Supporting Information


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General information

The reactions were conducted in Schlenk tube under N₂ atmosphere. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). GC-MS spectra were recorded on a Varian GC-MS 3900-2100T. GC analyses were performed on Varian GC 2000 gas chromatography instrument with a FID detector. ¹H and ¹³C NMR data were recorded with Bruker ADVANCE III (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks. High resolution mass spectra (HRMS) were measured with a Thermo Fisher Scientific LTQ FT Ultra, accurate masses are reported for the molecular ion ([M+H]+).
General procedure of the oxidative cross S-H/S-H coupling

To a Schlenk tube charged with mercapto arene (0.5 mmol) was added CH₂Cl₂ (1.0 mL), alkyl mercaptan (0.5 mmol) and TBHP (0.55 mmol, 70% solution in water) under N₂ atmosphere. After 30 seconds, NIS (0.05 mmol) was added in one batch. Then the Schlenk tube was allowed to react for 1 h at 25 °C. After the completion of the reaction, it was quenched by water (3.0 mL) and extracted with ethyl acetate (3 × 3.0 mL). The organic layers were combined and evaporated under vacuum. The pure product was obtained by flash chromatography on silicagel using petroleum ether and ethyl acetate as the eluent.
Condition Screening of the oxidative cross S-H/S-H coupling

Table S1. Condition screening of the cross S-H/S-H coupling

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxidant</th>
<th>Catalyst</th>
<th>Yield(^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TBHP</td>
<td>none</td>
<td>35%</td>
</tr>
<tr>
<td>2</td>
<td>TBHP</td>
<td>I(_2)</td>
<td>83%</td>
</tr>
<tr>
<td>3</td>
<td>TBHP</td>
<td>NIS</td>
<td><strong>89%</strong></td>
</tr>
<tr>
<td>4</td>
<td>TBHP</td>
<td>KI</td>
<td>86%</td>
</tr>
<tr>
<td>5</td>
<td>TBHP</td>
<td>(\text{\textsuperscript{a}}\text{Bu}_4\text{NI})</td>
<td>86%</td>
</tr>
<tr>
<td>6</td>
<td>TBHP</td>
<td>PhI</td>
<td>35%</td>
</tr>
<tr>
<td>7</td>
<td>DTBP</td>
<td>NIS</td>
<td>5%</td>
</tr>
<tr>
<td>8</td>
<td>CHP</td>
<td>NIS</td>
<td>87%</td>
</tr>
</tbody>
</table>

\(^a\)Reaction conditions: 1a (0.5 mmol), 2a (0.5 mmol), oxidant (0.55 mmol), catalyst (0.05 mmol), CH\(_2\)Cl\(_2\) (1 mL) at 25 °C for 1 h under N\(_2\),. \(^b\)The yields were determined by GC analysis with biphenyl as the internal standard. TBHP = tert-butyl hydroperoxide, NIS = N-iodosuccinimide, DTBP = di-tert-butyl peroxide, CHP = cumene hydroperoxide.
**Procedure of the synthesis of cumene mercaptan 2d**

To a Schlenk tube charged with Lawesson’s reagent (3.3 mmol) was added 3.0 mL dimethoxy ethane (DME) under N₂ atmosphere. After stirring for 3 minutes at 25 °C, cumene alcohol (3 mmol) was added in 1 batch. Then the Schlenk tube was allowed to react for 18 h at 25 °C. After the completion of the reaction, the solvent was removed under vacuum. Then flash chromatography was performed to obtain the product using petroleum ether as the eluent.
Procedure of the control experiments

Procedure of eq. 1
To a Schlenk tube charged with 2-mercapto-benzothiazole 1a (0.5 mmol) was added CH$_2$Cl$_2$ (1.0 mL) and TBHP (0.55 mmol, 70% solution in water) under N$_2$ atmosphere. After 30 seconds, NIS (0.05 mmol) was added in one batch. Then the Schlenk tube was allowed to react for 1 h at 25 °C. After the completion of the reaction, it was analyzed by GC.

Procedure of eq. 2
To a Schlenk tube was added CH$_2$Cl$_2$ (1.0 mL), tert-butyl mercaptan 2 (0.5 mmol) and TBHP (0.55 mmol, 70% solution in water) under N$_2$ atmosphere. After 30 seconds, NIS (0.05 mmol) was added in one batch. Then the Schlenk tube was allowed to react for 1 h at 25 °C. After the completion of the reaction, it was analyzed by GC.

Procedure of eq. 3
To a Schlenk tube charged with 2-benzothiazolyl disulfide 4 (0.25 mmol) was added CH$_2$Cl$_2$ (1.0 mL), alkyl mercaptan (0.5 mmol) and TBHP (0.55 mmol, 70% solution in water) under N$_2$ atmosphere. After 30 seconds, NIS (0.05 mmol) was added in one batch. Then the Schlenk tube was allowed to react for 1 h at 25 °C. After the completion of the reaction, it was analyzed by GC.

Procedure of eq. 4
To a Schlenk tube charged with 2-mercapto-benzothiazole 1a (0.5 mmol) was added CH$_2$Cl$_2$ (1.0 mL), tert-butyl disulfide 5 (0.25 mmol) and TBHP (0.55 mmol, 70% solution in water) under N$_2$ atmosphere. After 30 seconds, NIS (0.05 mmol) was added
in one batch. Then the Schlenk tube was allowed to react for 1 h at 25 °C. After the completion of the reaction, it was analyzed by GC.

**Procedure of eq. 5**

To a Schlenk tube charged with 2-benzothiazolyl disulfide 4 (0.5 mmol) was added CH₂Cl₂ (1.0 mL), tert-butyl mercaptan 2 (0.5 mmol) under N₂ atmosphere. Then the Schlenk tube was allowed to react for 1 h at 25 °C. After the completion of the reaction, it was analyzed by GC.
Detailed descriptions for products

![Chemical Structure](image)

**2-(tert-butyldisulfanyl)benzothiazole (3aa)**: product was obtained with 89% yield. Eluent: petroleum ether: ethyl acetate = 40:1. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.91 – 7.86\) (m, 1H), \(7.83 – 7.78\) (m, 1H), \(7.49 – 7.42\) (m, 1H), \(7.37 – 7.32\) (m, 1H), \(1.45\) (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 174.5, 154.9, 135.7, 126.2, 124.5, 122.1, 121.1, 50.3, 29.8\). HRMS (EI) calculated for C\(_{11}\)H\(_{14}\)NS\(_3\) [M+H]^+: 257.0283; found: 257.0280.

**2-(tert-butyldisulfanyl)benzoxazole (3ba)**: product was obtained with 82% yield. Eluent: petroleum ether: ethyl acetate = 40:1. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.70 – 7.64\) (m, 1H), \(7.52 – 7.47\) (m, 1H), \(7.34 – 7.27\) (m, 2H), \(1.42\) (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 163.9, 152.2, 142.0, 124.6, 124.6, 119.3, 110.2, 49.6, 29.6\). HRMS (EI) calculated for C\(_{11}\)H\(_{14}\)ONS\(_2\) [M+H]^+: 240.0511; found: 240.0510.

**2-(tert-butyldisulfanyl)-1-methyl-imidazole (3ca)**: product was obtained with 85% yield. Eluent: petroleum ether: ethyl acetate = 4:1. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.01\) (d, \(J = 1.3\) Hz, 1H), \(6.97\) (d, \(J = 1.2\) Hz, 1H), \(3.75\) (s, 3H), \(1.34\) (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 141.2, 129.1, 123.7, 49.1, 34.2, 29.9\). HRMS (EI) calculated for C\(_8\)H\(_{15}\)N\(_2\)S\(_2\) [M+H]^+: 203.0671; found: 203.0670.

**5-(tert-butyldisulfanyl)-1-methyl- tetrazole (3da)**: product was obtained with 90% yield. Eluent: petroleum ether: ethyl acetate = 4:1. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 4.11\) (s, 3H), \(1.34\) (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 153.5, 50.5, 34.6, 29.6\). HRMS (EI) calculated for C\(_6\)H\(_{13}\)N\(_4\)S\(_2\) [M+H]^+: 205.0576; found: 205.0575.
6-chloro-2-(tert-butyldisulfanyl)benzoxazole (3ea): product was obtained with 84% yield. Eluent: petroleum ether: ethyl acetate = 40:1. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.55$ (d, $J = 8.5$ Hz, 1H), 7.49 (d, $J = 1.9$ Hz, 1H), 7.30 – 7.25 (m, 1H), 1.40 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 164.8$, 152.2, 140.8, 130.3, 125.2, 119.7, 110.9, 49.7, 29.6. HRMS (EI) calculated for C$_{11}$H$_{13}$ClNOS$_2$ [M+H]$^+$: 274.0122; found: 274.0119.

2-(tert-butyldisulfanyl)-5-methyl-1,3,4-thiadiazole (3fa): product was obtained with 80% yield. Eluent: petroleum ether: ethyl acetate = 40:1. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 2.74$ (s, 3H), 1.41 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 174.2$, 166.4, 50.6, 29.8, 15.9. HRMS (EI) calculated for C$_7$H$_{13}$N$_2$S$_3$ [M+H]$^+$: 221.0235; found: 221.0234.

2-(tert-butyldisulfanyl)-pyridine (3ga): product was obtained with 75% yield. Eluent: petroleum ether: ethyl acetate = 40:1. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.41$ (ddd, $J = 4.9$, 1.9, 0.9 Hz, 1H), 7.82 – 7.75 (m, 1H), 7.61 (ddd, $J = 8.1$, 7.4, 1.8 Hz, 1H), 7.04 (ddd, $J = 7.4$, 4.8, 1.1 Hz, 1H), 1.33 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 161.6$, 149.2, 136.8, 120.4, 119.6, 49.3, 29.8. HRMS (EI) calculated for C$_9$H$_{14}$NS$_2$ [M+H]$^+$: 200.0562; found: 200.0560.

2-(tert-butyldisulfanyl)-pyrazine (3ha): product was obtained with 77% yield. Eluent: petroleum ether: ethyl acetate = 40:1. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.98$ – 8.94 (m, 1H), 8.41 – 8.35 (m, 1H), 8.34 – 8.30 (m, 1H), 1.34 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 158.3$, 143.4, 142.3, 140.8, 49.6, 29.7. HRMS (EI) calculated for C$_8$H$_{13}$N$_2$S$_2$ [M+H]$^+$: 201.0515; found: 201.0514.
2-(tert-butyldisulfanyl)-4,6-dimethylpyrimidine (3ia): product was obtained with 77% yield. Eluent: petroleum ether: ethyl acetate = 40:1. $^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 6.78 (s, 1H), 2.44 (s, 6H), 1.35 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta =$ 170.7, 167.5, 117.1, 48.9, 29.8, 23.9. HRMS (EI) calculated for C$_{10}$H$_{17}$N$_2$S$_2$ [M+H]$^+$: 229.0828; found: 229.0826.

2,5-di(tert-butyldisulfanyl)-1,3,4-thiadiazole (3ja): product was obtained with 87% yield. Eluent: petroleum ether: ethyl acetate = 40:1. $^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 1.39 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta =$ 175.1, 50.8, 29.7. HRMS (EI) calculated for C$_{10}$H$_{19}$N$_2$S$_5$ [M+H]$^+$: 327.0146; found: 327.0144.

2-(isopropyldisulfanyl)-1-methyl-imidazole (3db): product was obtained with 61% yield. Eluent: petroleum ether: ethyl acetate = 3:1. $^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 7.06 (d, $J =$ 1.3 Hz, 1H), 7.02 (d, $J =$ 1.3 Hz, 1H), 3.78 (s, 3H), 3.24 (hept, $J =$ 6.7 Hz, 1H), 1.34 (d, $J =$ 6.8 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta =$ 141.1, 129.6, 123.8, 41.5, 34.2, 22.3. HRMS (EI) calculated for C$_7$H$_{13}$N$_2$S$_2$ [M+H]$^+$: 189.0515; found: 189.0513.

2-(isopropyldisulfanyl)-1-methyl-imidazole (3dc): product was obtained with 50% yield. Eluent: petroleum ether: ethyl acetate = 3:1. $^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 7.06 (d, $J =$ 1.2 Hz, 1H), 7.01 (d, $J =$ 1.2 Hz, 1H), 3.77 (s, 3H), 3.05 – 2.95 (m, 1H), 2.12 – 2.04 (m, 2H), 1.79 – 1.71 (m, 2H), 1.64 – 1.56 (m, 1H), 1.43 – 1.21 (m, 5H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta =$ 141.3, 129.5, 123.8, 49.6, 34.2, 32.4, 25.9, 25.6. HRMS (EI) calculated for C$_{10}$H$_{17}$N$_2$S$_2$ [M+H]$^+$: 229.0828; found: 229.0825.
2-(cumenedisulfanyl)-1-methyl-imidazole (3dd): product was obtained with 84% yield. Eluent: petroleum ether: ethyl acetate = 3:1. $^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 7.50 – 7.44 (m, 2H), 7.33 – 7.24 (m, 2H), 7.24 – 7.18 (m, 1H), 7.03 (d, $J = 1.2$ Hz, 1H), 6.90 (d, $J = 1.2$ Hz, 1H), 3.59 (s, 3H), 1.80 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta =$ 144.2, 140.9, 129.4, 128.3, 127.3, 126.6, 123.6, 54.2, 34.1, 28.8. HRMS (EI) calculated for C$_{13}$H$_{17}$N$_2$S$_2$ [M+H]$^+$: 265.0833; found: 265.0830.

2-[(triphenylmethyl)disulfanyl]-1-methyl-imidazole (3de): product was obtained with 80% yield. Eluent: petroleum ether: ethyl acetate = 1:1. $^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 7.27 – 7.20 (m, 15H), 7.08 (d, $J = 1.3$ Hz, 1H), 6.82 (d, $J = 1.2$ Hz, 1H), 3.15 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta =$ 143.4, 140.4, 130.3, 130.1, 127.8, 127.2, 122.9, 72.5, 33.6. HRMS (EI) calculated for C$_{23}$H$_{21}$N$_2$S$_2$ [M+H]$^+$: 389.1141; found: 389.1136.

2-(tert-nonyldisulfanyl)-1-methyl-imidazole, mixture of isomers (3df): product was obtained with 87% yield. Eluent: petroleum ether: ethyl acetate = 3:1. $^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 7.15 – 6.89 (m, 2H), 3.94 – 3.59 (m, 3H), 1.85 – 0.60 (m, 19H). HRMS (EI) calculated for C$_{13}$H$_{25}$N$_2$S$_2$ [M+H]$^+$: 273.1459; found: 273.1455.

2-(tert-dedecyldisulfanyl)-1-methyl-imidazole, mixture of isomers (3dg): product was obtained with 81% yield. Eluent: petroleum ether: ethyl acetate = 3:1. $^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 7.07 – 6.93 (m, 2H), 4.01 – 3.62 (m, 3H), 1.84 – 0.60 (m, 25H). HRMS (EI) calculated for C$_{16}$H$_{31}$N$_2$S$_2$ [M+H]$^+$: 315.1923; found: 315.1919.
Copies of NMR spectrums

$^1$H NMR of 2-(tert-butyldisulfanyl)benzothiazole (3aa)

$^{13}$C NMR of 2-(tert-butyldisulfanyl)benzothiazole (3aa)
$^1$H NMR of 2-(tert-butyldisulfanyl)benzoxazole (3ba)

$^{13}$C NMR of 2-(tert-butyldisulfanyl)benzoxazole (3ba)
$^1$H NMR of $2$-(tert-butyldisulfanyl)-1-methyl-imidazole (3ca)

$^{13}$C NMR of $2$-(tert-butyldisulfanyl)-1-methyl-imidazole (3ca)
$^1$H NMR of 5-(tert-butyldisulfanyl)-1-methyl-tetrazole (3da)

$^{13}$C NMR of 5-(tert-butyldisulfanyl)-1-methyl-tetraazole (3da)
$^1$H NMR of 5-chloro-2-(tert-butyldisulfanyl)benzoxazole (3ea)

$^{13}$C NMR of 5-chloro-2-(tert-butyldisulfanyl)benzoxazole (3ea)
$^1$H NMR of 2-(tert-butyldisulfanyl)-5-methyl-1,3,4- thiadiazole (3fa)

$^{13}$C NMR of 2-(tert-butyldisulfanyl)-5-methyl-1,3,4-thiadiazole (3fa)
$^1$H NMR of 2-(tert-butyldisulfanyl)-pyridine (3ga)

$^{13}$C NMR of 2-(tert-butyldisulfanyl)-pyridine (3ga)
$^1$H NMR of 2-(tert-butyl disulfanyl)-pyrazine (3ha)

$^{13}$C NMR of 2-(tert-butyl disulfanyl)-pyrazine (3ha)
$^1$H NMR of 2-(tert-butyldisulfanyl)-4,6-dimethylpyrimidine (3ia)

$^{13}$C NMR of 2-(tert-butyldisulfanyl)-4,6-dimethylpyrimidine (3ia)
$^1$H NMR of 2,5-di(tert-butyldisulfanyl)-1,3,4-thiadiazole (3ja)

$^{13}$C NMR of 2-(tert-butyldisulfanyl)-5-methyl-1,3,4-thiadiazole (3ja)
$^1$H NMR of 2-(isopropyldisulfanyl)-1-methyl-imidazole (3db)

$^{13}$C NMR of 2-(isopropyldisulfanyl)-1-methyl-imidazole (3db)
$^1$H NMR of 2-(cyclohexyl disulfanyl)-1-methyl-imidazole (3dc)

$^{13}$C NMR of 2-(cyclohexyl disulfanyl)-1-methyl-imidazole (3dc)
$^1$H NMR of 2-(cumenedisulfanyl)-1-methyl-imidazole (3dd)

$^{13}$C NMR of 2-(cumenedisulfanyl)-1-methyl-imidazole (3dd)
$^1$H NMR of 2-[(triphenylmethyl)disulfanyl]-1-methyl-imidazole (3de)

$^{13}$C NMR of 2-[(triphenylmethyl)disulfanyl]-1-methyl-imidazole (3de)
$^1$H NMR of 2-(tert-nonyldisulfanyl-1-methyl-imidazole, mixture of isomers (3df)
$^1$H NMR of 2-(tert-nonyldisulfanyl)-1-methyl-imidazole, mixture of isomers (3dg)
Reference

