Supporting Information

Novel Use of CF_3SO_2Cl for the Metal-Free Electrophilic Trifluoromethylthiolation

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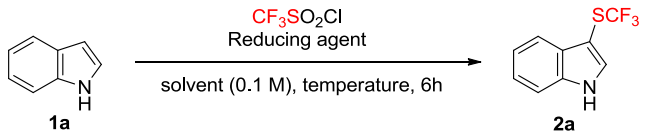
General information

Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Alfa Aesar, TCI and used as received unless otherwise stated. The reactions were monitored by thin-layer chromatography (TLC) performed with 0.20 mm silica gel 60 with fluorescent indicator UV_{254}. The TLC plates were visualized with UV light (254 nm). Column chromatography was performed on a column packed with silica gel 60M spherical neutral size 40-63 µm. ^{1}H (300 MHz), ^{13}C (75.5 MHz) and ^{19}F (282 MHz) NMR spectra for solution in $CDCl_3$ or DMSO-d_6 were recorded on Bruker Avance 300. Chemical shifts (δ) are expressed in ppm downfield from $CDCl_3$ or DMSO-d_6 or upfield from $CFCl_3$. The following abbreviations were used to show the multiplicities: s: singlet, d: doublet, t: triplet, q: quadruplet, dd: doublet of doublets, td: triplet of doublets, dt: doublet of triplets, m: multiplet, b: broad. The residual solvent signals were used as references ($CDCl_3$: δH = 7.26 ppm, δC = 77.00 ppm ; DMSO-d_6: δH = 2.50 ppm, δC = 39.52 ppm and $CFCl_3$: δF = 0.00 ppm). High resolution mass spectrometry (HRMS) was carried out on an electrospray ionization mass spectrometer with a micro-TOF analyzer. 2-Phenylimidazo[1,2-a]pyridine,[1] methyl indolizine-1-carboxylate,[2] and enamines[3] were prepared referring to previously reported procedures.

Optimization of the reaction conditions



run	reducing agent[a]	solvent	temperature	yield (%)[b]
Variation of the temperature				
1	PMe_3 (1:1.5:3)	toluene	–78 °C to rt	70
2	PMe_3 (1:1.5:3)	toluene	–40 °C to rt	62
3	PMe_3 (1:1.5:3)	toluene	–20 °C to rt	40
Variation of the amount of CF_3SO_2Cl and of the ratio CF_3SO_2Cl / reducing agent				
4	PMe_3 (1:1.5:1.5)	toluene	–78 °C to rt	41
5	PMe_3 (1:1.5:3)	toluene	–78 °C to rt	70
6	PMe_3 (1:1.5:3.75)	toluene	–78 °C to rt	77
7	PMe_3 (1:1.8:3.6)	toluene	–78 °C to rt	78
8	PMe_3 (1:1.8:4.5)	toluene	–78 °C to rt	73
9	PMe_3 (1:2.2:4.4)	toluene	–78 °C to rt	78
Variation of the concentration				
10	PMe_3 (1:1.8:3.6)	toluene	–78 °C to rt	64[c]
11	PMe_3 (1:1.8:3.6)	toluene	–78 °C to rt	80[d]
Screening of the reducing agent and solvent				
12	PMe_3 (1:1.8:3.6)	THF	–78 °C to rt	89
13	PMe_3 (1:1.8:3.6)	DCM/toluene (5:3)	–78 °C to rt	67
14	PMe_3 (1:1.8:3.6)	THF/toluene (5:3)	–78 °C to rt	66
15	PMe_3 (1:1.8:3.6)	Et_2O/toluene (5:3)	–78 °C to rt	83
16	PMe_3 (1:1.8:3.6)	ACN/toluene (5:3)	–78 °C to rt	55
17	PPh_3 (1:1.5:3)	toluene	–78 °C to rt	35
18	PPh_3 (1:1.5:3)	DCM	–78 °C to rt	51
19	PPh_3 (1:1.5:3)	$CHCl_3$	–78 °C to rt	21

20	PPh_3 (1:2:4)	DCM	–78 °C to rt	56
21	nBu$_3$N (1:1.8:3.6)	toluene	–78 °C to rt	25
22	PCy_3 (1:1.8:3.6)	toluene	–78 °C to rt	34
23	$P(OMe)_3$ (1:1.8:3.6)	toluene	–78 °C to rt	21
24	$P(OMe)_3$ (1:1.8:3.6)	DCM	–78 °C to rt	46
25	Et_3N	toluene	–78 °C to rt	0
26	$(EtO)_2P(O)H$	toluene	–78 °C to rt	0
27	TMSCl + NaI	toluene	–78 °C to rt	0
28	Me_2S	toluene	–78 °C to rt	0

[a] Ratio indole/CF_3SO_2Cl/reducing agent. [b] Yields were determined by ^{19}F NMR using trifluorotoluene as an internal standard. [c] Concentration: 0.25 M. [d] Concentration: 0.05 M.

General procedure for trifluoromethylthiolation

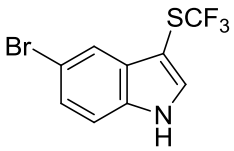
To a solution of substrate (0.85 mmol) in THF (5 mL) were added dropwise trimethylphosphine 1.0 M solution in THF (**Procedure A**: 3.6 equiv. or **Procedure B**: 4.4 equiv.) and trifluoromethanesulfonyl chloride (**Procedure A**: 1.8 equiv. or **Procedure B**: 2.2 equiv.) at –78 °C. The reaction mixture was stirred until the full consumption of the starting material (TLC monitored), as the temperature was let to increase to room temperature. The reaction mixture was quenched with water. The aqueous layer was extracted twice with ethyl acetate. The combined organic layers were dried over magnesium sulfate, and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel (cyclohexane/ethyl acetate).

Characterization data for SCF_3 products

3-((trifluoromethyl)thio)-1*H*-indole (2a).[4] CAS [62665-49-0]

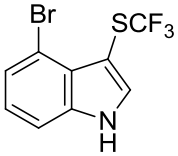
Procedure A. Brown solid. 157 mg, 85% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 8.53 (s, 1H), 7.88–7.76 (m, 1H), 7.56 (s, 1H), 7.51–7.39 (m, 1H), 7.38–7.22 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 136.0, 132.7, 129.4, 129.4 (q, J = 309.8 Hz), 123.4, 121.6, 119.3, 111.6, 95.6 (q, J = 2.8 Hz) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ –45.1 (s, 3F) ppm.

5-bromo-3-((trifluoromethyl)thio)-1*H*-indole (2b).[4] CAS [1045822-97-6]



Procedure B. Brown solid. 217 mg, 86% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 8.60 (s, 1H), 7.94 (s, 1H), 7.56 (s, 1H), 7.39 (d, J = 8.5 Hz, 1H), 7.32 (d, J = 8,5 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 134.6, 133.8, 131.2, 129.2 (q, J = 309.8 Hz), 126.5, 122.0, 115.2, 113.1, 95.4 (q, J = 2.8 Hz) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –45.0 (s, 3F) ppm.

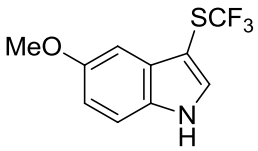
4-bromo-3-((trifluoromethyl)thio)-1*H*-indole (2c). New compound.



Procedure B. White solid. 186 mg, 74% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 7.63 (d, J = 1.9 Hz, 1H), 7.44 (d, J = 7.9 Hz, 1H), 7.40 (d, J = 8.7 Hz, 1H), 7.13 (t, J = 7.9 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ.137.1, 135.3, 129.0 (q, J = 309.8 Hz),

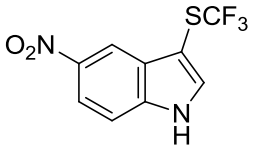
126.7, 126.1, 124.2, 114.4, 111.3, 96.4 (q, J = 2.8 Hz) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –46.0 (s, 3F) ppm. HRMS (ESI): Calculated for $C_9H_5BrF_3NS$: 294.92782; Found: 294.92667.

5-methoxy-3-((trifluoromethyl)thio)-1*H*-indole (2d).[4] CAS [1045822-99-8]



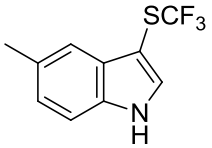
Procedure A. Brown solid. 160 mg, 76% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52 (s, 1H), 7.56 (s, 1H), 7.37 (d, J = 8.9 Hz, 1H), 7.29 (d, J = 12.1 Hz, 1H), 6.99 (d, J = 8.7 Hz, 1H), 3.95 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 155.6, 133.2, 130.8, 130.3, 129.4 (q, J = 310.3 Hz), 114.0, 112.5, 100.4, 95.0 (q, J = 2.2 Hz), 55.8 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –45.2 (s, 3F) ppm.

5-nitro-3-((trifluoromethyl)thio)-1*H*-indole (2e).[5] CAS [1045823-05-9]



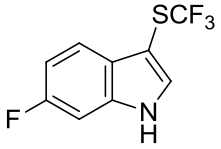
Procedure B. Yellow solid. 151 mg, 65% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.76 (s, 1H), 8.23 (d, J = 8.9 Hz, 1H), 7.76 (s, 1H), 7.55 (d, J = 8.9 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 142.3, 139.7, 139.1, 129.2 (q, J = 309.8 Hz), 128.6, 118.0, 114.6, 113.6, 94.3 (q, J = 2.8 Hz) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –44.7 (s, 3F) ppm.

5-methyl-3-((trifluoromethyl)thio)-1H-indole (2f).[4] CAS [1443036-44-9]



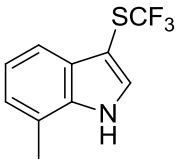
Procedure A. Brown solid. 140 mg, 71% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ.8.38 (bs, 1H), 7.58 (s, 1H), 7.45 (s, 1H), 7.28 (d, J = 8.4 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H), 2.49 (s, 3H) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 134.4, 132.9, 131.3, 129.8, 129.6 (q, J = 309.9 Hz), 125.2, 118.9, 111.5, 95.0 (q, J = 2.4 Hz), 21.6 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –45.2 (s, 3F) ppm.

6-fluoro-3-((trifluoromethyl)thio)-1H-indole (2g).[5] CAS [1802140-07-3]



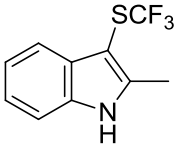
Procedure B. Brown solid. 193 mg, 96% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.51 (bs, 1H), 7.73 (dd, J = 8.5, 5.3 Hz, 1H), 7.54 (d, J = 2.3 Hz, 1H), 7.13 (d, J = 9.3 Hz, 1H), 7.06 (t, J = 8.9 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 162.1 (d, J = 239.9 Hz), 135.9 (d, J = 12.7 Hz), 133.0 (d, J = 3.3 Hz), 129.3 (q, J = 309.8 Hz) 125.9, 120.4 (d, J = 10.5 Hz), 110.6 (d, J = 24.8 Hz), 97.1 (d, J = 26.4 Hz), 96.0 (q, J = 2.2 Hz) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –44.9 (s, 3F), –110.4 (s, 1F) ppm.

7-methyl-3-((trifluoromethyl)thio)-1H-indole (2h).[4] CAS [1443036-45-0]



Procedure B. Yellow oily solid. 159 mg, 80% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.50 (bs, 1H), 7.68 (d, J = 7.9 Hz, 1H), 7.55 (d, J = 2.3 Hz, 1H), 7.22 (t, J = 7.7 Hz, 1H), 7.12 (d, J = 7.0 Hz, 1H), 2.53 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 135.6, 132.4, 129.4 (q, J = 309.7 Hz), 129.0, 123.9, 121.8, 120.8, 117.0, 96.0 (q, J = 2.2 Hz), 16.3 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –45.10 (s, 3F) ppm.

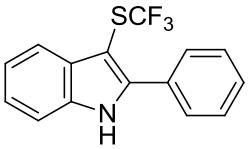
2-methyl-3-trifluoromethylthio-1*H*-indole (2i).[4] CAS [1443036-43-8]



Procedure B. Brown solid. 118 mg, 60% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (s, 1H), 7.78–7.67 (m, 1H), 7.39–7.30 (m, 1H), 7.29–7.18 (m, 2H), 2.60 (s, 3H)

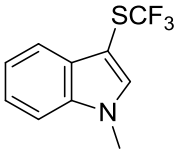
ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 143.5, 135.0, 130.6, 129.8 (q, *J* = 310.9 Hz), 122.6, 121.3, 118.7, 110.7, 92.5 (q, *J* = 2.2 Hz), 12.0 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –45.0 (s, 3F) ppm.

2-phenyl-3-trifluoromethylthio-1*H*-indole (2j).[5] CAS [1516898-91-1]



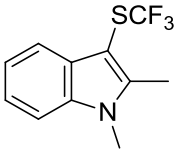
Procedure A. White solid. 72 mg, 29% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.59 (bs, 1H), 7.92–7.85 (m, 1H), 7.81–7.75 (m, 2H), 7.58–7.40 (m, 4H), 7.37–7.24 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.5, 135.4, 131.6, 130.8, 129.9 (q, *J* = 311.4 Hz), 129.4, 129.0, 128.8, 123.8, 121.9, 119.9, 111.3, 92.6 (q, *J* = 2.3 Hz) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –43.9 (s, 3F) ppm.

1-methyl-3-trifluoromethylthio-1*H*-indole (2l).[6] CAS [1631056-90-0]



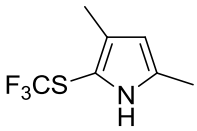
Procedure B. Pink solid. 187 mg, 94% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.4 Hz, 1H), 7.31–7.10 (m, 4H), 3.72 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 137.2, 136.9, 130.2, 129.4 (q, *J* = 309.8 Hz), 122.9, 121.3, 119.4, 109.9, 93.0 (q, *J* = 2.8 Hz), 33.3 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –45.5 (s, 3F) ppm.

1,2-dimethyl-3-trifluoromethylthio-1*H*-indole (2m).[7] CAS [1820750-76-2]



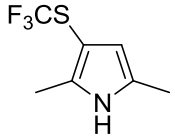
Procedure B. Brown solid. 132 mg, 63% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.8 Hz, 1H), 7.38–7.19 (m, 3H), 3.76 (s, 3H), 2.59 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 145.1, 136.8, 130.1, 129.7 (q, *J* = 310.9 Hz), 122.1, 121.1, 118.6, 109.2, 91.1 (q, *J* = 2.2 Hz), 30.4, 10.8 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –45.4 (s, 3F) ppm.

3,5-dimethyl-2-((trifluoromethyl)thio)-1H-pyrrole (3a).[8] CAS [62665-43-4]



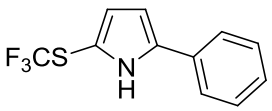
Procedure A. Colorless liquid. 57% NMR yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (bs, 1H), 5.88 (s, 1H), 2.25 (s, 3H), 2.15 (s, 3H) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 133.2, 131.7, 128.8 (q, *J* = 312.3 Hz), 110.4, 102.8 (q, *J* = 3.0 Hz), 13.4, 11.6 ppm ; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –46.0 (s, 3F) ppm.

2,5-dimethyl-3-((trifluoromethyl)thio)-1H-pyrrole (3b).[8] CAS [62665-41-2]



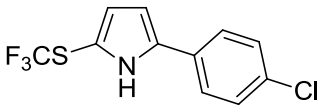
Procedure A. Pale yellow liquid. 50% NMR yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (s, 1H), 5.96 (s, 1H), 2.30 (s, 3H), 2.21 (s, 3H) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 134.5, 129.9 (q, *J* = 309.3 Hz), 126.8, 112.7, 97.9 (q, *J* = 3.0 Hz), 13.0, 11.4 ppm ; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –45.5 (s, 3F) ppm.

2-phenyl-5-((trifluoromethyl)thio)-1H-pyrrole (4a).[8] CAS [1659179-57-3]



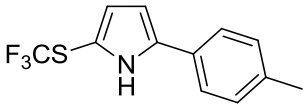
Procedure A. Violet solid. 120 mg, 58% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.60 (s, 1H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.71 (dd, *J* = 2.7, 1.8 Hz, 1H), 6.57 (dd, *J* = 3.6, 2.7 Hz, 1H) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 138.0, 131.6, 129.2, 128.5 (q, *J* = 312.3 Hz), 127.8, 124.6, 123.2, 108.5, 108.4 (d, *J* = 1.5 Hz) ppm ; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –45.6 (s, 3F) ppm.

2-(4-chlorophenyl)-5-((trifluoromethyl)thio)-1H-pyrrole (4b).[8] CAS [150618-98-7]



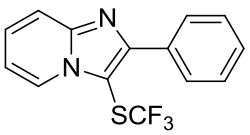
Procedure A. Violet solid. 97 mg, 41% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.60 (s, 1H), 7.46–7.26 (m, 4H), 6.71 (dd, *J* = 2.7, 2.7 Hz, 1H), 6.55 (dd, *J* = 2.7, 2.7 Hz, 1H) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 136.8, 133.6, 130.0, 129.4, 128.4 (q, *J* = 310.8 Hz), 125.8, 123.3, 109.0 (q, *J* = 3.0 Hz), 108.8 ppm ; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –45.5 (s, 3F) ppm.

2-(p-tolyl)-5-((trifluoromethyl)thio)-1H-pyrrole (4c).[8] CAS [1659179-98-2]



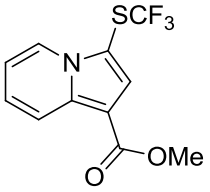
Procedure A. Violet solid. 127 mg, 58% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.55 (s, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.69 (dd, *J* = 2.7, 2.7 Hz, 1H), 6.51 (dd, *J* = 2.7, 2.7 Hz, 1H), 2.37 (s, 3H) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 138.2, 137.7, 129.9, 128.7, 128.4 (q, *J* = 310.8 Hz), 124.5, 123.1, 107.9, 107.8 (q, *J* = 3.0 Hz), 21.3 ppm ; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –45.7 (s, 3F) ppm.

2-phenyl-3-((trifluoromethyl)thio)imidazo[1,2-a]pyridine (5).[9] CAS [1383719-54-7]



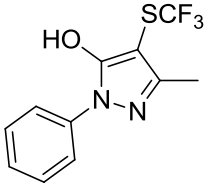
Procedure B. Yellow solid. 163 mg, 65% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.55 (d, *J* = 6.8 Hz, 1H), 8.17 (d, *J* = 7.4 Hz, 2H), 7.75 (d, *J* = 9.1Hz, 1H), 7.54–7.40 (m, 4H), 7.05 (t, *J* = 6.8 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 154.1, 148.0, 132.6, 129.1, 128.7, 128.6 (q, *J* = 315.3 Hz), 128.4, 124.6, 117.9, 113.7, 99.0 (q, *J* = 2.8 Hz) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –43.7 (s, 3F) ppm. HRMS (ESI): Calculated for $C_{14}H_{10}F_3N_2S$: 295.0517; Found: 295.0514.

Methyl 3-((trifluoromethyl)thio)indolizine-1-carboxylate (6).[5] CAS [1686143-31-6]



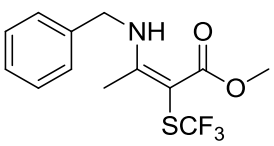
Procedure B. White solid. 159 mg, 68% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.55 (d, *J* = 7.0 Hz, 1H), 8.32 (d, *J* = 9.1 Hz, 1H), 7.73 (s, 1H), 7.29 (t, *J* = 7.7 ppm, 1H), 6.97 (t, *J* = 6.8 Hz, 1H), 3.92 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 164.3, 139.4, 129.2, 128.3 (q, *J* = 313.6 Hz), 125.0, 124.5, 122.1, 119.9, 113.8, 105.6, 102.5 (q, *J* = 2.8 Hz), 51.2 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –44.9 (s, 3F) ppm.

3-methyl-1-phenyl-4-((trifluoromethyl)thio)-1H-pyrazol-5-ol (7).[10] CAS [42092-89-7].



Procedure B. Orange solid. 182 mg, 77% yield. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.69 (d, *J* = 7.9 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 2.23 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 152.4, 137.6, 129.3 (q, *J* = 311.4 Hz), 129.1, 126.3, 121.2, 117.8, 92.2, 12.2 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ –45.60 (s, 3F) ppm. Calculated for $C_{11}H_{10}F_3N_2OS$ ($M+H^+$): 275.0466; Found: 275.0466.

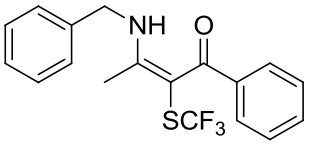
3-methyl 3-(benzylamino)-2-((trifluoromethyl)thio)but-2-enoate (8).[4] CAS [1443036-06-3]



Procedure B. Yellow solid. 171 mg, 65% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.76 (s, 1H), 7.44–7.21 (m, 5H), 4.54 (d, *J* = 5.9 Hz, 2H), 3.74 (s, 3H), 2.41 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 171.5, 171.2, 136.7,

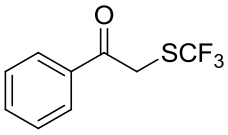
129.9 (q, *J* = 312.0 Hz), 129.0, 127.9, 126.8, 76.2 (q, J = 2.2 Hz), 51.5, 48.3, 17.7 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –47.9 (s, 3F) ppm.

3-(benzylamino)-1-phenyl-2-((trifluoromethyl)thio)but-2-en-1-one (9).[4] CAS [1443036-28-9]



Procedure A. Slightly yellow semi-solid. 185 mg, 62% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.01 (bs, 1H), 7.42-7.26 (m, 10H), 4.65 (d, *J* = 6.0 Hz, 2H), 2.51 (s, 3H) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 197.9, 173.9, 142.2, 136.0, 129.7 (q, *J* = 310.9 Hz), 129.2, 129.1, 128.2, 127.6, 127.5, 127.1, 87.9 (q, *J* = 1.6 Hz), 48.7, 18.3 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –48.1 (s, 3F) ppm.

1-phenyl-2-((trifluoromethyl)thio)ethanone (10).[11] CAS [39566-16-0]



Procedure B. Yellow oil. 99 mg, 53 % yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 4.54 (s, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 191.9, 134.2, 130.7 (q, *J* = 306.5 Hz), 128.9, 128.3, 38.4 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) : δ –41.9 (s, 3F) ppm.

References

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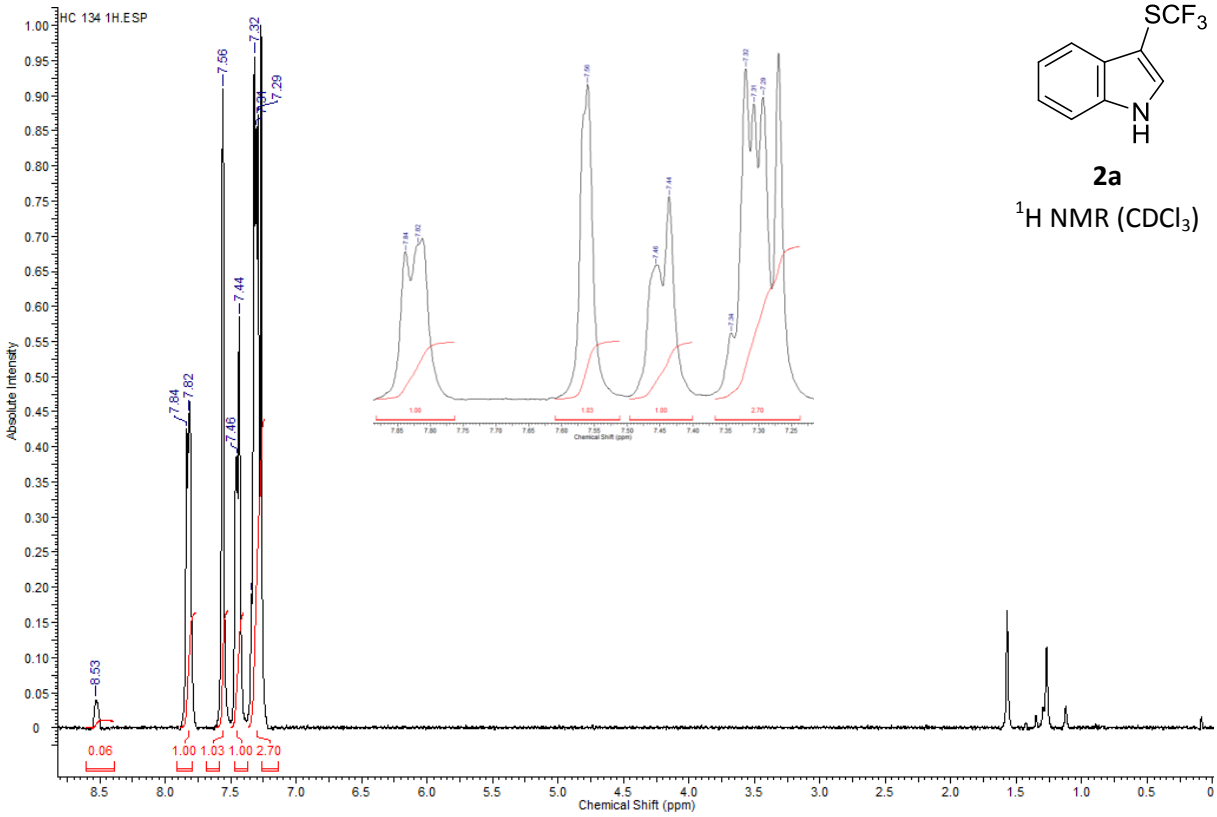
Copies of ^{1}H, ^{13}C, ^{19}F NMR



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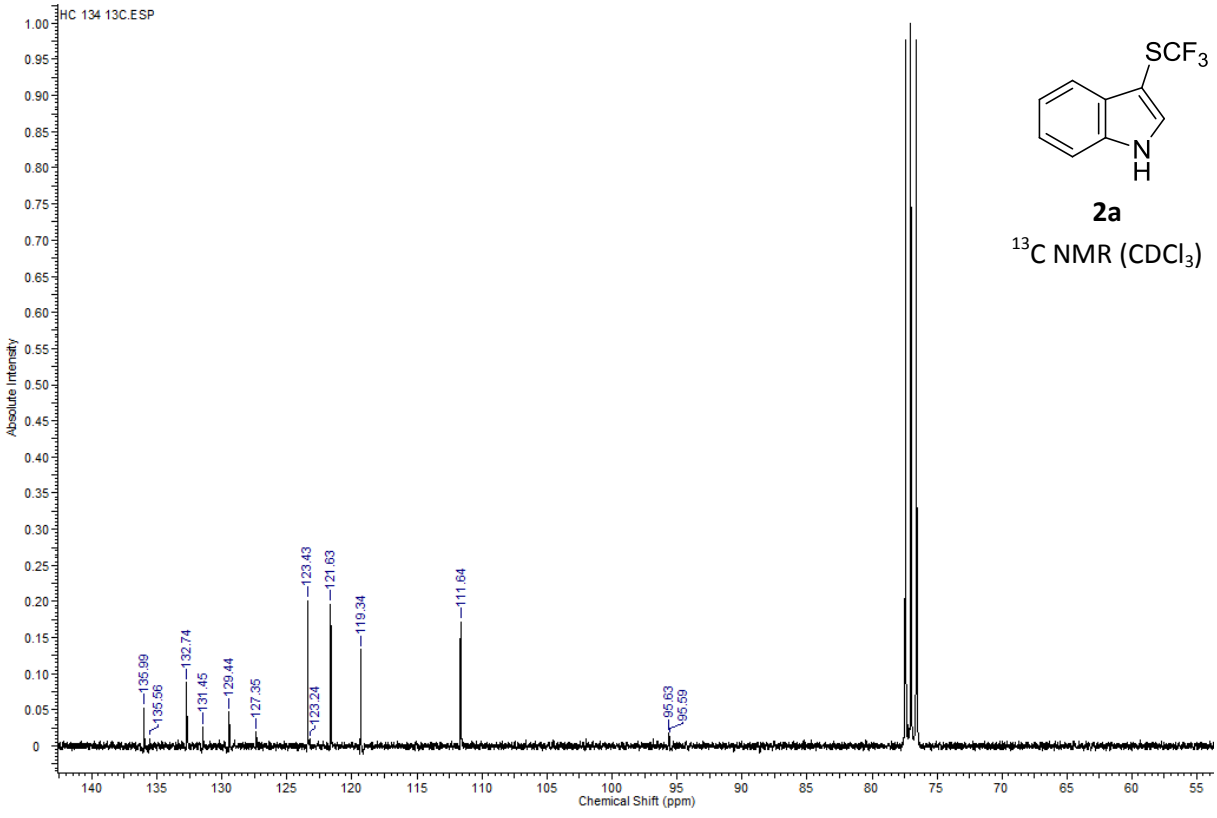
^{1}H NMR ($CDCl_3$)



2a

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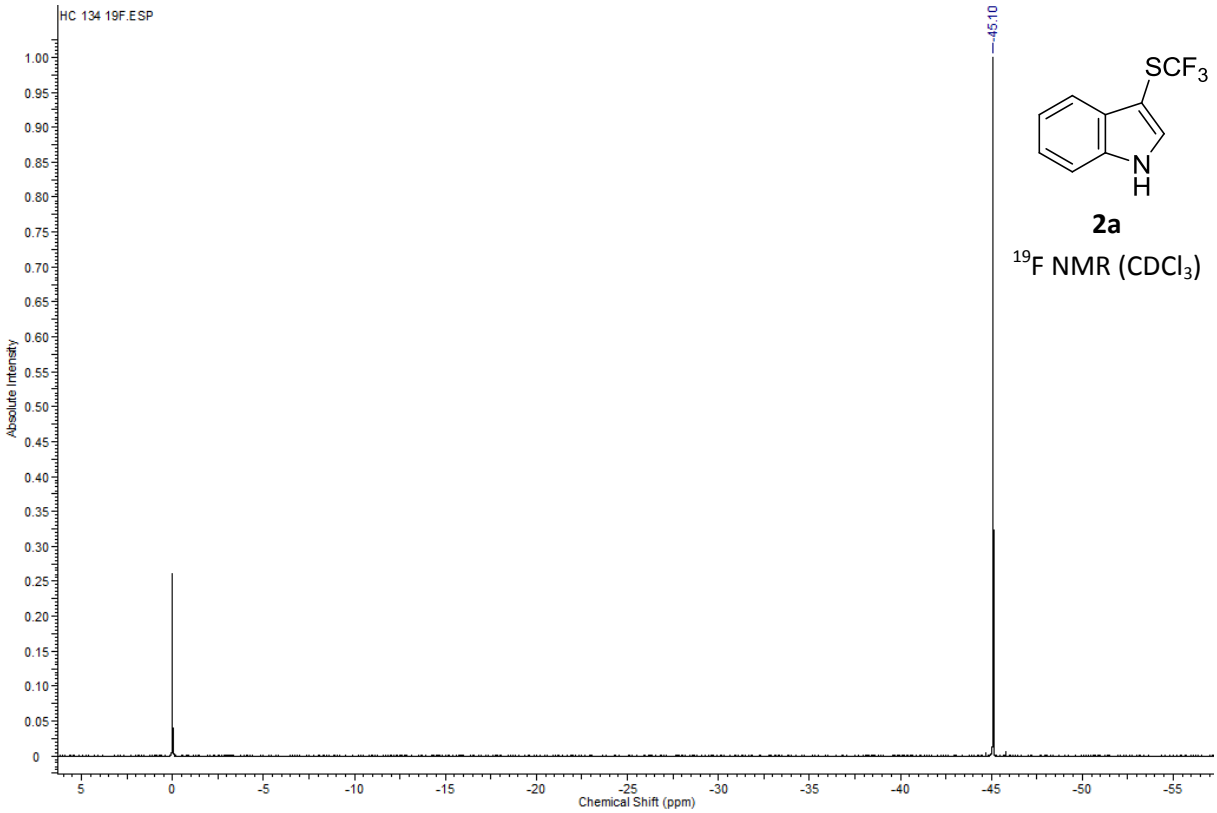

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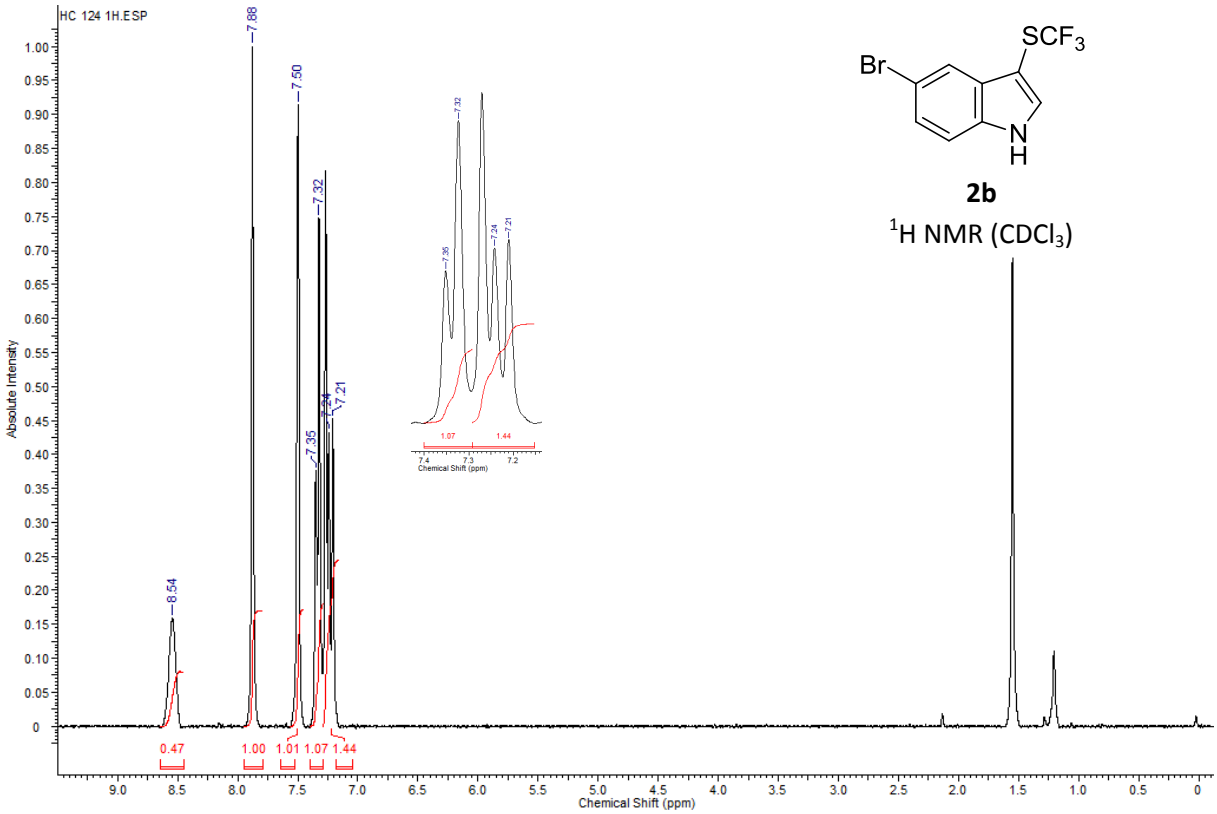

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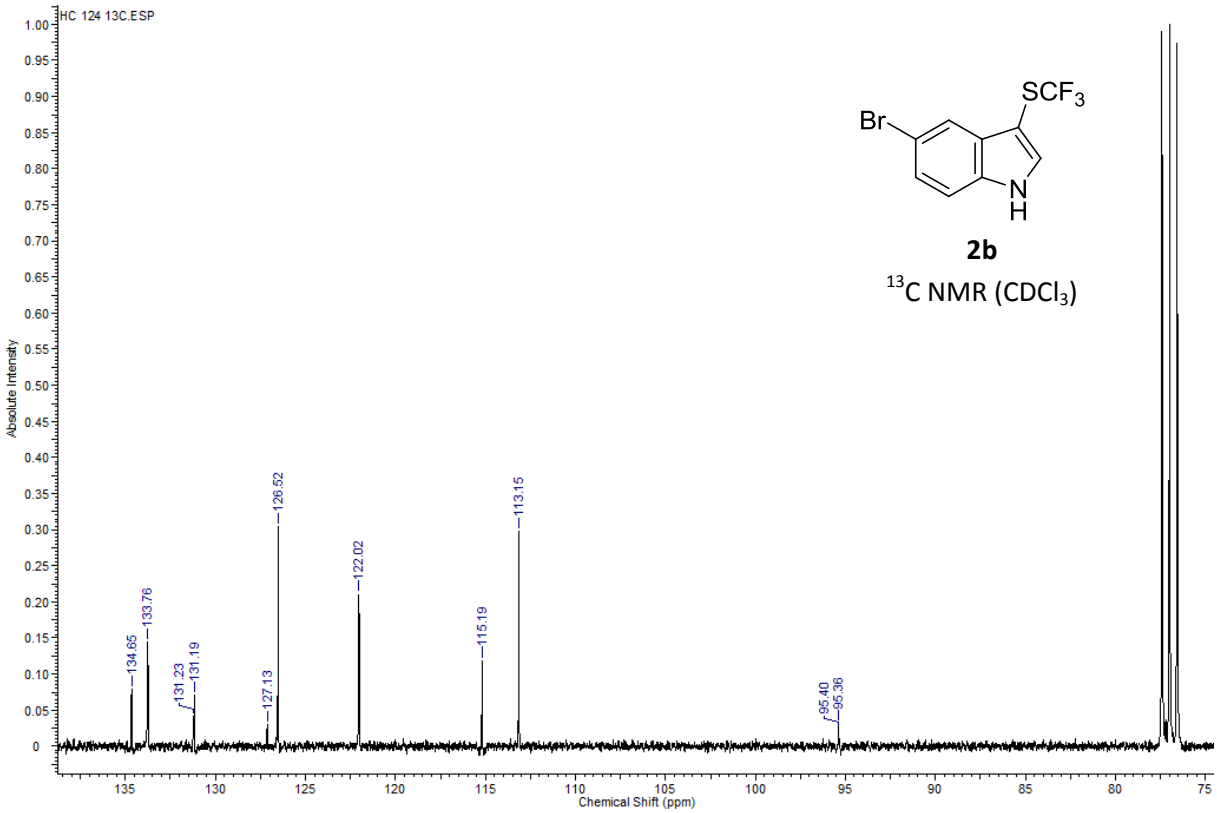

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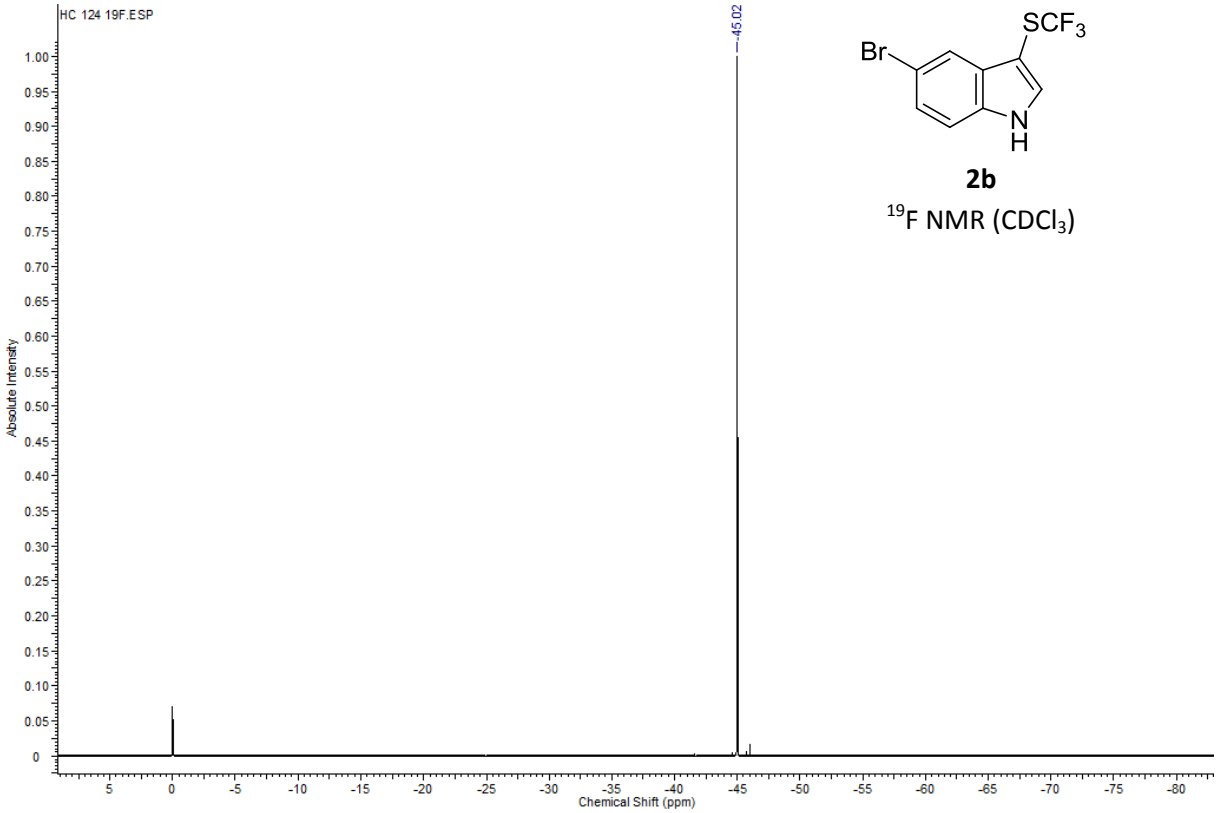

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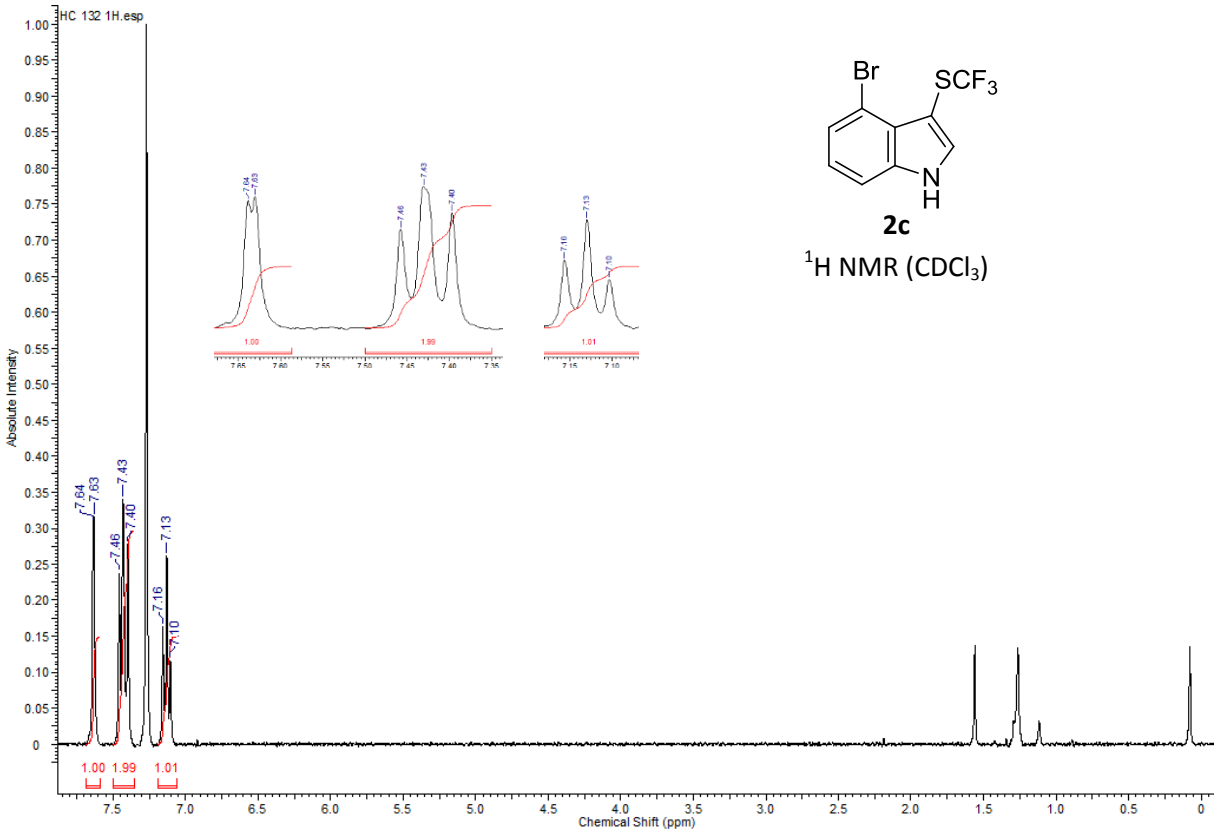

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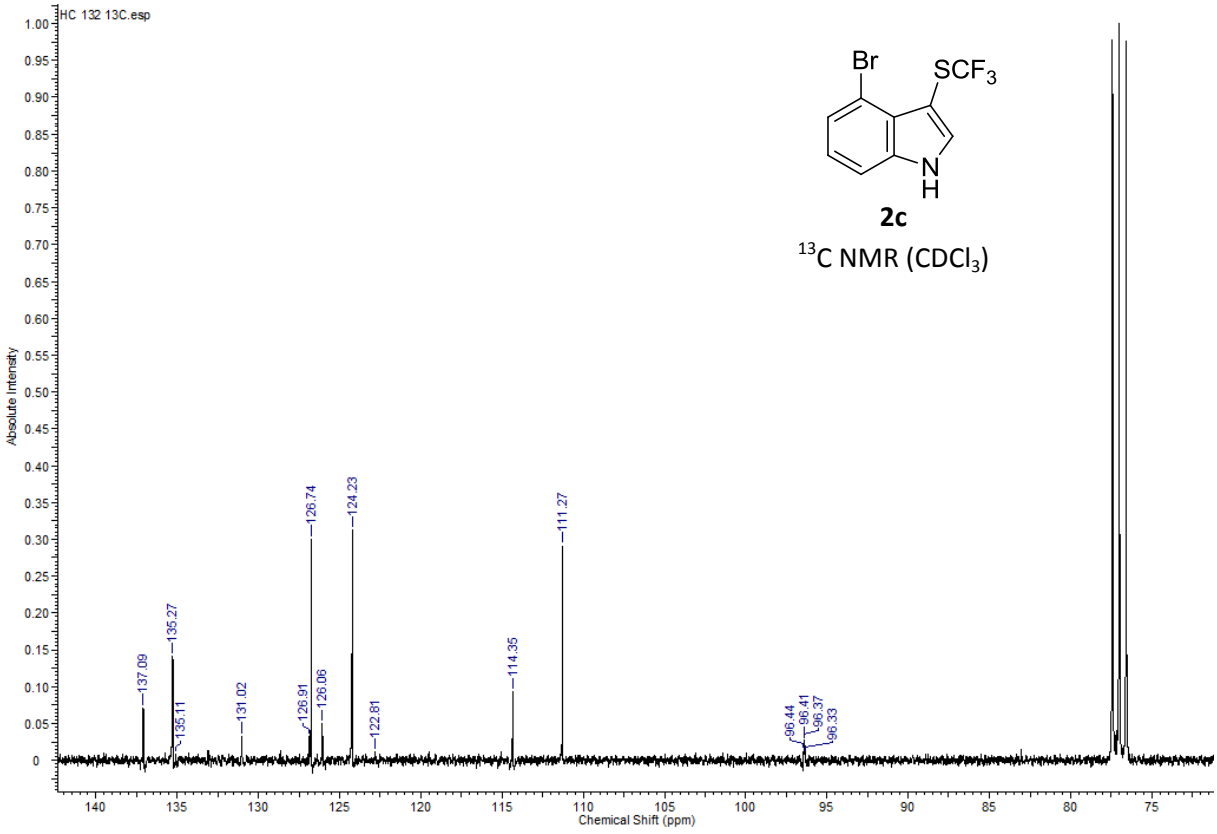

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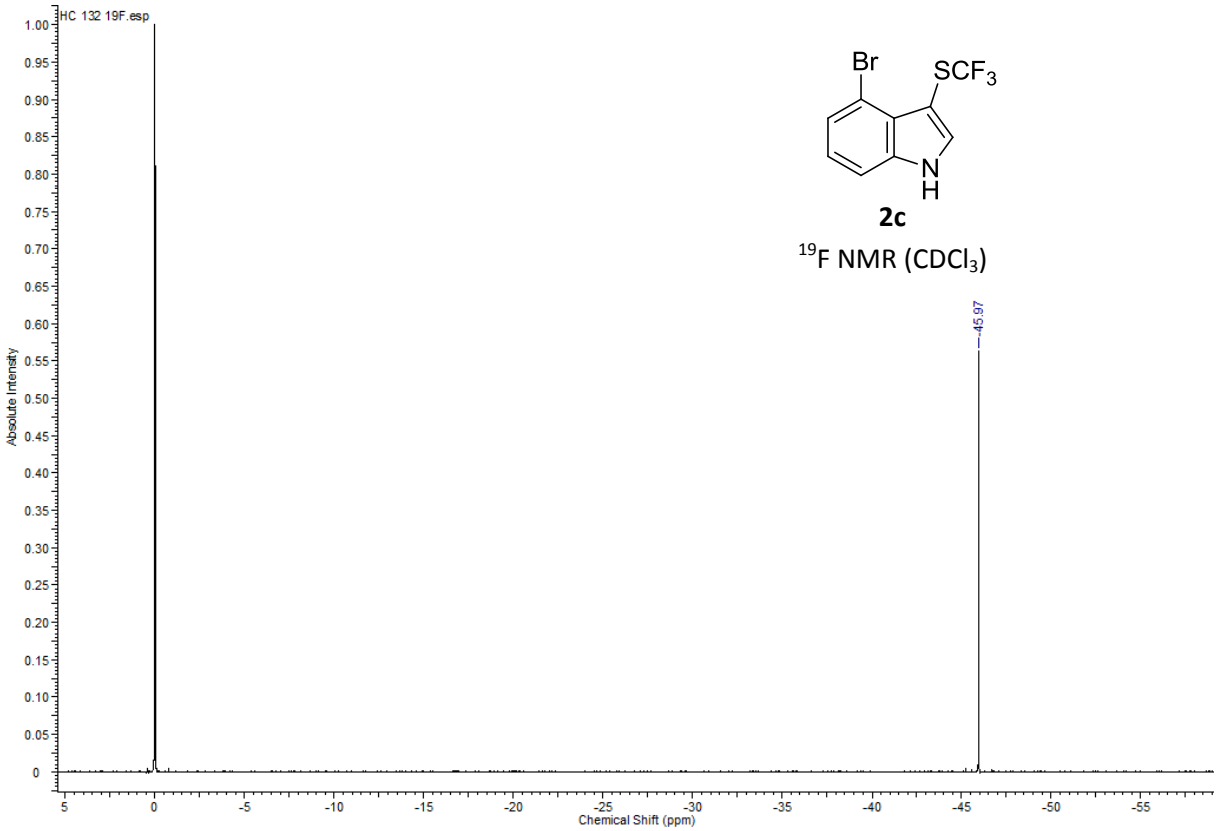

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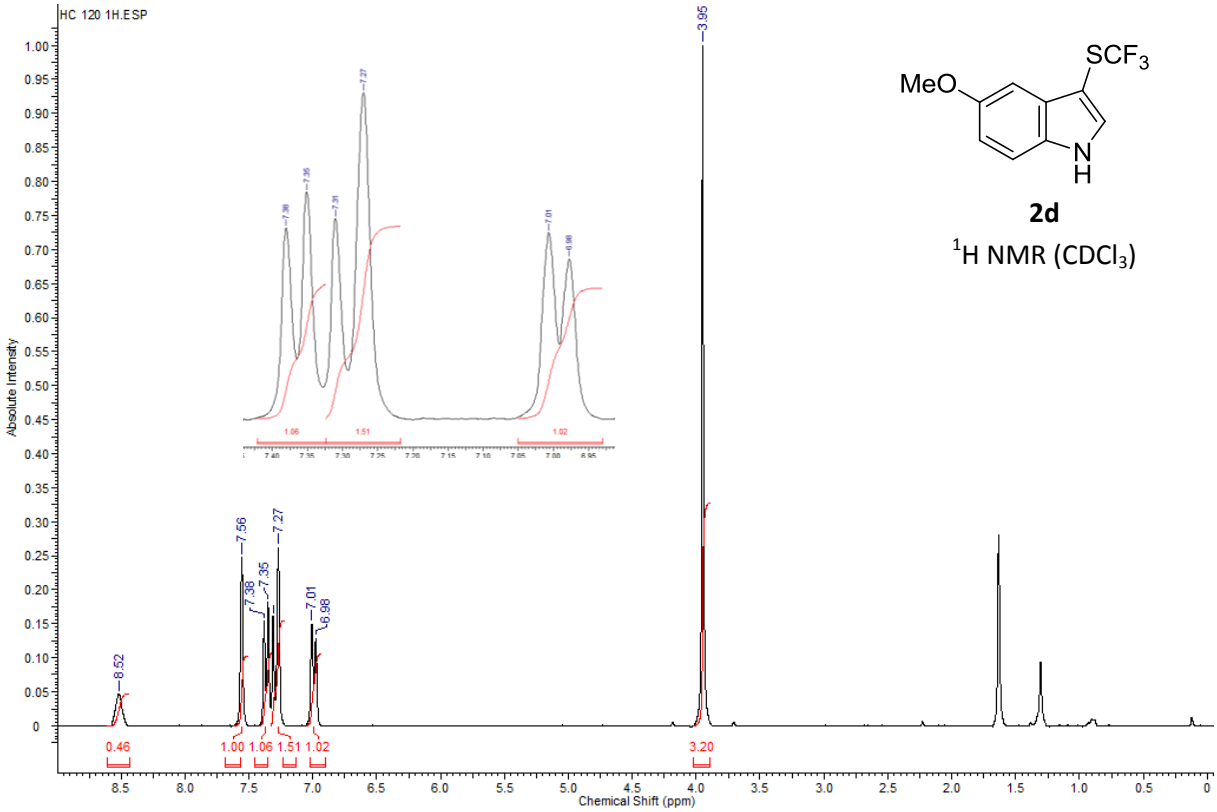

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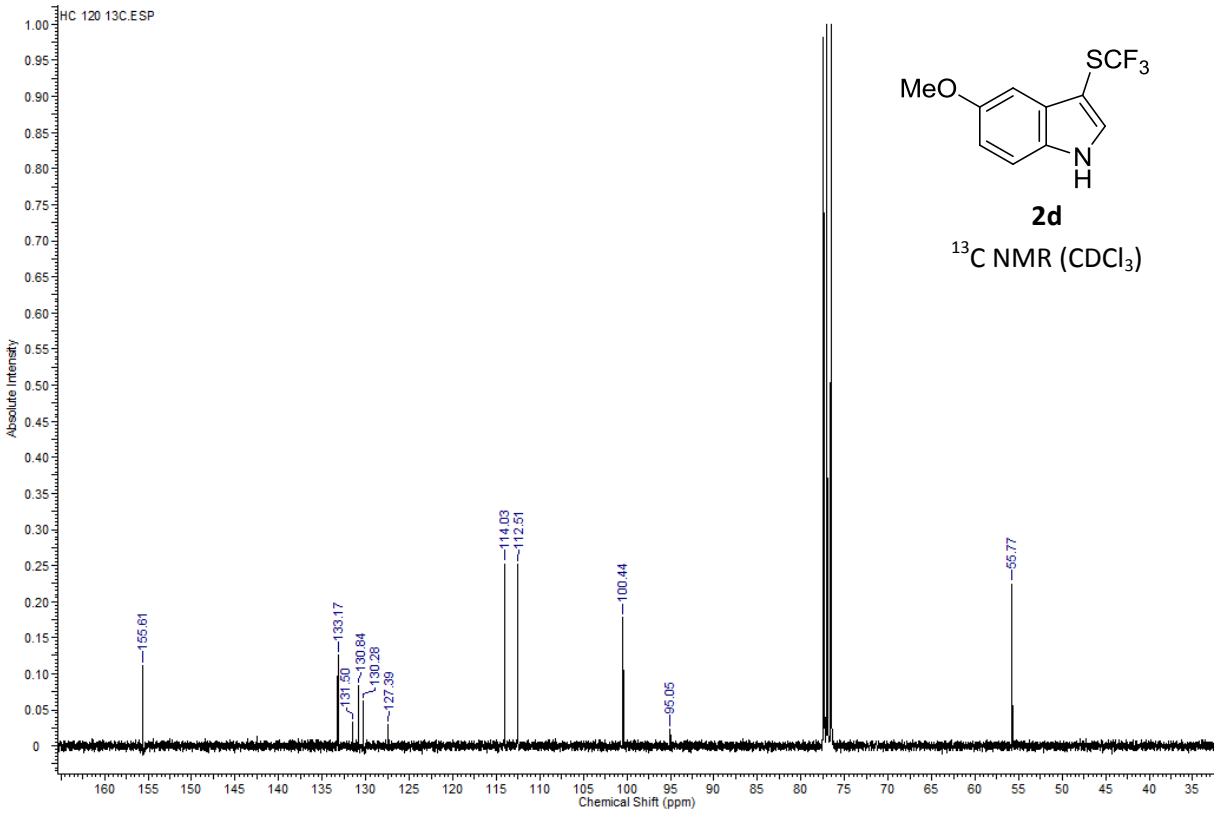

2d

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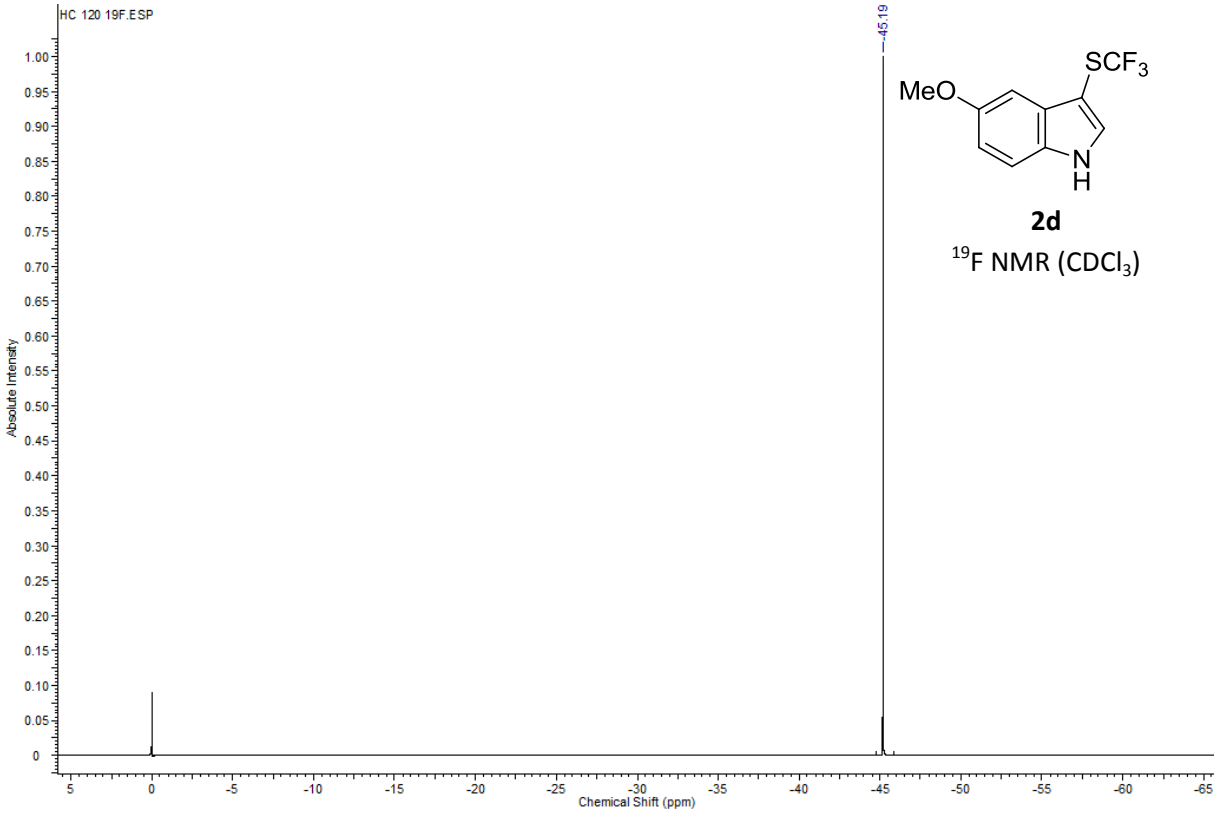

2d

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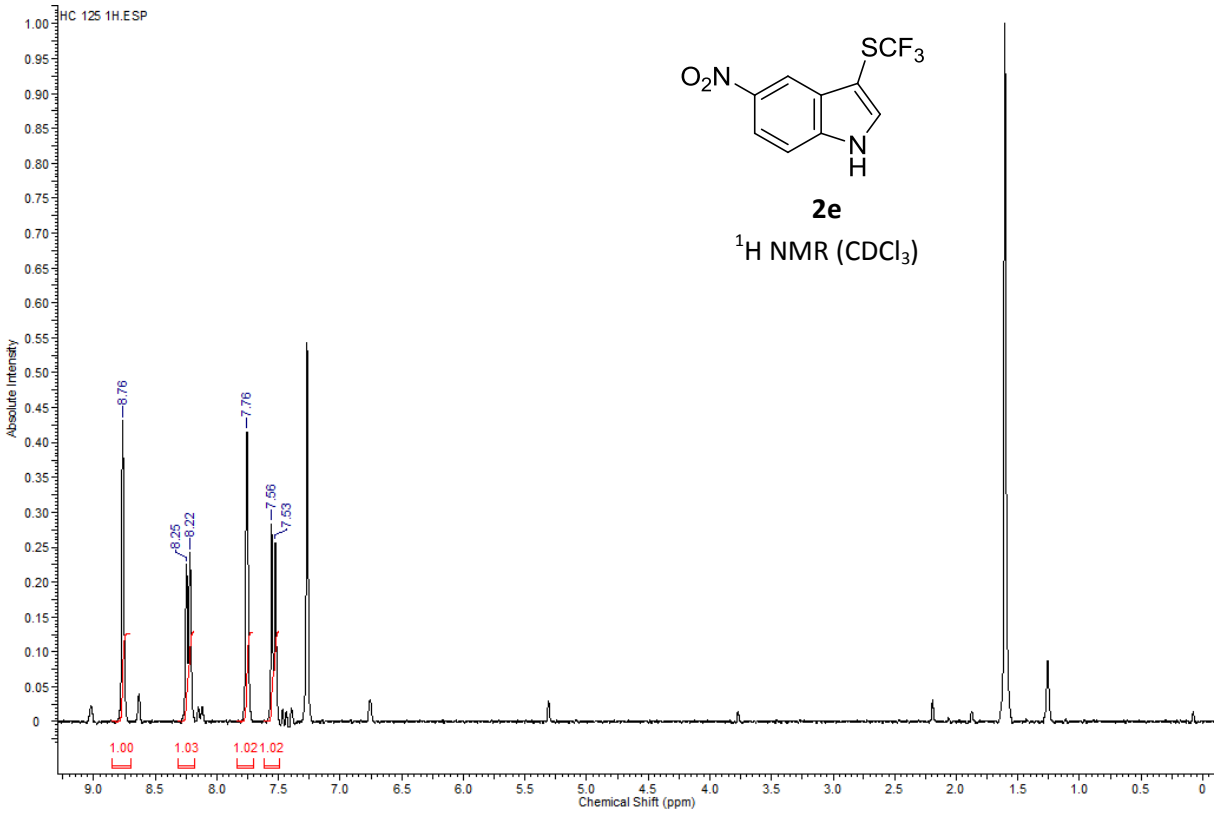

2e

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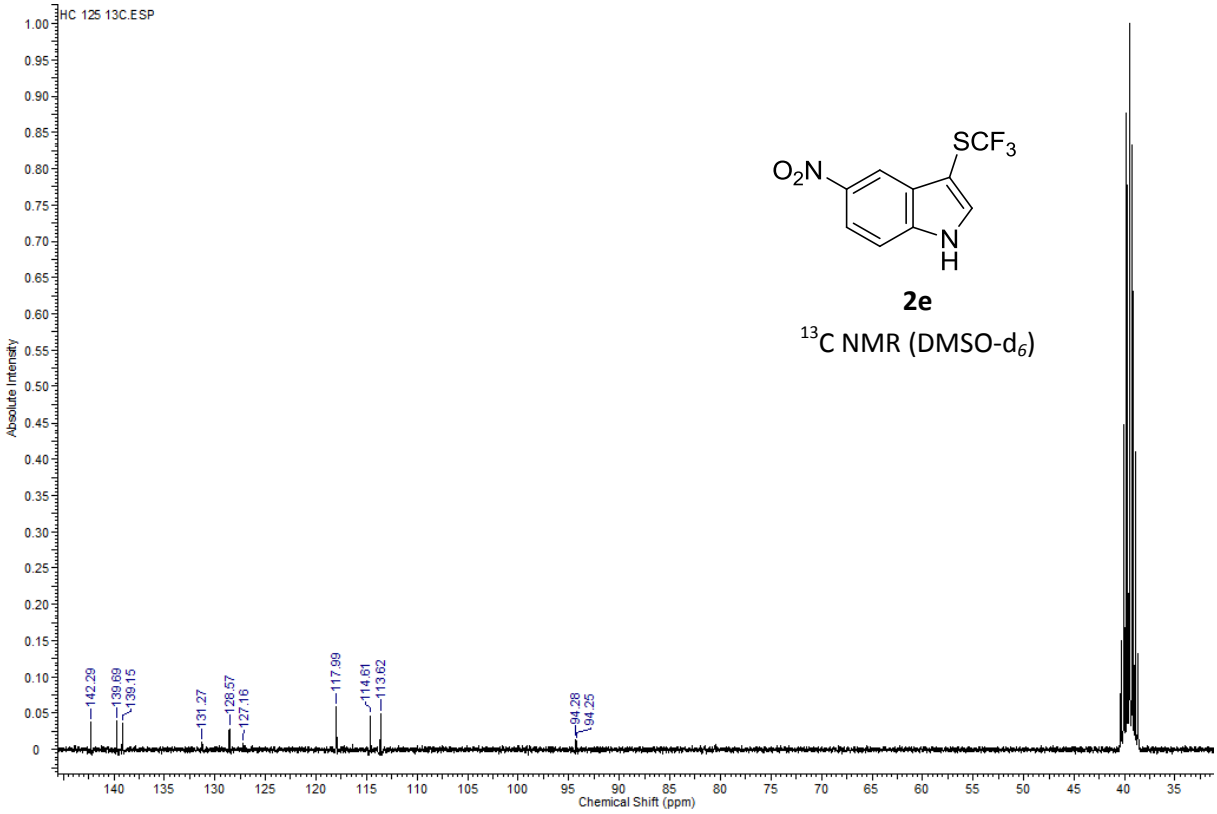

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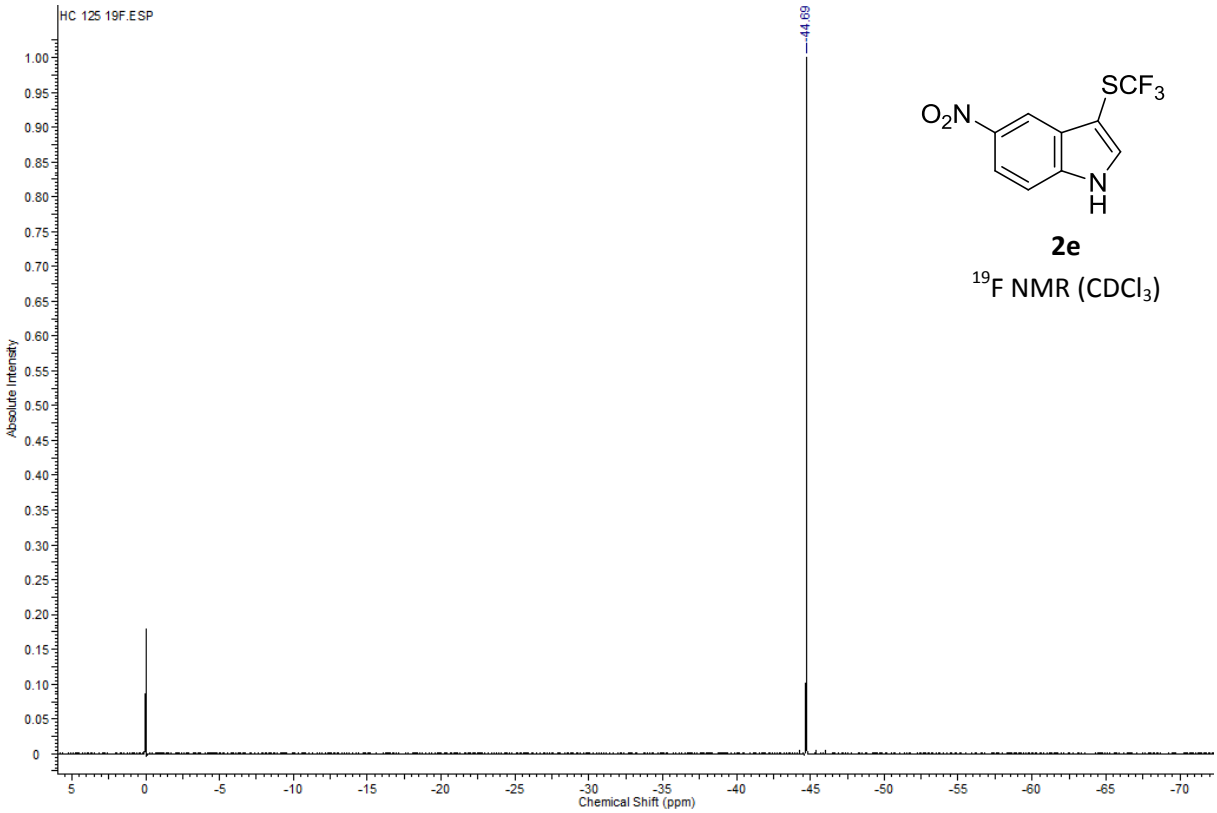

2e

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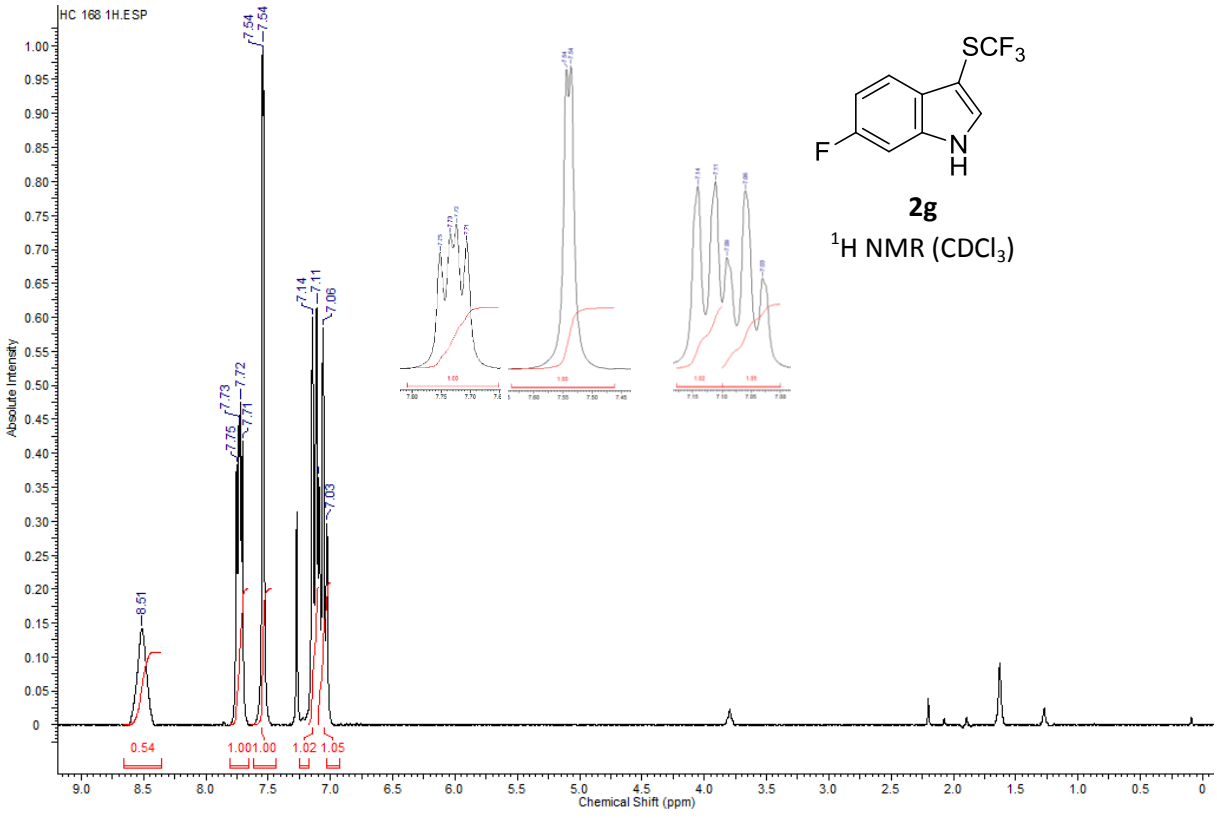

2g

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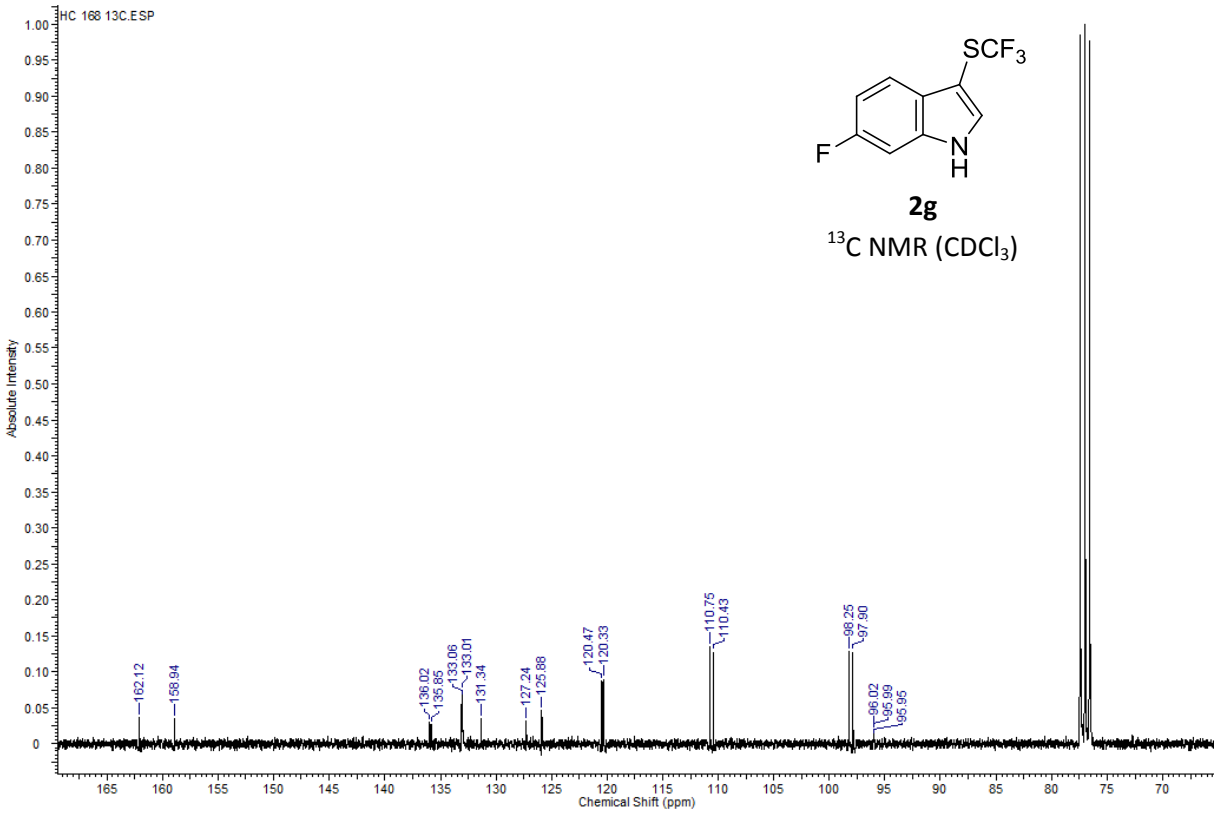

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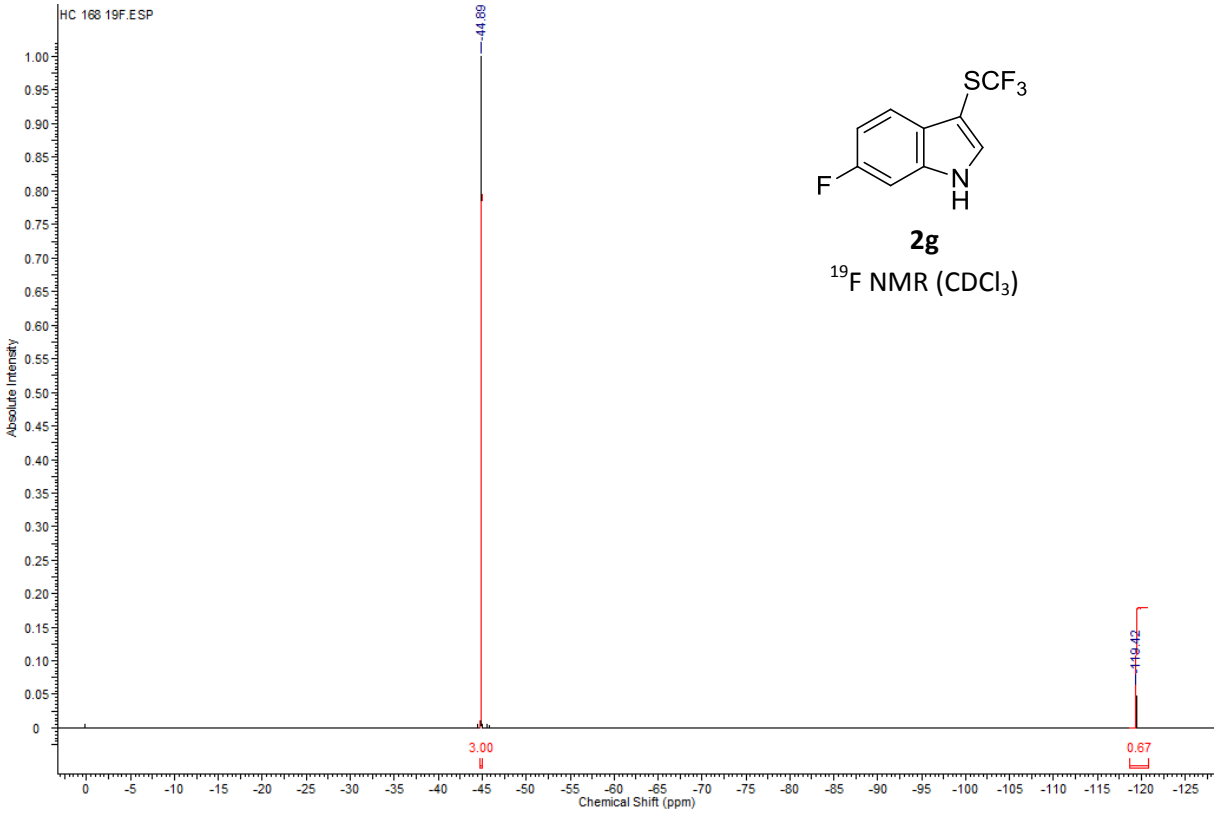

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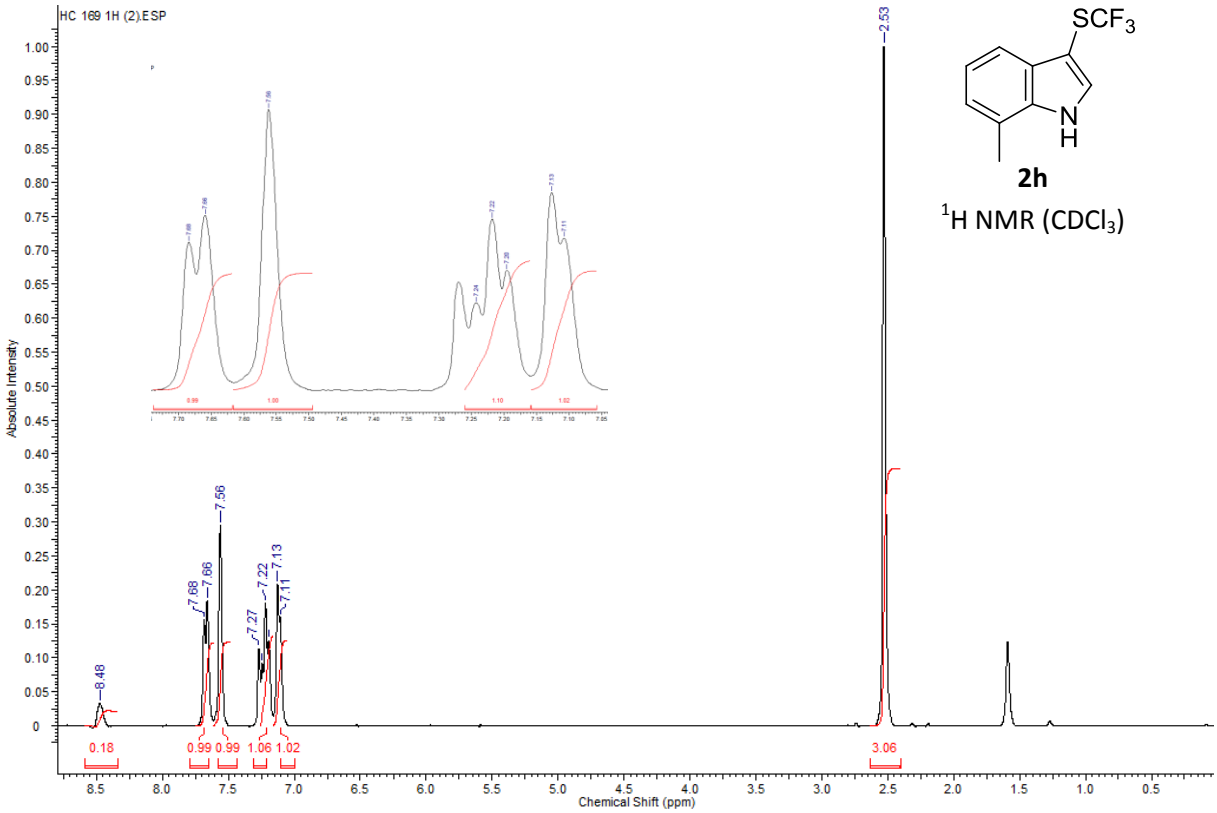
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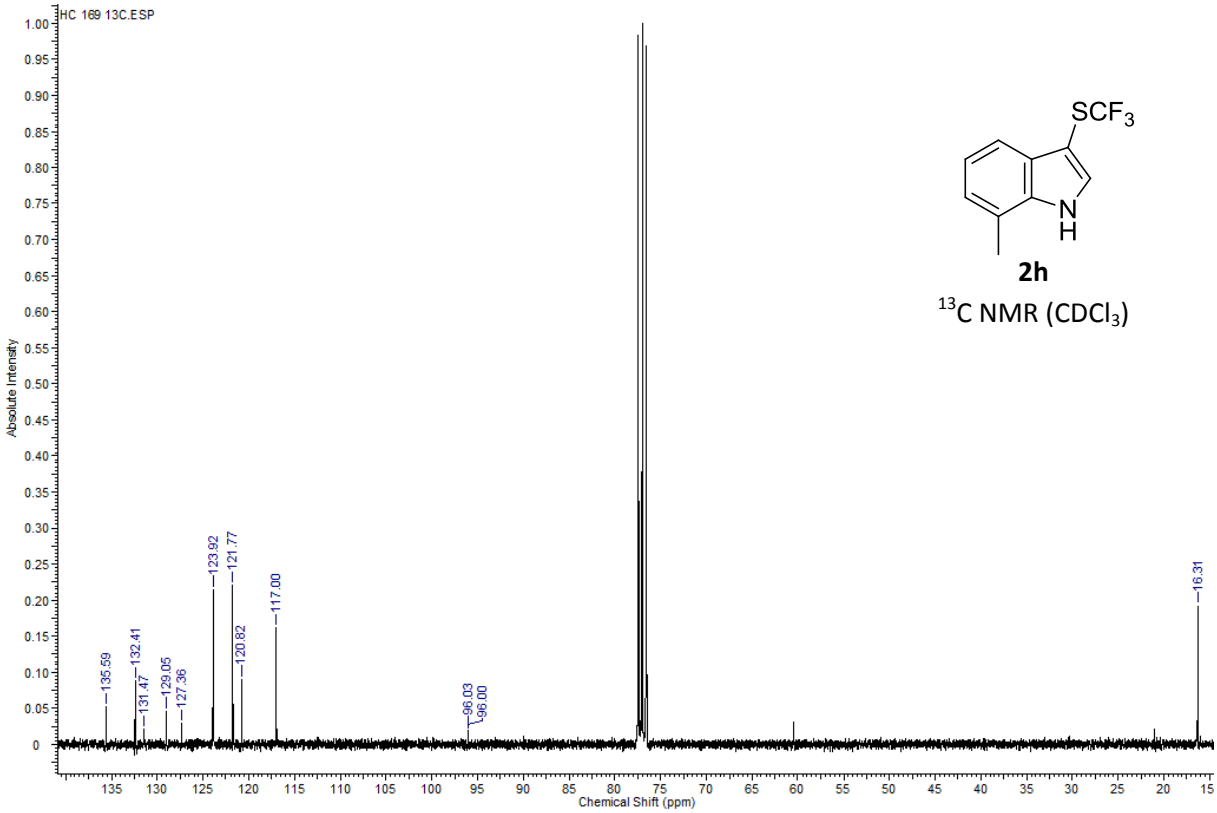
7.56
7.27
7.22
7.13
7.11
2.53
0.18
0.99
0.99
1.06
1.02
3.06
SCF3
N
H
2h
1H NMR (CDCl3)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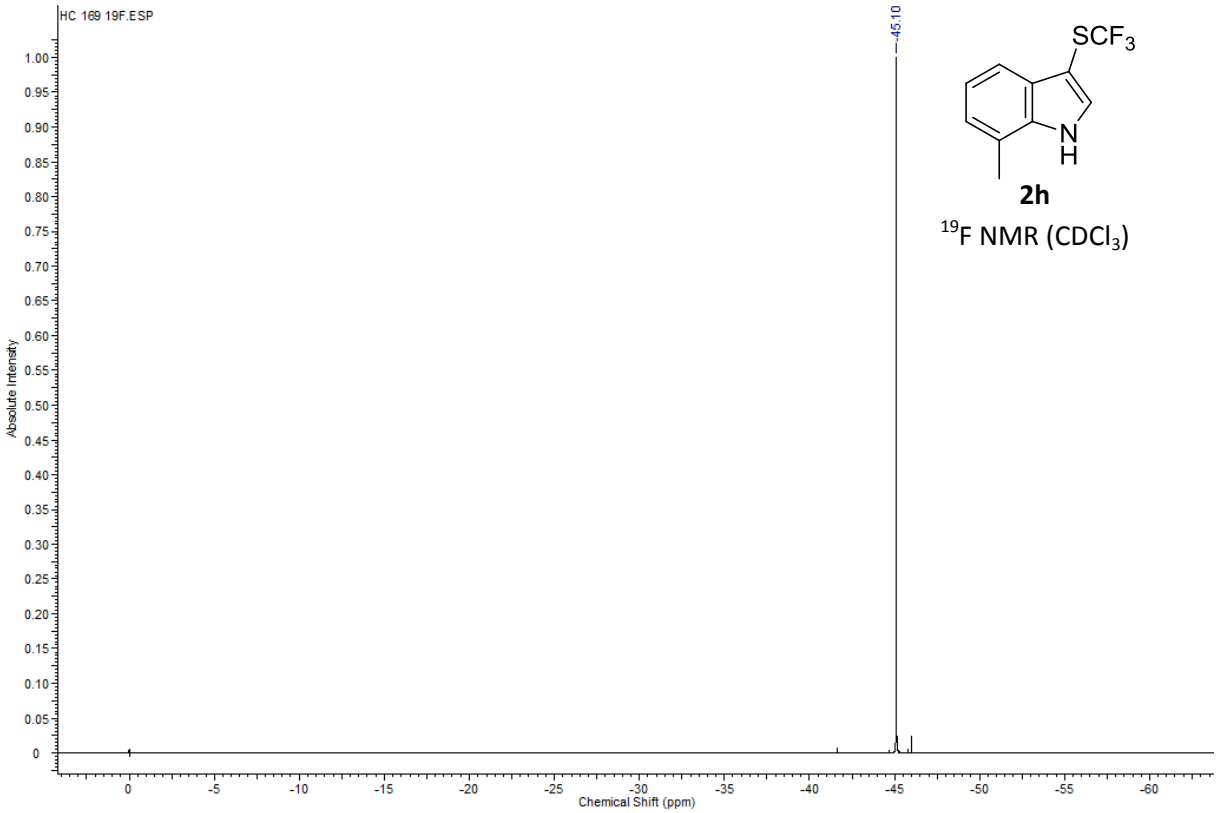
SCF3
N
H
2h
13C NMR (CDCl3)



2h

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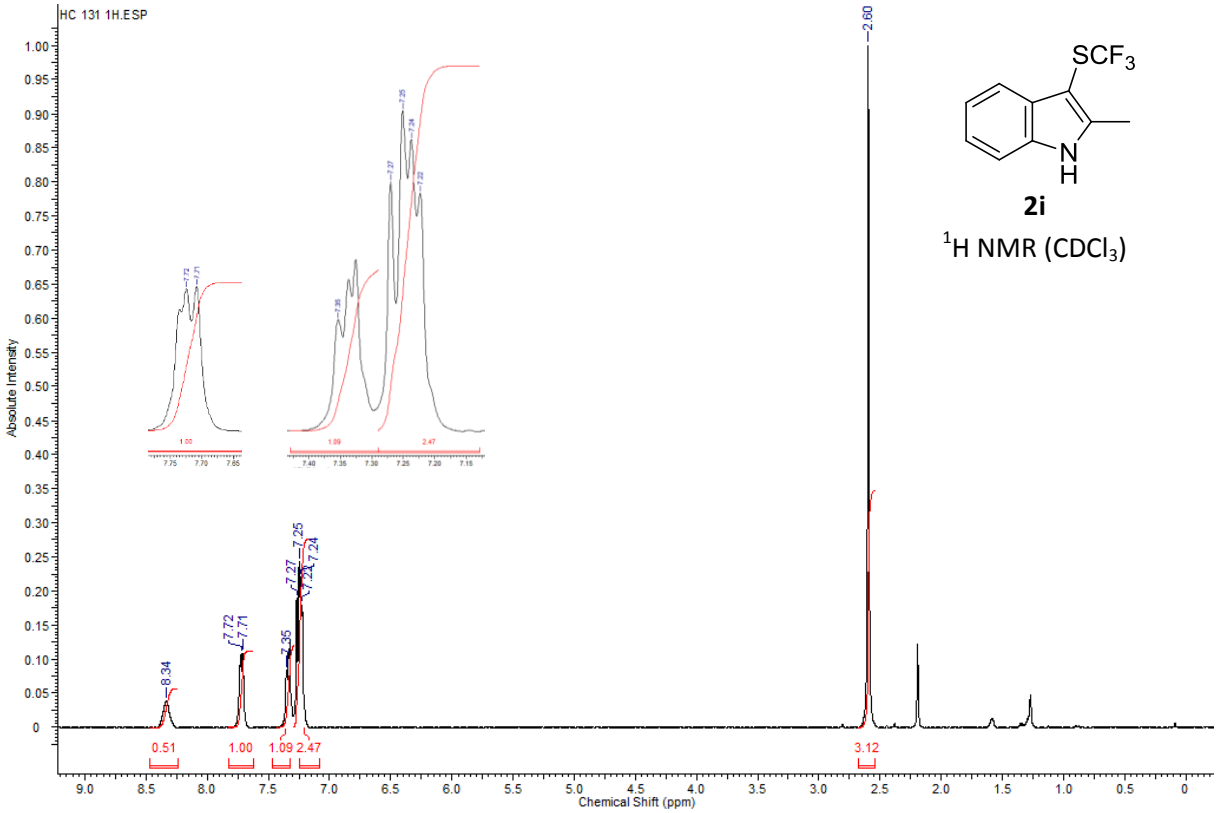

2i

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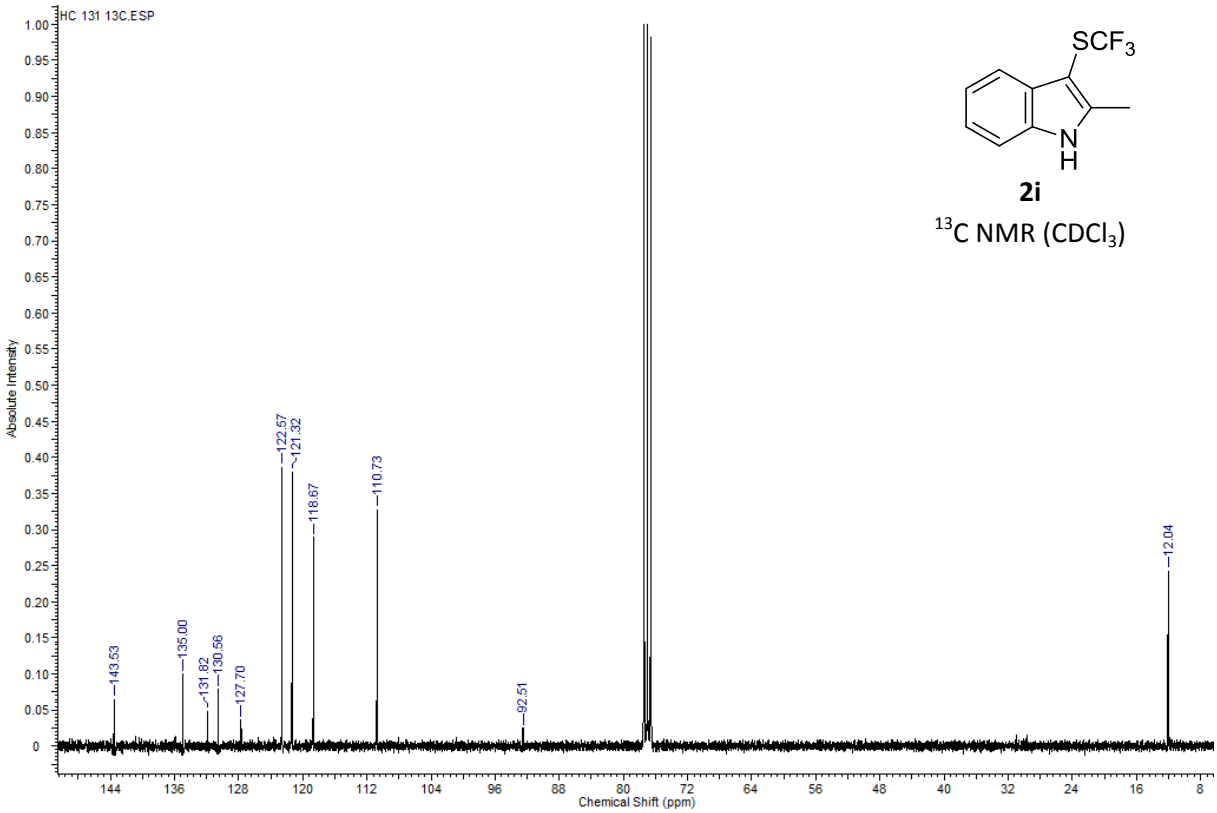

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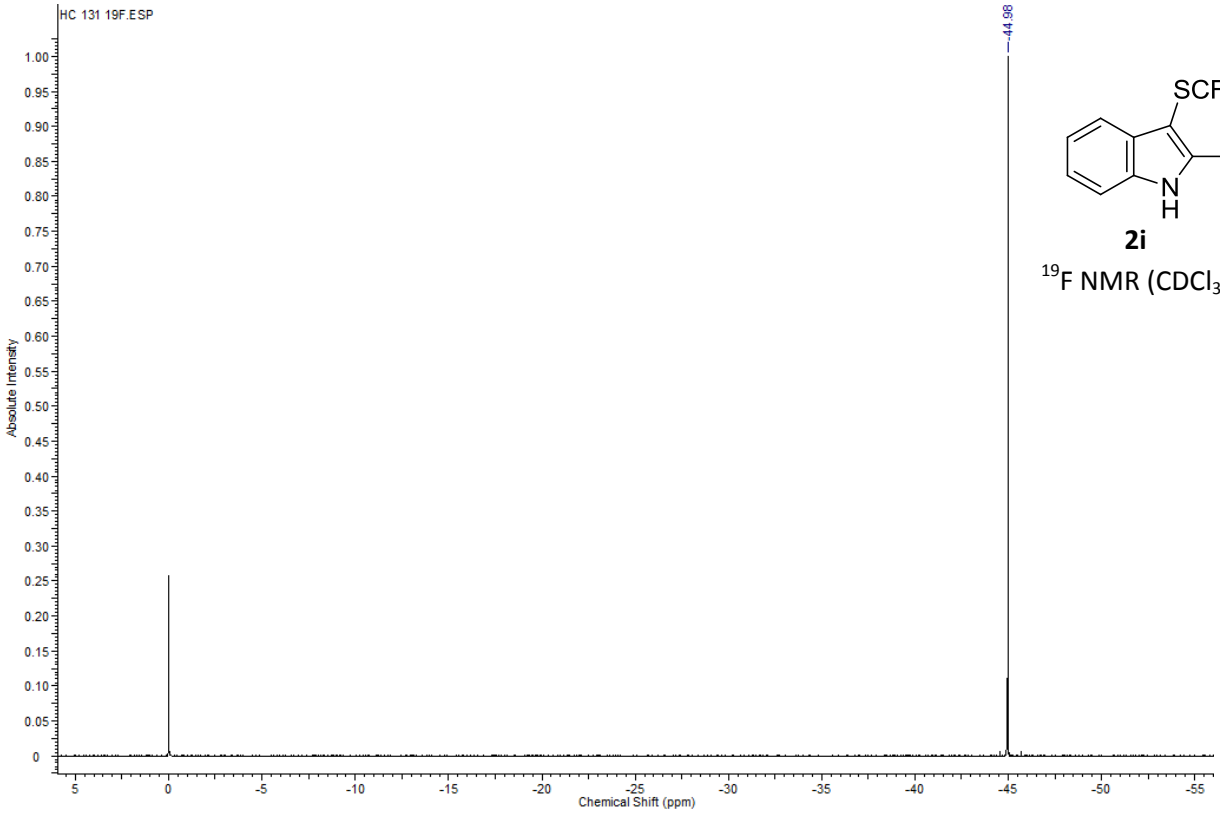

2i

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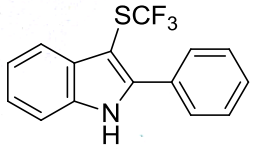

2j

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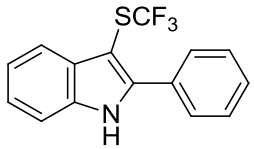

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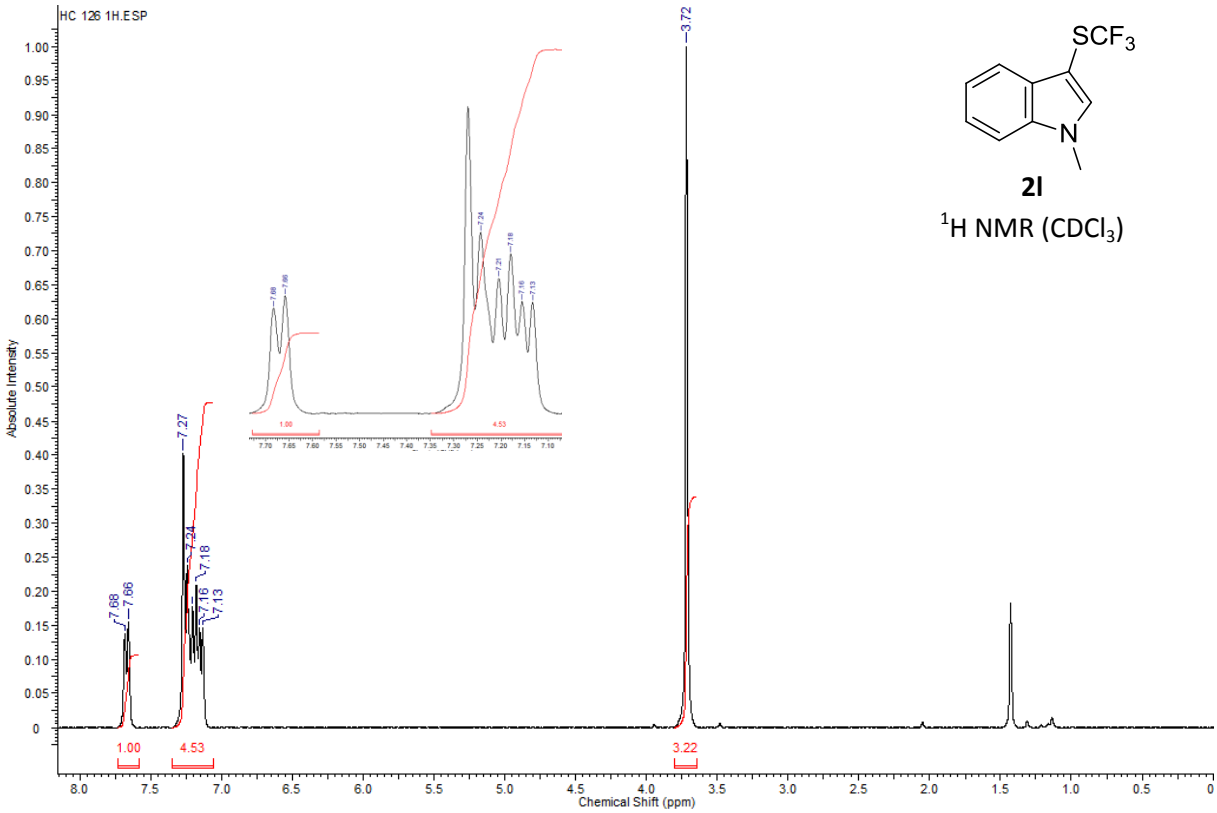

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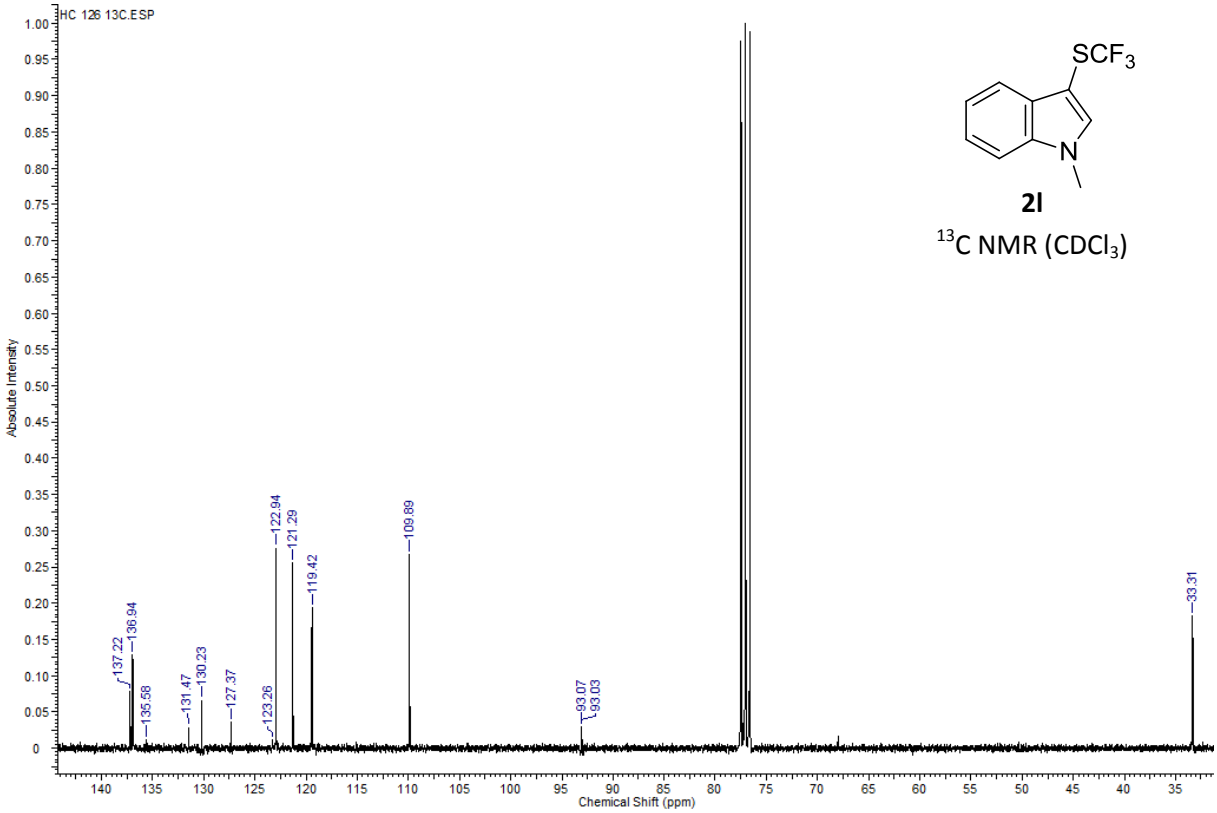

2l

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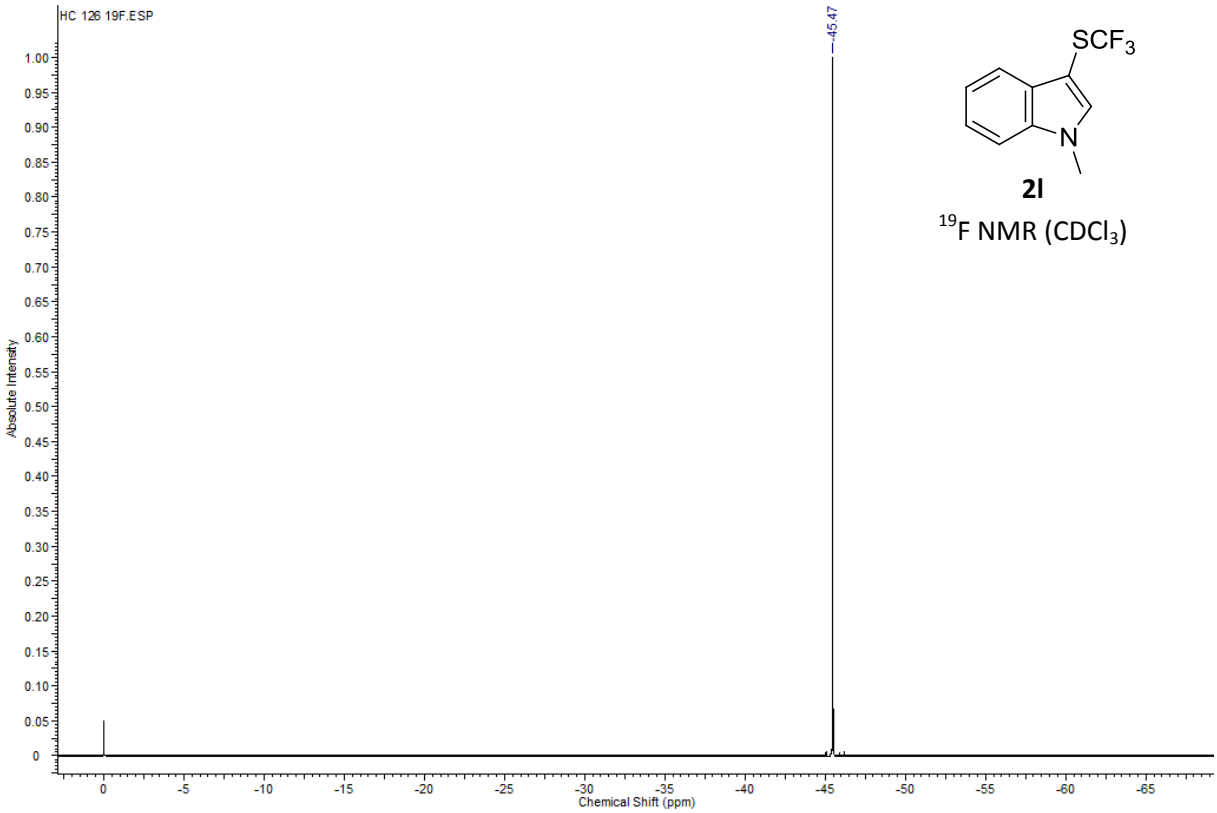

2l

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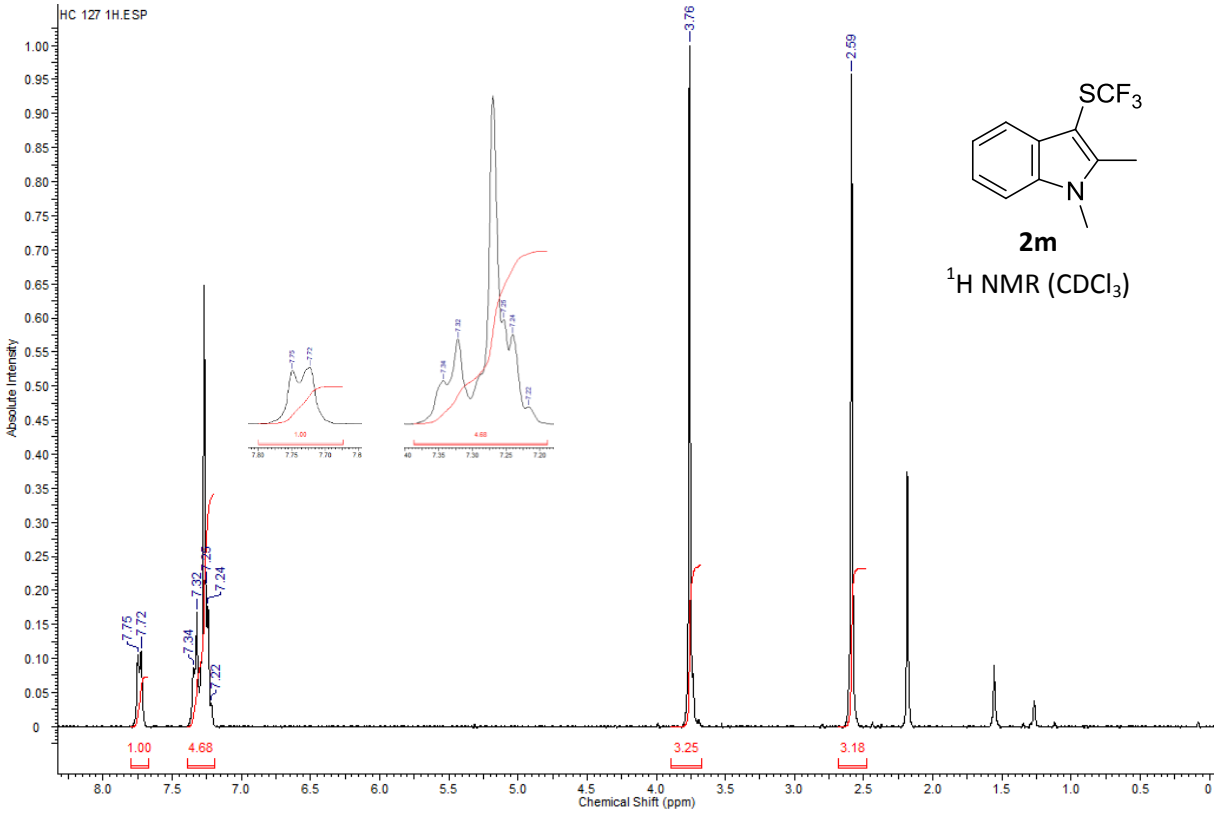

2m

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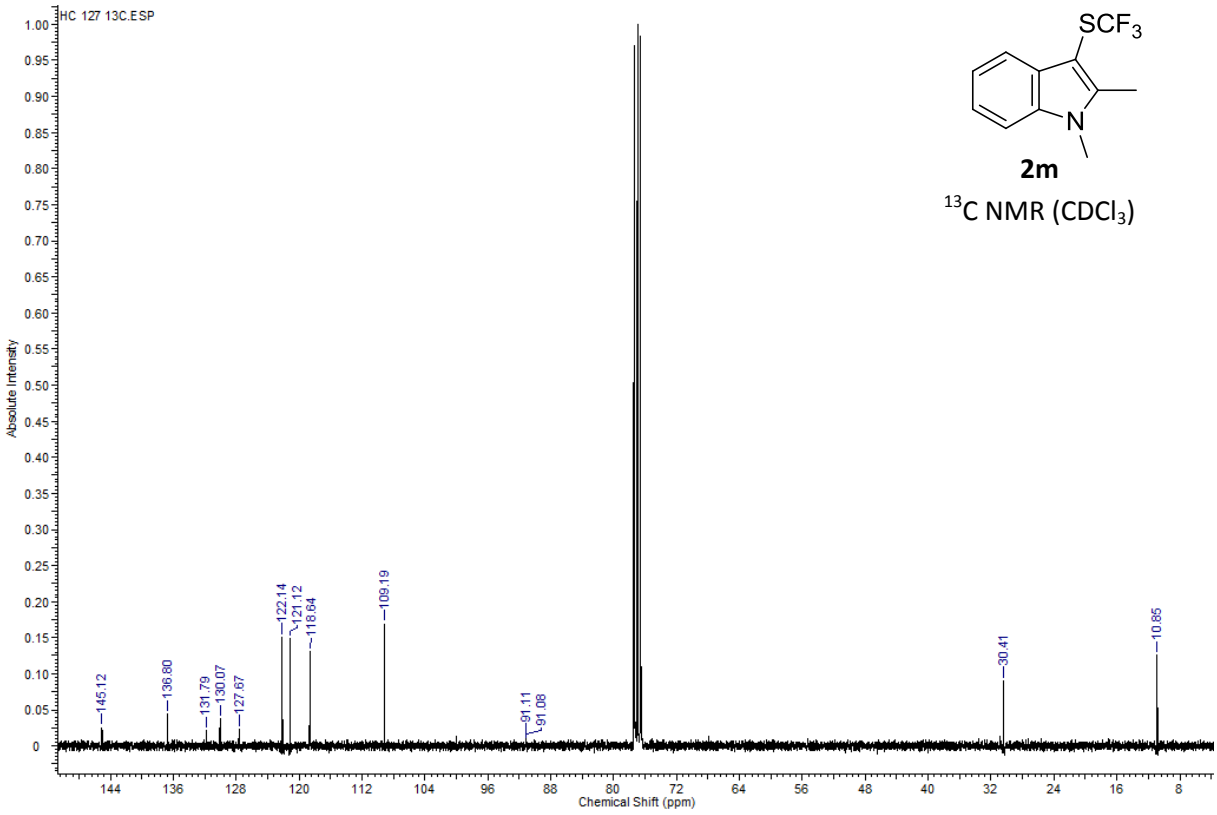
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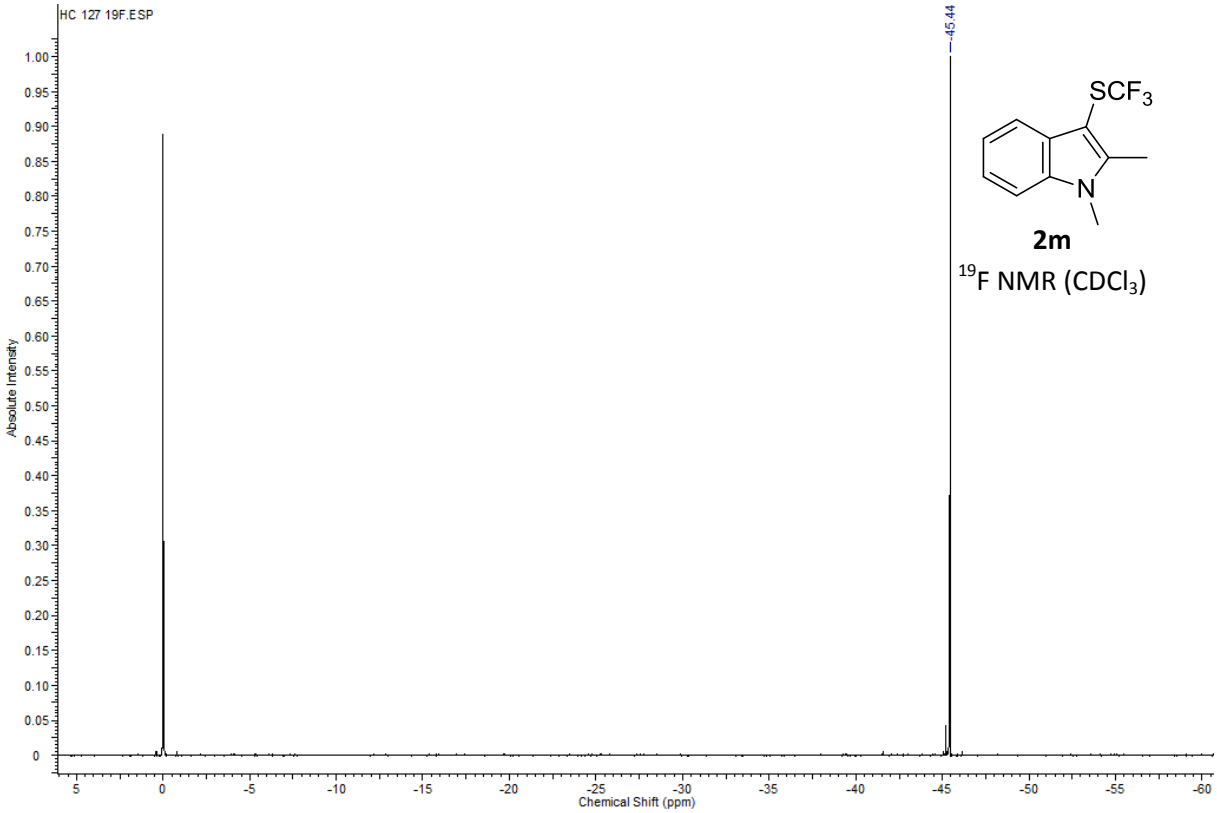
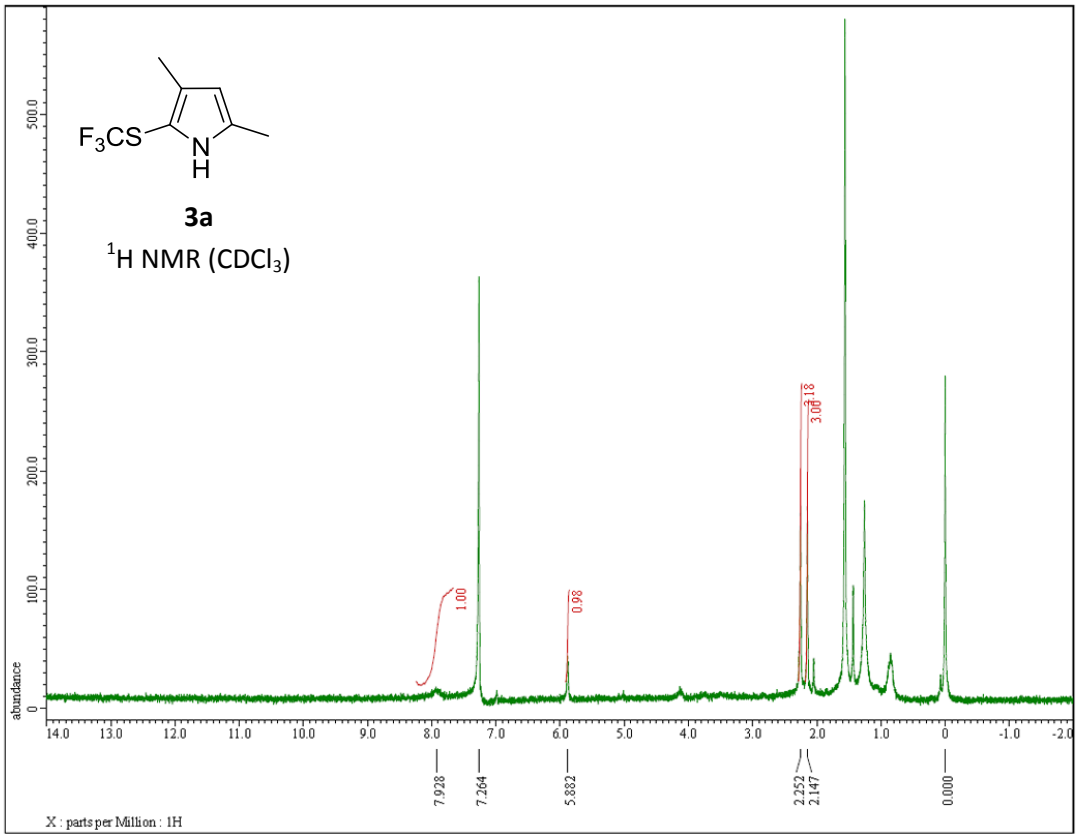
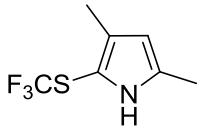
145.12
136.80
131.79
130.07
127.67
122.14
121.12
118.64
109.19
91.11
91.08
30.41
10.85
SCF3
N
2m
13C NMR (CDCl3)

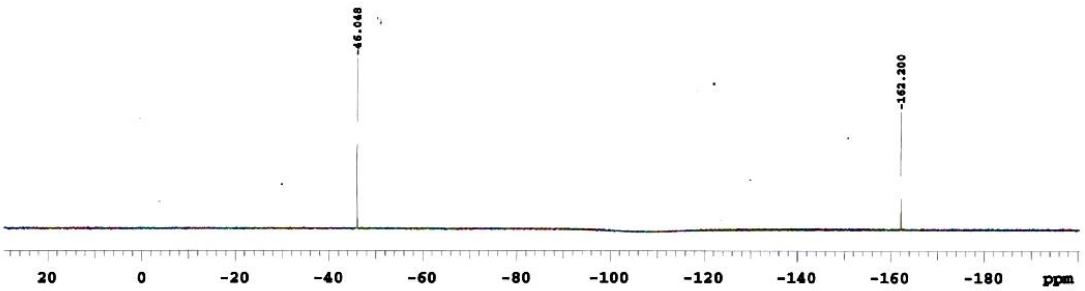

HC 127 19F.ESP
Absolute Intensity
Chemical Shift (ppm)
-45.44
SCF3
N
2m
19F NMR (CDCl3)

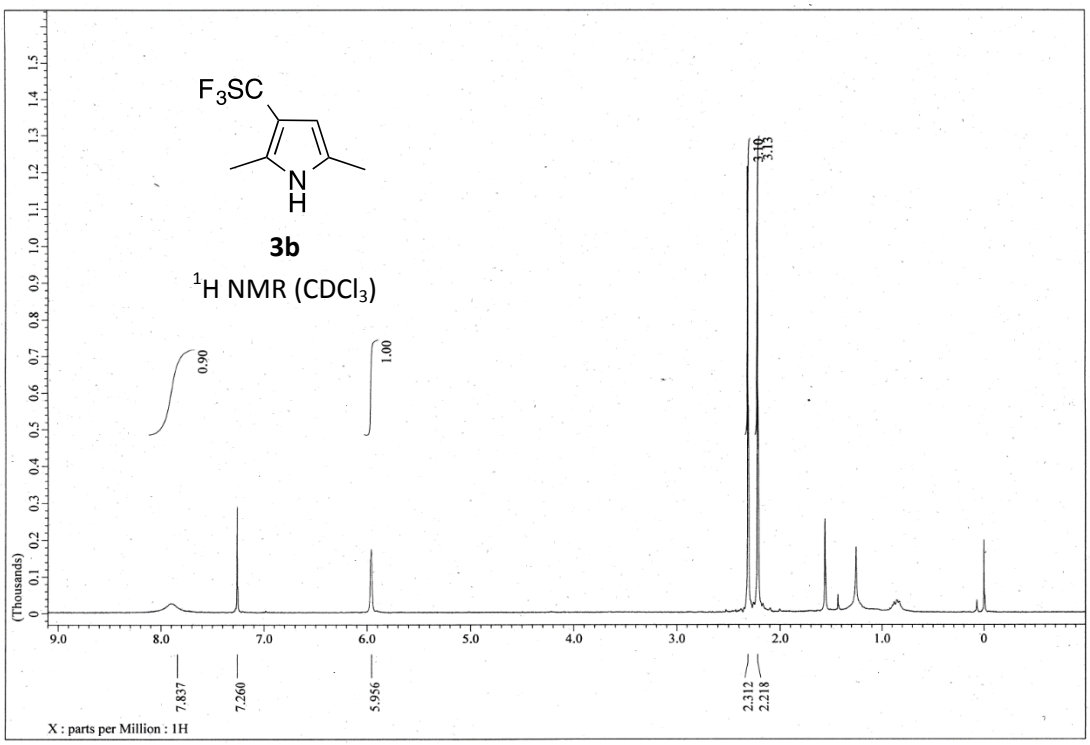


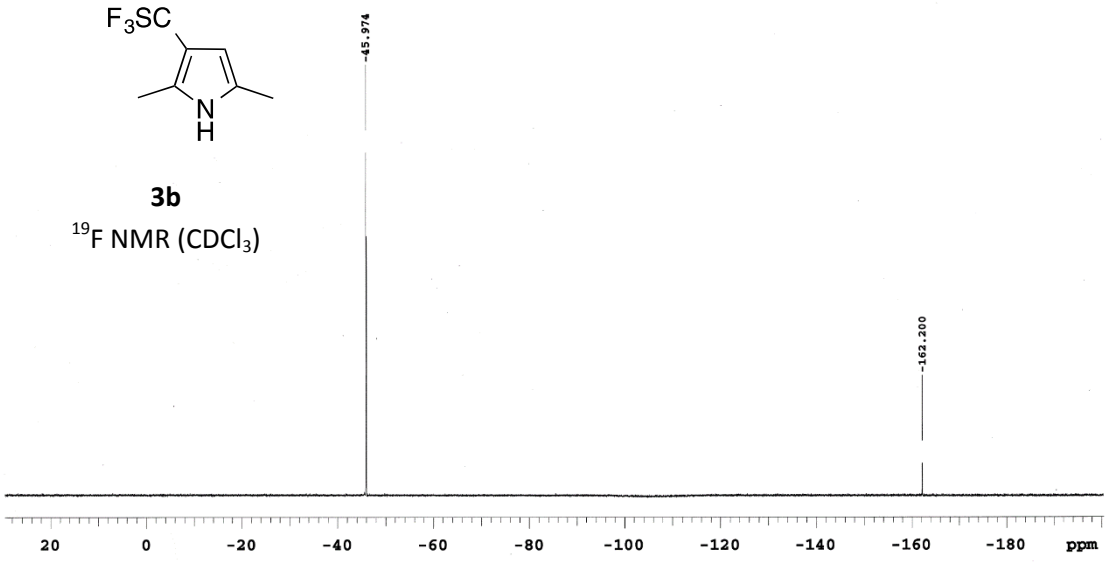


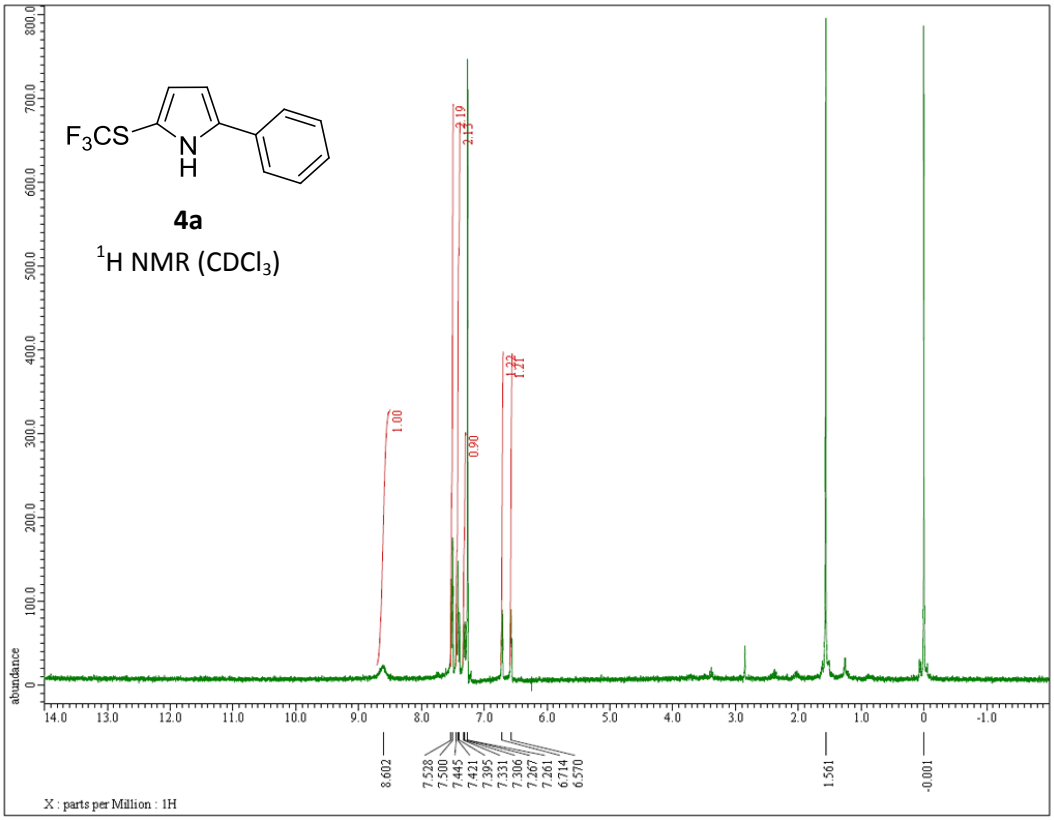
3a

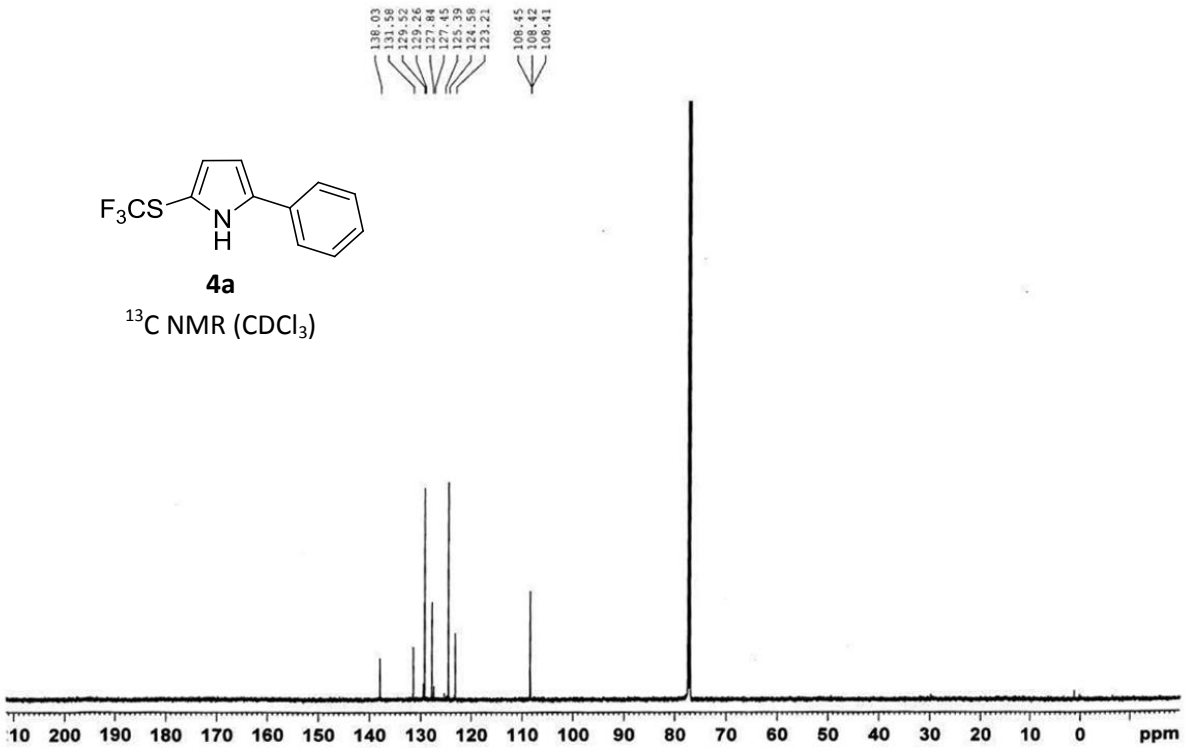
^{19}F NMR ($CDCl_3$)

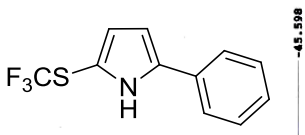



F3SC
N
H
3b
1H NMR (CDCl3)
0.90
1.00
3.10
3.13
(Thousands)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.837
7.260
5.956
2.312
2.218
X : parts per Million : 1H


F3SC
N
H
3b
19F NMR (CDCl3)
-45.974
-162.200
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

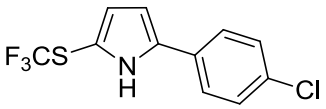

F3CS
N
H
4a
1H NMR (CDCl3)
abundance
X : parts per Million : 1H


F3CS
N
H
4a
13C NMR (CDCl3)
ppm



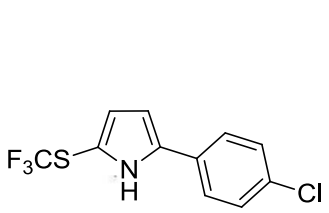
4a

^{19}F NMR ($CDCl_3$)



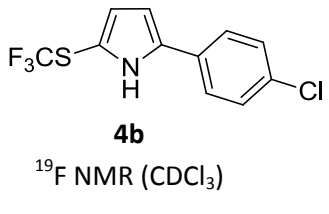
4b

^{1}H NMR ($CDCl_3$)



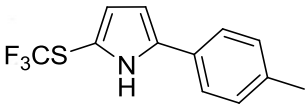
4b

^{13}C NMR ($CDCl_3$)



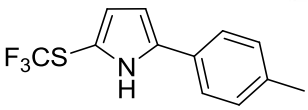
4b

^{19}F NMR ($CDCl_3$)



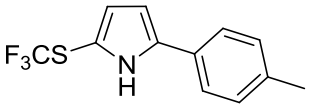
4c

^{1}H NMR ($CDCl_3$)



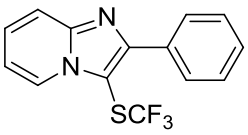
4c

^{13}C NMR ($CDCl_3$)



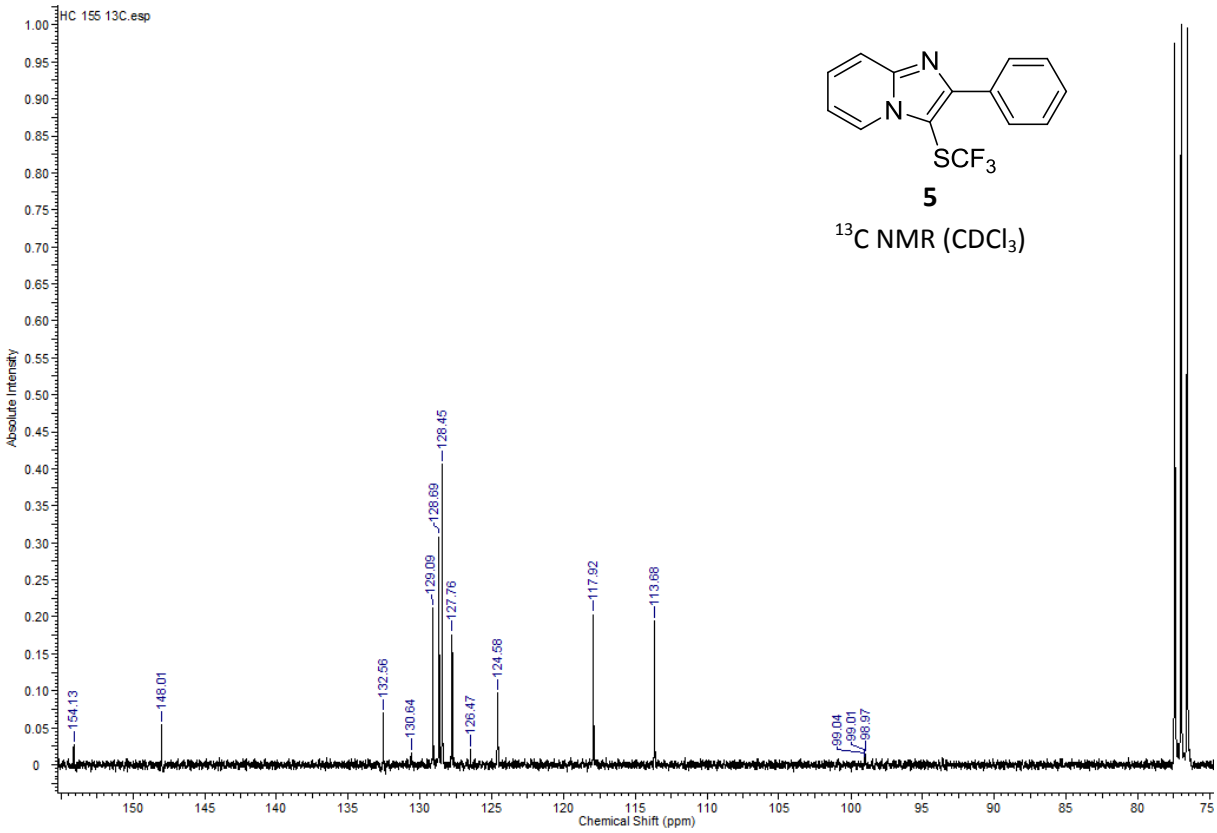
4c

^{19}F NMR ($CDCl_3$)



5

^{1}H NMR ($CDCl_3$)

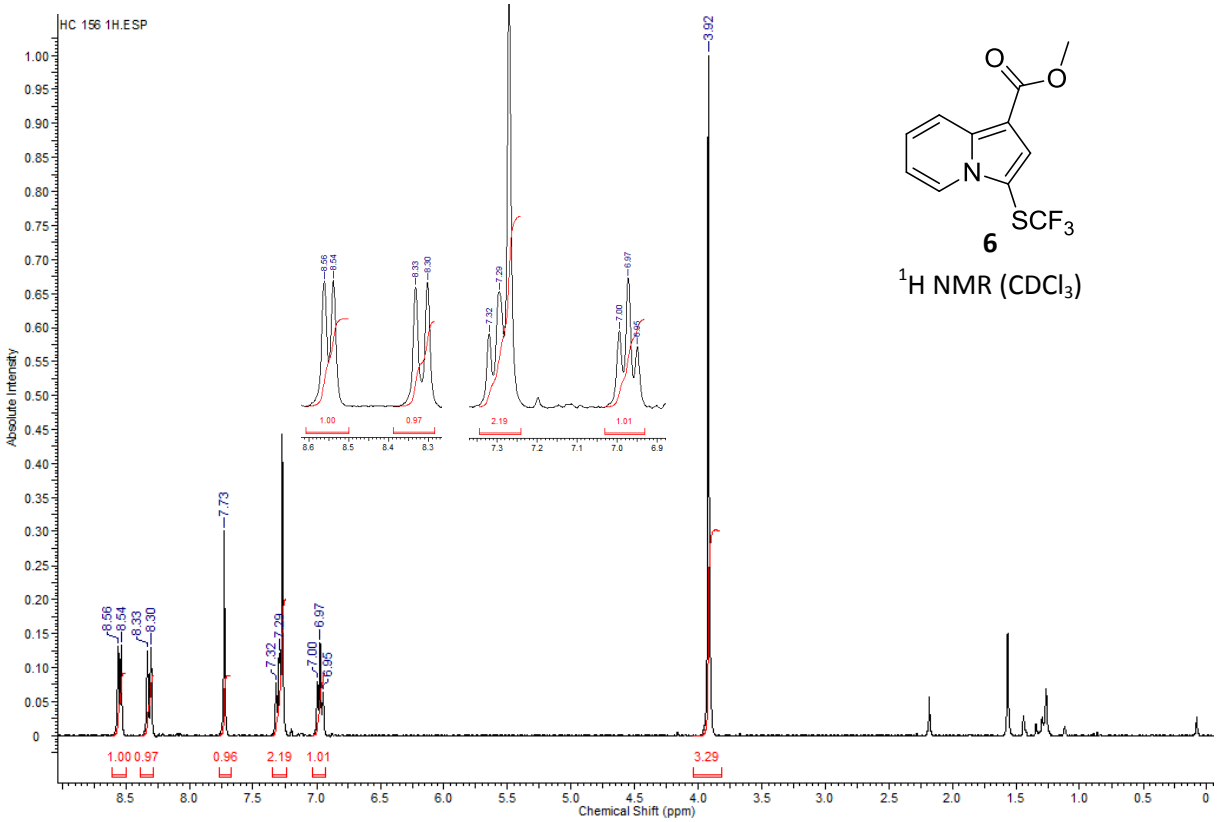


5

^{13}C NMR ($CDCl_3$)

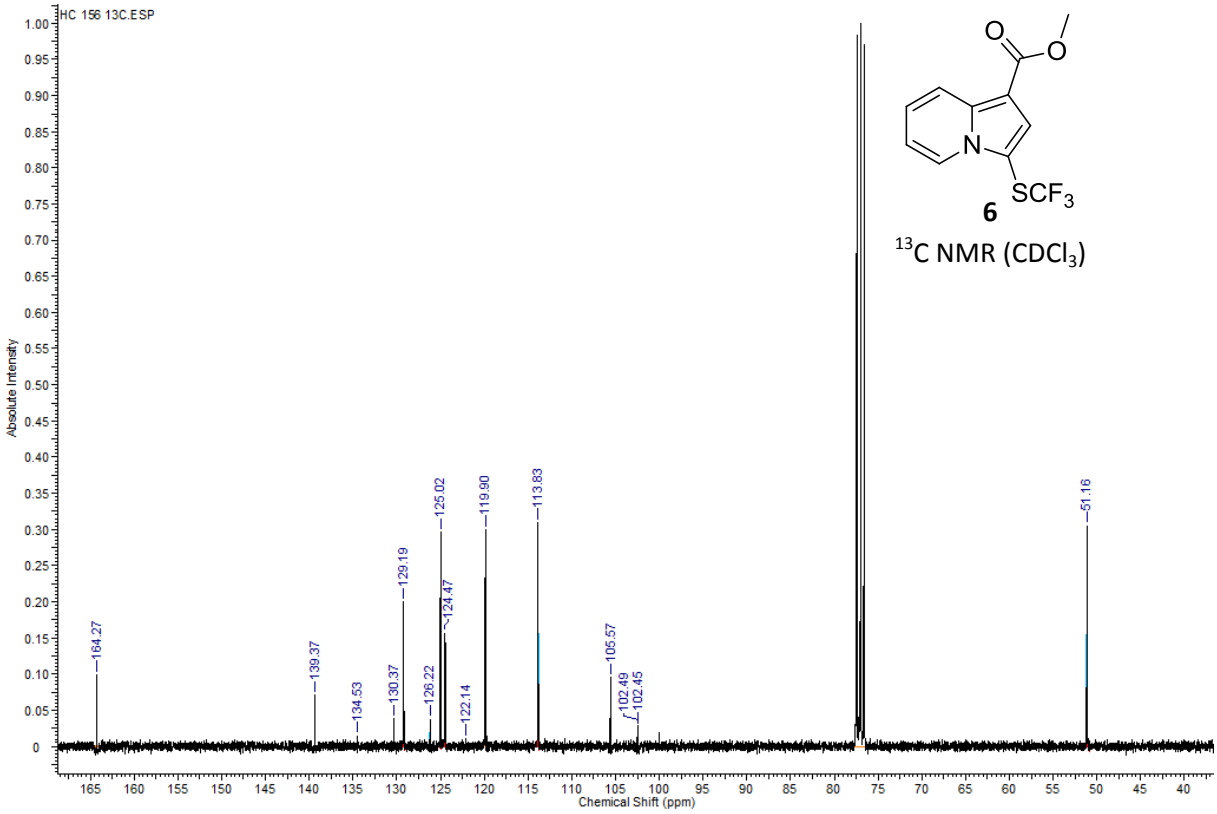
5

^{19}F NMR ($CDCl_3$)



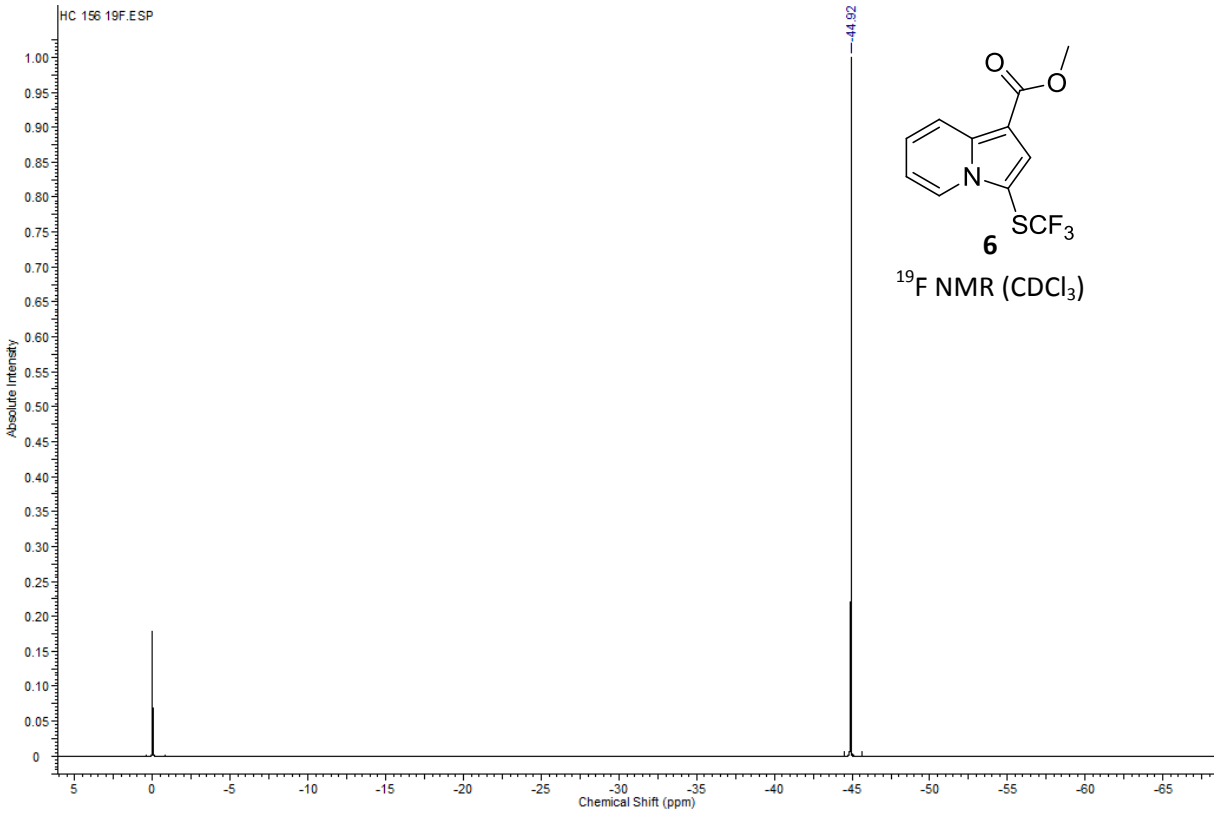
6

^{1}H NMR ($CDCl_3$)



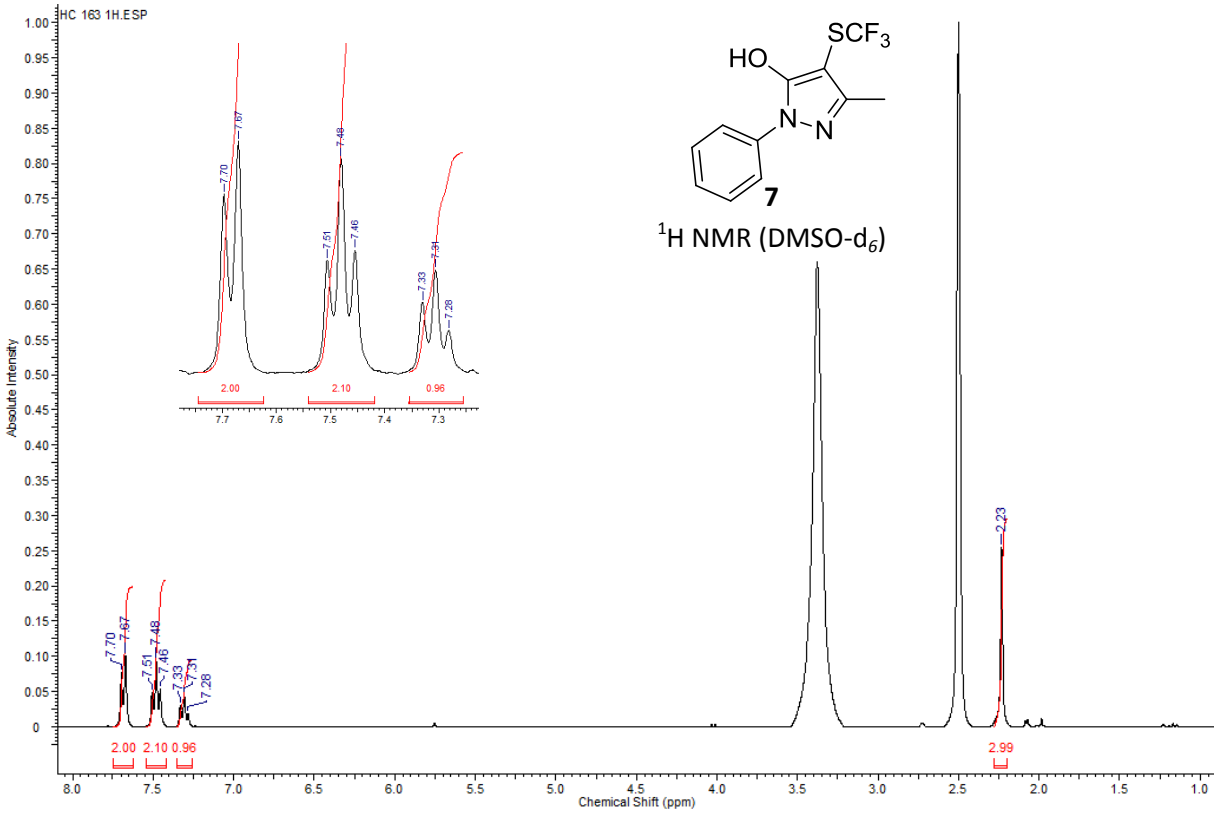
6

^{13}C NMR ($CDCl_3$)



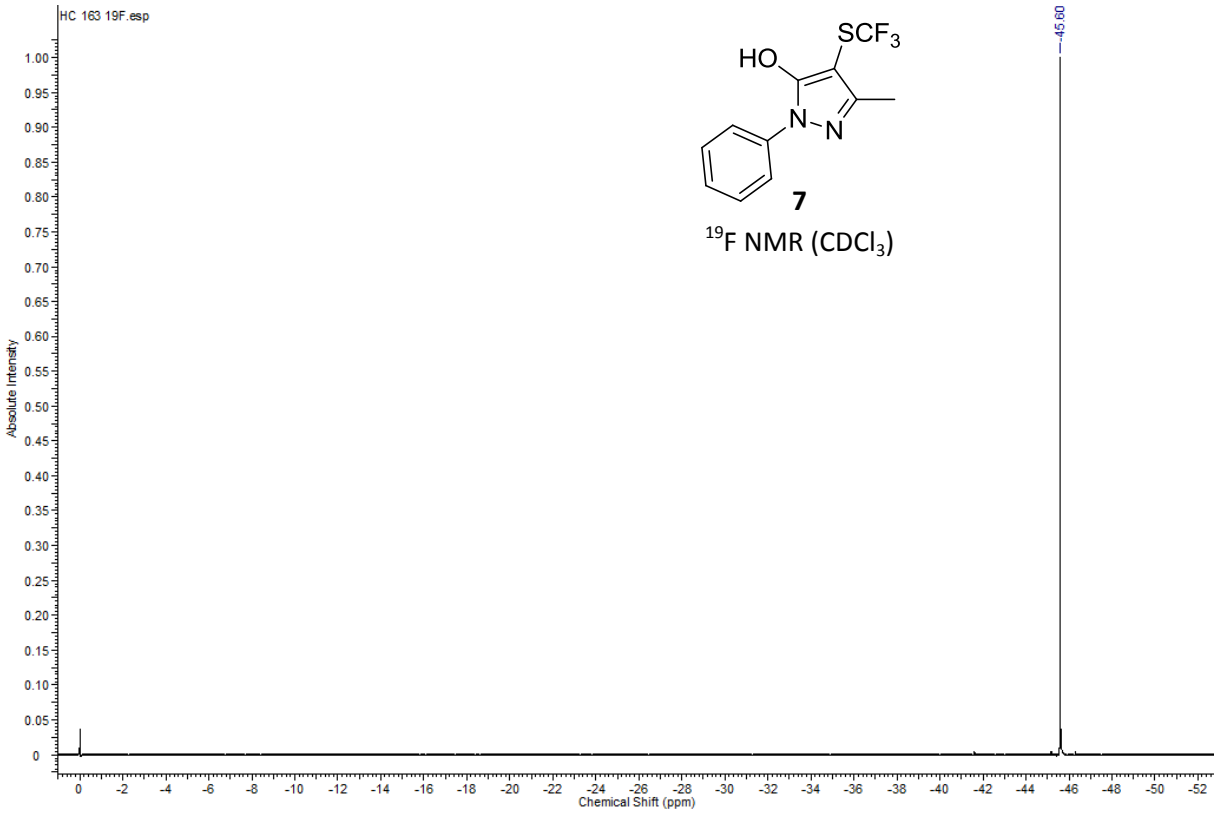
6

^{19}F NMR ($CDCl_3$)



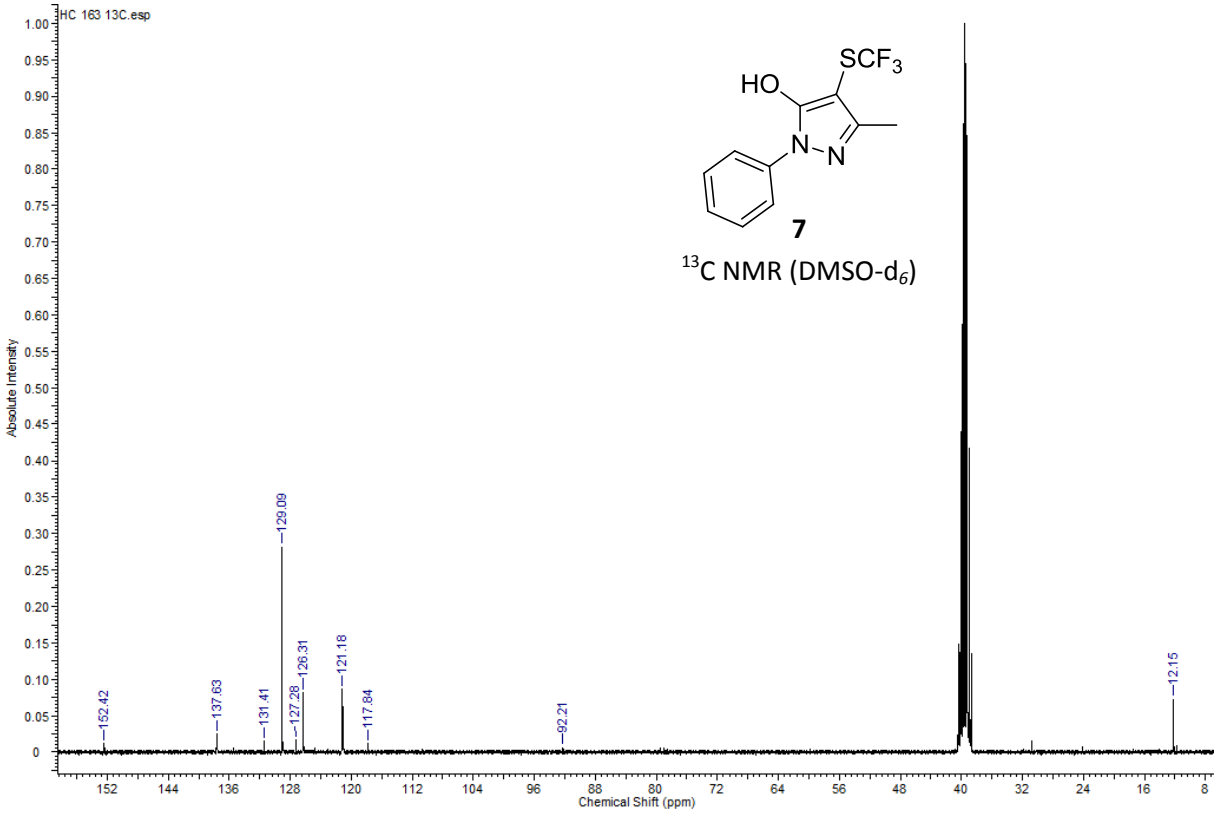
7

^{1}H NMR (DMSO-d_6)



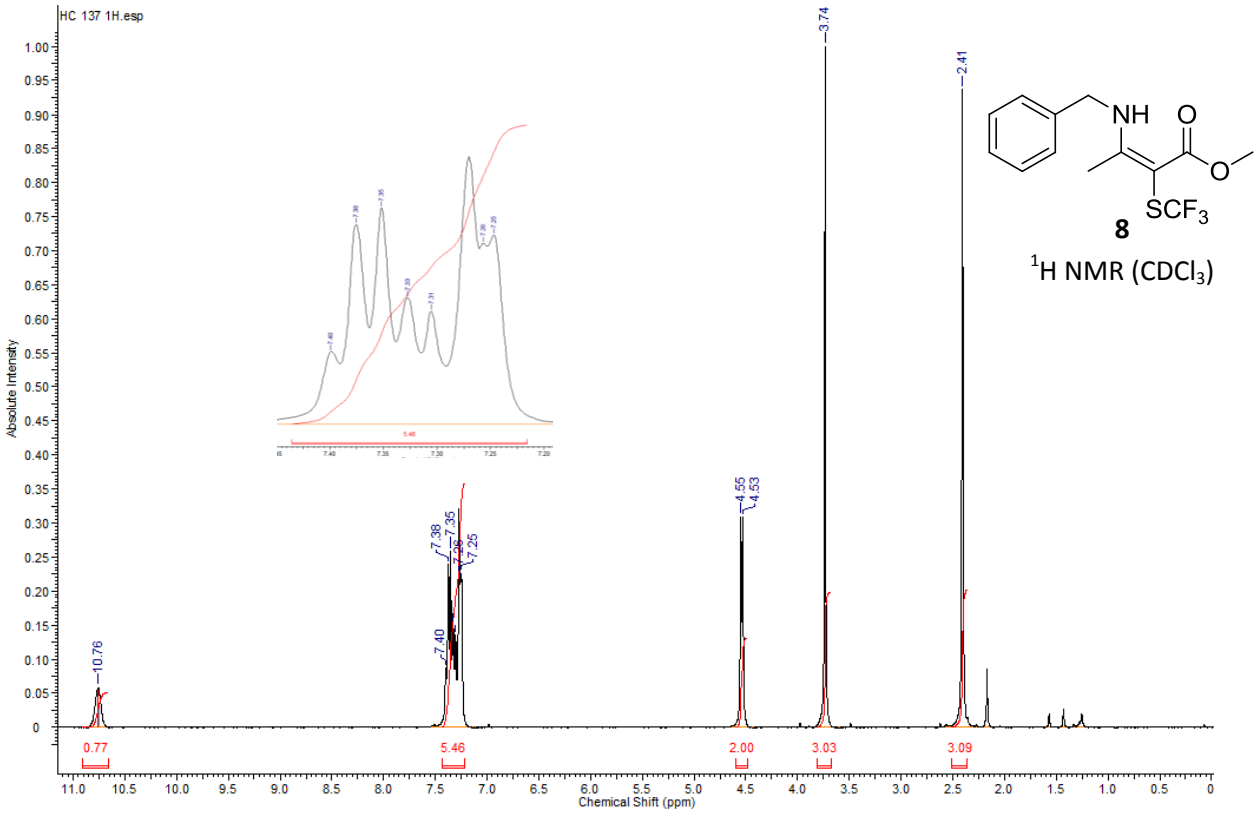
7

^{19}F NMR ($CDCl_3$)



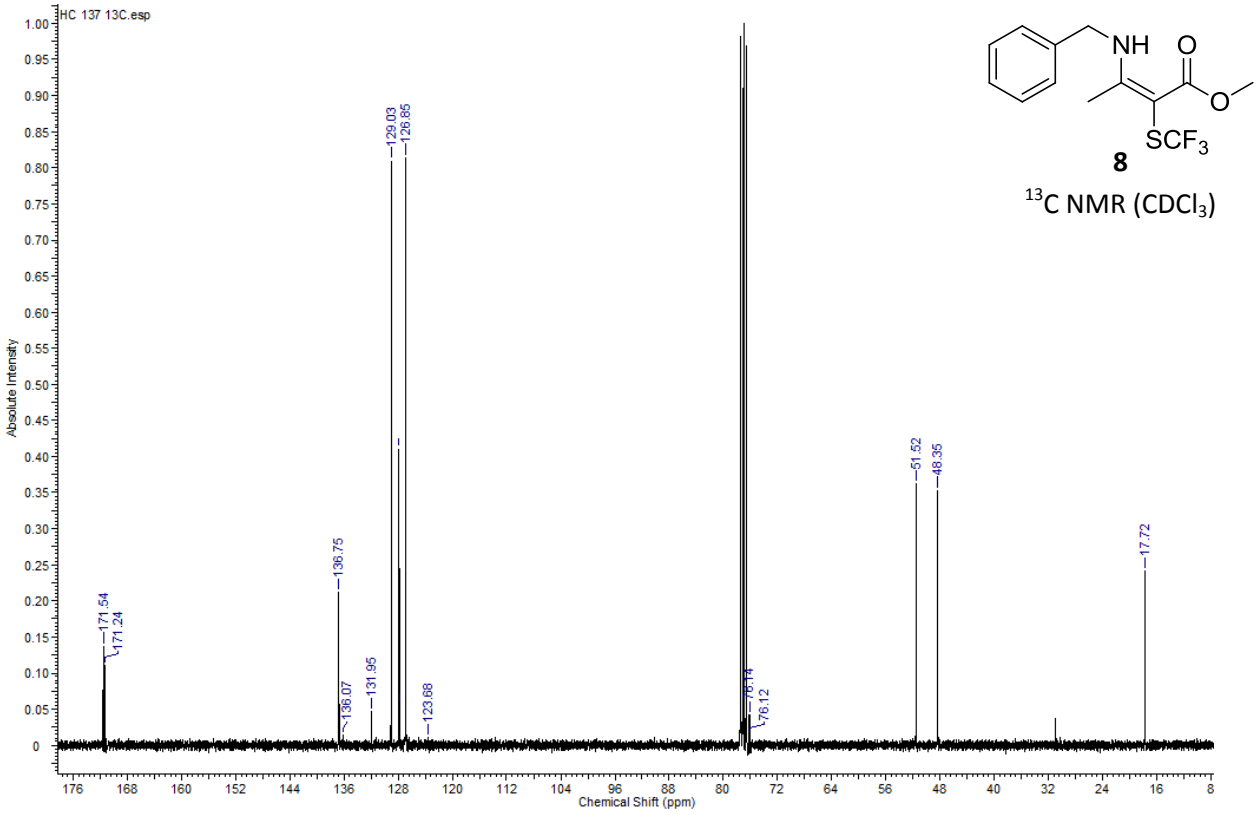
7

^{13}C NMR (DMSO-d_6)



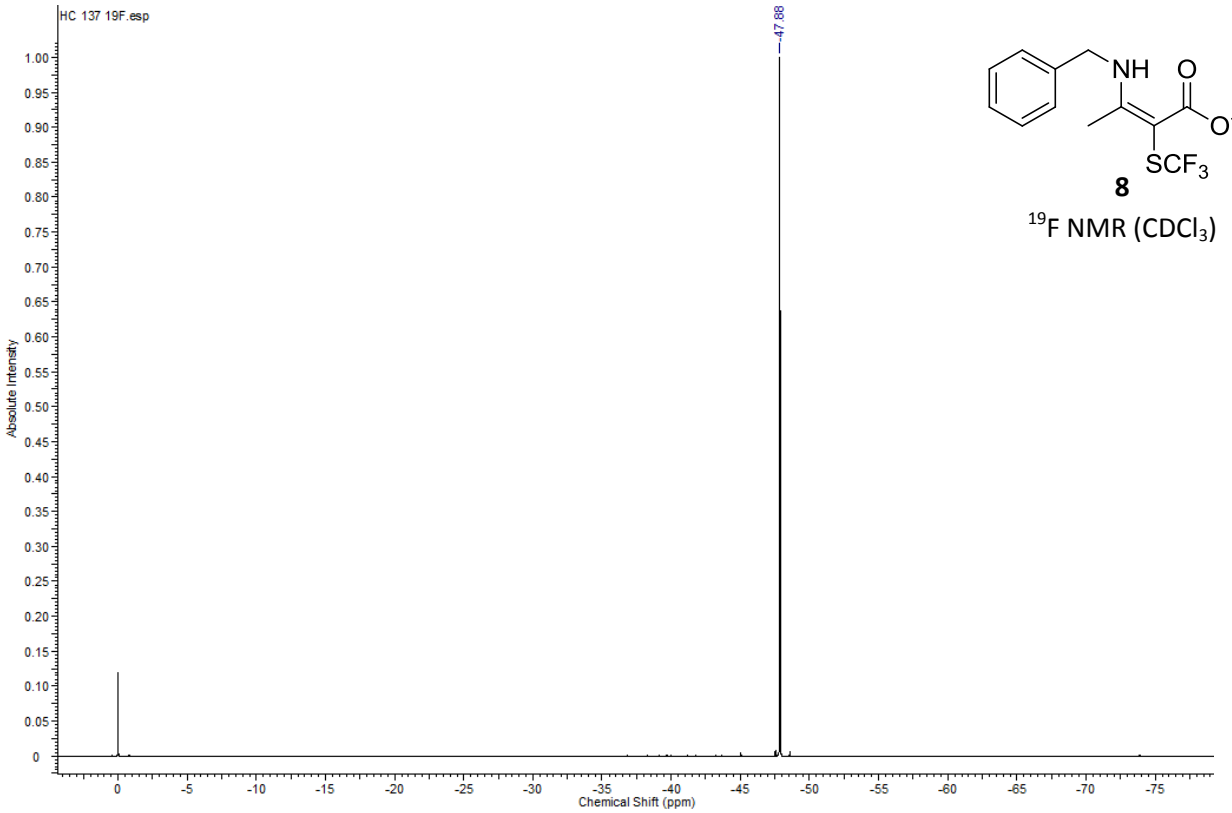
8

^{1}H NMR ($CDCl_3$)



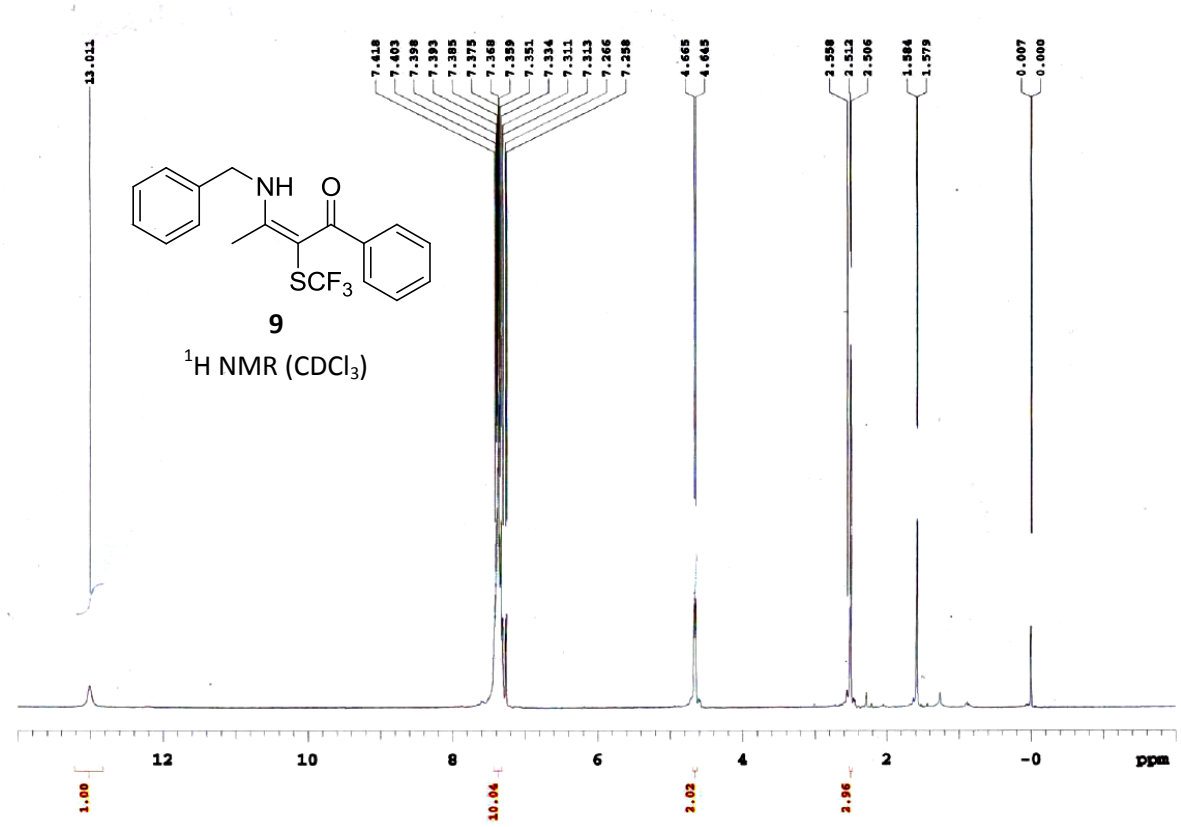
8

^{13}C NMR ($CDCl_3$)



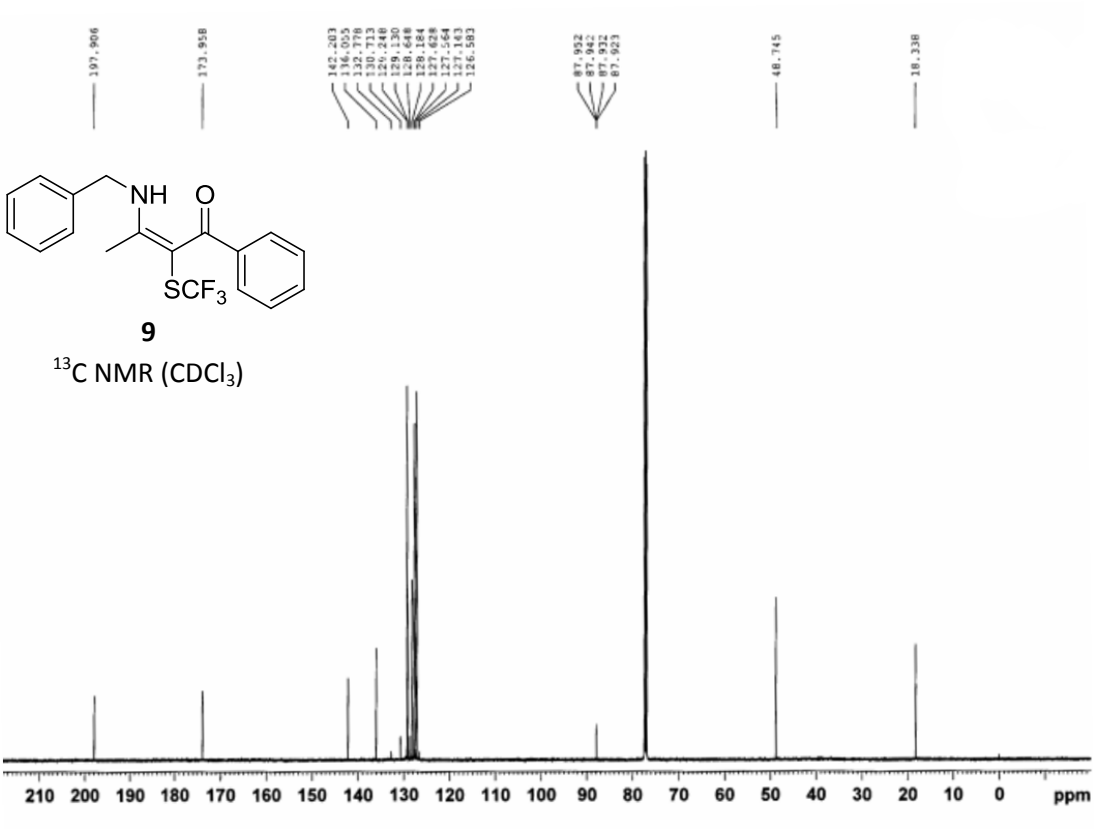
8

^{19}F NMR ($CDCl_3$)



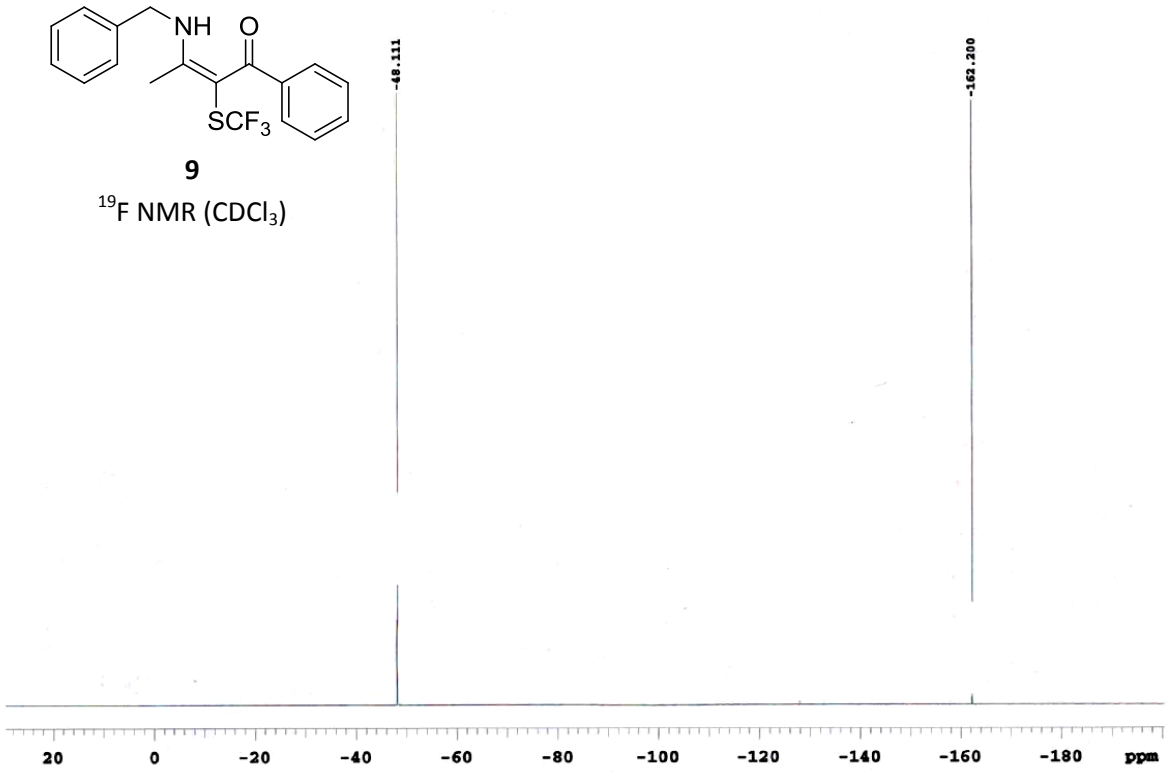
9

^{1}H NMR ($CDCl_3$)



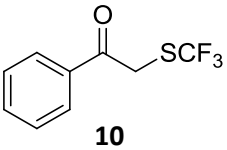
9

^{13}C NMR ($CDCl_3$)



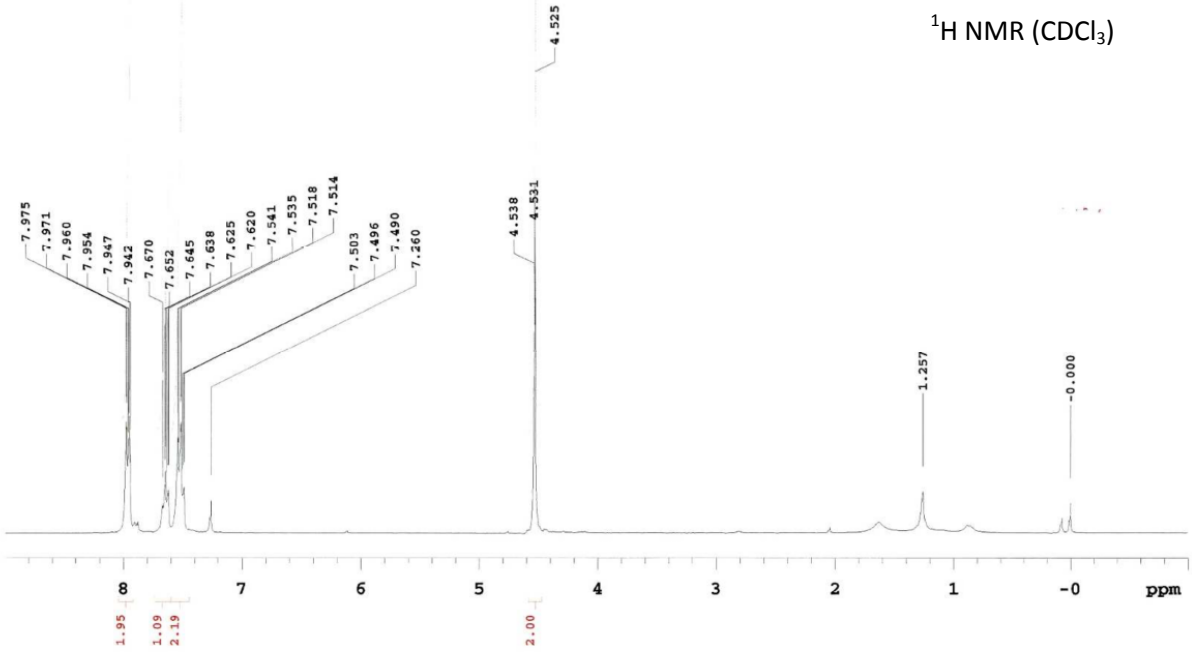
9

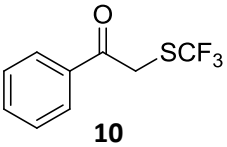
^{19}F NMR ($CDCl_3$)



10

^{1}H NMR ($CDCl_3$)





10

^{19}F NMR ($CDCl_3$)