Efficient Silver-Catalyzed Direct Sulfenylation and Selenylation of Rich Arenes

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**General** 1-methoxynaphthalene, aryl iodides and aryl thiols were purchased from Alfa Aesar and Shaoyuan Webstore. Chloroform-\(d\) was purchased from Cambridge Isotope Laboratories. All solvents were distilled prior to use. All reactions with air- and moisture-sensitive components were performed under a nitrogen atmosphere in a flame-dried reaction flask. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. \(^1\)H NMR (300 MHz) and \(^{13}\)C NMR (75 MHz) spectra were measure on Bruker 300 M spectrometers. CDCl\(_3\) was used as solvent with tetramethylsilane (TMS) as internal standard.

**General procedure for the preparation of diaryl disulfides**\(^{[1]}\)

![Diagram](image)

To the stirred solution of thiols (5 mmol) in dichloromethane (10 mL), NCS (0.5 eq.) was added. The mixture was then stirred for 30 min. The progress of the reaction was monitored by TLC. After completion of the reaction, CH\(_2\)Cl\(_2\) (10 mL) was added and the mixture was washed successively with water (2×20mL). The organic layer was separated and dried by adding anhydrous Na\(_2\)SO\(_4\). Evaporation of the solvent under reduced pressure gave almost pure product. Further purification was achieved by column chromatography on silica gel (ethyl acetate: hexane (1:30)) to give pure product in good to excellent yield.

**General procedure for the preparation of diaryl diselenides**\(^{[2]}\)

![Diagram](image)

To a stirred solution of Se (0) metal (4.0 mmol) and aryl iodides (2.0 mmol) in dry DMSO (3.0 mL) was added CuO (10 mol %) followed by KOH (2.0 equiv) under nitrogen atmosphere at 90 °C. The progress of the reaction was monitored by TLC. After the reaction was complete, Et\(_2\)O (10 mL) was added and the mixture was washed successively with water (2×20mL). The organic layer was separated and dried by adding anhydrous Na\(_2\)SO\(_4\). Evaporation of the solvent under reduced pressure gave...
almost pure product. Further purification was achieved by column chromatography on silica gel (ethylacetate: hexane (1:50)) to give pure product in good to excellent yield.

**Typical procedure for sulfenylation of sp² C-H bonds**

Under air atmosphere, 1-methoxynaphthalene (47.4 mg, 0.3 mmol), diaryl disulfides (0.3 mmol), AgSbF₆ (15.4 mg, 15 mol%), Cu(OAc)₂·H₂O (24 mg, 0.4 eq.) were added to a screw-capped vial, followed by addition of a stir bar and DCE (2 mL). The reaction vial was placed in a temperature-controlled aluminum-heating block set at 100 °C. After 12 h of stirring, the vial was removed from the heating block and was left to cool to the ambient temperature. The solvents were removed under reduced pressure and the crude reaction mixture was purified by silica gel column chromatography with Petroleum ether/EtOAc as an eluent to give the desired product.

**Typical procedure for selenylation of sp² C-H bonds**

Under air atmosphere, 1-methoxynaphthalene (47.4 mg, 0.3 mmol), diaryl diselenides (0.3 mmol), AgSbF₆ (20.6 mg, 20 mol%), Cu(OAc)₂·H₂O (60 mg, 1.0 eq.) were added to a screw-capped vial, followed by addition of a stir bar and DCE (2 mL). The reaction vial was placed in a temperature-controlled aluminum-heating block set at 120 °C. After 12 h of stirring, the vial was removed from the heating block and was left to cool to ambient temperature. The solvents were removed under reduced pressure and the crude reaction mixture was purified by silica gel column chromatography with Petroleum ether/EtOAc as an eluent to give the desired product.
Spectral data for the products

(4-chlorophenyl)(1-methoxynaphthalen-4-yl)sulfane (3a)

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm: 8.37-8.31 (m, 2H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.60-7.53 (m, 2H), 7.18-7.13 (m, 2H), 7.01-6.98 (m, 2H), 6.84 (d, $J = 8.0$ Hz, 1H), 4.07 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ ppm: 157.4, 137.8, 136.1, 135.1, 130.9, 129.0, 127.9, 127.9, 126.7, 125.9, 125.9, 122.8, 119.6, 104.1, 55.8. MS(EI): 300(100), 285(7), 257(4), 220(12). HRMS calcd for C$_{17}$H$_{13}$ClOS [M $^+$]: 300.0376, found: 300.0374.

(3-chlorophenyl)(1-methoxynaphthalen-4-yl)sulfane (3b)

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm: 8.41-8.32 (m, 2H), 7.86 (d, $J = 8.0$ Hz, 1H), 7.58 (t, $J = 4.0$ Hz, 2H), 7.07 (t, $J = 6.8$ Hz, 3H); 6.92 (d, $J = 7.8$ Hz, 1H), 6.87 (d, $J = 8.0$ Hz, 1H), 4.07 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ ppm: 157.6, 141.6, 136.5, 135.2, 134.8, 129.9, 128.0, 126.8, 126.0, 126.0, 125.8, 125.2, 124.5, 122.8, 104.2, 55.8. MS(EI): 300(60), 221(50), 145(100), 114(70), 63(55). HRMS calcd for C$_{17}$H$_{13}$ClOS [M $^+$]: 300.0376, found: 300.0375.

(2-chlorophenyl)(1-methoxynaphthalen-4-yl)sulfane (3c)
$^1$H NMR (300 MHz, CDCl$_3$) δ ppm: 8.39-8.27 (m, 2H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.59-7.53 (m, 2H), 7.40-7.38 (m, 1H), 7.03-6.98 (m, 1H), 6.92-6.87 (m, 2H), 6.42-6.39 (m, 1H), 4.07 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ ppm: 157.7, 138.6, 136.9, 135.4, 130.4, 129.4, 128.0, 127.0, 126.8, 126.0, 125.9, 125.6, 122.8, 118.3, 104.3, 55.8. MS(EI): 300(60), 145(100), 113(1.5). HRMS calcd for C$_{17}$H$_{13}$ClOS [M$^+$]: 300.0376, found: 300.0373.

(4-bromophenyl)(1-methoxynaphthalen-4-yl)sulfane (3d)

$^1$H NMR (300 MHz, CDCl$_3$) δ ppm: 8.38-8.27 (m, 2H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.58-7.53 (m, 2H), 7.30-7.25 (m, 2H), 6.94-6.85 (m, 3H), 4.07 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ ppm: 157.5, 138.5, 136.2, 135.1, 131.8, 128.1, 127.9, 126.7, 125.9, 125.8, 122.7, 118.6, 104.1, 55.8. MS(EI): 344(2.5), 145(100), 113(48), 63(18). HRMS calcd for C$_{17}$H$_{13}$BrOS [M$^+$]: 343.9871, found: 343.9873.

(2-bromophenyl)(1-methoxynaphthalen-4-yl)sulfane (3e)
$^1$H NMR (300 MHz, CDCl$_3$) δ ppm: 8.39-8.24(m, 2H), 7.87 (d, J = 8.0 Hz, 1H), 7.58-7.53(m, 3H), 6.94-6.88(m, 3H), 6.39-6.36(m, 1H), 4.09 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ ppm: 157.7, 140.5, 136.8, 135.3, 132.7, 128.0, 127.6, 126.8, 126.0, 125.9, 125.8, 122.7, 120.0, 118.8, 104.3, 55.8. MS(EI): 344(2.5), 210(30), 145(100), 113(33). HRMS calcd for C$_{17}$H$_{13}$BrOS [M$^+$]: 343.9871, found: 343.9874.

(4-fluorophenyl)(1-methoxynaphthalen-4-yl)sulfane (3f)

M$_3$O$_2$S

$^1$H NMR (300 MHz, CDCl$_3$) δ ppm: 8.37-8.33(m, 2H), 7.79 (d, J = 8.0 Hz, 1H), 7.57-7.53(m, 2H), 7.10-7.05(m, 2H), 6.93-6.83(m, 3H), 4.06 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ ppm: 162.8, 159.5, 157.2, 135.4, 135.0, 133.9, 133.8, 129.0, 129.0, 127.8, 126.7, 125.9, 125.8, 122.7, 120.8, 116.2, 115.9, 104.1, 55.7. MS(EI): 284(100), 269(53), 239(28), 144(25), 113(27), 102(18), 63(24). HRMS calcd for C$_{17}$H$_{13}$FOS [M$^+$]: 284.0671, found: 284.0668.

(2-fluorophenyl)(1-methoxynaphthalen-4-yl)sulfane (3g)

M$_3$O$_2$S

$^1$H NMR (300 MHz, CDCl$_3$) δ ppm: 8.39-8.37(m, 2H), 7.85 (d, J = 8.0 Hz, 1H), 7.60-7.53(m, 2H), 7.10-7.06(m, 2H), 6.90-6.82(m, 2H), 6.66-6.63(m, 1H), 4.07 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ ppm: 160.8, 157.5, 236.3, 135.3, 128.8, 127.9, 126.7, 126.6, 125.9, 125.8, 124.5, 124.5, 122.7, 118.2, 115.4, 115.2, 104.2, 55.8.
MS(EI): 284(45), 269(50), 241(100), 221(55), 145(50), 113(55), 102(55), 75(55), 63(55). HRMS calcd for C_{17}H_{13}FOS [M⁺]: 284.0671, found: 284.0669.

(1-methoxynaphthalen-4-yl)(4-nitrophenoxy)sulfane (3h)

\[
\begin{align*}
\text{MeO} & \quad \text{S} \\
\text{3h} & \quad \text{NO}_2
\end{align*}
\]

\( ^1 \text{H NMR (300 MHz, CDCl}_3 \) \( \delta \) ppm: 8.41-8.17 (m, 2H), 7.99 (d, \( J = 8.9 \) Hz, 2H), 7.87 (d, \( J = 8.0 \) Hz, 1H), 7.58-7.55 (m, 2H), 7.03 (d, \( J = 8.9 \) Hz, 2H), 6.91 (d, \( J = 8.0 \) Hz, 1H), 4.11 (s, 3H). \( ^{13} \text{C NMR (75 MHz, CDCl}_3 \) \( \delta \) ppm: 158.2, 149.7, 137.0, 135.1, 128.3, 126.8, 126.5, 126.2, 125.4, 124.5, 124.0, 123.0, 104.2, 55.9. MS(EI): 311(5), 145(90), 115(100), 102(90), 63(80). HRMS calcd for C_{17}H_{13}NO_3S [M⁺]: 311.0616, found: 311.0615

(1-methoxynaphthalen-4-yl)(p-tolyl)sulfane (3i)

\[
\begin{align*}
\text{MeO} & \quad \text{S} \\
\text{3i} & \quad \text{Me}
\end{align*}
\]

\( ^1 \text{H NMR (300 MHz, CDCl}_3 \) \( \delta \) ppm: 8.41-8.35 (m, 2H), 7.80 (d, \( J = 8.0 \) Hz, 1H), 7.57-7.53 (m, 2H), 7.03 (s, 4H), 6.84 (d, \( J = 8.0 \) Hz, 1H), 4.06 (s, 3H), 2.29 (s, 3H). \( ^{13} \text{C NMR (75 MHz, CDCl}_3 \) \( \delta \) ppm: 156.9, 135.2, 135.2, 135.1, 129.7, 127.6, 127.4, 126.6, 126.0, 125.7, 122.6, 121.1, 104.1, 55.7, 21.0. MS(EI): 280(100), 265(25), 220(25), 145(13), 113(10), 89(15), 63(15). HRMS calcd for C_{18}H_{16}OS [M⁺]: 280.0922, found: 280.0919.
(1-methoxynaphthalen-4-yl)(m-tolyl)sulfane (3j)

$^1$H NMR (300 MHz, CDCl$_3$) δ ppm: 8.40-8.30 (m, 2H), 7.75 (d, $J$ = 8.0 Hz, 1H), 7.59-7.55 (m, 2H), 7.22 (d, $J$ = 7.3 Hz, 1H), 7.08-7.03 (m, 1H), 6.95-6.90(m, 1H), 6.87(d, $J$ = 8.0 Hz, 1H), 6.62 (d, $J$ = 7.5 Hz, 1H), 4.07 (s, 3H), 2.56 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ ppm: 157.0, 137.9, 135.3, 135.2, 135.2, 130.1, 127.7, 126.8, 126.7, 126.5, 125.9, 125.8, 125.1, 122.7, 120.1, 104.3, 55.7, 20.2. MS(EI): 280(100), 265(23), 220(25), 115(4), 92(2), 65(4). HRMS calcd for C$_{18}$H$_{16}$OS [M$^+$]: 280.0922, found: 280.0920.

(1-methoxynaphthalen-4-yl)(o-tolyl)sulfane (3k)

$^1$H NMR (300 MHz, CDCl$_3$) δ ppm: 8.33-8.29 (m, 2H), 7.75 (d, $J$ = 8.0 Hz, 1H), 7.59-7.51 (m, 2H), 7.22(d, $J$ = 7.2 Hz, 1H), 7.07-7.02(m, 1H), 6.95-6.90 (m, 1H), 6.86 (d, $J$ = 8.0 Hz, 1H); 6.61 (d, $J$ = 7.8 Hz, 1H), 4.07 (s, 3H), 2.55 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ ppm: 157.0, 137.9, 135.3, 135.2, 135.2, 130.1, 127.7, 126.8, 126.7, 126.5, 125.9, 125.8, 125.1, 122.7, 120.1, 104.3, 55.7, 20.2. MS(EI): 280(100), 265(16), 189(65), 220(10), 147(13), 121(9), 92(9), 65(4). HRMS calcd for C$_{18}$H$_{16}$OS [M$^+$]: 280.0922, found: 280.0920.
(1-methoxynaphthalen-4-yl)(phenyl)sulfane (3m)

\[
\text{MeO-}[\text{S}]-[\text{Ar}]-[\text{Ar}]-\text{MeO}
\]

\(\delta\) ppm: 8.44-8.40 (m, 2H), 7.87 (d, \(J = 8.0\) Hz, 1H), 7.60-7.56 (m, 2H), 7.24-7.19 (m, 2H), 7.14-7.11 (m, 3H), 6.87 (d, \(J = 8.0\) Hz, 1H), 4.07 (s, 3H). 13C NMR (75 MHz, CDCl\(_3\)) \(\delta\) ppm: 157.2, 139.2, 135.9, 135.3, 128.9, 127.8, 126.8, 126.7, 126.1, 125.8, 125.2, 122.7, 120.2, 104.2, 55.7. MS(EI): 266(60), 221(28), 189(65), 145(100), 114(67), 63(52). HRMS calcd for C\(_{17}\)H\(_{14}\)Os \([M^+]: 266.0765\), found: 266.0763.

(4-chlorophenyl)(1-methoxynaphthalen-4-yl)selane (5a)

\[
\text{MeO-}[\text{Se}]-[\text{Ar}]-[\text{Cl}]-\text{MeO}
\]

\(\delta\) ppm: 8.40-8.33 (m, 2H), 7.94 (d, \(J = 8.0\) Hz, 1H), 7.60-7.56 (m, 2H), 7.19-7.12 (m, 4H), 6.80 (d, \(J = 8.0\) Hz, 1H); 4.05 (s, 3H). 13C NMR (75 MHz, CDCl\(_3\)) \(\delta\) ppm: 157.3, 136.9, 135.4, 132.0, 131.9, 130.9, 129.3, 128.1, 127.9, 126.7, 125.9, 122.7, 118.2, 104.4, 55.7. MS(EI): 348(12), 127(100), 114(80), 103(39), 87(40), 63(55). HRMS calcd for C\(_{17}\)H\(_{13}\)ClOSe \([M^+]: 347.9820\), found: 347.9818.

(4-fluorophenyl)(1-methoxynaphthalen-4-yl)selane (5b)
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm: 8.36-8.33 (m, 2H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.59-7.53 (m, 2H), 7.28-7.23 (m, 2H), 6.92-6.86 (m, 2H), 6.80 (d, $J = 8.0$ Hz, 1H); 4.05 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ ppm: 163.4, 160.2, 157.0, 136.2, 135.3, 132.1, 132.0, 128.0, 127.7, 126.6, 125.8, 122.6, 119.1, 116.4, 116.2, 104.3, 55.7. MS(EI): 332(19), 143(18), 114(55), 102(45), 75(40), 62(100). HRMS calcd for C$_{17}$H$_{13}$FOSe [M$^+$]: 332.0116, found: 332.0118.

(1-methoxynaphthalen-4-yl)(p-tolyl)selane (5c)

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm: 8.43-8.36 (m, 2H), 7.90 (d, $J = 8.0$ Hz, 1H), 7.60-7.52 (m, 2H), 7.23 (d, $J = 8.0$ Hz, 2H), 7.02 (d, $J = 8.0$ Hz, 2H), 6.80 (d, $J = 8.0$ Hz, 1H), 4.05 (s, 3H); 2.31 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ ppm: 156.8, 136.1, 136.0, 135.4, 130.4, 130.0, 129.4, 128.2, 127.6, 126.6, 125.7, 122.6, 119.3, 104.4, 55.7, 21.1. MS(EI): 328(2.5), 142(8), 128(26), 113(100), 89(30), 65(48). HRMS calcd for C$_{18}$H$_{16}$OSe [M$^+$]: 328.0366, found: 328.0363.

(1-methoxynaphthalen-4-yl)(o-tolyl)selane (5d)
(1-methoxynaphthalen-4-yl)(2-methoxyphenyl)selane (5e)

$^1$H NMR (300 MHz, CDCl$_3$) δ ppm: 8.37-8.3 (m, 2H), 8.00 (d, $J = 7.9$ Hz, 1H), 7.58-7.53 (m, 2H), 7.15-7.10 (m, 1H), 4.07 (s, 3H), 4.00 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ ppm: 157.4, 138.0, 136.2, 128.7, 128.5, 127.8, 126.6, 126.5, 125.8, 123.3, 122.6, 121.7, 121.6, 110.1, 104.5, 56.0, 55.7. MS(EI): 344(10), 146(45), 114(100), 64(46). HRMS calcd for C$_{18}$H$_{16}$O$_2$Se [M$^+$]: 344.0316, found: 344.0313.

(3-(trifluoromethyl)phenyl)(1-methoxynaphthalen-4-yl)selane (5f)

$^1$H NMR (300 MHz, CDCl$_3$) δ ppm: 8.37-8.36 (m, 2H), 8.00 (d, $J = 7.9$ Hz, 1H), 7.58-7.53 (m, 2H), 7.15-7.10 (m, 1H), 4.07 (s, 3H), 4.00 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ ppm: 157.4, 138.0, 136.2, 128.7, 128.5, 127.8, 126.6, 126.5, 125.8, 123.3, 122.6, 121.7, 121.6, 110.1, 104.5, 56.0, 55.7. MS(EI): 344(10), 146(45), 114(100), 64(46). HRMS calcd for C$_{18}$H$_{16}$O$_2$Se [M$^+$]: 344.0316, found: 344.0313.
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm: 8.38-8.30 (m, 2H), 7.96 (d, $J$ = 8.0 Hz, 1H), 7.57-7.52 (m, 2H), 7.38 (d, $J$ = 6.8 Hz, 1H), 7.28-7.18 (m, 2H), 6.84 (d, $J$ = 8.0 Hz, 1H), 4.07 (s, 3H).$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ ppm: 157.5, 137.3, 135.5, 135.1, 132.5, 129.4, 128.0, 127.9, 126.7, 125.9, 125.8, 125.2, 122.7, 122.6, 122.6, 117.3, 104.4, 55.7. MS(EI): 382(3), 145(4), 125(8), 113(100), 89(3). HRMS calcd for C$_{18}$H$_{13}$F$_3$OSe [M$^+$]: 382.0084, found: 382.0086.

(4-chlorophenyl)(2,4,6-trimethoxyphenyl)sulfane (6a)

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm: 7.13 (d, $J$ = 8.6 Hz, 2H), 6.96 (d, $J$ = 8.6 Hz, 2H), 6.23(s, 2H), 3.88 (s, 3H), 3.82(s, 6H).$^3$C NMR (75 MHz, CDCl$_3$) $\delta$ ppm: 163.2, 162.5, 137.5, 130.1, 128.6, 127.0, 91.3, 56.3, 55.5. MS(EI): 310(20), 155(38), 141(50), 125(75), 109(100), 97(57), 81(35), 69(30). HRMS calcd for C$_{15}$H$_{15}$ClO$_3$S [M$^+$]: 310.0430, found: 310.0427.

(4-chlorophenyl)(mesityl)sulfane (6b)

S12
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm: 7.16 (d, $J = 8.5$ Hz, 2H), 7.05 (s, 2H), 6.87 (d, $J = 8.5$ Hz, 1H), 2.41 (s, 6H), 2.36 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ ppm: 143.7, 139.7, 137.1, 130.3, 129.5, 129.4, 129.0, 126.7, 21.7, 21.2. MS(EI): 262(40), 194(20)50(100), 13491(55), 76(30). HRMS calcd for C$_{15}$H$_{15}$ClSe $[M^+]$: 262.0583, found: 262.0580.

(2,4,6-trimethoxyphenyl)(p-tolyl)selane (7a)

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm: 7.14 (d, $J = 8.0$ Hz, 2H), 6.98 (d, $J = 8.0$ Hz, 2H), 6.22(s, 2H), 3.88(s, 3H), 3.81 (s, 6H), 2.27(s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ ppm: 162.9, 161.9, 135.1, 129.7, 129.7, 129.6, 91.3, 56.4, 55.5, 21.0. MS(EI): 338(75), 181(40), 138(50), 125(55), 109(55), 103(60), 90(100), 65(25). HRMS calcd for C$_{16}$H$_{18}$O$_3$Se $[M^+]$: 338.0421, found: 338.0419.

References:

