Electronic Supplementary Information

Efficient Dehydrative Alkylation of Thiols with Alcohols Catalyzed by Alkyl Halides

Yaqi Yang, a Zihang Ye, a Xu Zhang, b Yipeng Zhou, a Xiantao Ma, a,b Hongen Cao, b Huan Li, a Lei Yu, b and Qing Xu a,b,*

a College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, Zhejiang 325035, P. R. China
b Institute of Pesticide, School of Horticulture and Plant Protection and School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, Jiangsu 225002, P. R. China

Email: qing-xu@wzu.edu.cn

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Experimental

**General.** The starting alcohols, thiols, alkyl halides, hydrobromic acid (33 wt% in HOAc) and solvents were all purchased and used without further purification. Et₃N-HBr was prepared from the reaction of Et₃N and HBr (33 wt% in HOAc) in EtOAc according to our previous method (Q. Xu, H. Xie, E.-L. Zhang, X. Ma, J. Chen, X.-C. Yu, H. Li, *Green Chem.* 2016, 18, 3940). Most of the reactions were carried out in sealed 10 mL Schlenk tubes and then monitored by TLC and/or GC-MS. All products were purified by column chromatography on silica gel using petroleum ether (PE) as the eluent. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance III AV500 instrument (500 MHz for ¹H and 125.4 MHz for ¹³C NMR spectroscopy) by using CDCl₃ or d₆-DMSO as the solvent. Chemical shift values for ¹H and ¹³C NMR were referred to internal Me₄Si (0 ppm). Mass spectra were measured on a Shimadzu GCMS-QP2010 Plus or a Shimadzu GCMS-QP2010 Ultra spectrometer (EI).

**General Procedure for Alkyl Halide-Catalyzed Dehydrative S-Alkylation of Thiols with Alcohols for the Synthesis of Unsymmetrical Thioethers.** The neat mixture of an alcohol 1 (2.4 mmol), a thiol 2 (2 mmol), and an alkyl halide 3 (0.4 mmol, 20 mol%, corresponds to the alcohol 1) in a 10 mL Schlenk tube was sealed under air and then heated at 120 °C for 12 h. The reaction was then monitored by TLC and/or GC-MS. Column chromatography of the crude products using petroleum ether as the eluent gave the corresponding thioether 4.

**Typical Procedure for Alkyl Halide-Catalyzed Dehydrative S-Alkylation of Thiols with Alcohols for the Synthesis of Unsymmetrical Thioethers.** The neat mixture of benzyl alcohol 1a (0.2592 g, 2.4 mmol), p-tolylthiol 2a (0.2480 g, 2 mmol), and PhCH₂Br 3a (0.048 mL, 0.4 mmol, 20 mol%, the alkyl halide corresponds to alcohol 1a) in a 10 mL Schlenk tube was sealed under air and then heated at 120 °C for 12 h. The reaction was then monitored by TLC and/or GC-MS. Column chromatography of the crude products using petroleum ether as the eluent gave 4aa in 95% isolated yield.

**Benzyl 4-tolyl thioether (4aa).** ¹H NMR (500 MHz, CDCl₃): δ 7.21-7.13 (m, 7H), 6.98 (d, J = 8.0 Hz, 2H), 3.99 (s, 2H), 2.22 (s, 3H). ¹³C NMR (125.4 MHz, CDCl₃): δ 138.0, 136.6, 132.9, 130.8, 129.9, 129.1, 128.7, 127.3, 39.9, 21.3. MS (EI): m/z (%) 214 (45), 123 (3), 91 (100), 65 (12). This
compound was known: Panova, Y. S.; Kashin, A. S.; Vorobev, M. G.; Degtyareva, E. S.; Ananikov, V. P. *ACS Catal.*, 2016, 6, 3637.

2-Methylbenzyl 4-tolyl thioether (4ba). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.22 (dd, $J$ = 6.0, 1.5 Hz, 2H), 7.14 (dd, $J$ = 5.0, 1.0 Hz, 2H), 7.12-7.06 (m, 4H), 4.05 (s, 2H), 2.38 (s, 3H), 2.31 (s, 3H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 136.7, 136.7, 135.4, 132.8, 131.1, 130.5, 129.8, 192.6, 127.4, 126.0, 38.2, 21.1, 19.2. MS (EI): $m/z$ (%) 228 (32), 123 (3), 105 (100), 77 (11). This compound was known: Yao, J.; Yu, M.; Zhang, Y. *Adv. Synth. Catal.* 2012, 354, 3205.

3-Methylbenzyl 4-tolyl thioether (4ca). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.21 (d, $J$ = 8.0 Hz, 2H), 7.16 (t, $J$ = 7.5 Hz, 1H), 7.06 (m, 5H), 4.03 (s, 2H), 2.31 (s, 6H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 138.1, 137.6, 136.5, 132.8, 130.5, 129.6, 128.3, 127.9, 125.9, 39.8, 21.4, 21.1. MS (EI): $m/z$ (%) 228 (34), 123 (3), 105 (100), 77 (12). This compound was known: Yu, M.; Xie, Y.; Xie, C.; Zhang, Y. *Org. Lett.* 2012, 14, 2164.

4-Methylbenzyl 4-tolyl thioether (4da). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.21 (d, $J$ = 8.0 Hz, 2H), 7.16 (d, $J$ = 7.5 Hz, 2H), 7.07 (m, 4H), 4.04 (s, 2H), 2.31 (s, 3H), 2.30 (s, 3H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 136.7, 136.4, 134.6, 132.8, 130.5, 129.6, 129.2, 128.7, 39.4, 21.1, 21.0. MS (EI): $m/z$ (%) 228 (32), 123 (3), 105 (100), 77 (10). This compound was known: Miyazaki, T.; Kasai, S.; Ogiwara, Y.; Sakai, N. *Eur. J. Org. Chem.* 2016, 5, 1043.

2-Chlorobenzyl 4-tolyl thioether (4ea). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.34 (d, $J$ = 8.0 Hz, 1H), 7.22 (m, 2H), 7.18-7.10 (m, 3H), 7.06 (d, $J$ = 8.0 Hz, 2H), 4.16 (s, 2H), 2.31 (s, 3H). $^{13}$C NMR
(125.4 MHz, CDCl$_3$): $\delta$ 137.0, 135.6, 134.0, 131.9, 131.6, 130.7, 129.7, 129.6, 128.5, 126.7, 37.7, 21.1. MS (EI): $m/z$ (%) 248 (43), 125 (100), 89 (12), 63 (4), 51 (1). This compound was known: Miyazaki, T.; Kasai, S.; Ogiwara, Y.; Sakai, N. *Eur. J. Org. Chem.* **2016**, 5, 1043.

3-Chlorobenzyl 4-tolyl thioether (4fa). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.24 (s, 1H), 7.20-7.18 (m, 4H), 7.07 (d, $J$ = 8.0 Hz, 2H), 4.00 (s, 2H), 2.31 (s, 3H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 140.0, 137.0, 134.2, 131.7, 131.2, 129.7, 129.6, 128.9, 127.2, 127.0, 39.5, 21.1. MS (EI): $m/z$ (%) 248 (49), 125 (100), 89 (12), 77 (5), 51 (1). This compound was known: Miyazaki, T.; Kasai, S.; Ogiwara, Y.; Sakai, N. *Eur. J. Org. Chem.* **2016**, 5, 1043.

4-Chlorobenzyl 4-tolyl thioether (4ga). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.26 (d, $J$ = 8.0 Hz, 2H), 7.21 (dd, $J$ = 8.0, 12.0 Hz, 4H), 7.10 (d, $J$ = 8.0 Hz, 2H), 4.04 (s, 2H), 2.34 (s, 3H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 140.0, 136.5, 132.8, 131.8, 131.2, 130.1, 129.7, 128.5, 39.3, 21.0. MS (EI): $m/z$ (%) 248 (28), 125 (100), 89 (12), 63 (3), 51 (1). This compound was known: Miyazaki, T.; Kasai, S.; Ogiwara, Y.; Sakai, N. *Eur. J. Org. Chem.* **2016**, 5, 1043.

4-Fluorobenzyl 4-tolyl thioether (4ha). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.20-7.18 (m, 4H), 7.06 (d, $J$ = 8.0 Hz, 2H), 6.96-6.92 (m, 2H), 4.01 (s, 2H), 2.30 (s, 3H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 161.9 ($J_{C-F}$ = 244.6 Hz), 136.9, 133.6 ($J_{C-F}$ = 3.3 Hz), 132.0, 131.1, 130.4 ($J_{C-F}$ = 8.0 Hz), 129.7, 115.3 ($J_{C-F}$ = 21.3 Hz), 39.2, 21.1. MS (EI): $m/z$ (%) 232 (32), 109 (100), 83 (11), 57 (2). This compound was known: Oderinde, M. S.; Frenette, M.; Robbins, D. W.; Aquila, B.; Johannes, J. W. *J. Am. Chem. Soc.* **2016**, 138, 1760.

O₄N
4-Nitrobenzyl 4-tolyl thioether (4ia). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.10 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.06 (d, $J = 8.0$ Hz, 2H), 4.07 (s, 2H), 2.31 (s, 3H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 147.0, 145.9, 137.7, 133.7, 131.9, 129.9, 129.6, 123.6, 39.6, 21.1. MS (EI): m/z (%) 259 (100), 213 (23), 136 (27), 123 (29), 90 (28), 78 (20). This compound was known: Santoni, G.; Mba, M.; Bonchio, M.; Nugent, W. A.; Zonta, C.; Licini, G. Chem. Eur. J. 2010, 16, 645.

![Structure of 4-Nitrobenzyl 4-tolyl thioether (4ia)](image)

Cinnamyl 4-tolyl thioether (4ja). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.33-7.26 (m, 6H), 7.23-7.19 (m, 1H), 7.09 (d, $J = 8.0$ Hz, 2H), 6.38 (d, $J = 16.0$ Hz, 1H), 6.27-6.21 (m, 1H), 3.66 (dd, $J = 7.0$, 1.0 Hz, 2H), 2.31 (s, 3H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 136.8, 136.7, 132.6, 132.0, 131.2, 129.6, 128.5, 127.5, 126.3, 125.4, 37.9, 21.1. MS (EI): m/z (%) 240 (16), 117 (100), 91 (12), 65 (3), 51 (1). This compound was known: Gholinejad, M. Eur. J. Org. Chem. 2015, 19, 4162.

![Structure of Cinnamyl 4-tolyl thioether (4ja)](image)

Pentyl 4-tolyl thioether (4ka). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.24 (d, $J = 8.0$ Hz, 2H), 7.09 (d, $J = 8.0$ Hz, 2H), 2.87 (t, $J = 7.5$ Hz, 2H), 2.31 (s, 3H), 1.65-1.59 (m, 2H), 1.42-1.26 (m, 4H), 0.88 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 135.8, 133.2, 129.8, 129.6, 34.4, 31.0, 29.0, 22.2, 21.0, 14.0. MS (EI): m/z (%) 194 (54), 137 (25), 124 (100), 91 (43), 77 (5). This compound was known: Sakai, N.; Miyazaki, T.; Sakamoto, T.; Yatsuda, T.; Moriya, T.; Ikeda, R.; Konakahara, T. Org. Lett. 2012, 14, 4366.

![Structure of Pentyl 4-tolyl thioether (4ka)](image)

Octyl 4-tolyl thioether (4la). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.25 (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 2.87 (t, $J = 7.5$ Hz, 2H), 2.32 (s, 3H), 1.65-1.59 (m, 2H), 1.42-1.38 (m, 2H), 1.31-1.27 (m, 8H), 0.88 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 135.8, 133.2, 129.8, 129.6, 34.4, 31.9, 29.3, 29.2, 29.1, 28.8, 22.6, 21.0. MS (EI): m/z (%) 236 (59), 137 (21), 124 (100), 91 (26), 57 (7). This compound was known: Oderinde, M. S.; Frenette, M.; Robbins, D. W.; Aquila, B.; Johannes, J. W. J. Am. Chem. Soc. 2016, 138, 1760.
Benzhydryl 4-tolyl thioether (4ma). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.40 (d, $J = 7.5$ Hz, 4H), 7.28 (t, $J = 7.5$ Hz, 4H), 7.21 (dd, $J = 16.0$, 7.5 Hz, 2H), 7.13 (d, $J = 8.0$ Hz, 2H), 6.97 (d, $J = 8.0$ Hz, 2H), 5.46 (s, 1H), 2.25 (s, 3H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 141.2, 136.9, 132.3, 131.4, 129.5, 128.5, 128.4, 127.2, 58.1, 21.1. MS (El): $m/z$ (%) 290 (4), 167 (100), 152 (16), 123 (4). This compound was known: Firouzabadi, H.; Iranpoor, N.; Jafarpour, M. *Tetrahedron Lett.* 2006, 47, 93.

$t$-Butyl 4-tolyl thioether (4pa). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.41 (d, $J = 7.5$ Hz, 2H), 7.13 (d, $J = 7.5$ Hz, 2H), 2.36 (s, 3H), 1.27 (s, 9H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 138.7, 137.4, 129.8, 129.2, 45.5, 30.9, 21.2. MS (El): $m/z$ (%) 180 (22), 179 (35), 125 (32), 124 (100), 123 (41), 91 (46). This compound was known: Venkanna, G. T.; Arman, H. D.; Tonzetich, Z. J. *ACS Catal.* 2014, 4, 2941.

Benzyl 2-tolyl thioether (4ab). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.30-7.21 (m, 6H), 7.15-7.07 (m, 3H), 4.07 (s, 2H), 2.31 (s, 3H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 138.0, 137.3, 135.8, 130.1, 129.0, 128.9, 128.5, 127.2, 126.4, 126.1, 38.4, 20.3. MS (El): $m/z$ (%) 214 (38), 91 (100), 65 (12), 51 (2). This compound was known: Sayah, M.; Organ, M. G. *Chem. Eur. J.* 2011, 17, 11719.

Benzyl 4-methoxyphenyl thioether (4ac). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.20-7.10 (m, 7H), 6.71 (dt, $J = 9.0$, 3.0 Hz, 2H), 3.91 (s, 2H), 3.70 (s, 3H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 159.2, 138.2, 134.1, 128.9, 128.4, 127.0, 126.1, 114.4, 55.3, 41.2. MS (El): $m/z$ (%) 230 (41), 91 (100), 65 (10), 51 (1). This compound was known: Miyazaki, T.; Kasai, S.; Ogiwara, Y.; Sakai, N. *Eur. J. Org. Chem.* 2016, 5, 1043.

Benzyl 2-chlorophenyl thioether (4ad). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.36 (s, 1H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.29 (t, $J = 8.0$ Hz, 2H), 7.24 (t, $J = 7.5$ Hz, 2H), 7.16-7.08 (m, 2H), 4.14 (s, 2H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 136.4, 135.8, 133.7, 129.7, 129.3, 128.9, 128.6, 127.4, 127.1, 126.9, 37.5. MS (El): $m/z$ (%) 234 (24), 91 (100), 65 (12), 51 (1). This compound was known: Naso, F.;

![Benzyl 3-chlorophenyl thioether (4ae).](image1)

Benzyl 3-chlorophenyl thioether (4ae). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.30-7.22 (m, 6H), 7.18-7.12 (m, 3H), 4.13 (s, 2H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 138.6, 136.8, 134.6, 129.8, 129.0, 128.8, 128.6, 127.4, 127.4, 126.3, 38.7. MS (EI): $m/z$ (%) 234 (23), 91 (100), 65 (12), 51 (1). This compound was known: Li, Y.; Xie, W.; Jiang, X. *Chem. Eur. J.* 2015, 21, 16059.

![Benzyl 4-chlorophenyl thioether (4af).](image2)

Benzyl 4-chlorophenyl thioether (4af). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.30-7.20 (m, 9H), 4.07 (s, 2H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 137.1, 134.7, 132.5, 131.4, 129.0, 128.8, 128.6, 127.3, 39.3. MS (EI): $m/z$ (%) 234 (23), 91 (100), 65 (13), 51 (1). This compound was known: Miyazaki, T.; Kasai, S.; Ogiwara, Y.; Sakai, N. *Eur. J. Org. Chem.* 2016, 5, 1043.

![Benzyl 4-nitrophenyl thioether (4ag).](image3)

Benzyl 4-nitrophenyl thioether (4ag). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.10 (d, $J = 7.5$ Hz, 2H), 7.39 (d, $J = 7.5$ Hz, 2H), 7.35-7.29 (m, 5H), 4.25 (s, 2H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 147.2, 135.5, 128.8, 127.8, 126.8, 123.9, 37.1. MS (EI): $m/z$ (%) 245 (11), 91 (100), 92 (8), 65 (10). This compound was known: Naso, F.; Capozzi, M. A. M.; Bottoni, A.; Calvaresi, M.; Bertolasi, V.; Capitelli, F.; Cardellicchio, C. *Chem. Eur. J.* 2009, 15, 13417.

![Benzyl naphthalen-2-yl thioether (4ah).](image4)

Benzyl naphthalen-2-yl thioether (4ah). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.77 (d, $J = 7.5$Hz, 1H), 7.73-7.68 (m, 3H), 7.46-7.38 (m, 3H), 7.33-7.21 (m, 5H), 4.21 (s, 2H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 137.4, 133.9, 133.7, 131.9, 128.9, 128.6, 128.3, 127.8, 127.75, 127.73, 127.2, 127.2, 126.5, 125.8, 39.0. MS (EI): $m/z$ (%) 250 (47), 115 (14), 91 (100), 65 (11), 51 (1). This compound was known: Bryliakov, K. P.; Talsi, E. P. *Eur. J. Org. Chem.* 2011, 24, 4693.
Benzyl pyridin-2-yl thioether (4ai). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.47 (d, $J = 5.0$ Hz, 1H), 7.51-7.47 (m, 1H), 7.42 (d, $J = 7.0$ Hz, 2H), 7.31-7.28 (m, 2H), 7.25-7.22 (m, 1H), 7.18 (dd, $J = 1.0$, 8.0 Hz, 1H), 7.02-7.00 (m, 1H), 4.46 (s, 2H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 158.8, 149.2, 137.8, 136.2, 129.0, 128.5, 127.1, 122.2, 119.6, 34.6. MS (EI): $m/z$ (%) 200 (23), 167(92), 124 (20), 91 (100), 79 (27), 65 (30), 51 (10). This compound was known: Rostami, A.; Rostami, A.; Ghaderi, A. *J. Org. Chem.* 2015, 80, 8694.

Dibenzyl thioether (4aj). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.32-7.26 (m, 8H), 7.25-7.22 (m, 2H), 3.59 (s, 4H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 138.2, 129.0, 128.5, 127.0, 35.6. MS (EI): $m/z$ (%) 214 (41), 123 (28), 91 (100), 65 (15), 51 (3). This compound was known: Miyazaki, T.; Kasai, S.; Ogiwara, Y.; Sakai, N. *Eur. J. Org. Chem.* 2016, 5, 1043.

Benzyl cyclohexyl thioether (4ak). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.32-7.20 (m, 5H), 3.74 (s, 2H), 2.56 (t, $J = 10.0$ Hz, 1H), 1.94 (d, $J = 12.5$Hz, 2H), 1.74 (s, 2H), 1.59 (s, 1H), 1.36-1.23 (m, 6H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 139.0, 128.8, 128.4, 126.8, 43.0, 34.6, 33.4, 26.0, 25.9. MS (EI): $m/z$ (%) 206 (33), 124 (20), 115 (26), 91 (100), 81 (17), 67 (15), 65 (10), 55 (17). This compound was known: Bhat, V. T.; Duspara, P. A.; Seo, S.; Binti, N. S.; Bakara, A.; Greaney, M. F. *Chem. Commun.* 2015, 51, 4383.

Benzyl $n$-octyl thioether (4al). $^1$H NMR (500 MHz, CDCl$_3$): 7.31-7.22 (m, 5H), 3.70 (s, 2H), 2.40 (t, $J = 7.5$ Hz, 2H), 1.58-1.52 (m, 2H), 1.36-1.25 (m, 10H), 0.88 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 138.7, 128.8, 128.4, 126.8, 36.3, 31.8, 31.4, 29.3, 28.9, 22.6, 14.1. MS (EI): $m/z$ (%) 236 (18), 145 (55), 124 (7), 91 (100), 69 (28), 55 (8).This compound was known: Miyazaki, T.; Kasai, S.; Ogiwara, Y.; Sakai, N. *Eur. J. Org. Chem.* 2016, 5, 1043.
Di(p-tolyl) disulfide (5a). $^1$H NMR (500 MHz, CDCl$_3$): 7.38 (d, $J = 8.5$ Hz, 4H), 7.10 (d, $J = 8.5$ Hz, 4H), 2.32 (s, 6H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 137.4, 134.0, 129.8, 128.6, 21.0. MS (EI): $m/z$ (%) 247 (10), 246 (18), 245 (100), 182 (11), 124 (20), 123 (98), 91 (19), 79 (20), 77 (16). This compound was known: Li, X.-.B.; Li, Z.-.J.; Gao, Y.-.J.; Meng, Q.-.Y.; Yu, S.; Weiss, R. G.; Tung, C.-.H.; Wu, L.-.Z. Angew. Chem. Int. Ed. 2014, 53, 2085.

Dibenzyl ether (6a). $^1$H NMR (500 MHz, CDCl$_3$): 7.50-7.42 (m, 10H), 4.69 (s, 4H). $^{13}$C NMR (125.4 MHz, CDCl$_3$): $\delta$ 138.5, 128.5, 127.9, 127.8, 72.3. MS (EI): $m/z$ (%) 107 (15), 92 (100), 91 (74), 79 (14), 77 (10), 65 (15). This compound was known: Gellert, B. A.; Kahlcke, N.; Feurer, M.; Roth, S. Chem. Eur. J. 2011, 17, 12203.
Control Reactions

1. Analysis on the Transformation of Thiols (2) to Didulfides (5)

1.1 GC-MS Analysis of the Commercial p-Tolylthiol (2a): The commercial p-tolylthiol (2a) was directly measured by GC-MS without any treatment after purchased.

**Result:** $p$-TolSH/$p$-TolS$_2$ = ca. 84/16

### GC spectra:

**Mass Spectra:**

- Ret. Time = 4.615, m/z = 124, $p$-TolSH
- Ret. Time = 8.001, m/z = 246, ($p$-TolS)$_2$

1.2 Heating the Commercial p-Tolylthiol (2a) in Air under the Standard Conditions:

**Detailed procedure:** The commercial $p$-tolylthiol (2a, 0.248 g, 2.0 mmol) was sealed in a 10 mL Schlenk tube under air and then heated at 120 °C for 12 h. The mixture was then dissolved in EtOAc and analyzed by TLC and/or GC-MS.

**GC spectra:**
2. S-Alkylation of p-Tolythiol (2a) with Dibenzyl Ether (6a) with or without PhCH$_2$Br (3a) Catalysis

Ph\(\begin{array}{c}O \end{array}\)\(\begin{array}{c}Ph \end{array}\) + \(\begin{array}{c}Ph \end{array}\)Me \(\begin{array}{c}Ph \end{array}\)Me \(\begin{array}{c}O \end{array}\)\(\begin{array}{c}Ph \end{array}\) + \(\begin{array}{c}Ph \end{array}\)Me \(\begin{array}{c}Ph \end{array}\)Me \(\begin{array}{c}O \end{array}\)\(\begin{array}{c}Ph \end{array}\)

under air \(\begin{array}{c}120 \degree C, 12 \text{ h} \end{array}\)

(1) PhCH$_2$Br (3a, 20 mol%): 66%
(2) blank: trace (<5%)

**Detailed procedure**: The mixture of benzyl ether (6a, 0.4752 g, 2.4 mmol), p-tolythiol (2a, 0.2480 g, 2.0 mmol), and benzyl bromide (3a, 0.0684 g, 20 mol%) was sealed in a 10 mL Schlenk tube under air and heated at 120 $^\circ$C for 12 h. The mixture was then dissolved in EtOAc and analyzed by TLC and/or GC-MS. The solvent was evaporated under vacuum and the residue purified by flash column chromatography on silica gel using petroleum ether as the eluent, giving 66% isolated yield of 4aa. Only trace 4aa could be observed in another control reaction without addition of benzyl bromide (3a) (entry 2).

3. S-Alkylation of Disulfide (5a) with Benzyl Alcohol (1a) with or without PhCH$_2$Br (3a) Catalysis
Detailed procedure: The mixture of benzyl alcohol (1a, 0.2160 g, 2 mmol), di(p-tolyl) disulfide (5a, 0.5904 g, 2.4 mmol) and benzyl bromide (3a, 0.0684 g, 20 mol%) was sealed in a 10 mL Schlenk tube under air and heated at 120 °C for 12 h. The mixture was then dissolved in EtOAc and analyzed by TLC and/or GC-MS. The solvent was evaporated under vacuum and the residue purified by flash column chromatography on silica gel using petroleum ether as the eluent, giving 35% isolated yield of 4aa (entry 1). Only trace 4aa could be observed in another control reaction without addition of benzyl bromide (3a) (entry 2).

4. S-Alkylation of Disulfide with Benzyl bromide

Detailed procedure: The mixture of benzyl bromide (3a, 0.4104 g, 2.4 mmol) and di(p-tolyl) disulfide (5a, 0.2460 g, 1 mmol) was sealed in a 10 mL Schlenk tube under air and heated at 120 °C for 12 h. The mixture was then dissolved in EtOAc and analyzed by TLC and/or GC-MS. The solvent was evaporated under vacuum and the residue purified by flash column chromatography on silica gel using petroleum ether as the eluent, giving 23% isolated yield of 4aa.
$^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of All Products

$^1\text{H}$ NMR

$^{13}\text{C}$ NMR
$^1$H NMR

$^{13}$C NMR
$^{1}H$ NMR

$^{13}C$ NMR
$^1$H NMR

$^{13}$C NMR
$^1$H NMR

$^{13}$C NMR
$^1$H NMR

$^{13}$C NMR
$^1$H NMR

$^{13}$C NMR

S21
\(^1\)H NMR

(1-phenylethyl)(p-tolyl)sulfane phenethyl(p-tolyl)sulfane=9:1
$^1$H NMR

$^1$C NMR
$^1$H NMR

$^{13}$C NMR
\[ ^1H\text{NMR} \]

\[ ^{13}C\text{NMR} \]
\[ ^1H \text{NMR} \]

\[ ^{13}C \text{NMR} \]
\[ ^1H \text{ NMR} \]

\[ ^{13}C \text{ NMR} \]
$^1$H NMR

$^{13}$C NMR
$^1$H NMR

$^{13}$C NMR
$^1$H NMR

$^{13}$C NMR
$^1$H NMR

$^{13}$C NMR