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Chemoselective annulation of 1,3-dithiin, -thiazine and -oxathiin rings on thiazoles using a green protocol

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Abstract—Tandem Knoevenagel and Michael reactions of 3-arylrhodanines, aromatic aldehydes and ammonium *N*-aryldithiocarbamates diastereoselectively yield dithioesters, thiazol-5-ylmethyl *N*-aryldithiocarbamates, under solvent-free microwave irradiation conditions in a one-pot procedure. Under the same conditions, the dithioesters are chemoselectively and expeditiously annulated with montmorillonite K-10 clay, Li^+-montmorillonite clay and I_2 to give thiazolo-1,3-dithiins, -thiazines and -oxathiins, respectively.

1. Introduction

Recently, a number of oxathiin, thiazine and dithiin derivatives have been reported to exhibit antiviral activity against human immunodeficiency virus type 1 (HIV-1), poliovirus type 1 (PV-1), coxsackie B virus type 3 (CoxB-3), vesicular stomatitis virus (VSV) and herpes simplex virus type 1 (HSV-1).[1] Moreover, dithiocarbamates have been extensively investigated for their fungitoxicity and many of these, viz., maneb, mancozeb, ziram, thiram and vapam, have attained major recognition as agricultural fungicides.[2,3] Compounds bearing the dithiocarbamate group, as part of a heterocyclic structure have been relatively less studied although some of these compounds, e.g., rhodanines and mylone are known to display useful pesticidal properties.[4,5] The thiazole nucleus is a well-known active core of various bioactive molecules. Thus, heterocyclic systems resulting from the annulation of oxathiin, thiazine and dithiin rings on biologically versatile thiazole nuclei provide an attractive scaffold that can be utilised for exploiting chemical diversity and generating drug-like screening libraries to generate lead candidates.

One-pot multi-component reactions (MCRs) have emerged as an improved synthetic strategy for drug discovery processes, [6–12] because multi-step synthesis produces considerable amounts of environmentally unfavourable wastes predominantly due to complex isolation procedures that often involve expensive, toxic and hazardous solvents after each step.

The application of microwave (MW) irradiation as a non-conventional energy source for activation of reactions, in general and under solvent-free conditions in particular, has now gained popularity over the usual homogeneous and heterogeneous reactions. It provides chemical processes with special attributes, such as enhanced reaction rates, higher yields of pure products, better selectivity, improved ease of manipulation, rapid optimisation of reactions in parallel and several ecofriendly advantages in the context of green chemistry.[13–20] The application of MW irradiation has recently been extended to modern drug discovery processes,[21,22] and has proved successful in the formation of carbon–heteroatom and carbon–carbon bonds.[23,24]

Considering the above reports and the recently reported results concerning MW accelerated Ugi three-component coupling (3cc) reactions,[25–27] in addition to continuing our work on new solvent-free cyclisation procedures,[28–32] we devised a solvent-free MW-activated expeditious synthesis of thiazolo-1,3-dithiins **5**, -thiazines **6** and -oxathiins **7** via one-pot Knoevenagel and Michael reactions (Scheme 1).

2. Results and discussion

After some preliminary experimentation, it was found that the envisaged synthesis (Scheme 1) was successful on intermittent MW irradiation of an intimate mixture of 3-arylrhodanines **1**, aromatic aldehydes **2** and ammonium *N*-aryldithiocarbamates **3** under solvent-free conditions for the time specified in Table 1, followed by heterocyclisations

Keywords: Microwaves; Mineral supported; Solvent-free; Chemoselective annulation; Thiazoles.
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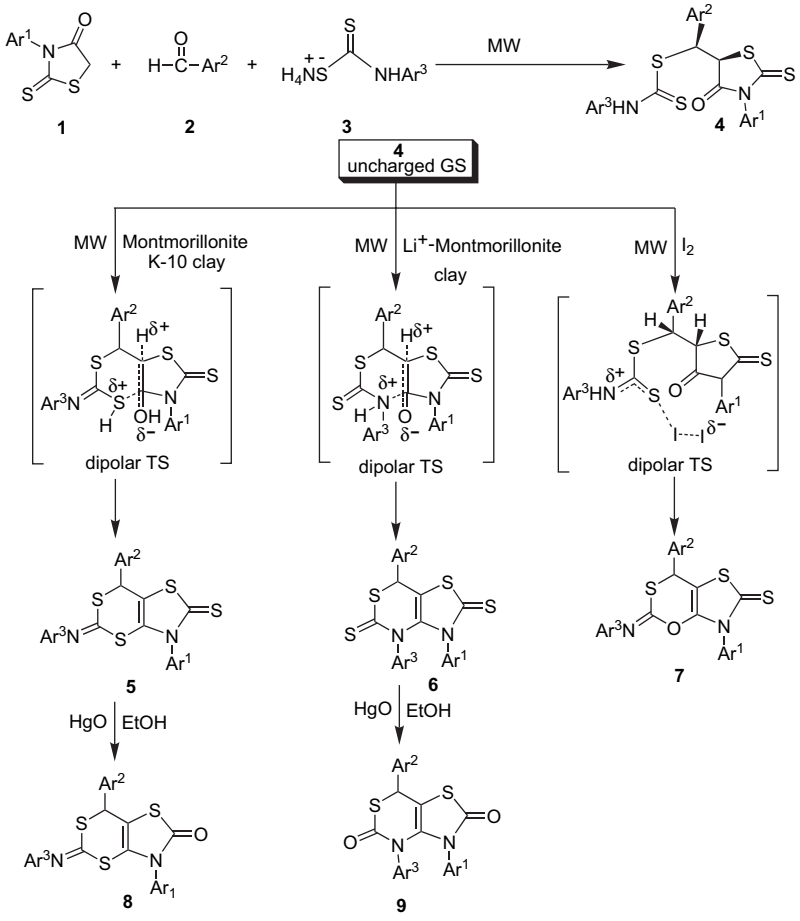

4- 7	Ar^1	Ar^2	Ar^3
a	Ph	4-ClC_6H_4	Ph
b	Ph	4-$MeOC_6H_4$	Ph
c	2-MeC_6H_4	Ph	2-MeC_6H_4
d	2-MeC_6H_4	4-ClC_6H_4	2-MeC_6H_4
e	2-MeC_6H_4	4-$MeOC_6H_4$	2-MeC_6H_4

Scheme 1.

of the resulting dithioesters **4** with montmorillonite K-10 clay, Li^+-montmorillonite, or I_2 under the same conditions. Isolation and purification by recrystallisation from ethanol afforded the desired products **4–7** in 77–89% yield (Table 1).

For comparative purposes, the final temperature of the reaction mixture was recorded immediately after the MW irradiation for 2 min and was found to reach about 90 °C. Reactions were also carried out using a thermostated oil bath at the same temperature (90 °C) as the MW-activated method, but for a longer (optimised) period of time (Table 1) to ascertain whether the MW method improved the yield or simply increased the conversion rates. It was found that significantly lower yields (42–52%) were obtained using the oil baths rather compared to the MW-activated method (Table 1). This observation may be rationalised by considering the formation of a dipolar transition state (TS) from an uncharged ground state (GS) in these reactions (Scheme 1). The greater stabilisation of more polar TS by dipole–dipole interactions with the electric field of microwaves as compared to the less polar GS, may reduce the activation energy ($\Delta G^{\neq}$), resulting in rate enhancement.[17]

Compounds **5–7** were synthesised from the same precursors **4** by intramolecular chemoselective heterocyclizations (Scheme 1). The isomeric compounds **5** and **6** clearly differ in their IR spectra; **5** exhibited a strong band attributed to C=N (1635 cm^{-1}), whereas **6** was devoid of this band. Further, the representative compounds **5a** and **6a** were converted into their -6-one and -2,5-dione analogs **8a** and **9a**, respectively, on treatment with HgO. This conversion, involving desulfurisation of the exocyclic sulfur, provides chemical evidence for the assigned structures of the isomeric **5a** and **6a** as the desulfurated products **8a** and **9a** are not isomeric.

Table 1. Solvent-free microwave-activated synthesis of products **4–7**

Product	Time		Yield (%)[a]		mp (°C)[b]
	MW (min)[c]	Thermal (h)[d]	MW	Thermal	
4a	6	2	88	51	118–120
4b	6	3	79	43	127–128
4c	4	2	82	42	133–135
4d	4	2	87	46	138–139
4e	6	3	80	43	130–131
5a	12	3	89	52	139–140
5b	10	3	80	47	143–144
5c	10	5	83	48	148–150
5d	12	4	85	50	150–152
5e	12	4	80	42	145–146
6a	10	5	88	45	154–156
6b	10	4	81	43	159–160
6c	12	3	82	42	153–154
6d	12	3	85	48	164–166
6e	10	4	78	45	162–163
7a	10	5	87	51	158–159
7b	10	5	83	48	167–168
7c	8	4	80	43	175–176
7d	8	5	85	48	152–153
7e	10	3	77	43	170–171

[a] Yield of isolated and purified products.
[b] All compounds gave C, H and N analyses within ±0.35% and satisfactory spectral (IR, ^{1}H NMR, ^{13}C NMR and EIMS) data.
[c] Microwave irradiation time (power = 100 W).
[d] Time for oil-bath heating at 90 °C.

3. Conclusion

In summary, we have developed a green protocol for an expeditious synthesis of various potentially, pharmaceutically and agrochemically useful thiazolo-1,3-dithiins, -thiazines and -oxathiins starting from readily available simple substrates employing solvent-free MW irradiation conditions.

4. Experimental

4.1. General

Melting points were determined by open glass capillary method and are uncorrected. IR spectra in KBr were recorded on a Perkin–Elmer 993 IR spectrophotometer, ^{1}H NMR spectra were recorded on a Bruker WM-40 C (400 MHz) FT spectrometer in DMSO-d_6 using TMS as internal reference. ^{13}C NMR spectra were recorded on the same instrument at 100 MHz using the same solvent and internal reference. Mass spectra were recorded on a JEOL D-300 mass spectrometer. Elemental analyses were carried out in a Coleman automatic carbon, hydrogen and nitrogen analyser. A CEM Discover Focused Microwave Synthesis System operating at 2450 MHz was used at an output of 100 W for all the experiments. All chemicals used were reagent grade and were used as received without further purification. Silica gel-G was used for TLC.

4.2. (3-Arylperhydro-4-oxo-2-thioxothiazol-5-yl)arylmethyl *N*-aryldithiocarbamates 4. General procedure

An intimate mixture of a 3-arylrhodanine **1** (2.0 mmol), an aromatic aldehyde **2** (2.0 mmol) and an ammonium *N*-aryldithiocarbamate **3** (2.0 mmol) were taken in a 20 mL vial and subjected to MW irradiation at 100 W in a CEM Discover microwave system for 2 min. The reaction mixture was then thoroughly mixed outside the MW oven for 2 min and again irradiated for another 2 min. This intermittent irradiation-mixing cycle was repeated for the total irradiation time of 4–6 min (Table 1). After completion of the reaction as indicated by TLC (hexane/AcOEt, 8:2, v/v), water (10 mL) was added to the reaction mixture and stirred well. The yellowish precipitate thus obtained was washed with water to give the crude product, which was recrystallised from ethanol to afford a diastereomeric mixture (>96:<4). The crude product ratios were >95:<5 as determined by ^{1}H NMR spectroscopy. The product on second recrystallisation from ethanol furnished an analytically pure sample of a single diastereomer **4** (Table 1). Comparison of the *J* values to that reported in the literature,[33–38] led to the assignment of cis stereochemistry for **4**, as the coupling constant ($Jcyclic_{SCH}$, $acyclic_{SCH}$=5 Hz) of the major isomer was lower than that for the minor trans diastereomer ($Jcyclic_{SCH}$, $acyclic_{SCH}$=10 Hz).

4.2.1. Compound 4a. White needles (88%), mp 118–120 °C. IR (KBr) ν_{max} 3147, 3025, 1700, 1602, 1580, 1451, 1055 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 5.94 (d, 1H, *J*=5 Hz, acyclic SCH), 6.05 (d, 1H, *J*=5 Hz, cyclic SCH), 7.13–8.02 (m, 14H$_{arom}$), 9.30 (br s, 1H, NH, exchanges with D$_2$O). ^{13}C NMR (DMSO-d_6/TMS) δ: 43.6, 79.0, 126.6, 127.2, 127.8, 129.5, 130.2, 130.9, 131.7, 132.5, 133.2, 133.8, 134.4, 135.1, 173.7, 192.9, 195.8. Mass (*m*/*z*): 500, 502 (M, M+2). Anal. Calcd for $C_{23}H_{17}ClN_2OS_4$: C, 55.13; H, 3.42; N, 5.59%. Found: C, 57.43; H, 3.34; N, 5.34%.

4.2.2. Compound 4b. White needles (79%), mp 127–128 °C. IR (KBr) ν_{max} 3143, 3022, 1705, 1601, 1575, 1445, 1050 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 3.70 (s, 3H, OMe), 5.91 (d, 1H, *J*=5 Hz, acyclic SCH), 6.08 (d, 1H, *J*=5 Hz, cyclic SCH), 7.03–7.99 (m, 14H$_{arom}$), 9.28 (br s, 1H, NH, exchanges with D$_2$O). ^{13}C NMR (DMSO-d_6/TMS) δ: 43.5, 55.3, 79.3, 125.9, 126.8, 127.5, 128.2, 129.0, 129.7, 130.3, 131.0, 131.6, 132.3, 133.0, 133.8, 173.5, 192.5, 195.7. Mass (*m*/*z*): 496 (M$^+$). Anal. Calcd for $C_{24}H_{20}N_2O_2S_4$: C, 58.04; H, 4.06; N, 5.64%. Found: C, 58.37; H, 3.86; N, 5.46%.

4.2.3. Compound 4c. White needles (82%), mp 133–135 °C. IR (KBr) ν_{max} 3140, 3020, 1707, 1600, 1580, 1450, 1057 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 2.29 (s, 6H, 2×Me), 5.89 (d, 1H, *J*=5 Hz, acyclic SCH), 6.11 (d, 1H, *J*=5 Hz, cyclic SCH), 7.13–8.11 (m, 13H$_{arom}$), 9.35 (br s, 1H, NH, exchanges with D$_2$O). ^{13}C NMR (DMSO-d_6/TMS) δ: 20.3, 21.4, 43.1, 79.8, 125.3, 125.9, 126.6, 127.2, 128.8, 128.5, 129.1, 129.8, 130.4, 131.0, 131.8, 132.6, 133.3, 134.0, 134.7, 135.2, 173.4, 192.5, 195.4. Mass (*m*/*z*): 494 (M$^+$). Anal. Calcd for $C_{25}H_{22}N_2OS_4$: C, 60.70; H, 4.48; N, 5.66%. Found: C, 61.01; H, 4.29; N, 5.89%.

4.2.4. Compound 4d. White needles (87%), mp 138–139 °C. IR (KBr) ν_{max} 3142, 3026, 1702, 1605, 1587, 1455, 1058 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 2.32 (s, 6H, 2×Me), 5.90 (d, 1H, *J*=5 Hz, acyclic SCH), 6.07 (d, 1H, *J*=5 Hz, cyclic SCH), 7.03–8.12 (m, 12H$_{arom}$), 9.30 (br s, 1H, NH, exchanges with D$_2$O). ^{13}C NMR

(DMSO-d_6/TMS) δ: 20.5, 21.6, 43.7, 80.0, 125.5, 126.1, 126.7, 127.4, 128.0, 128.6, 129.3, 130.0, 130.6, 131.3, 131.9, 132.5, 133.1, 133.8, 134.5, 135.2, 173.3, 192.8, 195.7. Mass (*m*/*z*): 528, 530 (M, M+2). Anal. Calcd for $C_{25}H_{21}ClN_2OS_4$: C, 56.74; H, 4.00; N, 5.29%. Found: C, 56.99; H, 3.89; N, 5.48%.

4.2.5. Compound 4e. White needles (80%), mp 130–131 °C. IR (KBr) ν_{max} 3147, 3028, 1706, 1608, 1579, 1449, 1051 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 2.37 (s, 6H, 2×Me), 3.68 (s, 3H, OMe), 5.85 (d, 1H, J=5 Hz, acyclic SCH), 6.01 (d, 1H, J=5 Hz, cyclic SCH), 7.01–8.11 (m, 12H$_{arom}$), 9.28 (br s, 1H, NH, exchanges with D_2O). ^{13}C NMR (DMSO-d_6/TMS) δ: 20.4, 21.5, 43.5, 55.1, 79.6, 125.4, 126.1, 126.7, 127.4, 127.9, 128.5, 129.2, 129.9, 130.5, 131.8, 132.4, 133.1, 133.7, 134.4, 135.1, 135.8, 173.2, 192.7, 195.5. Mass (*m*/*z*): 524 (M$^+$). Anal. Calcd for $C_{26}H_{24}N_2O_2S_4$: C, 59.51; H, 4.61; N, 5.34%. Found: C, 59.79; H, 4.48; N, 5.54%.

4.3. 3,7-Diaryl-5-(arylamino)-2,3,5,7-tetrahydrothiazolo[4,5-*d*][1,3]dithiin-2-thiones 5. General procedure

Thoroughly mixed dithioesters **4** (2.0 mmol) and montmorillonite K-10 clay (0.2 g) were taken in a 20 mL vial and subjected to intermittent MW irradiation at 100 W at the intervals of 2 min for the total irradiation time of 10–12 min (Table 1). After completion of the reaction as indicated by TLC (hexane/AcOEt, 8:2, v/v), water (10 mL) was added to the reaction mixture and stirred well. The yellowish precipitate thus obtained was washed with water to give the crude product, which was recrystallised from ethanol to afford analytically pure sample of **5**.

4.3.1. Compound 5a. Yellowish needles (89%), mp 139–140 °C. IR (KBr) ν_{max} 3025, 1635, 1604, 1585, 1456, 1060 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 4.45 (s, 1H, Ar-CH), 7.13–7.95 (m, 14H$_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 42.5, 80.5, 126.7, 127.4, 128.0, 128.6, 129.3, 130.1, 130.7, 131.5, 132.3, 133.0, 133.6, 134.3, 158.5, 159.8, 192.5. Mass (*m*/*z*): 482, 484 (M, M+2). Anal. Calcd for $C_{23}H_{15}ClN_2S_4$: C, 57.18; H, 3.13; N, 5.80%. Found: C, 57.47; H, 3.34; N, 5.49%.

4.3.2. Compound 5b. Yellowish needles (80%), mp 143–144 °C. IR (KBr) ν_{max} 3021, 1631, 1603, 1584, 1455, 1058 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 3.73 (s, 3H, OMe), 4.41 (s, 1H, Ar-CH), 7.11–7.93 (m, 14H$_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 42.4, 54.9, 81.3, 126.6, 127.3, 128.1, 128.7, 129.4, 130.1, 130.8, 131.6, 132.2, 132.9, 133.5, 134.2, 158.4, 159.6, 192.3. Mass (*m*/*z*): 478 (M$^+$). Anal. Calcd for $C_{24}H_{18}N_2OS_4$: C, 60.22; H, 3.79; N, 5.85%. Found: C, 59.87; H, 3.88; N, 5.65%.

4.3.3. Compound 5c. Yellowish needles (83%), mp 148–150 °C. IR (KBr) ν_{max} 3020, 1630, 1598, 1579, 1449, 1056 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 2.30 (s, 6H, 2×Me), 4.43 (s, 1H, Ar-CH), 7.15–7.89 (m, 13H$_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 20.3, 21.5, 42.2, 79.9, 125.4, 126.0, 126.6, 127.3, 128.0, 128.6, 129.4, 130.0, 130.7, 131.3, 131.9, 132.7, 133.3, 134.0, 134.6, 135.2, 158.1, 159.8, 192.5. Mass (*m*/*z*): 476 (M$^+$). Anal. Calcd for $C_{25}H_{20}N_2S_4$: C, 62.99; H, 4.23; N, 5.88%. Found: C, 62.72; H, 4.09; N, 5.98%.

4.3.4. Compound 5d. Yellowish needles (85%), mp 150–152 °C. IR (KBr) ν_{max} 3024, 1633, 1605, 1581, 1451, 1059 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 2.33 (s, 6H, 2×Me), 4.48 (s, 1H, Ar-CH), 7.10–7.91 (m, 12H$_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 20.2, 21.7, 42.4, 81.4, 125.3, 126.0, 126.7, 127.4, 128.1, 128.7, 129.3, 130.0, 130.8, 131.4, 132.0, 132.7, 133.4, 134.1, 134.7, 135.3, 157.9, 160.0, 192.8. Mass (*m*/*z*): 510, 512 (M, M+2). Anal. Calcd for $C_{25}H_{19}ClN_2S_4$: C, 58.74; H, 3.75; N, 5.48%. Found: C, 57.79; H, 3.58; N, 5.67%.

4.3.5. Compound 5e. Yellowish needles (80%), mp 145–146 °C. IR (KBr) ν_{max} 3021, 1631, 1601, 1580, 1448, 1061 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 2.31 (s, 6H, 2×Me), 3.70 (s, 3H, OMe), 4.42 (s, 1H, Ar-CH), 7.09–7.95 (m, 12H$_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 20.3, 21.6, 42.3, 54.8, 80.8, 125.5, 126.1, 126.7, 127.3, 128.0, 128.7, 129.4, 130.0, 130.6, 131.2, 131.9, 132.5, 133.2, 133.8, 134.4, 135.1, 158.8, 159.9, 192.6. Mass (*m*/*z*): 506 (M$^+$). Anal. Calcd for $C_{26}H_{22}N_2OS_4$: C, 61.63; H, 4.38; N, 5.53%. Found: C, 61.90; H, 4.23; N, 5.31%.

4.4. 3,4,7-Triaryl-2,3,4,5,7-pentahydrothiazolo[4,5-*d*]-[1,3]thiazine-2,5-dithiones 6. General procedure

An intimate mixture of dithioesters **4** (2.0 mmol) and Li$^+$-montmorillonite clay (0.2 g) was taken in a 20 mL vial and intermittently irradiated at the intervals of 2 min in a CEM Discover MW system at 100 W for the total irradiation time of 10–12 min (Table 1). To obtain analytically pure sample of compounds **6**, the same procedure was adopted as described for **5**.

4.4.1. Compound 6a. Yellowish needles (88%), mp 154–156 °C. IR (KBr) ν_{max} 3027, 1605, 1585, 1445, 1057 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 4.39 (s, 1H, Ar-CH), 7.02–7.91 (m, 14H$_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 42.1, 78.9, 125.8, 126.6, 127.3, 128.0, 128.8, 129.7, 130.4, 131.1, 131.9, 132.8, 133.6, 134.9, 151.9, 191.5, 192.3. Mass (*m*/*z*): 482, 484 (M, M+2). Anal. Calcd for $C_{23}H_{15}ClN_2S_4$: C, 57.18; H, 3.13; N, 5.80%. Found: C, 56.83; H, 3.25; N, 5.56%.

4.4.2. Compound 6b. Yellowish needles (81%), mp 159–160 °C. IR (KBr) ν_{max} 3021, 1598, 1583, 1451, 1051 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 3.75 (s, 3H, OMe), 4.43 (s, 1H, Ar-CH), 7.13–7.95 (m, 14H$_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 42.0, 54.7, 80.2, 125.7, 126.5, 127.3, 128.0, 128.8, 129.7, 130.4, 131.1, 131.9, 132.8, 133.6, 134.9, 151.9, 191.5, 192.3. Mass (*m*/*z*): 478 (M$^+$). Anal. Calcd for $C_{24}H_{18}N_2OS_4$: C, 60.22; H, 3.79; N, 5.85%. Found: C, 60.57; H, 3.64; N, 5.61%.

4.4.3. Compound 6c. Yellowish needles (82%), mp 153–154 °C. IR (KBr) ν_{max} 3022, 1601, 1579, 1450, 1053 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 2.32 (s, 6H, 2×Me), 4.37 (s, 1H, Ar-CH), 7.05–7.98 (m, 13H$_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 20.1, 21.3, 41.5, 78.8, 125.4, 126.0, 126.7, 127.3, 127.9, 128.6, 129.4, 130.0, 130.6, 131.2, 131.9, 132.5, 133.1, 133.8, 134.6, 135.0, 151.8, 191.5, 192.2. Mass (*m*/*z*): 476 (M$^+$). Anal. Calcd for $C_{25}H_{20}N_2S_4$: C, 62.99; H, 4.23; N, 5.88%. Found: C, 62.69; H, 4.11; N, 5.68%.

4.4.4. Compound 6d. Yellowish needles (85%), mp 164–166 °C. IR (KBr) ν_{max} 3026, 1604, 1584, 1448, 1059 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 2.31 (s, 6H, 2×Me), 4.42 (s, 1H, Ar-CH), 7.09–7.85 (m, 12H$_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 20.6, 21.5, 41.9, 81.0, 125.3, 125.9, 126.5, 127.2, 127.8, 128.5, 129.1, 129.8, 130.5, 131.1, 131.8, 132.4, 133.0, 133.7, 134.3, 135.0, 151.6, 191.7, 192.4. Mass (*m*/*z*): 510, 512 (M, M+2). Anal. Calcd for $C_{25}H_{19}ClN_2S_4$: C, 58.74; H, 3.75; N, 5.48%. Found: C, 58.36; H, 3.85; N, 5.73%.

4.4.5. Compound 6e. Yellowish needles (78%), mp 162–163 °C. IR (KBr) ν_{max} 3020, 1602, 1580, 1446, 1052 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 2.28 (s, 6H, 2×Me), 3.72 (s, 3H, OMe), 4.36 (s, 1H, Ar-CH), 7.11–7.88 (m, 12H$_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 20.4, 21.4, 41.7, 54.6, 81.1, 125.4, 126.1, 126.7, 127.3, 127.9, 128.6, 129.3, 130.0, 130.6, 131.3, 132.0, 132.6, 132.8, 133.6, 134.3, 135.0, 151.7, 191.6, 192.3. Mass (*m*/*z*): 506 (M$^+$). Anal. Calcd for $C_{26}H_{22}N_2OS_4$: C, 61.63; H, 4.38; N, 5.53%. Found: C, 61.30; H, 4.51; N, 5.73%.

4.5. 3,7-Diaryl-5-(arylamino)-2,3,5,7-tetrahydrothiazolo[4,5-*e*][1,3]oxathiin-2-thiones 7. General procedure

Thoroughly mixed dithioesters **4** (2 mmol) and I_2 (0.56 g) were taken in a 20 mL vial and subjected to intermittent MW irradiation at 100 W at the intervals of 2 min for the total irradiation time of 8–10 min (Table 1). To obtain analytically pure sample of compounds **7**, the same procedure was adopted as described for **5**.

4.5.1. Compound 7a. Yellowish needles (87%), mp 158–159 °C. IR (KBr) ν_{max} 3025, 1639, 1605, 1586, 1455, 1058 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 4.39 (s, 1H, Ar-CH), 7.03–7.85 (m, 14H$_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 42.7, 79.5, 125.9, 126.6, 127.4, 128.2, 128.9, 129.7, 130.5, 131.4, 132.1, 132.9, 133.7, 134.6, 161.2, 162.9, 191.8. Mass (*m*/*z*): 466, 468 (M, M+2). Anal. Calcd for $C_{23}H_{15}ClN_2OS_3$: C, 59.15; H, 3.24; N, 6.00%. Found: C, 60.10; H, 3.39; N, 5.78%.

4.5.2. Compound 7b. Yellowish needles (83%), mp 167–168 °C. IR (KBr) ν_{max} 3022, 1635, 1601, 1578, 1448, 1056 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 3.79 (s, 3H, OMe), 4.51 (s, 1H, Ar-CH), 7.32–7.95 (m, 14H$_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 42.5, 55.2, 81.2, 125.8, 126.5, 127.5, 128.3, 129.2, 130.1, 130.9, 131.7, 132.5, 133.2, 133.9, 134.7, 161.0, 162.7, 191.7. Mass (*m*/*z*): 462 (M$^+$). Anal. Calcd for $C_{24}H_{18}N_2O_2S_3$: C, 62.31; H, 3.92; N, 6.06%. Found: C, 62.66; H, 3.79; N, 6.26%.

4.5.3. Compound 7c. Yellowish needles (80%), mp 175–176 °C. IR (KBr) ν_{max} 3020, 1635, 1603, 1581, 1449, 1053 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 2.27 (s, 6H, 2×Me), 4.44 (s, 1H, Ar-CH), 7.05–7.99 (m, 13H$_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 20.3, 21.4, 42.2, 80.0, 125.3, 125.9, 126.6, 127.3, 128.0, 128.7, 129.4, 130.0, 130.6, 131.2, 131.9, 132.5, 133.2, 133.8, 134.4, 135.2, 160.9, 162.5, 191.3. Mass (*m*/*z*): 460 (M$^+$). Anal. Calcd for $C_{25}H_{20}N_2OS_3$: C, 65.19; H, 4.38; N, 6.08%. Found: C, 65.38; H, 4.22; N, 5.90%.

4.5.4. Compound 7d. Yellowish needles (85%), mp 152–153 °C. IR (KBr) ν_{max} 3026, 1633, 1599, 1585, 1445, 1054 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 2.36 (s, 6H, 2×Me), 4.52 (s, 1H, Ar-CH), 7.19–7.81 (m, 12H$_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 20.5, 21.7, 42.9, 81.3, 125.4, 126.0, 126.7, 127.3, 127.9, 128.5, 129.2, 129.8, 130.5, 131.1, 131.7, 132.3, 133.0, 133.6, 134.3, 134.9, 169.8, 162.7, 191.5. Mass (*m*/*z*): 494, 496 (M, M+2). Anal. Calcd for $C_{25}H_{19}ClN_2OS_3$: C, 60.65; H, 3.87; N, 5.66%. Found: C, 60.34; H, 3.72; N, 5.87%.

4.5.5. Compound 7e. Yellowish needles (77%), mp 170–171 °C. IR (KBr) ν_{max} 3023, 1636, 1600, 1580, 1451, 1056 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 2.29 (s, 6H, 2×Me), 3.82 (s, 3H, OMe), 4.48 (s, 1H, Ar-CH), 6.99–7.85 (m, 12H$_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 20.2, 21.5, 42.7, 54.8, 79.9, 125.2, 125.8, 126.4, 127.1, 127.7, 128.3, 129.0, 129.6, 130.3, 130.9, 131.6, 132.2, 133.5, 133.8, 134.1, 134.8, 161.5, 162.6, 191.7. Mass (*m*/*z*): 490 (M$^+$). Anal. Calcd for $C_{26}H_{22}N_2O_2S_3$: C, 63.64; H, 4.52; N, 5.71%. Found: C, 61.90; H, 4.40; N, 5.46%.

4.6. Conversion of 5a and 6a into their 2-one and 2,5-dione analogs 8a and 9a, respectively

Compounds **5a** (2.0 mmol) and HgO (4.0 mmol) were refluxed in ethanol (25 mL) for 13 h.[39] The precipitated HgS was filtered off, and the filtrate was concentrated and cooled to furnish **8a**, which was recrystallised from ethanol as white needles. Compound **9a** was similarly prepared from **6a** and recrystallised from ethanol.

4.6.1. Compound 8a. Yellowish needles, mp 138 °C. IR (KBr) ν_{max} 3024, 1705, 1638, 1604, 1585, 1451 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 4.49 (s, 1H, Ar-CH), 7.03–7.95 (m, 14H$_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 41.9, 80.9, 126.2, 126.8, 127.6, 128.5, 129.3, 130.0, 130.6, 131.3, 132.1, 132.7, 133.6, 134.5, 158.4, 160.0, 164.9. Mass (*m*/*z*): 466, 468 (M, M+2). Anal. Calcd for $C_{23}H_{15}ClN_2OS_3$: C, 59.15; H, 3.24; N, 6.00%. Found: C, 59.50; H, 3.13; N, 5.79%.

4.6.2. Compound 9a. Yellowish needles, mp 182–183 °C. IR (KBr) ν_{max} 3022, 1707, 1676, 1605, 1580, 1448 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 4.50 (s, 1H, Ar-CH), 7.12–7.98 (m, 14H$_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 43.7, 80.5, 126.3, 126.9, 127.7, 128.5, 129.4, 130.2, 130.9, 131.6, 132.5, 133.5, 133.9, 134.9, 152.1, 165.3, 166.2. Mass (*m*/*z*): 450, 452 (M, M+2). Anal. Calcd for $C_{23}H_{15}ClN_2O_2S_2$: C, 61.26; H, 3.35; N, 6.21%. Found: C, 6098; H, 3.49; N, 5.99%.

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References and notes

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