Sulfur-directed carbon-sulfur bond cleavage
for Rh-catalyzed regioselective alkynylthiolation of alkynes

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i) Condition screening for the intermolecular reaction of 1a with 2a

\[
\text{MeS} \quad \begin{array}{c}
\text{n-C}_5\text{H}_{11} \quad \text{S} \\
1a
\end{array}
\quad + 
\quad \begin{array}{c}
\text{H} \\
2a
\end{array}
\quad \xrightarrow{\text{Rh cat. (10 mol%)}} 
\quad \begin{array}{c}
\text{MeS} \quad \text{p-tolyl} \\
3aa
\end{array}
\]

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<th>Entry</th>
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<th>Solvent</th>
<th>Time (h)</th>
<th>Yield (%)</th>
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<td>19</td>
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<tr>
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<td>8</td>
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<td>1,4-dioxane</td>
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<td>81</td>
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</tbody>
</table>

a The ratio of sulfide 1a/alkyne 2a was 1/3. b BIPHEP: 2,2'-bis(diphenylphosphino)-1,1'-biphenyl, DPPE: 1,2-bis(diphenylphosphino)ethane, DPPE: 1,2-bis(diphenylphosphino)ethane.

ii) Condition screening for the intramolecular reaction of 6a

\[
\text{n-C}_5\text{H}_{11} \quad \begin{array}{c}
\text{S} \\
6a
\end{array}
\quad \xrightarrow{\text{Rh cat. (x mol%)}} 
\quad \begin{array}{c}
\text{n-C}_5\text{H}_{11} \quad \text{S} \\
7a
\end{array}
\]

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<th>Entry</th>
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<th>n (M)</th>
<th>Yield (%)</th>
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<td>5</td>
<td>[Rh(cod)]OTf + rac-BINAP</td>
<td>5</td>
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<td>93</td>
</tr>
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</table>

a The initial concentration of diyne 6a.

iii) Experimental details and characterization data for new compounds

**General:** $^1$H NMR spectra were recorded on JEOL ECX-500 (500 MHz) spectrometers. The chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm) for CDCl$_3$. The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; dt, doublet of triplet; m, multiplet; q, quartet. The coupling constants, $J$, are reported in Hertz (Hz). $^{13}$C NMR spectra were obtained by JEOL ECX-500 (125 MHz) spectrometers and referenced to the internal solvent signals (central peak is 77.16 ppm in CDCl$_3$). CDCl$_3$ was used as a NMR solvent. High-resolution mass spectra (HRMS) were measured on an ESI (Electro Spray Ionization) – Orbitrap mass spectrometer method. X-ray structures were determined...
were obtained by a Rigaku R-AXIS RAPID diffractometer. Preparative thin-layer chromatography (PTLC) was performed with silica gel-precoated glass plates (Merck 60 GF254) prepared in our laboratory. Flash column chromatography was performed over silica gel 200-300. All reagents were weighed and handled in air and backfilled under argon at room temperature. Unless otherwise noted, all reactions were performed under an argon atmosphere. All reagents were purchased from Wako, Kanto, Aldrich and TCI and used without further purification.

**General procedure for the syntheses of substrate (GP):**

\[
\begin{align*}
\text{R}_2\text{S} \leftrightarrow \text{n-C}_6\text{H}_{11} & + \text{Turbo Grignard Reagent (1.5 eq.)} \\
\text{THF, 0 °C-rt} & \rightarrow \text{R}_2\text{S} \leftrightarrow \text{n-C}_6\text{H}_{11}
\end{align*}
\]

Tetrahydrofuran (3.0 ml) was added to bromide derivatives (1.0 mmol) and Turbo Grignard Reagent (1.5 eq.) in round-bottom flask at 0 °C, then stirred for 2 hours at room temperature. Disulfide (or diselenide) (2.0 eq.) was added to the reaction vessel at 0 °C, then the mixture was stirred at room temperature for 2 hours. After reaction was completed, water was added and the mixture was extracted with AcOEt. The extract was dried (Na$_2$SO$_4$), and concentrated under reduced pressure. The crude products were purified by column chromatography on silica gel.

**[Hept-1-ynyl][2-(methylsulfanyl)phenyl]sulfane (1a).** GP was used. Isolated by preparative TLC (hexane only). The title compound was obtained as a yellow oil (65%). $^1$H NMR $\delta$ 7.68 (dd, $J = 1.3$, 7.9 Hz, 1H), 7.32 (dd, $J = 1.3$, 7.6 Hz, 1H), 7.26 (dt, $J_d = 1.4$ Hz, $J_t = 7.6$ Hz, 1H), 7.16 (dt, $J_d = 1.4$ Hz, $J_t = 7.9$ Hz, 1H), 2.46 (t, $J = 7.5$ Hz, 2H), 2.44 (s, 3H). $^{13}$C NMR $\delta$ 136.4, 134.0, 130.4, 127.6, 126.6, 126.3, 101.2, 64.9, 31.2, 28.5, 22.4, 20.5, 17.9, 14.2; HRMS(ESI) calcd for C$_{14}$H$_{19}$S$_2$(M+H): 251.0923; found: 251.0923.

**[Hept-1-ynyl][2-(Phenylsulfanyl)phenyl]sulfane (1b).** GP was used. Isolated by preparative TLC (hexane only). The title compound was obtained as a pale yellow oil (20%). $^1$H NMR $\delta$ 7.77 (dd, $J = 1.3$, 8.0 Hz, 1H), 7.44-7.37 (m, 2H), 7.27-7.22 (m, 2H), 7.20-7.15 (m, 4H), 2.46 (t, $J = 7.0$ Hz, 2H), 1.65-1.57 (m, 2H), 1.47-1.30 (m, 4H), 0.92 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR $\delta$ 140.0, 135.7, 135.4, 129.6, 129.3, 129.1, 128.7,
126.5, 126.4, 126.2, 101.5, 64.7, 31.1, 28.3, 22.2, 20.3, 14.0; HRMS(ESI) calcd for C_{19}H_{21}S_{2} (M+H): 313.1079; found: 313.1080.

[Hept-1-ynyl][2-(methylselenyl)phenyl]sulfane (1c). GP was used. Isolated by preparative TLC (hexane only). The title compound was obtained as a yellow oil (63%). $^1$H NMR $\delta$ 7.68 (dd, $J = 1.2, 7.7$ Hz, 1H), 7.46 (dd, $J = 1.4, 7.7$ Hz, 1H), 7.29 (dt, $J_d = 1.4$ Hz, $J_t = 7.5$ Hz, 1H), 7.11 (dt, $J_d = 1.4$ Hz, $J_t = 7.5$ Hz, 1H), 2.46 (t, $J = 7.2$ Hz, 2H), 2.31 (s, 3H), 1.64-1.59 (m, 2H), 1.46-1.33 (m, 4H), 0.92 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR $\delta$ 137.9, 133.1, 127.9, 125.9, 100.6, 65.0, 30.8, 28.0, 21.9, 20.0, 13.7, 8.4; HRMS(ESI) calcd for C_{14}H_{19}Se (M+H): 299.0367; found: 299.0368.

[Hept-1-ynyl][2-methoxyphenyl]sulfane (1d). Tetrahydrofuran (4.0 ml) was added to 1-heptyne (2.0 mmol) and n-BuLi (0.9 eq.) in round-bottom flask at -78 °C, then stirred for 1 hour. Bis(2-methoxyphenyl) disulfide (0.7 eq.) in tetrahydrofuran (3 ml) was added to the reaction, then the mixture was stirred and warmed to room temperature. After reaction was completed, water was added and the mixture was extracted with diethyl ether. The extract was dried (Na$_2$SO$_4$), and concentrated under reduced pressure. The crude products were purified by column chromatography on silica gel (hexane/CH$_2$Cl$_2$ = 3/1) to give title compound (47%) as a colorless oil. $^1$H NMR $\delta$ 7.60 (dd, $J = 1.6, 7.8$ Hz, 1H), 7.19-7.15 (m, 1H), 7.01 (dt, $J_d = 1.2$ Hz, $J_t = 7.7$ Hz, 1H), 6.82 (dd, $J = 1.1, 8.1$ Hz, 1H), 3.87 (s, 3H), 2.46 (t, $J = 7.0$ Hz, 2H), 1.66-1.58 (m, 2H), 1.47-1.32 (m, 4H), 0.92 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR $\delta$ 155.0, 126.8, 126.2, 122.5, 121.5, 110.2, 100.5, 64.2, 55.8, 31.1, 28.4, 22.2, 20.3, 13.9; HRMS(ESI) calcd for C_{14}H_{19}OS (M+H): 235.1151; found: 235.1152.

[Hept-1-ynyl][2-(methylsulfonyl)phenyl]sulfane (1e). Tetrahydrofuran (2.0 ml) was added to (2-bromophenyl)(hept-1-ynyl)sulfane (1.0 mmol) and Turbo Grignard Reagent (1.5 eq.) in round-bottom flask at 0 °C, then stirred for 2 hour at room temperature. Methanesulfonyl chloride (2.2 eq.) was added to the reaction, then the mixture was stirred and warmed to room temperature. After reaction was completed, saturated aq.NaHCO$_3$ was added and the mixture was extracted with diethyl ether. The extract was dried (Na$_2$SO$_4$), and concentrated under reduced pressure. The crude products were purified by column chromatography on silica gel (hexane/CH$_2$Cl$_2$ = 3/1) to give title compound (57%) as a colorless oil. $^1$H NMR $\delta$ 7.60 (dd, $J = 1.6, 7.8$ Hz, 1H), 7.19-7.15 (m, 1H), 7.01 (dt, $J_d = 1.2$ Hz, $J_t = 7.7$ Hz, 1H), 6.82 (dd, $J = 1.1, 8.1$ Hz, 1H), 3.87 (s, 3H), 2.46 (t, $J = 7.0$ Hz, 2H), 1.66-1.58 (m, 2H), 1.47-1.32 (m, 4H), 0.92 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR $\delta$ 155.0, 126.8, 126.2, 122.5, 121.5, 110.2, 100.5, 64.2, 55.8, 31.1, 28.4, 22.2, 20.3, 13.9; HRMS(ESI) calcd for C_{14}H_{19}OS (M+H): 235.1151; found: 235.1152.
chromatography on silica gel (hexane/EtOAc = 5/1) to give title compound (17%) as a colorless oil. $^1$H NMR δ 8.03-7.99 (m, 2H), 7.63 (dt, $J_d = 1.3$ Hz, $J_t = 7.4$ Hz, 1H), 7.41-7.36 (m, 1H), 3.17 (s, 3H), 2.49 (t, $J = 7.1$ Hz, 2H), 1.67-1.62 (m, 2H), 1.48-1.33 (m, 4H), 0.93 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR δ 136.2, 136.0, 134.0, 129.9, 128.4, 126.4, 102.3, 63.7, 42.1, 31.1, 28.1, 22.1, 20.3, 14.0; HRMS(ESI) calcd for C$_{14}$H$_{18}$O$_2$Na$_2$(M+Na): 305.0640; found: 305.0640.

[2-(Methylsulfanyl)phenyl][phenylethynyl]sulfane (1f). GP was used. Isolated by preparative TLC (hexane only). The title compound was obtained as a pale yellow oil (78%). $^1$H NMR δ 7.75 (dd, $J = 1.1$, 7.9 Hz, 1H), 7.53-7.50 (m, 2H), 7.36-7.33 (m, 4H), 7.27 (dt, $J_d = 1.4$ Hz, $J_t = 7.5$ Hz, 1H), 7.19 (dt, $J_d = 1.4$ Hz, $J_t = 7.5$ Hz, 1H), 2.46 (s, 3H); $^{13}$C NMR δ 135.6, 134.5, 131.9, 130.7, 128.8, 128.5, 127.8, 127.1, 126.8, 123.0, 98.8, 75.8, 18.0; HRMS(ESI) calcd for C$_{15}$H$_{13}$S$_2$(M+H): 257.0453; found: 257.0454.

[2-(Methylsulfanyl)phenyl][trimethylsilylethynyl]sulfane (1g). GP was used. Isolated by preparative TLC (hexane only). The title compound was obtained as a pale yellow oil (73%). $^1$H NMR δ 7.68 (dd, $J = 1.3$, 7.8 Hz, 1H), 7.37-7.34 (m, 1H), 7.32-7.27 (m, 1H), 7.23-7.18 (m, 1H), 2.45 (s, 3H), 0.27 (s, 9H); $^{13}$C NMR δ 135.1, 134.3, 130.8, 127.9, 127.0, 126.4, 107.3, 90.5, 18.0, 0.0; HRMS(ESI) calcd for C$_{12}$H$_{17}$S$_2$Si (M+H): 253.0535; found: 253.0536.

[Ethynyl][2-(methylsulfanyl)phenyl]sulfane (1h). Substrate (1g, 252.5 mg, 1.0 mmol) was dissolved in methanol (4.0 ml) and tetrahydrofuran (2.0 ml). After addition of KOH (62.1 mg, 1.1 mmol) and water (1.4 ml), the mixture was stirred at room temperature. After 2 h, the solvents were removed, and the residue was purified by preparative TLC (hexane/toluene = 5/1) to give corresponding substrate (1h, 94%) as a yellow oil. $^1$H NMR δ 7.71 (dd, $J = 1.0$, 7.7 Hz, 1H), 7.36-7.32 (m, 1H), 7.28-7.24 (m, 1H), 7.20 (dt, $J_d = 1.2$ Hz, $J_t = 7.5$ Hz, 1H), 3.28 (s, 1H), 2.44 (s, 3H); $^{13}$C NMR δ 134.9, 133.9, 130.4, 127.6, 127.3, 127.0, 87.7, 71.2, 17.8; HRMS(ESI) calcd for C$_9$H$_9$S$_2$(M+H): 181.0140; found: 181.0140.
(Z)-[2-(Methylsulfanyl)phenyl][1-(4-methylphenyl)non-1-en-3-ynyl]sulfane (3aa). Isolated by preparative TLC (hexane/CH₂Cl₂ = 5/1). The title compound was obtained as a yellow oil (98%). \(^1\)H NMR δ 7.37 (d, J = 7.9 Hz, 2H), 7.10-7.03 (m, 3H), 7.00 (d, J = 7.9 Hz, 2H), 6.87 (dt, J₉ = 1.4 Hz, J₇ = 7.4 Hz, 1H), 6.22 (t, J = 2.2 Hz, 1H), 2.47 (s, 3H), 2.37 (dt, J₉ = 2.2 Hz, J₇ = 7.1 Hz, 2H), 2.25 (s, 3H), 1.57-1.51 (m, 2H), 1.41-1.29 (m, 4H), 0.88 (t, J = 7.3 Hz, 3H); \(^{13}\)C NMR δ 144.8, 139.3, 138.3, 135.6, 133.6, 131.4, 128.8, 127.5, 126.9, 125.9, 125.1, 113.0, 100.1, 78.5, 31.1, 28.3, 22.2, 21.1, 20.0, 16.2, 14.0; HRMS(ESI) calcd for C\(_{23}\)H\(_{26}\)NaS\(_2\) (M+Na): 389.1368; found: 389.1368.

(Z)-[2-(Phenylsulfanyl)phenyl][1-(4-methylphenyl)non-1-en-3-ynyl]sulfane (3ba). Purified by preparative TLC (hexane/CH₂Cl₂ = 5/1). The title compound and dimer of 1b were obtained as a mixture, and the yield was determined to be 67% by the NMR analysis using tetrachloroethylene as an internal standard. Only the discriminable \(^1\)H NMR and \(^{13}\)C NMR peaks for compound 3ba were listed. \(^1\)H NMR δ 6.19 (t, J = 2.0 Hz, 1H), 2.36 (dt, J₉ = 2.0 Hz, J₇ = 7.0 Hz, 2H), 2.25 (s, 3H), 1.56-1.46 (m, 2H), 1.41-1.26 (m, 4H), 0.87 (t, J = 7.5 Hz, 3H); \(^{13}\)C NMR δ 100.4, 78.8, 31.3, 28.5, 22.4, 21.3, 20.2, 14.2; HRMS(ESI) calcd for C\(_{28}\)H\(_{28}\)NaS\(_2\) (M+Na): 451.1525; found: 451.1526.

(Z)-[2-(Methylselenyl)phenyl][1-(4-methylphenyl)non-1-en-3-ynyl]sulfane (3ca). Isolated by preparative TLC (hexane/CH₂Cl₂ = 4/1). The title compound was obtained as a yellow oil (89%). \(^1\)H NMR δ 7.37 (d, J = 8.1 Hz, 2H), 7.18 (dd, J = 1.2, 7.8 Hz, 1H), 7.06 (dd, J = 1.4, 7.8 Hz, 1H), 7.01-6.98 (m, 3H), 6.90 (dt, J₉ = 1.4 Hz, J₇ = 7.6 Hz, 1H), 6.12 (t, J = 2.2 Hz, 1H), 2.38 (dt, J₉ = 2.2 Hz, J₇ = 7.0 Hz, 2H), 2.32 (s, 3H), 2.25 (s, 3H), 1.58-1.52 (m, 2H), 1.42-1.29 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H); \(^{13}\)C NMR δ 145.1, 138.3, 135.5, 135.3, 134.9, 131.7, 128.8, 128.6, 127.5, 127.1, 125.8, 112.9, 100.2, 78.5, 31.1, 28.4, 22.2, 21.1, 20.0, 14.0, 7.1; HRMS(ESI) calcd for C\(_{23}\)H\(_{26}\)NaSe (M+Na): 437.0810; found: 437.0811.
(Z)-[2-(Methylsulfanyl)phenyl][1-(3-methylphenyl)non-1-en-3-ynyl]sulfane (3ab). Isolated by preparative TLC (hexane/CH$_2$Cl$_2$ = 5/1). The title compound was obtained as a yellow oil (89%). $^1$H NMR δ 7.30-7.26 (m, 2H), 7.09-7.03 (m, 4H), 6.98 (d, $J = 7.4$ Hz, 1H), 6.89-6.86 (m, 1H), 6.15-6.14 (m, 1H), 2.47 (s, 3H), 2.37 (dt, $J_d = 2.2$ Hz, $J_l = 7.1$ Hz, 2H), 2.24 (s, 3H), 1.57-1.51 (m, 2H), 1.42-1.29 (m, 4H), 0.89 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR δ 145.2, 139.6, 138.4, 137.6, 133.4, 131.7, 129.1, 128.3, 127.9, 127.0, 125.9, 125.0, 124.8, 113.3, 100.3, 78.4, 31.1, 28.3, 22.2, 21.3, 20.0, 16.2, 14.0; HRMS(ESI) calcd for C$_{23}$H$_{26}$NaS$_2$ (M+Na): 389.1368; found: 389.1368.

(Z)-[2-(Methylsulfanyl)phenyl][1-(2-methylphenyl)non-1-en-3-ynyl]sulfane (3ac). Isolated by preparative TLC (hexane/CH$_2$Cl$_2$ = 5/1). The title compound was obtained as a red brown oil (96%). $^1$H NMR δ 7.18-7.14 (m, 2H), 7.10 (dt, $J_d = 1.4$ Hz, $J_l = 7.5$ Hz, 1H), 7.03-6.98 (m, 3H), 6.95-6.91 (m, 1H), 6.83 (dt, $J_d = 1.3$ Hz, $J_l = 7.4$ Hz, 1H), 5.72-5.71 (m, 1H), 2.46 (dt, $J_d = 2.2$ Hz, $J_l = 7.1$ Hz, 2H), 2.43 (s, 3H), 2.40 (s, 3H), 1.66-1.60 (m, 2H), 1.51-1.45 (m, 2H), 1.40-1.36 (m, 2H), 0.95 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR δ 146.6, 143.4, 137.9, 136.2, 135.1, 129.9, 129.8, 128.5, 128.7, 124.3, 124.1, 110.9, 99.7, 77.4, 31.1, 28.5, 22.3, 20.0, 20.0, 15.7, 14.1; HRMS(ESI) calcd for C$_{23}$H$_{26}$NaS$_2$ (M+Na): 389.1368; found: 389.1368.

(Z)-[2-(Methylsulfanyl)phenyl][1-(phenyl)non-1-en-3-ynyl]sulfane (3ad). Isolated by preparative TLC (hexane/CH$_2$Cl$_2$ = 5/1). The title compound was obtained as a yellow oil (96%). $^1$H NMR δ 7.48-7.44 (m, 2H), 7.20-7.14 (m, 3H), 7.08-7.00 (m, 3H), 6.87-6.82 (m, 1H), 6.14 (t, $J = 1.8$ Hz, 1H), 2.45 (s, 3H), 2.38 (dt, $J_d = 1.8$ Hz, $J_l = 6.8$ Hz, 2H), 1.58-1.50 (m, 2H), 1.43-1.27 (m, 4H), 0.88 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR δ 145.3, 139.9, 138.6, 133.2, 132.0, 128.5, 128.2, 127.8, 127.3, 125.9, 125.1, 113.6, 100.6, 78.6, 31.3, 28.5, 22.4, 20.2, 16.3, 14.2; HRMS(ESI) calcd for C$_{22}$H$_{24}$NaS$_2$ (M+Na): 375.1212; found: 375.1212.
(Z)-[2-(Methylsulfanyl)phenyl][1-(1-naphthyl)non-1-en-3-ynyl]sulfane (3ac). Isolated by preparative TLC (hexane/CH₂Cl₂ = 5/1). The title compound was obtained as a yellow oil (83%). ¹H NMR δ 8.34-8.33 (m, 1H), 7.68-7.66 (m, 1H), 7.57-7.56 (m, 1H), 7.48-7.44 (m, 1H), 7.41-7.37 (m, 1H), 7.35 (dd, J = 1.1, 7.1 Hz, 1H), 7.18-7.15 (m, 1H), 6.97 (dd, J = 1.3, 7.7 Hz, 1H), 6.91 (dt, Jₖ = 1.4 Hz, Jₗ = 7.9 Hz, 1H), 6.84 (dd, J = 1.3, 7.9 Hz, 1H), 6.52 (dt, Jₖ = 1.4 Hz, Jₗ = 7.5 Hz, 1H), 5.88 (dt, J = 2.2 Hz, 1H), 2.48 (dt, Jₖ = 2.2 Hz, Jₗ = 7.1 Hz, 2H), 2.34 (s, 3H), 1.67-1.62 (m, 2H), 1.52-1.46 (m, 2H), 1.41-1.34 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ¹³C NMR δ 145.9, 143.7, 135.9, 135.5, 133.1, 131.5, 129.5, 128.6, 127.9, 127.1, 125.9, 125.8, 125.6, 124.5, 124.2, 123.8, 111.2, 100.1, 77.5, 31.1, 28.5, 22.3, 20.0, 15.7, 14.0; HRMS(ESI) calcd for C₂₉H₂₈NaS₂ (M+Na): 425.1368; found: 425.1368.

(Z)-[2-(Methylsulfanyl)phenyl][1-(4-bromophenyl)non-1-en-3-ynyl]sulfane (3af). Isolated by preparative TLC (hexane/CH₂Cl₂ = 5/1). The title compound was obtained as a yellow oil (87%). ¹H NMR δ 7.33-7.28 (m, 4H), 7.09-7.03 (m, 3H), 6.89-6.85 (m, 1H), 6.10 (t, J = 2.2 Hz, 1H), 2.45-2.44 (m, 3H), 2.39 (dt, Jₖ = 2.2 Hz, Jₗ = 7.2 Hz, 2H), 1.59-1.52 (m, 2H), 1.43-1.27 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H); ¹³C NMR δ 144.2, 140.1, 137.4, 132.2, 132.0, 131.2, 129.2, 127.5, 125.5, 125.0, 122.3, 113.8, 101.0, 78.3, 31.1, 28.3, 22.2, 20.0, 16.0, 14.0; HRMS(ESI) calcd for C₂₂H₂₃BrNaS₂ (M+Na): 453.0317; found: 453.0318.

(Z)-[2-(Methylsulfanyl)phenyl][1-(4-trifluoromethylphenyl)non-1-en-3-ynyl]sulfane (3ag). Isolated by preparative TLC (hexane/CH₂Cl₂ = 5/1). The title compound was obtained as a yellow oil (81%). ¹H NMR δ 7.56 (d, J = 7.9 Hz, 2H), 7.43 (d, J = 7.9 Hz, 2H), 7.09-7.07 (m, 3H), 6.89-6.86 (m, 1H), 6.17 (t, J = 2.3 Hz, 1H), 2.47 (s, 3H), 2.41 (dt, Jₖ = 2.3 Hz, Jₗ = 7.2 Hz, 2H), 1.60-1.54 (m, 2H), 1.44-1.29 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H); ¹³C NMR δ 143.9, 142.0 (d, J₉ = 1.5 Hz), 140.3, 132.1, 131.9, 130.0 (q, J₉ = 32.8 Hz), 127.9, 127.6, 125.6, 125.0 (q, J₉ = 3.9 Hz), 123.9 (d, J₉ = 276.9 Hz), 115.0, 101.8, 78.1, 31.1, 28.2, 22.2, 20.0, 16.0, 13.9 (a pair of peaks at the aromatic region is overlapped); HRMS(ESI) calcd for C₂₃H₂₃F₃NaS₂ (M+Na): 443.1088; found: 443.1089.
(Z)-[2-(Methylsulfanyl)phenyl][1-(2-methyl-4-methoxyphenyl)non-1-en-3-ynyl]sulfane (3ah). Isolated by preparative TLC (hexane/CH$_2$Cl$_2$ = 5/1). The title compound was obtained as a pale yellow oil (95%). $^1$H NMR $\delta$ 7.14-7.12 (m, 1H), 7.08-7.05 (m, 2H), 6.97-6.95 (m, 1H), 6.83-6.79 (m, 1H), 6.52-6.51 (m, 1H), 6.46 (dd, $J_d = 2.4$, 8.3 Hz, 1H), 5.66 (t, $J = 2.1$ Hz, 1H), 3.67 (s, 3H), 2.42 (dt, $J_d = 2.1$ Hz, $J_t = 7.1$ Hz, 2H), 2.39 (s, 3H), 2.35 (s, 3H), 1.62-1.55 (m, 2H), 1.47-1.29 (m, 1H), 0.91 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR $\delta$ 159.1, 146.5, 143.2, 138.0, 135.0, 131.2, 130.7, 128.5, 124.5, 115.3, 111.1, 110.4, 99.7, 77.7, 55.2, 31.3, 28.6, 22.4, 20.5, 20.1, 15.9, 14.2; HRMS(ESI) calcd for C$_{23}$H$_{28}$ONa$_2$S (M+Na): 419.1474; found: 419.1472.

(Z)-[2-(Methylsulfanyl)phenyl][1-(pentyl)non-1-en-3-ynyl]sulfane (3ai). Isolated by preparative TLC (hexane/CH$_2$Cl$_2$ = 5/1). The title compound was obtained as a yellow oil (81%). $^1$H NMR $\delta$ 7.42 (dd, $J = 1.1$, 7.7 Hz, 1H), 7.30-7.29 (m, 1H), 7.15-7.13 (m, 1H), 7.09-7.05 (m, 1H), 5.66-5.64 (m, 1H), 2.44 (s, 3H), 2.36 (dt, $J_d = 2.0$ Hz, $J_t = 6.9$ Hz, 2H), 2.02 (t, $J = 7.1$ Hz, 2H), 1.58-1.51 (m, 2H), 1.43-1.28 (m, 6H), 1.21-1.07 (m, 4H), 0.89 (t, $J = 7.1$ Hz, 3H), 0.80 (t, $J = 6.9$ Hz, 3H); $^{13}$C NMR $\delta$ 147.5, 143.4, 134.6, 129.7, 129.6, 128.4, 124.2, 107.6, 97.4, 77.1, 35.2, 30.8, 30.7, 28.2, 27.8, 22.0, 21.9, 19.5, 15.3, 13.7, 13.6; HRMS(ESI) calcd for C$_{21}$H$_{30}$NaS$_2$ (M+Na): 369.1681; found: 369.1681.

(Z)-[2-(Methylsulfanyl)phenyl][1-(2-methyl-2-propanyl)non-1-en-3-ynyl]sulfane (3aj). Isolated by preparative TLC (hexane/CH$_2$Cl$_2$ = 5/1). The title compound was obtained as a yellow oil (86%). $^1$H NMR $\delta$ 7.20-7.16 (m, 2H), 7.11-7.03 (m, 2H), 6.12 (t, $J = 2.3$ Hz, 1H), 2.49 (s, 3H), 2.04 (dt, $J_d = 2.3$ Hz, $J_t = 7.0$ Hz, 2H), 1.23 (s, 9H), 1.22-1.09 (m, 6H), 0.81 (t, $J = 6.9$ Hz, 3H); $^{13}$C NMR $\delta$ 154.6, 136.7, 136.4, 127.7, 126.9, 125.6, 125.6, 114.5, 99.2, 78.1, 39.4, 30.9, 29.2, 28.0, 22.2, 19.6, 16.4, 13.9; HRMS(ESI) calcd for C$_{20}$H$_{28}$NaS$_2$ (M+Na): 355.1525; found: 355.1525.
(Z)-[2-(Methylsulfanyl)phenyl][1-(trimethylsilyl)non-1-en-3-ynyl]sulfane (3ak). Isolated by preparative TLC (hexane/CH₂Cl₂ = 5/1). The title compound was obtained as a yellow oil (76%). ¹H NMR δ 7.31 (dd, J = 1.4, 7.5 Hz, 1H), 7.21-7.18 (m, 1H), 7.14 (dd, J = 1.3, 7.6 Hz, 1H), 7.04 (dt, Jₜ = 1.4 Hz, Jₛ = 7.5 Hz, 1H), 6.22 (t, J = 2.3 Hz, 1H), 2.46 (s, 3H), 2.23 (dt, Jₜ = 2.3 Hz, Jₛ = 7.2 Hz, 2H), 1.45-1.32 (m, 2H), 1.32-1.24 (m, 4H), 0.86 (t, J = 7.1 Hz, 3H), 0.04 (s, 9H); ¹³C NMR δ 148.6, 142.2, 134.4, 133.7, 128.6, 126.2, 125.6, 123.9, 102.2, 79.1, 32.1, 29.2, 23.2, 20.8, 16.9, 15.0, 0.0; HRMS(ESI) calcd for C₁₉H₂₈Na₂SiS₂ (M+Na): 371.1294; found: 371.1295.

(Z)-[1-(4-Methylphenyl)-4-(phenyl)but-1-en-3-ynyl][2-(methylsulfanyl)phenyl]sulfane (3fa). Isolated by preparative TLC (hexane/CH₂Cl₂ = 4/1). The title compound was obtained as a pale yellow solid (91%). Mp 103 °C; ¹H NMR δ 7.45-7.42 (m, 4H), 7.30-7.28 (m, 3H), 7.13-7.02 (m, 5H), 6.90-6.86 (m, 1H), 6.32 (s, 1H), 2.47 (s, 3H), 2.26 (s, 3H); ¹³C NMR δ 147.1, 139.8, 138.7, 135.5, 133.1, 131.9, 131.6, 128.9, 128.2, 127.6, 127.3, 125.8, 125.1, 123.5, 111.6, 98.1, 87.6, 21.2, 16.1 (a pair of peaks at the aromatic region is overlapped); HRMS(ESI) calcd for C₂₄H₂₀Na₂S (M+Na): 395.0899; found: 395.0900.

(Z)-[1-(4-Methylphenyl)-4-(trimethylsilyl)but-1-en-3-ynyl][2-(methylsulfanyl)phenyl]sulfane (3ga). Isolated by preparative TLC (hexane/CH₂Cl₂ = 4/1). The title compound was obtained as a yellow oil (90%). ¹H NMR δ 7.35 (d, J = 8.1 Hz, 2H), 7.09-7.06 (m, 3H), 7.00 (d, J = 8.1 Hz, 2H), 6.89-6.85 (m, 1H), 6.09 (s, 1H), 2.47 (s, 3H), 2.25 (s, 3H), 0.19 (s, 9H); ¹³C NMR δ 148.6, 140.0, 138.0, 135.5, 133.1, 132.3, 129.0, 127.8, 127.4, 125.9, 125.1, 111.2, 104.1, 102.4, 21.3, 16.3, 0.0; HRMS(ESI) calcd for C₂₃H₂₄Na₂S₂Si (M+Na): 391.0981; found: 391.0982.
(Z)-[1-(4-Methylphenyl)but-1-en-3-ynyl][2-(methylsulfanyl)phenyl]sulfane (3ha). Isolated by preparative TLC (hexane/CH₂Cl₂ = 3/1). The title compound was obtained as a yellow oil (12%). ¹H NMR δ 7.35 (d, J = 8.1 Hz, 2H), 7.11-7.06 (m, 3H), 7.00 (d, J = 8.1 Hz, 2H), 6.91-6.85 (m, 1H), 6.05 (d, J = 2.2 Hz, 1H), 3.45 (dt, J = 2.2 Hz, 1H), 2.47 (s, 3H), 2.25 (s, 3H); ¹³C NMR δ 149.5, 140.4, 138.9, 134.9, 132.5, 132.1, 128.9, 127.7, 127.6, 125.6, 124.9, 110.1, 85.5, 81.1, 21.2, 16.1; HRMS(ESI) calcd for C₁₈H₁₆NaS₂ (M+Na): 319.0586; found: 319.0587.

[1-((2-Methylsulfanylphenyl)sulfanyl)but-1-en-3-ynyl][2-(methylsulfanyl)phenyl]sulfane (3hh). Isolated by preparative TLC (hexane/CH₂Cl₂ = 3/1). The title compound was obtained as a yellow oil (64%). ¹H NMR δ 7.43 (dd, J = 1.3, 7.7 Hz, 1H), 7.36-28 (m, 3H), 7.20 (dd, J = 1.0, 7.7 Hz, 1H), 7.14 (dd, J = 1.2, 7.9 Hz, 1H), 7.12-7.06 (m, 2H), 5.48 (d, J = 2.5 Hz, 1H), 3.42 (d, J = 2.5 Hz, 1H), 2.45 (s, 3H), 2.35 (s, 3H); ¹³C NMR δ 146.5, 144.2, 143.4, 135.6, 134.6, 130.0, 129.6, 129.2, 128.9, 125.6, 125.3, 125.2, 124.9, 107.9, 85.5, 80.1, 16.1, 15.6; HRMS(ESI) calcd for C₁₈H₁₆NaS₄ (M+Na): 383.0027; found: 383.0027.

Ethyl (E)-3-((2-(methylsulfanyl)phenyl)sulfanyl)undec-2-en-5-ynoate (5). Isolated by preparative TLC (hexane/EtOAc = 5/1). The title compound was obtained as a yellow oil (54%). ¹H NMR δ 7.51 (dd, J = 1.4, 7.5 Hz, 1H), 7.43 (dt, Jₛ = 1.6 Hz, Jₜ = 7.8 Hz, 1H), 7.24-7.21 (m, 1H), 7.17 (dt, Jₛ = 1.2 Hz, Jₜ = 7.5 Hz, 1H), 5.08-5.07 (m, 1H), 4.07 (q, J = 7.2 Hz, 2H), 3.95-3.93 (m, 2H), 2.44 (s, 3H), 2.23-2.18 (m, 2H), 1.57-1.50 (m, 2H), 1.44-1.30 (m, 4H), 1.20 (t, J = 7.2 Hz, 3H), 0.90 (t, J = 7.3 Hz, 3H); ¹³C NMR δ 165.0, 158.0, 146.1, 137.6, 131.1, 126.5, 125.3, 124.9, 110.6, 83.5, 75.1, 60.0, 31.2, 28.6, 23.4, 22.4, 19.0, 15.4, 14.4, 14.2; HRMS(ESI) calcd for C₂₀H₂₆O₂NaS₂ (M+Na): 385.1266; found: 385.1267.
[Hept-1-ynyl][2-(2-(heptynyl)phenyl)sulfanyl]phenyl)sulfane (6a). Tetrahydrofuran solution (2.5 ml) of [Hept-1-ynyl][2-(2-bromophenyl)sulfanyl]phenyl)sulfane (1.48 g, 3.8 mmol) was added to a dry and argon-flushed flask, then cooled to -20 °C. iPrMgCl • LiCl (tetrahydrofuran solution (abt. 14%), 4.7 ml, 4.9 mmol) was added at –20 °C and the resulting mixture was stirred for 2 h warming to rt. Then, a solution of I₂ (2.45 g, 9.6 mmol) in THF (9.0 ml) was added and stirred for 15 min. The reaction mixture was quenched with sat. Na₂S₂O₃ and the resulting mixture was extracted with diethyl ether. The combined organic layer was dried (Na₂SO₄), and concentrated under reduced pressure. Tetrahydrofuran 1.9 mL) and diisopropylamine (0.7 mL) were added to a part of crude mixture (303.0 mg, 0.6 mmol), Pd(PPh₃)Cl₂ (56.4 mg, 0.08 mmol) and CuI (30.8 mg, 0.16 mmol) under an Ar atmosphere. 1-heptyne (0.25 ml, 1.8 mmol) was added, and the resulting mixture was stirred at 60 °C. After 4 h, the solvents were removed, and the residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂ = 5/1) to give diyne (106.6 mg, 44%) as a yellow oil. ¹H NMR δ 7.84-7.78 (m, 1H), 7.48-7.41 (m, 2H), 7.40-7.35 (m, 1H), 7.24-7.18 (m, 1H), 7.09-7.04 (m, 2H), 6.67-6.62 (m, 1H), 2.52-2.44 (m, 4H), 1.67-1.59 (m, 4H), 1.51-1.28 (m, 8H), 0.92 (t, J = 7.2 Hz, 6H); ¹³C NMR δ 141.1, 138.8, 136.3, 132.4, 130.0, 128.0, 128.0, 126.5, 126.1, 126.1, 125.3, 122.6, 101.6, 97.7, 78.0, 64.8, 31.1, 31.1, 28.3, 22.2, 20.3, 19.7, 14.0, 14.0 (a pair of peaks at the aliphatic region is overlapped); HRMS(ESI) calcd for C₂₆H₃₀NaS₂ (M+Na): 429.1681; found: 429.1682.

[Hept-1-ynyl][2-(2-(phenylethynyl)phenyl)sulfanyl]phenyl)sulfane (6b). Isolated by preparative TLC (hexane/CH₂Cl₂ = 5/1). The title compound was obtained as a pale yellow oil (39%). ¹H NMR δ 7.82 (dd, J = 1.1, 8.0 Hz, 1H), 7.61-7.30 (m, 8H), 7.21 (dt, Jd = 1.3 Hz, Jf = 7.5 Hz, 1H), 7.14-7.10 (m, 2H), 6.72-6.68 (m, 1H), 2.45 (t, J = 7.0 Hz, 2H), 1.65-1.57 (m, 2H), 1.46-1.30 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H); ¹³C NMR δ 141.3, 139.4, 136.6, 132.5, 131.8, 130.3, 128.9, 128.6, 128.4, 127.8, 126.7, 126.4, 126.3, 125.6, 123.1, 121.8, 101.9, 96.1, 86.9, 64.8, 31.2, 28.4, 22.3, 20.4, 14.1; HRMS(ESI) calcd for C₂₇H₂₃NaS₂ (M+Na): 435.1212; found: 435.1212.
[Hept-1-ynyl][(2-(2-(4-methylphenylethynyl)phenyl)sulfanyl)phenyl]sulfane (6c). Isolated by preparative TLC (hexane/CH₂Cl₂ = 5/1). The title compound was obtained as a yellow oil (40%). ¹H NMR δ 7.81 (dd, J = 0.9, 7.9 Hz, 1H), 7.50-7.41 (m, 5H), 7.23-7.09 (m, 5H), 6.70-6.67 (m, 1H), 2.45 (t, J = 7.1 Hz, 2H), 2.36(s, 3H), 1.64-1.59 (m, 2H), 1.46-1.30 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H); ¹³C NMR δ 141.3, 139.2, 138.7, 136.5, 132.4, 131.6, 130.2, 129.2, 128.7, 127.9, 126.7, 126.4, 126.2, 125.5, 122.0, 120.0, 101.8, 96.4, 86.2, 64.8, 31.1, 28.4, 22.3, 21.6, 20.4, 14.1; HRMS(ESI) calcd for C₂₈H₂₆NaS₂ (M+Na): 449.1368; found: 449.1368.

![n-C₅H₁₁][S=S](o-toly)_2

[Hept-1-ynyl][(2-(2-(methylphenylethynyl)phenyl)sulfanyl)phenyl]sulfane (6d). Isolated by preparative TLC (hexane/CH₂Cl₂ = 5/1). The title compound was obtained as a yellow oil (38%). ¹H NMR δ 7.82 (dd, J = 1.2, 8.0 Hz, 1H), 7.57-7.48 (m, 3H), 7.43 (dt, Jₙ = 1.5 Hz, Jᵢ = 7.9 Hz, 1H), 7.24-7.20 (m, 3H), 7.19-7.14 (m, 1H), 7.12-7.08 (m, 2H), 6.70-6.66 (m, 1H), 2.58(s, 3H), 2.44 (t, J = 7.2 Hz, 2H), 1.63-1.56 (m, 2H), 1.45-1.30 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H); ¹³C NMR δ 141.4, 140.5, 139.2, 136.6, 132.5, 132.1, 130.2, 129.5, 128.8, 128.5, 127.7, 126.6, 126.3, 126.1, 125.5, 125.4, 122.9, 121.9, 101.8, 95.0, 90.6, 64.8, 31.1, 28.3, 22.2, 21.1, 20.3, 14.0; HRMS(ESI) calcd for C₂₈H₂₆NaS₂ (M+Na): 449.1368; found: 449.1369.

![n-C₅H₁₁][S=S](TMS)_2

[Hept-1-ynyl][(2-(2-(trimethylsilyl)ethynyl)phenyl)sulfanyl)phenyl]sulfane (6e). Isolated by preparative TLC (hexane only). The title compound was obtained as a pale yellow oil (40%). ¹H NMR δ 7.80 (d, J = 7.9 Hz, 1H), 7.48-7.41 (m, 3H), 7.22-7.18 (m, 1H), 7.11-7.04 (m, 2H), 6.66 (d, J = 7.8 Hz, 1H), 2.46 (t, J = 7.6 Hz, 2H), 1.64-1.57 (m, 2H), 1.46-1.32 (m, 4H), 0.92 (t, J = 7.7 Hz, 3H), 0.28 (s, 9H); ¹³C NMR δ 141.3, 139.7, 136.4, 132.9, 130.1, 129.1, 128.0, 126.6, 126.4, 126.3, 125.4, 121.7, 102.0, 101.8, 101.7, 64.9, 31.2, 28.4, 22.3, 20.4, 14.1, 0.0; HRMS(ESI) calcd for C₂₉H₂₆NaS₂Si (M+Na): 431.1294; found: 431.1294.
[Hept-1-ynyl][(2-(2-ethynylphenyl)sulfanyl)phenyl]sulfane (6f). Diyne having trimethylsilyl group (6e, 100.8 mg, 0.3 mmol) was dissolved in methanol (1.3 ml) and tetrahydrofuran (1.3 ml). After addition of KOH (30.5 mg, 0.5 mmol) and water (0.13 ml), the mixture was stirred at room temperature. After 2 h, the solvents were removed, and the residue was purified by preparative TLC (hexane/CH₂Cl₂) to give corresponding diyne (6f, 78%) as a yellow oil. ¹H NMR δ 7.87-7.85 (m, 1H), 7.54-7.48 (m, 3H), 7.29-7.24 (m, 1H), 7.19-7.10 (m, 2H), 6.70-6.68 (m, 1H), 3.53 (s, 1H), 2.50 (t, J = 7.1 Hz, 2H), 1.68-1.61 (m, 2H), 1.50-1.36 (m, 4H), 0.95 (t, J = 7.2 Hz, 3H); ¹³C NMR δ 141.6, 139.9, 136.8, 133.4, 130.5, 129.5, 127.3, 126.8, 126.4, 126.2, 125.5, 125.0, 101.9, 83.9, 80.9, 64.8, 31.2, 28.4, 22.3, 20.4, 14.1; HRMS(ESI) calcd for C₂₁H₂₀NaS₂ (M+Na): 359.0899; found: 359.0899.

(Z)-11-(1-Pentyl-1-oct-2-ynylidene)-11H-dibenzo[b,e][1,4]dithiepine (7a). [Rh(cod)₂]OTf (3.1 mg, 0.005 mmol) and rac-BINAP (3.1 mg, 0.005 mmol) were placed in Schlenk tube, which was then evacuated and backfilled with argon (3×), the reaction vessel was filled with argon. 1,2-Dichloroethane (0.1 mL) was added to the flask and the mixture was stirred to give a yellowish solution. Then, a 1,2-dichloroethane solution (0.9 mL) of diyne (0.10 mmol) was added and the mixture was stirred at 80 °C. The volatiles were removed under reduced pressure, and the crude products were isolated by preparative TLC (hexane/toluene = 3/1). The title compound was obtained as a colorless oil (93%). ¹H NMR δ 7.60-7.55 (m, 1H), 7.52 (dd, J = 1.5, 7.6 Hz, 1H), 7.33 (m, 2H), 7.25-7.19 (m, 2H), 7.08 (dt, J₁ = 1.6 Hz, J₂ = 7.6 Hz, 1H), 7.01 (dt, J₁ = 1.5 Hz, J₂ = 7.4 Hz, 1H), 2.50 (t, J = 7.2 Hz, 2H), 2.03 (t, J = 7.9 Hz, 2H), 1.69-1.45 (m, 6H), 1.41-1.32 (m, 2H), 1.25-1.08 (m, 4H), 0.92 (t, J = 6.9 Hz, 3H), 0.82 (t, J = 7.2 Hz, 3H); ¹³C NMR δ 140.4, 138.9, 137.4, 137.0, 136.9, 134.3, 133.8, 130.2, 130.2, 129.4, 129.2, 128.9, 126.9, 120.2, 100.2, 79.0, 33.8, 31.2, 31.1, 28.6, 28.2, 22.4, 22.3, 20.0, 14.2, 14.1; HRMS(ESI) calcd for C₂₆H₃₀NaS₂ (M+Na): 429.1681; found: 429.1681.

(Z)-11-(1-Phenyl-1-oct-2-ynylidene)-11H-dibenzo[b,e][1,4]dithiepine (7b). Isolated by preparative TLC (hexane/toluene = 3/1). The title compound was obtained as a pale yellow oil (76%). ¹H NMR δ 7.62 (dd, J = 1.6, 7.1 Hz, 1H), 7.56 (dd, J = 1.1, 7.8 Hz, 1H), 7.42 (dd, J = 1.7, 7.8 Hz, 1H), 7.17-7.01 (m, 8H), 6.96 (dt, J₁ = 1.2 Hz, J₂ = 7.5 Hz, 1H), 6.78 (dd, J₁ = 1.1, 7.9 Hz, 1H), 2.56 (t, J = 7.2 Hz, 2H), 1.73-1.66 (m, 2H), 1.55-1.48 (m, 2H), 1.42-1.33 (m, 2H), 0.93 (t, J = 7.6 Hz, 3H); ¹³C NMR δ 138.9, 138.5, 136.2, 136.2, 136.0, 135.6, 132.1, 131.5, 129.7, 128.9, 127.6, 127.4, 127.1, 127.0, 125.6, 125.5, 124.6, 116.0, 99.5, 77.4, 29.2, 26.4, 20.2, 18.0, 12.1; HRMS(ESI) calcd for C₂₇H₃₄NaS₂ (M+Na): 435.1212; found: 435.1212.
(Z)-11-(1-(4-Methylphenyl)-1-oct-2-ynylidene)-11H-dibenzo[b,e][1,4]dithiepine (7c). Isolated by preparative TLC (hexane/toluene = 3/1). The title compound was obtained as a pale yellow oil (67%). $^1$H NMR δ 7.62 (dd, $J = 1.7, 7.2$ Hz, 1H), 7.57 (dd, $J = 1.1, 7.5$ Hz, 1H), 7.41 (dd, $J = 1.7, 7.8$ Hz, 1H), 7.17-7.08 (m, 3H), 6.90-6.56 (m, 4H), 6.81 (dd, $J = 1.3, 7.8$ Hz, 1H), 2.55 (t, $J = 7.3$ Hz, 2H), 2.21 (s, 3H), 1.73-1.65 (m, 2H), 1.54-1.48 (m, 2H), 1.42-1.34 (m, 2H), 0.93 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR δ 140.9, 140.2, 138.5, 138.0, 137.6, 136.5, 135.4, 134.2, 133.7, 131.8, 131.0, 129.8, 129.4, 129.2, 129.1, 128.4, 127.6, 118.2, 101.5, 79.6, 31.4, 28.6, 22.4, 21.3, 20.2, 14.2; HRMS(ESI) calcd for C$_{28}$H$_{26}$NaS$_2$ (M+Na): 449.1368; found: 449.1368.

(E)-11-(1-(2-Methylphenyl)-1-oct-2-ynylidene)-11H-dibenzo[b,e][1,4]dithiepine (7d). Isolated by preparative TLC (hexane/toluene = 3/1). The title compound was obtained as a pale yellow oil (59%). $^1$H NMR δ 7.61 (dd, $J = 1.5, 7.5$ Hz, 1H), 7.47 (d, $J = 7.7$ Hz, 1H), 7.43 (dd, $J = 1.3, 7.7$ Hz, 1H), 7.17-7.13 (m, 1H), 7.12-7.08 (m, 1H), 7.03-6.97 (m, 3H), 6.95-6.85 (m, 3H), 6.71 (d, $J = 7.4$ Hz, 1H), 2.50 (t, $J = 7.1$ Hz, 2H), 2.31 (s, 3H), 1.68-1.62 (m, 2H), 1.50-1.44 (m, 2H), 1.39-1.32 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR δ 141.8, 139.8, 138.3, 138.2, 138.0, 137.0, 136.8, 134.1, 133.4, 131.3, 131.0, 130.0, 129.9, 129.1, 129.0, 128.9, 127.6, 127.1, 125.3, 118.1, 102.0, 78.9, 31.2, 28.5, 22.3, 20.1, 19.9, 14.1; HRMS(ESI) calcd for C$_{28}$H$_{26}$NaS$_2$ (M+Na): 449.1368; found: 449.1368.

(E)-11-(1-Trimethylsilyl-1-oct-2-ynylidene)-11H-dibenzo[b,e][1,4]dithiepine (7e). Isolated by preparative TLC (hexane/toluene = 3/1). The title compound was obtained as a pale yellow oil (90%). $^1$H NMR δ 7.84 (dt, $J_d = 1.7$ Hz, $J_t = 7.2$ Hz, 1H), 7.82-7.80 (m, 1H), 7.65 (dd, $J = 1.6, 7.4$ Hz, 1H), 7.58-7.50 (m, 3H), 7.84 (dt, $J_d = 1.7$ Hz, $J_t = 7.4$ Hz, 1H), 7.35 (dt, $J_d = 1.6$ Hz, $J_t = 7.3$ Hz, 1H), 2.82 (t, $J = 7.7$ Hz, 2H), 1.97-1.88 (m, 2H), 1.84-1.60 (m, 4H), 1.20 (t, $J = 7.7$ Hz, 3H), 0.15 (s, 9H); $^{13}$C NMR δ 152.4, 142.1,
139.2, 139.0, 137.9, 134.5, 133.9, 131.3, 131.3, 130.2, 129.7, 129.3, 127.9, 120.4, 104.8, 80.7, 31.6, 29.1, 22.6, 20.6, 14.5, 0.0; HRMS(ESI) calcd for C$_{24}$H$_{28}$NaS$_{2}$Si (M+Na): 431.1294 found: 431.1294.

(Z)-11-(Oct-2-ynylidene)-11H-dibenzo[b,e][1,4]dithiepine (7f). Isolated by preparative TLC (hexane/toluene = 3/1). The title compound was obtained as a yellow oil (92%). $^1$H NMR δ 7.63-7.62 (m, 1H), 7.56-7.54 (m, 1H), 7.49-7.48 (m, 1H), 7.31-7.28 (m, 2H), 7.23-7.19 (m, 1H), 7.18-7.13 (m, 2H), 5.50 (t, $J = 2.3$ Hz, 1H), 2.51 (dt, $J_d = 2.3$ Hz, $J_t = 7.1$ Hz, 2H), 1.68-1.63 (m, 2H), 1.52-1.46 (m, 2H), 1.41-1.34 (m, 2H), 0.93 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR δ 146.7, 141.3, 139.7, 139.5, 137.2, 136.4, 133.9, 133.8, 131.8, 131.0, 129.7, 129.5, 129.3, 128.4, 105.6, 101.2, 77.0, 31.2, 28.5, 22.3, 20.0, 14.1; HRMS(ESI) calcd for C$_{32}$H$_{20}$NaS$_{2}$ (M+Na): 359.0899; found: 359.0899.

iv) Experimental details and characterization data for complex A

A 1,2-dichloroethane solution (0.5 mL) of sulfide 1a (7.5 mg, 0.01 mmol) and [Rh(cod)(dppe)]OTf (9.5 mg, 0.01 mmol) was stirred at 80 °C for 30 minutes. Then, acetonitrile (0.5 ml) was added and stirred at 80 °C for 2 h. After removing all volatiles under reduced pressure, reprecipitation using gave complex A (4.2 mg, 33%) as an orange solid: $^1$H NMR δ 8.30-8.15 (m, 4H), 7.97-7.90 (m, 2H), 7.57-7.40 (m, 5H), 7.38-7.31 (m, 2H), 7.21-7.08 (m, 3H), 6.90-6.82 (m, 3H), 6.74-6.62 (m, 3H), 6.60-6.54 (m, 1H), 6.40-6.34 (m, 1H), 3.33-2.63 (m, 4H), 1.78 (s, 3H), 1.35 (t, $J = 6.8$ Hz, 2H), 1.03-0.93 (m, 2H), 0.80-0.64 (m, 4H), 0.71 (t, $J = 7.5$ Hz, 3H); $^{31}$P NMR δ 48.94 (d, $J_{PRh} = 100.3$ Hz), 42.87 (d, $J_{PRh} = 95.9$ Hz). HRMS(ESI) calcd for C$_{40}$H$_{42}$P$_2$RhS$_2$ (M): 751.1253; found: 751.1248.
iv) Copies of $^1$H NMR and $^{13}$C NMR spectra for new compounds

![Spectrum Image]

1a
n-C₃H₁₁

3ad

ppm (¹H)

ppm (¹³C)
3ak
3ga
$n$-C$_5$H$_{11}$

S-p-tolyl

6c
$\text{o-tolyl} - \text{n-C}_5\text{H}_{11}$

$7d$
vi) Copies of $^1$H NMR and $^{31}$P NMR spectra for complex A