Supporting information for

Micellar catalysis: green solution to enable undirected and mild C–H activation of (oligo)thiophenes at challenging β -position.

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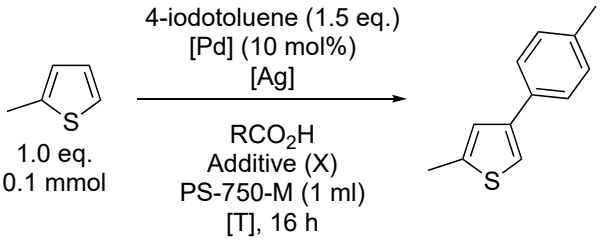
General information

All reactions from the optimization and scope were carried out under air. PS-750-M solutions were previously prepared with PS-750-M from Merck and from distilled and degassed H_2O and stored in a Schlenk flask under argon at 7 °C. Optimization reactions were carried out with 2 mL flasks using 11 mm diameter and 8 mm stirring bars. Scope reactions were performed in 5 mL round bottom flasks with 15 mm stirring bars. Volatile reagents were added as last to the reaction before air-tight sealing the reaction vessel. Room temperature was set at 25 °C. Screening reactions were carried out in a metal block from DrySyn and scope reactions were kept in a water bath to ensure a constant reaction temperature. Technical grade solvents for purifications and extractions (cyclohexane, ethyl acetate, toluene, and dichloromethane) were used without further purification. All reagents were purchased from commercial suppliers (Merck, Sigma Aldrich, Fluorochem, TCI, Alfa Aesar and Apollo Scientific) and used without purification and assumed to have a purity higher than 95%. TLCs were performed with silica coated aluminum plates (0.25 mm, Merck silica-gel 60-F254). Flash column chromatography was performed on VWR silica gel (40 – 63 µm) and with the indicated solvents. Spots were visualized by UV light irradiation (254 or 390 nm). **^{1}H NMR** (400 MHz), **^{19}F NMR** (377 MHz) and **^{13}C NMR** (101 MHz) spectra were recorded on Bruker Avance III HD 400 instrument. Chemical shifts are reported as δ-values in parts per million (ppm) and are referred to partially deuterated chloroform (chloroform δ[^{1}H] = 7.26 ppm and δ[^{13}C] = 77.0 ppm). The spectra were processed with MestreNova 14.3.0 (Mestrelab). Multiplicities were abbreviated as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *m* (multiplet), *dd* (doublet of doublets), *ddd* (doublet of doublets of doublets). Coupling constants *J* were given in Hz. Coupling constants are given for H-H and H-F for proton signals and C-F for carbon signals. Quantitative NMR. (QNMR) were performed by adding CH_2Br_2 to the crude product in $CDCl_3$ and integrated with respect to characteristic peaks of the thiophene. Regioselectivity of the products were analyzed by the GC/MS trace and integrated with Agilent MassHunter Qualitative Analysis 10.0 software. High resolution mass spectrometry (HRMS) analysis was performed with a Bruker MicroTOF mass analyser under ESI in positive ionization mode detection (measurement accuracy ≤ 15 ppm) by the analytical facility at the University of Strasbourg. All measures were carried on at 25 °C. The absorption spectra were recorded on spectrophotometer Cary 5000 UV-visible-NIR (Agilent Technologies). Emission and excitation measurements were carried on a fluorescence spectrometer LS55 (Perkin Elmer). The X-ray crystallographic structure analysis was performed by the radio- crystallographic facility at the Université de Strasbourg. The analysis was carried out on a Bruker PHOTON III DUO CPAD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo-Kα radiation (λ = 0.71073 Å).

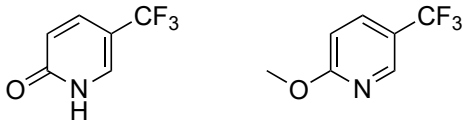
Optimization of the direct arylation of thiophenes

Initial Screening



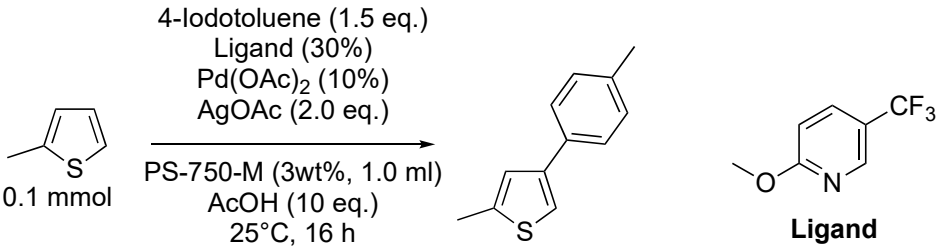
Entry	[Pd]	[Ag]	RCO_2H	Additive	[t]	[T]	Yield
1	$Pd(OAc)_2$	AgOAc (2 eq.)	-	L1	62h	50 °C	19%*
2	$Pd(OAc)_2$	AgOAc (2 eq.)	-	L2	62h	50 °C	12%*
3	$Pd(OAc)_2$	AgOAc (2 eq.)	AcOH 10 eq.l	L2	62h	50 °C	35%*
4	$Pd(OAc)_2$	AgOAc (2 eq.)	AcOH 10 eq.l	-	45h	50 °C	22%*
5	$Pd(OAc)_2$	AgOAc (2 eq.)	AcOH 10 eq.l	L2	45h	25 °C	32%*
6	$Pd(OAc)_2$	AgOAc (2 eq.)	AcOH 10 eq.l	L2	45h	25 °C	32%*
7	**$Pd(OAc)_2$**	**AgOAc (2 eq.)**	**AcOH 10 eq.l**	**L2**	**16h**	**25 °C**	**44%***
8	$Pd(OAc)_2$	AgOAc (2 eq.)	AcOH 10 eq.l	L2	41h	50 °C	21%*
9	1%	AgOAc (2 eq.)	AcOH 10 eq.l	L2	16h	50 °C	2%*
10	2%	AgOAc (2 eq.)	AcOH 10 eq.l	L2	16h	50 °C	5%*
11	25%	AgOAc (2 eq.)	AcOH 10 eq.l	L2	16h	50 °C	44%*

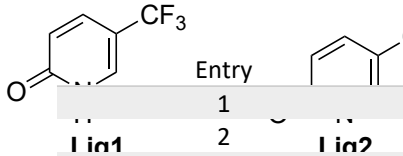
*Yield determined by ^1H NMR using an internal standard



L1 **L2**

Ligand Screening

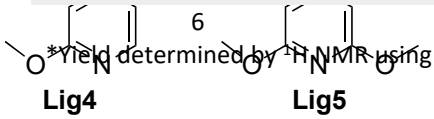




Lig1 **Lig2** **Lig3**

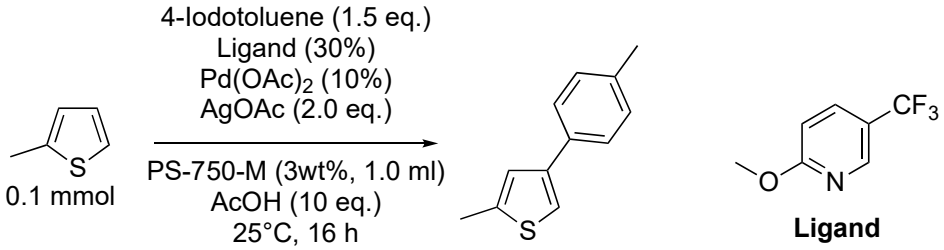
Entry	Deviation	Yield
1	Ligand free	31%*
2	Pyridine	1%*
3	Lig3	6%*
4	Lig4	13%*
5	**Lig2**	**43%***
6	Lig5	37%*

*Yield determined by ^1H NMR using an internal standard



Lig4 **Lig5**

Silver quantity



Entry	Deviation	Yield
1	No Silver	7%*
2	AgOAc 0.5 eq.	41%*
3	**AgOAc 1.0 eq.**	**53% ***
4	AgOAc 1.5 eq.	51% *
5	AgOAc 2.0 eq.	43% *

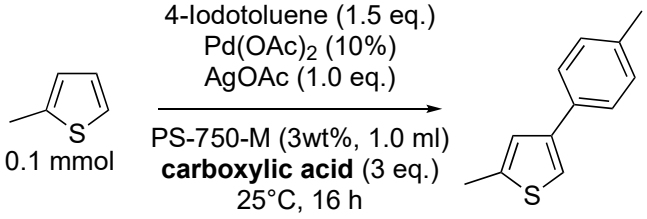
*Yield determined by ^{1}H NMR using an internal standard

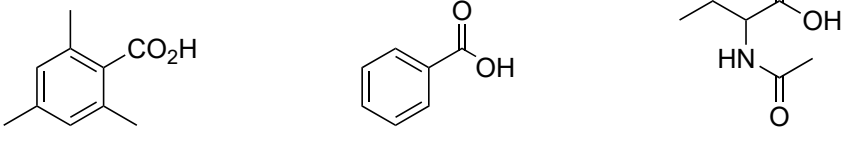
Silver/oxidant source

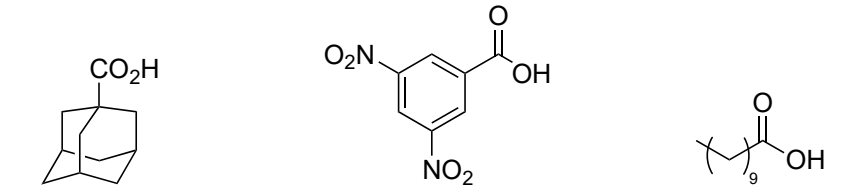
Entry	Deviation	Yield
1	Ag_2O 1.0 eq.	5%*
2	AgI 1.0 eq.	6%*
3	Ag_2SO_4 1.0 eq.	27%*
4	AgTFA 1.0 eq.	52%*
5	**AgOAc 1.0 eq.**	**53%***
6	No Silver	7%*
7	CuOAc	0%*
8	$Cu(OAc)_2$	8%*
9	BQ	0%*
10	O_2 balloon	9%*

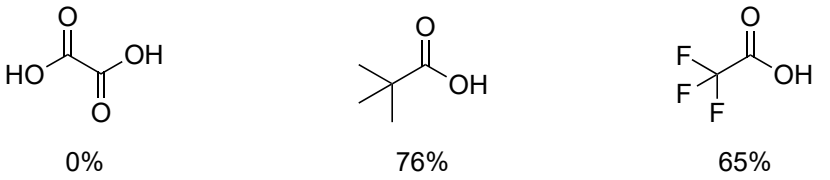
*Yield determined by ^{1}H NMR using an internal standard

Carboxylic acid screening





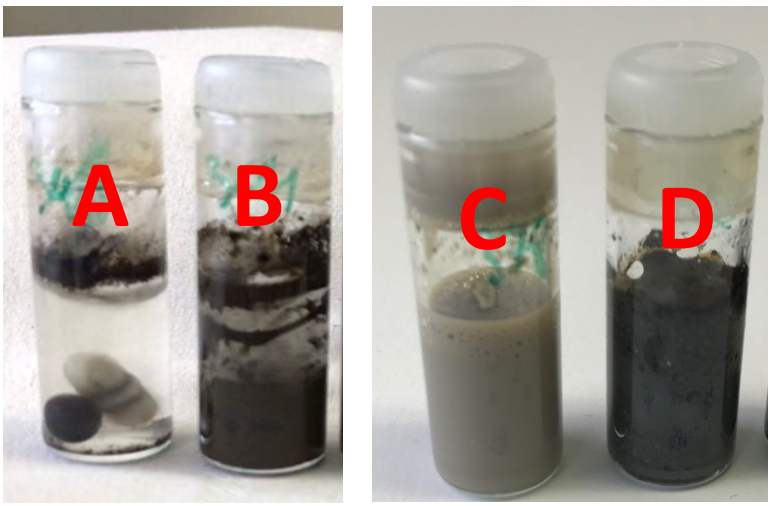




Alternative acids screening

Entry	Deviation	Yield
1	HCl 37% 50 yl	0%*
2	*p*TsOH 50 mg	8%*
3	CF_3CO_2H 10 eq + CF_3CO_2Ag 1.0 eq.	62%*
4	Sodium laurate	47%*

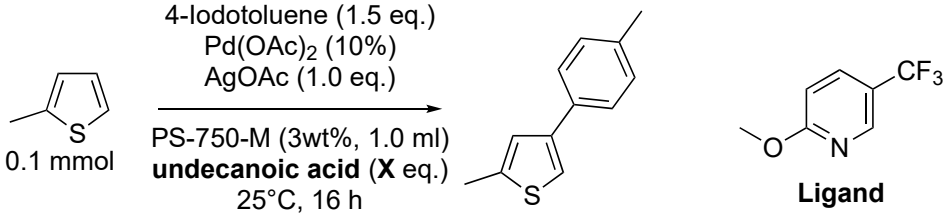
*Yield determined by 1H NMR using an internal standard



Homogeneity of reaction mixture, standard reaction condition (1.0 eq. 2-methylthiophene, 1.5 eq. 4-iodotoluene, $Pd(OAc)_2$ 10%, AgOAc 1.0 eq, undecanoic acid 1.0 eq, 3 wt% PS-750-M, 0.1 mmol scale),

A. In water instead of PS-750-M
B. With benzoic acid instead of undecanoic acid
C. Optimized conditions
D. With 5.0 eq. undecanoic instead of 1.0 eq.

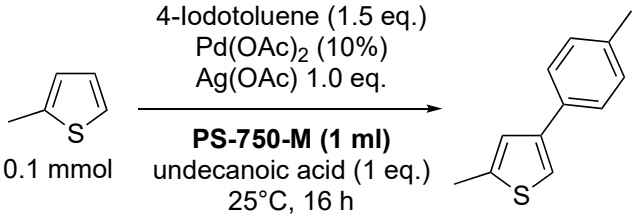
Carboxylic acid quantity



Entry	Deviation	Yield
1	5 eq. acid	90%
2	3 eq. acid	79%
3	1 eq. acid	79%
4	0.5 eq. acid	69%
5	3 eq. acid, ligand free	84%
6	acid free	24%
7	**1.0 eq. acid,ligand free**	**80%**
8	3.0 eq. acid, ligand free	86%
9	5.0 eq. acid, ligand free	89%
10	10.0 eq. acid, ligand free	84%

*Yield determined by ^1H NMR using an internal standard

Reaction media

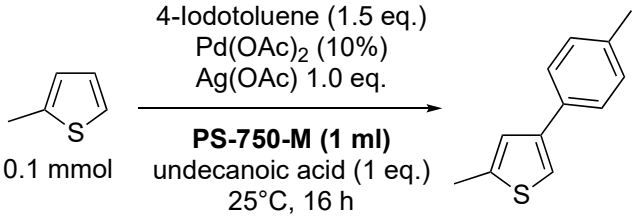


Entry	Deviation	Yield
1	In water	86%*
2	In water, 0.2 mmol scale	50%**
3	5% PS-750-M	83%*
4	EtOH as solvent	55%*
5	0.5 mL 3% PS-750-M	83%*

*Yield determined by ^{1}H NMR using an internal standard

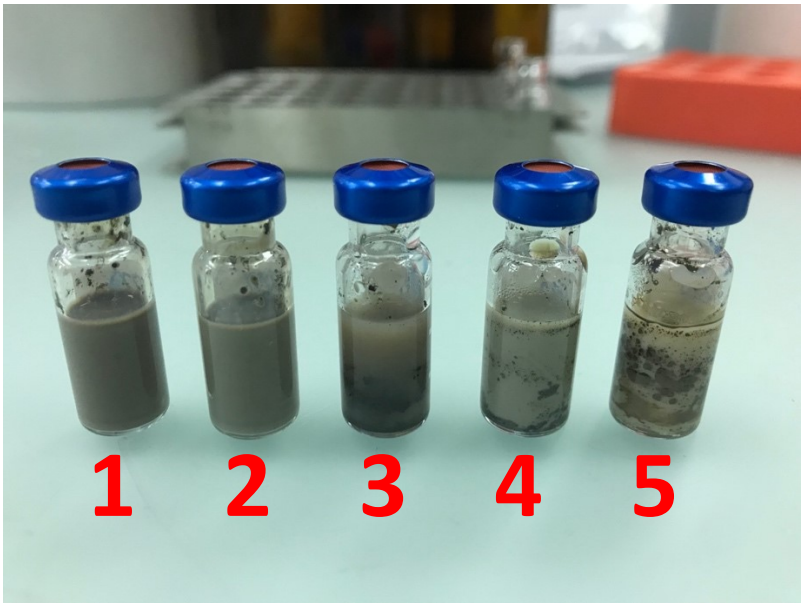
**The absence of surfactant resulted in an inhomogeneous mixture, which could not be reproduced on 0.5 mmol scale

Surfactant concentration

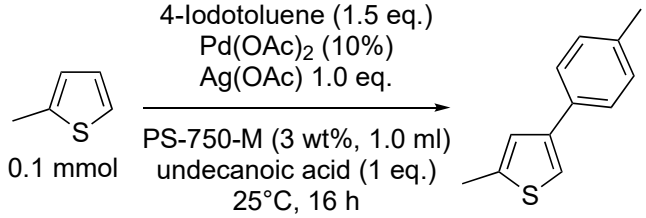


Entry	Deviation	Yield
1	3% PS-750-M	88%
2	2% PS-750-M	87%
3	1% PS-750-M	86%
4	2% TPGS-750-M	81%
5	2% SPGS-550-M	86%

*Yield determined by ^{1}H NMR using an internal standard



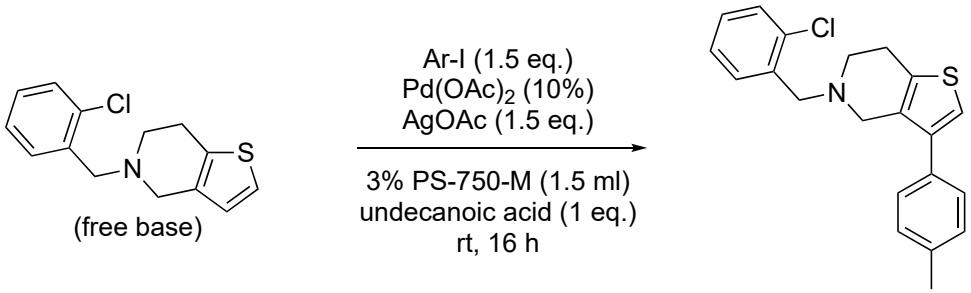
Control experiments



Entry	Deviation	Yield
1	4-bromotoluene	0%*
2	No [Pd]	0%*
3	No Silver	5%*
4	Solvent free (10 eq. undecanoic acid)	0%*
5	1.0 eq. Iodotoluene	86%*
6	1.1 eq. Thiophene 1.0 eq 4-iodotoluene	92%*

*Yield determined by ^{1}H NMR using an internal standard

Optimization of the reaction conditions for direct arylation of Ticlopidine

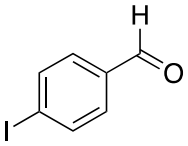


Entry	Deviation	Yield (SM:Pr)
1	Ticlopidine* HCl	7%* (10:1)
2	3 days	36%* (1:1)
3	2 mL 5% PS-750-M	32%* (1.4:1)
4	AcOH (3 eq.)	27%* (1.8:1)
5	benzoic acid	18%* (3.7:1)
6	PivOH	30%* (1.3:1)
7	At 40 °C, 1 eq. undecanoic acid	36%* (1.2:1)
8	1 eq. AgOAc	36%* (1.3:1)
9	1.5 eq. AgOAc	44%* (0.9:1)
10	2.0 eq AgOAc	37%* (0.8:1)
11	3.0 eq AgOAc	39%* (0.8:1)
12	1.5 eq. AgOAc 41 hours	40%* (0.8:1)
13	1.5 eq. AgOAc and 0.2 eq Pd	47%* (0.5:1)
14	1.5 eq. AgOAc 3 eq. undecanoic acid	20%* (3:1)
15	1.5 eq. AgOAc, 3 eq. acid Dppf (0.3 eq.) ligand	1%* (99:1)
16	under Argon	37%* (1.1:1)
17	0.5 eq. acid	34%* (1:1)
18	0.1 eq. acid	33%* (0.9:1)
19	no acid	21%* (1.8:1)
20	0.2 eq. Pd/C (10%)	0%* (98:0)
21	$Pd(Acac)_2$	0%* (100:0)
22	$PdCl_2$	10%* (8:1)

23	$Pd(dba)_2$	20%* (4:1)
24	$Pd(TFA)_2$	38%* (1.5:1)
25	Ag_2CO_3	44%* (0.8:1)
26	AgTFA	26%* (2.6:1)
27	AgBenzoate	25%* (2.1:1)
28	Ag_2O	5%* (14:1)
29	K_2CO_3 (2.0 eq.) additive	26%* (1.7:1)
30	Ag_2CO_3 (1.0 eq.) $Pd_2(dba)_3$ (5%)	10%* (7:1)
31	10 yl EtOAc cosolvent	41%* (0.8:1)
32	10% $Pd(OAc)_2$ after 16h, 41h	40%* (0.3:1)
33	60 °C	30%* (1.2:1)
34	80 °C	21%* (1.9:1)
35	8h	44%* (1:1)
36	3.0 eq. AgOAc, 8h	33%* (1.4:1)
37	1.5 eq. AgOAc 8h, then 1.5 eq. AgOAc, 8h	38%* (0.7:1)
38	H_2O, 80 °C	24%* (1.6:1)
39	1 mL PS-750-M, 10% MeOH	41%* (0.9:1)
40	1 mL PS-750-M, 10% EtOH	43%* (1:1)
41	1 mL PS-750-M, 10% iPrOH	46%* (0.7:1)
42	1 mL PS-750-M, 10% THF	37%* (1:1)
43	1 mL PS-750-M, 10% Toluene	26%* (2:1)
44	1 mL PS-750-M, 10% Acetone	41%* (1:1)
45	1 mL PS-750-M, 10% ACN	44%* (0.9:1)
46	1 mL HFIP	14%* (4:1)
47	**3 eq. ArI**	**50%* (1:1)**

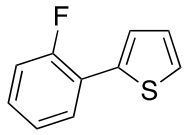
*Yield determined by ^1H NMR using an internal standard

Synthesis of thiophenes and aryl iodine substrates



4-iodobenzaldehyde

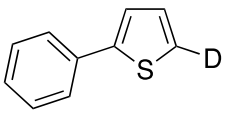
4-iodobenzonitrile (687 mg, 3.00 mmol, 1.0 eq) was dissolved in dry CH_2Cl_2 and cooled to 0 °C before DIBAL-H (3.0 mL, 1.2 M in hexane, 3.60 mmol. 1.2 eq.) was added slowly. After full addition, the reaction was allowed to stir for 2 h at rt before it was transferred to an Erlenmeyer flask with ice and concentrated HCl (20 mL) and stirred for another 30 min. The reaction was quenched with sat. aq. $NaHCO_3$, extracted with CH_2Cl_2 and dried over $MgSO_4$. The product was isolated as white solid (563 mg, 2.43 mmol, 81 %) and used without further purification. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.96 – 7.88 (m, 2H), 7.63 – 7.56 (m, 2H). Spectral data were consistent with the literature.[1]



2-(2-fluorophenyl)thiophene

2-fluorophenylboronic acid (700 mg, 5.00 mmol, 1.0 eq.), 2-bromothiophene (815 mg, 5.00 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (86.6 mg, 75.0 µmol, 1.5%) and K_2CO_3 (898 mg, 6.50 mmol, 1.3 eq.) were dissolved in a 1:1 mixture of dioxane/water (10mL) and heated for 14 h at 100 °C. The reaction was extracted with EtOAc, dried over $MgSO_4$, and purified by flash column chromatography (cyclohexane/EtOAc 95:5) to obtain the product as white solid (750 mg, 4.20 mmol, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (td, *J* = 8.0, 1.9 Hz, 1H), 7.49 (dt, *J* = 3.7, 1.3 Hz, 1H), 7.37 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.21 – 7.10 (m, 3H). Spectral data were consistent with the literature.[2]



2-phenylthiophene-5-d

2-Phenylthiophene (401 mg, 2.50 mmol, 1.0 eq.) was dissolved in DMSO- *d*6 (2.8 mL, 40.0 mmol, 16 eq.) and K_3PO_4 (265 mg, 1.25 mmol, 0.5 eq.) was added. The reaction mixture was stirred for 60h at 130°C and quenched with sat. aq. $NaHCO_3$. The organic layer was extracted with cyclohexane and the product was isolated without further purification as white solid (317 mg, 1.97 mmol, 79%). **^{1}H NMR**

(400 MHz, Chloroform-*d*) δ 7.64 – 7.61 (m, 2H), 7.41 – 7.36 (m, 2H), 7.32 (d, *J* = 3.6 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.09 (d, *J* = 3.6 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.49, 134.56, 129.02, 127.98, 127.59, 126.10, 123.21. **HRMS (ESI)** m/z calc. for $C_{10}H_8DS^+$ $[M+H]^+$: 162.0482, found: 162.0457.

General procedures

General procedure A: Thiophene (1.0 eq.), aryl iodide (1.5 eq.), silver acetate (1.0 eq.), palladium diacetate (10%) and undecanoic acid (1.0 eq.) were added in a 10 mL RBF with a 15 mm stirring bar. A degassed solution of 3 wt% PS-750-M (0.1 M) was added, and the reaction stirred for 16h at room temperature. After this time, the mixture was diluted with EtOAc, dried with $MgSO_4$, filtered over a plug of celite and washed several times with EtOAc. The crude mixture was then analysed by quantitative NMR with CH_2Br_2 as internal standard. The crude product was purified by column chromatography with the specified solvent and further purified on preparative TLC if necessary to obtain the pure product.

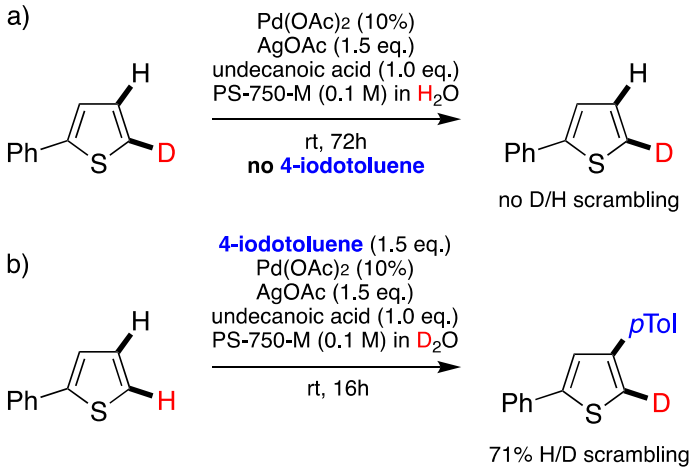
General procedure B: An excess of thiophene (2.4 – 5.0 eq.), aryl iodide (1.0 eq.), silver acetate (3.0 eq.), palladium diacetate (10%) and undecanoic acid (3.0 eq.) were added in a 10 mL RBF with a 15 mm stirring bar. A degassed solution of 3 wt% PS-750-M (0.1 M) was added and the reaction stirred for three days at room temperature. After this time, the mixture was diluted with EtOAc, dried with $MgSO_4$, filtered over a plug of celite and washed several times with EtOAc. The crude mixture was then analysed by quantitative NMR with CH_2Br_2 as internal standard. The crude product was purified by column chromatography with the specified solvent and further purified on preparative TLC if necessary to obtain the pure product.

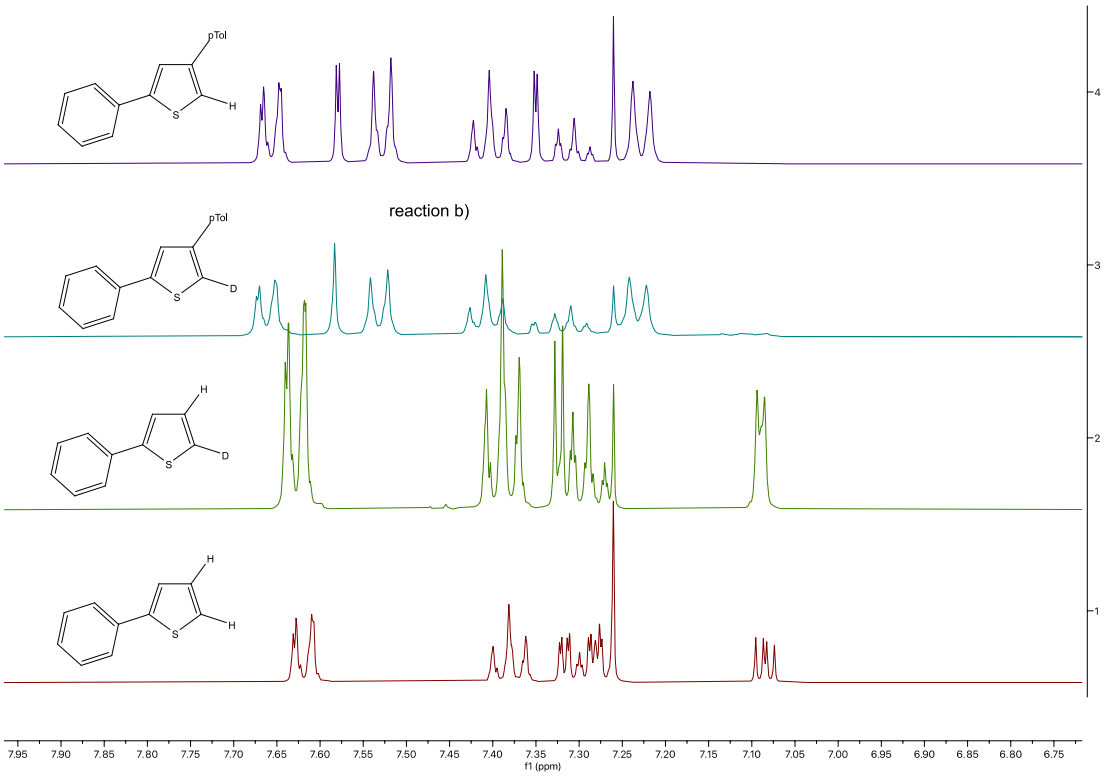
General procedure C: Thiophene (1.0 eq.), aryl iodide (5.0 eq.), silver acetate (3.0 eq.), palladium diacetate (10%) and undecanoic acid (3.0 eq.) were added in a 10 mL RBF with a 15 mm stirring bar. A degassed solution of 3 wt% PS-750-M (0.1 M) was added, and the reaction stirred for the indicated time at room temperature. After this time, the mixture was diluted with EtOAc, dried with $MgSO_4$, filtered over a plug of celite and washed several times with EtOAc. The crude mixture was then analysed by quantitative NMR with CH_2Br_2 as internal standard. The crude product was purified by column chromatography with the specified solvent and further purified on preparative TLC if necessary to obtain the pure product.

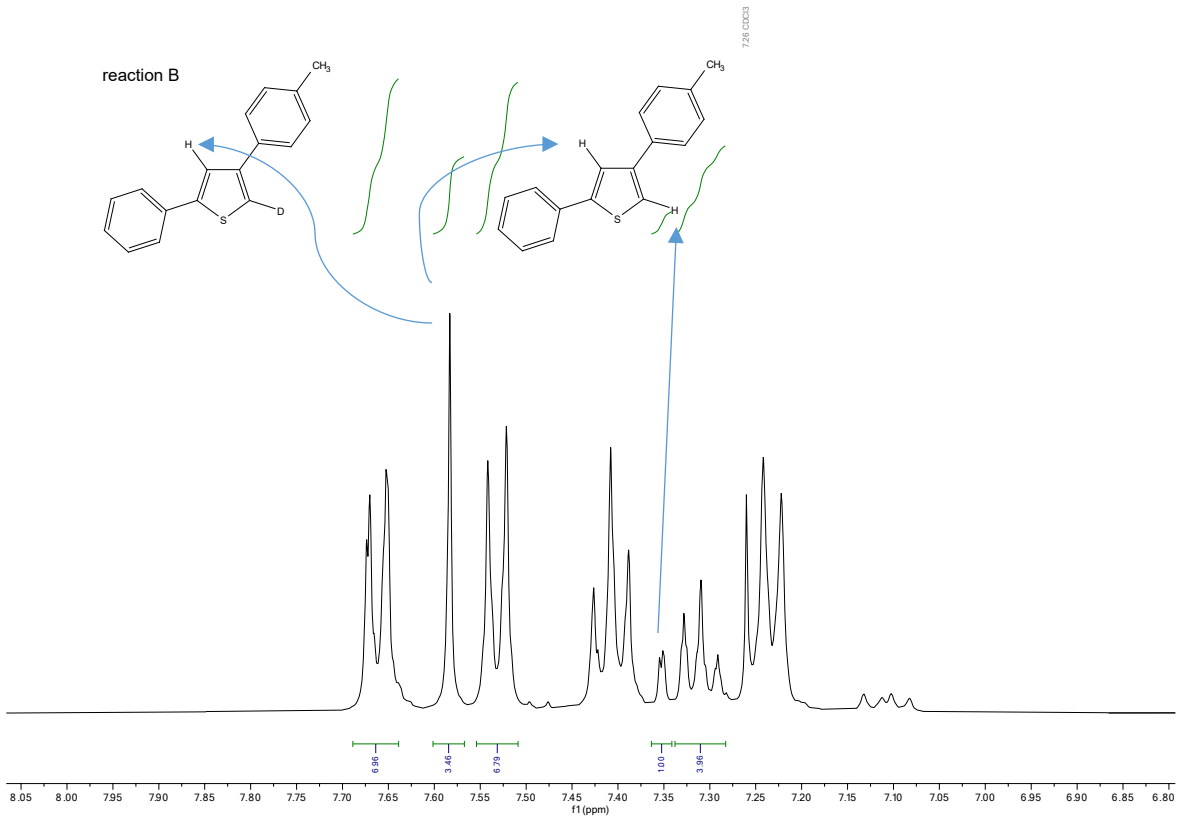
General procedure D: Thiophene (1.0 eq.), aryl iodide (3.0 eq.), silver acetate (1.5 eq.), palladium diacetate (10%) and undecanoic acid (1.0 eq.) were added in a 2 mL vial with an 8 mm stirring bar. A degassed solution of 3 wt% PS-750-M (0.1 M) was added, and the reaction stirred for 16 h at room temperature. After this time, the mixture was diluted with EtOAc, dried with $MgSO_4$, filtered over a plug of celite and washed several times with EtOAc. The crude mixture was then analysed by quantitative NMR

with CH_2Br_2 as internal standard. The crude product was purified by column chromatography with the specified solvent and further purified on preparative TLC if necessary to obtain the pure product.

Kinetic measurements

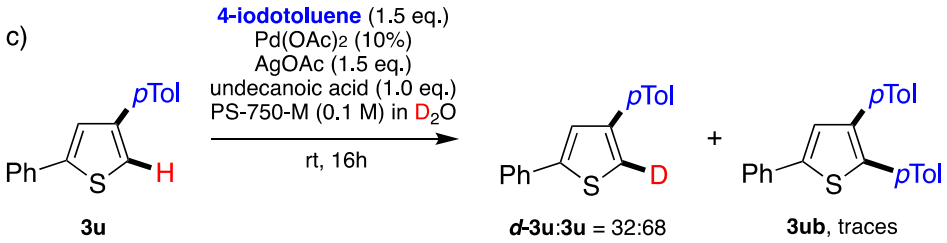




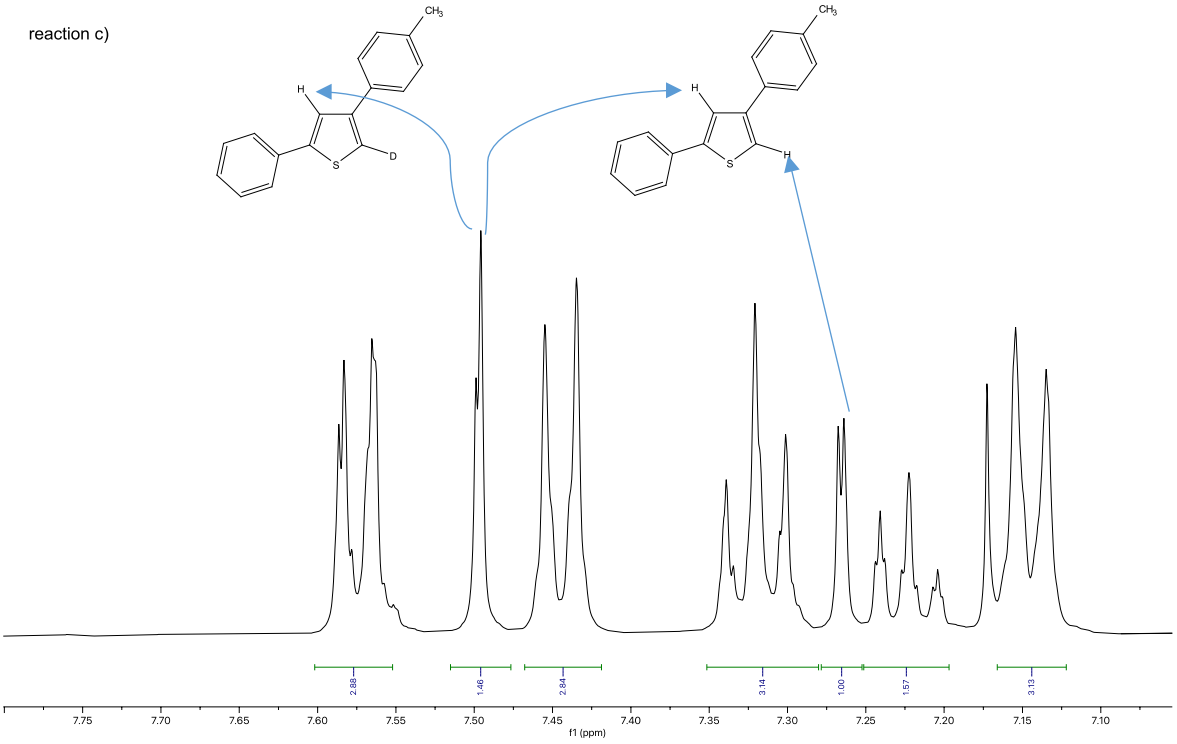


$$\frac{D}{H} = \frac{d3u}{3u} = \frac{3.46 - 1}{3.46} = 71\%$$

c)



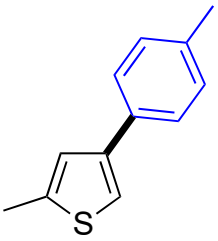
3u **d-3u**:**3u** = 32:68 **3ub**, traces



$$\frac{D}{H} = \frac{d3u}{3u} = \frac{1.46 - 1}{1.46} = 32\%$$

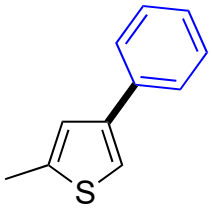
Compound characterization

2-methyl-4-(p-tolyl)thiophene (3a)



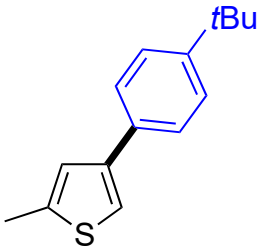
The product **3a** was synthesized via the general procedure A using 2-methylthiophene (49 mg, 0.5 mmol, 1.0 eq.), 4-iodotoluene (163 mg, 0.75 mmol, 1.5 eq.) and isolated by column chromatography (100% cyclohexane). The product was isolated as white solid (82 mg, 0.43 mmol, 86%). **(QNMR: 99%)**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 1.5 Hz, 1H), 7.07 (d, *J* = 1.4 Hz, 1H), 2.55 (d, *J* = 1.2 Hz, 3H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.18, 140.49, 136.79, 133.51, 129.55, 126.27, 124.78, 117.52, 21.28, 15.59. **GC/MS** regioselectivity by integration β/α > 99:1. Spectral data were consistent with the literature.[3]

2-methyl-4-phenylthiophene (3b)



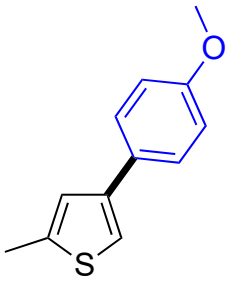
The product **3b** was synthesized via the general procedure A using 2-methylthiophene (49 mg, 0.5 mmol, 1.0 eq.), iodobenzene (153 mg, 0.75 mmol, 1.5 eq.) and isolated by column chromatography (100% cyclohexane). The product was isolated as white solid (79 mg, 0.45 mmol, 91%). **(QNMR: 95%)**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 – 7.54 (m, 2H), 7.44 – 7.35 (m, 2H), 7.33 – 7.24 (m, 2H), 7.21 (d, *J* = 1.5 Hz, 1H), 7.08 (p, *J* = 1.1 Hz, 1H), 2.55 (d, *J* = 1.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.20, 140.63, 136.28, 128.85, 127.06, 126.38, 124.76, 118.15, 15.57. **GC/MS** regioselectivity by integration β/α > 99:1. Spectral data were consistent with the literature.[4]

4-(4-(tert-butyl)phenyl)-2-methylthiophene (3c)



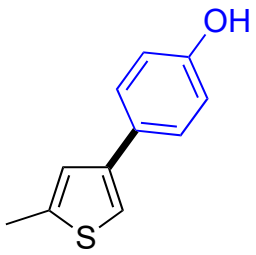
The product **3c** was synthesized via the general procedure A using 2-methylthiophene (49 mg, 0.5 mmol, 1.0 eq.), 1-(*tert*-butyl)-4-iodobenzene (195 mg, 0.75 mmol, 1.5 eq.) and isolated by column chromatography (100% cyclohexane). The product was isolated as white solid (104 mg, 0.45 mmol, 90%). **(QNMR: 99%)**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.18 (s, 1H), 7.07 (s, 1H), 2.55 (s, 3H), 1.37 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.02, 142.11, 140.39, 133.54, 126.08, 125.76, 124.80, 117.65, 34.65, 31.47, 15.58. **GC/MS** regioselectivity by integration β/α > 99:1. Spectral data were consistent with the literature.[5]

4-(4-methoxyphenyl)-2-methylthiophene (3d)



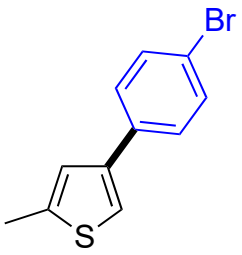
The product **3d** was synthesized via the general procedure A using 2-methylthiophene (49 mg, 0.5 mmol, 1.0 eq.), 1-iodoanisole (175 mg, 0.75 mmol, 1.5 eq.) and isolated by column chromatography (100% cyclohexane). The product was isolated as white solid (55 mg, 0.27 mmol, 54%) **(QNMR: 63%).^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.51 – 7.48 (m, 2H), 7.09 (d, *J* = 1.5 Hz, 1H), 7.03 – 7.01 (m, 1H), 6.94 – 6.91 (m, 2H), 3.84 (s, 3H), 2.53 (d, *J* = 1.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.86, 141.83, 140.48, 129.18, 127.47, 124.71, 116.76, 114.24, 55.44, 15.56. **GC/MS** regioselectivity by integration β/α > 99:1. Spectral data were consistent with the literature.[4]

4-(5-methylthiophen-3-yl)phenol (3e)



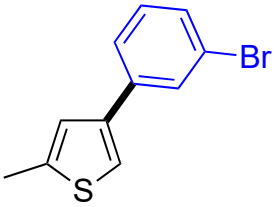
The product **3e** was synthesized via the general procedure A using 2-methylthiophene (49 mg, 0.5 mmol, 1.0 eq.), 1-iodoanisole (175 mg, 0.75 mmol, 1.5 eq.) and isolated by column chromatography (90% cyclohexane, 10% EtOAc). The product was isolated as white solid white oil (68 mg, 0.36 mmol, 72%). The product was further purified by preparative HPLC (ACN/H_2O). **(QNMR: 72%).^{1}H NMR** (600 MHz, DMSO-*d*6) δ: 9.43 (s, 1H), 7.45 (br d, *J* = 8.4 Hz, 2H), 7.33 (s, 1H), 7.13 (s, 1H), 6.77 (br d, *J* = 8.4 Hz, 2H), 2.46 (s, 3H). **^{13}C NMR** (151 MHz, DMSO-*d*6) δ 156.55, 141.24, 139.62, 127.02, 126.63, 124.38, 116.16, 115.50, 15.04. **GC/MS** regioselectivity by integration β/α > 99:1. **HRMS (ESI)** m/z calc. for $C_{11}H_{10}OS^+$ $[M]^+$, 190.0452, measured: 190.0446.

4-(4-bromophenyl)-2-methylthiophene (3f)



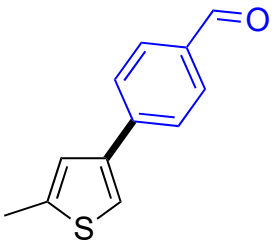
The product **3f** was synthesized via the general procedure A using 2-methylthiophene (49 mg, 0.5 mmol, 1.0 eq.), 1-bromo-4-iodobenzene (212 mg, 0.75 mmol, 1.5 eq.) and isolated by column chromatography (100% cyclohexane). The product was isolated as white solid (70 mg, 0.28 mmol, 55%) **(QNMR: 70%) ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.51 – 7.48 (m, 2H), 7.43 – 7.40 (m, 2H), 7.19 (d, *J* = 1.5 Hz, 1H), 7.02 (s, 1H), 2.53 (d, *J* = 1.1 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 141.06, 140.92, 135.16, 131.93, 127.91, 124.45, 120.90, 118.54, 15.55. **GC/MS** regioselectivity by integration β/α > 99:1. Spectral data were consistent with the literature.[4]

4-(3-bromophenyl)-2-methylthiophene (3g)



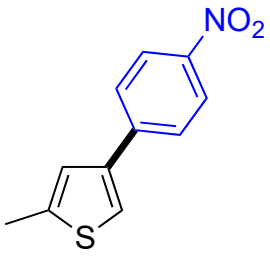
The product **3g** was synthesized via the general procedure A using 2-methylthiophene (49 mg, 0.5 mmol, 1.0 eq.), 3-bromoiodobenzene (283 mg, 0.75 mmol, 1.5 eq.) and isolated by column chromatography (100% cyclohexane). The product was isolated as clear oil (110 mg, 0.43 mmol, 87%) **(QNMR: 88%).** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (t, *J* = 1.8 Hz, 1H), 7.52 (ddd, *J* = 7.8, 1.8, 1.1 Hz, 1H), 7.44 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 1.6 Hz, 1H), 7.07 (s, 1H), 2.57 (d, *J* = 1.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.07, 140.59, 138.28, 130.36, 129.93, 129.38, 124.91, 124.48, 122.99, 119.05, 15.54. **GC/MS** regioselectivity by integration β/α > 99:1. Spectral data were consistent with the literature.[6]

1-(4-(5-methylthiophen-3-yl)phenyl)ethan-1-one (3h)



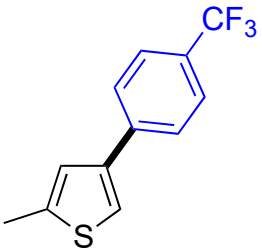
The product **3h** was synthesized via the general procedure A using 2-methylthiophene (49 mg, 0.5 mmol, 1.0 eq.), 4-iodobenzaldehyde (174 mg, 0.75 mmol, 1.5 eq.) and isolated by column chromatography (95:5 Cyclohexane/EtOAc). The product was isolated as white solid (86 mg, 0.43 mmol, 85%) **(QNMR: 91%)**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.00 (s, 1H), 7.90 – 7.88 (m, 2H), 7.72 – 7.70 (m, 2H), 7.36 (d, *J* = 1.6 Hz, 1H), 7.11 (s, 1H) 2.54 (d, *J* = 1.1 Hz, 3H)., **^{13}C NMR** (101 MHz, Chloroform-*d*) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.90, 141.94, 141.45, 140.72, 134.95, 130.53, 126.68, 124.46, 120.56, 15.56. **GC/MS** regioselectivity by integration β/α > 99:1. **HRMS (ESI)** m/z calc. for $C_{12}H_{11}OS^+$ $[M+H]^+$: 203.0525, found: 203.0529.

2-methyl-4-(4-nitrophenyl)thiophene (3i)



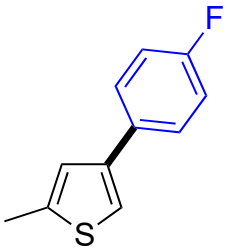
The product **3i** was synthesized via the general procedure A using 2-methylthiophene (49 mg, 0.5 mmol, 1.0 eq.), 1-iodo-4-nitrobenzene (187 mg, 0.75 mmol, 1.5 eq.), isolated by column chromatography (95:5 Cyclohexane/EtOAc) and further purified by preparative TLC (100% toluene). The product was isolated as white solid (22 mg, 0.10 mmol, 20%) **(QNMR: 20%).** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.26 – 8.22 (m, 2H), 7.71 – 7.67 (m, 2H), 7.38 (d, *J* = 1.5 Hz, 1H), 7.10 (t, *J* = 1.3 Hz, 1H), 2.55 (d, *J* = 1.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.64, 142.33, 141.90, 139.78, 126.72, 124.41, 124.35, 121.25, 15.57. **GC/MS** regioselectivity by integration β/α = 97:3. Spectral data were consistent with the literature.[4]

2-methyl-4-(4-(trifluoromethyl)phenyl)thiophene (3j)



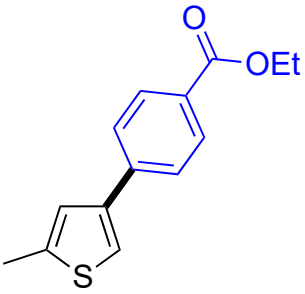
The product **3j** was synthesized via the general procedure A using 2-methylthiophene (49 mg, 0.5 mmol, 1.0 eq.), 1-iodobenzotrifluoride (204 mg, 0.75 mmol, 1.5 eq.) and isolated by column chromatography (100% cyclohexane). The product was isolated as white solid (92 mg, 0.40 mmol, 80%) **(QNMR: 87%).** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.63 (m, 4H), 7.29 (d, *J* = 1.6 Hz, 1H), 7.09 (s, 1H), 2.56 (d, *J* = 1.2 Hz, 3H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 141.25, 140.55, 139.44 (d, *J* = 1.5 Hz), 128.84 (q, *J* = 32.5 Hz), 126.34, 125.74 (q, *J* = 3.8 Hz), 124.35, 124.35 (q, *J* = 271.8 Hz), 119.65, 15.36.. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -62.42. **GC/MS** regioselectivity by integration β/α > 99:1. Spectral data were consistent with the literature.[4]

4-(4-fluorophenyl)-2-methylthiophene (3k)



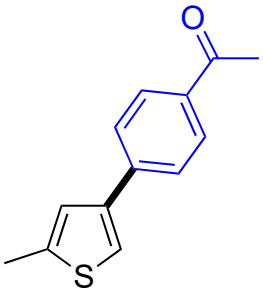
The product **3k** was synthesized via the general procedure A using 2-methylthiophene (49 mg, 0.5 mmol, 1.0 eq.), 1-fluoro-4-iodobenzene (166 mg, 0.75 mmol, 1.5 eq.) and isolated by column chromatography (100% cyclohexane). The product was isolated as clear oil (85 mg, 0.44 mmol, 88%) **(QNMR: 99%)** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 – 7.48 (m, 1H), 7.13 (d, *J* = 1.6 Hz, 1H), 7.09 – 7.03 (m, 1H), 7.00 (p, *J* = 1.2 Hz, 1H), 2.53 (d, *J* = 1.1 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.14 (d, *J* = 245.8 Hz), 141.16, 140.89, 132.52 (d, *J* = 3.3 Hz), 127.90 (d, *J* = 8.0 Hz), 124.69, 117.91 (d, *J* = 1.0 Hz), 115.70 (d, *J* = 21.6 Hz), 15.55. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -115.75. **GC/MS** regioselectivity by integration β/α > 99:1. Spectral data were consistent with the literature.[4]

ethyl 4-(5-methylthiophen-3-yl)benzoate (3l)



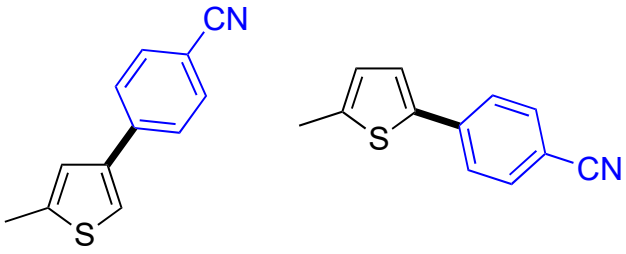
The product **3l** was synthesized via the general procedure A using 2-methylthiophene (49 mg, 0.5 mmol, 1.0 eq.), ethyl 4-iodobenzoate (207 mg, 0.75 mmol, 1.5 eq.) and isolated by column chromatography (95:5 Cyclohexane/EtOAc). The product was isolated as white solid (107 mg, 0.44 mmol, 88%). **(QNMR: 90%)**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.09 – 8.01 (m, 2H), 7.65 – 7.58 (m, 2H), 7.31 (d, *J* = 1.6 Hz, 1H), 7.10 (p, *J* = 1.1 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.54 (d, *J* = 1.1 Hz, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.62, 141.18, 141.07, 140.35, 130.26, 128.91, 126.07, 124.56, 119.81, 61.05, 15.57, 14.51. **GC/MS** regioselectivity by integration β/α > 99:1. **HRMS (ESI)** m/z calc. for $C_{14}H_{15}O_2S^+$ $[M+H]^+$: 247.0787, found: 247.0784

1-(4-(5-methylthiophen-3-yl)phenyl)ethan-1-one (3m)



The product **3m** was synthesized via the general procedure A using 2-methylthiophene (49 mg, 0.5 mmol, 1.0 eq.), 4-iodoacetophenone (184mg, 0.75 mmol, 1.5 eq.) and isolated by column chromatography (100% toluene). The product was isolated as white solid (60 mg, 0.28 mmol, 55%) **(QNMR: 88%)**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 – 7.94 (m, 2H), 7.67 – 7.60 (m, 2H), 7.32 (d, *J* = 1.5 Hz, 1H), 7.13 – 7.07 (m, 1H), 2.61 (s, 3H), 2.54 (d, *J* = 1.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 197.69, 141.27, 140.87, 140.59, 135.58, 129.13, 126.25, 124.48, 120.03, 26.71, 15.55. **GC/MS** regioselectivity by integration β/α > 99:1. **HRMS (ESI)** m/z calc. for $C_{13}H_{13}OS^{+}$ $[M+H]^{+}$: 217.0682, found: 217.0686.

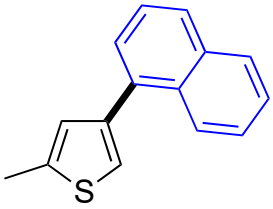
4-(5-methylthiophen-3-yl)benzonitrile (3na) and 4-(5-methylthiophen-2-yl)benzonitrile (3nb)



The product **3na** was synthesized via the general procedure A using 2-methylthiophene (49 mg, 0.5 mmol, 1.0 eq.) and 4-iodobenzonitrile (172 mg, 0.75 mmol, 1.5 eq.). The product was purified by column chromatography (90:10 cyclohexane/EtOAc) and further purified by preparative TLC (90:10 Cyclohexane/EtOAc). The compound was isolated as an inseparable mixture of **3na** and the alpha-arylated product **3nb** (**3na**/**3nb**: 4.2:1, 40mg, 0.2 mmol, 40%) **(QNMR: 38% 3na, 9% 3nb).** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.61 (m, 5H, **3na** + **3nb**), 7.32 (d, *J* = 1.5 Hz, 1H, **3na**), 7.22 (d, *J* = 3.6 Hz, 0.22H, **3nb**), 7.06 (s, 1H, **3na**), 6.78 (dd, *J* = 3.6, 1.2 Hz, 0.21H, **3nb**), 2.54 (d, *J* = 1.1 Hz, 3H, **3na**), 2.53 (d, *J* = 1.1 Hz, 0.7H, **XY**). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.36 (**3nb**), 141.71 (**3na**), 140.41 (**3na**), 140.15 (**3na**), 139.72 (**3nb**), 139.08 (**3nb**), 132.81 (**3nb**), 132.77 (**3na**), 126.97 (**3nb**), 126.74 (**3na**), 125.65 (**3nb**), 125.26 (**3nb**),

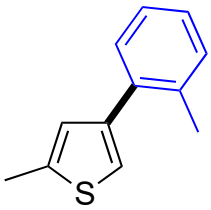
124.23 (**3na**), 120.61 (**3na**), 119.16 (**3na**), 119.12 (**3nb**), 110.35 (**3na**), 110.04 (**3nb**), 15.70 (**3nb**), 15.55 (**3na**). **GC/MS** regioselectivity by integration β/α = 81:19. Spectral data were consistent with the literature.[4,7]

2-methyl-4-(naphthalen-1-yl)thiophene (3o)



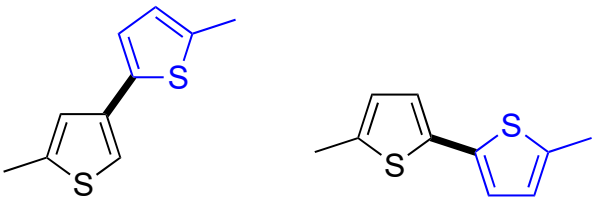
The product **3o** was synthesized via the general procedure A using 2-methylthiophene (49 mg, 0.5 mmol, 1.0 eq.), 1-iodonaphthalene (190 mg, 0.75 mmol, 1.5 eq.) and isolated by column chromatography (100% cyclohexane The product was isolated as clear oil (45 mg, 0.2 mmol, 40%) **(QNMR: 47%)**. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 8.12 (m, 1H), 7.93 – 7.90 (m, 1H), 7.86 – 7.84 (m, 1H), 7.54 – 7.47 (m, 4H), 7.16 (d, *J* = 1.4 Hz, 1H), 7.01 (s, 1H), 2.61 (d, *J* = 1.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 141.12, 139.68, 135.50, 133.94, 131.91, 128.40, 128.05, 127.72, 126.86, 126.16, 126.12, 125.91, 125.52, 121.39, 15.53. **GC/MS** regioselectivity by integration β/α > 99:1. Spectral data were consistent with the literature.[4]

2-methyl-4-(2-methylphenyl)thiophene (3p)



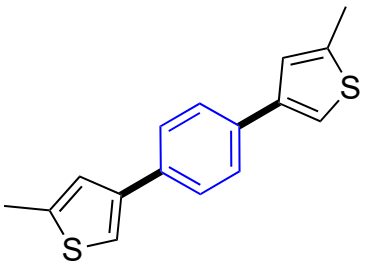
The product **3p** was synthesized via the general procedure A using 2-methylthiophene (49 mg, 0.5 mmol, 1.0 eq.), 2-iodotoluene (164 mg, 0.75 mmol, 1.5 eq.) and isolated by column chromatography (100% cyclohexane). The product was isolated as clear oil (40 mg, 0.21 mmol, 42%) **(QNMR: 49%).**^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.20 (m, 4H), 6.95 (d, *J* = 1.4 Hz, 1H), 6.82 (s, 1H), 2.54 (d, *J* = 1.1 Hz, 3H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.18, 139.25, 137.08, 135.76, 130.55, 129.75, 127.37, 127.28, 125.87, 120.50, 20.93, 15.47. **GC/MS** regioselectivity by integration β/α > 99:1. Spectral data were consistent with the literature.[8]

5,5'-dimethyl-2,3'-bithiophene (3qa) and 5,5'-dimethyl-2,2'-bithiophene (3qb)



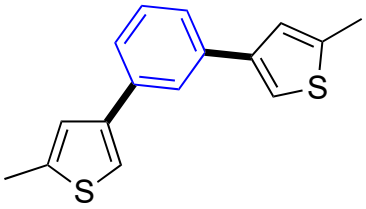
The product **3qa** was synthesized via the general procedure A using 2-methylthiophene (49 mg, 0.5 mmol, 1.0 eq.), 2-iodo-5-methylthiophene (168 mg, 0.75 mmol, 1.5 eq.) and isolated by column chromatography (100% cyclohexane) as an inseparable mixture of **3qa** and **3qb** (**3qa**/**3qb**: 8:1, 19.0 mg, 0.1 mmol, 20%) **(QNMR: 39%)**. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.03 (d, *J* = 1.2 Hz, 1H, **3qa**), 6.94 – 6.92 (m, 2H, **3qa**), 6.88 (d, *J* = 3.5 Hz, 0.24H, **3qb**), 6.66 (dd, *J* = 3.5, 1.2 Hz, 1H, **3qa**), 6.64 (dd, *J* = 3.5, 1.1 Hz, 0.24H, **3qb**), 2.49 (d, *J* = 1.1 Hz, 3H, **3qa**), 2.48 (d, *J* = 1.1 Hz, 3H, **3qa**), 2.47 (d, *J* = 1.0 Hz, 0.82H, **3qb**). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.54 (**3qa**), 138.60 (**3qb**), 138.30 (**3qa**), 137.45 (**3qa**), 135.73 (**3qa**), 135.64 (**3qb**), 125.87 (**3qb**), 125.78 (**3qa**), 124.35 (**3qa**), 122.99 (**3qb**), 122.75 (**3qa**), 116.58 (**3qa**), 31.04 (**3qa**), 15.45 (**3qb**), 15.43 (**3qa**). **HRMS (ESI) 3qa** m/z calc. for $C_{10}H_{11}S_2^+$ $[M+H]^+$: 195.0297, found: 195.0302. **GC/MS** regioselectivity by integration β/α = 87:13. Spectral data were consistent with the literature.[9]

1,4-bis(5-methylthiophen-3-yl)benzene (3r)



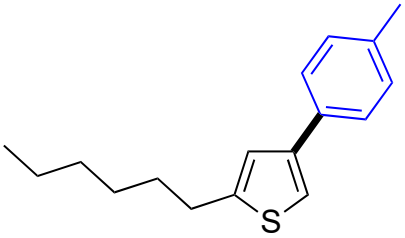
The product **3r** was synthesized via the general procedure B using 2-methylthiophene (245 mg, 2.5 mmol, 5.0 eq.), 1,4-diiodobenzene (165 mg, 0.5 mmol, 1.0 eq.) and isolated by column chromatography (100% cyclohexane). Compound **3r** was further purified by preparative TLC obtaining the product as white solid (35.2 mg, 0.13 mmol, 26%). **(QNMR: 50%)**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 (s, 4H), 7.21 (d, *J* = 1.5 Hz, 2H), 7.09 – 7.07 (m, 2H), 2.54 (d, *J* = 1.1 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 141.78, 140.70, 134.84, 126.67, 124.64, 117.99, 15.60. **GC/MS** regioselectivity by integration β/α > 99:1. **HRMS (ESI)** m/z calc. for $C_{16}H_{15}S_2^+$ $[M]^+$: 271.0610, found: 271.0613.

1,3-bis(5-methylthiophen-3-yl)benzene (3s)



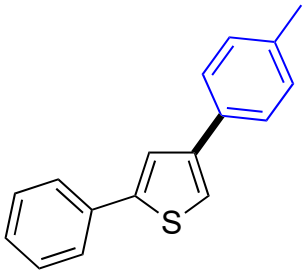
The product **3s** was synthesized via the general procedure B using 2-methylthiophene (118 mg, 1.2 mmol, 2.4 eq.), 1,3-diiodobenzene (165 mg, 0.5 mmol, 1.0 eq.) and isolated by column chromatography (100% cyclohexane). The product was isolated as white solid (78 mg, 0.29 mmol, 58%) **(QNMR: 73%) ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (t, *J* = 1.8 Hz, 1H), 7.52 – 7.50 (m, 2H), 7.42 (dd, *J* = 8.5, 6.7 Hz, 1H), 7.28 (d, *J* = 1.5 Hz, 2H), 7.14 (s, 2H), 2.59 (d, *J* = 1.2 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.14, 140.71, 136.74, 129.24, 125.07, 124.84, 124.42, 118.37, 15.59. **GC/MS** regioselectivity by integration β/α > 99:1. Spectral data were consistent with the literature.[10]

2-hexyl-4-(p-tolyl)thiophene (3t)



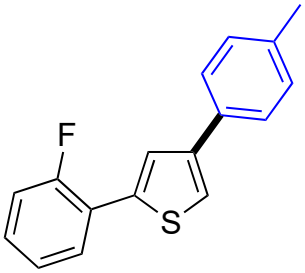
The product **3t** was synthesized via the general procedure A using 2-hexylthiophene (84 mg, 0.5 mmol, 1.0 eq.), 4-iodotoluene (163 mg, 0.75 mmol, 1.5 eq.) and isolated by column chromatography (100% cyclohexane The product was isolated as clear oil (114 mg, 0.44 mmol, 88%) **(QNMR: 100%)**. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.46 (m, 2H), 7.21 – 7.19 (m, 3H), 7.07 (dt, *J* = 1.5, 0.7 Hz, 1H), 2.87 – 2.83 (m, 2H), 1.77 – 1.69 (m, 2H), 1.44 – 1.32 (m, 6H), 0.93 (t, *J* = 7.1, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.71, 141.90, 136.72, 133.60, 129.53, 126.27, 123.51, 117.22, 31.77, 31.74, 30.39, 28.97, 22.73, 21.27, 14.23. **GC/MS** regioselectivity by integration β/α > 99:1. Spectral data were consistent with the literature.[11]

2-phenyl-4-(p-tolyl)thiophene (3u)



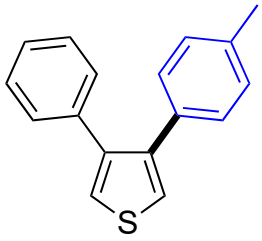
The product **3u** was synthesized via the general procedure A using 2-phenylthiophene (80 mg, 0.5 mmol, 1.0 eq.), 4-iodotoluene (163 mg, 0.75 mmol, 1.5 eq.) and isolated by column chromatography (100% cyclohexane). The product was isolated as white solid (105 mg, 0.42 mmol, 84%) **(QNMR: 99%) ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.67 – 7.64 (m, 2H), 7.58 (d, *J* = 1.5 Hz, 1H), 7.54 – 7.51 (m, 2H), 7.43 – 7.38 (m, 2H), 7.35 (d, *J* = 1.5 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.24 – 7.22 (m, 2H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145.04, 143.26, 137.18, 134.54, 133.23, 129.65, 129.06, 127.77, 126.34, 125.99, 122.49, 119.26, 21.31. **GC/MS** regioselectivity by integration β/α > 99:1. Spectral data were consistent with the literature.[12]

2-(2-fluorophenyl)-4-(p-tolyl)thiophene (3v)



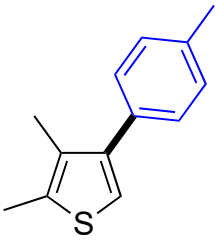
The product **3v** was synthesized via the general procedure A using 2-(2-fluorophenyl)thiophene (89 mg, 0.5 mmol, 1.0 eq.), 4-iodotoluene (163 mg, 0.75 mmol, 1.5 eq.) and isolated by column chromatography (100% cyclohexane). The product was isolated as white solid (89 mg, 0.33 mmol, 66%) **(QNMR: 72%) ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (s, 1H), 7.71 (td, *J* = 8.0, 1.9 Hz, 1H), 7.58 – 7.56 (m, 2H), 7.46 (d, *J* = 1.4 Hz, 1H), 7.33 – 7.17 (m, 5H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.24 (d, *J* = 250.2 Hz), 142.97, 137.82 (d, *J* = 3.3 Hz), 137.19, 133.13, 129.66, 128.92 (d, *J* = 8.4 Hz), 128.81 (d, *J* = 3.4 Hz), 126.39, 125.72 (d, *J* = 6.5 Hz), 124.59 (d, *J* = 3.5 Hz), 122.37 (d, *J* = 12.5 Hz), 120.15 (d, *J* = 4.0 Hz), 116.51 (d, *J* = 22.5 Hz), 21.30. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -113.70. **GC/MS** regioselectivity by integration β/α > 99:1. **HRMS (ESI)** m/z calc. for $C_{17}H_{13}FS^{+}$ $[M]^{+}$: 268.0717, found: 268.0715.

3-phenyl-4-(p-tolyl)thiophene (3w)



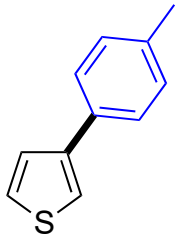
The product **3w** was synthesized via the general procedure A with the exception of using 1.0 eq. of 4-iodotoluene (109 mg, 0.5 mmol) and 3-phenylthiophene (80.1 mg, 0.5 mmol, 1.0 eq). The product was purified by preparative HPLC (ACN/H_2O) to obtain a clean sample for analysis **(QNMR: 45%)**. **^{1}H NMR** (600 MHz, DMSO-*d*6) δ: 7.62 – 7.59 (m, 1H), 7.58 – 7.55 (m, 1H), 7.28 – 7.24 (m, 1H), 7.32 – 7.23 (m, 2H), 7.18 – 7.13 (m, 2H), 7.11 – 7.07 (m, 2H), 7.06 – 7.00 (m, 2H), 2.29 – 2.25 (m, 3H). **^{13}C NMR** (151 MHz, DMSO-*d*6) δ 140.8 (C3, C4), 136.3 (C9, C12), 133.4, 128.9, 128.6, 128.5, 128.2, 126.8, 124.4, 20.7. **GC/MS** regioselectivity by integration β/α > 99:1.

2,3-dimethyl-4-(p-tolyl)thiophene (3ya)



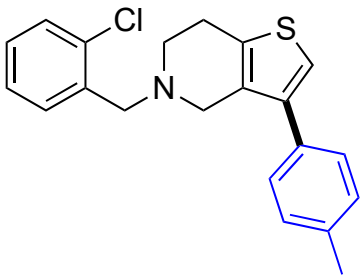
The product **3ya** was synthesized via the general procedure A using 2,3 dimethylthiophene (11.6 mg, 0.1 mmol, 1.0 eq.), 2-iodotoluene (32.7 mg, 0.15 mmol, 1.5 eq.) in a 2 mL vial and isolated by preparative TLC (100% toluene). The product was isolated as white solid (15 mg, 0.07 mmol, 74%) **(QNMR: 74%). ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.28 – 7.26 (m, 2H), 7.23 – 7.21 (m, 2H), 6.94 (s, 1H), 2.42 (d, *J* = 0.8 Hz, 3H), 2.40 (s, 3H), 2.13 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.88, 136.66, 135.14, 133.69, 131.81, 129.10, 128.71, 118.27, 21.31, 13.96, 13.25. **GC/MS** regioselectivity by integration β/α > 99:1. **HRMS (ESI)** m/z calc. for $C_{13}H_{14}OS^+$ $[M]^+$: 202.0811, found: 202.0832.

3-(p-tolyl)thiophene (3x)



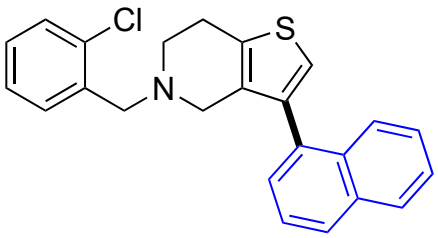
The product **3x** was synthesized via the general procedure A with the exception of using an excess of thiophene (84.1 mg, 1.0 mmol, 2.0 eq.) and 4-iodotoluene (109 mg, 0.5 mmol, 1.0 eq.). The title product was isolated as the mayor regioisomer by column chromatography (100% cyclohexane). The product was isolated as white solid (21.7 mg, 0.12 mmol, 25%) **(QNMR: 56%). ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 – 7.48 (m, 2H), 7.42 – 7.41 (m, 1H), 7.40 – 7.37 (m, 2H), 7.23 – 7.21 (m, 2H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.49, 137.00, 133.23, 129.62, 126.47, 126.18, 119.78, 21.28. **GC/MS** regioselectivity by integration β/α = 97:3. Spectral data were consistent with the literature.[4]

5-(2-chlorobenzyl)-3-(p-tolyl)-4,5,6,7-tetrahydrothieno[3,2-c]pyridine (3za)



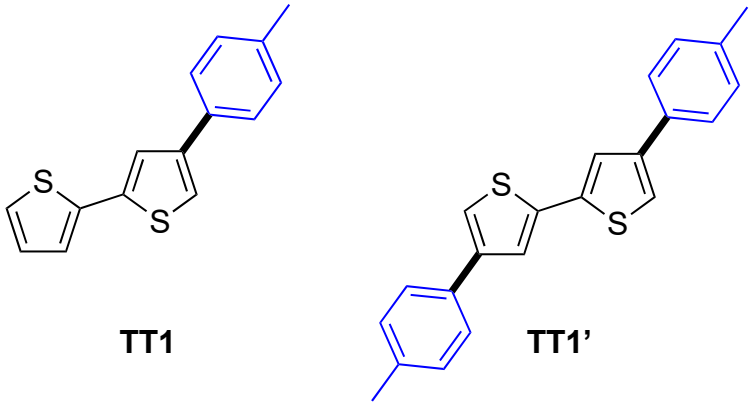
The product **3za** was synthesized via the general procedure D using Ticlopidine (free base) (26.4 mg, 0.1 mmol, 1.0 eq.), 4-iodotoluene (65.4 mg, 0.3 mmol, 3.0 eq.) and purified by preparative TLC (5% EtOAc/cyclohexane). The product was obtained as clear oil (17.7 mg, 0.05 mmol, 50%). **(QNMR: 50%**, 50% SM recovered). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.51 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.34 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.26 – 7.15 (s, 6H), 7.02 (s, 1H), 3.82 (s, 2H), 3.69 (s, 2H), 2.97 – 2.94 (m, 2H), 2.86 (t, *J* = 5.6 Hz, 2H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.80, 136.92, 136.28, 134.89, 134.29, 133.68, 132.53, 130.57, 129.55, 129.32, 128.27, 128.07, 126.87, 119.49, 58.63, 54.20, 50.16, 26.24, 21.31. **GC/MS** regioselectivity by integration β/α > 99:1. **HRMS (ESI)** m/z calc. for $C_{21}H_{21}ClNS^{+}$ $[M+H]^{+}$: 354.1078, found: 354.1066.

5-(2-chlorobenzyl)-3-(naphthalen-1-yl)-4,5,6,7-tetrahydrothieno[3,2-c]pyridine (3zb)



The product **3zb** was synthesized via the general procedure D using Ticlopidine (free base) (26.4 mg, 0.1 mmol, 1.0 eq.), 1-iodonaphthalene (76.2 mg, 0.3 mmol, 3.0 eq.) and purified by preparative TLC (10% EtOAc/cyclohexane). The product was obtained as clear oil (9.2 mg, 0.024 mmol, 24%) (**QNMR**: 39%, 46% Sm recovered). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.7 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.50 – 7.40 (m, 4H), 7.37 (dd, *J* = 7.0, 1.1 Hz, 1H), 7.29 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.191 – 7.11 (m, 2H), 7.07 (s, 1H), 3.66 (s, 2H), 3.37 (s, 2H), 3.00 (t, *J* = 5.5 Hz, 2H), 2.86 (t, *J* = 5.7 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 138.73, 136.28, 134.45, 134.22, 134.19, 134.19, 133.75, 132.39, 130.44, 129.46, 128.32, 128.17, 128.02, 127.29, 126.77, 126.28, 126.25, 125.99, 125.42, 121.39, 58.39, 53.50, 50.17, 26.12. **GC/MS** regioselectivity by integration β/α > 99:1. **HRMS (ESI)** m/z calc. for $C_{25}H_{20}ClNS^{+}$ $[M]^{+}$: 389.10, found: 386.08.

4,4'-di-p-tolyl-2,2'-bithiophene (TT$_1$') and 4-(p-tolyl)-2,2'-bithiophene (TT$_1$)

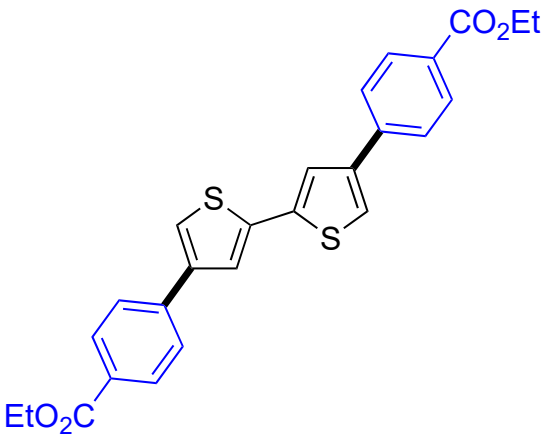


TT1 **TT1'**

The products **TT$_1$'** and **TT$_1$** were synthesized via the general procedure C using 2,2'-bithiophene (83 mg, 0.5 mmol, 1.0 eq.), 4-iodotoluene (545 mg, 2.50 mmol, 5.0 eq.) and a reaction time of 3 days and isolated by column chromatography (100% to 98% cyclohexane/EtOAc). Product **TT$_1$'** was isolated as white solid that is barely soluble in EtOAc and $CDCl_3$ (61mg, 0.18 mmol, 35%) and product **TT$_1$** was obtained as white solid (46 mg, 0.18 mmol, 36%). Due to the different solubility of **TT$_1$'** and **TT$_1$**, the quantitative ^{1}H NMR could not deliver reliable results. **TT$_1$' ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 – 7.50 (m, 4H), 7.47 (d, *J* = 1.5 Hz, 2H), 7.30 (d, *J* = 1.5 Hz, 2H), 7.24 – 7.21 (m, 4H), 2.39 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.08, 138.04,

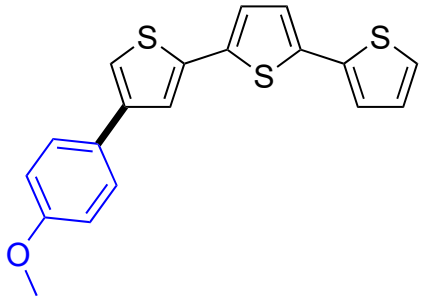
137.32, 132.89, 129.67, 126.34, 123.14, 118.82, 21.32. **TT_1 ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 – 7.47 (m, 2H), 7.42 (d, *J* = 1.5 Hz, 1H), 7.26 (d, *J* = 1.5 Hz, 1H), 7.23 – 7.19 (m, 4H), 7.02 (dd, *J* = 5.1, 3.6 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.02, 138.03, 137.54, 137.27, 132.91, 129.65, 127.94, 126.32, 124.64, 123.98, 123.07, 118.68, 21.30. **TT_1 HRMS (ESI)** m/z calc. for $C_{15}H_{12}OS_2^+$ $[M]^+$: 256.0375, found: 256.0376. **TT_1' HRMS (ESI)** m/z calc. for $C_{22}H_{19}S_2^+$ $[M]^+$: 347.0923, found: 347.0922.

diethyl 4,4'-([2,2'-bithiophene]-4,4'-diyl)dibenzoate (TT_2)



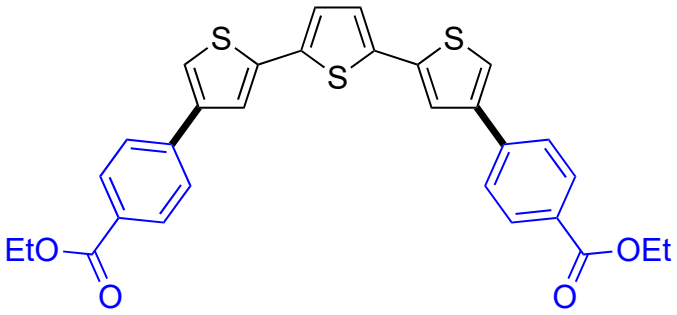
The product **TT_2** was synthesized via the general procedure C using 2,2'-bithiophene (83 mg, 0.5 mmol, 1.0 eq.), ethyl 4-iodobenzoate (690 mg, 2.50 mmol, 5.0 eq.) and a reaction time of 3 days and isolated by column chromatography (10% to 100% cyclohexane/EtOAc). The product was further purified by crystallization from cyclohexane. **TT_2** was isolated as yellow solid that is barely soluble in cyclohexane (143 mg, 0.31 mmol, 62%). (**QNMR: 72%**). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.11 – 8.07 (m, 4H), 7.69 – 7.66 (m, 4H), 7.53 (d, *J* = 1.5 Hz, 2H), 7.47 (d, *J* = 1.5 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 4H), 1.42 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.49, 142.05, 139.62, 138.26, 130.37, 129.45, 126.22, 123.13, 121.18, 61.16, 14.51. **HRMS (ESI)** m/z calc. for $C_{26}H_{22}NaO_4S_2^+$ $[M+Na]^+$: 485.0852, found: 485.0841.

4-(4-methoxyphenyl)-2,2':5',2''-terthiophene (TTT_1)



The product **TTT_1** was synthesized via the general procedure C using 2,2':5',2''-terthiophene (124 mg, 0.5 mmol, 1.0 eq.), 4-iodoanisole (545 mg, 2.50 mmol, 5.0 eq.) and a reaction time of 5 days and isolated by column chromatography (10% to 100% EtOAc/cyclohexane). Product **TTT_1** was isolated as red solid that is barely soluble in EtOAc and $CDCl_3$ (100 mg, 0.28 mmol, 56%) (**QNMR: 44%**). **TTT_1** can be further purified by vacuum sublimation. Due to the low solubility in $CDCl_3$, quantitative ^{1}H NMR could not deliver reliable results**. ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.55 – 7.52 (m, 2H), 7.40 (d, *J* = 1.5 Hz, 1H), 7.23 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.22 (d, *J* = 1.5 Hz, 1H), 7.19 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.11 (d, *J* = 3.7 Hz, 1H), 7.10 (d, *J* = 3.8 Hz, 1H), 7.03 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.97 – 6.93 (m, 2H), 3.85 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.23, 142.82, 137.73, 137.25, 136.48, 136.33, 128.47, 128.04, 127.60, 124.68, 124.50, 124.47, 123.88, 122.90, 118.07, 114.37, 55.49. **HRMS (ESI)** m/z calc. for $C_{19}H_{14}OS_3^+$ $[M]^+$: 354.0201, found: 354.0196.

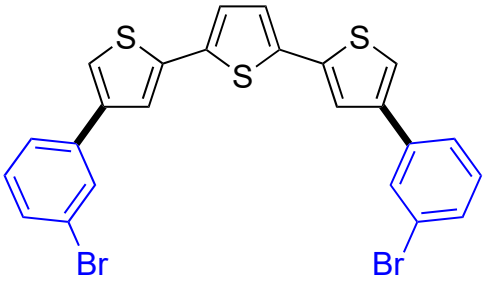
diethyl 4,4'-([2,2':5',2''-terthiophene]-4,4''-diyl)dibenzoate (TTT_2)



The product **TTT_2** was synthesized via the general procedure C using 2,2':5',2''-terthiophene (124 mg, 0.5 mmol, 1.0 eq.), ethyl 4-iodobenzoate (690 mg, 2.50 mmol, 5.0 eq.) and a reaction time of 3 days and isolated by column chromatography (10% EtOAc/cyclohexane to 10% CH_2Cl_2/MeOH). The product was further purified by crystallization from cyclohexane/CH_2Cl_2 and isolated as orange solid that is barely soluble in EtOAc and well soluble in CH_2Cl_2 (142 mg, 0.26 mmol, 52%). **(QNMR: 85%). ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.11 – 8.08 (m, 4H), 7.68 – 7.66 (m, 4H), 7.50 (d, *J* = 1.5 Hz, 2H), 7.45 (d, *J* = 1.5 Hz, 2H), 7.16 (s, 2H), 4.41 (q, *J* = 7.1 Hz, 4H), 1.42 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.51, 142.10, 139.63,

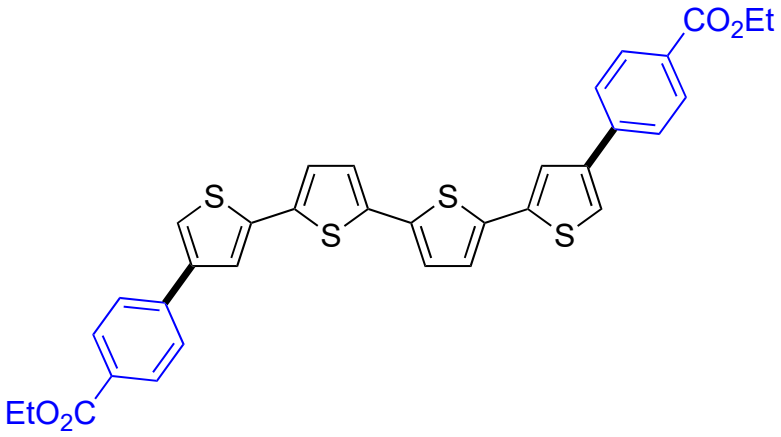
138.26, 136.34, 130.38, 129.46, 126.22, 124.89, 122.82, 121.03, 61.17, 14.52. **HRMS (ESI)** m/z calc. for $C_{30}H_{25}O_4S_3^+$ [M+H]$^+$: 545.0909, found: 545.0920.

4,4''-bis(3-bromophenyl)-2,2':5',2''-terthiophene (TTT_3)



The product **TTT_3** was synthesized via the general procedure C using 2,2':5',2''-terthiophene (124 mg, 0.5 mmol, 1.0 eq.), 3-bromoiodobenzene (707 mg, 2.50 mmol, 5.0 eq.) and a reaction time of 3 days and isolated by column chromatography (10% EtOAc/cyclohexane to 90% CH_2Cl_2/MeOH). The product was further purified by a crystallization from cyclohexane and isolated as brownish solid (168 mg, 0.29 mmol, 58%) **(QNMR: 68%)**. Further purification can be achieved by vacuum sublimation to obtain a clear yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (t, *J* = 1.8 Hz, 2H), 7.52 (ddd, *J* = 7.8, 1.8, 1.1 Hz, 2H), 7.44 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 2H), 7.41 (d, *J* = 1.5 Hz, 2H), 7.34 (d, *J* = 1.5 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.14 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.47, 138.05, 137.43, 136.18, 130.39, 130.35, 129.35, 124.89, 124.67, 123.02, 122.59, 120.17. **HRMS (ESI)** m/z calc. for $C_{24}H_{14}Br_2S_3^+$ [M]$^+$: 555.8619, found: 555.8584.

diethyl 4,4'-([2,2':5',2'':5'',2'''-quaterthiophene]-4,4'''-diyl)dibenzoate ($TTTT_1$)



The product **$TTTT_1$** was synthesized via the general procedure C using 2,2':5',2'':5'',2'''-quaterthiophene (165 mg, 0.5 mmol, 1.0 eq.), ethyl 4-iodobenzoate (690 mg, 2.50 mmol, 5.0 eq.) and a reaction time of 3 days and was isolated by column chromatography (10/90/0 to 50/25/25 EtOAc/cyclohexane/CH_2Cl_2). The product was further purified by crystallization from cyclohexane and isolated as brownish solid (59.0 mg,

94.1 µmol, 19%) **(QNMR: 20%)** as the main product. Unreacted 2,2':5',2'':5'',2'''-quaterthiophene could be recovered and purified by sublimation (127 mg, 0.38 mmol, 77%) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.11 – 8.08 (m, 4H), 7.69 – 7.66 (m, 4H), 7.49 (d, *J* = 1.5 Hz, 2H), 7.45 (d, *J* = 1.5 Hz, 2H), 7.15 (d, *J* = 3.8 Hz, 2H), 7.12 (d, *J* = 3.8 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 4H), 1.42 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.37, 141.95, 139.49, 138.15, 136.22, 136.00, 130.24, 129.31, 126.07, 124.82, 124.47, 122.63, 120.86, 61.02, 14.37. **HRMS (ESI)** m/z calc. for $C_{34}H_{27}O_4S_4^+$ $[M+H]^+$: 627.0787, found: 627.0787.

Fluorescence measurements

Materials and methods

Reagent

Spectroscopic grade of 1,2 dichloroethane (DCE) was purchase from VWR. It was contacted with K_2CO_3 to remove HCl for 12 hours and then filtered.

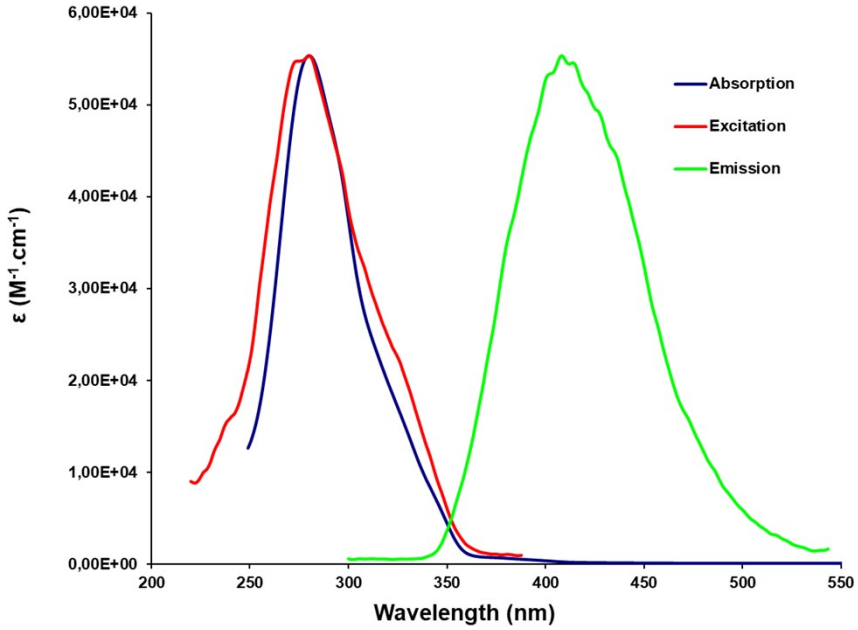
Sample preparation

An aliquot (~0.5mg) of synthesis product was precisely weight on an XA105 balance (Mettler Toledo) and dilute in a 5 ml volumetric flask with DCE. The solutions were freshly prepared before using. All volumes were collected with Hamilton syringe in order to prepare the samples in quartz suprasil cuvette (Hellma) to measure absorption, excitation and emission spectra. The optical path length was 1 cm.

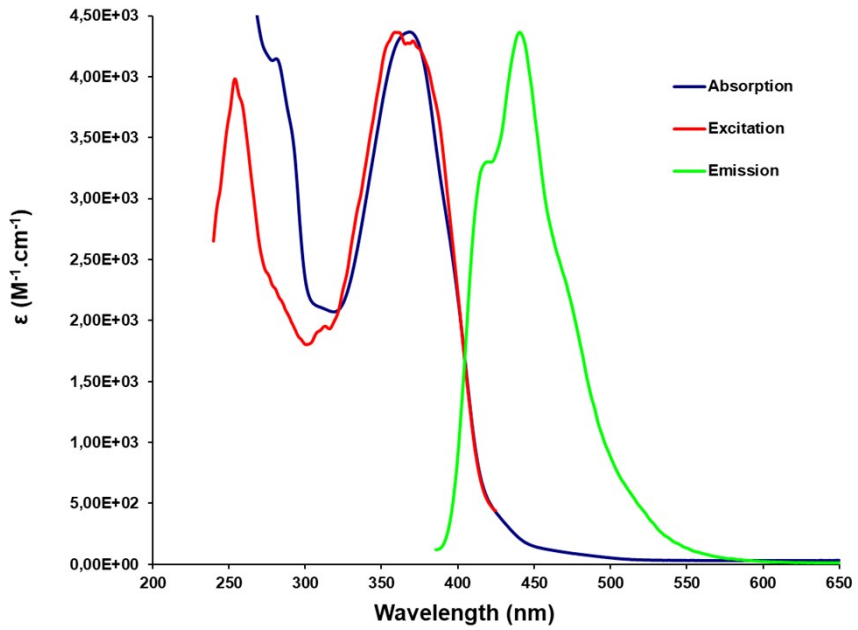
Optical properties of synthesis products

To remain under linear conditions, excitation and emission spectra recorded with solution with an absorbance of less than 0.1 in DCE.[13]

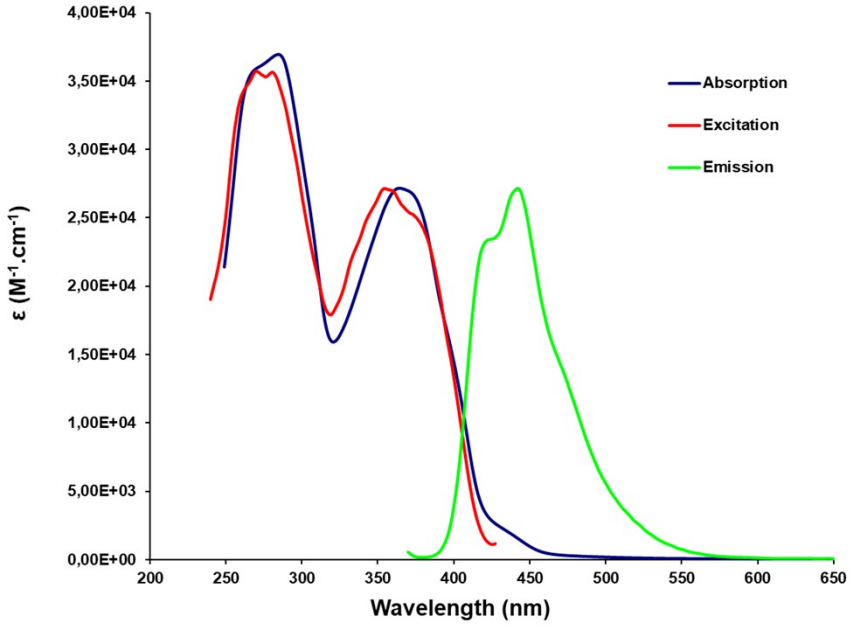
All absorption spectra were converted in electronics spectrum by dividing the values of absorbance by concentration (M) of product. All excitation and emission spectra were normalised to those of spectra absorption. So, following figures, on the vertical axis, the emission and excitation values are normalized intensities.



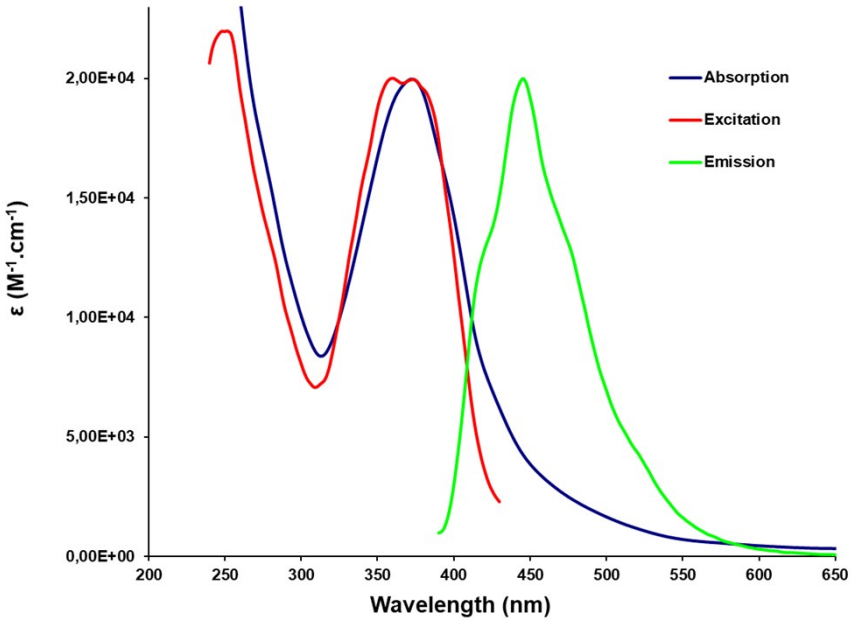
Electronic spectrum from absorption (blue), excitation spectrum (red) λ_{em} = 408 nm and emission spectrum (green) λ_{exc} = 280 nm of **TT_2**. 1% attenuation, slit 11 nm



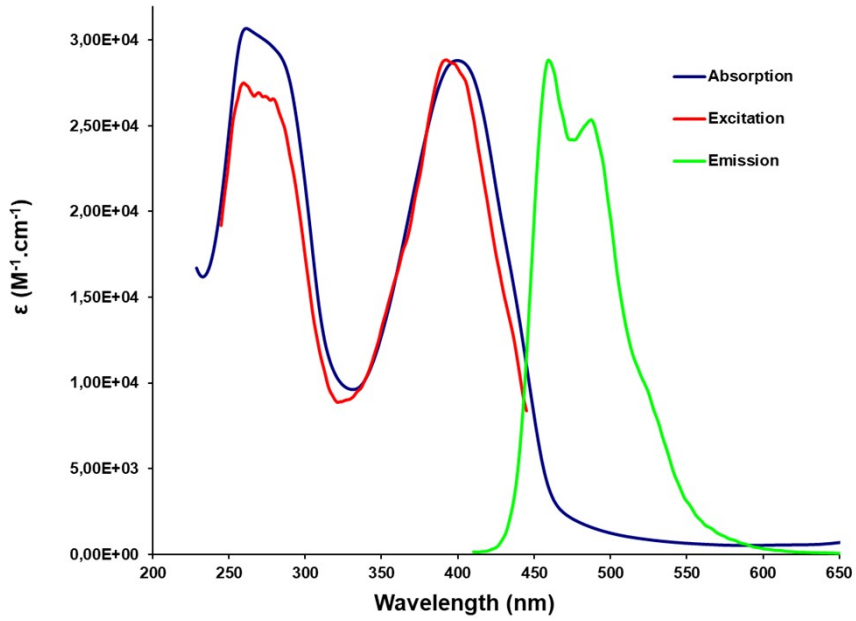
Electronic spectrum from absorption (blue), excitation spectrum (red) λ_{em} = 440 nm and emission spectrum (green) λ_{exc} = 360 nm of **TTT_1**. Slit 8 nm



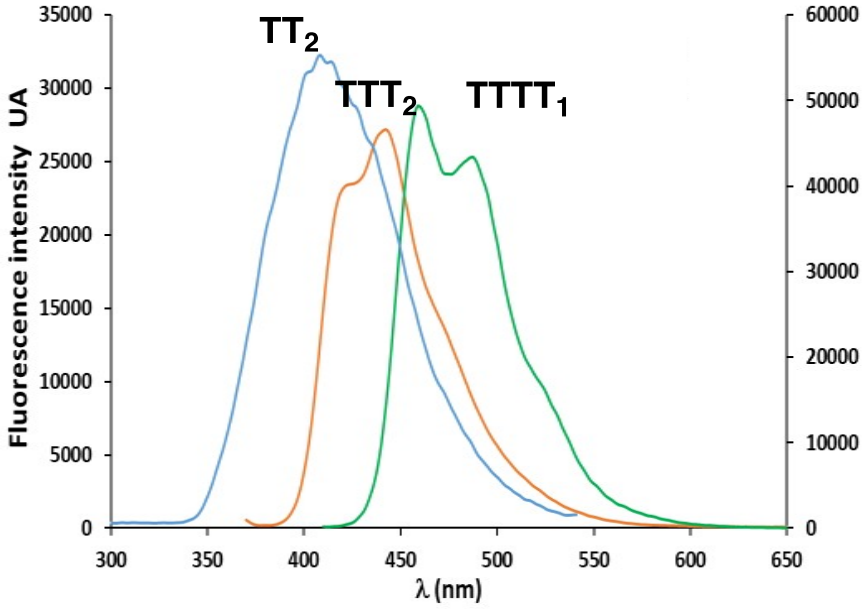
Electronic spectrum from absorption (blue), excitation spectrum (red) λ_{em} = 442 nm and emission spectrum (green) λ_{exc} = 355 nm of **TTT_2**. 1% attenuation, slit 12 nm



Electronic spectrum from absorption (blue), excitation spectrum (red) λ_{em} = 445 nm and emission spectrum (green) λ_{exc} = 373 nm of **TTT_3**. 1% attenuation, slit 13 nm

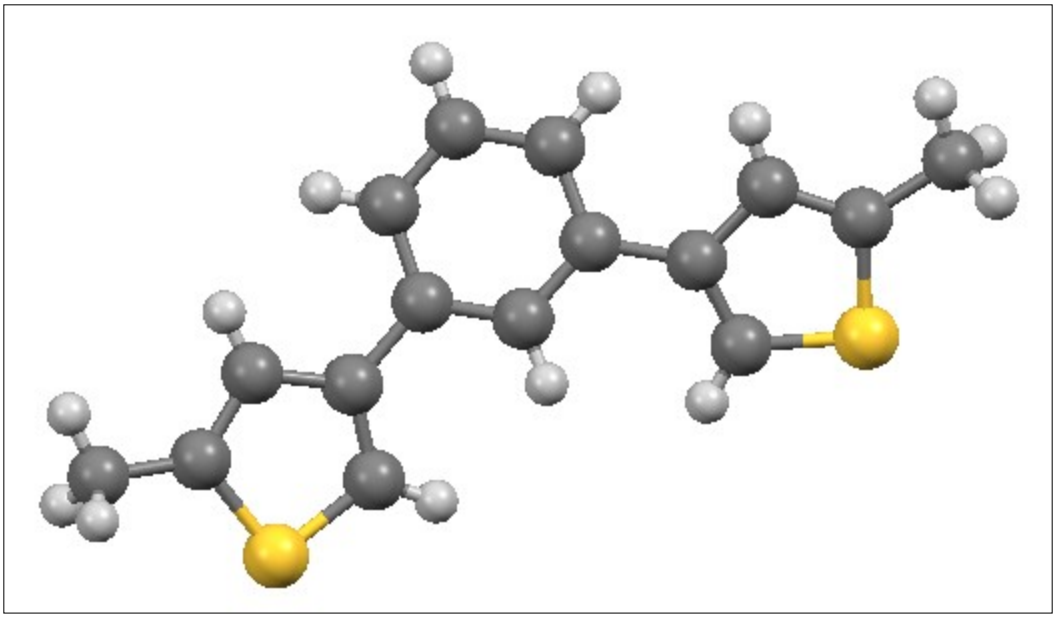


Electronic spectrum from absorption (blue), excitation spectrum (red) λ_{em} = 460 nm and emission spectrum (green) λ_{exc} = 392 nm of **$TTTT_1$**. 1% attenuation, slit 10 nm



Superposition of emission spectra from **TT_2**, **TTT_2** and **$TTTT_1$**.

X-Ray data



Crystal data and structure refinement for **3s** (CCDC 2253044).

Identification code	**3s** (CCDC 2253044).
Empirical formula	$C_{16}H_{14}S_2$
Formula weight	270.39
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 5.93940(10) Å alpha = 90 deg. b = 17.7242(4) Å beta = 95.7350(10) deg. c = 25.3518(6) Å gamma = 90 deg.
Volume	2655.45(10) $Å^3$
Z, Calculated density	8, 1.353 Mg/m^3
Absorption coefficient	0.379 mm^1
F(000)	1136
Crystal size	0.200 x 0.200 x 0.160 mm
Theta range for data collection	1.982 to 27.939 deg.
Limiting indices	-7<=h<=7, -23<=k<=20, -33<=l<=33
Reflections collected / unique	51644 / 6355 [R(int) = 0.0271]
Completeness to theta = 25.242	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.7145
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6355 / 0 / 323
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0321, wR2 = 0.0874
R indices (all data)	R1 = 0.0357, wR2 = 0.0907
Extinction coefficient	n/a
Largest diff. peak and hole	0.573 and -0.323 e. $Å^3$

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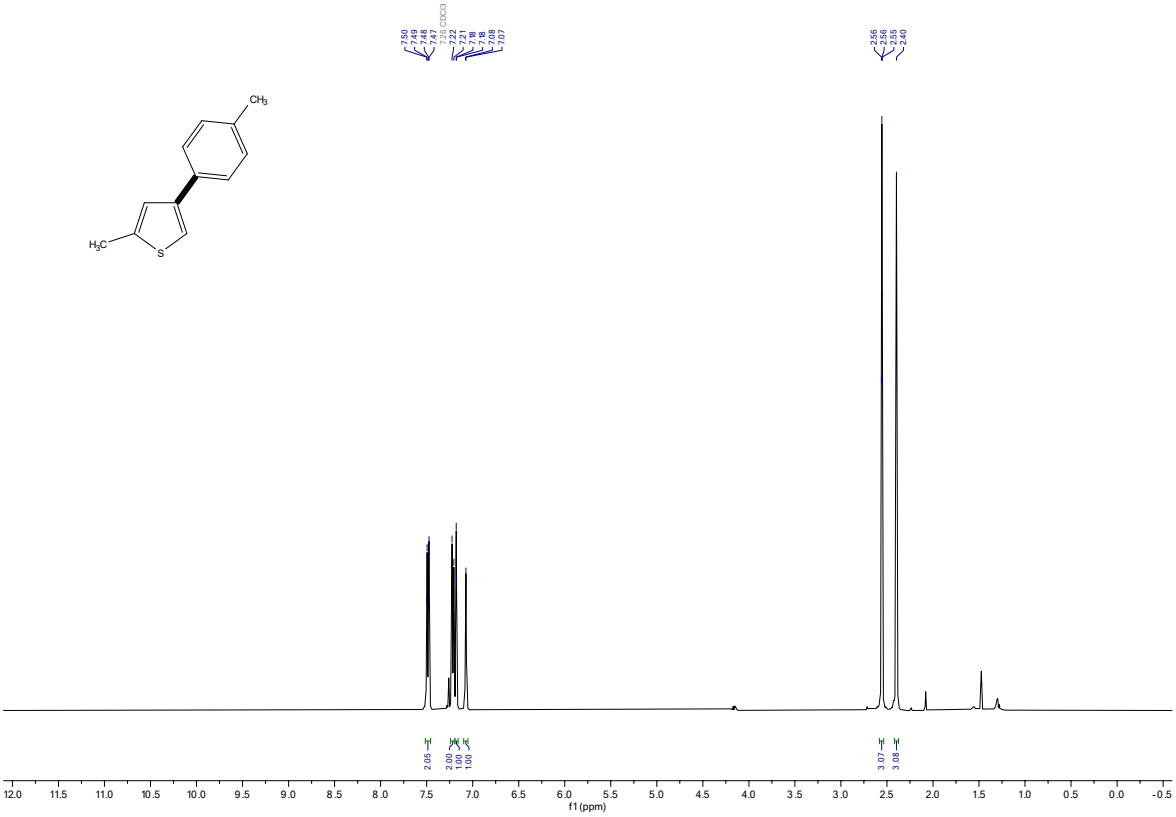
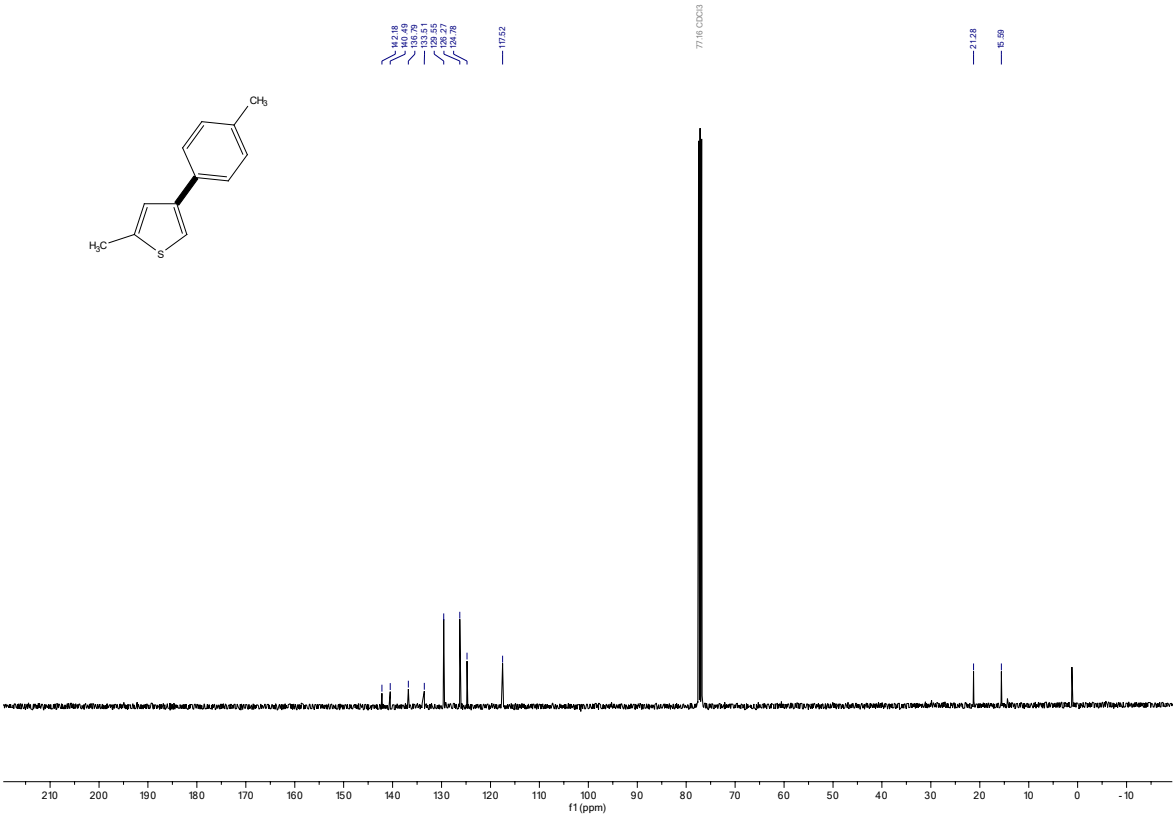
Spectra


7.50
7.49
7.48
7.47
7.22
7.21
7.19
7.18
7.08
7.07
CDCl3
2.56
2.56
2.55
2.55
2.40
CH3
H3C
S
2.05
2.00
1.03
1.00
3.07
3.08
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 -0.5
f1 (ppm)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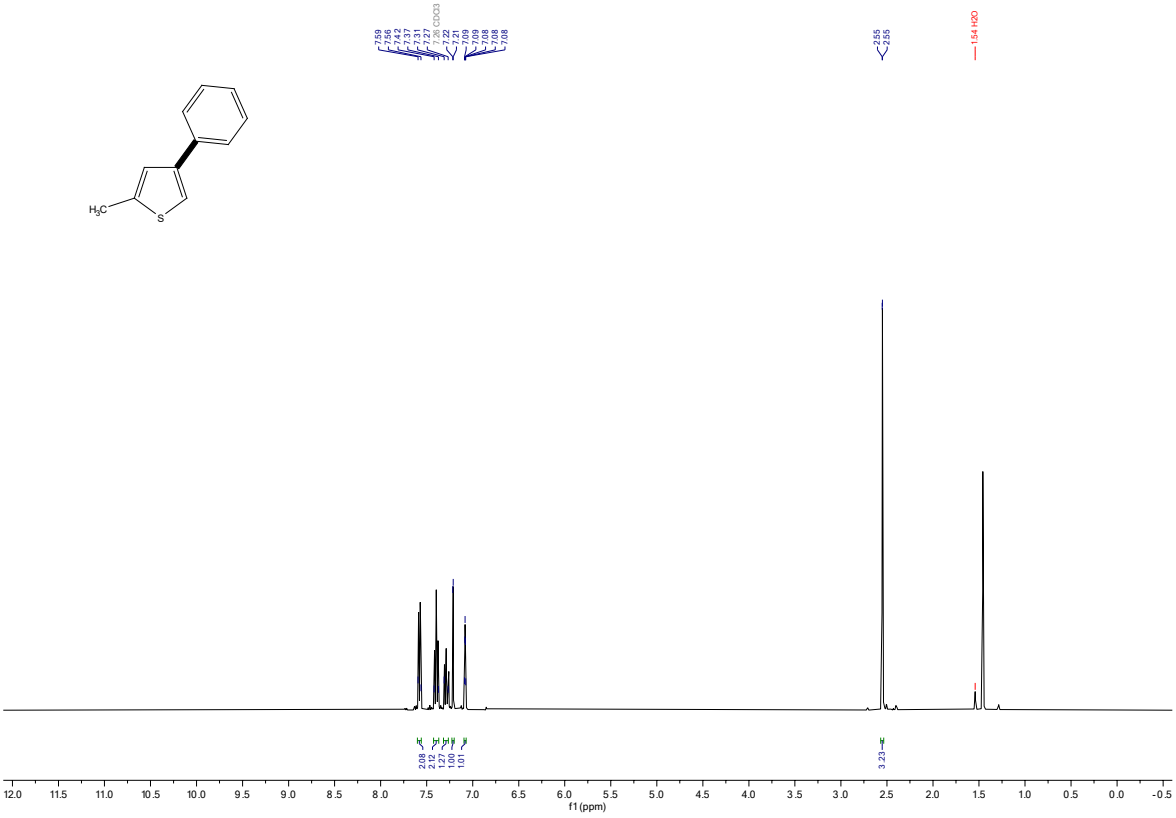
140.40
136.79
133.51
128.35
126.27
124.78
117.52
77.16 CDCl3
21.28
15.59
CH3
H3C
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.58
7.42
7.37
7.31
7.27
7.26 CDCl3
7.23
7.21
7.09
7.09
7.08
7.08
7.08
2.55
2.55
1.54 H2O
H3C
S
2.08
2.13
1.27
1.00
1.01
3.23
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
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3.0
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2.0
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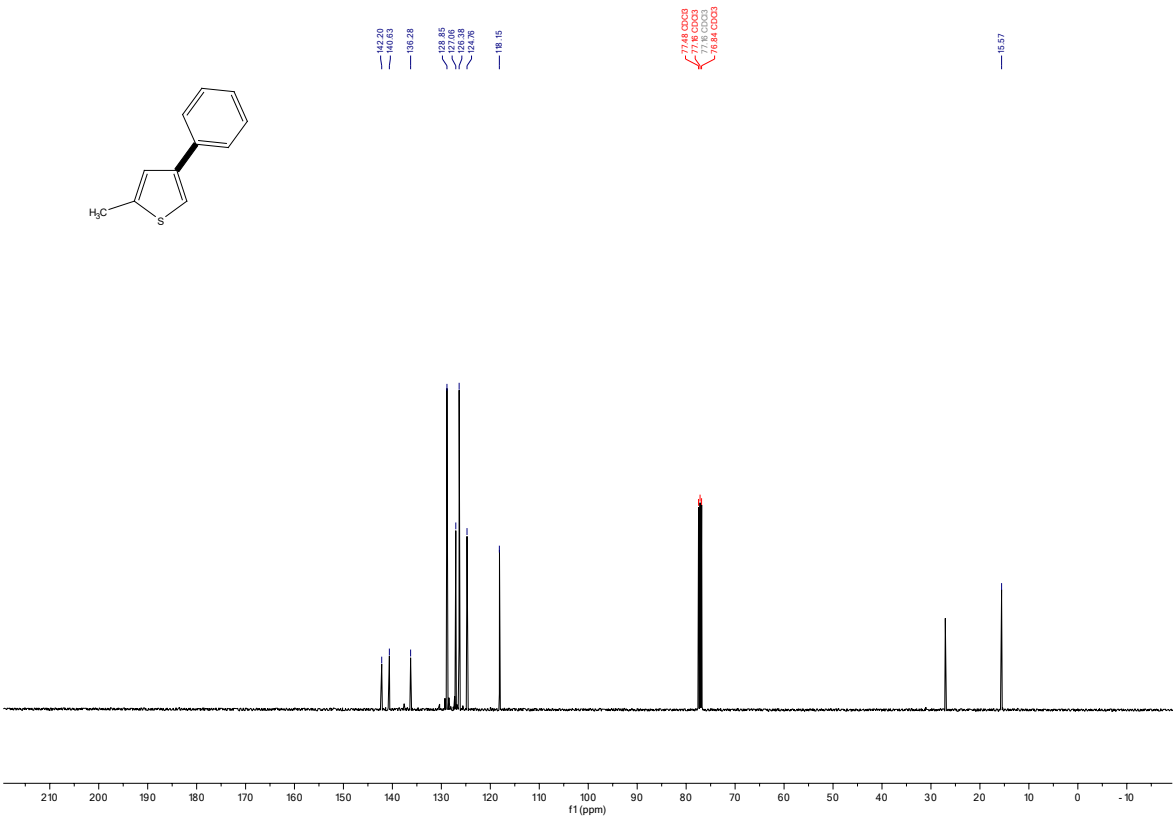
1.0
0.5
0.0
-0.5
f1 (ppm)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128.85
127.06
125.38
124.36
118.15
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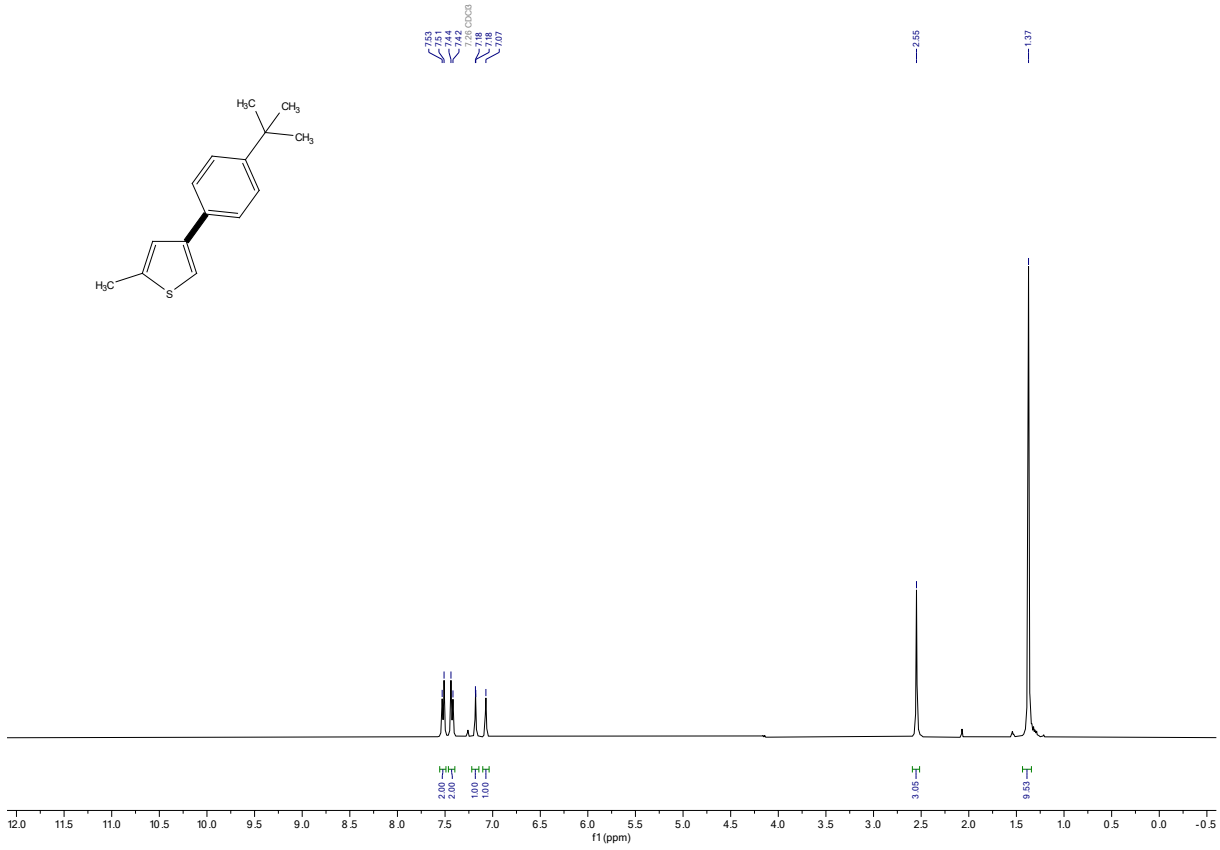
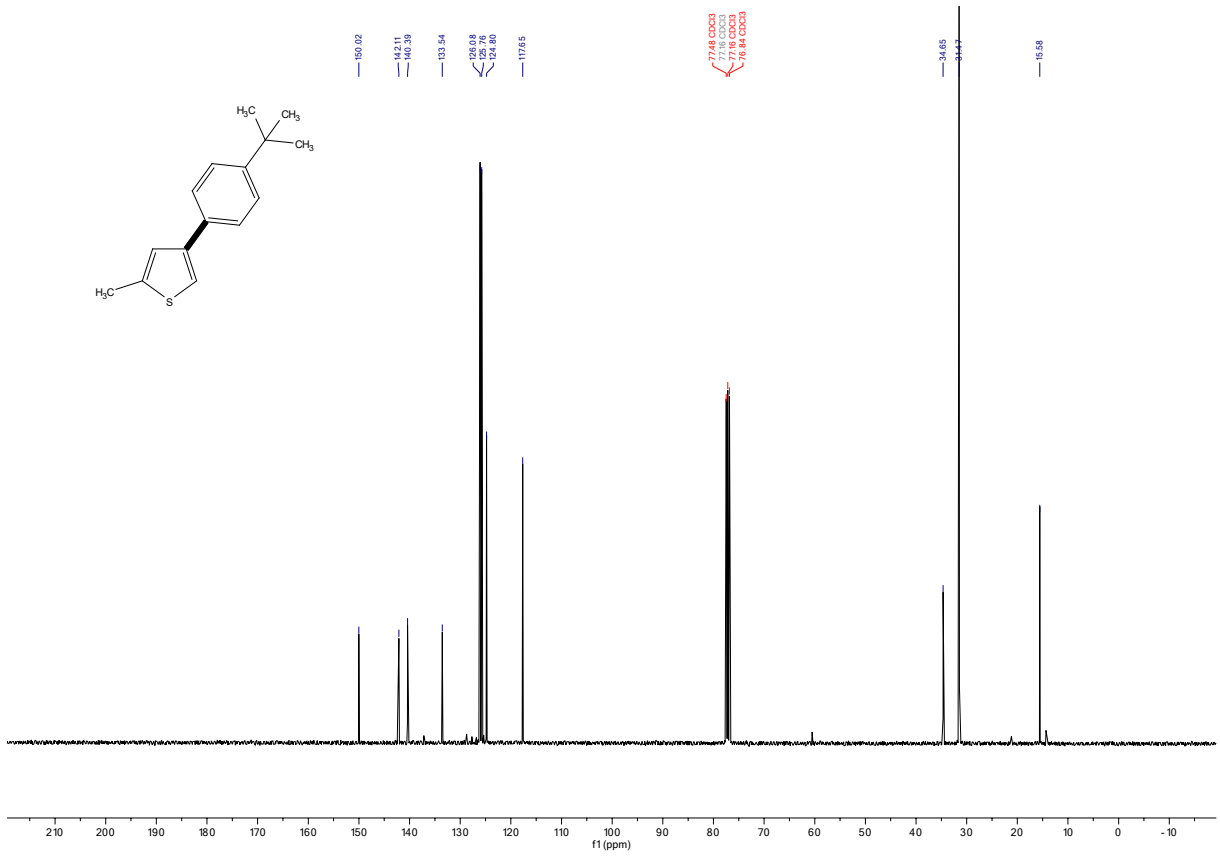
77.16 CDCl3
76.84 CDCl3
15.57
H3C
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.53
7.51
7.44
7.42
7.26 CDCl3
7.18
7.18
7.07
2.55
1.37
H3C
CH3
CH3
H3C
S
2.00
2.00
1.00
1.00
3.05
9.53
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 -0.5
f1 (ppm)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142.11
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126.18
125.76
124.80
117.65
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77.16 CDCl3
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34.65
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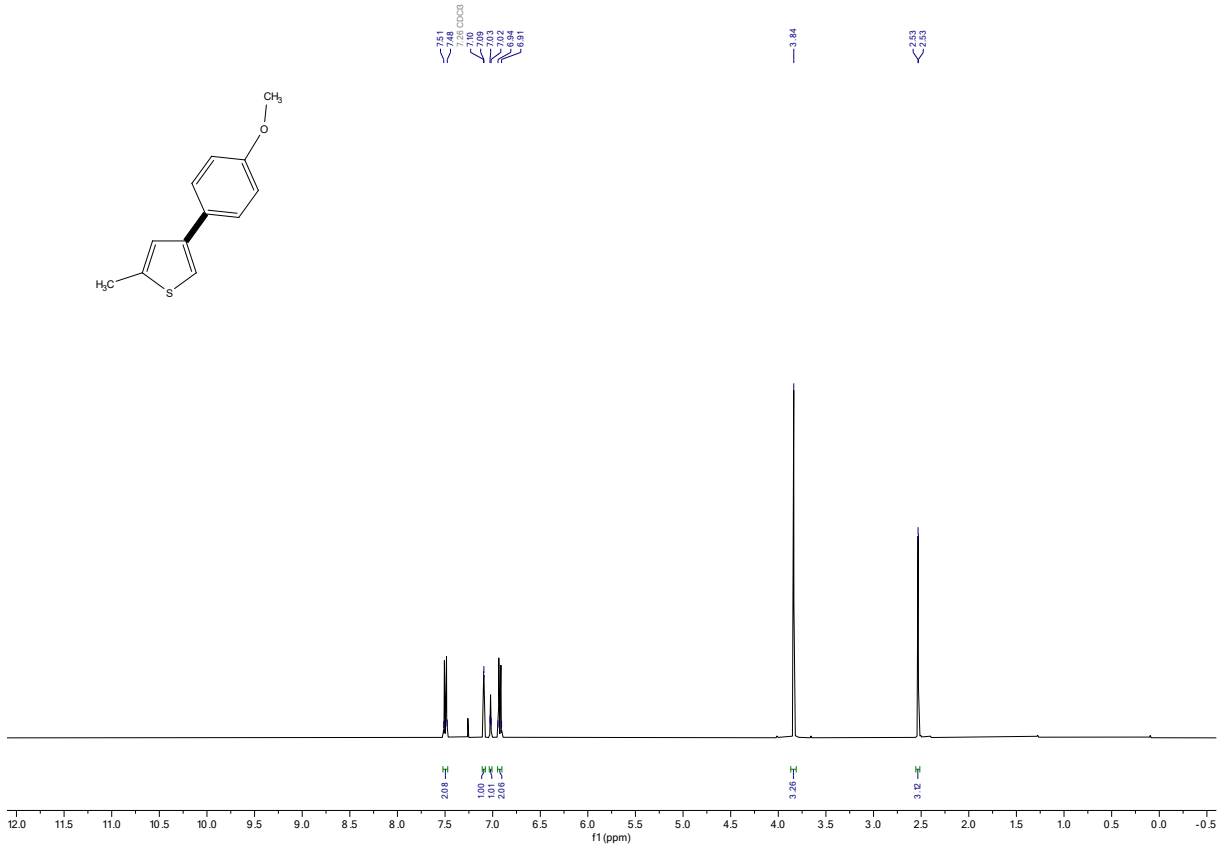
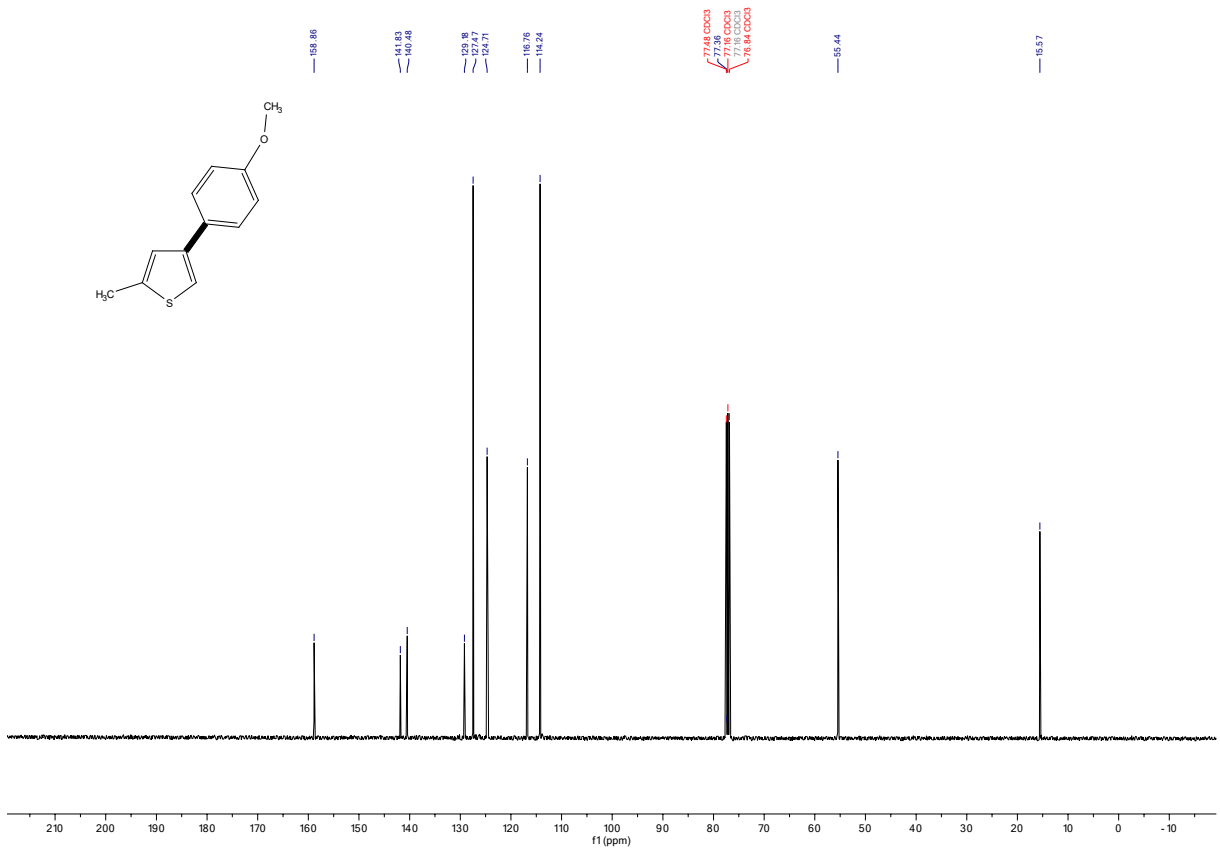
f1 (ppm)


7.51
7.48
7.26 CDCl3
7.09
7.09
7.03
7.03
7.02
6.94
6.91
3.84
2.53
2.53
CH3
O
H3C
S
2.08
1.00
1.01
2.06
3.26
3.12
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 -0.5
f1 (ppm)


158.86
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140.48
129.18
127.47
124.71
118.76
114.24
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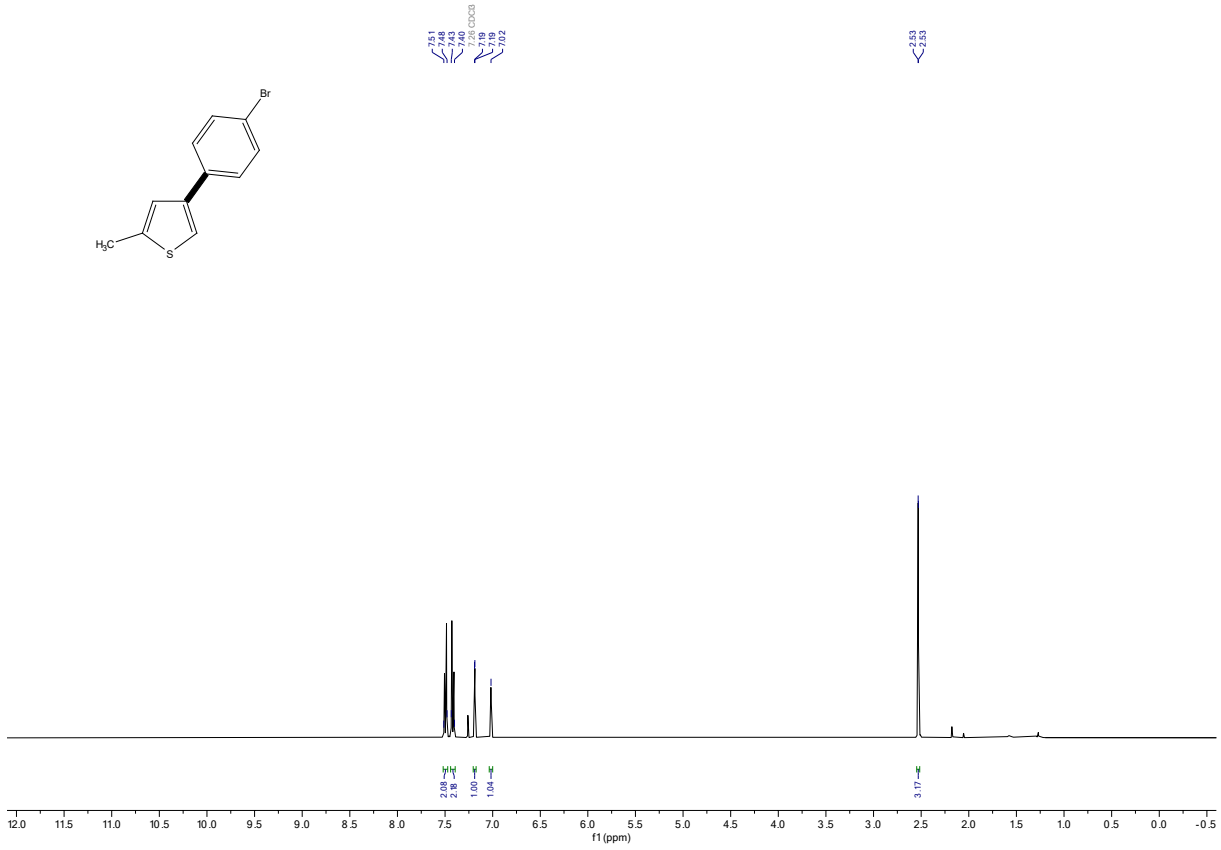
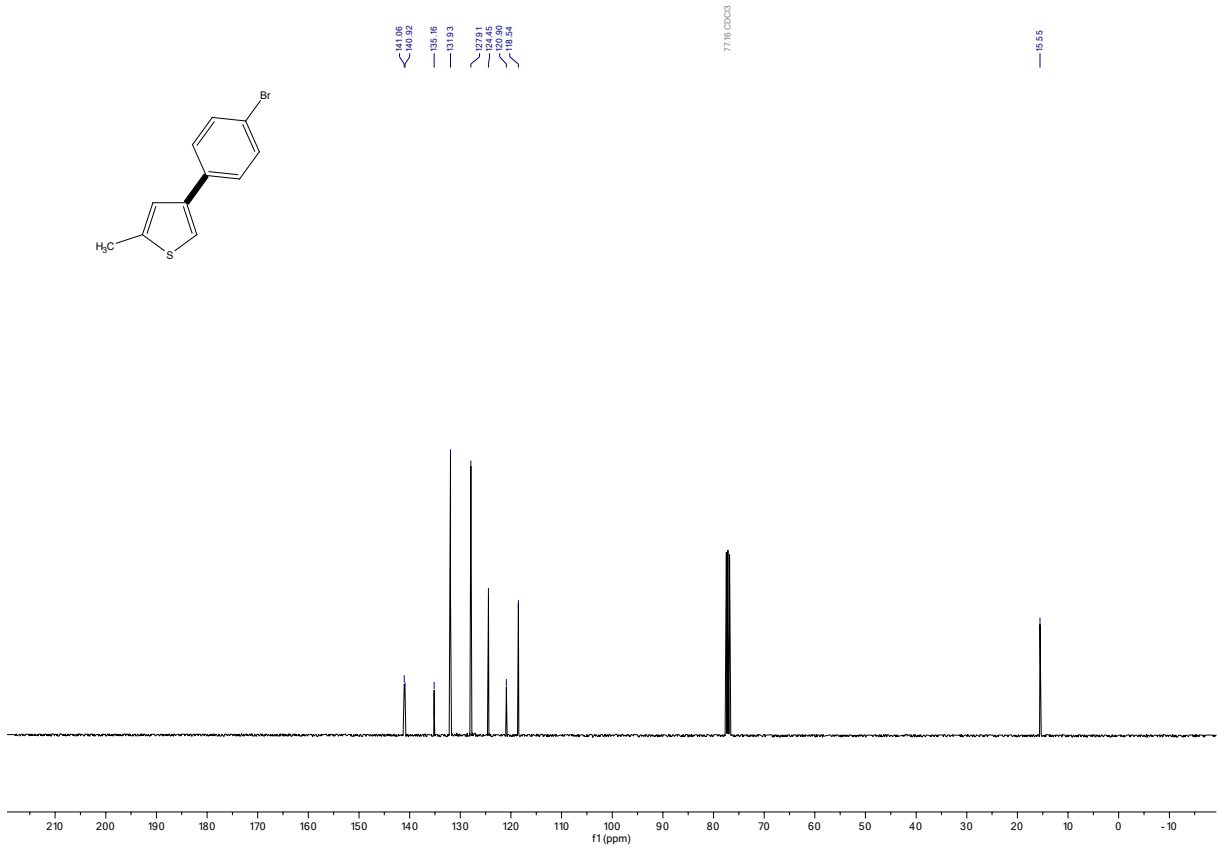
77.36
77.16 CDCl3
76.95 CDCl3
76.84 CDCl3
55.44
15.57
CH3
O
H3C
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.51
7.48
7.43
7.40
7.26 CDCl3
7.19
7.19
7.02
2.53
2.53
Br
H3C
S
2.08
2.16
1.00
1.04
3.17
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 -0.5
f1 (ppm)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15.55
Br
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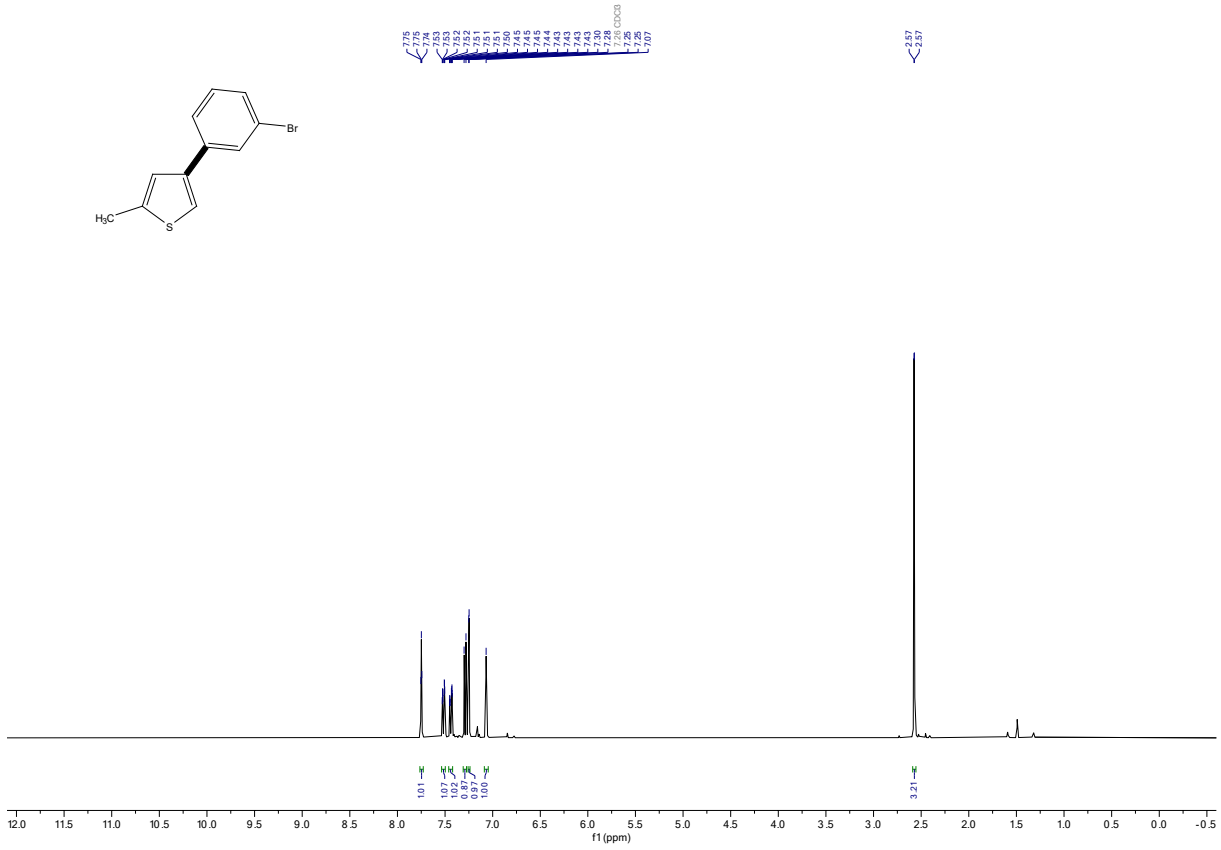
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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H3C
S
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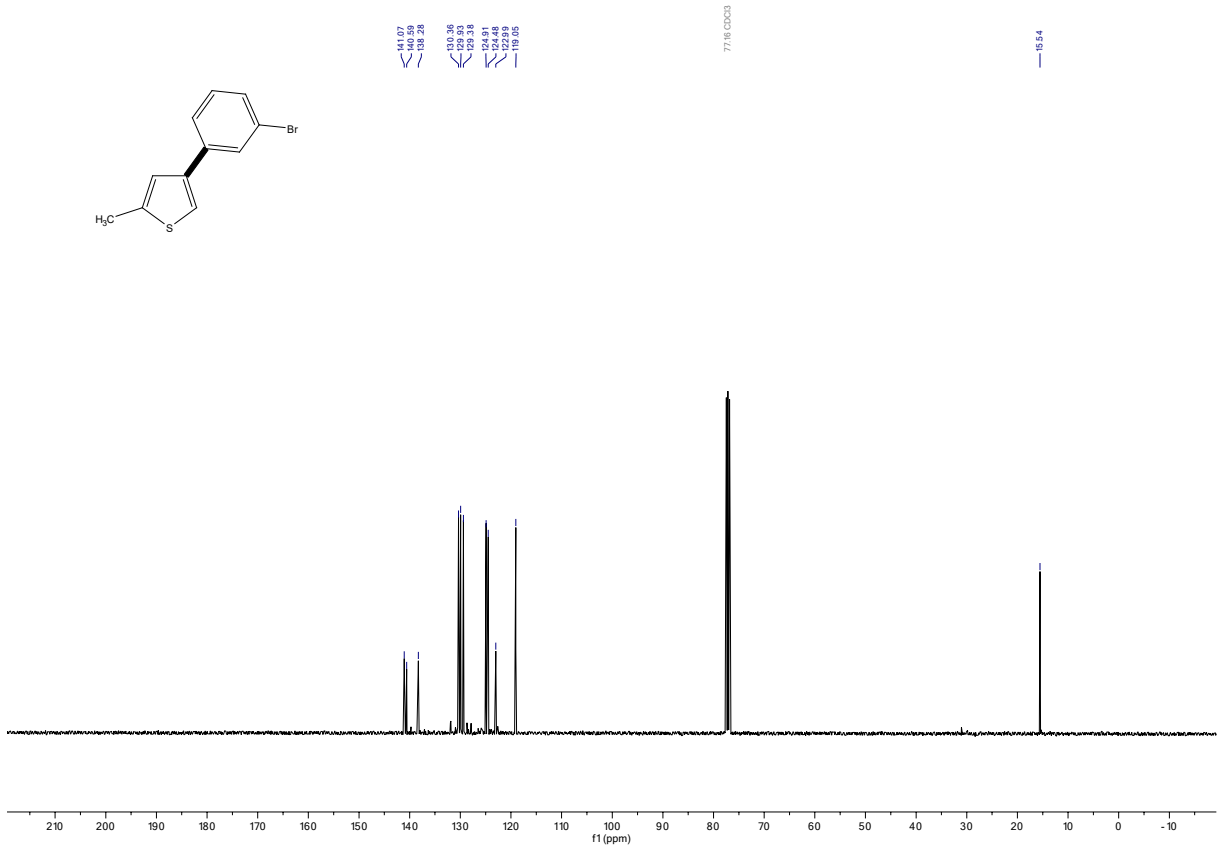
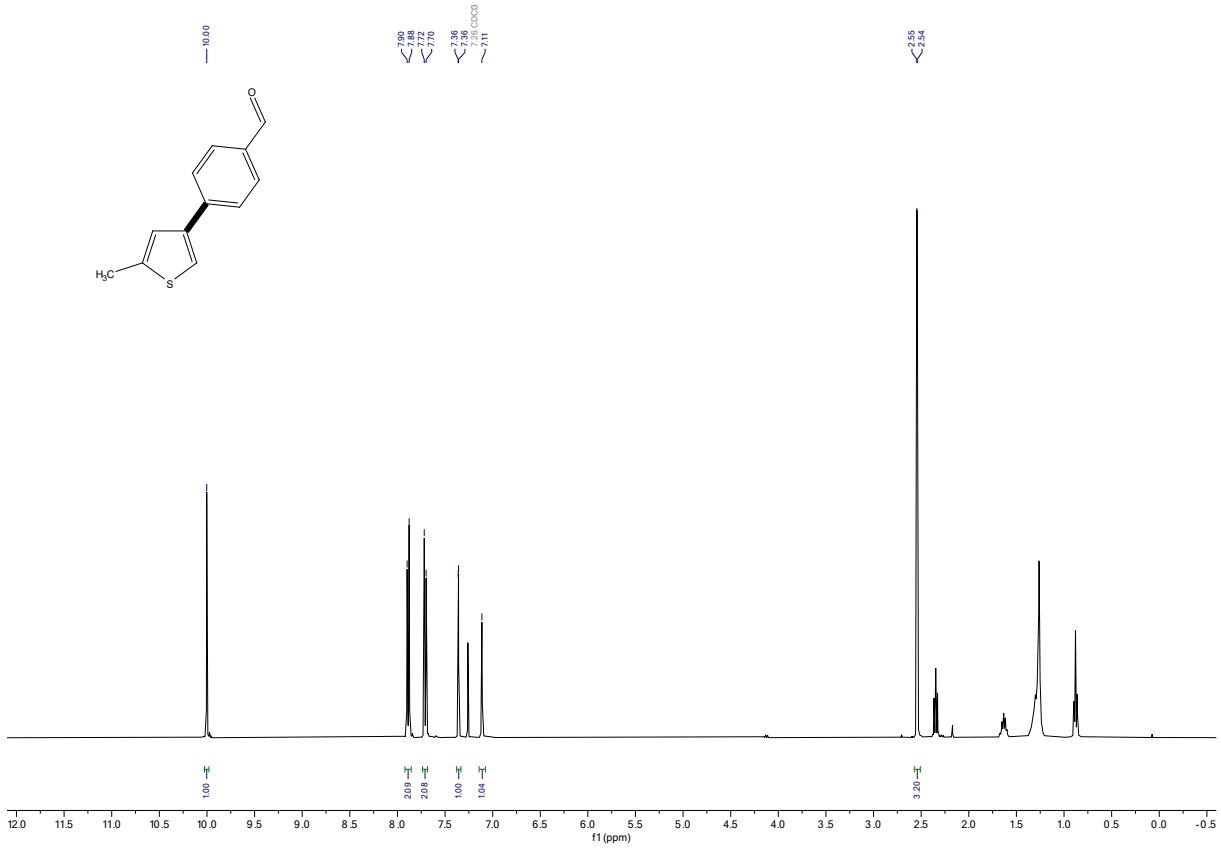
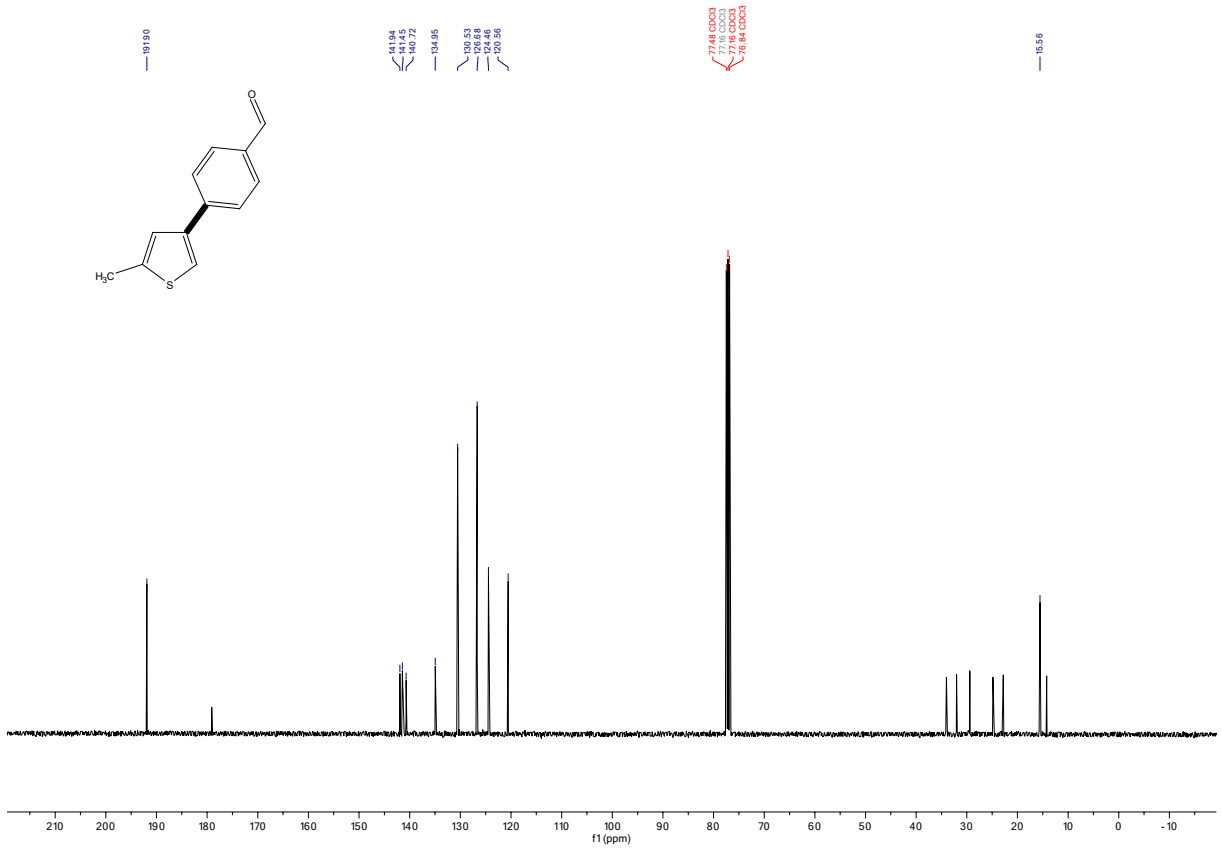
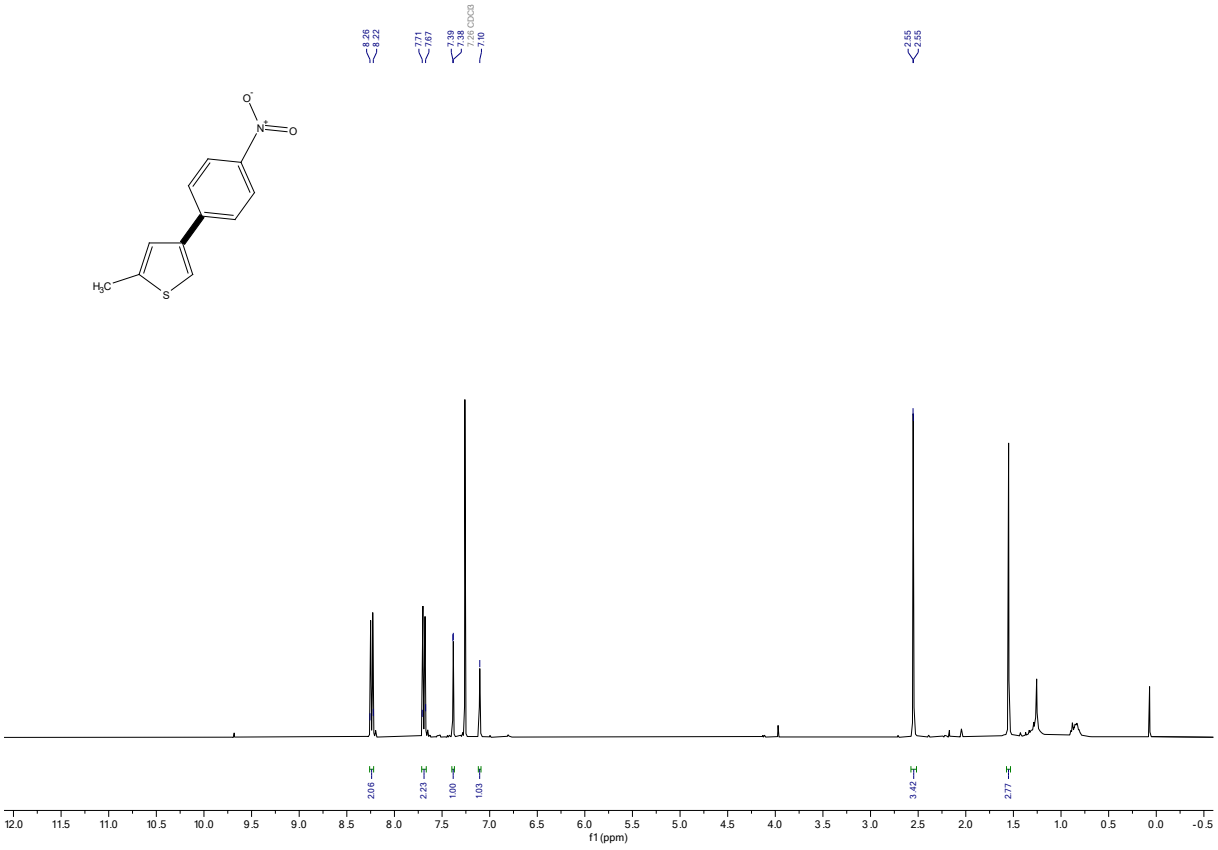
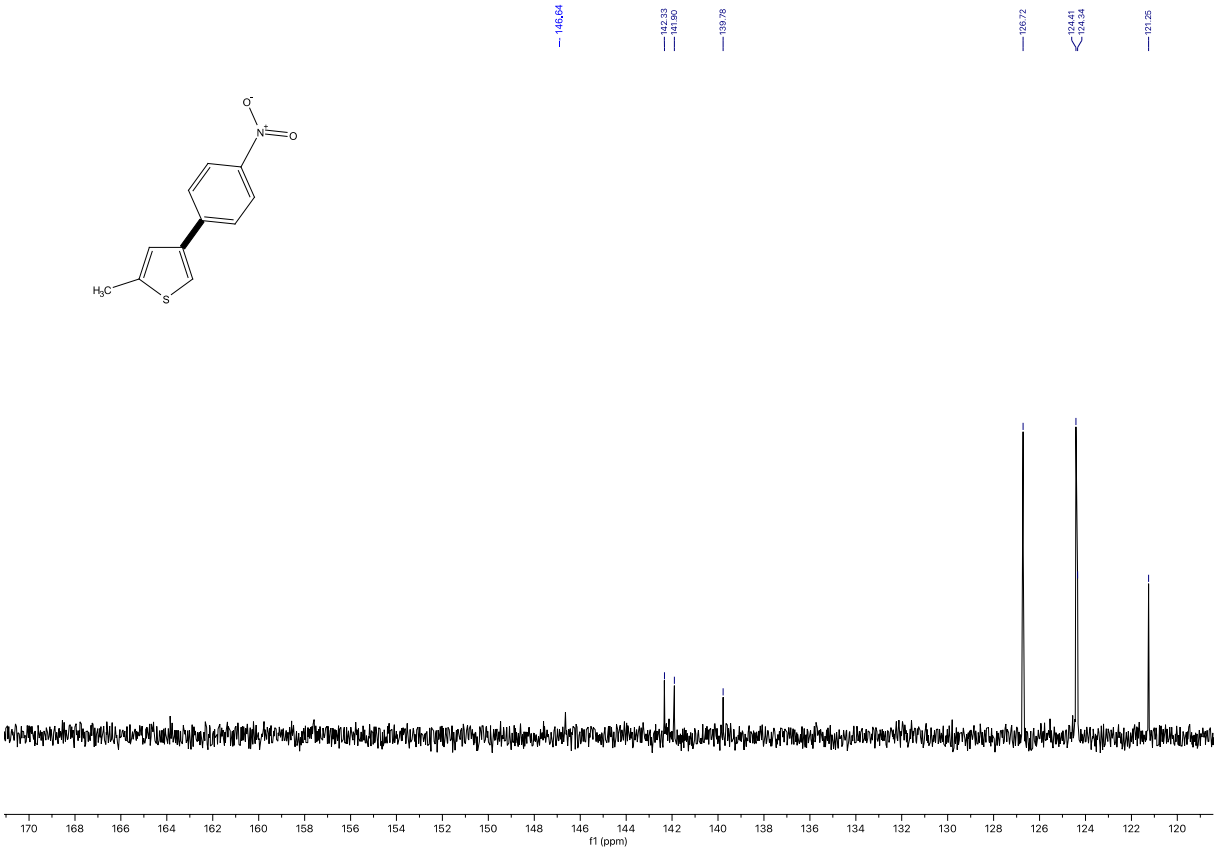
7.75
7.74
7.53
7.53
7.52
7.52
7.51
7.51
7.51
7.50
7.45
7.45
7.45
7.44
7.43
7.43
7.43
7.43
7.30
7.28 CDCl3
7.26
7.25
7.25
7.07
2.57
2.57
1.01
1.07
1.02
0.87
0.97
1.00
3.21
f1 (ppm)


Br
H3C
S
141.07
140.59
138.28
130.36
129.93
129.38
125.71
124.48
122.99
119.05
77.16 CDCl3
15.54
f1 (ppm)


10.00
7.90
7.88
7.72
7.70
7.36
7.36
7.26 CDCl3
7.11
2.55
2.54
O
H3C
S
1.00
2.09
2.08
1.00
1.04
3.20
f1 (ppm)


191.90
141.94
141.45
140.72
134.95
130.53
126.68
124.46
120.56
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
15.56
O
H3C
S
f1 (ppm)


8.26
8.22
7.71
7.67
7.39
7.38
7.26 CDCl3
7.10
2.55
2.55
2.06
2.23
1.00
1.03
3.42
2.77
f1 (ppm)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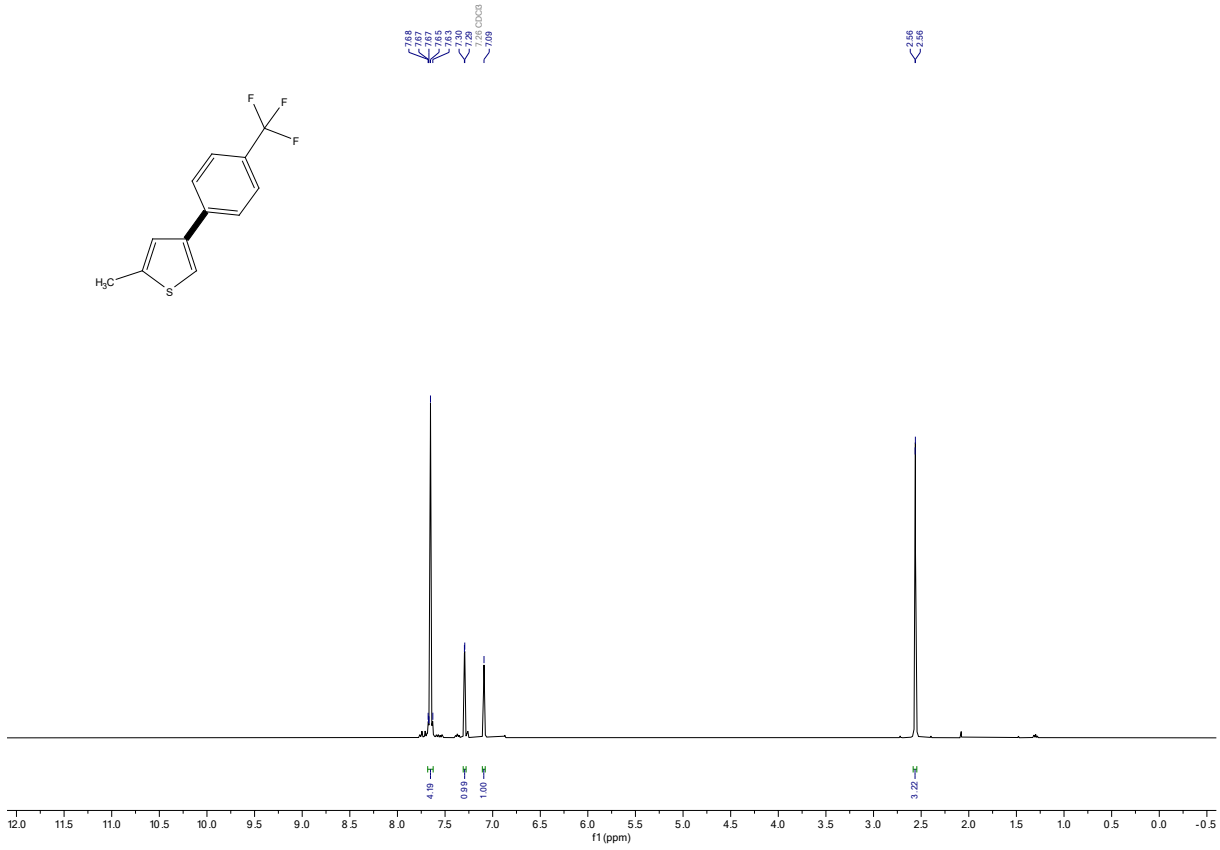
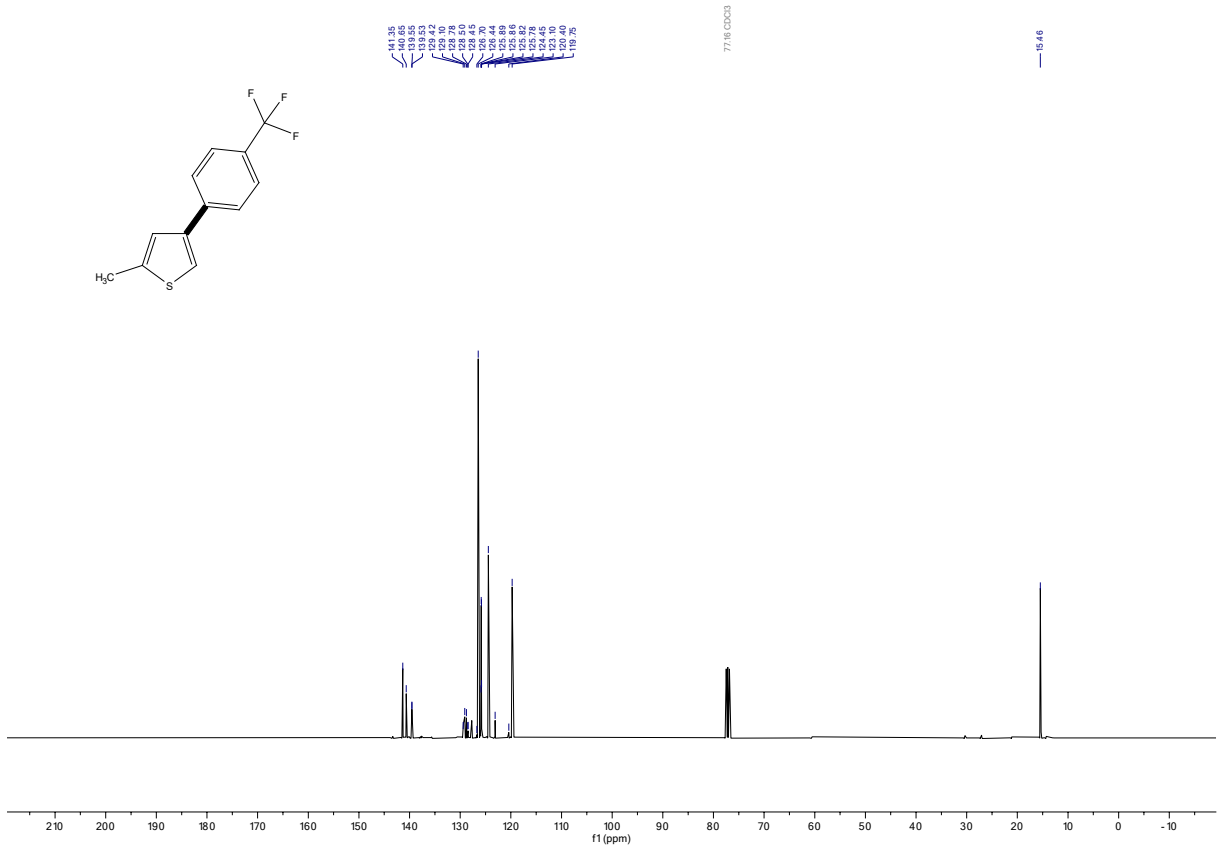
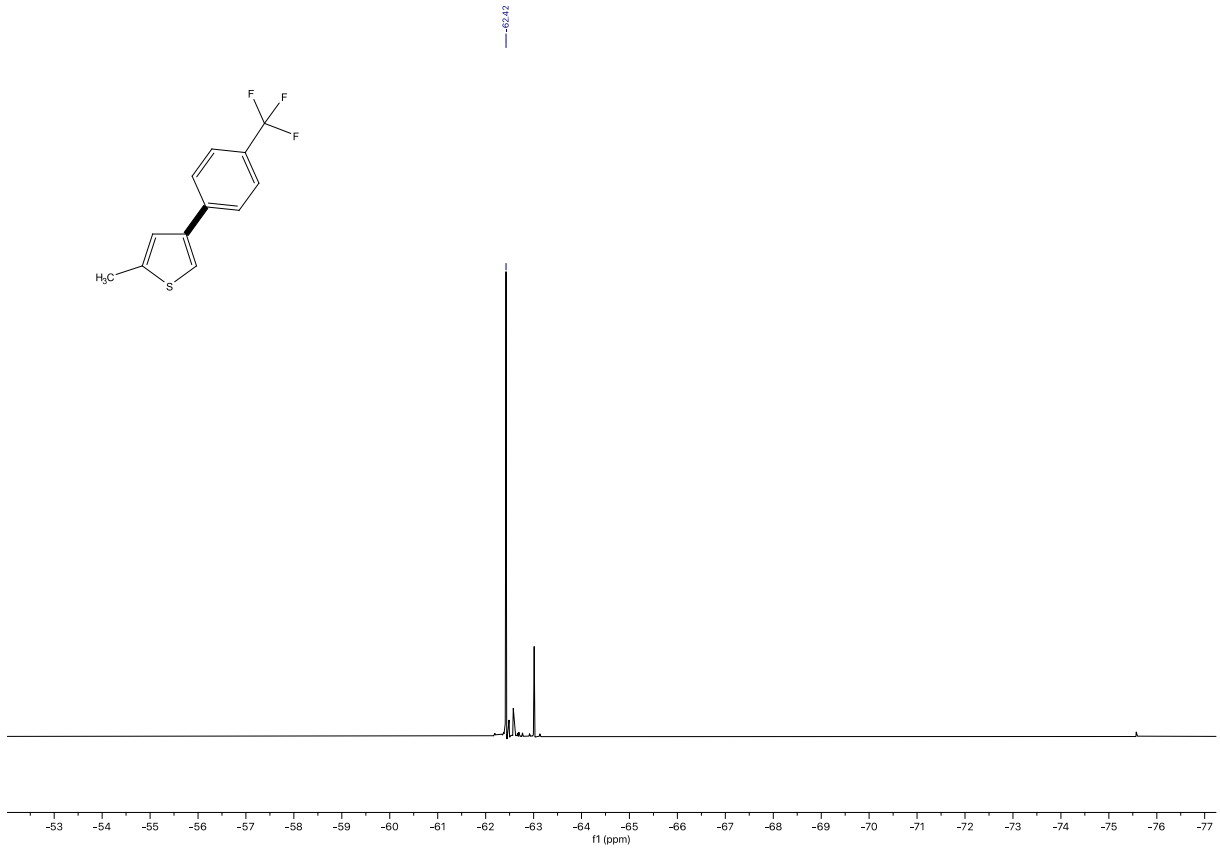
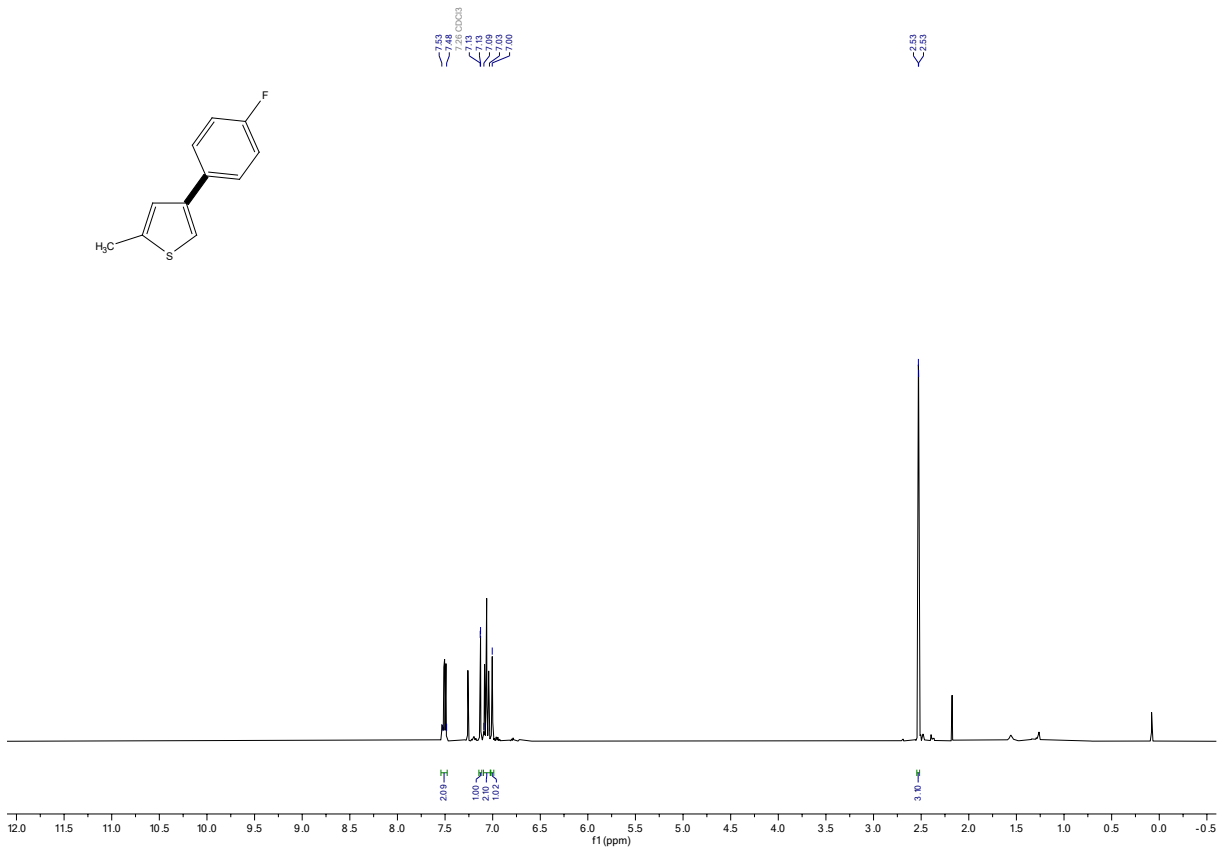
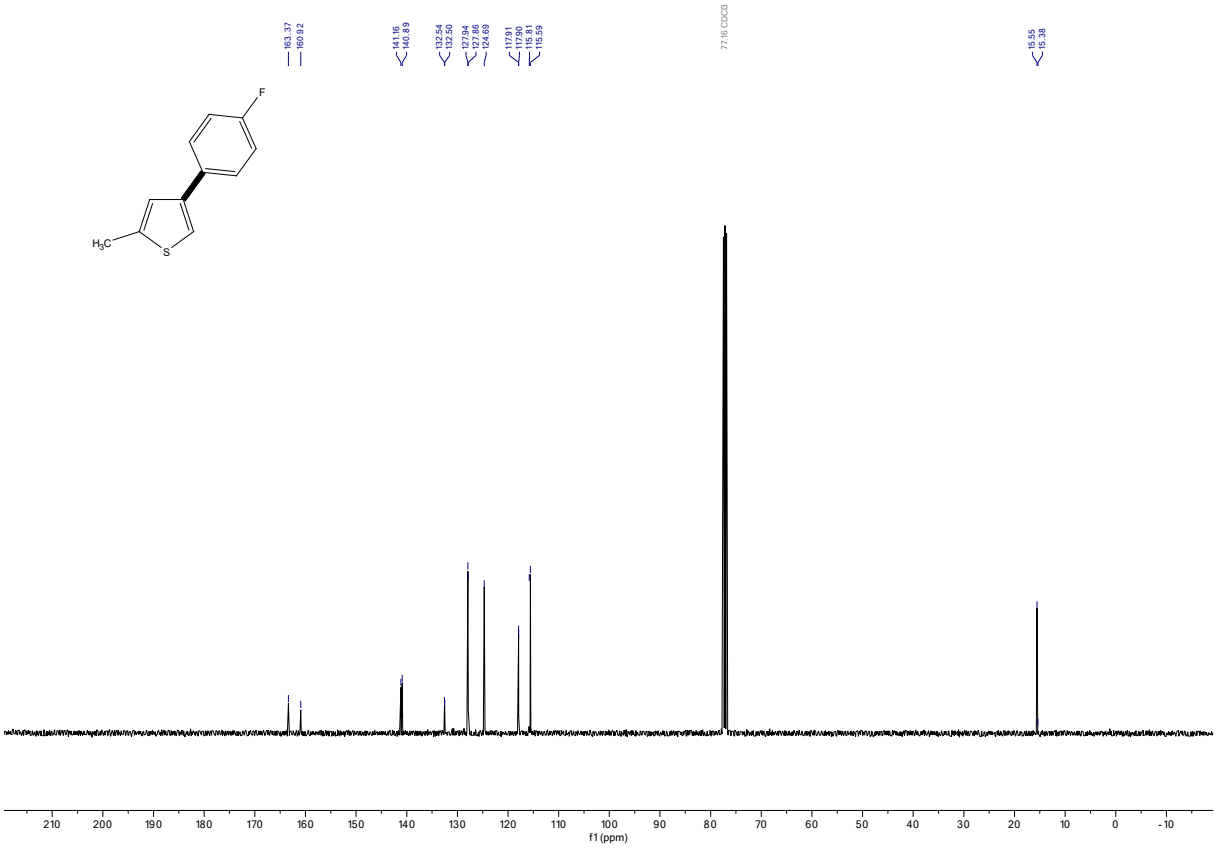
142.33
141.90
139.78
126.72
124.41
124.34
121.25
f1 (ppm)

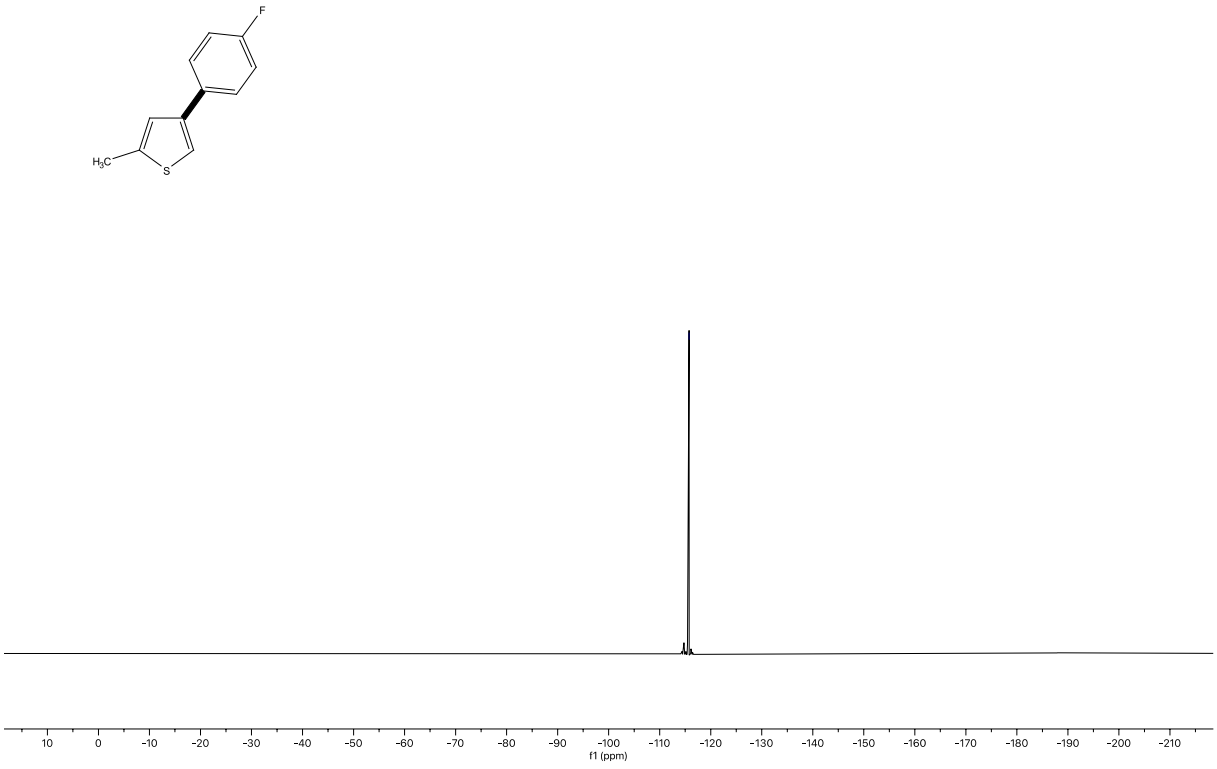

7.68
7.67
7.67
7.65
7.63
7.30
7.29
7.26 CDCl3
7.09
2.56
2.56
F
F
F
H3C
S
4.19
0.99
1.00
3.22
f1 (ppm)

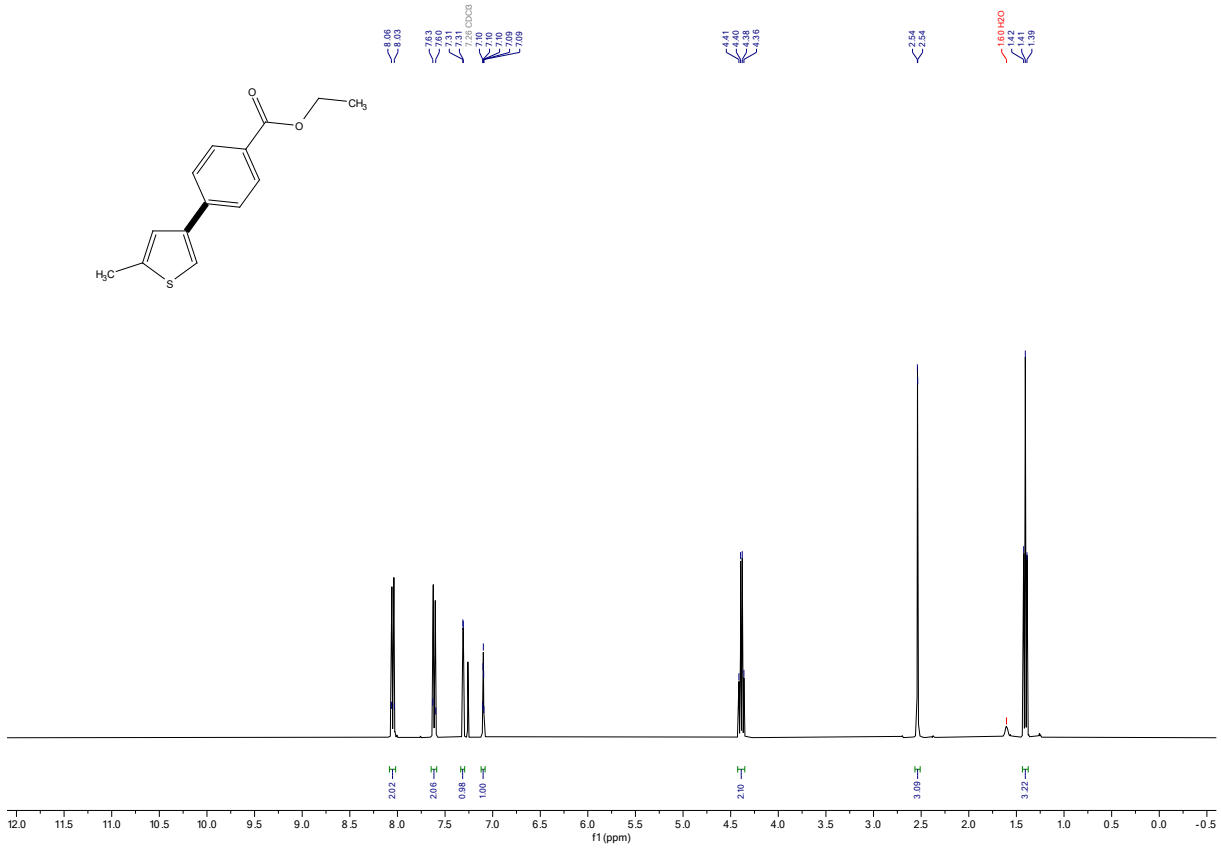

141.35
140.65
139.55
139.53
129.42
129.39
128.78
128.50
128.45
128.30
126.44
125.89
125.86
125.82
125.78
124.45
123.30
120.40
119.75
77.16 CDCl3
15.46
F
F
F
H3C
S
f1 (ppm)

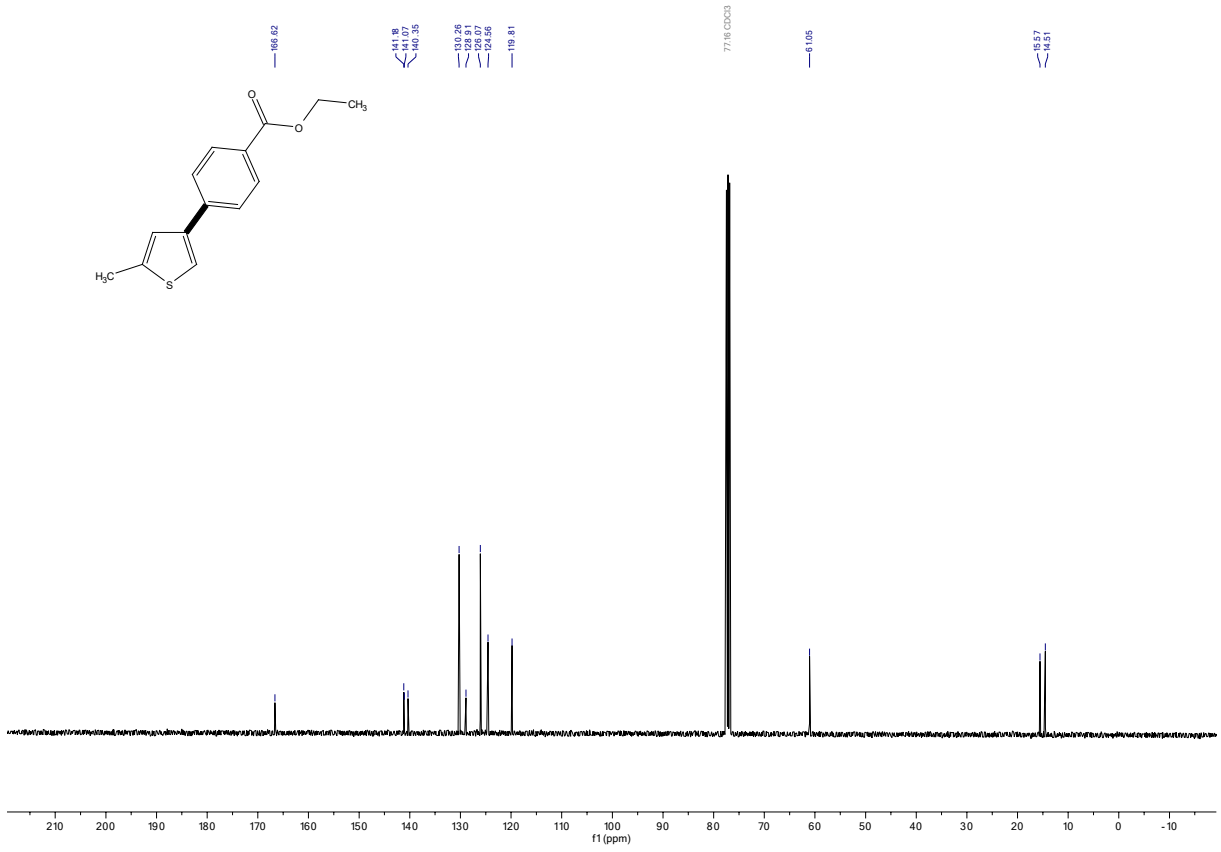

-62.42
F
F
F
H3C
S
-53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77
f1 (ppm)


7.53
7.48
7.26 CDCl3
7.13
7.13
7.09
7.03
7.00
2.53
2.53
F
H3C
S
2.09
1.00
2.03
1.02
3.10
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 -0.5
f1 (ppm)


163.37
160.92
141.16
140.89
132.54
132.50
127.94
127.86
124.69
117.91
117.90
115.81
115.59
77.16 CDCl3
15.55
15.38
F
H3C
S
f1 (ppm)


F
H3C
S
f1 (ppm)


8.06
8.03
7.63
7.60
7.31
7.28
CDCl3
7.10
7.10
7.09
7.09
4.41
4.40
4.38
4.36
2.54
2.54
1.60 H2O
1.42
1.41
1.39
O
O
CH3
H3C
S
2.02
2.06
0.98
1.00
2.10
3.09
3.22
f1 (ppm)


166.62
141.18
141.07
140.35
130.26
129.31
126.07
124.56
119.81
77.16 CDCl3
61.05
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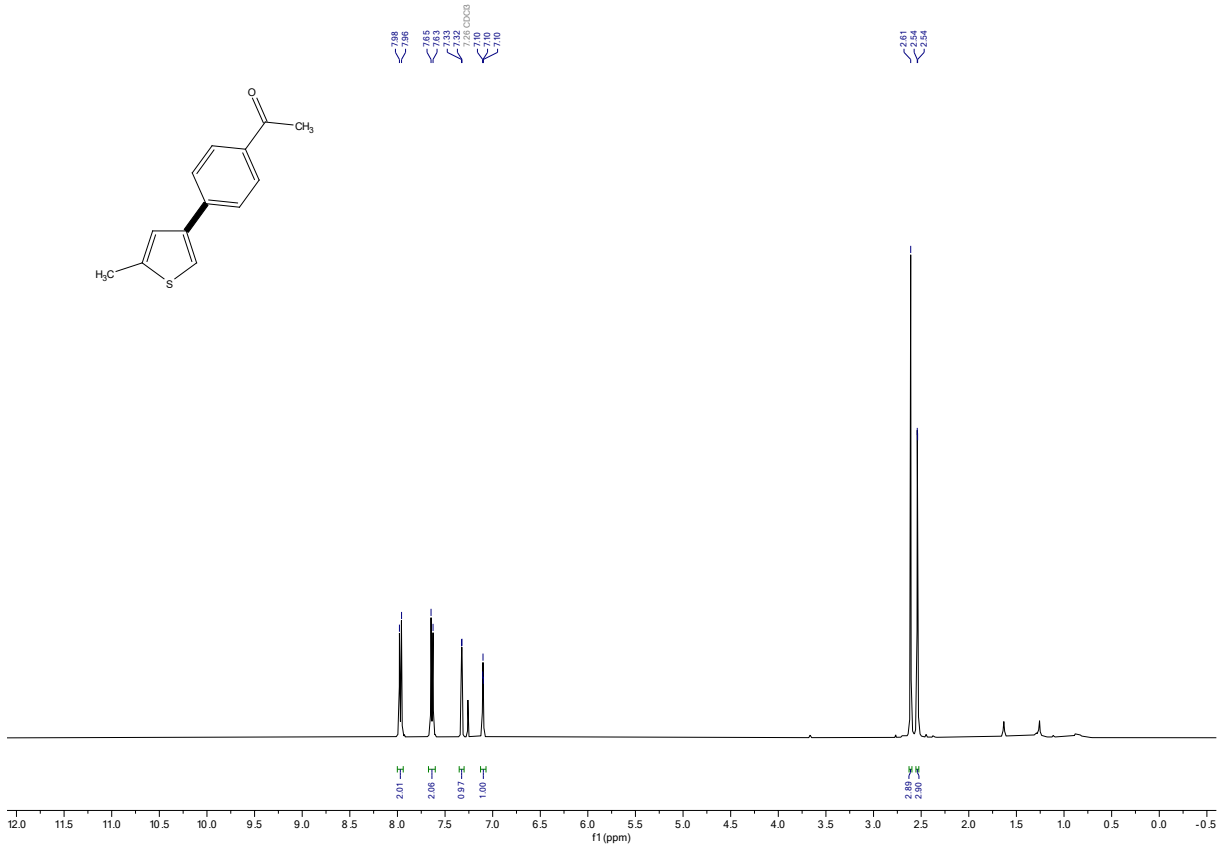
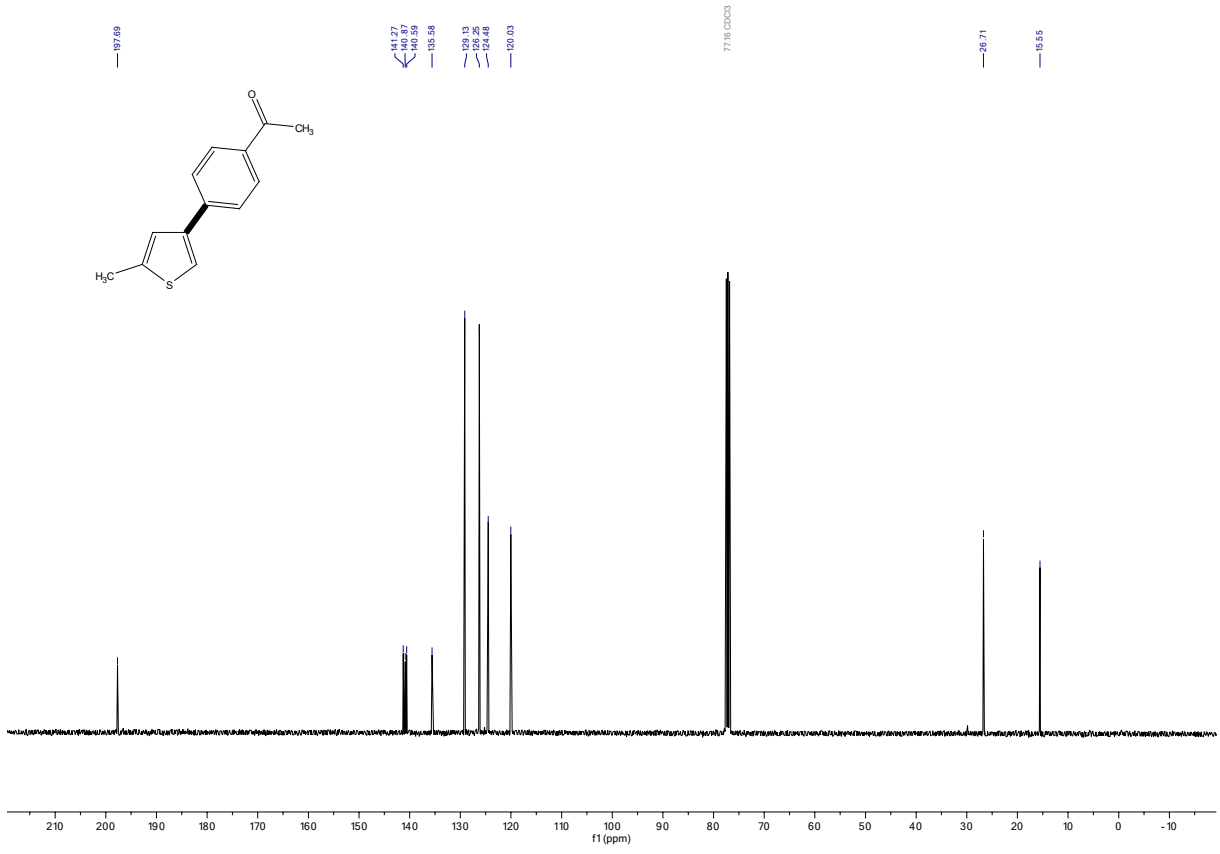
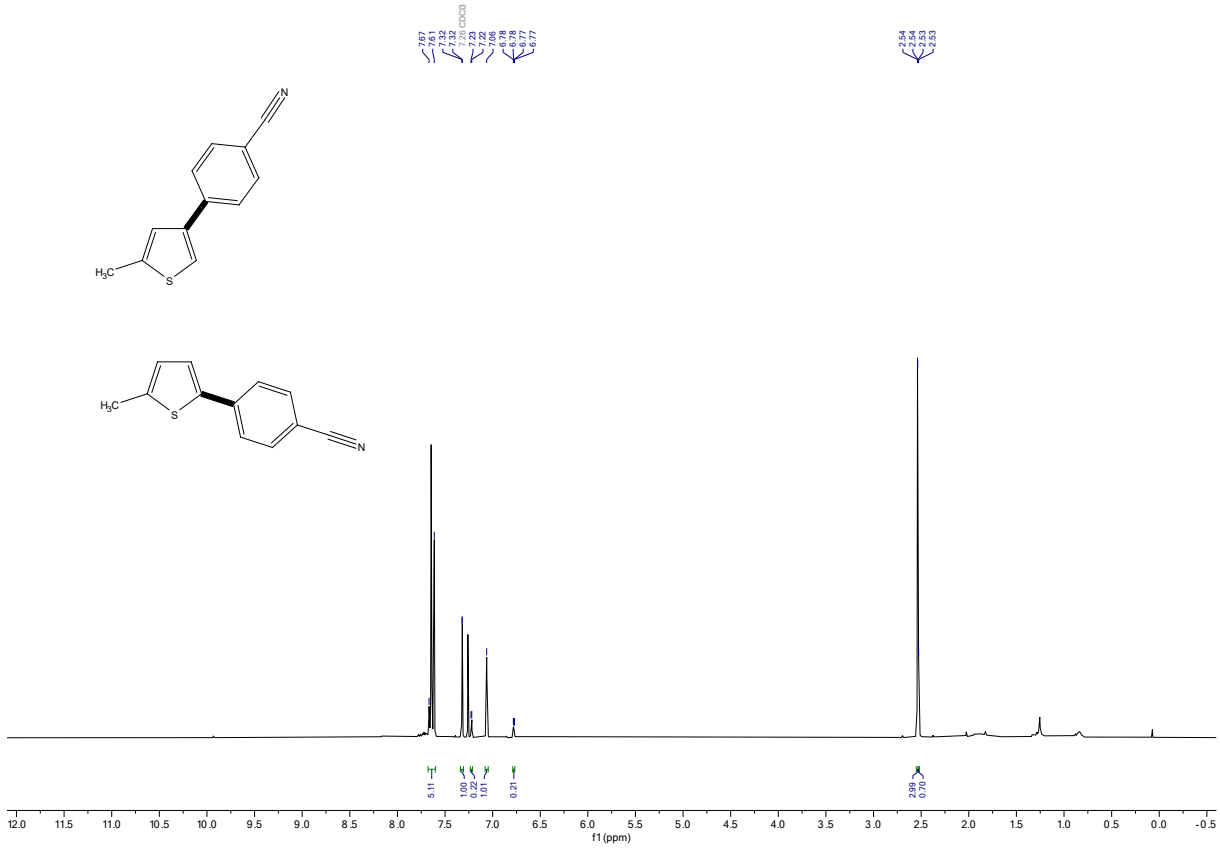
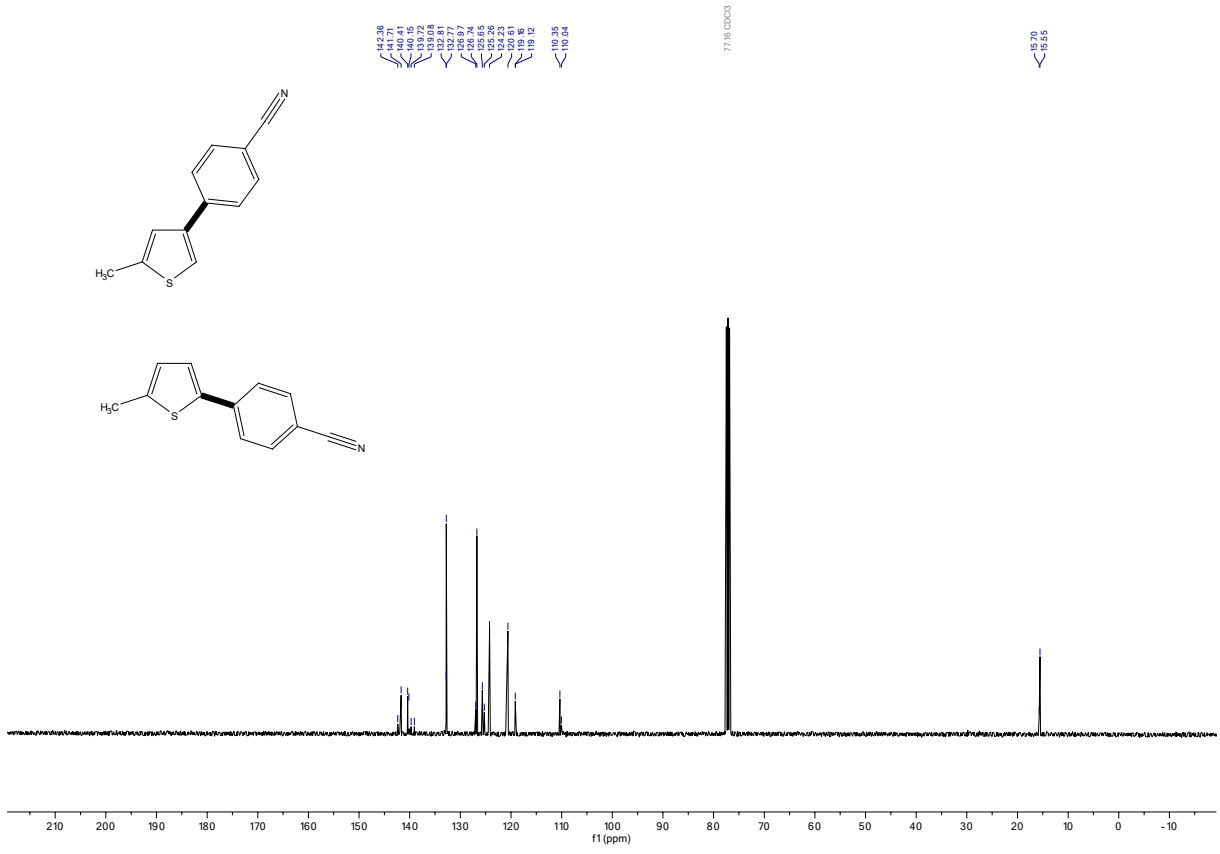
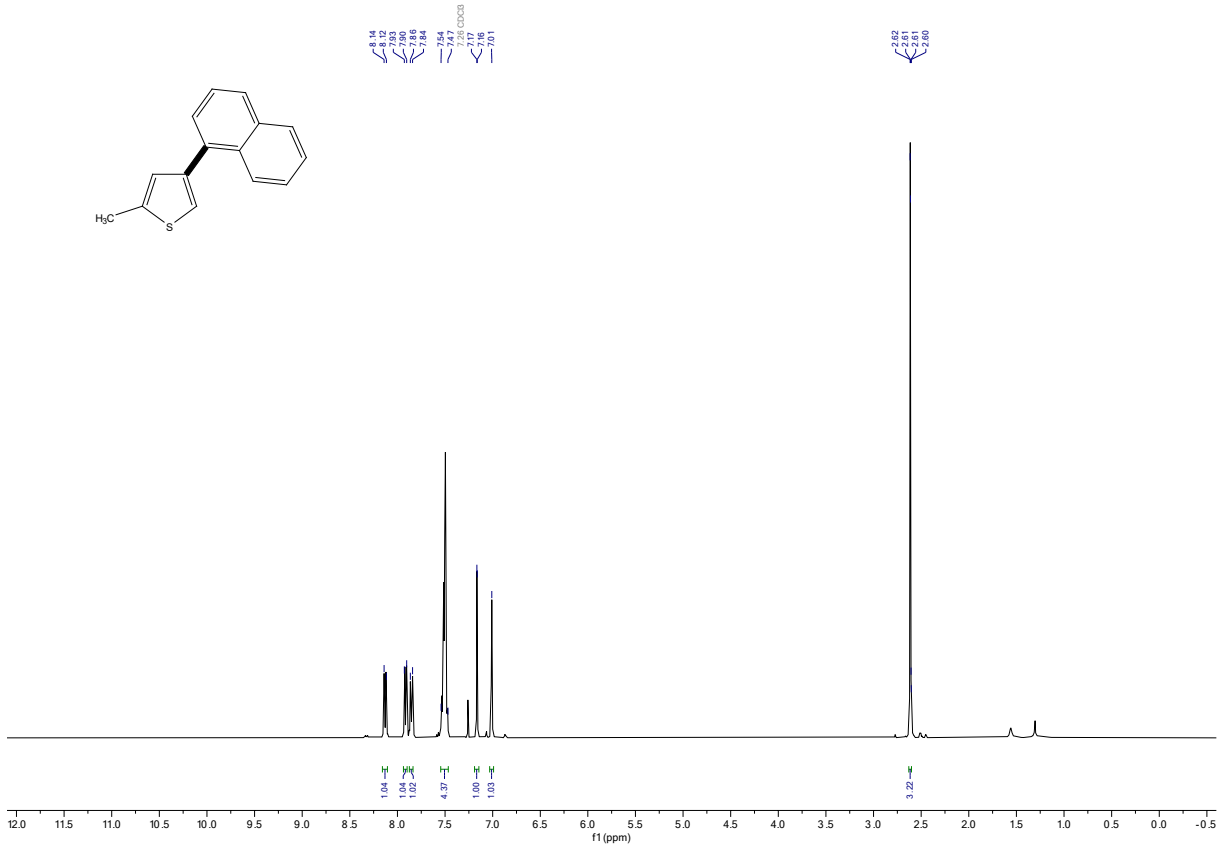
14.51
O
O
CH3
H3C
S
f1 (ppm)

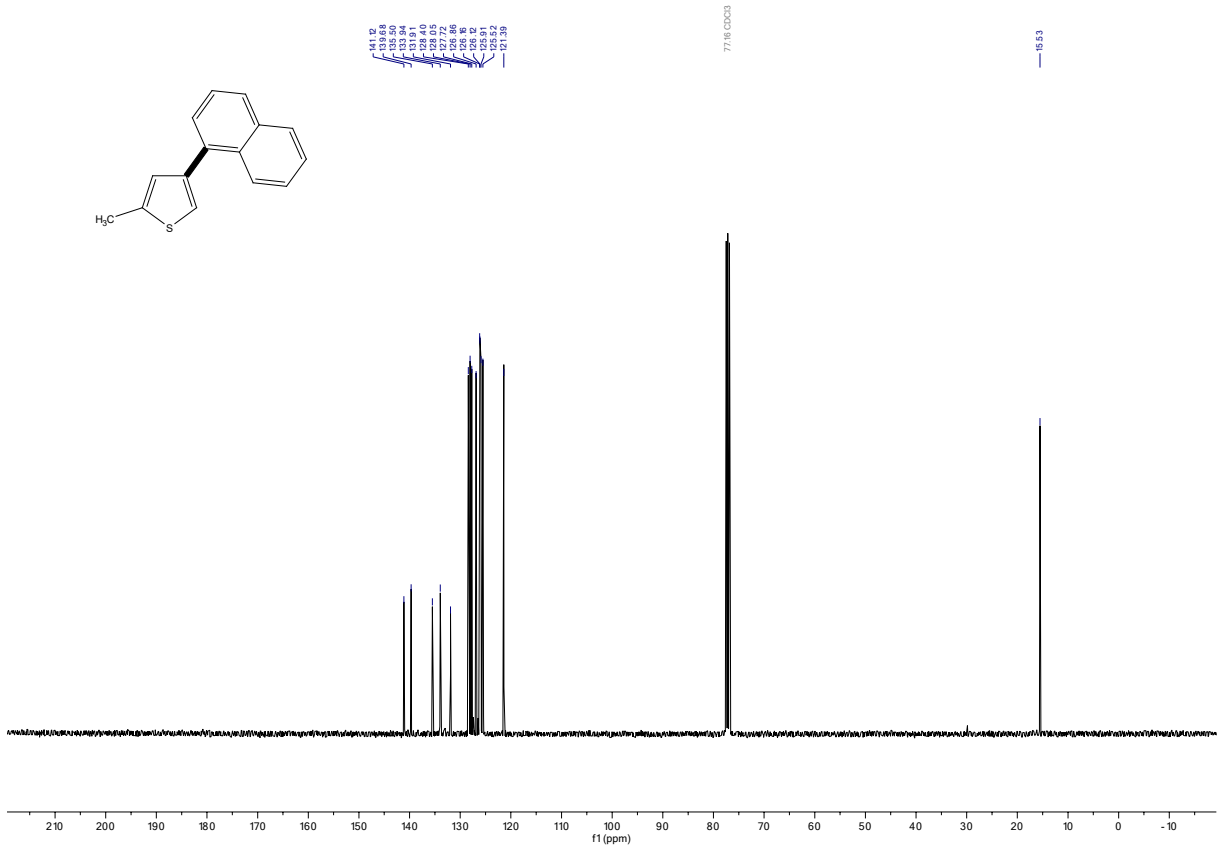

7.98
7.96
7.65
7.63
7.33
7.32
7.26 CDCl3
7.10
7.10
7.10
2.61
2.54
2.54
O
CH3
H3C
S
2.01
2.06
0.97
1.00
2.89
2.90
f1 (ppm)


197.69
141.27
140.87
140.39
135.58
129.13
126.25
124.48
120.03
77.16 CDCl3
26.71
15.55
O
CH3
H3C
S
f1 (ppm)


7.67
7.61
7.32
7.26 CDCl3
7.23
7.22
7.06
6.78
6.78
6.77
6.77
2.54
2.54
2.53
2.53
N
H3C
S
5.11
1.00
0.22
1.01
0.21
2.99
0.70
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 -0.5
f1 (ppm)


142.36
141.71
140.41
140.15
139.72
139.08
138.81
132.77
128.97
128.74
125.65
125.26
124.23
120.61
119.16
119.12
110.35
110.04
77.16 CDCl3
15.70
15.55
N
H3C
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.14
8.12
7.93
7.90
7.85
7.84
7.54
7.47
7.26 CDCl3
7.17
7.16
7.01
2.62
2.61
2.61
2.60
1.04
1.04
1.02
4.37
1.00
1.03
3.22
f1 (ppm)


141.12
139.68
135.50
133.94
133.41
128.40
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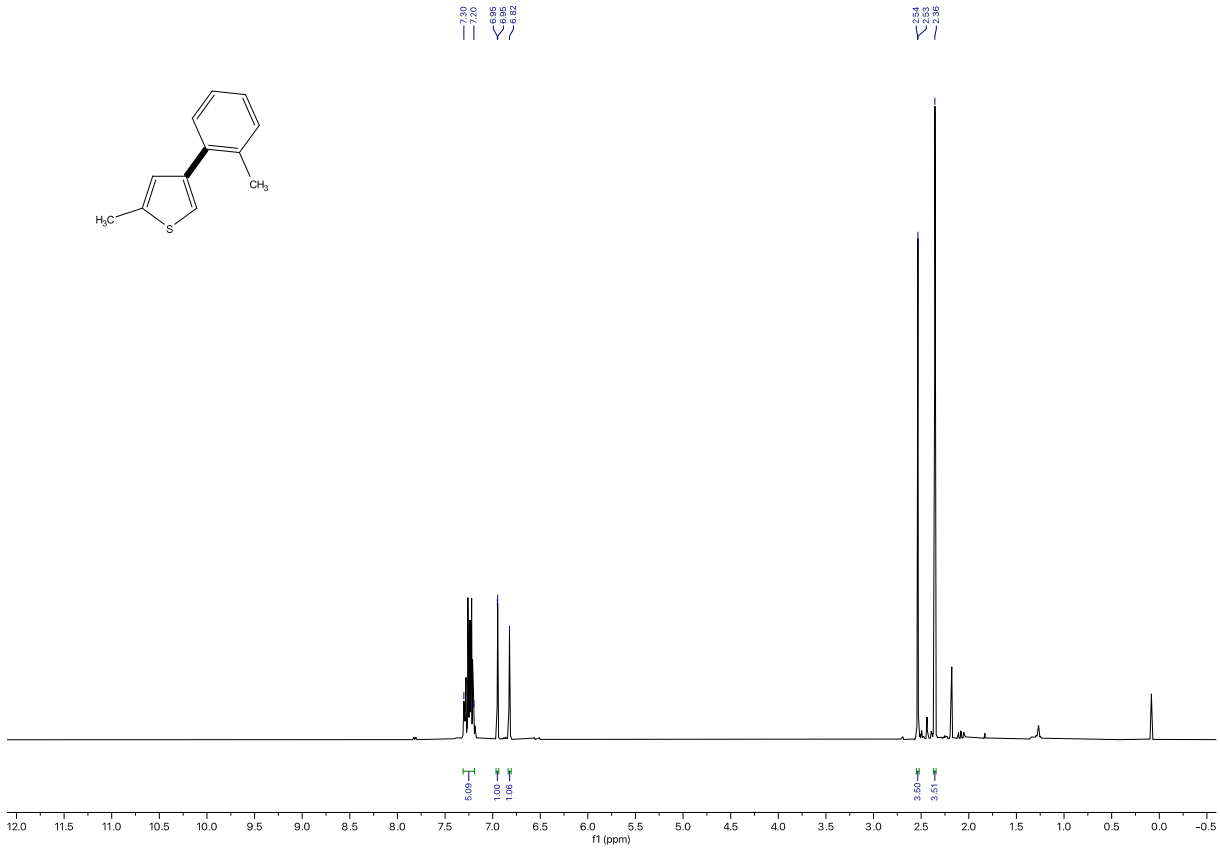
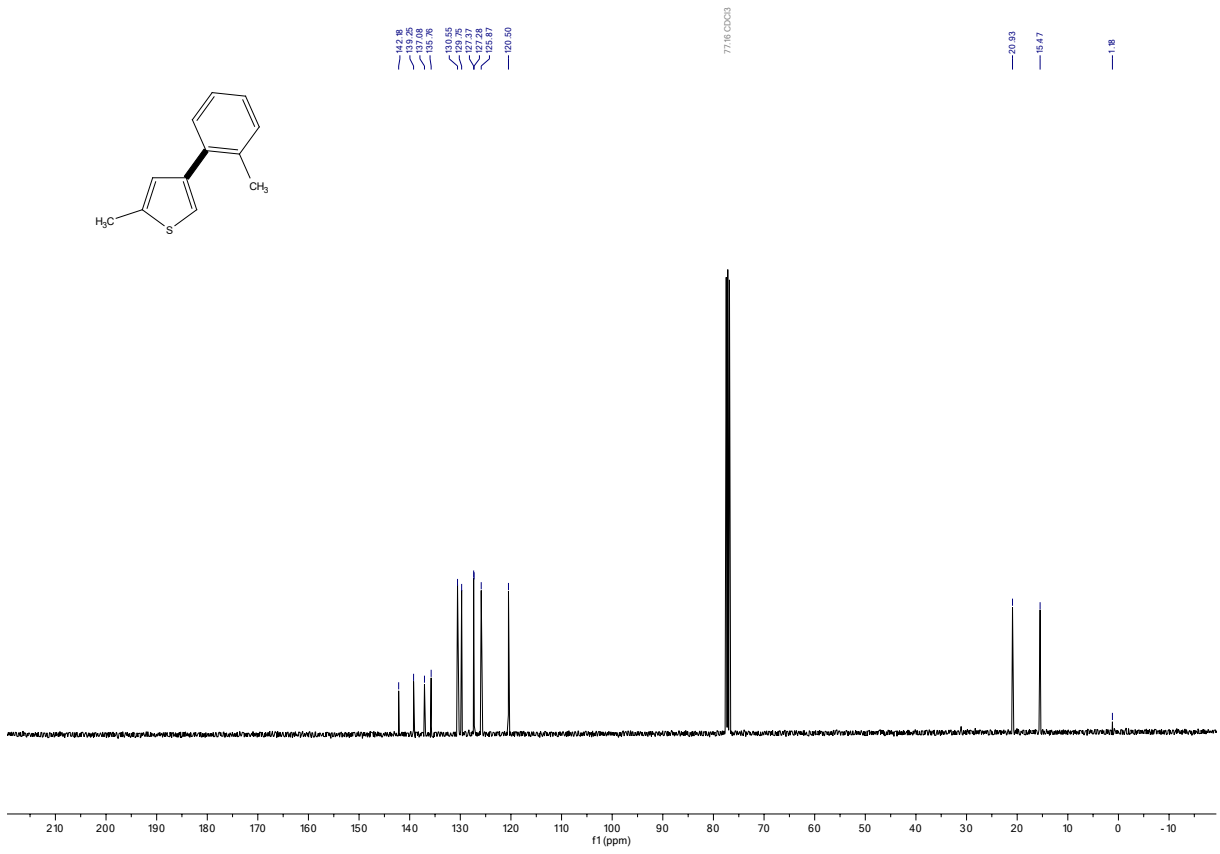
127.73
127.46
126.16
126.12
125.91
125.52
121.39
77.16 CDCl3
15.53
f1 (ppm)


7.30
7.20
6.95
6.95
6.82
2.54
2.53
2.36
CH3
H3C
S
5.09
1.00
1.06
3.50
3.51
f1 (ppm)


14.2.18
139.25
137.08
135.76
130.55
129.75
129.77
127.28
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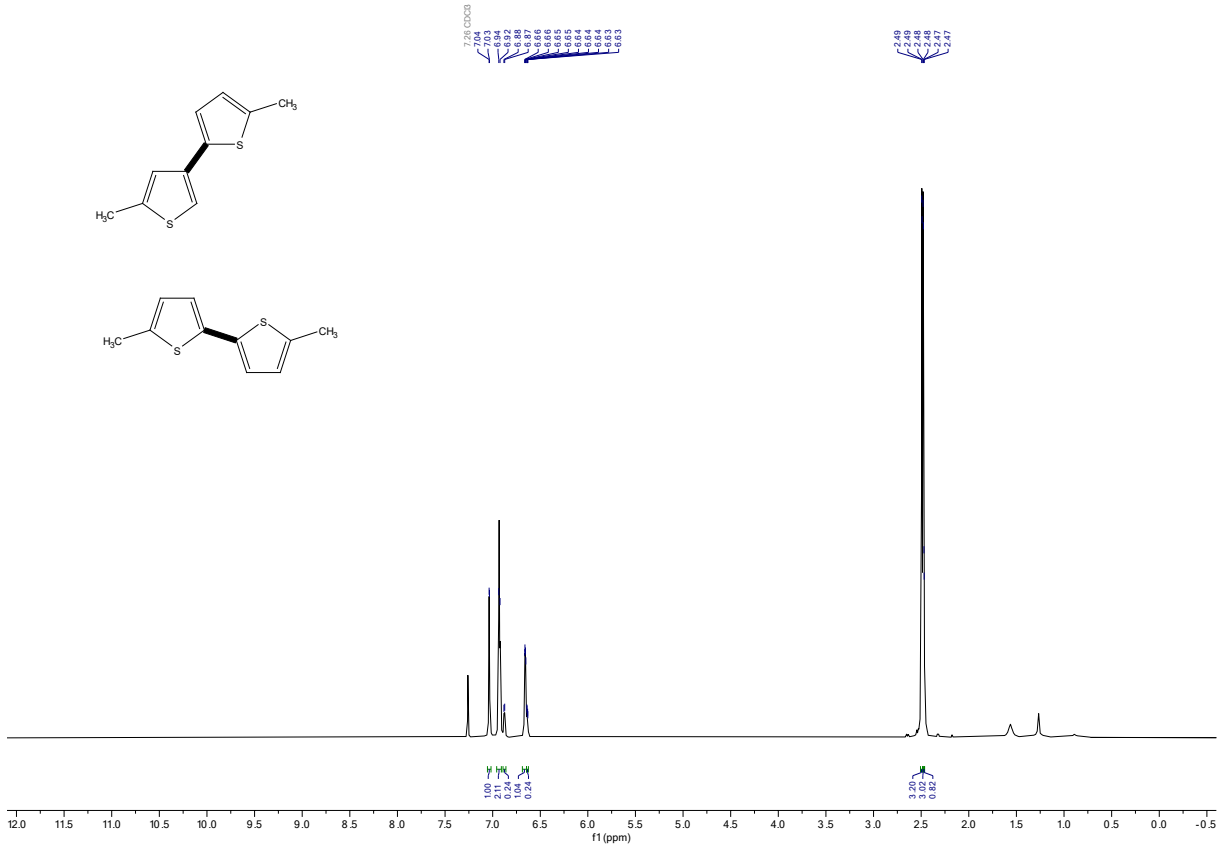
120.50
77.16 CDCl3
20.93
15.47
1.18
CH3
H3C
S
f1 (ppm)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7.03
6.94
6.92
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6.87
6.67
6.66
6.66
6.65
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6.64
6.64
6.64
6.63
6.63
2.49
2.49
2.48
2.48
2.48
2.47
2.47
CH3
S
H3C
S
H3C
S
S
CH3
1.00
2.11
0.24
1.04
0.24
3.20
3.02
0.82
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
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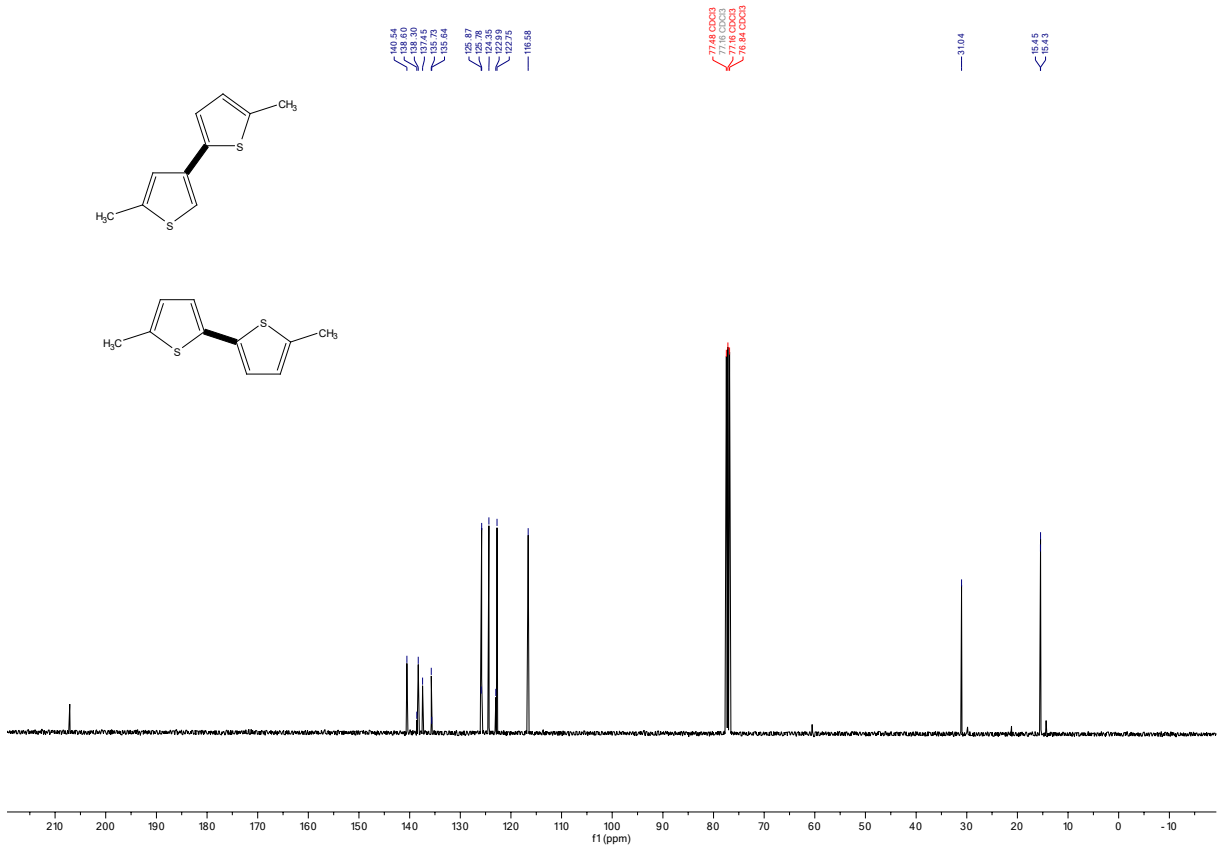
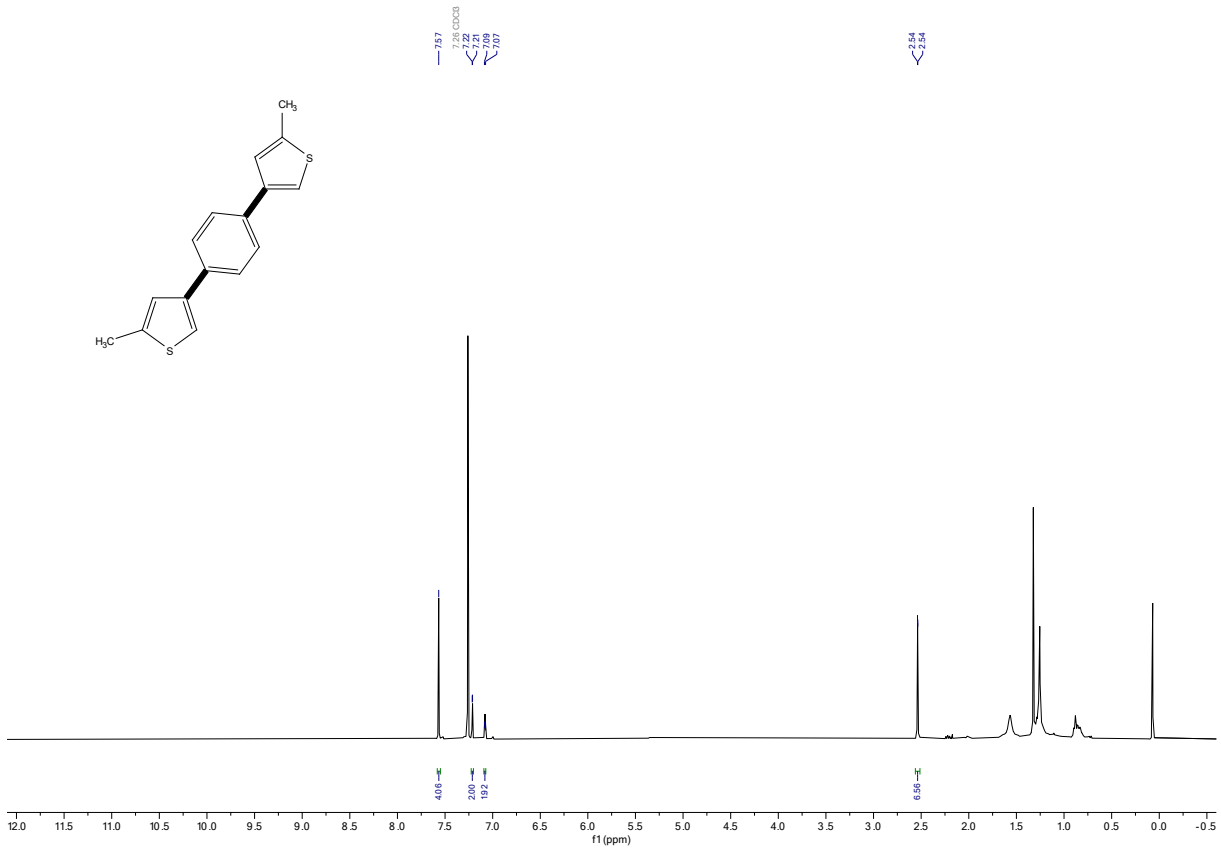
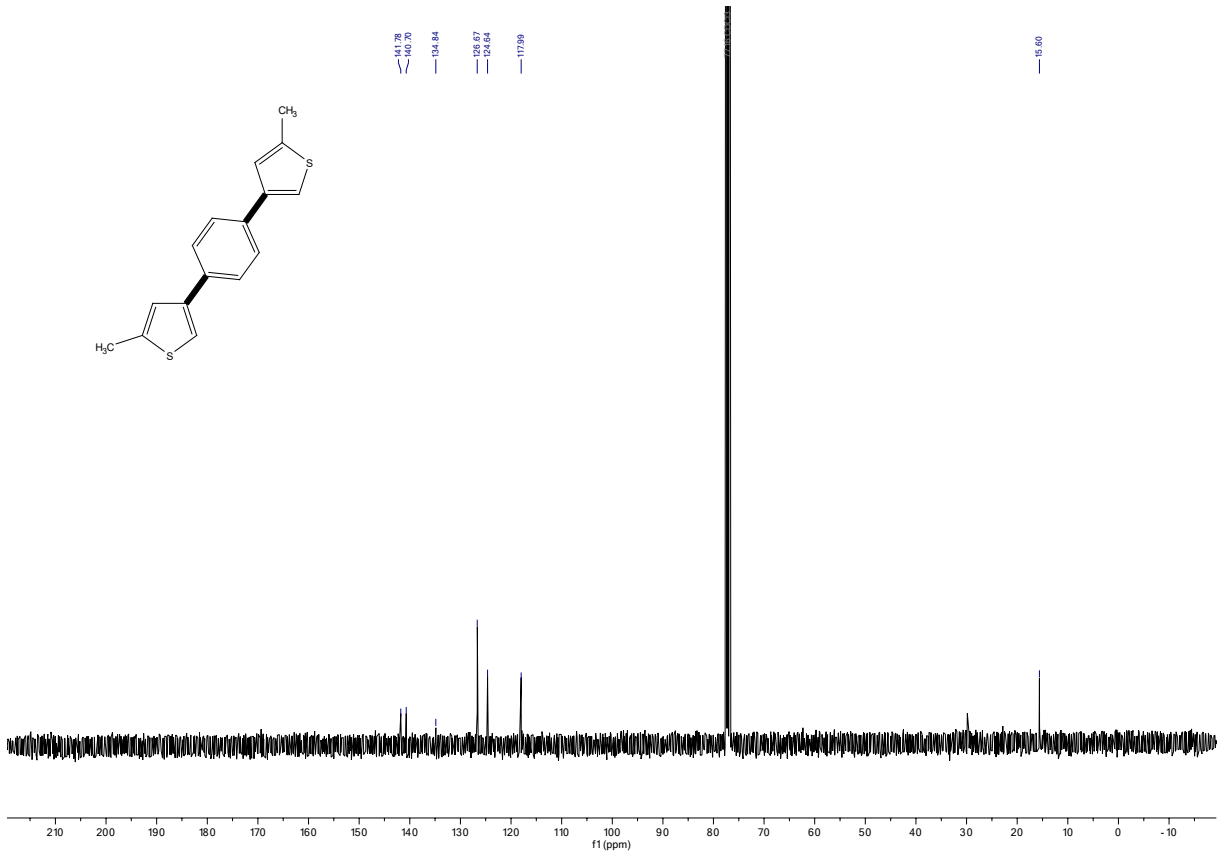
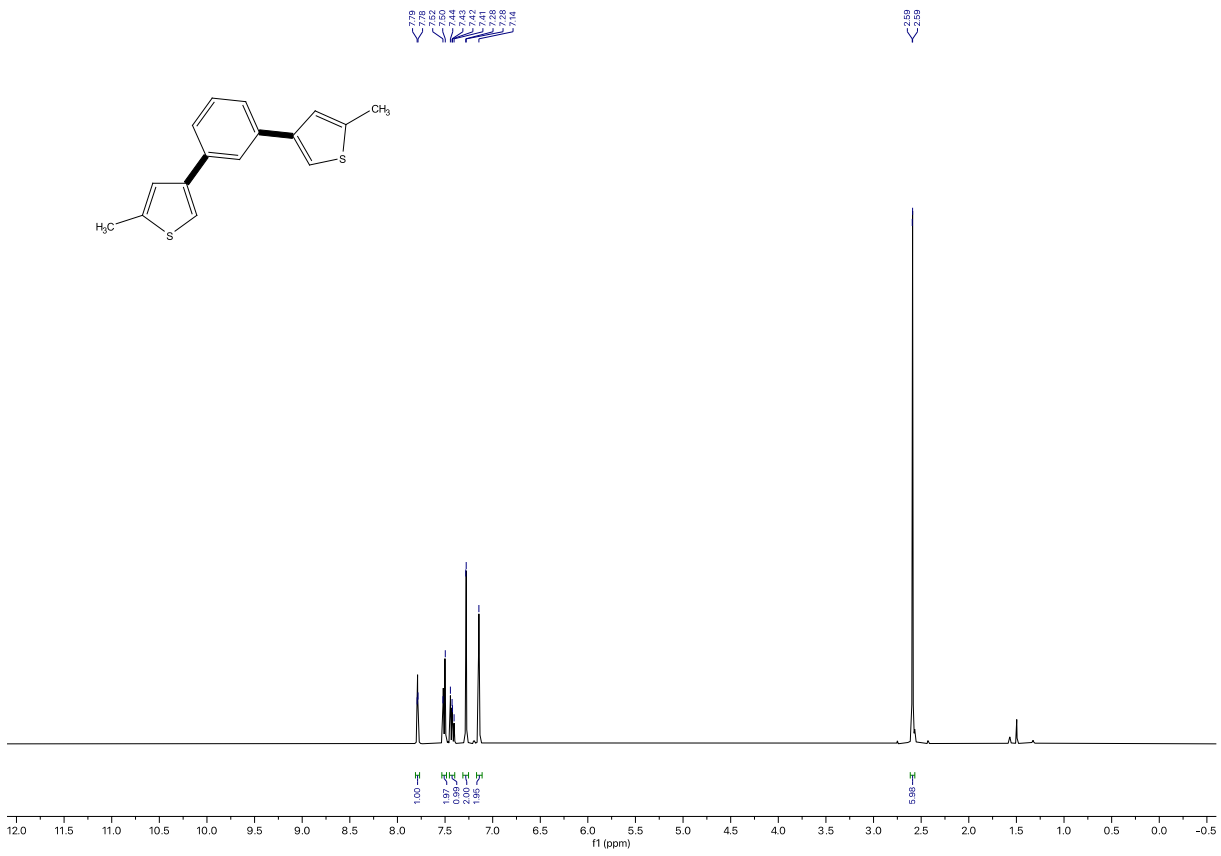
-0.5
f1 (ppm)


140.54
138.60
138.30
137.43
135.73
135.64
125.87
125.78
124.35
123.99
122.75
116.58
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
31.04
15.45
15.43
CH3
S
H3C
S
H3C
S
S
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.57
7.26 CDCl3
7.22
7.21
7.09
7.07
2.54
2.54
CH3
S
H3C
S
4.06
2.00
1.92
6.56
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 -0.5
f1 (ppm)


141.78
140.70
134.84
126.67
124.64
117.99
15.60
CH3
S
H3C
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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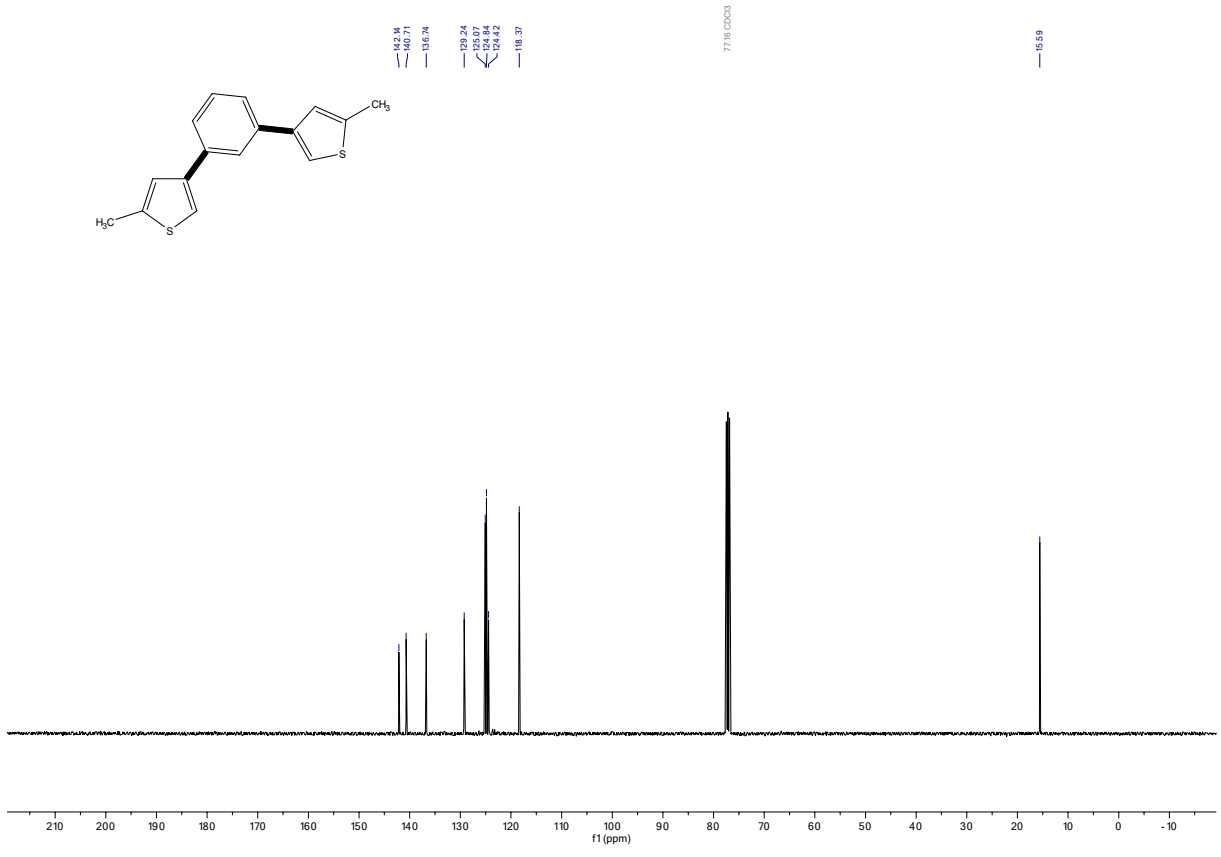
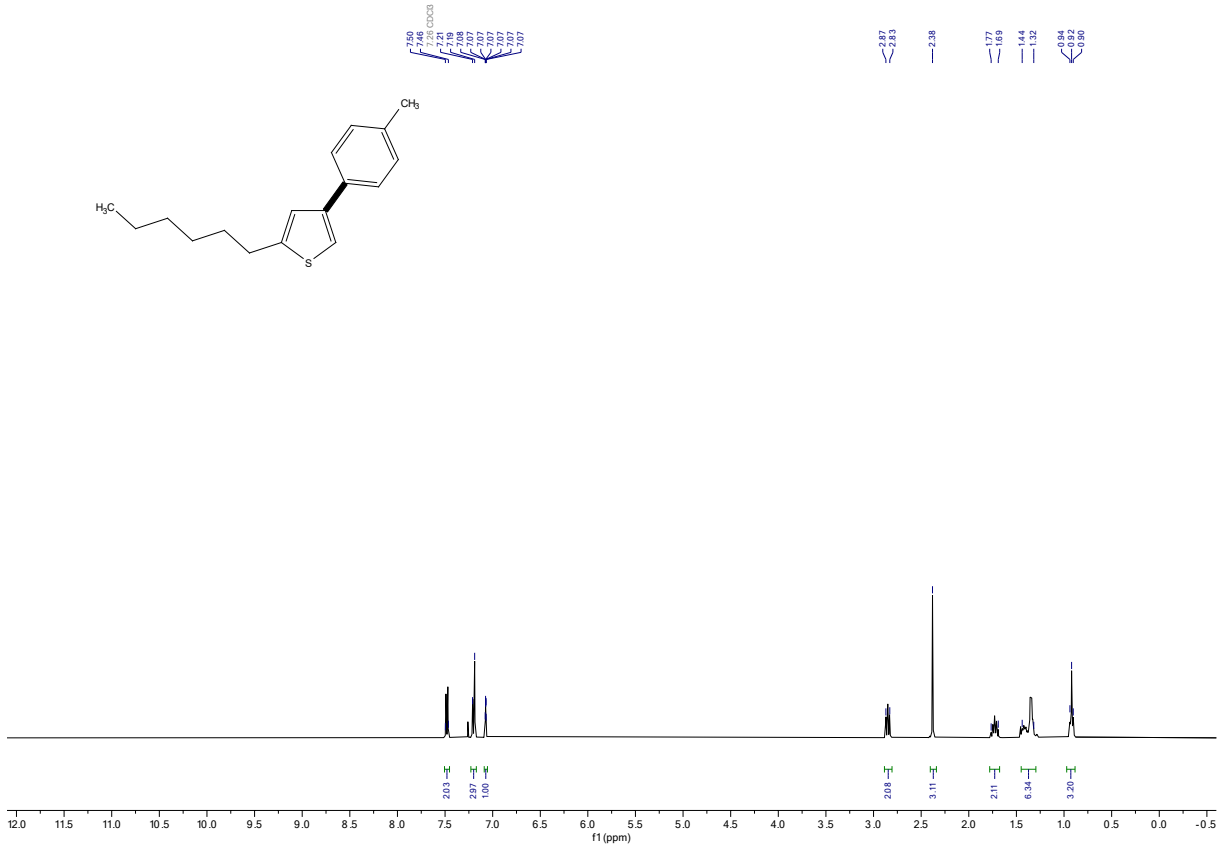
7.78
7.62
7.55
7.44
7.43
7.42
7.41
7.28
7.14
2.59
2.59
CH3
S
H3C
S
1.00
1.97
0.99
2.00
1.95
5.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


142.14
140.71
136.74
129.24
125.07
124.84
124.42
118.37
77.16 CDCl3
15.59
CH3
S
H3C
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.50
7.46
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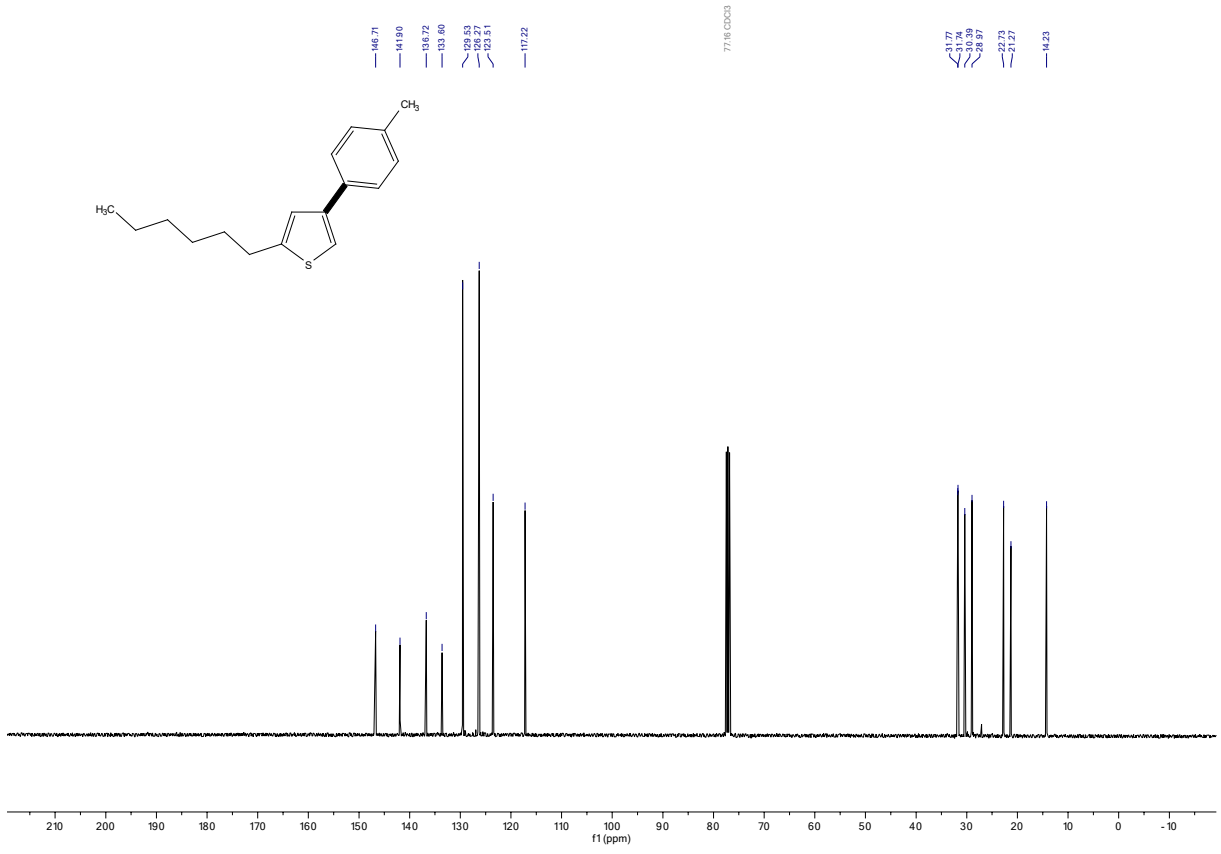
7.22
7.19
7.08
7.07
7.07
7.07
7.07
7.07
7.07
7.07
2.87
2.83
2.38
1.77
1.69
1.44
1.32
0.94
0.92
0.90
CH3
H3C
S
2.03
2.97
1.00
2.08
3.11
2.11
6.34
3.20
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


146.71
141.90
136.72
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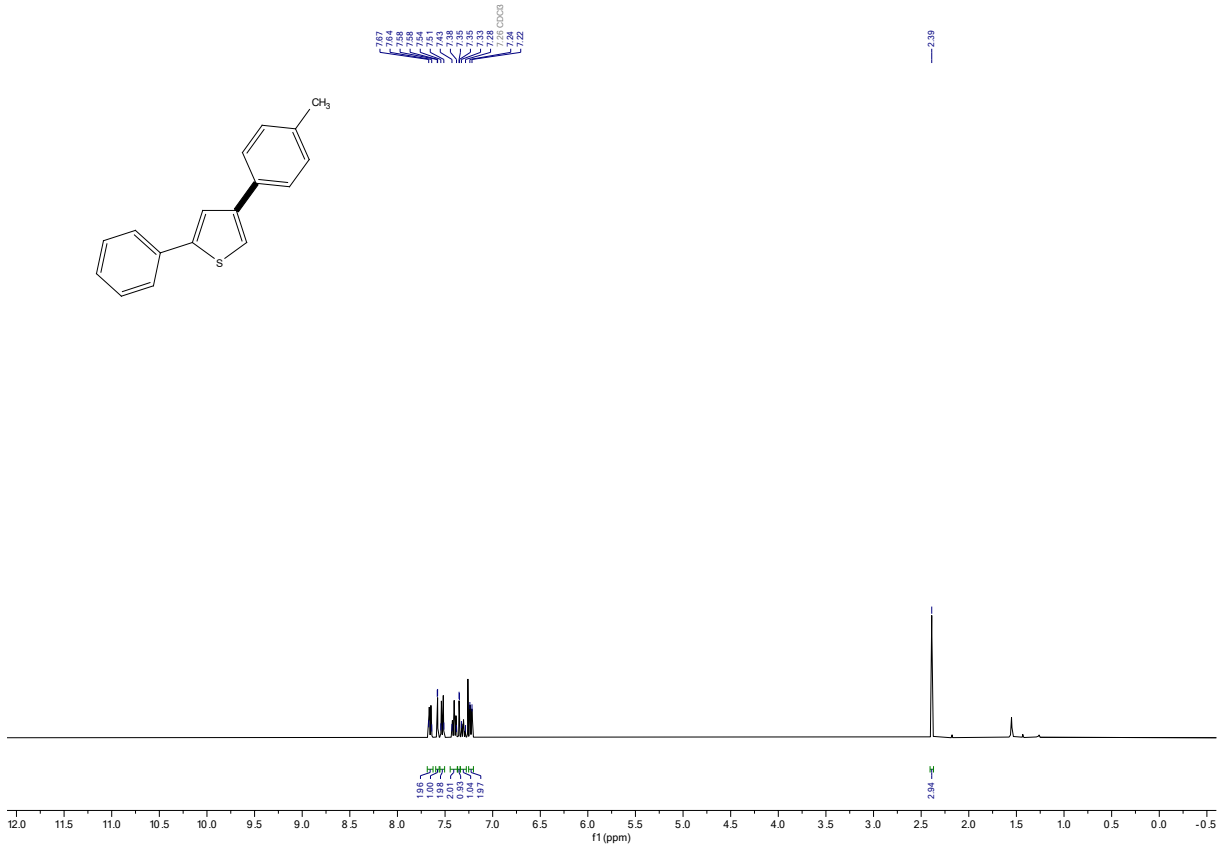
129.53
126.27
123.51
117.22
77.16 CDCl3
31.77
30.76
30.39
28.97
22.73
21.27
14.23
CH3
H3C
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.67
7.64
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7.58
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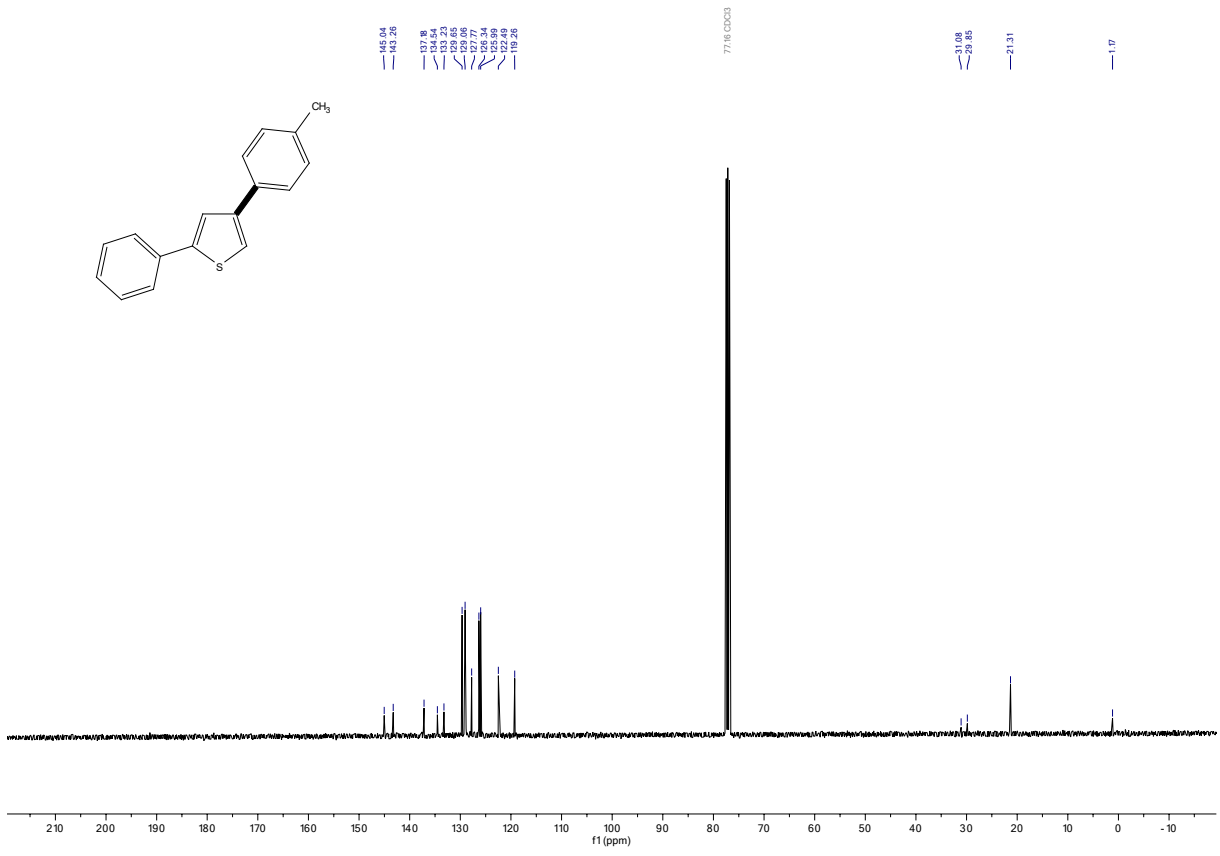
7.43
7.38
7.35
7.33
7.33
7.28
7.26 CDCl3
7.22
2.39
CH3
S
1.95
1.00
1.94
2.01
0.93
1.04
1.97
2.94
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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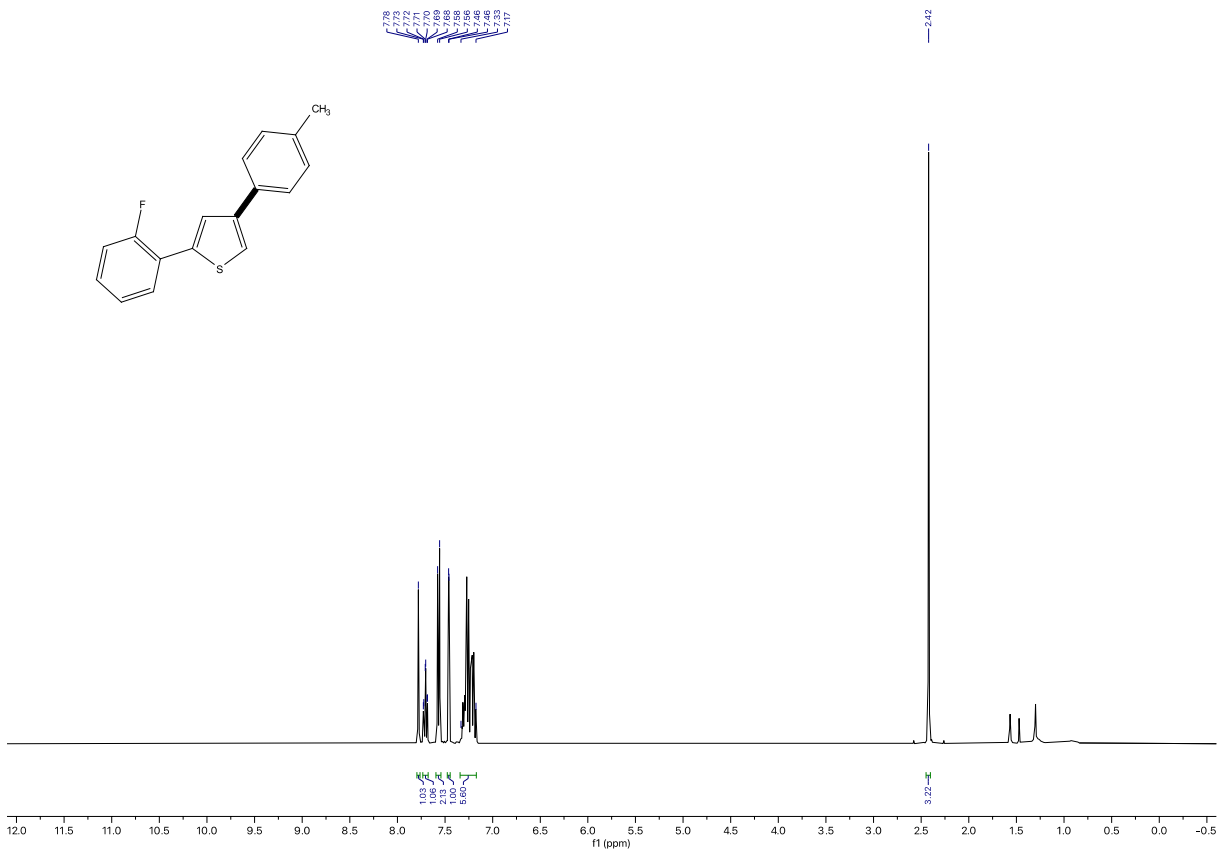
137.18
134.54
133.23
130.65
129.06
127.77
126.14
125.99
122.49
119.26
77.16 CDCl3
31.08
29.85
21.31
1.17
CH3
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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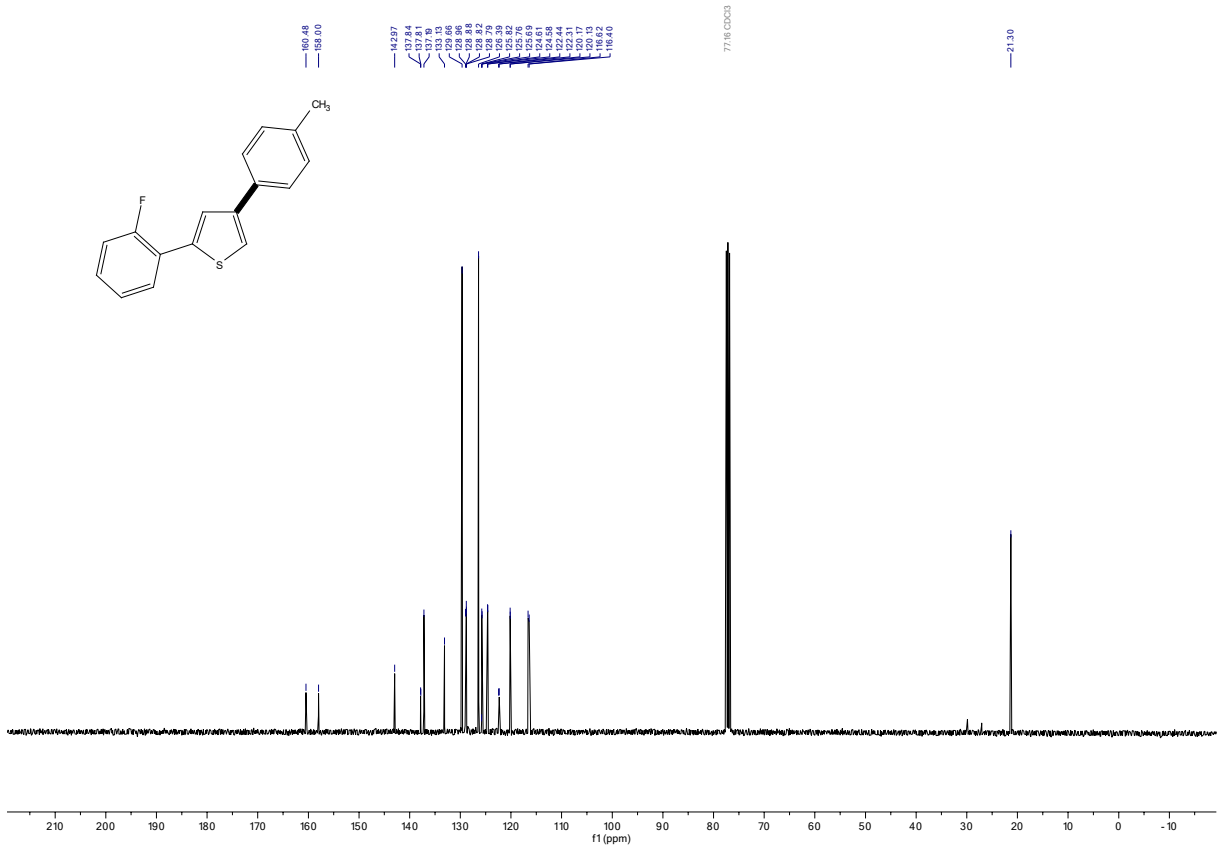
7.69
7.68
7.58
7.56
7.46
7.33
7.17
2.42
CH3
F
S
1.03
1.06
2.03
1.00
5.60
3.22
f1 (ppm)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158.00
142.97
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137.78
131.13
129.66
128.96
128.84
128.82
128.79
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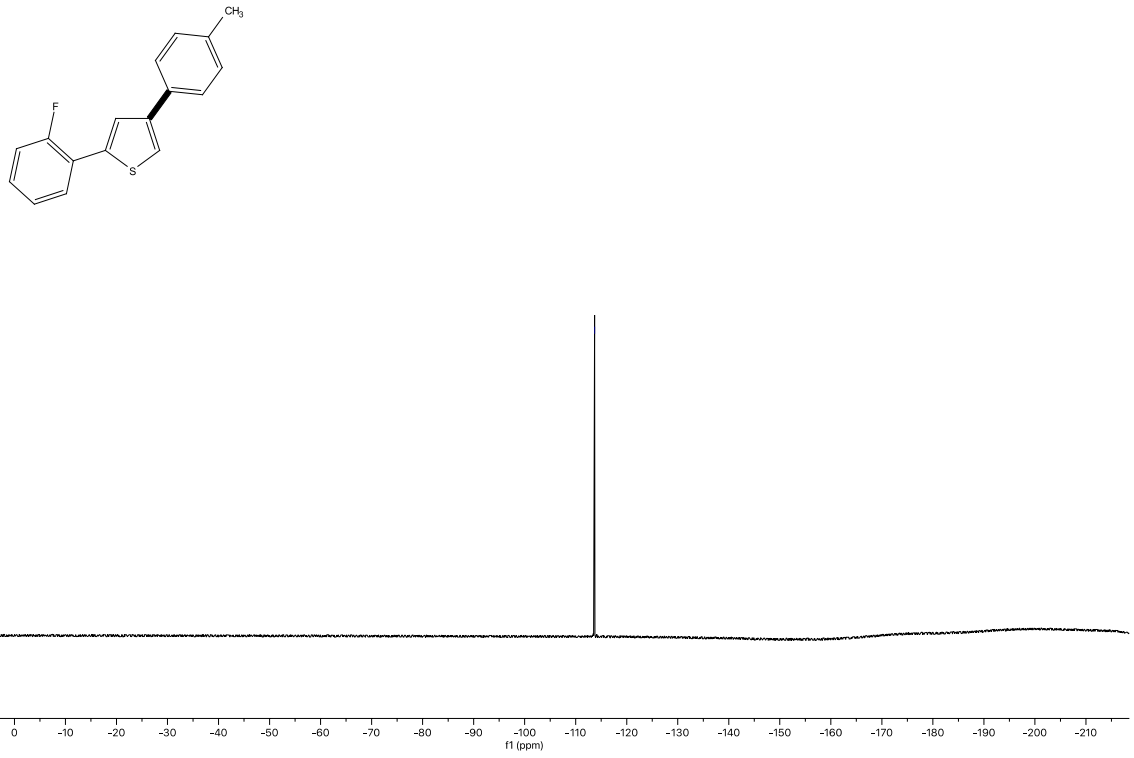
125.92
125.76
125.69
124.61
124.58
122.44
122.11
120.17
120.13
116.62
116.40
77.16 CDCl3
21.30
CH3
F
S
f1 (ppm)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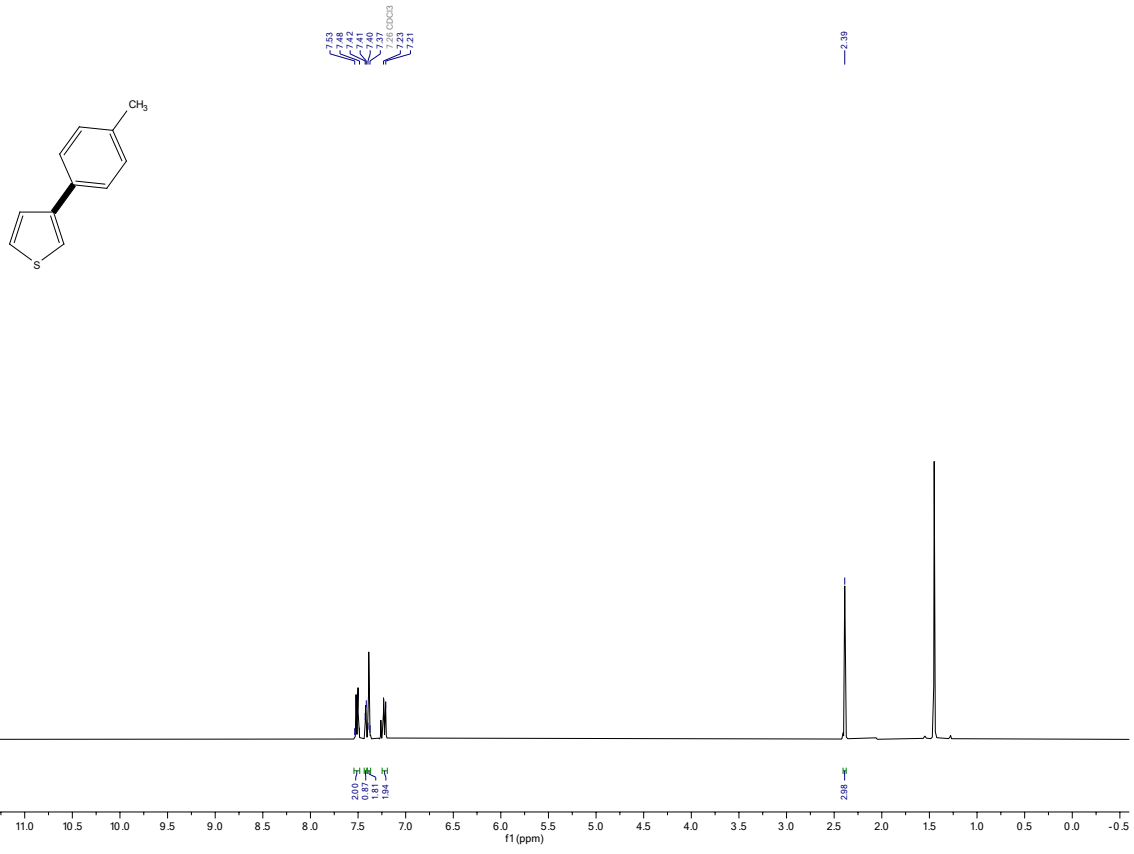
CH3
F
S
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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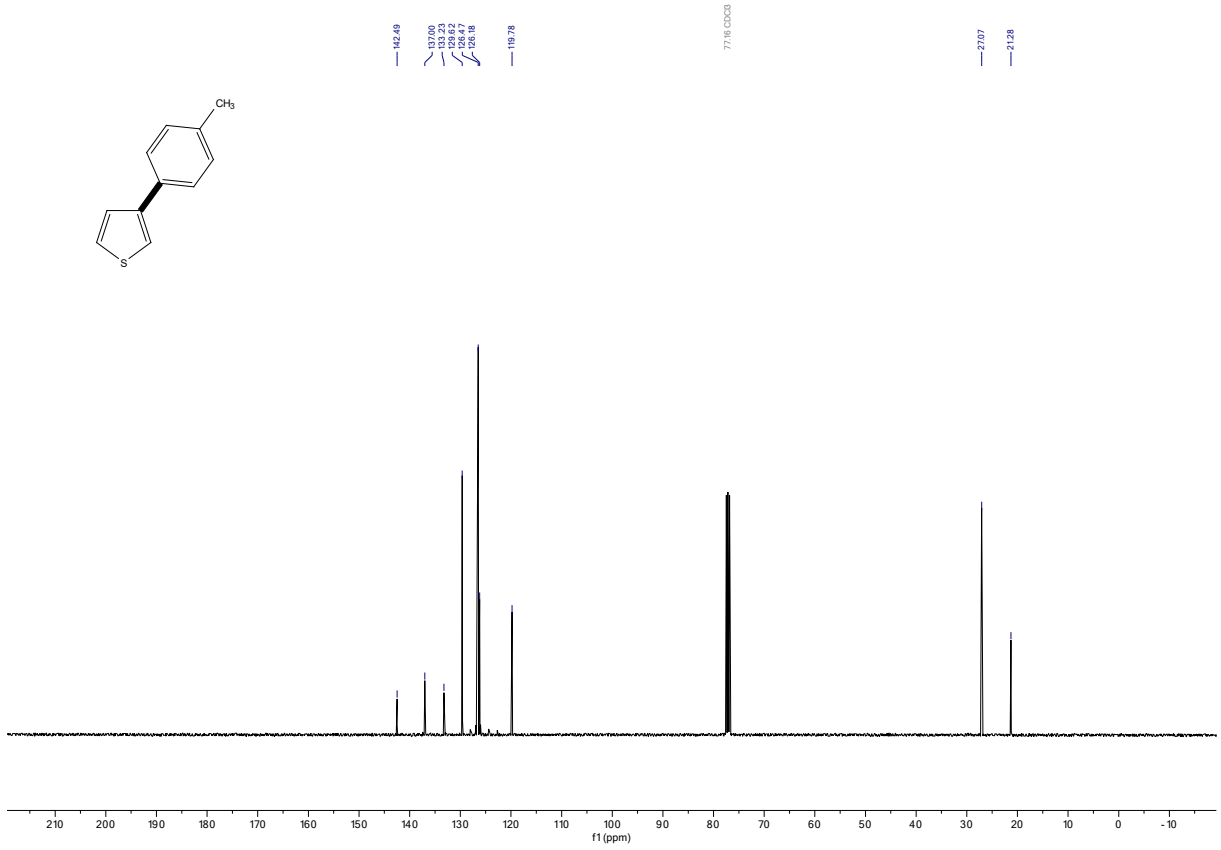
7.48
7.42
7.41
7.40
7.37
7.26 CDCl3
7.23
7.21
2.39
CH3
S
2.00
0.87
1.81
1.94
2.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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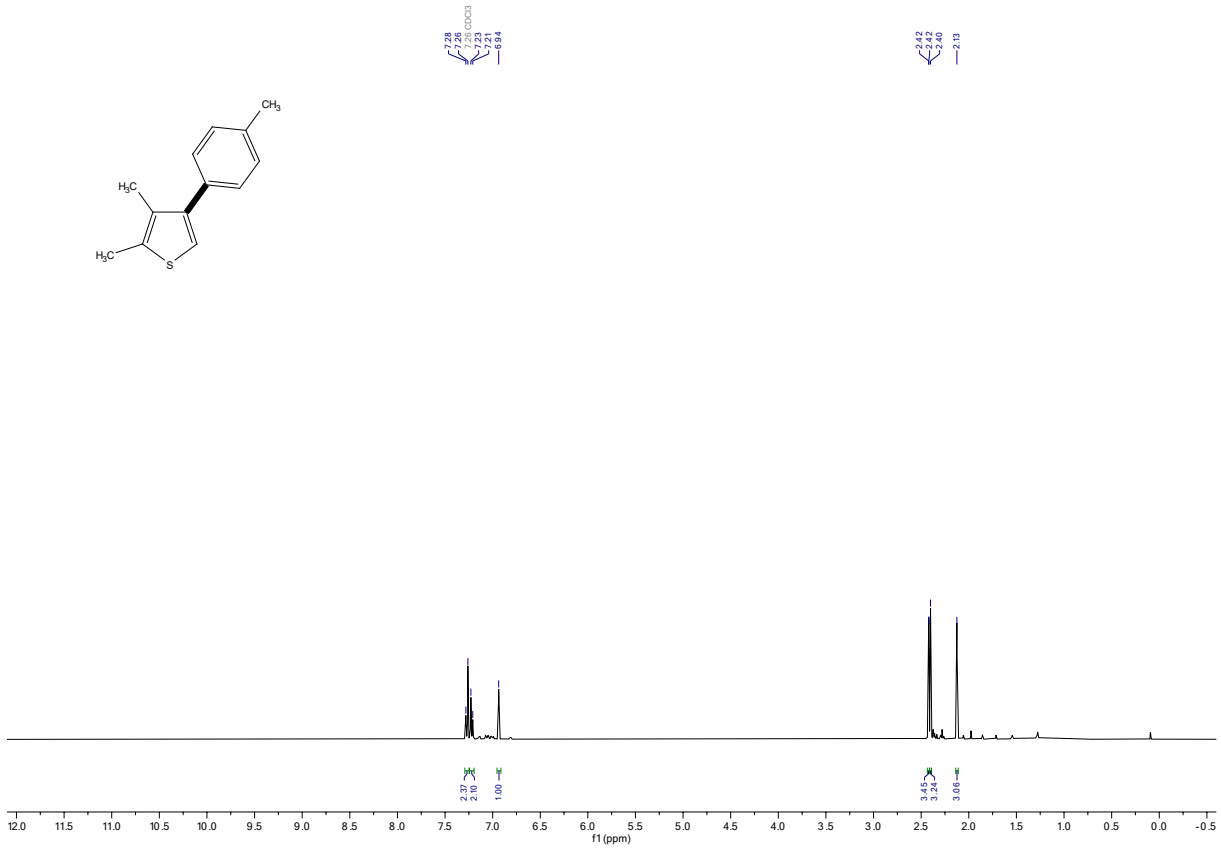
126.18
119.78
77.16 CDCl3
27.07
21.28
CH3
S
f1 (ppm)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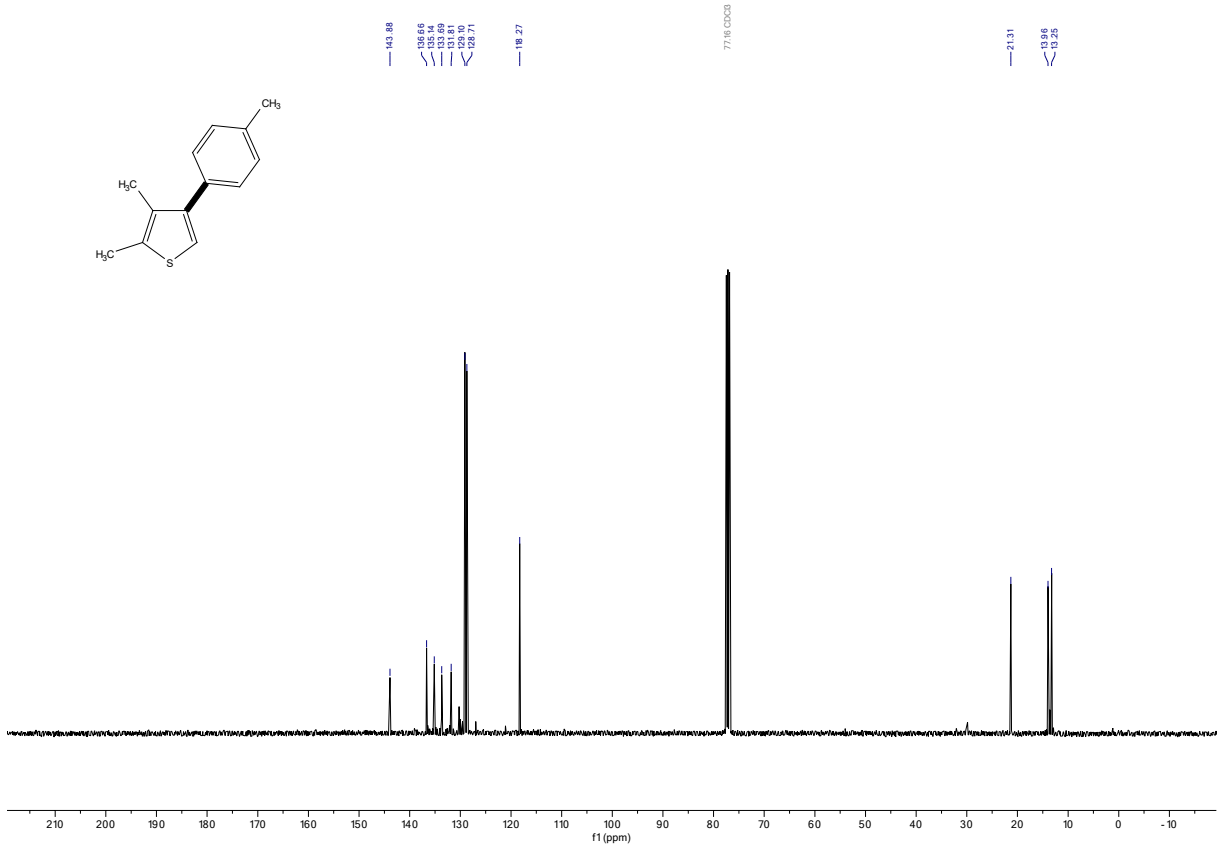
7.23
7.21
6.94
2.42
2.42
2.40
2.13
CH3
H3C
H3C
S
2.37
2.10
1.00
3.45
3.24
3.06
f1 (ppm)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131.81
129.10
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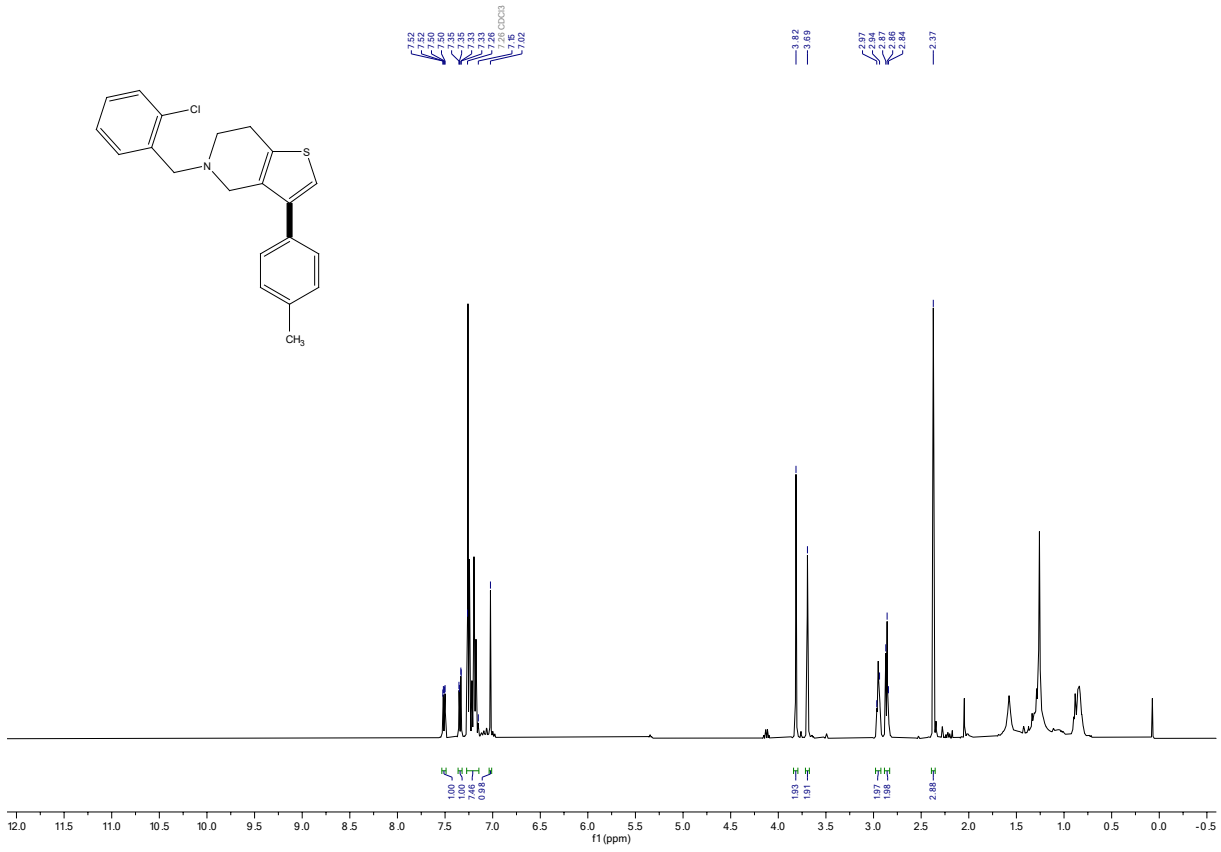
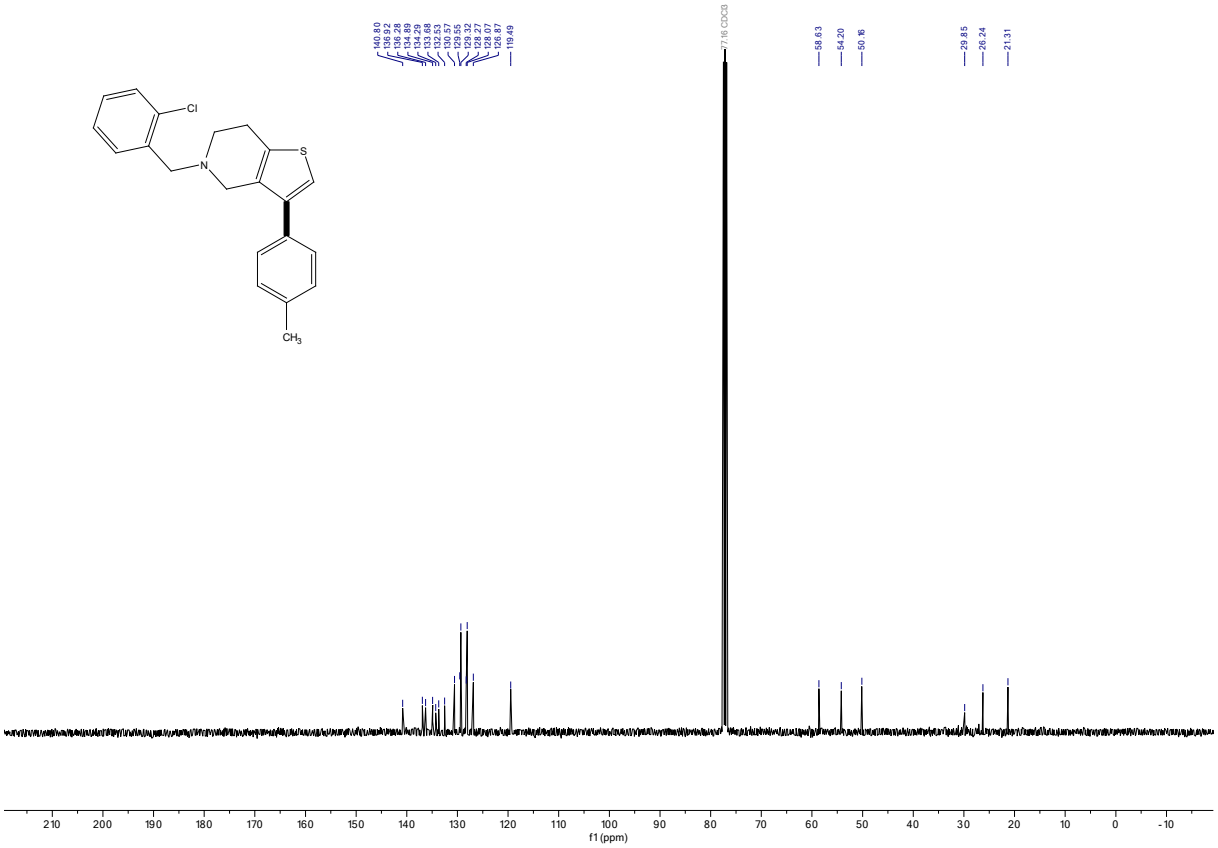
118.27
77.16 CDCl3
21.31
13.96
13.25
CH3
H3C
H3C
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.52
7.52
7.50
7.50
7.35
7.33
7.33
7.26
7.26 CDCl3
7.5
7.02
3.82
3.69
2.97
2.94
2.87
2.86
2.84
2.37
Cl
N
S
CH3
1.00
1.00
1.48
0.88
1.93
1.91
1.97
1.96
2.88
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 -0.5
f1 (ppm)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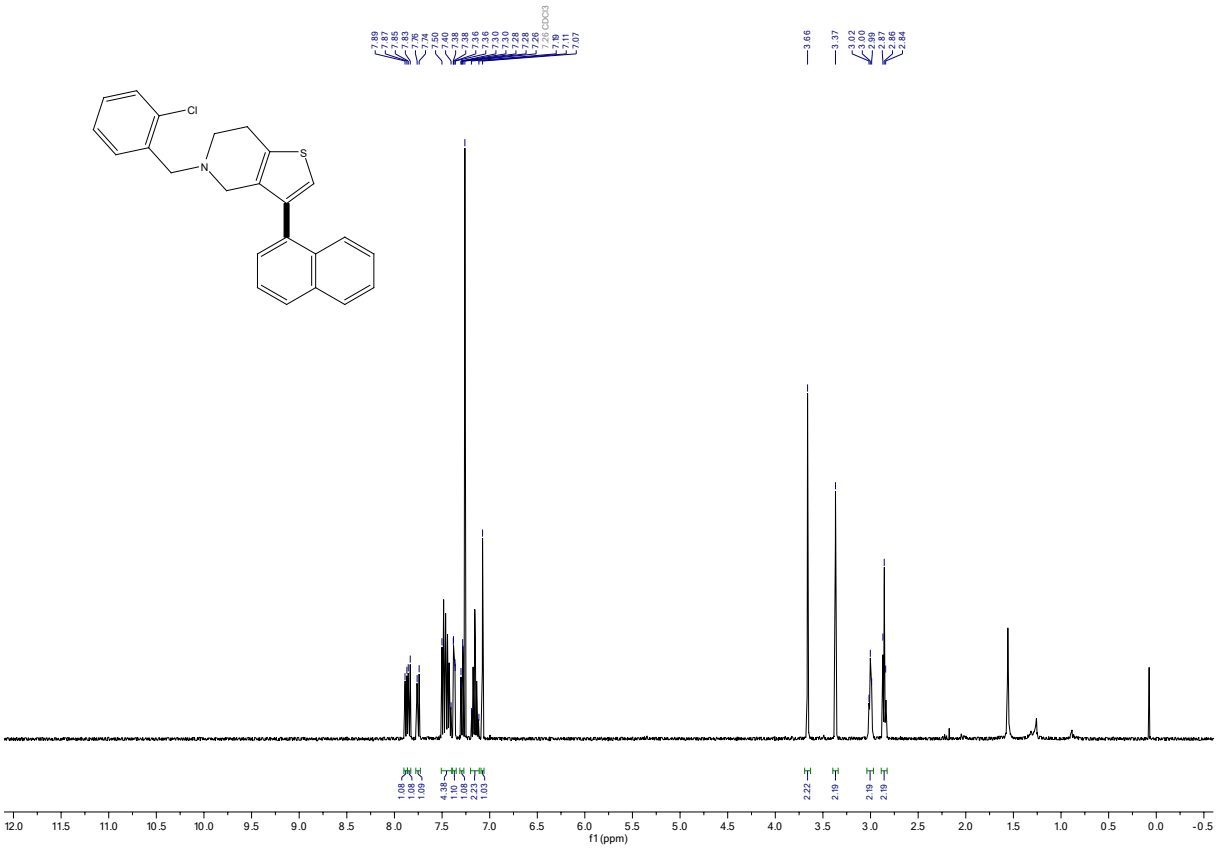
134.29
133.68
132.53
130.57
129.55
129.32
128.27
128.07
126.87
119.49
77.16 CDCl3
58.63
54.20
50.16
29.85
26.24
21.31
Cl
N
S
CH3
f1 (ppm)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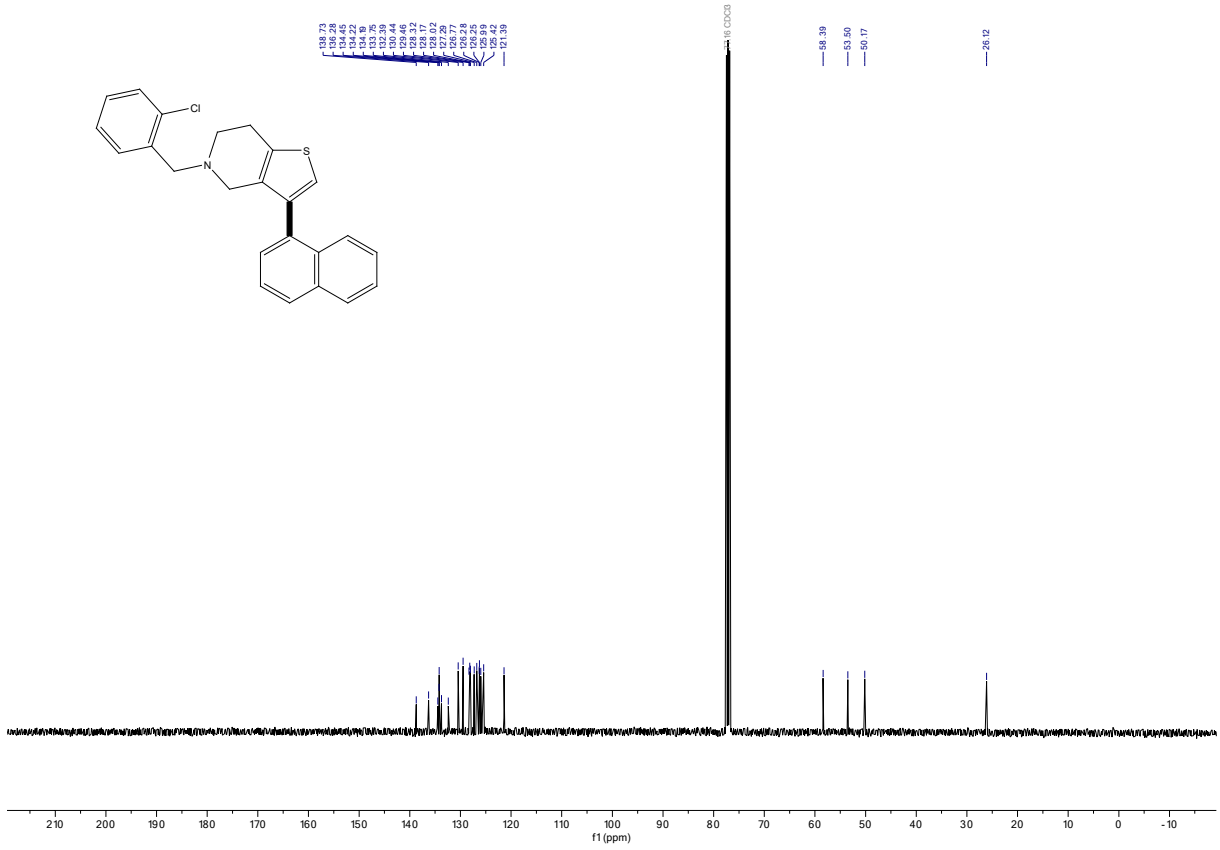
7.38
7.36
7.36
7.30
7.30
7.28
7.28
7.26
7.26 CDCl3
7.19
7.11
7.07
3.66
3.37
3.02
3.00
2.89
2.87
2.86
2.84
1.08
1.08
1.04
1.09
4.38
1.00
1.00
2.23
1.03
2.22
2.19
2.19
2.19
Cl
N
S
f1 (ppm)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134.22
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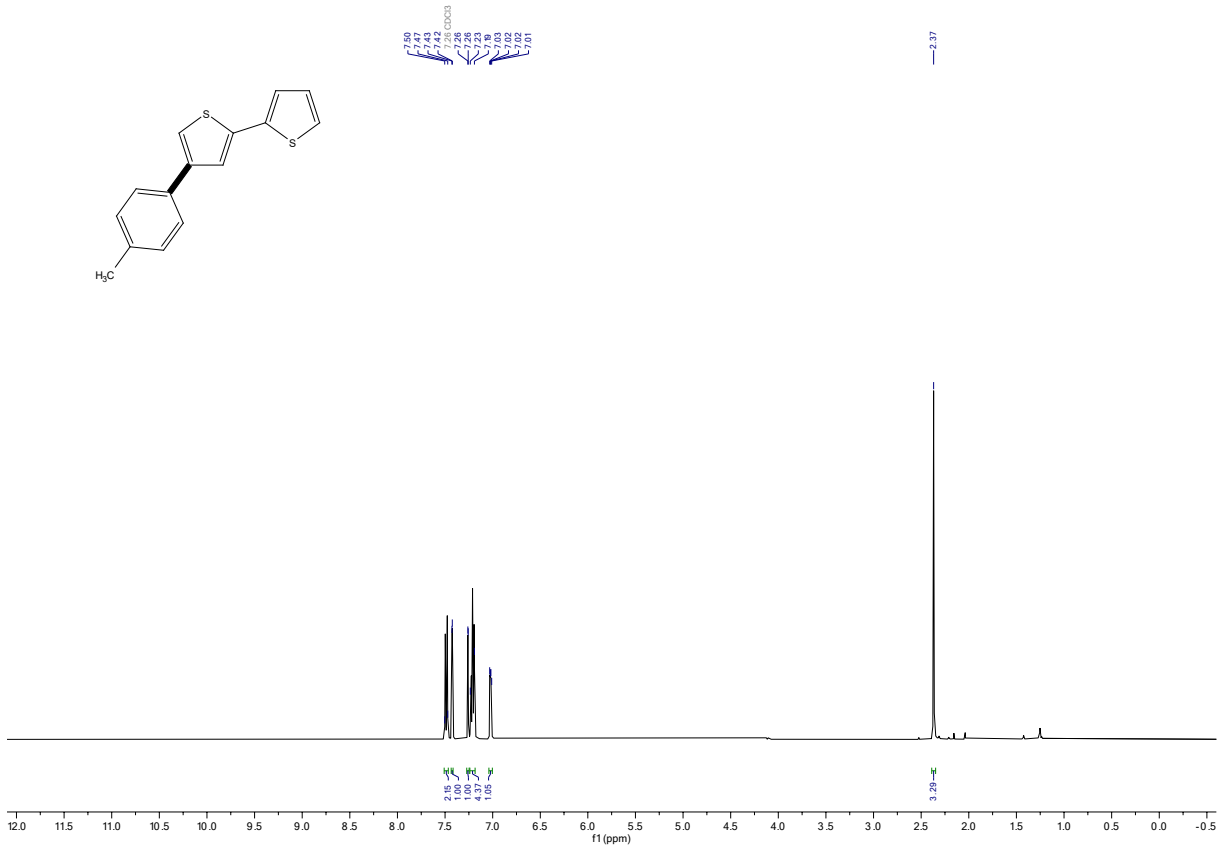
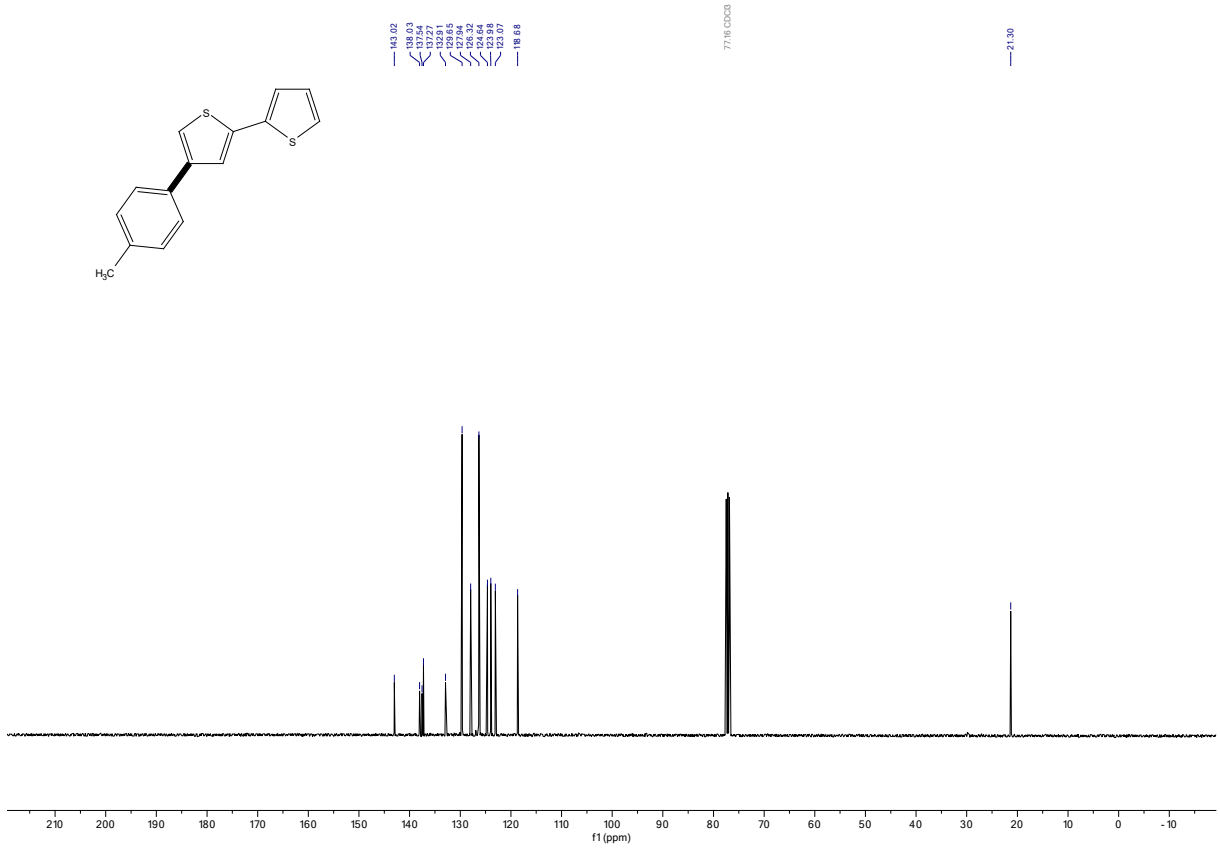
132.35
132.39
130.44
129.46
128.32
128.17
128.02
127.79
126.77
126.28
126.25
125.89
125.42
121.39
77.16 CDCl3
58.39
53.50
50.17
26.12
Cl
N
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.50
7.47
7.43
7.42
7.26 CDCl3
7.26
7.25
7.23
7.19
7.03
7.02
7.01
2.37
S
S
H3C
2.15
1.00
1.00
4.37
1.05
3.29
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 -0.5
f1 (ppm)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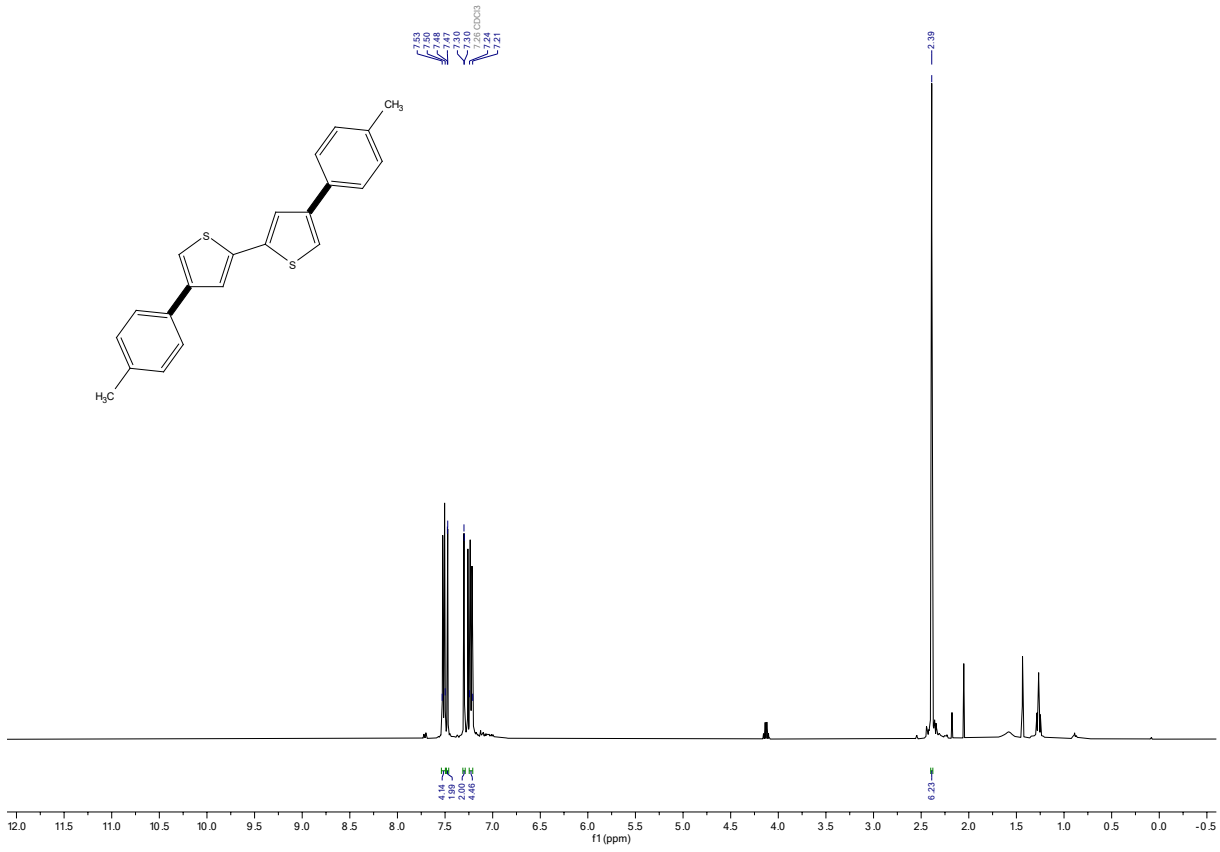
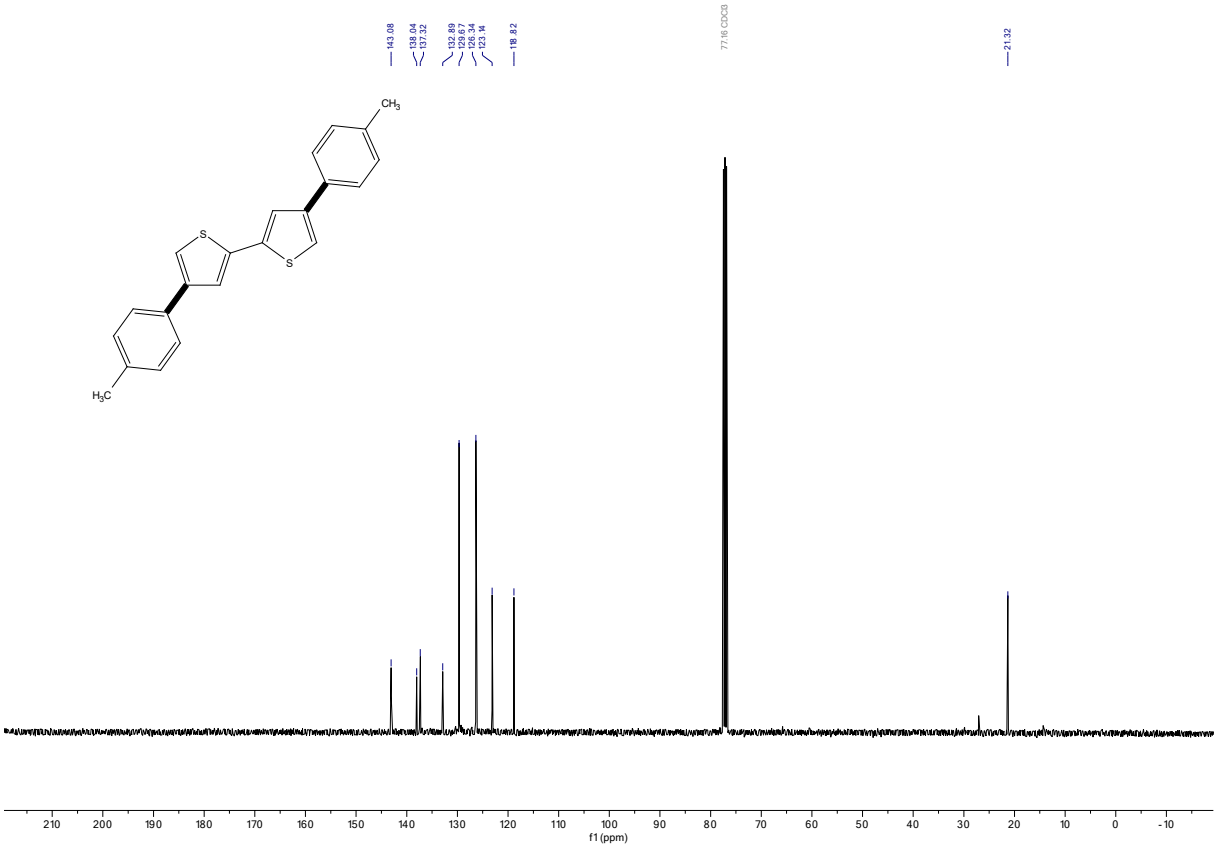
138.03
137.54
137.27
132.51
129.65
127.94
126.72
124.64
123.98
123.07
118.68
77.16 CDCl3
21.30
S
S
H3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.53
7.50
7.48
7.47
7.30
7.26 CDCl3
7.24
7.21
2.39
CH3
S
S
H3C
4.14
1.99
2.00
4.46
6.23
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 -0.5
f1 (ppm)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137.32
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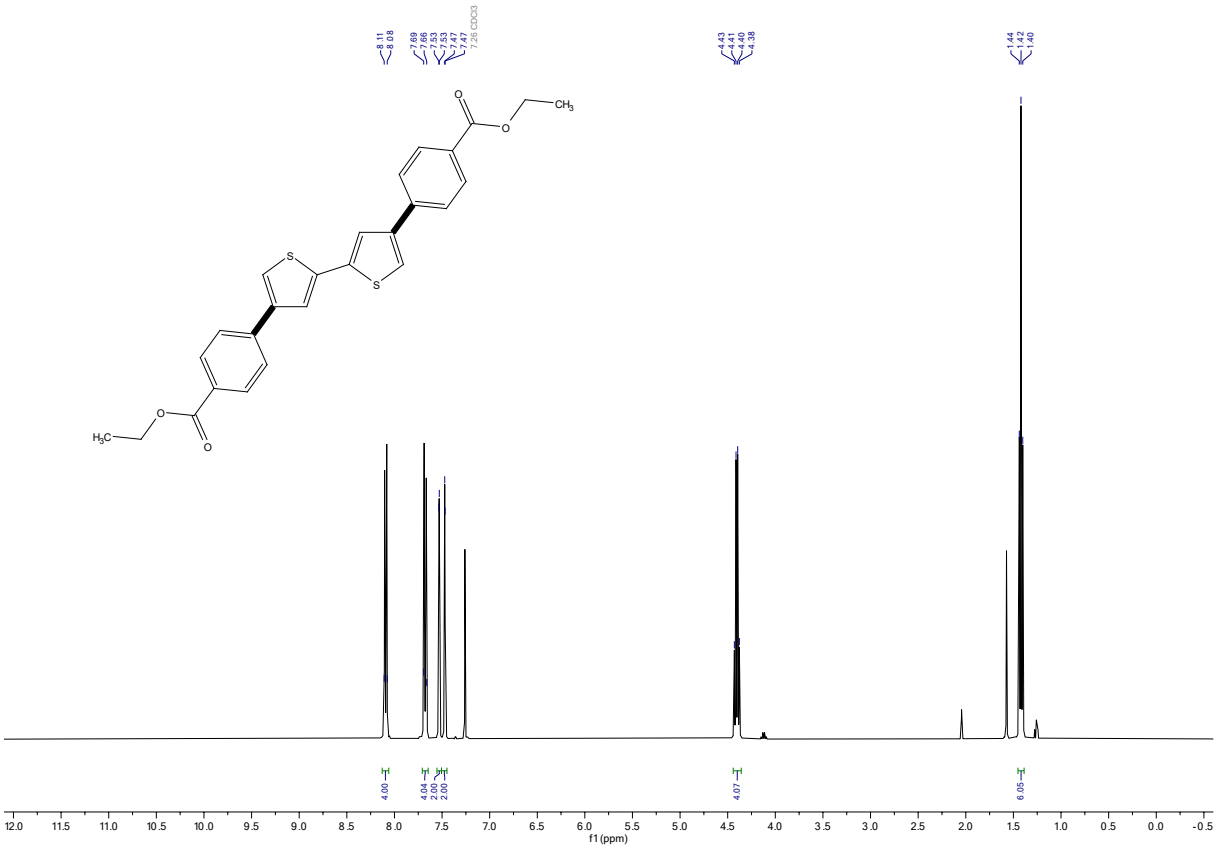
123.14
118.82
77.16 CDCl3
21.32
CH3
H3C
S
S
f1 (ppm)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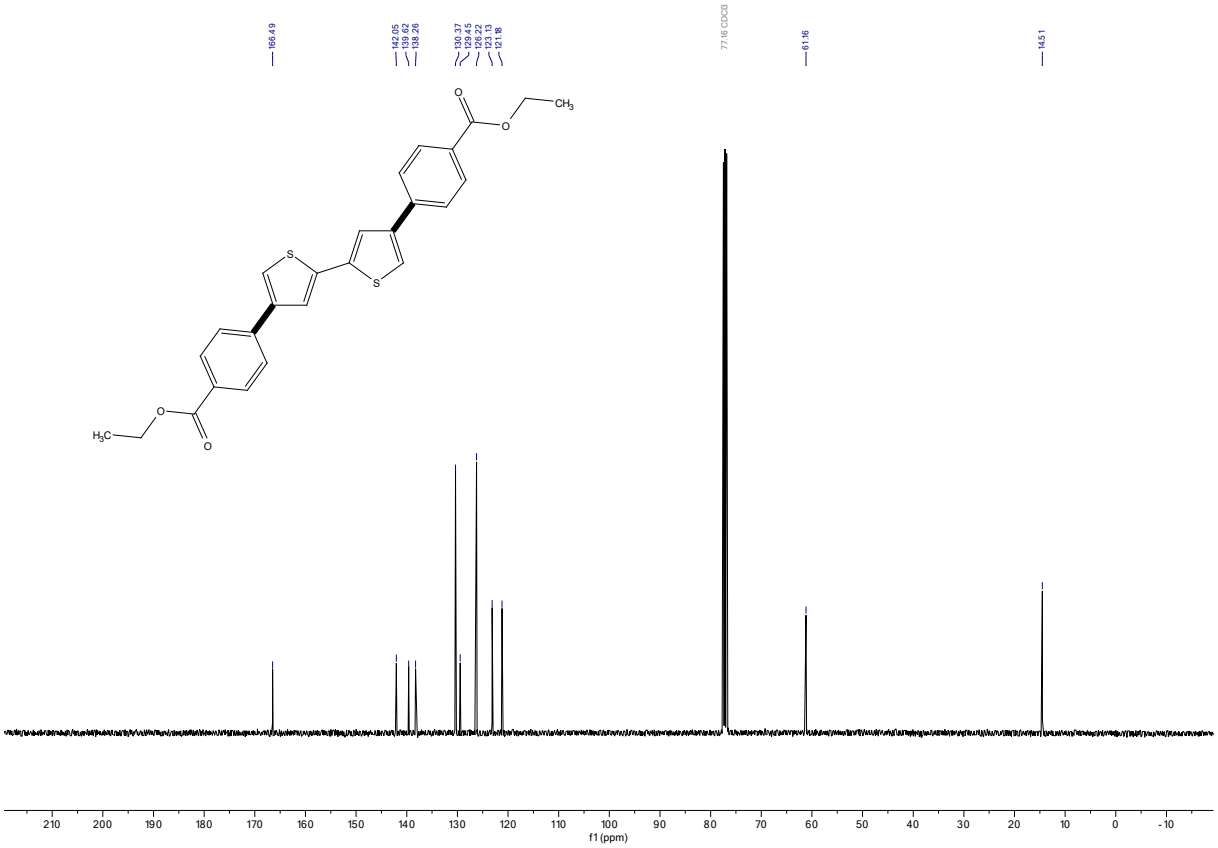
8.08
7.69
7.66
7.53
7.51
7.47
7.45
7.26 CDCl3
4.43
4.41
4.40
4.38
1.44
1.42
1.40
4.00
4.04
2.00
2.00
4.07
6.05
CH3
H3C
O
O
S
S
f1 (ppm)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142.05
139.62
138.26
130.37
129.45
126.22
123.13
121.18
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61.16
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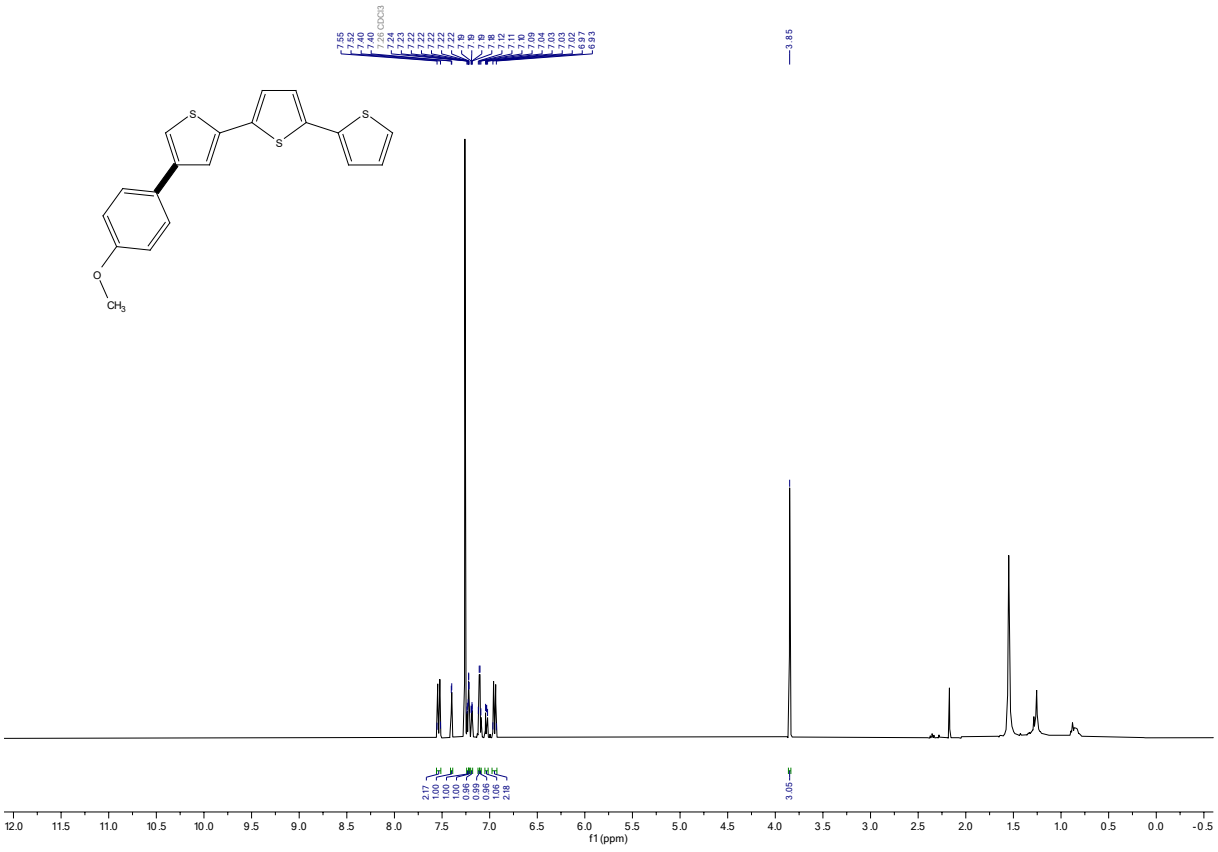
CH3
S
S
O
H3C
O
f1 (ppm)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CDCl3
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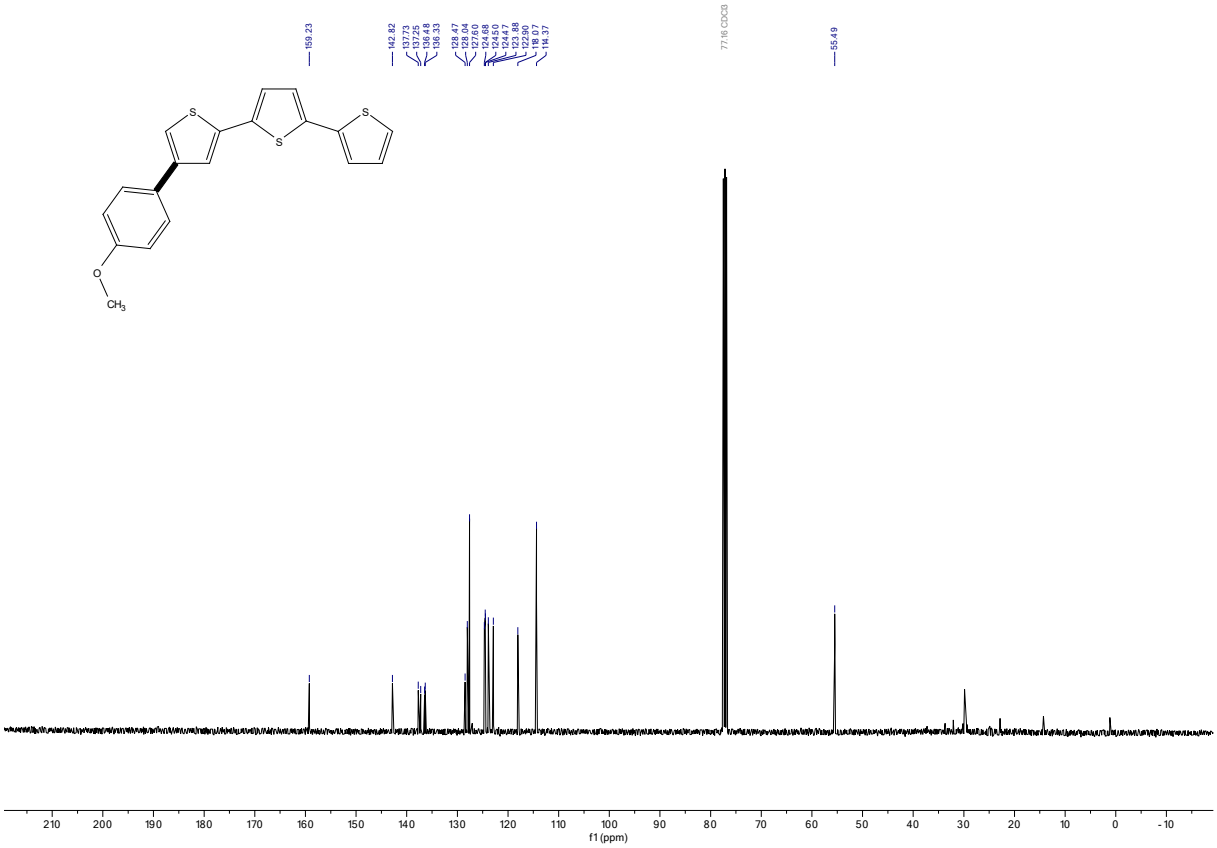
7.23
7.22
7.22
7.22
7.22
7.19
7.19
7.18
7.18
7.12
7.11
7.11
7.09
7.04
7.03
7.03
7.02
6.97
6.93
3.85
S
S
S
O
CH3
2.17
1.00
1.00
1.00
0.98
0.98
0.98
1.06
2.93
3.05
f1 (ppm)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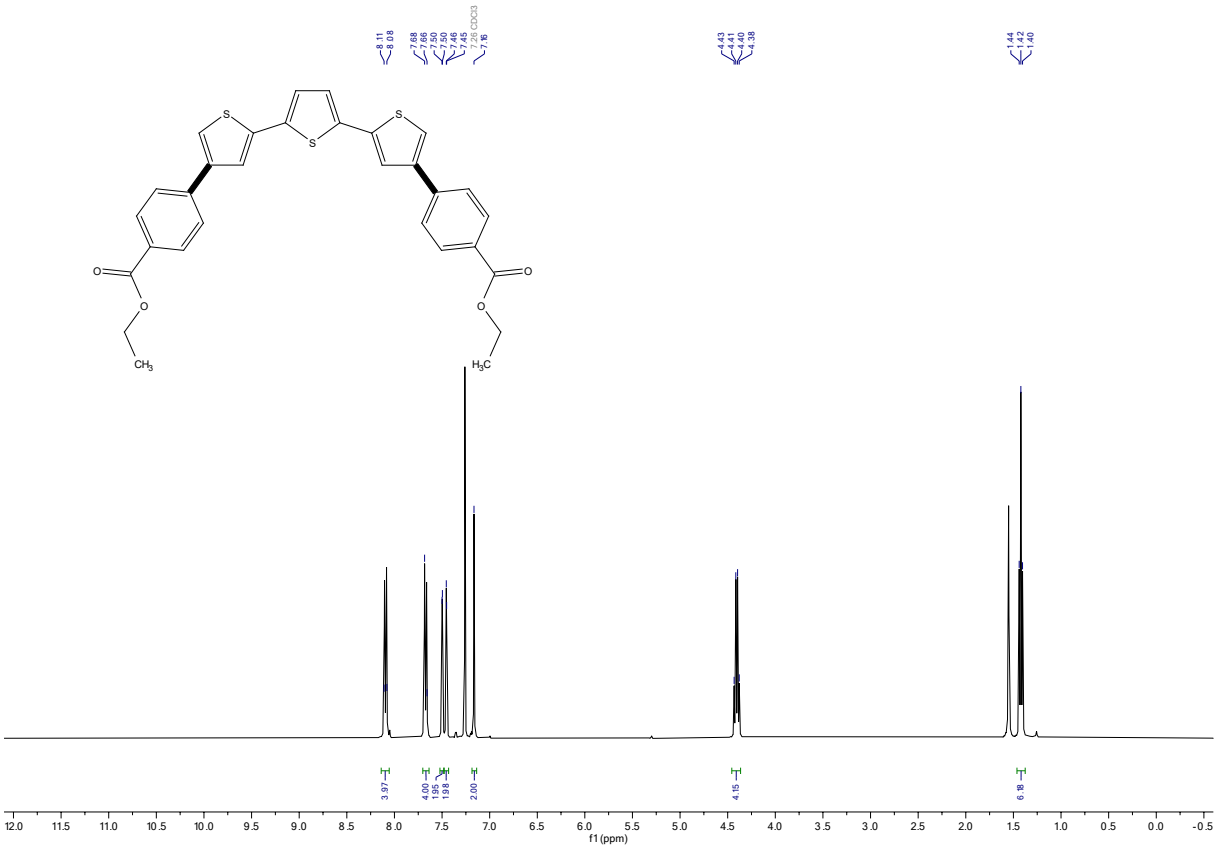
124.65
124.47
123.88
122.90
118.77
114.37
77.16 CDCl3
55.49
S
S
S
O
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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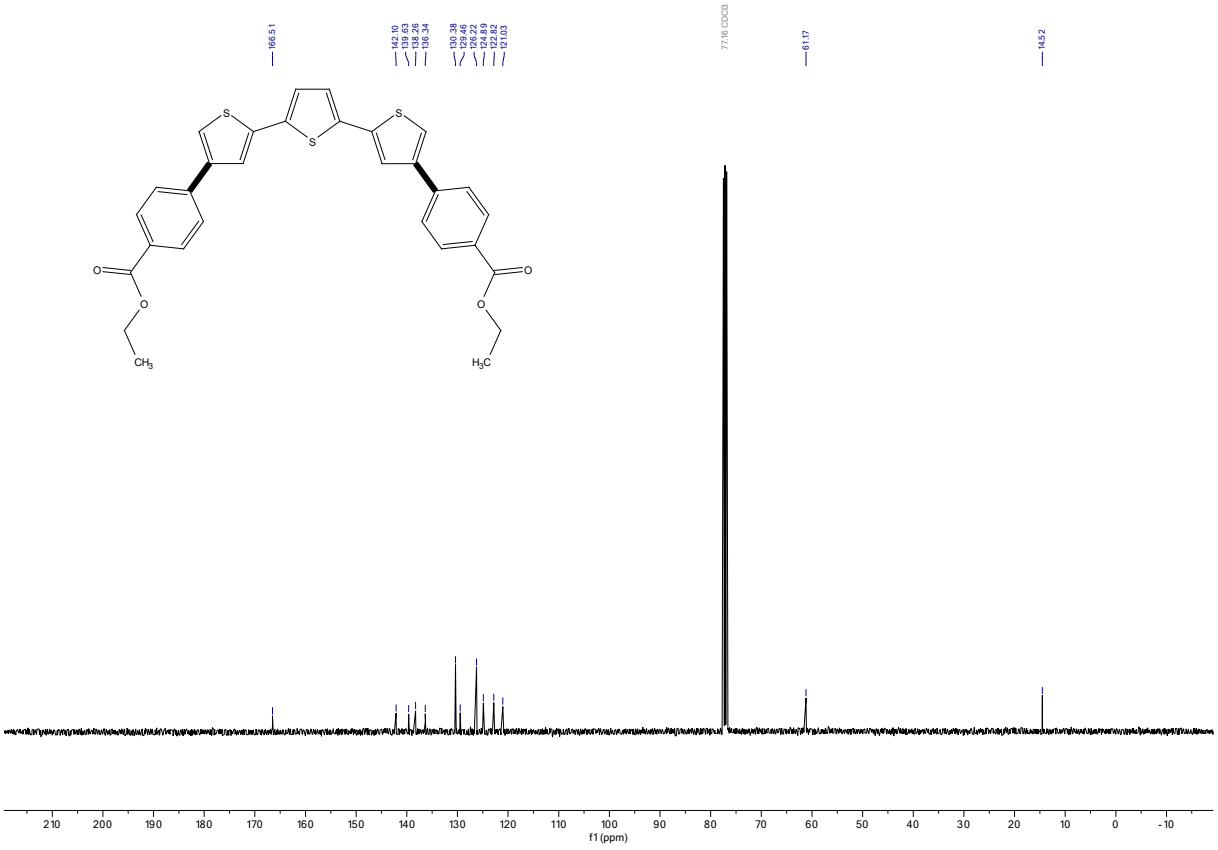
8.08
7.68
7.66
7.50
7.48
7.45
7.26 CDCl3
7.16
4.43
4.41
4.40
4.38
1.44
1.42
1.40
S
S
S
O
O
O
O
CH3
H3C
3.97
4.00
1.95
1.98
2.00
4.15
6.18
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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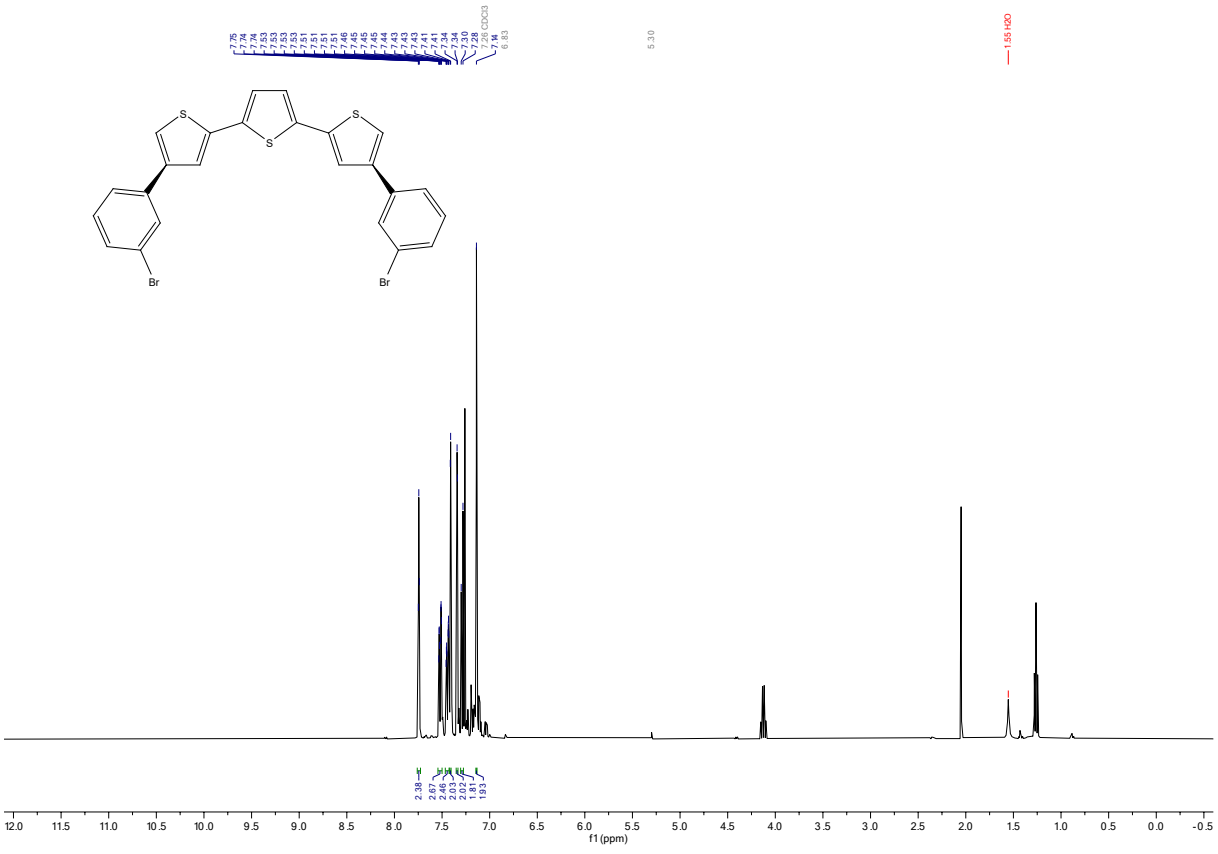
139.63
138.26
136.34
130.38
129.46
126.22
124.89
122.82
121.03
77.16 CDCl3
61.17
14.52
O
O
O
O
S
S
S
CH3
H3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.74
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7.44
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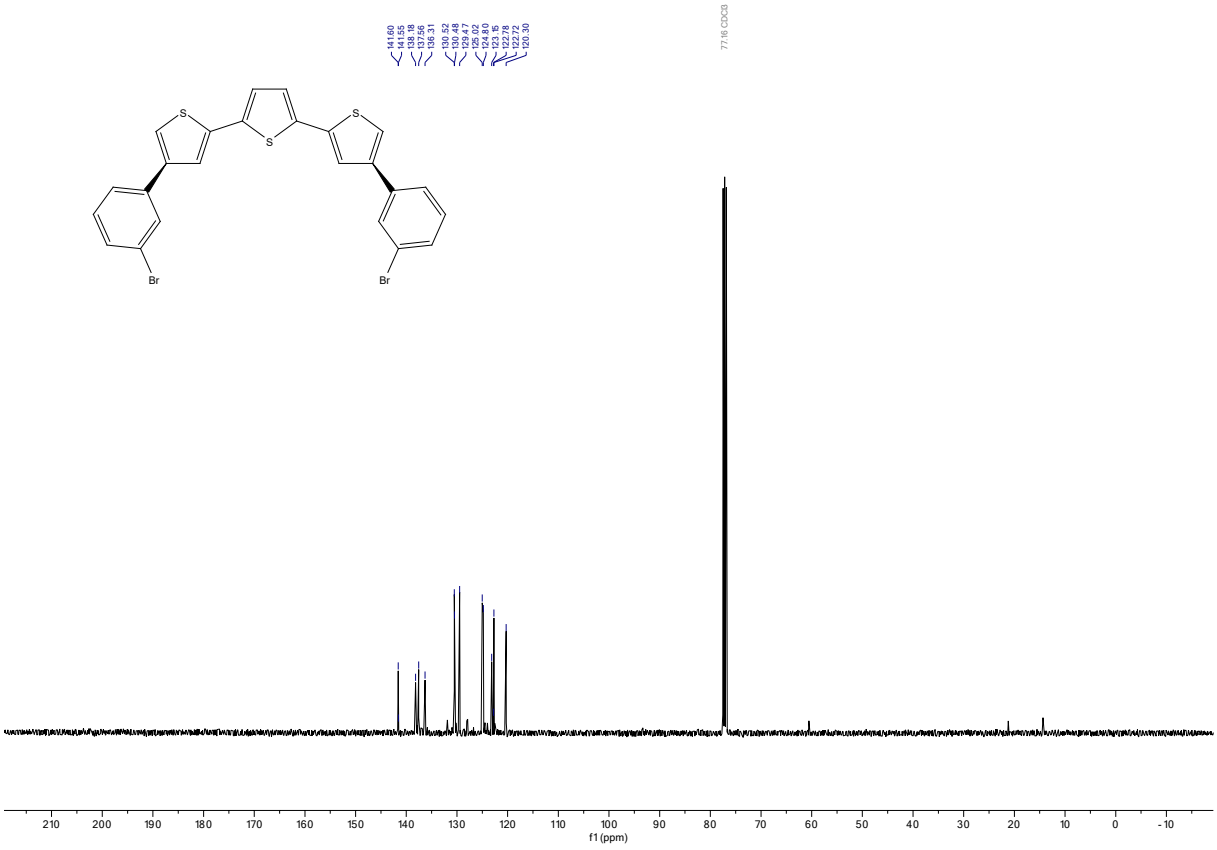
7.43
7.43
7.41
7.41
7.34
7.34
7.30
7.28
7.26 CDCl3
7.14
6.83
5.30
1.55 H2O
S
S
S
Br
Br
2.38
2.67
2.46
2.03
2.02
1.81
1.93
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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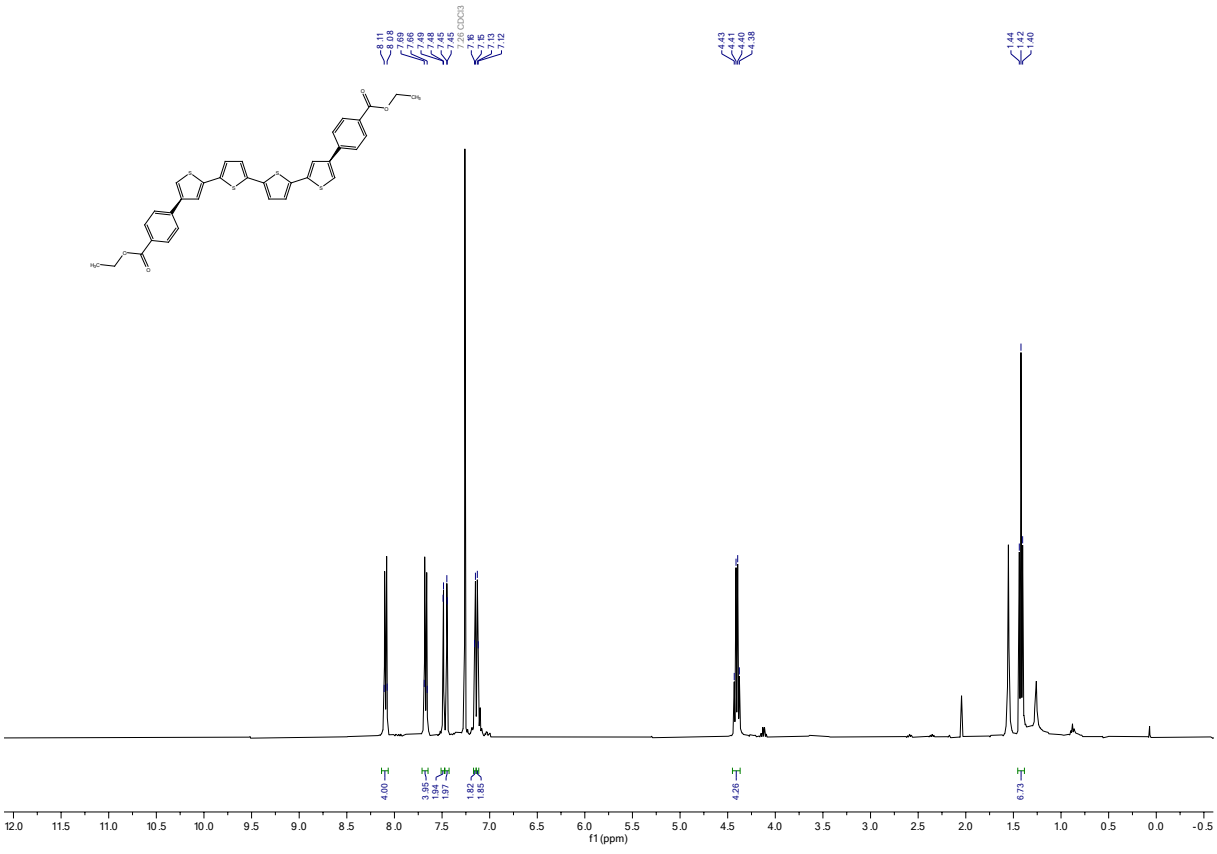
130.48
129.47
125.02
124.80
123.5
122.78
122.72
120.30
77.16 CDCl3
S
S
S
Br
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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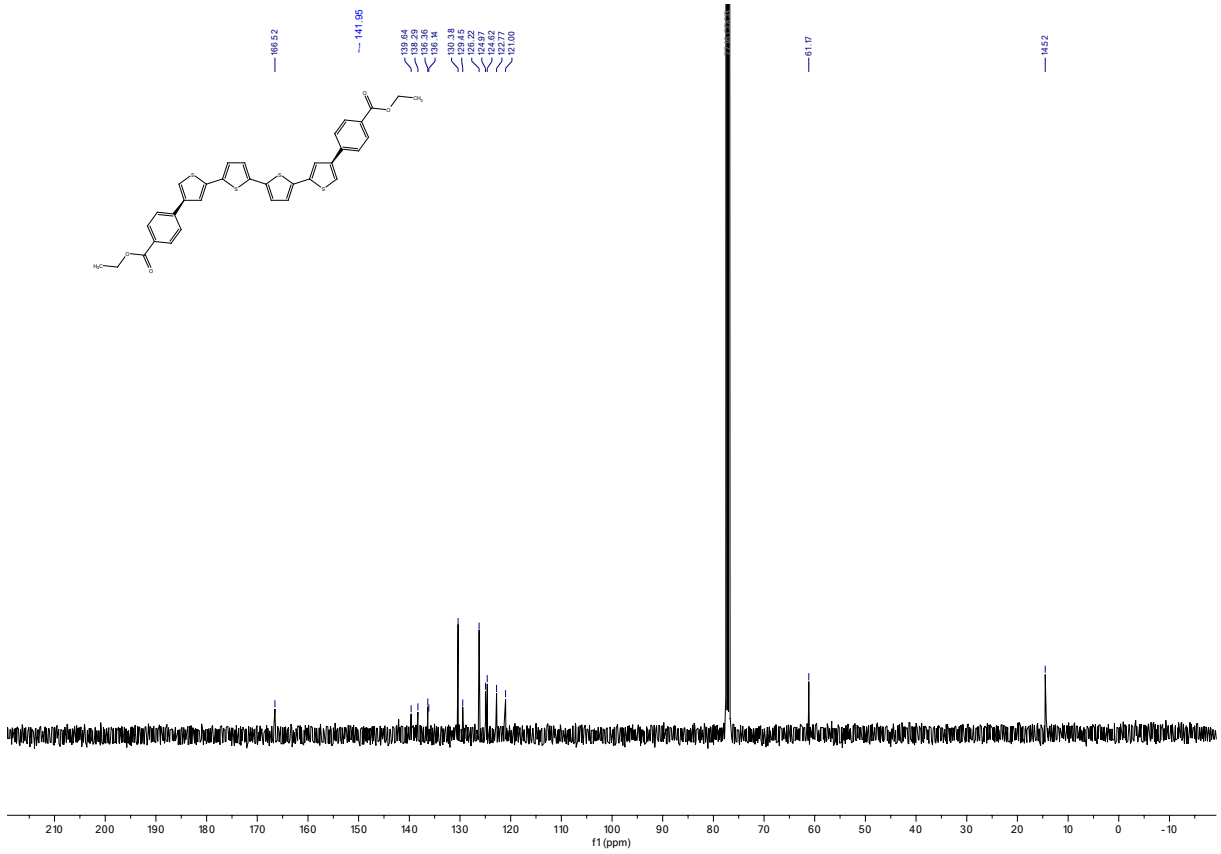
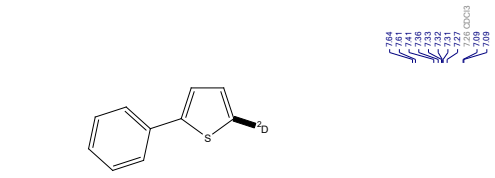
8.08
7.69
7.66
7.49
7.48
7.45
7.43
7.26 CDCl3
7.16
7.15
7.13
7.12
4.43
4.41
4.40
4.38
1.44
1.42
1.40
O
O
O
O
4.00
3.95
1.94
1.97
1.82
1.83
4.26
6.73
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


166.52
141.95
139.64
139.20
138.39
136.14
130.38
129.45
126.22
124.97
124.62
122.77
121.00
77.26
61.17
14.52
f1 (ppm)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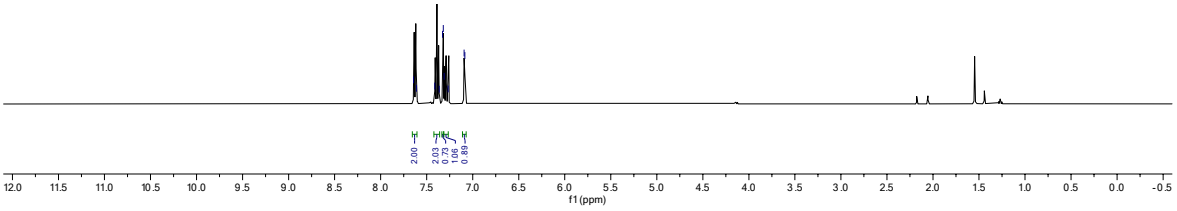
7.32
7.31
7.27
7.26 CDCl3
7.09
7.09
D


2.00
2.03
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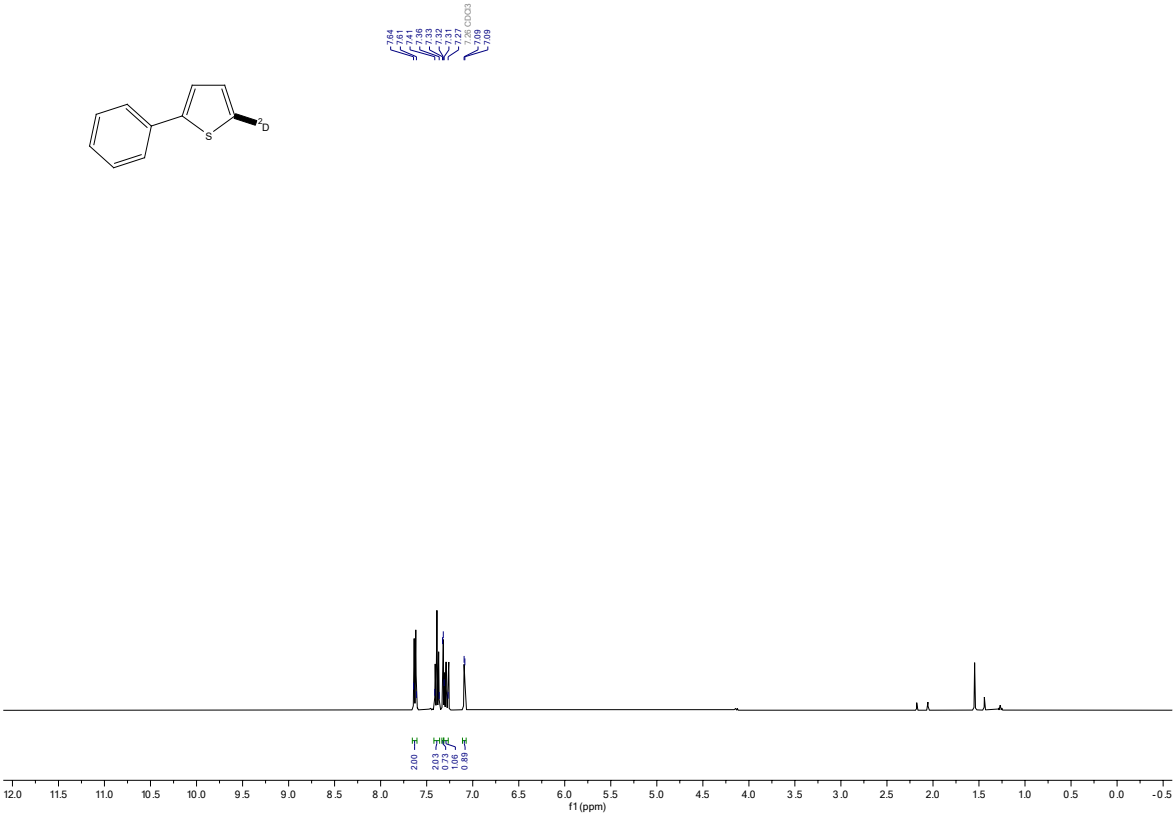
0.89
f1 (ppm)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7.38
7.32
7.31
7.27
7.26 CDCl3
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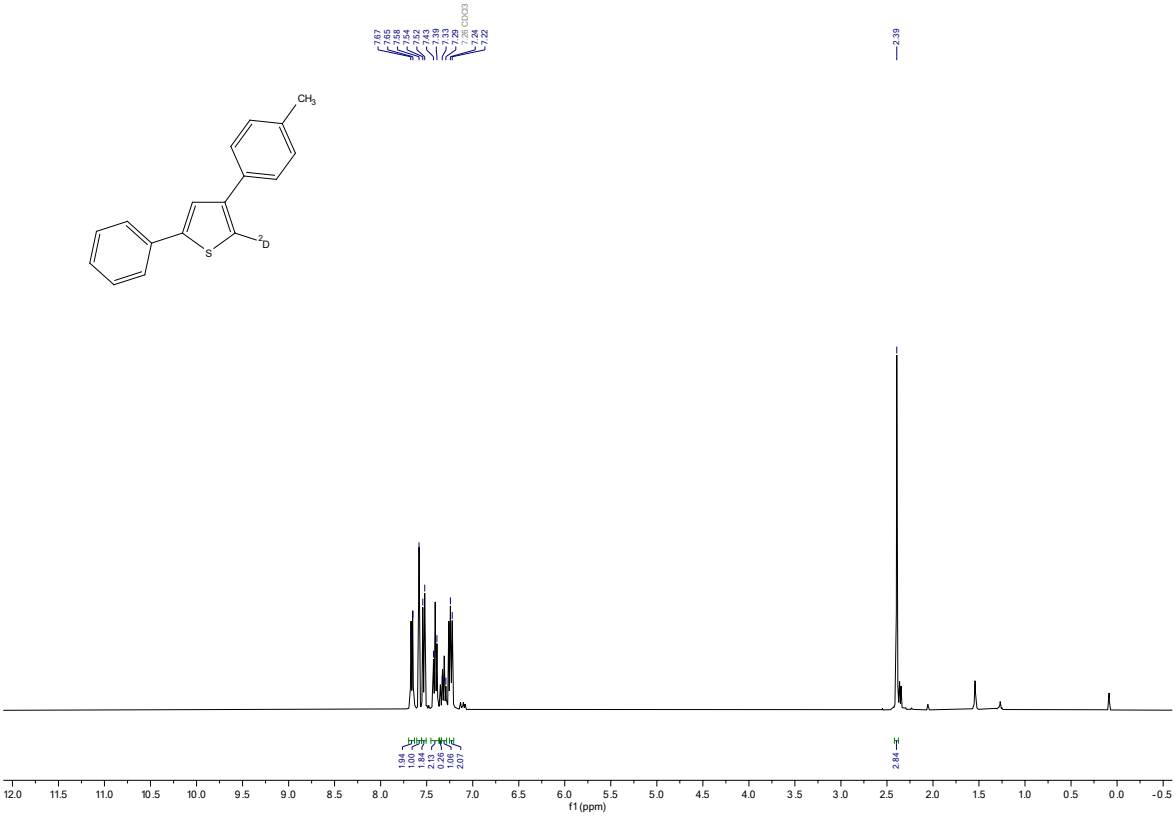
7.09
S
2D
2.00
2.03
2.13
1.06
0.89
f1 (ppm)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7.65
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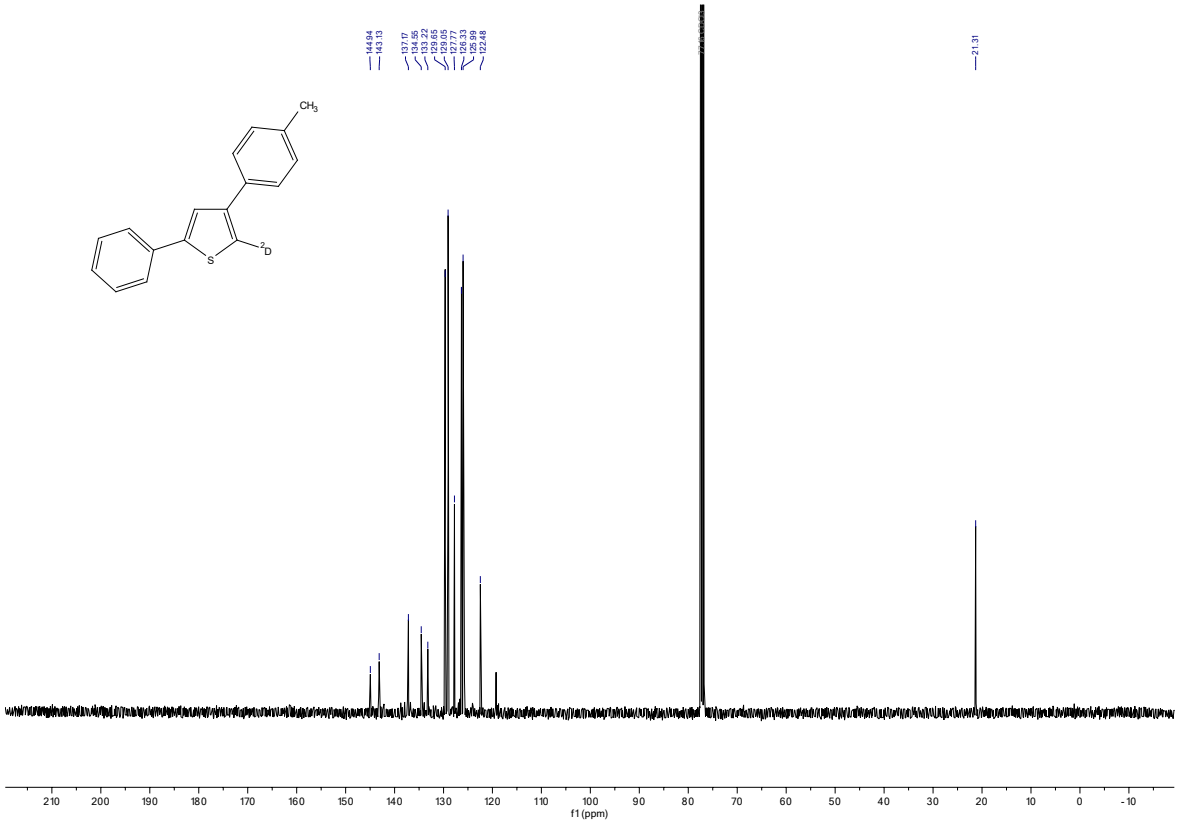
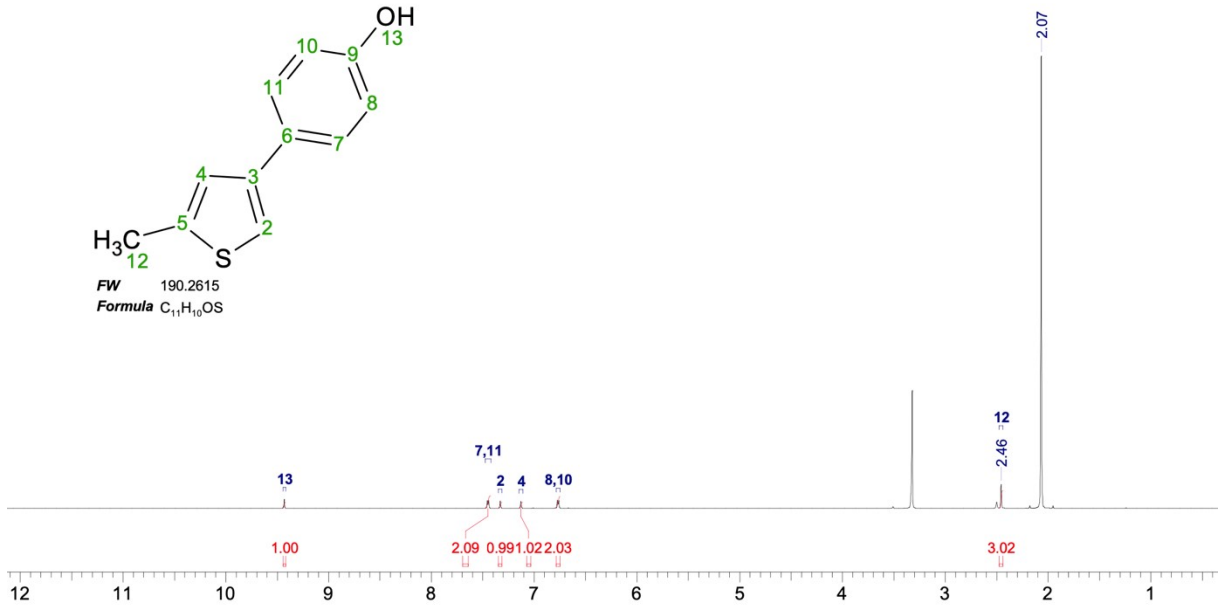
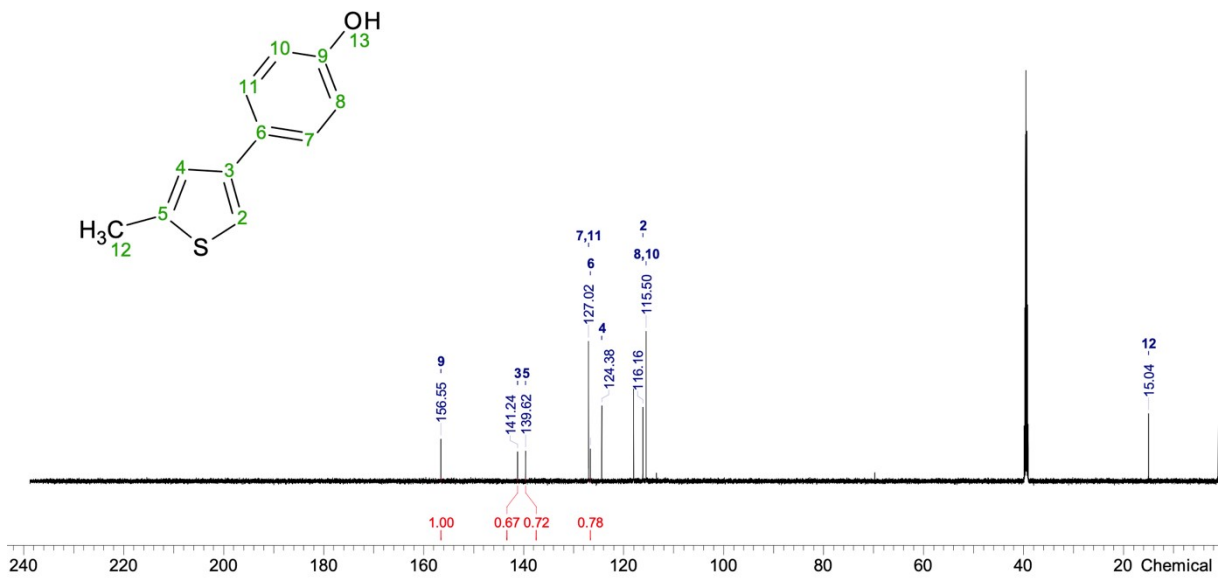
7.43
7.39
7.33
7.29
7.26 CDCl3
7.24
7.22
2.39
CH3
S
2D
1.94
1.00
1.84
1.13
0.26
1.06
2.07
2.84
f1 (ppm)


144.94
143.13
137.17
134.95
133.22
129.65
129.05
127.77
125.53
125.39
122.48
77.00
21.31
CH3
S
2D
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OH
13
10
9
11
8
6
7
4
3
5
2
H3C
12
S
FW 190.2615
Formula C11H10OS
2.07
12
2.46
7,11
13
2
4
8,10
1.00
2.09
0.99
1.02
2.03
3.02
12 11 10 9 8 7 6 5 4 3 2 1


OH
13
10
9
11
8
6
7
4
3
5
2
H_3C
12
S
7,11
6
2
8,10
127.02
115.50
4
124.38
116.16
9
156.55
35
141.24
139.62
12
15.04
1.00
0.67
0.72
0.78
240
220
200
180
160
140
120
100
80
60
40
20
Chemical