Efficient synthesis of 6-hydroxy-6-aryloxymethyl-1,5-diaryl-1,3,5-triazinane-2,4-dithiones

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An efficient and convenient method for the synthesis of 6-hydroxy-6-aryloxymethyl-1,5-diaryl-1,3,5-triazinane-2,4-dithiones via condensation of 2 equiv. of 1-arylthioureas with aryloxyacetic acids using ferric chloride hexahydrate as catalyst is described. Triazine derivatives have important medicinal properties, are widely used in the textile, plastic and rubber industries, and have applications as pesticides, dyestuffs, optical bleaches, explosives and surface active agents.

Keywords: 1,3,5-triazinane-2,4-dithione, thiourea, aryloxyacetic acid, synthesis

Triazine derivatives have attracted much attention due to their antimalarial,[1] antiplasmodial,[2] antimicrobial,[3] anti-angiogenesis[4] and antitumour[5] activities. They also have widespread applications in the textile, plastic and rubber industries, and are used as pesticides, dyestuffs, optical bleaches, explosives and surface active agents.[6] Meanwhile, heterocycles containing a thiourea structural unit show powerful antiproliferative,[7] antibacterial[8] and anticancer activities.[9] Hence, triazinane derivatives incorporating a thiourea unit may be important in many fields.

The general synthetic methods for 1,3,5-triazinane derivatives involve the reactions of *N*,*N*′-bis(arylmethylidene)arylmethane diimines with thioureas,[10] the multi-component reactions of phosphonates, nitriles, aldehydes and isocyanates,[11] the condensation of trifluoromethanesulfonamide with formaldehyde,[12] or the reactions of thiosemicarbazones with potassium thiocyanate and benzoyl chloride.[13] However, some methods use expensive reagents, toxic organic solvents, rigorous conditions, tedious workup procedure and long reaction time. Therefore, it is necessary to develop simple and efficient synthetic methods to 1,3,5-triazinane derivatives.

In continuation of an ongoing programme to synthesise biologically active compounds and develop synthetic strategy for important heterocyclic compounds,[14–18] we now report the simple and efficient synthesis of novel heterocyclic compounds including 1,3,5-triazinane-2,4-dithiones by reactions of 1-arylthioureas with aryloxyacetic acids in ethyl acetate using ferric chloride hexahydrate as a catalyst.

Results and discussion

Initially, the synthesis of 6-hydroxy-6-aryloxymethyl-1,5-diaryl-1,3,5-triazinane-2,4-dithiones was attempted by reaction of 1-phenylthiourea and phenoxyacetic acid at room temperature under catalyst-free condition. However, none of the desired product was detected. Subsequently, when a mixture of 1-phenylthiourea and phenoxyacetic acid was heated at 80 °C for several hours, a new compound was isolated in low yield, which was identified as a novel heterocyclic compound, 6-hydroxy-6-phenoxymethyl-1,5-diphenyl-1,3,5-triazinane-2,4-dithione. In the latter research, it was found that some Bronsted acids such as *p*-toluenesulfonic acid (PTSA) and trichloroacetic acid (TCA), and Lewis acids, such as $AlCl_3$, $NiCl_2$, $FeCl_3$ and $FeCl_3 \cdot 6H_2O$, could catalyse the reaction. Among them, $FeCl_3 \cdot 6H_2O$ could efficiently give product in highest yield (Table 1, entry 8).

Solvents also played a crucial role in the synthesis of 6-hydroxy-6-phenoxymethyl-1,5-diphenyl-1,3,5-triazinane-2,4-dithione (Table 2). The reactions in CH_2Cl_2 and MeOH could not give the desired products. However, the reactions in EtOH, MeCN, THF, $C_2H_4Cl_2$ and EtOAc could give the corresponding products. Among them, the reaction in EtOAc gave the product in highest yield.

Table 1 The effect of catalysts on the yield of 6-hydroxy-6-phenoxymethyl-1,5-diphenyl-1,3,5-triazinane-2,4-dithione[a]

Entry	Catalyst	Amount of catalyst/mol%	Yield/%[b]
1	–	–	38
2	PTSA	10	60
3	TCA	10	56
4	$AlCl_3$	10	55
5	$NiCl_2$	10	70
6	$FeCl_3$	10	74
7	$FeCl_3 \cdot 6H_2O$	5	78
8	$FeCl_3 \cdot 6H_2O$	10	88
9	$FeCl_3 \cdot 6H_2O$	15	80

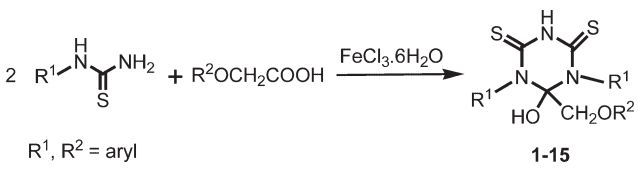
[a]Reaction conditions: 1-phenylthiourea (2 mmol), phenoxyacetic acid (1.5 mmol) in EtOAc (5 mL) at 80 °C using different catalysts.
[b]Isolated yields.

To explore the generality and scope of the synthetic reactions and synthesis of a series of novel 6-hydroxyl-6-aryloxy-1,5-diaryl-1,3,5-triazinane-2,4-dithiones (Scheme 1), various 1-arylthioureas and different aryloxyacetic acids as substrates were examined under optimal conditions (Table 3). It was found that various 1-arylthioureas could efficiently react with aryloxyacetic acids at 80 °C to give the corresponding

Table 2 The effect of solvents on the yield of 6-hydroxy-6-phenoxymethyl-1,5-diphenyl-1,3,5-triazinane-2,4-dithione[a]

Entry	Solvent	Time/h	Yield/%[b]
1	CH_2Cl_2	20	0
2	MeOH	20	0
3	EtOH	10	46
4	MeCN	10	50
5	THF	10	40
6	CH_2ClCH_2Cl	10	62
7	EtOAc	10	88

[a]Reaction conditions: 1-phenylthiourea (2 mmol), phenoxyacetic acid (1.5 mmol) and $FeCl_3 \cdot 6H_2O$ (0.2 mmol) in 5 mL of solvents.
[b]Isolated yields.



Scheme 1 Synthesis of 6-hydroxyl-6-aryloxy-1,5-diaryl-1,3,5-triazinane-2,4-dithiones

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Table 3 Synthesis of 6-hydroxy-6-aryloxymethyl-1,5-diaryl-1,3,5-triazinane-2,4-dithiones[a]

Compd.	R^1	R^2	Time/h	M.p./°C	Yield /%[b]
1	C_6H_5	C_6H_5	7	165–166	88
2	C_6H_5	4-$CH_3C_6H_4$	8	188–190	72
3	C_6H_5	2-ClC_6H_4	9	154–156	76
4	C_6H_5	4-ClC_6H_4	6	249–251	80
5	4-$CH_3C_6H_4$	C_6H_5	7	131–133	81
6	4-$CH_3C_6H_4$	3-$CH_3C_6H_4$	10	176–178	78
7	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	8	231–233	80
8	4-$CH_3C_6H_4$	2-ClC_6H_4	9	82–84	73
9	4-$CH_3C_6H_4$	3-ClC_6H_4	9	195–196	81
10	4-$CH_3C_6H_4$	4-ClC_6H_4	8	157–159	84
11	4-ClC_6H_4	C_6H_5	7	150–152	76
12	4-ClC_6H_4	3-$CH_3C_6H_4$	9	181–182	78
13	4-ClC_6H_4	4-$CH_3C_6H_4$	8	246–248	80
14	4-ClC_6H_4	2-ClC_6H_4	9	210–211	72
15	4-ClC_6H_4	4-ClC_6H_4	7	223–224	75

[a]Reaction conditions: 1-arylthiourea (2 mmol), aryloxyacetic acid (1.5 mmol), and ferric chloride hexahydrate (0.2 mmol) in EtOAc (5 mL) at 80 °C.
[b]Isolated yields.

products in good to high yields. 1-Arylthioureas and aryloxyacetic acids bearing either electron-donating or electron-withdrawing groups have no obvious influence on the efficiency of the reactions. However, it was found that, for *ortho*-substituted aryloxyacetic acids, the corresponding products were obtained in slightly lower yield than *para*-substituted ones (Table 3, entries 3, 8 and 14), presumably due to the steric effect. In addition, the similar reactions of 1-arylthioureas with aromatic carboxylic acids, such as (un)substituted benzoic acids, were also attempted for the reactions, but no desired products were observed.

A possible mechanism for the synthesis of 6-hydroxy-6-aryloxymethyl-1,5-diaryl-1,3,5-triazinane-2,4-dithiones is shown in Scheme 2. Presumably, condensation of 2 equiv. of 1-arylthioureas releasing ammonia generates intermediates **A**, One of amino groups of **A** subsequent reacts with a mole of complexes **B**, which are formed from aryloxyacetic acid and ferric chloride in the solution, to give intermediates **C** by loss of water. Subsequently the carbonyl group of **C** undergoes the nuleophilic addition of another amino group to form a six-membered heterocyclic compounds, 6-hydroxy-6-aryloxymethyl-1,5-diaryl-1,3,5-triazinane-2,4-dithiones.

Conclusion

An efficient and concise method for the synthesis of 6-hydroxy-6-aryloxymethyl-1,5-diaryl-1,3,5-triazinane-2,4-dithiones via reactions of 2 equiv. of 1-arylthioureas with aryloxyacetic acids in EtOAc using ferric chloride hexahydrate as a catalyst has been developed. This protocol has the advantages of using easily obtainable materials, simple work-up procedure, mild condition and high yield.

Experimental

IR spectra were recorded using KBr pellets on an Alpha Centauri FTIR spectrophotometer and ^{1}H NMR and ^{13}C NMR spectra on a Mercury-400BB instrument using $CDCl_3$ or DMSO-d_6 as solvents and Me_4Si as internal standard. Elemental analyses were performed on a Vario El Elemental Analysis instrument. Melting points were observed in an electrothermal melting point apparatus. All reactions were monitored by TLC. Flash column chromatography was carried out using 200–300 mesh silica gel at increased pressure. 1-Arylthioureas[19–20] and aryloxyacetic acids[21] were synthesised according to the literature methods.

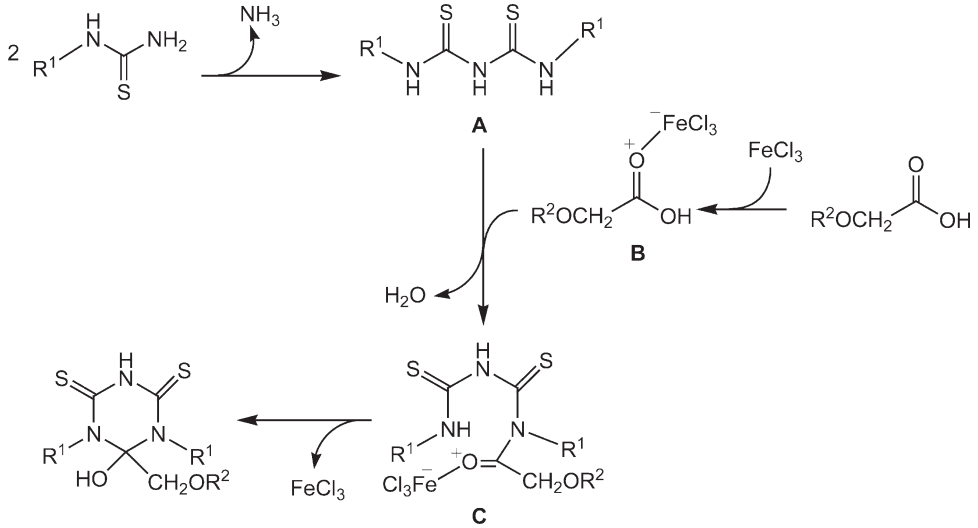
Synthesis of 6-hydroxy-6-aryloxymethyl-1,5-diaryl-1,3,5-triazinane-2,4-dithiones; general procedure

A mixture of 1-arylthiourea (2 mmol), aryloxyacetic acid (1.5 mmol) and ferric chloride hexahydrate (0.2 mmol) in EtOAc (5 mL) was stirred at 80 °C for the time indicated in Table 3. The progress of the reaction was monitored by TLC. After the completion of the reaction, the mixture was cooled to room temperature, washed with 15% of sodium carbonate solution. Then the organic layer was concentrated, and the residue was subjected to silica gel flash column chromatography (ethyl acetate-petroleum ether, 1:8) to obtain the pure product. The analytical and spectral data of the products are given below.

6-Hydroxy-6-phenoxymethyl-1,5-diphenyl-1,3,5-triazinane-2,4-dithione (**1**)*:* White solid, m.p. 165–166 °C; IR (KBr, ν, cm^{-1}): 3419 (OH), 3257 (NH), 1238 (C=S). ^{1}H NMR ($CDC1_3$, 400 MHz): δ 7.67–6.85 (m, 15H, Ph-H), 6.16 (s, 1H, OH), 4.78 (s, 2H, OCH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.3, 178.2, 158.3, 146.0, 137.5, 133.4, 130.9, 130.8, 129.3, 129.2, 128.1, 123.9, 121.0, 118.9, 114.7, 69.1. Anal. Calcd for $C_{22}H_{19}N_3O_2S_2$: C, 62.68; H, 4.54; N, 9.97. Found: C, 62.56; H, 4.55; N, 9.94%.

6-Hydroxy-1,5-diphenyl-6-(4-tolyloxymethyl)-1,3,5-triazinane-2,4-dithione (**2**): White solid, m.p. 188–190 °C; IR (KBr, ν, cm^{-1}): 3422 (OH), 3257 (NH), 1238 (C=S). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63–6.68 (m, 14H, Ph-H), 6.08 (s, 1H, OH), 4.67 (s, 2H, OCH_2), 2.19 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.4, 178.1, 156.2, 145.9, 137.5, 133.4, 130.9, 130.8, 130.2 129.8, 129.2, 128.1, 123.9, 118.9, 114.5, 69.3, 20.5. Anal. Calcd for $C_{23}H_{21}N_3O_2S_2$: C, 63.42; H, 4.86; N, 9.65. Found: C, 63.49; H, 4.85; N, 9.63%.

6-(2-Chlorophenoxymethyl)-6-hydroxy-1,5-diphenyl-1,3,5-triazinane-2,4-dithione (**3**): White solid, m.p. 154–156 °C; IR (KBr, ν, cm^{-1}): 3414



Scheme 2 The possible mechanism for the synthesis of 6-hydroxy-6-aryloxymethyl-1,5-diaryl-1,3,5-triazinane-2,4-dithiones.

(OH), 3058 (NH), 1255 (C=S). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60–6.66 (m, 14H, Ph-H), 6.07 (s, 1H, OH), 4.68 (s, 2H, OCH_2).^{13}C NMR ($CDCl_3$, 100 MHz): δ 181.2, 177.9, 156.9, 146.6, 141.3, 134.9, 133.7, 131.4, 131.1, 130.6, 130.3, 129.7, 129.3, 127.7, 125.8, 119.2, 116.0, 69.2. Anal. Calcd for $C_{22}H_{18}ClN_3O_2S_2$: C, 57.95; H, 3.98; N, 9.22. Found: C, 57.88; H, 3.97; N, 9.25%.

6-(4-Chlorophenoxymethyl)-6-hydroxy-1,5-diphenyl-1,3,5-triazinane-2,4-dithione (**4**): White solid, m.p. 249–251 °C; IR (KBr, ν, cm^{-1}): 3396 (OH), 3320 (NH), 1238 (C=S). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67–6.75 (m, 14H, Ph-H), 6.15 (s, 1H, OH), 4.74 (s, 2H, OCH_2).^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.8, 178.3, 156.9, 146.1, 137.5, 133.3, 130.9, 130.8, 129.2, 129.1, 128.0, 125.8, 124.0, 118.9, 116.0, 69.2. Anal. Calcd for $C_{22}H_{18}ClN_3O_2S_2$: C, 57.95; H, 3.98; N, 9.22. Found: C, 58.03; H, 3.99; N, 9.20%.

6-Hydroxy-6-phenoxymethyl-1,5-di(4-tolyl)-1,3,5-triazinane-2,4-dithione (**5**): White solid, m.p. 131–133 °C; IR (KBr, ν, cm^{-1}): 3422 (OH), 3313 (NH), 1225 (C=S). ^{1}H NMR ($CDC1_3$, 400 MHz): δ 7.44–6.85 (m, 13H, Ph-H), 6.12 (s, 1H, OH), 4.76 (s, 2H, OCH_2), 2.50 (s, 3H, CH_3), 2.30 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 180.1, 178.3, 158.2, 146.5, 141.2, 134.9, 133.6, 131.4, 130.6, 129.6, 129.3, 127.7, 120.9, 119.2, 114.6, 69.1, 21.4, 20.8. Anal. Calcd for $C_{24}H_{23}N_3O_2S_2$: C, 64.12; H, 5.16; N, 9.35. Found: C, 64.20; H, 5.17; N, 9.32%.

6-Hydroxy-1,5-di(4-tolyl)-6-(3-tolyloxymethyl)-1,3,5-triazinane-2,4-dithione (**6**): White solid, m.p. 176–178 °C; IR (KBr, ν, cm^{-1}): 3414 (OH), 3059 (NH), 1256 (C=S). ^{1}H NMR ($CDC1_3$, 400 MHz): δ 7.45–6.65 (m, 12H, Ph-H), 6.11 (s, 1H, OH), 4.75 (s, 2H, OCH_2), 2.51 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.29 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.1, 178.3, 158.2, 146.5, 141.2, 139.3, 135.0, 133.6, 131.4, 130.7, 129.6, 129.0, 127.7, 121.8, 119.2, 115.5, 111.4, 69.0, 21.5, 21.4, 20.8. Anal. Calcd for $C_{25}H_{25}N_3O_2S_2$: C, 64.77; H, 5.44; N, 9.06. Found: C, 64.80; H, 5.43; N, 9.08%.

6-Hydroxy-1,5-di(4-tolyl)-6-(4-tolyloxymethyl)-1,3,5-triazinane-2,4-dithione (**7**): White solid, m.p. 231–233 °C; IR (KBr, ν, cm^{-1}): 3442 (OH), 3035 (NH), 1234 (C=S). ^{1}H NMR ($CDC1_3$, 400 MHz): δ 7.45–6.75 (m, 12H, Ph-H), 6.10 (s, 1H, OH), 4.74 (s, 2H, OCH_2), 2.51 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.27 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.3, 178.3, 156.2, 146.5, 141.3, 135.0, 133.6, 131.4, 130.7, 130.1, 129.7, 129.6, 127.7, 119.2, 114.5, 69.3, 21.4, 20.8, 20.5. Anal. Calcd for $C_{25}H_{25}N_3O_2S_2$: C, 64.77; H, 5.44; N, 9.06. Found: C, 64.88; H, 5.45; N, 9.05%.

6-(2-Chlorophenoxymethyl)-6-hydroxy-1,5-di(4-tolyl)-1,3,5-triazinane-2,4-dithione (**8**): White solid, m.p. 82–84 °C; IR (KBr, ν, cm^{-1}): 3414 (OH), 3059 (NH), 1238 (C=S). ^{1}H NMR ($CDC1_3$, 400 MHz): δ 7.44–6.76 (m, 12H, Ph-H), 6.09 (s, 1H, OH), 4.74 (s, 2H, OCH_2), 2.51 (s, 3H, CH_3), 2.30 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 183.7, 181.2, 156.9, 146.6, 141.3, 135.0, 133.6, 131.4, 131.1, 130.6, 130.3, 129.7, 129.3, 129.1, 127.7, 119.2, 116.0, 69.2, 21.5, 20.8. Anal. Calcd for $C_{24}H_{22}ClN_3O_2S_2$: C, 59.55; H, 4.58; N, 8.68. Found: C, 59.63; H, 4.59; N, 8.65%.

6-(3-Chlorophenoxymethyl)-6-hydroxy-1,5-di(4-tolyl)-1,3,5-triazinane-2,4-dithione (**9**): White solid, m.p. 195–196 °C; IR (KBr, ν, cm^{-1}): 3414 (OH), 3059 (NH), 1256 (C=S). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45–6.65 (m, 12H, Ph-H), 6.11 (s, 1H, OH), 4.75 (s, 2H, OCH_2), 2.30 (s, 3H, CH_3), 2.29 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.1, 178.3, 158.2, 146.5, 141.2, 139.3, 135.0, 133.6, 131.4, 130.7, 129.6, 129.0, 127.7, 121.8, 119.2, 115.5, 111.4, 69.0, 21.5, 21.4. Anal. Calcd for $C_{24}H_{22}ClN_3O_2S_2$: C, 59.55; H, 4.58; N, 8.68. Found: C, 59.50; H, 4.58; N, 8.70%.

6-(4-Chlorophenoxymethyl)-6-hydroxy-1,5-di(4-tolyl)-1,3,5-triazinane-2,4-dithione (**10**): White solid, m.p. 157–159 °C; IR (KBr, ν, cm^{-1}): 3444 (OH), 1236 (C=S). ^{1}H NMR ($CDC1_3$, 400 MHz): δ 7.44–6.78 (m, 12H, Ph-H), 6.10 (s, 1H, OH), 4.76 (s, 2H, OCH_2), 2.51 (s, 3H, CH_3), 2.30 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.7, 178.5, 157.0, 146.6, 141.3, 135.0, 133.7, 131.4, 130.6, 129.7, 129.1, 127.7, 125.8, 119.2, 116.0, 69.3, 21.4, 20.8. Anal. Calcd for $C_{24}H_{22}ClN_3O_2S_2$: C, 59.55; H, 4.58; N, 8.68. Found: C, 59.48; H, 4.57; N, 8.71%.

6-Hydroxyl-6-phenoxymethyl-1,5-di(4-chlorophenyl)-1,3,5-triazinane-2,4-dithione (**11**): White solid, m.p. 150–152 °C; IR (KBr, ν, cm^{-1}): 3427 (OH), 3063 (NH), 1238 (C=S). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.59 (s, 1H, OH), 7.61–6.80 (m, 13H, Ph-H), 4.74 (s, 2H, OCH_2).^{13}C NMR ($CDCl_3$-DMSO-d_6, 100 MHz): δ 178.3, 176.8, 156.8, 146.2, 136.5, 134.4, 131.1, 128.9, 128.1, 127.0, 126.3, 120.3, 119.6, 113.1, 67.5. Anal. Calcd for $C_{22}H_{17}Cl_2N_3O_2S_2$: C, 53.88; H, 3.49; N, 8.57. Found: C, 53.78; H, 3.48; N, 8.55%.

6-Hydroxy-6-(3-tolyloxymethyl)-1,5-di(4-chlorophenyl)-1,3,5-triazinane-2,4-dithione (**12**): White solid, m.p. 181–182 °C; IR (KBr, ν, cm^{-1}): 3414 (OH), 3061 (NH), 1256 (C=S). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45-6.65 (m, 12H, Ph-H), 6.11 (s, 1H, OH), 4.75 (s, 2H, OCH_2), 2.29 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.1, 178.3, 158.2, 146.5, 141.2, 139.3, 135.0, 133.6, 131.4, 130.7, 129.6, 129.0, 127.7, 121.8, 119.2, 115.5, 111.4, 69.0, 21.4. Anal. Calcd for $C_{23}H_{19}Cl_2N_3O_2S_2$: C, 54.76; H, 3.80; N, 8.33. Found: C, 54.68; H, 3.81; N, 8.31%.

6-Hydroxy-6-(4-tolyloxymethyl)-1,5-di(4-chlorophenyl)-1,3,5-triazinane-2,4-dithione (**13**): White solid, m.p. 256–258 °C; IR (KBr, ν, cm^{-1}): 3415 (OH), 3060 (NH), 1238 (C=S). ^{1}H NMR ($CDCl_3$-DMSO-d_6, 400 MHz): δ 8.67 (s, 1H, OH), 7.65–6.69 (m, 12H, Ph-H), 4.70 (s, 2H, OCH_2), 2.23 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$-DMSO-d_6, 100 MHz): δ 177.6, 175.9, 154.1, 145.6, 136.2, 133.2, 130.7, 128.7, 128.1, 127.7, 127.5, 126.4, 124.9, 119.6, 112.4, 66.9, 18.3. Anal. Calcd for $C_{23}H_{19}Cl_2N_3O_2S_2$: C, 54.76; H, 3.80; N, 8.33. Found: C, 54.82; H, 3.79; N, 8.35%.

6-(2-Chlorophenoxymethyl)-6-hydroxy-1,5-di(4-chlorophenyl)-1,3,5-triazinane-2,4-dithione (**14**): White solid, m.p. 210–211 °C; IR (KBr, ν, cm^{-1}): 3414 (OH), 3060 (NH), 1256 (C=S). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45–6.73 (m, 12H, Ph-H), 6.10 (s, 1H, OH), 4.75 (s, 2H, OCH_2).^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.7, 178.5, 156.9, 146.6, 141.4, 134.9, 133.7, 130.6, 129.7, 129.7, 129.3, 129.1, 127.7, 125.8, 119.2, 115.9, 114.6, 69.2. Anal. Calcd for $C_{22}H_{16}Cl_3N_3O_2S_2$: C, 50.34; H, 3.07; N, 8.01. Found: C, 50.27; H, 3.08; N, 8.04%.

6-(4-Chlorophenoxymethyl)-6-hydroxy-1,5-di(4-chlorophenyl)-1,3,5-triazinane-2,4-dithione (**15**): White solid, m.p. 223–224 °C; IR (KBr, ν, cm^{-1}): 3435 (OH), 1234 (C=S). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63–6.75 (m, 12H, Ph-H), 6.09 (s, 1H, OH), 4.75 (s, 2H, OCH_2). ^{13}C NMR ($CDCl_3$-DMSO-d_6, 100 MHz): δ 177.1, 175.9, 155.0, 145.7, 136.2, 133.2, 130.7, 128.7, 128.1, 127.1, 126.3, 124.9, 122.8, 119.6, 114.3, 67.0. Anal. Calcd for $C_{22}H_{16}Cl_3N_3O_2S_2$: C, 50.34; H, 3.07; N, 8.01. Found: C, 50.40; H, 3.06; N, 7.99%.

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