Supporting Information

Ruthenium-catalyzed Decarboxylative C-S Cross-Coupling of carbonothioate: Synthesis of allyl(Aryl)sulfide

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**GENERAL.** Ethyl acetate (ACS grade), petroleum ether (ACS grade) and dichloromethane (ACS grade) were obtained commercially and used without further purification. Anhydrous 1,2-dichloroethane (HPLC grade) was purified by distillation over calcium hydride. Tetrahydrofuran was distilled over sodium/benzophenone. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using Silicycle precoated silica gel plates. Flash column chromatography was performed over Silicycle silica gel (300-400 mesh). 

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer using tetramethylsilane (TMS) as internal standards. Infrared spectra were recorded with a Nicolet 5700 spectrometer and are reported in reciprocal centimeter (cm$^{-1}$). HRESI-MS data were measured on a Synapt G2-Si instrument.

**PROCEDURE FOR THE SYNTHESIS**

1. **Preparation of unsubstituted allyl carbonothioates**

\[
\begin{align*}
R^+ \text{SH} + \text{CHCl=CHCOCl} & \quad \text{CTAB} \\
3 & \quad 4 \\
\text{0°C, 2h} & \quad 1
\end{align*}
\]

1a-1l was prepared according to the literature procedure$^1$.

The thiophenol 3 (5 mmol) and tetra-$n$-butyl ammonium chloride hydrate (0.035 mmol) were dissolved in dichloromethane (10 mL) and 4M sodium hydroxide (2mL) at 0 °C. Allyl chloroformate 4 (6 mmol) was slowly added and the reaction mixture was stirred for 2 hr. After 2 hr, the two layers were separated and the organic layer was washed with 2M sodium hydroxide (5 mL) and dried over MgSO$_4$. A yellow oil remained after evaporation of the solvent under reduced pressure. This oil was purified by flash column chromatography using ethyl acetate and petroleum ether as an eluent.

O-allyl S-(p-tolyl) carbonothioate (1a)
Purified by flash column chromatography (petroleum ether/ethyl acetate, 20/1) to afford 1a (0.91g, 88%) as pale yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.41 (d, \(J=7.8\) Hz, 2H), 7.20 (d, \(J=7.8\) Hz, 2H), 6.00 – 5.85 (m, 1H), 5.40 – 5.23 (m, 2H), 4.71 (d, \(J=5.8\) Hz, 2H), 2.37 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 169.90, 139.97, 134.89, 131.37, 130.01, 124.10, 119.28, 68.20, 21.33; IR (film) \(v\): 2939, 1722, 1448, 1132, 937, 812 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{11}\)H\(_{12}\)O\(_2\)S ([M+Na]\(^{+}\)): 231.0486; found: 231.0487.

O-allyl S-(4-methoxyphenyl) carbonothioate (1b)

\[
\begin{align*} \text{O} & \text{-} \text{allyl} \quad \text{S-} \quad \text{O} \quad \text{alkyl} \quad \text{carbonothioate} \quad (1b) \end{align*}
\]

Purified by flash column chromatography (petroleum ether) to afford 1b (1.0g, 91%) as pale yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.50 – 7.39 (m, 2H), 6.96 – 6.85 (m, 2H), 5.97 – 5.84 (m, 1H), 5.39 – 5.22 (m, 2H), 4.70 (dt, \(J=5.8, 1.3\) Hz, 2H), 3.81 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.25, 160.88, 136.67, 131.40, 119.25, 118.27, 114.83, 68.17, 55.37; IR (film) \(v\): 2945, 2839, 1724, 1593, 1456, 1249, 831 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{11}\)H\(_{12}\)O\(_3\)S ([M+Na]\(^{+}\)): 247.0405; found: 247.0403.

O-allyl S-(naphthalen-2-yl) carbonothioate (1c)

\[
\begin{align*} \text{O} & \text{-} \text{allyl} \quad \text{S-} \quad \text{O} \quad \text{alkyl} \quad \text{carbonothioate} \quad (1c) \end{align*}
\]

Purified by flash column chromatography (petroleum ether) to afford 1c (1.07g, 88%) as pale yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.05 (s, 1H), 7.87 – 7.80 (m, 3H), 7.58 – 7.50 (m, 3H), 6.01 – 5.84 (m, 1H), 5.38 – 5.26 (m, 2H), 4.75 – 4.69 (m, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 169.58, 134.70, 133.45, 133.41, 131.32, 131.21, 128.88, 128.02, 127.79, 127.30, 126.67, 124.90, 119.41, 68.34; IR (film) \(v\): 3053, 2922, 1624, 1587, 1425, 1226, 920, 812, 742 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{14}\)H\(_{12}\)O\(_2\)S ([M+Na]\(^{+}\)): 267.0456; found: 267.0455.

O-allyl S-(2,6-dimethylphenyl) carbonothioate (1d)
Purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1) to afford 1d (0.91 g, 82%) as pale yellow oil. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.31 – 7.17 (m, 2H), 7.16 – 7.14 (m, 1H), 5.96 – 5.88 (m, 1H), 5.41 – 5.20 (m, 2H), 4.70 (d, \(J=5.6\) Hz, 2H), 2.45 (s, 6H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 158.41, 143.33, 131.46, 130.08, 128.34, 126.81, 119.02, 68.01, 21.91; IR (film) \(\nu\): 2954, 1722, 1460, 1136, 937, 773 cm\textsuperscript{-1}; HRMS (ESI) calcd for C\textsubscript{12}H\textsubscript{14}O\textsubscript{2}S ([M+H+Na]\textsuperscript{+}): 246.0690; found: 246.0692.

O-allyl S-(4-bromophenyl) carbonothioate (1e)

Purified by flash column chromatography (petroleum ether) to afford 1e (1.22 g, 89%) as pale yellow oil. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.52 (d, \(J=8.4\) Hz, 2H), 7.39 (d, \(J=8.4\) Hz, 2H), 5.95 – 5.87 (m, 1H), 5.37 – 5.28 (m, 2H), 4.73 – 4.71 (m, 2H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 168.80, 136.26, 132.40, 131.14, 126.79, 124.34, 119.58, 68.52; IR (film) \(\nu\): 3086, 2947, 1726, 1471, 1132, 939, 819 cm\textsuperscript{-1}; HRMS (ESI) calcd for C\textsubscript{10}H\textsubscript{9}BrO\textsubscript{2}S ([M +Na]\textsuperscript{+}): 294.9404; found: 294.9402.

O-allyl S-(2-bromophenyl) carbonothioate (1f)

Purified by flash column chromatography (petroleum ether) to afford 1f (1.13 g, 87%) as pale yellow oil. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.73 – 7.65 (m, 2H), 7.35 – 7.24 (m, 2H), 6.00 – 5.86 (m, 1H), 5.41 – 5.24 (m, 2H), 4.74 (d, \(J=5.9\) Hz, 1H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 167.86, 137.34, 133.62, 131.36, 131.17, 129.94, 129.34, 128.02, 119.40, 68.54; IR (film) \(\nu\): 3086, 2949, 1728, 1450, 1267, 1141, 1022, 939, 754 cm\textsuperscript{-1}; HRMS (ESI) calcd for C\textsubscript{10}H\textsubscript{9}BrO\textsubscript{2}S ([M +Na]\textsuperscript{+}): 294.9404; found: 294.9406.
**O-allyl S-(4-chlorophenyl) carbonothioate (1g)**

Purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1) to afford 1g (1.04g, 90%) as pale yellow oil. \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.50 – 7.42 (m, 2H), 7.40 – 7.34 (m, 2H), 5.98 – 5.88 (m, 1H), 5.41 – 5.25 (m, 2H), 4.72 (dt, \(J=5.9, 1.3\) Hz, 2H); \(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 168.97, 136.10, 136.06, 131.14, 129.44, 126.15, 119.56, 68.50; \(\text{IR}\) (film) \(\nu\): 3086, 2947, 1726, 1475, 1136, 939, 825 cm\(^{-1}\); \(\text{HRMS (ESI)}\) calcd for C\(_{10}\)H\(_9\)ClO\(_2\)S ([M + Na]\(^+\)): 250.9909; found: 250.9906.

**O-allyl S-benzyl carbonothioate (1h)**

Purified by flash column chromatography (petroleum ether) to afford 1h (0.87g, 83%) as pale yellow oil. \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.38 – 7.21 (m, 5H), 5.99 – 5.83 (m, 1H), 5.42 – 5.21 (m, 2H), 4.71 (d, \(J=5.8, 1.4\) Hz, 2H), 4.11 (s, 2H); \(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 170.56, 137.13, 131.45, 128.86, 128.64, 127.46, 119.17, 67.97, 35.41; \(\text{IR}\) (film) \(\nu\): 2927, 1710, 1452, 1136, 935, 704 cm\(^{-1}\); \(\text{HRMS (ESI)}\) calcd for C\(_{11}\)H\(_{12}\)O\(_2\)S ([M+Na]\(^+\)): 231.0456; found: 231.0453.

**O-allyl S-butyl carbonothioate (1i)**

Purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1) to afford 1i (0.79g, 90%) as pale yellow oil. \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 5.99 – 5.86 (m, 1H), 5.39 – 5.22 (m, 2H), 4.71 – 4.69 (m, 2H), 2.87 (t, \(J=7.4\) Hz, 2H), 1.69-1.56 (m, 2H), 1.44 – 1.39 (m, 2H), 0.93 (t, \(J=7.3\) Hz, 3H); \(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 171.12, 131.60, 118.94, 67.63, 31.80, 30.73, 21.80, 13.54; \(\text{IR}\) (film) \(\nu\): 2960, 2873, 1712, 1458, 1138, 935 cm\(^{-1}\); \(\text{HRMS (ESI)}\) calcd for C\(_{8}\)H\(_{14}\)O\(_2\)S ([M+Na]\(^+\)): 197.0612; found: 197.0615.
O-allyl S-(4-nitrophenyl) carbonothioate (1j)

\[
\begin{align*}
&\text{Purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1) to afford} \\
&\text{1j (1.04g, 87%) as pale yellow solid. Mp: 68-70 °C; } ^1\text{H NMR (400 MHz, CDCl}_3) \delta 8.24 \\
&(\text{d, } J=8.9 \text{ Hz, 2H}), 7.73 (\text{d, } J=8.9 \text{ Hz, 2H}), 5.96 – 5.89 \text{ (m, 1H)}, 5.56 – 5.18 \text{ (m, 2H), 4.77} \\
&(\text{d, } J=5.9 \text{ Hz, 2H}); ^13\text{C NMR (101 MHz, CDCl}_3) \delta 167.38, 148.16, 136.35, 134.61, \\
&130.82, 123.94, 120.00, 68.97; \text{ IR (film) } \nu: 3097, 1720, 1512, 1344, 1161, 943, 846 \text{ cm}^{-1}; \\
&\text{HRMS (ESI) calcd for C}_{10}\text{H}_9\text{NO}_4\text{S ([M+Na]^+): 262.0150; found: 262.0153.}
\end{align*}
\]

O-allyl S-(pyridin-3-yl) carbonothioate (1k)

\[
\begin{align*}
&\text{Purified by flash column chromatography (petroleum ether/ethyl acetate, 10/1) to afford} \\
&\text{1k (0.85g, 86%) as pale yellow oil. } ^1\text{H NMR (400 MHz, CDCl}_3) \delta 8.64 – 8.56 \text{ (m, 1H),} \\
&7.77 – 7.69 \text{ (m, 2H), 7.29 – 7.25 (m, 1H), 6.00 – 5.87 (m, 1H), 5.39 – 5.27 (m, 2H), 4.76} \\
&(\text{d, } J= 5.9 \text{ Hz, 2H}); ^13\text{C NMR (101 MHz, CDCl}_3) \delta 168.25, 151.71, 150.16, 137.26, \\
&131.10, 129.38, 123.46, 119.55, 68.42; \text{ IR (film) } \nu: 2949, 1724, 1570, 1450, 1145, 941, \\
&767 \text{ cm}^{-1}; \text{ HRMS (ESI) calcd for C}_{9}\text{H}_9\text{NO}_2\text{S ([M+H]^+): 196.0432; found: 196.0431.}
\end{align*}
\]

O-allyl S-(benzo[d]thiazol-2-yl) carbonothioate (1l)

\[
\begin{align*}
&\text{Purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1) to afford} \\
&\text{1l (1.08g, 86%)} \text{ as pale yellow oil. } ^1\text{H NMR (400 MHz, CDCl}_3) \delta 8.08–7.95 \text{ (m, 1H),} \\
&7.94 – 7.82 \text{ (m, 1H), 7.52 – 7.40 (m, 2H), 6.02 – 5.92 (m, 1H), 5.48–5.31 (m, 2H), 4.84} \\
&(\text{dt, } J=6.0, 1.3 \text{ Hz, 2H}); ^13\text{C NMR (101 MHz, CDCl}_3) \delta 166.00, 157.78, 152.08, 136.51, \\
&130.52, 126.41, 125.62, 123.08, 121.14, 120.41, 69.44; \text{ IR (film) } \nu: 3062, 1728, 1419, \\
&1147, 1001, 1147, 759 \text{ cm}^{-1}; \text{ HRMS (ESI) calcd for C}_{11}\text{H}_9\text{NO}_2\text{S}_2 ([M+H]^+): 252.0153; \\
&\text{found: 252.0152.}
\end{align*}
\]
2. Preparation of substituted allyl carbonothioates

\[
\begin{align*}
\text{R}_1\text{S} - \text{R}_2 \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{R}_4 \quad \text{R}_3 \quad \text{OH} & \quad \text{DMAP} \\
0^\circ\text{C}, 2\text{h} & \quad \rightarrow \text{R}_1\text{S} - \text{R}_2 \quad \text{O} \quad \text{R}_3 \\
\end{align*}
\]

1m-1t was prepared according to the literature procedure².

To a solution of a substituted thiophenol 3 (5 mmol) and triphosgene (1.8 mmol) in dry dichloromethane (30 mL) was added 4-dimethylaminopyridine (DMAP) (5 mmol) dropwise at 0 °C. The resulting mixture was stirred for 30 min at that temperature, and then an allylic alcohol 5 (5 mmol) and DMAP (6 mmol) were sequentially added. After stirring for 2 h, the reaction mixture was quenched by adding H₂O (20 mL). The organic phase was separated, dried over Na₂SO₄, concentrated in vacuo, and the residue was purified by flash chromatography. The following compounds were synthesized:

S-(2-methoxyphenyl) O-(2-methylallyl) carbonothioate (1m)

\[
\begin{align*}
\text{O} & \quad \text{S} \\
\text{R}_1\text{S} - \text{R}_2 & \quad \text{O} \quad \text{R}_4 \\
\end{align*}
\]

Purified by flash column chromatography (petroleum ether/ethyl acetate, 80/1) to afford 1m as pale yellow oil (0.83g, 70%). \(^1\text{H NMR} (400\text{ MHz, CDCl}_3) \delta 7.51 (dd, J = 8.2, 1.6 \text{ Hz, } 1\text{H}), 7.41 (dd, J = 8.2, 1.6 \text{ Hz, } 1\text{H}), 7.01 – 6.93 (m, 2\text{H}), 4.99 (s, 1\text{H}), 4.94 (s, 1\text{H}), 4.62 (s, 2\text{H}), 3.88 (d, J = 8.6 \text{ Hz, } 3\text{H}), 1.75 (s, 3\text{H}); \(^{13}\text{C NMR} (101\text{ MHz, CDCl}_3) \delta 168.84, 159.63, 139.33, 137.06, 131.92, 121.02, 115.87, 113.77, 111.56, 70.75, 56.00, 19.36; \text{IR (film) } \nu: 2939, 1726, 1479, 1277, 1139, 1069, 1024, 754 \text{ cm}^{-1}; \text{HRMS (ESI) calcd for C}_{12}\text{H}_{14}\text{O}_3\text{S ([M+Na]}^+): 261.0561; \text{found: 261.0563.}
\]

S-(4-bromophenyl) O-(2-methylallyl) carbonothioate (1n)
Purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1) to afford \( \text{1n} \) as pale yellow oil (1.06g, 74%). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.53 (d, \( J = 8.5 \) Hz, 2H), 7.39 (d, \( J = 8.5 \) Hz, 2H), 4.99 (d, \( J = 6.1 \) Hz, 1H), 4.97 (s, 1H), 4.64 (s, 2H), 1.76 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 168.83, 139.03, 136.28, 132.40, 126.86, 124.33, 114.31, 71.21, 19.39; IR (film) \( \nu \): 2976, 2941, 1726, 1472, 1387, 1138, 1090, 912, 817 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{11}\)H\(_{11}\)BrO\(_2\)S ([M+Na]\(^{+}\)): 308.9561; found: 308.9560.

\textbf{O-cinnamyl S-(p-tolyl) carbonothioate (1o)}

\[
\begin{align*}
\text{S} & \quad \text{O} \\
\text{O-C} & \quad \text{S} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\end{align*}
\]

Purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1) to afford \( \text{1o} \) as pale yellow oil (0.97g, 68%). Mp: 83-85 °C; \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.48 – 7.15 (m, 9H), 6.64 (d, \( J = 15.7 \) Hz, 1H), 6.38 – 6.16 (m, 1H), 4.85 (d, \( J = 5.6 \) Hz, 2H), 2.36 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 170.01, 140.00, 136.04, 135.31, 134.97, 130.07, 128.67, 128.31, 126.78, 124.26, 122.29, 68.26, 21.38; IR (film) \( \nu \): 2941, 1726, 1472, 1386, 1138, 1069, 912, 817 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{17}\)H\(_{16}\)O\(_2\)S ([M+Na]\(^{+}\)): 307.0769; found: 307.0766.

\textbf{S-(4-bromophenyl) O-cinnamyl carbonothioate (1p)}

\[
\begin{align*}
\text{Br} & \quad \text{S} \\
\text{O-C} & \quad \text{S} \\
\text{O-C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\end{align*}
\]

Purified by flash column chromatography (petroleum ether) to afford \( \text{1p} \) as white solid (1.12g, 64%). Mp: 86-89 °C; \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.54 – 7.52 (m, 2H), 7.41 – 7.25 (m, 7H), 6.66 (d, \( J = 15.8 \) Hz, 1H), 6.38 – 6.19 (m, 1H), 4.88 (d, \( J = 6.1 \) Hz, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 168.92, 136.31, 135.88, 135.64, 132.43, 128.68, 128.39, 126.77, 124.38, 121.94, 68.60; IR (film) \( \nu \): 2853, 1717, 1472, 1163, 1092, 923, 819, 740 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{16}\)H\(_{13}\)BrO\(_2\)S ([M+Na]\(^{+}\)): 370.9717; found: 370.9716.
S-(4-chlorophenyl) O-cinnamylcarbonothioate (1q)

\[
\begin{align*}
&\text{Cl} \quad \text{S} \quad \text{O} \quad \text{O} \quad \text{O} \\
&\text{C} \quad \text{C} \quad \text{C} \quad \text{C} \\
&\text{H} \quad \text{H} \quad \text{H} \quad \text{H}
\end{align*}
\]

Purified by flash column chromatography (petroleum ether) to afford 1q as white solid (1.01 g, 66%). Mp: 83-85 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.48 – 7.46 (m, 2H), 7.43 – 7.23 (m, 7H), 6.67 (d, \( J = 15.9 \) Hz, 1H), 6.32 – 6.26 (m, 1H), 4.88 (d, \( J = 6.6 \) Hz, 2H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 169.08, 136.12, 135.89, 135.63, 129.48, 128.68, 128.39, 126.78, 126.22, 121.96, 68.59; \textbf{IR} (film) \( \nu \): 2920, 1737, 1468, 1383, 1087, 970, 808, 756 cm\textsuperscript{-1}; \textbf{HRMS} (ESI) calcd for C\textsubscript{16}H\textsubscript{13}ClO\textsubscript{2}S ([M+Na]\textsuperscript{+}): 327.0222; found: 327.0220.

S-(2-bromophenyl) O-(but-3-en-2-yl) carbonothioate (1r)

\[
\begin{align*}
&\text{Br} \quad \text{S} \quad \text{O} \quad \text{O} \\
&\text{C} \quad \text{C} \quad \text{C} \quad \text{C} \\
&\text{H} \quad \text{H} \quad \text{H} \quad \text{H}
\end{align*}
\]

Purified by flash column chromatography (petroleum ether/ethyl acetate, 80/1) to afford 1r as pale yellow oil (1.05 g, 73%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.73 – 7.63 (m, 2H), 7.37 – 7.23 (m, 2H), 5.93 – 5.79 (m, 1H), 5.46 – 5.40 (m, 1H), 5.30 – 5.26 (m, 1H), 5.20 – 5.17 (m, 1H), 1.38 (d, \( J = 6.5 \) Hz, 3H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 167.27, 137.31, 136.67, 133.58, 131.25, 127.97, 116.97, 75.73, 20.00; \textbf{IR} (film) \( \nu \): 2984, 1730, 1449, 1429, 1149, 1022, 845, 752 cm\textsuperscript{-1}; \textbf{HRMS} (ESI) calcd for C\textsubscript{11}H\textsubscript{11}BrO\textsubscript{2}S ([M+Na]\textsuperscript{+}): 308.9561; found: 308.9563.

O-(but-3-en-2-yl) S-(4-chlorophenyl) carbonothioate (1s)

\[
\begin{align*}
&\text{Cl} \quad \text{S} \quad \text{O} \quad \text{O} \\
&\text{C} \quad \text{C} \quad \text{C} \quad \text{C} \\
&\text{H} \quad \text{H} \quad \text{H} \quad \text{H}
\end{align*}
\]

Purified by flash column chromatography (petroleum ether/ethyl acetate, 80/1) to afford 1s as pale yellow oil (0.89 g, 73%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.46 (t, \( J =8.5 \) Hz, 2H), 7.36 (d, \( J = 8.5 \) Hz, 2H), 5.89 – 5.81 (m, 1H), 5.45 – 5.39 (m, 1H), 5.30 – 5.17 (m, 2H), 1.38 (d, \( J = 6.5 \) Hz, 3H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 168.39, 136.64, 136.05, 129.39,
126.42, 117.11, 75.69, 19.98; \textbf{IR} (film) ν: 2985, 1726, 1477, 1150, 1094, 1037, 847, 819 cm⁻¹; \textbf{HRMS} (ESI) calcd for C₁₁H₁₁ClO₂S ([M+Na]⁺): 265.0066; found: 265.0069.

\(\text{(E)-O-(but-2-en-1-yl) S-(4-chlorophenyl) carbonothioate (1t)}\)

Purified by flash column chromatography (petroleum ether/ethyl acetate, 80/1) to afford 1t as pale yellow oil (0.91 g, 75%). \(\text{¹H NMR} (400 \text{ MHz, CDCl}_3) \delta \text{ 7.44 (d, } J = 8.3 \text{ Hz, 2H), 7.37 (, } J = 8.3 \text{ Hz, 2H), 5.90 – 5.76 (m, 1H), 5.67 – 5.54 (m, 1H), 4.65 (d, } J = 6.7 \text{ Hz, 2H), 1.73 (d, } J = 6.5 \text{ Hz, 3H); ¹³C NMR} (101 \text{ MHz, CDCl}_3) \delta 168.96, 136.05, 133.14, 129.41, 126.36, 124.19, 68.79, 17.82. \text{IR} (film) ν: 2945, 1724, 1477, 1136, 1092, 1015, 966, 821 cm⁻¹; \text{HRMS} (ESI) calcd for C₁₁H₁₁ClO₂S ([M+Na]⁺): 265.0066; found: 265.0067.

3. General procedure for ruthenium-catalyzed decarboxylative allylic etherification

\[
\begin{array}{c}
\text{R}^\text{−} \text{S} \text{O} \text{O} \text{R}_\text{2} \text{R}_\text{3} \text{Cp*RuCl(PPh}_3\text{)}\text{2} (3 \text{ mol%}) \text{DCE} \\
\text{1} \quad \text{2}
\end{array}
\]

To a 2 dram septum-capped vial were added sequentially 1 (0.3 mmol), Cp*RuCl(PPh₃)₂ (0.009 mmol, 3 mol%) and 3 mL of dry DCE, and the resulting homogenous solution was stirred at 50 °C until 1 disappeared on TLC. After complete reaction, the solvent was removed under reduced pressure, and the crude product was purified through flash chromatography on silica gel to afford target compounds 2 series as following.

\(\text{allyl(p-tolyl)sulfane (2a)}\)

Purified by flash column chromatography (petroleum ether) to afford 2a (47.3mg, 96%) as pale yellow oil. \(\text{¹H NMR} (400 \text{ MHz, CDCl}_3) \delta 7.26 (d, J=8.0 \text{ Hz, 2H), 7.09 (d, } J=8.0 \text{ Hz, 2H, 7.81 (dd, } J=8.0,8.0 \text{ Hz, 2H) \text{; IR} (film) \nu: 2945, 1724, 1477, 1136, 1092, 1015, 966, 821 \text{ cm}⁻¹ \text{; HRMS} (ESI) calcd for C}_{13}H_{15}ClO₂S ([M+Na]⁺): 294.0112; found: 294.0112.}\)
Hz, 2H), 5.91 – 5.81 (m, 1H), 5.13 – 4.98 (m, 1H), 5.07 – 5.02 (m, 1H), 3.50 (d, J=6.9 Hz, 2H), 2.31 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 136.43, 133.84, 132.03, 130.70, 129.58, 117.42, 37.91, 21.04. IR (film) ν: 3018, 2920, 1636, 1492, 1224, 987, 918, 804 cm$^{-1}$.

**allyl(4-methoxyphenyl)sulfane (2b)**

Purified by flash column chromatography (petroleum ether/ethyl acetate, 60/1) to afford 2b (52.0mg, 94%) as pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.32 (m, 1H), 6.85 – 6.81 (m, 1H), 5.93 – 5.77 (m, 1H), 5.06 – 4.93 (m, 2H), 3.79 (s, 3H), 3.43 (d, $J$ = 7.1, 1.1 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.08, 134.04, 133.91, 125.81, 117.26, 114.41, 55.30, 39.35; IR (film) ν: 2922, 1573, 1461, 1205, 1125, 809, 742 cm$^{-1}$.

**allyl(naphthalen-2-yl)sulfane (2c)**

Purified by flash column chromatography (petroleum ether) to afford 2c (57.7mg, 96%) as pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.79 – 7.71 (m, 4H), 7.48 – 7.41 (m, 3H), 5.99 – 5.86 (m, 1H), 5.20-5.05 (m, 2H), 3.65 (d, $J$ = 6.8 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 133.71, 133.48, 133.44, 131.86, 128.28, 127.78, 127.72, 127.71, 127.13, 126.49, 125.71, 117.84, 37.07; IR (film) ν: 3053, 2922, 1624, 1587, 1425, 1226, 920, 812, 742 cm$^{-1}$.

**allyl(2,6-dimethylphenyl)sulfane (2d)**

Purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1) to afford 2d (47.1mg, 88%) as pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.12 – 10 (m, 3H), 5.88 – 5.77 (m, 1H), 4.95-4.82 (m, 2H), 3.28 (d, $J$=7.3 Hz, 2H), 2.53 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.32, 134.03, 132.86, 128.24, 116.80, 38.37, 22.16; IR (film) ν: 2953, 2920, 1635, 1460, 1224, 916, 769 cm$^{-1}$.
allyl(4-bromophenyl)sulfane (2e)

Purified by flash column chromatography (petroleum ether) to afford 2e (61.9mg, 90%) as pale yellow oil. \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.39 (d, \( J = 8.5 \) Hz, 2H), 7.19 (d, \( J = 8.5 \) Hz, 2H), 5.88 – 5.79 (m, 1H), 5.14 – 5.07 (m, 2H), 3.53 – 3.51 (m, 2H); \( ^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 135.07, 133.18, 131.82, 131.44, 120.15, 117.99, 37.24; IR (film) \( \nu \): 2922, 1473, 1226, 1091, 920, 808 cm\(^{-1}\).

allyl(2-bromophenyl)sulfane (2f)

Purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1) to afford 2f (59.1mg, 86%) as pale yellow oil. \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.54 (s, 1H), 7.30 – 7.23 (m, 2H), 7.03 (s, 1H), 5.99 – 5.82 (m, 1H), 5.33 – 5.05 (m, 2H), 3.60 (d, \( J = 6.7 \) Hz, 2H); \( ^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 137.41, 132.96, 132.59, 128.91, 127.60, 126.82, 123.89, 118.48, 36.16; IR (film) \( \nu \): 2922, 1573, 1448, 1109, 921, 742 cm\(^{-1}\).

allyl(4-chlorophenyl)sulfane (2g):

Purified by flash column chromatography (petroleum ether) to afford 2g (48.7mg, 89%) as pale yellow oil. 1H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.30 – 7.17 (m, 4H), 5.89 – 5.79 (m, 1H), 5.18 - 5.01 (m, 2H), 3.51 (d, \( J = 6.8 \) Hz, 2H); \( ^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 134.34, 133.25, 132.30, 131.34, 128.91, 117.94, 37.45; IR (film) \( \nu \): 3082, 2922, 1635, 1475, 1095, 814, 731 cm\(^{-1}\).

allyl(benzyl)sulfane (2h)
Purified by flash column chromatography (petroleum ether) to afford 2h (45.2mg, 91%) as pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31 – 7.30 (m, 4H), 7.26 – 7.22 (m, 1H), 5.88 – 5.71 (m, 1H), 5.18 – 5.04 (m, 2H), 3.66 (s, 2H), 3.03 (d, $J$ = 7.1 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 138.32, 134.21, 129.02, 128.47, 126.93, 117.30, 34.94, 34.09; IR (film) $\nu$: 2924, 1726, 1454, 1271, 916, 769 cm$^{-1}$.

allyl(butyl)sulfane (2i)

Purified by flash column chromatography (petroleum ether) to afford 2i (34.0 mg, 87%) as pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.85 – 5.74 (m, 1H), 5.14 – 5.08 (m, 1H), 5.06 (d, $J$ = 1.2 Hz, 1H), 3.14 – 3.10 (m, 2H), 2.46 (t, $J$ = 8.0 Hz, 2H), 1.61-1.48 (m, 2H), 1.46-1.32 (m, 2H), 0.91 (t, $J$ = 7.3 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 134.59, 116.64, 34.76, 31.42, 30.38, 21.99, 13.70; IR (film) $\nu$: 3358, 2922, 2852, 1656, 1462 cm$^{-1}$.

allyl(4-nitrophenyl)sulfane (2j)

Purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1) to afford 2j (48.6 mg, 83%) as pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (d, $J$ = 8.9 Hz, 2H), 7.35 (d, $J$ = 8.9 Hz, 2H), 5.94 – 5.84 (m, 1H), 5.35 – 5.30 (m, 1H), 5.23 – 5.20 (m, 1H), 3.68 (d, $J$ = 6.9 Hz 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 146.82, 145.22, 131.95, 126.80, 119.05, 35.21; IR (film) $\nu$: 2920, 1640, 1512, 1336, 1087, 842, cm$^{-1}$.

3-(allylthio)pyridine (2k)

Purified by flash column chromatography (petroleum ether/ethyl acetate, 10/1) to afford 2k (42.8 mg, 86%) as pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.44 – 8.42 (m, 1H),
7.52 – 7.41 (m, 1H), 7.18 – 7.16 (m, 1H), 7.03 – 6.92 (m, 1H), 6.05 – 5.88 (m, 1H), 5.31 – 5.26 (m, 1H), 5.12 – 5.09 (m, 1H), 3.85 – 3.83 (m, 2H); \(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 158.58, 149.43, 135.93, 133.84, 122.28, 119.50, 117.51, 33.05; \(\text{IR (film)}\) \(\nu\) 2942, 1491, 1224, 987, 913, 803, 765 cm\(^{-1}\).

2-(allylthio)benzo[d]thiazole (2l)

Purified by flash column chromatography (petroleum ether) to afford 2l (53.90 mg, 87%) as pale yellow oil. \(^{1}\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.88 (dd, \(J=8.0, 1.2\) Hz, 1H), 7.75 (dd, \(J=8.0, 1.2\) Hz, 1H), 7.43 – 7.39 (m, 1H), 7.34-7.22 (m, 1H), 6.08 – 5.97 (m, 1H), 5.41 – 5.36 (m, 1H), 5.22 – 5.19 (m, 1H), 4.00 (dt, \(J=7.0, 1.2\) Hz, 2H); \(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 166.18, 153.21, 135.33, 132.32, 126.05, 124.28, 121.59, 120.97, 119.17, 36.26; \(\text{IR (film)}\) \(\nu\) 3062, 2922, 1460, 1236, 995, 756 cm\(^{-1}\).

(2-methoxyphenyl)(2-methylallyl)sulfane (2m)

Purified by flash column chromatography (petroleum ether/ethyl acetate, 80/1) to afford 2m (53.1mg, 91%) as pale yellow oil. \(^{1}\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.30 – 7.26 (m, 1H), 7.23 – 7.15 (m, 1H), 6.93 – 6.82 (m, 2H), 4.79 (d, \(J=8.9\) Hz, 2H), 3.89 (s, 3H), 3.51 (s, 2H), 1.85 (s, 3H); \(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 157.75, 140.95, 130.87, 127.56, 124.22, 120.89, 113.75, 110.46, 55.74, 40.11, 21.29; \(\text{IR (film)}\) \(\nu\) 2954, 2924, 2854, 1579, 1471, 1244, 1026, 894, 748 cm\(^{-1}\); \(\text{IR (film)}\) \(\nu\) 2954, 2924, 2854, 1579, 1471, 1244, 1026, 894, 748 cm\(^{-1}\).

(4-bromophenyl)(2-methylallyl)sulfane (2n)
Purified by flash column chromatography (petroleum ether) to afford 2n (68.6mg, 94%) as pale yellow oil. \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.38 (d, \( J \) = 8.4 Hz, 2H), 7.19 (d, \( J \) = 8.4 Hz, 2H), 4.81 (d, \( J \) = 5.2 Hz, 2H), 3.49 (s, 2H), 1.84 (s, 3H); \( ^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 204.12, 140.39, 135.57, 131.78, 131.63, 120.16, 114.34, 41.99, 21.07. IR (film) \( \nu \): 3078, 2972, 2918, 1647, 1566, 1471, 1091, 1006, 898, 810, 771 cm\(^{-1}\).

\( \text{cinnamyl(p-tolyl)sulfane (2o)} \)

Purified by flash column chromatography (petroleum ether) to afford 2o (67.1mg, 93%) as pale yellow oil. \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.33 – 7.17 (m, 7H), 7.08 (d, \( J \) = 7.8 Hz, 2H), 6.38 (d, \( J \) = 15.7 Hz, 1H), 6.29 – 6.17 (m, 1H), 3.65 (d, \( J \) = 7.0 Hz, 2H), 2.30 (s, 3H); \( ^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 136.87, 136.67, 132.60, 131.96, 131.16, 129.66, 128.53, 127.53, 126.36, 125.41, 37.88, 21.07; IR (film) \( \nu \): 3026, 2922, 1701, 1678, 1490, 1450, 1122, 966, 806, 750, 696 cm\(^{-1}\).

\( \text{(4-bromophenyl)(cinnamyl)sulfane (2p)} \)

Purified by flash column chromatography (petroleum ether) to afford 2p (78.4mg, 89%) as white solid. \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 77.41 – 7.36 (m, 2H), 7.34 – 7.28 (m, 4H), 7.26 – 7.20 (m, 3H), 6.42 (d, \( J \) = 15.7 Hz, 1H), 6.27 – 6.16 (m, 1H), 3.68 (d, \( J \) = 7.1 Hz, 2H); \( ^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 136.55, 135.02, 133.13, 131.90, 131.86, 128.59, 127.73, 126.37, 124.62, 120.41, 37.20; IR (film) \( \nu \): 2920, 1468, 1383, 1213, 1088, 970, 808 cm\(^{-1}\).

\( \text{(4-chlorophenyl)(cinnamyl)sulfane (2q)} \)
Purified by flash column chromatography (petroleum ether) to afford 2q (68.9 mg, 87%) as white solid. \( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.35 – 7.17 (m, 9H), 6.40 (d, \( J = 15.7 \) Hz, 1H), 6.28 – 6.14 (m, 1H), 3.67 (d, \( J = 7.0 \) Hz, 2H); \( ^{13}\text{C NMR} \) (101 MHz, CDCl\(_3\)) \( \delta \) 136.57, 134.27, 133.08, 132.56, 131.80, 128.99, 128.58, 127.72, 126.36, 124.69, 37.43; IR (film) \( \nu \): 2922, 1475, 1389, 1221, 1097, 968, 810, 756 cm\(^{-1}\).

(2-bromophenyl)(but-3-en-2-yl)sulfane (2r-1)

Purified by flash column chromatography (petroleum ether) to afford 2r-1 (32.5 mg, 45%) as pale yellow oil. \( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.45 – 7.35 (m, 1H), 7.31 – 7.17 (m, 3H), 5.89 – 5.75 (m, 1H), 5.08 – 4.93 (m, 2H), 3.91 (p, \( J = 7.0 \) Hz, 1H), 1.44 (d, \( J = 6.9 \) Hz, 3H); \( ^{13}\text{C NMR} \) (101 MHz, CDCl\(_3\)) \( \delta \) 139.32, 132.89, 129.97, 128.54, 127.58, 126.56, 124.98, 115.31, 35.43, 17.79; IR (film) \( \nu \): 2920, 2852, 1573, 1446, 1220, 1020, 962, 744 cm\(^{-1}\).

(2-bromophenyl)(but-2-en-1-yl)sulfane (2r-2)

Purified by flash column chromatography (petroleum ether) to afford 2r-2 (32.8 mg, 45%) as pale yellow oil. \( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.59 – 7.51 (m, 2H), 7.10 – 6.97 (m, 2H), 5.73 – 5.61 (m, 1H), 5.59 – 5.48 (m, 1H), 3.62 – 3.51 (m, 2H), 1.66 (d, \( J = 6.3 \) Hz, 3H); \( ^{13}\text{C NMR} \) (101 MHz, CDCl\(_3\)) \( \delta \) 138.01, 136.50, 133.08, 132.60, 127.86, 127.50, 123.59, 115.31, 45.39, 20.03; IR (film) \( \nu \): 2920, 2852, 1573, 1446, 1220, 1020, 962, 744 cm\(^{-1}\).

but-3-en-2-yl(4-chlorophenyl)sulfane (2s-1)
Purified by flash column chromatography (petroleum ether) to afford 2s-1 (27.1mg, 45.5%) as pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.25 – 7.23 (m, 4H), 5.85 – 5.70 (m, 1H), 4.95 – 4.88 (m, 2H), 3.74 – 3.67 (m, 1H), 1.38 (d, $J = 6.9$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 134.16, 131.13, 129.37, 128.84, 128.83, 114.95, 46.71, 20.04; IR (film) $\nu$: 2966, 2992, 1475, 1386, 1220, 1095, 962, 920, 815 cm$^{-1}$.

(E)-but-2-en-1-yl(4-chlorophenyl)sulfane (2s-2)

Purified by flash column chromatography (petroleum ether) to afford 2s-2 (27.1mg, 45.5%) as pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 (d, $J = 8.5$ Hz, 2H), 7.25 (d, $J = 8.5$ Hz, 2H), 5.64 – 5.42 (m, 2H), 3.56 – 3.42 (m, 2H), 1.65 (d, $J = 5.4$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 139.60, 134.16, 131.13, 128.83, 125.81, 114.95, 36.67, 17.72; IR (film) $\nu$: 2966, 2992, 1475, 1386, 1220, 1095, 962, 920, 815 cm$^{-1}$.

20170707-1.2.fid

O\textsubscript{2}N

\[
\begin{align*}
167.38 & & 181.46 & & 168.35 & & 131.61 & & 130.82 & & 123.94 & & 130.00 & & 126.97
\end{align*}
\]
20170710-3.2.fid

166.31  157.38  152.98  138.51  

120.42  121.14  123.08  125.62  126.43

130.52  136.51  152.08  157.78  166.01

![](image)

f1 (ppm)
20170703-6.2.fid

![Chemical Structure](image)

- f1 (ppm)
  - 20.98
  - 23.94
  - 26.71
  - 28.81
  - 39.35
  - 55.30
  - 114.41
  - 117.26
  - 125.81
  - 133.91
  - 134.04
  - 159.08

- 0
  - 500
  - 1000
  - 1500
  - 2000
  - 2500
  - 3000
  - 3500
  - 4000
  - 4500

- 220
  - 210
  - 200
  - 190
  - 180
  - 170
  - 160
  - 150
  - 140
  - 130
  - 120
  - 110
  - 100
  - 90
  - 80
  - 70
  - 60
  - 50
  - 40
  - 30
  - 20
  - 10
  - 0
  - -10
  - -20
20170726-1.1.fid

[Chemical structure image]

f1 (ppm)