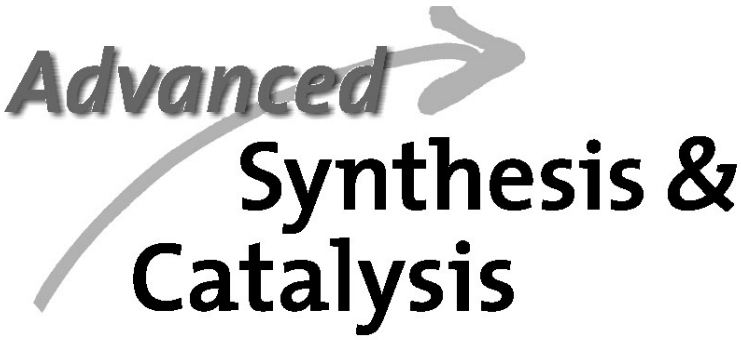

Supporting Information

Supporting Information

The Chan-Lam Reaction of Chalcogen Elements Leading to Aryl Chalcogenides

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1. General information

All chemicals were used as received without further purification unless stated otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a 300 MHz NMR spectrometer (75 MHz for ^{13}C). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0 ppm) as the internal standard. The coupling constants J are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh).

2. Synthetic procedures

General procedure for the synthesis of aryl sulfides/selenides: Under N_2, the mixture of arylboronic acid (0.4 mmol), sulfur/selenium powder (0.8 mmol), CuF_2 (10 mol %) in Py/DMSO (2 mL, 2 : 1) was stirred under 100 ^{o}C for 12 h. After the completion of the reaction (monitored by TLC), the solvent was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc as the eluent to give the desired product.

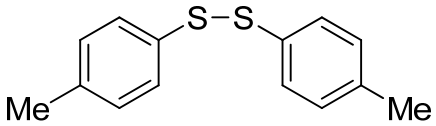
General procedure for the synthesis of aryl thiols: Under N_2, the mixture of arylboronic acid (0.4 mmol), sulfur powder (0.8 mmol), CuF_2 (10 mol %) in Py/DMSO (2 mL, 2 : 1) was stirred at 100 ^{o}C for 12 h. To this reaction mixture, $NaBH_4$ (1 mmol) was added. After the resultant reaction solution was stirred at 40 ^{o}C for 5 h, water was added to quench the reaction. The mixture was extracted with ethyl acetate, and the combined organic layer was washed with H_2O and brine, dried over Na_2SO_4. The solvent was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel to give the desired product.

General procedure for the synthesis of unsymmetrical monosulfides: Under N_2, the mixture of arylboronic acid (0.4 mmol), sulfur powder (0.8 mmol), CuF_2 (10 mol %) in Py/DMSO (2 mL, 2 : 1) was stirred at 100 ^{o}C for 12 h. To this reaction mixture,

$NaBH_4$ (1 mmol) was added. After the resultant reaction solution was stirred at 40 ^oC for 5 h, aryl/alkyl iodide (0.6 mmol) was added and stirred at 100 ^oC for another 20 h. The reaction mixture was extracted with ethyl acetate. The organic layer was washed with H_2O and brine, dried over Na_2SO_4. After removal of the solvent in vacuum, the residue was purified by flash column chromatography on silica gel to give the desired unsymmetrical monosulfides.

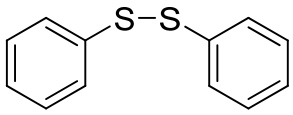
3. Characterization data for the products

dis(4-methylphenyl) disulfide (2a)[1]



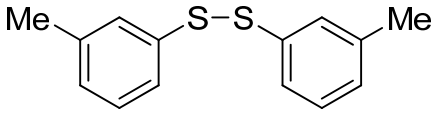
White solid (46.3 mg, 94% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.39 (d, J = 8.2 Hz, 4H), 7.11 (d, J = 8.0 Hz, 4H), 2.32 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.4, 133.8, 129.8, 128.5, 21.1.

diphenyl disulfide (2b)[1]



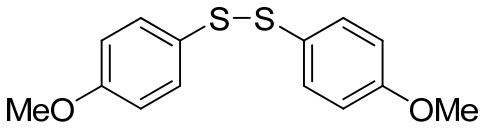
White solid (41.4 mg, 95% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.55-7.53 (m, 4H), 7.36-7.27 (m, 4H), 7.25-7.23 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 136.9, 129.0, 127.4, 127.1.

bis(3-methylphenyl) disulfide (2c)[2]



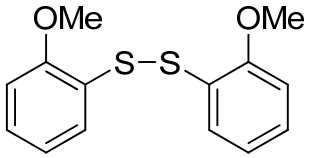
White solid (34.9 mg, 71% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.48 (s, 4H), 7.32 (t, J = 7.6 Hz, 2H), 7.16 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.7, 136.8, 128.7, 127.9, 124.4, 21.2.

bis(4-methoxyphenyl) disulfide (2d)[1]



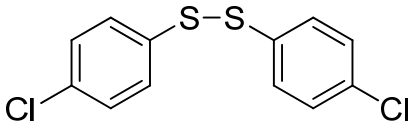
White solid (52.8 mg, 95% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.40 (d, J = 8.9 Hz, 4H), 6.84 (d, J = 8.8 Hz, 4H), 3.80 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.9, 132.7, 128.4, 114.6, 55.4.

bis(2-methoxyphenyl) disulfide (2e)[3]



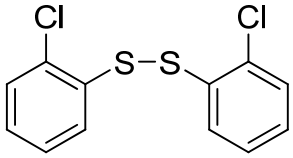
White solid (36.1 mg, 65% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.53 (d, J = 7.7 Hz, 2H), 7.19 (t, J = 7.5 Hz, 2H), 6.93-6.84 (m, 4H), 3.90 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.2, 129.2, 128.0, 120.4, 118.4, 117.1, 55.3.

bis(4-chlorophenyl) disulfide (2f)[1]



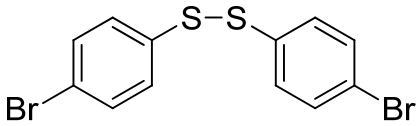
White solid (51.5 mg, 90% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.40 (d, J = 8.6 Hz, 4H), 7.29 (d, J = 8.7 Hz, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 135.0, 133.6, 129.3 (One carbon is invisible because of overlapping.).

bis(2-chlorophenyl) disulfide (2g)[1]



White solid (53.8 mg, 94% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.55 (d, J = 7.9 Hz, 2H), 7.37 (d, J = 7.6 Hz, 2H), 7.16-7.23 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 134.4, 131.8, 129.7, 127.8, 127.6, 127.2.

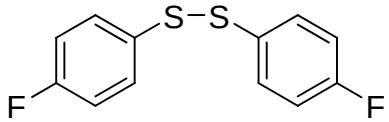
bis(4-bromophenyl) disulfide (2h)[4]



White solid (63.6 mg, 85% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.43 (d, J = 8.6 Hz, 4H), 7.33 (d, J = 8.6 Hz, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 135.7, 132.2, 129.4,

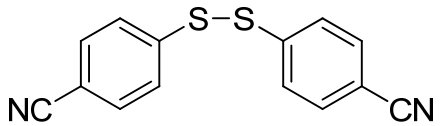
121.5.

bis(4-fluophenyl) disulfide (2i)[4]



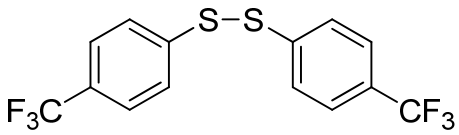
White solid (40.6 mg, 80% yield). ^{1}HNMR ($CDCl_3$, 300MHz): δ 6.95-6.89 (m, 2H), 6.80-6.75 (m, 2H), 0.25 (s, 9H); ^{13}CNMR ($CDCl_3$, 75MHz): δ 163.0 (d, $J_{C\text{-}F}$ = 245.7 Hz), 133.2 (d, $J_{C\text{-}F}$ = 8.4 Hz), 131.2 (d, $J_{C\text{-}F}$ = 8.3 Hz), 116.2 (d, $J_{C\text{-}F}$ = 23.3 Hz).

bis(4-cyanophenyl) disulfide (2j)[6]



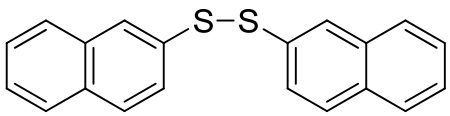
White solid (36.4 mg, 68% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.61 (d, J = 8.8 Hz, 4H), 7.55 (d, J = 8.8 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 142.1, 132.8, 126.5, 117.9, 110.9.

bis(4-(trifluoromethyl)phenyl) disulfide (2k)[6]



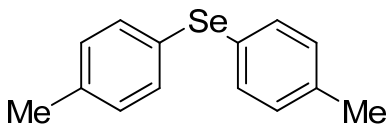
White solid (31.9 mg, 45% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.60-7.26 (m, 8H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 140.8, 129.8, 128.4, 126.6, 123.8 ($J_{C\text{-}F}$ = 270 Hz).

bis(2-naphthyl phenyl) disulfide (2l)[1]



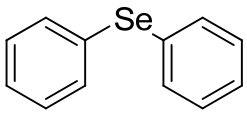
White solid (53.4 mg, 84% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.99 (s, 2H), 7.80-7.72 (m, 6H), 7.64-7.60 (m, 2H), 7.49-7.42 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 134.3, 133.3, 131.0, 129.9, 129.2, 128.9, 127.8, 127.6, 127.3, 127.1.

di(4-methylphenyl) selenide (4a)[7]



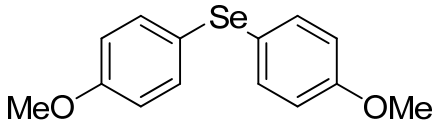
White solid (44.5 mg, 85% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.38 (d, J = 8.1 Hz, 4H), 7.10 (d, J = 7.8 Hz, 4H), 2.34 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.2, 132.9, 130.1, 127.7, 21.1.

diphenyl selenide (4b)[7]



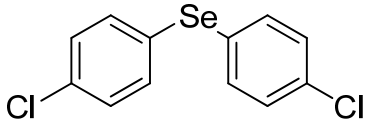
White solid (34.2 mg, 73% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.63-7.59 (m, 4H), 7.29-7.25 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 132.8, 131.5, 129.1, 127.6.

di(4-methoxyphenyl) selenide (4c)[7]



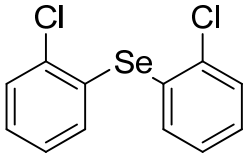
White solid (46.5 mg, 79% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): 7.40 (d, J = 8.8 Hz, 4H), 6.81 (d, J = 8.8 Hz, 4H), 3.79 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.2, 134.6, 122.1, 115.0, 55.3.

di(4-chlorophenyl) selenide (4d)[7]



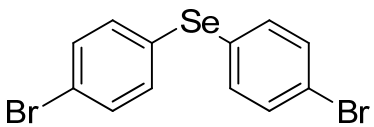
White solid (51.3 mg, 83% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): 7.38 (d, J = 8.5 Hz, 4H), 7.25 (d, J = 8.4 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 134.3, 133.9, 129.6, 129.0.

di(2-chlorophenyl) selenide (4e)[8]



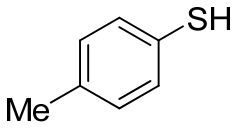
White solid (50.1 mg, 83% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.62-7.59 (m, 4H), 7.35-7.32 (m, 2H), 7.18-7.15 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ. 133.2, 130.7, 129.3, 129.1, 128.4, 127.9.

di(4-bromophenyl) selenide (4f)[7]



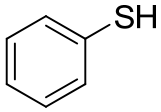
White solid (49.9 mg, 64 % yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.40 (d, J = 8.6 Hz, 4H), 7.30 (d, J = 8.6 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 134.6, 132.6, 129.6, 122.0.

4-methylbenzenethiol (5a)[9]



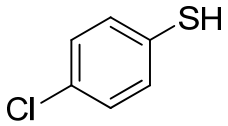
White solid (39.2 mg, 79% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.19 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 3.39 (s, 1H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 135.1, 129.8, 129.7, 126.5, 21.0.

benzenethiol (5b)[9]



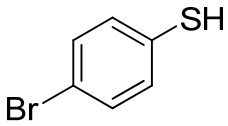
Colorless liquid (35.2 mg, 80% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.27-7.10 (m, 5H), 3.43 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 130.7, 129.3, 129.0, 125.5.

4-chlorobenzenethiol (5c)[9]



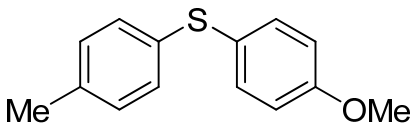
White solid (46.6 mg, 81% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.20 (s, 4H), 3.45 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 131.7, 130.7, 129.1, 129.1.

4-bromobenzenethiol (5d)[10]



White solid (59.7 mg, 79% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.5 Hz, 2H), 3.44 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 132.1, 131.0, 129.9, 119.4.

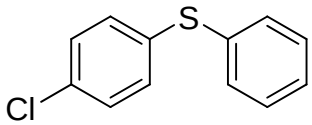
4-methoxyphenyl 4-methylphenyl sulfide (3ab)[11]



Colorless oil (73.6 mg, 80% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.42 (d, J = 8.9 Hz, 2H), 7.23 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.1 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 3.83

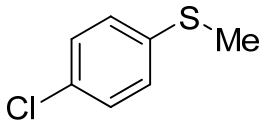
(s, 3H), 2.35 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.4, 136.0, 134.3 (2C), 134.2, 129.7 (2C), 129.3 (2C), 125.5, 114.8 (2C), 55.2, 20.9.

4-chlorophenyl phenyl sulfide (3bc)[11]



Colorless oil (68.6 mg, 78% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.38-7.26 (m, 8H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 135.1, 134.6, 132.9, 132.0, 131.3, 129.3, 129.3, 127.4.

4-chlorophenyl methyl sulfide (3cd)[12]



Colorless oil (48.7 mg, 77% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.24 (d, J = 8.7 Hz, 2H), 7.16 (d, J = 8.7 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 136.9, 130.7, 128.8, 127.7, 15.9.

4. References

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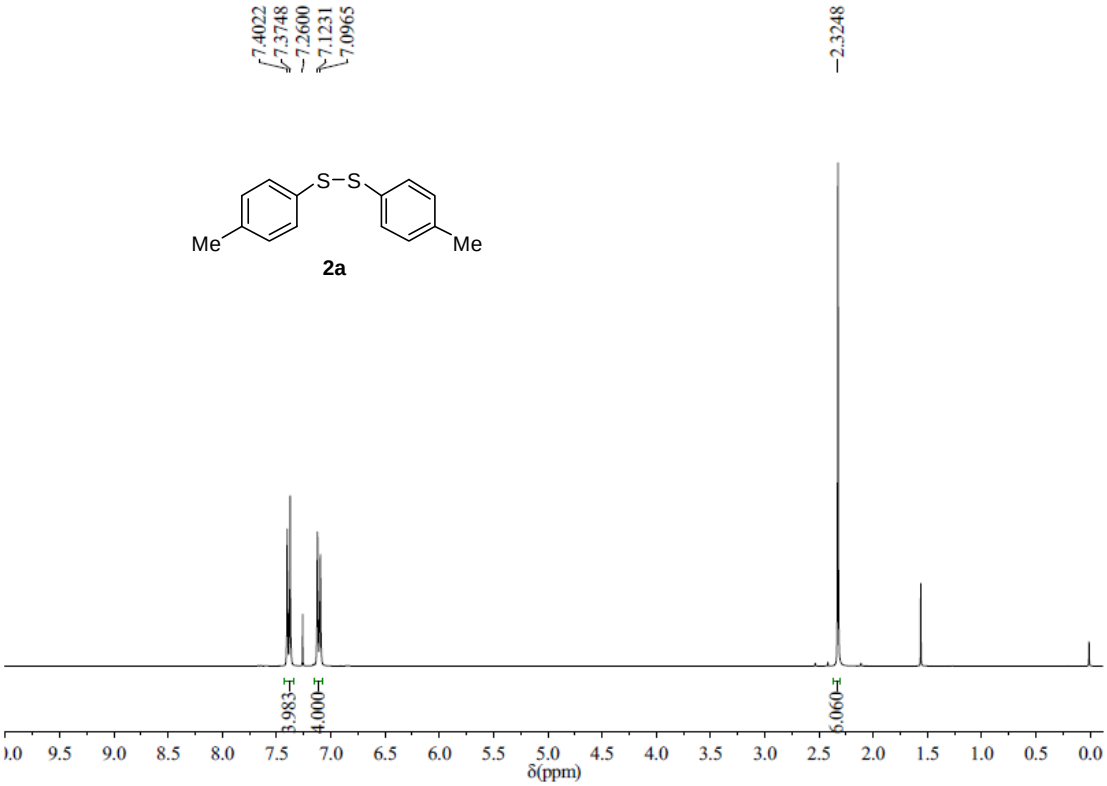
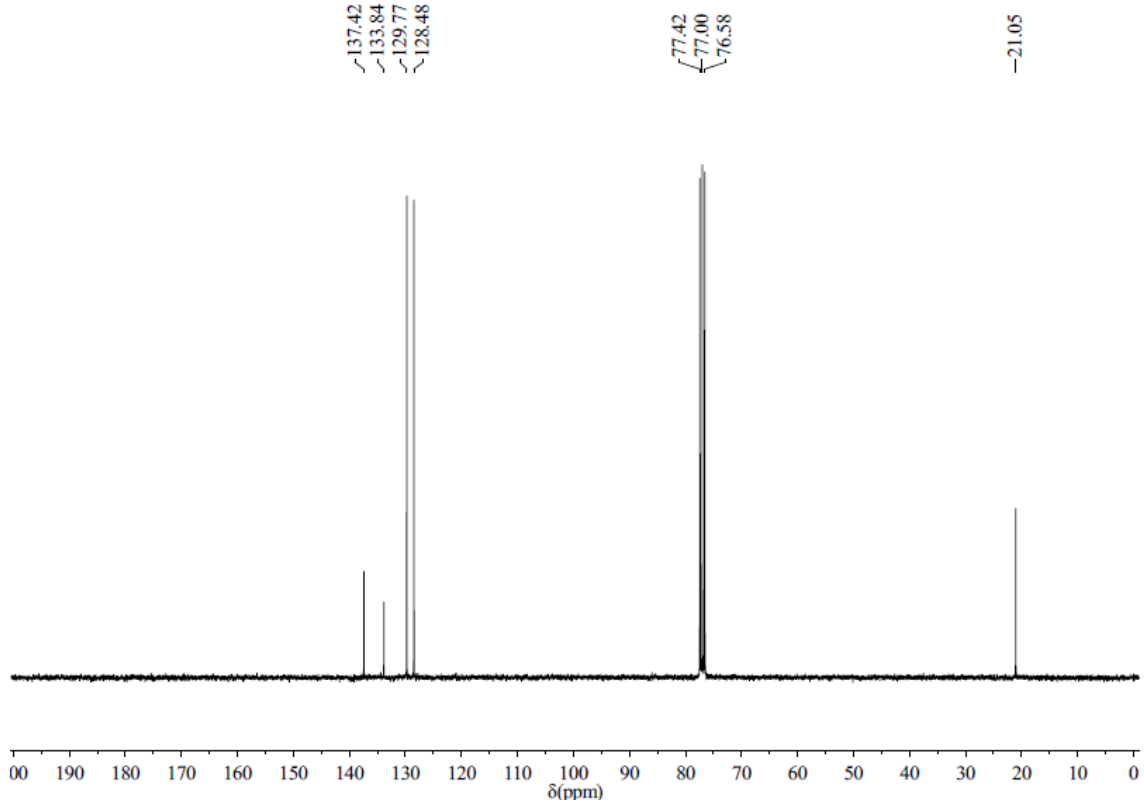
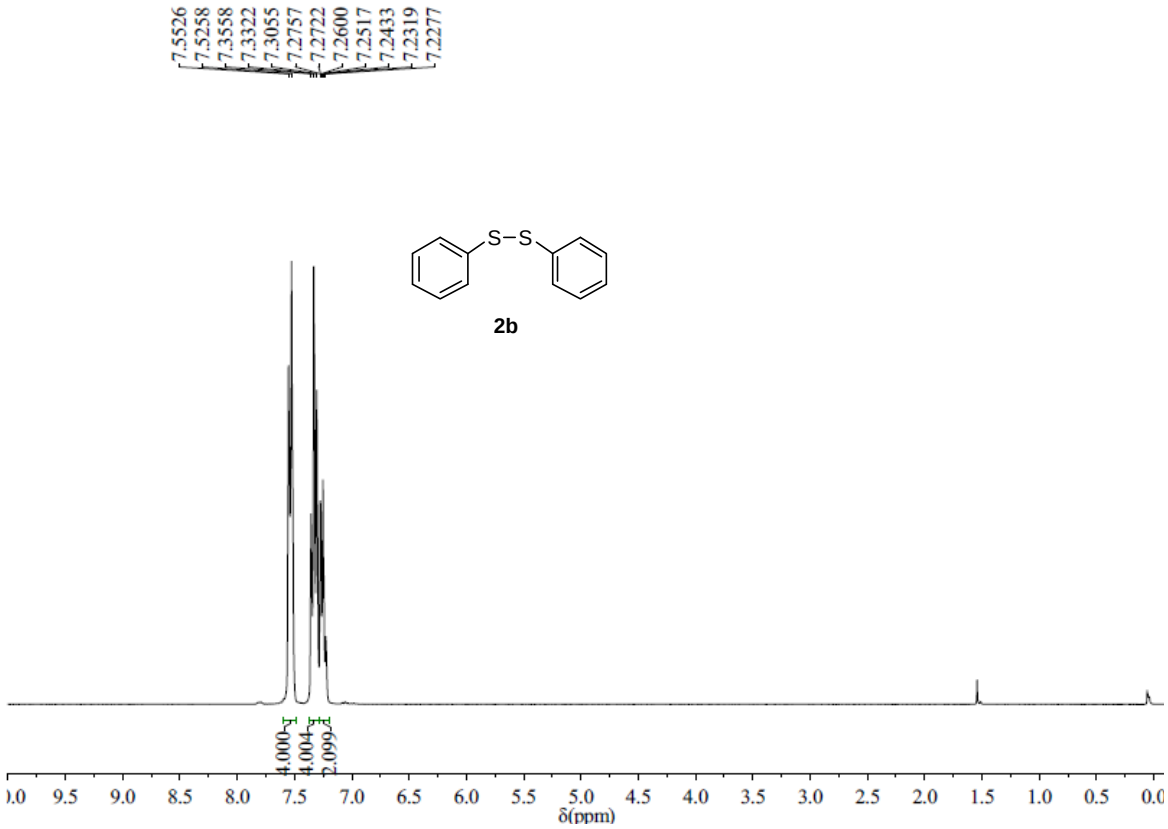
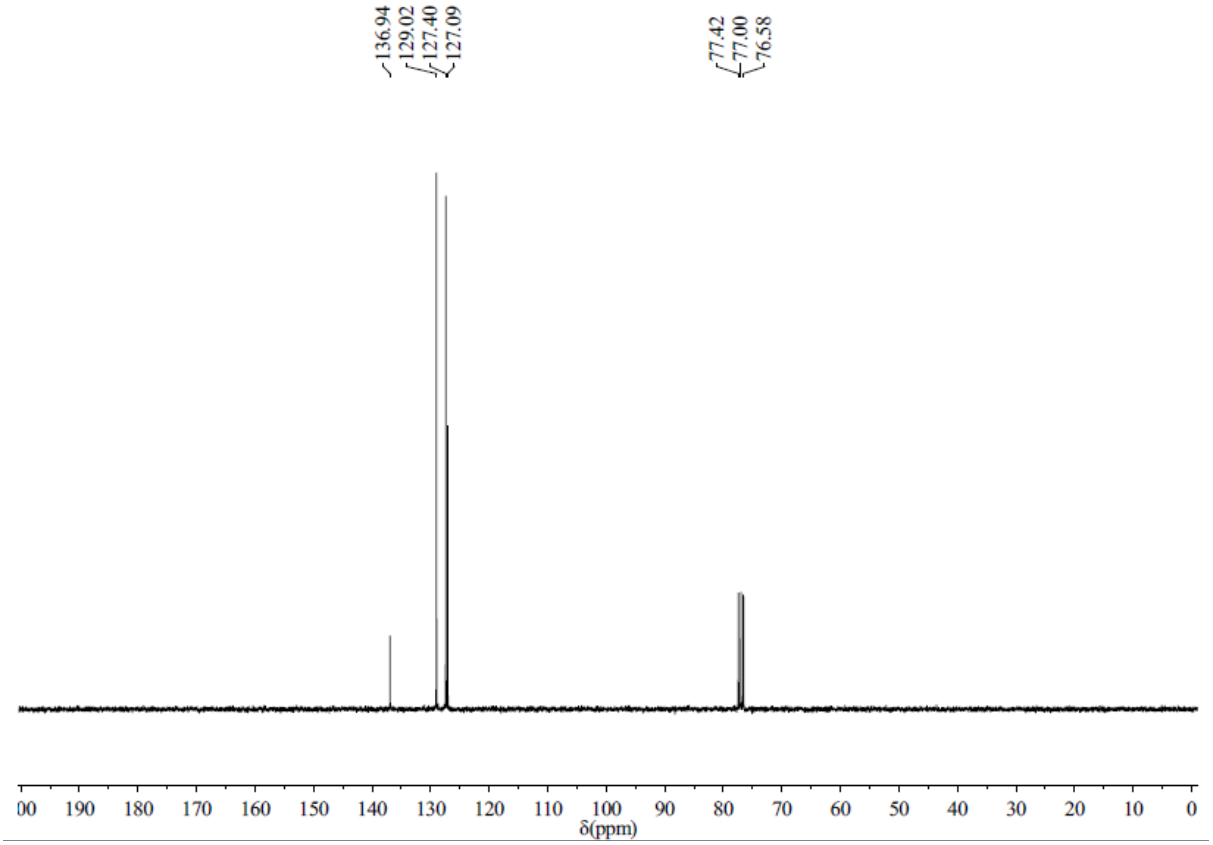
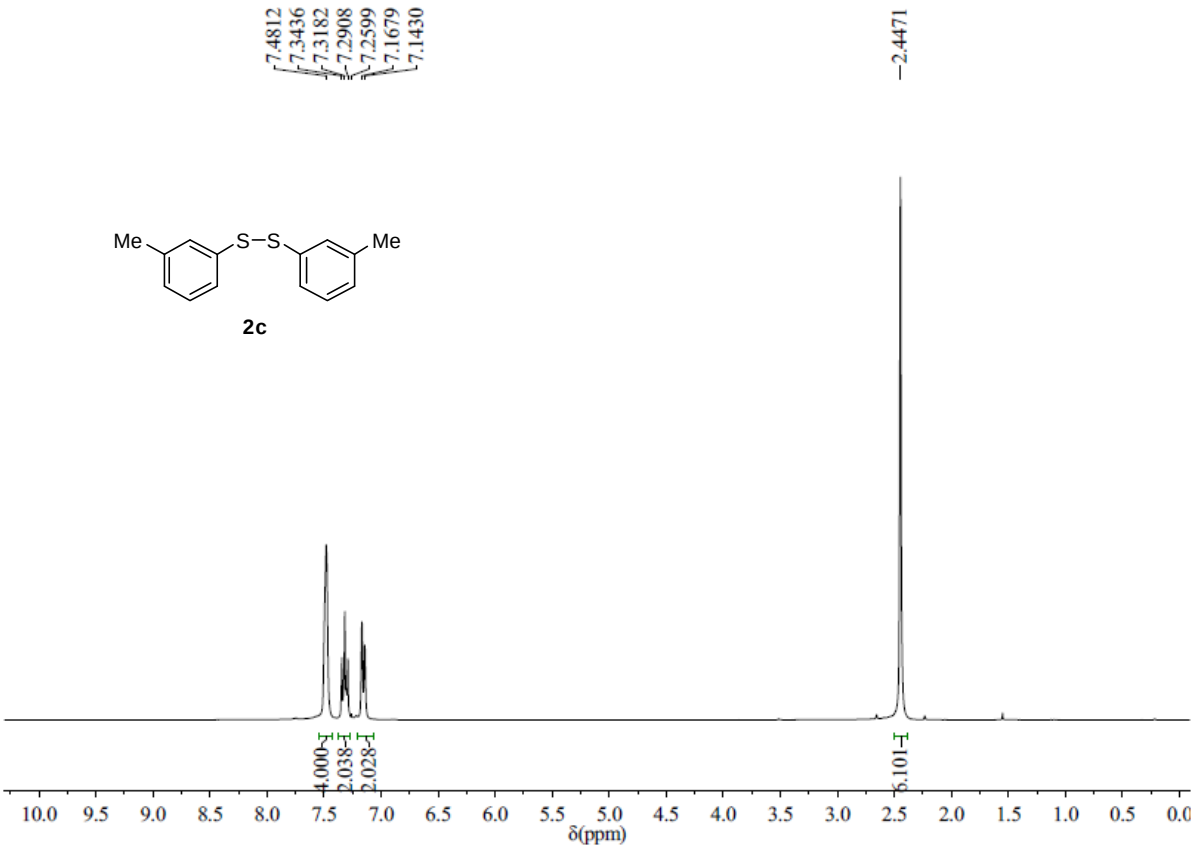
5. Copies of the ^{1}H NMR and ^{13}C NMR spectra

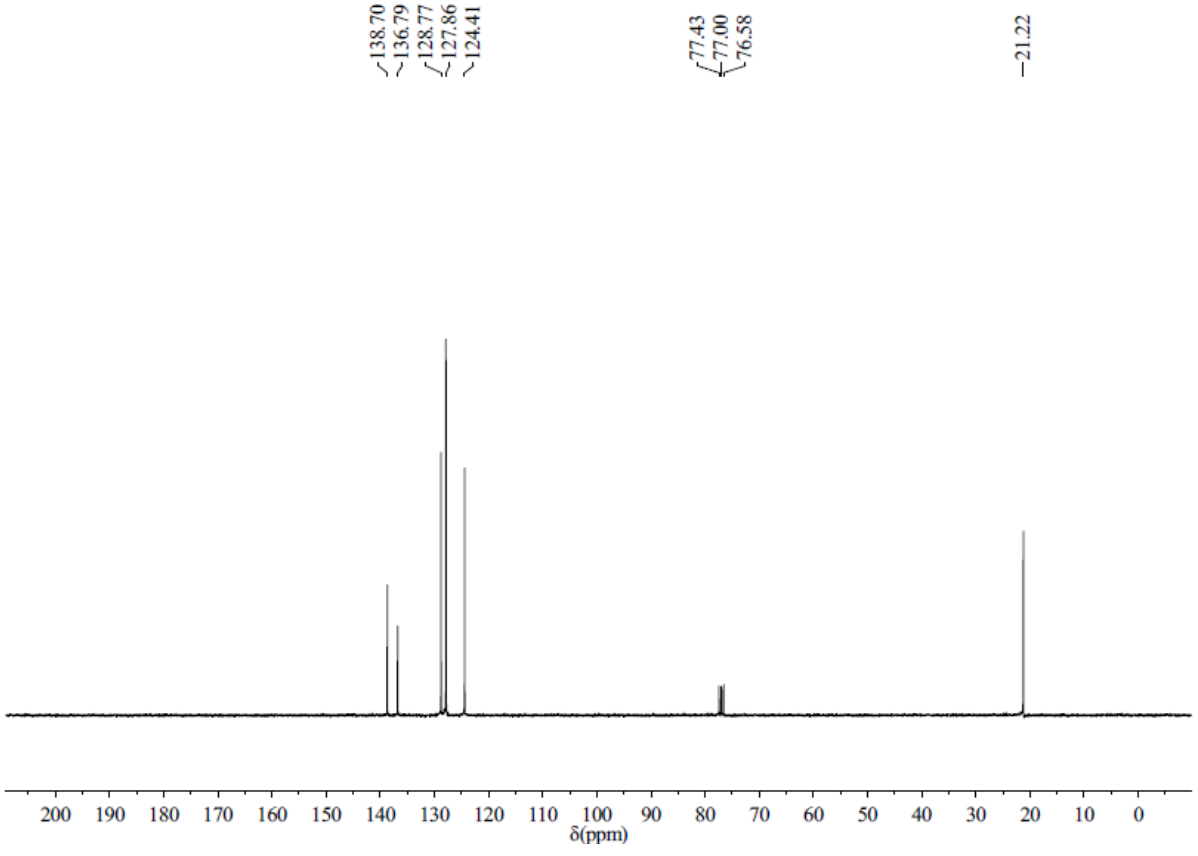


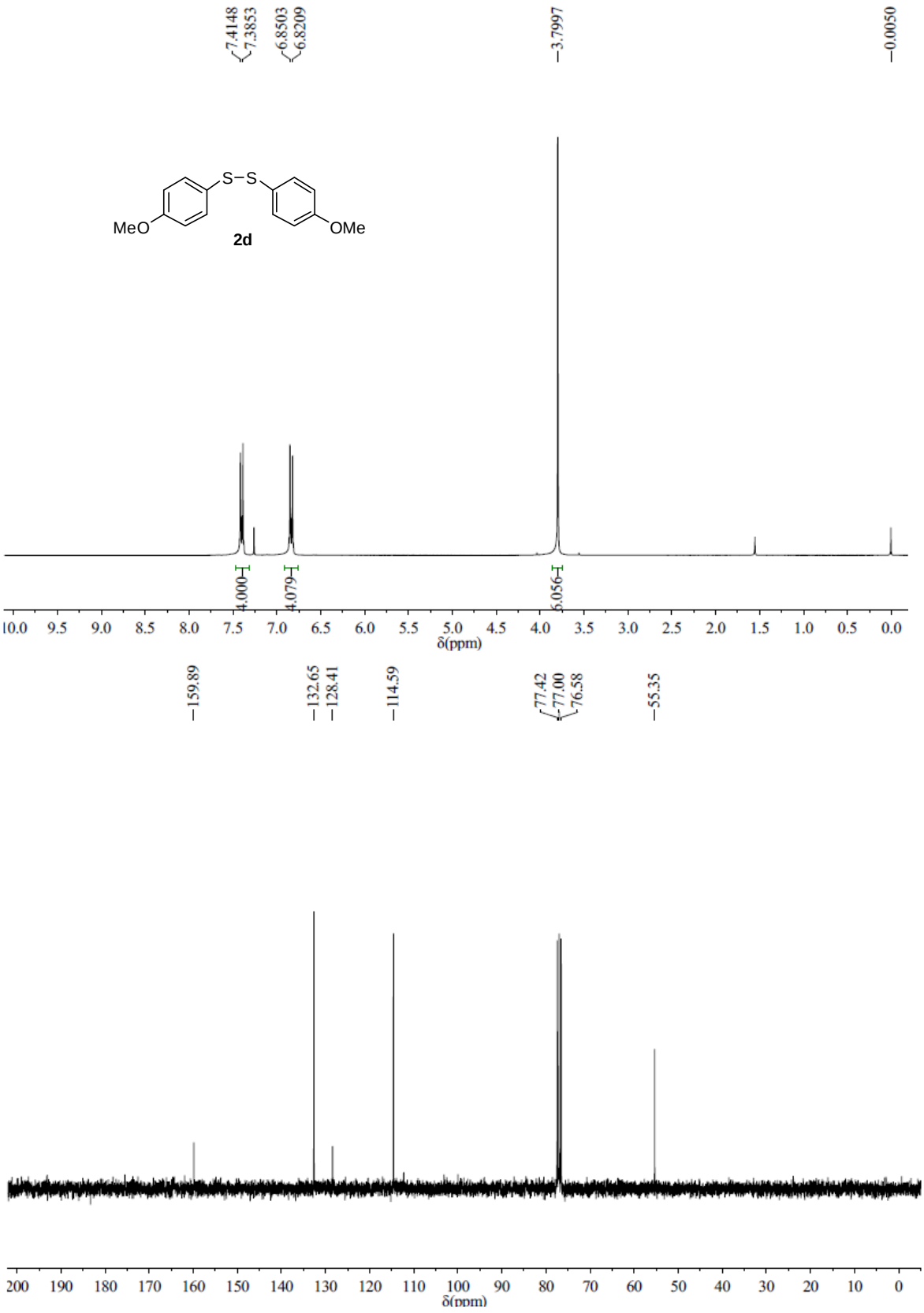


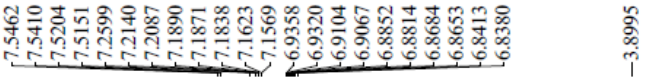

7.5526
7.5258
7.3558
7.3322
7.3055
7.2757
7.2722
7.2600
7.2517
7.2433
7.2319
7.2277
S–S
2b
4.000
4.004
2.099
δ(ppm)

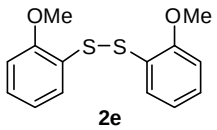

136.94
129.02
127.40
127.09
77.42
77.00
76.58
δ(ppm)


7.4812
7.3436
7.3182
7.2908
7.2599
7.1679
7.1430
2.4471
Me
S–S
Me
2c
4.000
2.038
2.028
6.101
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
δ(ppm)

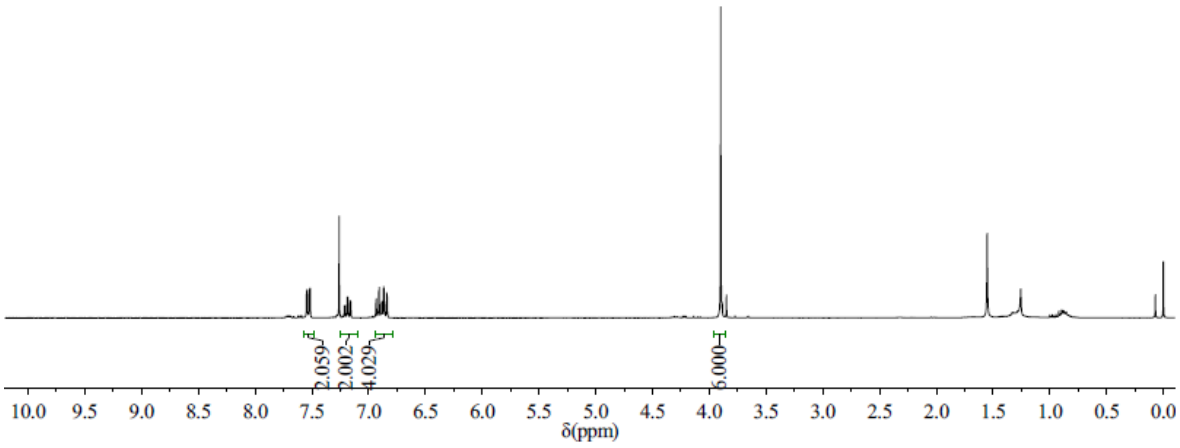

138.70
136.79
128.77
127.86
124.41
77.43
77.00
76.58
21.22
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ(ppm)

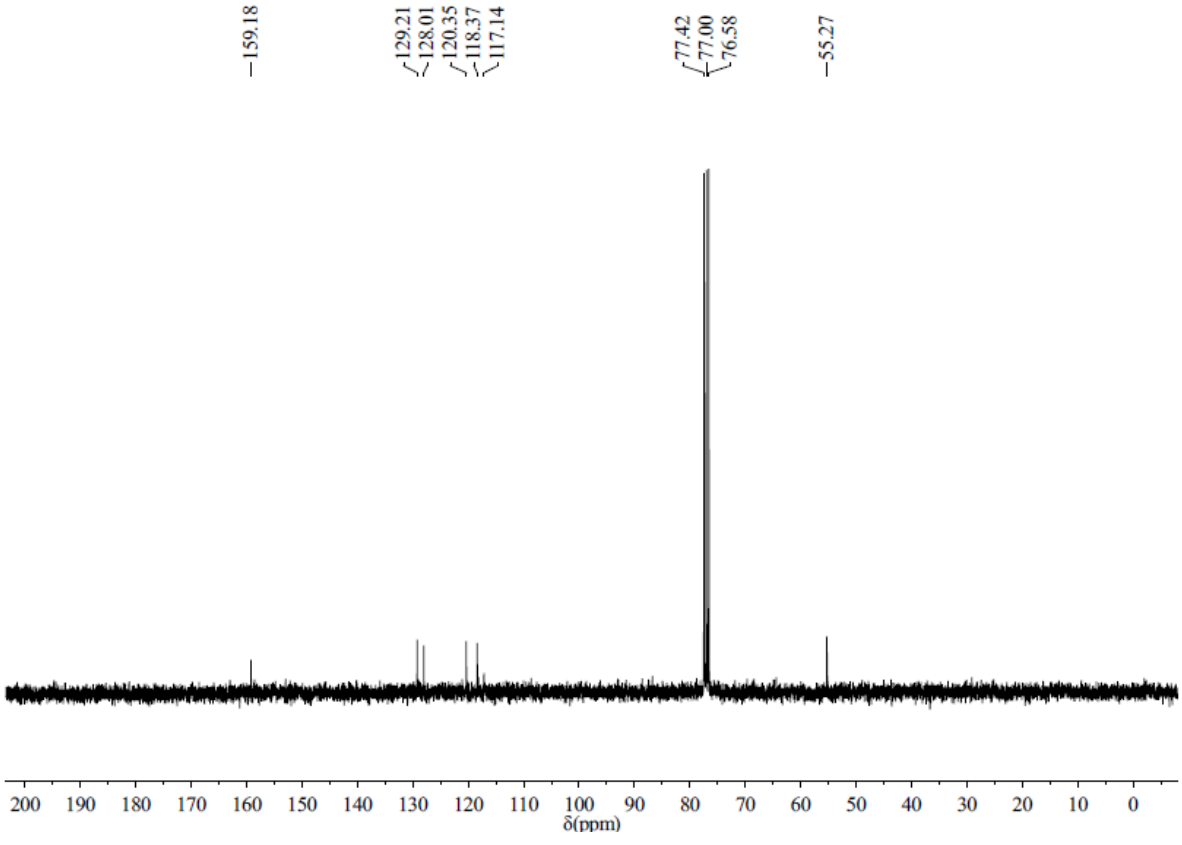

7.4148
7.3853
6.8503
6.8209
3.7997
0.0050
S–S
MeO
OMe
2d
4.000
4.079
6.056
δ(ppm)
159.89
132.65
128.41
114.59
77.42
77.00
76.58
55.35
δ(ppm)

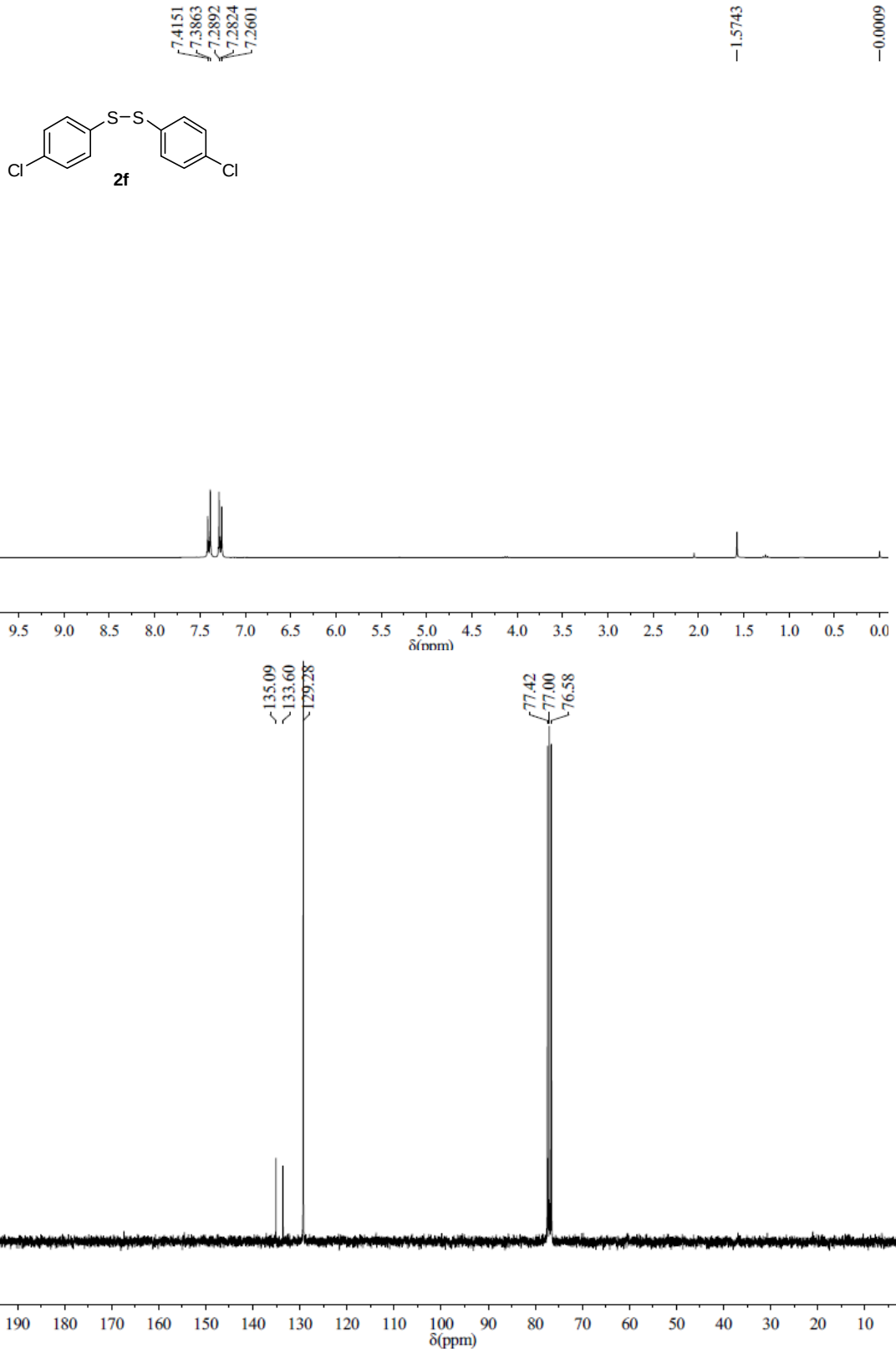

7.5462
7.5410
7.5204
7.5151
7.2599
7.2140
7.2087
7.1890
7.1871
7.1838
7.1623
7.1569
6.9358
6.9320
6.9104
6.9067
6.8852
6.8814
6.8684
6.8653
6.8413
6.8380
3.8995

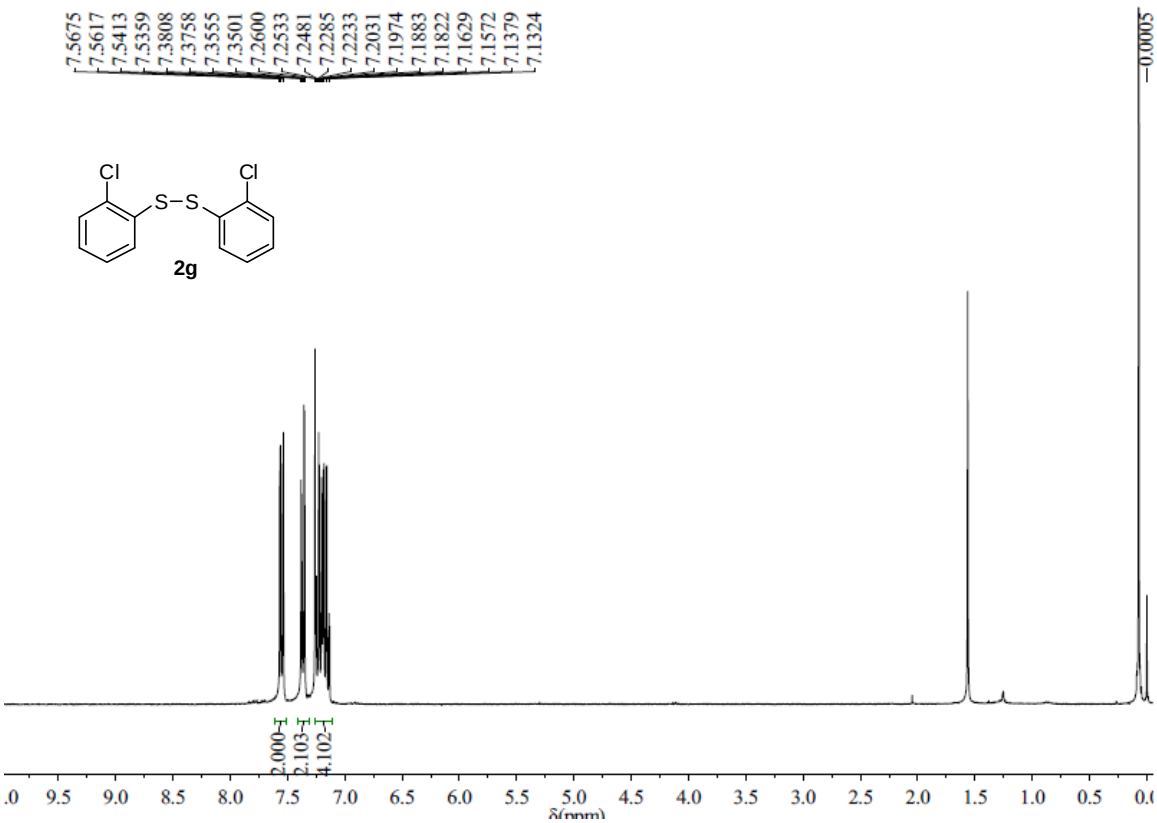

OMe
OMe
S–S

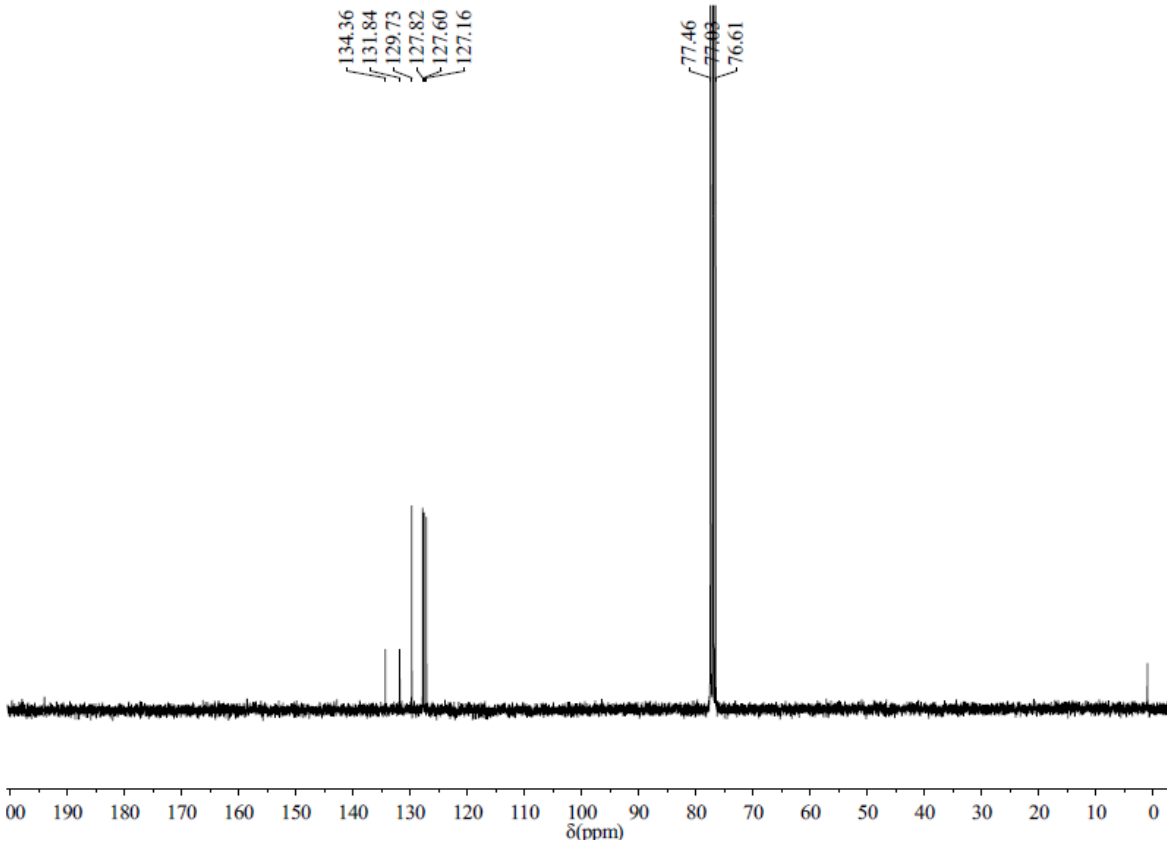
2e

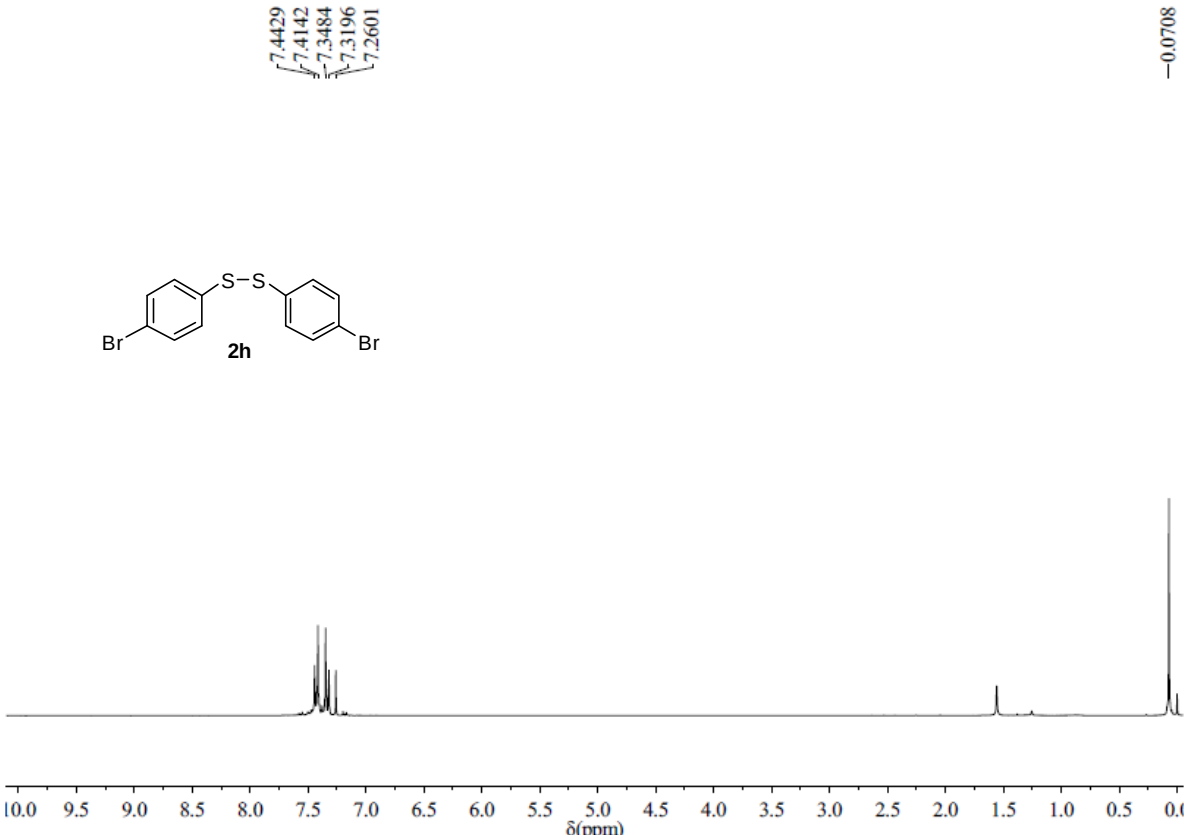

2.059
2.002
4.029
6.000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ(ppm)


159.18
129.21
128.01
120.35
118.37
117.14
77.42
77.00
76.58
55.27
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ(ppm)


7.4151
7.3863
7.2892
7.2824
7.2601
1.5743
0.0009
S–S
Cl
Cl
2f
δ(ppm)
135.09
133.60
129.28
77.42
77.00
76.58
δ(ppm)


7.5675
7.5617
7.5413
7.5359
7.3808
7.3758
7.3555
7.3501
7.2600
7.2533
7.2481
7.2285
7.2233
7.2031
7.1974
7.1883
7.1822
7.1629
7.1572
7.1379
7.1324
0.0005
Cl
S–S
Cl
2g
2.000
2.103
4.102
δ(ppm)


134.36
131.84
129.73
127.82
127.60
127.16
77.46
77.03
76.61
δ(ppm)


7.4429
7.4142
7.3484
7.3196
7.2601
-0.0708
S–S
Br
Br
2h
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
δ(ppm)
135.71
132.21
129.38
121.53
77.42
77.20
77.00
76.58
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ(ppm)


7.5618
7.5428
7.5331
7.5154
7.5053
7.4876
7.4764
7.4587
7.4474
7.4301
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7.0873
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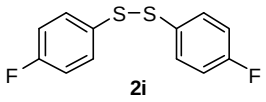
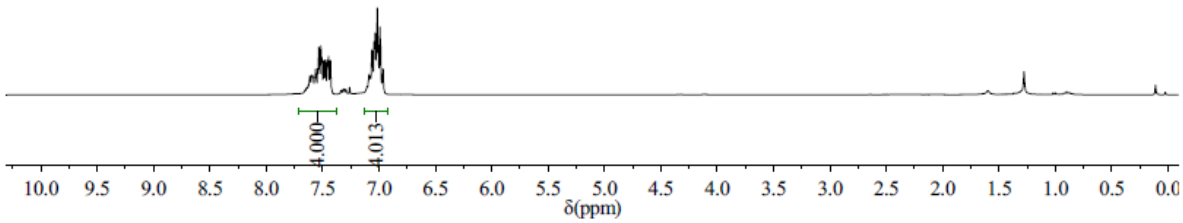
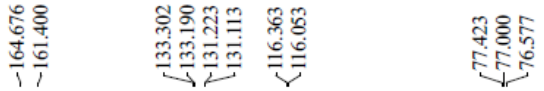
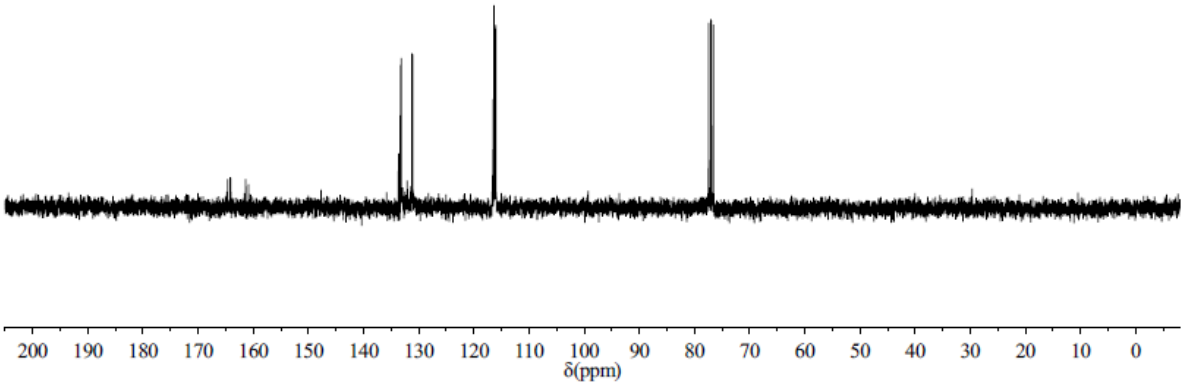
7.0434
7.0348
7.0150
6.9921
6.9638

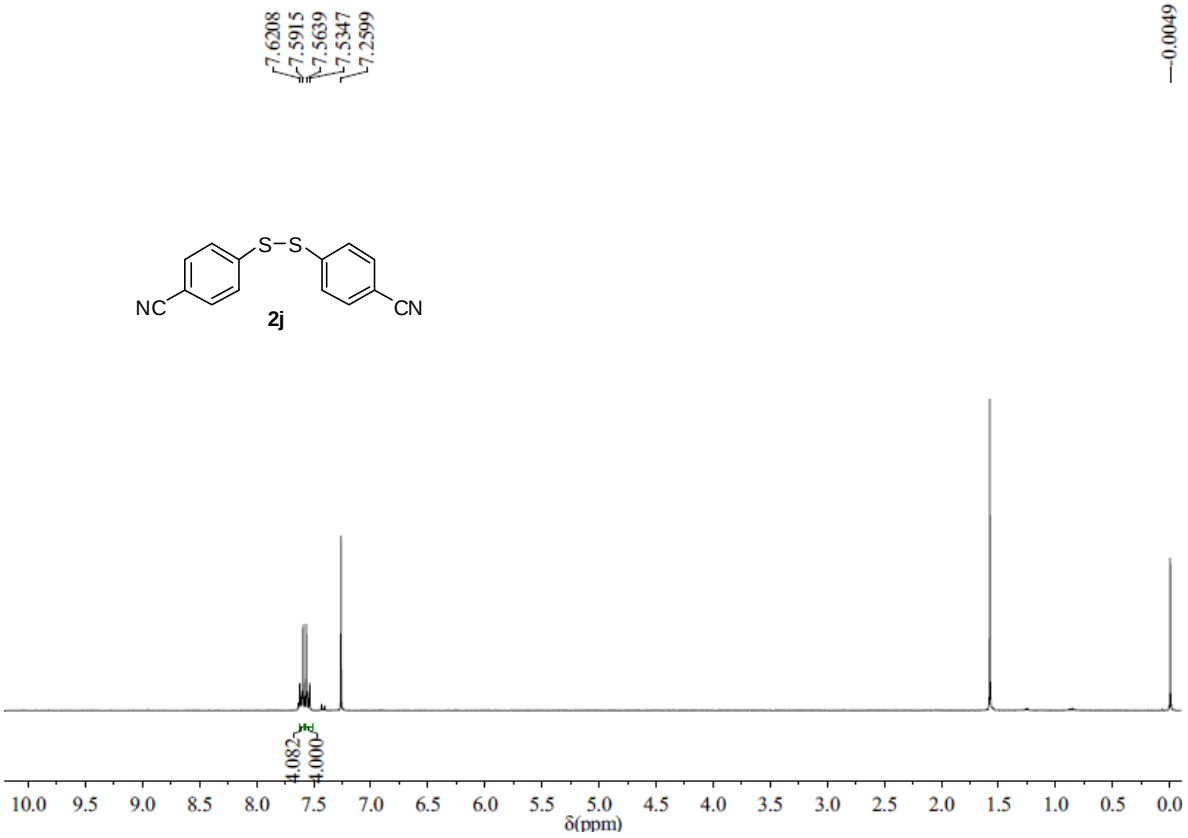

S–S
F
F

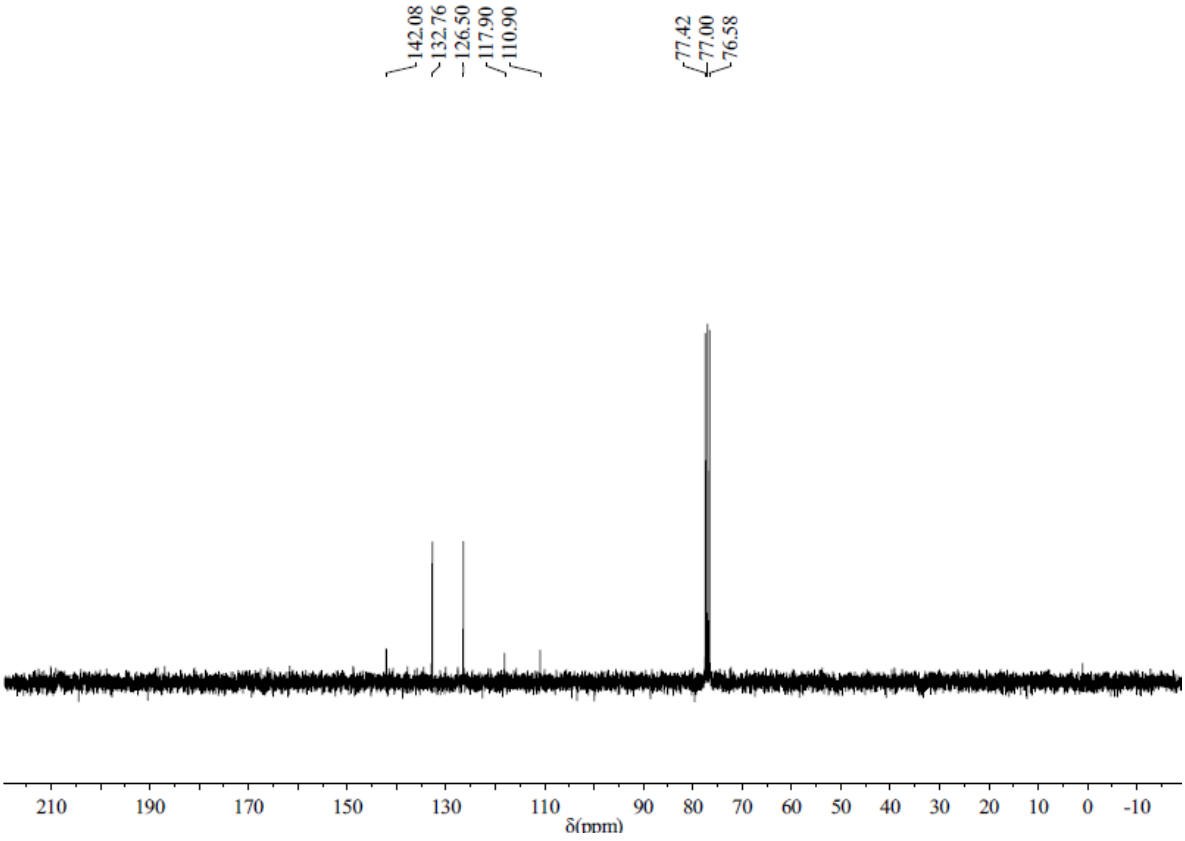
2i

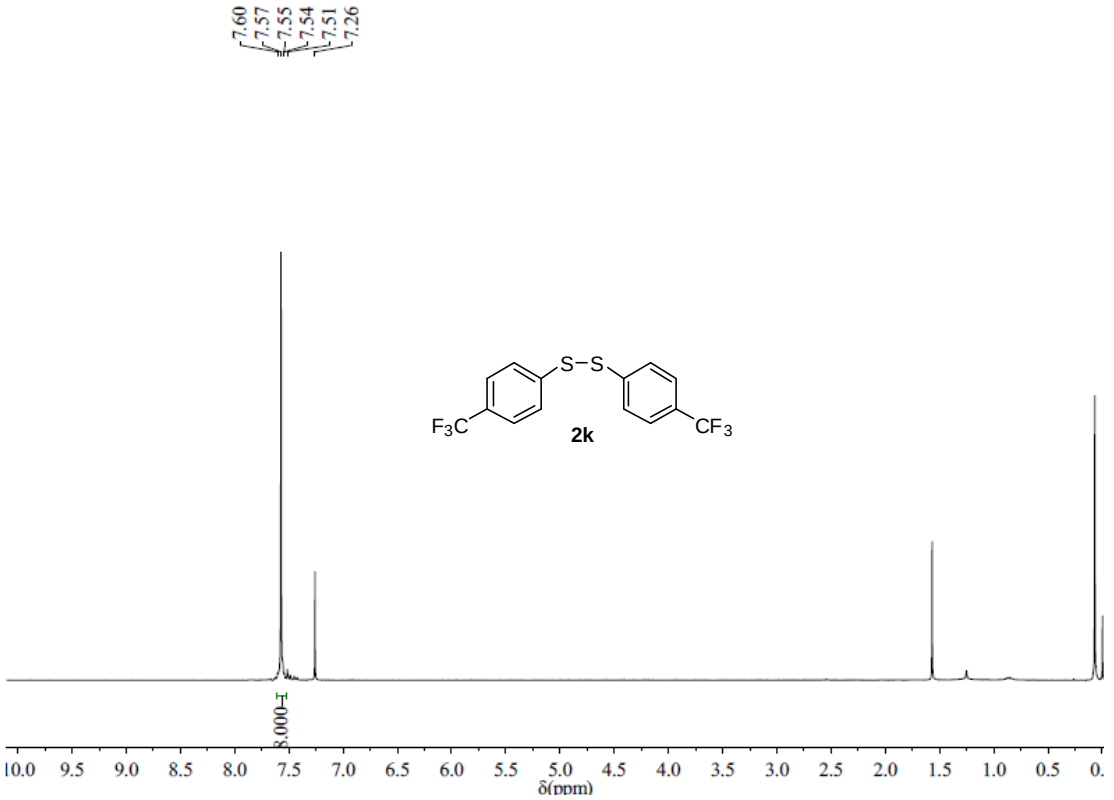

4.000
4.013
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ(ppm)

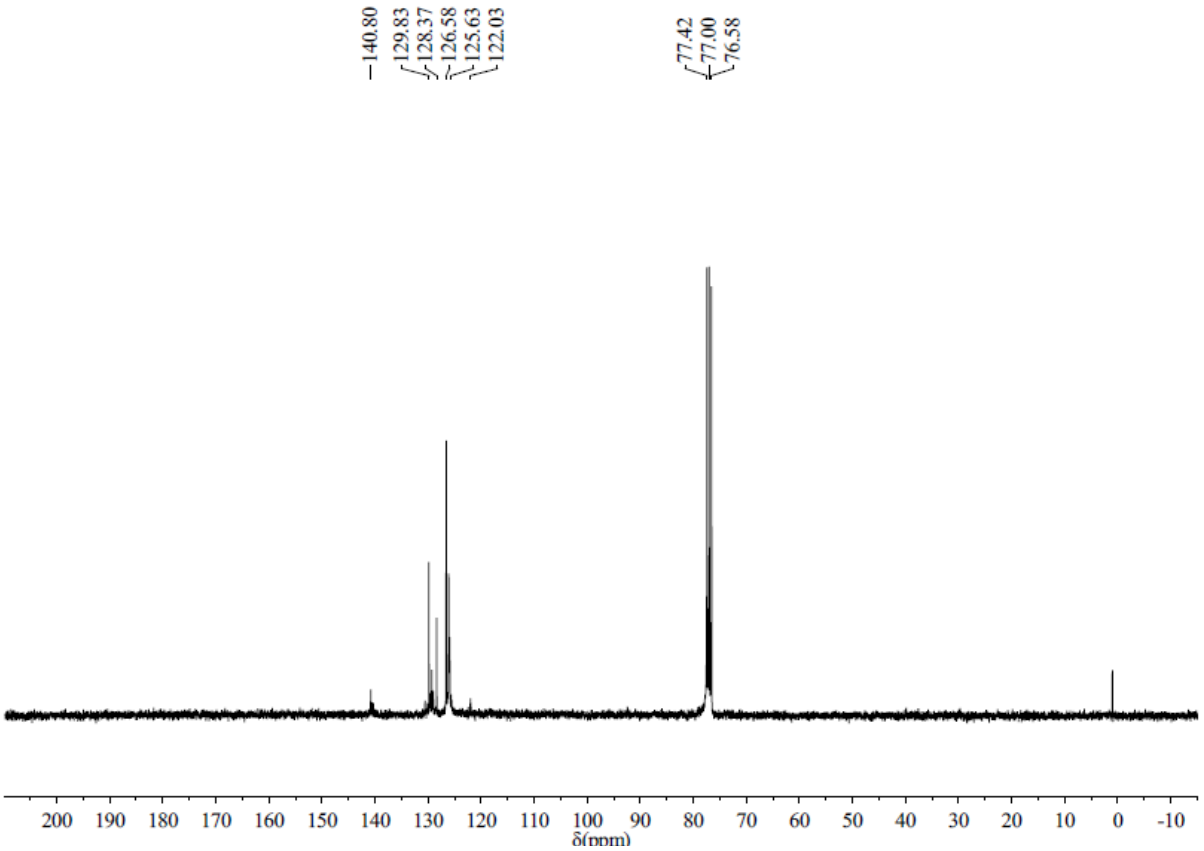

164.676
161.400
133.302
133.190
131.223
131.113
116.363
116.053
77.423
77.000
76.577

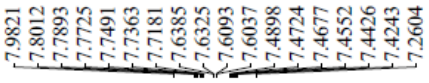

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ(ppm)


7.6208
7.5915
7.5639
7.5347
7.2599
0.0049
S–S
NC
CN
2j
4.082
4.000
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
δ(ppm)

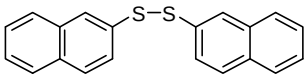

142.08
132.76
126.50
117.90
110.90
77.42
77.00
76.58
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
δ(ppm)


7.60
7.57
7.55
7.54
7.51
7.26
S−S
F3C
CF3
2k
8.000
δ(ppm)

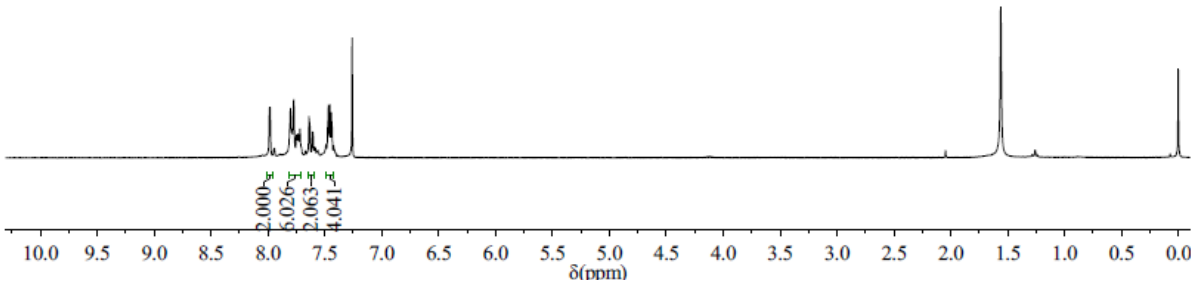

140.80
129.83
128.37
126.58
125.63
122.03
77.42
77.00
76.58
δ(ppm)

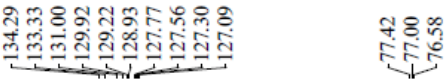

7.9821
7.8012
7.7893
7.7725
7.7491
7.7363
7.7181
7.6385
7.6325
7.6093
7.6037
7.4898
7.4724
7.4677
7.4552
7.4426
7.4243
7.2604


1.5614
0.0027

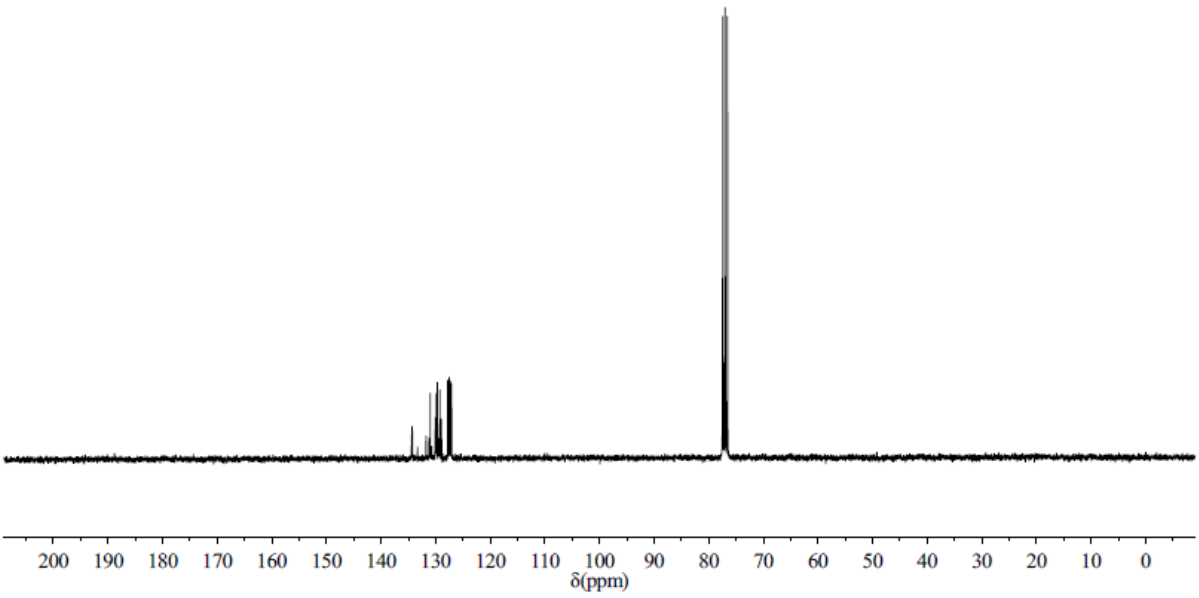

S–S

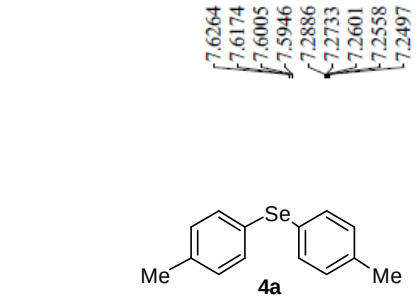
2l


2.000
6.026
2.063
4.041
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
δ(ppm)

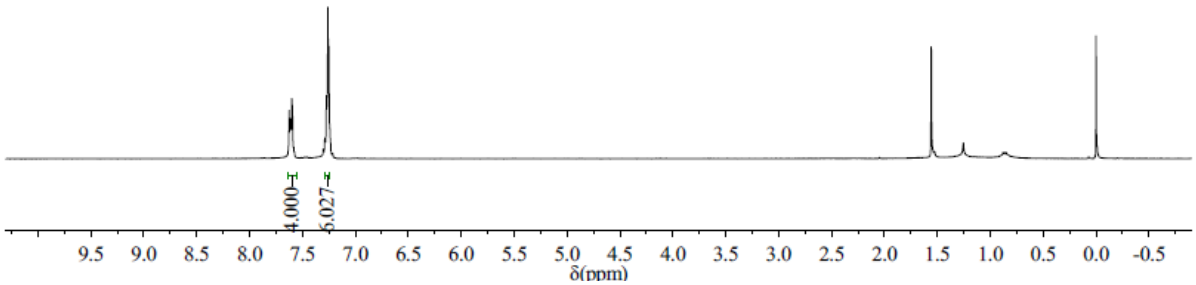

134.29
133.33
131.00
129.92
129.22
128.93
127.77
127.56
127.30
127.09

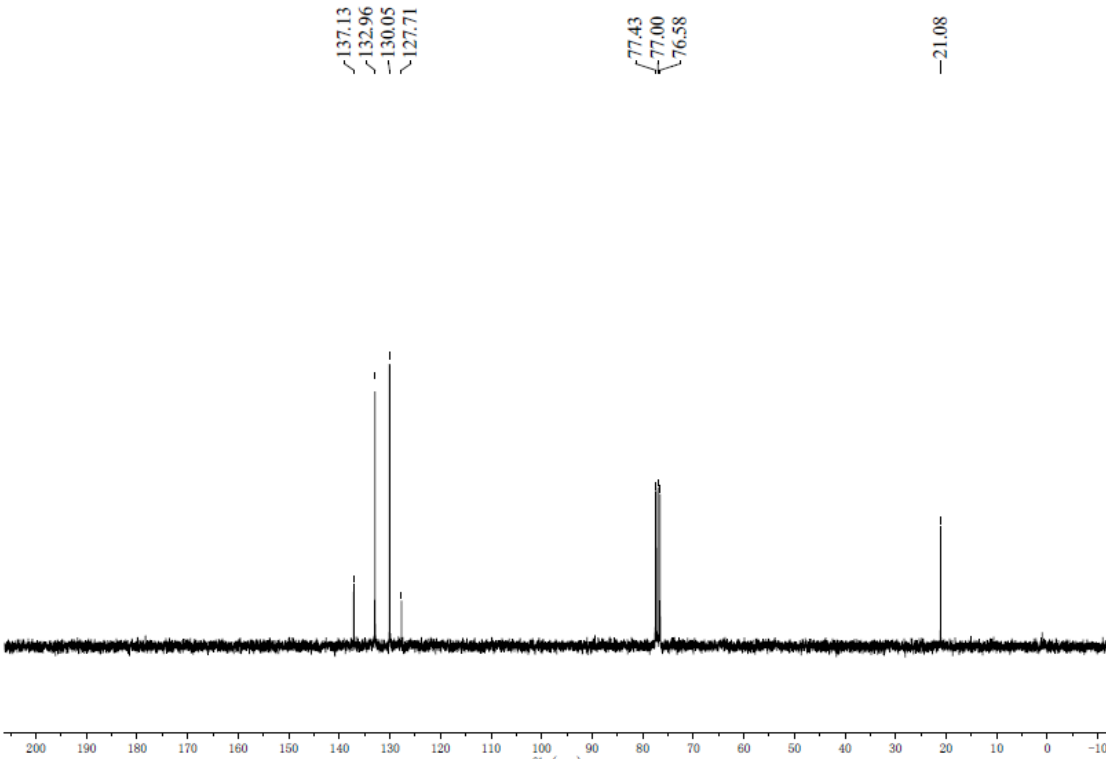
77.42
77.00
76.58

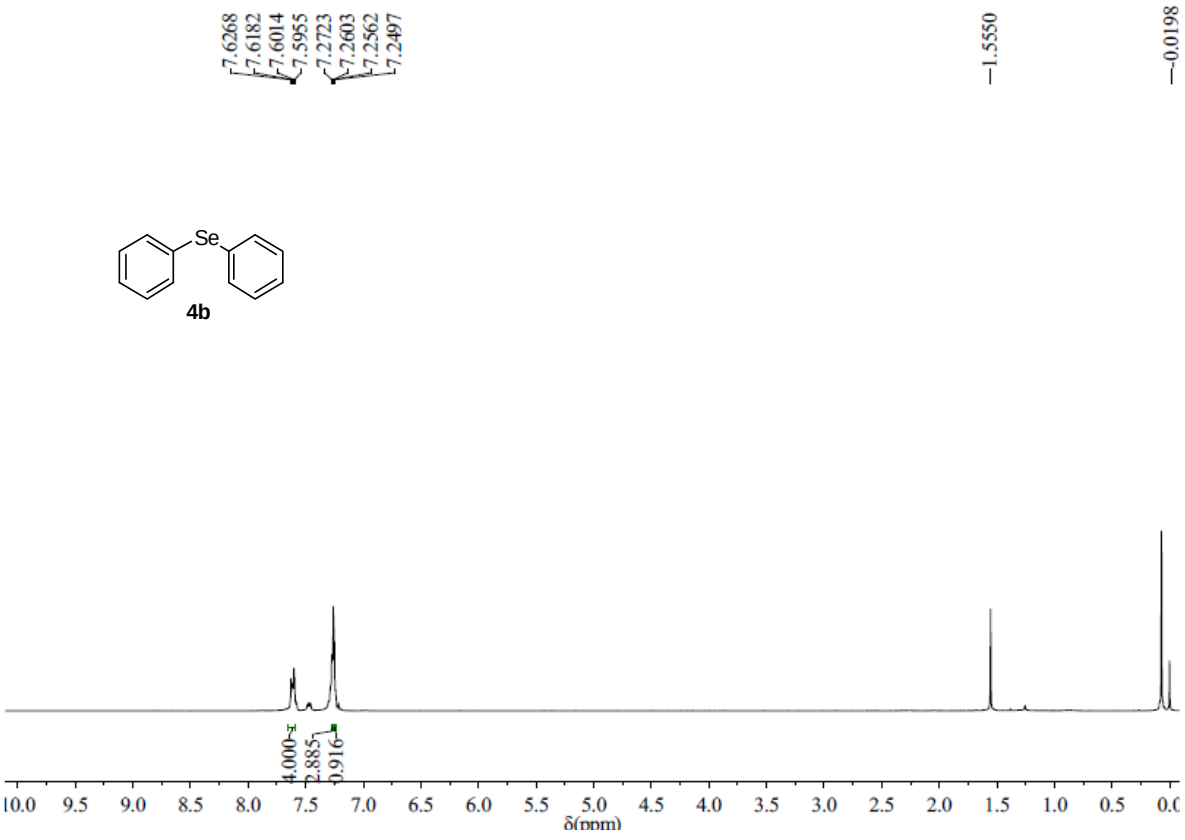

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ(ppm)

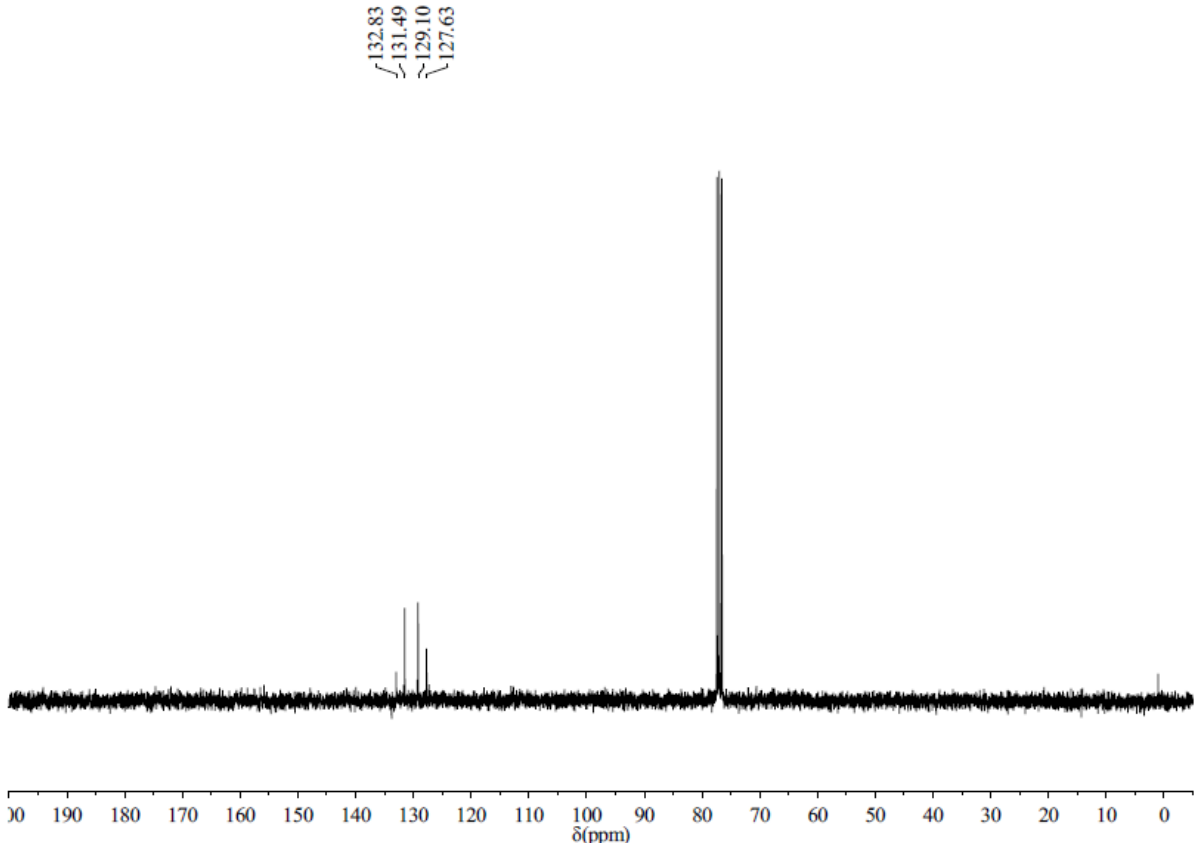

7.6264
7.6174
7.6005
7.5946
7.2886
7.2733
7.2601
7.2558
7.2497
Se
Me
Me

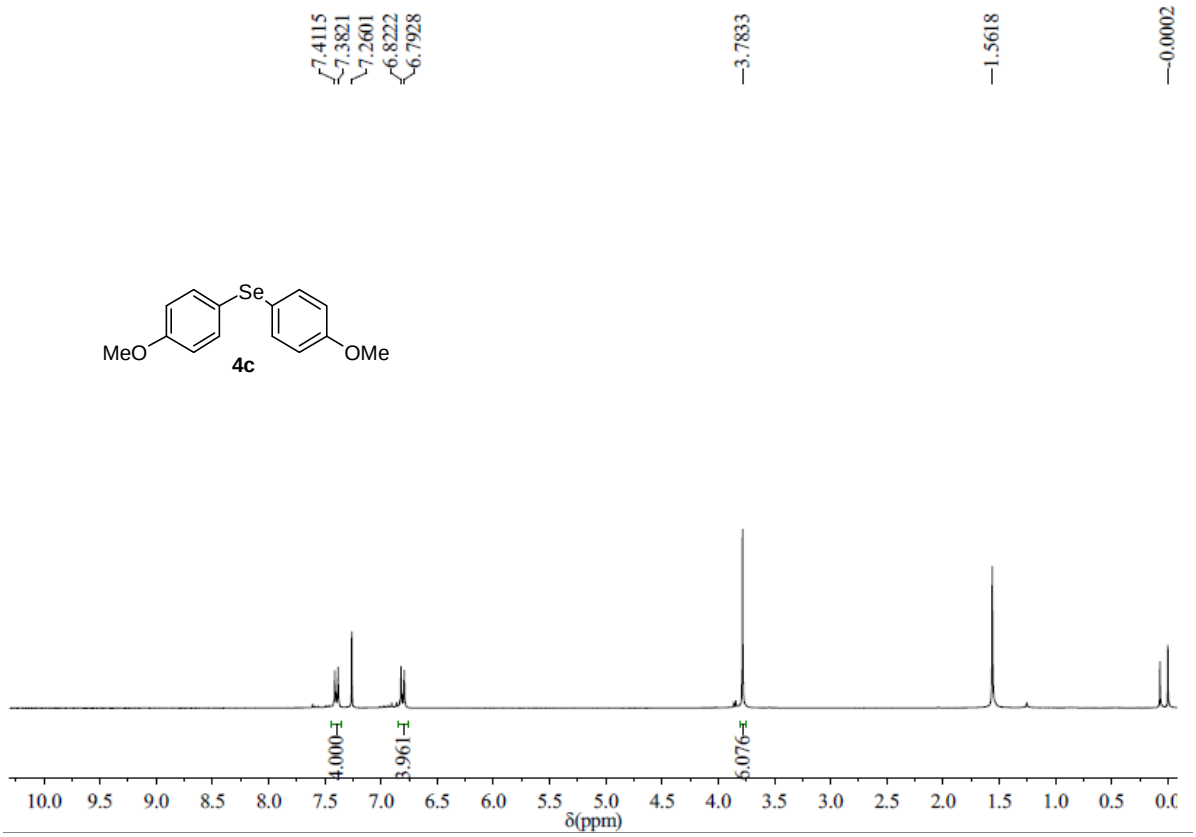
4a

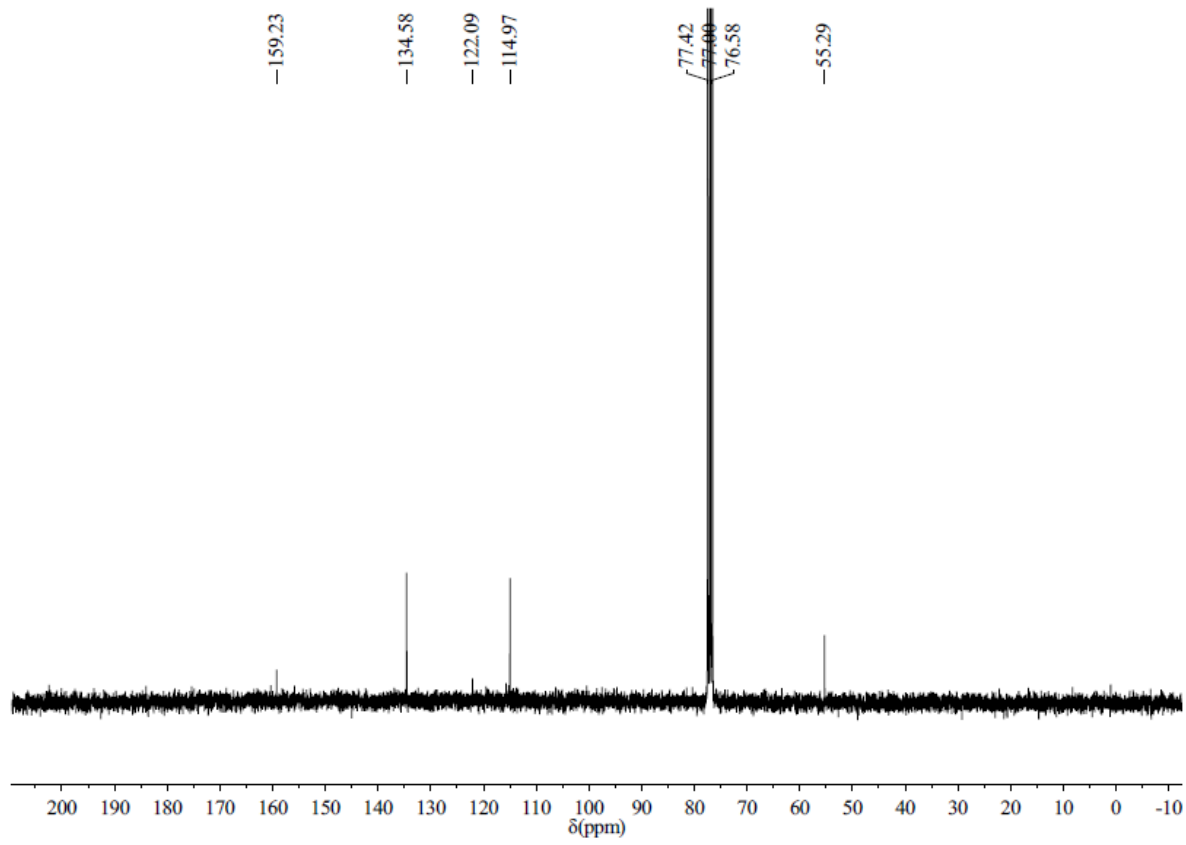

4.000
6.027
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ(ppm)

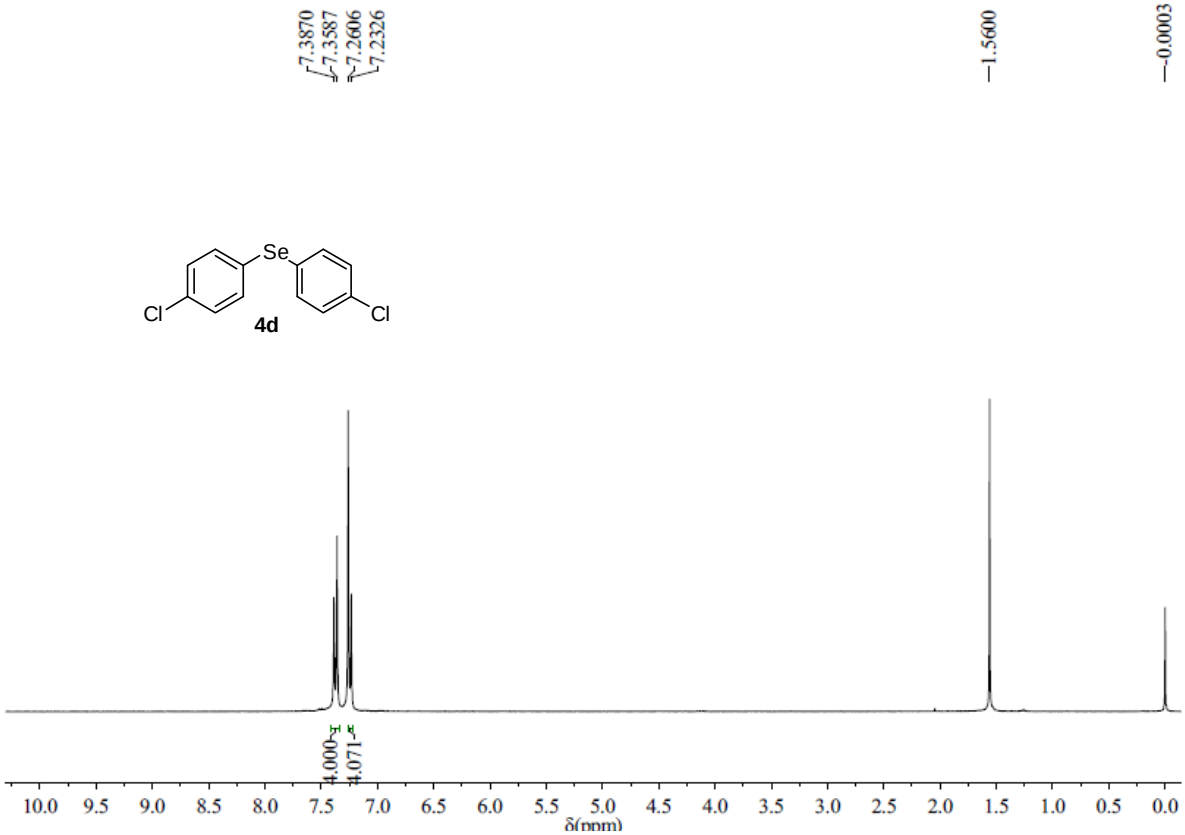

137.13
132.96
130.05
127.71
77.43
77.00
76.58
21.08
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

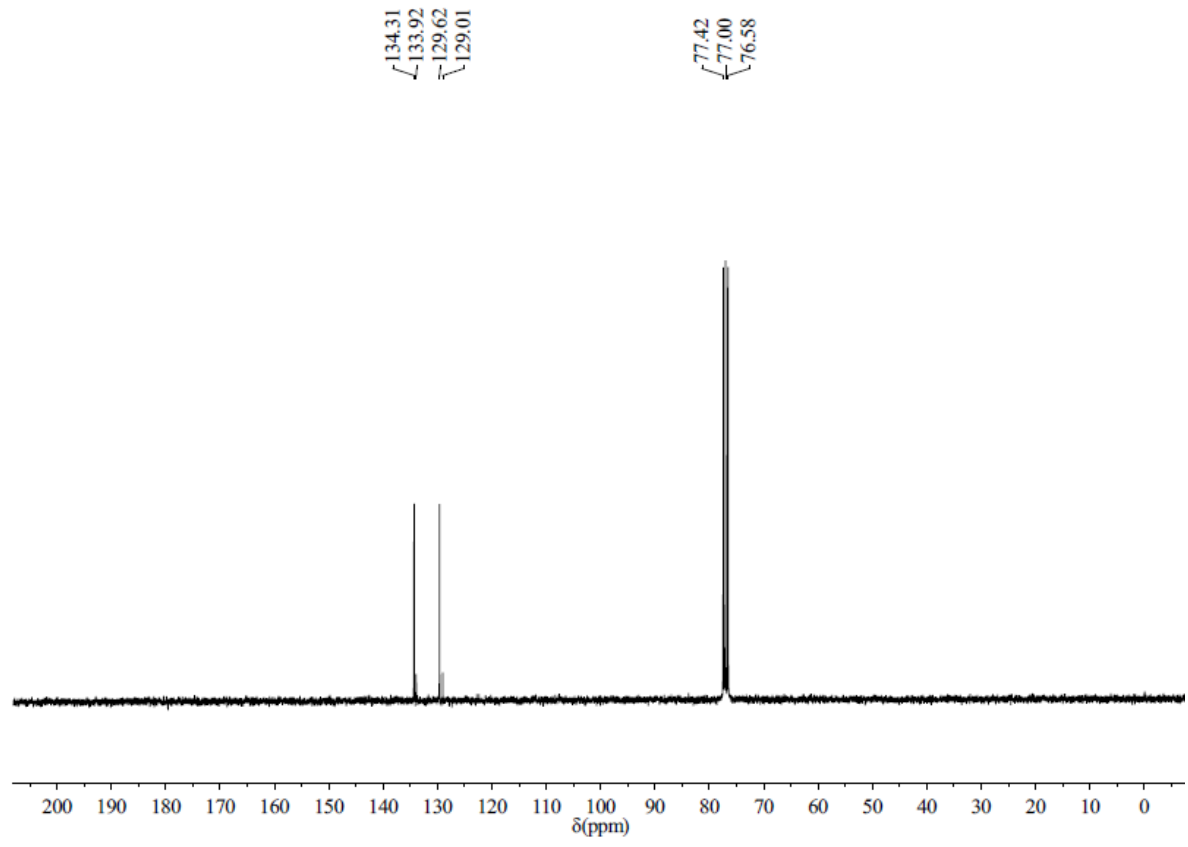

7.6268
7.6182
7.6014
7.5955
7.2723
7.2603
7.2562
7.2497
1.5550
0.0198
Se
4b
4.000
2.885
0.916
δ(ppm)

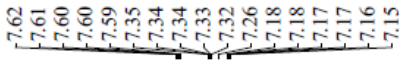

132.83
131.49
129.10
127.63
δ(ppm)

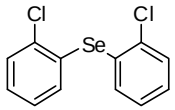

7.4115
7.3821
7.2601
6.8222
6.7928
3.7833
1.5618
0.0002
Se
MeO
OMe
4c
4.000
3.961
6.076
δ(ppm)


159.23
134.58
122.09
114.97
77.42
77.00
76.58
55.29
δ(ppm)


7.3870
7.3587
7.2606
7.2326
1.5600
0.0003
Se
Cl
Cl
4d
4.000
4.071
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
δ(ppm)

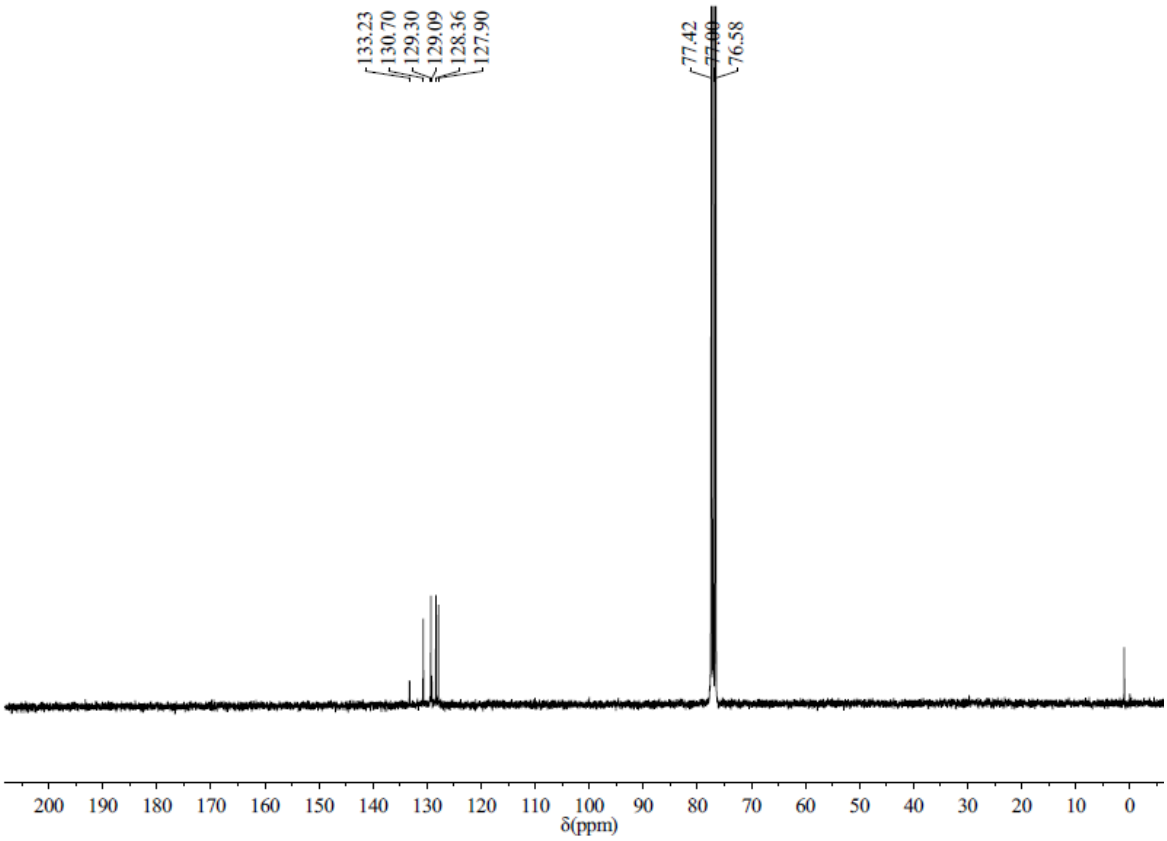

134.31
133.92
129.62
129.01
77.42
77.00
76.58
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ(ppm)

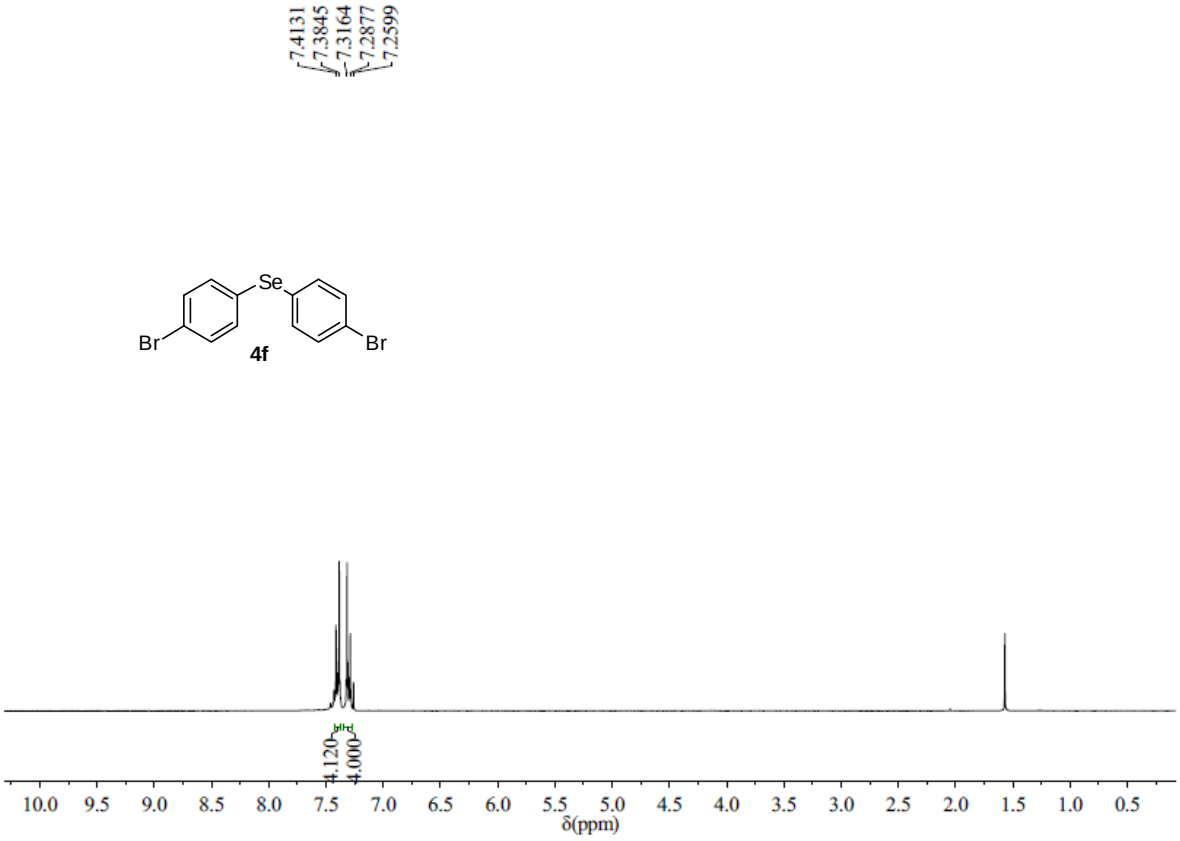

7.62
7.61
7.60
7.60
7.59
7.35
7.34
7.34
7.33
7.32
7.26
7.18
7.18
7.17
7.17
7.16
7.15

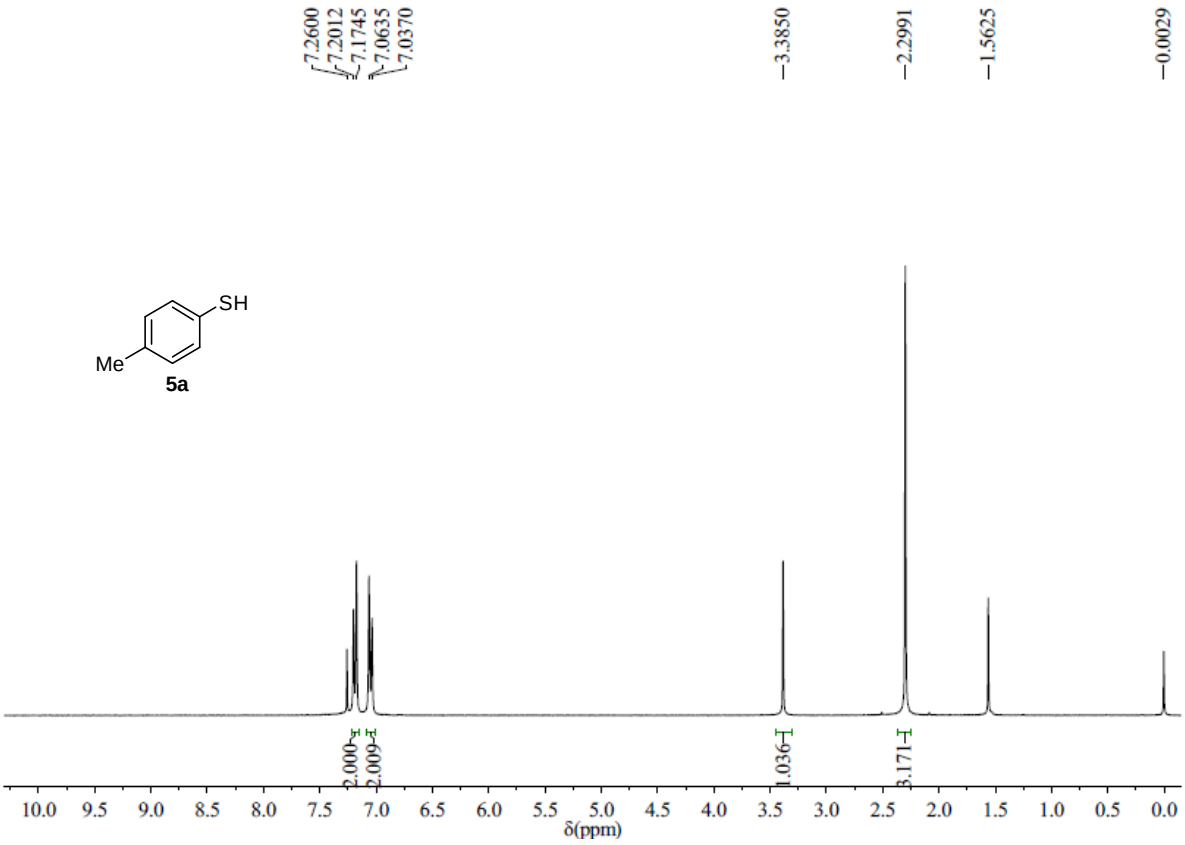

Cl
Se
Cl

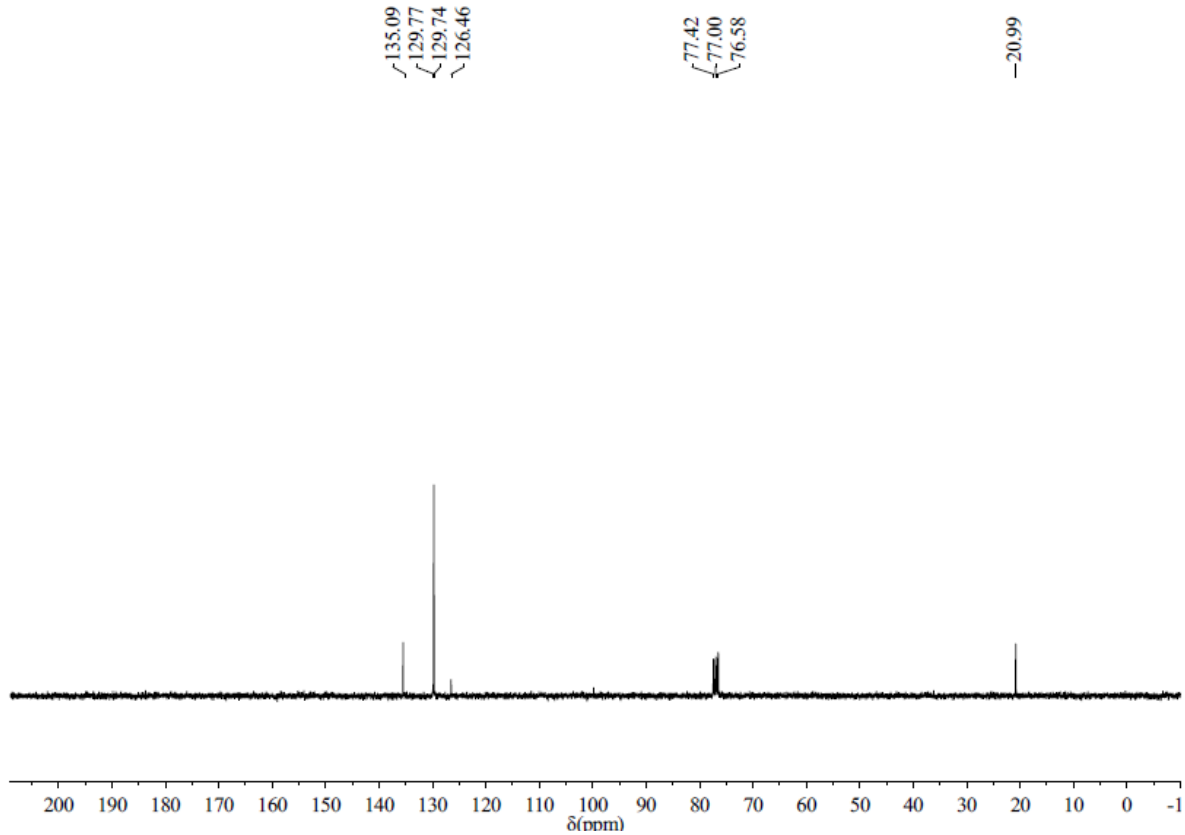
4e

2.000
2.133
4.015
δ(ppm)

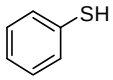

133.23
130.70
129.30
129.09
128.36
127.90
77.42
77.00
76.58
δ(ppm)


7.4131
7.3845
7.3164
7.2877
7.2599
Se
Br
Br
4f
4.120
4.000
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
δ(ppm)
134.56
132.55
129.60
121.97
77.42
77.00
76.58
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ(ppm)

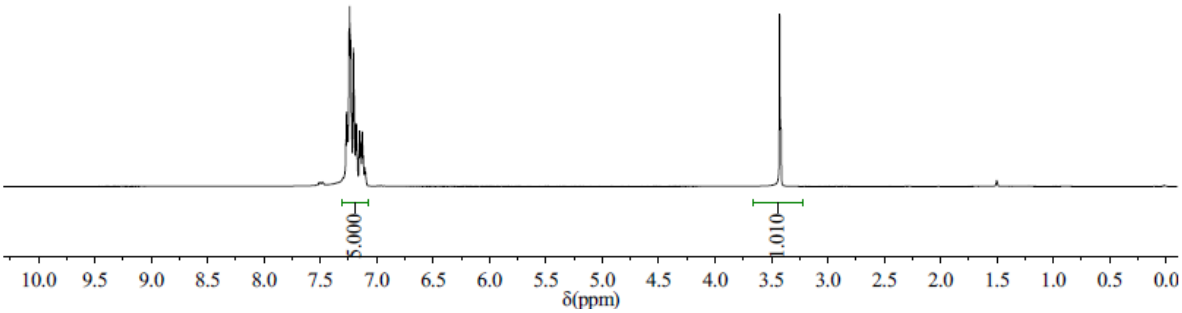

7.2600
7.2012
7.1745
7.0635
7.0370
3.3850
2.2991
1.5625
0.0029
SH
Me
5a
2.000
2.009
1.036
3.171
δ(ppm)

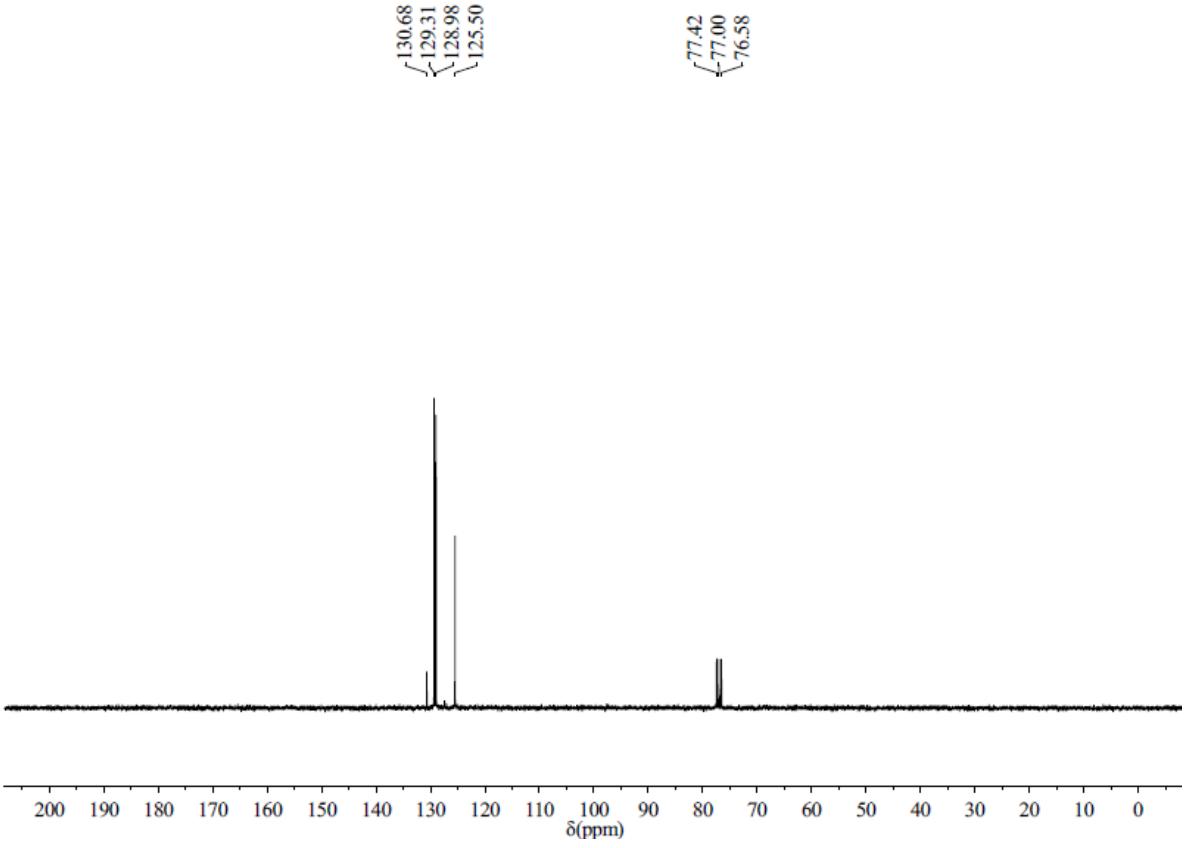

135.09
129.77
129.74
126.46
77.42
77.00
76.58
20.99
δ(ppm)

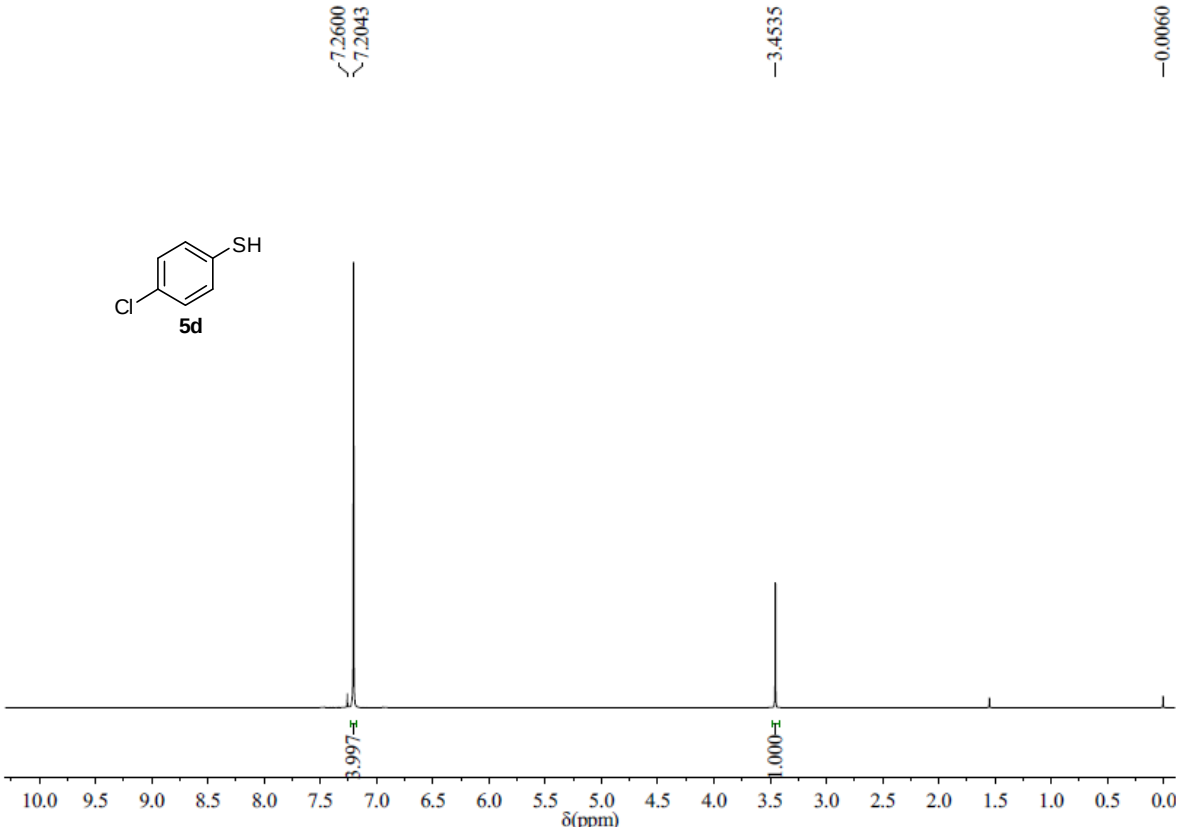

7.2733
7.2672
7.2445
7.2398
7.2334
7.2300
7.2066
7.2007
7.1869
7.1802
7.1566
7.1511
7.1451
7.1380
7.1275
7.1186
7.1052
7.0998
3.4276

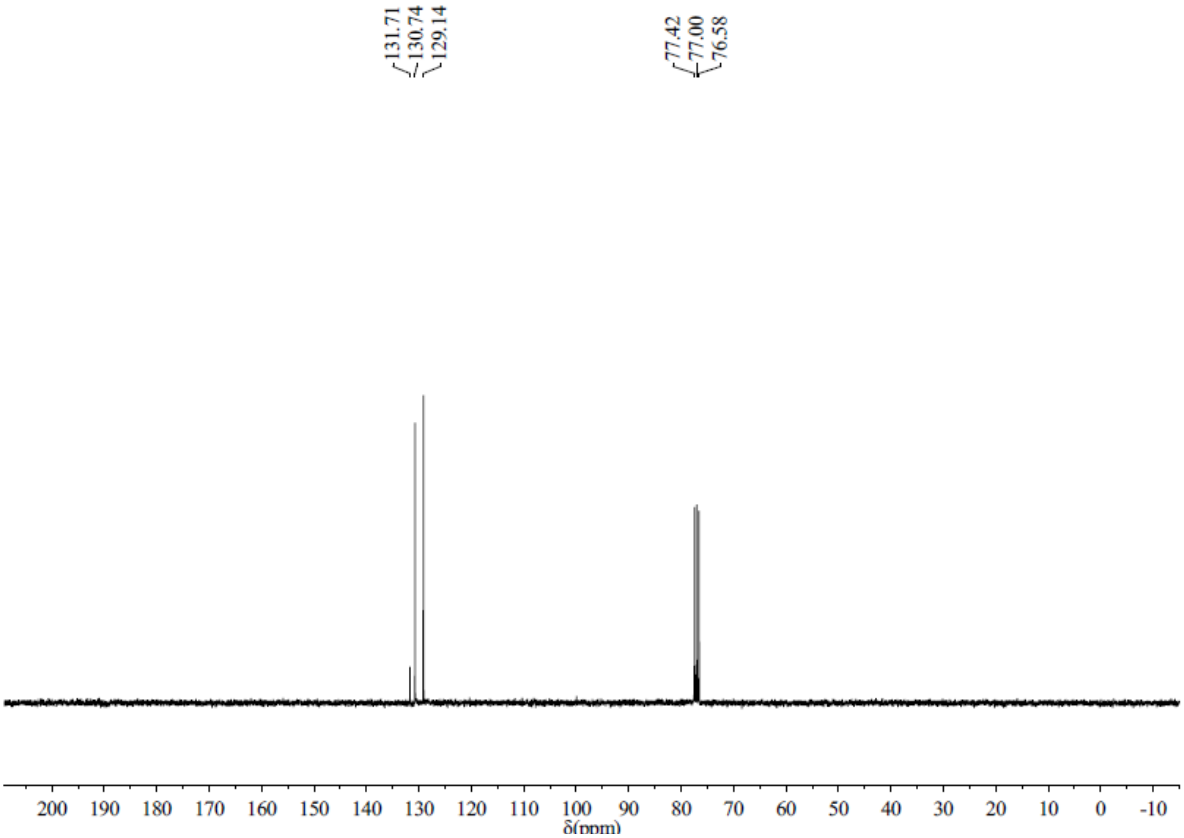

SH

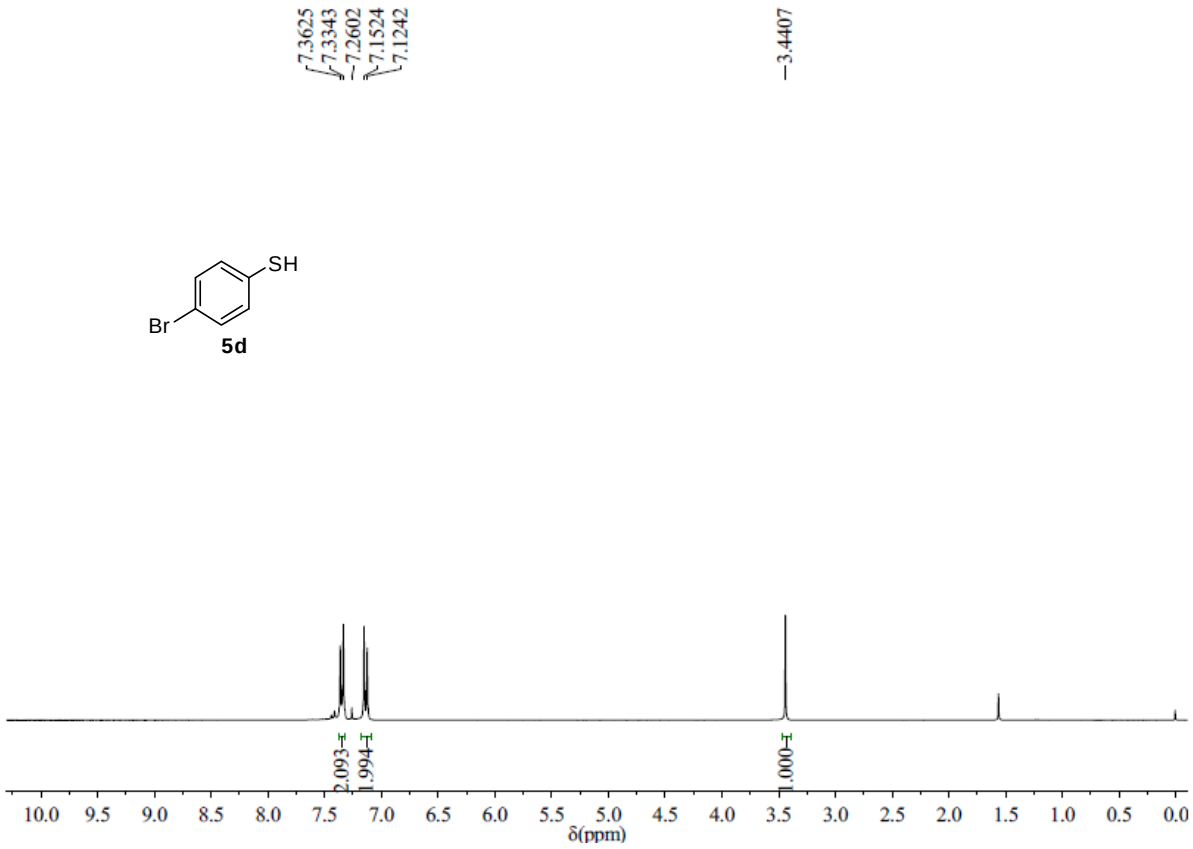
5b

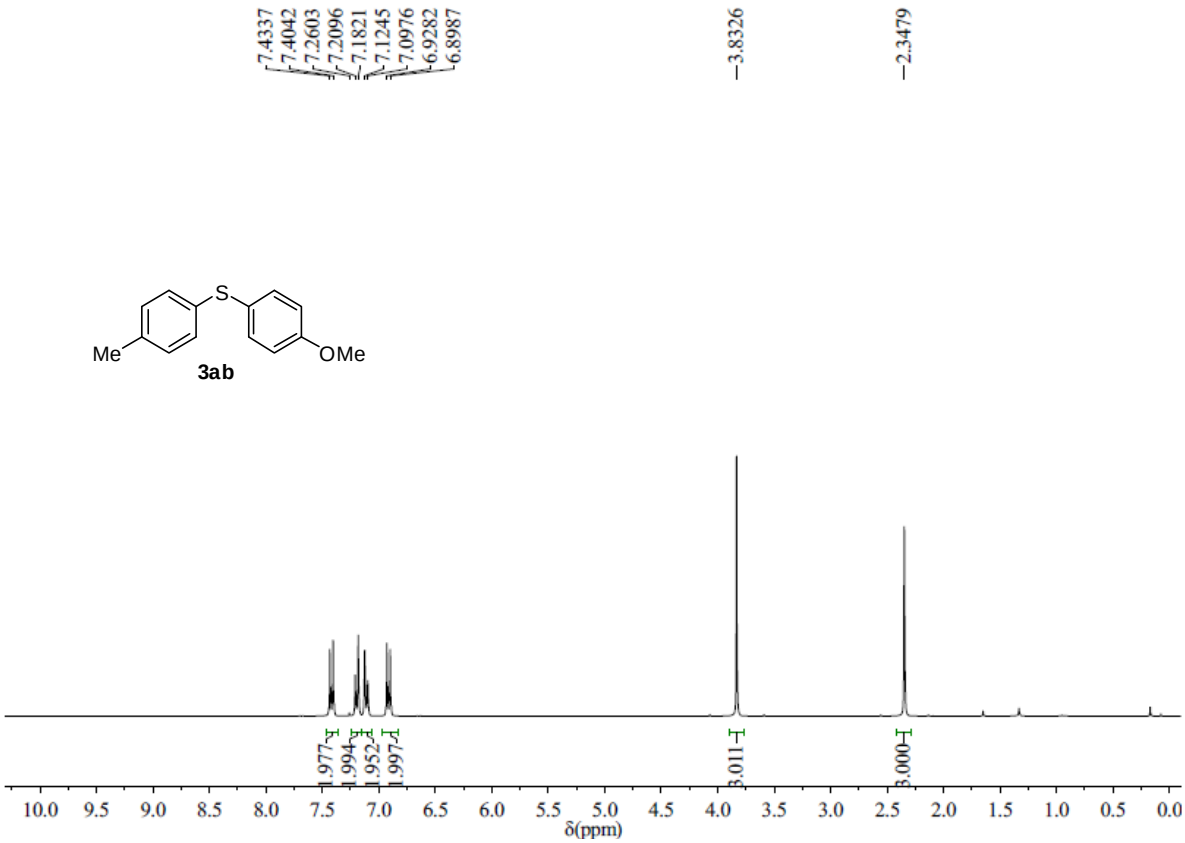

5.000
1.010
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ(ppm)

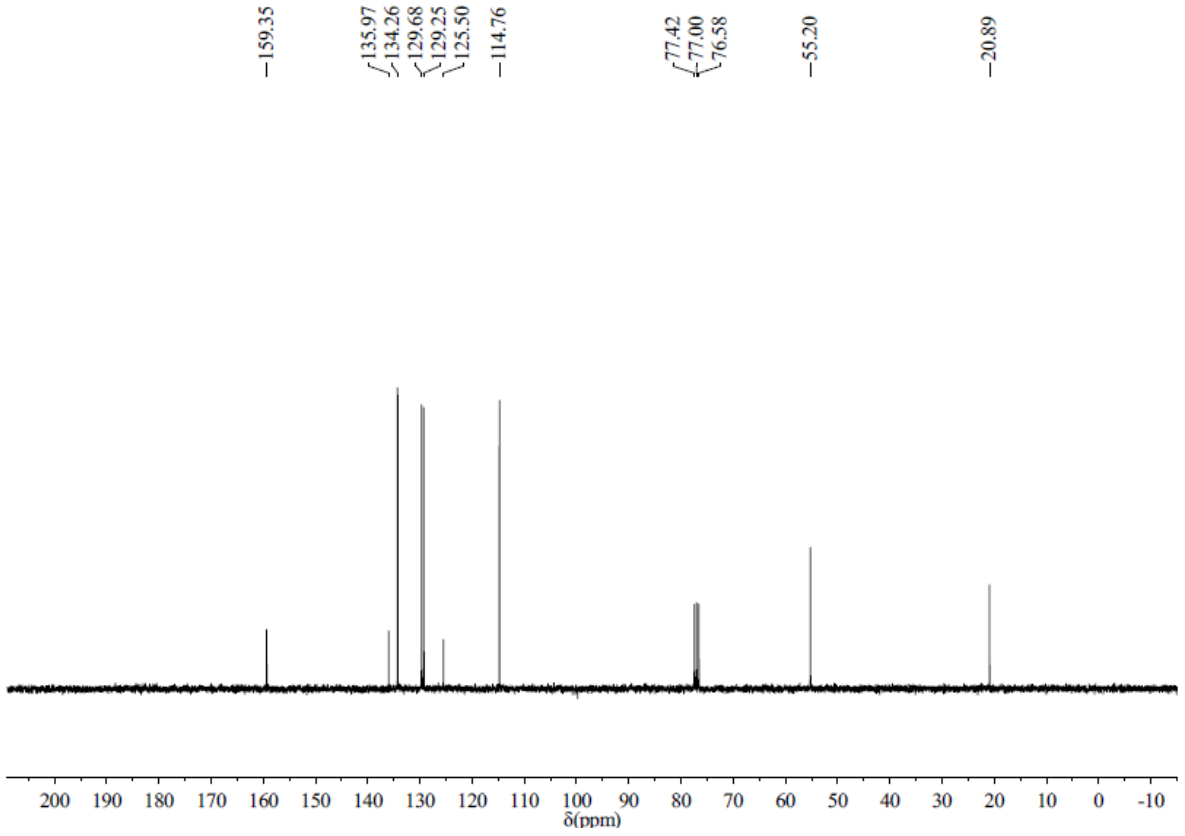

130.68
129.31
128.98
125.50
77.42
77.00
76.58
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ(ppm)

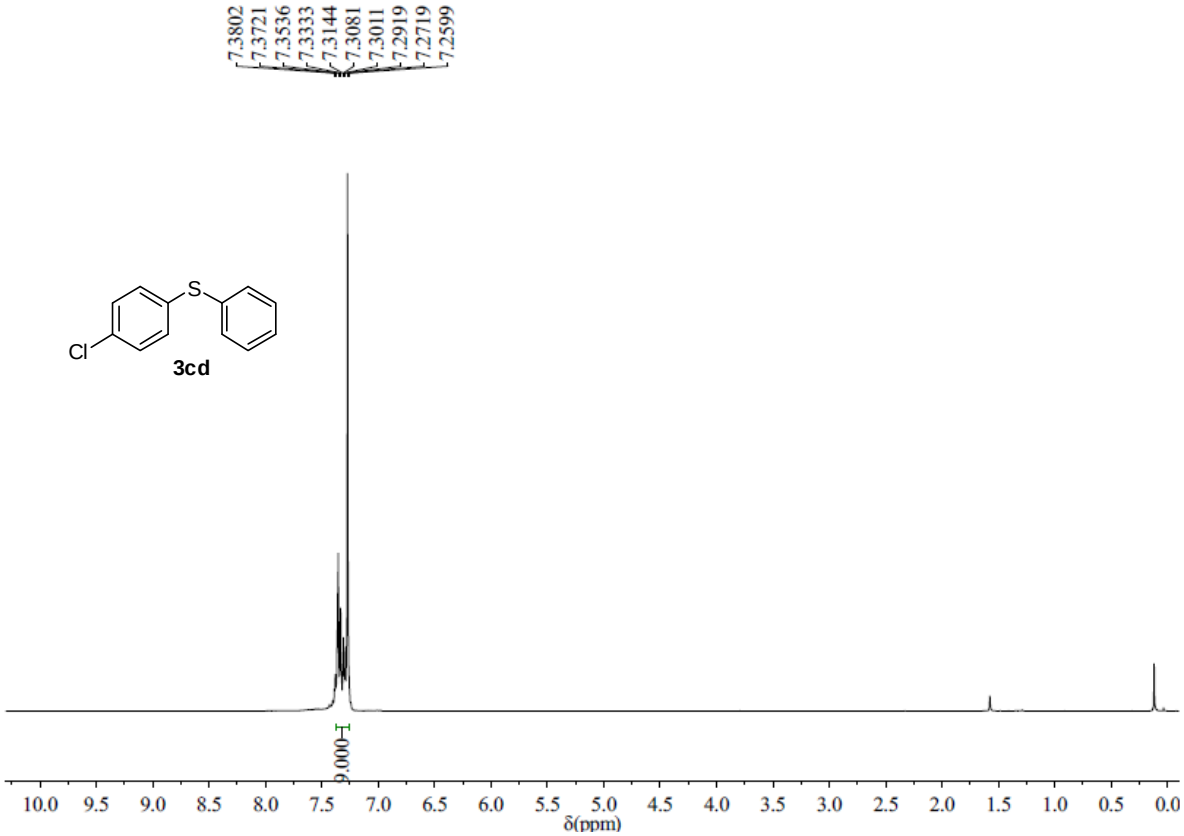

7.2600
7.2043
3.4535
0.0060
SH
Cl
5d
3.997
1.000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ(ppm)

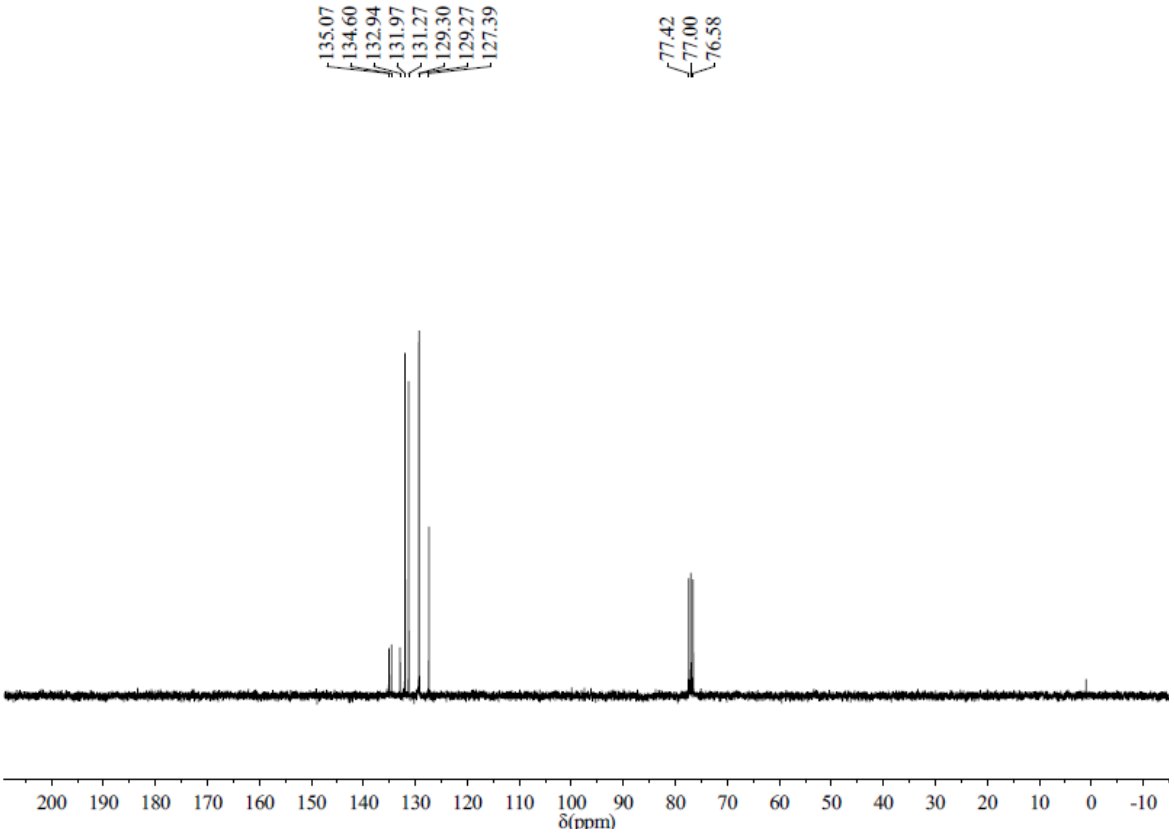

131.71
130.74
129.14
77.42
77.00
76.58
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ(ppm)

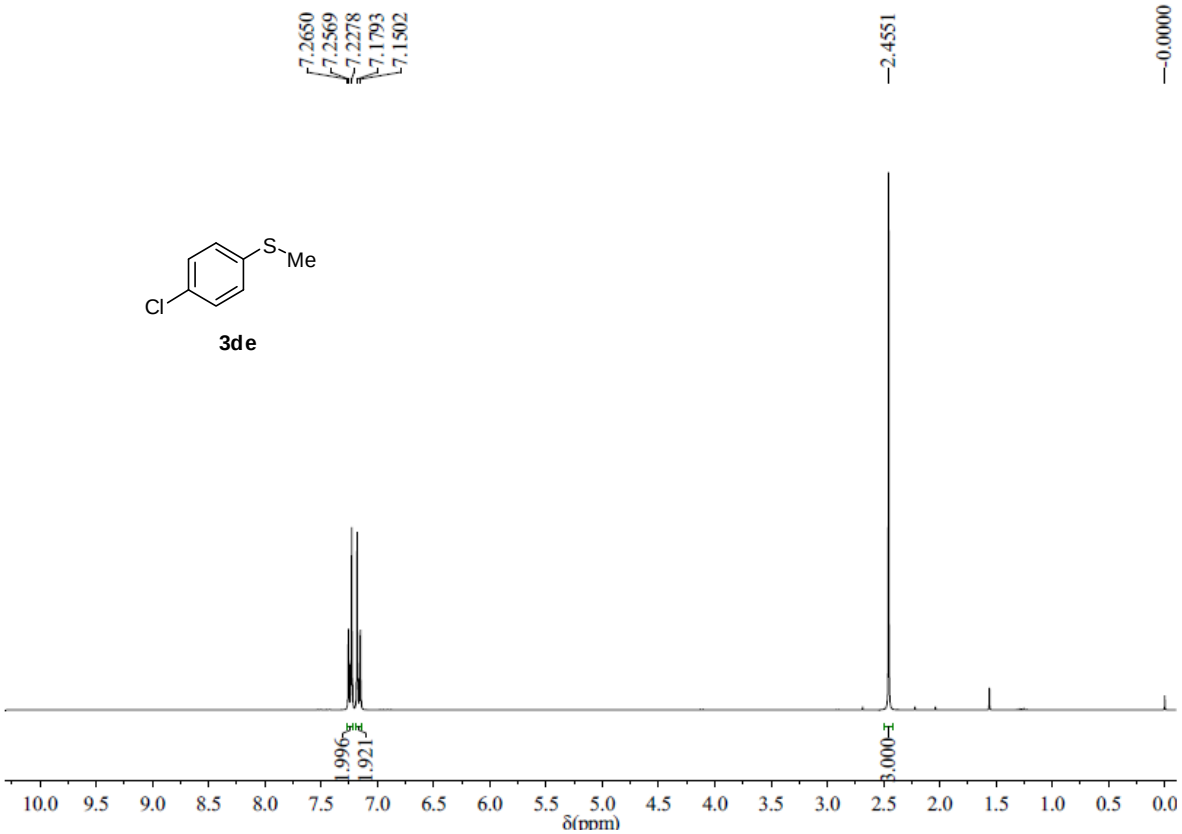

7.3625
7.3343
7.2602
7.1524
7.1242
3.4407
SH
Br
5d
2.093
1.994
1.000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ(ppm)
132.05
130.98
129.88
119.44
77.42
77.00
76.58
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ(ppm)


7.4337
7.4042
7.2603
7.2096
7.1821
7.1245
7.0976
6.9282
6.8987
3.8326
2.3479
S
Me
OMe
3ab
1.977
1.994
1.952
1.997
3.011
3.000
δ(ppm)

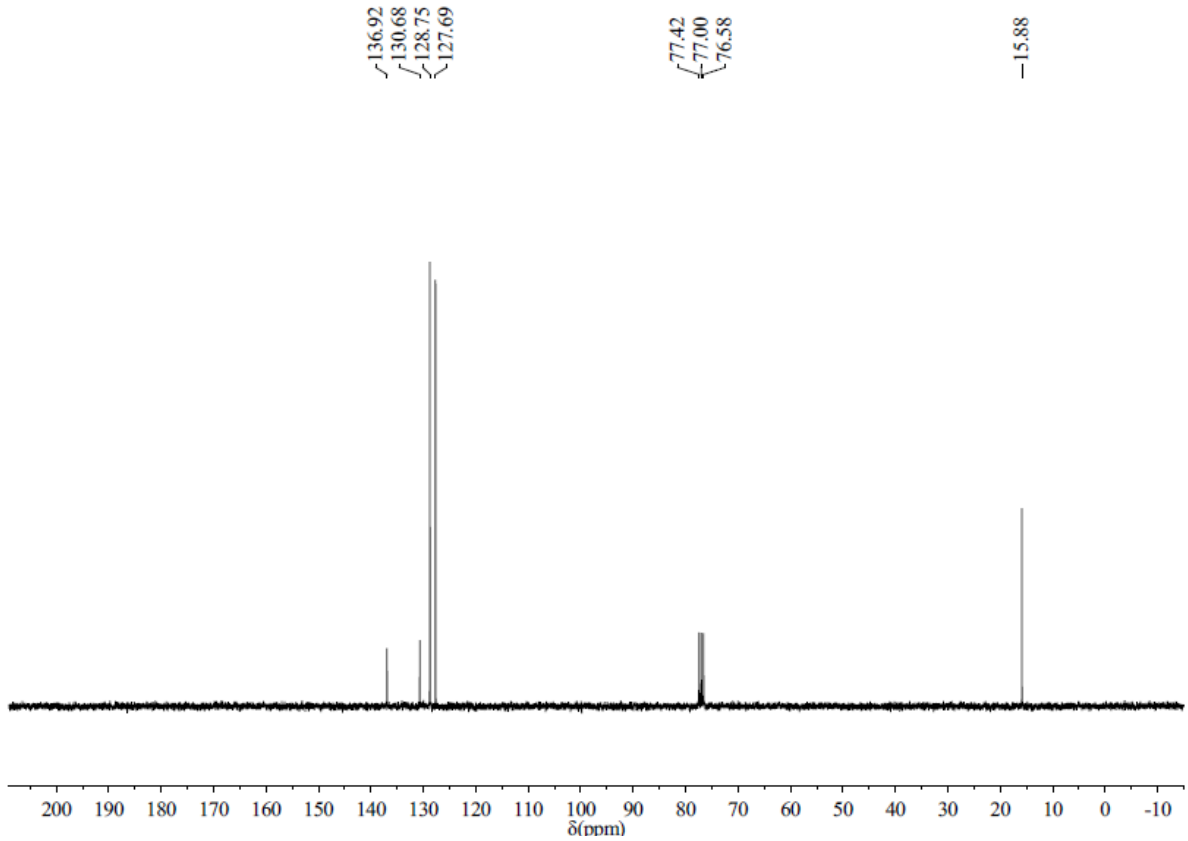

159.35
135.97
134.26
129.68
129.25
125.50
114.76
77.42
77.00
76.58
55.20
20.89
δ(ppm)


7.3802
7.3721
7.3536
7.3333
7.3144
7.3081
7.3011
7.2919
7.2719
7.2599
S
Cl
3cd
9.000
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
δ(ppm)


135.07
134.60
132.94
131.97
131.27
129.30
129.27
127.39
77.42
77.00
76.58
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ(ppm)

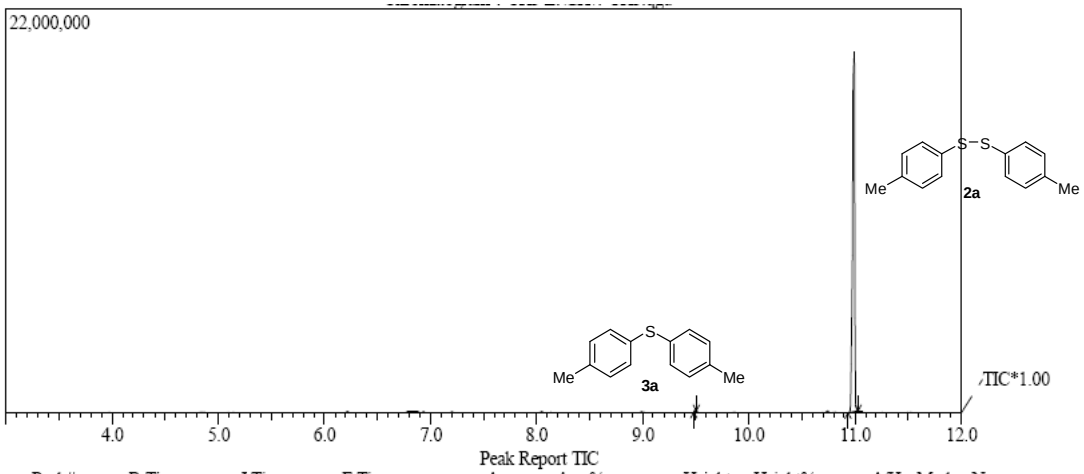

7.2650
7.2569
7.2278
7.1793
7.1502
2.4551
0.0000
S
Me
Cl
1.996
1.921
3.000
δ(ppm)

3de


136.92
130.68
128.75
127.69
77.42
77.00
76.58
15.88
δ(ppm)

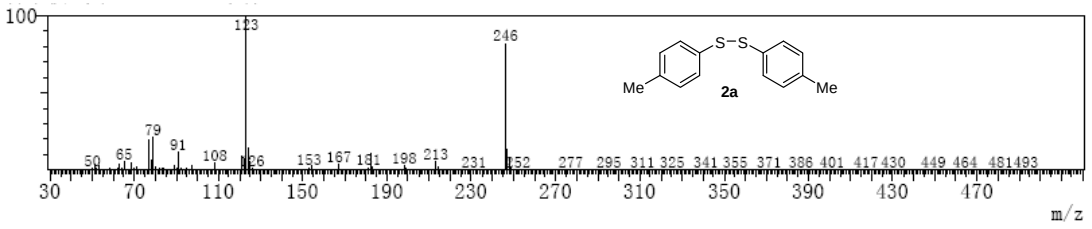
6. GC-MS analysis of the coupling compounds

GC-MS spectra of **2a** and **3a**

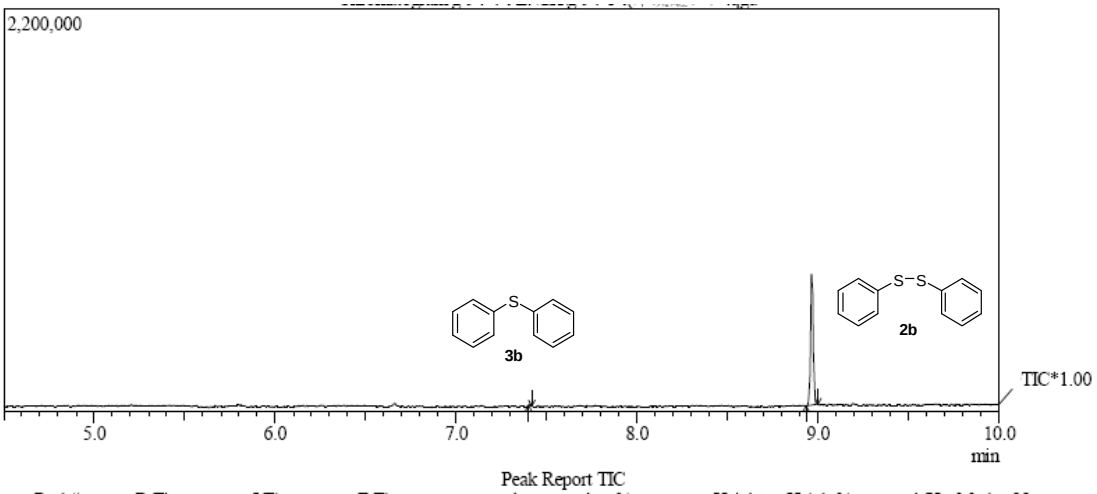


Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	9.498	9.483	9.508	138643	0.50	140229	0.71	0.99	MI	
2	10.988	10.933	11.033	27463717	99.50	19621062	99.29	1.40	MI	
				27602360	100.00	19761291	100.00			

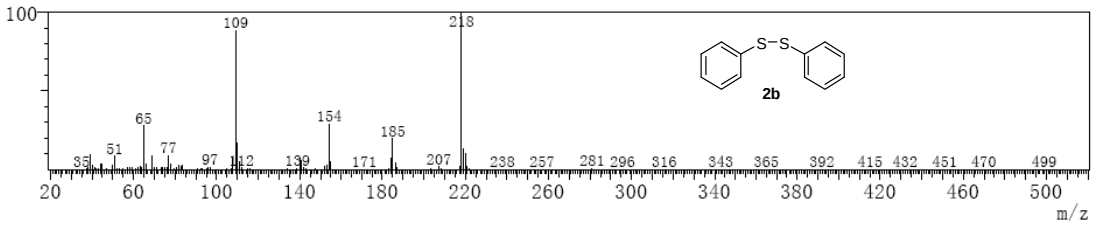


GC-MS spectra of **2b** and **3b**

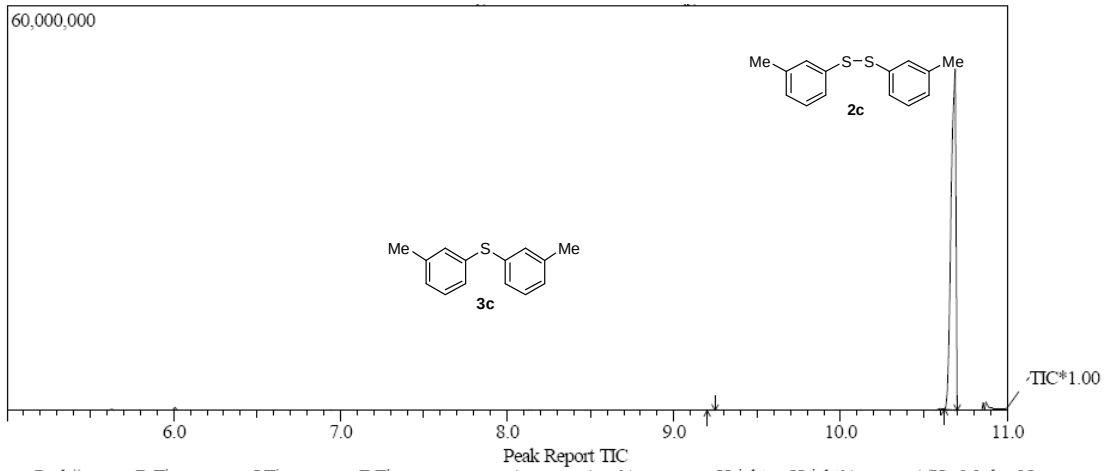


Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	7.410	7.400	7.420	6614	0.91	11544	1.58	0.57	MI	
2	8.966	8.935	9.000	724028	99.09	717218	98.42	1.01	MI	
				730642	100.00	728762	100.00			

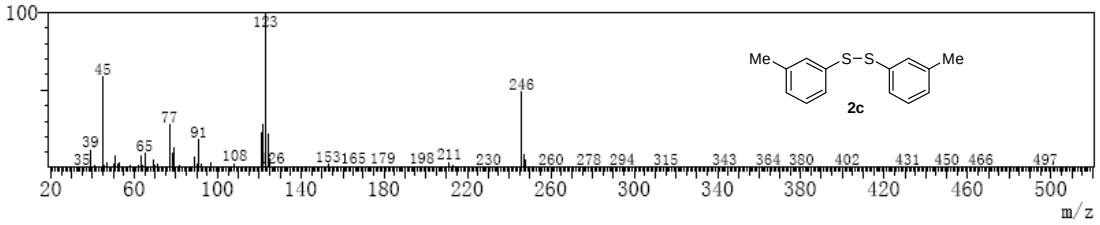


GC-MS spectra of **2c** and **3c**

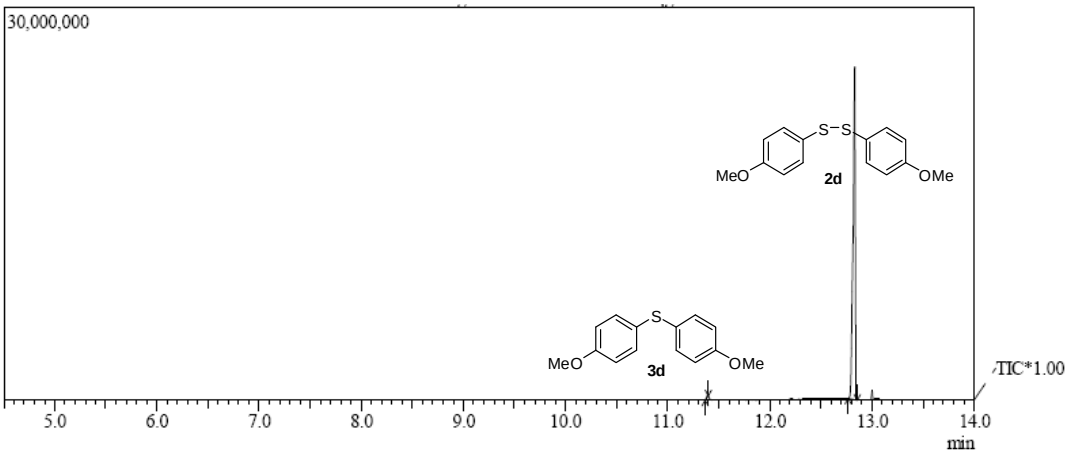


Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	9.224	9.200	9.250	125465	0.13	102958	0.20	1.22	MI	
2	10.688	10.625	10.700	99492097	99.87	50647340	99.80	1.96	MI	
				99617562	100.00	50750298	100.00			

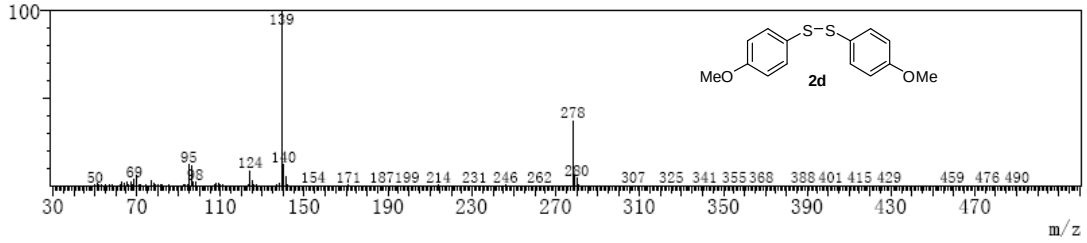


GC-MS spectra of **2d** and **3d**

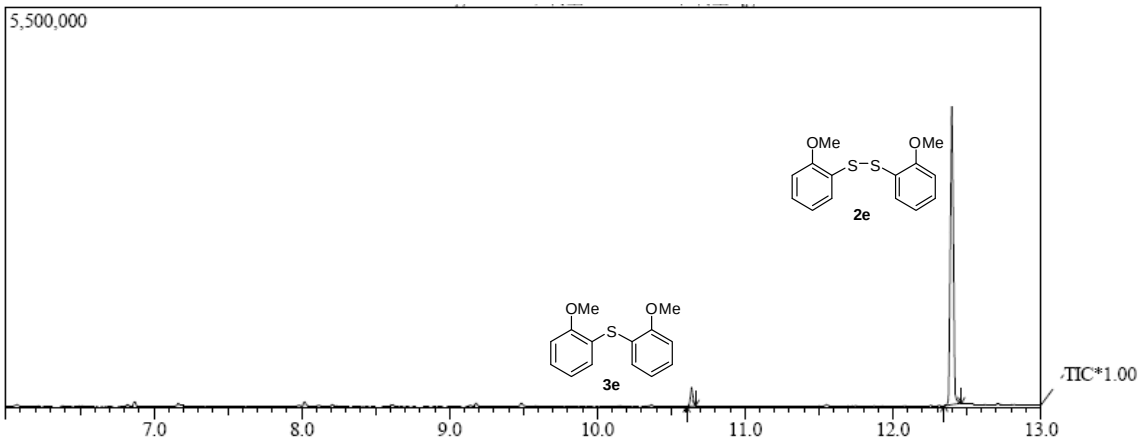


Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	11.392	11.367	11.400	260384	0.70	245199	0.95	1.06	MI	
2	12.830	12.767	12.858	36762725	99.30	25483689	99.05	1.44	MI	
				37023109	100.00	25728888	100.00			

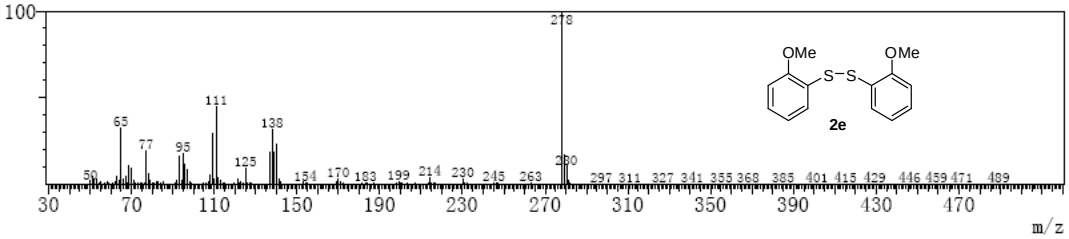


GC-MS spectra of **2e** and **3e**

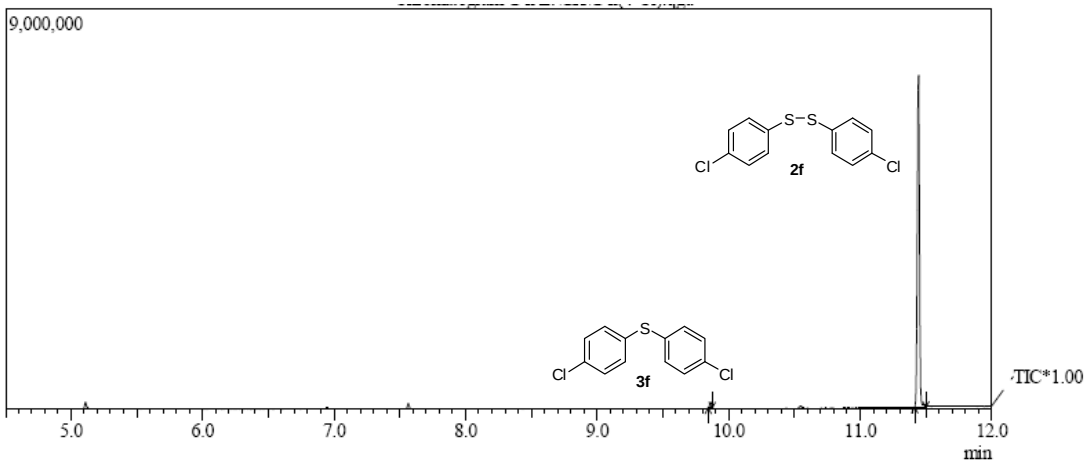


Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	10.641	10.608	10.667	324202	5.72	256512	5.90	1.26	MI	
2	12.400	12.350	12.467	5342002	94.28	4092973	94.10	1.31	MI	
				5666204	100.00	4349485	100.00			

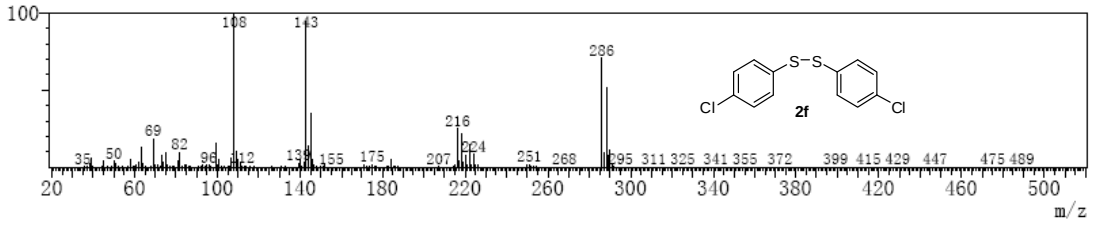


GC-MS spectra of **2f** and **3f**

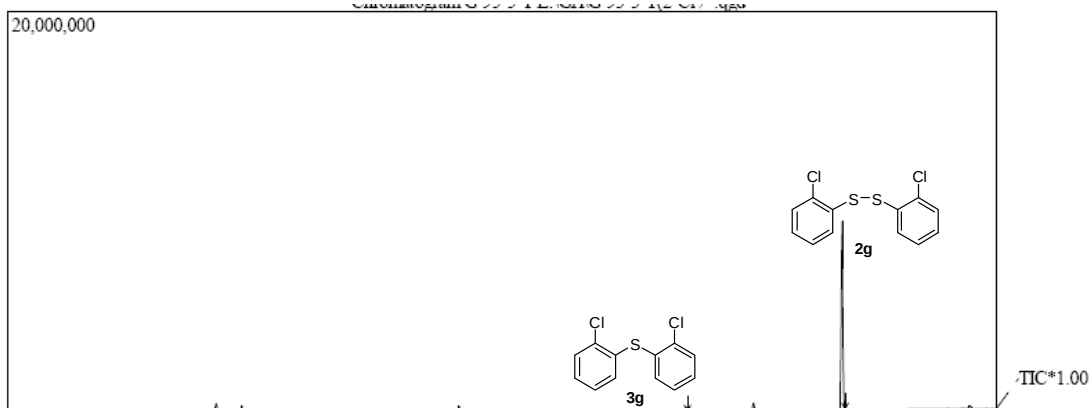


Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	9.863	9.845	9.875	146059	1.66	146204	1.92	1.00	MI	
2	11.443	11.415	11.500	8644293	98.34	7476350	98.08	1.16	MI	
				8790352	100.00	7622554	100.00			

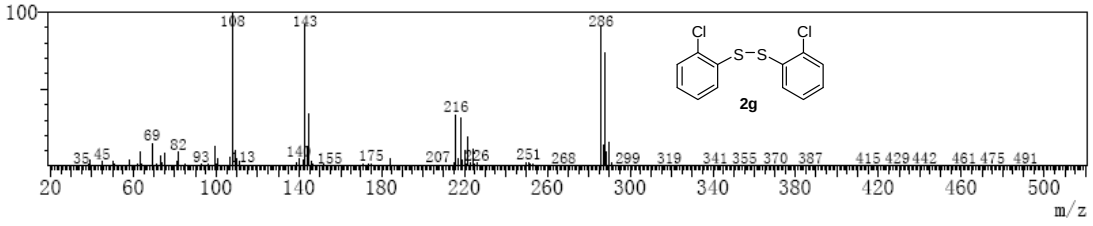


GC-MS spectra of **2g** and **3g**

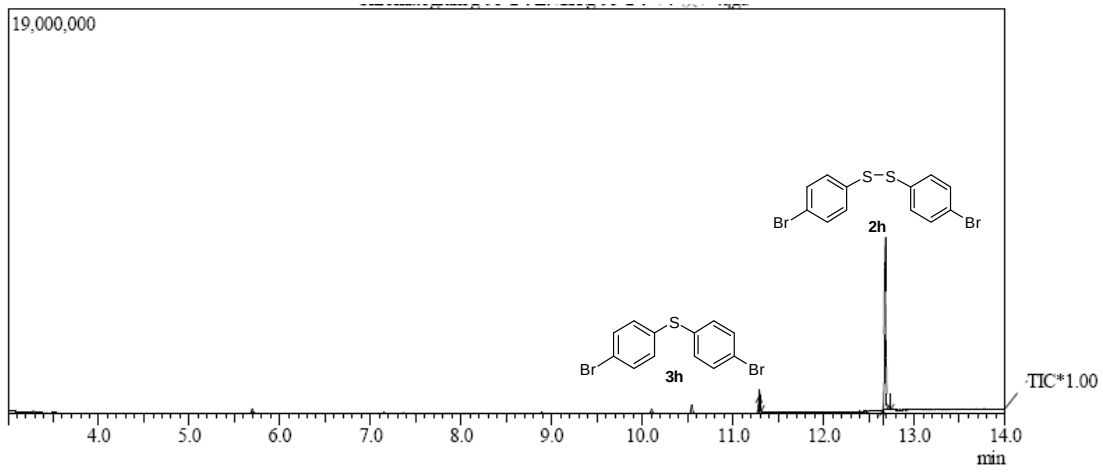


Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	9.859	9.845	9.875	157694	1.47	173408	1.81	0.91	MI	
2	11.439	11.410	11.470	10592252	98.53	9431426	98.19	1.12	MI	
				10749946	100.00	9604834	100.00			

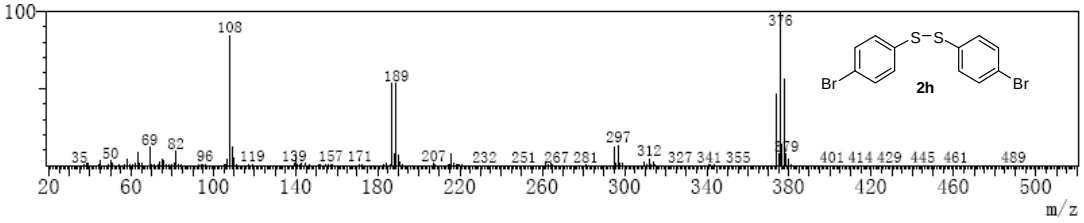


GC-MS spectra of **2h** and **3h**

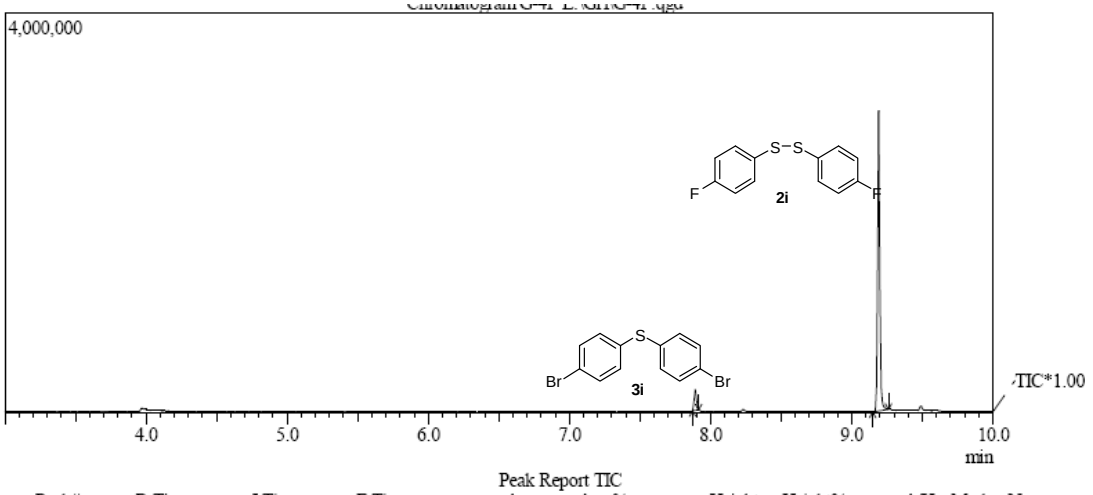


Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	11.291	11.285	11.310	236085	2.62	512622	5.94	0.46	MI	
2	12.679	12.655	12.740	8784501	97.38	8111797	94.06	1.08	MI	
				9020586	100.00	8624419	100.00			

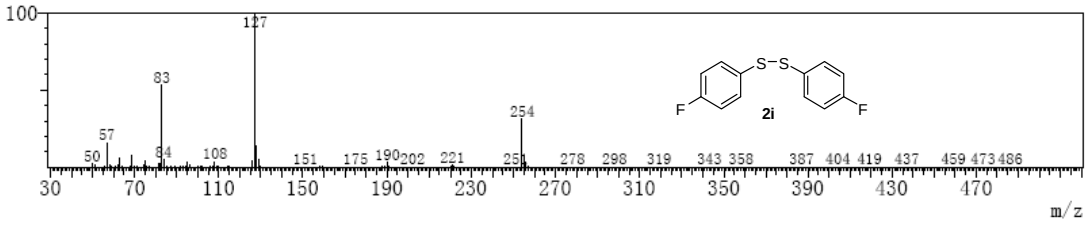


GC-MS spectra of **2i** and **3i**

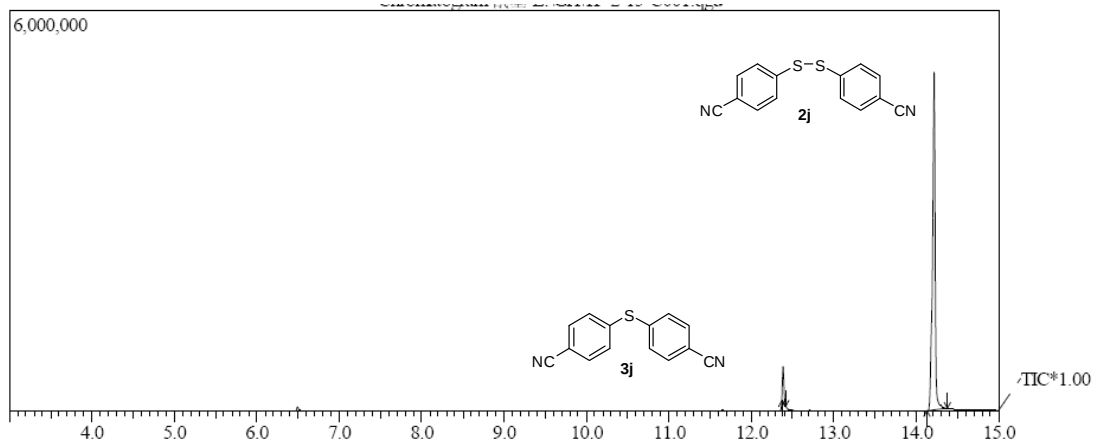


Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	7.892	7.875	7.917	218277	6.03	210901	6.55	1.03	MI	
2	9.191	9.150	9.258	3401850	93.97	3008217	93.45	1.13	MI	
				3620127	100.00	3219118	100.00			

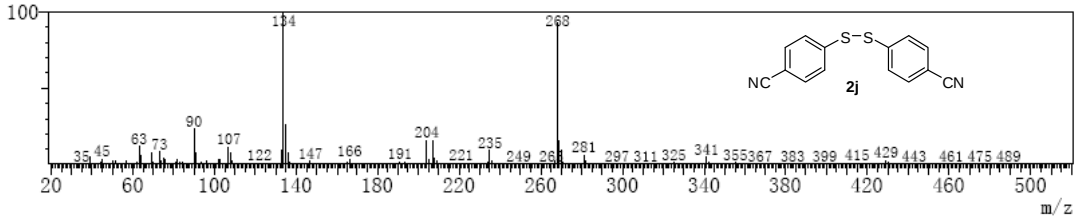


GC-MS spectra of **2j** and **3j**

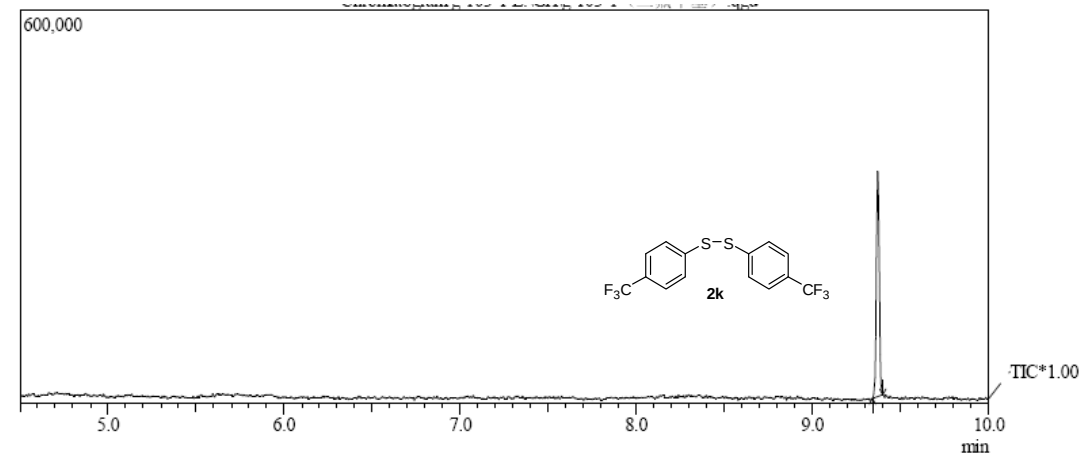


Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	12.383	12.367	12.417	665484	5.72	542468	9.72	1.23	MI	
2	14.216	14.133	14.383	10961737	94.28	5038870	90.28	2.18	MI	
				11627221	100.00	5581338	100.00			

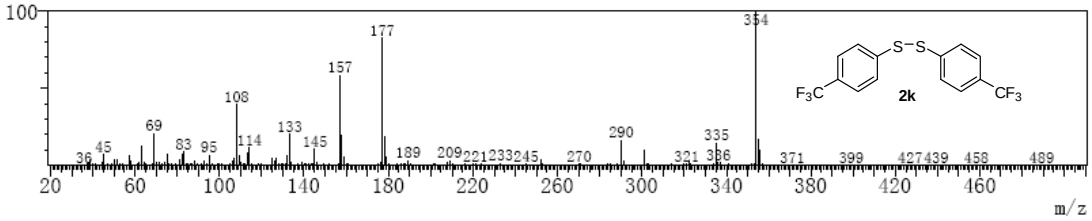


GC-MS spectra of **2k** and **3k**

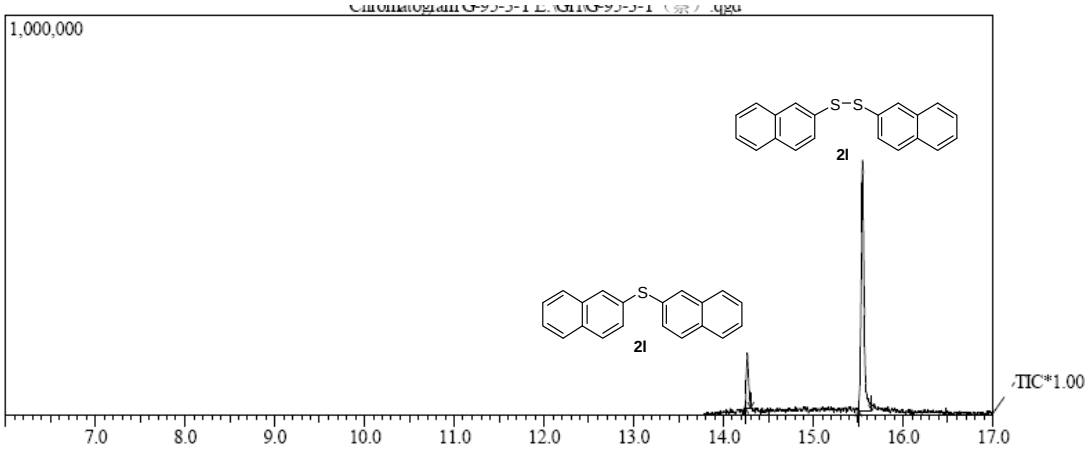


Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	9.372	9.340	9.400	377920	100.00	343613	100.00	1.10	MI	
				377920	100.00	343613	100.00			



GC-MS spectra of **2l** and **3l**



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	14.267	14.245	14.300	189286	13.15	121912	18.05	1.55	MI	
2	15.551	15.505	15.650	1250691	86.85	553545	81.95	2.26	MI	
				1439977	100.00	675457	100.00