Electronic Supplementary Material (ESI) for Chemical Science
This journal is © The Royal Society of Chemistry 2014

Sandmeyer Trifluoromethylthiolation of Arenediazonium Salts with Sodium Thiocyanate and Ruppert-Prakash Reagent

Grégory Danoun, Bilguun Bayarmagnai, Matthias F. Grünberg, and Lukas J. Gooßen*

FB Chemie – Organische Chemie, TU Kaiserslautern, Erwin-Schrödinger-Str. Geb. 54,

67663 Kaiserslautern, Germany, Fax: (+49) 631-205-3921, e-mail: goossen@chemie.uni-kl.de.

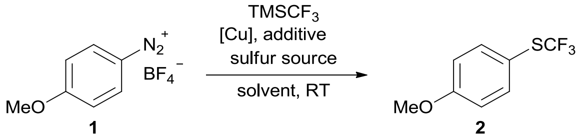
Supporting Information

General Methods

The reactions were performed in oven-dried glassware containing a Teflon-coated stirrer bar and dry septum under a nitrogen atmosphere. Acetonitrile was dried by refluxing over CaH_2 and subsequent fractionally distillation. Three freeze-pump-thaw cycles were performed before the reagents were mixed. All reactions were monitored by TLC (0.20 mm silica gel plates, POLYGRAM® SIL G/UV_{254}), GC and the yields were determined by ^{19}F NMR using 1,3-difluorobenzene as internal standard. GC analyses were carried out using a HP-5 capillary column (Phenyl Methyl Siloxane 30 m x 320 x 0.25, 100/2.3-30- 300/3) and a time program beginning with 2 min at 60 °C followed by 30 °C/min ramp to 300 °C, then 3 min at this temp. Column chromatography was performed using a Combi Flash Companion-Chromatography-System (Isco-Systems) and Grace Reveleris packed flash columns (12 g). NMR spectra were obtained on a Bruker AMX 400 system using chloroform-*d* or DMSO-d_6 as deuterated solvents, with proton, carbon and fluorine resonances at 400 MHz, 101 MHz and 151 MHz, respectively. Melting points were measured on a Mettler FP 61. Infrared spectra were recorded on a Perkin Elmer Fourier transform spectrometer. Mass spectral data were acquired on a Varian Saturn 2100 T. The high resolution mass (HRMS) was determined on a Finnigan MAT 90 (70 eV) spectrometer.

The diazonium salts were prepared from the corresponding anilines following the procedure below and were directly used. All other starting materials were commercially available. All the anilines and solvents were purified by distillation or sublimation prior to use. The other chemicals were used without further purification.

Table 1. Optimization of the reaction conditions.



entry	[Cu]	sulfur source	additive	solvent	yield of **2** [%][a]
1[b]	CuSCN	S_8	CsF	MeCN	5
2[b]	"	Lawesson's reagent	"	"	traces
3[b]	"	Na_2S	"	"	0
4	"	NaSCN	"	"	30
5	"	KSCN	"	"	traces
6	"	NH_4SCN	"	"	traces
7	"	NaSCN	Cs_2CO_3	"	98
8	"	"	"	DMF	81
9	"	"	"	acetone	18
10	Cu(0)	"	"	MeCN	1
11	$CuSO_4$	"	"	"	10
12	CuOAc	"	"	"	85
13	CuI	"	"	"	6
14	CuSCN	"	–	"	0
15	"	–	Cs_2CO_3	"	0
16	–	NaSCN	"	"	0
17[c]	CuSCN	"	"	"	34
18[d]	"	"	"	"	98
19[e]	"	"	"	"	67

Reaction conditions: 0.5 mmol [Cu], 2 equiv. additive, 1.5 equiv. sulfur source, 2 mL solvent, RT, dropwise addition of 0.5 mmol **1** in 2 mL of solvent, then 2 equiv. $TMSCF_3$, 12h. [a] Yields were determined by ^{19}F NMR using 1,3-difluorobenzene as internal standard. [b] $TMSCF_3$ added before **1**. [c] 1 equiv. Cs_2CO_3. [d] 0.5 equiv. CuSCN. [e] 0.1 equiv. CuSCN., Lawesson's reagent = 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-dithione.

Synthesis of arenediazonium tetrafluoroborates

In a 50 mL round-bottom flask, the aniline (10 mmol) was dissolved in a mixture of absolute ethanol (3 mL) and an aqueous solution of HBF_4 (50%, 2.5 mL, 20 mmol) and *tert*-butyl nitrite (2.7 mL, 20 mmol) was added dropwise to the solution at 0 °C. The reaction was stirred at room temperature for 1 h and diethyl ether (20 mL) was added to precipitate the arenediazonium tetrafluoroborate that was filtered off and washed with diethyl ether (3 × 10 mL). The arenediazonium tetrafluoroborate was dried in vacuo (10^{-3} mbar) for 10 minutes and was then directly used without further purification.

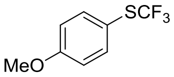
Synthesis of 1,3-benzothiazole-2-diazonium tetrafluoroborate [CAS: 29163-72-2].

Benzothiazole-2-diazonium tetrafluoroborate was prepared from 2-Amino-benzothiazole [CAS: 136-95-8].[1]

Synthesis of trifluoromethyl thioethers

Standard procedure for the synthesis of trifluoromethyl thioethers from the corresponding arenediazonium salts. An oven-dried 20 mL crimp cap vessel with Teflon-coated stirrer bar was charged with copper thiocyanate (61.4 mg, 0.50 mmol), caesium carbonate (652 mg, 2.00 mmol) and sodium thiocyanate (122 mg, 1.50 mmol) and was brought under an atmosphere of dry nitrogen. Acetonitrile (4 mL) was added *via* syringe and the resulting suspension was stirred at room temperature for 10 minutes. A solution of the arenediazonium tetrafluoroborate (1.00 mmol) in acetonitrile (4 mL) was added dropwise *via* syringe and the reaction mixture was stirred for another 10 minutes. Trifluoromethyltrimethylsilane (321 µL, 2.00 mmol) was added at once *via* syringe and the mixture was then stirred at ambient temperature for 16 h. The resulting mixture was filtered through a short pad of celite (5 g) and rinsed with diethyl ether (20 mL). The resulting organic solution was washed with water (10 mL) and brine (10 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated (700 mbar, 40 °C). The residue was further purified by flash chromatography (SiO_2, diethyl ether/hexane gradient), yielding the corresponding trifluoromethyl thioethers.

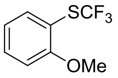
Synthesis of 1-methoxy-4-[(trifluoromethyl)thio]benzene (2) [CAS: 78914-94-0].



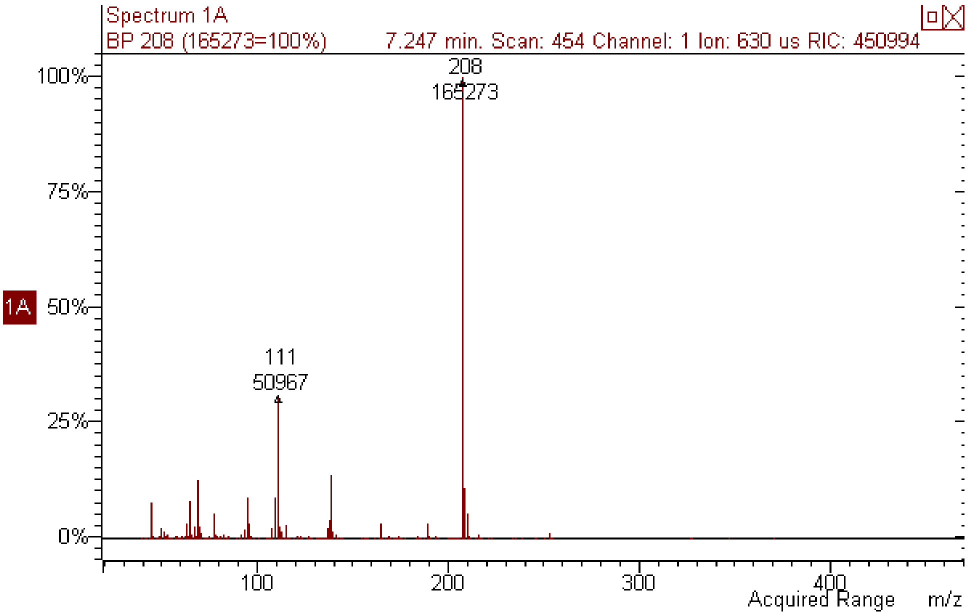
Compound **2** was prepared following the standard procedure, starting from 4-methoxybenzenediazonium tetrafluoroborate [CAS: 459-64-3] (222 mg, 1.00 mmol). After purification, **2** was isolated as colorless liquid (171 mg, 0.82 mmol, 82%). TLC (Et_2O:hexane, 1:4 vol/vol): R_f = 0.43; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.59 (d, ^3J(H,H)=8.8 Hz, 2H), 6.95 (d, ^3J(H,H)=8.8 Hz, 2H), 3.85 ppm (s, 3H); ^{19}F NMR (151 MHz, $CDCl_3$): δ=–44.0 ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ=161.8, 138.3 (2C), 129.6 (q,

^{1}J(C,F)=308.8 Hz, 1C), 115.0 (2C), 114.8 (q, ^{3}J(C,F)=1.8 Hz, 1C), 55.4 ppm.

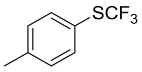
Synthesis of 1-methoxy-2-[(trifluoromethyl)thio]benzene (3) [CAS: 75168-99-9].



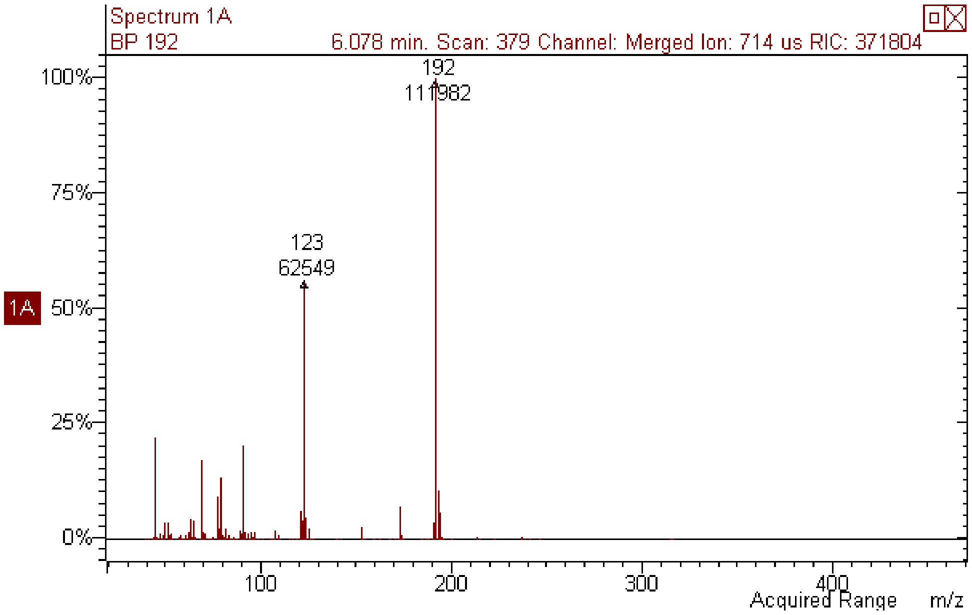
Compound **3** was prepared following the standard procedure, starting from 2-methoxybenzenediazonium tetrafluoroborate [CAS: 492-95-5] (222 mg, 1.00 mmol). After the reaction, 1,3-difluorobenzene as internal standard (100 µL, 1.00 mmol) was added to the reaction mixture and product **3** was formed in 77% yield as determined by ^{19}F NMR spectroscopic analysis and confirmed by GC-MS analytics. ^{19}F NMR (151 MHz, DMSO-d_6): δ =–43.3 ppm.



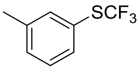
Synthesis of 4-[(trifluoromethyl)thio]toluene (4) [CAS: 352-68-1].



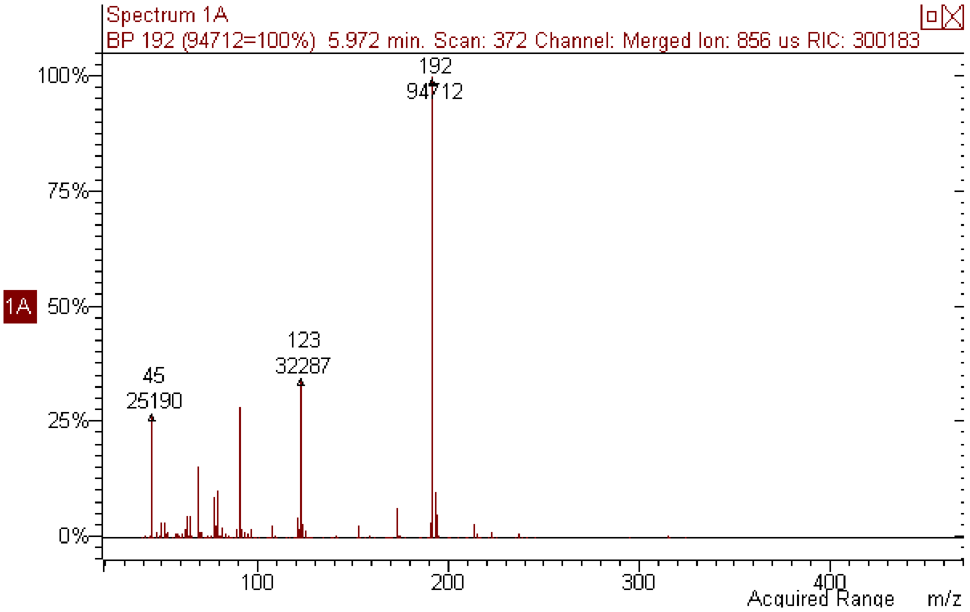
Compound **4** was prepared following the standard procedure, starting from 4-methylbenzenediazonium tetrafluoroborate [CAS: 459-44-9] (206 mg, 1.00 mmol). After the reaction, 1,3-difluorobenzene as internal standard (100 µL, 1.00 mmol) was added to the reaction mixture and product **4** was formed in 98% yield as determined by ^{19}F NMR spectroscopic analysis and confirmed by GC-MS analytics. ^{19}F NMR (151 MHz, DMSO-d_6): δ =–44.0 ppm.



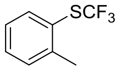
Synthesis of 3-[(trifluoromethyl)thio]toluene (5) [CAS: 705-46-4].



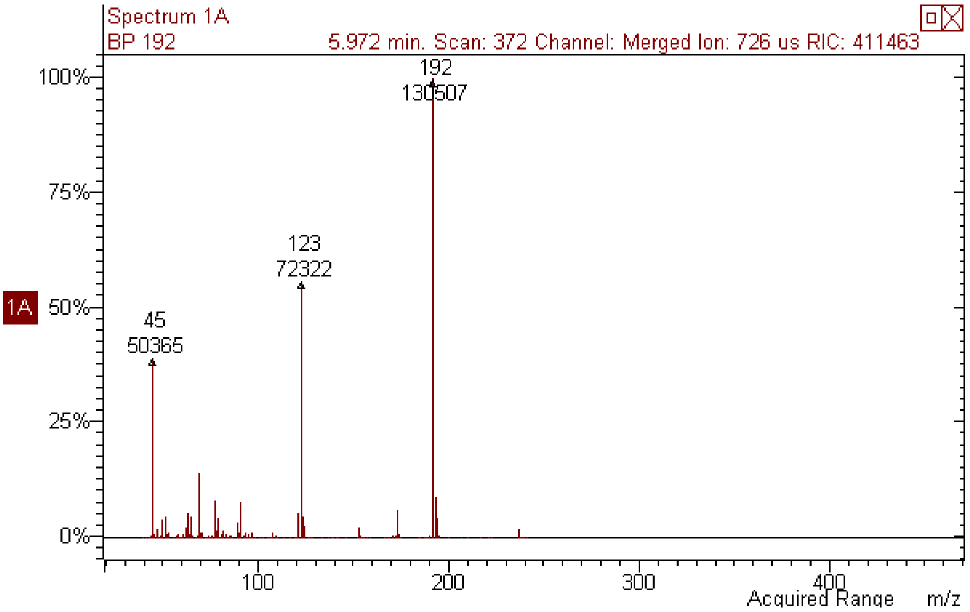
Compound **5** was prepared following the standard procedure, starting from 3-methylbenzenediazonium tetrafluoroborate [CAS: 1422-76-0] (206 mg, 1.00 mmol). After the reaction, 1,3-difluorobenzene as internal standard (100 µL, 1.00 mmol) was added to the reaction mixture and product **5** was formed in 98% yield as determined by ^{19}F NMR spectroscopic analysis and confirmed by GC-MS analytics. ^{19}F NMR (151 MHz, DMSO-d_6): δ =–43.6 ppm.



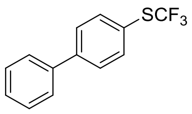
Synthesis of 2-[(trifluoromethyl)thio]toluene (6) [CAS: 1736-75-0].



Compound **6** was prepared following the standard procedure, starting from 2-methylbenzenediazonium tetrafluoroborate [CAS: 2093-46-1] (206 mg, 1.00 mmol). After the reaction, 1,3-difluorobenzene as internal standard (100 µL, 1.00 mmol) was added to the reaction mixture and product **6** was formed in 92% yield as determined by ^{19}F NMR spectroscopic analysis and confirmed by GC-MS analytics. ^{19}F NMR (151 MHz, DMSO-d_6): δ =–43.3 ppm.

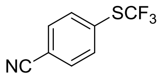


Synthesis of 4-[(trifluoromethyl)thio]biphenyl (7) [CAS: 177551-63-2].



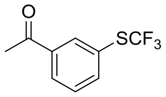
Compound **7** was prepared following the standard procedure, starting from [1,1’-biphenyl]-4-diazonium tetrafluoroborate [CAS: 52053-64-2] (268 mg, 1.00 mmol). After purification, **7** was isolated as colorless solid (187 mg, 0.74 mmol, 74%). TLC (Et_2O:hexane, 1:4 vol/vol): R_f = 0.57; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.79 (d, ^3J(H,H)=8.3 Hz, 2H), 7.67 (m, 4H), 7.53 (m, 2H), 7.47 ppm (m, 1H); ^{19}F NMR (151 MHz, $CDCl_3$): δ=–42.6 ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ=143.8, 139.6, 136.7 (2C), 129.6 (q, ^1J(C,F)=308.8 Hz, 1C), 128.9 (2C), 128.1, 128.1 (2C), 127.2 (2C), 123.0 ppm (q, ^3J(C,F)=1.8 Hz, 1C).

Synthesis of 4-[(trifluoromethyl)thio]benzonitrile (8) [CAS: 332-26-3].



Compound **8** was prepared following the standard procedure, starting from 4-cyanobenzenediazonium tetrafluoroborate [CAS: 2252-32-6] (217 mg, 1.00 mmol). After purification, **8** was isolated as colorless liquid (175 mg, 0.86 mmol, 86%). TLC (Et_2O:hexane, 1:4 vol/vol): R_f = 0.32; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.77 (d, ^3J(H,H)=8.6 Hz, 2H), 7.71 ppm (d, ^3J(H,H)=8.6 Hz, 2H); ^{19}F NMR (151 MHz, $CDCl_3$): δ=–41.5 ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ=135.9 (2C), 132.9 (2C), 130.5 (q, ^3J(C,F)=1.8 Hz, 1C), 129.0 (q, ^1J(C,F)=308.8 Hz, 1C), 117.6, 114.6 ppm.

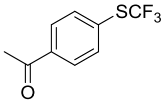
Synthesis of 3-[(trifluoromethyl)thio]acetophenone (9) [CAS: 56773-33-2].



Compound **9** was prepared following the standard procedure, starting from 3-acetylbenzenediazonium tetrafluoroborate [CAS: 59206-56-3] (234 mg, 1.00 mmol). After purification, **9** was isolated as colorless liquid

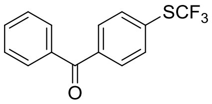
(136 mg, 0.62 mmol, 62%). TLC (Et_2O:hexane, 1:4 vol/vol): R_f = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.22 (s, 1H), 8.07 (d, ^3J(H,H)=7.8 Hz, 1H), 7.85 (d, ^3J(H,H)=7.8 Hz, 1H), 7.54 (t, ^3J(H,H)=7.8 Hz, 1H), 2.63 ppm (s, 3H); ^{19}F NMR (151 MHz, $CDCl_3$): δ=–42.5 ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ=196.6, 140.4, 138.2, 136.0, 130.5, 129.8, 129.3 (q, ^1J(C,F)=307.9 Hz, 1C), 125.3 (q, ^3J(C,F)=1.8 Hz, 1C), 26.6 ppm.

Synthesis of 4-[(trifluoromethyl)thio]acetophenone (10) [CAS: 713-67-7].



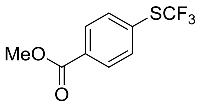
Compound **10** was prepared following the standard procedure, starting from 4-acetylbenzenediazonium tetrafluoroborate [CAS: 350-47-0] (234 mg, 1.00 mmol). After purification, **10** was isolated as colorless liquid (156 mg, 0.71 mmol, 71%). TLC (Et_2O:hexane, 1:4 vol/vol): R_f = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.98 (d, ^3J(H,H)=8.2 Hz, 2H), 7.74 (d, ^3J(H,H)=8.3 Hz, 2H), 2.62 ppm (s, 3H); ^{19}F NMR (151 MHz, $CDCl_3$): δ=–41.8 ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ=197.0, 138.4, 135.7 (2C), 129.9 (q, ^3J(C,F)=1.8 Hz, 1C), 129.2 (q, ^1J(C,F)=308.8 Hz, 1C), 129.0 (2C), 26.6 ppm.

Synthesis of 4-[(trifluoromethyl)thio]benzophenone (11) [CAS: 41830-99-3].



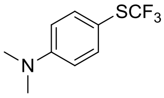
Compound **11** was prepared following the standard procedure, starting from 4-benzoylbenzenediazonium tetrafluoroborate [CAS: 38246-74-1] (296 mg, 1.00 mmol). After purification, **11** was isolated as colorless solid (165 mg, 0.59 mmol, 59%). TLC (Et_2O:hexane, 1:4 vol/vol): R_f = 0.41; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.81 (m, 6H), 7.62 (m, 1H), 7.51 ppm (m, 2H); ^{19}F NMR (151 MHz, $CDCl_3$): δ=–41.8 ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ=195.5, 139.4, 136.7, 135.5 (2C), 132.9, 130.6 (2C), 130.0 (2C), 129.3 (q, ${}^{1}J$(C,F)=308.8 Hz, 1C), 129.0 (q, ${}^{3}J$(C,F)=1.8 Hz, 1C), 128.4 ppm (2C).

Synthesis of methyl 4-[(trifluoromethyl)thio]benzoate (12) [CAS: 88489-60-5].



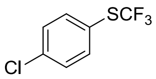
Compound **12** was prepared following the standard procedure, starting from 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate [CAS: 369-48-2] (250 mg, 1.00 mmol). After purification, **12** was isolated as colorless liquid (187 mg, 0.79 mmol, 79%). TLC (Et_2O:hexane, 1:4 vol/vol): R_f = 0.37; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.06 (d, ${}^{3}J$(H,H)=8.5 Hz, 2H), 7.71 (d, ${}^{3}J$(H,H)=8.3 Hz, 2H), 3.93 ppm (s, 3H); ^{19}F NMR (151 MHz, $CDCl_3$): δ=–41.9 ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ=166.9, 135.5 (2C), 132.1, 130.4 (2C), 129.8 (q, ${}^{3}J$(C,F)=1.8 Hz, 1C), 129.3 (q, ${}^{1}J$(C,F)=308.8 Hz, 1C), 52.4 ppm.

Synthesis of *N,N*-dimethyl-4-[(trifluoromethyl)thio]aniline (13) [CAS: 2677-71-6].

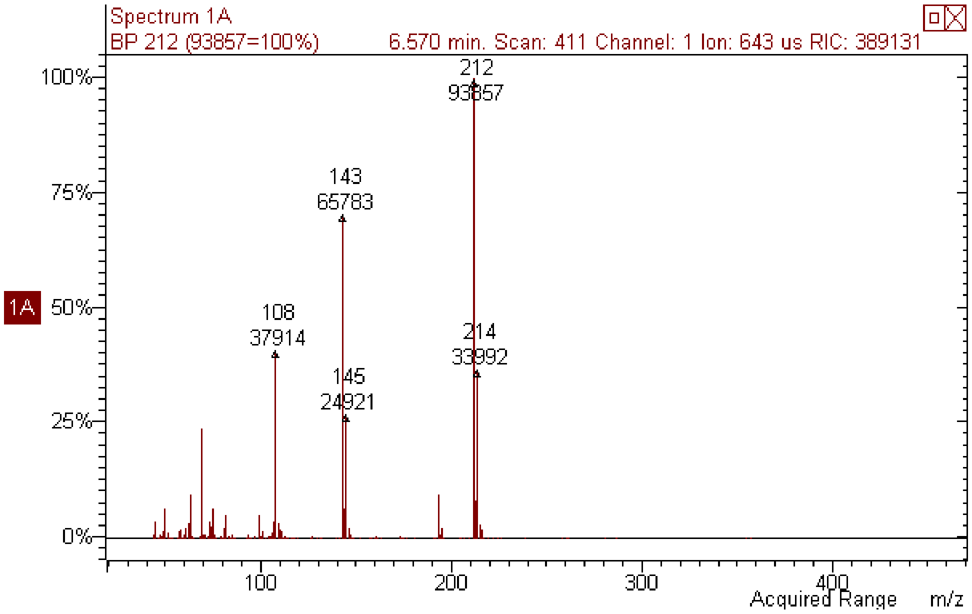


Compound **13** was prepared following the standard procedure, starting from 4-(dimethylamino)benzenediazonium tetrafluoroborate [CAS: 24564-52-1] (235 mg, 1.00 mmol). After purification, **13** was isolated as colorless liquid (183 mg, 0.83 mmol, 83%). TLC (Et_2O:hexane, 1:4 vol/vol): R_f = 0.40; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.51 (d, ${}^{3}J$(H,H)=8.8 Hz, 2H), 6.70 (d, ${}^{3}J$(H,H)=8.8 Hz, 2H), 3.03 ppm (s, 6H); ^{19}F NMR (151 MHz, $CDCl_3$): δ=–44.7 ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ=151.9, 137.9 (2C), 129.8 (q, ${}^{1}J$(C,F)=308.8 Hz, 1C), 112.3 (2C), 108.2 (q, ${}^{3}J$(C,F)=1.8 Hz, 1C), 40.0 ppm (2C).

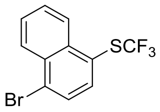
Synthesis of 1-chloro-4-[(trifluoromethyl)thio]benzene (14) [CAS: 407-16-9].



Compound **14** was prepared following the standard procedure, starting from 4-chlorobenzenediazonium tetrafluoroborate [CAS: 673-41-6] (226 mg, 1.00 mmol). After the reaction, 1,3-difluorobenzene as internal standard (100 µL, 1.00 mmol) was added to the reaction mixture and product **14** was formed in 98% yield as determined by ^{19}F NMR spectroscopic analysis and confirmed by GC-MS analytics. ^{19}F NMR (151 MHz, DMSO-d_6): δ =–43.7 ppm.



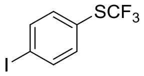
Synthesis of 1-bromo-4-[(trifluoromethyl)thio]naphthalene (15).



Compound **15** was prepared following the standard procedure, starting from 4-bromonaphthalen-1-yldiazonium tetrafluoroborate [CAS: 341-89-9] (321 mg, 1.00 mmol). After purification, **15** was isolated as colorless liquid (227 mg, 0.74 mmol, 74%). TLC (Et_2O:hexane, 1:4 vol/vol): R_f = 0.62; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.57 (m, 1H), 8.32 (m, 1 H), 7.81 (m, 2 H), 7.69 ppm (m, 2H); ^{19}F NMR (151 MHz, $CDCl_3$): δ=–42.1 ppm;

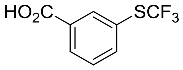
^{13}C NMR (101 MHz, $CDCl_3$): δ=137.5, 136.1, 132.7, 129.7, 129.2 (q, ^1J(C,F)=309.7 Hz, 1C), 128.4, 128.1, 128.0, 127.9, 126.4, 121.6 ppm (q, ^3J(C,F)=1.8 Hz, 1C); IR (NaCl): *ν*=3073 (w), 1497 (s), 1370 (m), 1158 (s), 1146 (s), 1130 (vs), 1110 (vs), 976 (s), 828 (m), 760 cm^{-1} (s); MS (70 eV): *m*/*z* (%): 308 (12), 307 (100) [M^+], 239 (66), 237 (57), 158 (46), 114 (15), 69 (22); HRMS-EI (TOF) (*m*/*z*): [M+] calcd for $C_{11}H_6{}^{79}Br_1F_3{}^{32}S_1$, 305.9320; found, 305.9336.

Synthesis of 1-iodo-4-[(trifluoromethyl)thio]benzene (16) [CAS: 372-15-6].



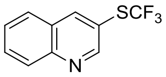
Compound **16** was prepared following the standard procedure, starting from 4-iodobenzenediazonium tetrafluoroborate [CAS: 1514-50-7] (318 mg, 1.00 mmol). After chromatography, **16** was obtained as colorless liquid (238 mg, 0.78 mmol, 78%) which contained traces of iodobenzene. TLC (Et_2O:hexane, 1:4 vol/vol): R_f = 0.61; ^1H NMR (400 MHz, $CDCl_3$): δ=7.63 (d, ^3J(H,H)=8.5 Hz, 2H), 7.23 ppm (d, ^3J(H,H)=8.3 Hz, 2H); ^{19}F NMR (151 MHz, $CDCl_3$): δ=–42.6 ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ=138.7 (2C), 137.7 (2C), 129.1 (q, ^1J(C,F)=308.8 Hz, 1C), 124.1 (q, ^3J(C,F)=1.8 Hz, 1C), 98.0 ppm.

Synthesis of 3-[(trifluoromethyl)thio]benzoic acid (17) [CAS: 946-65-6].



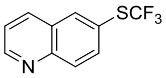
Compound **17** was prepared following the standard procedure, starting from 3-carboxybenzenediazonium tetrafluoroborate [CAS: 20873-47-6] (236 mg, 1.00 mmol). After chromatography, **17** was obtained as colorless solid (52 mg, 0.23 mmol, 23%) which contained 5% of benzoic acid. TLC (Et_2O:hexane, 1:4 vol/vol): R_f = 0.05; ^1H NMR (400 MHz, $CDCl_3$): δ=8.43 (bs, 1H), 8.26 (dt, $^{3,4}J$(H,H)=7.9, 1.4 Hz, 1H), 7.93 (d, ^3J(H,H)=7.8 Hz, 1H), 7.59 ppm (d, ^3J(H,H)=7.8 Hz, 1H); ^{19}F NMR (151 MHz, $CDCl_3$): δ=–42.4 ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ=170.9, 141.4, 137.9, 132.5, 130.8, 129.8, 129.4 (q, ^1J(C,F)=308.8 Hz, 1C), 125.4 ppm (q, ^3J(C,F)=2.2 Hz, 1C).

Synthesis of 3-[(trifluoromethyl)thio]quinoline (18) [CAS: 1333415-90-9].



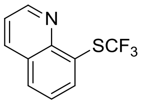
Compound **18** was prepared following the standard procedure, starting from quinoline-3-diazonium tetrafluoroborate [CAS: 398-41-4] (243 mg, 1.00 mmol). After purification, **18** was isolated as colorless solid (142 mg, 0.62 mmol, 62%). TLC (Et_2O:hexane, 1:4 vol/vol): R_f = 0.13; ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.03 (d, ^4J(H,H)=2.3 Hz, 1H), 8.50 (d, ^4J(H,H)=2.0 Hz, 1H), 8.15 (m, 1H), 7.82 (m, 2H), 7.62 ppm (m, 1H); ^{19}F NMR (151 MHz, $CDCl_3$): δ=–43.3 ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ=154.5, 148.3, 144.7, 131.6, 129.5, 129.1 (q, ^1J(C,F)=308.8 Hz, 1C), 128.0, 127.7, 127.7, 118.2 ppm (q, ^3J(C,F)=1.8 Hz, 1C).

Synthesis of 6-[(trifluoromethyl)thio]quinoline (19).



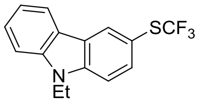
Compound **19** was prepared following the standard procedure, starting from quinoline-6-diazonium tetrafluoroborate [CAS: 2366-78-1] (243 mg, 1.00 mmol). After purification, **19** was isolated as colorless solid (125 mg, 0.55 mmol, 55%). m.p. 54.4 °C; TLC (Et_2O:hexane, 1:4 vol/vol): R_f = 0.08; ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.02 (br. s, 1H), 8.17 (m, 3H), 7.9 (dd, $^{3,4}J$(H,H)=8.5, 1.8 Hz, 1H), 7.49 ppm (dd, $^{3,4}J$(H,H)=8.0, 4.0 Hz, 1H); ^{19}F NMR (151 MHz, $CDCl_3$): δ=–42.3 ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ=152.2, 148.6, 136.7, 136.2, 135.4, 130.9, 129.5 (q, ^1J(C,F)=308.8 Hz, 1C), 128.3, 122.7 (q, ^3J(C,F)=1.8 Hz, 1C), 122.1 ppm; IR (KBr): ν=1489 (m), 1158 (vs), 1132 (vs), 1116 (vs), 1106 (vs), 1070 (s), 894 (s), 836 (vs), 794 (s), 754 cm^{-1} (s); MS (70 eV): *m*/*z* (%): 230 (5), 229 (100) [M^+], 160 (46), 116 (21), 89 (11), 69 (16), 63 (5); HRMS-EI (TOF) (*m*/*z*): [M+] calcd for $C_{10}H_6N_1F_3{}^{32}S_1$, 229.0168; found, 229.0165.

Synthesis of 8-[(trifluoromethyl)thio]quinoline (20).



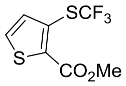
Compound **20** was prepared following the standard procedure, starting from quinoline-8-diazonium tetrafluoroborate [CAS: 27388-19-8] (243 mg, 1.00 mmol). After purification, **20** was isolated as colorless liquid (72 mg, 0.31 mmol, 31%). TLC (Et_2O:hexane, 1:4 vol/vol): R_f = 0.15; ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.02 (dd, $^{3,4}J$(H,H)=4.2, 1.7 Hz, 1H), 8.20 (dd, $^{3,4}J$(H,H)=8.3, 1.7 Hz, 1H), 8.08 (d, ^3J(H,H)=7.3 Hz, 1H), 7.88 (m, 1H), 7.63–7.45 ppm (m, 2H); ^{19}F NMR (151 MHz, $CDCl_3$): δ=–41.1 ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ=150.7, 146.7, 136.5, 134.0, 129.9 (q, ^1J(C,F)=308.8 Hz, 1C), 129.6, 128.8, 126.9 (q, ^3J(C,F)=1.8 Hz, 1C), 126.6, 122.1 ppm; IR (NaCl): ν=1607 (m), 1595 (m), 1491 (s), 1459 (m), 1306 (w), 1108 (vs), 980 (m), 822 (m), 788 (m), 756 cm^{-1} (w); MS (70 eV): *m*/*z* (%):230 (5), 229 (100) [M^+], 161 (6), 160 (48), 116 (21), 89 (11), 69 (13); HRMS-EI (TOF) (*m/z*): [M+] calcd for $C_{10}H_6N_1F_3{}^{32}S_1$, 229.0166; found, 229.0168.

Synthesis of 9-ethyl-3-[(trifluoromethyl)thio]-9*H*-carbazole (21).



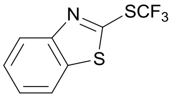
Compound **21** was prepared following the standard procedure, starting from 9-ethyl-9*H*-carbazol-3-diazonium tetrafluoroborate [CAS: 115771-91-0] (309 mg, 1.00 mmol). After purification, **21** was isolated as colorless solid (195 mg, 0.66 mmol, 66%). m.p. 71.6 °C; TLC (Et_2O:hexane, 1:4 vol/vol): R_f = 0.26; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.45 (d, ^4J(H,H)=1.8 Hz, 1H), 8.15 (d, ^3J(H,H)=7.8 Hz, 1H), 7.78 (dd, $^{3,4}J$(H,H)=8.5, 1.8 Hz, 1H), 7.57 (m, 1H), 7.44 (d, ^3J(H,H)=8.3 Hz, 1H), 7.41 (d, ^3J(H,H)=8.5 Hz, 1H), 7.35 (d, $^{3,4}J$(H,H)=7.5, 0.9 Hz, 1H), 4.32 (q, ^3J(H,H)=7.2 Hz, 2H), 1.45 ppm (t, ^3J(H,H)=7.2 Hz, 3H); ^{19}F NMR (151 MHz, $CDCl_3$): δ=–43.9 ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ=141.0, 140.3, 133.7, 130.0 (q, ^1J(C,F)=308.8 Hz, 1C), 129.5, 126.6, 123.8, 122.1, 120.6, 119.7, 112.4 (q, ^3J(C,F)=1.8 Hz, 1C), 109.2, 108.8, 37.6, 13.7 ppm. IR (KBr): ν=2975 (w), 1475 (s), 1449 (s), 1234 (s), 1134 (vs), 1124 (vs), 1108 (vs), 744 (vs), 722 (vs), 604 cm^{-1} (s); MS (70 eV): *m*/*z* (%):296 (6), 295 (100) [M^+], 281 (5), 280 (31), 227 (7), 226 (47), 69 (14); HRMS-EI (TOF) (*m/z*): [M+] calcd for $C_{15}H_{12}N_1F_3{}^{32}S_1$, 295.0637; found, 295.0636.

Synthesis of methyl 3-[(trifluoromethyl)thio]thiophene-2-carboxylate (22).



Compound **22** was prepared following the standard procedure, starting from 2-(methoxycarbonyl)thiophene-3-diazonium tetrafluoroborate [CAS: 100421-50-9] (256 mg, 1.00 mmol). After purification, **22** was isolated as colorless liquid (142 mg, 0.59 mmol, 59%). TLC (Et$_2$O:hexane, 1:4 vol/vol): R_f = 0.33; ^{1}H NMR (400 MHz, CDCl$_3$): δ=7.60 (d, ^3J(H,H)=5.3 Hz, 1H), 7.25 (dq, ^3J(H,H)=5.3 Hz, ^5J(H,F)=1.4 Hz, 1H), 3.91 ppm (s, 3H); ^{19}F NMR (151 MHz, CDCl$_3$): δ=–41.4 ppm; ^{13}C NMR (101 MHz, CDCl$_3$): δ=161.7, 131.7, 130.6 (q, ^3J(C,F)=1.8 Hz, 1C), 129.6 (q, ^1J(C,F)=308.8 Hz, 1C), 129.2 (q, ^3J(C,F)=1.8 Hz, 1C), 128.4, 52.5 ppm; IR (NaCl): ν=3105 (m), 2957 (s), 1701 (vs), 1501 (s), 1439 (s), 1407 (s), 1274 (s), 1152 (s), 1136 (s), 1106 cm^{-1} (s); MS (70 eV): *m*/*z* (%):243 (10), 241 (100) [M^+], 211 (50), 173 (42), 143 (11), 142 (15), 69 (23); HRMS-EI (TOF) (*m/z*): [M+] calcd for $C_7H_5O_2F_3{}^{32}S_2$, 241.9675; found, 241.9678.

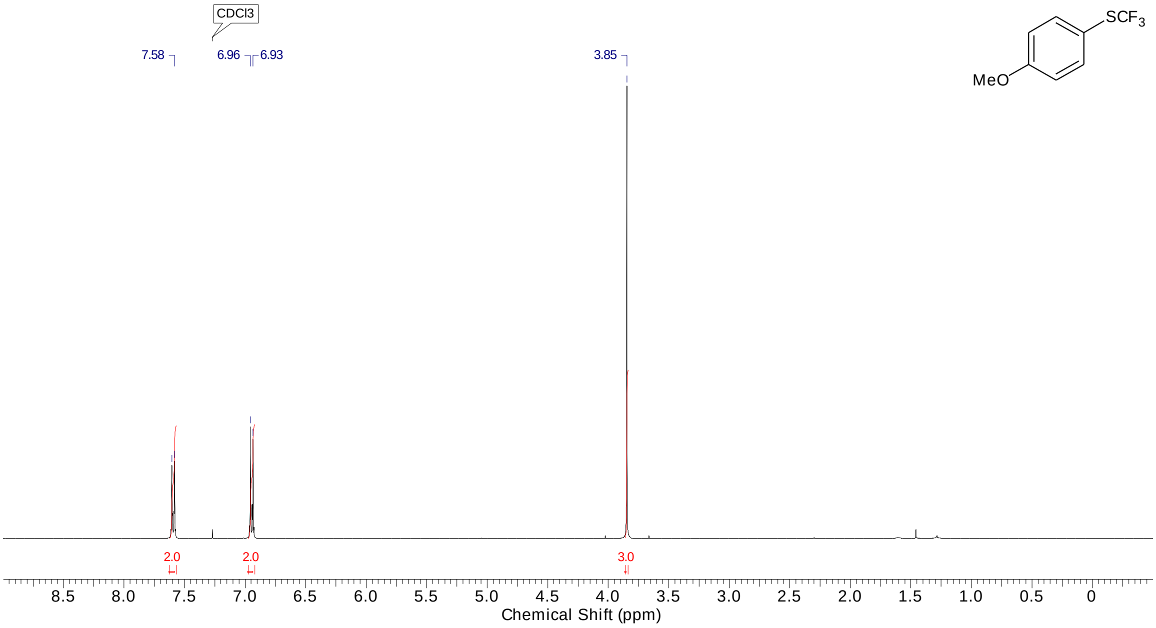
Synthesis of 2-[(Trifluoromethyl)thio]benzothiazole (23) [CAS: 63647-63-2].

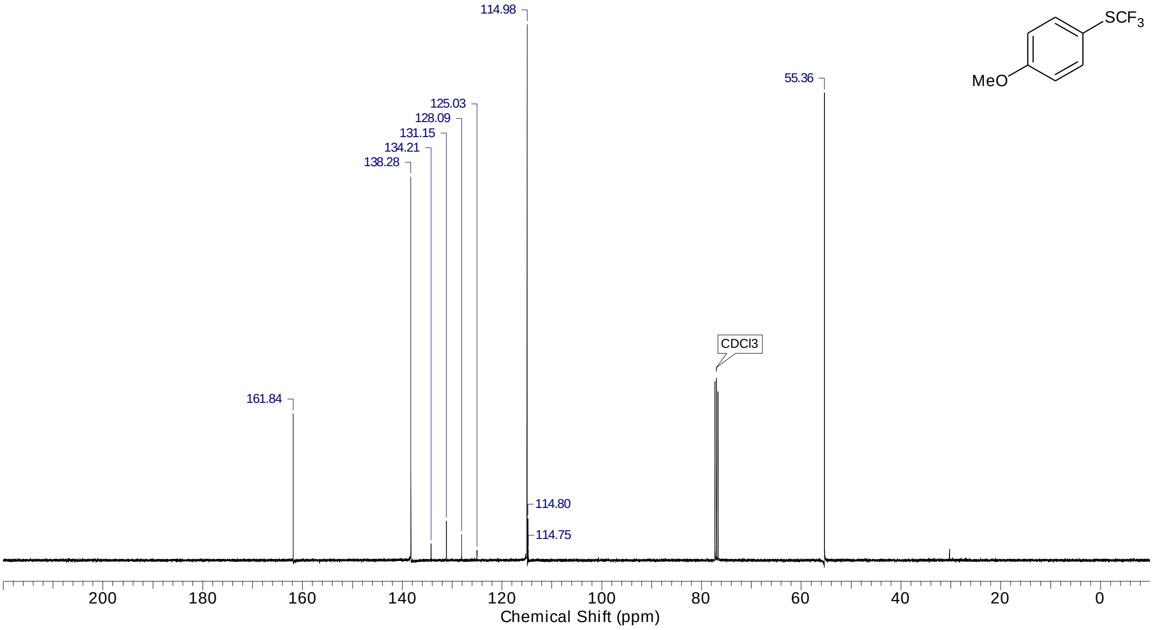


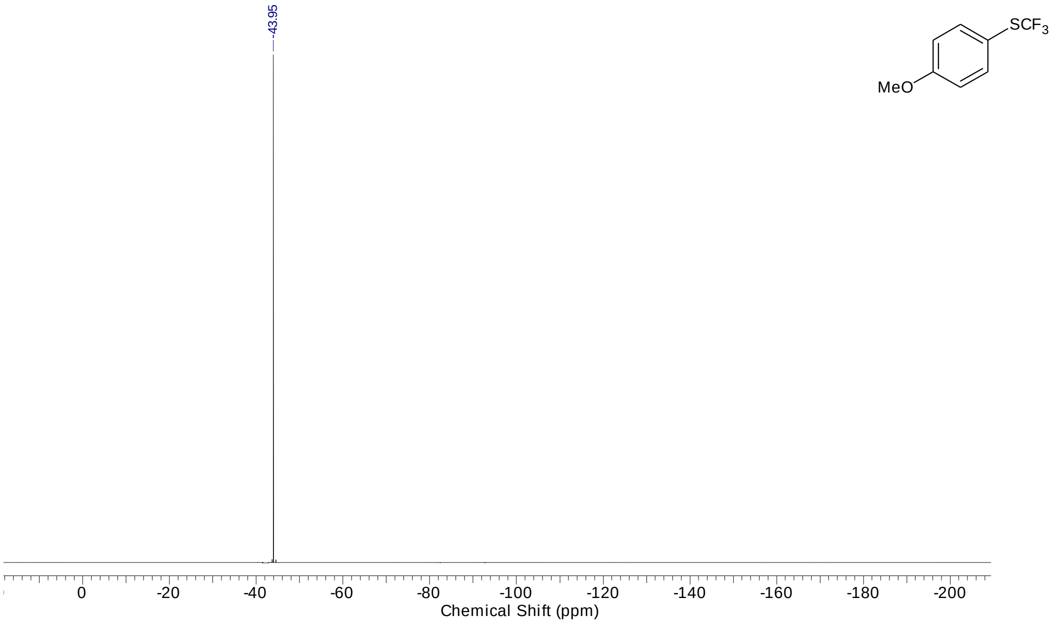
Compound **23** was prepared following the standard procedure, starting from 1,3-benzothiazole-2-diazonium tetrafluoroborate [CAS: 29163-72-2] (249 mg, 1.00 mmol). After purification, **23** was isolated as colorless solid (98 mg, 0.42 mmol, 42%). TLC (Et$_2$O:hexane, 1:4 vol/vol): R_f =0.40; ^{1}H NMR (400 MHz, CDCl$_3$): δ=8.15 (d, ^3J(H,H)=8.0 Hz, 1H), 7.91

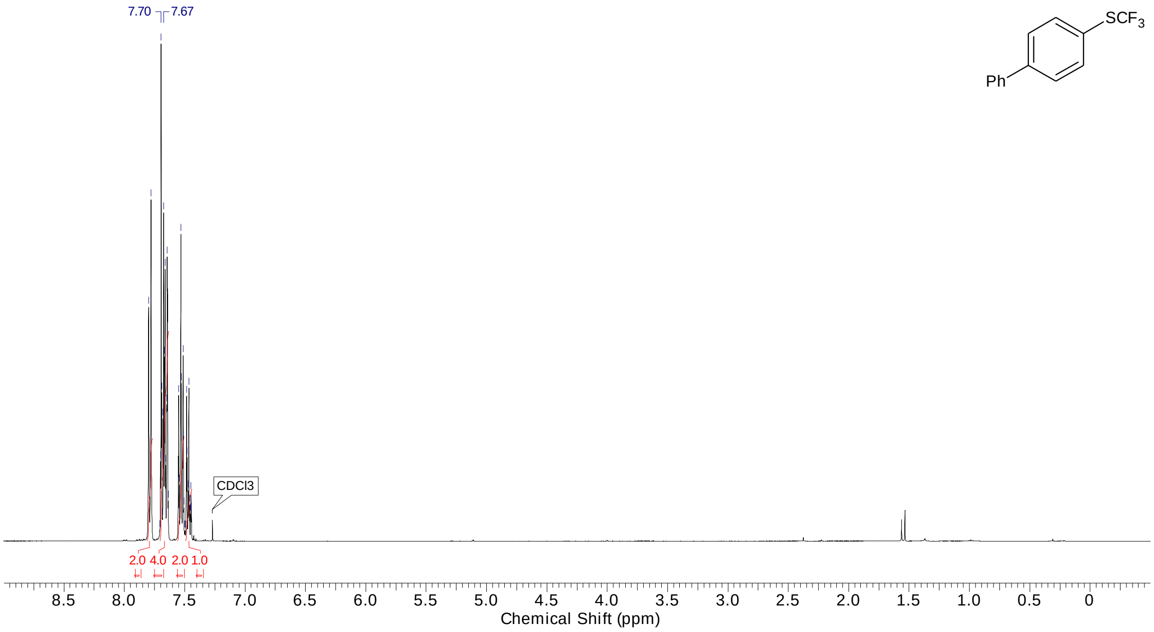
(d, ^{3}J(H,H)=8.03 Hz, 1H), 7.54 ppm (m, 2H); ^{19}F NMR (151 MHz, $CDCl_3$): δ=–40.2 ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ=153.1, 151.7 (q, ^{3}J(C,F)=2.7 Hz, 1C), 137.9, 129.7 (q, ^{1}J(C,F)=310.6 Hz, 1C), 127.0, 126.7, 124.1, 121.3 ppm.

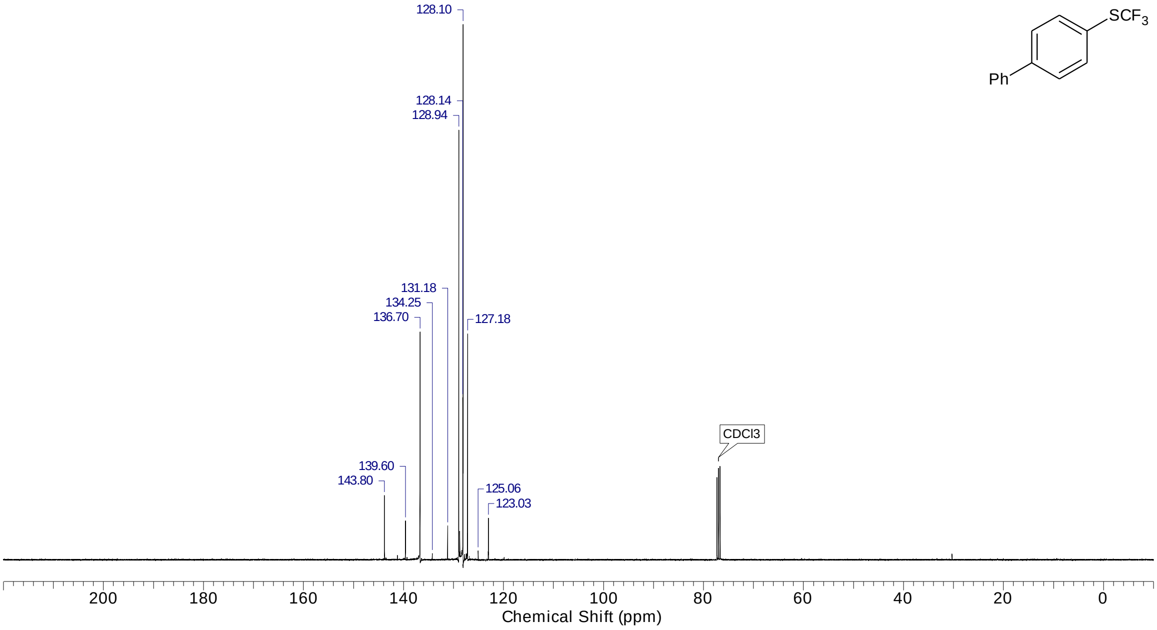
Spectroscopic data

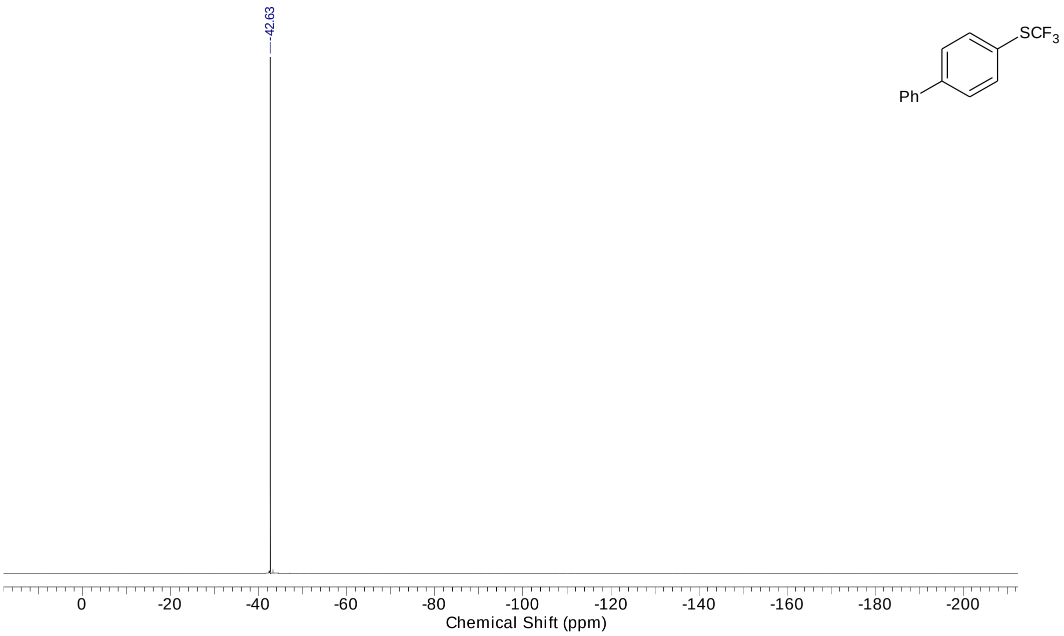


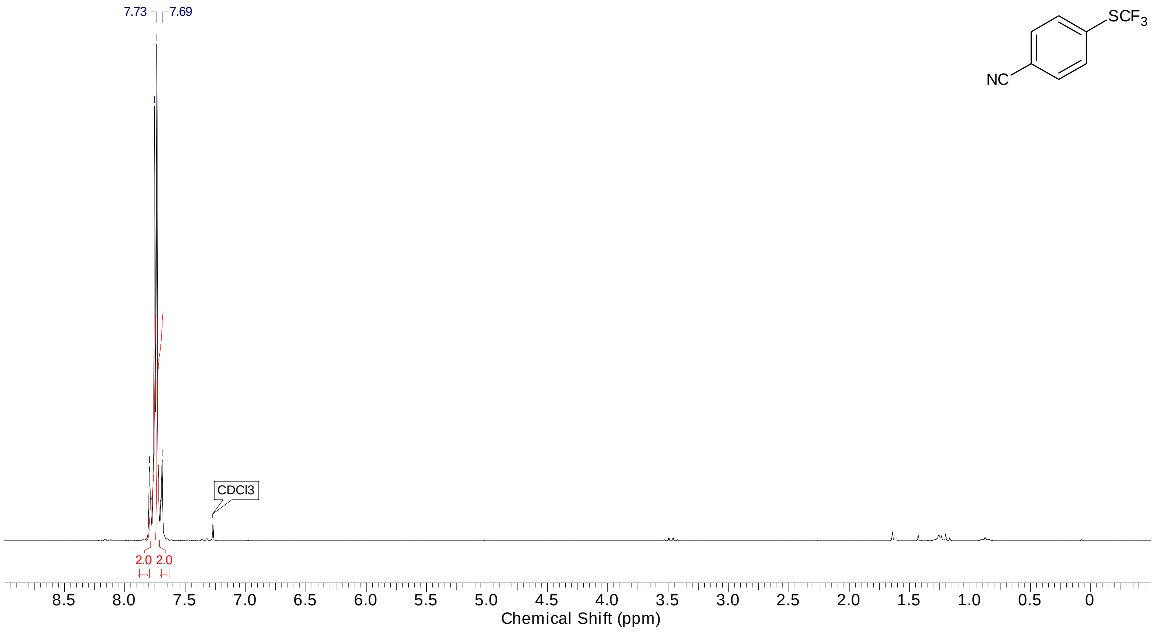


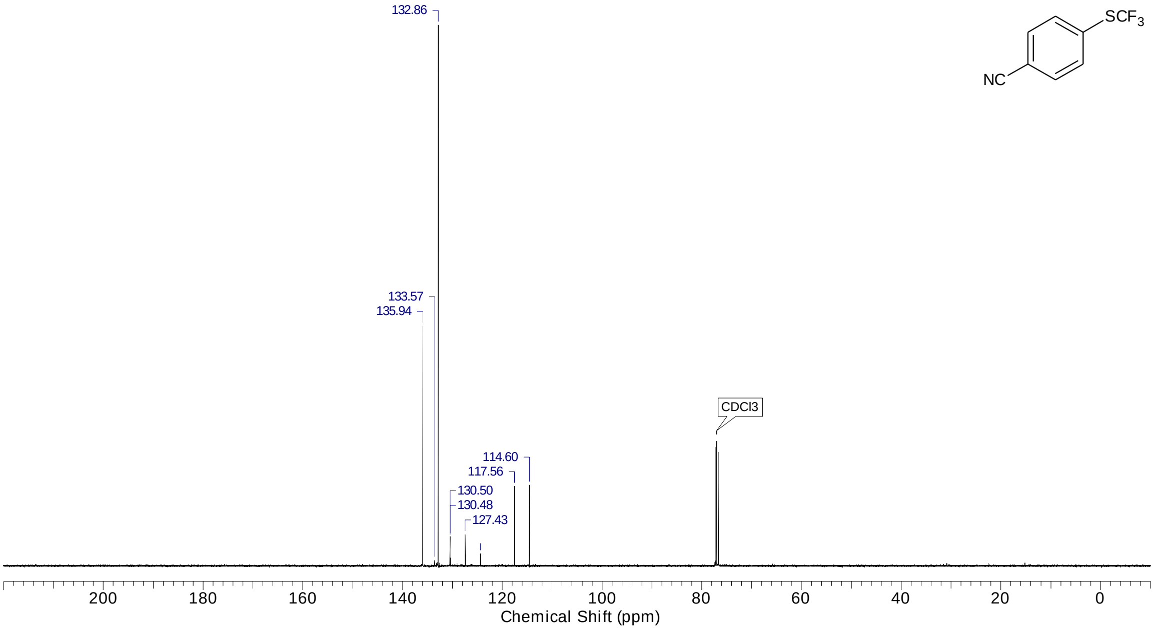

-43.95
SCF$_3$
MeO
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

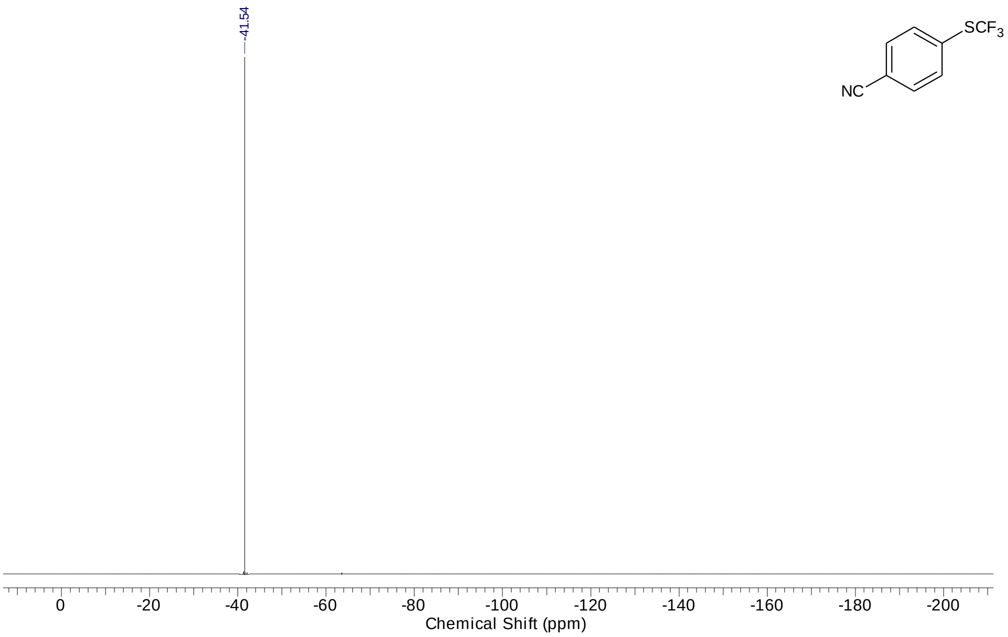

7.70
7.67
SCF$_3$
Ph
CDCl3
2.0
4.0
2.0
1.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

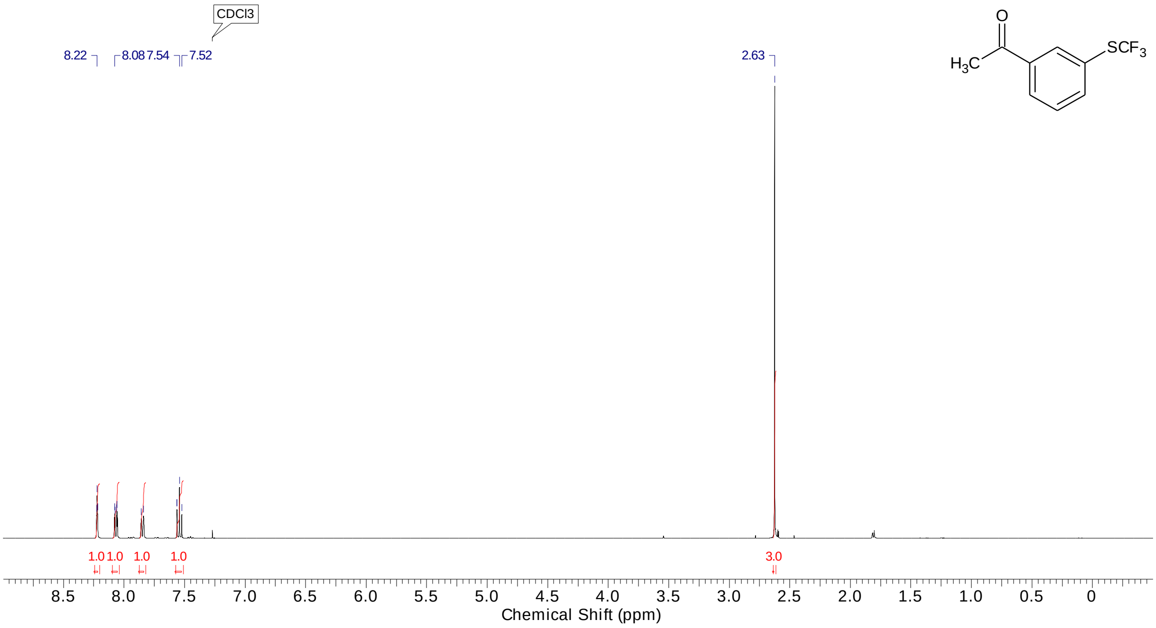

128.10
128.14
128.94
131.18
134.25
136.70
127.18
139.60
143.80
125.06
123.03
SCF$_3$
Ph
CDCl3
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

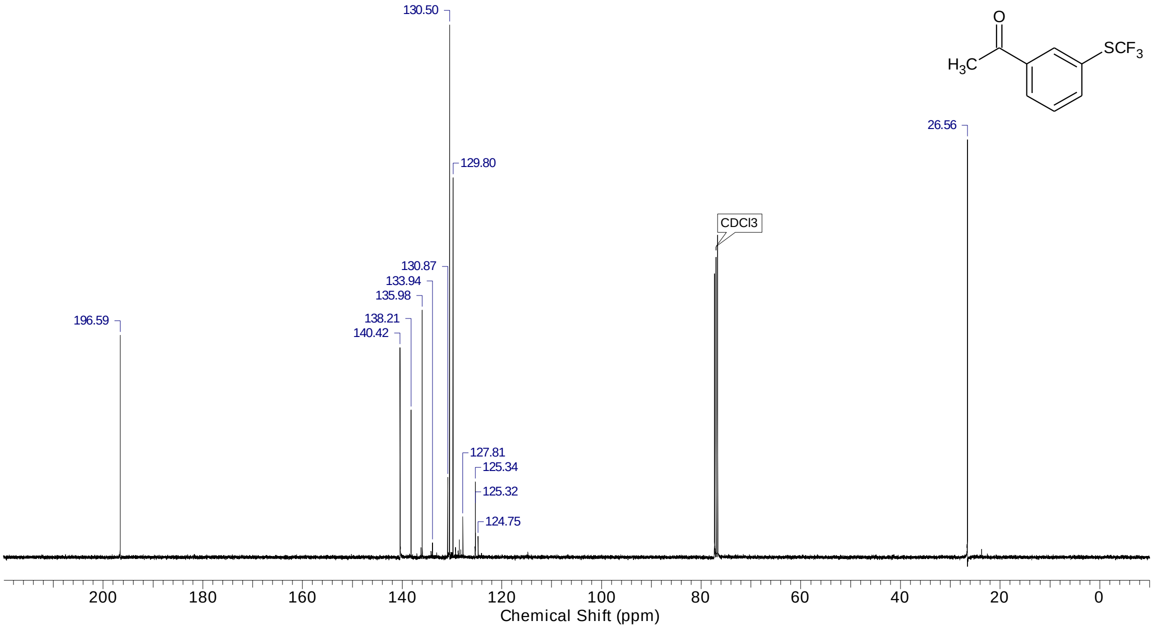

-42.63
SCF$_3$
Ph
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

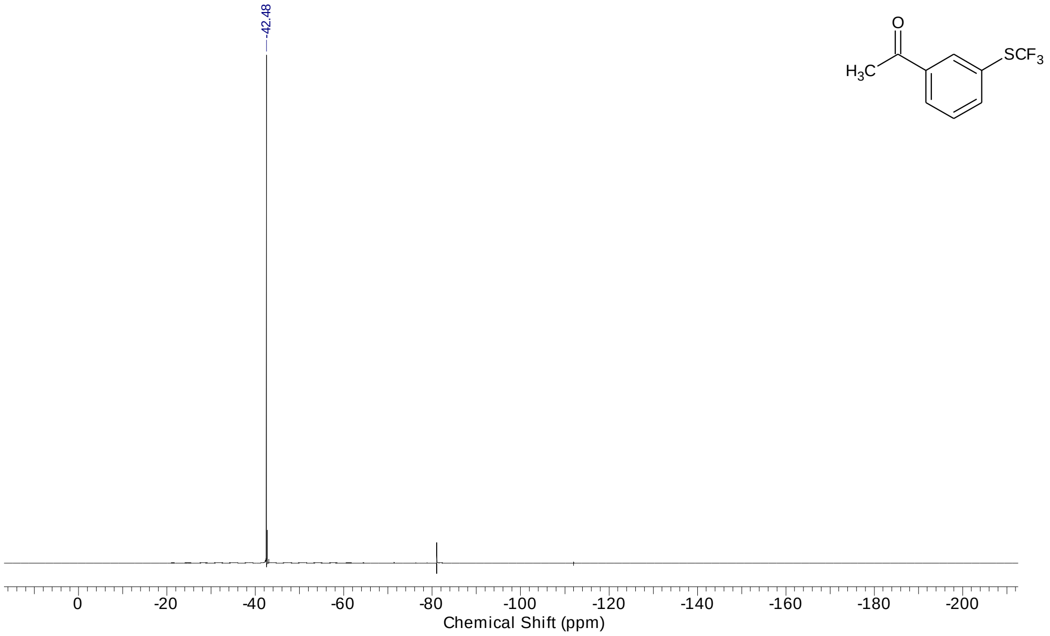

7.73
7.69
SCF3
NC
CDCl3
2.0
2.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

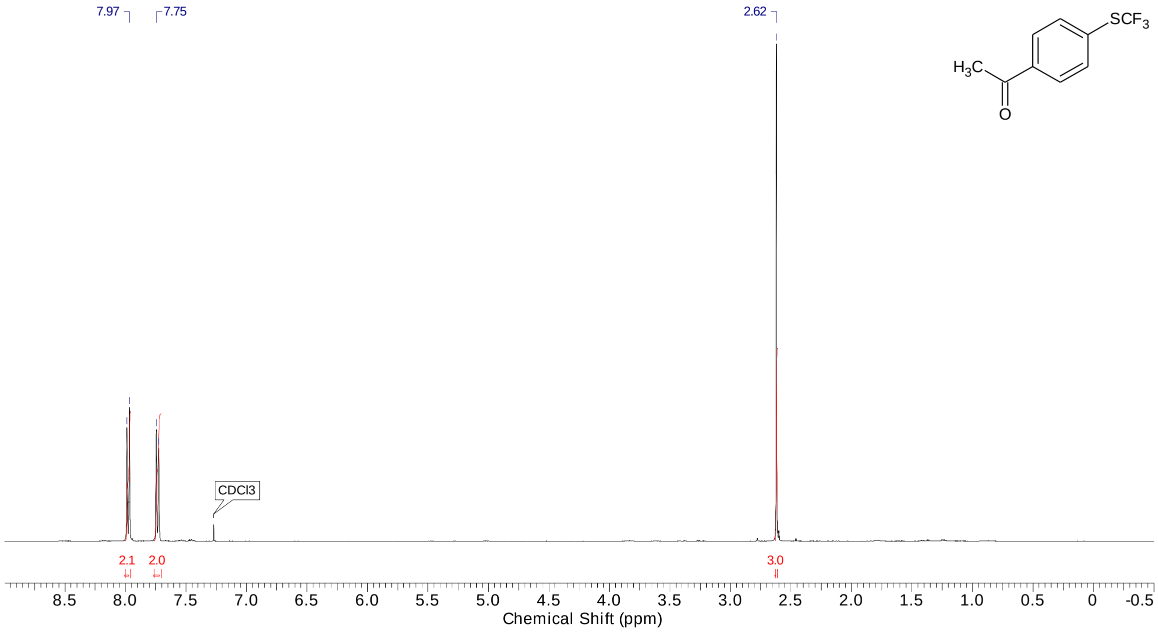

132.86
SCF3
NC
133.57
135.94
CDCl3
114.60
117.56
130.50
130.48
127.43
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

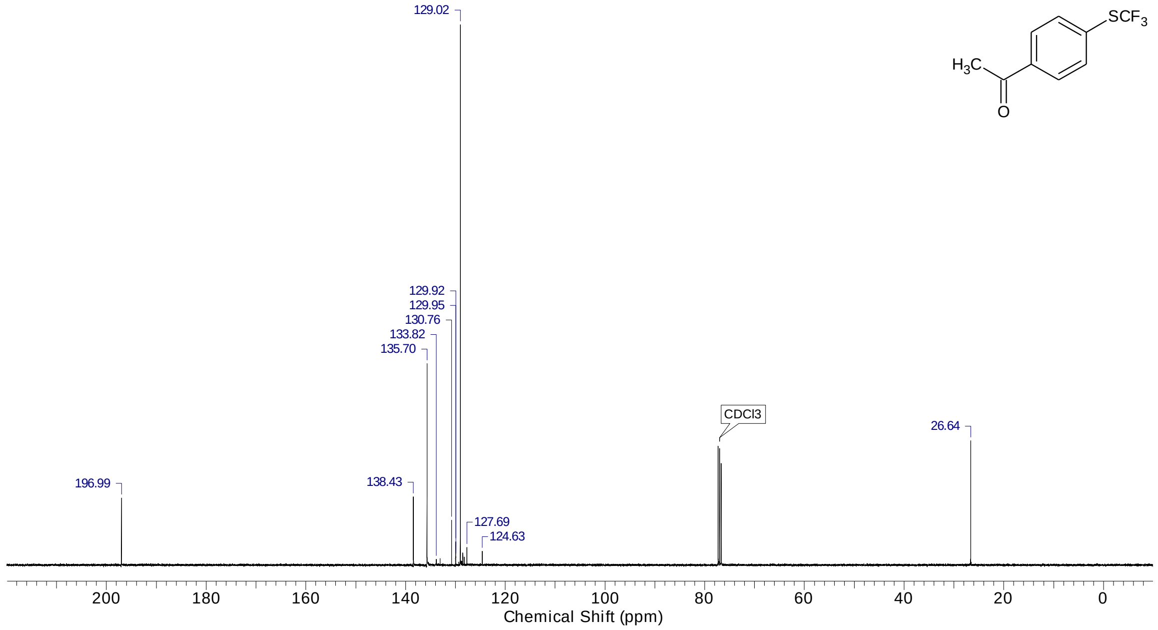

-41.54
SCF3
NC
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

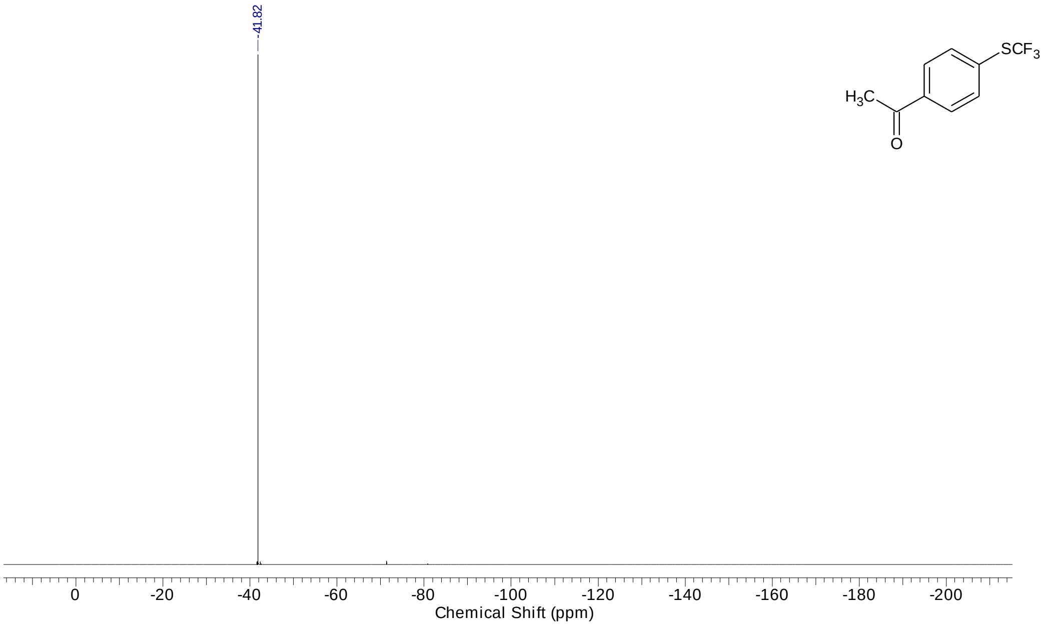

CDCl3
8.22
8.08
7.54
7.52
2.63
O
H_3C
SCF_3
1.0
1.0
1.0
1.0
3.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

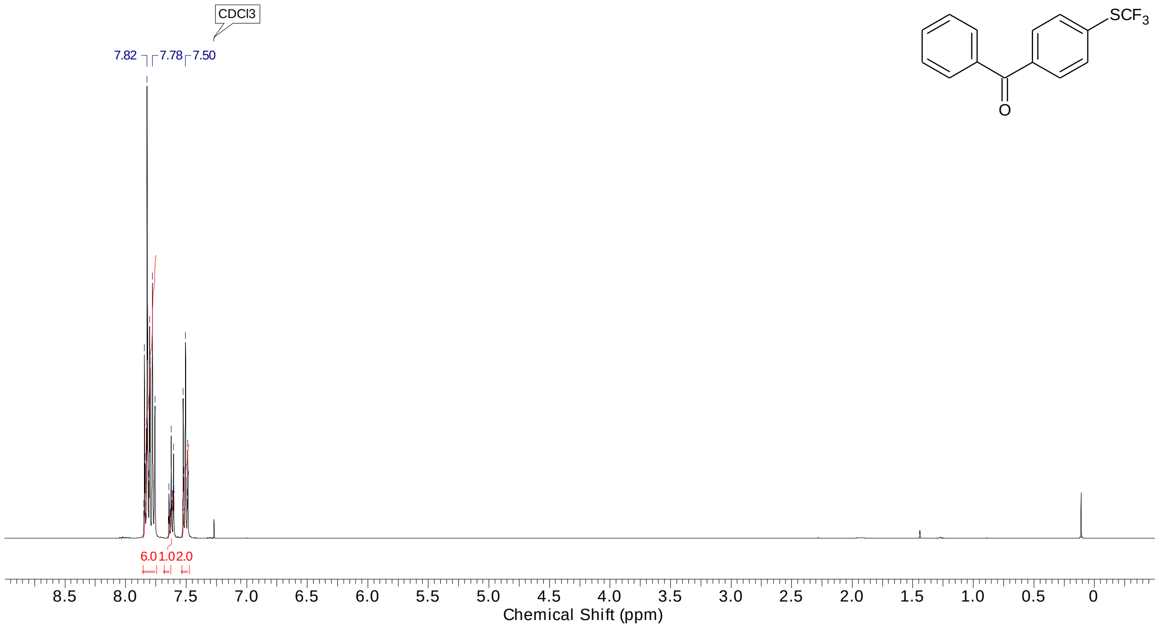

130.50
O
H_3C
SCF_3
26.56
129.80
CDCl3
130.87
133.94
135.98
138.21
140.42
196.59
127.81
125.34
125.32
124.75
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

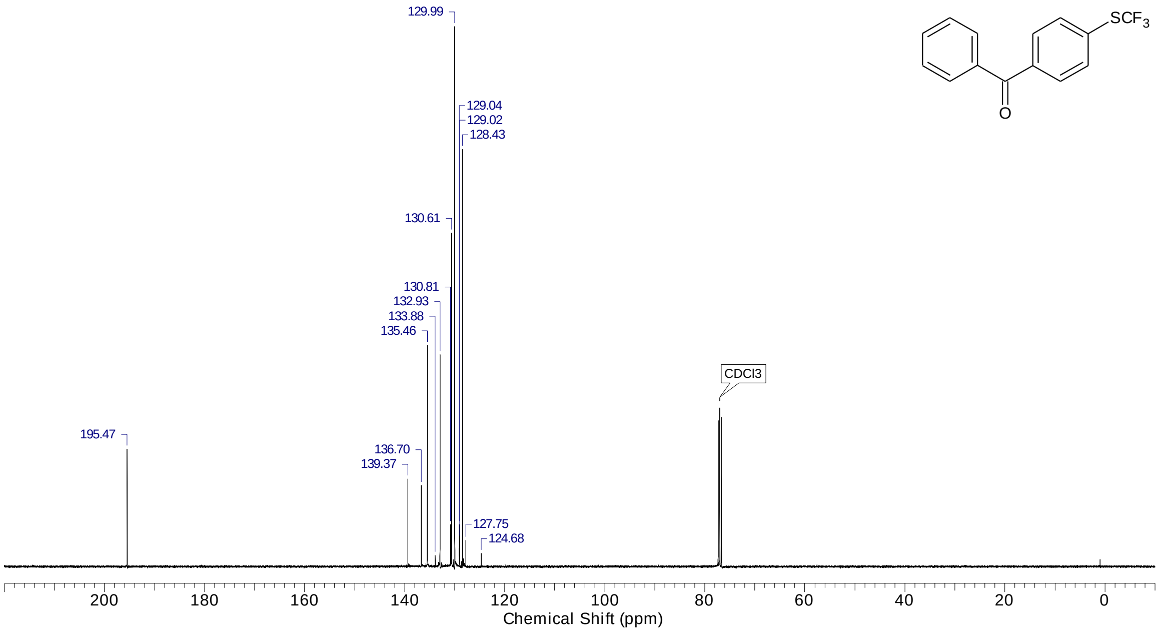

-42.48
O
H_3C
SCF_3
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

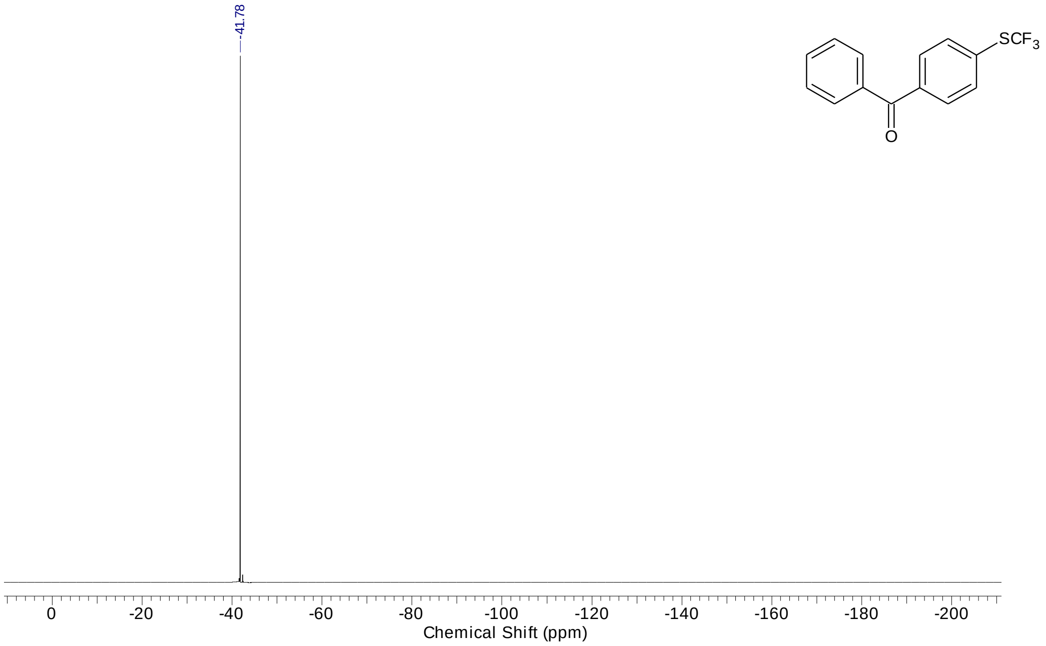

7.97
7.75
2.62
SCF$_3$
H$_3$C
O
CDCl3
2.1
2.0
3.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)

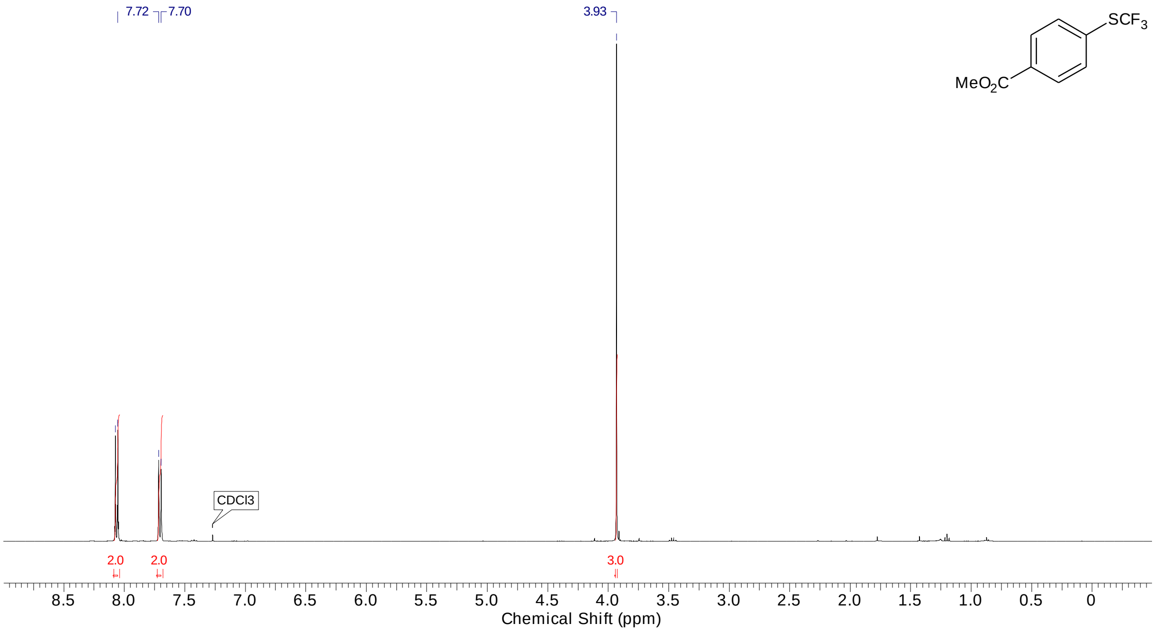

129.02
SCF$_3$
H$_3$C
O
129.92
129.95
130.76
133.82
135.70
CDCl3
26.64
196.99
138.43
127.69
124.63
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

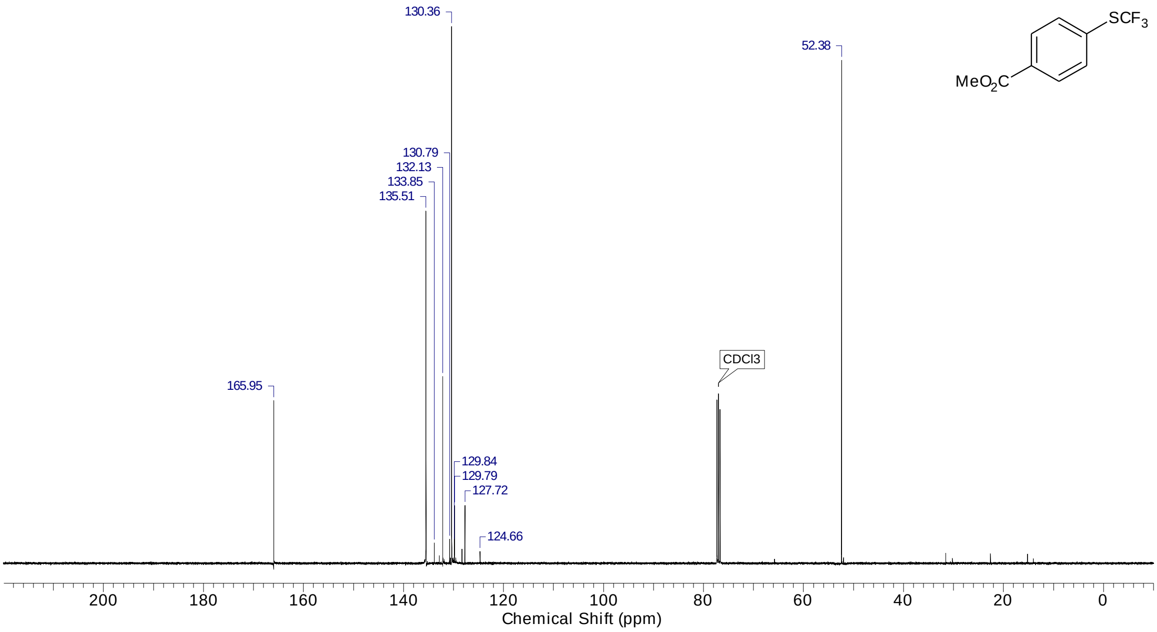

-41.82
SCF3
H3C
O
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

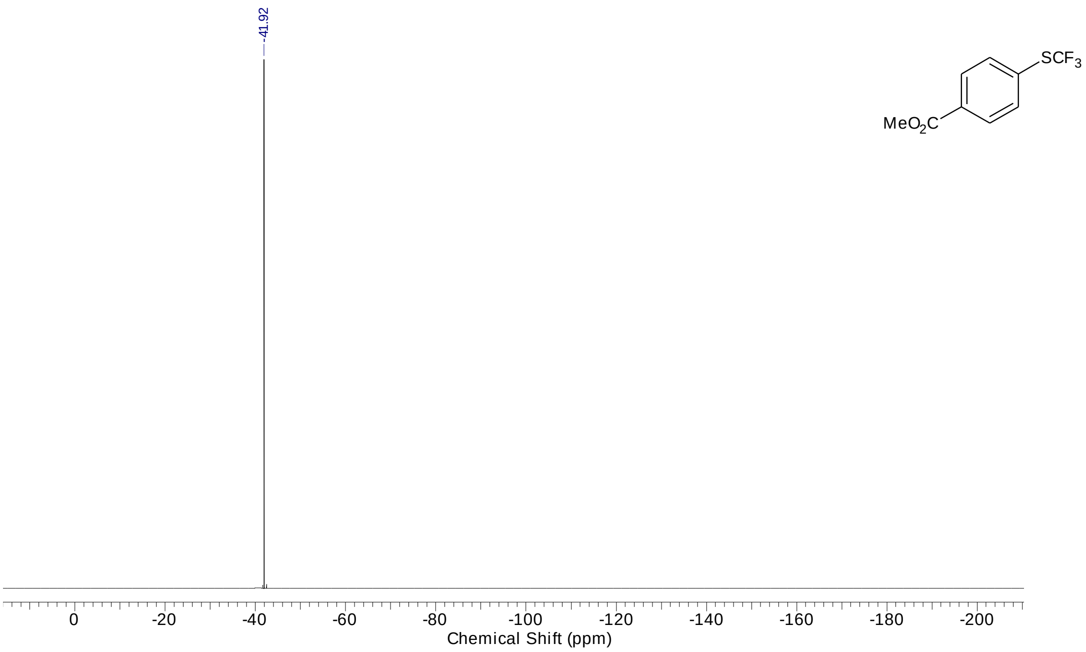

CDCl3
7.82
7.78
7.50
SCF$_3$
O
6.0
1.0
2.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

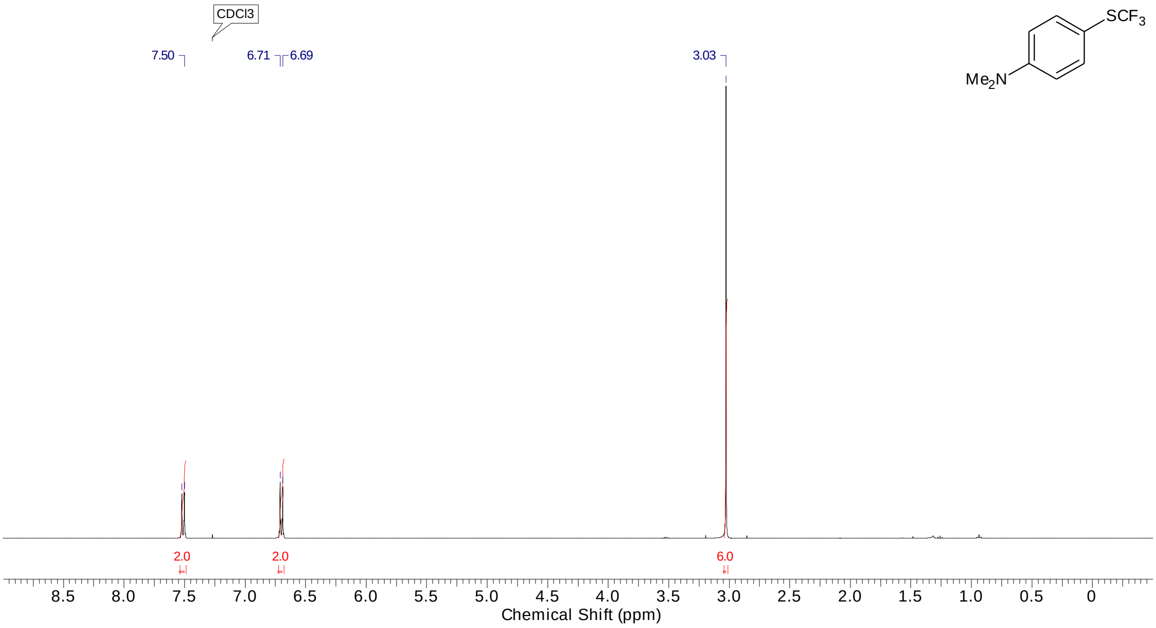

129.99
SCF$_3$
O
129.04
129.02
128.43
130.61
130.81
132.93
133.88
135.46
CDCl3
195.47
136.70
139.37
127.75
124.68
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

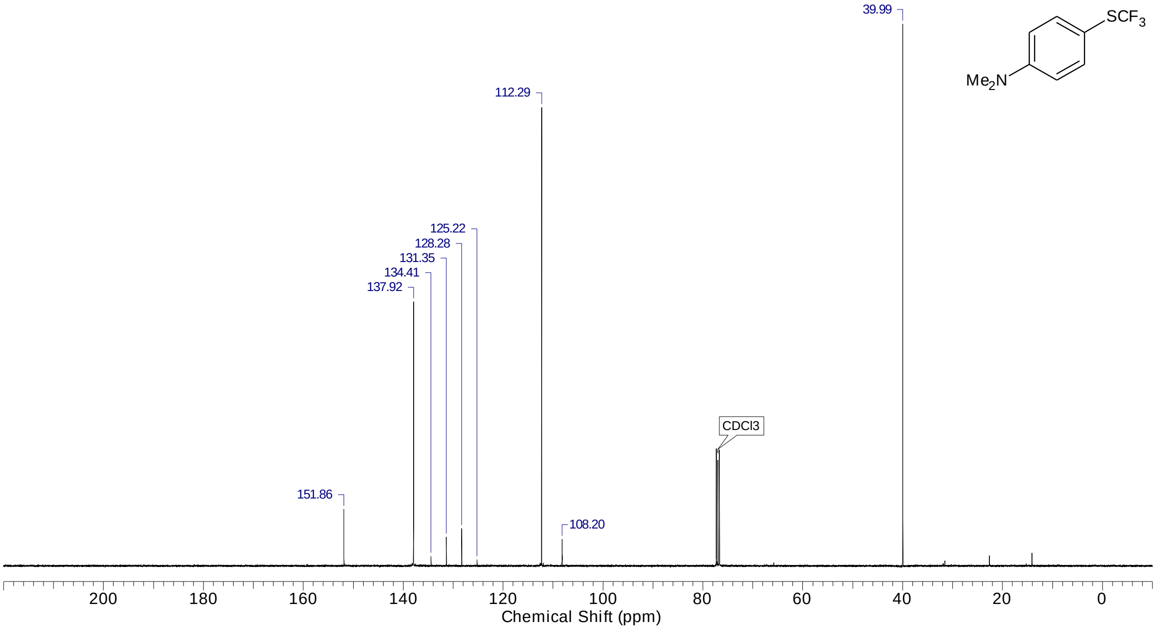

-41.78
SCF3
O
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

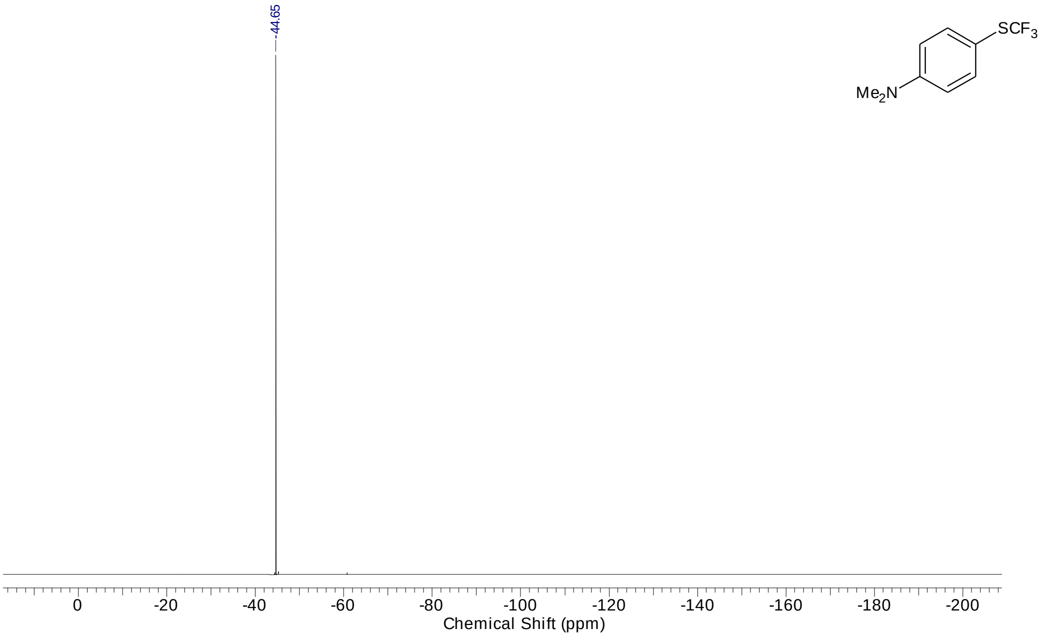

7.72
7.70
3.93
SCF$_3$
MeO$_2$C
CDCl3
2.0
2.0
3.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

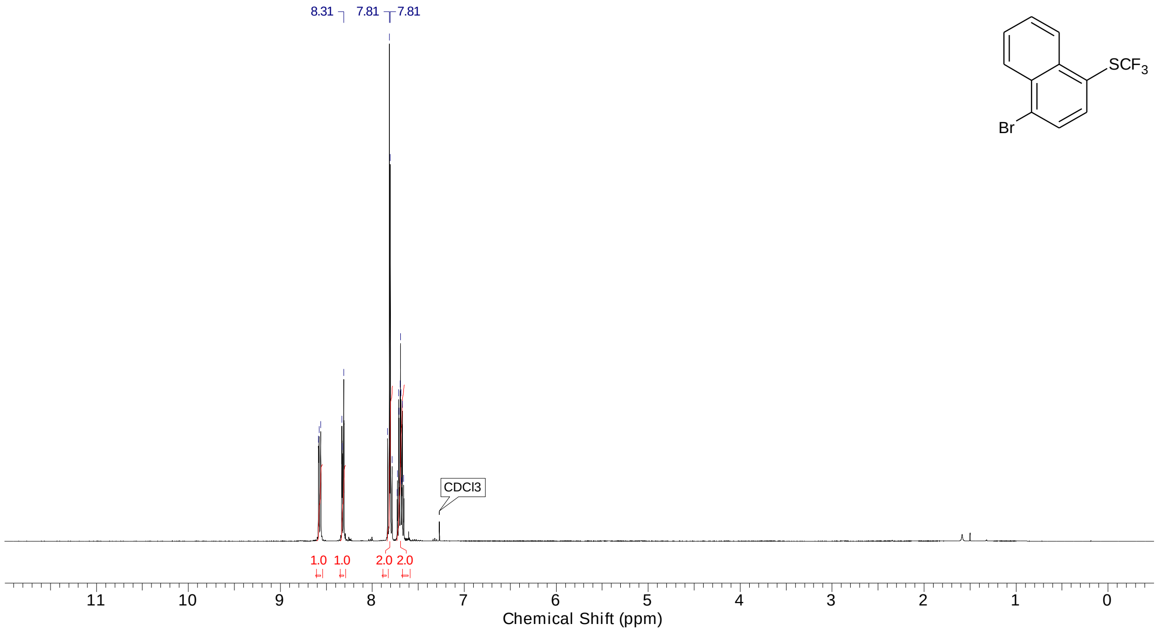

130.36
SCF$_3$
52.38
MeO$_2$C
130.79
132.13
133.85
135.51
CDCl3
165.95
129.84
129.79
127.72
124.66
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

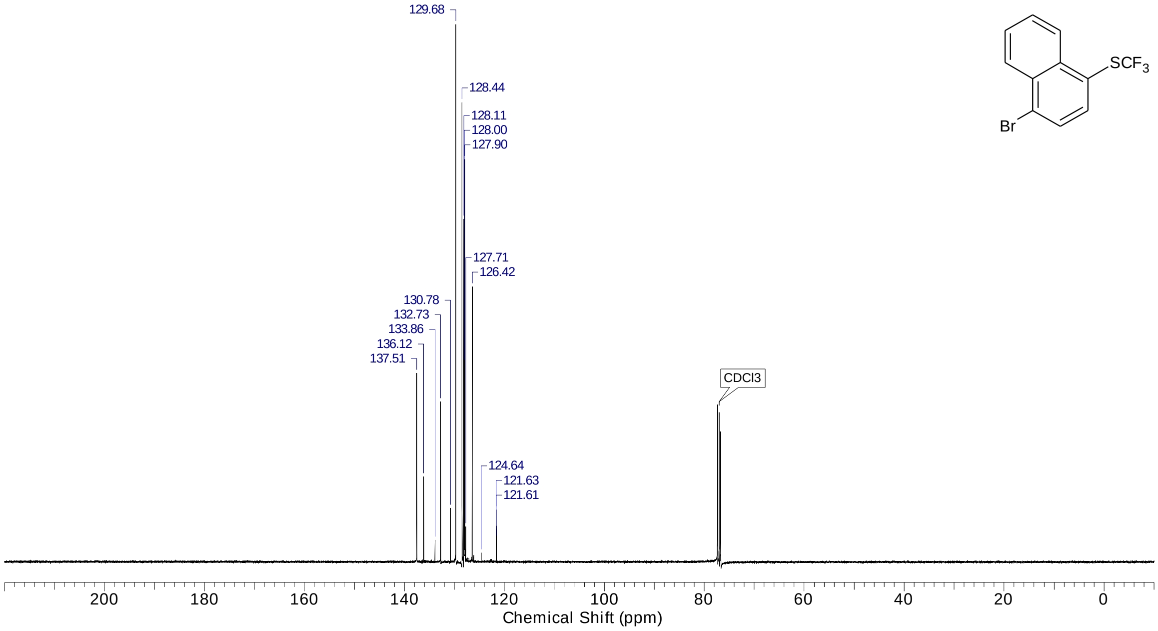

-41.92
SCF$_3$
MeO$_2$C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

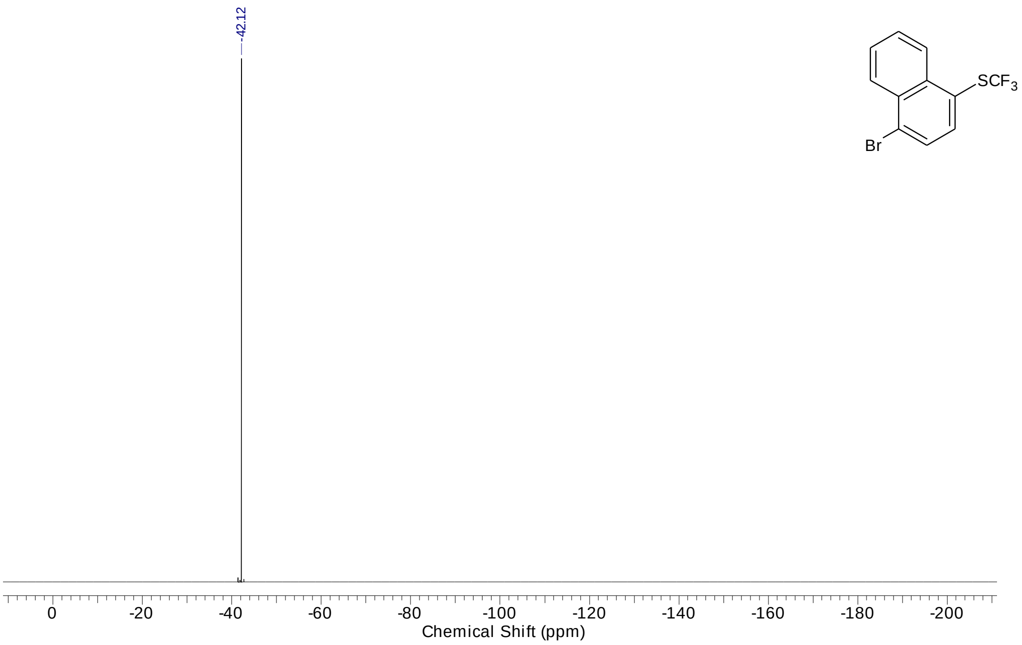

CDCl3
7.50
6.71
6.69
3.03
SCF3
Me2N
2.0
2.0
6.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

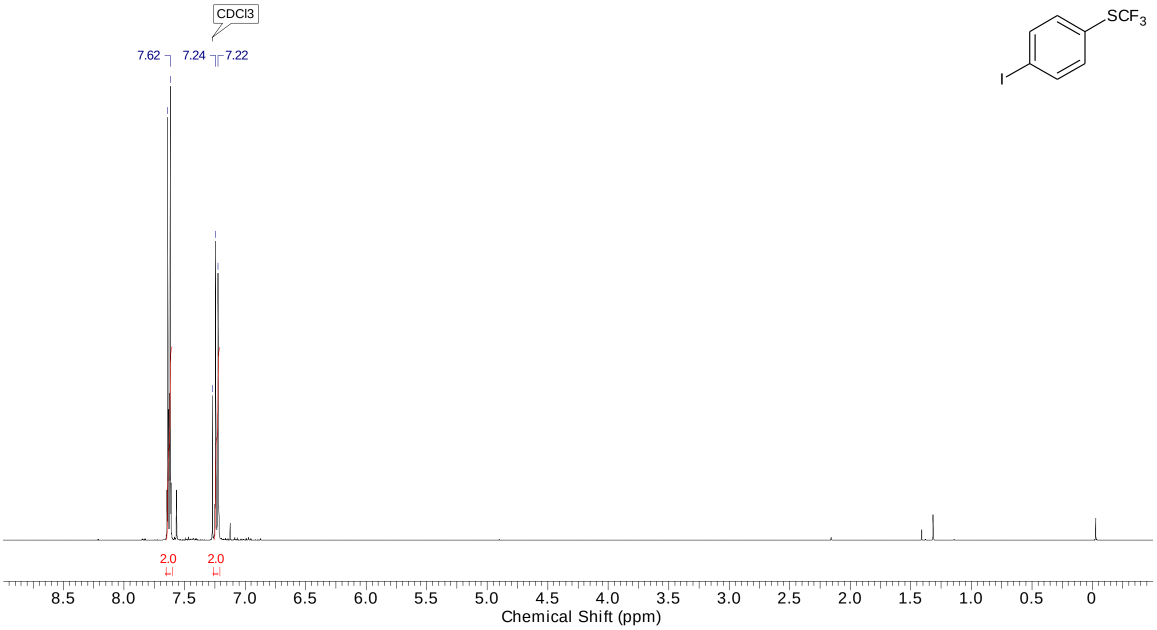

39.99
SCF3
Me2N
112.29
125.22
128.28
131.35
134.41
137.92
CDCl3
151.86
108.20
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

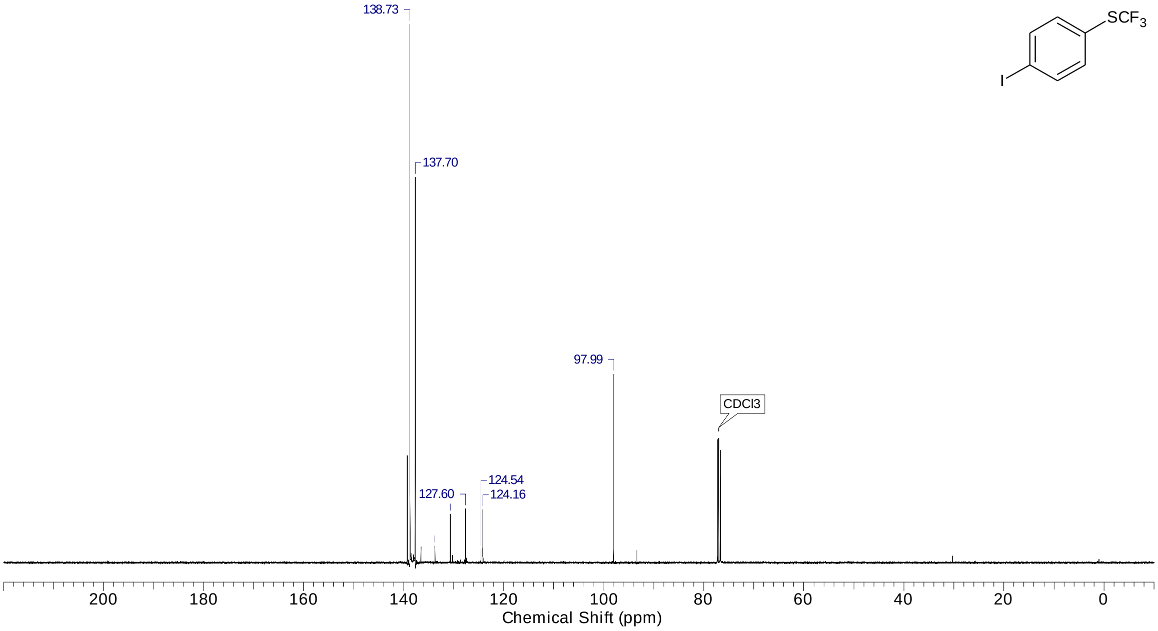

-44.65
SCF3
Me2N
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

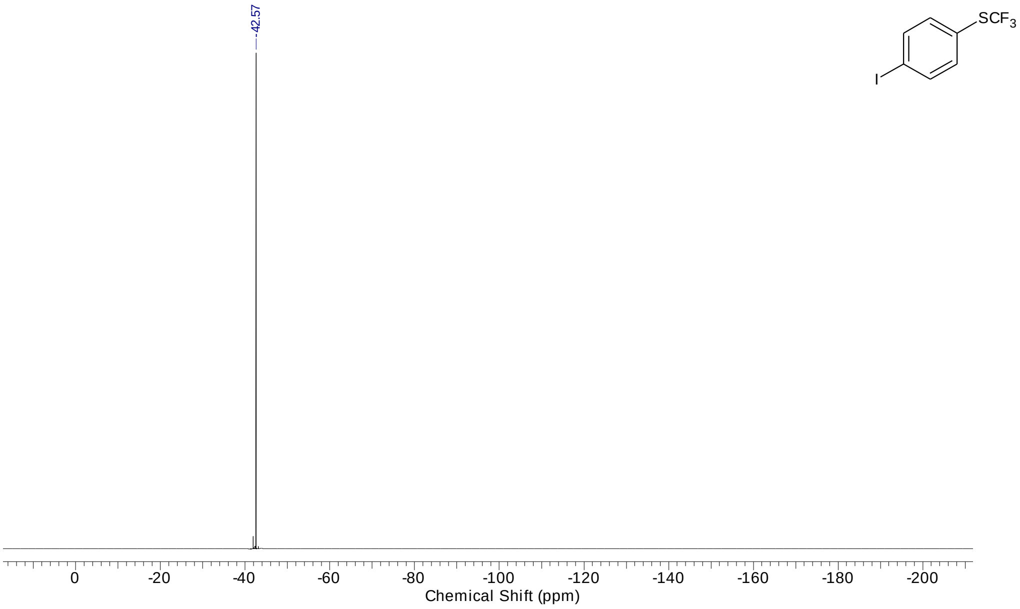

8.31
7.81
7.81
SCF3
Br
CDCl3
1.0
1.0
2.0
2.0
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

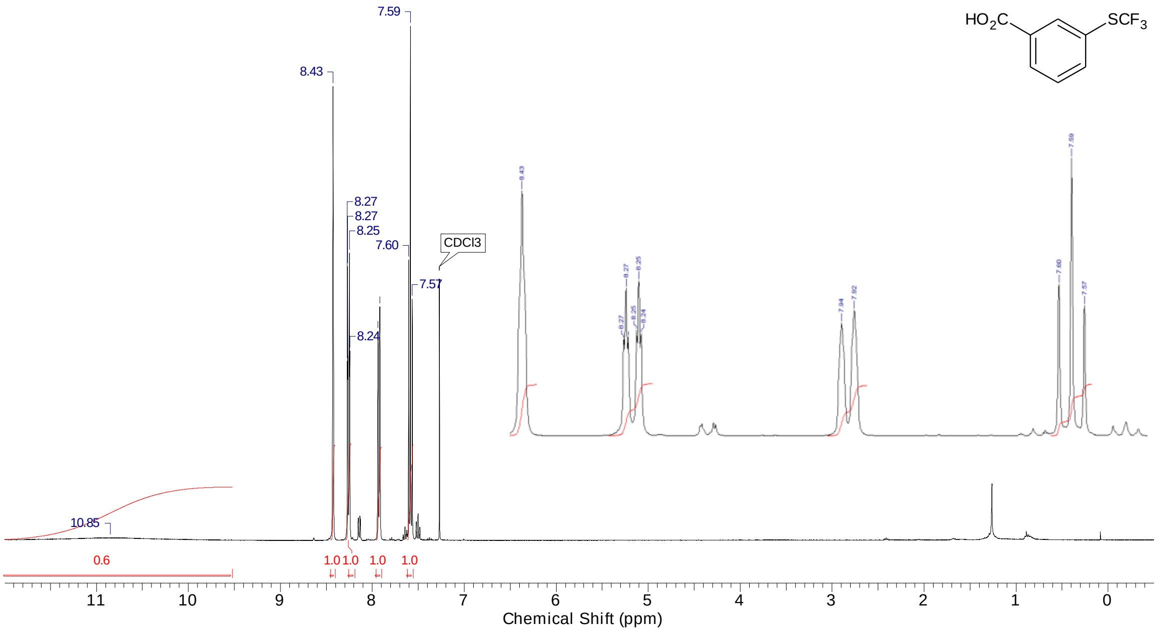

129.68
128.44
128.11
128.00
127.90
127.71
126.42
130.78
132.73
133.86
136.12
137.51
124.64
121.63
121.61
SCF3
Br
CDCl3
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

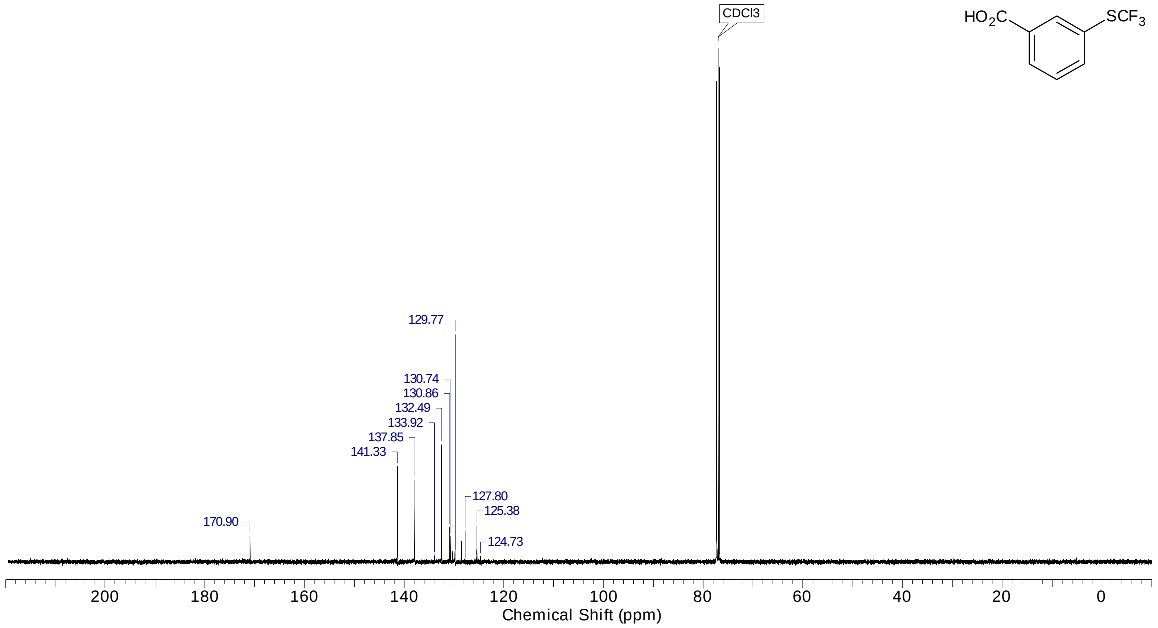

-42.12
SCF$_3$
Br
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

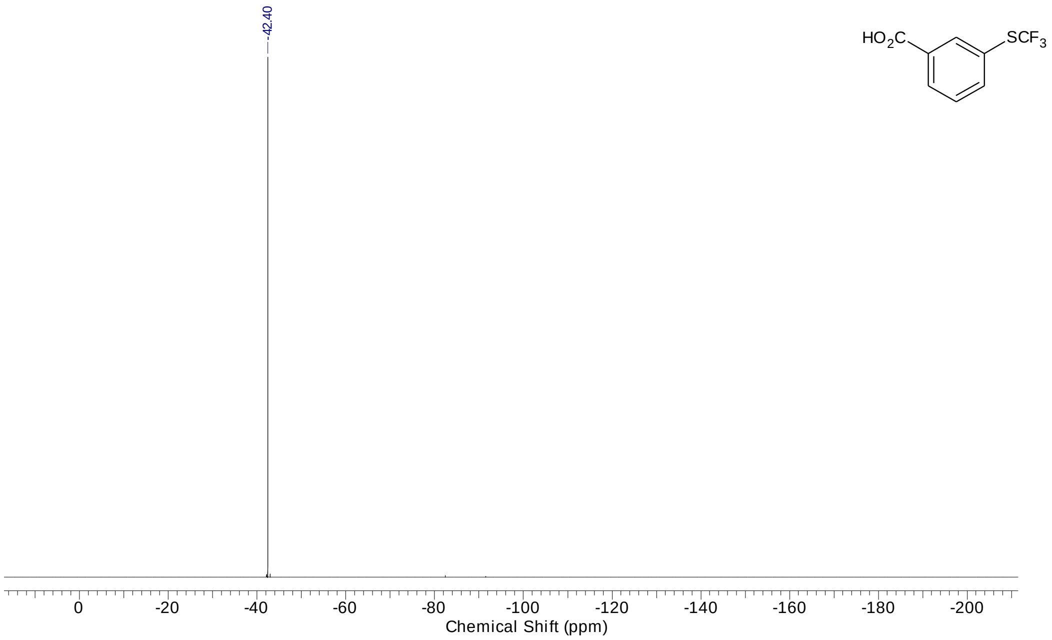

CDCl3
7.62
7.24
7.22
SCF3
I
2.0
2.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

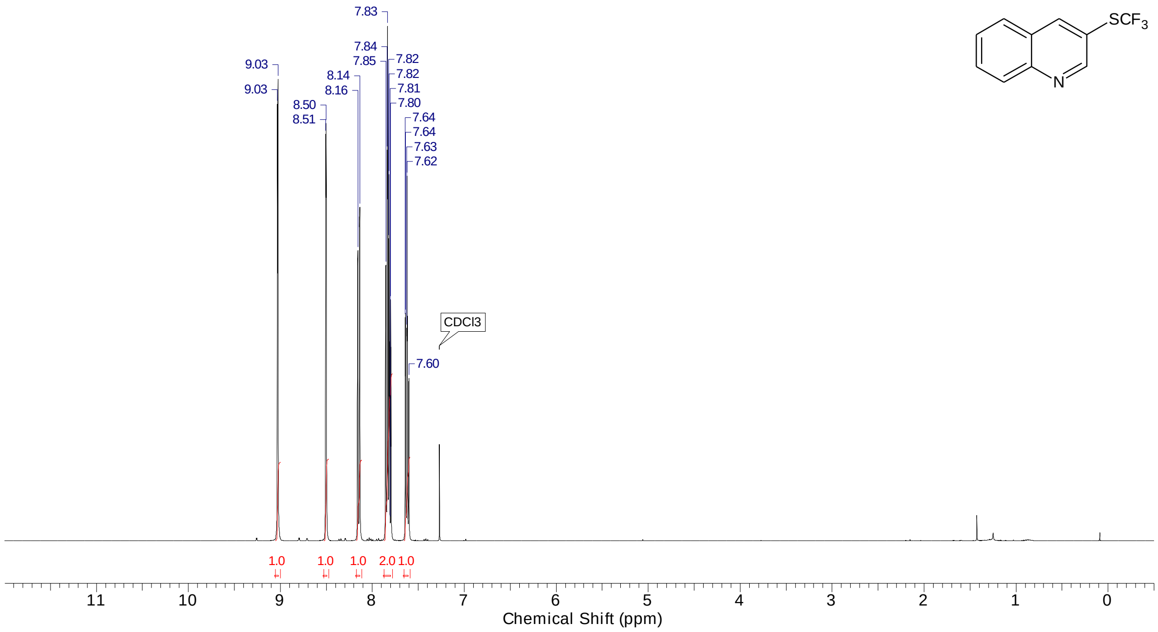

138.73
137.70
127.60
124.54
124.16
97.99
CDCl3
SCF3
I
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

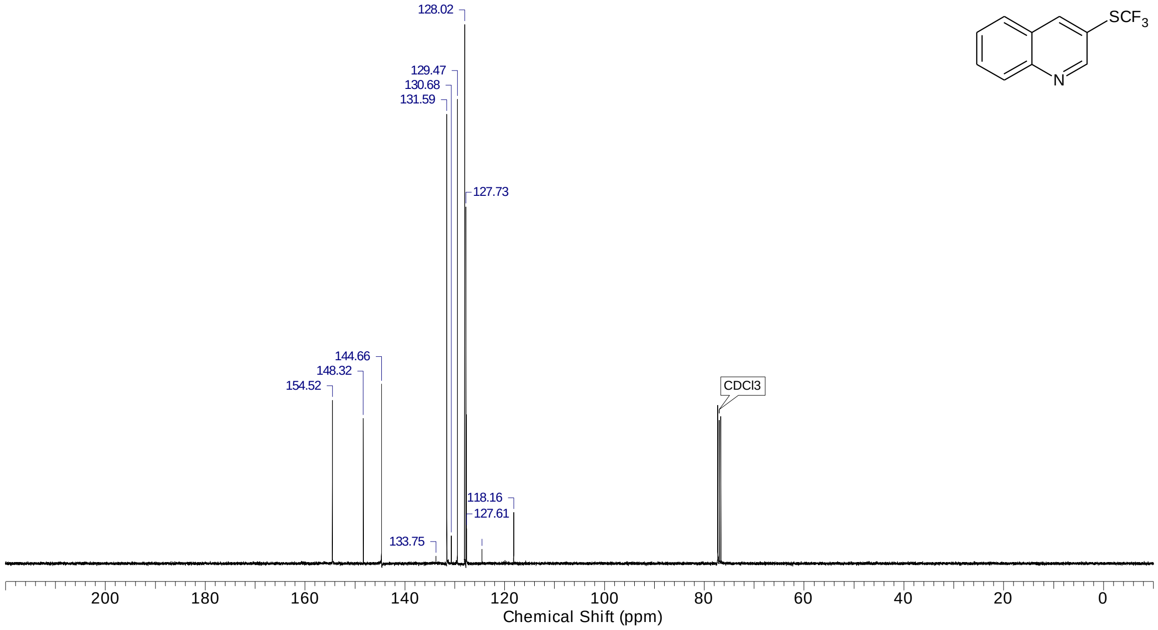

-42.57
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)
SCF3
I

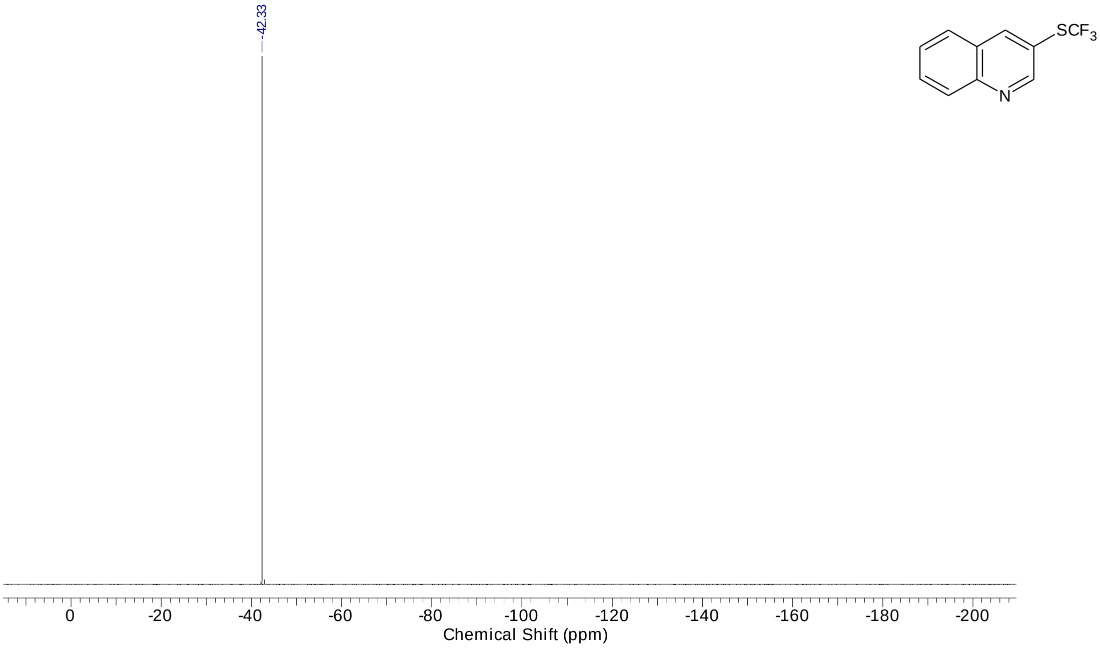

HO_2C
SCF_3
7.59
8.43
8.27
8.27
8.25
7.60
7.57
8.24
CDCl3
10.85
0.6
1.0
1.0
1.0
1.0
7.94
7.92
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

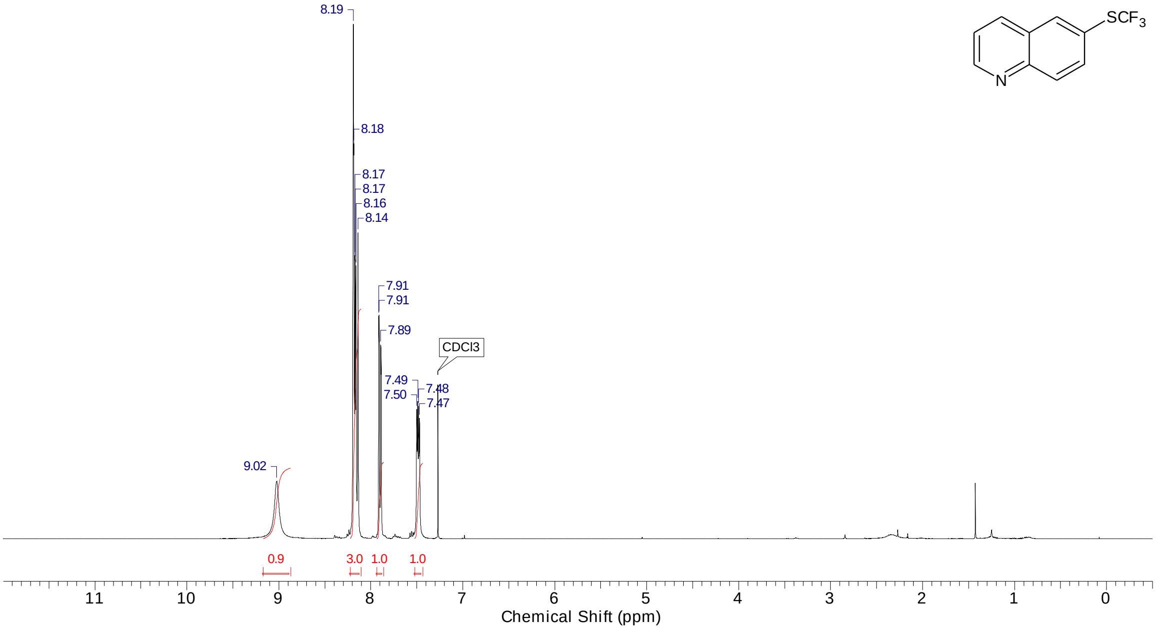

CDCl3
HO_2C
SCF_3
129.77
130.74
130.86
132.49
133.92
137.85
141.33
127.80
125.38
170.90
124.73
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

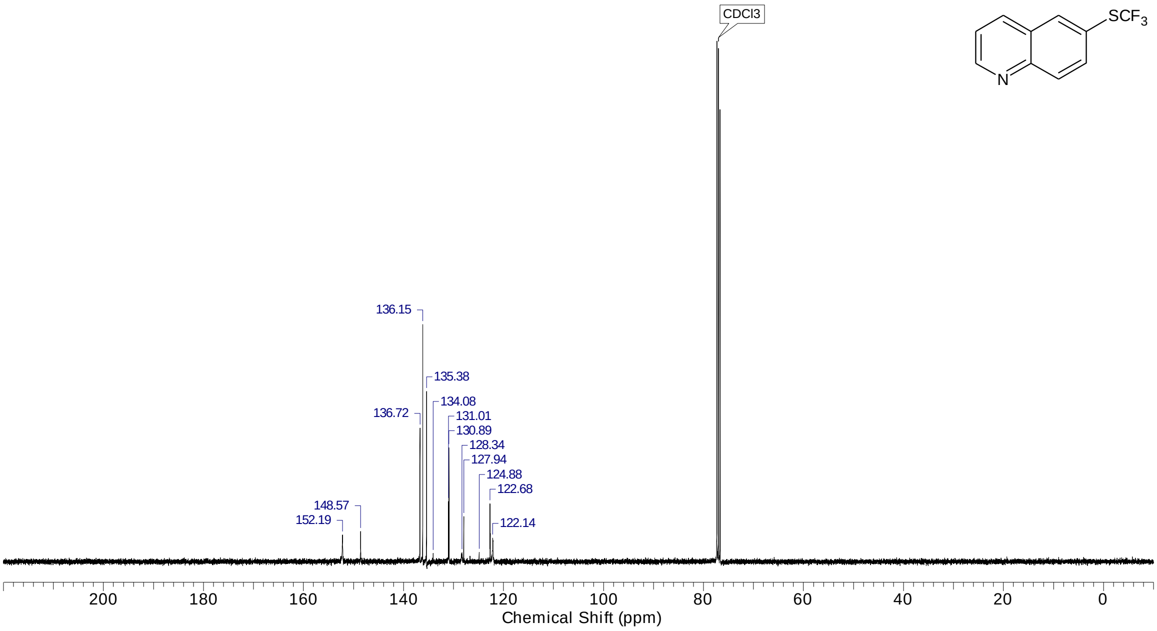

-42.40
HO2C
SCF3
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

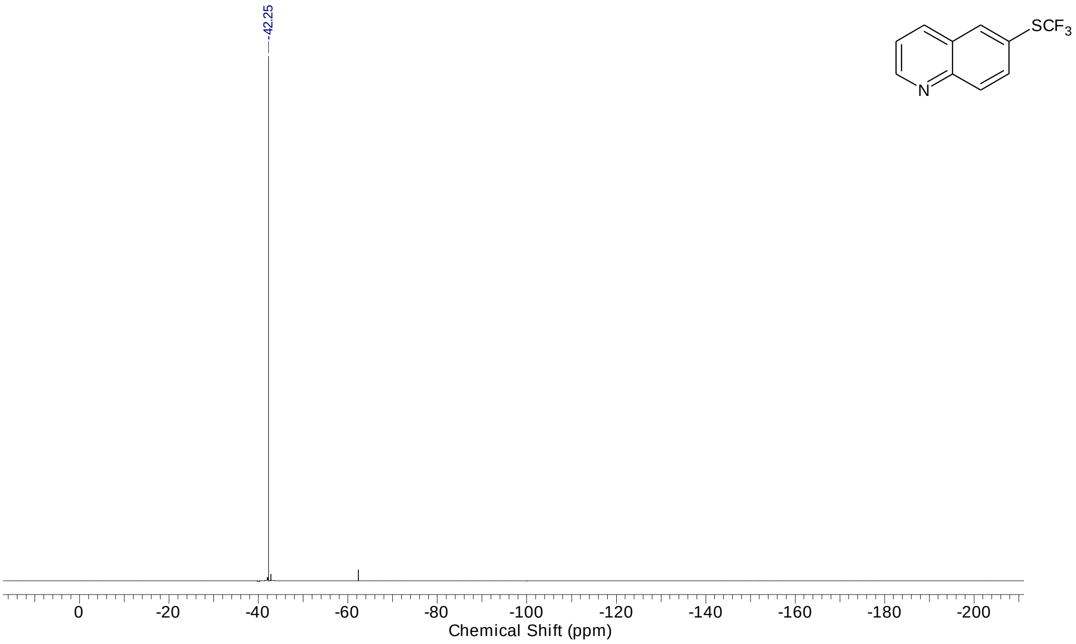

7.83
9.03
9.03
8.14
8.16
8.50
8.51
7.84
7.85
7.82
7.82
7.81
7.80
7.64
7.64
7.63
7.62
7.60
CDCl3
SCF3
N
1.0
1.0
1.0
2.0
1.0
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

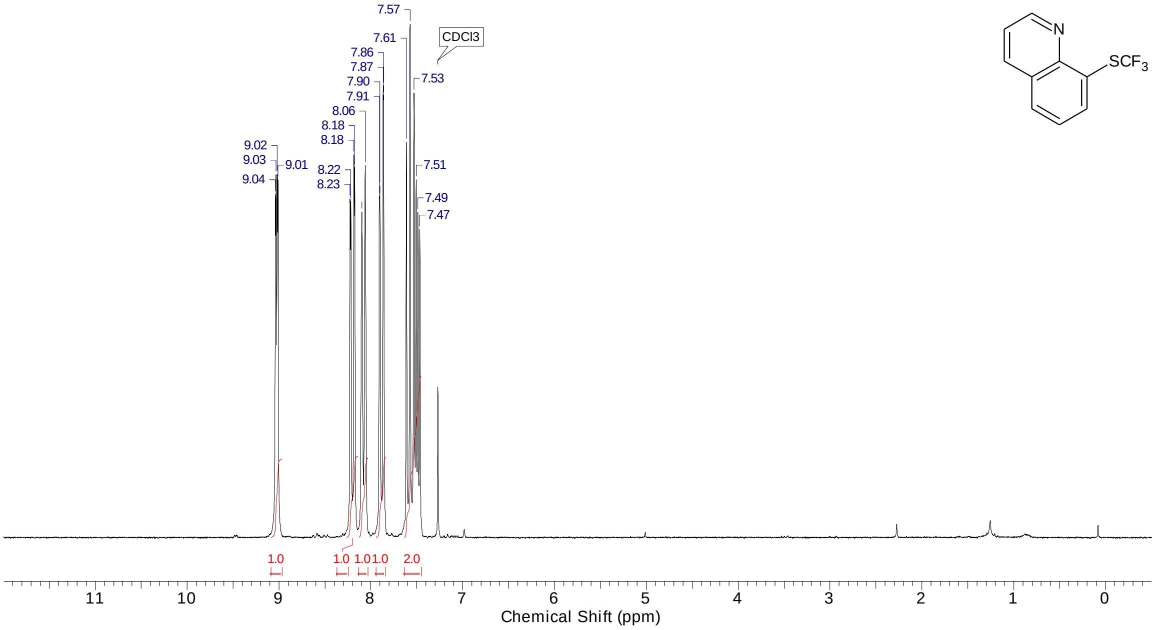

128.02
129.47
130.68
131.59
127.73
144.66
148.32
154.52
CDCl3
118.16
127.61
133.75
SCF3
N
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

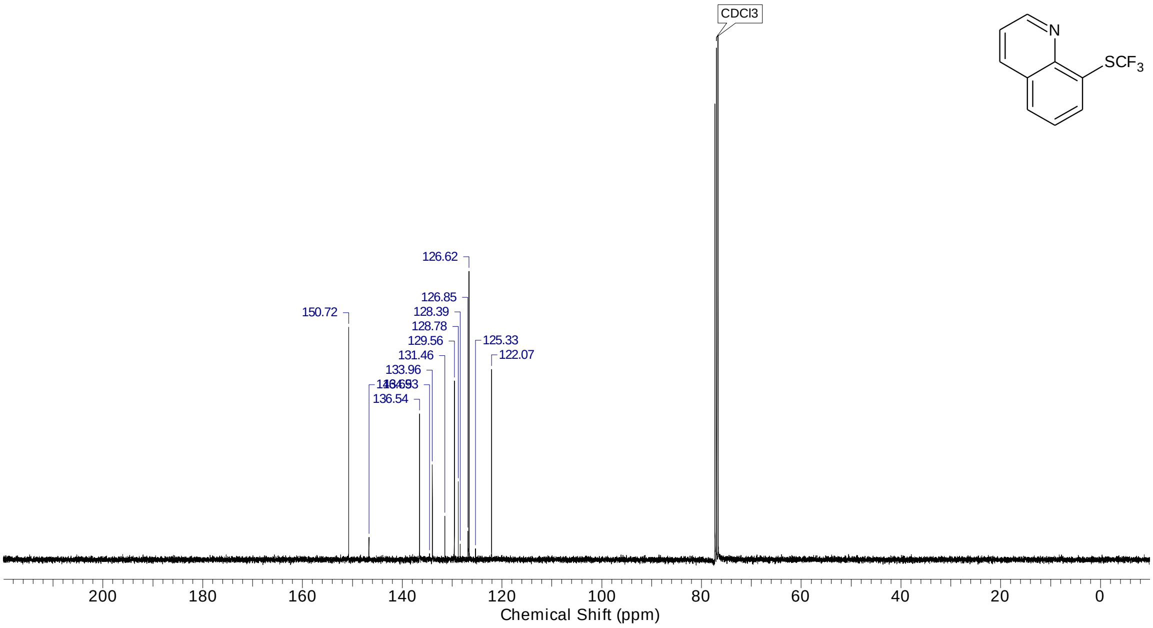

-42.33
SCF3
N
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

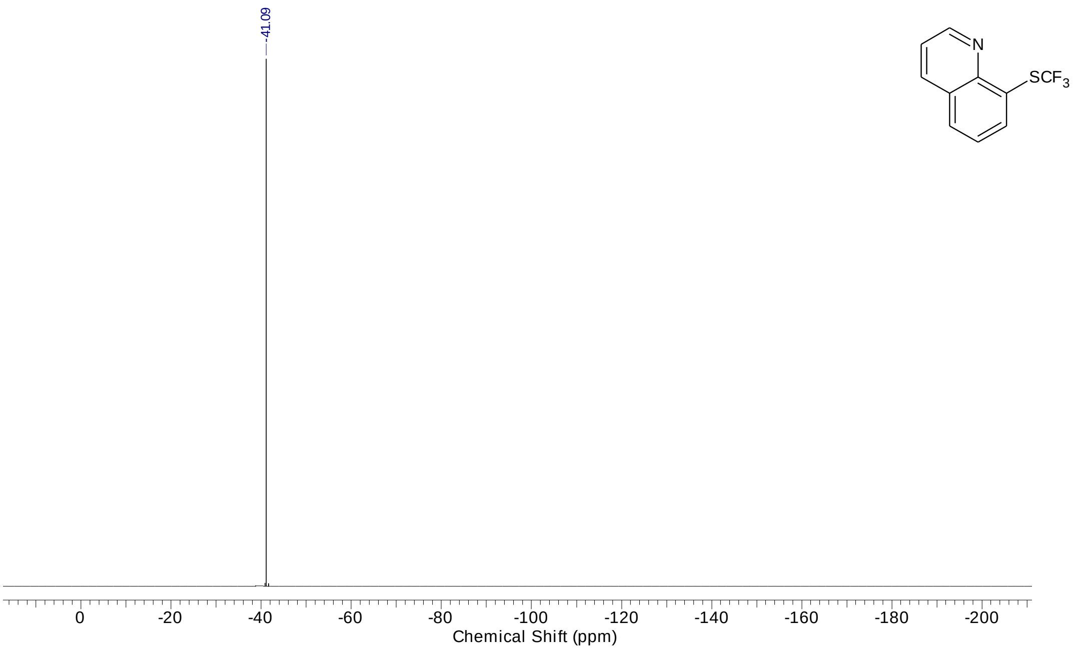

8.19
8.18
8.17
8.17
8.16
8.14
7.91
7.91
7.89
CDCl3
7.49
7.50
7.48
7.47
9.02
0.9
3.0
1.0
1.0
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)
SCF3
N

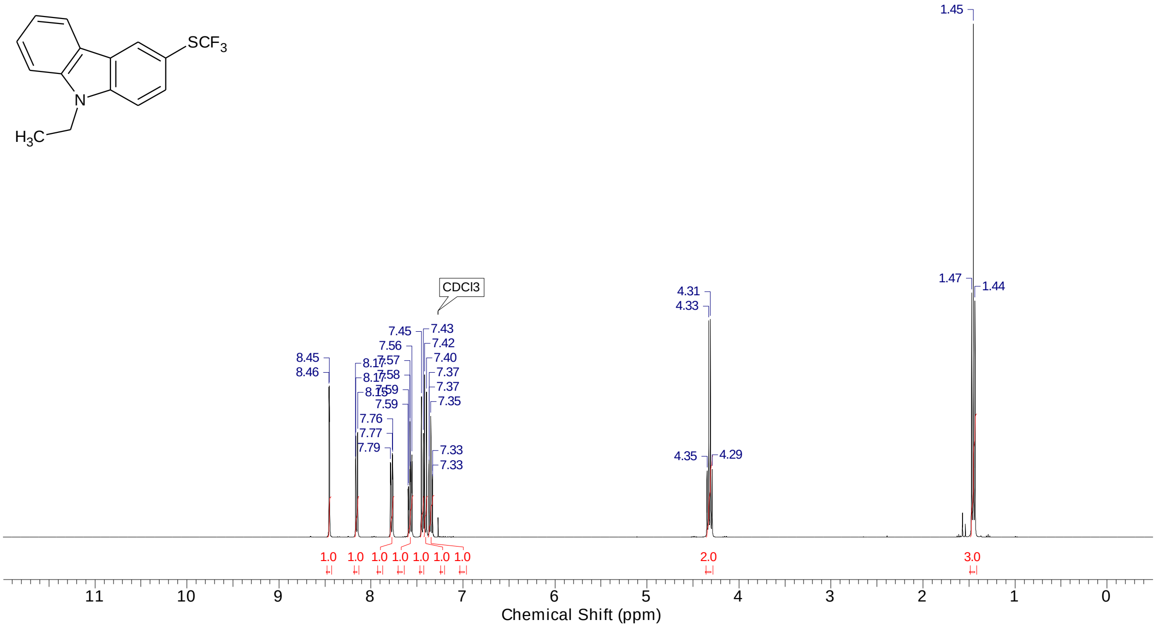

CDCl3
SCF3
N
136.15
135.38
134.08
136.72
131.01
130.89
128.34
127.94
124.88
122.68
148.57
152.19
122.14
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

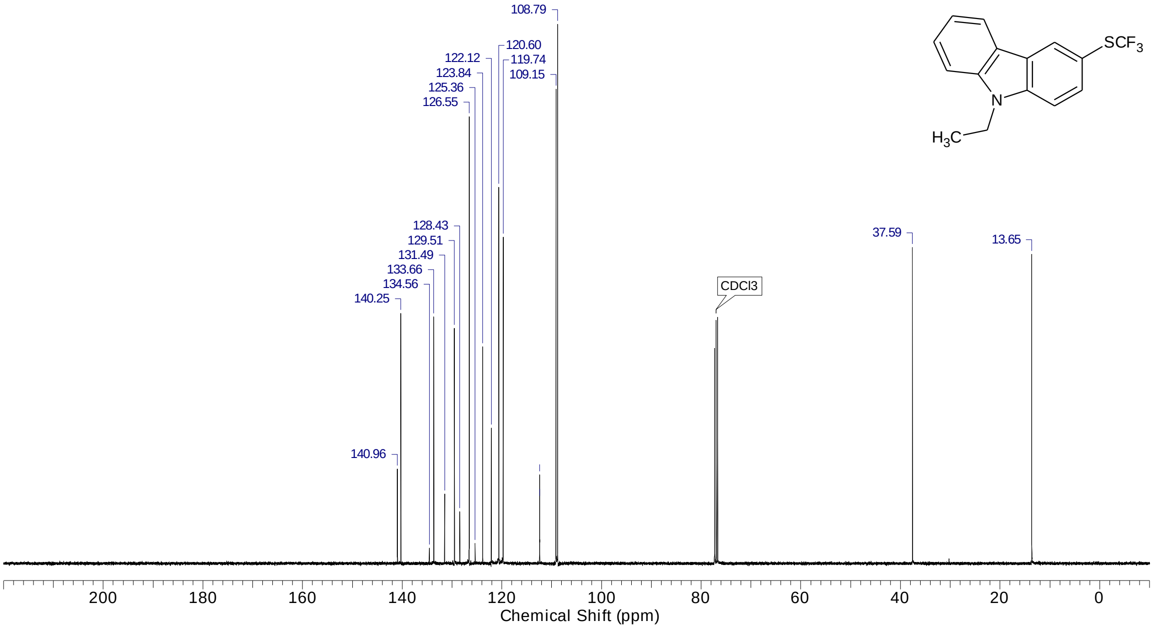

-42.25
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)
SCF$_3$
N

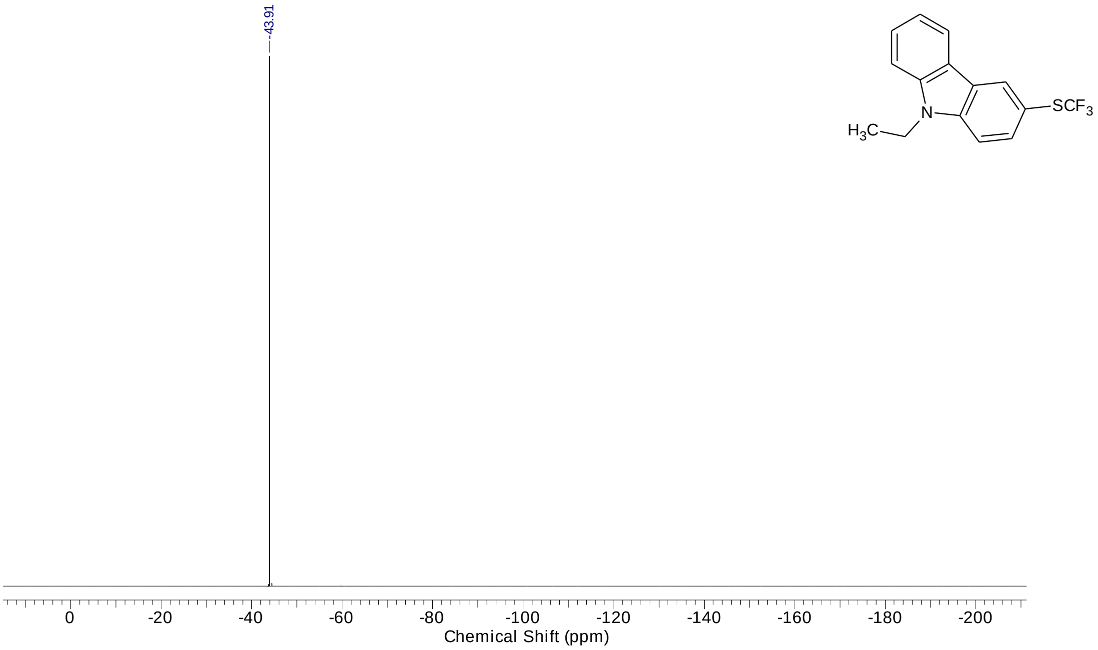

7.57
7.61
CDCl3
7.86
7.87
7.90
7.91
7.53
8.06
8.18
8.18
9.02
9.03
9.01
8.22
8.23
7.51
9.04
7.49
7.47
1.0
1.0
1.0
1.0
2.0
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)
N
SCF_3

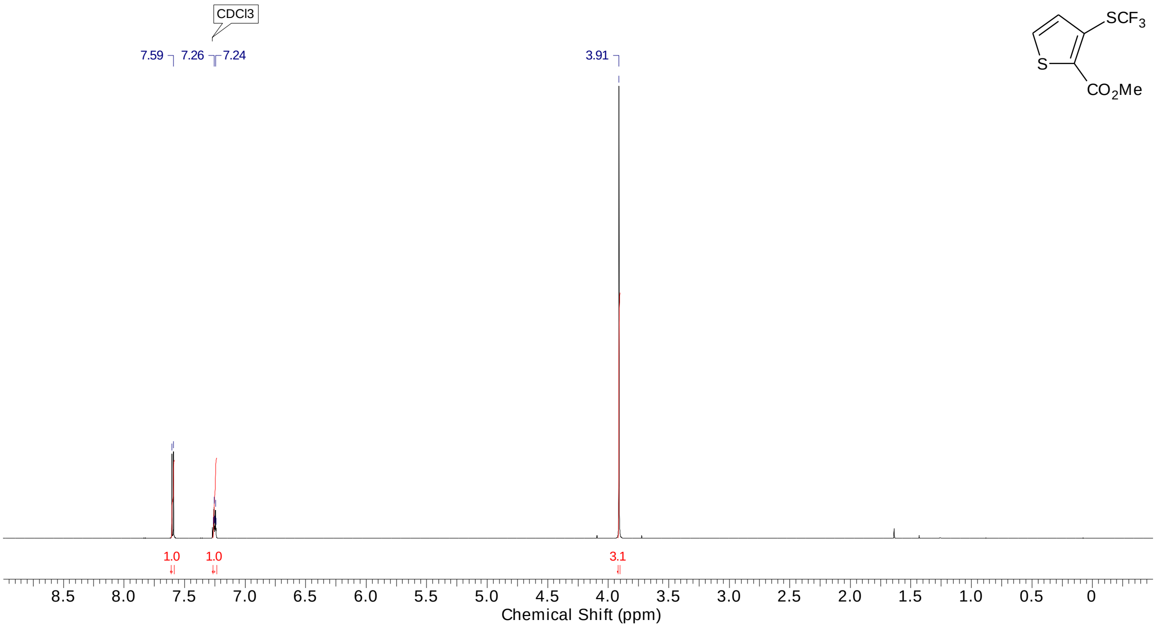

CDCl3
N
SCF_3
126.62
126.85
150.72
128.39
128.78
129.56
125.33
131.46
122.07
133.96
146.69
133.93
136.54
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

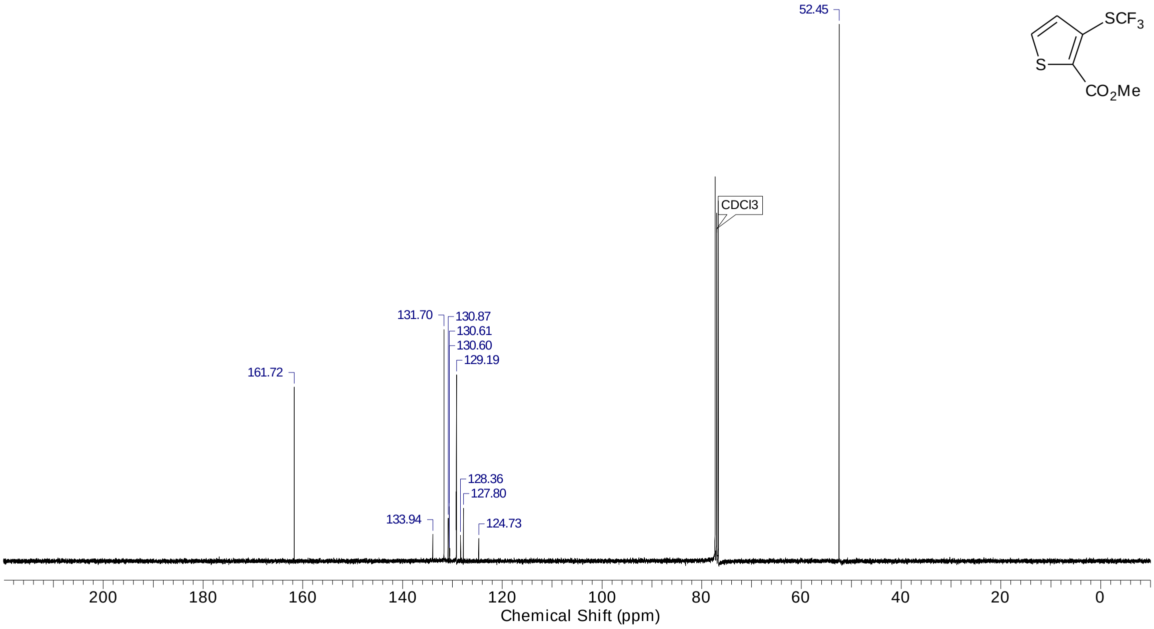

-41.09
N
SCF$_3$
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

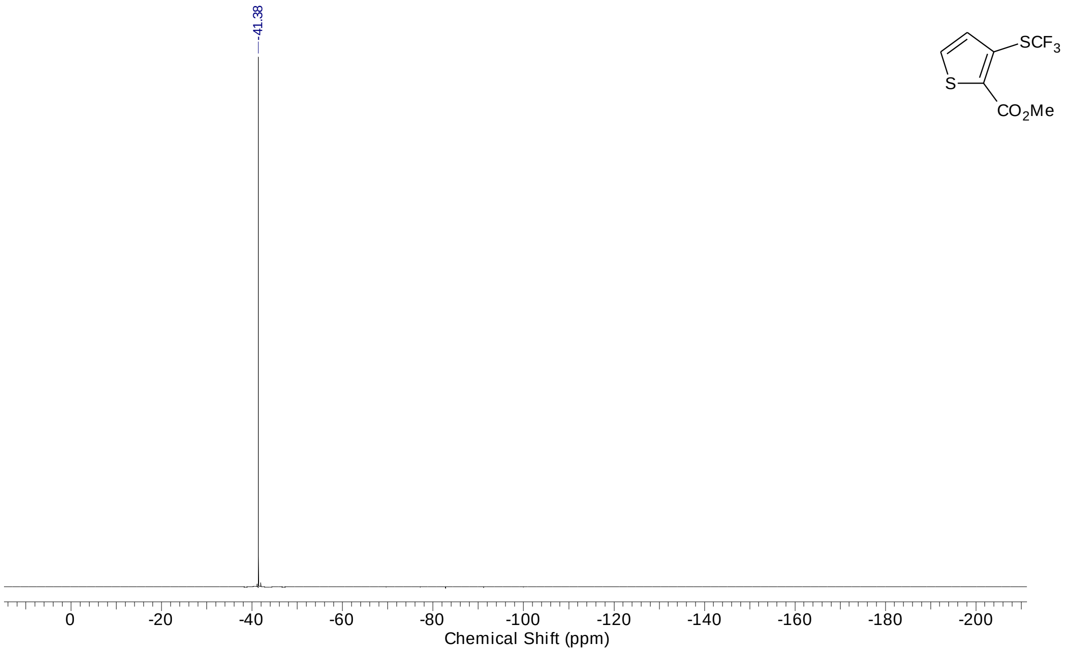

SCF3
N
H3C
1.45
1.47
1.44
4.31
4.33
4.35
4.29
CDCl3
8.45
8.46
8.17
8.17
8.15
7.45
7.56
7.57
7.58
7.59
7.59
7.76
7.77
7.79
7.43
7.42
7.40
7.37
7.37
7.35
7.33
7.33
1.0
1.0
1.0
1.0
1.0
1.0
1.0
2.0
3.0
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

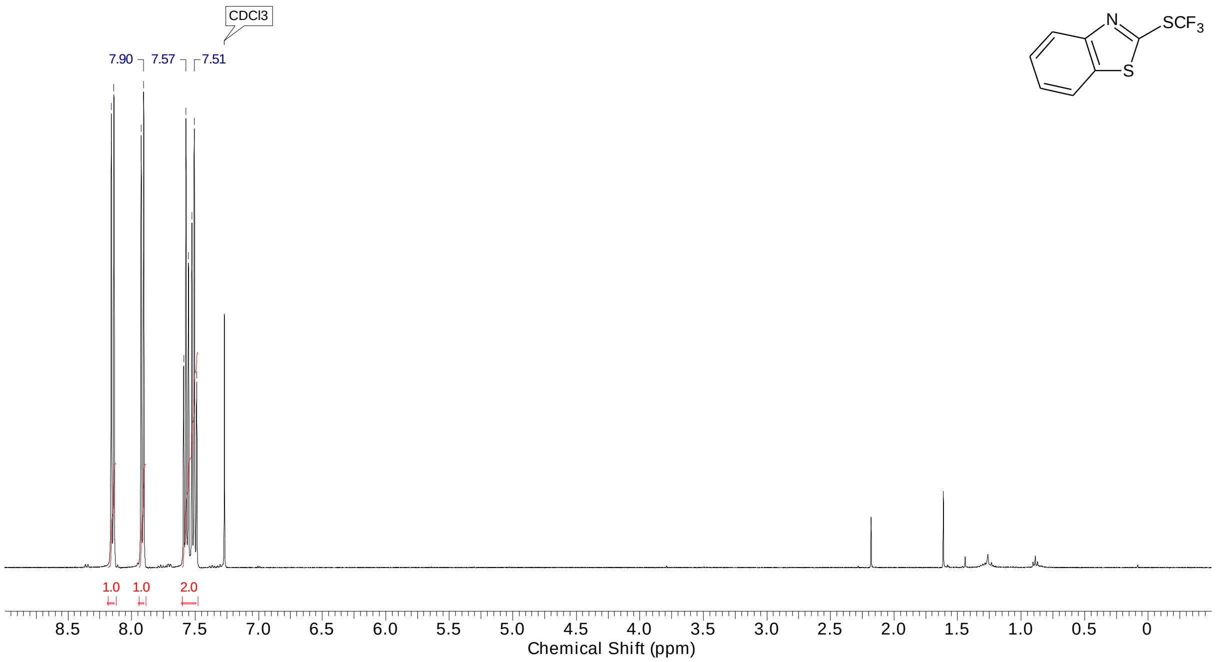

108.79
120.60
119.74
109.15
122.12
123.84
125.36
126.55
128.43
129.51
131.49
133.66
134.56
140.25
140.96
CDCl3
37.59
13.65
SCF3
N
H3C
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

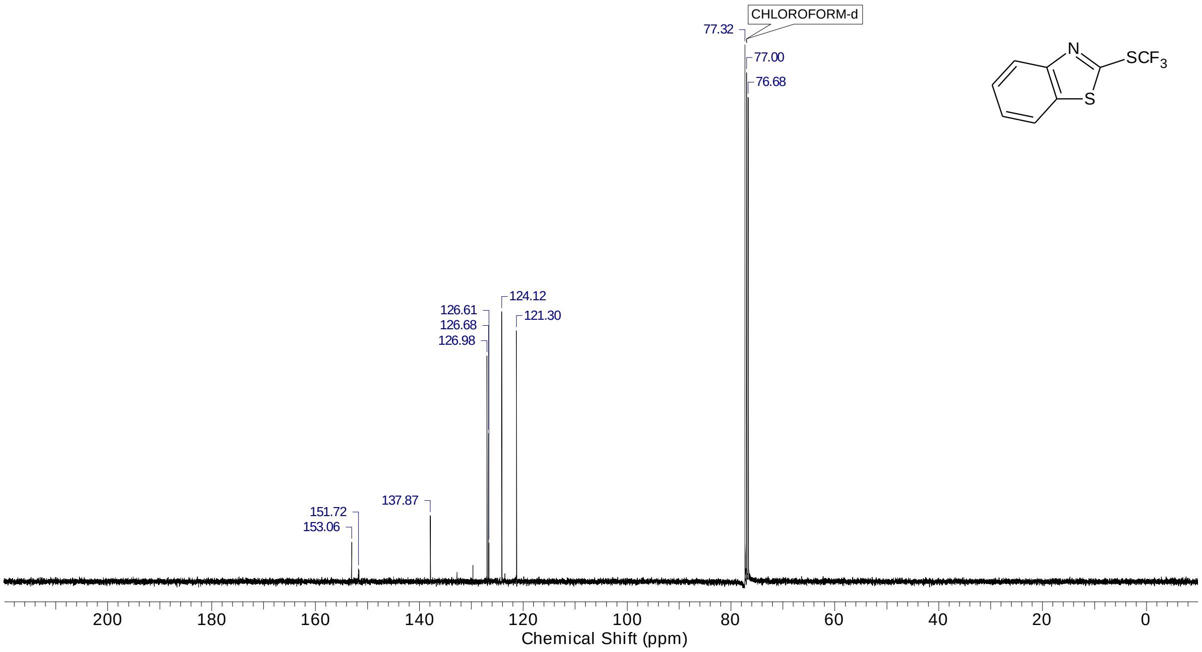

-43.91
H$_3$C
N
SCF$_3$
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

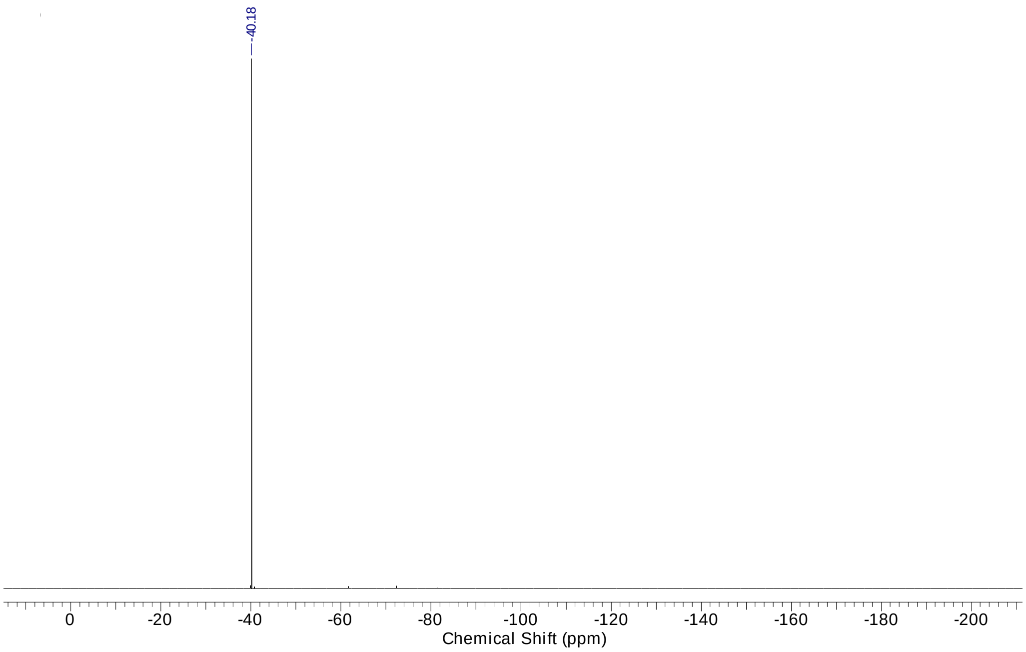

CDCl3
7.59
7.26
7.24
3.91
1.0
1.0
3.1
SCF$_3$
S
CO$_2$Me
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


52.45
SCF$_3$
S
CO$_2$Me
CDCl3
131.70
130.87
130.61
130.60
129.19
161.72
128.36
127.80
133.94
124.73
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


-41.38
SCF$_3$
S
CO$_2$Me
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)


CDCl3
7.90
7.57
7.51
1.0
1.0
2.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)
N
SCF3
S


CHLOROFORM-d
77.32
77.00
76.68
124.12
121.30
126.61
126.68
126.98
137.87
151.72
153.06
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)
N
SCF3
S



---

[1] V. V. Shaburov, O. V. Vasil'eva, A. V. El'tsov, *Chemistry of Heterocyclic Compounds,* 1974 , **10**, 320.