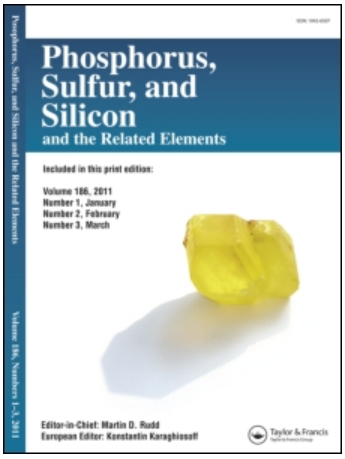

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DIBUTADIENYL PIPERAZINE, DIBUTADIENYL HOMOPIPERAZINES AND BUTADIENYL-SUBSTITUTED PIPERIDINES FROM MONOSUBSTITUTED HALODIENES

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*Compounds **3a–k** were obtained from the reactions of compounds **1a–k** with homopiperazine (**2**) in CH_2Cl_2. Compounds **1a–b**, **1d–f**, and **1h–l** gave compounds **5a–b**, **5d–f**, and **5h–l** with 2-methylpiperazine (**4**) in dichloromethane. Compounds **7c** and **9c** were obtained from the reactions of compound **1c** with 4-ethoxycarbonyl piperazine (**6**) and 4-piperidinol (**8**) in CH_2Cl_2. Compounds **1a** and **1f** gave compounds **11a** and **11f** with 4-methylpiperazine (**10**), and compound **13f** was obtained from the reactions of compound **1f** with 4-methylpiperidine (**12**) in CH_2Cl_2.*

Keywords: Homopiperazine; N,S-substituted-1,3-halodienes; piperazine; piperidine; thiosubstituted nitrodiene

The reactions of perhalogenated butadienes, butenes, and butines with thiols have been described.[1–5] We have informed that S,S,S-,S-, and S,S-substituted nitrodienes were obtained from the reactions of nitrodienes and S-nucleophiles.[6–9] It was known that N-, N,N-substituted dienes were obtained from the reactions of nitrodienes and some nitrogen nucleophiles.[10–14]

We have reported the reactions of some thiosubstituted nitrohalodienes and N-nucleophiles before.[15–18]

The aim of this work was to synthesize novel compounds from the reactions of some aromatic and aliphatic monosubstituted nitrodiene compounds with homopiperazine and derivatives of piperazine and piperidine, and also to establish the structure of these novel compounds.

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It is known that some derivatives of homopiperazine exhibit biological activity and are used in medicinal chemistry,[19,20] and derivatives of piperazine are important in clinical chemistry.[21] Also it has been reported that some piperazine compounds have been used in gen-transfer before.[22] It is known that substituted piperidines have shown biological activity.[23]

We have reported compounds **1a–l** before.[24–27] **1a–k** gave **3a–k** with homopiperazine (**2**) in CH_2Cl_2 (Scheme 1).

Dibutadienyl homopiperazines **3a–k** are yellow, novel compounds. **5a–b**, **5d–f**, **5h**, **5i**, **5k**, and **5l** were obtained from the reactions of **1a–b**, **1d–f**, **1h**, **1i**, **1k**, and **1l** with derivatives of piperazine (**4**), respectively. The structures of these compounds were determined by microanalysis and spectroscopic data.

Compound **1c** gave **7c** with piperazine **6. 9c** was obtained from compound **1c** and piperidine **8**. Compounds **11a** and **11f** were obtained in the reactions of **1a** and **1f** with piperazine **10**. Compound **1f** gave **13f** with piperidine **12**. Compounds **7c**, **9c**, **11a**, **11f**, and **13f** were stable and are novel compounds.

The infrared (IR) spectra of compound **7c** shows a characteristic band for C=O at 1700 cm^{-1}. Butadienylpiperazine **9c** shows a characteristic band for OH at 3450 cm^{-1} in the IR spectrum. The ^{1}H NMR spectrum of compounds **3f** and **5f** show multiplet signals at $\delta \cong 5.6$–6.0 ppm and $\delta \cong 5.1$–5.4 ppm for the protons of the vinyl groups.

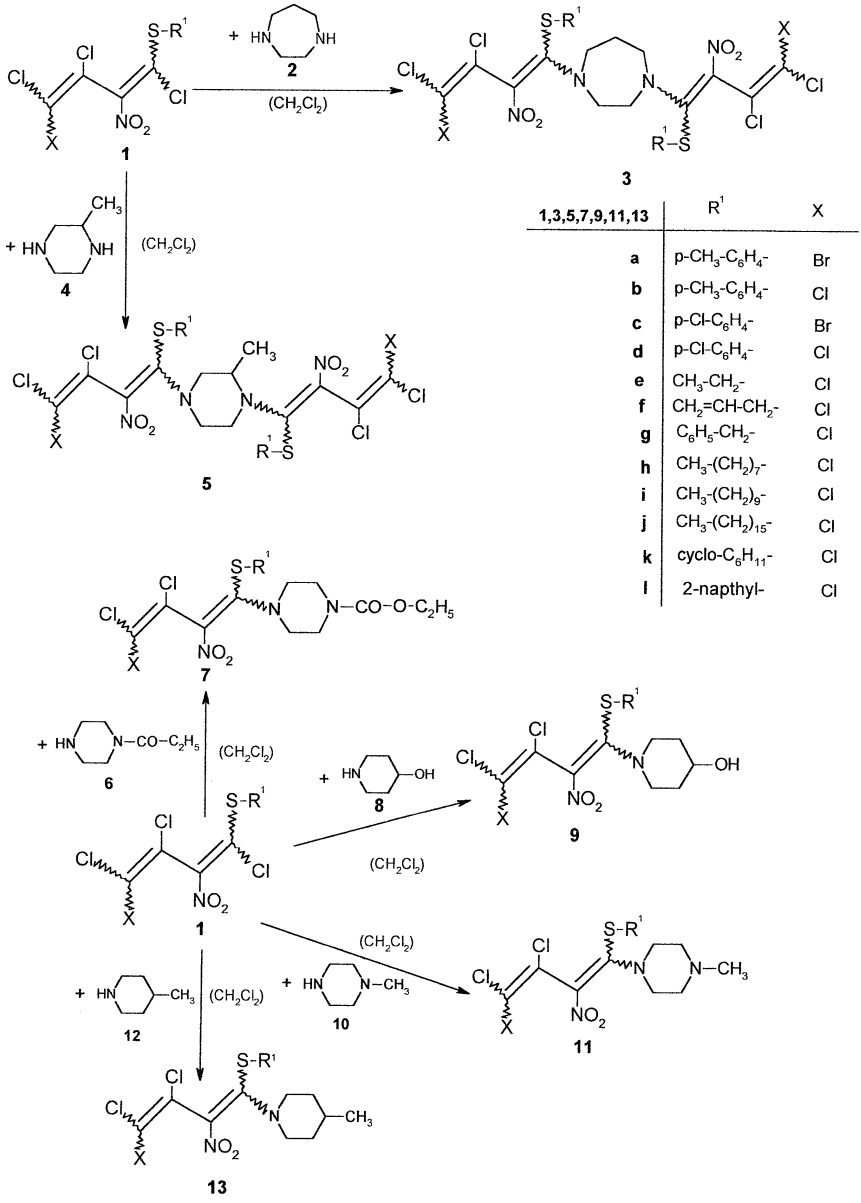
The reactions of nitrodienes with S- and N-nucleophiles occurred according to the addition–elimination mechanism. At first amine was added to the nitrovinyldiene group, and then HCl was eliminated from the additional compounds.

EXPERIMENTAL SECTION

^{1}H NMR: Varian (Inova) 500 MHz. IR: Shimadzu Fourier transform infrared (FTIR)-8101. Microanalyses: Carlo-Erba 1106 elemental analyzer. Melting Points: Büchi SMP 20. Products were isolated by column chromatography on SiO_2 (Fluka Kieselgel 60, particle size 63–200 μm). TLC plates silica 60 F_{254} (Merck, Darmstadt).

Preperation of N,S-Substituted Polyhalonitrodienes: General Procedure

One mole S-substituted polyhalonitrodiene and 1 mol piperazine derivative or piperidine derivative were stirred in dichloromethan until completion of the reaction (TLC). Chloroform was added to the reaction mixture. The organic layer was separated and washed with water



1,3,5,7,9,11,13	R^1	X
a	p-CH_3-C_6H_4-	Br
b	p-CH_3-C_6H_4-	Cl
c	p-Cl-C_6H_4-	Br
d	p-Cl-C_6H_4-	Cl
e	CH_3-CH_2-	Cl
f	CH_2=CH-CH_2-	Cl
g	C_6H_5-CH_2-	Cl
h	CH_3-$(CH_2)_7$-	Cl
i	CH_3-$(CH_2)_9$-	Cl
j	CH_3-$(CH_2)_{15}$-	Cl
k	cyclo-C_6H_{11}-	Cl
l	2-napthyl-	Cl

SCHEME 1

(4 × 30 ml), and dried with $MgSO_4$. The solvent was evaporated and the residue was either crystallized in methanol or purified by column chromatography on silica gel. **3a** to **3k** were synthesized in the same way.

N,N′-Bis(4-Bromo-3,4-dichloro-1-(4-methylphenylthio)-2-nitro-1,3-butadienyl)-homopiperazine (3a)

3a: Yield: 0.06 g (30%); m.p. 182–184°C. $R_f = 0.7917$ (CH_2Cl_2). IR(KBr): $\nu = 2850$, 2950 cm^{-1} (C—H), 1290, 1530 (C—NO_2). ^{1}HNMR ($CDCl_3$): $\delta = 7.1$–7.4 ppm (m, 8H, 2Ar—H), 3.3–3.8 (m, 10H, $5CH_2$), 2.3–2.6 (t, 6H, $2CH_3$)—$C_{27}H_{24}Br_2Cl_4N_4O_4S_2$ (834.26) calcd:C, 38.87; H, 2.90; N, 6.72; S, 7.63. Found: C, 38.46; H, 2.18; N, 6.17; S, 7.93.

N,N′-Bis(3,4,4-trichloro-1-(4-methylphenylthio)-2-nitro-1,3-butadienyl)-homopiperazine (3b)

3b: Yield: 0.1 g (25%); m.p. 240–241°C. $R_f = 0.4545$ (CH_2Cl_2/CH_3OH 5:1). IR(KBr): $\nu = 2800$, 2900 cm^{-1} (C—H), 1600 (C=C), 1290, 1525 (C—NO_2). ^{1}HNMR ($CDCl_3$): $\delta = 7.05$–7.4 ppm (m, 8H, 2Ar—H), 3.3–3.8 (m, 10H, $5CH_2$), 2.3–2.6 (t, 6H, $2CH_3$)—$C_{27}H_{24}Cl_6N_4O_4S_2$ (745.36) calcd: C, 43.51; H, 3.25; N, 7.52; S, 8.60. Found: C, 43.59; H, 2.47; N, 7.13; S, 8.90.

N,N′-Bis(4-Bromo-3,4-dichloro-1-(4-chlorophenylthio)-2-nitro-1,3-butadienyl)-homopiperazine (3c)

3c: Yield: 0.02 g (10%); m.p. 200–202°C. $R_f = 0.5789$ ($CHCl_3$). IR(KBr): $\nu = 2800$, 2850 cm^{-1} (C—H), 1290, 1520 (C—NO_2). ^{1}HNMR ($CDCl_3$): $\delta = 7.2$–7.5 ppm (m, 8H, 2Ar—H), 3.4–4.0 (m, 10H, $5CH_2$). —$C_{25}H_{18}Br_2Cl_6N_4O_4S_2$ (875.1) calcd: C, 34.21; H, 2.07; N, 6.40; S, 7.33. Found: C, 34.17; H, 2.18; N, 6.31; S, 7.83.

N,N′-Bis(3,4,4-trichloro-1-(4-chlorophenylthio)-2-nitro-1,3-butadienyl)-homopiperazine (3d)

3d: Yield: 0.1 g (24%); m.p. 195–197°C. $R_f = 0.6296$ (CH_2Cl_2). IR(KBr): $\nu = 3100$ cm^{-1} (Ar CH), 2990 (C—H), 1560, 1600 (C=C), 1290, 1520 (C—NO_2). ^{1}HNMR ($CDCl_3$): $\delta = 7.15$–7.5 ppm (m, 8H, 2Ar—H), 3.4–4.0 (m, 10H, $5CH_2$). —$C_{25}H_{18}Cl_8N_4O_4S_2$ (786.2) calcd:C, 38.19; H, 2.31; N, 7.13; S, 8.16. Found: C, 38.34; H, 2.10; N, 7.15; S, 8.14.

N,N′-Bis(3,4,4-trichloro-1-(ethylthio)-2-nitro-1,3-butadienyl)-homopiperazine (3e)

3e: Yield: 0.06 g (32%); m.p. 135–137°C. $R_f = 0.6190$ (CH_2Cl_2). IR(KBr): $\nu = 2990$ cm^{-1} (C—H), 1300, 1510 (C—NO_2). ^{1}HNMR ($CDCl_3$): $\delta = 3.6$–4.0 ppm (m, 10H, $5CH_2$), 2.9–3.1 (m, 4H, $2CH_2$), 2.0–2.2 (m, 6H, $2CH_3$). —$C_{17}H_{20}Cl_6N_4O_4S_2$ (621.22) calcd:C, 32.87; H, 3.25; N, 9.02; S, 10.32. Found: C, 32.26; H, 3.46; N, 9.75; S, 10.35.

N,N′-Bis(3,4,4-trichloro-1-(allylthio)-2-nitro-1,3-butadienyl)-homopiperazine (3f)

3f: Yield: 0.09 g (22%); m.p. 118–120°C. $R_f = 0.4615$ (CH_2Cl_2). IR(KBr): $\nu = 2990$, 3000 cm^{-1} (C—H), 1650 (C=C), 1290, 1510 (C—NO_2). ^{1}HNMR ($CDCl_3$): $\delta = 5.6$–6.0 ppm (m, 2H, 2CH=), 5.1–5.4 (m, 4H, $2CH_2$=), 3.4–4.1 (m, 14H, $7CH_2$). —$C_{19}H_{20}Cl_6N_4O_4S_2$ (645.24) calcd: C, 35.37; H, 3.12; N, 8.68; S, 9.94. Found: C, 35.02; H, 2.87; N, 8.56; S, 9.79.

N,N′-Bis(3,4,4-trichloro-1-(benzylthio)-2-nitro-1,3-butadienyl)-homopiperazine (3g)

3g: Yield: 0.03 g (14%); m.p. 103–105°C. $R_f = 0.4444$ (CH_2Cl_2/CCl_4 10:1). IR(KBr): $\nu = 2950$, 3010 cm^{-1} (C—H), 1300, 1510 (C—NO_2). ^{1}HNMR ($CDCl_3$): $\delta = 7.0$–7.4 ppm (m, 10H, 2ArH), 4.1–4.4 (s, 4H, $2CH_2$), 3.3–3.8 (m, 10H, $5CH_2$). —$C_{27}H_{24}Cl_6N_4O_4S_2$ (745.36) calcd: C, 43.51; H, 3.25; N, 7.52; S, 8.60. Found: C, 43.88; H, 3.39; N, 7.21; S, 8.80.

N,N′-Bis(3,4,4-trichloro-1-(octylthio)-2-nitro-1,3-butadienyl)-homopiperazine (3h)

3h: Yield: 0.08 g (20%); oil. $R_f = 0.6363$ (CH_2Cl_2/CH_3OH 5:1). IR(film): $\nu = 2950$, 2900 cm^{-1} (C—H), 1290, 1510 (C—NO_2). ^{1}HNMR ($CDCl_3$): $\delta = 2.8$–3.2 ppm (m, 38H, $19CH_2$), 1.0–2.0 (m, 6H, $2CH_3$). —$C_{29}H_{44}Cl_6N_4O_4S_2$ (789.54) calcd: C, 44.12; H, 5.62; N, 7.10; S, 8.12. Found: C, 44.97; H, 5.20; N, 6.89; S, 7.98.

N,N′-Bis(3,4,4-trichloro-1-(decanylthio)-2-nitro-1,3-butadienyl)-homopiperazine (3i)

3i: Yield: 0.18 g (46%); oil. $R_f = 0.6551$ (CH_2Cl_2/CH_3OH 5:1). IR(film): $\nu = 2990$, 2950 cm^{-1} (C—H), 1650 (C=C), 1290, 1510 (C—NO_2). ^{1}HNMR ($CDCl_3$): $\delta = 3.2$–5.0 ppm (m, 36H, $18CH_2$), 2.8–3.2 (m, 10H, $5CH_2$),

2.0–2.6 (m, 6H, $2CH_3$). —$C_{33}H_{52}Cl_6N_4O_4S_2$ (845.85) calcd: C, 46.87; H, 6.20; N, 6.63; S, 7.58. Found: C, 46.45; H, 6.70; N, 6.53; S, 7.20.

N,N′-Bis(3,4,4-trichloro-1-(hexadecanylthio)-2-nitro-1,3-butadienyl)-homopiperazine (3j)

3j: Yield: 0.05 g (13%); m.p. 88–90°C. $R_f = 0.7692$ ($CHCl_3/CH_3OH$ 10:1). IR(KBr): ν = 2990, 2900 cm^{-1} (C—H), 1290, 1510 (C—NO_2). ^{1}HNMR ($CDCl_3$): δ = 3.2–4.8 ppm (m, 70H, $35CH_2$), 2.0–3.0 (m, 6H, $3CH_3$). —$C_{45}H_{76}Cl_6N_4O_4S_2$ (1013.98) calcd:C, 53.31; H, 7.55; N, 5.53; S, 6.32. Found: C, 53.22; H, 7.49; N, 5.51; S, 6.40.

N,N′-Bis(3,4,4-trichloro-1-(cyclohexylthio)-2-nitro-1,3-butadienyl)-homopiperazine (3k)

3k: Yield: 0.18 g (43%), m.p. 80–82°C. $R_f = 0.7333$ ($CHCl_3/CH_3OH$ 5:1). IR(KBr): ν = 2990, 2950 cm^{-1} (C—H), 1290, 1510 (C—NO_2). ^{1}HNMR ($CDCl_3$): δ = 2.9–4.5 ppm (m, 2H, 2CH), 1.1–2.7 (m, 30H, $15CH_2$). —$C_{25}H_{32}Cl_6N_4O_4S_2$ (729.40) calcd:C, 41.17; H, 4.42; N, 7.68; S, 8.79. Found: C, 41.25; H, 4.38; N, 7.14; S, 8.79.

5a–b, **5d–f**, **5h–l** were synthesized in the same way.

N,N′-Bis(4-Bromo-3,4-dichloro-1-(4-methylphenylthio)-2-nitro-1,3-butadienyl)-2-methylpiperazine (5a)

5a: Yield: 0.06 g (15%); m.p. 165–167°C. R_f = 0.3330 ($CHCl_3/CH_3OH$ 5:1). IR(KBr): ν = 2950, 2800 cm^{-1} (C—H), 1290, 1520 (C—NO_2). ^{1}HNMR ($CDCl_3$): δ = 7.2–7.4 ppm (m, 8H, 2Ar—H), 2.1–2.4 (m, 7H, $3CH_2$, 1CH), 1.1–1.4 (m, 9H, $3CH_3$)—$C_{27}H_{24}Br_2Cl_4N_4O_4S_2$ (834.26) calcd: C, 38.87; H, 2.90; N, 6.72. Found: C, 38.2; H, 2.49; N, 6.94.

N,N′-Bis(3,4,4-trichloro-1-(4-methylphenylthio)-2-nitro-1,3-butadienyl)-2-methyl-piperazine (5b)

5b: Yield: 0.15 g (36%); oil. R_f = 0.4285 ($CHCl_3/CH_3OH$ 5:1). IR (film): ν = 2950, 2900 cm^{-1} (C—H), 1290, 1520 (C—NO_2). ^{1}*HNMR*(*CDCl*$_3$): δ = 7.05–7.4 ppm (q, 8H, 2Ar—H), 3.3–3.8 (m, 10H, $5CH_2$), 2.3–2.6 (t, 6H, $2CH_3$). —$C_{27}H_{24}Cl_6N_4O_4S_2$ (745.36) calcd: C, 43.51; H, 3.25; N, 8.60. Found: C, 44.01; H, 3.98; N, 9.10.

N,N′-Bis(3,4,4-trichloro-1-(4-chlorophenylthio)-2-nitro-1,3-butadienyl)-2-methylpiperazine (5d)

5d: Yield: 0.3 g (73%); m.p. 203–205°C. R_f = 0.6000 (CH_2Cl_2/CH_3OH 10:1). IR(KBr): ν = 2900 (C—H), 1600 (C=C), 1290, 1520 (C—NO_2).

^{1}HNMR ($CDCl_3$): δ = 7.2–7.4 ppm (m, 8H, 2Ar—H), 2.0–2.6 (m, 6H, $3CH_2$), 1.0–1.6 (m, 4H, CH_3, CH). —$C_{25}H_{18}Cl_8N_4O_4S_2$ (786.2) calcd: C, 38.19; H, 2.31; N, 7.13; S, 8.16. Found: C, 38.04; H, 2.59; N, 7.65; S, 7.94.

N,N′-Bis(3,4,4-trichloro-1-(ethylthio)- 2-nitro-1,3-butadienyl)-2-methylpiperazine (5e)

5e: Yield: 0.1 g (23%); Oil. R_f = 0.2727 (CH_2Cl_2/CH_3OH 5:1). IR(): ν = 2950 cm^{-1} (C—H), 1290, 1510 (C—NO_2). ^{1}HNMR ($CDCl_3$): δ = 3.2–4.0 ppm (m, 10H, $5CH_2$), 2.8–3.0 (m, H, CH), 1.0–1.6 (m, 9H, $3CH_3$). —$C_{17}H_{20}Cl_6N_4O_4S_2$ (621.22) calcd: C, 32.87; H, 3.25; N, 9.02. Found: C, 32.97; H, 3.11; N, 9.89.

N,N′-Bis(3,4,4-trichloro-1-(allylthio)- 2-nitro-1,3-butadienyl)-2-methylpiperazine (5f)

5f: Yield: 0.1 g (24%); m.p. 198–200°C. R_f = 0.3850 (CH_2Cl_2/CH_3OH 10:1). IR(KBr): ν = 2950, 2900 cm^{-1} (C—H), 1290, 1510 (C—NO_2). ^{1}HNMR ($CDCl_3$): δ = 5.7–5.9 ppm (m, 2H, 2CH=), 5.1–5.3 (m, 4H, $2CH_2$=), 3.0–3.8 (m, 10H, $5CH_2$), 0.8–1.6 (m, 4H, CH_3 CH). —$C_{19}H_{20}Cl_6N_4O_4S_2$ (645.24) calcd:C, 35.37; H, 3.12; N, 8.68. Found: C, 35.36; H, 3.42; N, 8.71.

N,N′-Bis(3,4,4-trichloro-1-(octylthio)-2-nitro- 1,3-butadienyl)-2-methylpiperazine (5h)

5h: Yield: 0.15 g (38%); oil. R_f = 0.3181 (CH_2Cl_2/CH_3OH 5:1). IR (film): ν = 2950, 2900 cm^{-1} (C—H), 1290, 1510 (C—NO_2). ^{1}HNMR ($CDCl_3$): δ = 2.4–4.0 ppm (m, 35H, $17CH_2$, CH), 1.1–1.6 (m, 9H, $3CH_3$). —$C_{29}H_{44}Cl_6N_4O_4S_2$ (789.54) calcd: C, 44.12; H, 5.62; N, 7.10. Found: C, 44.45; H, 6.06; N, 7.24.

N,N′-Bis(3,4,4-trichloro-1-(decanylthio)- 2-nitro-1,3-butadienyl)-2-methy-lpiperazine (5i)

5i: Yield: 0.25 g (61%); oil. R_f = 0.7727 (CH_2Cl_2/CH_3OH 5:1). IR(film): ν = 2950, 2900 cm^{-1} (C—H), 1290, 1510 (C—NO_2). ^{1}HNMR ($CDCl_3$): δ = 2.4–3.0 ppm (m, 43H, $21CH_2$, CH), 1.0–1.6 (m, 6H, $2CH_3$). —$C_{33}H_{52}Cl_6N_4O_4S_2$ (845.85) calcd: C, 46.87; H, 6.20; N, 6.63. Found: C, 46.97; H, 6.12; N, 7.01.

N,N′-Bis(3,4,4-trichloro-1-(hexadecanylthio)-2-nitro- 1,3-butadienyl)-2-methylpiprazine (5j)

5j: Yield: 0.2 g (49%); oil. R_f = 0.5000 ($CHCl_3/CH_3OH$ 5:1). IR(film): ν = 2900, 2800 cm^{-1} (C—H), 1600 (C=C), 1290, 1520 (C—NO_2). ^{1}HNMR

($CDCl_3$): $\delta = 2.4$–3.0 ppm (m, 66H, $33CH_2$), 1.0–1.6 (m, 10H, $3CH_3$, CH). —$C_{45}H_{76}Cl_6N_4O_4S_2$ (1013.98) calcd: C, 53.31; H, 7.55; N, 5.53. Found: C, 53.36; H, 7.74; N, 6.2.

N,N′-Bis(3,4,4-trichloro-1-(cyclohexylthio)-2-nitro-1,3-butadienyl)-2-methylpiperazine (5k)

5k: Yield: 0.25 g (61%); oil. $R_f = 0.5357$ ($CHCl_3/CH_3OH$ 5:1). IR(film): $\nu = 2950$, 2800 cm^{-1} (C—H), 1290, 1510 (C—NO_2). ^{1}HNMR ($CDCl_3$): $\delta = 3.0$–4.0 ppm (m, 26H, $13CH_2$), 1.0–2.0 (m, 6H, CH_3, 3CH). —$C_{25}H_{32}Cl_6N_4O_4S_2$ (729.40) calcd: C, 41.17; H, 4.42; N, 7.68. Found: C, 41.46; H, 4.66; N, 8.25.

N,N′-Bis(3,4,4-trichloro-1-(napthylthio)-2-nitro-1,3-butadienyl)-2-methylpiperazine (5l)

5l: Yield: 0.15 g (37%), m.p. 168–170°C. $R_f = 0.5240$ ($CHCl_3/CH_3OH$ 10:1). IR(KBr): $\nu = 2950$, 2900 cm^{-1} (C—H), 1600 (C=C), 1290, 1530 (C—NO_2). ^{1}HNMR ($CDCl_3$): $\delta = 7.2$–8.0 ppm (m, 14H, 4Ar—H), 2.0–2.4 (m, 6H, $3CH_2$), 0.8–1.6 (m, 4H, CH_3, CH). —$C_{33}H_{24}Cl_6N_4O_4S_2$ (817.43) calcd: C, 48.49; H, 2.96; N, 6.85. Found: C, 48.45; H, 3.2; N, 6.88.

1-(4-Bromo-3,4-dichloro-1-(4-chlorophenylthio)-2-nitro-1,3-butadienyl)-4-ethoxycarbonylpiperazine (7c)

7c: Yield: 0.1 g (78%); oil. $R_f = 0.5882$ (CH_2Cl_2). IR(film): $\nu = 3050$ cm^{-1} (Ar—CH), 3000, 2950, 2900 (C—H), 1600 (C=C), 1280, 1510 (C—NO_2). ^{1}HNMR ($CDCl_3$): $\delta = 7.2$–7.4 ppm (m, 4H, Ar—H), 3.0–3.6 (m, 10H, $5CH_2$), 1.0–1.3 (m, 3H, CH_3). —$C_{17}H_{17}BrCl_3N_3O_4S$ (545.67) calcd: C, 37.42; H, 3.14; N, 7.70. Found: C, 37.02; H, 3.24; N, 7.97.

1-(4-Bromo-3,4-dichloro-1-(4-chlorophenylthio)-2-nitro-1,3-butadienyl)-4-piperidinol (9c)

9c: Yield: 0.1 g (83%); m.p. 132–133°C. $R_f = 0.4138$ ($CHCl_3$). IR(KBr): $\nu = 3450$ cm^{-1} (OH), 2850, 2800 (C—H), 1250, 1530 (C—NO_2). ^{1}HNMR ($CDCl_3$): $\delta = 7.2$–7.4 ppm (m, 4H, Ar—H), 3.1–3.9 (m, 8H, $4CH_2$), 2.1 (s, 1H, CH), 1.1–1.4 (m, 1H, OH). —$C_{15}H_{14}BrCl_3N_2O_3S$ (492.65) calcd: C, 36.57; H, 3.68; N, 5.69. Found: C, 36.39; H, 3.20; N, 5.39.

1-(4-Bromo-3,4-dichloro-1-(4-methylphenylthio)-2-nitro-1,3-butadienyl)-4-methylpiperazine (11a)

11a: Yield: 0.05 g (45%); m.p. 171–173°C. $R_f = 0.3428$ ($CHCl_3$). IR(KBr): $\nu = 3050$ cm^{-1} (Ar-CH=), 3000, 2900, 2850, 2800 (C—H), 1595 (C=C),

1290, 1530 (C—NO_2). ^{1}HNMR ($CDCl_3$): $\delta = 7.1$–7.3 ppm (m, 4H, Ar—H), 3.3–3.4 (m, 8H, $4CH_2$), 2.0–2.3 (m, 6H, $2CH_3$). —$C_{16}H_{18}BrCl_2N_3O_2S$ (467.21) calcd: C, 41.10; H, 3.80; N, 8.90. Found: C, 41.02; H, 3.26; N, 8.34.

1-(3,4,4-trichloro-1-(allylthio)-2-nitro-1,3-butadienyl)-4-methylpiperazine (11f)

11f: Yield: 0.09 g (75%); oil. $R_f = 0.6667$ ($CHCl_3/CH_3OH$ 2:1). IR(film): $\nu = 2950$, 2900 cm^{-1} (C—H), 1600 (C=C), 1300, 1510 (C—NO_2). ^{1}HNMR ($CDCl_3$): $\delta = 5.7$–5.9 ppm (m, H, CH=), 5.2–5.4 (m, 2H, CH_2=), 3.2–4.0 (m, 10H, $5CH_2$), 2.0 (s, 3H, CH_3). —$C_{12}H_{16}Cl_3N_3O_2S$ (372.70) calcd: C, 38.67; H, 4.33; N, 11.27. Found: C, 38.20; H, 4.02; N, 10.92.

1-(3,4,4-trichloro-1-(allylthio)-2-nitro-1,3-butadienyl)-4-methylpiperidine (13f)

13f: Yield: 0.08 g (64%); oil. $R_f = 0.5757$ (CH_2Cl_2). IR(film): $\nu = 2900$, 2800 (C—H), 1595 (C=C), 1290, 1520 (C—NO_2). ^{1}HNMR ($CDCl_3$): $\delta =$ 5.7–5.9 ppm (m, H, CH=), 5.1–5.3 (m, 2H, CH_2=), 3.1–3.6 (m, 11H, $5CH_2$, CH), 1.6–1.8 (m, 3H, CH_3=), —$C_{13}H_{17}Cl_3N_2O_2S$ (371.72) calcd: C, 42.01; H, 4.61; N, 7.54. Found: C, 41.97; H, 4.01; N, 6.93.

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