

# The synthesis of new thiosubstituted butadienes, butenyne and butatrienes

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## Abstract

By treatment of the pentachlorobutadiene **1** and of the tetrachlorobromobutadiene **9** with thiolates in ethanol, a very fast and extensive replacement of chlorine was observed even at room temperature. The reaction of **1** with three molar equivalents of thiolates lead to butadienes with two, three, four and five organylthio groups. Tris(thio)-substituted butadienes **3a-c** tetrakis(thio)-substituted butadiene **4a** were treated with potassium *tert*-butoxide to form tris(thio)-substituted butatrienyl halide compounds **12a-c** and tetrakis(thio)-substituted butatriene **14a**, respectively. The butatrienyl halides **12a-c** obtained partly isomerizes to give butenyne **13a-c** at room temperature and without catalyst.

**Keywords:** Thiosubstituted butadienes, butenyne, butatrienes, thiols, HCl elimination

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## Introduction

Polyhalogenobutadienes have been used as model substrates for studying of the process of vinylic substitution ( $S_NVin$ ). There are various possibilities of the use of these compounds for the synthesis of numerous polyfunctional products. The reactions of *2H*- and *1H*-pentachlorobutadienes, 1,3-di-*H*- and 2,3-di-*H*-hexachlorobutenes with some thiols are well documented and mono- and polythiosubstituted compounds, mostly butadiene derivatives, have been obtained by this way.<sup>1-7</sup>

It is known that some thiosubstituted butadienes exhibit high biological activity. Industrial research has long focused on biological applications of thiosubstituted compounds as insecticides, herbicides, fungicides, and bactericides.<sup>8</sup> 5-lipoxygenase inhibition effect of 1-thiosubstituted butadienes also reported.<sup>9</sup> Butenyne and butatrienes are very valuable compounds for their use in polymer chemistry. Unlike alkanes and most alkenes, cumulenes tends to be rigid, which makes them appealing for molecular nanotechnology.<sup>10-12</sup> Thiosubstituted compounds are used as

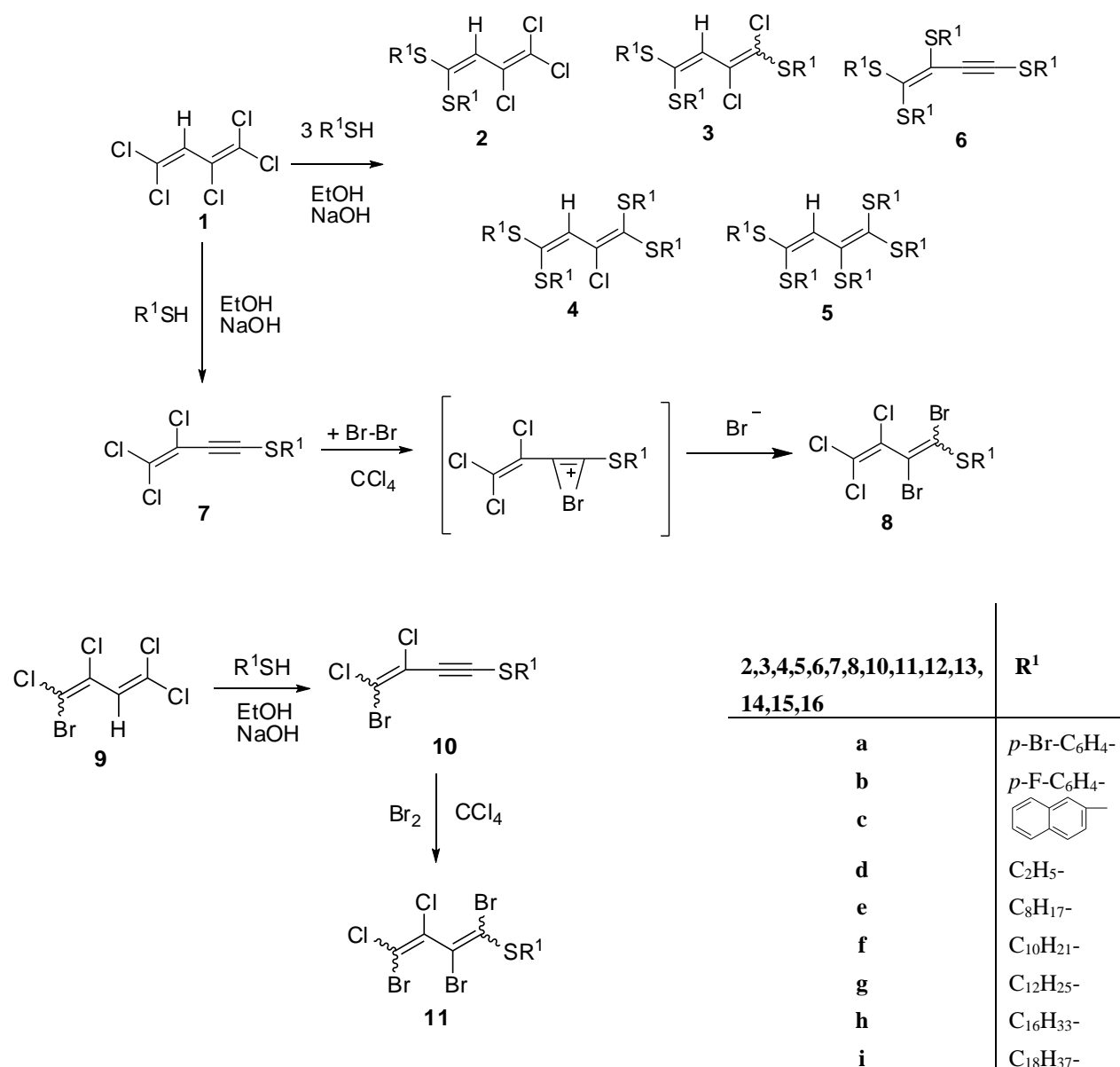
electronic conductors, ferromagnets, electron-accepting supramolecules, optical materials in material chemistry and as stabilizers in polymer chemistry.<sup>13</sup>

Schmidt et al. have synthesised thiosubstituted butatrienes and 1,3-butadienes from the reaction of a tetrakis(pyridinium)-substituted butadiene with some thiolates.<sup>14</sup> In an earlier study, Block et al. have used perchalcogenohydrocarbons as starting material to obtain perthio-1,3-butadienes, -1-buten-3-yne and -1,2,3-butatrienes.<sup>15</sup> In this work, we report another efficient method for the synthesis of novel thiosubstituted butadiene, butenyne and butatriene compounds.

## Results and Discussion

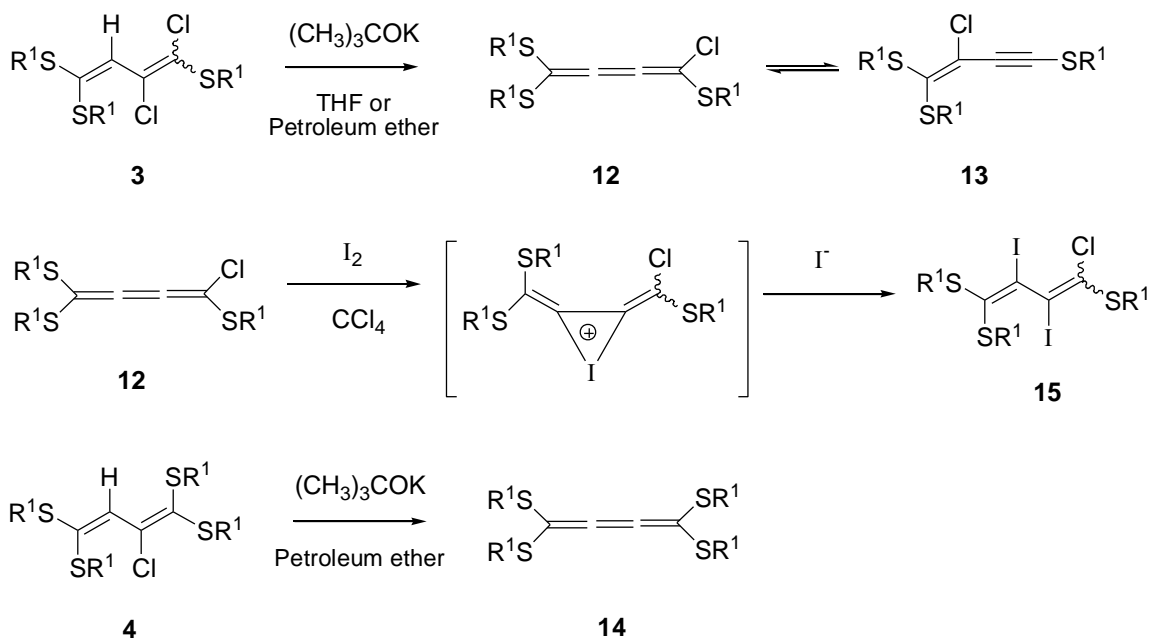
The reactions of 2*H*-pentachlorobutadiene with three molar equivalents of thiols in the presence of NaOH in ethanol at room temperature were carried out to give bis-, tris-, tetrakis- and pentakis(thio)-substituted butadienes, **2d**, **3a-c**, **4a**, **5a** and tetrakis(thio)-substituted butenyne **6d**. New mono(thio)-substituted butenyne compounds **7a**, **7c**, **7e-i** were obtained from the reactions of 2*H*-pentachlorobutadiene and **10e-i**, from the reactions of 2*H*-1,1,3,4-tetrachloro-4-bromobutadiene with one molar equivalent of thiols at the same reaction conditions. Monothiosubstituted polyhalogenobutadienes **8a**, **8c**, **8e-i** and **11h** were synthesized from the bromination of mono(thio)-substituted butenyne compounds in an apolar solvent (Scheme 1).

Compounds **3a**, **4a** and **5a** were obtained from the reaction of 2*H*-pentachlorobutadiene with three molar equivalents of thiol **a**. In the possible reaction mechanism of **5a**, it is thought that perchlorobutenyne formed by HCl elimination from 2*H*-pentachlorobutadiene firstly and then tetrakis(thio)-substituted butenyne and tetrakis(thio)-substituted butatriene intermediates were occurred via addition of four molar of thiol **a** to perchlorobutenyne. These intermediates both were stabilized by mesomery. In the last step of the mechanism, **5a** was obtained by addition of one molar of thiol **a** to tetrakis(thio)-substituted butenyne or tetrakis(thio)-substituted butatriene. <sup>1</sup>H-NMR spectra of **2d**, **3a-c**, **4a** and **5a** exhibited the presence of vinyl proton as a singlet at approximately 6.50 ppm. The mass spectrum of **3a** confirmed the estimated structure; two main peaks were observed at *m/z* 683.62 and 648.77 corresponding to [M]<sup>+</sup> and [M-Cl]<sup>+</sup>, respectively. The IR spectra of butenyne derivatives **6d**, **7a**, **7c**, **7e-i** and **10e-i** showed the characteristic strong band at 2147 and 2152 cm<sup>-1</sup> for C≡C group. In the <sup>13</sup>C-NMR spectra of these compounds, two alkyne carbons provide chemical shift values around 85.11 and 92.07 ppm. In the ESI-MS spectrum of **10h** showed a molecular ion peak at *m/z* 455.93 and the fragmentation of molecular ion peak at *m/z* 375 corresponding to the loss of a bromine atom. New thiosubstituted polyhalobutadiene compounds **8a**, **8c**, **8e-i** and **11e-i** were formed by the electrophilic addition of Br<sub>2</sub> to butenyne. It is evidence for succesful bromination reaction that the IR spectra of these compounds showed no absorbtion band around 2147 or 2152 cm<sup>-1</sup>.



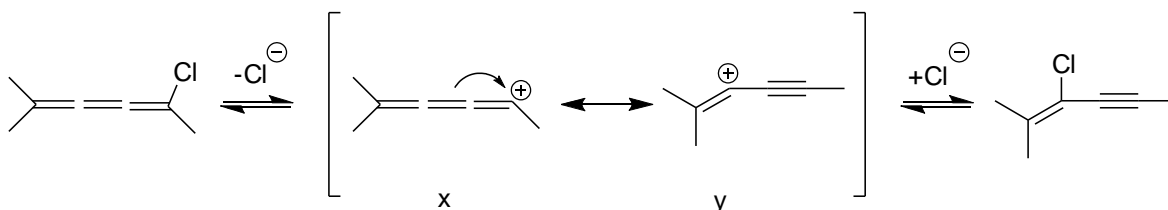
**Scheme 1.** General synthesis methods of butadienes and butenyne.

Tris(thio)-substituted butatriene compounds **12a-c** were formed by HCl elimination in the presence of potassium *tert*-butoxide from tris(thio)-substituted butadienes **3a-c**. These butatriene compounds **12a-c** partly isomerize to the tris(thio)-substituted butenyne **13a-c** even at room temperature, in a solvent medium. Tetrakis(thio)-substituted butatriene **14a**, obtained from **4a** by HCl elimination, is more stable than **12a-c**. This stability was proved by IR spectrum of **14a** that there was no typical absorption band at 2142-2157 cm<sup>-1</sup> region corresponding to C≡C group. Addition of I<sub>2</sub> to butatriene compounds **12a** and **14a** were performed in apolar solvent at room temperature to give **15a** and **16a**. Electrophilic addition reaction mechanism proceeds via an iodonium cation (Scheme 2).



**Scheme 2.** The synthesis and iodination of butatriene compounds.

The solvolysis of butatrienyl halides gives the ambident vinyl cation which has positive charge on a disubstituted carbon in both mesomeric structures (x and y). The possible isomerization mechanism of 1-chloro-1,4,4-tris(4-methylphenylthio)butatriene have been explained in the previous study by our group (Scheme 3).<sup>5</sup>



**Scheme 3.** The possible isomerization mechanism of butatrienyl halides to butenyne.

**12a** and **12c** obtained under the action of potassium *tert*-butoxide, are stable solid compounds. The peaks at 2037 and 2043  $\text{cm}^{-1}$  in the IR spectra of **12a** and **12c** was assigned to  $\text{C}=\text{C}=\text{C}=\text{C}$  stretching vibration, respectively. **12b**, yellow oily compound, easily isomerizes to 1-buten-3-yne **13b** at room temperature without catalyst. IR spectrum of **12b** showed  $\text{C}\equiv\text{C}$  stretching band at 2143  $\text{cm}^{-1}$  next to butatriene band at 2043  $\text{cm}^{-1}$ . However, in the solvent medium, stable butatrienyl halides **12a** and **12c** are solvolyzed to give the ambident allenyl cation which isomerizes to butenyne compounds **13a** and **13c**.

**12a-c** cannot be isolated from the isomeric mixture by the chromatographic techniques. IR, Mass spectra and elemental analyses results confirmed that these compounds are the isomeric mixture

of tris(thio)-substituted butatriene and tris(thio)-substituted butenyne. IR spectrum of the isomeric mixture of **12a** and **13a** showed characteristic absorption bands at 2037 and 2142  $\text{cm}^{-1}$  due to  $\text{C}=\text{C}=\text{C}$  and  $\text{C}\equiv\text{C}$  groups, respectively. The ESI-MS in the positive ion mode of the mixture of compounds **12a** and **13a**, displays an ion of  $m/z$  648.84 assigned to the protonated molecular ion peak  $[\text{M}+\text{H}]^+$ . The major ion of  $m/z$  459.90 in the ESI-MS/MS of **12a** and **13a** indicates the loss of  $-\text{SC}_6\text{H}_4\text{Br}$  group. The presence of isomer mixture was also confirmed by the  $^{13}\text{C}$ -NMR spectrum, in which more signals than expected chemical shifts were observed and two internal alkynes appeared at 86.24 and 93.19 ppm.

Thiosubstituted butadiene and butenyne compounds showed maximum absorption of the range 244-266 nm in  $\text{CHCl}_3$ , the maximum absorption wavelengths of butatriene compounds were observed between 367-392 nm.

## Experimental Section

**General.** Melting points were measured on Buchi B-540 capillary apparatus and are uncorrected. IR-spectras were recorded on Shimadzu FTIR-8101. NMR spectra were recorded on Varian Unity Inova 500 MHz. Mass spectra were obtained on a Thermo Finnigan LCQ Advantage MAX LC/MS/MS Spectrometer using ion-trap mass analyzer for both APCI or ESI source. UV spectra were recorded on UV-VIS Spectrophotometer TU-1901. Microanalyses were obtained by using a Carlo-Erba 1110 element analyser. Thin-layer chromatography (TLC) : E. Merck silica gel 60 F<sub>254</sub> foils. Column chromatography: Silica gel 60 ( particle size 0.063-0.20 mm, E. Merck ).

### General procedure 1

2*H*-pentachlorobutadiene **1** (1 g, 4.4 mmol) and thiols (13.2 mmol) were stirred in a mixture of EtOH (30 mL) and aqueous solution of NaOH (1.2 g and 8 ml water) for 30 min. at room temperature. Ether was added to the reaction mixture and the organic layer was separated, washed with water (4x30 mL), and dried with  $\text{MgSO}_4$ . The solvent was evaporated and the residue was purified by column chromatography over silica gel (petroleum ether/chloroform or petroleum ether).

**1,2-Dichloro-1,4,4-tris(4-bromophenylthio)-1,3-butadiene (3a).** Yield 40%; White solid, mp: 80-82°C.  $R_f$  (Petroleum ether): 0.35; IR (KBr,  $\text{cm}^{-1}$ ): 1580 (C=C), 3100 (=C-H<sub>arom</sub>); UV-vis( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  (log $\epsilon$ ) = 244 nm (5.1), 266 (5.0), 330 (4.8);  $^1\text{H}$  NMR (499.83 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.49 (s, 1H, vinyl-H), 7.02-7.42 (m, 12H, H<sub>arom</sub>);  $^{13}\text{C}$  NMR (125.68 MHz,  $\text{CDCl}_3$ ):  $\delta$  130.91, 131.01, 131.38, 131.45, 132.81, 133.05, 133.34, 133.40 (CH<sub>arom</sub>), 121.48, 122.12, 122.26, 126.32, 126.69, 130.32, 130.52, 130.91, 139.69 (C<sub>arom</sub> and C<sub>butad</sub>); MS (+ESI):  $m/z$  683.62  $[\text{M}]^+$ , 648.77  $[\text{M}-\text{Cl}]^+$ ;  $\text{C}_{22}\text{H}_{13}\text{S}_3\text{Cl}_2\text{Br}_3$  (M, 684.15). Calcd. C, 38.62; H, 1.91; S, 14.06. Found C, 38.61; H, 1.85; S, 14.66.

**2-Chloro-1,1,4,4-tetrakis(4-bromophenylthio)-1,3-butadiene (4a).** Yield 12%; Yellow solid, mp: 135-137°C.  $R_f$ [Petroleum ether/ $\text{CCl}_4$  (1:1)]: 0.42; IR (KBr,  $\text{cm}^{-1}$ ): 1502, 1563 (C=C), 3079 (=C- $\text{H}_{\text{arom}}$ );  $^1\text{H}$  NMR (499.83 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.76 (s, 1H, vinyl-H), 6.78-7.34 (m, 16H,  $\text{H}_{\text{arom}}$ );  $^{13}\text{C}$  NMR (125.68 MHz,  $\text{CDCl}_3$ ):  $\delta$  121.59, 122.61, 123.16, 123.20, 129.85, 130.98, 131.13, 131.79, 131.82, 132.03, 132.16, 132.21, 132.25, 132.52, 133.04, 133.96, 134.49, 135.41 ve 139.61 ( $\text{CH}_{\text{arom}}$ ,  $\text{C}_{\text{arom}}$  and  $\text{C}_{\text{butad}}$ );  $\text{C}_{28}\text{H}_{17}\text{S}_4\text{ClBr}_4$  (M, 836.76). Calcd. C, 40.19; H, 2.05; S, 15.33. Found C, 40.87; H, 1.95; S, 15.59.

**1,1,2,4,4-Pentakis(4-bromophenylthio)-1,3-butadiene (5a).** Yield 6%; Yellow solid, mp: 157-159°C.  $R_f$ [Petroleum ether/ $\text{CHCl}_3$  (1:1)]: 0.13, IR (KBr,  $\text{cm}^{-1}$ ): 1561 (C=C), 3074 (=C- $\text{H}_{\text{arom}}$ );  $^1\text{H}$  NMR (499.83 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.34 (s, 1H, vinyl-H), 6.81-7.44 (m, 20H,  $\text{H}_{\text{arom}}$ );  $^{13}\text{C}$  NMR (125.68 MHz,  $\text{CDCl}_3$ ):  $\delta$  121.92, 122.06, 122.64, 122.77, 123.07, 130.15, 131.28, 131.50, 131.90, 132.10, 132.27, 132.38, 132.51, 132.67, 133.20, 133.29, 134.06, 134.38, 135.17, 137.83, 141.31 ( $\text{CH}_{\text{arom}}$ ,  $\text{C}_{\text{arom}}$ ,  $\text{C}_{\text{butad}}$ );  $\text{C}_{34}\text{H}_{21}\text{S}_5\text{Br}_5$  (M, 989.39). Calcd. C, 41.28; H, 2.14; S, 16.20. Found C, 40.93; H, 2.05; S, 16.82.

**1,2-Dichloro-1,4,4-tris(4-fluorophenylthio)-1,3-butadiene (3b).** Yield 42%; Oil,  $R_f$ [Petroleum ether/ $\text{CHCl}_3$  (1:1)]: 0.40; IR (film,  $\text{cm}^{-1}$ ): 1589 (C=C), 3068 (=C- $\text{H}_{\text{arom}}$ ); UV-vis( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  (log $\epsilon$ ) = 257 nm (4.6), 326 (4.5);  $^1\text{H}$  NMR (499.83 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.48 (s, 1H, vinyl-H), 7.02-7.48 (m, 12H,  $\text{H}_{\text{arom}}$ );  $^{13}\text{C}$  NMR (125.68 MHz,  $\text{CDCl}_3$ ):  $\delta$  116.15, 116.32, 116.58, 116.65, 116.76, 116.83, 125.69, 127.03, 127.64, 128.36, 133.94, 135.19, 135.25, 135.71, 135.77, 135.98, 136.05, 142.56, 162.37, 164.13, 164.37 ( $\text{CH}_{\text{arom}}$ ,  $\text{C}_{\text{arom}}$  and  $\text{C}_{\text{butad}}$ ); MS (+ESI):  $m/z$  500.97 [ $\text{M}$ ] $^+$ , 464.96 [ $\text{M}-\text{Cl}$ ] $^+$ , 373.93 [ $\text{M}-\text{SC}_6\text{H}_4\text{F}$ ] $^+$ ;  $\text{C}_{22}\text{H}_{13}\text{Cl}_2\text{S}_3\text{F}_3$  (M, 500.7). Calcd. C, 52.69; H, 2.61; S, 19.18. Found C, 53.19; H, 2.99; S, 18.14.

**1,2-Dichloro-1,4,4-tris(2-naphtylthio)-1,3-butadiene (3c).** Yield 34%; White solid, mp: 143-145°C.  $R_f$ [Petroleum ether/ $\text{CCl}_4$  (1:1)]: 0.30; IR (KBr,  $\text{cm}^{-1}$ ): 1580 (C=C), 3050 (=C- $\text{H}_{\text{arom}}$ ); UV-vis( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  (log $\epsilon$ ) = 259 nm (4.9);  $^1\text{H}$  NMR (499.83 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.55 (s, 1H, vinyl-H), 7.25-7.84 (m, 21H,  $\text{H}_{\text{arom}}$ );  $^{13}\text{C}$  NMR (125.68 MHz,  $\text{CDCl}_3$ ):  $\delta$  126.71, 126.79, 126.86, 126.96, 127.09, 127.17, 127.80, 127.95, 127.99, 128.36, 128.61, 129.02, 129.11, 129.23, 129.66, 129.75, 129.88, 129.93, 130.11, 132.08, 132.29, 132.48, 132.99, 133.13, 133.19, 133.63, 133.74, 133.77, 142.11 ( $\text{CH}_{\text{arom}}$ ,  $\text{C}_{\text{arom}}$  and  $\text{C}_{\text{butad}}$ ); MS (+ESI):  $m/z$  597.80 [ $\text{M}$ ] $^+$ , 560.97 [ $\text{M}-\text{Cl}$ ] $^+$ ;  $\text{C}_{34}\text{H}_{22}\text{Cl}_2\text{S}_3$  (M, 597.64). Calcd. C, 68.33; H, 3.71; S, 16.10. Found C, 68.24; H, 3.82; S, 16.07.

**1,1,2-Trichloro-4,4-bis(*n*-ethylthio)-1,3-butadiene (2d).** Yield 41%; Oil,  $R_f$ (Hexane): 0.70; IR (film,  $\text{cm}^{-1}$ ): 1546 (C=C), 2870, 2927, 2971 (C-H).  $^1\text{H}$  NMR (499.83 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.18 (s, 1H, vinyl-H), 2.74-2.82 (m,  $J = 7.32$  Hz, 4H, S- $\text{CH}_2$ ), 1.19-1.25 (m,  $J = 7.32$  Hz, 6H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (125.68 MHz,  $\text{CDCl}_3$ ):  $\delta$  119.28, 121.53, 124.98, 142.34 ( $\text{C}_{\text{butad}}$ ), 12.86, 13.98 ( $\text{CH}_3$ ), 26.93, 27.03 ( $\text{CH}_2$ ); MS (+ESI):  $m/z$  279.41 [ $\text{M}+\text{H}$ ] $^+$ ;  $\text{C}_8\text{H}_{11}\text{Cl}_3\text{S}_2$  (M, 277.66); Calcd. C, 34.61; H, 3.99; S, 23.10. Found C, 34.92; H, 4.02; S, 23.65.

**1,1,2,4-Tetrakis(*n*-ethylthio)-1-buten-3-yne (6d).** Yield 27%; Oil,  $R_f$ (Hexane): 0.35; IR (film,  $\text{cm}^{-1}$ ): 1531 (C=C), 2144 (C $\equiv$ C), 2872, 2930, 2958 (C-H).  $^1\text{H}$  NMR (499.83 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.62-2.90 (m,  $J = 7.32$  Hz, 8H, S- $\text{CH}_2$ ), 1.18-1.47 (m,  $J = 7.32$  Hz, 12H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (125.68 MHz,  $\text{CDCl}_3$ ):  $\delta$  87.59, 89.40, 124.60, 139.82 ( $\text{C}_{\text{butenyne}}$ ); 27.59, 27.18, 27.03, 26.92 ( $\text{CH}_2$ ); 13.95,

13.93, 13.62, 13.13 (CH<sub>3</sub>); MS (+ESI): *m/z* 292.94 [M]<sup>+</sup>; C<sub>12</sub>H<sub>20</sub>S<sub>4</sub> (M, 292.55); Calcd. C, 49.27; H, 6.89; S, 43.84. Found 49.85; H, 6.02; S, 44.05.

### General procedure 2

2*H*-pentachlorobutadiene **1** (1 g, 4.4 mmol) or 2*H*-1,1,3,4-tetrachloro-4-bromobutadiene **9** (1 g, 3.7 mmol) and thiols (4.4 mmol for the reaction with **1**, 3.7 mmol for the reaction with **9**) were stirred in a mixture of EtOH (30 mL) and aqueous solution of NaOH (1.2 g and 8 ml water) for 30 min. at room temperature. Ether was added the reaction mixture. The organic layer was separated and washed with water (4x30 mL), and dried with MgSO<sub>4</sub>. The solvent was evaporated and the products were purified by column chromatography over silica gel (petroleum ether).

**1,1,2-Trichloro-4-(4-bromophenylthio)-1-buten-3-yne (7a)**. Yield 65%; White solid, mp: 68-69 °C. *R<sub>f</sub>* (Petroleum ether): 0.67; IR (KBr, cm<sup>-1</sup>): 2157 (C≡C), 3025 (=C-H<sub>arom</sub>); UV-vis(CHCl<sub>3</sub>): λ<sub>max</sub> (logε) = 266 nm (4.0); <sup>1</sup>H NMR (499.83 MHz, CDCl<sub>3</sub>): δ 7.20-7.45 (m, 4H, H<sub>arom</sub>); <sup>13</sup>C NMR (125.68 MHz, CDCl<sub>3</sub>): δ 128.50, 128.66, 132.67, 132.87 (CH<sub>arom</sub>), 87.78, 91.03, 112.85, 121.66, 130.39, 134.58 (C<sub>arom</sub> and C<sub>butenyne</sub>); EIMS: *m/z* 341.9 [M]<sup>+</sup>; C<sub>10</sub>H<sub>4</sub>Cl<sub>3</sub>SBr (M, 342.50). Calcd. C, 35.07; H, 1.17; S, 9.36. Found C, 35.67; H, 1.12; S, 9.25.

**1,1,2-Trichloro-4-(2-naphtylthio)-1-buten-3-yne (6c)**. Yield 43%; White solid, mp: 71-73 °C. *R<sub>f</sub>*(Petroleum ether): 0.71; IR (KBr, cm<sup>-1</sup>): 2149 (C≡C), 3032 (=C-H<sub>arom</sub>); UV-vis(CHCl<sub>3</sub>): λ<sub>max</sub> (logε) = 259 nm (5.2); <sup>1</sup>H NMR (499.83 MHz, CDCl<sub>3</sub>): δ 7.39-7.85 (m, 7H, H<sub>arom</sub>); <sup>13</sup>C NMR (125.68 MHz, CDCl<sub>3</sub>): δ 88.88, 90.67, 113.04, 124.64, 125.94, 126.74, 127.36, 127.52, 128.00, 128.13, 128.26, 129.63, 132.62, 133.97 (C<sub>arom</sub>, CH<sub>arom</sub>, C<sub>butenyne</sub>); C<sub>14</sub>H<sub>7</sub>Cl<sub>3</sub>S (M, 313.5). Calcd. C, 53.20; H, 2.85; S, 10.40. Found C, 53.68; H, 2.38; S, 9.63.

**1,1,2-Trichloro-4-(1-octylthio)-1-buten-3-yne (7e)**. Yield 52%; Oil, *R<sub>f</sub>* (Petroleum ether): 0.87; IR (film, cm<sup>-1</sup>): 2152 (C≡C), 2855, 2925 (C-H). UV-vis(CHCl<sub>3</sub>): λ<sub>max</sub> (logε) = 244 nm (4.6); <sup>1</sup>H NMR (499.83 MHz, CDCl<sub>3</sub>): δ 0.8 (t, *J* = 7.32 Hz, 3H, CH<sub>3</sub>), 1.2-1.4 (m, 10H, -(CH<sub>2</sub>)<sub>5</sub>-), 1.70 (m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>), 2.75 (t, *J* = 7.32, 2H, S-CH<sub>2</sub>) <sup>13</sup>C NMR (125.68 MHz, CDCl<sub>3</sub>): δ 13.04 (CH<sub>3</sub>); 21.62, 27.14, 27.99, 28.08, 28.33, 30.75, 35.09 (CH<sub>2</sub>); 85.08, 92.04, 112.01, 123.88 (C<sub>butenyne</sub>); EIMS: *m/z* 300.1 [M]<sup>+</sup>; C<sub>12</sub>H<sub>17</sub>Cl<sub>3</sub>S (M, 299.69); Calcd. C, 48.09; H, 5.72; S, 10.69. Found. C, 48.31; H, 5.82; S 10.44.

**1,1,2-Trichloro-4-(1-decylthio)-1-buten-3-yne (7f)**. Yield 41%; Oil, *R<sub>f</sub>* (Petroleum ether): 0.75; IR (film, cm<sup>-1</sup>): 2147 (C≡C), 2855, 2925 (C-H). UV-vis(CHCl<sub>3</sub>): λ<sub>max</sub> (logε) = 244 nm (4.1); <sup>1</sup>H NMR (499.83 MHz, CDCl<sub>3</sub>): δ 0.81 (t, *J* = 7.32Hz, 3H, CH<sub>3</sub>), 1.2-1.4 (m, 14H, -(CH<sub>2</sub>)<sub>7</sub>-), 1.69 (m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>), 2.73 (t, *J* = 7.32, 2H, S-CH<sub>2</sub>) <sup>13</sup>C NMR (125.68 MHz, CDCl<sub>3</sub>): δ 13.09 (CH<sub>3</sub>); 21.67, 27.15, 28.05, 28.09, 28.29, 28.44, 28.52, 30.89, 35.09 (CH<sub>2</sub>); 85.10, 92.07, 112.03, 123.84 (C<sub>butenyne</sub>); EIMS: *m/z* 326.1 [M]<sup>+</sup>; C<sub>14</sub>H<sub>21</sub>Cl<sub>3</sub>S (M, 327, 743); Calcd. C, 51.30; H, 6.46; S, 9.78. Found C, 51.37; H, 6.81; S, 9.93.

**1,1,2-Trichloro-4-(1-dodecylthio)-1-buten-3-yne (7g)**. Yield 48%; Oil, *R<sub>f</sub>* (Petroleum ether): 0.85; IR (film, cm<sup>-1</sup>): 2152 (C≡C), 2854, 2925 (C-H). UV-vis(CHCl<sub>3</sub>): λ<sub>max</sub> (logε) = 244 nm (5.1); <sup>1</sup>H NMR (499.83 MHz, CDCl<sub>3</sub>): δ 0.79 (t, *J*=7.32Hz, 3H, CH<sub>3</sub>), 1.2-1.4 (m, 18H, -(CH<sub>2</sub>)<sub>9</sub>-), 1.69 (m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>), 2.75 (t, *J* = 7.32, 2H, S-CH<sub>2</sub>) <sup>13</sup>C NMR (125.68 MHz, CDCl<sub>3</sub>): δ 13.07

(CH<sub>3</sub>); 21.67, 27.14, 28.03, 28.32, 28.34, 28.42, 28.54, 28.60, 28.62, 30.90, 35.10 (CH<sub>2</sub>); 85.10, 92.06, 112.02, 123.87 (C<sub>butenyne</sub>); EIMS: *m/z* 354.2 [M]<sup>+</sup>; C<sub>16</sub>H<sub>25</sub>Cl<sub>3</sub>S (M, 355.80); Calcd. C, 54.01; H, 7.08; S, 9.01. Found C, 54.14; H, 7.22; S, 9.49.

**1,1,2-Trichloro-4-(1-hexadecylthio)-1-buten-3-yne (7h).** Yield 32%; Oil, R<sub>f</sub> (Petroleum ether); 0.86; IR (film, cm<sup>-1</sup>): 2152 (C≡C), 2855, 2925 (C-H). UV-vis(CHCl<sub>3</sub>): λ<sub>max</sub> (logε) = 243 nm (4.1); <sup>1</sup>H NMR (499.83 MHz, CDCl<sub>3</sub>): δ 0.88 (t, *J* = 7.32Hz, 3H, CH<sub>3</sub>), 1.2-1.4 (m, 26H, -(CH<sub>2</sub>)<sub>13</sub>-), 1.76 (m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>), 2.80 (t, *J* = 7.32, 2H, S-CH<sub>2</sub>) <sup>13</sup>C NMR (125.68 MHz, CDCl<sub>3</sub>): δ 13.09 (CH<sub>3</sub>); 21.69, 27.15, 28.05, 28.08, 28.35, 28.36, 28.44, 28.47, 28.56, 28.64, 28.67, 28.69, 28.71, 30.93, 35.10 (CH<sub>2</sub>); 85.11, 92.07, 112.04, 123.86 (C<sub>butenyne</sub>); C<sub>20</sub>H<sub>33</sub>Cl<sub>3</sub>S (M, 411.50) Calcd. C, 58.30; H, 8.02; S, 7.77. Found. C, 58.25; H, 7.85; S, 7.55.

**1,1,2-Trichloro-4-(1-octadecylthio)-1-buten-3-yne (7i).** Yield 23%; Oil, R<sub>f</sub> (Petroleum ether); 0.82; IR (film, cm<sup>-1</sup>): 2157 (C≡C), 2855, 2925 (C-H). UV-vis(CHCl<sub>3</sub>): λ<sub>max</sub> (logε) = 243 nm (4.5); <sup>1</sup>H NMR (499.83 MHz, CDCl<sub>3</sub>): δ 0.86 (t, *J* = 7.32Hz, 3H, CH<sub>3</sub>), 1.2-1.4 (m, 30H, -(CH<sub>2</sub>)<sub>15</sub>-), 1.76 (m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>), 2.80 (t, *J* = 7.32, 2H, S-CH<sub>2</sub>) <sup>13</sup>C NMR (125.68 MHz, CDCl<sub>3</sub>): δ 13.09 (CH<sub>3</sub>); 21.69, 27.15, 27.54, 28.05, 28.09, 28.35, 28.37, 28.44, 28.47, 28.56, 28.59, 28.60, 28.64, 28.67, 28.71, 30.94, 35.10 (CH<sub>2</sub>); 85.11, 92.06, 112.03, 123.85 (C<sub>butenyne</sub>); C<sub>22</sub>H<sub>37</sub>Cl<sub>3</sub>S (M, 439.96) Calcd. C, 60.06; H, 8.47; S, 7.28. Found C, 60.61; H, 8.49; S, 7.29.

**1-Bromo-1,2-dichloro-4-(1-octylthio)-1-buten-3-yne (10e).** Yield 67%; Oil, R<sub>f</sub> (Petroleum ether): 0.85; IR(film, cm<sup>-1</sup>): 2146 (C≡C), 2855, 2956 (C-H). UV-vis(CHCl<sub>3</sub>): λ<sub>max</sub> (logε) = 242 nm (4.5); <sup>1</sup>H NMR (499.83 MHz, CDCl<sub>3</sub>): δ 0.82 (t, *J* = 7.32 Hz, 3H, CH<sub>3</sub>), 1.22-1.47 (m, 10H, -(CH<sub>2</sub>)<sub>5</sub>-), 1.70 (m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>), 2.74 (t, *J* = 7.32, 2H, S-CH<sub>2</sub>) <sup>13</sup>C NMR (125.68 MHz, CDCl<sub>3</sub>): δ 13.04 (CH<sub>3</sub>); 21.62, 27.14, 28.00, 28.08, 28.09, 30.75, 35.22 (CH<sub>2</sub>); 86.70, 91.37, 112.55, 123.27 (C<sub>butenyne</sub>); C<sub>12</sub>H<sub>17</sub>SCl<sub>2</sub>Br (M, 344.14); Calcd. C, 41.88; H, 4.98; S, 9.32. Found. C, 41.31; H, 5.02; S 9.63.

**1-Bromo-1,2-dichloro-4-(1-decylthio)-1-buten-3-yne (10f).** Yield 60%; Oil, R<sub>f</sub> (Petroleum ether): 0.77; IR(film, cm<sup>-1</sup>): 2146 (C≡C), 2855, 2925 (C-H). UV-vis(CHCl<sub>3</sub>): λ<sub>max</sub> (logε) = 242 nm (4.0); <sup>1</sup>H NMR (499.83MHz, CDCl<sub>3</sub>): δ 0.81 (t, *J*=7.32Hz, 3H, CH<sub>3</sub>), 1.2-1.4 (m, 14H, -(CH<sub>2</sub>)<sub>7</sub>-), 1.70 (m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>), 2.74 (t, *J*=7.32, 2H, S-CH<sub>2</sub>) <sup>13</sup>C NMR (125.68 MHz, CDCl<sub>3</sub>): δ 13.07 (CH<sub>3</sub>); 21.65, 27.13, 28.04, 28.27, 28.42, 28.43, 28.49, 30.87, 35.21 (CH<sub>2</sub>); 86.69, 92.23, 113.84, 123.27 (C<sub>butenyne</sub>); C<sub>14</sub>H<sub>21</sub>Cl<sub>2</sub>BrS (M, 372.19) Calcd. C, 45.18; H, 5.68; S, 8.61. Found C, 45.22; H, 5.42; S 8.42.

**1-Bromo-1,2-dichloro-4-(1-dodecylthio)-1-buten-3-yne (10g).** Yield 63%; Oil, R<sub>f</sub> (Petroleum ether): 0.82; IR (film, cm<sup>-1</sup>): 2147 (C≡C), 2853, 2924 (C-H). UV-vis(CHCl<sub>3</sub>): λ<sub>max</sub> (logε) = 243 nm (5.1); <sup>1</sup>H NMR (499.83 MHz, CDCl<sub>3</sub>): δ 0.81 (t, *J* = 7.32Hz, 3H, CH<sub>3</sub>), 1.19-1.35 (m, 18H, -(CH<sub>2</sub>)<sub>9</sub>-), 1.71 (m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>), 2.74 (t, *J* = 7.32, 2H, S-CH<sub>2</sub>) <sup>13</sup>C NMR (125.68 MHz, CDCl<sub>3</sub>): δ 13.08 (CH<sub>3</sub>); 21.67, 27.14, 28.05, 28.33, 28.40, 28.43, 28.55, 28.61, 28.62, 30.91, 35.04 (CH<sub>2</sub>); 86.70, 91.38, 112.54, 122.68 (C<sub>butenyne</sub>); C<sub>16</sub>H<sub>25</sub>Cl<sub>2</sub>BrS (M, 400.25); Calcd. C, 48.01; H, 6.29; S, 8.01. Found C, 47.96; H, 6.18; S, 8.27.

**1-Bromo-1,2-dichloro-4-(1-hexadecylthio)-1-buten-3-yne (10h).** Yield 50%; Oil, R<sub>f</sub> (Petroleum ether); 0.83; IR (film, cm<sup>-1</sup>): 2146 (C≡C), 2851, 2921 (C-H). UV-vis(CHCl<sub>3</sub>): λ<sub>max</sub>



(log $\epsilon$ ) = 244 nm (4.1);  $^1\text{H}$  NMR (499.83 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.81 (t,  $J = 7.32\text{Hz}$ , 3H,  $\text{CH}_3$ ), 1.2-1.4 (m, 26H,  $-(\text{CH}_2)_{13}-$ ), 1.71 (m, 2H,  $\text{S-CH}_2\text{-CH}_2$ ), 2.73 (t,  $J = 7.32$ , 2H,  $\text{S-CH}_2$ )  $^{13}\text{C}$  NMR (125.68 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.08 ( $\text{CH}_3$ ); 21.67, 27.13, 27.15, 28.04, 28.35, 28.40, 28.42, 28.44, 28.54, 28.62, 28.65, 28.67, 28.68, 30.92, 35.03 ( $\text{CH}_2$ ); 86.70, 92.24, 112.54, 124.10 ( $\text{C}_{\text{butenyne}}$ ); MS (+APCI):  $m/z$  455.93 [ $\text{M}$ ] $^+$ ;  $\text{C}_{20}\text{H}_{33}\text{Cl}_2\text{BrS}$  (M, 456.36); Calcd. C, 52.64; H, 7.29; S, 7.02. Found C, 52.69; H, 7.69; S, 7.58.

**1-Bromo-1,2-dichloro-4-(1-octadecylthio)-1-buten-3-yne (10i).** Yield 44%; Oil,  $R_f$  (Petroleum ether); 0.79; IR (film,  $\text{cm}^{-1}$ ): 2148 ( $\text{C}\equiv\text{C}$ ), 2853, 2923 ( $\text{C-H}$ ). UV-vis( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  (log $\epsilon$ ) = 244 nm (3.9);  $^1\text{H}$  NMR (499.83 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.81 (t,  $J = 7.32\text{Hz}$ , 3H,  $\text{CH}_3$ ), 1.2-1.4 (m, 30H,  $-(\text{CH}_2)_{15}-$ ), 1.71 (m, 2H,  $\text{S-CH}_2\text{-CH}_2$ ), 2.74 (t,  $J = 7.32$ , 2H,  $\text{S-CH}_2$ )  $^{13}\text{C}$  NMR (125.68 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.09 ( $\text{CH}_3$ ) 21.68, 27.13, 27.15, 28.04, 28.24, 28.33, 28.35, 28.39, 228.42, 28.44, 28.55, 28.63, 28.65, 28.67, 28.69, 30.92, 35.07 ( $\text{CH}_2$ ); 86.69, 91.36, 110.60, 125.47 ( $\text{C}_{\text{butenyne}}$ );  $\text{C}_{22}\text{H}_{37}\text{Cl}_2\text{BrS}$  (M, 484.41); Calcd. C, 54.55; H, 7.69; S, 6.62. Found C, 54.78; H, 7.67; S, 6.04.

### General procedure 3

Tris- or tetrakis-thiosubstituted butadiene compound (0.9 mmol) in 50 mL Petroleum ether (30-50  $^\circ\text{C}$ ) was mixed with potassium *tert*-butoxide (0.2 g, 1.8 mmol) for 4h at room temperature. For **12-13c**, Tetrahydrofuran was used as solvent instead of Petroleum ether. Ether and water added to the reaction mixture and then organic layer was separated, dried with anhydrous  $\text{MgSO}_4$ . The solvent was evaporated and the residue was purified by column chromatography over silica gel (petroleum ether/chloroform).

**1-Chloro-1,4,4-tris(4-bromophenylthio)-1,2,3-butatriene (12a)** and **2-Chloro-1,1,4-tris(4-bromophenylthio)-1-buten-3-yne (13a).** Yield 82%; Bright yellow crystalline solid, mp: 119-121 $^\circ\text{C}$ .  $R_f$  (Petroleum ether): 0.35; IR (KBr,  $\text{cm}^{-1}$ ): 2037, 859 ( $\text{C}=\text{C}=\text{C}=\text{C}$ ), 2142 ( $\text{C}\equiv\text{C}$ ), 1576 ( $\text{C}=\text{C}$ ), 3073 ( $=\text{C-H}_{\text{arom}}$ ). UV-vis( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  (log $\epsilon$ ) = 384 nm (4.9);  $^1\text{H}$  NMR (499.83 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.12-7.44 (m, 12H,  $\text{H}_{\text{arom}}$ )  $^{13}\text{C}$  NMR (125.68 MHz,  $\text{CDCl}_3$ ):  $\delta$  86.24, 93.19, 101.80, 115.53, 120.08, 120.76, 122.19, 122.49, 123.25, 127.17, 128.47, 128.97, 129.15, 129.81, 130.07, 130.22, 130.57, 130.83, 130.97, 131.23, 131.31, 131.45, 131.46, 131.47, 131.60, 132.19, 133.00, 134.23, 134.52, 137.53, 145.88, 153.13 ( $\text{C}_{\text{arom}}$ ,  $\text{CH}_{\text{arom}}$ ,  $\text{C}_{\text{butatriene}}$ ,  $\text{C}_{\text{butenyne}}$ ); MS (+ESI):  $m/z$  648.84 [ $\text{M}+\text{H}$ ] $^+$ ;  $\text{C}_{22}\text{H}_{12}\text{ClBr}_3\text{S}_3$  (M, 647.50); Calcd. C, 40.80; H, 1.85; S, 14.83. Found C, 40.67; H, 1.23; S, 15.03.

**1-Chloro-1,4,4-tris(4-fluorophenylthio)-1,2,3-butatriene (12b)** and **2-Chloro-1,1,4-tris(4-fluorophenylthio)-1-buten-3-yne (13b).** Yield 76%; Oil,  $R_f$  [Petroleum ether/ $\text{CHCl}_3$  (1:1)]: 0.40; IR (film,  $\text{cm}^{-1}$ ): 2043, 870 ( $\text{C}=\text{C}=\text{C}=\text{C}$ ), 2143 ( $\text{C}\equiv\text{C}$ ), 1589 ( $\text{C}=\text{C}$ ), 3068 ( $=\text{C-H}_{\text{arom}}$ ). UV-vis( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  (log $\epsilon$ ) = 316 nm (5.0);  $^1\text{H}$  NMR (499.83 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.12-7.51 (m, 12H,  $\text{H}_{\text{arom}}$ )  $^{13}\text{C}$  NMR (125.68 MHz,  $\text{CDCl}_3$ ):  $\delta$  86.07, 93.75, 110.00, 114.69, 115.93, 116.11, 116.29, 116.57, 116.75, 116.82, 126.95, 127.49, 128.53, 129.10, 129.16, 130.94, 132.51, 132.57, 133.90, 133.97, 135.12, 135.92, 135.99, 136.58, 140.26, 143.03, 161.64, 162.35, 163.37, 163.62, 164.33, 164.43 ( $\text{C}_{\text{arom}}$ ,  $\text{CH}_{\text{arom}}$ ,  $\text{C}_{\text{butatriene}}$ ,  $\text{C}_{\text{butenyne}}$ ); MS (+ESI):  $m/z$  465.13 [ $\text{M}$ ] $^+$ ;  $\text{C}_{22}\text{H}_{12}\text{ClF}_3\text{S}_3$  (M, 464.97); Calcd. C, 56.83; H, 2.60; S, 20.69. Found C, 57.0; H, 2.93; S, 21.07.

**1-Chloro-1,4,4-tris(2-naphthylthio)-1,2,3-butatriene (12c)** and **2-Chloro-1,1,4-tris(2-naphthylthio)-1-buten-3-yne (13c)**. Yield 67%; Yellow crystalline solid, mp: 185-187 °C.  $R_f$  [Petroleum ether/ $\text{CHCl}_3$  (1:1)]: 0.30; IR (KBr,  $\text{cm}^{-1}$ ): 2043, 856 (C=C=C=C), 2141 (C≡C), 1588 (C=C), 3055 (=C-H<sub>arom</sub>). UV-vis( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 392 nm (4.2);  $^1\text{H}$  NMR (499.83 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.29–7.85 (m, 21H, H<sub>arom</sub>)  $^{13}\text{C}$  NMR (125.68 MHz,  $\text{CDCl}_3$ ):  $\delta$  84.02, 94.63, 115.05, 124.39, 125.35, 126.34, 126.55, 126.60, 126.69, 126.72, 126.76, 126.78, 126.83, 126.86, 126.91, 126.93, 127.04, 127.06, 127.07, 127.14, 127.42, 127.63, 127.78, 127.80, 127.87, 127.89, 127.90, 127.92, 127.97, 128.03, 128.32, 128.57, 128.62, 128.99, 129.01, 129.08, 129.20, 129.28, 129.64, 129.72, 129.86, 129.90, 129.91, 130.06, 131.14, 132.06, 132.26, 132.46, 133.16, 134.30 (C<sub>arom</sub>, CH<sub>arom</sub>, C<sub>butatriene</sub>, C<sub>butenyne</sub>); MS (+APCI):  $m/z$  561.31 [M]<sup>+</sup>; C<sub>43</sub>H<sub>21</sub>ClS<sub>3</sub> (M, 561.18); Calcd. C, 72.77; H, 3.77; S, 17.14. Found C, 73.21; H, 3.93; S, 17.07.

**1,1,4,4-Tetrakis(4-bromophenylthio)butatriene (14a)**. Yield 94%; Bright yellow crystalline solid, mp: 179-181°C.  $R_f$  [Petroleum ether/ $\text{CCl}_4$  (1:1)]: 0.42; IR (KBr): 867 (C=C=C=C), 3048 (=C-H<sub>arom</sub>).  $^1\text{H}$  NMR (499.83MHz,  $\text{CDCl}_3$ ):  $\delta$  7.09 (d, 8H, H<sub>arom</sub>), 7.31 (d, 8H, H<sub>arom</sub>);  $^{13}\text{C}$  NMR (125.68 MHz,  $\text{CDCl}_3$ ):  $\delta$  109.76, 122.07, 130.70, 131.30, 132.69 and 149.91 (C<sub>arom</sub>, CH<sub>arom</sub> and C<sub>butatriene</sub>); MS (+ESI):  $m/z$  800.11 [M]<sup>+</sup>; C<sub>28</sub>H<sub>16</sub>Br<sub>4</sub>S<sub>4</sub> (M, 800.30). Calcd. C, 40.80; H, 1.85; S, 14.83. Found C, 40.67; H, 1.23; S, 15.03.

#### General procedure 4

Monothiosubstituted butenyne compound (1.5 mmol) and bromine (0.25 g, 1.5 mmol) were stirred in  $\text{CCl}_4$  (30mL) for 3h at room temperature. Ether was added to the reaction mixture and extracted with 100 ml of 3% aqueous solution of  $\text{Na}_2\text{S}_2\text{O}_5$  twice. The organic layer was separated, washed with water (4x30 mL), dried with anhydrous  $\text{MgSO}_4$ . The solvent was evaporated and the residue was purified by column chromatography over silica gel (petroleum ether).

**1,2-Dibromo-3,4,4-trichloro-1-(4-bromophenylthio)-1,3-butadiene 8a**. Yield 82%; White solid, mp: 60-62 °C.  $R_f$  (Petroleum ether): 0.67; IR (film,  $\text{cm}^{-1}$ ): 1599, 1564 (C=C), 3080 (=C-H<sub>arom</sub>); UV-vis( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 243 (4.02);  $^1\text{H}$  NMR (499.83MHz,  $\text{CDCl}_3$ ):  $\delta$  7.18-7.48 (m, 4H, H<sub>arom</sub>);  $^{13}\text{C}$  NMR (125.68 MHz,  $\text{CDCl}_3$ ):  $\delta$  111.62, 119.87, 121.83, 123.36, 129.67, 131.57, 131.78, 132.88, 134.79; C<sub>10</sub>H<sub>4</sub>Br<sub>3</sub>Cl<sub>3</sub>S (M, 502, 27) Calcd. C, 23.91; H, 0.80; S, 6.38. Found C, 24.51; H, 0.86; S, 6.75.

**1,2-Dibromo-3,4,4-trichloro-1-(2-naphthylthio)-1,3-butadiene (8c)**. Yield 63%; White solid, mp: 65-67 °C.  $R_f$  (Petroleum ether): 0.71; IR (KBr,  $\text{cm}^{-1}$ ): 1585, 1538 (C=C), 3054 (=C-H<sub>arom</sub>); UV-vis( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 241 (4.05);  $^1\text{H}$  NMR (499.83MHz,  $\text{CDCl}_3$ ):  $\delta$  7.16-7.92 (m, 7H, H<sub>arom</sub>);  $^{13}\text{C}$  NMR (125.68 MHz,  $\text{CDCl}_3$ ):  $\delta$  110.75, 118.94, 122.85, 125.97, 126.28, 126.44, 126.84, 126.97, 127.80, 128.03, 129.43, 131.15, 132.94; C<sub>14</sub>H<sub>7</sub>Br<sub>2</sub>Cl<sub>3</sub>S (M, 473.44) Calcd. C, 35.52; H, 1.49; S, 6.77. Found C, 34.92; H, 1.03; S, 7.22.

**1,2-Dibromo-3,4,4-trichloro-1-(1-octylthio)-1,3-butadiene (8e)**. Yield 65%; Oil,  $R_f$  (Petroleum ether): 0.85; IR (film,  $\text{cm}^{-1}$ ): 2855, 2927 (C-H), 1538, 1599 (C=C), UV-vis( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 246 nm (5.3);  $^1\text{H}$  NMR (499.83 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.8 (t,  $J$  = 7.32Hz, 3H, CH<sub>3</sub>), 1.20-1.35 (m, 10H, -(CH<sub>2</sub>)<sub>5</sub>-), 1.58 (m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>), 2.89 (t,  $J$  = 7.32, 2H, S-CH<sub>2</sub>)  $^{13}\text{C}$  NMR (125.68 MHz,

CDCl<sub>3</sub>):  $\delta$  13.05 (CH<sub>3</sub>); 21.61, 27.46, 28.00, 28.04, 28.08, 30.74, 35.76 (CH<sub>2</sub>); 109.84, 116.85, 123.69, 128.43 (C<sub>butadiene</sub>); C<sub>12</sub>H<sub>17</sub>Cl<sub>3</sub>Br<sub>2</sub>S (M, 459.50) Calcd. C, 31.37; H, 3.73; S, 6.98. Found C, 31.61; H, 3.49; S, 7.09.

**1,2-Dibromo-3,4,4-trichloro-1-(1-decylthio)-1,3-butadiene (8f).** Yield 78%; Oil, R<sub>f</sub> (Petroleum ether): 0.75; IR (film, cm<sup>-1</sup>): 2854, 2924 (C-H), 1538, 1599 (C=C), UV-vis(CHCl<sub>3</sub>):  $\lambda_{\max}$  (log $\epsilon$ ) = 244nm (5.1); <sup>1</sup>H NMR (499.83 MHz, CDCl<sub>3</sub>):  $\delta$  0.81 (t, *J* = 7.32Hz, 3H, CH<sub>3</sub>), 1.19-1.34 (m, 10H, -(CH<sub>2</sub>)<sub>5</sub>-), 1.58 (m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>), 2.89 (t, *J* = 7.32, 2H, S-CH<sub>2</sub>) <sup>13</sup>C NMR (125.68 MHz, CDCl<sub>3</sub>):  $\delta$  13.08 (CH<sub>3</sub>); 21.65, 28.05, 28.08, 28.27, 28.42, 28.49, 28.62, 30.87, 35.75 (CH<sub>2</sub>); 109.82, 116.85, 123.69, 128.48 (C<sub>butadiene</sub>); C<sub>14</sub>H<sub>21</sub>Cl<sub>3</sub>Br<sub>2</sub>S (M, 487.50) Calcd. C, 34.46; H, 4.30; S, 6.56. Found C, 34.09; H, 4.97; S, 7.08.

**1,2-Dibromo-3,4,4-trichloro-1-(1-dodecylthio)-1,3-butadiene (8g).** Yield 92%; Oil, R<sub>f</sub> (Petroleum ether); 0.90; IR (film, cm<sup>-1</sup>): 1598, 1539 (C=C), 2854, 2954 (C-H). UV-vis(CHCl<sub>3</sub>):  $\lambda_{\max}$  (log $\epsilon$ ) = 243 nm (5.0); <sup>1</sup>H NMR (499.83 MHz, CDCl<sub>3</sub>):  $\delta$  0.82 (t, *J* = 7.32Hz, 3H, CH<sub>3</sub>), 1.19-1.34 (m, 26H, -(CH<sub>2</sub>)<sub>13</sub>-), 1.58 (m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>), 2.92 (t, *J* = 7.32, 2H, S-CH<sub>2</sub>) <sup>13</sup>C NMR (125.68 MHz, CDCl<sub>3</sub>):  $\delta$  13.09 (CH<sub>3</sub>); 21.67, 27.45, 28.04, 28.07, 28.32, 28.41, 28.45, 28.53, 28.61, 30.90, 35.75 (CH<sub>2</sub>); 109.81, 116.85, 123.69, 128.48 (C<sub>butadiene</sub>); C<sub>16</sub>H<sub>25</sub>Cl<sub>3</sub>Br<sub>2</sub>S (M, 515.50) Calcd. C, 37.24; H, 4.84; S, 6.20. Found C, 38.01; H, 4.85; S, 6.55.

**1,2-Dibromo-3,4,4-trichloro-1-(1-hexadecylthio)-1,3-butadiene (8h).** Yield 86%; Oil, R<sub>f</sub> (Petroleum ether); 0.86; IR (film, cm<sup>-1</sup>): 1598 (C=C), 2853, 2923 (C-H). UV-vis(CHCl<sub>3</sub>):  $\lambda_{\max}$  (log $\epsilon$ ) = 245 nm (4.8); <sup>1</sup>H NMR (499.83 MHz, CDCl<sub>3</sub>):  $\delta$  0.81 (t, *J* = 7.32Hz, 3H, CH<sub>3</sub>), 1.18-1.35 (m, 26H, -(CH<sub>2</sub>)<sub>13</sub>-), 1.56 (m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>), 2.89 (t, *J* = 7.32, 2H, S-CH<sub>2</sub>) <sup>13</sup>C NMR (125.68 MHz, CDCl<sub>3</sub>):  $\delta$  13.09 (CH<sub>3</sub>); 21.68, 27.45, 28.04, 28.07, 28.35, 28.41, 28.46, 28.53, 28.62, 28.65, 28.67, 28.68, 28.69, 30.92, 35.75 (CH<sub>2</sub>); 109.82, 116.85, 123.68, 128.47 (C<sub>butadiene</sub>); C<sub>20</sub>H<sub>33</sub>Cl<sub>3</sub>Br<sub>2</sub>S (M, 571.50) Calcd. C, 42.03; H, 5.78; S, 5.60. Found C, 41.95; H, 5.85; S, 5.55.

**1,2-Dibromo-3,4,4-trichloro-1-(1-otcadecylthio)-1,3-butadiene (8i).** Yield 76%; Oil, R<sub>f</sub> (Petroleum ether); 0.80; IR (film, cm<sup>-1</sup>): 2855, 2925 (C-H), 1550 (C=C). UV-vis(CHCl<sub>3</sub>):  $\lambda_{\max}$  (log $\epsilon$ ) = 244 nm (4.4); <sup>1</sup>H NMR (499.83 MHz, CDCl<sub>3</sub>):  $\delta$  0.81 (t, *J* = 7.32Hz, 3H, CH<sub>3</sub>), 1.18-1.38 (m, 30H, -(CH<sub>2</sub>)<sub>15</sub>-), 1.58 (m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>), 2.92 (t, *J* = 7.32, 2H, S-CH<sub>2</sub>) <sup>13</sup>C NMR (125.68 MHz, CDCl<sub>3</sub>):  $\delta$  13.09 (CH<sub>3</sub>); 21.68, 27.46, 27.53, 28.04, 28.08, 28.35, 28.42, 28.46, 28.53, 28.62, 28.63, 28.65, 28.67, 28.69, 28.76, 30.92, 35.76 (CH<sub>2</sub>); 109.84, 116.85, 123.69, 128.48 (C<sub>butadiene</sub>); C<sub>22</sub>H<sub>37</sub>Cl<sub>3</sub>Br<sub>2</sub>S (M, 599.77) Calcd. C, 44.05; H, 6.22; S, 5.34. Found C, 44.52; H, 6.35; S, 5.12.

**1,2-Dibromo-3,4,4-trichloro-1-(1-hexadecylthio)-1,3-butadiene (11h).** Yield 88%; Oil, R<sub>f</sub> (Petroleum ether); 0.83; IR (film, cm<sup>-1</sup>): 1594 (C=C), 2853, 2923 (C-H). UV-vis(CHCl<sub>3</sub>):  $\lambda_{\max}$  (log $\epsilon$ ) = 244 nm (5.3); <sup>1</sup>H NMR (499.83 MHz, CDCl<sub>3</sub>):  $\delta$  0.81 (t, *J* = 7.32Hz, 3H, CH<sub>3</sub>), 1.19-1.35 (m, 26H, -(CH<sub>2</sub>)<sub>13</sub>-), 1.58 (m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>), 2.89 (t, *J* = 7.32, 2H, S-CH<sub>2</sub>) <sup>13</sup>C NMR (125.68 MHz, CDCl<sub>3</sub>):  $\delta$  13.11 (CH<sub>3</sub>); 21.69, 27.46, 28.06, 28.10, 28.36, 28.43, 28.44, 28.47, 28.55, 28.63, 28.66, 28.68, 28.70, 30.93, 35.75 (CH<sub>2</sub>); 109.58, 118.25, 123.64, 128.41 (C<sub>butadiene</sub>); C<sub>20</sub>H<sub>33</sub>Cl<sub>2</sub>Br<sub>3</sub>S (M, 616.36); Calcd. C, 38.93; H, 5.35; S, 5.19. Found C, 38.25; H, 5.69; S, 4.97.

### General procedure 5

Arylthiosubstituted butatriene compound (1.5 mmol) and iodine (0.38 g, 1.5 mmol) were stirred in  $\text{CCl}_4$  (30 mL) for 3h at room temperature. Ether was added to the reaction mixture and extracted with 100 ml of 3% aqueous solution of  $\text{Na}_2\text{S}_2\text{O}_5$  twice. The organic layer was separated, washed with water (4x30 mL), dried with anhydrous  $\text{MgSO}_4$ . The solvent was evaporated and the residue was purified by column chromatography over silica gel (petroleum ether/chloroform).

**1-Chloro-2,3-diiodo-1,4,4-tris(4-bromophenylthio)-1,3-butadiene (15a).** Yield 87%; Oil,  $R_f$  (Petroleum ether): 0.35; IR (film,  $\text{cm}^{-1}$ ): 1563 (C=C), 3077 (=C-H<sub>arom</sub>).  $^1\text{H}$  NMR (499.83 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.84-7.46 (m, 12H, H<sub>arom</sub>);  $^{13}\text{C}$  NMR (125.68 MHz,  $\text{CDCl}_3$ ):  $\delta$  61.92, 67.46, 99.76, 102.30, 102.54, 102.79, 121.41, 121.65, 121.70, 122.58, 129.37, 129.86, 130.19, 130.47, 130.49, 130.55, 130.60, 130.69, 130.73, 130.76, 130.80, 131.50, 131.54, 131.61, 132.20, 132.30, 133.07, 133.13, 133.18, 133.39, 133.84, 133.92, 134.18, 138.46, 139.45; (CH<sub>arom</sub>, C<sub>arom</sub>, C<sub>butadiene</sub>) MS (+ESI):  $m/z$  775.32 [M-I]<sup>+</sup>;  $\text{C}_{22}\text{H}_{12}\text{Br}_3\text{ClI}_2\text{S}_3$  (M, 901.50); Calcd. C, 29.31; H, 1.34; S, 10.67. Found C, 29.88; H, 1.93; S, 11.09.

**2,3-Diiodo-1,1,1,4-tetrakis(4-bromophenylthio)-1,3-butadiene (16a).** Yield 76%; Light yellow crystalline solid, mp: 135-137 °C;  $R_f$  [Petroleum ether/ $\text{CCl}_4$  (1:1)]: 0.42; IR (KBr,  $\text{cm}^{-1}$ ): 1564 (C=C), 3076 (=C-H<sub>arom</sub>).  $^1\text{H}$  NMR (499.83 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.88-7.25 (m, 16H, H<sub>arom</sub>);  $^{13}\text{C}$  NMR (125.68 MHz,  $\text{CDCl}_3$ ):  $\delta$  131.98, 132.02, 133.58, 134.16 (CH<sub>arom</sub>), 68.40, 106.04, 122.67, 122.74, 131.81, 139.28 (C<sub>arom</sub> and C<sub>butadiene</sub>); MS (+ESI):  $m/z$  1052 [M]<sup>+</sup>;  $\text{C}_{28}\text{H}_{16}\text{Br}_4\text{I}_2\text{S}_4$  (M, 1054.11). Calcd. C, 31.90; H, 1.53; S, 12.17. Found C, 32.23; H, 1.75; S, 12.88.

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