Fe_3O_4@ABA-Aniline-CuI nanocomposite as a highly efficient and reusable nanocatalyst for synthesis of benzothiazole-sulfide aryls and heteroaryls

Mingzhe Sun [1] *, Wei Liu [2], Wei Wu [1], Qun Li [1], Li Shen [3]*

[1] College of Food and Biology, Changchun Polytechnic, Changchun, Jilin 130033, China

[2] Jilin Normal University, Siping, Jilin 136000, China

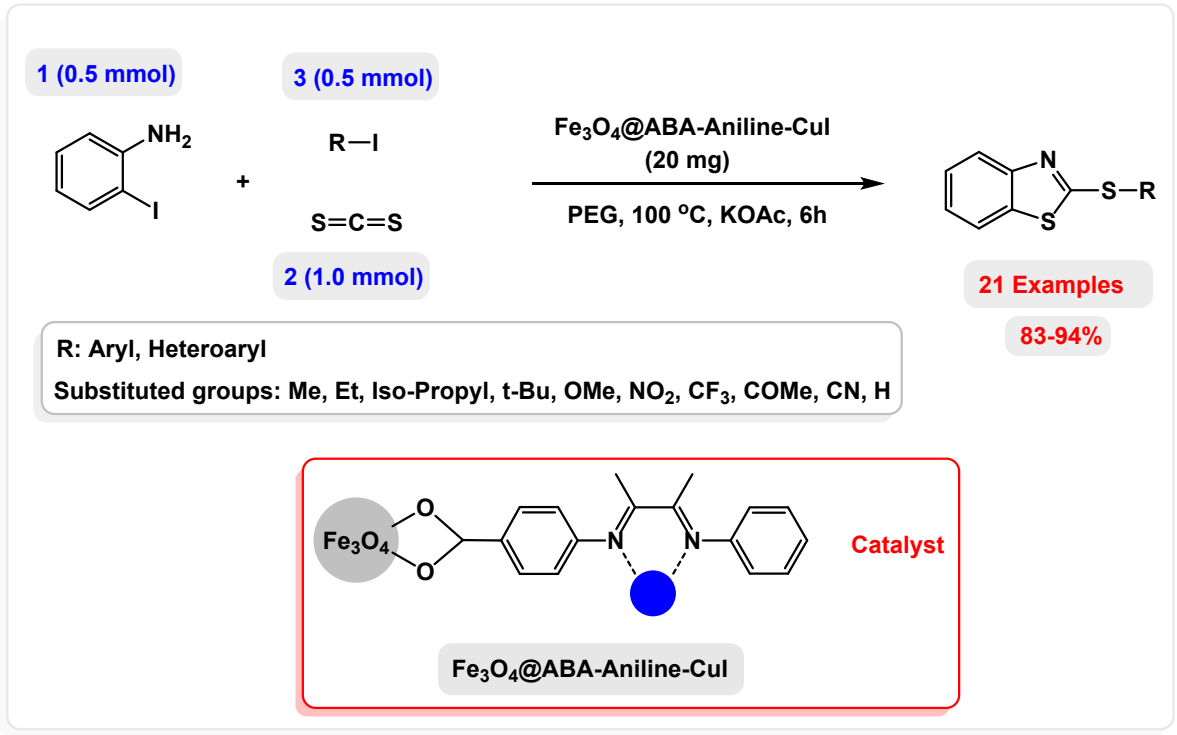
[3] Institute Chemical and Nanotechnology, Beijing, China.

Mail: lshenl1985@gmail.com and mingzhesun2021@163.com

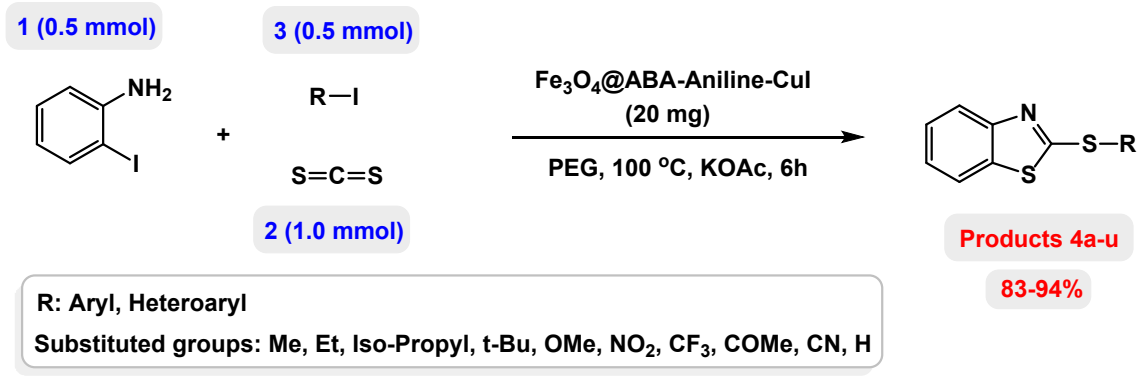
Abstract

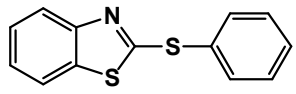
Studying diaryl sulfides and benzothiazoles is important in organic synthesis because a large number of natural and medicinal products contain these scaffolds. Over the past few years, the research on the synthesis of compounds containing benzothiazole-sulfide aryls as important biological molecules have received a significant attention. Multicomponent reactions are the most popular strategy for the performance of difficult reactions and the synthesis of complexed-molecules such as benzothiazole-sulfide aryls. In this work, CuI immobilized on the surface of magnetic Fe_3O_4 nanoparticles modified with aniline and 4-aminobenzoic acid [Fe_3O_4@ABA-Aniline-CuI nanocomposite] were successfully constructed and its catalytic activity were investigated in the preparation of a broad range of benzothiazole-sulfide aryls and heteroaryls through the one-pot three-component reactions of 2-iodoaniline with carbon disulfide and aryl or heteroaryl iodides in the presence of KOAc as base in PEG as solvent. TEM and SEM images revealed that the shape of the Fe_3O_4@ABA-Aniline-CuI particles is spherical and the size of the particles is approximately between 12-25 nanometers.

Keywords: Fe_3O_4@ABA-Aniline-CuI nanocatalyst, benzothiazole-sulfide aryls, Magnetically recoverable catalyst, Nanometer range, Multicomponent reactions.



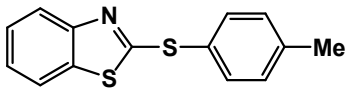
Scope of Fe_3O_4@ABA-Aniline-CuI nanocatalyst in synthesis of benzothiazole-sulfide aryls. [a]





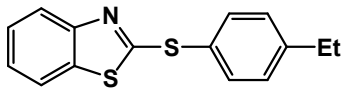
Product 4a

94%



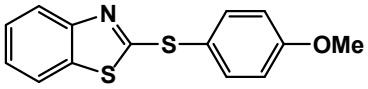
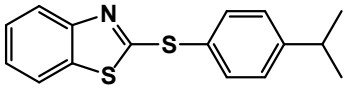
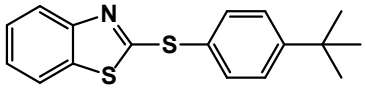
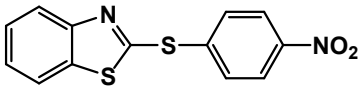
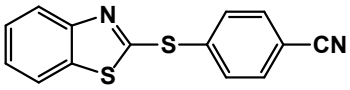
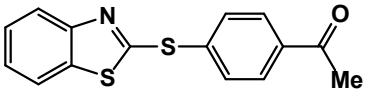
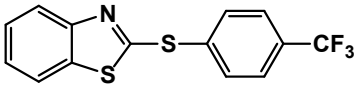
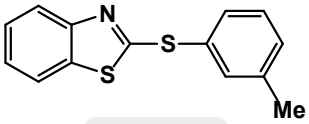
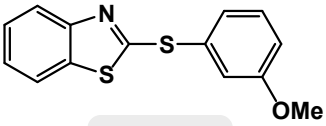
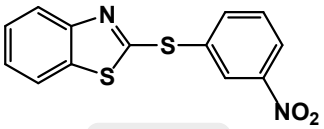
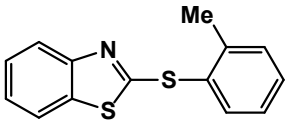
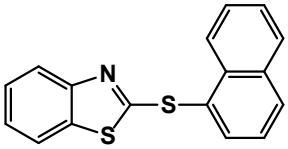
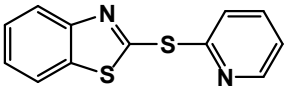
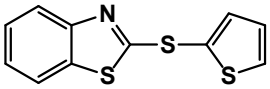
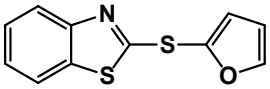
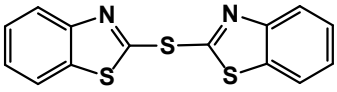
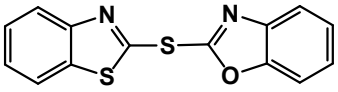
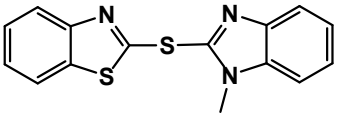
Product 4b

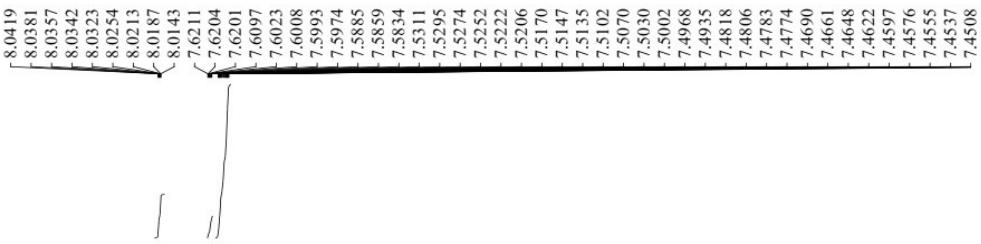
97%

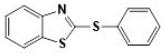


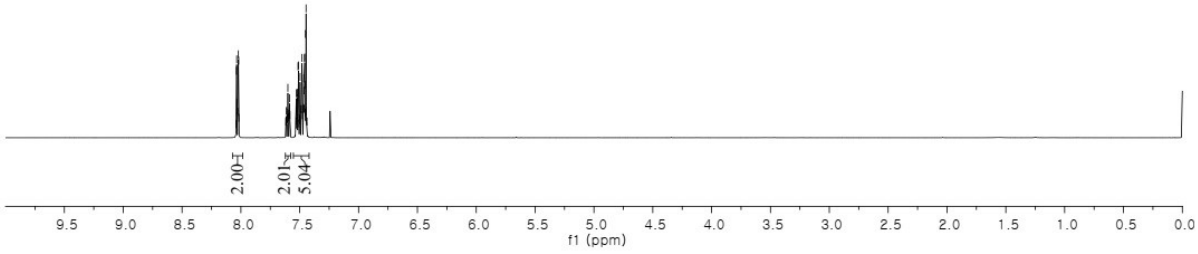
Product 4c

95%

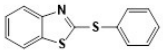
 Product 4d 97%	 Product 4e 88%	 Product 4f 83%
 Product 4g 90%	 Product 4h 91%	 Product 4i 90%
 Product 4j 86%	 Product 4k 95%	 Product 4l 93%
 Product 4m 86%	 Product 4n 96%	 Product 4o 91%
 Product 4p 93%	 Product 4q 91%	 Product 4r 89%
 Product 4s 90%	 Product 4t 87%	 Product 4u 91%

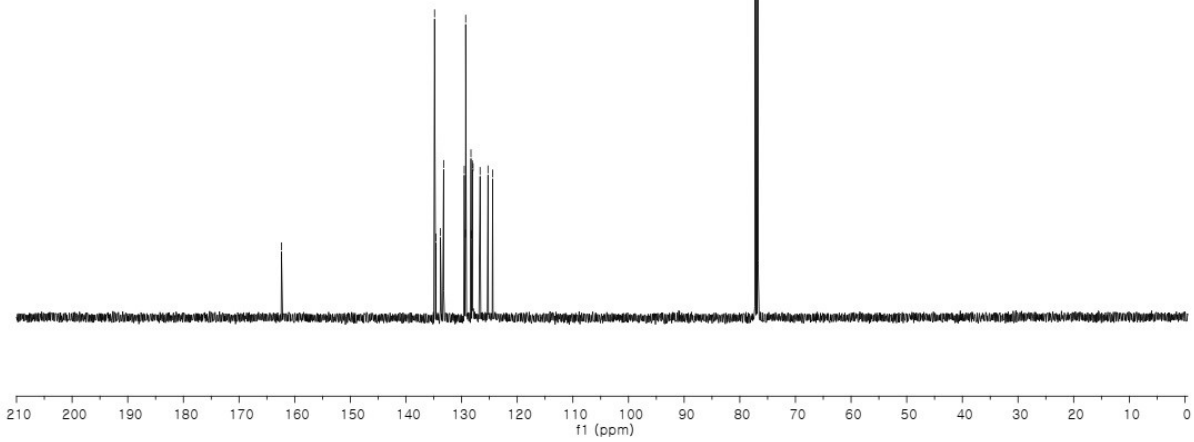

8.0419
8.0381
8.0357
8.0342
8.0323
8.0254
8.0213
8.0187
8.0143
7.6211
7.6204
7.6201
7.6097
7.6023
7.6008
7.5993
7.5974
7.5885
7.5859
7.5834
7.5311
7.5295
7.5274
7.5252
7.5222
7.5206
7.5170
7.5147
7.5135
7.5102
7.5070
7.5030
7.5002
7.4968
7.4935
7.4818
7.4806
7.4783
7.4774
7.4690
7.4661
7.4648
7.4622
7.4597
7.4576
7.4555
7.4537
7.4508


N
S
S

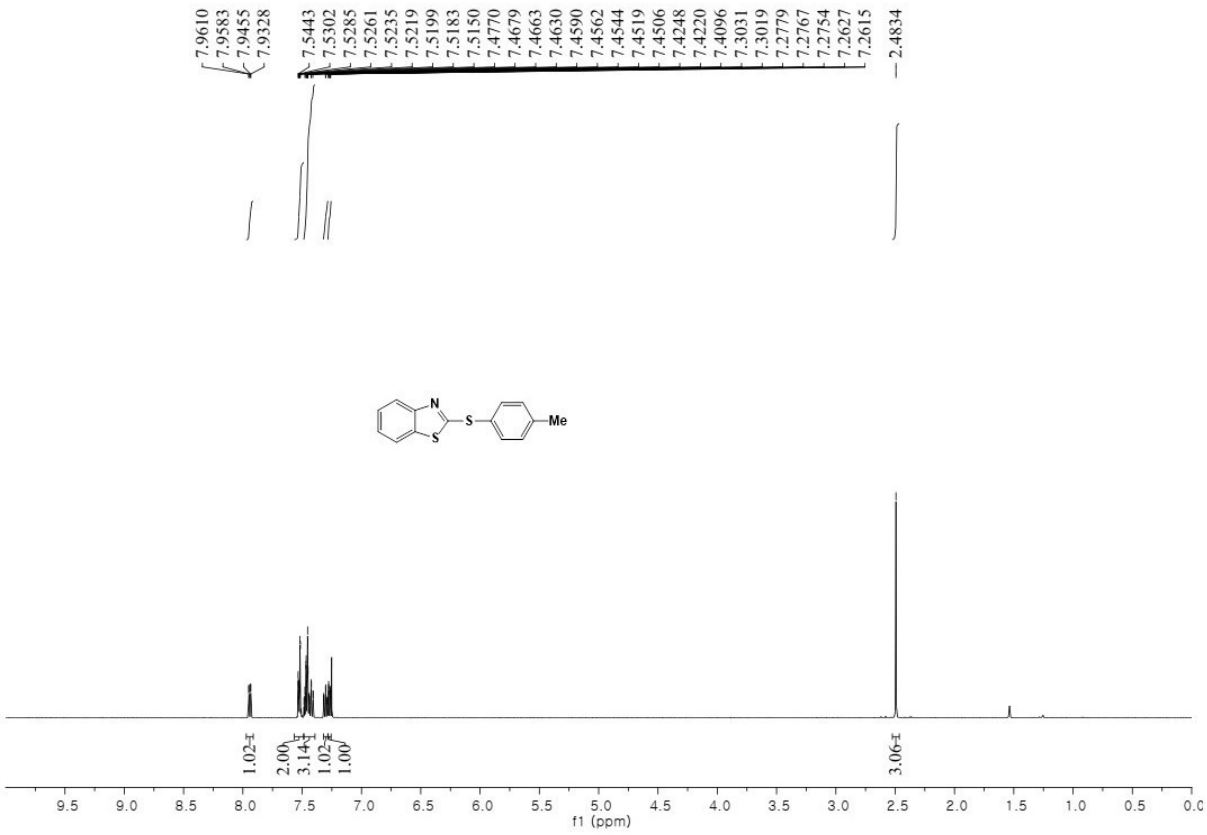

2.00
2.01
5.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

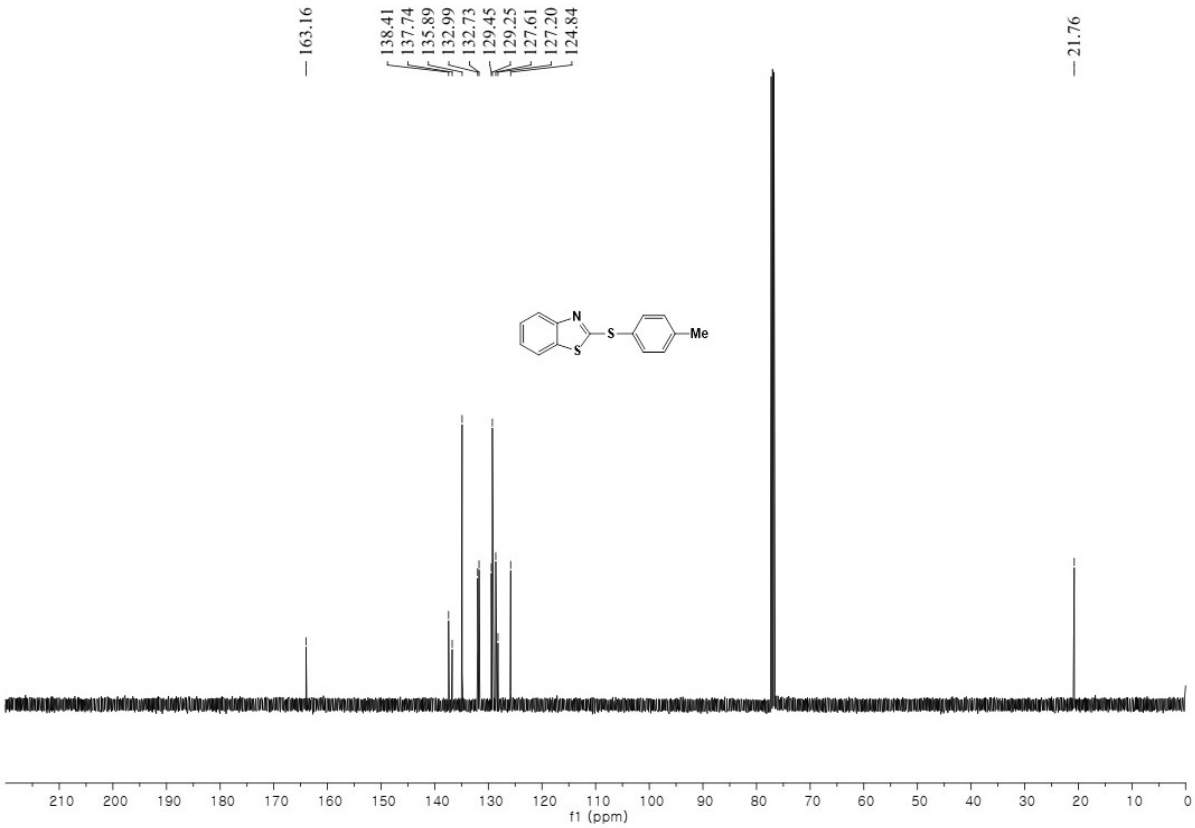

162.13
135.86
135.63
134.79
134.23
130.52
129.31
129.27
128.32
127.26
127.06
126.94
125.68
124.26
123.42


N
S
S

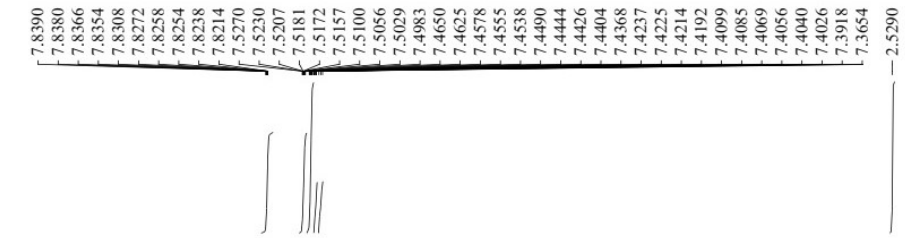

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

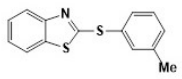
2-(phenylthio)benzo[d]thiazole: 1H NMR (500 MHz, CDCl3) δ 8.04–8.01 (m, 2H), 7.62–7.60 (m, 2H), 7.59–7.45 (m, 5H); 13C{1H} NMR (126 MHz, CDCl3) δ 162.1, 135.9, 135.6, 134.8, 134.2, 130.5, 129.3, 129.2, 128.3, 127.2, 127.0, 126.1, 125.7, 124.3, 123.4

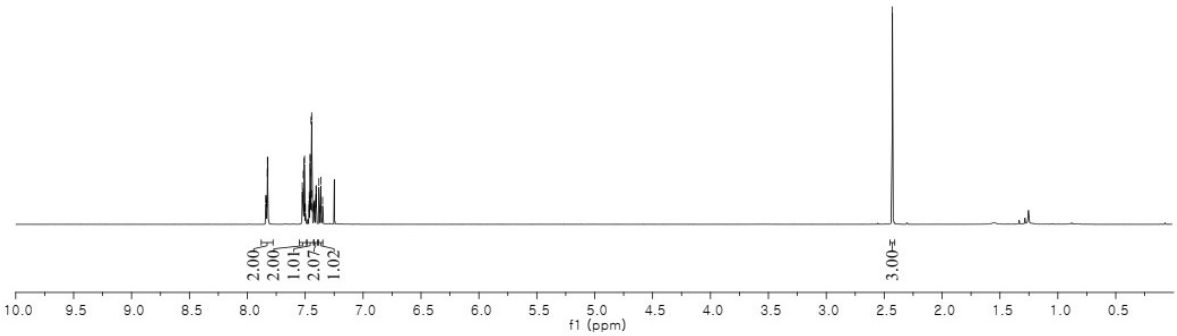




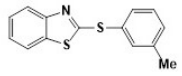
2-(p-tolylthio)benzo[d]thiazole: 1H NMR (500 MHz, CDCl3) δ 7.96 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.54–7.51 (m, 2H), 7.51–7.47 (m, 3H), 7.46–7.42 (m, 2H), 7.40–7.26 (m, 1H), 2.49 (s, 3H); 13C{1H} NMR (126 MHz, CDCl3) δ 163.2, 138.4, 137.7, 135.9, 132.9, 132.7, 129.5, 129.3, 127.6, 1272, 124.8, 21.8.

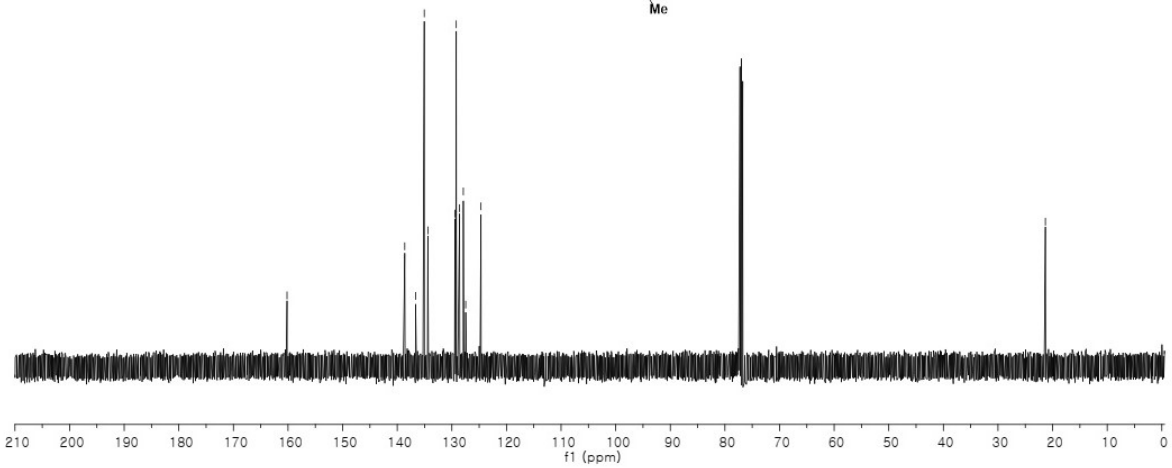

7.8390
7.8380
7.8366
7.8354
7.8308
7.8272
7.8258
7.8254
7.8238
7.8214
7.5270
7.5230
7.5207
7.5181
7.5172
7.5157
7.5100
7.5056
7.5029
7.4983
7.4650
7.4625
7.4578
7.4555
7.4538
7.4490
7.4444
7.4426
7.4404
7.4368
7.4237
7.4225
7.4214
7.4192
7.4099
7.4085
7.4069
7.4056
7.4040
7.4026
7.3918
7.3654
2.5290


N
S
S
Me

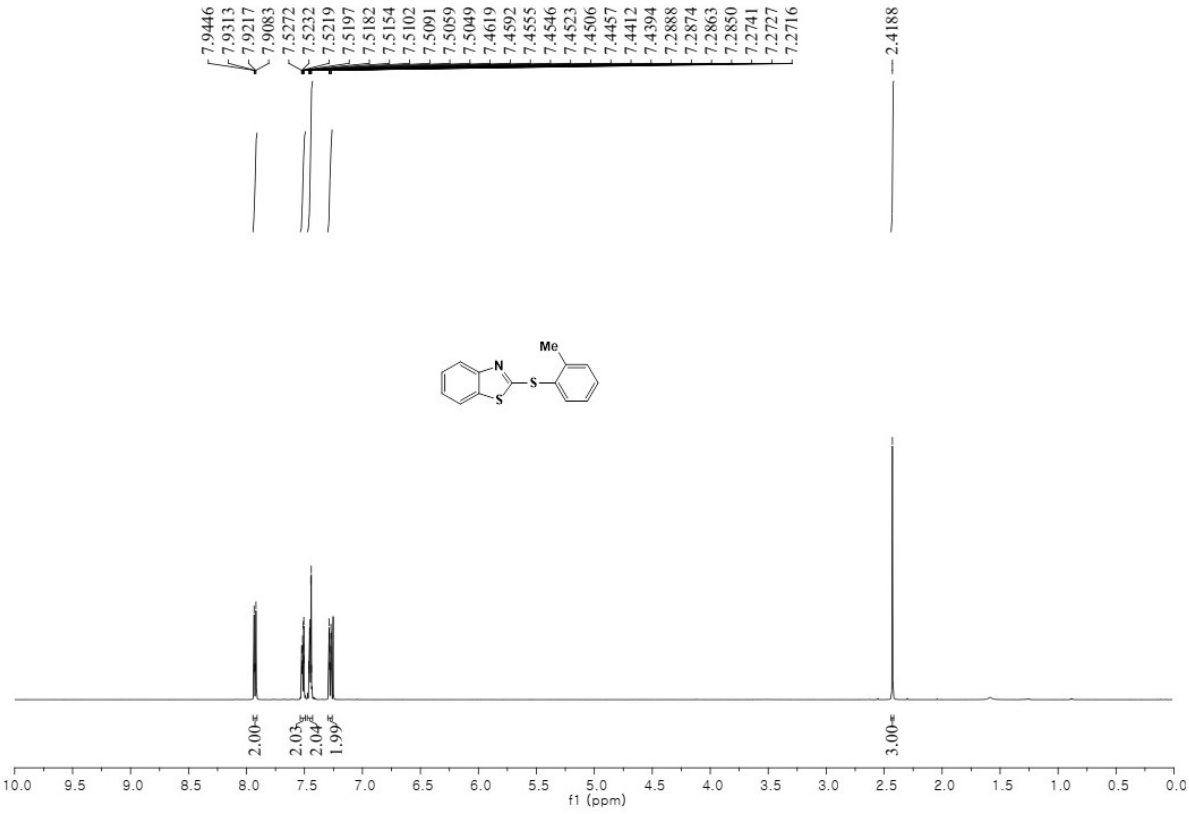

2.00
2.00
1.01
2.07
1.02
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

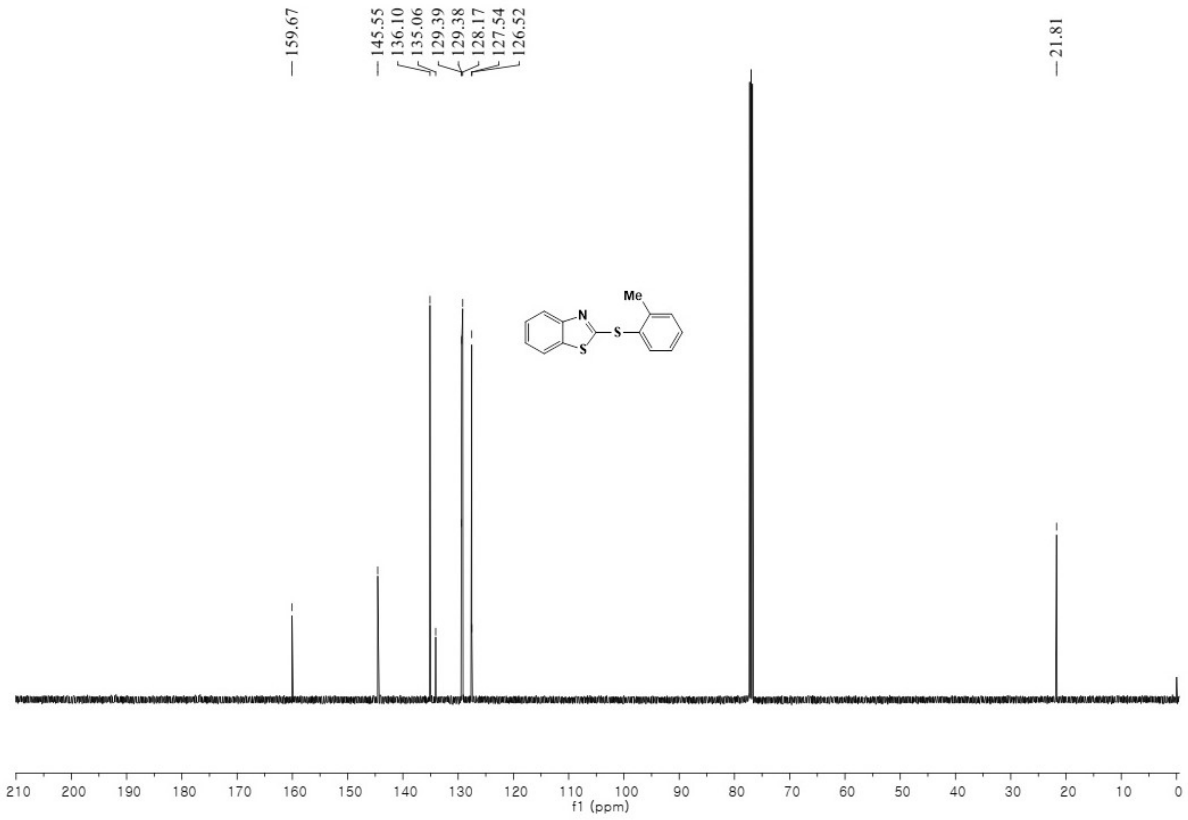

160.21
137.62
135.63
134.05
133.39
129.43
128.19
127.59
126.90
126.46
125.67
21.62


N
S
S
Me

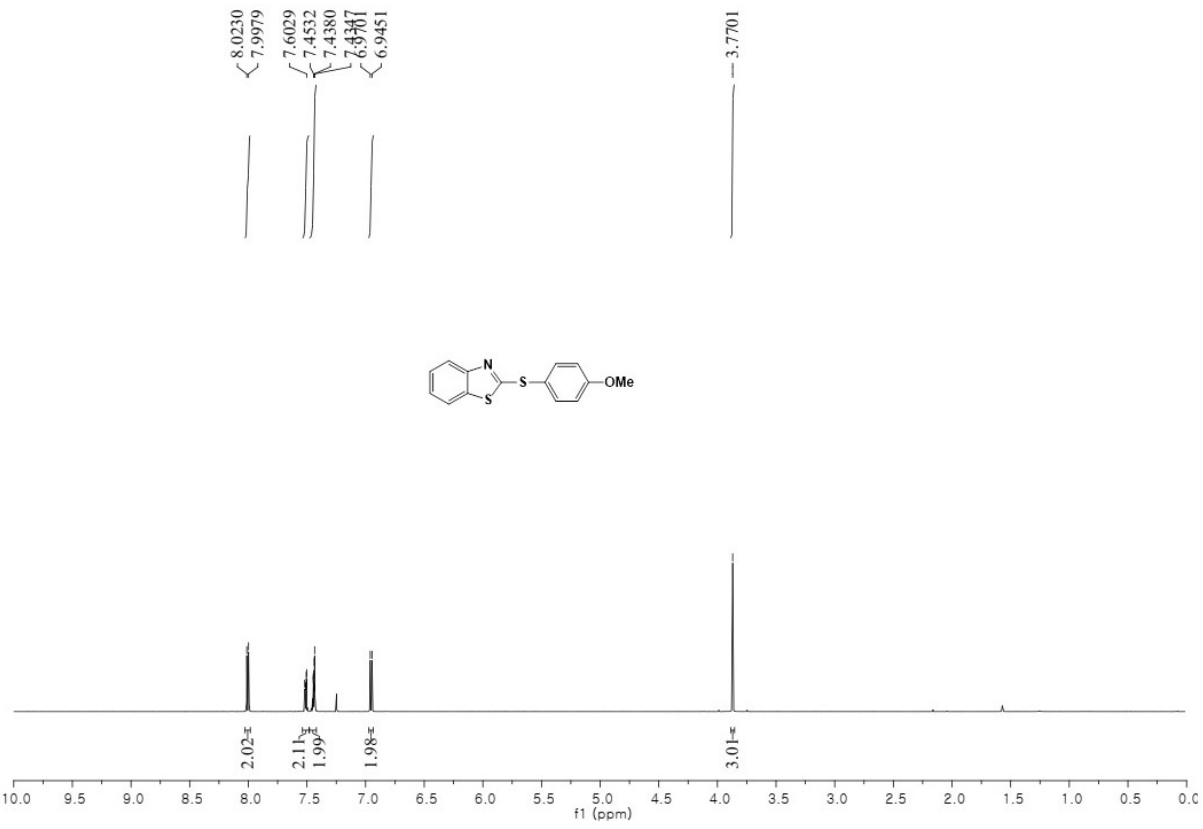

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

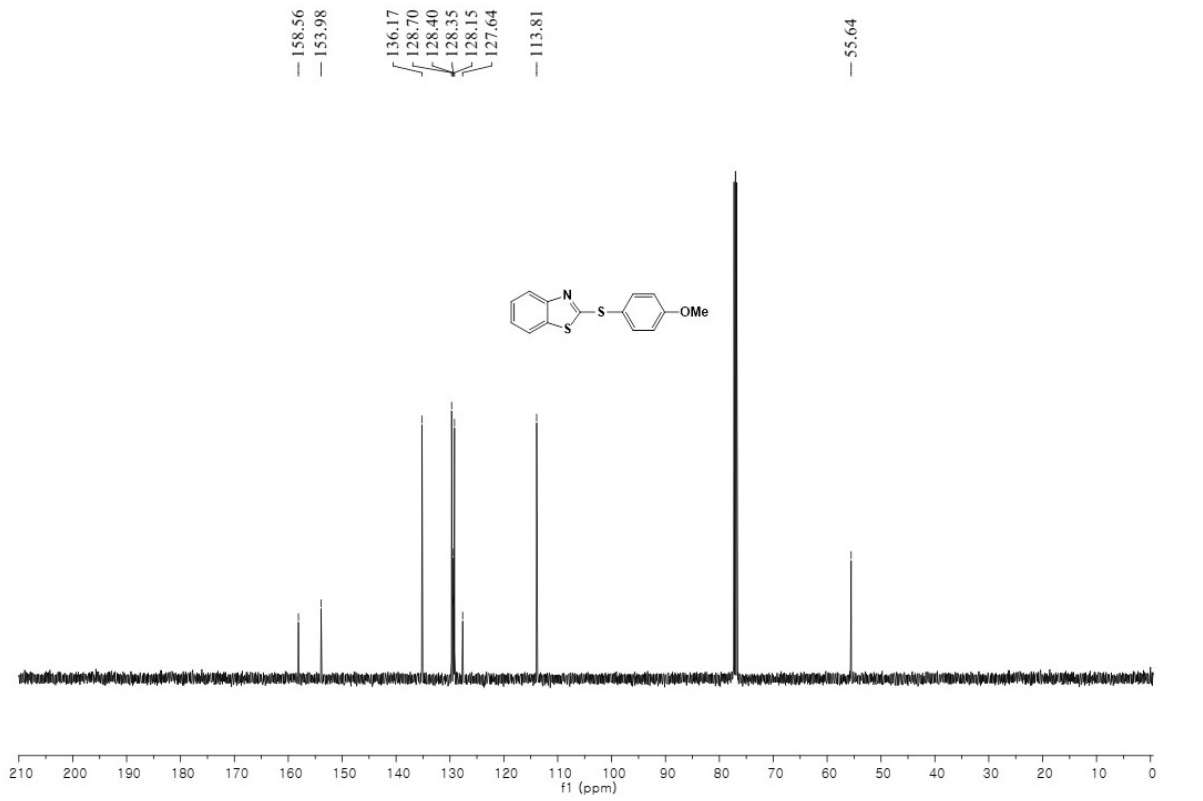
2-(m-tolylthio)benzo[d]thiazole: 1H NMR (500 MHz, cdcl3) δ 7.84–7.82 (m, 2H), 7.52–7.51 (m, 2H), 7.50–7.43 (m, 1H), 7.42–7.41 (m, 2H), 7.39–7.36 (m, 1H), 2.52 (s, 3H); 13C{1H} NMR (126 MHz, CDCl3) δ 160.2, 137.6, 135.6, 134.1, 133.4, 129.4, 128.2, 127.6, 126.9, 126.5, 125.7, 21.6.



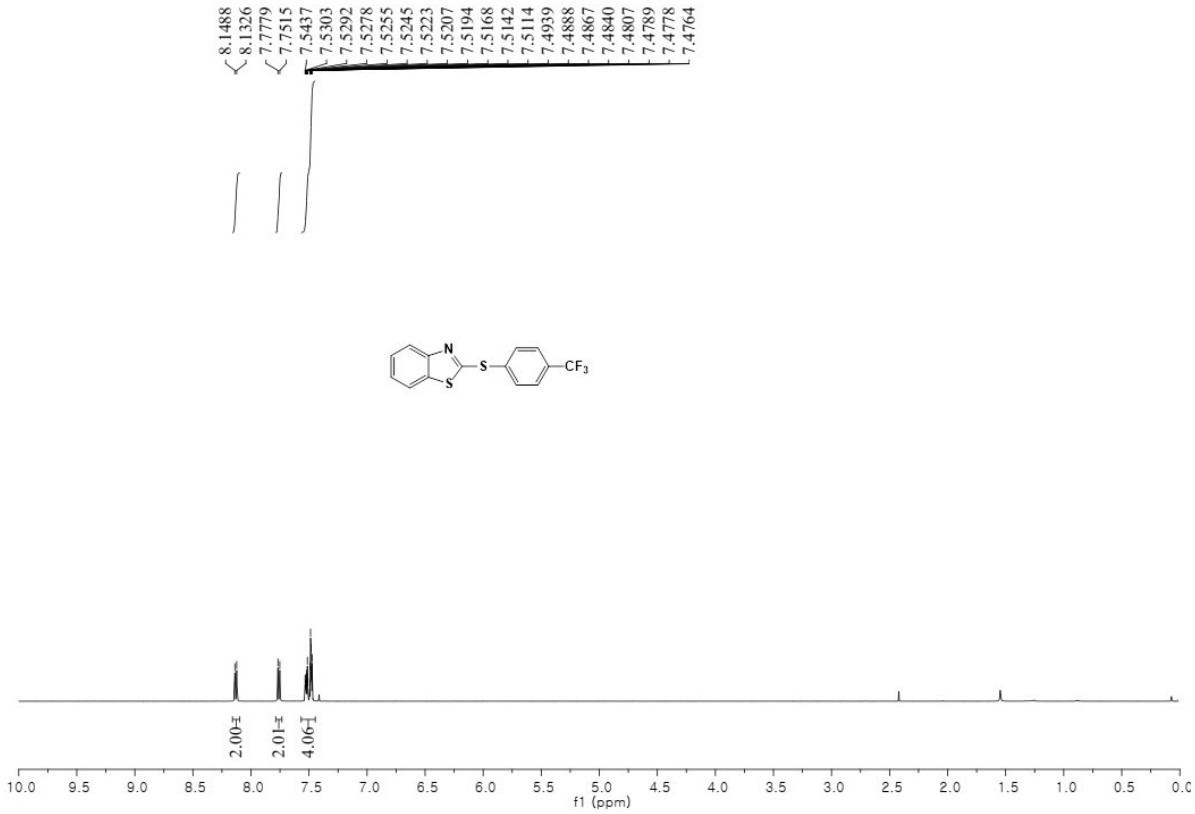


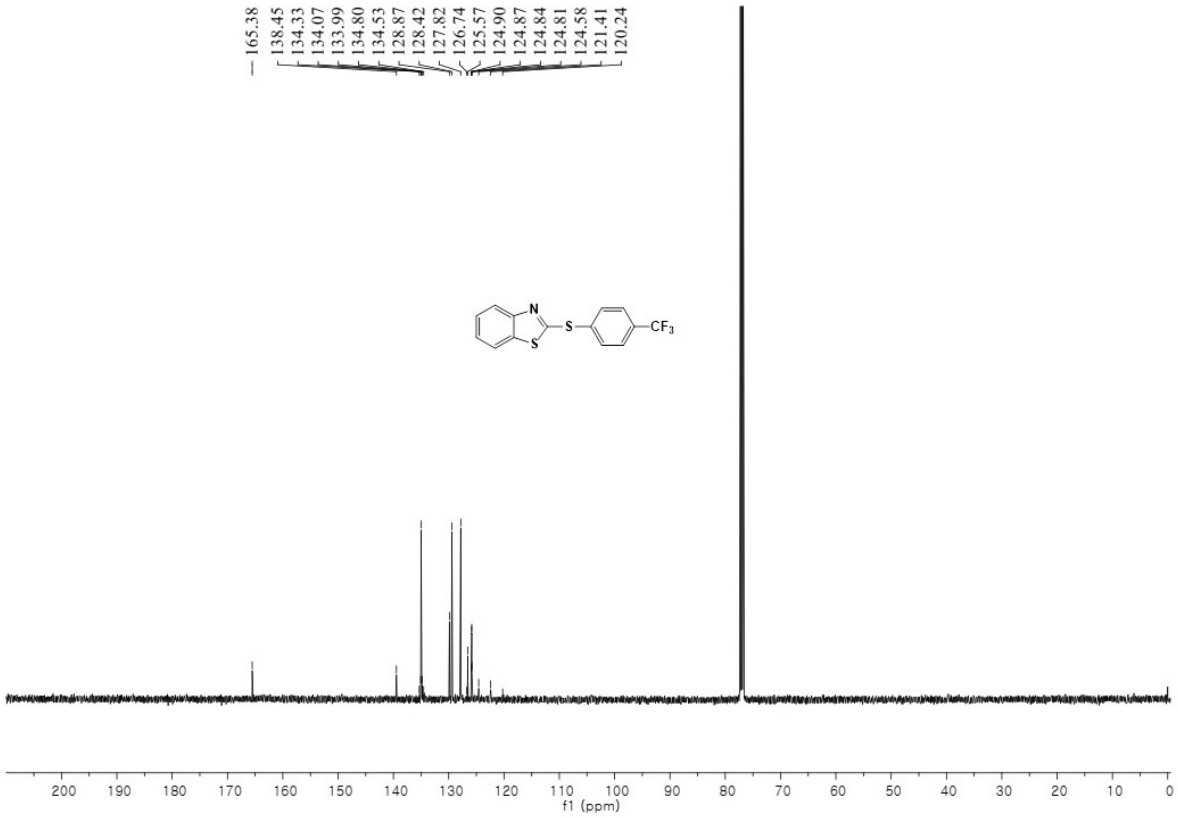
2-(o-tolylthio)benzo[d]thiazole: 1H NMR (500 MHz, CDCl3) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.53–7.48 (m, 2H), 7.48–7.42 (m, 2H), 7.31–7.27 (m, 2H), 2.41 (s, 3H); 13C{1H} NMR (126 MHz, CDCl3) δ 159.7, 145.6, 136.1, 135.1, 129.39, 129.38, 128.2, 127.54, 126.52, 21.8.


8.0230
7.9979
7.6029
7.4532
7.4380
6.9451
3.7701
N
S
S
OMe
2.02
2.11
1.99
1.98
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

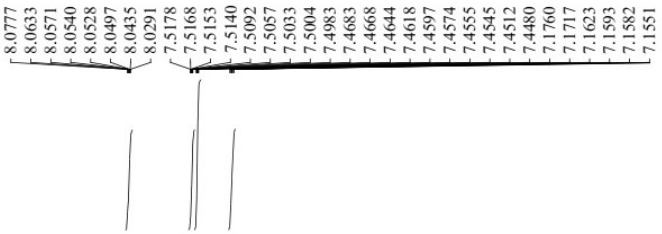

158.56
153.98
136.17
128.70
128.40
128.35
128.15
127.64
113.81
55.64
N
S
S
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

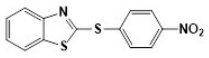
2-((4-methoxyphenyl)thio)benzo[d]thiazole: 1H NMR (600 MHz, CDCl3) δ 8.02 (d, *J* = 9.1 Hz, 2H), 7.60 (m, 2H), 7.45–7.43 (m, 2H), 6.97 (d, *J* = 9.0 Hz, 2H), 3.77 (s,3H); 13C{1H} NMR (126 MHz, CDCl3) δ 158.6, 154.0, 136.1, 128.7, 128.4, 128.4, 128.2, 127.6, 113.8, 55.6.

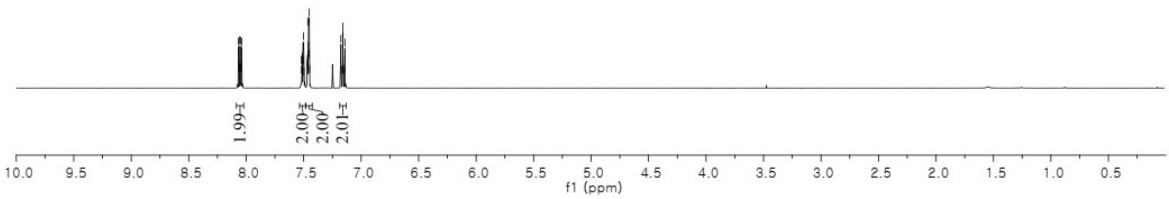


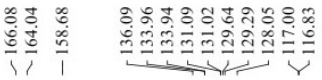


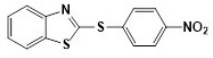
2-((4-(trifluoromethyl)phenyl)thio)benzo[d]thiazole: 1H NMR (500 MHz, cdcl3) δ 8.14 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.54–7.47 (m, 4H); 13C{1H} NMR (126 MHz, CDCl3) δ 165.4, 138.4, 134.3, 134.0, 128.9, 128.4, 127.8, 126.7, 125.6, 124.9, 124.8, 124.6, 121.4, 120.2.


8.0777
8.0633
8.0571
8.0540
8.0528
8.0497
8.0435
8.0291
7.5178
7.5168
7.5153
7.5140
7.5092
7.5057
7.5033
7.5004
7.4983
7.4683
7.4668
7.4644
7.4618
7.4597
7.4574
7.4555
7.4545
7.4512
7.4480
7.1760
7.1717
7.1623
7.1593
7.1582
7.1551


N
S
S
NO2

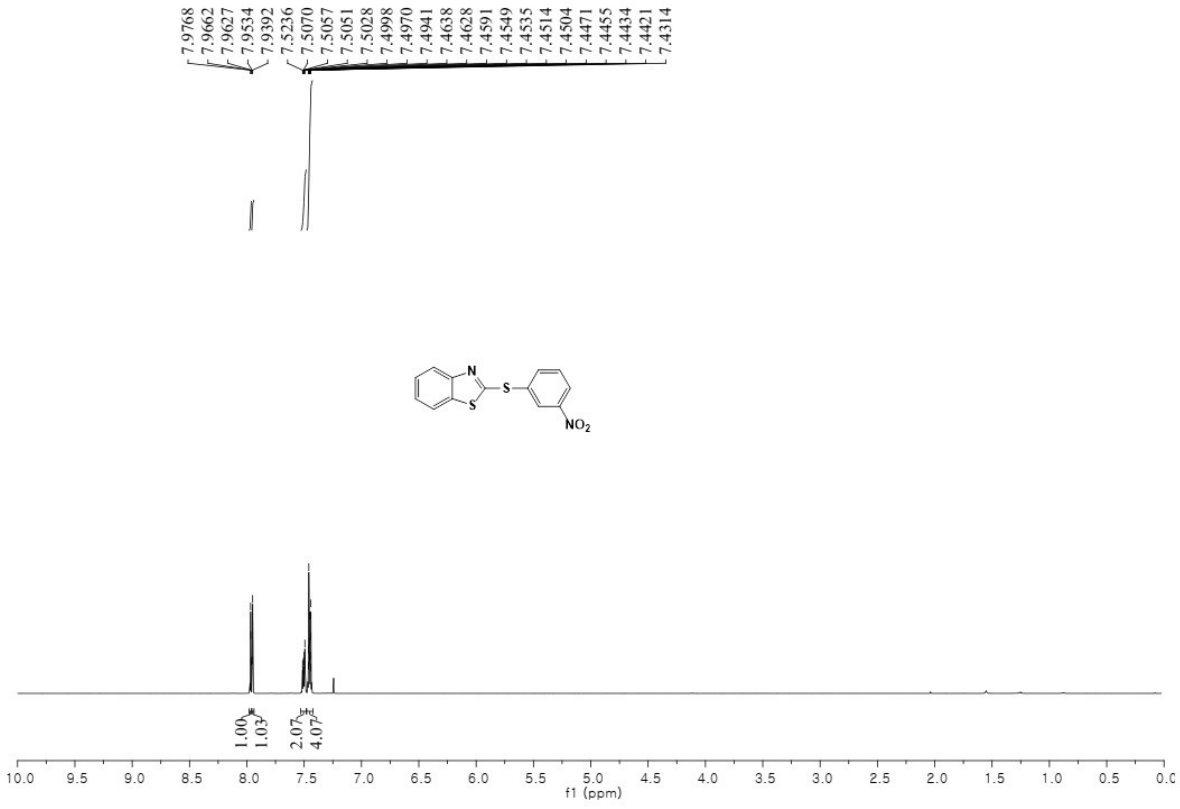

1.99
2.00
2.00
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

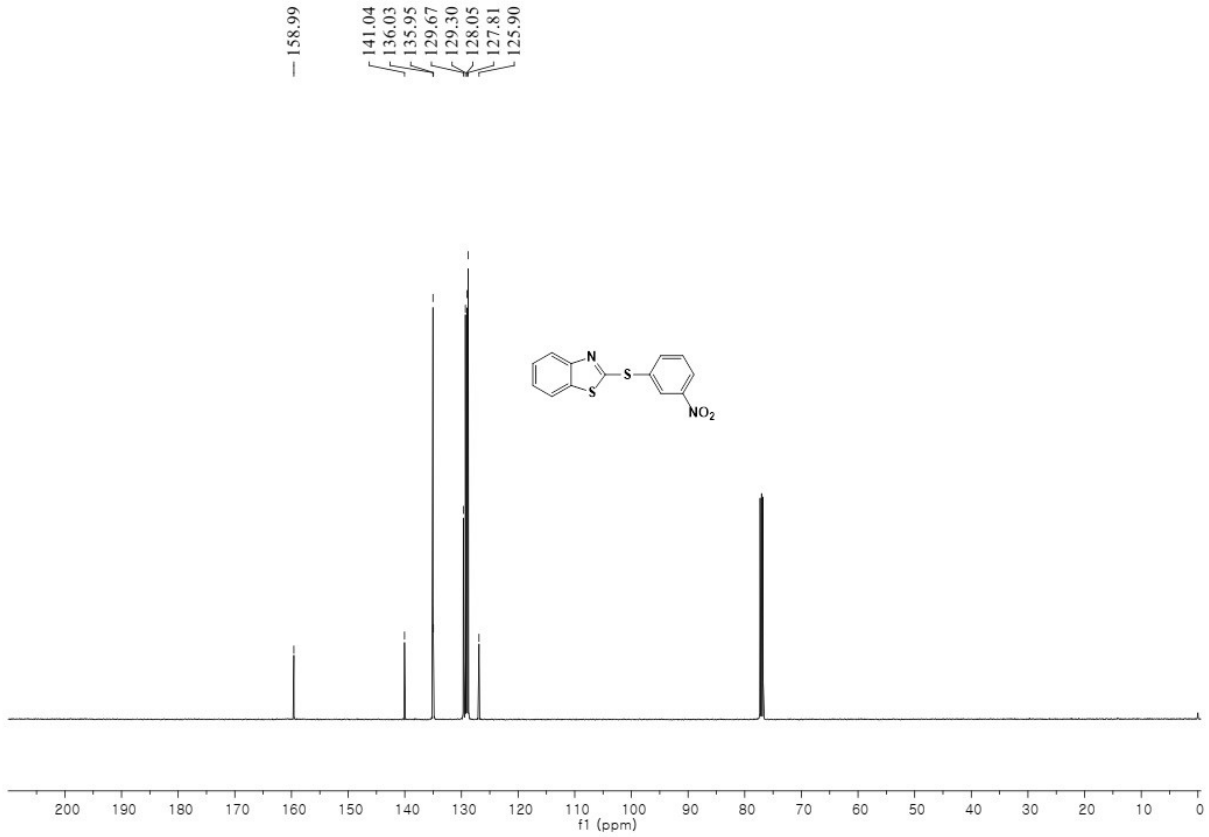

166.08
164.04
158.68
136.09
133.96
133.94
131.09
131.02
129.64
129.29
128.05
117.00
116.83


N
S
S
NO2

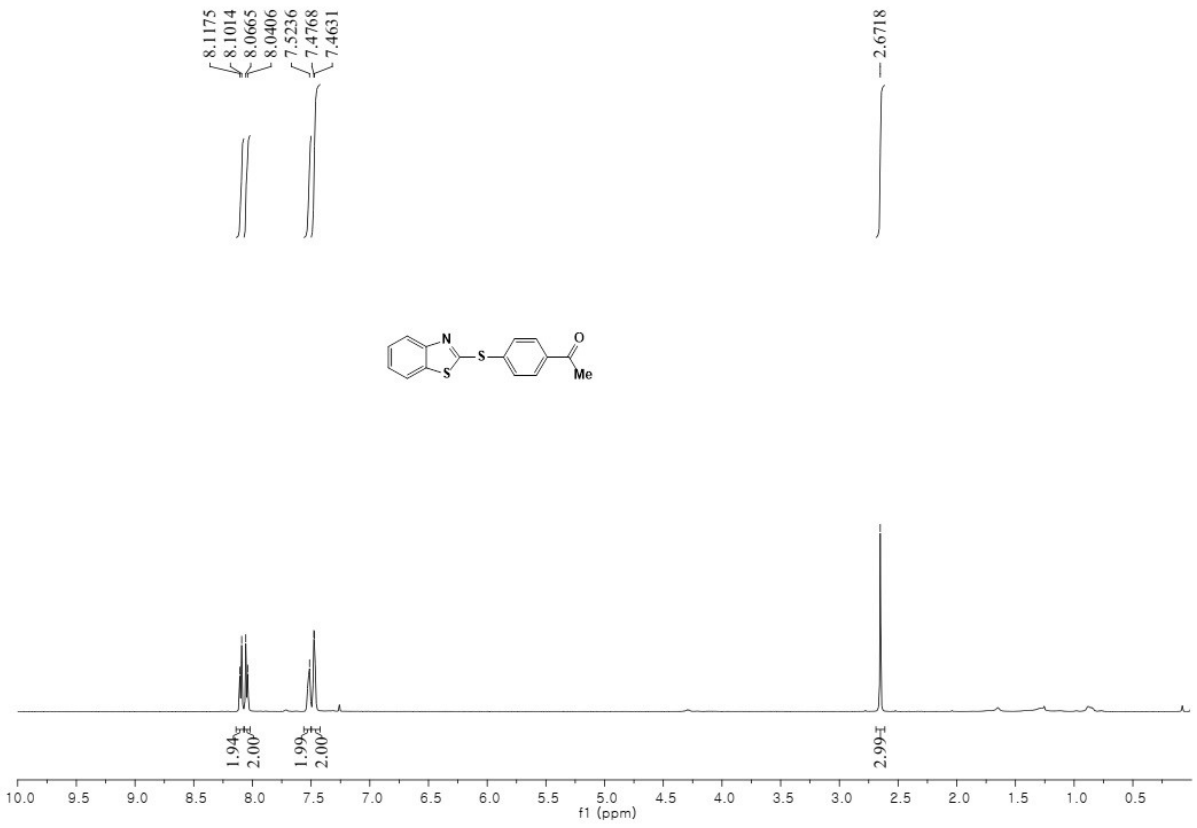
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

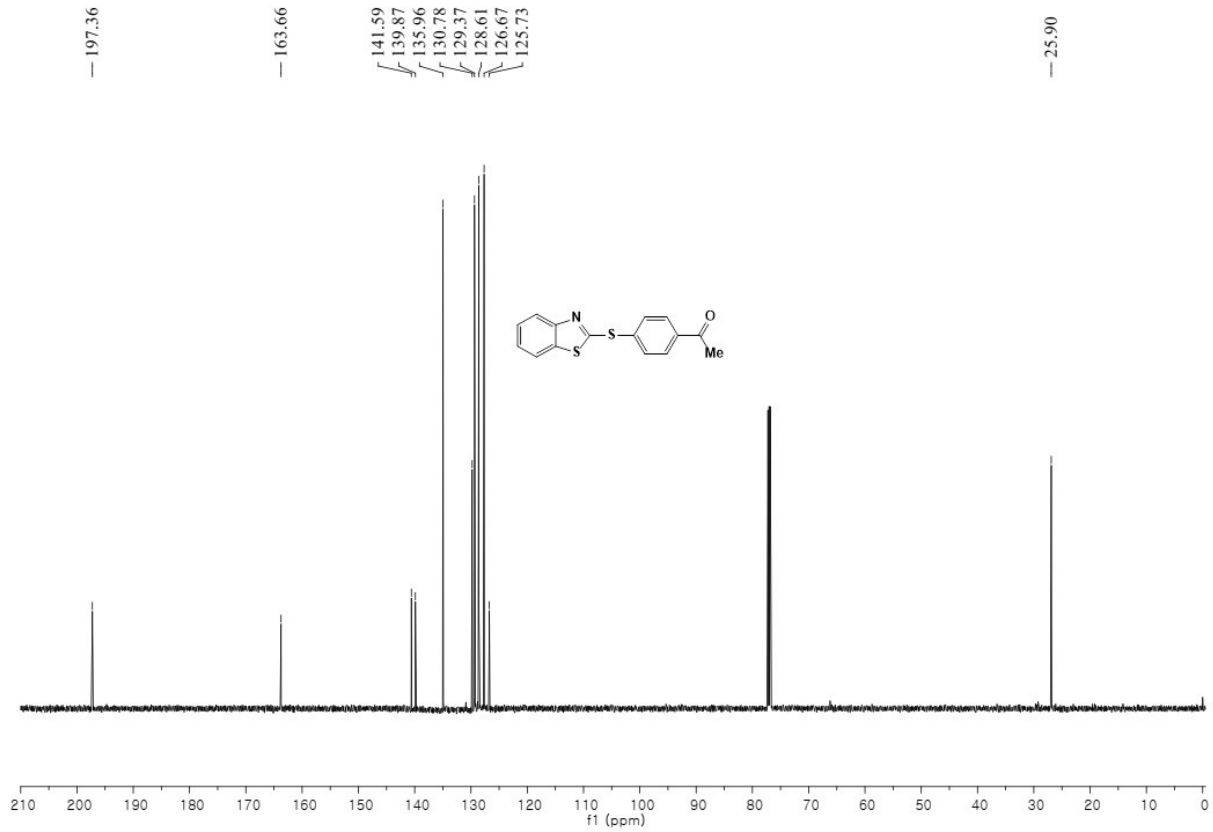
2-((4-nitrophenyl)thio)benzo[d]thiazole: 1H NMR (500 MHz, CDCl3) δ 8.07–8.02 (m, 2H), 7.51–7.50 (m, 2H), 7.50–7.43 (m, 2H), 7.19–7.15 (m, 2H); 13C{1H} NMR (126 MHz, CDCl3) δ 166.1, 164.0, 158.7, 136.1, 133.1, 133.1, 131.1, 131.0, 129.6, 129.3, 128.0, 117.0, 116.9.



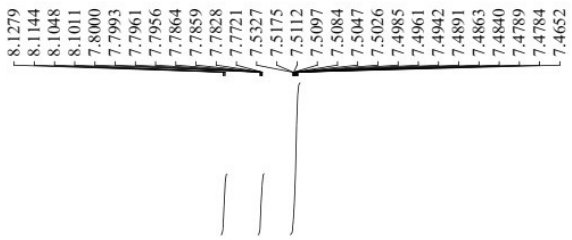


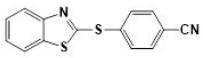
2-((3-nitrophenyl)thio)benzo[d]thiazole: 1H NMR (500 MHz, CDCl3) δ 7.97 (d, *J* = 2.1 Hz, 1H), 7.96 (d, *J* = 2.1 Hz, 1H), 7.52–7.48 (m, 2H), 7.47–7.43 (m, 4H); 13C{1H} NMR (126 MHz, CDCl3) δ 158.9, 141.0, 136.0, 135.9, 129.7, 129.3, 128.1, 127.8, 125.9.

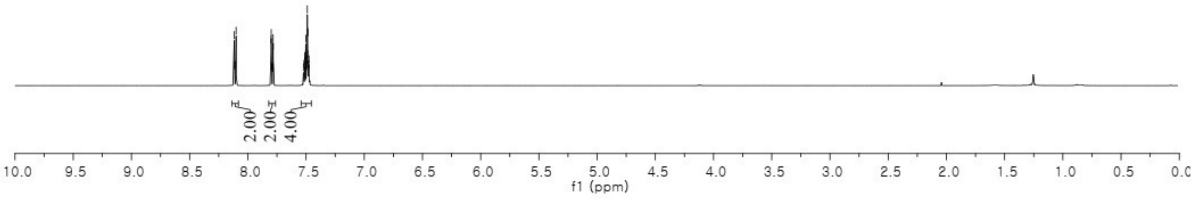

8.1175
8.1014
8.0665
8.0406
7.5236
7.4768
7.4631
2.6718
N
S
S
O
Me
1.94
2.00
1.99
2.00
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



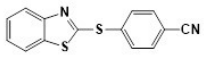
1-(4-(benzo[d]thiazol-2-ylthio)phenyl)ethan-1-one: 1H NMR (500 MHz, CDCl3) δ 8.11 (d, *J* = 8.0 Hz, 2H), 8.06 (d, *J* = 7.9 Hz, 2H), 7.52 (m, 2H), 7.50–7.46 (m, 2H), 2.67 (s, 3H); 13C{1H} NMR (151 MHz, CDCl3) δ 197.4, 163.7, 141.6, 139.9, 135.0, 130.8, 129.4, 128.6, 126.7, 125.7, 25.9.


8.1279
8.1144
8.1048
8.1011
8.0000
7.7993
7.7961
7.7956
7.7864
7.7859
7.7828
7.7721
7.5327
7.5175
7.5112
7.5097
7.5084
7.5047
7.5026
7.4985
7.4961
7.4942
7.4891
7.4863
7.4840
7.4789
7.4784
7.4652


N
S
S
CN

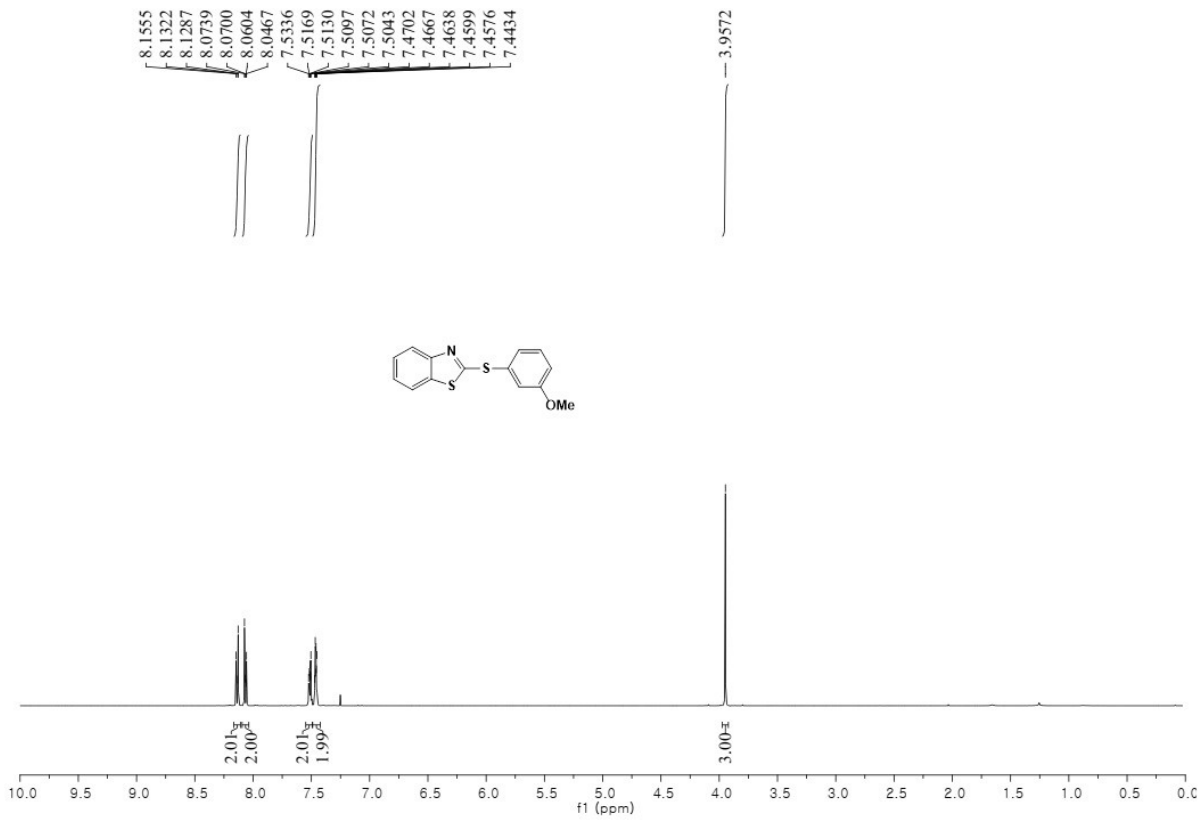

2.00
2.00
4.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

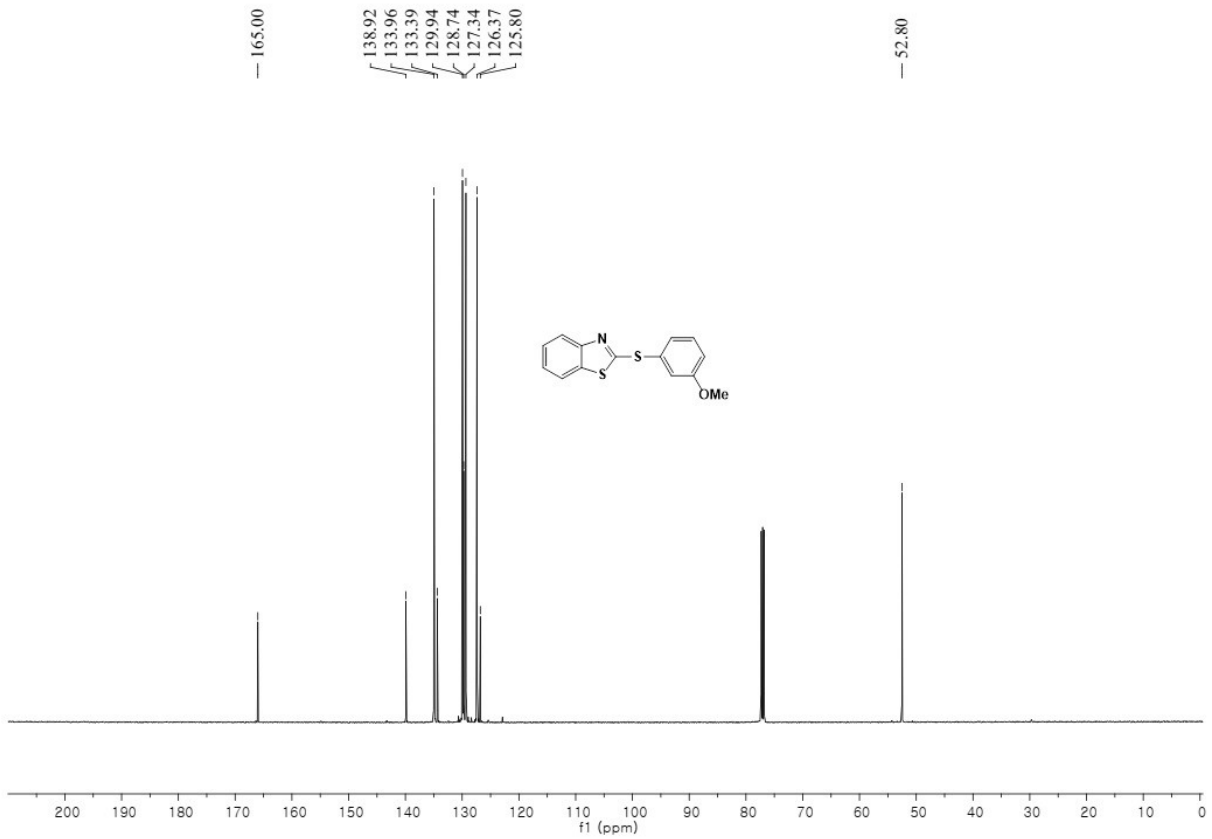

163.05
138.78
133.92
132.62
130.01
128.48
126.90
125.22
116.77
115.89


N
S
S
CN

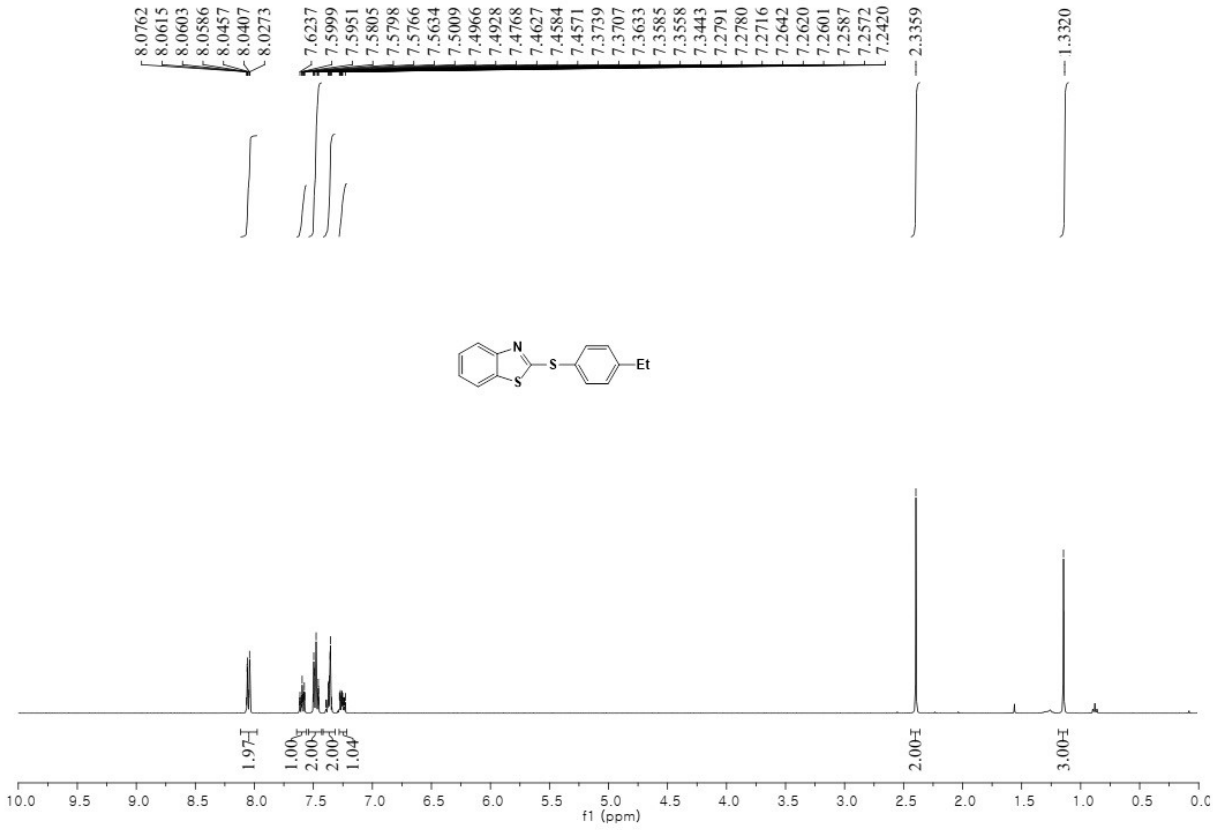
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

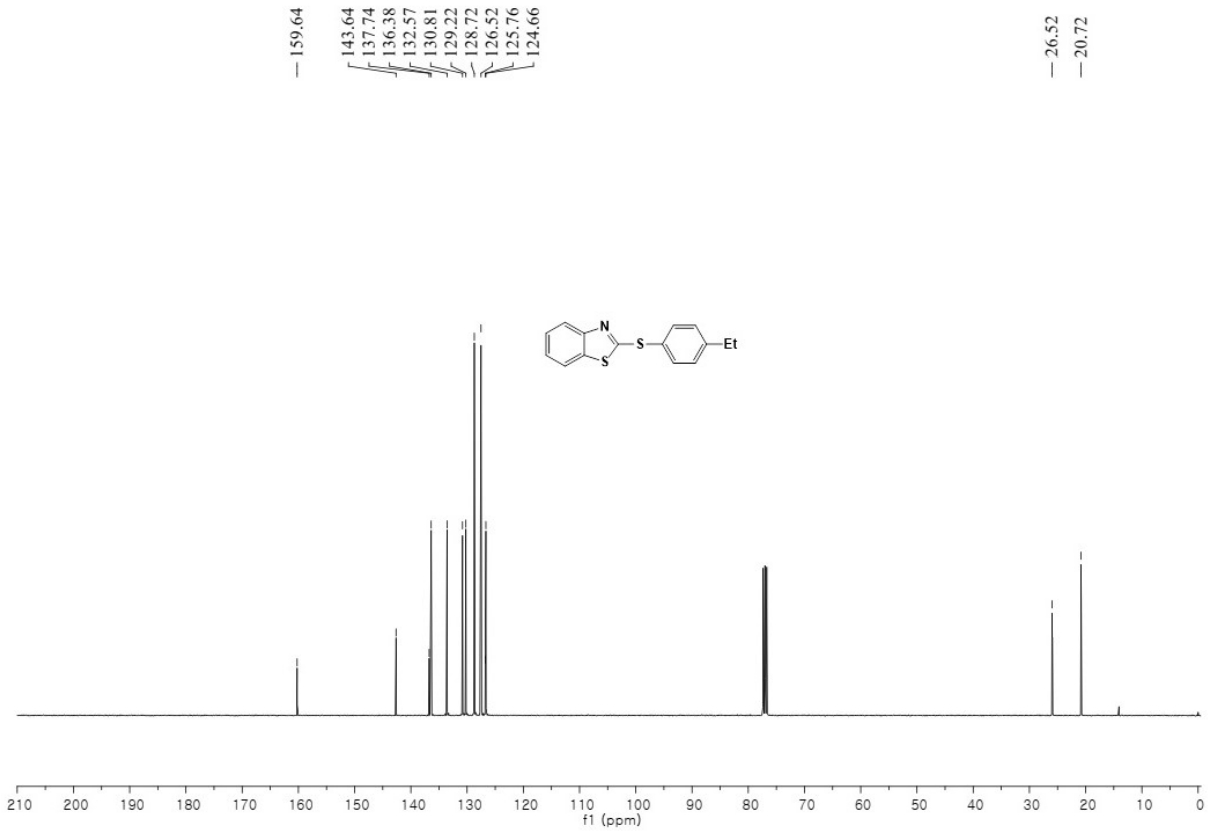
4-(benzo[d]thiazol-2-ylthio)benzonitrile: 1H NMR (500 MHz, CDCl3) δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.53–7.46 (m, 4H); 13C{1H} NMR (126 MHz, CDCl3) δ 163.1, 138.8, 133.9, 132.6, 130.0, 128.5, 126.9, 125.2, 116.8, 115.9.



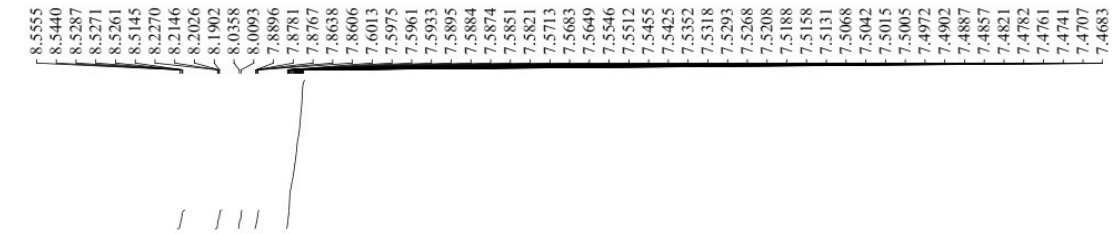


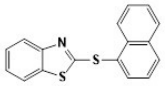
2-((3-methoxyphenyl)thio)benzo[d]thiazole: 1H NMR (500 MHz, CDCl3) δ 8.15 (d, *J* = 8.4 Hz, 2H), 8.06 (d, *J* = 8.6 Hz, 2H), 7.53–7.49 (m, 2H), 7.49–7.44 (m, 2H), 3.96 (s, 3H); 13C{1H} NMR (126 MHz, CDCl3) δ 165.1, 166.0, 138.9, 133.0, 133.4, 129.9, 128.7, 127.3, 126.4, 125.8, 52.8.

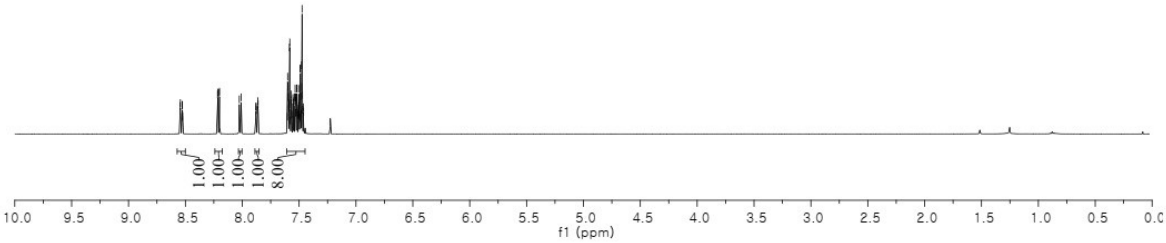

8.0762
8.0615
8.0603
8.0586
8.0457
8.0407
8.0273
7.6237
7.5999
7.5951
7.5805
7.5798
7.5766
7.5634
7.5009
7.4966
7.4928
7.4768
7.4627
7.4584
7.4571
7.3739
7.3707
7.3633
7.3585
7.3558
7.3443
7.2791
7.2780
7.2716
7.2642
7.2620
7.2601
7.2587
7.2572
7.2420
2.3359
1.3320
N
S
S
Et
1.97
1.00
2.00
2.00
1.04
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



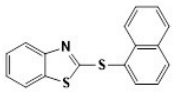
2-((4-ethylphenyl)thio)benzo[d]thiazole: 1H NMR (400 MHz, CDCl3) δ 8.08–8.02 (m, 2H), 7.62–7.56 (m, 1H), 7.56–7.42 (m, 2H), 7.42–7.30 (m, 2H), 7.28–7.24 (m, 1H), 2.30 (s, 2H), 1.3 (s, 3H); 13C{1H} NMR (101 MHz, CDCl3) δ 159.6, 143.6, 137.7, 136.4, 132.6, 130.8, 129.2, 128.7, 126.5, 125.8, 124.7, 26.5, 20.7.

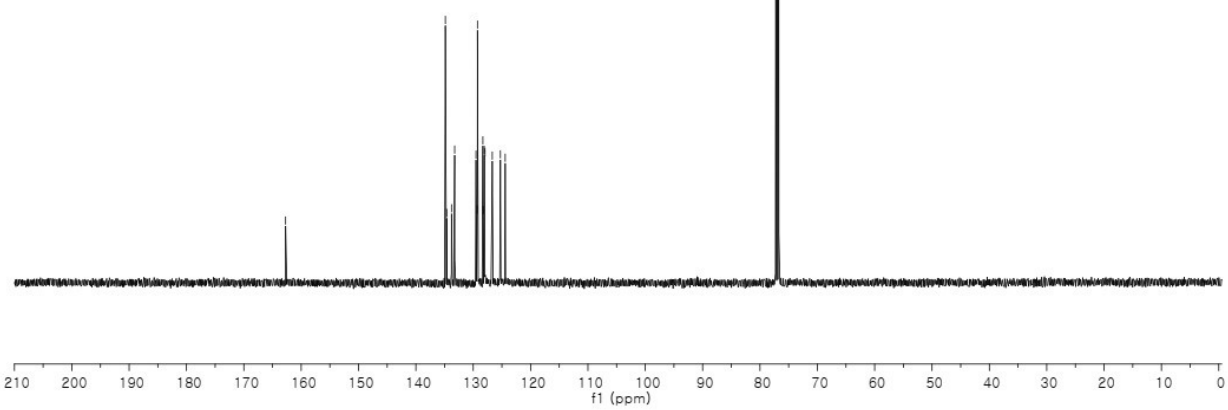

8.5555
8.5440
8.5287
8.5271
8.5261
8.5145
8.2270
8.2146
8.2026
8.1902
8.0358
8.0093
7.8896
7.8781
7.8767
7.8638
7.8606
7.6013
7.5975
7.5961
7.5933
7.5895
7.5884
7.5874
7.5851
7.5821
7.5713
7.5683
7.5649
7.5546
7.5512
7.5455
7.5425
7.5352
7.5318
7.5293
7.5268
7.5208
7.5188
7.5158
7.5131
7.5068
7.5042
7.5015
7.5005
7.4972
7.4902
7.4887
7.4857
7.4821
7.4782
7.4761
7.4741
7.4707
7.4683


N
S
S

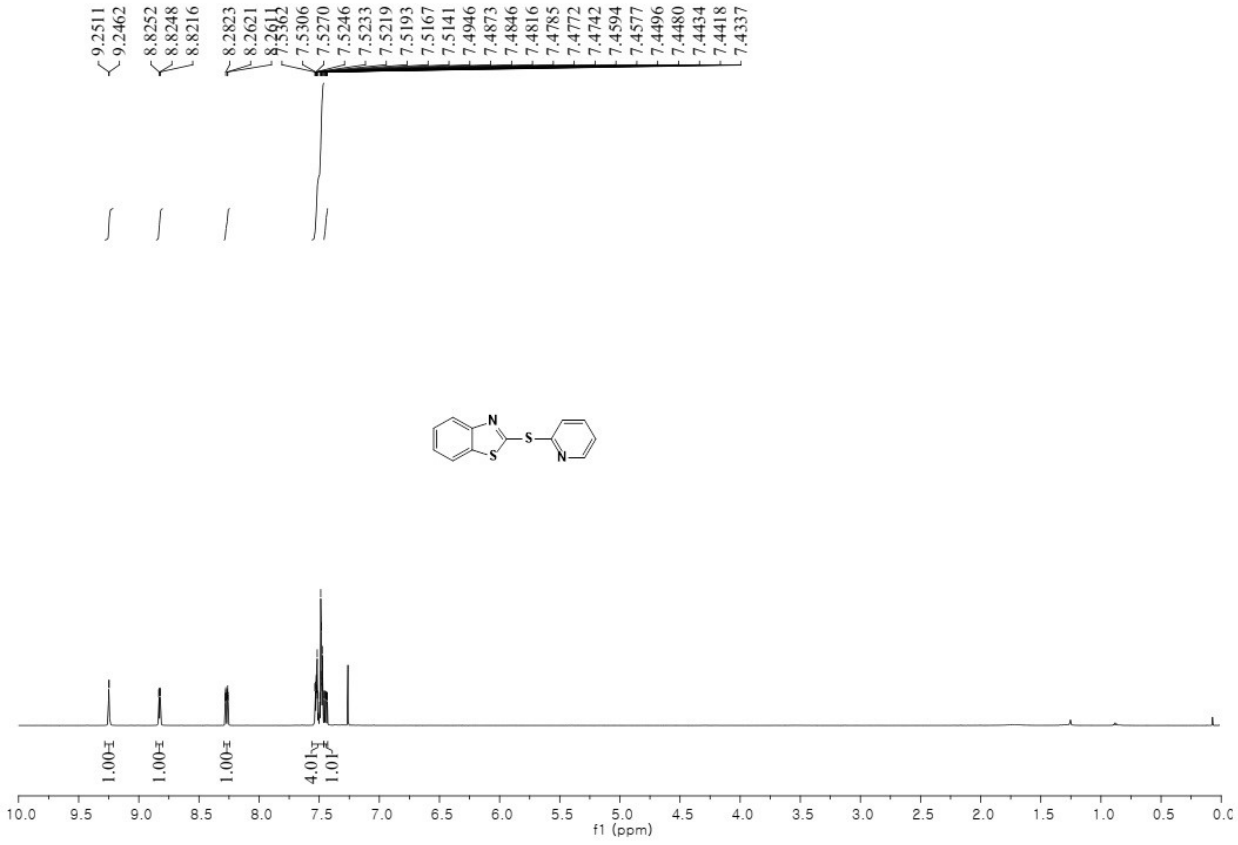

1.00
1.00
1.00
1.00
8.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

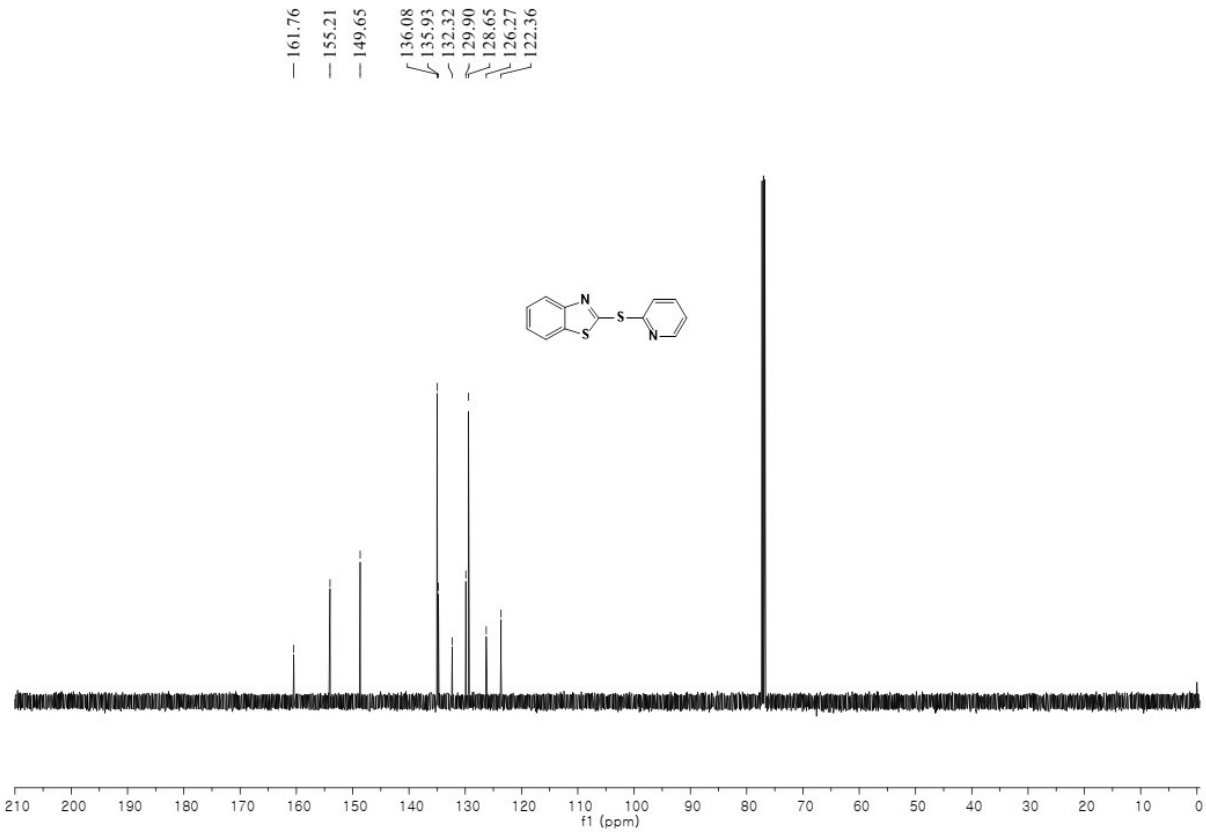

162.13
135.86
135.63
133.79
132.23
129.52
128.31
128.27
127.32
127.26
127.06
126.94
125.68
125.26
123.42


N
S
S

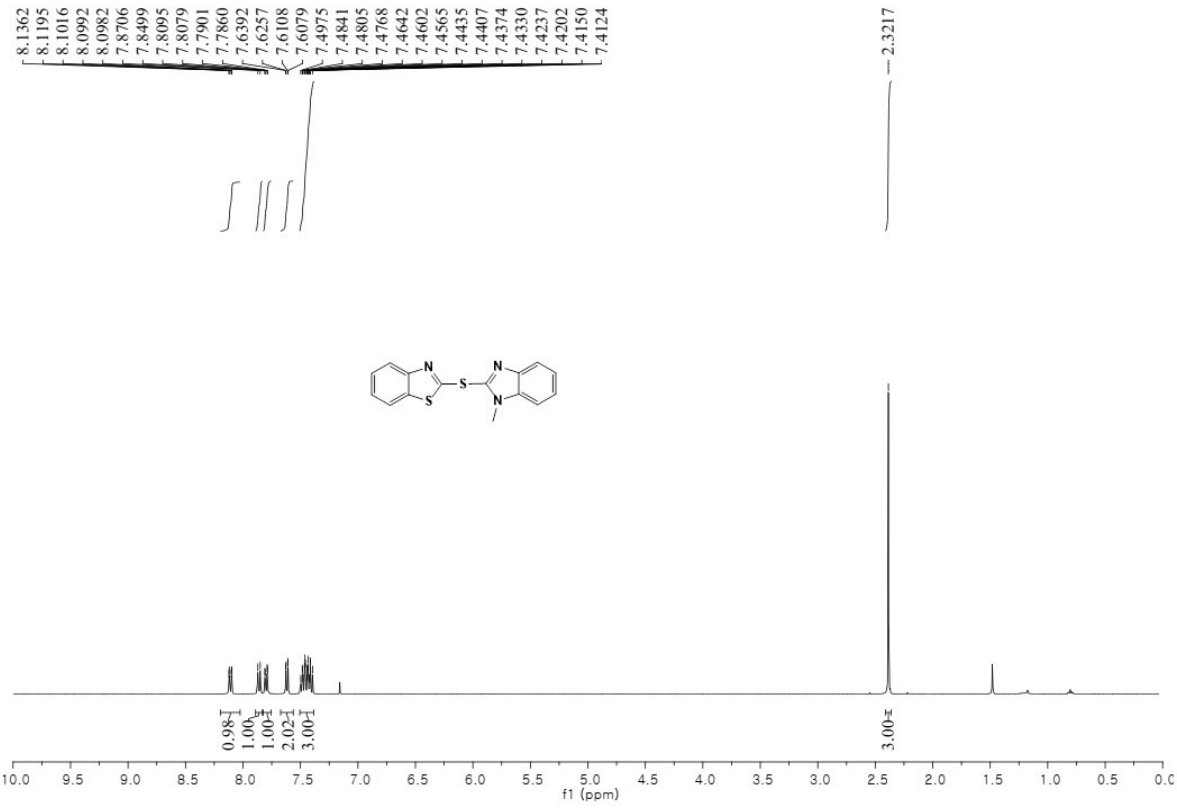

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

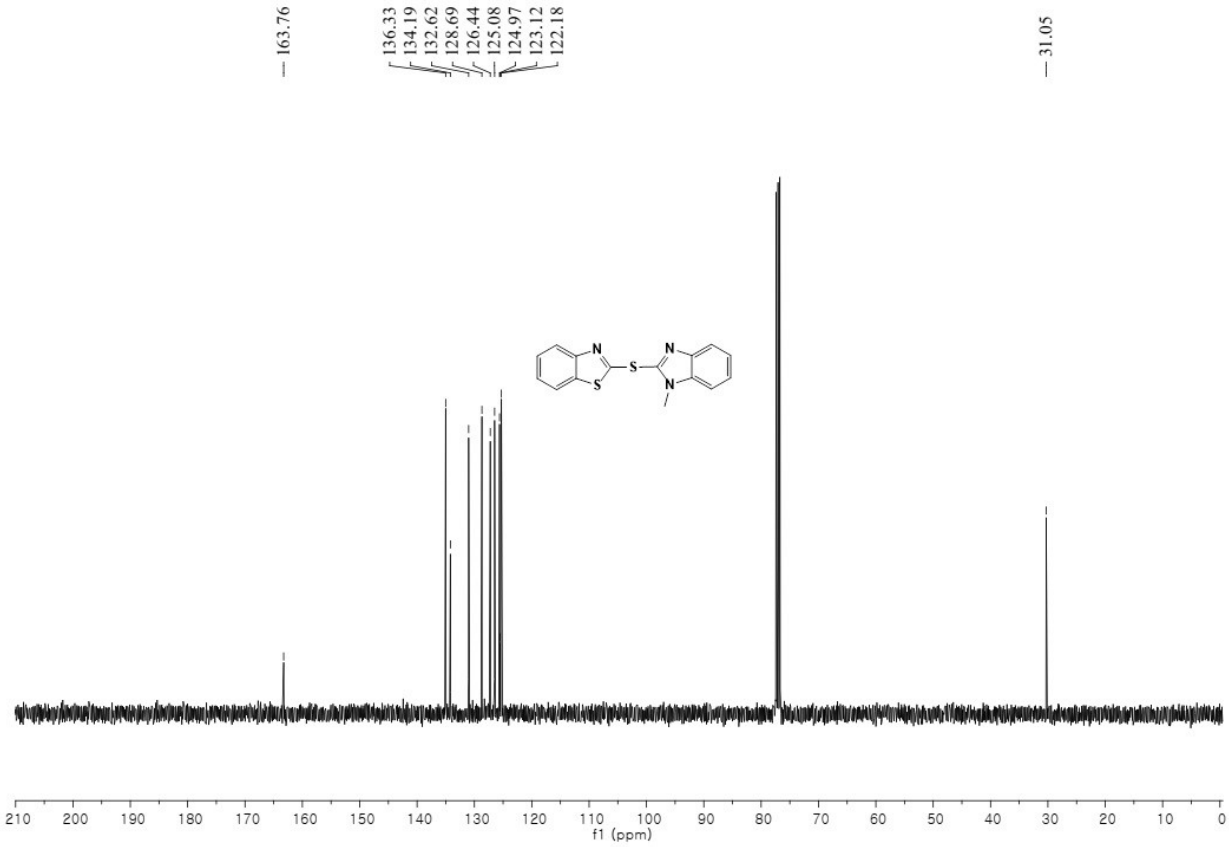
2-(naphthalen-1-ylthio)benzo[d]thiazole: 1H NMR (500 MHz, CDCl3) δ 8.55 (d, *J* = 7.6 Hz, 1H), 8.20 (dd, *J* = 7.2, 1.2 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.60–7.46 (m, 8H); 13C{1H} NMR (126 MHz, CDCl3) δ 162.1, 135.9, 135.6, 133.8, 132.2, 129.5, 128.3, 128.3, 127.3, 127.3, 127.1, 126.9, 125.7, 125.3, 123.4.



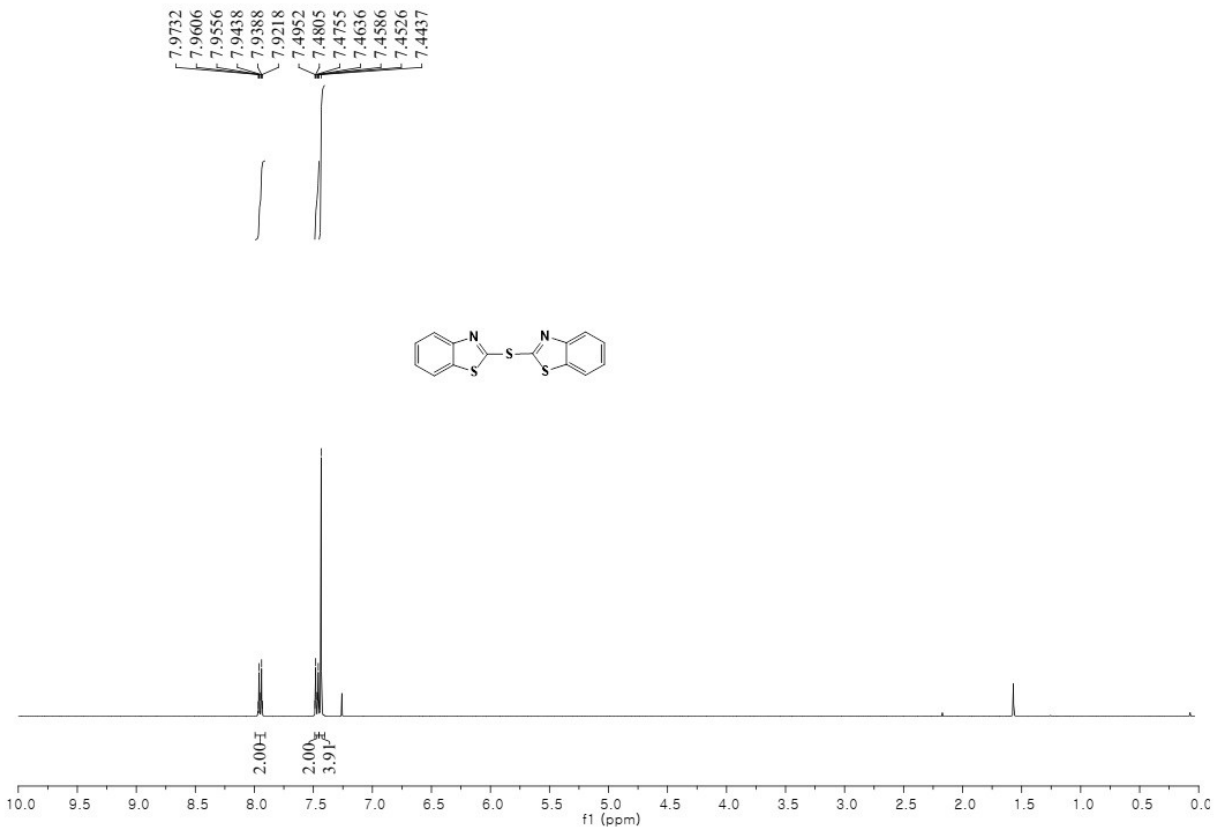


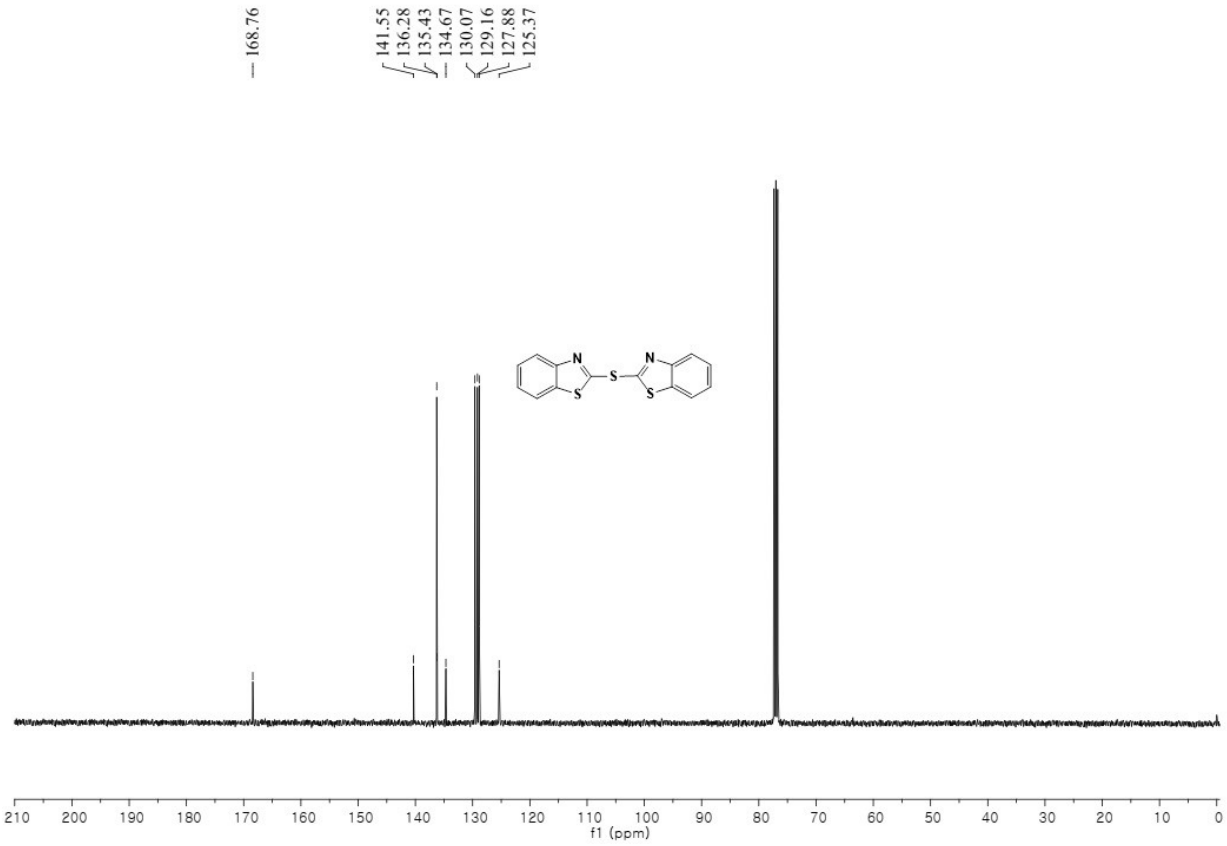
2-(pyridin-2-ylthio)benzo[d]thiazole: 1H NMR (500 MHz, CDCl3) δ 9.24 (d, *J* = 1.7 Hz, 1H), 8.82 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.28 (ddd, *J* = 8.0, 2.2, 1.7 Hz, 1H), 7.57–7.45 (m, 4H), 7.44 (ddd, *J* = 8.0, 4.9, 0.8 Hz, 1H); 13C{1H} NMR (126 MHz, CDCl3) δ 161.8, 155.2, 149.7, 136.0, 135.8, 132.3, 129.9, 128.4, 126.3, 122.6.


8.1362
8.1195
8.1016
8.0992
8.0982
7.8706
7.8499
7.8095
7.8079
7.7901
7.7860
7.6392
7.6257
7.6108
7.6079
7.4975
7.4841
7.4805
7.4768
7.4642
7.4602
7.4565
7.4435
7.4407
7.4374
7.4330
7.4237
7.4202
7.4150
7.4124
2.3217
N
S
S
N
N
0.98
1.00
1.00
2.02
3.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

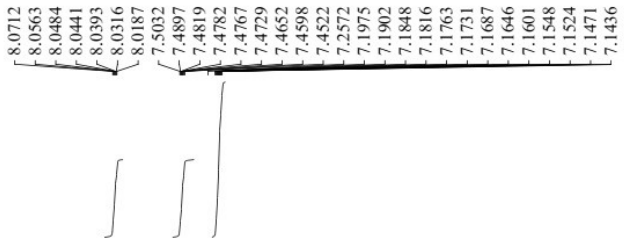


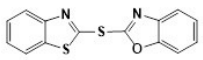
2-((1-methyl-1H-benzo[d]imidazol-2-yl)thio)benzo[d]thiazole: 1H NMR (400 MHz, CDCl3) δ 8.13 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.79 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.60 (dd, *J* = 7.1, 1.2 Hz, 1H), 7.51–7.41 (m, 3H), 2.32 (s, 3H); 13C{1H} NMR (101 MHz, CDCl3) δ 163.8, 136.0, 134.2, 132.6, 128.7, 126.4, 125.1, 124.9, 123.1, 122.1, 31.0.

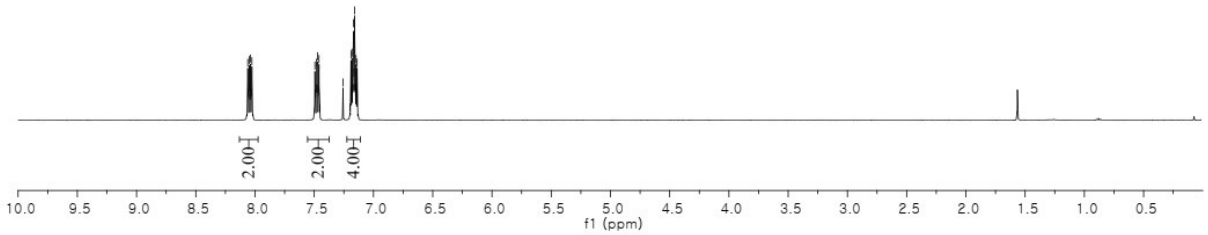

7.9732
7.9606
7.9556
7.9438
7.9388
7.9218
7.4952
7.4805
7.4755
7.4636
7.4586
7.4526
7.4437
N
S
S
N
2.00
2.00
3.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

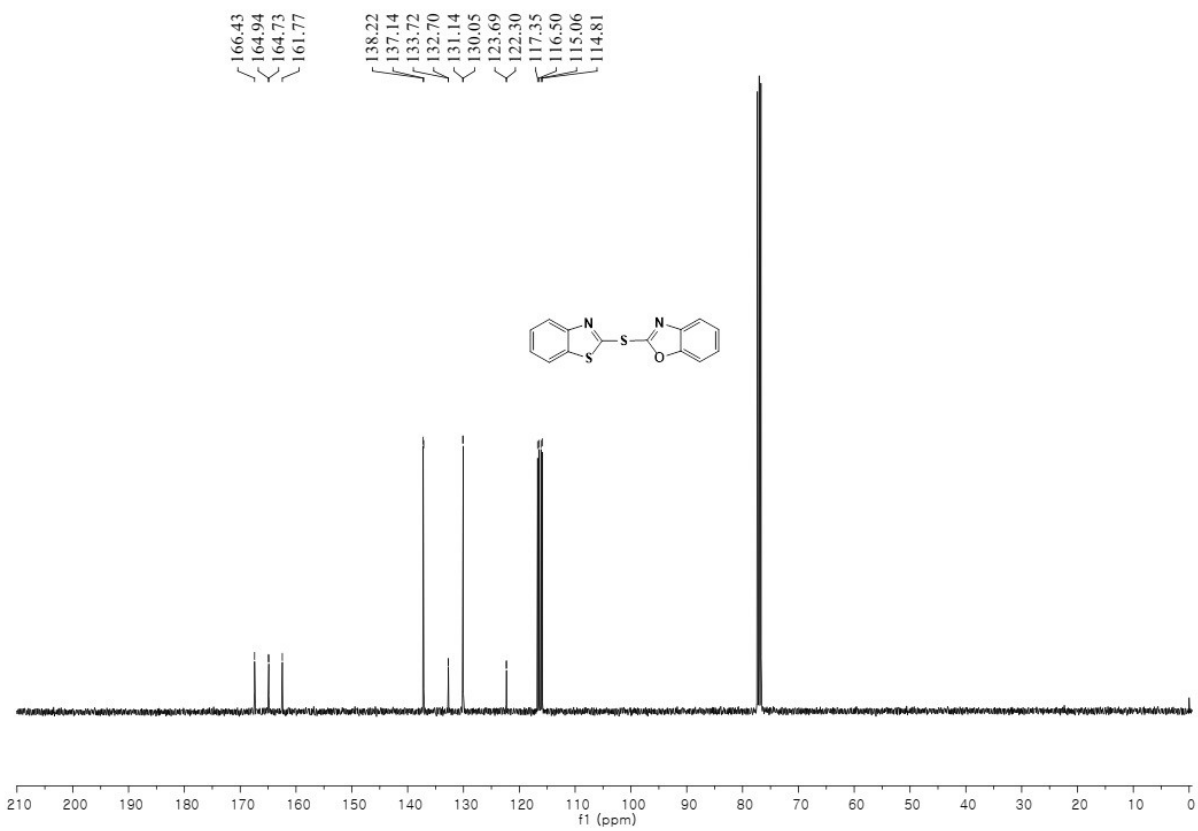


bis(benzo[d]thiazol-2-yl)sulfane: 1H NMR (400 MHz, CDCl3) δ 7.97 (d, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.48–7.44 (m, 4H); 13C{1H} NMR (101 MHz, CDCl3) δ 168.8, 141.5, 136.3, 135.4, 134.7, 130.7, 129.2, 128.8, 125.4.

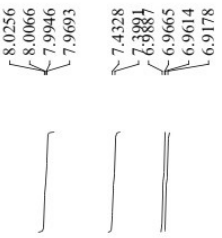

8.0712
8.0563
8.0484
8.0441
8.0393
8.0316
8.0187
7.5032
7.4897
7.4819
7.4782
7.4767
7.4729
7.4652
7.4598
7.4522
7.2572
7.1975
7.1902
7.1848
7.1816
7.1763
7.1731
7.1687
7.1646
7.1601
7.1548
7.1524
7.1471
7.1436

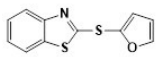

N
S
S
N
O

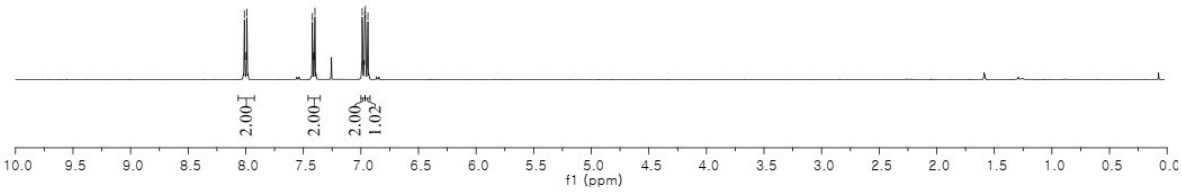

2.00
2.00
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

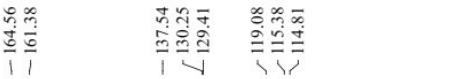


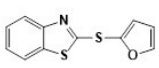
2-(benzo[d]thiazol-2-ylthio)benzo[d]oxazole: 1H NMR (400 MHz, CDCl3) δ 8.07 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.50 (dd, *J* = 8.9, 5.2 Hz, 2H), 7.23–7.14 (m, 4H); 13C{1H} NMR (101 MHz, CDCl3) δ 188.7, 166.2 (d, *J*C-F = 249.6 Hz), 166.4, 165.0, 164.7, 161.8, 138.2, 137.4, 133.7, 132.7, 131.4, 130.0, 123.7, 122.3, 117.3, 116.5, 115.0, 114.8.


8.0256
8.0066
7.9946
7.9693
7.4328
7.3991
6.9665
6.9614
6.9178




2.00
2.00
2.00
1.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


164.56
161.38
137.54
130.25
129.41
119.08
115.38
114.81



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2-(furan-2-ylthio)benzo[d]thiazole: 1H NMR (400 MHz, CDCl3) δ 8.02 (d, *J* = 9.0 Hz, 2H), 7.43 (d, *J* = 8.9 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 1H); 13C{1H} NMR (101 MHz, CDCl3) δ 164.6, 161.4, 137.5, 130.1, 129.4, 119.1, 115.4, 114.1.