Supporting Information

For

H₂O₂-Mediated Metal-free Protocol towards Unsymmetrical Thiosulfonates from Sulfonyl Hydrazides and Disulfides in PEG-400

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General information

All product mixtures were analyzed by thin layer chromatography glass-backed silica TLC plates with a fluorescent indicator from Branch of Qingdao Haiyang Chemical CO. LTD. UV-active compounds were detected with a UV lamp ($\lambda=254$ nm). For flash column chromatography, silica gel (200 - 300 mesh) was used as stationary phase and a mixture of petroleum and ethyl acetate was used as eluent. $^1$H and $^{13}$C NMR spectra were recorded on a Varian INOVA-400 in deuterated chloroform at 25 °C with residue solvent peaks as internal standards ($\delta=7.26$ ppm for $^1$H-NMR and $\delta=77.16$ ppm for $^{13}$C-NMR). Chemical shifts $\delta$ are reported in ppm, and spin-spin coupling constants ($J$) are given in Hz, while multiplicities are abbreviated by s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Mass spectra were recorded on a ThermoFinnigan MAT95XP microspectrometer and High resolution mass spectra (HRMS) were recorded on Agilent Technologies Accurate Mass Q-TOF 6530 microspectrometer. Melting points were recorded on a national standard melting point apparatus (Model: Taike XT-4) and were uncorrected.

All solvents were dried according to known methods.[S1] All the chemicals were purchased commercially and were used without further purification.

General procedure towards thiosulfonates 3

A Schlenk tube (25 mL) equipped with a magnetic bar was loaded with sulfonyl hydrazide 1 (1.0 mmol, 2 equiv), and disulfide 2 (0.5 mmol) in PEG-400 (1.5 mL), then $\text{H}_2\text{O}_2$ (30% in $\text{H}_2\text{O}$, 950 mg, 4.2 mmol) were added dropwise and the reaction mixture was allowed to stir at 100 °C for 2 h. After the completion of the reaction (monitored by TLC), the solution was washed with $\text{H}_2\text{O}$ and saturated sodium chloride, then extracted with dichloromethane (15 mL × 3) and dried over anhydrous sodium sulfate. The organic phase was combined and then concentrated. The crude product was purified by column chromatography using silica gel (200 - 300 mesh) as stationary phase and petroleum ether/ethyl acetate (40/1) used as eluent to give the desired product in noted yields.

Compounds EXCEPT 3ca, 3ma, 3na, 3oa, 3pa, 3an, 3ao, 3ap were known compounds and the data obtained herein were in accordance with the previous reports.[S2 - S5]

References:

Data

\( p\)-Tolyl sulfonothioic phenyl ester (3aa)

\[
\begin{align*}
\text{\includegraphics[width=0.3\textwidth]{figure1.png}}
\end{align*}
\]

Follow the general procedure, 3aa was obtained as yellow liquid with petroleum ether/ethyl acetate (40/1) used as eluent in 78% yield (103.2 mg).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 7.45 \) (t, \( J = 7.1 \) Hz, 3H), 7.39 – 7.31 (m, 4H), 7.20 (d, \( J = 7.9 \) Hz, 2H), 2.42 (s, 3H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 144.7, 140.3, 136.6, 131.3, 129.4, 129.4, 128.1, 127.6, 21.7 \) ppm.

IR (in KBr): \( \nu = 1590, 1428, 1313, 1127 \) (cm\(^{-1}\)).

MS (EI) m/z (%) = 77.0 (4), 91.0 (37), 109.0 (27), 155.0 (68), 264.0 (100, M\(^+\)).

HRMS (ESI) (m/z)[C\(_{13}\)H\(_{12}\)S\(_2\)O\(_2\) + H\(^+\)]: Calcd. 265.0351, Found. 265.0345.

Phenyl sulfonothioic phenyl ester (3ba)

\[
\begin{align*}
\text{\includegraphics[width=0.3\textwidth]{figure2.png}}
\end{align*}
\]

Follow the general procedure, 3ba was obtained as yellow liquid with petroleum ether/ethyl acetate (40/1) used as eluent in 79% yield (99.3 mg).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 7.61 – 7.53 \) (m, 3H), 7.47 (t, \( J = 7.2 \) Hz, 1H), 7.41 (t, \( J = 7.5 \) Hz, 2H), 7.38 – 7.28 (m, 4H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 142.9, 136.6, 133.7, 131.5, 129.5, 128.8, 127.8, 127.6 \) ppm.

IR (in KBr): \( \nu = 3080, 1315, 1130, 780 \) (cm\(^{-1}\)).

MS (ESI) m/z (%) = 77.0 (24), 109.0 (47), 141.0 (84), 250.0 (100, M\(^+\)).

HRMS (ESI) (m/z)[C\(_{12}\)H\(_{10}\)S\(_2\)O\(_2\) + H\(^+\)]: Calcd. 251.0195, Found. 251.0198.

\( p\)-\( tert \)-Butylphenyl sulfonothioic phenyl ester (3ca)

\[
\begin{align*}
\text{\includegraphics[width=0.3\textwidth]{figure3.png}}
\end{align*}
\]

Follow the general procedure, 3ca was obtained as white solid with petroleum ether/ethyl acetate (40/1) used as eluent in 81% yield (124.2 mg).

m.p.: 42 - 44 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 7.47 \) (t, \( J = 9.3 \) Hz, 3H), 7.41 (d, \( J = 8.2 \) Hz, 2H), 7.36 (d, \( J = 6.3 \) Hz, 3H), 7.31 (d, \( J = 7.5 \) Hz, 1H), 1.33 (s, 9H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 157.7, 140.2, 136.6, 131.3, 129.4, 128.1, 127.5, 125.7, 35.3, 31.1 \) ppm.

IR (in KBr): \( \nu = 2960, 1594, 1457, 1324, 1148 \) (cm\(^{-1}\)).

MS (ESI) m/z (%) = 109.0 (25), 133.1 (48), 197.0 (100), 306.0 (95, M\(^+\)).

HRMS (ESI) (m/z) [C\(_{16}\)H\(_{18}\)S\(_2\)O\(_2\) + H\(^+\)]: Calcd. 307.0821, Found. 307.0829.
p-Methoxyphenyl sulfonothioic phenyl ester (3da)

Follow the general procedure, 3da was obtained as yellow liquid with petroleum ether/ethyl acetate (40/1) used as eluent in 72% yield (101.5 mg).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.48 (t, J = 10.0\text{ Hz}, 3\text{H}), 7.35 (q, J = 7.4\text{ Hz}, 4\text{H}), 6.86 (d, J = 7.8\text{ Hz}, 2\text{H}), 3.86 (s, 3\text{H})\) (ppm).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 163.6, 136.7, 134.9, 131.3, 129.9, 129.4, 128.2, 113.8, 55.7\) (ppm).

IR (in KBr): \(\nu = 1596, 1494, 1327, 1148, 720\) (cm\(^{-1}\)).

MS (ESI) \(m/z\) = 77.0 (8), 107.0 (42), 109.0 (61), 171.0 (100), 280.0 (92, M\(^+\)).

HRMS (ESI) (m/z)[C\(_{13}\)H\(_{12}\)S\(_2\)O\(_2\) + H\(^+\)]: Calcd. 281.0301, Found. 281.0306.

p-Fluorophenyl sulfonothioic phenyl ester (3ea)

Follow the general procedure, 3ea was obtained as yellow liquid with petroleum ether/ethyl acetate (40/1) used as eluent in 64% yield (86.2 mg).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.61 – 7.54 (m, 2\text{H}), 7.49 (s, 1\text{H}), 7.37 (d, J = 3.5\text{ Hz}, 4\text{H}), 7.09 (t, J = 8.3\text{ Hz}, 2\text{H})\) (ppm).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 165.5 (d, J = 256.8\text{ Hz}), 139.0 (J\_C\_F = 3.2\text{ Hz}), 136.6, 131.6, 130.5 (J\_C\_F = 9.7\text{ Hz}), 129.6, 127.7, 116.1 (J\_C\_F = 22.8\text{ Hz})\) (ppm).

IR (in KBr): \(\nu = 1712, 1587, 1430, 1127\) (cm\(^{-1}\)).

MS (ESI) \(m/z\) = 77.0 (7), 95.0 (26), 109.0 (56), 158.0 (85), 268.0 (100, M\(^+\)).

HRMS (ESI) (m/z)[C\(_{12}\)H\(_9\)FO\(_2\)S\(_2\) + H\(^+\)]: Calcd. 269.0101, Found. 269.0110.

m-Chlorophenyl sulfonothioic phenyl ester (3ga)

Follow the general procedure, 3ga was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 71% yield (100.4 mg).

m.p.: 65 - 67 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.51 – 7.44 (m, 2\text{H}), 7.42 (s, 1\text{H}), 7.37 (d, J = 7.8\text{ Hz}, 1\text{H}), 7.33 – 7.26 (m, 5\text{H})\) (ppm).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 144.2, 136.6, 135.1, 133.7, 131.8, 130.1, 129.6, 127.6, 127.4, 125.6\) (ppm).

IR (in KBr): \(\nu = 1599, 1484, 1343, 1126\) (cm\(^{-1}\)).

MS (ESI) \(m/z\) = 77.0 (9), 109.0 (26), 111.0 (56), 174.0 (100), 264.0 (68, M\(^+\)).

HRMS (ESI) (m/z)[C\(_{12}\)H\(_9\)ClO\(_2\)S\(_2\) + H\(^+\)]: Calcd. 284.9805, Found. 284.9814.
**p-Chlorophenyl sulfonothioic phenyl ester (3ha)**

Follow the general procedure, 3ha was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 73% yield (103.2 mg).

m.p.: 80 – 82 °C.

1H NMR (400 MHz, CDCl3) δ = 7.48 (d, J = 7.5 Hz, 3H), 7.42 – 7.34 (m, 6H) (ppm).

13C NMR (100 MHz, CDCl3) δ = 141.4, 140.3, 136.6, 131.7, 129.6, 129.1, 129.0, 127.6 (ppm).

IR (in KBr): ν = 1584, 1450, 1340, 1128 (cm⁻¹).

MS (ESI) m/z (%) = 77.0 (7), 109.0 (24), 111.0 (57), 174.0 (100), 264.0 (75, M⁺).

HRMS (ESI) (m/z) [C12H9ClO2S2 + H⁺]: Calcd. 284.9805, Found. 284.9801.

**m-Bromophenyl sulfonothioic phenyl ester (3ja)**

Follow the general procedure, 3ja was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 70% yield (114.6 mg).

m.p.: 57 – 59 °C.

1H NMR (400 MHz, CDCl3) δ = 7.70 (d, J = 7.9 Hz, 1H), 7.62 (s, 1H), 7.51 (dd, J = 14.3, 5.9 Hz, 2H), 7.38 (d, J = 4.2 Hz, 4H), 7.30 (t, J = 8.0 Hz, 1H) (ppm).

13C NMR (100 MHz, CDCl3) δ = 144.3, 136.6, 136.6, 131.8, 130.5, 130.3, 129.7, 127.5, 125.9, 122.7 (ppm).

IR (in KBr): ν = 1594, 1450, 1334, 1126 (cm⁻¹).

MS (ESI) m/z (%) = 77.0 (6), 109.0 (28), 154.0 (43), 218.0 (67), 328.0 (100, M⁺).

HRMS (ESI) (m/z) [C12H9BrO2S2 + H⁺]: Calcd. 328.9300, Found. 328.9308.

**p-Bromophenyl sulfonothioic phenyl ester (3ka)**

Follow the general procedure, 3ka was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 71% yield (116.4 mg).

m.p.: 76 – 77 °C.

1H NMR (400 MHz, CDCl3) δ = 7.56 (d, J = 7.8 Hz, 2H), 7.49 (d, J = 5.4 Hz, 1H), 7.40 (d, J = 7.9 Hz, 2H), 7.39 – 7.31 (m, 4H) (ppm).

13C NMR (100 MHz, CDCl3) δ = 142.0, 136.6, 132.1, 131.6, 129.6, 129.0, 128.9, 127.6 (ppm).

IR (in KBr): ν = 1595, 1442, 1310, 1138 (cm⁻¹).

MS (ESI) m/z (%) = 77.0 (4), 109.0 (32), 154.0 (21), 218.0 (72), 328.0 (100, M⁺).

HRMS (ESI) (m/z) [C12H9BrO2S2 + H⁺]: Calcd. 328.9300, Found. 328.9296.
p-Nitrophenyl sulfonothioic phenyl ester (3la)

Follow the general procedure, 3la was obtained as yellow liquid with petroleum ether/ethyl acetate (40/1) used as eluent in 68% yield (100.5 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.27$ (d, $J = 7.8$ Hz, 2H), 7.73 (d, $J = 7.8$ Hz, 2H), 7.53 (d, $J = 3.0$ Hz, 1H), 7.40 (t, $J = 6.3$ Hz, 4H). ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 150.4$, 147.9, 136.5, 132.1, 129.9, 128.8, 126.9, 124.1 bbpm.

IR (in KBr): $\nu = 1590$, 1456, 1320, 1132 (cm$^{-1}$).

MS (ESI) m/z (%) = 77.0 (5), 109.0 (54), 122.0 (43), 185.0 (100), 295.0 (86, M$^+$).

HRMS (ESI) (m/z)[C$_{12}$H$_9$NO$_2$S$_2$ + H$^+$]: Calcd. 296.0046, Found. 296.0054.

4-Biphenyl sulfonothioic phenyl ester (3ma)

Follow the general procedure, 3ma was obtained as white solid with petroleum ether/ethyl acetate (40/1) used as eluent in 77% yield (125.6 mg).

m.p.: 102 – 103 $^\circ$C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.51$ (dd, $J = 16.6$, 9.1 Hz, 6H), 7.40 (t, $J = 7.3$ Hz, 3H), 7.38 – 7.31 (m, 3H), 7.27 (t, $J = 7.4$ Hz, 2H) (ppm).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 146.5$, 141.6, 138.9, 137.0, 131.5, 129.5, 129.1, 128.8, 128.1, 127.4, 127.3 (ppm).

IR (in KBr): $\nu = 1589$, 1445, 1321, 1143 (cm$^{-1}$).

MS (ESI) m/z (%) = 77.0 (12), 109.0 (25), 153.0 (56), 217.0 (100), 327.0 (76, M$^+$).

HRMS (ESI) (m/z)[C$_{18}$H$_{14}$S$_2$O$_2$ + H$^+$]: Calcd. 327.0508, Found. 327.0512.

2-Napthyl sulfonothioic phenyl ester (3na)

Follow the general procedure, 3na was obtained as white solid with petroleum ether/ethyl acetate (40/1) used as eluent in 68% yield (102.3 mg).

m.p.: 51 – 53 $^\circ$C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.95$ (s, 1H), 7.90 (d, $J = 8.5$ Hz, 2H), 7.79 (d, $J = 8.1$ Hz, 1H), 7.70 – 7.63 (m, 2H), 7.59 (d, $J = 7.6$ Hz, 1H), 7.45 (t, $J = 7.1$ Hz, 1H), 7.32 (t, $J = 7.3$ Hz, 2H), 7.31 – 7.26 (m, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 139.6$, 136.7, 136.6, 135.1, 131.6, 131.4, 129.5, 129.4, 129.3, 128.1, 128.0, 127.7, 122.4 (ppm).

IR (in KBr): $\nu = 1590$, 1452, 1311, 1145, 761 (cm$^{-1}$).

MS (ESI) m/z (%) = 77.0 (8), 109.0 (28), 127.0 (35), 191.0 (72), 300.0 (100, M$^+$).
HRMS (ESI) (m/z)[C_{16}H_{12}S_{2}O_{2} + H^+]: Calcd. 301.0351, Found. 301.0353.

3-Pyridinyl sulfonothioic phenyl ester (3oa)

Follow the general procedure, 3oa was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 72% yield (90.2 mg).

m.p.: 87 – 88 °C.

^1^H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta = 7.58 \text{ (t, } J = 8.4 \text{ Hz, 3H), 7.47 \text{ (d, } J = 6.6 \text{ Hz, 1H), 7.42 \text{ (t, } J = 7.4 \text{ Hz, 2H), 7.38 – 7.31 \text{ (m, 3H) (ppm).}} \)

^1^C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta = 143.0, 136.6, 133.7, 131.5, 129.5, 128.8, 127.8, 127.6 \text{ (ppm).} \)

IR (in KBr): \( \nu = 1593, 1467, 1331, 1145, 731 \text{ (cm}^{-1}). \)

MS (ESI) m/z (%) = 77.0 (6), 78.0 (35), 109.0 (42), 141.0 (100), 251.0 (87, M\textsuperscript{+}).

HRMS (ESI) (m/z)[C\textsubscript{11}H\textsubscript{9}NO\textsubscript{2}S\textsubscript{2} + H\textsuperscript{+}]: Calcd. 252.0147, Found. 252.0154.

2-Thiophenyl sulfonothioic phenyl ester (3pa)

Follow the general procedure, 3pa was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 64% yield (82.3 mg).

m.p.: 72 – 73 °C.

^1^H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta = 7.63 \text{ (d, } J = 4.8 \text{ Hz, 1H), 7.49 \text{ (d, } J = 7.0 \text{ Hz, 1H), 7.44 \text{ (d, } J = 7.4 \text{ Hz, 2H), 7.38 \text{ (t, } J = 7.4 \text{ Hz, 2H), 7.27 \text{ (s, 1H), 6.99 \text{ (s, 1H) (ppm).}} \)

^1^C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta = 136.6, 134.0, 133.8, 131.6, 129.6, 128.1, 127.0 \text{ (ppm).} \)

IR (in KBr): \( \nu = 1578, 1483, 1315, 1130, 745 \text{ (cm}^{-1}). \)

MS (ESI) m/z (%) = 82.0 (24), 91.0 (6), 123.0 (47), 146.0 (76), 255.0 (100, M\textsuperscript{+}).

HRMS (ESI) (m/z)[C\textsubscript{10}H\textsubscript{8}O\textsubscript{2}S\textsubscript{3} + H\textsuperscript{+}]: Calcd. 256.9759, Found. 256.9753.

4-Tolyl sulfonothioic 4-tolyl ester (3ab)

Follow the general procedure, 3ab was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 80% yield (111.5 mg).

m.p.: 76 – 77 °C.

^1^H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta = 7.46 \text{ (d, } J = 7.5 \text{ Hz, 2H), 7.22 \text{ (t, } J = 8.9 \text{ Hz, 4H), 7.14 \text{ (d, } J = 7.6 \text{ Hz, 2H), 2.42 \text{ (s, 3H), 2.38 \text{ (s, 3H) (ppm).}} \)

^1^C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta = 144.6, 142.1, 140.5, 136.5, 130.2, 129.4, 127.6, 124.6, 21.7, 21.5 \text{ (ppm).} \)

IR (in KBr): \( \nu = 1594, 1490, 1328, 1143 \text{ (cm}^{-1}). \)

MS (ESI) m/z (%) = 91.0 (35), 123.0 (52), 155.0 (78), 278.0 (100, M\textsuperscript{+}).
HRMS (ESI) (m/z)[C_{14}H_{14}O_{2}S_{2} + H^+] : Calcd. 279.0508, Found. 279.0502.

4-Tolyl sulfonothioic 3-tolyl ester (3ac)

Follow the general procedure, 3ac was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 78% yield (108.6 mg).

m.p.: 76 – 77 °C.

1H NMR (400 MHz, CDCl₃) δ = 7.46 (d, J = 7.3 Hz, 2H), 7.22 (d, J = 10.3 Hz, 4H), 7.14 (d, J = 7.5 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H) (ppm).

13C NMR (100 MHz, CDCl₃) δ = 144.6, 142.1, 140.5, 136.5, 130.2, 129.4, 127.6, 124.6, 21.7, 21.5 (ppm).

IR (in KBr): ν = 1598, 1494, 1326, 1140 (cm⁻¹).

MS (ESI) m/z (%) = 91.0 (100), 123.0 (73), 155.0 (68), 278.0 (46, M⁺).

HRMS (ESI) (m/z)[C_{14}H_{14}O_{2}S_{2} + H^+] : Calcd. 279.0508, Found. 279.0514.

4-Tolyl sulfonothioic 2-tolyl ester (3ad)

Follow the general procedure, 3ad was obtained as white solid with petroleum ether/ethyl acetate (40/1) used as eluent in 65% yield (90.4 mg).

m.p.: 101 – 102 °C.

1H NMR (400 MHz, CDCl₃) δ = 7.43 (d, J = 7.7 Hz, 2H), 7.39 – 7.31 (m, 2H), 7.22 (t, J = 7.8 Hz, 3H), 7.16 (t, J = 7.4 Hz, 1H), 2.42 (s, 3H), 2.15 (s, 3H) (ppm).

13C NMR (100 MHz, CDCl₃) δ = 144.8, 144.2, 140.7, 138.3, 131.9, 131.0, 123.0, 127.5, 127.3, 126.9, 21.7, 20.7 (ppm).

IR (in KBr): ν = 1590, 1492, 1341, 1138 (cm⁻¹).

MS (ESI) m/z (%) = 91.0 (76), 123.0 (31), 155.0 (27), 278.0 (100, M⁺).

HRMS (ESI) (m/z)[C_{12}H_{10}S_{2}O_{2} + H^+] : Calcd. 279.0508, Found. 279.0516.

4-Tolyl sulfonothioic 4-methoxyphenyl ester (3ae)

Follow the general procedure, 3ae was obtained as white solid with petroleum ether/ethyl acetate (40/1) used as eluent in 75% yield (110.4 mg).

m.p.: 127 – 128 °C.

1H NMR (400 MHz, CDCl₃) δ = 7.45 (d, J = 7.5 Hz, 2H), 7.26 (d, J = 7.4 Hz, 2H), 7.22 (d, J = 7.7 Hz, 2H), 6.84 (d, J = 7.6 Hz, 2H), 3.83 (s, 3H), 2.42 (s, 3H) (ppm).

13C NMR (100 MHz, CDCl₃) δ = 162.3, 144.6, 140.3, 138.4, 129.4, 127.6, 118.7, 115.0, 55.5, 21.7 (ppm).

IR (in KBr): ν = 1598, 1494, 1326, 1140 (cm⁻¹)
IR (in KBr): ν = 1590, 1493, 1325, 1141 cm\(^{-1}\).
MS (ESI) m/z (%) = 91.0 (56), 107.0 (25), 139.0 (43), 155.0 (100), 294.0 (78, M\(^+\)).
HRMS (ESI) (m/z) [C\(_{14}\)H\(_{14}\)O\(_2\)S\(_2\) + H\(^+\)]: Calcd. 295.0457, Found. 295.0450.

4-Tolyl sulfonothioic 2-fluorophenyl ester (3af)

Follow the general procedure, 3af was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 64% yield (90.1 mg).
m.p.: 65 – 67 °C.
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.49\) (t, \(J = 7.7\) Hz, 4H), 7.23 (d, \(J = 7.8\) Hz, 2H), 7.18 (t, \(J = 7.6\) Hz, 1H), 7.06 (t, \(J = 8.6\) Hz, 1H), 2.43 (s, 3H) (ppm).
\(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 162.9\) (\(J_{C-F} = 253.7\) Hz), 145.1, 140.7, 139.1, 134.2 (\(J_{C-F} = 8.3\) Hz), 129.5, 127.5, 125.0 (\(J_{C-F} = 3.9\) Hz), 116.4 (\(J_{C-F} = 22.7\) Hz), 115.3 (\(J_{C-F} = 17.8\) Hz), 21.7 (ppm).
IR (in KBr): ν = 1725, 1587, 1493, 1329, 1141 cm\(^{-1}\).
MS (ESI) m/z (%) = 91.0 (100), 95.0 (48), 127.0 (25), 155.0 (67), 282.0 (24, M\(^+\)).
HRMS (ESI) (m/z) [C\(_{13}\)H\(_{11}\)FO\(_2\)S\(_2\) + H\(^+\)]: Calcd. 283.0257, Found. 283.0249.

4-Tolyl sulfonothioic 4-fluorophenyl ester (3ag)

Follow the general procedure, 3ag was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 60% yield (85.5 mg).
m.p.: 92 – 93 °C.
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.45\) (d, \(J = 7.4\) Hz, 2H), 7.38 – 7.32 (m, 2H), 7.23 (d, \(J = 7.6\) Hz, 2H), 7.04 (t, \(J = 8.0\) Hz, 2H), 2.43 (s, 3H) (ppm).
\(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 164.8\) (\(J_{C-F} = 253.7\) Hz), 145.0, 140.1, 138.9 (\(J_{C-F} = 9.1\) Hz), 129.5, 127.6, 123.6 (\(J_{C-F} = 3.6\) Hz), 116.8 (\(J_{C-F} = 22.2\) Hz), 21.7 (ppm).
IR (in KBr): ν = 1725, 1584, 1498, 1326, 1140 cm\(^{-1}\).
MS (ESI) m/z (%) = 91.0 (100), 95.0 (39), 127.0 (34), 155.0 (52), 282.0 (23, M\(^+\)).
HRMS (ESI) (m/z) [C\(_{14}\)H\(_{11}\)FO\(_2\)S\(_2\) + H\(^+\)]: Calcd. 283.0257, Found. 283.0264.

4-Tolyl sulfonothioic 3-chlorophenyl ester (3ai)

Follow the general procedure, 3ai was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 71% yield (105.5 mg).
m.p.: 77 – 79 °C.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.47$ (d, $J = 8.1$ Hz, 3H), 7.30 (d, $J = 5.8$ Hz, 3H), 7.25 (d, $J = 8.0$ Hz, 2H), 2.44 (s, 3H) (ppm).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 145.2$, 140.0, 136.1, 134.9, 134.7, 131.5, 130.4, 129.7, 129.5, 127.7, 21.7 (ppm).

IR (in KBr): $\nu = 1572$, 1429, 1330, 1142 cm$^{-1}$.

MS (ESI) m/z (%) = 91.0 (100), 111.0 (37), 142.0 (56), 155.0 (38), 297.0 (65, M$^+$).

HRMS (ESI) (m/z)[C$_{13}$H$_{11}$ClO$_2$S$_2$ + H$^+$]: Calcd. 298.9962, Found. 298.9957.

4-Tolyl sulfonothioic 4-chlorophenyl ester (**3aj**)

Follow the general procedure, **3aj** was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 68% yield (101.4 mg).

m.p.: 86 – 87 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.47$ (d, $J = 7.6$ Hz, 2H), 7.34 – 7.28 (m, 4H), 7.26 – 7.22 (m, 2H), 2.43 (s, 3H) (ppm).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 145.0$, 140.2, 138.2, 137.7, 129.7, 129.5, 127.6, 126.6, 21.7 (ppm).

IR (in KBr): $\nu = 1576$, 1421, 1338, 1149 (cm$^{-1}$).

MS (ESI) m/z (%) = 91.0 (84), 154.0 (24), 155.0 (38), 186.0 (68), 341.0 (100, M$^+$).

HRMS (ESI) (m/z)[C$_{13}$H$_{11}$BrO$_2$S$_2$ + H$^+$]: Calcd. 342.9457, Found. 342.9459.

4-Tolyl sulfonothioic 3-bromophenyl ester (**3ak**)

Follow the general procedure, **3ak** was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 71% yield (121.6 mg).

m.p.: 73 – 74 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.60$ (d, $J = 8.0$ Hz, 1H), 7.47 (d, $J = 8.0$ Hz, 2H), 7.41 – 7.34 (m, 2H), 7.23 (d, $J = 9.2$ Hz, 3H), 2.44 (s, 3H) (ppm).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 145.2$, 139.9, 138.9, 135.3, 134.3, 130.7, 129.9, 129.5, 127.7, 122.7, 21.7 (ppm).

IR (in KBr): $\nu = 1528$, 1421, 1338, 1149 (cm$^{-1}$).

MS (ESI) m/z (%) = 91.0 (84), 154.0 (24), 155.0 (38), 186.0 (68), 341.0 (100, M$^+$).

HRMS (ESI) (m/z)[C$_{13}$H$_{11}$BrO$_2$S$_2$ + H$^+$]: Calcd. 342.9457, Found. 342.9459.

4-Tolyl sulfonothioic 4-bromophenyl ester (**3al**)

Follow the general procedure, **3al** was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 68% yield (101.4 mg).

m.p.: 86 – 87 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.47$ (d, $J = 8.1$ Hz, 3H), 7.30 (d, $J = 5.8$ Hz, 3H), 7.25 (d, $J = 8.0$ Hz, 2H), 2.44 (s, 3H) (ppm).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 145.2$, 140.0, 136.1, 134.9, 134.7, 131.5, 130.4, 129.7, 129.5, 127.7, 21.7 (ppm).

IR (in KBr): $\nu = 1576$, 1421, 1338, 1149 (cm$^{-1}$).

MS (ESI) m/z (%) = 91.0 (100), 111.0 (37), 142.0 (56), 155.0 (38), 297.0 (65, M$^+$).

HRMS (ESI) (m/z)[C$_{13}$H$_{11}$BrO$_2$S$_2$ + H$^+$]: Calcd. 298.9962, Found. 298.9957.
Follow the general procedure, 3al was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 70% yield (119.3 mg).
m.p.: 102 – 103 °C.

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta = 7.51 - 7.45 (m, 4H), 7.23 (t, J = 6.9 Hz, 4H), 2.43 (s, 3H) (ppm). \]

\[ \text{C NMR (100 MHz, CDCl}_3\text{)} \delta = 145.1, 140.2, 137.9, 132.7, 129.6, 127.6, 127.2, 126.6, 21.7 (ppm). \]

IR (in KBr): \( \nu = 1524, 1420, 1336, 1149 \text{ cm}^{-1} \).

MS (ESI) m/z (%) = 91.0 (73), 154.0 (36), 155.0 (45), 186.0 (81), 341.0 (100, M\(^+\)).

HRMS (ESI) (m/z)[C\(_{13}\)H\(_{11}\)BrO\(_2\)S\(_2\) + H\(^+\)]: Calcd. 342.9457, Found. 342.9463.

4-Tolyl sulfonothioic 2-thiophenyl ester (3am)

Follow the general procedure, 3am was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 62% yield (83.2 mg).
m.p.: 51 – 52 °C.

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta = 7.61 (d, J = 5.1 Hz, 1H), 7.53 (d, J = 7.9 Hz, 2H), 7.26 (d, J = 7.4 Hz, 2H), 7.15 (s, 1H), 7.07 (s, 1H), 2.44 (s, 3H) (ppm). \]

\[ \text{C NMR (100 MHz, CDCl}_3\text{)} \delta = 145.1, 139.5, 139.4, 135.1, 129.6, 128.4, 127.9, 21.7 (ppm). \]

IR (in KBr): \( \nu = 1545, 1421, 1332, 1179, 727 \text{ cm}^{-1} \).

MS (ESI) m/z (%) = 82.0 (56), 91.0 (100), 114.0 (47), 155.0 (28), 269.0 (61, M\(^+\)).

HRMS (ESI) (m/z)[C\(_{11}\)H\(_{10}\)O\(_2\)S\(_3\) + H\(^+\)]: Calcd. 270.9916, Found. 270.9907.

4-Tolyl sulfonothioic 2-benzothiazolyl ester (3an)

Follow the general procedure, 3an was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 58% yield (93.2 mg).
m.p.: 62 – 63 °C.

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta = 8.15 (d, J = 7.8 Hz, 1H), 8.04 (d, J = 7.5 Hz, 2H), 7.95 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 7.3 Hz, 1H), 7.54 (d, J = 9.2 Hz, 1H), 7.38 (d, J = 7.8 Hz, 2H), 2.43 (s, 3H) (ppm). \]

\[ \text{C NMR (100 MHz, CDCl}_3\text{)} \delta = 166.7, 151.9, 144.9, 136.0, 134.4, 129.2, 128.0, 126.7, 126.4, 124.5, 121.2, 20.7 (ppm). \]

IR (in KBr): \( \nu = 1556, 1428, 1334, 1140 \text{ cm}^{-1} \).

MS (ESI) m/z (%) = 91.0 (56), 134.0 (81), 155.0 (45), 165.0 (100), 320.0 (23, M\(^+\)).

HRMS (ESI) (m/z)[C\(_{14}\)H\(_{11}\)NO\(_2\)S\(_3\) + H\(^+\)]: Calcd. 322.0025, Found. 322.0028.

4-Tolyl sulfonothioic benzyl ester (3ao)
Follow the general procedure, **3ao** was obtained as white solid with petroleum ether/ethyl acetate (40/1) used as eluent in 77% yield (97.2 mg).

m.p.: 62 – 63 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.72 (d, $J$ = 7.7 Hz, 2H), 7.27 (d, $J$ = 8.0 Hz, 2H), 7.22 (s, 3H), 7.18 (s, 2H), 4.24 (s, 2H), 2.43 (s, 3H) (ppm).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 144.7, 142.0, 133.7, 129.8, 129.2, 128.8, 128.0, 127.0, 40.3, 21.7 (ppm).

IR (in KBr): $\nu$ = 3120, 1423, 1348, 1127 cm$^{-1}$.

MS (ESI) m/z (%) =91.0 (68), 123.0 (41), 155.0 (100), 264.0 (46, M$^+$)

HRMS (ESI) (m/z)[$C_{14}H_{24}O_2S_2+ H^+$]: Calcd. 279.0508, Found. 279.0517.

4-Tolyl sulfonothioic decane ester (**3ap**)

Follow the general procedure, **3ba** was obtained as colorless liquid with petroleum ether/ethyl acetate (40/1) used as eluent in 48% yield (122.4 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.81 (d, $J$ = 7.6 Hz, 2H), 7.34 (d, $J$ = 7.6 Hz, 2H), 2.98 (t, $J$ = 7.1 Hz, 2H), 2.45 (s, 3H), 1.23 (d, $J$ = 18.1 Hz, 2H), 0.88 (t, $J$ = 5.9 Hz, 3H) (ppm).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 144.6, 142.2, 129.8, 127.0, 36.1, 31.9, 29.6, 29.5, 29.4, 28.9, 28.6, 28.5, 22.7, 21.7, 14.2 (ppm).

IR (in KBr): $\nu$ = 3080, 1415, 1130,780 (cm$^{-1}$).

MS (ESI) m/z (%) = 91.0 (24), 155.0 (56), 201.0 (37),356 (100, M$^+$).

HRMS (ESI) (m/z)[$C_{12}H_{10}S_2O_2 + H^+$]: Calcd. 357.1916, Found. 357.1909.

**EPR sample preparation and spectra**

**p-Tolyl sulfonyl hydrazide in PEG-400:**

A Schlenk tube (25 mL) equipped with a magnetic bar was loaded with $p$-tolyl sulfonyl hydrazide (110.4 mg) and PEG-400 (1.0 mL) and the mixture was allowed to stir at 100 °C for 1 h in air. Then the mixture was introduced in an EPR tube, and the spectrum was measured at room temperature but no signal was observed.

**Dphenyl disulfide:**

A Schlenk tube (25 mL) equipped with a magnetic bar was loaded with diphenyl disulfide (65.4 mg) and PEG-400 (1.0 mL). the mixture was allowed to stir at 100 °C for 1 h in air, then was introduced in an EPR tube, and the spectrum was measured at room temperature. A broad spectrum centered at $g_e$ value = 2.0072 with additional weak narrow signals stemming from the solution was observed.
$p$-Tolyl sulfonyl hydrazide + H$_2$O$_2$ (30% in water): 

A Schlenk tube (25 mL) equipped with a magnetic bar was loaded with $p$-tolyl sulfonyl hydrazide (110.4 mg), H$_2$O$_2$ (476.1 mg, 30% in water) in PEG-400 (1.0 mL). The mixture was allowed to stir at 100 °C for 1 h in air, then was introduced in an EPR tube, and the spectrum was measured at room temperature. A broad spectrum centered at $g_e$ value = 2.0086 with additional weak narrow signals stemming from the solution was observed.

Diphenyl disulfide + 30%H$_2$O$_2$: 

A Schlenk tube (25 mL) equipped with a magnetic bar was loaded with diphenyl disulfide (65.4 mg), 30% H$_2$O$_2$ (476.1 mg) in PEG-400 (1.0 mL) and the mixture was allowed to stir at 100 °C for 1 h. Then the mixture was introduced in an EPR tube, and the spectrum was measured at room temperature. No signal was observed.

Reaction mixtures: 

A Schlenk tube (25 mL) equipped with a magnetic bar was loaded with $p$-tolyl sulfonyl hydrazide (110.4 mg), diphenyl disulfide (65.4 mg) and H$_2$O$_2$(476.1 mg, 30% in water) in PEG-400 (1.0 mL). The mixture was allowed to stir at 100 °C for 1 h in air, then was introduced in an EPR tube, and the spectrum was measured at room temperature. A broad spectrum centered at $g$-Value = 2.007 with additional weak narrow signals stemming from the solution was observed.
Spectra:

$^1$H, $^{13}$C and spectra of 3aa
$^1$H, $^{13}$C and spectra of 3ba
$^{1}H$, $^{13}C$ and spectra of 3ca
$^1$H, $^{13}$C and spectra of 3da
$^1$H, $^{13}$C and spectra of 3ea
$^1$H, $^{13}$C and spectra of 3ga
$^1\text{H}, ^{13}\text{C}$ and spectra of 3ha
$^1$H, $^{13}$C and spectra of 3ja
$^1$H, $^{13}$C and spectra of 3ka
$^{1}\text{H}, ^{13}\text{C}$ and spectra of 3la
$^1$H, $^{13}$C and spectra of 3ma
$^1$H, $^{13}$C and spectra of 3na
$^{1}$H, $^{13}$C and spectra of 3oa
$^{1}H$, $^{13}C$ and spectra of 3pa
$^{1}H$, $^{13}C$ and spectra of 3ab
$^{1}$H, $^{13}$C and spectra of 3ac
$^{1}H$, $^{13}C$ and spectra of 3ad
$^1\text{H}, ^{13}\text{C}$ and spectra of 3ae
$^{1}H$, $^{13}C$ and spectra of 3af
$^1$H, $^{13}$C and spectra of 3ag
$^1$H, $^{13}$C and spectra of 3ai
$^1$H, $^{13}$C and spectra of 3aj
$^1$H, $^{13}$C and spectra of 3ak
$^1$H, $^{13}$C and spectra of 3al
$^1$H, $^{13}$C and spectra of 3am
$^1$H, $^{13}$C and spectra of 3an
$^1$H, $^{13}$C and spectra of 3ao
$^1$H, $^{13}$C and spectra of 3ap