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

Metal-Free Catalytic Synthesis of Diaryl Thioethers under Mild Conditions

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Supporting Information

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1 General experimental procedure

All reagents were purchased from commercial suppliers and used without further purification. All products were characterized by NMR. ^{1}H NMR spectra were recorded at 500 MHz and ^{13}C NMR spectra were recorded at 126 MHz (Bruker AV400) with $CDCl_3$ or DMSO-d_6 as solvent. Chemical shifts are reported in ppm using TMS as internal standard. Gas chromatography/mass spectra (GC/MS) were recorded on an Agilent Technologies 7890A instrument with an Agilent 5975C mass detector (EI) and a HP5-MS 30 m x 0.25 mm capillary apolar column (Stationary phase: 5% diphenyldimethylpolysiloxane film, 0.25 μm).

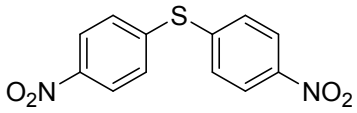
2 General procedure for the synthesis of products

General procedure for preparation of ionic liquid [DBUH][OAc]: To a 150 mL three-necked flask was added 20 mmol of DBU. Acetic acid (20 mmol) was then added slowly dropwise in ice bath. After dropwise addition, the ice bath was removed and the reaction mixture was stirred at room temperature for 24 h. The oil residue was dried in vacuo at 60℃ for 24 h to afford [DBU][OAc] as a light yellow, viscous liquid.

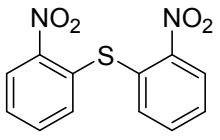
The general procedure is similar for all products. As an example, the synthesis of compound 2a was carried out in a 10 mL tube with a magnetic stirrer. As a typical experiment, we describe the procedures for the reaction of CS_2 and 1-iodo-4-nitrobenzene. 1-iodo-4-nitrobenzene (1 mmol), [DBUH][OAc] (1 mL) and CS_2 (0.5 mmol)were added into the reactor. The reactor was placed in a heating magnetic stirrer at the desired temperature and the reaction mixture was stirred. When the reaction ended, the reactor was cooled at room temperature. The residue was extracted with Et_2O to separate the IL from the product, and the mixture was purified by column chromatography (Different products needed different eluents which were presented in the following characteristic section). The IL ([DBUH][OAc]) was recovered and reused in the next reaction as the catalyst.

3 Characterization data

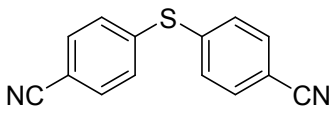
1, 8-diazabicyclo [5, 4, 0] undec-7-enium acetate. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.35– 3.27 (m, 6H), 2.70-2.63 (m, 2H), 1.89 – 1.54 (m, 12H).



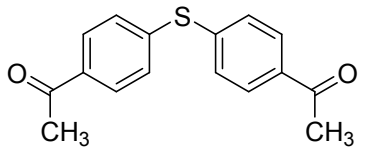
***Bis(4-nitrophenyl)sulfide*[1]**. Purification by column chromatography (petroleum ether/ethyl acetate 40:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 8.8 Hz, 4H), 7.49 (d, J = 8.8 Hz, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 147.24, 142.60, 131.82, 125.18. MS (EI) m/z: 276 [M^+]



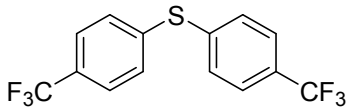
***2,2'-Dinitro diphenyl sulfide*[3]**. Purification by column chromatography (petroleum ether/ethyl acetate 40:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.21 (d, J = 8.1 Hz, 2H), 7.74-7.63 (m, 4H), 7.40 (d, J = 7.9 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.33, 139.59, 138.92, 135.14, 134.70, 130.75. MS (EI) m/z: 276 [M^+]



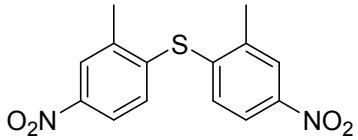
***Di(4-nitrilophenyl)sulfide*[1]**. Purification by column chromatography (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.87 (d, *J* = 8.5 Hz, 4H), 7.54 (d, *J* = 8.5 Hz, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 140.48, 133.86, 131.64, 118.81, 110.82. MS (EI) m/z: 236 [M^+]



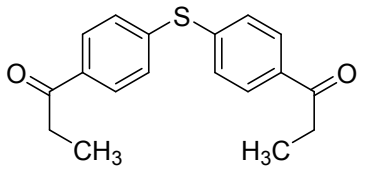
***4,4'-Diacetyl diphenyl sulfide*[1]**. Purification by column chromatography (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.97 (d, *J* = 8.5 Hz, 4H), 7.49 (d, *J* = 8.5 Hz, 4H), 2.58 (s, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 197.55, 140.37, 136.24, 130.92, 129.85, 27.15. MS (EI) m/z: 270 [M^+]



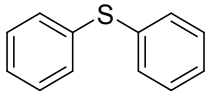
***Bis(4-(trifluoromethyl)phenyl)sulfide*[1]**. Purification by column chromatography (petroleum ether). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.76 (d, *J* = 8.3 Hz, 4H), 7.58 (d, *J* = 8.2 Hz, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 139.69 (s), 131.67 (s), 128.59 (q, *J* = 32.3 Hz), 126.98 (q, *J* = 3.7 Hz), 123.90 (q, *J* = 272.0 Hz). MS (EI) m/z: 322 [M^+]



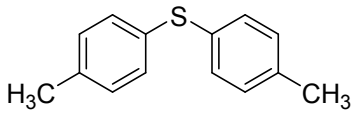
***Bis(2-methyl-4-nitrophenyl)sulfide*[4]**. Purification by column chromatography (petroleum ether/ethyl acetate 40:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.27 (s, 2H), 8.04 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 2.46 (s, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 147.25, 141.47, 140.71, 131.99, 125.65, 122.52, 20.33. MS (EI) m/z: 304 [M^+]



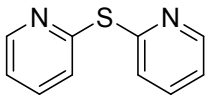
***4,4'-Dipropionyl diphenyl sulfide*[5]**. Purification by column chromatography (petroleum ether/ethyl acetate 20:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.97 (d, *J* = 8.5 Hz, 4H), 7.48 (d, *J* = 8.5 Hz, 4H), 3.03 (q, *J* = 7.2 Hz, 4H), 1.09 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 200.06, 140.14, 136.01, 130.93, 129.51, 31.71, 8.50. MS (EI) m/z: 298 [M^+]



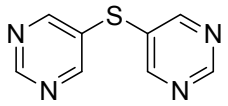
***Diphenylsulfide*[1]**. Purification by column chromatography (petroleum ether). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.40-7.30 (m, 10H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 135.30, 131.20, 130.02, 127.88. MS (EI) m/z: 186 [M^+]



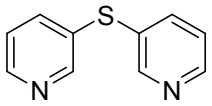
***Di-p-tolyl sulfide*[2]**. Purification by column chromatography (petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.1 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 1H), 2.32 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.91, 132.72, 131.09, 129.91, 21.06. MS (EI) m/z: 214 [M^+]



***Bis(2-pyridyl) sulfide*[2]**. Purification by column chromatography (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.52-8.51 (m, 2H), 7.80-7.76 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.32-7.30 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 156.40, 150.59, 138.13, 126.13, 122.68. MS (EI) m/z: 187 [M^+]



***Dipyrimidin-5-ylsulfane*[6]**. Purification by column chromatography (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.16 (s, 2H), 8.75 (s, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 159.46, 157.85, 130.43. MS (EI) m/z: 190 [M^+]



***Bis(3-pyridyl) sulfide*[3]**. Purification by column chromatography (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 2H), 8.53-8.52 (m, 2H), 7.66-7.64 (m, 2H), 7.27 – 7.25 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.68, 148.66, 138.77, 131.94, 124.16. MS (EI) m/z: 188 [M^+]

4 References

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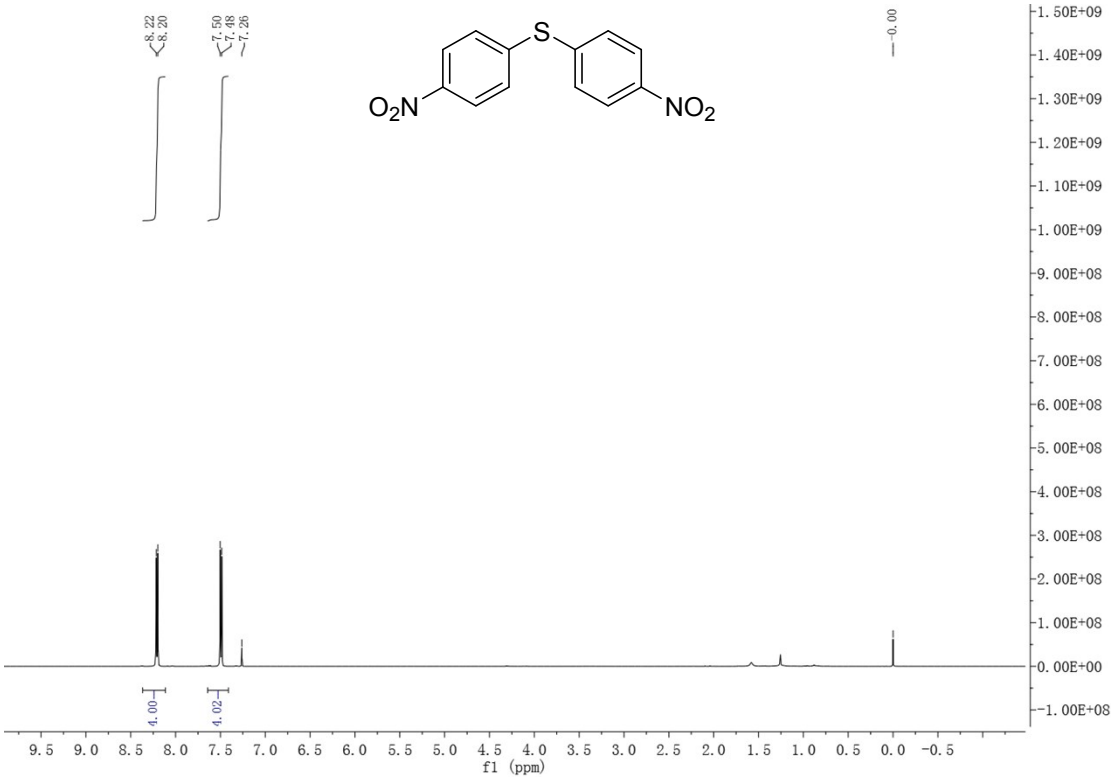
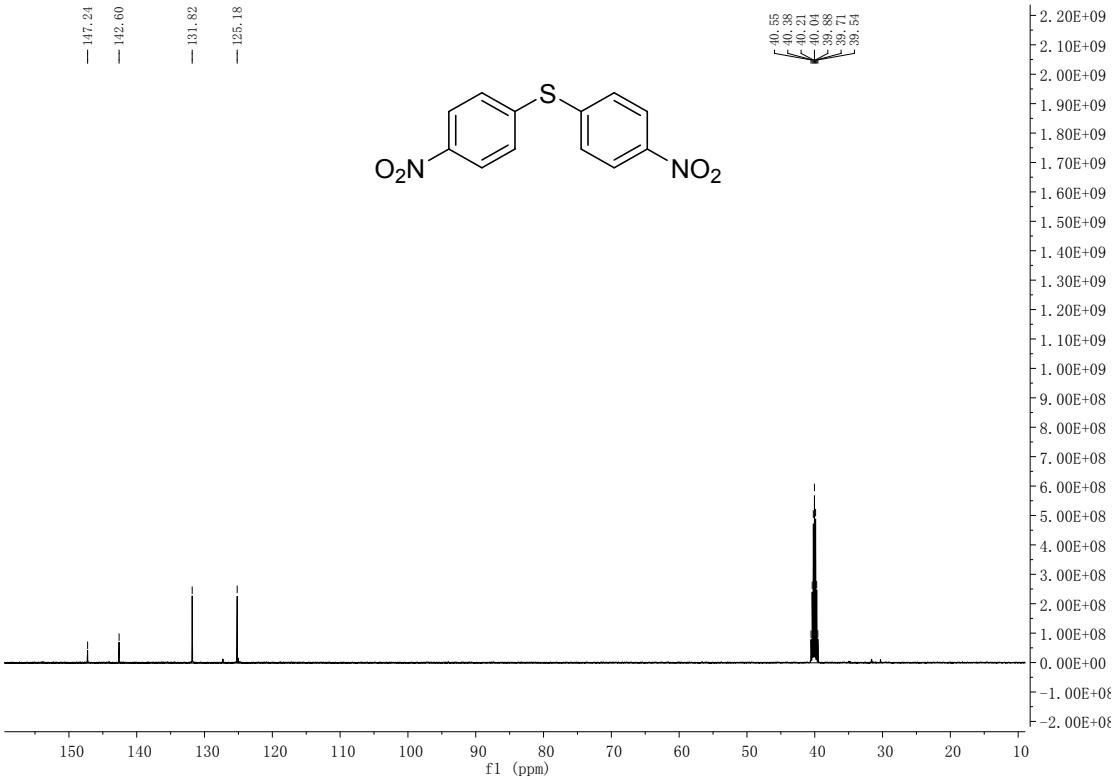
5 ^{1}H NMR and ^{13}C NMR spectra for the products and [DBUH][OAc]

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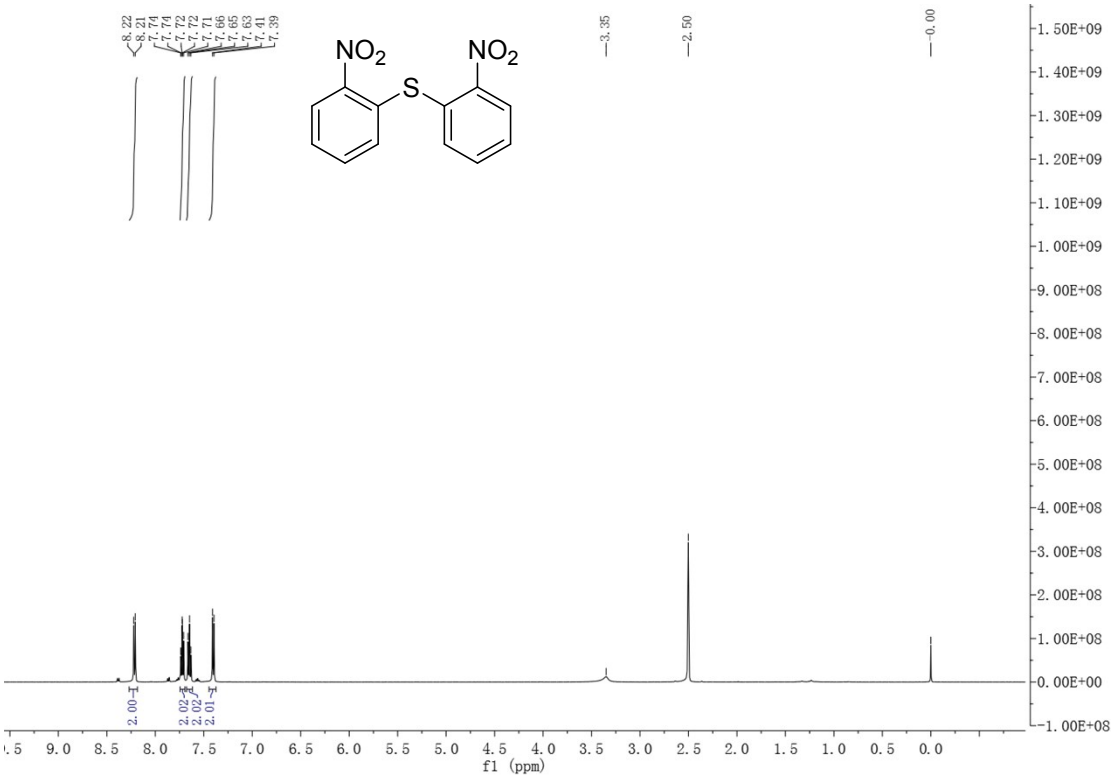
NO2
f1 (ppm)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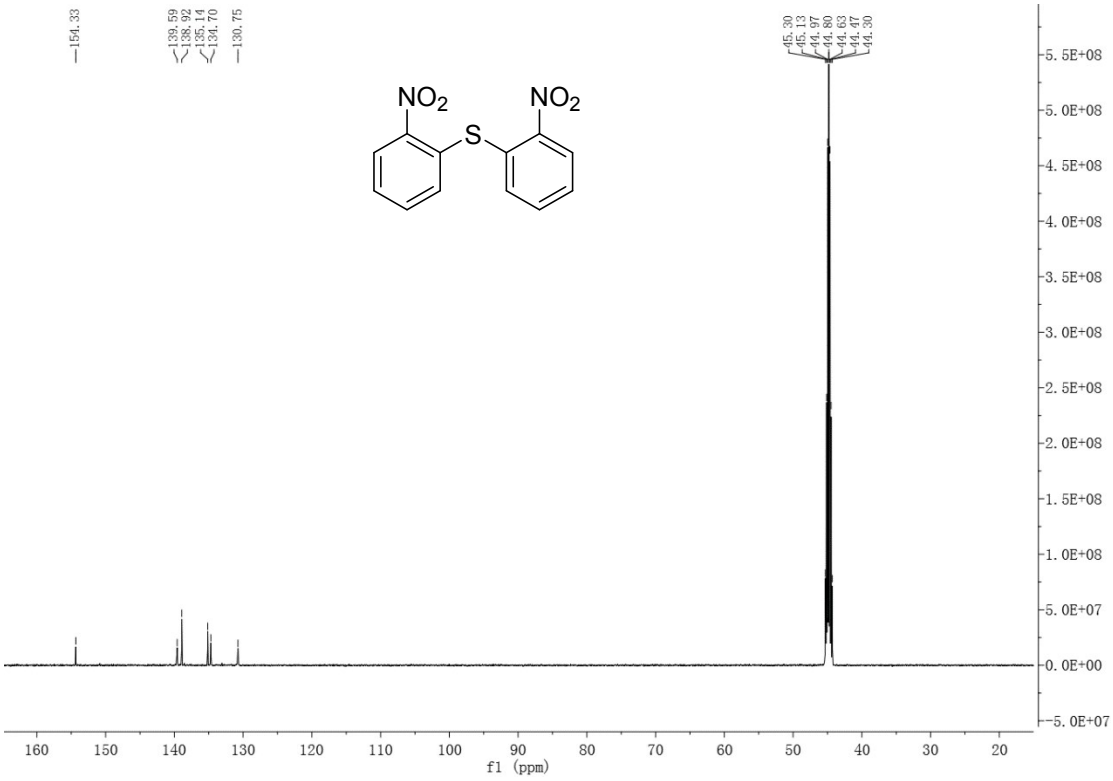
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NO2
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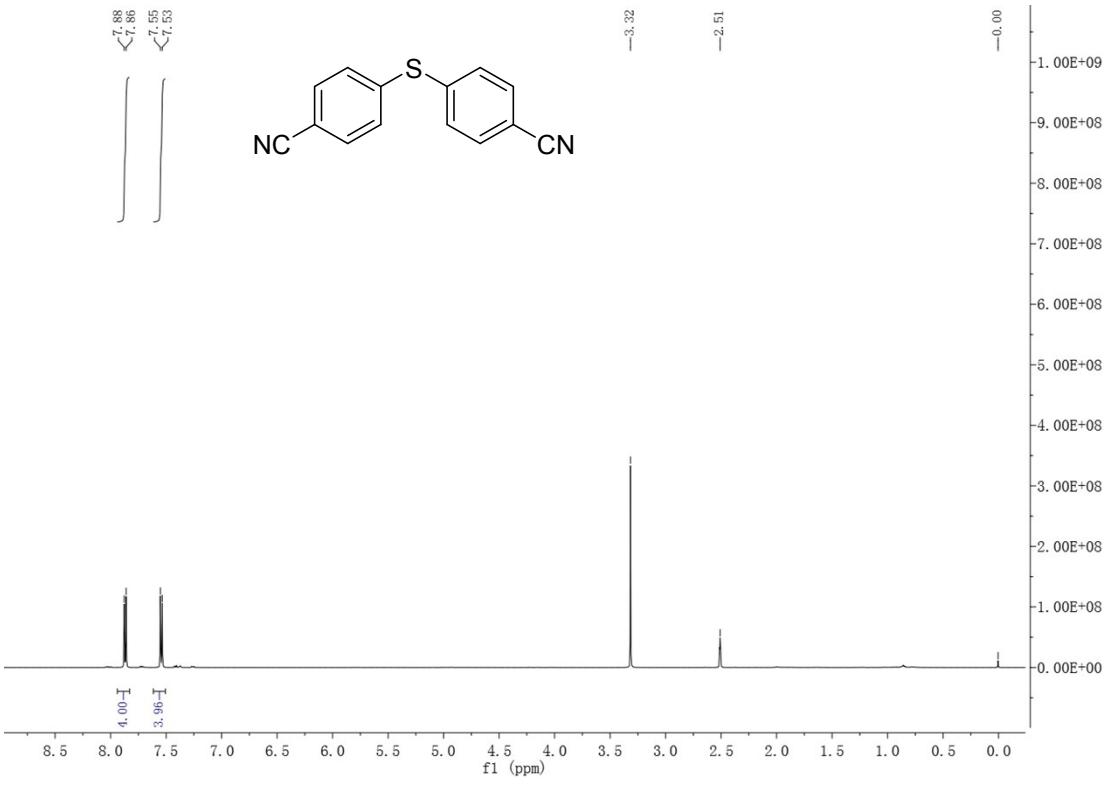
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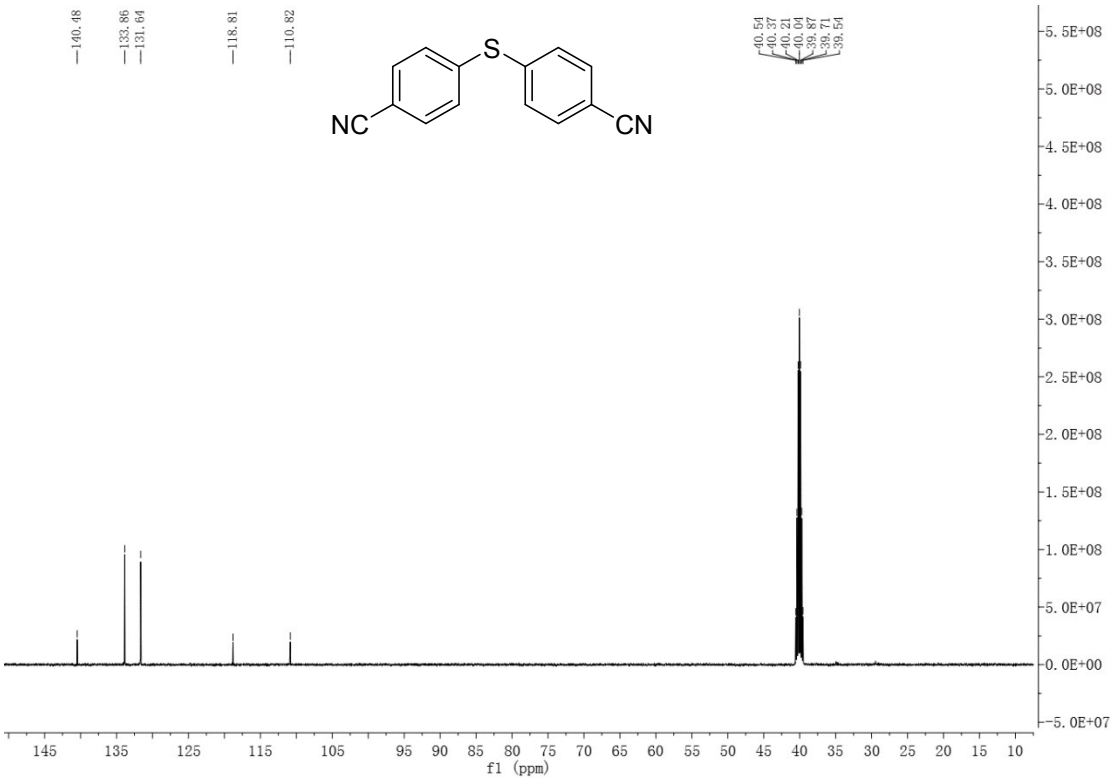
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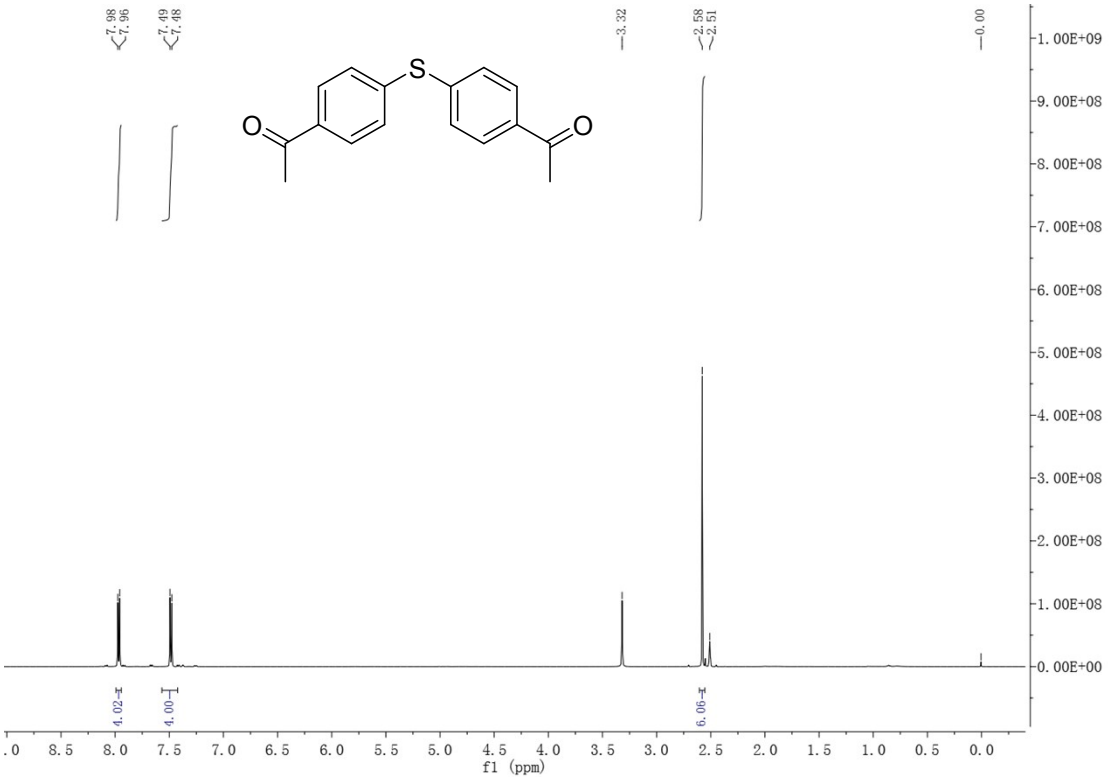
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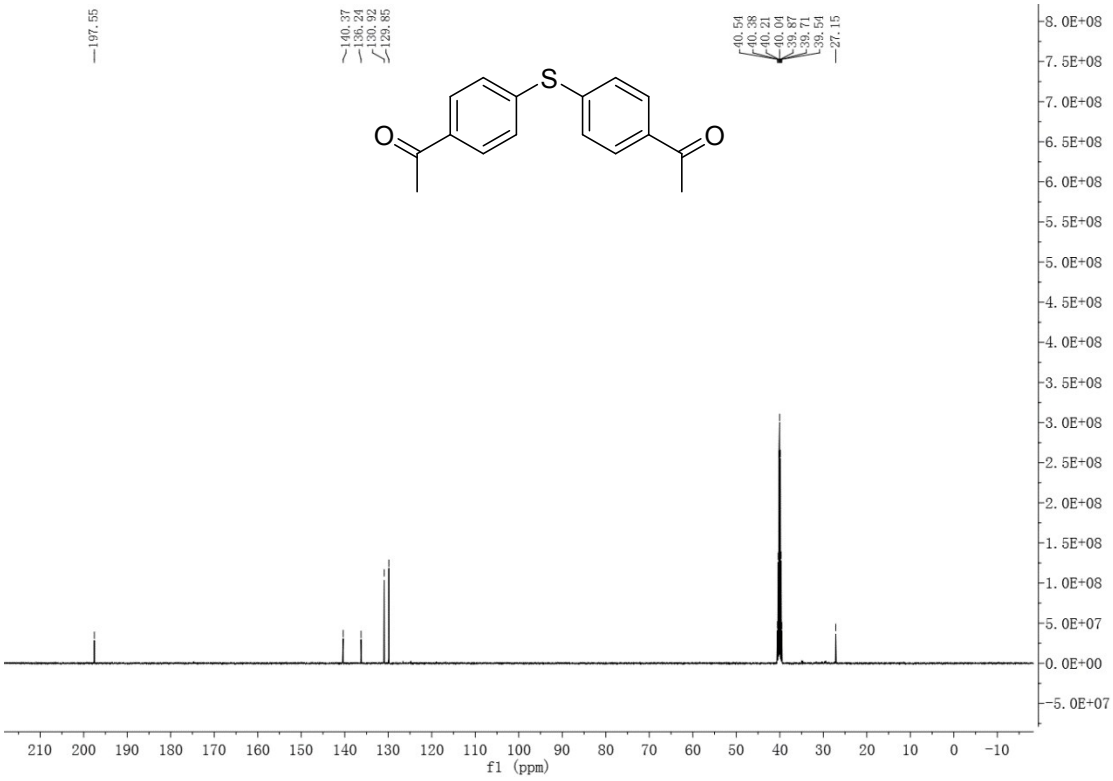
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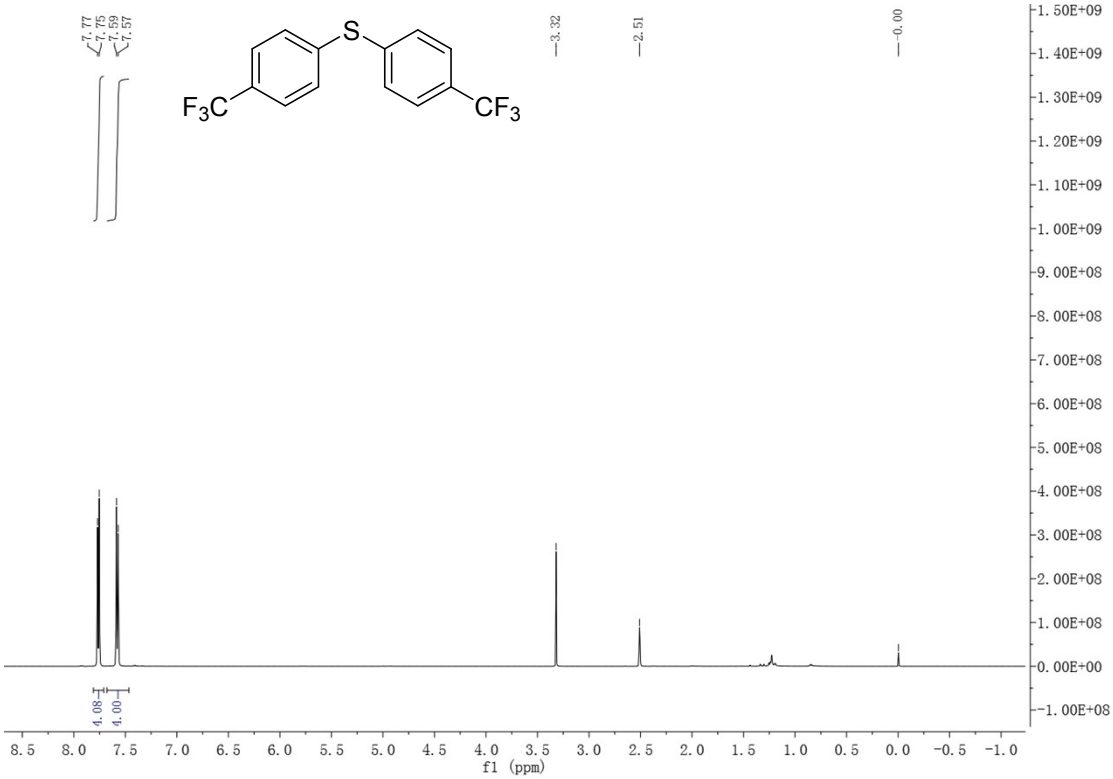
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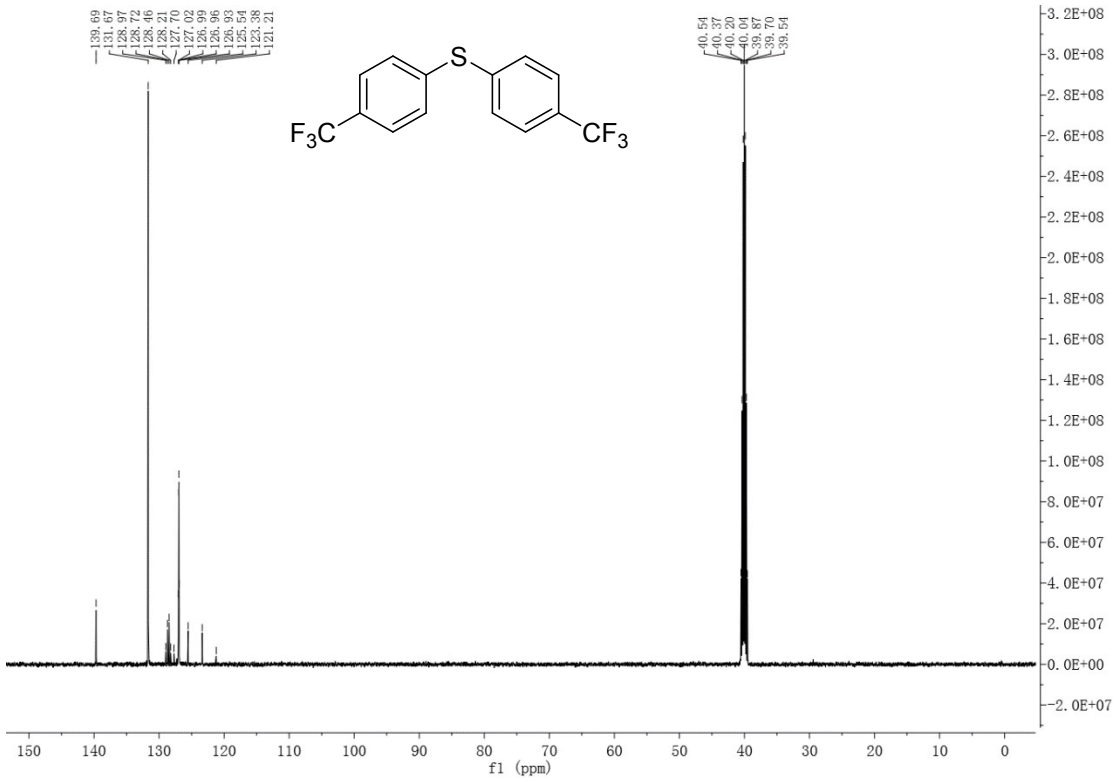
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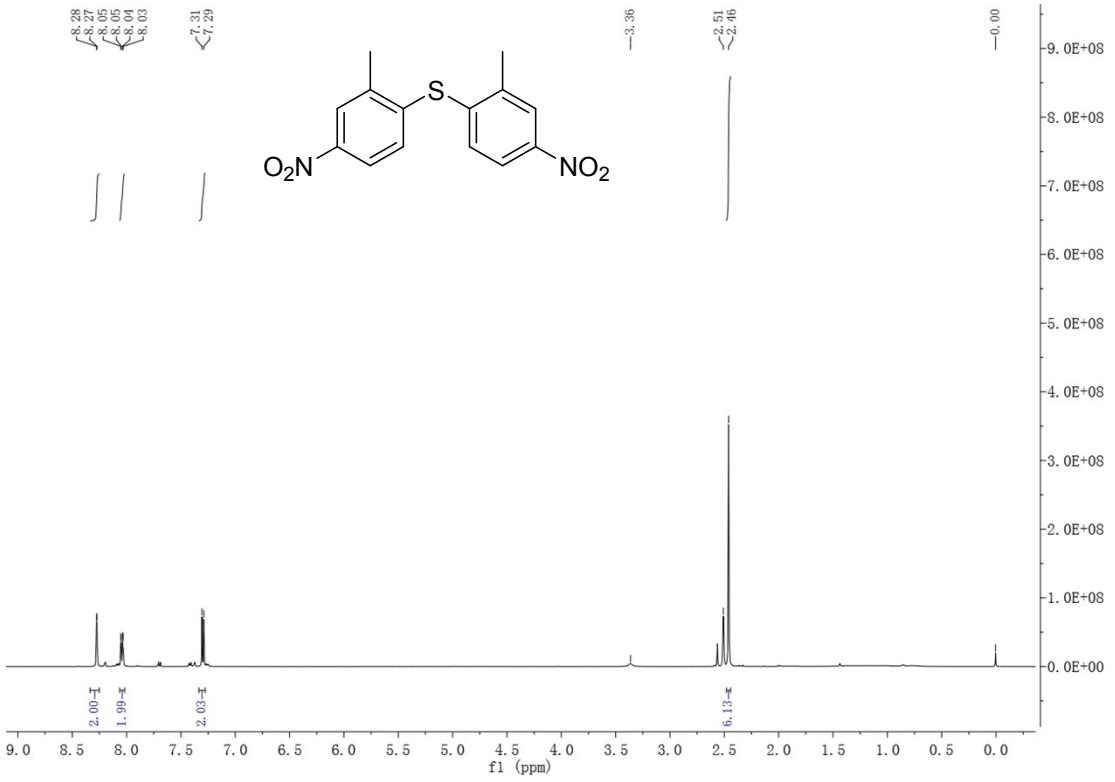
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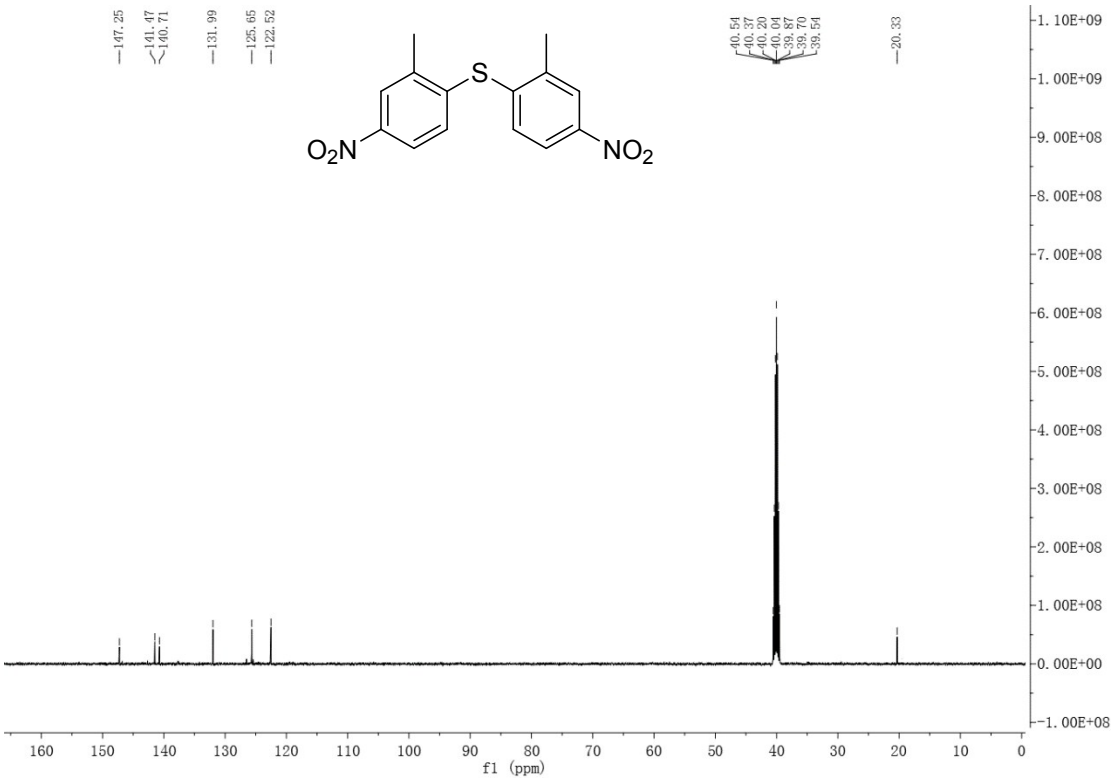
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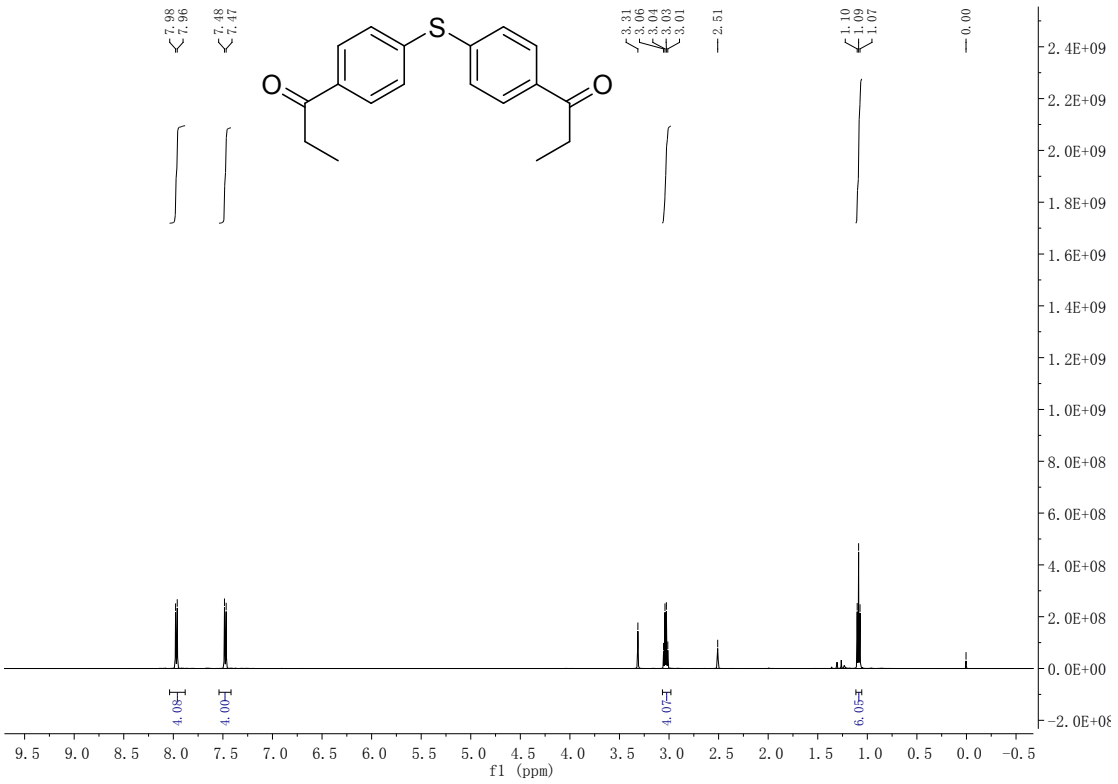
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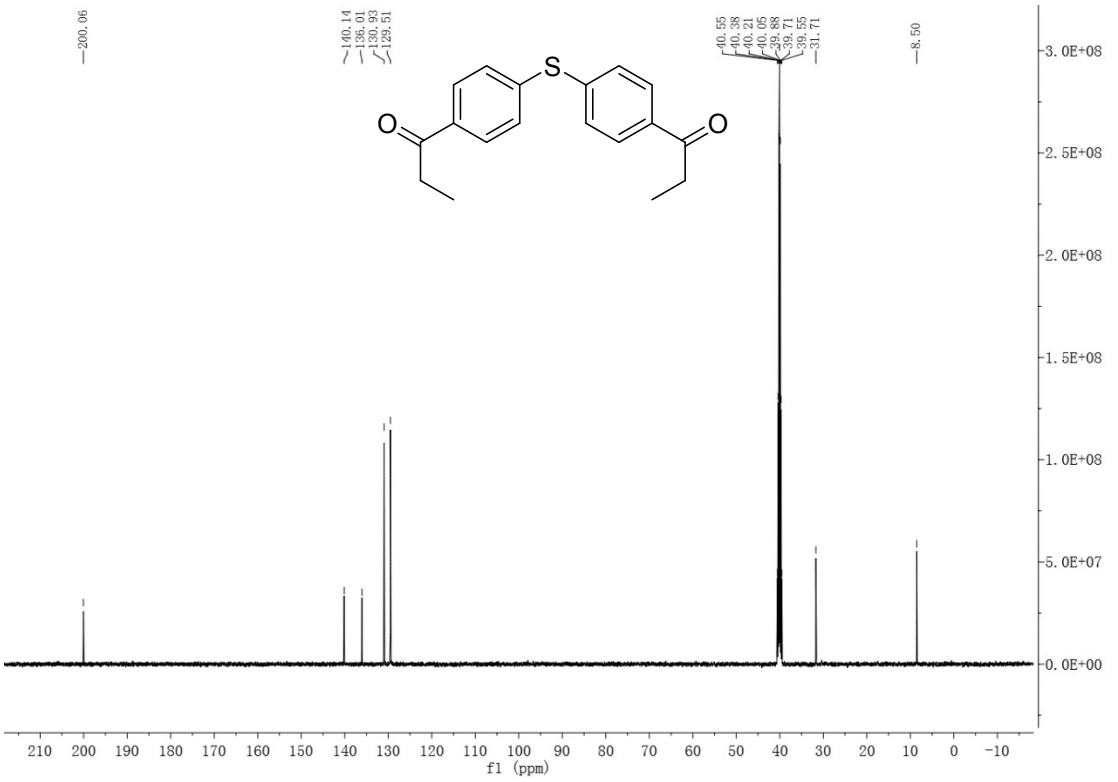
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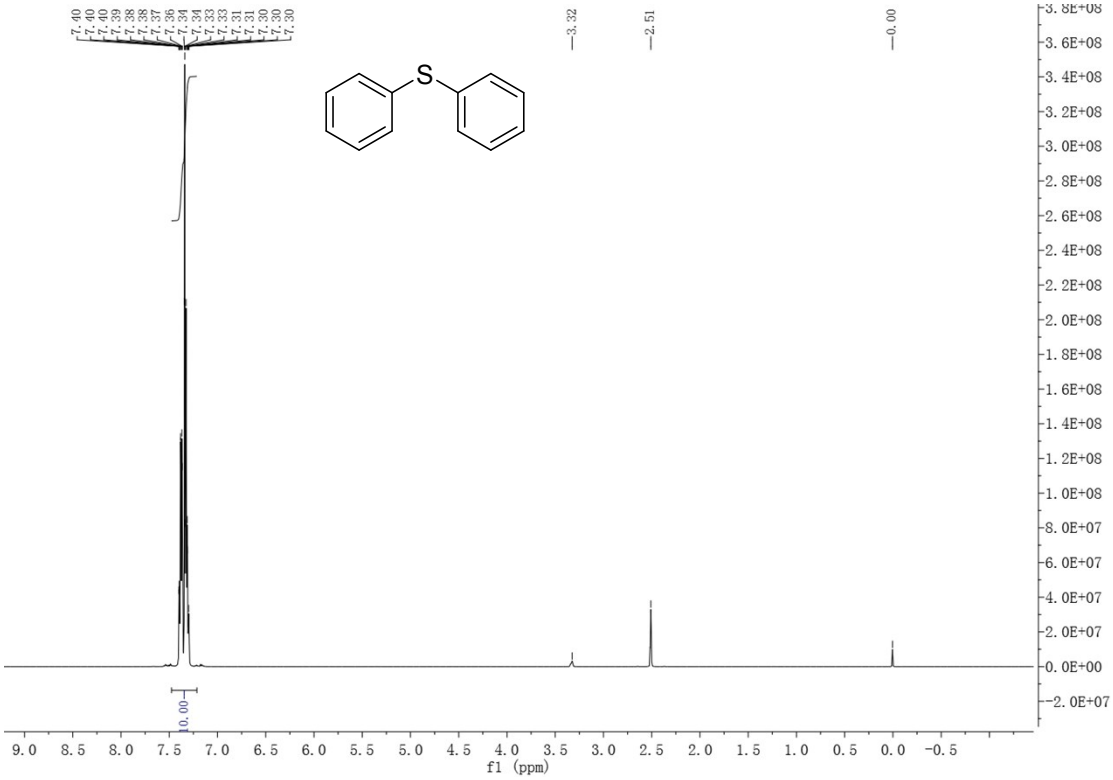
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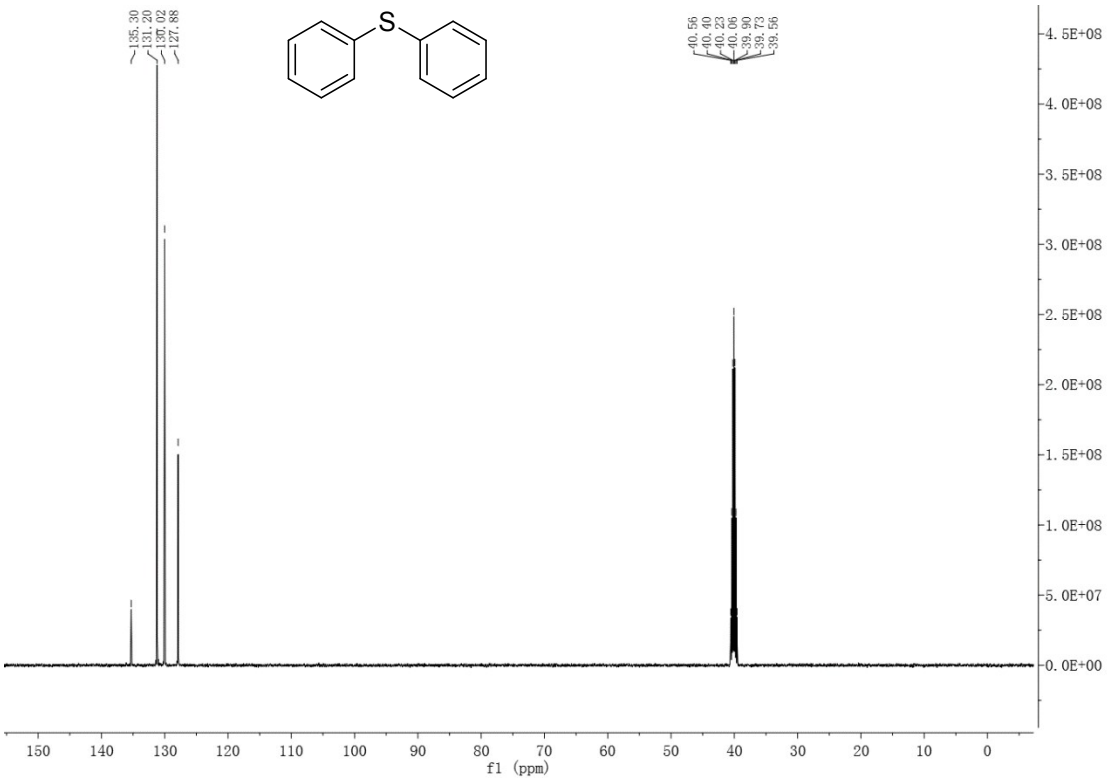
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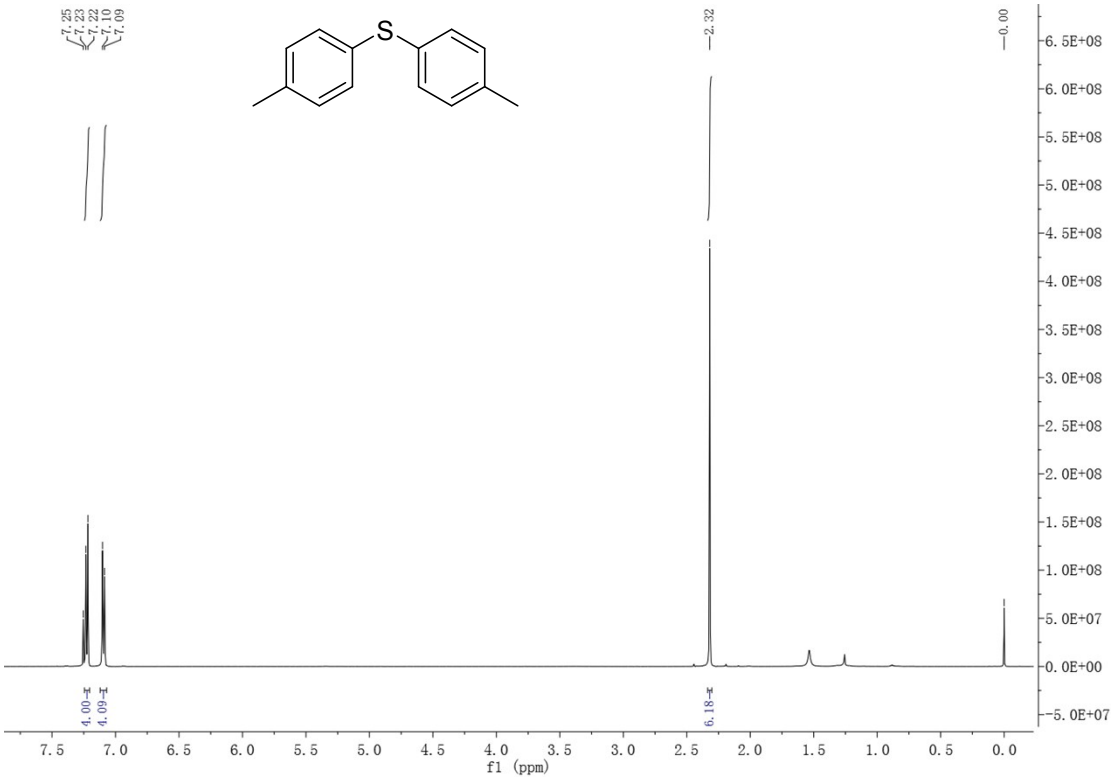
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S
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132.72
131.09
129.91
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77.02
76.77
21.06
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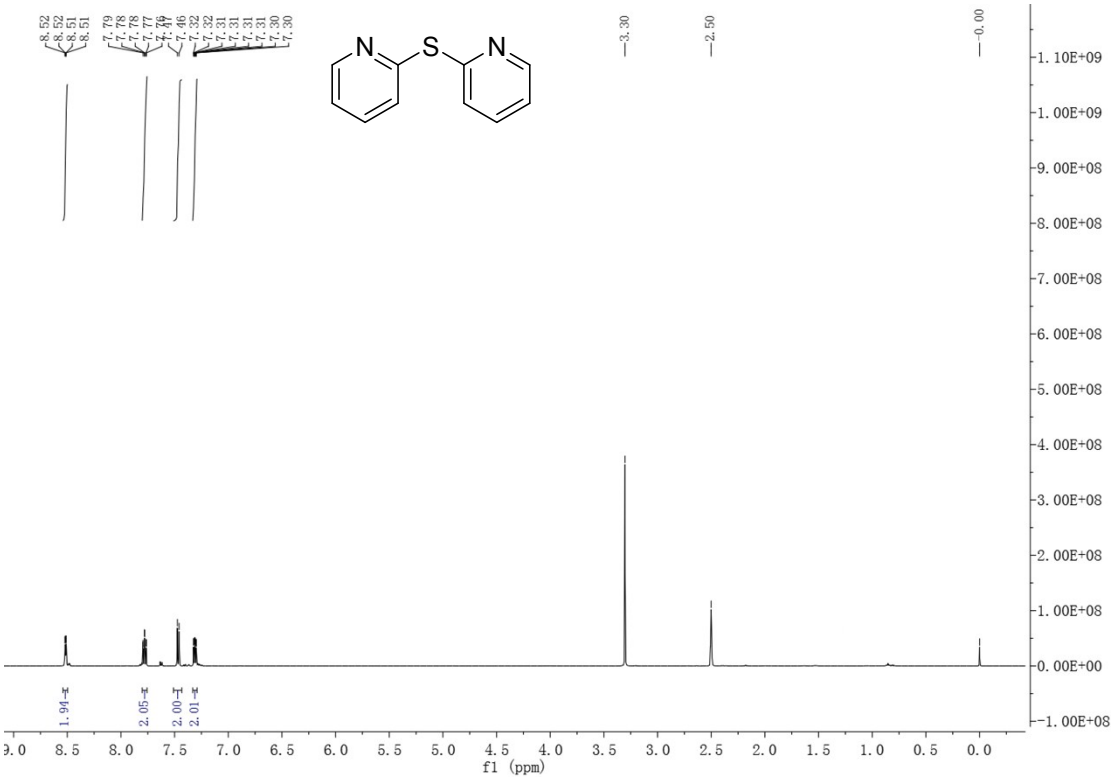
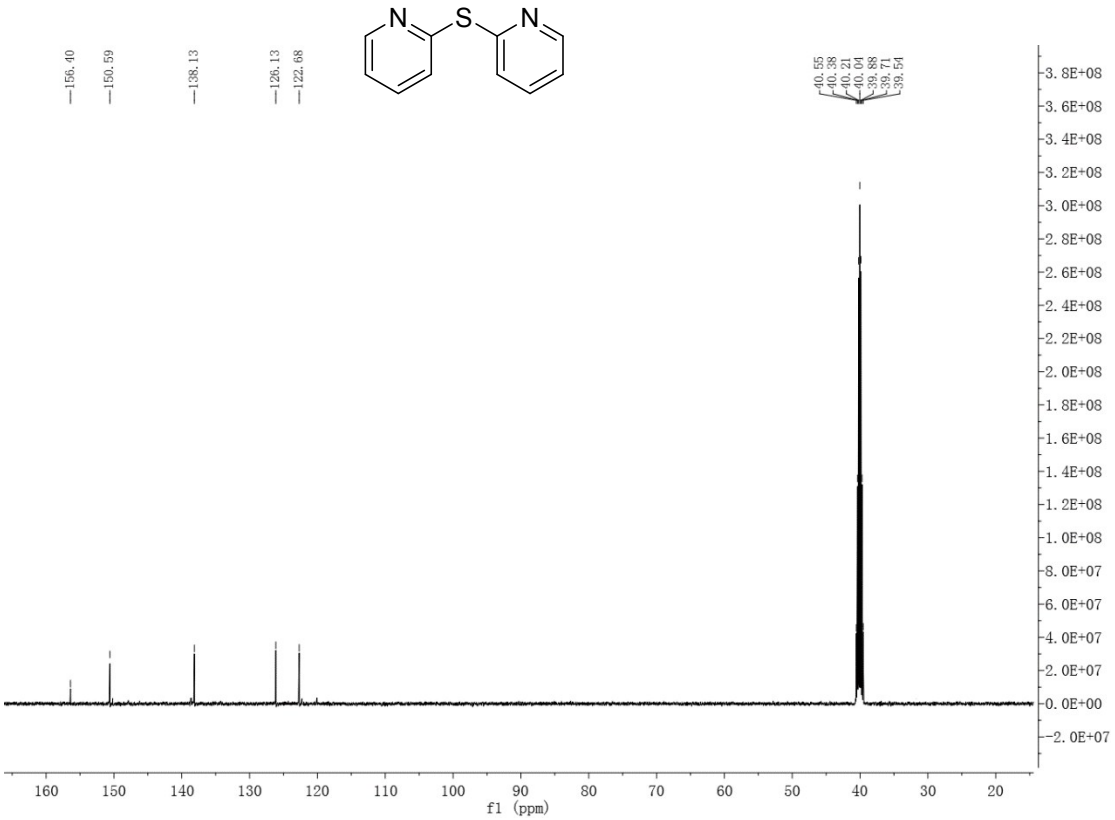
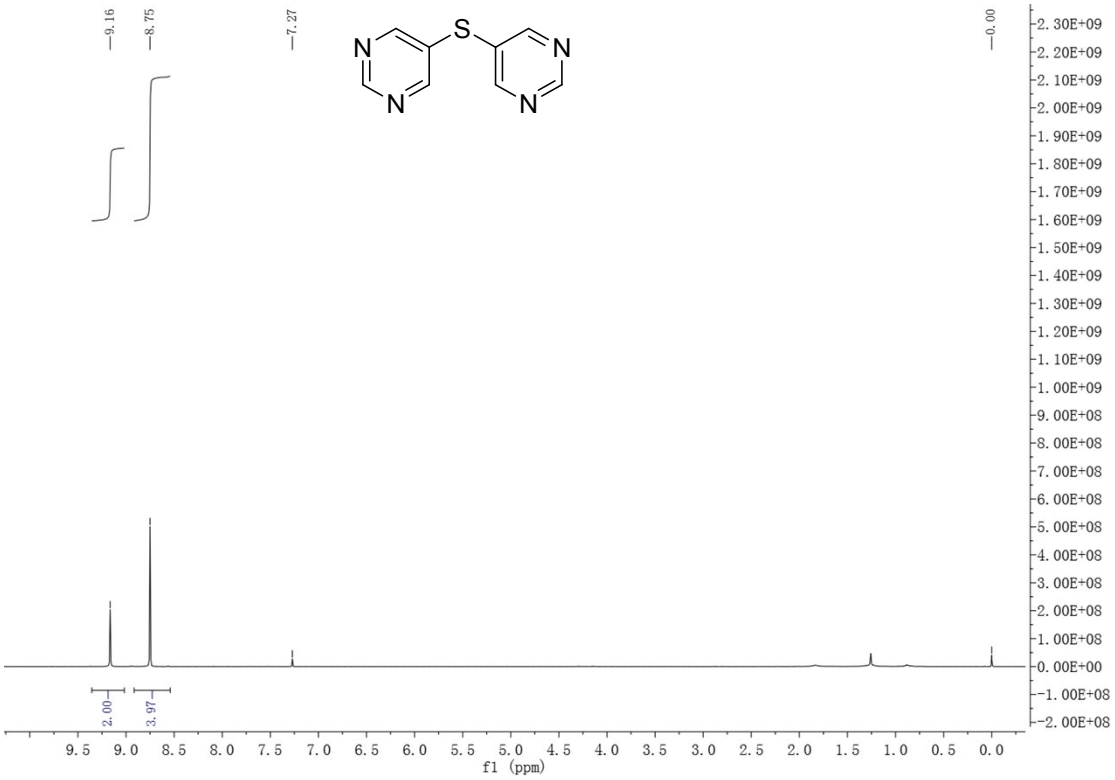
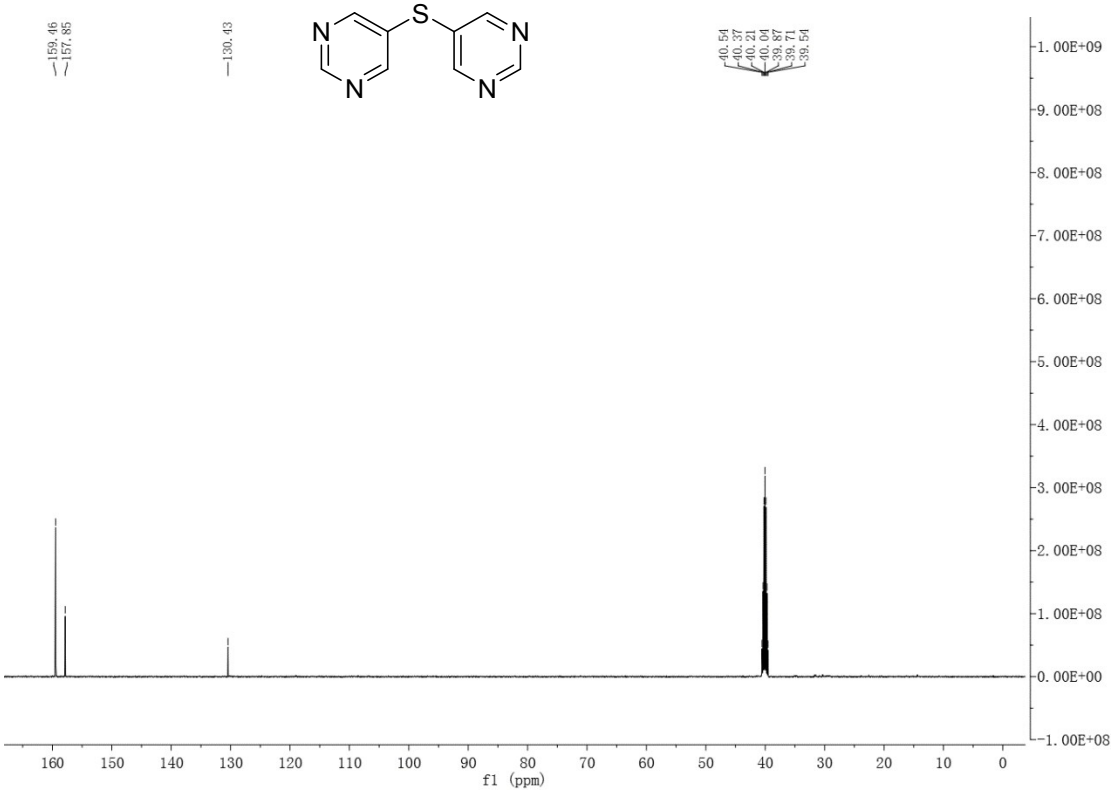
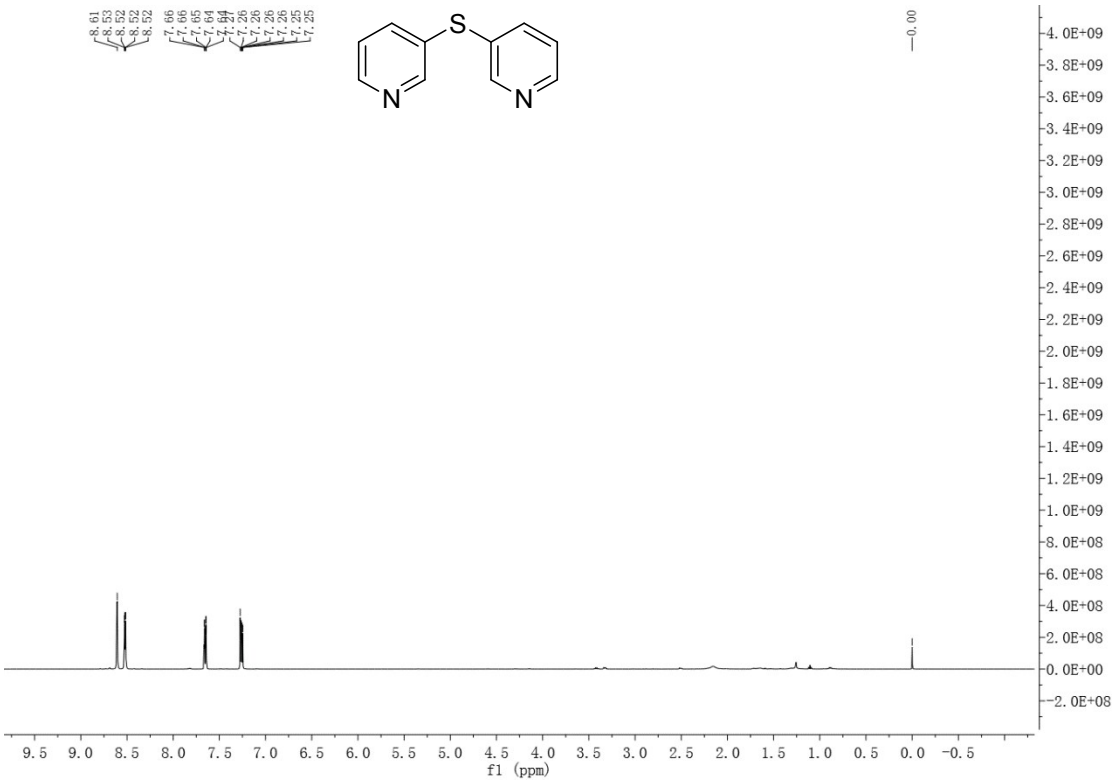
S
f1 (ppm)

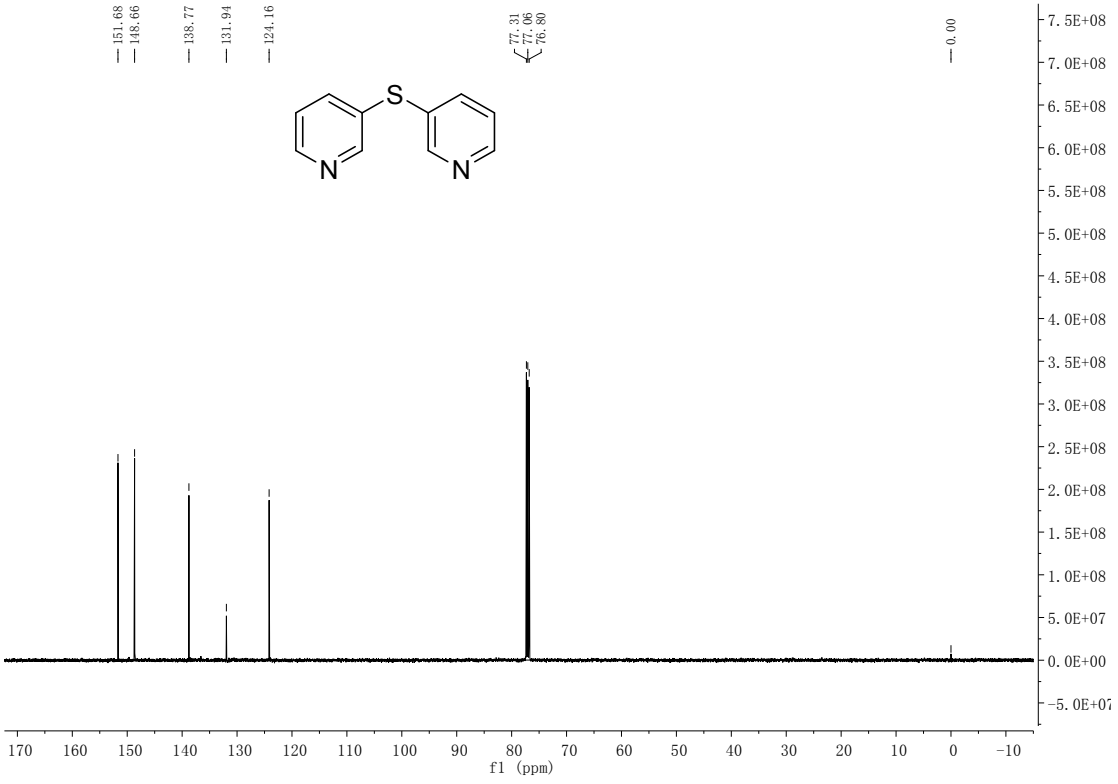

8.52
8.52
8.51
8.51
7.79
7.78
7.78
7.77
7.46
7.32
7.32
7.31
7.31
7.31
7.30
7.30
3.30
2.50
0.00
N
S
N
1.94
2.05
2.00
2.01
f1 (ppm)


156.40
150.59
138.13
126.13
122.68
40.55
40.38
40.21
40.04
39.88
39.71
39.54
N
S
N
f1 (ppm)

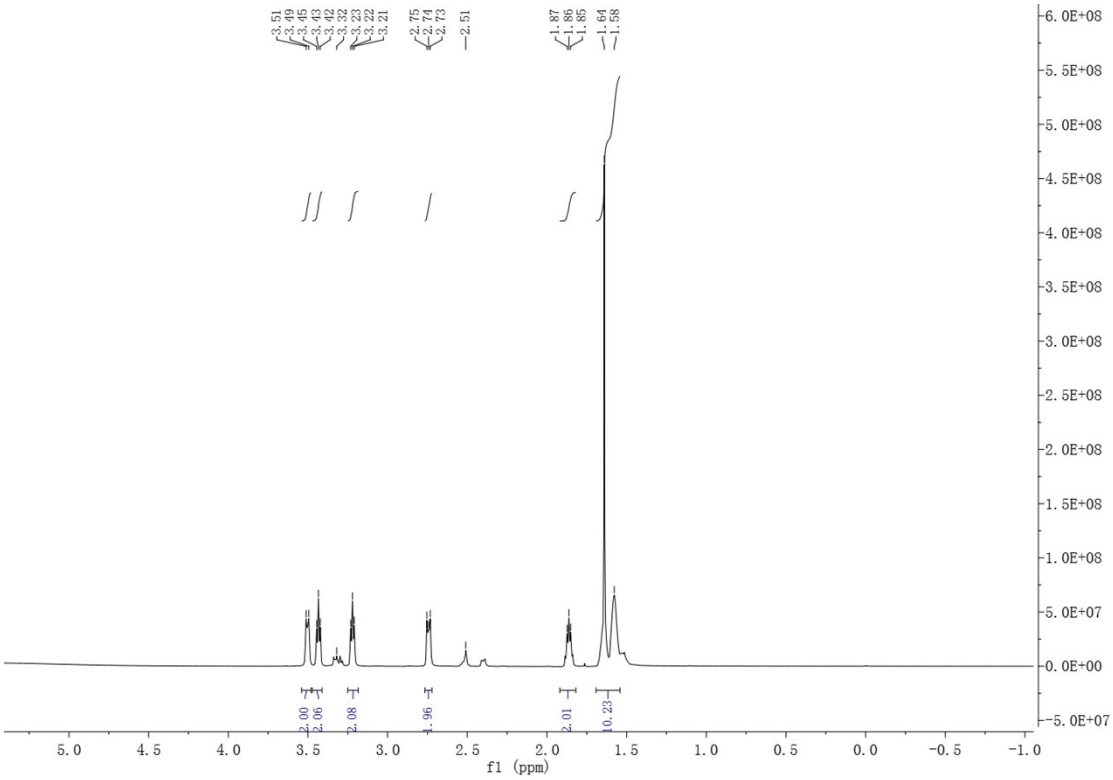

9.16
8.75
7.27
0.00
2.00
3.97
f1 (ppm)

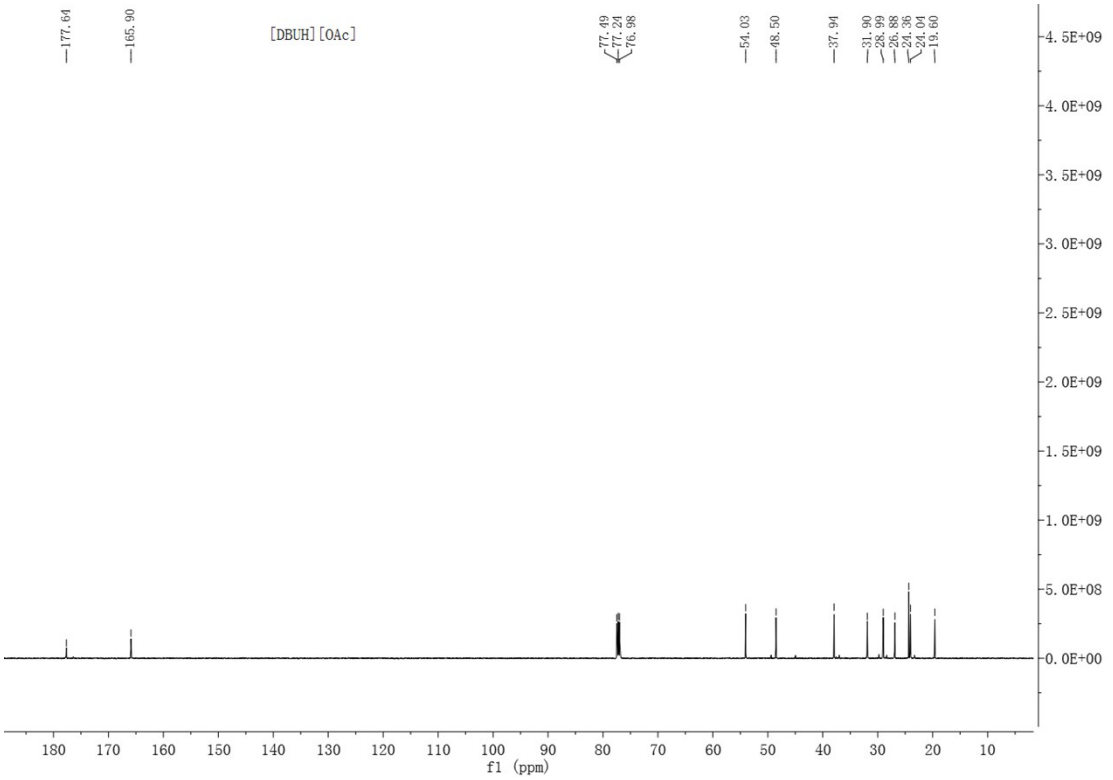

159.46
157.85
130.43
40.54
40.37
40.21
40.04
39.87
39.71
39.54
f1 (ppm)


8.61
8.53
8.52
8.52
8.52
7.66
7.66
7.65
7.64
7.64
7.27
7.26
7.26
7.26
7.26
7.25
7.25
S
N
N
0.00
4.0E+09
3.8E+09
3.6E+09
3.4E+09
3.2E+09
3.0E+09
2.8E+09
2.6E+09
2.4E+09
2.2E+09
2.0E+09
1.8E+09
1.6E+09
1.4E+09
1.2E+09
1.0E+09
8.0E+08
6.0E+08
4.0E+08
2.0E+08
0.0E+00
-2.0E+08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


151.68
148.66
138.77
131.94
124.16
77.31
77.06
76.80
0.00
S
N
N
7.5E+08
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

[DBUH][OAc]


3.51
3.49
3.45
3.43
3.42
3.32
3.23
3.22
3.21
2.75
2.74
2.73
2.51
1.87
1.86
1.85
1.64
1.58
2.00
2.06
2.08
4.96
2.01
10.23
f1 (ppm)


177.64
165.90
[DBUH][OAc]
77.49
77.24
76.98
54.03
48.50
37.94
31.90
28.99
26.88
24.36
24.04
19.60
f1 (ppm)