Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Tunable Photophysical Properties of Thiophene Based Chromophores: Conjoined Experimental and Theoretical Investigation

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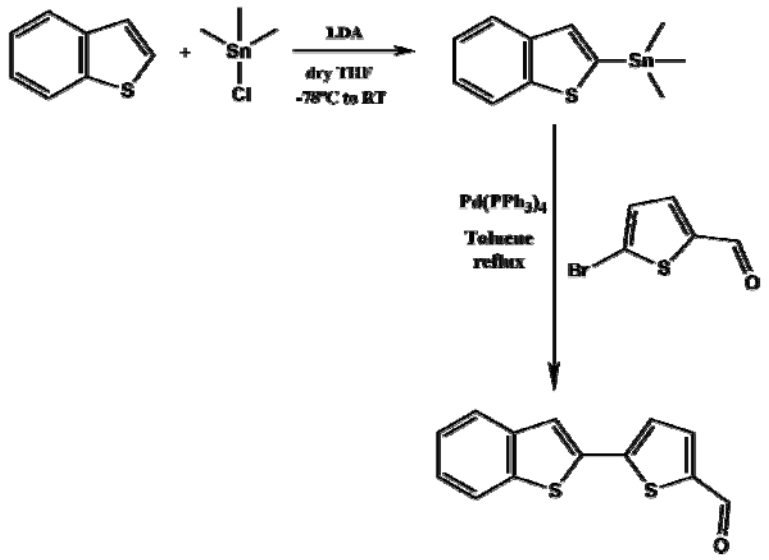
5-(benzothiophen-2-yl)thiophene-2-carbaldehyde: reaction path and ^{1}H NMR

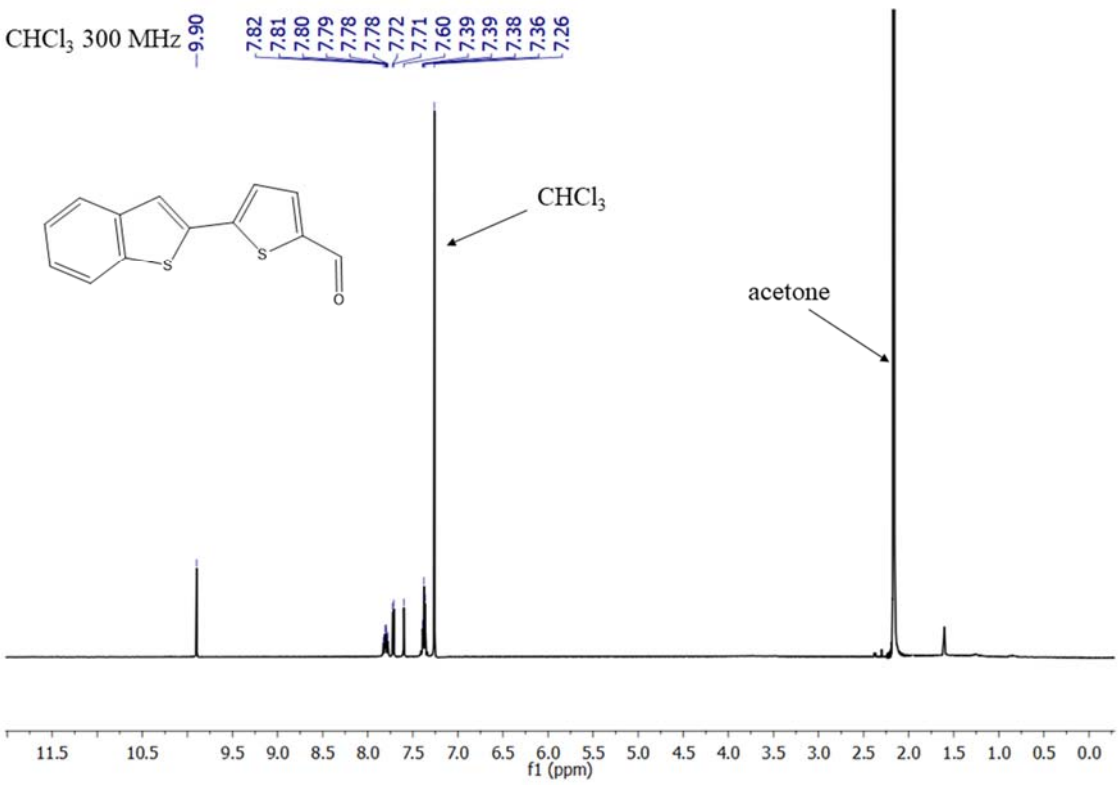


Scheme S1. Synthesis route for 5-(benzothiophen-2-yl)thiophene-2-carbaldehyde

Under argon, in a Schlenk flask 1 eq of benzothiophene (500 mg, 3.73 mmol) was dissolved in 20 mL of dry THF. The reaction mixture was cooled to -78°C and 1.1eq of lithium diisopropylamide (LDA) (439 mg, 4.1 mmol) was added dropwise. The mixture was stirred 1h at -78°C. Afterwards 1.9eq of trimethyltinchloride (1.41 g, 7.08 mmol) was added dropwise. The mixture was stirred at -78°C for 1h and then at room temperature overnight. After that, 20 mL of NaF saturated aqueous solution was added and the reaction mixture was stirred for 1h. Followed by extraction using 100 mL of ethyl acetate, solution was washed 3 times by distilled water (3x100 mL), then dried over $MgSO_4$ and filtrated. Solvents were evaporated to obtain a yellow oil. Then under argon 1eq of benzo[b]thiophen-2-yltrimethylstannane (1.11 g, 3.73 mmol) was dissolved in 20 mL of dry toluene followed by the addition of 1eq of 5-bromothiophene-2-carbaldehyde (712 mg, 3.73 mmol) and 0.08eq of $Pd(PPh_3)_4$ (345 mg, 0.29 mmol). Reaction mixture was refluxed for 48hrs. Solvent was evaporated. Then reaction was purified by column chromatography on silica gel using 3:1 pentane/CH_2Cl_2 as eluent. Product was obtained as a yellow powder with 70% yield (638 mg)[1,2].

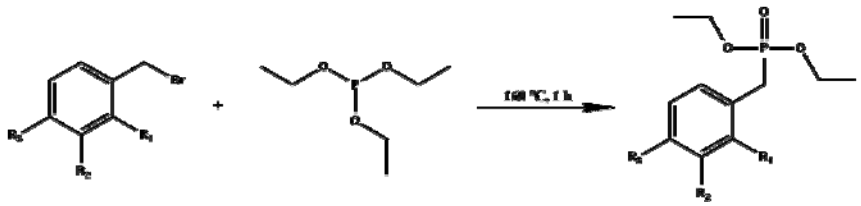
[1] M. Iyoda, *J. Solid State Chem.*, 2002, **168**, 597–607.

[2] A. Miyazaki, K. Enomoto, K. Okabe, H. Yamazaki, J. Nishijo, T. Enoki, E. Ogura, K. Ugawa, Y. Kuwatani and M. Iyoda, *J. Solid State Chem.*, 2002, **168**, 547–562.



^{1}H NMR ($CDCl_3$, 300 MHz) δ/ppm: 9.90(s, 1H), 7.81(d, 1H, J= 4.8Hz), 7.78(d, 1H, J= 4.8 Hz), 7.71(d, 1H, J= 4.0Hz), 7.60(s, 1H), 7.38(m, 2H), 7.36(d, 1H, J= 4.0Hz)

Phosphonates: reaction scheme, chemical structure, reactants ratio & yield



Scheme S2. Synthetic route for phosphonates

All of the used phosphonates were synthesized in the same way. The reaction scheme and specific proportions of reactants can be find in SI (Scheme S2 and Table S2). Under argon, in the flask with distillation column a benzyl bromide derivative (1 eq) was mixed with four equivalents of triethyl phosphate and stirred for 1 hour in the temperature of 160ºC. During the reaction ethyl bromide might be produced as a side product. Afterwards mixture was cooled down to the room temperature and dried (~5mbar, 60ºC). At this point product should look like yellow oil. The mixture was dissolved in ethyl acetate (100 mL) and washed 6 times with saturated $NaHCO_3$ (6x30 mL). The organic phase was dried with $MgSO_4$ and then on rotatory evaporator (~5mbar, 60ºC). Obtained yellow oil was additionally washed with petroleum ether (5x20 mL) and dried once again (~5 mbar, 60ºC). The structure of the compounds was confirmed by ^{1}H and ^{31}P NMR spectroscopy[3].

Table S1. The chemical structure of synthesized compounds

Compound	**R_1**	**R_2**	**R_3**
1	CN	H	H
2	H	CN	H
3	H	H	CN
4	NO_2	H	H
5	H	NO_2	H
6	H	H	NO_2

Table S2. Reaction yield of phosphonates synthesis

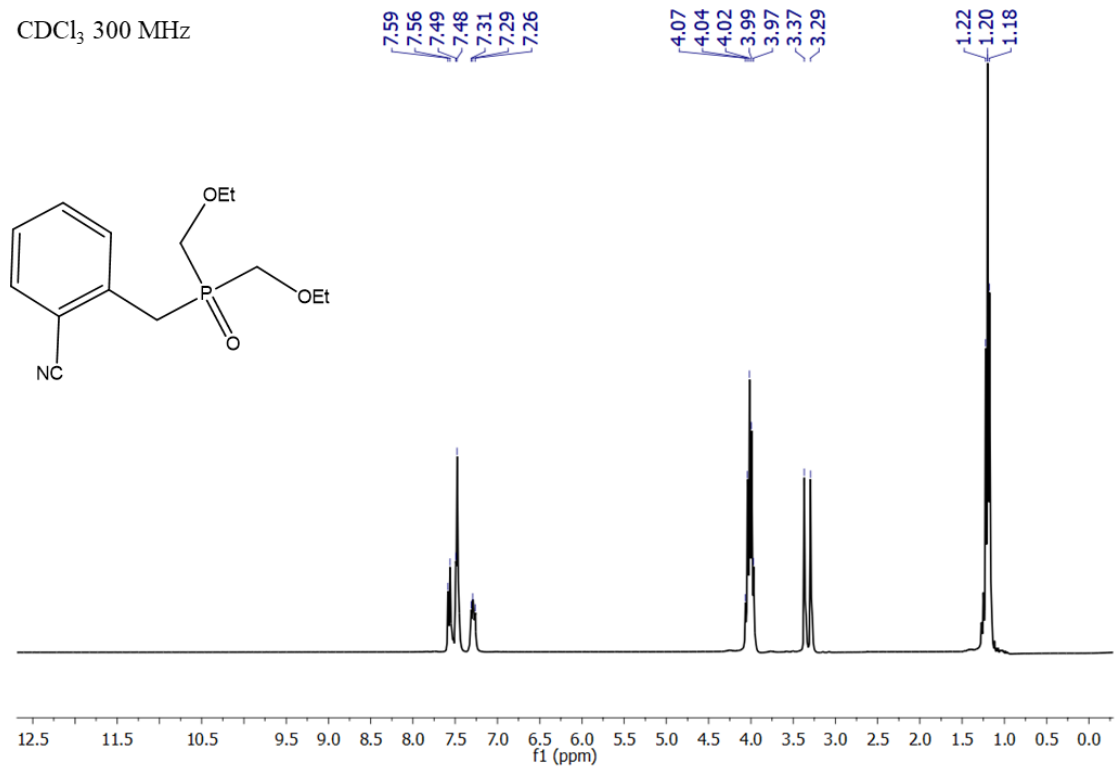
Compound			**Triethyl phosphate**	**Yield**	
eq	1		4	%	g
1	2-(bromomethyl)benzonitrile	3g	10.50 ml	81	3.14
2	3-(bromomethyl)benzonitrile	3g	10,50 ml	78	3.02
3	4-(bromomethyl)benzonitrile	3g	10.50 ml	80	3.10
4	1-(bromomethyl)-2-nitrobenzene	3g	9.60 ml	79	3.00
5	1-(bromomethyl)-3-nitrobenzene	3g	9.60 ml	69	2.62
6	1-(bromomethyl)-4-nitrobenzene	3g	9.60 ml	74	2.81

[3] A. Szukalski, K. Parafiniuk, K. Haupa, W. Goldeman, B. Sahraoui, F. Kajzar and J. Mysliwiec, *Dyes Pigments*, 2017, **142**, 507–515.

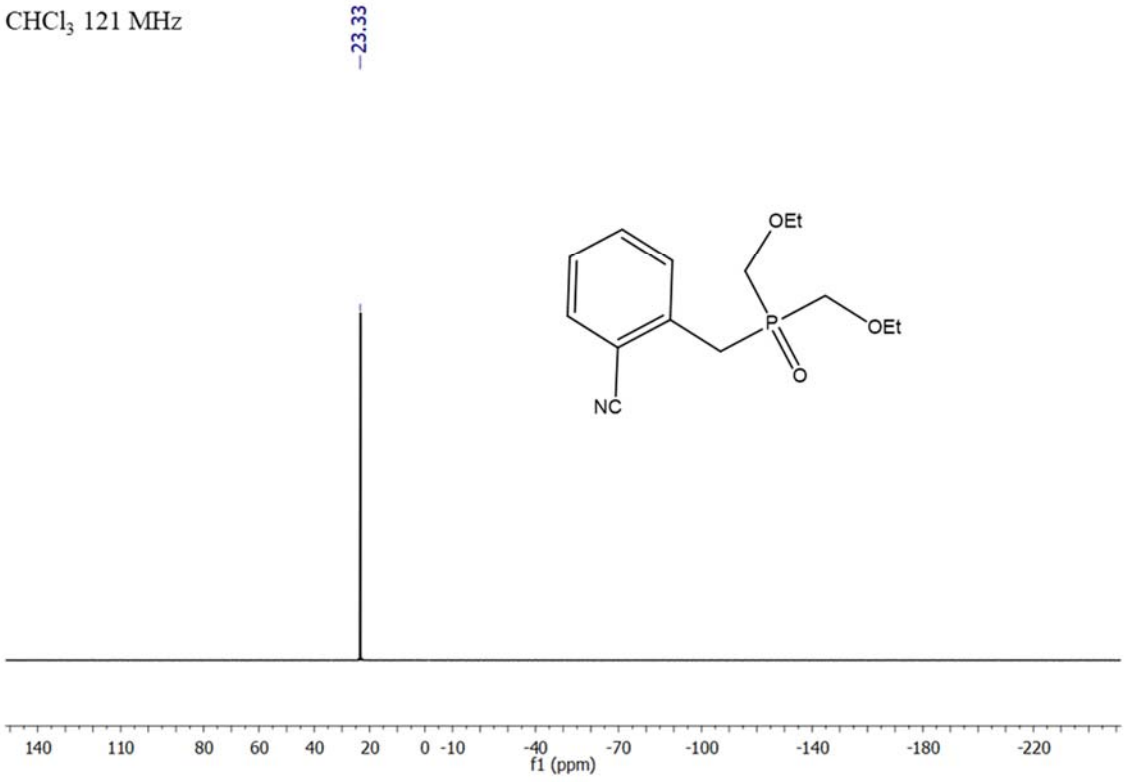
Phosphonates NMR Spectra

2-(bromomethyl)benzonitrile

^{1}H

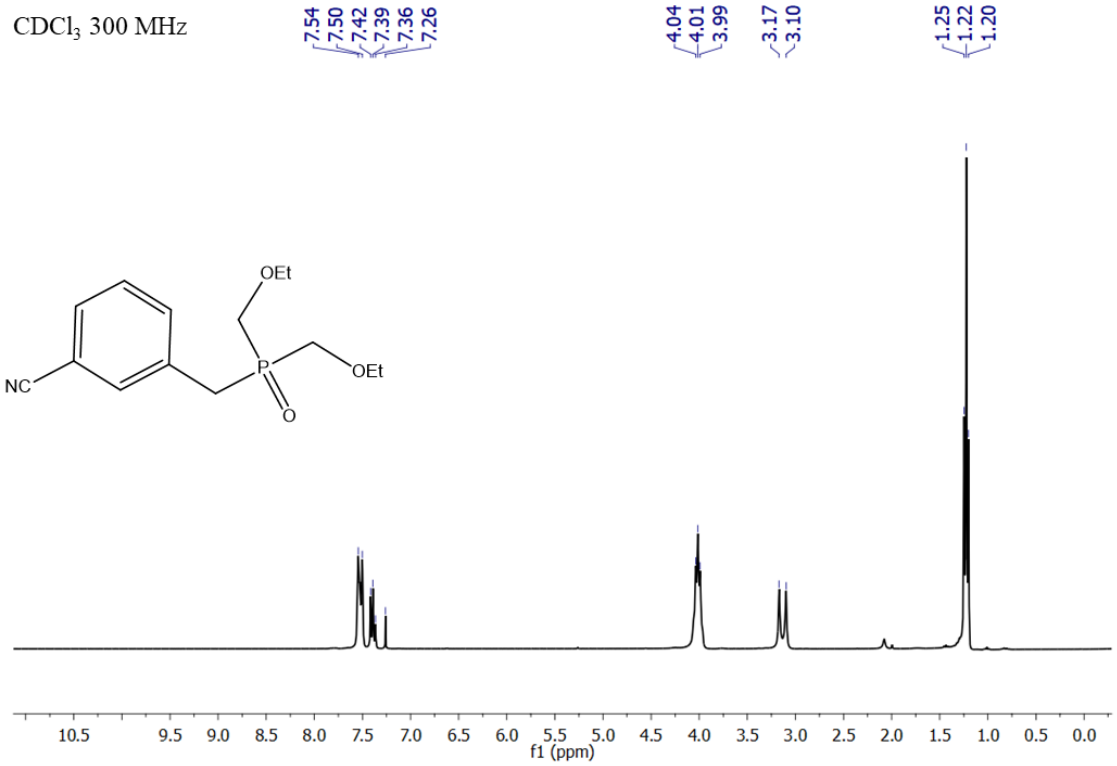


^{31}P

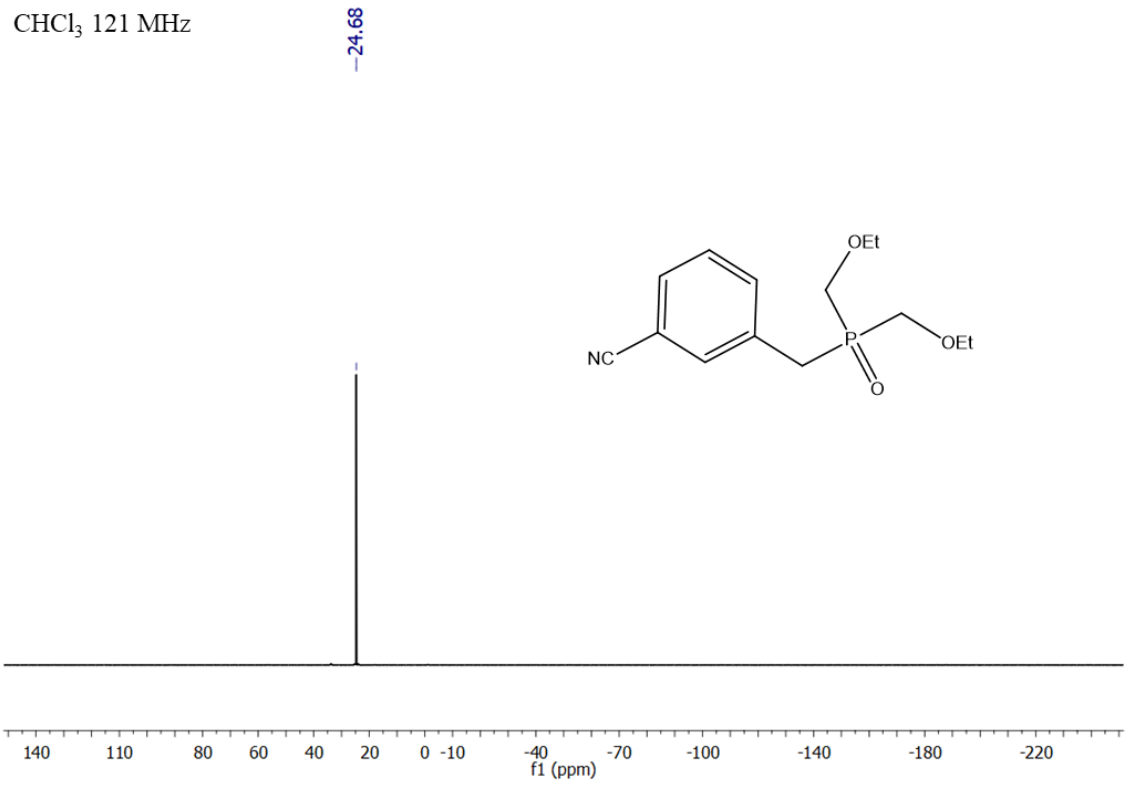


3-(bromomethyl)benzonitrile

^{1}H

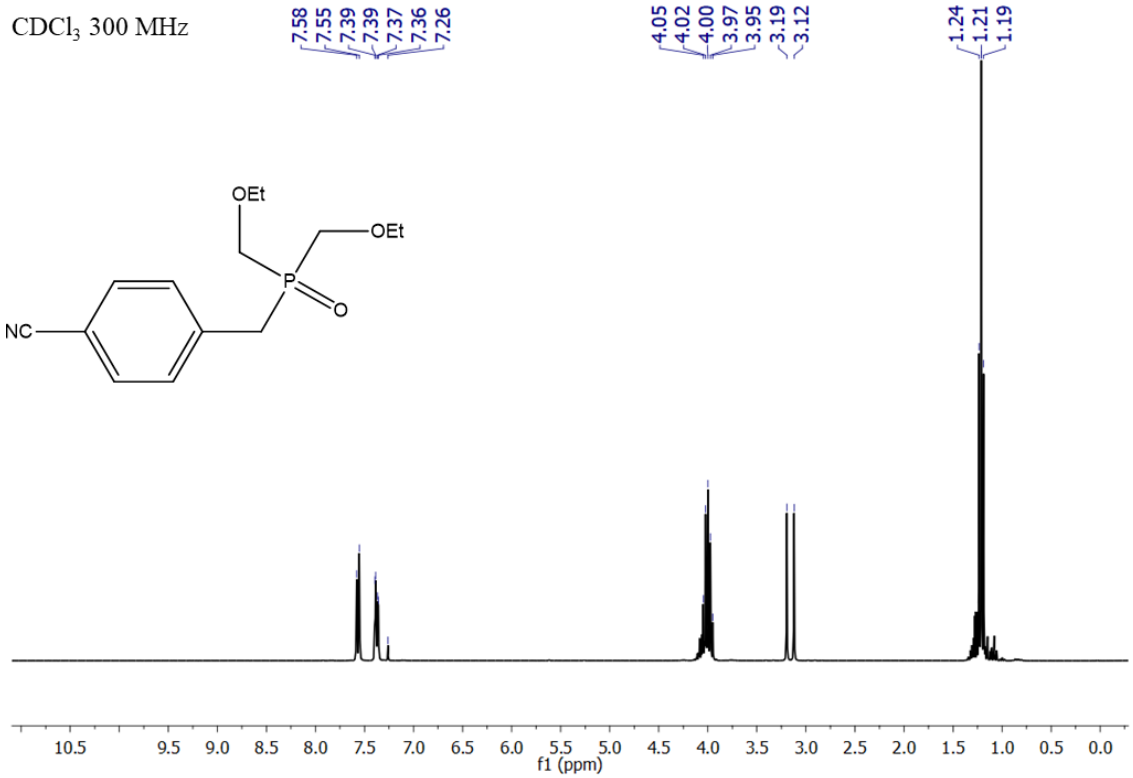


^{31}P

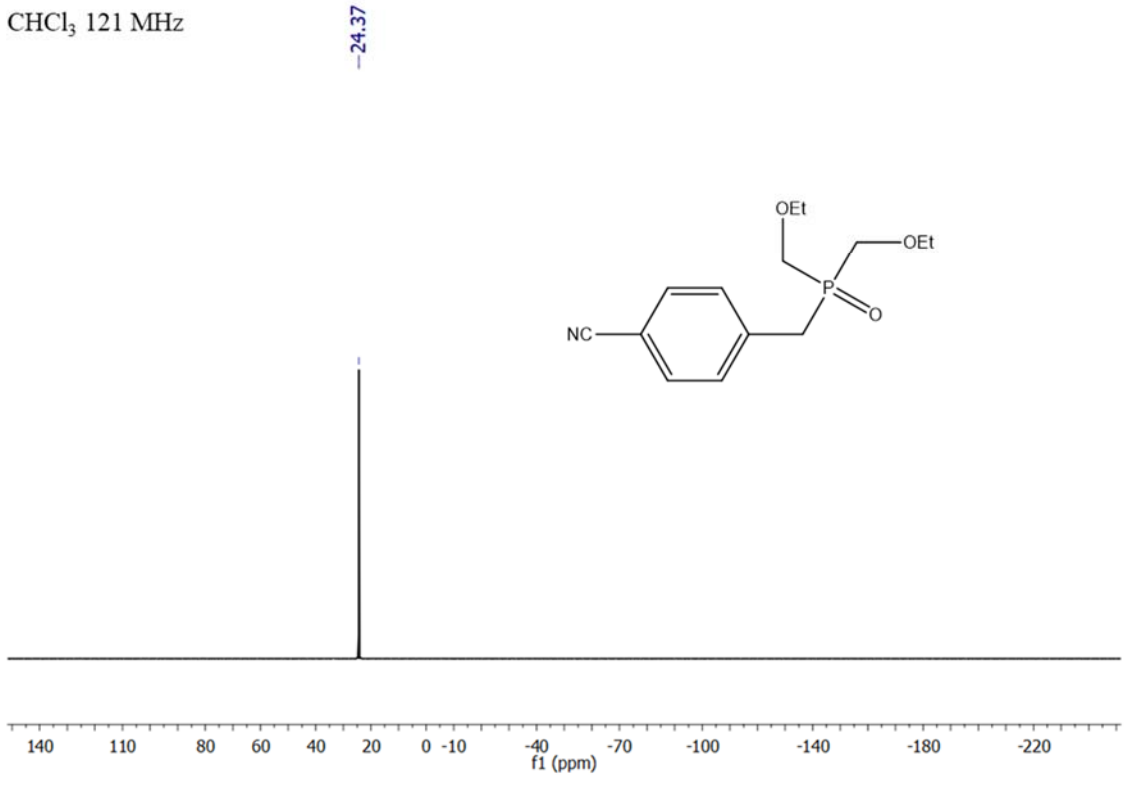


4-(bromomethyl)benzonitrile

^{1}H

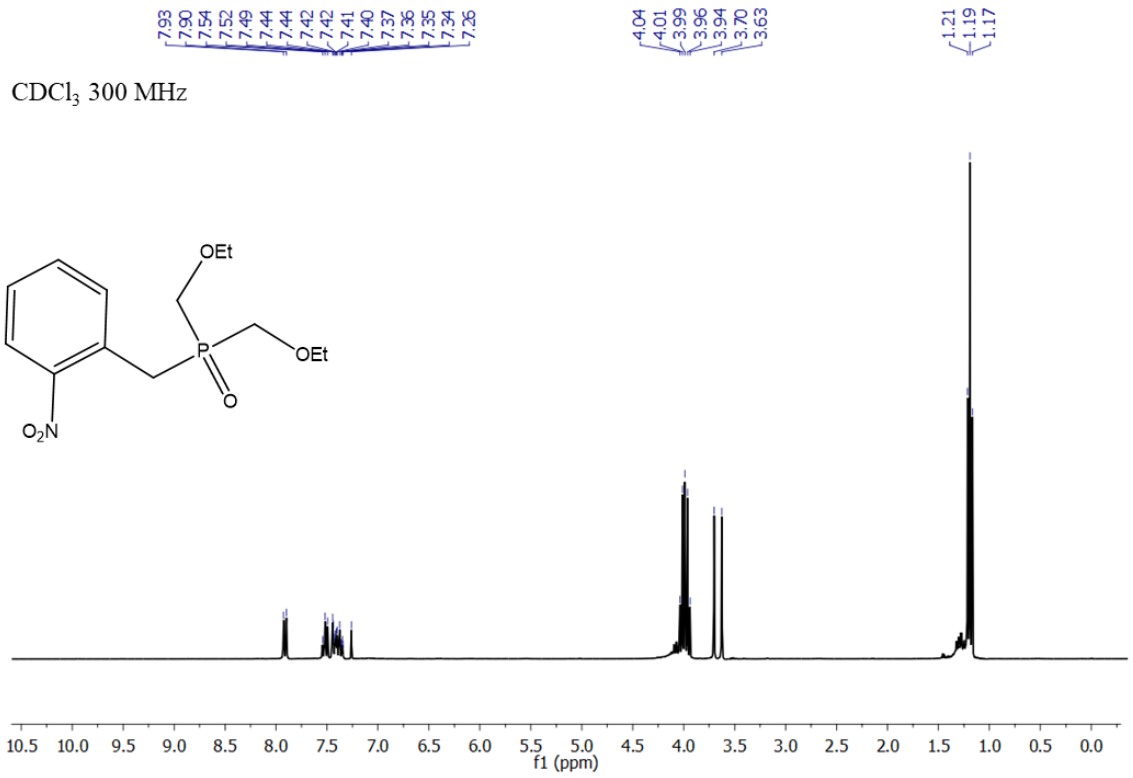


^{31}P

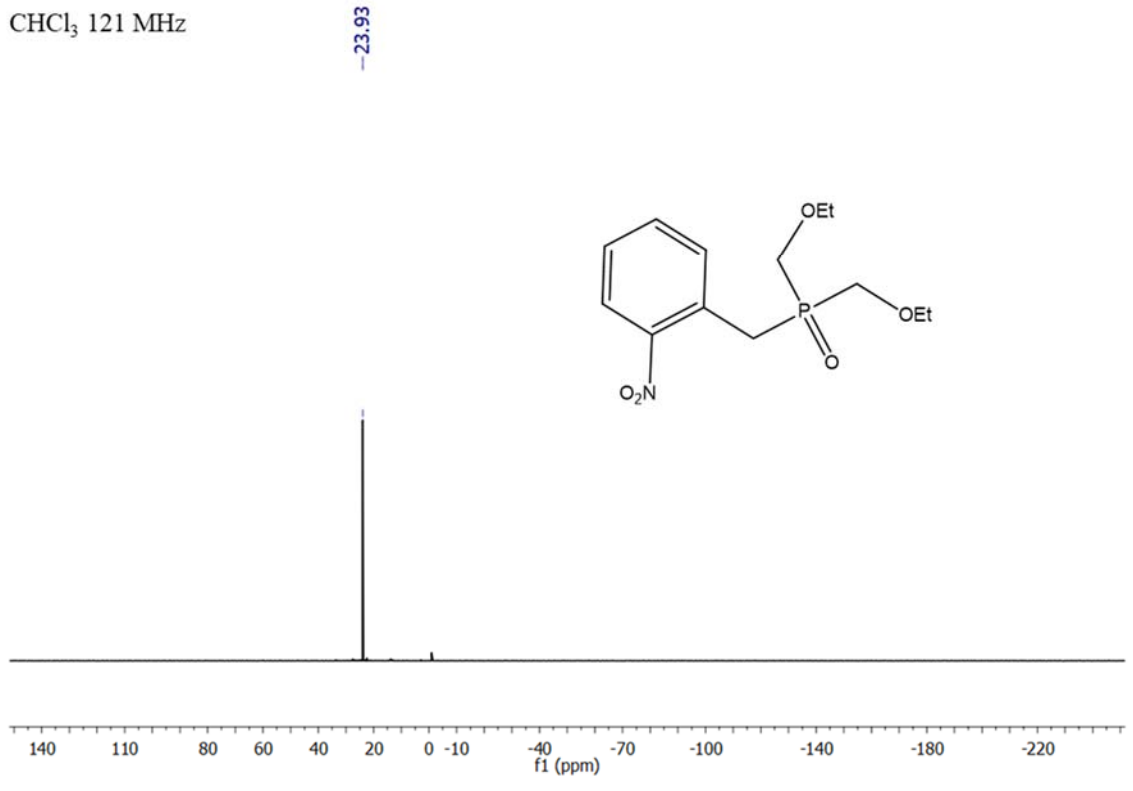


1-(bromomethyl)-2-nitrobenzene

^{1}H

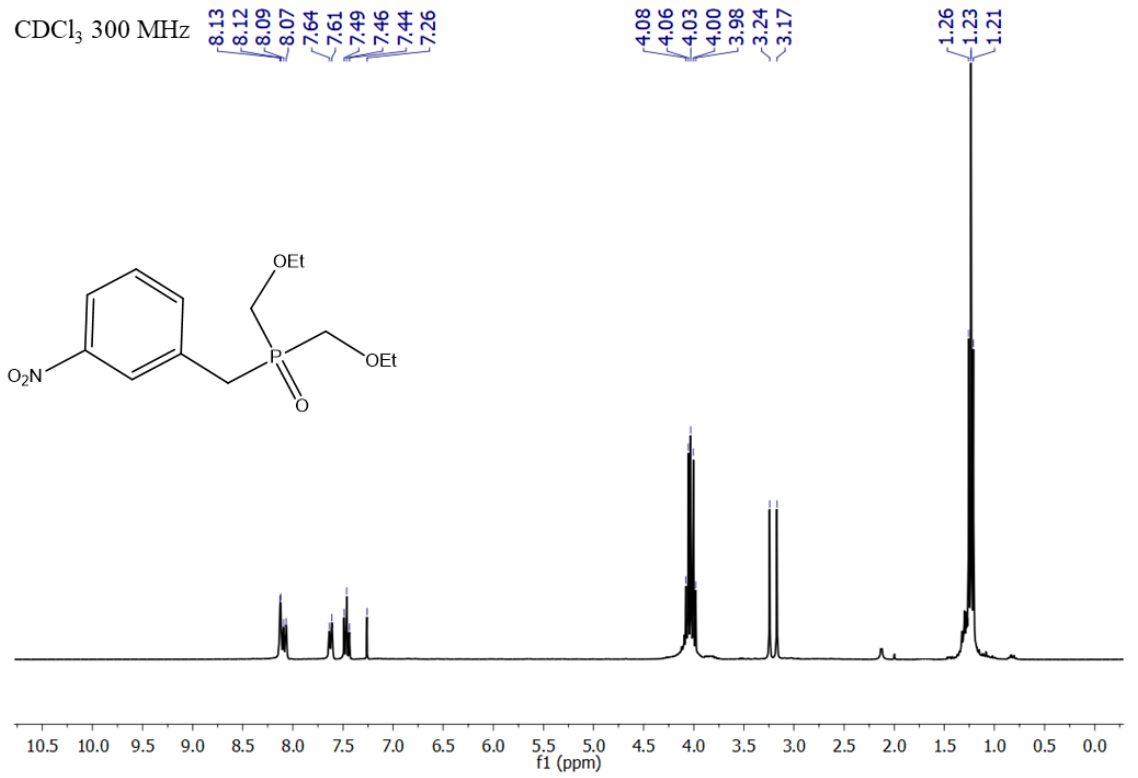


^{31}P

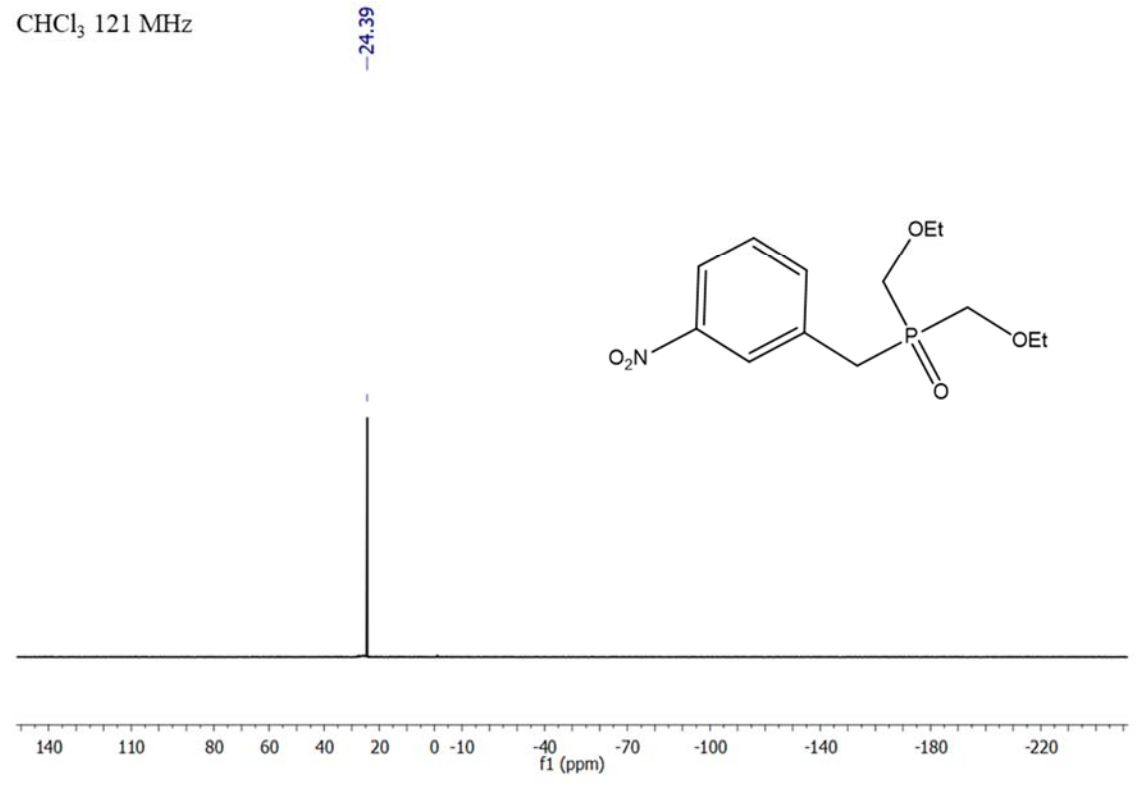


1-(bromomethyl)-3-nitrobenzene

^{1}H

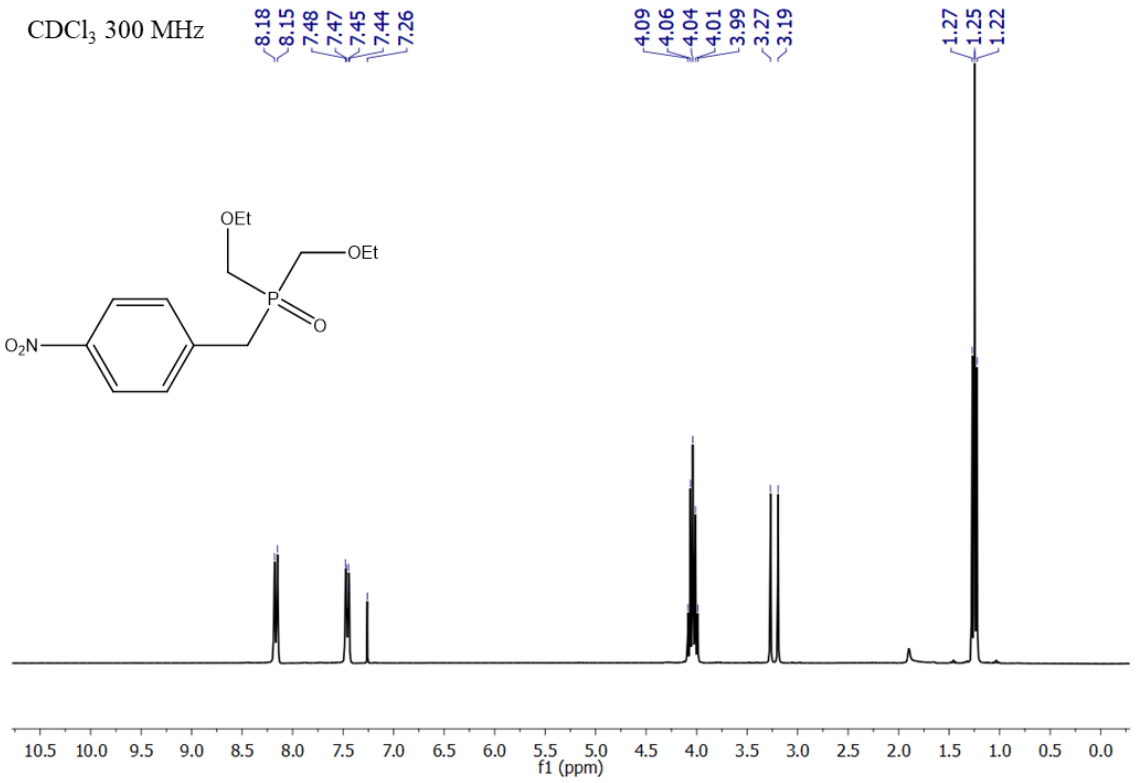


^{31}P

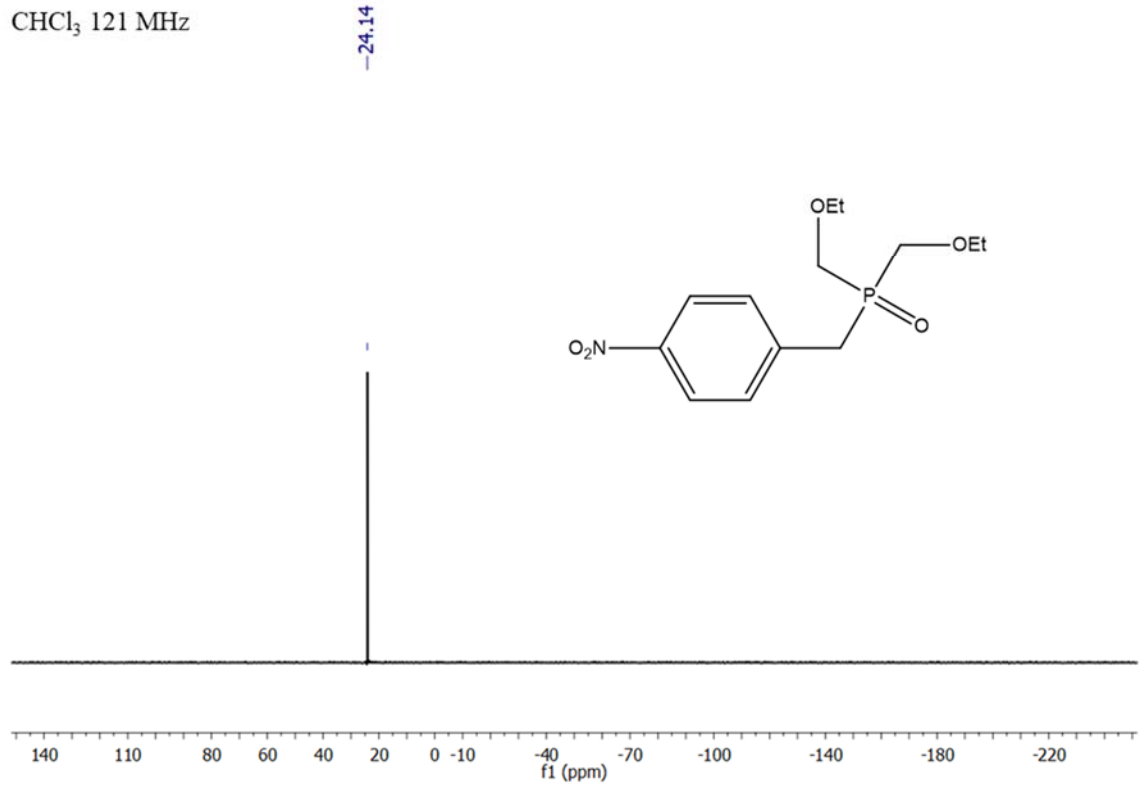


1-(bromomethyl)-4-nitrobenzene

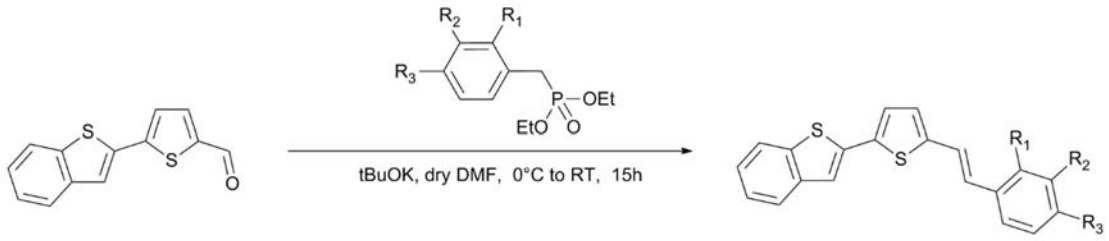
^{1}H



^{31}P



Thiophene derivatives: synthesis route and reaction yield



Scheme 3. Synthetic route for novel push-pull thiophene derivatives.

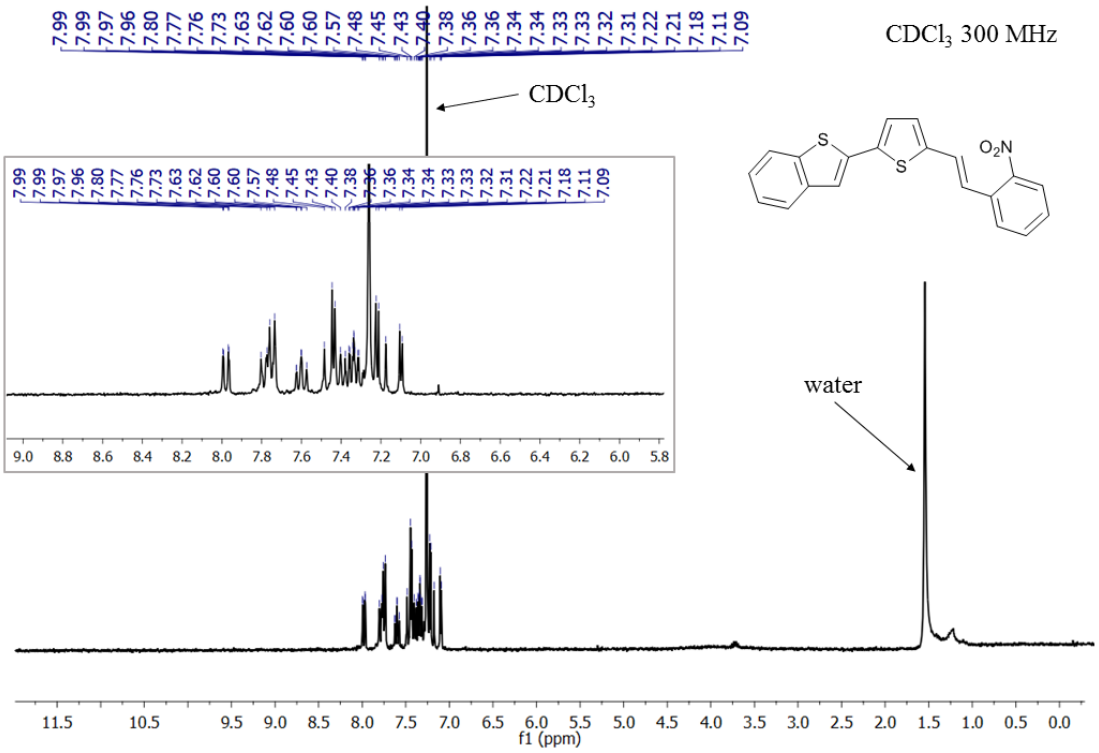
Table 4. The chemical structure of obtained ThDs.

Compound	R_1	R_2	R_3	Yield [%]	Yield [mg]
1a	NO_2	H	H	79	118
1b	H	NO_2	H	65	97
1c	H	H	NO_2	68	101
2a	CN	H	H	84	118
2b	H	CN	H	77	109
2c	H	H	CN	69	97

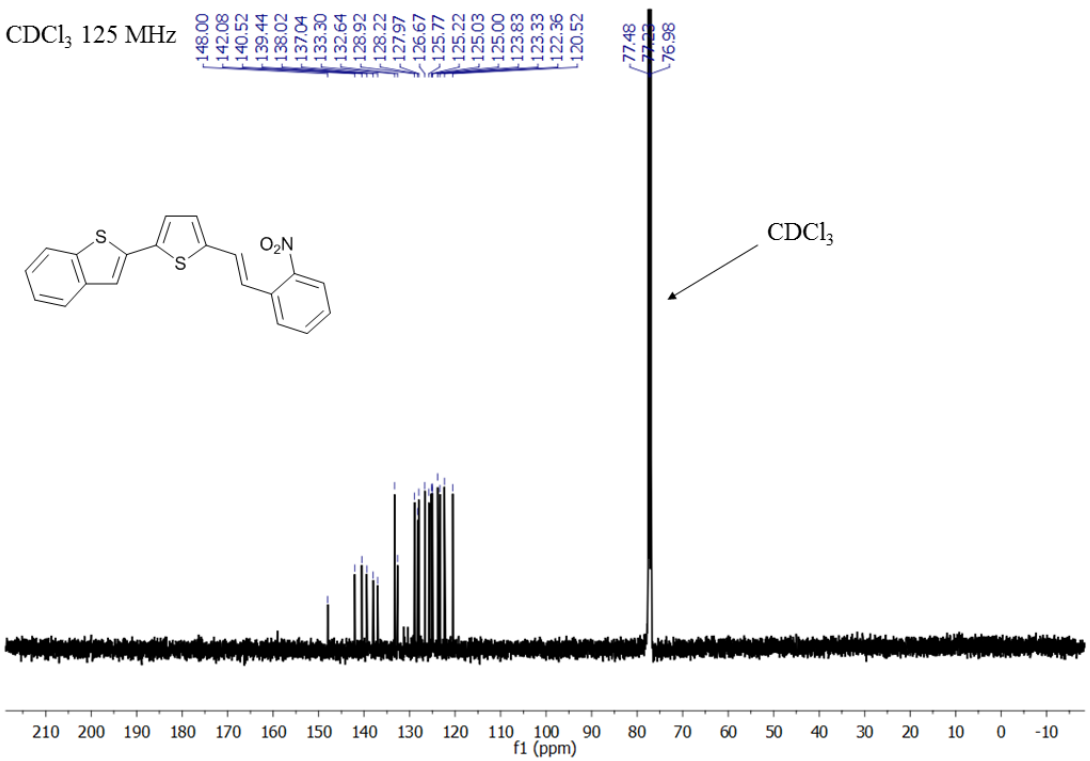
Thiophene derivatives ^{1}H and ^{13}C NMR

1a

^{1}H

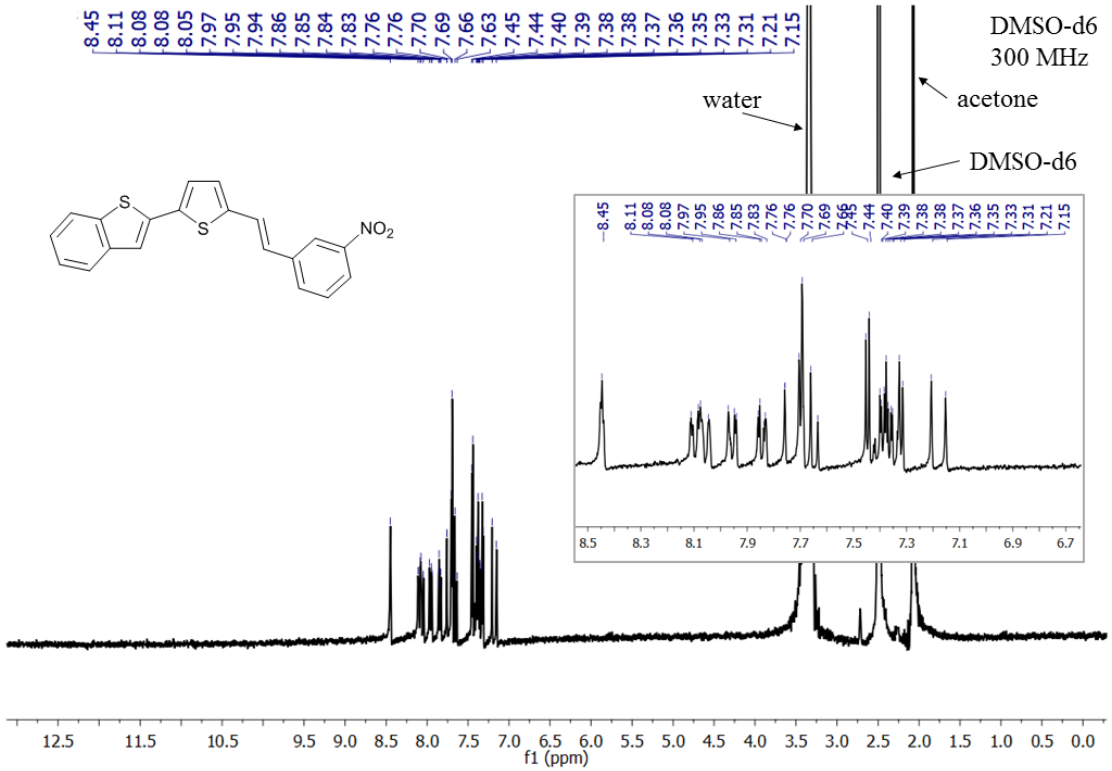


^{13}C



1b

^{1}H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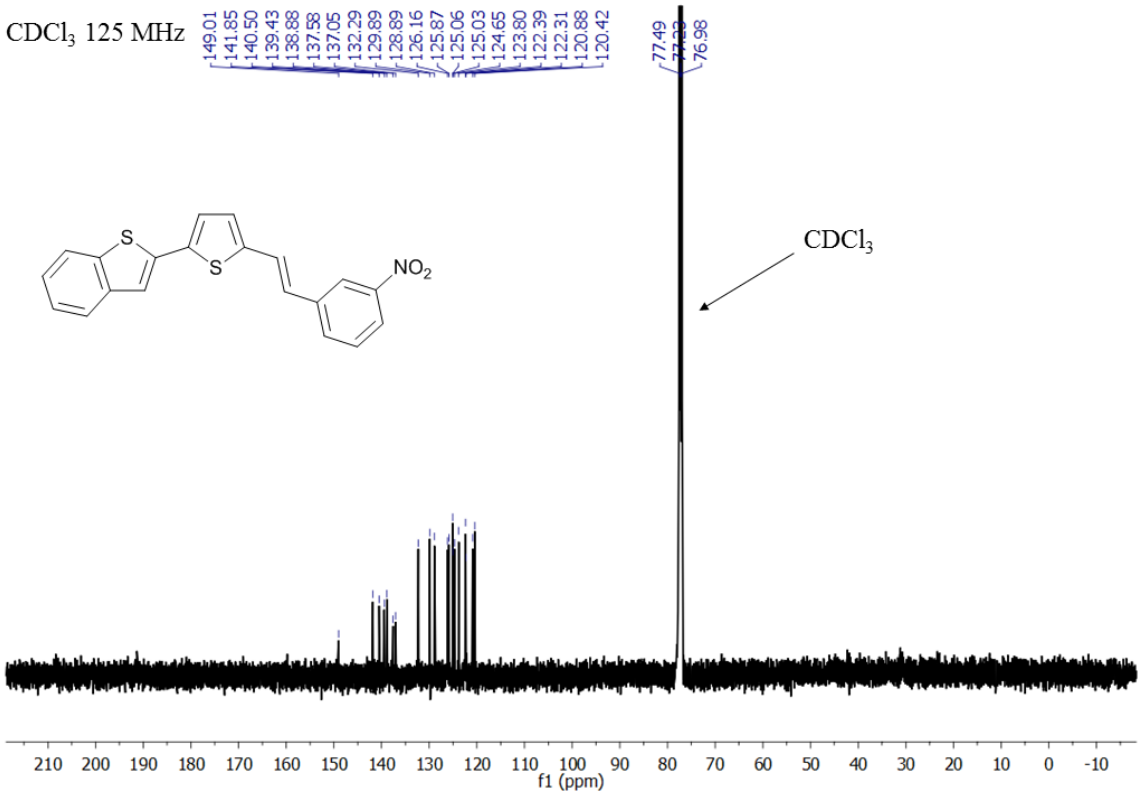
acetone
DMSO-d6
NO2
f1 (ppm)

^{13}C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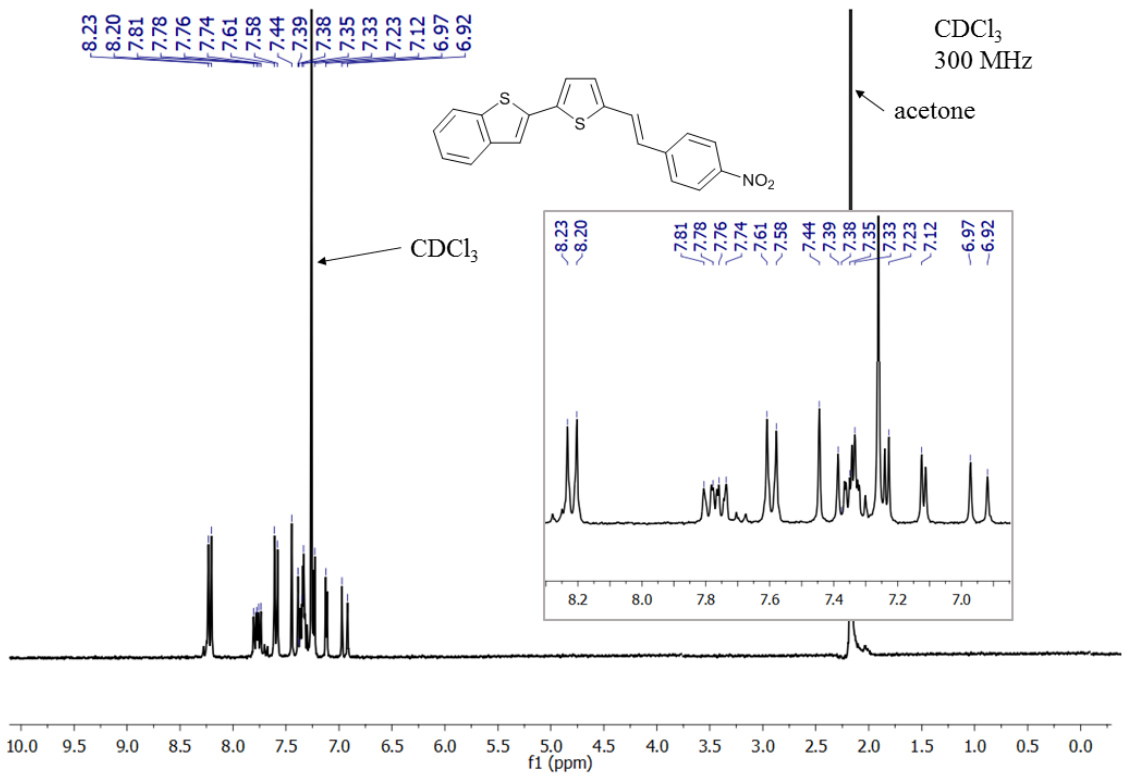
CDCl3
NO2
f1 (ppm)

1c

^{1}H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7.74
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7.33
7.23
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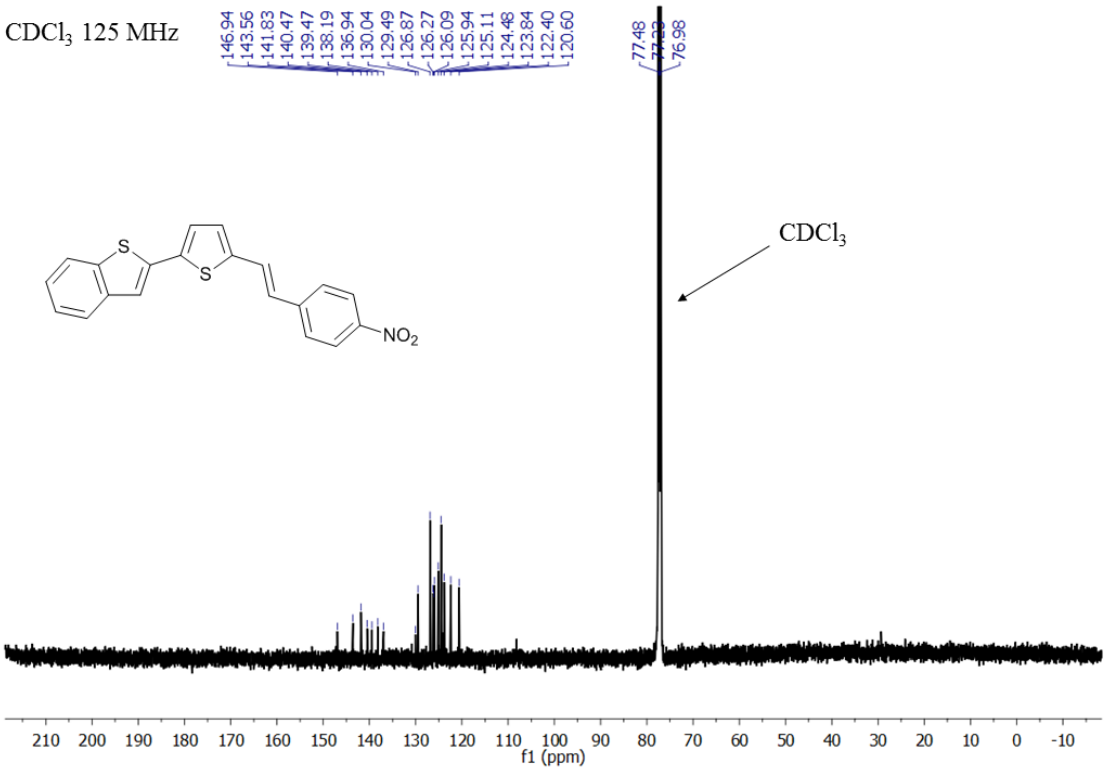
6.97
6.92
CDCl3
300 MHz
acetone
CDCl3
S
S
NO2
f1 (ppm)

^{13}C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141.83
140.47
139.47
138.19
136.94
130.04
129.49
126.87
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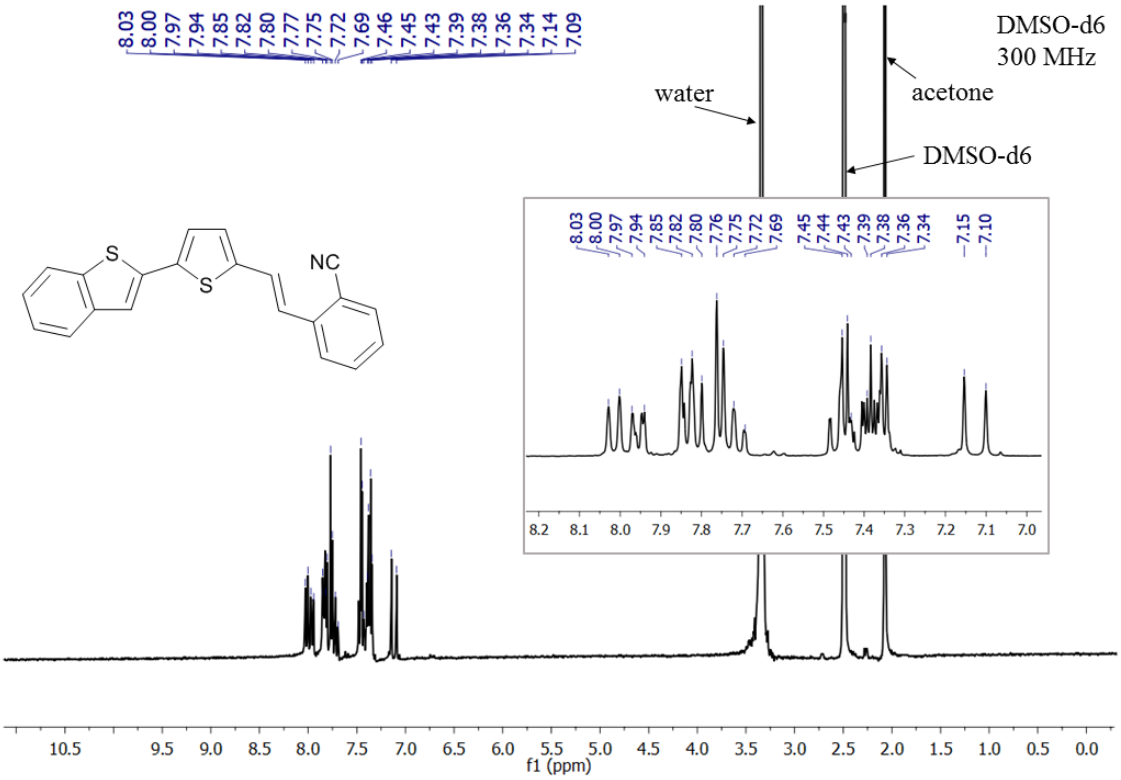
126.09
125.94
125.11
124.48
123.84
122.40
120.60
77.48
77.23
76.98
CDCl3
S
S
NO2
f1 (ppm)

2a

^{1}H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8.00
7.97
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7.75
7.72
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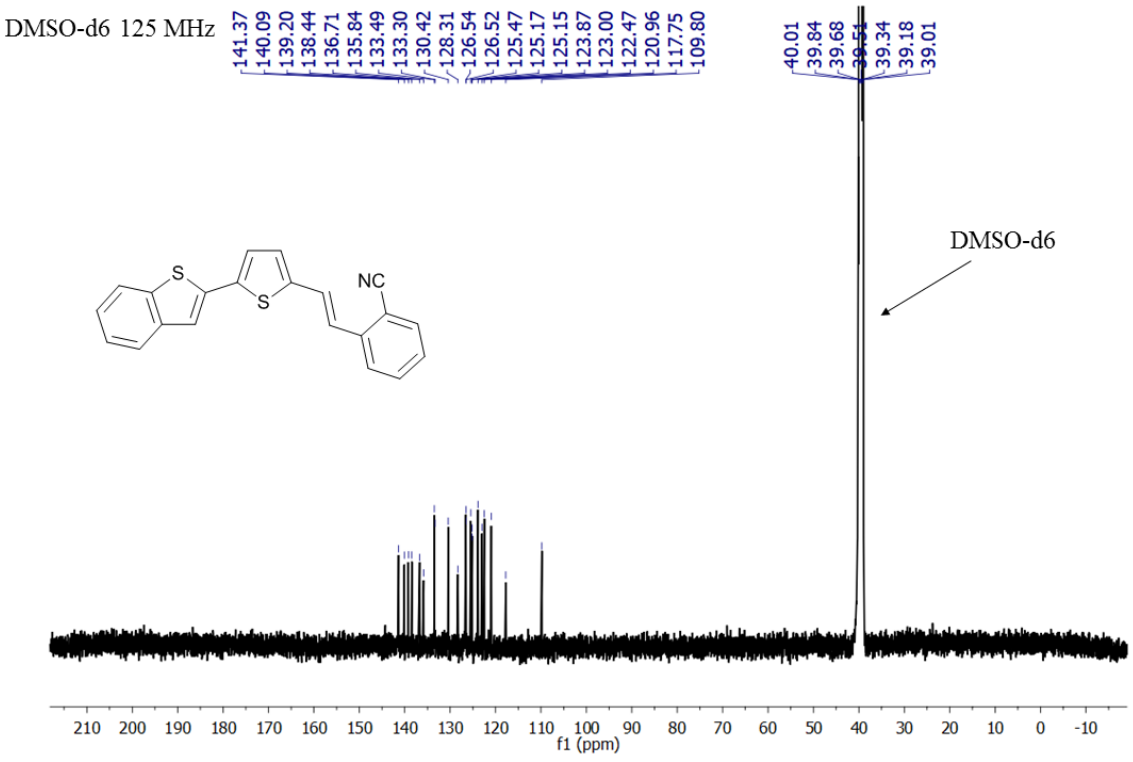
7.46
7.45
7.43
7.39
7.38
7.36
7.34
7.14
7.09
DMSO-d6
300 MHz
water
acetone
DMSO-d6
S
S
NC
f1 (ppm)

^{13}C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125.47
125.17
125.15
123.87
123.00
122.47
120.96
117.75
109.80
40.01
39.84
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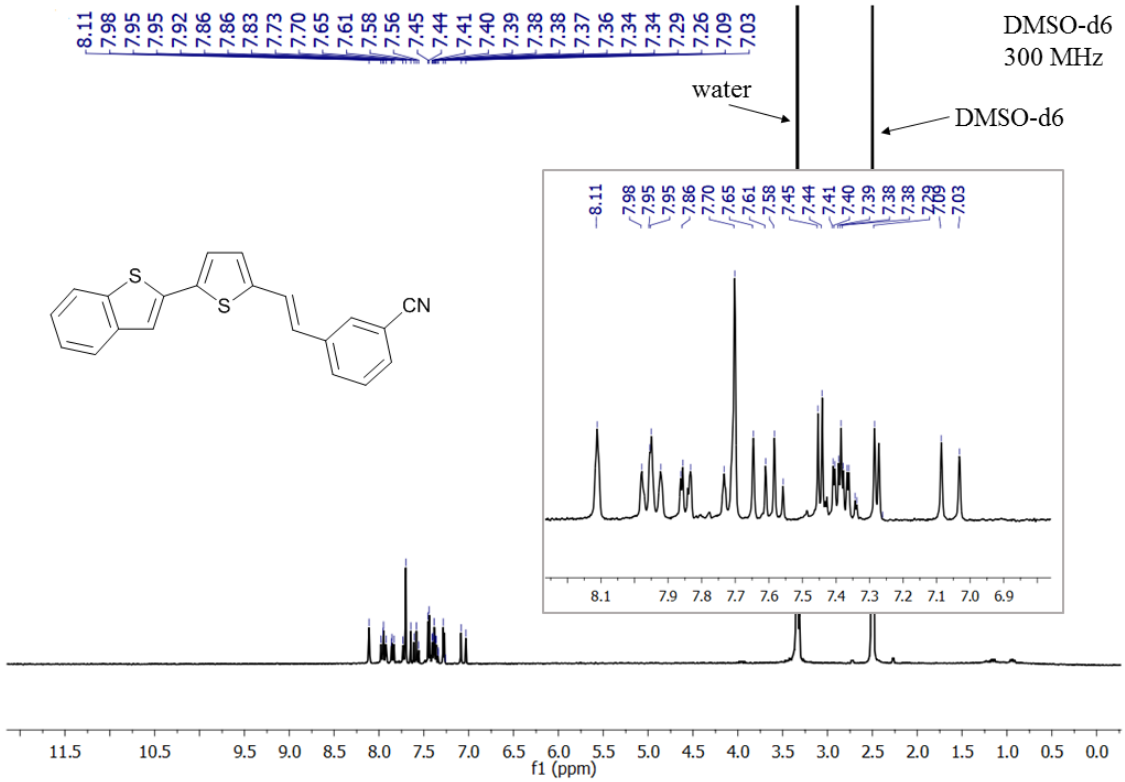
39.34
39.18
39.01
DMSO-d6
S
S
NC
f1 (ppm)

2b

^{1}H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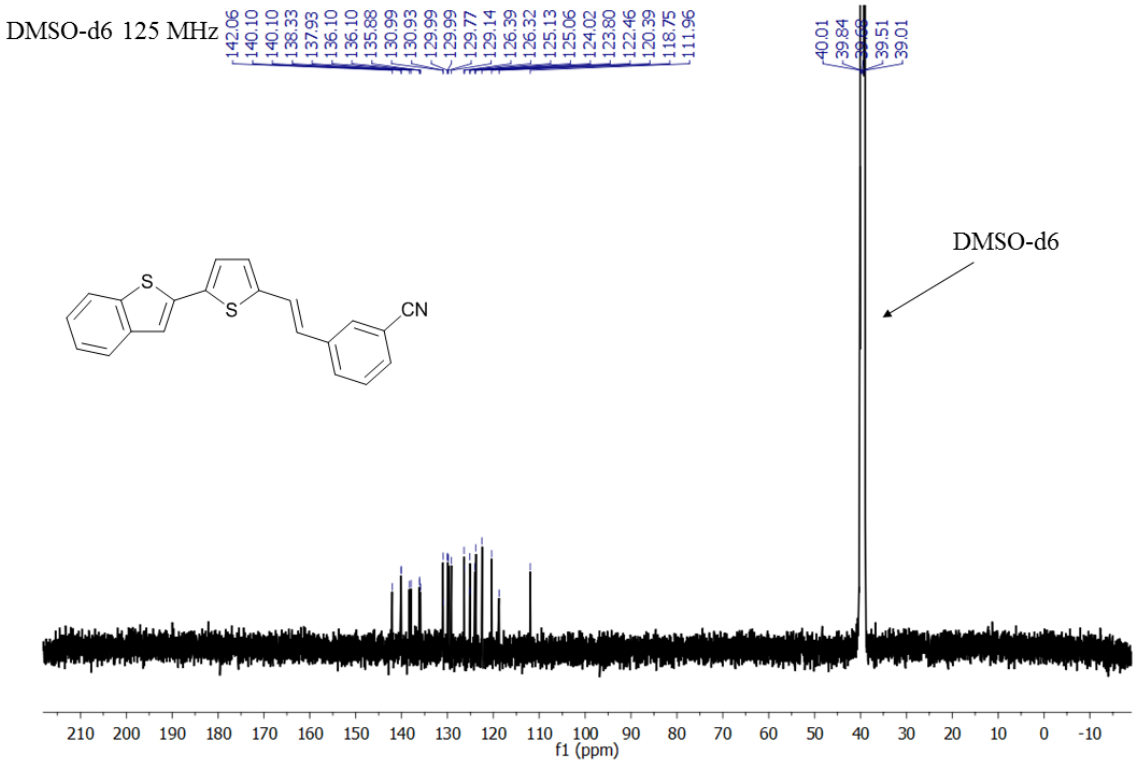
DMSO-d6
300 MHz
water
DMSO-d6
S
S
CN
f1 (ppm)

^{13}C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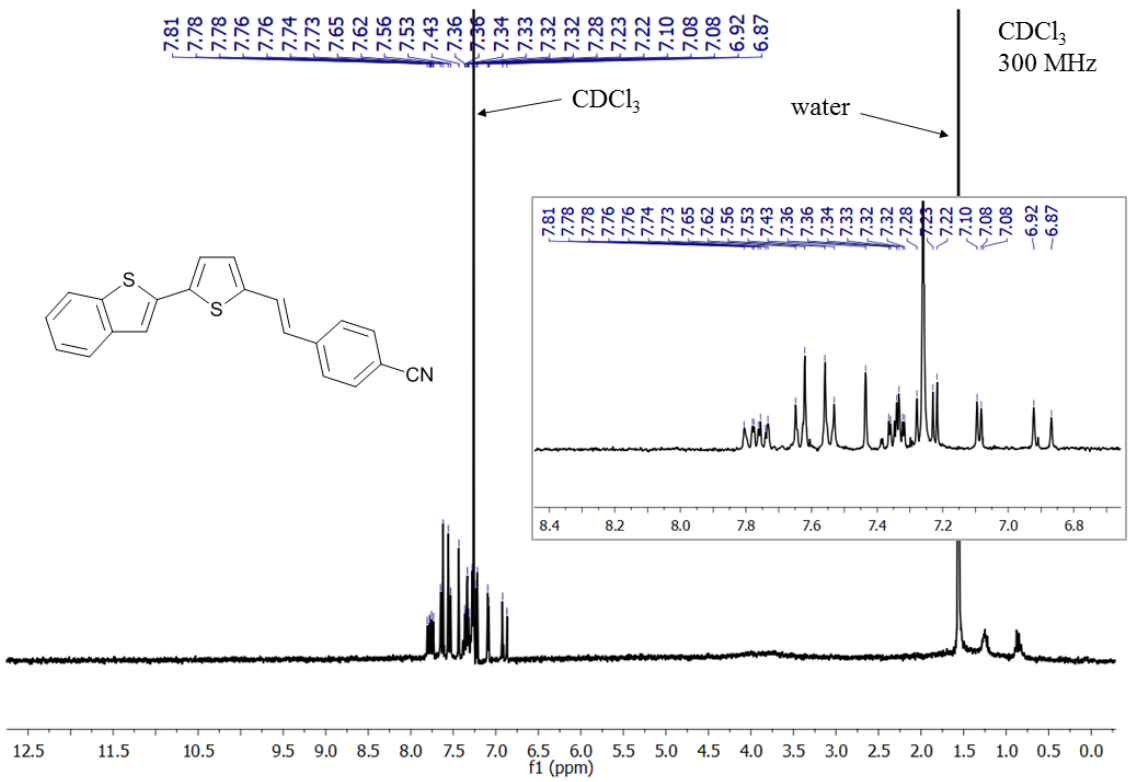
40.01 39.84 39.68 39.51 39.01
DMSO-d6
S
S
CN
f1 (ppm)

2c

^{1}H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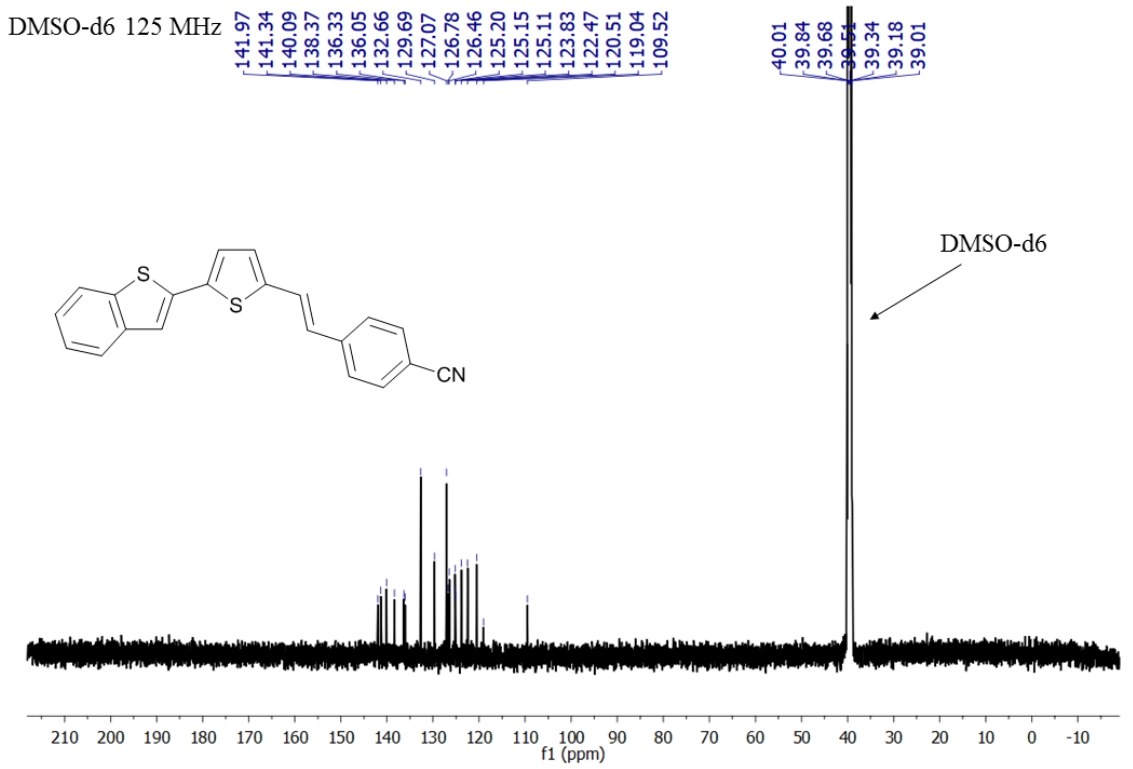
CDCl3
300 MHz
CDCl3
water
S
S
CN
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

^{13}C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40.01 39.84 39.68 39.51 39.34 39.18 39.01
DMSO-d6
S
S
CN
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)

High-resolution mass spectrometry

1a

RT : 3.32 min Scan# : (287,348)
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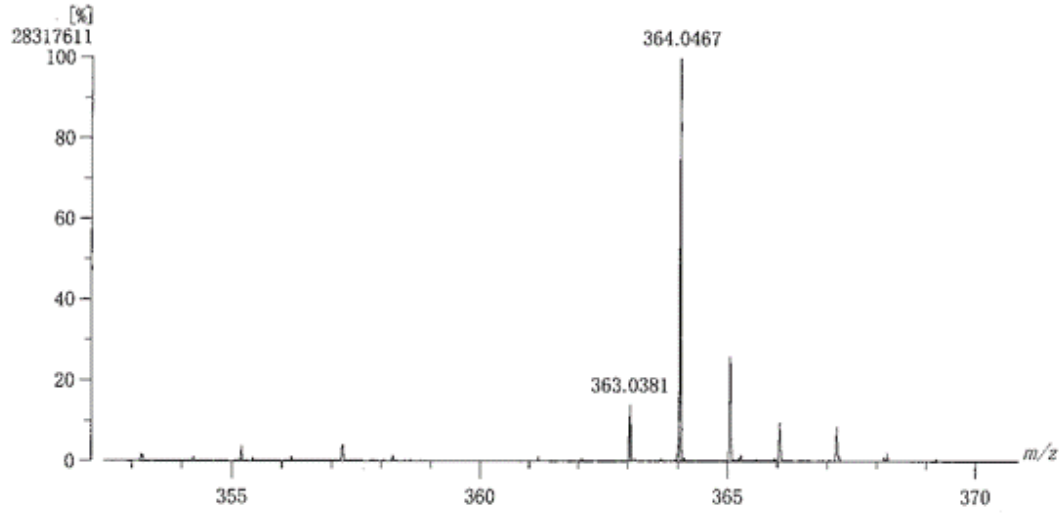

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1	363.0381	13.97	-1.9 / -0.7	17.0	C20 H13 N O2 S2
2	364.0467	100.00	+0.3 / +0.1	16.5	C20 H14 N O2 S2

1b

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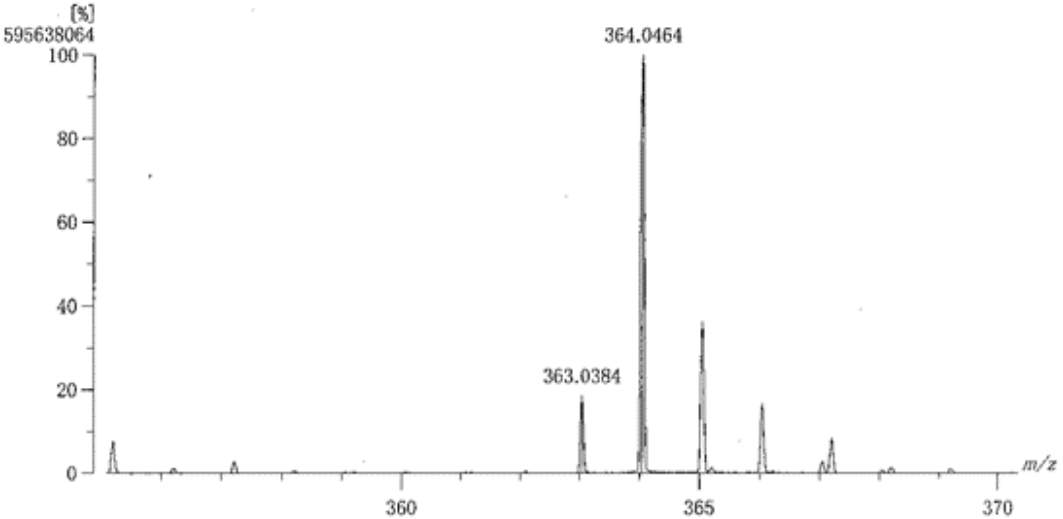

	Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
1	363.0384	18.57	-1.0 / -0.4	17.0	C20 H13 N O2 S2
2	364.0464	100.00	-0.5 / -0.2	16.5	C20 H14 N O2 S2

1c

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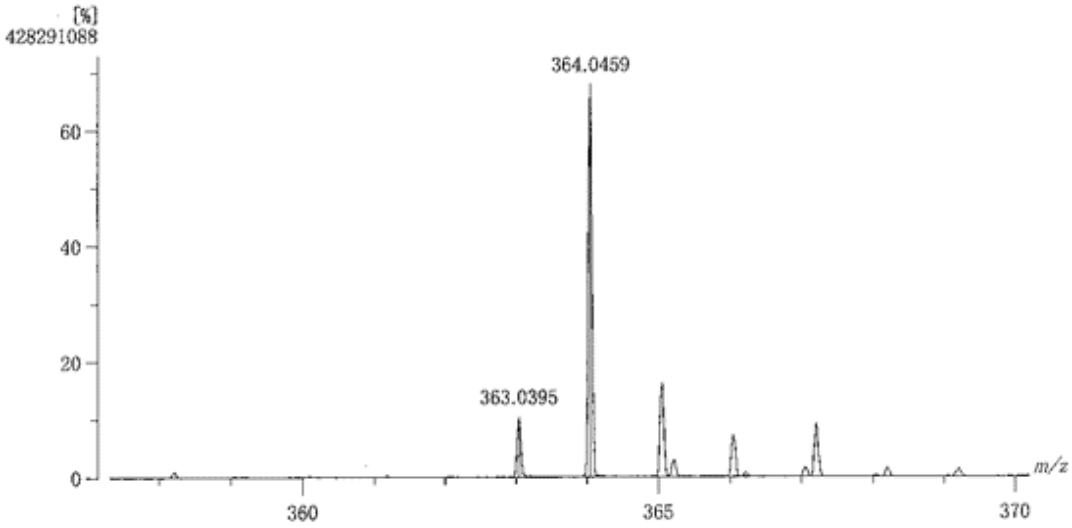

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2a

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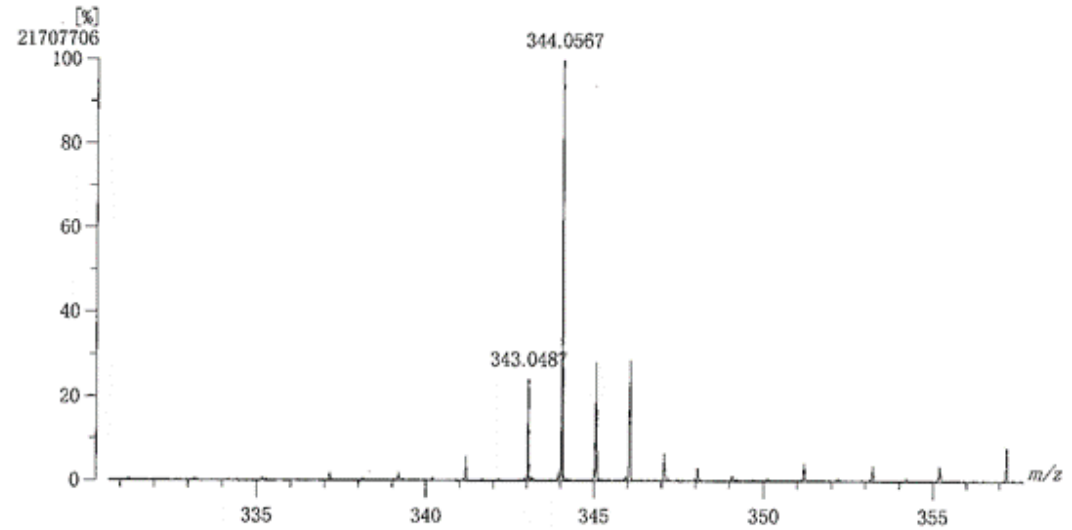

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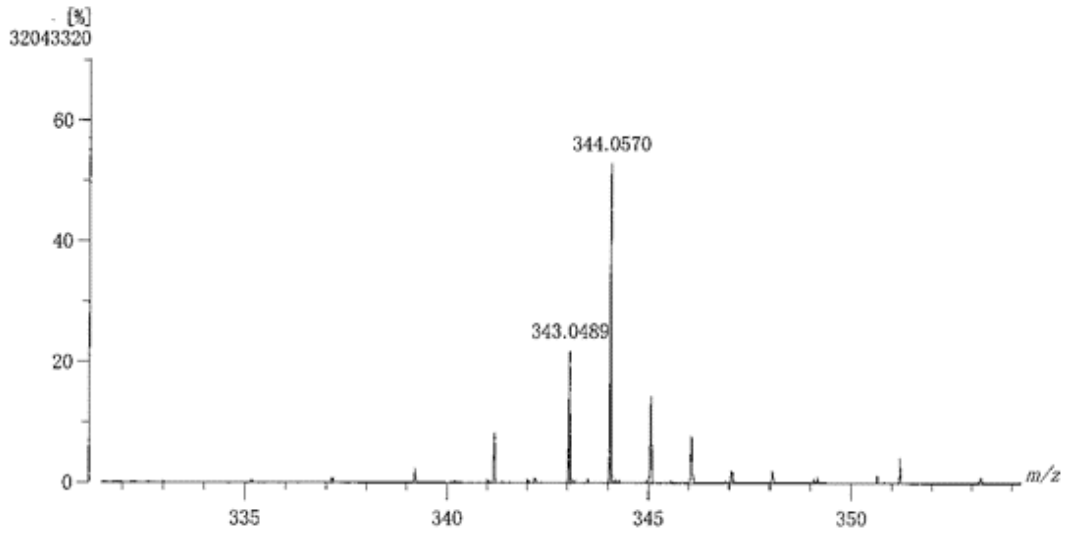
2b

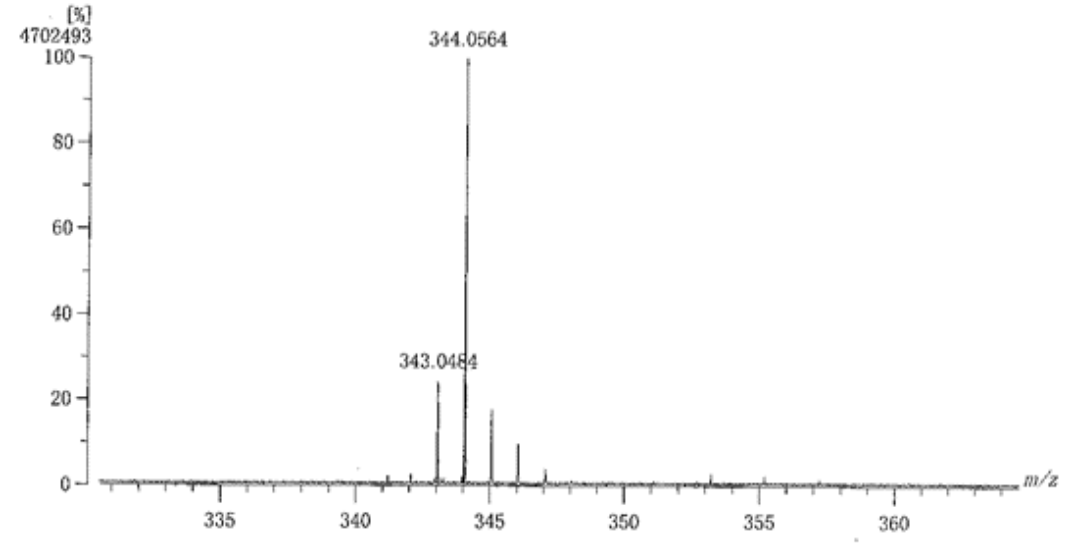
RT : 1.31 min Scan# : (114,229)
Elements : C 24/0, H 49/0, N 1/0, S 2/0
Mass Tolerance : 1000ppm, 1mmu if m/z > 1
Unsaturation (U.S.) : -0.5 - 20.0



	Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
1	343.0489	21.87	-0.1 / -0.0	18.0	C21 H13 N S2
2	344.0570	52.92	+0.7 / +0.2	17.5	C21 H14 N S2

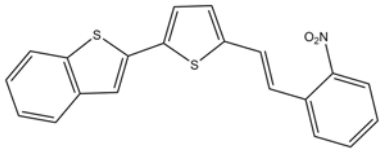
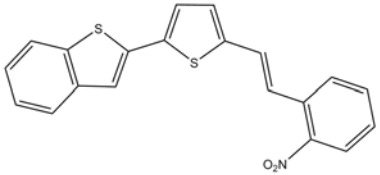
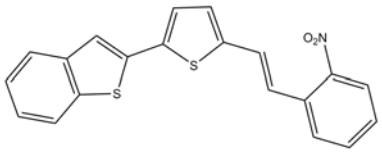
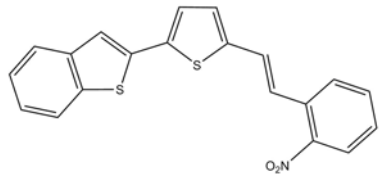
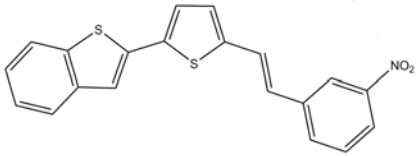
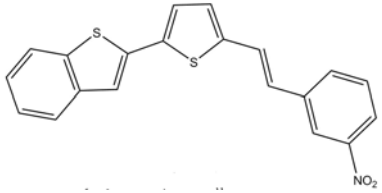
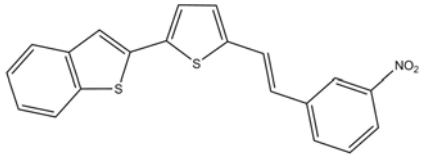
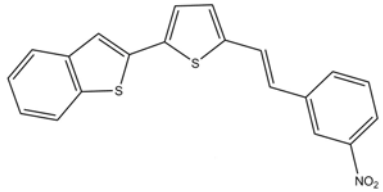
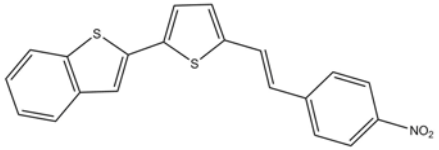
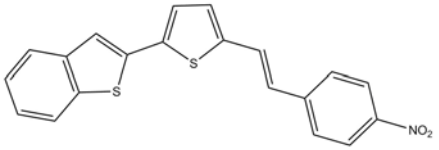
2c

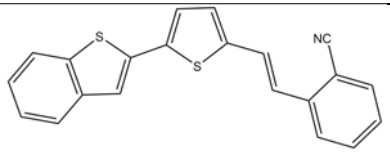
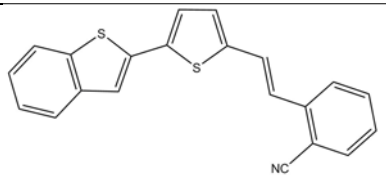
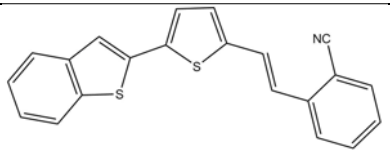
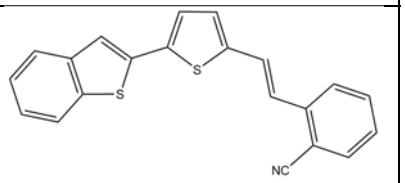
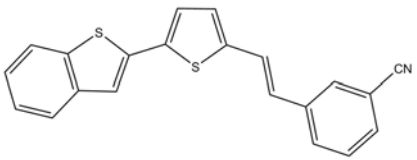
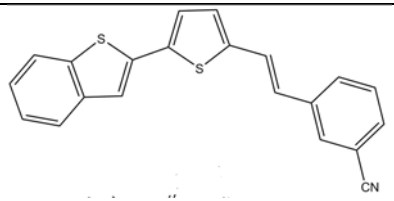
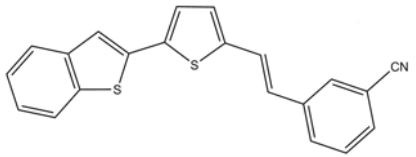
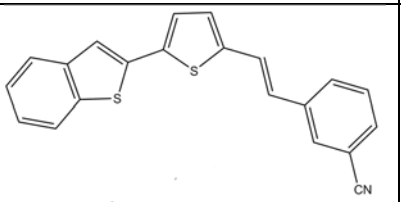
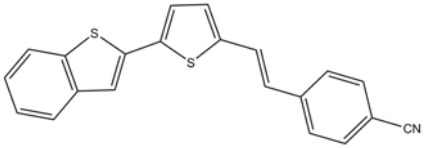
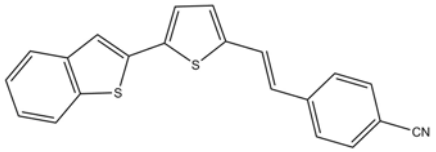
RT : 3.82 min Scan# : (330,387)
Elements : C 24/0, H 49/0, N 1/0, S 2/0
Mass Tolerance : 1000ppm, 1mmu if m/z > 1
Unsaturation (U.S.) : -0.5 - 20.0



	Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
1	343.0484	24.45	-1.6 / -0.5	18.0	C21 H13 N S2
2	344.0564	100.00	-1.1 / -0.4	17.5	C21 H14 N S2

Examined conformers

position	Examined NO_2-substituted structures			
ortho				
meta				
para				

position	Examined CN-substituted structures			
ortho				
meta				
para				

Optimized geometries

All geometries included below were optimized with M06-2X/6-31G(d) method, using LR-PCM approach to take into account chloroform solution[1,2]. The coordinates are given in Å units.

1a

Total energy + ZPE = -1770.682325

6	-4.7253471558	1.8773171446	0.4839859602
6	-4.5493463259	0.5159872067	0.1861047005
6	-5.7167419710	-0.1881681338	-0.1562641855
6	-6.9741171906	0.4049094613	-0.2092985795
6	-7.1006529288	1.7588783149	0.0630423756
6	-5.9670615142	2.4934774317	0.4090316648
6	-3.2186907814	-0.0963999397	0.3100491764
6	-2.0796693051	0.5787935142	0.0822105465
6	-0.7483024512	0.0172199152	0.2464594184
16	0.6379839724	0.9589579468	-0.2162565404
6	1.7338360310	-0.3014746385	0.2519003384
6	1.0445368522	-1.3902116695	0.7312745717
6	-0.3599586489	-1.2097264704	0.7301518959
6	3.1689232914	-0.1324628296	0.1180105952
6	3.8619409030	1.0022993631	-0.1747254652
6	5.2841746506	0.8033885054	-0.2264085354
6	5.6393813990	-0.5346059436	0.0435342256
16	4.2273398792	-1.5189794082	0.3424009980
6	6.9711169147	-0.9541680043	0.0509459664
6	7.9553998742	-0.0146373995	-0.2168731630
6	7.6213540220	1.3234283176	-0.4872300206
6	6.3005862856	1.7362539739	-0.4931043896
7	-5.6659095277	-1.6107633660	-0.5163122633
8	-6.6806136667	-2.2690403787	-0.3617090829
8	-4.6254728250	-2.0583077714	-0.9689408904
1	7.2283766697	-1.9875038529	0.2602331942
1	8.9971578795	-0.3185746676	-0.2171762662
1	8.4103557289	2.0394250306	-0.6932871480
1	6.0420018943	2.7702473675	-0.7011454504
1	-1.0597840346	-1.9586451908	1.0819310578
1	1.5351097291	-2.2899297065	1.0869677874
1	3.3885758047	1.9646279728	-0.3410047074
1	-2.1287051124	1.6062074943	-0.2734120557
1	-3.1743728375	-1.1424843272	0.5922425207
1	-3.8642771198	2.4494302677	0.8125300783
1	-6.0534845101	3.5497454120	0.6418558296
1	-8.0742060270	2.2331347539	0.0122635273
1	-7.8300432487	-0.2017970748	-0.4777066198

1b

Total energy + ZPE = -1770.687995

6	-4.4980280081	1.7764532207	-0.0546727536
6	-4.2405048869	0.3955081364	-0.0022623083
6	-5.3332693289	-0.4780990391	0.0233107158
6	-6.6196835172	0.0394015773	-0.0058159180
6	-6.8852974454	1.4000055963	-0.0593967125
6	-5.7969851299	2.2683850245	-0.0833195924
6	-2.8898060473	-0.1755481934	0.0279613433
6	-1.7388397823	0.5167134293	-0.0135645962
6	-0.4161640594	-0.0852989183	0.0216366418
6	-0.0414065801	-1.4051720061	0.1167015966
6	1.3627262857	-1.5879557498	0.1232043830
6	2.0663181646	-0.4099718963	0.0340217290
16	0.9842853143	0.9417658055	-0.0675846108
6	3.5045115046	-0.2175633900	0.0209523685
6	4.1997918144	0.9496292409	0.1101205421
6	5.6245146421	0.7683965791	0.0667455835
6	5.9793791716	-0.5910442624	-0.0566429157
16	4.5642119662	-1.6132730576	-0.1275097036
6	7.3133149532	-0.9998990736	-0.1127278569
6	8.2998875036	-0.0275974914	-0.0437240186
6	7.9660442734	1.3319085091	0.0801866475
6	6.6431222566	1.7338572140	0.1359408948
7	-7.7514043434	-0.8982066963	0.0219053363
8	-7.5034529739	-2.0901030547	0.0705449905
8	-8.8763598508	-0.4313656272	-0.0051928216
1	-3.6732851341	2.4813038798	-0.0717268876
1	-5.9667858129	3.3387003784	-0.1236785539
1	-7.9070998613	1.7565736900	-0.0801046753
1	-5.1892546724	-1.5515995147	0.0652034897
1	-2.8513966259	-1.2615886131	0.0874793892
1	-1.7613475826	1.6022278491	-0.0786130317
1	-0.7499058369	-2.2223582827	0.1854053743
1	1.8424070714	-2.5577056092	0.2020636012
1	3.7257952913	1.9201912550	0.2157232621
1	6.3844971187	2.7841289870	0.2324097053
1	8.7568706362	2.0731601981	0.1329156687
1	9.3433896240	-0.3225157078	-0.0858659242
1	7.5707376418	-2.0498571768	-0.2077917263

1c

Total energy + ZPE = -1770.688929

6	6.5229869695	2.0620124086	-0.0108731352
6	5.6105043056	0.9933407531	-0.0085063603
6	6.1047617797	-0.3268842698	-0.0511191414
6	7.4737983076	-0.5977242513	-0.0963456472
6	8.3536582032	0.4742752815	-0.0990074799
6	7.8802870882	1.7968891705	-0.0563513094
16	4.8043611472	-1.4933878226	-0.0419290829
6	3.6049815831	-0.2087714820	0.0287382710
6	4.1748916728	1.0277766253	0.0380794327
6	2.1949578319	-0.5487560569	0.0691612101
16	0.9760832161	0.6781517385	-0.0557428207
6	-0.3070662750	-0.4873232151	0.0843928198
6	0.2059641896	-1.7571002530	0.2157358491
6	1.6207343078	-1.7912790774	0.2055057830
6	-1.6861060107	-0.0333245119	0.0510257149
6	-2.7556380342	-0.8489233981	0.0626338264
6	-4.1562949629	-0.4227999610	0.0398179589
6	-5.1516972898	-1.4010900497	-0.1201917800
6	-6.4960639158	-1.0634598369	-0.1594756174
6	-6.8430998509	0.2752837475	-0.0317562420
6	-5.8903142056	1.2754777628	0.1374656829
6	-4.5528270842	0.9199487931	0.1753226491
7	-8.2578133133	0.6460670323	-0.0697474982
8	-8.5423210367	1.8260846910	0.0498417127
8	-9.0775641308	-0.2444940040	-0.2195398726
1	7.8389754951	-1.6191186028	-0.1282461616
1	9.4220459392	0.2873366592	-0.1343071433
1	8.5896350867	2.6181365805	-0.0588568581
1	6.1567016321	3.0837577422	0.0228481601
1	-0.4121071082	-2.6403046173	0.3268006296
1	2.2009735287	-2.7020173563	0.3078611864
1	3.6027989071	1.9488359708	0.0858755389
1	-1.8288295966	1.0440487604	0.0055449116
1	-2.5994033164	-1.9259541375	0.0744093312
1	-4.8613452330	-2.4425468525	-0.2193185332
1	-7.2668962181	-1.8133738549	-0.2858028968
1	-6.2042990564	2.3064884862	0.2422144463
1	-3.8120970315	1.6978847012	0.3240307029

2a

Total energy + ZPE = -1658.481218

6	5.1570272101	-1.7051611045	-0.3130887152
6	4.8932791025	-0.3457054233	-0.0932708732
6	5.9993750842	0.4878466062	0.1812688147
6	7.3017505266	-0.0194695452	0.2503214461
6	7.5266263309	-1.3724236376	0.0432638939
6	6.4475311708	-2.2113604991	-0.2402920530
6	3.5418746739	0.2174193707	-0.1500509854
6	2.4066880282	-0.5009716346	-0.0918671402
6	1.0726590902	0.0688408367	-0.1701101977
16	-0.3079107741	-0.9547026584	0.0956141412
6	-1.4131803302	0.3592280225	-0.1505688975
6	-0.7311232112	1.5228491011	-0.4191155722
6	0.6749075542	1.3589521728	-0.4328325858
6	-2.8472801248	0.1548538706	-0.0670069425
6	-3.5242457973	-1.0149287694	0.0982454499
6	-4.9507368441	-0.8471138238	0.1349925310
6	-5.3260414564	0.5045379089	-0.0112045384
16	-3.9279022046	1.5375693076	-0.1841166632
6	-6.6651936021	0.8997786277	-0.0076207108
6	-7.6364648883	-0.0783996204	0.1448543617
6	-7.2822959622	-1.4305228267	0.2911423258
6	-5.9541920837	-1.8189995747	0.2870313933
6	5.8018730866	1.8951544482	0.4070941847
7	5.6463665379	3.0287294159	0.5863072376
1	-6.9382589272	1.9439491147	-0.1210821566
1	-8.6836973903	0.2060359079	0.1508113411
1	-8.0613824762	-2.1767965342	0.4084115835
1	-5.6801014249	-2.8636971486	0.3996973592
1	1.3689626706	2.1649391340	-0.6406299854
1	-1.2274470905	2.4678983082	-0.6120959682
1	-3.0357279219	-1.9800557316	0.1868668770
1	2.4570593835	-1.5801468143	0.0363541398
1	3.4778296552	1.3011392951	-0.2211364801
1	4.3400317812	-2.3727430208	-0.5655752554
1	6.6162573066	-3.2686447376	-0.4173923347
1	8.5342808772	-1.7697791956	0.0937898748
1	8.1236103798	0.6545020320	0.4667595710

2b

Total energy + ZPE = -1658.480817

6	-4.9639029684	1.6499174402	-0.0732643564
6	-4.6858429938	0.2744519095	-0.0034442717
6	-5.7649620252	-0.6145506836	0.0372924518
6	-7.0780563220	-0.1386262436	0.0069359467
6	-7.3425743242	1.2318130351	-0.0642152486
6	-6.2709125689	2.1189360570	-0.1035868242
6	-3.3260258015	-0.2748451088	0.0299417421
6	-2.1855828494	0.4337735819	-0.0229657449
6	-0.8540378427	-0.1486716803	0.0144412466
16	0.5312765089	0.8989636419	-0.0731448449
6	1.6332410085	-0.4365740251	0.0305089745
6	0.9470349127	-1.6247098520	0.1188191393
6	-0.4596883853	-1.4627816427	0.1099782845
6	3.0685315787	-0.2236101575	0.0199587518
6	3.7478076917	0.9522672898	0.1178589547
6	5.1750114450	0.7905790889	0.0749376194
6	5.5482946057	-0.5631300969	-0.0570322028
16	4.1471994654	-1.6037659343	-0.1370825141
6	6.8875889414	-0.9539128774	-0.1138680750
6	7.8611131994	0.0308688867	-0.0369490821
6	7.5089783775	1.3849226017	0.0955565889
6	6.1807104541	1.7689011319	0.1520780288
6	-8.1707754663	-1.0756083429	0.0502269091
7	-9.0497462914	-1.8279018272	0.0850952692
1	7.1589792619	-1.9997378210	-0.2155503497
1	8.9085064125	-0.2498679281	-0.0795168320
1	8.2897622273	2.1362984611	0.1544291885
1	5.9081750999	2.8150012159	0.2552694867
1	-1.1559867489	-2.2905576017	0.1764504347
1	1.4410007149	-2.5872009932	0.1986716845
1	3.2603985483	1.9154367885	0.2300834477
1	-2.2241851029	1.5180672391	-0.0997430166
1	-3.2697941846	-1.3594349041	0.1030898379
1	-4.1502378103	2.3672711540	-0.1028192283
1	-6.4584697395	3.1859296122	-0.1574859318
1	-8.3662541020	1.5883885109	-0.0869199515
1	-5.5849905566	-1.6839060677	0.0927590974

2c

Total energy + ZPE = -1658.481649

6	5.6347176016	-1.3014145572	0.0967448844
6	4.6305782895	-0.3292059585	-0.0343764393
6	5.0163665474	1.0187566890	-0.1345877808
6	6.3513947571	1.3819436675	-0.0911291460
6	7.3379838179	0.3961948052	0.0483026606
6	6.9756735537	-0.9515063065	0.1402466297
6	3.2328576433	-0.7665183811	-0.0644052793
6	2.1548506037	0.0370159082	-0.0401336084
6	0.7806118883	-0.4327200859	-0.0810986897
16	-0.5168403800	0.7154613762	0.0718763188
6	-1.7210385475	-0.5243283928	-0.0710017588
6	-1.1317814804	-1.7579710035	-0.2200448215
6	0.2827571275	-1.7066986447	-0.2275177241
6	-3.1353848349	-0.2024942922	-0.0315943498
6	-3.7241937471	1.0241491210	-0.0811301318
6	-5.1590132121	0.9695088563	-0.0235593943
6	-5.6326079309	-0.3557926507	0.0686675672
16	-4.3143119917	-1.5017015561	0.0950911294
6	-6.9969823020	-0.6459780882	0.1310973344
6	-7.8935705998	0.4116121312	0.1008273144
6	-7.4410544636	1.7389402043	0.0085377616
6	-6.0882490172	2.0231964998	-0.0541922453
6	8.7247507979	0.7719333983	0.0908612844
7	9.8417854754	1.0752764376	0.1254297710
1	-7.3458764427	-1.6711982744	0.2009798707
1	-8.9587095054	0.2095469689	0.1488063744
1	-8.1630595338	2.5487724209	-0.0141052785
1	-5.7383520857	3.0486633513	-0.1266354647
1	0.9113843090	-2.5811313308	-0.3481200683
1	-1.7012666303	-2.6739163860	-0.3358143412
1	-3.1662556933	1.9508847385	-0.1690928662
1	2.2852904312	1.1151297878	0.0215773194
1	3.0869125114	-1.8447877602	-0.0953030945
1	5.3536831327	-2.3479152442	0.1691932262
1	7.7418423762	-1.7120908068	0.2443852687
1	6.6397619815	2.4246038352	-0.1696598092
1	4.2685861084	1.7946090625	-0.2587831180

References

(1) Jacquemin, D.; Bahers, T. L.; Adamo, C.; Ciofini, I. What Is the "Best" Atomic Charge Model to Describe through-Space Charge-Transfer Excitations? *Phys. Chem. Chem. Phys.* **2012**, *14*, 5383. https://doi.org/10.1039/c2cp40261k.

(2) Le Bahers, T.; Adamo, C.; Ciofini, I. A Qualitative Index of Spatial Extent in Charge-Transfer Excitations. *J. Chem. Theory Comput.* **2011**, *7* (8), 2498–2506. https://doi.org/10.1021/ct200308m.