Benign and efficient preparation of thioethers by solvent-free S-alkylation of thiols with alkyl halides catalyzed by potassium fluoride on alumina

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ABSTRACT

The preparation of thioethers by S-alkylation of various thiols with alkyl halides under solvent-free reaction conditions using potassium fluoride on alumina (KF/Al\(_2\)O\(_3\)) as a solid catalyst has been investigated in detail with respect to three different modes of reaction activation (ultrasound irradiation, microwave irradiation, and conventional heating) for obtaining maximum yield of the thioether. The importance of KF/Al\(_2\)O\(_3\) as a particularly efficient catalyst was corroborated for all three modes of reaction activation, although the reaction time was found to be strongly dependent on the mode of activation. The yield of the thioethers was also found to depend on the amount of the solid catalyst relative to the equimolar amounts of the two reactants.

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1. Introduction

Thioethers (sulfides) are the sulfur analogs of ethers and constitute an important class of organosulfur compounds.[1,2] Thioethers have large applications, for example, as potential hypocholesterolemic agents,[3] antagonists of leukocyte function-associated antigen-1 (LFA-1),[4] nicotinic acetylcholine receptors,[5] precursors of sulfoxides and sulfones,[6–8] and in general useful synthetic reagents and/or intermediates in organic synthesis, agro-chemistry and heterocyclic chemistry.[9–12]
Many categories of thioethers are mainly synthesized by S-alkylation of thiols/thiolates with alkyl halides,[13–25] or with alcohols,[26–37] S-arylation (Ullmann cross-coupling) of thiols and aryl halides catalyzed by KF/alumina as base [38–40] or promoted by metal compounds/complexes,[41–48] and cleavage of disulfides to react with alkyl halides or alkyl tosylate.[49–53] However, the base-promoted S-alkylation of thiols with alkyl halides is the classical and most common method to produce thioethers. The previous works on the catalyst-free S-alkylation of thiols and alkyl halides illustrated that the presence of a catalyst is necessary in order to reduce the reaction time.[13] A variety of inorganic or organic base catalysts in the presence of phase transfer catalyst,[14–17] or solid supports have been investigated in solvent media.[18,19] Moreover, solvent-promoted S-alkylation of thiols by alkyl halides can take place in the presence of Zn powder.[20] In recent years, solvent-free S-alkylation of thiols with alkyl halides by using Mg–Al Hydrotalcite,[21] KF/Al2O3 ground in a mortar as primary tests,[22] or magnetic iron oxide nanoparticles has been developed.[25] In addition, the application of ionic liquid [pmIm]Br as a catalyst and reaction medium for the conversion of thiols to thioethers has been investigated.[23,24]

Solid-phase organic syntheses are preferable due to simple handling, cheaper operation, easy product isolation (avoiding the removal of the polar organic solvent at the work up step), highly efficient catalyst recycling, and especially of importance in the chemical industry.[54–56] Since the invention of ultrasound and microwave irradiation, many categories of solid phase syntheses or heterogeneous reactions accelerated by ultrasound or microwave irradiation have been launched in order to reduce the reaction time, generate fewer by-products, giving higher yield of the main products, or produce other products incidentally compared with reactions under the conventional methods (stirring or thermal heating methods).[57–61]

In this work, we report the influences of ultrasound or microwave irradiation on the solvent-free S-alkylation of thiols with alkyl halides catalyzed by potassium fluoride absorbed on alumina (KF/Al2O3) to form the corresponding thioethers (Scheme 1). KF/Al2O3 was introduced as a useful base reagent by Ando et al. in 1979. Subsequently, the applications of KF/Al2O3 in organic synthesis became popular and widely used in the formation of carbon–carbon bonds, carbon–oxygen bonds, carbon–nitrogen bonds, carbon–phosphor bonds,[62,63] carbon–sulfur bonds via solvent S-alkylation of thiols with alkyl halides,[19] or solvent-free Ullmann cross-coupling,[38–40] and sulfur–sulfur bonds.[64]

\[
\begin{align*}
R^1\text{SH} + R^2\text{X} & \xrightarrow{\text{KF/Al}_2\text{O}_3} R^1\text{S} \text{R}^2 \quad \text{(MW or HIHI)} \\
& \xrightarrow{\text{R}^1\text{S} \text{S} \text{R}^1} \\
R^1 & : n-C_4H_9, t-C_4H_9, n-C_8H_{17}, c-C_6H_{11}, C_6H_{13}, p-CH_3C_6H_4, ... \\
R^2 & : n-C_4H_9, C_6H_5CH_3 \\
X & : \text{Cl, Br}
\end{align*}
\]

**Scheme 1.** S-alkylation of thiols with alkyl/aryl halides catalyzed by KF/Al2O3.
2. Result and discussion

At the beginning of this research, \( p \)-thiocresol was arbitrarily selected as the test substance in order to find the most efficient reaction molar ratios. A series of experiments was performed under microwave irradiation, in which the molar ratio between \( p \)-thiocresol, 1-chlorobutane and the amount of catalyst (KF/Al\(_2\)O\(_3\)) was varied. Obviously, an increasing amount of KF/Al\(_2\)O\(_3\) affected the reaction conversion and hence the reaction yield more drastically than excessive amounts of the alkyl halide and the thiol. However, an excessive amount of KF/Al\(_2\)O\(_3\) catalyst led to an increase in the formation of the disulfide from the self-coupling reaction of the thiol (Figure 1). This observation is comparable with the observation of E. J. Lenardão et al. on the synthesis of symmetrical disulfide from thiols by using KF/Al\(_2\)O\(_3\) as the base, although the self-coupling reaction of thiols occurred only slowly.[60] Further experiments demonstrated that the appropriate amount of KF/Al\(_2\)O\(_3\)-promoted solvent-free \( S \)-alkylation of \( p \)-thiocresol into 4-(butylthio)toluene to take place most efficiently is 0.6 g.

Altogether nine thiols were subjected to solvent-free \( S \)-alkylation with three alkyl halides under three different reaction conditions. In the first series of solvent-free \( S \)-alkylation reactions, the mixture of reactants was allowed to react under the assistance of ultrasound irradiation (Method A, Table 1). Some experiments on the effects of ultrasound irradiation were compared with magnetic stirring at room temperature. The results showed that the yields obtained by the heterogeneous reactions between \( p \)-thiocresol and 1-chlorobutane with KF/Al\(_2\)O\(_3\) catalyst was 77% after 2 h of ultrasound irradiation, while it was 63% after 5 h of magnetic stirring. Thus, ultrasound irradiation is selected to activate the further experiments of solvent-free \( S \)-alkylation of thiols with alkyl halides. The second series of solvent-free \( S \)-alkylation reaction was performed under the assistance

![Figure 1. Influence of the catalyst amount in the \( S \)-alkylation of \( p \)-thiocresol into 4-(butylthio)toluene under solvent-free reaction conditions and assistance by microwave irradiation (50° 4 W, 6 min, \( p \)-thiocresol: 1.5 mmol, 1-chlorobutane: 1.5 mmol).](image)
Table 1. Yields of sulfides obtained by the solvent-free alkylation of thiols by various methods.\(^a\)

\[
\text{R}^1\text{-SH} + \text{R}^2\text{-X} \xrightarrow{\text{KF/Al}_2\text{O}_3} \text{MW, )) or } \Delta \quad \xrightarrow{\text{Method A}^d} \quad \text{R}^1\text{-S-R}^2 + \text{HX}
\]

| Entry | \(\text{R}^1\text{-SH}\) | \(\text{R}^2\text{-X}\) | Yield of \(3^b\) (time\(^c\)) |
|-------|-----------------|-----------------|------------------|
|       |                 |                 | Method \(A^d\)  | Method \(B^d\)  | Method \(C^d\)  |
| 1     | \(\text{C}_6\text{H}_5\) \(\text{SH}\) | \(\text{CH}_3\) \(\text{Cl}\) | 72 (120) | 85 (13) | 63 (13); 72 (60) |
| 2     |                 | \(\text{CH}_3\) \(\text{Br}\) | 82 (120) | 88 (8)  | 64 (8); 86 (60) |
| 3     | \(\text{C}_6\text{H}_4\text{CH}_2\text{Cl}\) | \(\text{CH}_3\) \(\text{Cl}\) | 72\(^e\) (120) | 75\(^e\) (13) | 52\(^e\) (13); 63\(^e\) (60) |
| 4     | \(\text{C}_6\text{H}_4\) \(\text{SH}\) | \(\text{CH}_3\) \(\text{Br}\) | 77 (120) | 89 (7)  | 40 (7); 70 (60) |
| 5     | \(\text{C}_6\text{H}_4\) \(\text{SH}\) | \(\text{CH}_3\) \(\text{Cl}\) | 89 (120) | 95 (8)  | 58 (8); 92 (60) |
| 6     | \(\text{C}_6\text{H}_4\text{CH}_2\text{Cl}\) | \(\text{CH}_3\) \(\text{Cl}\) | 71\(^e\) (120) | 71\(^e\) (13) | 42\(^e\) (13); 62\(^e\) (60) |
| 7     | \(\text{C}_6\text{H}_4\text{CH}_2\text{Cl}\) | \(\text{CH}_3\) \(\text{Br}\) | 72\(^e\) (120) | 70\(^e\) (13) | 68\(^e\) (60) |
| 8     | \(\text{C}_6\text{H}_4\text{CH}_2\text{Cl}\) | \(\text{CH}_3\) \(\text{Cl}\) | 80\(^e\) (120) | 82\(^e\) (13) | 73\(^e\) (60) |
| 9     | \(\text{C}_6\text{H}_4\text{CH}_2\text{Cl}\) | \(\text{CH}_3\) \(\text{Br}\) | 75\(^e\) (180) | 77\(^e\) (16) | 60\(^e\) (90) |
| 10    | \(\text{C}_6\text{H}_4\text{CH}_2\text{Cl}\) | \(\text{CH}_3\) \(\text{Br}\) | 76\(^e\) (150) | 78\(^e\) (14) | 64\(^e\) (75) |
| 11    | \(\text{CH}_3\) \(\text{SH}\) | \(\text{C}_6\text{H}_4\text{CH}_2\text{Cl}\) | 96 (90) | 95 (12) | 96 (45) |
| 12    | \(\text{CH}_3\) \(\text{SH}\) | \(\text{C}_6\text{H}_4\text{CH}_2\text{Cl}\) | 97 (90) | 98 (12) | 97 (45) |
| 13    | \(\text{C}_6\text{H}_2\text{O}\) \(\text{SH}\) | \(\text{CH}_3\) \(\text{Cl}\) | 96 (120) | 97 (13) | 98 (60) |
| 14    | \(\text{CH}_3\) \(\text{SH}\) | \(\text{CH}_3\) \(\text{Cl}\) | 92 (120) | 96 (13) | 96 (60) |

\(^a\)Ratio of thiol : alkyl/aryl halides : KF/Al\(_2\)O\(_3\) = 1.5 mmol : 1.5 mmol : 0.6 g.  
\(^b\)Yields were calculated based on GC/MS.  
\(^c\)Time = reaction time in minutes.  
\(^d\)Method A: ultrasound irradiation; Method B: Microwave irradiation at 4 W, 50°C; Method C: Conventional heating at 50°C.  
\(^e\)Yields of isolated products.
Figure 2. Influence of the catalyst cycles on the S-alkylation of thiophenol into 1-(phenylthio)butane under solvent-free reaction conditions and assistance by microwave irradiation (50°C, 4 W, 8 min, thiophenol: 1.5 mmol, 1-bromobutane: 1.5 mmol).

of microwave irradiation (Method B, Table 1). A series of experiments on testing reaction temperatures from room temperature to 40°C, 50°C, 60°C and 70°C was carried out. The results of the experiments clearly demonstrated that a conveniently increased reaction temperature (50°C) could shorten the time of the solvent-free S-alkylation. Consequently, the yields of the products were comparable to those of experiments on Method A, but the reaction times appeared shortened drastically from some hours down to some minutes at 50°C. Microwave irradiation inevitably affects the temperature rise of the reaction mixture, and it would be of interest to check whether the drastically shortened reaction times could be affected simply by the higher reaction temperatures. A series of experiments was performed under conventional heating (Entries 1–6, Method C, Table 1) at the same reaction times and temperatures with those under microwave irradiation. The results showed that microwave irradiation affected considerably the yields of the thioethers and reaction times owing to the efficient internal heating of microwave irradiation by direct coupling of microwave energy with molecules present in the reaction mixture.

With advantages of KF/Al₂O₃ on enhanced reactivity, a straightforward work-up procedure and milder reaction conditions, the reusability of KF/Al₂O₃ was paid attention and needs to be examined. The KF/Al₂O₃ collected after filtration from the previous reaction was washed sequentially with diethyl ether, ethyl acetate and acetone at room temperature, subsequently dried in an oven at 100°C for 1, 2 and 3 h. The structure of the recovered catalyst after 2-h drying was comparable with that of the fresh KF/Al₂O₃ by the X-ray diffraction pattern. The recycled KF/Al₂O₃ was used for solvent-free S-alkylation of thiophenol with 1-bromobutane under microwave irradiation as that of the optimized experiment presented in Entry 2, Table 1. The catalytic efficiency of KF/Al₂O₃ did not drop significantly even after four cycles of being reused and recycled (Figure 2).

3. Experimental

3.1. Instrumentation and chemicals

3.1.1. Instrumentation

Microwave irradiations were performed by means of a CEM Discover microwave oven. Ultrasound irradiation was performed by means of a BRANSON 1510 ultrasonic bath,
operating at frequency 40 kHz. GC/MS analyses were performed on a Hewlett Packard 6890 GC series II, apparatus of MS 5975C with Triple-Axis detector equipped with a J&W DB-5MS capillary column (30 m, 0.25 mm i.d., 0.25 μm film thickness) and a Hewlett Packard 7683B autosampler. HPLC analyses were performed on a micrOTOF-QII (Bruker) with UV/VIS and MS detector, the heated capillary of iron trap mass spectrometer was set to 350°C, reverse column ACE 3C18 (5 μm × 4.6 × 150 mm) and ESI (electrospray ionization): μQTOF Bruker. NMR spectra were recorded on a Bruker 500 NMR spectrometer at 500 MHz (1H) and 125 MHz (13C).

3.1.2. Chemicals
All commercially available chemicals used were from Aldrich and analyzed for authenticity and purity by GC/MS before being used.

3.1.3. Preparation of base catalyst KF/Al₂O₃ (40% w/w)
KF (20 g) was dissolved completely in de-ionized water (150 mL, pH of solution: 6.5). Neutral Al₂O₃ (30 g) was stirred regularly in de-ionized water (150 mL) for around 5 min. Then the KF solution was poured into the solution containing Al₂O₃ under continuous stirring for 30–45 min, until the pH of the mixture of the solutions was 11.5–11.7. Subsequently, water was removed from the solution mixture by rotatory evaporation, until the weight of the remaining solid mass was 53–55 g. The wet solid mass was dried at 100–110°C for 6 h. Finally, the obtained solid mass (50.5–51.5 g) was ground in a mortar into a fine powder.

3.2. Typical procedures

3.2.1. S-alkylation of thiols into corresponding thioethers by KF/Al₂O₃ under solvent-free reaction conditions assisted by ultrasound irradiation (Method A).
A suitable quantity of alkyl halide (1.5 mmol) and KF/Al₂O₃ (0.6 g) was added to the 5 mL round-bottom flask containing thiol (1.5 mmol). The flask was placed into an ultrasound bath where the mixture of reactants was exposed to ultrasound irradiation for a specific period of time (Table 1). Subsequently, the reaction mixture was extracted with dichloromethane (4 × 15 mL). The combined extracts were filtered, washed with water until neutral, and then dried by anhydrous Na₂SO₄. After removal of the solvent by rotary evaporation, the remaining crude product was analyzed by GC/MS and NMR spectroscopy.

3.2.2. S-alkylation of thiols into corresponding thioethers by KF/Al₂O₃ under solvent-free reaction conditions assisted by microwave irradiation (Method B)
A suitable quantity of alkyl halides (1.5 mmol) and KF/Al₂O₃ (0.6 g) was added to a specific test tube (h = 9 cm, d = 1.5 cm) containing the thiol (1.5 mmol). The test tube was placed into a Discover CEM microwave oven. For each of the thiols, an irradiation program was fixed to operate at power of oven (4 W), reaction temperature (50°C) and reaction time (minutes), see Table 1. After cooling, the reaction mixture was worked up as described in method A.
3.2.3. **S-alkylation of thiols into corresponding thioethers by KF/Al₂O₃ under solvent-free reaction conditions assisted by conventional heating (Method C)**

A test tube \((h = 18 \text{ cm}, d = 2 \text{ cm})\) containing a suitable quantity of thiols, alkyl halides and KF/Al₂O₃ (following the molar ratio as in Table 1) was placed in an oil bath heated to the temperature applied for the reactions under microwave irradiation. The test tube was kept in the oil bath for a period of time corresponding exactly to that found at optimum in Method B or for a period of time to optimize the reaction yields. After cooling, the reaction mixture was worked up as described in Method A.

3.3. **Spectroscopic data**

The identity and purity of all of the thioethers synthesized were ensured by \(^1\)H and \(^{13}\)C NMR spectroscopy as well as by GC/MS or HPLC/ESI. The observed data of \(^1\)H, \(^{13}\)C NMR spectroscopic and mass spectra for the 12 thioethers synthesized are listed below, and most of them were found compatible with those reported in the literature.[65–68]

**1-(Phenylthio)butane**
(Entry 1 or 2, Table 1): \(^1\)H NMR (CDCl₃): \(\delta_H = 7.14–7.33 \text{ (m, 5H)}, 2.93 \text{ (t, } J = 7.5 \text{ Hz, 2H}), 1.64 \text{ (quintet, } J = 7 \text{ Hz, 2H}), 1.45 \text{ (sextet, } J = 7.5 \text{ Hz, 2H}), 0.92 \text{ (t, } J = 7.5 \text{ Hz, 3H})\). \(^{13}\)C NMR (CDCl₃): \(\delta_C = 137.04, 128.85 \text{ (2C)}, 128.78 \text{ (2C)}, 125.60, 33.26, 31.21, 21.93, 13.60\). MS: \(m/z = 166\)[M]⁺, 123, 110.

**Benzylthiobenzene**
(Entry 3, Table 1): \(^1\)H NMR (CDCl₃): \(\delta_H = 7.19–7.34 \text{ (m, 10H)}, 4.14 \text{ (s, 2H)}\). \(^{13}\)C NMR (CDCl₃): \(\delta_C = 137.46, 136.37, 129.84 \text{ (2C)}, 128.79 \text{ (4C)}, 128.44 \text{ (2C)}, 127.13, 126.31, 39.05\). MS: \(m/z = 200\)[M]⁺, 91, 65.

**4-Butylthiotoluene**
(Entry 4 or 5, Table 1): \(^1\)H NMR (CDCl₃): \(\delta_H = 7.25 \text{ (d, } J = 8.0 \text{ Hz, 2H}), 7.09 \text{ (d, } J = 8.0 \text{ Hz, 2H}), 2.88 \text{ (t, } J = 7.5 \text{ Hz, 2H}), 2.32 \text{ (s, 3H)}, 1.61 \text{ (quintet, } J = 7 \text{ Hz, 2H}), 1.44 \text{ (sextet, } J = 7.5 \text{ Hz, 2H}), 0.91 \text{ (t, } J = 7.5 \text{ Hz, 3H})\). \(^{13}\)C NMR (CDCl₃): \(\delta_C = 135.81, 133.14, 129.77 \text{ (2C)}, 129.58 \text{ (2C)}, 34.04, 31.34, 21.91, 20.96, 13.62\). MS: \(m/z = 180\)[M]⁺, 137, 124, 91.

**4-Benzylthiotoluene**
(Entry 6, Table 1): \(^1\)H NMR (CDCl₃): \(\delta_H = 7.24–7.32 \text{ (m, 7H)}, 7.09 \text{ (d, } J = 8.0 \text{ Hz, 2H}), 4.10 \text{ (s, 2H)}, 2.34 \text{ (s, 3H)}\). \(^{13}\)C NMR (CDCl₃): \(\delta_C = 137.78, 136.50, 132.49, 130.68 \text{ (2C)}, 129.56 \text{ (2C)}, 128.79 \text{ (2C)}, 128.38 \text{ (2C)}, 127.01, 39.76, 20.98\). MS: \(m/z = 214\)[M]⁺, 123, 91.

**2-Butylthiobenzimidazole**
(Entry 7, Table 1): \(^1\)H NMR (CDCl₃): \(\delta_H = 9.06 \text{ (s, 1H)}, 7.52–7.55 \text{ (m, 2H)}, 7.18–7.21 \text{ (m, 2H)}, 3.35 \text{ (t, } J = 7.5 \text{ Hz, 2H}), 1.72 \text{ (quintet, } J = 7.5 \text{ Hz, 2H}), 1.39 \text{ (sextet, } J = 7.5 \text{ Hz, 2H}), 0.86 \text{ (t, } J = 7.5 \text{ Hz, 3H})\). \(^{13}\)C NMR (CDCl₃): \(\delta_C = 150.99, 139.17 \text{ (2C)}, 122.25 \text{ (2C)}, 113.98 \text{ (2C)}, 32.47, 31.56, 21.75, 13.48\). MS (ESI⁺): \(m/z = 207.0986 \text{ ([M+H]⁺, 6%)}\), 151.0378 (100%).
2-Benzylthiobenzimidazole
(Entry 8, Table 1): 1H NMR (DMSO-\textit{d}_6): \(\delta_H = 12.55\) (s, 1H), 7.09–7.57 (m, 9H), 4.55 (s, 2H). \(^{13}\text{C}\) NMR (CDCl\textsubscript{3}): \(\delta_C = 149.68, 143.61, 137.66, 135.44, 128.81\) (2C), 128.45 (2C), 127.29, 121.65, 121.13, 117.40, 110.32, 35.13. MS (ESI\(^+\)): \(m/z = 241.0769\) ([M]\(^+\), 100%), 198.0791 (34%), 150.0339 (18%).

2-Butylthio-4,5-dihydrothiazole
(Entry 9, Table 1): 1H NMR (CDCl\textsubscript{3}): \(\delta_H = 4.20\) (t, \(J = 7.5\) Hz, 2H), 3.36 (t, \(J = 8.0\) Hz, 2H), 3.09 (t, \(J = 7.5\) Hz, 2H), 1.66 (quintet, \(J = 7.5\) Hz, 2H), 1.41 (sextet, \(J = 7.5\) Hz, 2H), 0.91 (t, \(J = 7.5\) Hz, 3H). \(^{13}\text{C}\) NMR (CDCl\textsubscript{3}): \(\delta_C = 166.34, 64.10, 35.19, 32.52, 31.23, 21.82, 13.52\). MS (ESI\(^+\)): \(m/z = 176.0537\) ([M]\(^+\), 98%).

2-Butylthio-4-phenylimidazole
(Entry 10, Table 1): 1H NMR (CDCl\textsubscript{3}): \(\delta_H = 7.68\) (dm, \(J = 8\) Hz, 2H), 7.34 (tm, \(J = 7.25\) Hz, 3H), 7.23 (tt, \(J = 7.5\) Hz, \(J = 1\) Hz, 1H), 6.52 (s, 1H), 3.00 (t, \(J = 7.5\) Hz, 2H), 2.18 (s, 1H), 1.58 (quintet, \(J = 7.5\) Hz, 2H), 1.35 (sextet, \(J = 7.5\) Hz, 2H), 0.85 (t, \(J = 7.5\) Hz, 3H). \(^{13}\text{C}\) NMR (CDCl\textsubscript{3}): \(\delta_C = 141.13, 139.57, 132.19, 128.69\) (2C), 127.06, 124.80 (2C), 117.86, 34.84, 31.96, 21.67, 13.53. MS (ESI\(^+\)): \(m/z = 233.1144\) ([M]\(^+\), 9%), 177.0581 (100%).

1-(Benzylthio)butane
(Entry 11, Table 1): 1H NMR (CDCl\textsubscript{3}): \(\delta_H = 7.30–7.33\) (m, 4H), 7.22–7.27 (m, 1H), 3.71 (s, 1H), 2.43 (t, \(J = 7.0\) Hz, 2H), 1.56 (quintet, \(J = 7.0\) Hz, 2H), 1.38 (sextet, \(J = 7.0\) Hz, 2H), 0.90 (t, \(J = 7.0\) Hz, 3H). \(^{13}\text{C}\) NMR (CDCl\textsubscript{3}): \(\delta_C = 138.69, 128.83(2C), 128.44(2C), 126.85, 36.31, 31.34, 31.07, 22.03, 13.68\). MS: \(m/z = 180\) [M]\(^+\), 91, 77, 65, 45.

1-(Benzylthio)octane
(Entry 12, Table 1): 1H NMR (CDCl\textsubscript{3}): \(\delta_H = 7.29–7.36\) (m, 4H), 7.22–7.26 (m, 1H), 3.71 (s, 1H), 2.41 (t, \(J = 7.0\) Hz, 2H), 1.56 (quintet, \(J = 7.0\) Hz, 2H), 1.22–1.37 (m, 10H), 0.89 (t, \(J = 7.2\) Hz, 3H). \(^{13}\text{C}\) NMR (CDCl\textsubscript{3}): \(\delta_C = 138.72, 128.84(2C), 128.45(2C), 126.86, 36.34, 31.82, 31.45, 29.26, 29.20, 29.18, 28.91, 22.66, 14.10\). MS: \(m/z = 236\) [M]\(^+\), 145, 91, 69.

Benzylthiocyclohexane
(Entry 13, Table 1): 1H NMR (CDCl\textsubscript{3}): \(\delta_H = 7.29–7.35\) (m, 4H), 7.22–7.26 (m, 1H), 3.75 (s, 1H), 2.54–2.60 (m, 1H), 1.94–1.97 (m, 2H), 1.75–1.77 (m, 2H), 1.60–1.75 (m, 1H), 1.24–1.33 (m, 5H). \(^{13}\text{C}\) NMR (CDCl\textsubscript{3}): \(\delta_C = 138.97, 128.76(2C), 128.44(2C), 126.77, 42.93, 34.61, 33.39(2C), 26.00, 25.89(2C)\). MS: \(m/z = 206\) [M]\(^+\), 115, 91, 67.

2-Benzylthio-2-methylpropane
(Entry 14, Table 1): 1H NMR (CDCl\textsubscript{3}): \(\delta_H = 7.20–7.36\) (m, 5H), 3.77 (s, 2H), 1.36 (s, 9H). \(^{13}\text{C}\) NMR (CDCl\textsubscript{3}): \(\delta_C = 138.61, 128.96(2C), 128.45(2C), 126.76, 42.87, 33.45, 30.92(3C)\). MS: \(m/z = 180\) [M]\(^+\), 124, 91, 77, 57.
Conclusion

Comprehensive experimental work has made it possible for us to introduce an fast and efficient synthetic method for the preparation of thioethers in fair to high yields by solvent-free S-alkylation of thiols with alkyl halides by means of KF/Al₂O₃ as a green catalyst (safety for use and high recyclability) under the assistance of ultrasound or microwave irradiation, subsidiarily also under the influence of conventional heating.

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