Journal of Chemical Crystallography
https://doi.org/10.1007/s10870-020-00859-w

ORIGINAL PAPER

Methods, Syntheses and Characterization of Diaryl, Aryl Benzyl, and Dibenzyl Sulfides

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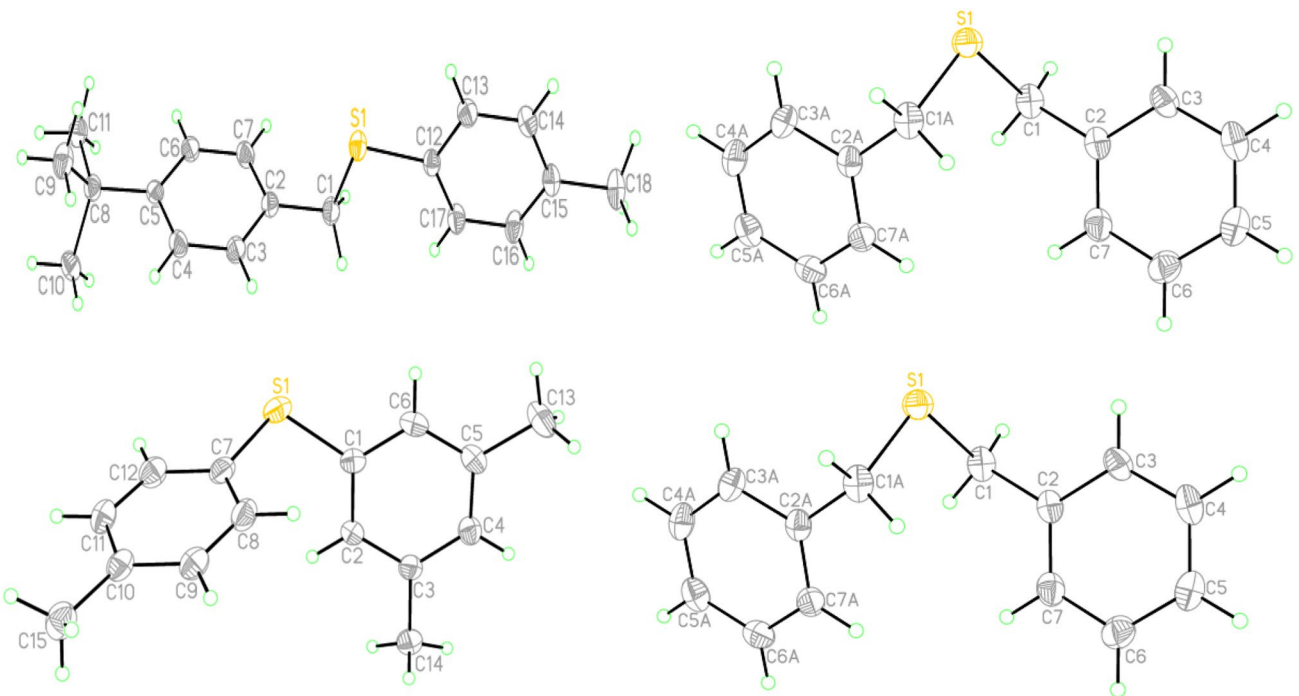
Received: 7 May 2020 / Accepted: 25 August 2020

Abstract

Twenty-four aryl benzyl sulfides, diaryl sulfides and dibenzyl sulfides were synthesized by four methods and characterized by ^{1}H NMR, FT-IR and Gas chromatography. The reaction conditions of different synthesis methods were studied from the aspects of time, solvent, base and dispersant. The molecular structures of benzylphenyl sulfide (**2S**), (4-*tert*-butylbenzyl) (4-methylphenyl) sulfide (**4S**), (4-methylbenzyl)(4-methylphenyl) sulfide (**9S**), di(4-methylphenyl) sulfide (**11S**), (3,5-dimethylphenyl)(4-methyl phenyl) sulfide (**15S**), and dibenzyl sulfide (**19S**) [22] have been determined by single-crystal X-ray crystallography. Compounds **2S** and **15S** crystallize in the monoclinic space group $P2_1/c$, with $a = 12.278(3)$, $b = 15.894(3)$, $c = 5.6056(11)$ Å, $\beta = 94.532(2)°$, and $Z = 4$ for **2S**, and $a = 9.800(9)$, $b = 7.950(7)$, $c = 16.690(15)$ Å, $\beta = 100.890(12)°$, and $Z = 4$ for **15S**. The unit cell of **4S** has a triclinic $P\bar{1}$ symmetry with the cell parameters $a = 6.0436(10)$, $b = 8.7871(14)$, $c = 15.535(2)$ Å, $\alpha = 81.921(2)°$, $\beta = 81.977(2)°$, $\gamma = 80.889(2)°$, and $Z = 2$. Compounds **9S** and **11S** both crystallize in the orthorhombic space group $P2_12_12_1$, with $a = 6.188(3)$, $b = 8.041(4)$, $c = 26.005(14)$ Å, and $Z = 4$ for **9S**, and $a = 5.835(2)$, $b = 8.010(3)$, $c = 25.131(9)$ Å, and $Z = 4$ for **11S**.

Graphic Abstract

Twenty-four aryl sulfide compounds with different substituents were synthesized and characterized, and the molecular structures of six different sulfide compounds have been determined by single-crystal X-ray crystallography.



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Published online: 31 August 2020

Keywords Aryl benzyl sulfide · Diaryl sulfide · Dibenzyl sulfide · Synthesis · Characterization · Crystal structure

Introduction

Sulfides (R-S-R), the R group can be various functional groups, such as alkyl, alkenyl, alkynyl, aryl and benzyl. They are useful starting materials for the synthesis of many organic compounds [1, 2]. Typically, they can be oxidized into sulfoxides or sulfones, which have received extensive attention as essentially synthetic intermediates in some important organic molecule syntheses, such as lansoprazole and omeprazole [3–5]. Due to the diversity of its own functional groups and the substitution of different functional groups, such as nitro, amino, chloro and alkyl, the free combination makes a wide range of sulfides, accordingly their synthetic methods are different. However, traditional methods for formation of C–S bond have some problems such as tedious reaction operation, unfriendly ecological environment, excessive raw materials, high toxicity and expensive catalysts [6]. Recently, several new synthetic methods of sulfides have been explored [7, 8]. Herein, we report four methods for the syntheses of twenty-four diaryl sulfides, aryl benzyl sulfides, and dibenzyl sulfides based on literature methods [9–12]. And the reaction conditions of different synthesis methods were studied from the aspects of time, solvent, base and dispersant to improve the reaction yield. It is found that thirteen diaryl sulfides and dibenzyl sulfides could be synthesized in a quantitative yield by the following method: 5 mol% CuI as a catalyst, PEG_{400} as a reaction medium, iodobenzene/benzyl bromide and tolthiol/benzylthiol as the reactant at a molar ratio of 1:1 at 120 °C. This method is simple, environment friendly, and economical. The synthesized twenty-four diaryl sulfides, aryl benzyl sulfides, and dibenzyl sulfides were characterized by ^{1}H NMR, FT-IR and Gas chromatography, of which the structures of six sulfides were established by X–ray crystallography in this paper.

Experimental

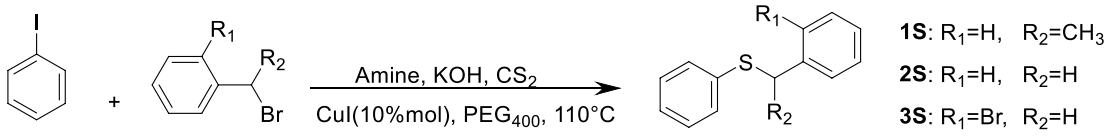
General Considerations

All syntheses were carried out under nitrogen by standard Schlenk techniques. Iodobenzene, 2-iodotoluene, 3-iodotoluene, 4-iodotoluene, 2,4-dimethyliodobenzene, 3,5-dimethyliodobenzene, benzyl bromide, 2-bromobenzyl bromide, 2-methylbenzyl bromide, 3-methylbenzyl bromide, 4-methylbenzyl bromide, 4-*tert*-butylbenzyl bromide, (1-bromoethyl)benzene, bromobenzene, 4-bromotoluene, *p*-toluenethiol, benzylthiol, 1-ethyl-4-iodobenzene, 4-iodoanisole, CuI, $Pd(PPh_3)_4$ and PEG_{400} were purchased from Alfa Aesar Ltd. and used without further purification. ^{1}H NMR spectra were recorded on a Bruker ALX 400 spectrometer. The ^{1}HNMR measurements were performed at room temperature. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^{1}H). Infrared spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer using KBr pellets. Gas chromatography analyses were performed with an FID detector on a Shimadzu GC-2010 Plus spectrometer using the RTX-5 column (15 m × 0.25 mm, film thickness 0.25 μm). The initial temperature of the column was 110 °C and increased to 260 °C with a rate of 20 °C min^{-1}.

Synthesis by Method A (See Scheme 1) [9]

Phenyl(1-Phenylethyl) Sulfide (1S)

A solution of CS_2 (0.92 g, 12 mmol), NaOH (10% aq. solution, 10 mL) and diethylamine (1.2 mL, 12 mmol) were stirred for 1 h at room temperature. CuI (0.19 g, 0.99 mmol, 10% mol), iodobenzene (2.0 g, 10 mmol) and PEG_{400} (20 mL) were added, and the reaction mixture was stirred



Scheme 1 Synthesis of aryl benzyl sulfides 1S–3S

at reflux. After 15 h, KOH (2.2 g, 40 mmol) was added and the mixture was stirred at 110 °C for 4 h. After cooling, (1-bromoethyl)benzene (2.8 g, 15 mmol) was added to the solution, which was stirred at room temperature for 1 h, and the reaction solution was diluted with water (20 mL) and further extracted with ethyl acetate (10 mL × 2). The solvent was removed in *vacuo*, and the residue was washed by cool diethyl ether (8 mL × 3). Yield: 50%. GC: purity 93.4%, t_R = 4.708 min. IR (cm^{-1}): 1175 *v*(–S–Ar), 836 *v*(–CH(CH_3)–S–). ^{1}H NMR (400 MHz, C*D*Cl_3) *δ* (ppm): 1.61 (d, *J* = 7.2 Hz, 3H, CH_3), 4.35 (q, *J* = 21 Hz, 1H, C*H*), 7.05 (d, *J* = 8.0 Hz, 2H, Ar–*H*), 7.19–7.27 (m, 8H, Ar–*H*).

Benzylphenyl Sulfide (2S)

The method was similar to that used for **1S**, employing benzyl bromide (2.6 g, 15 mmol) instead of (1-bromoethyl)benzene. Colorless crystals suitable for X-ray diffraction were obtained by slow evaporation of its dichloromethane/methanol solution (v:v = 2:5) at room temperature in five days. Yield: 67%. GC: purity 96.0%, t_R = 4.161 min. IR (cm^{-1}): 1171 *v*(–S–Ar), 839 *v*(–CH_2–S–). ^{1}H NMR (400 MHz, C*D*Cl_3) *δ* (ppm): 4.10 (s, 2H, CH_2), 7.16–7.30 (m, 10H, Ar–*H*).

(2-Bromobenzyl)phenyl Sulfide (3S)

The method was similar to that used for **1S**, employing 2-bromobenzyl bromide (3.8 g, 15 mmol) instead of (1-bromoethyl)benzene. Yield: 60%. GC: purity 93.5%, t_R = 8.263 min. IR (cm^{-1}): 1180 *v*(–S–Ar), 835 *v*(–CH_2–S–). ^{1}H NMR (400 MHz, C*D*Cl_3) *δ* (ppm): 4.21 (s, 2H, CH_2), 7.09–7.34 (m, 8H, Ar–*H*), 7.54 (d, *J* = 8.0 Hz, 1H, Ar–*H*).

Synthesis by Method B (See Scheme 2) [10]

(4-Tert-Butylbenzyl)(4-Methylphenyl) Sulfide (4S)

To a solution of THF (30 mL) was added sodium *p*-tolylthiolate (0.90 g, 6.0 mmol) and 4-*tert*-butylbenzyl bromide (1.1 g, 5.0 mmol), which was then stirred at reflux for 6 h. After cooling and extraction with dichloromethane (10 mL × 2), the solvent was removed in *vacuo*, and the residue was washed with cool methanol. Crystals suitable for X-ray diffraction were obtained by slow evaporation of its dichloromethane/methanol solution (v:v = 1:3) at room temperature in three days. Yield: 75%. GC: purity 100%, t_R = 6.347 min. IR (cm^{-1}): 1173 *v*(–S–Ar), 831 *v*(–CH_2–S–). ^{1}H NMR (400 MHz, C*D*Cl_3) *δ* (ppm): 1.30 (s, 9H, (CH_3)$_3$), 2.31 (s, 3H, CH_3), 4.06 (s, 2H, CH_2), 7.06–7.31 (m, 8H, Ar–*H*).

Benzyl(4-Methylphenyl) Sulfide (5S)

The method was similar to that used for **4S**, employing benzyl bromide (0.86 g, 5.0 mmol) instead of 4-*tert*-butylbenzyl bromide. Yield: 70%. GC: purity 100%, t_R = 8.401 min. IR (cm^{-1}): 1179 *v*(–S–Ar), 835 *v*(–CH_2–S–). ^{1}H NMR (400 MHz, C*D*Cl_3) *δ* (ppm): 2.31 (s, 3H, CH_3), 4.16 (s, 2H, CH_2), 7.08–7.25 (m, 9H, Ar–*H*).

(2-Bromobenzyl)(4-Methylphenyl) Sulfide (6S)

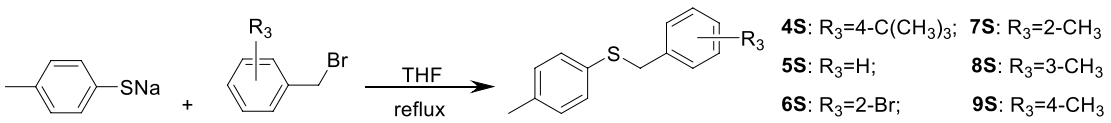
The method was similar to that used for **4S**, employing 2-bromobenzyl bromide (1.3 g, 5.0 mmol) instead of 4-*tert*-butylbenzyl bromide. Yield: 78%. GC: purity 98.4%, t_R = 7.472 min. IR (cm^{-1}): 1175 *v*(–S–Ar), 837 *v*(–CH_2–S–). ^{1}H NMR (400 MHz, C*D*Cl_3) *δ* (ppm): 2.33 (s, 3H, CH_3), 4.07 (s, 2H, CH_2), 7.08–7.26 (m, 8H, Ar–*H*).

(2-Methylbenzyl)(4-Methylphenyl) Sulfide (7S)

The method was similar to that used for **4S**, employing 2-methylbenzyl bromide (0.93 g, 5.0 mmol) instead of 4-*tert*-butylbenzyl bromide. Yield: 65%. GC: purity 100%, t_R = 7.398 min. IR (cm^{-1}): 1172 *v*(–S–Ar), 840 *v*(–CH_2–S–). ^{1}H NMR (400 MHz, C*D*Cl_3) *δ* (ppm): 2.38 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 4.00 (s, 2H, CH_2), 7.05–7.22 (m, 8H, Ar–*H*).

(3-Methylbenzyl)(4-Methylphenyl) Sulfide (8S)

The method was similar to that used for **4S**, employing 3-methylbenzyl bromide (0.93 g, 5.0 mmol) instead of 4-*tert*-butylbenzyl bromide. Yield: 87%. GC: purity 99.4%, t_R = 7.410 min. IR (cm^{-1}): 1176 *v*(–S–Ar), 833 *v*(–CH_2–S–). ^{1}H NMR (400 MHz, C*D*Cl_3) *δ* (ppm): 2.32 (s, 3H, Ar–CH_3), 2.37 (s, 3H, CH_3), 4.05 (s, 2H, CH_2), 7.04–7.24 (m, 8H, Ar–*H*).



Scheme 2 Synthesis of aryl benzyl sulfides 4S–9S

(4-Methylbenzyl)(4-Methylphenyl) Sulfide (9S)

The method was similar to that used for **4S**, employing 4-methylbenzyl bromide (0.93 g, 5.0 mmol) instead of 4-*tert*-butylbenzyl bromide. Crystals suitable for X-ray diffraction were obtained by slow evaporation of its dichloromethane/methanol solution (v:v = 1:3) at room temperature in three days. Yield: 73%. GC: purity 99.5%, t_R = 7.403 min. IR (cm^{-1}): 1173 *v*(–S–Ar), 835 *v*(–CH_2–S–). ^{1}H NMR (400 MHz, C*D*Cl_3) *δ* (ppm): 2.35 (s, 3H, Ar–CH_3), 2.30 (s, 3H, CH_3), 4.03 (s, 2H, CH_2), 7.05–7.29 (m, 8H, Ar–*H*).

Synthesis by Method C (See Scheme 3) [11]

Phenyl(4-Methylphenyl) Sulfide (10S)

A mixture of $Pd(PPh_3)_4$ (0.46 g, 0.40 mmol), bromobenzene (1.6 g, 10 mmol) and tolthiol (0.70 g, 6.0 mmol) were stirred in methanol for 6 h at reflux. After cooling, the solution was filtered, and the filtrate was washed with water (10 mL × 2) and further extracted with dichloromethane (10 mL × 3). After removal of solvents in *vacuo*, a white powder was obtained. Yield: 65%. GC: purity 95.4%, t_R = 6.382 min. IR (cm^{-1}): 1180 *v*(–S–Ar). ^{1}H NMR (400 MHz, C*D*Cl_3) *δ* (ppm): 2.33 (s, 3H, CH_3), 7.12–7.30 (m, 9H, Ar–*H*).

Di(4-Methylphenyl) Sulfide (11S)

The method was similar to that used for **10S**, employing 4-bromotoluene (1.7 g, 10 mmol) instead of bromobenzene. Crystals suitable for X-ray diffraction were obtained by slow evaporation of its dichloromethane/methanol solution (v:v = 1:3) at room temperature in five days. Yield: 60%. GC: purity 90.0%, t_R = 4.796 min. IR (cm^{-1}): 1179 *v*(–S–Ar). ^{1}H NMR (400 MHz, C*D*Cl_3) *δ* (ppm): 2.32 (s, 6H, CH_3), 7.09–7.26 (m, 8H, Ar–*H*).

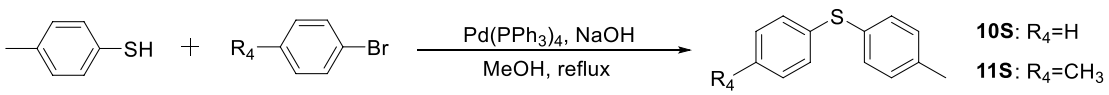
Synthesis by Method D (See Scheme 4) [12]

(2-Methylphenyl)(4-Methylphenyl) Sulfide (12S)

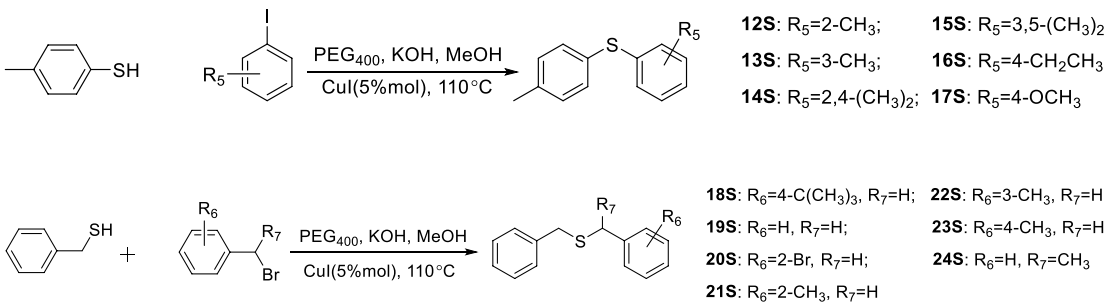
A mixture of *p*-toluenethiol (1.2 g, 10 mmol), KOH (2.2 g, 40 mmol), PEG_{400} (20 mL) were stirred in methanol at 70 °C for 15 min. Then 2-iodotoluene (2.2 g, 10 mmol) and CuI (0.10 g, 5% mol) were added, and the reaction mixture was stirred at 110 °C for 12 h. After cooling and extraction with hexane (10 mL × 6), the solvent was removed in *vacuo* and the desired product was obtained. Yield: 100%. GC: purity 97.8%, t_R = 6.839 min. IR (cm^{-1}): 1183 *v*(–S–Ar). ^{1}H NMR (400 MHz, C*D*Cl_3) *δ* (ppm): 2.33 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 7.10–7.23 (m, 8H, Ar–*H*).

(3-Methylphenyl)(4-Methylphenyl) Sulfide (13S)

The method was similar to that used for **12S**, employing 3-iodotoluene (2.2 g, 10 mmol) instead of 2-iodotoluene. Yield: 100%. GC: purity 97.3%, t_R = 6.927 min. IR (cm^{-1}):



Scheme 3 Synthesis of diaryl sulfides 10S and 11S



Scheme 4 Synthesis of diaryl sulfides 12S–17S and dibenzyl sulfides 18S–24S

1178 ν(–S–Ar). ^{1}H NMR (400 MHz, C*D*Cl$_3$) δ (ppm): 2.22 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 6.89–7.23 (m, 8H, Ar–*H*).

(2,4-Dimethylphenyl)(4-Methylphenyl) Sulfide (14S)

The method was similar to that used for **12S**, employing 2,4-dimethyliodobenzene (2.3 g, 10 mmol) instead of 2-iodotoluene. Yield: 100%. GC: purity 94.5%, t_R = 7.424 min. IR (cm^{-1}): 1180 ν(–S–Ar). ^{1}H NMR (400 MHz, C*D*Cl$_3$) δ (ppm): 2.31 (s, 6H, CH_3), 2.34 (s, 3H, CH_3), 6.94–7.26 (m, 7H, Ar–*H*).

(3,5-Dimethylphenyl)(4-Methylphenyl) Sulfide (15S)

The method was similar to that used for **12S**, employing 3,5-dimethyliodobenzene (2.3 g, 10 mmol) instead of 2-iodotoluene. Crystals suitable for X-ray diffraction were obtained by slow evaporation of its dichloromethane/methanol solution (v:v = 1:3) at room temperature in four days. Yield: 100%. GC: purity 100%, t_R = 5.168 min. IR (cm^{-1}): 1175 ν(–S–Ar). ^{1}H NMR (400 MHz, C*D*Cl$_3$) δ (ppm): 2.25 (s, 6H, CH_3), 2.34 (s, 3H, CH_3), 6.84–7.28 (m, 7H, Ar–*H*).

(4-Ethylphenyl)(4-Methylphenyl) Sulfide (16S)

The method was similar to that used for **12S**, employing 1-ethyl-4-iodobenzene (2.3 g, 10 mmol) instead of 2-iodotoluene. Yield: 100%. GC: purity 99.4%, t_R = 7.567 min. IR (cm^{-1}): 1181 ν(–S–Ar). ^{1}H NMR (400 MHz, C*D*Cl$_3$) δ (ppm): 1.22 (t, J = 15 Hz, 3H,–CH$_2$CH_3), 2.32 (s, 3H, Ar–CH_3), 2.65 (q, J = 22 Hz, 2H,–CH_2CH$_3$), 7.10–7.13 (m, 4H, Ar–*H*), 7.23–7.24 (m, 4H, Ar–*H*).

(4-Methoxyphenyl)(4-Methylphenyl) Sulfide (17S)

The method was similar to that used for **12S**, employing 4-iodoanisole (2.3 g, 10 mmol) instead of 2-iodotoluene. Yield: 100%. GC: purity 94.7%, t_R = 5.644 min. IR (cm^{-1}): 1179 ν(–S–Ar), 1253 ν(–O–CH$_3$). ^{1}H NMR (400 MHz, C*D*Cl$_3$) δ (ppm): 2.22 (s, 3H, Ar–CH_3), 3.73 (s, 3H,–OCH_3), 6.78–7.29 (m, 8H, Ar–*H*).

(4-Tert-Butylbenzyl)Benzyl Sulfide (18S)

The method was similar to that used for **12S**, employing benzylthiol (1.2 g, 10 mmol) instead of *p*-toluenethiol, 4-*tert*-butylbenzyl bromide (2.3 g, 10 mmol) instead of 2-iodotoluene. Yield: 97.5%. GC: purity 97.5%, t_R = 6.507 min. IR (cm^{-1}): 837 ν(–CH$_2$–S–). ^{1}H NMR (400 MHz, C*D*Cl$_3$) δ (ppm): 1.32 (s, 9H, CH_3), 3.58 (s, 2H, CH_2), 3.61 (s, 2H, CH_2), 7.13–7.32 (m, 9H, Ar–*H*).

Dibenzyl Sulfide (19S)

The method was similar to that used for **18S**, employing benzyl bromide (1.7 g, 10 mmol) instead of 4-*tert*-butylbenzyl bromide. Crystals suitable for X-ray diffraction were obtained by slow evaporation of its dichloromethane/methanol solution (v:v = 1:3) at room temperature in four days. Yield: 100%. GC: purity 100%, t_R = 4.837 min. IR (cm^{-1}): 835 ν(–CH$_2$–S–). ^{1}H NMR (400 MHz, C*D*Cl$_3$) δ (ppm): 3.60 (s, 4H, CH_2), 7.22–7.37 (m, 10H, Ar–*H*).

(2-Bromobenzyl)Benzyl Sulfide (20S)

The method was similar to that used for **18S**, employing 2-bromobenzyl bromide (2.5 g, 10 mmol) instead of 4-*tert*-butylbenzyl bromide. Yield: 99.0%. GC: purity 99.0%, t_R = 6.973 min. IR (cm^{-1}): 839 ν(–CH$_2$–S–). ^{1}H NMR (400 MHz, C*D*Cl$_3$) δ (ppm): 3.69 (s, 2H, CH_2), 3.74 (s, 2H, CH_2), 7.11–7.33 (m, 8H, Ar–*H*), 7.56 (d, J = 8.0 Hz, 1H, Ar–*H*).

(2-Methylbenzyl)Benzyl Sulfide (21S)

The method was similar to that used for **18S**, employing 2-methylbenzyl bromide (1.9 g, 10 mmol) instead of 4-*tert*-butylbenzyl bromide. Yield: 93.2%. GC: purity 93.2%, t_R = 5.398 min. IR (cm^{-1}): 833 ν(–CH$_2$–S–). ^{1}H NMR (400 MHz, C*D*Cl$_3$) δ (ppm): 2.30 (s, 3H, CH_3), 3.60 (s, 2H, CH_2), 3.66 (s, 2H, CH_2), 7.14–7.32 (m, 9H, Ar–*H*).

(3-Methylbenzyl)Benzyl Sulfide (22S)

The method was similar to that used for **18S**, employing 3-methylbenzyl bromide (1.9 g, 10 mmol) instead of 4-*tert*-butylbenzyl bromide. Yield: 94.5%. GC: purity 94.5%, t_R = 5.304 min. IR (cm^{-1}): 836 ν(–CH$_2$–S–). ^{1}H NMR (400 MHz, C*D*Cl$_3$) δ (ppm): 2.35 (s, 3H, CH_3), 3.58 (s, 2H, CH_2), 3.62 (s, 2H, CH_2), 7.13–7.32 (m, 9H, Ar–*H*).

(4-Methylbenzyl)Benzyl Sulfide (23S)

The method was similar to that used for **18S**, employing 4-methylbenzyl bromide (1.9 g, 10 mmol) instead of 4-*tert*-butylbenzyl bromide. Yield: 93.5%. GC: purity 93.5%, t_R = 5.401 min. IR (cm^{-1}): 835 ν(–CH$_2$–S–). ^{1}H NMR (400 MHz, C*D*Cl$_3$) δ (ppm): 2.36 (s, 3H, CH_3), 3.58 (s, 2H, CH_2), 3.61 (s, 2H, CH_2), 7.13–7.33 (m, 9H, Ar–*H*).

Benzyl(1-Phenylethyl) Sulfide (24S)

The method was similar to that used for **18S**, employing (1-bromoethyl)benzene (1.9 g, 10 mmol) instead of 4-*tert*-butylbenzyl bromide. Yield: 100%. GC: purity 100%,

t_R = 4.848 min. IR (cm^{-1}): 835 ν(–CH(CH_3)–S–). ^{1}H NMR (400 MHz, C*D*Cl_3) δ (ppm): 1.54 (d, J = 18 Hz, 3H, CH_3), 3.50 (s, 2H, CH_2), 3.81 (q, J = 14 Hz, 1H, C*H*), 7.21–7.32 (m, 10H, Ar–*H*).

X-Ray Crystallography

A summary of crystallographic data and experimental details for compounds **2S**, **4S**, **9S**, **11S**, **15S**, and **19S** is summarized in Table 1. Intensity data were collected on a Bruker SMART APEX 2000 CCD diffractometer using graphite-monochromated Mo–Kα radiation (λ = 0.71073 Å) at 296(2) K. The collected frames were processed with the software SAINT [13]. The data was corrected for absorption using the program SADABS [14]. Structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [15, 16]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C_{sp3}–H = 0.96 Å and C_{sp2}–H = 0.93 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon atoms before the final cycle of least-squares refinement.

Results and Discussion

Firouzabadi and coworkers [9] presented a one-pot preparation of aryl benzyl sulfides employing CS_2 as the sulfur surrogate, and CuI as the catalyst in PEG_{200}. However, PEG_{200} was expensive and products were difficult to extract from it. In this paper, PEG_{400} was used as the dispersant, which was cheaper and easier to separate than PEG_{200}. Method A: as shown in Scheme 1, the reaction of different substituted benzyl bromide and iodobenzene in the presence of CS_2 at reflux afforded aryl benzyl sulfides **1S**–**3S**, after repeated several times, the experiment results showed that the yield could achieve 67%, comparable to the yields reported by Firouzabadi (70%). O'Mahony [10] reported the synthesis of aryl benzyl sulfides by reacting sodium *p*-tolylthiolate

Table 1 Crystallographic data and experimental details for complexes

Complex	**2S**	**4S**	**9S**	**11S**	**15S**	**19S**
Empirical formula	$C_{13}H_{12}S$	$C_{18}H_{22}S$	$C_{15}H_{16}S$	$C_{14}H_{14}S$	$C_{15}H_{16}S$	$C_{14}H_{14}S$
Formula weight	200.29	270.42	228.34	214.31	228.34	214.31
Crystal system	Monoclinic	Triclinic	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
a (Å)	12.278(3)	6.0436(10)	6.188(3)	5.835(2)	9.800(9)	14.169(13)
b (Å)	15.894(3)	8.7871(14)	8.041(4)	8.010(3)	7.950(7)	11.476(10)
c (Å)	5.6056(11)	15.352(2)	26.005(14)	25.131(9)	16.690(15)	7.300(7)
α (°)		81.921(2)				
β(°)	94.532(2)	81.977(2)			100.890(12)	
γ (°)		80.889(2)				
V (Å^3)	1090.5(4)	791.2(2)	1293.9(12)	1174.6(8)	1277(2)	1187.0(18)
Space group	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$	$Pbcn$
Z	4	2	4	4	4	4
D_{calc} (g cm^{-3})	1.220	1.135	1.172	1.212	1.188	1.199
Temperature (K)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
F(000)	424	292	488	456	488	456
μ(Mo-Kα) (mm^{-1})	0.253	0.190	0.221	0.239	0.224	0.236
Total refln	6659	4922	7761	7215	7673	6327
Independent refln	2469	3486	2931	2642	2945	1336
R_{int}	0.0233	0.0174	0.0322	0.0232	0.0287	0.0350
$R1$[a],$wR2$[b]($I > 2\sigma(I)$)	0.0364, 0.0926	0.0408, 0.1047	0.0469, 0.1116	0.0333, 0.0845	0.0486, 0.1389	0.0398, 0.1039
$R1$, $wR2$ (all data)	0.0486, 0.1006	0.0517, 0.1143	0.0979, 0.1376	0.0399, 0.0892	0.0783, 0.1608	0.0664, 0.1157
GoF[c]	1.026	1.033	1.024	1.039	1.023	1.021
Flack parameter	–	–	− 0.10(14)	0.04(8)	–	-

[a] $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$

[b] $wR2 = \left[\sum w\left(|F_o^2| - |F_c^2|\right)^2 \Big/ \sum w|F_o^2|^2 \right]^{1/2}$

[c] $\text{GoF} = \left[\sum W\left(|F_o| - F_c\right)^2 \Big/ N_{obs} - N_{param} \right]^{1/2}$

with substituted benzyl bromide, the reaction time was 16 h, and the highest yield was only 50%. We changed the solvent, as shown in Method B (Scheme 2), THF was used as the solvent, the reaction time shortened to be 8 h, and the yield of compounds **4S**–**9S** was up to 87%. Migita and coworkers [11] reported a traditional palladium-based catalytic reaction, and a series of diaryl sulfides were synthesized (11%–59%). However, the solvent they used were DMSO and DMF, which was difficult to remove. In Method C, we selected methanol as the solvent, which was easy to remove and much cheaper. As shown in Scheme 3, bromobenzene and tolthiol were reacted in methanol at reflux for 6 h catalyzed by $Pd(PPh_3)_4$ afforded diaryl sulfides **10S** and **11S** (60%–65%). Wang and coworkers [12] reported the synthesis of diaryl and dibenzyl sulfides catalyzed by CuI, PEG_{1000} was used as the dispersant and K_3PO_4 was used as the base. Although PEG_{1000} was cheaper than PEG_{400}, it also has a higher viscosity and hard to process. Besides, we found that when KOH was used as the base, the catalytic efficiency of the reaction was higher. So in Method D, we selected PEG_{400} as the dispersant and KOH as the base, as shown in Scheme 4, reaction of substituted iodobenzene/benzyl bromide and tolthiol/benzylthiol gave diaryl sulfides **12S**–**17S** (100%) and dibenzyl sulfides **18S**–**24S** (93.2%–100%) in high yields. In addition, the manipulations of Method D were simple, and the product could be obtained in a one-pot reaction, which was obviously economical and applicable.

The infrared spectra of aryl benzyl sulfides **1S**–**9S** and diaryl sulfides **10S**–**17S** showed–S–Ar peaks at around 1176 cm^{-1}. The aryl benzyl sulfides **1S**–**9S** and dibenzyl sulfides **18S**–**24S** showed–CH_2–S–or–$CH(CH_3)$–S–peaks at about 835 cm^{-1} [17, 18]. The ^1H NMR spectra of compounds **2S**–**9S**, **18S**–**24S** all showed -CH_2–S- protons as a single peak ranging from 4.00–4.21 ppm, which are comparable to those in the related compounds [19]. The signal of a -C*H*(CH_3)–S- proton in compound **1S** showed a doublet at 1.61 ppm with $J = 7.2$ Hz, while the –CH(C*H*$_3$)–S- protons in dibenzyl sulfide **24S** showed a doublet at 1.54 ppm with $J = 14$ Hz. GC analysis showed that the average retention time of aryl benzyl sulfide compounds (6.840 min) was normally longer than those of diaryl sulfide compounds (6.343 min) and dibenzyl sulfide compounds (5.610 min), and the isomers of **21S**, **22S** and **23S** have almost the same retention time: 5.398, 5.304 and 5.401 min, respectively, indicating that *o*-, *m*-, or *p*-positions of a methyl group have little effect on the retention time of similar compounds.

Molecular structures and packing views of compounds **2S**, **4S**, **9S**, **11S**, **15S**, and **19S** were further confirmed by single crystal X-ray crystallography, as shown in Figs. 1, 2, 3, 4, 5, 6, respectively. Selected bond lengths and angles are given in Tables 2, 3, 4, 5, 6, 7. The C(sp^2)–S bond lengths in aryl benzyl sulfides **2S**, **4S** and **9S** are 1.7606(15), 1.7640(15), 1.752(4) Å, respectively, which are similar to

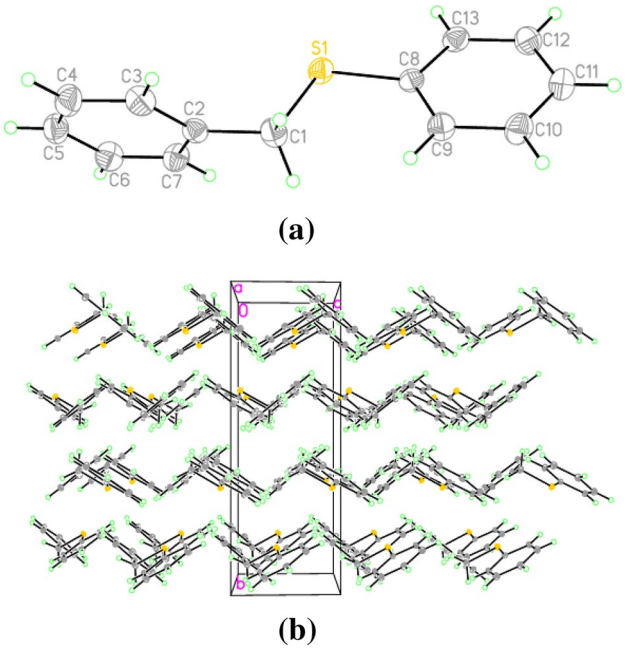


Fig. 1 **a** Molecular structure of benzylphenyl sulfide **2S**, showing the atom labeling scheme and 40% thermal ellipsoids. **b** Packing mode of compound **2S** projected along with *bc* plane

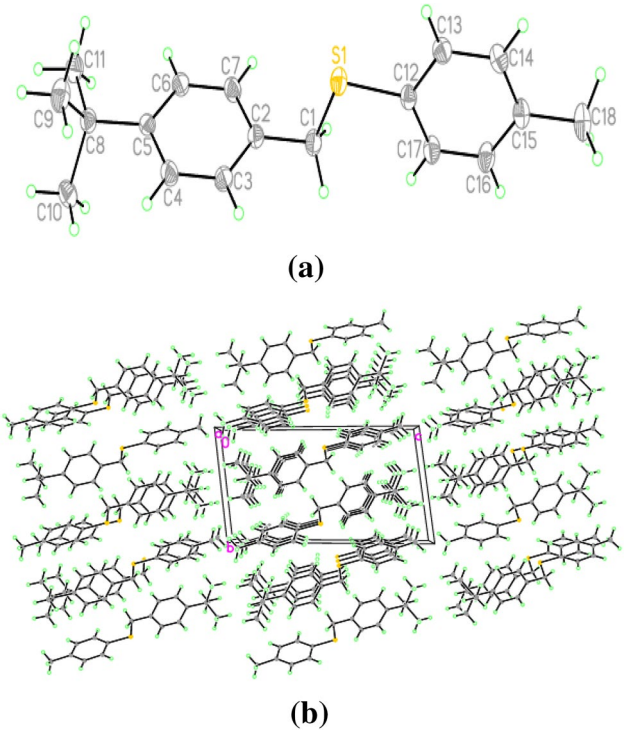


Fig. 2 **a** Molecular structure of (4-*tert*-butylbenzyl)(4-methylphenyl) sulfide **4S**, showing the atom labeling scheme and 40% thermal ellipsoids. **b** Packing mode of compound **4S** projected along with *bc* plane

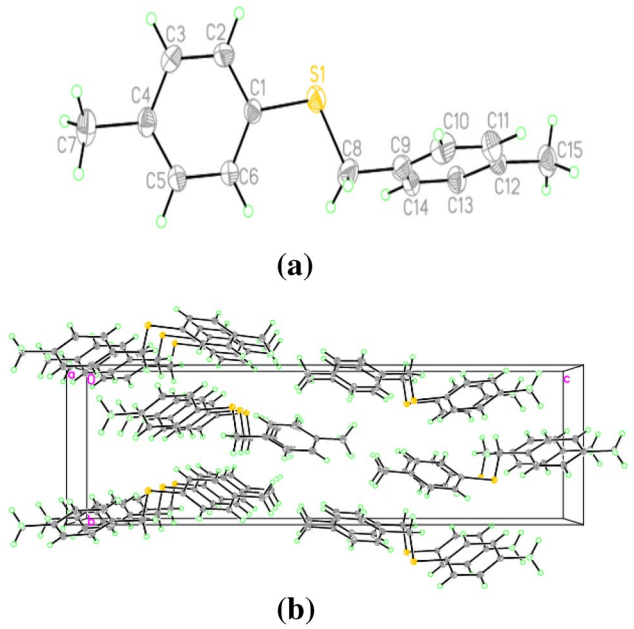


Fig. 3 **a** Molecular structure of (4-methylbenzyl)(4-methylphenyl) sulfide **9S**, showing the atom labeling scheme and 40% thermal ellipsoids. **b** Packing mode of compound **9S** projected along with *bc* plane

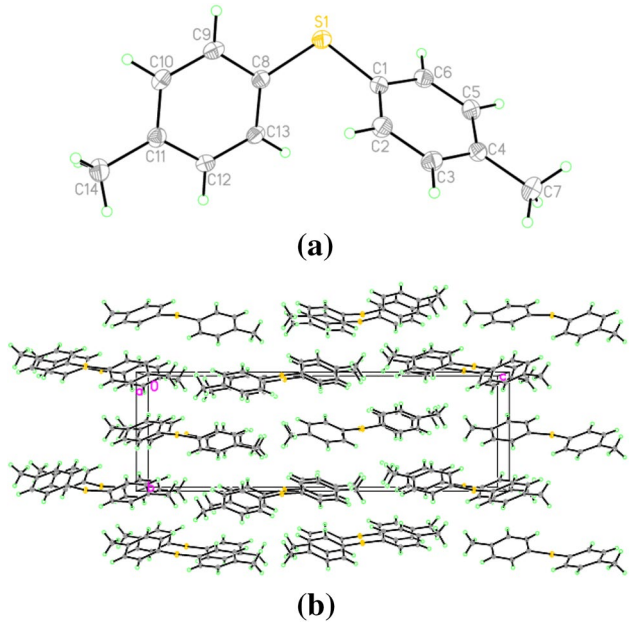


Fig. 4 **a** Molecular structure of di(4-methylphenyl) sulfide **11S**, showing the atom labeling scheme and 40% thermal ellipsoids. **b** Packing mode of compound **11S** projected along with *bc* plane

those in analogous compounds [20, 21], and a little shorter than the corresponding C(sp^3)–S bond lengths (1.8039(15) Å for **2S**, 1.8108(16) Å for **4S**, 1.760(3) Å for **9S**). The average C(sp^2)–S bond lengths are 1.7768(16) Å and 1.768(2) Å in diaryl sulfides **11S** and **15S**, respectively, which are

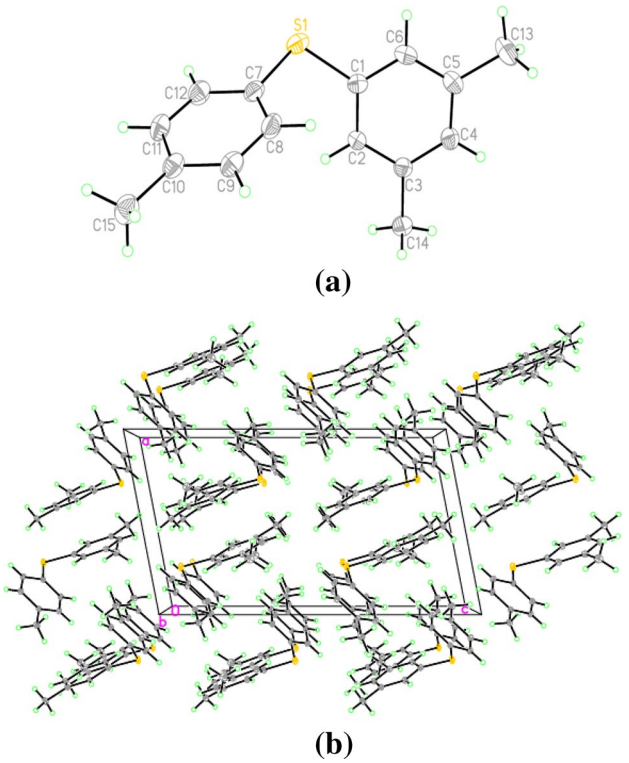


Fig. 5 **a** Molecular structure of (3,5-dimethylphenyl)(4-methylphenyl) sulfide **15S**, showing the atom labeling scheme and 40% thermal ellipsoids. **b** Packing mode of compound **15S** projected along with *ac* plane

compared to those in aryl benzyl sulfides **2S**, **4S** and **9S**. In dibenzyl sulfide compound **19S**, the C(sp^3)–S bond length is 1.798(2) Å, which is similar to the same structure reported by Hansson (1.8098(12) Å) [22]. The C(sp^3)–S–C(sp^3) bond angle is 101.67(14)° in dibenzyl sulfide **19S**, which agrees well to those in related dibenzyl sulfides (101.23(8)°) [20] and di-4-cyanobenzyl sulfide (101.64°) [23], smaller than those in aryl benzyl sulfides **2S** (103.94(7)°), **4S** (104.58(7)°), **9S** (104.84(14)°), and diaryl sulfides **11S** (104.65(8)°), and **15S** (104.58(9)°), which may be due to the steric hindrance of the two benzyl rings.

In summary, twenty-four sulfides were synthesized based on four synthetic methods and characterized by ^{1}H NMR, FT-IR and Gas chromatography. Six of the sulfides involving diaryl sulfide, aryl benzyl sulfide, and dibenzyl sulfide compounds were characterized by the single crystal X–ray diffraction analysis. Method A employing PEG_{400} as the dispersant to replace PEG_{200} could synthesize aryl benzyl sulfides **1S**–**3S** in a cheaper and easier way without decreasing the yields [9]. Method B using the solvent THF to replace dichloromethane-H_2O (v:v = 1:1) led to isolation of aryl benzyl sulfides **4S**–**9S** with improved yields (87% *vs.* 50%) [10]. Method C could be used to synthesize diaryl sulfides **10S** and **11S** in better yields by using methanol

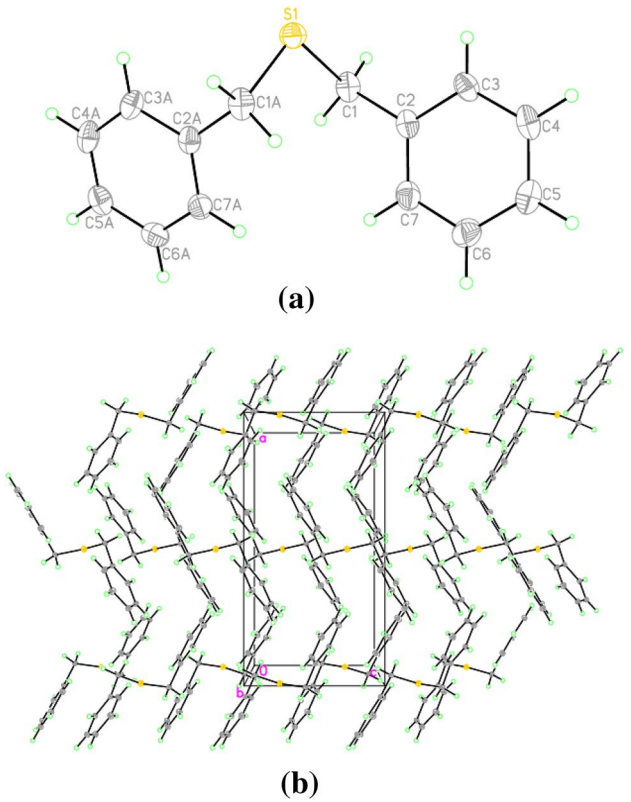


Fig. 6 **a** Molecular structure of dibenzyl sulfide **19S**, showing the atom labeling scheme and 40% thermal ellipsoids. **b** Packing mode of compound **19S** projected along with *ac* plane

Table 2 Selected bond lengths (Å) and angles (°) for benzylphenyl sulfide **2S**

S(1)–C(1)	1.8039(15)	C(8)–S(1)–C(1)	103.94(7)
S(1)–C(8)	1.7606(15)	C(2)–C(1)–S(1)	108.92(10)
C(1)–C(2)	1.507(2)		

Table 3 Selected bond lengths (Å) and angles (°) for (4-*tert*-butylbenzyl)(4-methylphenyl) sulfide **4S**

S(1)–C(1)	1.8108(16)	C(12)–S(1)–C(1)	104.58(7)
S(1)–C(12)	1.7640(15)	C(2)–C(1)–S(1)	107.57(11)
C(1)–C(2)	1.502(2)	C(4)–C(5)–C(8)	119.67(13)
C(5)–C(8)	1.528(2)	C(10)–C(8)–C(9)	109.20(15)
C(8)-C(9)	1.535(2)	C(14)–C(15)–C(18)	121.10(16)
C(14)-C(15)	1.387(2)		

Table 4 Selected bond lengths (Å) and angles (°) for (4-methylbenzyl)(4-methylphenyl) sulfide **9S**

S(1)–C(1)	1.752(4)	C(8)–S(1)–C(1)	104.84(14)
S(1)–C(8)	1.760(3)	C(2)–C(1)–S(1)	117.1(2)
C(4)–C(7)	1.524(4)	C(3)–C4)–C(7)	120.4(3)
C(8)–C(9)	1.499(4)	C(9)–C(8)–S(1)	110.2(2)
C(12)–C(15)	1.517(4)	C(11)–C(12)–C(15)	122.2(3)

Table 5 Selected bond lengths (Å) and angles (°) for di(4-methylphenyl) sulfide **11S**

S(1)–C(1)	1.7749(17)	C(1)–S(1)–C(8)	104.65(8)
S(1)–C(8)	1.7786(16)	C(5)–C(4)–C(7)	121.93(17)
C(4)–C(7)	1.509(2)	C(10)–C(11)–C(14)	121.26(16)
C(11)–C(14)	1.512(2)		

Table 6 Selected bond lengths (Å) and angles (°) for (3,5-dimethylphenyl)(4-methylphenyl) sulfide **15S**

S(1)–C(1)	1.770(2)	C(7)–S(1)–C(1)	104.58(9)
S(1)–C(7)	1.765(3)	C(4)–C(3)–C(14)	120.32(19)
C(3)–C(14)	1.504(3)	C(6)–C(5)–C(13)	121.1(2)
C(5)–C(13)	1.504(3)	C(9)–C(10)–C(15)	121.3(2)
C(10)–C(15)	1.498(3)		

Table 7 Selected bond lengths (Å) and angles (°) for dibenzyl sulfide **19S**

S(1)–C(1)	1.798(2)	C(1)–S(1)–C(1A)	101.67(14)
S(1)–C(1A)	1.798(2)	C(2)–C(1)–S(1)	114.87(11)
C(1)–C(2)	1.507(2)		

as the solvent [11]. Method D using PEG_{400} and KOH to replace PEG_{1000} and K_3PO_4 is an efficient method to synthesize diaryl sulfides **12S**–**17S** and dibenzyl sulfides **18S**–**24S** due to its quantitative yield and environment friendly [12].

Supplementary Material

Crystallographic data for a summary of crystallographic data and experimental details for benzylphenyl sulfide (**2S**), (4-*tert*-butylbenzyl)(4-methylphenyl) sulfide (**4S**), (4-methylbenzyl)(4-methylphenyl) sulfide (**9S**), di(4-methylphenyl) sulfide (**11S**), (3,5-dimethylphenyl)(4-methylphenyl) sulfide (**15S**) and dibenzyl sulfide (**19S**) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 2001056-2001061, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44)1233-336-033; e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements This project was supported by the National Natural Science Foundation of China (21372007).

Compliance with Ethical Standards

Conflict of Interests The authors declare that they have no conflict of interests.

References

1. Choghamarani AG, Seydyosefi Z, Tahmasbi B (2018) Appl Organomet Chem 32:e4396–4404
2. Ghaderi A (2016) Tetrahedron 72:4758–4782
3. Salom-Roig X, Bauder C (2020) Synthesis-Stuttgart 52(7): 964–978
4. Wojaczyńska E (2010) J Wojaczyński Chem Rev 110:4303–4356
5. Rozen S (2014) Acc Chem Res 47:2378–2389
6. Percec V, Bae JY, Hill DH (1995) J Org Chem 60(21):6895–6903
7. Choghamarani AG, Heidarnezhad Z, Tahmasbi B (2019) ChemistrySelect 4:8860–8869
8. Velasco N, Virumbrales C, Sanz R (2018) Organic Lett 20(10):2848–2852
9. Firouzabadi H, Iranpoor N, Samadi A (2014) Tetrahedron Lett 55:1212–1217
10. O'Mahony GE, Ford A, Maguire AR (2012) J Org Chem 77:3288–3296
11. Migita T, Shimizu T, Asami Y, Shiobara J, Kato Y, Kosugi M (1980) Bull Chem Soc Jpn 53:1385–1389
12. She J, Jiang Z, Wang YG (2009) Tetrahedron Lett 50:593–596
13. SMART and SAINT+ for Windows NT Version 6.02a. Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1998.
14. Sheldrick GM (1996) Sadabs. University of Göttingen, Göttingen, Germany
15. G.M. Sheldrick. Shelxtl (version 5.1), Software Reference Manual, Bruker AXS Inc., Madison, Wisconsin, USA, 1997.
16. Sheldrick GM (2015) Acta Cryst C 71:3–8
17. Zhang XY, Song HB, Li QS, Liu XF, Tang LF (2007) Polyhedron 26:3743–3749
18. Yan YG, Xie MJ, Chen YR, Wu QX, Yu ZL (1999) J. Sichuan Univ. (Nat. Sci. Ed.) 36(3):535–540
19. Gogoi P, Hazarika S, Sarma MJ, Barman P (2014) Tetrahedron 70(41):7484–7489
20. Ramirez AA, Cross ED, Bierenstiel M (2014) Dalton Trans 43(8):3104–3113
21. Kumar S, Kandasamy K, Singh HB, Butcher RJ (2004) New J Chem 28:640–645
22. Hansson C (2006) Acta Cryst E62:o2377–o2379
23. Lee E, Ju H, Kim S, Park KM, Lee SS (2015) Cryst. Growth Des 15(11):5427–5436

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