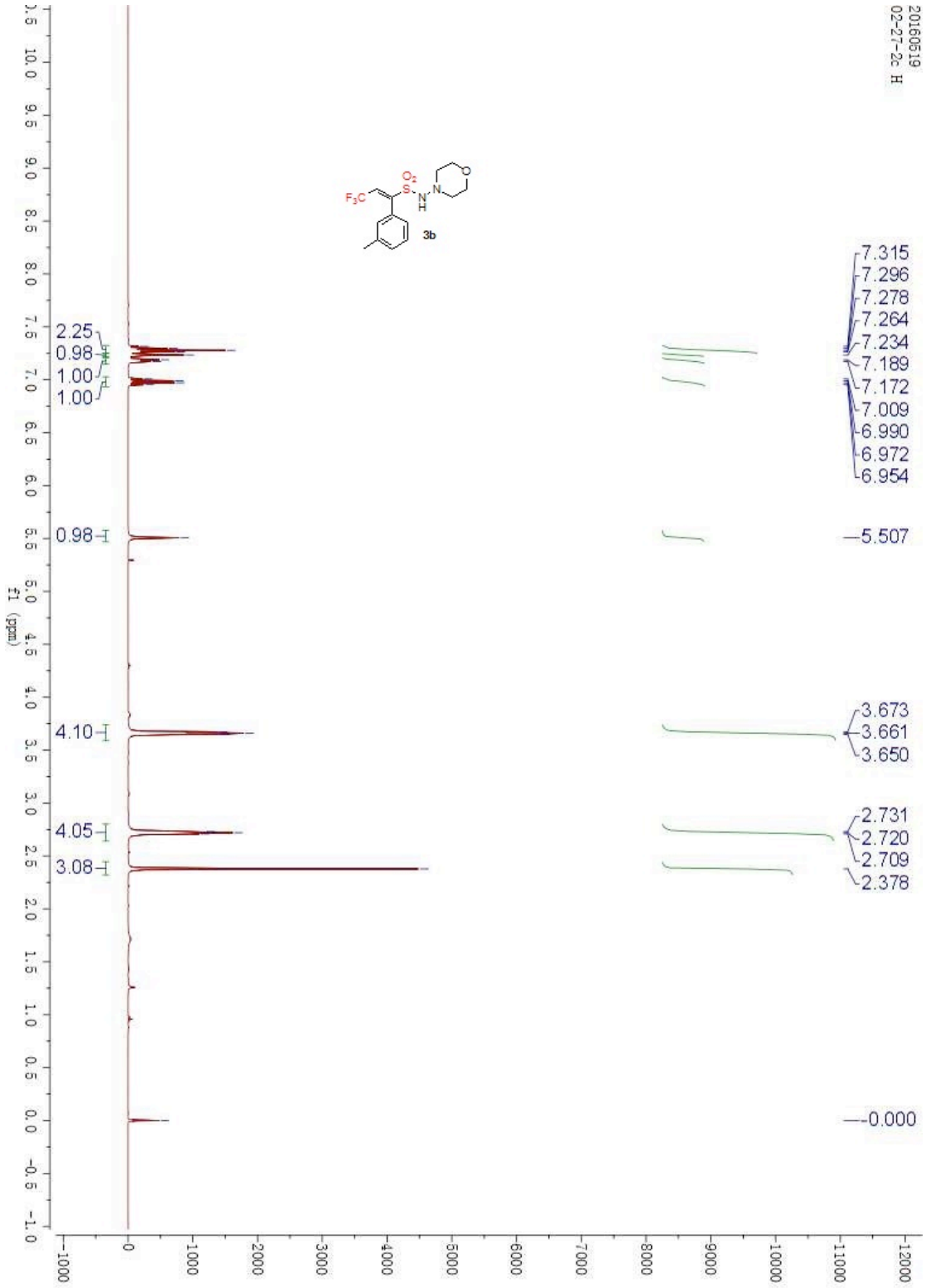
3,3,3-trifluoro-N-morpholinoprop-1-ene-1-sulfonamide (**3t**)

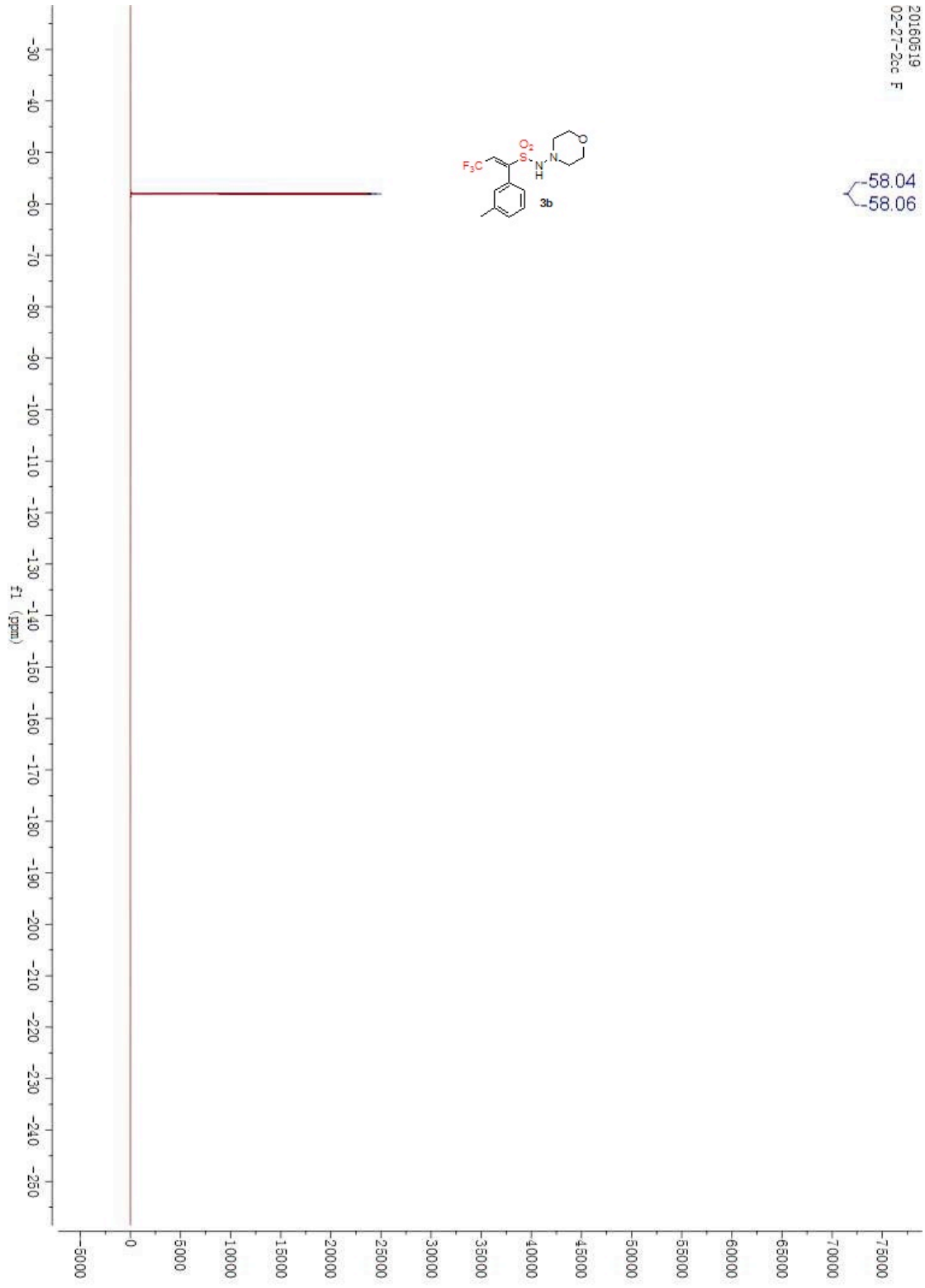
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (dq, *J* = 15.2, 2.0, 1H), 6.79 (dq, *J* = 15.3, 6.1 Hz, 1H), 6.06 (s, 1H), 3.75 (t, *J* = 4.6, 4H), 2.86 (t, *J* = 4.6, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.11 (dd, *J* = 6.1, 1.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.1 (q, *J* = 6.0 Hz), 130.2 (q, *J* = 36.5 Hz), 121.2 (q, *J* = 271.7 Hz), 66.4, 57.2;


20160411-14
02-27-0 H
3a
7.323
7.302
7.261
7.231
7.211
7.017
6.999
6.980
6.962
5.286
3.691
3.679
3.667
2.746
2.735
2.724
2.393
-0.000
1.89
1.98
1.00
1.02
3.96
4.00
2.94
f1 (ppm)


20160411-14
02-27-0 F
-57.98
-58.00
3a
f1 (ppm)


20160411-14
02-27-0 C
3a
149.91
149.86
140.69
129.56
129.55
128.98
127.30
126.95
126.59
126.24
125.34
124.98
122.82
120.11
117.39
77.32
77.00
76.68
66.48
57.21
21.39
f1 (ppm)


20160619
02-27-2c H
3b
7.315
7.296
7.278
7.264
7.234
7.189
7.172
7.009
6.990
6.972
6.954
5.507
3.673
3.661
3.650
2.731
2.720
2.709
2.378
0.000
2.25
0.98
1.00
1.00
0.98
4.10
4.05
3.08
f1 (ppm)


20160619
02-27-2cc F
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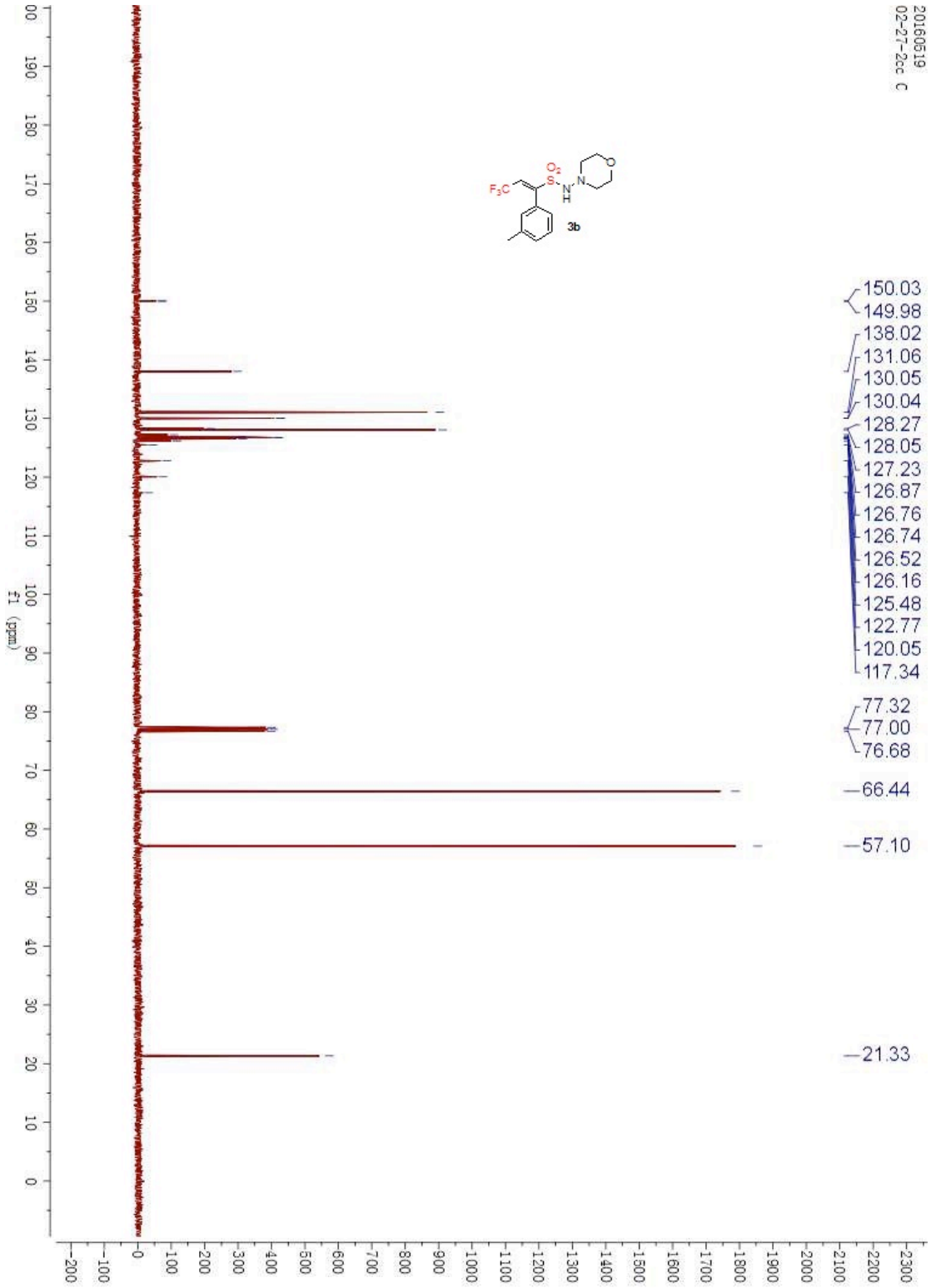
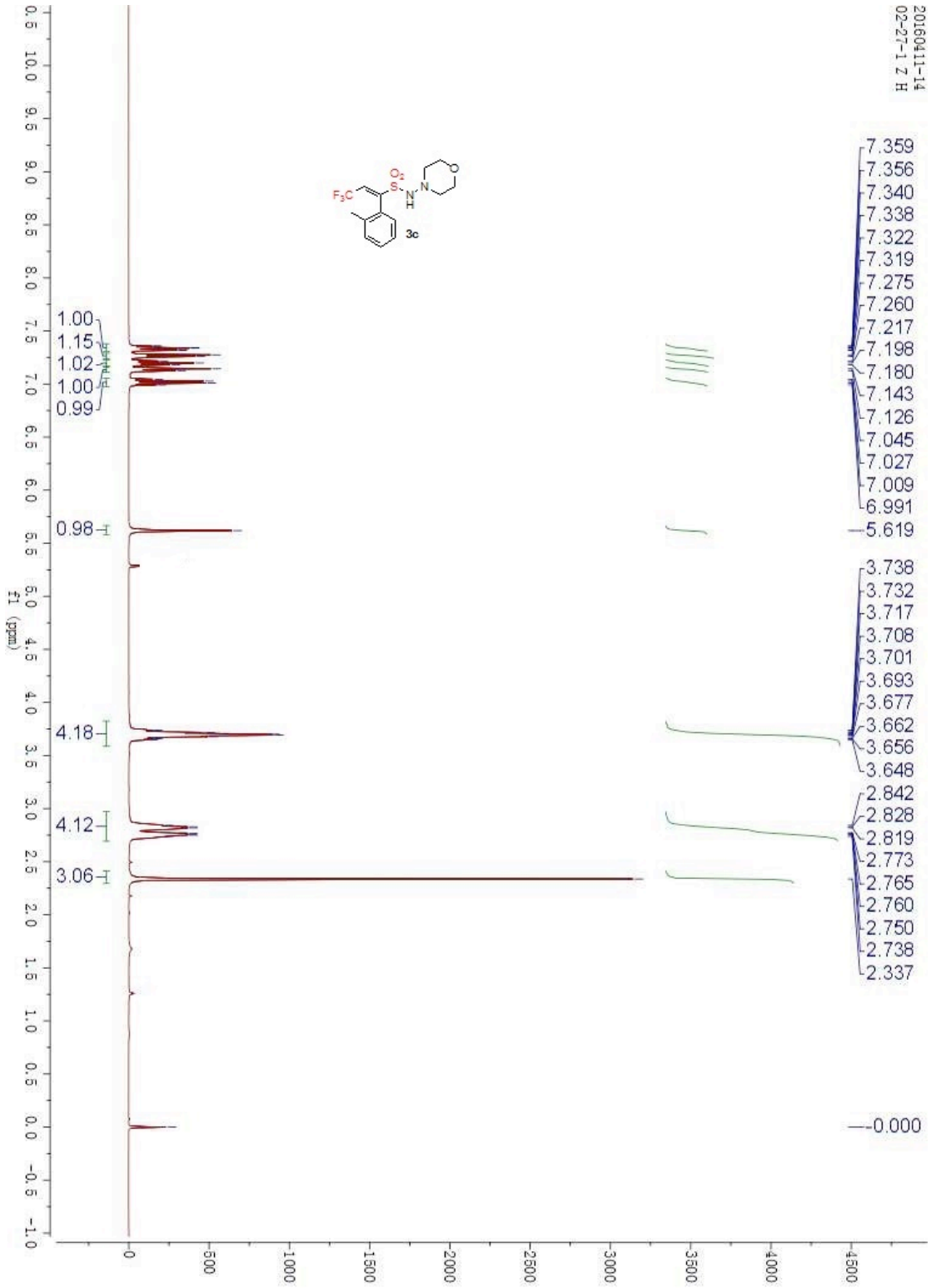
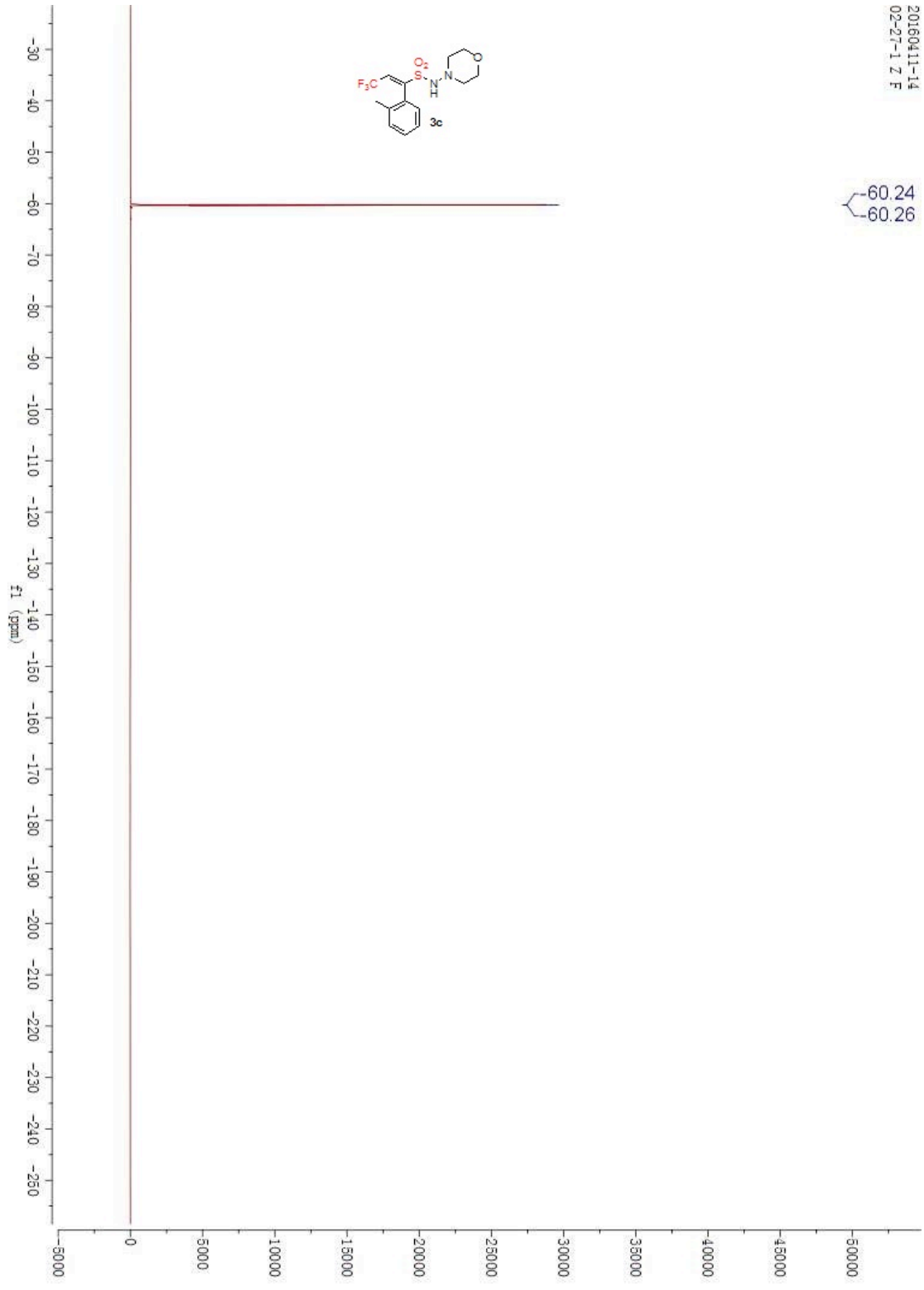
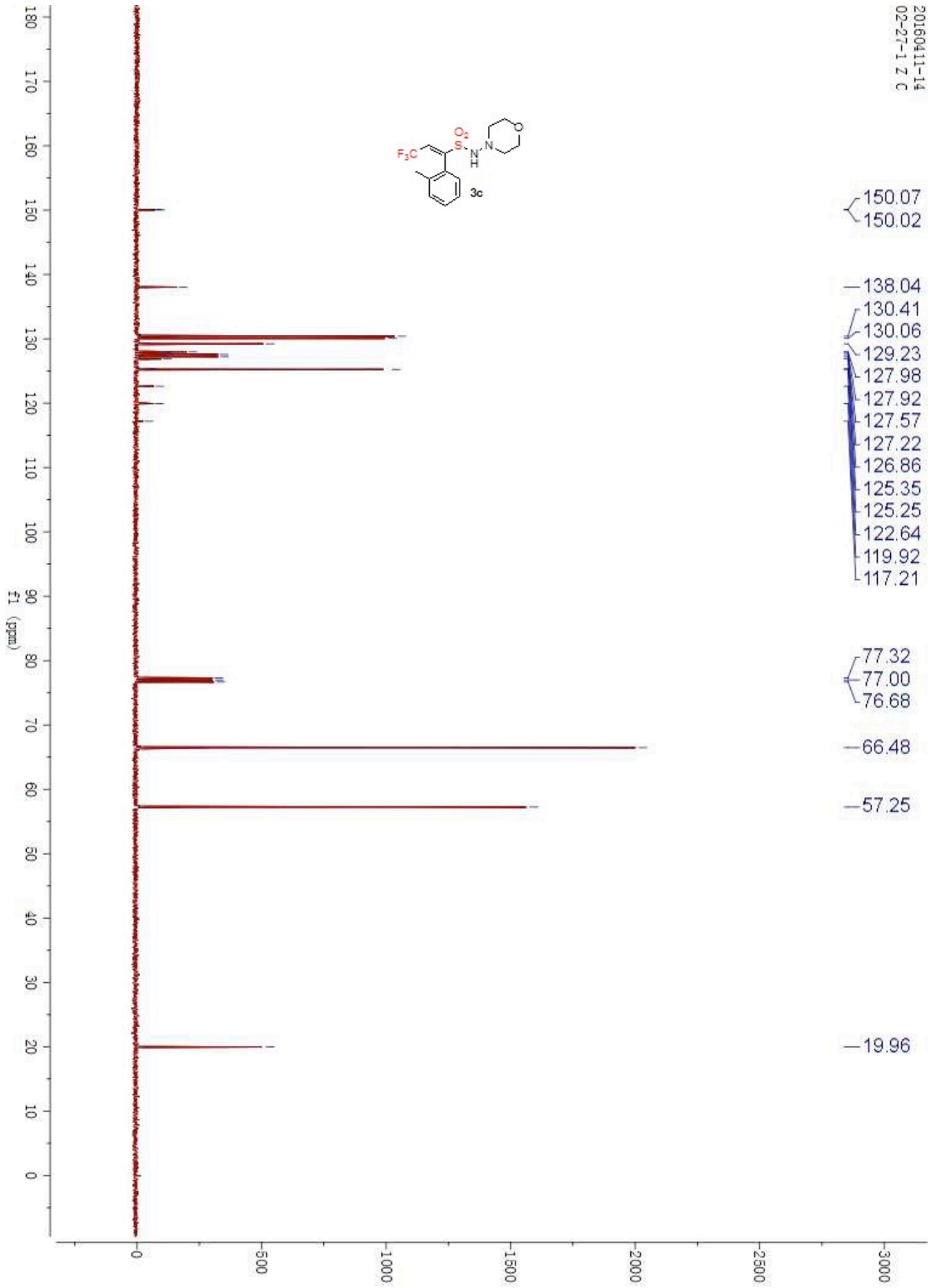
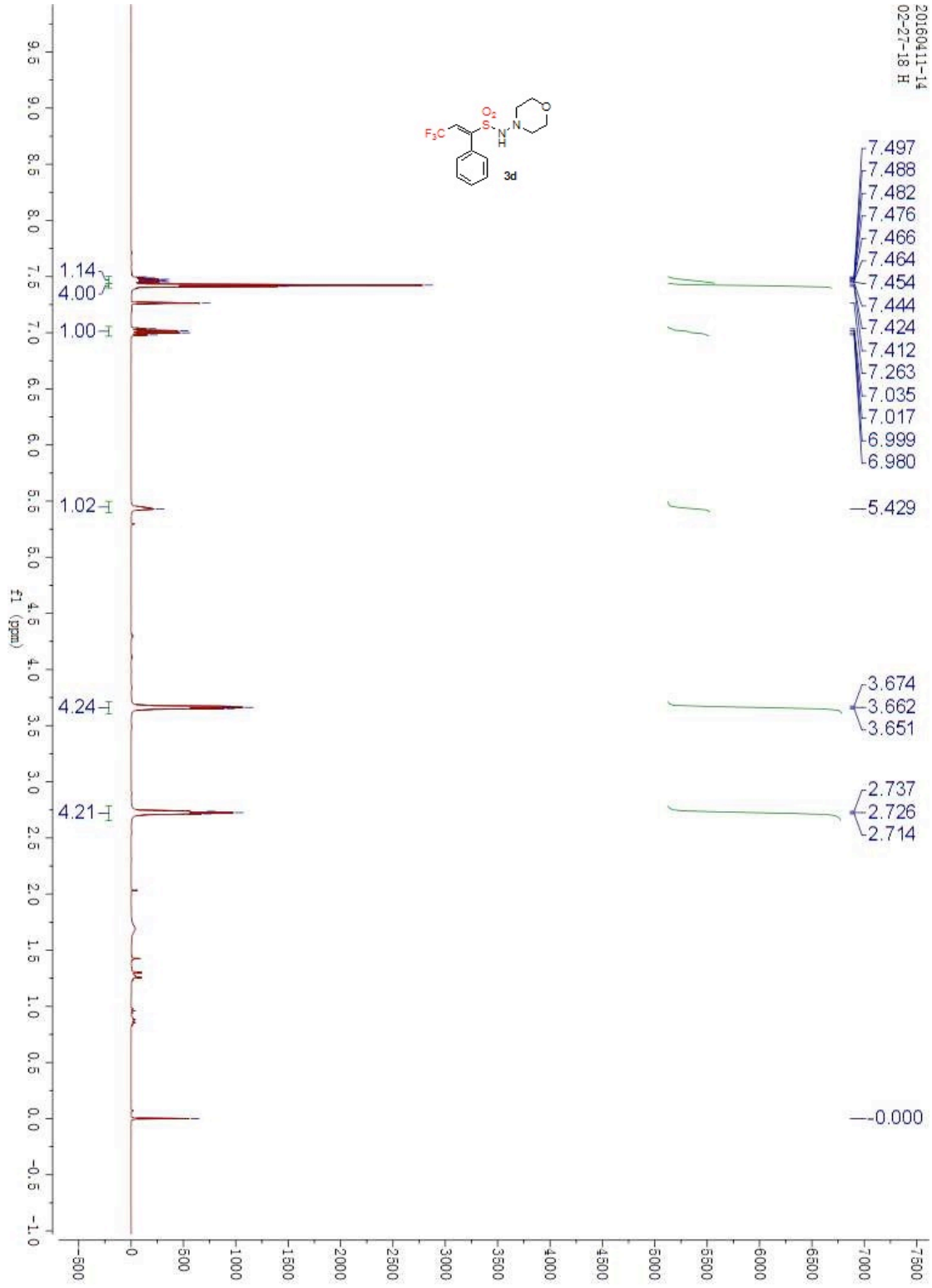
-58.06
3b
f1 (ppm)

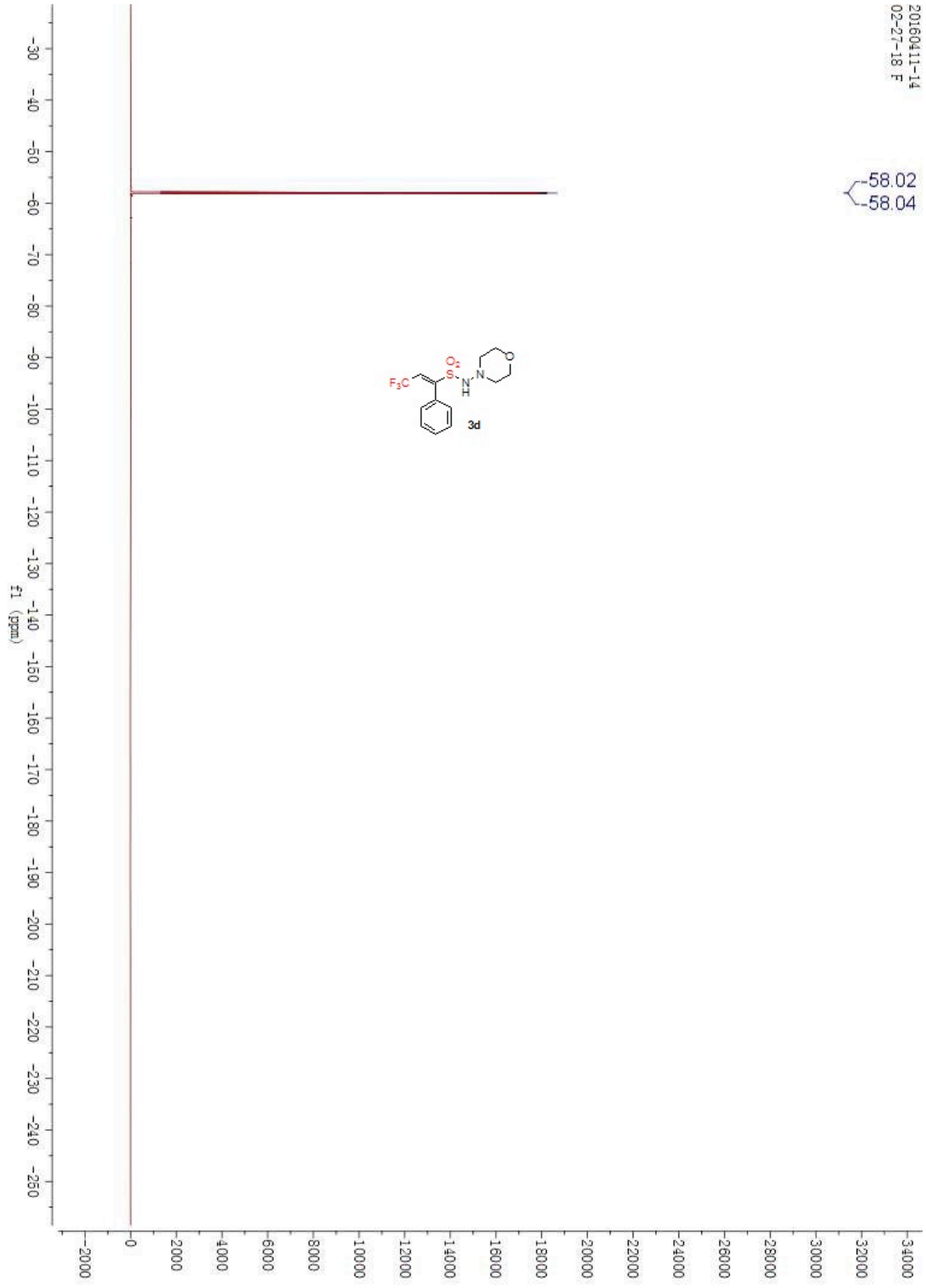

20160619
02-27-2cc C
3b
150.03
149.98
138.02
131.06
130.05
130.04
128.27
128.05
127.23
126.87
126.76
126.74
126.52
126.16
125.48
122.77
120.05
117.34
77.32
77.00
76.68
66.44
57.10
21.33
f1 (ppm)

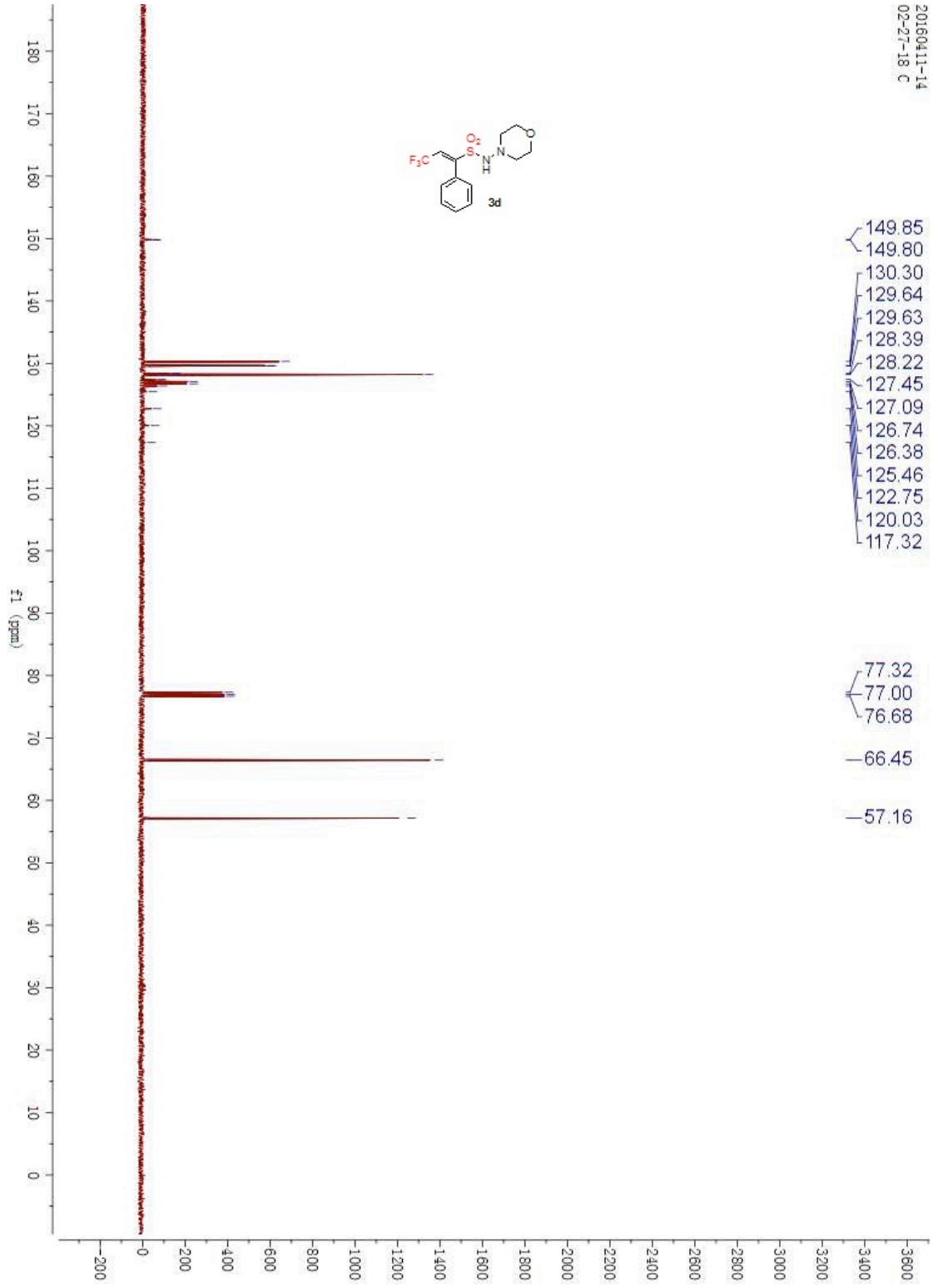

20160411-14
02-27-1 Z H
3c
7.359
7.356
7.340
7.338
7.322
7.319
7.275
7.260
7.217
7.198
7.180
7.143
7.126
7.045
7.027
7.009
6.991
5.619
3.738
3.732
3.717
3.708
3.701
3.693
3.677
3.662
3.656
3.648
2.842
2.828
2.819
2.773
2.765
2.760
2.750
2.738
2.337
0.000
1.00
1.15
1.02
1.00
0.99
0.98
4.18
4.12
3.06
f1 (ppm)

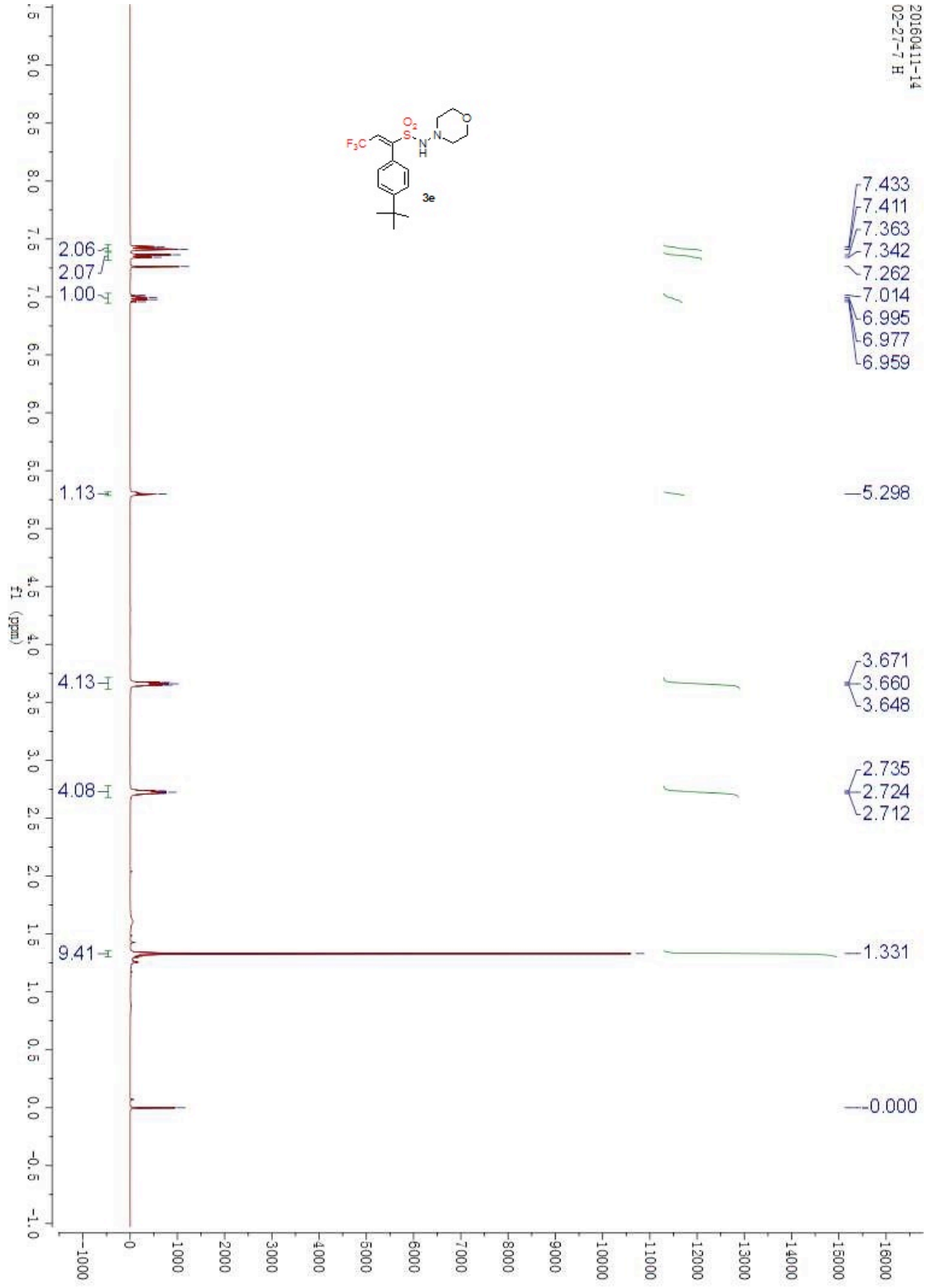

20160411-14
02-27-1 Z F
-60.24
-60.26
3c
f1 (ppm)

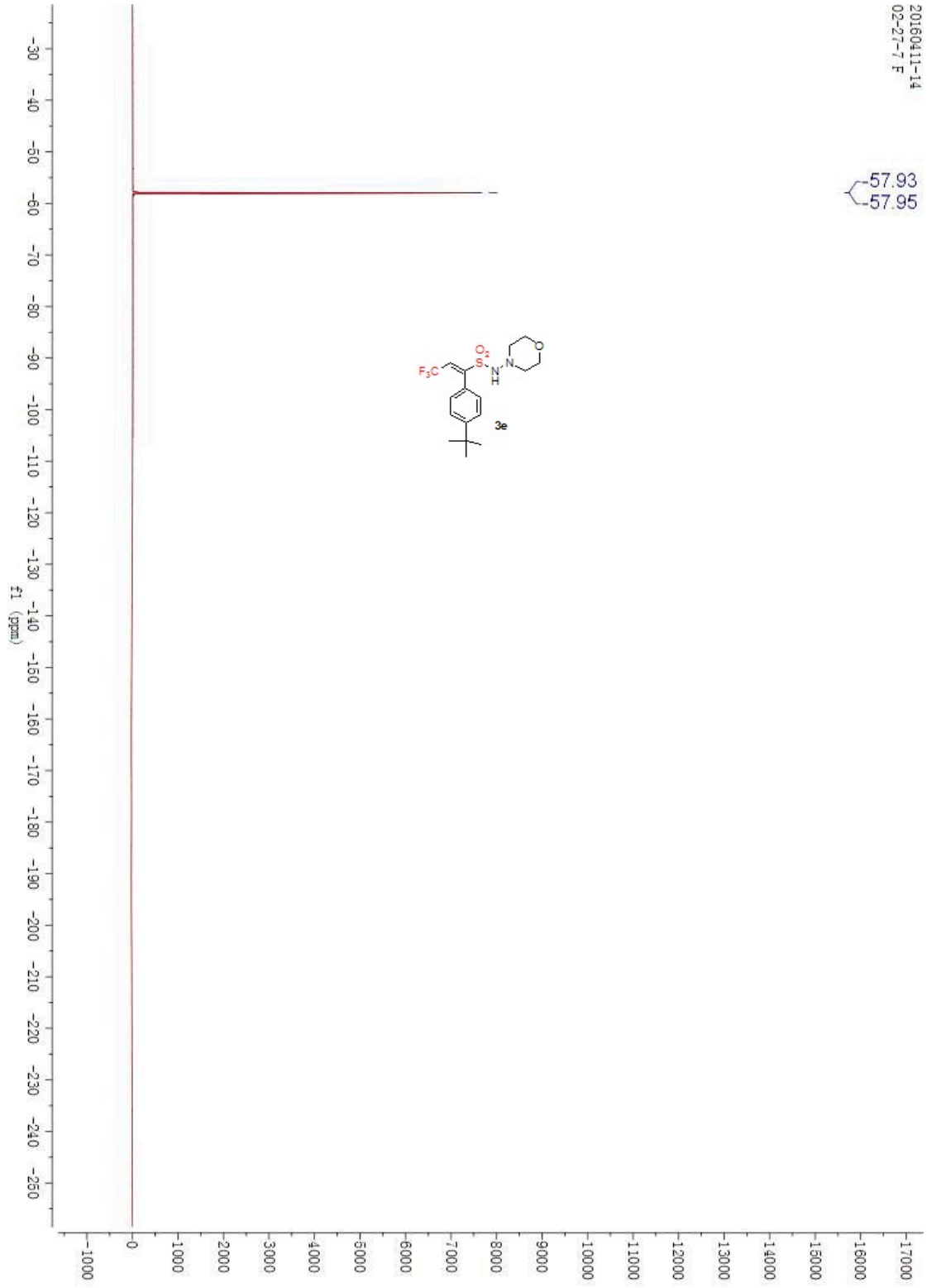

20160411-14
02-27-1 Z C
3c
150.07
150.02
138.04
130.41
130.06
129.23
127.98
127.92
127.57
127.22
126.86
125.35
125.25
122.64
119.92
117.21
77.32
77.00
76.68
66.48
57.25
19.96
f1 (ppm)

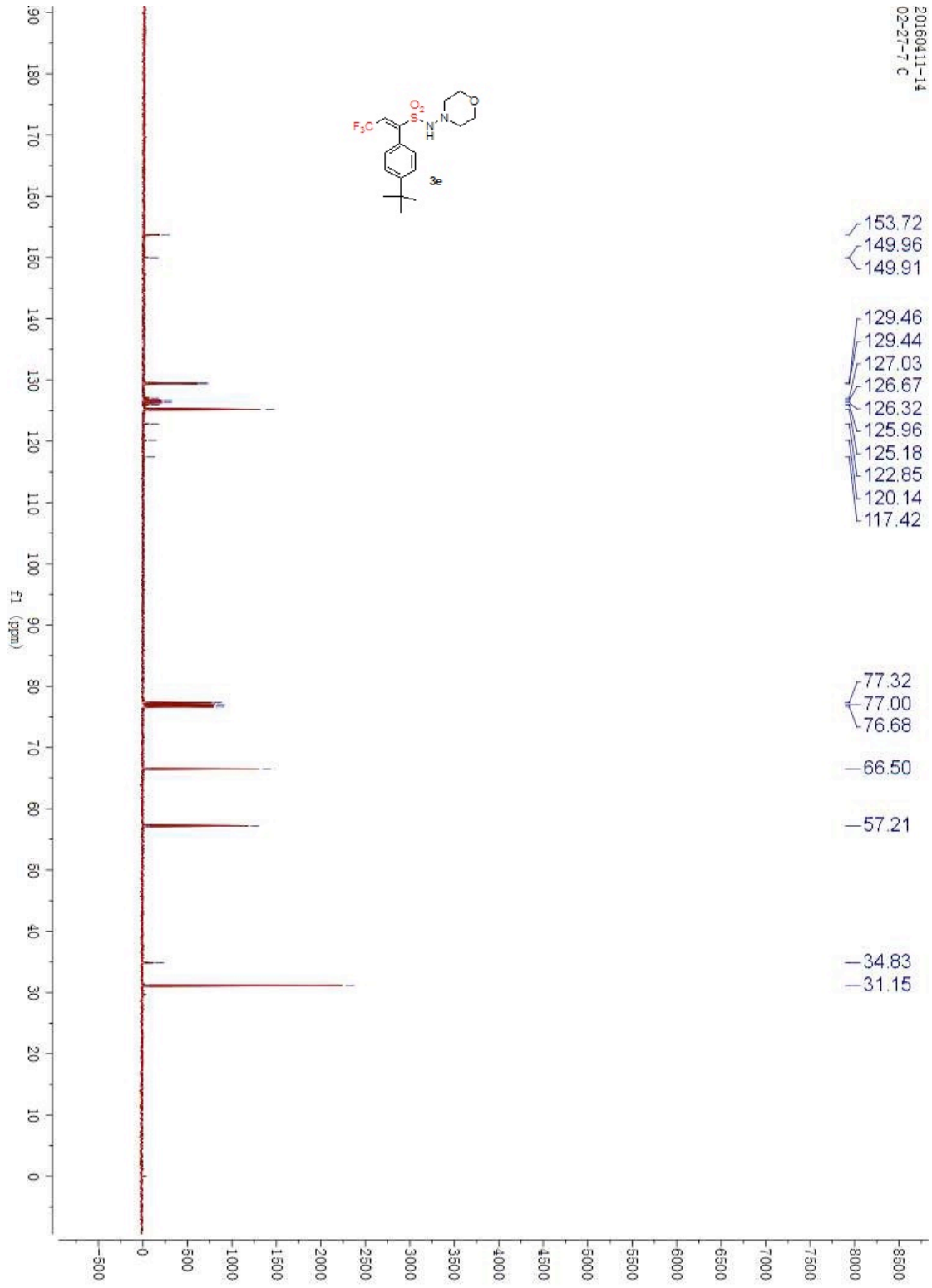

20160411-14
02-27-18 H
3d
7.497
7.488
7.482
7.476
7.466
7.464
7.454
7.444
7.424
7.412
7.263
7.035
7.017
6.999
6.980
5.429
3.674
3.662
3.651
2.737
2.726
2.714
0.000
1.14
4.00
1.00
1.02
4.24
4.21
f1 (ppm)

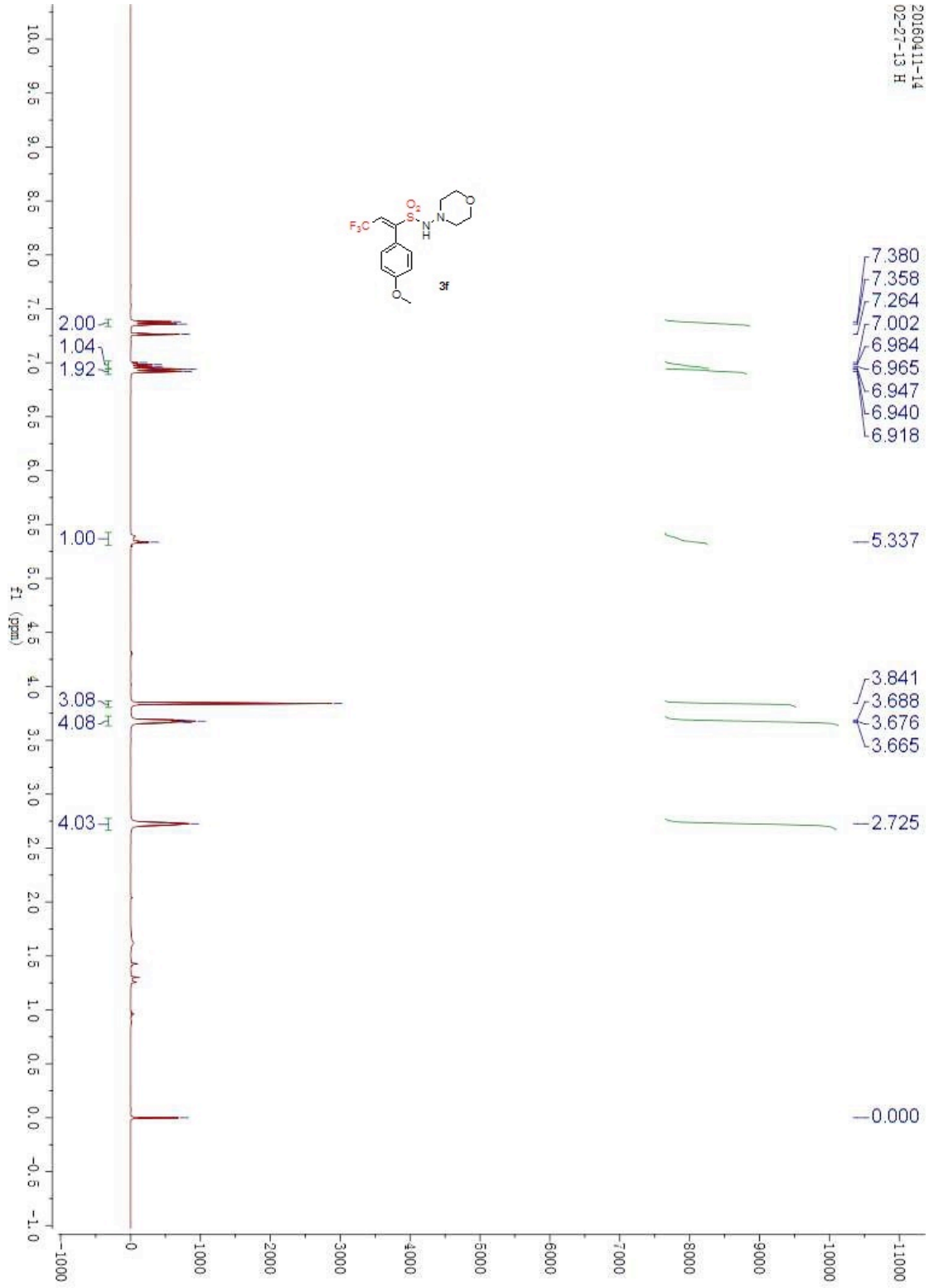

20160411-14
02-27-18 F
-58.02
-58.04
3d
f1 (ppm)

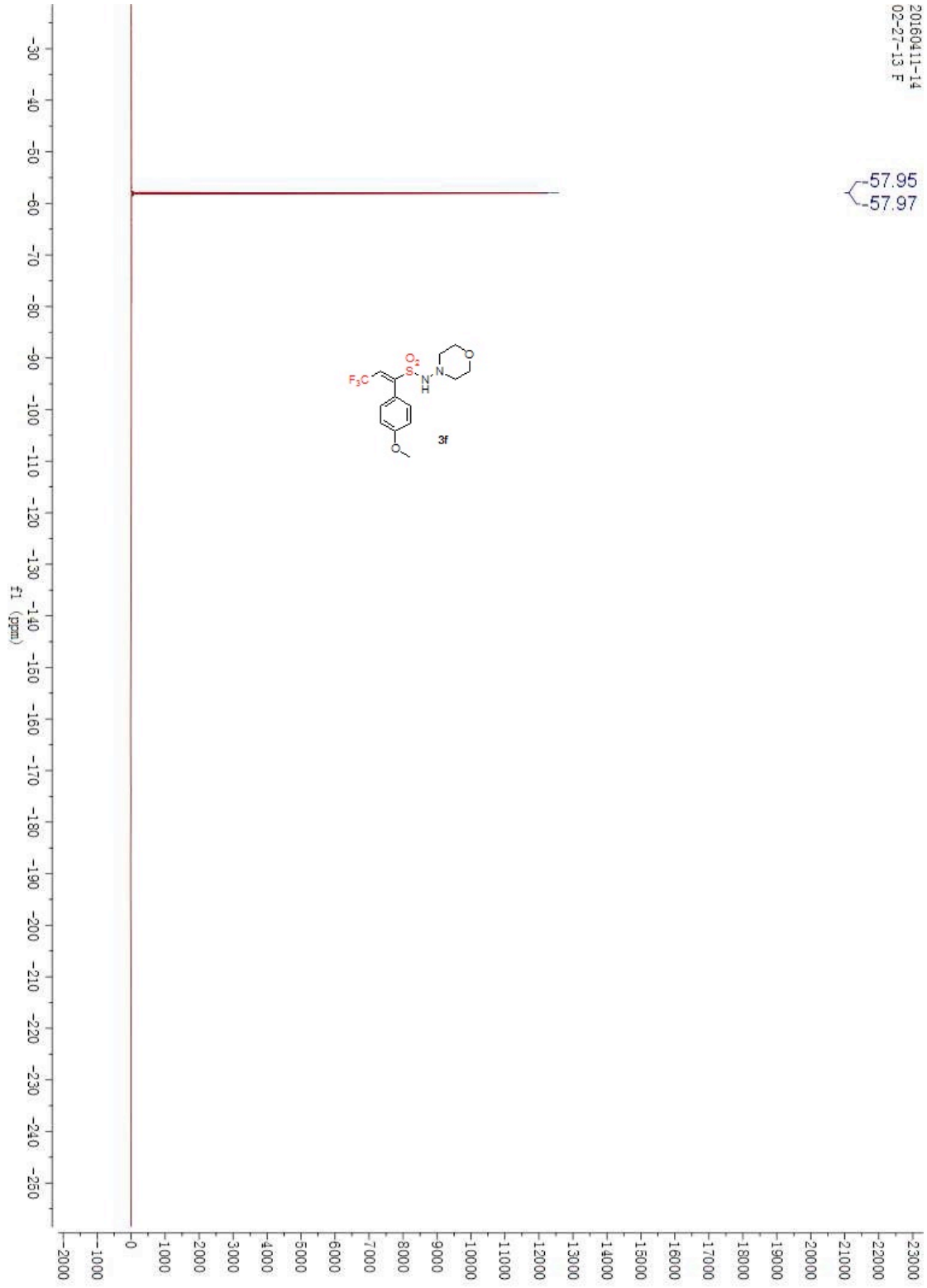

20160411-14
02-27-18 C
3d
149.85
149.80
130.30
129.64
129.63
128.39
128.22
127.45
127.09
126.74
126.38
125.46
122.75
120.03
117.32
77.32
77.00
76.68
66.45
57.16
f1 (ppm)

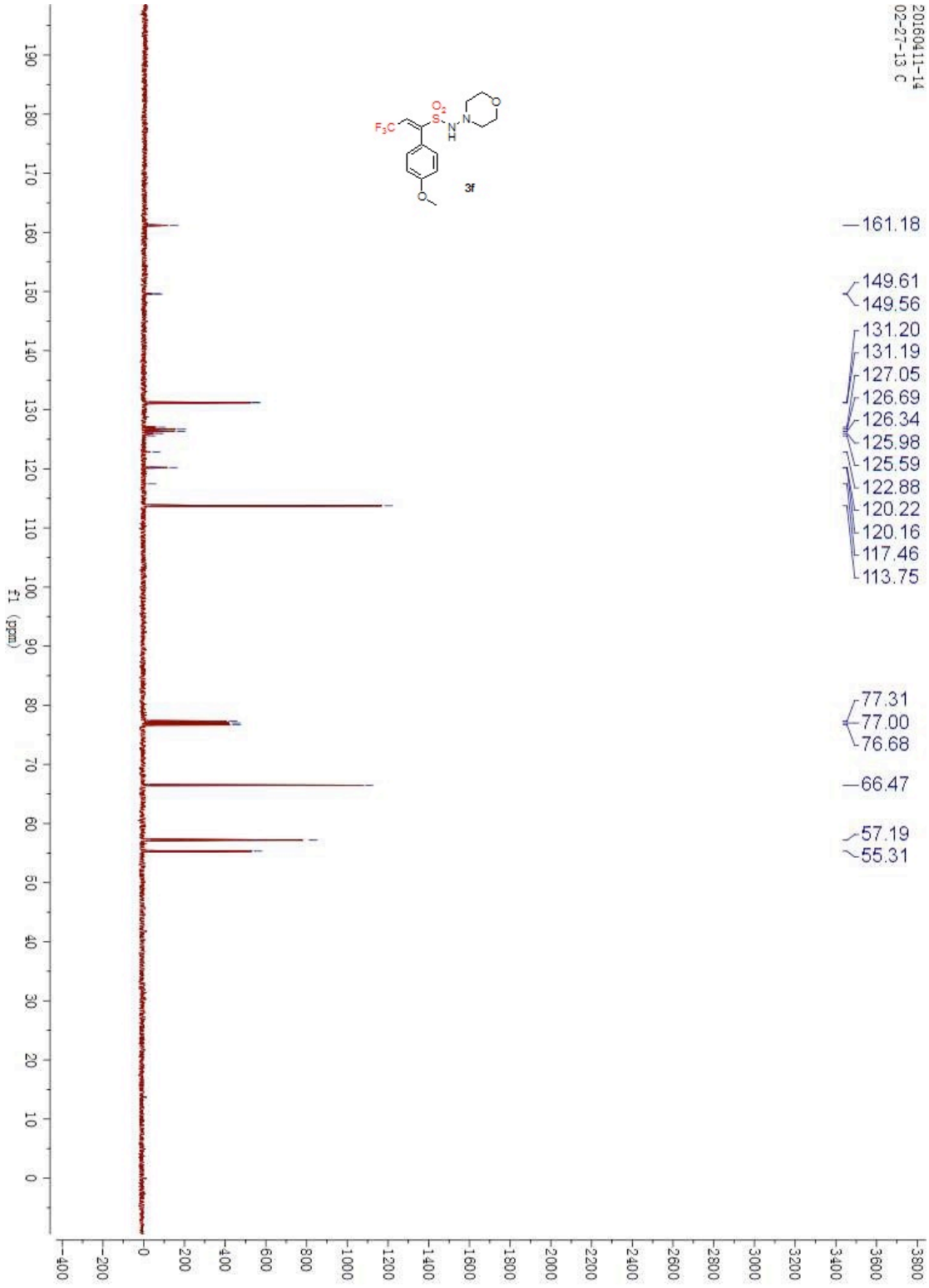

20160411-14
02-27-7 H
3e
7.433
7.411
7.363
7.342
7.262
7.014
6.995
6.977
6.959
5.298
3.671
3.660
3.648
2.735
2.724
2.712
1.331
0.000
2.06
2.07
1.00
1.13
4.13
4.08
9.41
f1 (ppm)

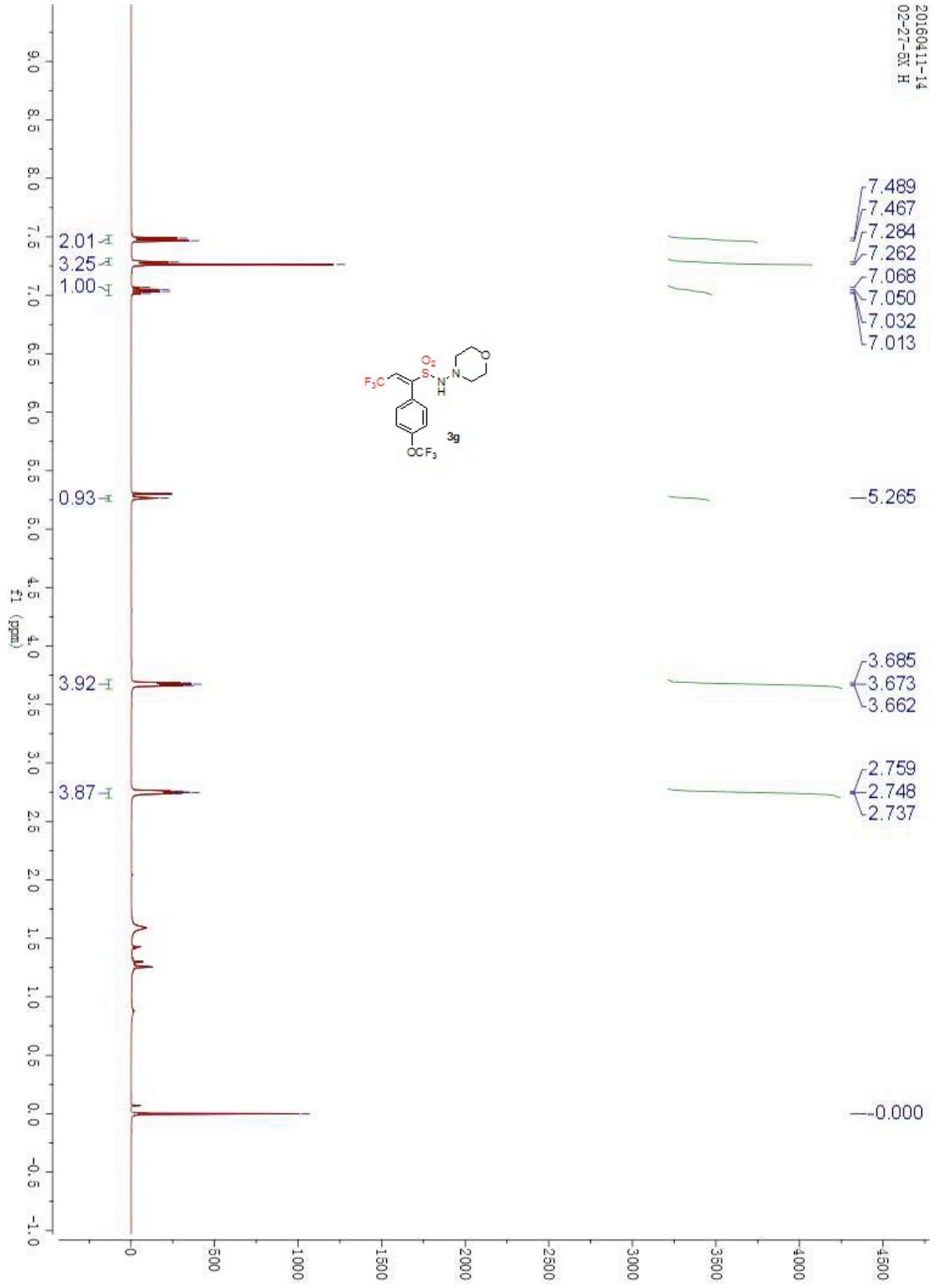

20160411-14
02-27-7 F
-57.93
-57.95
3e
f1 (ppm)

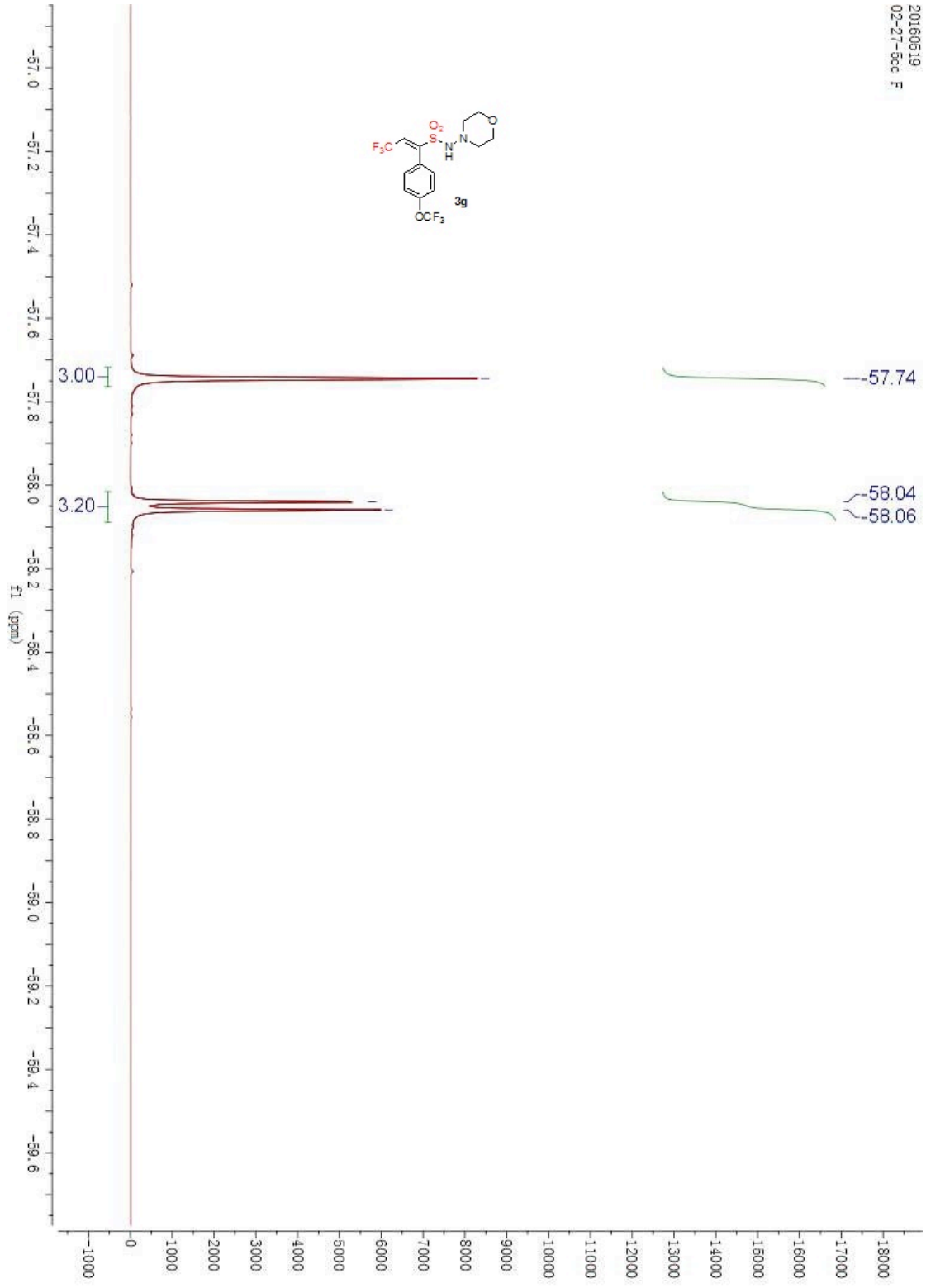

20160411-14
02-27-7 C
3e
153.72
149.96
149.91
129.46
129.44
127.03
126.67
126.32
125.96
125.18
122.85
120.14
117.42
77.32
77.00
76.68
66.50
57.21
34.83
31.15
f1 (ppm)

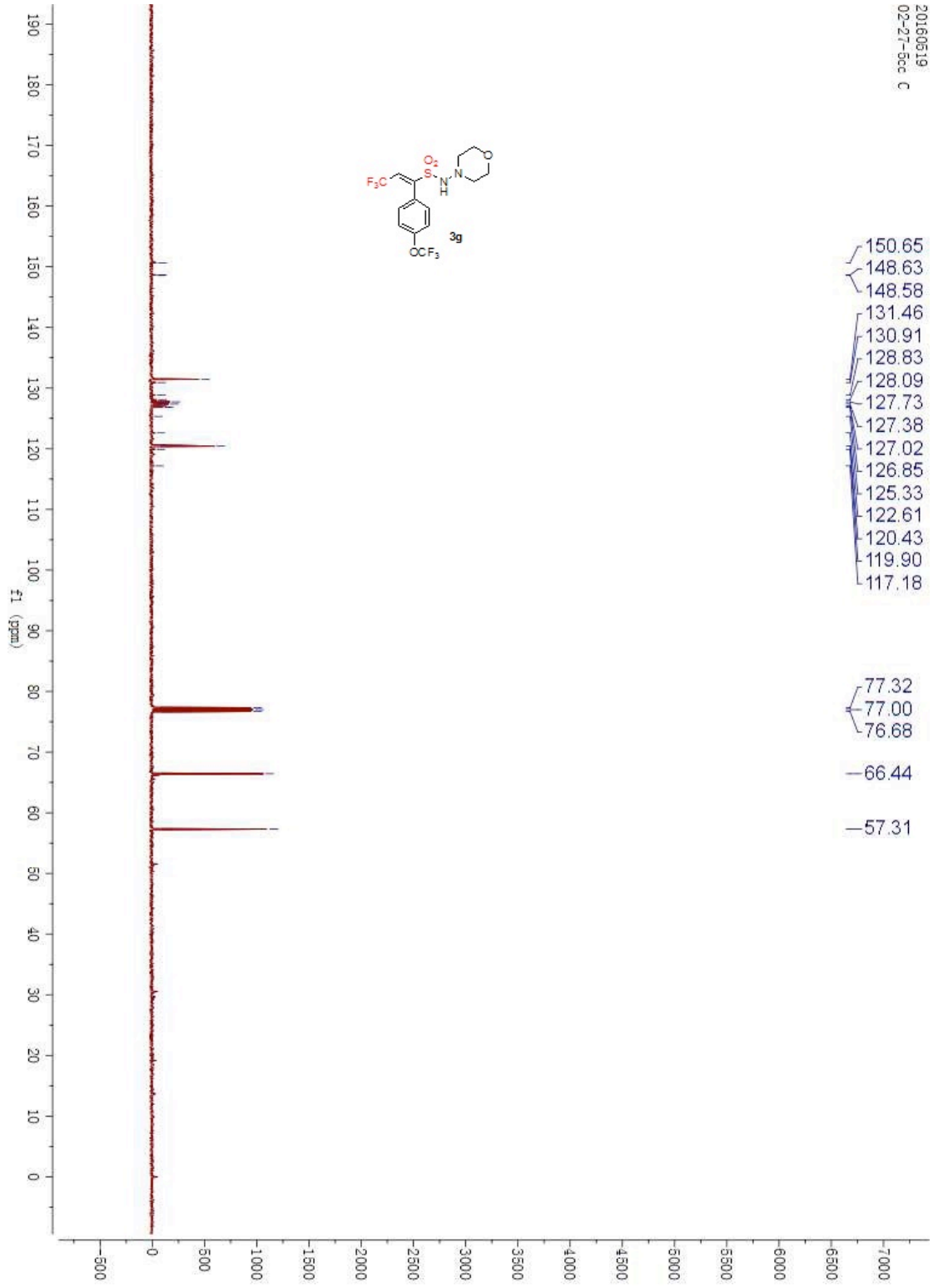

20160411-14
02-27-13 H
3f
7.380
7.358
7.264
7.002
6.984
6.965
6.947
6.940
6.918
5.337
3.841
3.688
3.676
3.665
2.725
0.000
2.00
1.04
1.92
1.00
3.08
4.08
4.03
f1 (ppm)

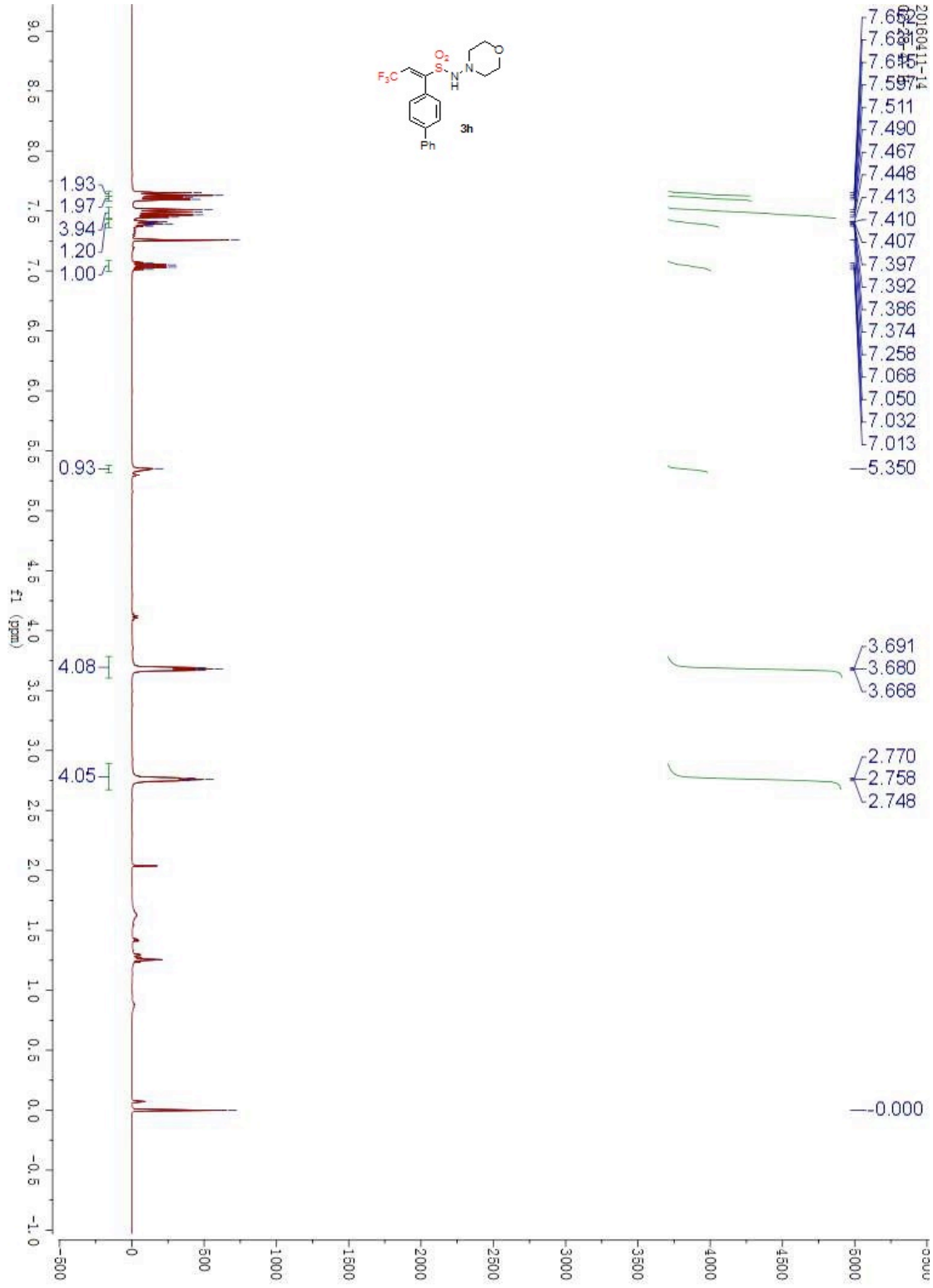

20160411-14
02-27-13 F
-57.95
-57.97
3f
f1 (ppm)

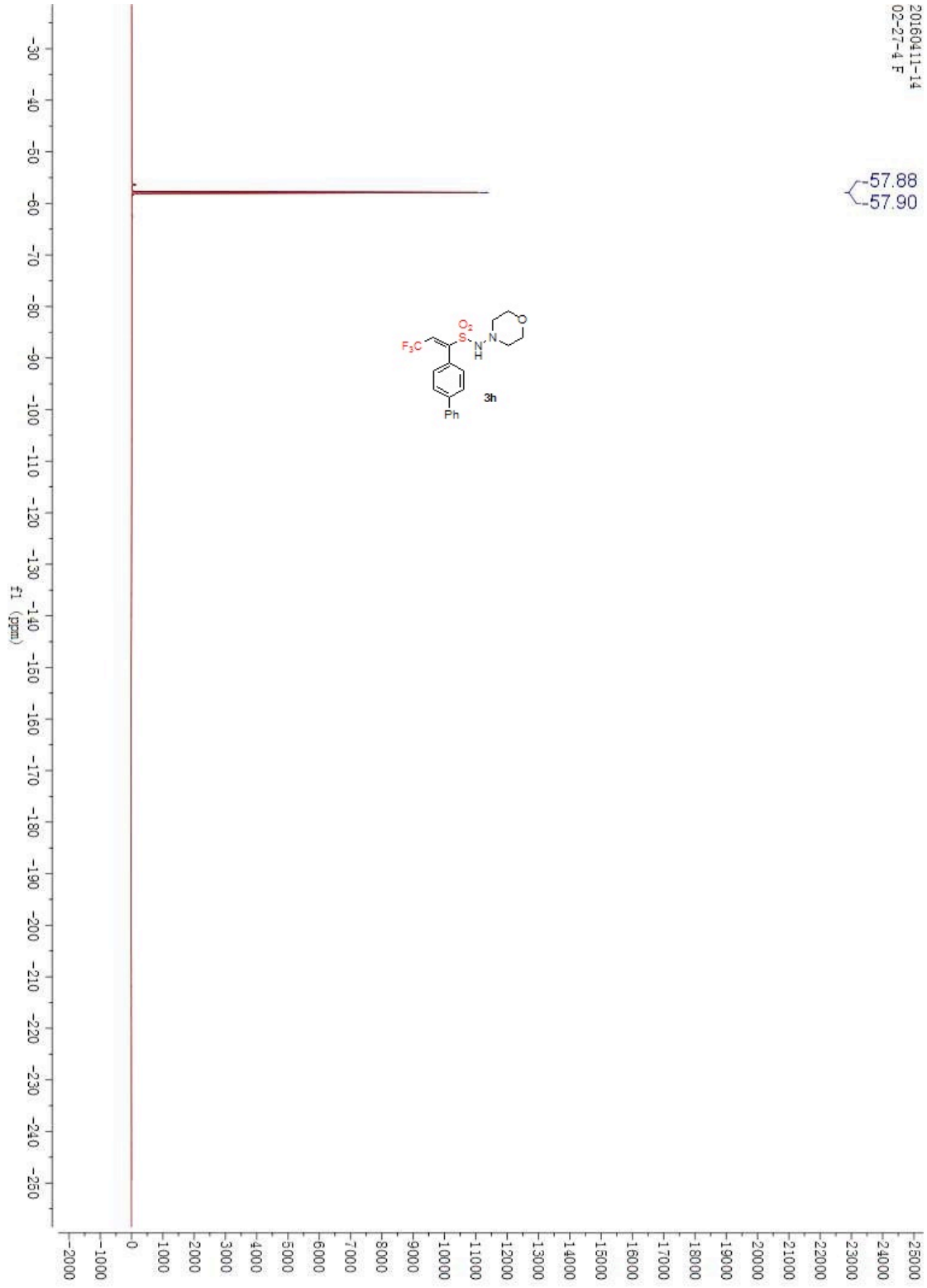

20160411-14
02-27-13 C
3f
161.18
149.61
149.56
131.20
131.19
127.05
126.69
126.34
125.98
125.59
122.88
120.22
120.16
117.46
113.75
77.31
77.00
76.68
66.47
57.19
55.31
f1 (ppm)

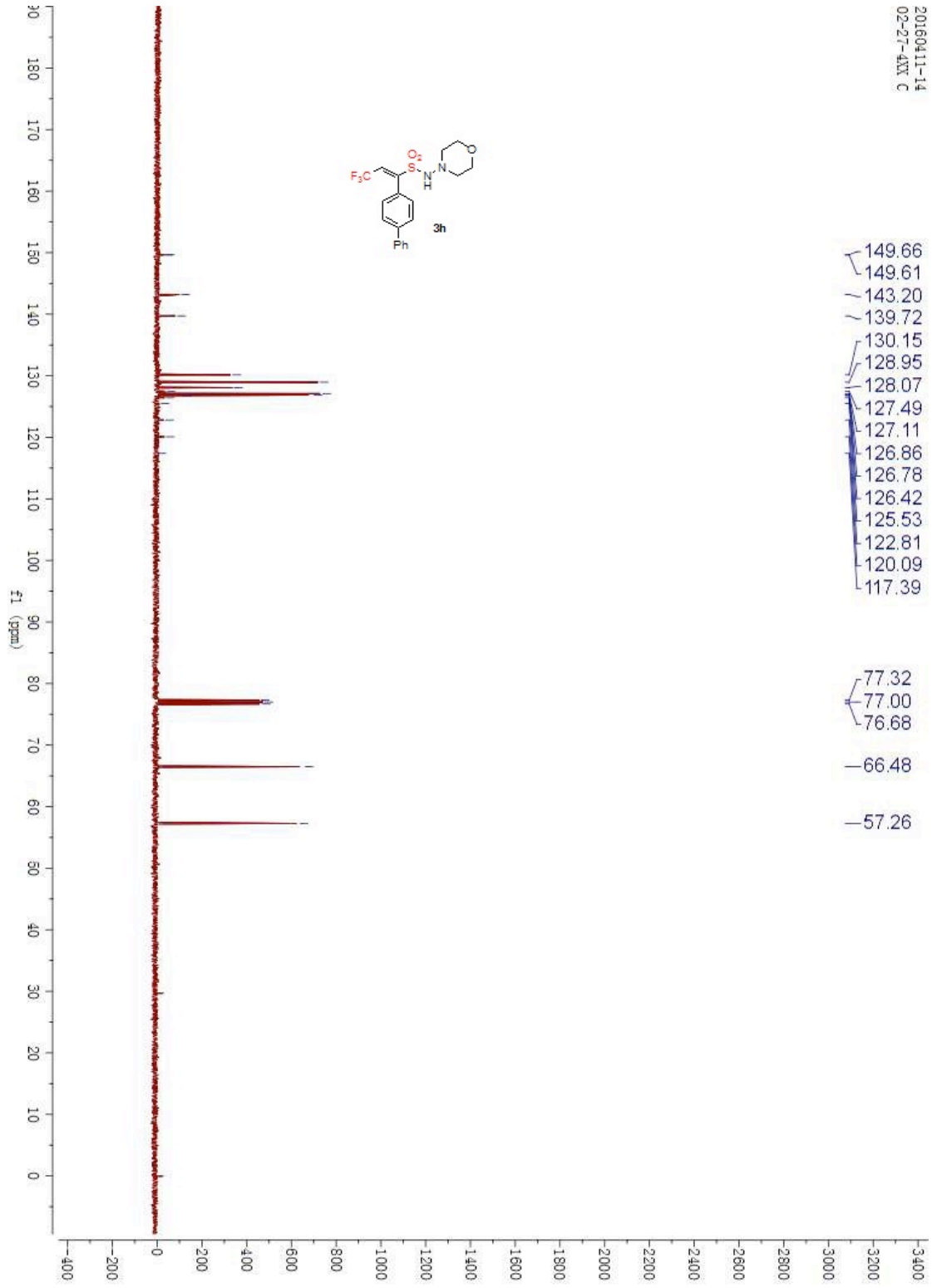

20160411-14
02-27-SX H
7.489
7.467
7.284
7.262
7.068
7.050
7.032
7.013
5.265
3.685
3.673
3.662
2.759
2.748
2.737
0.000
2.01
3.25
1.00
0.93
3.92
3.87
3g
f1 (ppm)

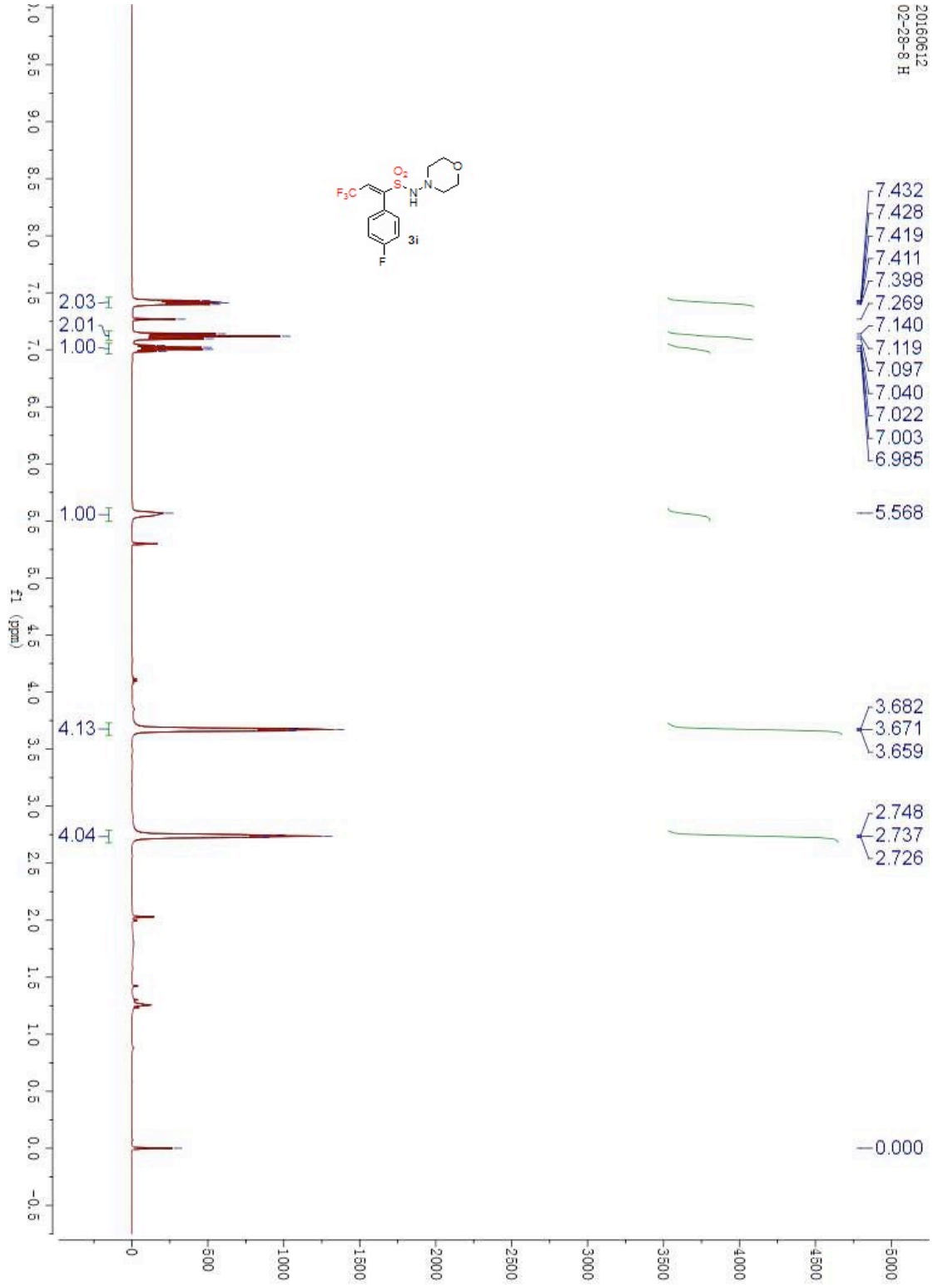

20160919
02-27-5cc F
3g
3.00
3.20
-57.74
-58.04
-58.06
f1 (ppm)

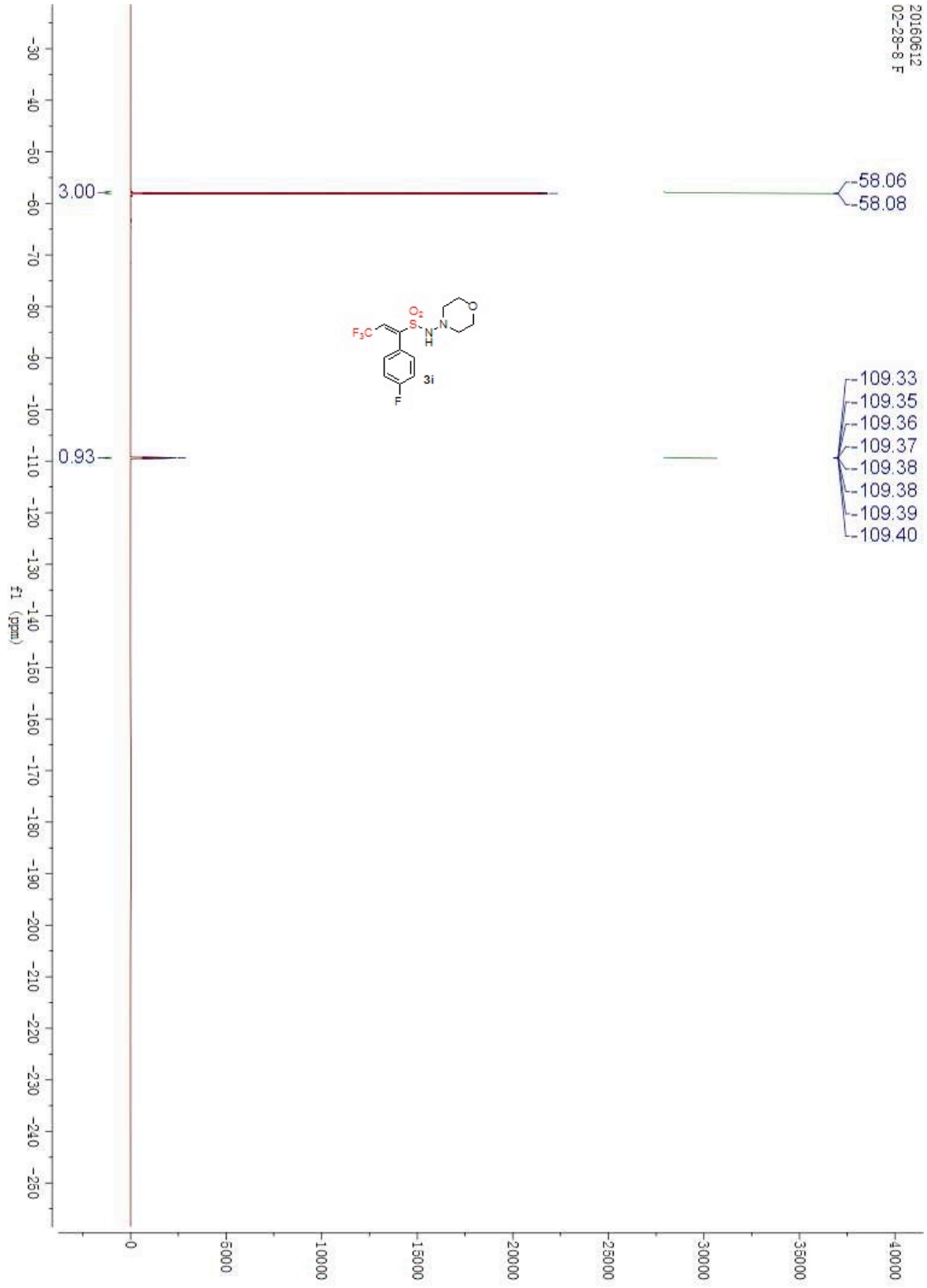

20160919
02-27-5cc C
3g
150.65
148.63
148.58
131.46
130.91
128.83
128.09
127.73
127.38
127.02
126.85
125.33
122.61
120.43
119.90
117.18
77.32
77.00
76.68
66.44
57.31
f1 (ppm)

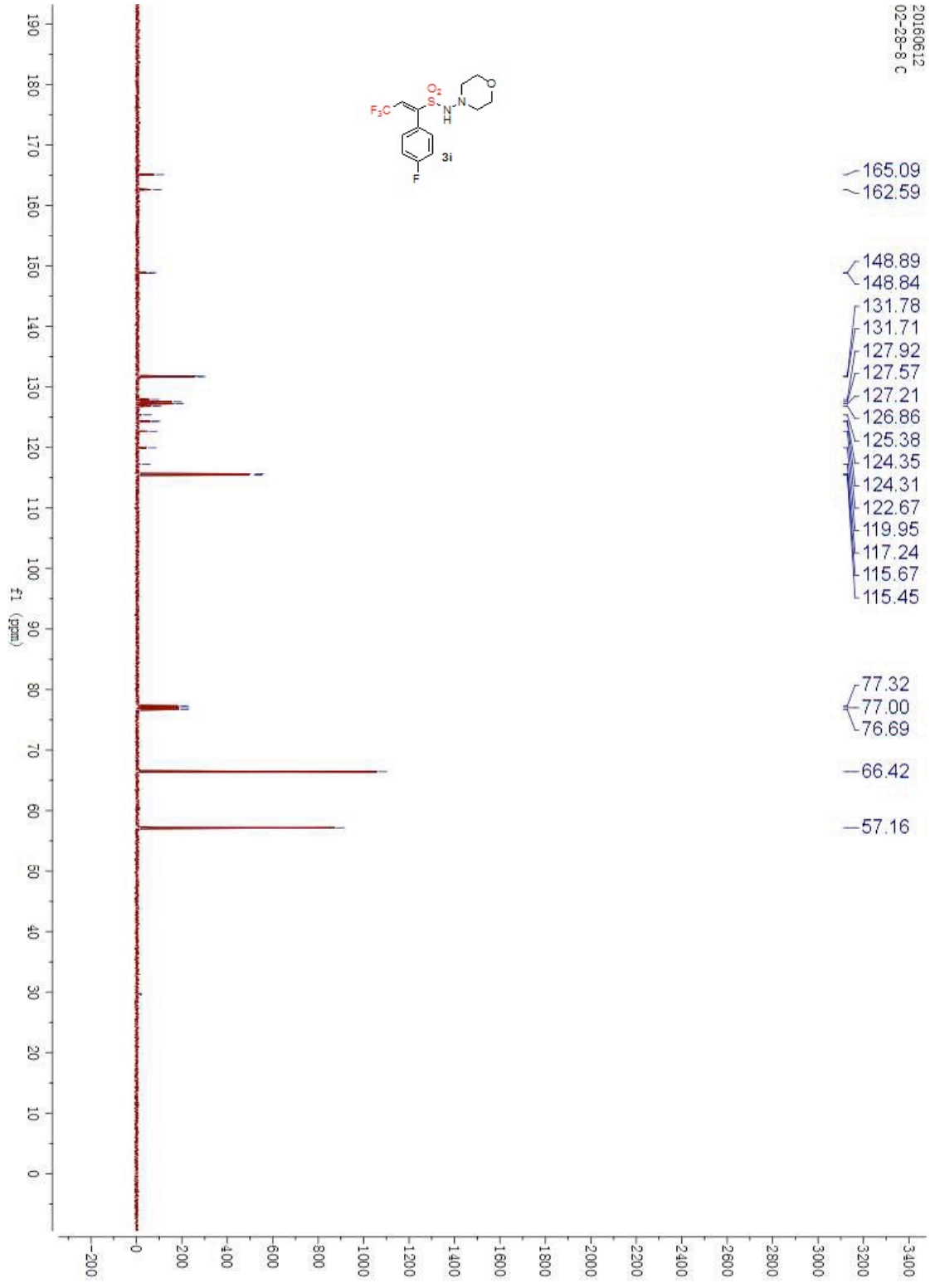

3h
1.93
1.97
3.94
1.20
1.00
0.93
4.08
4.05
7.652
7.633
7.615
7.597
7.511
7.490
7.467
7.448
7.413
7.410
7.407
7.397
7.392
7.386
7.374
7.258
7.068
7.050
7.032
7.013
5.350
3.691
3.680
3.668
2.770
2.758
2.748
0.000
f1 (ppm)

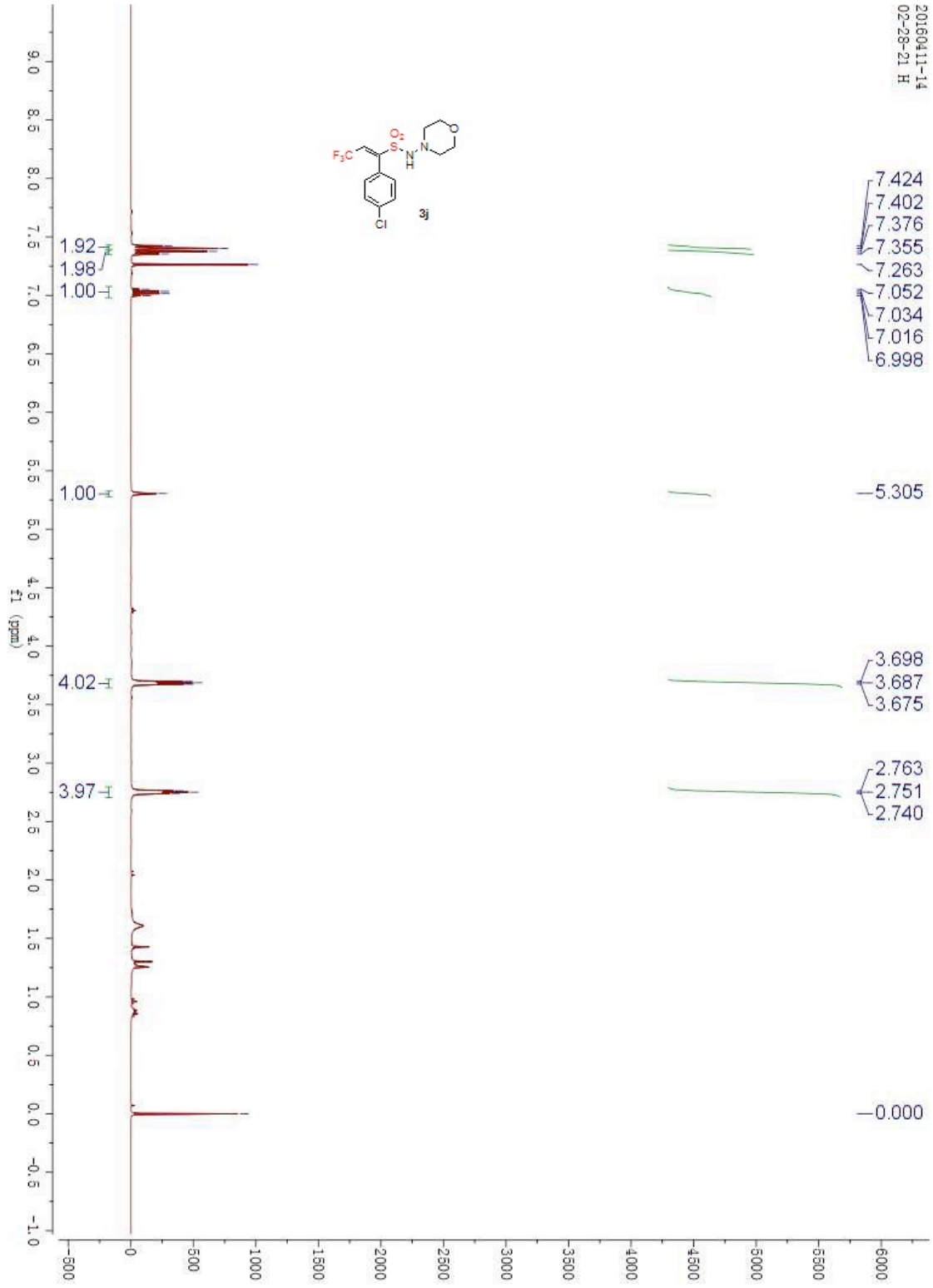

20160411-14
02-27-4 F
-57.88
-57.90
3h
f1 (ppm)

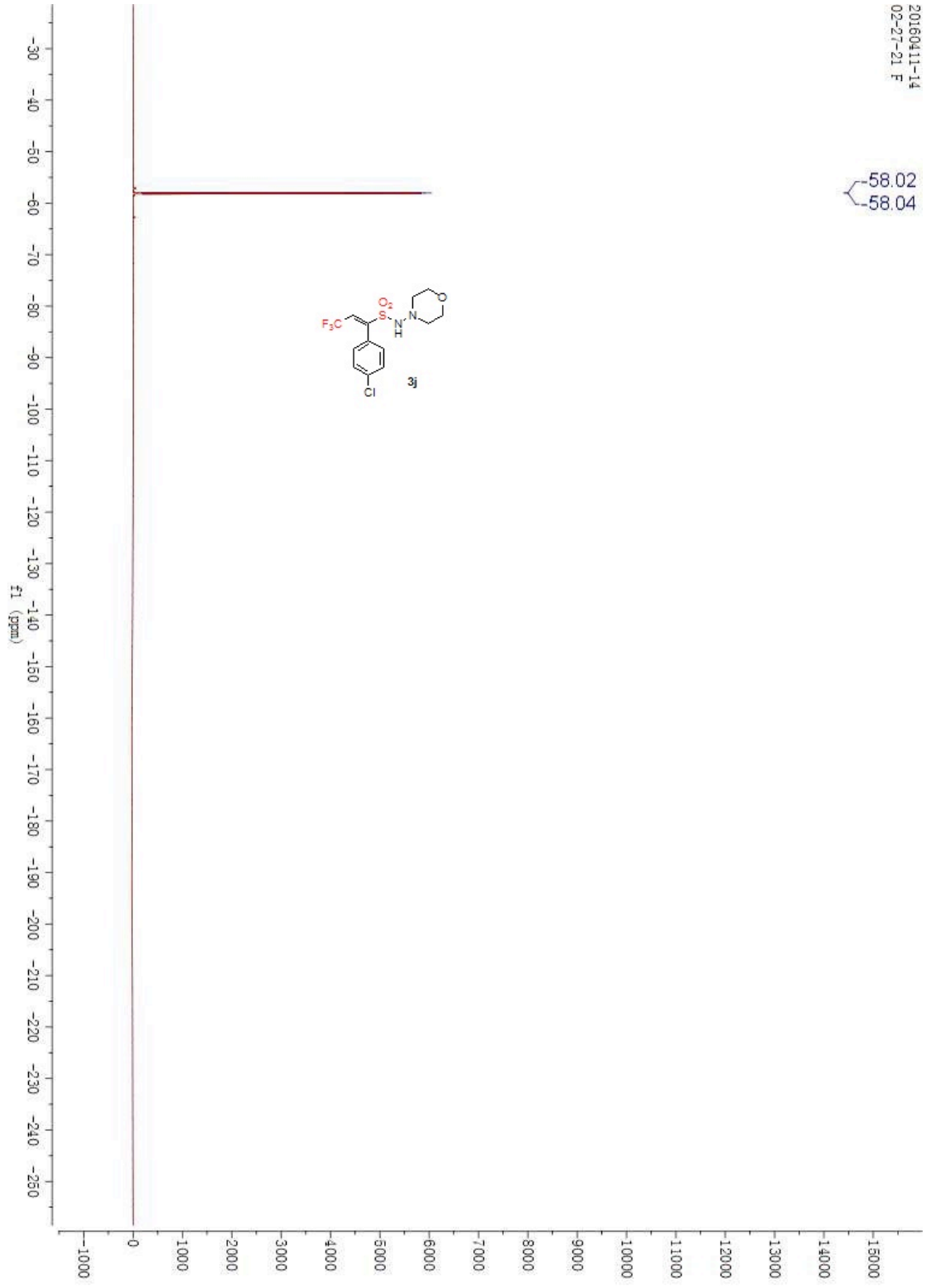

20160411-14
02-27-4XX C
3h
149.66
149.61
143.20
139.72
130.15
128.95
128.07
127.49
127.11
126.86
126.78
126.42
125.53
122.81
120.09
117.39
77.32
77.00
76.68
66.48
57.26
f1 (ppm)

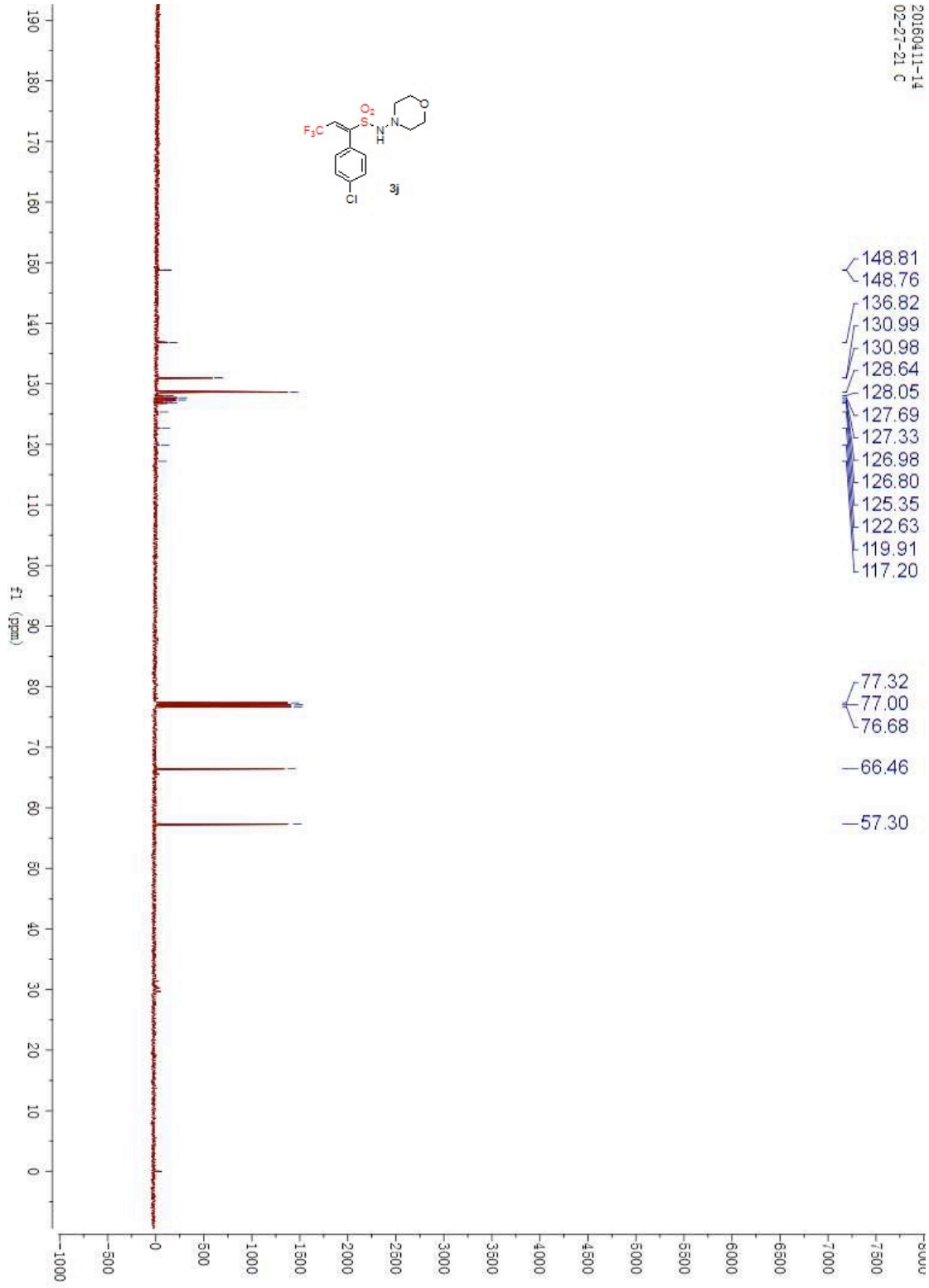

20160612
02-28-8 H
3i
7.432
7.428
7.419
7.411
7.398
7.269
7.140
7.119
7.097
7.040
7.022
7.003
6.985
5.568
3.682
3.671
3.659
2.748
2.737
2.726
0.000
2.03
2.01
1.00
1.00
4.13
4.04
f1 (ppm)

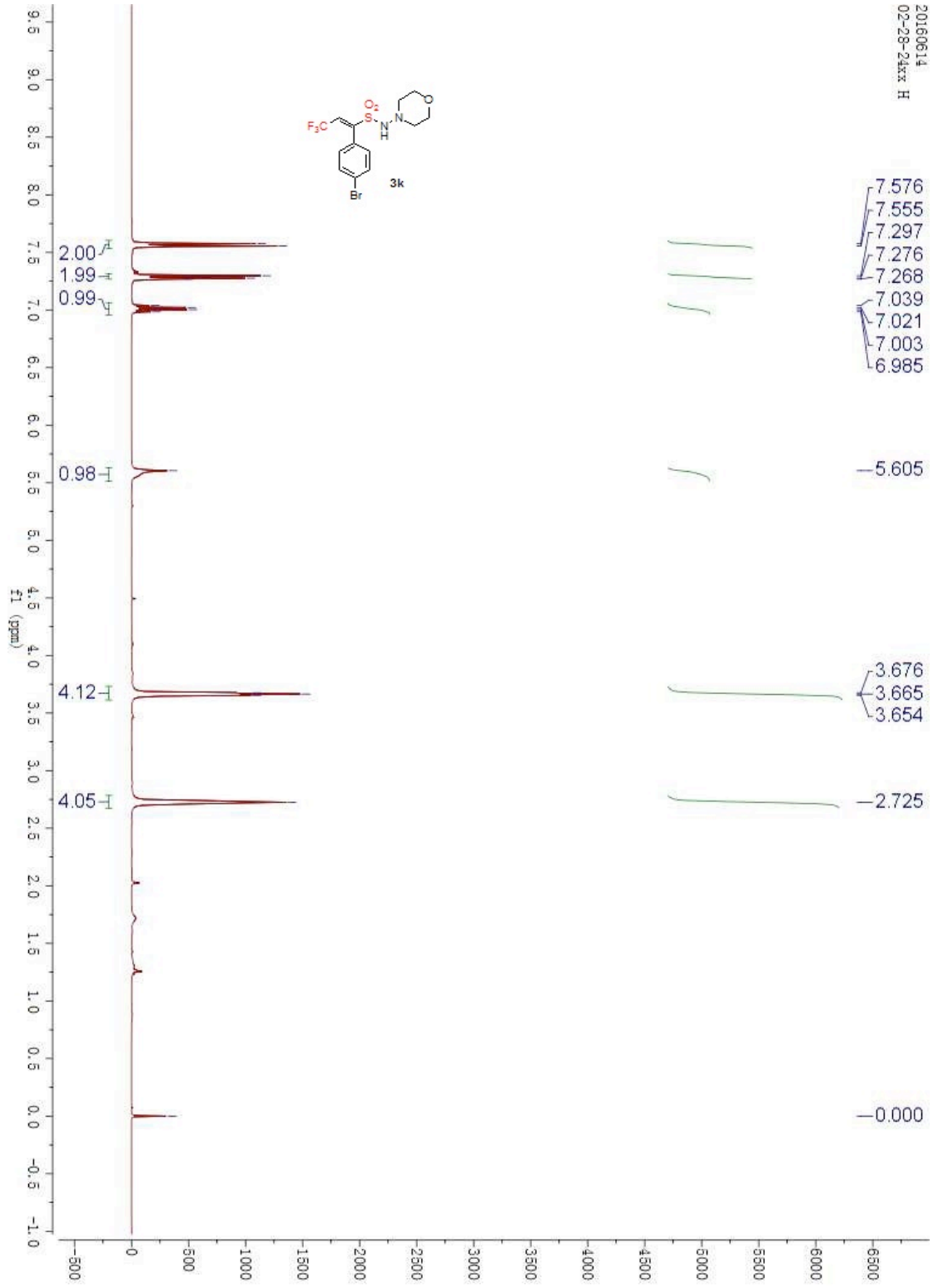

20160912
02-28-8 F
3.00
0.93
58.06
58.08
109.33
109.35
109.36
109.37
109.38
109.38
109.39
109.40
3i
f1 (ppm)

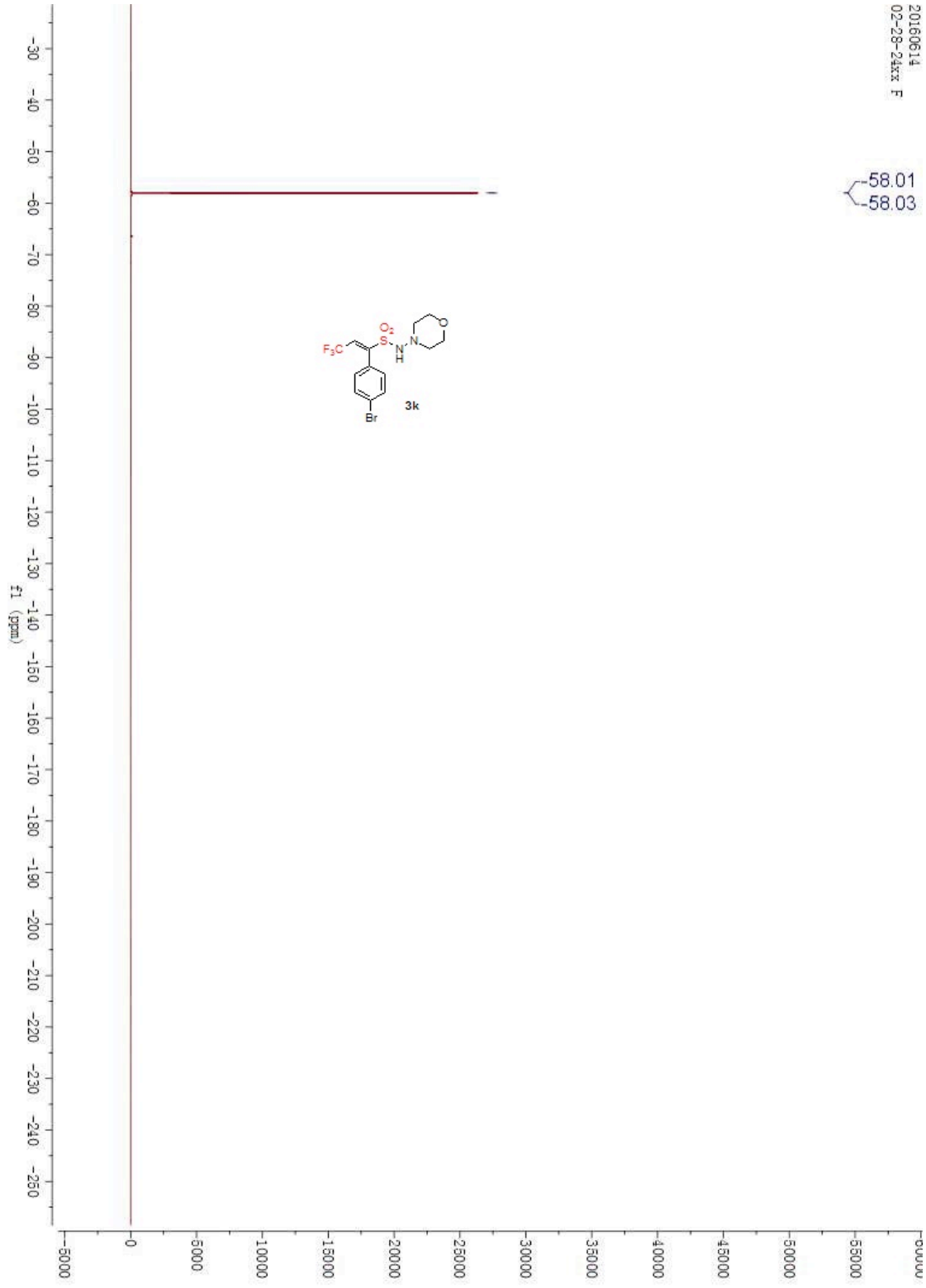

20160612
02-28-8 C
3i
165.09
162.59
148.89
148.84
131.78
131.71
127.92
127.57
127.21
126.86
125.38
124.35
124.31
122.67
119.95
117.24
115.67
115.45
77.32
77.00
76.69
66.42
57.16
f1 (ppm)

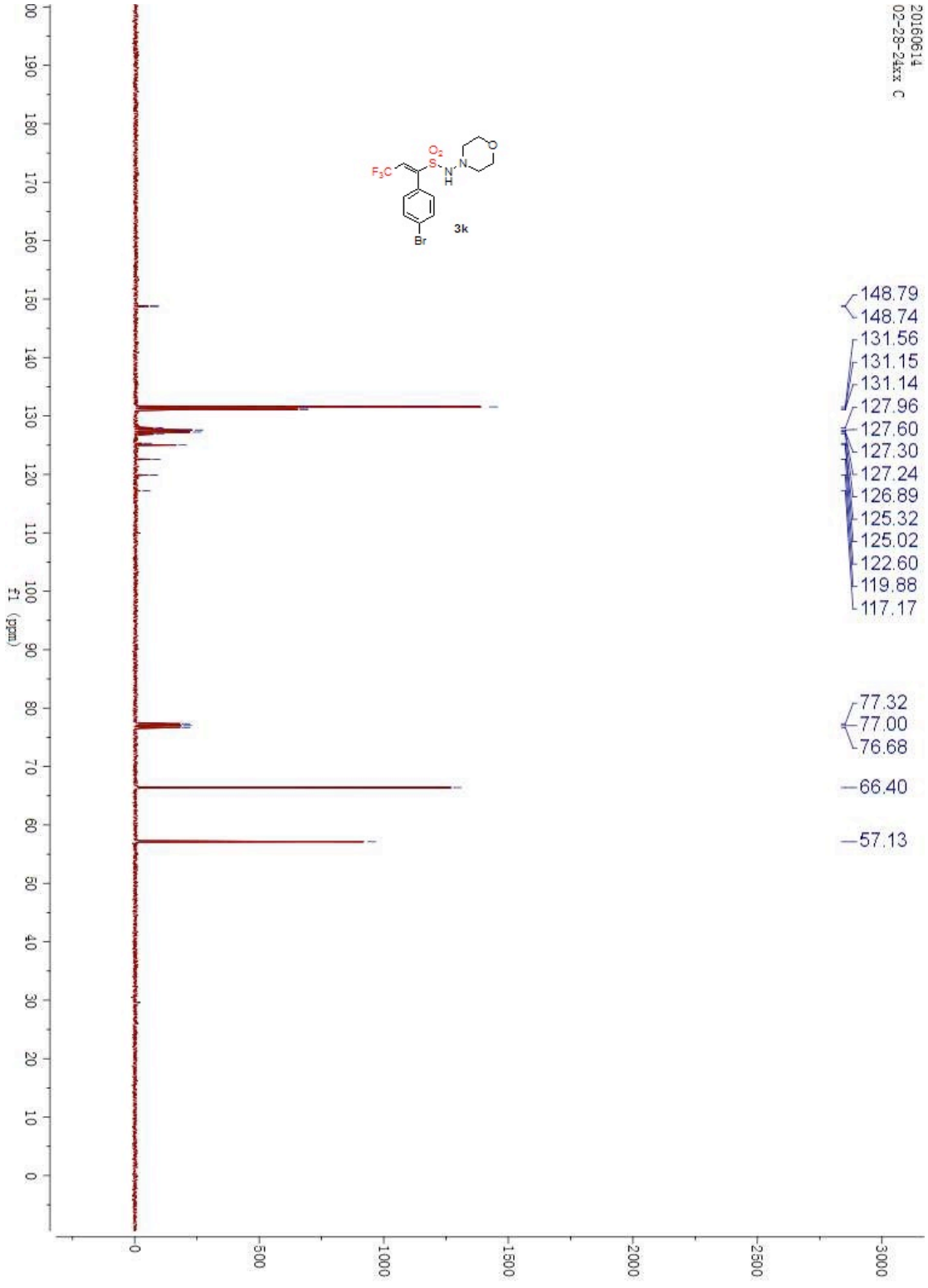

20160411-14
02-28-21 H
3j
7.424
7.402
7.376
7.355
7.263
7.052
7.034
7.016
6.998
5.305
3.698
3.687
3.675
2.763
2.751
2.740
0.000
1.92
1.98
1.00
1.00
4.02
3.97
f1 (ppm)

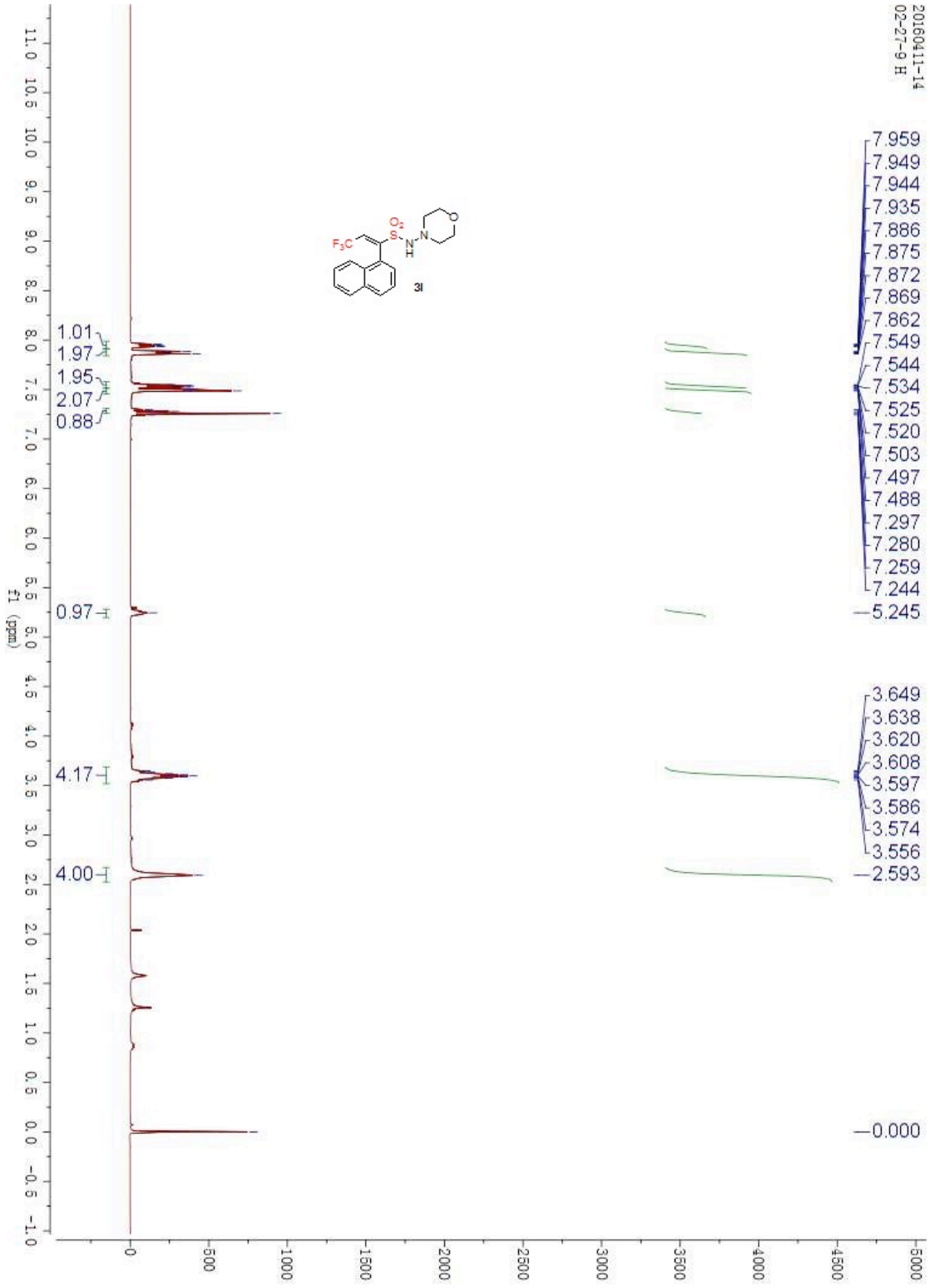

20160411-14
02-27-21 F
-58.02
-58.04
3j
f1 (ppm)

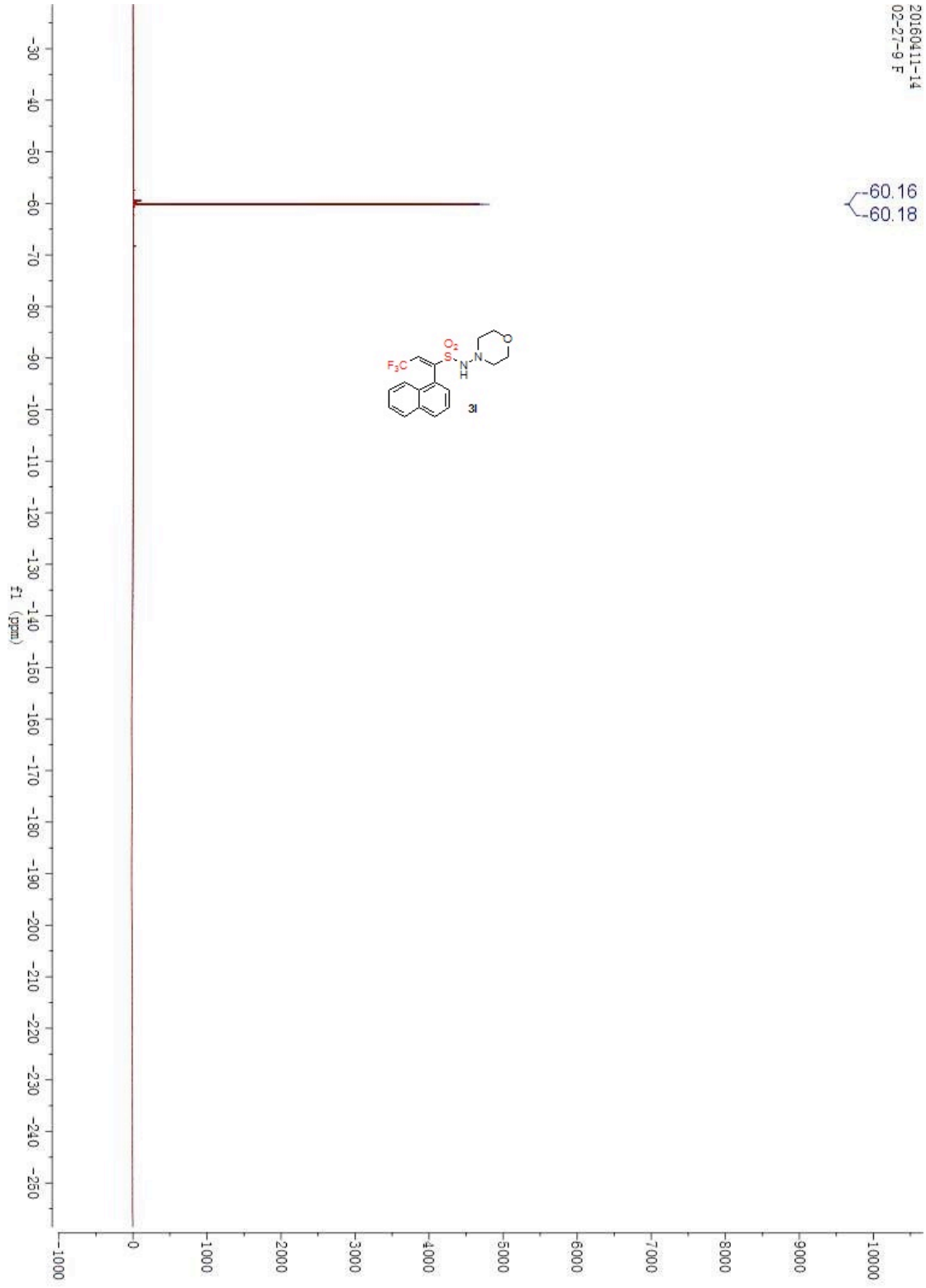

20160411-14
02-27-21 C
148.81
148.76
136.82
130.99
130.98
128.64
128.05
127.69
127.33
126.98
126.80
125.35
122.63
119.91
117.20
77.32
77.00
76.68
66.46
57.30
f1 (ppm)
3j

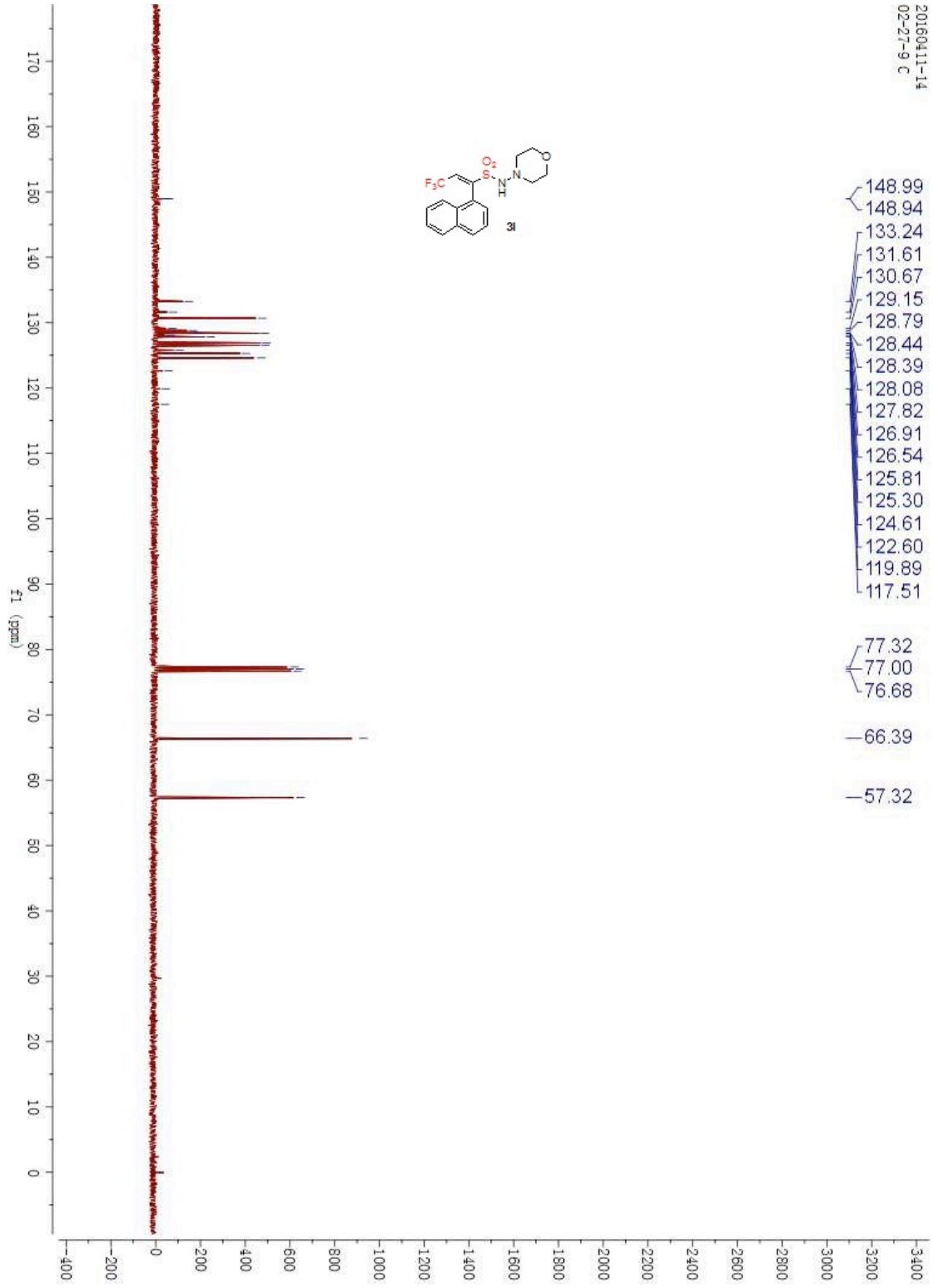

20160614
02-28-24xx H
3k
7.576
7.555
7.297
7.276
7.268
7.039
7.021
7.003
6.985
5.605
3.676
3.665
3.654
2.725
0.000
2.00
1.99
0.99
0.98
4.12
4.05
f1 (ppm)

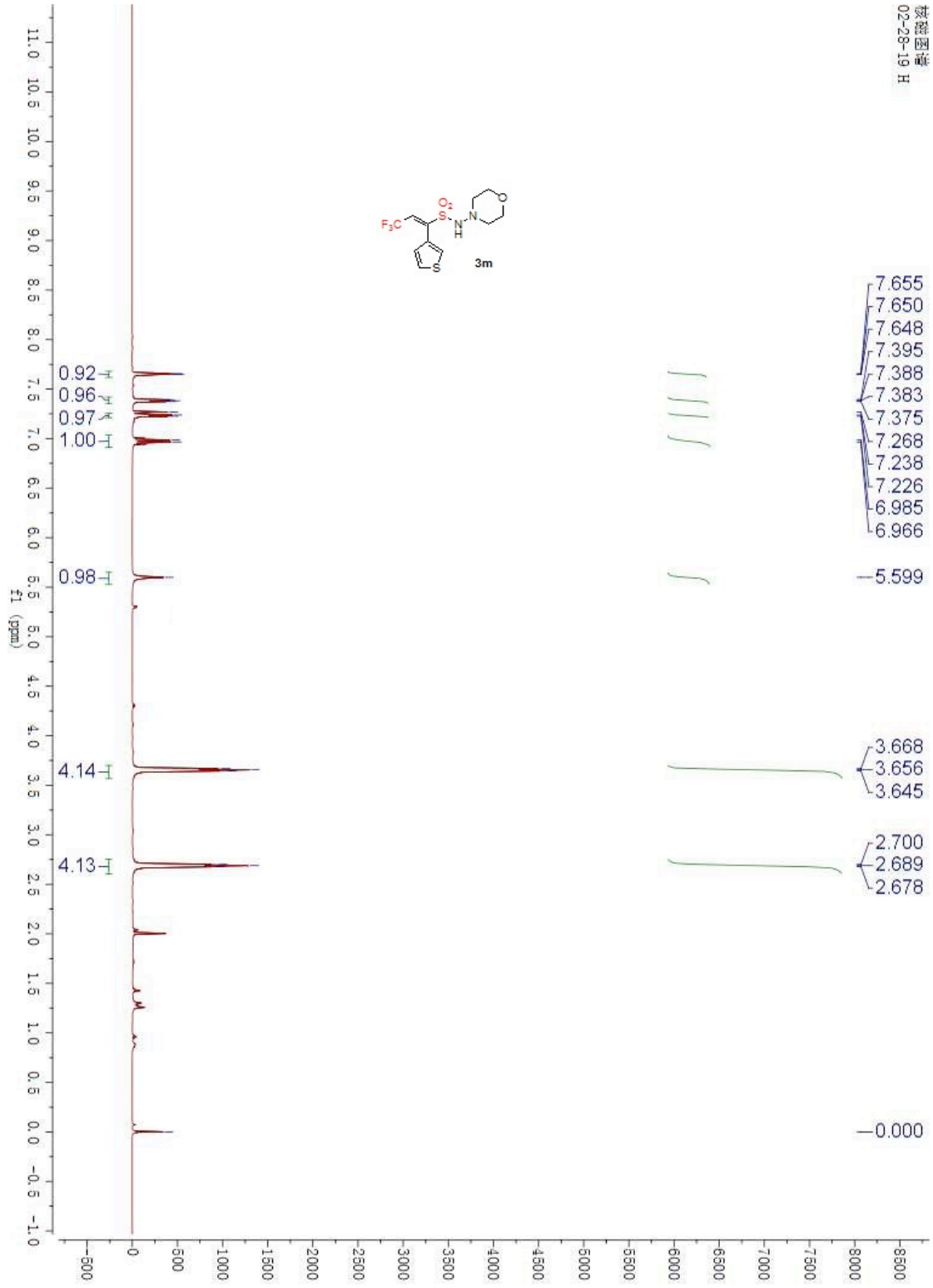

20160614
02-28-24xx F
-58.01
-58.03
3k
f1 (ppm)

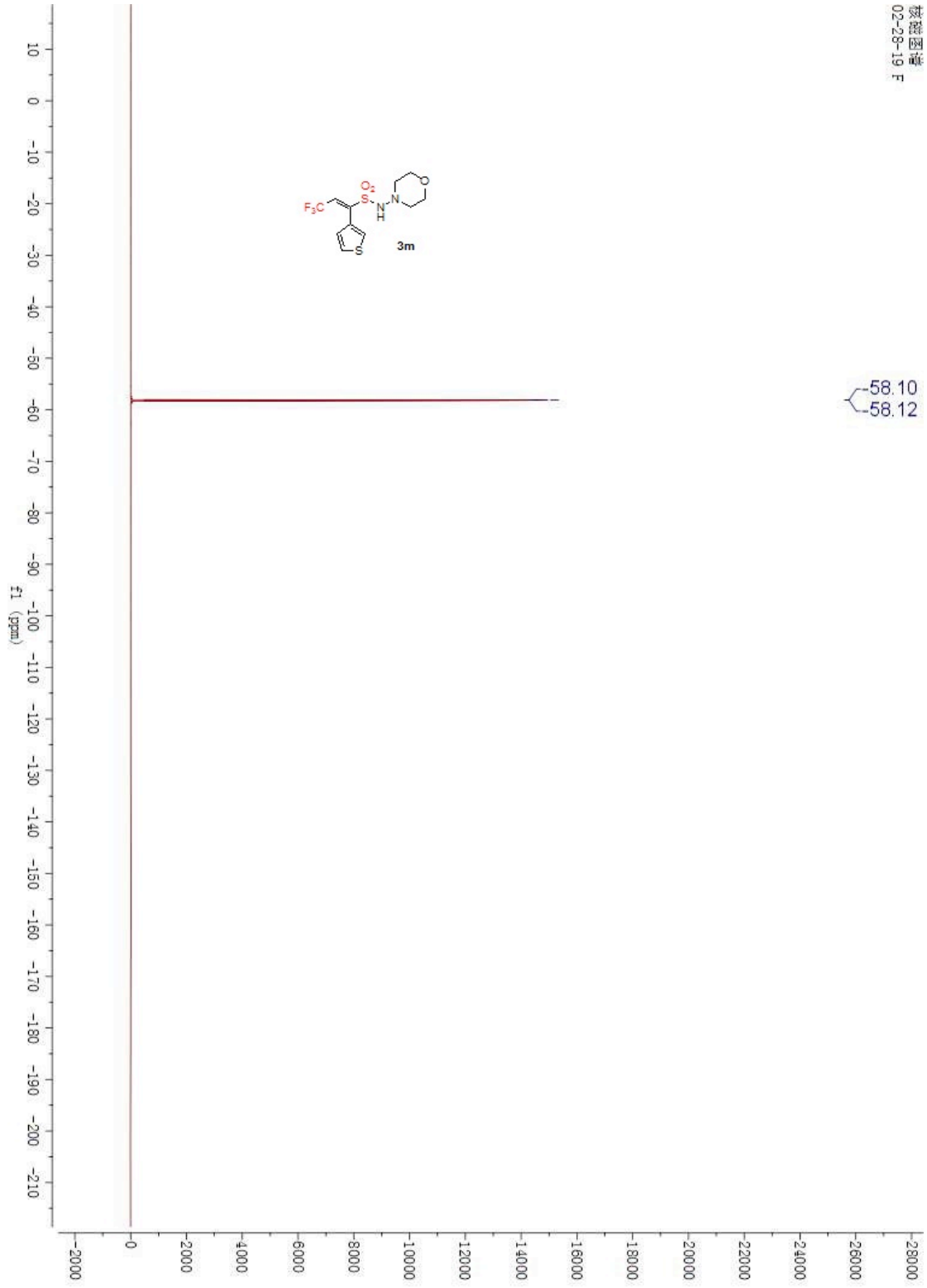

20160614
02-28-24xx C
3k
148.79
148.74
131.56
131.15
131.14
127.96
127.60
127.30
127.24
126.89
125.32
125.02
122.60
119.88
117.17
77.32
77.00
76.68
66.40
57.13
f1 (ppm)

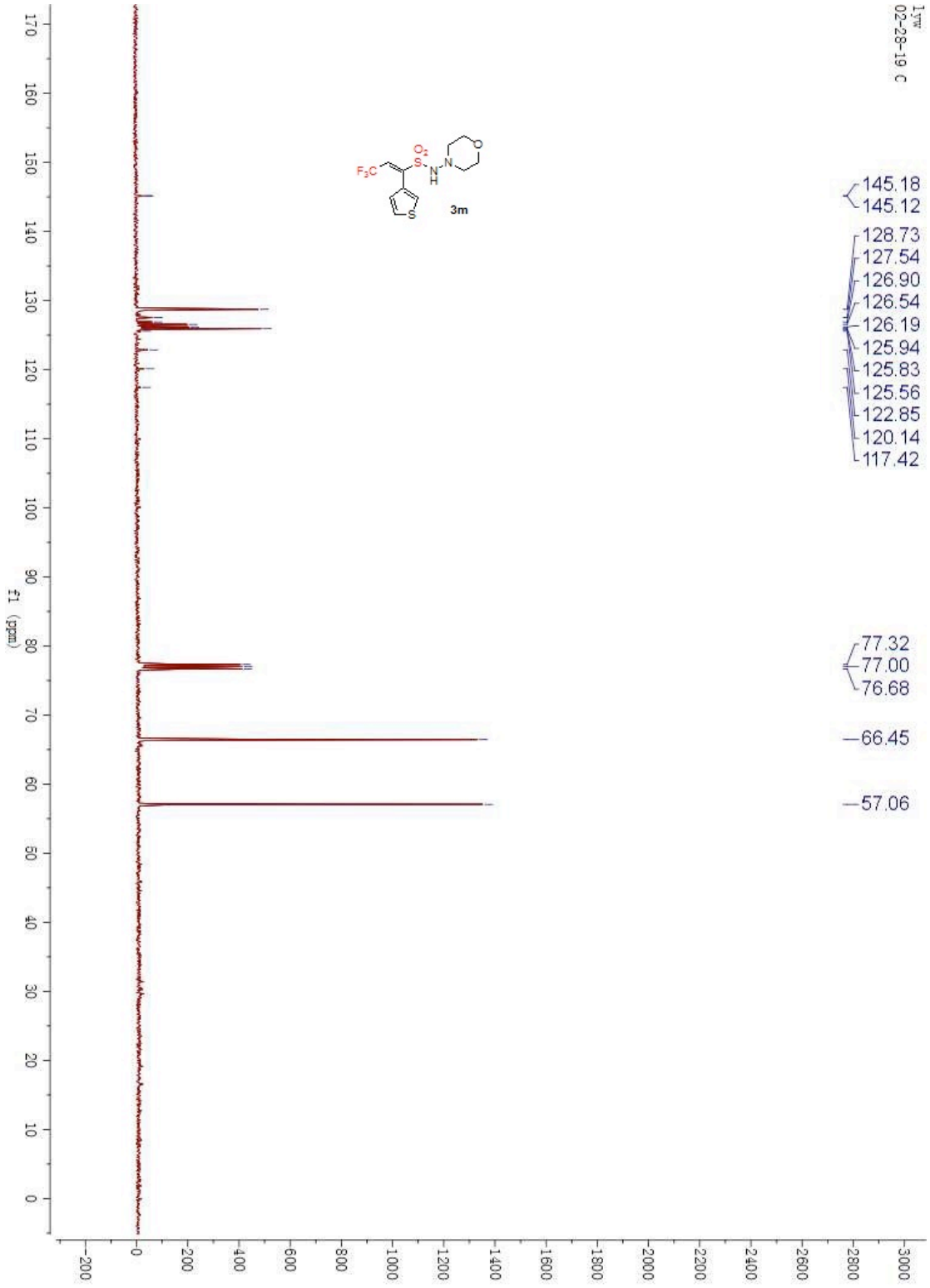

20160411-14
02-27-9 H
7.959
7.949
7.944
7.935
7.886
7.875
7.872
7.869
7.862
7.549
7.544
7.534
7.525
7.520
7.503
7.497
7.488
7.297
7.280
7.259
7.244
5.245
3.649
3.638
3.620
3.608
3.597
3.586
3.574
3.556
2.593
0.000
1.01
1.97
1.95
2.07
0.88
0.97
4.17
4.00
3l
f1 (ppm)

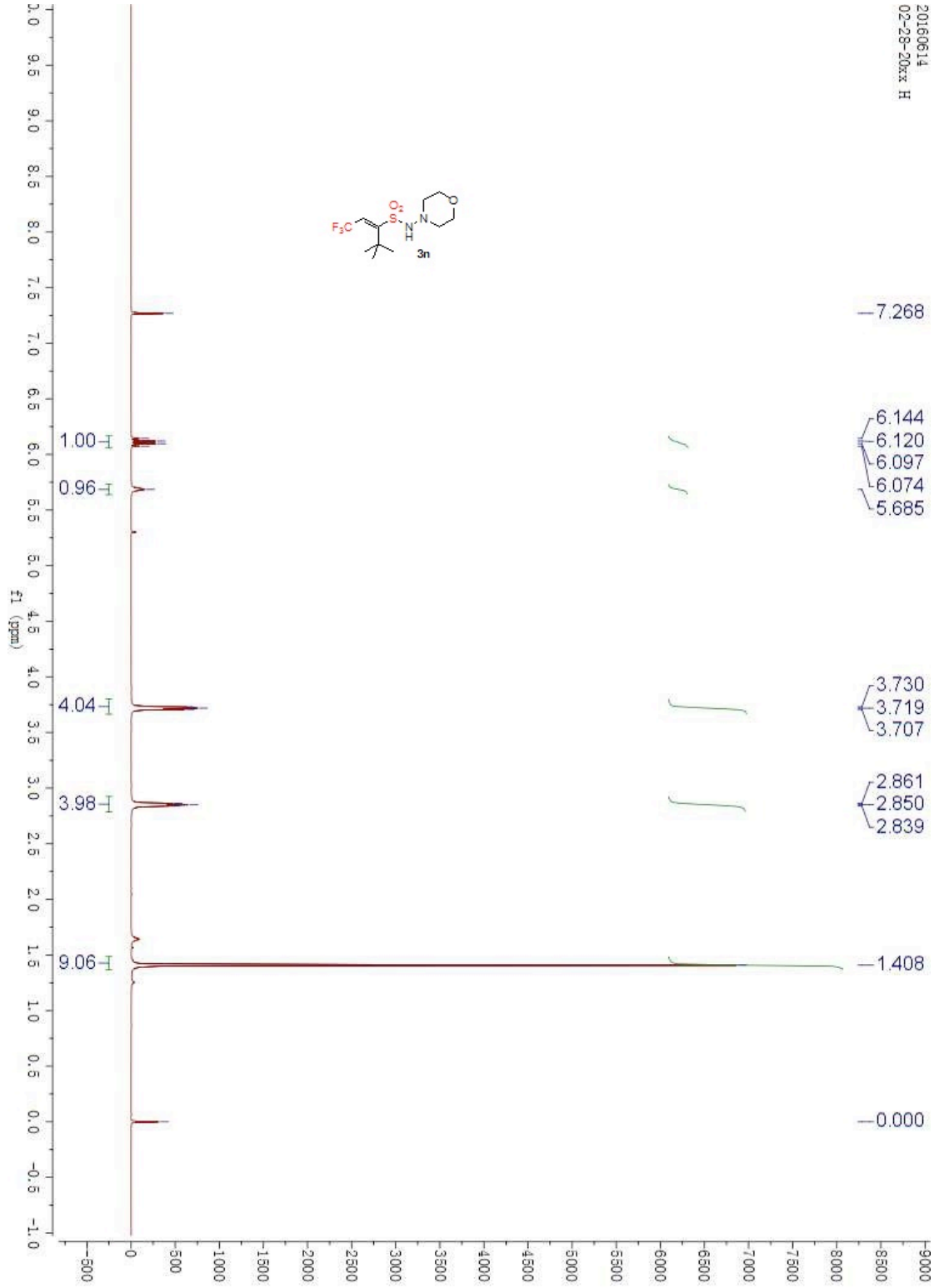

20160411-14
02-27-9 F
-60.16
-60.18
3l
f1 (ppm)

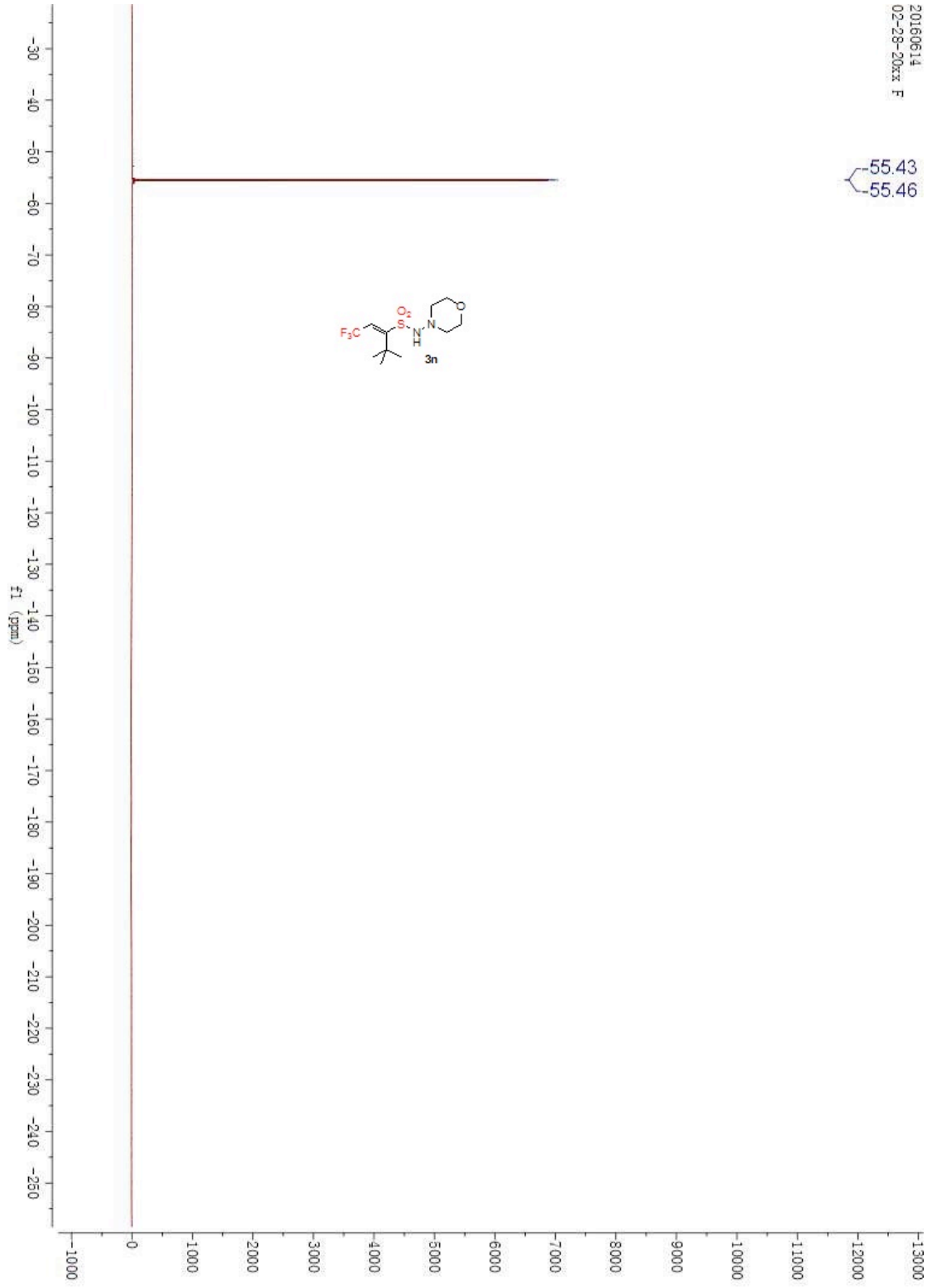

20160411-14
02-27-9 C
148.99
148.94
133.24
131.61
130.67
129.15
128.79
128.44
128.39
128.08
127.82
126.91
126.54
125.81
125.30
124.61
122.60
119.89
117.51
77.32
77.00
76.68
66.39
57.32
3l
f1 (ppm)

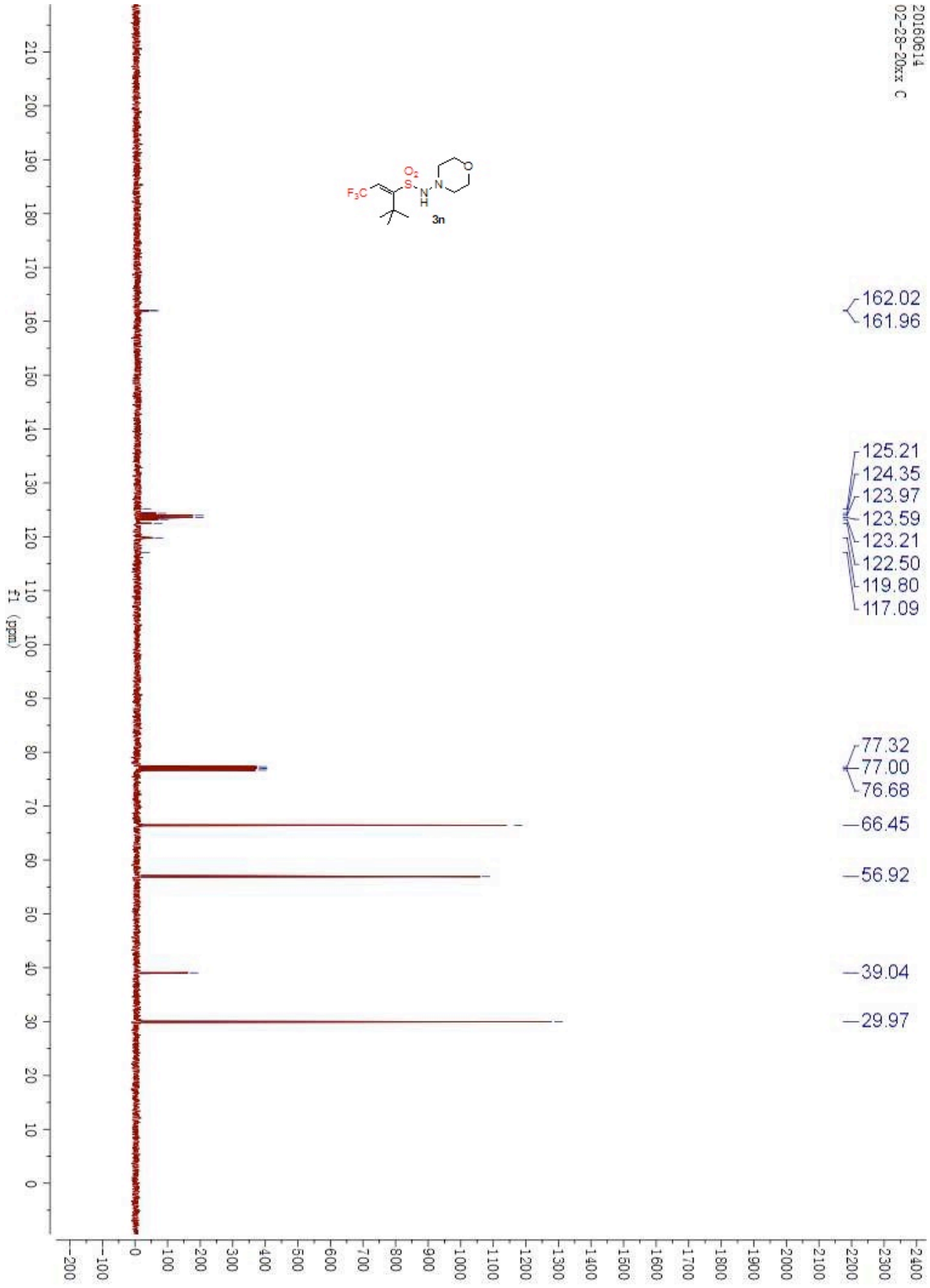

3m
7.655
7.650
7.648
7.395
7.388
7.383
7.375
7.268
7.238
7.226
6.985
6.966
5.599
3.668
3.656
3.645
2.700
2.689
2.678
0.000
0.92
0.96
0.97
1.00
0.98
4.14
4.13
f1 (ppm)

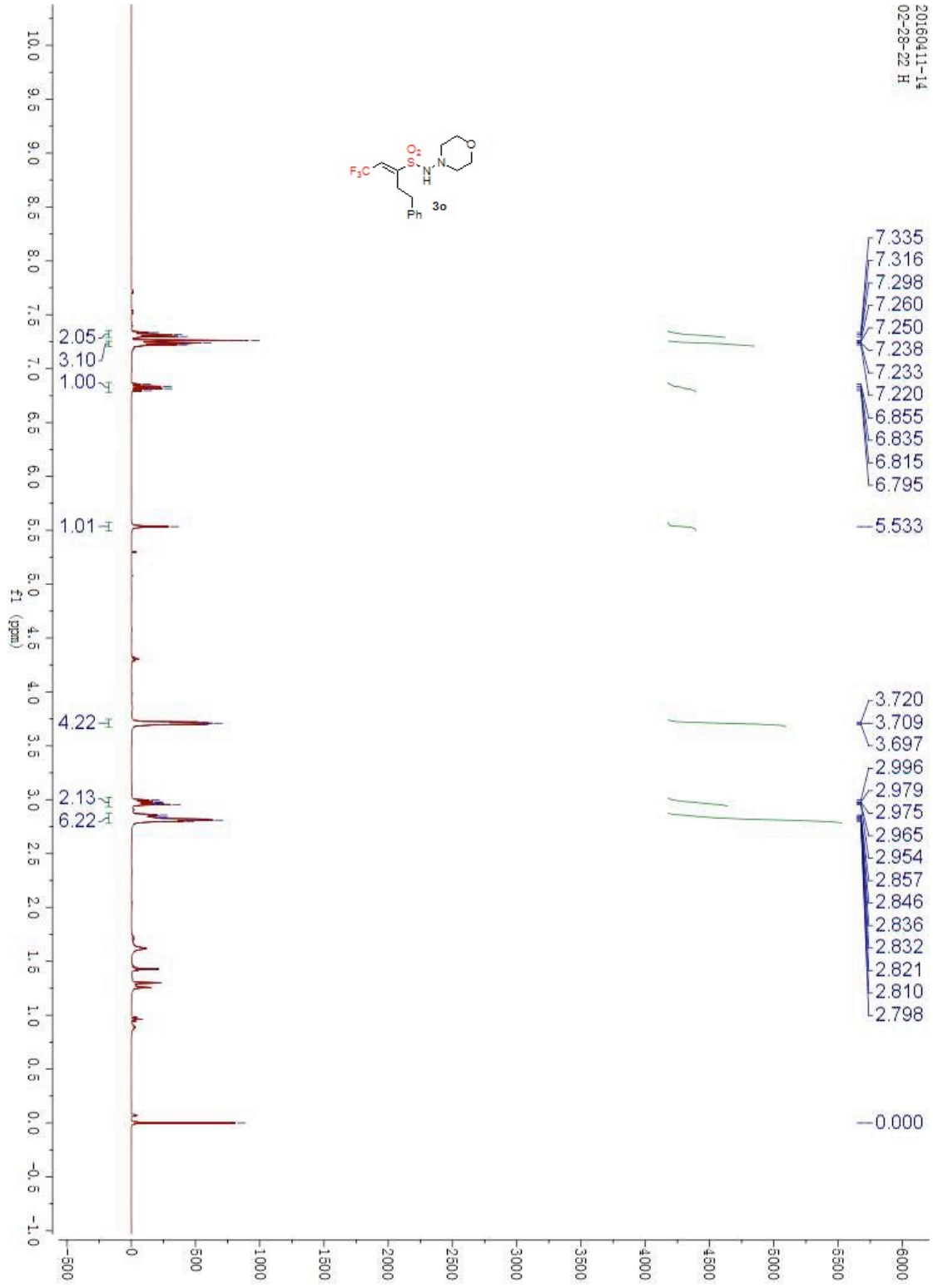

02-28-19 F
3m
-58.10
-58.12
f1 (ppm)

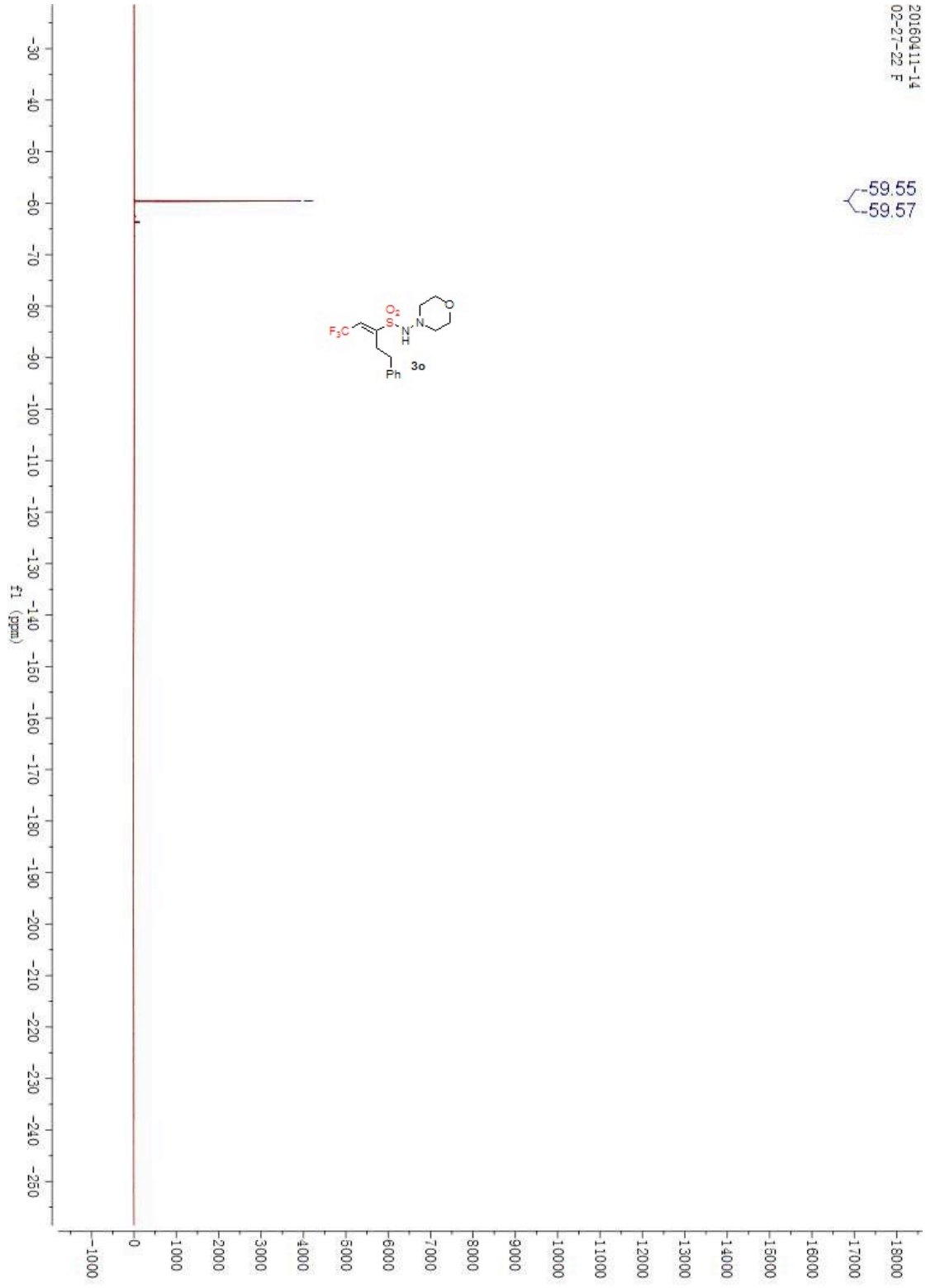

lyw
02-28-19 C
3m
145.18
145.12
128.73
127.54
126.90
126.54
126.19
125.94
125.83
125.56
122.85
120.14
117.42
77.32
77.00
76.68
66.45
57.06
f1 (ppm)

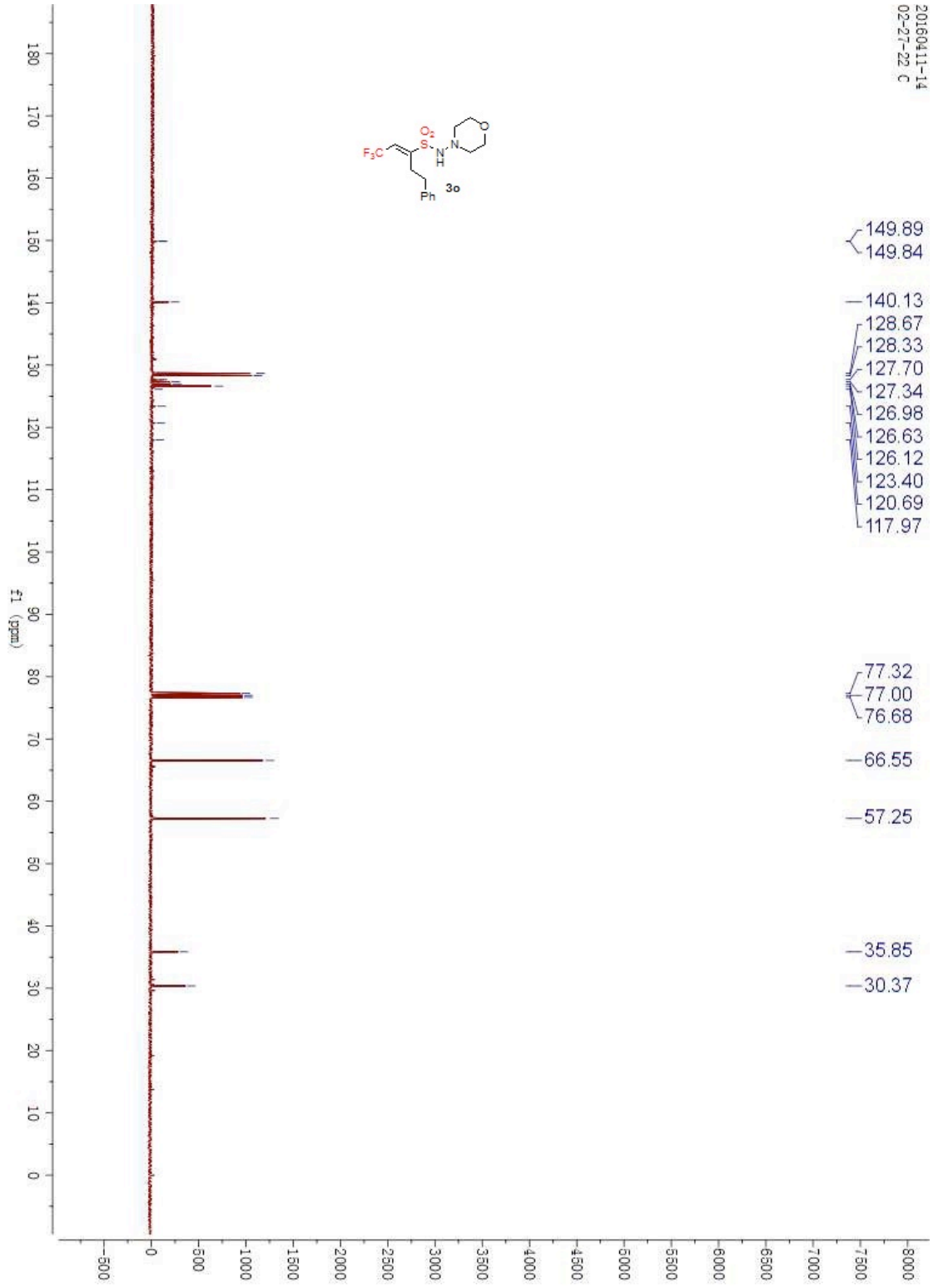

20160614
02-28-20xx H
3n
7.268
6.144
6.120
6.097
6.074
5.685
3.730
3.719
3.707
2.861
2.850
2.839
1.408
0.000
1.00
0.96
4.04
3.98
9.06
f1 (ppm)

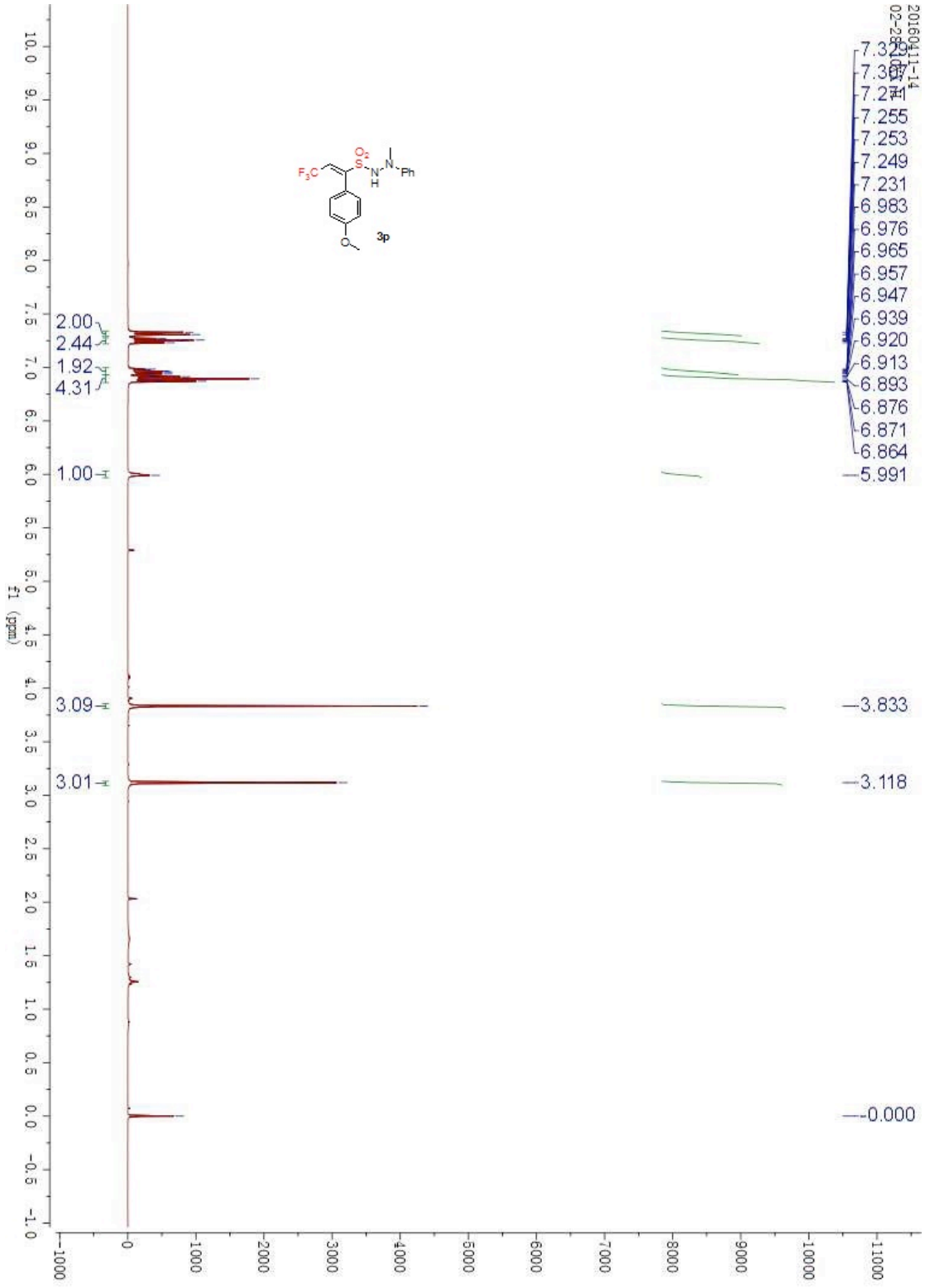

20160614
02-28-20xx F
-55.43
-55.46
3n
f1 (ppm)

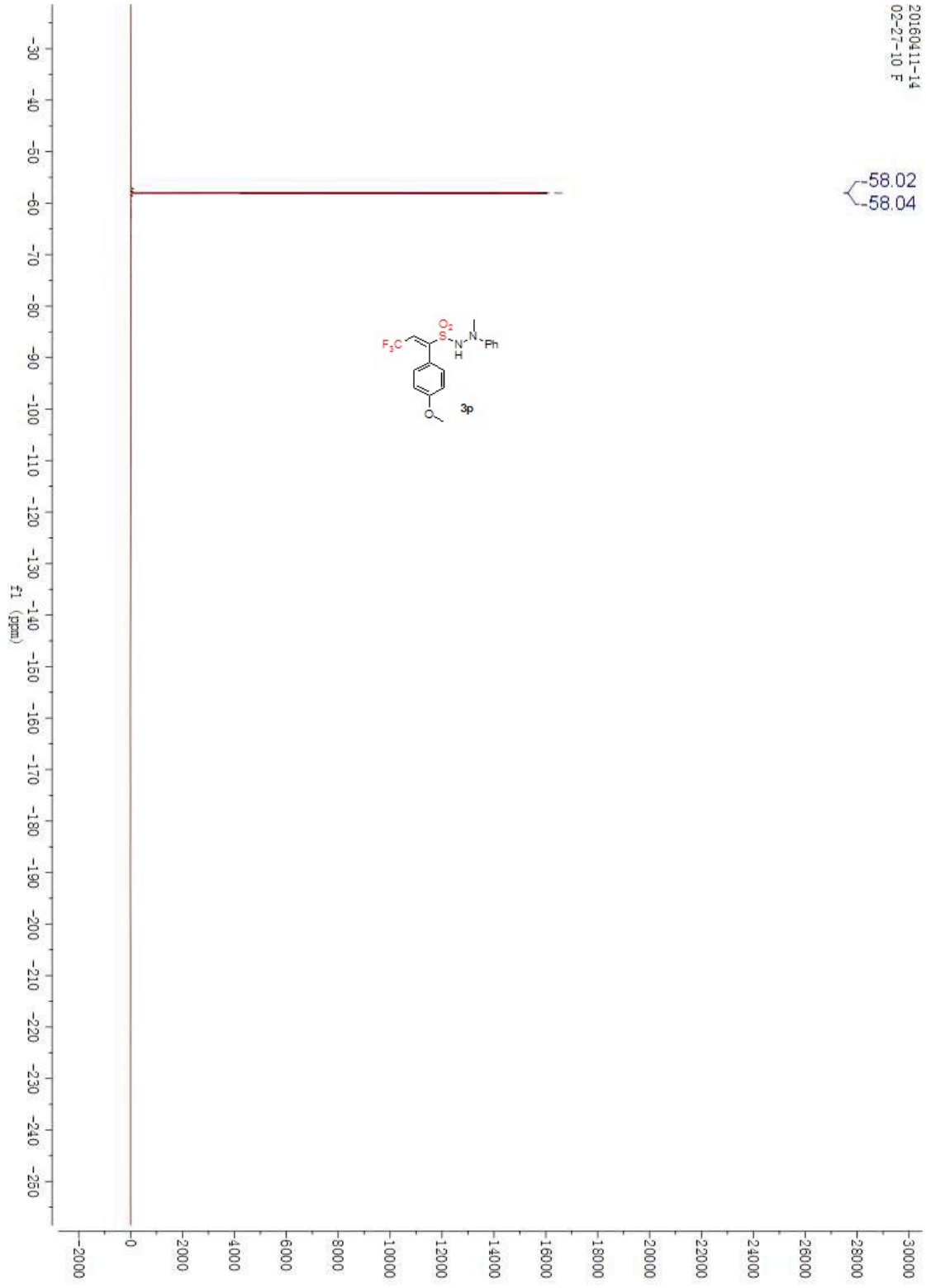

20160614
02-28-20xx C
3n
162.02
161.96
125.21
124.35
123.97
123.59
123.21
122.50
119.80
117.09
77.32
77.00
76.68
66.45
56.92
39.04
29.97
f1 (ppm)

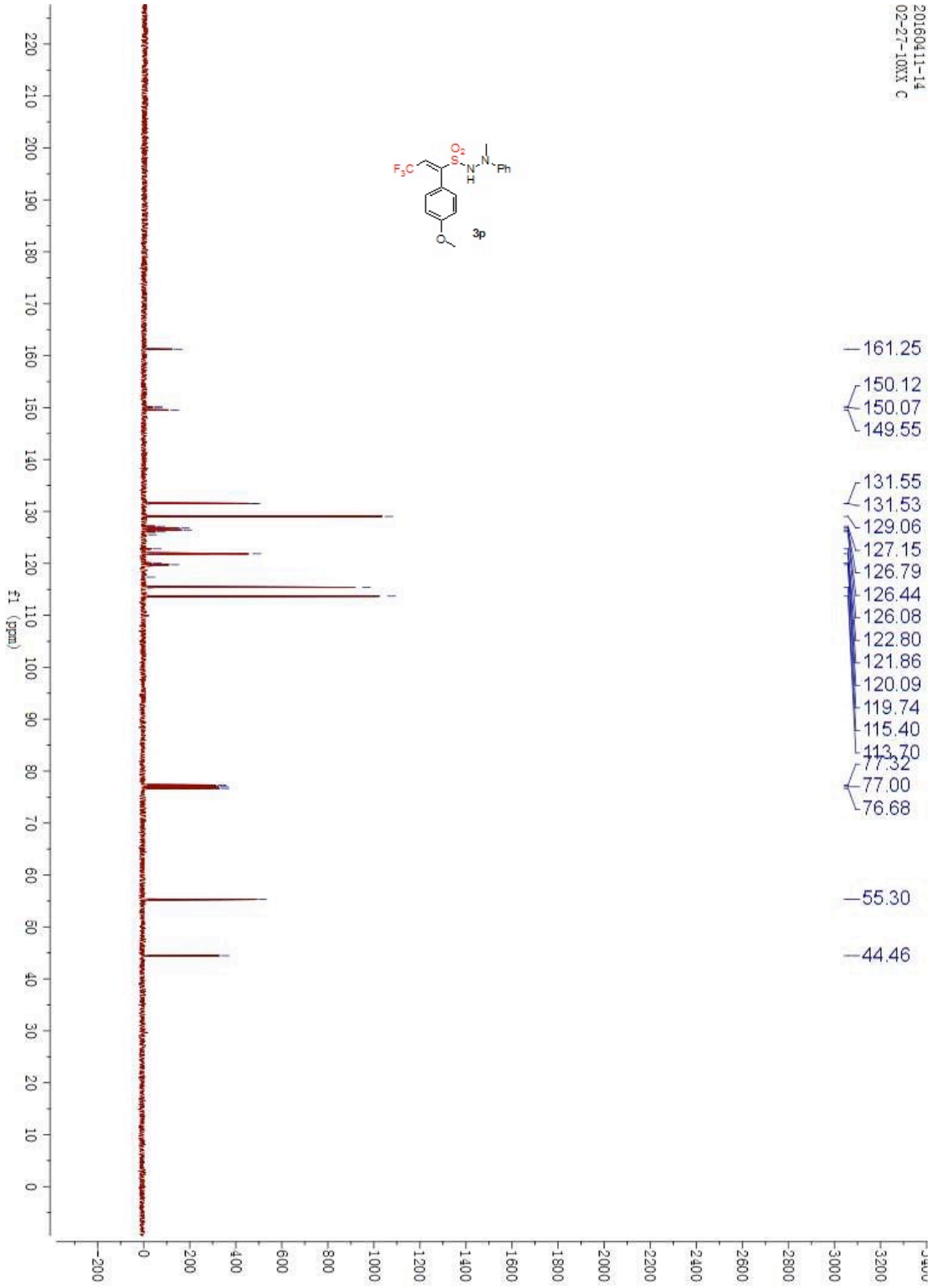

20160411-14
02-28-22 H
3o
7.335
7.316
7.298
7.260
7.250
7.238
7.233
7.220
6.855
6.835
6.815
6.795
5.533
3.720
3.709
3.697
2.996
2.979
2.975
2.965
2.954
2.857
2.846
2.836
2.832
2.821
2.810
2.798
0.000
2.05
3.10
1.00
1.01
4.22
2.13
6.22
f1 (ppm)

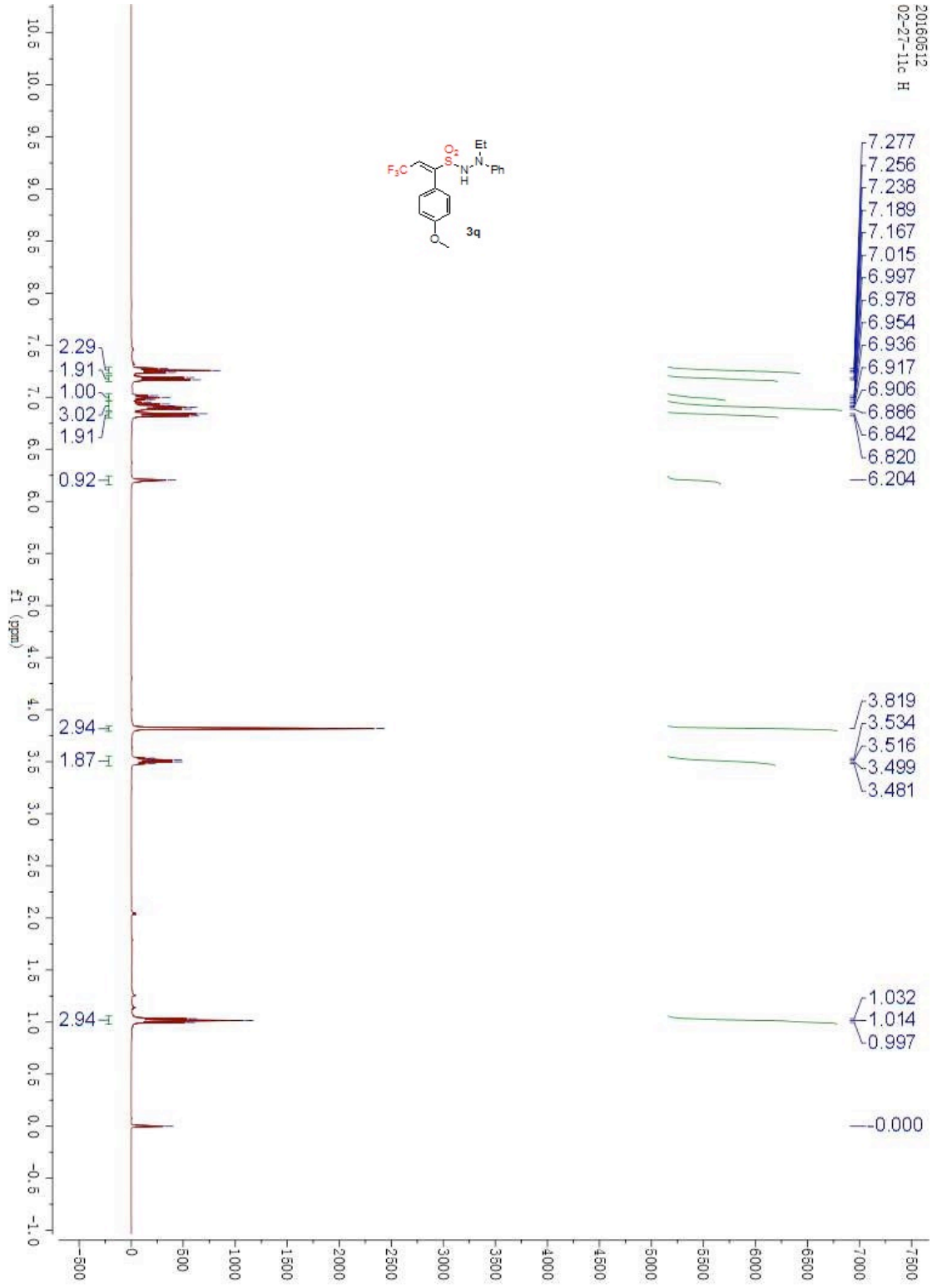

20160411-14
02-27-22 F
-59.55
-59.57
3o
f1 (ppm)

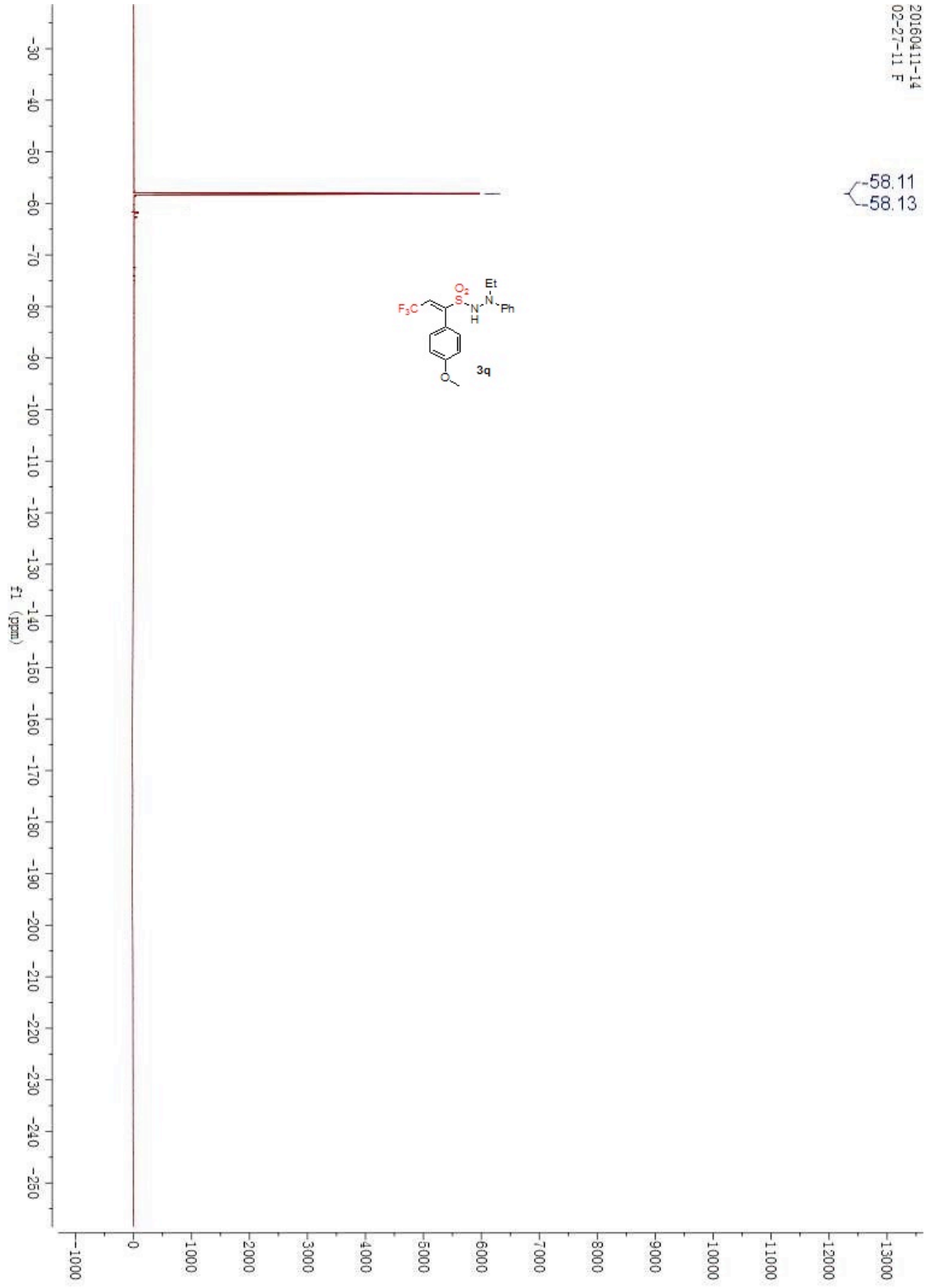

20160411-14
02-27-22 C
3o
149.89
149.84
140.13
128.67
128.33
127.70
127.34
126.98
126.63
126.12
123.40
120.69
117.97
77.32
77.00
76.68
66.55
57.25
35.85
30.37
f1 (ppm)

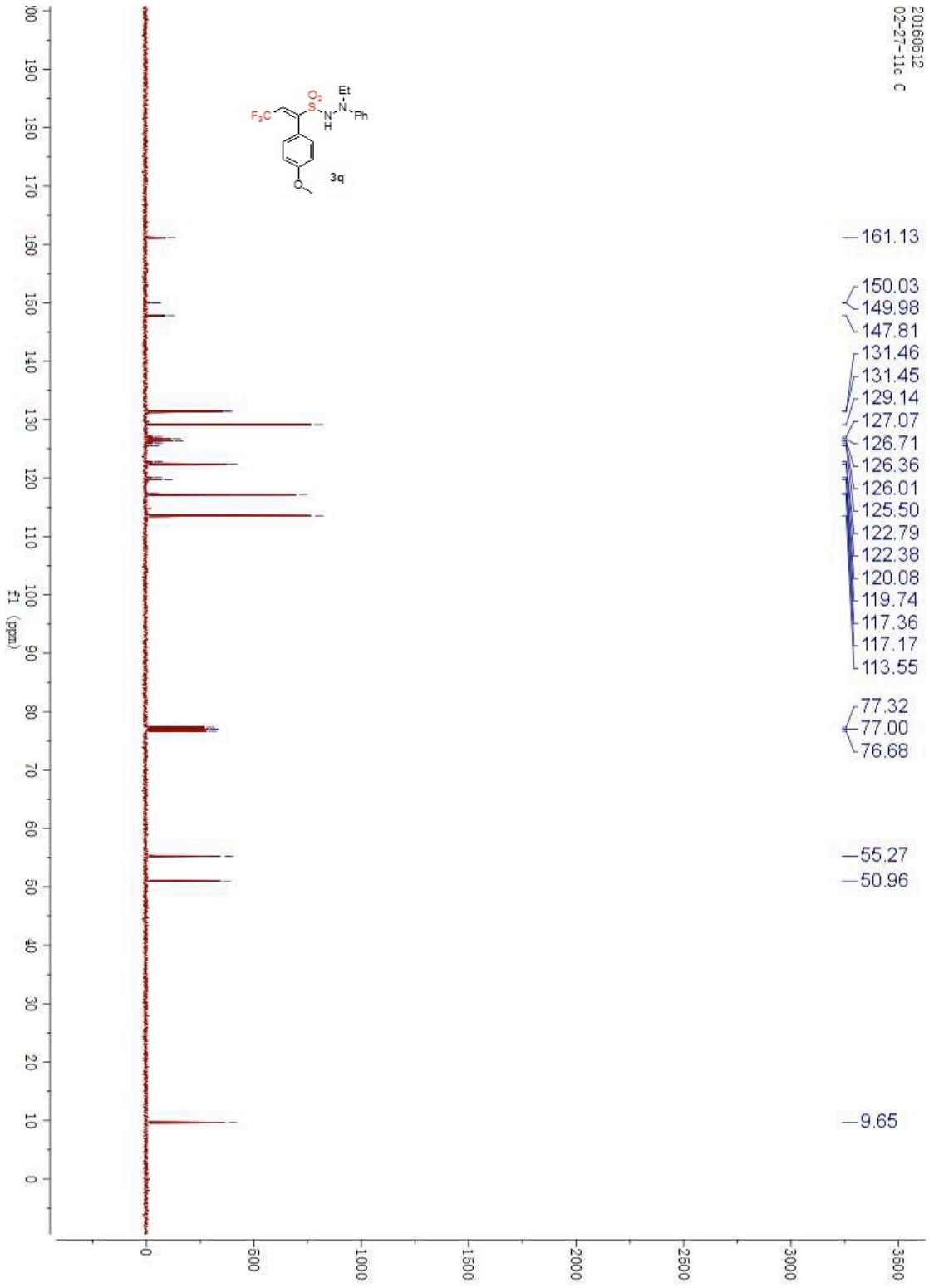

3p
2.00
2.44
1.92
4.31
1.00
3.09
3.01
7.329
7.307
7.274
7.255
7.253
7.249
7.231
6.983
6.976
6.965
6.957
6.947
6.939
6.920
6.913
6.893
6.876
6.871
6.864
5.991
3.833
3.118
0.000
f1 (ppm)

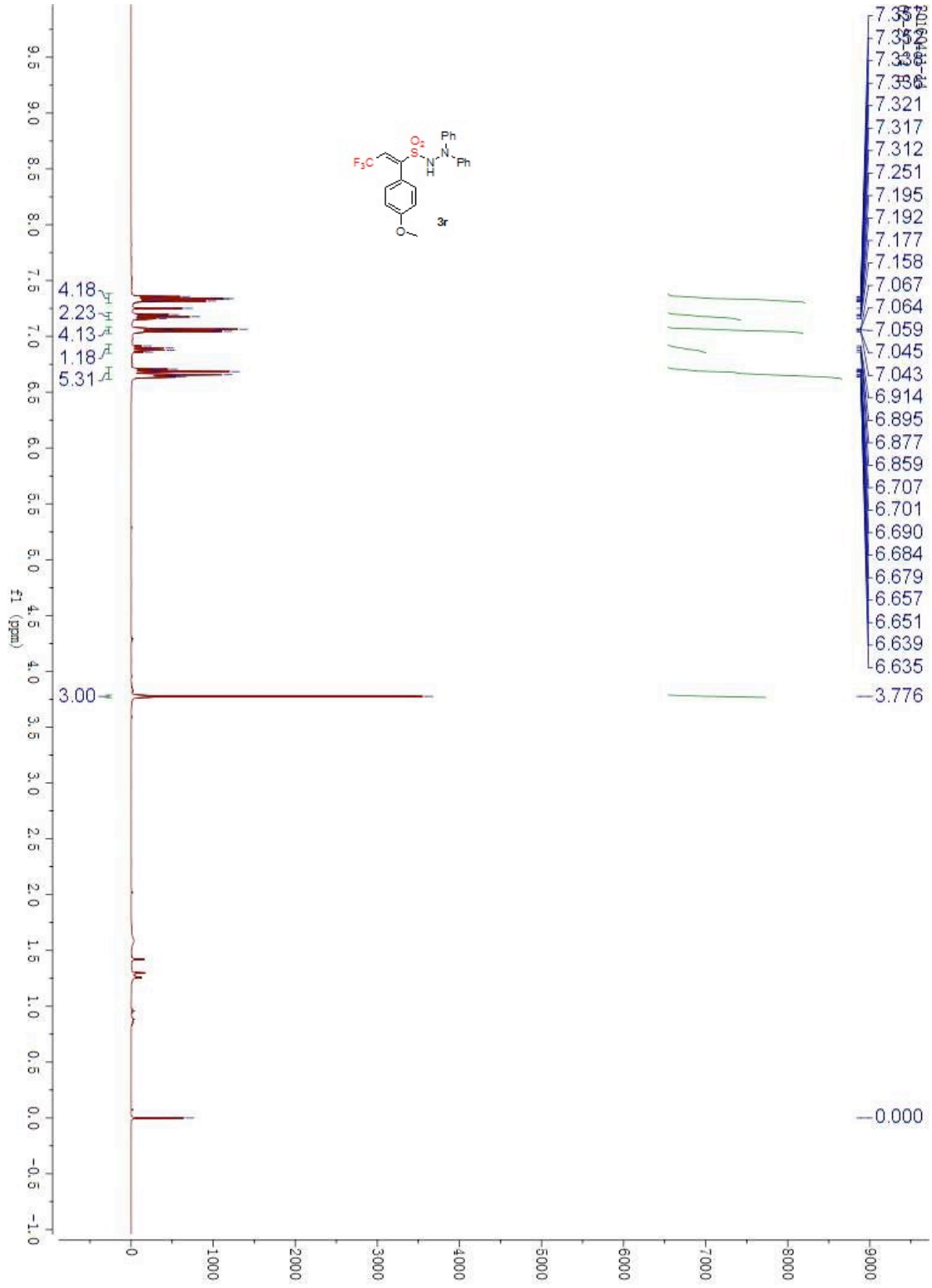

20160411-14
02-27-10 F
-58.02
-58.04
3p
f1 (ppm)

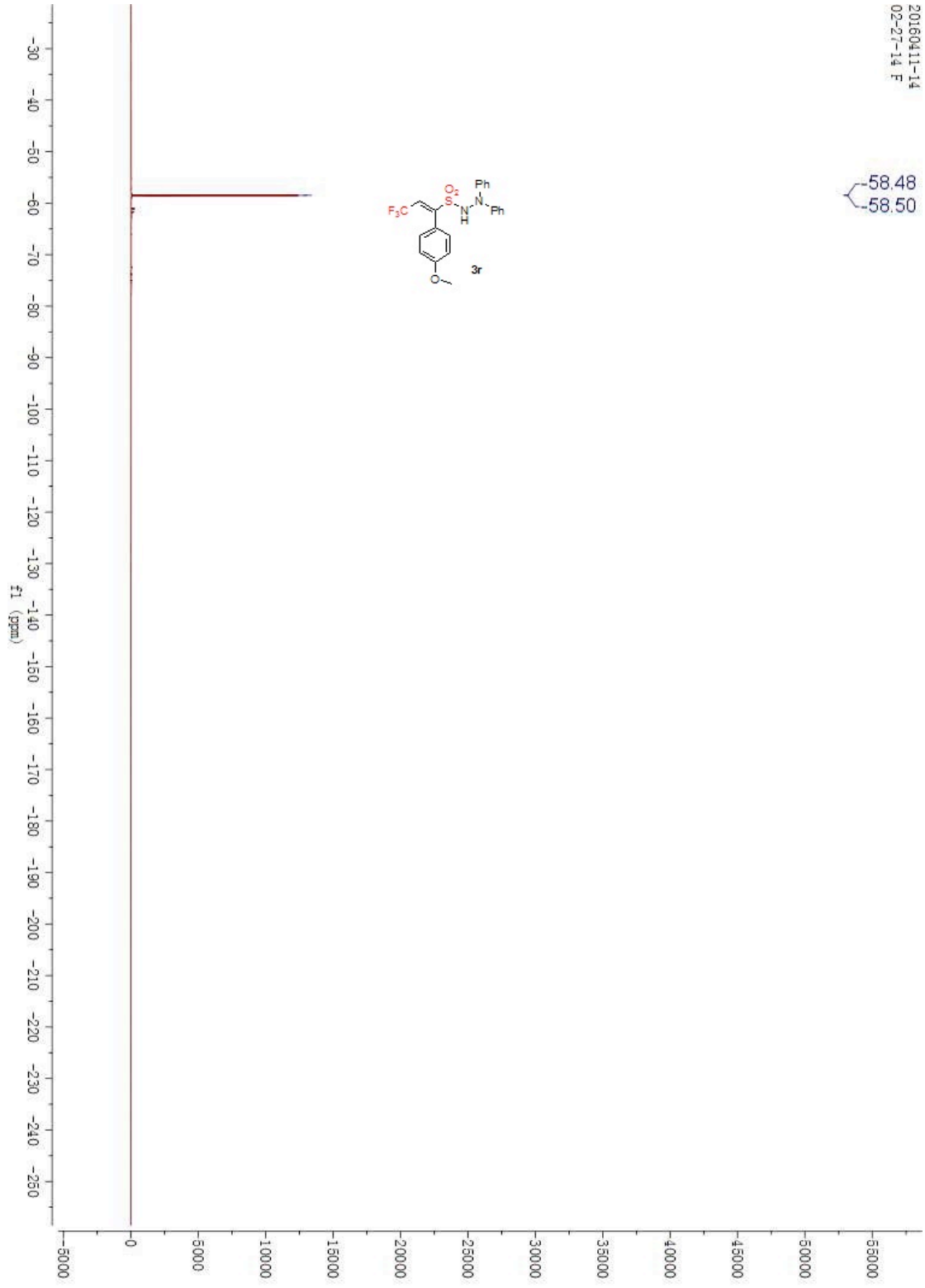

20160411-14
02-27-10XX C
3p
161.25
150.12
150.07
149.55
131.55
131.53
129.06
127.15
126.79
126.44
126.08
122.80
121.86
120.09
119.74
115.40
113.70
77.32
77.00
76.68
55.30
44.46
f1 (ppm)

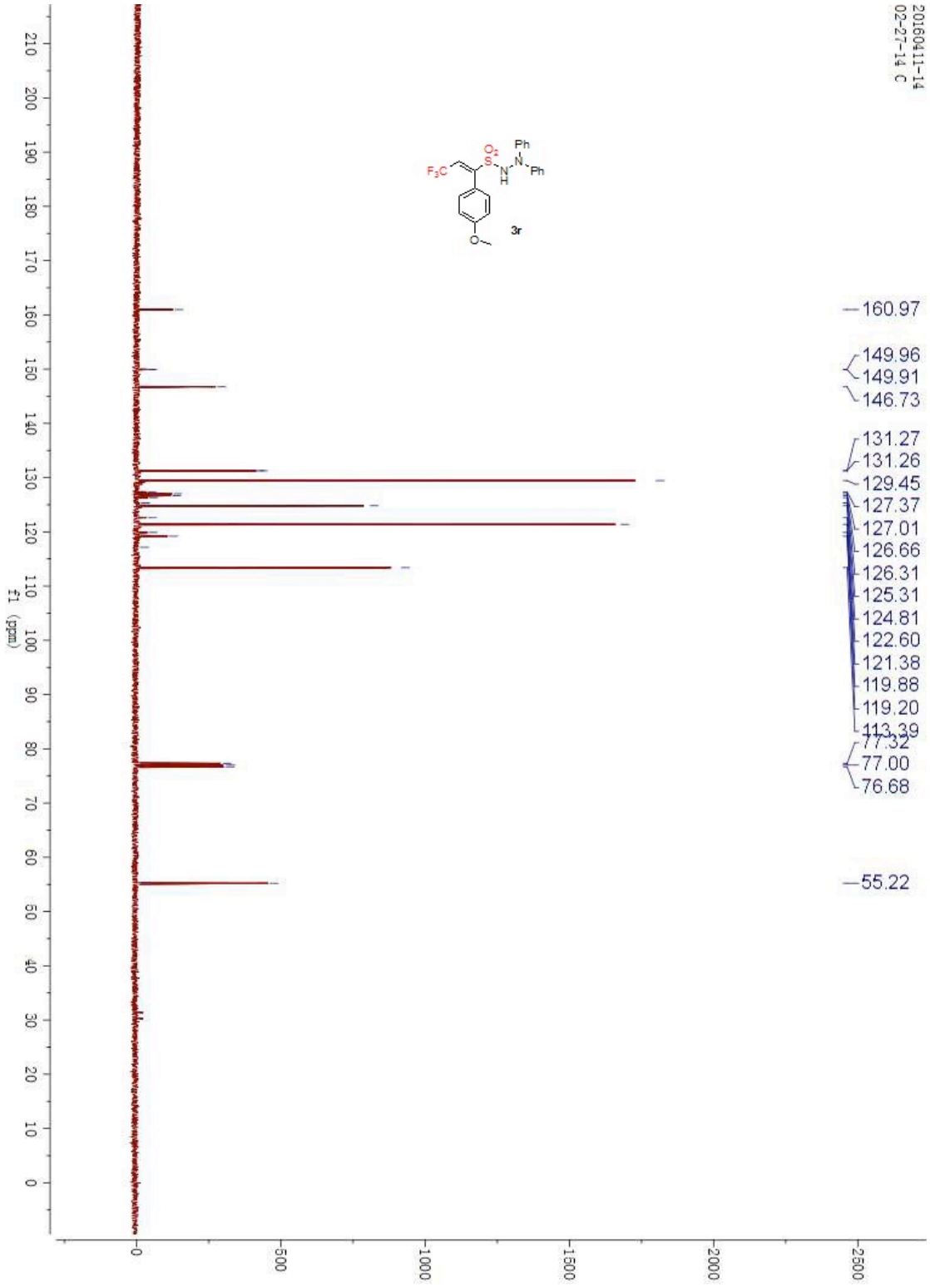

20160512
02-27-11c H
3q
7.277
7.256
7.238
7.189
7.167
7.015
6.997
6.978
6.954
6.936
6.917
6.906
6.886
6.842
6.820
6.204
3.819
3.534
3.516
3.499
3.481
1.032
1.014
0.997
0.000
2.29
1.91
1.00
3.02
1.91
0.92
2.94
1.87
2.94
f1 (ppm)

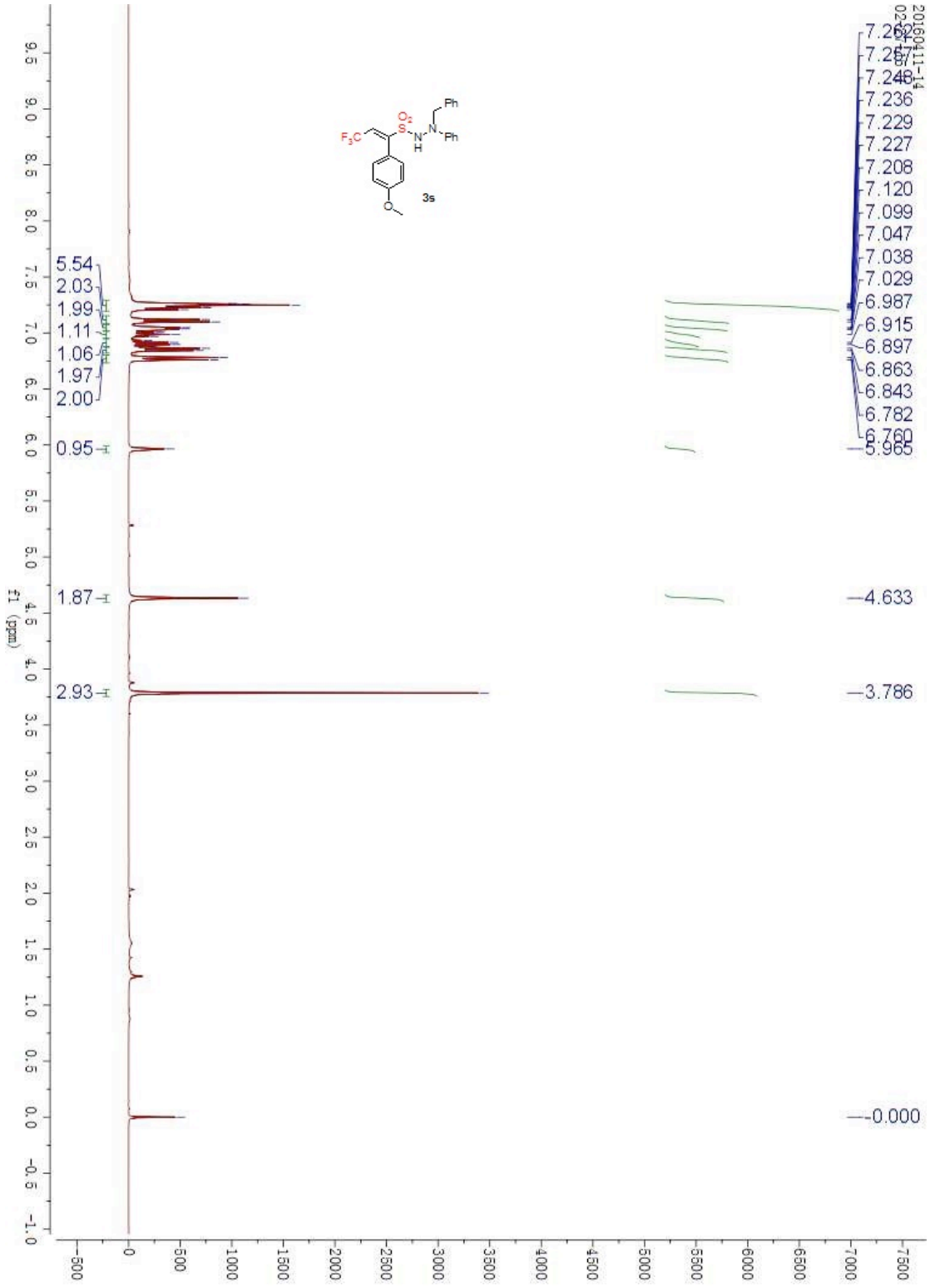

20160411-14
02-27-11 F
-58.11
-58.13
Et
N
Ph
O
S
N
H
F3C
3q
f1 (ppm)

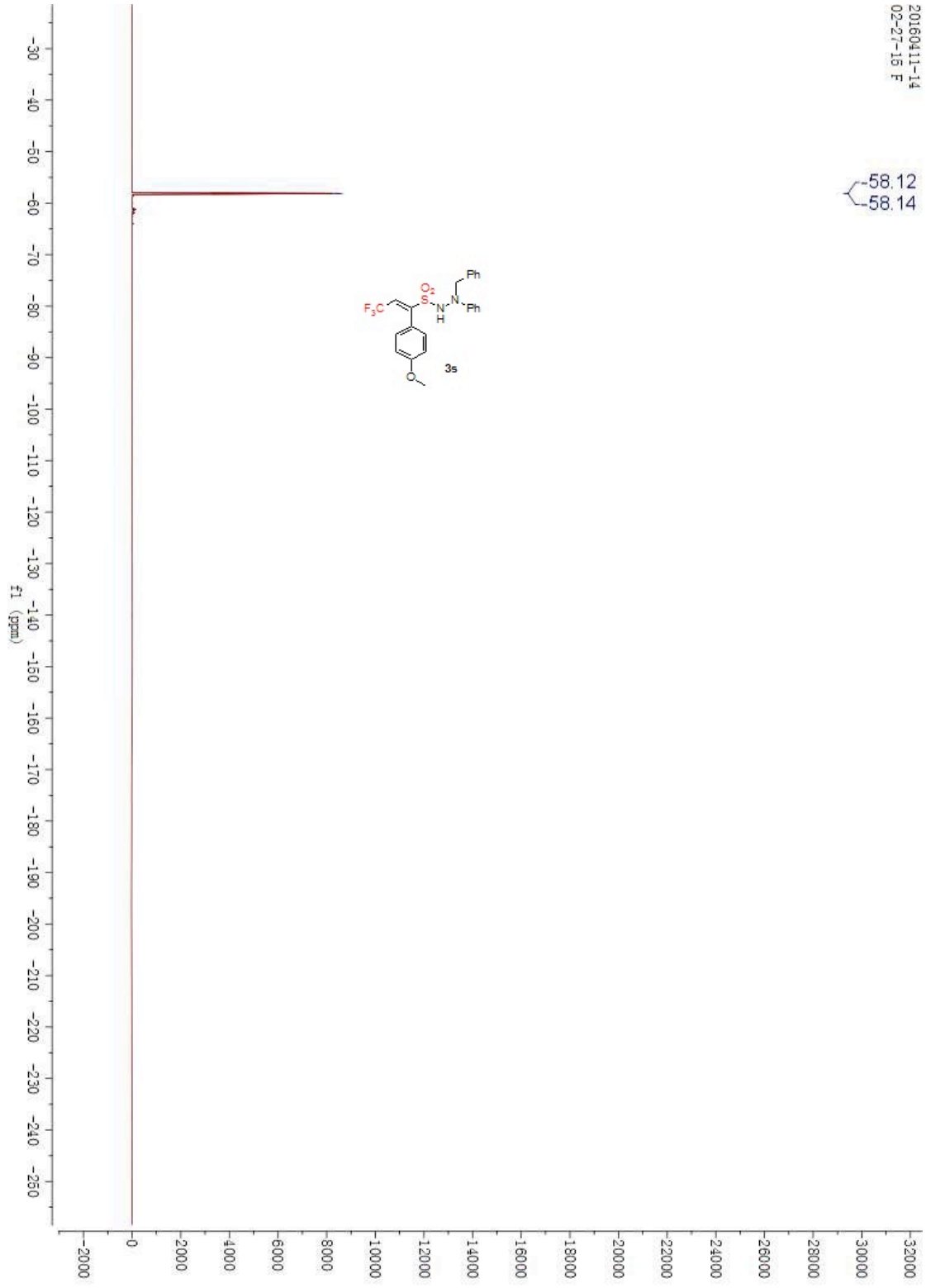

20160612
02-27-11c C
3q
161.13
150.03
149.98
147.81
131.46
131.45
129.14
127.07
126.71
126.36
126.01
125.50
122.79
122.38
120.08
119.74
117.36
117.17
113.55
77.32
77.00
76.68
55.27
50.96
9.65
f1 (ppm)

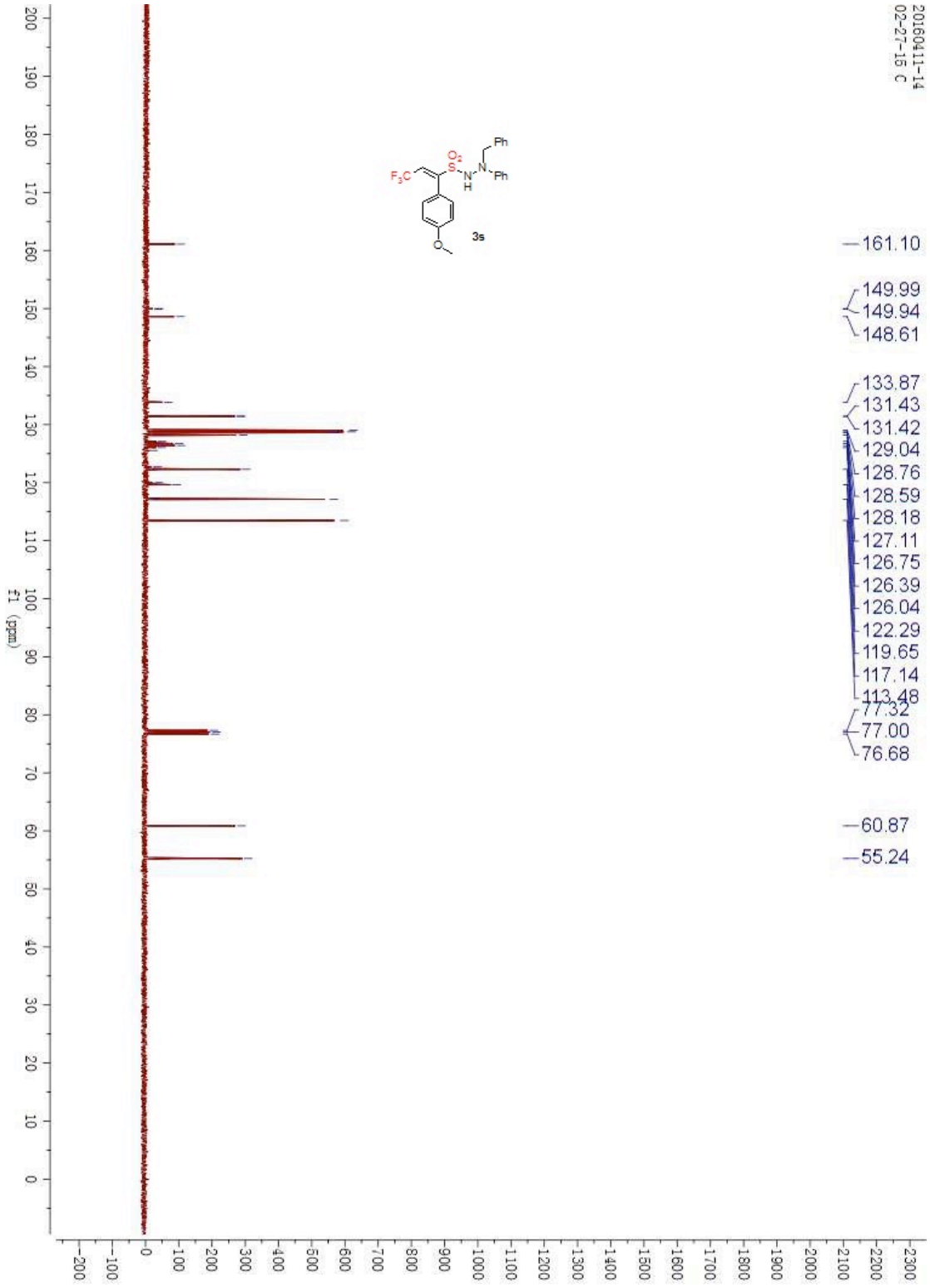

3r
4.18
2.23
4.13
1.18
5.31
3.00
7.321
7.317
7.312
7.251
7.195
7.192
7.177
7.158
7.067
7.064
7.059
7.045
7.043
6.914
6.895
6.877
6.859
6.707
6.701
6.690
6.684
6.679
6.657
6.651
6.639
6.635
3.776
0.000
f1 (ppm)

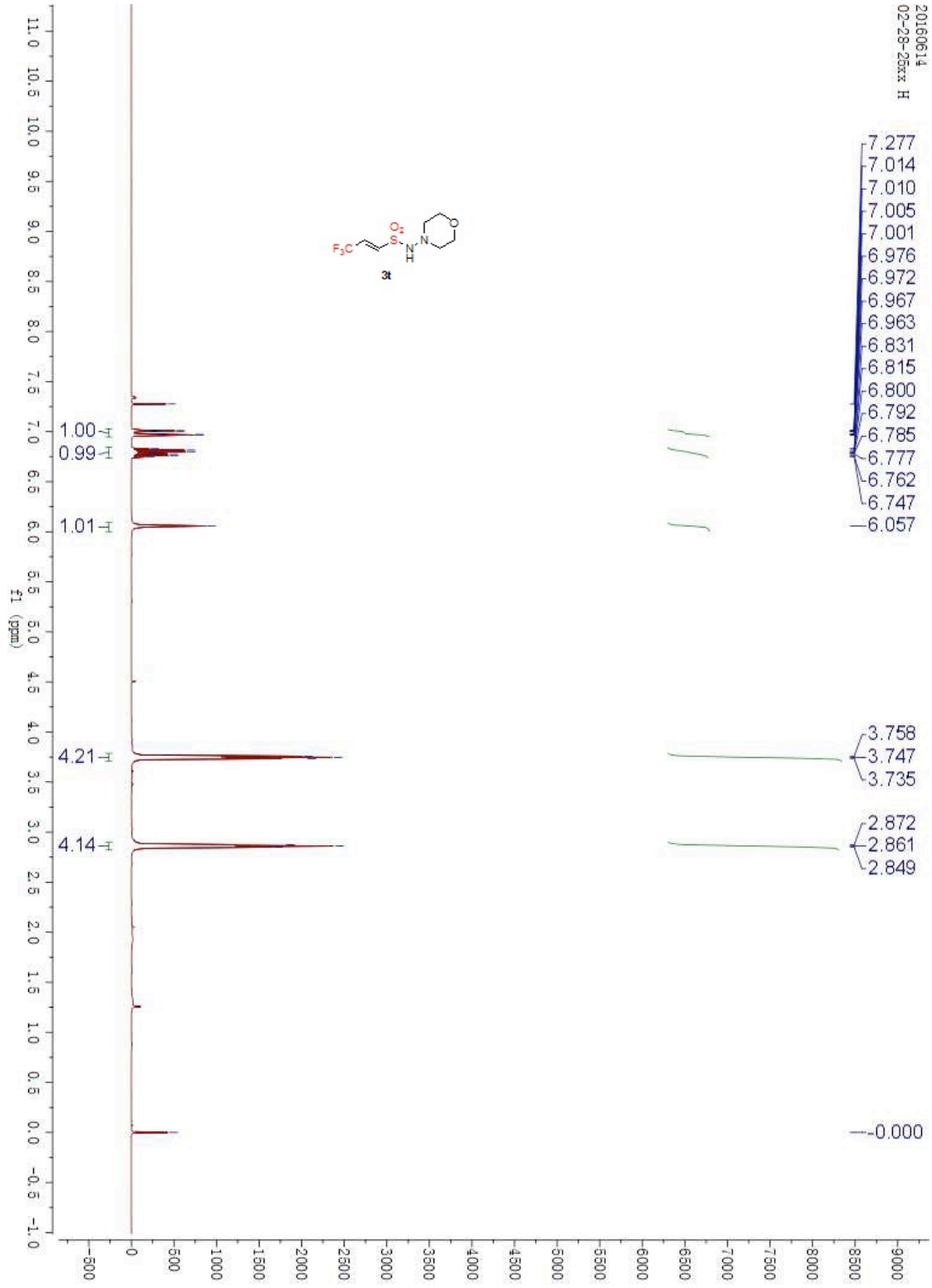

20160411-14
02-27-14 F
-58.48
-58.50
3r
f1 (ppm)

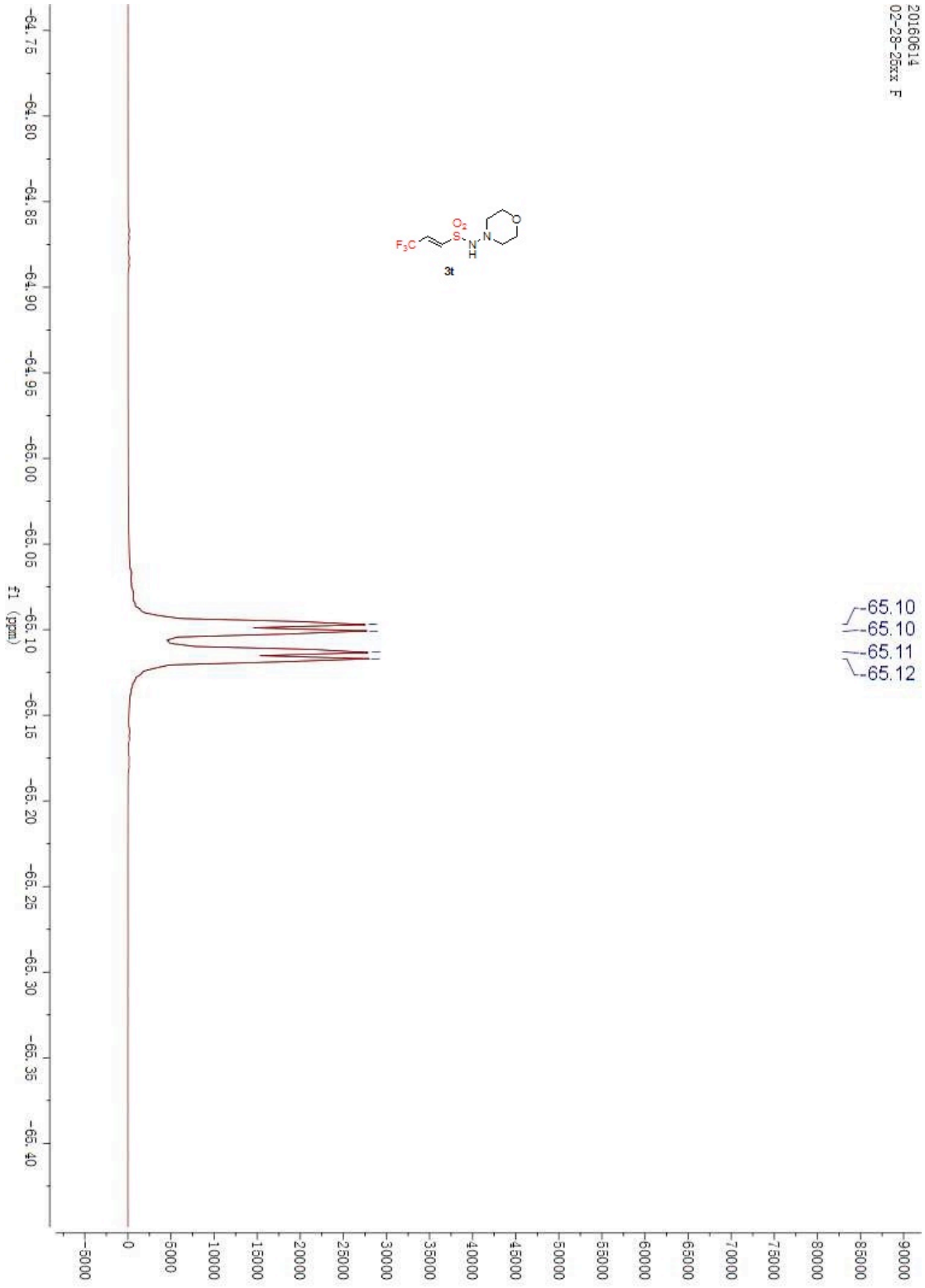

20160411-14
02-27-14 C
3r
160.97
149.96
149.91
146.73
131.27
131.26
129.45
127.37
127.01
126.66
126.31
125.31
124.81
122.60
121.38
119.88
119.20
113.39
77.32
77.00
76.68
55.22
f1 (ppm)

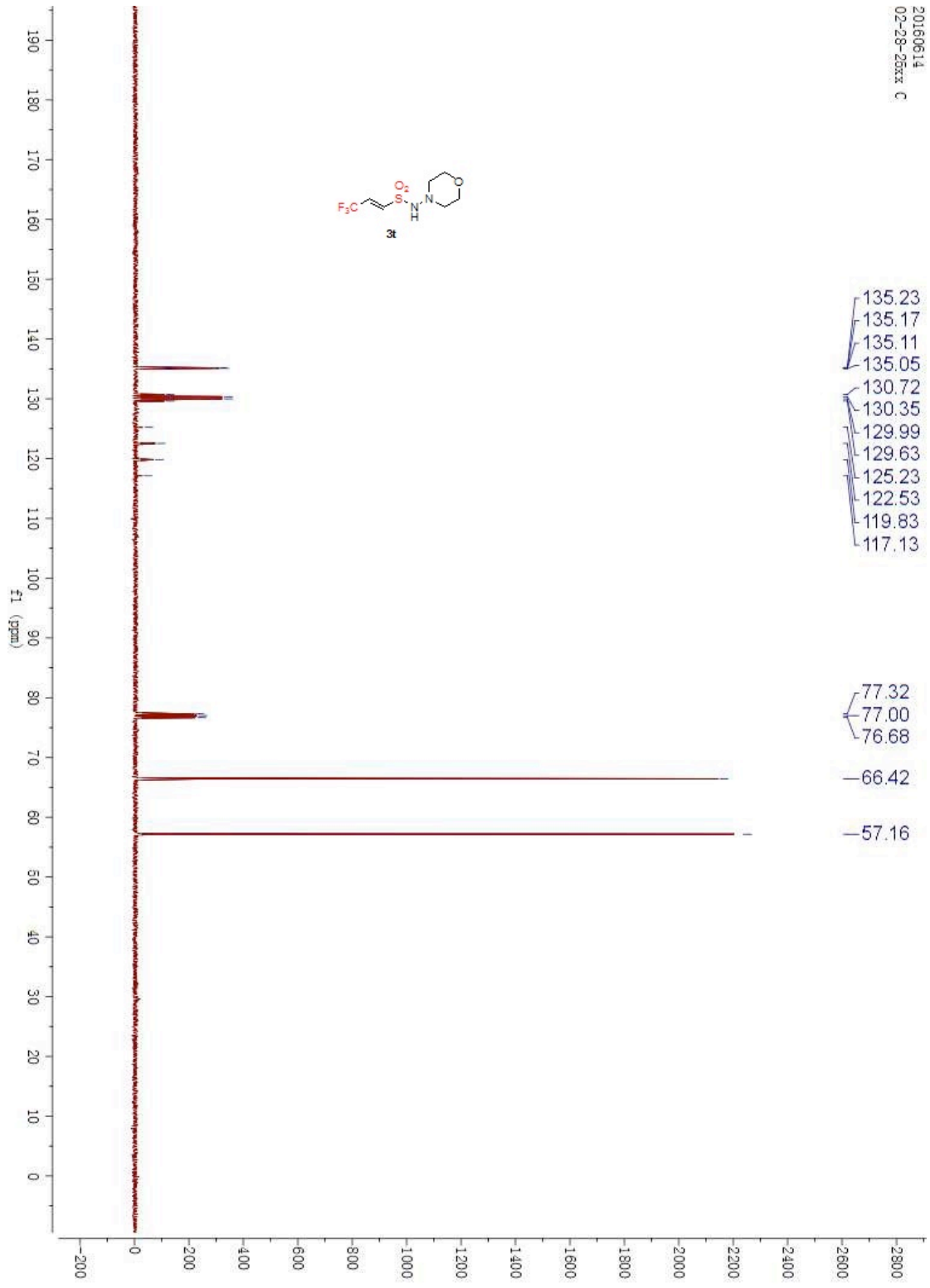

3s
5.54
2.03
1.99
1.11
1.06
1.97
2.00
0.95
1.87
2.93
7.262
7.257
7.248
7.236
7.229
7.227
7.208
7.120
7.099
7.047
7.038
7.029
6.987
6.915
6.897
6.863
6.843
6.782
6.760
5.965
4.633
3.786
0.000
f1 (ppm)


20160411-14
02-27-15 F
-58.12
-58.14
Ph
Ph
3s
f1 (ppm)

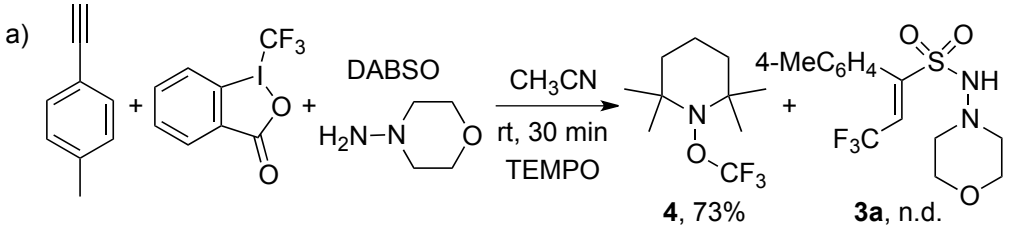

20160411-14
02-27-15 C
3s
161.10
149.99
149.94
148.61
133.87
131.43
131.42
129.04
128.76
128.59
128.18
127.11
126.75
126.39
126.04
122.29
119.65
117.14
113.48
77.32
77.00
76.68
60.87
55.24
f1 (ppm)


20160614
02-28-25xxx H
7.277
7.014
7.010
7.005
7.001
6.976
6.972
6.967
6.963
6.831
6.815
6.800
6.792
6.785
6.777
6.762
6.747
6.057
3.758
3.747
3.735
2.872
2.861
2.849
-0.000
1.00
0.99
1.01
4.21
4.14
3t
f1 (ppm)

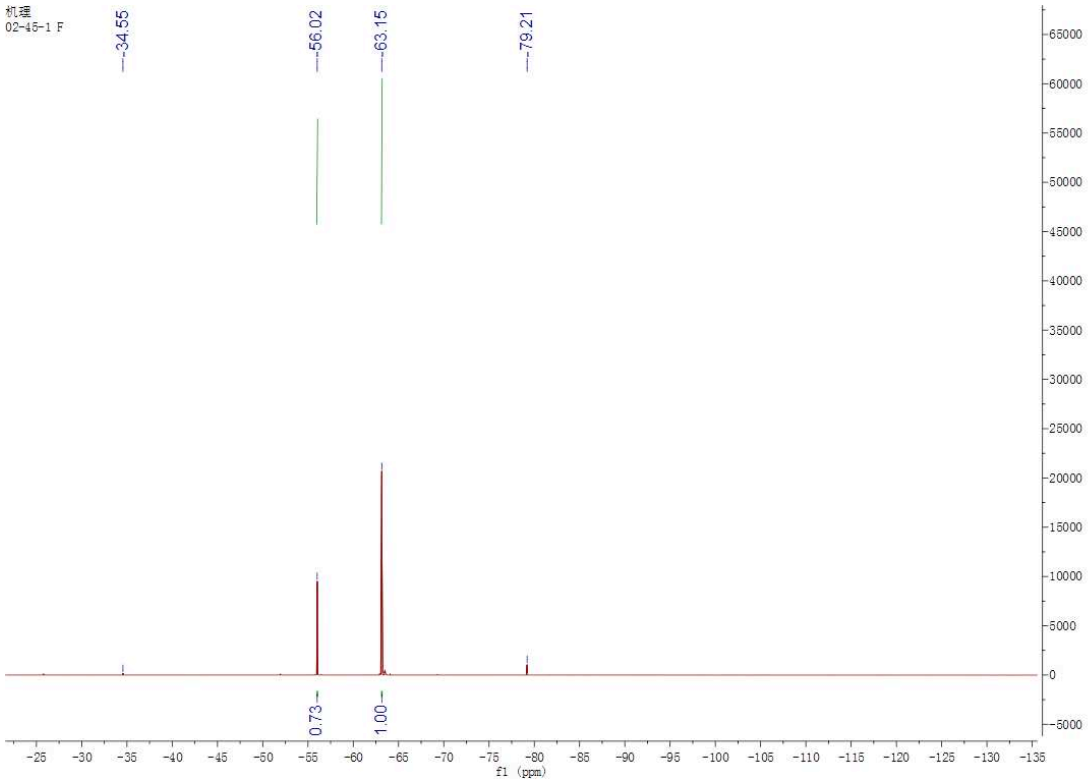

20160614
02-28-25xx F
3t
-65.10
-65.10
-65.11
-65.12
f1 (ppm)


20160614
02-28-26xx C
3t
135.23
135.17
135.11
135.05
130.72
130.35
129.99
129.63
125.23
122.53
119.83
117.13
77.32
77.00
76.68
66.42
57.16
f1 (ppm)

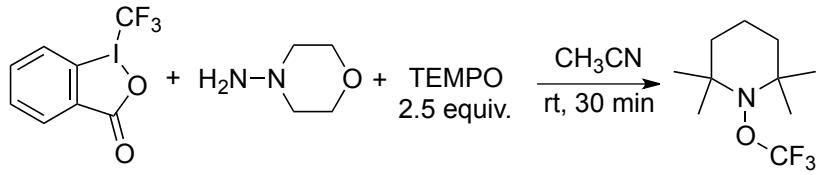
Scheme S1. Investigation of mechanism.



Alkyne **1** (0.2 mmol) was combined with Togni's reagent (96.0 mg, 0.3 mmol), TEMPO (0.50 mmol) and DABSO (0.16 mmol) in a tube. The tube was evacuated and backfilled with N_2 three times before the addition of CH_3CN (4.0 mL). Then the solution was stirred for several minutes at room temperature. Subsequently, morpholin-4-amine **2a** (1.5 equiv.) was added dropwisely to the solution. The reaction continued to stir for 30 minutes. The solvent was evaporated in vacuo, and 1-(trifluoromethyl)benzene (0.2 mmol) and deuterotrichloromethane (1.0 mL) was added. The solution was transferred into NMR tube to perform the ^{19}F NMR.

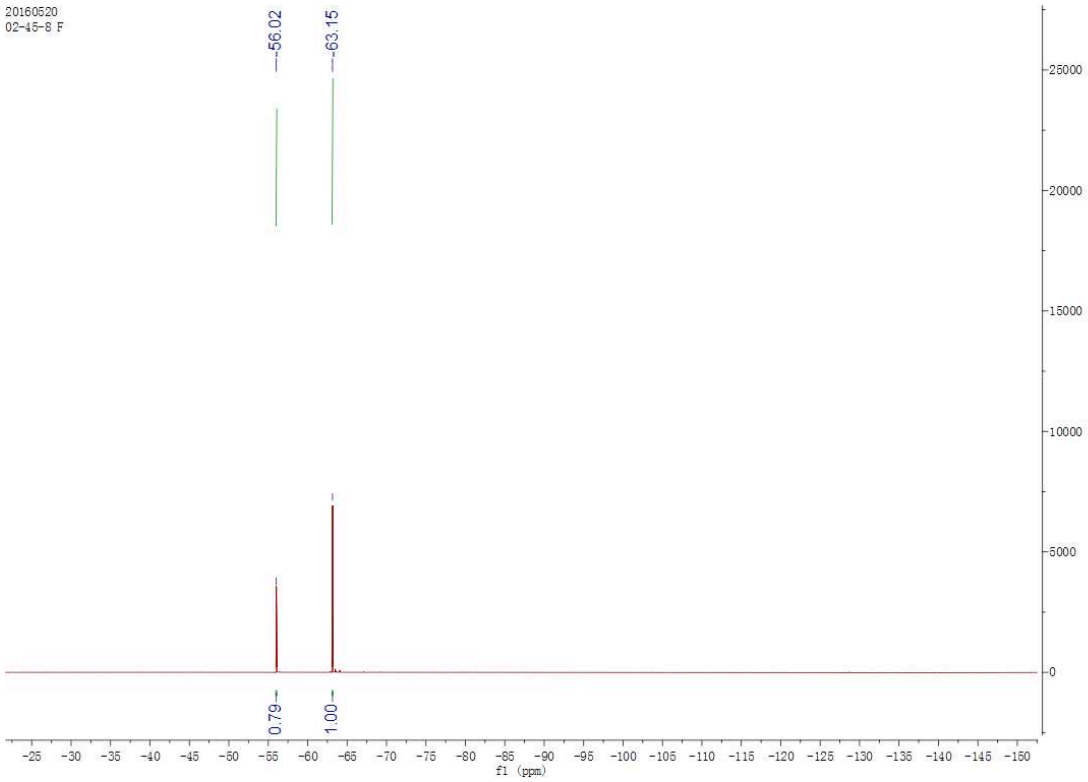


b)

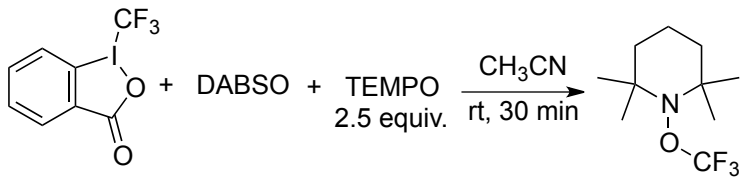


4, 79%

Togni's reagent (96.0 mg, 0.3 mmol) was combined with TEMPO (0.50 mmol) in a tube. The tube was evacuated and backfilled with N_2 three times before the addition of CH_3CN (4.0 mL). Then the solution was stirred for several minutes at room temperature. Subsequently, morpholin-4-amine **2a** (1.5 equiv.) was added dropwisely to the solution. The reaction continued to stir for 30 minutes. The solvent was evaporated in vacuo, 1-(trifluoromethyl)benzene (0.2 mmol) and deuterotrichloromethane (1.0 mL) was added. The solution was transferred into NMR tube to perform the ^{19}F NMR.



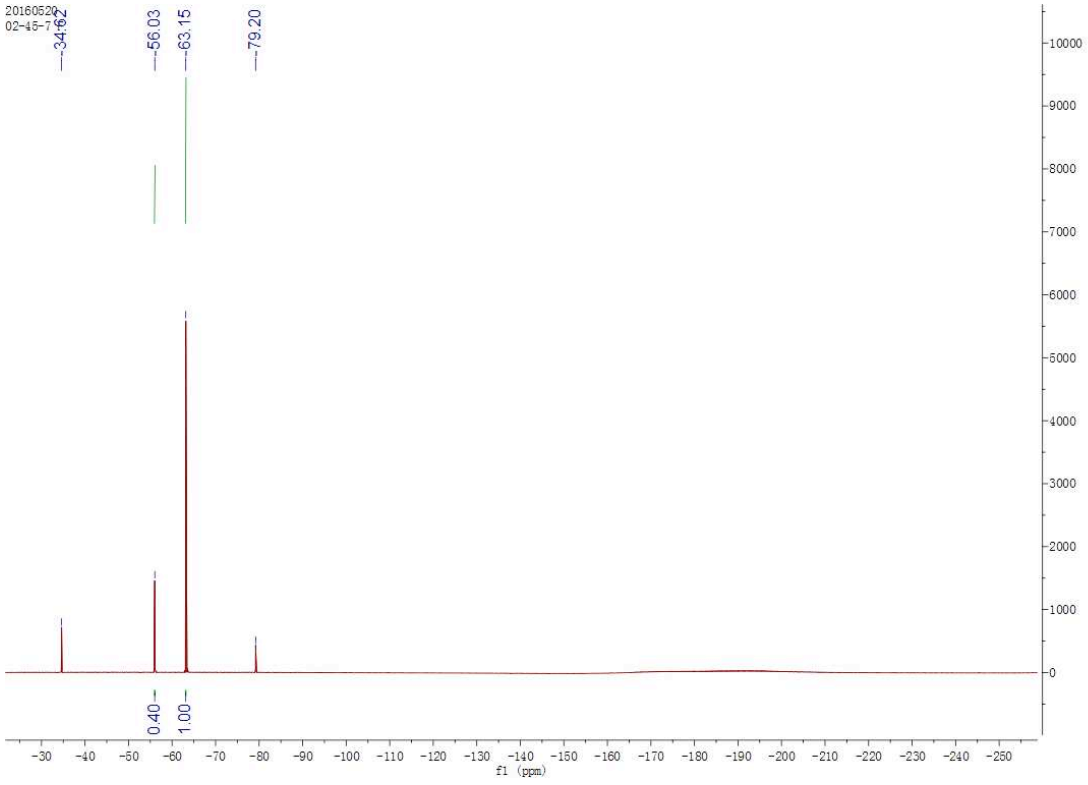
c)



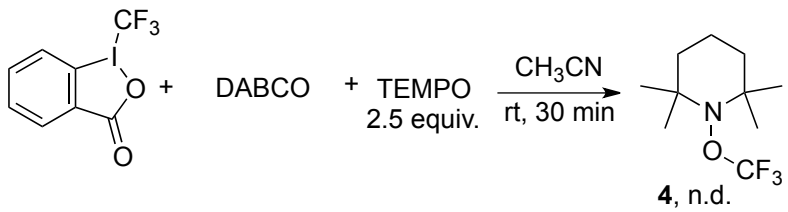
4, 40%

Togni's reagent (96.0 mg, 0.3 mmol) was combined with TEMPO (0.50 mmol) and

DABSO (0.16 mmol) in a tube. The tube was evacuated and backfilled with N_2 three times before the addition of CH_3CN (4.0 mL). The reaction was stirred for 30 minutes. The solvent was evaporated in vacuo, 1-(trifluoromethyl)benzene (0.2 mmol) and deuterotrichloromethane (1.0 mL) was added. The solution was transferred into NMR tube to perform the ^{19}F NMR.



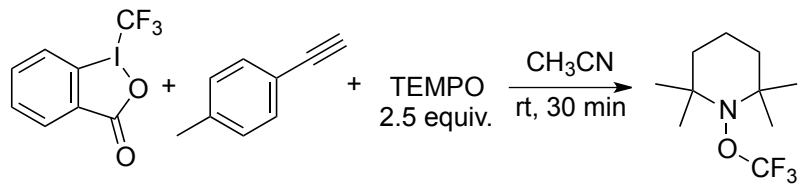
d)



4, n.d.

Togni's reagent (96.0 mg, 0.3 mmol) was combined with TEMPO (0.50 mmol) and DABCO (0.16 mmol) in a tube. The tube was evacuated and backfilled with N_2 three times before the addition of CH_3CN (4.0 mL). The reaction was stirred for 30 minutes. The solvent was evaporated in vacuo, 1-(trifluoromethyl)benzene (0.2 mmol) and deuterotrichloromethane (1.0 mL) was added. The solution was transferred into NMR tube to perform the ^{19}F NMR.

e)



4, n.d.

Togni's reagent (96.0 mg, 0.3 mmol) was combined with TEMPO (0.50 mmol) and 1-ethynyl-4-methylbenzene (0.2 mmol) in a tube. The tube was evacuated and backfilled with N_2 three times before the addition of CH_3CN (4.0 mL). The reaction was stirred for 30 minutes. The solvent was evaporated in vacuo, 1-(trifluoromethyl)benzene (0.2 mmol) and deuterotrichloromethane (1.0 mL) was added. The solution was transferred into NMR tube to perform the ^{19}F NMR.

Computational details

The M06-2X density functional theory calculations were performed with the Gaussian09 package using 6-31+G(d,p) basis set for C, H, O, N, F, S.[1,2] For I, we used the Lanl2DZ pseudo potential with the associated double-z basis set.[3] The geometry optimizations were performed without symmetry constraints, and the nature of the extrema was checked by analytical frequency calculations. The intrinsic reaction coordinate (IRC)[4] pathways have been traced to verify two desired minima connected by the transition states. To account for solvation effect, the calculations were performed with the IEFPCM solvation model[5] in the CH_3CN solution with radii and non-electrostatic terms for Truhlar and coworkers' SMD solvation model.[6]

A possible pathway was proposed and the corresponding free energy reaction profile is shown in Figure 1. First, reactant **2** and Togni reagent **B** can form complex **2B-COM**, which is 9.5 kcal/mol more stable than the reactants. One of the two hydrogen atoms in amino group forms a strong hydrogen bond with the saturated oxygen atom of Togni reagent, the distance between the H atom and the O atom is 2.13 Å. And the N-I distance is 3.01 Å. Then **B** is reduced via single-electron transfer (SET)[13] and gives out **C**, free radical **D** and CF_3· as well. It can be inferred that this step is rate-determining. Subsequently, CF_3· attacks alkyne **1** to afford **F** free radical. Then formation of intermediate **G** occurs smoothly via **TS2** from interaction of free radical F and hydrazine-SO_2 complex **A**.[8a] The breaking of bond S-N in **G** leads to free radical **H**. Finally, **H** combines with radical **D** to produce complex **I** first and then form product **3**. Another pathway affording CF_3· from hydrazine-SO2 **A** and **B** was also studied (Figure S1, see Supporting Information). Obviously, the step giving CF_3· radical is more difficult than that in the former pathway, and this step is rate-determining too. So this path is less favoured, which is in good line with the experimental fact that hydrazine **2** is a good reagent producing CF_3· radical, and the yield of CF_3-TEMPO is high up to 79%. It is also worth noting in Figure S1 that the free energy profile is bifurcated from radical **F**, corresponding two modes producing **H** radical. In one branch SO_2 comes from dissociation of **AB**-**COM** (in black), and the other one from the second molecule **A** (in red). The profile shows that the former is

more favoured.

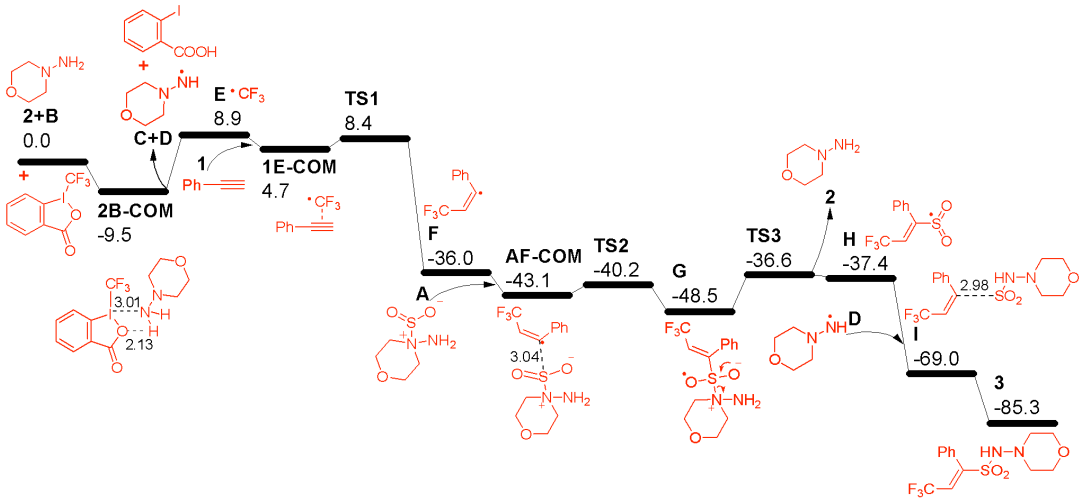


Figure 1 Free energy reaction profile (kcal/mol) in acetonitrile from reactants 1, 2, A and B to product 3, calculated at the M06-2X/6-31+G(d,p) with LANL2DZ (for I) level.

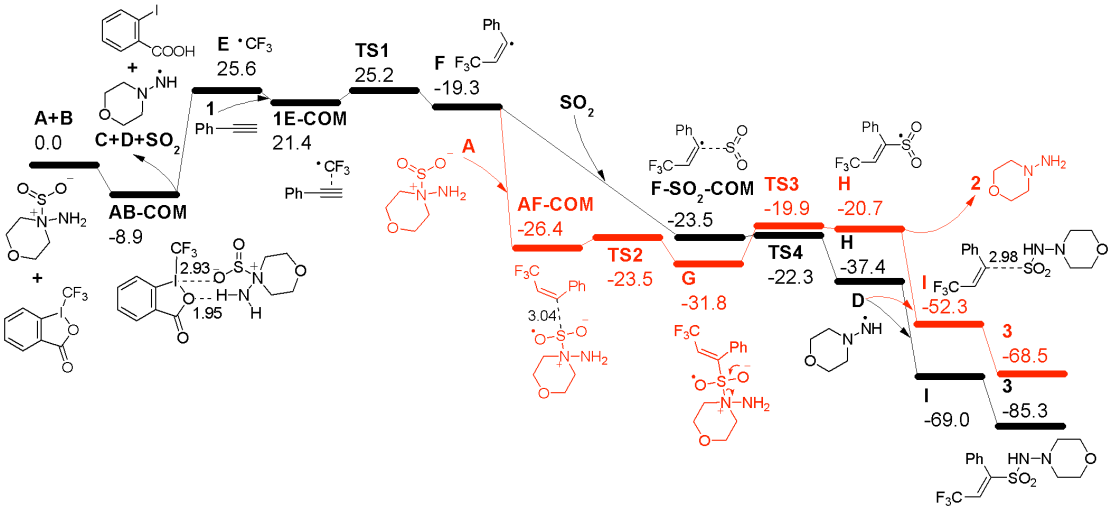
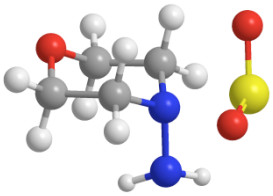


Figure S1 The detailed free free energy reaction profile (kcal/mol) from **A** to compound **VIII**, calculated at the PCM(DCE) B3LYP /6-31G(d,p) with LANL2DZ (for Pd and Br) level. The first pathway is in black, and the second one is in red.

Table S1 Coordinate data sets for DFT optimized complexes.

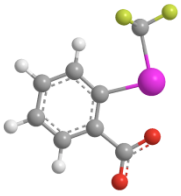
A



0 1

C	0.41436	-1.163632	0.599158
C	-0.834857	-1.208101	-0.272947
C	-1.003508	1.122347	-0.282975
C	0.234235	1.260225	0.593665
O	-1.675624	-0.096036	-0.007825
N	1.145638	0.104365	0.414478
N	1.887449	0.090548	-0.801157
H	0.130471	-1.210214	1.656501
H	1.097335	-1.98241	0.366301
H	-0.570724	-1.229847	-1.341163
H	-1.404823	-2.109836	-0.041093
H	-0.739767	1.17228	-1.350314
H	-1.697328	1.935631	-0.061285
H	0.788158	2.174143	0.359835
H	-0.05474	1.270099	1.648853
H	1.248753	0.066546	-1.597852
H	2.391528	0.975856	-0.858966
S	2.656223	0.156272	1.911314
O	3.084466	-1.251812	1.823628
O	1.780896	0.441156	3.066479

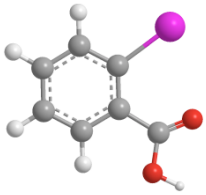
B



0 1

C	-0.658321	0.734061	-1.245759
C	-1.96309	0.237365	-1.25602
C	-2.206582	-1.13652	-1.249965
C	-1.145955	-2.035622	-1.23398
C	0.166644	-1.56335	-1.223562
C	0.367197	-0.196744	-1.229468
C	1.344978	-2.518844	-1.206566
O	2.493124	-1.904493	-1.198405
I	2.455078	0.297418	-1.20984
C	2.000606	2.483371	-1.225292
F	3.18927	3.100655	-1.213478
F	1.312091	2.899075	-0.155506
F	1.339638	2.887492	-2.31691
O	1.165621	-3.71878	-1.202029
H	-0.485337	1.802137	-1.25106
H	-2.790406	0.939328	-1.269075
H	-3.227806	-1.502487	-1.257939
H	-1.294366	-3.110914	-1.229122

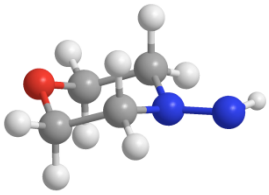
C



0 1

C	-0.698588	1.661482	0.013023
C	-1.884106	0.932759	0.004976
C	-1.849276	-0.45923	0.002044
C	-0.623399	-1.108929	0.006739
C	0.582704	-0.391077	0.00257
C	0.536289	1.010877	0.008388
I	2.234452	2.274717	0.048577
C	1.858786	-1.166835	-0.030301
O	2.953341	-0.726664	-0.279608
O	1.669065	-2.476129	0.24321
H	-0.730897	2.745425	0.023227
H	-2.833025	1.459973	0.003665
H	-2.768346	-1.035175	-0.002437
H	-0.579244	-2.191476	0.007249
H	2.538562	-2.899123	0.179491

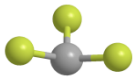
D



0 2

C	-0.969545	-1.062578	-0.598576
C	0.166602	-0.903878	-1.597798
C	0.91953	1.046049	-0.567971
C	-0.179759	0.980074	0.485517
O	0.492606	0.462344	-1.780759
N	-0.617488	-0.402585	0.650999
N	-1.354792	-0.77598	1.701009
H	-1.890847	-0.615668	-1.003816
H	-1.160527	-2.113755	-0.372122
H	1.054447	-1.451888	-1.245702
H	-0.126163	-1.291473	-2.575732
H	1.816536	0.524791	-0.198156
H	1.17648	2.084418	-0.788266
H	0.195705	1.342933	1.447774
H	-1.032577	1.605895	0.177362
H	-1.142256	-0.105229	2.447464

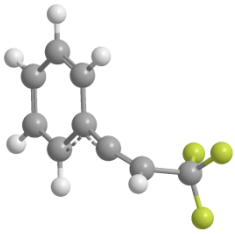
E



0 2

C	0.380693	0.320174	-0.124697
F	-0.934296	0.239795	-0.185612
F	0.822528	-0.038473	1.065479
F	0.943318	-0.400037	-1.075239

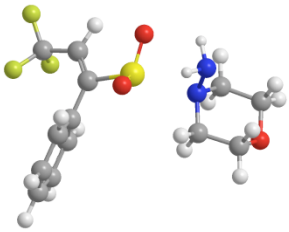
F



0 2

C	-0.660727	0.192776	-0.829902
C	-1.765283	-0.216386	-0.269563
C	0.682141	0.507005	-1.010402
C	1.578433	-0.439355	-1.574827
C	2.905659	-0.101805	-1.778994
C	3.376139	1.171303	-1.441411
C	2.501562	2.113888	-0.890605
C	1.170196	1.79866	-0.678092
C	-1.807568	-0.758014	1.13521
F	-2.268975	-2.023371	1.156543
F	-2.641066	-0.035005	1.907764
F	-0.607254	-0.757063	1.726083
H	-2.733563	-0.194828	-0.768987
H	1.208613	-1.425374	-1.835807
H	3.584242	-0.834491	-2.204058
H	4.417534	1.426616	-1.606664
H	2.8661	3.100961	-0.624549
H	0.487509	2.525643	-0.25095

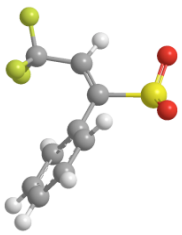
G



0 2

N	0.312046	-2.779323	1.006491
N	0.065664	-3.114248	2.362681
S	-0.004468	-0.420186	1.094102
O	1.02796	-0.283376	2.154116
O	-1.411695	-0.614015	1.537141
C	-0.009511	1.198133	0.192073
C	1.674871	-3.140268	0.60943
C	1.812141	-4.656711	0.477453
O	0.850513	-5.152031	-0.435684
C	-0.467761	-4.887308	0.00835
C	-0.688525	-3.379975	0.120579
C	0.931916	2.059994	0.572894
C	-0.969954	1.303477	-0.92485
C	-2.348125	1.182296	-0.707457
C	-3.229224	1.291174	-1.779581
C	-2.746991	1.504571	-3.070489
C	-1.375061	1.611866	-3.291671
C	-0.488138	1.511016	-2.224014
C	1.116283	3.427088	-0.021645
F	1.923943	3.395007	-1.104528
F	1.702371	4.242814	0.871364
F	-0.027462	4.008789	-0.402697
H	-0.861205	-2.736109	2.574258
H	0.715346	-2.542986	2.909346
H	2.369761	-2.720431	1.343267
H	1.85724	-2.66347	-0.359208
H	1.682454	-5.133918	1.458938
H	2.794232	-4.916032	0.07618
H	-0.641043	-5.36792	0.981495
H	-1.145035	-5.317138	-0.732488
H	-0.566043	-2.908177	-0.860026
H	-1.681415	-3.12701	0.505343
H	1.623051	1.802465	1.371087
H	-2.714498	1.003325	0.297282
H	-4.297286	1.208611	-1.604886
H	-3.43965	1.586385	-3.902361
H	-0.993257	1.77602	-4.294254
H	0.581678	1.597326	-2.390761

H

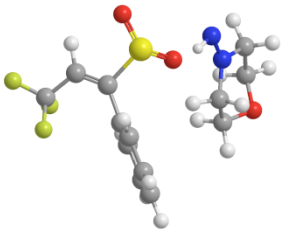


0 2

C	-1.314227	0.849237	0.216138
C	-1.985487	-0.180613	-0.297015
C	0.10791	1.209896	0.068963
C	0.633595	1.376667	-1.21895
C	1.979054	1.688365	-1.384837
C	2.802654	1.835141	-0.270169
C	2.279188	1.676466	1.012609
C	0.933331	1.371775	1.187611
C	-1.34018	-1.304654	-1.063347
F	-2.073647	-2.420193	-0.93424
F	-0.099501	-1.588106	-0.655695
F	-1.277617	-1.023037	-2.379749
S	-2.375306	2.059131	1.116718
O	-1.605323	2.518979	2.285241
O	-3.704155	1.447883	1.272922
H	-3.061193	-0.268593	-0.172995

H	-0.01374	1.26016	-2.083187
H	2.383061	1.815559	-2.383745
H	3.852707	2.076839	-0.401081
H	2.919838	1.791958	1.880647
H	0.519338	1.259617	2.183682

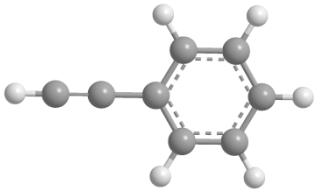
I



0 1

C	-0.351206	-1.861092	0.421846
C	-0.512442	-3.175898	0.517248
C	0.790512	-1.094853	-0.106198
C	1.134738	-1.180739	-1.460881
C	2.175465	-0.409317	-1.970684
C	2.87734	0.46329	-1.138251
C	2.538689	0.555389	0.211398
C	1.497732	-0.217313	0.724967
C	0.512934	-4.188135	0.109978
F	1.778579	-3.766118	0.268194
F	0.381301	-4.539211	-1.188234
F	0.381993	-5.317745	0.828672
S	-1.783146	-0.822438	0.968679
O	-2.834776	-1.815858	1.333155
O	-2.053911	-0.07266	-0.340143
N	-2.673775	1.963094	1.542079
N	-2.236315	2.144104	0.401694
C	-3.223147	2.324718	-0.693272
C	-2.601774	2.093067	-2.069725
O	-1.373974	2.790382	-2.170825
C	-0.420737	2.192216	-1.317477
C	-0.805193	2.439175	0.135894
H	-1.457895	-3.568453	0.888878
H	0.575079	-1.851815	-2.105604
H	2.438378	-0.487753	-3.021013
H	3.691181	1.060808	-1.537382
H	3.096722	1.216066	0.868659
H	1.24806	-0.169329	1.782404
H	-1.884977	1.91163	2.201427
H	-3.55731	3.364369	-0.598394
H	-4.038478	1.635507	-0.475089
H	-3.273989	2.512049	-2.821262
H	-2.449641	1.023397	-2.253338
H	0.544322	2.666373	-1.507888
H	-0.350817	1.115306	-1.500506
H	-0.224534	1.810059	0.818049
H	-0.684021	3.498523	0.391325

1



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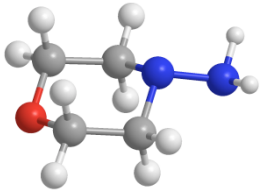
C	-0.074234	-0.000066	-0.00676
C	0.631918	-1.211217	-0.01015
C	2.02299	-1.207157	-0.016701
C	2.721051	0.000013	-0.019958
C	2.022924	1.207147	-0.016797
C	0.631853	1.211129	-0.010246
C	-1.510633	-0.000022	0.000324
C	-2.718846	0.000018	0.006414
H	0.080333	-2.145648	-0.007502
H	2.56368	-2.148292	-0.019221
H	3.806449	0.000042	-0.025047
H	2.563563	2.148312	-0.019393
H	0.080207	2.145527	-0.007672
H	-3.785765	0.000215	0.011764

2



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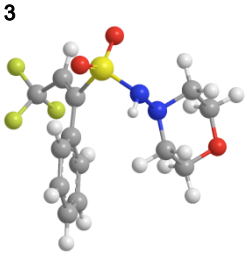
N	0.789282	0.493728	-0.523956
N	1.577836	1.058915	-1.605556
C	-0.508046	1.164545	-0.535312
C	-1.409588	0.522083	0.508771
O	-1.583079	-0.857212	0.249394
C	-0.3363	-1.523994	0.223929
C	0.583657	-0.91993	-0.826802
H	2.489915	0.606043	-1.537434
H	1.756736	2.025317	-1.330467
H	-0.971836	1.095163	-1.534601
H	-0.361504	2.223867	-0.29235
H	-2.403784	0.974107	0.485957
H	-0.973636	0.661998	1.510111
H	-0.544343	-2.571414	-0.005433
H	0.141652	-1.460527	1.213955
H	1.553269	-1.431976	-0.803654
H	0.146344	-1.042661	-1.832807

3



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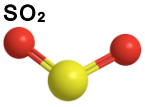
C	-0.66375	-1.349821	0.728409
C	-1.293904	-2.473224	0.387343
C	0.703158	-0.907794	0.381494
C	1.115164	-0.979197	-0.955534
C	2.369253	-0.50627	-1.32778
C	3.218604	0.050227	-0.371019
C	2.812368	0.12276	0.960687
C	1.558646	-0.352072	1.341301
C	-0.662531	-3.633695	-0.328187
F	-1.280466	-4.773908	0.01749
F	0.639451	-3.787313	-0.0593
F	-0.783065	-3.515775	-1.667361
S	-1.647616	-0.215493	1.745659
O	-1.064618	-0.165076	3.079025
O	-3.04216	-0.563607	1.544082
N	-1.40674	1.316118	1.103852
N	-1.499932	1.34129	-0.313642
C	-2.777245	1.946086	-0.714102
C	-2.847891	1.926982	-2.233165
O	-1.762103	2.638926	-2.799755
C	-0.527175	2.081996	-2.402417
C	-0.382612	2.093154	-0.886991
H	-2.344476	-2.60634	0.629639
H	0.438459	-1.385307	-1.701421
H	2.679702	-0.564691	-2.366251
H	4.194999	0.423669	-0.663096
H	3.474707	0.545926	1.70905
H	1.243175	-0.304333	2.379421
H	-0.540721	1.715783	1.465101
H	-2.848008	2.980392	-0.341842
H	-3.585675	1.352944	-0.279273
H	-3.760118	2.415823	-2.580516
H	-2.839313	0.885915	-2.590704
H	0.258049	2.685477	-2.863143
H	-0.44369	1.045347	-2.765428
H	0.561285	1.618785	-0.597375
H	-0.392246	3.137112	-0.525872

SO_2



0 1

S	-0.393038	0	0.636286
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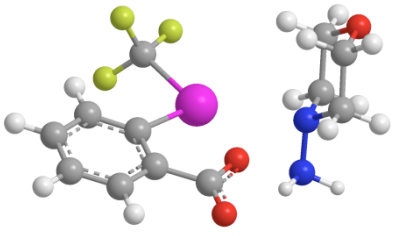
O	-1.061117	0	-0.647089

2B-COM



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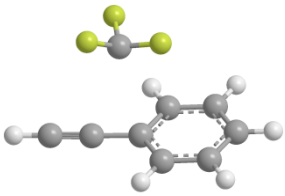
C	-1.504913	-0.42105	2.007
C	-2.733978	-0.600382	2.643708
C	-2.812722	-0.698023	4.032736
C	-1.658336	-0.615827	4.803374
C	-0.419799	-0.434622	4.187631
C	-0.373889	-0.34248	2.806125
C	0.846472	-0.34292	5.012911
O	1.916442	-0.159023	4.291954
I	1.619985	-0.068335	2.073168
C	0.886795	-0.023551	-0.036764
F	0.291203	-1.154155	-0.435562
F	1.984815	0.146267	-0.790025
F	0.052214	0.990016	-0.303178
O	0.809099	-0.43804	6.22378
H	-1.466432	-0.348662	0.928176
H	-3.633113	-0.662491	2.039262
H	-3.776596	-0.838357	4.510488
H	-1.676706	-0.688388	5.886297
C	4.801598	1.179517	3.885408
C	4.752183	2.510047	3.148842
C	5.352658	1.486758	1.145458
C	5.416789	0.122108	1.817979
O	5.652751	2.522071	2.057856
N	4.499255	0.096498	2.949345
N	4.533406	-1.188753	3.553055
H	5.807105	1.03737	4.323852
H	4.054765	1.152609	4.685651
H	3.727022	2.693962	2.786821
H	5.042819	3.329831	3.808821
H	4.346714	1.646737	0.720474
H	6.084382	1.553707	0.33739
H	5.126055	-0.671768	1.121928
H	6.453793	-0.072846	2.149076
H	5.40507	-1.297463	4.08223
H	3.761142	-1.215616	4.218975

1E-COM

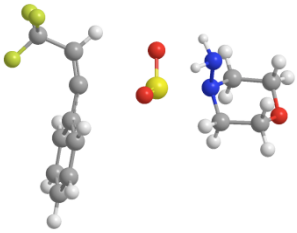


0 2

C	-1.061984	0.314605	-1.686361
C	-2.235042	0.121772	-1.903595
C	0.328631	0.535834	-1.401476
C	1.284325	-0.429014	-1.749365
C	2.624853	-0.224418	-1.438731
C	3.023283	0.93912	-0.781301
C	2.076092	1.902383	-0.435598
C	0.733863	1.706281	-0.743388
C	-0.492741	-0.605452	1.378838
F	-1.232146	-1.676674	1.59895
F	-1.030927	0.460956	1.942647

F	0.742042	-0.791169	1.805816
H	-3.270308	-0.046917	-2.100407
H	0.964328	-1.333417	-2.256794
H	3.359824	-0.976309	-1.708221
H	4.069471	1.094202	-0.53749
H	2.382712	2.807747	0.07847
H	-0.011723	2.446792	-0.471469

AF-COM



0 2

N	0.435869	-3.019813	0.911531
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S	0.299311	-0.999838	0.256729
O	1.543337	-0.601918	0.947747
O	-0.933878	-0.739723	1.024712
C	0.088884	1.939551	-0.490553
C	1.667575	-3.639984	0.389269
C	1.715133	-5.125446	0.730367
O	0.559079	-5.776837	0.238168
C	-0.614487	-5.25291	0.830827
C	-0.759178	-3.77432	0.49027
C	0.889535	2.439176	0.409762
C	-0.916556	1.849264	-1.451755
C	-2.217178	1.412631	-1.085972
C	-3.203217	1.298705	-2.052336
C	-2.927855	1.595822	-3.391303
C	-1.645552	2.012267	-3.763524
C	-0.643927	2.136066	-2.814891
C	0.829621	3.884179	0.822851
F	2.022922	4.488487	0.655711
F	0.517659	4.008216	2.126557
F	-0.073994	4.586867	0.126195
H	-0.343603	-2.407979	2.60479
H	1.274867	-2.312523	2.53724
H	2.51875	-3.086413	0.79743
H	1.650228	-3.50256	-0.697439
H	1.793755	-5.263167	1.817424
H	2.57429	-5.593485	0.245693
H	-0.582273	-5.389806	1.920278
H	-1.456075	-5.81555	0.421508
H	-0.84701	-3.642242	-0.59369
H	-1.629222	-3.314448	0.96866
H	1.629644	1.831743	0.932564
H	-2.411205	1.159446	-0.048962
H	-4.197383	0.972405	-1.763516
H	-3.706963	1.501012	-4.140568
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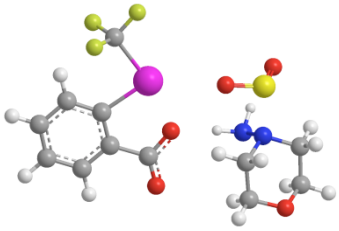
H	0.352122	2.462256	-3.095791

AB-COM



0 1

C	-0.369694	-0.654587	-0.252398
C	-1.315405	-1.681417	-0.247095
C	-0.943599	-2.996083	0.0302
C	0.385708	-3.299414	0.302374
C	1.348063	-2.290301	0.296006
C	0.947641	-0.99086	0.021746
C	2.798983	-2.607163	0.574935
O	3.575345	-1.570833	0.456124
I	2.56364	0.417489	0.092902
C	1.172825	2.110123	-0.299386
F	1.924888	3.21485	-0.282598
F	0.22357	2.242198	0.634588
F	0.566344	2.043789	-1.490728
O	3.157098	-3.730759	0.878035
S	6.813558	0.695163	0.980958
O	5.331954	0.770231	0.987833
O	7.402679	0.723606	-0.372157
H	-0.683457	0.357404	-0.469543
H	-2.35102	-1.43972	-0.463071
H	-1.69213	-3.781483	0.031908
H	0.71686	-4.309469	0.522818
C	8.37569	-1.735489	1.359533
C	8.504486	-3.223542	1.667269
C	6.364222	-3.298918	2.597025
C	6.146995	-1.814129	2.33635
O	7.742353	-3.559861	2.808948
N	6.953191	-1.369801	1.176871
N	6.468023	-1.942074	-0.030755
H	8.754093	-1.137627	2.196018
H	8.910022	-1.454386	0.447297
H	8.172834	-3.809993	0.800346
H	9.544949	-3.466723	1.893652
H	5.978998	-3.892549	1.757778
H	5.839364	-3.594804	3.507413
H	5.102864	-1.579321	2.119131
H	6.488597	-1.224221	3.19419
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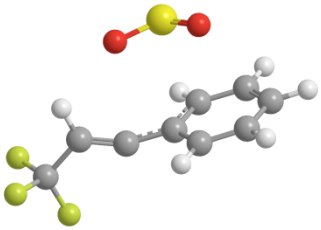
H	6.826918	-1.341894	-0.78105

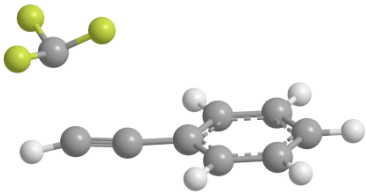
F-SO_2-COM



0 2

C	0.092399	-0.939572	-0.423931
C	-1.082953	-1.497566	-0.521305
C	1.016413	0.060399	-0.121
C	1.344749	1.046685	-1.089106
C	2.25516	2.048974	-0.782448
C	2.856213	2.098714	0.477519
C	2.542233	1.130811	1.436759
C	1.642534	0.116374	1.149913
C	-1.284096	-2.865588	-1.107526
F	-1.8876	-3.685451	-0.227062
F	-0.138242	-3.447684	-1.480741
F	-2.082241	-2.812489	-2.191639
S	-0.923491	2.533664	0.554517
O	-0.114399	2.942107	1.684428
O	-1.766715	1.36265	0.713276
H	-1.994137	-0.996978	-0.185296
H	0.877771	0.998342	-2.068053
H	2.49415	2.799994	-1.52906
H	3.557738	2.891248	0.714497
H	2.996457	1.178215	2.421049
H	1.389209	-0.630055	1.895249

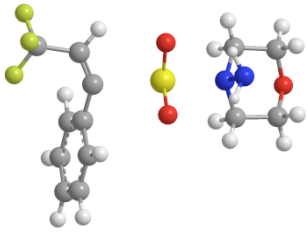
TS1



0 2

C	-1.407827	-0.187914	-1.258311
C	-2.572345	-0.483611	-1.047135
C	-0.02019	0.124039	-1.385372
C	0.878173	-0.833173	-1.884316
C	2.227118	-0.52123	-2.007202
C	2.692899	0.740712	-1.637381
C	1.804024	1.694907	-1.141418
C	0.453188	1.393073	-1.014755
C	-2.585519	-1.319324	1.168841
F	-3.170602	-2.511854	1.207444
F	-3.229051	-0.476993	1.968359
F	-1.320671	-1.422454	1.541399
H	-3.625117	-0.64172	-1.151103
H	0.506851	-1.812084	-2.169182
H	2.917926	-1.264423	-2.392132
H	3.747265	0.979427	-1.734203
H	2.164985	2.676181	-0.850705
H	-0.245807	2.127678	-0.628693

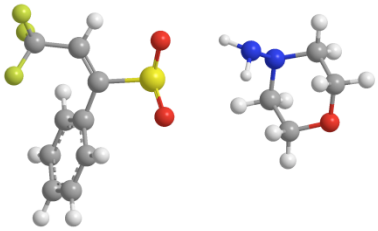
TS2



0 2

N	-0.312	-1.565321	-1.034105
N	-0.54653	-1.795959	0.355196
S	-0.489476	0.615134	-1.258227
O	0.554156	0.860307	-0.238637
O	-1.874239	0.601705	-0.738884
C	-0.597865	2.842052	-2.172235
C	1.036045	-2.021466	-1.406635
C	1.122897	-3.54428	-1.387452
O	0.135286	-4.100525	-2.235986
C	-1.167	-3.749888	-1.804647
C	-1.341344	-2.235621	-1.843777
C	0.285499	3.561318	-1.520974
C	-1.615531	2.859603	-3.168624
C	-2.971886	2.774459	-2.796671
C	-3.955461	2.764016	-3.776557
C	-3.606165	2.813841	-5.127758
C	-2.261922	2.873849	-5.502801
C	-1.267878	2.88956	-4.534487
C	0.414851	5.048009	-1.702195
F	1.668124	5.378816	-2.071032
F	0.166598	5.700513	-0.552345
F	-0.415797	5.540138	-2.630549
H	-1.456093	-1.363952	0.544842
H	0.12795	-1.19532	0.839558
H	1.751189	-1.554125	-0.722487
H	1.225203	-1.64615	-2.418437
H	0.992985	-3.917441	-0.362238
H	2.091399	-3.872838	-1.770143
H	-1.34198	-4.126721	-0.787535
H	-1.868262	-4.2281	-2.491741
H	-1.219443	-1.870464	-2.869602
H	-2.320307	-1.913492	-1.475776
H	0.959128	3.119318	-0.787698
H	-3.224556	2.705005	-1.743976
H	-5.00014	2.71084	-3.487441
H	-4.380432	2.802082	-5.888553
H	-1.991281	2.912262	-6.553127
H	-0.220088	2.942898	-4.813606

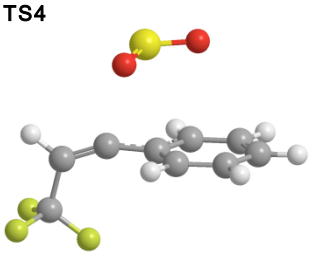
TS3



0 2

N	1.053446	-2.559883	-1.17439
N	0.726253	-1.813129	-0.007614
S	-0.388616	1.316707	-1.993243
O	0.640869	1.303687	-0.939931
O	-1.650052	0.57414	-1.814736
C	-0.829964	3.075453	-2.31903
C	1.523965	-3.895859	-0.795546
C	0.38826	-4.792815	-0.318325
O	-0.619087	-4.894524	-1.315764
C	-1.153907	-3.622722	-1.636205
C	-0.053811	-2.684959	-2.130307
C	-0.015156	3.953395	-1.736264
C	-1.937955	3.302553	-3.264609
C	-3.234719	2.854432	-2.987634
C	-4.261833	3.122143	-3.886787
C	-4.000398	3.820068	-5.065369
C	-2.706841	4.254454	-5.349184
C	-1.675112	3.99654	-4.452694
C	-0.182396	5.446926	-1.843028
F	0.484544	5.934662	-2.906329
F	0.327312	6.037178	-0.752054
F	-1.455851	5.834785	-1.956365
H	-0.260084	-1.889163	0.241385
H	0.930907	-0.835972	-0.190977
H	2.283577	-3.776313	-0.019983
H	1.985052	-4.346818	-1.682903
H	-0.048338	-4.390617	0.610979
H	0.737301	-5.810264	-0.12398
H	-1.663282	-3.203301	-0.751004
H	-1.909462	-3.781515	-2.40993
H	0.359547	-3.089813	-3.061988
H	-0.462728	-1.690324	-2.334165
H	0.825746	3.628292	-1.13017
H	-3.433272	2.304259	-2.074304
H	-5.268551	2.782778	-3.666568
H	-4.805337	4.022062	-5.764886
H	-2.499399	4.794357	-6.267073
H	-0.664994	4.333186	-4.666366

TS4



0 2

C	-1.20018	0.264169	-0.365362
C	-2.007362	-0.717586	-0.66217
C	0.012118	0.9294	-0.176007
C	0.584643	1.700051	-1.222013
C	1.742133	2.424449	-0.993444
C	2.349238	2.411844	0.265976
C	1.793188	1.657285	1.303941
C	0.638299	0.922728	1.098271
C	-1.504876	-2.063824	-1.116062
F	-1.9299	-3.041053	-0.294206
F	-0.169306	-2.126038	-1.161649
F	-1.967204	-2.365431	-2.344059
S	-1.895272	3.152656	1.124737
O	-0.755218	4.040622	1.032515
O	-2.052067	2.369523	2.333813
H	-3.091966	-0.641484	-0.600004
H	0.102645	1.710808	-2.194365
H	2.175135	3.009977	-1.798017
H	3.248704	2.992628	0.440643
H	2.262422	1.652047	2.28232
H	0.18943	0.350656	1.903699

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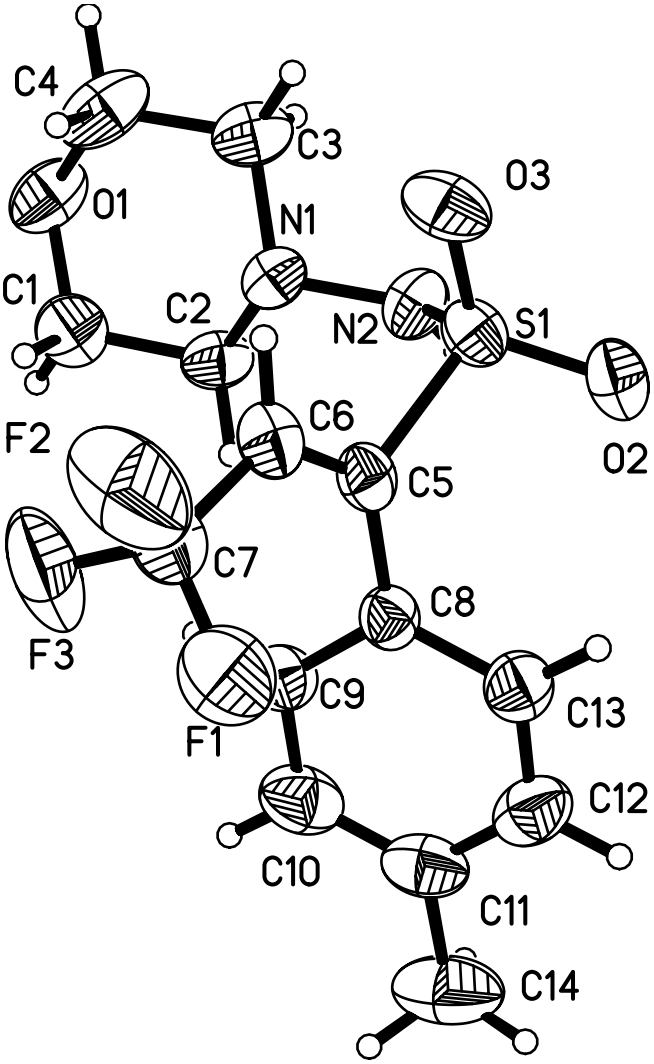
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C3
O1
N1
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C11
C14