

Supporting Information for:

Nickel-catalyzed synthesis of aryl trifluoromethyl sulfides at room temperature

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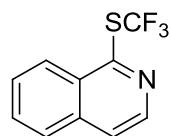
Experimental Procedures

General Considerations. All manipulations were performed using standard Schlenk and high vacuum techniques or in a nitrogen filled glovebox. Solvents were distilled from Na/benzophenone or CaH₂. All reagents were used as received from commercial vendors, unless otherwise noted. ¹H NMR spectra were recorded at ambient temperature (unless otherwise noted) on a Varian Oxford 300 MHz spectrometer and referenced to residual proton solvent signals. ¹³C NMR spectra were recorded on the Varian Oxford spectrometers operating 75 MHz or 126 MHz and referenced to solvent signals. ¹⁹F spectra were recorded on the Varian Oxford spectrometer operating at 282 MHz and were referenced to α,α,α-trifluorotoluene as an internal standard (δ = -63.7). [NMe₄][SCF₃] was prepared according to a previously published procedure,¹ and care was taken that no elemental sulfur was present after work-up.

General procedure for the trifluoromethylthiolations:

Under nitrogen atmosphere, [NMe₄]⁺[SCF₃]⁻ (43.0 mg, 0.24 mmol), Ni(COD)₂ (8.5 mg, 0.03 mmol) and 4,4'-dimethoxyl-2,2'-bipyridine (13.2 mg, 0.06 mmol) were added into a solution of 1-iodoisoquinoline (51.0 mg, 0.20 mmol) in dry THF (4.0 mL). The suspension was stirred at room temperature for 22 hours. Then diethyl ether (50 mL) was added. The mixture was washed with water and dried over anhydrous Na₂SO₄. After evaporation of the solvent, the crude product was purified by flash column chromatography using diethyl ether : pentane = 1 : 20 (v/v) as eluent. The desired product was obtained as a light yellow liquid (25.0 mg, 0.11 mmol, 55% yield).

Analytical data for the new compound in this manuscript:

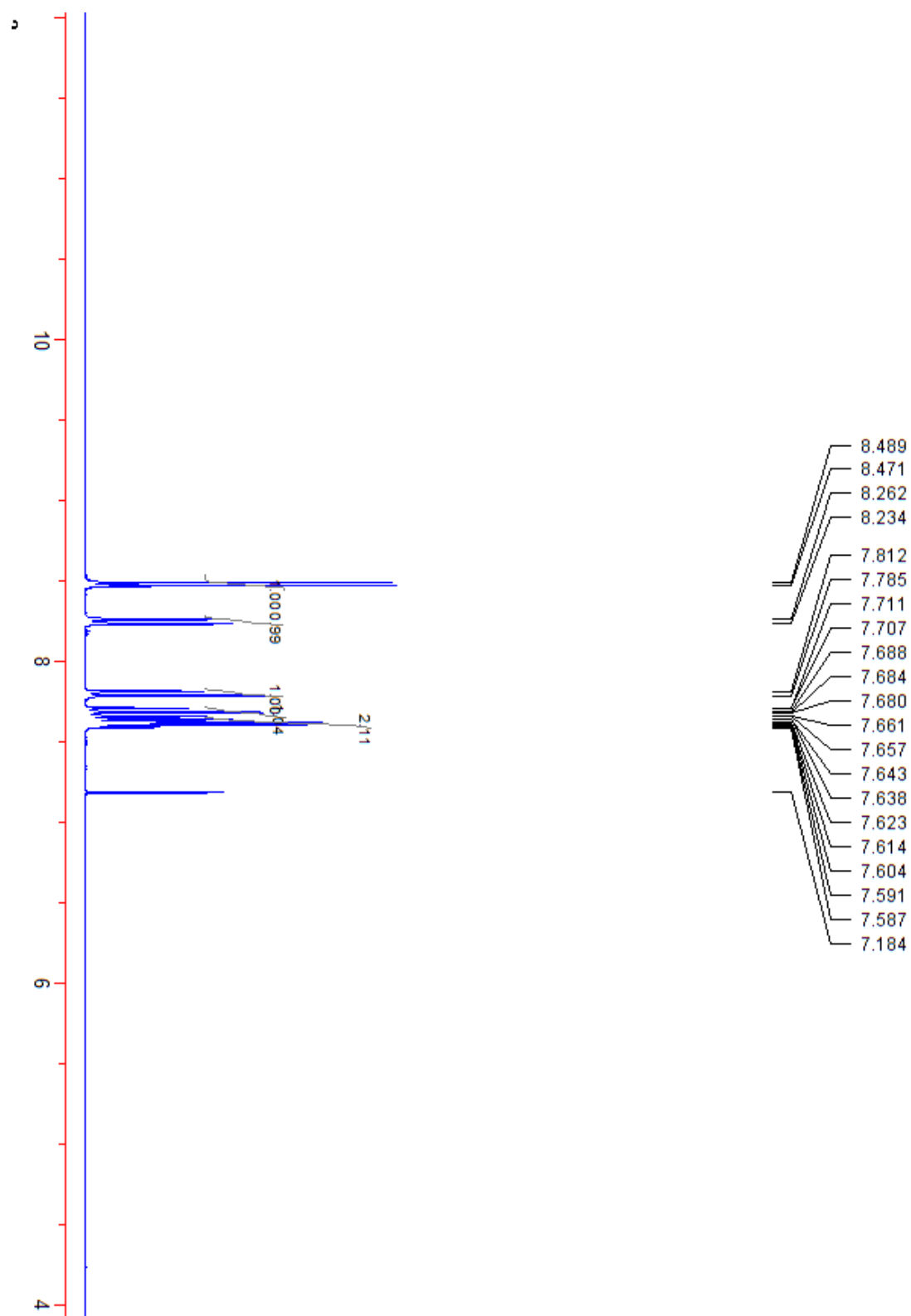


: ¹H NMR (CDCl₃, 300 Hz): δ 8.48 (d, *J* = 5.5 Hz, 1H), 8.25 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.68 (td, *J* = 7.5, 1.2 Hz, 1H), 7.61 (d, *J* = 5.5 Hz, 1H), 7.61 (td, *J* = 7.8, 1.2 Hz, 1H). ¹⁹F NMR (CDCl₃, 282 Hz): δ -39.4 (s, 3F). ¹³C NMR (CDCl₃, 75 Hz): δ 150.2, 142.9, 137.0, 131.3, 130.0, 129.5 (q, *J* = 308.6 Hz, SCF₃), 128.8, 127.6, 126.1, 122.1. HRMS: 229.0178.

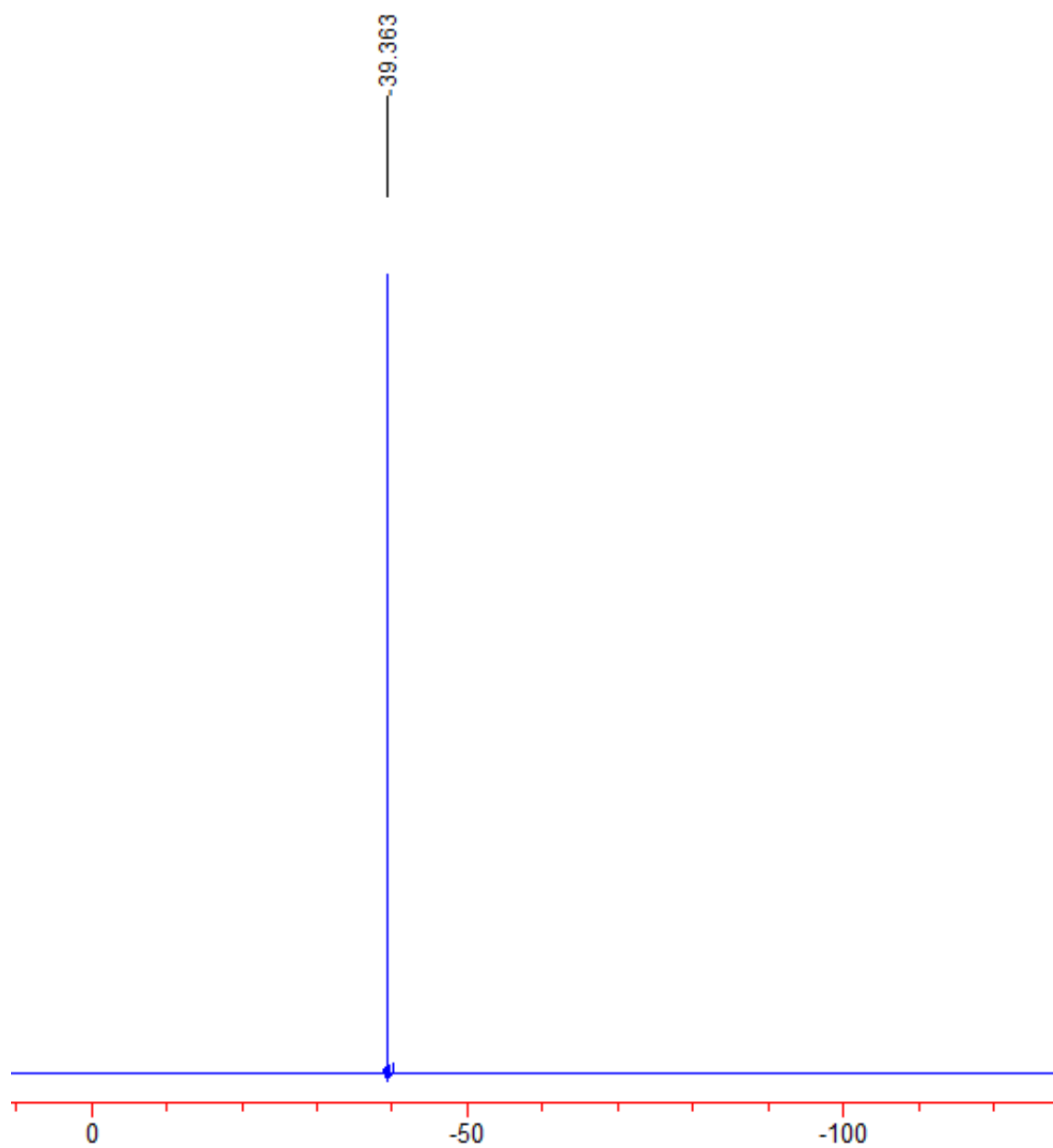
Reference:

- (1) Tyrre, W.; Naumann, D.; Hoge, B.; Yagupolskii, Y. L. *Journal of Fluorine Chemistry* **2003**, *119*, 101.

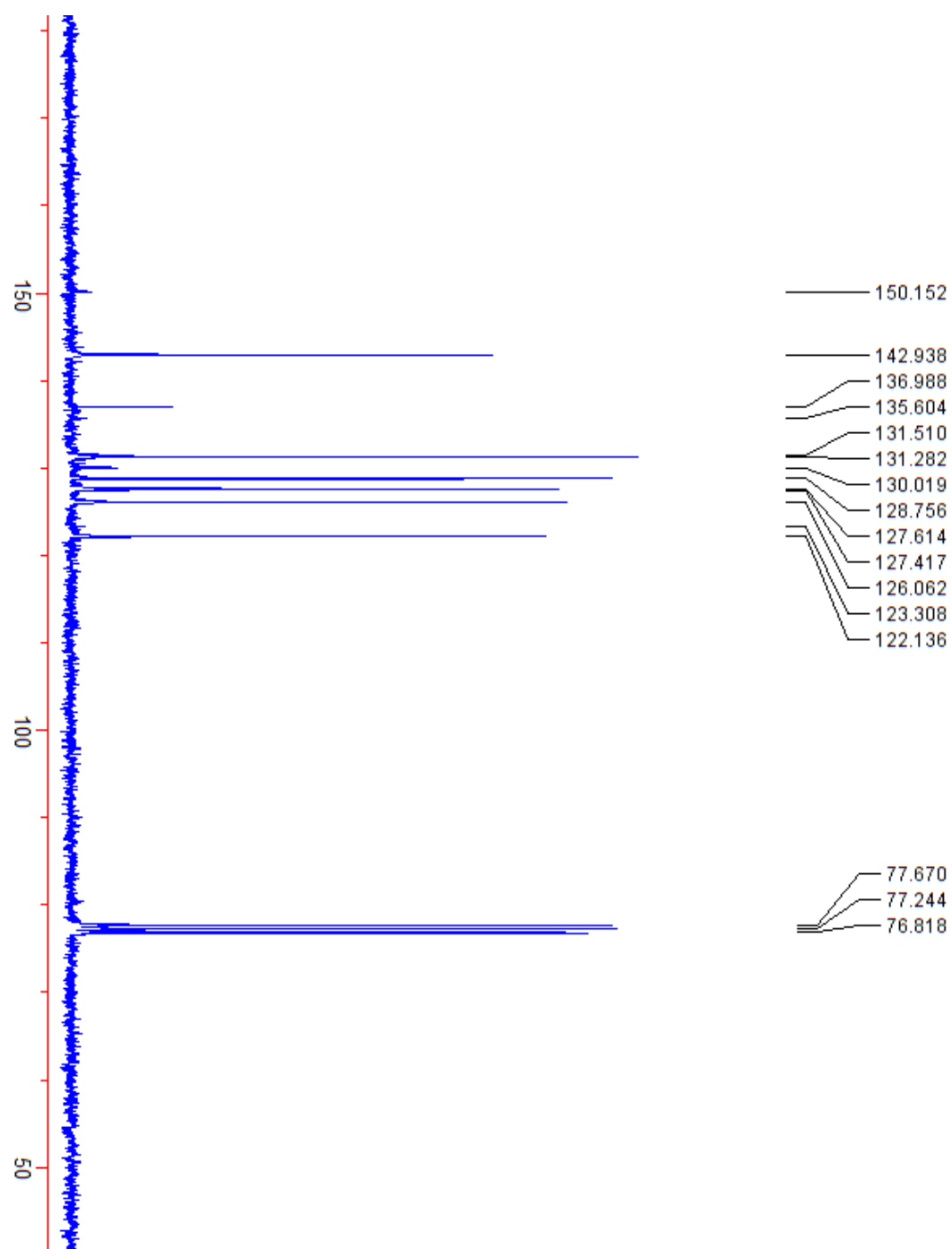
^1H NMR spectrum (CDCl_3):

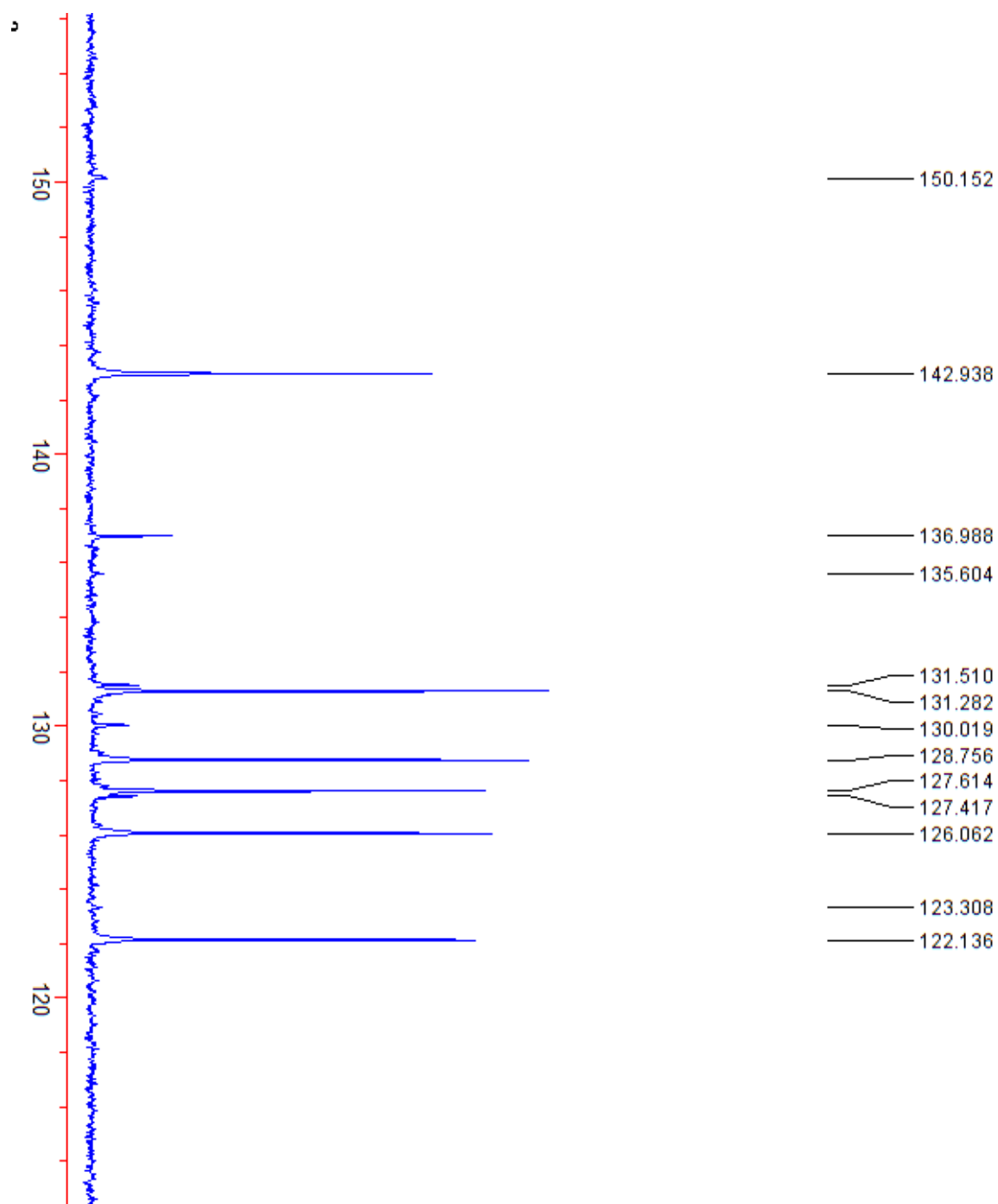


^{19}F NMR spectrum (CDCl_3):



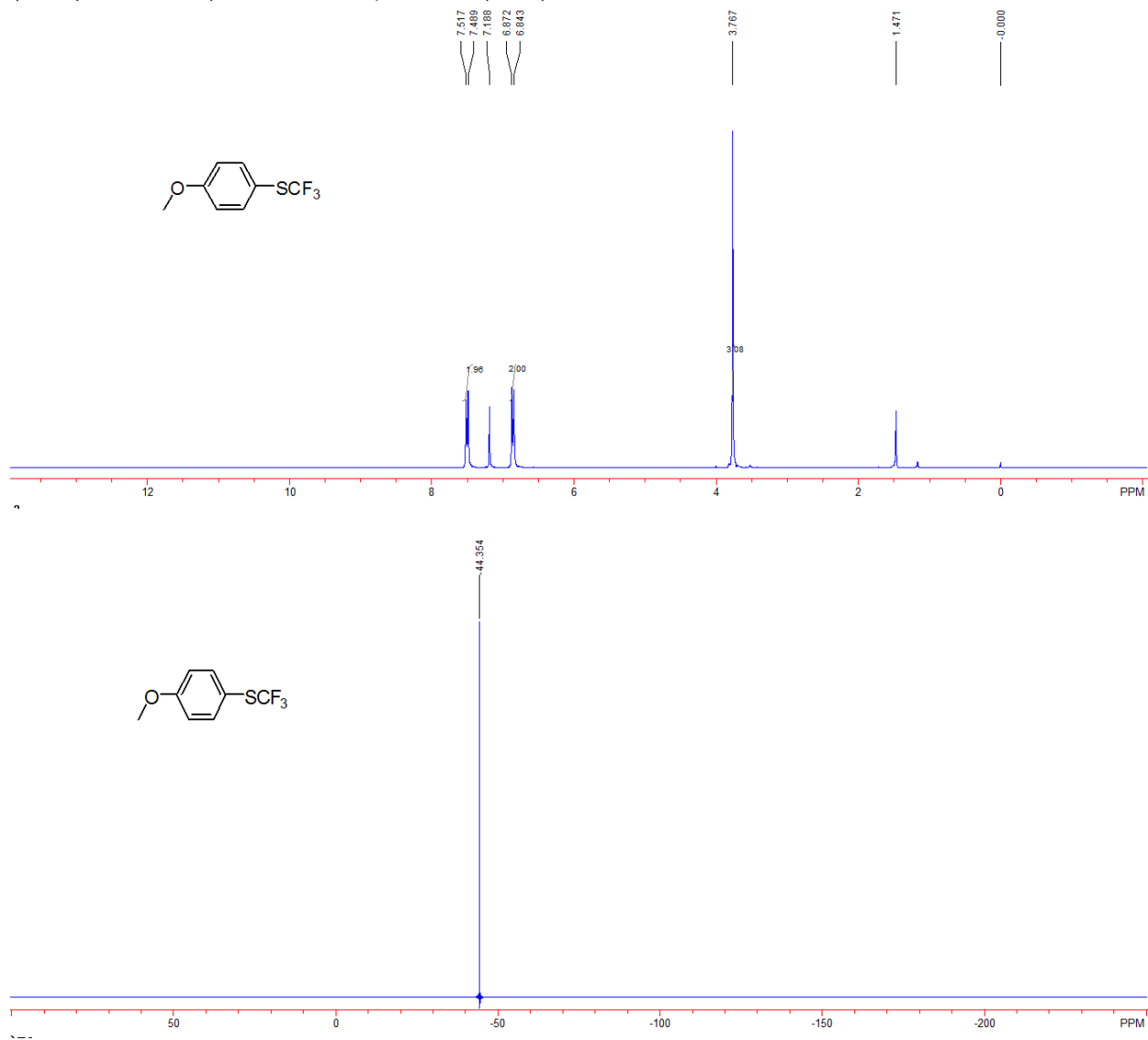
^{13}C NMR spectrum (CDCl_3):



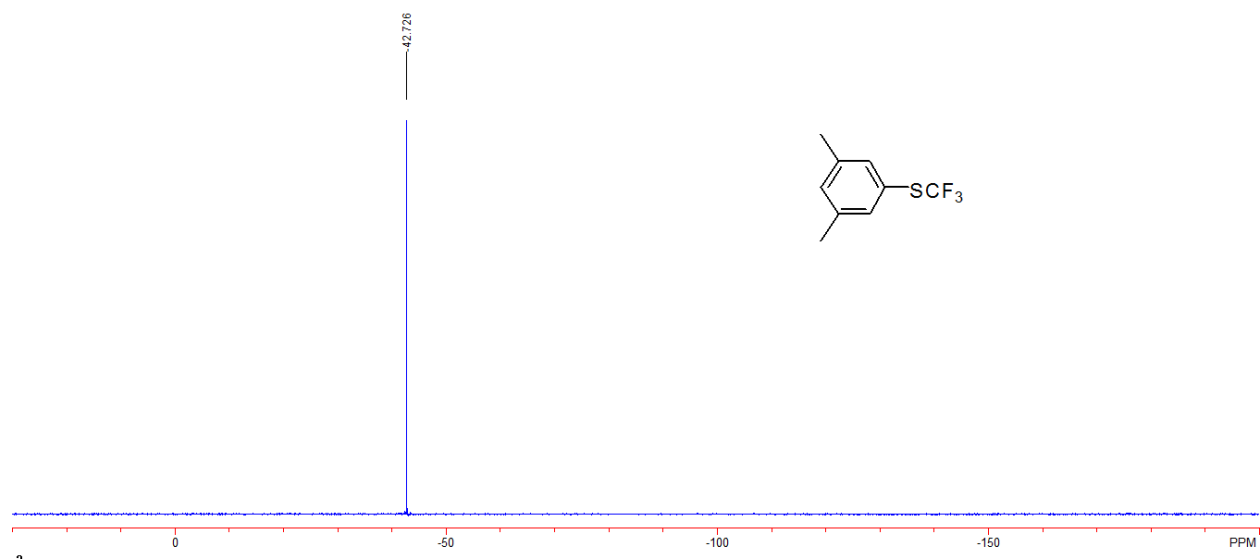
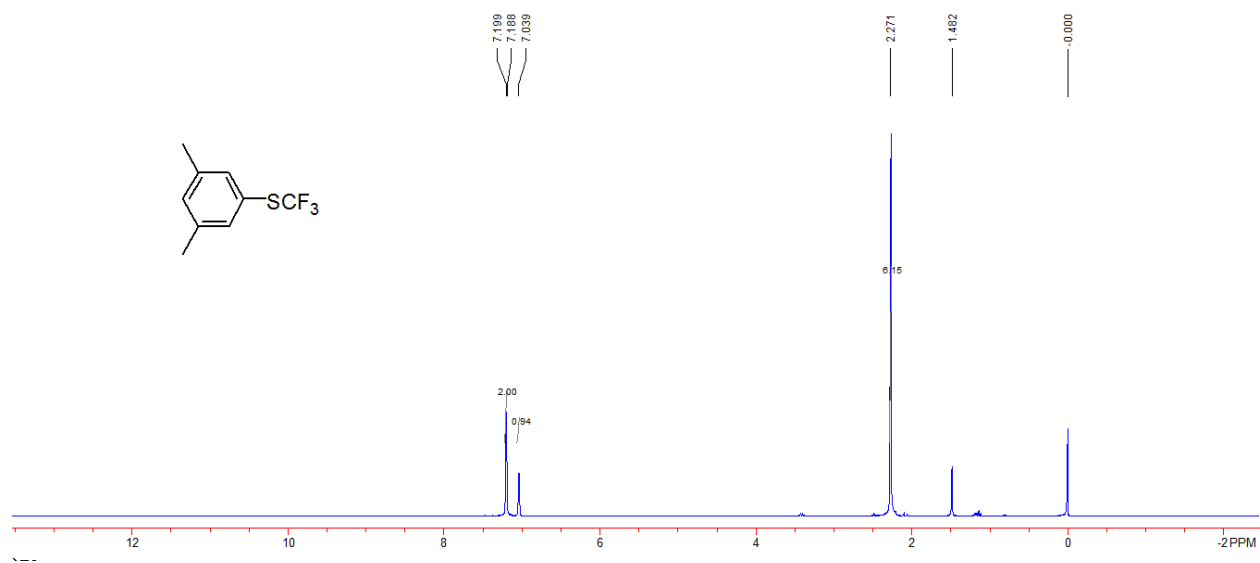


NMR data showing the purity of material from the reactions reporting isolated yields.

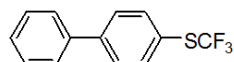
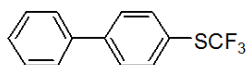
COc1ccc(SCF3)cc1: ^1H NMR (CDCl_3 , 300 Hz): δ 7.50 (d, $J = 8.5$ Hz, 2H), 6.86 (d, $J = 8.5$ Hz, 2H), 3.77 (s, 3H). ^{19}F NMR (CDCl_3 , 282 Hz): δ -44.4 (s, 3F).



Cc1cc(C)ccc(SCF3)c1: ^1H NMR (CDCl_3 , 300 Hz): δ 7.20 (s, 2H), 7.04 (s, 1H), 2.27 (s, 6H). ^{19}F NMR (CDCl_3 , 282 Hz): δ -42.7 (s, 3F).



Cc1cc(C)cc(S(=O)(=O)F)c1: ¹H NMR (CDCl₃, 300 Hz): δ 7.64 (d, *J* = 7.6 Hz, 2H), 7.56-7.50 (m, 4H), 7.39 (t, *J* = 6.8 Hz, 2H), 7.32 (t, *J* = 6.8 Hz, 1H). ¹⁹F NMR (CDCl₃, 282 Hz): δ -43.1 (s, 3F).

SC(F)(F)c1ccc(cc1)N2CCOCC2

