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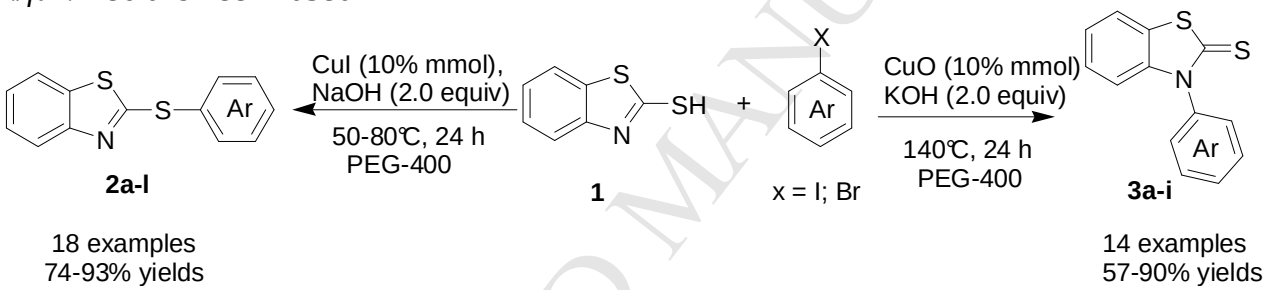

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Novel copper/PEG-400 catalyst systems for chemoselective S- and N-arylation of 2-mercaptobenzothiazole

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ABSTRACT

A novel approach for chemoselective S- and N-arylation of 2-mercaptobenzothiazole was developed by copper/PEG-400 catalyst systems. Copper source and reaction temperature play an important role in this protocol, selective S-arylation of 2-mercaptobenzothiazole was achieved by using CuI/PEG-400/50 °C catalyst system, while selective N-arylation was achieved with CuO/ PEG-400/140 °C catalyst system. Both are compatible with a variety of aryl halides and selectively give the desired S- and N-arylation products in good to excellent yields, respectively.

1. Introduction

In the last decades, transition-metal-catalyzed carbon-carbon and carbon-heteroatom bond coupling reaction constitutes an important methodology,[1] which has vast applications in pharmaceuticals, materials science as well as in the synthesis of biologically active compounds.[2-9] However, as for substrates with multiple heteroatom sites capable of undergoing reaction, the desirable coupling reaction compounds were not frequently obtained. Recently, with the development of more effective catalyst systems for transition-metal-catalyzed cross-coupling reactions, the substrate scope and generality of these processes has greatly improved.[10] Furthermore, many chemoselective C-O versus C-N[11b,c] and C-N versus C-C[10d] coupling reactions in the same substrates can be performed without the need to employ protecting groups. For example, Buchwald and workers reported sets of procedures for the Pd- and Cu-catalyzed chemoselective arylation of aminobenzamides,[11a] 5-aminoindole,[11a] 4-(2-

aminoethyl)aniline,[11a] amino alcohols,[11b] aminophenols[11c] and oxindoles.[11d] Recently, Buchwald have developed a catalyst-controlled protocol for chemoselective N-arylations of 2-aminobenzimidazoles and related aminoazoles, wherein selective N-arylation of the amino group with a Pd-catalyzed method, while selective N-arylation of azole nitrogen with a Cu-catalyzed procedure.[12]

Although transition-metal-catalyzed chemoselective carbon-carbon versus carbon-heteroatom bond coupling reactions show some advantages, some specific ligands and different transition-metals were required, importantly, the resulting chemoselectivities were generally low.[13] On the other hand, the chemoselective C-N versus C-S coupling reactions in the same substrates is a relatively unexplored area and the N- and S-arylated products constitute a common structural motif in various potentially useful therapeutic agents and/or drug candidates.[14] They have also been applied as building blocks for the preparation of organic materials.[15] Thus, it is desired to exploit a simple and efficient catalyst system for chemoselective C-N versus C-S coupling reactions in the same substrates in view of green and sustainable chemistry.

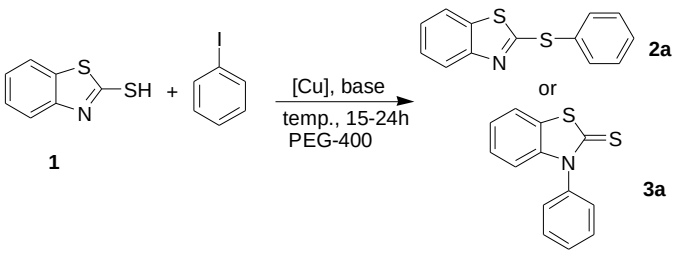
The 1,3-benzothiazole derivatives are an important class of molecules and are a common heterocyclic scaffold in biologically active and medicinally significant compounds.[16] Particularly, several 2-thio-substituted mercaptobenzothiazoles such as 2-arylthiobenzothiazoles have received much attention due to their unique structure and its uses as radioactive amyloid imagining agents,[17] and anticancer agents.[18] Some therapeutic agents containing this core structure include potent heat shock protein-90 inhibitors[19] and an inhibitor of Cathepsin-D.[20] They also act as antimicrobial agents especially against Piricularia oryzae and Xanthomonasoryzae.[21] Furthermore, 3-amino-substituted mercaptobenzothiazoles such as 3-aryl-2-benzothiazolthions are a kind of important organic intermediates[22] and important redox-active compounds with broad chemical, material, and biomedical applications. For example, 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) and its derivatives have been used as the electrochromic component in smart windows,[23] as a chromogenic substrate in assays for enzymatic activity,[24] and as a mediator for electron transfer in bioelectrocatalysis.[25] Although 2-thio-substituted mercaptobenzothiazoles play an important role in the field of pharmaceutical science, the available synthetic methods for these compounds are very limited. Two typical methods have generally been applied for the elaboration of 2-thio-substituted mercaptobenzothiazoles. One by the nucleophilic attack of arylthiols with a preformed 2-halobenzothiazoles and the second by a nucleophilic attack of mercapto-benzothiazole upon haloarenes containing electron-withdrawing substituents under strongly basic conditions.[26] Alternatively, Wang developed a method for the synthesis of 2-arylthiobenzothiazoles by the thio-arylation of benzothiazol-2-thiol with diaryliodonium salts in an ioinic liquid [bmim]BF.[27] Recent approaches have focused on the use of transition-metal (Cu, Pd, and Fe)-catalyzed, intermolecular, C-S bond formations for

the synthesis of 2-(arylthio)-1,3-benzothiazoles under milder conditions with better efficiency and selectivity.[28] Additionally, Patel developed a single catalytic system for two sequential intra- and intermolecular S-arylations leading to a direct synthesis of 2-arylthiobenzothiazoles from dithiocarbamates.[29] However, specific ligand and transition metal were needed for obtaining high yields. Furthermore, to the best of our knowledge, the synthesis of 3-animo-substituted mercaptobenzothiazoles has not so far been reported. In a continuation of our endeavors to develop copper-catalyzed carbon-heteroatom bonds cross-coupling reactions in PEG-400,[30] we, herein, report a novel Cu-catalyzed chemoselective condition for S- or N-arylation of unprotected 2-mercaptobenzothiazole with aryl halides using different copper salts, bases, and varied temperatures.

2. Results and discussion

The optimization of the reaction conditions was carried out with 2-mercaptobenzothiazole **1** and iodobenzene as model substrates using different copper sources and bases at varied temperatures in Table 1. Initially, the reaction was conducted under the action of 10 mol % of CuI, and two equivalent of NaOH in PEG-400 at 140 °C. It was found that most of the 2-mercaptobenzothiazole was consumed after 15 h. Unexpectedly, the desired product of the S-arylation coupling reaction, **2a**, was obtained in only 41% yield, together with the corresponding N-arylation product, **3a** (47% yield on the basis of **1** used, Table 1, entry 1). To our delight, decreasing the temperature of the coupling reaction to 120 °C resulted the S-arylation product with 46% yield, while the yield of **3a** was decrease to 38% (Table 1, entry 2). Further decreasing the temperature to 100 °C and 80 °C, the yields of the S-arylation coupling reaction was increased to 51% and 78%, respectively (Table 1, entries 3 and 4). However, under the same conditions, lowering of the reaction temperature (50 °C) led to low conversion. Gratifyingly, the yield of S-arylation product was increased to 89% through longer reaction time to 24 h, only small amounts of N-arylation product was detected (Table 1, entry 5). When the reaction was carried out using different copper salts such as $CuCl_2$, $CuSO_4$, and CuO, affording the S-arylation and N-arylation products in very low yields (Table 1, entries 6-8). Then, various bases were also screened at the above same reaction condition, moderate yield was obtained using KOH as base (Table 1, entry 9), while K_3PO_4, K_2CO_3 or NaOAc as bases afforded the S- and N-arylation products in lower yields (table 1, entries 10-12).

Table 1: Reaction optimization



1

Entry [a]	[Cu]	base	Temp (℃)	Yield [b] (%)
1	CuI	NaOH	140	**2**a/41, **3**a/47
2	CuI	NaOH	120	**2**a/46, **3**a/38
3	CuI	NaOH	100	**2**a/51, **3**a/29
4	CuI	NaOH	80	**2**a/78, **3**a/11
5	**CuI**	**NaOH**	**50**	**2a/89, 3a/7**
6	$CuCl_2$	NaOH	50	**2**a/<5, **3**a/3
7	$CuSO_4$	NaOH	50	**2**a/15, **3**a/6

8	CuO	NaOH	50	**2**a/16, **3**a/10
9	CuI	KOH	50	**2**a/68, **3**a/19
10	CuI	K_3PO_4	50	**2**a+**3**a /<5
11	CuI	K_2CO_3	50	**2**a+**3**a /<5
12	CuI	NaOAc	50	**2**a+**3**a /<5
13	CuI	KOH	140	**2**a/12, **3**a/61
14	**CuO**	**KOH**	**140**	**2a/16, 3a/81**
15	$CuCl_2$	KOH	140	**2**a/13, **3**a/15
16	$Cu(NO_3)_2$	KOH	140	**2**a/19, **3**a/12
17	Cu_2SO_4	KOH	140	**2**a/11, **3**a/8

[a] 2-Mercaptobenzothiazole (1.0 mmol), iodobenzene (1.1 mmol), copper salt (10 mol%), base (2.0 mmol), PEG-400 (2.0 mL), entries 1-4 for 15 h, others for 24h.

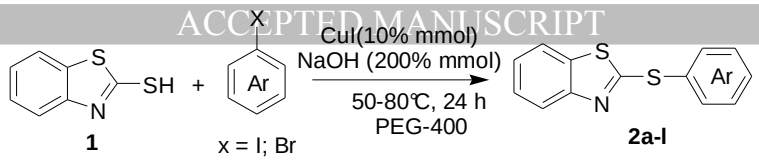
[b] Yield of isolated product based on 2-mercaptobenzothiazole, average of two runs.

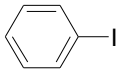
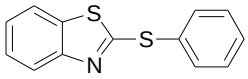
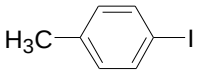
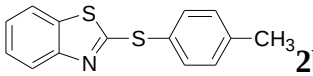
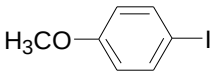
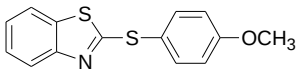
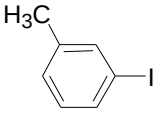
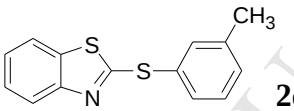
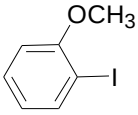
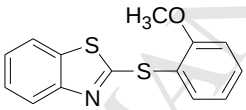
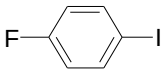
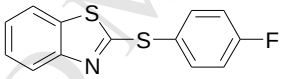
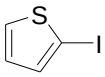
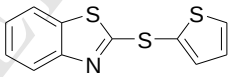
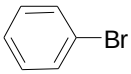
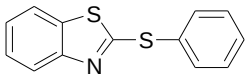
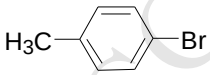
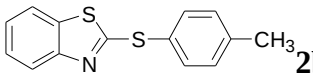
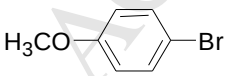
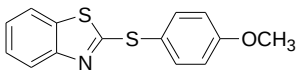
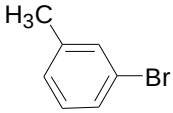
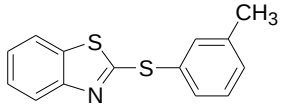
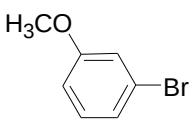
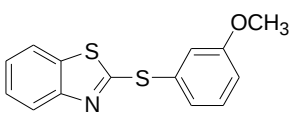
Finally, by a systematic variation of the reaction parameters we establish CuI/PEG-400/50 °C an effective catalytic system for chemoselective S-arylation of 2-mercaptobenzothiazole.

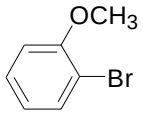
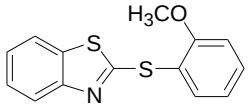
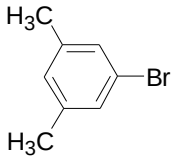
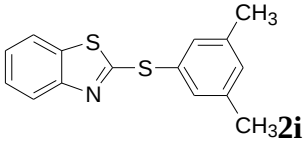
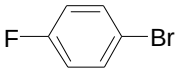
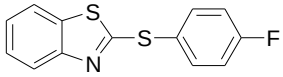
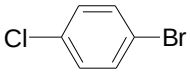
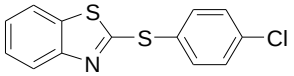
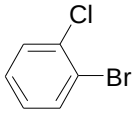
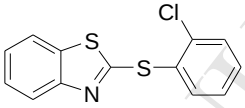
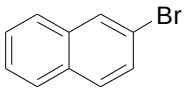
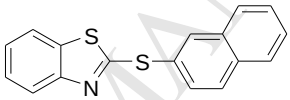
Then, we turned our attention to finding conditions for the selective formation of the N-arylation product. Obviously, higher reaction temperature was of great benefit to the N-arylation. Unexpectedly, switching the base to KOH provided an improved yield (Table 1, entries 1 vs 13). Thus, we selected KOH as the base at 140 °C in the following studies. The effect of the copper salts on this reaction was evaluated, we found that copper salt also plays a crucial role for this coupling reaction, as is evident from CuO affording 81% yield (Table 1, entries 14), while a moderate yield was observed in the case of CuI, and a relatively low yield was observed when $CuCl_2$, $Cu(NO_3)_2$ or Cu_2SO_4 were employed (Table 1, entries 15-17). Finally, we established that CuO/KOH/140 °C was an effective catalytic system for chemoselective N-arylation of 2-mercaptobenzothiazole.

Next, we firstly explored the scope of the Cu-catalyzed chemoselective S-arylation of 2-mercaptobenzothiazole using 10 mol% CuI, 200 mol% NaOH as the base, and PEG-400 as the solvent at temperatures 50 °C for 24h. Our catalytic system efficiently promotes highly chemoselective S-arylation cross-coupling reactions between 2-mercaptobenzothiazole and aryl halides with either electron-donating or electron-withdrawing substituents, thus giving the corresponding S-arylation products in 74-93 % yields upon isolation (Table 2, entries 1-18). Particularly interesting was that *ortho*-substituted aryl iodides provided better yields than *para*- and *meta*- substituted aryl halides (Table 2, entries 2 vs 5; 10 vs 12 or 13), presumably because of the steric effect on S-arylation. A heterocyclic compound, such as 2-iodothiophene, could also afford the corresponding S-arylation products in 89% yield (Table 2, entry 7). However, some electron-deficient aryl bromides such as *p*-fluoro bromobenzene, *p*-chloro bromobenzene, and *o*-chloro bromobenzene exhibited relatively weak reactivity and also gave relatively good yields by increasing reaction temperature to 80 ℃ (Table 2, entries15-17). Remarkably, 2-bromo naphthalene also proved to be good substrate in the reaction, giving the desired product in satisfactory yield (Table 2, entry 18). It was worth mentioning that the process showed good functional group compatibility (Table 2, entries15-17).

Table 2 Scope of the Cu-catalyzed S-arylation of 2-mercaptobenzothiazol



Entry [a]	ArX	Product	Yield [b] (%)
1		 **2a**	89
2		 **2b**	86
3		 **2c**	91
4		 **2d**	87
5		 **2e**	93
6		 **2f**	82
7		 **2g**	89
8		 **2a**	85
9		 **2b**	87
10		 **2c**	87
11		 **2d**	91
12		 **2h**	89

13		 **2e**	91
14		 **2i**	90
15[c]		 **2f**	80
16[c]		 **2j**	84
17[c,]		 **2k**	85
18[c]		 **2l**	74

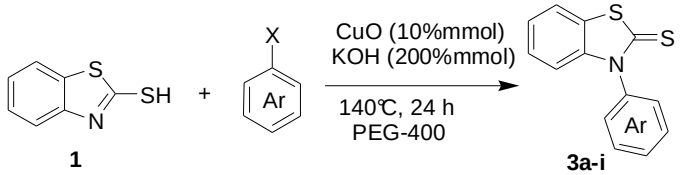
[a] Reaction condiction: 2-mercaptobenzothiazole (1.0 mmol), aryl halide (1.1 mmol), NaOH (2.0 mmol), CuI (10 mol%), PEG-400 (2.0 mL), 50 ℃, 24 h under N_2.

[b] Yield of isolated product based on 2-mercaptobenzothiazole, average of two runs.

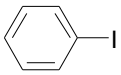
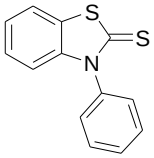
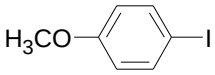
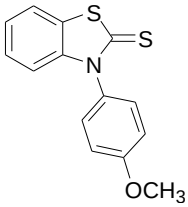
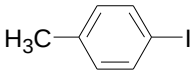
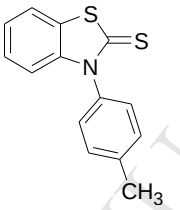
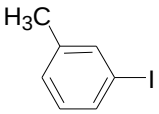
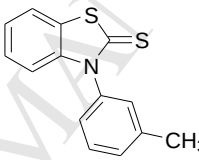
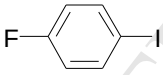
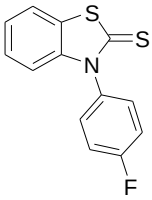
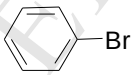
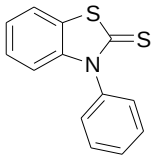
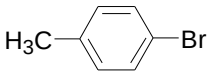
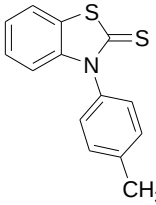
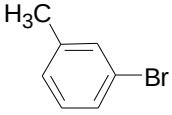
[c] Reaction temperature at 80 ℃, 24 h.

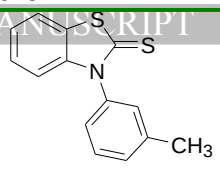
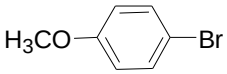
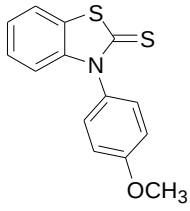
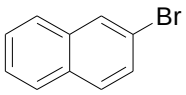
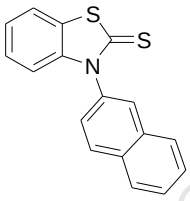
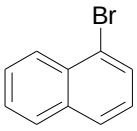
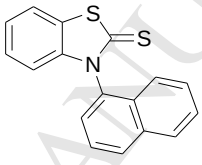
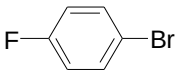
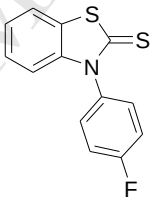
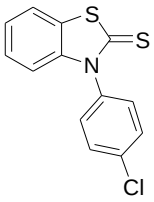
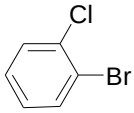
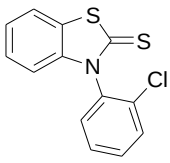
The scope of the Cu-catalyzed N-selective arylation was also investigated using 10 mol% CuO, 200 mol% KOH as the base, and PEG-400 as the solvent at temperatures 140 °C (Table 3). In these reactions, we found that reactions of 2-mercaptobenzothiazole with a variety of electron-neutral, and -rich aryl halides generally underwent N-arylation in excellent yields and with high levels of chemoselectivity (Table 3, entries 1-9). However, bromonaphthalenes as substrates gave only moderate yields (58%, 57%, respectively Table 3, entries 10-11). Electron-deficient aryl halides, such as *p*-fluoroiodobenzene, *p*-fluorobromobenzene, and *p*-chlorobromobenzene afforded good yields (Table 3, entries 12-13), *o*-chlorobramobenzene also gave the N-arylation product in high yield.

Table 3 Scope of the Cu-catalyzed N-arylation of 2-mercaptobenzothiazole



1 **3a-i**

Entry [a]	ArX	Product	Yield [b](%)
1		 **3a**	85
2		 **3b**	81
3		 **3c**	80
4		 **3d**	81
5		 **3e**	87
6		 **3a**	90
7		 **3c**	81
8			86

		 **3**d		
9		 **3**b	83	
10		 **3**e	58	
11		 **3**f	57	
12		 **3**g	73	
13		 **3**h	86	
14		 **3**i	80	

[a] Reaction condiction: 2-mercaptobenzothiazole (1.0 mmol), aryl halide (1.1 mmol), KOH (2.0 mmol), CuO (10 mol%), PEG-400 (2.0 mL), 140 ℃, 24 h under N_2.

[b] Yield of isolated product based on 2-mercaptobenzothiazole, average of two runs.

3. Conclusions

We have developed a novel approach for chemoselective S- and N-arylation of 2-mercaptobenzothiazole by copper/PEG-400 catalyst systems. Copper source and reaction temperature play an important role in this protocol,

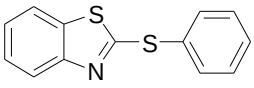
selective S-arylation of 2-mercaptobenzothiazole was achieved by using CuI/PEG-400/50 °C catalyst system, while selective N-arylation was achieved with CuO/PEG-400/140 °C catalyst system. Both are compatible with a variety of aryl halides and selectively give the desired S- or N-arylation products in good to excellent yields. Application of this protocol for other coupling reactions involving chemoselective S- versus N-arylation and a detailed mechanistic study are currently under investigation.

4. Experimental section

4.1. *General Procedure A: Cu-catalyzed S-arylation of 2-mercaptobenzothiazole*

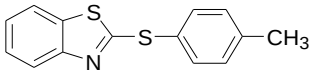
A flask equipped a magnetic stirring bar was charged with 2-mercaptobenzothiazole (1.0 mmol), aryl halide (1.1 mmol), CuI (0.1 mmol), NaOH (2 mmol) and PEG-400 (2 ml). The reaction mixture was stirred under a nitrogen atmosphere at 50 °C for 24 h. The reaction mixture was cooled to room temperature, diluted with Et_2O, washed with brine and dried over $MgSO_4$. Silica gel (1.0 g) was added to the mixture and the mixture was concentrated in vacuo. The silica gel-adsorbed product was purified through flash chromatography with petroleum ether/ethyl acetate as eluent to give the desired S-arylation products.

4.1.1. *2-(Phenylthio)benzo[d]thiazole* (**2**a)



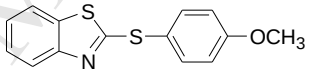
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.0 Hz, 1H), 7.26-7.20 (m, 3H), 7.13-7.07 (m, 3H), 6.80-6.74 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d6): δ 169.39, 150.84, 137.39, 131.81, 131.44, 129.50, 128.28, 126.73, 125.83, 117.17, 115.37. IR (KBr): 3057, 1581, 1458, 1433, 1311, 1235, 1019, 1004, 753 cm^{-1}. HR EIMS: 243.0153 *m/z* (calcd for $C_{13}H_9NS_2$: 243.0156).

4.1.2. *2-(p-Tolylthio)benzo[d]thiazole* (**2**b).



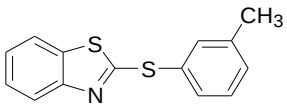
White solid, M.p. 71-72 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.25-7.19 (m, 1H), 7.02 (t, *J* = 7.6 Hz, 4H), 6.78-6.72 (m, 2H), 2.28 (s, 3H); ^{13}C NMR (100MHz, DMSO-d6): δ 169.26, 150.41, 136.97, 135.43, 133.37, 131.15, 130.14, 127.54, 117.13, 115.31, 113.44, 20.93. IR (KBr): 3064, 2912, 1595, 1426, 1315, 1239, 817, 761 cm^{-1}. HR EIMS: 257.0326 *m/z* (calcd for $C_{14}H_{11}NS_2$: 257.0333).

4.1.3. *2-(4-Methoxyphenylthio)benzo[d]thiazole* (**2**c).



White solid, M.p. 61-63 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.4Hz, 1H), 7.66-7.61 (m, 3H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.25-7.23 (m, 1H), 7.00-6.98 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 171.81, 161.74, 154.22, 137.57, 135.47, 126.10, 124.09, 121.79, 120.76, 120.26, 115.54, 55.49. IR (KBr): 3056, 2922, 1589, 1496, 1453, 1425, 1252, 1003, 833, 758 cm^{-1}. HR EIMS: 273.0338 *m/z* (calcd for $C_{14}H_{11}NOS_2$: 273.0341).

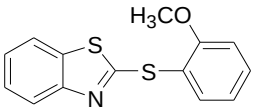
4.1.4. *2-(3-Methylphenylthio)benzo[d]thiazole* (**2**d).



White solid, M.p. 87-91°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6

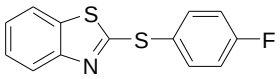
Hz, 1H), 7.103 (t, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 11.2 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.75 (t, J_1 = 7.6 Hz, J_2 = 6.8 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d6): δ 169.02, 150.66, 138.77, 137.31, 136.93, 131.40, 129.34, 127.44, 126.70, 124.04, 117.15, 115.34, 112.63, 21.42. IR (KBr): 3454.60, 2925.87, 1570.31, 1426.05, 1158.26, 1076.87, 950.90, 859.14, 754.50, 546.46. HR EIMS: 257.0328 *m/z* (calcd for $C_{14}H_{11}NS_2$: 257.0333).

4.1.5. *2-(2-Methoxyphenylthio)benzo[d]thiazole* (**2**e).



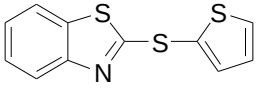
Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.11-7.10 (m, 1H), 6.87-6.77 (m, 4H), 6.66 (d, *J* = 8.0 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d6): δ 169.46, 155.85, 151.10, 137.67, 131.48, 126.60, 126.05, 125.16, 121.47, 117.32, 115.25, 111.36, 111.30, 56.17. IR (KBr): 3061, 2954, 1590, 1428, 1239, 812, 765 cm^{-1}. HR EIMS: 273.0337 *m/z* (calcd for $C_{14}H_{11}NOS_2$: 273.0341).

4.1.6. *2-(4-fluorophenylthio)benzo[d]thiazole* (**2**f).



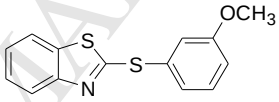
Brown liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.54-7.47 (m, 1H), 7.45-7.38 (m, 2H), 7.36-7.34 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d6): δ 168.71, 162.26, 159.84, 150.55, 137.10, 132.51, 131.46, 129.34, 117.19, 116.63, 115.42. IR (KBr): 3056, 2923, 1582, 1457, 1433, 1258, 1104, 1015, 813, 746 cm^{-1}. HR EIMS: 261.0144. *m/z* (calcd for $C_{13}H_9FNS_2$ 261.0156).

4.1.7. *2-(2-thiophenylthio)benzo[d]thiazole* (**2**g).



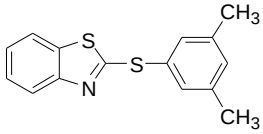
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.29 (m, 2H), 7.19-7.18 (m, 2H), 6.96-6.91 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d6): δ 169.36, 149.11, 134.57, 134.24, 132.82, 130.49, 130.14, 128.21, 117.15, 117.03, 115.42. IR (KBr): 3058, 2947, 1590, 1423, 1237, 813, 754 cm^{-1}. HR EIMS: 249.3746 *m/z* (calcd for $C_{11}H_7NS_3$: 249.3750).

4.1.8. *2-(3-Methoxyphenylthio)benzo[d]thiazole* (**2**h).



Yellow liquid, ^{1}H NMR (400MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.25-7.22 (m, 1H), 7.15-7.11 (m, 1H), 6.79-6.73 (m, 2H), 6.67-6.64 (m, 3H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.09, 148.90, 138.29, 137.52, 131.22, 129.81, 118.78, 118.73, 115.37, 114.16, 112.10, 111.03, 55.18. IR (KBr): 3468, 3369, 3063, 2936, 2834, 1609, 1589, 1478, 1247, 1042, 751 cm^{-1}. HR EIMS: 273.0338 *m/z* (calcd for $C_{14}H_{11}NOS_2$: 273.0341).

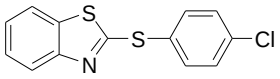
4.1.9. *2-(3,5-Dimethylphenylthio)benzo[d]thiazole* (**2**i).



Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.43 (m, 1H), 7.23 (d, *J* = 12.0 Hz, 1H), 6.79-6.72 (m, 5H), 2.22 (s, 6H); ^{13}C NMR (100 MHz;

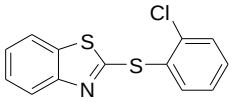
$CDCl_3$): δ 148.70, 138.67, 137.27, 136.21, 130.87, 127.54, 124.38, 128.66, 115.33, 114.81, 21.27. HR EIMS: 271.0481 *m/z* (calcd for $C_{15}H_{13}NS_2$: 271.0489).

4.1.10. *2-(4-Chlorophenylthio)benzo[d]thiazole* (**2**j).



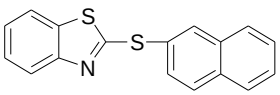
Brown liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.27-7.17 (m, 2H), 7.01-6.91 (m, 2H), 6.80-6.74 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d6): δ 169.32, 150.84, 137.45, 136.41, 131.81, 130.36, 129.39, 128.28, 117.21, 115.49, 111.70. IR (KBr): 3470, 3370, 2924, 1608, 1574, 1474, 1309, 1091, 1010, 814, 750 cm^{-1}. HR EIMS: 276.9782 *m/z* (calcd for $C_{13}H_8ClNS_2$:276.9786).

4.1.11. *2-(2-Chlorophenylthio)benzo[d]thiazole* (**2**k).



Brown liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 12.0 Hz, 1H), 7.35-7.26 (m, 2H), 7.06-7.04 (m, 2H), 6.83-6.78 (m, 2H), 6.65-6.62 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d6): δ 168.95, 151.31, 137.83, 136.33, 132.21, 130.25, 129.96, 128.07, 126.76, 126.35, 117.45, 115.58, 109.99. IR (KBr): 3485, 3375, 2931, 1607, 1556, 1476, 1301, 1090, 1015, 812, 786, 753 cm^{-1}. HR EIMS: 276.9783 *m/z* (calcd for $C_{13}H_8ClNS_2$:276.9786).

4.1.12. *2-(2-Naphthalenylthio)benzo[d]thiazole* (**2**l).

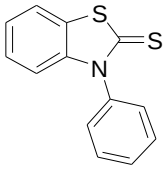


Brown liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.72 (m, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.51-7.47 (m, 2H), 7.41-7.37 (m, 2H), 7.28-7.21 (m, 2H), 6.81-6.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.90, 137.47, 134.26, 133.84, 131.62, 131.25, 128.70, 127.78, 127.07, 126.60, 125.48, 125.19, 124.41, 118.85, 115.51, 114.35. IR (KBr): 3468, 3371, 3053, 1607, 1479, 1448, 1309, 1063, 851, 813, 747. cm^{-1}. HR EIMS: 293.0327 *m/z* (calcd for $C_{17}H_{11}NS_2$: 293.0334).

4.2. *General Procedure B: Cu-catalyzed N-arylation of 2-mercaptobenzothiazole*

A flask equipped a magnetic stirring bar was charged with 2-mercaptobenzothiazole (1.0 mmol), aryl halide (1.1 mmol), CuO (0.1 mmol), KOH (2 mmol) and PEG-400 (2 ml). The reaction mixture was stirred under a nitrogen atmosphere at 140 °C for 24 h. The reaction mixture was cooled to room temperature, diluted with Et_2O, washed with brine and dried over $MgSO_4$. Silica gel (1.0 g) was added to the mixture and the mixture was concentrated in vacuo. The silica gel-adsorbed product was purified through flash chromatography with petroleum ether/ethyl acetate as eluent to give the desired N-arylation products.

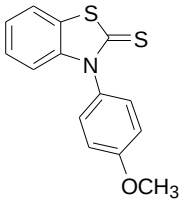
4.2.1. *3-Phenyl-3H-benzothiazole-2-thione* (**3**a).



Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.33 (m, 4H), 7.31-7.29 (m, 3H), 7.27-7.23 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d6): δ 169.31, 153.87, 135.69, 135.32, 131.38, 130.77, 129.34, 126.89, 124.97, 122.18, 121.87. IR (KBr): 3061, 2924, 2854, 1581, 1476, 1440, 1377, 1081,

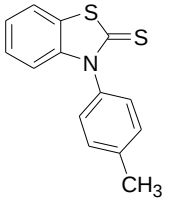
1024, 737, 689, 516. cm^{-1}. HR EIMS: 243.0152 *m/z* (calcd for $C_{13}H_9NS_2$: 243.0156).

4.2.2. *3-(4-Methoxy-phenyl)-3H-benzothiazole-2-thione* (**3**b).



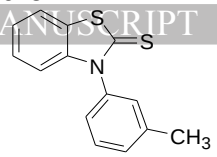
White solid, M.p. 57-59℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.67-7.61 (m, 3H), 7.40-7.36 (m, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.01, 161.73, 154.20, 137.63, 135.41, 126.12, 124.09, 121.76, 120.77, 120.18, 115.54, 55.51. IR (KBr): 3445, 2458, 1642, 1567, 1426, 1161, 1070, 951, 861, 547. cm^{-1}. HR EIMS: 273.0336 *m/z* (calcd for $C_{14}H_{11}NOS_2$: 273.0341).

4.2.3. *3-p-Tolyl-3H-benzothiazole-2-thione* (**3**c).



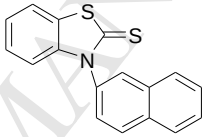
White solid, M.p. 49-50℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.6 Hz, 1H), 7.22 (m, 1H), 7.027 (dd, *J* = 8.4 Hz, 8Hz, 4H), 6.77 (t, *J* = 8.0 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d6): δ 170.30, 153.98, 141.68, 135.91, 135.24, 131.45, 126.87, 125.74, 124.84, 122.17, 121.17, 21.33. IR (KBr): 3450, 2952, 2451, 1567, 1447, 1160, 951, 860, 547, 521. cm^{-1}. HR EIMS: 257.0325 *m/z* (calcd for $C_{14}H_{11}NS_2$: 257.0333).

4.2.4. *3-m-Tolyl-3H-benzothiazole-2-thione* (**3**d)



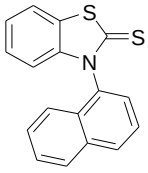
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.80-6.76 (m, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.66, 138.84, 137.38, 136.50, 131.02, 128.88, 127.20, 126.43, 123.63, 118.78, 115.42, 114.67, 75.88, 21.42. IR (KBr): 3468, 3370, 1609, 1449, 1082, 953, 864, 564, 519. cm^{-1}. HR EIMS: 257.0324 *m/z* (calcd for $C_{14}H_{11}NS_2$: 257.0333).

4.2.5. *3-Naphthalen-2-yl-3H-benzothiazole-2-thione* (**3**e)



Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76-7.62 (m, 3H), 7.51-7.36 (m, 4H), 7.28-7.21 (m, 2H), 6.80-6.76 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d6): δ 170.45, 150.76, 137.30, 137.24, 134.74, 133.75, 131.58, 129.03, 128.09, 127.24, 127.18, 125.98, 125.63, 124.59, 117.24, 115.48, 112.40. IR (KBr): 3057, 1456, 1425, 1310, 1238, 1020, 1007, 771, 755, 726, 665, 477. cm^{-1}. HR EIMS: 293.0325 *m/z* (calcd for $C_{17}H_{11}NS_2$: 293.0334).

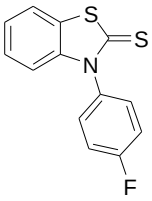
4.2.6. *3-Naphthalen-1-yl-3H-benzothiazole-2-thione* (**3**f)



Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.74-

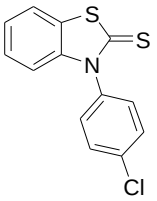
7.38 (m, 5H), 7.26 (d, *J* = 8.0 Hz,2H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.79 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d6): δ 169.34, 153.82, 137.03, 137.02, 135.35, 134.72, 133.99, 132.93, 129.51, 128.71, 127.56, 126.86, 126.14, 125.14, 124.87, 122.16, 121.82. IR (KBr): 3121, 2982, 1659, 1454, 1315, 1285, 1007, 852, 756, 716, 582, 516, 455. cm^{-1}. HR EIMS: 293.0325 *m/z* (calcd for $C_{17}H_{11}NS_2$: 293.0334).

4.2.7. *3-(4-Fluoro-phenyl)-3H-benzothiazole-2-thione* (**3**g)



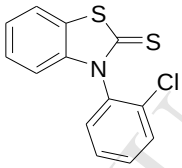
White solid, M.p. 98-100℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.4 Hz, 2H), 8.84 (d, *J* = 7.6 Hz, 2H), 7.53-7.49 (m, 2H), 7.434-7.40 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d6): δ 169.76, 150.84, 137.45, 136.41, 131.81, 130.35, 139.39, 128.28, 117.20, 115.49, 111.69. IR (KBr): 3444, 1642, 1566, 1428, 1410, 1159, 1074, 991, 952, 861, 755, 547, 520. cm^{-1}. HR EIMS: 261.0141. *m/z* (calcd for $C_{13}H_9FNS_2$ 261.0156).

4.2.8. *3-(4-Chloro-phenyl)-3H-benzothiazole-2-thione* (**3**h)



Brown liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.43 (m, 1H), 7.43-7.23 (m, 1H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 6.81-6.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ148.76, 137.46, 135.45, 131.46, 131.25, 129.09, 127.67, 118.90, 115.51, 113.86. IR (KBr): 3470, 3372, 3065, 1608, 1475, 1447, 1309, 1092, 1011, 814, 750, 553, 482. cm^{-1}. HR EIMS: 276.9781 *m/z* (calcd for $C_{13}H_8ClNS_2$:276.9786).

4.2.9. *3-(2-Chloro-phenyl)-3H-benzothiazole-2-thione* (**3**i)



Brown liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.460 (d, *J* = 7.6 Hz, 1H), 7.35-7.26 (m, 2H), 7.06-7.03 (m, 2H), 6.86-6.79 (m, 2H), 6.65-6.62 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d6): δ 170.16, 151.32, 137.84, 136.35, 132.21, 130.27, 129.93, 128.05, 126.74, 126.36, 117.46, 115.59, 110.02. IR (KBr): 3468, 3371, 3061, 1609, 1574, 1479, 1449, 1431, 1309, 1252, 1115, 1032, 747, 660. cm^{-1}. HR EIMS: 276.9784 *m/z* (calcd for $C_{13}H_8ClNS_2$:276.9786).

Acknowledgements

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Novel copper/PEG-400 catalyst systems for chemoselective S- and N-arylation of 2-mercaptobenzothiazole

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General information

All reactions were carried out under an Ar atmosphere using a standard Schlenk tube techniques. All reagents and solvents PEG-400 were purchased from Alfa, Acros, Aldrich or TCI, and used without further purification. Flash chromatography was performed on silca gel (silca gel, 200-300 mesh).^{1}H NMR and^{13}C NMR spectra were recorded on Bruker 400 MHz and Bruker 100 MHz spectrometers with $CDCl_3$ or DMSO-d6 as the solvent. Mass spectra were determined on a Finnigan 8230 mass spectrometer. Melting points were determined on an XT-4 electrothermal Micro-melting-point apparatus.

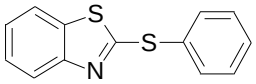
General Procedure A: Cu-catalyzed S-arylation of 2-mercaptobenzothiazole

A flask equipped a magnetic stirring bar was charged with 2-mercaptobenzothiazole (1 mmol), aryl halide (1.1 mmol), CuI (0.1 mmol), NaOH (2 mmol) and PEG-400 (2 ml). The reaction mixture was stirred under a nitrogen atmosphere at 50 ℃ for 24 h. The reaction mixture was cooled to room temperature, diluted with Et_2O, washed with brine and dried over $MgSO_4$. Silica gel (1.0 g) was added to the mixture and the mixture was concentrated in vacuo. The Silica gel-adsorbed product was purified through flash chromatography with petroleum ether/ethyl acetate as eluent to give **2**a-l.

General Procedure B: Cu-catalyzed N-arylation of 2-mercaptobenzothiazole

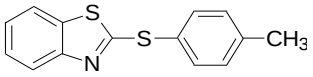
A flask equipped a magnetic stirring bar was charged with 2-mercaptobenzothiazole (1 mmol), aryl halide (1.1 mmol), CuO (0.1 mmol), KOH (2 mmol) and PEG-400 (2 ml). The reaction mixture was stirred under a nitrogen atmosphere at 140 ℃ for 24 h. The reaction mixture was cooled to room temperature, diluted with Et_2O, washed with brine and dried over $MgSO_4$. Silica gel (1.0 g) was added to the mixture and the mixture was concentrated in vacuo. The Silica gel-adsorbed product was purified through flash chromatography with petroleum ether/ethyl acetate as eluent to give **3**a-i.

2-(Phenylthio)benzo[*d*]thiazole (**2**a) [1]



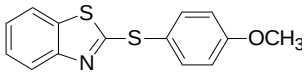
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.0 Hz, 1H), 7.26-7.20 (m, 3H), 7.13-7.07 (m, 3H), 6.80-6.74 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d6): δ 169.39, 150.84, 137.39, 131.81, 131.44, 129.50, 128.28, 126.73, 125.83, 117.17, 115.37. IR (KBr): 3057, 1581, 1458, 1433, 1311, 1235, 1019, 1004, 753 cm^{-1}. HR EIMS: 243.0153 *m/z* (calcd for $C_{13}H_9NS_2$: 243.0156).

2-(*p*-Tolylthio)benzo[*d*]thiazole (**2**b) [1]



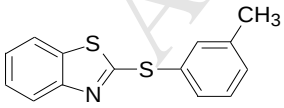
White solid, M.p. 71-72 ℃. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.25-7.19 (m, 1H), 7.02 (t, *J* = 7.6 Hz, 4H), 6.78-6.72 (m, 2H), 2.28 (s, 3H); ^{13}C NMR (100MHz, DMSO-d6): δ 169.26, 150.41, 136.97, 135.43, 133.37, 131.15, 130.14, 127.54, 117.13, 115.31, 113.44, 20.93. IR (KBr): 3064, 2912, 1595, 1426, 1315, 1239, 817, 761 cm^{-1}. HR EIMS: 257.0326 *m/z* (calcd for $C_{14}H_{11}NS_2$: 257.0333).

2-(4-Methoxyphenylthio)benzo[*d*]thiazole (**2**c) [1]



White solid, M.p. 61–63 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.4Hz, 1H), 7.66-7.61 (m, 3H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.25-7.23 (m, 1H), 7.00-6.98 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 171.81, 161.74, 154.22, 137.57, 135.47, 126.10, 124.09, 121.79, 120.76, 120.26, 115.54, 55.49. IR (KBr): 3056, 2922, 1589, 1496, 1453, 1425, 1252, 1003, 833, 758 cm^{-1}. HR EIMS: 273.0338 *m/z* (calcd for $C_{14}H_{11}NOS_2$: 273.0341).

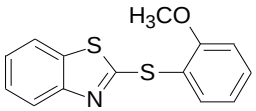
2-(3-Methylphenylthio)benzo[*d*]thiazole (**2**d) [1]



White solid, M.p. 87-91 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.103 (t, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 11.2 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.75 (t, J_1 = 7.6 Hz, J_2 = 6.8 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d6): δ 169.02, 150.66, 138.77, 137.31, 136.93,

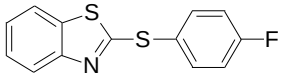
131.40, 129.34, 127.44, 126.70, 124.04, 117.15, 115.34, 112.63, 21.42. IR (KBr): 3454.60, 2925.87, 1570.31, 1426.05, 1158.26, 1076.87, 950.90, 859.14, 754.50, 546.46. HR EIMS: 257.0328 *m/z* (calcd for $C_{14}H_{11}NS_2$: 257.0333).

2-(2-Methoxyphenylthio)benzo[*d*]thiazole (**2**e) [2]



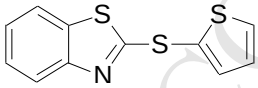
Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.11-7.10 (m, 1H), 6.87-6.77 (m, 4H), 6.66 (d, *J* = 8.0 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d6): δ 169.46, 155.85, 151.10, 137.67, 131.48, 126.60, 126.05, 125.16, 121.47, 117.32, 115.25, 111.36, 111.30, 56.17. IR (KBr): 3061, 2954, 1590, 1428, 1239, 812, 765 cm^{-1}. HR EIMS: 273.0337 *m/z* (calcd for $C_{14}H_{11}NOS_2$: 273.0341).

2-(4-fluorophenylthio)benzo[*d*]thiazole (**2**f). [3]



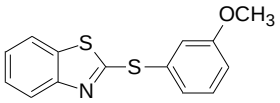
Brown liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.54-7.47 (m, 1H), 7.45-7.38 (m, 2H), 7.36-7.34 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d6): δ 168.71, 162.26, 159.84, 150.55, 137.10, 132.51, 131.46, 129.34, 117.19, 116.63, 115.42. IR (KBr): 3056, 2923, 1582, 1457, 1433, 1258, 1104, 1015, 813, 746 cm^{-1}. HR EIMS: 261.0144. *m/z* (calcd for $C_{13}H_9FNS_2$ 261.0156).

2-(2-thiophenylthio)benzo[*d*]thiazole (**2**g).



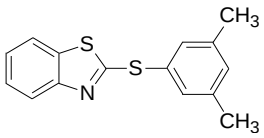
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.29 (m, 2H), 7.19-7.18 (m, 2H), 6.96-6.91 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d6): δ 169.36, 149.11, 134.57, 134.24, 132.82, 130.49, 130.14, 128.21, 117.15, 117.03, 115.42. IR (KBr): 3058, 2947, 1590, 1423, 1237, 813, 754 cm^{-1}. HR EIMS: 249.3746 *m/z* (calcd for $C_{11}H_7NS_3$: 249.3750).

2-(3-Methoxyphenylthio)benzo[*d*]thiazole (**2**h) [2]



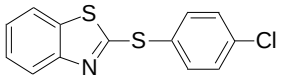
Yellow liquid, ^{1}H NMR (400MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.25-7.22 (m, 1H), 7.15-7.11 (m, 1H), 6.79-6.73 (m, 2H), 6.67-6.64 (m, 3H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.09, 148.90, 138.29, 137.52, 131.22, 129.81, 118.78, 118.73, 115.37,114.16, 112.10,111.03,55.18. IR (KBr): 3468, 3369, 3063, 2936, 2834, 1609, 1589, 1478, 1247, 1042, 751 cm^{-1}. HR EIMS: 273.0338 *m/z* (calcd for $C_{14}H_{11}NOS_2$: 273.0341).

2-(3,5-Dimethylphenylthio)benzo[*d*]thiazole (**2**i) [2]



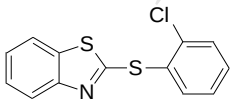
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.43 (m, 1H), 7.23 (d, *J* = 12.0 Hz, 1H), 6.79-6.72 (m, 5H), 2.22 (s, 6H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 148.70, 138.67, 137.27, 136.21, 130.87, 127.54, 124.38, 128.66, 115.33, 114.81, 21.27. IR (KBr): 3452.58, 2924.82, 1570.51, 1425.83, 1075.82, 954.95, 757.84, 525.82. HR EIMS: 271.0481 *m/z* (calcd for $C_{15}H_{13}NS_2$: 271.0489).

2-(4-Chlorophenylthio)benzo[*d*]thiazole (**2**j) [2]



Brown liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.27-7.17 (m, 2H), 7.01-6.91 (m, 2H), 6.80-6.74 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d6): δ 169.32, 150.84, 137.45, 136.41, 131.81, 130.36, 129.39, 128.28, 117.21, 115.49, 111.70. IR (KBr): 3470, 3370, 2924, 1608, 1574, 1474, 1309, 1091, 1010, 814, 750 cm^{-1}. HR EIMS: 276.9782 *m/z* (calcd for $C_{13}H_8ClNS_2$:276.9786).

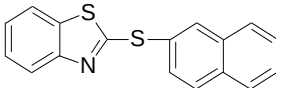
2-(2-Chlorophenylthio)benzo[*d*]thiazole (**2**k) [2]



Brown liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 12.0 Hz, 1H), 7.35-7.26 (m, 2H), 7.06-7.04 (m, 2H), 6.83-6.78 (m, 2H), 6.65-6.62 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d6): δ 168.95, 151.31, 137.83, 136.33, 132.21, 130.25, 129.96, 128.07,

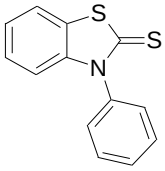
126.76, 126.35, 117.45, 115.58, 109.99. IR (KBr): 3485, 3375, 2931, 1607, 1556, 1476, 1301, 1090, 1015, 812, 786, 753 cm^{-1}. HR EIMS: 276.9783 *m/z* (calcd for $C_{13}H_8ClNS_2$:276.9786).

2-(2-Naphthalenylthio)benzo[*d*]thiazole (**2**l) [2]



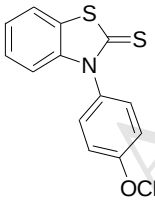
Brown liquid, ^1H NMR (400 MHz, $CDCl_3$): δ 7.75-7.72 (m, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.51-7.47 (m, 2H), 7.41-7.37 (m, 2H), 7.28-7.21 (m, 2H), 6.81-6.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.90, 137.47, 134.26, 133.84, 131.62, 131.25, 128.70, 127.78, 127.07, 126.60, 125.48, 125.19, 124.41, 118.85, 115.51, 114.35. IR (KBr): 3468, 3371, 3053, 1607, 1479, 1448, 1309, 1063, 851, 813, 747. cm^{-1}. HR EIMS: 293.0327 *m/z* (calcd for $C_{17}H_{11}NS_2$: 293.0334).

3-Phenyl-3H-benzothiazole-2-thione (**3**a)



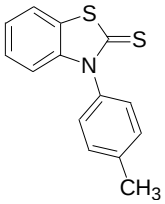
Yellow liquid, ^1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.33 (m, 4H), 7.31-7.29 (m, 3H), 7.27-7.23 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d6): δ 169.31, 153.87, 135.69, 135.32, 131.38, 130.77, 129.34, 126.89, 124.97, 122.18, 121.87. IR (KBr): 3061, 2924, 2854, 1581, 1476, 1440, 1377, 1081, 1024, 737, 689, 516. cm^{-1}. HR EIMS: 243.0152 *m/z* (calcd for $C_{13}H_9NS_2$: 243.0156).

3-(4-Methoxy-phenyl)-3H-benzothiazole-2-thione (**3**b)



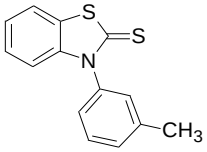
White solid, M.p. 57-59℃; ^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.67-7.61 (m, 3H), 7.40-7.36 (m, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.01, 161.73, 154.20, 137.63, 135.41, 126.12, 124.09, 121.76, 120.77, 120.18, 115.54, 55.51. IR (KBr): 3445, 2458, 1642, 1567, 1426, 1161, 1070, 951, 861, 547. cm^{-1}. HR EIMS: 273.0336 *m/z* (calcd for $C_{14}H_{11}NOS_2$: 273.0341).

3-*p*-Tolyl-3H-benzothiazole-2-thione (**3**c)



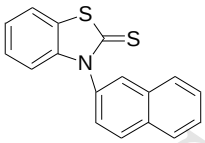
White solid, M.p. 49-50℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.6 Hz, 1H), 7.22 (m, 1H), 7.027 (dd, *J* = 8.4 Hz, 8Hz, 4H), 6.77 (t, *J* = 8.0 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d6): δ 170.30, 153.98, 141.68, 135.91, 135.24, 131.45, 126.87, 125.74, 124.84, 122.17, 121.17, 21.33. IR (KBr): 3450, 2952, 2451, 1567, 1447, 1160, 951, 860, 547, 521. cm^{-1}. HR EIMS: 257.0325 *m/z* (calcd for $C_{14}H_{11}NS_2$: 257.0333).

3-*m*-Tolyl-3H-benzothiazole-2-thione (**8**d)



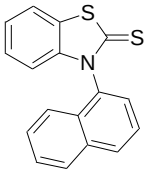
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.80-6.76 (m, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.66, 138.84, 137.38, 136.50, 131.02, 128.88, 127.20, 126.43, 123.63, 118.78, 115.42, 114.67, 75.88, 21.42. IR (KBr): 3468, 3370, 1609, 1449, 1082, 953, 864, 564, 519. cm^{-1}. HR EIMS: 257.0324 *m/z* (calcd for $C_{14}H_{11}NS_2$: 257.0333).

3-Naphthalen-2-yl-3H-benzothiazole-2-thione (**3**e)



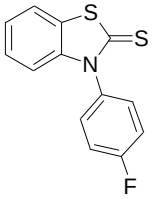
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76-7.62 (m, 3H), 7.51-7.36 (m, 4H), 7.28-7.21 (m, 2H), 6.80-6.76 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d6): δ 170.45, 150.76, 137.30, 137.24, 134.74, 133.75, 131.58, 129.03, 128.09, 127.24, 127.18, 125.98, 125.63, 124.59, 117.24, 115.48, 112.40. IR (KBr): 3057, 1456, 1425, 1310, 1238, 1020, 1007, 771, 755, 726, 665, 477. cm^{-1}. HR EIMS: 293.0325 *m/z* (calcd for $C_{17}H_{11}NS_2$: 293.0334).

3-Naphthalen-1-yl-3H-benzothiazole-2-thione (**3**f)



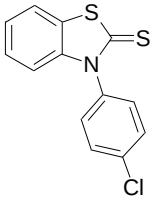
Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.74-7.38 (m, 5H), 7.26 (d, *J* = 8.0 Hz,2H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.79 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d6): δ 169.34, 153.82, 137.03, 137.02, 135.35, 134.72, 133.99, 132.93, 129.51, 128.71, 127.56, 126.86, 126.14, 125.14, 124.87, 122.16, 121.82. IR (KBr): 3121, 2982, 1659, 1454, 1315, 1285, 1007, 852, 756, 716, 582, 516, 455. cm^{-1}. HR EIMS: 293.0325 *m/z* (calcd for $C_{17}H_{11}NS_2$: 293.0334).

3-(4-Fluoro-phenyl)-3H-benzothiazole-2-thione (**3**g)



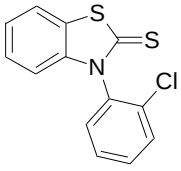
White solid, M.p. 98-100℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.4 Hz, 2H), 8.84 (d, *J* = 7.6 Hz, 2H), 7.53-7.49 (m, 2H), 7.434-7.40 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d6): δ 169.76, 150.84, 137.45, 136.41, 131.81, 130.35, 139.39, 128.28, 117.20, 115.49, 111.69. IR (KBr): 3444, 1642, 1566, 1428, 1410, 1159, 1074, 991, 952, 861, 755, 547, 520. cm^{-1}. HR EIMS: 261.0141. *m/z* (calcd for $C_{13}H_9FNS_2$ 261.0156).

3-(4-Chloro-phenyl)-3H-benzothiazole-2-thione (**3**h)

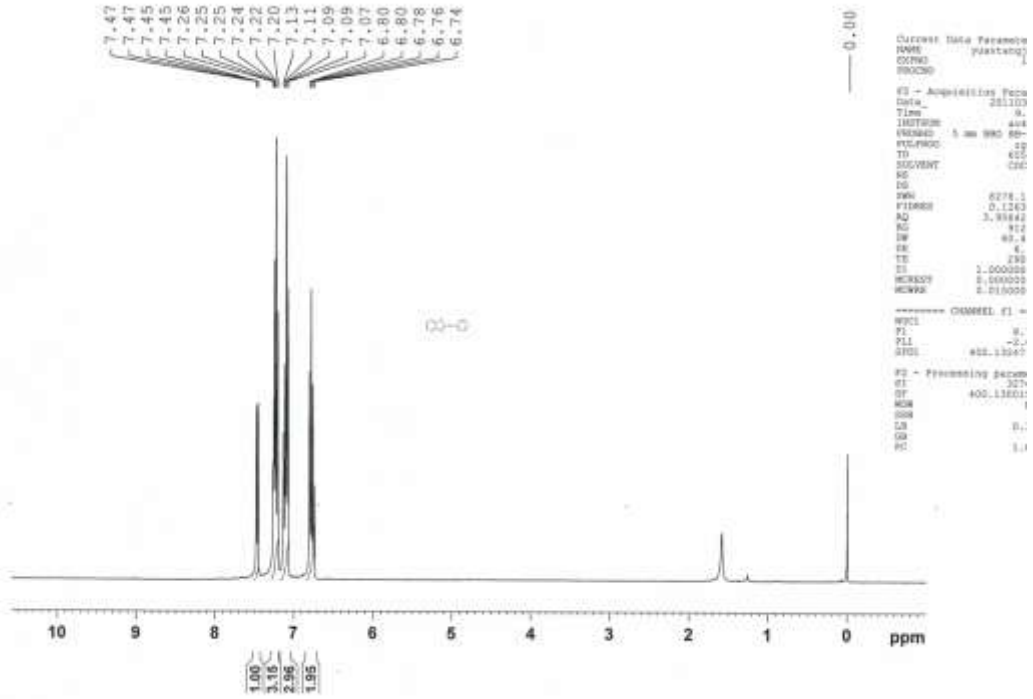


Brown liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.43 (m, 1H), 7.43-7.23 (m, 1H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 6.81-6.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.56, 137.43, 135.40, 131.43, 131.27, 129.09, 127.71, 119.01, 115.59, 114.02. IR (KBr): 3470, 3372, 3065, 1608, 1475, 1447, 1309, 1092, 1011, 814, 750, 553, 482. cm^{-1}. HR EIMS: 276.9781 *m/z* (calcd for $C_{13}H_8ClNS_2$:276.9786).

3-(2-Chloro-phenyl)-3H-benzothiazole-2-thione (**3**i)



Brown liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.460 (d, *J* = 7.6 Hz, 1H), 7.35-7.26 (m, 2H), 7.06-7.03 (m, 2H), 6.86-6.79 (m, 2H), 6.65-6.62 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d6): δ 170.16, 151.32, 137.84, 136.35, 132.21, 130.27, 129.93, 128.05, 126.74, 126.36, 117.46, 115.59, 110.02. IR (KBr): 3468, 3371, 3061, 1609, 1574, 1479, 1449, 1431, 1309, 1252, 1115, 1032, 747, 660. cm^{-1}. HR EIMS: 276.9784 *m*/*z* (calcd for $C_{13}H_8ClNS_2$:276.9786).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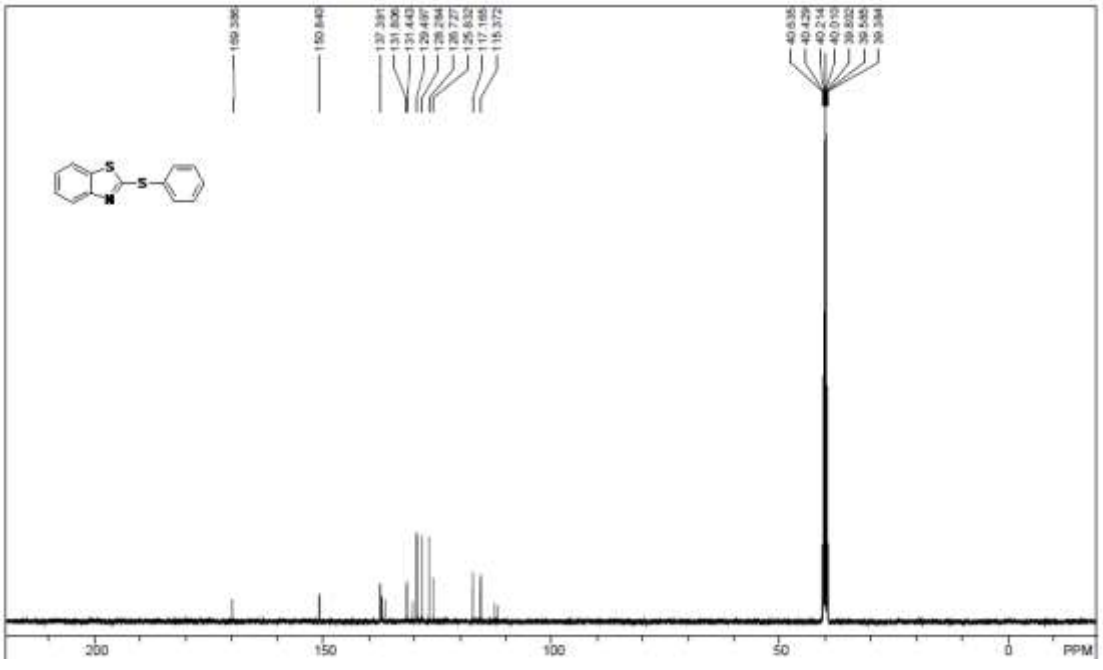
7.45
7.45
7.26
7.25
7.25
7.24
7.22
7.20
7.13
7.11
7.09
7.09
7.07
6.80
6.80
6.78
6.76
6.74
0.00
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
3.15
2.96
1.95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137.391
131.806
131.443
129.497
126.294
126.727
125.632
117.166
115.372
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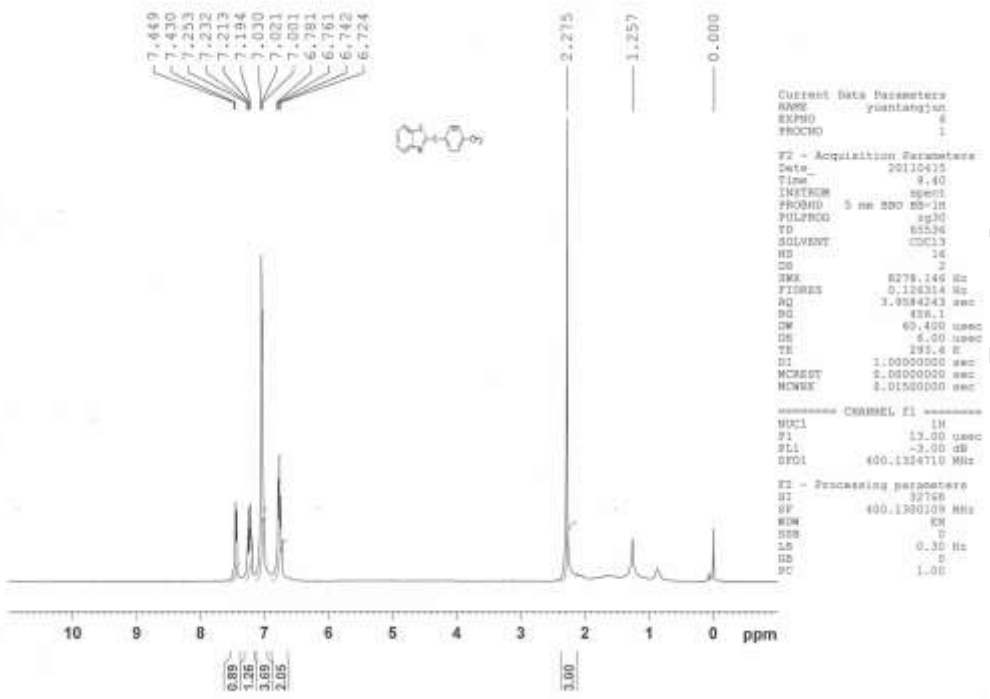
40.429
40.214
40.010
39.802
39.585
39.384
200
150
100
50
0
PPM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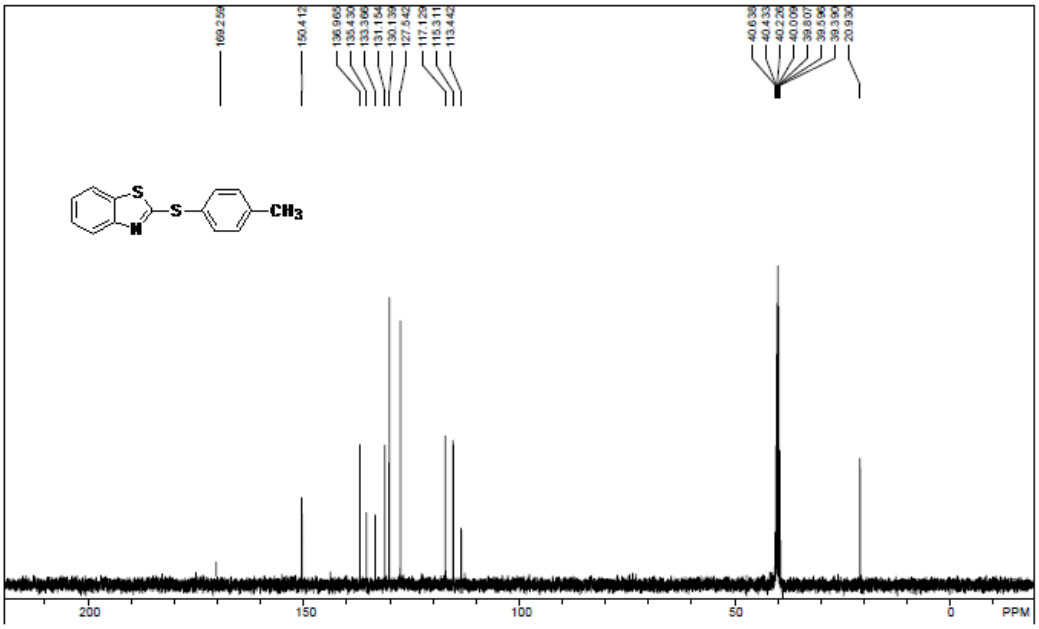
7.430
7.253
7.232
7.213
7.194
7.030
7.021
7.001
6.781
6.761
6.742
6.724
2.275
1.257
0.000
10
9
8
7
6
5
4
3
2
1
0
ppm
0.89
1.26
3.69
2.05
3.00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127.542
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115.311
113.442
40.636
40.433
40.229
40.009
39.807
39.596
39.390
20.930
S
N
S
CH3
200
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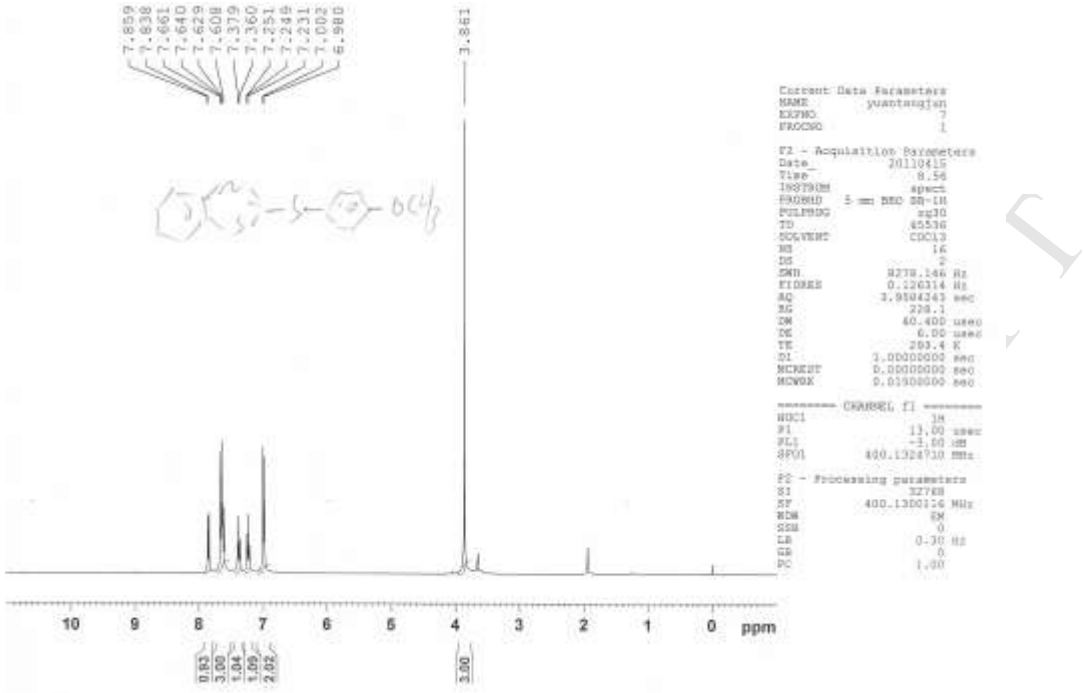
100
50
0
PPM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7.661
7.640
7.629
7.608
7.379
7.360
7.251
7.249
7.231
7.002
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3.861
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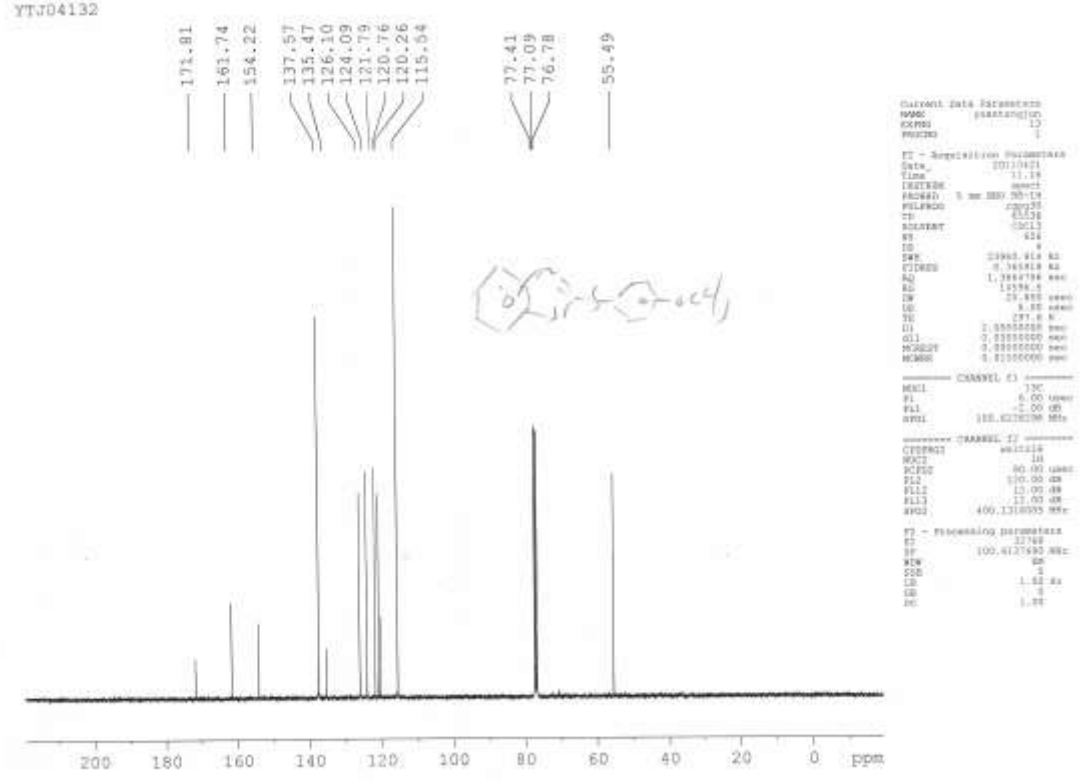
0.83
3.00
1.04
1.09
2.02
3.00


YTJ04132
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161.74
156.22
137.57
135.47
126.10
124.09
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120.76
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115.54
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77.09
76.78
55.49
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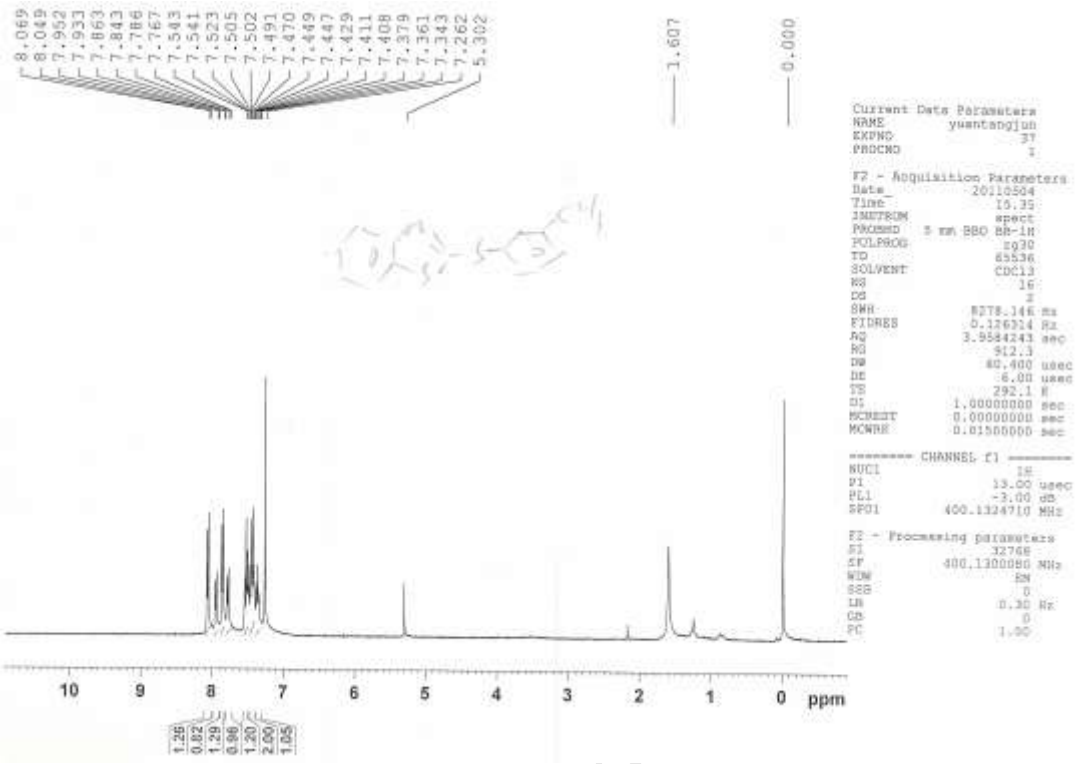
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7.933
7.863
7.843
7.786
7.767
7.543
7.541
7.523
7.505
7.502
7.491
7.470
7.449
7.447
7.429
7.411
7.408
7.379
7.361
7.343
7.262
5.302
1.607
0.000
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PROCNO 1
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DE 6.00 usec
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MCREST 0.00000000 sec
MCWRK 0.01500000 sec
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SF 400.1300000 MHz
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LB 0.30 Hz
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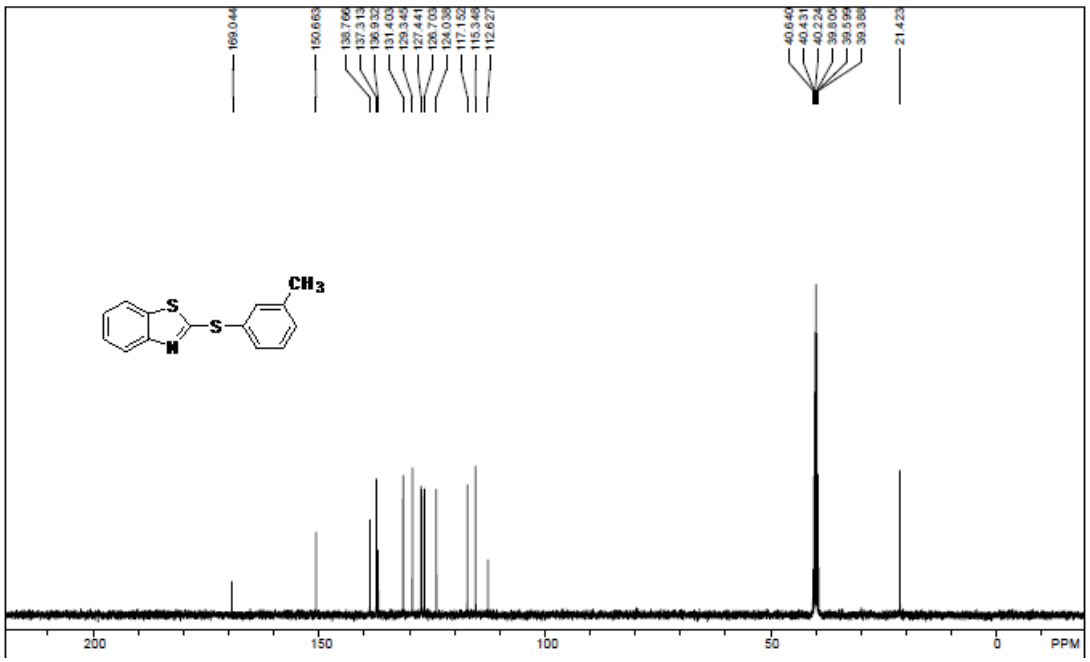
2.00
1.05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40.224
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39.599
39.388
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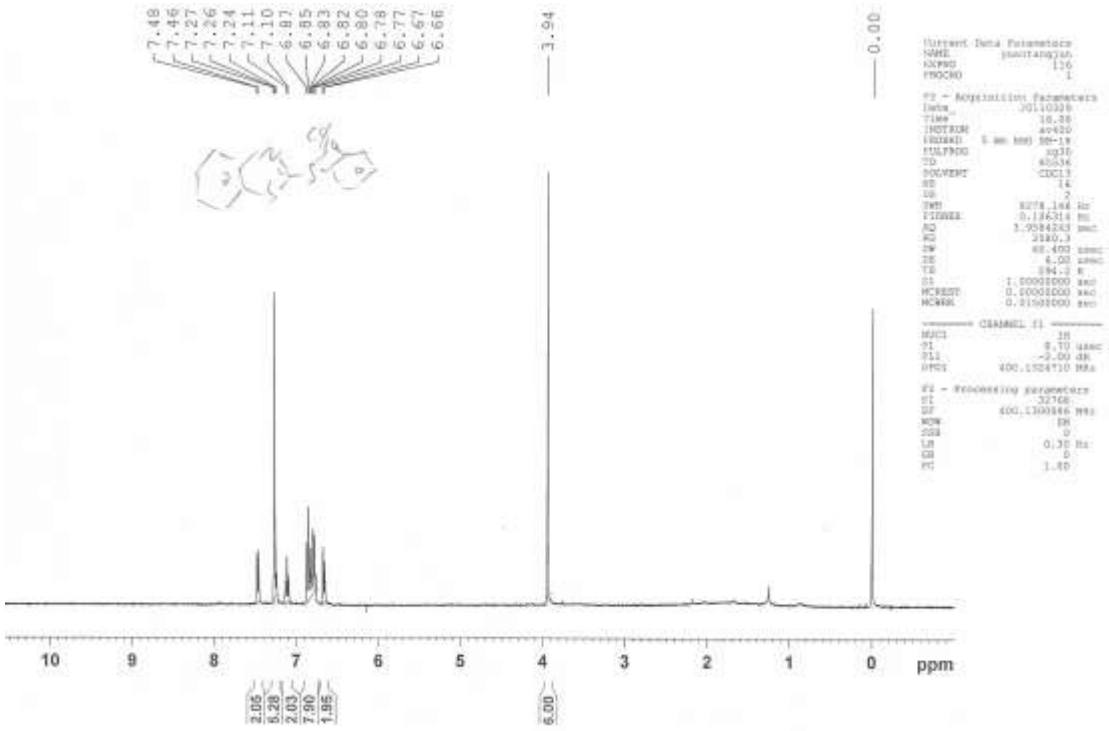
CH3
S
S
H
200 150 100 50 0 PPM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6.87
6.85
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6.80
6.78
6.77
6.67
6.66
3.94
0.00
10
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8
7
6
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4
3
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0
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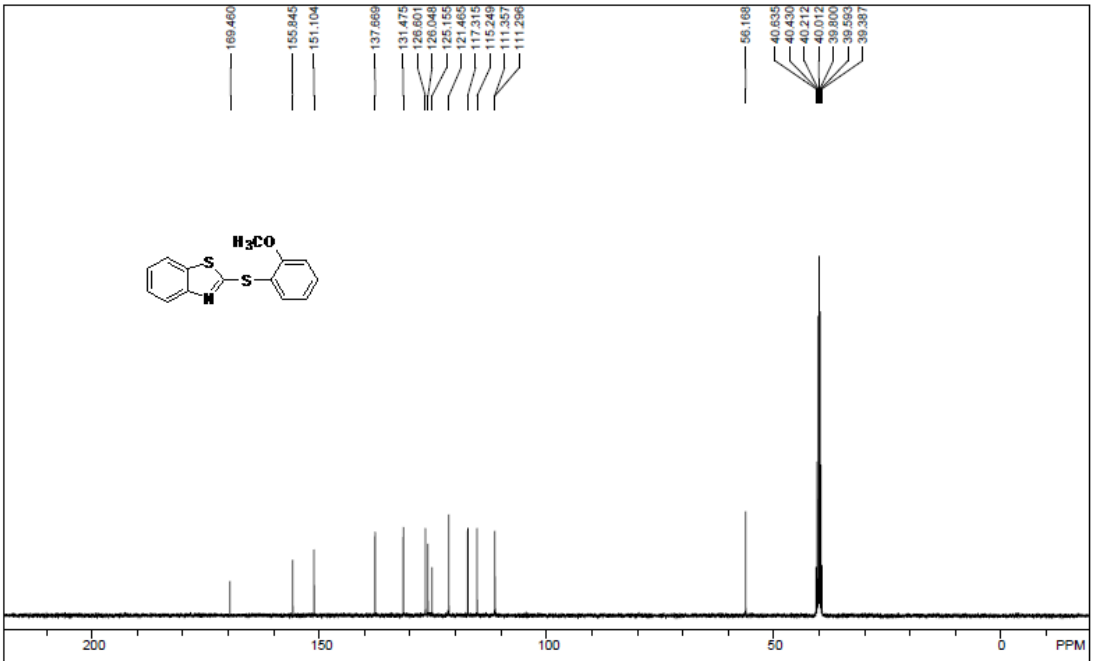
6.00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125.155
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115.249
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111.296
56.168
40.635
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39.593
39.387
H3CO
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S
H
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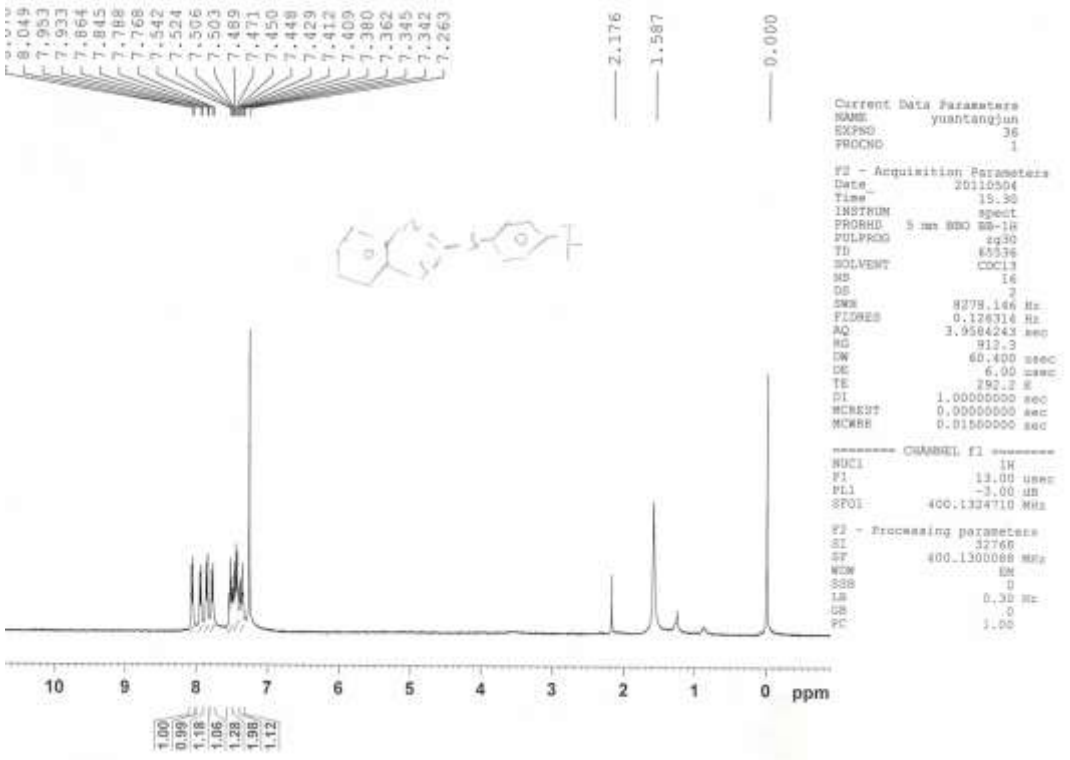
150
100
50
0
PPM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7.524
7.506
7.503
7.489
7.471
7.450
7.448
7.429
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7.380
7.362
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7.342
7.263
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PROCNO 1
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DE 6.00 usec
TE 292.2 K
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MCREST 0.00000000 sec
MCWRK 0.01500000 sec
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NUC1 1H
P1 13.00 usec
PL1 -3.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
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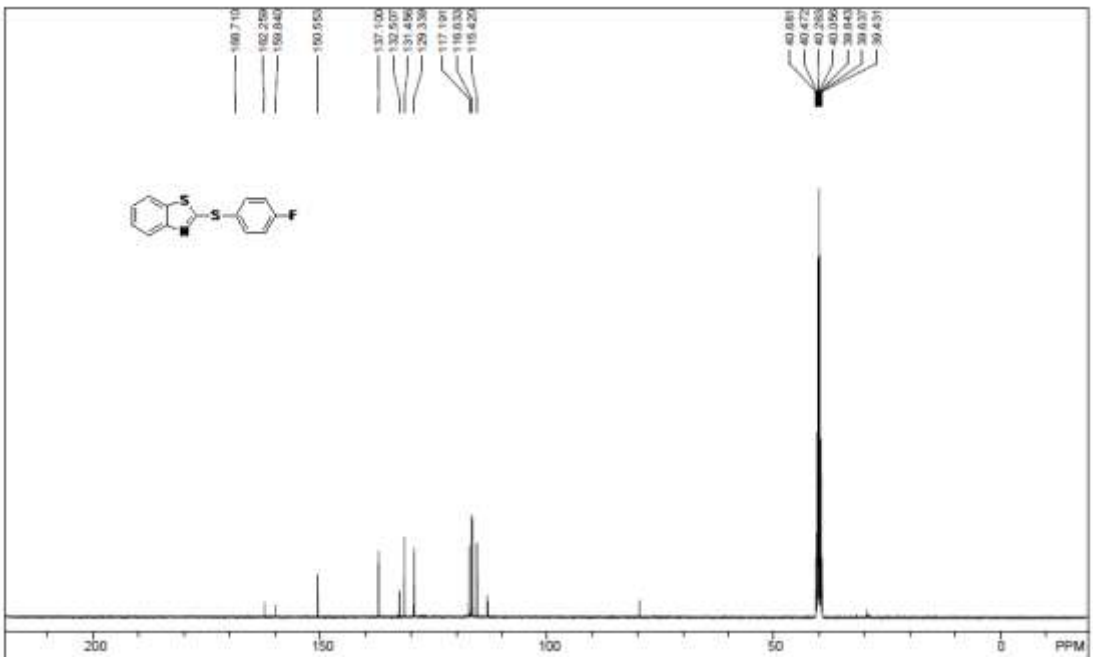
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40.263
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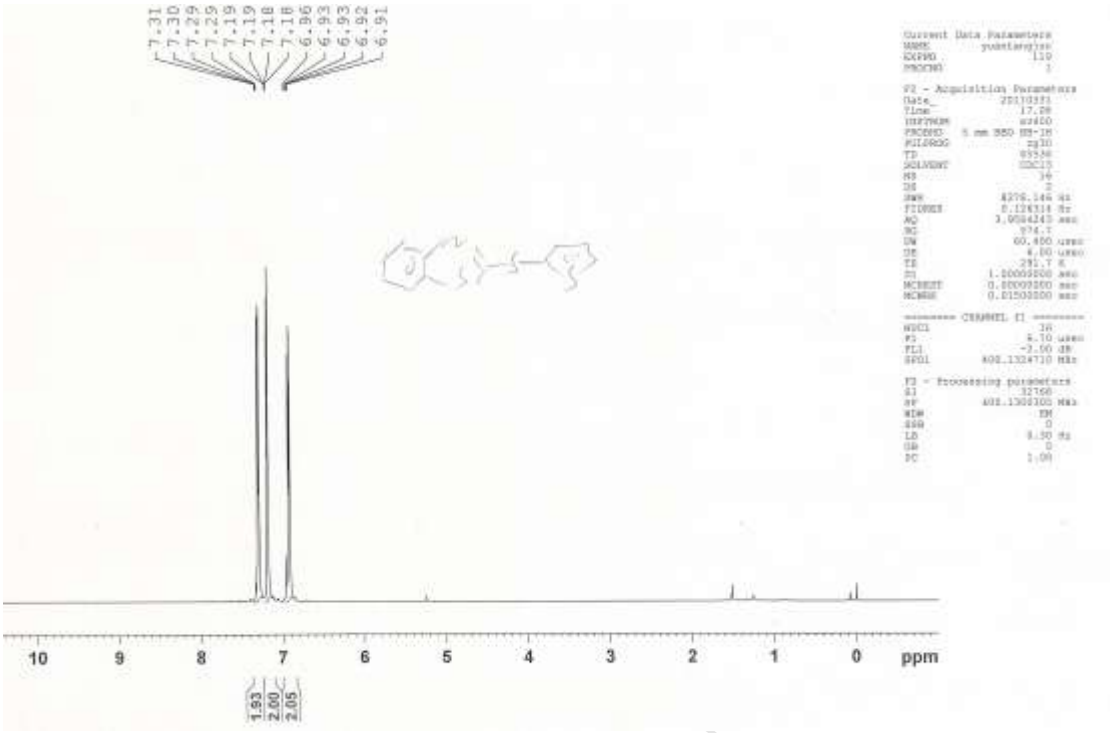
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7.29
7.19
7.19
7.18
7.18
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6.93
6.93
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6.91
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9
8
7
6
5
4
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1
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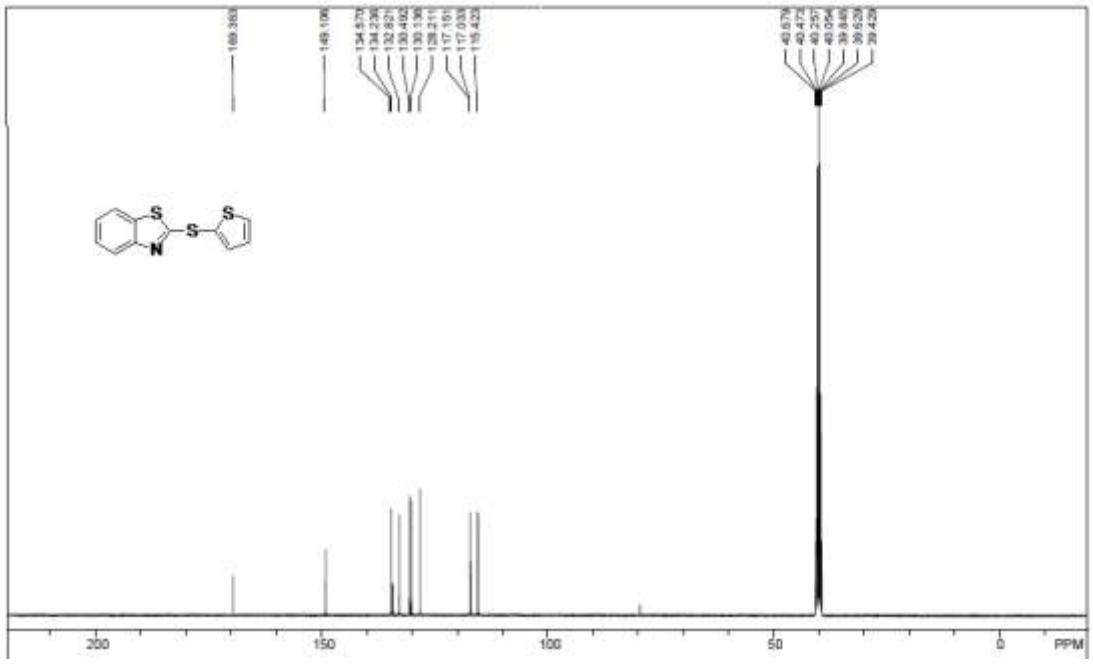
2.00
2.05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130.130
128.211
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40.472
40.257
40.054
39.849
39.629
39.429
S
N
S
S
200
150
100
50
0
PPM


ytj04133
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7.443
7.254
7.233
7.215
7.152
7.132
7.112
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6.752
6.734
6.673
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6.636
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PROCNO 1
F2 - Acquisition Parameters
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Time 9.02
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PULPROG zg30
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SOLVENT CDCl3
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DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 645.1
DW 60.400 usec
DE 6.00 usec
TE 293.4 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 13.00 usec
PL1 -3.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300118 MHz
WDW EM
SSB 0
LB 0.30 Hz
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1.90
2.86
3.00
160.09
148.90
138.29
137.52
131.22
129.81
118.78
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114.16
112.10
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77.02
76.71
55.18
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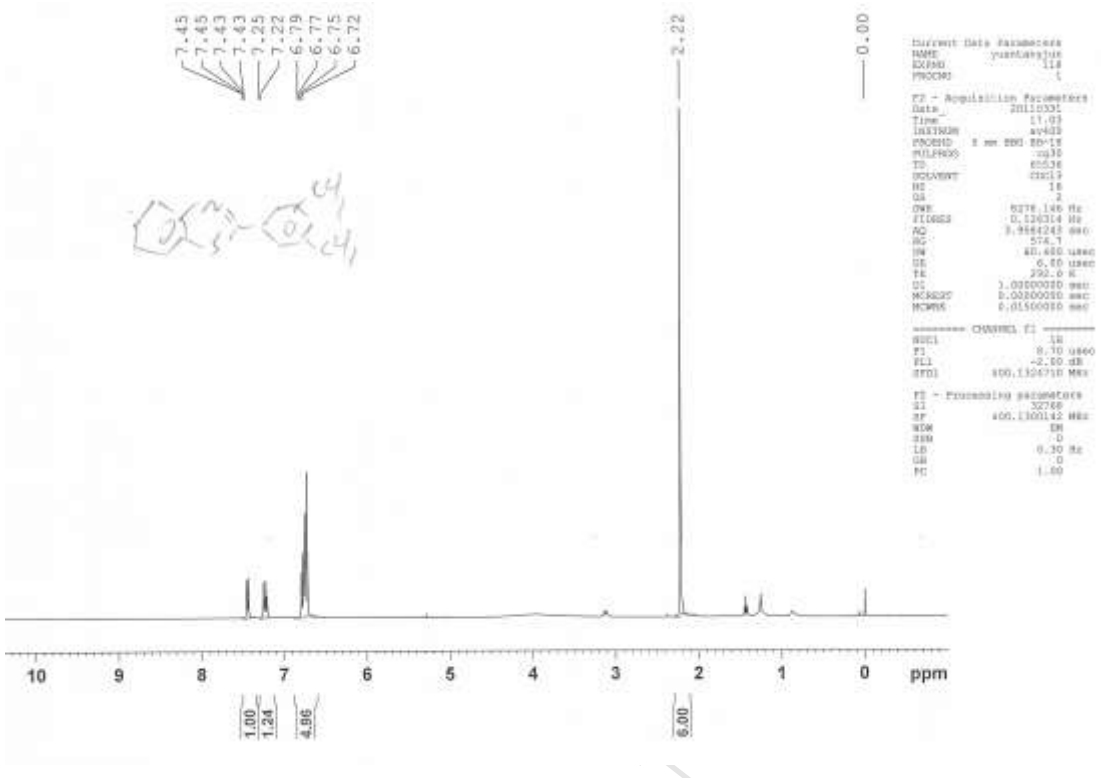
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7
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4
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ppm
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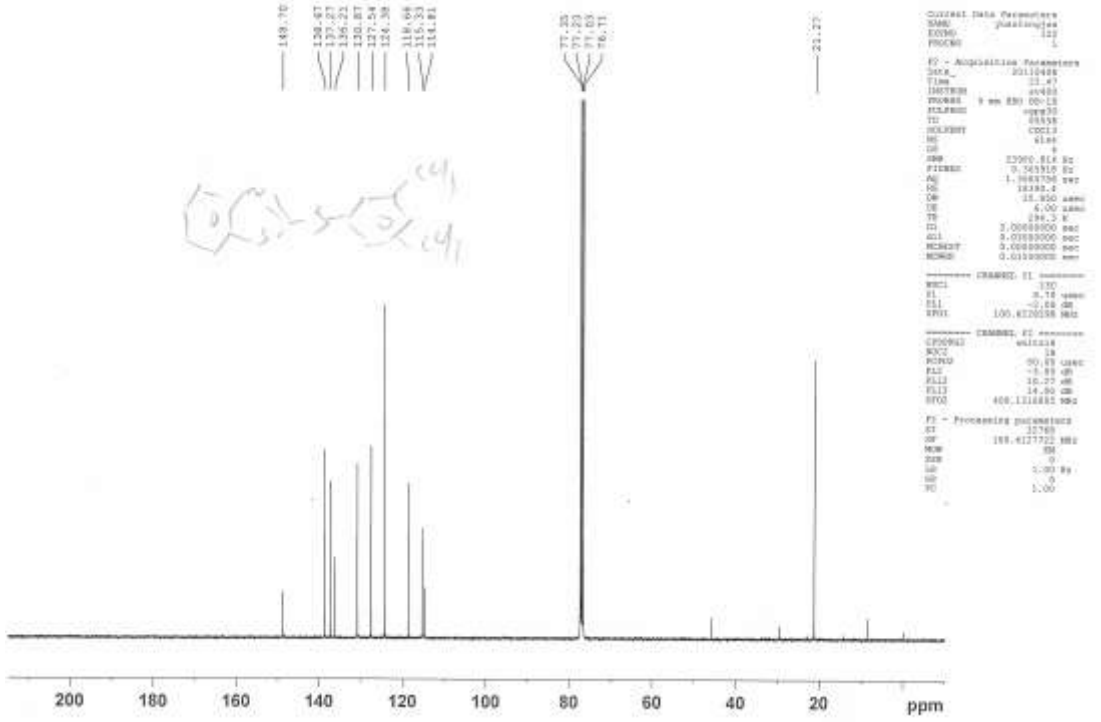
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140
120
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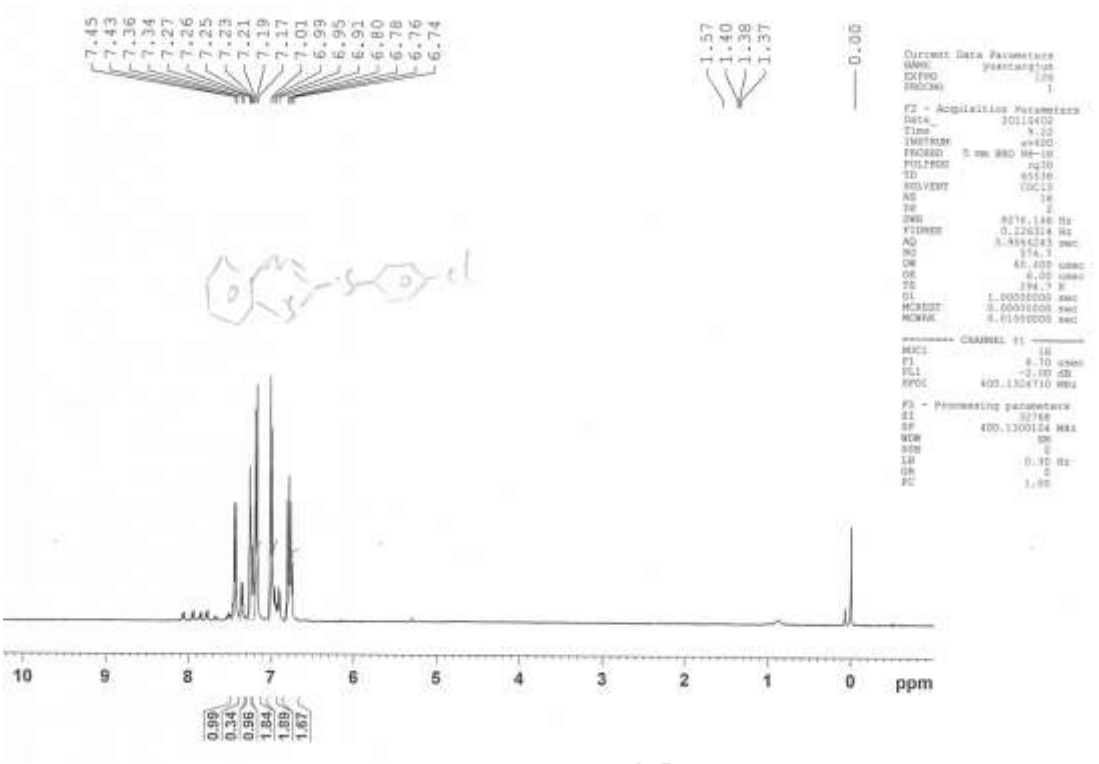
80
60
40
20
ppm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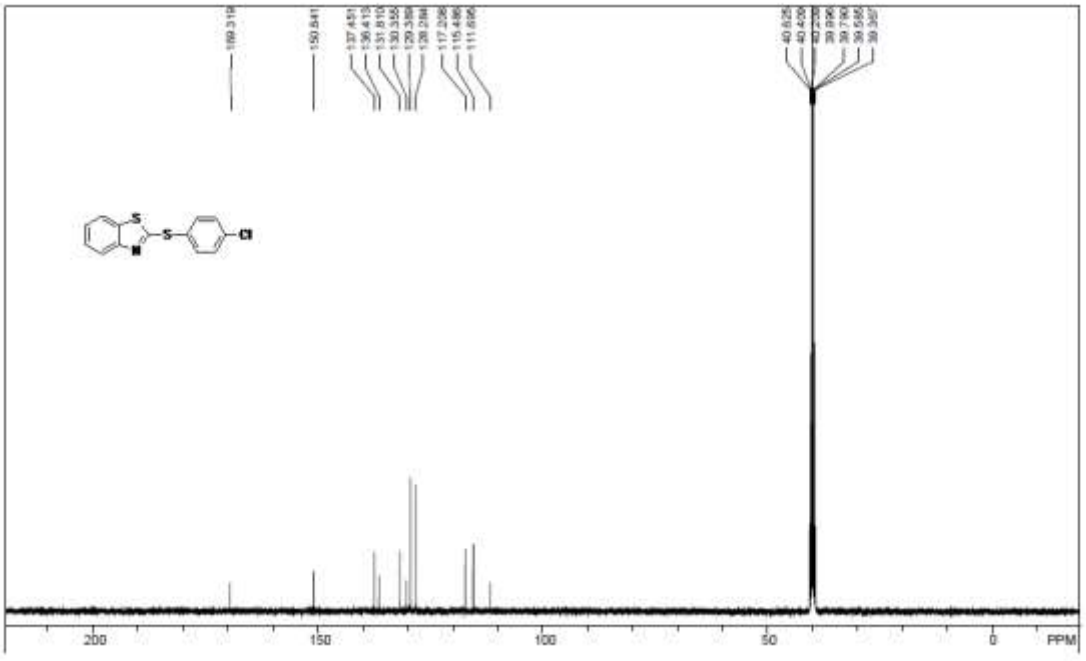
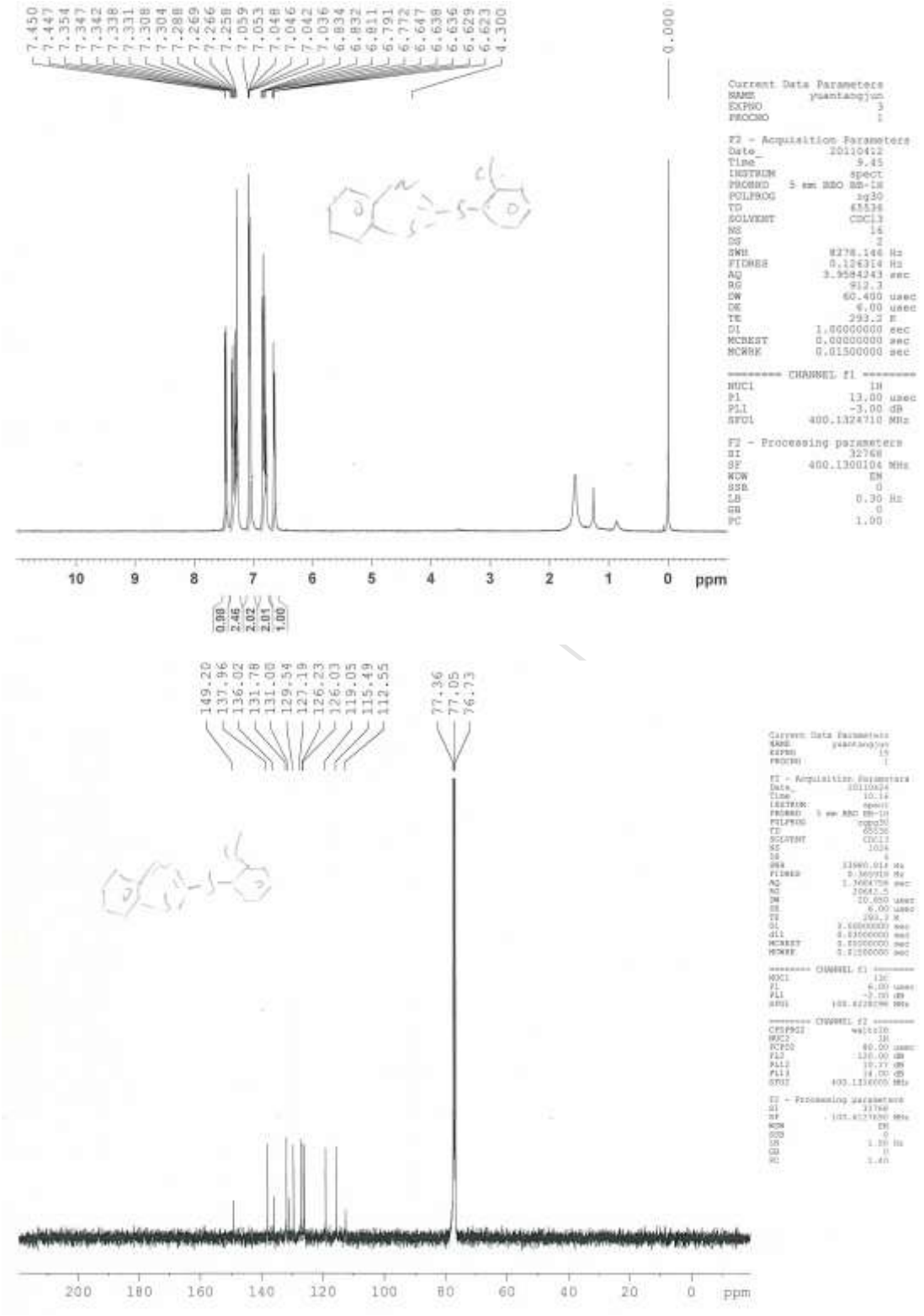
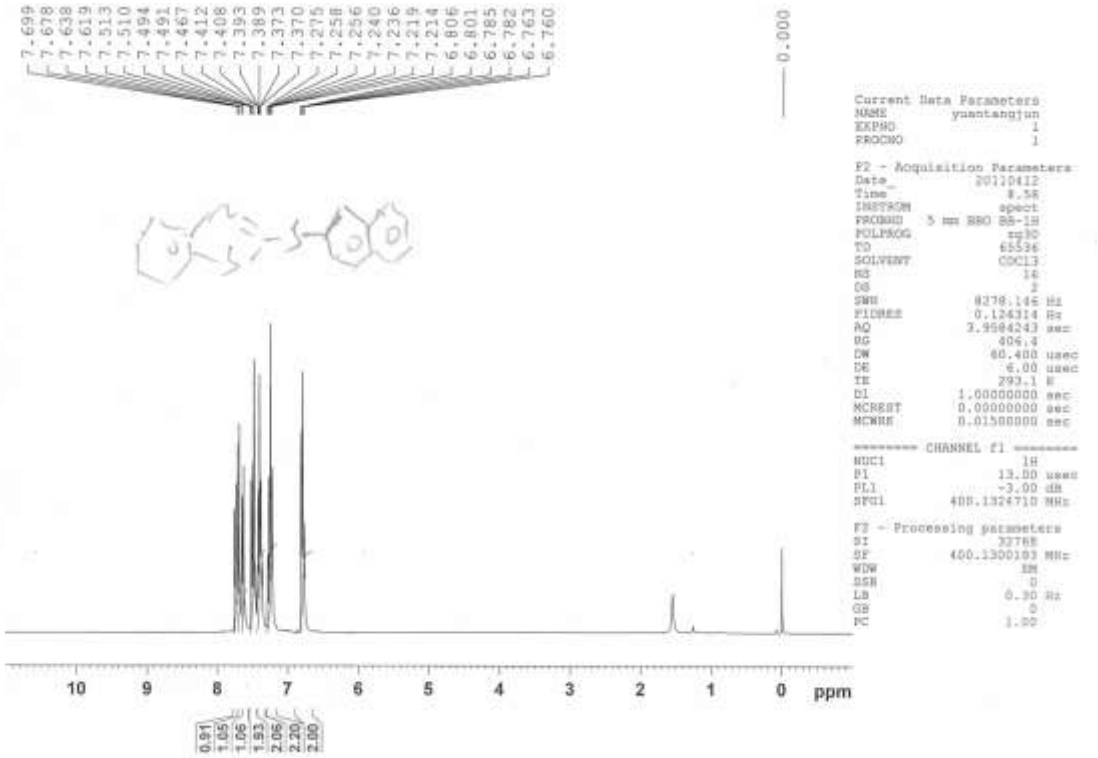
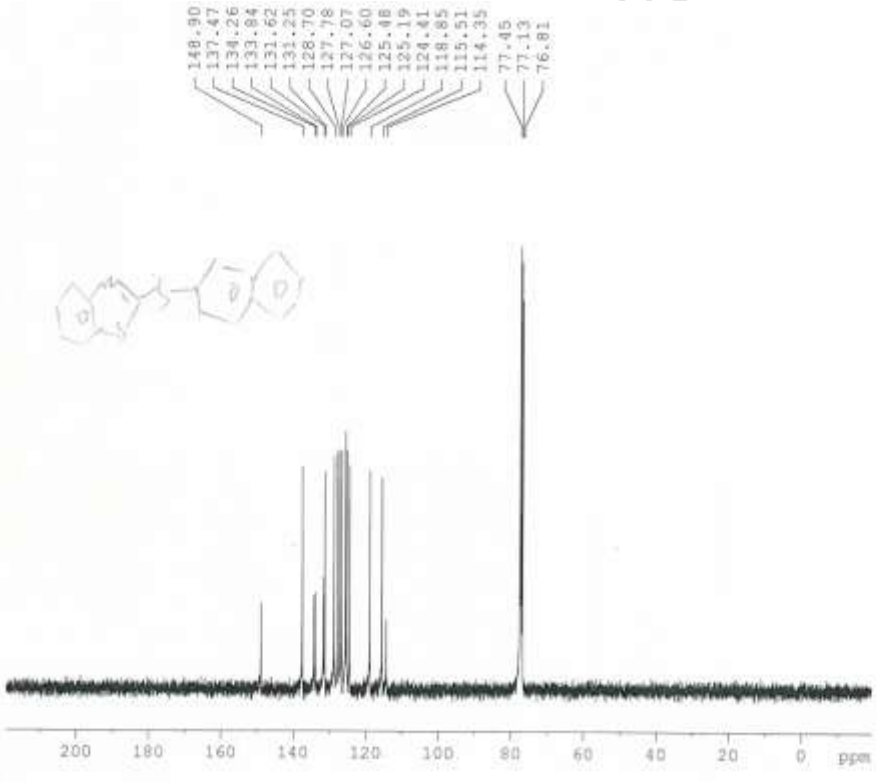
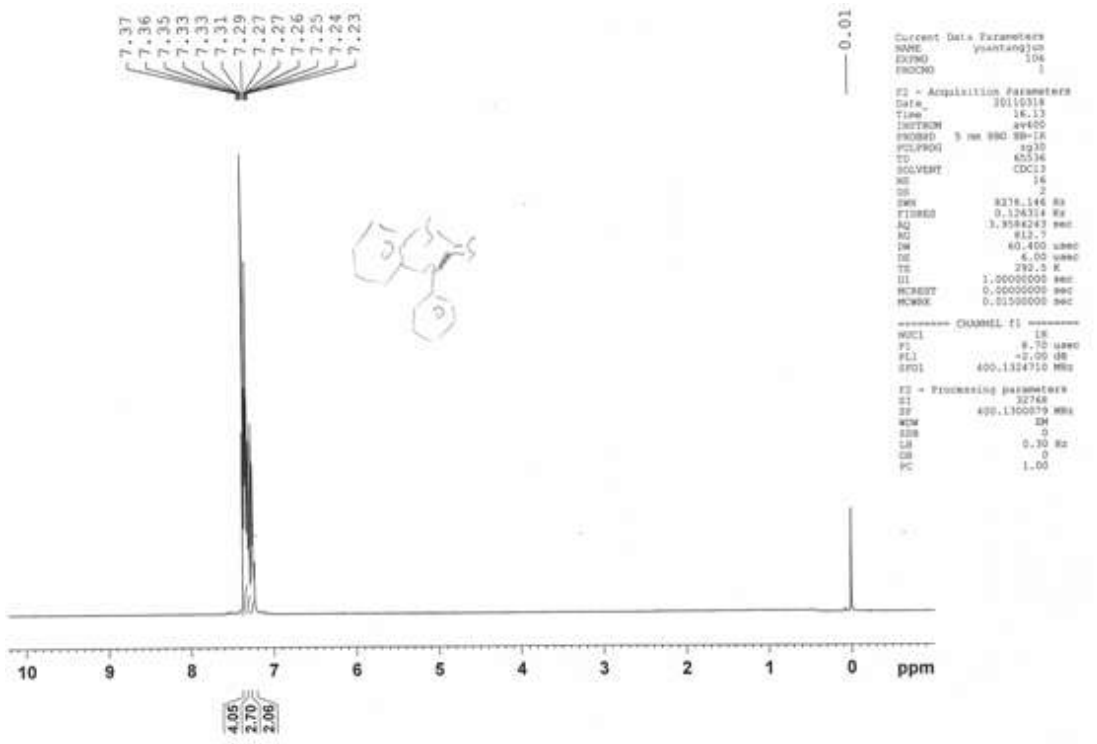
6.76
6.74
1.57
1.40
1.38
1.37
0.00
10
9
8
7
6
5
4
3
2
1
0
ppm
0.99
0.34
0.96
1.84
1.89
1.67

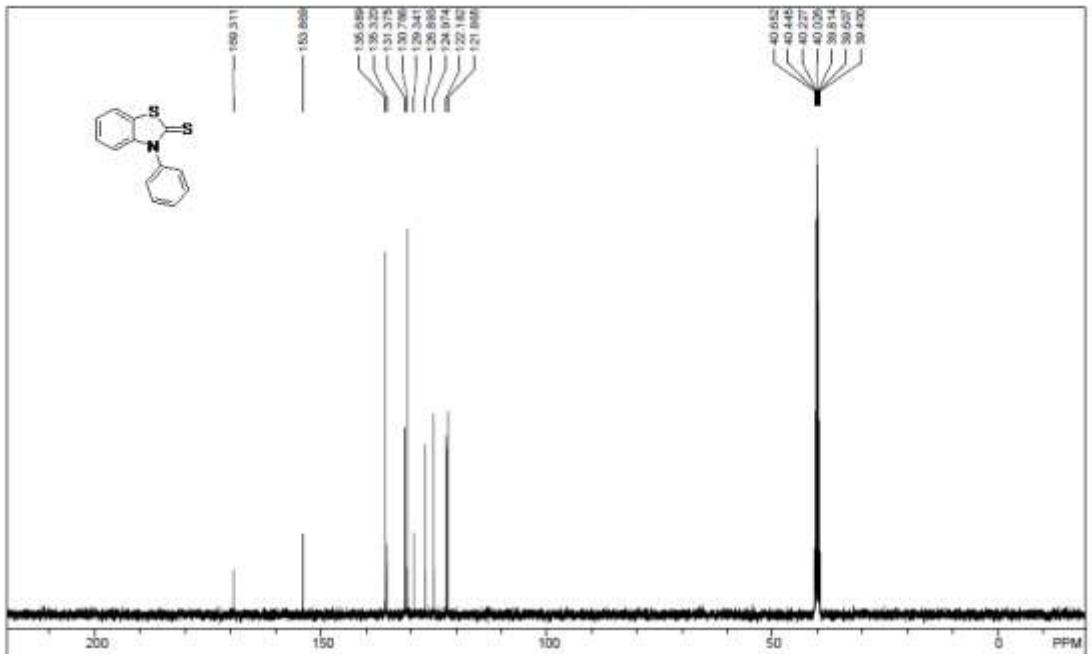

199.319
150.841
137.451
136.413
131.810
130.355
129.389
128.294
117.208
115.486
111.696
40.825
40.409
40.209
39.996
39.790
39.585
39.367
S
S
Cl
200
150
100
50
0
PPM

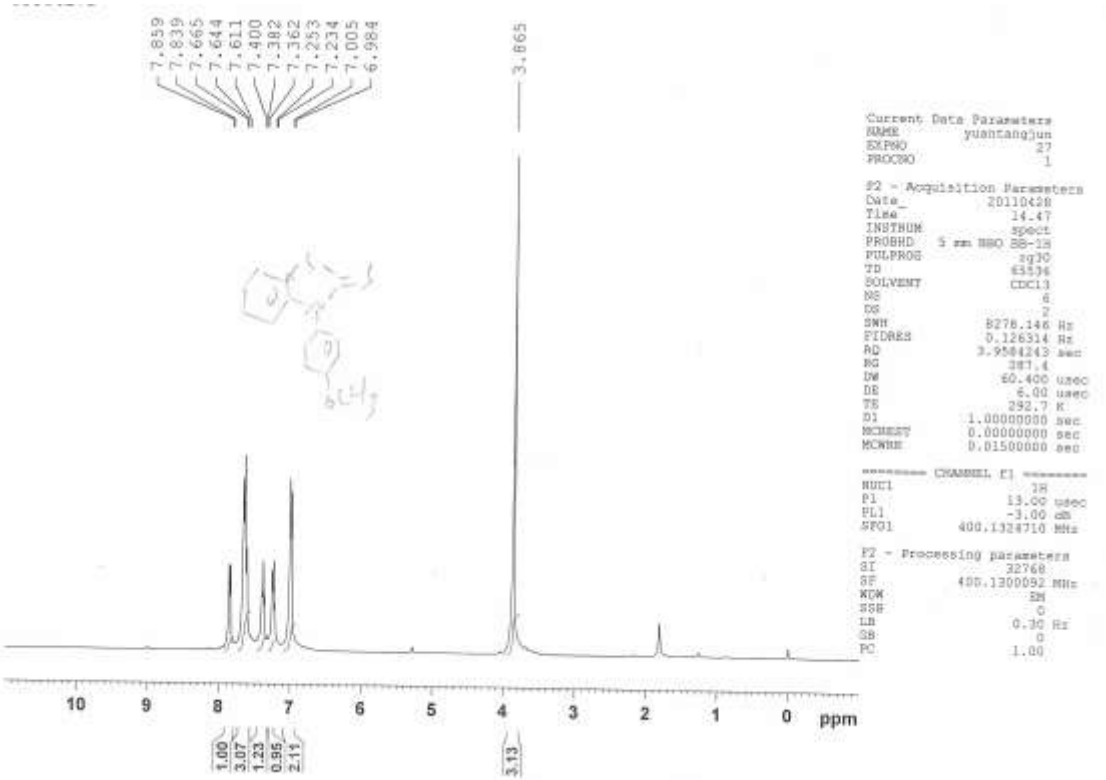

7.450
7.447
7.354
7.347
7.342
7.338
7.331
7.308
7.304
7.288
7.269
7.266
7.258
7.059
7.053
7.048
7.046
7.042
7.036
6.834
6.832
6.811
6.791
6.772
6.647
6.638
6.636
6.629
6.623
4.300
0.000
Current Data Parameters
NAME yuantaojun
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110412
Time 9.45
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 912.3
DW 60.400 usec
DE 6.00 usec
TE 293.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -3.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300104 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 0 ppm
0.98
2.46
2.02
2.01
1.00
149.20
137.96
136.02
131.78
131.00
129.59
127.19
126.23
126.03
119.05
115.49
112.55
77.36
77.05
76.73
200 180 160 140 120 100 80 60 40 20 0 ppm

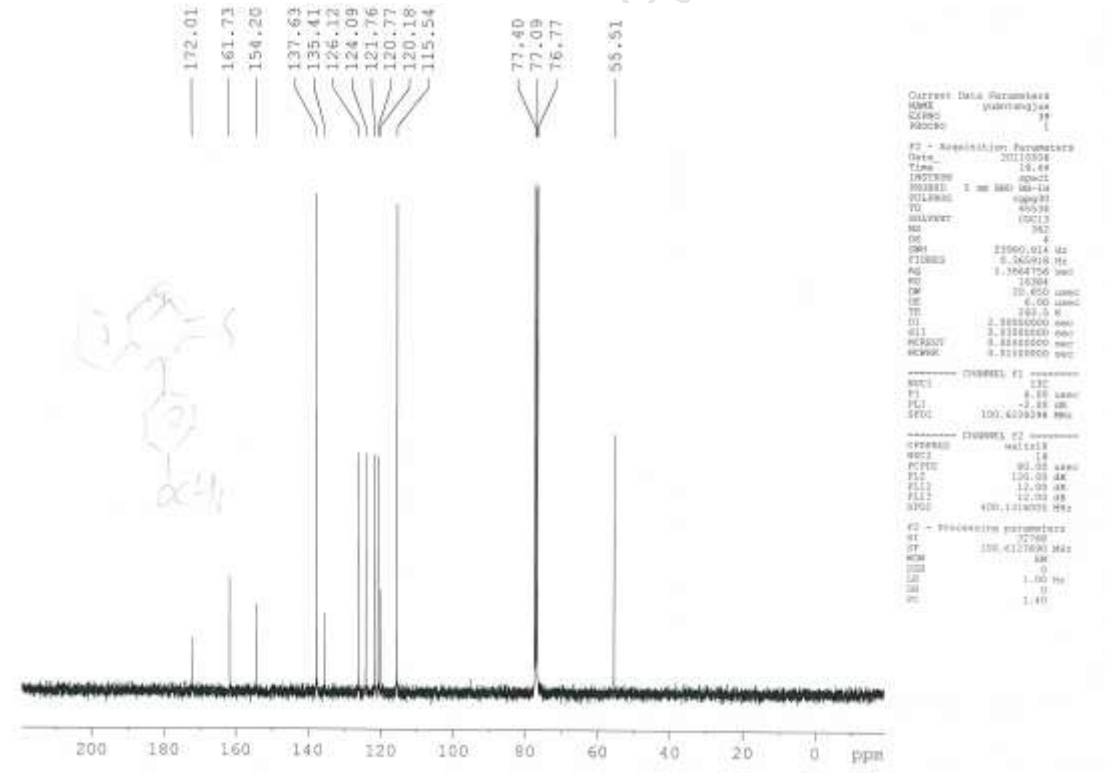

7.699
7.678
7.638
7.619
7.513
7.510
7.494
7.491
7.467
7.412
7.408
7.393
7.389
7.373
7.370
7.275
7.258
7.256
7.240
7.236
7.219
7.214
6.806
6.801
6.785
6.782
6.763
6.760
0.000
10 9 8 7 6 5 4 3 2 1 0 ppm
0.91
1.05
1.06
1.53
2.05
2.20
2.00

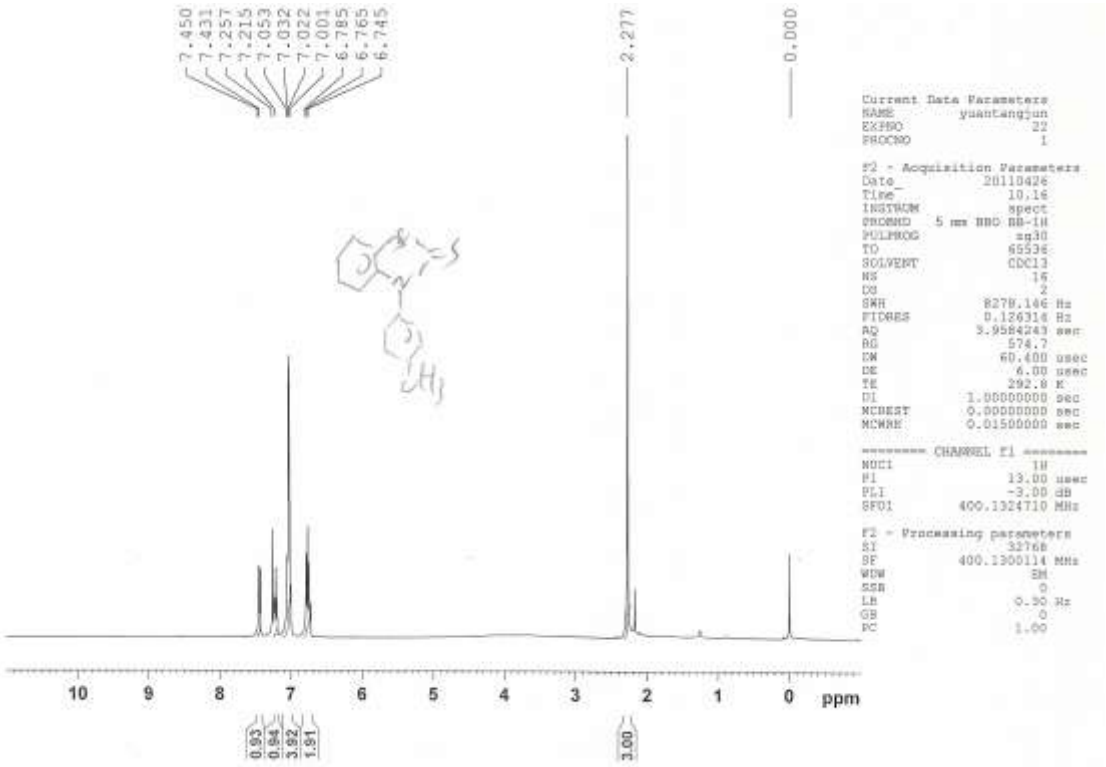

148.90
137.47
134.26
133.84
131.62
131.25
128.70
127.78
127.07
126.60
125.48
125.19
124.41
118.85
115.51
114.35
77.45
77.13
76.81
200 180 160 140 120 100 80 60 40 20 0 ppm

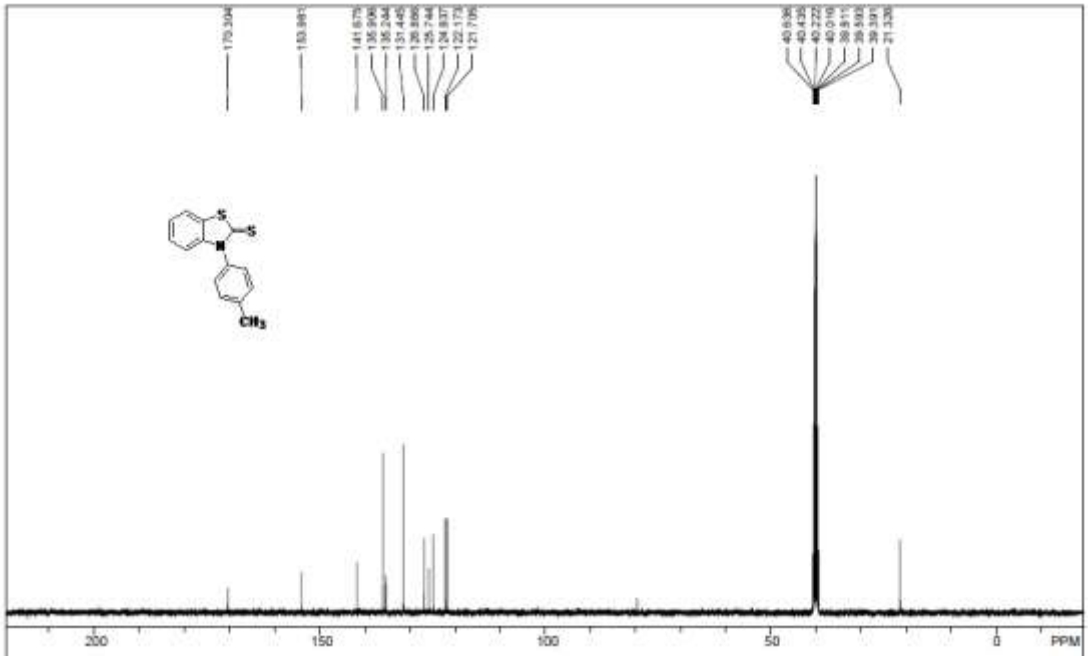

7.37
7.36
7.35
7.33
7.33
7.31
7.29
7.27
7.27
7.26
7.25
7.24
7.23
0.01
10
9
8
7
6
5
4
3
2
1
0
ppm
4.05
2.70
2.06

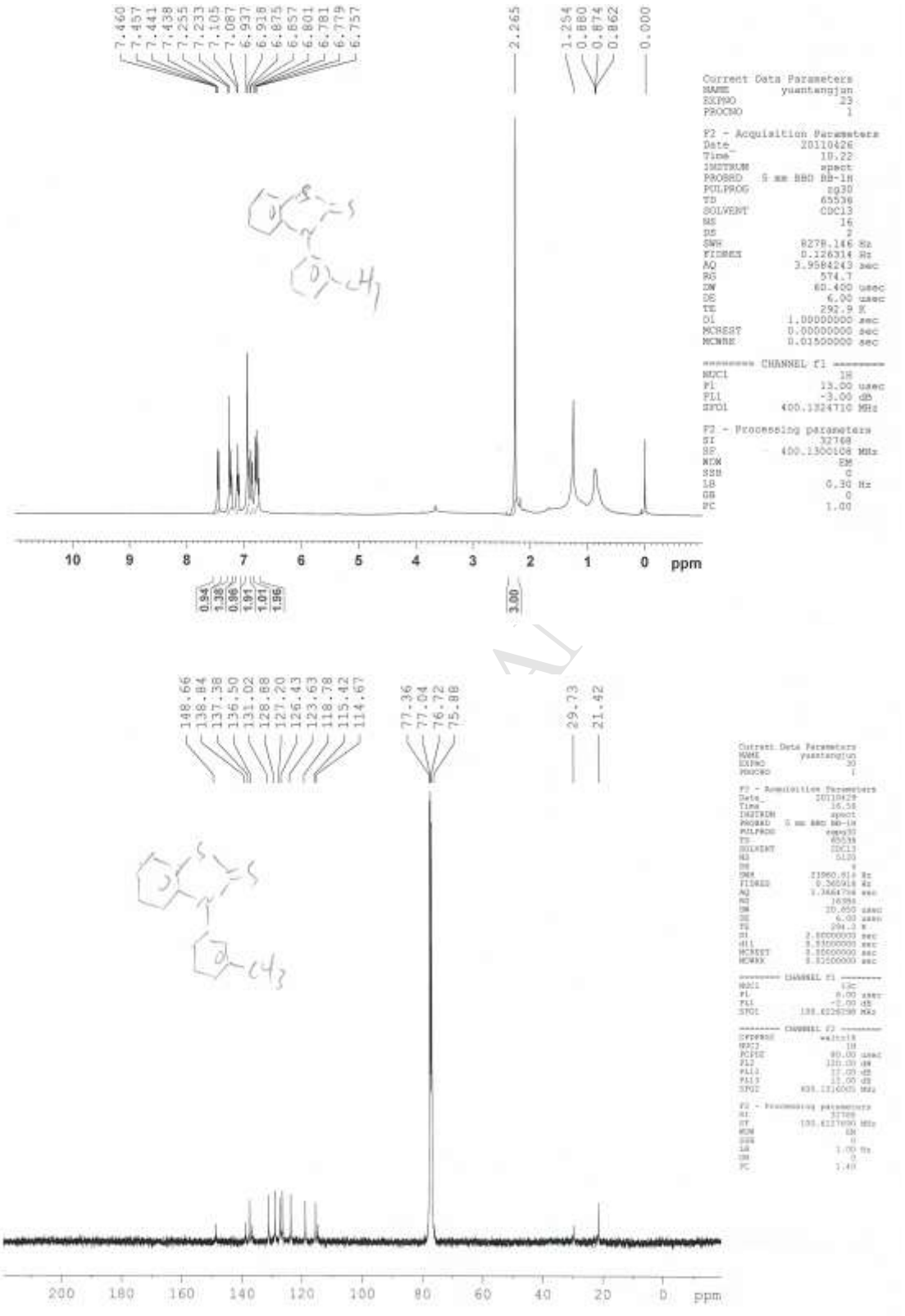

169.311
153.868
135.659
135.320
131.375
130.786
129.341
126.869
124.914
122.182
121.885
40.652
40.448
40.227
40.026
39.814
39.597
39.430
S
S
N
200
150
100
50
0
PPM

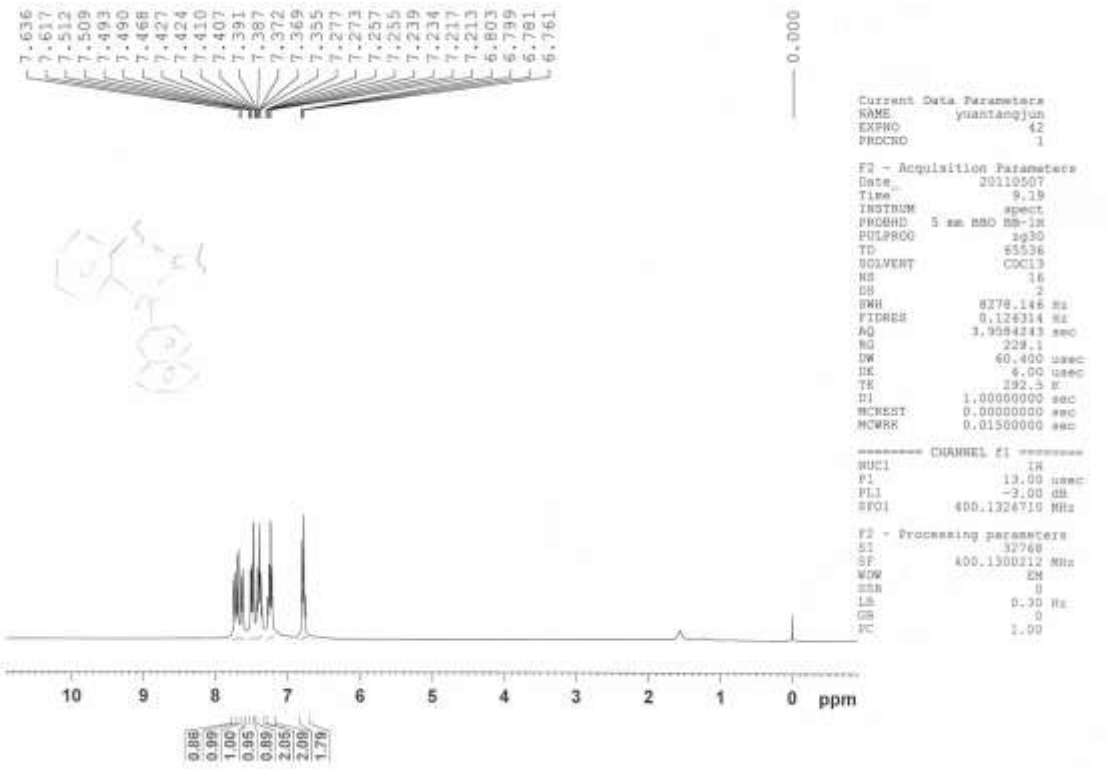

7.859
7.839
7.665
7.644
7.611
7.400
7.382
7.362
7.253
7.234
7.005
6.984
3.865
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
3.07
1.23
0.95
2.11
3.13

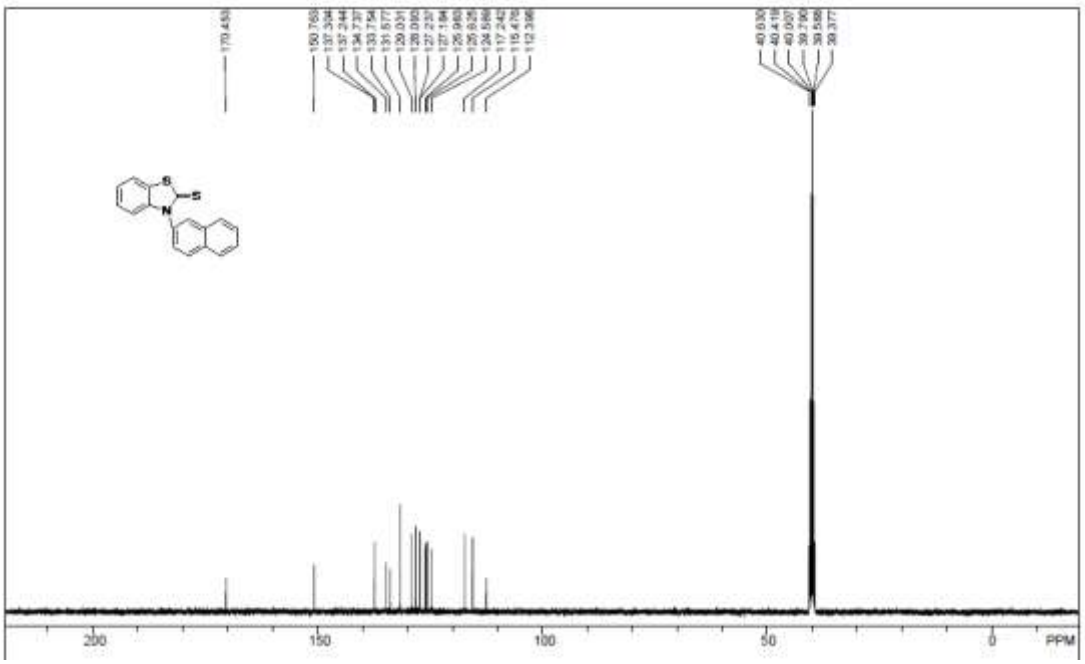

172.01
161.73
154.20
137.63
135.41
126.12
124.09
121.76
120.77
120.18
115.54
77.40
77.09
76.77
55.51
200 180 160 140 120 100 80 60 40 20 0 ppm

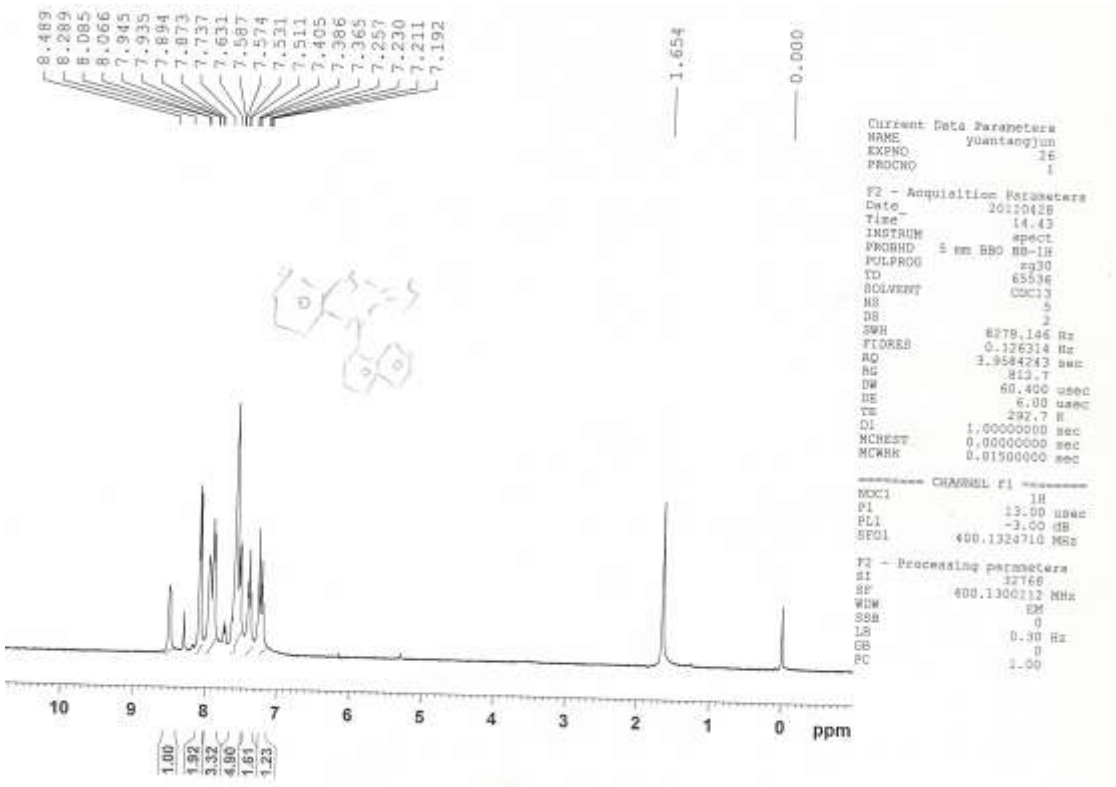

7.450
7.431
7.257
7.215
7.053
7.032
7.022
7.001
6.785
6.765
6.745
2.277
0.000
Current Data Parameters
NAME yuantangjun
EXPNO 22
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110426
Time 10.16
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126316 Hz
AQ 3.9584243 sec
RG 574.7
DW 60.400 usec
DE 6.00 usec
TE 292.8 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 13.00 usec
PL1 -3.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300114 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 0 ppm
0.93
0.94
3.92
1.91
3.00

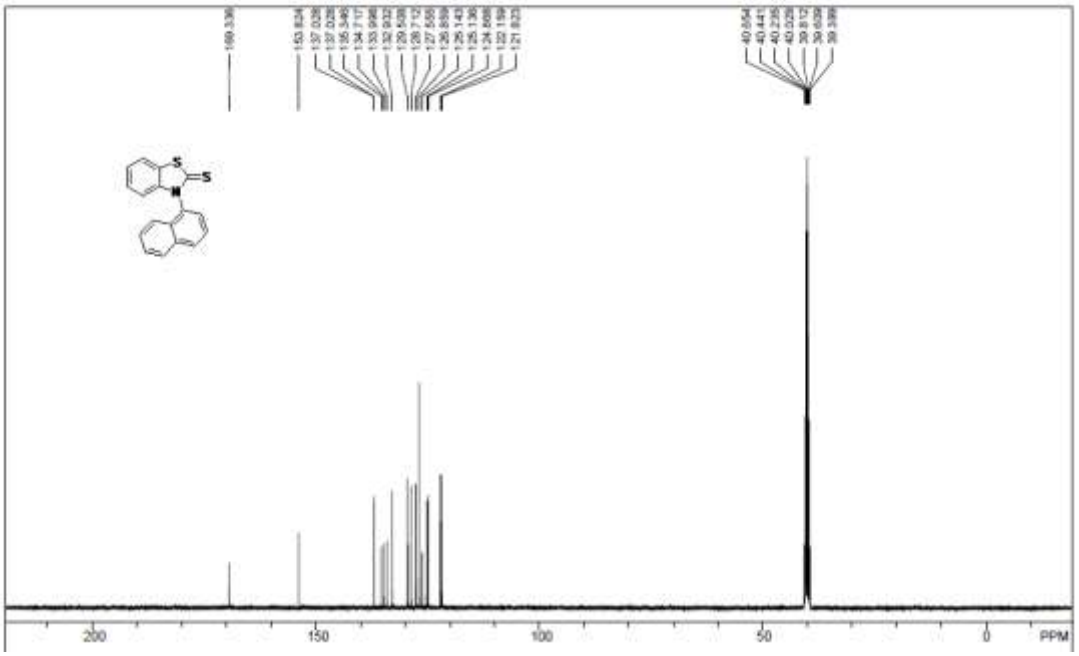

170.304
153.981
141.675
135.906
135.244
131.445
126.866
125.744
124.837
122.173
121.705
40.636
40.436
40.222
40.010
39.811
39.593
39.391
21.336
200 150 100 50 0 PPM

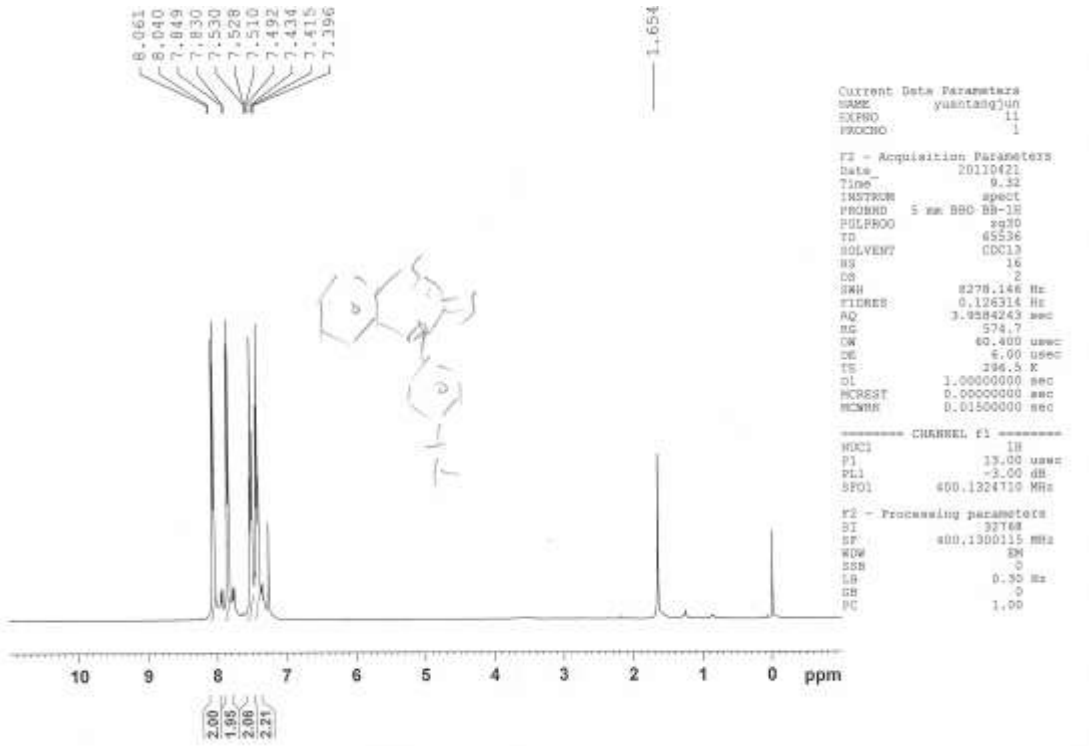

7.460
7.457
7.441
7.438
7.255
7.233
7.105
7.087
6.937
6.918
6.875
6.857
6.801
6.781
6.779
6.757
2.265
1.254
0.880
0.874
0.862
0.000
Current Data Parameters
NAME yuantangjun
EXPNO 23
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110426
Time 10.22
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 574.7
DW 60.400 usec
DE 6.00 usec
TE 292.9 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 13.00 usec
PL1 -3.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300108 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 0 ppm
0.94
1.38
0.96
1.91
1.01
1.86
3.00
148.66
138.84
137.38
136.50
131.02
128.88
127.20
126.43
123.63
118.78
115.42
114.67
77.36
77.04
76.72
75.88
29.73
21.42
200 180 160 140 120 100 80 60 40 20 0 ppm

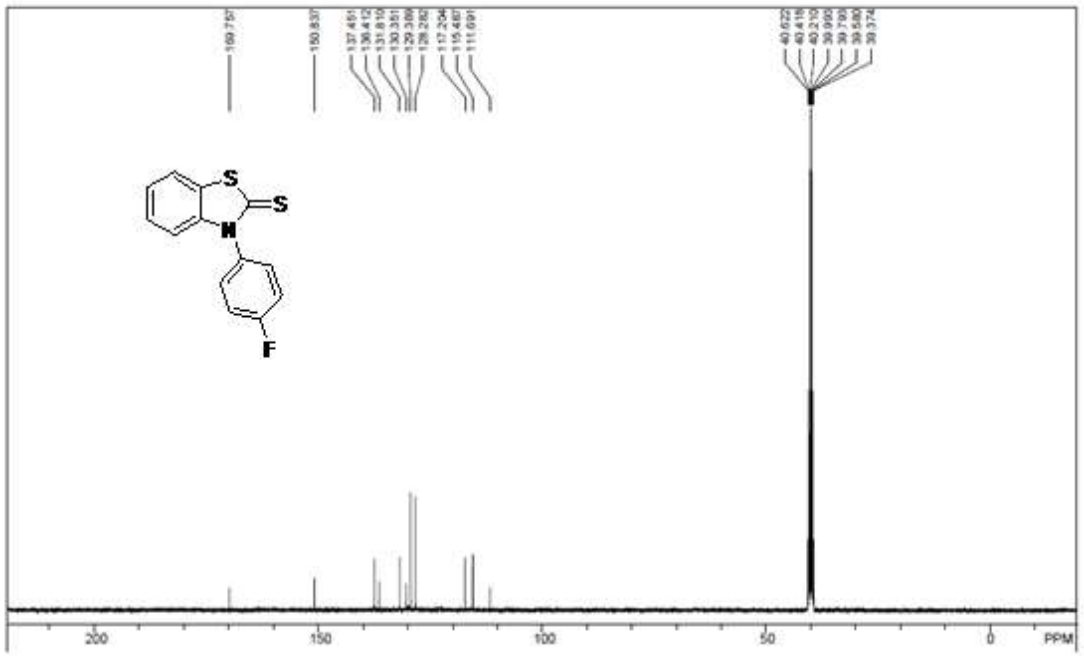

7.636
7.617
7.512
7.509
7.493
7.490
7.468
7.427
7.424
7.410
7.407
7.391
7.387
7.372
7.369
7.355
7.277
7.273
7.257
7.255
7.239
7.234
7.217
7.213
6.803
6.799
6.781
6.761
0.000
Current Data Parameters
NAME yuantangjun
EXPNO 42
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110507
Time 9.19
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 228.1
DW 60.400 usec
DE 6.00 usec
TE 292.5 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -3.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300212 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 0 ppm
0.88 0.99 1.00 0.95 0.89 2.05 2.08 1.79

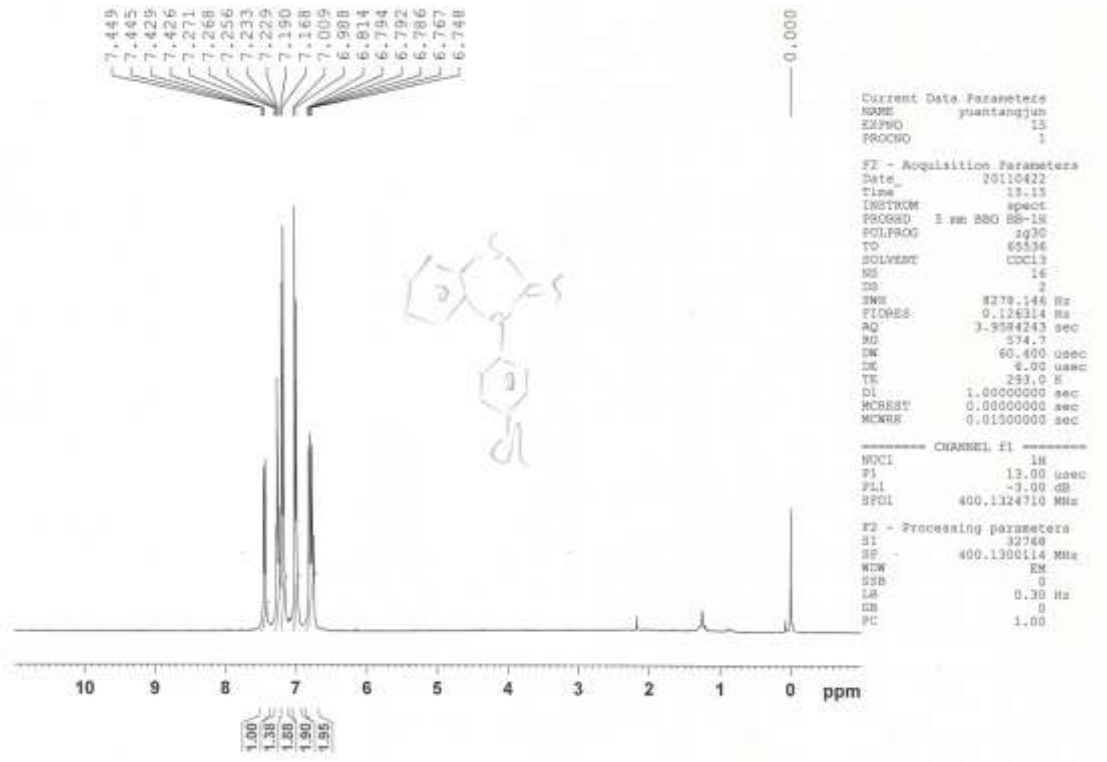

170.453
150.769
137.304
137.244
134.737
133.754
131.677
129.031
128.093
127.257
127.184
125.663
125.625
124.586
117.242
115.470
112.398
40.630
40.419
40.207
39.790
39.588
39.377
200 150 100 50 0 PPM

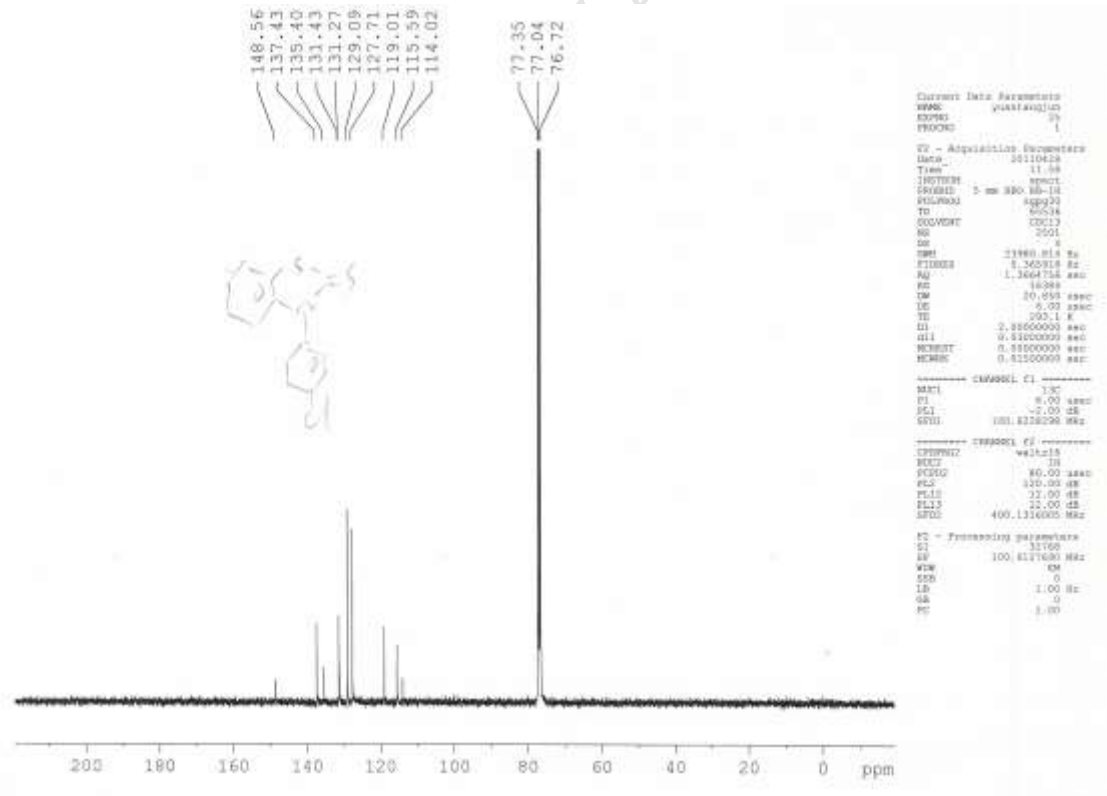

8.489
8.289
8.085
8.066
7.945
7.935
7.894
7.873
7.737
7.631
7.587
7.574
7.531
7.511
7.405
7.386
7.365
7.257
7.230
7.211
7.192
1.654
0.000
Current Data Parameters
NAME yuantangjun
EXPNO 26
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120428
Time 14.43
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 5
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 813.7
DW 60.400 usec
DE 6.00 usec
TE 292.7 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 13.00 usec
PL1 -3.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300212 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00 1.92 3.32 4.90 1.61 1.23

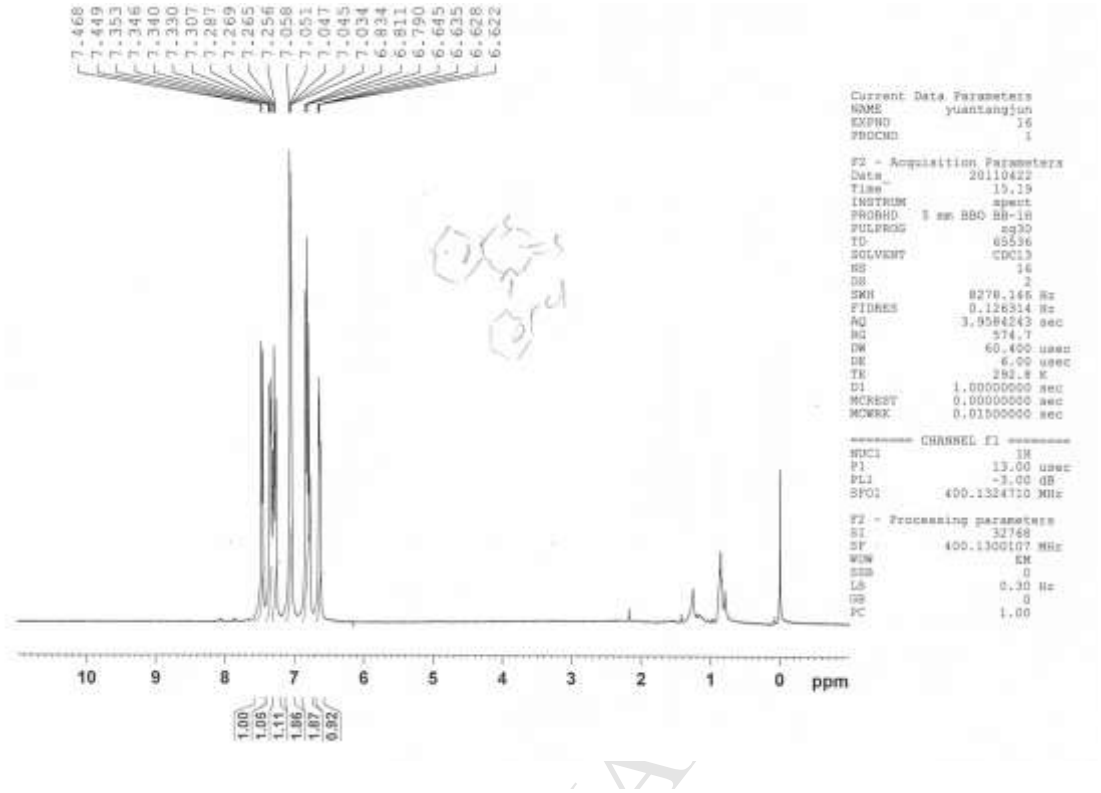

169.336
153.834
137.038
137.026
136.546
134.717
133.998
132.932
129.508
128.712
127.558
126.859
125.143
125.130
124.606
122.199
121.825
40.654
40.441
40.228
40.015
39.802
39.589
39.376
S
S
N
200 150 100 50 0 PPM

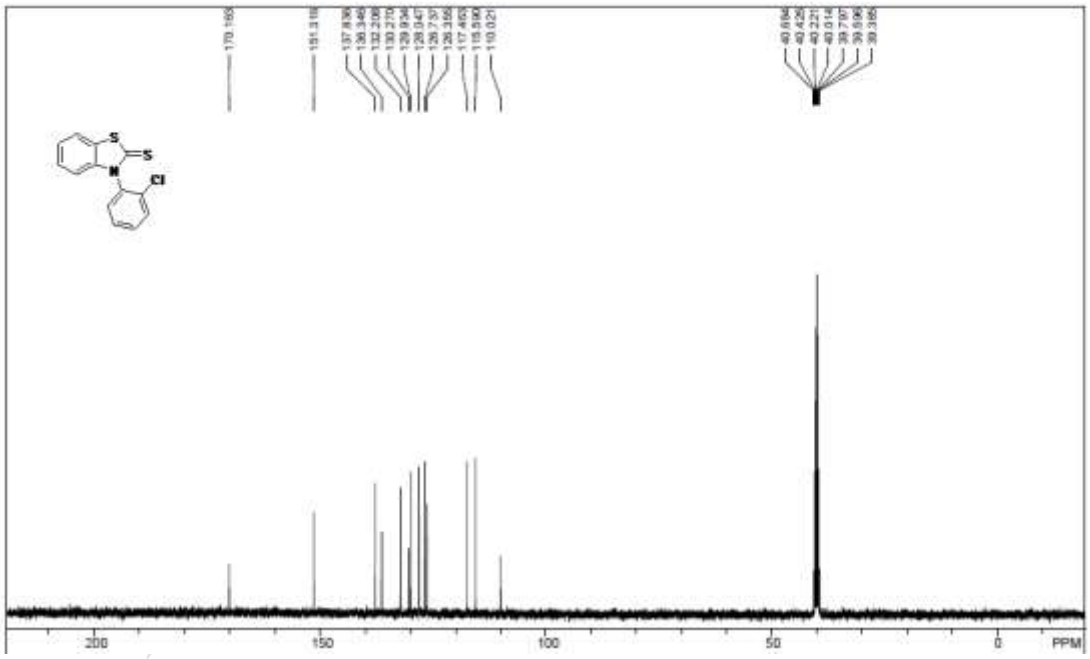

8.061
8.040
7.849
7.830
7.530
7.528
7.510
7.492
7.434
7.415
7.396
1.654
Current Data Parameters
NAME yuantangjun
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110421
Time 9.32
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 574.7
DW 60.400 usec
DE 6.00 usec
TE 296.5 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 13.00 usec
PL1 -3.00 dB
SFO1 600.1324710 MHz
F2 - Processing parameters
SI 32768
SF 600.1300115 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 0 ppm
2.00
1.95
2.06
2.21


169.757
150.837
137.491
136.412
131.810
130.351
129.389
128.282
117.254
115.467
111.691
40.622
40.416
40.210
39.998
39.790
39.580
39.374
S
S
N
F
200 150 100 50 0 PPM


7.449
7.445
7.429
7.426
7.271
7.268
7.256
7.233
7.229
7.190
7.168
7.009
6.988
6.814
6.794
6.792
6.786
6.767
6.748
0.000
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00 1.38 1.88 1.90 1.95


148.56
137.43
135.40
131.43
131.27
129.09
127.71
119.01
115.59
114.02
77.35
77.04
76.72
200 180 160 140 120 100 80 60 40 20 0 ppm





[1] S. Murru, H. Ghosh, S. K. Sahoo, and B. K. Patel, *Org. Lett.* **2011**, *11*, 5254-5257.

[2] S. Ranjit, R. Lee, D. Heryadi, C. Shen, J. Wu, P. Zhang, K.-W. Huang, X. Liu, *J. Org. Chem.* **2011**, *76*, 8999-9007.

[3] H. Inomata, A. Toh, T. Mitsui, S. Fukuzawa, *Tetrahedron Letters*, **2013**, *54*, 4729-4731.