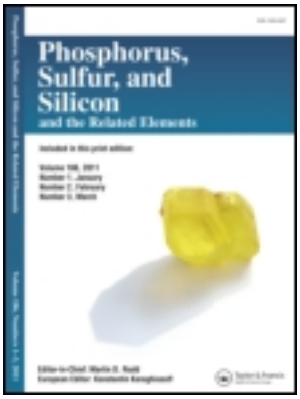

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SYNTHESIS AND FUNGICIDAL ACTIVITIES OF DERIVATIVES OF 2-ALKYLTHIO-3-AMINO-4H-IMIDAZOL-4-ONE

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SYNTHESIS AND FUNGICIDAL ACTIVITIES OF DERIVATIVES OF 2-ALKYLTHIO-3-AMINO-4*H*-IMIDAZOL-4-ONE

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2-Alkylthio-3-phenylamino-5-arylmethylene-4H-imidazol-4-ones ***5*** *were synthesized by S-alkylation of 3-phenylamino-2-thioxo-4-imidazolidinones* ***4****, which were obtained via cyclization of isothiocyanates* ***2*** *with phenylhydrazine in presence of solid potassium carbonate. Compound* ***5*** *exhibited fungicidal activity.*

Keywords: 4*H*-Imidazol-4-one; aza-Wittig reaction; fungicidal activities; synthesis

INTRODUCTION

Many 4*H*-imidazol-4-ones have shown biological and pharmaceutical activities, especially some 2-alkylthioimidazolones.[1–3] Since a new imidazolone (Fenamidone; Figure 1) was found to show high fungicidal activities, many other 2-alkylthio-3-aminoimidazolones were synthesized to evaluate their fungicidal activities.[4–7]

Most of the 2-alkylthio-3-aminoimidazolones reported are 5,5-disubstituted types. They were generally synthesized from corresponding amino acetic acid[6,7] (Scheme 1). Unfortunately, 5-arylmethylene-2-alkylthio-3-aminoimidazolones cannot be prepared by this general method because corresponding starting materials needed are unstable vinyl amino acetic acids. Recently, we became interested in the

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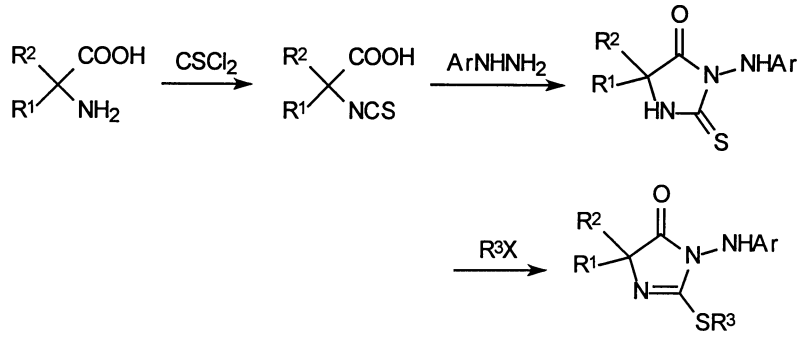


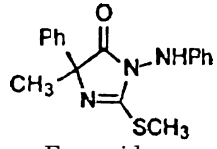
SCHEME 1

synthesis of biologically active imidazolones via a tandem aza-Wittig reaction.[8–10] We wish to report a new efficient synthesis of unreported 5-arylmethylene-2-alkylthio-3-aminoimidazolones **5** from the stable vinyliminophosphorane **1**.

RESULTS AND DISCUSSION

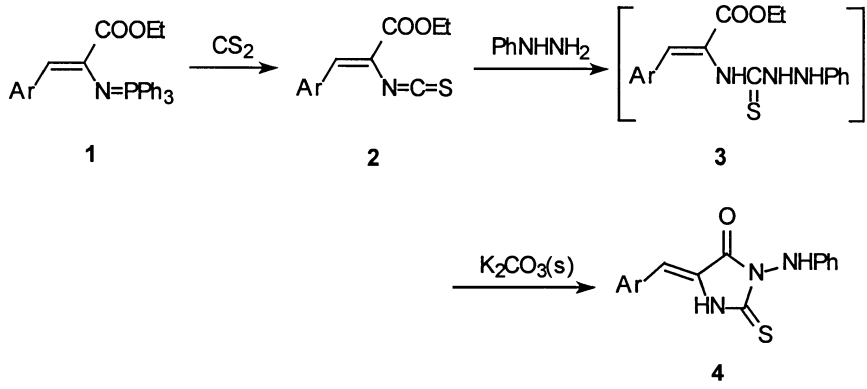
The easily accessible vinyliminophosphorane **1** reacted with carbon disulfide to give vinyl isothiocyanates **2**, which were allowed to react with phenylhydrazine in presence of catalytic solid potassium carbonate to give the 3-phenylamino-2-thioxo-4-imidazolidinones **4** at 40–50°C. The formation of **4** can be rationalized in terms of an initial nucleophilic addition of phenylhydrazine to give the intermediates **3**, which cyclize to give **4**, catalyzed by potassium carbonate (Scheme 2). Since the direct reaction of isothiocyanates **2** with phenylhydrazine often give a mixture of intermediates **3** and imidazolidinones **4**, the presence of catalytic solid potassium carbonate is necessary for the cyclization to occur completely.

S-Alkylation of **4** with alkyl halides in the presence of potassium carbonate provided 2-alkylthio-3-phenylamino-5-arylmethylene-4*H*-imidazol-4-ones **5** in satisfactory yields (Scheme 3). With alkylating

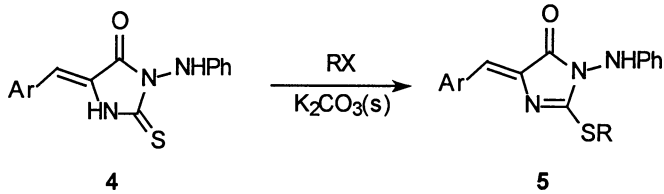


Fenamidone

FIGURE 1



SCHEME 2



SCHEME 3

reagents such as RI and $BrCH_2COR$, the alkylation could be carried out at room temperature; with other reagents the alkylation had to be carried out at 50°C (See Table I).

The structures of **5** have been characterized spectroscopically. For example, the ^1H NMR spectral data in **5a** show the signals for $-SCH_3$ and —NH at δ 2.68 and δ 6.36 as singlets. The signals of alkenyl hydrogen were overlapped with the signals of Ar (δ 8.20–6.76). In the IR spectral data of **5a**, the stretching resonance peak of N—H appears at 3344 cm^{-1}. The strong stretching resonance peak of imidazolone C=O appears at 1725 cm^{-1}. The stretching of C=C shows relatively strong absorbtion at about 1638 cm^{-1} due to resonance effect. The MS spectrum of **5a** shows a molecule ion peak at *m/z* 309 with 20% abundance.

The biological activities of **5** were investigated, and the results showed that they exhibited fungicidal activities, especially against *Botrytis Cinerea Pers*. For example, **5l** showed 91% inhibition of *Botrytis Cinerea Pers* in 50 mg/l (See Table II).

TABLE I Preparation of 2-Thioxo-4-imidazolidinones **4** and 4*H*-Imidazol-4-ones **5**

	Ar	RX	Condition	Yield (%)*
4a	Ph		2 h/40–50°C	76
4b	4-Cl-C_6H_4		3 h/40–50°C	72
5a	Ph	CH_3I	2 h/rt	87
5b	Ph	EtBr	5 h/50°C	65
5c	Ph	*n*-PrBr	3 h/50°C	83
5d	Ph	*n*-BuBr	3 h/50°C	86
5e	Ph	*n*-$C_6H_{13}Br$	3 h/50°C	70
5f	Ph	$PhCH_2Cl$	2 h/50°C	71
5g	Ph	$ClCH_2CN$	2 h/50°C	81
5h	Ph	$PhCOCH_2Br$	2 h/rt	82
5i	Ph	$ClCH_2CONH_2$	2 h/50°C	75
5j	Ph	$ClCH_2COOEt$	2 h/50°C	86
5k	Ph	$BrCH_2COOMe$	2 h/rt	80
5l	Ph	BrCH(Me)COOEt	3 h/50°C	74
5m	4-Cl-C_6H_4	CH_3I	2 h/rt	85
5n	4-Cl-C_6H_4	EtBr	5 h/50°C	68
5o	4-Cl-C_6H_4	*n*-PrBr	3 h/50°C	73
5p	4-Cl-C_6H_4	*n*-BuBr	3 h/50°C	87
5q	4-Cl-C_6H_4	$PhCH_2Cl$	2 h/50°C	77
5r	4-Cl-C_6H_4	$ClCH_2COOEt$	3 h/50°C	83

*Isolated yields of **4** or **5** based on iminophosphosphorane **1** or imidazolidinone **4**, respectively.

EXPERIMENTAL

Melting points were uncorrected. MS were measured on a Finnigan Trace MS spectrometer. IR were recorded on a PE-983 infrared spectrometer as KBr pellets with absorption in cm^{-1}. NMR were recorded in $CDCl_3$ or dimethylsulfoxide (DMSO)-d_6 on a Varian Mercury 400 spectrometer, and resonances are given in ppm (δ) relative to tetramethyl silane (TMS). Elementary analyses were taken on a Vario EL III elementary analysis instrument.

Preparation of 3-Phenylamino-2-thioxo-4-imidazolidinones 4

To a solution of vinyliminophosphorane **1**[10] (5 mmol) in dry methylene chloride (15 ml) was added excess carbon disufide (5 ml). After the reaction mixture was refluxed for 28 h, the solvent was removed under reduced pressure, and ether/petroleum ether (1:2, 20 ml) was added to precipitate triphenylphosphine sulfide, which was removed by filtration. The filtrate was evaporated to give isothiocyanate **2**, which was

TABLE II Fungicidal Activities of 4*H*-imidazol-4-ones **5** (50 mg/l, Relative Inhibition of Growth %)

Compound	*Fusarium oxysporum*	*Pyricularia oryzae*	*Botrytis Cinerea Pers.*	*Gibberella zeae*	*Cercospora beticola Sacc.*
5a	37	53	47	14	39
5b	34	47	61	22	44
5c	43	55	73	43	51
5d	40	60	45	49	41
5e	29	38	55	0	54
5f	26	43	64	22	34
5g	43	53	66	32	41
5h	40	45	64	27	49
5i	54	64	77	43	56
5j	57	68	84	38	78
5k	29	43	64	30	51
5l	54	77	91	49	61
5m	34	47	55	38	54
5n	19	38	52	43	32
5o	23	31	45	31	26
5p	46	53	77	41	46
5q	31	47	84	43	52
5r	35	50	84	40	39
Carbendazim	100	81	85	100	11

used directly without further purification. To a solution of the crude **2** in CH_3CN (15 ml) was added phenylhydrazine (0.54 g, 5 mmol) and solid potassium carbonate (0.05 g). The mixture was stirred for 2–3 h at 40–50°C and was filtered. The filtrate was condensed, and the residual was recrystallized from methylene chloride/petroleum ether to give 3-phenylamino-2-thioxo-4-imidazolidinones **4**.

3-Phenylamino-5-phenylmethylene-2-thioxo-4-imidazolidinone (4a)

Yellow crystals, m.p. 195–196°C. ^{1}H NMR ($CDCl_3$, 400 MHz); δ 8.87 (s, 1H, NH), 7.50–6.86 (m, 11H, Ar—H and =CH), 6.54 (s, 1H, NHPh). IR (cm^{-1}); 3330 and 3209 (NH), 1734 (C=O), 1653, 1466, 1266. MS (m/z, %): 295 (M^+, 100), 262 (7), 234 (11), 160 (54), 77 (88). Elemental Anal. Calcd. for $C_{16}H_{13}N_3OS$: C, 65.06; H, 4.44; N, 14.23. Found: C, 65.12; H, 4.35; N, 14.27.

3-Phenylamino-5-(4-chlorophenylmethylene)-2-thioxo-4-imidazolidinone (4b)

Yellow crystals, m.p. 231–232°C. ^{1}H NMR ($CDCl_3$, 400 MHz); δ 8.84 (s, 1H, NH), 7.49–6.84 (m, 10H, Ar—H and =CH), 6.51 (s, 1H, NHPh). IR (cm^{-1}); 3294 and 3212 (NH), 1722 (C=O), 1651, 1460, 1263. MS (m/z,

%): 331 (35), 329 (M^+, 100), 238 (7), 194 (25), 151 (59), 93 (82). Elemental Anal. Calcd. for $C_{16}H_{12}ClN_3OS$: C, 58.27; H, 3.67; N, 12.74. Found: C, 58.16; H, 3.69; N, 12.81.

Preparation of 2-Alkylthio-3-phenylamino-5-arylmethylene-4*H*-imidazol-4-ones 5

A mixture of **4** (4 mmol), alkyl halide (5 mmol), and solid potassium carbonate (1.11 g, 8 mmol) in CH_3CN (30 ml) was stirred for 2–5 h at room temperature or 50°C and was filtered. The filtrate was condensed, and the residue was recrystallized from methylene chloride/petroleum ether to give 2-alkylthio-3-phenylamino-5-arylmethylene-4*H*-imidazol-4-ones **5**.

*2-Methylthio-3-phenylamino-5-phenylmethylene-4*H*-imidazol-4-one (5a)*

Yellow crystals, m.p. 180–181°C. ^{1}H NMR ($CDCl_3$, 400 MHz); δ 8.20–6.76 (m, 11H, Ar—H and =CH), 6.36 (s, 1H, NH), 2.68 (s, 3H, SCH_3). IR (cm^{-1}); 3344 (NH), 1725 (C=O), 1638, 1499, 1240, 1140. MS (*m*/*z*, %): 309 (M^+, 20), 234 (7), 165 (11), 116 (66), 92 (100). Elemental Anal. Calcd. for $C_{17}H_{15}N_3OS$: C, 66.00; H, 4.89; N, 13.58. Found: C, 66.16; H, 4.81; N, 13.63.

*2-Ethylthio-3-phenylamino-5-phenylmethylene-4*H*-imidazol-4-one (5b)*

Light yellow crystals, m.p. 169–170°C, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.13–6.71 (m, 11H, Ar—H and =CH), 6.18 (s, 1H, NH), 3.25 (q, 2H, $J = 7.2$ Hz, SCH_2), 1.44 (t, 3H, $J = 7.2$ Hz, CH_3). IR (cm^{-1}): 3282 (NH), 1719 (C=O), 1638, 1497, 1244, 1142. MS (*m*/*z*, %): 323 (M^+, 89), 295 (19), 262 (23), 234 (42), 179 (61), 92 (100). Elemental Anal. Calcd. for $C_{18}H_{17}N_3OS$: C, 66.85; H, 5.30; N, 12.99. Found: C, 66.91; H, 5.48; N, 12.92.

*2-(*n*-Propylthio)-3-phenylamino-5-phenylmethylene-4*H*-imidazol-4-one (5c)*

Light yellow crystals, m.p. 150–151°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.12–6.69 (m, 11H, Ar—H and =CH), 6.24 (s, 1H, NH), 3.21 (*t*, 2H, $J = 7.2$ Hz, SCH_2), 1.84–1.78 (m, 2H, CH_2), 1.03 (t, 3H, $J = 7.2$ Hz, CH_3). IR (cm^{-1}): 3284 (NH), 1711 (C=O), 1628, 1492, 1253, 1138. MS (*m*/*z*, %): 337 (M^+, 58), 295 (52), 262 (36), 234 (41), 193 (49), 92 (100). Elemental Anal. Calcd. for $C_{19}H_{19}N_3OS$: C, 67.63; H, 5.68; N, 12.45. Found: C, 67.71; H, 5.69; N, 12.31.

*2-(*n*-Butylthio)-3-phenylamino-5-phenylmethylene-4*H-*imidazol-4-one (5d)*

Light yellow crystals, m.p. 126–128°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.20–6.76 (m, 11H, Ar—H and =CH), 6.29 (s, 1H, NH), 3.30 (t, 2H, $J = 7.2$ Hz, SCH_2), 1.86–1.49 (m, 4H, CH_2CH_2), 1.00 (t, 3H, $J = 7.2$ Hz, CH_3). IR (cm^{-1}), 3278 (NH), 1711 (C=O), 1637, 1497, 1252, 1141. MS (m/z, %): 351 (M^+, 29), 295 (17), 234 (6), 151 (19), 92 (100). Elemental Anal. Calcd. for $C_{20}H_{21}N_3OS$: C, 68.35; H, 6.02; N, 11.96. Found: C, 68.28; H, 6.14; N, 12.05.

*2-(*n*-Hexylthio)-3-phenylamino-5-phenylmethylene-4*H-*imidazol-4-one (5e)*

Light yellow crystals, m.p. 106–107°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.20–6.76 (m, 11H, Ar—H and =CH), 6.31 (s, 1H, NH), 3.28 (*t*, 2H, $J = 7.2$ Hz, SCH_2), 1.87–1.35 (m, 8H, $(CH_2)_4$), 0.91 (t, 3H, $J = 7.2$ Hz, CH_3). IR (cm^{-1}): 3325 (NH), 1733 (C=O), 1637, 1493, 1245, 1143. MS (m/z, %): 379 (M^+, 37), 295 (41), 234 (8), 151 (24), 92 (100). Elemental Anal. Calcd. for $C_{22}H_{25}N_3OS$: C, 69.62; H, 6.64; N, 11.07. Found: C, 69.48; H, 6.67; N, 11.14.

*2-Phenylmethylthio-3-phenylamino-5-phenylmethylene-4*H-*imidazol-4-one (5f)*

Light yellow crystals, m.p. 200–201°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.22–6.74 (m, 16H, Ar—H and =CH), 6.27 (s, 1H, NH), 4.54 (s, 2H, SCH_2). IR (cm^{-1}): 3332 (NH), 1720 (C=O), 1638, 1494, 1252, 1141. MS (m/z, %): 385 (M^+, 29), 295 (9), 236 (58), 116 (30), 91 (100). Elemental Anal. Calcd. for $C_{23}H_{19}N_3OS$: C, 71.66; H, 4.97; N, 10.90. Found: C, 71.73; H, 4.88; N, 10.95.

*2-Cyanomethylthio-3-phenylamino-5-phenylmethylene-4*H-*imidazol-4-one (5g)*

Light yellow crystals, m.p. 218–220°C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.04 (s, 1H, NH), 8.33–6.70 (m, 11H, Ar—H and =CH), 4.41 (s, 2H, SCH_2). IR (cm^{-1}): 3272 (NH), 2246 (CN), 1718 (C=O), 1637, 1499, 1258, 1139. MS (m/z, %): 334 (M^+, 45), 295 (4), 236 (13), 116 (60), 92 (100). Elemental Anal. Calcd. for $C_{18}H_{14}N_4OS$: C, 64.65; H, 4.22; N, 16.75. Found: C, 64.77; H, 4.39; N, 16.92.

*2-Benzoylmethylthio-3-phenylamino-5-phenylmethylene-4*H-*imidazol-4-one (5h)*

Light yellow crystals, m.p. 201–202°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.14–6.82 (m, 16H, Ar—H and =CH), 6.26 (s, 1H, NH), 4.77 (s, 2H, SCH_2). IR (cm^{-1}): 3312 (NH), 1722 and 1688 (C=O), 1637, 1492, 1256,

1143; MS (*m/z*, %), 413 (M^+, 4), 381 (13), 296 (4), 116 (17), 105 (100). Elemental Anal. Calcd. for $C_{24}H_{19}N_3O_2S$: C, 69.71; H, 4.63; N, 10.16. Found: C, 69.75; H, 4.51; N, 10.15.

2-Aminocarbonylmethylthio-3-phenylamino-5-phenylmethylene-4 H-*imidazol-4-one (5i)*

Light yellow crystals, m.p. 182–184°C, ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.94 (s, 1H, NHPh), 7.81 and 7.32 (s, 2H, NH_2), 8.28–6.69 (m, 11H, Ar—H and =CH), 4.02 (s, 2H, SCH_2); IR (cm^{-1}), 3433 and 3327 (NH and NH_2), 1738 and 1661 (C=O), 1639, 1493, 1260, 1143. MS (*m/z*, %), 352 (M^+, 7), 295 (48), 207 (12), 116 (78), 92 (100). Elemental Anal. Calcd. for $C_{18}H_{16}N_4O_2S$: C, 61.35; H, 4.58; N, 15.90. Found: C, 61.31; H, 4.64; N, 15.74.

2-Ethoxycarbonylmethylthio-3-phenylamino-5-phenylmethylene-4 H-*imidazol-4-one (5j)*

Light yellow crystals, m.p. 159–160°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.15–6.80 (m, 11H, Ar—H and =CH), 6.28 (s, 1H, NH), 4.27 (q, 2H, $J = 7.2$ Hz, OCH_2), 4.06 (s, 2H, SCH_2), 1.32 (t, 3H, $J = 7.2$ Hz, CH_3). IR (cm^{-1}): 3270 (NH), 1737 and 1724 (C=O), 1633, 1502, 1258, 1140. MS (*m/z*, %): 381 (M^+, 93), 353 (12), 336 (15), 295 (24), 262 (54), 191 (76), 92 (100). Elemental Anal. Calcd. for $C_{20}H_{19}N_3O_3S$: C, 62.98; H, 5.02; N, 11.02. Found: C, 62.84; H, 5.24; N, 10.06.

2-Methoxycarbonylmethylthio-3-phenylamino-5-phenylmethylene-4 H-*imidazol-4-one (5k)*

Light yellow crystals, m.p. 136–138°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.15–6.79 (m, 11H, Ar—H and =CH), 6.32 (s, 1H, NH), 4.05 (s, 2H, SCH_2), 3.82 (s, 3H, OCH_3). IR (cm^{-1}): 3283 (NH), 1744 and 1721 (C=O), 1634, 1504, 1258, 1141. MS (*m/z*, %): 367 (M^+, 7), 331 (100), 116 (81), 92 (84). Elemental Anal. Calcd. for $C_{19}H_{17}N_3O_3S$: C, 62.11; H, 4.66; N, 11.44. Found: C, 62.10; H, 4.85; N, 11.37.

2-(1-Ethoxycarbonylethylthio)-3-phenylamino-5-phenylmethylene-4 H-*imidazol-4-one (5l)*

Light yellow crystals, m.p. 139–140°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.16–6.78 (m, 11H, Ar—H and =CH), 6.29 (s, 1H, NH), 4.62 (q, 1H, $J = 7.6$ Hz, SCH), 4.29–4.19 (m, 2H, OCH_2), 1.73 (d, 3H, $J = 7.6$ Hz, CH_3), 1.29 (t, 3H, $J = 7.2$ Hz, $COOCH_2C\underline{H}_3$). IR (cm^{-1}): 3279 (NH), 1728 and 1711 (C=O), 1635, 1495, 1254, 1139. MS (*m/z*, %): 395 (M^+, 53), 350 (12), 295 (45), 262 (25), 151 (46), 92 (100). Elemental Anal.

Calcd. for $C_{21}H_{21}N_3O_3S$: C, 63.78; H, 5.35; N, 10.62. Found: C, 63.65; H, 5.29; N, 10.74.

2-Methylthio-3-phenylamino-5-(4-chlorophenylmethylene)-4 H-*imidazol-4-one (5m)*

Yellow crystals, m.p. 187–189°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.13–6.76 (m, 10H, Ar—H and =CH), 6.33 (s, 1H, NH), 2.67 (s, 3H, SCH_3). IR (cm^{-1}): 3359 (NH), 1714 (C=O), 1626, 1488, 1248, 1139. MS (*m*/*z*, %): 345 (30), 343 (M^+, 99), 296 (31), 268 (34), 150 (51), 92 (100). Elemental Anal. Calcd. for $C_{17}H_{14}ClN_3OS$: C, 59.39; H, 4.10; N, 12.22. Found: C, 59.33; H, 4.23; N, 12.14.

2-Ethylthio-3-phenylamino-5-(4-chlorophenylmethylene)-4 H-*imidazol-4-one (5n)*

Light yellow crystals, m.p. 189–191°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.12–6.75 (m, 10H, Ar—H and =CH), 6.33 (s, 1H, NH), 3.29 (q, 2H, $J = 7.2$ Hz, SCH_2), 1.50 (*t*, 3H, $J = 7.2$ Hz, CH_3). IR (cm^{-1}): 3330 (NH), 1713 (C=O), 1635, 1486, 1250, 1144. MS (*m*/*z*, %): 359 (3), 357 (M^+, 10), 150 (82), 92 (100). Elemental Anal. Calcd. for $C_{18}H_{16}ClN_3OS$: C, 60.41; H, 4.51; N, 11.74. Found: C, 60.56; H, 4.54; N, 11.64.

*2-(*n-*Propylthio)-3-phenylamino-5-(4-chlorophenylmethylene)-4* H-*imidazol-4-one (5o)*

Light yellow crystals, m.p. 171–173°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.14–6.77 (m, 10H, Ar—H and =CH), 6.24 (s, 1H, NH), 3.28 (*t*, 2H, $J = 7.2$ Hz, SCH_2), 1.92–1.86 (m, 2H, CH_2), 1.10 (t, 3H, $J = 7.2$ Hz, CH_3). IR (cm^{-1}): 3282 (NH), 1715 (C=O), 1634, 1493, 1251, 1143. MS (*m*/*z*, %): 373 (10), 371 (M^+, 28), 329 (16), 151 (30), 92 (100). Elemental Anal. Calcd. for $C_{19}H_{18}ClN_3OS$: C, 61.37; H, 4.88; N, 11.30. Found: C, 61.43; H, 4.72; N, 11.33.

*2-(*n-*Butylthio)-3-phenylamino-5-(4-chlorophenylmethylene)-4* H-*imidazol-4-one (5p)*

Light yellow crystals, m.p. 170–172°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.14–6.77 (m, 10H, Ar—H and =CH), 6.23 (s, 1H, NH), 3.29 (*t*, 2H, $J = 7.2$ Hz, SCH_2), 1.86–1.50 (m, 4H, CH_2CH_2), 1.01 (t, 3H, $J = 7.2$ Hz, CH_3). IR (cm^{-1}): 3286 (NH), 1716 (C=O), 1637, 1494, 1252, 1144. MS (*m*/*z*, %): 387 (18), 385 (M^+, 46), 329 (25), 268 (8), 151 (46), 92 (100). Elemental Anal. Calcd. for $C_{20}H_{20}ClN_3OS$: C, 62.25; H, 5.22; N, 10.89. Found: C, 62.31; H, 5.28; N, 10.75.

2-Phenylmethylthio-3-phenylamino-5-(4-chlorophenylmethylene)-4 H-*imidazol-4-one (5q)*

Light yellow crystals, m.p. 208–210°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.15–6.76 (m, 15H, Ar—H and =CH), 6.22 (s, 1H, NH), 4.53 (s, 2H, SCH_2). IR (cm^{-1}): 3283 (NH), 1722 (C=O), 1632, 1492, 1258, 1139. MS (m/z, %): 421 (3), 419 (M^+, 8), 270 (18), 150 (13), 91 (100). Elemental Anal. Calcd. for $C_{23}H_{18}ClN_3OS$: C, 65.79; H, 4.32; N, 10.01. Found: C, 65.75; H, 4.24; N, 10.18.

2-Ethoxycarbonylmethylthio-3-phenylamino-5-(4-chlorophenylmethylene)-4 H-*imidazol-4-one (5r)*

Light yellow crystals, m.p. 168–169°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09–6.80 (m, 10H, Ar—H and =CH), 6.29 (s, 1H, NH), 4.26 (q, 2H, $J = 7.2$ Hz, OCH_2), 4.04 (s, 2H, SCH_2), 1.31 (t, 3H, $J = 7.2$ Hz, CH_3). IR (cm^{-1}): 3342 (NH), 1743 and 1717 (C=O), 1636, 1499, 1257, 1140. MS (m/z, %): 417 (14), 415 (M^+, 38), 267 (8), 191 (12), 150 (34), 92 (100). Elemental Anal. Calcd. for $C_{20}H_{18}ClN_3O_3S$: C, 57.76; H, 4.36; N, 10.10. Found: C, 57.88; H, 4.42; N, 10.03.

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