Supporting Information
for DOI: 10.1055/s-0035-1561268
© Georg Thieme Verlag KG Stuttgart · New York 2015
A highly efficient copper-catalyzed synthesis of unsymmetrical diaryl- and aryl alkyl chalcogenides from aryl iodides and diorganyl disulfides and diselenides

Barahman Movassagh,* Zhila Hosseinzadeh

Department of Chemistry, K. N. Toosi University of Technology, P. O. Box 16315-1618, Tehran, Iran; Tel: +98-21-23064323; Fax: +98-21-22853650; E-mail: bmovass1178@yahoo.com

Table of Contents

1. Experimental Procedure S2
   1.1. General S2
   1.2. General procedure for the preparation of diorgano chalcogenides S2
2. Spectral data for Table 2 S3
3. Copy of $^1$H and $^{13}$C NMR spectra of diorgano chalcogenides S8
1. Experimental Procedure:

1.1. General

All chemicals were purchased from Merck and Aldrich Chemical Companies. Melting points were determined on a Büchi melting point B-540 apparatus. NMR spectra were recorded at 500, 400 and 300 (\(\text{^1H}\)), 125, 100.6 and 75.5 (\(\text{^{13C}}\)) MHz, on a commercial Bruker DMX-500, DMX-400 and DMX-300, respectively using CDCl\(_3\) as solvent. IR spectra were recorded on an ABB Bomem Model FTLA 2000 spectrophotometer.

1.2. General procedure for the preparation of diorgano chalcogenides

A flame-dried test tube containing a magnetic stirring bar was charged with diorgano dichalcogenide (0.5 mmol), aryl halide (1.0 mmol), KOH (1.0 mmol), and dry DMSO (2 mL) [For aryl bromides or chlorides, TBAB (1.0 mmol) was also added]. Then, CuI (10 mol%) and Mtpy (10 mol%) were added to the above mixture, and the reaction mixture was heated at 110 °C under nitrogen. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the mixture was cooled to r.t., poured into H\(_2\)O (10 mL), and extracted with ethyl acetate (3 × 8 mL). The combined organic layers were dried over MgSO\(_4\), filtered, and concentrated in vacuo to give the crude product which was further purified by preparative TLC (silica gel, \(n\)-hexane-EtOAc = 9:1). The identity of the products were confirmed by IR, \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopic analysis.
2. Spectral data for Table 2:

**Di-p-tolyl sulfide**

![Di-p-tolyl sulfide structure]

White solid; m.p. 55-57 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta_H = 7.30$ (d, $J = 8.4$ Hz, 4H), 7.16 (d, $J = 8.4$ Hz, 4H), 2.38 (s, 6H); $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta_C = 136.9, 132.7, 131.1, 130.0, 21.1$.

**(4-Methoxyphenyl)(phenyl)sulfide**

![4-Methoxyphenyl)(phenyl)sulfide structure]

Colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta_H = 7.49$ (dt, $J = 6.9, 1.8$ Hz, 2H), 7.19-7.29 (m, 5H), 6.96 (dt, $J = 6.9, 1.8$ Hz, 2H), 3.85 (s, 3H); $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta_C = 159.8, 138.6, 135.3, 128.9, 128.2, 125.7, 124.3, 115.0, 55.3$.

**Naphthalen-2-yl(p-tolyl)sulfide**

![Naphthalen-2-yl(p-tolyl)sulfide structure]

White solid; m.p. 69-71 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta_H = 7.75-7.86$ (m, 4H), 7.41-7.52 (m, 5H), 7.21 (d, $J = 9.0$ Hz, 2H), 2.42 (s, 3H); $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta_C = 137.6, 134.3, 133.7, 132.1, 132.0, 131.4, 130.1, 128.7, 128.3, 127.9, 127.7, 127.3, 126.5, 125.9, 21.1$.

**(4-Methoxyphenyl)(octyl)sulfide**

![4-Methoxyphenyl)(octyl)sulfide structure]

Colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta_H = 7.34$ (dt, $J = 9.9, 2.1$ Hz, 2H), 6.85 (dt, $J = 9.9, 2.1$ Hz, 2H), 3.80 (s, 3H), 2.82 (t, $J = 6$ Hz, 2H), 1.54-1.63 (m, 2H), 1.27-1.41 (m, 10H), 0.88 (t, $J = 6$ Hz, 3H); $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta_C = 158.6, 132.8, 126.9, 114.4, 55.2, 35.7, 31.7, 29.3, 29.14, 29.11, 28.6, 22.6, 14.0$. 
1-(4-(Phenylthio)phenyl)ethanone

Yellow solid; m.p. 62-64 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta_H = 7.82$ (d, $J = 8.4$ Hz, 2H), 7.48-7.50 (m, 2H), 7.39-7.41 (m, 3H), 7.21 (d, $J = 8.4$ Hz, 2H), 2.55 (s, 3H); $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta_C = 197.1$, 144.9, 134.4, 133.9, 132.0, 129.7, 128.9, 128.8, 127.4, 26.5.

(4-Nitrilephenyl)(phenyl)sulfide

Colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta_H = 7.58$-7.64 (m, 4H), 7.50-7.26 (m, 5H); $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta_C = 141.1$, 139.5, 133.4, 129.7, 128.7, 127.2, 127.1, 118.0, 110.8.

(4-Chlorophenyl)(p-tolyl)sulfide

White solid; m.p. 69-70 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta_H = 7.33$ (d, $J = 8.2$ Hz, 2H), 7.17-7.24 (m, 6H), 2.35 (s, 3H); $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta_C = 138.0$, 136.0, 132.5, 132.3, 130.8, 130.7, 130.2, 129.1, 21.2.

2-(Butylthio)thiophene

Colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta_H = 7.20$-7.29 (m, 3H), 2.82 (t, $J = 6.0$ Hz, 2H), 1.27-1.34 (m, 4H), 0.84-0.91 (m, 3H); $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta_C = 139.9$, 132.9, 129.5, 127.8, 53.3, 34.2, 22.4, 13.9.
Diphenyl sulfide

\[ \begin{array}{c}
\text{S} \\
\text{C} \text{C} \\
\text{C} \text{C}
\end{array} \]

Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta_H = 7.40 \) (d, \(J = 8.0\) Hz, 4H), \(7.35 \) (t, \(J = 8.0\) Hz, 4H), \(7.30 \) (t, \(J = 8.0\) Hz, 2H); \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)): \(\delta_C = 135.9, 131.1, 129.3, 127.1\).

Naphthalen-2-yl (phenyl)sulfide

\[ \begin{array}{c}
\text{S} \\
\text{C} \text{C} \\
\text{C} \text{C}
\end{array} \]

White solid; m.p. 63-65 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta_H = 7.91 \) (s, 1H), 7.77-7.83 (m, 3H), 7.43-7.53 (m, 5H), 7.27-7.37 (m, 3H); \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)): \(\delta_C = 135.9, 133.8, 133.0, 132.3, 131.0, 129.9, 129.3, 128.9, 128.8, 127.8, 127.4, 127.1, 126.6, 126.2\).

Benzyl(phenyl)sulfide

\[ \begin{array}{c}
\text{S} \\
\text{C} \text{C} \\
\text{C} \text{C}
\end{array} \]

White solid; m.p. 53-55 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta_H = 7.24-7.40 \) (m, 10H), 4.18 (s, 2H); \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)): \(\delta_C = 137.5, 136.4, 129.8, 128.9, 128.5, 127.2, 126.3, 36.0\).

(4-Bromophenyl)(phenyl)sulfide

\[ \begin{array}{c}
\text{S} \\
\text{C} \text{C} \\
\text{C} \text{C}
\end{array} \]

Colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta_H = 7.60 \) (dt, \(J = 6.0, 2.7\) Hz, 1H), 7.24-7.44 (m, 6H), 7.19 (dt, \(J = 6.0, 2.7\) Hz, 1H), 7.05 (dt, \(J = 6.0, 2.7\) Hz, 1H); \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)): \(\delta_C = 135.4, 134.7, 133.0, 131.9, 131.7, 129.3, 127.6, 120.8\).
Phenyl(o-tolyl)sulfide

![Phenyl(o-tolyl)sulfide structure]

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta_H = 7.28$-$7.54$ (m, 5H), 7.26 (d, $J = 8.0$ Hz, 3H), 7.19 (t, $J = 8.0$ Hz, 1H), 2.43 (s, 3H); $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta_C = 140.0$, 136.2, 133.8, 133.1, 131.1, 130.7, 129.7, 129.3, 126.8, 126.4, 20.7.

(4-Methylphenyl)(phenyl)sulfide

![4-Methylphenyl)(phenyl)sulfide structure]

Colorless oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta_H = 7.41$-$7.43$ (m, 5H), 7.20-$7.32$ (m, 4H), 2.42 (s, 3H); $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta_C = 137.61$, 137.2, 132.3, 131.3, 130.1, 129.8, 129.0, 126.4, 21.1.

(4-Methoxyphenyl)(phenyl)selenide

![4-Methoxyphenyl)(phenyl)selenide structure]

Yellow oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta_H = 7.55$ (dd, $J = 6.9$, 2.1 Hz, 2H), 7.39 (dd, $J = 7.4$, 1.4 Hz, 2H), 7.21-$7.29$ (m, 3H), 6.90 (dd, $J = 6.9$, 2.1 Hz, 2H), 3.84 (s, 3H); $^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta_C = 159.8$, 136.6, 133.2, 130.9, 129.2, 126.4, 119.9, 115.1, 55.3.

(2-Methoxyphenyl)(phenyl)selenide

![2-Methoxyphenyl)(phenyl)selenide structure]

Yellow oil; $^1$HNMR (500 MHz, CDCl$_3$): $\delta_H = 7.27$-$7.70$ (m, 5H), 7.08-$7.10$ (m, 1H), 6.88-$6.95$ (m, 3H), 3.95 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta_C = 157.1$, 135.9, 131.3, 130.0, 128.8, 128.6, 128.3, 122.4, 122.1, 110.9, 56.4.
(4-Methylphenyl)(phenyl)selenide

\[
\text{Se} \quad \text{CH}_3
\]

Yellow oil; \(^1\text{H} \) NMR (500 MHz, CDCl\(_3\)): \( \delta_H = 7.56 \) (d, \( J = 7.6 \) Hz, 4H), 7.36 (d, \( J = 6.4 \) Hz, 3H), 7.23 (d, \( J = 7.6 \) Hz, 2H), 2.46 (s, 3H); \(^{13}\text{C} \) NMR (125 MHz, CDCl\(_3\)): \( \delta_C = 138.2, 134.5, 134.4, 132.5, 132.6, 130.7, 129.8, 127.4, 21.7 \).

(4-Chlorophenyl)(phenyl)selenide

\[
\text{Se} \quad \text{Cl}
\]

Yellow oil; \(^1\text{H} \) NMR (500 MHz, CDCl\(_3\)): \( \delta_H = 7.55-7.79 \) (m, 4H), 7.17-7.37 (m, 5H); \(^{13}\text{C} \) NMR (125 MHz, CDCl\(_3\)): \( \delta_C = 134.8, 134.6, 134.0, 133.7, 131.2, 130 \).

3. Copy of \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of and diorgano chalcogenides
Se

OMe