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Thiourea to bicyclic scaffolds: highly regio- and stereoselective routes to dithiazolopyrimidines

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Abstract—Microwave-activated solvent-free Michael addition of 3-imino-1,4,2-dithiazoles to 4-arylidene-5(4*H*)-oxazolones furnished isolable adducts regio- and diastereoselectively, which underwent ring transformation to yield the target dithiazolopyrimidines. Alternatively, the similar conjugate addition of methanesulfinylmethylisothioureas to 4-arylidene-5(4*H*)-oxazolones diastereoselectively afforded Michael adducts, which underwent ring transformation followed by heterocyclization via deoxygenative demethylation with thionyl chloride to yield the same products dithiazolopyrimidines regio- and diastereoselectively.

1. Introduction

In general, heterocycles encompassing a pyrimidine unit have found applications in a wide spectrum of biological and therapeutic areas.[1–3] Cancer and AIDS have long been recognized as the most common cause of death. Accordingly, many diverse strategies have been employed to develop new drugs or to improve existing treatments. A literature survey described a variety of substituted thiazoles and antimetabolite thiazolopyrimidine derivatives that received a great deal of attention for their anticancer,[4,5] antiviral,[6,7] antiinflammatory and antimicrobial[8] activities. Highly substituted heterocycles are interesting as potentially biodegradable pharmaceuticals and agrochemicals.[9–11]

Thus, we envisaged the synthesis of a new highly substituted dithiazolopyrimidine system, incorporating the biologically versatile pyrimidine nucleus fused with a dithiazole ring, as it is an attractive scaffold that can be utilized for exploiting chemical diversity and generating a drug-like library to screen for lead candidates.

Recent years have witnessed a considerable upsurge of interest in the application of microwave (MW) irradiation as a non-conventional energy source for the activation of reactions, in solution and under solvent-free conditions in particular, over the usual homogeneous and heterogeneous reactions. Microwave irradiation provides chemical processes with special attributes such as enhanced reaction rates, higher yields of pure products, better selectivity, improved ease of manipulation, rapid optimization of reactions in parallel, and several ecofriendly advantages in the context of green chemistry.[12–19] The application of MW irradiation to provide enhanced reaction rates and improved product yields in chemical synthesis has been extended to modern drug discovery processes,[20,21] and is proving quite successful in the formation of carbon–carbon and carbon–heteroatom bonds.[22,23]

Considering the above valid points and our continued interest in devising new solvent-free cyclization methods,[24–28] we report herein the MW assisted highly diastereoselective formation of pyrimidines **8** and **6** under catalyst and solvent-free conditions. The cornerstone in our approach is the conversion of thiourea into isothioureas **2** bearing a sulfinyl (>S=O) function for effecting the desired heterocyclizations via deoxygenative demethylation using thionyl chloride. Interestingly, the present stereoselective synthetic protocols yielding dithiazolopyrimidines **6** starting from thiourea **1** are hitherto unreported to the best of our knowledge, and are among the few examples showing increased stereoselectivity under MW irradiation compared to conventional heating.

2. Results and discussion

After some preliminary experimentation, it was found that the synthesis of dithiazolopyrimidines **6** could be effected by MW-activated solvent-free Michael addition of 3-imino-1,4,2-dithiazoles **3** to 4-arylidene-5(4*H*)-oxazolones **4** to

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furnish adducts **5** regio- and diastereoselectively, which underwent ring transformation to yield products **6** (route 1). Alternatively, MW-activated Michael addition of isothioureas **2** to 4-arylidene-5-(4*H*)-oxazolones **4** diastereoselectively afforded adducts **7**, which underwent ring transformation followed by heterocyclization via deoxygenative demethylation with thionyl chloride to yield regioselectively the same products **6** (route 2). However, the highly regio- and diastereoselective synthesis of target compound **6** is equally feasible by both routes.

2.1. Route 1

The envisaged synthetic route in its entirety involves irradiation of a mixture of 3-imino-1,4,2-dithiazoles **3** and 4-arylidene-5(4*H*)-oxazolones **4** for 8–12 min in a CEM Discover Focused Microwave Synthesis System at 85 °C (Table 1) to afford 6-acet(benz)amido-7-aryl-6,7-dihydro-5*H*-1,3,4-dithiozolo[4,5-*a*]pyrimdin-5-ones **6** in 79–90% yields with >96:4 diastereoselectivity (Table 1) and total regiocontrol (Scheme 1). The Michael adducts **5** were isolated in 81–90% yields, with >96:4 diastereoselectivity (Table 1) and total regiocontrol (Scheme 1). The procedure followed was the same as that for **6** except that the time of MW irradiation in this case was 4 min.

2.2. Route 2

In an alternate route, the envisaged annulation was successful with a mixture of isothioureas **2** and 4-arylidene-5(4*H*)-oxazolones **4** under MW irradiation in a CEM Discover Focused Microwave Synthesis System at 85 °C for 4–8 min (Table 1) to furnish 5-acet(benz)amido-6-aryl-2-methane-(phenylmethane)sulfinylmethyl(phenylmethyl)thio-5,6-dihydropyrimidin(4*H*)-4-ones **8** in 73–90% yields with >95:5 diastereoselectivity (Scheme 2). The compounds **8** underwent heterocyclization via deoxygenative demethylation with thionyl chloride in the presence of pyridine to give the target compounds 6-acet(benz)amido-7-aryl-6,7-dihydro-5*H*-1,4,2-dithiozolo[4,5-*a*]pyrimdin-5-ones **6** in 76–92% yields with >95:5 diastereoselectivity and total regiocontrol (Scheme 2).

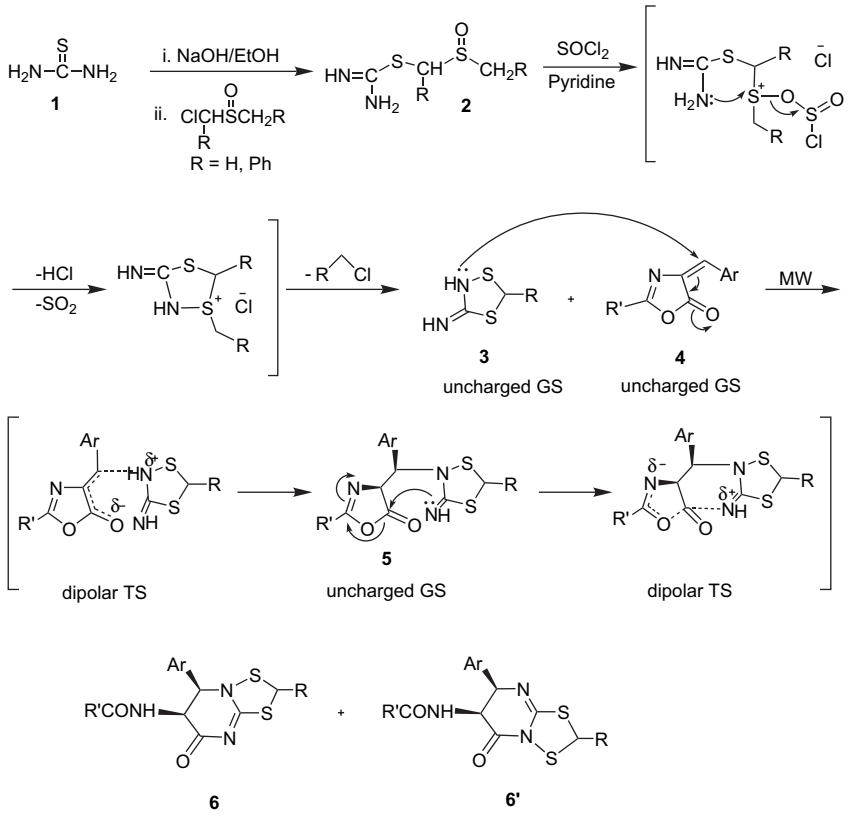
For comparison purposes, the temperature of the reaction mixture was maintained at 85 °C in the case of the MW method and the reactions were also carried out using a thermostated oil-bath at the same temperature (85 °C) of the reaction mixture but for a longer (optimized) period of time (Table 1). This was to ascertain whether the MW method improves the yield and regio-/diastereoselectivity or simply increases conversion rates. It was found that significantly lower yields (35–48%) and diastereoselectivity (>53:47) in route 1 and 34–50% yields and >56:44 diastereoselectivity in route 2 were obtained using oil-bath heating rather than the MW-activated method (Table 1). However, total regiocontrol was observed in the MW-activated method as well as by using oil-bath heating.

This observation may be rationalized on the basis of the formation of a dipolar transition state (TS) from an uncharged ground state (GS) in these reactions (Schemes 1 and 2), and the greater stabilization of more polar TS by dipole–dipole interactions with the oscillating electric field of microwaves as compared to the less polar GS, which may reduce the activation energy ($\Delta G^{\neq}$) resulting in the rate enhancement.[16] The formation of **6** involves the conjugate addition of the

Table 1. Microwave-activated synthesis of products **5–8**

Product	Time		Route 1				Route 2				Mp (°C)
	MW (min)[a]	Thermal (h)[b]	Yield (%)[c,d]		cis:trans ratio[e]		Yield (%)[c,d]		cis:trans ratio[e]		
			MW	Thermal	MW	Thermal	MW	Thermal	MW	Thermal	
5a	4	3	90	49	98:2	59:41	—	—	—	—	177–178
5e	4	2	81	35	98:2	57:43	—	—	—	—	217–218
5h	4	2	85	45	97:3	53:47	—	—	—	—	185–186
7a	6	3	—	—	—	—	77	42	96:4	59:41	146–147
7e	6	2	—	—	—	—	87	44	97:3	57:43	208–210
7h	6	3	—	—	—	—	74	38	97:3	58:42	167–168
6a	8	4	79	35	97:3	55:45	89	50	96:4	60:40	160–162
6b	10	6	81	37	97:3	55:45	76	48	97:3	57:43	139–140
6c	10	6	90	48	98:2	56:46	92	52	96:4	58:42	145–146
6d	8	5	83	41	99:1	54:46	78	34	97:3	58:42	155–157
6e	10	5	89	45	99:1	55:45	82	39	97:3	57:43	197–199
6f	12	6	79	39	97:3	54:46	87	36	96:4	58:42	163–164
6g	12	4	88	44	98:2	57:43	79	44	99:1	59:41	188–189
6h	10	4	90	38	98:2	56:44	85	46	99:1	59:41	166–167
8a	4	3	—	—	—	—	78	41	96:4	59:41	131–133
8b	4	2	—	—	—	—	88	48	97:3	57:43	115–116
8c	6	3	—	—	—	—	90	51	97:3	52:48	143–144
8d	8	3	—	—	—	—	75	46	96:4	51:49	151–152
8e	8	2	—	—	—	—	85	44	98:2	57:43	190–192
8f	6	2	—	—	—	—	73	38	99:1	51:49	170–171
8g	8	2	—	—	—	—	87	50	98:2	52:48	178–179
8h	4	3	—	—	—	—	74	39	98:2	58:42	148–150

[a] Microwave irradiation time at 85 °C.
[b] Time for oil-bath heating at 85 °C.
[c] Yield of isolated and purified products.
[d] All compounds gave C, H and N analyses within ±0.32% and satisfactory spectral (IR, ^{1}H NMR, ^{13}C NMR and EIMS) data.
[e] As determined by ^{1}H NMR spectroscopy.



2-6	R	R'	Ar	2-6	R	R'	Ar
a	H	Ph	Ph	**e**	H	Me	Ph
b	Ph	Ph	Ph	**f**	Ph	Me	Ph
c	H	Ph	4-ClC$_6$H$_4$	**g**	H	Me	4-ClC$_6$H$_4$
d	Ph	Ph	4-ClC$_6$H$_4$	**h**	Ph	Me	4-ClC$_6$H$_4$

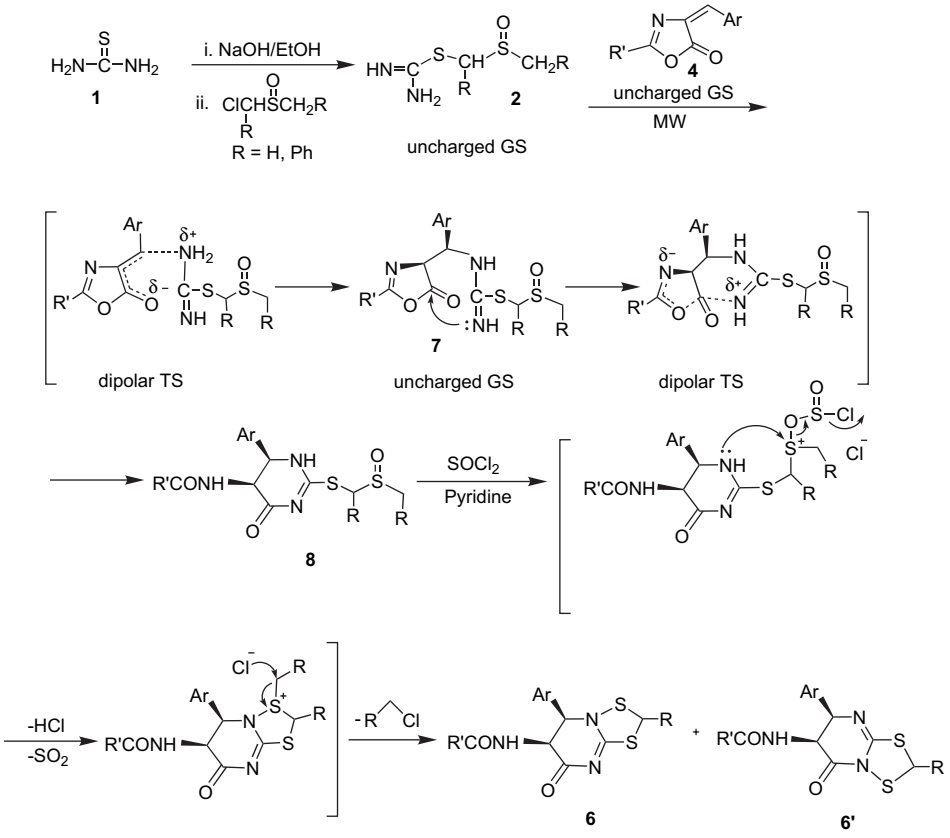
Scheme 1.

ring nitrogen (*N*-2) of 3-imino-1,4,2-dithiazoles **3** to 4-arylidene-5(4*H*)-oxazolones **4** via intermolecular nucleophilic attack of the 3-imino nitrogen atom at the carbonyl carbon (*C*-5) of oxazolones **4** followed by ring transformation of the Michael adducts **5** to yield **6** (Scheme 1). Alternatively, Michael addition of the nitrogen of isothioureas **2** to oxazolones **4** gives adducts **7**, which undergo ring transformation followed by heterocyclization via deoxgenative demethylation with thionyl chloride to yield the title compounds **6** (Scheme 2).

The formation of adducts **5** and **7** and their transformations to **6** were highly diastereoselective in favour of the cis isomers. The diastereomeric ratios of the crude products were checked by ^{1}H NMR prior to purification, to ensure accurate and true diastereomeric ratios. The diastereomeric ratio for compounds **6** in the case of MW activation was significantly higher (>96:4 in route 1 and >95:5 in route 2) than that from oil-bath heating (>53:47 in route 1 and >56:44 in route 2) as determined by ^{1}H NMR spectroscopy. The high diastereoselectivity (>96% in route 1 and >95% in route 2) in favour of the cis isomers under MW irradiation may be plausibly explained by considering that MW irradiation favours the reactions occurring via more polar TS[16] and that the TS leading to the formation of the cis isomers is more polar than that leading to the trans isomers because, in general, cis isomers are more polar than the trans isomers.[29] However, we wish to make it clear that this explanation, based on the tentative rationalization proposed by Loupy and Perreux,[16] is not substantiated and many experts in the field may not agree to it.

It was found that there was no evolution of any trans form under prolonged MW-induced and oil-bath heating of compounds **6** at 85 °C. This indicates that there is no equilibrium between the cis and trans forms. The cis stereochemistry of the products **6** was also supported by NOE experiments as described below.

The exclusive formation of regioisomers **6** instead of **6′** is mechanistically expected and further supported by the NOE experiments. The 8% NOE at 7-H upon irradiation of 2-H, combined with the absence of any measurable intensity enhancement of 6-H signal, indicates that 7-H and 2-H are located on the same face of the molecule, and that 2-H is in closer spatial proximity with 7-H as compared with 6-H (Fig. 1). However, if the regioisomers **6′** would have been formed, then one would have expected almost the same NOE at both 6-H and 7-H upon irradiation of 2-H because they are structurally almost at the same distance from



2-8	R	R'	Ar	2-8	R	R'	Ar
a	H	Ph	Ph	**e**	H	Me	Ph
b	Ph	Ph	Ph	**f**	Ph	Me	Ph
c	H	Ph	4-ClC$_6$H$_4$	**g**	H	Me	4-ClC$_6$H$_4$
d	Ph	Ph	4-ClC$_6$H$_4$	**h**	Ph	Me	4-ClC$_6$H$_4$

Scheme 2.

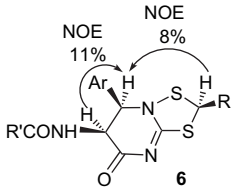


Figure 1.

2-H. Furthermore, the 11% NOE at 7-H (and ~0% at 2-H) upon irradiation of 6-H indicates that 6-H and 7-H are cis to each other. The NOE experiments clearly indicate that the R group in **6** is trans to 6-H and 7-H.

3. Conclusion

In summary, we have developed a general method for mild, rapid and efficient regio- and diastereoselective synthesis of potentially pharmaceutically and agrochemically useful highly functionalized dithiazolopyrimidines starting from thiourea employing microwave irradiations under solvent-free conditions.

4. Experimental

4.1. General

Melting points were determined in open glass capillaries 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 an 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 for all the experiments. All chemicals used were of reagent grade and were used as received without further purification. Silica gel-G was used for TLC.

4.2. *S*-Methane(phenylmethane)sulfinylmethyl(phenylmethyl)isothioureas 2: general procedure

Chloromethyl methyl sulfoxide (2.2 mmol) was added to a solution of NaOH (2.0 mmol) in ethanol (50 mL) and

refluxed for 4–5 h. The solvent was evaporated and the residue was washed well with H_2O and recrystallized from EtOH to give a product, which on second recrystallization from EtOH furnished an analytically pure sample of **2** as yellowish needles.

4.2.1. Compound 2a. Yield 65%, mp 176–177 °C. IR (KBr) ν_{max} 3390, 3360, 1635, 1030 cm^{-1}. ^1H NMR (DMSO-d_6/TMS) δ: 2.31 (br s, 3H, NH_2 and =NH exchanges with D_2O), 2.56 (s, 3H, Me), 4.28 (s, 2H, CH_2). ^{13}C NMR (DMSO-d_6/TMS) δ: 35.2 (Me), 48.8 (CH_2), 162.9 (C=N). Mass (*m*/*z*): 152 (M^+). Anal. Calcd for $C_3H_8N_2OS_2$: C, 23.67; H, 5.30; N, 18.40%. Found: C, 23.91; H, 5.17; N, 18.53%.

4.2.2. Compound 2b. Yield 73%, mp 152–153 °C. IR (KBr) ν_{max} 3393, 3362, 1632, 1605, 1585, 1453, 1030 cm^{-1}. ^1H NMR (DMSO-d_6/TMS) δ: 2.5 (br s, 3H, NH_2 and =NH exchanges with D_2O), 3.80 (s, 2H, $PhCH_2$), 4.58 (s, 1H, CHPh), 7.02–8.12 (m, $10H_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 53.5 (CH_2Ph), 61.8 (CHPh), 128.1, 129.0, 129.8, 130.5, 131.2, 131.9, 132.6, 133.0 (2×Ph), 163.1 (C=N). Mass (*m*/*z*): 304 (M^+). Anal. Calcd for $C_{15}H_{16}N_2OS_2$: C, 59.18; H, 5.30; N, 9.20%. Found: C, 58.83; H, 5.51; N, 9.07%.

4.3. 3-Imino-1,4,2-dithiazoles 3: general procedure

A solution of isothioureas (2.0 mmol) and thionyl chloride (2.5 mmol) in pyridine was refluxed for 8 h. Pyridine was evaporated under reduced pressure and the residue was washed with water to give crude product, which was recrystallized from ethanol to obtain the analytically pure sample of **3**.

4.3.1. Compound 3a. Yield 74%, mp 160–161 °C. IR (KBr) ν_{max} 3375, 1640 cm^{-1}. ^1H NMR (DMSO-d_6/TMS) δ: 2.5 (br s, 2H, NH_2 exchanges with D_2O), 4.18 (s, 2H, CH_2). ^{13}C NMR (DMSO-d_6/TMS) δ: 19.7 (CH_2), 163.0 (C=N). Mass (*m*/*z*): 120 (M^+). Anal. Calcd for $C_2H_4N_2S_2$: C, 19.99; H, 3.35; N, 23.31%. Found: C, 20.25; H, 3.19; N, 23.63%.

4.3.2. Compound 3b. Yield 70%, mp 149–150 °C. IR (KBr) ν_{max} 3385, 1633, 1603, 1581, 1455 cm^{-1}. ^1H NMR (DMSO-d_6/TMS) δ: 2.2 (br s, 2H, NH_2 exchanges with D_2O), 4.75 (s, 1H, CHPh), 7.68–7.86 (m, $5H_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 37.0 (CHPh), 126.7, 127.8, 128.6, 130.8 (Ph), 164.2 (C=N). Mass (*m*/*z*): 196 (M^+). Anal. Calcd for $C_8H_8N_2S_2$: C, 48.95; H, 4.11; N, 14.27%. Found: C, 48.71; H, 4.40; N, 14.09%.

4.4. 6-Acet(benz)amido-7-aryl-6,7-dihydro-5*H*-1,3,4-dithiozolo[4,5-*a*]pyrimidin-5-ones 6: general procedure

Route 1: thoroughly mixed 4-arylidene-5(4*H*)-oxazolones **4** (1.0 mmol) and 3-imino-1,4,2-dithiazoles **3** (1.0 mmol) was taken in a 20 mL vial and subjected to MW irradiation at 85 °C for 8–12 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 recrystallized from ethanol to afford a diastereomeric mixture (>96:4, in the crude products the ratio was >94:6 as determined by ^1H NMR spectroscopy). The product on second recrystallization from ethanol furnished an analytically pure sample of a single diastereomer **6** (Table 1). On the basis of comparison of *J* values to literature ones,[30–35] and NOE experiments (an NOE of ~11% at 7-H upon irradiation of 6-H), the cis stereochemistry was assigned to **6**, as the coupling constant ($J_{6,7}$=5 Hz) of the major cis isomer was lower than that for the minor trans diastereomer ($J_{6,7}$=10 Hz), and there was no measurable intensity enhancement of 7-H signal upon irradiation of 6-H in case of the latter.

Route 2: the procedure followed was the same as described above for the synthesis of **3**, except that the starting material in this case was 5,6-dihydroyrimidin(4*H*)-4-ones **8** instead of isothioureas **2** (2.0 mmol) for **3**. Pyridine was evaporated under reduced pressure and the residue was washed with water to give crude product (diastereomeric ratio >92:8). To obtain analytically pure sample of **6** (diastereomeric ratio >95:5) the same procedure was adopted as described in route 1.

4.4.1. Compound 6a. Yellowish needles, mp 160–162 °C. IR (KBr) ν_{max} 3340, 3023, 1745, 1642, 1633, 1603, 1586, 1457 cm^{-1}. ^1H NMR (DMSO-d_6/TMS) δ: 4.21 (s, 2H, CH_2), 6.60 (d, 1H, *J*=5 Hz, H-6), 6.72 (dd, 1H, *J*=5, 10 Hz, H-5), 7.34–8.20 (m, $10H_{arom}$), 8.60 (br s, 1H, $NH_{acyclic}$, exchanges with D_2O). ^{13}C NMR (DMSO-d_6/TMS) δ: 51.0 (CH_2), 59.9 (6-C), 60.2 (5-C), 126.1, 127.2, 128.4, 129.6, 130.4, 131.3, 132.1, 133.0 (2×Ph), 163.0 (SC=N), 167.9, 177.0 (2×C=O). Mass (*m*/*z*): 369 (M^+). Anal. Calcd for $C_{18}H_{15}N_3O_2S_2$: C, 58.52; H, 4.09; N, 11.37%. Found: C, 58.80; H, 4.27; N, 11.22%.

4.4.2. Compound 6b. Yellowish needles, mp 139–140 °C. IR (KBr) ν_{max} 3342, 3025, 1743, 1651, 1629, 1601, 1581, 1452 cm^{-1}. ^1H NMR (DMSO-d_6/TMS) δ: 4.48 (s, 1H, CHPh), 6.61 (d, 1H, *J*=5 Hz, H-6), 6.73 (dd, 1H, *J*=5, 10 Hz, H-5), 7.28–7.99 (m, $15H_{arom}$), 8.61 (br s, 1H, $NH_{acyclic}$, exchanges with D_2O). ^{13}C NMR (DMSO-d_6/TMS) δ: 53.7 (*CH*Ph), 60.5 (6-C), 61.2 (5-C), 126.3, 127.0, 128.1, 128.8, 129.5, 130.2, 131.0, 131.6, 132.3, 133.1, 134.0, 134.8 (3×Ph), 162.8 (SC=N), 168.1, 180.0 (2×C=O). Mass (*m*/*z*): 445 (M^+). Anal. Calcd for $C_{24}H_{19}N_3O_2S_2$: C, 64.70; H, 4.30; N, 9.43%. Found: C, 64.38; H, 4.11; N, 9.55%.

4.4.3. Compound 6c. Yellowish needles, mp 145–146 °C. IR (KBr) ν_{max} 3347, 3021, 1747, 1641, 1628, 1599, 1580, 1453 cm^{-1}. ^1H NMR (DMSO-d_6/TMS) δ: 4.24 (s, 2H, CH_2), 6.60 (d, 1H, *J*=5 Hz, H-6), 6.76 (dd, 1H, *J*=5, 10 Hz, H-5), 7.31–8.24 (m, $9H_{arom}$), 8.56 (br s, 1H, $NH_{acyclic}$, exchanges with D_2O). ^{13}C NMR (DMSO-d_6/TMS) δ: 50.8 (CH_2), 59.7 (6-C), 60.1 (5-C), 126.5, 127.3, 128.9, 129.6, 130.5, 131.2, 132.0, 133.0 (Ph, 4-ClC_6H_4), 162.9 (SC=N), 167.7, 179.9 (2×C=O). Mass (*m*/*z*): 403, 405 (M, M+2). Anal. Calcd for $C_{18}H_{14}ClN_3O_2S_2$: C, 53.53; H, 3.49; N, 10.40%. Found: C, 53.35; H, 3.68; N, 10.29%.

4.4.4. Compound 6d. Yellowish needles, mp 155–157 °C. IR (KBr) ν_{max} 3341, 3018, 1744, 1644, 1635, 1597, 1585, 1455 cm^{-1}. ^1H NMR (DMSO-d_6/TMS) δ: 4.50 (s, 1H, CHPh), 6.63 (d, 1H, *J*=5 Hz, H-6), 6.75 (dd, 1H, *J*=5, 10 Hz, H-5), 7.31–8.10 (m, $14H_{arom}$), 8.63 (br s, 1H,

$NH_{acyclic}$, exchanges with D_2O). ^{13}C NMR (DMSO-d_6/TMS) δ: 53.5 (*CH*Ph), 60.3 (6-C), 61.6 (5-C), 126.0, 127.1, 127.8, 128.0, 129.1, 129.6, 130.3, 131.1, 132.0, 132.6, 133.4, 134.5 (2×Ph, 4-ClC_6H_4), 163.2 (SC=N), 168.2, 180.5 (2×C=O). Mass (*m*/*z*): 479, 481 (M, M+2). Anal. Calcd for $C_{24}H_{18}ClN_3O_2S_2$: C, 60.05; H, 3.78; N, 8.75%. Found: C, 60.37; H, 3.93; N, 8.69%.

4.4.5. Compound 6e. Yellowish needles, mp 197–199 °C. IR (KBr) ν_{max} 3345, 3025, 1748, 1652, 1634, 1604, 1583, 1458 cm^{-1}. ^1H NMR (DMSO-d_6/TMS) δ: 2.12 (s, 3H, Me), 4.18 (s, 2H, CH_2), 6.63 (d, 1H, *J*=5 Hz, H-6), 6.67 (dd, 1H, *J*=5, 10 Hz, H-5), 7.35–8.29 (m, $5H_{arom}$), 8.54 (br s, 1H, $NH_{acyclic}$, exchanges with D_2O). ^{13}C NMR (DMSO-d_6/TMS) δ: 21.2 (Me), 50.6 (CH_2), 59.5 (6-C), 60.0 (5-C), 127.0, 129.9, 132.1, 133.5 (Ph), 162.7 (SC=N), 167.3, 181.2 (2×C=O). Mass (*m*/*z*): 307 (M^+). Anal. Calcd for $C_{13}H_{13}N_3O_2S_2$: C, 50.79; H, 4.26; N, 13.67%. Found: C, 50.57; H, 4.43; N, 13.52%.

4.4.6. Compound 6f. Yellowish needles, mp 163–164 °C. IR (KBr) ν_{max} 3340, 3027, 1742, 1648, 1628, 1602, 1582, 1451 cm^{-1}. ^1H NMR (DMSO-d_6/TMS) δ: 2.14 (s, 3H, Me), 4.47 (s, 1H, CHPh), 6.62 (d, 1H, *J*=5 Hz, H-6), 6.74 (dd, 1H, *J*=5, 10 Hz, H-5), 7.30–8.21 (m, $10H_{arom}$), 8.59 (br s, 1H, $NH_{acyclic}$, exchanges with D_2O). ^{13}C NMR (DMSO-d_6/TMS) δ: 21.5 (Me), 51.3 (*CH*Ph), 59.8 (6-C), 62.1 (5-C), 126.8, 127.6, 128.4, 129.1, 130.0, 130.7, 131.9, 133.0 (2×Ph), 162.9 (SC=N), 168.0, 182.3 (2×C=O). Mass (*m*/*z*): 383 (M^+). Anal. Calcd for $C_{19}H_{17}N_3O_2S_2$: C, 59.51; H, 4.47; N, 10.96%. Found: C, 59.79; H, 4.19; N, 10.79%.

4.4.7. Compound 6g. Yellowish needles, mp 188–189 °C. IR (KBr) ν_{max} 3343, 3020, 1746, 1643, 1631, 1598, 1579, 1450 cm^{-1}. ^1H NMR (DMSO-d_6/TMS) δ: 2.15 (s, 3H, Me), 4.21 (s, 2H, CH_2), 6.62 (d, 1H, *J*=5 Hz, H-6), 6.68 (dd, 1H, *J*=5, 10 Hz, H-5), 7.34–8.26 (m, $4H_{arom}$), 8.55 (br s, 1H, $NH_{acyclic}$, exchanges with D_2O). ^{13}C NMR (DMSO-d_6/TMS) δ: 21.4 (Me), 51.2 (CH_2), 59.6 (6-C), 62.5 (5-C), 126.1, 127.4, 131.4, 133.1 (4-ClC_6H_4), 163.0 (SC=N), 168.0, 182.1 (2×C=O). Mass (*m*/*z*): 341, 343 (M, M+2). Anal. Calcd for $C_{13}H_{12}ClN_3O_2S_2$: C, 45.68; H, 3.54; N, 12.29%. Found: C, 45.93; H, 3.29; N, 12.41%.

4.4.8. Compound 6h. Yellowish needles, mp 166–167 °C. IR (KBr) ν_{max} 3346, 3022, 1745, 1647, 1630, 1600, 1583, 1455 cm^{-1}. ^1H NMR (DMSO-d_6/TMS) δ: 2.16 (s, 3H, Me), 4.49 (s, 1H, CHPh), 6.63 (d, 1H, *J*=5 Hz, H-6), 6.71 (dd, 1H, *J*=5, 10 Hz, H-5), 7.26–8.09 (m, $9H_{arom}$), 8.64 (br s, 1H, $NH_{acyclic}$, exchanges with D_2O). ^{13}C NMR (DMSO-d_6/TMS) δ: 21.7 (Me), 51.5 (*CH*Ph), 60.1 (6-C), 62.8 (5-C), 126.5, 127.2, 128.0, 129.1, 129.7, 131.3, 132.2, 133.8 (Ph, 4-ClC_6H_4), 163.2 (SC=N), 168.2, 182.3 (2×C=O). Mass (*m*/*z*): 417, 419 (M, M+2). Anal. Calcd for $C_{19}H_{16}ClN_3O_2S_2$: C, 54.60; H, 3.86; N, 10.05%. Found: C, 54.92; H, 4.05; N, 9.97%.

4.5. Isolation of Michael adducts 5a, 5e and 5h and their transformation into the corresponding final products 6a, 6e and 6h: general procedure

The procedure followed was the same as described above for the synthesis of **6** except that the time of MW irradiation in this case was 4 min instead of 8–12 min for **6** (route 1). Adducts **5** were recrystallized from ethanol to give a diastereomeric mixture (>96:4, in the crude isolates the ratio was >94:6 as determined by ^1H NMR spectroscopy), which was again recrystallized from ethanol to obtain an analytical sample of **5a**, **5e** and **5h**. Adducts **5a**, **5e** and **5h** were assigned the *syn* stereochemistry, as their ^1H NMR spectra exhibited lower values of coupling constant $J_{cyclic\ NCH,}$ $J_{acyclic\ NCH}$=5 Hz, than that of the very minor (<4%) diastereomer (*anti*), $J_{cyclic\ NCH,}$ $J_{acyclic\ NCH}$=9 Hz.[30–35] Finely powdered intermediate compounds **5a**, **5e** and **5h** were MW irradiated for 6 min in the same way as described for the synthesis of **6** (route 1) to give the corresponding annulated products **6a**, **6e** and **6h** quantitatively.

4.5.1. Compound 5a. Pale yellow needles, mp 177–178 °C. IR (KBr) ν_{max} 3342, 3020, 1746, 1632, 1603, 1580, 1450 cm^{-1}. ^1H NMR (DMSO-d_6/TMS) δ: 4.23 (s, 2H, CH_2), 6.67 (d, 1H, *J*=5 Hz, acyclic NCH), 6.78 (d, 1H, *J*=5 Hz, cyclic NCH), 7.11–7.90 (m, $10H_{arom}$), 8.45 (br s, 1H, NH, exchanges with D_2O). ^{13}C NMR (DMSO-d_6/TMS) δ: 51.3 (CH_2), 64.4 (Ar-*C*), 69.7 (O=C–*C*), 126.2, 126.9, 127.9, 129.0, 129.6, 130.3, 131.0, 132.5 (2×Ph), 159.2 (SC=N), 160.7 (OC=N), 172.5 (C=O). Mass (*m*/*z*): 369 (M^+). Anal. Calcd for $C_{18}H_{15}N_3O_2S_2$: C, 58.52; H, 4.09; N, 11.37%. Found: C, 58.84; H, 4.31; N, 11.21%.

4.5.2. Compound 5e. Pale yellow needles, mp 217–218 °C. IR (KBr) ν_{max} 3340, 3021, 1742, 1630, 1601, 1578, 1455 cm^{-1}. ^1H NMR (DMSO-d_6/TMS) δ: 2.15 (s, 3H, Me), 4.25 (s, 2H, CH_2), 6.65 (d, 1H, *J*=5 Hz, acyclic NCH), 6.77 (d, 1H, *J*=5 Hz, cyclic NCH), 7.08–7.91 (m, $5H_{arom}$), 8.46 (br s, 1H, NH, exchanges with D_2O). ^{13}C NMR (DMSO-d_6/TMS) δ: 20.3 (Me), 51.1 (CH_2), 64.2 (Ar-*C*), 69.5 (O=C–*C*), 126.0, 127.5, 130.0, 132.7 (Ph), 159.0 (SC=N), 160.8 (OC=N), 172.1 (C=O). Mass (*m*/*z*): 307 (M^+). Anal. Calcd for $C_{13}H_{13}N_3O_3S_2$: C, 50.79; H, 4.26; N, 13.67%. Found: C, 50.51; H, 4.41; N, 13.52%.

4.5.3. Compound 5h. Pale yellow needles, mp 185–186 °C. IR (KBr) ν_{max} 3344, 3024, 1747, 1635, 1605, 1585, 1451 cm^{-1}. ^1H NMR (DMSO-d_6/TMS) δ: 2.33 (s, 3H, Me), 4.50 (s, 1H, CHPh), 6.68 (d, 1H, *J*=5 Hz, acyclic NCH), 6.79 (d, 1H, *J*=5 Hz, cyclic NCH), 7.30–8.08 (m, $9H_{arom}$), 8.48 (br s, 1H, NH, exchanges with D_2O). ^{13}C NMR (DMSO-d_6/TMS) δ: 20.5 (Me), 53.8 (CHPh), 64.7 (Ar-*C*), 70.1 (O=C–*C*), 126.5, 127.3, 128.8, 129.7, 130.5, 131.4, 132.0, 132.9 (Ph, 4-ClC_6H_4), 159.8 (SC=N), 160.9 (OC=N), 172.3 (C=O). Mass (*m*/*z*): 417, 419 (M, M+2). Anal. Calcd for $C_{19}H_{16}ClN_3O_3S_2$: C, 54.60; H, 3.86; N, 10.05%. Found: C, 54.89; H, 3.73; N, 10.17%.

4.6. 5-Acet(benz)amido-6-aryl-2-methane(phenylmethane)sulfinylmethyl(phenylmethyl)thio-5,6-dihydropyrimidin(4*H*)-4-ones 8: general procedure

A mixture of isothioureas **2** (1.0 mmol) and 4-arylidene-5(4*H*)-oxazolones **4** (1.0 mmol) was taken in a 20 mL vial and subjected to MW irradiation at 85 °C for 4–8 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 recrystallized from ethanol to afford a diastereomeric mixture (>95:5, in the crude products the ratio was >92:8 as determined by ^{1}H NMR spectroscopy). The product on second recrystallization from ethanol furnished an analytically pure sample of a single diastereomer **8** (Table 1). On the basis of comparison of *J* values to literature ones,[30–35] and NOE experiments (an NOE of ~10% at 5-H upon irradiation of 6-H), the cis stereochemistry was assigned to **8**, as the coupling constant ($J_{5,6}$=4 Hz) of the major cis isomer was lower than that for the minor trans diastereomer ($J_{5,6}$=8 Hz), and there was no measurable intensity enhancement of 5-H signal upon irradiation of 6-H in case of the latter.

4.6.1. Compound 8a. Yellowish needles, mp 131–133 °C. IR (KBr) ν_{max} 3341, 3021, 1748, 1645, 1632, 1605, 1580, 1455 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 2.58 (s, 3H, Me), 4.21 (s, 2H, CH_2), 6.60 (d, 1H, *J*=5 Hz, H-6), 6.72 (dd, 1H, *J*=5, 10 Hz, H-5), 7.31–8.23 (m, 10H$_{arom}$), 8.43 (br s, 1H, cyclic NH, exchanges with D_2O), 8.62 (br s, 1H, acyclic NH, exchanges with D_2O). ^{13}C NMR (DMSO-d_6/TMS) δ: 41.2 (*Me*S=O), 58.0 (CH_2), 59.5 (6-C), 64.2 (5-C), 126.7, 127.5, 128.8, 129.5, 130.2, 130.9, 131.7, 132.8 (2×Ph), 159.5 (SC=N), 170.1, 172.6 (2×C=O). Mass (*m*/*z*): 401 (M$^+$). Anal. Calcd for $C_{19}H_{19}N_3O_3S_2$: C, 56.84; H, 4.77; N, 10.47%. Found: C, 56.52; H, 4.55; N, 10.31%.

4.6.2. Compound 8b. Yellowish needles, mp 115–116 °C. IR (KBr) ν_{max} 3343, 3022, 1747, 1646, 1635, 1603, 1585, 1459 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 2.85 (s, 2H, CH_2), 4.53 (s, 1H, SCH), 6.65 (d, 1H, *J*=5 Hz, H-6), 6.71 (dd, 1H, *J*=5, 10 Hz, H-5), 7.20–7.98 (m, 20H$_{arom}$), 8.66 (br s, 1H, cyclic NH, exchanges with D_2O), 8.44 (br s, 1H, acyclic NH, exchanges with D_2O). ^{13}C NMR (DMSO-d_6/TMS) δ: 51.5 (CH_2), 58.0 (S=O*CH*), 60.1 (6-C), 64.5 (5-C), 126.2, 126.8, 127.5, 128.1, 128.9, 129.5, 130.1, 130.8, 131.2, 131.8, 132.5, 133.2, 134.0, 134.6, 135.1, 135.8 (4×Ph), 160.2 (SC=N), 170.2, 172.8 (2×C=O). Mass (*m*/*z*): 553 (M$^+$). Anal. Calcd for $C_{31}H_{27}N_3O_3S_2$: C, 67.24; H, 4.92; N, 7.59%. Found: C, 67.51; H, 4.71; N, 7.44%.

4.6.3. Compound 8c. Yellowish needles, mp 143–144 °C. IR (KBr) ν_{max} 3347, 3025, 1751, 1650, 1634, 1608, 1588, 1461 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 2.55 (s, 3H, Me), 4.19 (s, 2H, CH_2), 6.63 (d, 1H, *J*=5 Hz, H-6), 6.69 (dd, 1H, *J*=5, 10 Hz, H-5), 7.34–8.21 (m, 9H$_{arom}$), 8.41 (br s, 1H, cyclic NH, exchanges with D_2O), 8.65 (br s, 1H, acyclic NH, exchanges with D_2O). ^{13}C NMR (DMSO-d_6/TMS) δ: 41.4 (*Me*S=O), 58.4 (CH_2), 60.5 (6-C), 64.8 (5-C), 126.4, 127.2, 128.1, 128.8, 129.5, 130.3, 131.7, 133.8 (Ph, 4-ClC_6H_4), 160.5 (SC=N), 170.6, 173.2 (2×C=O). Mass (*m*/*z*): 435, 437 (M, M+2). Anal. Calcd for $C_{19}H_{18}ClN_3O_3S_2$: C, 52.35; H, 4.16; N, 9.64%. Found: C, 52.08; H, 4.36; N, 9.48%.

4.6.4. Compound 8d. Yellowish needles, mp 151–152 °C. IR (KBr) ν_{max} 3345, 3027, 1750, 1652, 1635, 1607, 1589, 1460 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 2.88 (s, 2H, CH_2), 4.55 (s, 1H, SCH), 6.68 (d, 1H, *J*=5 Hz, H-6), 6.75 (dd, 1H, *J*=5, 10 Hz, H-5), 7.28–8.11 (m, 19H$_{arom}$), 8.67 (br s, 1H, cyclic NH, exchanges with D_2O), 8.48 (br s, 1H, acyclic NH, exchanges with D_2O). ^{13}C NMR (DMSO-d_6/TMS) δ: 52.5 (CH_2), 58.5 (S=O*CH*), 60.2 (6-C), 64.7 (5-C), 126.0, 126.7, 127.3, 128.0, 128.6, 129.2, 129.9, 130.6, 131.2, 132.0, 132.7, 133.3, 134.0, 134.7, 135.3, 136.0 (3× Ph, 4-ClC_6H_4), 160.5 (SC=N), 170.5, 172.3 (2×C=O). Mass (*m*/*z*): 587, 589 (M, M+2). Anal. Calcd for $C_{31}H_{26}ClN_3O_3S_2$: C, 63.31; H, 4.46; N, 7.14%. Found: C, 63.12; H, 4.66; N, 7.27%.

4.6.5. Compound 8e. Yellowish needles, mp 190–192 °C. IR (KBr) ν_{max} 3338, 3018, 1749, 1641, 1630, 1603, 1578, 1448 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 2.15 (s, 3H, *Me*CO), 2.61 (s, 3H, *Me*SO), 4.24 (s, 2H, CH_2), 6.57 (d, 1H, *J*=5 Hz, H-6), 6.69 (dd, 1H, *J*=5, 10 Hz, H-5), 7.31–8.26 (m, 5H$_{arom}$), 8.42 (br s, 1H, cyclic NH, exchanges with D_2O), 8.55 (br s, 1H, acyclic NH, exchanges with D_2O). ^{13}C NMR (DMSO-d_6/TMS) δ: 21.3 (*Me*C=O), 41.3(*Me*S=O), 58.2 (CH_2), 60.1 (6-C), 64.5 (5-C), 127.5, 129.4, 131.5, 132.8 (Ph), 160.3 (SC=N), 171.0, 173.5 (2× C=O). Mass (*m*/*z*): 339 (M$^+$). Anal. Calcd for $C_{14}H_{17}N_3O_3S_2$: C, 49.54; H, 5.05; N, 12.38%. Found: C, 49.86; H, 5.27; N, 12.22%.

4.6.6. Compound 8f. Yellowish needles, mp 170–171 °C. IR (KBr) ν_{max} 3339, 3020, 1747, 1640, 1629, 1604, 1581, 1450 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 2.17 (s, 3H, MeC=O), 2.81 (s, 2H, CH_2), 4.49 (s, 1H, SCH), 6.61 (d, 1H, *J*=5 Hz, H-6), 6.73 (dd, 1H, *J*=5, 10 Hz, H-5), 7.30–8.15 (m, 15H$_{arom}$), 8.53 (br s, 1H, cyclic NH, exchanges with D_2O), 8.40 (br s, 1H, acyclic NH, exchanges with D_2O). ^{13}C NMR (DMSO-d_6/TMS) δ: 21.5 (Me), 51.4 (CH_2), 58.1 (S=O*CH*), 60.3 (6-C), 64.2 (5-C), 126.3, 127.0, 127.8, 128.6, 129.7, 130.5, 131.2, 132.0, 132.7, 133.1, 133.7, 134.3 (3×Ph), 160.3 (SC=N), 170.7, 172.9 (2×C=O). Mass (*m*/*z*): 491 (M$^+$). Anal. Calcd for $C_{26}H_{25}N_3O_3S_2$: C, 63.52; H, 5.13; N, 8.55%. Found: C, 63.81; H, 5.29; N, 8.39%.

4.6.7. Compound 8g. Yellowish needles, mp 178–179 °C. IR (KBr) ν_{max} 3341, 3022, 1748, 1642, 1630, 1605, 1580, 1455 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 2.18 (s, 3H, *Me*C=O), 2.58 (s, 3H, *Me*S=O), 4.20 (s, 2H, CH_2), 6.63 (d, 1H, *J*=5 Hz, H-6), 6.72 (dd, 1H, *J*=5, 10 Hz, H-5), 7.22–8.26 (m, 4H$_{arom}$), 8.45 (br s, 1H, cyclic NH, exchanges with D_2O), 8.57 (br s, 1H, acyclic NH, exchanges with D_2O). ^{13}C NMR (DMSO-d_6/TMS) δ: 21.4 (*Me*C=O), 41.5 (*Me*S=O), 58.5 (CH_2), 60.8 (6-C), 64.9 (5-C), 127.9, 129.5, 132.2, 133.8 (4-ClC_6H_4), 160.1 (SC=N), 170.9, 173.1 (2×C=O). Mass (*m*/*z*): 373, 375 (M, M+2). Anal. Calcd for $C_{14}H_{16}ClN_3O_3S_2$: C, 44.97; H, 4.31; N, 11.24%. Found: C, 45.29; H, 4.06; N, 11.09%.

4.6.8. Compound 8h. Yellowish needles, mp 148–150 °C. IR (KBr) ν_{max} 3343, 3021, 1746, 1643, 1633, 1603, 1583, 1453 cm^{-1}. ^{1}H NMR (DMSO-d_6/TMS) δ: 2.19 (s, 3H, MeCO), 2.83 (s, 2H, CH_2), 4.51 (s, 1H, SCH), 6.64 (d, 1H, *J*=5 Hz, H-6), 6.76 (dd, 1H, *J*=5, 10 Hz, H-5), 7.31–8.32 (m, 14H$_{arom}$), 8.54 (br s, 1H, cyclic NH, exchanges with D_2O), 8.39 (br s, 1H, acyclic NH, exchanges with D_2O). ^{13}C NMR (DMSO-d_6/TMS) δ: 21.7 (Me), 51.6 (CH_2), 58.3 (S=O*CH*), 60.5 (6-C), 64.7 (5-C), 126.7, 127.4, 127.2, 129.0, 129.6, 130.3, 131.0, 131.8, 132.4, 133.2, 134.0, 134.6 (2×Ph, 4-ClC_6H_4), 160.7 (SC=N), 170.5, 173.2 (2×C=O). Mass (*m*/*z*): 525, 527 (M, M+2). Anal. Calcd for $C_{26}H_{24}ClN_3O_3S_2$: C, 59.36; H, 4.60; N, 7.99%. Found: C, 59.65; H, 4.41; N, 7.89%.

4.7. Isolation of Michael adducts 7a, 7e and 7h and their transformation into the corresponding products 8a, 8e and 8h

The procedure followed was the same as described above for the isolation of **5a**, **5e** and **5h** but the time of MW irradiation in this case was 3 min instead of 4 min. To obtain analytically pure sample of **7a**, **7e** and **7h** (diastereomeric ratio >95:5) and to assign the stereochemistry the same procedure was adopted as described for **5a**, **5e** and **5h**. Finely powdered intermediate compounds **7a**, **7e** and **7h** were MW irradiated for 5 min in the same way as described for the synthesis of **8** to give the corresponding annulated products **8a**, **8e** and **8h** quantitatively.

4.7.1. Compound 7a. Pale yellow needles, mp 146–147 °C. IR (KBr) ν_{max} 3344, 3025, 1745, 1631, 1604, 1581, 1458 cm^{-1}. ^1H NMR (DMSO-d_6/TMS) δ: 2.30 (br s, 2H, NH_2, exchanges with D_2O), 2.55 (s, 3H, Me), 4.26 (s, 2H, CH_2), 6.65 (d, 1H, J=5 Hz, acyclic NCH), 6.79 (d, 1H, J=5 Hz, cyclic NCH), 7.05–7.88 (m, $10H_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 41.0 (*Me*S=O), 57.7 (CH_2), 64.6 (Ar-*C*), 69.8 (O=C–*C*), 126.2, 127.0, 128.8, 129.5, 130.3, 131.0, 132.1, 133.0 (2×Ph), 160.5 (OC=N), 162.5 (SC=N), 172.3 (C=O). Mass (*m*/*z*): 401 (M^+). Anal. Calcd for $C_{19}H_{19}N_3O_3S_2$: C, 56.84; H, 4.77; N, 10.47%. Found: C, 57.09; H, 4.65; N, 10.29%.

4.7.2. Compound 7e. Pale yellow needles, mp 208–210 °C. IR (KBr) ν_{max} 3342, 3024, 1746, 1635, 1601, 1578, 1453 cm^{-1}. ^1H NMR (DMSO-d_6/TMS) δ: 2.16 (s, 3H, MeC=N), 2.32 (br s, 2H, NH_2, exchanges with D_2O), 2.51 (s, 3H, MeS=O), 4.23 (s, 2H, CH_2), 6.64 (d, 1H, J=5 Hz, acyclic NCH), 6.78 (d, 1H, J=5 Hz, cyclic NCH), 7.15–7.79 (m, $5H_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 20.2 (*Me*C=N), 41.2 (*Me*S=O), 57.8 (CH_2), 64.3 (Ar-*C*), 69.7 (O=C–*C*), 126.5, 128.2, 130.3, 132.5 (Ph), 160.6 (OC=N), 162.3 (SC=N), 172.1 (C=O). Mass (*m*/*z*): 339 (M^+). Anal. Calcd for $C_{14}H_{17}N_3O_3S_2$: C, 49.54; H, 5.05; N, 12.38%. Found: C, 49.29; H, 5.26; N, 12.24%.

4.7.3. Compound 7h. Pale yellow needles, mp 167–168 °C. IR (KBr) ν_{max} 3345, 3027, 1742, 1633, 1605, 1585, 1455 cm^{-1}. ^1H NMR (DMSO-d_6/TMS) δ: 2.18 (s, 3H, Me), 2.35 (br s, 2H, NH_2, exchanges with D_2O), 2.85 (s, 2H, CH_2), 4.55 (s, 1H, SCH), 6.67 (d, 1H, J=5 Hz, acyclic NCH), 6.81 (d, 1H, J=5 Hz, cyclic NCH), 7.35–7.48 (m, $14H_{arom}$). ^{13}C NMR (DMSO-d_6/TMS) δ: 20.5 (Me), 53.7 (CH_2Ph), 62.0 (CHPh), 64.7 (Ar-*C*), 70.1 (O=C–*C*), 126.8, 127.7, 128.5, 129.2, 130.0, 131.2, 132.1, 133.0 (Ph, 4-ClC_6H_4), 160.8 (OC=N), 162.7 (SC=N), 172.5 (C=O). Mass (*m*/*z*): 525, 527 (M, M+2). Anal. Calcd for $C_{26}H_{24}ClN_3O_3S_2$: C, 59.36; H, 4.60; N, 7.99%. Found: C, 59.62; H, 4.45; N, 8.07%.

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