Supporting Information

Aryne Triggered [2,3]-Sigmatropic Rearrangement of Allyl and Propargyl Thioethers

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I. General Methods.

All reactions were carried out in schlenk tubes. The reactions were monitored either by thin-layer chromatography on silica gel 60-F254 coated 0.2 mm plates (Yantai Chemical Industry Research Institute) or GC-MS (Thermo Fisher Trace 1300-ISQ). Visualization was accomplished by UV light (254 nm). The crude products were purified either using a preparative thin-layer chromatography (TLC) plate or flash column chromatography using silica gel (normal phase, 200-300 mesh, Branch of Qingdao Haiyang Chemical). $^1$H NMR spectra was recorded on a 400/500 MHz spectrometer at ambient temperature. Data are reported as follows: (1) chemical shift in parts per million (δ, ppm) from CDCl$_3$ (7.26 ppm) (2) multiplicity (s = singlet, br = broad, d = doublet, t = triplet, q = quartet, and m = multiplet); (3) coupling constants (Hz). $^{13}$C NMR spectra were recorded on a 100/125 MHz spectrometer at ambient temperature. Chemical shifts are reported in ppm from CDCl$_3$ (77.16 ppm). HR-MS data were obtained on a QTOF mass spectrometer. All commercial materials were used as received unless otherwise noted. Aryne precursors are all prepared following the literature procedures.

II. Substrates Preparation

1) General procedure A:

\[
\begin{align*}
&\text{R}_1\text{R}_2\text{Br} + \text{HS-\text{EtCOO}} \\
&\text{THF, 0°C} \quad \text{NaH} \\
&\text{R}_1\text{R}_2\text{OEt} \quad \text{S-\text{EtCOO}}
\end{align*}
\]

A mixture of sodium hydride (NaH, 5.25 mmol, 60% in mineral, 0.21 g, 1.05 equiv.) and anhydrous tetrahydrofuran (THF) was added ethyl 2-mercaptoacetate (5 mmol, 0.55 mL, 1 equiv.) under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube with a magnetic stir bar. The minutes was kept stirring for 30 minutes until allyl bromide (5.25 mmol, 1.05 equiv.) was added to the solution dropwise. The reaction was kept stirring overnight at 0 °C. The reaction was then quenched with saturated NH$_4$Cl (30 mL) and extracted with ethyl acetate (3×30 mL), dried over sodium
sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (petroleum ether (PE) and ethyl acetate (EA) as the eluent).

\[
\text{OEt}
\]

**Ethyl 2-(allylthio)acetate (2d)**

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=20:1 as the eluent) to give 2d (95% yield) as a colorless oil. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.76 (td, $J = 16.4, 7.7$ Hz, 1H), 5.20-5.10 (m, 2H), 4.19 (q, $J = 7.1$ Hz, 2H), 3.25 (d, $J = 7.3$ Hz, 2H), 3.16 (s, 2H), 1.29 (t, $J = 7.1$ Hz, 3H). 

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 170.45, 132.93, 118.27, 61.22, 34.93, 31.74, 14.16.

HR-MS (ESI): Calcd for C$_7$H$_{13}$O$_2$S$^+ [M+H]$^+$ requires 161.0631; found 161.0623.

\[
\text{Br}
\]

**Ethyl 2-((2-bromoallyl)thio)acetate (2i)**

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=20:1 as the eluent) to give 2i (98% yield) as a yellow oil. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.84 (s, 1H), 5.59 (s, 1H), 4.19 (q, $J = 7.1$ Hz, 2H), 3.60 (s, 2H), 3.20 (s, 2H), 1.30 (t, $J = 7.1$ Hz, 3H). 

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 169.98, 128.29, 120.18, 61.45, 42.17, 31.91, 14.17. HR-MS (ESI): Calcd for C$_7$H$_{12}$BrO$_2$S$^+ [M+H]$^+$ requires 238.9736; found 238.9723.

\[
\text{OEt}
\]

**Ethyl 2-((2-methylallyl)thio)acetate (2j)**
Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=10:1 as the eluent) to give 2j (85% yield) as a colorless oil. 

$^1$H NMR (400 MHz, CDCl$_3$): δ 4.91 (s, 1H), 4.87 (s, 1H), 4.18 (q, $J$ = 7.1 Hz, 2H), 3.23 (s, 2H), 3.14 (s, 2H), 1.82 (s, 3H), 1.29 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 170.50, 139.96, 114.72, 61.21, 39.53, 31.98, 20.55, 14.18. HR-MS (ESI): Calcd for C$_8$H$_{15}$O$_2$S$^+$ [M+H]$^+$ requires 175.0787; found 175.0783.

![Ethyl 2-(cinnamylthio)acetate (2k)](image)

**Ethyl 2-(cinnamylthio)acetate (2k)**

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=20:1 as the eluent) to give 2k (70% yield) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.37 (d, $J$ = 7.7 Hz, 2H), 7.30 (t, $J$ = 7.5 Hz, 2H), 7.22 (t, $J$ = 7.2 Hz, 1H), 6.48 (d, $J$ = 15.7 Hz, 1H), 6.14 (dt, $J$ = 15.3, 7.5 Hz, 1H), 4.15 (q, $J$ = 7.1 Hz, 2H), 3.41 (d, $J$ = 7.5 Hz, 2H), 3.17 (s, 2H), 1.25 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 170.55, 136.54, 133.77, 128.62, 127.75, 126.42, 124.47, 61.30, 34.64, 31.87, 14.21. HR-MS (ESI): Calcd for C$_{13}$H$_{17}$O$_2$S$^+$ [M+H]$^+$ requires 237.0944; found 237.0948.

![Ethyl 2-((3-methylbut-2-en-1-yl)thio)acetate (2l)](image)

**Ethyl 2-((3-methylbut-2-en-1-yl)thio)acetate (2l)**

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=50:1 as the eluent) to give 2l (85% yield) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$): δ 5.26-5.15 (m, 1H), 4.19 (q, $J$ = 7.1 Hz, 2H), 3.27 (d, $J$ = 7.8 Hz, 2H), 3.16 (s, 2H), 1.75 (s, 3H), 1.67 (s, 3H), 1.29 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 170.78, 136.78, 119.51, 61.23, 32.44, 30.06, 25.71, 17.67,
14.18. HR-MS (ESI): Calcd for C₉H₁₇O₂S⁺ [M+H]⁺ requires 189.0944; found 189.0948.

Ethyl 2-(prop-2-yn-1-ylthio)acetate (5b)

Following the general procedure A, the crude product was purified by silica gel flash chromatography (PE: EA=20:1 as the eluent) to give 5b (81% yield) as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 4.21 (q, J = 7.1 Hz, 2H), 3.42 (s, 2H), 3.41 (d, J = 2.7 Hz, 2H), 2.28 (t, J = 2.5 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 169.95, 78.95, 71.78, 61.47, 32.63, 19.91, 14.15. HR-MS (ESI): Calcd for C₇H₁₁O₂S⁺ [M+H]⁺ requires 159.0474; found 159.0477.

2) General procedure B:

A mixture of NaH (5.25 mmol, 60% in mineral, 0.21 g, 1.05 equiv.) in anhydrous THF was added prop-2-ene-1-thiol (5 mmol, wt% =50%, 0.74 g, 1 equiv.) under nitrogen atmosphere at 0 °C for 30 minutes in a flame-dried schlenk tube with a magnetic stir bar. The reaction was kept stirring for 30 minutes until the electrophile compound (5.25 mmol, 1.05 equiv.) was added dropwise. The resultant solution was kept stirring overnight and then quenched with saturated NH₄Cl solution (30 mL), extracted with EA (3×30 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The crude product was then further purified by silica gel flash chromatography (PE and EA as the eluent).
2-(Allylthio)-N,N-diethylacetamide (2b)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=5:1 as the eluent) to give 2b (85% yield) as a colorless oil. 

$1^H$ NMR (400 MHz, CDCl$_3$): $\delta$ 5.87-5.73 (m, 1H), 5.15 (dd, $J = 25.2, 13.5$ Hz, 2H), 3.43-3.30 (m, 4H), 3.23 (dd, $J = 12.9, 4.8$ Hz, 4H), 1.19 (td, $J = 7.0, 2.3$ Hz, 4H), 1.11 (td, $J = 6.9, 2.5$ Hz, 3H). 

$13^C$ NMR (100 MHz, CDCl$_3$): $\delta$ 168.32, 133.35, 117.98, 42.52, 40.31, 34.72, 31.73, 14.39, 12.88. HR-MS (ESI): Calcd for C$_9$H$_{18}$NOS$^+$ [M+H]$^+$ requires 188.1104; found 188.1114.

2-(Allylthio)-1-phenylethan-1-one (2c)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=10:1 as the eluent) to give 2c (45% yield) as a deep yellow oil. 

$1^H$ NMR (400 MHz, CDCl$_3$): $\delta$ 7.99-7.93 (m, 2H), 7.57 (dd, $J = 10.9, 3.7$ Hz, 1H), 7.46 (t, $J = 7.7$ Hz, 2H), 5.77 (ddt, $J = 17.1, 9.9, 7.2$ Hz, 1H), 5.25-5.12 (m, 2H), 3.76 (s, 2H), 3.18 (d, $J = 7.2$ Hz, 2H). 

$13^C$ NMR (100 MHz, CDCl$_3$): $\delta$ 194.49, 135.52, 133.32, 132.97, 128.68, 118.49, 35.58, 34.75. HR-MS (ESI): Calcd for C$_{11}$H$_{13}$OS$^+$ [M+H]$^+$ requires 193.0682; found 193.0689.

2-(Allylthio)-1-morpholinoethan-1-one (2e)
Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=5:1 as the eluent) to give 2e (46% yield) as an orange oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.66 (ddt, $J$ = 17.1, 9.9, 7.2 Hz, 1H), 5.05 (ddd, $J$ = 13.5, 10.6, 1.0 Hz, 2H), 3.59-3.50 (m, 4H), 3.49-3.43 (m, 2H), 3.40-3.34 (m, 2H), 3.13 (s, 2H), 3.10 (d, $J$ = 7.2 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.68, 133.04, 118.13, 66.61, 66.45, 46.66, 42.04, 34.66, 31.50. HR-MS (ESI): Calcd for C$_9$H$_{16}$NO$_2$S$^+$ [M+H]$^+$ requires 202.0896; found 202.0902.

![2-(Allylthio)acetonitrile (2f)](image)

**2-(Allylthio)acetonitrile (2f)**

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=50:1 as the eluent) to give 2f (49% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.81-5.66 (m, 1H), 5.31-5.20 (m, 2H), 3.39-3.31 (m, 2H), 3.23 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 131.74, 119.51, 116.33, 34.76, 15.40. HR-MS (ESI): Calcd for C$_5$H$_8$NS$^+$ [M+H]$^+$ requires 114.0372; found 114.0382.

![2-((Allylthio)methyl)benzo[d]oxazole (2h)](image)

**2-((Allylthio)methyl)benzo[d]oxazole (2h)**

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=20:1 as the eluent) to give 2h (58% yield) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.70 (dd, $J$ = 6.1, 3.0 Hz, 1H), 7.51 (dd, $J$ = 6.2, 3.0 Hz, 1H), 7.33 (dt, $J$ = 4.8, 3.6 Hz, 2H), 5.81 (ddt, $J$ = 17.1, 9.9, 7.2 Hz, 1H), 5.23 (dd, $J$ = 25.5, 13.5 Hz, 2H), 3.87 (s, 2H), 3.27 (d, $J$ = 7.2 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 163.72, 151.04, 141.25, 132.77, 125.06, 124.39, 120.00, 118.66, 110.59, 34.71, 26.69.

HR-MS (ESI): Calcd for C$_{11}$H$_{12}$NOS$^+$ [M+H]$^+$ requires 206.0634; found 206.0630.
2-(Allylthio)cyclohexan-1-one (2m)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=50:1 as the eluent) to give 2m (28% yield) as a pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.76 (ddt, $J = 17.1$, 9.9, 7.2 Hz, 1H), 5.24-5.06 (m, 2H), 3.33 (t, $J = 4.8$ Hz, 1H), 3.11 (d, $J = 7.2$ Hz, 2H), 2.95 (ddd, $J = 14.5$, 10.7, 5.8 Hz, 1H), 2.29-1.67 (m, 7H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 205.73, 133.32, 117.99, 50.53, 37.97, 34.20, 32.96, 26.94, 22.09. HR-MS (ESI): Calcd for C$_9$H$_{15}$OS$^+$ [M+H]$^+$ requires 171.0838; found 171.0848.

3-(Allylthio)dihydrofuran-2(3H)-one (2n)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE: EA=10:1 as the eluent) to give 2n (38% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.83 (ddd, $J = 16.4$, 9.2, 6.0 Hz, 1H), 5.23 (dd, $J = 30.3$, 13.5 Hz, 2H), 4.42 (dd, $J = 16.1$, 7.9 Hz, 1H), 4.33 (td, $J = 8.5$, 4.6 Hz, 1H), 3.57 (dd, $J = 13.8$, 8.5 Hz, 1H), 3.48 (dd, $J = 8.6$, 4.8 Hz, 1H), 3.23 (dd, $J = 13.8$, 5.9 Hz, 1H), 2.65 (dq, $J = 13.7$, 8.1 Hz, 1H), 2.13 (ddt, $J = 11.9$, 7.1, 4.7 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 175.56, 132.69, 118.74, 66.74, 37.47, 33.93, 29.74. HR-MS (ESI): Calcd for C$_7$H$_{11}$O$_2$S$^+$ [M+H]$^+$ requires 159.0474; found 159.0480.
Allyl(benzhydryl)sulfane (2o)

Following the general procedure B, the crude product was purified by silica gel flash chromatography (PE as the eluent) to give 2o (48% yield) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.41 (d, $J = 7.5$ Hz, 4H), 7.30 (t, $J = 7.5$ Hz, 4H), 7.21 (t, $J = 7.1$ Hz, 2H), 5.82 (td, $J = 17.0$, 7.2 Hz, 1H), 5.11 (s, 1H), 5.11-4.92 (m, 2H), 2.98 (d, $J = 7.1$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 141.21, 133.97, 128.58, 128.53, 127.18, 117.39, 52.73, 35.10. HR-MS (ESI): Calcd for C$_{16}$H$_{17}$S$^+$ [M+H]$^+$ requires 241.1045; found 241.1050.

3) Synthesis of 2g

Diethyl ((allylthio)methyl)phosphonate (2g)

A mixture of anhydrous potassium carbonate (K$_2$CO$_3$, 10 mmol, 1.38 g, 2.0 equiv.) and Tetrabutylammonium Hydrogen Sulfate (1 mmol, 0.34 g, 0.1 equiv.) in 10mL anhydrous dichloromethane (DCM) was added prop-2-ene-1-thiol (5 mmol, wt% =50%, 0.74 g, 1.0 equiv.) dropwise under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube with a magnetic stir bar. After 30 minutes, the triflate (5 mmol, 1.0 equiv.) was added to the solution dropwise and stirred at room temperature until TLC indicate the reactant was over. The mixture was then treated with water (30 mL), extracted with EA (3×30 mL), washed by brine (30 mL), dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude product was then purified by Aluminum oxide flash chromatography (PE: EA=4:1 as the eluent) to give 2g (56% yield) as a pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.74 (ddd, $J = 14.5$, 9.5, 7.3 Hz, 1H), 5.20-5.13 (m, 2H), 4.20-4.15 (m, 4H), 3.31 (dd, $J = 7.2$, 0.6 Hz, 2H), 2.66 (d, $J = 13.1$ Hz, 2H).
Hz, 2H), 1.35 (t, J = 7.1 Hz, 6H). $^{31}$P NMR (162 MHz, CDCl$_3$): δ 24.80. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 132.99, 118.52, 62.59, 62.53, 35.65, 35.61, 23.98, 22.49, 16.51, 16.45. HR-MS (ESI): Calcd for C$_8$H$_{18}$O$_3$PS$^+$ [M+H]$^+$ requires 225.0709; found 225.0719.

4) Synthesis of 5a

\[
\begin{align*}
\text{Di(prop-2-yn-1-yl)sulfane (5a)}
\end{align*}
\]

3-Bromoprop-1-yne (80 wt% in toluene, 1.25 mL, 11.2 mmol) was added dropwise to a solution of Na$_2$S•H$_2$O (1.24 g, 5.2 mmol) in methanol at 0 °C. The mixture was stirred at room temperature for 1 hour and the solvent was evaporated. The residue was treated with water (20 mL), extracted with Et$_2$O (3×30 mL), washed with brine, dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (PE: EA =20:1) to give 5a (23%) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 3.44 (d, J = 2.5 Hz, 1H), 2.27 (t, J = 2.5 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 78.98, 71.47, 18.85. HR-MS (ESI): Calcd for C$_6$H$_7$S$^+$ [M+H]$^+$ requires 111.0263; found 111.0268.

5) Synthesis of 5c

\[
\begin{align*}
\text{allyl(prop-2-yn-1-yl)sulfane (5c)}
\end{align*}
\]

A mixture of NaH (5.25 mmol, 60% in mineral, 0.21 g, 1.05 equiv.) in anhydrous THF was added prop-2-ene-1-thiol (5 mmol, wt% =50%, 0.74 g, 1 equiv.)
under nitrogen atmosphere at 0 °C for 30 minutes in a flame-dried schlenk tube with a magnetic stir bar. The reaction was kept stirring for 30 minutes until 3-Bromoprop-1-yne (80 wt% in toluene, 1.25 mL, 11.2 mmol) was added dropwise. The resultant solution was kept stirring overnight and then quenched with saturated NH₄Cl solution (30 mL), extracted with EA (3×30 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The crude product was then further purified by vacuum distillation to give 5c (25%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 5.84-5.71 (m, 1H), 5.20-5.06 (m, 2H), 3.32-3.28 (m, 2H), 3.18 (d, J = 2.6 Hz, 2H), 2.23 (t, J = 2.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 132.94, 117.95, 79.91, 70.99, 33.87, 17.77.

III. General Procedure for Aryne Reaction

A mixture of cesium fluoride (CsF, 0.5 mmol, 0.076 g, 0.25 equiv.) in 1 mL anhydrous acetonitrile was added aryne (0.2 mmol, 49 µL, 1.0 equiv.) dropwise under nitrogen atmosphere at room temperature in a flame-dried schlenk tube with a magnetic stir bar. After 10 minutes, the sulfide (0.4 mmol, 2.0 equiv.) was added to the solution dropwise, which was then kept stirring at 30 °C or 70 °C (18 h or 48 h). The reaction mixture was then treated with water (20 mL), extracted with EA (3×20 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography.

Hexa-1,5-dien-3-yl(phenyl)sulfane (3a)
Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=20:1 as the eluent) to give 3a (90% yield) as a colorless oil. \[^1\text{H}\] NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.42-7.37 (m, 2H), 7.29 (dd, \(J = 8.5, 1.6\) Hz, 2H), 7.26-7.16 (m, 1H), 5.84 (ddt, \(J = 17.1, 10.2, 7.0\) Hz, 1H), 5.71 (ddd, \(J = 17.0, 10.1, 8.7\) Hz, 1H), 5.16-5.03 (m, 2H), 5.01-4.85 (m, 2H), 3.65 (dd, \(J = 14.5, 8.1\) Hz, 1H), 2.53-2.35 (m, 2H). \[^{13}\text{C}\] NMR (100 MHz, CDCl\(_3\)): \(\delta\) 138.14, 135.03, 134.47, 132.91, 128.72, 127.21, 117.24, 116.03, 51.77, 38.62. HR-MS (ESI): Calcd for C\(_{12}\)H\(_{15}\)S\(^+\) [M+H]\(^+\) requires 191.0889; found 191.0900.

\[\text{S} \quad \text{O} \quad \text{N,N-Diethyl-2-(phenylthio)pent-4-enamide (3b)}\]

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=10:1 as the eluent) to give 3b (84% yield) as a yellow oil. \[^1\text{H}\] NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.54-7.46 (m, 2H), 7.35-7.30 (m, 3H), 5.88-5.74 (m, 1H), 5.19-5.01 (m, 2H), 3.82 (dd, \(J = 9.0, 5.7\) Hz, 1H), 3.50 (dq, \(J = 13.9, 7.1\) Hz, 1H), 3.41-3.18 (m, 2H), 3.11 (dq, \(J = 14.4, 7.2\) Hz, 1H), 2.87-2.72 (m, 1H), 2.49 (td, \(J = 13.2, 6.6\) Hz, 1H), 1.11 (q, \(J = 7.1\) Hz, 6H). \[^{13}\text{C}\] NMR (100 MHz, CDCl\(_3\)): \(\delta\) 169.46, 135.01, 134.14, 132.83, 128.91, 128.31, 117.60, 47.37, 42.01, 40.82, 37.05, 14.75, 12.94. HR-MS (ESI): Calcd for C\(_7\)H\(_{13}\)O\(_2\)S\(^+\) [M+H]\(^+\) requires 161.0631; found 161.0623.

\[\text{S} \quad \text{O} \quad \text{1-Phenyl-2-(phenylthio)pent-4-en-1-one (3c)}\]
Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give 3c (71% yield) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.94-7.87 (m, 1H), 7.60-7.22 (m, 8H), 5.88 (ddt, $J$ = 17.0, 10.2, 6.8 Hz, 1H), 5.17-5.04 (m, 2H), 4.50 (dd, $J$ = 7.7, 6.9 Hz, 1H), 2.76 (ddd, $J$ = 14.6, 7.7, 6.8 Hz, 1H), 2.66-2.54 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 195.19, 136.11, 134.83, 133.10, 131.51, 128.98, 128.81, 128.60, 117.78, 50.83, 35.08. HR-MS (ESI): Calcd for C$_{17}$H$_{17}$OS$^+$ [M+H]$^+$ requires 269.0995; found 269.0998.

![Ethyl 2-(phenylthio)pent-4-enoate (3d)](image)

**Ethyl 2-(phenylthio)pent-4-enoate (3d)**

Following the general procedure, ethyl 2-(allylthio)acetate (0.2 mmol, 0.032 g, 1.0 equiv.) was added and the mixture was stirred at 70 °C for 18 h. The crude product was purified by silica gel chromatography (PE: EA=20:1 as the eluent) to give 3d (51% yield) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.56-7.38 (m, 2H), 7.36-7.16 (m, 3H), 5.81 (ddt, $J$ = 17.0, 10.2, 6.8 Hz, 1H), 5.20-5.04 (m, 2H), 4.14-4.07 (m, 2H), 3.70 (dd, $J$ = 8.7, 6.4 Hz, 1H), 2.70-2.40 (m, 2H), 1.16 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.63, 133.90, 133.16, 133.11, 128.95, 128.04, 118.03, 61.15, 50.27, 35.86, 14.09. HR-MS (ESI): Calcd for C$_{13}$H$_{17}$O$_2$S$^+$ [M+H]$^+$ requires 237.0944; found 237.0958.

![1-Morpholino-2-(phenylthio)pent-4-en-1-one (3e)](image)

**1-Morpholino-2-(phenylthio)pent-4-en-1-one (3e)**
Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=5:1 as the eluent) to give 3e (72% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.53-7.40 (m, 2H), 7.36-7.29 (m, 3H), 5.88-5.75 (m, 1H), 5.10 (dd, $J = 22.5$, 5.4 Hz, 2H), 3.86 (dd, $J = 8.5$, 6.1 Hz, 1H), 3.77-3.35 (m, 8H), 2.87-2.42 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 169.00, 134.89, 134.11, 132.31, 129.09, 128.60, 117.72, 66.88, 66.51, 46.69, 46.39, 42.47, 36.36. HR-MS (ESI): Calcd for C$_{15}$H$_{20}$NO$_2$S$^+$ [M+H]$^+$ requires 278.1209; found 278.1219.

![2-(Phenylthio)pent-4-enenitrile (3f)](image)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=20:1 as the eluent) to give 3f (84% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.66-7.57 (m, 2H), 7.44-7.35 (m, 3H), 5.96-5.79 (m, 1H), 5.24 (dd, $J = 8.5$, 6.7 Hz, 2H), 3.73 (t, $J = 7.3$ Hz, 1H), 2.61-2.55 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 134.70, 131.83, 130.48, 129.64, 129.52, 120.02, 118.79, 36.91, 36.62. HR-MS (ESI): Calcd for C$_{11}$H$_{12}$NS$^+$ [M+H]$^+$ requires 190.0685; found 190.0685.

![Diethyl (1-(phenylthio)but-3-en-1-yl)phosphonate (3g)](image)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=5:1 as the eluent) to give 3g (81% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.53 (m, 2H), 7.33-7.26 (m, 3H), 5.98 (ddt, $J = 17.0$, 10.1, 6.8 Hz, 1H), 5.20-5.11 (m, 2H), 4.17 (ddd, $J = 22.0$, 14.5, 7.2 Hz, 2H).
4H), 3.19 (ddd, \( J = 16.3, 9.3, 4.6 \) Hz, 1H), 2.78 (ddd, \( J = 19.8, 14.3, 5.6 \) Hz, 1H), 2.50 (td, \( J = 16.3, 9.3 \) Hz, 1H), 1.31 (td, \( J = 7.0, 1.8 \) Hz, 6H). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \( \delta \) 24.87. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 134.86, 134.82, 134.59, 134.47, 131.99, 128.93, 127.45, 117.84, 63.08, 63.01, 62.76, 62.69, 45.39, 43.92, 34.44, 16.49, 16.44, 16.39. HR-MS (ESI): Calcd for \( \text{C}_{14}\text{H}_{22}\text{O}_{3}\text{PS}^+ \) [M+H]\(^+\) requires 301.1022; found 301.1014.

![Structure of 2-(1-(Phenylthio)but-3-en-1-yl)benzo[d]oxazole (3h)](image)

**2-(1-(Phenylthio)but-3-en-1-yl)benzo[d]oxazole (3h)**

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give 3h (86% yield) as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.70-7.62 (m, 1H), 7.52-7.46 (m, 1H), 7.40-7.34 (m, 2H), 7.33-7.28 (m, 2H), 7.27-7.23 (m, 3H), 5.86 (ddt, \( J = 17.0, 10.1, 6.8 \) Hz, 1H), 5.11 (dd, \( J = 28.7, 13.6 \) Hz, 2H), 4.51-4.36 (m, 1H), 2.90 (ddt, \( J = 27.9, 14.2, 7.2 \) Hz, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 165.50, 150.74, 140.94, 133.72, 133.38, 132.55, 129.03, 128.28, 125.06, 124.36, 120.08, 118.44, 110.61, 46.14, 37.07. HR-MS (ESI): Calcd for \( \text{C}_{17}\text{H}_{16}\text{NOS}^+ \) [M+H]\(^+\) requires 282.0947; found 282.0940.

![Structure of Ethyl 4-bromo-2-(phenylthio)pent-4-enoate (3i)](image)

**Ethyl 4-bromo-2-(phenylthio)pent-4-enoate (3i)**

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give 3i (94% yield) as a yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.49 (m, 2H), 7.32 (m, 3H), 5.68 (s, 1H), 5.52 (d, \( J = 1.7 \) Hz, 1H), 4.12 (q, \( J = 7.1 \), 2H), 3.98 (dd, \( J = 8.4, 6.7 \) Hz, 1H), 2.91
(ddd, $J = 21.0, 14.6, 7.3$ Hz, 2H), 1.18 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 170.97, 133.61, 132.39, 129.16, 129.03, 128.44, 120.16, 61.39, 48.76, 43.18, 14.04. HR-MS (ESI): Calcd for C$_{13}$H$_{16}$BrO$_2$S$^+$ [M+H]$^+$ requires 315.0049; found 315.0060.

**Ethyl 4-methyl-2-(phenylthio)pent-4-enoate (3j)**

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give 3j (93% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.50-7.43 (m, 2H), 7.31 (m, 3H), 4.83 (s, 1H), 4.77 (s, 1H), 4.08 (q, $J = 7.1$ Hz, 2H), 3.84 (dd, $J = 9.5, 6.1$ Hz, 1H), 2.63 (dd, $J = 14.6, 9.6$ Hz, 1H), 2.45 (dd, $J = 14.6, 6.0$ Hz, 1H), 1.75 (s, 3H), 1.15 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.85, 141.45, 133.30, 133.03, 128.93, 128.01, 113.21, 61.09, 49.07, 39.72, 22.31, 14.05. HR-MS (ESI): Calcd for C$_{14}$H$_{19}$O$_2$S$^+$ [M+H]$^+$ requires 251.1100; found 251.1105.

**Ethyl 3-phenyl-2-(phenylthio)pent-4-enoate (3k)**

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give 3k (88% yield) as a deep yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53-7.43 (m, 2H), 7.37-7.15 (m, 18 h), 6.13 (ddd, $J = 17.0, 10.1, 8.4$ Hz, 1H), 6.01 (ddd, $J = 17.2, 10.1, 8.3$ Hz, 1H), 5.15 (m, 4H), 4.11-3.96 (m, 4H), 3.83-3.72 (m, 4H), 1.14 (t, $J = 7.1$ Hz, 3H), 0.86 (t, $J = 7.1$ Hz, 3H).
Hz, 4H). $^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.32, 170.88, 140.79, 139.85, 138.00, 137.90, 133.58, 133.54, 133.23, 133.17, 128.95, 128.79, 128.63, 128.59, 128.30, 127.99, 127.95, 127.23, 127.15, 117.69, 117.06, 61.12, 60.85, 56.44, 56.05, 52.00, 51.70, 14.07, 13.73. HR-MS (ESI): Calcd for C$_{19}$H$_{21}$O$_2$S$^+$ [M+H]$^+$ requires 313.1257; found 313.1260.

![Ethyl 3,3-dimethyl-2-(phenylthio)pent-4-enoate (3l)](image)

**Ethyl 3,3-dimethyl-2-(phenylthio)pent-4-enoate (3l)**

Following the general procedure at 70 °C for 48 h, the mixture was stirred for 48 h and the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give 3l (83% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.44 (m, 2H), 7.33-7.14 (m, 3H), 6.03 (dd, $J$ = 17.4, 10.7 Hz, 1H), 5.13-5.04 (m, 2H), 4.10 (m, 2H), 3.58 (s, 1H), 2.17 (s, 1H), 1.28 (s, 3H), 1.26 (s, 3H), 1.16 (t, $J$ = 7.1 Hz, 3H). $^1$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.72, 144.09, 135.29, 131.94, 128.98, 127.38, 113.17, 62.20, 60.81, 40.01, 25.35, 24.37, 14.13. HR-MS (ESI): Calcd for C$_{15}$H$_{21}$O$_2$S$^+$ [M+H]$^+$ requires 265.1257; found 265.1255.

![2-Allyl-2-(phenylthio)cyclohexan-1-one (3m)](image)

**2-Allyl-2-(phenylthio)cyclohexan-1-one (3m)**

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give 3m (43% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38-7.27 (m, 5H), 5.85 (ddt, $J$ = 17.2, 10.2, 7.1 Hz, 1H), 5.07 (dd, $J$ = 21.7, 13.6 Hz, 2H), 3.37 (td, $J$ = 14.3, 5.8 Hz, 1H), 2.34 (m, 1H), 2.35-1.53 (m, 8H). $^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 207.15, 136.28,
3-Allyl-3-(phenylthio)dihydrofuran-2(3H)-one (3n)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give 3n (81% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.56 (d, $J$ = 7.4 Hz, 2H), 7.43 (t, $J$ = 7.3 Hz, 1H), 7.36 (t, $J$ = 7.5 Hz, 2H), 5.80 (ddt, $J$ = 17.3, 10.2, 7.1 Hz, 1H), 5.22 - 5.13 (m, 2H), 4.26-4.19 (m, 2H), 2.59-2.52 (m, 2H), 2.50 (m, 1H), 2.19 (ddd, $J$ = 13.9, 5.2, 3.1 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 175.56, 137.27, 132.15, 130.17, 129.05, 120.14, 65.05, 52.95, 39.44, 33.48. HR-MS (ESI): Calcd for C$_{13}$H$_{15}$O$_2$S$^+$ [M+H]$^+$ requires 235.0787; found 235.0786.

(1,1-Diphenylbut-3-en-1-yl)(phenyl)sulfane (3o)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE as the eluent) to give 3o (33% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.45-7.01 (m, 15H), 5.65 (dt, $J$ = 13.8, 9.8 Hz, 1H), 4.75 (dd, $J$ = 43.8, 13.4 Hz, 2H), 4.44-4.10 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 137.26, 135.26, 133.51, 132.10, 131.25, 128.61, 128.53, 128.50, 128.39, 128.35, 128.14, 127.75, 127.50, 127.34, 126.78, 126.63, 126.58, 125.85, 116.46, 57.19, 55.92. HR-MS (ESI): Calcd for C$_{22}$H$_{21}$S$^+$ [M+H]$^+$ requires 317.1358; found 317.1360.
5-(Hexa-1,5-dien-3-ylthio)benzo[d][1,3]dioxole (4a)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=20:1 as the eluent) to give 4a (73% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.99-6.88 (m, 2H), 6.76 (d, $J$ = 7.9 Hz, 1H), 5.98 (s, 2H), 5.85 (ddt, $J$ = 17.2, 10.3, 6.9 Hz, 1H), 5.71 (ddd, $J$ = 17.1, 9.9, 9.0 Hz, 1H), 5.12 (dd, $J$ = 13.1, 5.6 Hz, 2H), 4.93 (dd, $J$ = 51.4, 13.6 Hz, 2H), 3.51 (dd, $J$ = 14.6, 8.3 Hz, 1H), 2.54-2.35 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 147.74, 147.65, 138.19, 135.12, 128.70, 125.96, 117.10, 115.93, 114.72, 108.45, 101.31, 53.03, 38.37. HR-MS (ESI): Calcd for C$_{13}$H$_{15}$O$_2$S$^+$ [M+H]$^+$ requires 235.0787; found 235.0786.

(3,4-Dimethylphenyl)(hexa-1,5-dien-3-yl)sulfane (4b)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give 4b (78% yield) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.21-6.99 (m, 3H), 5.83 (ddt, $J$ = 17.1, 10.2, 6.9 Hz, 1H), 5.70 (ddd, $J$ = 17.0, 10.1, 8.8 Hz, 1H), 5.12-5.03 (m, 2H), 4.93 (dd, $J$ = 30.9, 13.6 Hz, 2H), 3.58 (dd, $J$ = 14.4, 8.2 Hz, 1H), 2.51-2.39 (m, 2H), 2.22 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.30, 137.04, 136.06, 135.23, 134.56, 130.87, 130.74, 129.98, 117.04, 115.80, 51.94, 38.59, 19.66, 19.44. HR-MS (ESI): Calcd for C$_{14}$H$_{19}$S$^+$ [M+H]$^+$ requires 219.1202; found 219.1207.
2-(Benzo[d][1,3]dioxol-5-ythio)-1-morpholinopent-4-en-1-one (4c)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give 4c (69% yield) as a colorless oil. 1H NMR (400 MHz, CDCl3) δ 7.01 (dd, J = 8.0, 1.7 Hz, 1H), 6.96 (d, J = 1.6 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 6.00 (s, 2H), 5.17-5.02 (m, 2H), 3.80-3.72 (m, 1H), 3.70-3.41 (m, 8H), 2.79 -2.41 (m, 2H). 13C NMR (100 MHz, CDCl3) δ 167.93, 147.76, 146.90, 133.96, 128.75, 122.40, 116.61, 114.32, 107.68, 100.54, 65.92, 65.54, 46.05, 45.36, 41.40, 34.99, 28.67. HR-MS (ESI): Calcd for C16H20NO4S+ [M+H]+ requires 322.1108; found 322.1116.

2-(1-((3,4-Dimethylphenyl)thio)but-3-en-1-yl)benzo[d]oxazole (4d)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give 4d (65% yield) as a colorless oil. 1H NMR (400 MHz, CDCl3) δ 7.60-7.53 (m, 1H), 7.42 (ddd, J = 4.2, 2.1, 0.5 Hz, 1H), 7.27-7.19 (m, 2H), 7.00 (d, J = 4.9 Hz, 2H), 6.95-6.88 (m, 1H), 5.78 (ddt, J = 17.0, 10.2, 6.8 Hz, 1H), 5.10-4.95 (m, 2H), 4.32-4.26 (m, 1H), 2.91-2.67 (m, 2H), 2.11 (s, 3H), 2.03 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 164.62, 149.68, 139.95, 136.37, 134.33, 132.91, 130.63, 129.22, 127.57, 123.92, 123.24, 118.97, 117.19, 109.52, 45.43, 35.91, 18.47, 18.44. HR-MS (ESI): Calcd for C18H20NOS+ [M+H]+ requires 298.1260; found 298.1260.
**Hexa-1,5-dien-3-yl(p-tolyl)sulfane (4e) and hexa-1,5-dien-3-yl(m-tolyl)sulfane (4e’)**

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give 4e and 4e’ (4e:4e’=1.3:1, 92% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (t, $J = 5.9$ Hz, 2.3H), 7.22 (t, $J = 7.9$ Hz, 1H), 6.99 (dd, $J = 11.5$, 4.9 Hz, 2.3H), 6.86 (t, $J = 5.8$ Hz, 2.6H), 6.80 (dd, $J = 8.1$, 2.2 Hz, 1H), 5.91-5.81 (m, 2.3H), 5.73 (ddd, $J = 18.6$, 9.6, 5.1 Hz, 2.3H), 5.15-5.09 (m, 4.6H), 5.05-4.92 (m, 3.3H), 4.82 (d, $J = 17.0$ Hz, 1.3H), 3.82 (s, 3.9H), 3.82 (s, 3H), 3.71 (dd, $J = 14.4$, 8.0 Hz, 1H), 3.50 (dd, $J = 14.6$, 8.2 Hz, 1.3H), 2.45 (ddt, $J = 16.0$, 14.7, 7.1 Hz, 4.6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.31, 138.15, 136.27, 135.25, 134.96, 129.47, 124.64, 124.40, 117.61, 117.26, 117.00, 116.11, 115.76, 114.25, 112.97, 55.28, 52.93, 51.46, 38.62, 38.40. HR-MS (ESI): Calcd for C$_{13}$H$_{17}$S$^+$ [M+H]$^+$ requires 205.1045; found 205.1049.

**Hexa-1,5-dien-3-yl(4-methoxyphenyl)sulfane (4f) and hexa-1,5-dien-3-yl(3-methoxyphenyl)sulfane (4f’)**

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give 4f and 4f’ (4f:4f’=1.3:1, 75% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (d, $J = 8.8$ Hz, 2.6H), 7.22 (t, $J = 8.0$ Hz, 1H), 7.04-6.93 (m, 2H), 6.88-6.82 (m, 2.6H), 6.82-6.75 (m, 1H), 5.94-5.80 (m, 2.3H), 5.78-5.63 (m, 2.3H), 5.18-5.07 (m, 4.6H), 5.05-4.77 (m, 4.6H), 3.82 (s, 3.9H), 3.82 (s, 3H), 3.71 (dd, $J = 14.4$, 8.1 Hz, 1H), 3.50 (dd, $J = 14.6$, 8.3 Hz, 1.3H), 2.55-2.34 (m, 4.6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$

(4-Fluorophenyl)(hexa-1,5-dien-3-yl)sulfane (4g) and (3-fluorophenyl)(hexa-1,5-dien-3-yl)sulfane (4g’)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give 4g and 4g’ (4g:4g’=2.4:1, 86% yield) as a colorless oil. ^1H NMR (400 MHz, CDCl3) δ 7.43-7.35 (m, 4.4H), 7.25-7.20 (m, 1H), 7.10 (ddd, J = 10.9, 9.3, 4.7 Hz, 2.4H), 7.03-6.94 (m, 4.8H), 6.91 (td, J = 8.3, 1.7 Hz, 1H), 5.89-5.77 (m, 3.4H), 5.74-5.59 (m, 3.4H), 5.15-5.06 (m, 6.8H), 5.03-4.93 (m, 4.4H), 4.80 (d, J = 17.0 Hz, 2.4H), 3.68 (dd, J = 14.7, 7.9 Hz, 1H), 3.52 (dd, J = 14.7, 8.1 Hz, 2.4H), 2.49-2.33 (m, 6.8H). ^19F NMR (376 MHz, CDCl3) δ -112.66, -113.97. ^13C NMR (100 MHz, CDCl3) δ 163.76, 161.30, 138.02, 137.79, 136.01, 135.93, 134.91, 134.66, 129.92, 129.83, 129.17, 127.72, 118.89, 118.67, 117.49, 117.26, 116.42, 116.06, 115.89, 115.67, 114.06, 113.85, 52.79, 51.51, 38.55, 38.41. HR-MS (ESI): Calcd for C_{12}H_{14}FS^+ [M+H]^+ requires 209.0795; found 209.0788.

(3-fluorophenyl)(hexa-1,5-dien-3-yl)sulfane (4h’)

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE as the eluent) to give 4h and 4h’ (4h:4h’=1:1, 71% yield)
as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.52 (d, $J = 8.4$ Hz, 1H), 7.91-7.81 (m, 2H), 7.80-7.70 (m, 4H), 7.66 (dd, $J = 7.1$, 0.8 Hz, 1H), 7.58-7.36 (m, 6H), 5.95-5.79 (m, 2H), 5.72 (dd, $J = 18.4$, 9.7, 5.2 Hz, 2H), 5.15-5.05 (m, 4H), 5.01-4.65 (m, 4H), 3.77 (dd, $J = 14.5$, 8.1 Hz, 1H), 3.67 (dd, $J = 14.6$, 8.2 Hz, 1H), 2.58-2.40 (m, 4H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 138.07, 138.03, 135.07, 135.00, 134.55, 134.08, 133.62, 133.28, 132.35, 131.95, 131.66, 131.55, 130.18, 128.71, 128.56, 128.18, 127.70, 127.43, 126.54, 126.41, 126.12, 125.88, 125.40, 117.32, 117.27, 116.22, 116.03, 52.14, 51.68, 38.90, 38.67. HR-MS (ESI): Calcd for C$_{16}$H$_{17}$S$^+$ [M+H]$^+$ requires 241.1045; found 241.1050.

**Hexa-4,5-dien-1-yn-3-yl(phenyl)sulfane (6a)**

Following the general procedure at 30 °C for 18 h, the crude product was purified by silica gel chromatography (PE as the eluent) to give 6a (75% yield) as a yellow oil. For 1mmol scale reaction, the same procedure was followed. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.60-7.49 (m, 2H), 7.38-7.29 (m, 3H), 5.27 (dd, $J = 13.9$, 6.6 Hz, 1H), 4.78 (dt, $J = 6.4$, 2.1 Hz, 1H), 4.38 (dd, $J = 7.1$, 4.5, 2.2 Hz, 1H), 2.46 (d, $J = 2.4$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 208.65, 134.20, 132.82, 128.76, 128.41, 89.92, 81.13, 78.26, 73.49, 38.29. HR-MS (ESI): Calcd for C$_{12}$H$_{11}$S$^+$ [M+H]$^+$ requires 187.0576; found 187.0566.

**(4-fluorophenyl)(hexa-4,5-dien-1-yn-3-yl)sulfane (6b)** and **(3-fluorophenyl)(hexa-4,5-dien-1-yn-3-yl)sulfane (6b’)**
Following the general procedure at 30 °C for 18 h, the crude product was purified by silica gel chromatography (PE as the eluent) to give 6b and 6b' (6b:6b'=5.5:1, 61% yield) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.51-7.44 (m, 12H), 7.25-7.20 (m, 2H), 7.00-6.92 (m, 12H), 5.22-5.18 (m, 1H), 5.17 (dd, J = 7.3, 6.6 Hz, 5.5H), 4.77 (dd, J = 6.5, 2.3 Hz, 2H), 4.71-4.68 (m, 11H), 4.35 (dq, J = 7.1, 2.3 Hz, 1H), 4.22 (dq, J = 7.1, 2.3 Hz, 5.5H), 2.42 (d, J = 2.4 Hz, 1H), 2.39 (d, J = 2.4 Hz, 5.5H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 208.67, 137.40, 137.32, 115.95, 115.73, 89.83, 80.90, 78.26, 73.76, 38.87. HR-MS (ESI): Calcd for C$_{12}$H$_9$FS$^+$ [M+H]$^+$ requires 204.0409; found 204.0418.

![Ethyl (Z)-2-(phenylthio)penta-2,4-dienoate (6c)](ethylethyl_diienylthiophosphate.png)

**Ethyl (Z)-2-(phenylthio)penta-2,4-dienoate (6c)**

Following the general procedure at 30 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give 6c (56% yield) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.69 (d, J = 10.9 Hz, 1H), 7.27-7.15 (m, 5H), 7.14-7.04 (m, 1H), 5.78 (dd, J = 17.0, 0.7 Hz, 1H), 5.64 (dd, J = 10.1, 1.0 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 1.08 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.60, 147.39, 135.82, 133.29, 128.94, 128.54, 127.66, 126.30, 126.24, 61.64, 13.92. HR-MS (ESI): Calcd for C$_{13}$H$_{15}$O$_2$S$^+$ [M+H]$^+$ requires 235.0787; found 235.0758.

![Hex-5-en-1-yn-3-yl(phenyl)sulfane (6d)](hex-5-en-1-yn-3-yl(phenyl)sulfane.png)

**Hex-5-en-1-yn-3-yl(phenyl)sulfane (6d)**

Following the general procedure at 70 °C for 18 h, the crude product was purified by silica gel chromatography (PE: EA=50:1 as the eluent) to give 6c (80% yield) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.53 (dt, J = 4.3, 2.3 Hz, 1H), 7.37-7.27 (m,
2H), 6.00-5.87 (m, 1H), 5.21-5.10 (m, 1H), 3.82 (ddd, $J = 8.3, 6.1, 2.4$ Hz, 1H),
2.57-2.48 (m, 1H), 2.37 (dd, $J = 2.4$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 133.98,
133.45, 133.00, 128.91, 127.91, 118.09, 83.13, 72.73, 39.16, 38.16. HR-MS (ESI):
Calcd for C$_{12}$H$_{13}$S$^+$ [M+H]$^+$ requires 189.0732; found 188.0760.

IV. Sulfide Oxidation
To demonstrate the synthetic utility of our method, we have further studied the
rearrangement product functionalization. Oxidation reaction of 3a using commercially
available hydrogen peroxide or MCPBA gave the corresponding sulfone product in
moderate yield respectively.

![Sulfone Product](image)

(hexa-1,5-dien-3-ylsulfonyl)benzene (7)

Procedure A:

To a stirred solution of the sulfide 3a (0.019g, 0.1mmol, 1 equiv.) in 1mL
CH$_2$Cl$_2$ was added m-CPBA (0.041g, 0.2mmol, 2 equiv.) at 0°C. The reaction was
kept stirring for 4h at 0 ºC. The reaction was then quenched with saturated NaHCO$_3$
(20 mL), extracted with ethyl acetate (20 mL), washed with saturated NaHCO$_3$ (3×20
mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product
was further purified by silica gel flash chromatography (PE: EA=10:1 as the eluent) to
give 7 (60% yield) as a white solid.
Procedure B:

To a stirred solution of the sulfide 3a (0.019g, 0.1mmol, 1 equiv.) in 1mL ethanol was added H₂O₂ (30% in water, 0.05 mL, 0.5mmol, 5.0 equiv.) at room temperature. The reaction was stirred for 24h and then concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA=10:1 as the eluent) to give 7 (61% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.91-7.80 (m, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 5.72-5.57 (m, 1H), 5.33-4.98 (m, 2H), 3.57 (td, J = 10.3, 3.5 Hz, 1H), 2.94-2.39 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 137.21, 133.72, 132.90, 129.85, 129.29, 128.85, 123.83, 118.44, 69.30, 31.59. HR-MS (ESI): Calcd for C₁₂H₁₃O₂S⁺ [M+H]⁺ requires 221.0631; found 221.0656.
V. Spectrum