Supporting Information

Highly regio- and stereoselective hydrothiolation of acetylenes with thiols catalyzed by a well-defined supported Rh complex

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1 General information

Unless otherwise noted, all chemicals were purchased from commercial sources and used as received without further purification. Analytical thin-layer chromatography (TLC) was performed on silica gel plates and compounds were visualized by irradiation with UV light. Flash chromatography was carried out utilizing 200-300 mesh silica gel.

2 Catalyst Preparation

SBA-15 was synthesized according to a published procedure. Preparation of the supported rhodium complex on SBA-15 was performed under a nitrogen atmosphere in a step-by-step manner, as shown in Scheme S1.

2.1 Preparation of Cl-SBA-15

The as-prepared SBA-15 silica (2.0 g) was calcined at 473 K for 6 h under vacuum, and then refluxed in an anhydrous toluene solution of 3-chloropropyltriethoxysilane (5.33 mL) at 383 K for 24 h under a N₂ atmosphere. The SBA-15 was filtrated by Soxhlet extraction with anhydrous dichloromethane and then dried under vacuum for 24 h. The solid powder was labeled as Cl-SBA-15 and stored under a N₂ atmosphere.

2.2 Preparation of N-SBA-15

The as-prepared SBA-15 silica (1.0 g) was calcined at 473 K for 6 h under vacuum, and then refluxed in an anhydrous toluene solution of 3-amino-propyltriethoxysilane (1.0 mL) at 383 K for 24 h under a N₂ atmosphere. The SBA-15 was filtrated by Soxhlet extraction with anhydrous

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dichloromethane and then dried under vacuum for 24 h. The solid powder was labeled as N-SBA-15 and stored under a N\textsubscript{2} atmosphere.

### 2.3 Preparation of 2N-SBA-15

The as-prepared SBA-15 silica (1.0 g) was calcined at 473 K for 6 h under vacuum, and then refluxed in an anhydrous toluene solution of [3-(2-aminoethylamino)-propyl]triethoxysilane (1.0 mL) at 383 K for 24 h under a N\textsubscript{2} atmosphere. The SBA-15 was filtrated by Soxhlet extraction with anhydrous dichloromethane and then dried under vacuum for 24 h. The solid powder was labeled as 2N-SBA-15 and stored under a N\textsubscript{2} atmosphere.

### 2.4 Preparation of P-SBA-15

A THF solution of lithium diphenylphosphide (16 mL, 0.5 M) was added to a solid sample of Cl-SBA-15 (1.5 g) under a N\textsubscript{2} atmosphere. The resulting mixture was stirred at room temperature for 20 h. The solid was filtrated by Soxhlet extraction with anhydrous dichloromethane and then dried under vacuum for 24 h. The solid powder was labeled as P-SBA-15 and stored under a N\textsubscript{2} atmosphere.

### 2.5 Preparation of Rh-N-SBA-15

An anhydrous toluene solution of Wilkinson complex RhCl(PPh\textsubscript{3})\textsubscript{3} (0.10 g, 0.11 mmol) was added to N-SBA-15 (1.0 g) under a N\textsubscript{2} atmosphere. The resulting mixture was refluxed for 3 h. The solid was filtrated by Soxhlet extraction with anhydrous toluene and then dried under vacuum for 24 h. The solid powder was labeled as Rh-N-SBA-15 and stored under a N\textsubscript{2} atmosphere.

### 2.6 Preparation of Rh-2N-SBA-15

An anhydrous toluene solution of Wilkinson complex RhCl(PPh\textsubscript{3})\textsubscript{3} (0.10 g, 0.11 mmol) was added to 2N-SBA-15 (1.0 g) under a N\textsubscript{2} atmosphere. The resulting mixture was refluxed for 3 h.

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The solid was filtrated by Soxhlet extraction with anhydrous toluene and then dried under vacuum for 24 h. The solid powder was labeled as Rh-2N-SBA-15 and stored under a N2 atmosphere.

2.7 Preparation of Rh-P-SBA-15

An anhydrous dichloromethane solution of Wilkinson complex RhCl(PPh3)3 (0.15 g, 0.16 mmol) was added to P-SBA-15 (1.5 g) under a N2 atmosphere. The resulting mixture was stirred at room temperature for 2 days. The solid was filtrated by Soxhlet extraction with anhydrous dichloromethane and then dried under vacuum for 24 h. The solid powder was labeled as Rh-P-SBA-15 and stored under a N2 atmosphere.

3 Catalytic hydrothiolation reaction

In a typical catalytic reaction, a given amount of supported catalyst and 1,2-dichloroethane were combined in a 10 mL Schlenk tube equipped with a magnetic stir bar. Alkyne (0.5 mmol), and thiol (0.55 mmol) were then added under a N2 atmosphere. The progress of the reaction was monitored by 1H NMR. The catalyst was separated by centrifugation after reaction, the solvent was removed and the resulting mixture was purified by column chromatography with hexane/ethyl acetate to afford the pure product. The compound was structurally confirmed by 1H NMR, 13C NMR, and high resolution mass spectrometry (HR-MS).

4 Characterization

4.1 NMR characterization

1H NMR, 13C NMR spectra were performed on a Bruker Advance 300 or 400 NMR spectrometer. The spectra were recorded in CDCl3 as solvent at room temperature, 1H and 13C NMR chemical shifts are reported in ppm relative to either the residual solvent peak (13C) (δ = 77.00 ppm) or...
TMS ($^1$H) ($\delta = 0.0$ ppm) as an internal standard. Data for $^1$H NMR are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. Regioselectivity and stereoselectivity of the product was determined by NMR analysis of the crude product.

4.2 HR-MS

High resolution mass spectral analysis (HR-MS) was performed on Waters LCT Classic TOF Mass Spectrometer.

4.3 Physical Adsorption characterization

Nitrogen adsorption was performed on a Micromeritics ASAP-2020 analyzer at 77 K. Each sample (150 mg) was degassed at 473 K for 3 h before an adsorption measurement.

4.4 Solid-state NMR characterization

$^{13}$C, $^{29}$Si and $^{31}$P solid-state MAS NMR spectra (MAS rate: 5 kHz) were recorded with a Chemagnetics Bruker AV-300 spectrometer operating at 75.5, 59.7, and 121.6 MHz, respectively. $^{13}$C MAS NMR spectra with cross polarization (CP) were acquired with the contact time of 3.0 ms. A cross polarization detection method with hydrogen decoupling was used in $^{29}$Si NMR measurements, using contact time of 4.0 s. The rotor spin rate was 5 kHz, with the delay time of 5 s ($^{13}$C) or 4 s ($^{29}$Si). Hexamethylbenzene ($^{13}$C: 17.4 and 132.2 ppm), Tetrakis-silane ($^{29}$Si: -9.7 and -135.2 ppm) and H$_3$PO$_4$ were used as external standards for the calibration of chemical shifts.

4.5 XRD characterization

The low-angle powder XRD patterns were recorded at room temperature on an X’Pert PRO X-ray diffractometer with Cu-K\(\alpha\) radiation at 45 kV and 40 mA. The $2\theta$ angles were scanned from $0.5^\circ$ to $8^\circ$ at a rate of 1°/min.

4.6 HRTEM characterization
High resolution transmission electron microscopy (HRTEM) was performed on a JEOL JEM-2010F operating at an accelerating voltage of 200 kV. The sample was dispersed with dry ethanol and supported on holey carbon-coated Cu grids.

4.7 ICP-AES characterization

The Rh loading and leaching content were detected on Perkin-Elmer-Optima 5300, Inductively Coupled Plasma Emission Spectrometry (ICP-AES). A 40% hydrofluoric acid solution was used to dissolve the sample.
5. Schemes / Table / Figures captions

Scheme S1  Preparation of immobilized Rh-P-SBA-15 catalyst.

Table S1  Structural and textual properties of mesoporous silica samples

Figure S1  (A) N\textsubscript{2} adsorption-desorption isotherms and (B) pore diameter distribution of (a) SBA-15; (b) Cl-SBA-15; (c) P-SBA-15; and (d) Rh-P-SBA-15.

Figure S2  Low-angle XRD pattern of (a) SBA-15; (b) P-SBA-15; and (c) Rh-P-SBA-15.

Figure S3  High resolution TEM image of (A) SBA-15 and (B) Rh-P-SBA-15.

Figure S4  \textsuperscript{29}Si solid state NMR spectra of (a) Cl-SBA-15; (b) P-SBA-15; and (c) Rh-P-SBA-15.

Figure S5  \textsuperscript{31}P solid-state NMR spectra of (a) P-SBA-15; and (b) Rh-P-SBA-15.

Figure S6  Effect of removal of the Rh-P-SBA-15 catalyst on the hydrothiolation of thiophenol with phenylacetylene with and without removal of Rh-P-SBA-15 catalyst.

Figure S7  Demonstration of the recyclability of Rh-P-SBA-15 for hydrothiolation of phenylacetylene and thiophenol.
Scheme S1 Preparation of immobilized Rh-P-SBA-15 catalyst.
Table S1  Structural and textual properties of samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rh loading (wt%)</th>
<th>d\textsubscript{100} (Å)\textsuperscript{a}</th>
<th>a\textsubscript{0} (Å)\textsuperscript{b}</th>
<th>Wall thickness (Å)\textsuperscript{c}</th>
<th>S\textsubscript{BET} (m\textsuperscript{2} g\textsuperscript{-1})\textsuperscript{d}</th>
<th>D\textsubscript{BJH} (Å)\textsuperscript{e}</th>
<th>V\textsubscript{u} (cm\textsuperscript{3} g\textsuperscript{-1})\textsuperscript{f}</th>
<th>V\textsubscript{p} (cm\textsuperscript{3} g\textsuperscript{-1})\textsuperscript{g}</th>
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<tr>
<td>SBA-15</td>
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<td>51.1</td>
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<tr>
<td>P-SBA-15</td>
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<td>109.5</td>
<td>53.5</td>
<td>445</td>
<td>56</td>
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<td>Rh-P-SBA-15</td>
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<td>95.7</td>
<td>110.5</td>
<td>52.5</td>
<td>315</td>
<td>58</td>
<td>0.007</td>
<td>0.43</td>
</tr>
</tbody>
</table>

\(\textsuperscript{a}\) XRD (100) interplaner spacing, \(\lambda = 2d\textsubscript{100}\sin\theta\).

\(\textsuperscript{b}\) Hexagonal unit cell parameter, \(a\textsubscript{0} = \lambda / 2 \sin\theta\).

\(\textsuperscript{c}\) Size of wall thickness, wall thickness = \(a\textsubscript{0} - D\textsubscript{BJH}\).

\(\textsuperscript{d}\) BET specific surface area.

\(\textsuperscript{e}\) Mean pore diameter.

\(\textsuperscript{f}\) Micropore volume.

\(\textsuperscript{g}\) Total pore volume.
Figure S1. (A) N₂ adsorption-desorption isotherms and (B) pore diameter distribution of samples: (a) SBA-15; (b) Cl-SBA-15; (c) P-SBA-15; and (d) Rh-P-SBA-15.
Figure S2. Low-angle XRD pattern of (a) SBA-15; (b) P-SBA-15; and (c) Rh-P-SBA-15.
**Figure S3.** High resolution TEM image of (A) SBA-15 and (B) Rh-P-SBA-15.
**Figure S4.** $^{29}$Si solid state NMR spectra of (a) Cl-SBA-15; (b) P-SBA-15; and (c) Rh-P-SBA-15. The peaks at $\delta = -58$ and -68 ppm in the $^{29}$Si solid-state NMR spectrum are assignable to $T^2$ and $T^3$ organosilica species, respectively, confirming a condensation reaction between the surface silanol groups of SBA-15 and the ethoxy group of propyltriethoxysilane moiety in the linker to form the covalent Si-O-Si linkage occurred.
Figure S5. $^{31}$P solid-state NMR spectra of (a) P-SBA-15 and (b) Rh-P-SBA-15. Asterisks denote spinning sidebands.
**Figure S6.** Effect of removal of the Rh-P-SBA-15 catalyst on the hydrothiolation of thiophenol with phenylacetylene (□) without removal of Rh-P-SBA-15 catalyst and (●) after removal of Rh-P-SBA-15. The arrow indicates the time when the Rh-P-SBA-15 catalyst was removed from the Schlenk tube. Reaction conditions: 0.5 mmol phenylacetylene, 0.55 mmol thiophenol, 50 mg catalyst (4.5 µmol Rh), 2 mL DCE, and room temperature.
Figure S7. Demonstration of the recyclability of Rh-P-SBA-15 for the hydrothiolation of phenylacetylene and thiophenol; (○) conversion and (●) regioselectivity to \((E)\)-isomer vinyl sulfide. Reaction conditions: 0.5 mmol phenylacetylene, 0.55 mmol thiophenol, 50 mg catalyst (4.5 µmol Rh), 2 mL DCE, and room temperature.
6. $^1$H / $^{13}$C NMR and HR-MS Data for vinyl sulfides

\[
\begin{align*}
\text{Purified by column chromatography using SiO}_2 \text{ gel with hexane/EtOAc (10/1, v/v) as an eluent, colorless liquid; } & \text{ }^1\text{H NMR (300 MHz, CDCl}_3\text{): } 6.79 \text{ (d, 1H), 6.94 (d, 1H),} \\
& 7.29-7.46 \text{ (m, 10H). } ^{13}\text{C NMR (75 MHz, CDCl}_3\text{): } 123.4, 126.1, 127.0, 127.6, 128.7, 129.2, \\
& 129.9, 131.9, 135.3, 136.6. \text{ HR-MS (ESI): theoretical, C}_{14}\text{H}_{12}\text{S, 212.0660, found 212.0338.}
\end{align*}
\]

\[
\begin{align*}
\text{Purified by column chromatography using SiO}_2 \text{ gel with hexane/EtOAc (10/1, v/v) as an eluent, white solid; } & \text{ }^1\text{H NMR (300 MHz, CDCl}_3\text{): } 2.42 \text{ (s, 3H), 6.87 (d, 1H),} \\
& 7.06 \text{ (d, 1H), 7.23-7.43 (m, 9H). } ^{13}\text{C NMR (75 MHz, CDCl}_3\text{): } 21.3, 122.1, 126.0, 126.8, 129.1, \\
& 129.4, 129.6, 132.4, 133.8, 135.6, 136.6. \text{ HR-MS (ESI): theoretical, C}_{15}\text{H}_{14}\text{S, 226.0813, found 226.0319.}
\end{align*}
\]

\[
\begin{align*}
\text{Purified by column chromatography using SiO}_2 \text{ gel with hexane/EtOAc (10/1, v/v) as an eluent, yellow liquid; } & \text{ }^1\text{H NMR (300 MHz, CDCl}_3\text{): } 2.38 \text{ (s, 3H), 6.78 (d, 1H),} \\
& 6.86 \text{ (d, 1H), 7.16-7.46 (m, 9H). } ^{13}\text{C NMR (75 MHz, CDCl}_3\text{): } 20.3, 124.7, 125.8, 126.7, 127.5 \\
& (d), 128.0 \text{ (d), 129.6, 130.0, 130.5 \text{ (d), 130.9, 136.2 (d). HR-MS (ESI): theoretical, C}_{15}\text{H}_{14}\text{S,} \\
& 226.0813, \text{ found 226.0809.}
\end{align*}
\]

\[
\begin{align*}
\text{Purified by column chromatography using SiO}_2 \text{ gel with hexane/EtOAc (10/1, v/v) as an eluent, yellow liquid; } & \text{ }^1\text{H NMR (300 MHz, CDCl}_3\text{): } 2.39 \text{ (s, 3H), 6.77 (d, 1H),}
\end{align*}
\]
6.93 (d, 1H), 7.10-7.34 (m, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$): 21.9, 123.6 (d), 127.3 (d), 127.8 (d), 128.9, 129.6 (d), 130.2, 132.6, 135.9, 136.9, 138.7. HR-MS (ESI): theoretical, C$_{15}$H$_{14}$S, 226.0813, found 226.0319.

Purified by column chromatography using SiO$_2$ gel with hexane/EtOAc (10/1, v/v) as an eluent, white solid, $^1$H NMR (300 MHz, CDCl$_3$): 3.85 (s, 3H), 6.77 (d, 1H), 6.90 (d, 1H), 7.25-7.36 (m, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$): 55.8, 114.6, 120.5, 127.0, 127.8, 129.5, 129.6 (d), 129.8, 133.2, 136.4, 159.8. HR-MS (ESI): theoretical, C$_{15}$H$_{14}$SO, 242.0765, found 242.0278.

Purified by column chromatography using SiO$_2$ gel with hexane/EtOAc (18/1, v/v) as an eluent, colorless liquid, $^1$H NMR (300 MHz, CDCl$_3$): 3.88 (s, 3H), 6.95 (d, 1H), 7.06 (d, 1H), 7.26-7.46 (m, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$): 55.9, 111.3, 121.1, 124.2, 126.5 (d), 127.5 (d), 129.4 (d), 130.3, 136.4, 156.9. HR-MS (ESI): theoretical, C$_{15}$H$_{14}$SO, 242.0765, found 242.0795.

Purified by column chromatography using SiO$_2$ gel with hexane/EtOAc (10/1, v/v) as an eluent, colorless liquid, $^1$H NMR (300 MHz, CDCl$_3$): 6.73 (d, 1H), 6.84 (d, 1H), 7.03 (t, 2H), 7.28-7.37 (m, 7H). $^{13}$C NMR (75 MHz, CDCl$_3$): 115.9 (d), 123.6, 127.5, 129.5 (d), 130.3, 131.0, 133.2, 135.5, 136.6, 145.8. HR-MS (ESI): theoretical, C$_{14}$H$_{11}$FS, 230.0565, found 230.0488.
: Purified by column chromatography using SiO$_2$ gel with hexane/EtOAc (10/1, v/v) as an eluent, white solid, $^1$H NMR (300 MHz, CDCl$_3$): 6.65 (d, 1H), 6.93 (d, 1H), 7.23 (d, 2H), 7.29-7.47 (m, 7H). $^{13}$C NMR (75 MHz, CDCl$_3$): 123.4, 126.1, 127.0, 127.6, 128.7, 129.2, 129.9, 131.9, 135.3, 136.6. HR-MS (ESI): theoretical, C$_{14}$H$_{11}$BrS, 289.9765, found 289.9229.

: Purified by column chromatography using SiO$_2$ gel with hexane/EtOAc (18/1, v/v) as an eluent, colorless liquid, $^1$H NMR (300 MHz, CDCl$_3$): 0.93 (t, 3H), 1.32-1.48 (m, 4H), 1.92 (d, 2H), 2.19 (q, 2H), 6.04 (d, 1H), 6.16 (d, 1H), 7.21-7.37 (m, 5H). $^{13}$C NMR (75 MHz, CDCl$_3$): 14.5, 22.9, 29.1, 31.9, 33.5, 121.1, 126.5, 127.9, 128.9, 129.2, 130.3, 134.2. HR-MS (ESI): theoretical, C$_{13}$H$_{18}$S, 206.1129, found 206.1108.

: Purified by column chromatography using SiO$_2$ gel with hexane/EtOAc (10/1, v/v) as an eluent, colorless liquid, $^1$H NMR (300 MHz, CDCl$_3$): 0.91 (t, 3H), 1.30-1.49 (m, 14H), 1.51 (br, 2H), 2.21 (t, 2H), 5.96 (td, 1H), 6.17 (td, 1H), 7.22-7.37 (m, 5H). $^{13}$C NMR (75 MHz, CDCl$_3$): 14.2, 22.7, 29.2, 29.4, 29.5, 29.6, 31.9, 33.1, 122.5, 126.0, 126.1, 128.3, 128.7, 133.8, 137.9. HR-MS (ESI): theoretical, C$_{18}$H$_{28}$S, 276.1912, found 276.1513.

: Purified by column chromatography using SiO$_2$ gel with hexane/EtOAc (18/1, v/v) as an eluent, white solid, $^1$H NMR (300 MHz, CDCl$_3$): 6.74 (d, 1H), 6.85 (d, 1H), 7.03 (t, 2H), 7.259-7.37 (m, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$): 123.4, 126.1, 127.0, 127.6, 128.7,
129.2, 129.9, 131.9, 135.3, 136.6. HR-MS (ESI): theoretical, C_{11}H_{14}OS, 194.0765, found 194.0709.

: Purified by column chromatography using SiO_{2} gel with hexane/EtOAc (10/1, v/v) as an eluent, colorless liquid, \(^1\)H NMR (300 MHz, CDCl\(_3\)): 1.97 (quint, 2H), 2.36 (ddt, 2H), 3.58 (t, 2H), 5.93 (dt, 1H), 6.26 (dt, 1H), 7.26-7.41 (m, 5H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): 30.5, 32.1, 44.6, 123.5, 125.8, 127.6, 129.5, 131.4, 133.6. HR-MS (ESI): theoretical, C_{11}H_{13}ClS, 212.0426, found 212.0311.

: Purified by column chromatography using SiO_{2} gel with hexane/EtOAc (10/1, v/v) as an eluent, yellow liquid, \(^1\)H NMR (300 MHz, CDCl\(_3\)): 1.67-1.83 (m, 4H), 2.24 (m, 4H), 5.81 (br, s, 1H), 6.26 (s, 1H), 6.54 (d, 1H), 7.35-7.46 (m, 5H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): 22.8, 3.2, 24.9, 26.3, 118.1, 126.7, 127.7, 129.3, 130.2, 133.0, 135.4, 137.3. HR-MS (ESI): theoretical, C_{14}H_{16}S, 216.0973, found 216.0392.

: Purified by column chromatography using SiO_{2} gel with hexane/EtOAc (10/1, v/v) as an eluent, colorless liquid, \(^1\)H NMR (300 MHz, CDCl\(_3\)): 2.14 (s, 3H), 6.81 (s, 1H), 7.28-7.44 (m, 10H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): 20.1, 126.9, 127.6, 128.7, 129.3, 129.5, 129.7, 131.9, 132.6, 134.3, 136.8. HR-MS (ESI): theoretical, C_{15}H_{14}S, 226.0816, found 226.0513.

: Purified by column chromatography using SiO_{2} gel with hexane/EtOAc (40/1, v/v) as an eluent, colorless liquid; \(^1\)H NMR (300 MHz, CDCl\(_3\)): 1.21 (t, 3H), 2.56 (q, 2H), 6.44 (d,
1H), 7.09 (d, 1H), 7.48-7.44 (m, 5H). $^{13}$C NMR (75 MHz, CDCl$_3$): 25.3, 58.6, 108.6, 126.7, 128.7, 129.1, 131.9, 141.7. HR-MS (ESI): theoretical, C$_{10}$H$_{12}$S, 164.0660, found 164.0662.

![Structure 1](image1.png)

: Purified by column chromatography using SiO$_2$ gel with hexane/EtOAc (40/1, v/v) as an eluent, yellow liquid; $^1$H NMR (300 MHz, CDCl$_3$): 1.21 (t, 3H), 2.56 (q, 2H), 6.44 (d, 1H), 7.09 (d, 1H), 7.48-7.44 (m, 5H). $^{13}$C NMR (75 MHz, CDCl$_3$): 26.5, 33.3, 34.0, 45.8, 123.7, 126.0, 128.3, 128.8, 129.0, 131.9, 133.2. HR-MS (ESI): theoretical, C$_{14}$H$_{18}$S, 218.1129, found 218.1009.

![Structure 2](image2.png)

: Purified by column chromatography using SiO$_2$ gel with hexane/EtOAc (40/1, v/v) as an eluent, colorless liquid; $^1$H NMR (300 MHz, CDCl$_3$): 3.31 (q, 2H), 6.66 (d, 1H), 6.73 (d, 1H), 7.23-7.33 (m, 5H). $^{13}$C NMR (75 MHz, CDCl$_3$): 36.4, 54.6, 126.6, 128.8, 129.2, 131.9, 136.8. HR-MS (ESI): theoretical, C$_{10}$H$_{9}$F$_3$S, 218.1129, found 218.0351.

![Structure 3](image3.png)

: Purified by column chromatography using SiO$_2$ gel with hexane/EtOAc (10/1, v/v) as an eluent, yellow liquid; $^1$H NMR (300 MHz, CDCl$_3$): 2.43 (s, 1H), 6.73 (d, 1H), 6.94 (d, 1H), 7.22-7.43 (m, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$): 21.6, 124.9, 126.4, 127.9, 129.1, 130.5, 130.9, 131.1, 137.1, 137.8. HR-MS (ESI): theoretical, C$_{15}$H$_{14}$S, 226.0816, found 226.0809.
Purified by column chromatography using SiO$_2$ gel with hexane/EtOAc (10/1, v/v) as an eluent, white solid; $^1$H NMR (300 MHz, CDCl$_3$): 3.87 (s, 1H), 6.55 (d, 1H), 6.87 (d, 1H), 6.94 (d, 2H), 7.21-7.30 (m, 8H). $^{13}$C NMR (75 MHz, CDCl$_3$): 55.8, 115.3, 124.9, 126.2, 126.3, 127.6, 129.1, 129.4, 133.9, 137.2. HR-MS (ESI): theoretical, C$_{15}$H$_{14}$O$_2$, 242.0765, found 242.0759.

Purified by column chromatography using SiO$_2$ gel with hexane/EtOAc (10/1, v/v) as an eluent, white solid; $^1$H NMR (300 MHz, CDCl$_3$): 6.78 (d, 1H), 6.89 (d, 1H), 7.30-7.47 (m, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$): 122.9, 126.6, 128.3, 129.2, 129.8, 131.4, 133.2 (d), 134.4, 136.7. HR-MS (ESI): theoretical, C$_{15}$H$_{11}$ClS, 246.0270, found 246.0259.

Purified by column chromatography using SiO$_2$ gel with hexane/EtOAc (10/1, v/v) as an eluent, pale yellow solid; $^1$H NMR (300 MHz, CDCl$_3$): 6.83 (d, 1H), 6.89 (d, 1H), 7.31-7.50 (m, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$): 121.3, 122.6, 126.5, 128.3, 131.5, 132.6, 133.4, 135.0, 136.6. HR-MS (ESI): theoretical, C$_{15}$H$_{11}$BrS, 289.9765, found 289.9682.

Purified by column chromatography using SiO$_2$ gel with hexane/EtOAc (10/1, v/v) as an eluent, white solid; $^1$H NMR (300 MHz, CDCl$_3$): 4.08 (s, 2H), 6.61 (d, 1H), 6.80
(d, 1H), 7.29-7.43 (m, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$): 37.8, 124.8, 126.1, 127.5, 127.8, 128.4, 129.1, 129.2, 129.3, 137.6 (d). HR-MS (ESI): theoretical, C$_{15}$H$_{14}$S, 226.0816, found 226.0693.