## **Electronic Supplementary Information**

# Efficient Synthesis of Unsymmetrical Heteroaryl Thioethers and Chalcogenides by Alkali Hydroxide-Mediated S<sub>N</sub>Ar Reactions of HeteroarylHalides and Dichalcogenides

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#### Experimental

**General.**All the chemicals, bases, and solvents were purchased and used without further purification. Unless otherwise specified, all reactions were carried out in sealed Schlenk tubes under nitrogen atmosphere and then monitored by TLC and/or GC-MS. Products were purified by column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent. <sup>1</sup>H and<sup>13</sup>C NMR spectra were measured on a Bruker Avance-III 500 instrument (500 MHz for <sup>1</sup>H, 125.4 MHz for <sup>13</sup>C NMR spectroscopy) using CDCl<sub>3</sub> as the solvent. Chemical shifts for <sup>1</sup>H and<sup>13</sup>C NMR were referred to internal Me<sub>4</sub>Si (0 ppm) as the standard. Mass spectra were measured on a Shimadzu GC-MS-QP2010 Plus spectrometer (EI). HRMS (ESI) analysis was measured on a Bruker micrOTOF-Q II instrument.

Typical Procedure of Sodium Hydroxide-Mediated  $S_NAr$  Reaction of 2-Chloropyridine with Diphenyl Disulfide for Unsymmetrical Heteroaryl Thioether Synthesis. The mixture of 2-chloropyridine 1a (56.5 mg, 47.0 µL, 0.50 mmol), diphenyl disulfide 2a (65.4 mg, 0.30 mmol, 1.2 equiv.), and sodium hydroxide (30.0 mg, 0.75 mmol, 1.5 equiv.) in dimethyl sulfoxide (1.0 mL) was sealed under nitrogen in a Schlenk tube (20 mL) and then stirred at 120 °C for 24 h. The reaction was monitored by TLC and/or GC-MS. After completion of the reaction, solvent was evaporated under vacuum. The residue was then purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (100:0 ~ 20:1) as the eluent, giving the target product 3a in 80% isolated yield.



**2-(Phenylthio)pyridine (3a).** Colourless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.43 –8.41 (m, 1H), 7.62–7.56 (m, 2H), 7.47–7.38 (m, 4H), 7.01–6.96 (m, 1H), 6.88 (dt, *J* = 8.1 Hz, *J* = 0.9 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 161.4, 149.4, 136.6 134.8, 131.0, 129.5, 128.9, 121.3, 119.8; MS (EI): m/z (%) 187 (25), 186 (100), 154 (1), 115 (5), 109 (2), 93 (5), 78 (7), 65 (4), 52 (3), 51 (12). This compound was known: X. Jia, L. Yu, J. Liu, Q. Xu, M. Sickert, L. Chen, M. Lautens, *Green Chem.***2014**, *16*, 3444-3449.



**2-(Phenylthio)pyridin-3-amine (3b).** The mixture of 2-chloropyridin-3-amine (64.0 mg, 0.50 mmol), diphenyl disulfide **2a** (65.4 mg, 0.30 mmol, 1.2 equiv.), and sodium hydroxide (30.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (120 °C) for 60 h, affording 68.0 mg **3b** (67% isolated yield) as a brown oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.02 (dd, J = 4.5 Hz, J = 1.5 Hz, 1H), 7.27–7.25 (m, 4H), 7.24–7.16 (m, 1H), 7.10–7.00 (m, 2H), 4.24 (s, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  144.2, 140.2, 139.0, 134.0, 129.4, 129.0, 126.6, 124.2, 122.0; MS (EI): m/z (%) 202 (46), 201 (100), 186 (7), 168 (5), 140 (1), 115 (2), 101 (6), 77 (4), 66 (10), 51 (4). This compound was known: X. Jia, L. Yu, J. Liu, Q. Xu, M. Sickert, L. Chen, M. Lautens, *Green Chem.***2014**, *16*, 3444-3449.



**4-Methyl-2-(phenylthio)pyridine(3c).** The mixture of 2-chloro-4-methylpyridine (63.5 mg, 0.50 mmol), diphenyl disulfide **2a** (65.4 mg, 0.30 mmol, 1.2 equiv.), and sodium hydroxide (30.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording 67.0 mg **3c** (66% isolated yield) as a yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.28 (d, J = 5.0 Hz, 1H), 7.59–7.57 (m, 2H), 7.43–7.39 (m, 3H), 6.82 (d, J = 5.0 Hz, 1H), 6.74 (s, 1H), 2.20 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  160.9, 149.3, 148.0, 134.7, 131.4, 129.5, 128.8, 122.1, 121.3, 21.0; MS (EI): m/z (%)201 (26), 200 (100), 186 (4), 115 (2), 109 (3), 100 (4), 77 (4), 65 (19), 51 (6). This compound was known: B. Sreedhar, P. S. Reddy, M. A. Reddy, *Synthesis* **2009**, 1732-1738.

Me S-Ph

**5-Methyl-2-(phenylthio)pyridine (3d).** The mixture of 2-chloro-5-methylpyridine (63.5 mg, 0.50 mmol), diphenyl disulfide **2a** (65.4 mg, 0.30 mmol, 1.2 equiv.), and sodium hydroxide (30.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording 51.0 mg **3d** (51% isolated yield) as a brown oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.27 (d, J = 2.0 Hz, 1H), 7.56–7.54 (m, 2H), 7.40–7.37 (m, 3H), 7.28 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H),

6.86 (d, *J* = 8.0 Hz, 1H), 2.26 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 157.6, 150.0, 137.5, 134.3, 132.1, 129.7, 129.5, 128.6, 121.8, 17.8; MS (EI): m/z (%) 201 (27), 200 (100), 185 (2), 156 (1), 109 (3), 93 (2), 77 (4), 65 (18), 51 (6). This compound was known: S. Arai, M. Yamazaki, M. Hida, *J. Heterocyclic.Chem.***1990**, *27*, 1073-1078.



**6**-(**Phenylthio**)**nicotinonitrile** (**3e**). The mixture of 6-chloronicotinonitrile (69.0 mg, 0.50 mmol), diphenyl disulfide **2a** (65.4 mg, 0.30 mmol, 1.2 equiv.), and sodium hydroxide (30.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (150 °C) for 60 h, affording 61.0 mg **3e** (57% isolated yield) as a colourless solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.63 (dd, J = 2.0 Hz, J = 1.0 Hz, 1H), 7.64–7.59 (m, 3H), 7.51–7.47 (m, 3H), 6.90 (dd, J = 8.5 Hz, J = 0.5 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.0, 152.1, 138.9, 135.6, 130.2, 130.1, 128.5, 120.0, 116.8, 105.1; MS (EI): m/z (%) 212 (29), 211 (100), 179 (1), 140 (7), 109 (4), 92 (2), 82 (2), 77 (7), 69 (4), 51 (10). This compound was known: X. Jia, L. Yu, J. Liu, Q. Xu, M. Sickert, L. Chen, M. Lautens, *Green Chem.***2014**, *16*, 3444-3449.

**5-Nitro-2-(phenylthio)pyridine (3f).** The mixture of 2-chloro-5-nitropyridine (79.0 mg, 0.50 mmol), diphenyl disulfide **2a** (65.4 mg, 0.30 mmol, 1.2 equiv.), and sodium hydroxide (30.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (150 °C) for 60 h, affording 89.0 mg**3f**(77% isolated yield) as a colourless solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  9.20 (d, J = 2.5 Hz, 1H), 8.18 (dd, J = 9.0 Hz, J = 2.5 Hz, 1H), 7.63–7.61 (m, 2H), 7.56–7.49 (m, 3H), 6.92 (d, J = 9.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  170.3, 145.0, 141.0, 135.5, 131.2, 130.4, 130.1, 128.4, 119.7; MS (EI): m/z (%) 232 (38), 231 (100), 201 (11), 185 (49), 173 (5), 115 (11), 109 (29), 77 (10), 65 (17), 52 (1), 51 (8). This compound was known: X. Jia, L. Yu, J. Liu, Q. Xu, M. Sickert, L. Chen, M. Lautens, *Green Chem.***2014**, *16*, 3444-3449.

3-Chloro-2-(phenylthio)pyridine (3g). The mixture of 2,3-dichloropyridine (73.5 mg, 0.50

mmol), diphenyl disulfide **2a** (65.4 mg, 0.30 mmol, 1.2 equiv.), and sodium hydroxide (30.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording 87.0 mg **3g** (79% isolated yield) as a brown oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.22 (dd, J = 4.5Hz, J = 1.5 Hz, 1H), 7.60–7.56 (m, 3H), 7.49–7.42 (m, 3H), 7.05–6.95 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  158.5, 148.4, 137.2, 136.3, 130.7, 130.1, 130.0, 129.7, 121.6; MS (EI): m/z (%) 221 (29), 220 (100), 185 (15), 140 (2), 115 (5), 85 (2), 76 (7), 65 (6), 52 (1), 51 (9). This compound was known:X. Jia, L. Yu, J. Liu, Q. Xu, M. Sickert, L. Chen, M. Lautens, *Green Chem*.**2014**, *16*, 3444-3449.

**5-Chloro-2-(phenylthio)pyridine (3h).** The mixture of 2,5-dichloropyridine (73.5 mg, 0.50 mmol), diphenyl disulfide **2a** (65.4 mg, 0.30 mmol, 1.2 equiv.), and sodium hydroxide (30.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording 83.0 mg **3h** (75% isolated yield)as a yellow oil.<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.38 (dd, J = 2.4 Hz, J = 0.6 Hz, 1H), 7.61–7.55 (m, 2H), 7.48–7.40 (m, 4H), 6.83 (dd, J = 8.7 Hz, J = 0.9 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  160.6, 149.1, 135.3, 135.8, 131.7, 130.7, 130.3, 129.2, 123.1; MS (EI): m/z (%) 221 (28), 220 (100), 185 (13), 158 (1), 140 (4), 93 (11), 76 (12), 65 (10), 51 (12). This compound was known:X. Jia, L. Yu, J. Liu, Q. Xu, M. Sickert, L. Chen, M. Lautens, *Green Chem.***2014**, *16*, 3444-3449.



**4-Chloro-2-(phenylthio)pyridine (3i).** The mixture of 2,4-dichloropyridine (73.5 mg, 0.50 mmol), diphenyl disulfide **2a** (65.4 mg, 0.30 mmol, 1.2 equiv.), and sodium hydroxide (30.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording 76.0 mg **3i** (69% isolated yield) as a yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.10 (d, J = 5.0 Hz, 1H), 7.57–7.53 (m, 2H), 7.51–7.45 (m, 3H), 6.89 (d, J = 1.5 Hz, 1H), 6.84 (dd, J = 5.5 Hz, J = 1.5 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  153.8, 151.8, 148.9, 135.3, 130.2, 130.1, 128.4, 120.2, 119.3; MS (EI): m/z (%) 221 (100), 186 (44), 158 (6), 140 (14), 115 (25), 109 (19), 93 (7), 85 (10), 77 (21) 65 (22), 51 (34). This compound was known:X. Jia, L. Yu, J.

Liu, Q. Xu, M. Sickert, L. Chen, M. Lautens, Green Chem. 2014, 16, 3444-3449.



**2,4-Bis(phenylthio)pyridine (3i').** The mixture of 2,4-dichloropyridine (73.5 mg, 0.50 mmol), diphenyl disulfide **2a** (131.0 mg, 0.60 mmol, 2.4 equiv.), and sodium hydroxide (60.0 mg, 1.50 mmol, 3.0 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording 116.0 mg **3i'** (79% isolated yield) as a yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.15 (d, *J* = 5.0 Hz, 1H), 7.49–7.47 (m, 2H), 7.42–7.33 (m, 8H), 6.66 (dd, *J* = 5.5 Hz, *J* = 1.5 Hz, 1H), 6.40 (d, *J* = 1.5 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  161.9, 151.4, 148.8, 135.2, 135.0, 130.4, 129.8, 129.64, 129.58, 129.1, 128.9, 117.3, 117.1; MS (EI): m/z (%) 295 (36), 294 (100), 260 (1), 217 (4), 185 (12), 173 (4), 147 (5), 115 (10), 77 (8), 51 (7). This compound was known: X. Jia, L. Yu, J. Liu, Q. Xu, M. Sickert, L. Chen, M. Lautens, *Green Chem.***2014**, *16*, 3444-3449.



**2-Chloro-6-(phenylthio)pyridine (3j).** The mixture of 2,6-dichloropyridine (73.5 mg, 0.50 mmol), diphenyl disulfide **2a** (65.4 mg, 0.30 mmol, 1.2 equiv.), and sodium hydroxide (30.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording 88.0 mg **3j** (80% isolated yield) as a yellow oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.62–7.59 (m, 2H), 7,47–7.42 (m, 3H), 7.40–7.34 (m, 1H), 6.99 (dd, J = 7.8 Hz, J = 0.6 Hz, 1H), 6.68 (dd, J = 8.1 Hz, J = 0.6 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  162.8, 150.8, 138.8, 135.2, 130.0, 129.8, 129.5, 119.8, 119.1; MS (EI): m/z (%) 221 (54), 220 (100), 186 (20), 153 (4), 140 (8), 115 (10), 109 (10), 93 (9), 76 (15), 65 (13), 51 (17). This compound was known:X. Jia, L. Yu, J. Liu, Q. Xu, M. Sickert, L. Chen, M. Lautens, *Green Chem.***2014**, *16*, 3444-3449.

**2,6-Bis(phenylthio)pyridine (3j').** The mixture of 2,6-dichloropyridine (73.5 mg, 0.50 mmol), diphenyl disulfide **2a** (131.0 mg, 0.60 mmol, 2.4 equiv.), and sodium hydroxide (60.0 mg, 1.50 mmol, 3.0 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording 115.0 mg **3j'** (78% isolated yield) as a colourless solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ 

7.60–7.56 (m, 4H), 7.41–7.39 (m, 6H), 7.18 (t, J = 8.1 Hz, 1H), 6.52 (d, J = 8.1 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  161.5, 136.9, 135.0, 130.7, 129.4, 129.0, 117.0; MS (EI): m/z (%) 296 (24), 295 (88), 294 (100), 216 (16), 186 (58), 185 (36), 115 (22), 109 (16), 77 (17), 65 (11), 51 (11). This compound was known: X. Jia, L. Yu, J. Liu, Q. Xu, M. Sickert, L. Chen, M. Lautens, *Green Chem.***2014**, *16*, 3444-3449.



**4-(Phenylthio)pyridine (3k).** The mixture of 4-iodopyridine (102.5 mg, 0.50 mmol), diphenyl disulfide **2a** (65.4 mg, 0.30 mmol, 1.2 equiv.), and sodium hydroxide (30.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording 42.0 mg **3k** (45% isolated yield) as a brown oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.34 (d, J = 4.8 Hz, 2H), 7.57–7.51 (m, 2H), 7.48–7.40 (m, 3H), 6.93 (dd, J = 4.5 Hz, J = 1.5 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  150.2, 149.4, 135.1, 129.8, 129.6, 129.4, 120.8; MS (EI): m/z (%) 187 (100), 186 (68), 160 (7), 154 (7), 134 (2), 128 (3), 115 (14), 65 (7), 52 (2), 51 (28). This compound was known: G. R. Alfonso, F. I. M. Angeles, R. G. Arrayas, J. C. Carretero, *Chem. Eur. J.* **2011**, *17*, 3567-3570.



**2-(Phenylthio)quinoline (31).** The mixture of 2-chloroquinoline (81.5 mg, 0.50 mmol), diphenyl disulfide **2a** (65.4 mg, 0.30 mmol, 1.2 equiv.), and sodium hydroxide (30.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording 107.0 mg **3l** (90% isolated yield) as a yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.95 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 9.0 Hz, 1H), 7.68–7.63 (m, 4H), 7.45–7.41 (m, 4H), 6.98 (d, *J* = 9.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  161.4, 148.0, 136.3, 135.0, 130.8, 129.9, 129.5, 129.1, 128.2, 127.4, 125.7, 125.6, 119.4; MS (EI): m/z (%) 237 (44), 236 (100), 204 (3), 165 (2), 128 (13), 119 (5), 101 (17), 65 (3), 51 (6). This compound was known: X. Jia, L. Yu, J. Liu, Q. Xu, M. Sickert, L. Chen, M. Lautens, *Green Chem.***2014**, *16*, 3444-3449.

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**2-(Phenylthio)pyrimidine (3m).** The mixture of 2-chloropyrimidine (57.0 mg, 0.50 mmol), diphenyl disulfide **2a** (65.4 mg, 0.30 mmol, 1.2 equiv.), and sodium hydroxide (30.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording 57.0 mg **3m** (61% isolated yield) as a brown oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.48 (d, *J* = 4.5 Hz, 2H), 7.66–7.62 (m, 2H), 7.45–7.43 (m, 3H),6.96 (t, *J* = 5.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  172.8, 157.5, 135.2, 129.4, 129.3, 129.2, 116.9; MS (EI): m/z (%) 188 (35), 187 (100), 160 (3), 135 (4), 109 (10), 77 (16), 65 (9), 63 (4), 51 (11). This compound was known: M. Egi, L. S. Liebeskind, *Org. Lett.***2003**, *5*, 801-802.



**2-(Phenylthio)benzo[d]thiazole(3n).** The mixture of 2-chlorobenzo[d]thiazole (84.5 mg, 0.50 mmol), diphenyl disulfide **2a** (65.4 mg, 0.30 mmol, 1.2 equiv.), and sodium hydroxide (30.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording 107.0 mg **3n** (88% isolated yield) as a yellow oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.90–7.86 (m, 1H), 7.75–7.71 (m, 2H), 7.65–7.61 (m, 1H), 7.53–7.36 (m, 4H), 7.28–7.22 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  170.4, 154.9, 136.5, 136.2, 131.4, 130.8, 127.1, 125.3, 122.9, 121.7; MS (EI): m/z (%) 243 (56), 242 (100), 209 (2), 121 (8), 108 (9), 82 (4), 77 (6), 65 (8), 51 (8). This compound was known: X. Jia, L. Yu, J. Liu, Q. Xu, M. Sickert, L. Chen, M. Lautens, *Green Chem.***2014**, *16*, 3444-3449.



**4-(Pyridin-2-ylthio)aniline(30).** The mixture of 2-chloropyridine **1a** (56.5 mg, 47.0 µL, 0.50 mmol), di(4-aminophenyl) disulfide (74.4 mg, 0.30 mmol, 1.2 equiv.), and sodium hydroxide (30.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording 62.0 mg **30** (61% isolated yield)as a yellow oil.<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.39 –8.37 (m, 1H), 7.41–7.36 (m, 3H), 6.94–6.91 (m, 1H), 6.77 (dt, J = 8.5 Hz, J = 1.0 Hz, 1H), 6.73–6.70 (m, 2H), 3.66 (br, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  163.6, 149.2, 147.9, 137.2, 136.5, 120.0, 119.1, 117.4, 115.9; MS (EI): m/z (%) 203 (11), 202 (58), 201 (100), 184 (13), 124 (23), 101 (5), 97 (9), 91 (5), 88 (9), 80 (42), 79 (5), 78 (38), 73 (11), 70 (29), 69 (8), 67

(6), 65 (12), 64 (6), 63 (35), 62 (10), 61 (34), 53 (14), 52 (14), 51 (25). This compound was known: X. L. Fang, R. Y. Tang, X. G. Zhang, J. H. Li, *Synthesis***2011**, 7, 1099-1105.



**2-(Pyridin-2-ylthio)aniline (3p).** The mixture of 2-chloropyridine **1a** (56.5 mg, 47.0  $\mu$ L, 0.50 mmol), di(2-aminophenyl) disulfide (74.4 mg, 0.30 mmol, 1.2 equiv.), and sodium hydroxide (30.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (150 °C) for 24 h, affording52.5 mg **3p** (52% isolated yield) as a coloueless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.42 (d, *J* = 4.0 Hz, 1H), 7.50 (dd, *J* = 7.5Hz, *J* =1.0 Hz, 1H), 7.43 (dt, *J* = 9.0Hz, *J* = 1.5 Hz, 1H), 7.30–7.28 (m, 1H), 6.99 (dd, *J* = 7.5Hz, *J* = 5.0 Hz, 1H), 6.88–6.61 (m, 3H), 4.37 (brs, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ 160.5, 149.6, 149.2, 137.8, 136.8, 131.8, 119.9, 119.8, 118.9, 115.5, 112.8. This compound was known: H. W. Lee, K. F. Yung, F. Y. Kwong, *Synlett*. **2014**, *25*, 2743-2747.



**2-(4-Methoxyphenylthio)pyridine (3q).** The mixture of 2-chloropyridine **1a** (56.5 mg, 47.0 µL, 0.50 mmol), di(4-methoxyphenyl) disulfide (83.4 mg, 0.30 mmol, 1.2 equiv.), and sodium hydroxide (30.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording 81.5 mg **3q** (75% isolated yield) as a yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.40 (d, J = 4.5 Hz, 1H), 7.55–7.52 (m, 2H), 7.44–7.41 (m, 1H), 6.98 –6.94 (m, 3H), 6.79 (d, J = 8.0 Hz, 1H), 3.85 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  162.8, 160.7, 149.4, 137.2, 136.6, 121.2, 120.5, 119.4, 115.3, 55.4; MS (EI): m/z (%) 218 (11), 217 (53), 216 (100), 202 (8), 201 (23), 186 (5), 174 (7), 173 (12), 78 (17), 70 (12), 63 (6), 61 (11), 51 (6).This compound was known:X. Jia, L. Yu, J. Liu, Q. Xu, M. Sickert, L. Chen, M. Lautens, *Green Chem.***2014**, *16*, 3444-3449.



**2-(Thiophen-2-ylthio)pyridine (3s).** The mixture of **1a** (56.5 mg, 47.0  $\mu$ L, 0.50 mmol), di(thiophen-2-yl) disulfide (69.0 mg, 0.30 mmol, 1.2 equiv.), and sodium hydroxide (30.0 mg,

0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording 64.0 mg **3s** (66% isolated yield)as a yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.42 (d, J = 5.0 Hz, 1H), 7.58 (dd, J = 5.5 Hz, J = 1.5 Hz, 1H), 7.48 (dt, J = 7.5 Hz, J = 1.5 H, 1H), 7.37 (dd, J = 3.5 Hz, J = 1.0 Hz, 1H), 7.15 (dd, J = 5.5 Hz, J = 3.5 Hz, 1H), 7.02–6.99 (m, 1H), 6.87 (d, J = 8.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  162.1, 149.3, 137.2, 136.9, 132.4, 128.3, 120.02, 119.98. Calcd for C<sub>9</sub>H<sub>8</sub>NS<sub>2</sub> (M+H): 194.0093; found: 194.0100.



**2-(Benzylthio)pyridine(3t).** The mixture of 2-chloropyridine **1a** (56.5 mg, 47.0  $\mu$ L, 0.50 mmol), dibenzyl disulfide (73.8 mg, 0.30 mmol, 1.2 equiv.), and sodium hydroxide (30.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording 88.0 mg **3t** (88% isolated yield) as a yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.45–8.43 (m, 1H), 7.44–7.39 (m, 3H), 7.29–7.26 (m, 2H), 7.23–7.21 (m, 1H), 7.13 (d, *J* = 8.5 Hz, 1H), 6.97–6.94 (m, 1H), 4.43 (s, 2H); <sup>13</sup>C NMR (125.4 MHz, CDCl<sub>3</sub>):  $\delta$  158.7, 149.3, 137.9, 135.9, 128.9, 128.4, 127.0, 122.0, 119.5, 34.4; MS (EI): m/z (%) 202 (9), 201 (65), 169 (14), 168 (100), 167 (23), 124 (8), 91 (49), 79 (13), 65 (17), 51 (5). This compound was known:X. Jia, L. Yu, J. Liu, Q. Xu, M. Sickert, L. Chen, M. Lautens, *Green Chem.***2014**, *16*, 3444-3449.

Typical Procedure of Potassium Hydroxide-Mediated S<sub>N</sub>Ar Reaction of 2-Chloropyridine with Diphenyl Diselenide for Unsymmetrical Heteroaryl Selenide Synthesis. The mixture of 2-chloropyridine 1a (56.5 mg, 47.0  $\mu$ L, 0.50 mmol), diphenyl diselenide 4 (93.6 mg, 0.30 mmol, 1.2 equiv.), and potassium hydroxide (42.0 mg, 0.75 mmol, 1.5 equiv.) in dimethyl sulfoxide (1.0 mL) was sealed under nitrogen in a Schlenk tube (20 mL) and then stirred at 120 °C for 24 h. The reaction was monitored by TLC and/or GC-MS. After completion of the reaction, solvent was evaporated under vacuum. The residue was then purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (100:0 ~ 20:1) as the eluent, giving the target product 5a in 88% isolated yield.



**2-(Phenylselanyl)pyridine (5a).** Yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.43 (dd, *J* = 5.0 Hz, *J* =1.0 Hz, 1H), 7.72–7.70 (m, 2H), 7.42–7.37 (m, 4H), 7.03–6.99 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 158.8, 149.9, 136.6, 136.2, 129.7, 128.8, 127.8, 124.2, 120.4; This compound was known:N. Taniguchi, T. Onami, *J. Org. Chem.*, **2004**, 69, 915-920.

**5-Methyl-2-(phenylselanyl)pyridine (5b).** The mixture of 2-chloro-5-methylpyridine (63.5 mg, 0.50 mmol), diphenyl diselenide **4** (93.6 mg, 0.30 mmol, 1.2 equiv.), and potassium hydroxide (42.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording 110.0 mg **5b** (88% isolated yield) as a yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.29 (dd, J = 1.5 Hz, J = 0.5 Hz, 1H), 7.68–7.67 (m, 2H), 7.37–7.36 (m, 3H),7.25–7.23 (m, 1H), 6.97 (d, J = 8.0 Hz, 1H), 2.25 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  154.5, 150.3, 137.5, 135.7, 130.2, 129.6, 128.6, 128.5, 124.6, 17.9; This compound was known:K. K. Bhasin, S. Doomra, G. Kaur, E. Arora, N. Singh, Y. Nagpal, R. Kumar, Rishu, T. M. Klapoetke, S. K. Mehta, *Phosphorus, Sulfur, and Silicon and the Related Elements* **2008**, *183*, 992-997.

**3-Chloro-2-(phenylselanyl)pyridine (5c).** The mixture of 2,3-dichloropyridine (73.5 mg, 0.50 mmol), diphenyl diselenide **4** (93.6 mg, 0.30 mmol, 1.2 equiv.), and potassium hydroxide (42.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording 116.0 mg **5c** (86% isolated yield) as a yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.23 (dd, J = 4.5 Hz, J = 1.5 Hz, 1H), 7.71–7.66 (m, 2H), 7.54 (dd, J = 6.5 Hz, J = 1.5 Hz, 1H), 7.46–7.39 (m, 3H), 7.01–6.98 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  156.0, 147.9, 136.5, 135.7, 131.1, 129.2, 128.7, 127.1, 121.2; This compound was known: S. Thurow, R. Webber, G. Perin, E. J. Lenardão, D. Alves, *Tetrahedron Lett.* **2013**, *54*, 3215-3218.



4-(Phenylselanyl)pyridine (5d). The mixture of 4-iodopyridine (102.5 mg, 0.50 mmol),

diphenyl diselenide **4** (93.6 mg, 0.30 mmol, 1.2 equiv.), and potassium hydroxide (42.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording 49.5 mg **5d** (42% isolated yield) as a yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.31 (dd, J = 4.5 Hz, J = 1.5 Hz, 2H), 7.65–7.63 (m, 2H), 7.46–7.38 (m, 3H), 7.09 (dd, J = 4.5 Hz, J = 1.5 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  149.5, 145.7, 136.2, 129.9, 129.3, 126.2, 123.9; This compound was known: H.Zhao, Y. Jiang, Q. Chen, M. Cai, *New J. Chem.*, **2015**, *39*, 2106-2115



**2-(Phenylselanyl)quinoline (5e).** The mixture of 2-chloroquinoline (81.5 mg, 0.50 mmol), diphenyl diselenide **4** (93.6 mg, 0.30 mmol, 1.2 equiv.), and potassium hydroxide (42.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording110.0 mg **5e** (77% isolated yield) as a colourless solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.99 (d, J = 8.5 Hz, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.76 (dd, J = 8.0 Hz, J = 1.2 Hz, 2H), 7.72–7.58 (m, 2H), 7.54–7.33 (m, 4H), 7.05 (d, J = 8.5 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  159.7, 148.4, 136.5, 136.3, 130.1, 129.8, 129.1, 128.3, 127.8, 127.7, 126.1, 126.0, 121.9; This compound was known: A. B. Penenory, A. B. Pierini, R. A. Rossi, *J. Org. Chem.*, **1984**, *49*, 3834-3835.



**2-(Phenylselanyl)benzo[d]thiazole (5f).** The mixture of 2-chlorobenzo[d]thiazole (84.5 mg, 0.50 mmol), diphenyl diselenide **4** (93.6 mg, 0.30 mmol, 1.2 equiv.), and potassium hydroxide (42.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (120 °C) for 24 h, affording 102.0 mg **5f** (70% isolated yield) as a colourless solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 (d, *J* = 8.5 Hz, 1H), 7.88–7.80 (m, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.52–7.34 (m, 4H), 7.27 (t, *J* = 8.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  163.0, 154.4, 136.62, 136.56, 130.1, 130.0, 126.6, 126.1, 124.4, 121.9, 120.8; This compound was known: A. R. Rosario, K. K. Casola, C. E. Oliveira, G. Zeni, *Adv. Syn. Catal.*, **2013**, *355*, 2960-2966.



**2-(Phenyltelluranyl)pyridine (5g).** The mixture of 2-chloropyridine **1a** (56.5 mg, 47.0  $\mu$ L, 0.50 mmol), diphenyl ditelluride (124.0 mg, 0.30 mmol, 1.2 equiv.), and caesium hydroxide (112.5 mg, 0.75 mmol, 1.5 equiv.) in DMSO was heated following the typical procedure (150 °C) for 24 h, affording 41.0 mg **5g** (29% isolated yield) as a yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.47 (d, *J* = 3.5 Hz, 1H), 8.02–7.89 (m, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.35–7.26 (m, 3H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.02 (ddd, *J* = 7.5 Hz, *J* = 4.5 Hz, *J* = 1.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  150.6, 146.3, 140.6, 136.1, 130.3, 129.9, 128.9, 121.1, 113.7; MS (EI): m/z (%) 285 (55),283 (51), 281 (30), 280 (29), 207 (8), 155 (46), 154 (63), 127 (9), 78 (100), 77 (88), 51 (82). Calcd for C<sub>11</sub>H<sub>10</sub>NTe (M+H): 285.9875; found: 285.9873.

#### Control Reactions on Transformation of (RY)<sub>2</sub> by NaOH and Data Analysis

To check whether  $(PhS)_2$  was transformed by bases to  $PhSO_2H$  (25%) according to Danehy and Hunter's report (see equation below—eq. 6 in the manuscript, see also ref 22: *J. Org. Chem.*, 1967, **32**, 2047), the following reactions was performed and analyzed with great care.

 $2 R_2 S_2 + 4 OH^- \longrightarrow 3 RS^- + RSO_2^- + 2 H_2 O$  (6)

#### i) Reaction A (the standard reaction):

N CI +	(PhS) <sub>2</sub>	NaOH (1.5 equiv.) DMSO, N <sub>2</sub> , 120 <sup>o</sup> C, 24 h	N SPh +	. Ph <sup>S</sup> `Me	+ PhSO <sub>2</sub> H
<b>1a</b> m/z = 113	<b>2a</b> m/z = 218		<b>3a</b> m/z = 187	<b>8</b> m/z = 124	not observed

**Procedure (the standard conditions):** The mixture of 2-chloropyridine **1a** (56.5 mg, 47.0  $\mu$ L, 0.50 mmol), (PhS)<sub>2</sub> **2a** (65.4 mg, 0.30 mmol), and NaOH (30.0 mg, 0.75 mmol, 1.5 equiv.) in DMSO (1.0 mL) was sealed under nitrogen in a Schlenk tube (20 mL) and stirred at 120 °C for 24 h. The reaction mixture was then directly acidized with HCl (1 N) to pH = 1, and extracted with ethyl acetate (3 × 10 mL). The combined organic layer were then washed with brine (10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under vacuum and the oily residue analyzed by GC-MS (see below).







**Discussion:** Firstly, we re-investigated the above standard reaction. If PhSO<sub>2</sub>H is generated in the reaction according to Danehy and Hunter's report (ref 22: *J. Org. Chem.*, 1967, **32**, 2047), it should be firstly produced as PhSO<sub>2</sub>Na. Therefore, we acidized the crude reaction mixture to transfer the potential PhSO<sub>2</sub>Na to PhSO<sub>2</sub>H, which was then concentrated and analyzed by GC-MS (see above). However, only trace of the starting 2-chloropyridine **1a**, large amounts of product **3a**, and trace amount of PhSMe (**8**) were detected. No PhSO<sub>2</sub>H could be observed at all. PhSMe (**8**) was most possibly formed by reactions of DMSO that acted as the Me source (for literatures on DMSO as Me and CH<sub>2</sub> source, see ref. 25 in the manuscript).

#### ii) Reaction B (more amounts of 2a and NaOH in the standard reaction):

	(PhS)	NaOH (2.0 equiv.)	+	SS	+ PhSO₂H
N CI	(1110)2	DMSO, N <sub>2</sub> , 120 ºC, 24 h	N SPh	Pn ~ Ph	1 1100211
1a	2a		3a	9	not observed
m/z = 113	m/z = 218		m/z = 187	m/z = 232	

**Procedure:** The mixture of 2-chloropyridine **1a** (56.5 mg, 47.0  $\mu$ L, 0.50 mmol), (PhS)<sub>2</sub> **2a** (87.2 mg, 0.40 mmol), and NaOH (40.0 mg, 1.0 mmol, 2.0 equiv.) in DMSO (1.0 mL) was sealed under nitrogen in a Schlenk tube (20 mL) and then stirred at 120 °C for 24 h. After completion of the reaction, the reaction mixture was acidized with HCl (1 N) to pH = 1, and then extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine (10 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was then evaporated under vacuum and the oily residue analyzed by GC-MS.

#### GC-MS results and analysis: GC:



$$t = 7.825 \text{ min}, \text{m/z} = 232, (PhS)_2CH_2 9 \text{ (trace)}$$



**Discussion:** Since no PhSO<sub>2</sub>H was observed in reaction A, we conducted reaction B with more amounts of **2a** and NaOH added in the same reaction, hoping that more amounts of PhSO<sub>2</sub>H could be generated and detected. However, GC-MS analysis (see above) also showed that no PhSO<sub>2</sub>H could be observed. Only product **3a**, small amounts of unreacted (PhS)<sub>2</sub>(**2a**) and small amounts of (PhS)<sub>2</sub>CH<sub>2</sub> (**9**) were observed. (PhS)<sub>2</sub>CH<sub>2</sub> (**9**) was most possibly formed by reactions of DMSO when more (PhS)<sub>2</sub> was added (for literatures on DMSO as Me and CH<sub>2</sub> source, see ref. 25 in the manuscript).

#### iii) Reaction C (Doubled loading of the reactants in reaction B):



**Procedure:** The mixture of 2-chloropyridine **1a** (1.0 mmol), (PhS)<sub>2</sub> **2a** (0.80 mmol) and NaOH (2.0 mmol) in DMSO (2 mL) was also performed at 120 °C for 24 h. After completion of the reaction, 20 mL water was added to the reaction mixture (to solve the potential PhSO<sub>2</sub>Na). The organic layer and the aqueous layer were separated. The aqueous layer was washed with ethyl acetate ( $3 \times 10 \text{ mL}$ ), and then acidized with HCl (1 N) to pH = 1 to transfer the potential PhSO<sub>2</sub>Na to PhSO<sub>2</sub>H. The acidized aqueous layer was further extracted with ethyl acetate ( $3 \times 10 \text{ mL}$ ) (to transfer potential PhSO<sub>2</sub>H to the organic solvent). The organic extracts were then washed with brine ( $1 \times 10 \text{ mL}$ ) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Solvent was evaporated under vacuum, giving only small amounts of the oily reaction residue, which was unable to be purified by standard procedures (in contrast, PhSO<sub>2</sub>H should be white solid easy to purify). The oily residue was then analyzed by GC-MS (see below), TLC, and NMR.

#### GC-MS Analysis of the oily residue from the aqueous layer: GC:



t = 6.725 min, m/z = 187, product 3a (trace)



**Discussion:** In order to isolate the potential  $PhSO_2H$  from the reaction mixture, we doubled the loading of the reactants hoping that more amounts of  $PhSO_2H$  could be produced and detected. However, only trace product **3a**, the starting  $(PhS)_2$  **2a** and unreacted PhSH were observed from the oily residue of the aqueous layer of the reaction mixture by GC-MS. No PhSO<sub>2</sub>H could be isolated or even merely detected by GC-MS. The oily residue was also analyzed by TLC by comparison with the authentic sample of PhSO<sub>2</sub>H (freshly prepared from PhSO<sub>2</sub>Na and HCl), but no presence of PhSO<sub>2</sub>H could be observed. The oily residue was also analyzed by <sup>1</sup>H NMR, but the spectrum is very complex and hard to determine the presence of PhSO<sub>2</sub>H.

#### iv) Reaction D (the standard reaction without 1a added):



**Procedure:** The mixture of  $(PhS)_2$  **2a** (65.4 mg, 0.30 mmol), and NaOH (30.0 mg, 0.75 mmol) in DMSO (1.0 mL) was sealed under nitrogen in a Schlenk tube (20 mL) and then stirred at 120 <sup>o</sup>C for 24 h. The reaction mixture was then directly acidized with HCl (1 N) to pH = 1, and extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine (10 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the oily residue analyzed by GC-MS.





**Discussion:** Since no PhSO<sub>2</sub>H was observed in all the above reactions, we reckon that the addition of **1a** may reduce the formation of PhSO<sub>2</sub>H in the reaction mixtures (in this regard, this control reaction is not a good reference even PhSO<sub>2</sub>H was detected). However, GC-MS analysis of the acidized reaction mixture showed that, only PhSH, PhSMe **8**, (PhS)<sub>2</sub>CH<sub>2</sub> **9** and unreated (PhS)<sub>2</sub> **2a** were detected without any trance of PhSO<sub>2</sub>H observed.

#### v) Tentative Conclusion

As shown above, although we tried the above slightly different reactions under the standard conditions, and performed and analyzed the reactions with great care by means of NMR, GC-MS, TLC comparison with the authentic sample of sulfonic acid, even purification of the reaction residue containing the potential sulfonic acid, no any trace of PhSO<sub>2</sub>H could be observed in all the above reactions including the one without addition of 2-chloropyridine 1a (reaction D). This most likely suggestes that PhSO<sub>2</sub>H was not generated in the present reactions. This is possible because the conditions of the present MOH (M = Na, K, Cs)/DMSO systems are different to the literature report of aqueous alkali conditions (ref 22: J. Org. Chem., 1967, 32, 2047). However, due to the observation of some byproducts such as PhSMe 8 and (PhS)<sub>2</sub>CH<sub>2</sub> 9, which are most possibly formed by reactions of DMSO that acted as the Me and CH<sub>2</sub> source (for literatures on DMSO as Me and CH<sub>2</sub> source, see ref. 25 in the manuscript), DMSO might play an important role in the reactions. Although how disulfides are transformed into the corresponding thio anions by treatment with bases and how many thio anions (at least 1 equiv., up to 2 equiv.) could be generated in present reactions are still not clear at present, which is similar to the previous reports (ref. 15-16) and deserve further mechanistic studies in the future, it is certain that more than 1 equiv. up to 2 equiv. of this anions could be generated form  $(RS)_2$  as the this source.

Therefore, the mechanism section was revised by adding the discussions on this subject and citations, with the mechanism scheme revised not to show clearly the stoichiometry between dichalcogenides and anions 6.

# Copies of <sup>1</sup>H and <sup>13</sup>C NMR Spectra of the Products



<sup>1</sup>H NMR



















































NO<sub>2</sub>



























































<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)







































Cl













