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The Synthesis and Characterization of Some Novel Thioethers: Thio-Subsituted [3]Cumulenes, -1-Buten-3-ynes and Buta-1,3-dienes

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In this study, some novel thiosubstituted butenyne (**3a-d**, **7b**, **15b**), butadiene (**4a-b**, **4d**, **5a**, **5c**, **6b**, **8e**, **9c**, **10b**, **16b**, **18e**) and [3]cumulene (**11a-b** with isomer **3a-b**, **12a** with isomer **13a**, **14b**, **17e**) compounds were synthesized from the reaction of 2*H*-pentachloro-1,3-butadiene with thiols. The new compounds were characterized by elemental analysis, mass spectrometry, UV-vis, IR, ^{1}H NMR, NMR (^{13}C or APT) spectroscopy.

Key Words: 2*H*-Pentachloro-1,3-butadiene, Dienes and butenynes, [3]Cumulenes, Thioethers

Introduction

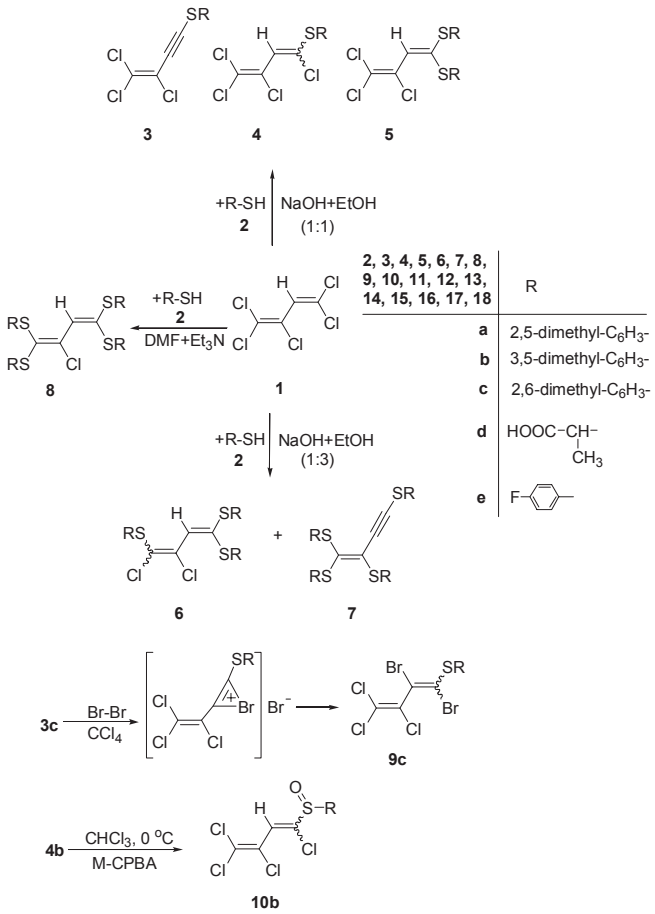
The ability to synthesize thioether functional groups is of special interest because of their importance in organic synthesis as a key entry point into many biologically active compounds.[1] Also, it was reported in the US patent that some tetrakismethyl (thio)substituted butadiene compounds exhibit interesting biological activity.[2] Furthermore, compounds with high sulfur content have received considerable attention because they play a crucial role in material chemistry, biochemistry, nanochemistry and polymer chemistry.[3] In addition, it is known that sulfoxides[4] and 1,3-Enynes[5] are useful synthetic intermediates in the synthesis of natural products.

It has been reported that some bis-, tris-, tetrakis-(thio)subsituted diene, triene and butenyne compounds were synthesized from polyhalodienes or butadiynes.[6-16] We describe herein the synthesis of mono-, bis-, tris- or tetrakis-(thio)substituted butadienes, butenynes and [3]cumulenes and their bromination, iodination or oxidation.

Results and Discussion

As shown Scheme 1, reactions of 2*H*-1,1,3,4,4-pentachloro-1,3-butadiene (Cl_2C=CH-CCl=CCl_2) **1** with dimethylbenzenethiols **2a-c** in EtOH in the presence of NaOH gave compounds **3a-c**, **4a-b**, **5a**, **5c**, **6b** and **7b**. The reaction of **1** with 2-mercaptopropionic acid **2d** under the same reaction condition provided **3d** and **4d**. The IR spectrum of compounds **3a-d** and **7b** show characteristic absorptions of acetylenic (C≡C) groups at around 2150 cm^{-1}. Also, the APT NMR signals of compounds **3a-d** and **7b** at about 80 and 90 ppm were assigned to the acetylenic groups. In the possible reaction mechanism, it is thougth that perchlorobutenyne was formed from the HCl elimination of compound **1**. The compounds **3a-d** and **7b** were constituted from the substitution of perchlorobutenyne compound.

Treatment of **3c** with bromine resulted in the formation of dibromo-mono(thio)substituted butadiene compound **9c**. In the IR and APT NMR spectra of **9c**, the disapperance of C≡C signals were a clear evidence for butadiene formation through bromination. Also, 2*H*-pentachloro-1,3-butadiene **1** reacted with **2e** to give tetrakis(thio)subsituted thioether **8e** in the presence of triethylamine, under the different reaction condition in the literature.[17] The singlet peak at 5.2 - 6.9 ppm in the ^{1}H NMR spectrum were assigned to the vinyl proton for compounds **4a-b**, **4d**, **5a**, **5c**, **6b**, **8e**, **10b**. Oxidation of sulfide compound **4b** was carried out using with 1 equivalent of metachloroperbenzoic acid (M-CPBA) to yield the sulfoxide compound **10b** at 0 °C. The IR spectrum of **10b** showed characteristic absorption of



Scheme 1. Formation of dienes and butenynes from **1**, bromination of **3c** and oxidation of **4b**

S=O group at 1076 cm^{-1}.

There are limited reports in the literature on the synthesis of (thio)subsituted [3]cumulene compounds. Herein, we report the synthesis of novel mono-, bis-, tris- and tetrakis-(thio) substituted [3]cumulene compounds by the reaction of thio(substituted)-buta-1,3-diene with thiols. As shown Scheme 2, some synthesized [3]cumulene compounds converted into partially butenyne compounds. It is known that an allenyl cation is involved as an intermediate in the room-temperature isomerization of butatriene to butenyne.[9,18]

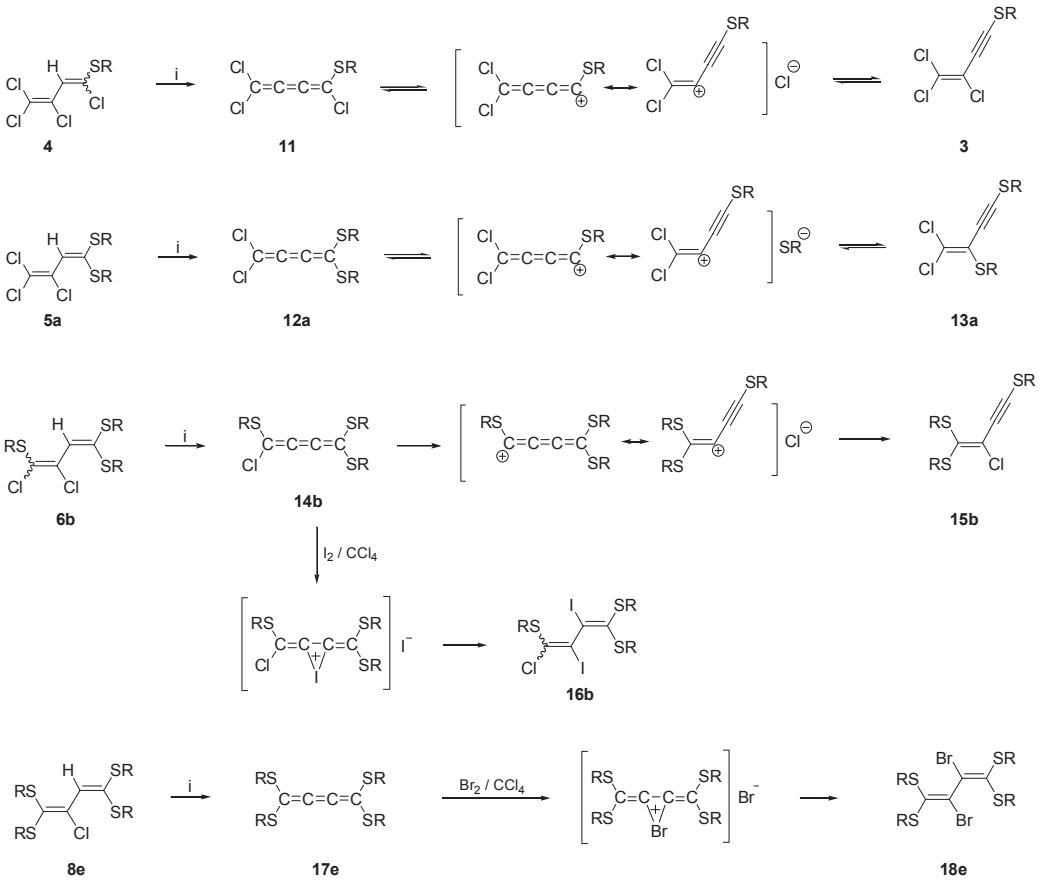
As shown Scheme 3, reaction of **4a-b** with potassium *tert*-butoxide resulted in the isomeric mixtures of mono(thio)-substituted [3]cumulenes (**11a-b**) and mono(thio)-substituted butenynes (**3a-b**). Similarly, reaction of **5a** with potassium *tert*-butoxide resulted in the isomer mixture of bis(thio)-substituted [3]cumulene (**12a**) and bis(thio)-substituted butenyne (**13a**). But, treatment of **6b** with potassium *tert*-butoxide resulted in the formation of tris(thio)-substituted [3]cumulene (**14b**). Compound **14b** was isolated but then it converted into tris(thio)-substituted butenyne compound (**15b**) at room temperature by solvolysis of butatrienyl cation.

Scheme 2. The butatrienyl cation with mesomeric form of vinyl cation

The IR spectrum of isomeric mixtures (**11a-b** with **3a-b**, **12a** with **13a**) showed characteristic buta-1,2,3-triene (C=C=C=C) absorptions at around 2060 cm^{-1} and C≡C absorptions at around 2150 cm^{-1}. Tris- and tetrakis (thio)-substituted [3]cumulenes (**14b** and **17e**) showed characteristic buta-1,2,3-triene (C=C=C=C) absorptions at around 2040 cm^{-1}. In the ^{1}H NMR spectrum of [3]cumulenes, the disapperance of vinyl proton signals are a clear evidence for buta- 1,2,3-trienes formation through HCl elimination. The GC-MS (+EI) spectrum obtained for **11a** and **3a** isomer mixture is shown in Figure 1(a). This isomer mixture showed a molecular ion of m/z = 291.8 ($C_{12}H_9Cl_3S$, 291.6 g·mol^{-1}). As shown in Figure 1(b), the absorption bands at 2061 cm^{-1} and 2155 cm^{-1} indicate the coexistence of buta-1,2,3-triene (C=C=C=C) and acetylenic (C≡C) groups in the isomer mixture (**11a** and **3a**), respectively. Also, treatment of **14b** and **17e** with iodine and bromine, respectively, resulted in the formations of diiodo- and dibromo-(thio)substituted butadiene compounds **16b** and **18e**. All compounds's structures are in accordance with the data given in the experimental part.

Experimental

Infrared spectra (IR) were measured using Perkin Elmer Precisely Spectrum One FTIR instrument. Mass spectra (MS) were recorded on a Thermo Finnigan LCQ Advantage MAX system using ion-trap mass analyzer for ESI source. GC-MS



Scheme 3. Formation of mono-, bis-, tris-, and tetrakis-(thio)subsituted buta-1,2,3-triene compounds (i: $(CH_3)_3COK$, Petroleum ether), iodination of **14b** and bromination of **17e**

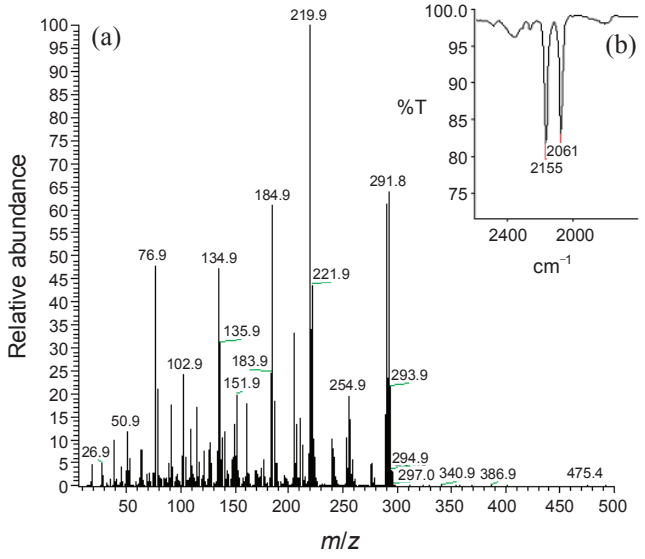


Figure 1. GC-MS (+EI) spectra (a) and FTIR spectra (b) of **11a** and **3a** isomer mixture.

spectra were obtained on a Thermo Finnigan Trace DSQ system equipped with an EI source. ^{1}H NMR, ^{13}C NMR and APT NMR spectra were obtained using a Varian Unity Inova (500 MHz) spectrometer by using TMS an the internal standard. Elemental analyses (C, H, S) were conducted using the Thermo Finnigan Flash EA 1112 Series Elemental Analyser, their results were found to be in good agreement (±0.2%) with the calculated values. UV-vis spectra were performed on a Perkin Elmer Lambda 35 UV-vis Spectrometer. Column chromatography on silica was carried out using silica gel (Merck Kieselgel 60, 70 - 230 mesh). Kieselgel 60 F-254 plates (Merck) were used for thin layer chromatography (TLC).

General procedure 1. A mixture of 1.0 g of 2*H*-pentachloro-1,3-butadiene (4.4 mmol) and 608 mg of dimethylbenzenethiol (4.4 mmol) in 25 mL of ethanol and 1.2 g NaOH (in 10 mL of water) was stirred for 24 h at room temperature. The reaction mixture was treated with about 50 mL of water and extracted with $CHCl_3$ (3 × 40 mL), and the organic layers were combined and dried (Na_2SO_4). After evaporation of chloroform, the residue was subjected to column chromatography to give the pure products.

Synthesis of 1,1,2-trichloro-4-(2,5-dimethylphenylthio)-1-buten-3-yne (3a), 1,1,2,4-tetrachloro-4-(2,5-dimethylphenylthio)-1,3-butadiene (4a), 1,1,2-trichloro-4,4-bis(2,5-dimethylphenylthio)-1,3-butadiene (5a). Compounds **3a**, **4a** and **5a** were synthesized from the reaction of 2*H*-pentachloro-1,3-butadiene (**1**) with 2,5-dimethylbenzenethiol (**2a**) according to the general procedure 1.

1,1,2-Trichloro-4-(2,5-dimethylphenylthio)-1-buten-3-yne (3a): Yellow oil; Yield: 300 mg (23%); R_f (*n*-Hexane): 0.8; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.25 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 6.93 (d, J = 6.8 Hz, H, Ar-H), 7.00 (d, J = 7.8 Hz, H, Ar-H), 7.36 (s, H, Ar-H); APT NMR (125 MHz, $CDCl_3$) δ 18.15, 19.92 (CH_3), 127.33, 127.51, 129.49 (CH_{arom}), 88.23, 88.55, 111.87, 126.25, 128.37, 132.13, 135.98; IR (KBr) ν 2155 (C≡C), 1552, 1605 (C=C), 1379, 2860, 2974 (C-H_{methyl}), 3019 (=C-H_{arom}) cm^{-1}; UV-vis ($CHCl_3$) λ_{max}/nm (log ε_{max}) 254 (4.45); GC-MS (EI) *m*/*z* (%) = 292.0 (57), 220.0 (100), 185.0 (50), 135.0 (32), 77.0 (46); ($C_{12}H_9Cl_3S$, 291.6); Calcd., %: C, 49.42; H, 3.11; S, 11.00; Found, %: C, 49.40; H, 3.10; S, 11.00.

1,1,2,4-Tetrachloro-4-(2,5-dimethylphenylthio)-1,3-butadiene (4a): Light yellow oil; Yield: 220 mg (15%); R_f (Petroleum ether): 0.7; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.24 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 6.46 (s, H, >C=CH), 7.02 (d, J = 7.8 Hz, H, Ar-H), 7.06 (d, J = 7.8 Hz, H, Ar-H), 7.20 (s, H, Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.20, 19.71 (CH_3), 121.03, 123.08, 123.46, 128.36, 129.52, 129.53, 134.28, 135.30, 136.95, 137.48 (C_{arom}, CH_{arom}, C_{butad}, CH_{butad}); IR (KBr) ν 1567, 1604 (C=C), 1379 (C-H_{methyl}), 3020 (=C-H_{arom}) cm^{-1}; UV-vis ($CHCl_3$) λ_{max}/nm (log ε_{max}) 239 (4.32), 268 (4.20); GC-MS (EI) *m*/*z* (%) = 327.9 (83), 293.0 (62), 256.0 (100), 220.0 (44), 148.0 (79), 105.0 (95), 77.0 (85); ($C_{12}H_{10}Cl_4S$, 328.1); Calcd, %: C, 43.93; H, 3.07; S, 9.77; Found, %: C, 43.92; H, 3.05; S, 9.77.

1,1,2-Trichloro-4,4-bis(2,5-dimethylphenylthio)-1,3-butadiene (5a): Light yellow oil; Yield: 340 mg, 18%; R_f (Petroleum ether): 0.6; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.13 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.21 (s, 6H, $2CH_3$), 5.83 (s, H, >C=CH), 6.94-7.04 (m, 5H, Ar-H), 7.09 (s, H, Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.67, 19.12, 19.68, 19.72 (CH_3), 128.74, 129.09, 129.47, 129.49, 134.08, 134.96 (CH_{arom}), 118.76 (CH_{butad}), 119.17, 125.06, 129.21, 134.75, 135.41, 137.27, 137.81, 143.15 (C_{arom}, C_{butad}); IR (KBr) ν 1546, 1604 (C=C), 1378, 2860, 2972 (C-H_{methyl}), 3016 (=C-H_{arom}) cm^{-1}; UV-vis ($CHCl_3$) λ_{max}/nm (log ε_{max}) 240 (4.51), 266 (4.47); MS (+ESI) *m*/*z* $[M+H]^+$= 431.0 ($C_{20}H_{19}Cl_3S_2$, 429.9); Calcd., %: C, 55.88; H, 4.46; S, 14.92; Found, %: C, 55.87; H, 4.47; S, 14.90.

Synthesis of 1,1,2-trichloro-4-(3,5-dimethylphenylthio)-1-buten-3-yne (3b), 1,1,2,4-tetrachloro-4-(3,5-dimethylphenylthio)-1,3-butadiene (4b). Compounds **3b** and **4b** were synthesized from the reaction of 2*H*-pentachloro-1,3-butadiene (**1**) with 3,5- dimethylbenzenethiol (**2b**) according to the general procedure 1.

1,1,2-Trichloro-4-(3,5-dimethylphenylthio)-1-buten-3-yne (3b): Light yellow oil; Yield: 400 mg, 31%; R_f (Petroleum ether): 0.8; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.22 (s, 6H, $2CH_3$), 6.80 (s, H, Ar-H), 6.97 (s, 2H, Ar-H); APT NMR (125 MHz, $CDCl_3$) δ 20.20 ($2CH_3$), 88.18, 89.14, 111.86, 126.23, 129.18, 138.35 (C_{arom}, $C_{butenyne}$), 123.54, 128.27 (CH_{arom}); IR (KBr) ν 2155 (C≡C), 1602, 1580 (C=C), 1376, 2860, 2952 (C-H_{methyl}), 3009 (=C-H_{arom}) cm^{-1}; UV-vis ($CHCl_3$) λ_{max}/nm (log ε_{max}) 256 (4.41); GC-MS (EI) *m*/*z* (%) = 292.0 (36), 220.1 (100), 185.1 (23), 135.1 (3), 77.0 (38); ($C_{12}H_9Cl_3S$, 291.6); Calcd., %: C, 49.42; H, 3.11; S, 11.00; Found, %: C, 49.42; H, 3.12; S, 11.01.

1,1,2,4-Tetrachloro-4-(3,5-dimethylphenylthio)-1,3-butadiene (4b): Light yellow oil; Yield: 73 mg, 5%; R_f (Petroleum ether): 0.7; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.25 (s, 6H, $2CH_3$), 6.49 (s, H, >C=CH), 6.91 (s, H, Ar-H), 7.00 (s, 2H, Ar-H); APT NMR (125 MHz, $CDCl_3$) δ 20.14 ($2CH_3$), 123.41, 129.18, 136.89, 137.93, 138.41 (C_{butad}, C_{arom}), 124.73 (CH_{butad}), 129.50, 129.76 (CH_{arom}); IR (KBr) ν 1601, 1567 (C=C), 3028 (=C-H_{arom}), 1377, 2860, 2952 (C-H_{methyl}) cm^{-1}; UV-vis ($CHCl_3$) λ_{max}/nm (log ε_{max}) 265 (4.13); GC-MS (EI) *m*/*z* (%) = 328.0 (28), 293.1 (25), 256.1 (100), 220.1 (22), 105.1 (27), 77.0 (48); ($C_{12}H_{10}Cl_4S$, 328.1); Calcd., %: C, 43.93; H, 3.07; S, 9.77; Found, %: C,

43.91; H, 3.06; S, 9.76.

Synthesis of 1,1,2-trichloro-4-(2,6-dimethylphenylthio)-1-buten-3-yne (3c), 1,1,2-Trichloro-4,4-bis(2,6-dimethylphenylthio)-1,3-butadiene (5c). Compounds **3c** and **5c** were synthesized from the reaction of 2*H*-pentachloro-1,3-butadiene (**1**) with 2,6- dimethylbenzenethiol (**2c**) according to the general procedure 1.

1,1,2-Trichloro-4-(2,6-dimethylphenylthio)-1-buten-3-yne (3c): Light yellow oil; Yield: 605 mg, 47%; R_f (Petroleum ether): 0.8; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.55 (s, 6H, $2CH_3$), 7.05 (d, J = 7.8 Hz, 2H, Ar-H), 7.12 (t, J = 7.6 Hz, H, Ar-H); APT NMR (125 MHz, $CDCl_3$) δ 20.86 ($2CH_3$), 127.30, 127.76, 128.70 (CH_{arom}), 82.65, 90.43, 112.09, 126.25, 127.14, 141.10, (C_{arom}, $C_{butenyne}$); IR (KBr) ν 2152 (C≡C), 1554, 1583 (C=C), 1378, 2977 (C-H_{methyl}), 3056 (=C-H_{arom}) cm^{-1}; UV-vis ($CHCl_3$) λ_{max}/nm (log ε_{max}) 262 (4.20); GC-MS (EI) *m/z* (%) = 292.0 (91), 290.0 (85), 220.0 (100), 185.0 (79), 135.0 (82), 76.9 (67); ($C_{12}H_9Cl_3S$, 291.6); Calcd., %: C, 49.42; H, 3.11; S, 11.00; Found, %: C, 49.40; H, 3.10; S, 11.00.

1,1,2-Trichloro-4,4-bis(2,6-dimethylphenylthio)-1,3-butadiene (5c): Yellow oil; Yield: 100 mg, 5%, R_f (*n*-Hexane): 0.5; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.26 (s, 6H, $2CH_3$), 2.48 (s, 6H, $2CH_3$), 5.21 (s, H, >C=CH), 7.03 (d, J = 7.3 Hz, 2H, Ar-H), 7.08 (d, J = 7.8 Hz, 2H, Ar-H), 7.12 (t, J = 7.6 Hz, H, Ar-H), 7.17 (t, J = 7.3 Hz, H, Ar-H); APT NMR (125 MHz, $CDCl_3$) δ 20.12 ($2CH_3$), 21.09 ($2CH_3$), 127.11, 127.60, 128.86, 129.10 (CH_{arom}), 118.20, 125.47, 127.63, 128.12, 142.79, 142.88, 143.76 (C_{arom}, C_{butad}), 111.22 (CH_{butad}); IR (KBr) ν 1376, 2963 (C-H_{methyl}), 1540 (C=C), 3056 (=C-H_{arom}) cm^{-1}; UV-vis ($CHCl_3$) λ_{max}/nm (log ε_{max}) 240 (4.18); MS (+ESI) *m/z* $[M+H]^+$ = 431.3 ($C_{20}H_{19}Cl_3S_2$, 429.9); Calcd., %: C, 55.88; H, 4.46; S, 14.92; Found, %: C, 55.86; H, 4.45; S, 14.91.

Synthesis of 2-(3,4,4-trichlorobut-3-en-1-ynylthio)-propanoic acid (3d), 2-(1,3,4,4-tetrachloro-buta-1,3-dienylthio)-propanoic acid (4d). A mixture of 1.0 g (4.4 mmol) of 2*H*-pentachloro-butadiene (**1**) and 469 mg (4.4 mmol) of 2-mercaptopropionic acid (**2d**) in 25 mL of ethanol and in the presence of NaOH (1.2 g in 10 mL of water) was stirred for 24 h at room temperature. The reaction mixture was adjusted to pH≅ 3 with aq. acetic acid and the resulting solution was extracted with chloroform. Then, the organic layer was washed with water, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give 2-(3,4,4-trichlorobut-3-en-1-ynylthio)-propanoic acid (**3d**) and 2-(1,3,4,4-tetrachloro-buta-1,3-dienylthio)-propanoic acid (**4d**).

2-(3,4,4-Trichlorobut-3-en-1-ynylthio)-propanoic acid (3d): Yellow oil; Yield: 230 mg, 20%; R_f (Ethylacetate): 0.2; ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.85 (C=O), 111.68, 126.68 (C=C), 87.46, 88.56 (C≡C), 44.12 (CH), 16.11 (CH_3); IR (KBr) ν 2155 (C≡C), 1715 (C=O), 2800-3400 (OH) cm^{-1}; UV-vis ($CHCl_3$) λ_{max}/nm (log ε_{max}) 272 (3.74), 244 (3.88); GC-MS (EI) *m/z* 259.8 (52), 185.8 (100); ($C_7H_5Cl_3SO_2$, 259.5); Calcd., %: C, 32.39; H, 1.94; S, 12.35; Found, %: C, 32.37; H, 1.92; S, 12.34.

2-(1,3,4,4-Tetrachloro-buta-1,3-dienylthio)-propanoic acid (4d): Yellow oil; Yield: 326 mg, 25%; R_f (Ethylacetate): 0.2; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.50 (d, 3H, CH_3), 4.07 (q, H, CH), 6.50 (s, H, >C=CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.94 (C=O), 135.26, 126.96, 126.45, 122.97 ($C_{butadiene}$), 43.09 (CH), 15.97 (CH_3); IR (KBr) ν 1721 (C=O), 2900-3600 (OH) cm^{-1}; UV-vis ($CHCl_3$) λ_{max}/nm (log ε_{max}) 279 (3.86), 243 (3.91); MS (+ESI) *m/z* $[M-H]^-$ = 294.7 ($C_7H_6Cl_4O_2S$, 296.0); Calcd., %: C, 28.40; H, 2.04; S, 10.83; Found, %: C, 28.41; H, 2.02; S, 10.81.

Synthesis of 1,2-dichloro-1,4,4-tris(3,5-dimethylphenylthio)-1,3-butadiene (6b), 1,1,2,4-tetrakis(3,5-dimethylphenylthio)-1-buten-3-yne (7b). A mixture of 2.0 g (8.8 mmol) of 2*H*-pentachloro-butadiene (**1**) and 3.65 g (26.4 mmol) of 3,5-dimethylbenzenethiol (**2b**) in 30 mL of ethanol and NaOH (1.3 g in 10 mL of water) was stirred for 24 h at room temperature. The reaction mixture was treated with about 50 mL of water and extracted with $CHCl_3$ (3 × 40 mL) and the organic layers were combined and dried (Na_2SO_4). After evaporation of chloroform, purification of the residue by silica gel column chromatography (*n*-Hexane) gave compounds **6b** and **7b**.

1,2-Dichloro-1,4,4-tris(3,5-dimethylphenylthio)-1,3-butadiene (6b): Yellow oil; Yield: 935 mg, 20%; R_f [$CHCl_3$/*n*-Hexane (1/2)]: 0.8; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.16 (s, 6H, $2CH_3$), 2.20 (s, 6H, $2CH_3$), 2.21 (s, 6H, $2CH_3$), 6.48 (s, H, >C=CH), 6.82-6.94 (m, 9H, Ar-H); APT NMR (125 MHz, $CDCl_3$) δ 20.13, 20.15, 20.19 (CH_3), 127.16, 128.78, 128.81, 129.01, 129.13, 129.24, 129.34, 130.06, 130.11 (CH_{arom}), 124.88 (CH_{butad}), 127.48, 130.97, 131.0, 131.05, 131.10, 131.15, 137.27, 137.75, 137.78, 137.90, 141.46, 141.80 (C_{arom} and C_{butad}); IR (KBr) ν 1579, 1600 (C=C), 1376, 2858, 2949 (C-H), 3033 (=C-H_{arom}) cm^{-1}; UV-vis ($CHCl_3$) λ_{max}/nm (log ε_{max}) 239 (4.51); MS (+ESI) *m/z* $[M+H]^+$ = 531.2 ($C_{28}H_{28}S_3Cl_2$, 531.6); Calcd., %: C, 63.26; H, 5.31; S, 18.09; Found, %: C, 63.24; H, 5.30; S, 18.08.

1,1,2,4-Tetrakis(3,5-dimethylphenylthio)-1-buten-3-yne (7b): Yellow oil; Yield: 158 mg, 3%; R_f (*n*-Hexane): 0.8; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.19 (s, 6H, $2CH_3$), 2.22 (s, 6H, $2CH_3$), 2.23 (s, 6H, $2CH_3$), 2.25 (s, 6H, $2CH_3$), 6.76-6.81 (m, 2H, Ar-H), 6.89 (s, H, Ar-H), 6.94 (s, H, Ar-H), 6.97-7.05 (m, 8H, Ar-H); APT NMR (125 MHz, $CDCl_3$) δ 20.15, 20.17, 20.21 (CH_3), 123.34, 124.25, 128.02, 128.04, 128.48, 129.56, 130.06, 130.17 (CH_{arom}), 91.16, 91.41, 128.96, 129.76, 129.79, 130.00, 133.48, 137.72, 138.03, 138.08, 138.26, 138.28 (C_{arom}, $C_{butenyne}$); IR (KBr) ν 2147 (C≡C), 1601, 1579 (C=C) cm^{-1}; UV-vis ($CHCl_3$) λ_{max}/nm 252; MS (+ESI) *m/z* $[M+H]^+$ = 597.2 ($C_{36}H_{36}S_4$, 596.9); Calcd., %: C, 72.43; H, 6.08; S, 21.49; Found, %: C, 72.41; H, 6.06; S, 21.47.

1,1,4,4-Tetrakis(4-fluorophenylthio)-2-chloro-1,3-butadiene (8e):[17] A mixture of 1.00 g (4.4 mmol) 2*H*-pentachloro-butadiene (**1**) and 2.26 g (17.6 mmol) of 4-fluorothiophenol (**2e**) in 25 mL of *N*,*N*-dimethylformamide (DMF) and triethylamine (2.5 mL) was stirred for 24 h at room temperature. The reaction mixture was treated with about 50 mL of water and extracted with $CHCl_3$ (3 × 40 mL) and the organic layers were combined and dried (Na_2SO_4). After the solvent was evaporated, crystallization from methanol gave **8e**: Yellow solid; Yield: 887 mg, 34% R_f ($CHCl_3$): 0.7; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74 (s, H, >C=CH), 6.84-7.02 (m, 10H, Ar-H), 7.06-7.12 (m, 2H, Ar-H), 7.16-7.22 (m, 2H, Ar-H), 7.24-7.30 (m, 2H, Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 115.59, 115.83, 115.86, 116.03, 116.38, 126.96, 128.03, 131.66, 131.73, 134.77, 134.84, 135.17, 135.24, 135.94, 136.00, 140.75, 161.25, 161.97, 163.23, 163.82, 163.98;

IR (KBr) ν 1589 (C=C) cm^{-1}; UV-vis ($CHCl_3$) λ_{max}/nm (log ε_{max}) 261 (4.34); MS (+ESI) *m/z* $[M+H]^+$ = 593.1 ($C_{28}H_{17}F_4S_4Cl$, 593.1); Calcd., %: C, 56.70; H, 2.89; S, 21.62; Found, %: C, 56.68; H, 2.87; S, 21.60.

1,2-Dibromo-3,4,4-trichloro-1-(2,6-dimethylphenylthio)-1,3-butadiene (9c): To 100 mg **3c** (0.34 mmol) a solution of 0.017 mL bromine (0.34 mmol) in 50 mL carbon tetrachloride was added. The reaction mixture was stirred 5 h, washed with solution (3g $Na_2S_2O_6$ in 100 mL water) and the organic layer was seperated, washed with water, dried with Na_2SO_4. After the solvent was evaporated, purification of the residue by silica gel column chromatography (*n*-Hexane) gave **9c**: Yellow oil; Yield: 123 mg, 80%; R_f (*n*-Hexane): 0.7; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.38 (s, 6H, $2CH_3$), 7.00-7.30 (m, 3H, Ar-H); APT NMR (125 MHz, $CDCl_3$) δ 17.48, 17.58 (CH_3), 104.48, 107.86, 120.10, 123.94, 124.00, 124.64, 125.80, 125.90, 126.08, 139.25, 139.45 (C_{butad}, C_{arom}, CH_{arom}); IR (KBr) ν 1590, 1538 (C=C), 3057 (=C-H_{arom}), 1377, 2955 (C-H) cm^{-1}; UV-vis ($CHCl_3$) λ_{max}/nm 268; GC-MS (EI) *m/z* (%) = 451.9 (23), 414.9 (41), 335.9 (14), 255.0 (23), 220.0 (38), 105.0 (100); ($C_{12}H_9Cl_3Br_2S$, 451.4); Calcd., %: C, 31.93; H, 2.01; S, 7.10; Found, %: C, 31.91; H, 2.00; S, 7.11.

1,1,2,4-Tetrachloro-4-(3,5-dimethylphenylsulfinyl)-1,3-butadiene (10b): Compound **4b** (70 mg, 0.21 mmol) in 10 mL of chloroform was added to m-chloroperbenzoic acid (36 mg, 0.21 mmol) at 0 °C for 48 h; 2 N NaOH added to the reaction mixture and then washed with water and the organic layer was seperated and dried with Na_2SO_4. After the solvent was evaporated, purification of the residue by silica gel column chromatography (*n*-Hexane) gave **10b**: Yellow oil; Yield: 50 mg, 68%; R_f ($CHCl_3$): 0.6; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.32 (s, 6H, $2CH_3$), 6.83 (s, H, >C=CH), 7.08 (s, H, Ar-H), 7.21 (s, 2H, Ar-H); APT NMR (125 MHz, $CDCl_3$) δ 20.33 ($2CH_3$), 132.62, 127.06, 122.62, 121.26 (CH_{arom}, CH_{butad}), 146.80, 139.30, 138.37, 124.33, 121.07 (C_{arom}, C_{butad}); IR (KBr) ν 1076 (S=O), 1605, 1577 (C=C) cm^{-1}; UV-vis ($CHCl_3$) λ_{max}/nm (log ε_{max}) 283 (4.46), 241 (4.32); MS (+ESI) *m/z* $[M+H]^+$ = 344.9 ($C_{12}H_{10}Cl_4SO$, 344.1); Calcd., %: C, 41.89; H, 2.93; S, 9.32; Found, %: C, 41.90; H, 2.92; S, 9.31.

1,1,4-Trichloro-4-(2,5-dimethylphenylthio)-1,2,3-butatriene (11a) and 1,1,2-trichloro-4-(2,5-dimethylphenylthio)-1-buten-3-yne (3a) (Isomer mixture): To 10 mg potassium *tert*-butoxide (0.09 mmol) a solution of **4a** (30 mg, 0.09 mmol) in 20 mL petroleum ether was added. The reaction mixture was stirred 4 h, washed with water and extracted with diethylether (3 × 40 mL). The organic layers were combined and dried (Na_2SO_4). After the solvent was evaporated, purification of the residue by silica gel column chromatography (*n*-Hexane) gave **11a** and **3a** isomer mixture: Yellow oil; Yield: 24 mg, 92%; R_f (*n*-Hexane): 0.3 (for **11a**); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.8-7.5 (m, 6H, Ar-H), 2.20-2.24 (m, 12H, $4CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 81.99, 84.39, 87.67, 88.23, 88.55, 89.69, 111.87, 126.23, 128.36, 131.68, 132.11, 135.78, 135.97, 165.27 (C_{arom}, $C_{butenyne}$, $C_{butatriene}$), 126.50, 126.98, 127.32, 127.50, 129.26, 129.49 (CH_{arom}), 27.64, 26.90, 19.92, 18.14 (CH_3); IR (KBr) ν 2061 (C=C=C=C), 2155 (C≡C), 1601 (C=C), 1369, 2870 (C-H) cm^{-1}; GC-MS (EI) *m/z* (%) = 291.8 (64), 254.9 (19), 219.9 (100), 134.9 (47), 76.9 (48), 184.9 (61); ($C_{12}H_9Cl_3S$, 291.6); Calcd., %: C, 49.42; H, 3.11; S, 11.00; Found, %: C, 49.40; H, 3.10; S, 10.99.

1,1,4-Trichloro-4-(3,5-dimethylphenylthio)-1,2,3-butatriene (11b) and 1,1,2-trichloro-4-(3,5-dimethylphenylthio)-1-buten-3-yne (3b) (Isomer mixture): To 34 mg potassium *tert*-butoxide (0.30 mmol) a solution of **4b** (98 mg, 0.30 mmol) in 20 mL petroleum ether was added. The reaction mixture was stirred 4 h, washed with water and extracted with diethylether (3 × 40 mL). The organic layers were combined and dried (Na_2SO_4). After the solvent was evaporated, purification of the residue by silica gel column chromatography (*n*-Hexane) gave **11b** and **3b** isomer mixture: Yellow oil; Yield: 79 mg, 90%; R_f(*n*-Hexane): 0.7 (for **11b**); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.24 (s, 6H, $2CH_3$), 2.26 (s, 6H, $2CH_3$), 6.79 (s, H, Ar-H), 6.82 (s, H, Ar-H), 6.99 (s, 4H, Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.21, 27.65 (CH_3), 87.68, 88.13, 89.14, 90.20, 108.75, 111.84, 123.22, 123.54, 126.24, 127.83, 128.28, 129.17, 138.12, 138.35; IR (KBr) ν 2063 (C=C=C=C), 2155 (C≡C), 1602, 1581 (C=C) cm^{-1}; GC-MS (EI) *m/z* (%) = 291.9 (49), 254.9 (19), 219.9 (100), 185.0 (25), 210.9 (41), 76.9 (41); ($C_{12}H_9Cl_3S$, 291.6); Calcd., %: C, 49.42; H, 3.11; S, 11.00; Found, %: C, 49.40; H, 3.10; S, 10.98.

1,1-Dichloro-4,4-bis(2,5-dimethylphenylthio)-1,2,3-butatriene (12a) and 1,1-dichloro-2,4-bis(2,5-dimethylphenylthio)-1-buten-3-yne (13a) (Isomer mixture): To 26 mg potassium *tert*-butoxide (0.23 mmol) a solution of **5a** (100 mg, 0.23 mmol) in 20 mL petroleum ether was added. The reaction mixture was stirred 4 h, washed with water and extracted with diethylether (3 × 40 mL). The organic layers were combined and dried (Na_2SO_4). After the solvent was evaporated, purification of the residue by silica gel column chromatography (*n*-Hexane) gave **12a** and **13a** isomer mixture: Yellow oil; Yield: 80 mg, 88%; R_f(*n*-Hexane): 0.4 (**12a**), 0.5 (**13a**); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.20-2.34 (m, 24H, $8CH_3$), 6.84-7.45 (m, 12H, Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.07, 19.64, 26.66, 26.91, 27.58, 28.15 (CH_3), 79.47, 80.44, 92.89, 92.90, 119.74, 127.02, 127.16, 127.18, 127.21, 128.02, 128.37, 129.33, 129.35, 129.60, 129.73, 129.94, 129.97, 135.00, 135.44, 135.46, 135.87, 137.74, 138.13, 143.51, 151.71, 153.72; IR (KBr) ν 2057 (C=C=C=C), 2148 (C≡C), 1635, 1587 (C=C) cm^{-1}; MS (+ESI) *m/z* $[M+H]^+$ = 392.9 ($C_{28}H_{18}S_2Cl_2$, 393.4); Calcd., %: C, 61.06; H, 4.61; S, 16.30; Found, %: C, 61.04; H, 4.60; S, 16.28.

1-Chloro-1,4,4-tris-(3,5-dimethylphenylthio)-1,2,3-butatriene (14b): To 10 mg potassium *tert*-butoxide (0.09 mmol) a solution of **6b** (48 mg, 0.09 mmol) in 20 mL petroleum ether was added. The reaction mixture was stirred 4 h, washed with water and extracted with diethylether (3 × 40 mL). The organic layers were combined, dried (Na_2SO_4) and the solvent was evaporated to give **14b**: Yellow oil; Yield: 40 mg, 90%; R_f [*n*-Hexane/$CHCl_3$ (1/1), isomer mixture]: 0.8; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.20 (s, 12H, $4CH_3$), 2.23 (s, 6H, $2CH_3$), 6.82 (s, H, Ar-H), 6.84 (s, H, Ar-H), 6.88 (s, 2H, Ar-H), 6.90 (s, H, Ar-H), 6.99 (s, 2H, Ar-H), 7.05 (s, 2H, Ar-H); APT NMR (125 MHz, $CDCl_3$) δ 21.33, 21.39, 21.46 (CH_3), 129.24, 130.38, 130.78, 131.01, 131.16, 131.62 (CH_{arom}), 101.18, 119.28, 130.88, 131.45, 132.22, 139.03, 139.05, 139.11, 145.67, 155.83 ($C_{butatriene}$, C_{arom}); IR (KBr) ν 2043 (C=C=C=C) cm^{-1}; MS(+ESI) *m/z* $[M+H]^+$ = 494.9 ($C_{28}H_{27}S_3Cl$, 495.2); Calcd., %: C, 67.92; H, 5.50; S, 19.43; Found, %: C, 67.90; H, 5.48; S, 19.41.

2-Chloro-1,1,4-tris-(3,5-dimethylphenylthio)-1-buten-3-yne (15b): Compound **14b** (40 mg, 0.08 mmol) converted into **15b** at room temperature by solvolysis. Compound **15b**: Dark yellow oil; Yield: 37 mg, 93%; R_f(*n*-Hexane): 0.2; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.15 (s, 6H, $2CH_3$), 2.14 (s, 12H, $4CH_3$), 7.01 (s, 2H, Ar-H), 6.83 (s, H, Ar-H), 6.74 (s, 2H, Ar-H), 6.70 (s, 2H, Ar-H), 6.61 (s, 2H, Ar-H); APT NMR (125 MHz, $CDCl_3$) δ 20.01, 20.08, 20.12 (CH_3), 123.08, 127.43, 127.73, 128.25, 129.23, 130.98 (CH_{arom}), 84.24, 93.30, 108.76, 113.17, 129.59, 130.35, 131.88, 137.02, 137.16, 138.10, 139.04 ($C_{butenyne}$, C_{arom}); IR (KBr) ν 2141 (C≡C), 1601, 1579 (C=C) cm^{-1}; MS (+ESI) *m*/*z* $[M+H]^+$ = 494.9 ($C_{28}H_{27}S_3Cl$, 495.2); Calcd., %: C, 67.92; H, 5.50; S, 19.43; Found, %: C, 67.91; H, 5.48; S, 19.42.

1-Chloro-2,3-diiodo-1,4,4-tris(3,5-dimethylphenylthio)-1,3-butadiene (16b): To 40 mg **14b** (0.08 mmol), a solution of 21 mg iodine (0.08 mmol) in 50 mL carbon tetrachloride was added. The reaction mixture was stirred 5 h, washed with solution (3 g $Na_2S_2O_6$ in 100 mL water) and the organic layer was seperated, washed with water, dried with Na_2SO_4. After the solvent was evaporated, purification of the residue by silica gel column chromatography (*n*-Hexane) gave **16b**: Yellow oil; Yield: 36 mg, 60%; R_f(*n*-Hexane): 0.2; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.12 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 6.64 (s, 2H, Ar-H), 6.68 (s, H, Ar-H), 6.78 (s, 2H, Ar-H), 7.03 (s, H, Ar-H), 7.04 (s, H, Ar-H), 7.07 (s, H, Ar-H), 7.08 (s, H, Ar-H); APT NMR (125 MHz, $CDCl_3$) δ 20.03, 20.07, 20.09, 20.17, 20.22 (CH_3), 124.23, 128.01, 128.96, 129.14, 129.18, 129.36, 129.42, 129.46, 129.60 (CH_{arom}), 60.36, 85.77, 136.91, 136.94, 137.01, 137.72, 137.87, 137.97 (C_{arom}, C_{butad}); IR (KBr) ν 1600, 1579 (C=C) cm^{-1}; UV-vis ($CHCl_3$) λ_{max} 243; MS (+ESI) *m*/*z* $[M\text{-}Cl]^+$ = 713.0, $[M\text{-}I]^+$ = 621.2 ($C_{28}H_{27}I_2ClS_3$, 749.0); Calcd., %: C 44.90; H, 3.63; S, 12.84; Found, %: C, 44.91; H, 3.62; S, 12.82.

1,1,4,4-Tetrakis(4-fluorophenylthio)-1,2,3-butatriene (17e): To 15 mg potassium *tert*-butoxide (0.13 mmol) a solution of 79 mg **8e** (0.13 mmol) in 20 mL petroleum ether was added. The reaction mixture was stirred 4 h, washed with water and diethylether and the organic layer was seperated and dried with Na_2SO_4. After the solvent was evaporated, purification of the residue by silica gel column chromatography (*n*-Hexane) gave **17e**: Yellow solid; Yield: 67 mg, 90%; R_f(*n*-Hexane): 0.8; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86-7.02 (m, 8H, Ar-H), 7.24-7.34 (m, 8H, Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.28, 162.30, 135.11, 135.04, 131.85, 127.85 (CH_{arom}, C_{arom}, $C_{butatriene}$); IR (KBr) ν 2036, 870 (C=C=C=C) cm^{-1}; MS(+ESI) *m*/*z* $[M+H]^+$ = 556.9 ($C_{28}H_{16}F_4S_4$, 556.7); Calcd., %: C, 60.41; H, 2.90; S, 23.04; Found, %: C, 60.42; H, 2.91; S, 23.06.

2,3-Dibromo-1,1,4,4-tetrakis(4-fluorophenylthio)-1,3-butadiene (18e): To 17 mg **17e** (0.03 mmol) a solution of 0.002 mL bromine (0.03 mmol) in 50 mL carbon tetrachloride was added. The reaction mixture was stirred 5 h, washed with solution (3 g $Na_2S_2O_6$ in 100 mL water) and the organic layer was seperated, washed with water, dried with Na_2SO_4. After the solvent was evaporated, purification of the residue by silica gel column chromatography (*n*-Hexane) gave **18e**: Yellow solid; Yield: 10 mg, 47%; R_f[$CHCl_3$/*n*-Hexane (1:2)]: 0.7; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.8-7.2 (m, 16H, Ar-H); IR (KBr) ν 1589 (C=C) cm^{-1}; UV-vis ($CHCl_3$) λ_{max}/nm 284, 242; MS(+ESI) *m*/*z* $[M+H]^+$ = 717.2, $[M\text{-}Br]^+$ = 637.2 ($C_{28}H_{16}Br_2S_4F_4$, 716.5); Calcd., %: C, 46.94; H, 2.25; S, 17.90; Found, %: C, 46.92; H, 2.23; S, 17.92.

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