Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Preparation of difluoromethylthioethers through difluoromethylation of disulfides using TMS-CF_2H

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General Methods

Reactions were performed in oven-dried glassware under a nitrogen atmosphere.

Caesium fluoride was dried at 200 °C, 5 mbar for 12 h prior to use. N-Methyl-2-pyrrolidone (NMP) was dried over oven-dried molecular sieves (4 Å) prior to use. Diglyme was distilled from calcium hydride before use. If not stated below, chemicals were commercially available and used without further purification.

^{1}H and ^{13}C NMR spectra were obtained on Bruker 400 Ultrashield^{TM} and Bruker 500 MHz spectrometers with chloroform-d as deuterated solvent. These were performed without ^{19}F decoupling, so fluorine coupling is observed. ^{19}F NMR spectra were obtained using an Oxford Instruments 300 MHz spectrometer. The obtained chemical shifts δ are reported in ppm and are referenced to the residual solvent signal. Spin-spin coupling constants J are given in Hz.

High resolution mass spectral (HRMS) data were obtained on a Thermo Scientific LTQ Orbitrap XL by the EPSRC UK National Mass Spectrometry Facility at Swansea University or on a Waters MALDI-TOF mx.

Infrared spectra were recorded on a Shimadzu IR-Affinity-1S FTIR spectrometer

Melting points were measured using a Gallenkamp apparatus and are reported uncorrected.

The microwave used for the synthesis of thiols was a CEM Discover SP.

Synthesis of difluoromethyltrimethylsilane (TMSCF$_2$H)

Following a known procedure[1] trimethylsilanetrifluoromethane (24.0 g, 169 mmol) was added slowly over 20 min to an ice cold solution of sodium borohydride (2.22 g, 59 mmol, 0.43 eq) in dry diglyme (50 mL). After 2 h the ice bath was removed and the reaction stirred for another 18 h. The reaction mixture was distilled twice at atmospheric pressure (set temperature 170 °C and 90 °C) to yield 13.1 g (62%, 105.4 mmol) of TMSCF$_2$H. Data in accordance with literature values.[2]

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.84 (t, *J* = 46.2 Hz, 1H), 0.17 (s, 9H).

^{13}C NMR (300 MHz, CDCl$_3$) δ 124.1 (t, *J* = 253.7 Hz), -5.4.

^{19}F NMR (283 MHz, CDCl$_3$) δ -139.79 (d, *J* = 46.0 Hz).

IR: 1256, 1080, 991, 862 cm^{-1}

Synthesis of thiols

Following a modified literature procedure[3], a microwave vial was charged with the corresponding alkyl bromide (35 mmol), thiourea (1.2 eq, 42 mmol, 3.2 g) and ethanol (15 mL) and irradiated to 140 °C for 30 min. Then NaOH (3 eq, 4.2 g, 105 mmol) and water (7 mL) were added and the solution was heated again to 140 °C for 10 min. The reaction mixture was neutralised with aqueous HCl and the product extracted with diethylether (3 x 50 mL). The organic layers were combined and washed with water (20 mL), dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure. The product was further purified by column chromatography (SiO_2 petroleum ether/ ethyl acetate).

2-bromobenzylmercaptan (3.026 g, 43 %, 14.9 mmol)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 1H), 7.37 – 7.31 (m, 1H), 7.28 – 7.22 (m, 1H), 7.11 – 7.05 (m, 1H), 3.80 (d, J = 8.2 Hz, 2H), 1.99 (t, J = 8.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 133.1, 130.1, 128.8, 128.0, 123.6, 29.7.

IR: 1466, 1435, 1026, 748, 725 cm^{-1}.

HRMS calcd for $C_7H_6Br_1S_1$ $[M-H]^+$: 200.9368, found: 200.9366.

4-bromobenzylmercaptan (1.910 g, 27 %, 9.4 mmol)

^{1}H NMR (400 MHz, $CDCl^3$) δ 7.50 - 7.44 (m, 1H), 7.26 – 7.19 (m, 2H), 3.72 (d, J = 3.7 Hz, 2H), 1.84 (t, J = 7.7 Hz, 1H).

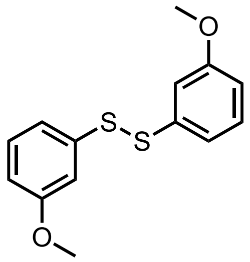
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 131.6 (d, *J* = 18.0 Hz), 129.7 (d, *J* = 21.5 Hz), 120.7, 28.3.

IR: 1481, 1072, 1011, 818, 494 cm^{-1}.

HRMS calcd for $C_7H_6Br_1S_1$ $[M-H]^+$: 200.9368, found: 200.9366.

Synthesis of disulfides

Standard procedure for the synthesis of disulfides from the corresponding thiol:
Following a modified literature procedure[4], a suspension of 1,3-dibromo-5,5-dimethylhydantoin (1.073 g, 3.75 mmol) in chloroform (10 mL) was added dropwise to a solution of the thiol (15 mmol) in chloroform (5 mL). The suspension was stirred at room temperature for 1 h and then washed with a saturated $NaHCO_3$ solution (2 x 15 mL) and brine (15 mL). The organic layer was dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure to yield the corresponding disulfide.



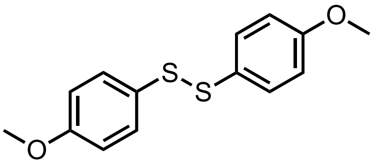
Bis(3-methoxyphenyl)disulfide[5] (2.040 g, 97%, 7.3 mmol), colourless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.22 (m, 2H), 7.19 – 7.10 (m, 4H), 6.89 – 6.75 (m, 2H), 3.82 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 138.7, 130.4, 120.0, 113.6, 113.0, 55.8

IR: 2932, 2924, 1568, 1468, 1221, 851, 766 cm^{-1}

HRMS (EI): [$C_{14}H_{14}O_2S_2$] calc. 278.0435, found 278.0434



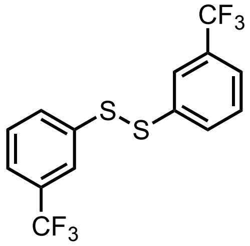
Bis(4-methoxyphenyl)disulfide[5] (1.815 g, 87%, 6.5 mmol) , brown oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.9 Hz, 4H), 6.88 (d, *J* = 8.9 Hz, 4H), 3.84 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 133.1, 128.8, 115.0, 55.8

IR: 2932, 2832, 1587, 1485, 1171, 1028, 817, 520 cm^{-1}

HRMS (EI): [$C_{14}H_{14}O_2S_2$] calc. 278.0435, found 278.0438



Bis(3-(trifluoromethyl)phenyl)disulfide[6] (2.382 g, 89%, 6.7 mmol), yellow oil

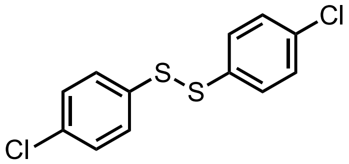
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 2H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 132.1 (q, *J* = 32.7 Hz), 131.0, 130.1, 124.7 (dd, *J* = 6.5, 3.7 Hz), 124.6 - 124.8 (m).

^{19}F NMR (283 MHz, $CDCl_3$) δ -63.14 (s).

IR: 1317, 1119, 1098, 791, 692 cm^{-1}

HRMS (EI): [$C_{14}H_8S_2F_6$] calc353.9972, found 353.9973



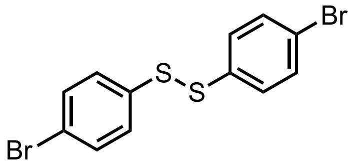
Bis(4-chlorophenyl)disulfide[5] (1.944 g, 91%, 6.8 mmol), white solid (mp: 74-75 °C, chloroform)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (m, 4H), 7.33 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.5, 134.1, 129.8, 129.7.

IR: 1468, 1377, 810, 486 cm^{-1}

HRMS (EI): [$C_{12}H_8S_2Cl_2$] calc 285.9444, found 285.9446



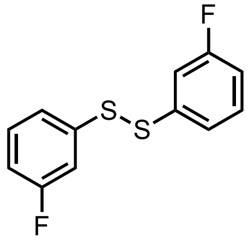
Bis(4-bromophenyl)disulfide[5] (2.601 g, 92%, 6.9 mmol), white solid (mp: 91-93 °C, chloroform)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (m, 4H), 7.38 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 132.7, 129.8, 122.0.

IR: 1464, 1377, 1067, 810, 494 cm^{-1}

HRMS (EI): [$C_{12}H_8S_2Br_2$] calc. 373.8434, found 373.8436



Bis(3-fluorophenyl)disulfide (1.680 g, 88%, 6.6 mmol), colourless oil

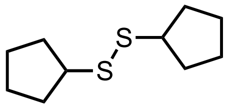
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.10 (m, 6H), 6.88 – 6.80 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5 (d, *J* = 249.5 Hz), 139.2 (d, *J* = 7.1 Hz), 131.0 (d, *J* = 8.4 Hz), 123.0 (d, *J* = 3.0 Hz), 114.8 (d, *J* = 21.4 Hz), 114.4 (d, *J* = 24.2 Hz).

^{19}F NMR (283 MHz, $CDCl_3$) δ -111.40 (s).

IR: 1578, 1470, 1213, 872, 772, 673, 494 cm^{-1}

HRMS (EI): [$C_{12}H_8F_2S_2$] calc. 254.0036, found 254.0036



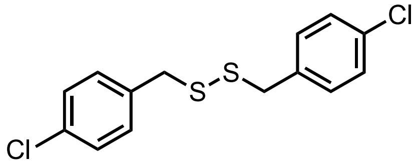
Dicyclopentyldisulfide (1.411 g, 89%, 6.7 mmol), colourless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.28 (dq, *J* = 7.1, 5.5 Hz, 2H), 2.10 – 1.86 (m, 4H), 1.84 – 1.49 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 50.8, 33.5, 25.1

IR: 2955, 2862, 1443, 1235, 481 cm^{-1}

HRMS (EI): [$C_{10}H_{10}S_2$] calc. 202.0850, found 202.0850



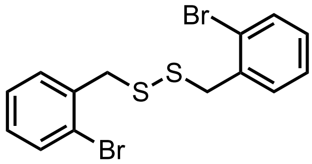
Bis(4-chlorobenzyl)disulfide[7] (2.199 g, 93%, 7.0 mmol), white solid (mp: 62-63 °C, chloroform)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 4H), 7.16 (m, 4H), 3.57 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.2, 133.8, 131.1, 129.1, 42.9

IR: 1489, 1088, 1015, 837, 505, 494 cm^{-1}

HRMS (EI): [$C_{14}H_{12}S_2Cl_2$] calc. 313.9757, found 313.9760



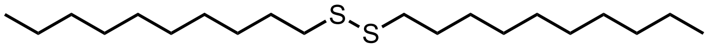
Bis(2-bromobenzyl)disulfide[8] (1.164 g, 82%, 2.88 mmol), white solid (mp: 86-87 °C, chloroform)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.9 Hz, 2H), 7.21 – 7.16 (m, 4H), 7.11 – 7.02 (m, 2H), 3.71 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 133.5, 132.1, 129.6, 127.8, 125.0, 44.1

IR: 1435, 1026, 756 648, 571, 440 cm^{-1}

HRMS (EI): [$C_{14}H_{12}S_2Br_2$] calc. 401.8747, found 401.8752



Didecyldisulfide[8] (1.238 g, 90%, 3.6 mmol), colourless oil

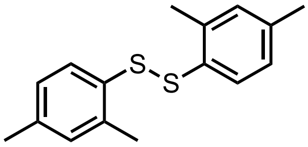
1,3-dibromo-5,5-dimethylhydantoin (0.574 g, 2 mmol) was added slowly to a solution of 1-decanethiol (1.394 g, 8 mmol) in chloroform (8 mL). The suspension was stirred at room temperature for 2 h, filtered and the solvent removed under reduced pressure to yield didecyldisulfide.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 – 2.65 (m, 4H), 1.71 (dt, *J* = 14.9, 7.2 Hz, 4H), 1.48 – 1.20 (m, 28H), 0.92 (t, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 39.6, 32.4, 30.0, 30.0, 29.8, 29.7, 29.7, 29.0, 23.1, 14.6.

IR: 2922, 2847, 1454, 762 cm^{-1}

HRMS (EI): [$C_{20}H_{42}S_2$] calc. 346.2728, found 346.2727



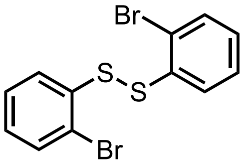
Bis(2,4-dimethylphenyl)disulfide (1.932 g, 93%, 7.0 mmol), yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.9 Hz, 2H), 7.07 (s, 2H), 7.01 (d, *J* = 7.5 Hz, 2H), 2.45 (s, 6H), 2.37 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 138.3, 132.8, 131.7, 130.9, 127.8, 21.5, 20.6

IR: 1472, 1045, 806, 546 cm^{-1}

HRMS (EI): [$C_{16}H_{18}S_2$] calc. 274.0850, found 274.0852



Bis(2-bromophenyl)disulfide (0.895 g, 80%, 2.4 mmol), white solid (mp: 95-96 °C, chloroform)

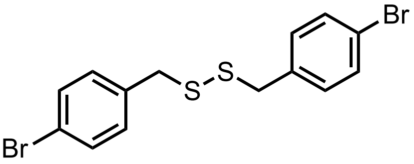
A suspension of 1,3-dibromo-5,5-dimethylhydantoin (0.429 g, 1.5 mmol) in chloroform (5 mL) was added dropwise to a solution of 2-bromothiophenol (1.126 g, 6 mmol) in chloroform (3 mL). The suspension was stirred at room temperature for 1 h and then washed with a saturated $NaHCO_3$ solution (2 x 15 mL) and brine (15 mL). The organic layer was dried over anhydrous $MgSO_4$ and solvent removed under reduced pressure to yield Bis(2-bromophenyl)disulfide.

^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (m, 4H), 7.23 – 7.15 (m, 2H), 7.00 (td, J = 7.8, 1.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 133.4, 128.7, 128.4, 127.3, 121.4

IR: 1420, 1011, 733, 648 cm^{-1}

HRMS (EI): [$C_{12}H_8S_2Br_2$] calc. 373.8434, found 373.8437



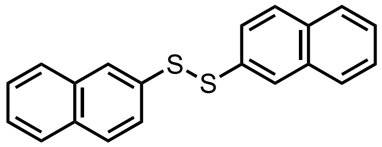
Bis(4-bromobenzyl)disulfide (0.9703 g, 98%, 2.4 mmol) , colourless oil

^1H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 4H), 7.13 – 7.05 (m, 4H), 3.55 (s, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.5, 131.8, 131.1, 121.6, 42.7

IR: 1481, 1065, 1011, 826, 802, 494, 401 cm^{-1}.

HRMS calcd for $C_{14}H_{11}Br_2S_2$ $[M-H]^+$: 400.8663, found: 400.8657.



1,2-di(naphthalen-2-yl)disulfide[9] (1.472 g, 46%, 4.6 mmol), pale yellow crystals (mp: 141-142 ^{o}C, chloroform).

Synthesised by the standard procedure on a 10 mmol scale.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 1.7 Hz, 1H), 7.83 – 7.77 (m, 2H), 7.76 – 7.71 (m, 1H), 7.62 (dd, J = 8.7, 1.9 Hz, 1H), 7.50 – 7.42 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.4, 133.6, 132.6, 129.1, 127.9, 127.6, 126.9, 126.6, 126.4, 125.8.

IR: 2970, 1738, 1366, 1352, 1229, 1217, 897, 862, 810, 735, 629, 475 cm^{-1}.

HRMS (EI+): $[C_{20}H_{14}S_2]^+$: calcd. 318.0537, found 318.0543

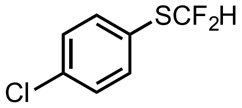
Synthesis of difluoromethyl thioethers

Standard procedure for the synthesis of difluoromethyl thioethers from the corresponding disulfide:

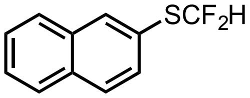
An oven-dried flask was charged with caesium fluoride (0.608 g, 4 mmol), the disulfide (0.5 mmol) and flushed with nitrogen. *N*-Methyl-2-pyrrolidone (1 mL) was added and the solution cooled to 0 ^{o}C. Difluoromethyltrimethylsilane (0.248 g, 4 mmol) was added dropwise. The suspension was stirred at 0 °C for 1 h and then at rt for a further 19 h. Trifluorotoluene (0.041 mL, 0.33 mmol) was added as a standard and conversion determined by ^{19}F-NMR spectroscopy. The spectra were referenced to trifluorotoluene at δ= -63.72 and the conversion determined by comparing the integral of the desired product peak (doublet at δ= -94 ppm) to the integral of the peak due to the standard (δ= -63.72). Other common materials noted in the ^{19}F NMR of the crude reaction mixture are $TMSCF_2H$ @ -139 ppm and CF_2H_2@ -140 ppm.

Isolation: The NMP was removed manually by a modified counter-current extraction method with diethyl ether (4 x 10 mL) and water (4 x 10 mL).[10] The organic layer was dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure. The crude

product was purified by flash column chromatography eluting with petroleum ether and ethyl acetate. Isolation of the products was complicated by the volatility of the product. To exemplify the volatility of the products a mixed column fraction containing ~ a 1:1 mixture of $ArSCF_2H$ and the ArSH byproduct (as analysed by ^1H NMR) were subject to rotary evaporation under standard operating conditions for 1 hour. Following this treatment, reevalution by ^1H NMR showed that there was none of the $ArSCF_2H$ remaining.
Alas in the following example we have isolated the material with solvent impurities



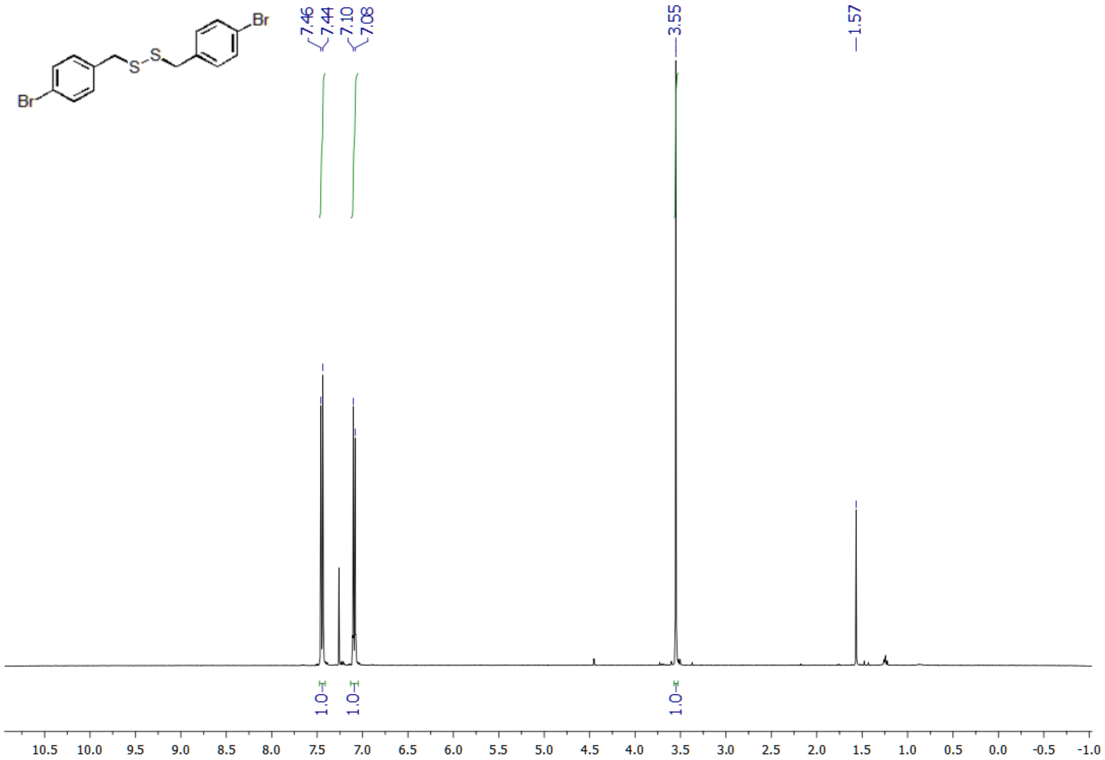
(4-chlorophenyl)(difluoromethyl)sulfane, 10 (0.065 g, 0.33 mmol, 67%), colourless oil
^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 6.81 (t, *J* = 56.6 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.7, 136.5, 129.6, 124.3, 120.4 (t, *J* = 275.8 Hz).
^{19}F NMR (283 MHz, $CDCl_3$) δ -95.09 (d, *J* = 54.1 Hz)).
IR: 2361, 1574, 1477, 1319, 1296, 1065, 1038, 907, 826, 733, 501 cm^{-1}.
HRMS (ASAP+): $[C_7H_5F_2SCl]^+$ calcd. 193.9769, found: 193.9771.

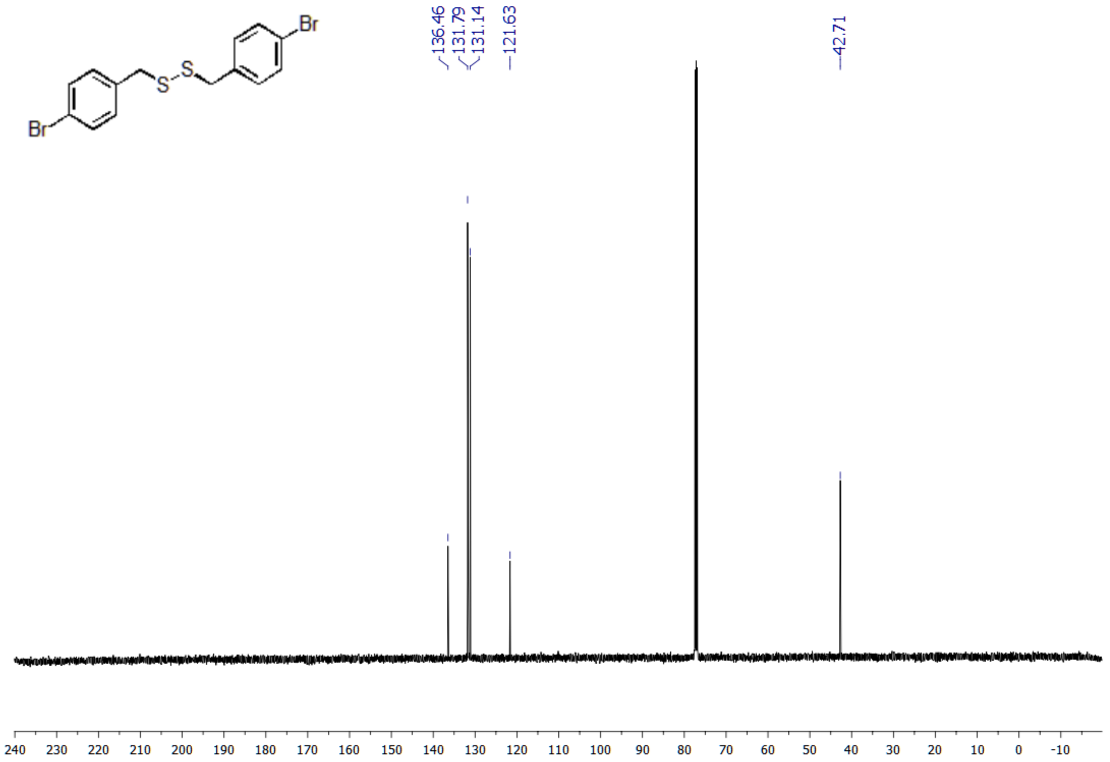


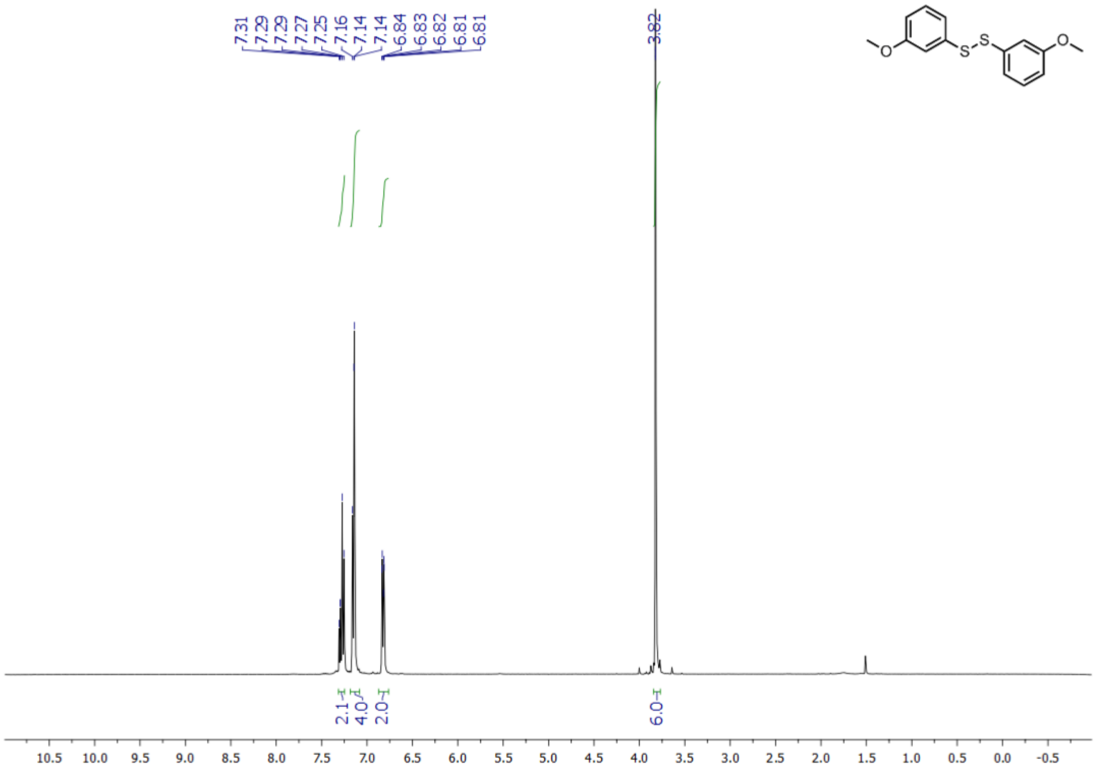
(difluoromethyl)(naphthalen-2-yl)sulfane, 18 (0.065 g, 0.31 mmol, 62%), colourless oil
^1H NMR (400 MHz, CDCl3) δ 8.00 (s, 1H), 7.80 – 7.69 (m, 3H), 7.54 – 7.46 (m, 1H), 7.46 – 7.38 (m, 2H), 6.78 (t, J = 56.9 Hz, 1H).
^{13}C NMR (75 MHz, CDCl3) δ 135.5, 133.5, 131.5, 129.1, 128.0, 127.8, 127.5, 126.9, 125.6, 123.3, 121.2 (t, J = 275.6 Hz).
^{19}F NMR (376 MHz, CDCl3) δ -91.09 (d, J = 56.8 Hz, 2F).
IR: 1501, 1318, 1296, 1061, 1030, 814, 754, 475 cm^{-1}.
HRMS (EI+): $[C_{11}H_8F_2S]^+$ calcd. 210.0315, found: 210.0316

Spectroscopic Data

Disulfides






7.31
7.29
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7.27
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7.16
7.14
7.14
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6.83
6.82
6.81
6.81
3.82
O
S
S
O
2.1
4.0
2.0
6.0
10.5
10.0
9.5
9.0
8.5
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7.0
6.5
6.0
5.5
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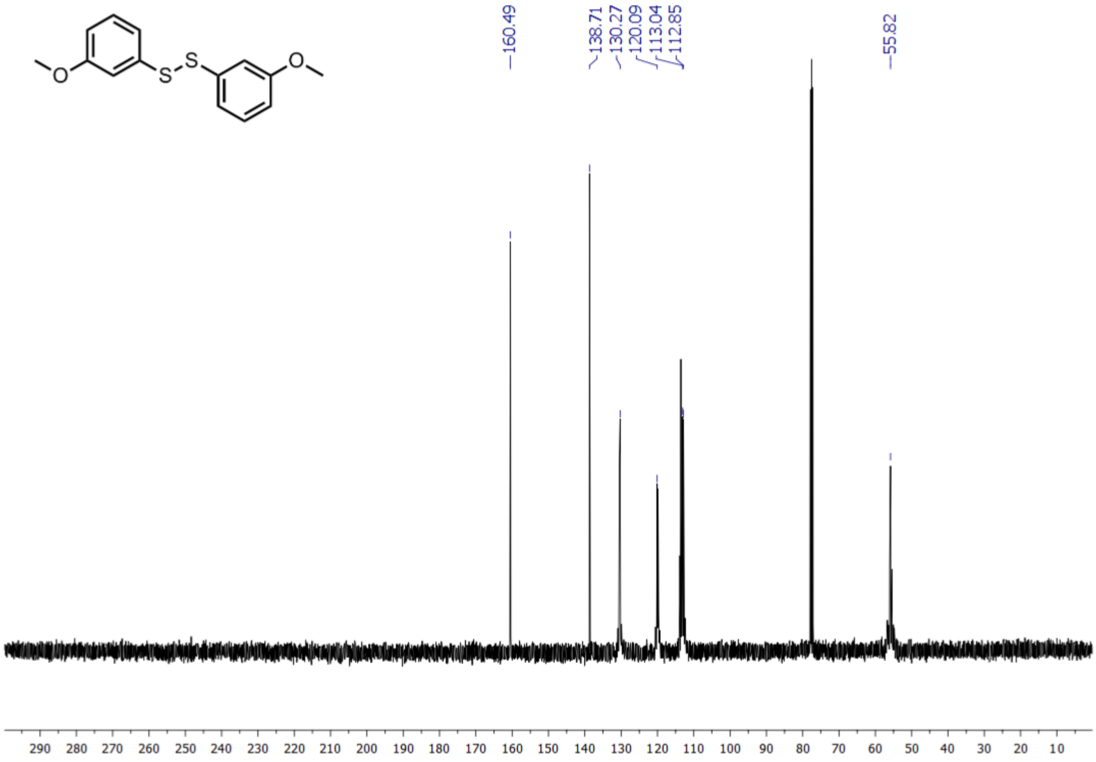
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130.27
120.09
113.04
112.85
55.82
O
S
S
O
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280
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230
220
210
200
190
180
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160
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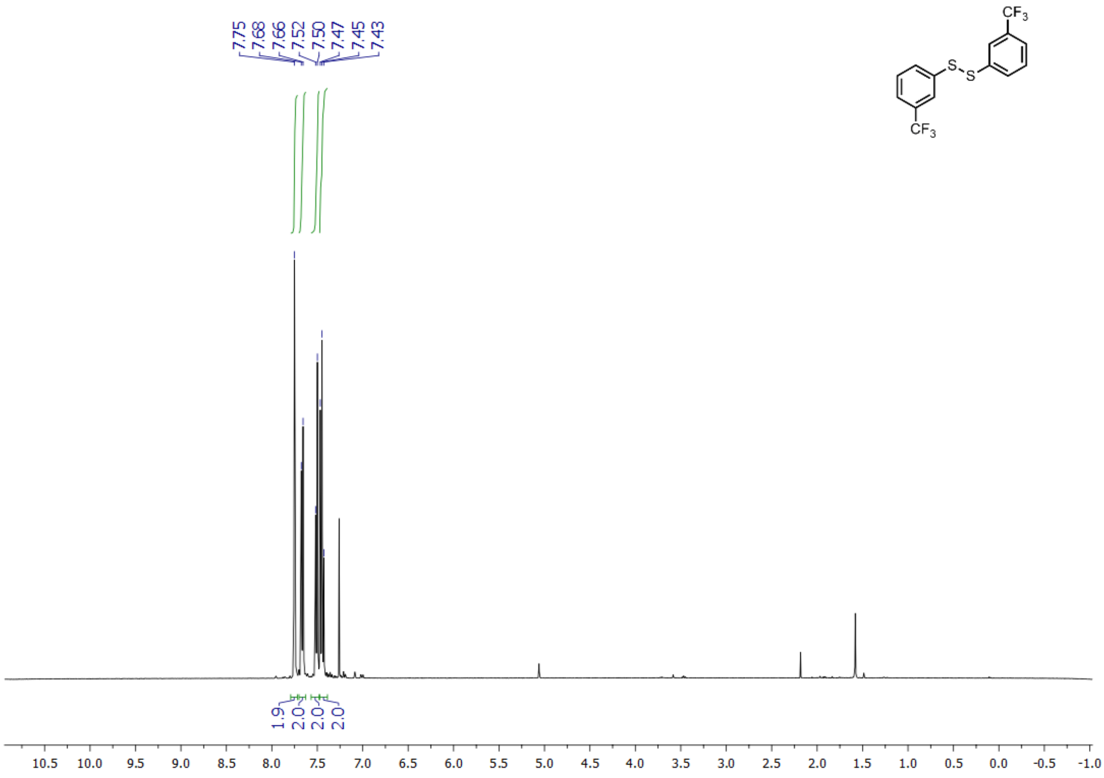

CF3
S
S
CF3
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7.52
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7.45
7.43
1.9
2.0
2.0
2.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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1.5
1.0
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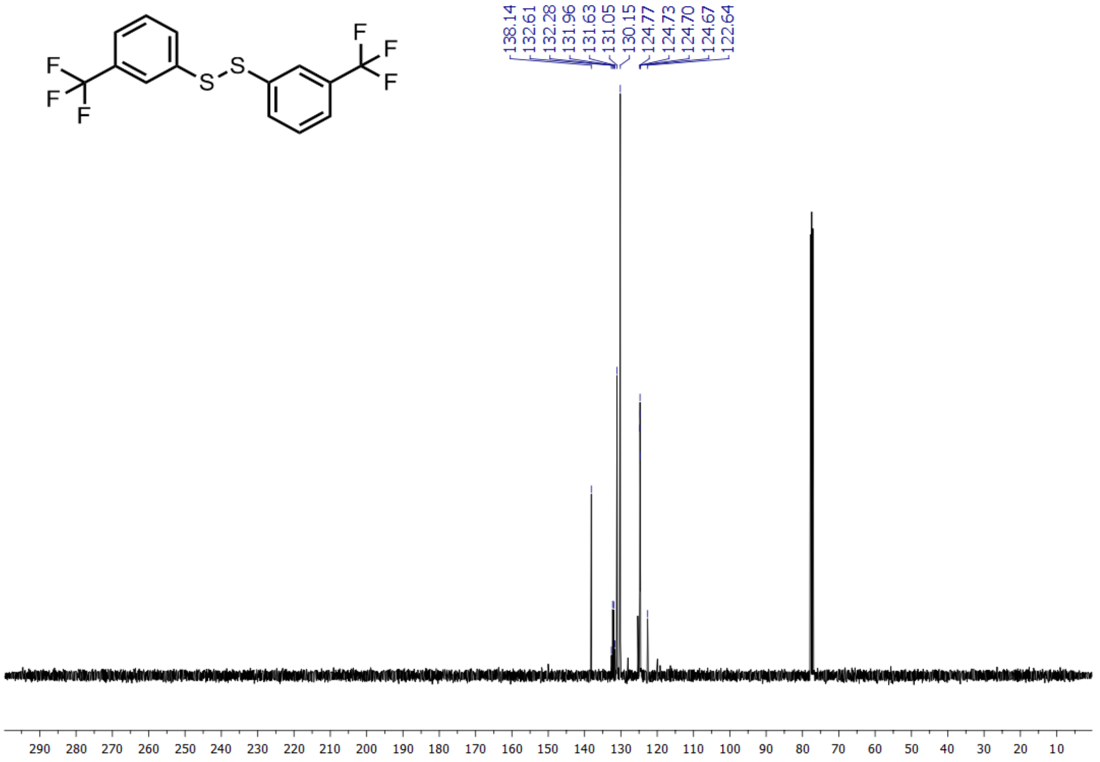
-0.5
-1.0



F
F
F
S
S
F
F
F
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132.61
132.28
131.96
131.63
131.05
130.15
124.77
124.73
124.70
124.67
122.64
290
280
270
260
250
240
230
220
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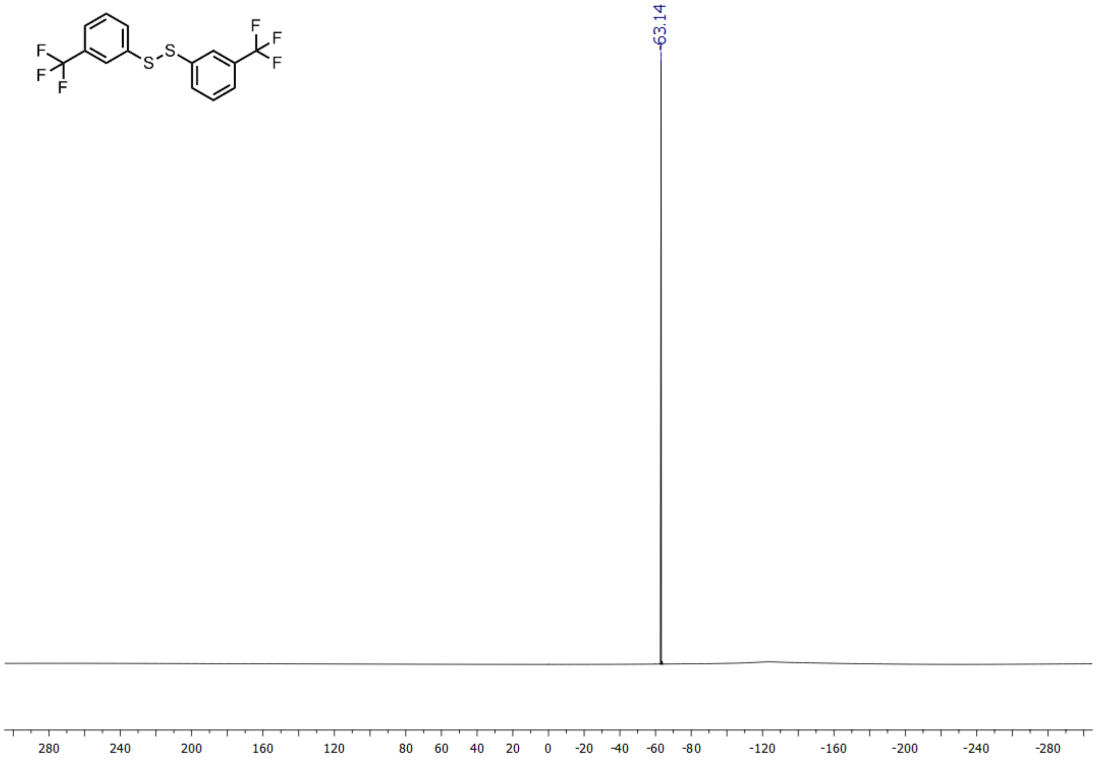
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F
F
S
S
F
F
F
-63.14
280
240
200
160
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60
40
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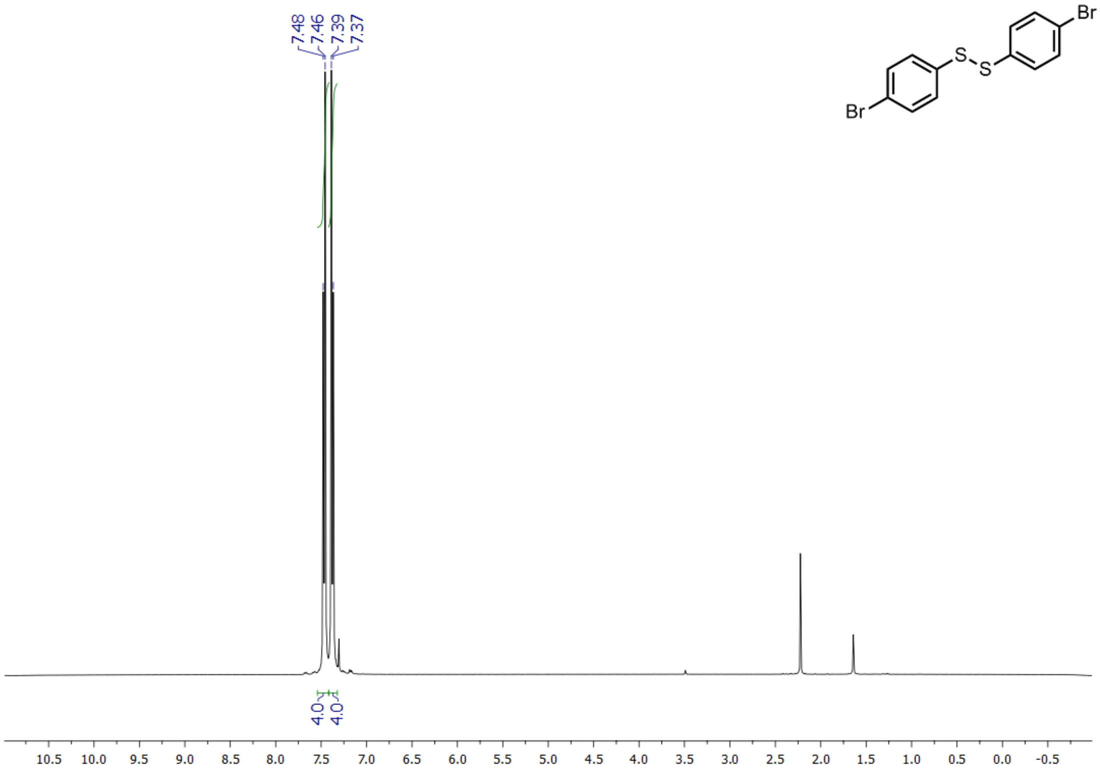
0
-20
-40
-60
-80
-120
-160
-200
-240
-280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7.46
7.39
7.37
4.0
4.0
Br
S
S
Br
10.5
10.0
9.5
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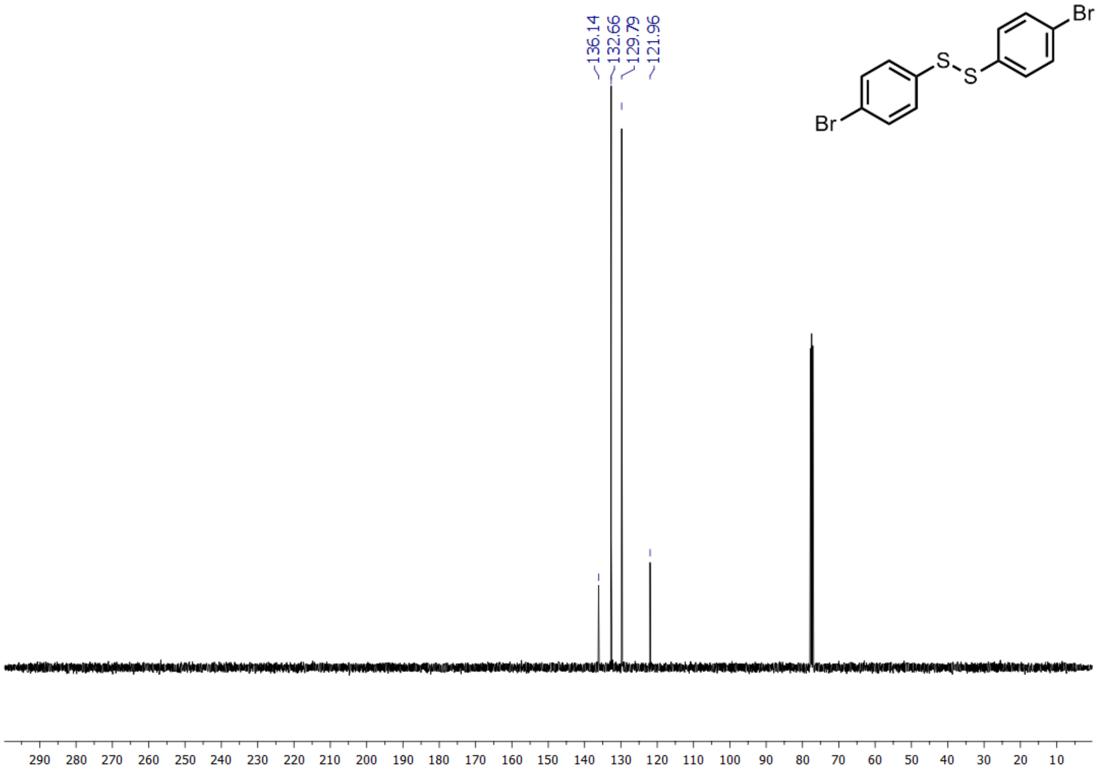
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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132.66
129.79
121.96
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S
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Br
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280
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260
250
240
230
220
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20
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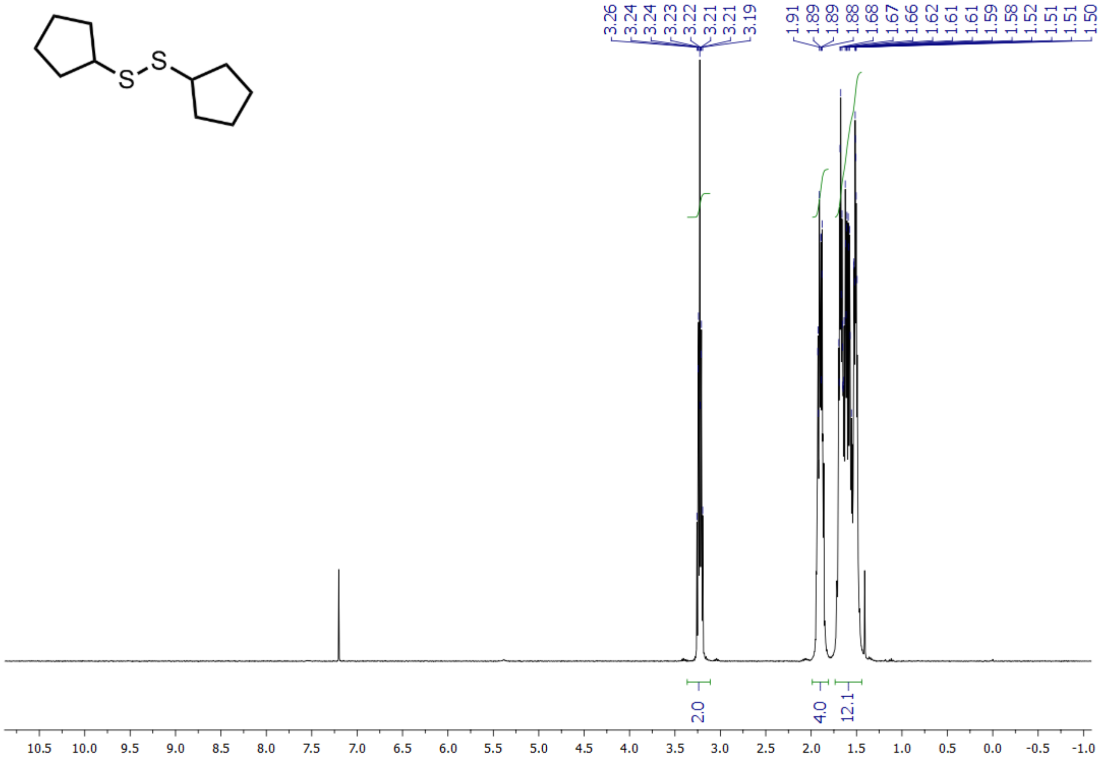
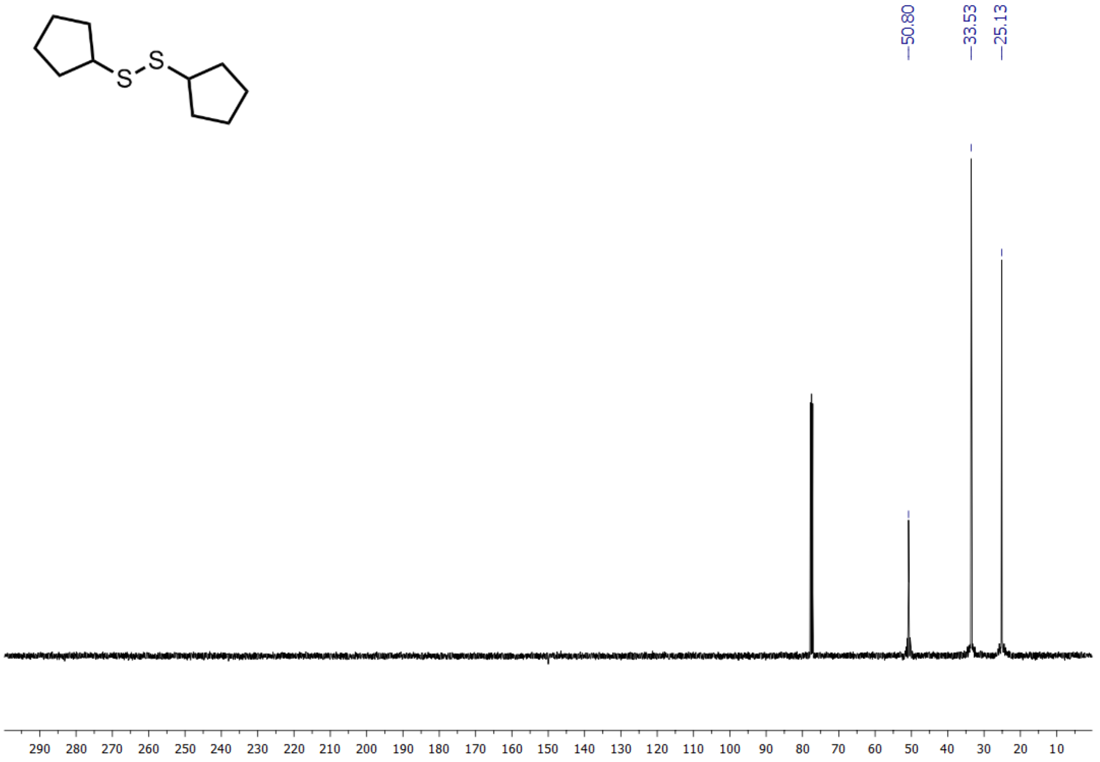
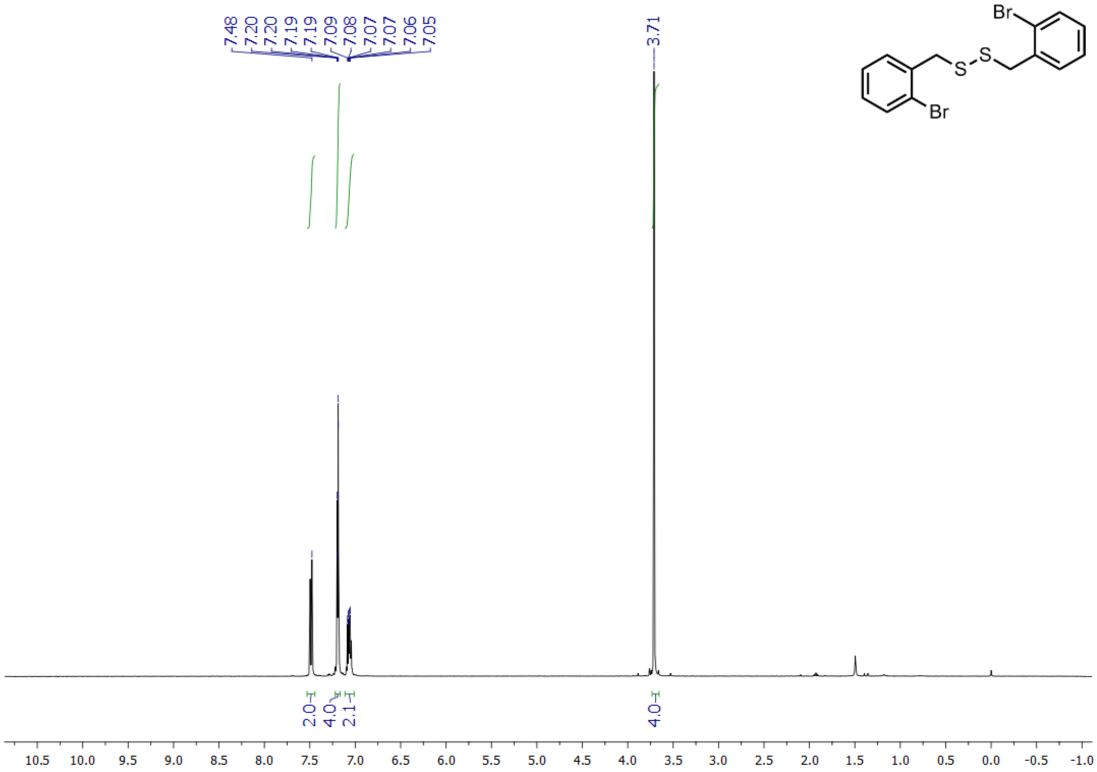


S
S
3.26
3.24
3.24
3.23
3.22
3.21
3.21
3.19
1.91
1.89
1.89
1.88
1.68
1.67
1.66
1.62
1.61
1.61
1.59
1.58
1.52
1.51
1.51
1.50
2.0
4.0
12.1
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0



S
S
50.80
33.53
25.13
290 280 270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


7.48
7.20
7.20
7.19
7.19
7.09
7.08
7.07
7.07
7.06
7.05
3.71
Br
S
S
Br
2.0
4.0
2.1
4.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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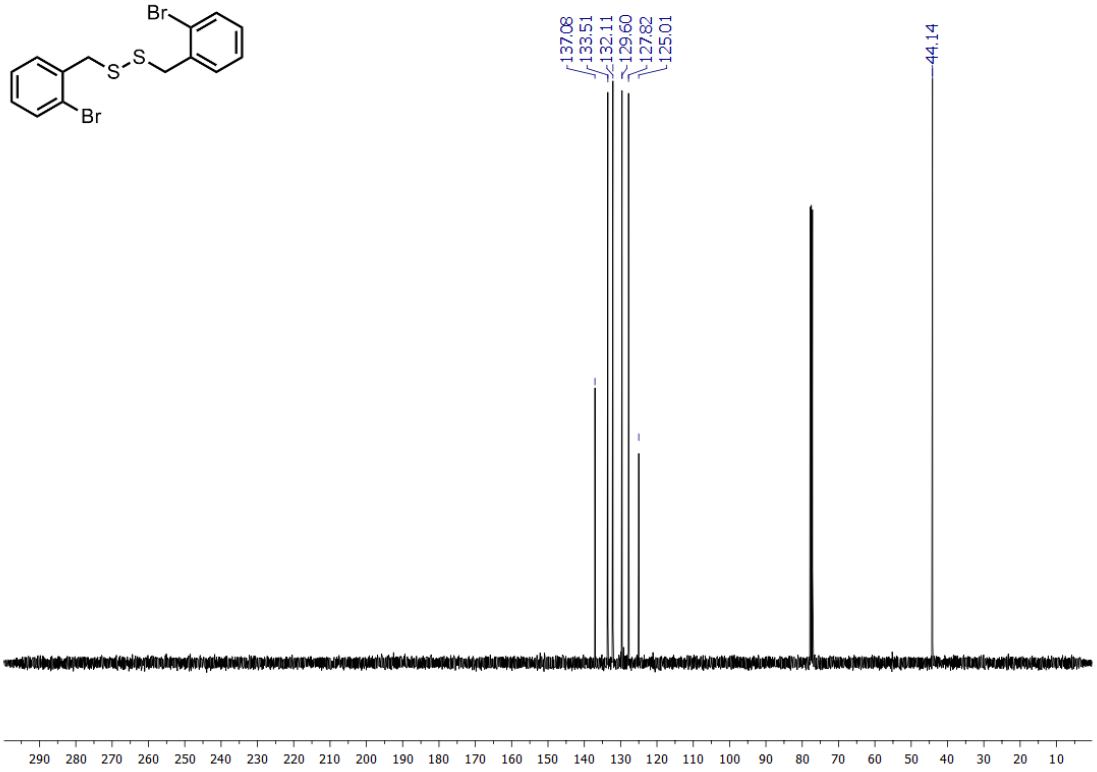
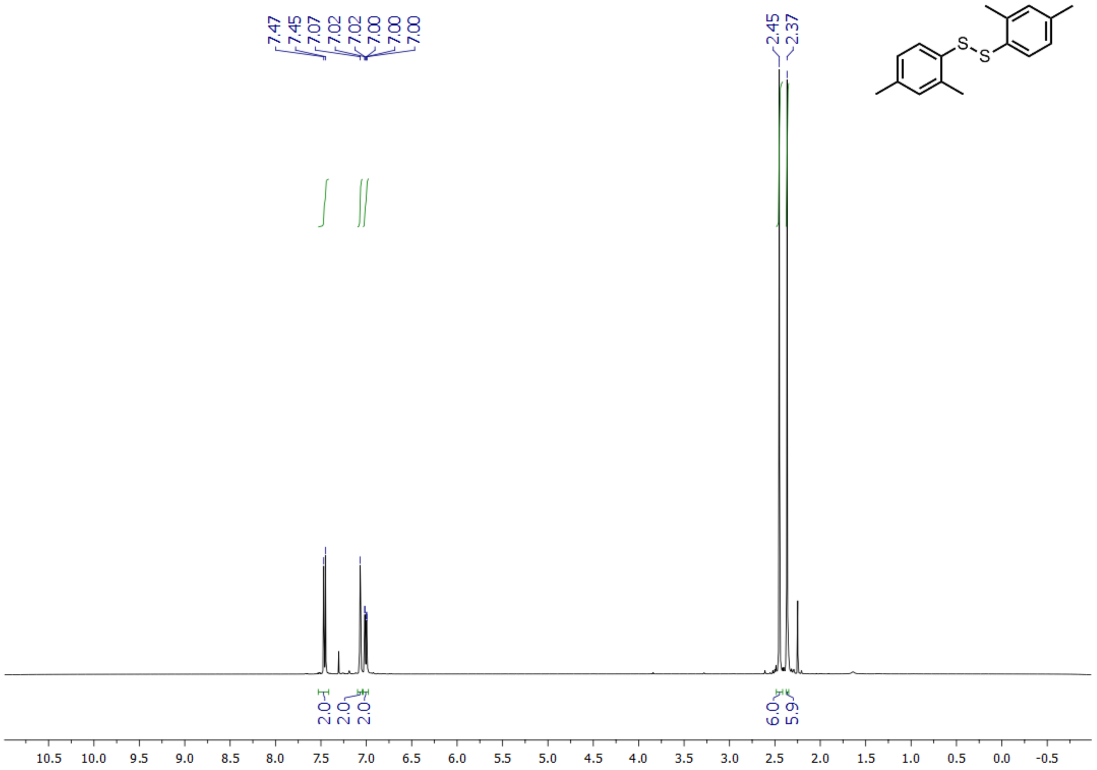
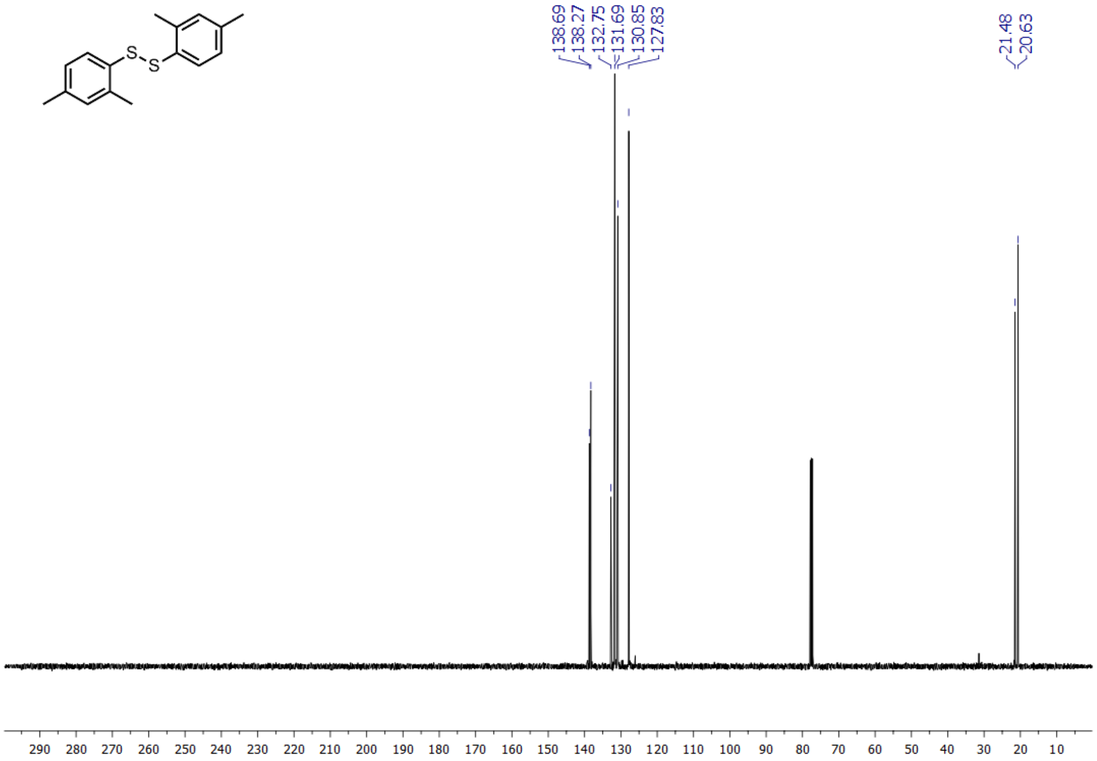
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0


Br
S
S
Br
137.08
133.51
132.11
129.60
127.82
125.01
44.14
290
280
270
260
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


7.47
7.45
7.07
7.02
7.02
7.00
7.00
7.00
2.45
2.37
S
S
2.0
2.0
2.0
6.0
5.9
10.5
10.0
9.5
9.0
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
-0.5


S
S
138.69
138.27
132.75
131.69
130.85
127.83
21.48
20.63
290
280
270
260
250
240
230
220
210
200
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180
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160
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80
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40
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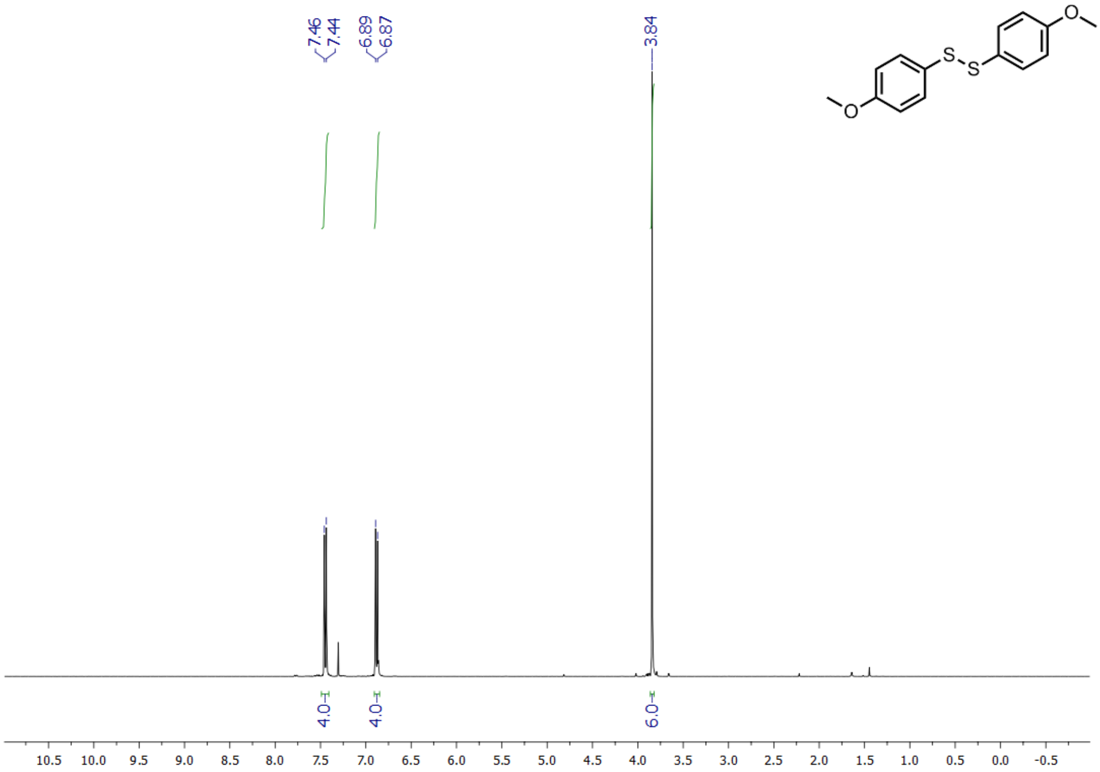
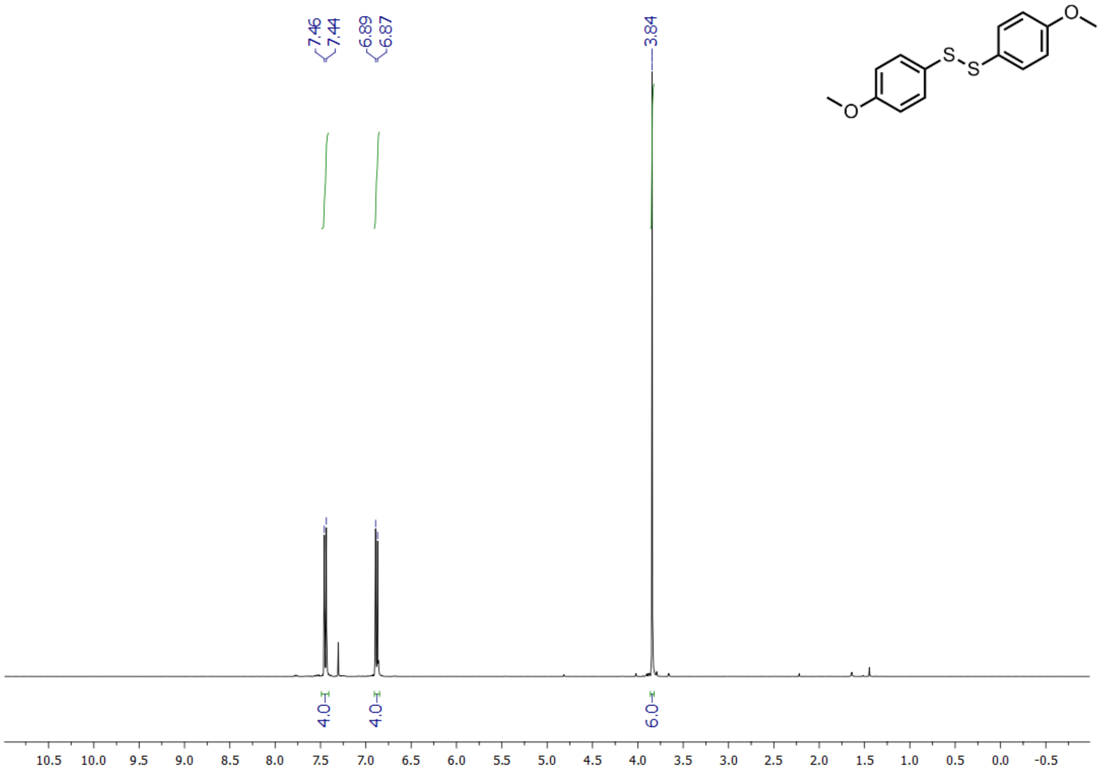
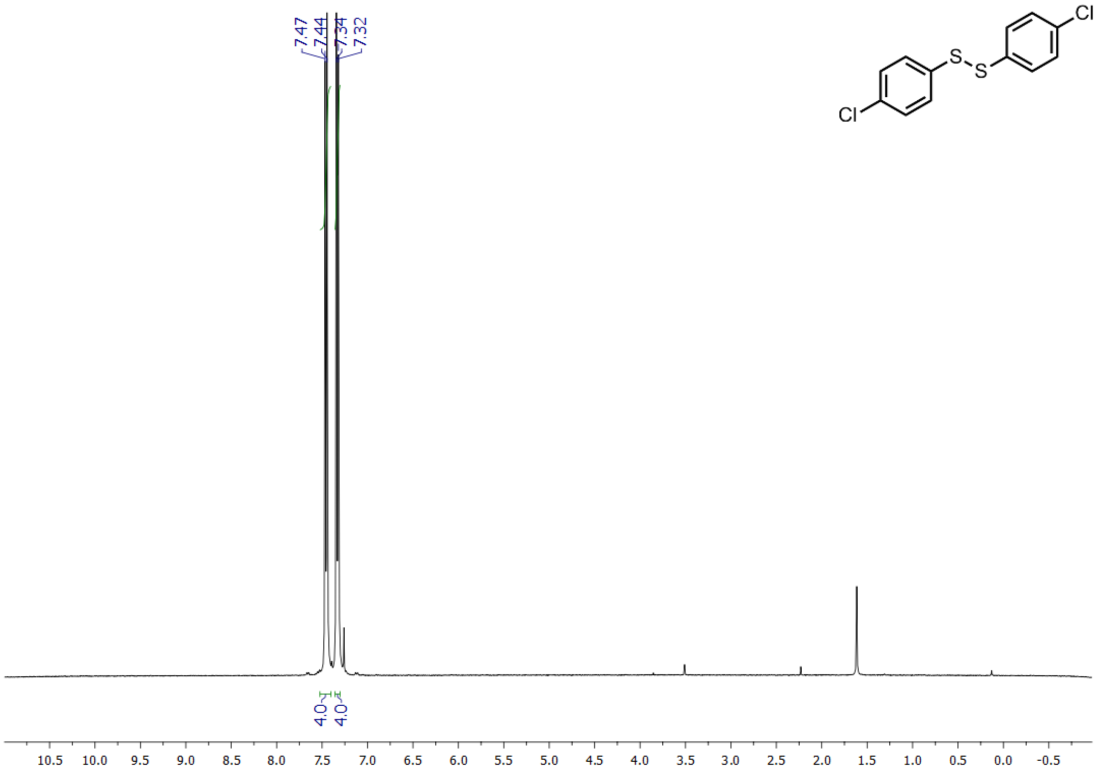
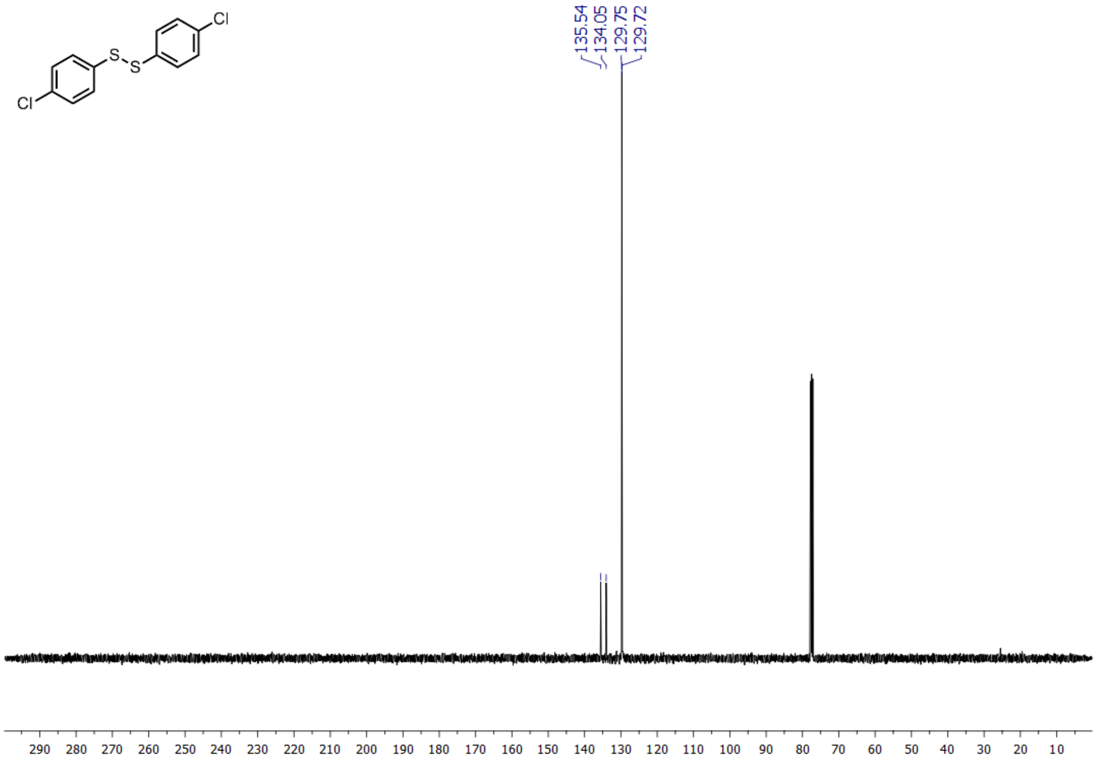
20
10


7.46
7.44
6.89
6.87
3.84
4.0
4.0
6.0
10.5 10.0 9.5 9.0 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 -0.5
O
S
S
O


7.46
7.44
6.89
6.87
3.84
4.0
4.0
6.0
10.5 10.0 9.5 9.0 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 -0.5
O
S
S
O


7.47
7.44
7.34
7.32
Cl
S
S
Cl
4.0
4.0
10.5
10.0
9.5
9.0
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
-0.5


135.54
134.05
129.75
129.72
Cl
S
S
Cl
290
280
270
260
250
240
230
220
210
200
190
180
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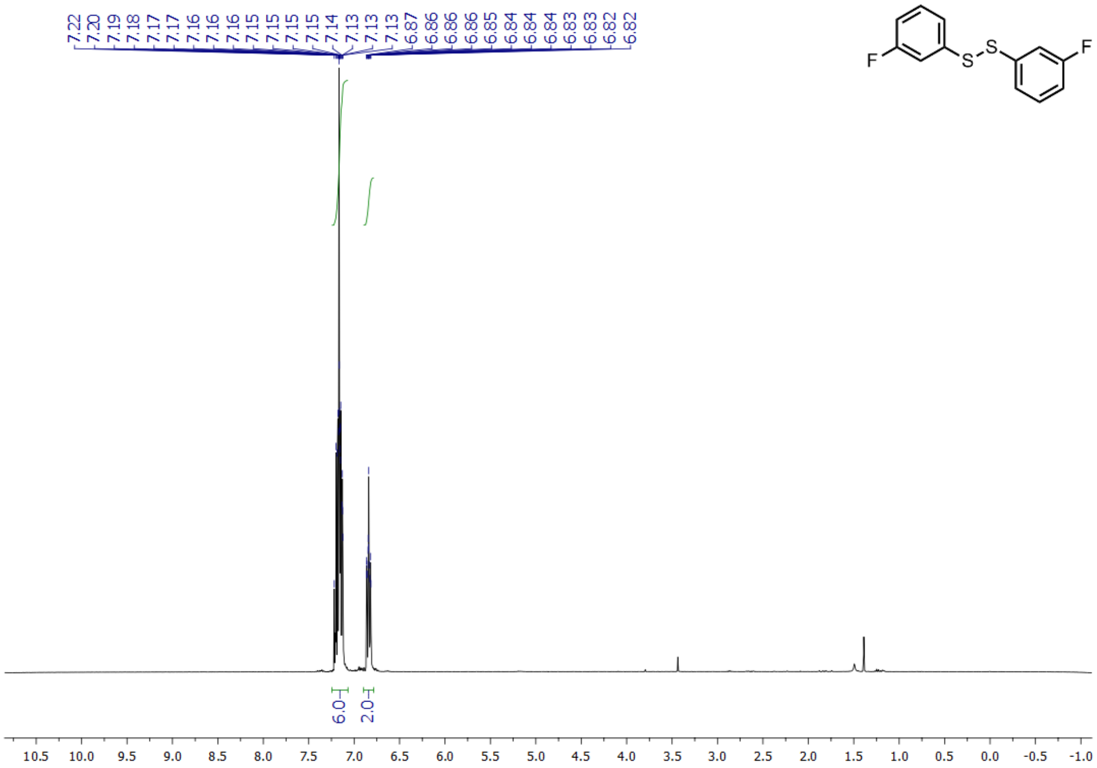
7.22
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7.19
7.18
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7.17
7.16
7.16
7.16
7.15
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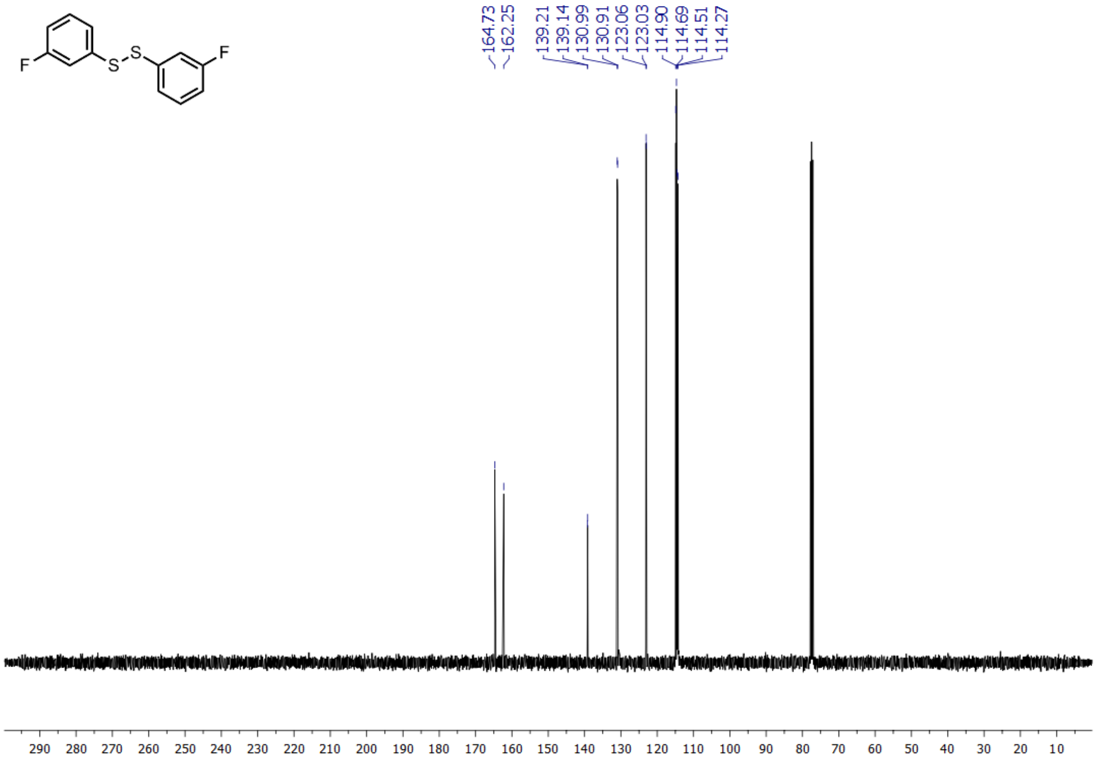
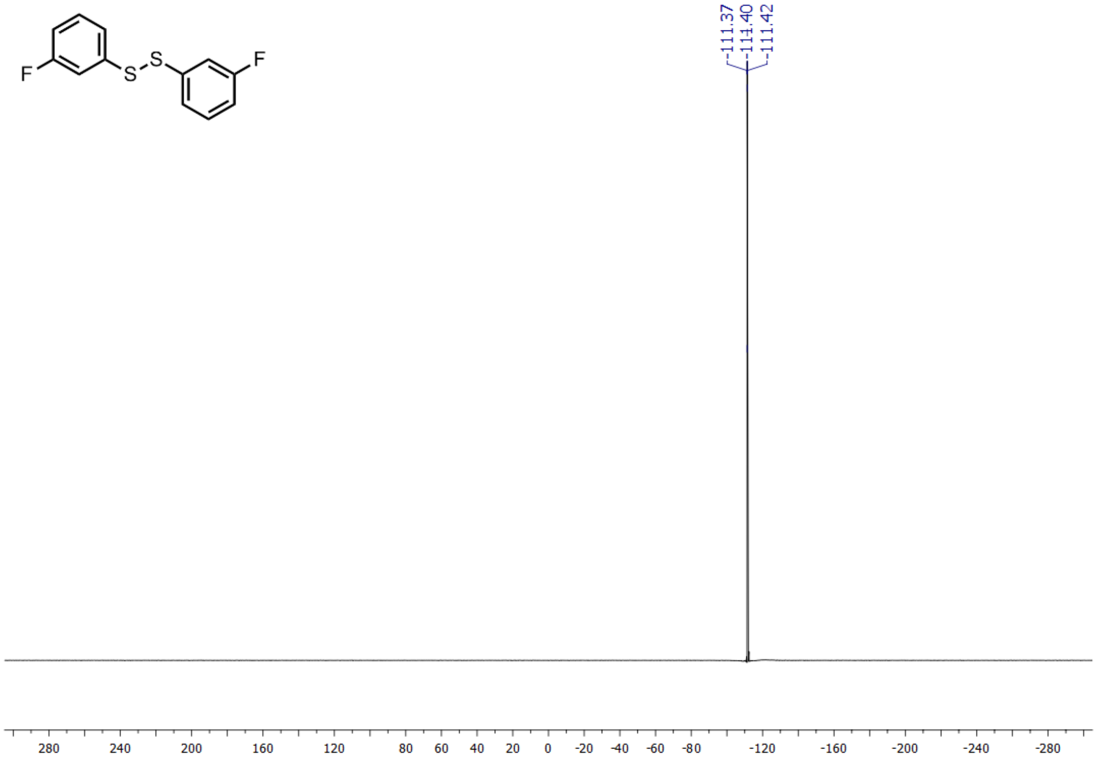
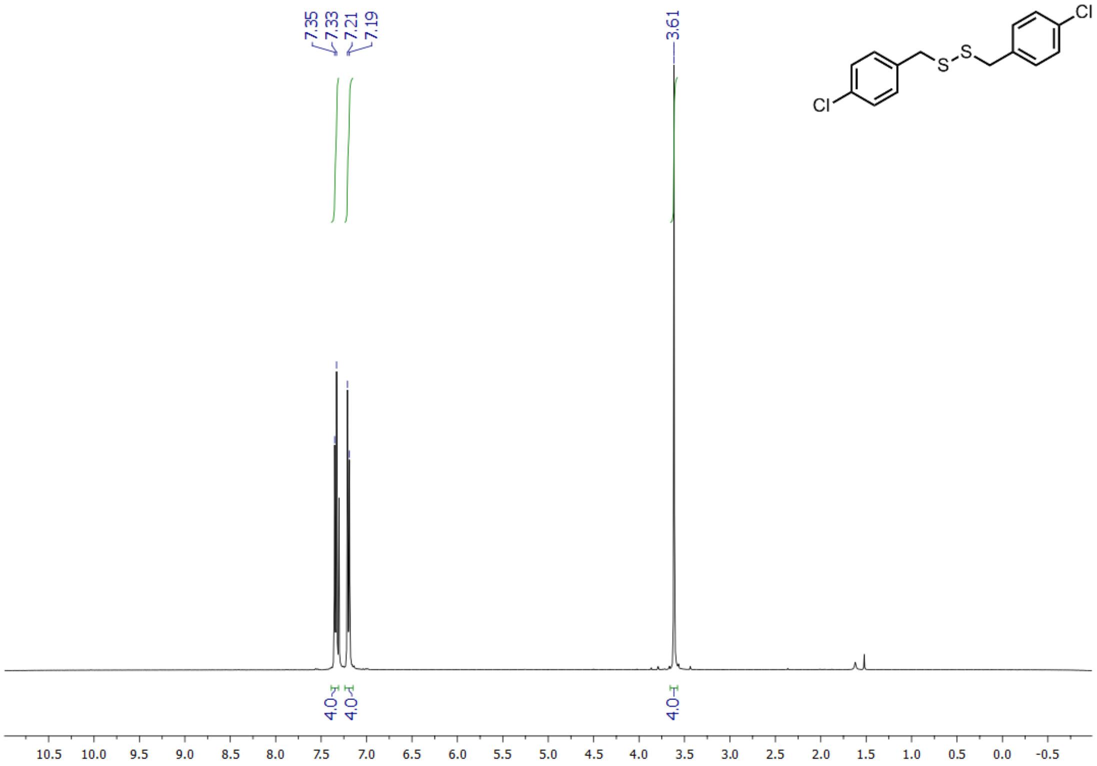
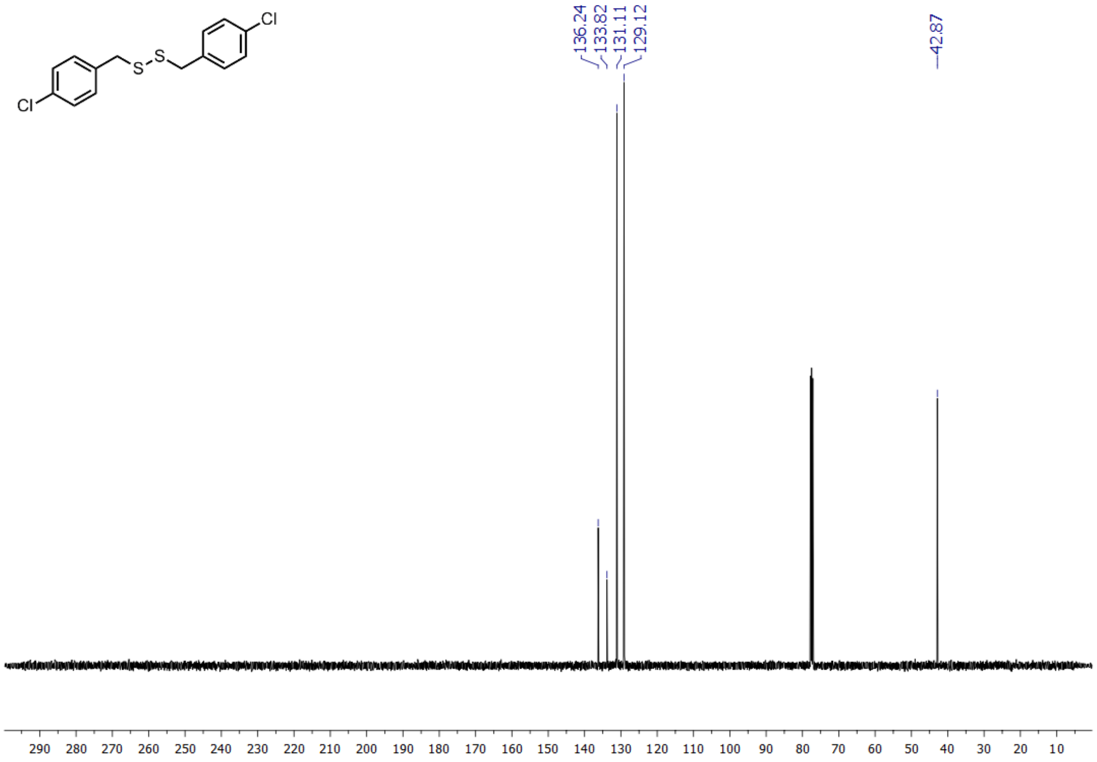
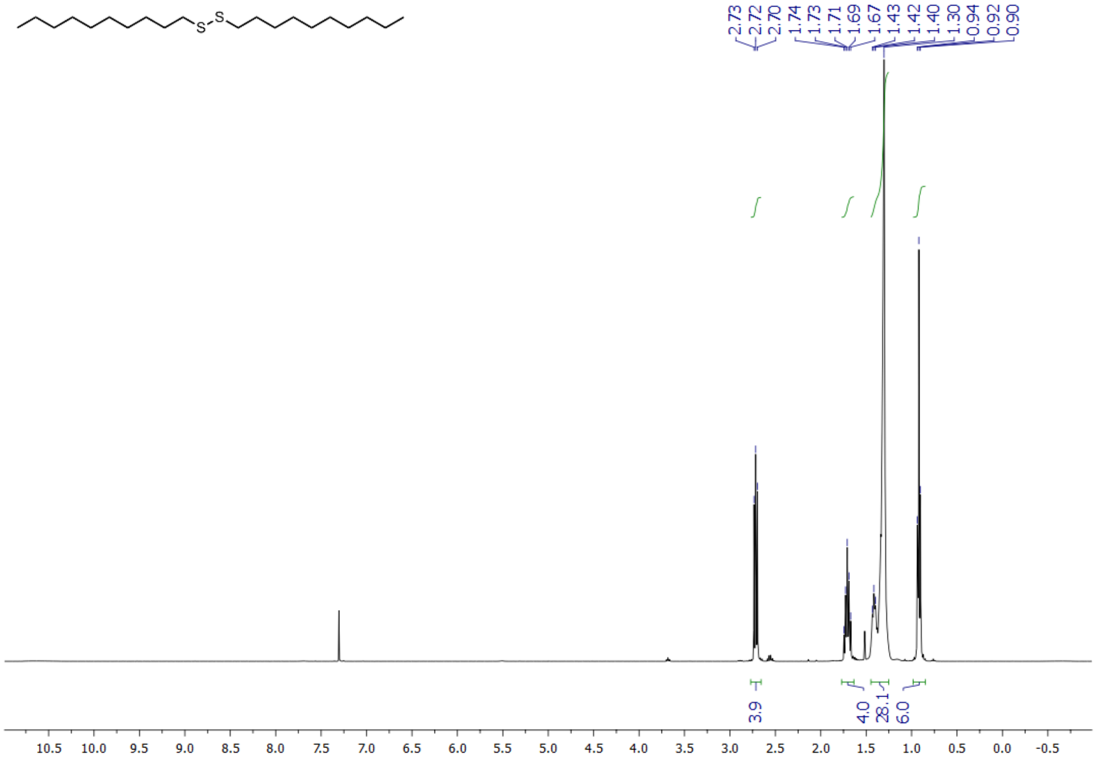
7.15
7.15
7.14
7.13
7.13
7.13
6.87
6.86
6.86
6.86
6.85
6.84
6.84
6.84
6.83
6.83
6.82
6.82
F
S
S
F
6.0
2.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

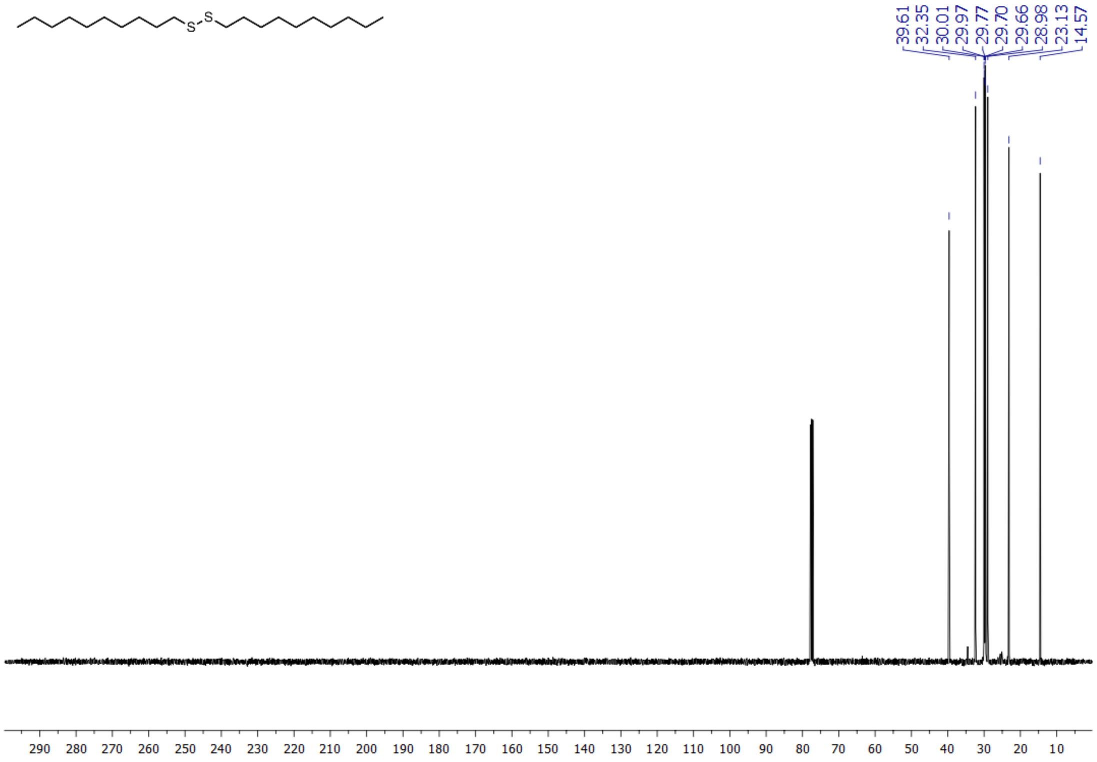

F
S
S
F
164.73
162.25
139.21
139.14
130.99
130.91
123.06
123.03
114.90
114.69
114.51
114.27
290
280
270
260
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


F
S
S
F
-111.37
-111.40
-111.42
280
240
200
160
120
80
60
40
20
0
-20
-40
-60
-80
-120
-160
-200
-240
-280


7.35
7.33
7.21
7.19
3.61
Cl
S
S
Cl
4.0
4.0
4.0
10.5 10.0 9.5 9.0 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 -0.5


136.24
133.82
131.11
129.12
42.87
Cl
S
S
Cl
290 280 270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


S
S
2.73
2.72
2.70
1.74
1.73
1.71
1.69
1.67
1.43
1.42
1.40
1.30
0.94
0.92
0.90
3.9
4.0
28.1
6.0
10.5
10.0
9.5
9.0
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
-0.5


S
S
39.61
32.35
30.01
29.97
29.77
29.70
29.66
28.98
23.13
14.57
290
280
270
260
250
240
230
220
210
200
190
180
170
160
150
140
130
120
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100
90
80
70
60
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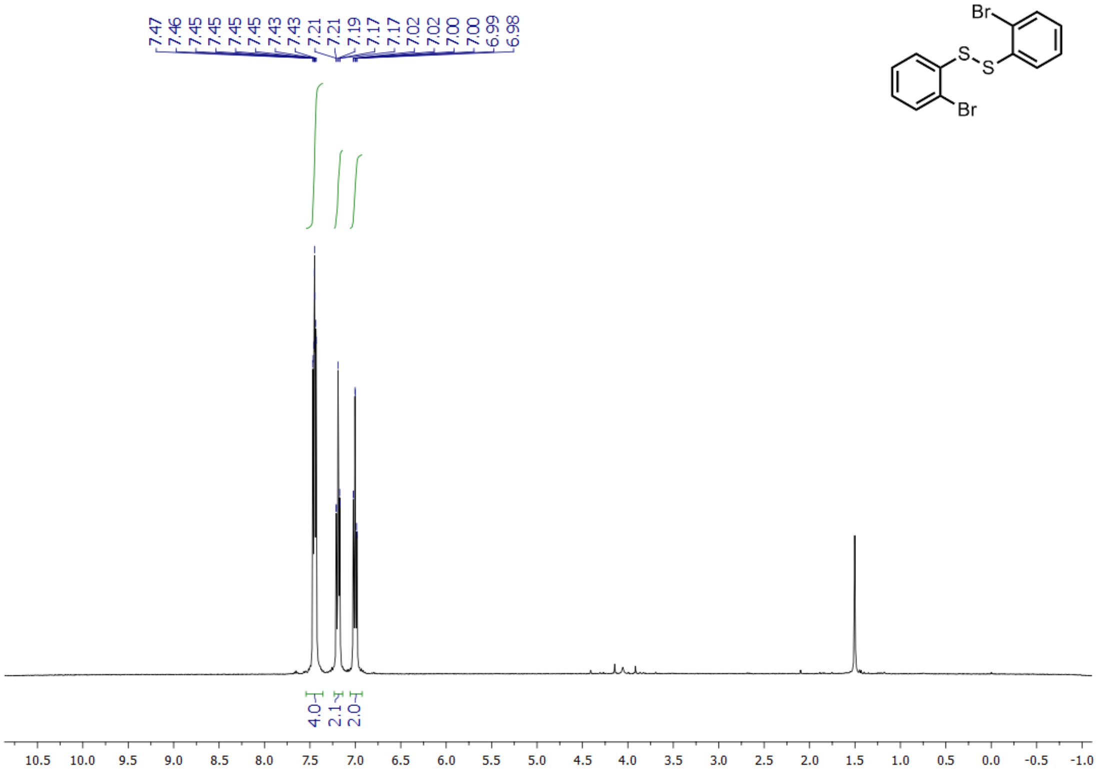
40
30
20
10


7.47
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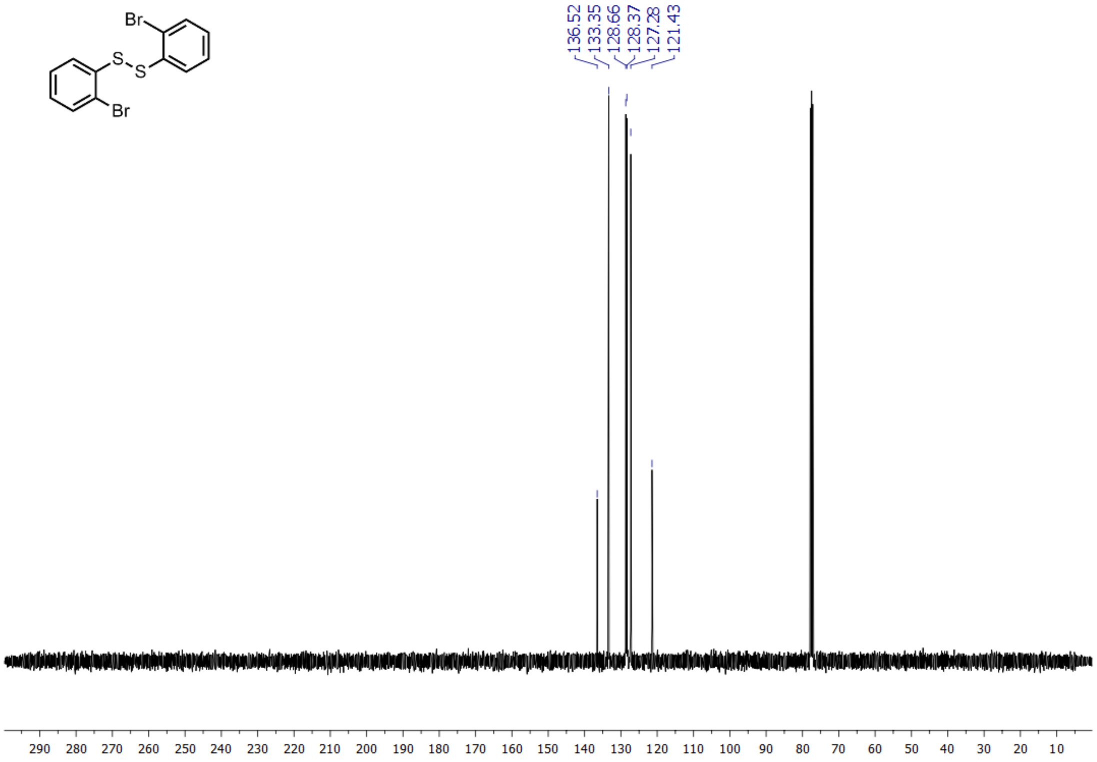
7.45
7.45
7.45
7.43
7.43
7.21
7.21
7.19
7.17
7.17
7.02
7.02
7.00
7.00
6.99
6.98
4.0
2.1
2.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
Br
S
S
Br


136.52
133.35
128.66
128.37
127.28
121.43
Br
S
S
Br
290
280
270
260
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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40
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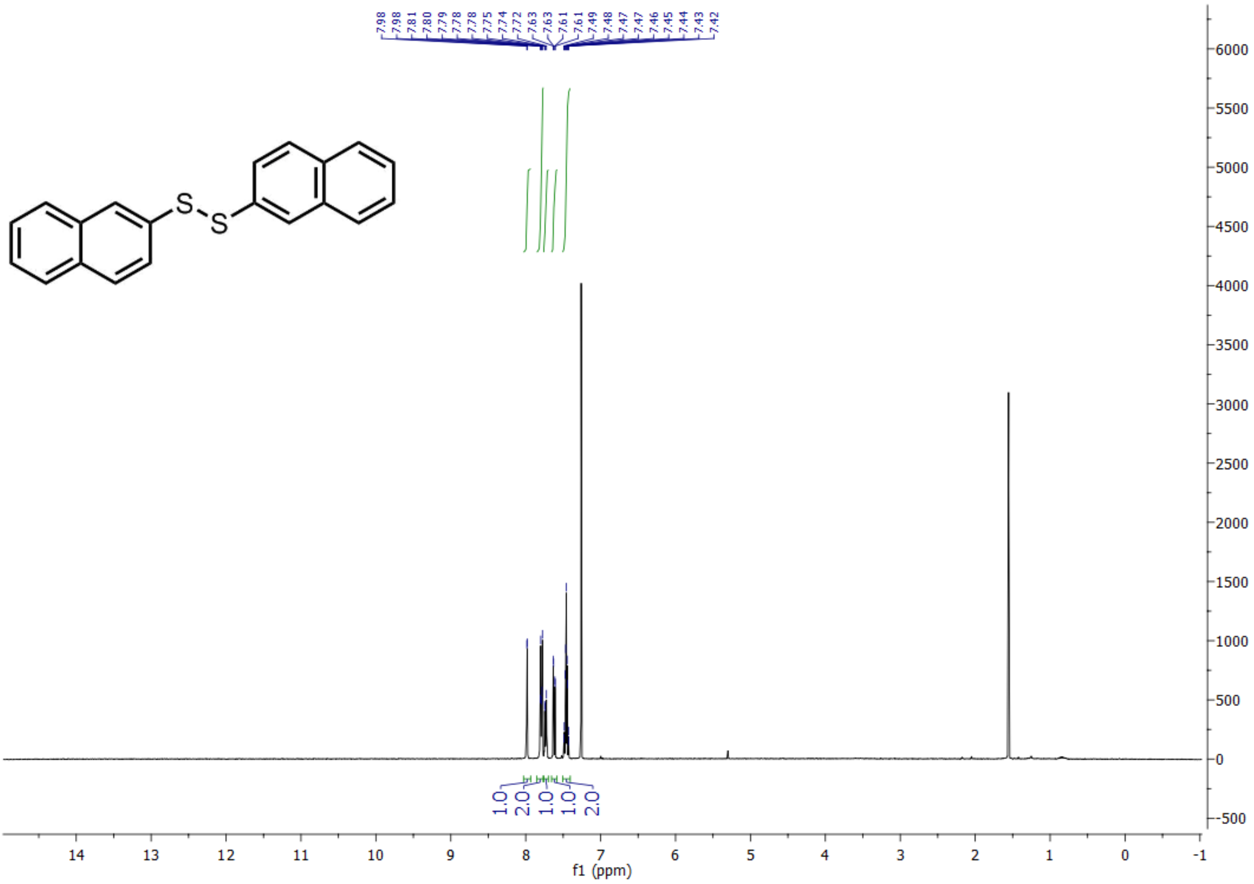
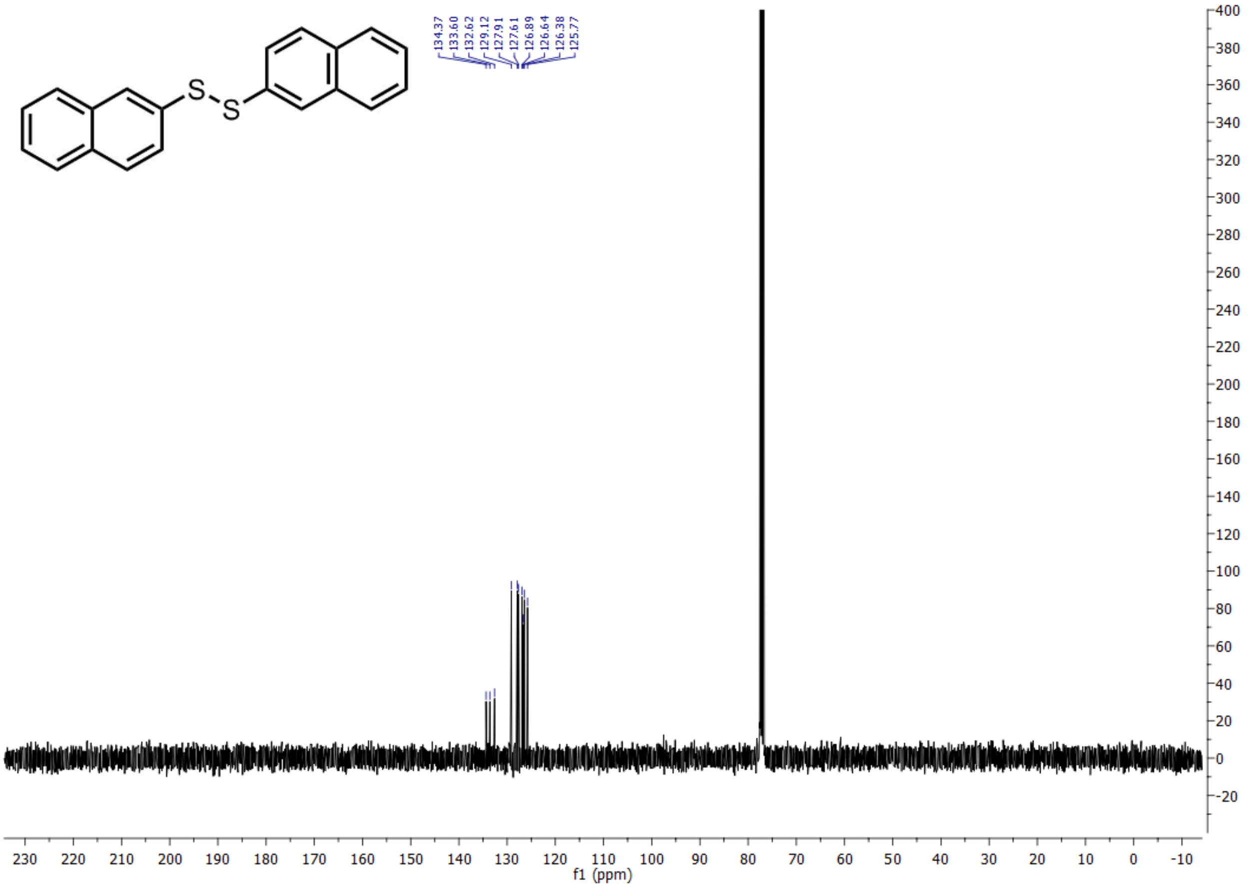
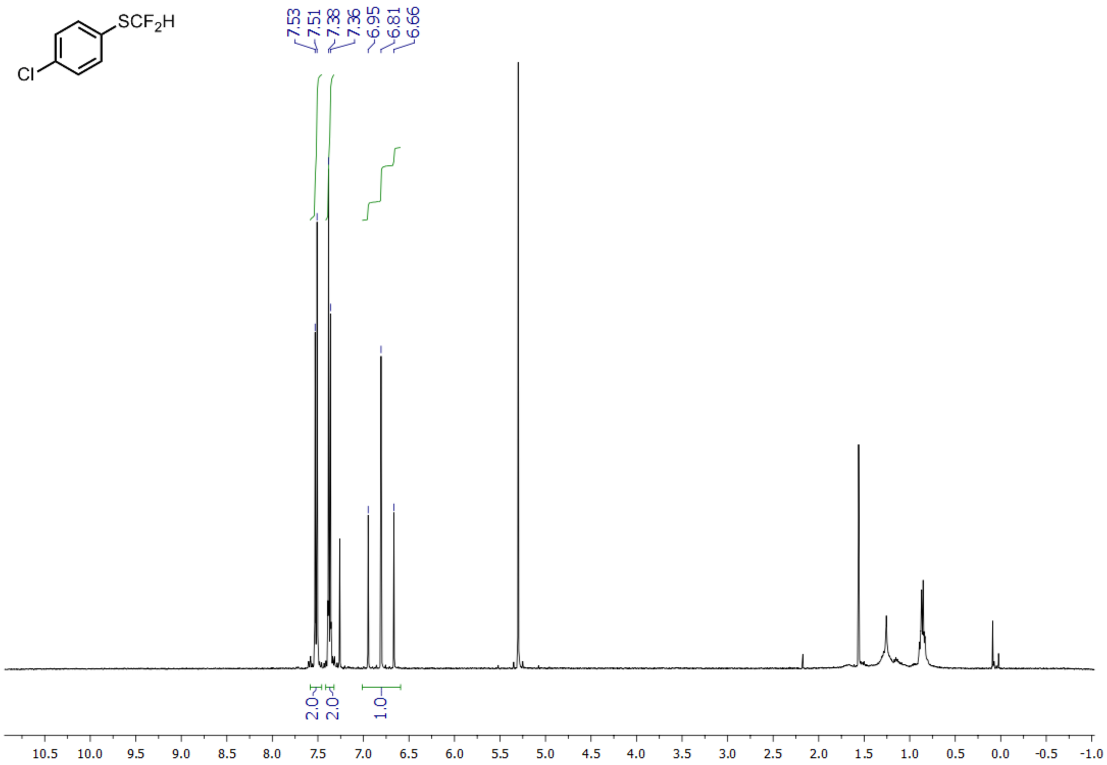
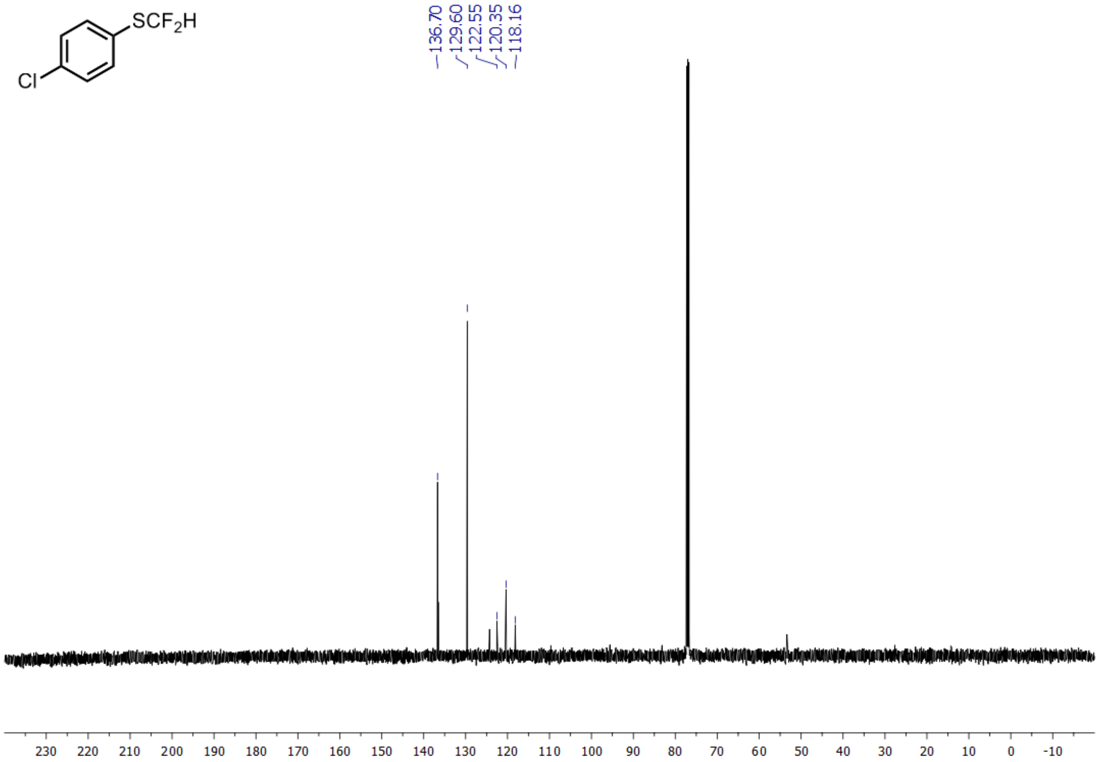
20
10

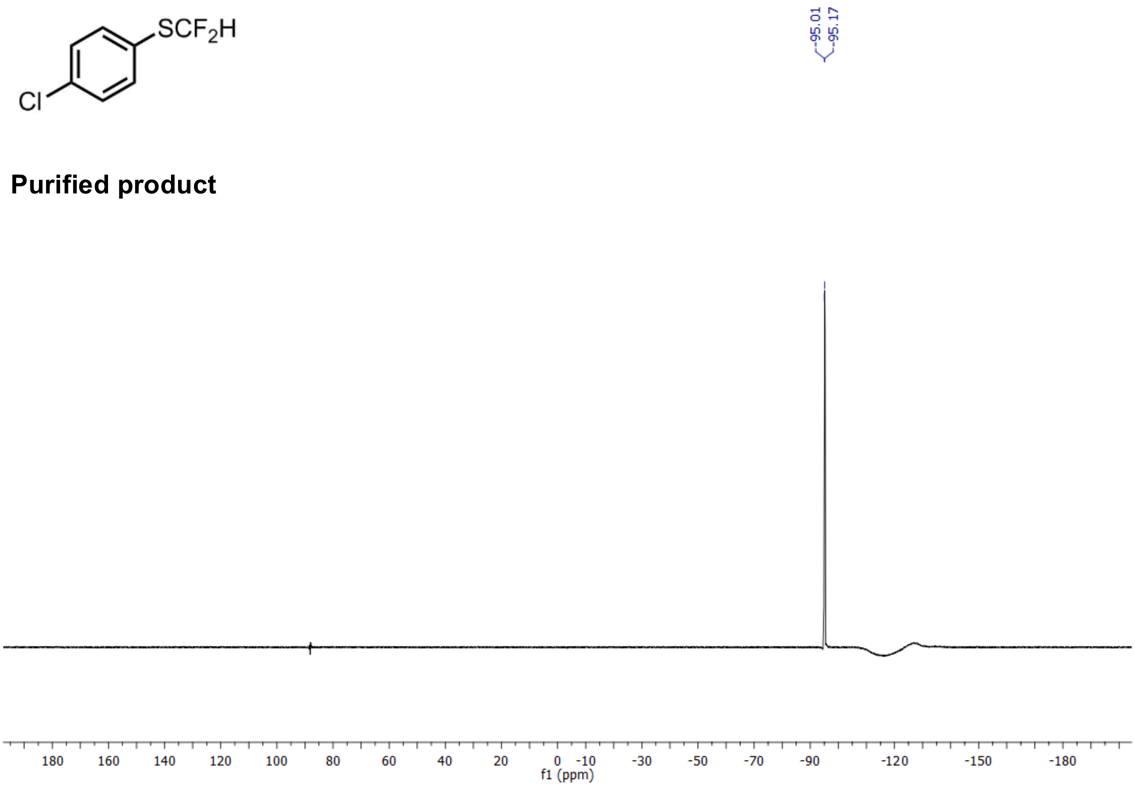

7.98
7.98
7.81
7.80
7.79
7.78
7.78
7.75
7.74
7.72
7.63
7.63
7.61
7.61
7.49
7.48
7.47
7.47
7.46
7.45
7.44
7.43
7.42
S
S
1.0
2.0
1.0
1.0
2.0
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

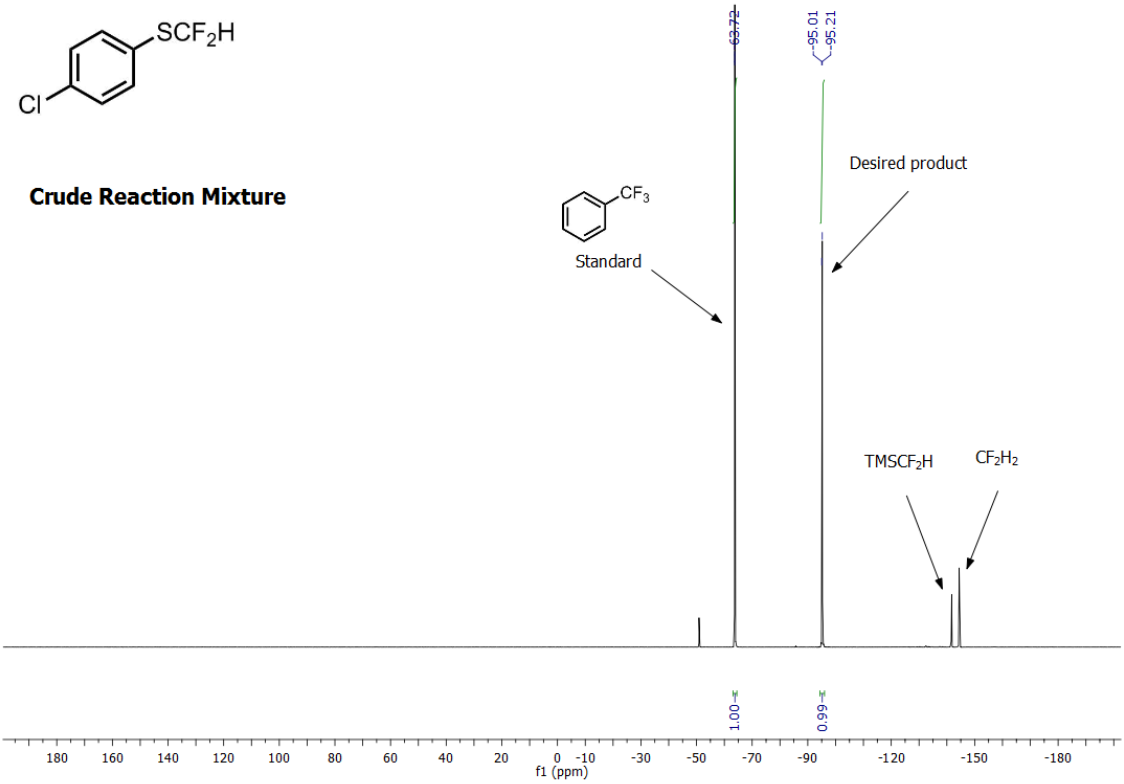

134.37
133.60
132.62
129.12
127.91
127.61
126.89
126.64
126.38
125.77
S
S
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

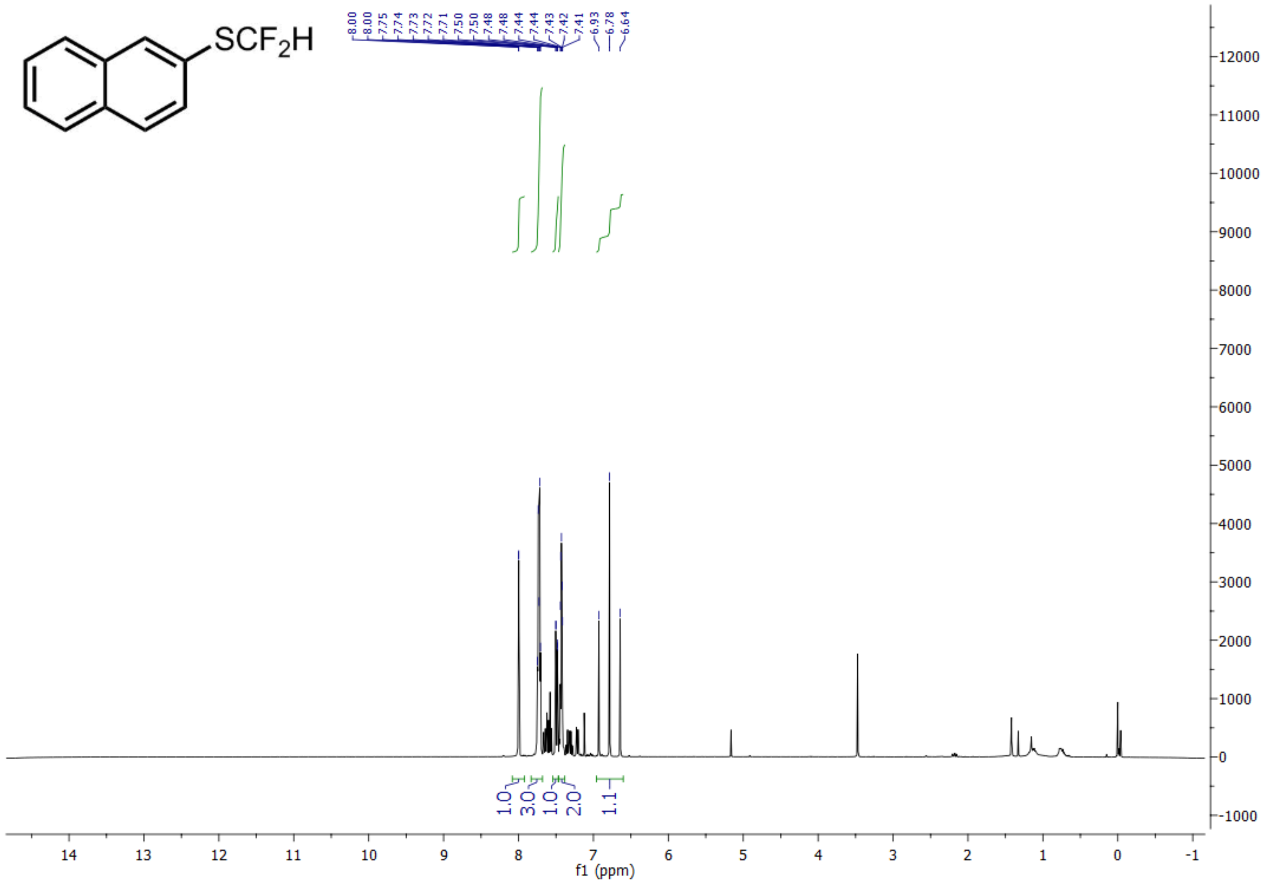
Difluoromethylthioethers

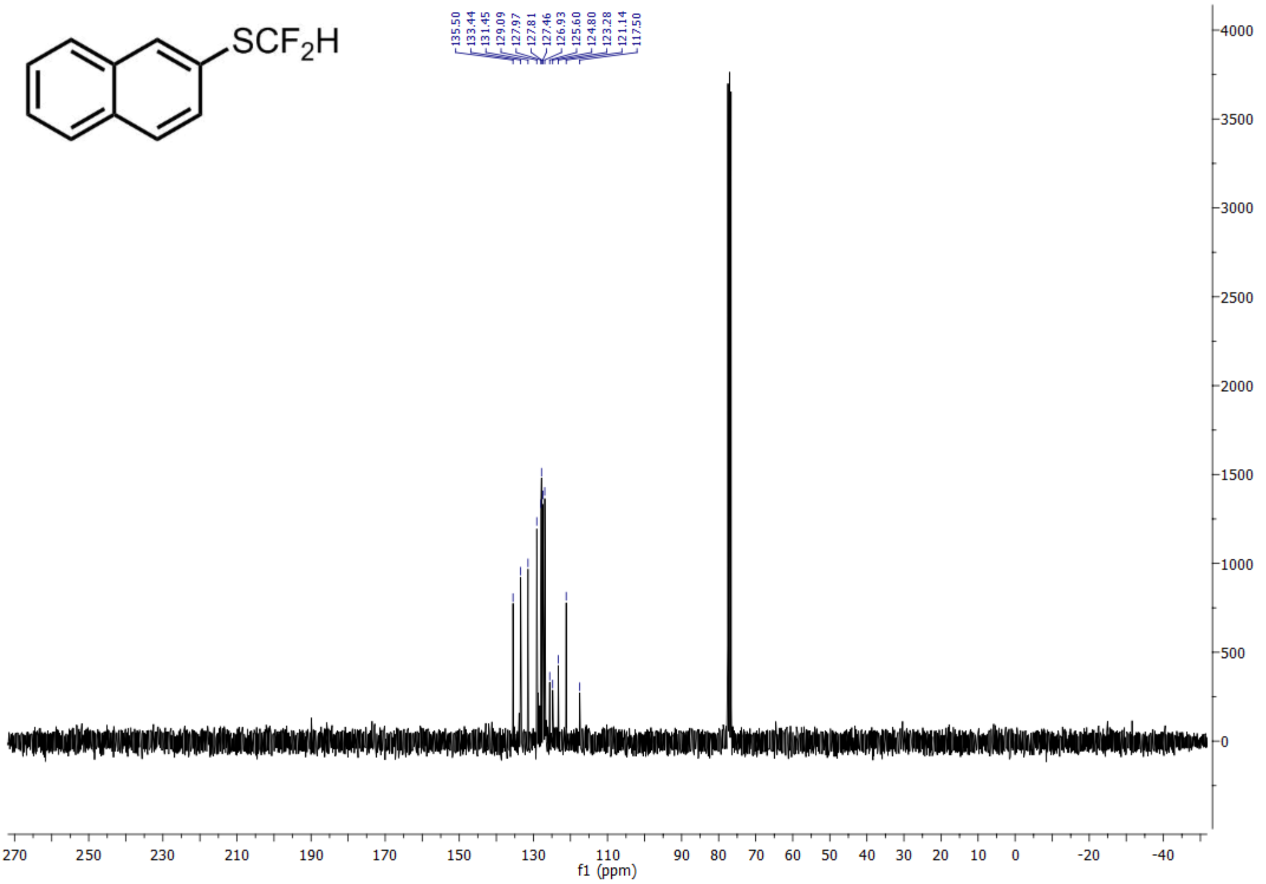


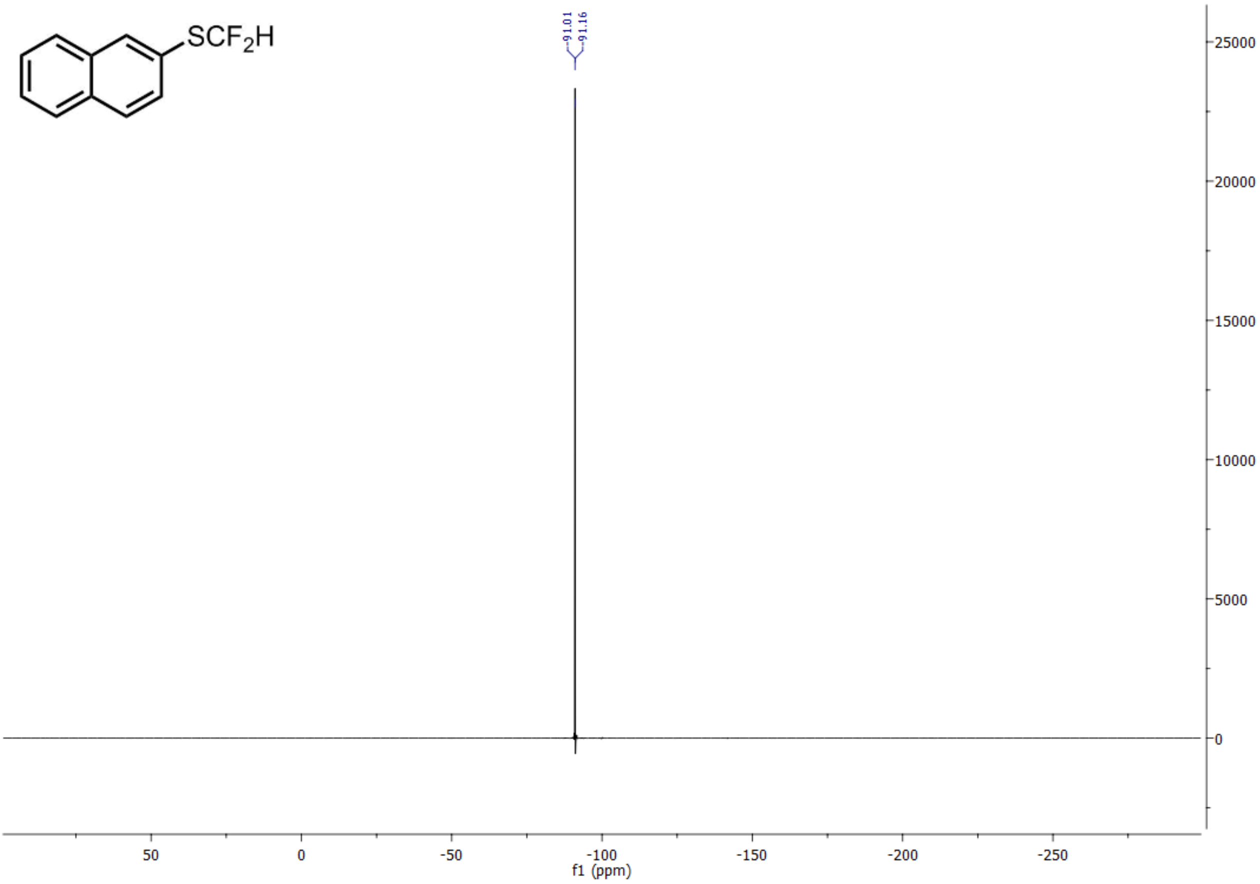



SCF$_2$H
Cl
Purified product
-95.01
-95.17
180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180
f1 (ppm)

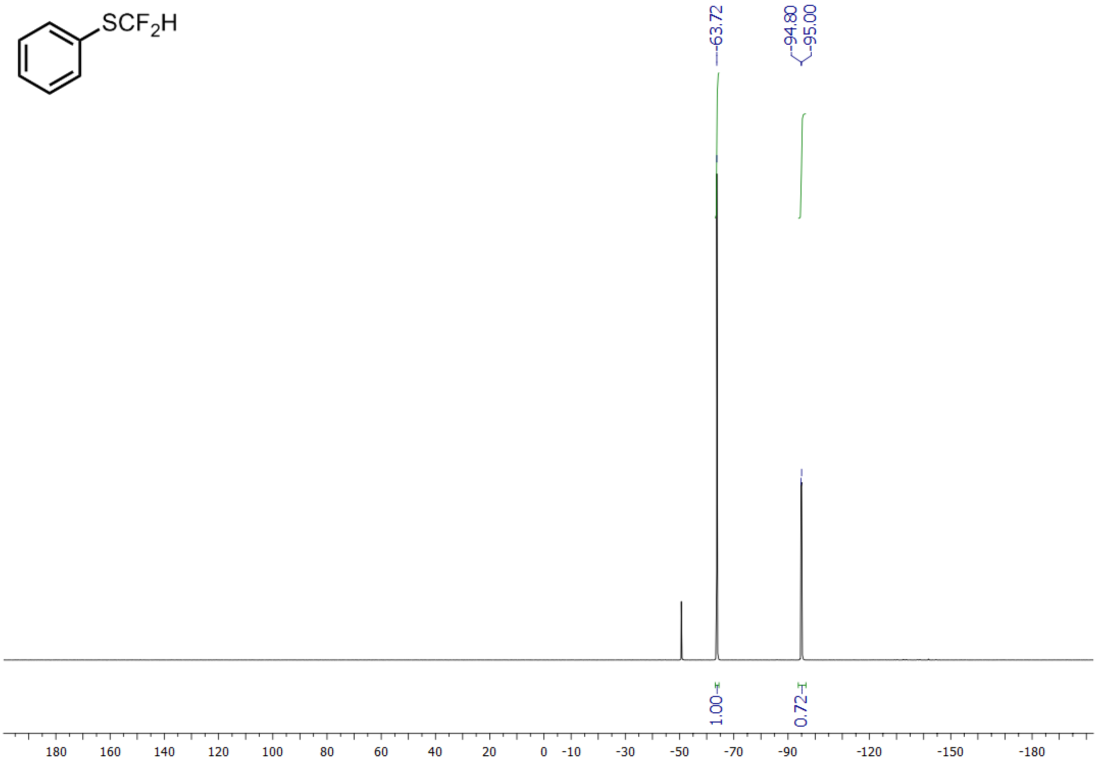

SCF$_2$H
Cl
Crude Reaction Mixture
-63.72
-95.01
-95.21
CF$_3$
Standard
Desired product
TMSCF$_2$H
CF$_2$H$_2$
1.00
0.99
180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180
f1 (ppm)

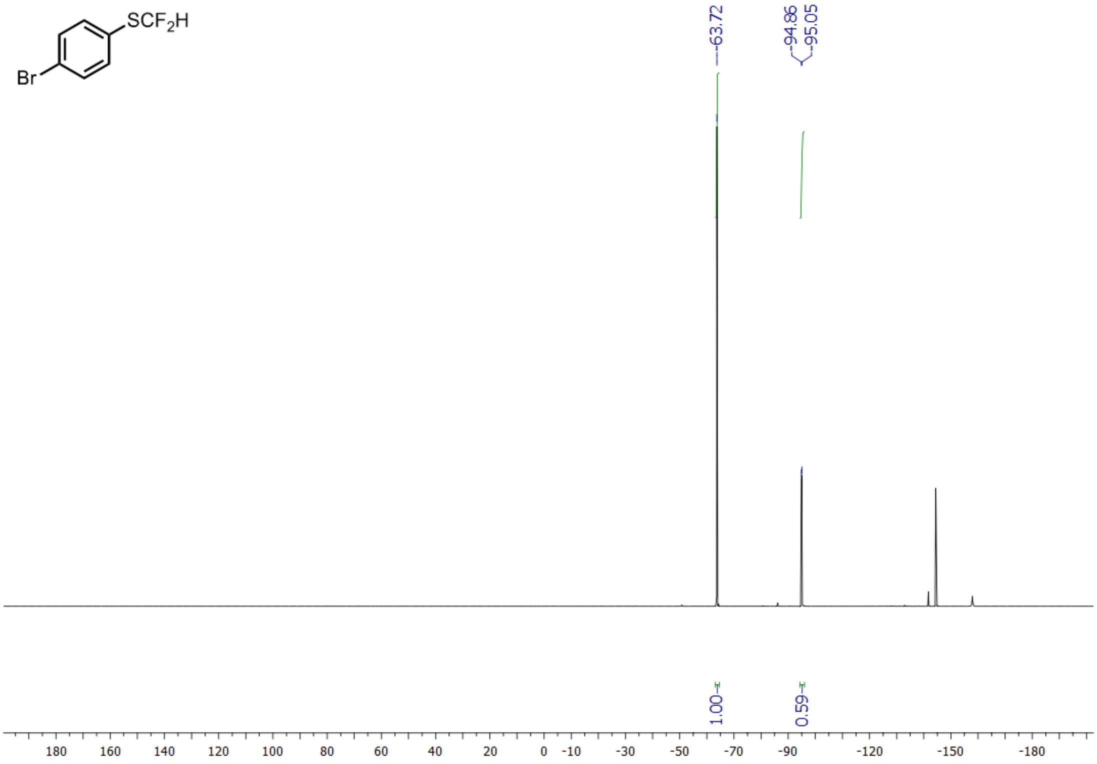

SCF$_2$H
8.00
8.00
7.75
7.74
7.73
7.72
7.71
7.50
7.50
7.48
7.48
7.44
7.44
7.43
7.42
7.41
6.93
6.78
6.64
1.0
3.0
1.0
2.0
1.1
f1 (ppm)

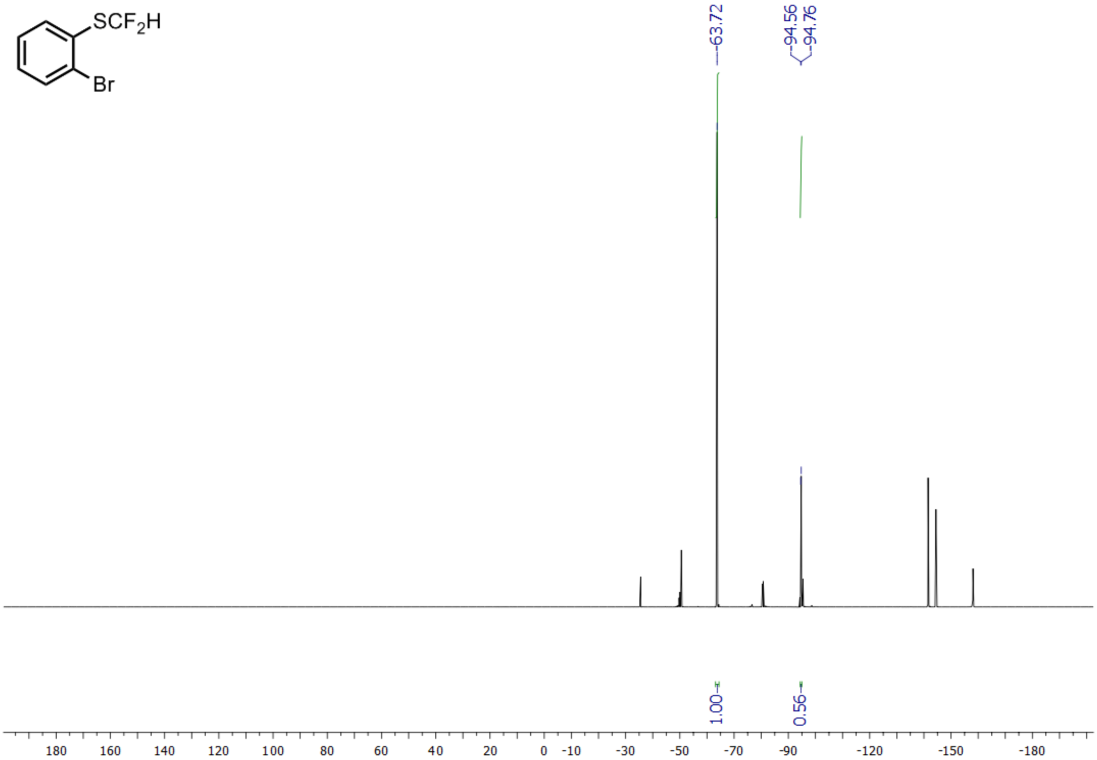

SCF$_2$H
135.50
133.44
131.45
129.09
127.97
127.81
127.46
126.93
125.60
124.80
123.28
121.14
117.50
f1 (ppm)

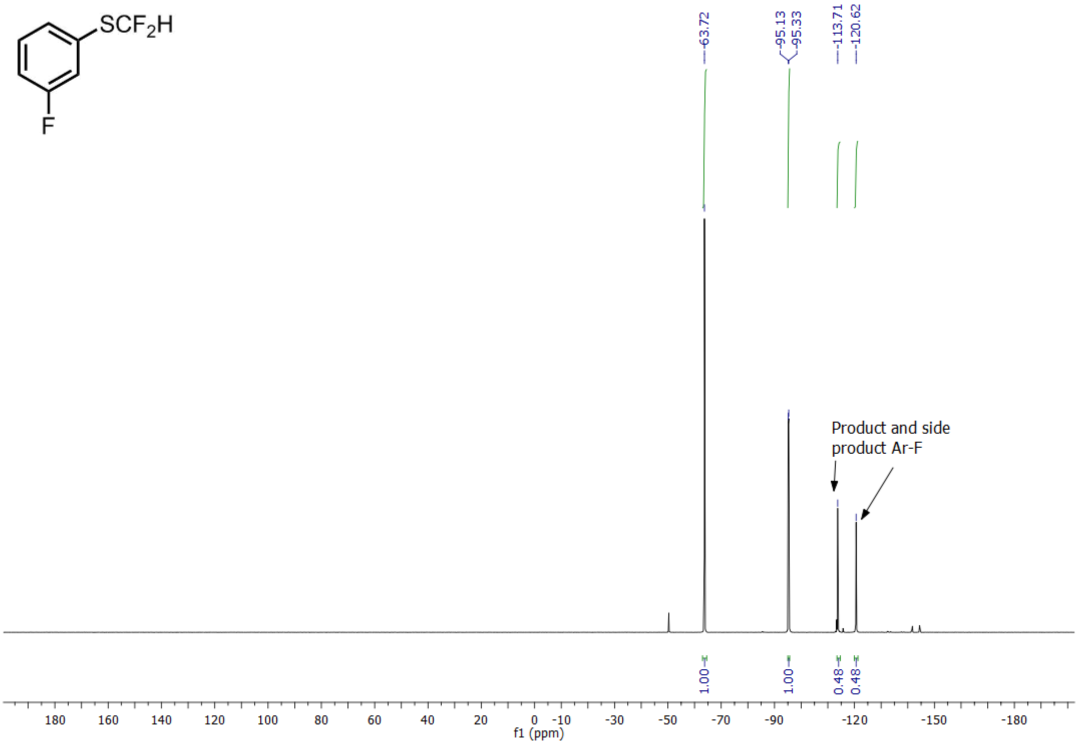

SCF$_2$H
-91.01
-91.16
25000
20000
15000
10000
5000
0
50
0
-50
-100
-150
-200
-250
f1 (ppm)

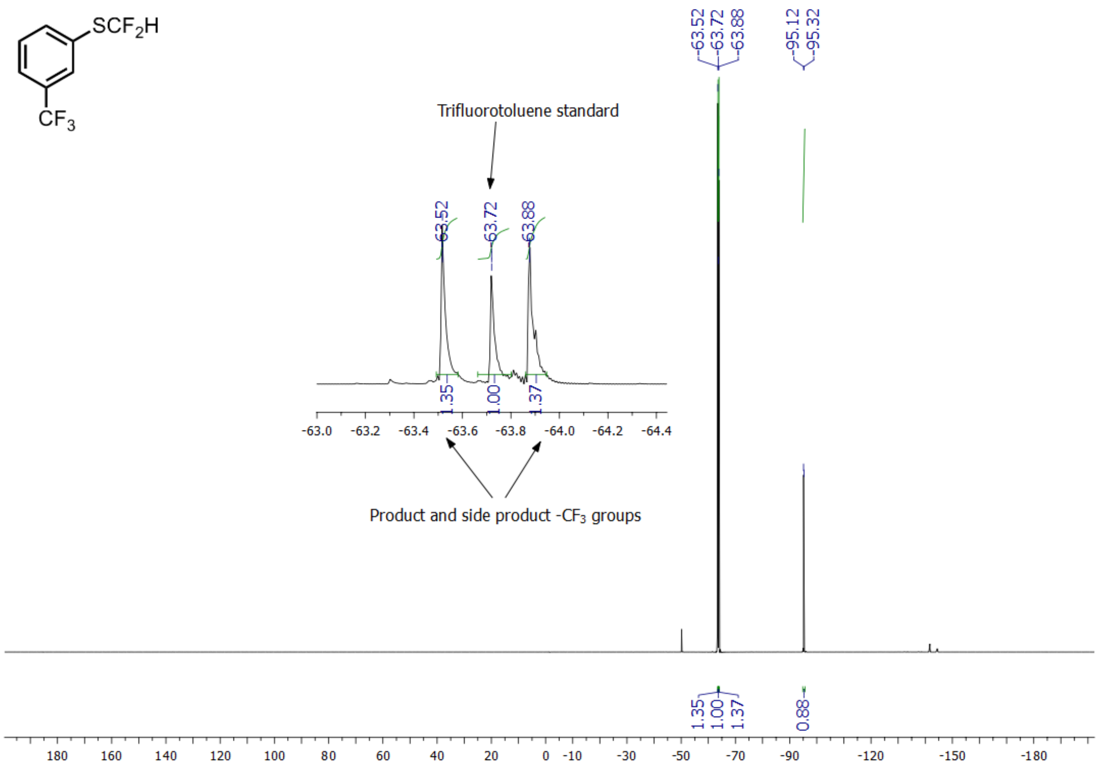
^{19}F NMR spectra of crude reaction mixtures with trifluorotoluene standard to determine conversion.





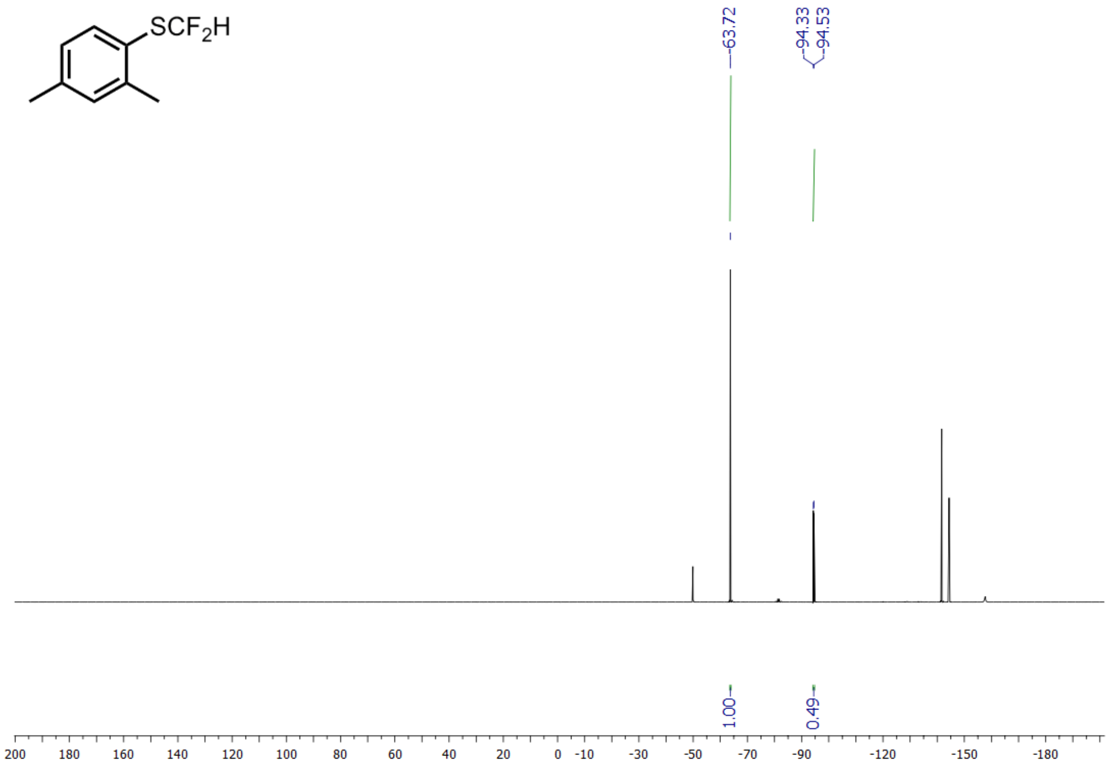


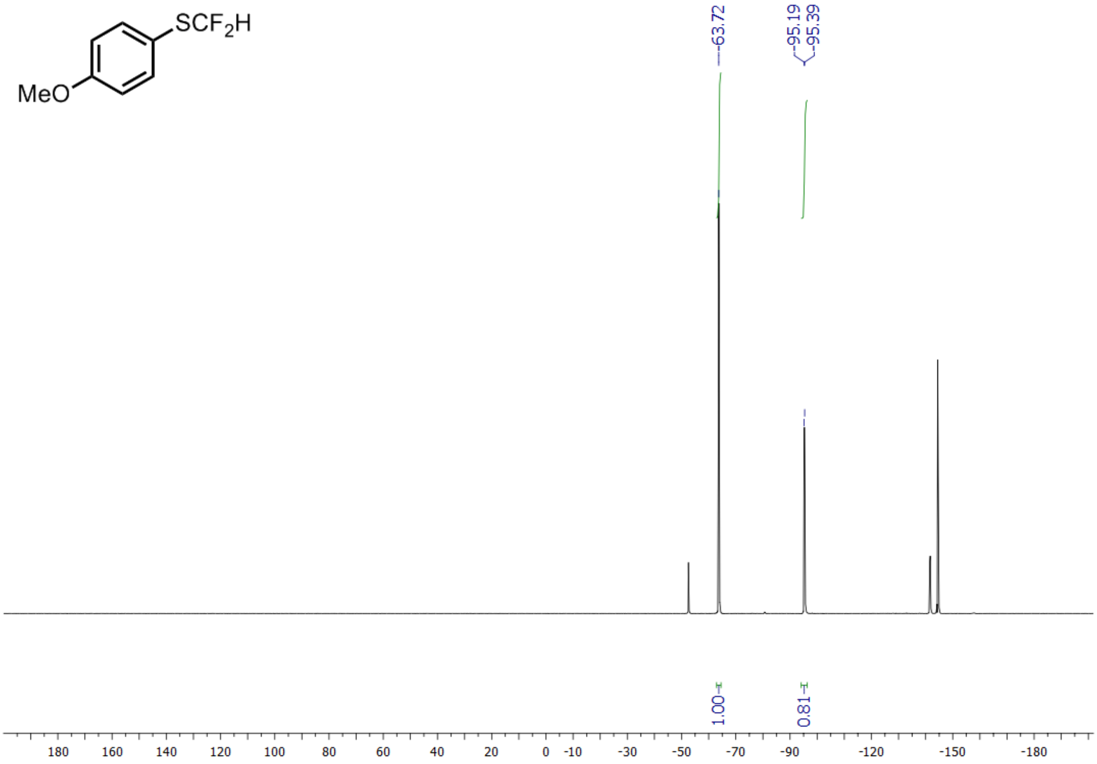

Product and side product Ar-F

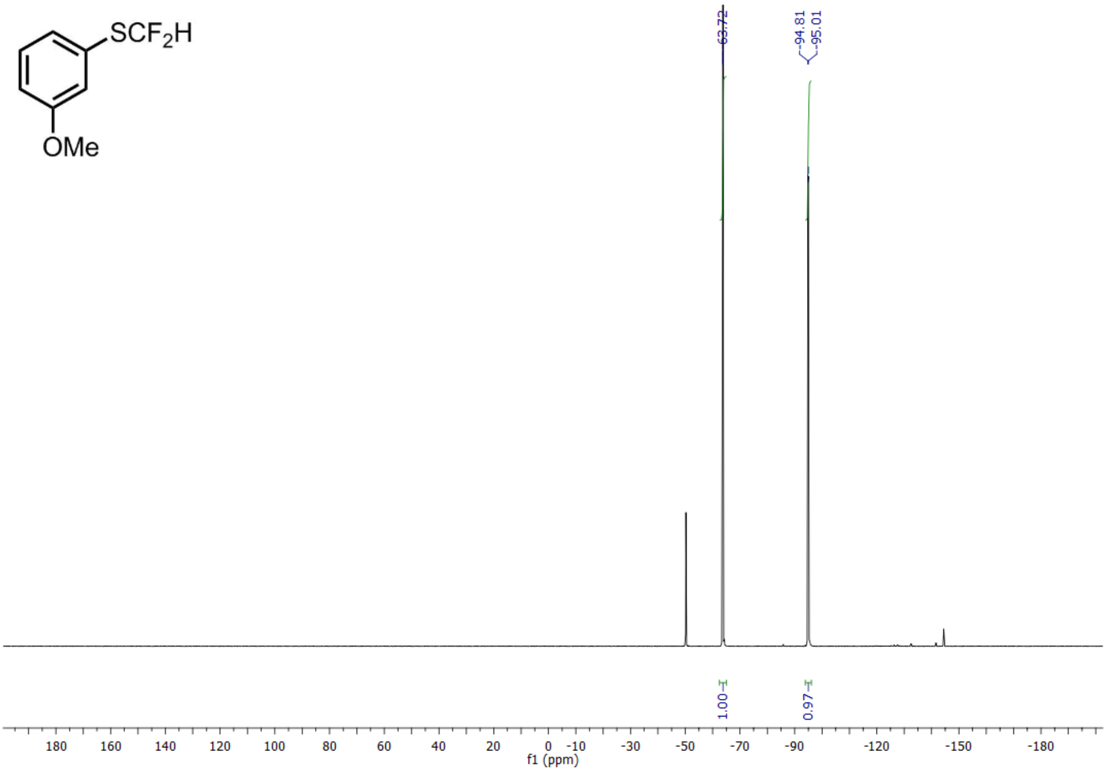


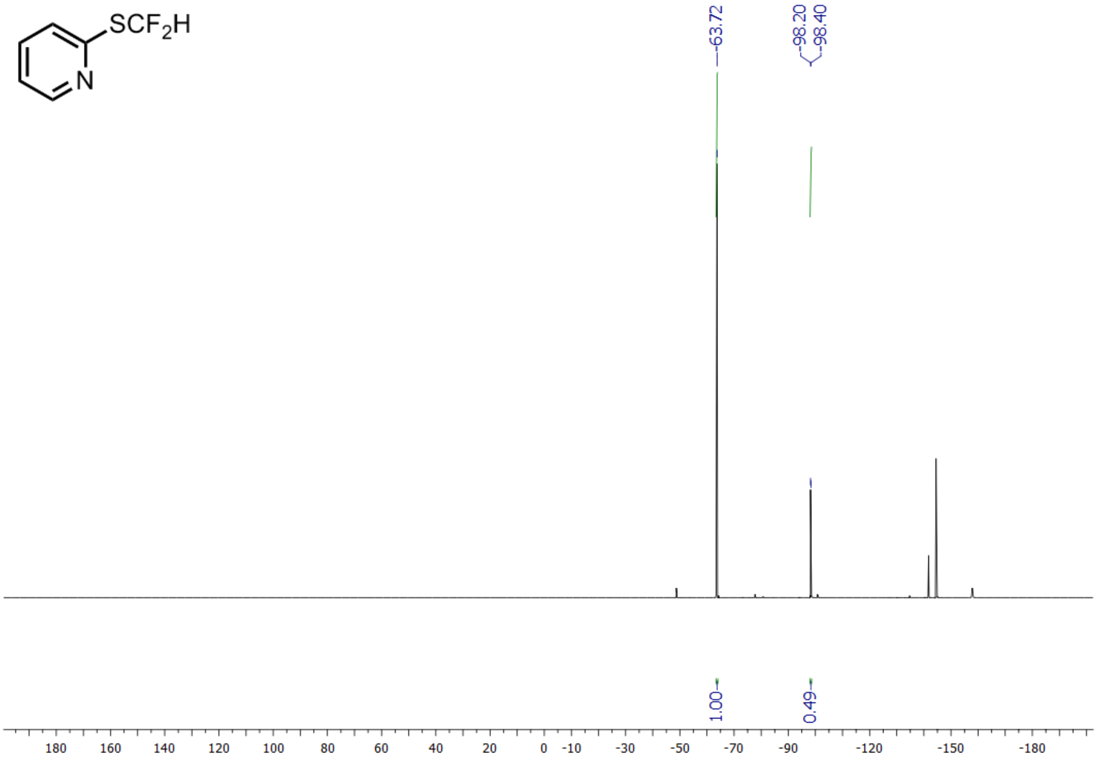
Trifluorotoluene standard

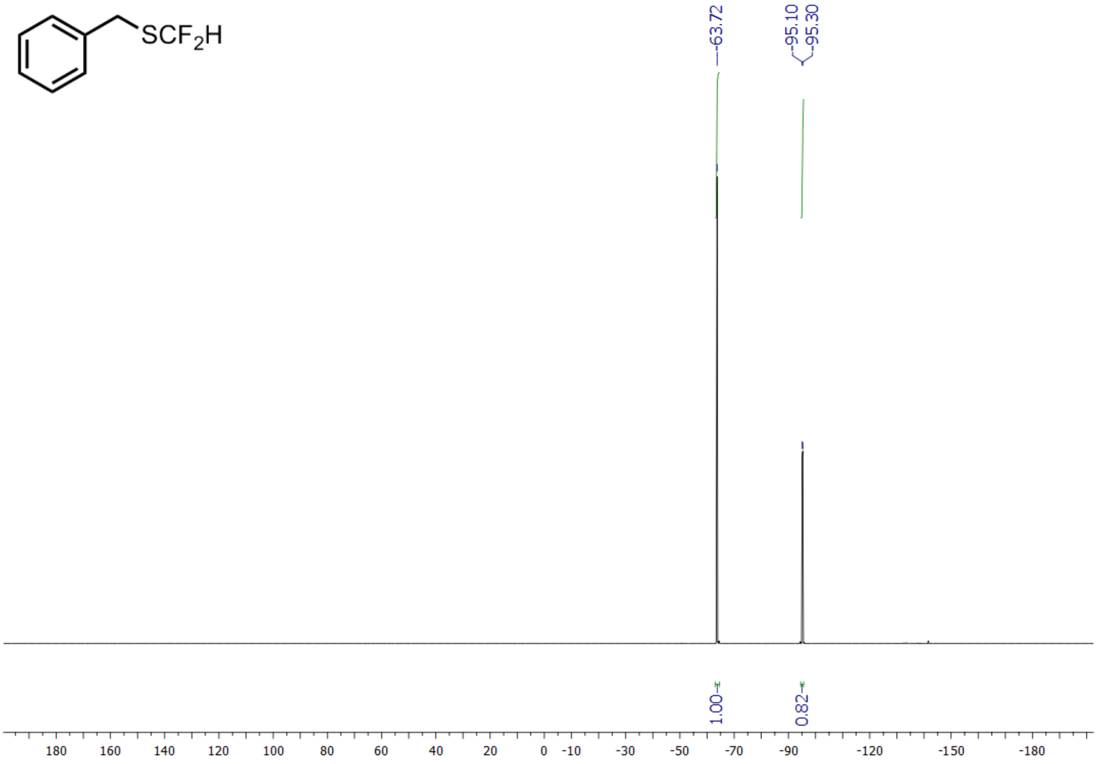
Product and side product -CF₃ groups

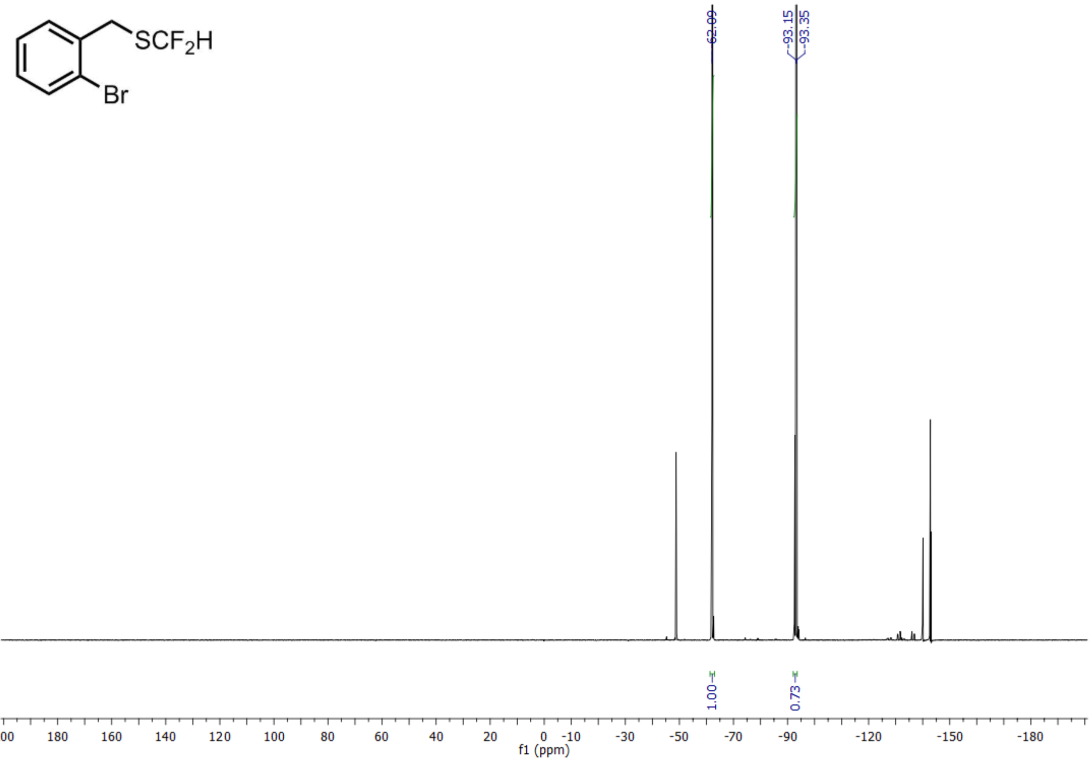


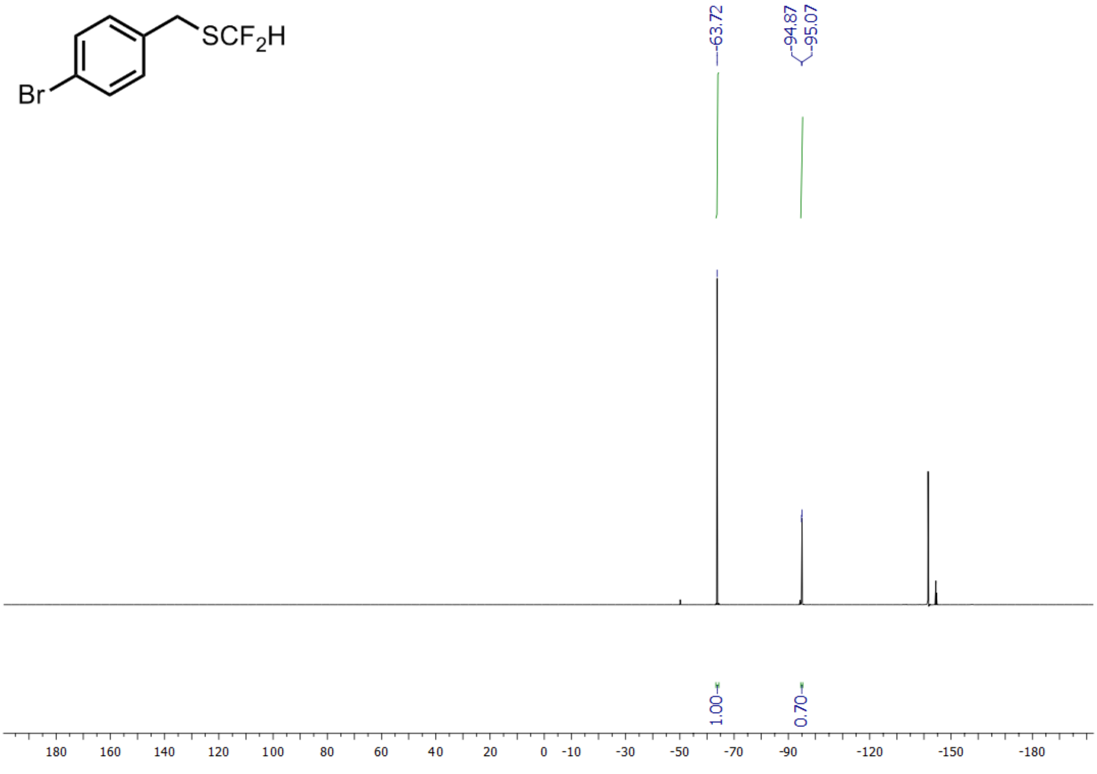

SCF2H
MeO
-63.72
-95.19
-95.39
1.00
0.81
180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180

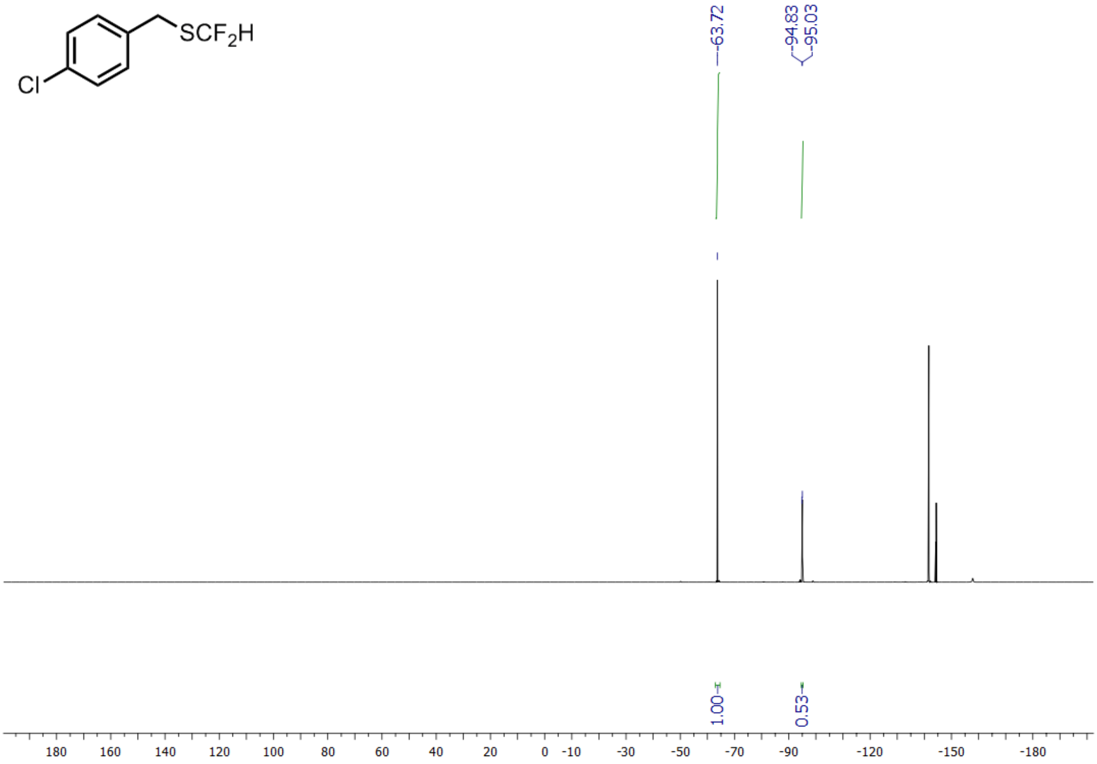

SCF2H
OMe
-63.72
-94.81
-95.01
1.00
0.97
180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180
f1 (ppm)

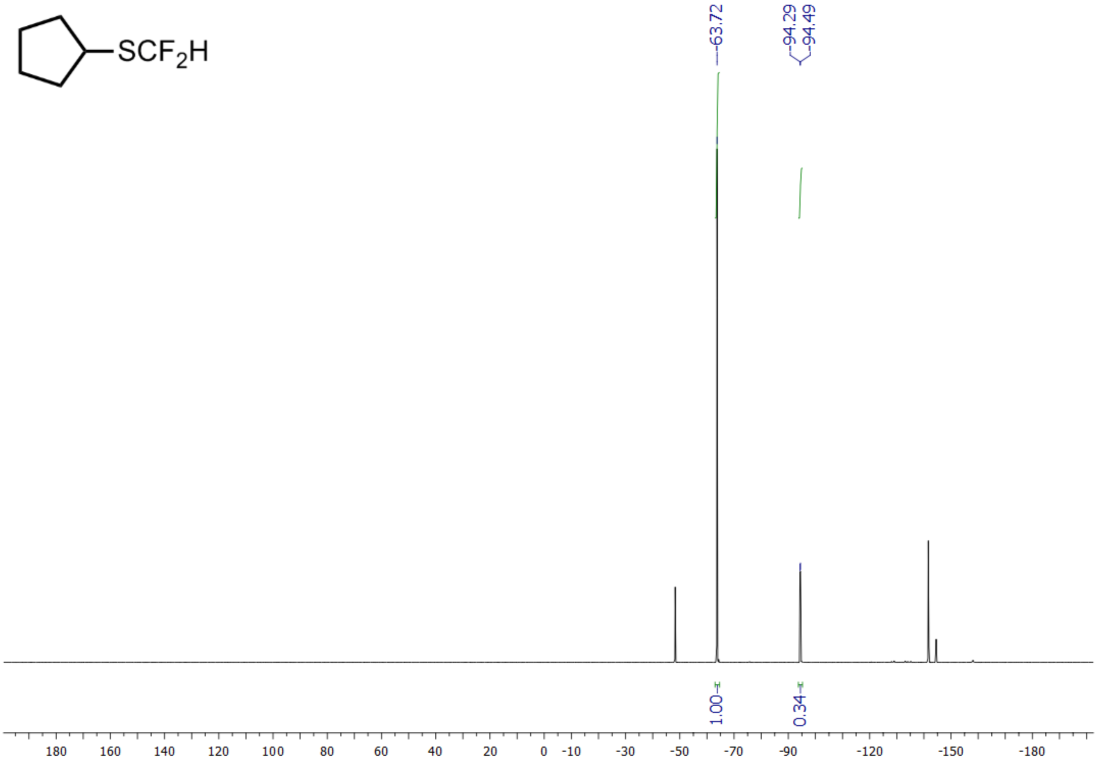

SCF2H
N
-63.72
-98.20
-98.40
1.00
0.49
180
160
140
120
100
80
60
40
20
0
-10
-30
-50
-70
-90
-120
-150
-180

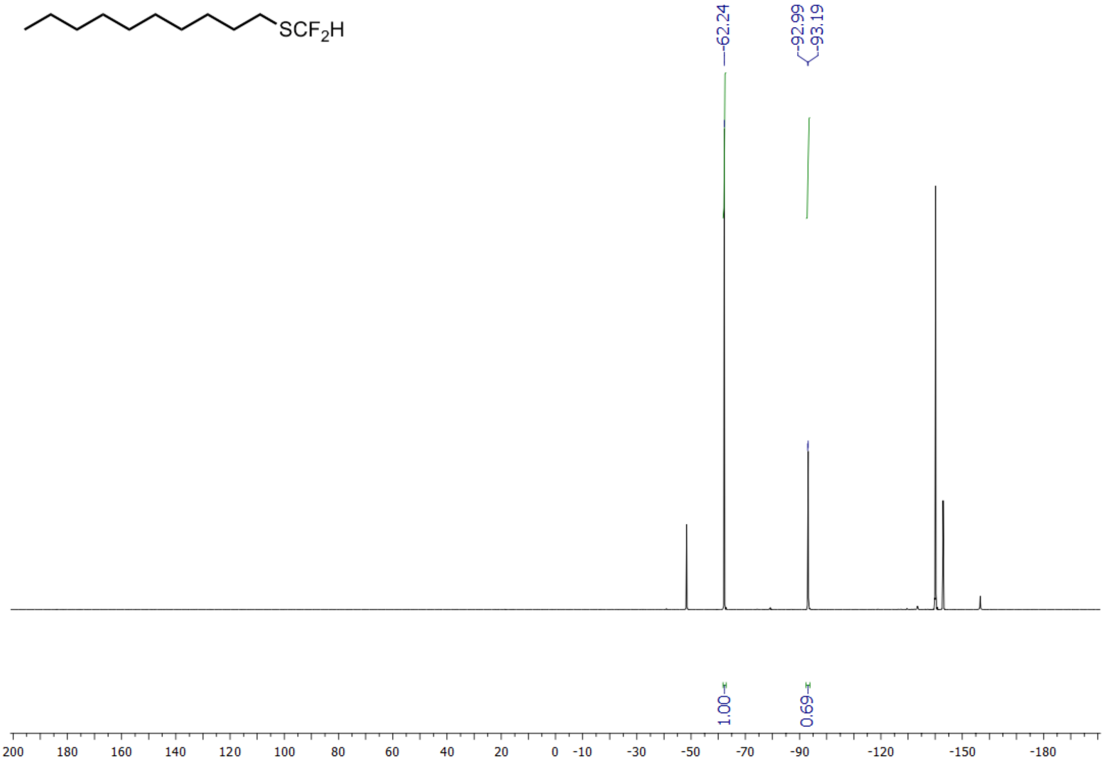

SCF2H
-63.72
-95.10
-95.30
1.00
0.82
180
160
140
120
100
80
60
40
20
0
-10
-30
-50
-70
-90
-120
-150
-180

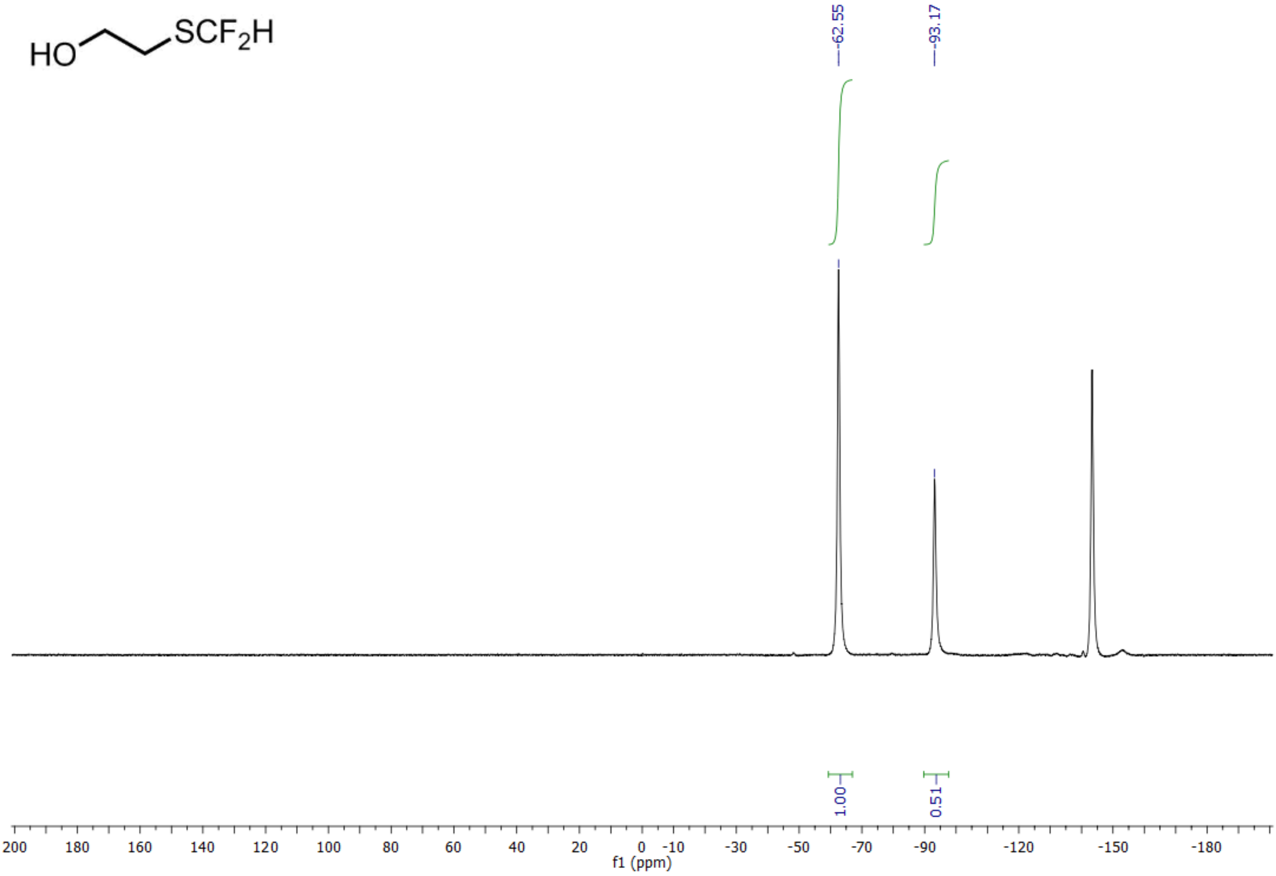

SCF2H
Br
-62.09
-93.15
-93.35
1.00
0.73
200 180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180
f1 (ppm)


SCF2H
Br
-63.72
-94.87
-95.07
1.00
0.70
180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180


SCF2H
Cl
-63.72
-94.83
-95.03
1.00
0.53
180
160
140
120
100
80
60
40
20
0
-10
-30
-50
-70
-90
-120
-150
-180


SCF2H
-63.72
-94.29
-94.49
1.00
0.34
180
160
140
120
100
80
60
40
20
0
-10
-30
-50
-70
-90
-120
-150
-180


SCF2H
-62.24
-92.99
-93.19
1.00
0.69
200 180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180


HO
SCF2H
-62.55
-93.17
1.00
0.51
200 180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180
f1 (ppm)

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