Silica-Assisted Reactions of Pyrroles with 1-Acyl-2-bromoacetylenes

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Abstract: Pyrroles react with 1-acyl-2-bromoacetylenes at room temperature on silica to give 2-acyl-1,1-di(pyrrol-2-yl)ethenes as major products in yields of up to 60%. Under reaction conditions employed, the intermediates (*E*)-2-(2-acyl-1-bromoethenyl)pyrroles (3–11% isolated yields) either readily exchange the bromine atom for the pyrrole molecule or eliminate HBr to afford 2-(2-acylethynyl)pyrroles, which can be isolated in 9–22% yields by chromatography of the reaction mixture on Al_2O_3.

Key words: pyrroles, 1-acyl-2-bromoacetylenes, 2-(2-acyl-1-bromoethenyl)pyrroles, 2-acyl-1,1-di(pyrrol-2-yl)ethenes, 2-(2-acylethynyl)pyrroles, silica

Silica plays an important role in organic synthesis and is widely used both in industrial processes and preparative organic reactions. Such reactions often proceed under mild conditions with high chemo-, regio-, and stereoselectivity and allow for simpler product isolation procedures as compared to analogous reactions in solution.[1–3] Synthetic application of solid supports and chromatographic sorbents, including their modified forms, are steadily growing.[4–6]

The use of silica as a solid support in the *C*-ethenylation of pyrroles with acylacetylenes proved to be advantageous; it allowed one to achieve significant reaction acceleration, improved regio- and stereoselectivity, and increased yields of adducts.[7,8]

Acyl-haloacetylenes have not yet been studied in the reaction with pyrroles, although this would not only contribute to understanding the reactivity of both pyrroles and acylhaloacetylenes, but also provide a route to novel functionalized vinylpyrroles, potent building blocks for design of drugs[9] and advanced materials.[10]

Generally, the interaction of haloacetylenes with nucleophiles can proceed via halogen substitution or addition to the triple bond.[11,12] Introduction of strong electron-withdrawing substituents into haloacetylenes not only enhances their reactivity, but also makes the halogen substitution a major pathway of their reactions with nucleophiles. Thus, the first step of interaction of 1-acyl-2-bromoacetylenes with nucleophiles is the exclusive formation of ethynylketones.[13]

In the present work, we have for the first time undertaken a study of the reaction of pyrroles **1a–c** with 1-acyl-2-bromoacetylenes **2a**,**b**.

Under solvent-free conditions, the process is accompanied by strong exothermic effect (sometimes up to explosion) and resinification, whereas in solvents it slows down drastically. For example, in Et_2O, the reactants **1a** and **2b** did not show any reaction at room temperature for 24 hours.

A successful application of silica as a reaction medium for the *C*-ethenylation of pyrroles with acylacetylenes[7,8] prompted us to employ this methodology for the addition of pyrroles to 1-acyl-2-bromoacetylenes.

According to Scheme 1, pyrroles **1a–c** reacted with acylbromoacetylenes **2a**,**b** on silica under mild conditions (room temperature, moderate self-heating, 15 to 30 minutes) to form unexpectedly 2-acyl-1,1-di(pyrrol-2-yl)ethenes **4a–f** as major products (in yields of up to 60%, based on a starting pyrrole).

The expected primary adducts, 2-(2-acyl-1-bromoethenyl)pyrroles **3a–f,** could be isolated (by chromatography on Al_2O_3) in 3–11% yields only.

Monitoring of the reaction of pyrrole (**1a**) with acetylene **2b** by ^1H NMR ($CDCl_3$ extracts of probes) confirmed (Figure 1) the primary adduct to be 2-(1-bromo-2-thenoylethenyl)pyrrole (**3d**), the content of which increased over the time studied (one hour). During the first five minutes, 1,1-di(pyrrol-2-yl)-2-thenoylethene (**4d**) (the **3d/4d** ratio, 2:1) and trace amounts of 2-(2-thenoylethynyl)pyrrole (**5d**) were detected in the reaction mixture. The content of the latter remained constant for one hour, whereas the **3d/4d** ratio had changed to 3:1 by the time the starting pyrrole (**1a**) (45 min) had disappeared completely. Additionally, the reaction mixture contained discernable (*Z*)-1,2-dibromo-2-thenoylethene (**6**), originating from HBr addition to the bromo-thenoylacetylene **2b** (HBr can be formed in the addition-elimination reaction of **3d** with **1a**). The final reaction mixture consisted of **3d**, **4d**, and **6** in a ratio of 7:2:4, thus indicating that the adduct **3d** remained a major component of the reaction mixture before work up.

However, in this case we failed to isolate the adduct **3d** in pure form. During chromatography on alumina, it partially underwent HBr elimination to form the acetylene **5d** in 12% yield, while the major part of **3d** polymerized.

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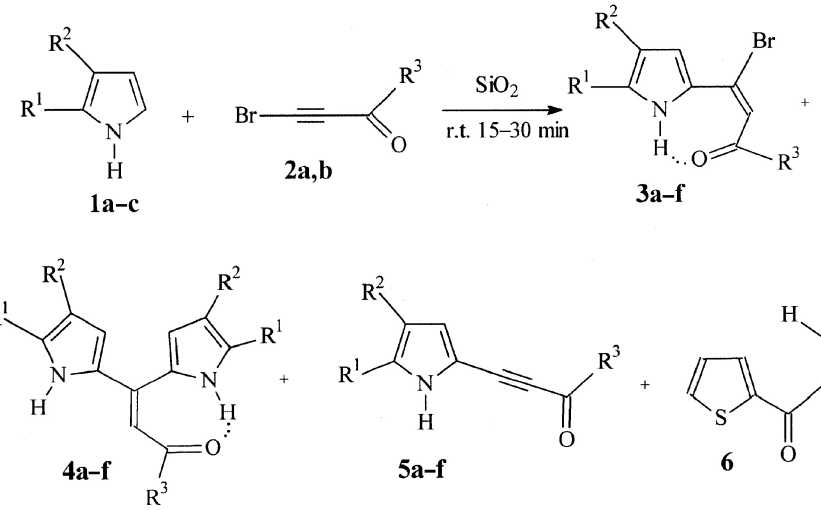


1	2	3-5	R^1	R^2	R^3	Yield, % 3	4	5
a	**a**	**a**	H	H	Ph	*	17	9
b	**a**	**b**	$(CH_2)_4$		Ph	3	19	19
c	**a**	**c**	Ph	H	Ph	6	39	17
a	**b**	**d**	H	H	2-thienyl	*	31	12
b	**b**	**e**	$(CH_2)_4$		2-thienyl	< 1	57	22
c	**b**	**f**	Ph	H	2-thienyl	11	60	20

* not isolated

Scheme 1

Still, 2-(2-acyl-1-bromoethenyl)pyrroles **3b**,**c**,**f** were stable enough to be isolated by chromatography on alumina in 3–11% yield.

The isolated yields of 2-acyl-1,1-di(pyrrol-2-yl)ethenes **4a–f** were also sensitive towards the nature of substituents in the pyrrole ring.

Thus, from the equimolar mixtures of pyrroles **1b**,**c** and acetylene **2b**, after their short contact (15 min) with silica, the adducts **4e**,**f** were prepared in 57% and 60% yields, respectively. Meanwhile, in order to attain a preparatively acceptable yield (31%) of the dipyrrolylethene **4d**, it was necessary to use a two-fold molar excess of the pyrrole (**1a**) and increase the reaction time to 30 minutes. However, further prolonging the process resulted in resinification of the products.

In the above-mentioned cases, acetylenes **5e** and **5f** were also formed in low yields (3% and 2%, respectively). The yields of these products increased to 20–22% after chromatographic treatment of reaction mixtures on alumina, again supporting the HBr elimination from the primary adducts **3** to be the source of acetylenes **5**.

Correspondingly, 2-acyl-1,1-di(pyrrol-2-yl)ethenes **4a–f** are mainly formed as a result of the exchange of bromine atom in 2-(2-acyl-1-bromoethenyl)pyrroles **3a–f** for a second molecule of the pyrrole **1** (presumably, through an addition-elimination two-step process). Another probable route to **4a–f** is the addition of the pyrrole **1** to acetylenes **5a–f**. It is also possible that both of these routes are followed.

According to ^{1}H NMR, 2-(2-acyl-1-bromoethenyl)pyrroles **3a–f** are (*E*)-isomers with *s-cis*-conformation by disposition of the carbonyl group and pyrrole ring.

Thus, 2D NOESY spectrum of the 2-(2-benzoyl-1-bromoethenyl)-5-phenylpyrrole (**3c**) shows the following characteristic nuclear Overhauser effects (NOE): the H_α atom only has a resonance with the benzoyl H_{ortho} atom. For H_{ortho} atoms in the 5-phenyl substituent, there are NOEs with the NH and the H-4 pyrrole atoms. Such a conformation implies a strong intramolecular hydrogen bond between the NH and the carbonyl group, which causes a considerable down-field shift of the NH signal to the region of δ = 13.5–14.5 ppm.[14] Indeed, in the case of pyrrole **3c** (Figure 2), a broadened singlet of the NH atom is observed at δ = 14.50 ppm.

The existence of such an interaction is supported by the absence of NH stretching vibrations at ν = 3100–3400 cm^{-1} in the IR spectrum of **3c**, as well as in the IR spectra of compounds **4b** and **5c**, all recorded in KBr pellets. Likewise, in IR spectra of 2-(2-acyl-1-phenylethenyl)-5-phenylpyrroles ($c = 10^{-3}$–10^{-4} mol /L solutions in CCl_4), having a similar strong intramolecular H-bond, the NH band was also anomalously shifted to the ν = 3000–3100 cm^{-1} region at low temperatures.[15] In the IR spectra of pyrroles **3a–f** the C=O stretches are correspondingly shifted to a very low frequency region, at ν = 1633–1620 cm^{-1}. The source of such spectral anomalies is assumed to be a contribution of the zwitterionic structure **3′c** (Scheme 2).

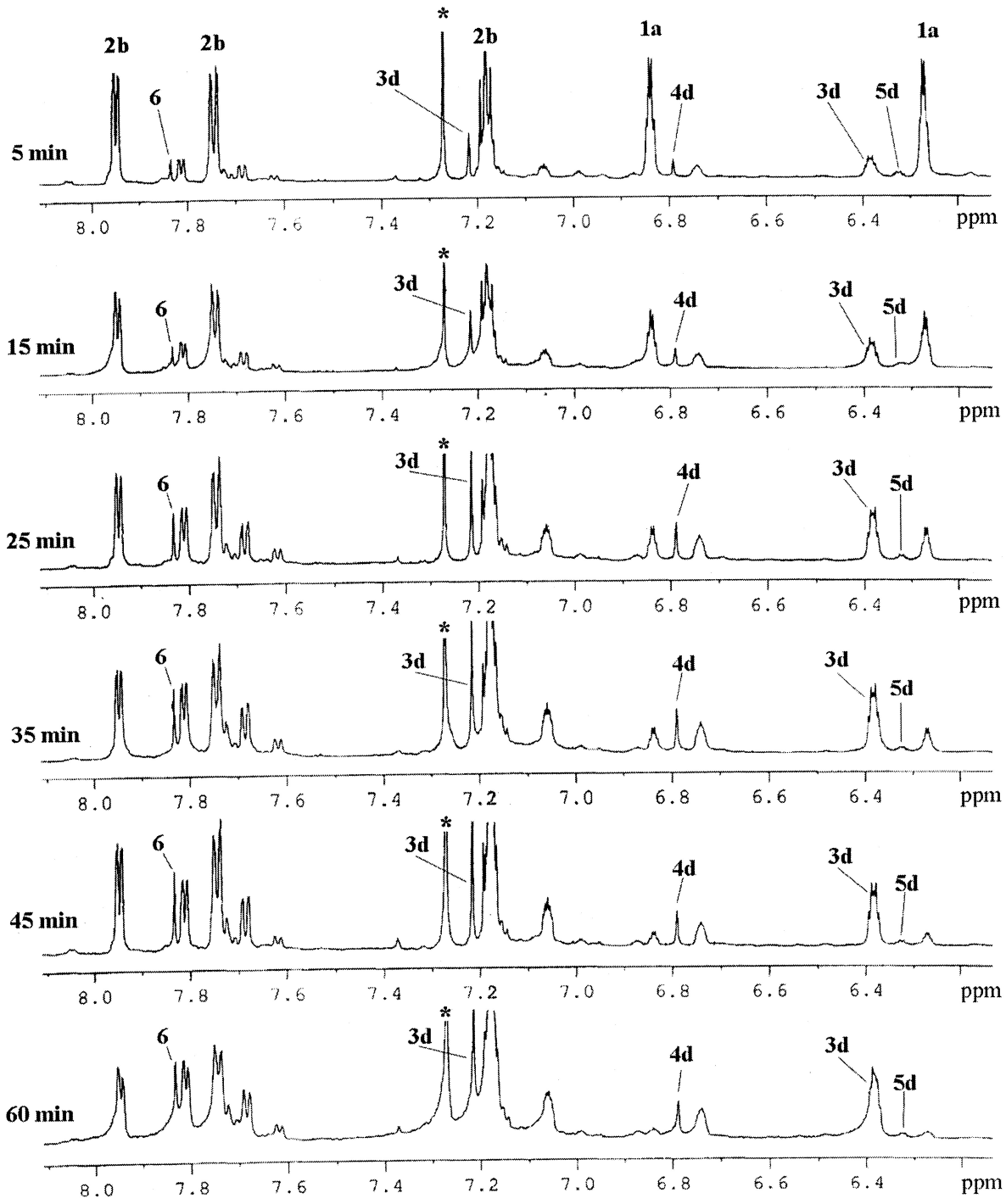
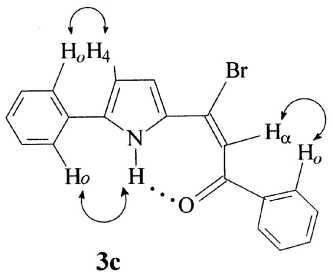
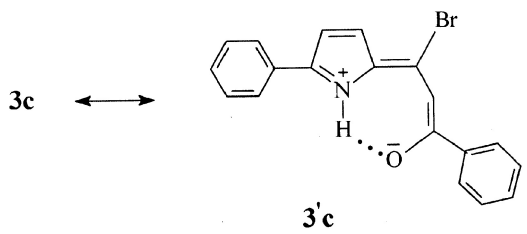


Figure 1 ^{1}H NMR monitoring of the reaction of the pyrrole (**1a**) with 2-bromo-1-thenoylacetylene (**2b**) on silica (the ratio **1a/2b**, 1:1). The ratio of the reaction products was determined by the integral intensity of atoms H_α (**3d**, **4d**, **6**). *: $CDCl_3$



3c

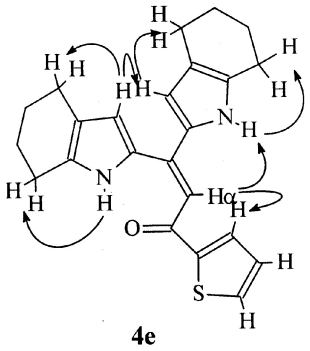
Figure 2



3'c

Scheme 2

In 2-acyl-1,1-di(pyrrol-2-yl)ethenes **4a–f** a similar intramolecular hydrogen bond of the NH group in one of the pyrrole rings with the carbonyl group causes the same very strong down-field shift of the NH signal (δ = 13.80–14.96 ppm), while the signal of the second NH group (a free one) appeared in the region of δ = 8.16–8.86 ppm. For these compounds, the spin systems of both pyrrole rings are reliably separated in 2D COSY spectra by cross-peaks between the NH and ring H atom signals. The major interactions observed are shown below by example of compound **4e** (Figure 3).



4e

Figure 3

IR spectra of solutions of compounds **4c** and **4f** in CCl_4 ($c = 10^{-3}$–10^{-4} mol/L) show absorption bands of the free NH group stretches at ν = 3460 cm^{-1} and 3440 cm^{-1}, respectively. The bands related to the second NH group participating in the intramolecular H-bond are supposed to be shifted to the low frequency region and do not show up in this solvent at room temperature, similar to compounds with the same type of H-bond.[14]

IR spectra (4000–400 cm^{-1}) were taken with KBr pellets or in solutions (CCl_4) using a Bruker IFS-25 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 250 [250.13 MHz for ^1H and 62.9 MHz for ^{13}C, respectively] instrument in trichloromethanol solutions with HMDS as an internal standard. Assignment of signals in ^1H NMR spectra was done using 2D COSY and NOESY homonuclear correlation techniques.[16] Resonance signals of carbon atoms in ^{13}C NMR spectra were assigned on the basis of analysis of 2D HSQC and HMBC spectra.[17]

Analysis of reaction mixtures and purity control of compounds obtained were performed by TLC using Silufol plates; eluent: *n*-hexane–Et_2O (2:1).

Preparative separation of compounds was carried out by chromatography (on column or in non-fixed thin layer) on Al_2O_3. Pyrrole (**1a**) was a commercial product (Aldrich). 4,5,6,7-Tetrahydroindole (**1b**) and 2-phenylpyrrole (**1c**) were prepared correspondingly from cyclohexanonoxime and acetophenonoxime by the Trofimov reaction.[18] Silica (silica gel, L 100/160 μ, pH 4.5–5, Chemapol) was washed with distilled water and EtOH and dried in an oven (180 °C) until a constant weight.

Reaction of Pyrroles with 1-Acyl-2-bromoacetylenes; General Procedure

Equimolar amounts of pyrrole **1a–c** (2 mmol) and 1-acyl-2-bromoacetylene **2a**,**b** (2 mmol) were vigorously rubbed up in a china mortar with a 10-fold exess of SiO_2 at r.t. over 1–2 min. The reaction paste self–heated (5–8 °C) and instantly acquired a bright colour, which then turned to yellow and further to orange-brown in ca. 10 min. The paste was allowed to stay for 15–30 min, then the products were successively extracted with *n*-hexane, *n*-hexane–Et_2O mixture (from 2:1–1:2) and Et_2O. The extracts were chromatographed on Al_2O_3 (column or TLC). Crystalline products were recrystallised from *n*-hexane–Et_2O mixture (1:1).

2-(2-Benzoyl-1-bromoethenyl)-4,5,6,7-tetrahydroindole (3b)

Red-orange solid; mp 127–128 °C.

IR (KBr): 3065, 3004, 2924, 2852, 1633, 1614, 1596, 1575, 1556, 1540, 1483, 1434, 1394, 1346, 1302, 1285, 1233, 1177, 1139, 1052, 1022, 973, 954, 906, 811, 780, 719, 698, 668 cm^{-1}.

^1H NMR: δ = 13.63 (br s, 1 H, NH), 7.97 (m, 2 H, H_{ortho}Ph), 7.55 (m, 1 H, H_{para}Ph), 7.47 (m, 2 H, H_{meta}Ph), 7.13 (s, 1 H, H-α), 6.84 (d, ^4J = 1.8 Hz, 1 H, H-3), 2.76 (m, 2 H, CH_2-7), 2.59 (m, 2 H, CH_2-4), 1.80 (m, 4 H, CH_2-5,6).

Anal. Calcd for $C_{17}H_{16}BrNO$: C, 61.83; H, 4.88; N, 4.24; Br, 24.19. Found: C, 61.51; H, 4.35; N, 3.99.

2-(2-Benzoyl-1-bromoethenyl)-5-phenylpyrrole (3c)

Red crystals; mp 124–125 °C.

IR (KBr): 3115, 3067, 3006, 2927, 2861, 1624, 1594, 1574, 1536, 1502, 1472, 1453, 1361, 1319, 1212, 1177, 1075, 1039, 1023, 1001, 967, 922, 896, 866, 814, 794, 760, 738, 691, 780, 668, 651, 602, 533 cm^{-1}.

^1H NMR: δ = 14.50 (br s, 1 H, NH), 8.00 (m, 2 H, H_{ortho}COPh), 7.78 (m, 2 H, H_{ortho}Ph-5), 7.56 (m, 1 H, H_{para}COPh), 7.51 (m, 2 H, H_{meta}COPh), 7.47 (m, 2 H, Ph-5), 7.32 (m, 1 H, H_{para}Ph-5), 7.28 (s, 1 H, H-α), 7.11 (dd, ^3J = 4.1 Hz, ^4J = 2.2 Hz, 1 H, H-3), 6.76 (dd, ^3J = 4.1 Hz, ^4J = 2.4 Hz, 1 H, H-4).

Anal. Calcd for $C_{19}H_{14}BrNO$: C, 64.79; H, 4.01; N, 3.98; Br, 22.68. Found: C, 65.15; H, 4.11; N, 3.86; Br, 22.21.

2-(1-Bromo-2-thenoylethenyl)-4,5,6,7-tetrahydroindole (3e)

^1H NMR: δ = 13.47 (br s, 1 H, NH), 7.73 (dd, ^3J = 3.9 Hz, ^4J = 1.2 Hz, 1 H, H-3 of thenoyl), 7.61 (dd, ^3J = 4.8 Hz, ^4J = 1.2 Hz, 1 H, -5 of thenoyl), 7.13 (dd, ^3J = 4.8 Hz, ^3J = 3.9 Hz, 1 H, H-4 of thenoyl), 7.02 (s, 1 H, H-α), 6.81 (d, ^4J = 2.0 Hz, 1 H, H-3), 2.71 (m, 2 H, CH_2-7), 2.55 (m, 2 H, CH_2-4), 1.89 (m, 2 H, CH_2-6), 1.74 (m, 2 H, CH_2-5).

2-(1-Bromo-2-thenoylethenyl)-5-phenylpyrrole (3f)

Red-orange crystals; mp 160–161 °C.

IR (KBr): 3099, 2918, 2856, 1620, 1602, 1579, 1537, 1504, 1474, 1452, 1409, 1375, 1348, 1314, 1303, 1283, 1263, 1242, 1214, 1187, 1077, 1060, 1042, 1028, 1017, 968, 921, 906, 886, 858, 841, 810, 753, 728, 705, 685, 656, 592, 578 cm^{-1}.

^1H NMR: δ = 14.41 (br s, 1 H, NH), 7.84 (dd, ^3J = 3.8 Hz, ^4J = 1.0 Hz, 1 H, H-3 of thenoyl), 7.79 (m, 2 H, H_{ortho}Ph-5), 7.69 (dd, ^3J = 4.7 Hz, ^4J = 1.0 Hz, 1 H, H-5 of thenoyl), 7.48 (m, 2 H, H_{meta}Ph-5), 7.35 (m, 1 H, H_{para}Ph-5), 7.21 (s, 1 H, H-α), 7.18 (dd, ^3J = 4.7 Hz, ^3J = 3.8 Hz, 1 H, H-4 of thenoyl), 7.11 (dd, ^3J = 3.9 Hz, ^4J = 2.0 Hz, 1 H, H-3), 6.76 (dd, ^3J = 3.9 Hz, ^4J = 2.6 Hz, 1 H, H-4).

^{13}C NMR: δ = 179.60 (C=O), 146.37 (C-2 of thenoyl), 139.07 (C-5 of pyrrole), 134.17 (C-5 of thenoyl), 133.95 ($C_β$), 131.86 (C-3 of thenoyl), 131.15 (C_{ipso}), 130.92 (C-2 of pyrrole), 129.21 (C_{meta}), 128.61 (C-4 of thenoyl), 128.31 (C_{para}), 125.00 (C_{ortho}), 124.65 (C-3 of pyrrole), 116.17 ($C_α$), 110.31 (C-4 of pyrrole).

Anal. Calcd for $C_{17}H_{12}BrNOS$: C, 56.99; H, 3.37; N, 3.91; S, 8.95; Br, 22.30. Found: C, 57.15; H, 3.49; N, 3.96; Br, 21.98.

1,1′-Di(pyrrol-2-yl)-2-benzoylethene (4a)
Red-orange oil.

IR (KBr): 3311, 3101, 3058, 1617, 1595, 1574, 1547, 1522, 1499, 1487, 1451, 1429, 1402, 1383, 1353, 1316, 1241, 1227, 1176, 1139, 1103, 1041, 1021, 1002, 973, 938, 899, 881, 843, 777, 763, 741, 698, 600 cm^{-1}.

^1H NMR: δ = 13.99 (br s, 1 H, NH), 8.67 (br s, 1 H, NH′), 7.98 (m, 2 H, H_{ortho}COPh), 7.52 (m, 1 H, H_{para}COPh), 7.47 (m, 2 H, H_{meta}-COPh), 7.15 (m, 1 H, H-5), 6.95 (m, 1 H, H-5′), 6.84 (s, 1 H, H-α), 6.73 (m, 2 H, H-3, H-3′), 6.38 (m, 1 H, H-4), 6.33 (m, 1 H, H-4′).

^{13}C NMR: δ = 189.82 (C=O), 140.75 ($C_β$), 140.75 (C_{ipso}COPh), 133.06 (C-2′), 132.11 (C_{para}COPh), 129.89 (C-2 of pyrrole), 128.57 (C_{meta}COPh), 128.20 (C_{ortho}COPh), 123.48 (C-5 of pyrrole), 120.69 (C-5′ of pyrrole), 118.90 (C-3 of pyrrole), 112.60 (C-3′ of pyrrole), 111.81 ($C_α$), 111.49 (C-4 of pyrrole), 110.23 (C-4′ of pyrrole).

Anal. Calcd for $C_{17}H_{14}N_2O$: C, 77.84; H, 5.38; N, 10.68. Found: C, 77.46; H, 5.49; N, 10.32.

1,1′-Di(4,5,6,7-tetrahydroindol-2-yl)-2-benzoylethene (4b)
Red crystals; mp 186–187 °C.

IR (KBr): 3309, 3065, 2927, 2851, 1592, 1570, 1541, 1517, 1500, 1479, 1446, 1429, 1336, 1319, 1286, 1267, 1235, 1176, 1140, 1073, 1052, 1035, 1021, 955, 925, 900, 822, 810, 780, 720, 701, 639, 604, 577 cm^{-1}.

^1H NMR: δ = 14.00 (br s, 1 H, NH), 8.25 (br s, 1 H, NH′), 7.97 (m, 2 H, H_{ortho}Ph), 7.50 (m, 1 H, H_{para}Ph), 7.48 (m, 2 H, H_{meta}Ph), 6.65 (s, 1 H, H-α), 6.62 (d, ^4J = 2.0 Hz, 1 H, H-3), 6.50 (d, ^4J = 2.2 Hz, 1 H, H-3′), 2.81 (m, 2 H, CH_2-7), 2.68 (m, 2 H, CH_2-7′), 2.60 (m, 2 H, CH_2-4), 2.58 (m, 2 H, CH_2-4′), 1.84 (m, 8 H, CH_2-5,6, CH_2-5,6′).

^{13}C NMR: δ = 188.34 (C=O), 141.86 ($C_β$), 141.15 (C_{ipso}COPh), 135.45 (C-5 of pyrrole), 131.48 (C-2 of pyrrole), 131.33 (C_{para}-COPh), 131.18 (C-5′ of pyrrole), 128.69 (C-2′ of pyrrole), 128.42 (C_{meta}COPh), 127.93 (C_{ortho}COPh), 122.26 (C-4 of pyrrole), 119.65 (C-4′ of pyrrole), 118.48 (C-3 of pyrrole), 112.48 (C-3′ of pyrrole), 108.24 ($C_α$), 23.76 (CH_2-7,7′), 23.22 (CH_2-5,5′), 23.18 (CH_2-6,6′), 22.94 (CH_2-4,4′).

Anal. Calcd for $C_{25}H_{26}N_2O$: C, 81.05; H, 7.07; N, 7.56. Found: C, 81.38; H, 7.50; N, 7.30.

1,1′-Di(5-phenylpyrrol-2-yl)-2-benzoylethene (4c)
Red crystals; mp 203–205 °C.

IR (KBr): 3270, 3066, 3039, 1600, 1573, 1562, 1539, 1517, 1484, 1474, 1454, 1413, 1384, 1375, 1314, 1288, 1271, 1252, 1236, 1203, 1179, 1158, 1101, 1074, 1051, 1022, 999, 961, 924, 815, 776, 762, 752, 717, 685, 670, 651, 603, 575, 499 cm^{-1}.

^1H NMR: δ = 14.96 (br s, 1 H, NH), 8.86 (br s, 1 H, NH′), 8.06 (m, 2 H, H_{ortho}COPh), 7.87–7.31 (m, 5 H, Ph-5), 7.57–7.29 (m, 5 H, Ph-5′), 7.53 (m, 1 H, H_{para}COPh), 7.48 (m, 2 H, H_{meta}COPh), 6.95 (d, 1 H, H-3), 6.89 (s, 1 H, H-α), 6.83 (d, 1 H, H-3′), 6.81 (d, 1 H, H-4), 6.67 (d, 1 H, H-4′).

^{13}C NMR: δ = 189.28 (C=O), 141.21 (C_{ipso}COPh), 140.25 ($C_β$), 137.39 (C-5 of pyrrole), 135.05 (C-5′ of pyrrole), 133.97 (C-2′ of pyrrole), 131.90 (C_{ipso}COPh), 131.85 (C_{para}COPh), 131.58 (C_{ipso}Ph-5′), 131.04 (C-2 of pyrrole), 129.17 (C_{meta}Ph-5, Ph-5′), 128.57 (C_{meta}COPh), 128.20 (C_{ortho}COPh), 127.83 (C_{para}Ph-5), 127.22 (C_{para}Ph-5′), 124.84 (C_{ortho}Ph-5), 124.33 (C_{ortho}Ph-5′), 120.98 (C-3 of pyrrole), 114.65 (C-3′ of pyrrole), 110.82 ($C_α$), 109.89 (C-4 of pyrrole), 108.12 (C-4′ of pyrrole).

Anal. Calcd for $C_{29}H_{22}N_2O$: C, 84.03; H, 5.35; N, 6.76. Found: C, 83.78; H, 5.67; N, 6.60.

1,1′-Di(pyrrol-2-yl)-2-thenoylethene (4d)
Orange-red oil.

IR (KBr): 3295, 3096, 2922, 1643, 1605, 1551, 1512, 1499, 1407, 1350, 1265, 1243, 1189, 1140, 1080, 1061, 1043, 995, 965, 885, 856, 815, 746, 722, 653, 589 cm^{-1}.

^1H NMR: δ = 13.85 (br s, 1 H, NH), 8.65 (br s, 1 H, NH′), 7.77 (dd, ^3J = 3.7 Hz, ^4J = 1.2 Hz, 1 H, H-3 of thenoyl), 7.58 (dd, ^3J = 4.9 Hz, ^4J = 1.2 Hz, 1 H, H-5 of thenoyl), 7.12 (dd, ^3J = 4.9 Hz, ^3J = 3.7 Hz, 1 H, H-4 of thenoyl), 7.09 (m, 1 H, H-5), 6.96 (m, 1 H, H-5′), 6.75 (s, 1 H, H-α), 6.70 (m, 2 H, H-3, H-3′), 6.35 (m, 2 H, H-4, H-4′).

^{13}C NMR: δ = 181.84 (C=O), 147.93 (C-2 of thenoyl), 140.80 ($C_β$), 133.00 (C-2′ of pyrrole), 132.97 (C-5 of thenoyl), 130.93 (C-3 of thenoyl), 129.88 (C-2 of pyrrole), 128.43 (C-4 of thenoyl), 123.71 (C-5 of pyrrole), 120.56 (C-5′ of pyrrole), 118.99 (C-3 of pyrrole), 112.60 (C-3′ of pyrrole), 111.58 (C-4 of pyrrole), 111.12 ($C_α$), 110.28 (C-4′ of pyrrole).

Anal. Calcd for $C_{15}H_{12}N_2OS$: C, 67.14; H, 4.51; N, 10.44; S, 11.95. Found: C, 66.74; H, 4.14; N, 10.02; S, 11.80.

1,1′-Di(4,5,6,7-tetrahydroindol-2-yl)-2-thenoylethene (4e)
Dark red crystals; mp 210–211 °C.

IR (KBr): 3225, 3162, 3100, 3072, 2926, 2851, 1613, 1575, 1558, 1535, 1513, 1483, 1456, 1409, 1334, 1295, 1233, 1142, 1089, 1056, 995, 952, 928, 843, 809, 745, 725, 676, 622 cm^{-1}.

^1H NMR: δ = 13.80 (br s, 1 H, NH), 8.16 (br s, 1 H, NH′), 7.71 (dd, ^3J = 3.7 Hz, ^4J = 1.2 Hz, 1 H, H-3 of thenoyl), 7.51 (dd, ^3J = 4.9 Hz, ^4J = 1.2 Hz, 1 H, H-5 of thenoyl), 7.08 (dd, ^3J = 4.9 Hz, ^3J = 3.7 Hz, 1 H, H-4 of thenoyl), 6.57 (d, ^4J = 2.2 Hz, 1 H, H-3), 6.56 (s, 1 H, H-α), 6.44 (d, ^4J = 2.4 Hz, 1 H, H-3′), 2.75 (m, 2 H, CH_2-7), 2.64 (m, 2 H, CH_2-7′), 2.54 (m, 4 H, CH_2-4, CH_2-4′), 1.80 (m, 8 H, CH_2-5,6, CH_2-5′,6′).

^{13}C NMR: δ = 180.07 (C=O), 148.75 (C-2 of thenoyl), 140.81 ($C_β$), 135.85 (C-5 of pyrrole), 131.78 (C-5 of thenoyl), 131.32 (C-2 of pyrrole), 131.20 (C- 5′ of pyrrole), 129.71 (C-3 thenoyl), 128.61 (C-2′ of pyrrole), 128.18 (C-4 thenoyl), 122.19 (C-4 of pyrrole), 119.36 (C-4′ of pyrrole), 118.56 (C-3 of pyrrole), 112.41 (C-3′ of pyrrole), 107.30 ($C_α$), 23.78 (CH_2-7), 23.70 (CH_2-5,5′), 23.26 (CH_2-6,6′), 23.16 (CH_2-7′), 22.92 (CH_2-4,4′).

Anal. Calcd for $C_{23}H_{24}N_2OS$: C, 73.37; H, 6.42; N, 7.44; S, 8.52. Found: C, 72.95; H, 6.64; N, 7.58; S, 8.86.

1,1′-Di(5-phenylpyrrol-2-yl)-2-thenoylethene (4f)
Dark red crystals; mp 195–198 °C.

IR (KBr): 3294, 3094, 2922, 2850, 1619, 1602, 1581, 1536, 1503, 1476, 1452, 1405, 1376, 1348, 1313, 1264, 1241, 1076, 1060, 1045, 1021, 968, 922, 907, 885, 856, 810, 789, 755, 728, 706, 684, 592 cm^{-1}.

^1H NMR: δ = 14.71 (br s, 1 H, NH), 8.84 (br s, 1 H, NH′), 7.82 (dd, ^3J = 3.8 Hz, ^4J = 1.0 Hz, 1 H, H-5 of thenoyl), 7.80 (m, 2 H, H_{ortho}Ph-5), 7.59 (dd, ^3J = 4.7 Hz, ^4J = 1.0 Hz, 1 H, H-3 of thenoyl), 7.55 (m, 2 H, H_{ortho}Ph-5′), 7.44 (m, 2 H, H_{meta}Ph-5), 7.41 (m, 2 H, H_{meta}Ph-5′), 7.29 (m, 1 H, H_{para}Ph-5), 7.26 (m, 1 H, H_{para}Ph-5′), 7.13 (dd, ^3J = 4.7 Hz, ^3J = 3.8 Hz, 1 H, H-4 of thenoyl), 6.87 (dd, ^3J = 3.7 Hz, ^4J = 2.4 Hz, 1 H, H-3 of pyrrole), 6.79 (s, 1 H, H-α), 6.77 (dd, ^3J = 3.1 Hz, ^4J = 2.2 Hz, 1 H, H-3′ of pyrrole), 6.72 (dd, ^3J = 3.7 Hz, ^4J = 2.0 Hz, 1 H, H-4 of pyrrole), 6.63 (dd, ^3J = 3.1 Hz, ^4J = 2.4 Hz, 1 H, H-4′ of pyrrole).

^{13}C NMR: δ = 180.87 (C=O), 147.97 (C-2 of thenoyl), 139.86 ($C_β$), 137.78 (C-5 of pyrrole), 134.99 (C-5′ of pyrrole), 134.15 (C-5 of thenoyl), 133.77 (C-2′ of pyrrole), 131.97 (C_{ipso}Ph-5), 131.54 (C_{ipso}Ph-5′), 130.97 (C-2 of pyrrole), 130.71 (C-3 of thenoyl), 129.20 (C_{meta}Ph-5,5′), 128.38 (C-4 of thenoyl), 127.82 (C_{para}Ph-5), 127.21 (C_{para}Ph-5′), 124.88 (C_{ortho}Ph-5), 124.31 (C_{ortho}Ph-5′), 120.99 (C-3 of pyrrole), 114.56 (C-3′ of pyrrole), 110.07 ($C_α$), 109.82 (C-4 of pyrrole), 108.08 (C-4′ of pyrrole).

Anal. Calcd For $C_{27}H_{20}N_2OS$: C, 77.12; H, 4.79; N, 6.66; S, 7.62. Found: C, 76.79; H, 5.09; N, 7.02; S, 7.67.

2-(2-Benzoylethynyl)pyrrole (5a)
Yellow crystals; mp 141–142 °C.

IR (KBr): 3317, 3059, 3030, 2919, 2172, 1628, 1595, 1577, 1560, 1512, 1502, 1448, 1425, 1351, 1316, 1261, 1223, 1176, 1138, 1088, 1038, 1010, 964, 896, 842, 768, 743, 693, 652, 599 cm^{-1}.

^1H NMR: δ = 8.89 (br s, 1 H, NH), 8.19 (m, 2 H, H_{ortho}COPh), 7.63 (m, 1 H, H_{para}COPh), 7.51 (m, 2 H, H_{meta}COPh), 7.00 (m, 1 H, H-5), 6.90 (m, 1 H, H-3), 6.33 (m, 1 H, H-4).

^{13}C NMR: δ = 177.99 (C=O), 136.81 (C_{ipso}COPh), 133.97 (C_{para}-COPh), 129.43 (C_{ortho}COPh), 128.63 (C_{meta}COPh), 123.91 (C-5 of pyrrole), 120.91 (C-3 of pyrrole), 110.72 (C-4 of pyrrole), 110.05 (C-2 of pyrrole), 95.15 ($C_α$), 89.02 ($C_β$).

Anal. Calcd for $C_{13}H_9NO$: C, 79.98; H, 4.65; N, 7.17. Found: C, 79.88; H, 4.78; N, 6.99.

2-(2-Benzoylethynyl)-4,5,6,7-tetrahydroindole (5b)
Orange-red crystals; mp 167–168 °C.

IR (KBr): 3280, 3065, 2948, 2920, 2839, 2155, 1612, 1596, 1567, 1505, 1468, 1445, 1364, 1316, 1304, 1271, 1250, 1224, 1164, 1138, 1042, 1022, 972, 929, 824, 805, 787, 692, 649, 633, 576 cm^{-1}.

^1H NMR: δ = 8.24 (br s, 1 H, NH), 8.13 (m, 2 H, H_{ortho}COPh), 7.56 (m, 1 H, H_{para}COPh), 7.46 (m, 2 H, H_{meta}COPh), 6.61 (d, ^4J = 1.8 Hz, 1 H, H-3), 2.59 (m, 2 H, CH_2-7), 2.49 (m, 2 H, CH_2-4), 1.79 (m, 2 H, CH_2-6), 1.74 (m, 2 H, CH_2-5).

^{13}C NMR: δ = 177.63 (C=O), 137.14 (C_{ipso}COPh), 134.82 (C-5 of pyrrole), 133.62 (C_{para}COPh), 129.31 (C_{ortho}COPh), 128.55 (C_{meta}-COPh), 120.33 (C-3 of pyrrole), 120.29 (C-4 of pyrrole), 107.83 (C-2 of pyrrole), 93.62 ($C_α$), 91.15 ($C_β$), 23.42 (CH_2-7), 23.21 (CH_2-5), 22.89 (CH_2-6), 22.71 (CH_2-4).

Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.56; H, 6.20; N, 5.78.

2-(2-Benzoylethynyl)-5-phenylpyrrole (5c)
Orange crystals; mp 180–181 °C.

IR (KBr): 3309, 3067, 2958, 2855, 2166, 1628, 1595, 1573, 1536, 1518, 1505, 1484, 1470, 1457, 1414, 1383, 1315, 1303, 1289, 1274, 1244, 1217, 1171, 1158, 1075, 1054, 1021, 967, 929, 901, 792, 759, 695, 684, 648, 613, 574, 535, 492 cm^{-1}.

^1H NMR: δ = 9.04 (br s, 1 H, NH), 8.22 (m, 2 H, H_{ortho}COPh), 7.65 (m, 1 H, H_{para}Ph-5), 7.59 (m, 2 H, H_{meta}COPh), 7.56 (m, 2 H, H_{ortho}-Ph-5), 7.46 (m, 2 H, H_{meta}COPh), 7.35 (m, 1 H, H_{para}Ph-5), 6.97 (dd, ^3J = 3.6 Hz, ^4J = 2.5 Hz, 1 H, H-3), 6.62 (dd, ^3J = 3.6 Hz, ^4J = 2.8 Hz, 1 H, H-4).

^{13}C NMR: δ = 177.62 (C=O), 137.50 (C-5 of pyrrole), 136.75 (C_{ipso}COPh), 133.80 (C_{para}COPh), 130.85 (C_{ipso}Ph-5), 129.32 (C_{ortho}COPh), 129.07 (C_{meta}Ph-5), 128.50 (C_{meta}COPh), 127.88 (C_{para}Ph-5), 124.62 (C_{ortho}Ph-5), 122.54 (C-3 of pyrrole), 110.72 (C-2 of pyrrole), 108.24 (C-4 of pyrrole), 93.25 ($C_α$), 89.12 ($C_β$).

Anal. Calcd for: $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 83.75; H, 5.09; N, 5.61.

2-(2-Thenoylethynyl)pyrrole (5d)
Yellow crystals; mp 143–144 °C.

IR (KBr): 3167, 3096, 3071, 3004, 2954, 2174, 1581, 1555, 1512, 1433, 1409, 1353, 1320, 1266, 1249, 1231, 1140, 1099, 1079, 1061, 1039, 996, 930, 883, 858, 820, 749, 728, 720, 703, 655, 599, 552 cm^{-1}.

^1H NMR: δ = 8.93 (br s, 1 H, NH), 7.92 (dd, ^3J = 3.9 Hz, ^4J = 1.2 Hz, 1 H, H-3 of thenoyl), 7.67 (dd, J = 4.9 Hz, J = 1.2 Hz, 1 H, H-5 of thenoyl), 7.14 (dd, ^3J = 4.9 Hz, ^4J = 3.9 Hz, 1 H, H-4 of thenoyl), 6.96 (m, 1 H, H-5), 6.83 (m, 1 H, H-3), 6.28 (m, 1 H, H-4).

^{13}C NMR: δ = 169.71 (C=O), 144.82 (C-2 of thenoyl), 134.84 (C-5 of thenoyl), 134.66 (C-3 of thenoyl), 128.36 (C-4 of thenoyl), 123.68 (C-5 of pyrrole), 120.77 (C-3 of pyrrole), 110.78 (C-4 of pyrrole), 110.03 (C-2 of pyrrole), 91.34 ($C_α$), 87.05 ($C_β$).

Anal. Calcd for $C_{11}H_7NOS$: C, 65.65; H, 3.51; N, 6.96; S, 15.93. Found: C, 65.80; H, 3.31; N, 6.57; S, 15.66.

2-(2-Thenoylethynyl)-4,5,6,7-tetrahydroindole (5e)
Dark yellow crystals; mp 147–148 °C.

IR (KBr) 3260, 3102, 2945, 2918, 2842, 2153, 1596, 1569, 1514, 1469, 1432, 1410, 1354, 1316, 1302, 1256, 1228, 1166, 1138, 1081, 1051, 1016, 943, 926, 858, 845, 823, 806, 760, 715, 667, 648, 630, 556 cm^{-1}.

^1H NMR: δ = 8.43 (br s, 1 H, NH), 7.87 (dd, ^3J = 3.7 Hz, ^4J = 1.2 Hz, 1 H, H-3 thenoyl), 7.63 (dd, ^3J = 4.9 Hz, ^4J = 1.2 Hz, 1 H, H-5 thenoyl), 7.11 (dd, ^3J = 4.9 Hz, ^3J = 3.7 Hz, 1 H, H-4 thenoyl), 6.58 (d, ^4J = 2.0 Hz, 1 H, H-3), 2.57 (m, 2 H, CH_2-7), 2.48 (m, 2 H, CH_2-4), 1.76 (m, 4 H, CH_2-5,6).

^{13}C NMR: δ = 169.56 (C=O), 145.09 (C-2 of thenoyl), 134.83 (C-5 of pyrrole), 134.21 (C-5 of thenoyl), 134.21 (C-3 of thenoyl), 128.23 (C-4 of thenoyl), 120.24 (C-3 of pyrrole), 120.17 (C-4 of pyrrole), 107.60 (C-2 of pyrrole), 92.72 ($C_α$), 89.82 ($C_β$), 23.36 (CH_2-7), 23.15 (CH_2-5), 22.84 (CH_2-6), 22.67 (CH_2-4).

Anal. Calcd for $C_{15}H_{13}NOS$: C, 70.56; H, 5.13; N, 5.48; S, 12.56. Found: C, 70.52; H, 5.48; N, 5.49; S, 12.90.

2-(2-Thenoylethynyl)-5-phenylpyrrole (5f)
Red-orange crystals; mp 183 °C.

IR (KBr): 3298, 3066, 2959, 2922, 2855, 2169, 1597, 1558, 1512, 1462, 1406, 1354, 1315, 1302, 1245, 1225, 1194, 1081, 1057, 1044, 1022, 966, 941, 919, 904, 860, 784, 755, 724, 691, 651, 647, 534, 492 cm^{-1}.

^1H NMR: δ = 9.04 (br s, 1 H, NH), 7.95 (dd, ^3J = 3.8 Hz, ^4J = 1.3 Hz, 1 H, H-3 of thenoyl), 7.68 (dd, ^3J = 4.8 Hz, ^4J = 1.3 Hz, 1 H, H-5 of thenoyl), 7.54 (m, 2 H, H_{ortho}Ph), 7.42 (m, 2 H, H_{meta}Ph), 7.30 (m, 1 H, H_{para}Ph), 7.17 (dd, ^3J = 4.8 Hz, ^3J = 3.8 Hz, 1 H, H-4 of thenoyl), 6.90 (dd, ^3J = 4.0 Hz, ^4J = 2.2 Hz, 1 H, H-3), 6.57 (dd, ^3J = 4.0 Hz, ^4J = 2.5 Hz, 1 H, H-4).

^{13}C NMR: δ = 169.51 (C=O), 144.90 (C-2 of thenoyl), 137.55 (C-5 of pyrrole), 134.79 (C-5 of thenoyl), 134.58 (C-3 of thenoyl), 130.98 (C_{ipso}Ph), 129.28 (C_{meta}Ph), 128.37 (C-4 of thenoyl), 128.09 (C_{para}Ph), 124.71 (C_{ortho}Ph), 122.53 (C-3 of pyrrole), 110.74 (C-2 of pyrrole), 108.38 (C-4 of pyrrole), 92.59 ($C_α$), 87.40 ($C_β$).

Anal. Calcd for $C_{17}H_{11}NOS$: C, 73.62; H, 4.00; N, 5.05; S, 11.56. Found: C, 73.51; H, 4.26; N, 5.16; S, 11.70.

1,2-Dibromo-2-thenoylethene (6)
^1H NMR: δ = 7.18 (dd, ^3J = 4.9 Hz, ^3J = 3.8 Hz, 1 H, H-4), 7.73 (dd, ^3J = 4.9 Hz, ^4J = 1.2 Hz, 1 H, H-5), 7.75 (dd, ^3J = 3.8 Hz, ^4J = 1.2 Hz, 1 H, H-3), 7.84 (s, 1 H, =CH).

^{13} NMR: δ = 179.34 (C=O), 144.26 (C-2), 135.28 (C-5), 133.84 (=CBr), 132.61 (C-3), 131.32 (=CHBr), 128.50 (C-4).

MS: *m/z* [M] calcd for $C_7H_4Br_2OS$: 295.98; found $[M]^+$: 296.

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