Supporting Information

Coupling of Thiols and Aromatic Halides Promoted by Diboron Derived Super Electron Donors

Mario Franco,[a] Emily L. Vargas,[a] Mariola Tortosa,*[a,b] M. Belén Cid*[a,b]

a. Department of Organic Chemistry, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid (Spain),
e-mail: belen.cid@uam.es, mariola.tortosa@uam.es
b. Institute for Advanced Research in Chemical Sciences (IAdChem), Universidad Autónoma de Madrid, 28049 Madrid, Spain.

1. General methods

NMR spectra were acquired using $CDCl_3$ as solvent, running at 300 and 75 or 100 MHz for ^1H and ^{13}C, respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$, 7.26 ppm for ^1H NMR, and 77.0 ppm for ^{13}C NMR). In all ^1H NMR spectra, multiplicity is indicated as follows: br (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet). Coupling constant values (in Hertz) and number of protons for each signal are also indicated.

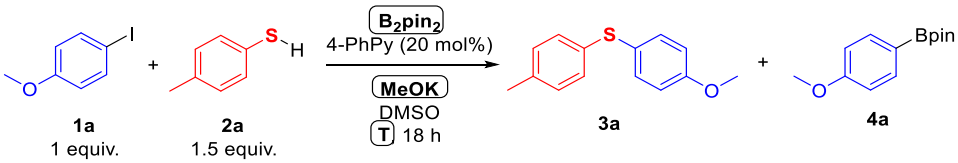
For thin layer chromatography (TLC) was performed using pre-coated aluminium backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet irradiation (254 nm) by treatment with a solution of $KMnO_4$ (1.5 g), K_2CO_3 (10 g), and 10% NaOH (1.25 mL) in H_2O (200 mL) or a solution of phosphomolybdic acid (12 g), in EtOH (250 mL) followed by heating. Flash column chromatography (FCC) was performed using Merck pore 60 Å, 40-63 µm silica gel and compressed air.

Cyclohexane and EtOAc were supplied by *Carlo Erba* and were used without previous purification. All solvents were purchased dry and with no stabilizers in *Acros Organics or Milipore Sigma*. Previous to their utilization, solvents were deoxygenated following the freeze-pump-thaw procedure, except DMSO, DMF and DMA, which were deoxygenated passing an argon flow through them for 15 minutes. All reagents were acquired from commercial sources and were used without further purification. For all described synthesized products, spectroscopic data are consistent with the references indicated next to the name of each compound.

High resolution mass spectra (HRMS) were acquired in a Waters-GCT Agilent Technologies 6890N mass spectrometer using Electron Ionization (EI) or in a Bruker-ULTRAFLEX III using MALDI-TOF as ionization source.

2. Optimization tables

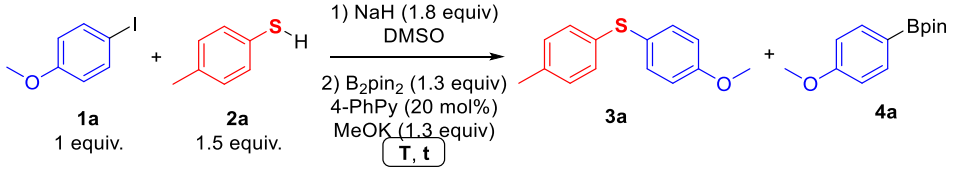
Table S1. *Preliminary optimization experiments using MeOK to deprotonate the thiol and form SED.*



Entry	Boron Source	Base	T (ºC)	Ratio 3a/4a	Conv[a] (%)	Yield 3a (%)
1	B_2pin_2 (1.3)	MeOK (3)	85	2/1	100	(40%)[b]
2	B_2pin_2 (0.2)	MeOK (2.3)	85	1/0	20	Trace
3	B_2pin_2 (1.3)	MeOK (3)	50	2/1	100	-
4	B_2pin_2 (1.3)	MeOK (3)	25	2/1	88	-

[a]Conversions measured by ^{1}H-NMR compared to the remaining starting material. [b] Isolated yield.

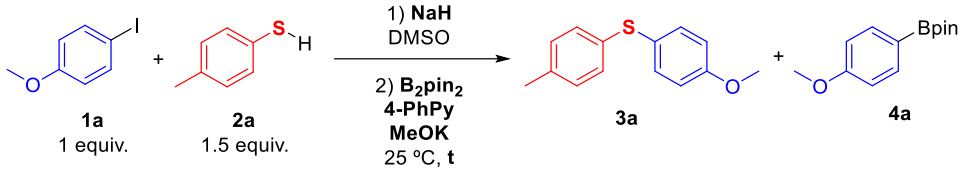
Table S2. *Optimization of time and temperature of the one-pot reaction.*



Entry	T (ºC)	t (h)	Ratio 3a:4a	Conv (%)[a]	Yield 3a (%)[b]
1	85	18	6:1	100	50
2	85	1	10:1	100	54
3	85	15 min	10:1	100	55
4	50	15 min	1:0	47	38
5	50	1	1:0	100	66
6	25	2.5	1:0	33	32
7	25	18	1:0	85	76
8	25	24	1:0	100	80 (68)[c]
9[d]	25	24	1:0	100	60[c]

[a]Conversions measured with ^{1}H-NMR compared to the remaining starting material. [b]Yields measured by ^{1}H-NMR using nitromethane as internal standard. [c]Isolated yield. [d]Out of glovebox.

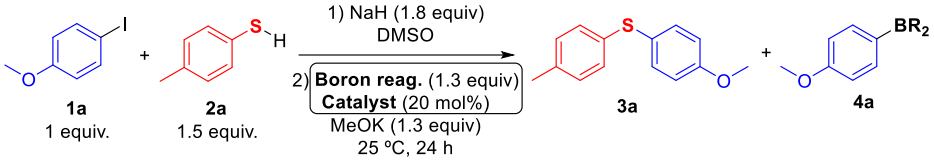
Table S3. *Optimization of the ratio of the reagents.*



Entry	Reagent Ratio	Boron Source	Catalyst	Base	t (h)	Ratio 3a:4a	Conv (%)[a]	Yield 3a (%)[b]
1	1:1.5	B_2pin_2 (1.3)	4-PhPy (30%)	NaH (1.8) MeOK (1.3)	18	1:0	100	84
2	1:1.5	B_2pin_2 (1.3)	4-PhPy (10%)	NaH (1.8) MeOK (1.3)	18	5:1	90	68
3	1:1.5	B_2pin_2 (0.5)	4-PhPy (20%)	NaH (1.8) MeOK (0.5)	24	1:0	67	44
4	1:1	B_2pin_2 (1.3)	4-PhPy (20%)	NaH (1.8) MeOK (1.3)	24	4:1	100	74
5	1:2	B_2pin_2 (1.3)	4-PhPy (20%)	NaH (2.2) MeOK (1.3)	18	7:1	100	70
6	1:2	B_2pin_2 (1.3)	4-PhPy (20%)	NaH (2.2) MeOK (2.6)	18	-	78	53
7	1:1.5	B_2pin_2 (1.3)	4-PhPy (20%)	NaH (1.8) MeOK (2.6)	18	-	100	67

[a] Conversions measured with ^{1}H-NMR compared to the remaining starting material. [b] Yields measured by ^{1}H-NMR using nitromethane as internal standard.

Table S4. *Pyridine catalyst and boron source screening.*



Entry	Boron Source	Catalyst	Conv (%)[a]	Yield 3a (%)[b]
1	B_2pin_2	4-CNPy	8	7
2	B_2pin_2	dpy	0	0
3	B_2pin_2	tbdpy	0	0
4	B_2pin_2	4,4'-dpy	100	68[c]
5	B_2cat_2	4-PhPy	0	0
6	B_2nep_2	4-PhPy	100	52[c]
7	B_2OH_4	4-PhPy	0	0
8	B_2eg_2	4-PhPy	0	0

[a] Conversions measured by ^{1}H-NMR compared to the remaining starting material. [b] Yields measured by ^{1}H-NMR using nitromethane as internal standard. [c] Isolated yields.

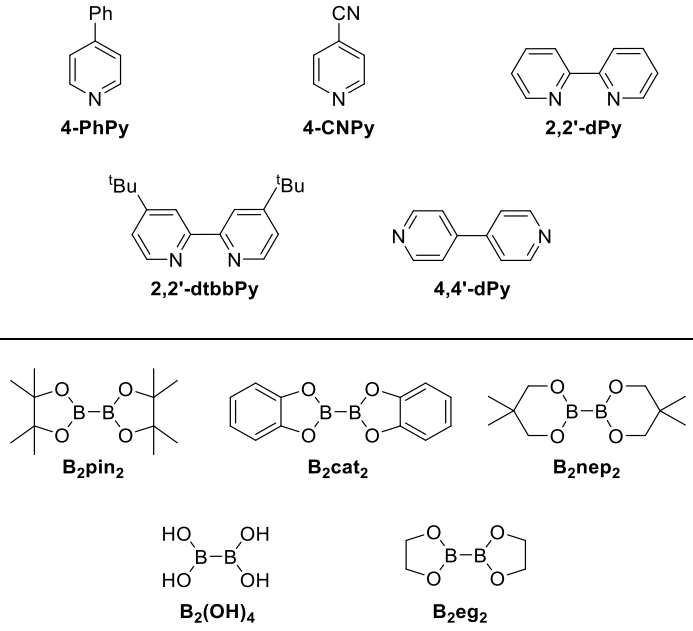
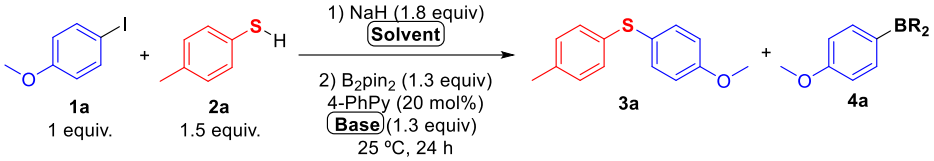


Figure S1. *Pyridine catalyst and boron source screening.*

Table S5. *Solvent and base screening.*

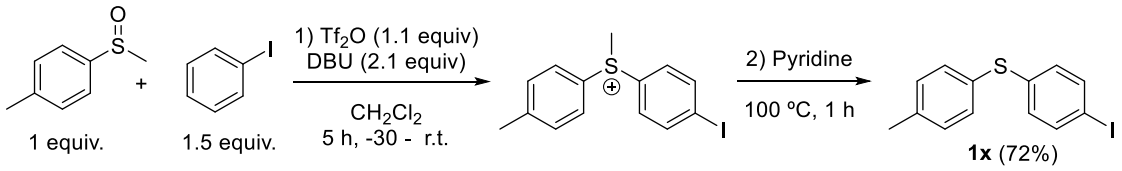


Entry	Solvent	Base	Ratio 3a/4a	Conv[a] (%)	Yield 3[a] (%)[b]
1	DMSO	MeOK	-	100	80 (68)
2	CF_3Tol	MeOK	-	6	-
3	CH_3CN	MeOK	-	0	-
4	DMF	MeOK	2/1	70	30
5	DMA	MeOK	-	100	66
6[c]	DMA	MeOK	4/1	64	40
7	THF	MeOK	-	32	-
8	HFIP	MeOK	-	0	-
9	MTBE	MeOK	-	0	0
10	MTBE:DMSO 2.5:1	MeOK	1/0	66	58
11	DMSO	MeONa	10/1	80	68
12[c]	DMSO	MeONa	4/1	100	80
13	DMSO	MeOLi	4/1	88	59
14	DMSO	C_2CO_3 MeOK	4/1	88	50
15[d]	DMSO	NaH MeOK	2/1	92	51

[a] Conversions measured by ^{1}H-NMR compared to the remaining starting material. [b] Yields measured by ^{1}H-NMR using nitromethane as internal standard. [c] 50 ºC, 18 h. [d] NaH 1.5 eq.

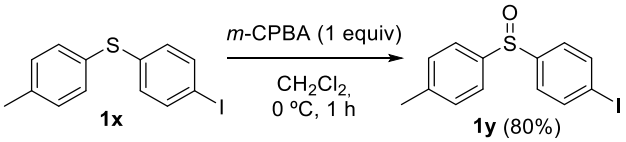
3. Preparation of precursors

Synthesis of (4-iodophenyl)(*p*-tolyl)sulfane (**1x**)[1]



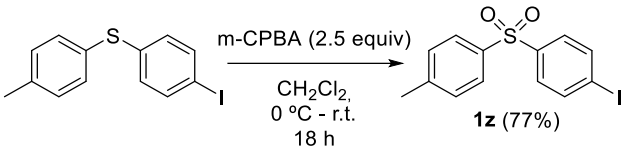
(4-Iodophenyl)(*p*-tolyl)sulfane (**1x**) was prepared following the procedure described in the literature.[2] Methyl *p*-tolyl sulfoxide (154 mg, 1 mmol) was dissolved in CH_2Cl_2 (5 mL) in an oven-dried sealed vial and the solution was cooled to -30 ºC. Tf_2O (310 mg, 1.1 mmol) was then added dropwise, followed by iodobenzene (306 mg, 1.5 mmol). After 15 minutes at -30 ºC, the reaction was stirred at r.t. for 1.5 h. Then, DBU was added, and the mixture was stirred for another 4 h. The solution was quenched with H_2O (10 mL) and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated at reduced pressure. The crude oil was then dissolved in pyridine (5 mL) and stirred at 100 ºC for 1 h. The solution was concentrated under vacuo and the resulting crude was purified by flash column chromatography using a cyclohexane : toluene 100:1 mixture as eluent. The spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 2.37 (s, 3H).

Synthesis of 1-iodo-4-(*p*-tolylsulfinyl)benzene (**1y**)[3]



To a solution of aryl iodide **1x** (80 mg, 0.25 mmol) in CH_2Cl_2 (1.25 mL) a solution of *m*-CPBA (43.2 mg, 0.25 mmol) in CH_2Cl_2 (1.25 mL) was added dropwise at 0 ºC. The mixture was stirred at the same temperature for 1 h and then quenched with saturated aqueous $NaHCO_3$. The mixture was extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated at reduced pressure. The resulting crude was purified by flash chromatography using a cyclohexane : ethyl acetate 20:1 mixture as eluent. The spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 2.37 (s, 3H).

Synthesis of 1-iodo-4-tosylbenzene (**1z**)[4]



To a solution of aryl iodide **1x** (158 mg, 0.5 mmol) in CH_2Cl_2 (2.5 mL) a solution of *m*-CPBA (259 mg, 1.5 mmol) in CH_2Cl_2 (2.5 mL) was added dropwise at 0 ºC. The mixture was stirred at room temperature for 18 h and then quenched with saturated aqueous $NaHCO_3$. The mixture was extracted with CH_2Cl_2 (3 x 10 mL) and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated at reduced pressure. The resulting crude was purified by flash chromatography using a cyclohexane : ethyl acetate 20:1 mixture as eluent. The spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.6 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 2.39 (s, 3H).

4. General procedures for the C-S coupling reaction

For convenience, most of the reactions have been performed in the glovebox. Nevertheless, we have demonstrated in several cases that the method can be translated to a Schlenk line with no significant drop in the yield.

Procedure in the glovebox

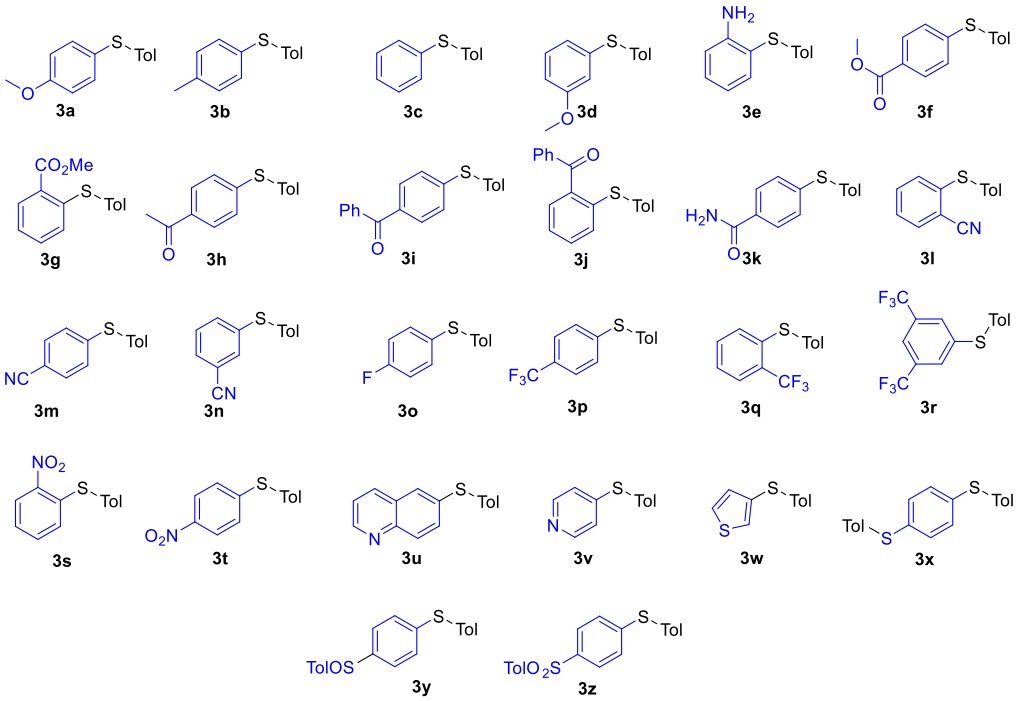
In a nitrogen filled glovebox at ambient temperature, the corresponding thiol (0.375 mmol) was added to a screw capped vial and diluted in 0.5 mL of dry and deoxygenated DMSO. Then, NaH (0.45 mmol, 10.8 mg) is added observing gas evolution, and the mixture is stirred at room temperature for 30 minutes. After complete deprotonation of the thiol; B_2pin_2 (0.325 mmol, 82.6 mg), 4-phenylpyridine (0.05 mmol, 7.8 mg), MeOK (0.325 mmol, 22.3 mg), and the corresponding iodide (0.25 mmol) were sequentially added to the thiolate solution. The vial was then sealed with a Teflon cap, and the mixture was stirred at room temperature for 24 h.

After this time, the reaction was diluted with 10 mL EtOAc and DMSO was eliminated following two different techniques specified in each case. In **method A** the solution was washed with H_2O, the organic phase was then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. In **method B** (for compounds partially soluble in water **3e, 3k, 3s, 3ar, 3as**) the solution was filtered through a short pad of silica. The pad is then washed with a 10:1 *c*Hex : EtOAc mixture, and the filtrate is concentrated in vacuo. Once eliminated the DMSO, the crude was finally purified by flash column chromatography using a *c*Hex : EtOAc mixture as eluent to afford the desired diaryl thioether.

Procedure outside the glovebox

In a screw capped vial, the corresponding thiol (0.375 mmol) is added along with NaH (0.45 mmol, 10.8 mg), and the vial is evacuated and backfilled with argon 3 times. Then, the mixture of solids is diluted with 0.5 mL of dry and deoxygenated DMSO, and the solution is stirred for 30 min at room temperature (gas evolution observed). After complete deprotonation of the thiol, B_2pin_2 (0.325 mmol, 82.6 mg), 4-phenylpyridine (0.05 mmol, 7.8 mg), MeOK (0.325 mmol, 22.3 mg), and the corresponding iodide (0.25 mmol) were sequentially added as solids to the thiolate solution under Ar positive pressure. The vial is then sealed with a Teflon cap, and the mixture was purged with argon for 5 minutes. After this, the mixture was stirred at room temperature for 24 h. After this time, the reaction is diluted with 10 mL EtOAc and the solution is treated according to either method A or B.

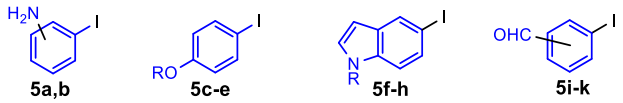
***Table S6**. Aromatic halide substrate scope.*



Unsuccessful substrates

Unlike the *o*-iodoaniline **1e**, the corresponding *m*- and *p*- substituted iodoanilines **5a-b** did not react under the reaction conditions. Different unprotected and protected *p*-iodo phenols **5c-e** probed to be ineffective, as well as some iodoindoles **5f-h.** Compounds **5i-k** underwent thiolation but partial reduction of the aldehyde was observed (Table S7).

***Table S7**. Unsuccessful halides.*



p-Aminothiophenol and *p*-nitrothiophenol also failed to form the corresponding thioether

Table S8. *Aromatic thiol substrate scope.*

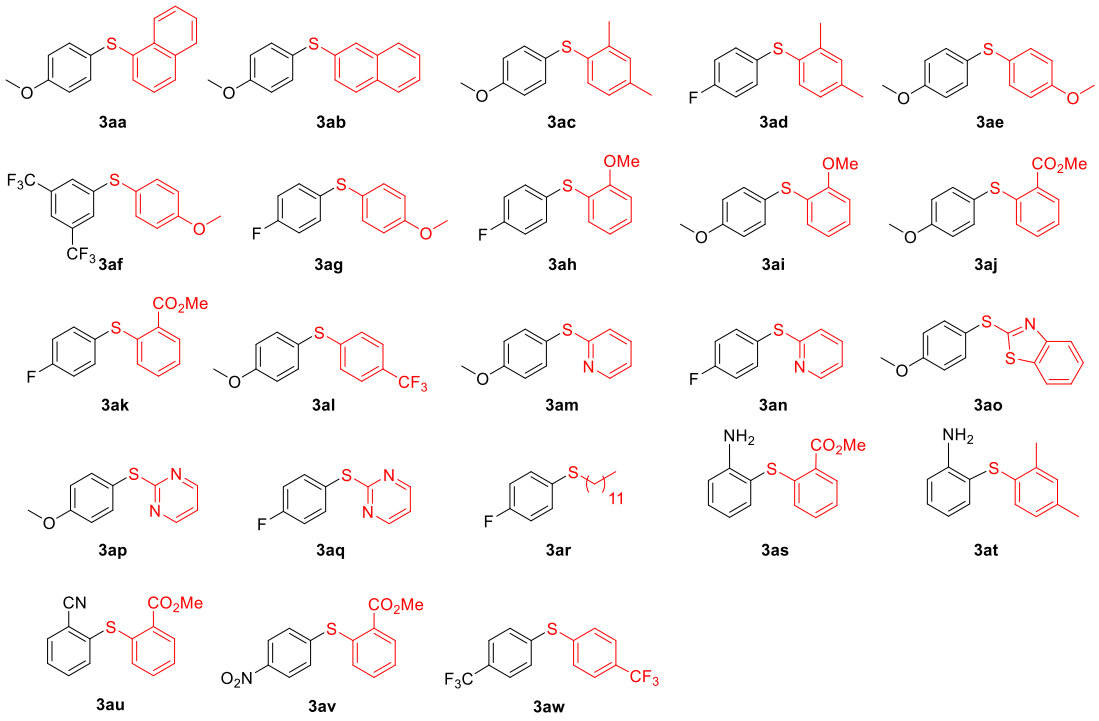
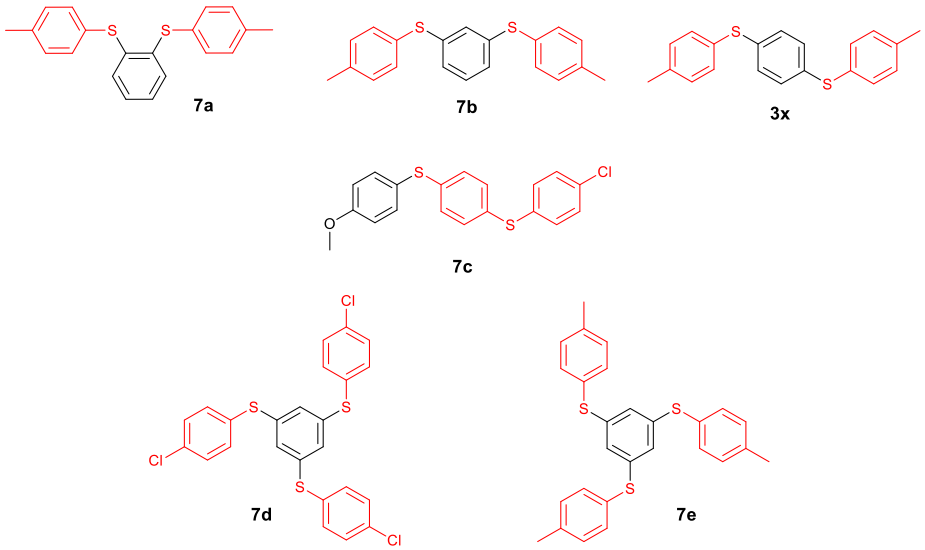
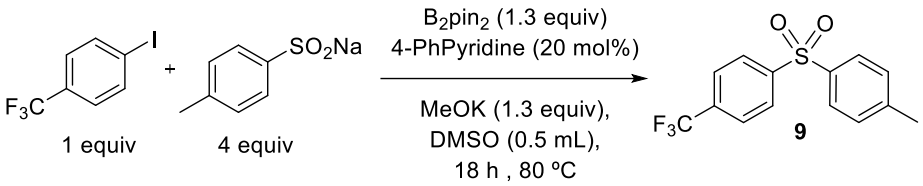


Table S9. *Thiother formation from multifunctionalized substrates.*



Preliminary attempt of the C-S coupling using sulfinate



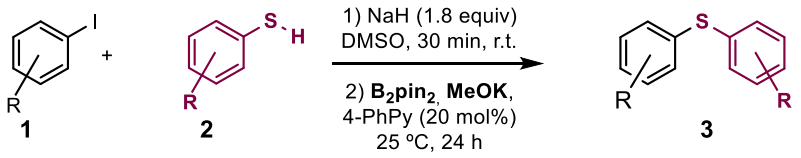
In a nitrogen filled glovebox at ambient temperature, sodium *p*-toluenesulfinate (1 mmol) was added to a screw capped vial and diluted in 0.8 mL of dry and deoxygenated DMSO. Then, B_2pin_2 (0.325 mmol, 82.6 mg), 4-phenylpyridine (0.05 mmol, 7.8 mg), MeOK (0.325 mmol, 22.3 mg), and -iodo-4-(trifluoromethyl)benzene (0.25 mmol) were sequentially added to the solution. The vial was then sealed with a Teflon cap, and the mixture was stirred at 80˚C for 24 h.

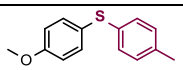
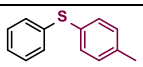
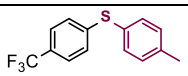
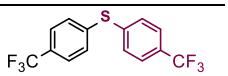
After this time, the reaction was diluted with 10 mL EtOAc and the solution was washed with H_2O, the organic phase was then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude was finally purified by flash column chromatography using a *c*Hex: EtOAc mixture as eluent (20:1 to 9:1) to afford the sulfone **9** (30 mg, 38 %). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.06 (d, *J* = 8.2 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 2.42 (s, 3H).

Experiments using catalytic amount of B_2pin_2 and base

As can be seen in the following table S10, it is possible to perform the reaction under substoichiometric amount of diboron reagent and base reagents. Nevertheless, the amount of B_2pin_2/ MeOK necessary for the reaction to proceed in high/moderated yields depends on the nature of the substituents.

Table S10. Catalytic modification of the C-S coupling reaction.

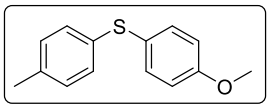


B_2pin_2/ MeOK (equiv)	 **3a**	 **3c**	 **3p**	 **3aw**
		Isolated yields (%)		
1.3	68	76	91	83
0.5	44	75	86	77
0.2	-	53	79	51

Using the reaction of 1-iodo-4-(trifluoromethyl)benzene and 4-methylbenzenethiol we have proven that the use of 0.5 or 0.2 equivalents of B_2pin_2 and MeOK provided **3p** with an insignificant erosion of the yield (86 and 79 % respectively, compared with the 91 % obtained when using 1 equivalent of B_2pin_2). The same happens when using 0.5 equivalents in the formation of **3c** and **3aw**, observing a more pronounced decrease when employing 0.2 equivalents. In the case of setting the reaction with catalytic amount of B_2pin_2 and MeOK to get product **3a** the yield erosion is bigger, although thioether could be obtained with moderate yield.

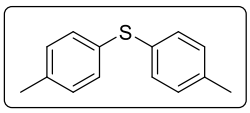
5. Characterization of compounds

(4-Methoxyphenyl)(*p*-tolyl)sulfane (3a)[5]



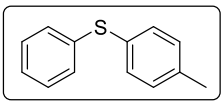
Synthesized according to general procedure, method A using either the combination of 4-iodoanisole and 4-methyl benzenethiol or 4-iodotoluene and 4-methoxybenzenethiol. The product was purified by column chromatography (cyclohexane:ethyl acetate 100:1) to get the product **3a** (39.1 mg, 68%). Spectroscopic data were in accordance with the literature.[1]**H NMR (300 MHz, $CDCl_3$)** δ 7.37 (d, *J* = 8.7 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 2.31 (s, 3H).

Di-*p*-tolylsulfane (3b)[6]



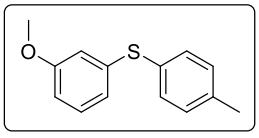
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:toluene 100:1) to get the product **3b** (32.1 mg, 60%). Spectroscopic data were in accordance with the literature.[1]**H NMR (300 MHz, $CDCl_3$)** δ 7.29 (d, *J* = 8.0 Hz, 4H), 7.16 (d, *J* = 8.0 Hz, 4H), 2.38 (s, 6H).

Phenyl(*p*-tolyl)sulfane (3c)[7]



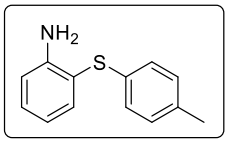
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane) to get the product **3c** (38 mg, 76%). Spectroscopic data were in accordance with the literature.[1]**H NMR (300 MHz, $CDCl_3$)** δ 7.38 – 7.08 (m, 9H), 2.37 (s, 3H).

(3-Methoxyphenyl)(*p*-tolyl)sulfane (3d)[8]



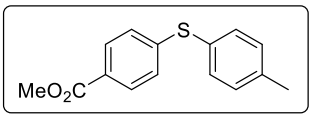
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 100:1) to get the product **3d** (53.4 mg, 93%). Spectroscopic data were in accordance with the literature.[1]**H NMR (300 MHz, $CDCl_3$)** δ 7.33 (d, *J* = 8.1 Hz, 2H), 7.22 – 7.11 (m, 3H), 6.83 (d, *J* = 8.3 Hz, 1H), 6.80 (t, *J* = 1.9 Hz, 1H), 6.73 (dd, *J* = 8.2, 2.5 Hz, 1H), 3.75 (s, 3H), 2.35 (s, 3H).

2-(*p*-Tolylthio)aniline (3e)[9]



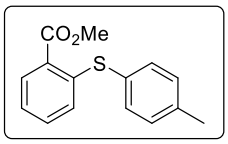
Synthesized according to general procedure, method B. The product was purified by column chromatography (cyclohexane:ethyl acetate 100:1) to get the product **3e** (33 mg, 64%). Spectroscopic data were in accordance with the literature.**^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.45 (dt, *J* = 9.4, 4.7 Hz, 1H), 7.26 – 7.18 (m, 1H), 7.08 – 7.00 (m, 4H), 6.83 – 6.70 (m, 2H), 4.28 (s br, 2H), 2.29 (s, 3H).

Methyl 4-(*p*-tolylthio)benzoate (3f)[10]



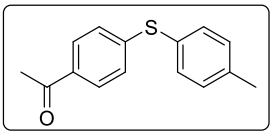
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 100:1) to get the product **3f** (46 mg, 71%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.87 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 3H), 2.39 (s, 3H).

Methyl 2-(*p*-tolylthio)benzoate (3g)[8]



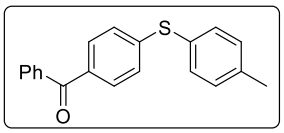
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 50:1) to get the product **(3g)** (37.6 mg, 65%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.98 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.23 (m, 3H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 3.96 (s, 3H), 2.41 (s, 3H).

1-(4-(*p*-Tolylthio)phenyl)ethan-1-one (3h)[8]



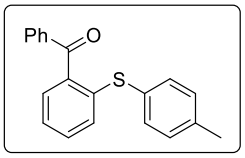
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 20:1) to get the product **3h** (37 mg, 62%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 2H), 2.54 (s, 3H), 2.40 (s, 3H).

Phenyl(4-(*p*-tolylthio)phenyl)methanone (3i)[10]



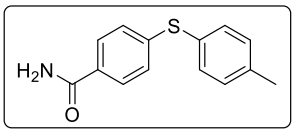
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 100:1) to get the product **3i** (52 mg, 68%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.81 – 7.72 (m, 2H), 7.72 – 7.64 (m, 2H), 7.63 – 7.53 (m, 1H), 7.53 – 7.40 (m, 4H), 7.32 – 7.14 (m, 4H), 2.40 (s, 3H).

Phenyl(2-(*p*-tolylthio)phenyl)methanone (3j)



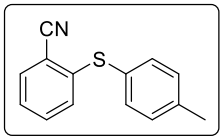
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 100:1) to get the product **3j** (57.7 mg, 76%) as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.82 (d, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.51 – 7.38 (m, 3H), 7.36 – 7.07 (m, 7H), 2.34 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 196.81 (CO), 138.90 (C), 138.66 (2C), 137.77 (C), 133.94 (CH), 133.35 (CH), 131.20 (CH), 130.83 (C), 130.74 (CH), 130.51 (CH), 130.48 (CH), 130.02 (CH), 128.71 (CH), 125.66 (CH), 21.51 (CH_3). **HRMS** (EI^+) Calcd for $C_{20}H_{16}OS$ $[M]^+$ 304.0922, Found 304.0928.

4-(*p*-Tolylthio)benzamide (3k)[11]



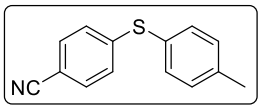
Synthesized according to general procedure, method B. The product was purified by column chromatography (cyclohexane:ethyl acetate 4:1) to get the product **3k** (45.8 mg, 75%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.66 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.20 (m, 4H), 6.01 (br s, 2H), 2.39 (s, 3H).

2-(*p*-Tolylthio)benzonitrile (3l)[10]



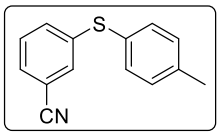
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 100:1) to get the product **3l** (46 mg, 82%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.61 (d, *J* = 7.7 Hz, 1H), 7.46 – 7.30 (m, 3H), 7.30 – 7.16 (m, 3H), 7.03 (d, *J* = 8.1 Hz, 1H), 2.39 (s, 3H).

4-(*p*-Tolylthio)benzonitrile (3m)[10]



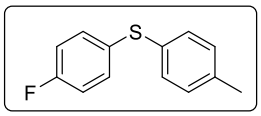
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 10:1) to get the product **3m** (44 mg, 78%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.45 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 2.41 (s, 3H).

3-(*p*-Tolylthio)benzonitrile (3n)[12]



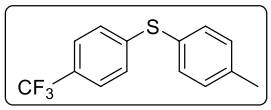
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 10:1) to get the product **3n** (43 mg, 77%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.44 – 7.27 (m, 6H), 7.22 (d, *J* = 7.9 Hz, 2H), 2.40 (s, 3H).

(4-Fluorophenyl)(*p*-tolyl)sulfane (3o)[13]



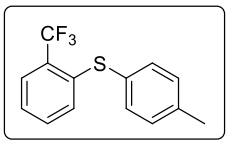
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:toluene 100:1) to get the product **3o** (46.2 mg, 85%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.32 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 7.00 (m, 2H), 2.35 (s, 3H).

***p*-Tolyl(4-(trifluoromethyl)phenyl)sulfane (3p)**[14]



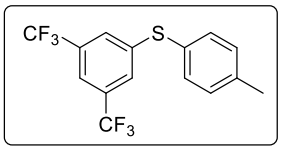
Synthesized according to general procedure starting from the iodide, bromide, or chloride, and in gram-scale following procedure outside the glovebox starting from 4 mmol (1088 mg) of iodide. The product was purified by column chromatography (cyclohexane:ethyl acetate 100:1) to get the product **3p** (61 mg, 91% / 1.005 g, 93%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.21 (m, 4H), 2.39 (s, 3H).

***p*-Tolyl(2-(trifluoromethyl)phenyl)sulfane (3q)**[15]



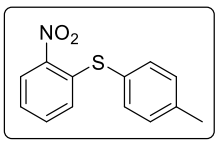
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 100:1) to get the product **3q** (55.6 mg, 83%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 7.7 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.22 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 1H), 2.39 (s, 3H).

(3,5-Bis(trifluoromethyl)phenyl)(*p*-tolyl)sulfane (3r)[10]



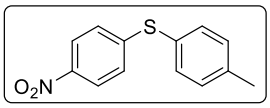
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane) to get the product **3r** (79 mg, 94%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.65 (s, 1H), 7.57 (s, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 2.46 (s, 3H).

(2-Nitrophenyl)(*p*-tolyl)sulfane (3s)[16]



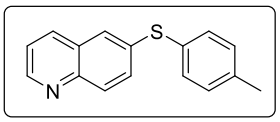
Synthesized according to general procedure, method B. The product was purified by column chromatography (cyclohexane:ethyl acetate 20:1) to get the product **3s** (35.5 mg, 58%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.24 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 7.9 Hz, 2H), 7.39 – 7.25 (m, 3H), 7.21 (t, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 2.45 (s, 3H).

(4-Nitrophenyl)(*p*-tolyl)sulfane (3t)[17]



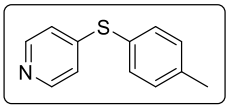
Synthesized according to general procedure, method B. The product was purified by column chromatography (cyclohexane:ethyl acetate 20:1) to get the product **3t** (38.6 mg, 63%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 9.0 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 9.0 Hz, 2H), 2.42 (s, 3H).

6-(*p*-Tolylthio)quinoline (3u)[18]



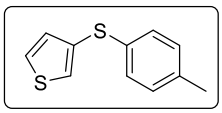
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 10:1) to get the product **3u** (32 mg, 55%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.84 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.12 – 7.88 (m, 2H), 7.69 – 7.48 (m, 2H), 7.48 – 7.30 (m, 3H), 7.19 (d, *J* = 8.2 Hz, 2H), 2.38 (s, 3H).

4-(*p*-Tolylthio)pyridine (3v)[19]



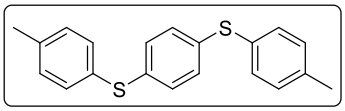
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 10:1) to get the product **3v** (22.2 mg, 44%). Spectroscopic data is in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** 8.31 (d, *J* = 6.2 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 6.91 (d, *J* = 6.2 Hz, 2H), 2.41 (s, 3H).

3-(*p*-Tolylthio)thiophene (3w)[20]



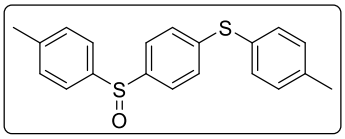
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane) to get the product **3w** (42.4 mg, 83%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.35 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.30 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.03 (dd, *J* = 5.0, 1.2 Hz, 1H), 2.33 (s, 3H).

1,4-Bis(*p*-tolylthio)benzene (3x)[21]



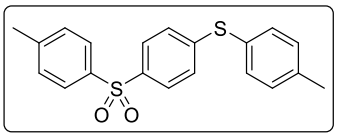
Synthesized according to general procedure, method A starting form iodide **1x,** or from iodide **6c** and adding 2.5 equivalents of the thiol and 3.25 equivalents of NaH. The product was purified by column chromatography (cyclohexane:toluene 100:1) to get the product **3x** (32 mg, 80%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.29 (d, *J* = 8.2 Hz, 4H), 7.18 – 7.10 (m, 8H), 2.34 (s, 3H).

_p_-Tolyl(4-(_p_-tolylsulfinyl)phenyl)sulfane (3y)



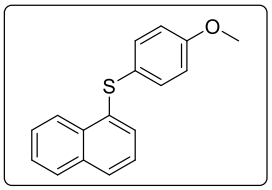
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 10:1) to get the product **3y** (20 mg, 45%). M.p. = 65 – 69 ºC. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.18 (m, 4H), 2.37 (s, 6H).**^{13}C NMR (75 MHz, $CDCl_3$)** δ 143.23 (C), 143.05 (C), 142.62 (C), 141.92 (C), 139.41 (C), 134.42 (CH), 130.75 (CH), 130.31 (CH), 128.68 (C), 128.31 (CH), 125.68 (CH), 125.17 (CH), 21.67 (CH_3), 21.51 (CH_3). **HRMS** (EI^+) Calcd for $C_{20}H_{18}OS_2$ $[M]^+$ 338.0799, Found 338.0810.

_p_-Tolyl(4-tosylphenyl)sulfane (3z)



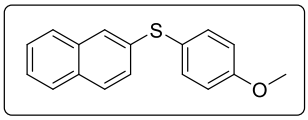
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 10:1) to get the product **3z** (41 mg, 92%). M.p. = 138 – 140 ºC. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 2.39 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 146.93 (C), 144.31 (C), 140.08 (C), 139.16 (C), 138.62 (C), 135.12 (CH), 130.95 (CH), 130.16 (CH), 128.17 (CH), 127.85 (CH), 127.33 (C), 127.03 (CH), 21.81 (CH_3), 21.56 (CH_3). **HRMS** (EI^+) Calcd for $C_{20}H_{18}O_2S_2$ $[M]^+$ 354.0748, Found 354.0763.

(4-Methoxyphenyl)(naphthalen-1-yl)sulfane (3aa)[22]



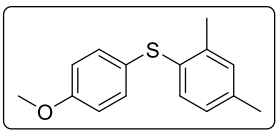
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 100:1) to get the product **3aa** (41 mg, 62%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.45 – 8.32 (m, 1H), 7.86 (m, 1H), 7.74 (dd, *J* = 6.6, 2.8 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.41 – 7.30 (m, 4H), 6.87 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H).

(4-Methoxyphenyl)(naphthalen-2-yl)sulfane (3ab)[10]



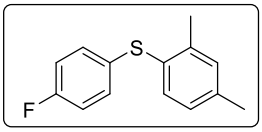
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 100:1) to get the product **3ab** (47 mg, 70%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.72 (m, 3H), 7.60 (s, 1H), 7.52 – 7.34 (m, 4H), 7.30 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H).

(2,4-Dimethylphenyl)(4-methoxyphenyl)sulfane (3ac)[23]



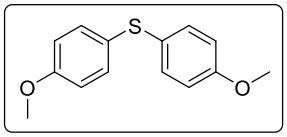
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 100:1) to get the product **3ac** (34 mg, 56%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.26 (d, *J* = 8.6 Hz, 2H), 7.03 (m, 2H), 6.91 (m, 1H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 2.35 (s, 3H), 2.30 (s, 3H).

(2,4-Dimethylphenyl)(4-fluorophenyl)sulfane (3ad)[24]



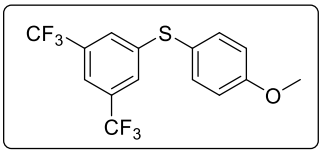
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 100:1) to get the product **3ad** (42.6 mg, 70%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.25 – 7.12 (m, 3H), 7.09 (m, 1H), 7.02 – 6.93 (m, 3H), 2.34 (s, 3H), 2.33 (s, 3H).

Bis(4-methoxyphenyl)sulfane (3ae)[8]



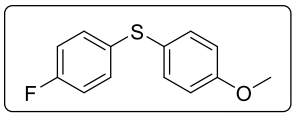
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 10:1) to get the product **3ae** (31 mg, 50%) as a 2.5:1 mixture with the *p*-Methoxyphenyl disulfide. Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.32 (d, *J* = 8.9 Hz, 4H), 6.88 (d, *J* = 8.8 Hz, 4H), 3.83 (s, 3H).

(3,5-Bis(trifluoromethyl)phenyl)(4-methoxyphenyl)sulfane (3af)[25]



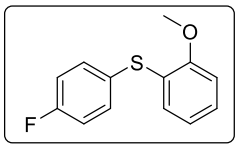
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 100:1) to get the product **3af** (50 mg, 57%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.65 (s, 1H), 7.57 (s, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 2.46 (s, 3H).

(4-Fluorophenyl)(4-methoxyphenyl)sulfane (3ag)[8]



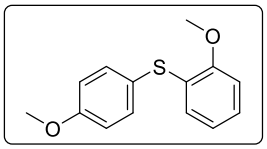
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 20:1) to get the product **3ag** (44 mg, 75%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.46 – 7.31 (m, 2H), 7.31 – 7.12 (m, 2H), 7.07 – 6.78 (m, 4H), 3.81 (s, 3H).

(4-Fluorophenyl)(2-methoxyphenyl)sulfane (3ah)[8]



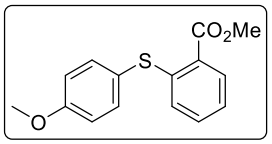
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 20:1) to get the product **3ah** (37 mg, 63%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.42 (m, 2H), 7.26 (m, 1H), 7.14 – 6.98 (m, 3H), 6.91 (m, 2H), 3.92 (s, 3H).

(2-Methoxyphenyl)(4-methoxyphenyl)sulfane (3ai)[26]



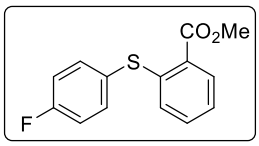
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 100:1) to get the product **3ai** (30.5 mg, 50%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.44 (d, *J* = 8.7 Hz, 2H), 7.16 – 7.01 (m, 1H), 6.95 – 6.67 (m, 5H), 3.91 (s, 3H), 3.83 (s, 3H).

Methyl 2-((4-methoxyphenyl)thio)benzoate (3aj)[27]



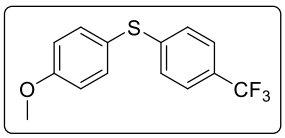
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 4:1) to get the product **3aj** (30 mg, 43%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.98 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.26 – 7.18 (m, 1H), 7.12 – 7.05 (m, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.74 (dd, *J* = 8.2, 1.0 Hz, 1H), 3.96 (s, 3H), 3.86 (s, 3H).

Methyl 2-((4-fluorophenyl)thio)benzoate (3ak)[8]



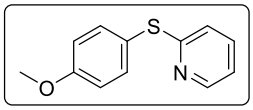
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 20:1) to get the product **3ak** (44 mg, 73%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.99 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.30 – 7.20 (m, 1H), 7.20 – 7.07 (m, 3H), 6.75 (d, *J* = 8.0, 1H), 3.96 (s, 3H).

(4-Methoxyphenyl)(4-(trifluoromethyl)phenyl)sulfane (3al)[28]



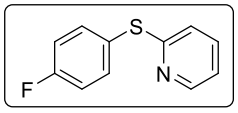
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 20:1) to get the product **3al** (53 mg, 76%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.50 (m, 4H), 7.18 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H).

2-((4-Methoxyphenyl)thio)pyridine (3am)[22]



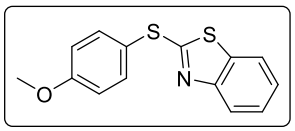
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 20:1) to get the product **3am** (32 mg, 60%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.44 – 8.35 (m, 2H), 7.53 (d, *J* = 8.9 Hz, 1H), 7.42 (td, *J* = 7.9, 1.9 Hz, 2H), 7.00 – 6.91 (m, 3H), 6.78 (d, *J* = 8.1 Hz, 1H), 3.84 (s, 3H).

2-((4-Fluorophenyl)thio)pyridine (3an)[29]



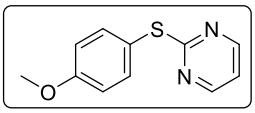
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:toluene 100:1) to get the product **3an** (43 mg, 79%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.41 (dd, *J* = 4.8, 0.9 Hz, 1H), 7.64 – 7.53 (m, 2H), 7.46 (td, *J* = 7.8, 1.9 Hz, 1H), 7.11 (m, 2H), 6.99 (ddd, *J* = 7.4, 4.9, 0.8 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H).

2-((4-Methoxyphenyl)thio)benzo[d]thiazole (3ao)[30]



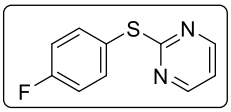
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 20:1) to get the product **3ao** (44 mg, 65%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 8.1 Hz, 1H), 7.64 (m, 3H), 7.38 (m, 1H), 7.24 (m, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H).

2-((4-Methoxyphenyl)thio)pyrimidine (3ap)[31]



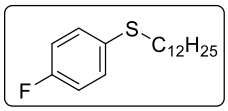
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 10:1) to get the product **3ap** (34.2 mg, 63%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.47 (d, *J* = 4.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.00 – 6.91 (m, 3H), 3.84 (s, 3H).

2-((4-Fluorophenyl)thio)pyrimidine (3aq)[32]



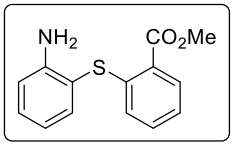
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 20:1) to get the product **3aq** (40 mg, 78%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.49 (d, *J* = 4.8 Hz, 2H), 7.66 – 7.52 (m, 2H), 7.13 (m, 2H), 6.98 (t, *J* = 4.9 Hz, 1H).

Dodecyl(4-fluorophenyl)sulfane (3ar)[33]



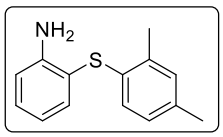
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 100:1) to get the product **3ar** (37 mg, 51%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.40 – 7.27 (m, 2H), 7.06 – 6.91 (m, 2H), 2.90 – 2.81 (m, 2H), 1.76 – 1.51 (m, 3H), 1.52 – 1.16 (m, 22H), 0.88 (t, *J* = 6.7 Hz, 3H).

Methyl 2-((2-aminophenyl)thio)benzoate (3as)[34]



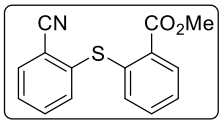
Synthesized according to general procedure, method B. The product was purified by column chromatography (cyclohexane:ethyl acetate 20:1) to get the product **3as** (56.3 mg, 77%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.02 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.46 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.34 – 7.22 (m, 2H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.90 – 6.71 (m, 3H), 3.97 (s, 3H), 3.80 (br, 2H).

2-((2,4-Dimethylphenyl)thio)aniline (3at)[35]



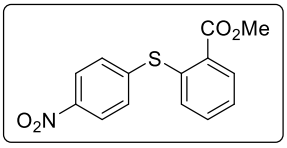
Synthesized according to general procedure, method B. The product was purified by column chromatography (cyclohexane:ethyl acetate 50:1) to get the product **3at** (35 mg, 65%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.38 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.29 – 7.19 (m, 1H), 7.02 (s, 1H), 6.90 – 6.65 (m, 4H), 4.14 (br, 2H), 2.41 (s, 3H), 2.28 (s, 3H).

Methyl 2-((2-cyanophenyl)thio)benzoate (3au)



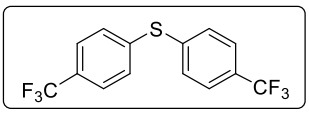
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 10:1) to get the product **3au** (52 mg, 78%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 7.7, 1H), 7.78 (d, *J* = 7.3 Hz, 1H), 7.68 – 7.55 (m, 2H), 7.55 – 7.43 (m, 1H), 7.40 – 7.18 (m, 2H), 6.82 (d, *J* = 8.0 Hz, 1H), 3.95 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 166.93 (CO), 139.60 (C), 138.31 (C), 136.12 (CH), 134.61 (CH), 133.68 (CH), 132.86 (CH), 131.54 (CH), 129.29 (CH), 128.93 (C), 128.91 (CH), 126.10 (CH), 118.45 (C), 117.06 (CN), 52.61 (CH_3). **HRMS** (EI^+) Calcd for $C_{15}H_{11}NO_2S$ $[M]^+$ 269.0510, Found 269.0504.

methyl 2-((4-nitrophenyl)thio)benzoate (3av)[36]



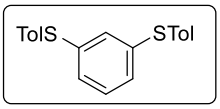
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 20:1) to get the product **3av** (35 mg, 50%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.98 (d, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.39 (m, 2H), 7.21 (d, *J* = 7.8 Hz, 1H), 3.92 (s, 3H).

bis(4-(trifluoromethyl)phenyl)sulfane (3aw)[37]



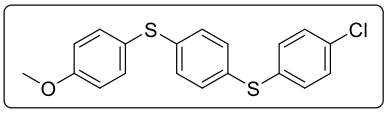
Synthesized according to general procedure, method A. The product was purified by column chromatography (cyclohexane:ethyl acetate 100:1) to get the product **3aw** (66 mg, 83%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.59 (d, *J* = 8.2 Hz, 4H), 7.45 (d, *J* = 8.2 Hz, 4H).

1,3-Bis(*p*-tolylthio)benzene (7b)[21]



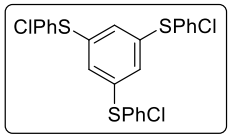
Synthesized according to general procedure, method A, but adding 2.5 equivalents of the thiol and 3.25 equivalents of NaH. The product was purified by column chromatography (cyclohexane) to get the product **7b** (44 mg, 73%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.29 (d, *J* = 8.0 Hz, 4H), 7.15 – 7.08 (m, 6H), 7.06 – 6.97 (m, 2H), 2.36 (s, 6H).

(4-Chlorophenyl)(4-((4-methoxyphenyl)thio)phenyl)sulfane (7c)



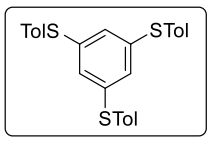
Synthesized according to general procedure, method A, but adding 2.5 equivalents of the thiol and 3.25 equivalents of NaH. The product was purified by column chromatography (cyclohexane:ethyl acetate 20:1) to get the product **7c** (59 mg, 66%). In the ^{13}C-NMR spectra an undetermined subproduct which could not be purified was observed. M.p. = 86 – 90 ºC. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.52 – 7.41 (m, 2H), 7.35 – 7.18 (m, 6H), 7.11 (d, *J* = 7.4 Hz, 2H), 6.96 (d, *J* = 7.7 Hz, 2H), 3.87 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 160.48 (CH_3), 139.36 (C) 136.15 (2 CH), 134.56 (C), 132.45 (2 CH), 132.01 (C), 131.87 (2 CH), 129.63 (C), 129.58 (2 CH), 128.65 (2 CH), 123.48 (C), 115.45 (2CH). **HRMS** (EI^+) Calcd for $C_{19}H_{15}ClOS_2$ $[M]^+$ 358.0253, Found 358.0262.

1,3,5-Tris((4-chlorophenyl)thio)benzene (7d)



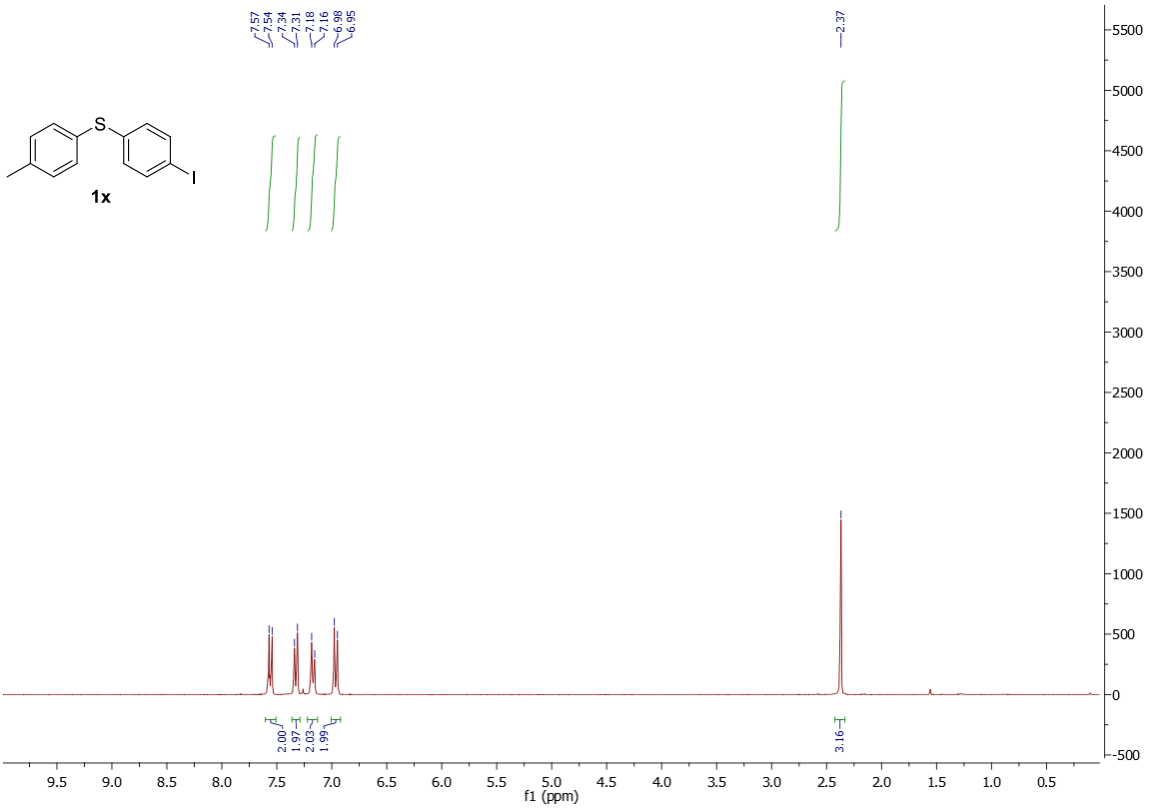
Synthesized according to general procedure, method A, but adding 3.5 equivalents of the thiol and 4.2 equivalents of NaH. The product was purified by column chromatography (cyclohexane:toluene 100:1) to get the product **7d** (30 mg, 33%). M.p. = 107 – 110 ºC. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.33 – 7.27 (m, 12H), 6.83 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 139.52 (C), 134.92 (C), 134.51 (CH), 131.81 (C), 129.93 (CH), 127.08 (CH). **HRMS** ($MALDI^+$) Calcd for $C_{24}H_{15}Cl_3S_3$ $[M]^+$ 503.9401, Found 503.9383.

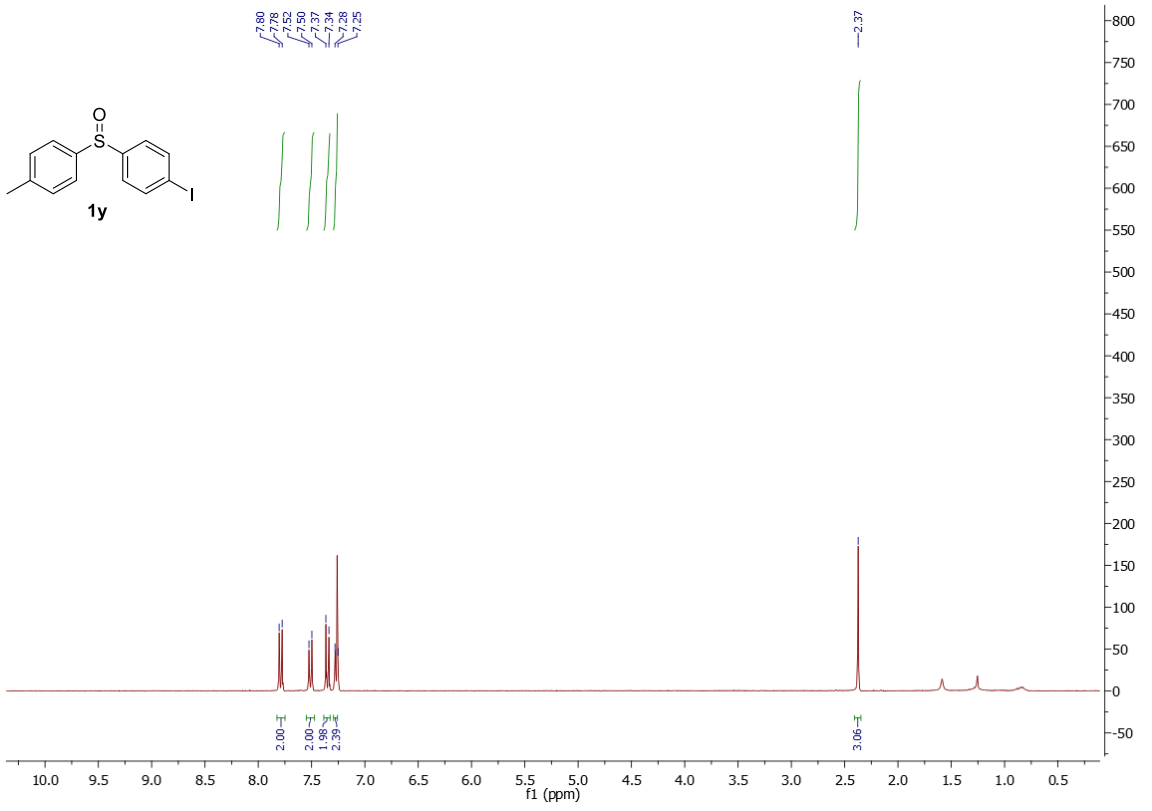
1,3,5-Tris(*p*-tolylthio)benzene (7e)[38]

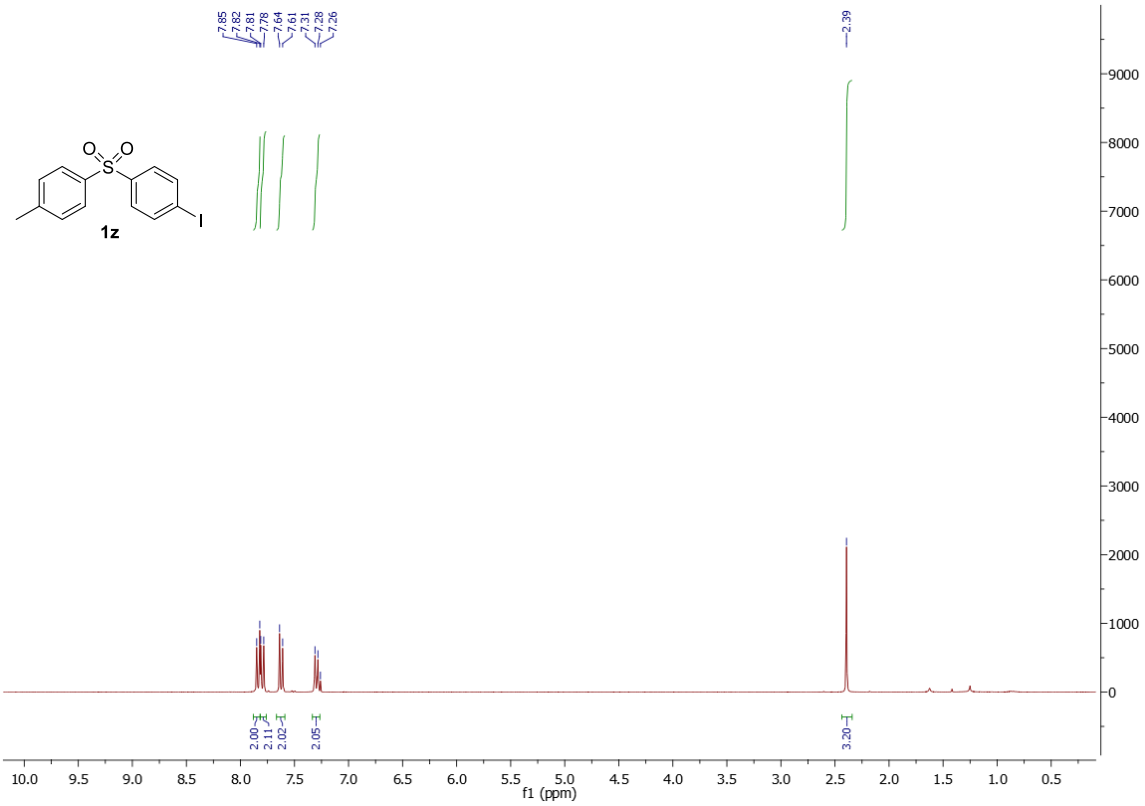


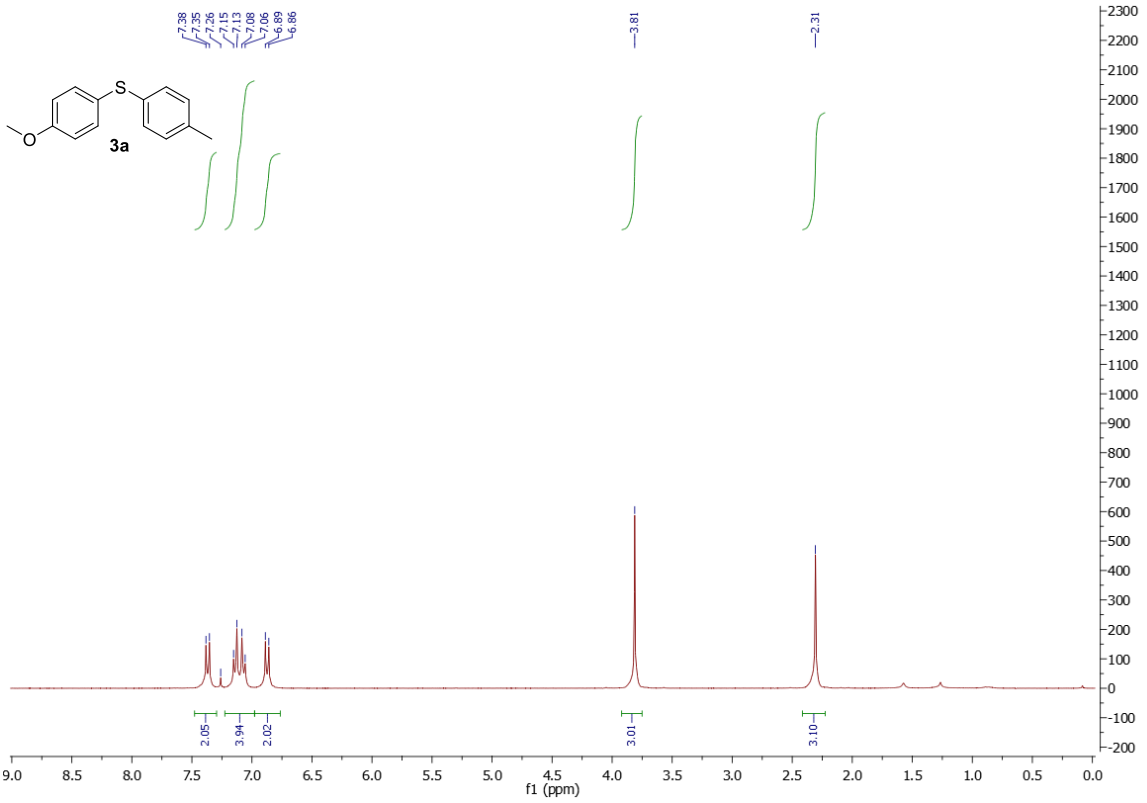
Synthesized according to general procedure, method A, but adding 4.5 equivalents of the thiol and 5.4 equivalents of NaH. The product was purified by column chromatography (cyclohexane:toluene 100:1) to get the product **7e** (41 mg, 47%). Spectroscopic data were in accordance with the literature. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.28 (d, *J* = 8.1 Hz, 6H), 7.14 (d, *J* = 8.0 Hz, 6H), 6.79 (s, 3H), 2.40 (s, 9H).

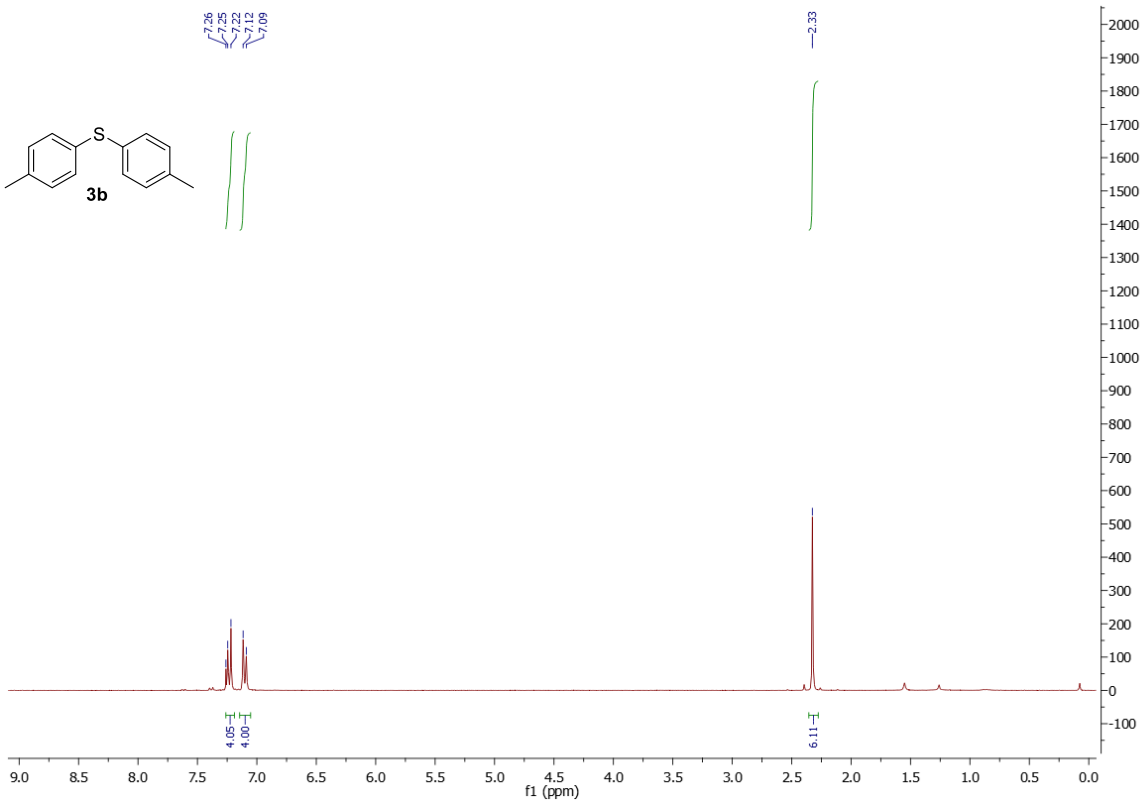
6. NMR Spectroscopic data






7.85
7.82
7.81
7.78
7.64
7.61
7.31
7.28
7.26
2.39
1z
2.00
2.11
2.02
2.05
3.20
f1 (ppm)


7.38
7.35
7.26
7.15
7.13
7.08
7.06
6.89
6.86
3.81
2.31
3a
2.05
3.94
2.02
3.01
3.10
f1 (ppm)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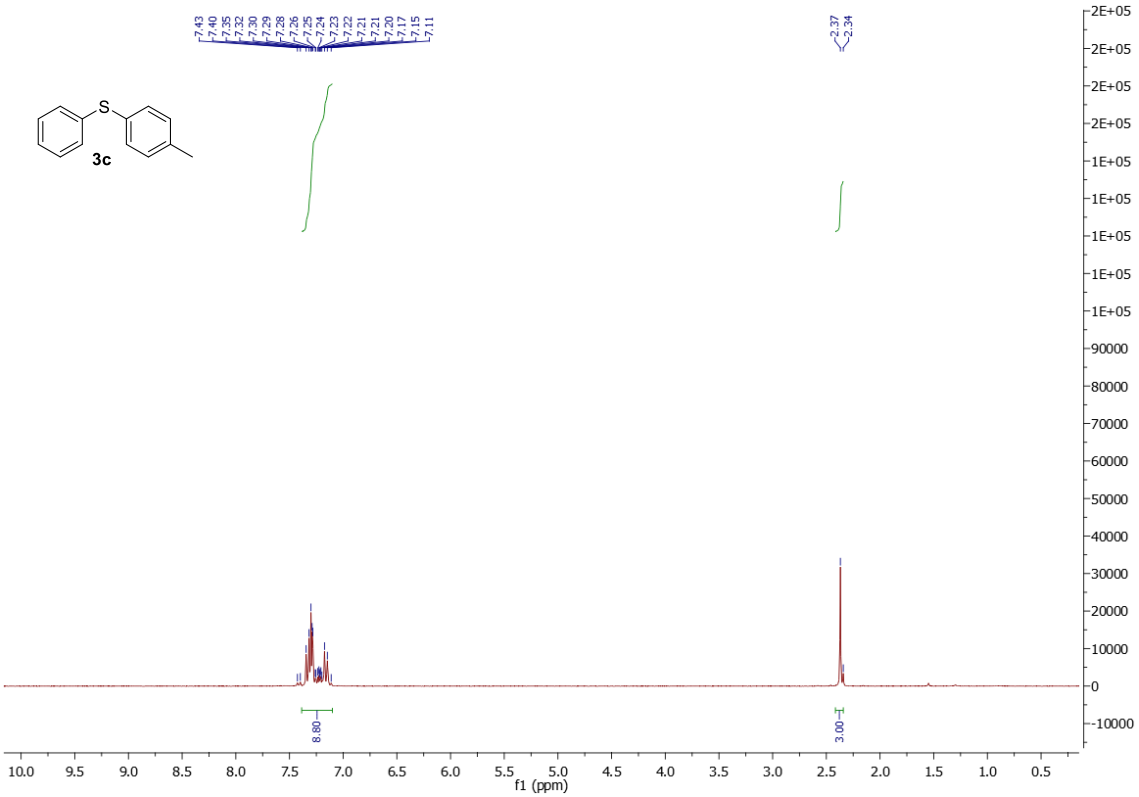
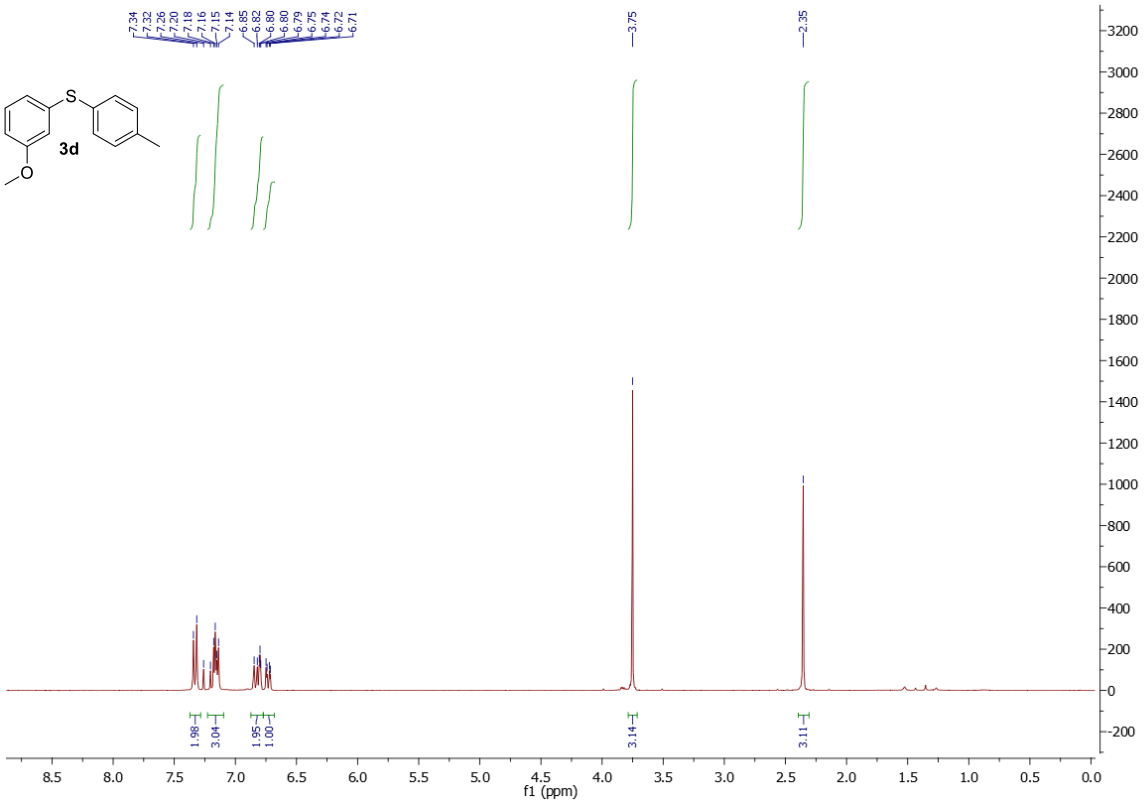
7.25
7.22
7.12
7.09
2.33
S
3b
4.05
4.00
6.11
f1 (ppm)


7.43
7.40
7.35
7.32
7.30
7.29
7.28
7.26
7.25
7.24
7.23
7.22
7.21
7.21
7.20
7.17
7.15
7.11
2.37
2.34
S
3c
8.80
3.00
f1 (ppm)


3d
S
O
7.34
7.32
7.26
7.20
7.18
7.16
7.15
7.14
6.85
6.82
6.80
6.80
6.79
6.75
6.74
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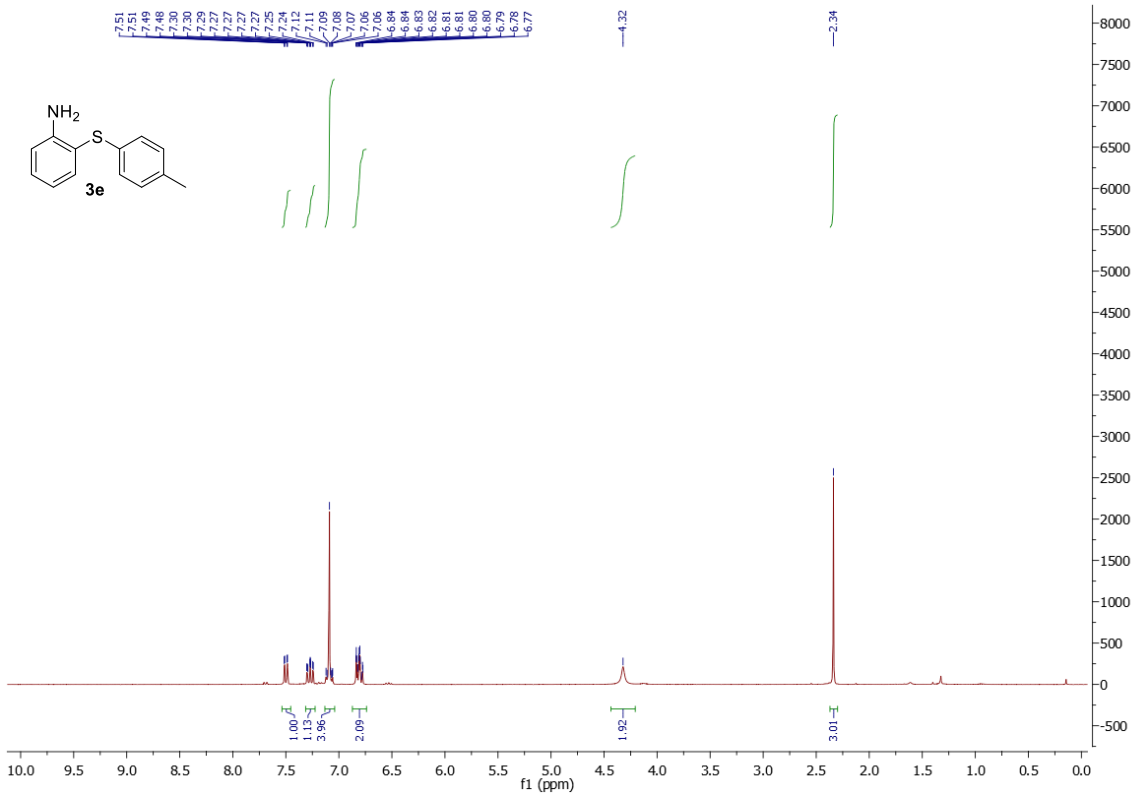
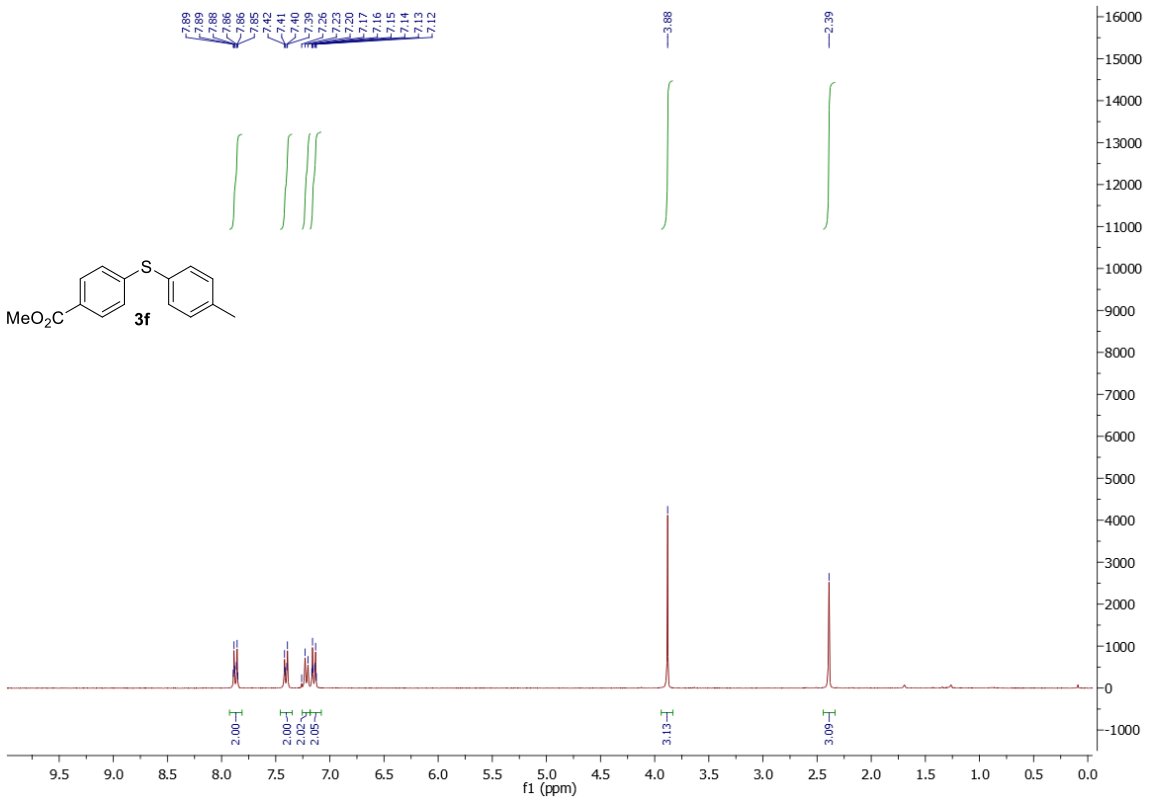
3.04
1.95
1.00
3.14
3.11
f1 (ppm)


3e
NH2
S
7.51
7.51
7.49
7.48
7.30
7.30
7.29
7.27
7.27
7.27
7.25
7.24
7.12
7.11
7.09
7.08
7.07
7.06
7.06
6.84
6.84
6.83
6.82
6.81
6.81
6.80
6.80
6.79
6.78
6.77
4.32
2.34
1.00
1.13
3.96
2.09
1.92
3.01
f1 (ppm)


7.89
7.89
7.88
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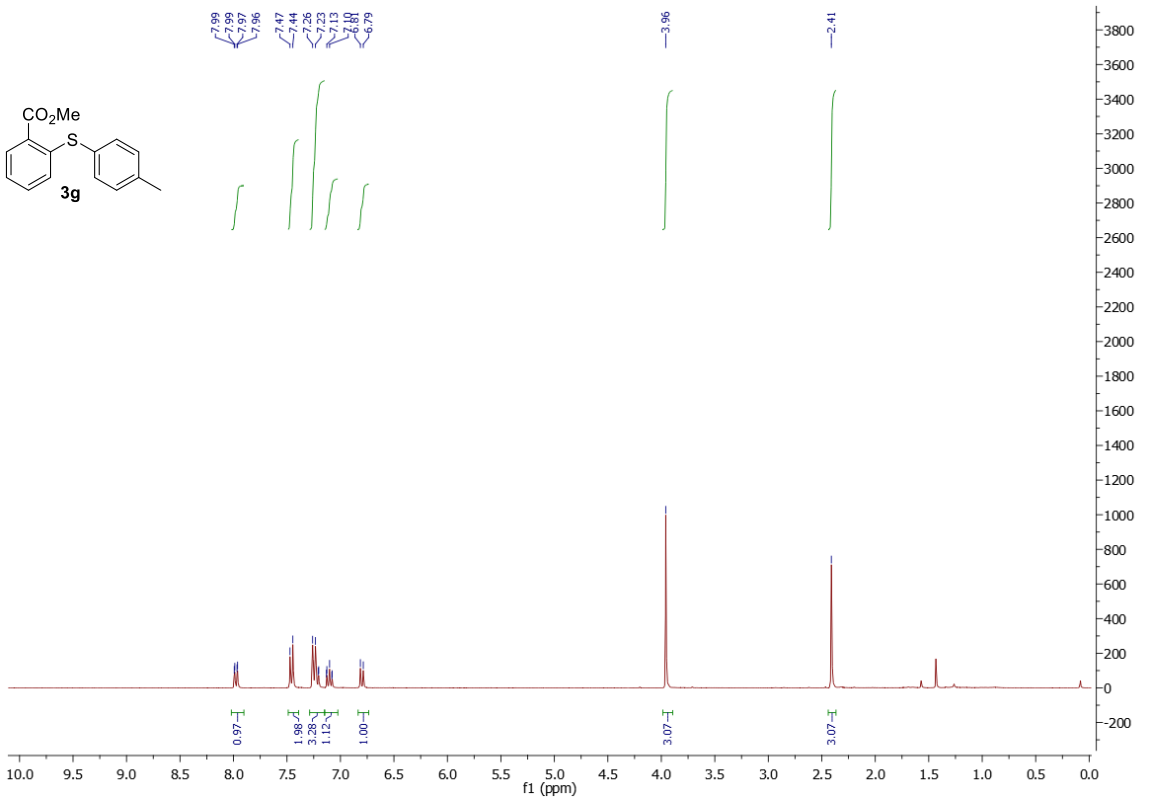
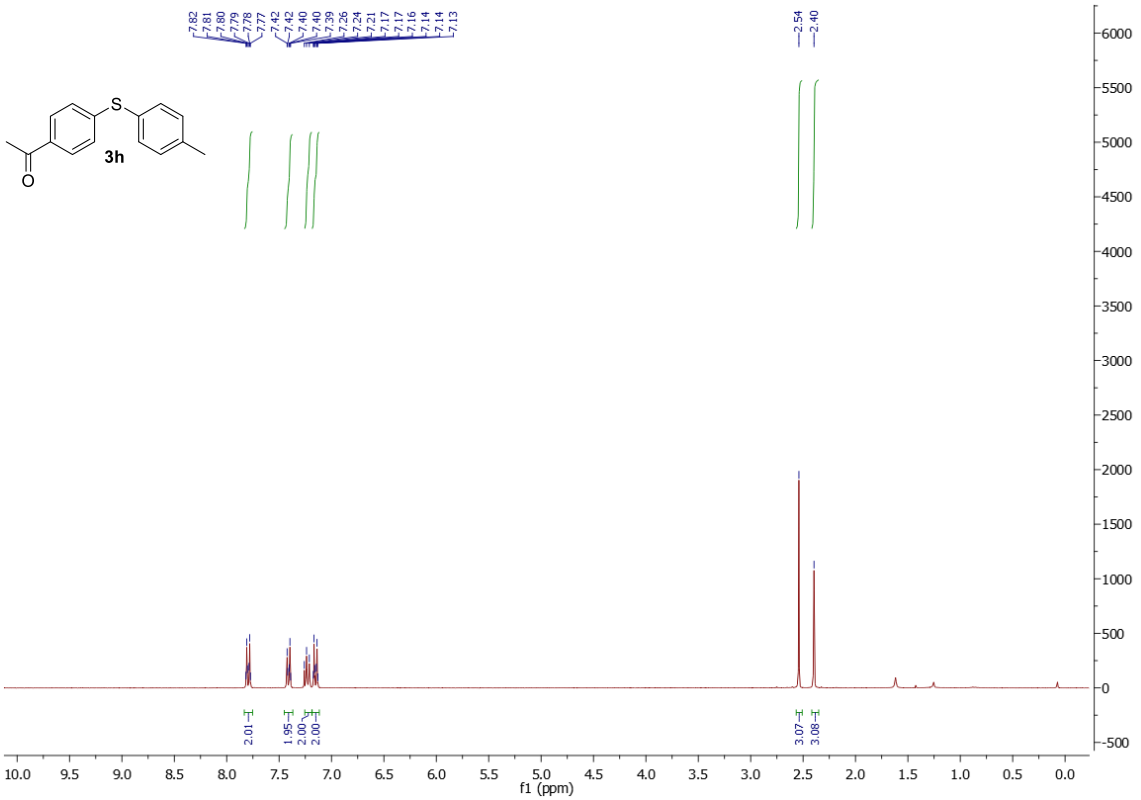
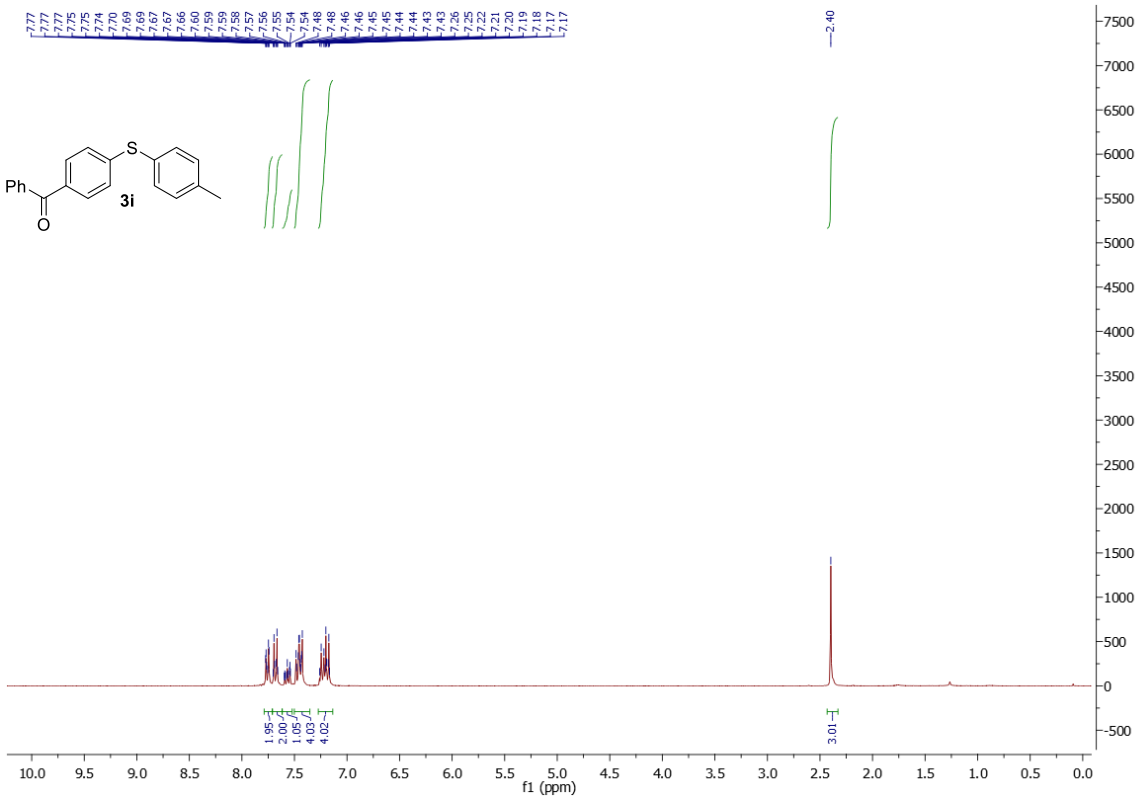
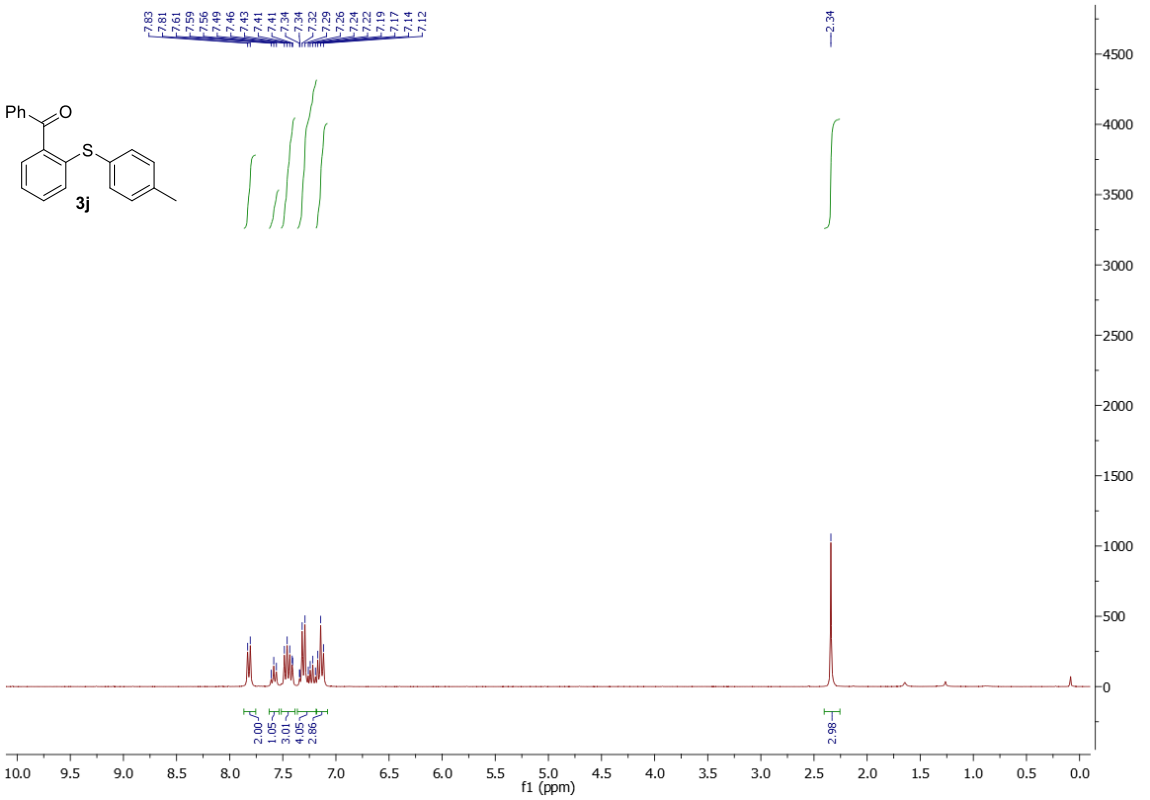
7.86
7.85
7.42
7.41
7.40
7.39
7.26
7.23
7.20
7.17
7.16
7.15
7.14
7.13
7.12
3.88
2.39
MeO2C
S
3f
2.00
2.00
2.02
2.05
3.13
3.09
f1 (ppm)


7.99
7.99
7.97
7.96
7.47
7.44
7.26
7.23
7.13
7.10
6.81
6.79
3.96
2.41
CO2Me
S
3g
0.97
1.98
3.28
1.12
1.00
3.07
3.07
f1 (ppm)


3h
f1 (ppm)


3i
f1 (ppm)


7.83
7.81
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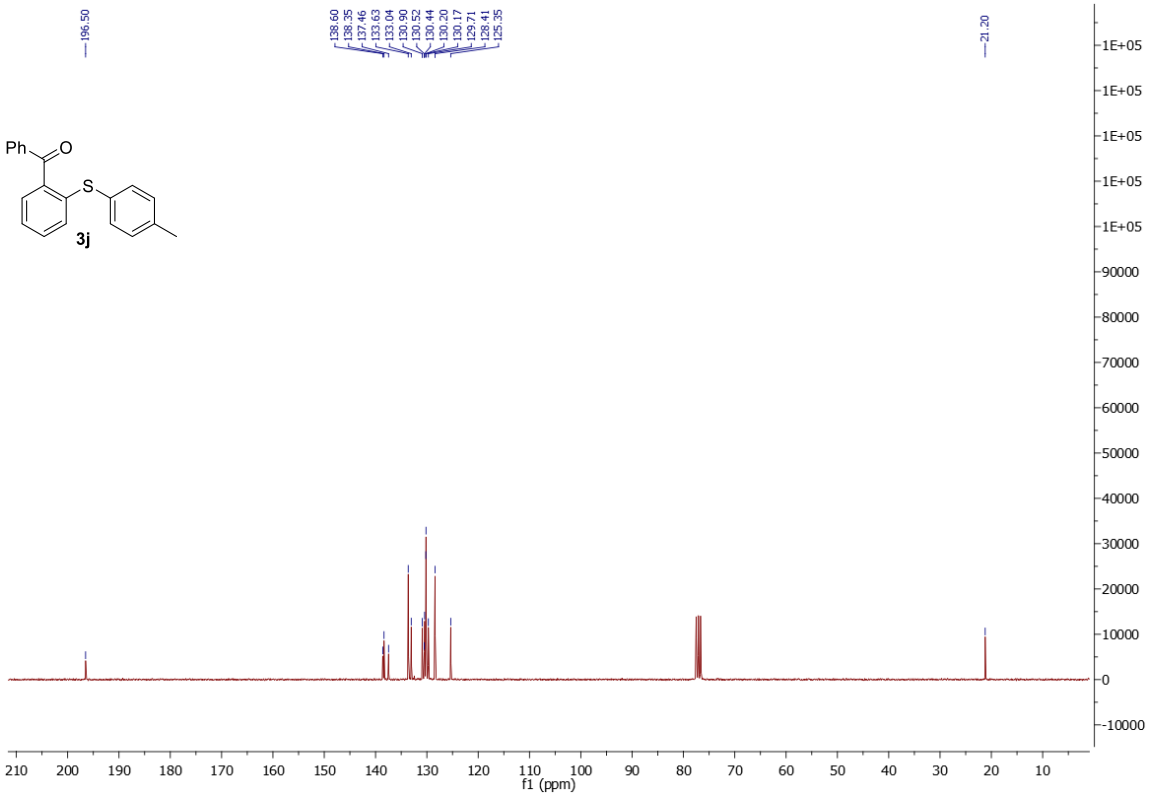
7.59
7.56
7.49
7.46
7.43
7.41
7.41
7.34
7.34
7.32
7.29
7.26
7.24
7.22
7.19
7.17
7.14
7.12
2.34
Ph
O
S
3j
2.00
1.05
3.01
4.05
2.86
2.98
f1 (ppm)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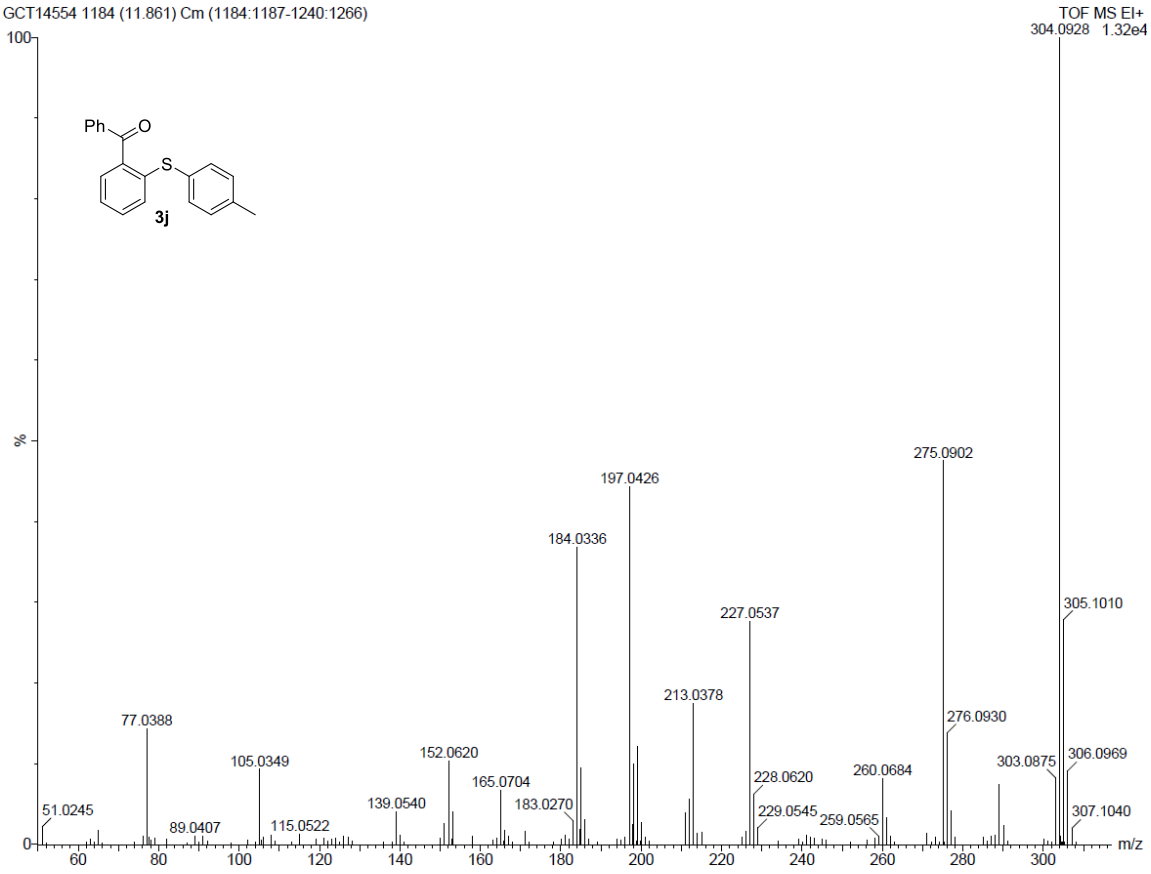
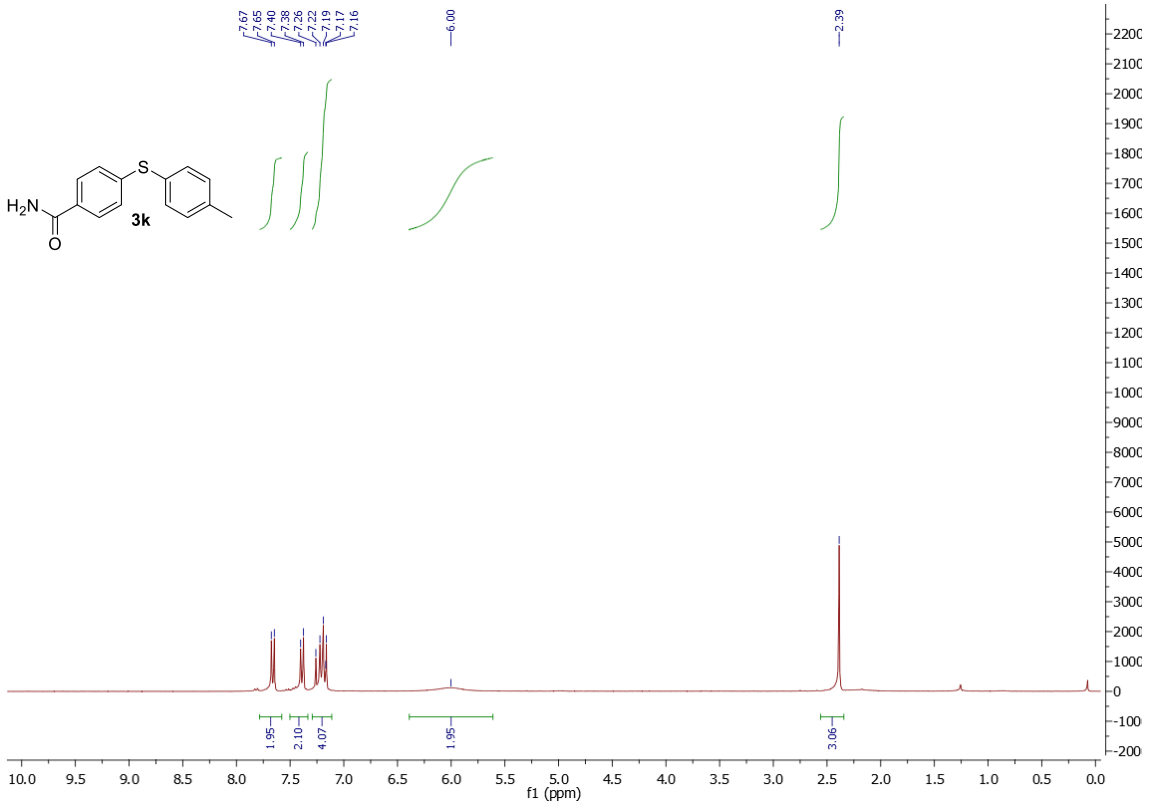
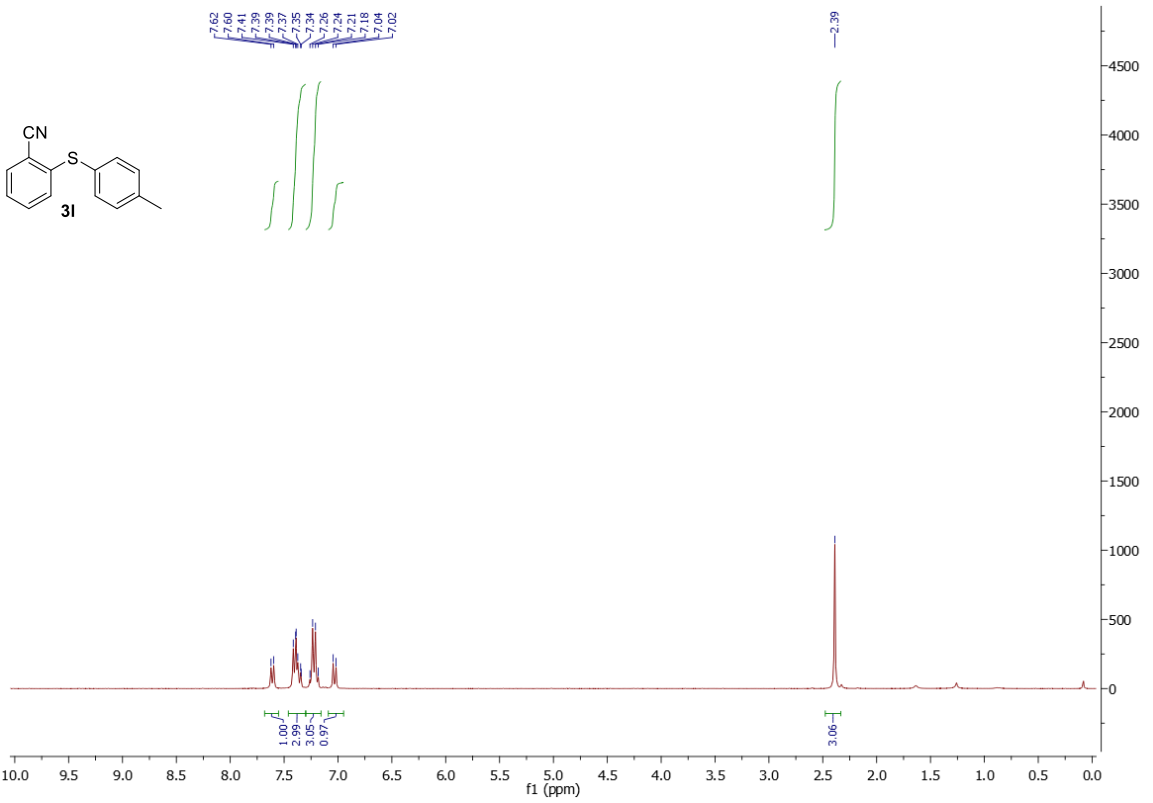
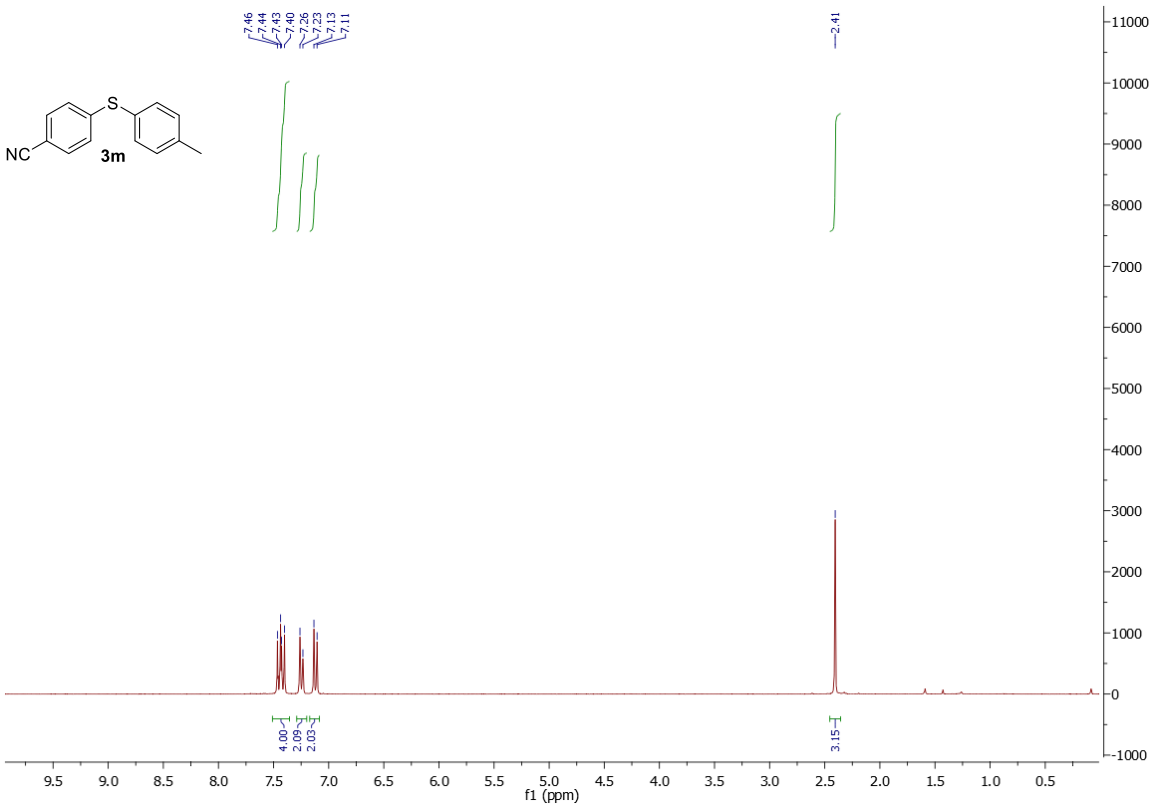
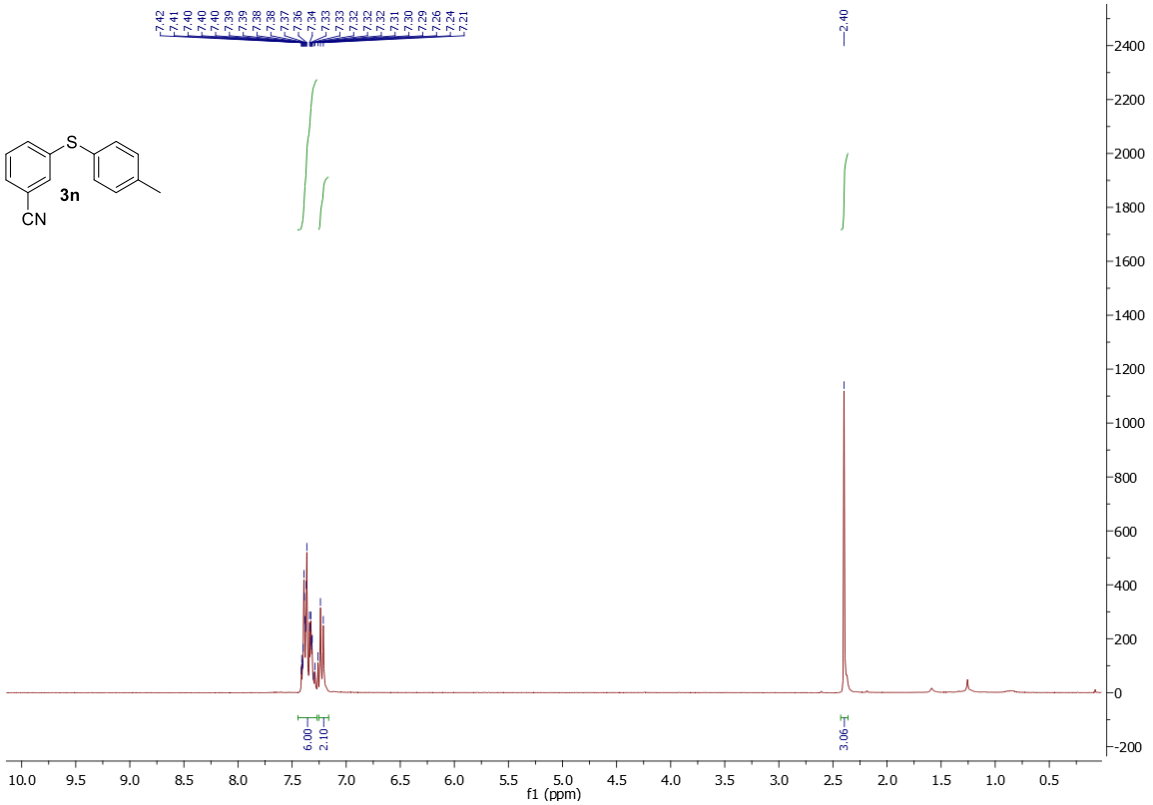
138.60
138.35
137.46
133.63
133.04
130.90
130.52
130.44
130.20
130.17
129.71
128.41
125.35
21.20
Ph
O
S
3j
f1 (ppm)


GCT14554 1184 (11.861) Cm (1184:1187-1240:1266)
TOF MS EI+
304.0928 1.32e4
100
%
0
Ph
O
S
3j
275.0902
197.0426
184.0336
305.1010
227.0537
213.0378
77.0388
276.0930
105.0349
152.0620
303.0875
306.0969
165.0704
228.0620
260.0684
139.0540
183.0270
229.0545
307.1040
51.0245
89.0407
115.0522
259.0565
60
80
100
120
140
160
180
200
220
240
260
280
300
m/z


7.67
7.65
7.40
7.38
7.26
7.22
7.19
7.17
7.16
6.00
2.39
H2N
O
S
3k
1.95
2.10
4.07
1.95
3.06
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)


CN
S
3l
7.62
7.60
7.41
7.39
7.39
7.37
7.35
7.34
7.26
7.24
7.21
7.18
7.04
7.02
2.39
1.00
2.99
3.05
0.97
3.06
f1 (ppm)


S
NC
3m
7.46
7.44
7.43
7.40
7.26
7.23
7.13
7.11
2.41
4.00
2.09
2.03
3.15
f1 (ppm)


3n
CN
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7.39
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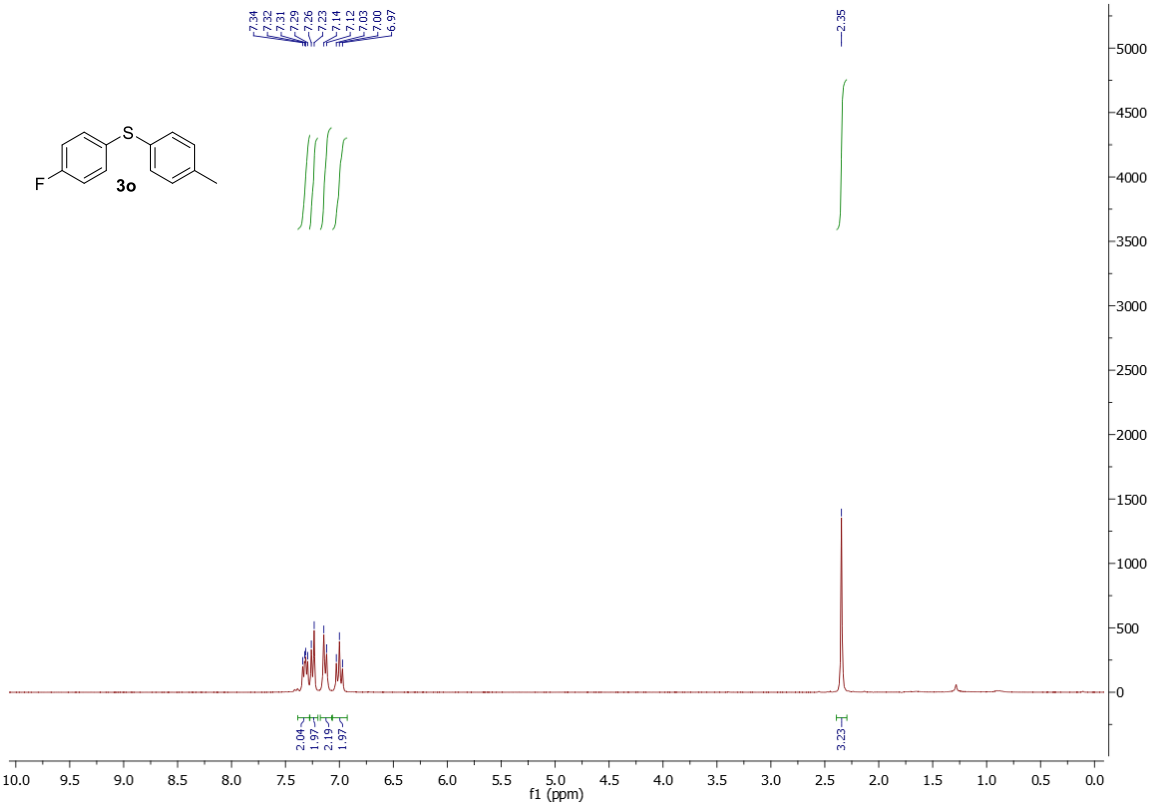
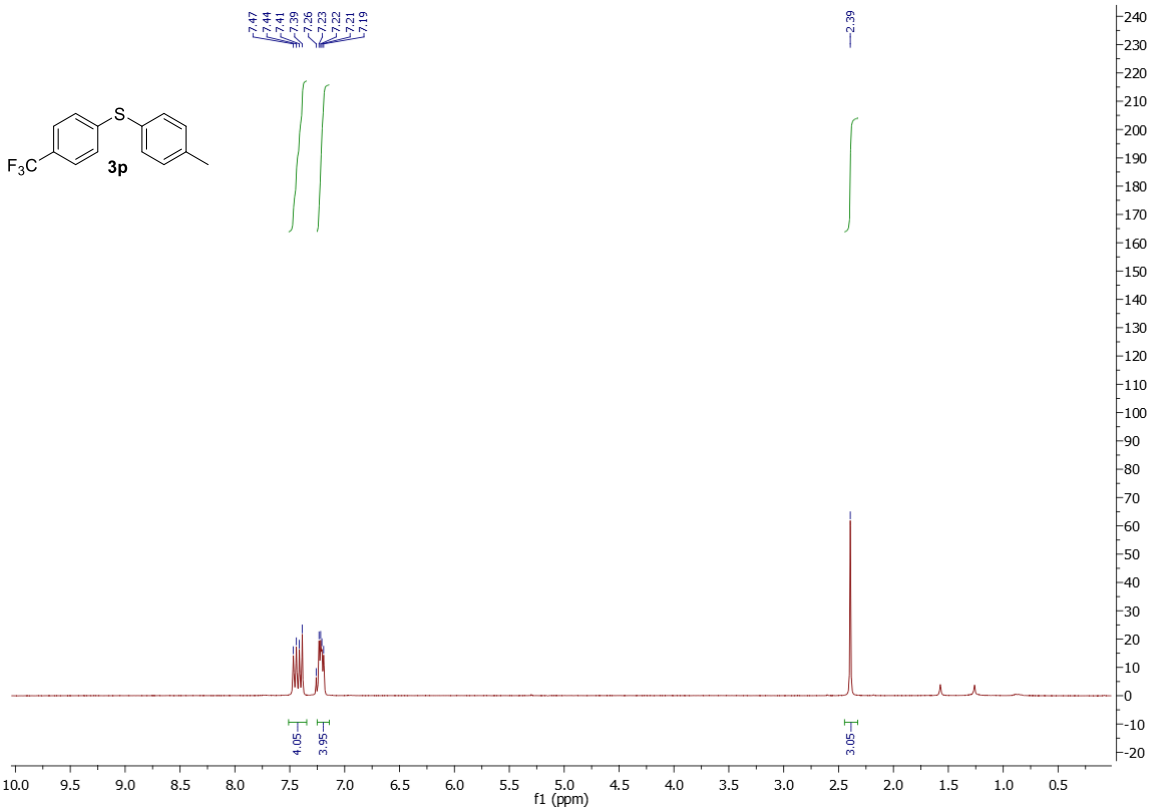
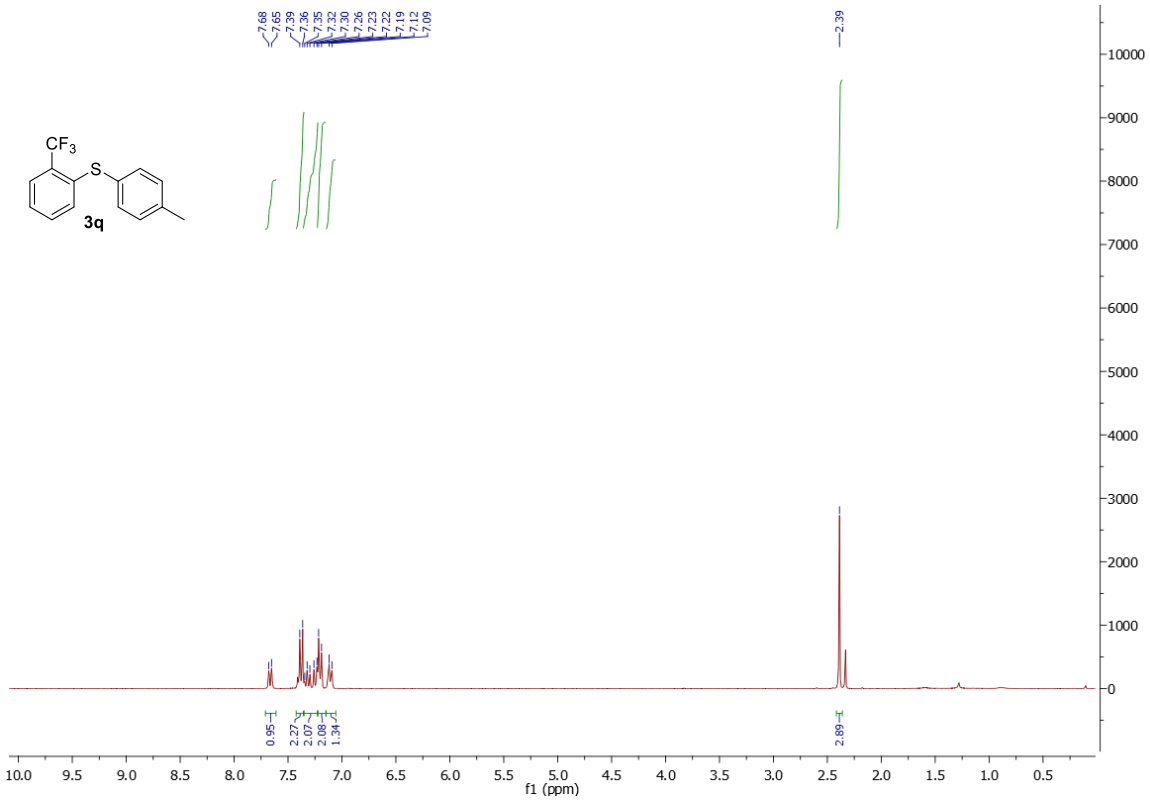
7.38
7.37
7.36
7.34
7.33
7.33
7.32
7.32
7.32
7.31
7.30
7.29
7.26
7.24
7.21
2.40
6.00
2.10
3.06
f1 (ppm)


3o
F
7.34
7.32
7.31
7.29
7.26
7.23
7.14
7.12
7.03
7.00
6.97
2.35
2.04
1.97
2.19
1.97
3.23
f1 (ppm)


7.47
7.44
7.41
7.39
7.26
7.23
7.22
7.21
7.19
2.39
S
F3C
3p
4.05
3.95
3.05
f1 (ppm)


7.68
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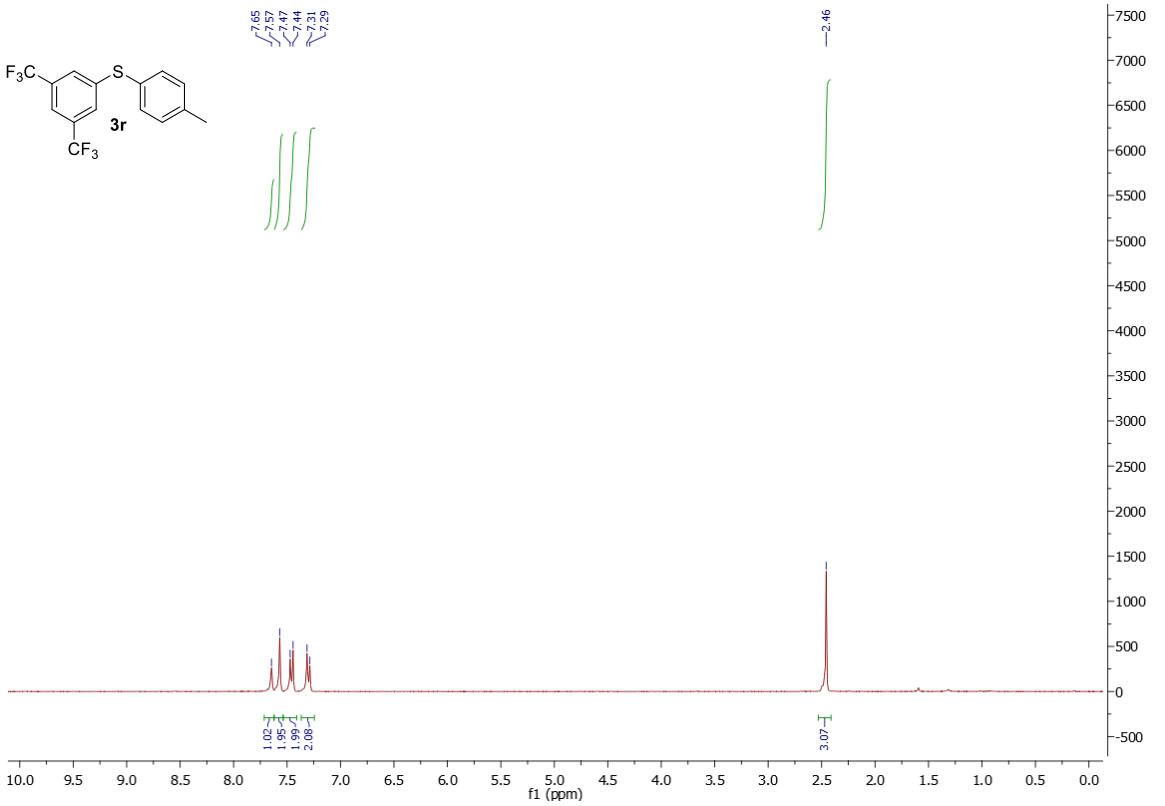
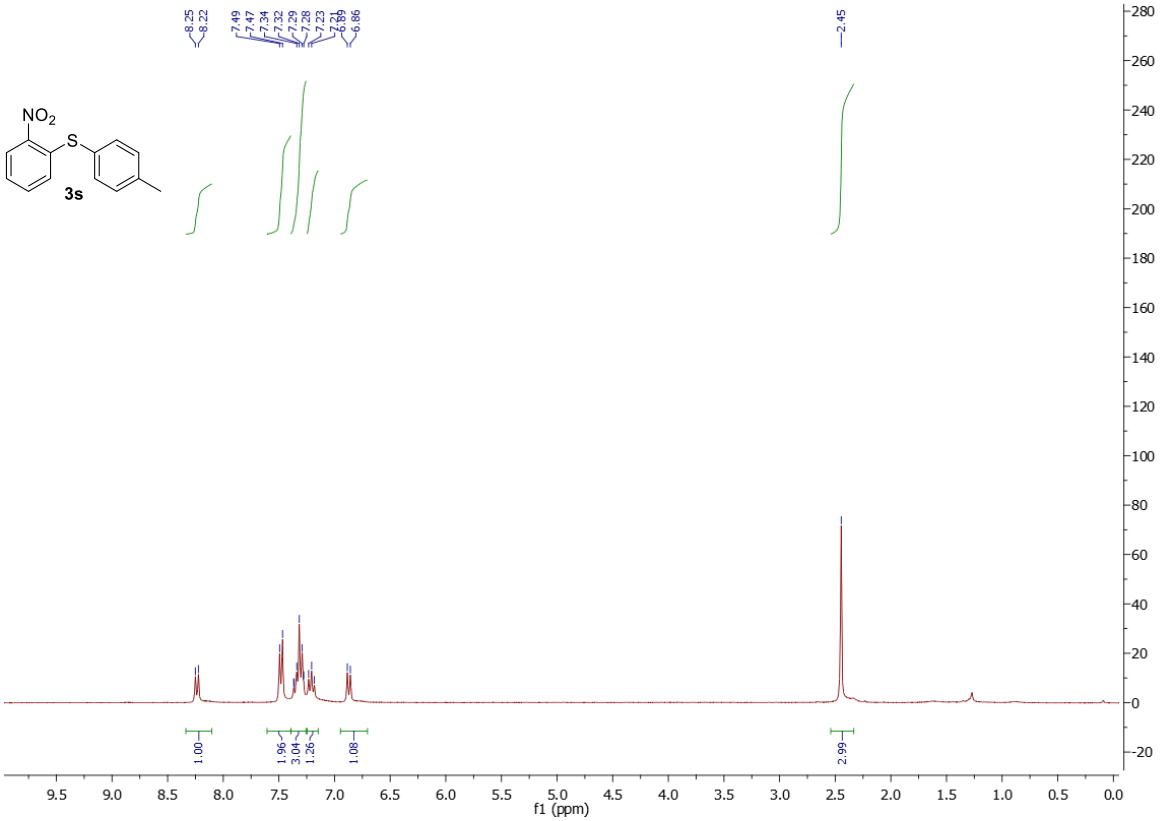
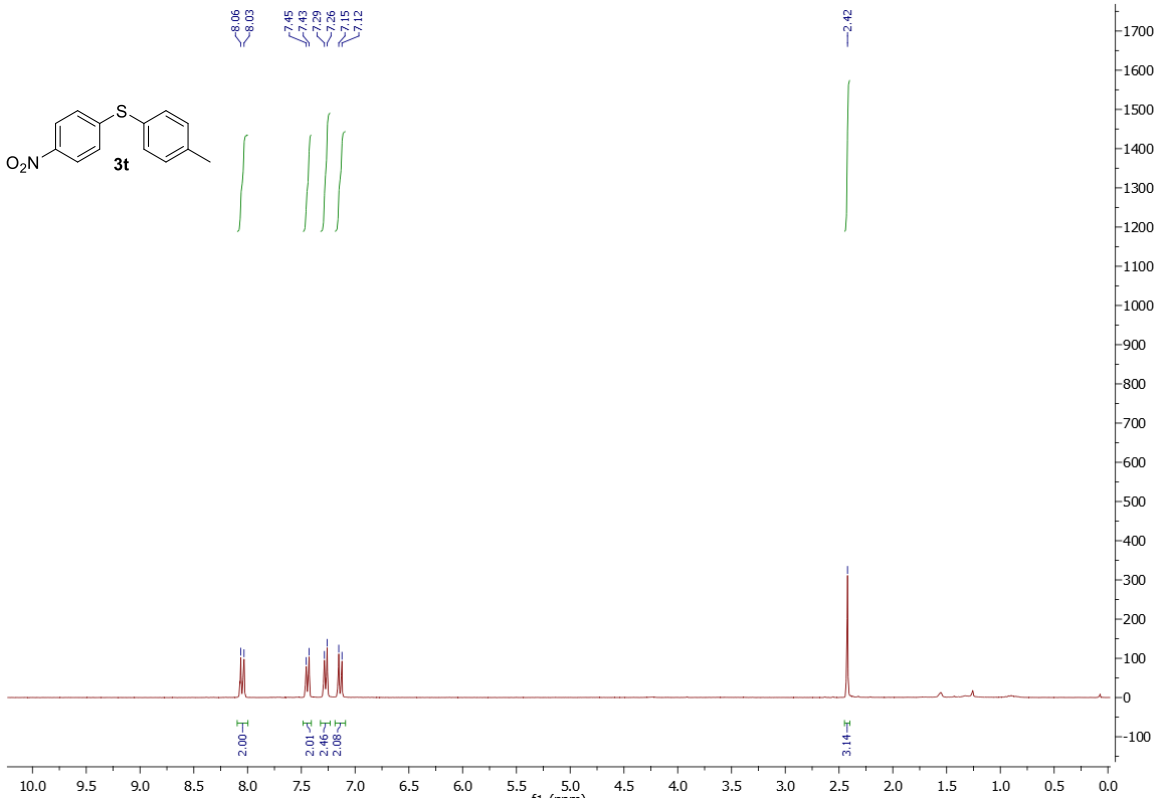
7.32
7.30
7.26
7.23
7.22
7.19
7.12
7.09
2.39
CF3
S
3q
0.95
2.27
2.07
2.08
1.34
2.89
f1 (ppm)


F3C
S
CF3
3r
7.65
7.57
7.47
7.44
7.31
7.29
2.46
1.02
1.95
1.99
2.08
3.07
f1 (ppm)


NO2
S
3s
8.25
8.22
7.49
7.47
7.34
7.32
7.29
7.28
7.23
7.21
6.89
6.86
2.45
1.00
1.96
3.04
1.26
1.08
2.99
f1 (ppm)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8.03
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7.29
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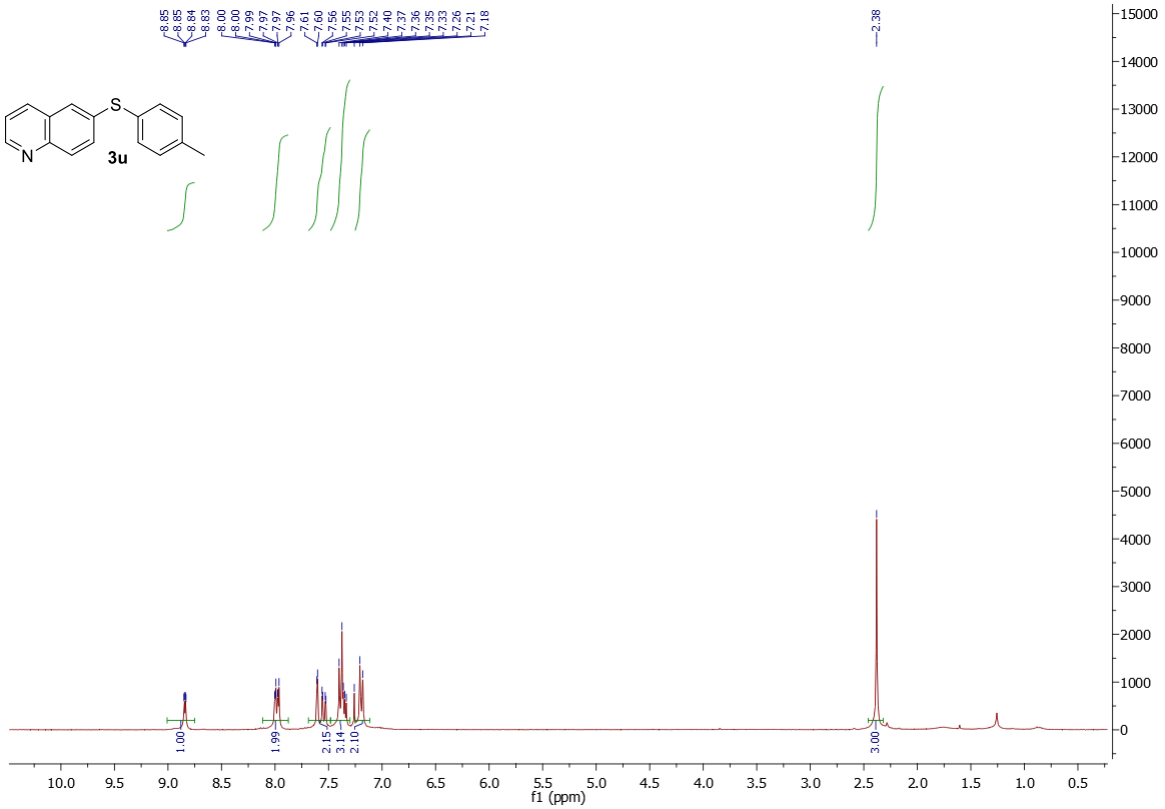
7.12
2.42
S
O_2N
3t
2.00
2.01
2.46
2.08
3.14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8.85
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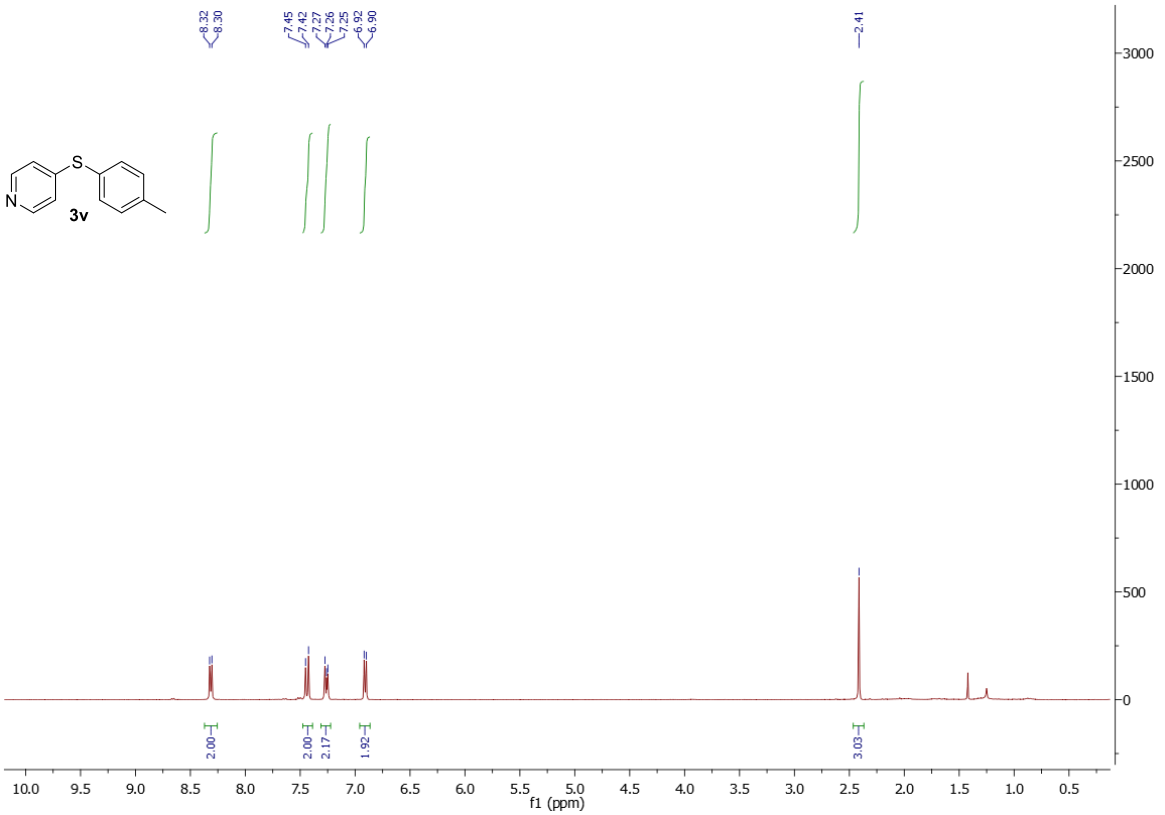
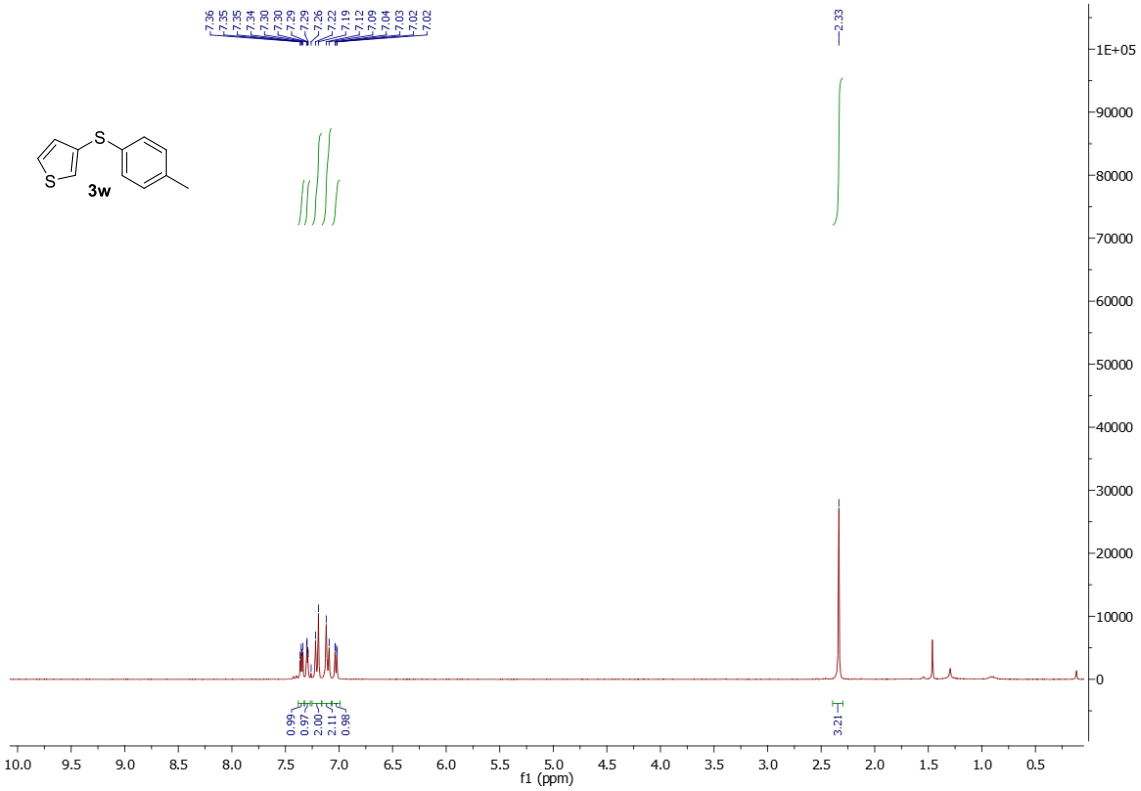
8.00
7.99
7.97
7.97
7.96
7.61
7.60
7.56
7.55
7.53
7.52
7.40
7.37
7.36
7.35
7.33
7.26
7.21
7.18
2.38
S
N
3u
1.00
1.99
2.15
3.14
2.10
3.00
f1 (ppm)


8.32
8.30
7.45
7.42
7.27
7.26
7.25
6.92
6.90
2.41
3v
2.00
2.00
2.17
1.92
3.03
f1 (ppm)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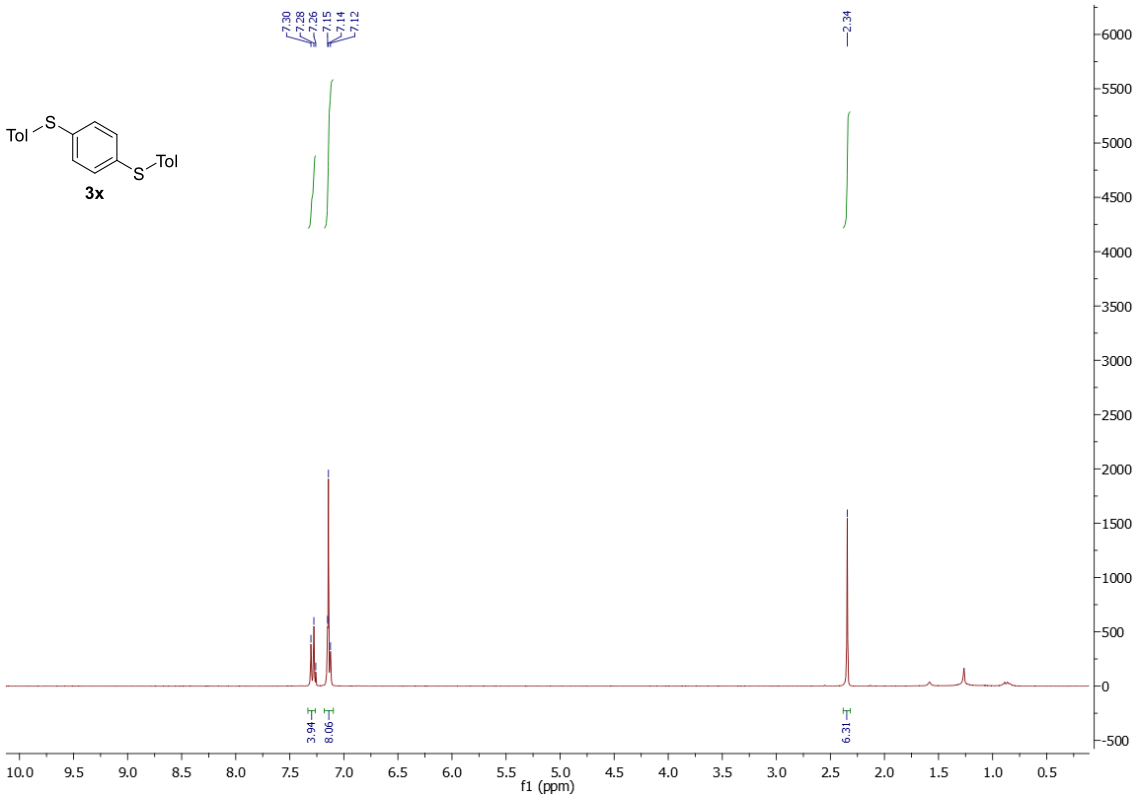
7.35
7.34
7.30
7.30
7.29
7.29
7.26
7.22
7.19
7.12
7.09
7.04
7.03
7.02
7.02
2.33
3w
0.99
0.97
2.00
2.11
0.98
3.21
f1 (ppm)


Tol
S
S
Tol
3x
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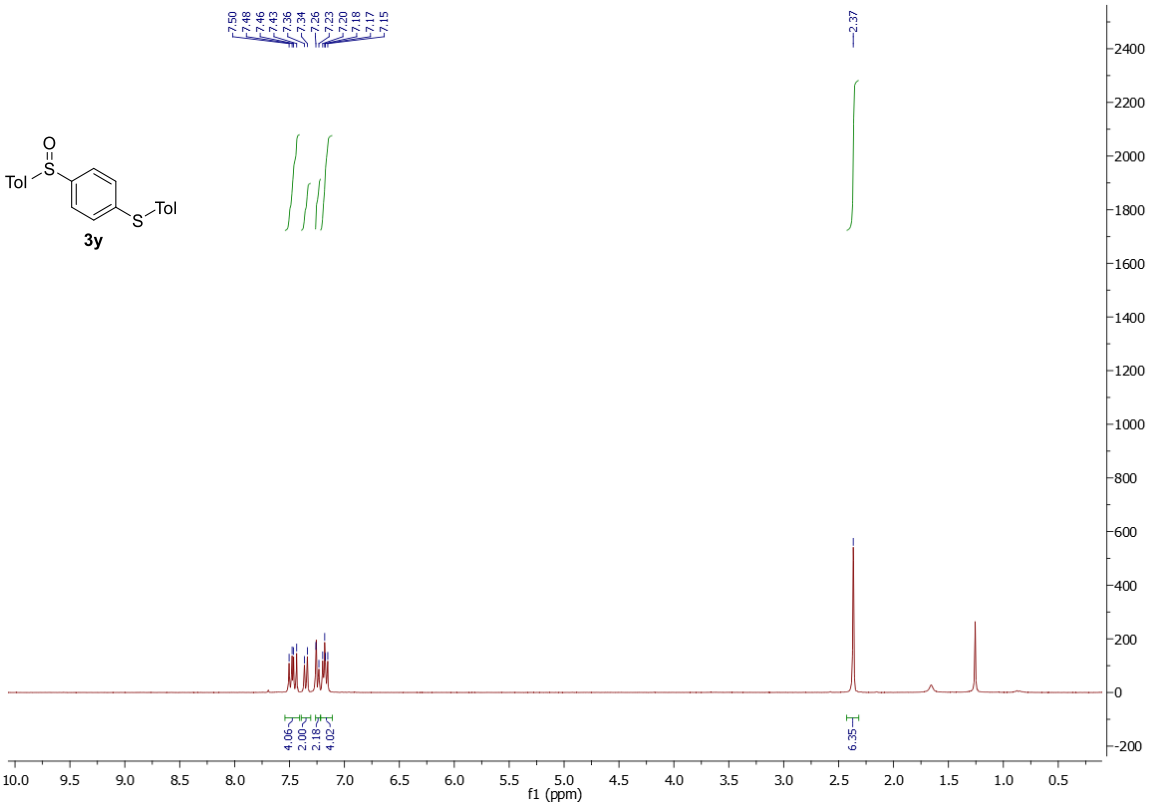
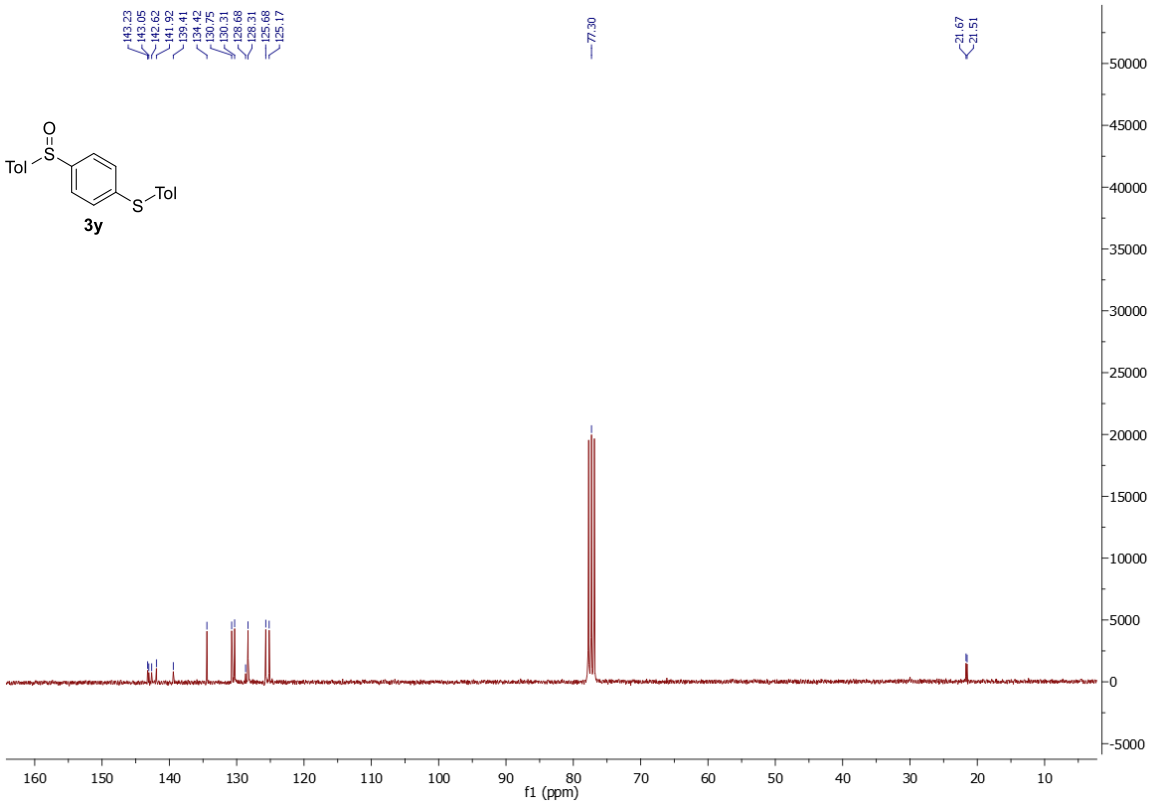
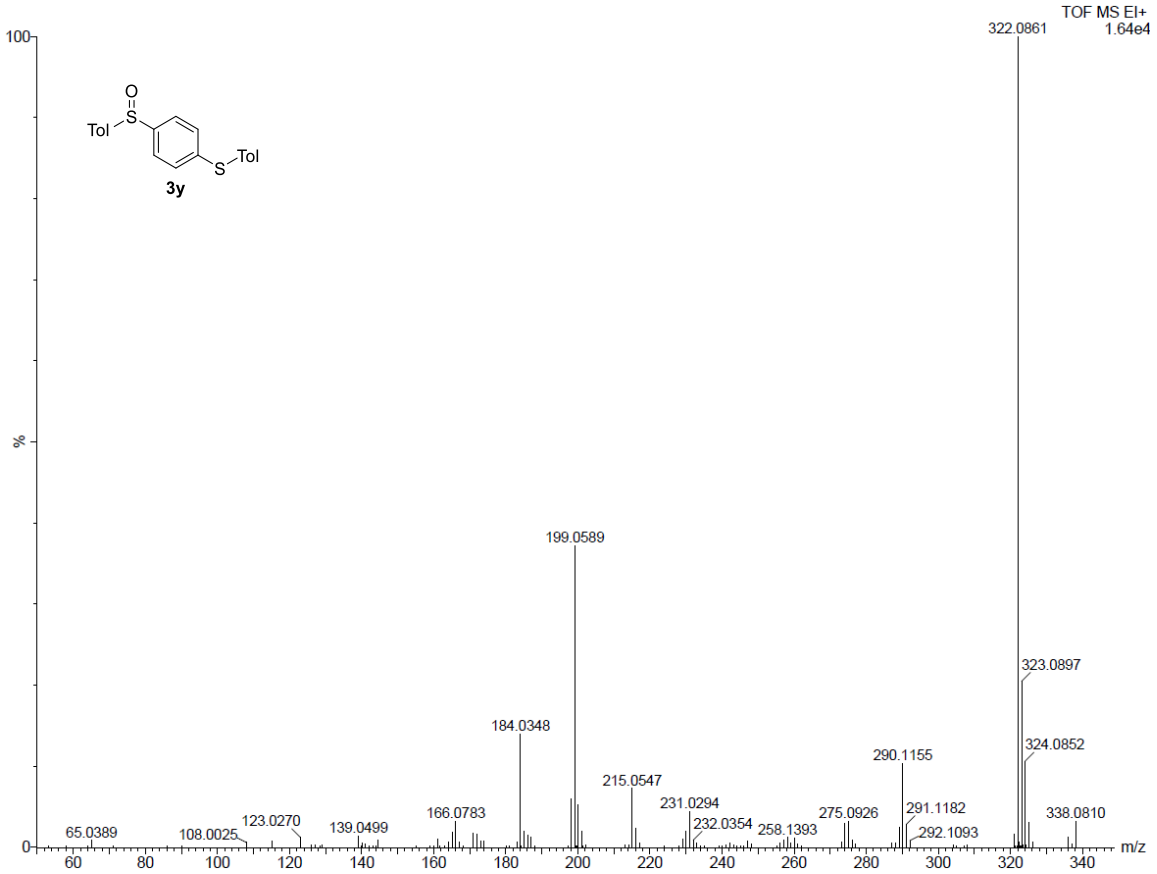
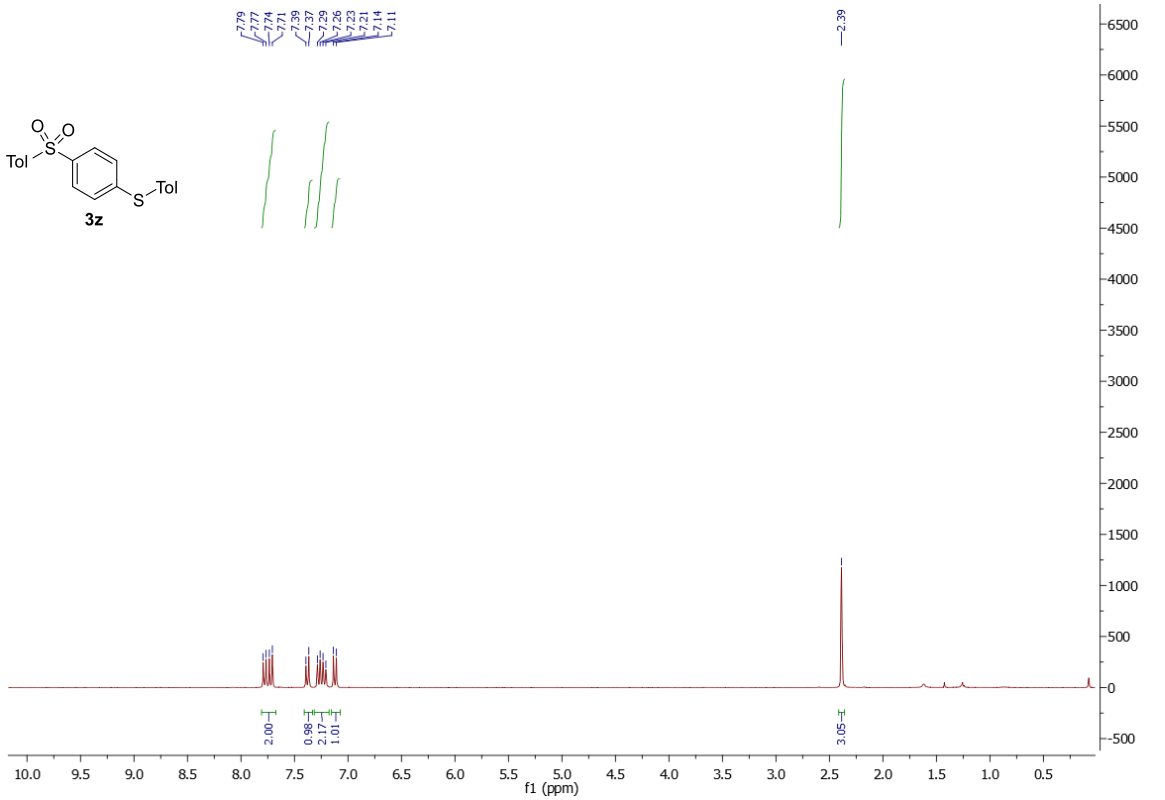
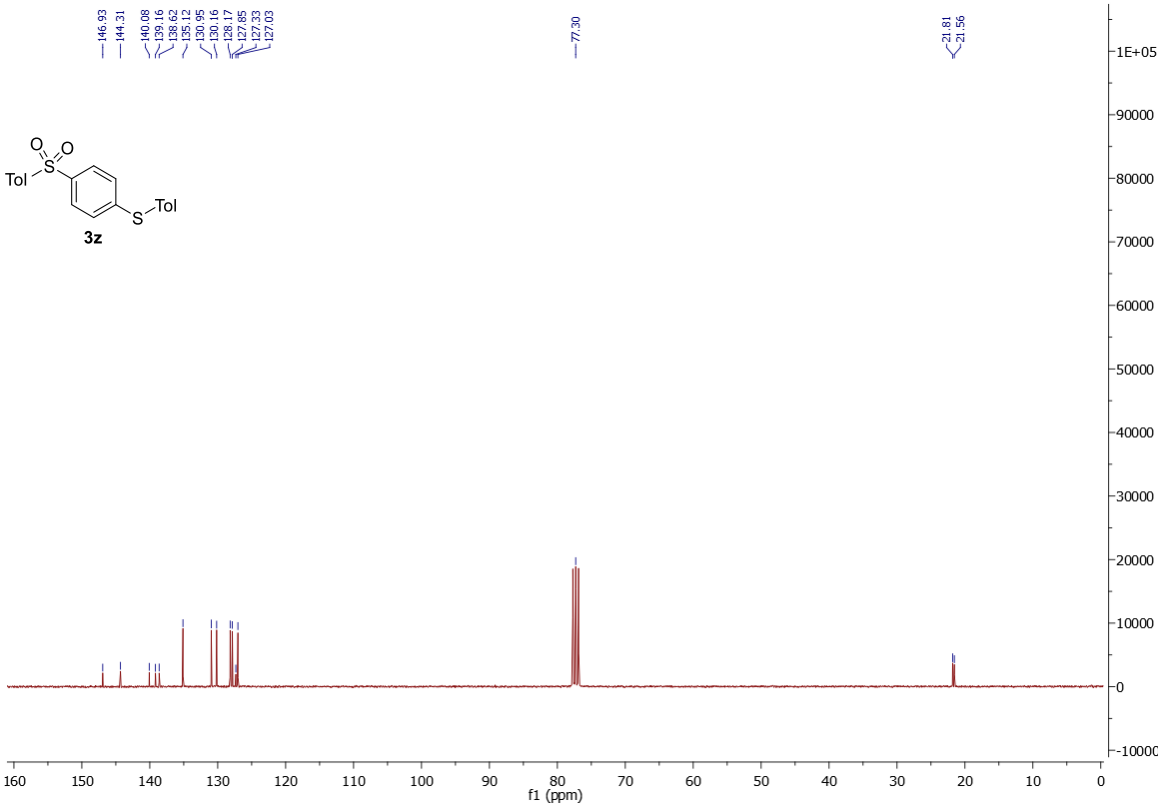
7.26
7.15
7.14
7.12
2.34
3.94
8.06
6.31
f1 (ppm)

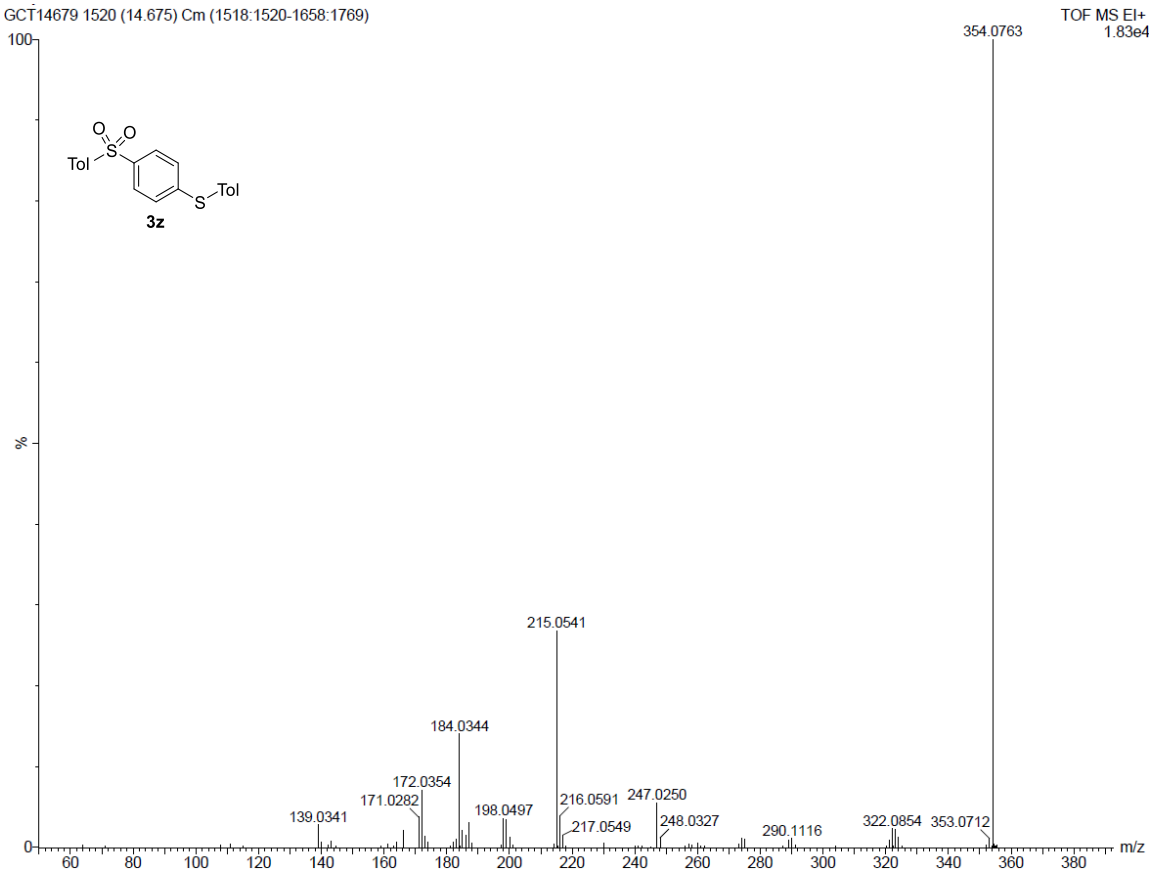

O
Tol
S
S
Tol
3y
7.50
7.48
7.46
7.43
7.36
7.34
7.26
7.23
7.20
7.18
7.17
7.15
2.37
4.06
2.00
2.18
4.02
6.35
f1 (ppm)

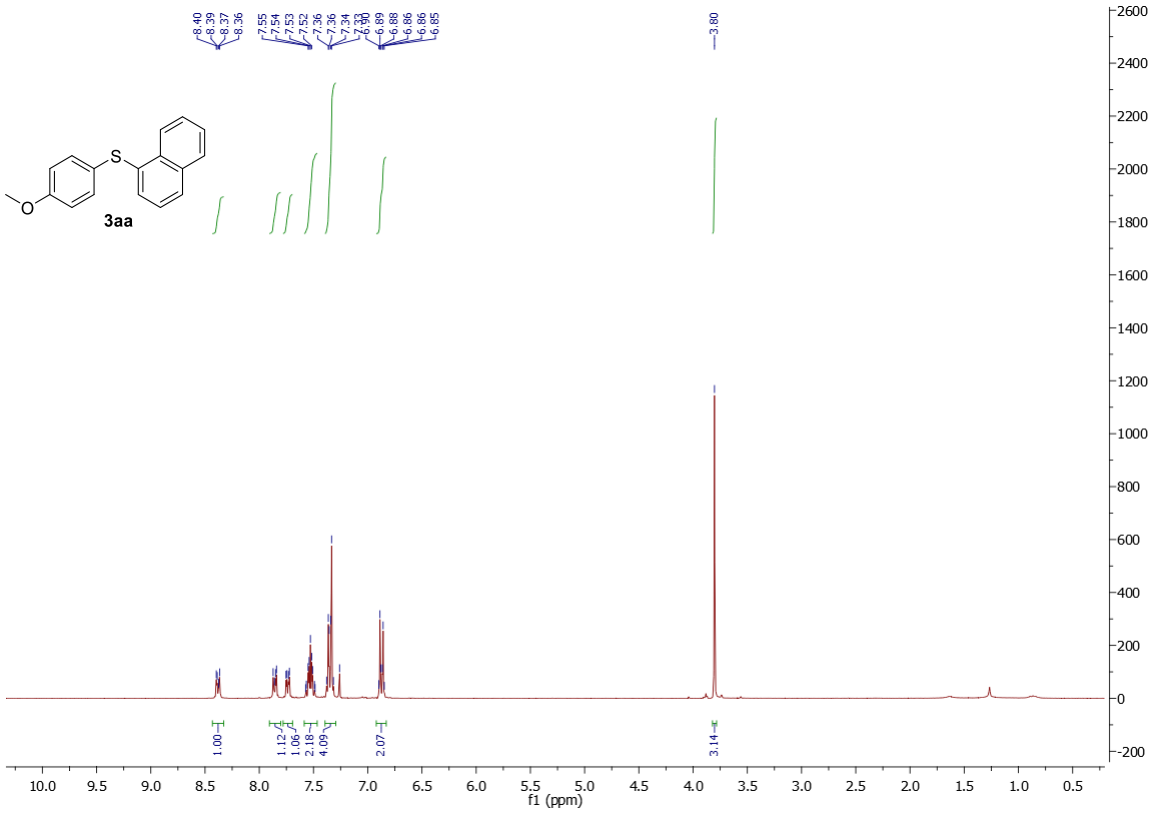

143.23
143.05
142.62
141.92
139.41
134.42
130.75
130.31
128.68
128.31
125.68
125.17
77.30
21.67
21.51
Tol
S
O
Tol
3y
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

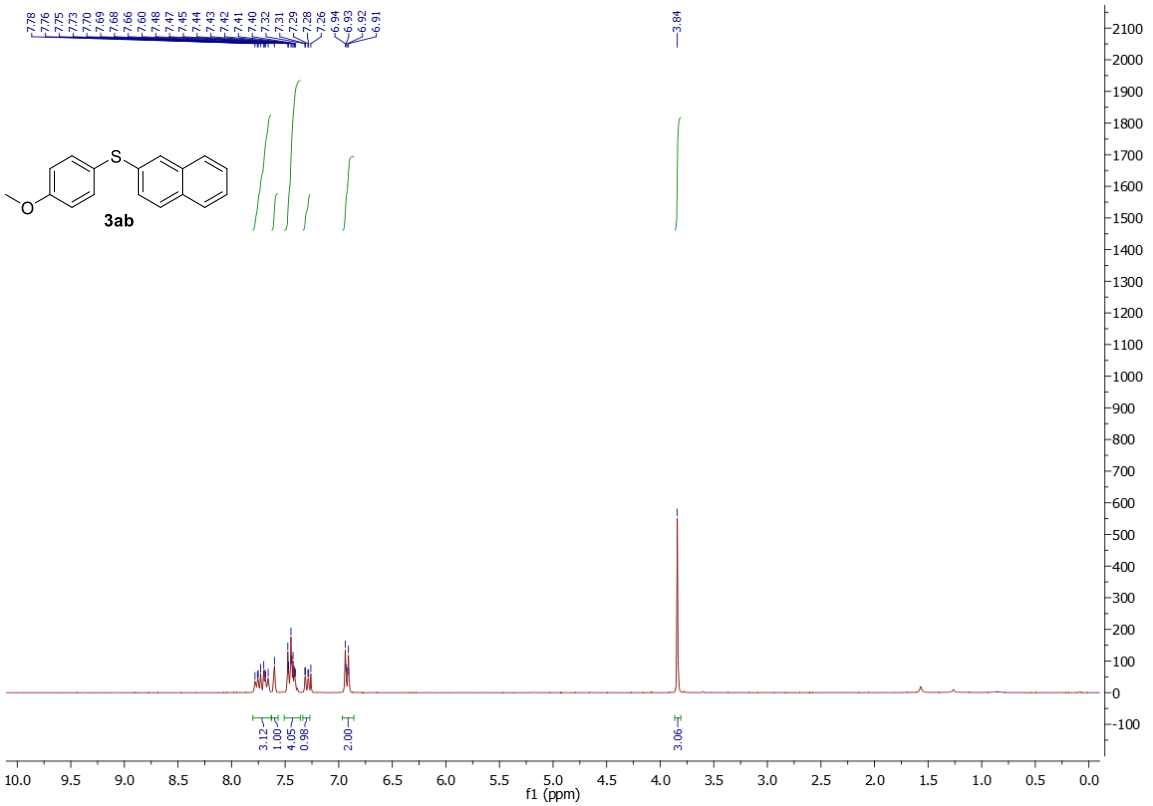

TOF MS EI+
1.64e4
322.0861
100
%
0
Tol
S
O
Tol
3y
199.0589
323.0897
184.0348
324.0852
290.1155
215.0547
231.0294
232.0354
166.0783
275.0926
291.1182
338.0810
65.0389
108.0025
123.0270
139.0499
258.1393
292.1093
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
m/z

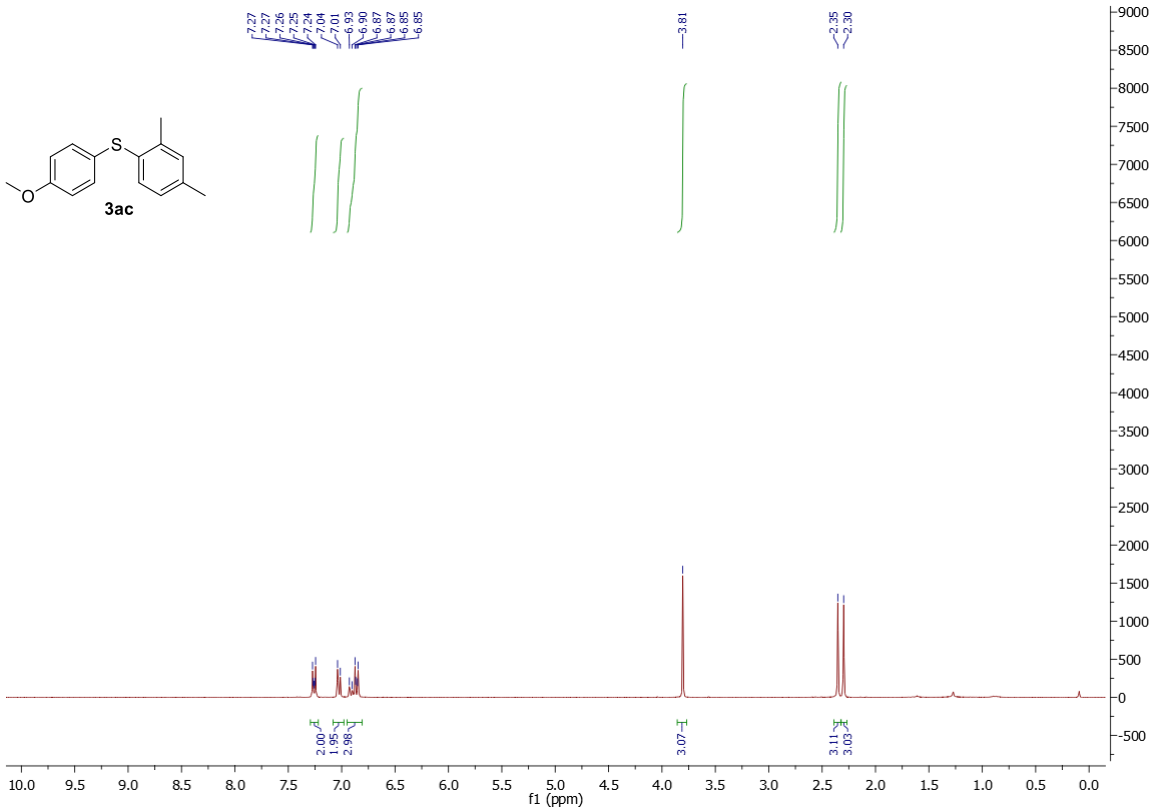

7.79
7.77
7.74
7.71
7.39
7.37
7.29
7.26
7.23
7.21
7.14
7.11
2.39
Tol
S
O
O
S
Tol
3z
2.00
0.98
2.17
1.01
3.05
f1 (ppm)

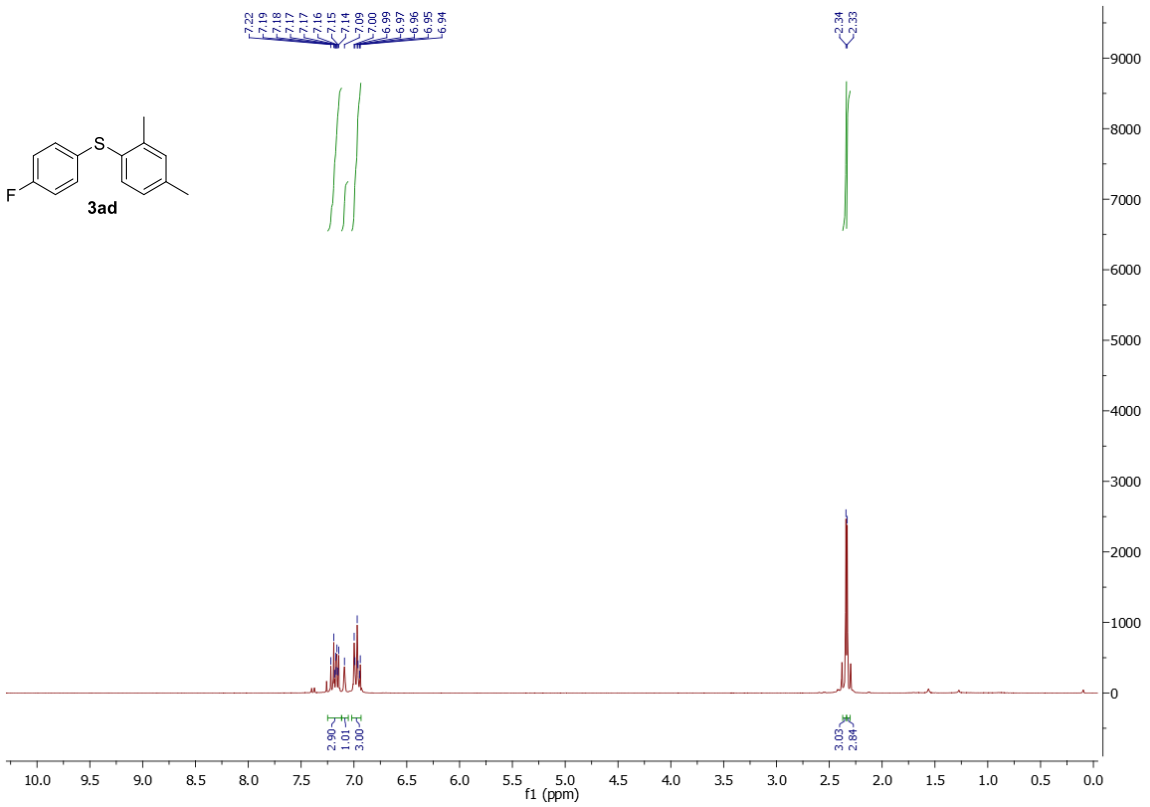

146.93
144.31
140.08
139.16
138.62
135.12
130.95
130.16
128.17
127.85
127.33
127.03
77.30
21.81
21.56
Tol
S
O
O
S
Tol
3z
f1 (ppm)

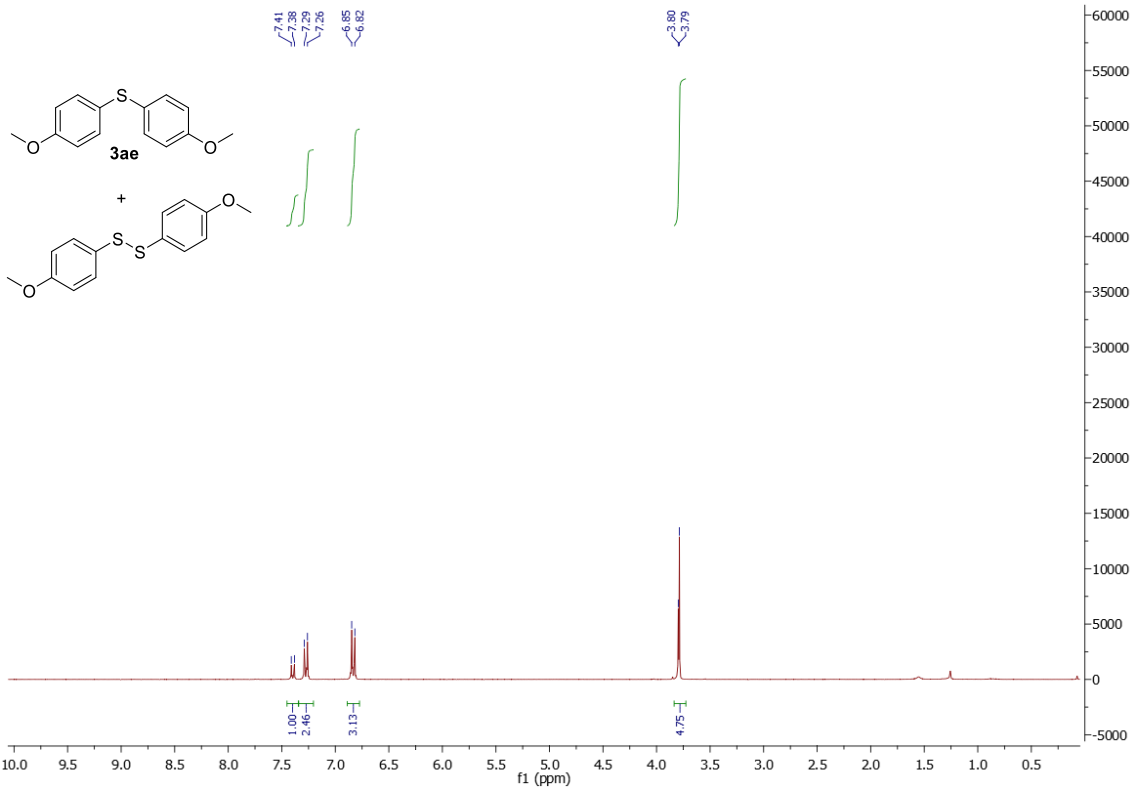

GCT14679 1520 (14.675) Cm (1518:1520-1658:1769)
TOF MS EI+
1.83e4
354.0763
100
%
0
Tol
S
O
O
S
Tol
3z
215.0541
184.0344
172.0354
171.0282
139.0341
198.0497
216.0591
247.0250
217.0549
248.0327
290.1116
322.0854
353.0712
m/z
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380

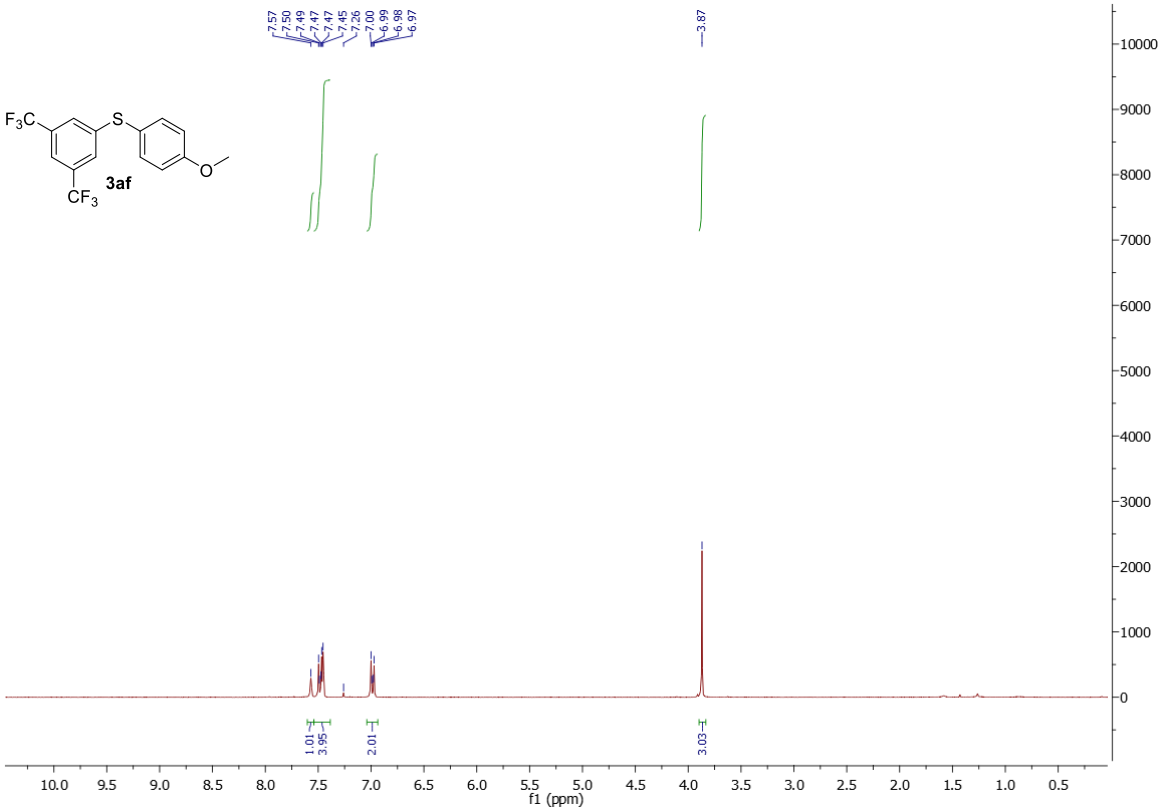

8.40
8.39
8.37
8.36
7.55
7.54
7.53
7.52
7.36
7.34
7.33
7.30
6.89
6.88
6.86
6.86
6.85
3.80
S
O
3aa
1.00
1.12
1.06
2.18
4.09
2.07
3.14
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

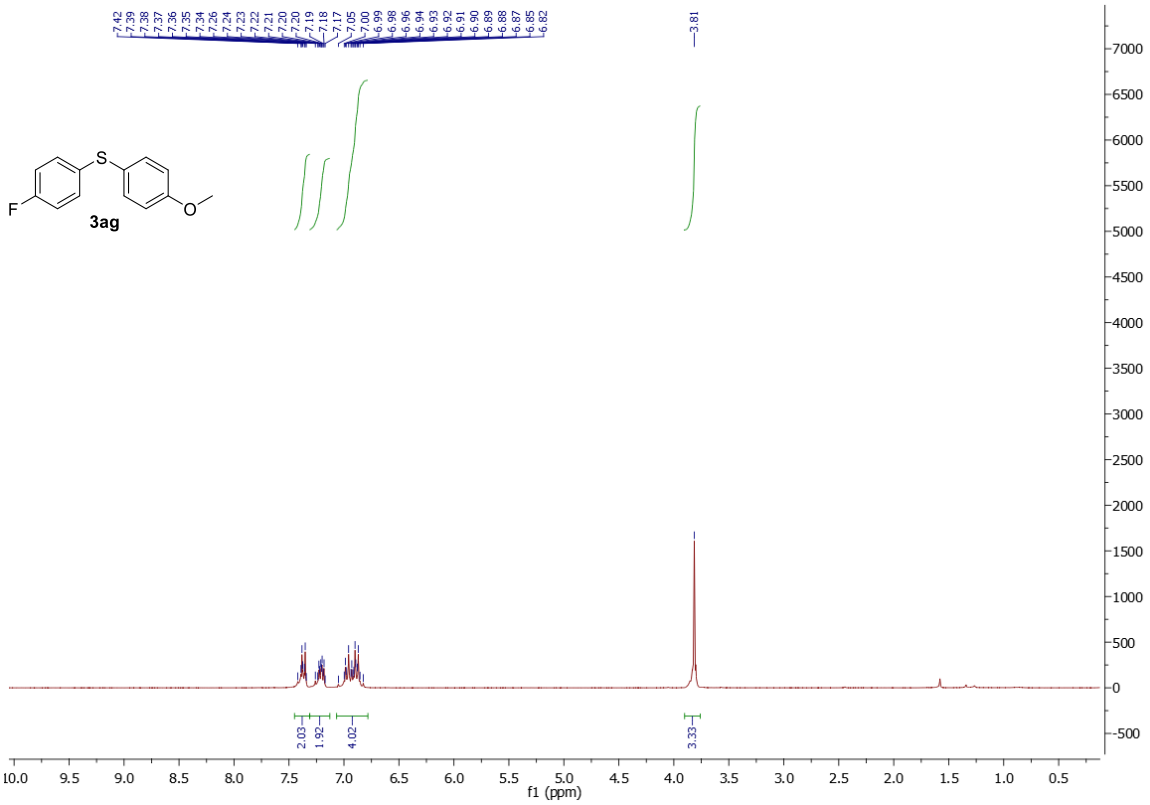

7.78
7.76
7.75
7.73
7.70
7.69
7.68
7.66
7.60
7.48
7.47
7.45
7.44
7.43
7.42
7.41
7.40
7.32
7.31
7.29
7.28
7.26
6.94
6.93
6.92
6.91
3.84
S
O
3ab
3.12
1.00
4.05
0.98
2.00
3.06
f1 (ppm)

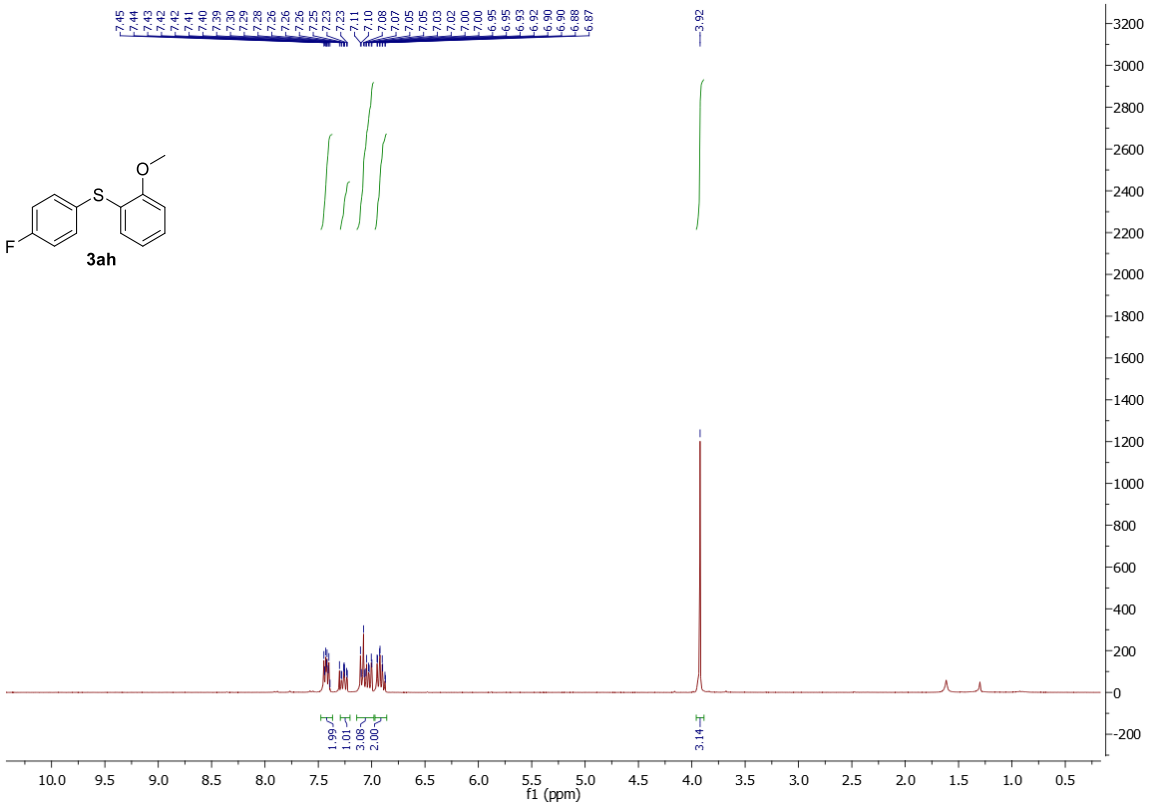

7.27
7.27
7.26
7.25
7.24
7.04
7.01
6.93
6.90
6.87
6.87
6.85
6.85
3.81
2.35
2.30
S
O
3ac
2.00
1.95
2.98
3.07
3.11
3.03
f1 (ppm)

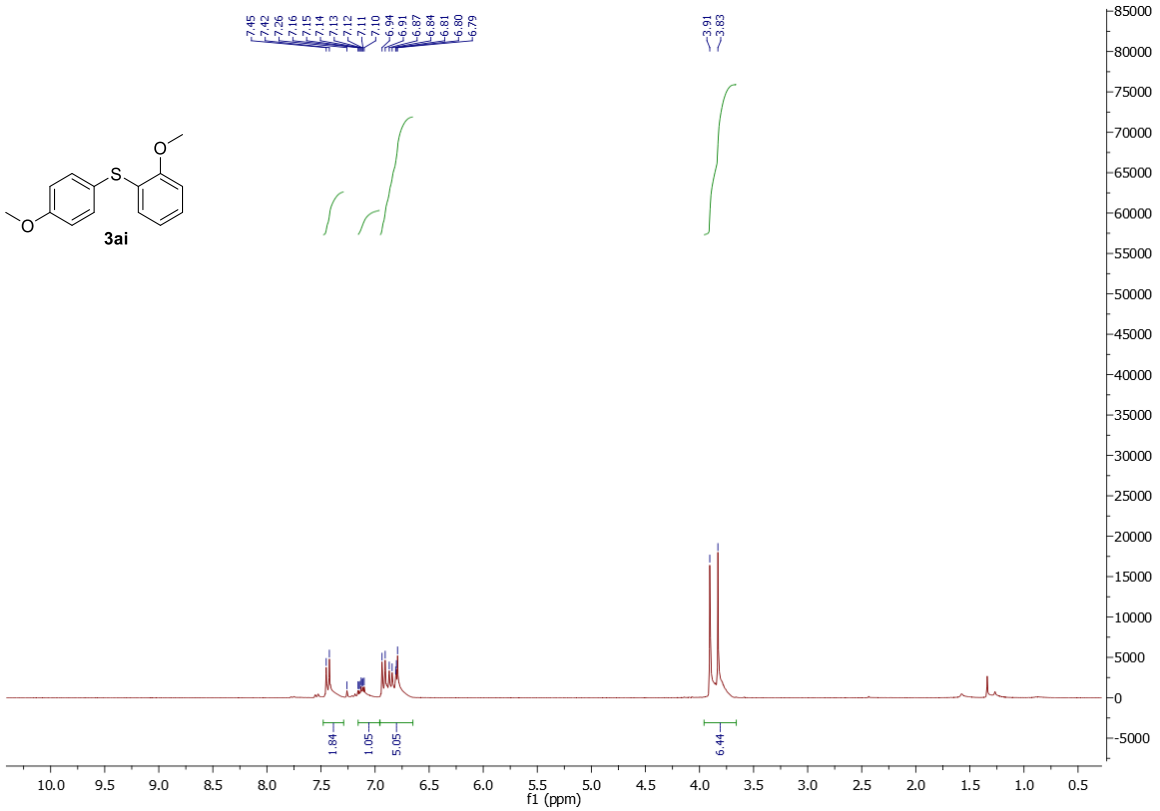

3ad
F
S
7.22
7.19
7.18
7.17
7.17
7.16
7.15
7.14
7.09
7.00
6.99
6.97
6.96
6.95
6.94
2.34
2.33
2.90
1.01
3.00
3.03
2.84
f1 (ppm)

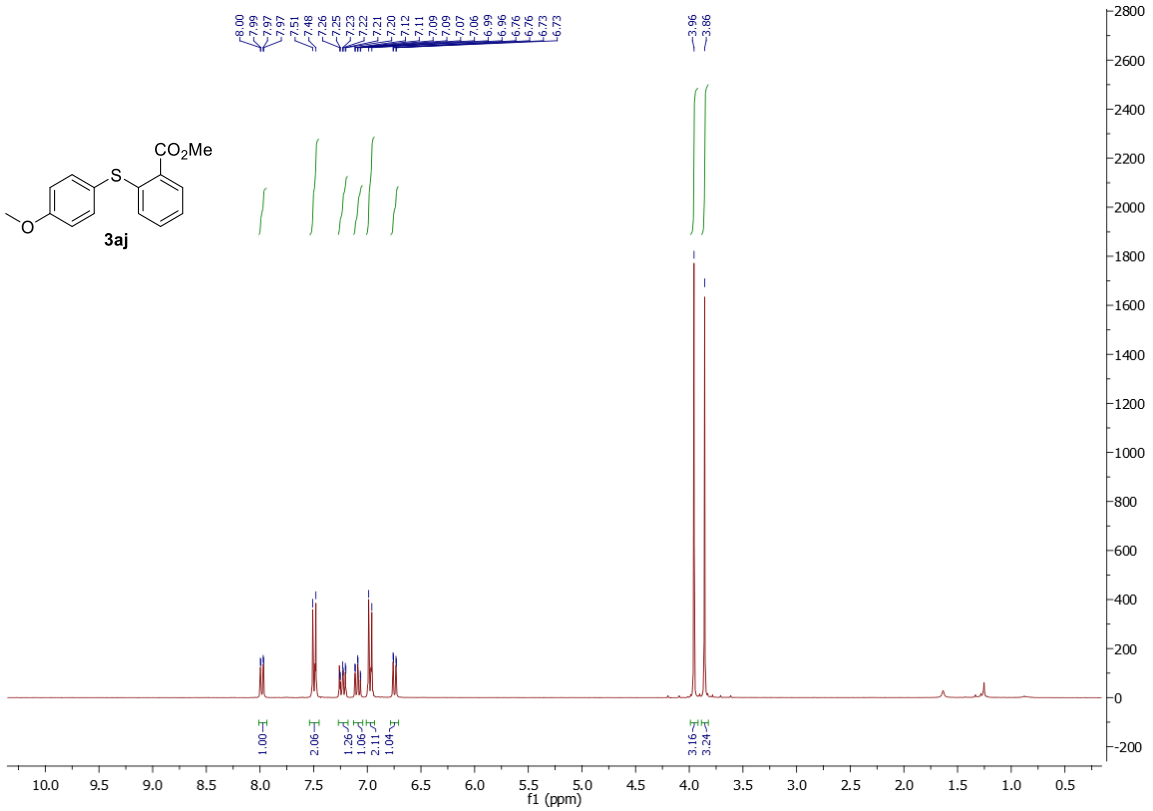

3ae
+
S
O
7.41
7.38
7.29
7.26
6.85
6.82
3.80
3.79
1.00
2.46
3.13
4.75
f1 (ppm)

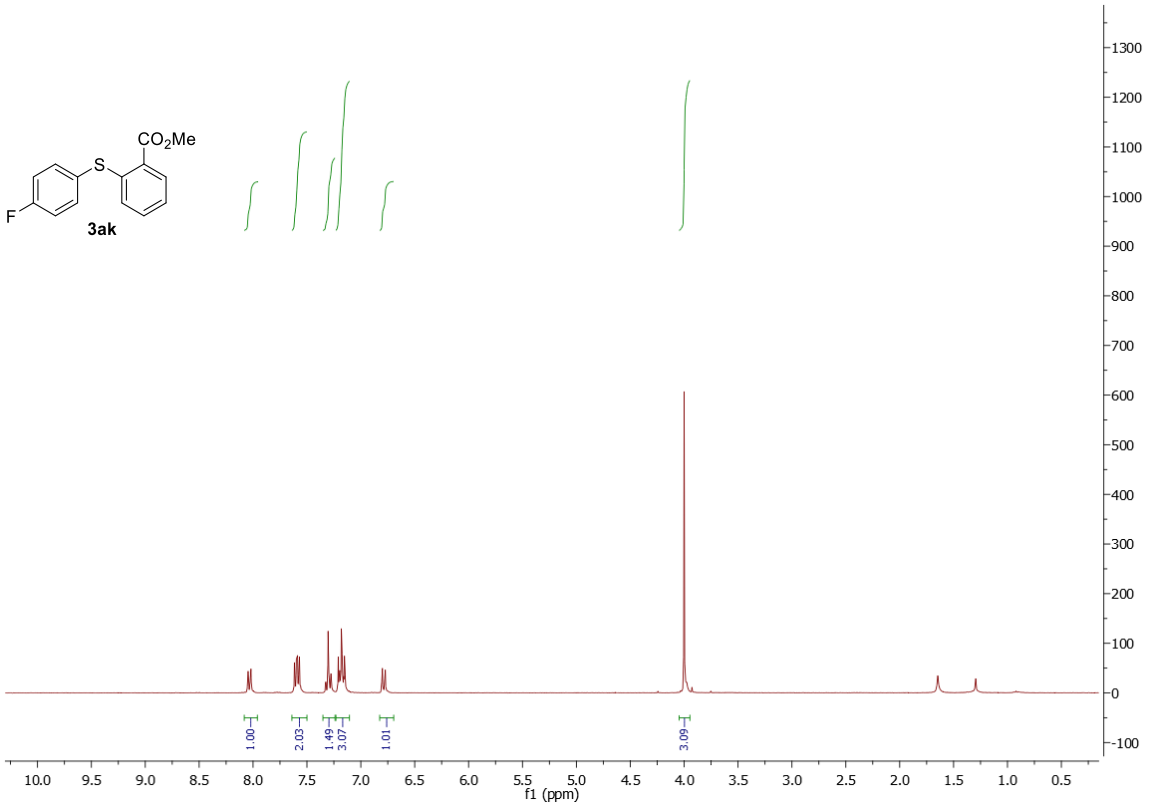

7.57
7.50
7.49
7.47
7.47
7.45
7.26
7.00
6.99
6.98
6.97
3.87
F3C
S
O
CF3
3af
1.01
3.95
2.01
3.03
f1 (ppm)

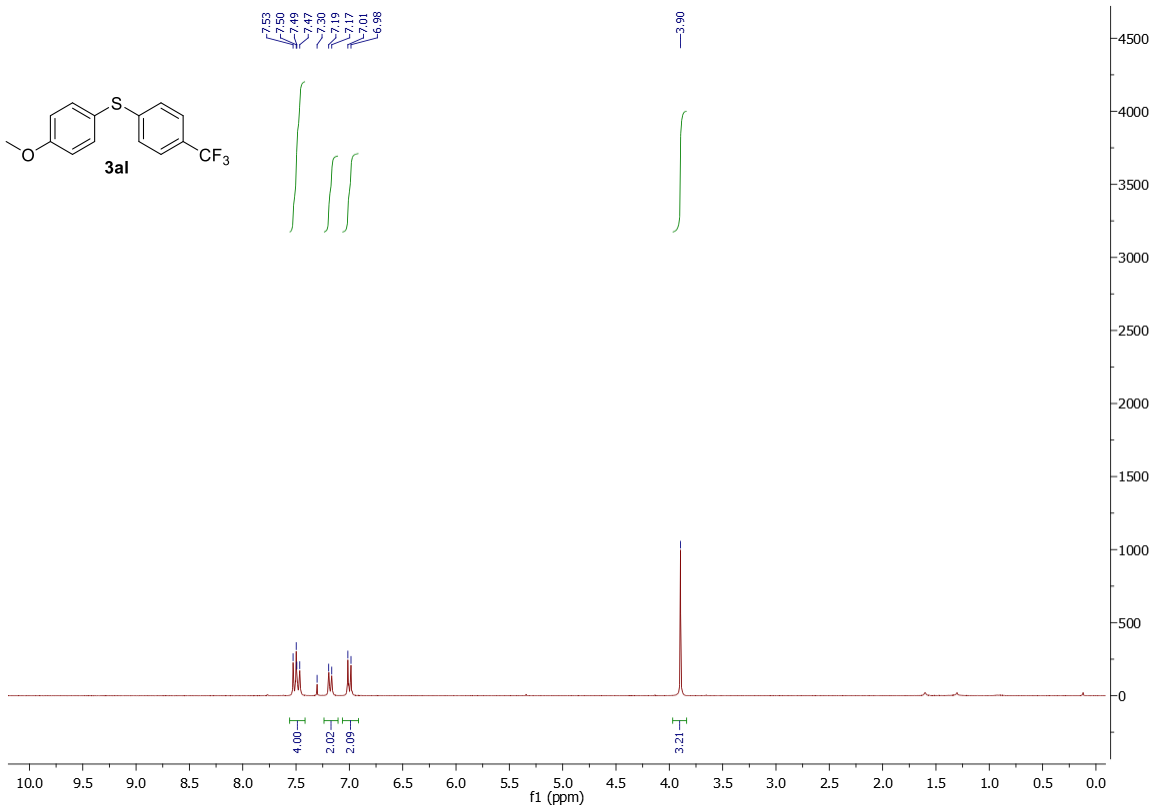

7.42
7.39
7.38
7.37
7.36
7.35
7.34
7.26
7.24
7.23
7.22
7.21
7.20
7.20
7.19
7.18
7.17
7.05
7.00
6.99
6.98
6.96
6.94
6.93
6.92
6.91
6.90
6.89
6.88
6.87
6.85
6.82
3.81
S
F
O
3ag
2.03
1.92
4.02
3.33
f1 (ppm)

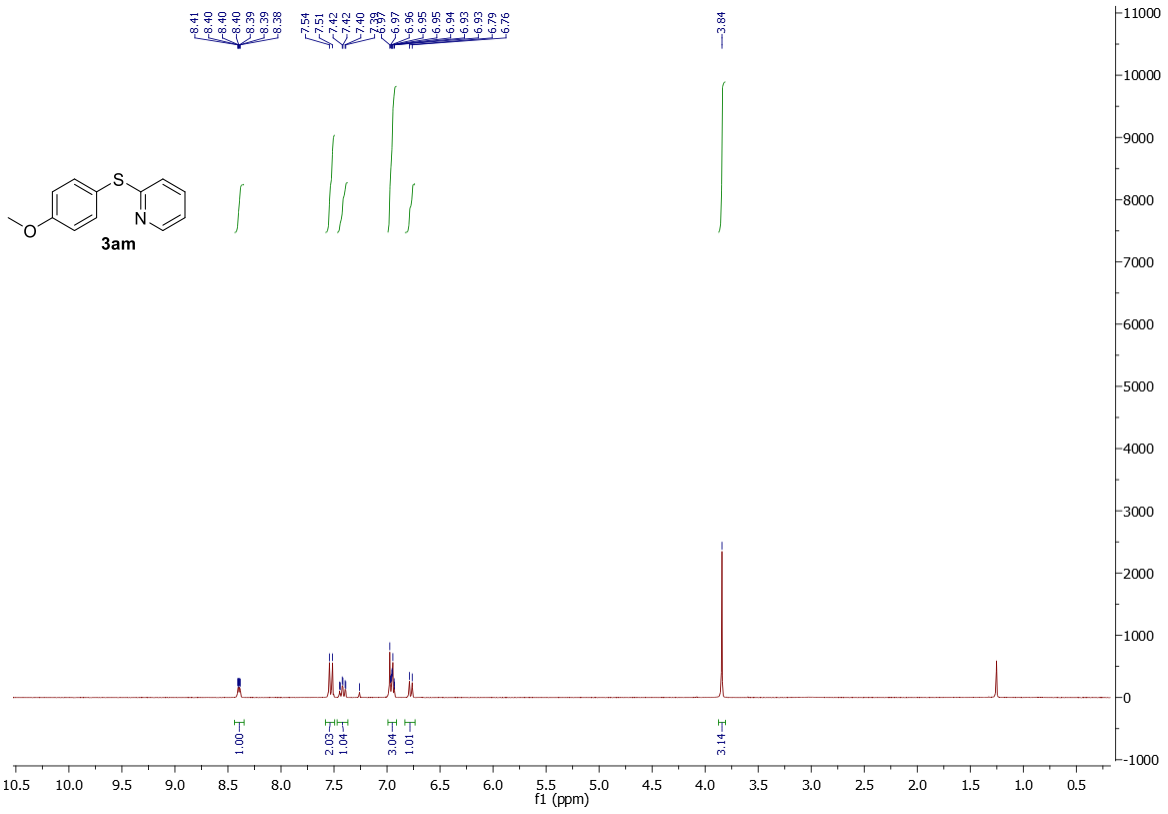

7.45
7.44
7.43
7.42
7.42
7.41
7.40
7.39
7.30
7.29
7.28
7.26
7.26
7.25
7.23
7.23
7.11
7.10
7.08
7.07
7.05
7.05
7.03
7.02
7.00
7.00
6.95
6.93
6.92
6.90
6.90
6.88
6.87
3.92
O
S
F
3ah
1.99
1.01
3.08
2.00
3.14
f1 (ppm)

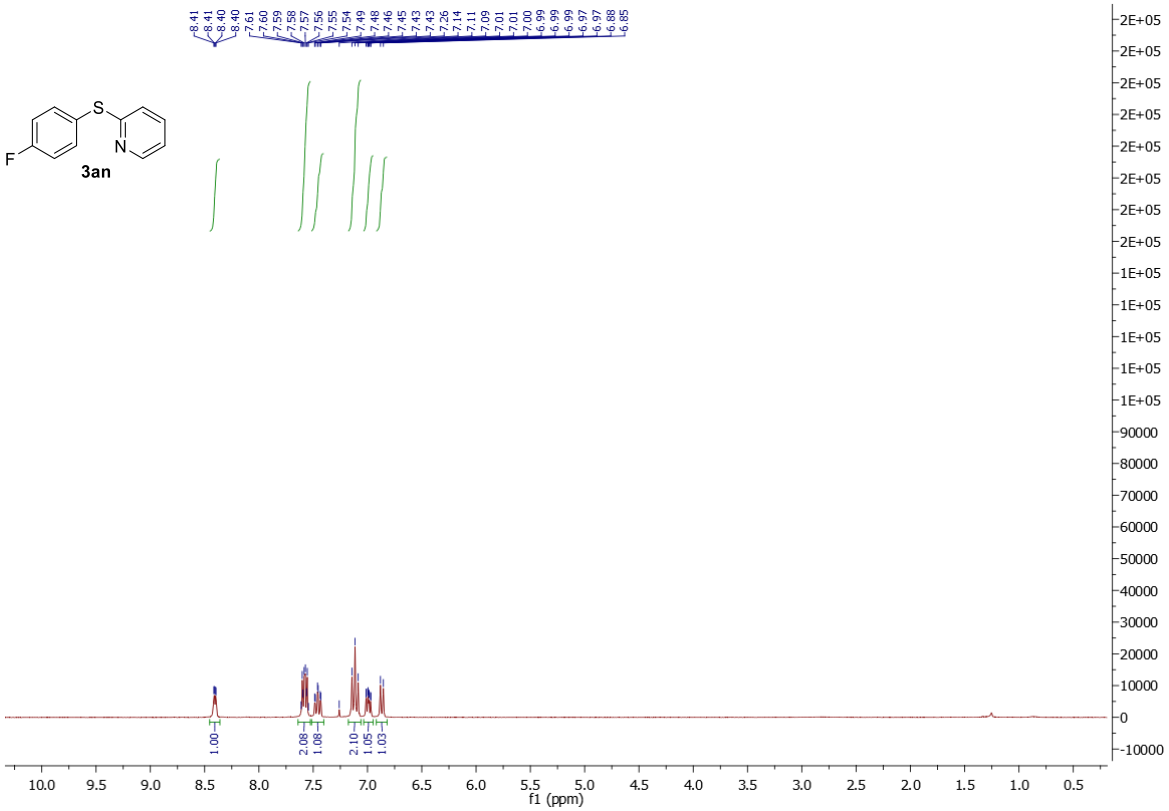

7.45
7.42
7.26
7.16
7.15
7.14
7.13
7.12
7.11
7.10
6.94
6.91
6.87
6.84
6.81
6.80
6.79
3.91
3.83
O
S
O
3ai
1.84
1.05
5.05
6.44
f1 (ppm)

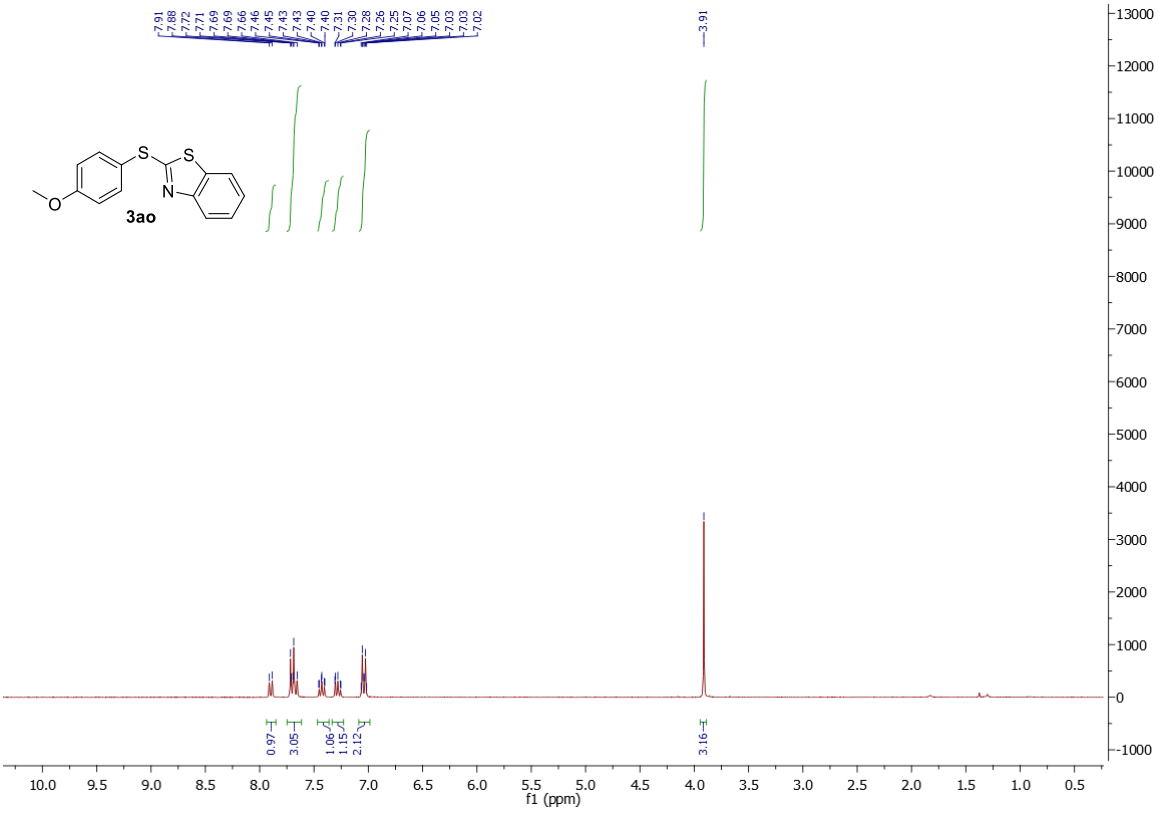

8.00
7.99
7.97
7.97
7.51
7.48
7.26
7.25
7.23
7.22
7.21
7.20
7.11
7.09
7.09
7.07
7.06
6.99
6.96
6.76
6.76
6.73
6.73
3.96
3.86
CO2Me
S
O
3aj
1.00
2.06
1.26
1.06
2.11
1.04
3.16
3.24
f1 (ppm)

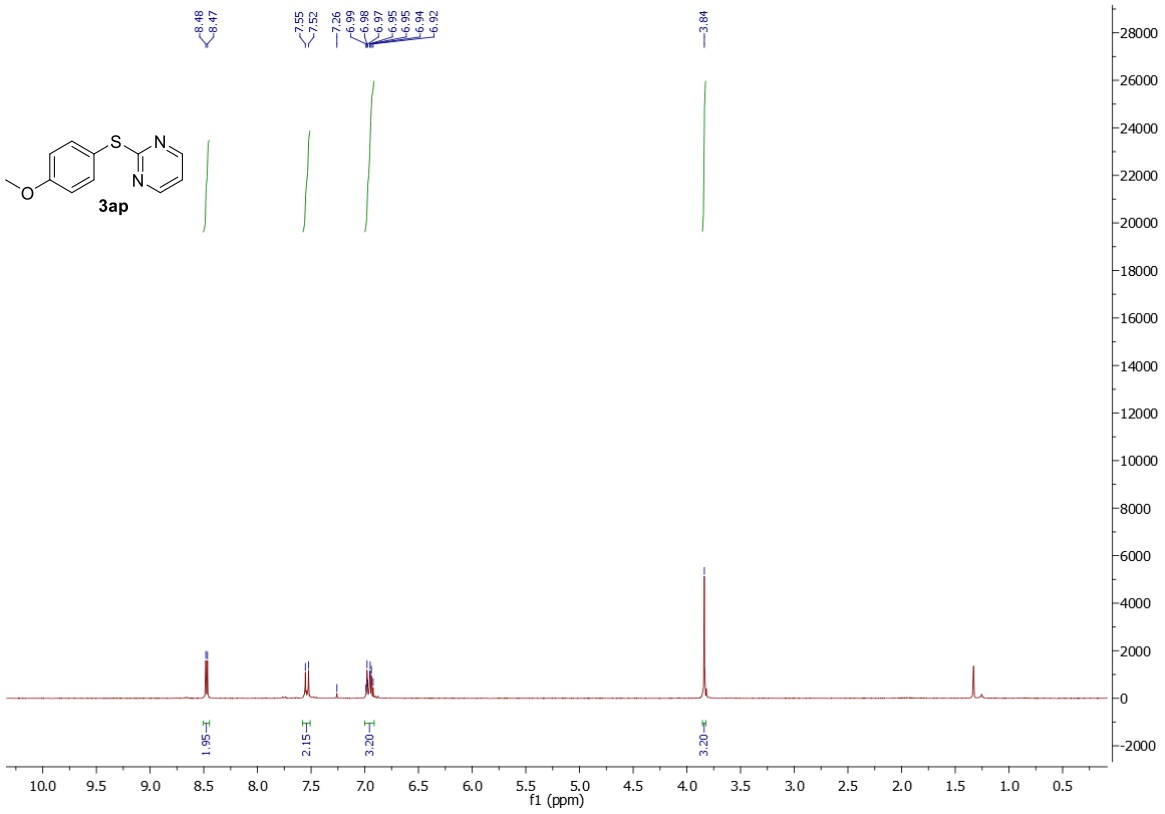

CO2Me
S
F
3ak
1.00
2.03
1.49
3.07
1.01
3.09
f1 (ppm)

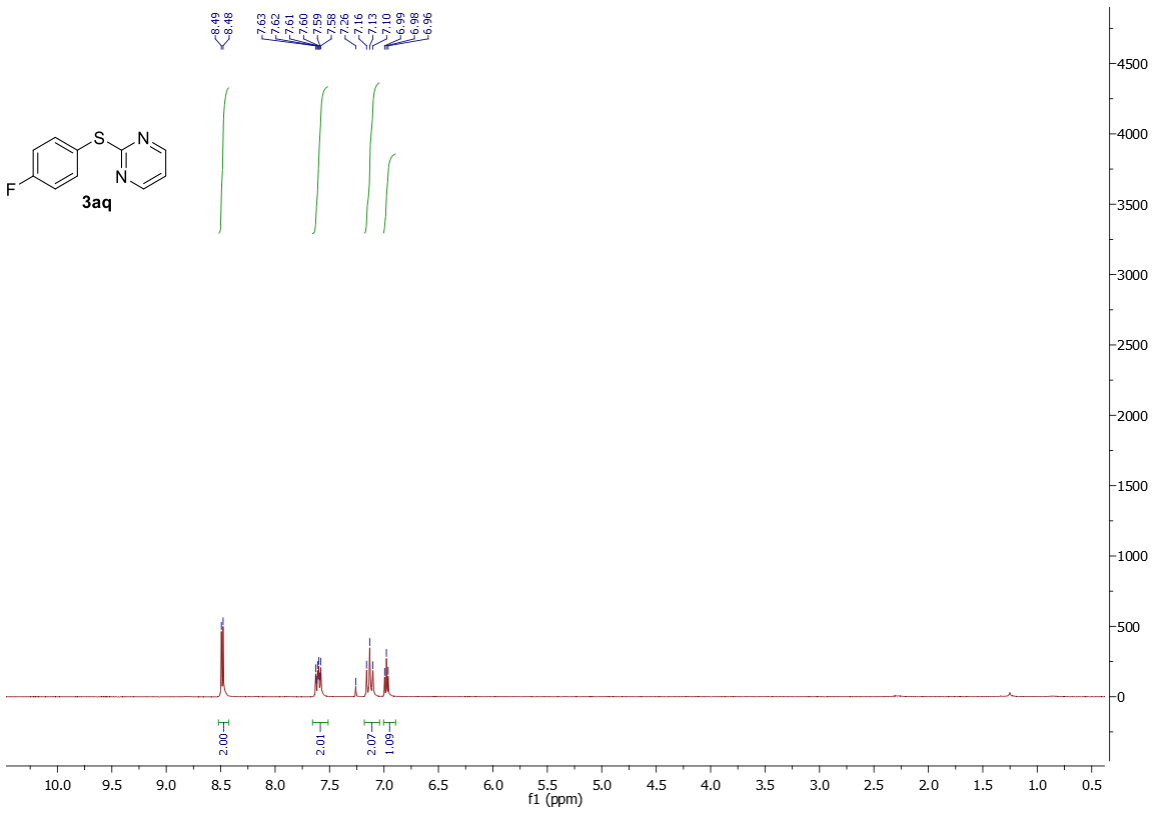

7.53
7.50
7.49
7.47
7.30
7.19
7.17
7.01
6.98
3.90
S
O
CF3
3al
4.00
2.02
2.09
3.21
f1 (ppm)

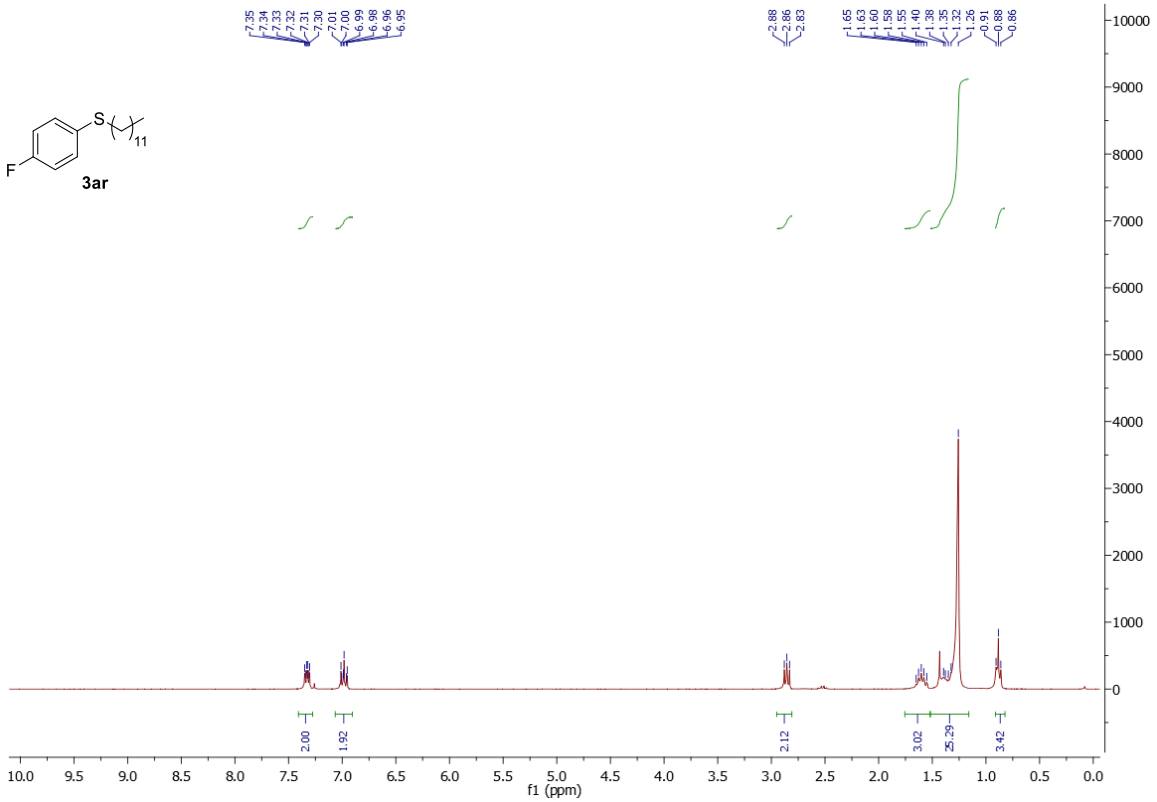

8.41
8.40
8.40
8.40
8.39
8.39
8.38
7.54
7.51
7.42
7.42
7.40
7.39
6.97
6.96
6.96
6.95
6.95
6.94
6.93
6.93
6.79
6.76
3.84
S
N
O
3am
1.00
2.03
1.04
3.04
1.01
3.14
f1 (ppm)

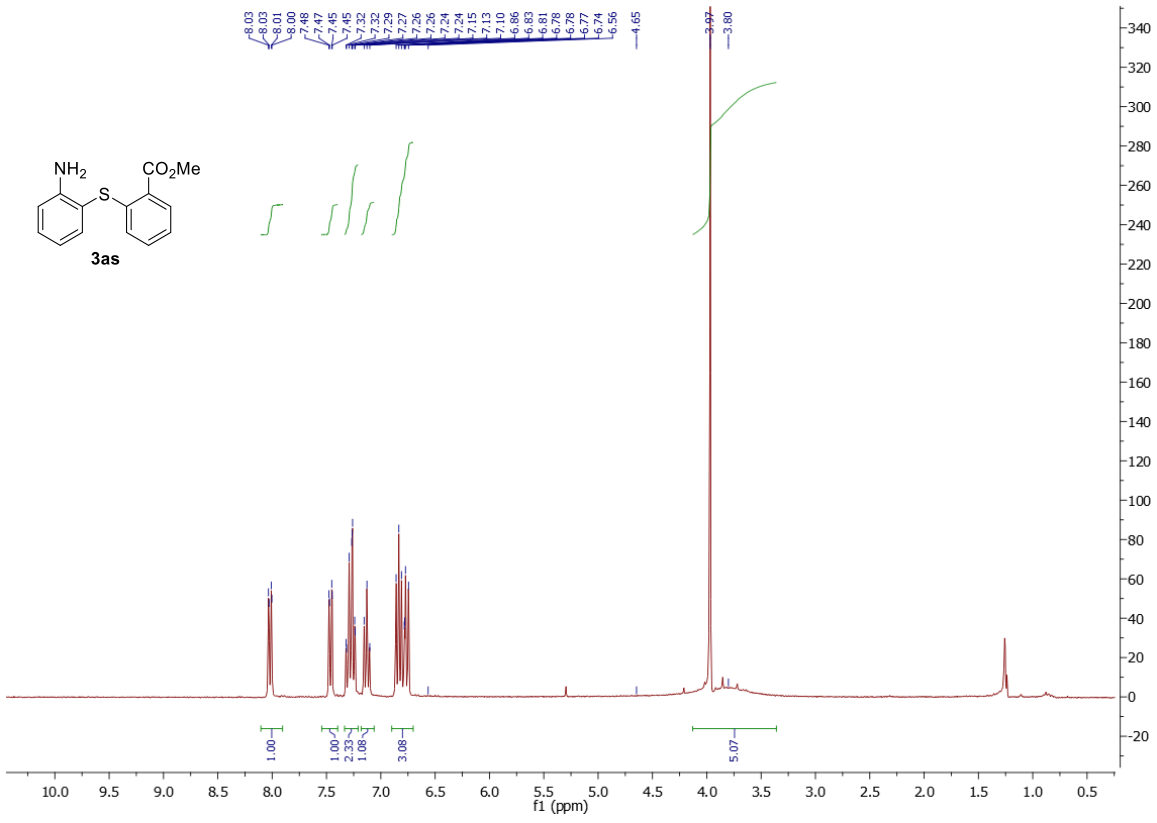

3an
f1 (ppm)

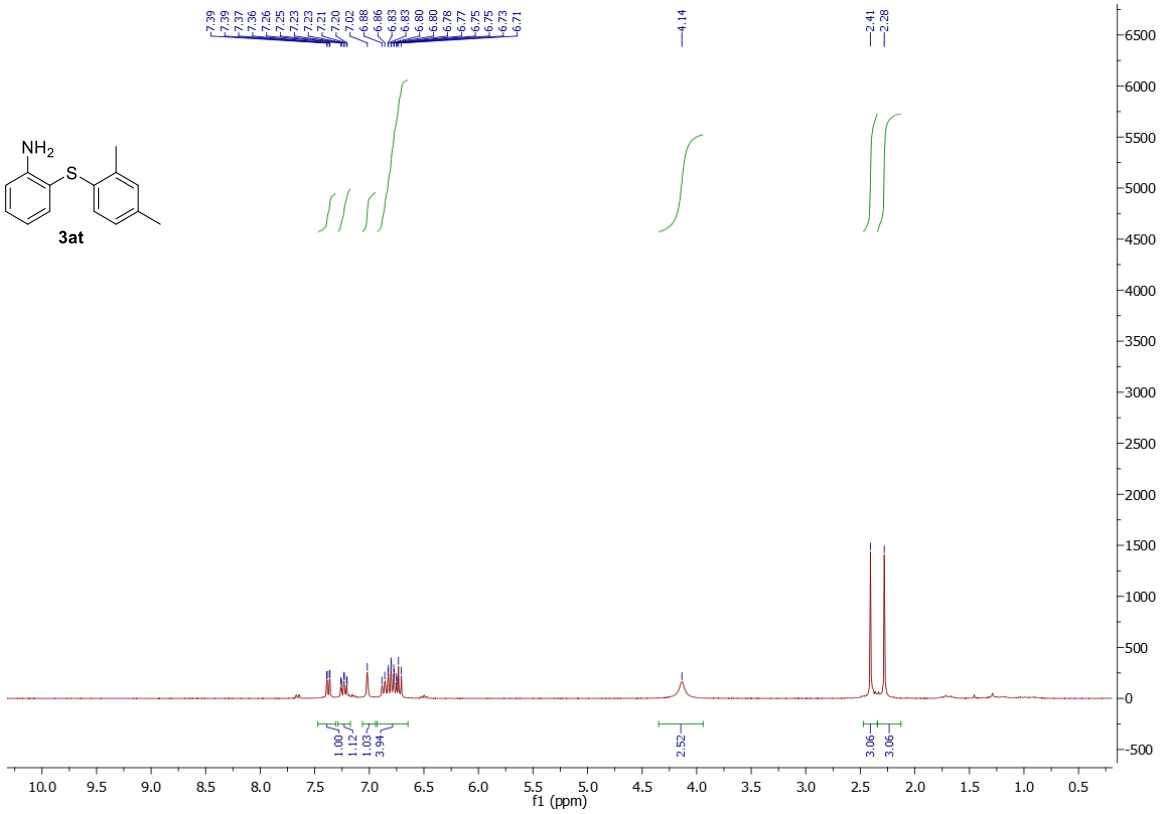

3ao
f1 (ppm)

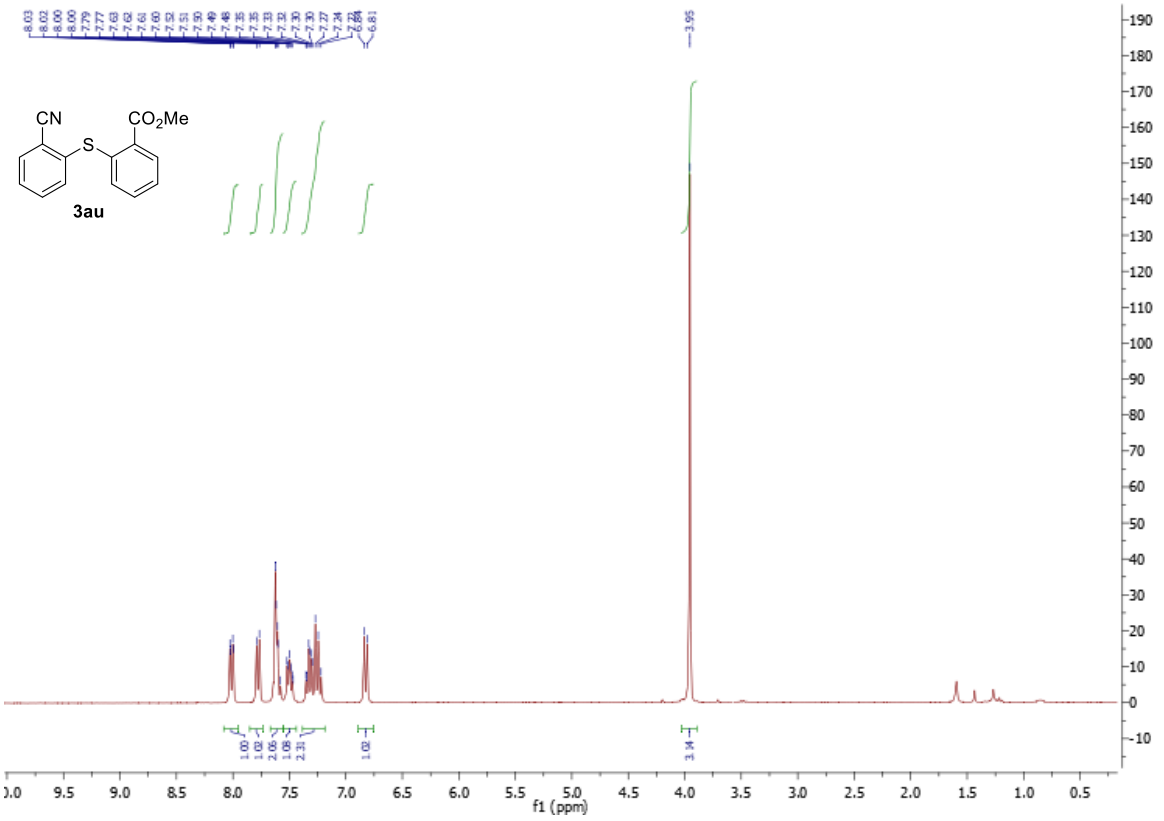

8.48
8.47
7.55
7.52
7.26
6.99
6.98
6.97
6.95
6.94
6.92
3.84
S
N
N
O
3ap
1.95
2.15
3.20
3.20
f1 (ppm)

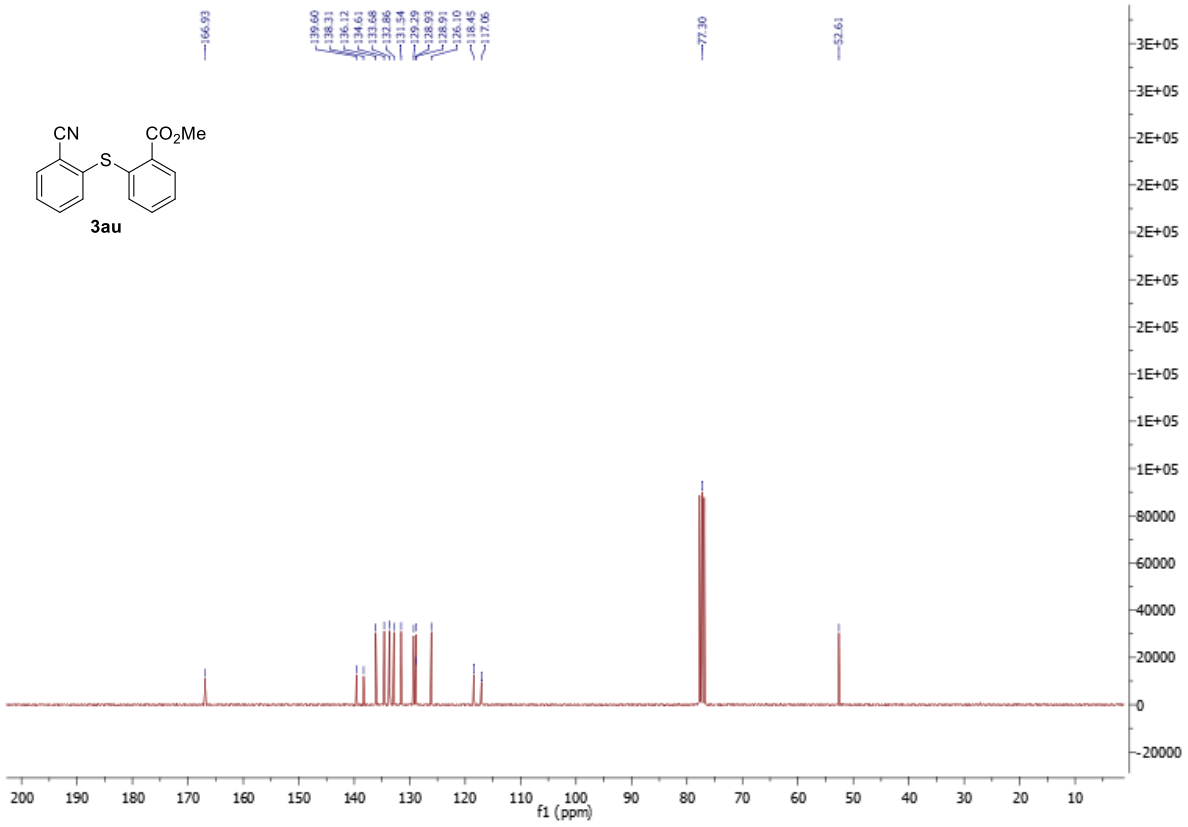

8.49
8.48
7.63
7.62
7.61
7.60
7.59
7.58
7.26
7.16
7.13
7.10
6.99
6.98
6.96
S
N
N
F
3aq
2.00
2.01
2.07
1.09
f1 (ppm)

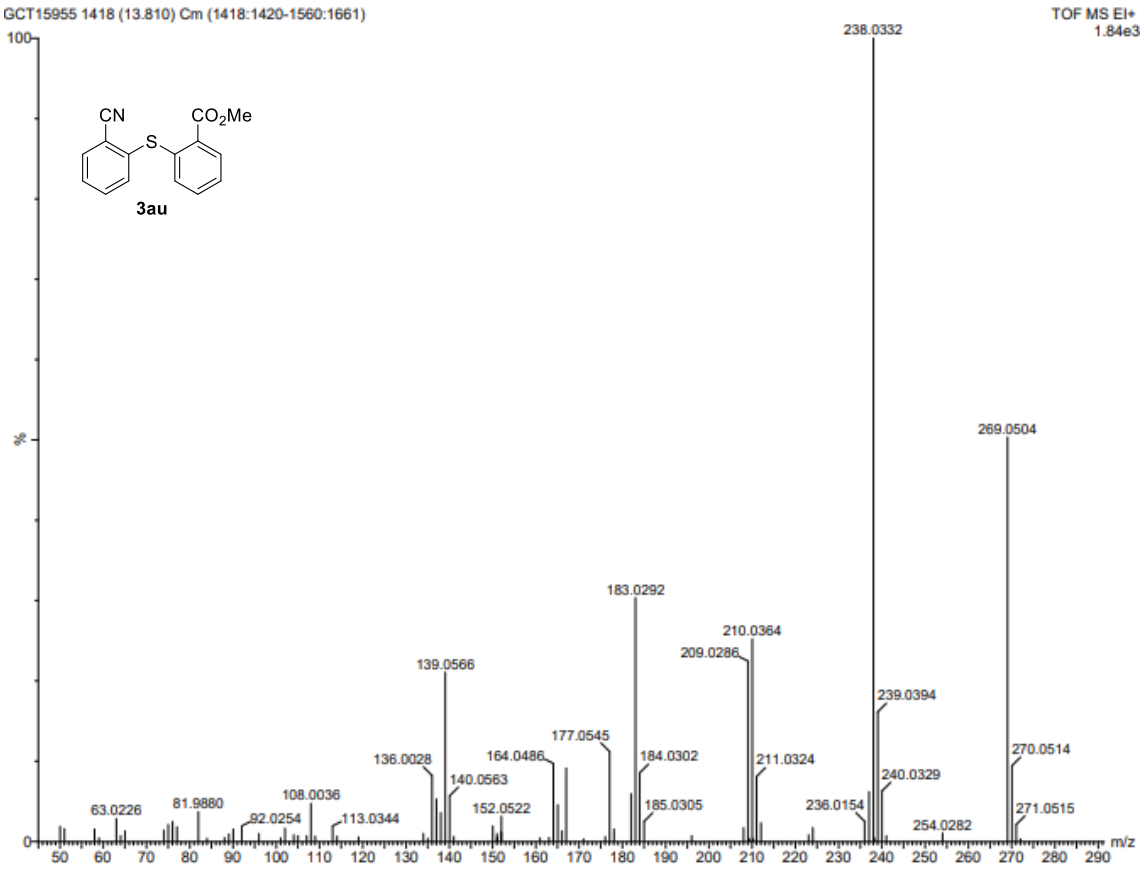

3ar
7.35
7.34
7.33
7.32
7.31
7.30
7.01
7.00
6.99
6.98
6.96
6.95
2.88
2.86
2.83
1.65
1.63
1.60
1.58
1.55
1.40
1.38
1.35
1.32
1.26
0.91
0.88
0.86
2.00
1.92
2.12
3.02
25.29
3.42
f1 (ppm)

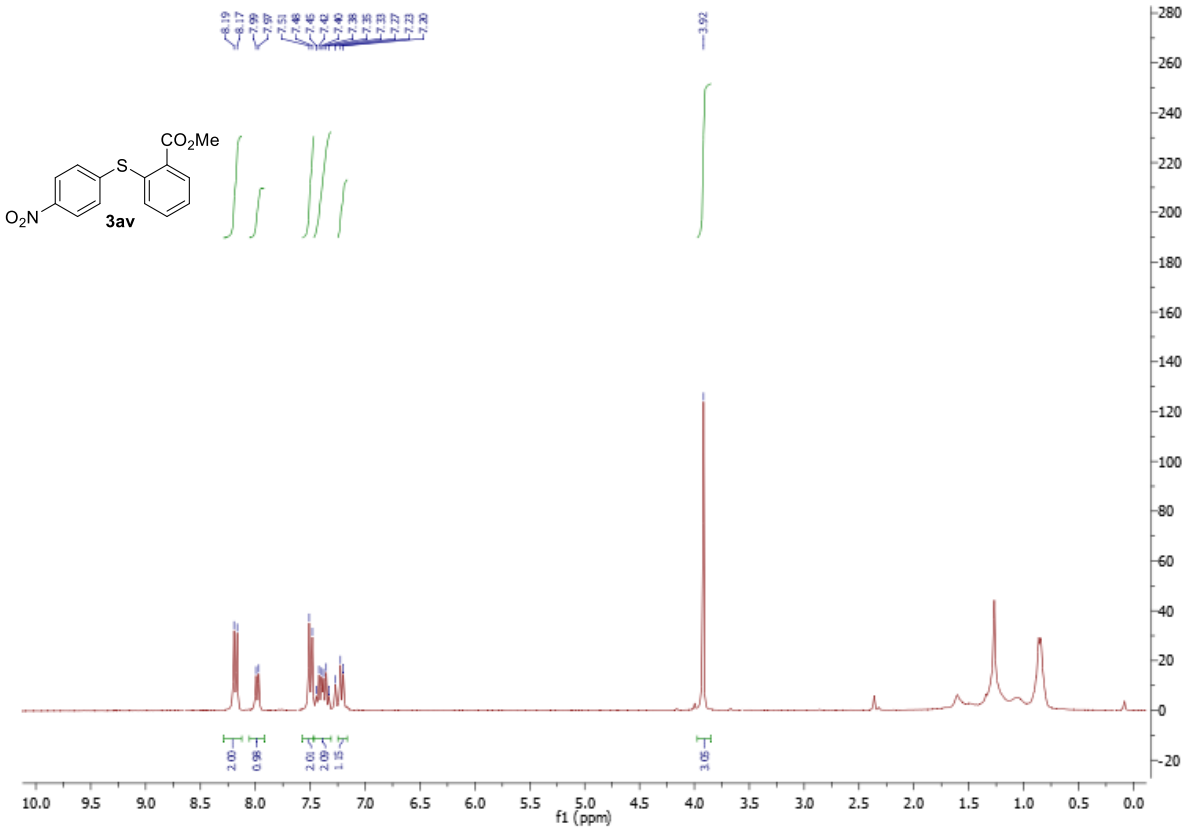

3as
8.03
8.03
8.01
8.00
7.48
7.47
7.45
7.45
7.32
7.29
7.27
7.26
7.24
7.15
7.13
7.10
6.86
6.83
6.81
6.78
6.78
6.77
6.74
6.56
4.65
3.97
3.80
1.00
1.00
2.33
1.08
3.08
5.07
f1 (ppm)

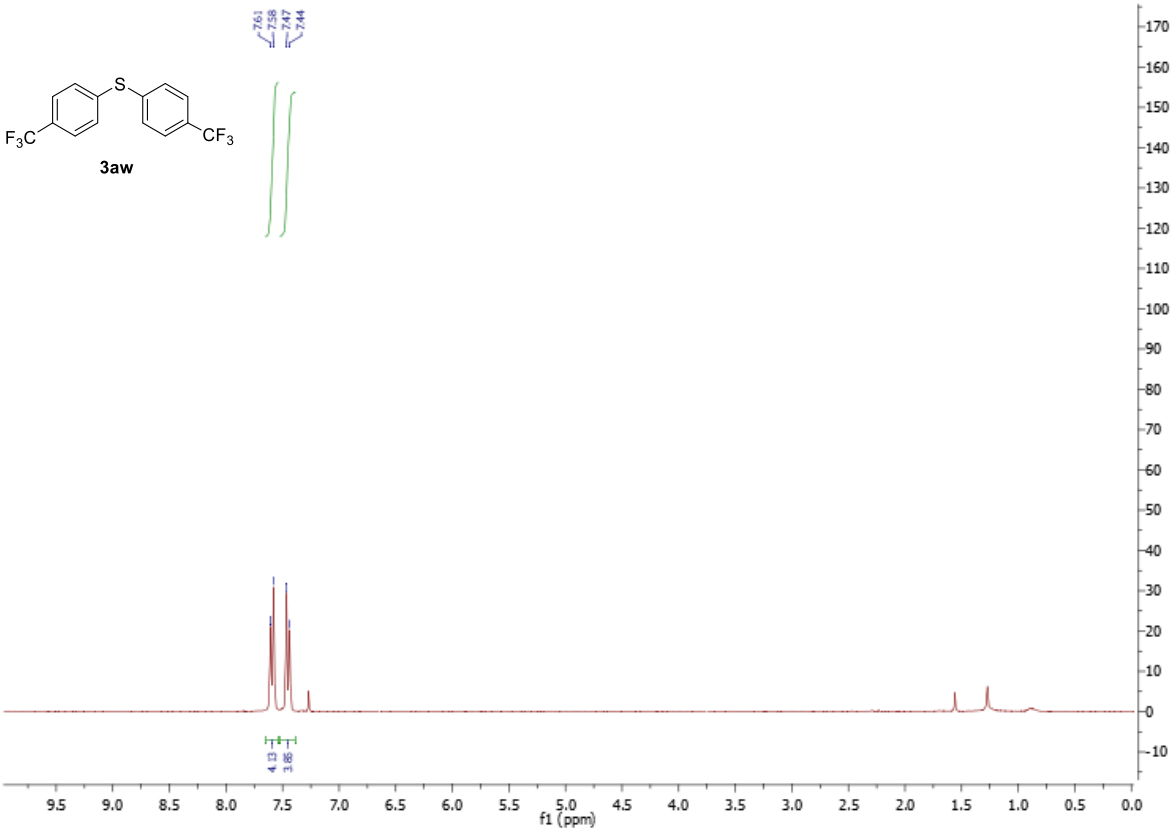

NH2
S
3at
f1 (ppm)

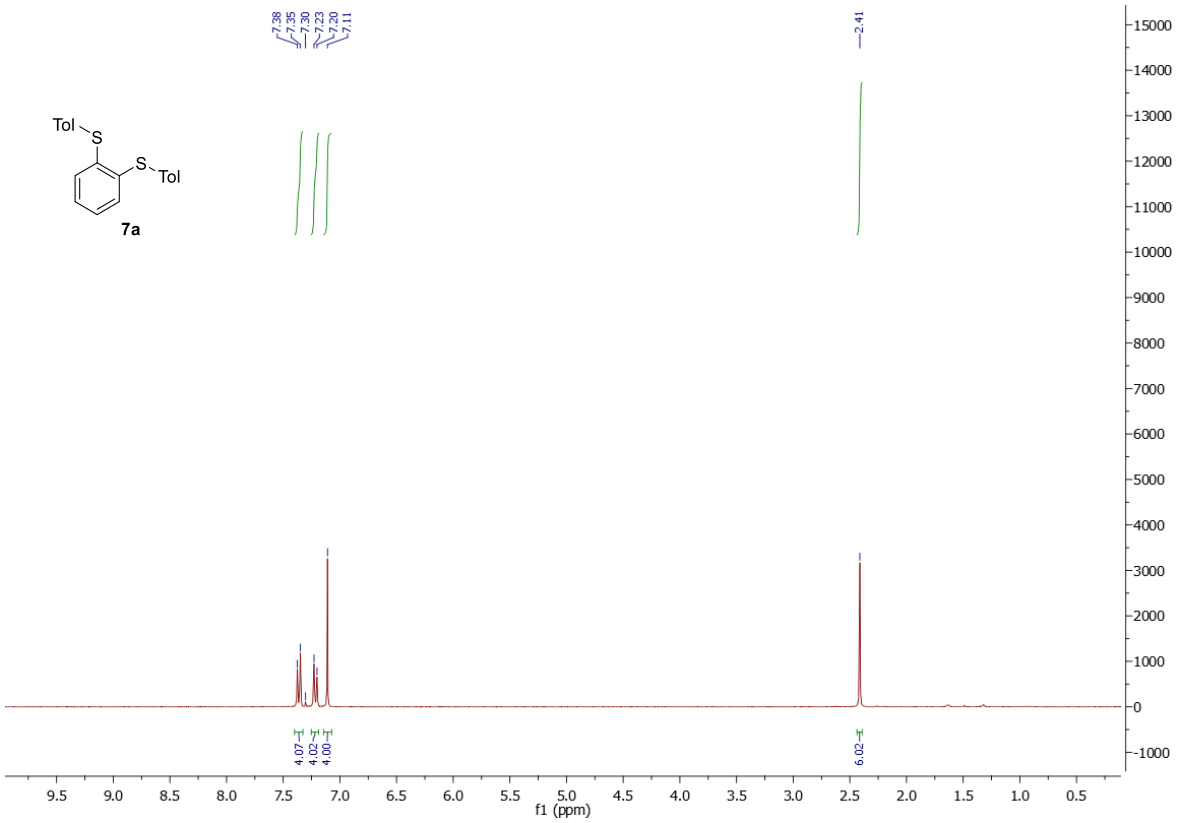

CN
CO2Me
S
3au
f1 (ppm)

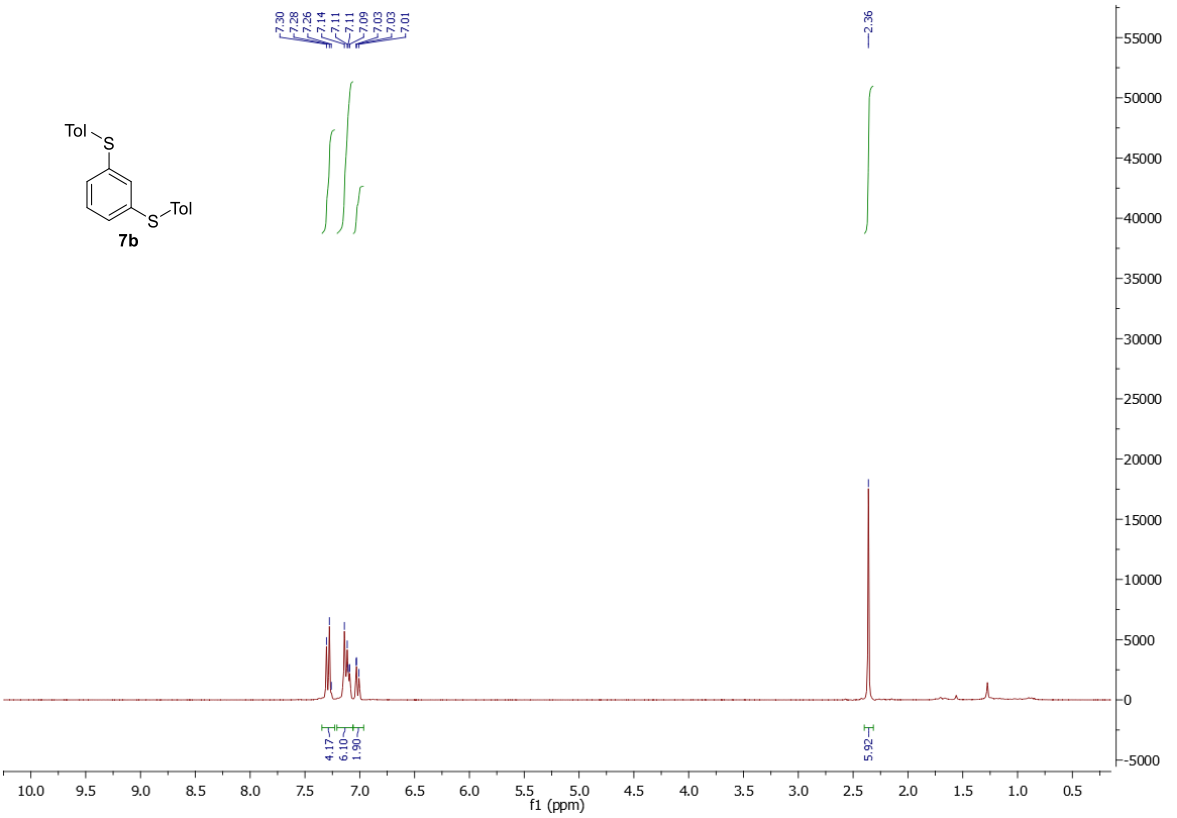

CN
CO2Me
S
3au
166.93
139.60
138.31
136.12
134.61
133.68
132.86
131.54
129.29
128.93
128.91
126.10
118.45
117.06
77.30
53.61
f1 (ppm)

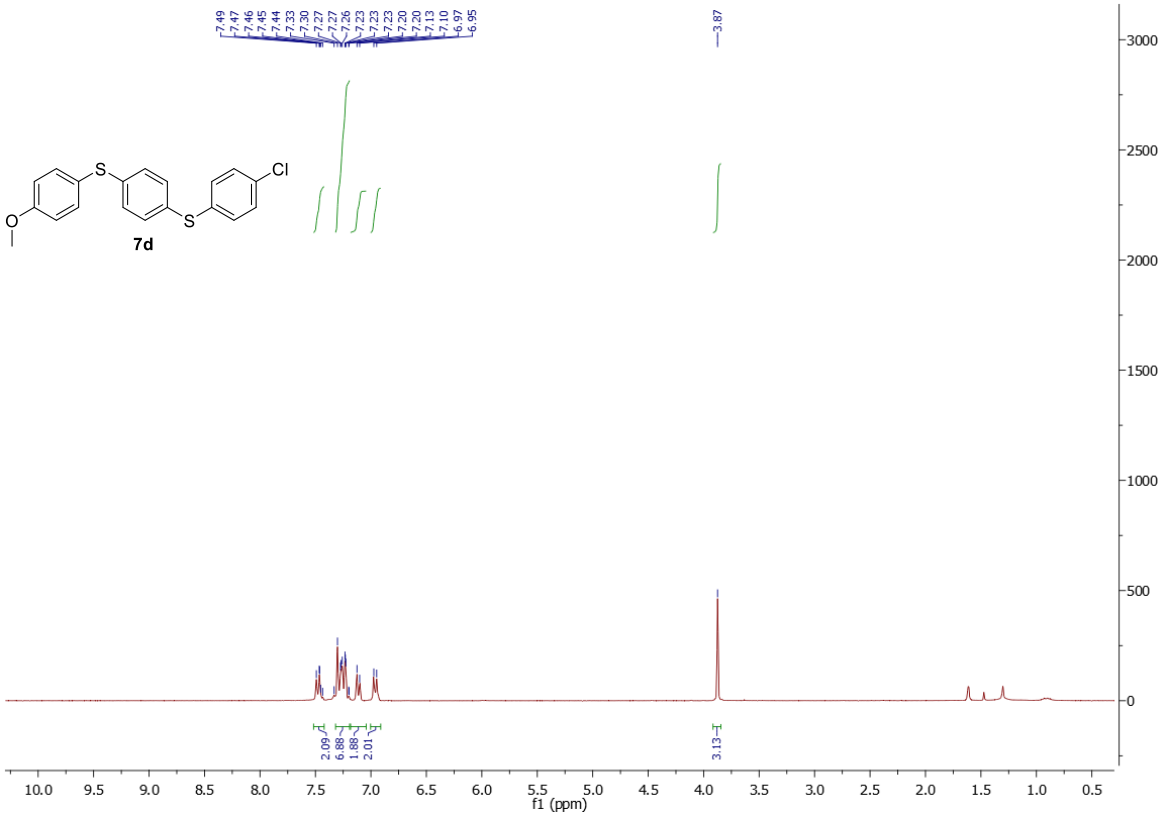

GCT15955 1418 (13.810) Cm (1418:1420-1560:1661)
TOF MS EI+
1.84e3
CN
CO2Me
S
3au
238.0332
269.0504
183.0292
210.0364
209.0286
139.0566
239.0394
177.0545
136.0028
164.0486
184.0302
211.0324
270.0514
140.0563
240.0329
108.0036
63.0226
81.9880
92.0254
113.0344
152.0522
185.0305
236.0154
271.0515
254.0282
%
m/z

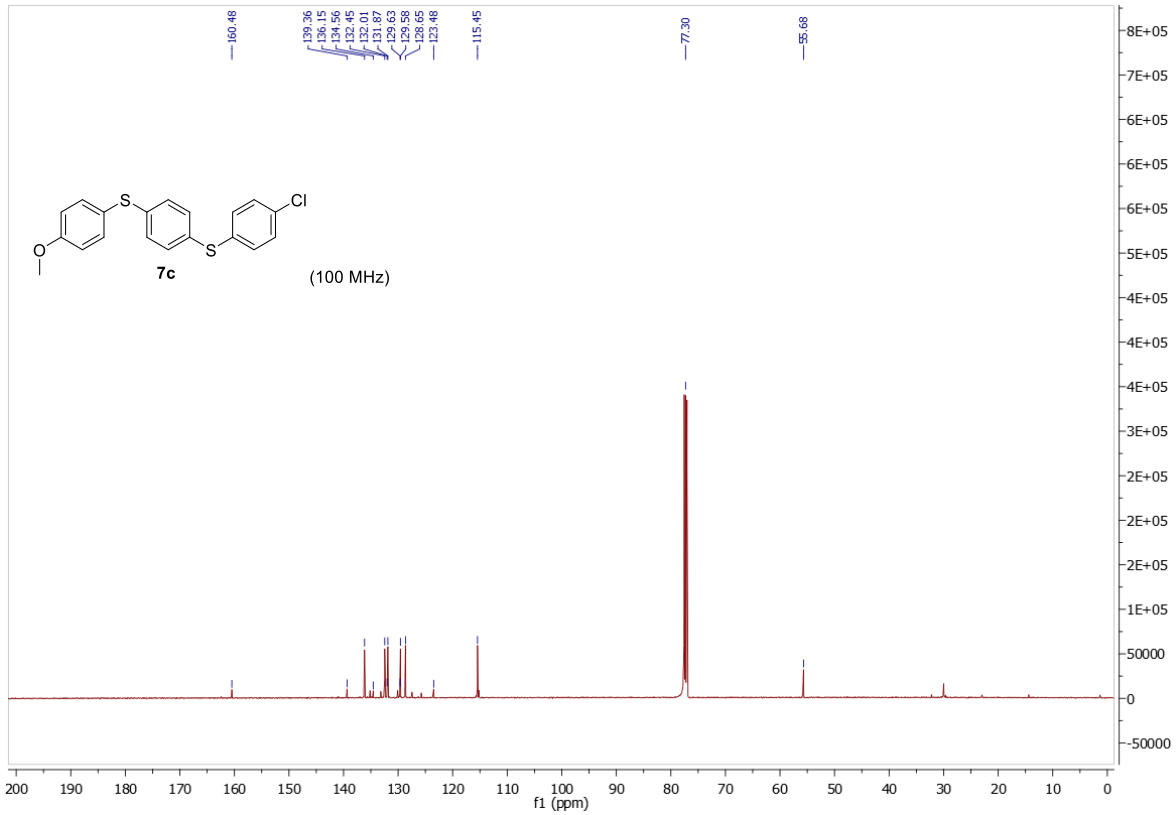

CO2Me
S
O2N
3av
8.19
8.17
7.99
7.97
7.51
7.48
7.46
7.42
7.40
7.38
7.35
7.33
7.27
7.23
7.20
3.92
2.00
0.98
2.01
2.09
1.15
3.05
f1 (ppm)

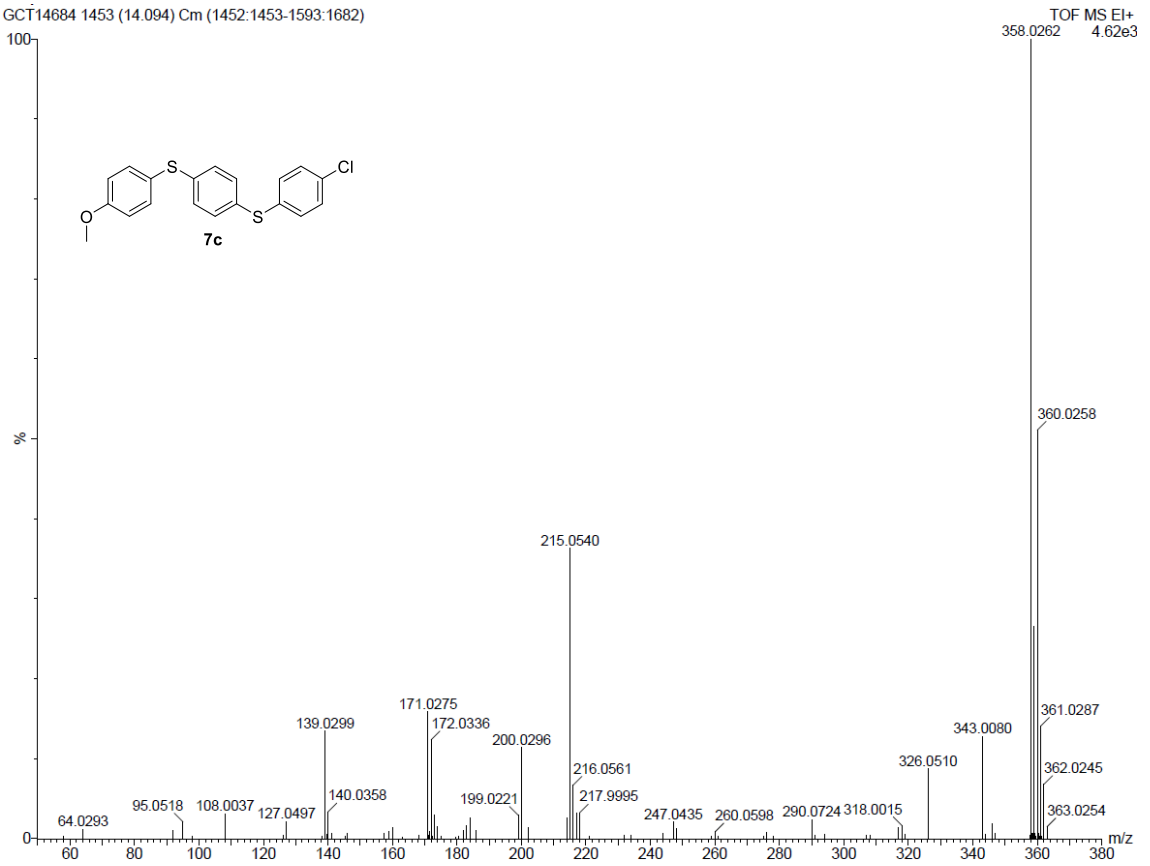

S
F3C
CF3
3aw
7.61
7.58
7.47
7.44
4.13
3.86
f1 (ppm)

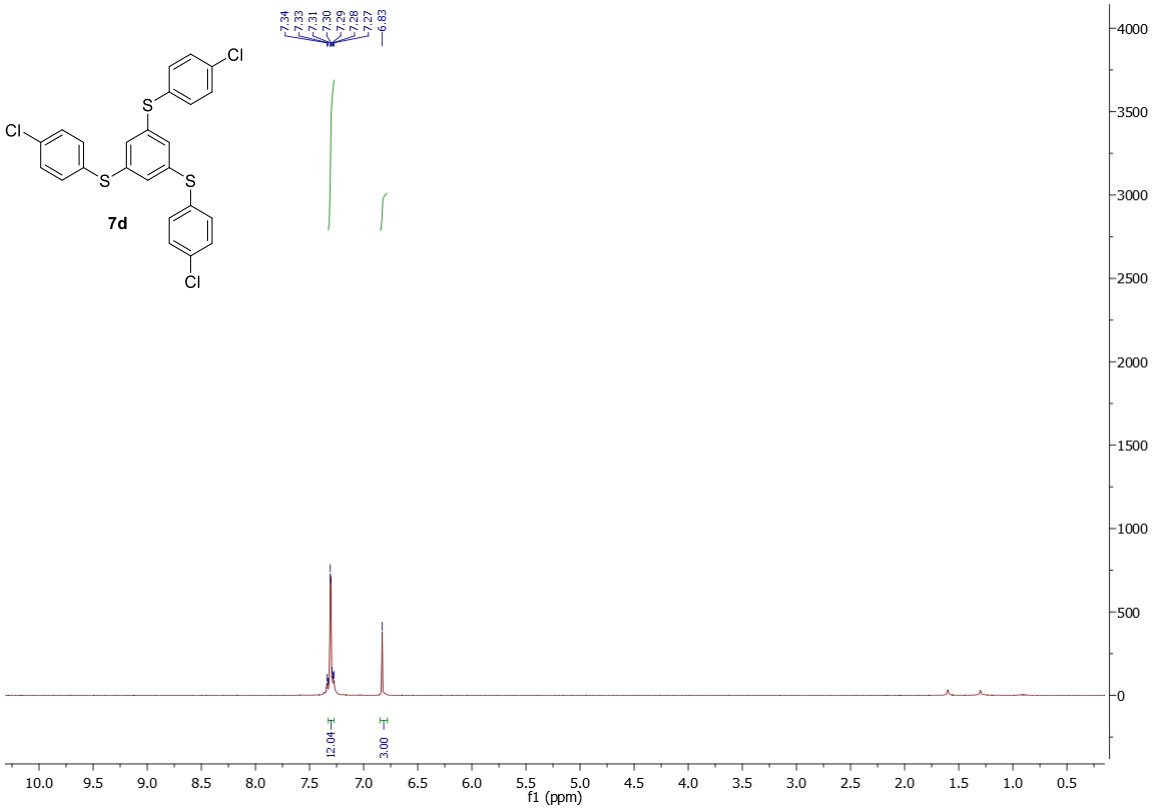

Tol
S
S
Tol
7a
7.38
7.35
7.30
7.23
7.20
7.11
2.41
4.07
4.02
4.00
6.02
f1 (ppm)

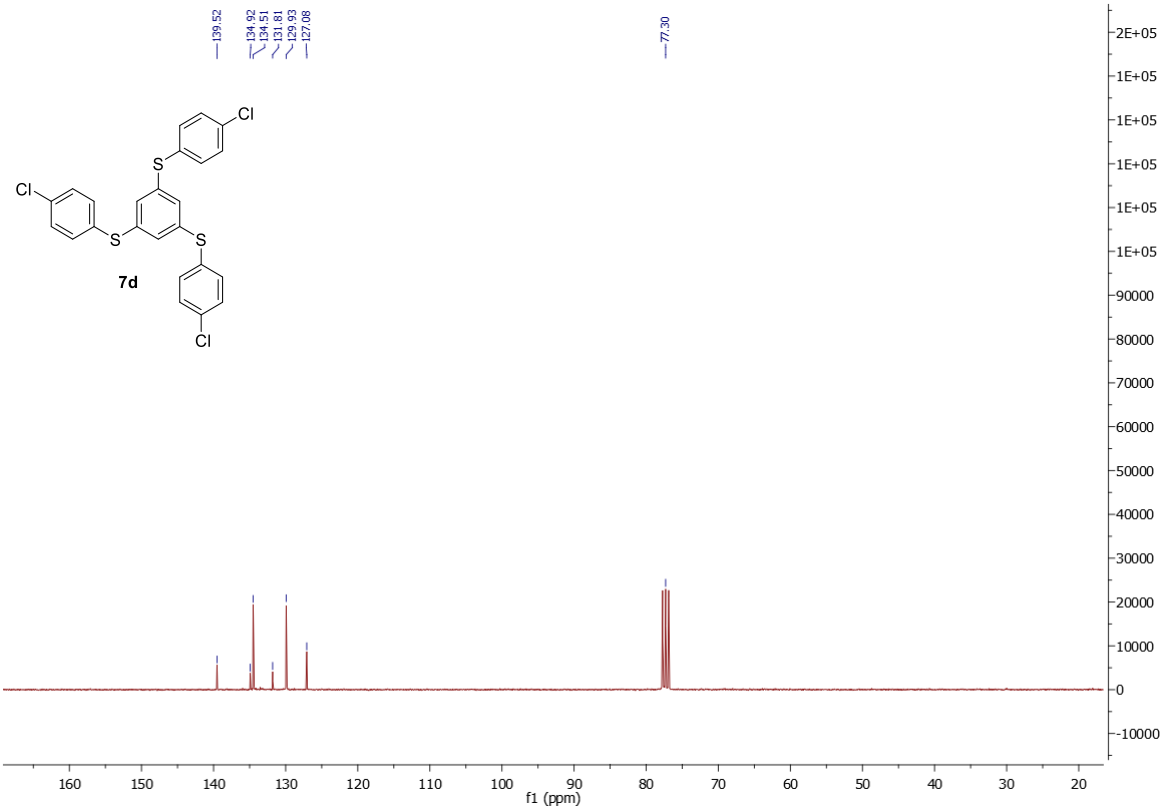

Tol
S
S
Tol
7b
7.30
7.28
7.26
7.14
7.11
7.11
7.09
7.03
7.03
7.01
2.36
4.17
6.10
1.90
5.92
f1 (ppm)

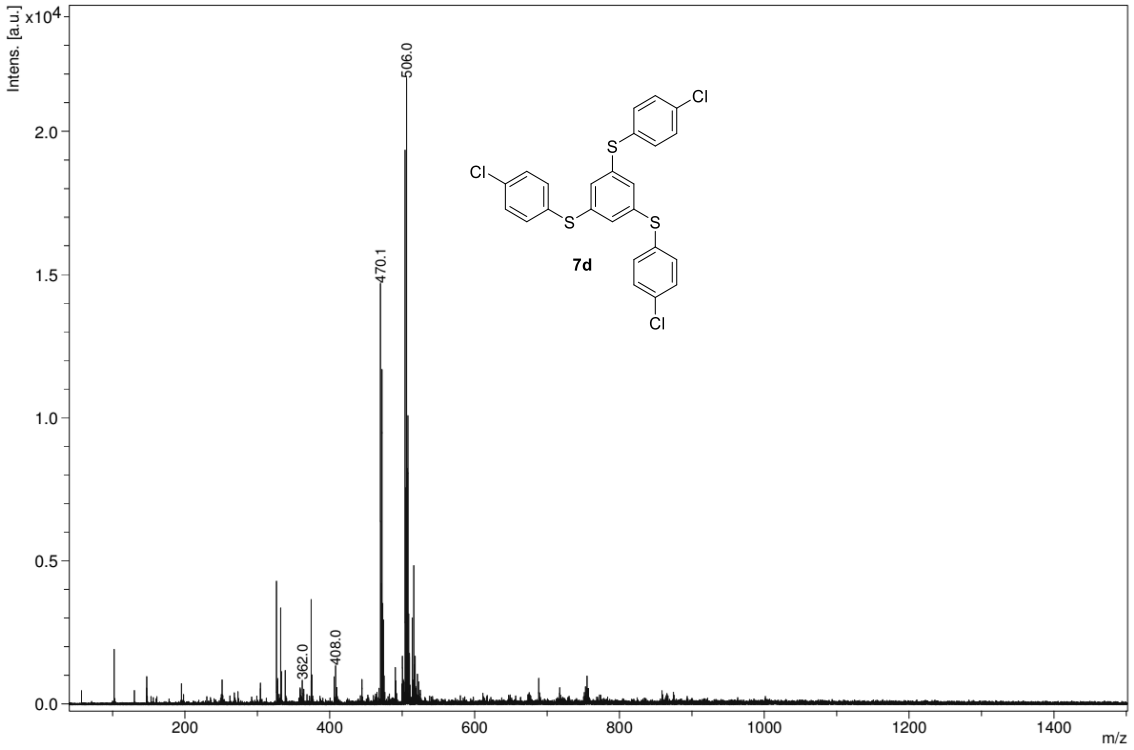

7.49
7.47
7.46
7.45
7.44
7.33
7.30
7.27
7.27
7.26
7.23
7.23
7.23
7.20
7.20
7.13
7.10
6.97
6.95
3.87
S
S
Cl
O
7d
2.09
6.88
1.88
2.01
3.13
f1 (ppm)

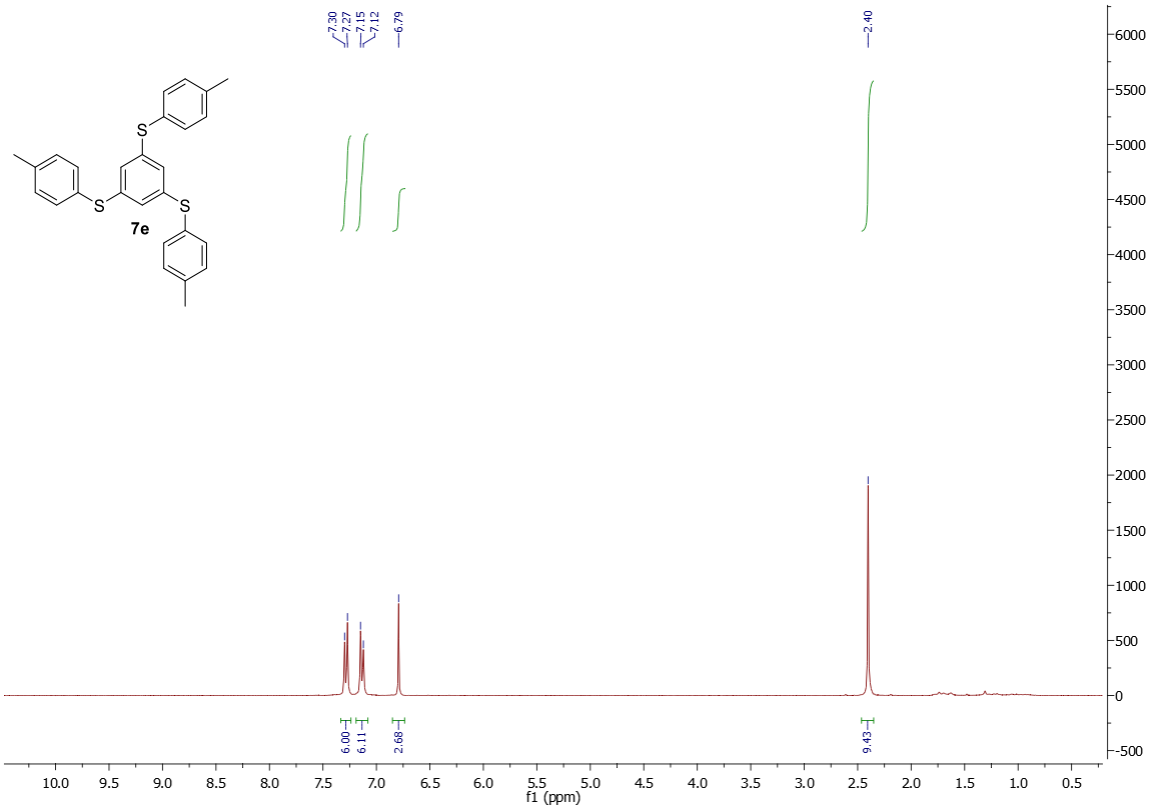

160.48
139.36
136.15
134.56
132.45
132.01
131.87
129.63
129.58
128.65
123.48
115.45
77.30
55.68
S
S
Cl
O
7c
(100 MHz)
f1 (ppm)

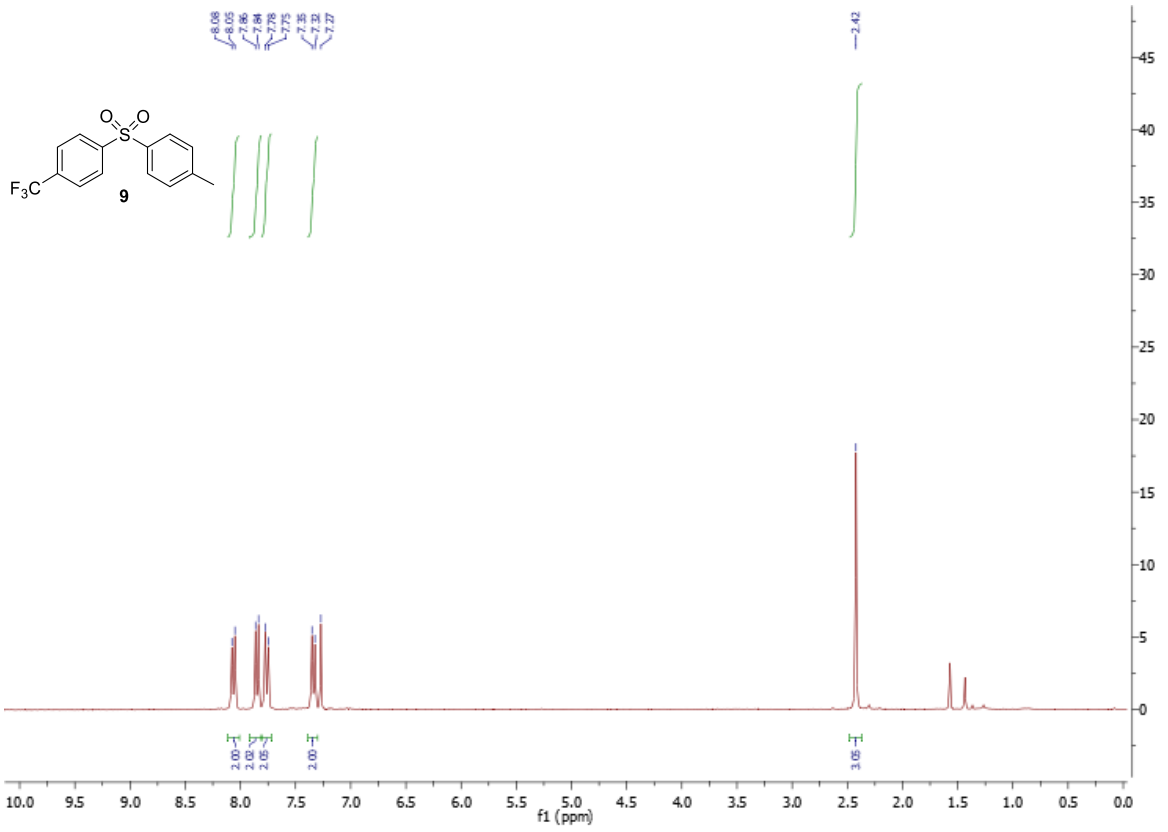

GCT14684 1453 (14.094) Cm (1452:1453-1593:1682)
TOF MS EI+
358.0262 4.62e3
100
%
0
S
S
Cl
O
7c
360.0258
215.0540
171.0275
172.0336
139.0299
200.0296
361.0287
343.0080
326.0510
216.0561
362.0245
140.0358
199.0221
217.9995
95.0518
108.0037
127.0497
64.0293
247.0435
260.0598
290.0724
318.0015
363.0254
60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380
m/z


7.34
7.33
7.31
7.30
7.29
7.28
7.27
6.83
Cl
Cl
S
S
S
7d
Cl
4000
3500
3000
2500
2000
1500
1000
500
0
12.04
3.00
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)


139.52
134.92
134.51
131.81
129.93
127.08
77.30
Cl
S
Cl
S
S
7d
Cl
2E+05
1E+05
1E+05
1E+05
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


Intens. [a.u.]
x10^4
2.0
1.5
1.0
0.5
0.0
506.0
470.1
362.0
408.0
Cl
S
Cl
S
S
7d
Cl
200
400
600
800
1000
1200
1400
m/z


7.30
7.27
7.15
7.12
6.79
2.40
S
S
S
7e
6.00
6.11
2.68
9.43
f1 (ppm)


8.08
8.05
7.86
7.84
7.78
7.75
7.35
7.32
7.27
2.42
O
O
S
F3C
9
2.00
2.02
2.05
2.00
3.05
f1 (ppm)

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