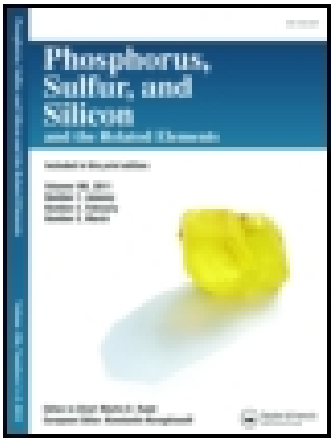

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One-Pot Metal-Free Synthesis of Benzyl Alkyl Sulfides

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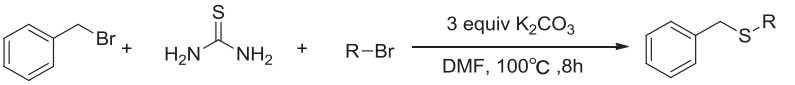
GRAPHICAL ABSTRACT



Abstract *The synthesis of sulfides is important in various fields. This paper reports an efficient, odorless, and viable protocol for the base-mediated synthesis of benzyl alkyl sulfides using thiourea. The reactions were carried out under transition-metal-free conditions, showing yields of asymmetric sulfides higher than 80%. Tertiary alkyl halides and aryl halides do not react with thiourea under formation of the corresponding isothiouronium salts; however, 5-bromopyrimidine and 2-bromopyrimidine lead to yields of 79.2% and 87.6%, respectively. This method is of significant importance from the both environmental and economic, green chemistry points of view.*

Keywords Asymmetric sulfides; thiourea; metal-free reaction

INTRODUCTION

There are a great number of natural and synthetic sulfur-containing compounds, some of which play a crucial role in the synthesis of drugs such as penicillin, sulfonamides, cephalosporins, and vitamin B1. Moreover, sulfides are useful in many other fields including in pesticides, dyes, organic optoelectronic materials, synthase inhibitors, and herbicides.[1–5]

The formation of C−S bonds is very important in the synthesis of thioethers that are of biological, pharmaceutical, and material science interest. During the past few decades, the generation of C−S bonds, especially C_{aryl}−S bonds involving an S_NAr reaction,[6] the coupling reaction,[7] and electrophilic substitution reaction of activated aryl halides and thiols[8] has received considerable attention. Among them, catalysts based on transition metals are widely used in the formation of C_{aryl}−S bonds by directly coupling aryl halides with thiols. Pd,[9] Ni,[10,11] Cu,[12,13] and Fe[14,15] have been successfully applied to the synthesis of aryl sulfides. However, there still exist some challenges in these reactions. For example, the use of highly volatile, environmentally harmful, and foul-smelling thiols is not desirable, especially in large-scale production

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processes. It becomes more and more unacceptable with respect to increasing environmental problems. Therefore, it is necessary to develop robust, simple, and sustainable procedures.

It is known that thiourea is an attractive starting material due to its low cost and ease of availability. Recently, it has been found that thiols can be replaced by thiourea, which is odorless and non-toxic, as a sulfur source for the formation of C−S bonds.[16,17] Although these pioneering studies provided highly promising strategies for the preparation of thioethers, the development of more efficient, environmentally benign, and simple processes that are viable to diverse products such as asymmetric thioethers remains challenging.

Herein, we report a novel and efficient route for the synthesis of asymmetric sulfides. The direct sulfonation of (bromomethyl)benzene with thiourea and a series of alkyl halides in DMF at 100°C yields asymmetric thioethers.

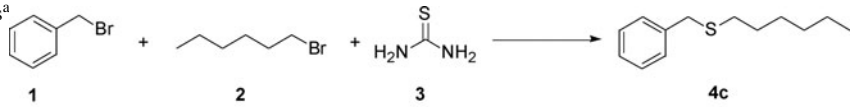
RESULTS AND DISCUSSION

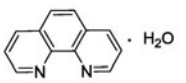
(Bromomethyl)benzene, 1-bromohexane, and thiourea were selected as a model system to optimize the reaction conditions, the results of which are summarized in Table 1. First, we investigated the effect of solvents and bases. DMF is found to be considerably superior to DMSO, THF, EtOH, acetone, and acetonitrile (Table 1, Entries 1–7). The results also indicate that the nature of the base has a pronounced impact on the reaction. Potassium carbonate leads to a better yield than cesium carbonate, potassium hydroxide, potassium *ortho*-phosphate, calcium oxide, and sodium carbonate (Table 1, Entries 2, 6, 10–13). Potassium hydroxide in DMSO forms a superbasic medium that allows cross-coupling reactions between aryl halides with various sulfur-, oxygen-, and nitrogen-based nucleophiles under transition metal-free conditions.[18] We conducted a similar reaction (Table 1, Entry 2); however, only a 74% yield was obtained. The reaction temperature also plays an important role in the reaction. The coupling proceeds slowly at 40°C, yielding only a little product even after 8 h (Table 1, Entry 7); however, the yield increased when the temperature was increased to 100°C, (Table 1, Entry 13).

Furthermore, copper(I) iodide, copper(I) chloride, iron(III) chloride, and $Pd(PPh_3)_3$ were used as ligands to catalyze the reaction (Table 1, Entries 14–27). The results reveal that the yields decrease compared to the use of potassium carbonate alone. Therefore, the optimal conditions can be concluded as follows: thiourea (1.2 equiv.), (bromomethyl)benzene (1.0 equiv.), and alkyl bromide (1.1 equiv.), potassium carbonate as the base without any metal catalysts. The best solvent is DMF; the optimum reaction temperature is 100°C; and the ideal reaction time is 8 h.

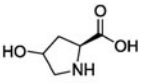
To investigate the generality and scope of the proposed protocol, reactions using a series of organic halides were explored. As summarized in Table 2, we found that alkyl halides can be easily transformed into their corresponding thioethers with yields higher than 80% at 100°C. The short-chain primary alkyl halides are more reactive substrates compared with those containing long chains because the reaction of primary alkyl halides with thiourea undergoes a mechanism of bimolecular nucleophilic substitution (S_N2) in which less steric hindrance results in higher reaction rates. High yields were also obtained when secondary alkyl halides including bromocyclopentane and bromocyclohexane were used as the reactants (Table 2, Entries 5–11). However, tertiary alkyl halides and aryl halides do not react

Table 1 Optimization of the reaction conditions for the synthesis of asymmetric thioethers[a]

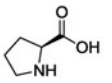




L1

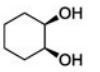


L2



L3

L3



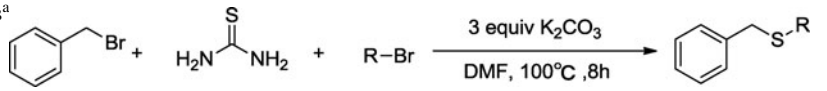
L4

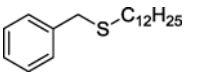
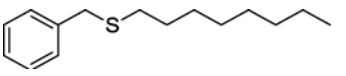
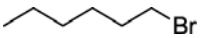
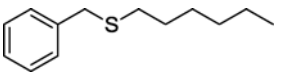
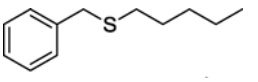
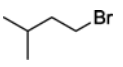
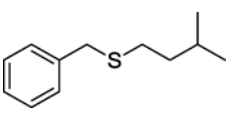
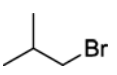
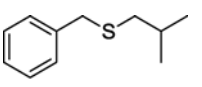
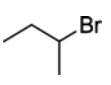
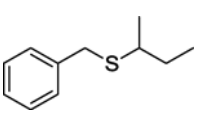
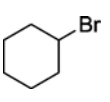
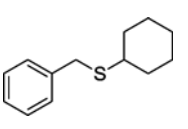
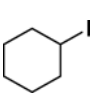
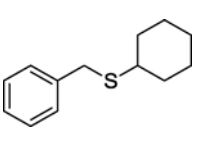
Entry	Catalyst	Ligand	Base	Solvent	Reaction temperature/°C	Yield[b](%)
1			K_2CO_3	EtOH	50	78
2			KOH	DMSO	80	74
3			K_2CO_3	Acetone	45	36
4			K_2CO_3	THF	45	0.4
5			K_2CO_3	Acetonitrile	50	0.25
6			Cs_2CO_3	DMF	80	49
7			K_2CO_3	DMF	40	27
8			K_2CO_3	DMF	60	74
9			K_2CO_3	DMF	80	82
10			K_3PO_4	DMF	100	50
11			CaO	DMF	100	88
12			Na_2CO_3	DMF	100	87
13			K_2CO_3	DMF	100	95
14	CuI		K_2CO_3	EtOH	50	53
15	CuCl		K_2CO_3	EtOH	50	62
16	$Pd(PPh_3)_3$		K_2CO_3	EtOH	50	88
17	$FeCl_3$		K_2CO_3	EtOH	50	81
18	$FeCl_3$	L1	K_2CO_3	DMF	100	90
19		L1	K_2CO_3	DMF	100	82
20		L2	K_2CO_3	DMF	100	85
21	CuI	L2	K_2CO_3	DMF	100	73
22	CuI	L3	K_2CO_3	DMF	100	74
23	CuI	L4	K_2CO_3	DMF	100	81
24	$FeCl_3$	L2	K_2CO_3	DMF	100	77
25		L3	K_2CO_3	DMF	100	62
26	$FeCl_3$	DMEDA	K_2CO_3	DMF	100	14
27	$FeCl_3$	TMEDA	K_2CO_3	DMF	100	62

[a]General reaction conditions: (bromomethyl)benzene (1.0 mmol), thiourea (1.2 mmol), 1-bromohexane (1.1 mmol), catalyst (0.1 mmol), ligand (0.1 mmol), and 3 equiv. base in solvent (5 mL) for 8 h. [b]GC yield.

with thiourea to produce isothiouronium salts, because of steric hindrance and electronic effects, respectively (Table 2, Entries 12 and 16). Interestingly, 5-bromopyrimidine and 2-bromopyrimidine lead to much better yields of 79.2% and 87.6%,respectively (Table 2, Entries 13 and 14).

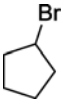
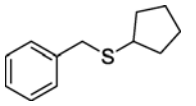
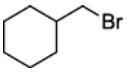
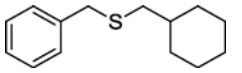
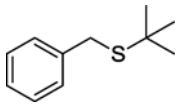
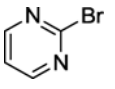
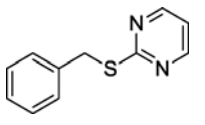
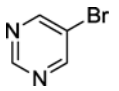
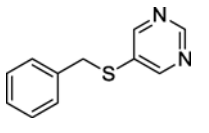
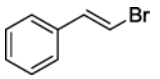
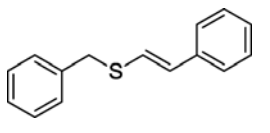
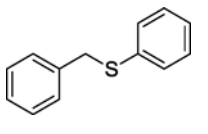
Table 2 Reactions of benzyl bromide with thioureas and alkyl halides Under Optimized Conditions[a]



Entry	Halide	Product Formula	Product No	Yield[b] (%)
1	n-$C_{12}H_{25}Br$		**4a**	87.6
2	n-$C_8H_{17}Br$		**4b**	87.1
3			**4c**	92.3
4			**4d**	96.2
5			**4e**	88.1
6			**4f**	95.4
7			**4g**	85.3
8			**4h**	80.6
9			**4i**	91.8

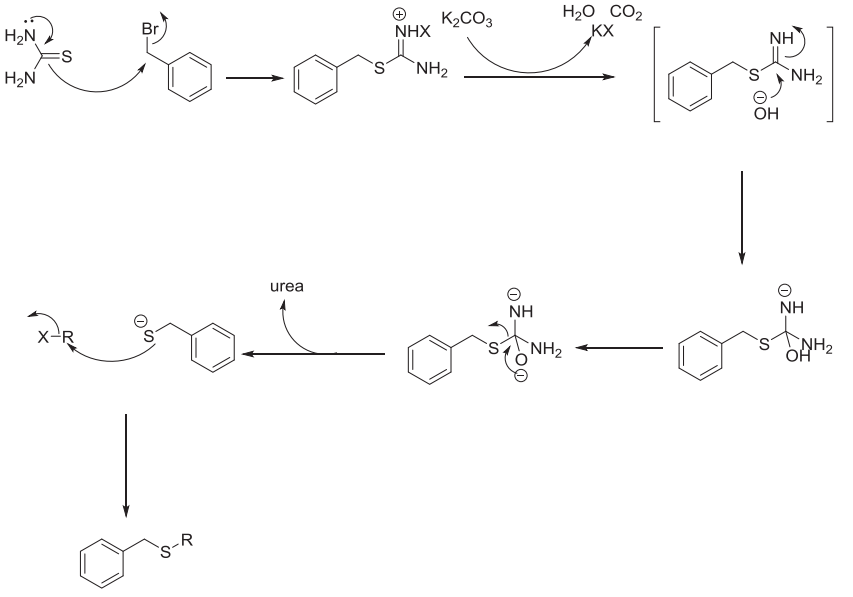
(Continued on next page)

Table 2 Reactions of benzyl bromide with thioureas and alkyl halides under optimized conditions[a] (*continued*)

Entry	Halide	Product Formula	Product No	Yield[b] (%)
10			**4j**	88.4
11			**4k**	89.8
12			**4l**	0
13			**4m**	87.6
14			**4n**	79.2
15			**4o**	85.6
16			**4p**	0

[a]General reaction conditions: (Bromomethyl)benzene (1.0 mmol), thiourea (1.2 mmol), alkyl bromide (1.1 mmol), and 3 equiv. K_2CO_3 in DMF at 100°C for 8 h.[b]Isolated yield.

We propose a general pathway for the reaction, which is shown in Scheme 1. The simultaneous reaction of thiourea with a mixture of two different alkylating agents selectively yields asymmetric thioethers as the main products. This may be explained by the fact that, by far, the most reactive halide benzyl bromide reacts with thiourea first and, in the following step, the less reactive halide leads to the formation of the benzyl alkyl thioether.



Scheme 1

CONCLUSION

In conclusion, we have identified an efficient, odorless, and viable protocol for the one-pot metal-free synthesis of benzyl alkyl thioethers. The most reactive halide benzyl bromide reacts with thiourea first and, in the following step, the less reactive halide leads to the formation of the benzyl alkyl thioether. The optimal conditions are as follows: thiourea (1.2 equiv.), (bromomethyl)benzene (1.0 equiv.), and the alkyl bromide (1.1 equiv.) are dissolved in DMF, potassium carbonate is added as the base and the reaction is run at 100°C for 8 h. Under optimal conditions, yields of asymmetric thioethers higher than 80% have been achieved.

EXPERIMENTAL

Materials and Methods

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance III spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C) in CD_3OD using TMS as the internal standard. Chemical shifts δ are reported in ppm, coupling constants J in Hertz. GC/MS Analyses were performed on a Polaris Q GC/MS instrument. All products are compounds that have been reported in the literature and were identified by comparing their spectra with those reported. All chemicals were commercially available and used without further purification.

Typical Procedure for the Reaction of Benzyl Bromide with Alkyl Halides and Thiourea

Benzyl bromide (1 mmol), alkyl halide (1.1 mmol), thiourea (1.2 mmol), and K_2CO_3 (3 mmol) were added to 5 mL of DMF at 100°C. The reaction was stopped after the consumption of the benzyl bromide, which was monitored by gas chromatography (GC). Then,

the reaction mixture was diluted with de-ionized water and extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation to generate a crude product. Purification by silica gel chromatography eluting with *n*-hexane afforded pure thioethers.

Characteristic Data of Compounds

Benzyl(dodecyl)sulfane (4a). Colorless oil. 256 mg (0.876 mmol, 87.6% yield). ^{1}H NMR: δ 7.32–7.17 (m, 5H), 3.69 (s, 2H), 2.38 (t, $J = 7.3$ Hz, 2H), 1.56–1.47 (m, 2H), 1.28 (m, 18H), 0.90 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR: δ 140.27, 129.94, 129.35, 127.80, 36.93, 33.09, 32.11, 30.78, 30.72, 30.64, 30.50, 30.32, 30.28, 29.86, 23.76, 14.48; HRMS (EI) calcd. for $[C_{19}H_{32}S + H]^+$ requires *m/z* 292.2225, found 291.7474.

Benzyl(octyl)sulfane (**4b**). Colorless oil. 206 mg (0.871 mmol, 87.1% yield). ^{1}H NMR: δ 7.78–6.87 (m, 5H), 3.69 (s, 2H), 2.41–2.36 (t, $J = 7.3$ Hz, 2H), 1.58–1.48 (m, 2H), 1.28 (s, 10H), 0.91 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR: δ 138.85, 128.59, 128.00, 126.45, 35.65, 31.66, 30.82, 29.01, 28.95, 28.56, 24.43, 22.39, 13.20; HRMS (EI) calcd. for $[C_{15}H_{24}S + H]^+$ requires *m/z* 236.1599, found 235.9009.

Benzyl(hexyl)sulfane (4c). Colorless oil. 190 mg (0.923 mmol, 92.3% yield). ^{1}H NMR: δ 7.31–7.16 (m, 5H), 3.66 (s, 1H), 2.40–2.32 (t, $J = 7.3$ Hz, 2H), 1.55–1.46 (m, 2H), 1.36–1.17 (m, 6H), 0.88 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR: δ 140.13, 129.89, 129.31, 127.75, 36.95, 32.52, 32.13, 30.27, 29.54, 23.59, 14.46; HRMS (EI) calcd. for $[C_{13}H_{20}S + H]^+$ requires *m/z* 208.1286, found 207.8443.

Benzyl(pentyl)sulfane (4d). Colorless oil. 187 mg (0.964 mmol, 96.4% yield). ^{1}H NMR: δ 7.32–7.15 (m, 5H), 3.67 (s, 2H), 2.36 (t, $J = 7.4$ Hz, 2H), 1.57–1.46 (m, 2H), 1.35–1.22 (m, 4H), 0.87 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR: δ 140.15, 129.89, 129.31, 127.76, 36.93, 32.09, 30.00, 23.28, 14.38; HRMS (EI) calcd. for $[C_{12}H_{18}S + H]^+$ requires *m/z* 194.1129, found 193.9804.

Benzyl(isopentyl)sulfane (4e). Colorless oil. 171 mg (0.881 mmol, 88.1% yield). ^{1}H NMR: δ 7.32–7.15 (m, 5H), 3.67 (s, 2H), 2.40–2.34 (m, 2H), 1.60 (dq, $J = 13.3$, 6.7 Hz, 1H), 1.40 (m, 2H), 0.84 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR: δ 140.12, 129.91, 129.30, 127.76, 39.39, 36.89, 30.07, 28.43, 22.68; HRMS (EI) calcd. for $[C_{12}H_{18}S + H]^+$requires *m/z* 194.1129, found 194.1001.

Benzyl(isobutyl)sulfane (**4f**). Colorless oil. 172 mg (0.954 mmol, 95.4% yield). ^{1}H NMR: δ 7.32–7.16 (m, 5H), 3.67 (s, 2H), 2.27 (d, $J = 6.8$ Hz, 2H), 1.73 (m, 1H), 0.93 (d, $J = 6.7$ Hz, 6H); ^{13}C NMR: δ 140.22, 129.95, 129.32, 127.79, 41.33, 37.36, 29.32, 22.35; HRMS (EI) calcd. for $[C_{11}H_{16}S + H]^+$ requires *m/z* 180.0973, found 179.9579.

Benzyl(*sec*-butyl)sulfane (**4g**). Colorless oil. 154 mg (0.853 mmol, 85.3% yield). ^{1}H NMR: δ 7.25 (m, 5H), 3.71 (s, 1H), 2.55 (m, 1H), 1.60–1.43 (m, 2H), 1.21 (d, $J = 6.8$ Hz, 3H), 0.92 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR: δ 140.32, 129.87, 129.32, 127.72, 42.10, 35.63, 30.51, 21.06, 11.61; HRMS (EI) calcd. for $[C_{11}H_{16}S + H]^+$ requires *m/z* 180.0973, found 179.9659.

Benzyl(cyclohexyl)sulfane (**4h, 4i**). Colorless oil. 166 mg (0.806 mmol, 80.6% yield), 189 mg (0.918mmol, 91.8% yield). ^{1}H NMR: δ 7.30–7.15 (m,5H), 3.65 (s, 1H), 2.37–2.33 (m, 1H), 1.54–1.45 (m, 2H), 1.35–1.19 (m, 6H), 0.87 (t, $J = 7.0$ Hz, 2H); ^{13}C NMR: δ 140.09, 129.88, 129.29, 127.74, 36.96, 32.51, 32.14, 30.26, 29.54, 23.58, 14.49; HRMS (EI) calcd. for $[C_{13}H_{18}S + H]^+$ requires *m/z* 206.1129, found 207.8443.

Benzyl(cyclopentyl)sulfane (**4j**). Colorless oil. 170 mg (0.884 mmol, 88.4% yield). ^{1}H NMR: δ 7.34–7.16 (m, 5H), 3.72 (s, 1H), 2.94 (p, $J = 6.8$ Hz, 1H), 1.99–1.85 (m, 2H), 1.74–1.67 (m, 2H), 1.59–1.42 (m, 4H); ^{13}C NMR: δ 140.39, 130.51, 129.86, 129.33,

127.72, 44.24, 37.12, 34.52, 25.74; HRMS (EI) calcd. for $[C_{12}H_{16}S + H]^+$ requires *m/z* 192.0973, found 191.9162.

Benzyl(cyclohexylmethyl)sulfane (**4k**). Colorless oil. 198 mg (0.898 mmol, 89.8% yield). ^{1}H NMR: δ 7.31–7.16 (m, 5H), 3.66 (s, 1H), 2.27 (d, $J = 6.8$ Hz, 2H), 1.79 (m, 2H), 1.69 (m, 3H), 1.44–1.33 (m, 1H), 1.28–1.08 (m, 3H), 0.88 (m, 2H); ^{13}C NMR: δ 140.28, 129.96, 129.32, 127.78, 39.79, 38.81, 37.51, 33.89, 27.51, 27.21; HRMS (EI) calcd. for $[C_{14}H_{20}S + H]^+$ requires *m/z* 220.1286, found 219.8657.

2-(Benzylthio)pyrimidine (**4m**). Colorless oil. 177 mg (0.876 mmol, 87.6% yield). ^{1}H NMR: δ 8.46 (d, $J = 4.9$ Hz, 2H), 7.37 (d, $J = 7.2$ Hz,2H), 7.26–7.13 (m, 3H), 6.98 (t, $J = 4.9$ Hz, 1H), 4.37 (s, 1H); ^{13}C NMR: δ 172.81, 158.49, 138.82, 129.97, 129.39, 128.13, 117.98, 35.86; HRMS (EI) calcd. for $[C_{11}H_{10}N_2S+ H]^+$ requires *m/z* 202.0565, found 201.9377.

5-(Benzylthio)pyrimidine (**4n**). Yellow oil. 87 mg (0.43 mmol, 79.2% yield). ^{1}H NMR: δ 8.92 (s, 1H), 8.60 (s, 2H), 7.29–7.17 (m, 5H), 4.19 (s, 1H); ^{13}C NMR: δ 159.10, 156.80, 137.85, 130.05, 129.64, 128.61, 38.94; HRMS (EI) calcd. for $[C_{11}H_{10}N_2S+ H]^+$ requires *m/z* 202.0565, found 201.8482.

(*E*)-Benzyl(styryl)sulfane (**4o**). White solid. 193 mg (0.856 mmol, 85.6% yield). ^{1}H NMR: δ 7.45–7.11 (m, 10H), 6.83 (d, $J = 15.6$ Hz, 0.5H), 6.48 (d, $J = 15.6$ Hz, 0.5H), 6.38 (d, $J = 11.0$ Hz, 0.5H), 6.31 (d, $J = 11.0$ Hz, 0.5H), 4.01 (d, $J = 8.3$ Hz, 2H).(E:Z = 1:1); ^{13}C NMR: δ 139.37, 139.11, 138.51, 138.48, 130.03, 129.96, 129.68, 129.61, 129.55, 129.40, 129.12, 128.59, 128.26, 128.19, 127.86, 127.55, 127.51, 126.53, 126.37, 125.87, 40.09, 37.84; HRMS (EI) calcd. for $[C_{15}H_{14}S + H]^+$ requires *m/z* 226.0816, found 225.8458.

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