Tandem sigmatropic shifts in [4 + 2] cycloaddition reactions of 1,3-diazabuta-1,3-dienes with butadienylketene: synthesis of pyrimidinone derivatives

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The reactions of 4-dialkylamino substituted 1,3-diazabuta-1,3-dienes **1** with butadienylketene **2**, are shown to undergo [4 + 2] cycloadditions to yield 5-(buta-1′,3′-dienyl)pyrimidinone **4** and tandem [1,5]H and [1,5]SCH_3 shifts are shown to accompany the [4 + 2] cycloaddition reactions of 4-dialkylamino-4-methylthio substituted 1,3-diazabuta-1,3-dienes **5** with **2**. The regioselective reactions of *N*-arylamino-1,3-diazabuta-1,3-dienes **11** and **14** with butadienylketene **2** are reported to yield 5-(buta-1′,3′-dienyl)-2-dialkylaminopyrimidin-4(3*H*)-one **13** and a mixture of 5-(buta-1′,3′-dienyl)-2-methylthiopyrimidin-4(3*H*)-one **17**, 2-methylthio-5-[1′-(*N*-phenylamino)but-2′-enyl]pyrimidin-4(3*H*)-one **19** and 2-methylthio-5-[3′-(*N*-phenylamino)but-1′-enyl]pyrimidin-4(3*H*)-one **20**, respectively. Tandem [1,5]H, [1,3]NHPh and [1,5]NHPh shifts are involved in the formation of pyrimidinones **19** and **20**. The Diels–Alder reactions of the 5-dienylpyrimidinones with dimethyl acetylenedicarboxylate (DMAD) and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) yielded corresponding cycloadducts.

Introduction

Functionalised 1,3-dienes continue to stimulate an increasing number of chemists because of their well documented synthetic potential and highly exceptional regio, stereo and facial selectivity in Diels–Alder cycloaddition reactions.[1] The development of suitable methods for the synthesis of hetero-atom and carbocyclic/heterocyclic ring substituted 1,3-dienes is of special interest because of their existence as intermediates in the synthesis/structures of various natural products.[1] Most of the reported methods for synthesis of such functionalised 1,3-dienes invariably suffer from multiplicity of the steps involved, cumbersome experimental procedures and low isolated yields. There has been a recent upsurge in the development of simpler methods for the synthesis of heteroatom and carbocyclic/heterocyclic ring substituted 1,3-dienes and as part of our ongoing studies on 1,3-diazabuta-1,3-dienes-ketenes cycloadditions,[2] it was felt that heterocyclic ring substituted 1,3-dienes may easily be obtained through the cycloaddition reactions of suitable substrates with butadienylketene. Recent disclosures from our laboratories have shown a convenient route for the generation and successful utilisation of butadienylketene in [2 + 2] and [4 + 2] cycloaddition reactions with imines and 1,3-diazabuta-1,3-dienes, respectively.[3,4] Herein, we report a detailed account of the [4 + 2] cycloaddition reactions of 1,3-diazabuta-1,3-dienes with butadienylketene, sigmatropic rearrangements accompanying these reactions and utilisation of 5-dienylpyrimidinones in Diels–Alder reactions with dimethyl acetylenedicarboxylate (DMAD) and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD).

Results and discussion

The reactions of 1,3-diazabuta-1,3-dienes **1** having a dimethylamino function at C-4 with butadienylketene **2**, generated *in situ* from sorbyl chloride (hexa-2,4-dienyl chloride) and triethylamine in dry methylene chloride, resulted in excellent yields of 5-(buta-1′,3′-dienyl)pyrimidinones **4** (Scheme 1). The detailed spectral features of these pyrimidinones are discussed in the Experimental section, however, only the salient features are mentioned here. The compound **4a**, for example, analysed for $C_{15}H_{14}N_2OS$ showed a molecular ion peak at *m*/*z* 270 in its mass spectrum. Its IR spectrum showed a strong absorption peak at 1683 cm^{-1} due to the α,β-unsaturated carbonyl group. The absence of *N*,*N*-dimethylamino protons and the presence of an olefinic proton at δ 7.90 in its ^1H NMR spectrum indicated the elimination of dimethylamine from the initially formed [4 + 2] cycloadduct **3** as an intermediate. The ^1H NMR spectrum also showed the presence of all dienyl protons. Its ^{13}C NMR spectrum was also in agreement with the assigned structure.

Interestingly, the reactions of 1-aryl-2-phenyl-4-dialkylamino-4-methylthio-1,3-diazabuta-1,3-dienes **5** with **2** resulted in the formation of a mixture (~1 : 1) of products. These products were assigned the pyrimidinone structures **7** and **10** on the basis of analytical data and spectral evidence. The separation of this mixture of pyrimidinones having very close R_f values was accomplished by a careful silica gel column chromatography with natural loss of yields. The compound **7a**, for example, analysed for $C_{22}H_{21}N_3O$ exhibited in its mass spectrum the molecular ion peak at *m*/*z* 343. Its IR spectrum showed a sharp peak at 1649 cm^{-1} due to α,β-unsaturated carbonyl group. The lower frequency carbonyl absorption in this case may possibly be due to the presence of a β-amino group in the α,β-unsaturated carbonyl unit. The ^1H and ^{13}C NMR spectra of **7a** exhibited peaks for dimethylamino and dienyl functionalities. The product **10a**, on the other hand, analysed for $C_{23}H_{25}N_3OS$ showed the molecular ion peak at *m*/*z* 391 in its mass spectrum and a sharp band at 1636 cm^{-1}, due to α,β-unsaturated carbonyl group in its IR spectrum. Its ^1H NMR spectrum exhibited a doublet (J = 6.8 Hz) at δ 1.42 for three $-CH_3$ protons and an unexpected presence of methylthio as well as dimethylamino groups as singlets at δ 2.04 and δ 3.11, respectively. ^{13}C NMR signals were also in agreement with the

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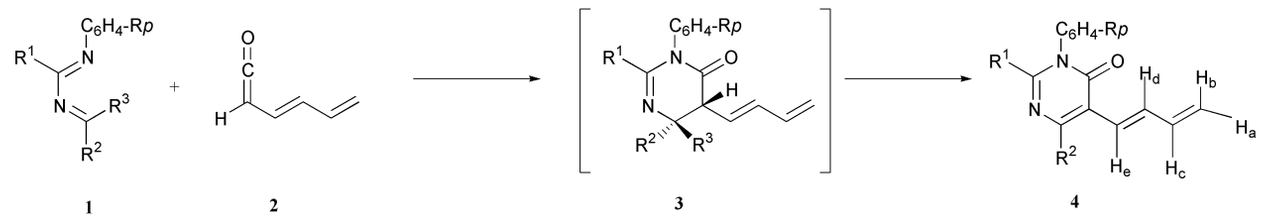


1 a. R = H, R^1 = SCH_3, R^2 = H, R^3 = $N(CH_3)_2$

b. R = H, R^1 = Ph, R^2 = H, R^3 = $N(CH_3)_2$

c. R = H, R^1 = Ph, R^2 = CH_3, R^3 = $N(CH_3)_2$

4 a. R = H, R^1 = SCH_3, R^2 = H

b. R = H, R^1 = Ph, R^2 = H

c. R = H, R^1 = Ph, R^2 = CH_3

Scheme 1

assigned structure. Further, the structure **10** for these pyrimidinones was unambiguously assigned by X-ray crystallographic data taken for pyrimidinone **10f** (Fig. 1). The crystals for pyrimidinone **10f** were grown in a mixture (1 : 5) of dichloromethane and hexane. S–C26 and S–C27 distances of 1.807 (10) and 1.782 (9) Å correspond to the normal S–C(sp^3) single bond distances. C24–C25 being 1.329(10) Å confirms the presence of a double bond. C30–C31 is 1.264(13) Å, which is shorter than the expected double bond, it may be due to relatively high thermal parameters of this terminally bonded allyl group leading to shortening of the distance. Shorter N2–C16 distance (1.298(9) Å) and C14–C15 distances 1.372(10) Å further ascertain the positions of double bonds in the pyrimidinones ring. All other bond lengths and angles are as expected. The torsional angle N3–C29–C30–C31 is 4.7°(17) indicating that the double bond C24–C25 is antiperiplanar with the pyrimidinone ring. The mean plane calculations indicate that the pyrimidinone ring varies significantly from planarity (maximum deviation is 0.04 Å). However, the segment O1–C13–N1–C16 is planar (179.3°(7)). All the three phenyl rings are planar. Phenyl groups make a propeller-like arrangement around the pyrimidinone ring. The phenyl rings A (C1–C6) and B (C7–C12) make dihedral angles 72.1(3) and 36.6°(3) with the pyrimidinone ring, respectively. Phenyl ring C (C17–C22) is rotated by 115.6°(2) with respect to the pyrimidinone ring. The torsion angle C15–C14–C24–C25 is *anti* (−178.3°(9)) but C13–C14–C24–C25 is *syn* (7.0°(13)) and this brings C25 quite close to O1. This gives rise to a short C25–H25A ··· O1 intramolecular contact with H25A ··· O1 2.20 Å. This is also indicated by a low field shift of this proton (δ 6.62) as compared to the adjacent olefinic proton (δ 5.82) attached to C24. C14–C24–C25–C26 is −173.3°(9) which shows that the (CH_3)–CH(SCH_3) and pyrimidinone rings are also *trans* to each other with respect to the C24–C25 double bond. Thus the two olefinic protons are also *trans* to each other (supplemented by 15 Hz coupling constant value for the *trans* protons). H-bonding calculations[5] show the presence of a weak intermolecular C ··· O interaction[6] C21–H21A ··· $O1^i$ 3.389(10) Å, H21 ··· $O1^i$ (2.57 Å) and C21–H21A ··· O^i 147° (where $i = -x + ½, y + ½, -z + ½$). Also present is a C–H ··· π interaction between the C27 methyl group and the phenyl ring C with CH_3 ··· π (H ··· centroid) distance of the order of 3.74(1) Å.

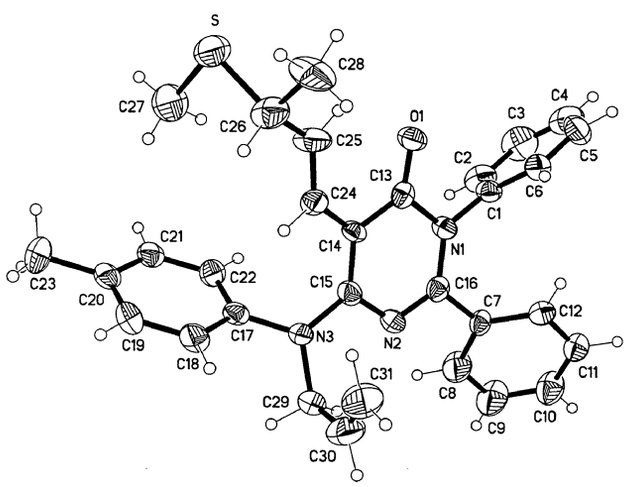
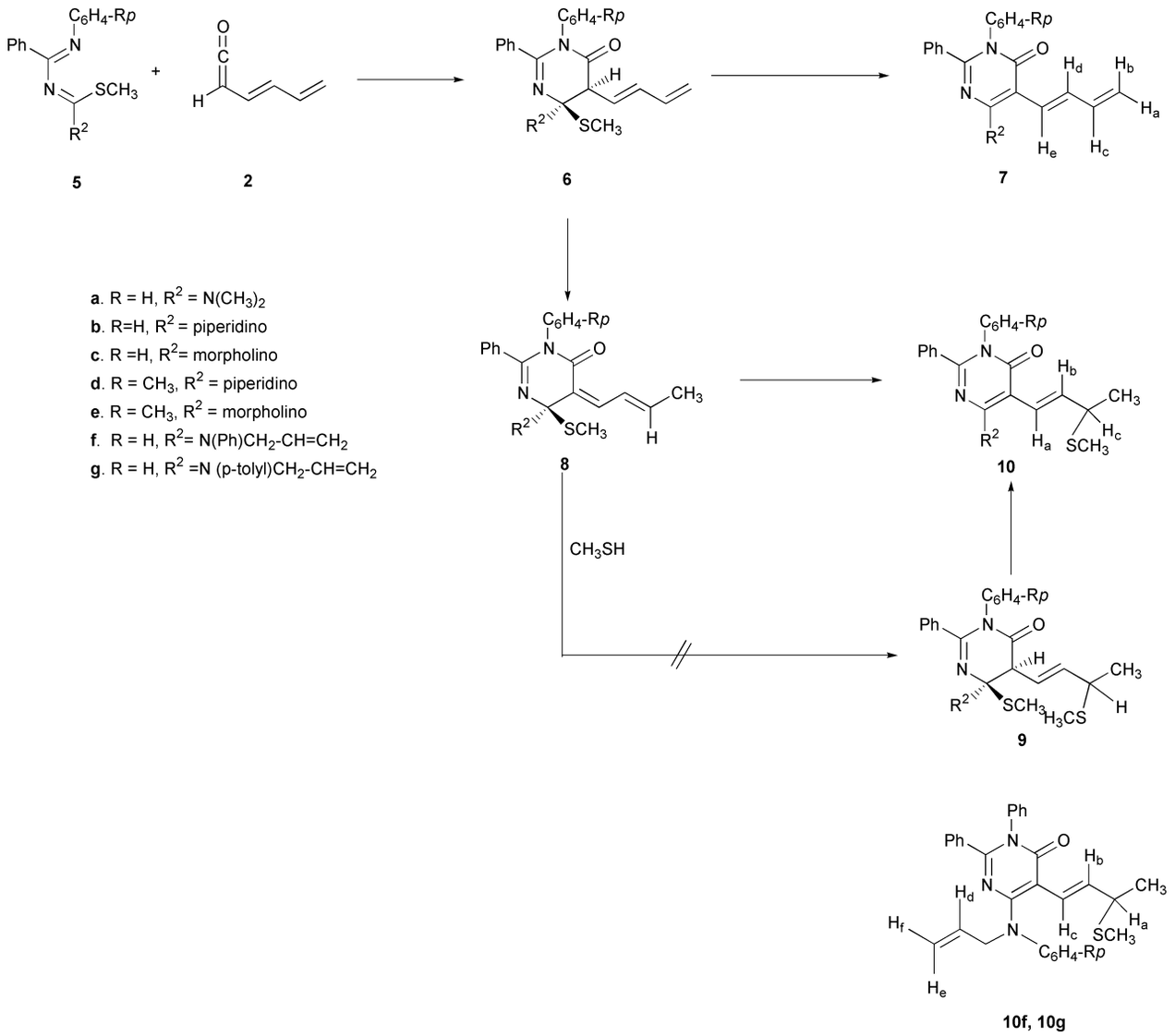


Fig. 1 A ORTEP diagram at 30% probability.

The plausible mechanistic pathways for the formation of pyrimidinones **7** and **10** are outlined in Scheme 2. In this Scheme it is assumed that the reactions of 1,3-diazabuta-1,3-dienes **5** with butadienylketene **2** leads to the initial formation of a [4 + 2] cycloadduct intermediate **6**, possibly consisting of a stereoisomeric mixture with H-5 *cis*/*trans* to the methylthio at C-6. It is conceivable that the *trans*-stereomer undergoes facile elimination of methanethiol to yield pyrimidinones **7**, while the *cis*-stereomer prefers a suprafacial [1,5]H shift over its equilibration to the *trans*-stereomer yielding another intermediate **8**, which undergoes [1,5] SCH_3 shift to yield pyrimidinone **10**. The formation of such a stereomeric mixture may be ruled out since the stereomer with H-5 *trans* to dialkylamino function should have resulted in a product corresponding to the elimination of dialkylamine as observed in reactions of 1,3-diazabuta-1,3-dienes **1** with **2**. It is also possible that the nucleophilic addition of the methanethiol, eliminated during the formation of pyrimidinone **7**, to the activated diene of intermediate **8** may form another intermediate **9** which on elimination of methanethiol yields pyrimidinone **10**. This mechanistic possibility is also discounted on the basis of a crossover experiment performed in the presence of propanethiol, wherein no addition product corresponding to the incorporation of propanethiol was isolated. It is more likely that the [4 + 2] cycloaddition of 1,3-diazabuta-1,3-dienes **5** with **2** is stereoselective, as evidenced from the exclusive elimination of methanethiol in cycloaddition reactions of **5** with other monosubstituted ketenes while the formation of pyrimidinones corresponding to the elimination of dialkylamine was never observed.[2] Recently, Rossi and co-workers have also reported the stereoselective formation of [4 + 2] cycloadducts in reactions of 1,3-diazabuta-1,3-dienes with ketenes.[7] These observations point towards an exclusive formation of an intermediate **6**, with H-5 *trans* to the methylthio at C-6. This intermediate then undergoes either elimination of methanethiol to form pyrimidinone **7** or a [1,5] H shift leading to an intermediate **8** followed by a [1,5]SCH_3 shift to form the pyrimidinone **10** and in the absence of a methylthio function at C-6 the intermediate **8** perhaps reverts back to **6**. A similar but acid catalysed [1,5] sulfenyl shift has recently been reported in the case of simple dienes.[8]

In continuation of these studies and our general interest[8] to understand regio/stereochemical aspects of such cycloaddition reactions, we have also examined the reactions of methylthio/dialkylamino substituted *N*-arylamino-1,3-diazabuta-1,3-dienes **11** and **14**, represented by a number of possible tautomeric forms,[9] and observed remarkable variation in their reactivity towards butadienylketene **2**. Thus, the treatment

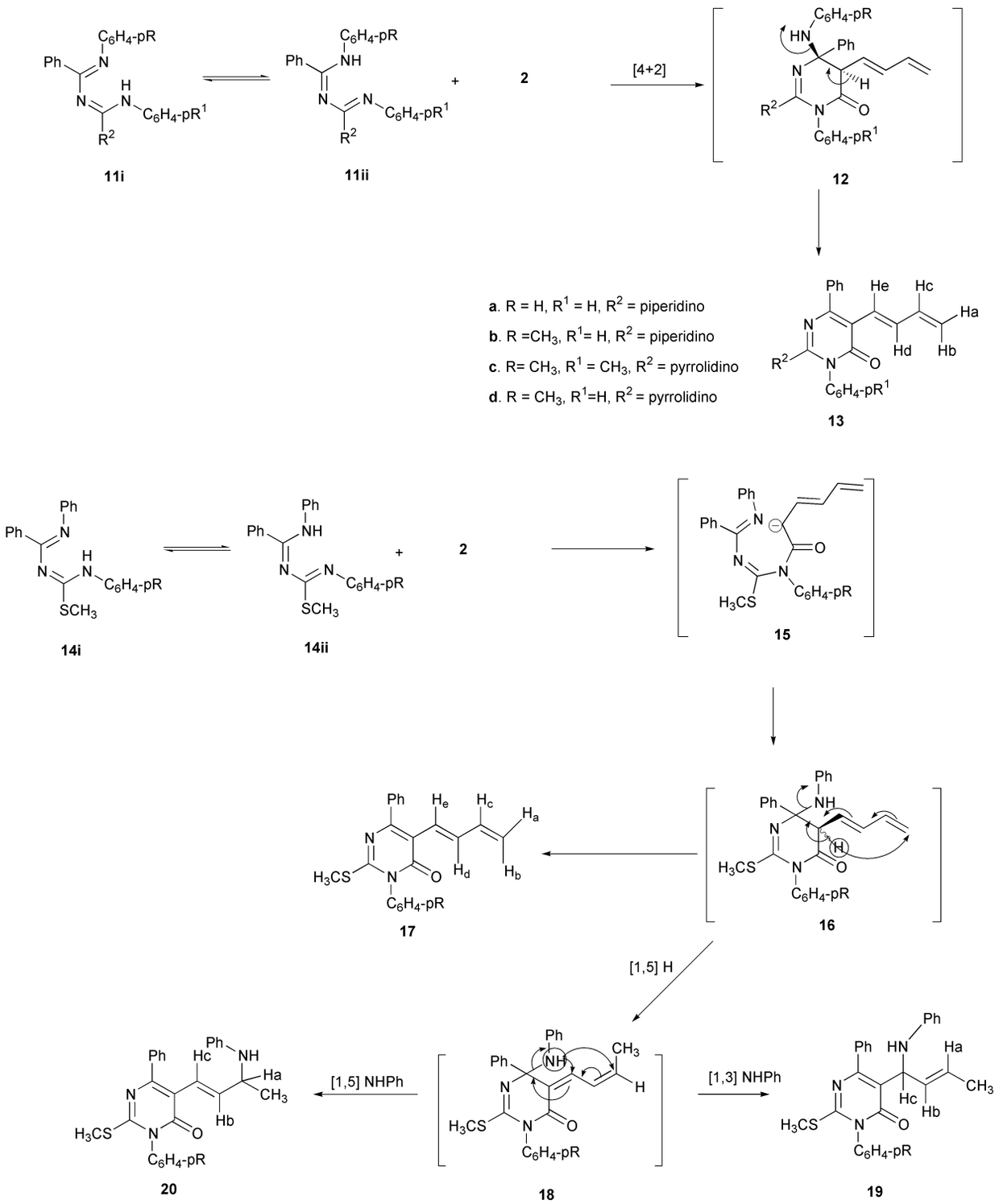


Scheme 2

of dialkylamino substituted *N*-arylamino-1,3-diazabuta-1,3-dienes **11** with butadienylketene **2** resulted in the exclusive formation of 2-dialkylamino-5-(buta-1′,3′-dienyl)pyrimidinone **13**. However, the reactions of methylthio substituted *N*-arylamino-1,3-diazabuta-1,3-dienes **14** with **2** resulted in the isolation of a mixture consisting of 5-(buta-1′,3′-dienyl)-2-methylthiopyrimidin-4(3*H*)-one **17**, 2-methylthio-5-[1′-(*N*-phenylamino)but-2′-enyl]pyrimidin-4(3*H*)-one **19** and 2-methylthio-5-[3′-(*N*-phenylamino)but-1′-enyl]pyrimidin-4(3*H*)-one **20**.

The structures for pyrimidinones **13**, **17**, **19** and **20** were established on the basis of spectral and analytical data. The compound **13a**, for example, analysed for $C_{25}H_{25}N_3O$ exhibited in its mass spectrum a molecular ion peak at *m*/*z* 383. Its IR spectrum showed a sharp peak at 1664 cm^{-1} due to α,β-unsaturated carbonyl group. The ^1H and ^{13}C NMR spectra of **13a** exhibited peaks for piperidino and dienyl functionalities. The product **19a** analysed for $C_{27}H_{25}N_2OS$ showed the molecular ion peak at *m*/*z* 425 in its mass spectrum and a sharp band at 1674 cm^{-1}, due to α,β-unsaturated carbonyl group in its IR spectrum. The ^1H and ^{13}C NMR spectra also attest to the assigned structure **19a**. The product **20a** analysed for $C_{27}H_{25}N_2OS$ showed the molecular ion peak at *m*/*z* 425 in its mass spectrum and a sharp band at 1667 cm^{-1} due to α,β-unsaturated carbonyl group in its IR spectrum. The ^1H and ^{13}C NMR spectra of **20a** were also in agreement with the assigned structure.

The probable mechanism that best explains the formation of these products is depicted in Scheme 3. In this Scheme, it is assumed that the more stable tautomeric form **11ii** of 1,3-diazabuta-1,3-dienes **11**,[9] undergoes a regio-/stereoselective [4 + 2] cycloaddition reaction with butadienylketene **2** to form an intermediate **12** which on elimination of aromatic amine results in formation of pyrimidinones **13**. However, in reactions of 1,3-diazabuta-1,3-dienes **14**, the more stable tautomeric form **14i** having higher electron density at the nitrogen atom attached to C-4,[9] undergoes initial nucleophilic attack at ketene carbonyl to yield an intermediate **15** which cyclises to a *cis–trans*-stereoisomeric mixture **16**. The *trans*-stereoisomer of this mixture **16** undergoes an expected facile elimination of aromatic amine to form dienyl pyrimidinone **17**, while the *cis*-stereoisomer prefers suprafacial [1,5]H shift over its equilibration to *trans*-isomer, yielding another intermediate **18**. This intermediate in turn undergoes [1,3]NHPh and [1,5]NHPh shifts to yield pyrimidinones **19** and **20**, respectively. The formation of rearranged pyrimidinones **19** and **20** in these reactions may also be explained by the nucleophilic addition of the eliminated aromatic amines to the activated diene of intermediate **18**. This mechanistic possibility is discounted since no such rearranged pyrimidinones were formed in reactions of **5**, **11** and **21** with **2**. Also, no addition product corresponding to the incorporation of external amine was observed in crossover experiments performed in the presence of an external amine. These mechanistic arguments are also in agreement with those advanced earlier to explain the regioselective reactions of



Scheme 3

N-arylamino-1,3-diazabuta-1,3-dienes with ketenes.[9] A simpler and perhaps more acceptable explanation for the observed variation in the products in reactions of 1,3-diazabuta-1,3-dienes **11** and **14** with **2**, depending on whether there is a sulfur or nitrogen substituent at the 2-position, would be that the initial pathways in both cases are identical and the additional nucleophilic push from nitrogen in intermediate **12** shortens its life time relative to that of **16** with respect to arylamine elimination. The enhanced lifetime of intermediate **16** then permits competition for alternative rearrangement pathways leading to compounds **19** and **20**.

In order to further establish the substituent dependent sigmatropic shifts followed in cycloaddition reactions of butadienylketene **2** with various 1,3-diazabuta-1,3-dienes, it was thought worthwhile to investigate the reactions of butadienylketene with 1,3-diazabuta-1,3-dienes **21** having two alkyl

amino functions at the 4-position. These reactions did not yield any rearranged pyrimidinone and resulted in an exclusive isolation of pyrimidinone **7b** and **7c**, presumably formed *via* elimination of dialkylamine from the initially obtained intermediate **22** (Scheme 4). The structures **7b** and **7c** for the products were established on the basis of undepressed mp and superimposable IR spectra of the products of the reactions of **4b** and **4c** with **2**.[10]

The 5-dienylpyrimidinones **4**, **7**, **13** and **17** were considered as useful synthons for a variety of substituted pyrimidinones and in order to establish their synthetic potential, we have carried out their Diels–Alder cycloaddition reactions with dimethyl acetylenedicarboxylate (DMAD) and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) which resulted in excellent yields (70–96%) of the corresponding cycloadducts. The reactions of **4a**, **4c**, **7b**, **13a** and **17b** with dimethyl acetylenedicarboxylate (DMAD), in refluxing toluene for 4–6 h, resulted in the isolation of products which could be assigned structures **24** and **26** on the basis of their spectral data and elemental analysis. The compound **24c**, was analysed for $C_{27}H_{24}N_2O_5$ and showed a molecular ion peak at *m*/*z* 456 in its mass spectrum, and strong peaks at 1719 and 1662 cm^{-1} due to methoxy carbonyl and α,β-unsaturated carbonyl groups, respectively, in its IR spectrum. The ^1H NMR spectrum exhibited the presence of signals for methyl (s, δ 2.41), methylene (m, δ 2.34–2.45), two methyls of methoxycarbonyls (s, δ 3.68 and s, δ 3.76), and olefinic protons (m, δ 5.58–5.64 and m, δ 5.83–5.89), in addition to the aromatic protons. Surprisingly, the methine proton could not be identified in the ^1H NMR spectra of **24b** and **24c**. However, their ^{13}C NMR spectra exhibited the presence of all carbons including the methine carbon. Any of the structures **23** or **24** may be assigned on the basis of the above spectral data. However, structure **24** was favoured to the cycloadducts on the basis of the observed doublet (J = 9 Hz) for the vinylic proton H_b in the ^1H NMR spectra of **24** which is unlikely for structure **23**. Also the structure **24a** is further supported by the $\{^1H\}$–$\{^1H\}$ homonuclear spin correlation spectrum (Fig. 2) which indicates the coupling of the methylene protons to Ha and the olefinic proton Hc. The structure **24** is further supported by the observed coupling constant values of approximately 7 Hz and 5 Hz between Ha and two methylene protons. This is possible only when Ha is adjacent to the methylene protons. Such a large coupling constant can not be anticipated on the basis of structure **23**. The more conjugated dienone adduct **24** presumably arises from the rearrangement of initially formed non-conjugated cyclohexa-2′,5′-dienyl Diels–Alder adduct **23**. Similarly in reactions of dienylpyrimidinone **13a** and **17b** with dimethyl acetylenedicarboxylate (DMAD), the formation of pyrimidinones **26** are supposed to proceed through initial formation of pyrimidinones **25**. The reactions of pyrimidinones **17b** and **17c** with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD), in methylene chloride at 0 °C, also resulted in the formation of the corresponding Diels–Alder adducts **27**. The compound **27a**, for example, exhibited strong absorption peaks at 1660 cm^{-1} and 1708 cm^{-1} in its IR spectrum due to the carbonyl groups. Its

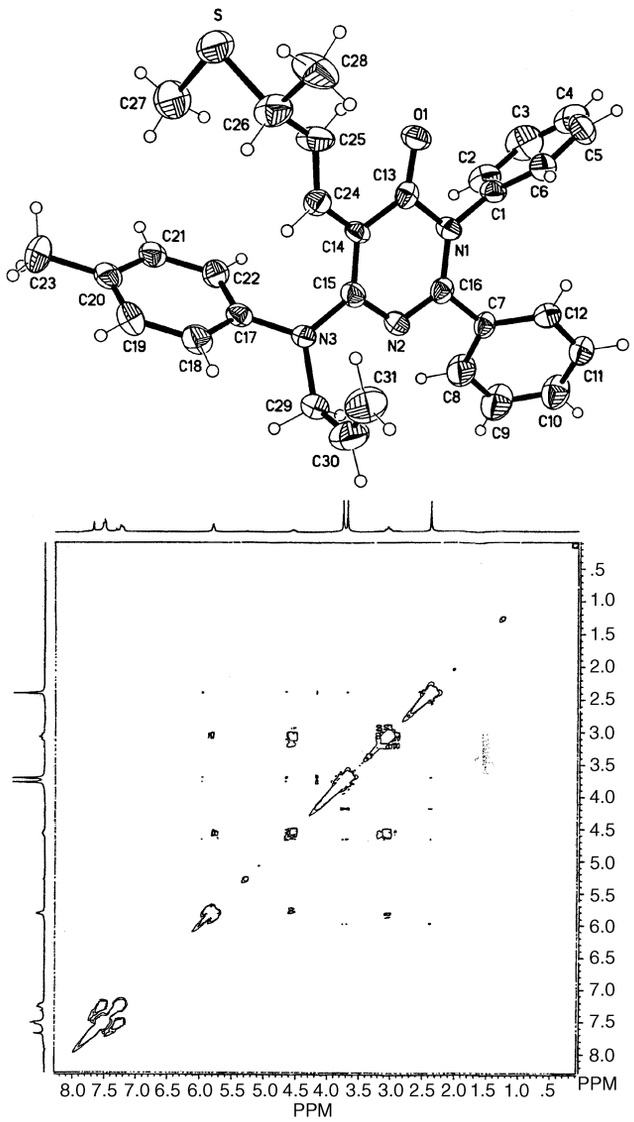


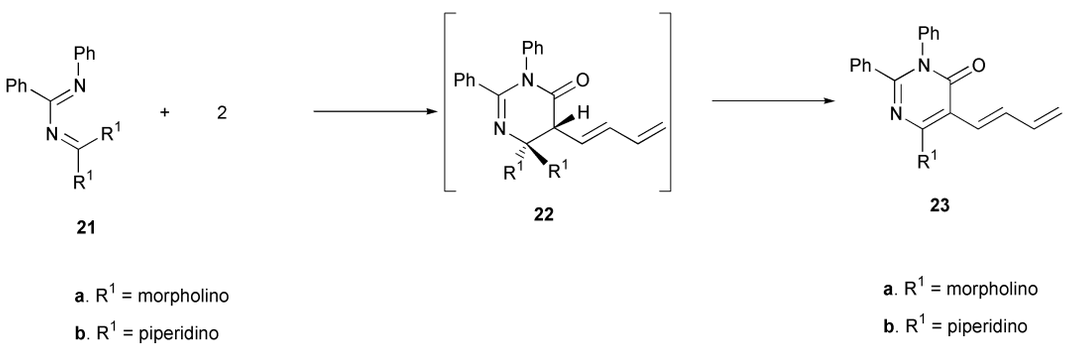
Fig. 2

mass spectrum exhibited a molecular ion peak at *m*/*z* 535 and a peak at 416 (M–Ph–N=C=O). Its ^1H and ^{13}C NMR spectra were in agreement with the assigned structure (Scheme 5).

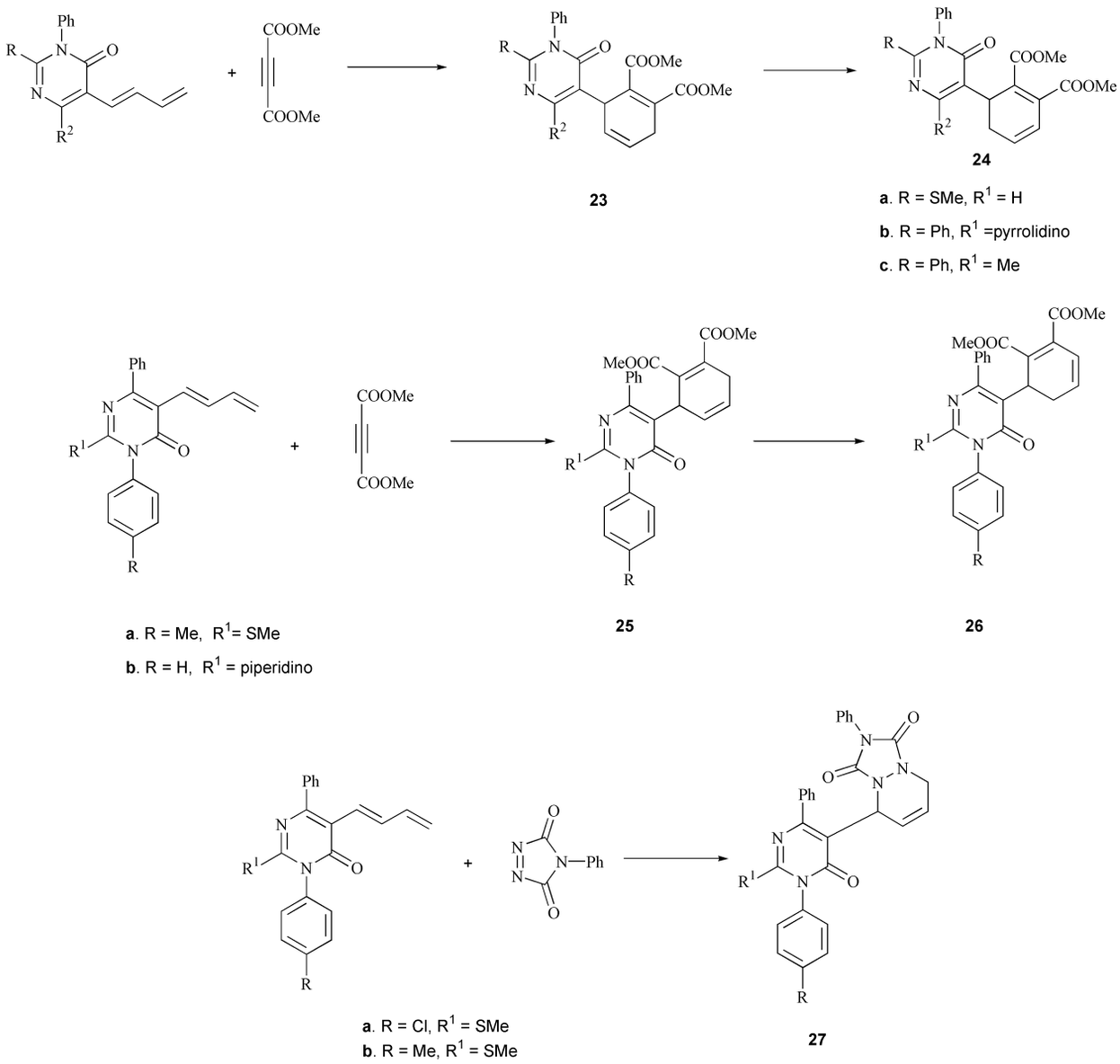
Experimental

General

Melting points were determined by an open capillary method and are uncorrected. Elemental analyses were performed on a Heraus CHN-O-Rapid Elemental Analyser. IR spectra were recorded in a Perkin–Elmer 983 and Shimadzu D-8001 Infrared



Scheme 4



Scheme 5

Spectrophotometer. ^{1}H and ^{13}C NMR were recorded in deuteriochloroform, with a Bruker AC–F 300 (300 MHz) and a Bruker AC–F200 (200 MHz) spectrometer using TMS as an internal standard. Chemical shifts are expressed as ppm downfield from TMS and *J* values are in Hz. Splitting patterns are expressed as s: singlet, d: doublet, t: triplet, m: multiplet, q: quartet and br: broad peak. Mass spectra were obtained by electron impact at 70 eV in a Shimadzu GCMS-QP-2000 mass spectrometer. Column chromatography was performed on a silica gel (60–120) mesh.

X-Ray diffraction experiment ‡

The crystal data, parameters of data collection and refinement results are given in Table 1. The unit cell dimensions were determined by least-square methods with twenty five centered reflections using graphite monochromated Mo-Kα radiation. The data were corrected for Lorentz and polarization effects. No correction was made for absorption. The structure was solved by direct methods. The non hydrogen atoms were refined anisotropically and the hydrogen atoms were located using geometric considerations and were not refined. All calculations were done using SHELXTL-PC.[5]

‡ CCDC reference number(s) 175135. See http://www.rsc.org/suppdata/p1/b1/b109922c/ for crystallographic files in .cif or other electronic format.

Starting Materials

1,3-Diazabuta-1,3-dienes **1**, **5**, **14** and **21** [2h,9a,9b] were prepared by following the reported procedures.[2b,2h,9a,9b]

Reactions of 1,3-diazabuta-1,3-dienes (1, 5, 11, 14 and 21) with butadienylketene

General procedure. To a well stirred solution of 1,3-diazabuta-1,3-diene (4 mmol) and triethylamine (10 mmol) in dry methylene chloride (30 ml), was added dropwise, a solution of sorbyl chloride (6 mmol) in dry methylene chloride (30 ml) over a period of 1 h at room temperature. After completion of the reaction (TLC), the reaction mixture was washed with a saturated sodium bicarbonate solution (2 × 25 ml) and water (5 × 50 ml) and the organic layer dried over anhydrous sodium sulfate. Removal of solvent under reduced pressure yielded the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane (1 : 10) as an eluent for pyrimidinones **4**, **10** and **23** and a mixture of ethyl acetate and hexane (1 : 50) for the separation of pyrimidinones **7**, **10**, **17**, **19** and **20**.

Table 1 Crystal data and structure refinement for **1**

Identification code	ak47	
Empirical formula	$C_{31}H_{31}N_3OS$	
Formula weight	493.65	
Temperature/K	293(2)	
Wavelength/ Å	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 12.411(3) Å	α = 90°
	b = 10.042(2) Å	β = 100.08(2)°
	c = 22.419(4) Å	γ = 90°
Volume/Å^3, Z	2751.0(10), 4	
Density (calculated)/Mg m^{-3}	1.192	
Absorption coefficient/mm^{-1}	0.145	
F(000)	1048	
Crystal size/mm	0.3 × 0.2 × 0.2	
θ/° range for data collection	1.85 to 20.01	
Limiting indices	$0 \le h \le 11$, $0 \le k \le 9$, $-21 \le l \le 21$	
Reflections collected	2730	
Independent reflections	2573 (R_{int} = 0.0357)	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2178/0/325	
Goodness-of-fit on F^2	1.087	
Final R indices [$I>2\sigma(I)$]	$R1$ = 0.0716, $wR2$ = 0.1558	
R indices (all data)	$R1$ = 0.1563, $wR2$ = 0.2182	
Largest diff. peak and hole/eÅ^{-3}	0.633 and −0.244	

5-(Buta-1′,3′-dienyl)-2-methylthio-3-phenylpyrimidin-4(3*H*)-one 4a. Yield 86%; mp 310–312 °C (Found: C, 66.73; H, 5.18; N, 10.30. $C_{15}H_{14}N_2OS$ requires: C, 66.64; H, 5.22; N, 10.36%); IR (KBr) ν_{max}: 1683 (C=O) and 1480 cm^{-1}; δ_H (300 MHz): 2.44 (s, 3H, –CH_3), 5.15 (d, J = 10.2, with fine splitting, 1H, H_a), 5.29 (d, J = 16.9, with fine splitting, 1H, H_b), 6.37–6.50 [m, 2H; consisting in signals at 6.40 (d, J = 15.6, 1H, H_e), 6.44 (ddd, J = 16.9, 10.6 and 10.2, 1H, H_c)], 7.25–7.28 (m, 2H, ArH), 7.39 (dd, J = 15.6 and 10.6, 1H, H_d), 7.51–7.56 (m, 3H, ArH), 7.90 (s, 1H, olefinic); δ_C (75.5 MHz): 15.3 (–SCH_3), 118.4 (C-4′), 119.6 (C-5), 125.1 (C-2′), 128.4, 129.8, 130.1, 133.3 (C-1′), 135.8, 137.8 (C-3′), 149.7 (C-6), 160.8 (C-2), 161.7 (C-4); *m*/*z* 270 (M^+).

5-(Buta-1′,3′-dienyl)-2,3-diphenylpyrimidin-4(3*H*)-one 4b. Yield 63%; mp 109–111 °C (Found: C, 79.83; H, 5.41; N, 9.39. $C_{20}H_{16}N_2O$ requires: C, 79.97; H, 5.36; N, 9.32%); IR (KBr) ν_{max}: 1660 (C=O) and 1481 cm^{-1}; δ_H (300 MHz): 5.23 (d, J = 10.0, 1H, H_a), 6.34–6.46 [m, 2H; consisting in signals at 5.41 (d, J 17.0, 1H, H_b) and 6.43 (ddd, J = 17.0, 10.3 and 10.0, 1H, H_c)], 6.58 (d, J = 15.4, 1H, H_e), 7.13–7.37 (m, 10H, ArH), 7.74 (dd, J = 15.4 and 10.3, 1H, H_d), 8.10 (s, 1H, olefinic); *m*/*z* 300 (M^+).

5-(Buta-1′,3′-dienyl)-2,3-diphenyl-6-methylpyrimidin-4(3*H*)-one 4c. Yield 89%; mp 114 °C (Found: C, 80.35; H, 5.72; N, 8.97. $C_{21}H_{18}N_2O$ requires: C, 80.23; H, 5.77; N, 8.91%); IR (KBr) ν_{max}: 1656 (C=O) and 1480 cm^{-1}; δ_H (300 MHz): 2.55 (s, 3H, –CH_3), 5.18 (d, J = 10.1, 1H, H_a), 5.34 (d, J = 16.9, 1H, H_b), 6.44–6.60 [m, 2H; consisting in signals at 6.50 (ddd, J = 16.9, 10.5 and 10.1, 1H, H_c) and 6.58 (d, J = 15.5, 1H, H_e)], 7.10–7.35 (m, 10H, ArH), 7.73 (dd, J = 15.5 and 10.5, 1H, H_d); δ_C (75.5 MHz): 22.4 (–CH_3), 118.6 (C-5), 118.8 (C-4′), 124.4 (C-2′), 127.9, 128.7, 129.0, 129.1, 129.5, 134.7, 136.2 (C-1′), 137.4, 138.5 (C-3′), 155.5 (C-6), 159.1 (C-2), 161.0 (C-4); *m*/*z* 314 (M^+).

5-(Buta-1′,3′-dienyl)-6-dimethylamino-2,3-diphenylpyrimidin-4(3*H*)-one 7a. Yield 29%; mp 135–137 °C (Found: C, 77.05; H, 6.12; N, 12.29. $C_{22}H_{21}N_3O$ requires: C, 76.94; H, 6.16; N, 12.23%); IR (KBr) ν_{max}: 1649 (C=O), 1517, 1473 and 1391 cm^{-1}; δ_H (300 MHz): 3.14 [s, 6H, $N(CH_3)_2$], 5.01 (d, J = 10.1, with fine splitting, 1H, H_a), 5.22 (d, J = 16.9, with fine splitting, 1H, H_b), 6.41–6.55 [m, 2H; consisting in signals at 6.43 (d, J = 15.5, 1H, H_e) and 6.47 (ddd, J = 16.9, 10.5 and 10.1, 1H, H_c)], 7.11–7.31 (m, 11H, H_d and ArH); δ_C (75.5 MHz): 41.3 [$N(CH_3)_2$], 96.9 (C-5), 115.2 (C-4′), 126.6 (C-2′), 127.7, 128.0, 128.7, 129.1, 129.3, 129.5, 130.5 (C-1′), 135.0, 137.8, 139.0 (C-3′), 153.9 (C-6), 161.1 (C-2), 162.5 (C-4); *m*/*z* 343 (M^+, 17%), 315 (4%), 300 (4%), 271 (2%), 180 (76%), 104 (5%), 77 (98%).

2,3-Diphenyl-5-(3′-methylthiobut-1′-enyl)-6-dimethylaminopyrimidin-4(3*H*)-one 10a. Yield 41%; mp 112–113 °C (Found: C, 70.70; N, 6.39; H, 10.81. $C_{23}H_{25}N_3OS$ requires: C, 70.55; H, 6.43; N, 10.73%); IR (KBr) ν_{max}: 1636 (C=O), 1548, 1517, 1473 and 1390 cm^{-1}; δ_H (300 MHz): 1.42 (d, J = 6.8, 3H, –CH_3), 2.04 (s, 3H, –SCH_3), 3.11 [s, 6H, $N(CH_3)_2$], 3.36–3.47 (m, 1H, H_a), 6.33–6.38 (m, 2H, olefinic), 7.09–7.30 (m, 10H, ArH); δ_C (75.5 MHz): 14.2 (–SCH_3), 20.8 (–CH_3), 41.2 [$N(CH_3)_2$], 45.3 (C-3′), 96.4 (C-5), 122.8 (C-2′), 127.6, 127.9, 128.6, 129.1, 129.2, 129.3, 133.0 (C-1′), 135.0, 137.8, 153.8 (C-6), 160.7 (C-2), 162.7 (C-4); *m*/*z* 391 (2%), 314 (4%), 180 (45%), 77 (98%).

5-(Buta-1′,3-dienyl)-2,3-diphenyl-6-piperidinopyrimidin-4(3*H*)-one 7b. Yield 31%; mp 163–164 °C (Found: C, 78.38; H, 6.55; N, 10.91. $C_{25}H_{25}N_3O$ requires: C, 78.30; H, 6.57; N, 10.95%); IR (KBr) ν_{max}: 1650 (C=O), 1545, 1507, 1486 and 1428 cm^{-1}; δ_H (300 MHz): 1.70 (br, 6H, –CH_2–CH_2–CH_2–), 3.57 (br, 4H, –CH_2–N–CH_2–), 5.03 (d, J = 10.1, 1H, H_a), 5.23 (d, J = 16.9, 1H, H_b), 6.33 (d, J = 15.5, 1H, H_e), 6.49 (ddd, J = 16.9, 10.6 and 10.1, 1H, H_c), 7.12–7.31 (m, 10H, ArH), 7.47 (dd, J = 15.5 and 10.6, 1H, H_d); δ_C (75.5 MHz): 24.7 (–CH_2), 26.4 (2 × –CH_2), 50.2 (–CH_2–N–CH_2–), 98.6 (C-5), 115.5 (C-4′), 126.5 (C-2′), 127.7, 128.1, 128.7, 129.1, 129.3, 129.4, 130.9 (C-1′), 135.1, 137.9, 139.2 (C-3′), 154.2 (C-6), 161.2 (C-2), 162.6 (C-4); *m*/*z* 383 (M^+).

2,3-Diphenyl-5-(3′-methylthiobut-1′-enyl)-6-piperidinopyrimidin-4(3*H*)-one 10b. Yield 26%; mp 101–102 °C (Found: C, 72.42; H, 6.71; N, 9.63. $C_{26}H_{26}N_3OS$ requires: C, 72.35; H, 6.77; N, 9.73%); IR (KBr) ν_{max}: 1649 (C=O), 1545, 1518, 1469 and 1390 cm^{-1}; δ_H (300 MHz): 1.42 (d, J = 6.8, 3H, –CH_3), 1.69 (br, 6H, –CH_2–CH_2–CH_2–), 2.06 (s, 3H, –SCH_3), 3.37–3.48 (m, 1H, H_a), 3.57 (br, 4H, –CH_2N–CH_2–), 6.24 (d, J = 15.7, 1H, H_c), 6.65 (dd, J = 15.7 and 8.5, 1H, H_b), 7.09–7.33 (m, 10H, ArH); *m*/*z* 431 (M^+).

5-(Buta-1′,3′-dienyl)-2,3-diphenyl-6-morpholinopyrimidin-4(3*H*)-one 7c. Yield 30%; mp 133–134 °C (Found: C, 74.74;

H, 6.05; N, 10.85. $C_{24}H_{23}N_3O_2$ requires: C, 74.78; H, 6.01; N, 10.90%); IR (KBr) ν_{max}: 1661 (C=O), 1541, 1504 and 1484 cm^{-1}; δ_H (300 MHz): 3.59–3.62 (m, 4H, $–CH_2–N–CH_2–$), 3.80–3.83 (m, 4H, $–CH_2–O–CH_2–$), 5.07 (d, J = 10.0, 1H, H_a), 5.25 (d, J = 16.9, 1H, H_b), 6.33 (d, J = 15.6, 1H, H_e), 6.48 (ddd, J = 16.9, 10.7 and 10.0, 1H, H_c), 7.12–7.33 (m, 10H, ArH), 7.46 (dd, J = 15.6 and 10.7, 1H, H_d); δ_C (75.5 MHz): 49.4 ($–CH_2–N–CH_2–$), 67.1 ($–CH_2–O–CH_2–$), 99.6 (C-5), 116.5 (C-4′), 125.5 (C-2′), 127.8, 128.3, 128.8, 129.0, 129.3, 129.6, 132.2 (C-1′), 134.8, 137.6, 138.8 (C-3′), 154.2 (C-6), 160.6 (C-2), 162.5 (C-4); m/z 385 (M^+).

2-3-Diphenyl-5-(3′-methylthiobut-1-enyl)-6-morpholino-pyrimidin-4(3*H*)-one 10c. Yield 33%; mp 116–117 °C (Found: C, 69.31; H, 65.24; N, 9.77. $C_{25}H_{27}N_3O_2S$ requires: C, 69.25; H, 6.27; N, 9.69%); IR (KBr) ν_{max}: 1660 (C=O), 1548, 1507 and 1487 cm^{-1}; δ_H (300 MHz): 1.42 (d, J = 6.9, 3H, $–CH_3$), 2.05 (s, 3H, $–CH_3$), 3.34–3.45 (m, 1H, H_a), 3.57–3.60 (m, 4H, $–CH_2–N–CH_2–$), 3.79–3.82 (m, 4H, $–CH_2–O–CH_2–$), 6.26 (d, J = 15.8, 1H, H_c), 6.66 (dd, J = 15.8 and 8.5, 1H, H_b), 7.11–7.33 (m, 10H, ArH); δ_C (75.5 MHz): 14.1 ($–SCH_3$), 20.7 ($–CH_3$), 45.2 (C-3′), 49 2 ($–CH_2–N–CH_2–$), 67.0 ($–CH_2–O–CH_2–$), 99.8 (C-5), 122.0 (C-2′), 127.8, 128.2, 128.8, 129.0, 129.2, 129.6, 134.6 (C-1′), 134.2, 137.7, 154.7 (C-6), 160.4 (C-2), 162.7 (C-4); m/z 433 (M^+).

5-(Buta-1′,3′-dienyl)-2-phenyl-3-(*p*-tolyl)-6-piperidino-pyrimidin-4(3*H*)-one 7d. Yield 36%; mp 156–158 °C (Found: C, 78.64; H, 6.82; N, 10.50. $C_{26}H_{27}N_3O$ requires: C, 78.56; H, 6.84; N, 10.57%); IR (KBr) ν_{max}: 1652 (C=O), 1548, 1507 and 1488 cm^{-1}; δ_H (300 MHz): 1.69 (br, 6H, $–CH_2–CH_2–CH_2–$), 2.29 (s, 3H, $–CH_3$), 3.55 (br, 4H, $–CH_2–N–CH_2–$), 5.02 (d, J = 10.1, with fine splitting, 1H, H_a), 5.22 (d, J = 16.9, with fine splitting, 1H, H_b), 6.32 (d, J = 15.4 with fine splitting, 1H, H_e), 6.47 (ddd, J = 16.9, 10.7 and 10.1, 1H, H_c), 7.00 (d, J = 8.4, with fine splitting, 2H, ArH), 7.08 (d, J = 8.4, with fine splitting, 2H, ArH), 7.14–7.32 (m, 5H, ArH), 7.46 (dd, J = 15.5 and 10.7, with fine splitting, 1H, H_d); δ_C (75.5 MHz): 21.1 ($–CH_3$), 24.7 ($–CH_2$), 26.4 (2 × $–CH_2$), 50.2 ($–CH_2–N–CH_2–$), 98.7 (C-5), 115.4 (C-4′), 126.6 (C-2′), 127.7, 128.8, 129.3, 129.4, 130.8, 132.1 (C-1′), 135.19, 135.22, 138.0, 139.2 (C-3′), 154.3 (C-6), 161.2 (C-2), 162.7 (C-4); m/z 397 (M^+).

5-(3′-Methylthiobut-1′-enyl)-2-phenyl-3-(*p*-tolyl)-6-piperidinopyrimidin-4(3*H*)-one 10d. Yield 28%; mp 101–103 °C (Found: C, 72.69; H, 6.98; N, 9.49. $C_{27}H_{31}N_3OS$ requires: C, 72.77; H, 7.01; N, 9.47%); IR (KBr) ν_{max}: 1653 (C=O), 1548, 1515 and 1481 cm^{-1}; δ_H (300 MHz): 1.41 (d, J = 6.8, 3H, $–CH_3$), 1.70 (m, 6H, $–CH_2–CH_2CH_2–$), 2.27 (s, 3H, $–CH_3$), 3.36–3.47 (m, 1H, H_a), 3.56 (m, 4H, $–CH_2–N–CH_2–$), 6.25 (d, J = 15.8, 1H, H_c), 6.64 (dd, J = 15.8 and 8.5, 1H, H_b), 7.04 (d, J = 8.4, with fine splitting, 2H, ArH), 7.09 (d, J = 8.4, with fine splitting, 2H, ArH), 7.14–7.30 (m, 8H, ArH); m/z 445 (M^+).

5-(1′,3′-Butadienyl)-3-(*p*-tolyl)-6-morpholino-2-phenyl-pyrimidin-4(3*H*)-one 7e. Yield 39%; mp 180–181 °C (Found: C, 75.07; H, 6.35; N, 10.58. $C_{25}H_{25}N_3O_2$ requires: C, 75.16; H, 6.30; N, 10.52%); IR (KBr) ν_{max}: 1652 (C=O), 1550 and 1507 cm^{-1}; δ_C (300 MHz): 2.29 (s, 3H, $–CH_3$), 3.57–3.61 (m, 4H, $–CH_2–N–CH_2–$), 3.78–3.82 (m, 4H, $–CH_2–O–CH_2–$), 5.06 (d, J = 10.0, 1H, H_a), 5.24 (d, J = 16.8, 1H, H_b), 6.31 (d, J = 15.6, 1H, H_e), 6.46 (ddd, J = 16.8, 10.6 and 10.0, 1H, H_c), 7.00 (d, J = 8.4, 2H, ArH), 7.09 (d, J = 8.4, 2H, ArH), 7.17–7.30 (m, 5H, ArH), 7.45 (dd, J = 15.67 and 10.6, 1H, H_d); δ_C (75.5 MHz): 21.1 ($–CH_3$), 49.4 ($–CH_2N–CH_2–$), 66.9 ($–CH_2–O–CH_2–$), 100.1 (C-5), 116.4 (C-4′), 125.4 (C-2′), 127.7, 128.6, 129.2, 129.4, 132.1 (C-1′), 134.9, 138.1, 138.8 (C-3′), 154.7 (C-6), 160.5 (C-2), 162.5 (C-4); m/z 339 (M^+).

5-(3′-Methylthiobut-1′-enyl)-3-(*p*-tolyl)-6-morpholino-pyrimidin-4(3*H*)-one 10e. Yield 32%; mp 130–132 °C (Found: C, 69.87; H, 6.59; N, 9.32. $C_{26}H_{29}N_3O_2S$ requires: C, 69.77; H, 6.53; N, 9.39%); IR (KBr) ν_{max}: 1667 (C=O), 1550, 1512 and 1487 cm^{-1}; δ_H (300 MHz): 1.41 (d, J = 6.8, 3H, $–CH_3$), 2.05 (s, 3H, $–SCH_3$), 2.29 (s, 3H, $–CH_3$), 3.34–3.45 (m, 1H, H_a), 3.56–3.60 (m, 4H, $–CH_2–N–CH_2–$), 3.79–3.82 (m, 4H, $–CH_2–O–CH_2–$), 6.26 (d, J = 15.7, 1H, H_c), 6.66 (dd, J = 15.7 and 8.5, 1H, H_b), 7.00 (d, J = 8.3, 2H, ArH), 7.09 (d, J = 8.3, 2H, ArH), 7.14–7.30 (m, 5H, ArH); δ_C (75.5 MHz): 14.1 ($–SCH_3$), 20.7 ($–CH_3$), 45.1 (C-3′), 49.3 ($–CH_2–N–CH_2–$), 67.0 ($–CH_2–O–CH_2–$), 99.9 (C-5), 122.0 (C-2′), 127.7, 128.6, 129.2, 129.5, 134.5 (C-1′), 135.0, 138.2, 154.8 (C-6), 160.4 (C-2), 162.8 (C-4); m/z 447 (M^+).

5-(Buta-1′3′-dienyl)-2,3-diphenyl-6-(*N*-allyl-*N*-phenylamino)-pyrimidin-4(3*H*)-one 7f. Yield 42% viscous liquid (Found: C, 80.65; H, 5.85; N, 9.79. $C_{29}H_{25}N_3O$ requires: C, 80.71; H, 5.84; N, 9.74%); IR (CCl_4) ν_{max} 1644 (C=O), 1547, 1488, 1439 and 1403 cm^{-1}; δ_H (300 MHz): 4.72 (m, 2H, $–CH_2–$), 4.85 (d, J = 10.0, 1H, H_a), 5.07 (d, J = 16.8, 1H, H_b), 5.14 (dd, J = 10.3, and 1.3, 1H, H_f), 5.23 (dd, J = 17.2 and 1.3, 1H, H_g), 5.85–6.09 (m, 3H, H_c, H_e and H_h), 6.94–7.01 (m, 1H, ArH), 7.10–7.32 (m, 14H, ArH), 7.44 (dd, J = 14.9 and 10.2, 1H, H_d); ^{13}C NMR (75.5 MHz): 54.8 ($–CH_2–$), 102.7 (C-5), 116.1, 116.5, 122.7, 123.5, 125.8, 127.7, 128.2, 128.3, 128.6, 128.8, 128.9, 129.0, 129.1, 129.3, 129.5, 132.5, 134.7, 135.0, 137.6, 138.8, 146.4, 154.6 (C-6), 157.3 (C-2), 162.5 (C-4); m/z: 431 (M^+).

5-(3′-Methylthiobut-1′-enyl)-2,3-diphenyl-6-(*N*-allyl-*N*-phenylamino)pyrimidin-4(3*H*)-one 10f. Yield 21% mp 110–111 °C (Found: C, 75.09; H, 6.08; N, 8.75. $C_{30}H_{29}N_3OS$ requires: C, 75.12; H, 6.09; N, 8.76%); IR (KBr) ν_{max}: 1657 (C=O) cm^{-1}; δ_H (300 MHz): 1.07 (d, J = 6.8, 3H, $–CH_3$), 1.68 (s, 3H, $–SCH_3$), 2.85–2.90 (m, 1H, H_a), 4.72 (dq, J = 16.5 and 5.3, 2H, $–CH_2–$), 5.15 (d, J = 10.3, 1H, H_f), 5.24 (d, J = 17.2, with fine splitting, 1H, H_e), 5.84 (d, J = 15.5, 1H, H_c), 6.06 (dddd, J = 17.2, 10.3, 5.2 and 5.2, 1H, H_d), 6.67 (dd, J = 15.5 and 8.7, 1H, H_b), 6.97–7.01 (m, 1H, ArH), 7.09–7.34 (m, 14H, ArH); ^{13}C NMR (75.5 MHz): 13.8 ($–CH_3$), 20.0 ($–SCH_3$), 45.1 (–CH–), 54.8 ($–CH_2–$), 103.2 (C-5), 116.5, 121.8, 122.6, 123.3, 127.8, 128.3, 128.9, 129.0, 129.2, 129.3, 129.5, 134.8, 135.3, 135.4, 137.7, 146.9, 154.8 (C-6), 157.3 (C-2), 162.7 (C-4); m/z 432 (M^+).

5-(Buta-1′,3′-dienyl)-2,3-diphenyl-6[*N*-allyl-*N*-(*p*-tolyl)-amino]pyrimidin-4(3*H*)-one 7g. Yield 40%; Viscous liquid (Found: C, 80.84; H, 6.08; N, 9.45. $C_{30}H_{27}N_3O$ requires: C, 80.87; H, 6.11; N, 9.43%); IR (CCl_4) ν_{max}: 1654 (C=O), 1548 and 1403 cm^{-1}; δ_H (300 MHz): 2.29 (s, 3H, $–CH_3$), 4.70 (m, 2H, $–CH_2–$), 4.86 (d, J = 9.9 with fine splitting, 1H, H_a), 5.05 (d, J = 16.9, with fine splitting, 1H, H_b), 5.15 (dd, J = 10.3 and 1.4, 1H, H_f), 5.21 (dd, J = 17.2 and 1.4, 1H, H_g), 5.86–6.11 (m, 3H, H_c, H_e and H_h), 7.08 (d, J = 8.7, with fine splitting, 2H, ArH), 7.15–7.37 (m, 10H, ArH), 7.41 (dd, J = 15.3 and 10.3, partially merged with arom, 1H, H_d); ^{13}C NMR (75.5 MHz): 20.8 ($–CH_3$), 55.1 ($–CH_2–$), 101.9 (C-5), 115.9 (C-10), 116.5 (C-13), 123.2, 125.9, 127.7, 128.3, 128.6, 128.8, 129.1, 129.4, 129.5, 129.6, 130.4, 132.1, 133.5, 134.8, 135.2, 137.8, 139.1, 144.0, 154.5 (C-6), 157.7 (C-2), 162.6 (C-4); m/z: 445 (M^+).

5-(3′-Methylthiobut-1′-enyl)-2,3-diphenyl-6-[*N*-allyl-*N*-(*p*-tolyl)amino]pyrimidin-4(3*H*)-one 10g. Yield 26%; mp 135 °C (Found: C, 75.69; H, 6.56; N, 8.27. $C_{33}H_{33}N_3OS$ requires: C, 75.70; H, 6.55; N, 8.28%); IR (KBr) ν_{max}: 1664 (C=O) and 1543 cm^{-1}; δ_H (300 MHz): 1.09 (d, J = 6.7, 3H, $–CH_3$), 1.66 (s, 3H, $–SCH_3$), 2.27 (s, 3H, $–CH_3$), 2.83–2.93 (m, 1H, H_a), 4.58–4.78 (m, 2H,$–CH_2–$), 5.14 (dd, J = 10.3 and 1.5, 1H, H_f), 5.21 (dd, J = 17.2 and 1.5, 1H, H_e), 5.82 (d, J = 15.5 with fine splitting, 1H, H_c), 6.05 (dddd, J = 17.2, 10.3, 5.4 and 5.4, 1H, H_d), 6.61 (dd, J = 15.5 and 8.8, 1H, H_b), 7.01 (d, J = 8.6, 2H, ArH), 7.07

(d, J = 8.6, 2H, ArH), 7.14–7.32 (m, 10H, ArH); ^{13}C NMR (75.5 MHz): 13.6 (–CH_3), 20.1 (–SCH_3), 20.7 (–CH_3), 45.3 (–CH–), 55.1 (–CH_2–), 102.1 (C-5), 116.5, 122.0, 123.2, 127.8, 128.3, 128.8, 129.1, 129.3, 129.5, 129.8, 133.2, 134.9, 135.4, 137.8, 144.5, 154.7 (C-6), 157.5 (C-2), 162.7 (C-4); m/z 447 (M^+).

5-(Buta-1′,3′-dienyl)-3,6-diphenyl-2-piperidinopyrimidin-4(3*H*)-one 13a. Yield 86%; mp 214–215 °C (Found: C, 78.29; H, 6.50; N, 10.95. $C_{25}H_{25}N_3O$ requires: C, 78.33; H, 6.53; N, 10.97%); IR (KBr) ν_{max}: 1664 (C=O) cm^{-1}; δ_H (300 MHz): 1.74–1.77 (m, 6H, –CH_2–CH_2–CH_2–), 3.09–3.11 (m, 4H, –CH_2, –N–CH_2), 4.94 (d, J = 10.6, 1H, Ha), 5.15 (d, J = 16.9, 1H, H_b), 6.27 (ddd, J = 16.9, 10.6 and 6.3, 1H, H_c), 6.39 (d, J = 15.4, 1H, H_e), 7.35–7.68 (m, 11H, ArH and H_d); δ_C (75.5 MHz): 25.4 (–CH_2–CH_2–CH_2–), 50.0 (–CH_2–N–CH_2–), 109.0 (C-5), 115.4 (C-4′), 127.2, 128.0, 128.5, 129.0, 129.4, 129.8, 131.0, 137.6, 139.3, 152.0 (C-6), 161.5 (C-2), 163.1 (C-4); m/z 383 (M^+).

5-(Buta-1′,3′-dienyl)-3-(*p*-tolyl)-6-phenyl-2-piperidinopyrimidin-4(3*H*)-one 13b. Yield 82%; mp 160–162 °C (Found: C, 78.54; H, 6.77; N, 10.53. $C_{26}H_{27}N_3O$ requires: C, 78.59; H, 6.80; N, 10.58%); IR (KBr) ν_{max}: 1662 (C=O) cm^{-1}; δ_H (300 MHz): 1.76–1.79 (m, 6H, –CH_2–CH_2–CH_2–), 2.41 (s, 3H, –CH_3), 3.17–3.19 (m, 4H, –CH_2–N–CH_2–), 4.99 (d, J = 10.3, 1H, H_a), 5.18 (d, J = 16.8, 1H, H_b), 6.28 (ddd, J = 16.9, 10.4, and 6.5, 1H, H_c), 6.40 (d, J = 15.4, 1H, H_e), 7.25 (d, J = 8.1, 2H, ArH), 7.36–7.67 (m, 8H, ArH and H_d); δ_C (75.5 MHz): 20.4 (–CH_3), 25.4 (–CH_2–CH_2–CH_2–), 50.0 (–CH_2–N–CH_2–), 109.0 (C-5), 114.8, 115.6 (C-4′), 126.9, 127.9, 128.3, 128.9, 129.1, 129.6, 130.9, 134.8, 135.1, 138.5, 139.3, 139.4, 151.3, 152.0, 158.8, 161.5 (C-2), 163.2 (C-4); m/z 397 (M^+).

5-(Buta-1′,3′-dienyl)-3-(*p*-tolyl)-6-phenyl-2-pyrrolidinopyrimidin-4(3*H*)-one 13c. Yield 80%; mp 158–160 °C (Found: C, 78.33; H, 6.53; N, 10.97. $C_{25}H_{25}N_3O$ requires: C, 78.29; H, 6.49; N, 10.94%); IR (KBr) ν_{max}: 1664 (C=O) cm^{-1}; δ_H (300 MHz): 1.67–1.71 (m, 4H, –CH_2–CH_2–), 2.28 (s, 3H, –CH_3), 3.17–3.19 (m, 4H, –CH_2–N–CH_2–), 4.99 (d, J = 10.2, 1H, H_a), 5.12 (d, J = 16.9, 1H, H_b), 6.25 (ddd, J = 16.9, 10.2 and 6.3, 1H, H_c), 6.40 (d, J = 15.4, 1H, H_e), 6.53–7.67 (m, 10H, ArH and H_d); δ_C (75.5 MHz): 15.5 (–CH_2–N–CH_2–), 21.2 (–CH_3), 25.4 (–CH_2–CH_2–), 108.8 (C-5), 115.0, 115.3 (C-4′), 127.2, 127.9, 128.2, 128.9, 129.0, 129.6, 130.9, 134.8, 135.0, 138.5, 139.2, 139.3, 151.5, 152.0, 158.9, 161.7 (C-2), 163.4 (C-4); m/z 383 (M^+).

5-(Buta-1′,3′-dienyl)-3,6-diphenyl-2-methylthiopyrimidin-4(3*H*)-one 17a. Yield 33%; mp 162–164 °C (Found: C, 72.80; H, 5.16; N, 8.07. $C_{21}H_{18}N_2OS$ requires: C, 72.83; H, 5.20; N, 8.09%); IR (KBr) ν_{max}: 1665 (C=O) cm^{-1}; δ_H (300 MHz): 2.52 (s, 3H, –SCH_3), 5.06 (d, J = 10.3, 1H, H_a), 5.24 (d, J = 16.9, 1H, H_b), 6.29 (ddd, J = 16.9, 10.4 and 6.4, 1H, H_c), 6.44 (d, J = 15.5, 1H, H_e), 7.16–7.66 (m, 11H, ArH and H_d); δ_C (75.5 MHz): 15.3 (–SCH_3), 115.3 (C-5), 118.0 (C-4), 122.0, 123.4, 124.1, 124.7, 125.8 (C-2), 128.1, 128.5, 128.9, 129.4, 129.5, 129.8, 130.0, 130.4, 135.2, 161.8 (C-4); m/z 346 (M^+).

5-(Buta-1′,3′-dienyl)-3-(*p*-tolyl)-2-methylthio-6-phenylpyrimidin-4(3*H*)-one 17b. Yield 29%; mp 190–192 °C (Found: C, 73.35; H, 5.52; N, 7.76. $C_{22}H_{20}N_2OS$ requires: C, 73.33; H, 5.56; N, 7.78%); IR (KBr) ν_{max}: 1664 (C=O) cm^{-1}; δ_H (300 MHz): 2.21 (s, 3H, –CH_3), 2.53 (s, 3H, –SCH_3), 5.06 (d, J = 10.1, 1H, H_a), 5.24 (d, J = 16.9, 1H, H_b), 6.28 (ddd, J = 16.9, 10.1 and 6.6, 1H, H_c), 6.44 (d, J = 15.5, 1H, H_e), 7.28 (d, J = 8.0, 2H, ArH), 7.47–7.60 (m, 8H, ArH and H_d); δ_C (75.5 MHz): 15.3 (–SCH_3), 21.39 (–CH_3), 115.30 (C-5), 117.93 (C-4′), 125.82 (C-2′), 128.11, 128.17, 129.35, 129.80, 130.48, 133.26, 135.19, 138.27, 138.68 (C-3), 158.81, 159.48 (C-2), 161.95 (C-4); m/z 360 (M^+).

5-(Buta-1′,3′-dienyl)-3-(*p*-chlorophenyl)-2-methylthio-6-phenylpyrimidin-4(3*H*)-one 17c. Yield 25%; mp 209–211 °C (Found: C, 66.18; H, 4.50; N, 7.23. $C_{21}H_{17}N_2OSC$ requires: C, 66.33; H, 4.44; N, 7.86%); IR (KBr) ν_{max}: 1663 (C=O) cm^{-1}; δ_H (200 MHz): 2.49 (s, 3H, –SCH_3), 5.08 (d, J = 10.2, 1H, H_a), 5.25 (d, J = 16.4, 1H, H_b), 6.30 (ddd, J = 16.9, 10.4 and 6.6, 1H, H_c), 6.42 (d, J = 15.5, 1H, H_e), 7.25–7.29 (d, J = 8.1, 2H, ArH), 7.47–7.68 (m, 8H, ArH and H_d); δ_C (50 MHz): 15.4 (–SCH_3), 115.4 (C-5), 118.2 (C-4′), 125.6 (C-2′), 128.2, 129.5, 129.8, 130.0, 133.1, 134.4, 135.4, 136.2, 138.6 (C-3′), 159.8, 160.2 (C-2), 162.6 (C-4); m/z 380 (M^+).

3,6-Diphenyl-2-methylthio-5-[1′-(*N*-phenylamino)but-2′-enyl]-pyrimidin-4(3*H*)-one 19a. Yield 21%; mp 160–162 °C (Found: C, 76.13; H, 5.90; N, 6.75. $C_{27}H_{25}N_2OS$ requires: C, 76.24; H, 5.88; N, 6.59%); IR (KBr) ν_{max}: 1674 (C=O) cm^{-1}; δ_H (300 MHz): 1.70 (dd, J = 6.4 and 1.2, 3H, –CH_3), 2.39 (s, 3H, –SCH_3), 5.09 (d, J = 6.5, 1H, H_c), 5.32 (br, 1H, NH exchangeable with D_2O), 5.70 (dq, J = 15.4 and 6.4, 1H, H_a), 5.97–6.02 (ddd, J = 15.4, 6.5 and 1.2, 1H, H_b), 6.33 (dd, J = 8.5 and 1.0, 2H, ArH), 6.60–6.65 (m, 1H, ArH), 7.00–7.05 (m, 2H, ArH), 7.24–7.34 (m, 2H, ArH), 7.50–7.56 (m, 6H, ArH), 7.62–7.65 (m, 2H, ArH); δ_C (75.5 MHz): 15.3 (–SCH_3), 17.9 (–CH_3), 54.5 (C-3′), 114.2, 117.4, 119.3, 127.5, 128.3, 128.5, 128.6, 128.9, 129.0, 129.5, 129.7, 129.8, 130.0, 130.2, 135.5, 138.0, 146.9 (arom), 159.1 (C-6), 160.5 (C-2), 162.5 (C-4); m/z 425.

3-(*p*-Tolyl)-2-methylthio-6-phenyl-5-[1′-(*N*-phenylamino)but-2′-enyl]pyrimidin-4(3*H*)-one 19b. Yield 26%; mp 194–196 °C (Found: C, 76.62; H, 6.09; N, 6.30. $C_{28}H_{27}N_2OS$ requires: C, 76.54; H, 6.15; N, 6.38%); IR (KBr) ν_{max}: 1676 (C=O) cm^{-1}; δ_H (200 MHz): 1.71 (d, J = 6.1, –CH_3), 2.19 (s, 3H, –CH_3), 2.42 (s, 3H, –SCH_3), 5.05 (d, J = 6.3, 1H, H_c), 5.30 (br, 1H, NH, exchangeable with D_2O), 5.62–5.70 (m, 1H, H_a), 5.95 (dd, J = 15.7 and 6.2, 1H, H_b), 6.25 (d, J = 8.2, 2H, ArH), 6.67 (m, 3H, ArH), 6.92–7.58 (m, 9H, ArH); δ_C (50.0 MHz): 15.4 (–SCH_3), 17.95 (–CH_3), 20.42 (–CH_3), 54.94 (C-1′), 114.46, 119.53, 126.70, 127.50, 128.29, 128.57, 128.97, 129.52, 129.84, 130.07, 130.45, 135.65, 138.12, 144.58 (ArC), 158.02 (C-6), 160.52 (C-2), 163.0 (C-4); m/z 439 (M^+).

3-(*p*-Chlorophenyl)-2-methylthio-6-phenyl-5-[1′-(*N*-phenylamino)but-2′-enyl]pyrimidin-4(3*H*)-one 19c. Yield 21%; mp 213–215 °C (Found: C, 70.51; H, 5.22; N, 6.09. $C_{27}H_{24}N_2OSCl$ requires: C, 70.51; H, 5.22; N, 6.09%); IR (KBr) ν_{max}: 1676 (C=O) cm^{-1}; δ_H (200 MHz): 1.70 (d, J = 6.1, 3H, –CH_3), 2.43 (s, 3H, –SCH_3), 5.06 (d, J = 6.0, 1H, H_c), 5.03 (br, 1H, –NH, exchangeable with D_2O), 5.61–5.73 (m, 1H, H_a), 5.97 (dd, J = 15.8 and 6.3, 1H, H_b), 6.25 (d, J = 8.2, 2H, ArH), 6.84 (d, J = 8.2, 2H, ArH), 7.27–7.64 (m, 10H, ArH); m/z 459 (M^+).

3,6-Diphenyl-2-methylthio-5-[3′-(*N*-phenylamino)but-1′-enyl]-pyrimidin-4(3*H*)-one 20a. Yield 30%; mp 181–183 °C (Found: C, 76.20; H, 5.93; N, 6.81. $C_{27}H_{25}N_2OS$ requires: C, 76.24; H, 5.88; N, 6.59%); IR (KBr) ν_{max}: 1667 (C=O) cm^{-1}; δ_H (300 MHz): 1.29 (d, J = 6.0, 3H, CH_3), 2.45 (s, 3H, –SCH_3), 3.96–4.03 (m, 1H, H_a), 6.43 (d, J = 15.7, 1H, H_c), 6.55 (d, J = 8.0, 2H, ArH), 6.71 (dd, J = 15.7 and 8.7, 1H, H_b), 7.04–7.56 (m, 14H, ArH and NH); δ_C (75.5 MHz): 15.3 (–SCH_3), 22.1 (–CH_3), 51.4 (C-3′), 113.4, 114.8, 117.0, 121.3, 127.9, 128.5, 128.6, 129.0, 129.1, 129.8, 130.0, 136.0, 137.9, 138.4, 147.3, 158.7 (C-6), 159.1 (C-2), 162.1 (C-4); m/z 425 (M^+)

3-(*p*-Tolyl)-2-methylthio-6-phenyl-5-[3′-(*N*-phenylamino)but-1′-enyl]pyrimidin-4(3*H*)-one 20b. Yield 29%; mp 150–152 °C (Found: C, 76.63; H, 6.10; N, 6.35. $C_{28}H_{27}N_2OS$ requires: C, 76.54; H, 6.15; N, 6.38%); IR (KBr) ν_{max}: 1666 (C=O) cm^{-1}; δ_H (200 MHz): 1.30 (d, J = 6.0, –CH_3), 2.41 (s, 3H, –SCH_3), 3.96–4.02 (m, 1H, H_a), 6.35 (d, J = 15.4, 1H, H_c), 6.58 (dd, J = 15.6 and 8.7, 1H, H_b), 6.69–7.53 (m, 14H, ArH); δ_C (50

MHz): 15.42 (–SCH_3), 20.44 (–CH_3), 22.40 (–CH_3), 51.54 (C-3′), 113.85, 115.13 (C-5), 117.42, 121.38, 128.02, 129.16, 129.98, 130.13, 130.32, 134.64, 136.29 (C-1′), 138.01, 138.73, 147.31, 158.52 (C-6), 159.17 (C-2), 162.24 (C-4); *m*/*z* 439 (M^+).

3-(*p*-Chlorophenyl)-2-methylthio-6-phenyl-5-[3′-(*N*-phenylamino)but-1′-enyl]pyrimidin-4(3*H*)-one 20c. Yield 27%; mp 213–215 °C (Found: C, 70.55; H, 5.09; N, 6.13. $C_{27}H_{24}N_2OSCl$ requires: C, 70.51; H, 5.22; N, 6.09%); IR (KBr) ν_{max}: 1676 (C=O) cm^{-1}; δ_H (200 MHz): 1.70 (d, *J* = 6.1, 3H, –CH_3), 2.43 (s, 3H, –SCH_3), 5.05 (d, *J* = 15.7, 1H, H_c), 5.03 (br s, 1H, NH, exchangable with D_2O), 5.61–5.72 (m, 1H, H_a), 5.96 (dd, *J* = 15.7 and 6.2, 1H, H_b), 6.25 (d, *J* = 8.1, 2H, ArH), 6.86 (d, *J* = 8.1, 2H, ArH), 7.25–7.64 (m, 10H, ArH); *m*/*z* 459 (M^+).

General procedure for Diels–Alder adducts 25 and 27

Equimolar amounts of 5-butadienyl pyrimidinones **4**, and DMAD were refluxed in dry toluene for 4–6 h. The solvent was removed under reduced pressure and the crude product thus obtained was purified by recrystallisation from a mixture (1 : 5) of ethyl acetate and hexane.

2,3-Diphenyl-5-[(2′,3′-bis(methoxycarbonyl)cyclohexa-2′,4′-dienyl]-6-methylpyrimidin-4(3*H*)-one 24a. Yield 96%; mp 185–186 °C (Found: C, 61.21; H, 4.81; N, 6.89. $C_{21}H_{20}N_2O_5S$ requires: C, 61.15; H, 4.89; N, 6.79%); IR (KBr) ν_{max}: 1732 (–CO_2CH_3), 1709 (–CO_2CH_3), 1675 (C=O) and 1490 cm^{-1}; δ_H (300 MHz): 2.40 (s, 3H, –SCH_3), 2.95–3.20 [m, 2H, –CH_2; consisting in signals at 3.01 (ddd, *J* = 23.1, 6.8 and 2.9, 1H) and 3.14 (ddd, *J* = 23.1, 7.5 and 2.0, 1H)], 3.72 (s, 3H, –OCH_3), 3.78 (s, 3H, –OCH_3), 4.55–4.62 (m, 1H, H_a), 5.77–5.86 (m, 2H, olefinic), 7.24–7.27 (m, 2H, ArH), 7.50–7.55 (m, 3H, ArH), 7.72 (s, 1H, olefinic); δ_C (75.5 MHz): 15.3 (–SCH_3), 27.3 (–CH_2), 35.8 (C-1′), 52.3 (–OCH_3), 122.7, 123.2, 125.1, 128.4, 129.8, 129.9, 130.1, 132.4, 135.4, 135.8, 150.5 (C-6), 161.4 (C-2), 162.8 (C-4), 167.6 (–CO_2CH_3), 168.0 (–CO_2CH_3); *m*/*z* 412 (M^+).

2,3-Diphenyl-5-[2′,3′-bis(methoxycarbonyl)cyclohexa-2′,4′-dienyl]-6-pyrrolidinopyrimidin-4(3*H*)one 24b. Yield 94%; mp 172–173 °C (Found: C, 70.52; H, 5.69; N, 8.15. $C_{30}H_{29}N_3O_5$ requires: C, 70.44; H, 5.71; N, 8.2%); IR (KBr) ν_{max}: 1728 (–CO_2CH_3), 1704 (–CO_2CH_3), 1642 (C=O), 1558 and 1524 cm^{-1}; δ_H (300 MHz): 1.80–1.87 (m, 2H, –CH_2), 1.98–2.03 (m, 2H, –CH_2), 3.44–3.50 (m, 2H, –NCH_2), 3.61 (s, 3H, –CO_2CH_3), 3.70 (s, 3H, –CO_2CH_3), 3.72–3.78 (m, 2H, –CH_2N), 4.33–4.36 (m, 2H, –CH_2), 6.01 (ddd, *J* = 9.5, 5.9 and 2.3, 1H, H_c), 6.21 (d, *J* = 9.5, 1H, H_b), 7.07–7.10 (m, 1H, ArH), 7.12–7.31 (m, 9H, ArH); δ_C (75.5 MHz): 25.6 (–CH_2–CH_2–), 38.0 (C-4′), 45.8 (C-1′), 50.5 (–CH_2–N–CH_2–), 51.6 (–OCH_3), 51.8 (–OCH_3), 96.7 (C-5), 120.4, 125.7, 127.7, 127.9, 128.6, 129.3, 129.5, 134.0, 135.1, 137.7, 138.4, 154.9 (C-6), 158.2 (C-2), 163.3 (C-4), 167.1 (–CO_2CH_3), 176.2 (–CO_2CH_3); *m*/*z* 511 (M^+).

5-[2′,3′-Bis(methoxycarbonyl)cyclohexa-2′,4′-dienyl]-2-methylthio-3-phenylpyrimidin-4(3*H*)-one 24c. Yield, 93%; mp 173–174 °C (Found: C, 70.95; H, 5.35; N, 6.20. $C_{27}H_{24}N_2O_5$ requires: C, 71.04; H, 5.30; N, 6.14%); IR (KBr) ν_{max}: 1719 (CO_2CH_3), 1662 (C=O) and 1524 cm^{-1}; δ_H (300 MHz): 2.41 (s, 3H, –CH_3), 2.34–2.45 (m, 2H, –CH_2), 3.68 (s, 3H, –CO_2CH_3), 3.76 (s, 3H, –CO_2CH_3), 5.58–5.64 (m, 1H, olefinic), 5.83–5.89 (m, 1H, olefinic), 7.05–7.28 (m, 10H, ArH); δ_C (75.5 MHz): 21.6 (–CH_3), 27.1 (–CH_2), 35.8 (C-1′), 52.1 (–CO_2CH_3), 52.1 (–OCH_3), 96.1 (C-5), 121.3, 122.8, 123.7, 127.9, 128.4, 128.7, 128.9, 129.0, 129.5, 130.6, 134.6, 136.2, 137.4, 156.8 (C-6), 161.0 (C-2), 162.1 (C-4), 167.3 (–CO_2CH_3), 168.1 (–CO_2CH_3); *m*/*z* 456 (M^+), 423, 409, 397 ($M^+ - CO_2CH_3$), 365, 337, 262, 180.

6-Phenyl-5-[2′,3′-bis(methoxycarbonyl)cyclohexa-2′,4′-dienyl]-3-(*p*-methylphenyl)-2-methylthiopyrimidin-4(3*H*)-one 26a. Yield, 69%; mp 225–226 °C (Found: C, 70.83; H, 5.96; N, 7.96; O, 15.23. Required C, 70.85; H, 5.90; N, 8.0; O, 15.24%); IR (KBr) ν_{max}: 1734 (–CO_2CH_3), 1708 (–CO_2CH_3), 1645 (C=O) cm^{-1}; δ_H (300 MHz): 1.74–1.77 (m, 6H, –CH_2–CH_2–CH_2), 2.85–2.88 (m, 2H,–CH_2), 3.10–3.13 (m, 4H, –CH_2–N–CH_2–), 3.64 (s, 3H, –$COOCH_3$), 3.68 (s, 3H, –$COOCH_3$), 4.52–4.56 (m, 1H, H_a), 5.57–5.61 (m, 1H, olefinic), 5.75–5.78 (m, 1H, olefinic), 7.29–7.62 (m, 9H, ArH); δ_C (75.5 MHz): 25.4 (–CH_2–CH_2–CH_2), 26.9 (–CH_2), 45.0 (C-1′), 50.0 (CH_2–N–CH_2–), 52.0 (–OCH_3), 52.1 (–OCH_3), 117.7, 124.0, 124.1, 128.3, 128.5, 129.1, 129.4, 130.4, 130.7, 137.6, 138.4, 140.2 (aromatic), 159.2 (C-6), 161.5 (C-2), 162.2 (C-4), 167.0 (–CO_2Me), 168.9 (–CO_2Me); *m*/*z* 525 (M^+).

3,6-Diphenyl-5-[(2′,3′-bis(methoxycarbonyl)cyclohexa-2′,4′-dienyl]-2-piperidinopyrimidin-4(3*H*)-one 26b. Yield 62%; mp 196–198 °C (Found: C, 66.90; H, 5.63; N, 5.55; S, 6.40; O, 15.91. Required C, 66.93; H, 5.18; N, 5.58; S, 6.37; O, 15.93); IR (KBr) ν_{max}: 1732 (–CO_2CH_3), 1709 (–CO_2CH_3) and 1640 (C=O) cm^{-1}; δ_H (300 MHz): 2.37 (s, 3H, –CH_3), 2.42 (s, 3H, –SCH_3), 2.84–2.87 (m, 2H, –CH_2), 3.63 (s, 3H, –$COOCH_3$), 3.67 (s, 3H, –$COOCH_3$), 4.53–4.55 (m, 1H, H_a), 5.57–5.61 (m, 1H, olefinic), 5.76–5.79 (m, 1H, olefinic), 7.16–7.19 (m, 2H, ArH), 7.25–7.51 (m, 7H, ArH); δ_C (75.5 MHz): 15.3 (–SCH_3), 21.4 (–CH_3), 26.9 (–CH_2), 45.0 (C-l′), 52.0 (–OCH_3), 52.1 (–OCH_3), 117.7, 123.6, 124.1, 128.2, 128.3, 129.0, 129.3, 130.3, 130.6, 133.0, 137.5, 138.4, 140.2 (aromatic), 158.2 (C-6), 160.7 (C-2), 161.4 (C-4), 167.0 (–CO_2CH_3), 168.9 (–CO_2CH_3); *m*/*z* 502 (M^+).

Reactions of butadienyl pyrimidinone 17 with 4-phenyl-1,2,4-triazoline-3,5-dione 27

Equimolar amounts of butadienyl pyrimidinone **17** and 4-phenyl-1,2,4-triazoline-3,5-dione were stirred at 0 °C for about 5 min in dry CH_2Cl_2. The solvent was removed and the crude product thus obtained was purified by recrystallisation from benzene–hexane (4 : 1) mixture.

3-(*p*-Chlorophenyl)-2-methylthio-6-phenyl-5-[7′,9′-dioxo-8′-phenyl-1,6,8-triazabicyclo[4.3.0]non-3-enyl]pyrimidin-4(3*H*)-one 27a. Yield 90%; mp 257–258 °C (Found: C, 67.27; H, 4.67; N, 13.04. $C_{30}H_{25}N_5O_3S$ requires: C, 67.29; H, 4.67; N, 13.08%); IR (KBr) ν_{max}: 1661 (C=O) and 1708 cm^{-1}; δ_H (90 MHz): 2.17 (s, 3H, CH_3), 2.40 (s, 3H, –SCH_3), 4.26 (m, 2H, –CH_2), 5.60–5.62 (m, 1H, H-2′), 5.79–5.85 (m, 1H, olefinic), 6.01–6.08 (m, 1H, olefinic), 7.17–7.50 (m, 2H, ArH), 7.64–7.68 (m, 2H, ArH); *m*/*z* 535.

3-(*p*-Tolyl)-2-methylthio-6-phenyl-5-[7′,9′-dioxo-8′-phenyl-1,6,8-triazabicyclo[4.3.0]non-3′-enyl]pyrimidin-4(3*H*)-one 27b. Yield 93%; mp 258–259 °C (Found: C, 62.64; H, 3.93; N, 12.4. $C_{29}H_{22}N_5O_3SCl$ requires: C, 62.65; H, 3.96; N, 12.6%); IR (KBr) ν_{max}: 1660 (C=O) and 1708 cm^{-1}; δ_H (300 MHz): 2.41 (s, 3H, –SCH_3), 4.25 (m, 2H, –CH_2), 5.60–5.62 (m, 1H, H_a), 5.81–5.84 (m, 1H, olefinic), 6.03–6.07 (m, 1H, olefinic), 7.26–7.66 (m, 14H, ArH); δ_C (75 MHz): 15.4 (SCH_3), 41.5 (CH_2), 52.4 (C-2′), 96.1, 114.5 (C-5), 120.9, 122.4, 125.5, 127.8, 128.4, 128.6, 129.0, 130.0, 130.3, 131.3, 133.7, 136.4, 137.7, 149.8, 150.2 (arom), 161.7, 163.9, 171.7, 174.7; *m*/*z* 555.

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10 The yields of **7b** and **7c** in reactions of **21a** and **21b** with butadienyl ketene are 31% and 30% respectively.