Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

One pot synthesis of trifluoromethyl aryl sulfoxides by trifluoromethylthiolation of arenes and subsequent oxidation with hydrogen peroxide

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Table of contents

Experimental section

General Information

TLC was performed on Merck-60-F_{254} plates using dichloromethane or mixtures of hexane:EtOAc (9:1). The crude products were purified by column chromatography on silica gel (63-200 μm, 70-230 mesh ASTM; Fluka). The melting points were determined on OptiMelt MPA100. Products were characterized by ^{1}H, ^{13}C and ^{19}F NMR spectra, HRMS and melting points of solids. ^{1}H spectra were recorded on Bruker Avance 300 DPX, ^{1}H, ^{13}C and ^{19}F NMR spectra on Bruker Avance III 500 instruments, C, H, N analysis were performed on Analizator Perkin-Elmer 2400 II. GC-MS was recorded on GC/MS Hewlett Packard 6890 (HP-1 MS column, initial temperature - 80 °C, 20 °C/min, final temperature - 270 °C).

The effect of reaction conditions on the oxidation of 1 to 2: To a solution of trifluoromethyl sulfide **1** (0.5 mmol) in 2 or 5 mL of solvent was added H_2O_2 (1-2 equiv.) or *m*-CPBA (1.2 equiv.) and activator (10 mol%). The reaction mixture was stirred for 3-24 h. After reaction was complete, the reaction mixture was washed with $NaHSO_3$, extracted with DCM (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuo. The product was analyzed by NMR spectroscopy. Results are presented in *Tables 1*, *2*, *3* and *4*.

Oxidation of thianthrene with 1.2 and 2 equivalent of *m*-CPBA and with H_2O_2

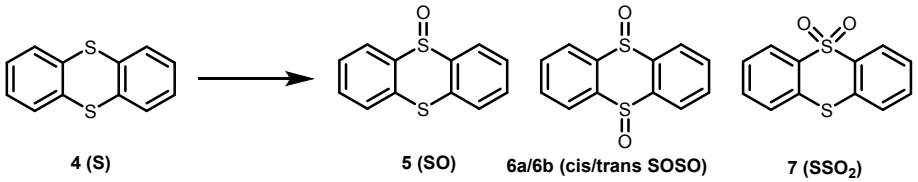


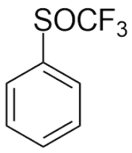
*Table 1. Selectivity of oxidation of thianthere **4**.*

Reaction conditions					Conversion				
oxidant	**eqiv.**	**solvent**	**temp.**	**time [h]**	**4**	**5** (SO)	**6a** (*cis*-SOSO)	**6b** (*trans*-SOSO)	**7** (SO_2)
m-CPBA	1.2	DCM	r.t.	24	8	81	3	7	1
m-CPBA	1.2	MeCN	r.t.	24	15	67	5	12	1
m-CPBA	1.2	TFA	0 °C	2.5	44	12	36	8	0
H_2O_2	1.2	TFA	0 °C	2.5	41	30	27	2	0
H_2O_2	1.2	TFA	r.t.	2.5	39	26	32	3	0
H_2O_2	1.2	TFA	r.t.	24	32	41	24	3	0
m-CPBA	2.0	DCM	r.t.	24	0	61	9	25	5
m-CPBA	2.0	MeCN	r.t.	24	0	57	8	28	7
m-CPBA	2.0	TFA	0 °C	2.5	19	7	61	13	0
H_2O_2	2.0	TFA	0 °C	2.5	10	14	71	5	0
H_2O_2	2.0	TFA	r.t.	2.5	9	25	47	19	0
H_2O_2	2.0	TFA	r.t.	24	7	27	53	13	0

Reaction conditions: 4 (0.5 mmol), oxidant (1.0 mmol), solvent (5 mL), time. Product distribution was determined by ^{1}H NMR spectroscopy.

Characterization Data for products

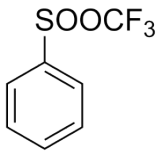
((trifluoromethyl)sulfinyl)benzene (2a)[1]



To a solution of phenyl(trifluoromethyl)sulfane (89 mg, 0.5 mmol) in 2 mL of solvent TFA at 0 °C was added 30% H_2O_2 (68 mg, 0.6 mmol). The reaction mixture was stirred at 0 °C for 6 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed with $NaHSO_3$ and extracted with DCM (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to provide the product (84 mg, 87%) as colorless, viscous liquid.

yield	84 mg, 87%
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C)	δ = 7.81 (d, J = 7.5 Hz, 2H), 7.59-7.72 (m, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)	δ = 133.9, 131.3, 130.2, 126.5, 121.6 (q, J = 333 Hz) ppm.
^{19}F NMR (471 MHz, $CDCl_3$, 25°C)	δ = –74.5 (s, 3F) ppm.
ESI-HRMS	$C_7H_6F_3OS$ $(M + H)^+$ calcd: 195.0086 found: 195.0084
IR	3065, 1788, 1584, 1447, 1172, 1085, 750, 686 cm^{-1}.

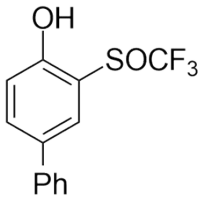
((trifluoromethyl)sulfonyl)benzene (3a)[2]



To a solution of phenyl(trifluoromethyl)sulfane (89 mg, 0.5 mmol) in 2 mL of solvent TFA was added 30% H_2O_2 (340 mg, 3.0 mmol). The reaction mixture was stirred at 25 °C for 5 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed with $NaHSO_3$ and extracted with DCM (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to provide the product (100 mg, 95%) as colorless, viscous liquid.

yield	100 mg, 95%
^{1}H NMR (500 MHz, $CDCl_3$, 25°C)	δ = 8.06 (d, J = 7.5 Hz, 2H), 7.85 (t, J = 7.5 Hz, 1H), 7.69 (t, J = 7.5 Hz, 2H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$, 25°C)	δ = 136.5, 131.4, 130.8, 129.9, 119.8 (q, J = 324 Hz) ppm.
^{19}F NMR (471 MHz, $CDCl_3$, 25°C)	δ = –78.9 (s, 3F) ppm.
GC-MS	m/z (%) = 210 [$M^{+\cdot}$] (100).
IR	3072, 1584, 1450, 1190, 1071, 720, 682 cm^{-1}.

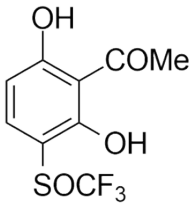
3-((trifluoromethyl)sulfinyl)-[1,1'-biphenyl]-4-ol (2b)[3]



To a solution of 3-((trifluoromethyl)thio)-[1,1'-biphenyl]-4-ol (55 mg, 0.2 mmol) in 2 mL of solvent TFA at 0 °C was added 30% H_2O_2 (27 mg, 0.24 mmol). The reaction mixture was stirred at 0 °C for 24 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed with $NaHSO_3$ and extracted with DCM (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to provide the product (48 mg, 84%) as white solid.

yield	48 mg, 84%
^{1}H NMR (500 MHz, $CDCl_3$, 25°C)	δ = 9.42 (s, 1H), 7.75 (dd, J = 9.0, 2.5 Hz, 1H), 7.35-7.52 (m, 6H), 7.10 (d, J = 8.5 Hz, 1H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$, 25°C)	δ = 156.7, 156.6, 140.0, 134.6, 134.0, 129.8, 128.2, 127.2, 126.3 (q, J = 337 Hz), 124.7, 117.9 ppm.
^{19}F NMR (471 MHz, $CDCl_3$, 25°C)	δ = –74.5 (s, 3F) ppm.
ESI-HRMS	$C_{13}H_{10}F_3O_2S$ $(M + H)^+$ calcd: 287.0354 found: 287.0350
IR	3181, 2919, 2378, 1608, 1484, 1035, 760, 696 cm^{-1}.

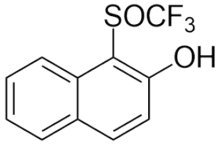
1-(2,6-dihydroxy-3-((trifluoromethyl)sulfinyl)phenyl)ethanone (2c)



To a solution of 1-(2,6-dihydroxy-3-((trifluoromethyl)thio)phenyl)ethanone (63 mg, 0.25 mmol) in 2 mL of solvent TFA at 0 °C was added 30% H_2O_2 (34 mg, 0.3 mmol). The reaction mixture was stirred at 0 °C for 24 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed with $NaHSO_3$ and extracted with DCM (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to provide the product (57 mg, 85%) as yellow solid.

yield	57 mg, 85%
^{1}H NMR (500 MHz, $CDCl_3$, 25°C)	δ = 14.10 (s, 1H), 11.31 (s, 1H), 7.83 (d, J = 8.5 Hz, 1H), 6.86 (d, J = 8.5 Hz, 1H), 2.76 (s, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$, 25°C)	δ = 206.9, 166.4, 164.5, 134.0, 126.4 (q, J = 335 Hz), 113.1, 110.6, 109.9, 33.6 ppm.
^{19}F NMR (471 MHz, $CDCl_3$, 25°C)	δ = –75.4 (s, 3F) ppm.
ESI-HRMS	$C_9H_8F_3O_4S$ $(M + H)^+$ calcd: 269.0095 found: 269.0098.

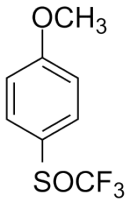
1-((trifluoromethyl)sulfinyl)naphthalen-2-ol (2d)



To a solution of 1-((trifluoromethyl)thio)naphthalen-2-ol (73 mg, 0.3 mmol) in 2 mL of solvent TFA at 0 °C was added 30% H_2O_2 (41 mg, 0.36 mmol). The reaction mixture was stirred at 0 °C for 22 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed with $NaHSO_3$ and extracted with DCM (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to provide the product (64 mg, 82%) as colorless, viscous liquid.

yield	64 mg, 82%
^{1}H NMR (500 MHz, $CDCl_3$, 25°C)	δ = 10.71 (s, 1H), 7.97 (d, J = 9 Hz, 1H), 7.82 (d, J = 8 Hz, 1H), 7.77 (d, J = 8.5 Hz, 1H), 7,56 (t, J = 8 Hz, 1H), 7.44 (t, J = 8 Hz, 1H), 7.14 (d, J = 9 Hz, 1H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$, 25°C)	δ = 163.3, 136.5, 131.4, 129.1, 128.8, 128.2, 126.0 (q, J = 335 Hz), 124.7, 121.1, 119.9, 103.4 ppm.
^{19}F NMR (471 MHz, $CDCl_3$, 25°C)	δ = –72.3 (s, 3F) ppm.
ESI-HRMS	$C_{11}H_8F_3O_2S$ $(M + H)^+$ calcd: 261.0197 found: 261.0193
IR	3094, 2928, 1621, 1178, 1118, 821, 744 cm^{-1}.

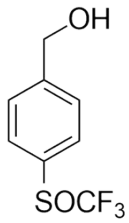
1-methoxy-4-((trifluoromethyl)sulfinyl)benzene (2e)[1]



To a solution of (4-methoxyphenyl)(trifluoromethyl)sulfane (112 mg, 0.5 mmol) in 5 mL of solvent TFA at 0 °C was added 30% H_2O_2 (68 mg, 0.6 mmol). The reaction mixture was stirred at 0 °C for 2 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed with $NaHSO_3$ and extracted with DCM (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude reaction was subjected to column chromathography with mobile phase dichloromethane. Solvent was evaporated in vacuo to provide the product (89 mg, 79%) as yellow, viscous liquid.

yield	89 mg, 79%
^{1}H NMR (500 MHz, $CDCl_3$, 25°C)	δ = 7.70 (d, J = 8.8 Hz, 2H), 7.07 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$, 25°C)	δ = 164.1, 128.2, 126.2, 124.8 (q, J = 335 Hz), 115.2, 55.7 ppm.
^{19}F NMR (471 MHz, $CDCl_3$, 25°C)	δ = –75.7 (s, 3F) ppm.
ESI-HRMS	$C_8H_8F_3O_2S$ $(M + H)^+$ calcd: 225.0192 found: 225.0190

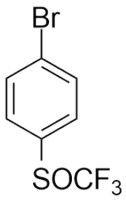
(4-((trifluoromethyl)sulfinyl)phenyl)methanol (2f)



To a solution of (4-((trifluoromethyl)thio)phenyl)methanol (104 mg, 0.5 mmol) in 2 mL of solvent TFA at 0 °C was added 30% H_2O_2 (68 mg, 0.6 mmol). The reaction mixture was stirred at 0 °C for 5.5 h. and at 25 °C for 1 h. Reaction time was determined with GC-MS. After that the reaction mixture was washed with $NaHSO_3$. The solvent was evaporated under vacuum. To the reaction mixture were added MeCN and distilled water. The solution was stirred at 25 °C for 24 h. After reaction was complete, the reaction mixture was extracted with DCM (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to provide the product (102 mg, 91%) as colorless, viscous liquid.

yield	102 mg, 91%
^{1}H NMR (500 MHz, $CDCl_3$, 25°C)	δ = 7.78 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 4.83 (s, 2H), 2.96 (s, 1H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$, 25°C)	δ = 147.1, 134.3, 127.6, 126.2, 124.6 (q, J = 333 Hz), 64.2 ppm.
^{19}F NMR (471 MHz, $CDCl_3$, 25°C)	δ = –75.0 (s, 3F) ppm.
ESI-HRMS	$C_8H_8F_3O_2S$ $(M + H)^+$ calcd: 225.0192 found: 225.0191
IR	3416, 2876, 1780, 1447, 1172, 1131, 807, 652 cm^{-1}.

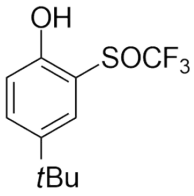
1-bromo-4-((trifluoromethyl)sulfinyl)benzene (2g)



To a solution of (4-bromophenyl)(trifluoromethyl)sulfane (129 mg, 0.5 mmol) in 2 mL of solvent TFA at 0 °C was added 30% H_2O_2 (68 mg, 0.6 mmol). The reaction mixture was stirred at 0 °C for 8.5 h and at 25 °C for 40 min. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed with $NaHSO_3$ and extracted with DCM (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to provide the product (130 mg, 95%) as colorless, viscous liquid.

yield	130 mg, 95%
^{1}H NMR (500 MHz, $CDCl_3$, 25°C)	δ = 7.77 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8 Hz, 2H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$, 25°C)	δ = 134.7, 133.0, 128.7, 127.4, 124.4 (q, J = 333 Hz) ppm.
^{19}F NMR (471 MHz, $CDCl_3$, 25°C)	δ = –74.9 (s, 3F) ppm.
ESI-HRMS	$C_7H_5BrF_3OS$ $(M + H)^+$ calcd: 272.9191 found: 272.9189
IR	3081, 2919, 1570, 1470, 1388, 1130, 1058, 726 cm^{-1}.

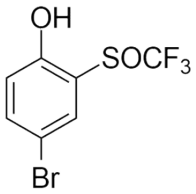
4-(*tert*-butyl)-2-((trifluoromethyl)sulfinyl)phenol (2h)



To a solution of 4-(*tert*-butyl)-2-((trifluoromethyl)thio)phenol (133 mg, 0.5 mmol) in 5 mL of solvent TFA at 0 °C was added 30% H_2O_2 (68 mg, 0.6 mmol). The reaction mixture was stirred at 0 °C for 3 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed with $NaHSO_3$ and extracted with DCM (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude reaction was subjected to column chromathography with mobile phase dichloromethane. Solvent was evaporated in vacuo to provide the product (102 mg, 77%) as brown, viscous liquid.

yield	102 mg, 77%
^{1}H NMR (500 MHz, $CDCl_3$, 25°C)	δ = 9.18 (s, 1H), 7.55 (dd, J = 8.8, 2.4 Hz, 1H), 7.19 (d, J = 2.1 Hz, 1H), 6.95 (d, J = 8.8 Hz, 1H), 1.29 (s, 9H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$, 25°C)	δ = 158.8, 143.9, 133.2, 125.2 (q, J = 336 Hz), 123.6, 119.6, 113.0, 34.5, 31.3 ppm.
^{19}F NMR (471 MHz, $CDCl_3$, 25°C)	δ = –74.0 (s, 3F) ppm.
ESI-HRMS	$C_{11}H_{14}F_3O_2S$ $(M + H)^+$ calcd: 267.0661 found: 267.0664
GC-MS	266 (M, 20 %), 197 (100 %), 182 (48 %), 149 (20 %).

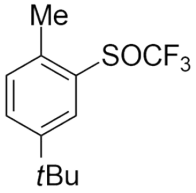
4-bromo-2-((trifluoromethyl)sulfinyl)phenol (2i)



To a solution of 4-bromo-2-((trifluoromethyl)thio)phenol (145 mg, 0.5 mmol) in 5 mL of solvent TFA at 0 °C was added 30% H_2O_2 (68 mg, 0.6 mmol). The reaction mixture was stirred at 0 °C for 4 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed with $NaHSO_3$ and extracted with DCM (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude reaction was subjected to column chromathography with mobile phase dichloromethane. Solvent was evaporated in vacuo to provide the product (124 mg, 86%) as brown solid. Mp 131.4–135.6 °C (Mp_{lit} = 140.0 °C).[3]

yield	124 mg, 86%
^{1}H NMR (500 MHz, $CDCl_3$, 25°C)	δ = 9.29 (s, 1H), 7.60 (dd, J = 8.9, 2.4 Hz, 1H), 7.38 (d, J = 2.1 Hz, 1H), 6.91 (d, J = 8.9 Hz, 1H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$, 25°C)	δ = 160.0, 138.5, 129.6, 125.2 (q, J = 336 Hz), 121.8, 115.6, 112.3 ppm.
^{19}F NMR (471 MHz, $CDCl_3$, 25°C)	δ = –73.5 (s, 3F) ppm.
ESI-HRMS	$C_7H_5BrF_3O_2S$ $(M + H)^+$ calcd: 288.9140, found: 288.9139
GC-MS	290 (M+2, 18 %), 221 (100 %), 193 (24 %), 143 (23 %), 112 (12 %), 95 (26 %), 69 (18 %).

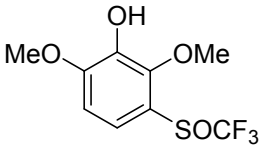
4-(*tert*-butyl)-1-methyl-2-((trifluoromethyl)sulfinyl)benzene (2j)



To a solution of (5-(*tert*-butyl)-2-methylphenyl)(trifluoromethyl)sulfane (132 mg, 0.5 mmol) in 5 mL of solvent TFA at 0 °C was added 30% H_2O_2 (68 mg, 0.6 mmol). The reaction mixture was stirred at 0 °C for 2.5 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed with $NaHSO_3$ and extracted with DCM (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude reaction was subjected to column chromathography with mobile phase dichloromethane. Solvent was evaporated in vacuo to provide the product (117 mg, 89%) as colorless, viscous liquid.

yield	117 mg, 89%
^{1}H NMR (500 MHz, $CDCl_3$, 25°C)	δ = 8.02 (d, J = 1.3 Hz, 1H), 7.54 (dd, J = 8.0, 2.1 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 2.43 (s, 3H), 1.35 (s, 9H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$, 25°C)	δ = 150.8, 134.9, 133.4, 131.1, 130.4, 125.3 (q, J = 335 Hz), 122.5, 35.0, 31.1, 17.7 ppm.
^{19}F NMR (471 MHz, $CDCl_3$, 25°C)	δ = –74.1 (s, 3F) ppm.
ESI-HRMS	$C_{12}H_{16}F_3OS$ $(M + H)^+$ calcd: 265.0868, found: 265.0869
GC-MS	264 (M, 10 %), 195 (100 %), 180 (38 %), 165 (14 %), 115 (15 %), 91 (16 %), 69 (15 %), 57 (54 %).

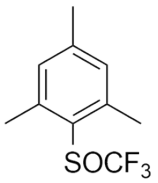
2,6-dimethoxy-3-((trifluoromethyl)sulfinyl)phenol (2k)



To a solution of 2,6-dimethoxy-4-((trifluoromethyl)thio)phenol (135 mg, 0.5 mmol) in 5 mL of solvent TFA at 0 °C was added 30% H_2O_2 (68 mg, 0.6 mmol). The reaction mixture was stirred at 0 °C for 5 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed with $NaHSO_3$ and extracted with DCM (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude reaction was subjected to column chromathography with mobile phase dichloromethane. Solvent was evaporated in vacuo to provide the product (117 mg, 87%) as brown solid. Mp 116.2–119.1°C.

yield	117 mg, 87%
^{1}H NMR (500 MHz, $CDCl_3$, 25°C)	δ = 7.42 (d, J = 8.8 Hz, 1H), 6.86 (d, J = 8.8 Hz, 1H), 4.03 (s, 3H), 3.98 (s, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$, 25°C)	δ = 152.0, 145.3, 138.0, 125.1 (q, J = 337 Hz), 120.7, 117.7, 106.6, 61.2, 56.7 ppm.
^{19}F NMR (471 MHz, $CDCl_3$, 25°C)	δ = –75.1 (s, 3F) ppm.
ESI-HRMS	$C_9H_{10}F_3O_4S$ $(M + H)^+$ calcd: 271.0246 found: 271.0243
GC-MS	270 (M, 10 %), 254 (12 %), 201 (100 %), 143 (13 %), 125 (14 %).

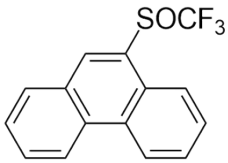
1,3,5-trimethyl-2-((trifluoromethyl)sulfinyl)benzene (2l)



To a solution of mesityl(trifluoromethyl)sulfane (118 mg, 0.5 mmol) in 5 mL of solvent TFA at 0 °C was added 30% H_2O_2 (68 mg, 0.6 mmol). The reaction mixture was stirred at 0 °C for 15 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed with $NaHSO_3$ and extracted with DCM (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude reaction was subjected to column chromathography with mobile phase dichloromethane. Solvent was evaporated in vacuo to provide the product (92 mg, 78%) as colorless, viscous liquid.

yield	92 mg, 78%
^{1}H NMR (500 MHz, $CDCl_3$, 25°C)	δ = 6.93 (s, 2H), 2.55 (s, 6H), 2.32 (s, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$, 25°C)	δ = 143.8, 130.7, 127.6, 126.6 (q, J = 338 Hz), 122.6, 21.3, 19.4 ppm.
^{19}F NMR (471 MHz, $CDCl_3$, 25°C)	δ = –70.5 (s, 3F) ppm.
ESI-HRMS	$C_{10}H_{12}F_3OS$ $(M + H)^+$ calcd: 237.0555 found: 237.0556

9-((trifluoromethyl)sulfinyl)phenanthrene (2m)



To a solution of phenanthren-9-yl(trifluoromethyl)sulfane (147 mg, 0.5 mmol) in 5 mL of solvent TFA at 0 °C was added 30% H_2O_2 (68 mg, 0.6 mmol). The reaction mixture was stirred at 0 °C for 15 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed with $NaHSO_3$ and extracted with DCM (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude reaction was subjected to column chromathography with mobile phase dichloromethane. Solvent was evaporated in vacuo to provide the product (125 mg, 85%) as brown, viscous liquid.

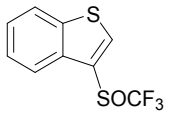
yield	125 mg, 85%
^{1}H NMR (500 MHz, $CDCl_3$, 25°C)	δ = 8.79 (d, J = 8.3 Hz, 1H), 8.73 (d, J = 8.4 Hz, 1H), 8.61 (s, 1H), 8.14 (d, J = 8.2 Hz, 1H), 8.09 (d, J = 7.9 Hz, 1H), 7.85-7.81 (m, 1H), 7.79 (t, J = 7.7 Hz, 1H), 7.75-7.68 (m, 2H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$, 25°C)	δ = 132.3, 130.9, 130.4, 130.3, 129.9, 129.0, 128.1, 128.0, 128.0, 127.8, 125.4 (q, J = 337 Hz), 123.8, 123.1, 122.9, 122.9 ppm.
^{19}F NMR (471 MHz, $CDCl_3$, 25°C)	δ = –72.9 (s, 3F) ppm.
ESI-HRMS	$C_{15}H_{10}F_3OS$ $(M + H)^+$ calcd: 295.0399, found: 295.0400
GC-MS	294 (M, 11 %), 278 (69 %), 225 (100 %), 209 (35 %), 181 (22 %), 165 (98 %).

3-((trifluoromethyl)sulfinyl)-1*H*-indole (2n)

To a solution of 3-((trifluoromethyl)thio)-1*H*-indole (108 mg, 0.5 mmol) in 5 mL of solvent TFA at 0 °C was added 30% H_2O_2 (68 mg, 0.6 mmol). The reaction mixture was stirred at 0 °C for 4 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed with $NaHSO_3$ and extracted with DCM (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude reaction was subjected to column chromatography with mobile phase heptane/ethyl acetate (2/1). Solvent was evaporated in vacuo to provide the product (38 mg, 33%) as black-brown, viscous liquid.

yield	38 mg, 33%
^{1}H NMR (500 MHz, $CDCl_3$, 25°C)	δ = 7.98 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 3.1 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.34 – 7.31 (m, 1H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$, 25°C)	136.7, 130.3, 127.0, 124.7, 124.5 (q, J = 337 Hz), 122.9, 120.6, 112.4, 109.4 ppm.
^{19}F NMR (471 MHz, $CDCl_3$, 25°C)	δ = –73.78 (s, 3F) ppm.
ESI-HRMS	$C_9H_6F_3NOS$ $(M + H)^+$ calcd: 234.0195 found: 234.0195

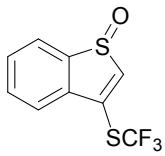
3-((trifluoromethyl)sulfinyl)benzo[*b*]thiophene (2o)



To a solution of 3-((trifluoromethyl)thio)benzo[b]thiophene (117 mg, 0.5 mmol) in 5 mL of solvent TFA at 0 °C was added 30% H_2O_2 (68 mg, 0.6 mmol). The reaction mixture was stirred at 0 °C for 1.5 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed with $NaHSO_3$ and extracted with DCM (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum. The crude reaction was subjected to column chromatography with mobile phase heptane/ethyl acetate (6/1). Solvent was evaporated in vacuo to provide the product (28 mg, 23%) as white solid.

yield	28 mg, 23%
^{1}H NMR (500 MHz, $CDCl_3$, 25°C)	δ = 8.33 (s, 1H), 8.10 (m, 1H), 7.98 (m, 1H), 7.55 – 7.50 (m, 2H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$, 25°C)	δ = 140.8, 135.0, 134.3, 126.3, 126.3 (q, J = 338 Hz), 126.0, 123.3, 122.6, 122.6 ppm.
^{19}F NMR (471 MHz, $CDCl_3$, 25°C)	δ = – 73.4 (s, 3F) ppm.
ESI-HRMS	$C_9H_5F_3OS_2$ $(M + H)^+$ calcd: 250.9807 found: 250.9806

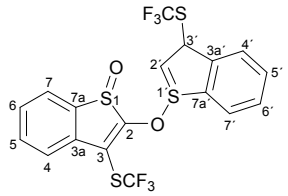
3-((trifluoromethyl)thio)benzo[*b*]thiophene 1-oxide (2o′)



To a solution of 3-((trifluoromethyl)thio)benzo[b]thiophene (117 mg, 0.5 mmol) in 5 mL of solvent TFA at 0 °C was added 30% H_2O_2 (68 mg, 0.6 mmol). The reaction mixture was stirred at 0 °C for 1.5 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed with $NaHSO_3$ and extracted with DCM (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum. The crude reaction was subjected to column chromatography with mobile phase heptane/ethyl acetate (from 6/1 to 0/1). Solvent was evaporated in vacuo to provide the product (43 mg, 34%) as white solid.

yield	43 mg, 34%
^{1}H NMR (500 MHz, DMSO, 25°C)	δ = 8.12 (m, 2H), 7.78 – 7.73 (m, 2H), 7.70 – 7.66 (m, 1H) ppm.
^{13}C NMR (126 MHz, DMSO, 25°C)	δ = 144.7, 144.0, 136.2, 133.2, 131.5, 130.4, 129.1 (q, J = 336 Hz), 127.2, 124.0 ppm.
^{19}F NMR (471 MHz, DMSO, 25°C)	δ = –39.6 (s, 3F) ppm.
ESI-HRMS	$C_9H_5F_3OS_2$ $(M + H)^+$ calcd: 250.9807 found: 250.9811

3-((trifluoromethyl)thio)-2-((3-((trifluoromethyl)thio)-3*H*-1l4-benzo[*b*]thiophen-1-yl)oxy)benzo[b]thiophene 1-oxide



the appearance of the sample	white solid
^{1}H NMR (500 MHz, $CDCl_3$, 25°C)	δ =8.12 (d, J = 7.8 Hz, 4), 7.99 (d, J = 7.8 Hz, 4′), 7.81 (d, J = 7.8 Hz, 7), 7.77 (m, 5), 7.64 (m, 6), 7.43 (m, 5′), 7.36 (d, J = 6.7 Hz, 2′), 7.29 (m, 6′), 7.08 (d, J = 7.7 Hz, 7′), 4.70 (d, J = 6.7 Hz, 3′) ppm.
^{13}C NMR (126 MHz, $CDCl_3$, 25°C)	δ = 144.3 (3a), 140.0 (7a), 134.9 (2′), 131.9 (5), 131.8 (7a′), 130.4 (5′), 130.2 (6), 130.2 (6′), 129.4 (3a′), 128.9 (q), 128.9 (q), 128.6 (7′), 128.4 (4), 128.2 (3), 127.7 (2), 127.6 (4′), 126.1 (7), 79.2 (3′) ppm.
^{19}F NMR (471 MHz, $CDCl_3$, 25°C)	δ = –37.5 (s, 3F), –41.7 (s, 3F) ppm.
ESI-HRMS	$C_{18}H_{10}F_6O_2S_4$ $(M + H)^+$ calcd: 500.9541 found: 500.9554

Characterization Data for products – One-pot

1-((trifluoromethyl)sulfinyl)naphthalen-2-ol (2d)

To a solution of naphthalen-2-ol (72 mg, 0.5 mmol) in 5 mL of DCM was added reagent 4-$ClC_6H_4NHSCF_3$ (126 mg, 0.65 mmol) and TfOH (98 mg, 0.65 mmol). The reagent and TfOH were added in one portion. The reaction mixture was stirred at room temperature for 21 h. Conversion was followed by GC-MS. After reaction was complete to a mixture 5 mL of solvent TFA and 30% H_2O_2 (85 mg, 0.75 mmol) was added. The reaction mixture was stirred at 25 °C for 8 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed first with water (5 mL), then with $NaHSO_3$, with aqueous HCl (5 mL), with water (5 mL) and with aqueous $NaHCO_3$ (5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum. The crude reaction was subjected to column chromatography with mobile phase hexane/EtOH (9/1). Solvent was evaporated in vacuum to provide the product (102 mg, 78%) as colorless, viscous liquid.

1-methoxy-4-((trifluoromethyl)sulfinyl)benzene (2e)[1]

To a solution of anisole (54.1 mg, 0.5 mmol) in dichloromethane (5 mL) was reagent 4-$ClC_6H_4NHSCF_3$ (148.0 mg, 0.65 mmol) and the TfOH (58 μL, 0.65 mmol) added slowly in 6 portions every 1 h. The mixture was stirred at room temperature for 20 h. Conversion was checked by GC-MS. After reaction was complete to a mixture 5 mL of solvent TFA and 30% H_2O_2 (68 mg, 0.6 mmol) was added. The reaction mixture was stirred at 0 °C for 2 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed first with water (5 mL), then with $NaHSO_3$, with aqueous HCl (5 mL), with water (5 mL) and with aqueous $NaHCO_3$ (5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum. The crude reaction was subjected to column chromatography with mobile phase dichloromethane. Solvent was evaporated in vacuo to provide the product (99 mg, 88%) as yellow, viscous liquid.

4-(*tert*-butyl)-2-((trifluoromethyl)sulfinyl)phenol (2h)

To a solution of 4-*tert*-butylphenol (75.1 mg, 0.5 mmol) in dichloromethane (5 mL) was reagent 4-$ClC_6H_4NHSCF_3$ (148.0 mg, 0.65 mmol) and the TfOH (58 μL, 0.65 mmol) added slowly in 5 portions every 1 h. The mixture was stirred at room temperature for 20 h. Conversion was checked by GC-MS. After reaction was complete to a mixture 5 mL of solvent TFA and 30% H_2O_2 (68 mg, 0.6 mmol) was added. The reaction mixture was stirred at 0 °C for 3 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed first with water (5 mL), then with $NaHSO_3$, with aqueous HCl (5 mL), with water (5 mL) and with aqueous $NaHCO_3$ (5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum. The crude reaction was subjected to column chromatography with mobile phase dichloromethane. Solvent was evaporated in vacuo to provide the product (120 mg, 90%) as brown, viscous liquid.

4-bromo-2-((trifluoromethyl)sulfinyl)phenol (2i)[3]

To a solution of 4-bromophenol (86.5 mg, 0.5 mmol) in hexane (5 mL) was reagent 4-$ClC_6H_4NHSCF_3$ (227.7 mg, 1.0 mmol), and the TfOH (134 µL, 1.5 mmol) added slowly in 6 portions every 1 h. The mixture was stirred at room temperature for 20 h. Conversion was checked by GC-MS. After reaction was complete to a mixture 5 mL of solvent TFA and 30% H_2O_2 (68 mg, 0.6 mmol) was added. The reaction mixture was stirred at 0 °C for 4 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed first with water (5 mL), then with $NaHSO_3$, with aqueous HCl (5 mL), with water (5 mL) and with aqueous $NaHCO_3$ (5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum. The crude reaction was subjected to column chromatography with mobile phase dichloromethane. Solvent was evaporated in vacuo to provide the product (131 mg, 91%) as brown solid.

4-(*tert*-butyl)-1-methyl-2-((trifluoromethyl)sulfinyl)benzene (2j)

To a solution of 4-*tert*-butyltoluene (74.1 mg, 0.5 mmol) in trifluoroacetic acid (5 mL) was reagent 4-$ClC_6H_4NHSCF_3$ (227.7 mg, 1.0 mmol) and the TfOH (134 µL, 1.5 mmol) added slowly in 6 portions every 1 h. The mixture was stirred at room temperature for 20 h. Conversion was checked by GC-MS. After reaction was complete to a mixture 5 mL of solvent TFA and 30% H_2O_2 (68 mg, 0.6 mmol) was added. The reaction mixture was stirred at 0 °C for 2.5 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed first with water (5 mL), then with $NaHSO_3$, with aqueous HCl (5 mL), with water (5 mL) and with aqueous $NaHCO_3$ (5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum. The crude reaction was subjected to column chromatography with mobile phase dichloromethane. Solvent was evaporated in vacuum to provide the product (123 mg, 93%) as colorless, viscous liquid.

2,6-dimethoxy-3-((trifluoromethyl)sulfinyl)phenol (2k)

To a solution of 2,6-dimethoxyphenol (77.1 mg, 0.5 mmol) in dichloromethane (5 mL) was added reagent 4-$ClC_6H_4NHSCF_3$ (148.0 mg, 0.65 mmol) and the TfOH (58 µL, 0.65 mmol). The mixture was stirred at room temperature for 20 h. Conversion was checked by GC-MS. After reaction was complete to a mixture 5 mL of solvent TFA and 30% H_2O_2 (68 mg, 0.6 mmol) was added. The reaction mixture was stirred at 0 °C for 5 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed first with water (5 mL), then with $NaHSO_3$, with aqueous HCl (5 mL), with water (5 mL) and with aqueous $NaHCO_3$ (5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum. The crude reaction was subjected to column chromatography with mobile phase dichloromethane. Solvent was evaporated in vacuum to provide the product (124 mg, 92%) as brown solid.

1,3,5-trimethyl-2-((trifluoromethyl)sulfinyl)benzene (2l)

To a solution of mesitylene (60.1 mg, 0.5 mmol) in dichloromethane (5 mL) was reagent 4-$ClC_6H_4NHSCF_3$ (148.0 mg, 0.65 mmol) and the TfOH (58 μL, 0.65 mmol) added slowly in 5 portions every 1 h. The mixture was stirred at room temperature for 20 h. Conversion was checked by GC-MS. After reaction was complete to a mixture 5 mL of solvent TFA and 30% H_2O_2 (68 mg, 0.6 mmol) was added. The reaction mixture was stirred at 0 °C for 15 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed first with water (5 mL), then with $NaHSO_3$, with aqueous HCl (5 mL), with water (5 mL) and with aqueous $NaHCO_3$ (5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum. The crude reaction was subjected to column chromatography with mobile phase dichloromethane. Solvent was evaporated in vacuo to provide the product (101 mg, 86%) as colorless, viscous liquid.

9-((trifluoromethyl)sulfinyl)phenanthrene (2m)

To a solution of phenanthrene (89.0 mg, 0.5 mmol) in dichloromethane (5 mL) was reagent 4-$ClC_6H_4NHSCF_3$ (148.0 mg, 0.65 mmol) and the TfOH (58 μL, 0.65 mmol) added slowly in 6 portions every 1 h. The mixture was stirred at room temperature for 20 h. Conversion was checked by GC-MS. After reaction was complete to a mixture 5 mL of solvent TFA and 30% H_2O_2 (68 mg, 0.6 mmol) was added. The reaction mixture was stirred at 0 °C for 15 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed first with water (5 mL), then with $NaHSO_3$, with aqueous HCl (5 mL), with water (5 mL) and with aqueous $NaHCO_3$ (5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum. The crude reaction was subjected to column chromatography with mobile phase dichloromethane. Solvent was evaporated in vacuo to provide the product (133 mg, 90%) as brown, viscous liquid.

3-((trifluoromethyl)sulfinyl)-1*H*-indole (2n)

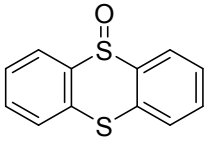
To a solution of 1*H*-indole (59 mg, 0.5 mmol) in dichloromethane (5 mL) was reagent 4-$ClC_6H_4NHSCF_3$ (148.0 mg, 0.65 mmol) and the TfOH (58 μL, 0.65 mmol) added slowly in 3 portions every 1 h. The mixture was stirred at room temperature for 6 h. Conversion was checked by GC-MS. After reaction was complete to a mixture 5 mL of solvent TFA and 30% H_2O_2 (68 mg, 0.6 mmol) was added. The reaction mixture was stirred at 0 °C for 4 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed first with water (5 mL), then with $NaHSO_3$, with aqueous HCl (5 mL), with water (5 mL) and with aqueous $NaHCO_3$ (5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum. The crude reaction was subjected to column chromatography with mobile phase heptane/ethyl acetate (2/1). Solvent was evaporated in vacuo to provide the product (43 mg, 37%) as black-brown, viscous liquid.

3-((trifluoromethyl)sulfinyl)benzo[*b*]thiophene (2o)

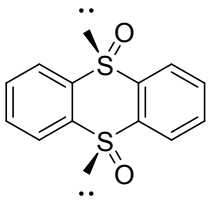
To a solution of benzo[*b*]thiophene (67 mg, 0.5 mmol) in dichloromethane (5 mL) was reagent 4-$ClC_6H_4NHSCF_3$ (148.0 mg, 0.65 mmol) and the TfOH (58 μL, 0.65 mmol) added slowly in 3 portions every 1 h. The mixture was stirred at room temperature for 24 h. Conversion was checked by GC-MS. After reaction was complete to a mixture 5 mL of solvent TFA and 30% H_2O_2 (68 mg, 0.6 mmol) was added. The reaction mixture was stirred at 0 °C for 1.5 h. Reaction time was determined with GC-MS. After reaction was complete, the reaction mixture was washed first with water (5 mL), then with $NaHSO_3$, with aqueous HCl (5 mL), with water (5 mL) and with aqueous $NaHCO_3$ (5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum. The crude reaction was subjected to column chromatography with mobile phase heptane/ethyl acetate (6/1). Solvent was evaporated in vacuo to provide the product (31 mg, 25%) as white solid.

The effect of reaction conditions on the oxidation of thianthrene 4

To a suspension of thianthrene **4** (0.5 mmol, 1 equiv.) in 5 mL of solvent (MeCN or TFA) was added oxidant (H_2O_2 or *m*-CPBA (0.5 mmol, 1.2 equiv.)). The reaction mixture was stirred for 2.5 or 24 h at 0 °C or rt. After reaction was complete, the reaction mixture was washed with $NaHSO_3$, extracted with DCM (3×5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuo. The crude reaction mixture was analyzed by NMR spectroscopy and product distribution determined from the NMR data in comparison with those in the literature. Results are presented in **Napaka! Vira sklicevanja ni bilo mogoče najti.**.

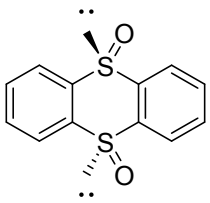


thianthrene 5-oxide (**5**).[4] ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.94 (d, J = 7.8 Hz, 2H), 7.63 (d, J = 7.6 Hz, 2H), 7.56 (m, 2H), 7.43 (m, 2H).

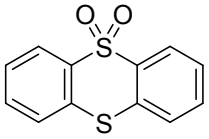


cis-thianthrene 5,10-dioxide (**6a**).[4] ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 8.07-8.09 (m, 4H), 7.72-7.74 (m, 4H).

trans-

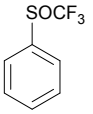


thianthrene 5,10-dioxide (**6b**).[4] ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 8.10-8.11 (m, 4H), 7.66-7.67 (m, 4H).

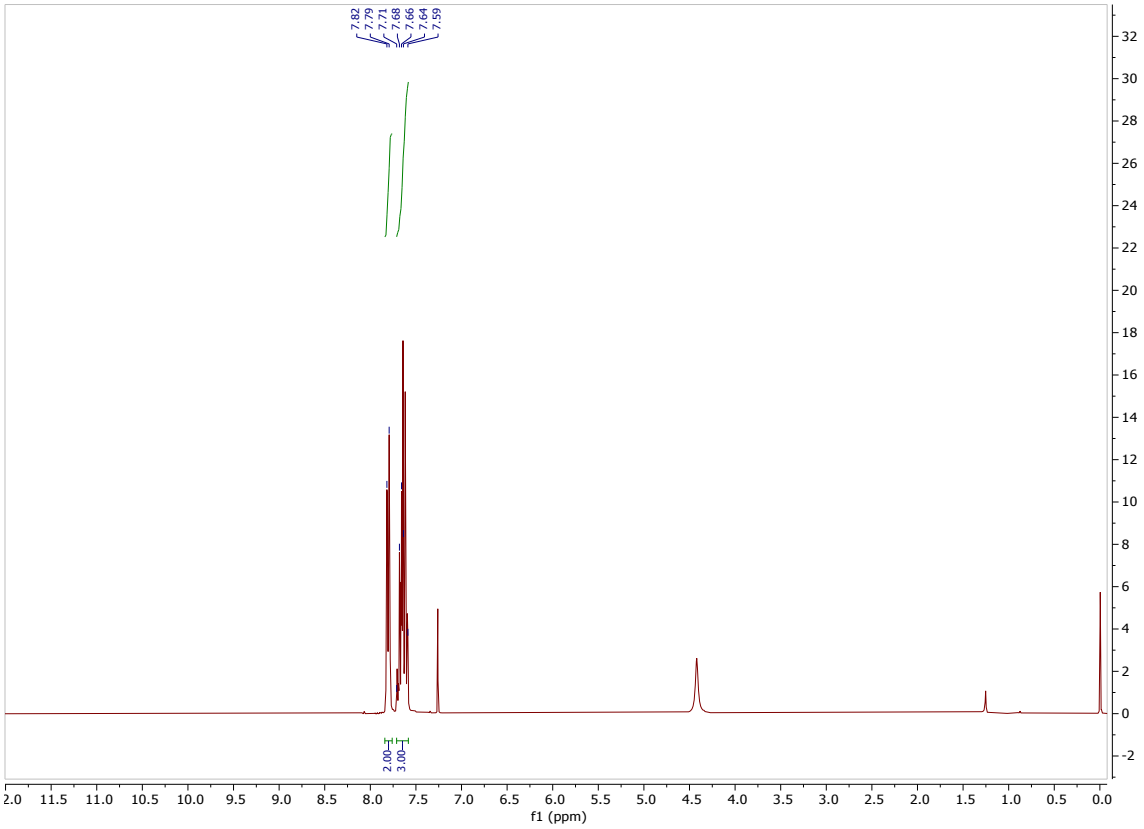


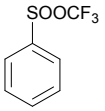
thianthrene 5,5-dioxide (**7**).[4] ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 8.26-8.20 (m, 2H), 7.75-7.61 (m, 2H), 7.59-7.53 (m, 4H).

1H, 13C and 19F spectra

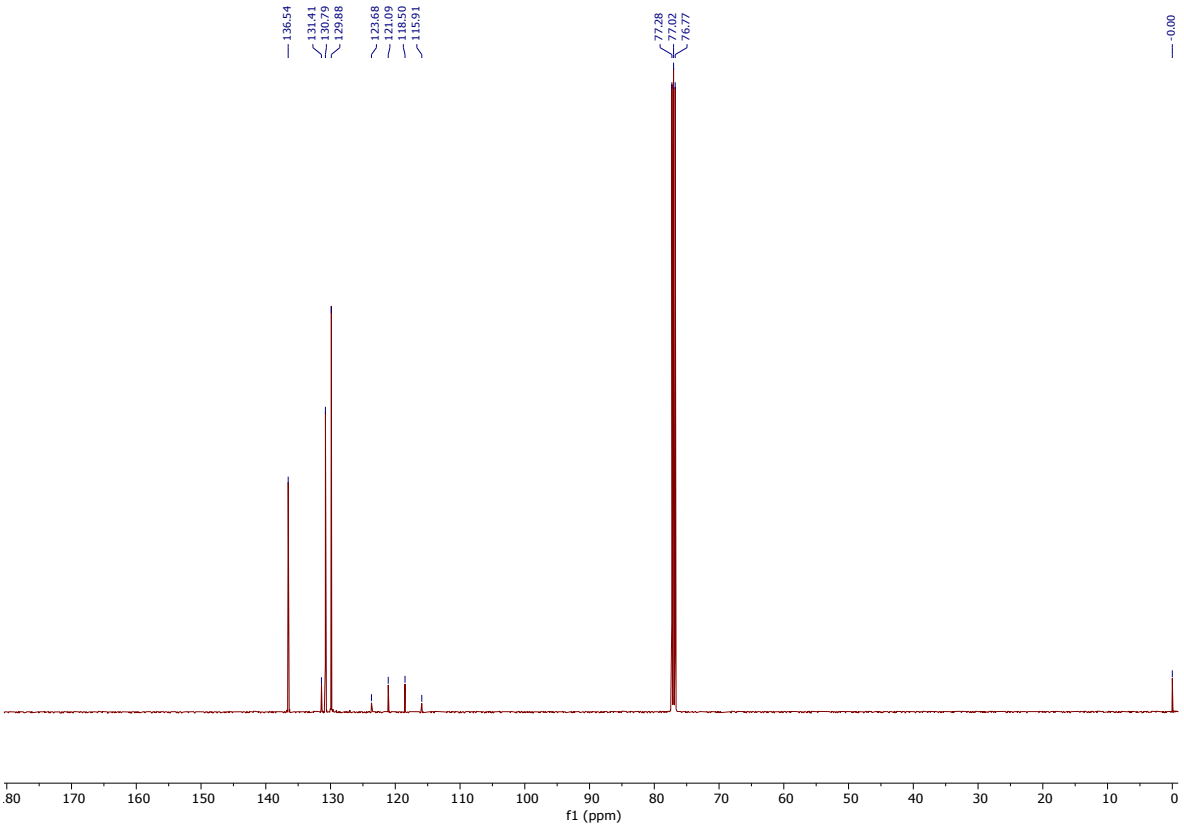


2a




SOOCF3

3a


136.54
131.41
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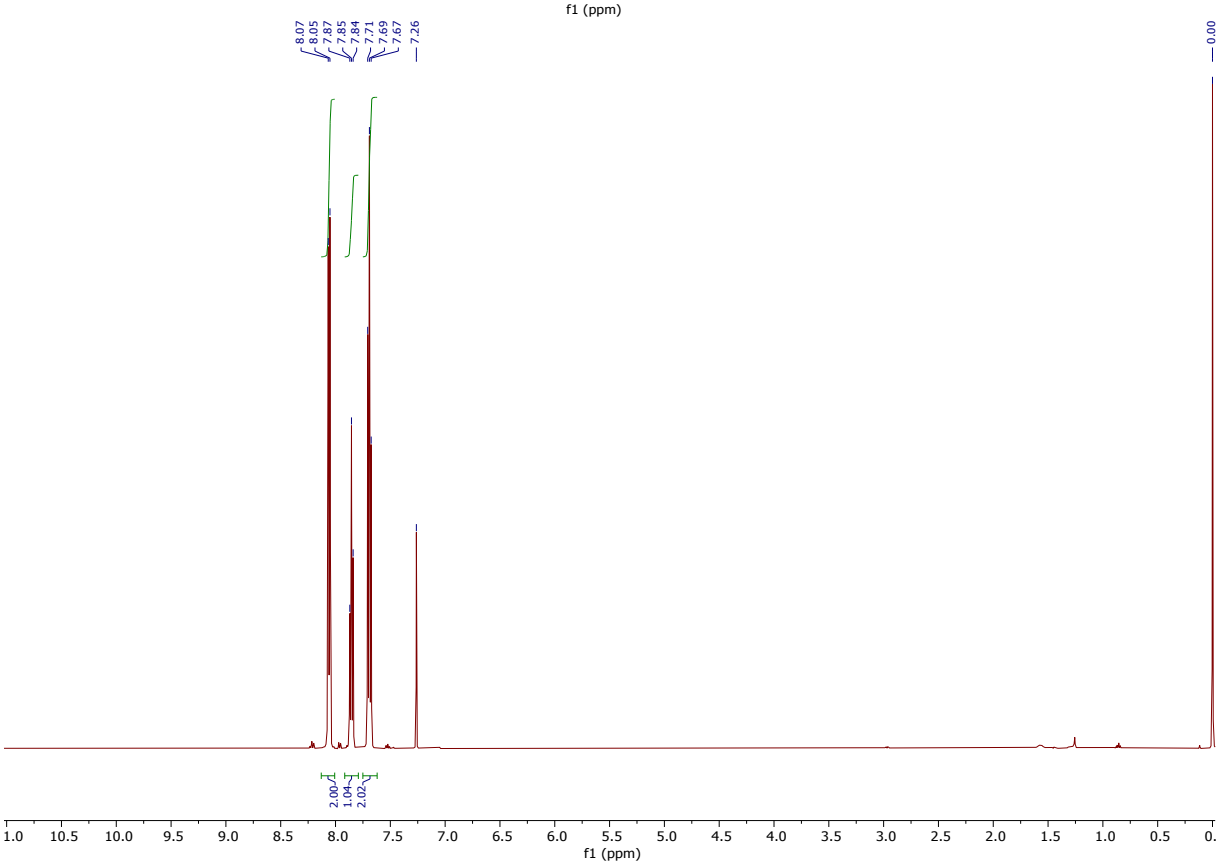
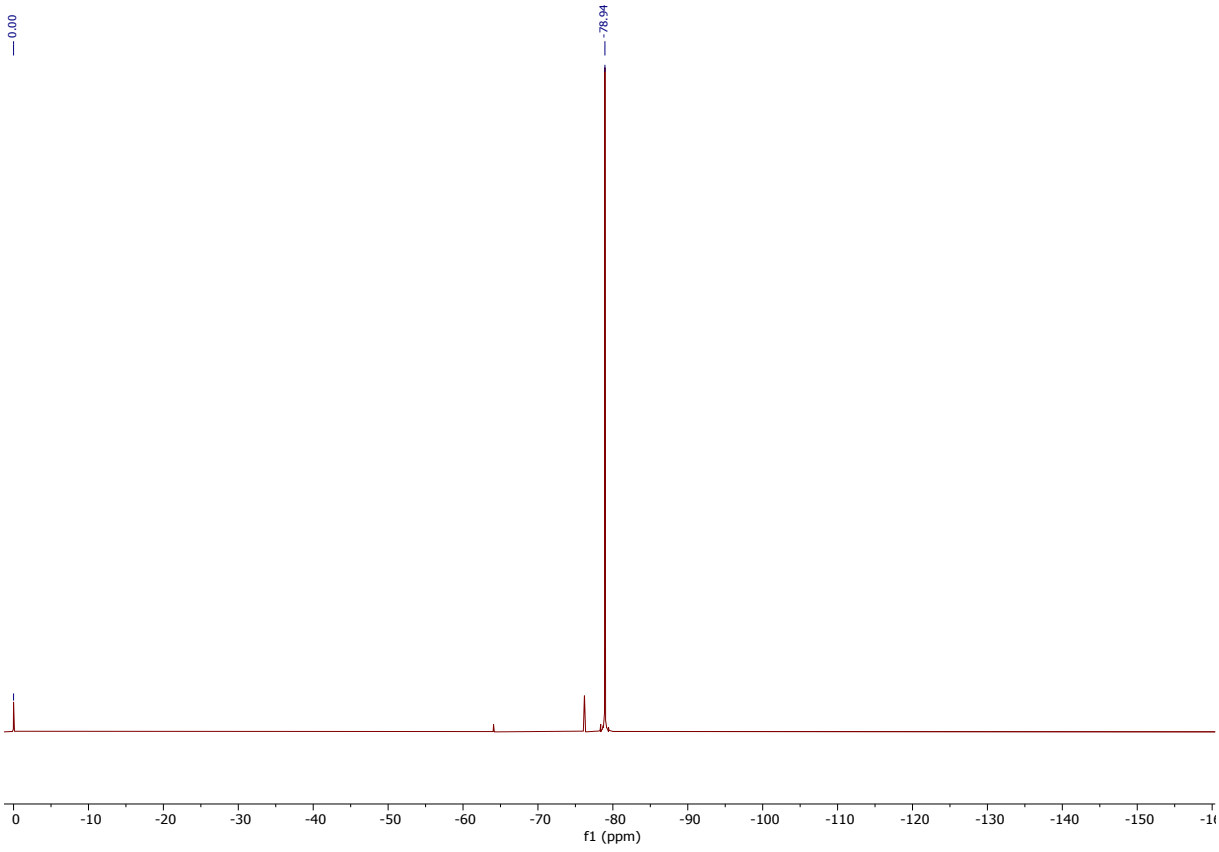
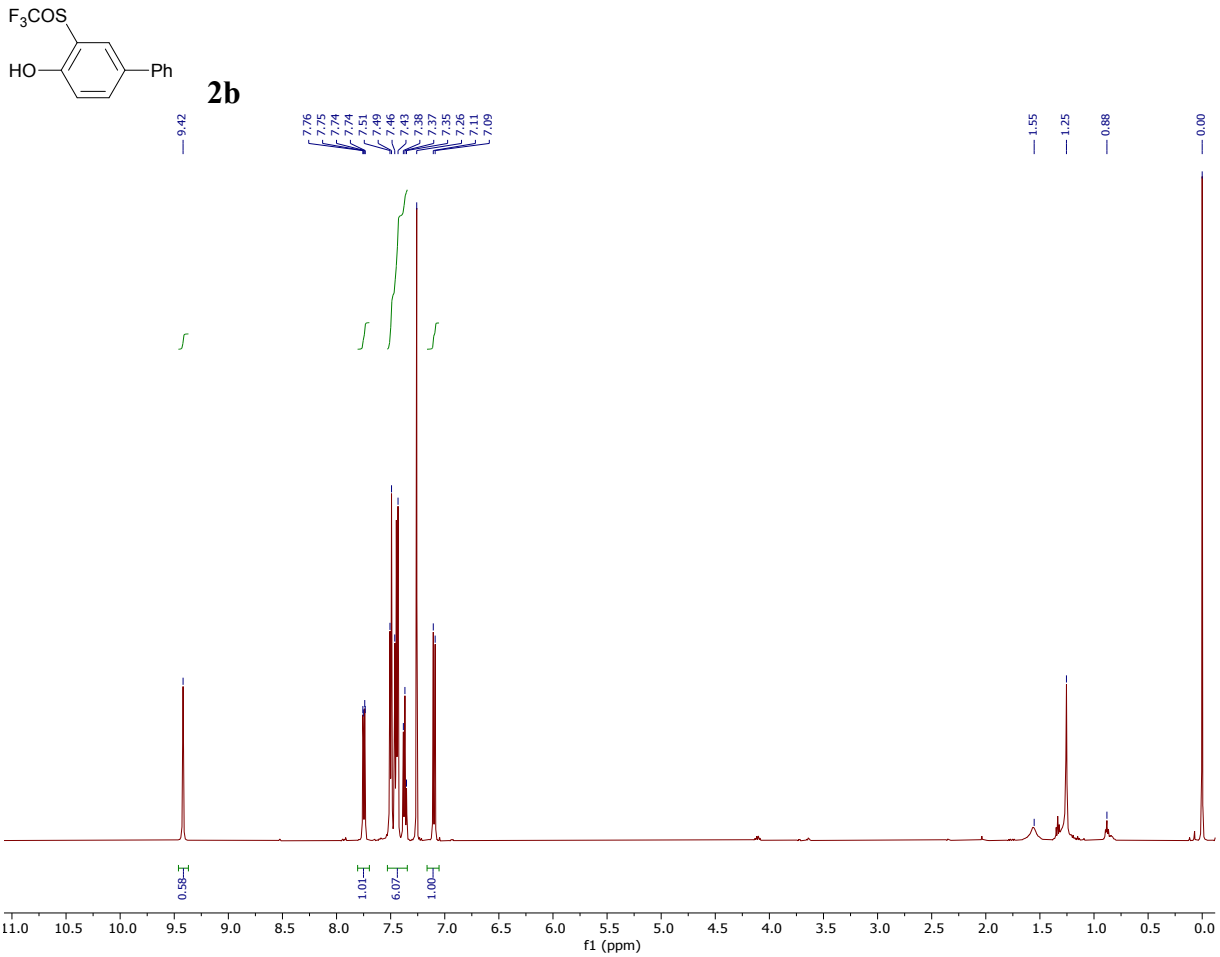
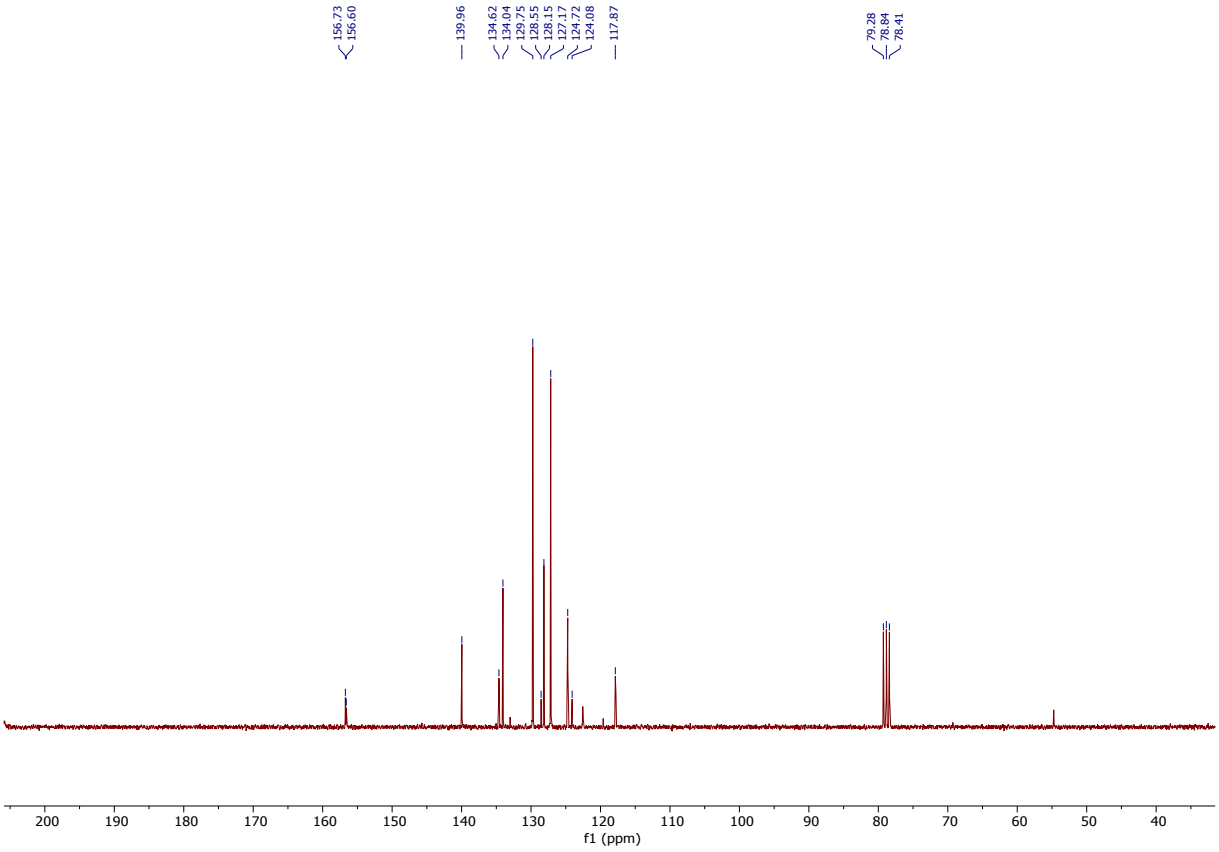
129.88
123.68
121.09
118.50
115.91
77.28
77.02
76.77
-0.00
f1 (ppm)


8.07
8.05
7.87
7.85
7.84
7.71
7.69
7.67
7.26
0.00
2.00
1.04
2.02
f1 (ppm)


0.00
-78.94
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)


F3COS
HO
Ph
2b
9.42
7.76
7.75
7.74
7.74
7.51
7.49
7.46
7.43
7.38
7.37
7.35
7.26
7.11
7.09
1.55
1.25
0.88
0.00
0.58
1.01
6.07
1.00
f1 (ppm)


156.73
156.60
139.96
134.62
134.04
129.75
128.55
128.15
127.17
124.72
124.08
117.87
79.28
78.84
78.41
200
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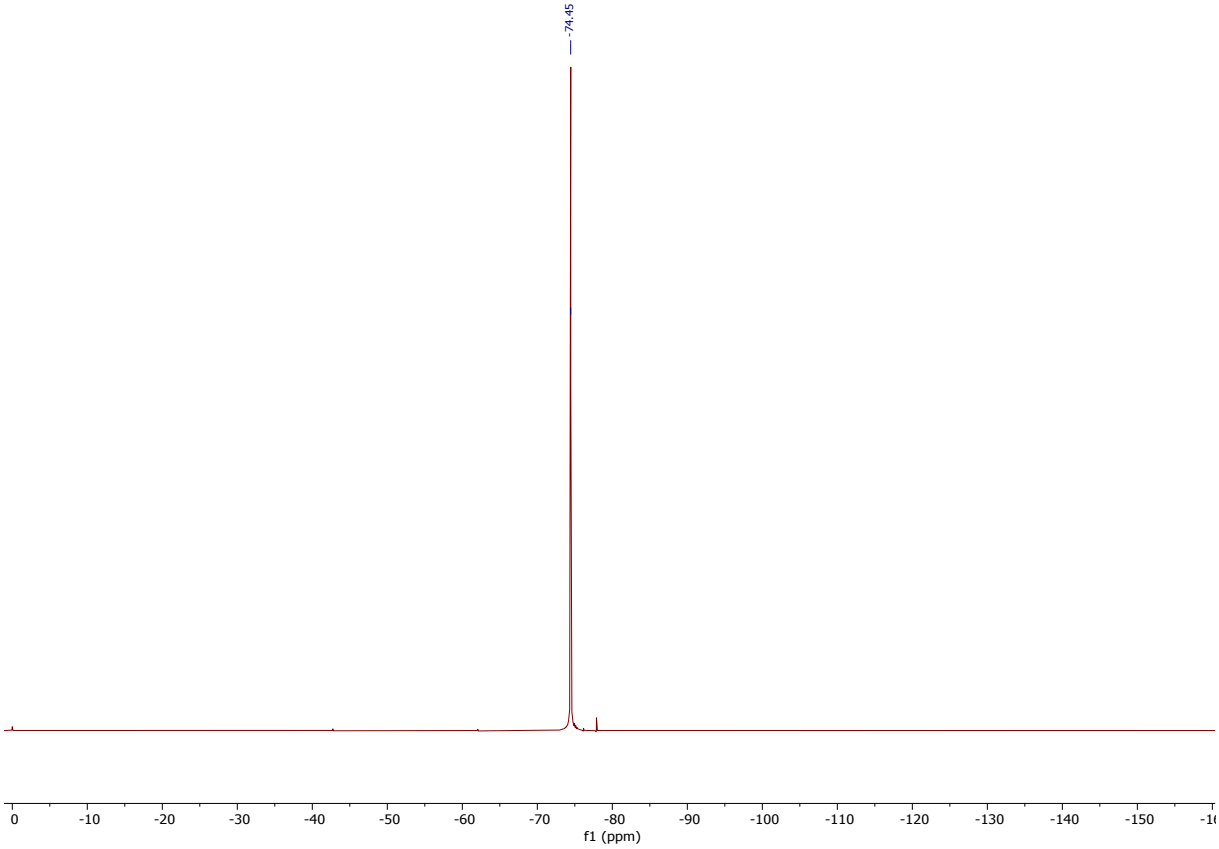
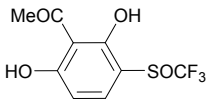
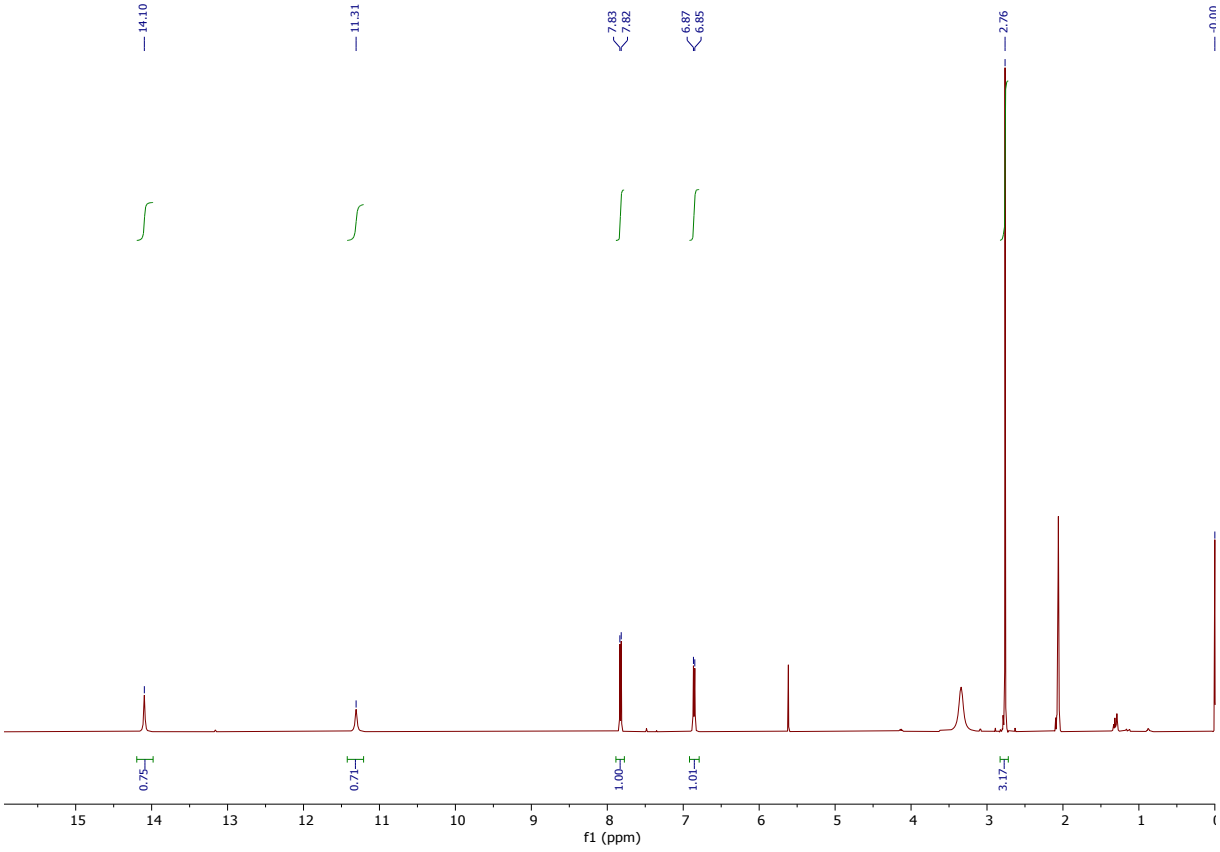
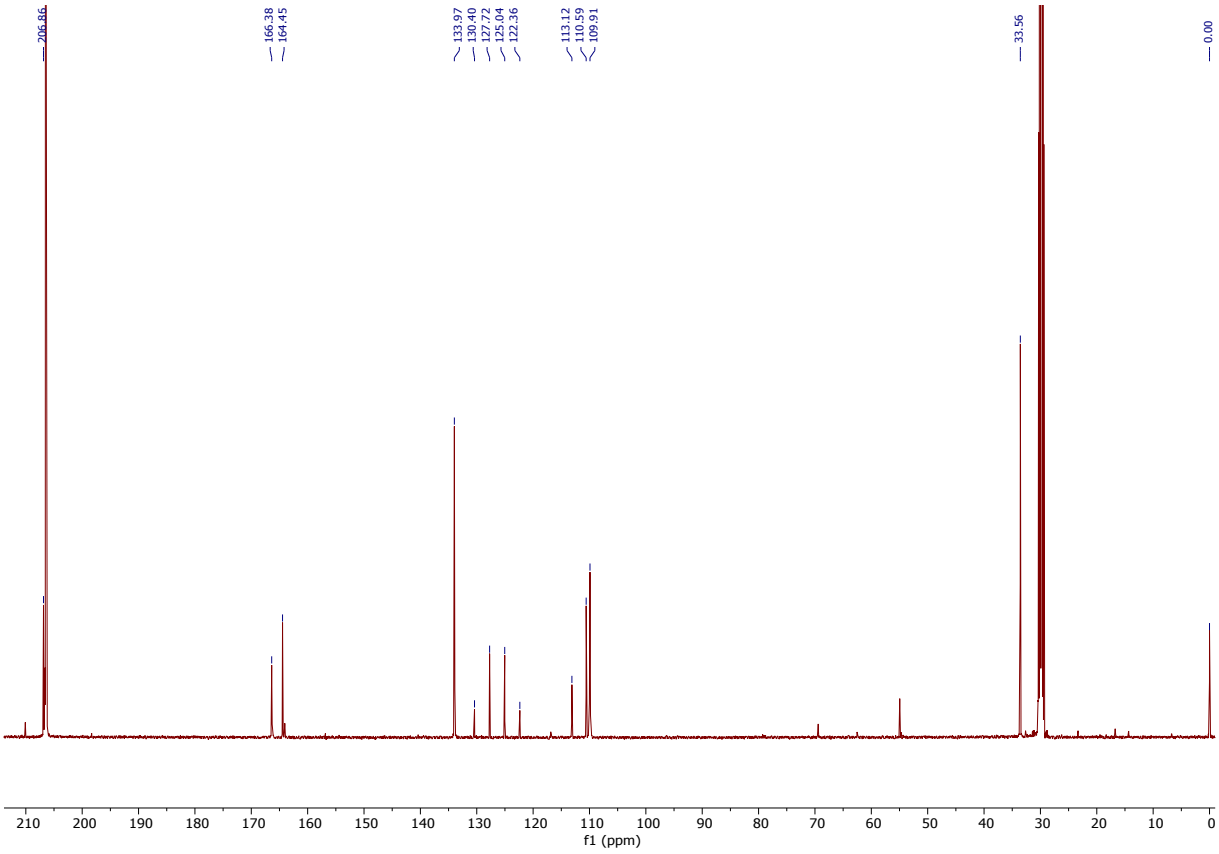
100
90
80
70
60
50
40
f1 (ppm)

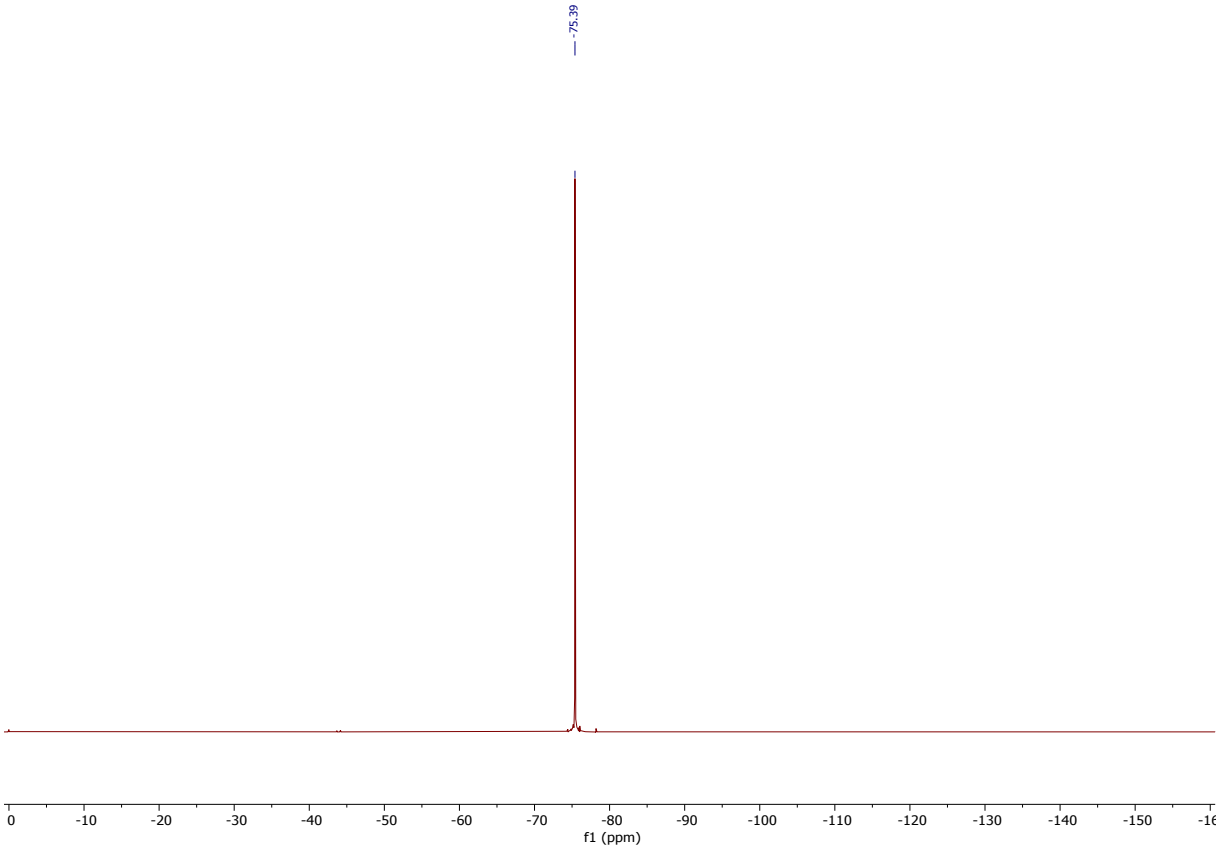

-74.45
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

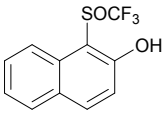

MeOC
OH
HO
SOCF3

2c

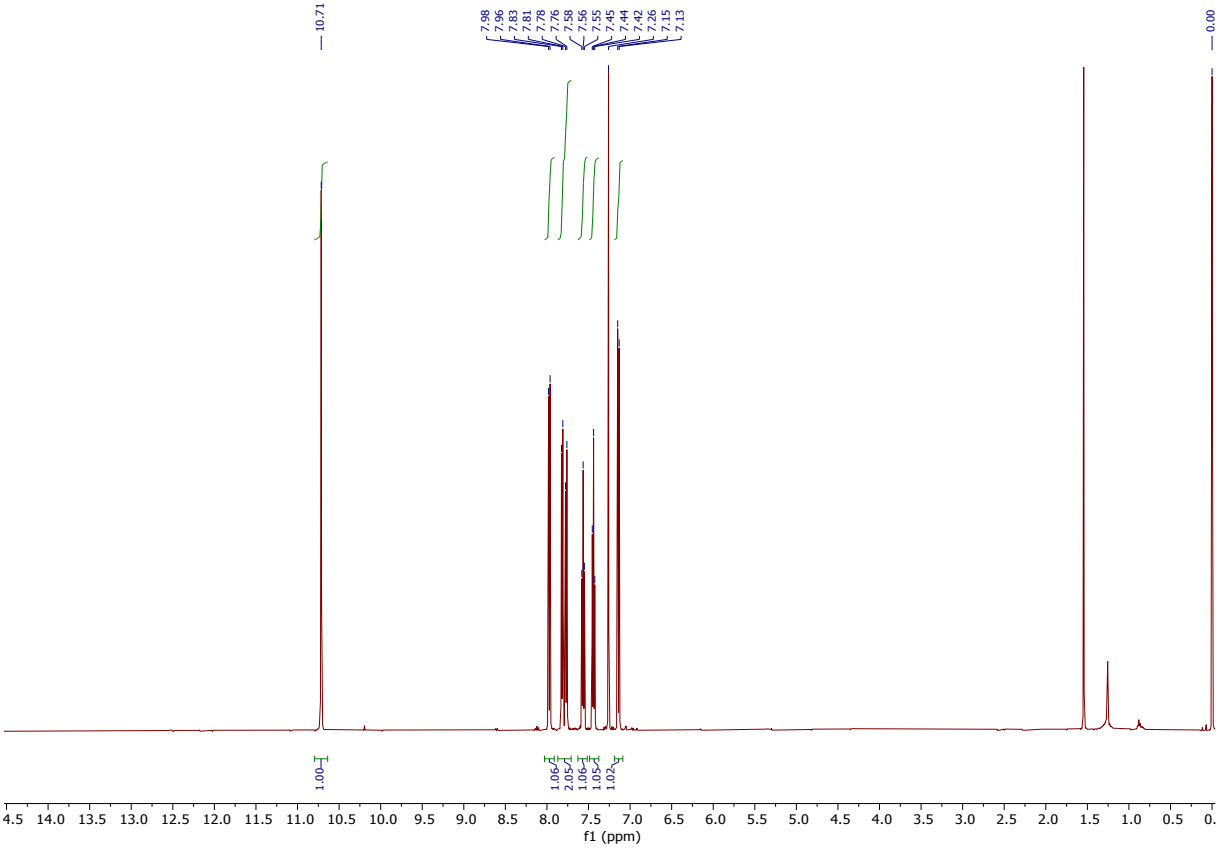

14.10
11.31
7.83
7.82
6.87
6.85
2.76
0.00
0.75
0.71
1.00
1.01
3.17
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
f1 (ppm)

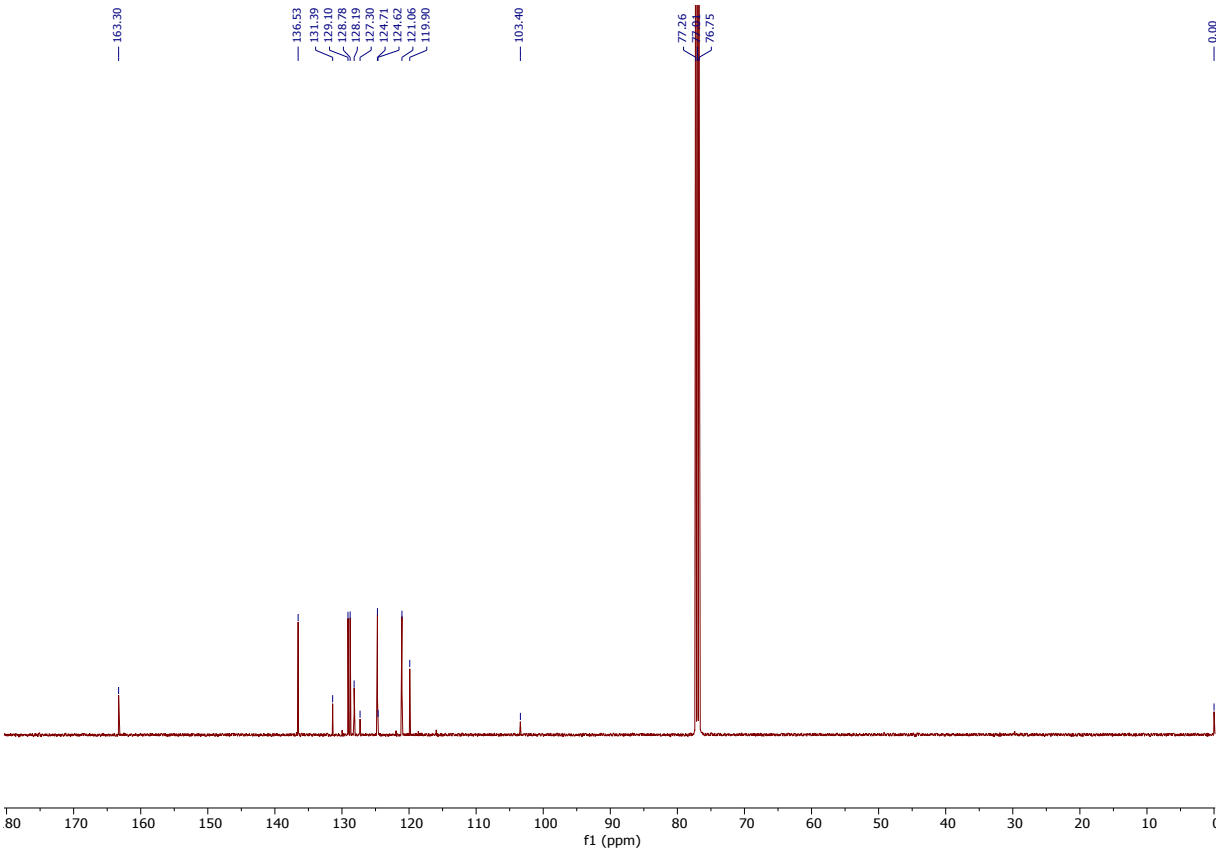

206.86
166.38
164.45
133.97
130.40
127.72
125.04
122.36
113.12
110.59
109.91
33.56
0.00
f1 (ppm)

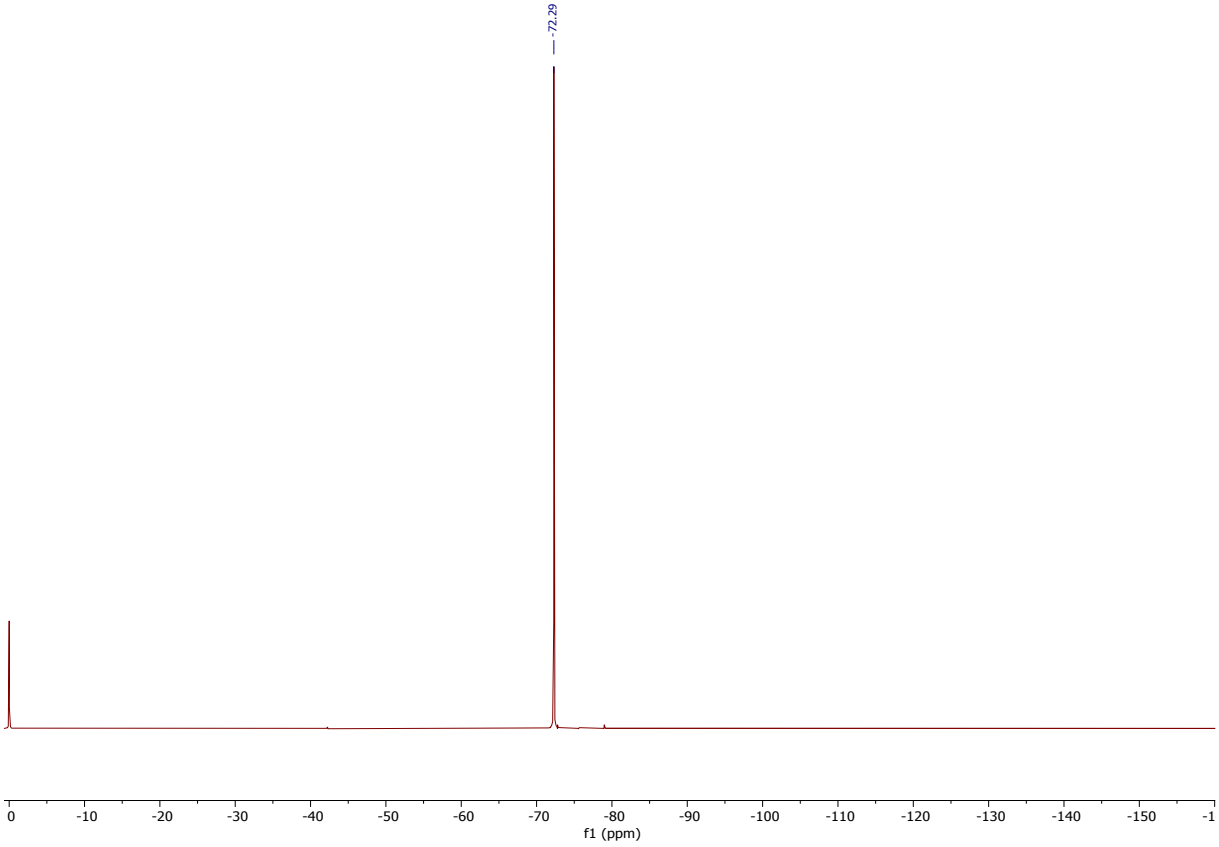

-75.39
f1 (ppm)

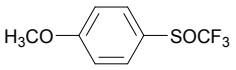

SOCF3
OH

2d

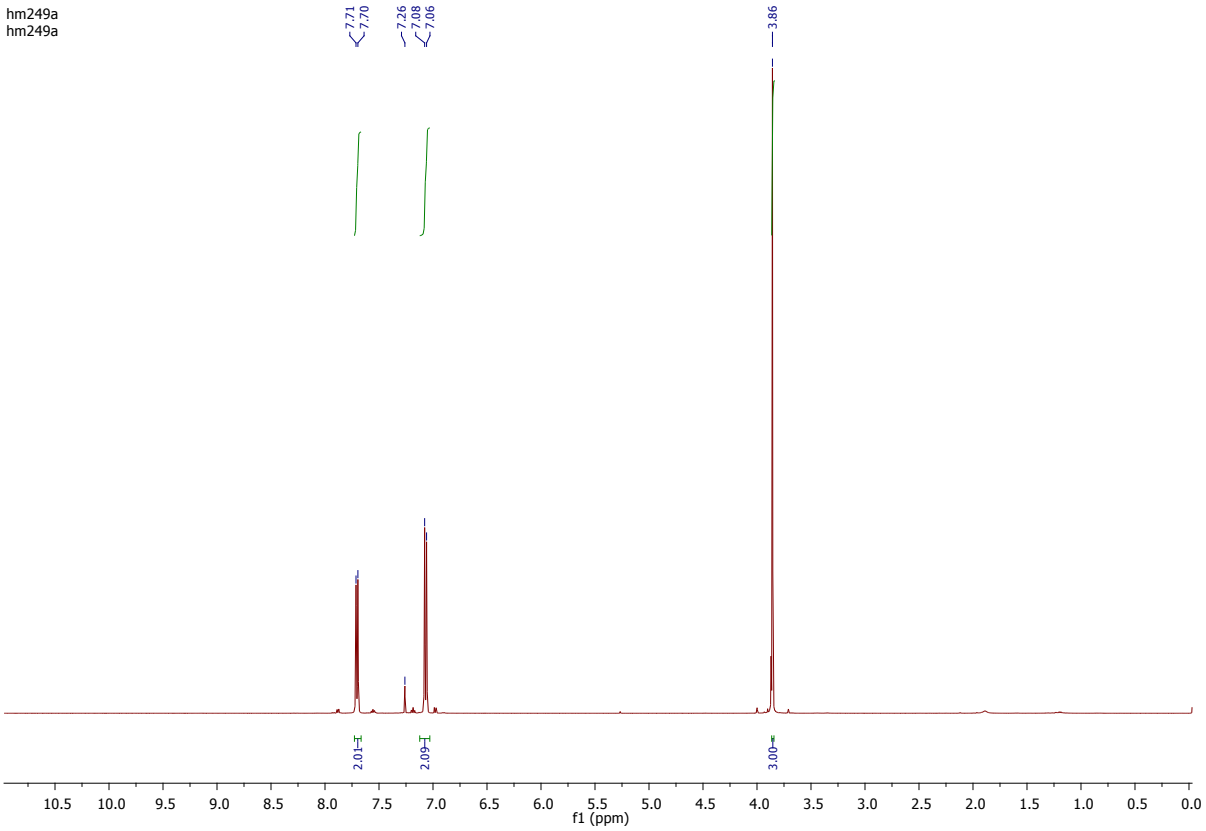

10.71
7.98
7.96
7.83
7.81
7.78
7.76
7.58
7.56
7.55
7.45
7.44
7.42
7.26
7.15
7.13
0.00
1.00
1.06
2.05
1.06
1.05
1.02
f1 (ppm)

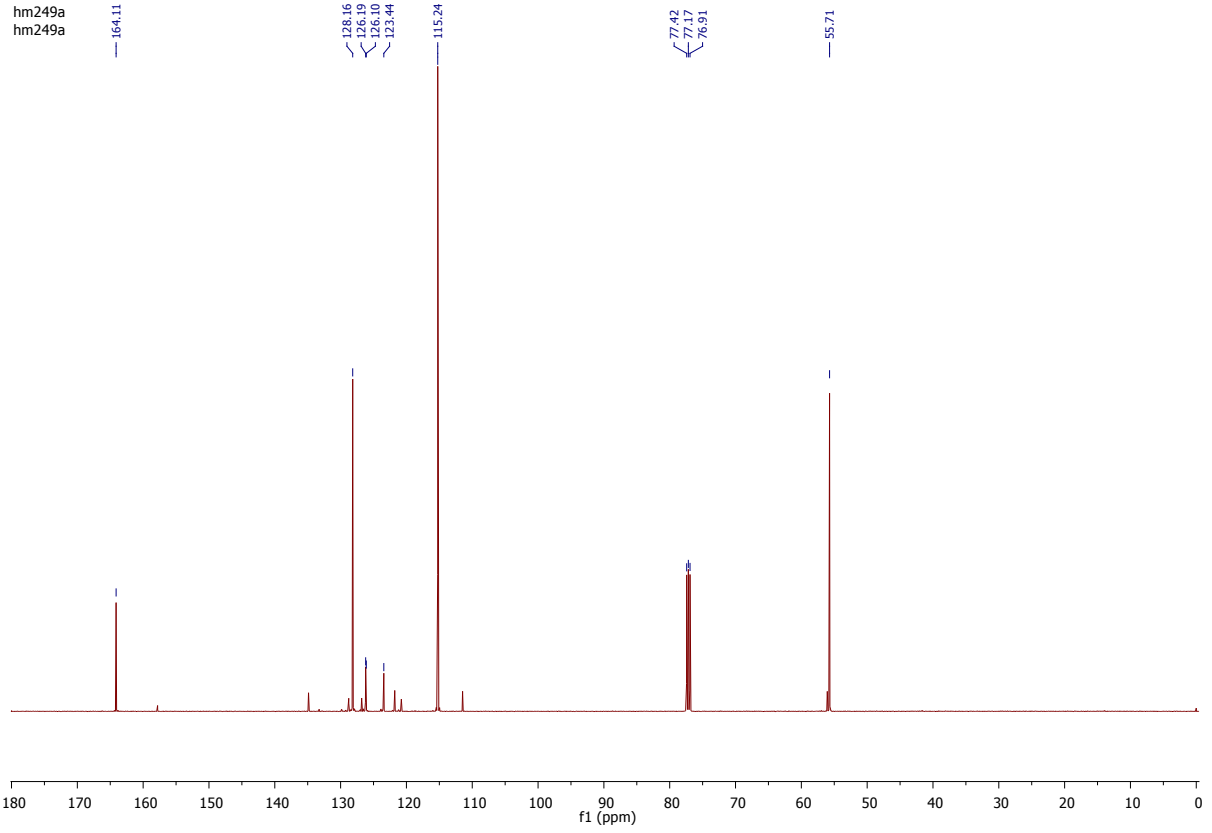

163.30
136.53
131.39
129.10
128.78
128.19
127.30
124.71
124.62
121.06
119.90
103.40
77.26
76.75
0.00
f1 (ppm)

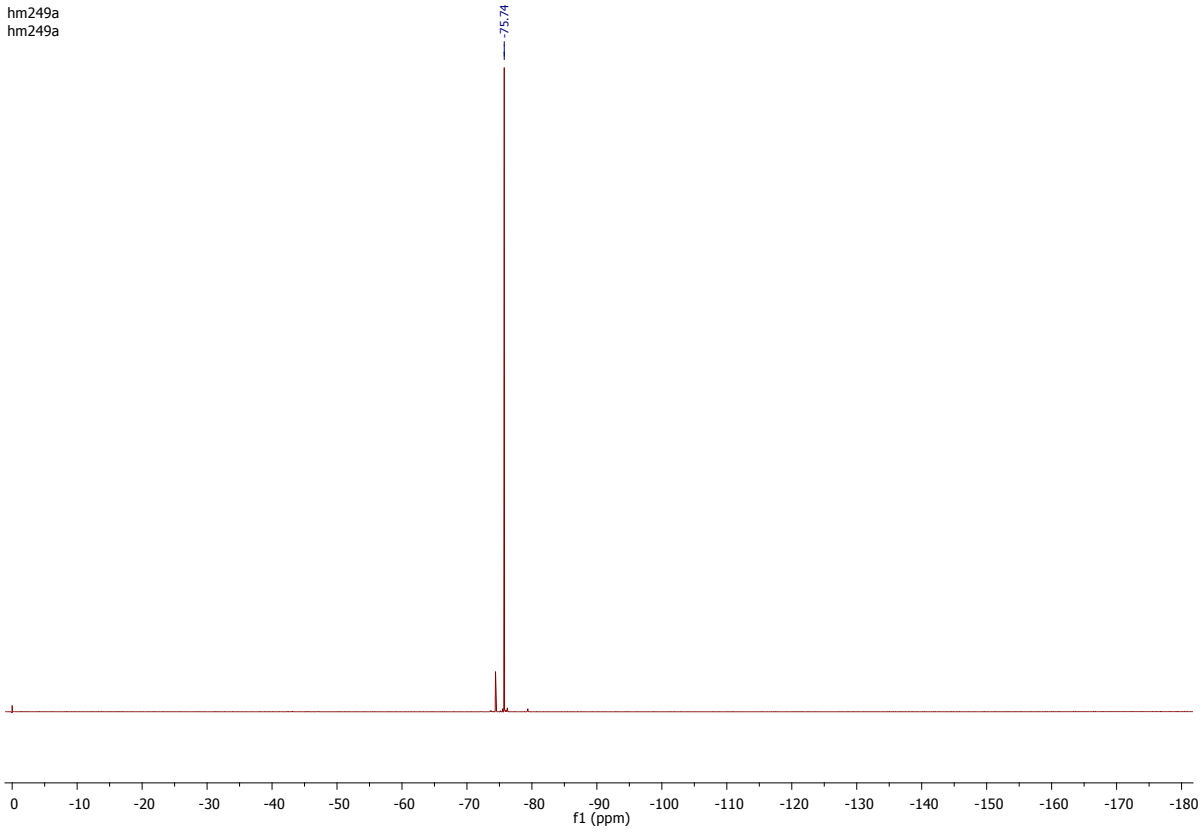

-72.29
f1 (ppm)


H3CO
SOCF3

2e


hm249a
hm249a
7.71
7.70
7.26
7.08
7.06
3.86
2.01
2.09
3.00
f1 (ppm)


hm249a
hm249a
164.11
128.16
126.19
126.10
123.44
115.24
77.42
77.17
76.91
55.71
f1 (ppm)


hm249a
hm249a
-75.74
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
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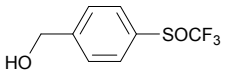
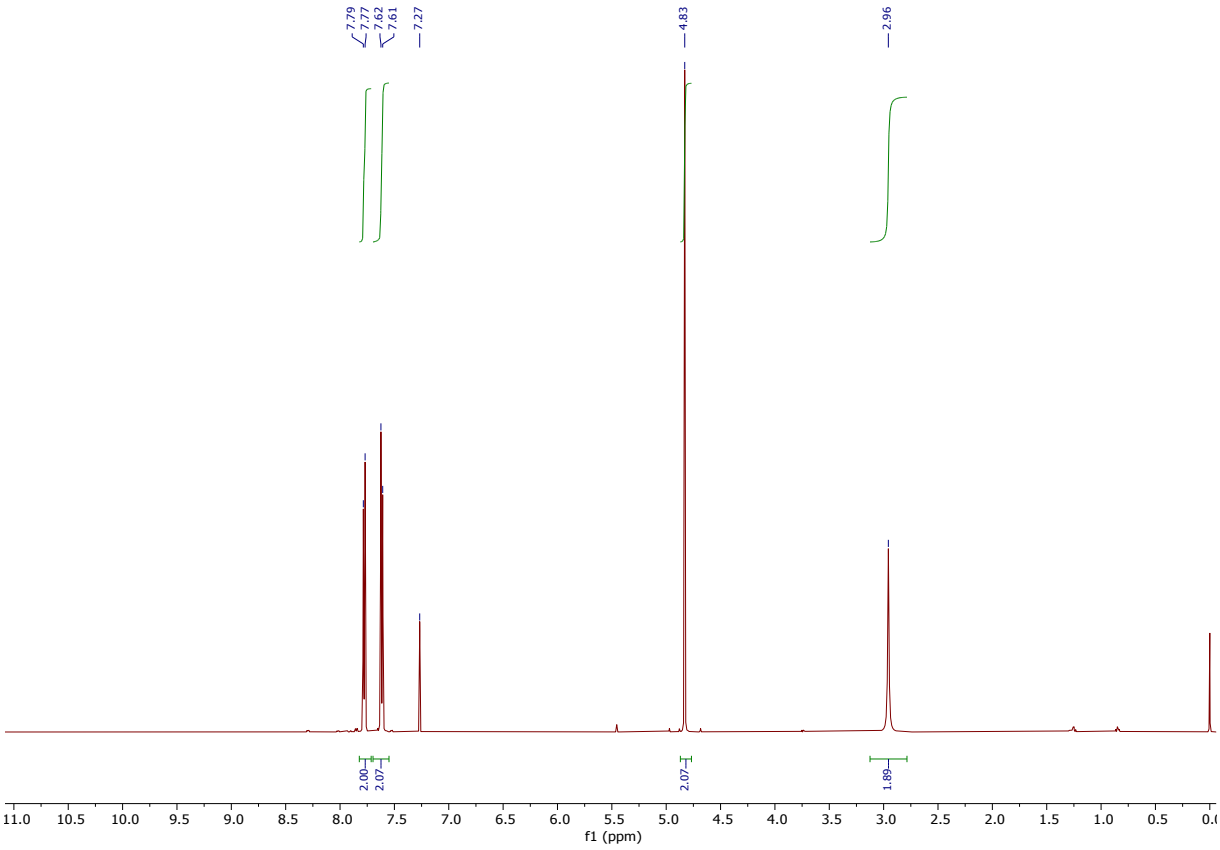
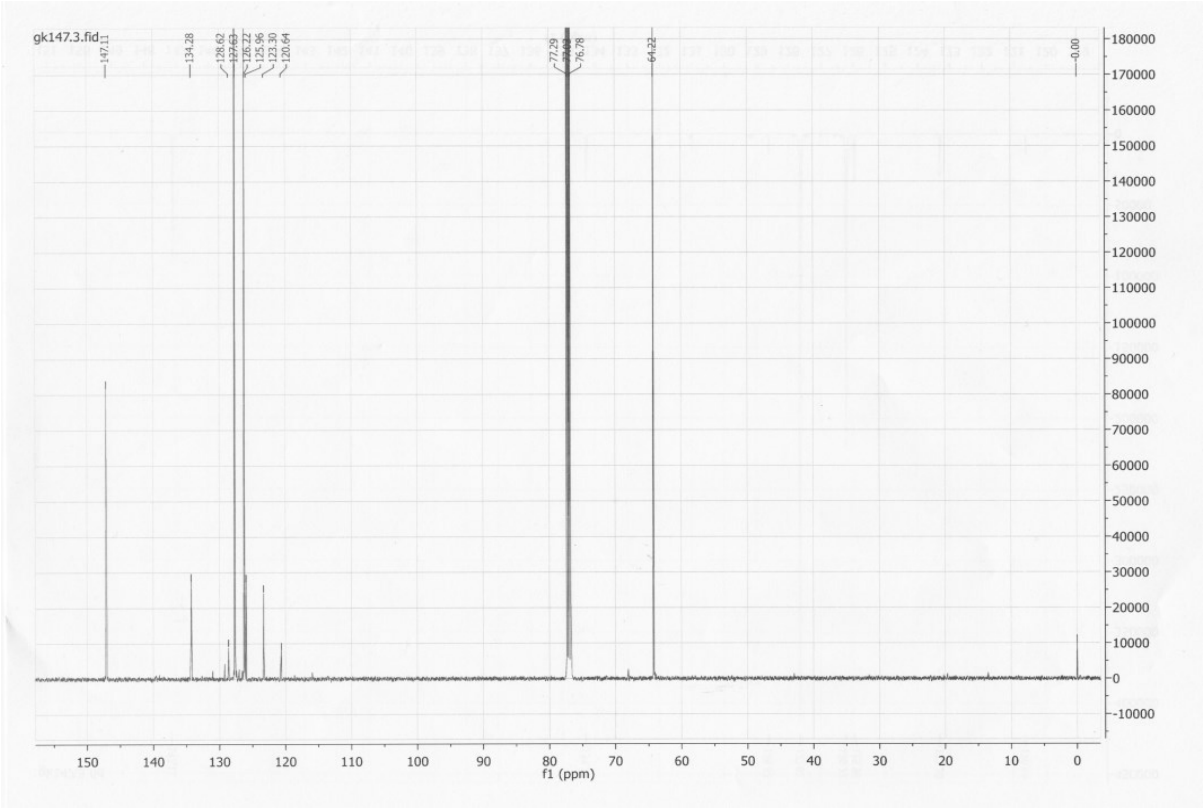
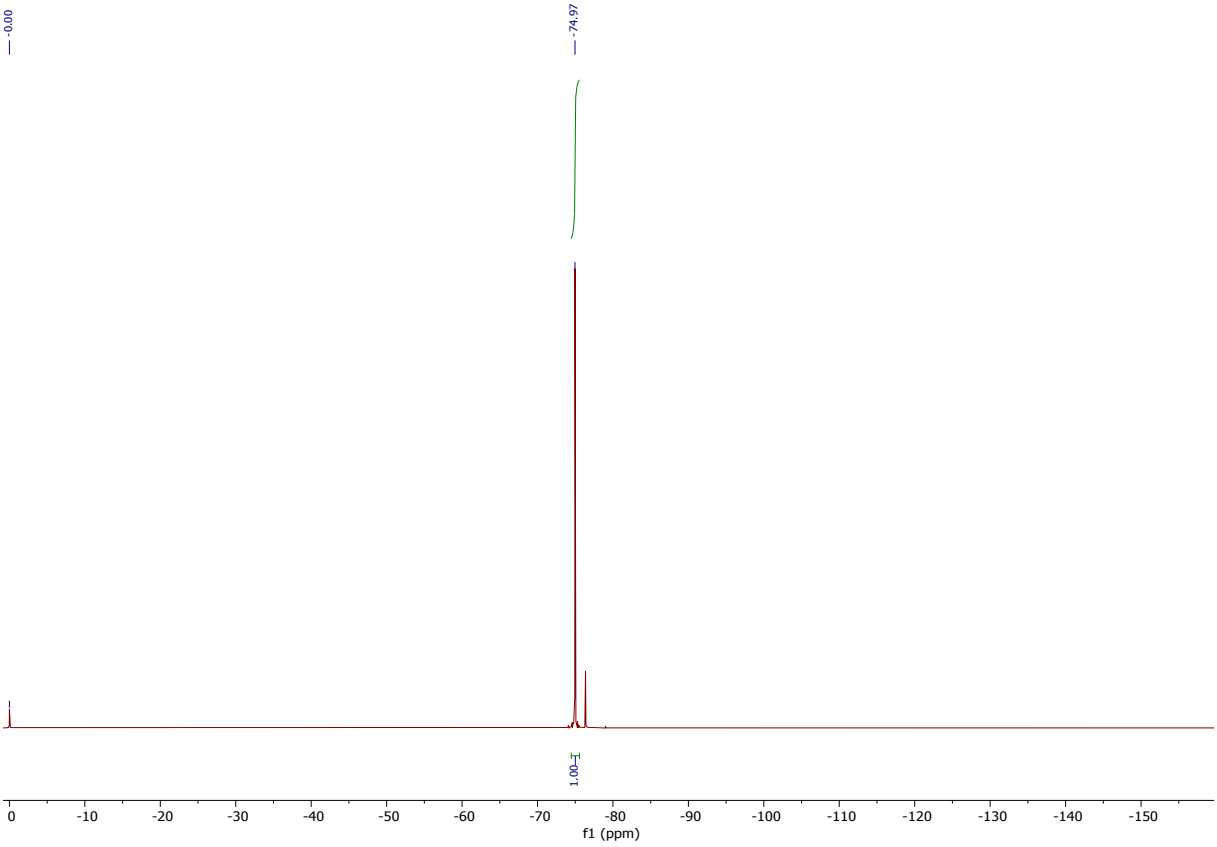
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

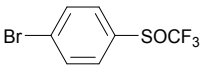

HO
SOCF3

2f

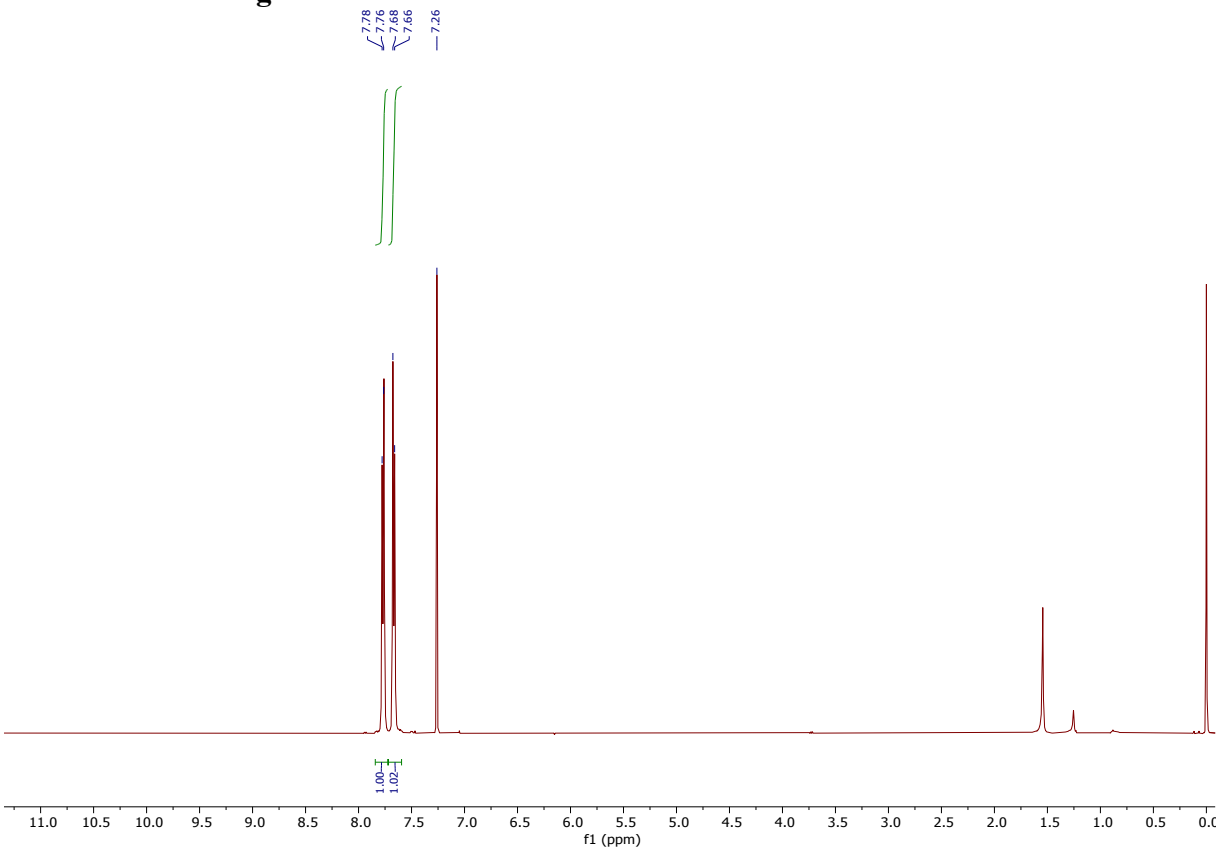

7.79
7.77
7.62
7.61
7.27
4.83
2.96
2.00
2.07
2.07
1.89
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

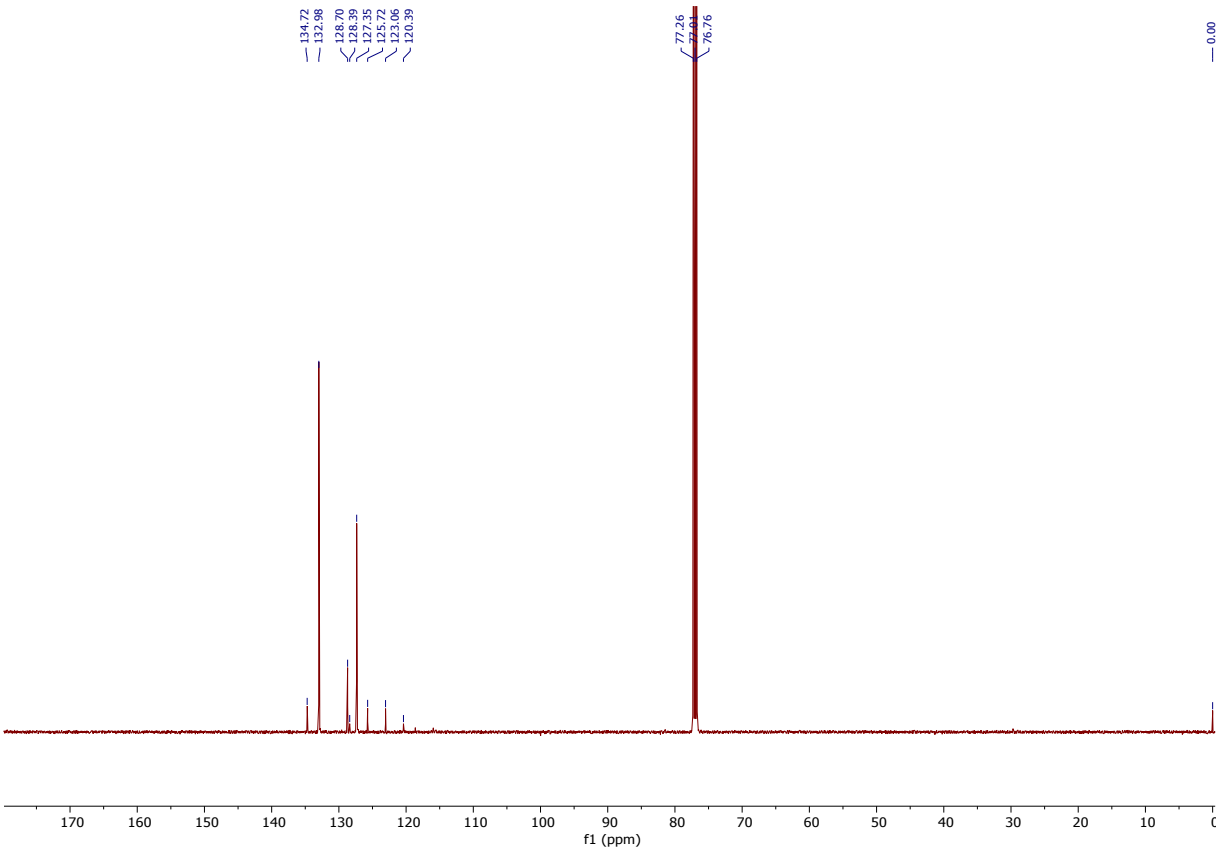

gk147.3.fid
147.11
134.28
128.62
127.67
126.27
125.96
123.30
120.64
77.29
77.03
76.78
64.22
0.00
f1 (ppm)

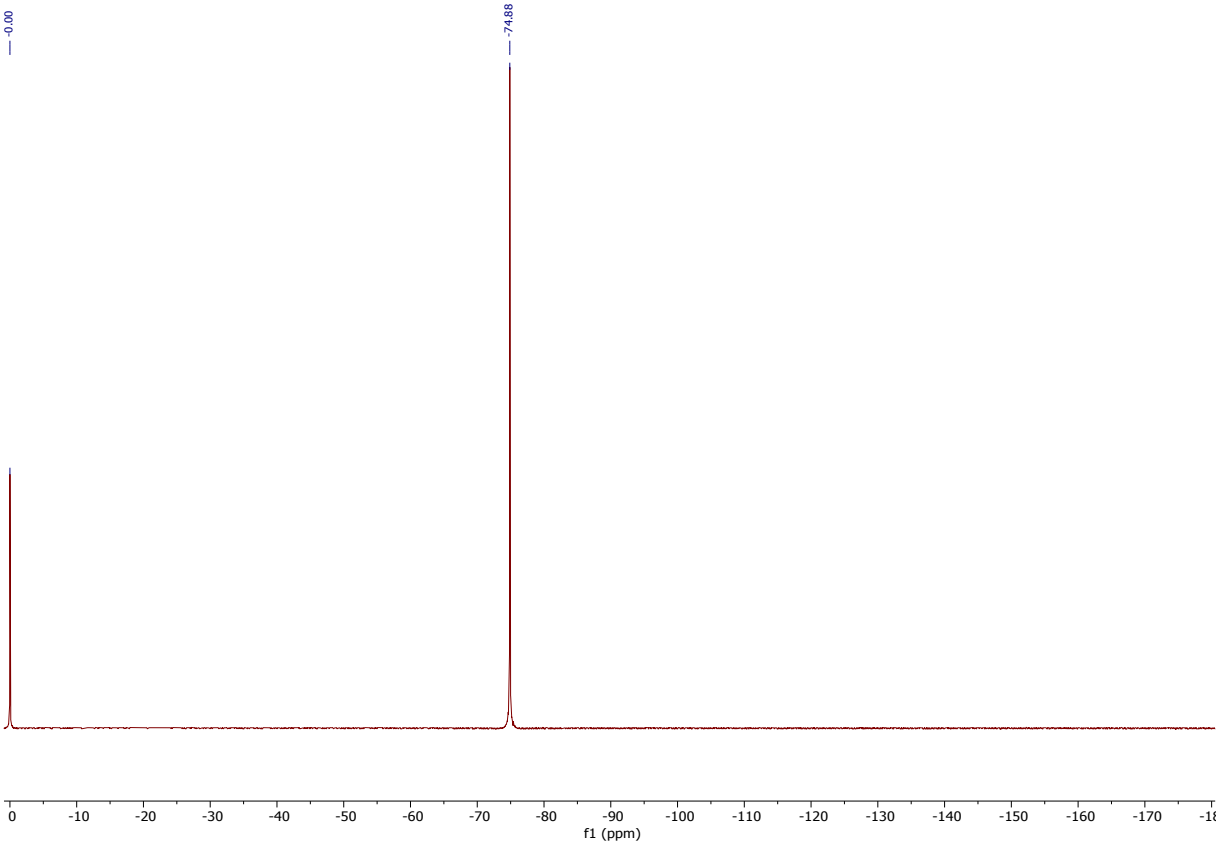

-0.00
-74.97
1.00
f1 (ppm)

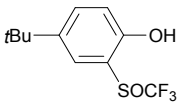

Br
SOCF3

2g

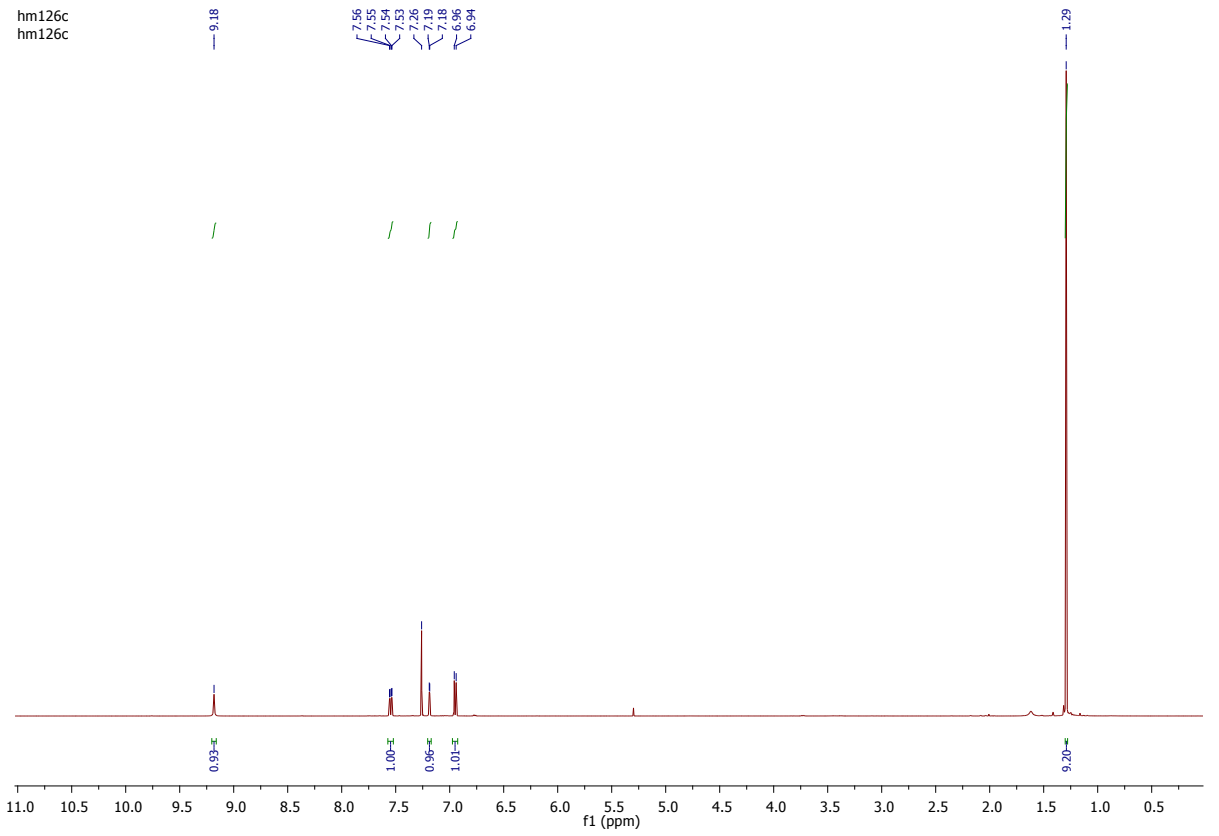

7.78
7.76
7.68
7.66
7.26
1.00
1.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

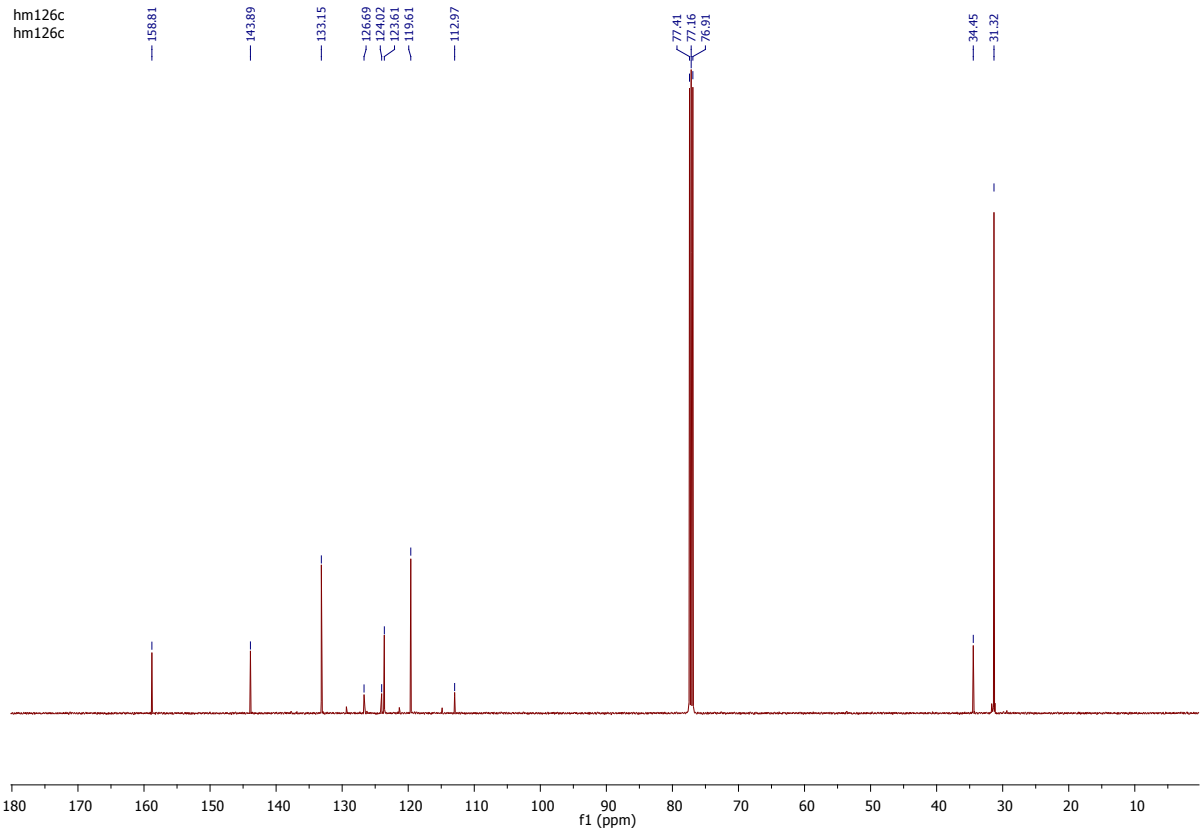

134.72
132.98
128.70
128.39
127.35
125.72
123.06
120.39
77.26
77.01
76.76
0.00
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

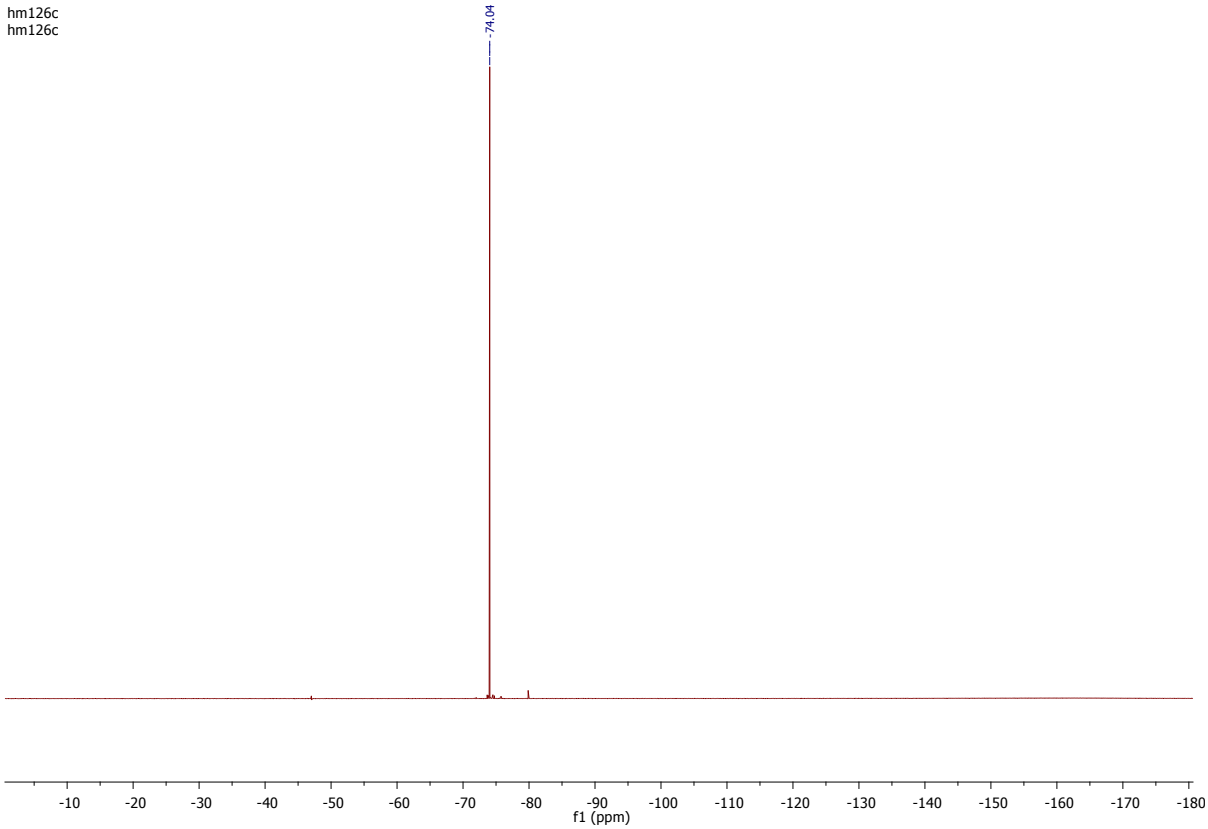

-0.00
-74.88
f1 (ppm)

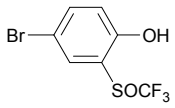

tBu
OH
SOCF3

2h

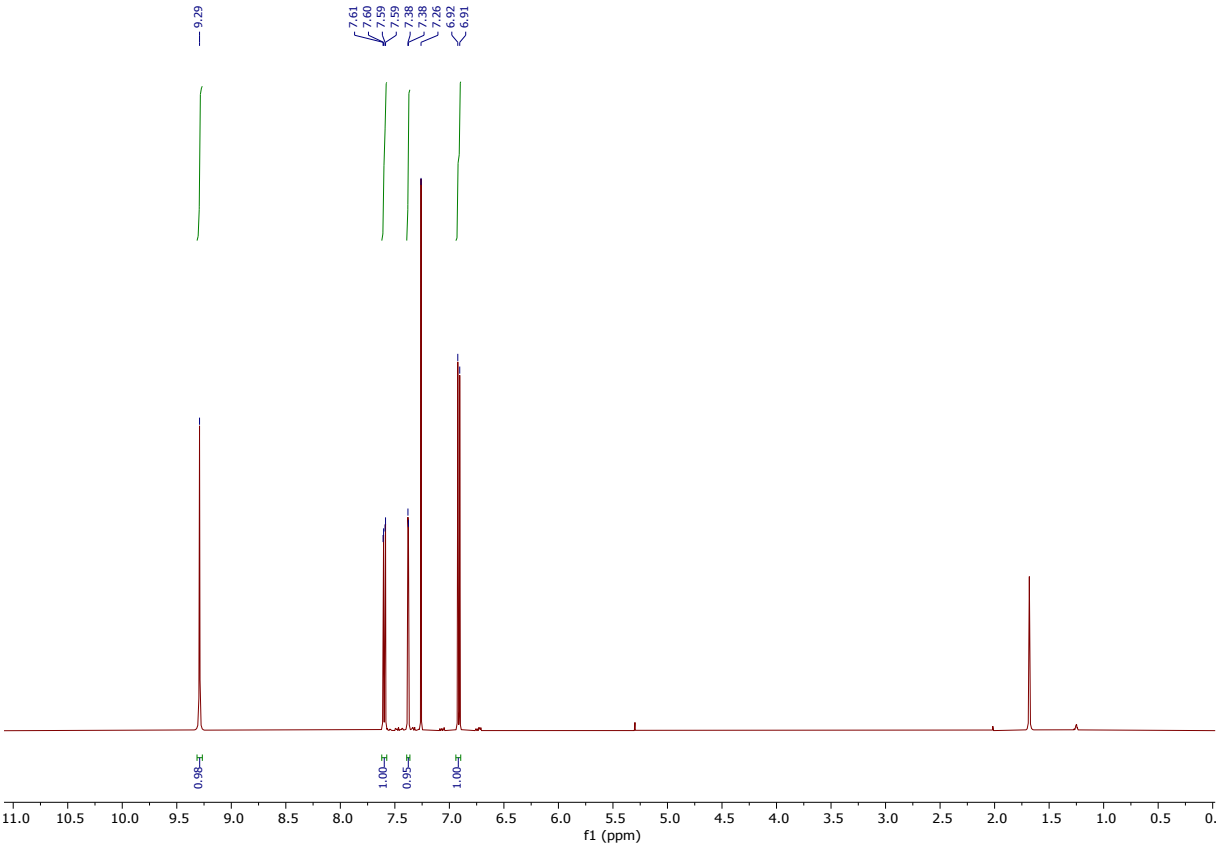

hm126c
hm126c
9.18
7.56
7.55
7.54
7.53
7.26
7.19
7.18
6.96
6.94
1.29
0.93
1.00
0.96
1.01
9.20
f1 (ppm)

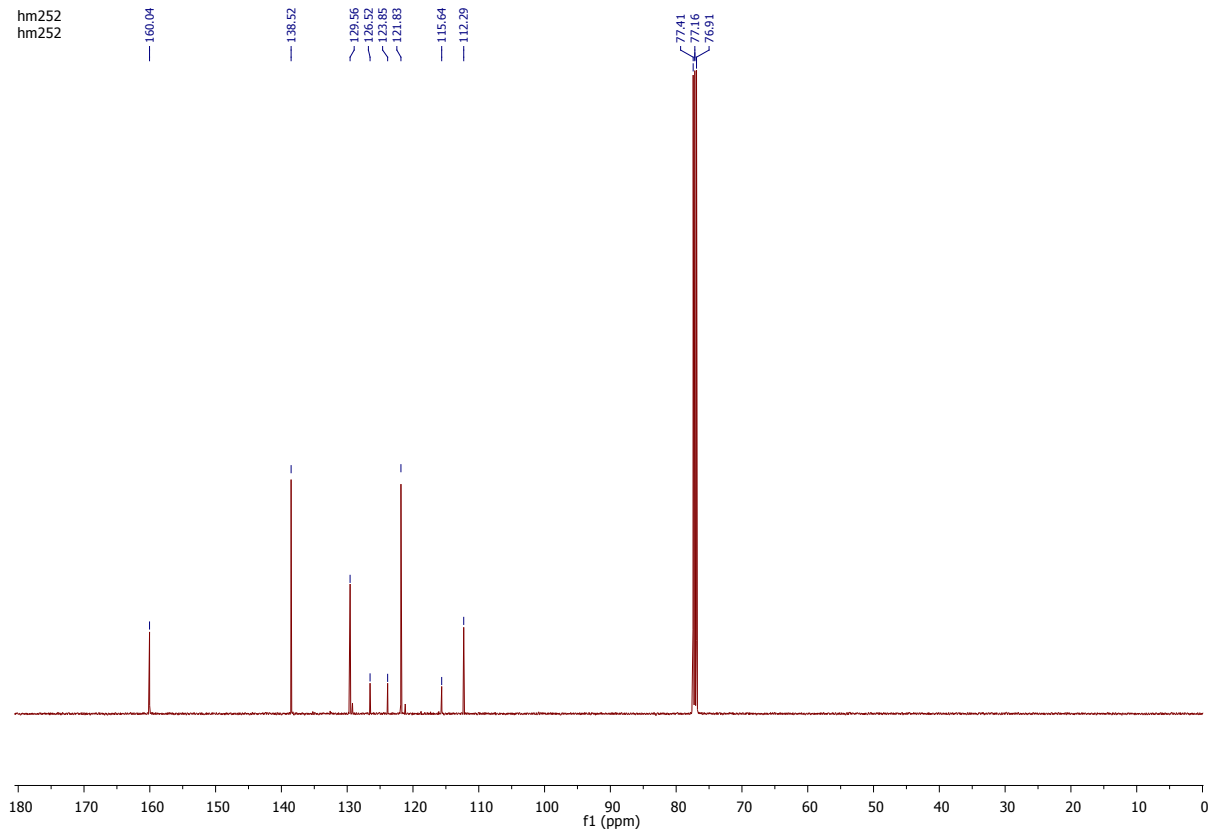

hm126c
hm126c
158.81
143.89
133.15
126.69
124.02
123.61
119.61
112.97
77.41
77.16
76.91
34.45
31.32
f1 (ppm)

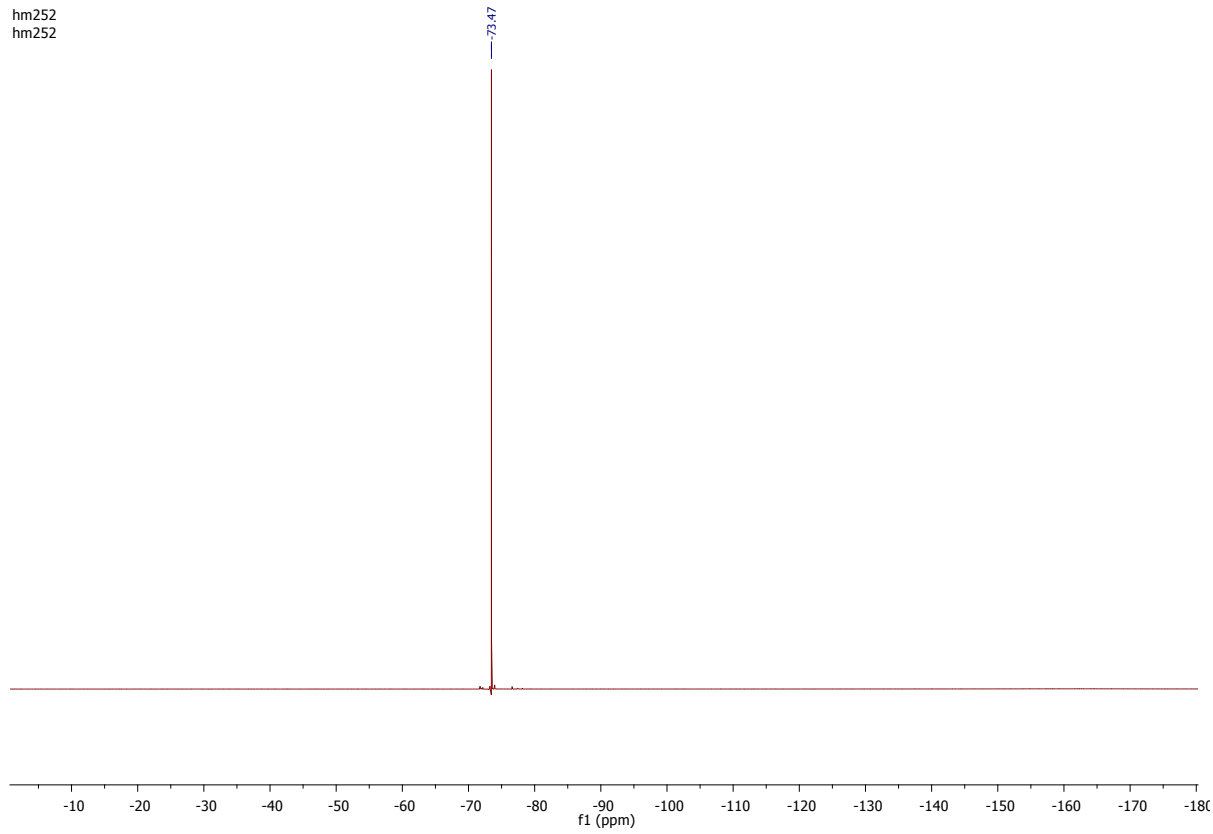

hm126c
hm126c
-74.04
f1 (ppm)

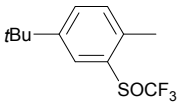

Br
OH
SOCF3

2i

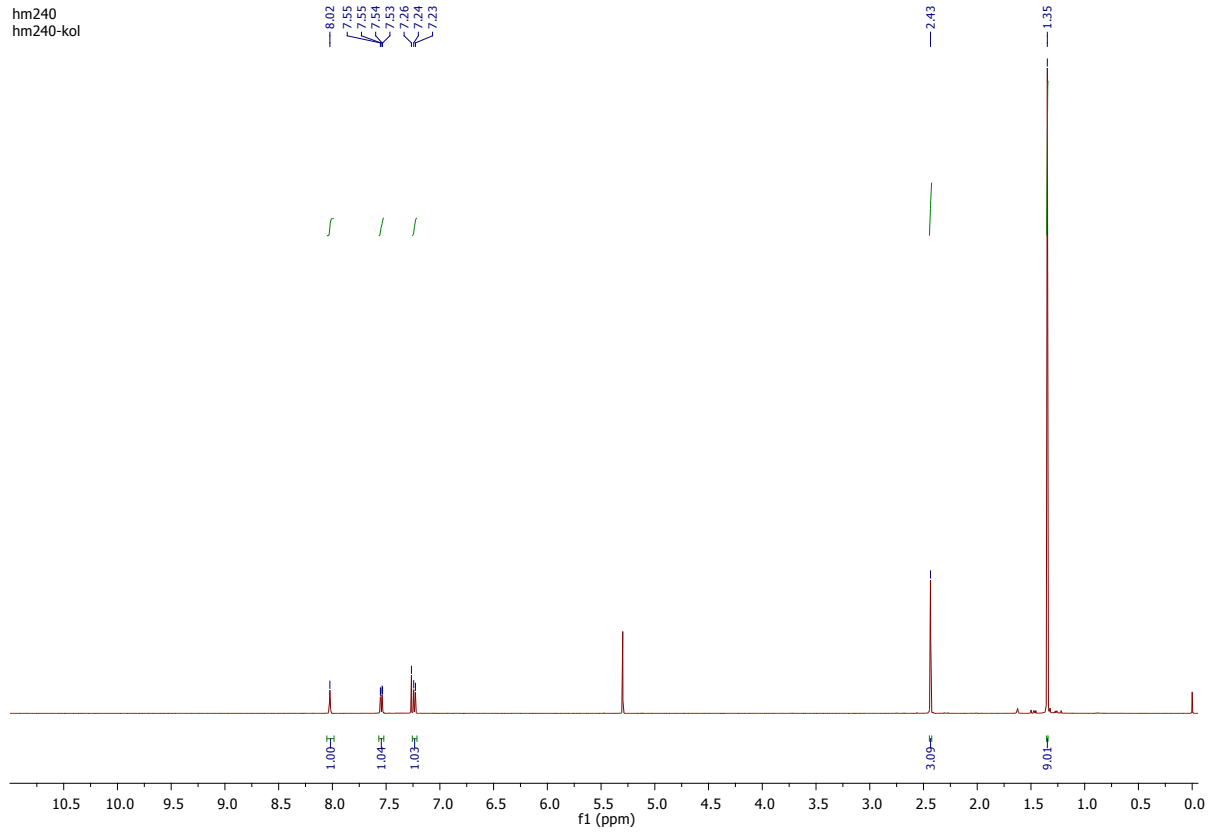

9.29
7.61
7.60
7.59
7.59
7.38
7.38
7.26
6.92
6.91
0.98
1.00
0.95
1.00
f1 (ppm)

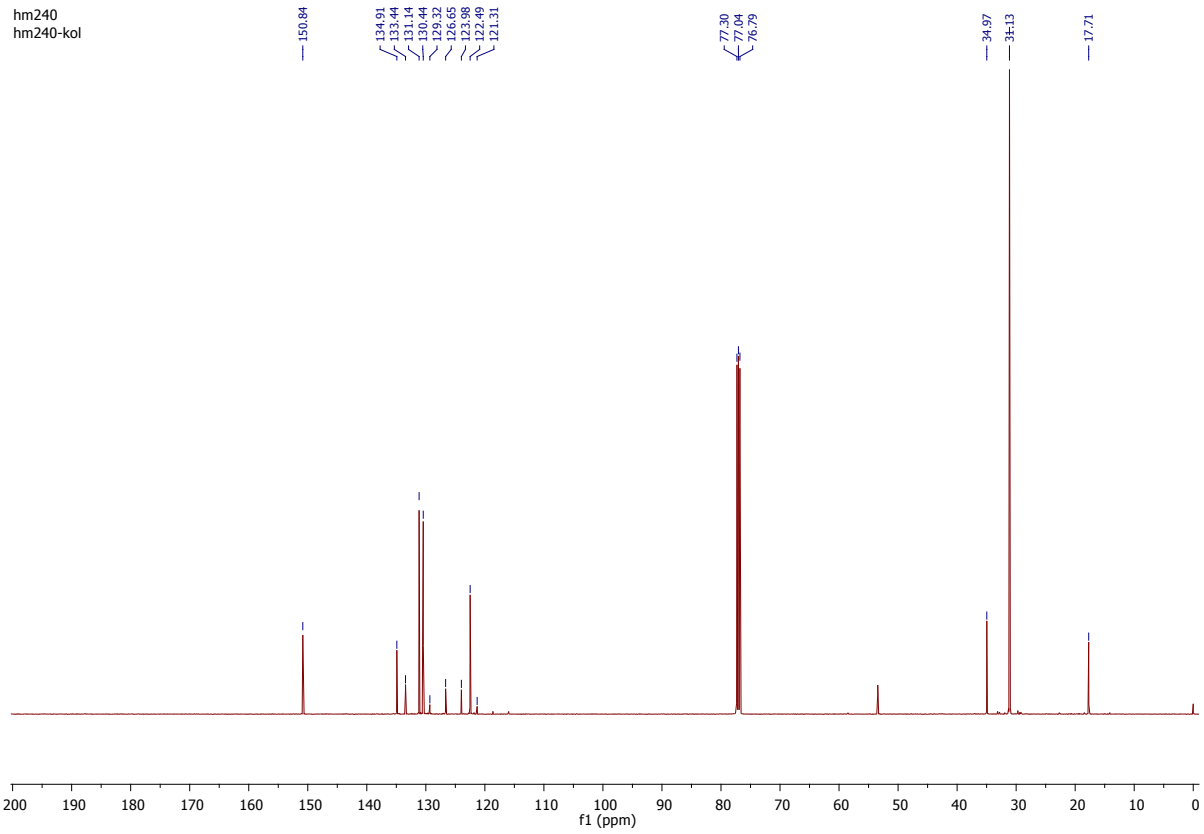

hm252
hm252
160.04
138.52
129.56
126.52
123.85
121.83
115.64
112.29
77.41
77.16
76.91
f1 (ppm)

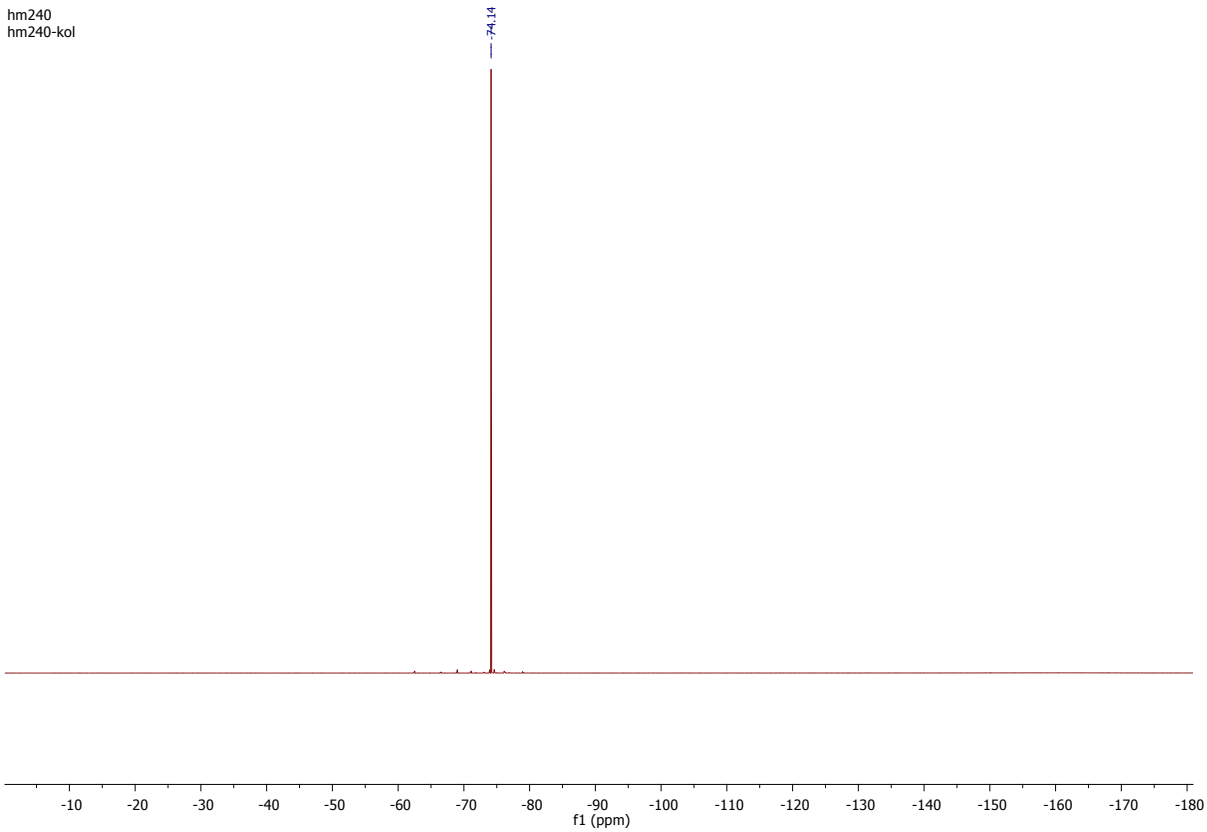

hm252
hm252
-73.47
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

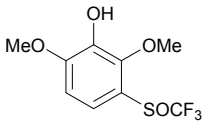

tBu
SOCF3

2j

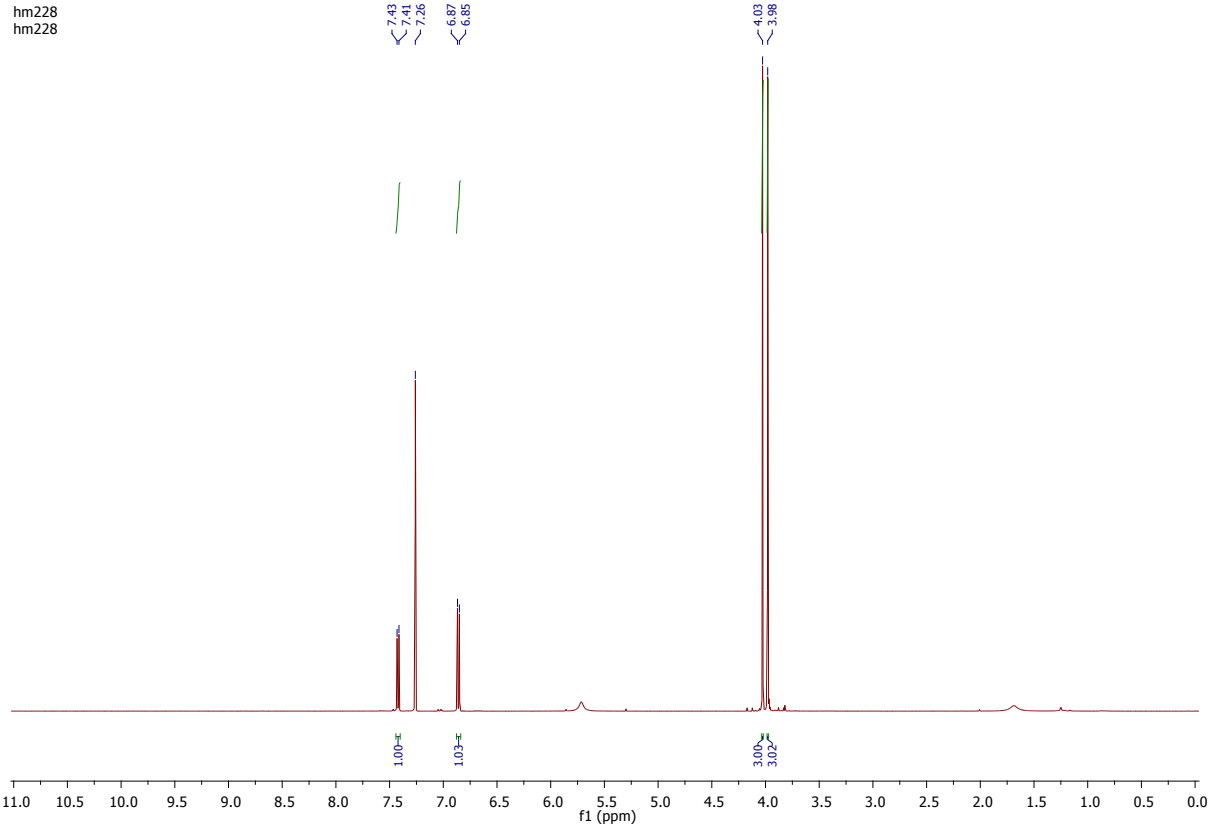

hm240
hm240-kol
8.02
7.55
7.55
7.54
7.53
7.26
7.24
7.23
2.43
1.35
1.00
1.04
1.03
3.09
9.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

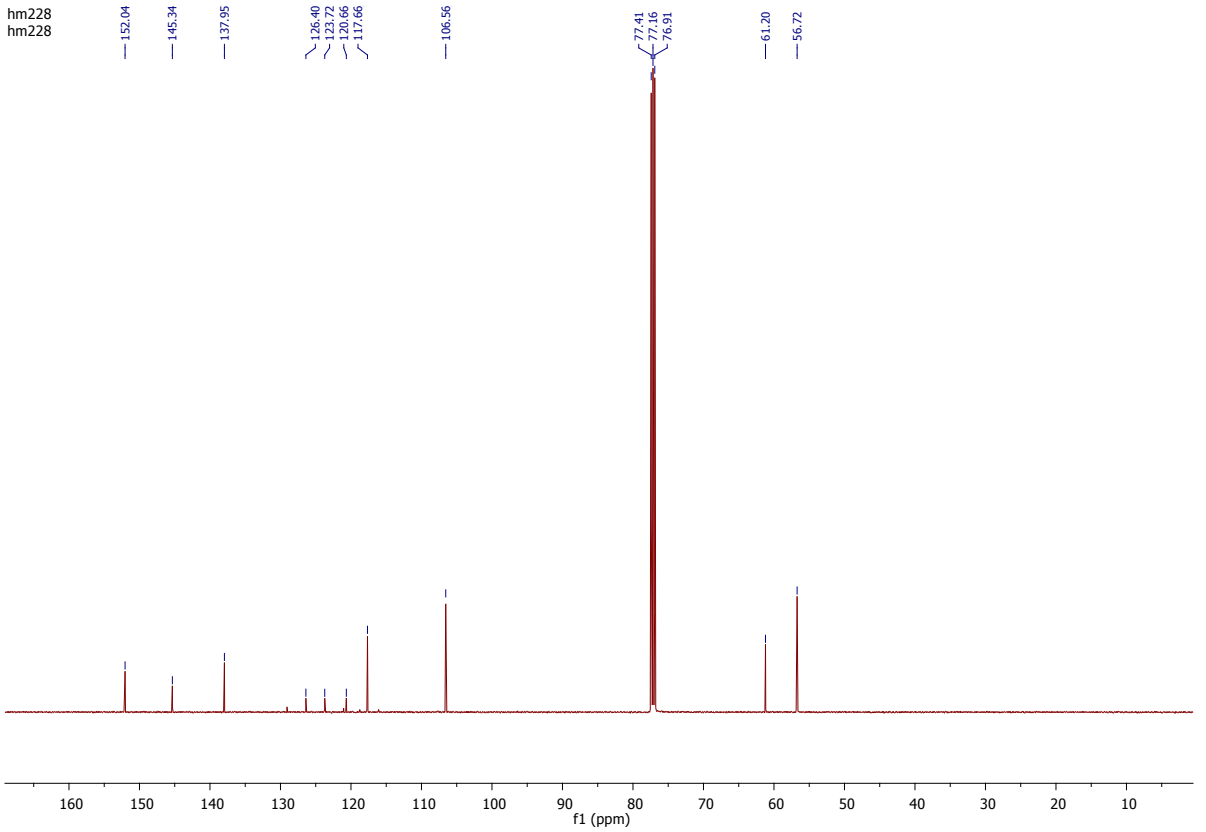

hm240
hm240-kol
150.84
134.91
133.44
131.14
130.44
129.32
126.65
123.98
122.49
121.31
77.30
77.04
76.79
34.97
31.13
17.71
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

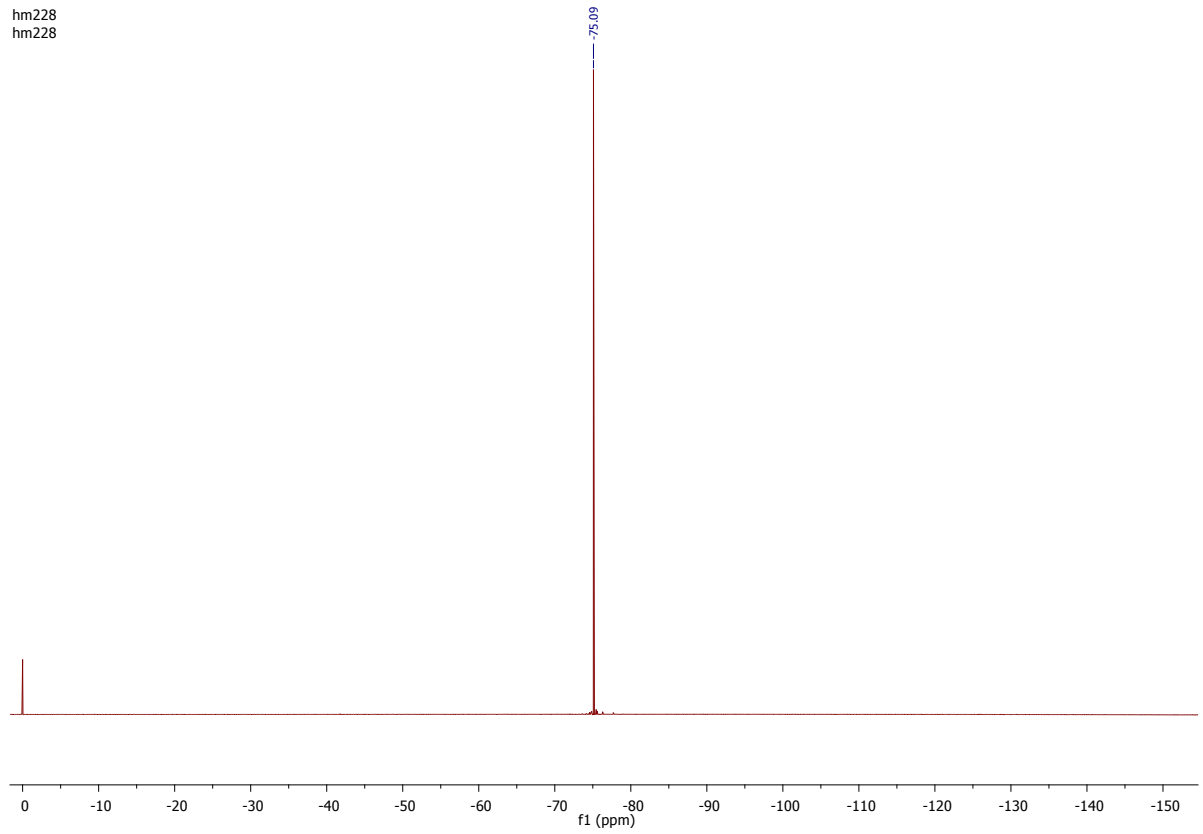

hm240
hm240-kol
-74.14
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

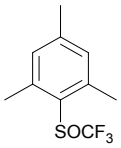

OH
MeO
OMe
SOCF3

2k

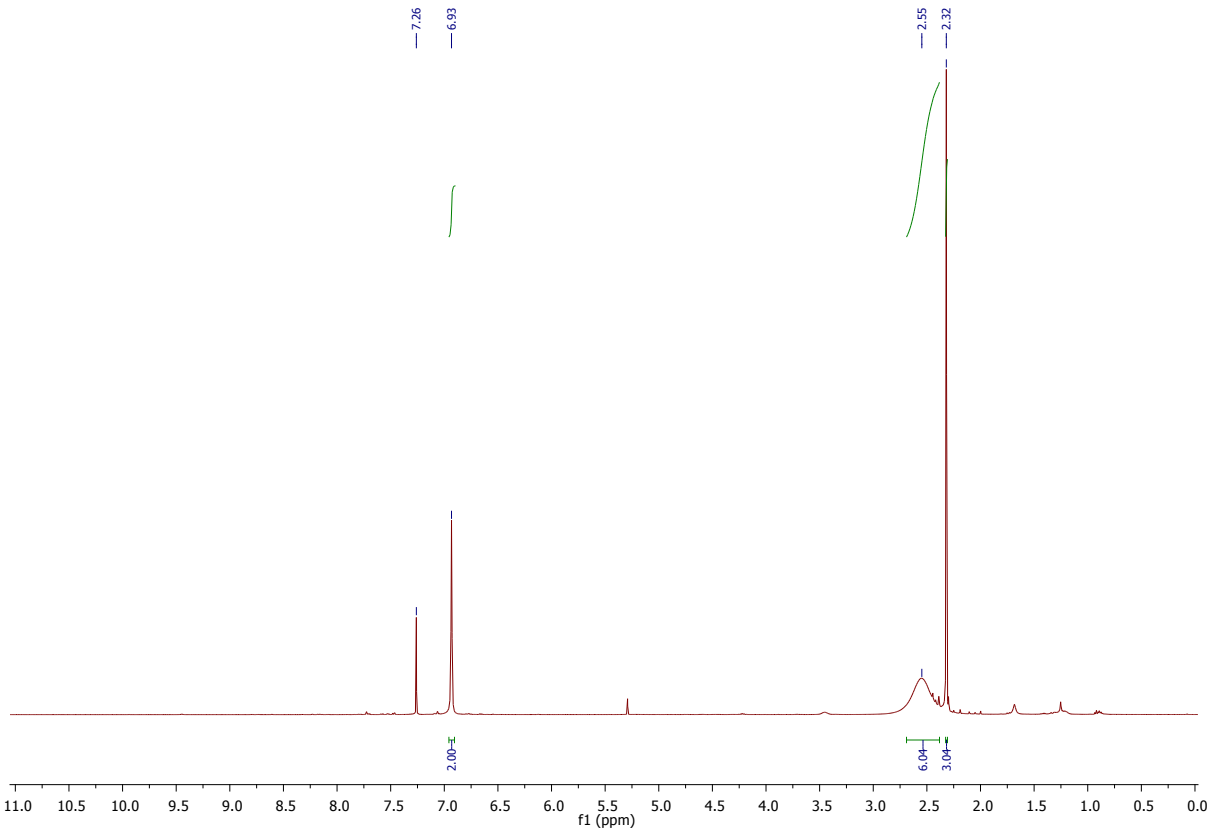

hm228
hm228
7.43
7.41
7.26
6.87
6.85
4.03
3.98
1.00
1.03
3.00
3.02
f1 (ppm)

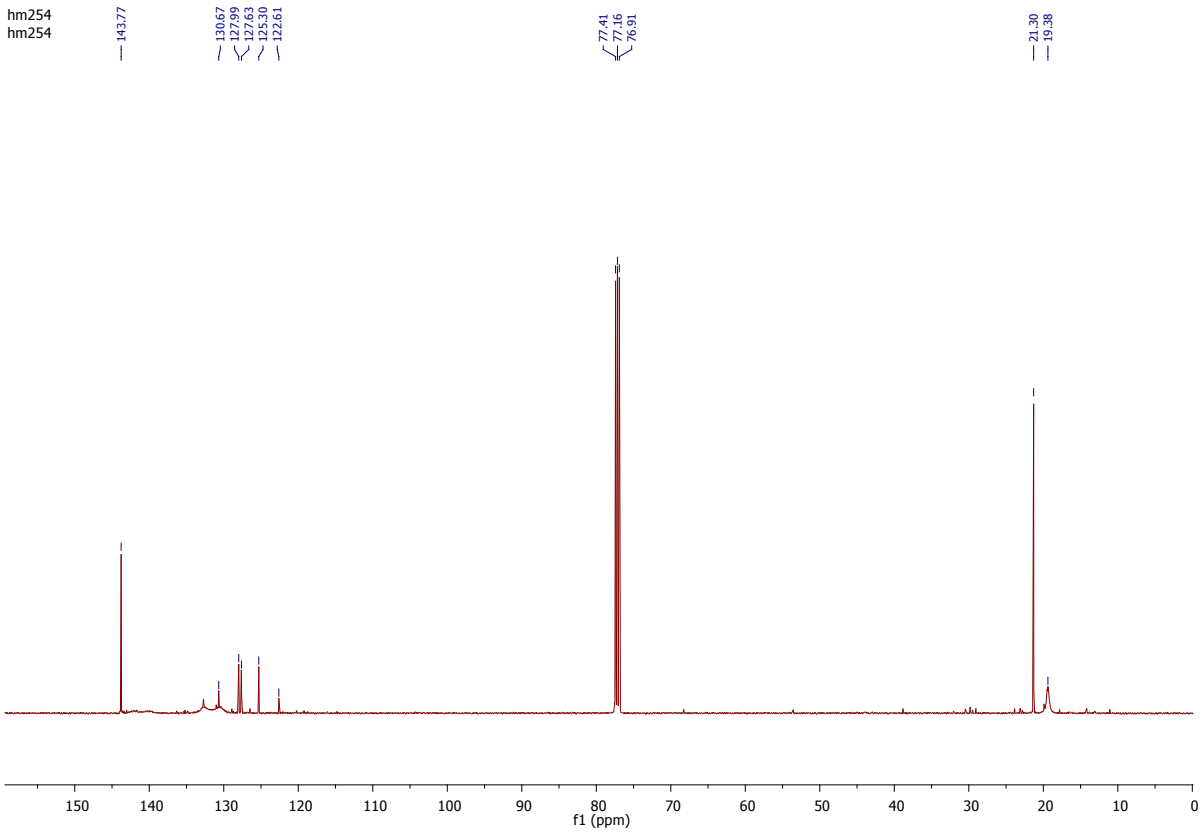

hm228
hm228
152.04
145.34
137.95
126.40
123.72
120.66
117.66
106.56
77.41
77.16
76.91
61.20
56.72
f1 (ppm)

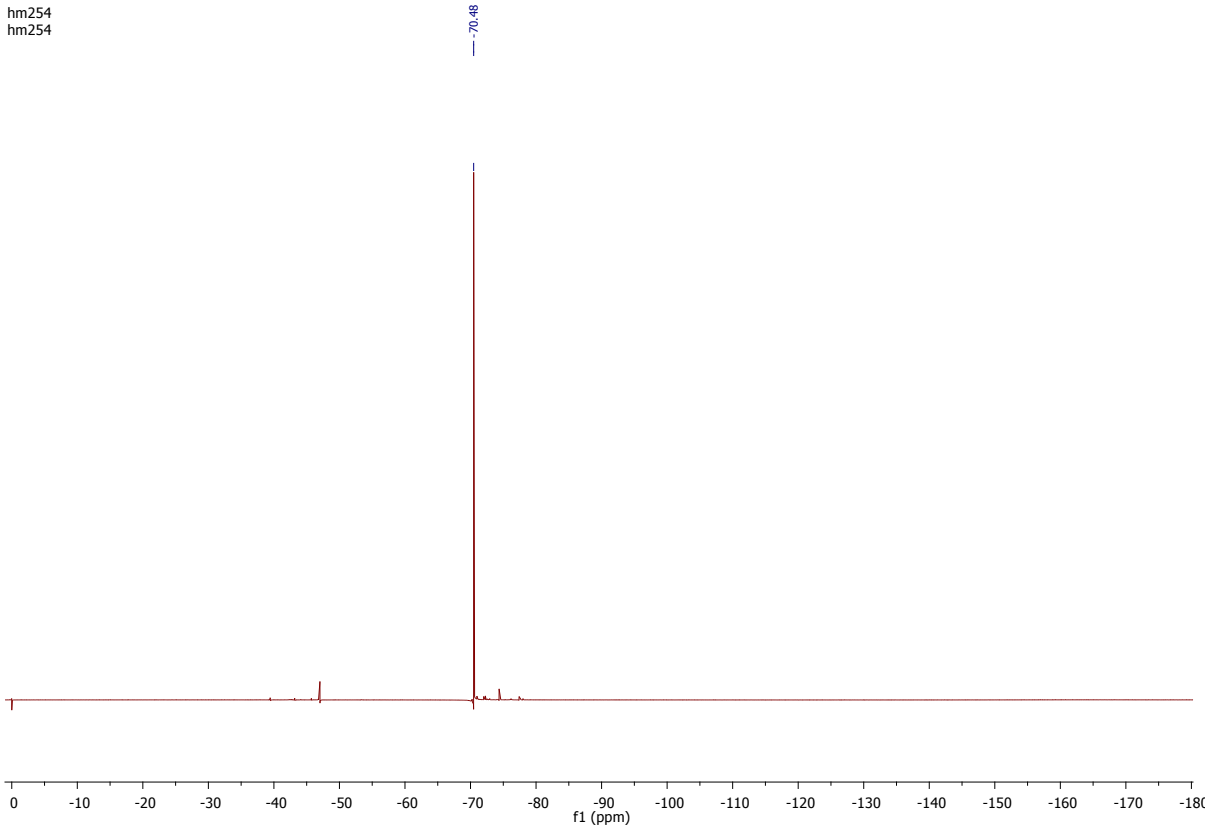

hm228
hm228
-75.09
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

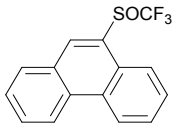

SOCF3

2l


7.26
6.93
2.55
2.32
2.00
6.04
3.04
11.0
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
f1 (ppm)

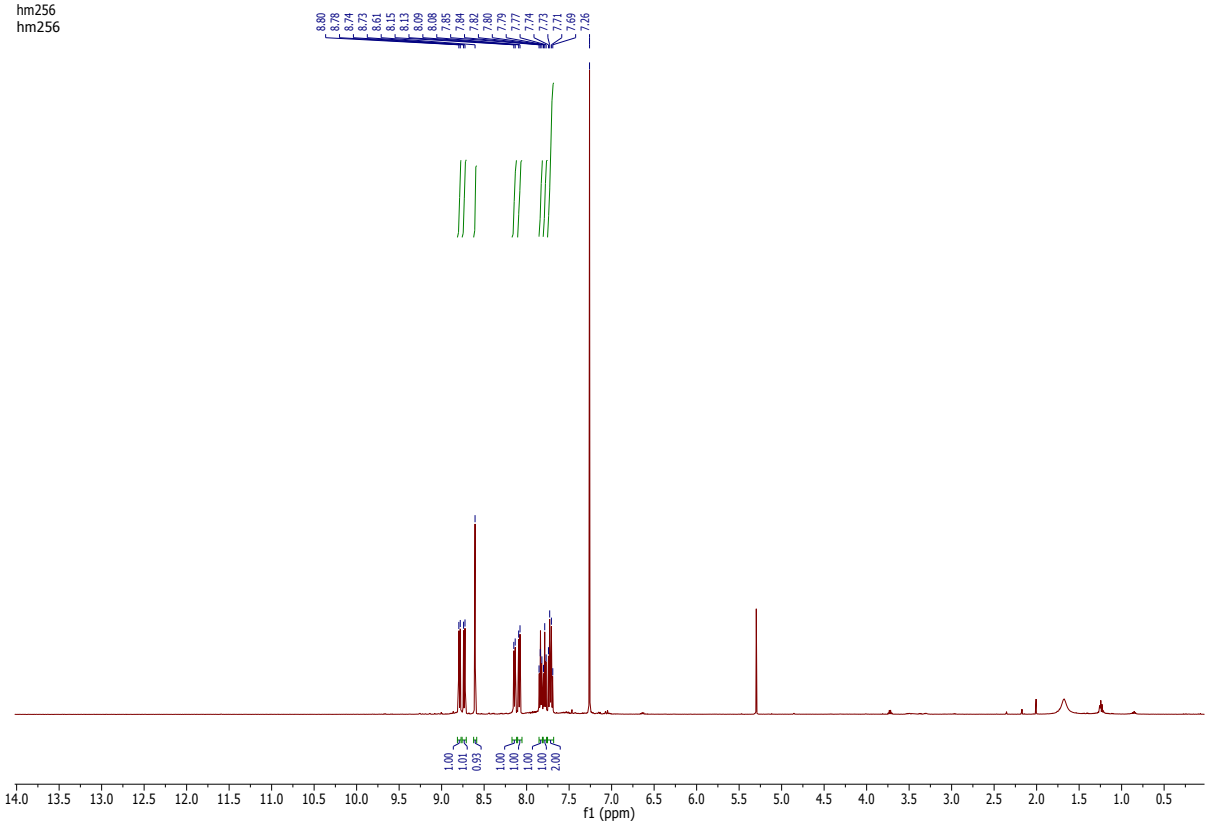

hm254
hm254
143.77
130.67
127.99
127.63
125.30
122.61
77.41
77.16
76.91
21.30
19.38
f1 (ppm)


hm254
hm254
-70.48
f1 (ppm)

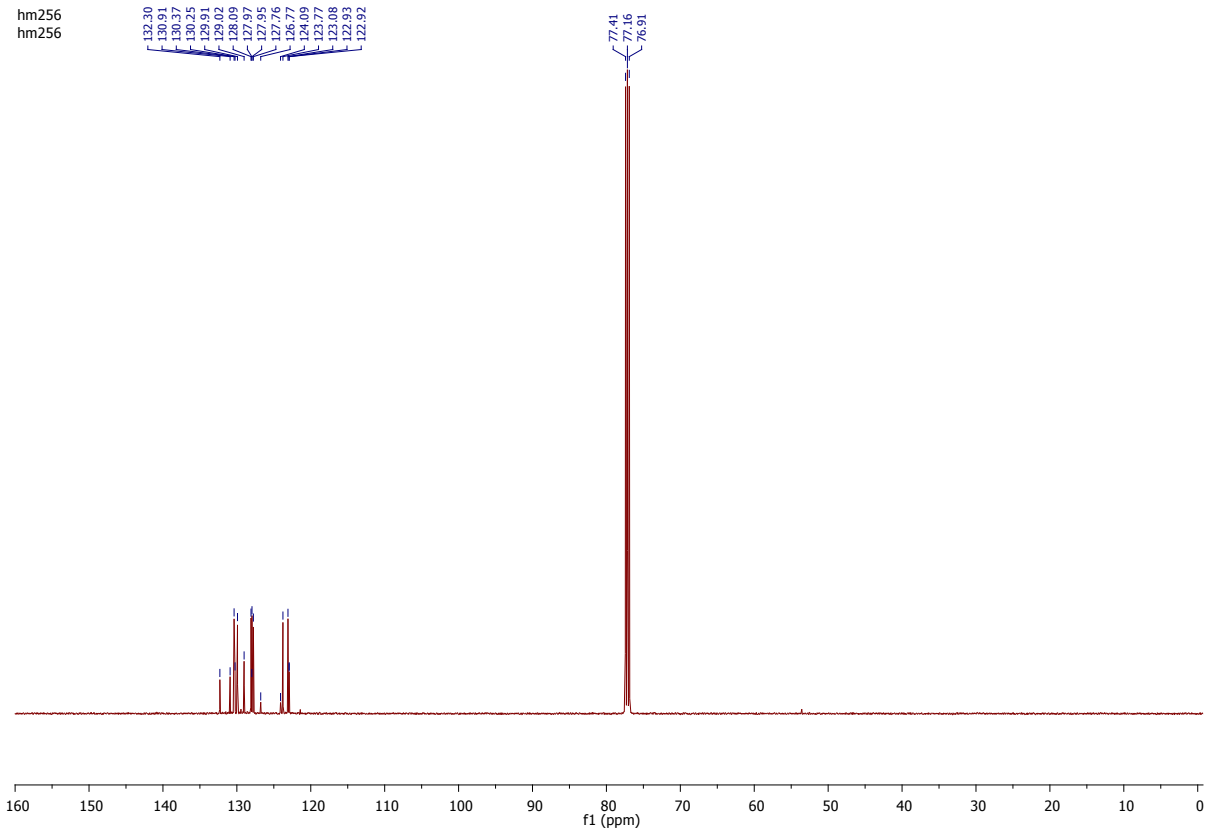


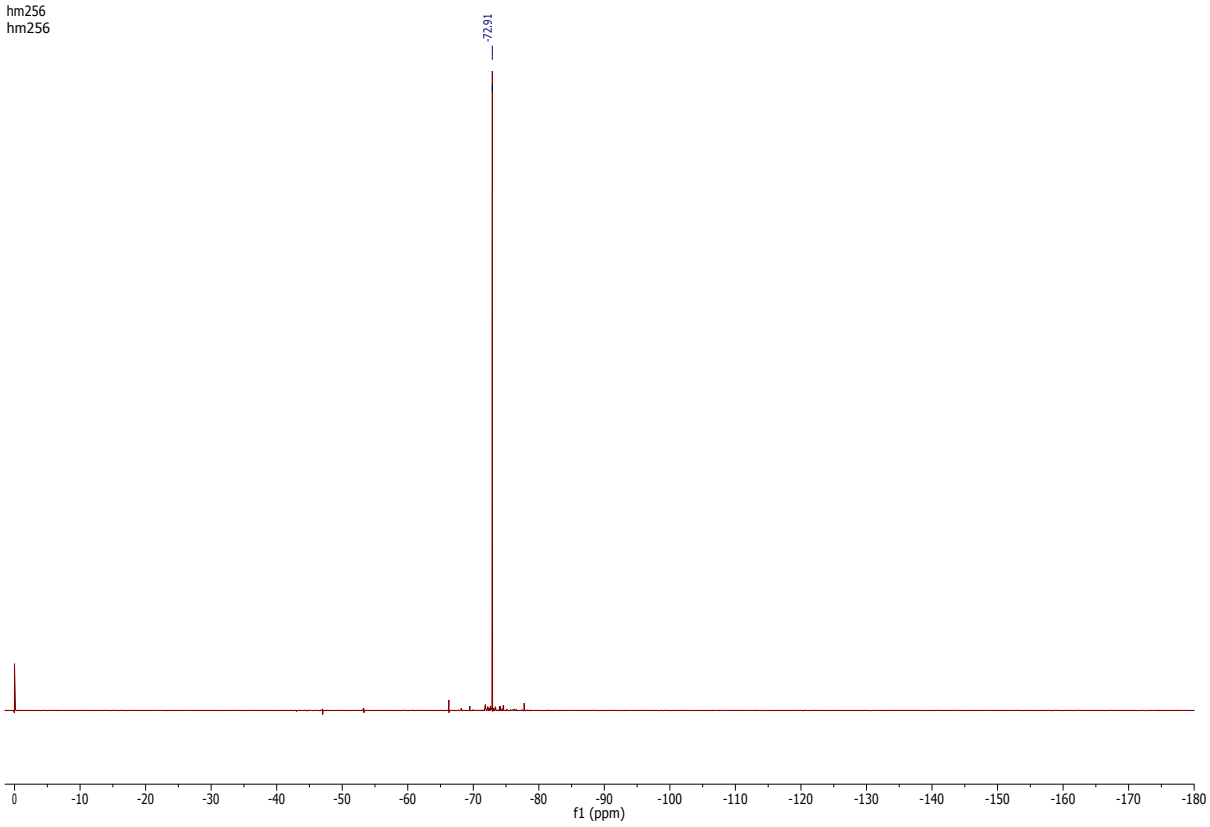
2m

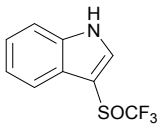
hm256
hm256



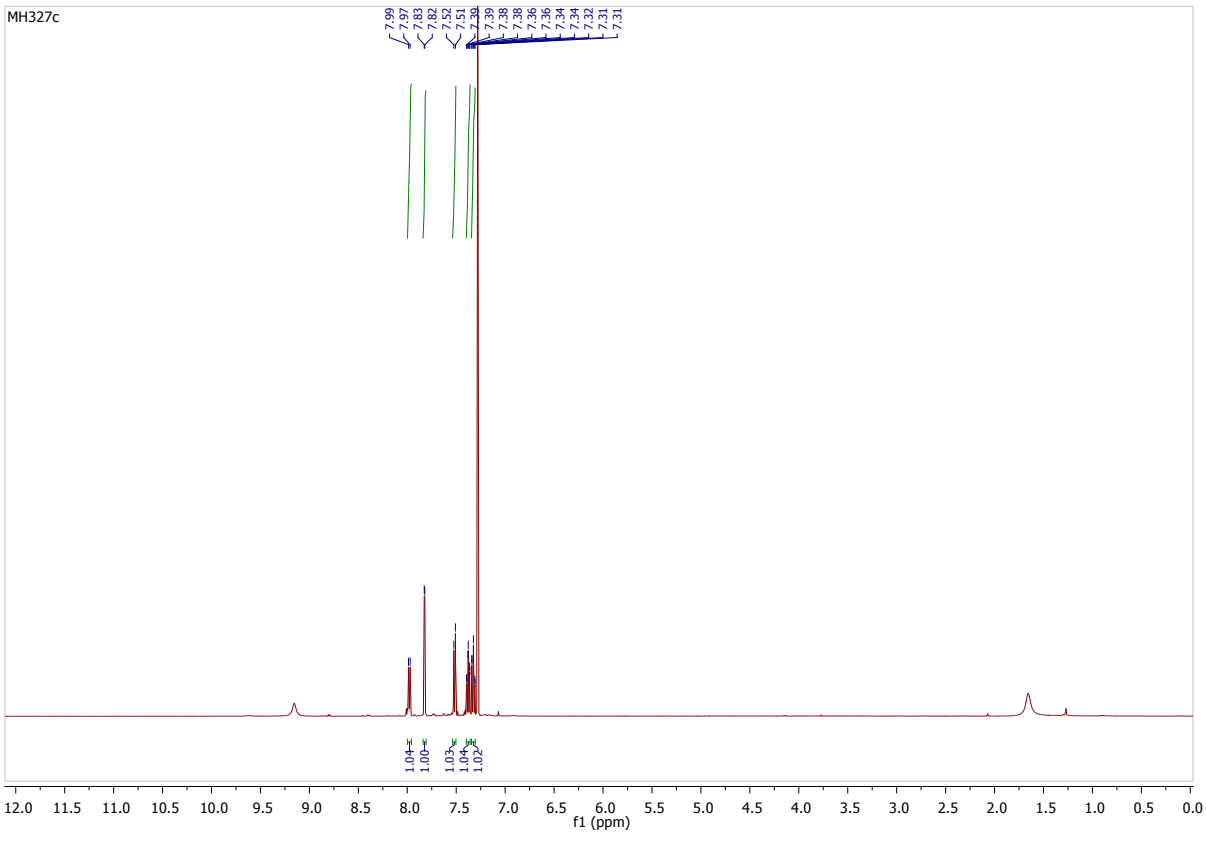
hm256
hm256

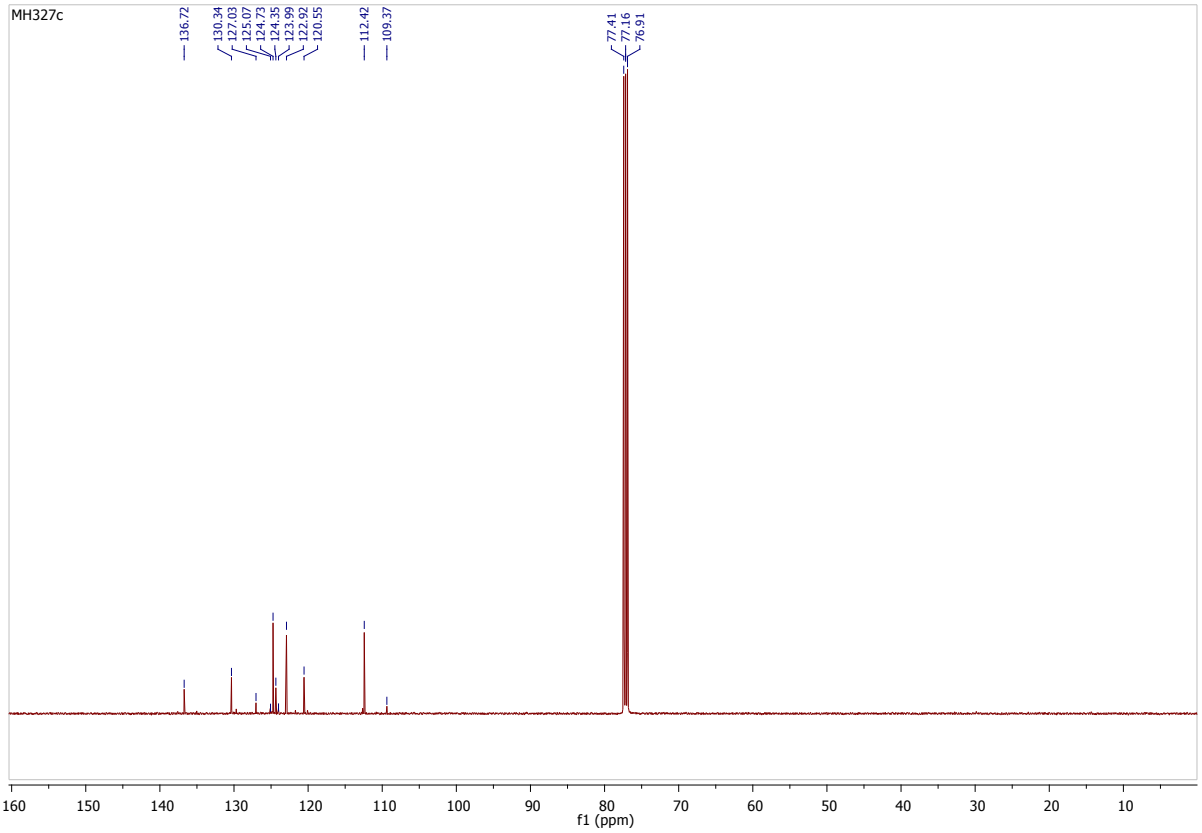


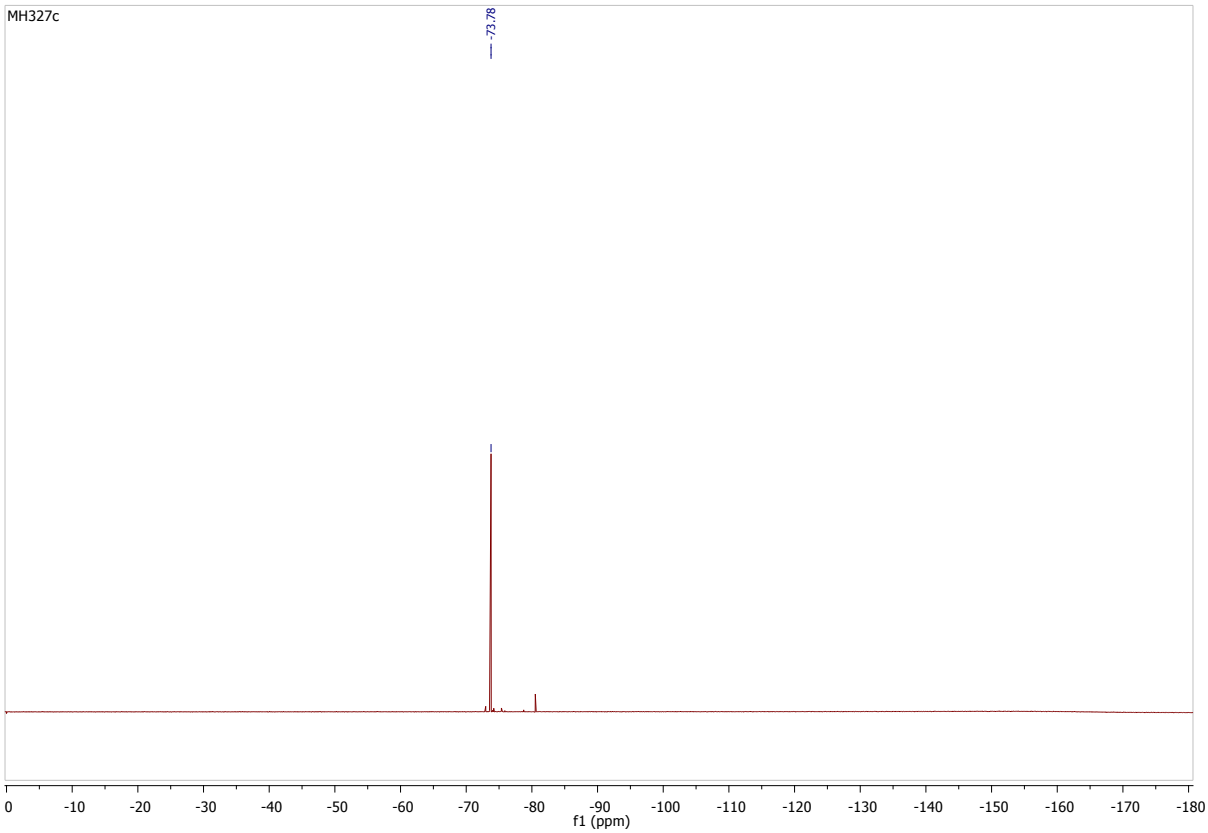

hm256
hm256
-72.91
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

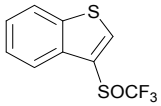

H
N
SOCF3

2n

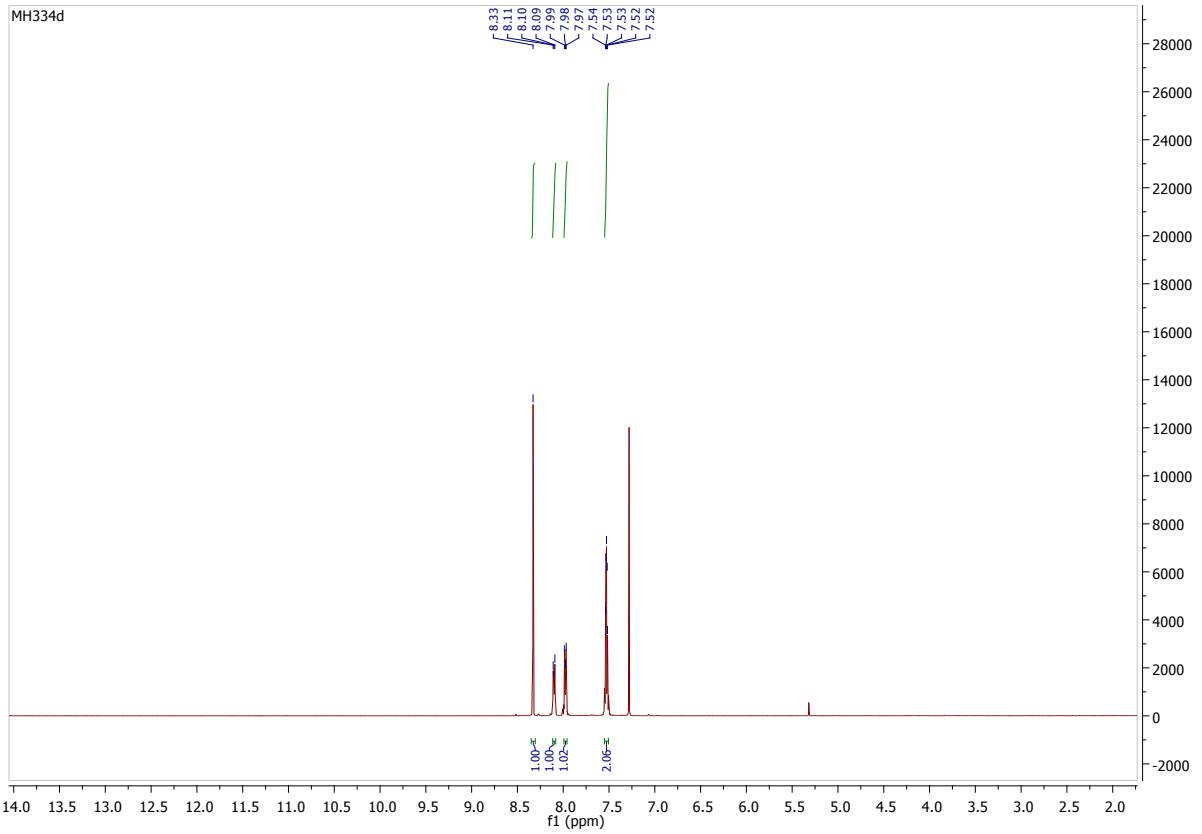

MH327c
7.99
7.97
7.83
7.82
7.52
7.51
7.39
7.39
7.38
7.38
7.36
7.36
7.34
7.34
7.32
7.31
7.31
1.04
1.00
1.03
1.04
1.02
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

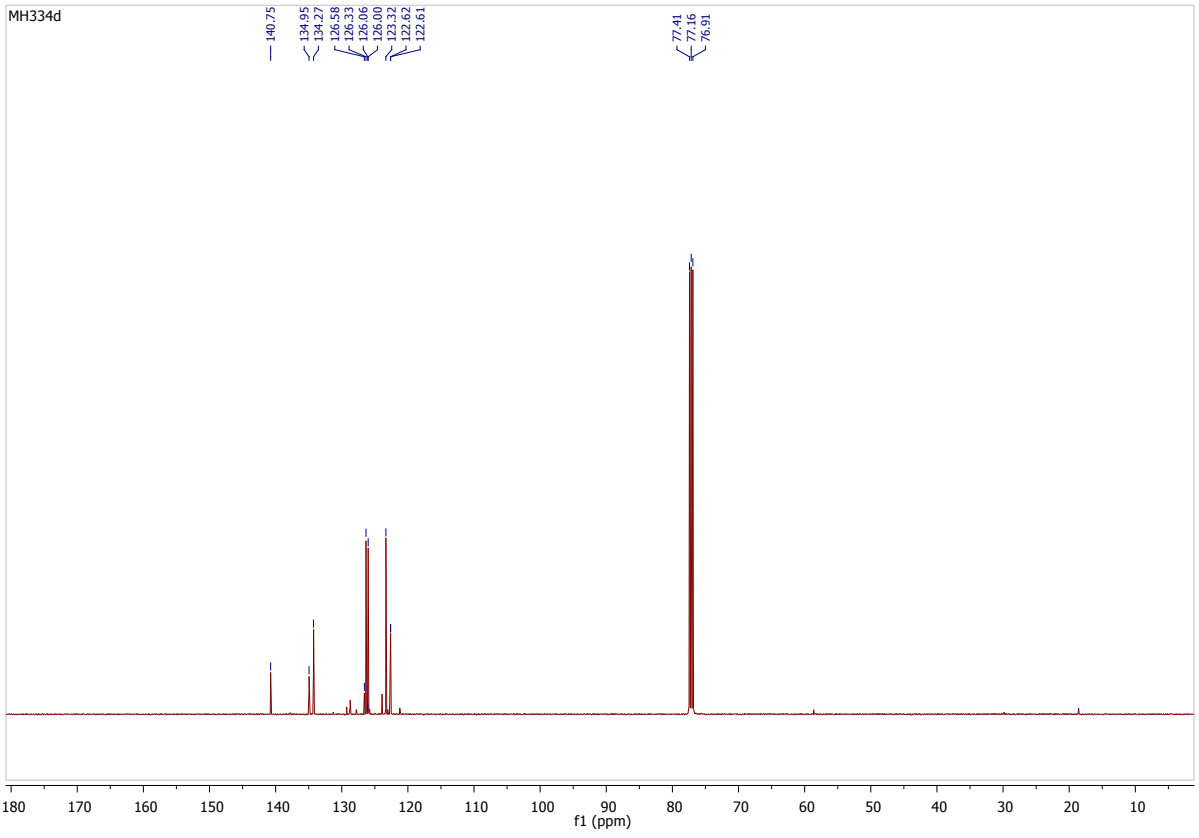

MH327c
136.72
130.34
127.03
125.07
124.73
124.35
123.99
122.92
120.55
112.42
109.37
77.41
77.16
76.91
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

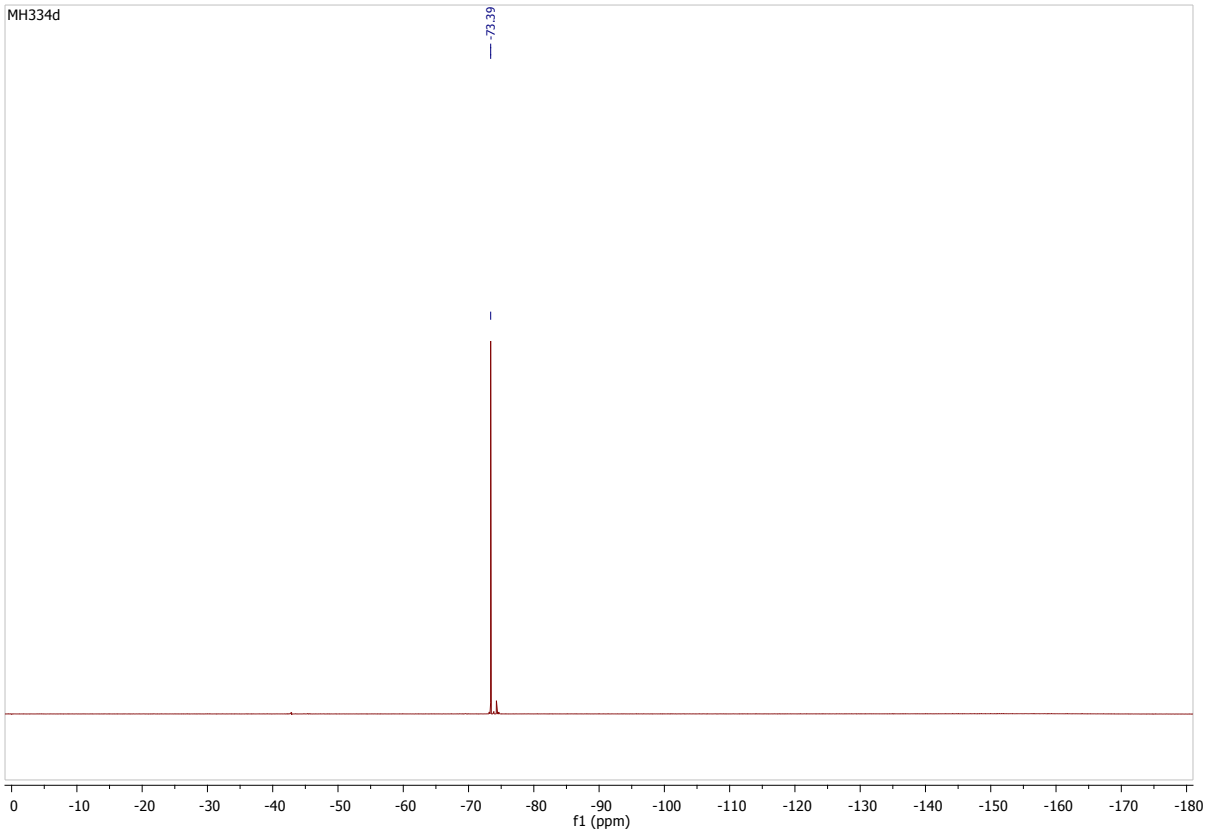

MH327c
-73.78
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

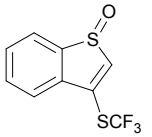

S
SOCF3

2o

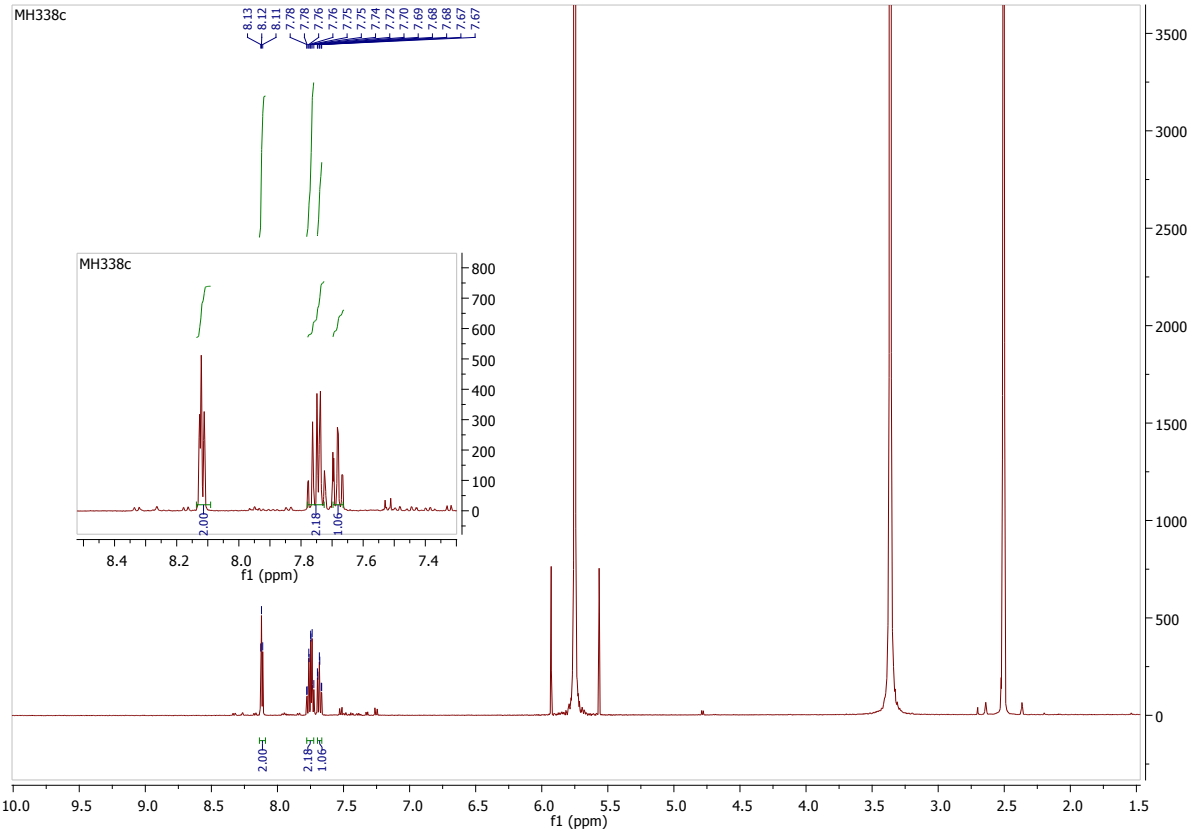

MH334d
8.33
8.11
8.10
8.09
7.99
7.98
7.97
7.54
7.53
7.53
7.52
7.52
1.00
1.00
1.02
2.06
f1 (ppm)

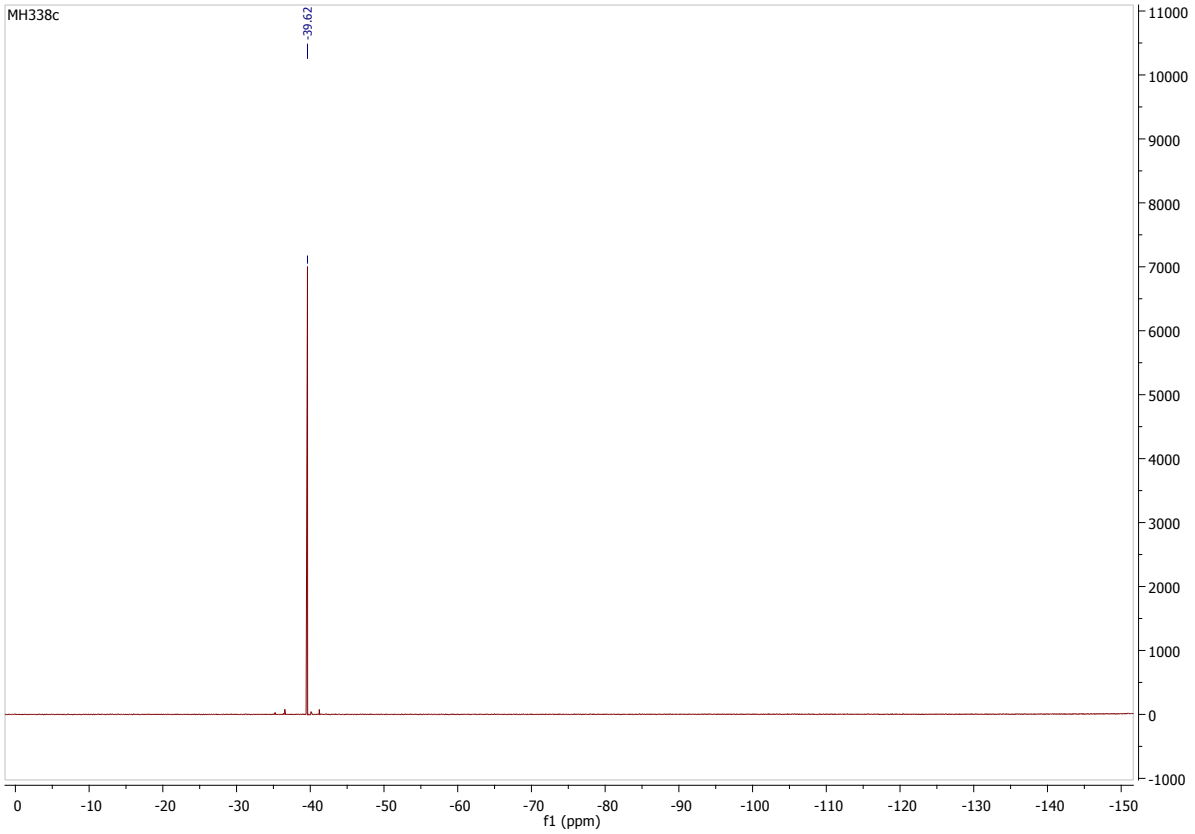

MH334d
140.75
134.95
134.27
126.58
126.33
126.06
126.00
123.32
122.62
122.61
77.41
77.16
76.91
f1 (ppm)

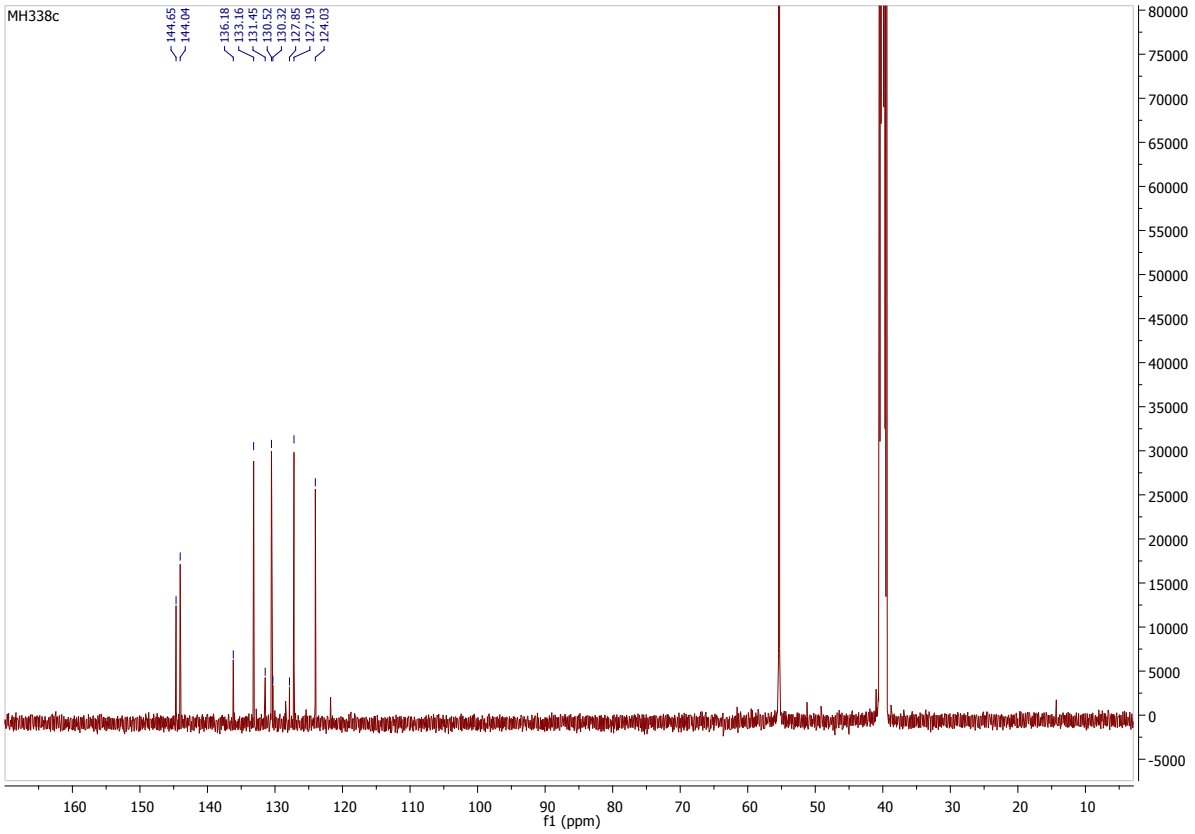

MH334d
-73.39
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

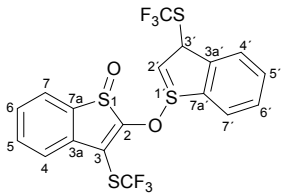

O
S
SCF3

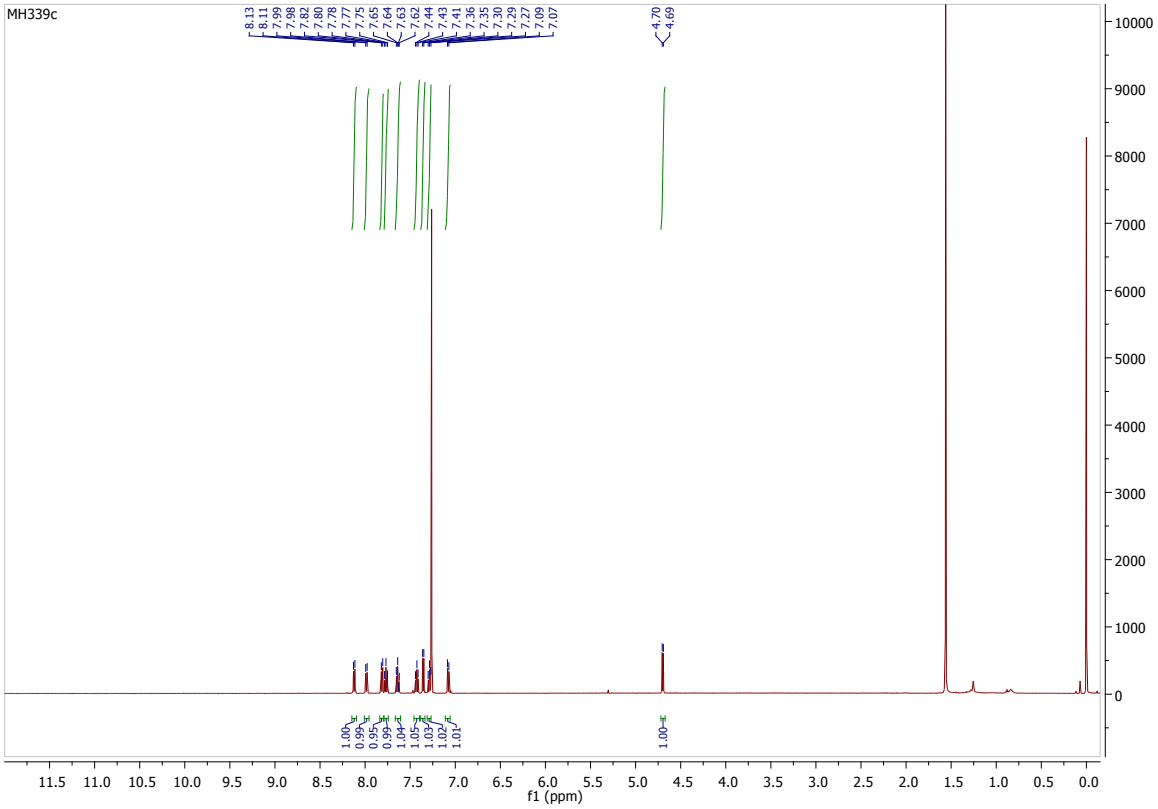
2o´

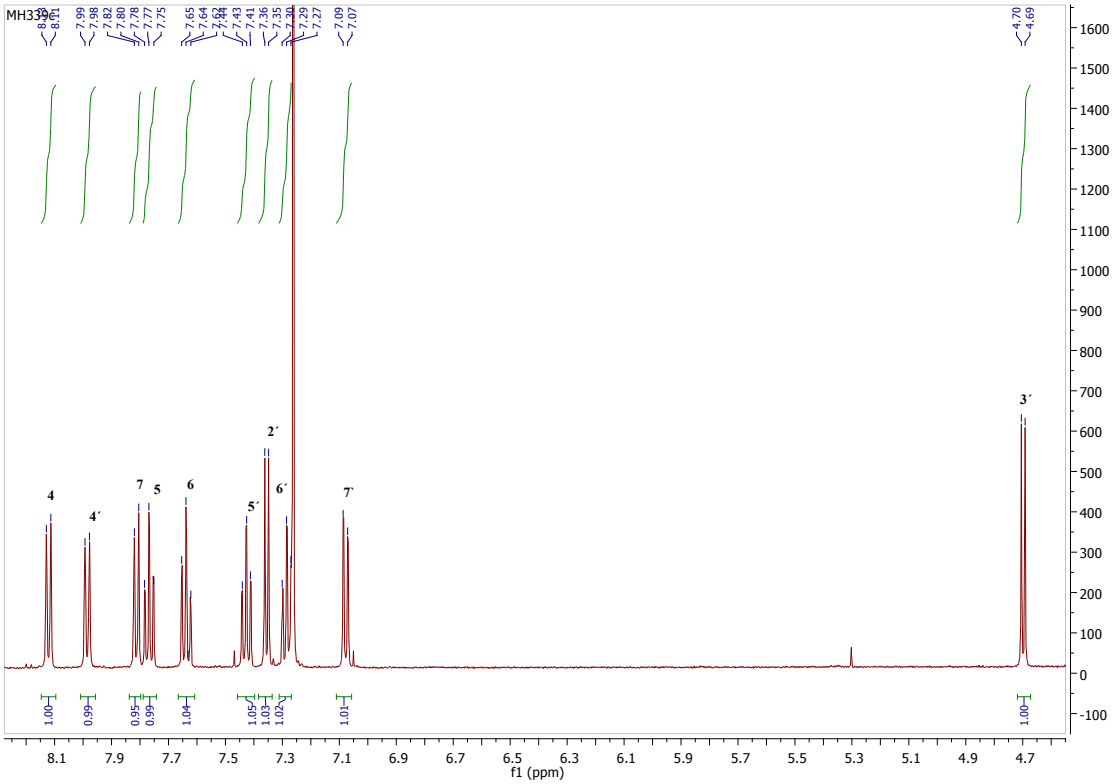

MH338c
8.13
8.12
8.11
7.78
7.78
7.76
7.76
7.75
7.75
7.74
7.72
7.70
7.69
7.68
7.68
7.67
7.67
MH338c
2.00
2.19
1.06
f1 (ppm)
2.00
2.19
1.06
f1 (ppm)

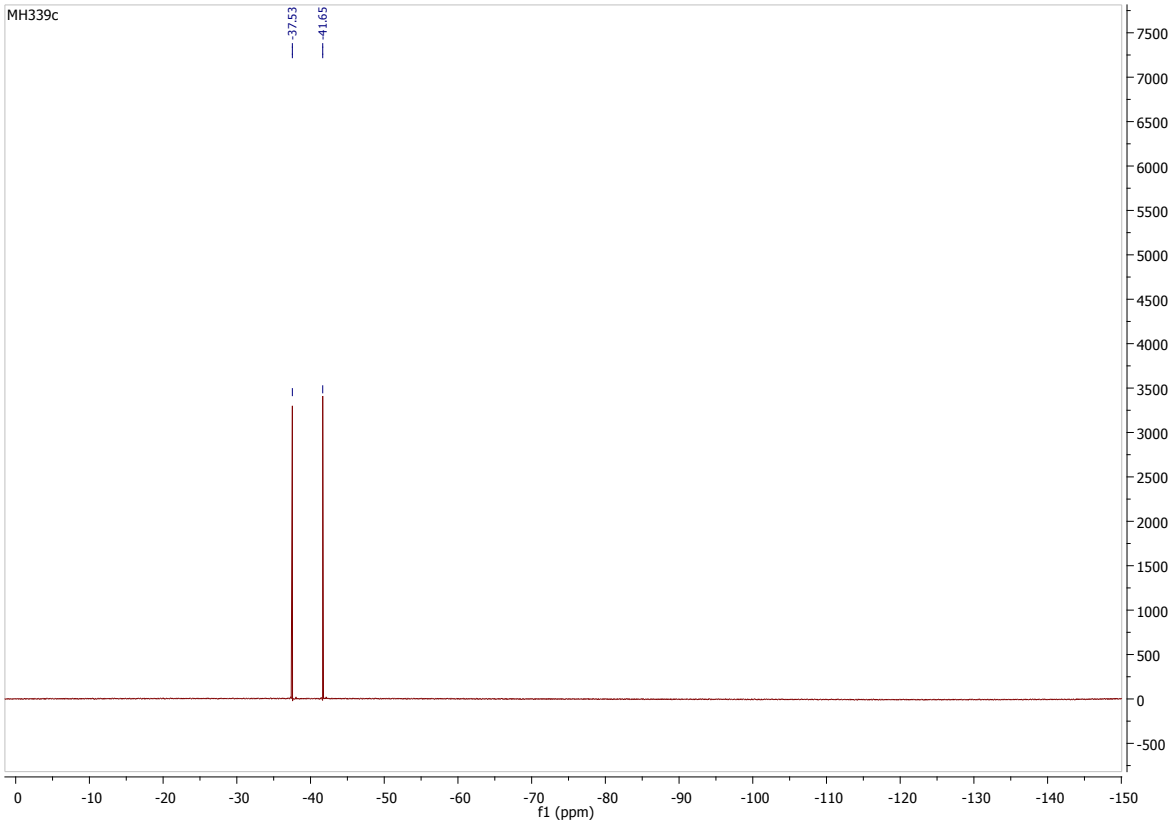

MH338c
-39.62
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)

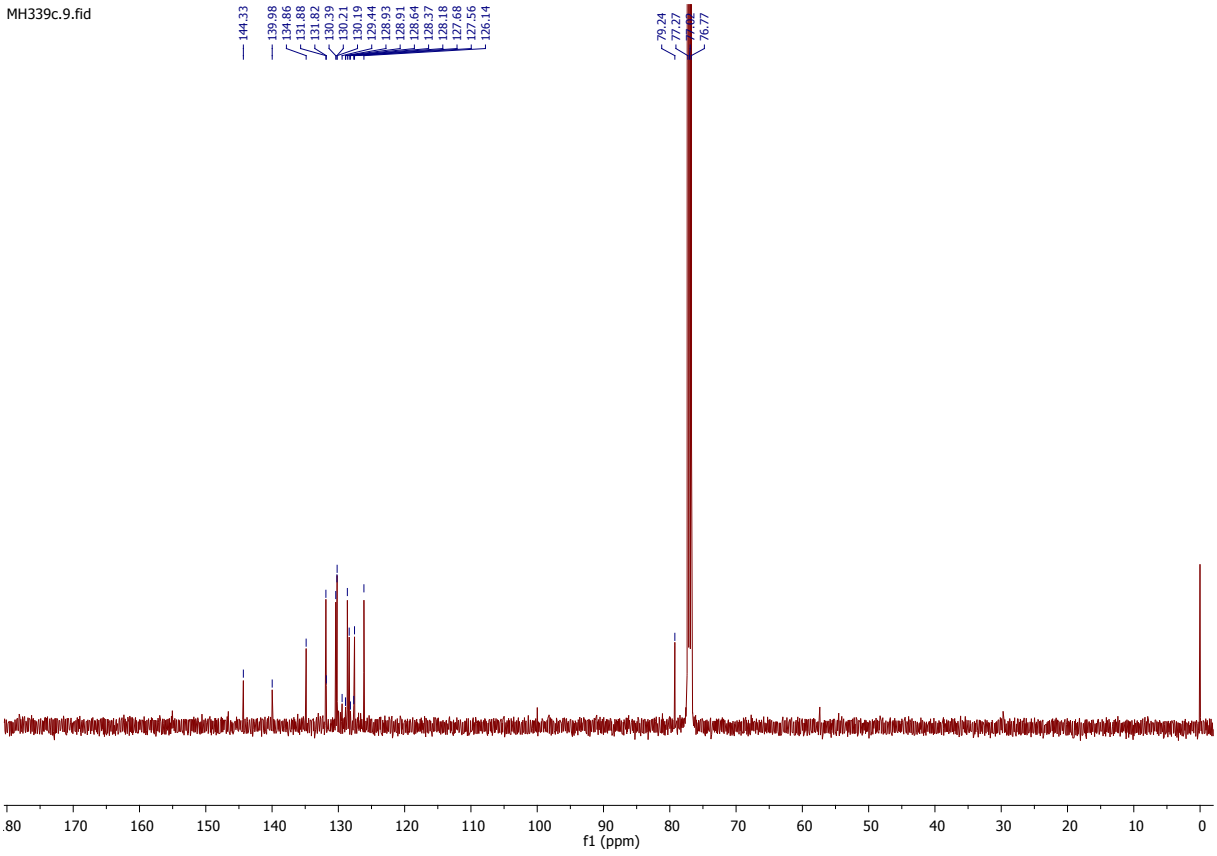

MH338c
144.65
144.04
136.18
133.16
131.45
130.52
130.32
127.85
127.19
124.03
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

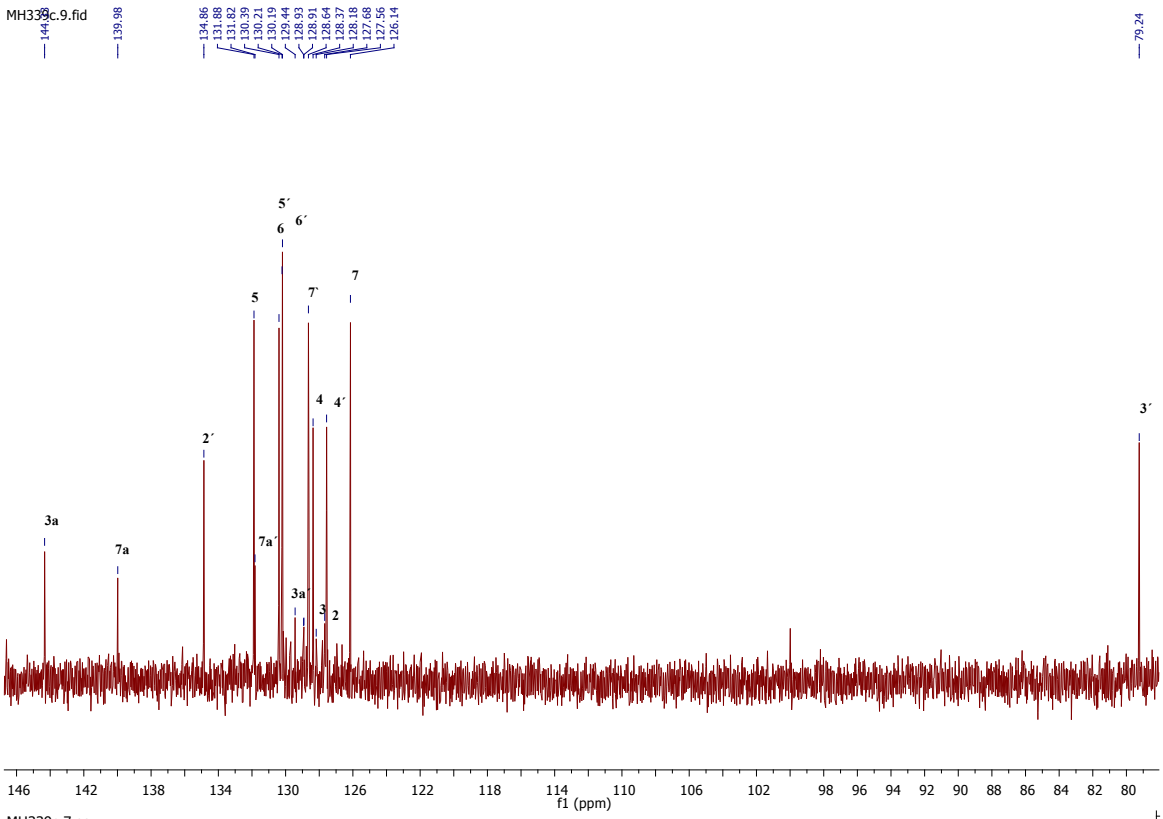

F3CS
3′
3a′
4′
2′
5′
7
6
7a
S1
O
1
S
7a′
6′
7′
5
2
O
4
3a
3
SCF3

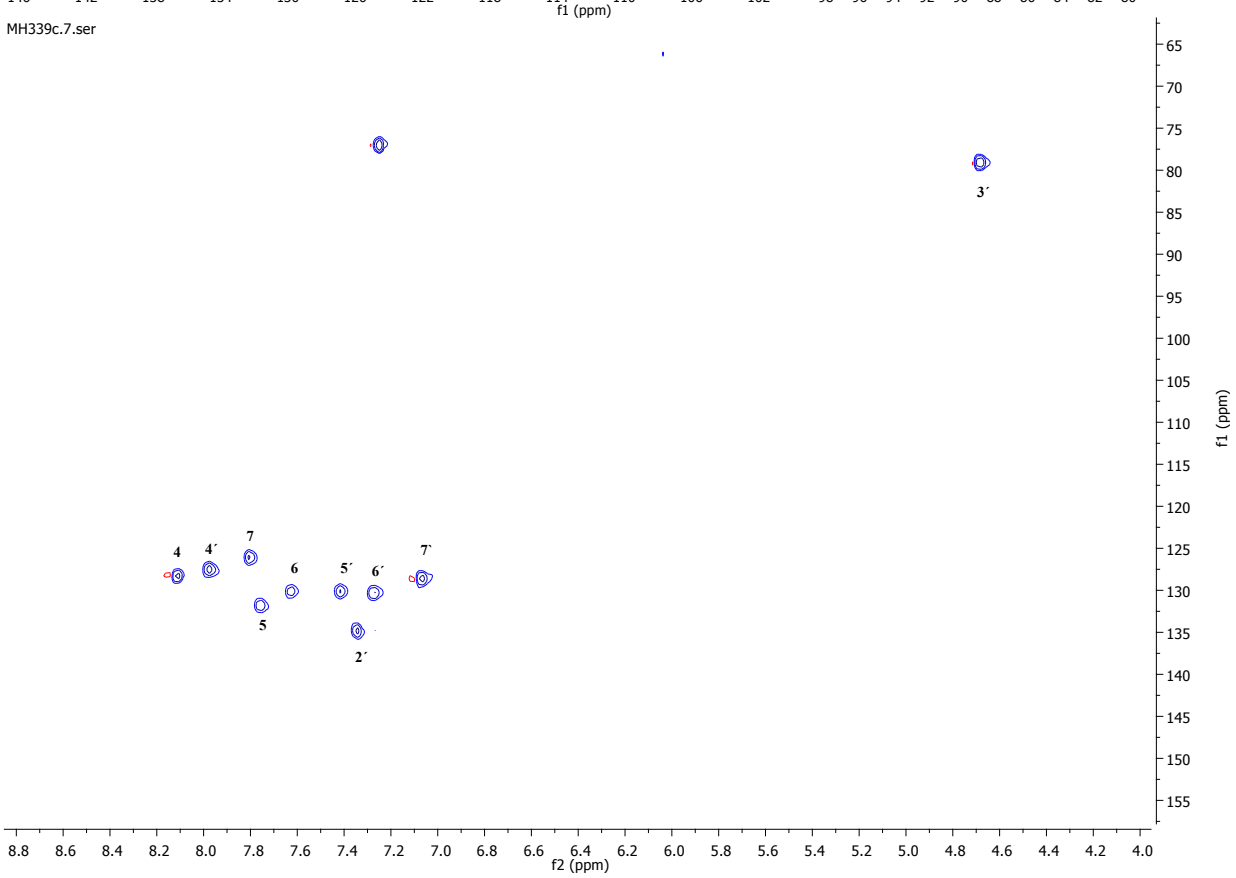

MH339c
f1 (ppm)

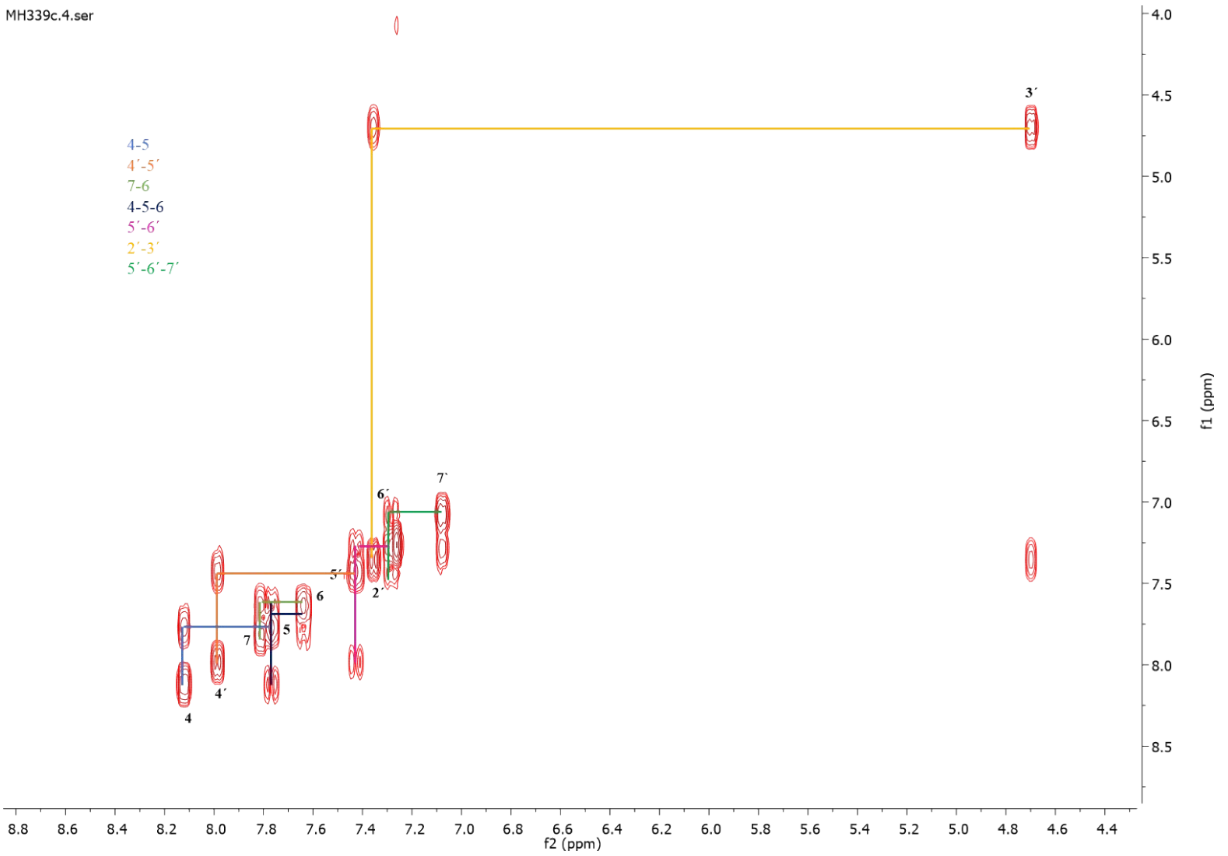

MH339c
4
4′
7
5
6
5′
2′
6′
7′
3′
f1 (ppm)

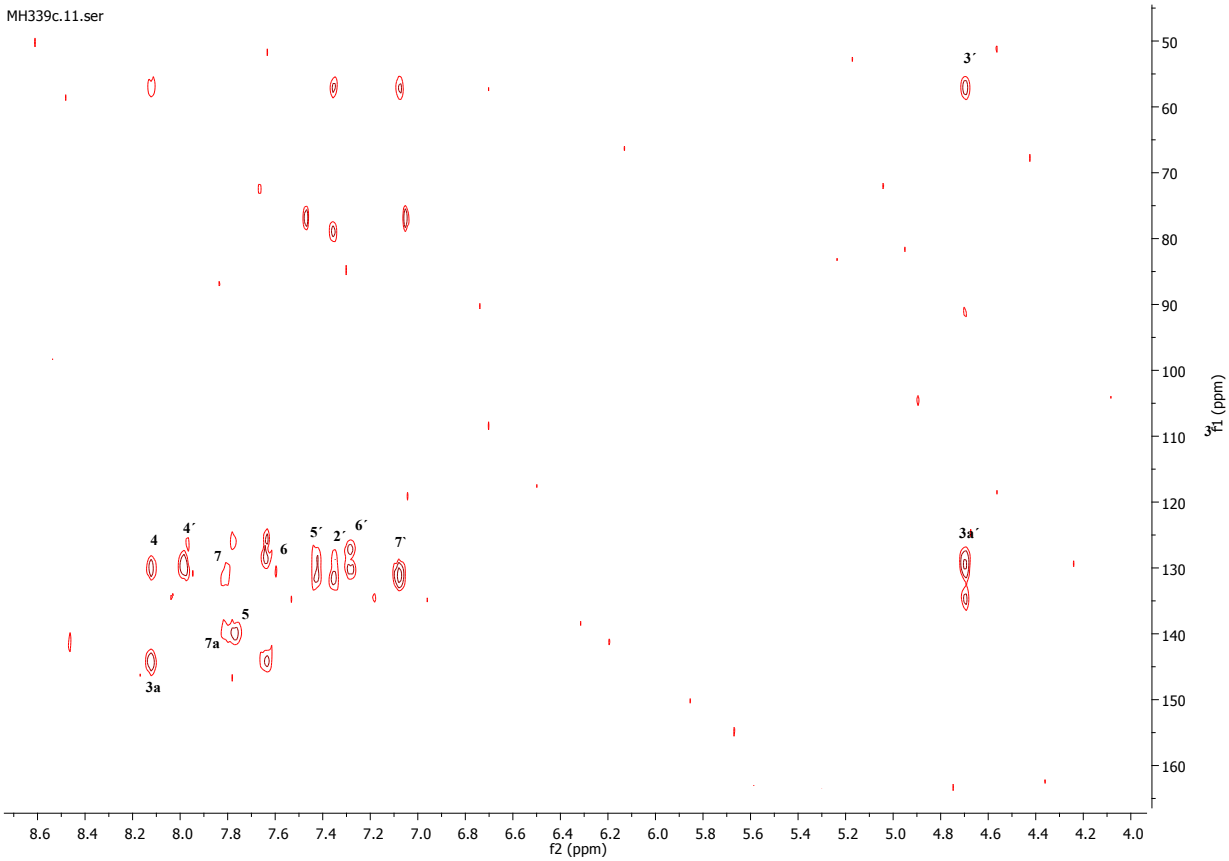

MH339c
-37.53
-41.65
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)


MH339c.9.fid
144.33
139.98
134.86
131.88
131.82
130.39
130.21
130.19
129.44
128.93
128.91
128.64
128.37
128.18
127.68
127.56
126.14
79.24
77.27
77.02
76.77
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MH339c.9.fid
144.73
139.98
134.86
131.88
131.82
130.39
130.21
130.19
129.44
128.93
128.91
128.64
128.37
128.18
127.68
127.56
126.14
79.24
5´
6
6´
7
5
7`
4
4´
3´
2´
3a
7a
7a´
3a`
3
2
146
142
138
134
130
126
122
118
114
110
106
102
98
96
94
92
90
88
86
84
82
80
f1 (ppm)


MH339c.7.ser
3´
4
4´
7
6
5´
6´
7`
5
2´
65
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
f1 (ppm)
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
f2 (ppm)


MH339c.4.ser
4-5
4´-5´
7-6
4-5-6
5´-6´
2´-3´
5´-6´-7´
f2 (ppm)
f1 (ppm)


MH339c.11.ser
f2 (ppm)
f1 (ppm)

References

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[2] X. Lin, G. Wang, H. Li, Y. Huang, W. He, D. Ye, K.-W. Huang, Y. Yuan, Z. Weng, *Tetrahedron* **2013**, *69*, 2628-2632.

[3] X. Chen, M. Tordeux, J.-R. Desmurs, C. Wakselman, *J. Fluorine Chem.* **2003**, *123*, 51-56.

[4] K. Kamata, M. Kotani, K. Yamaguchi, S. Hikichi, N. Mizuno, *Chemistry – A European Journal* **2007**, *13*, 639-648.