

The synthesis and spectral investigation of new thiosubstituted butadienes and butenyne

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Abstract

Poly(thio)substituted butadienes **3a** and **4b-g** were synthesized from 1,1,3,3,4,4-hexa-chloro-butene and aromatic thiols in dimethylformamide (DMF) within 2 hr at room temperature in the presence of triethylamine N(C₂H₅)₃. Thiosubstituted butenyne compounds **5e-g** and the butadiene compound **6h** were synthesized from 1,1,3,3,4,4-hexa-chloro-butene and aromatic thiols in EtOH/H₂O solution of NaOH. The thiosubstituted butenyne **8e**, **8g** and the thiosubstituted butadiene **9h** were obtained from the reactions of 1-bromo-1,2,4,4-tetrachloro-1,3-butadiene and aromatic thiols in EtOH/H₂O solution of NaOH. Structures of the novel compounds were characterized by microanalysis, FT-IR, UV/Vis, ¹H-NMR, ¹³C-NMR, MS and fluorescence spectroscopy.

Keywords: Thiosubstituted butadienes and butenyne, thiols, coumarin, spectroscopy

Introduction

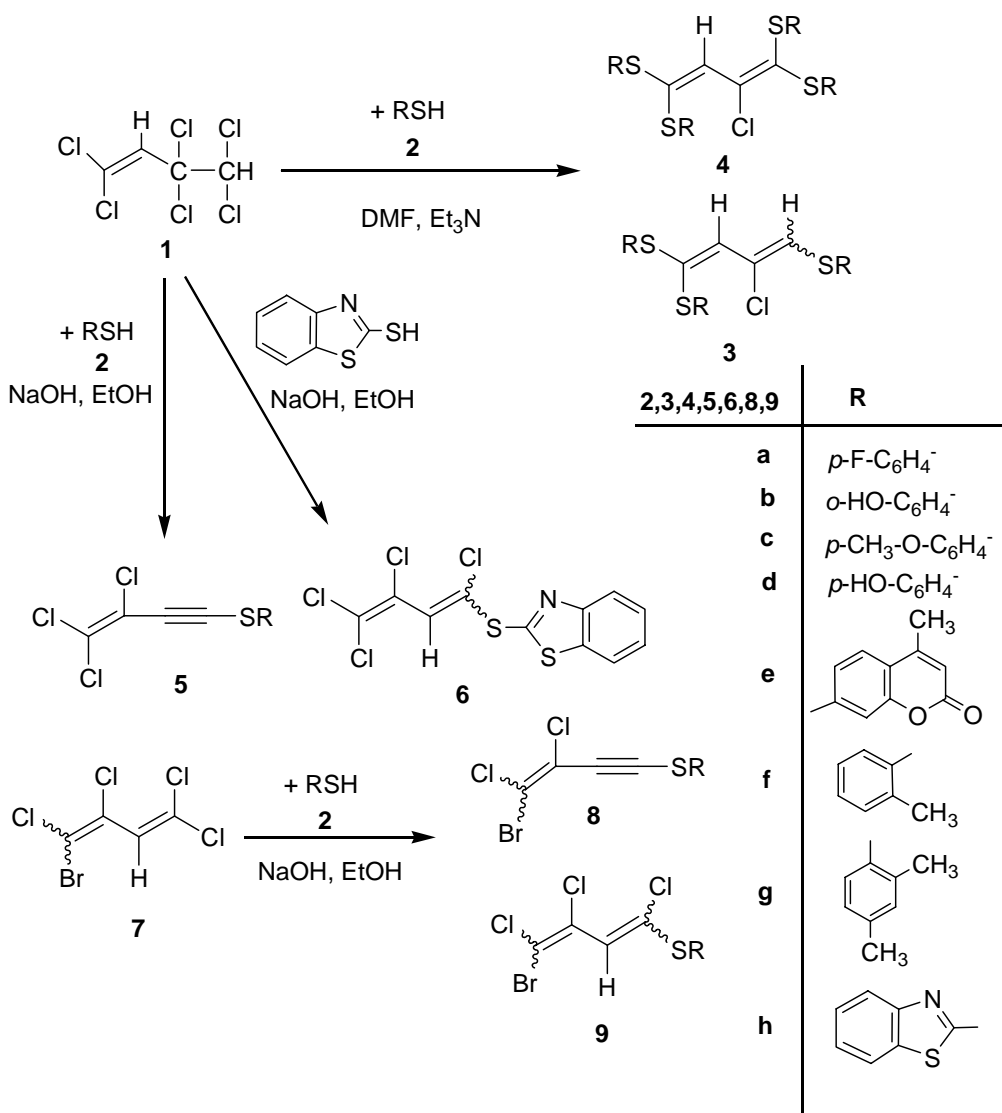
In recent years, synthesis of thiosubstituted, aliphatic and conjugated hydrocarbons has been widely studied because of the high reactivity of butadiene moiety or framework.¹ Dienes that contain sulfur or oxygen substituent show a greater reactivity.² Chemical literature contains many examples of attempts to prepare substituted butadienes.³⁻⁹ It is known from the US-Patent¹⁰ that some tetrakis(thio)substituted butadienes and some thiols¹¹ have biological activities such as fungicidal, insecticidal, herbicidal and nematocidal. Other sulfur containing molecules play an important role in redox mechanisms of biological systems.¹²

Coumarins, an old class of compounds, which we used our investigations, are naturally occurring benzopyrene derivatives. Coumarins have attracted a great interest in recent years because of their diverse pharmacological properties. The biological activities of coumarins and mercaptobenzoazoles are well known as antiviral, anticoagulant, antithrombic, antimicrobial, antibacterial, anticancer, antispasmodic and anti-HIV.¹³⁻¹⁷ The aim of this study is synthesis and characterization of novel thiosubstituted butadiene and butenyne compounds.

Result and Discussion

The tris(thio)substituted compound **3a** was prepared by the reaction between the halobutene compound **1** and *p*-fluorothiophenol **2a** in the presence of DMF and triethylamine $N(C_2H_5)_3$.¹⁸ Tetrakis(thio) substituted compounds **4b-g** were synthesized from the halobutene compound **1** and other aromatic thiols **2b-g** in the presence of $N(C_2H_5)_3$. New butenyne compounds **5e-g** and the thiosubstituted butadiene **6h** were obtained from the reaction of halobutene compounds **1** and **2e-h** in the presence of EtOH/H₂O solution of NaOH.

In the possible reaction mechanism, it is thought that *2H*-pentachlorobutadiene was formed from the HCl elimination of compound **1**. And then perchlorobutenyne was constituted from it. The compounds **5e-g** were constituted from the substitution of perchlorobutenyne compound. The new thiosubstituted butenyne compounds **8e, 8g** and the new butadiene compound **9h** were prepared by the reactions of 1-bromo-1,2,4,4-tetrachloro-1,3-butadiene **7** and **2e, 2g-h**, respectively (Scheme 1).



Scheme 1

The IR spectrum of the compound **3a** showed a characteristic band at 1593 cm^{-1} for the (C=C) stretching. The $^1\text{H-NMR}$ spectrum of the compound **3a** exhibited the presence of vinyl protons at 6.20 ppm. The IR spectra of compounds **4b** and **4d** showed broad bands at 3152 and 3326 cm^{-1} for the $-\text{OH}$ stretching, respectively. In $^1\text{H-NMR}$ spectra of **4b** and **4d**, singlets at 7.9 and 4.9 ppm were assigned to hydroxyl groups of this compounds. The IR spectrum of the compound **4c** showed a sharp peak at 1247 cm^{-1} indicating for the C-O stretching.

The mass spectra of **9h** in the positive ion mode for ESI confirmed the proposed structure; molecular peak was identified at m/z 401 (Figure 1). The fragmentation of molecular peak gave fragments corresponding to the cleavage of a chlorine atom at m/z 366. All compounds's spectral characterization are reported in experimental section.

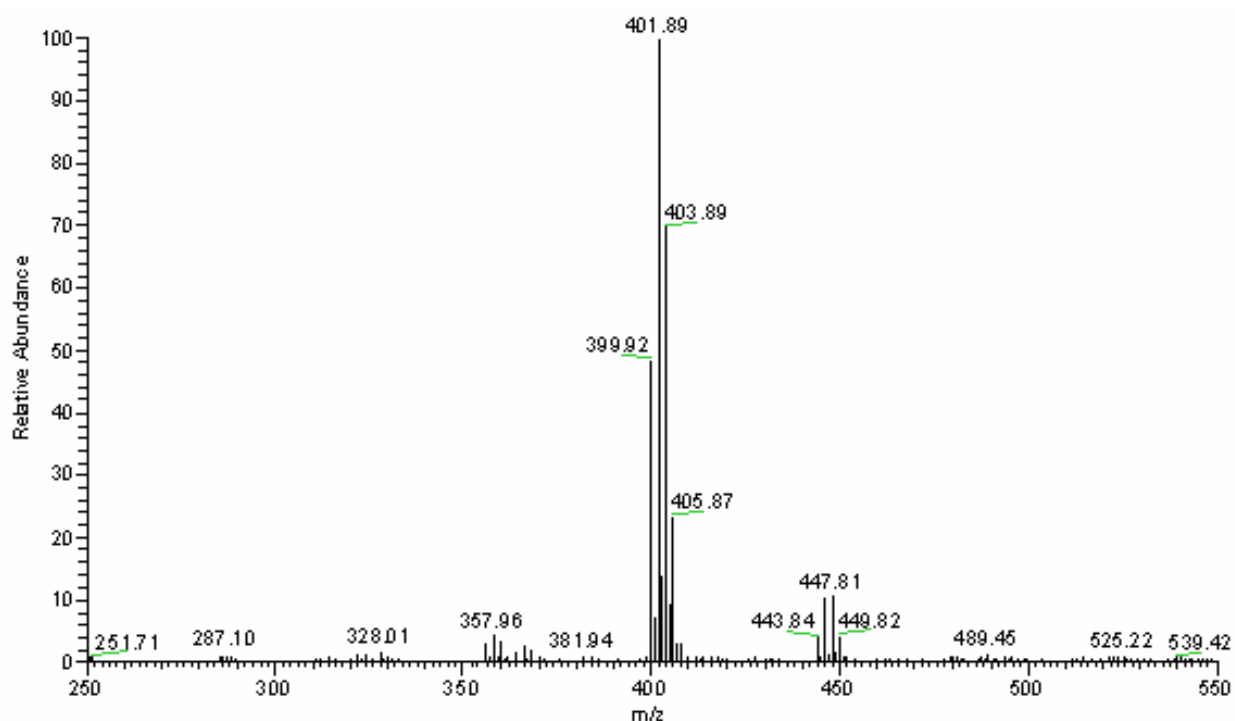


Figure 1. MS-ESI spectrum of the compound **9h**.

The coumarins showed maximum absorption with a single band at 270-310 nm.¹⁹ UV-Vis spectra of compounds **4e**, **5e** and **8e** in CHCl_3 showed broad bands at 277, 276 and 264 nm respectively (Table 1).

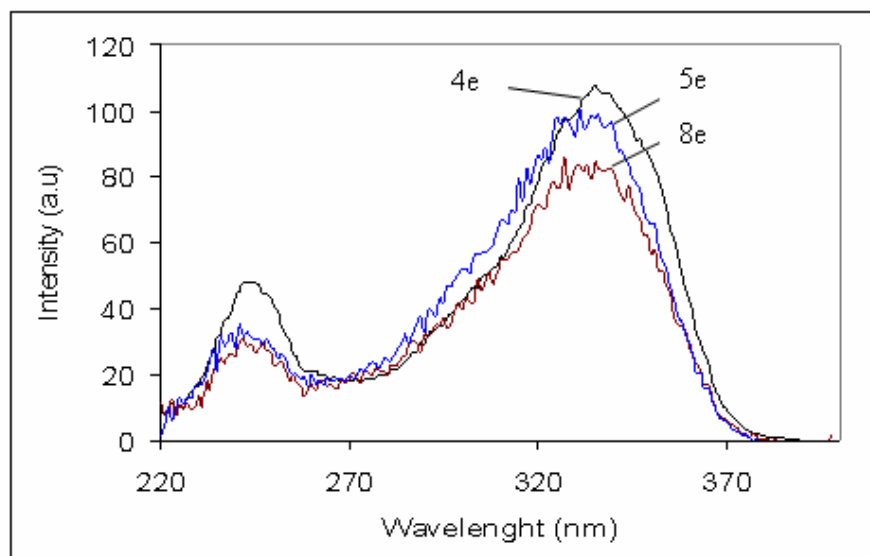
Table 1. UV-Vis data for different solvents

Compound	Absorption Maximum			Molar Absorptivity		
	$\lambda_{\text{max}}^{\text{a}}$	$\lambda_{\text{max}}^{\text{b}}$	$\lambda_{\text{max}}^{\text{c}}$	$\log \epsilon^{\text{a}}$	$\log \epsilon^{\text{b}}$	$\log \epsilon^{\text{c}}$
3a	240	293	-	4.21	4.16	-
4b	240	265	-	4.13	3.87	-
4c	241	265	-	4.46	3.34	-
4d	255	265	282	3.62	4.40	3.75
4e	277	327	-	5.57	4.39	-
4f	240	269	287	4.31	3.75	3.70
4g	240	267	246	4.54	4.13	4.29
5e	276	327	-	2.17	4.22	-
5f	265	256	246	3.82	2.78	3.53
5g	262	270	260	4.21	4.18	2.47
6h	262	281	258	4.56	4.14	2.38
8e	264	326	259	4.55	4.06	2.45
8g	263	265	251	4.07	4.00	1.56
9h	265	281	258	3.90	4.12	2.41

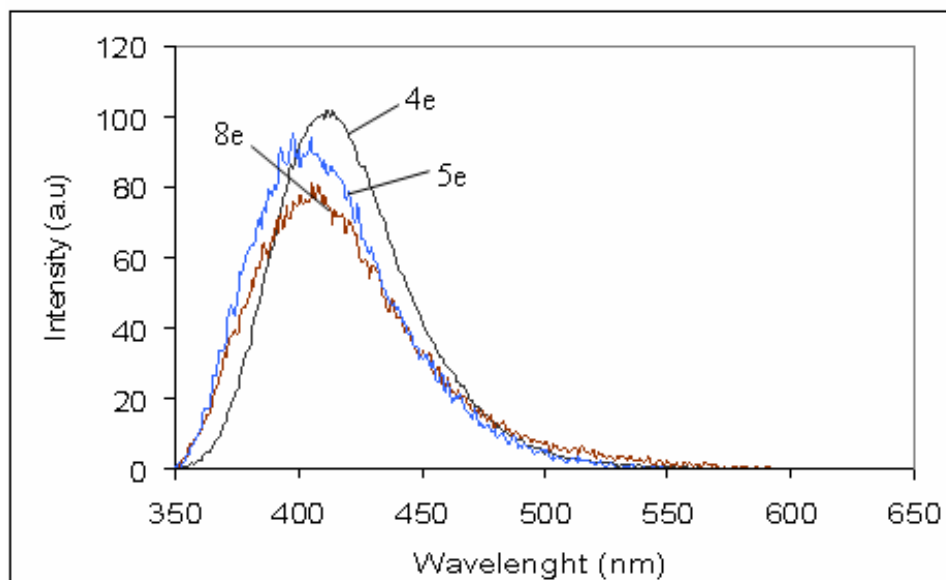
^aCHCl₃; ^bDMF; ^cHexane.

Table 2. Excitation and emission maximum wavelengths

Compound	Solvent	$\lambda_{\text{ex.}}(\text{max.})$	$\lambda_{\text{em.}}(\text{max.})$
4e	CHCl ₃	355	411
5e	CHCl ₃	327	405
8e	CHCl ₃	331	397



(a)



(b)

Figure 2. Excitation (a) and emission (b) spectra measured for 10^{-4} M solutions **4e**, **5e** and **8e** in CHCl_3 . Excitation and emission slit widths were set at 5 nm.

Experimental Section

General Procedures. Melting points were measured using a Buchi B-540 melting point apparatus and are uncorrected. Microanalyses were performed on a Thermo Finnigan Flash EA 1112 series elemental analyser. Infrared (IR) spectra were recorded in KBr pellets in Nujol mulls on a Perkin Elmer Precisely Spectrum One FTIR spectrometer. UV spectra were recorded in Perkin Elmer Precisely Lambda 35 UV-VIS spectrometer. Fluorescence Spectra were run on a VARIAN Cary Eclipse Fluorescence Spectrophotometer. $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ spectra were recorded in CDCl_3 or DMSO-d_6 on a Varian^{UNITY} INOVA spectrometer operating at 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. Products were isolated by column chromatography on silica gel (Fluka silica gel 60, particle size 63-200 μm). Thin-layer chromatography was performed on Merck silica gel plates (60F₂₅₄) and detection was carried out with ultraviolet light (254 nm). All reagents and solvents were of reagent-grade, obtained from commercial suppliers and used without further purification.

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. Finnigan Xcalibur® 1.4 was used to collect and process data. Experimental details of the analyses were 214.10 °C for capillary temperature and 9.29 V for capillary voltage. Sheath Gas and Aux/Sweep Gas flow rate were 39.55 and 19.50, respectively.

General procedure 1

1,1,3,3,4,4-Hexa-chloro-butene (1.0 g, 3.8 mmol) and aromatic thiols (15.2 mmol) were stirred in a mixture of DMF (30 mL) and triethylamine (3mL) for 2h at room temperature. Chloroform was added to the reaction mixture to separate the organic layer. Then, the organic layer was washed with water (4x30mL) and dried with MgSO₄. After filtering, the solvent was evaporated and the residue was purified by column chromatography on silica gel.

General procedure 2

Equimolar amounts of 1,1,3,3,4,4-Hexa-chloro-butene (1.0 g, 3.8 mmol) and thiols (3.8 mmol) were stirred in a mixture of EtOH (30 mL) and aqueous solution of NaOH (1.2 g NaOH and 8 mL water) for 2h at room temperature. Chloroform was added to the reaction mixture to separate the organic layer. Then the organic layer was washed with water(4x30mL) and dried with MgSO₄. The solvent was evaporated and the residue was purified by column chromatography on silica gel.

2-Chloro-1,4,4,-(4-fluorophenylthio)-1,3-butadiene (3a). Yield 0.60 g (34%); Oil, $R_f=0.40$ with CHCl₃/Petroleum ether (2:1) as an eluent; IR(KBr, cm⁻¹): 2927 (C-H), 1583 (C=C); UV-vis (CHCl₃) λ_{max} (nm) (log ϵ): 240(4.21), 214(4.02), 220(3.69); ¹H-NMR (499.74 MHz, CDCl₃): δ 6.2 (s, 2H, >C=CH), 6.8 (t, $J = 7.32$ Hz, 6H, H_{arom}), 6.9 (d, $J = 7.32$ Hz, 6H, H_{arom}), 7.2 (d, $J = 7.81$ Hz, 6H, H_{arom}), 7.3 (t, $J = 6.83$ Hz, 6H, H_{arom}); ¹³C-NMR (125.66 MHz, CDCl₃): δ 125.46, 125.93 (CH_{arom}), 135.16, 155.93 (C_{arom}), 114.78, 119.95, 133.44, 134.45 (C_{butad}); MS (-APCI): m/z 468 (M+H)⁺, 433 (M-Cl); C₂₂H₁₄S₃F₃Cl (M, 466.99). Calcd. C, 56.58; H, 3.02; S, 20.59. Found C, 56.49; H, 3.10; S, 20.44.

2-Chloro-1,1,4,4-(2-hydroxyphenylthio)-1,3-butadiene (4b). Yield 0.70 g (32%); Oil, $R_f=0.8$ with CHCl₃:Petroleum ether (2:1) as an eluent; IR(KBr, cm⁻¹): 3152 (O-H), 1219 (C-O), 1592 (C=C); UV-vis (CHCl₃) λ_{max} (nm) (log ϵ): 240(4.13), 205(4.09), 215(4.05); ¹H NMR (499.74 MHz, CDCl₃): δ 6.15 (s, 1H, >C=CH), 6.9 (d, $J = 8.3$ Hz, 8H, H_{arom}), 7.26 (t, $J = 7.32$ Hz, 8H, H_{arom}), 7.9 (s, 4H, OH); ¹³C NMR (125.66 MHz, CDCl₃): δ 120.05, 125.07, 129.88, 132.23 (CH_{arom}), 135.21, 155.96 (C_{arom}), 109.10, 111.78, 135.11, 136.24 (C_{butad}), MS (+ESI): m/z 584 (M)⁺; C₂₈H₂₁S₄O₄Cl (M, 585.19). Calcd. C, 57.47; H, 3.61; S, 21.91. Found C, 57.40; H, 3.59; S, 21.40.

2-Chloro-1,1,4,4-(4-methoxyphenylthio)-1,3-butadiene (4c). Yield 1.09 g (45%); Oil, $R_f=0.4$ with CCl₄ as an eluent ; IR(KBr, cm⁻¹): 2957, 2834 (C-H), 1030, 1247 (C-O), 1592 (C=C); UV-vis (CHCl₃) λ_{max} (nm) (log ϵ): 241(4.46), 212(4.31), 208(4.54); ¹H NMR (499.74 MHz, CDCl₃): δ 3.6 (s, 12H, OCH₃), 6.1 (s, 1H, >C=CH), 6.73 (d, $J = 8.78$ Hz, 8H, H_{arom}), 7.3 (d, $J = 8.78$ Hz, 8H, H_{arom}); ¹³C NMR (125.66 MHz, CDCl₃): δ 127.42, 127.50 (CH_{arom}), 131.58, 158.90 (C_{arom}), 113.61 (C_{butad}), 54.34 (-OCH₃); MS (+ESI): m/z 640 (M)⁺, 605 (M-Cl); C₃₂H₂₉S₄O₄Cl (M, 641.29). Calcd. C, 59.93; H, 4.56; S, 19.97. Found C, 59.62; H, 4.41; S, 19.89.

2-Chloro-1,1,4,4-(4-hydroxyphenylthio)-1,3-butadiene (4d). Yield 0.38 g (17.11%); Oil, $R_f=0.6$ with CHCl₃ as an eluent; IR(KBr, cm⁻¹): 3326 (O-H), 1224 (C-O), 1584 (C=C); UV-vis (CHCl₃) λ_{max} (nm) (log ϵ): 255(3.62), 228(3.55), 222(3.56); ¹H NMR (499.74 MHz, CD₃OD): δ 6.2 (s, 1H, >C=CH), 6.8 (d, $J = 8.7$ Hz, 8H, H_{arom}), 7.26 (t, $J = 8.7$ Hz, 8H, H_{arom}), 7.9 (s, 4H, OH); ¹³C NMR (125.66 MHz, CDCl₃): δ 115.91 (CH_{arom}), 133.46, 158.21 (C_{arom}), 127.09 (C_{butad}); C₂₈H₂₁S₄O₄Cl (M, 585.19). Calcd. C, 57.47; H, 3.61; S, 21.91. Found C, 57.20; H, 3.53; S, 21.80.

2-Chloro-1,1,4,4-(7-mercapto-4-methyl-coumarinyl)-1,3-butadiene (4e). Yield 0.72 g (22%); m.p.: 139-140°C. $R_f=0.5$ with CCl_4/EtAc (2:1) as an eluent; IR(KBr, cm^{-1}): 2920, 1385 (C-H), 1735 (C=O), 1592 (C=C); UV-vis (CHCl_3) λ_{max} (nm) ($\log\epsilon$): 277(5.57), 212(4.86), 209(4.69); ^1H NMR (499.74 MHz, CDCl_3): δ 2.33 (s, 12H, CH_3), 7.47 (d, $J = 8.29$ Hz, 4H, H_{arom}); ^{13}C NMR (125.66 MHz, CDCl_3): δ 121.12 (CH_{arom}), 124.27, 139.85, 150.76, 153.00, 159.07 (C_{arom}), 113.43, 113.95, 118.09 (C_{butad}), 17.58 ($-\text{CH}_3$); MS (+APCI): m/z 848 (M^+), 657, 622 (M-SR), (M-Cl); $\text{C}_{44}\text{H}_{29}\text{S}_4\text{O}_8\text{Cl}$ (M, 849.43). Calcd. C, 62.21; H, 3.44; S, 15.09. Found C, 62.14; H, 3.40; S, 15.60.

2-Chloro-1,1,4,4-(2-methylphenylthio)-1,3-butadiene (4f). Yield 0.60 g (27%); Oil, $R_f=0.65$ with Petroleum ether as an eluent; IR(KBr, cm^{-1}): 2921, 1379 (C-H), 1588 (C=C); UV-vis (CHCl_3) λ_{max} (nm) ($\log\epsilon$): 240(4.31); ^1H NMR (499.74 MHz, CDCl_3): δ 2.4 (s, 12H, CH_3), 6.1 (s, 1H, $>\text{C}=\text{CH}$), 7.30-7.55 (m, 16H, H_{arom}); ^{13}C NMR (125.66 MHz, CDCl_3): δ 130.60, 130.06 (CH_{arom}), 137.78, 135.76 (C_{arom}), 126.96, 127.66, 129.16 (C_{butad}), 20.28 ($-\text{CH}_3$); MS (+ESI): m/z 578 ($\text{M}+\text{H}^+$); $\text{C}_{32}\text{H}_{29}\text{S}_4\text{Cl}$ (M, 577.29). Calcd. C, 66.57; H, 5.06; S, 22.22. Found C, 66.43; H, 5.02; S, 22.10.

2-Chloro-1,1,4,4-(2,4-dimethylphenylthio)-1,3-butadiene (4g). Yield 0.42 g (18%); Oil, $R_f=0.7$ with Petroleum ether as an eluent; IR(KBr, cm^{-1}): 2919, 1376 (C-H), 1601 (C=C); UV-vis (CHCl_3) λ_{max} (nm) ($\log\epsilon$): 240(4.54); ^1H NMR (499.74 MHz, CDCl_3): δ 2.14-2.28 (s, 24H, CH_3), 6.85 (s, 1H, $>\text{C}=\text{CH}$), 7.26 (d, $J = 7.81$, 12H, H_{arom}); ^{13}C NMR (125.66 MHz, CDCl_3): δ 130.16 (CH_{arom}), 137.31, 136.78, 131.34 (C_{arom}), 130.13, 129.64, 126.29 (C_{butad}), 19.92 ($-\text{CH}_3$); $\text{C}_{36}\text{H}_{41}\text{S}_4\text{Cl}$ (M, 633.40). Calcd. C, 68.26; H, 5.89; S, 20.25. Found C, 68.12; H, 5.90; S, 20.23.

1,1,2-Trichloro-4-(7-mercapto-4-methyl-coumarinyl)-1-buten-3-in (5e). Yield 1.40 g (84%); m.p.: 136-37°C. $R_f=0.75$ with CH_2Cl_2 as an eluent; IR(KBr, cm^{-1}): 2158 ($\text{C}\equiv\text{C}$), 1601 (C=C), 1620 (C=O); UV-vis (CHCl_3) λ_{max} (nm) ($\log\epsilon$): 276(2.17), 230(2.00), 232(1.92); ^1H NMR (499.74 MHz, CDCl_3): δ 2.36 (s, 3H, CH_3), 6.71 (s, 1H, $>\text{C}=\text{CH}$), 7.1-7.6 (m, 3H, H_{arom}); ^{13}C NMR (125.66 MHz, CDCl_3): δ 120.73, 124.42, 125.63, 128.59 (CH_{arom}), 135.29, 150.66, 153.04 (C_{arom}), 158.99 (C=O), 84.79, 91.24 ($\text{C}\equiv\text{C}$), 17.58 ($-\text{CH}_3$); MS (+ESI): m/z 346 (M^+), 311 (M-Cl); $\text{C}_{14}\text{H}_7\text{O}_2\text{SCl}_3$ (M, 345.63). Calcd. C, 48.65; H, 2.04; S, 9.28. Found C, 48.57; H, 1.98; S, 9.17.

1,1,2-Trichloro-4-(2-methylphenylthio)-1-buten-3-in (5f). Yield 0.98 g (93%); Oil, $R_f=0.45$ with Petroleum ether as an eluent; IR(KBr, cm^{-1}): 3062 (C-H), 2155 ($\text{C}\equiv\text{C}$), 1588 (C=C); UV-vis (CHCl_3) λ_{max} (nm) ($\log\epsilon$): 265(3.82), 230(3.80), 212(3.76); ^1H NMR (499.74 MHz, CDCl_3): δ 2.36 (s, 3H, CH_3), 7.1-7.7 (m, 4H, H_{arom}); ^{13}C NMR (125.66 MHz, CDCl_3): δ 125.61, 126.64 (CH_{arom}), 128.62, 129.70, 133.76 (C_{arom}), 88.58, 87.88 ($\text{C}\equiv\text{C}$), 19.77 ($-\text{CH}_3$); MS (+APCI): m/z 278 ($\text{M}+\text{H}^+$), 243, 208 (M-Cl), (M-2Cl); $\text{C}_{11}\text{H}_7\text{SCl}_3$ (M, 277.60). Calcd. C, 47.83; H, 2.54; S, 11.59. Found C, 47.65; H, 2.43; S, 11.30.

1,1,2-Trichloro-4-(2,4-dimethylphenylthio)-1-buten-3-in (5g). Yield 0.52 g (47%); Oil, $R_f=0.4$ with Petroleum ether as an eluent; IR(KBr, cm^{-1}): 3009 (C-H), 2147 ($\text{C}\equiv\text{C}$), 1601 (C=C); UV-vis (CHCl_3) λ_{max} (nm) ($\log\epsilon$): 262(4.21), 226(4.01), 200(3.82); ^1H NMR (499.74 MHz, CDCl_3): δ 2.31-2.35 (d, $J = 7.81$ Hz, 6H, CH_3), 7.1-7.6 (m, 3H, H_{arom}); ^{13}C NMR (125.66 MHz, CDCl_3): δ 125.61, 126.64 (CH_{arom}), 128.62, 129.70, 133.76 (C_{arom}), 88.58, 87.88 ($\text{C}\equiv\text{C}$), 19.77 ($-\text{CH}_3$); MS (+ESI): m/z 292 ($\text{M}+\text{H}^+$), 257 (M-Cl); $\text{C}_{12}\text{H}_9\text{SCl}_3$ (M, 291.629). Calcd. C, 49.42; H, 3.11; S, 10.99. Found C, 49.27; H, 3.10; S, 10.53.

1,1,2,4-Tetrachloro-4-(benzo-1,3-thiazolyl-(2)-thio)-1,3-butadiene (6h). Yield 0.124 g (9.18%); Oil, $R_f=0.5$ with CHCl_3 as an eluent; IR(KBr, cm^{-1}): 3063 (C-H), 2157 (C \equiv C), 1572 (C=C), 1742 (C-N); UV-vis (CHCl_3) λ_{max} (nm) ($\log \epsilon$): 262(4.56), 230(4.37), 222(4.36); ^1H NMR (499.74 MHz, CDCl_3): δ 6.8 (s, 5H, >C=CH), 7.1-7.9 (m, 4H, H_{arom}); ^{13}C NMR (125.66 MHz, CDCl_3): δ 120.15, 120.21, 122.14, 124.62 (CH_{arom}), 158.69, 152.25, 135.94 (C_{arom}), 110.66, 123.25, 125.63, 131.44 (C_{butad}); MS (+ESI): m/z 357(M) $^+$, 322 (M-Cl); $\text{C}_{11}\text{H}_5\text{NS}_2\text{Cl}_4$ (M, 357.1). Calcd. C, 39.82; H, 1.13; S, 18.00. Found C, 39.20; H, 1.15; S, 18.03.

1-Bromo-1,2-dichloro-4-(7-mercapto-4-methyl-coumarinyl)-1-buten-3-in (8e). Yield 0.2 (20%); Oil, $R_f=0.75$ with CHCl_3 as an eluent; IR(KBr, cm^{-1}): 2152 (C \equiv C), 1601 (C=C), 1717 (C=O); UV-vis (CHCl_3) λ_{max} (nm) ($\log \epsilon$): 264(4.55), 227(4.39), 199(4.46); ^1H NMR (499.74 MHz, CDCl_3): δ 2.35 (d, $J=6.35$, 3H, CH_3), 6.1 (s, 1H, >C=CH), 7.1-7.6 (m, 3H, H_{arom}); ^{13}C NMR (125.66 MHz, CDCl_3): δ 112.01, 120.71, 125.69, 126.14 (CH_{arom}), 117.99, 132.63, 150.69, 152.54 (C_{arom}), 158.95 (C=O), 75.8, 76.05 (C \equiv C), 17.58 (- CH_3); MS (+ESI): m/z 390 (M) $^+$, 312 (M-Br); $\text{C}_{14}\text{H}_7\text{O}_2\text{SCl}_2\text{Br}$ (M, 390.08). Calcd. C, 43.10; H, 1.80; S, 8.22. Found C, 43.15; H, 1.73; S, 8.19.

1-Bromo-1,2-dichloro-4-(2,4-dimethylphenylthio)-1-buten-3-in (8g). Yield 0.25g (17%); Oil, $R_f=0.6$ with CHCl_3 as an eluent; IR(KBr, cm^{-1}): 1601 (C=C), 2144 (C \equiv C); UV-vis (CHCl_3) λ_{max} (nm) ($\log \epsilon$): 263(4.07), 212(4.05), 208(3.93); ^1H NMR (499.74 MHz, CDCl_3): δ 2.28 (d, $J=6.34$, 6H, CH_3), 6.8-7.4 (m, 3H, H_{arom}); ^{13}C NMR (125.66 MHz, CDCl_3): δ 19.94 (CH_3), 85.6, 89.9 (C \equiv C), 125.85, 124.91 (CH_{arom}), 141.43, 139.62, 134.76, 130.19 (C_{arom}); MS (+ESI): m/z 336(M) $^+$, 258(M-Br); $\text{C}_{12}\text{H}_9\text{SCl}_2\text{Br}$ (M, 336.08). Calcd. C, 42.80; H, 2.69; S, 9.54. Found C, 42.72; H, 2.65; S, 9.49.

1-Bromo-1,2-dichloro-4-(benzo-1,3-thiazolyl-(2)-thio)-1,3-butadiene (9h). Yield 0.25g (17%); Oil, $R_f=0.45$ with CHCl_3 as an eluent; IR(KBr, cm^{-1}): 3063 (C-H), 1565 (C=C), 1738 (C-N); UV-vis (CHCl_3) λ_{max} (nm) ($\log \epsilon$): 265(3.90), 215(3.81), 212(3.78); ^1H NMR (499.74 MHz, CDCl_3): δ 6.81 (d, $J=6.35$, 1H, >C=CH), 7.1-7.9 (m, 4H, H_{arom}); ^{13}C NMR (125.66 MHz, CDCl_3): δ 120.16, 122.20, 124.63, 125.57 (CH_{arom}), 158.65, 152.23, 135.97 (C_{arom}), 109.06, 121.50, 130.58, 132.06 (C_{butad}); MS (+ESI): m/z 401(M) $^+$, 366(M-Cl); $\text{C}_{11}\text{H}_5\text{NS}_2\text{Cl}_3\text{Br}$ (M, 401.55). Calcd. C, 32.90; H, 1.00; S, 15.96. Found C, 32.91; H, 1.18; S, 15.86.

Acknowledgements

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