Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information for

Sulfonate ester protecting groups that are rapidly cleaved by physiological glutathione

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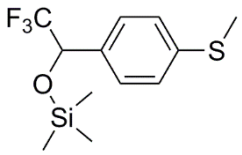
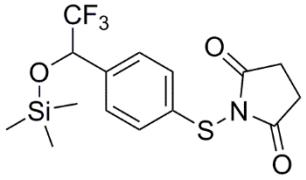
1. Synthetic Methods

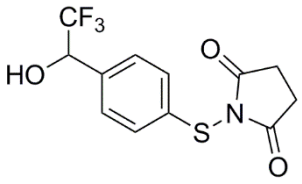
General. Compounds were purchased from Aldrich, Frontier Scientific, Matrix, Oakwood, Chem-Impex, Combi-Blocks, or TCI and used as received. NMR was performed on a Varian Mercury 400 or Bruker Ascend 500, and processed using MestReNova. High resolution mass spectrometry was performed at the UMass Mass Spectrometry core on a Thermo Scientific Orbitrap Velos Pro.



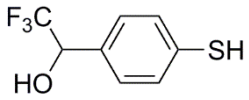
Trimethyl(2,2,2-trifluoro-1-(4-(methylthio)phenyl)ethoxy)silane (1)
In a 50 mL round bottom flask, 4-(Methylthio)benzaldehyde (2 g, 13.2 mmol) and trimethyl(trifluoromethyl)silane (3 mL, 20.3 mmol) were dissolved in anhydrous THF (13.5 mL) under argon. The temperature was lowered to 0°C, followed by the dropwise addition of 1 M TBAF in THF (70 µL, 0.07 mmol). The reaction was raised to room temperature and stirred for 10 minutes. The solvent was removed under reduced pressure and the product was purified by silica gel chromatography (0-7.5% EtOAc/hex) to afford a pale yellow oil (2.1 g, 7.14 mmol, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.26 (m, 2H), 4.91 (q, *J* = 6.4 Hz, 1H), 2.49 (s, 3H), 0.14 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.53 (d, *J* = 6.4 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.84, 132.06 – 131.96 (m), 128.08 – 127.88 (m), 125.88, 124.16 (q, *J* = 283.6 Hz), 72.88 (q, *J* = 32.3 Hz), 15.32, -0.33. HR-EIMS m/z calculated for C12H18F3OSSi+: 295.0794, found: 295.0779



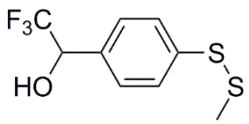
1-((4-(2,2,2-trifluoro-1-((trimethylsilyl)oxy)ethyl)phenyl)thio)pyrrolidine-2,5-dione (2)
In a 50 mL round bottom flask, compound **1** (860 mg, 2.9 mmol) and NBS (781 mg, 4.4 mmol) were dissolved in anhydrous DCM (6 mL) under argon. The reaction was stirred in the dark at room temperature for 24 hours. The solvent was removed under reduced pressure and the product was purified by silica gel chromatography (neat DCM) to afford a white solid (1.1 g, 2.9 mmol, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 4.88 (q, *J* = 6.4 Hz, 1H), 2.84 (s, 4H), 0.09 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.31 (d, *J* = 6.4 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.36, 137.03, 134.87, 131.27, 128.53 – 128.38 (m), 123.86 (q, *J* = 283.6 Hz), 72.60 (q, *J* = 32.4 Hz), 28.60, -0.32. HR-EIMS m/z calculated for C15H19F3NO3SSi+: 378.0802, found: 378.0808.



1-((4-(2,2,2-trifluoro-1-hydroxyethyl)phenyl)thio)pyrrolidine-2,5-dione (3)
In a round bottom flask, compound **2** (250 mg, 0.9 mmol) was dissolved in 1:1 1 M aq. HCl/THF (10 mL) and stirred at room temperature for 1.5 hours. THF was first removed under reduced pressure, then the product was extracted with EtOAc (3 x 25 mL). The organic layers were combined and washed with H_2O (3 x 50 mL) and brine (50 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the product was purified by silica gel chromatography (0-70% EtOAc/hex) to afford a white solid (200 mg, 0.65 mmol, 87%). ^{1}H NMR (400 MHz, CD_3OD) δ 7.47 (s, 4H), 5.04 (q, *J* = 7.2 Hz, 1H), 2.83 (s, 4H). ^{19}F NMR (376 MHz, CD_3OD) δ -79.61 (d, *J* = 7.1 Hz, 1H). ^{13}C NMR (101 MHz, CD_3OD) δ 177.71, 136.29 – 136.19 (m), 135.65, 128.51, 128.35 – 128.20 (m), 124.65 (q, *J* = 282.8 Hz), 71.00 (q, *J* = 31.5 Hz), 28.26. HR-EIMS m/z calculated for C12H11F3NO3S+: 306.0406, found: 306.0412.

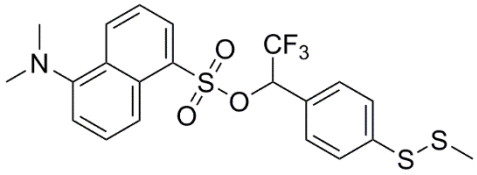


2,2,2-trifluoro-1-(4-mercaptophenyl)ethan-1-ol (4)
In a 200 mL round bottom flask, compound **3** (300 mg, 0.98 mmol) was dissolved in anhydrous methanol (20 mL) and degassed three times at -40°C. $NaBH_4$ (400 mg, 11 mmol) was added to the reaction in small proportions. The reaction was raised to room temperature and stirred under argon for 3 hours. The reaction was quenched using glacial acetic acid (20 mL). Toluene (50 mL) was added to the reaction mixture and the solvents were removed under reduced pressure. The crude product was dissolved in EtOAc (50 mL), washed with H_2O (3 x 50 mL) and brine (50 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the product was purified by silica gel chromatography (0–30% EtOAc/hex) afforded a white solid (100 mg, 0.48 mmol, 49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 4H), 4.98 (dq, *J* = 6.4, 4.4 Hz, 1H), 3.51 (s, 1H), 2.48 (d, *J* = 4.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.55 (d, *J* = 6.4 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.09, 131.14 – 131.05 (m), 129.13, 128.16 – 128.07 (m), 124.06 (q, *J* = 283.1 Hz)*, 72.36 (q, *J* = 32.2 Hz). [*Only 3 of the 4 peaks for the quartet at 124.06 are visible.] HR-EIMS m/z calculated for C8H6F3OS-: 207.0097, found: 207.0091.



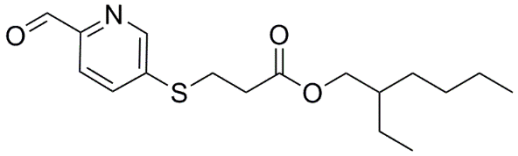
2,2,2-trifluoro-1-(4-(methyldisulfanyl)phenyl)ethan-1-ol (5)
In a 25 mL round bottom flask, compound **4** (58 mg, 0.24 mmol) and S-methyl methanethiosulfonate (42 mg, 0.33 mmol) were dissolved in anhydrous MeOH (3 mL) under argon. Degassed 100 mM sodium phosphate pH 8 buffer (4 mL) was added to the reaction. The reaction was stirred at room temperature under argon for 2.5 hours. The reaction mixture was poured into EtOAc (50 mL), washed with H_2O (3 x 25 mL) and brine (25 mL), then dried over

Na_2SO_4. The solvent was removed under reduced pressure and the product was purified by silica gel chromatography (0-30% EtOAc/hex) afforded a white solid (70 mg, 0.28 mmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 5.04 – 4.97 (m, 1H), 2.78 – 2.73 (m, 1H), 2.45 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.38 (d, *J* = 6.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.82, 132.31 – 132.22(m), 128.19 – 128.03 (m), 126.98, 124.10 (q, *J* = 283.2 Hz), 72.36 (q, *J* = 32.2 Hz), 22.86.



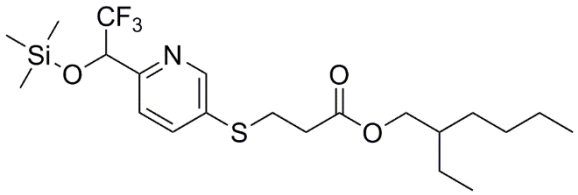
2,2,2-trifluoro-1-(4-(methyldisulfanyl)phenyl)ethyl 5-(dimethylamino)naphthalene-1-sulfonate (6)

In a 50 mL round bottom flask, compound **5** (18 mg, 0.07 mmol), DABCO (11 mg 0.1 mmol), and dansyl chloride (24 mg, 0.09 mmol) were dissolved in anhydrous DCM (3 mL) under argon. The reaction was stirred at room temperature under argon for 3 hours. The solvent was removed under reduced pressure and the product was purified by silica gel chromatography (0-30% EtOAc/hex) to afford a yellow solid (20 mg, 0.04 mmol, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (dt, *J* = 8.8, 1.2 Hz, 1H), 8.22 – 8.17 (m, 1H), 8.08 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.56 (dd, *J* = 8.4, 7.6 Hz, 1H), 7.36 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.18 – 7.09 (m, 3H), 7.03 (d, 8.4 Hz), 5.59 (q, *J* = 6.4 Hz, 1H), 2.83 (s, 6H), 2.37 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.86 (d, *J* = 6.4 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.69, 139.69, 132.00, 131.37, 130.26, 129.68, 129.49, 128.85, 128.60, 126.88, 125.66, 122.61, 122.09 (q, *J* = 282.3 Hz), 119.21, 115.45, 78.17 (q, *J* = 34.7 Hz), 45.40, 22.76. HR-EIMS m/z calculated for C21H21F3NO3S3+: 488.0630, found: 488.0666.



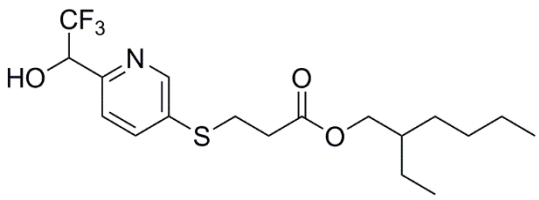
2-ethylhexyl 3-((6-formylpyridin-3-yl)thio)propanoate (7)

To a 200 mL round bottom flask equipped with a reflux condenser was added 5-Bromo-2-pyridinecarboxaldehyde (1 g, 5.4 mmol), 2-Ethylhexyl 3-Mercaptopropionate (1.3 g, 5.9 mmol), tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct ($Pd_2(dba)_3 \cdot CHCl_3$) (123 mg, 0.12 mmol) and Xantphos (156 mg, 0.27 mmol). The flask was first flushed with argon, then anhydrous toluene (30 mL) and DIPEA (1.4 g, 8 mmol) were added in series. The reaction was refluxed at 130°C under argon for 4.5 hours. The reaction was cooled to room temperature and filtered with Celite. The solvent was removed under reduced pressure and the product was purified by silica gel chromatography (0-30% EtOAc/hex) to afford a golden yellow oil (1.4 g, 4.33 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (d, *J* = 0.8 Hz, 1H), 8.56 (dd, *J* = 2.4, 0.8 Hz, 1H), 7.80 (dd, *J* = 8.0, 0.4 Hz, 1H), 7.66 (ddd, *J* = 8.4, 2.4, 0.8 Hz, 1H), 4.01 – 3.90 (m, 2H), 3.26 (t, *J* = 7.2 Hz, 2H), 2.66 (t, *J* = 7.2 Hz, 2H), 1.54 – 1.44 (m, 1H), 1.31 – 1.16 (m, 8H), 0.81 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.43, 171.09, 149.80, 148.07, 140.15, 134.59, 121.51, 67.39, 38.58, 33.65, 30.26, 28.80, 27.05, 23.65, 22.88, 14.00, 10.91. HR-EIMS m/z calculated for C17H26NO3S+: 324.1628, found: 324.1655.



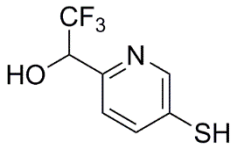
2-ethylhexyl 3-((6-(2,2,2-trifluoro-1-((trimethylsilyl)oxy)ethyl)pyridin-3-yl)thio)propanoate (8)

In a 200 mL round bottom flask, compound **7** (2.11 g, 6.5 mmol) and trifluoromethyltrimethylsilane (1.08 g, 7.6 mmol) were dissolved in anhydrous THF (50 mL) under argon. The temperature was lowered to 0°C, followed by the dropwise addition of 1 M TBAF in THF (100 µL, 0.1 mmol). The reaction was then raised to room temperature and stirred for 3 hours. The solvent was removed under reduced pressure and the product was purified by silica gel chromatography (0-20% EtOAc/hex) to afford a clear oil (2 g, 5.08 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 2.4, 0.8 Hz, 1H), 7.71 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 5.04 (q, *J* = 6.4 Hz, 1H), 4.04 – 3.95 (m, 2H), 3.19 (t, *J* = 7.2 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 1.59 – 1.50 (m, 1H), 1.37 – 1.20 (m, 8H), 0.86 (t, *J* = 7.6 Hz, 6H), 0.11 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.69 (d, *J* = 6.39 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.40, 153.53 – 153.41 (m), 149.05, 137.68, 133.36, 123.83 (q, *J* = 284.0 Hz), 122.36 – 122.22 (m), 74.32 (q, *J* = 31.7 Hz), 67.31, 38.65, 34.20, 30.31, 28.85, 28.73, 23.69, 22.92, 14.01, 10.93, -0.38. HR-EIMS m/z calculated for C21H35F3NO3SSi+: 466.2054, found: 466.2094.



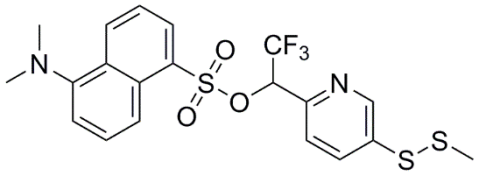
2-ethylhexyl 3-((6-(2,2,2-trifluoro-1-hydroxyethyl)pyridin-3-yl)thio)propanoate (9)

In a 200 mL round bottom flask, compound **8** (800 mg, 1.7 mmol) was dissolved in 1:1 aq.1M HCl/THF (100 mL) and stirred at room temperature overnight. THF was first removed under reduced pressure, then the product was extracted with EtOAc (3 x 50 mL). The organic extracts were combined, washed with H_2O (3 x 50 mL) and brine (50 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the product was purified by silica gel chromatography (0-30% EtOAc/hex) to afford a pale yellow oil (600 mg, 1.53 mmol, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 1.6 Hz, 1H), 7.74 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.35 (d, *J* = 8 Hz, 1H), 5.00 (q, *J* = 6.4 Hz, 1H), 4.08 – 3.91 (m, 2H), 3.21 (t, *J* = 7.2 Hz, 2H), 2.64 (t, *J* = 7.2 Hz, 2H), 1.60 – 1.50 (m, 1H), 1.37 – 1.21 (m, 8H), 0.86 (t, *J* = 7.2 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.05 (d, *J* = 6.39 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.38, 149.35- 148.77 (m), 148.56, 138.02, 134.30, 123.92 (q, *J* = 283.9 Hz), 122.62 - 122.53 (m), 70.63 (q, *J* = 31.9 Hz), 67.39, 38.64, 34.13, 30.31, 28.85, 28.75, 23.68, 22.92, 14.01, 10.92. HR-EIMS m/z calculated for C18H27F3NO3S+: 394.1658, found: 394.1694.



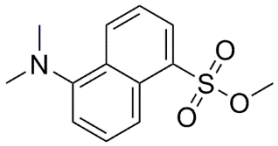
2,2,2-trifluoro-1-(5-mercaptopyridin-2-yl)ethan-1-ol (10)
In a 200 mL round bottom flask, compound **9** (432 mg, 1.1 mmol) was dissolved in anhydrous toluene (20 mL) and degassed 25% sodium methoxide in methanol (10 mL) under argon. The reaction was stirred at room temperature for 3 hours. The reaction was quenched with glacial acetic acid (10 mL). The solvents were removed under reduced pressure and the crude material was dissolved EtOAc (50 mL). The organic layer was washed with H_2O (3 x 50 mL) and brine (50 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the product was purified by silica gel chromatography (0-50% EtOAc/hex) afforded an off-white solid (120 mg, 0.57 mmol, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 – 8.46 (m, 1H), 7.69 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 5.16 (d, *J* = 7.2 Hz, 1H), 5.02 – 4.95 (m, 1H), 3.52 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.20 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.29 – 148.19 (m), 147.84, 137.55, 130.07, 123.88 (q, *J* = 284.0 Hz), 122.54 (m), 70.46 (q, *J* = 32.0 Hz). HR-EIMS m/z calculated for C7H7F3NOS+: 210.0195, found: 210.0215.

2,2,2-trifluoro-1-(5-(methyldisulfanyl)pyridin-2-yl)ethan-1-ol (11)
In a 50 mL round bottom flask, compound **10** (120 mg, 0.57 mmol) and S-methyl methanethiosulfonate (72 mg, 0.57 mmol) were dissolved in anhydrous MeOH (4 mL) under argon. Degassed 100 mM sodium phosphate pH 8 buffer (3 mL) was then added. The reaction was stirred at room temperature under argon for 3 hours. The reaction mixture was poured into EtOAc (50 mL), washed with H_2O (3 x 25 mL) and brine (25 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the product was purified by silica gel chromatography (0-20% EtOAc/hex) to afford an off-white solid (100 mg, 0.39 mmol 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 – 8.68 (m, 1H), 7.96 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.40 (d, *J* = 8 Hz, 1H), 5.30 – 5.20 (m, 1H), 5.07 – 4.98 (m, 1H), 2.48 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.04 (d, *J* = 7.52 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.47 (m), 146.87, 136.25, 135.80, 123.91 (q, *J* = 284.01 Hz), 122.66 (m), 70.60 (q, *J* = 32.1 Hz), 22.91. HR-EIMS m/z calculated for C8H9F3NOS2+: 256.0072, found: 256.0095.

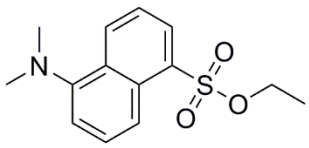


2,2,2-trifluoro-1-(5-(methyldisulfanyl)pyridin-2-yl)ethyl 5-(dimethylamino)naphthalene-1-sulfonate (12)

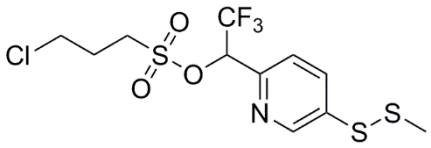
In a 50 mL round bottom flask, compound **11** (100 mg, 0.39 mmol), DABCO (44 mg, 0.39 mmol) and dansyl chloride (127 mg, 0.47 mmol) were dissolved in anhydrous DCM (6 mL) under argon. The reaction was stirred at room temperature under argon for 3 hours. The solvent was removed under reduced pressure and the product was purified by silica gel chromatography (0-25% EtOAc/hex) to afford a yellow solid (62 mg, 0.21 mmol, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.4 Hz, 1H), 8.36 (d, *J* = 1.6 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 8.18 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.50 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.44 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 5.71 (q, *J* = 6 Hz, 1H), 2.85 (s, 6H), 2.41 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.34 (d, *J* = 6.39 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.78, 147.46, 146.82, 135.94, 134.45, 132.22, 130.99, 130.79, 129.69, 129.54, 128.91, 122.85, 122.70, 121.89 (q, *J* = 280.13 Hz), 119.22, 115.53, 78.73 (q, *J* = 33.9 Hz), 45.41, 22.85. HR-EIMS m/z calculated for C20H20F3N2O3S3+: 489.0583, found: 489.0625.



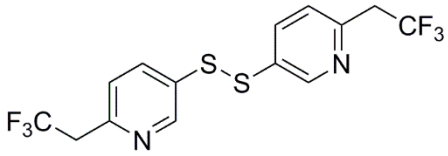
Methyl 5-(dimethylamino)naphthalene-1-sulfonate (13)
In a 50 mL round bottom flask, dansyl chloride (100 mg, 0.37 mmol) and DABCO (50 mg, 0.45 mmol) were dissolved in methanol (10 mL). The reaction was stirred for 6 hours at room temperature. The solvent was removed under reduced pressure and the crude mixture was dissolved in EtOAc (50 mL). The organic layer was washed with H_2O (3 x 50 mL) and brine (50 mL), then dried over Na_2SO_4. Removal of solvent under reduced pressure yielded a pure yellow oil (30 mg, 0.11 mmol, 30%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (dt, *J* = 8.8, 1.2 Hz, 1H), 8.28 (dd, *J* = 7.2, 1.2 Hz, 1H) 8.26 – 8.23 (m, 2H), 7.63 – 7.52 (m, 2H), 7.21 (dd, *J* = 7.6, 0.7 Hz, 1H), 3.72 (s, 3H), 2.89 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.78, 131.62, 130.83, 130.39, 129.90, 129.81, 128.76, 123.02, 119.32, 115.56, 56.40, 45.42. HR-EIMS m/z calculated for C13H16NO3S+: 266.0845, found: 266.0869



Methyl 5-(dimethylamino)naphthalene-1-sulfonate (14)
In a 50 mL round bottom flask, dansyl chloride (100 mg, 0.37 mmol) and DABCO (41 mg, 0.37 mmol) were dissolved in ethanol (5 mL). The reaction was stirred at room temperature for 4 hours. The solvent was removed under reduced pressure and the product was purified by silica gel chromatography (0-20% EtOAc/hex) to afford a yellow oil (100 mg, 0.29 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (dt, *J* = 8.8, 1.2 Hz, 1H), 8.27 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.56 (ddd, *J* = 18.4, 8.4, 7.6 Hz, 2H), 7.20 (dd, *J* = 7.6, 0.4 Hz, 1H), 4.07 (q, *J* = 6.8 Hz, 2H), 2.88 (s, 6H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.74, 131.46, 131.42, 130.39, 129.88, 129.80, 128.62, 123.04, 119.39, 115.49, 67.12, 45.42, 14.72. HR-EIMS m/z calculated for C14H18NO3S+: 280.1002, found: 280.1027



2,2,2-trifluoro-1-(5-(methyldisulfanyl)pyridin-2-yl)ethyl 3-chloropropane-1-sulfonate (15)
In a 25 mL round bottom flask, **10** (41 mg, 0.2 mmol) and TEA (41 mg, 0.4 mmol) were dissolved in anhydrous DCM (3 mL) at 0°C. 3-Chloropropanesulfonyl chloride (71 mg, 0.4 mmol) was separately dissolved in DCM (1 mL) and added drop-wise to the reaction. The reaction was stirred at 0°C for 2 hours and then poured in to aq. 1M HCl (20 mL). The product was extracted with DCM (3 x 20 mL) and the combined organic layers was washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the product was purified by silica gel chromatography (0-20% EtOAc/hex) to afford a pale yellow oil (69 mg, 0.17 mmol, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (dd, *J* = 2.4, 0.7 Hz, 1H), 8.02 (dd, *J* = 8.3, 2.4 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 6.00 (q, *J* = 6.2 Hz, 1H), 3.65 (t, *J* = 6.0 Hz, 2H), 3.45 – 3.37 (m, 2H), 2.49 (s,3H), 2.37 - 2.29 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.01 (d, *J* = 6.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.80-147.70 (m), 137.04, 135.64, 122.03 (q, *J* = 280 Hz), 122.92, 77.74 (q, *J* = 22.5 Hz), 49.46, 42.08, 26.51, 22.93. HR-EIMS m/z calculated for C11H14ClF3NO3S3+: 395.9771, found: 395.9755.



1,2-bis(6-(2,2,2-trifluoroethyl)pyridin-3-yl)disulfane (16)
In a 50 mL round bottom flask, **12** (50 mg, 0.1 mmol) was dissolved in ACN (9 mL). TCEP hydrochloride (286 mg, 1 mmol) was dissolved separately in H_2O (10 mL) and adjusted to pH 7. The two solutions were combined and stirred at room temperature for 2 hours. The reaction mixture was poured into brine (50 mL) and the product was extracted with diethyl ether (3 x 20 mL). The combined organic layers were washed with brine (50 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the product was purified by silica gel chromatography (0-20% EtOAc/hex) to afford an off-white solid (6 mg, 0.016 mmol, 16%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (dd, *J* = 2.4, 0.6 Hz, 2H), 7.83 (dd, *J* = 8.2, 2.5 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 3.60 (q, *J* = 10.6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.68 (t, *J* = 10.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.14-190.33 (m), 149.16, 136.99, 133.10, 125.21 (q, *J* = 275.6 Hz), 124.81, 42.29 (q, *J* = 29.5 Hz). HR-EIMS m/z calculated for C14H11F6N2S2+: 285.0262, found: 285.0251.

2. Excitation and Emission Spectra of Dansylates

Protocol:
Compounds at 1 mM stock concentration were diluted 1:500 in PBS pH 7.4 (6 µL into 3 mL) to a final concentration of 2 µM. For all acquisitions, the temperature was maintained at 20°C and slit widths were set to 1 mm (excitation) and 5 mm (emission).

Equipment and Conditions:
System: Horiba Scientific FluoroMax-4
Temperature Controller: Newport Model 350B
Acquisition software: FluorEssence
Temperature: 20°C

Compound	Peak Excitation (nm)	Peak Emission (nm)
Dansyl-sulfonate	324	498
TFMB-Dan	367	522
MeSSTFMB-Dan (**6)**	366	532
MeSSTFMP-Dan (**12**)	368	532
MeO-Dan (**13**)	324	518
EtO-Dan (**14**)	327	568

3. Fluorometric Detection of Dansylate Cleavage

Protocol:
Compounds at 1 mM stock concentration were diluted 1:500 in PBS pH 7.4 (6 µL into 3 mL) to a final concentration of 2 µM. The release of dansyl sulfonate was monitored using wavelengths of 324 nm (excitation) and 498 nm (emission). The temperature was maintained at 20°C and slit widths were set to 1 mm (excitation) and 5 mm (emission). Data points were collected every 10 seconds for 15 minutes. To establish fluorescence baseline, reducing agents were added 50 seconds after the initial time point.

Equipment and Conditions:
System: Horiba Scientific FluoroMax-4
Temperature Controller: Newport Model 350B
Acquisition software: FluorEssence
Temperature: 20°C

Concentrations and volumes of reducing agents:

Reducing Agent	Stock Concentration in PBS (mM)	Volume Added (µL)	Final Concentration (mM)
TCEP	500	6	1
DTT	500	6	1
BME	500	6	1
Glutathione	500	30	5

4. HPLC

Protocol:
Compounds at 10 mM stock concentration in DMF were diluted 1:1000 in PBS pH 7.4 (1 µL in 1 mL) with or without reducing agent to a final concentration of 10 µM. Compound standards were injected into the HPLC immediately after filtration through a 0.45 µM PTFE syringe filter. In all other conditions, compounds were incubated in the dark at room temperature for 15 minutes prior to filtration and injection. The HPLC column was equilibrated for at least 25 minutes at 1.4 mL/min prior to sample injection. TCEP was used at 1 mM and GSH was used at 5 mM.

Equipment and Conditions:
Injection volume: 200 µL
HPLC system: Agilent Series 1100
Filter: 13mm 0.45 µM PTFE
Column: Agilent Zorbax XDB-C8 µm 4.6 mm x 150 mm
Wavelength monitored: 290 nm / 800 nm (reference)
System: 0.1% TFA H_2O/acetonitrile

Ramp:

Time (m)	% Acetonitrile	Flow rate (mL/ min)
2	0	1.4
15	90	1.4
17	90	1.4
18	0	1.4
Post-run (25 minutes)	0	1.4

5. LCMS

Protocol:
Sample preparation and concentrations were identical to the HPLC protocol. The LCMS column was equilibrated for 5 minutes at 1.0 mL/min before each injection. TCEP, DTT and BME were used at 1 mM and GSH was used at 5 mM. Compound **10** was injected without prior incubation.

Note: The injection protocol of the LCMS auto-sampler took approximately 2 minutes to complete; total incubation time was therefore about 17 minutes for test samples and 2 minutes for control samples.

Equipment and Conditions:
Injection volume: 100 µL
LCMS system: Agilent 1260 Infinity with auto-sampler, 6130 Quadrupole LC/MS
Column: PoroShell 120 EC-C18 4.6x150 mm 2.7 µm
Wavelength monitored: 290 nm / 595 nm (reference)
System: 0.1% aq. formic acid/acetonitrile

Ramp:

Time (m)	% Acetonitrile	Flow rate (mL/ min)
0	0	1.0
8	100	1.0
10	100	1.0
Post-run (5 minutes)	0	1.0

6. Live cell imaging

Protocol:

Cell culture

HeLa cells were cultured with DMEM containing 10% FBS and 1% Pen/Strep at 37°C. Cells were first cultured in T-75 TC flasks to 70% confluency, then trypsinized and diluted to 50,000 cells/mL. Coverslips (#1.5 18 mm) were seeded in a 10 cm petri dish using 10 mL of cell solution. Cells were allowed to adhere for 20 hours at 37°C.

Staining

Coverslips were washed twice with HBSS and placed in a 35 mm petri plate containing HBSS (2 mL). Dansylates (2 µl of a 1 mM stock) were added to achieve a final concentration of 1 µM and then incubated for 15 minutes at 37°C. After incubation, the coverslips were washed twice with HBSS and mounted using a technique adapted from Chazotte (2011). Instead of using VALAP, Vaseline was used to seal the chamber and 200 µL of HBSS was used to fill the chamber to prevent the formation air bubbles.

Image processing

Raw 16-bit images were cropped to the desired 2 square inch frames (600 dpi) and normalized to the pixel intensity (min: 350, max: 3500), except for TFMB-Dan (min: 350, max: 6000). Those images were then converted to 8-bit images, and a scale bar was applied (7.85 pixel/µm). Composite pictures were prepared using the merge channel function in the FIJI software, and pseudocolored to match the fluorescence seen through the eyepiece (longpass emission filter).

Note: Fluorescence images were slightly misaligned with the DIC images due to hardware manipulation (opening and closing the shutter, focusing, etc.) during image acquisition. Images shown have been manually realigned to account for this shift.

Equipment

Coverslips: Deckgläser No. 1.5, 18 mm round glass
Microscope slides: Fisherfinest Premium Plain
Microscope: Nikon Eclipse E600
Camera: Hamamatsu Orca-ER with controller
Objective: Nikon Plan 50x oil immersion
Filer Set: Nikon UV-2A (330-380 nm bandpass excitation; 420 nm longpass emission)
Light Source: Chiu Technical Corporation 100W Mercury Lamp
Exposure time: 100 ms
Imaging processing software: FIJI

7. Toxicity Assay

Protocol:

Cell culture

HeLa cells were cultured with DMEM containing 10% FBS and 1% Pen/Strep at 37°C. Cells were first cultured in T-75 TC flasks to 70% confluency, then trypsinized and diluted to 50,000 cells/mL. 96-well plates were seeded with 5000 cells/well. Cells were allowed to adhere for 24 hours at 37°C.

XTT Assay

DMEM medium was removed via aspiration and the cells were washed once with HBSS (100 µL). After washing, the wells were filled with HBSS (50 µL). Compounds (50 µL) were added and incubated for 1 hr at 37°C. After treatment, the compounds were removed via aspiration and the cells were washed once with HBSS (100 µL). The cells were supplied with fresh DMEM (100 µL) and allowed to proliferate for 48 hours at 37°C. Activated XTT reagent (50 µL) were added and incubated at 37°C for 4 hour. Wells were read at 490 mm and 660 mm.

Compounds at 10 mM stock concentration in DMF were first diluted in HBSS (6 µL in 1 mL), then serially diluted (1:2) in HBSS. Concentrations ranged from 60 µM to 1.9 µM at 2X.

Equipment

Plates: BD 35-3072
Plate Reader: BioRad IMark
XTT Reagent: ATCC XTT Kit 30-1011K

7. Supplemental Reference

1) B. Chazotte, Mounting live cells onto microscope slides, *Cold Spring Harb. Protoc.* 2011, pdb.prot5554.

8. Supplemental Figures

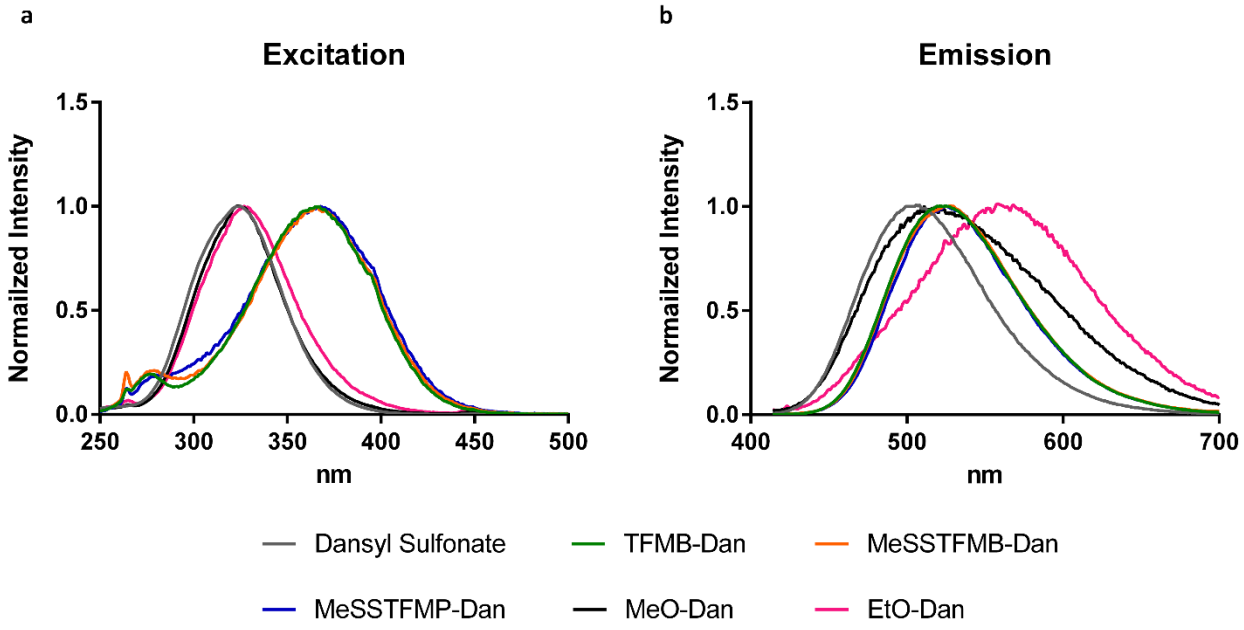


Figure S1: Excitation and Emission Spectra of Dansylates. Excitation (a) and emission (b) spectra were determined for each dansylate. Each spectrum was normalized to its respective peak intensity. Graphs were generated using GraphPad Prism 6.

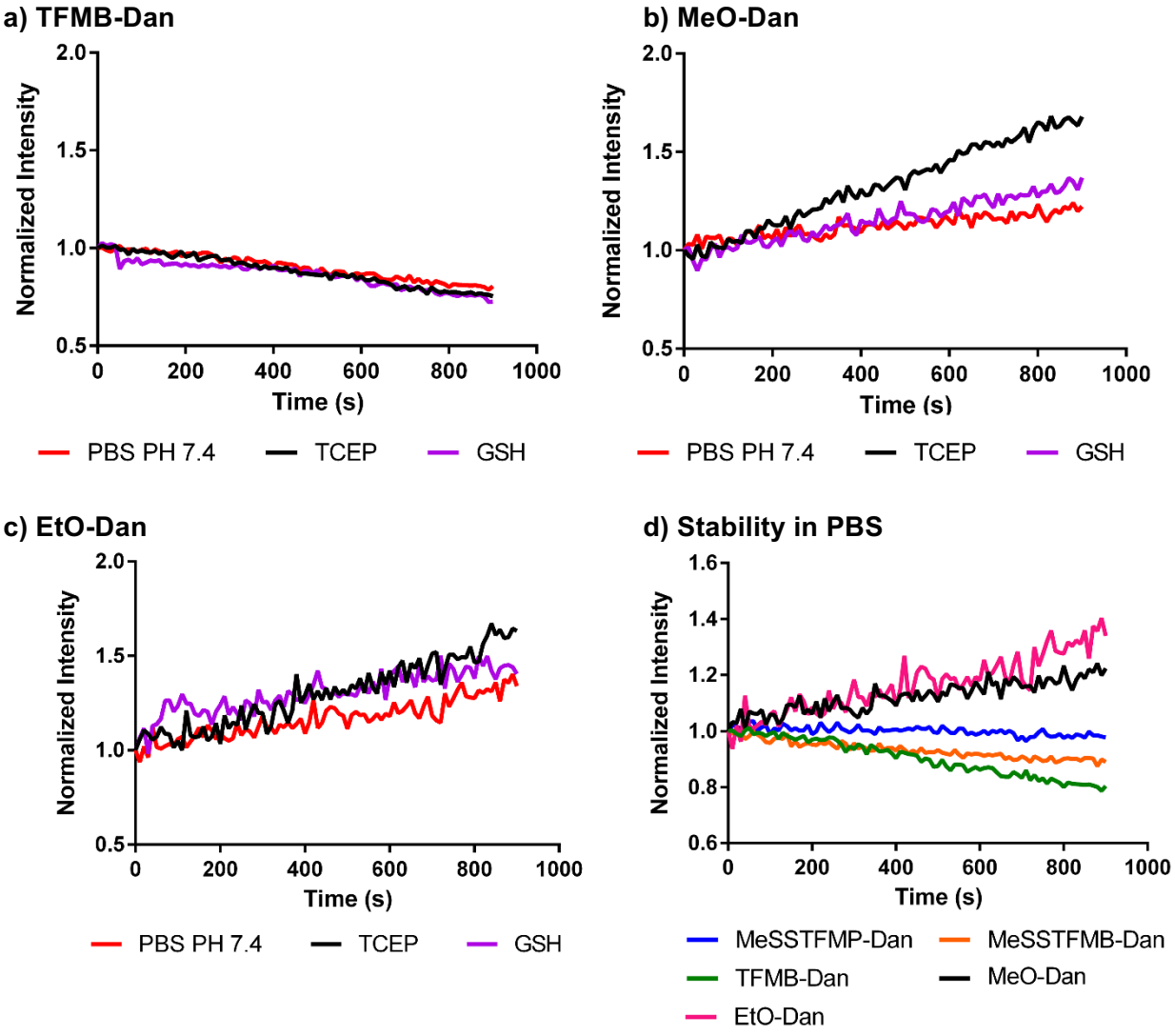


Figure S2: Stability of dansylates under reducing conditions. TFMB-Dan (a), MeO-Dan (b), EtO-Dan (c) were treated with 1 mM TCEP, 5 mM GSH, or PBS alone and the fluorescence of dansyl sulfonate was monitored (324 nm excitation; 498 nm emission). Comparison of the stability of all dansylates in PBS alone is shown in (d). Intensites were normalized to their initial (background) intensities at time zero. Graphs were generated using GraphPad Prism 6.

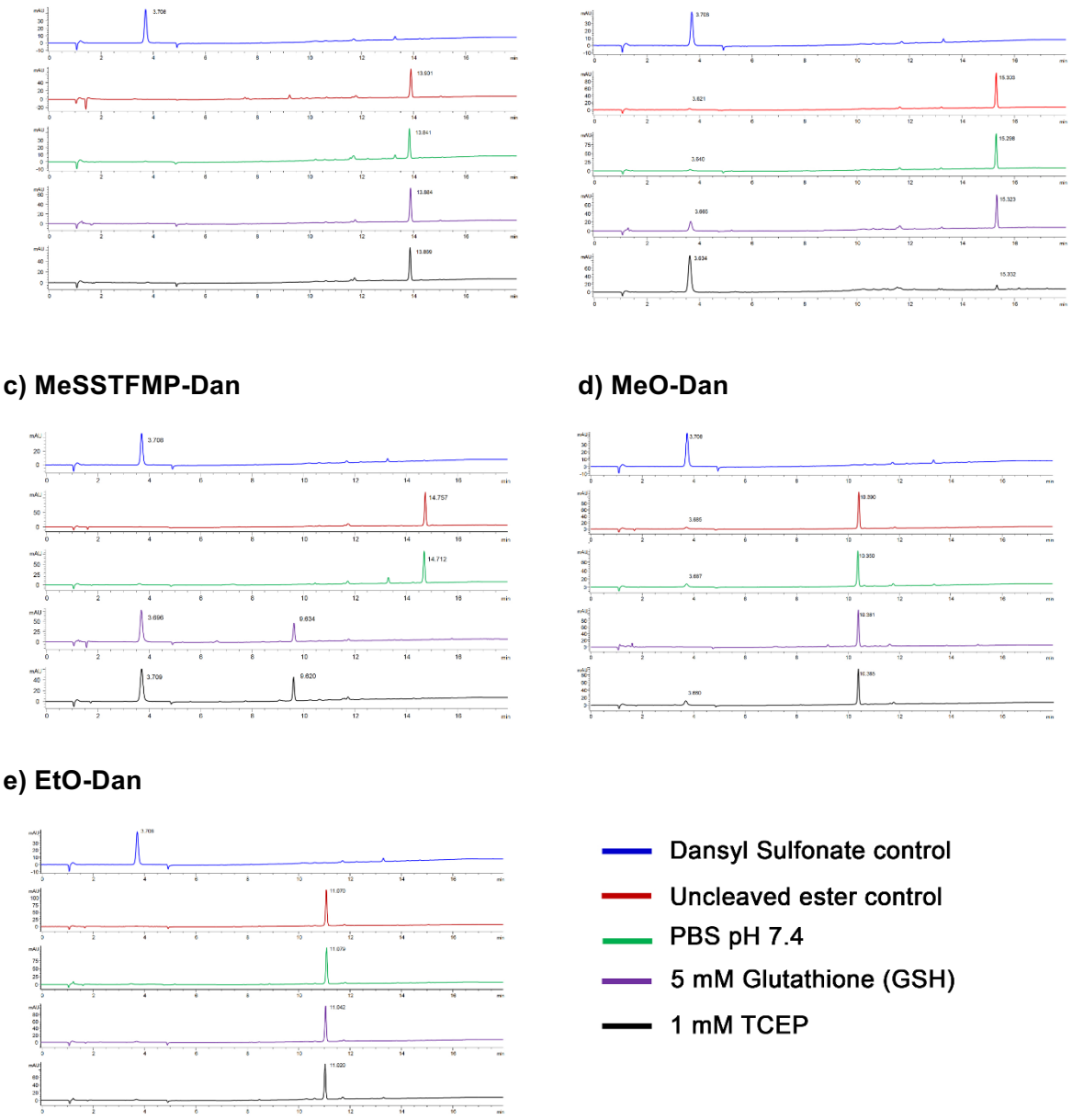


Figure S3: HPLC spectra of dansylates after treatment with reducing agents. TFMB-Dan (a), MeSSTFMB-Dan (b), MeSSTFMP-Dan (c), MeO-Dan (d), and EtO-Dan (e) were treated with reducing agents or PBS alone for 15 minutes. Control samples were injected immediately, without prior incubation. Each peak is labeled with its retention time. The peak at 9.8 minutes in (c) is presumed to be derived from the thioquinone methide cleavage product.

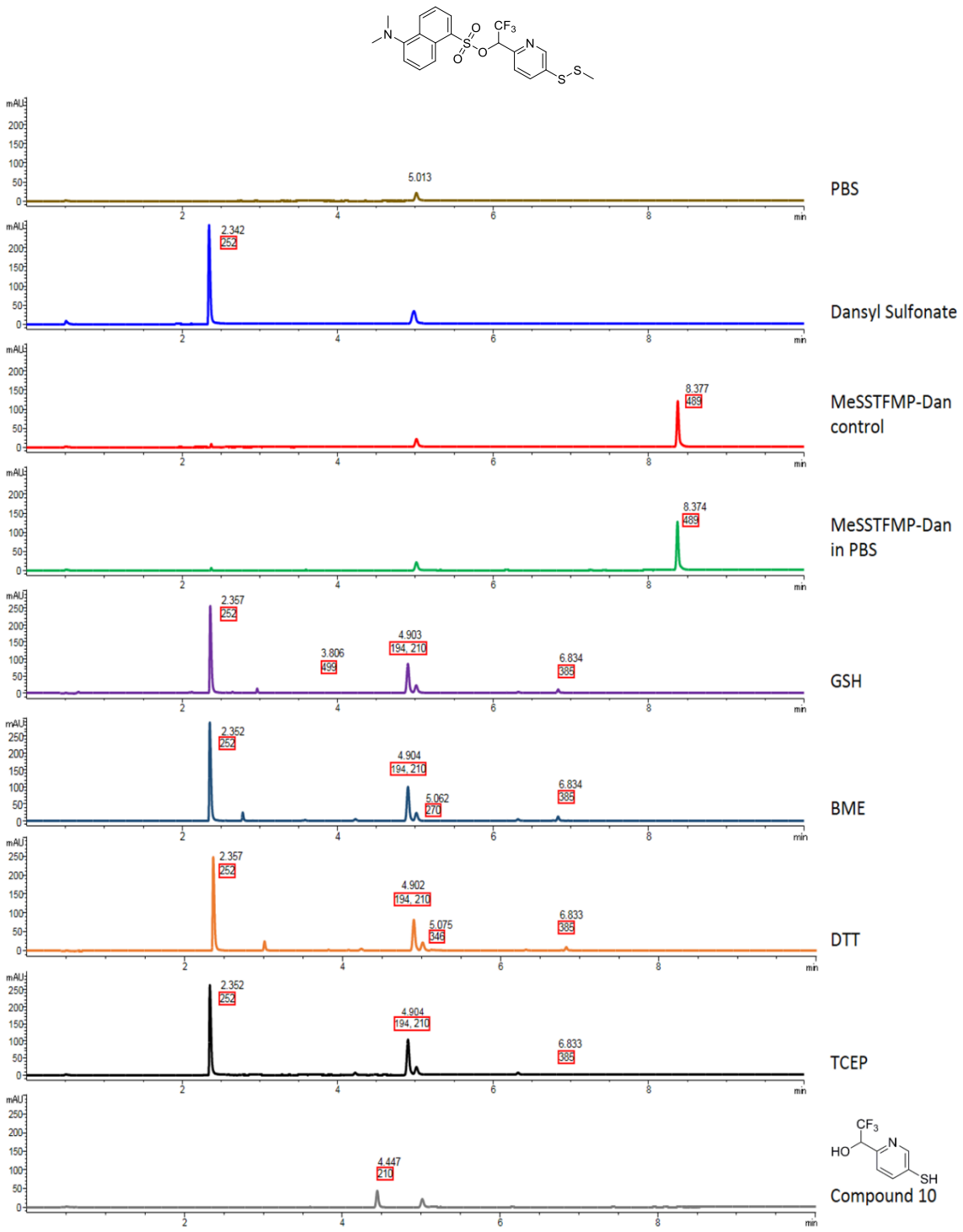


Figure S4: LCMS Spectra of MeSSTFMP-Dan (12) after treatment with reducing agents. Background spectrum of PBS alone (gold); purified dansyl sulfonate (blue); and MeSSTFMP-Dan control without pre-incubation (red). Treatment conditions included: PBS alone (green); 5 mM GSH (purple); 1 mM BME (navy blue); 1 mM DTT (orange); or 1 mM TCEP (black). Compound **10** (grey) was run as a control to confirm that it was not formed during the cleavage reaction. Retention times are labeled with their observed masses (MH+) in red boxes. A peak at 5.01 min is present in all traces and not derived from MeSSTFMP-Dan.

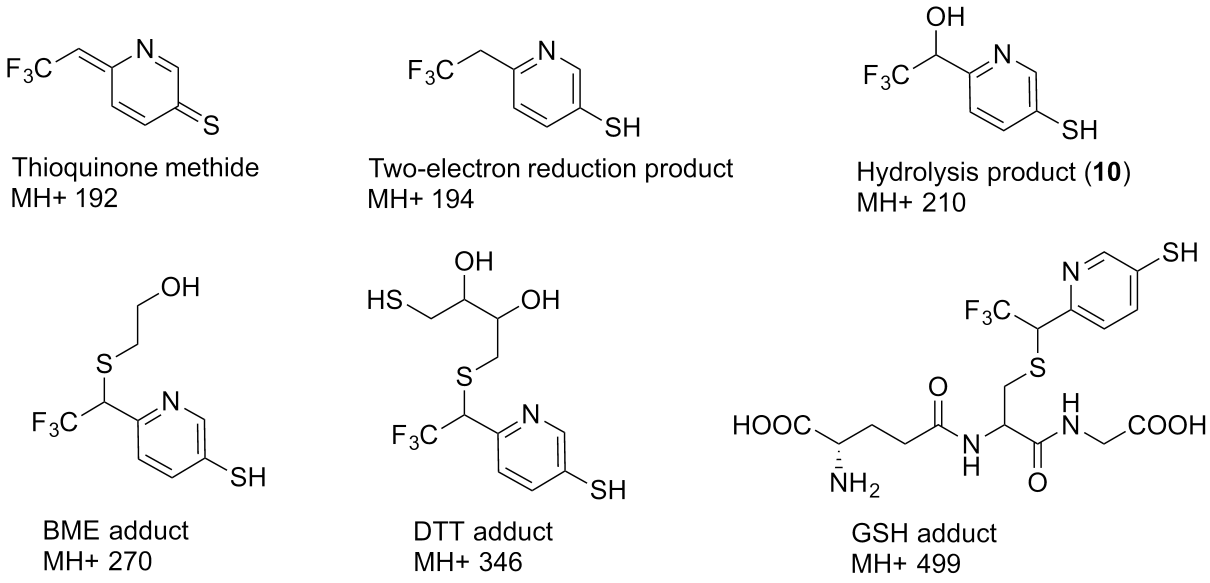


Figure S5: Possible byproducts of MeSSTFMP-Dan reductive cleavage. MeSSTFMP-Dan ester (retention time 8.37 min in Figure S4) is completely reduced by glutathione, BME, DTT, and TCEP to liberate the free dansyl sulfonate (2.36 min). The major byproduct of these reductions detected by LCMS (4.90 min) has a mass consistent with the two-electron reduction product of the thioquinone methide. The hydrolysis product equivalent to compound **10** was not observed. Reductant-specific byproducts were very minor, detectable only by MS and not by UV absorbance. GSH: A mass at 3.81 min consistent with the glutathione adduct with the thioquinone methide; BME: A mass at 5.06 min consistent with the BME adduct; DTT: A mass at 5.07 min consistent with the DTT adduct; TCEP: No TCEP-specific adducts were detected. Only one possible isomer of each potential reductant adduct is shown.

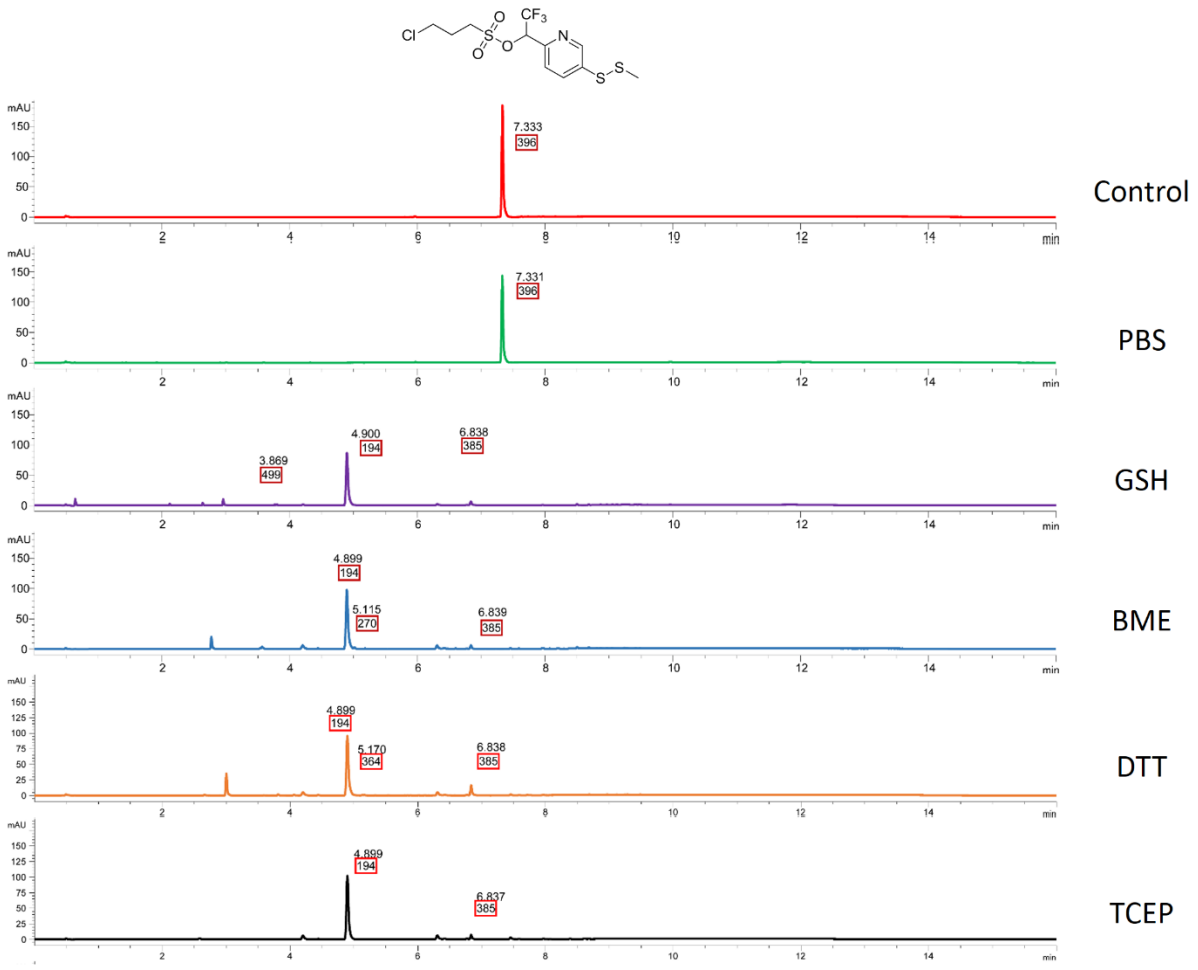


Figure S6: LCMS spectra of alkyl sulfonate 15 after treatment with reducing agents. Untreated control (red) compared to 15-minute incubations in: PBS alone (green); 5 mM GSH (purple); 1 mM BME (blue); 1 mM DTT (orange); 1 mM TCEP (black). Retention times are labeled with their observed masses (MH+) in red boxes.

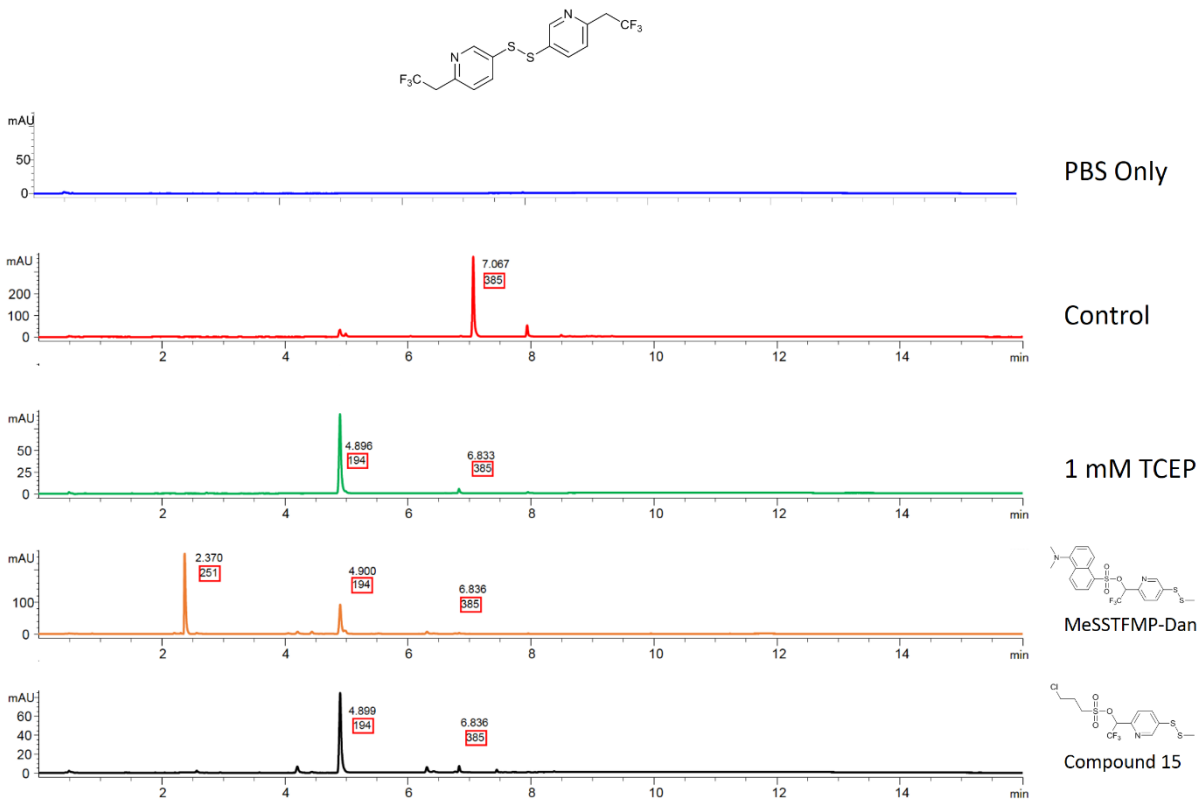


Figure S7: Comparison of the reduced thiol of disulfide 16 to the reduction byproduct of 12 and 15 by LCMS. PBS blank run (blue); Disulfide **16** alone in PBS (red); Reduction of **16** with 1 mM TCEP (green) compared to reduction of MeSSTFMP-Dan **12** (orange) and **15** (black). Retention times are labeled with their observed masses (MH+) in red boxes.

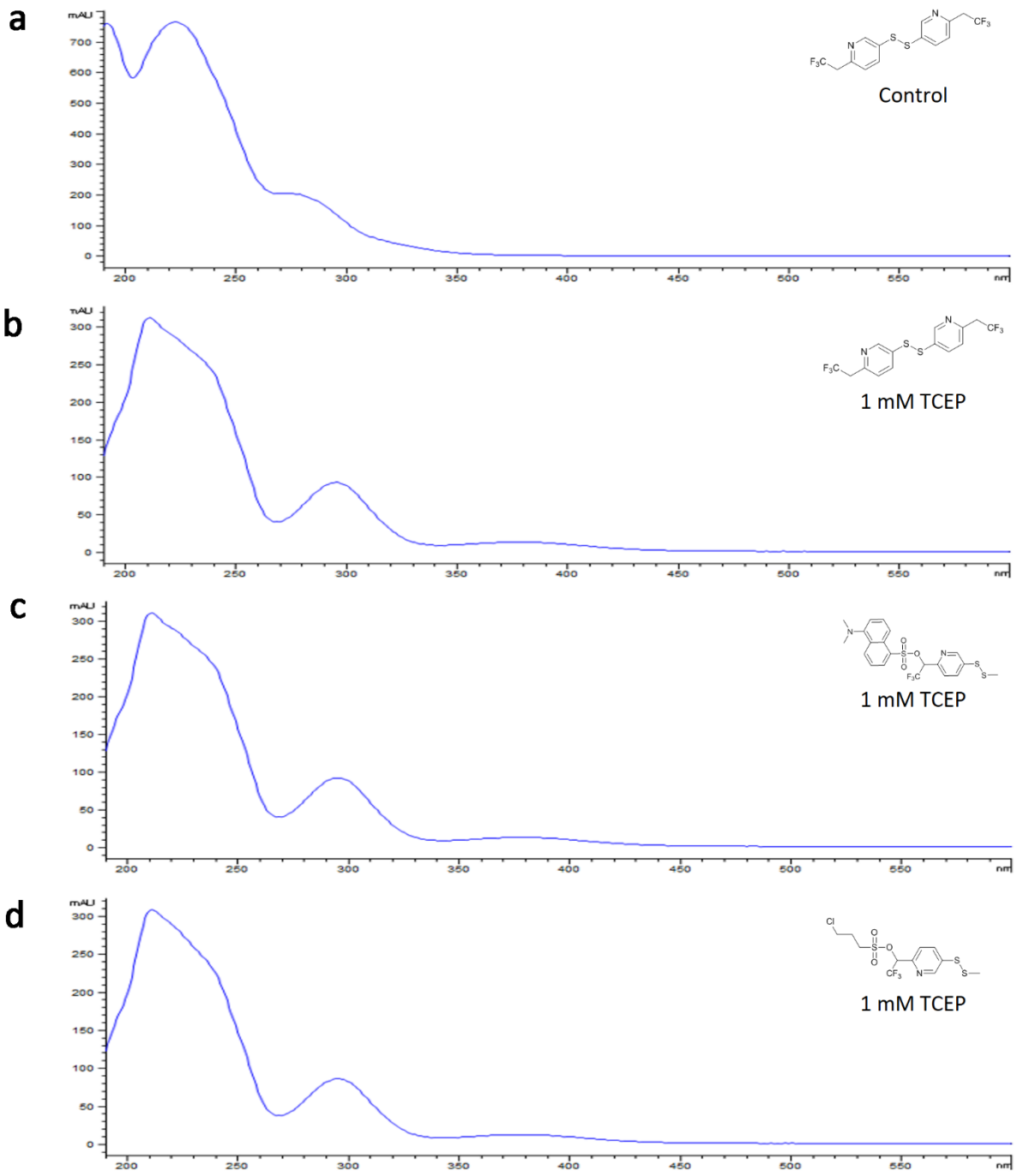


Figure S8: Absorbance spectra of the reduction product from Figure S7. Absorbance spectrum of disulfide **16** (a) compared to the spectra of the reduction product peaks at 4.90 min from Figure S7: b) 1 mM TCEP reduction of **16**; c) 1 mM TCEP reduction of MeSSTFMP-Dan **12**; and d) 1 mM TCEP reduction of **15**.

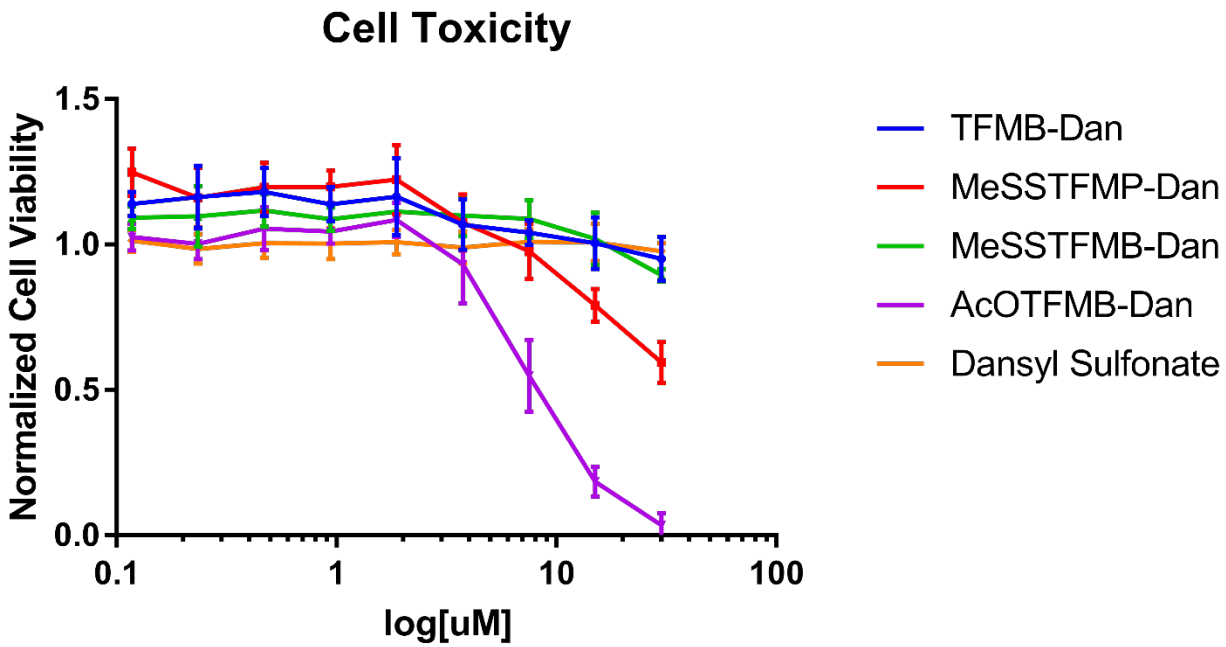


Figure S9: Toxicity of dansylates in live HeLa cells. Live HeLa cells were treated with different concentrations of each dansylate (30 μM – 0.11 μM) for 1 hour. Toxicity was assessed using an XTT cell proliferation assay 48 hours after treatment. Signals were normalized to the DMF vehicle control.

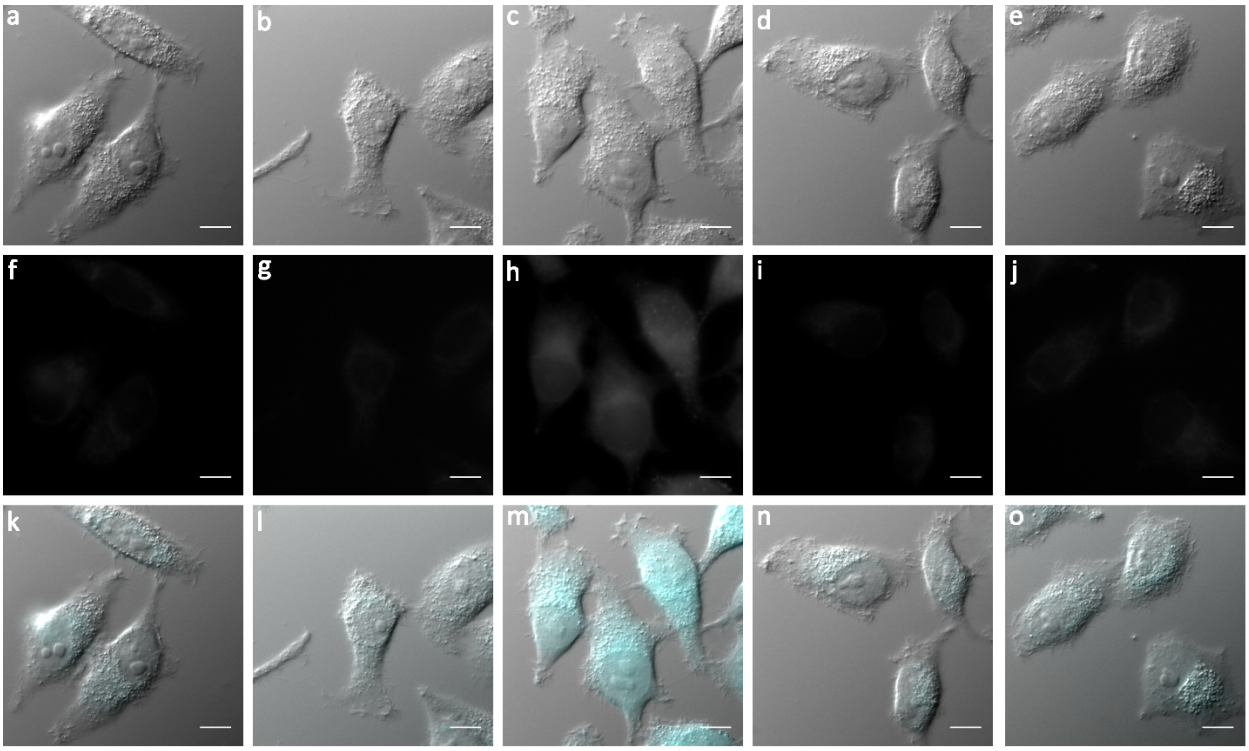
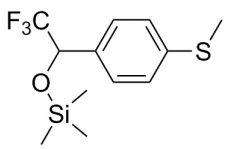
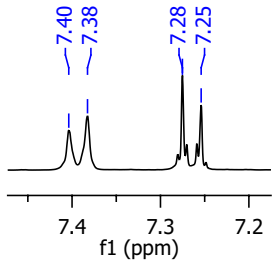


Figure S10: Live images of HeLa cells treated with different dansylates. DIC images (a-e), fluorescence images (f-j), and composite images (k-o) of cells treated with DMF vehicle (a, f, k); dansyl sulfonate (b, g, l); AcOTFMB-Dan (c, h, m); MeO-Dan (d, i, n); or EtO-Dan (e, j, o). Composite images are pseudocolored to match the fluorescence seen through the eyepiece. Scale bar = 10 μm.

^{1}H-NMR


F3C
O
Si
S

1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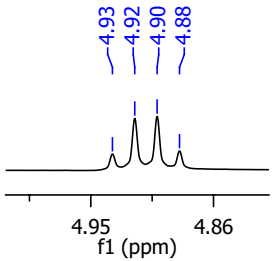
7.4
7.3
7.2
f1 (ppm)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f1 (ppm)

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4.92
4.90
4.88
2.49
0.14
2.07
2.05
1.00
3.25
8.37
13
12
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10
9
8
7
6
5
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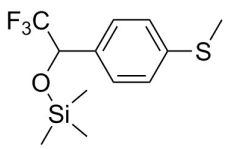
3
2
1
0
-1
f1 (ppm)

^{19}F-NMR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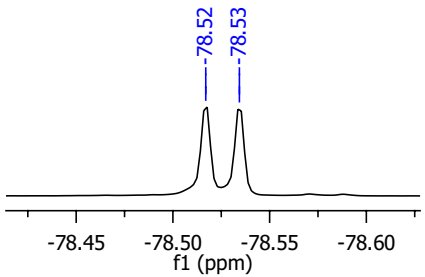
S
O
Si

1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f1 (ppm)

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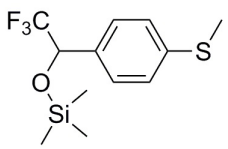
f1 (ppm)

^{13}C-NMR


F3C
S
O
Si

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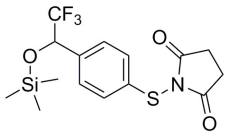
^{1}H-NMR



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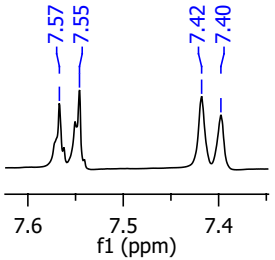
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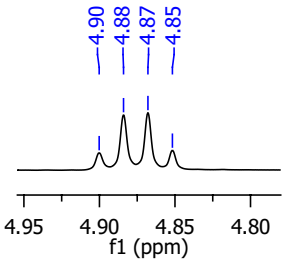
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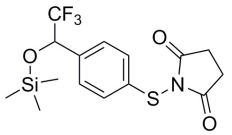
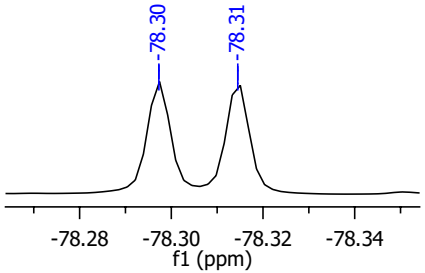
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

^{19}F-NMR

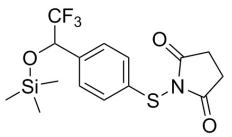

CF3
O
Si
O
N
S
O

2


-78.30
-78.31
-78.28
-78.30
-78.32
-78.34
f1 (ppm)

-78.30
-78.31
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

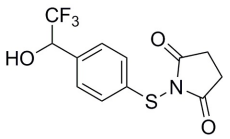
^{13}C-NMR



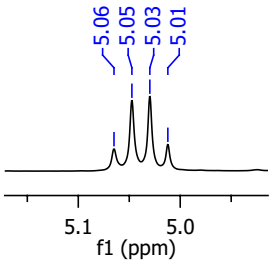
2

176.36
137.03
134.87
131.27
128.46
128.07
125.26
122.45
119.65
73.08
72.76
72.44
72.12
28.60
-0.32
f1 (ppm)

^{1}H-NMR

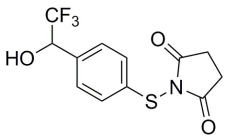

CF3
HO
O
N
S
O

3

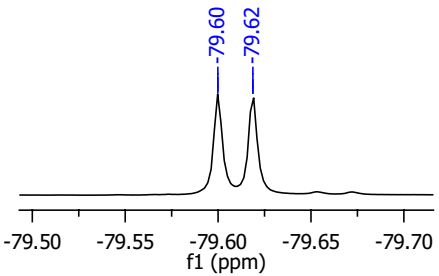

5.06
5.05
5.03
5.01
5.1
5.0
f1 (ppm)

7.47
5.06
5.05
5.03
5.01
2.83
3.94
1.00
4.45
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

^{19}F-NMR

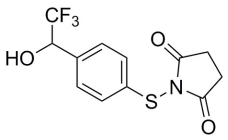

CF3
HO
O
N
S
O

3


-79.60
-79.62
-79.50
-79.55
-79.60
-79.65
-79.70
f1 (ppm)

-79.60
-79.62
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

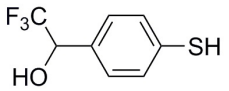
^{13}C-NMR


CF3
HO
O
N
S
O

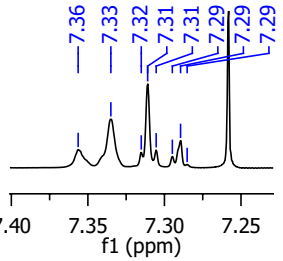
3

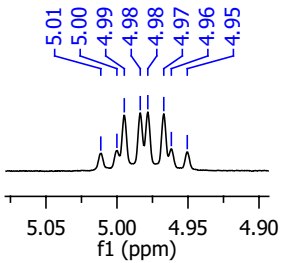
177.71
136.24
136.23
135.65
128.85
128.51
128.27
128.26
126.05
123.25
120.44
71.47
71.16
70.85
70.54
28.26
f1 (ppm)

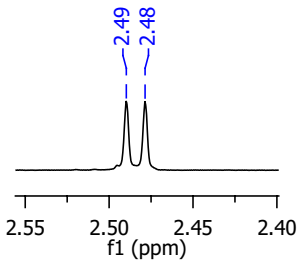
^{1}H-NMR


F3C
HO
SH

4

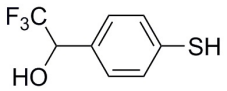

7.36
7.33
7.32
7.31
7.31
7.29
7.29
7.29
7.40
7.35
7.30
7.25
f1 (ppm)


5.01
5.00
4.99
4.98
4.98
4.97
4.96
4.95
5.05
5.00
4.95
4.90
f1 (ppm)

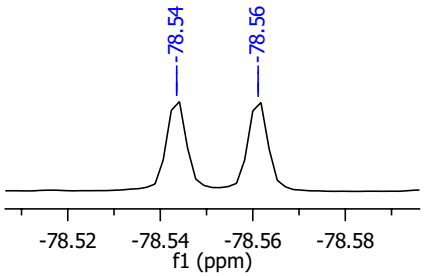

2.49
2.48
2.55
2.50
2.45
2.40
f1 (ppm)

7.36
7.33
7.32
7.31
7.31
7.29
7.29
7.29
5.01
5.00
4.99
4.98
4.98
4.97
4.96
4.95
3.51
2.49
2.48
4.01
1.00
0.88
0.96
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

^{19}F-NMR

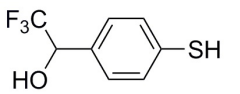

F3C
HO
SH

4


-78.54
-78.56
-78.52
-78.54
-78.56
-78.58
f1 (ppm)

-78.54
-78.56
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

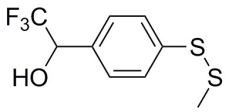
^{13}C-NMR


F3C
HO
SH

4

133.09
131.11
129.13
128.27
128.12
128.11
125.47
122.66
72.83
72.51
72.20
71.88
131.11
131.2
131.1
131.0
f1 (ppm)
72.83
72.51
72.20
71.88
74
73
72
71
70
f1 (ppm)
128.12
128.11
128.2
128.1
128.0
f1 (ppm)
129.13
128.12
128.11
125.47
122.66
128
124
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

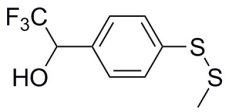
^{1}H-NMR


F3C
HO
S
S

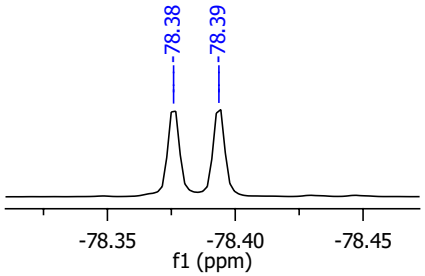
5

7.58
7.57
7.57
7.56
7.55
7.55
7.45
7.43
5.03
5.02
5.01
5.00
4.99
4.98
2.76
2.75
2.45
7.6
7.5
7.4
f1 (ppm)
5.1
5.0
4.9
f1 (ppm)
2.78
2.76
2.74
2.72
f1 (ppm)
1.98
2.09
1.00
0.95
3.18
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

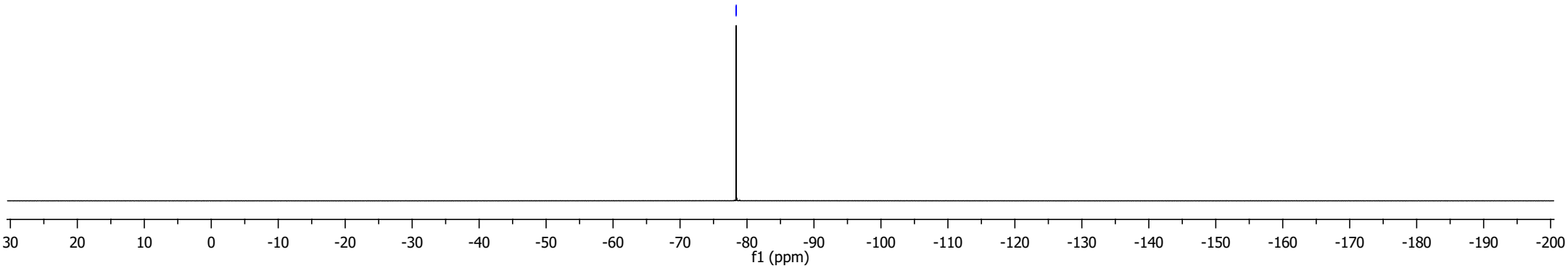
^{19}F-NMR


F3C
HO
S
S

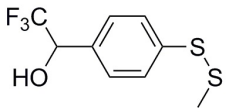
5


-78.38
-78.39
-78.35
-78.40
-78.45
f1 (ppm)


-78.38
-78.39


30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

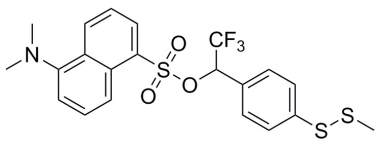
^{13}C-NMR


F3C
HO
S
S

5

138.82
132.27
132.26
128.31
128.11
128.10
126.98
125.50
122.70
119.89
72.84
72.52
72.20
71.88
22.86
132.4
132.2
f1 (ppm)
73
72
71
f1 (ppm)
128.2
128.1
128.0
f1 (ppm)
128
124
120
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

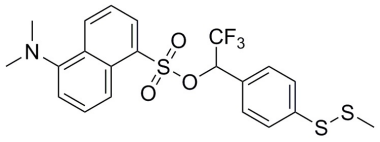
^{1}H-NMR



6

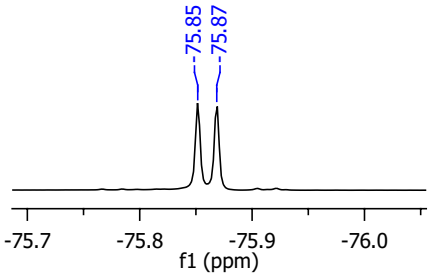
8.47
8.47
8.46
8.45
8.44
8.44
8.19
8.09
8.08
8.06
7.36
7.16
7.14
7.13
7.12
7.11
7.01
5.61
5.60
5.58
5.57
2.83
2.37
f1 (ppm)
1.02
0.99
0.99
1.06
1.04
3.14
2.15
1.00
6.81
3.15

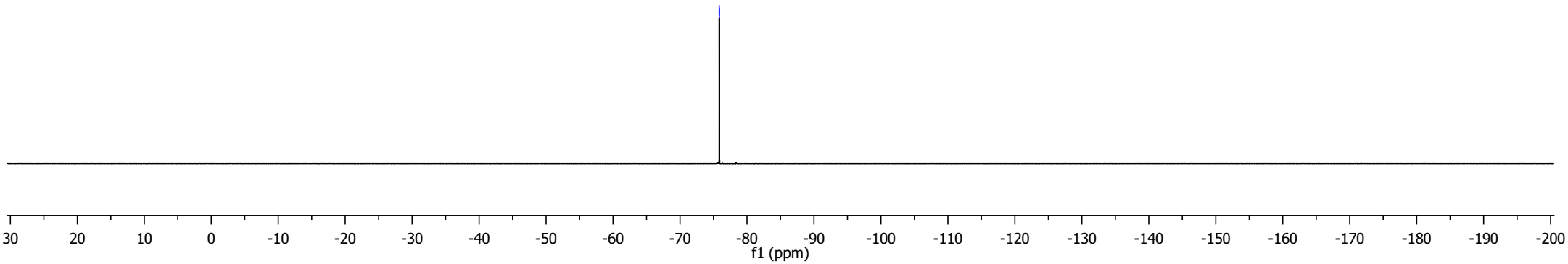
^{19}F-NMR



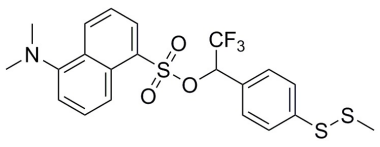
6

-75.85
-75.87





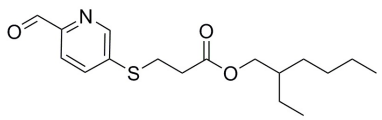
^{13}C-NMR



6

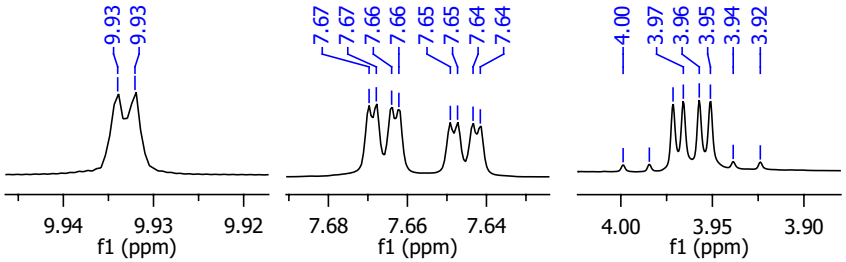
151.69
139.69
132.00
128.85
126.88
125.66
122.61
119.21
115.45
109.99
78.68
78.34
77.99
77.65
45.40
22.76
132.00
131.37
130.26
126.28
123.48
122.61
120.69
119.21
117.89
129.68
129.49
128.85
128.60
119.21
117.89
115.45
109.99
126.88
126.28
125.66
123.48
122.61
120.69
78.68
78.34
77.99
77.65
f1 (ppm)

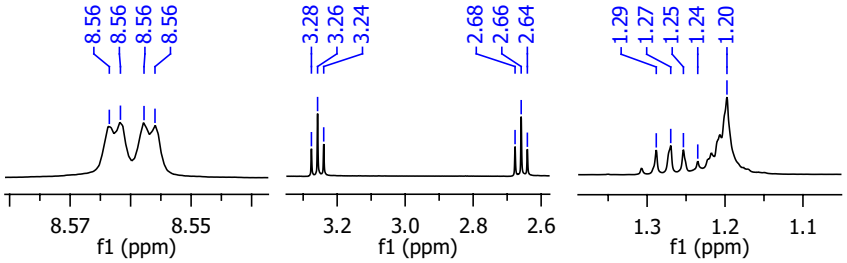
^{1}H-NMR

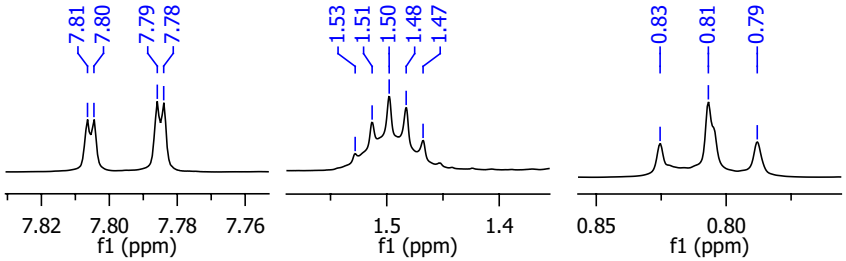


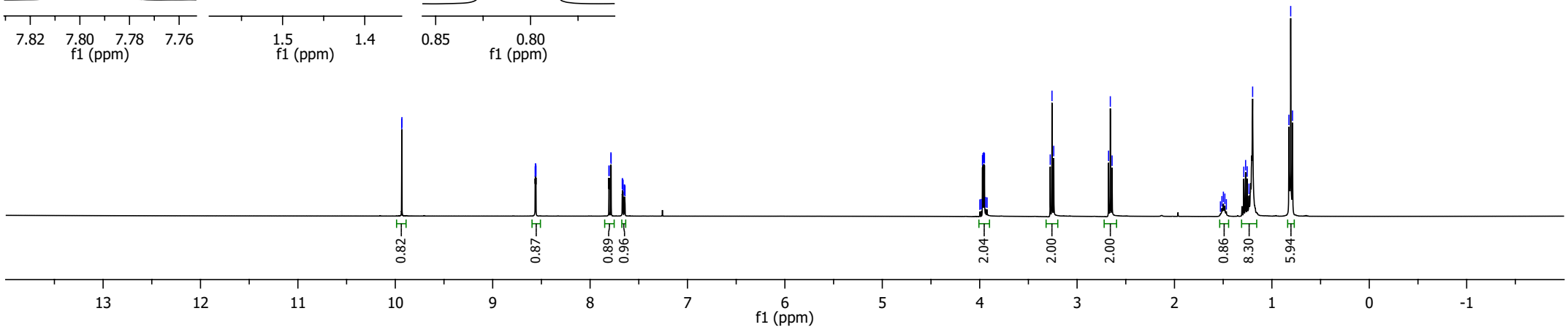
7


9.93
9.93
8.56
8.56
8.56
8.56
7.79
7.78
7.67
7.67
7.66
7.66
7.65
7.65
7.64
7.64
4.00
3.98
3.97
3.97
3.96
3.95
3.94
3.92
3.28
3.26
3.24
2.68
2.66
2.64
1.51
1.48
1.29
1.25
1.20
0.83
0.81
0.79

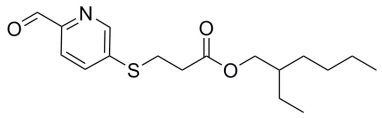

9.93
9.93
9.94
9.93
9.92
f1 (ppm)
7.67
7.67
7.66
7.66
7.65
7.65
7.64
7.64
7.68
7.66
7.64
f1 (ppm)
4.00
3.97
3.96
3.95
3.94
3.92
4.00
3.95
3.90
f1 (ppm)


8.56
8.56
8.56
8.56
8.57
8.55
f1 (ppm)
3.28
3.26
3.24
2.68
2.66
2.64
3.2
3.0
2.8
2.6
f1 (ppm)
1.29
1.27
1.25
1.24
1.20
1.3
1.2
1.1
f1 (ppm)


7.81
7.80
7.79
7.78
7.82
7.80
7.78
7.76
f1 (ppm)
1.53
1.51
1.50
1.48
1.47
1.5
1.4
f1 (ppm)
0.83
0.81
0.79
0.85
0.80
f1 (ppm)

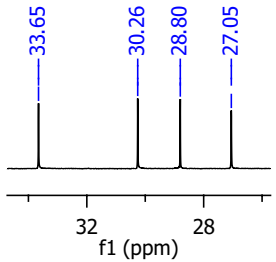

0.82
0.87
0.89
0.96
2.04
2.00
2.00
0.86
8.30
5.94
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

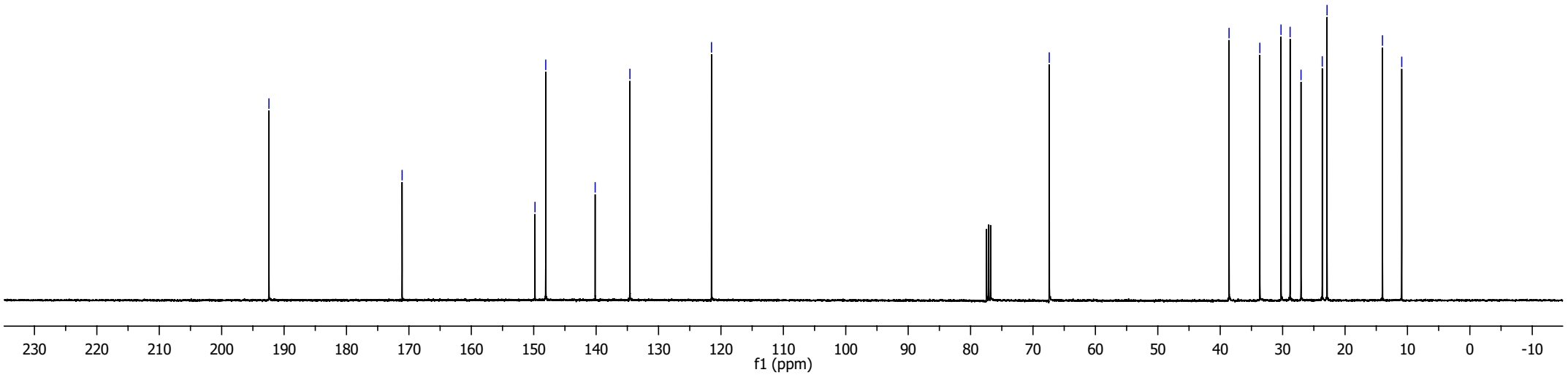
^{13}C-NMR



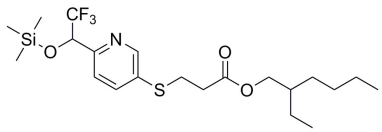
7

192.43
171.09
149.80
148.07
140.15
134.59
121.51
67.39
38.58
30.65
30.26
27.05
23.65
22.88
14.00
10.91





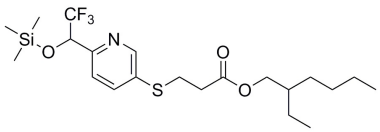
^{1}H-NMR



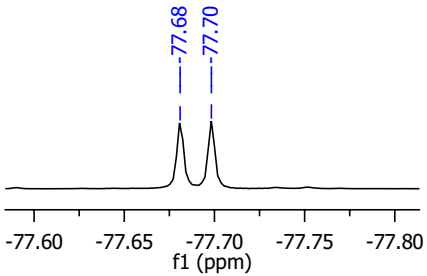
8

8.50 8.50 8.49 8.49 7.72 7.72 7.70 7.70 7.55 7.53
5.06 5.05 5.03 5.01 4.02 4.00 3.99 3.96 3.21 3.19 3.18 2.66 2.64 2.62 1.55 1.52 1.34 1.31 1.25 0.88 0.86 0.84 0.11
f1 (ppm)
0.88 0.96 0.91 0.86 2.00 2.00 1.96 0.78 8.47 6.13 8.19

^{19}F-NMR

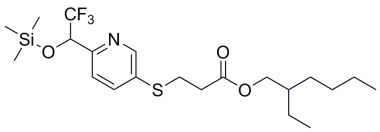


8


-77.68
-77.70
-77.60
-77.65
-77.70
-77.75
-77.80
f1 (ppm)

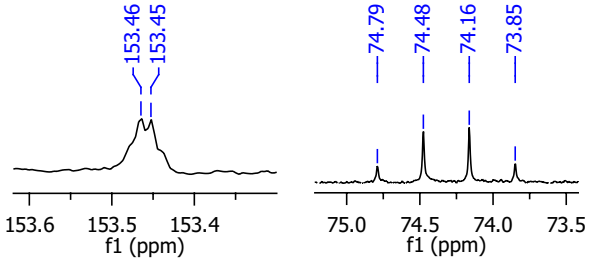
-77.68
-77.70
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

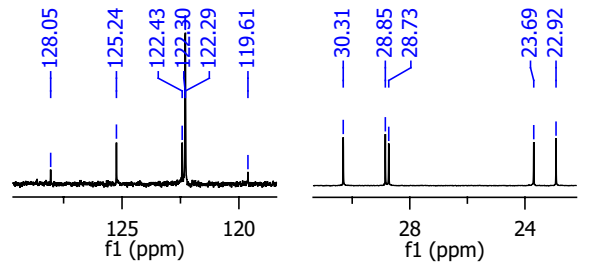
^{13}C-NMR

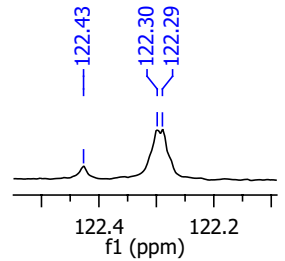


8

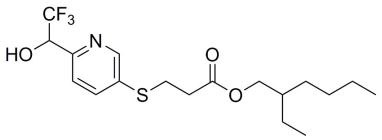
171.40
153.46
153.45
149.05
137.68
133.36
128.05
125.24
122.43
122.30
122.29
119.61
74.79
74.48
74.16
73.85
67.31
38.65
34.20
28.73
23.69
22.92
14.01
10.93
-0.38







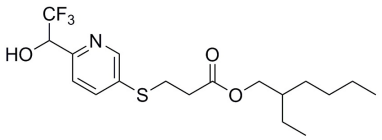
^{1}H-NMR


CF3
HO
N
O
S
O

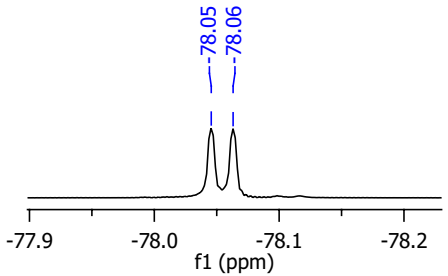
9

8.55
8.54
7.75
7.73
7.73
7.36
7.34
5.02
5.01
4.99
4.97
4.02
4.00
3.99
3.96
3.23
3.21
3.19
2.66
2.64
2.63
1.57
1.54
1.34
1.31
1.26
0.88
0.86
0.84
f1 (ppm)
0.90
0.88
0.88
0.88
2.03
1.94
2.03
0.87
8.40
6.00

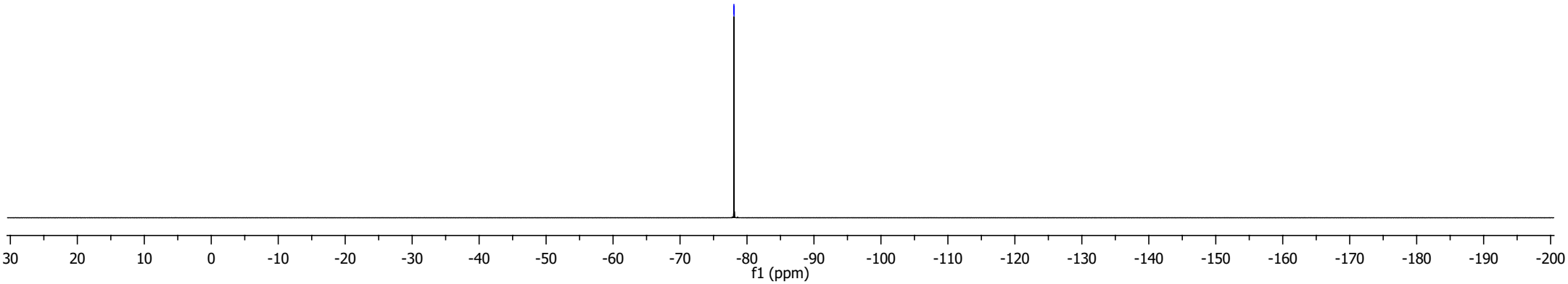
^{19}F-NMR


CF3
HO
N
S
O
O

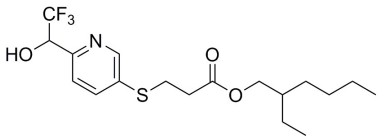
9


-78.05
-78.06
-77.9
-78.0
-78.1
-78.2
f1 (ppm)


-78.05
-78.06

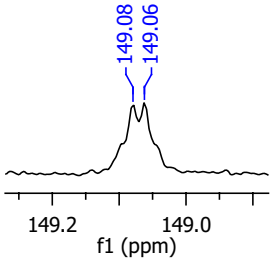

30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

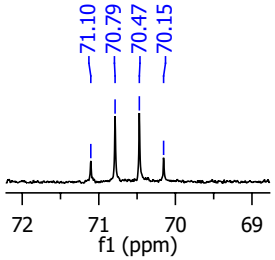
^{13}C-NMR

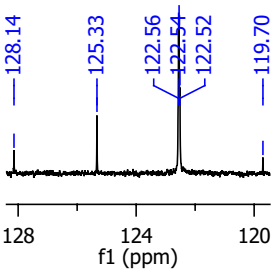


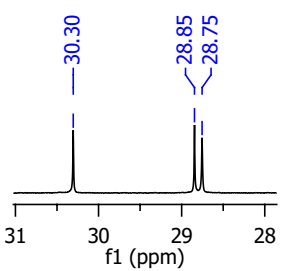
9

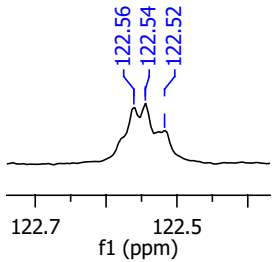
171.38
149.08
149.06
148.56
138.02
134.30
128.14
125.33
122.56
122.54
122.52
119.70
71.10
70.79
70.47
70.15
67.39
38.64
34.13
28.75
23.68
22.92
14.01
10.92



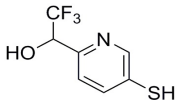








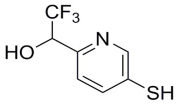
^{1}H-NMR


CF3
HO
N
SH

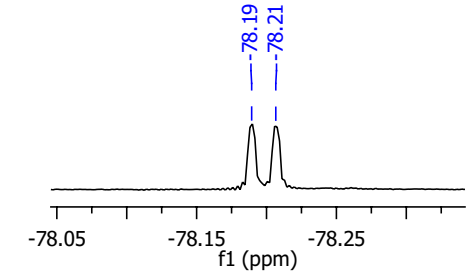
10

8.51
8.51
8.51
7.71
7.69
7.68
7.31
7.29
5.17
5.16
5.02
5.00
4.99
4.97
4.95
3.52
f1 (ppm)
1.00
1.07
1.15
1.02
1.10
1.03

^{19}F-NMR

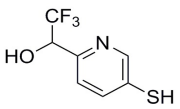

CF3
HO
N
SH

10


-78.19
-78.21
-78.05
-78.15
-78.25
f1 (ppm)

-78.19
-78.21
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

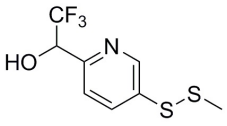
^{13}C-NMR


CF3
HO
N
SH

10

148.28
148.26
148.24
148.23
147.84
137.55
130.07
128.10
125.29
122.57
122.55
122.53
122.51
122.47
119.66
70.93
70.62
70.30
69.98
f1 (ppm)

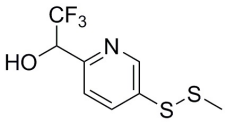
^{1}H-NMR


CF3
HO
N
S
S

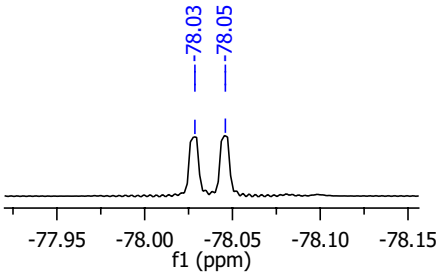
11

8.70
8.69
7.98
7.97
7.96
7.95
7.41
7.39
5.27
5.25
5.04
5.03
5.01
2.48
f1 (ppm)
0.96
1.00
1.05
0.91
1.02
3.23

^{19}F-NMR

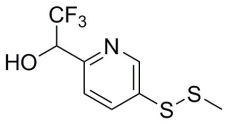

CF3
HO
N
S
S

11

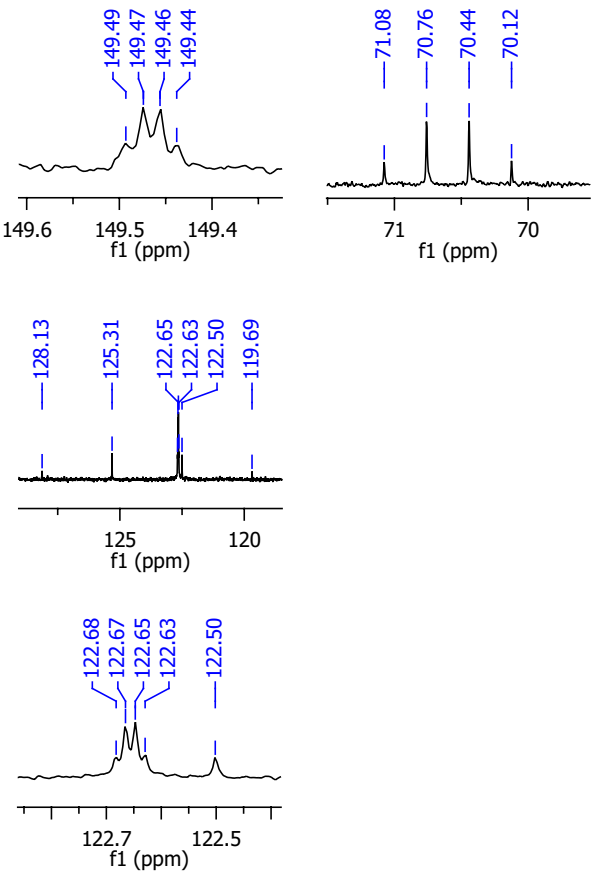

-78.03
-78.05
-77.95
-78.00
-78.05
-78.10
-78.15
f1 (ppm)

-78.03
-78.05
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

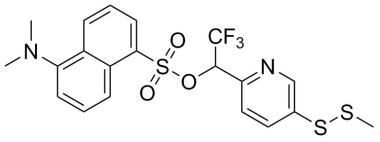
^{13}C-NMR


CF3
HO
N
S
S

11


149.49
149.47
149.46
149.44
146.87
136.25
135.80
128.13
125.31
122.68
122.67
122.65
122.63
122.50
119.69
71.08
70.76
70.44
70.12
22.91
149.6
149.5
149.4
f1 (ppm)
71
70
f1 (ppm)
125
120
f1 (ppm)
122.7
122.5
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

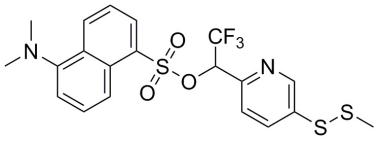
^{1}H-NMR



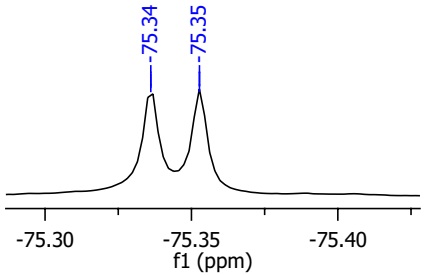
12

8.52
8.50
8.36
8.35
8.24
8.21
8.19
8.18
8.17
7.46
7.42
7.23
7.21
7.18
7.16
5.73
5.72
5.70
5.69
2.85
2.41
f1 (ppm)
1.03
0.90
1.07
1.08
1.15
1.07
1.15
1.17
1.12
1.00
6.99
3.29

^{19}F-NMR

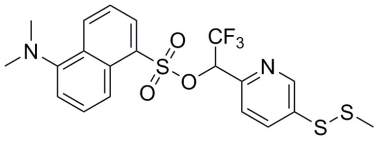


12


-75.34
-75.35
-75.30
-75.35
-75.40
f1 (ppm)

-75.34
-75.35
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

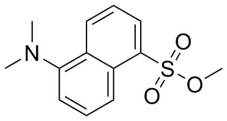
^{13}C-NMR



12

151.78
147.46
146.82
134.45
130.79
129.69
129.54
128.91
122.85
120.77
118.53
115.53
79.19
78.92
78.65
78.38
45.41
22.85
f1 (ppm)

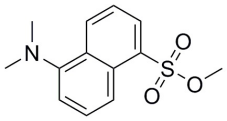
^{1}H-NMR



13

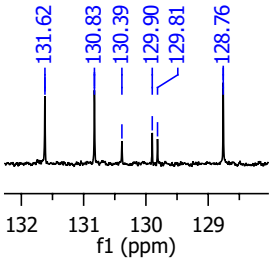
8.62
8.62
8.62
8.60
8.60
8.60
8.29
8.27
8.26
7.56
7.53
7.22
7.22
7.20
7.20
3.72
2.89
8.64
8.62
8.60
8.58
f1 (ppm)
7.24
7.22
7.20
f1 (ppm)
8.29
8.29
8.27
8.26
8.24
8.24
8.28
8.24
f1 (ppm)
7.61
7.59
7.57
7.55
7.53
7.60
7.55
f1 (ppm)
0.94
1.92
1.90
0.92
2.91
6.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

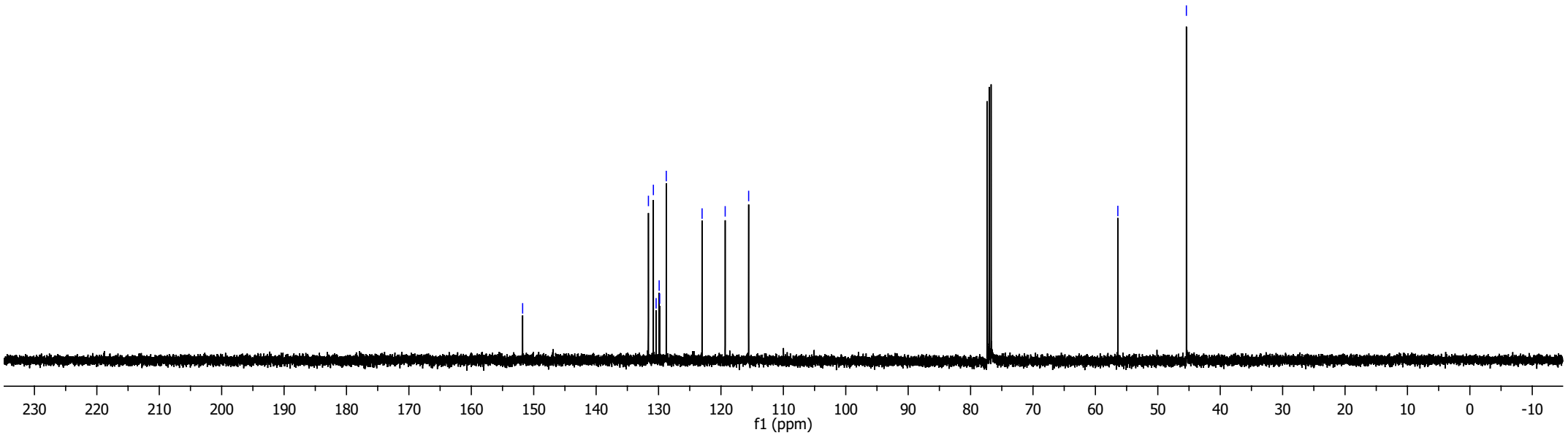
^{13}C-NMR



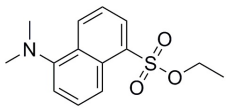
13

151.78
130.83
130.39
129.90
129.81
128.76
123.02
119.32
115.56
56.40
45.42

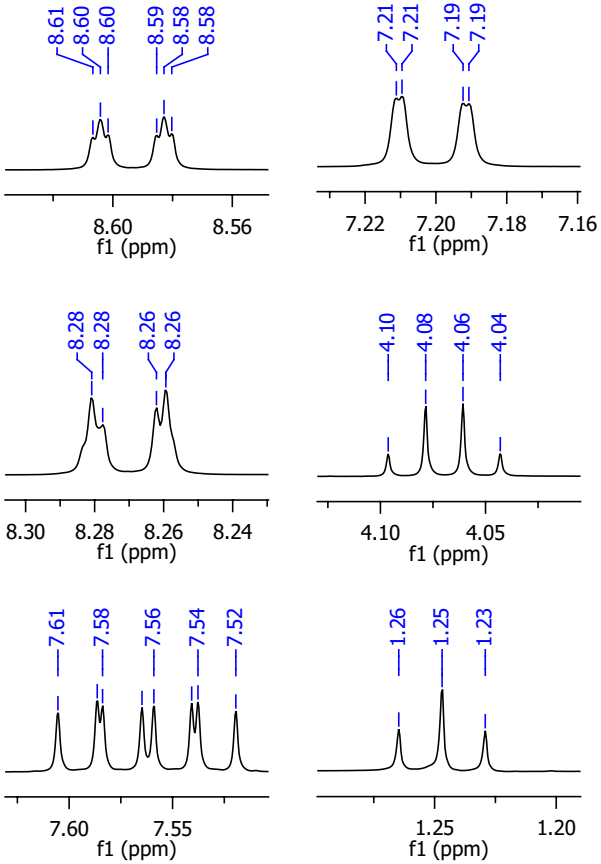




^{1}H-NMR

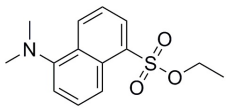


14


8.61
8.60
8.60
8.59
8.58
8.58
8.60
8.56
f1 (ppm)
7.21
7.21
7.19
7.19
7.22
7.20
7.18
7.16
f1 (ppm)
8.28
8.28
8.26
8.26
8.30
8.28
8.26
8.24
f1 (ppm)
4.10
4.08
4.06
4.04
4.10
4.05
f1 (ppm)
7.61
7.58
7.56
7.54
7.52
7.60
7.55
f1 (ppm)
1.26
1.25
1.23
1.25
1.20
f1 (ppm)

8.61
8.60
8.60
8.59
8.58
8.58
7.54
7.52
7.21
7.21
7.19
7.19
4.10
4.08
4.06
4.04
2.88
1.26
1.25
1.23
0.95
1.94
1.91
0.94
1.92
6.00
3.03
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

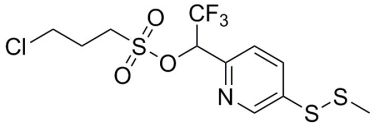
^{13}C-NMR



14

151.74
131.42
130.39
129.88
129.80
128.62
123.04
119.39
115.49
67.12
45.42
14.72
131.46
131.42
131.6
131.4
f1 (ppm)
130.39
129.88
129.80
130.4
130.0
f1 (ppm)
128.62
123.04
119.39
115.49
125
120
115
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

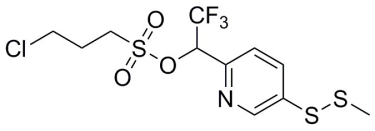
H^1-NMR


Cl
O
S
O
O
CF3
O
N
S
S

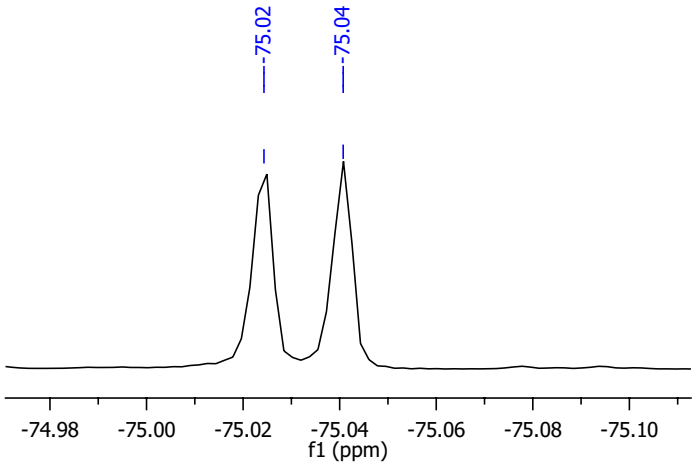
15

8.73
8.73
8.73
8.72
8.02
8.00
7.59
7.57
6.02
6.00
5.98
5.97
3.66
3.66
3.65
3.63
3.40
3.38
2.36
2.35
2.33
2.32
2.31
2.29
f1 (ppm)
0.96
1.02
1.09
1.00
2.31
2.38
3.26
2.35

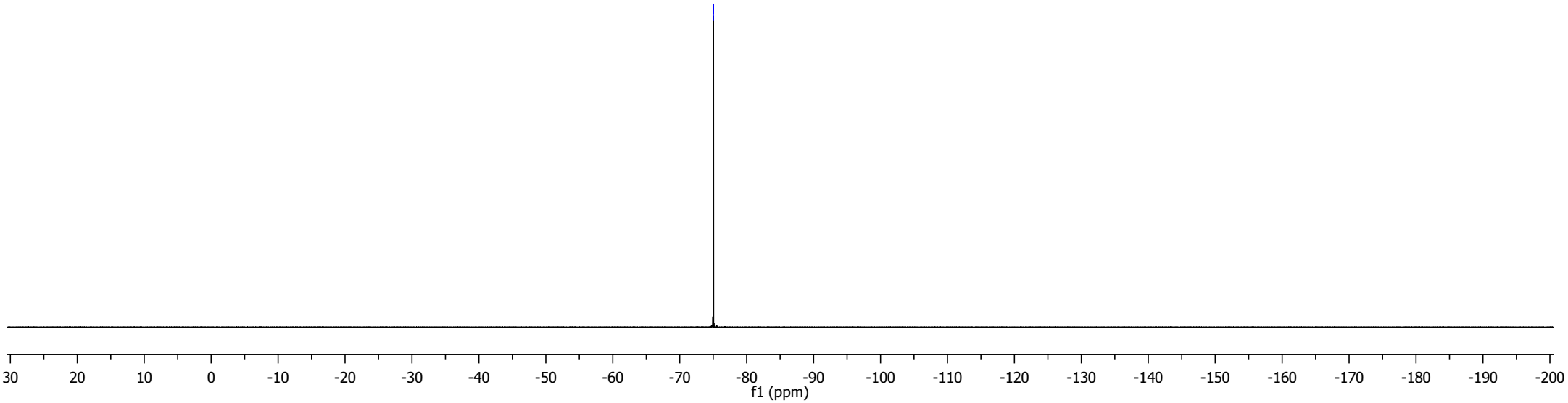
F^{19}-NMR


Cl
O
S
O
O
CF3
N
S
S

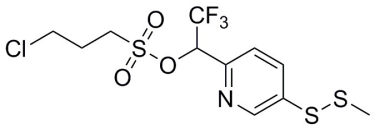
15


-75.02
-75.04
-74.98
-75.00
-75.02
-75.04
-75.06
-75.08
-75.10
f1 (ppm)


-75.02
-75.04

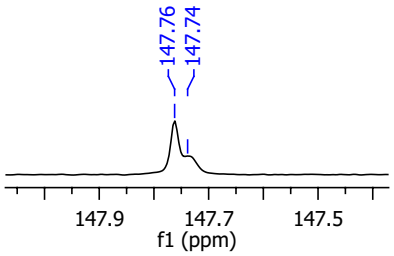

30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

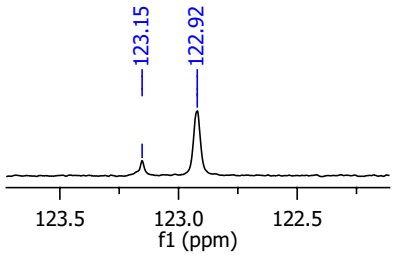
C^{13}-NMR

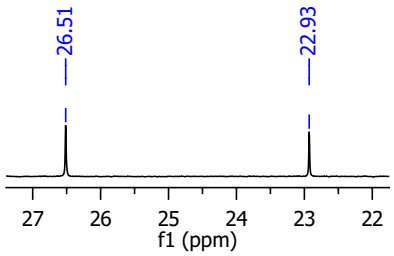


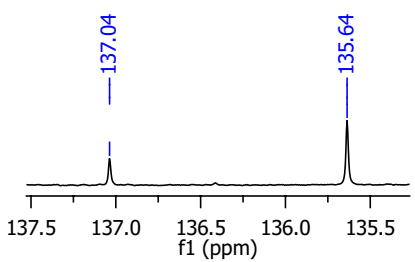
15

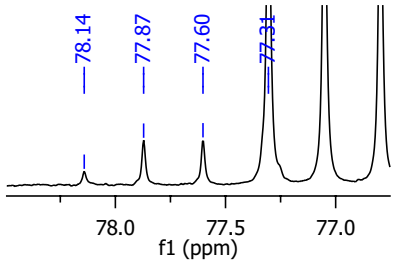
147.76
147.74
137.04
135.64
125.39
123.15
122.92
120.91
118.67
78.14
77.87
77.60
77.31
49.46
42.08
26.51
22.93

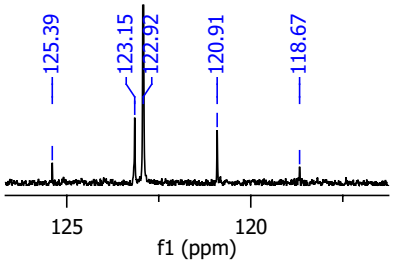


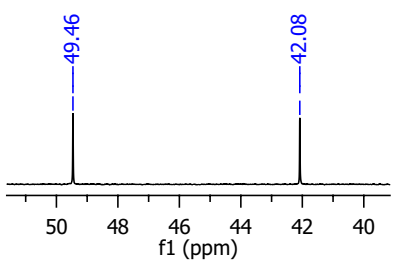




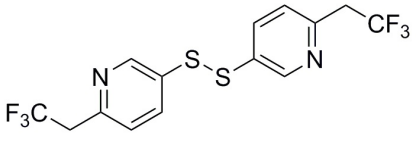




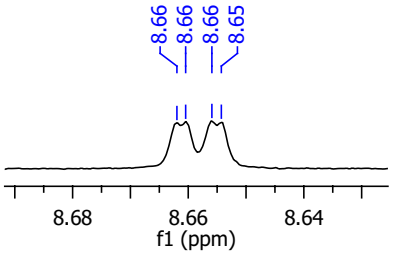


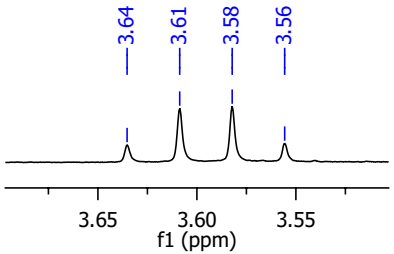


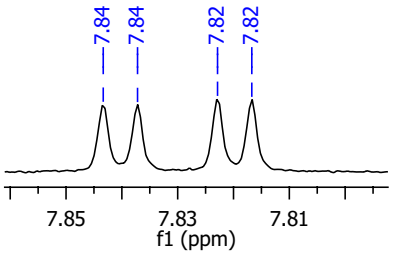
H^1-NMR

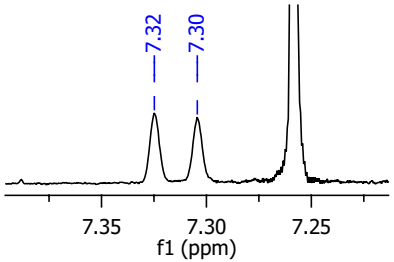

CF3
S
S
N
N
F3C

16


8.66
8.66
8.66
8.65
8.68
8.66
8.64
f1 (ppm)

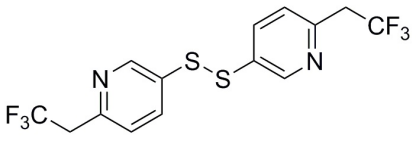

3.64
3.61
3.58
3.56
3.65
3.60
3.55
f1 (ppm)


7.84
7.84
7.82
7.82
7.85
7.83
7.81
f1 (ppm)

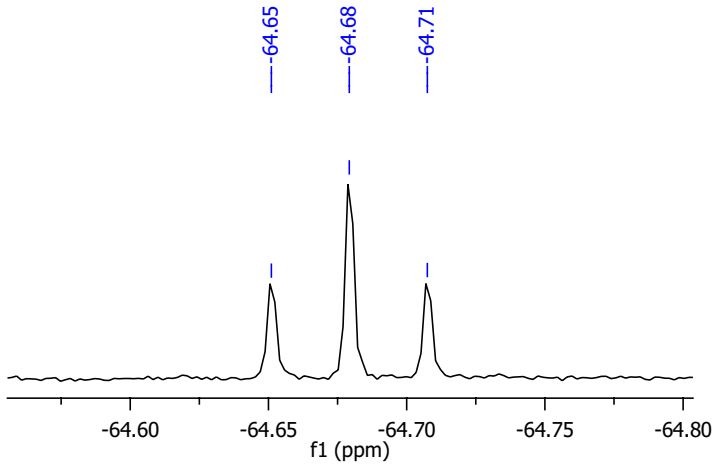

7.32
7.30
7.35
7.30
7.25
f1 (ppm)

8.66
8.66
8.66
8.65
7.84
7.84
7.82
7.82
7.32
7.30
3.64
3.61
3.58
3.56
1.75
2.01
2.13
4.63
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

F^{19}-NMR

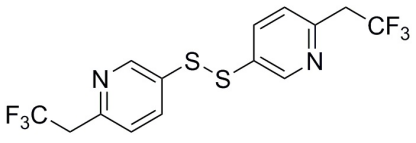

CF3
N
S
S
N
F3C

16


-64.65
-64.68
-64.71
-64.60
-64.65
-64.70
-64.75
-64.80
f1 (ppm)

-64.65
-64.68
-64.71
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

C^{13}-NMR


N
S
S
N
CF3
F3C

16

150.41
150.38
150.36
150.33
149.16
136.99
133.10
128.52
126.31
124.81
124.11
121.90
42.65
42.41
42.17
41.94
f1 (ppm)