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## IMINOPHOSPHORANES IN HETEROCYCLIC SYNTHESIS: SYNTHESIS OF PYRAZOLO[1,5-*a*]PYRIMIDINES, IMIDAZO[1,2-*b*]- PYRAZOLE AND PYRAZOLO[1,5-*b*][1,2,4]TRIAZINE DERIVATIVES VIA INTERMOLECULAR AZA-WITTIG REACTIONS

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**Abstract** – Series of pyrazolo[1,5-*a*]pyrimidine derivatives, imidazo[1,2-*b*]-pyrazole derivative and pyrazolo[1,5-*b*][1,2,4]triazine derivatives were obtained by the initial reaction of 5-(triphenylphosphoranylideneamino)-1*H*-pyrazole derivative with carbonyl compounds and hydrazonyl halides. The newly synthesized compounds were confirmed by spectral and analytical data.

### INTRODUCTION

The aza-Wittig reaction is a powerful tool for the synthesis of five to seven membered nitrogen heterocycles.<sup>1-8</sup> Annulation of ring systems with heterocycles by means of an aza-Wittig reaction has recently been widely utilized because of the availability of functionalized iminophosphoranes.<sup>9-12</sup> Many important fused nitrogen heterocycles such as pyrazole, indole, pyridine, pyrimidine and isoquinoline derivatives have been synthesized via the intermolecular aza-Wittig reaction,<sup>1-4,13-15</sup> as well as by the intermolecular aza-Wittig reaction followed by electrocyclization, intramolecular cycloaddition or heterocyclization.<sup>5-8</sup>

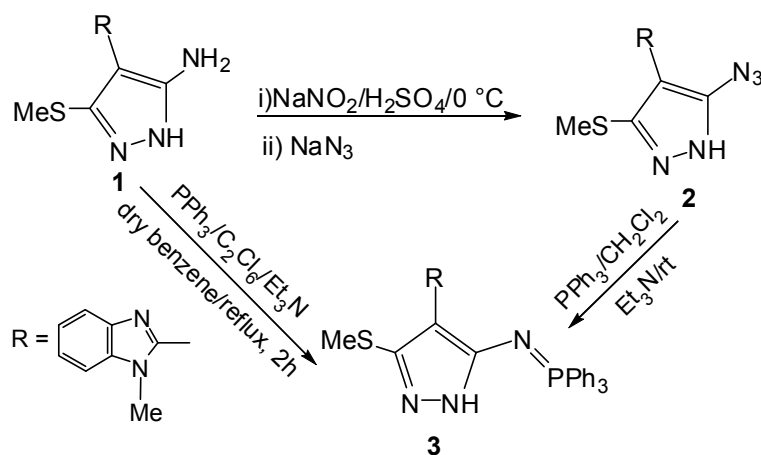
Pyrazole derivatives as an active branch of heterocyclic compounds has attracted wide attention. Besides, pyrimidine moiety has been widely employed in the design of biologically active agents, and compounds containing a fused pyrimidine possessing structural similarities with purines exhibit versatile bioactivities and have been widely used as potential pharmaceuticals such as selective and orally bioavailable mGluR1 antagonists,<sup>16</sup> selective inhibitors of PDE5,<sup>17,18</sup> antiviral,<sup>19,20</sup> antimicrobial,<sup>21,22</sup> anticancer,<sup>23</sup> anti-inflammatory,<sup>24</sup> and xanthine oxidase inhibitors.<sup>25</sup>

In addition, benzimidazole has been an important pharmacophore and privileged structure in medicinal chemistry<sup>26</sup> encompassing a diverse range of biological activities including antiarrhythmic, antiulcer, antihistamine, antifungal, antiviral and cytotoxicity.<sup>27</sup> Also, 1,2,4-triazine derivatives are well known to

possess biological activities, thus they have found use as herbicides.<sup>28,29</sup> In the last decade they have been screened *in vitro* supporting their anti-HIV and anticancer activities.<sup>30-33</sup> We have previously published the synthesis of fused pyrimidines based on the tandem aza-Wittig annulation strategy<sup>34</sup> and as a part of our ongoing studies we now describe a novel one-pot synthesis of new pyrazolo[1,5-*a*]pyrimidine, imidazo[1,2-*b*]pyrazole and pyrazolo[1,5-*b*][1,2,4]triazine derivatives. In connection with our previous studies<sup>35-37</sup> on polyfunctionally heteroaromatic compounds, we reported here pyrazolopyrimidine, imidazopyrazole and pyrazolotriazine with benzimidazole moiety in single molecular framework that are expected to have enhanced biological activities which is the goal of our study.

## RESULTS AND DISCUSSION

The iminophosphorane **3** was synthesized according to the Staudinger reaction<sup>38</sup> of 5-azidopyrazole derivative **2** with triphenylphosphine in dry methylene chloride at room temperature. Also, the iminophosphorane **3** was synthesized by the reaction of 5-aminopyrazole derivative **1** with triphenylphosphine/hexachloroethane and triethylamine reagent system according to Appel's procedure<sup>39</sup> (Scheme 1).



**Scheme 1**

The reaction of iminophosphorane **3** with ethyl 3-oxo-3-phenylpropanoate in dry toluene at reflux temperature yield the corresponding pyrazolopyrimidine derivative **4**. The formation of **4** proceed via an initial aza-Wittig reaction between the iminophosphorane **3** with ethyl 3-oxo-3-phenylpropanoate to give the intermediate, which readily undergoes heterocyclization with loss of ethanol rather than elimination of water. The structure of the product was assigned as 5-phenylpyrazolo[1,5-*a*]pyrimidin-7(6*H*)-one **4** based on the elemental analysis and spectral data which in agreement with this structure. Its IR spectrum showed absorption band in the region  $1693\text{ cm}^{-1}$  assignable to carbonyl function and its  $^1\text{H}$  NMR spectrum revealed the presence of three singlet signals at  $\delta$  3.86 ppm,  $\delta$  2.66 ppm and  $\delta$  2.45 ppm

assignable to the N-Me, CH<sub>3</sub>S and CH<sub>2</sub> protons, respectively. The mass spectrum of **4** showed the molecular ion at  $m/z$  387 (M<sup>+</sup>). Furthermore, the <sup>13</sup>C NMR spectrum also revealed signals at 188.8 ppm and 33.6 ppm due to carbonyl carbon and methylene carbon, respectively.

Similarly, **3** reacted with ethyl 3-oxobutanoate to give pyrazolo[1,5-*a*]pyrimidine **5** via intermediate which readily undergoes heterocyclization with loss of ethanol rather than elimination of water. The structure of the product was assigned as 5-methylpyrazolo[1,5-*a*]pyrimidin-7(6*H*)-one **7** based on the elemental analysis and spectral data which in agreement with this structure.

Reaction of compound **3** with 3-chloropentane-2,4-dione gave the corresponding pyrazolo[1,5-*a*]pyrimidine **6**. The formation of **6** proceed via an initial aza-Wittig reaction between the iminophosphorane **3** with 3-chloropentane-2,4-dione to give the intermediate, which readily undergoes heterocyclization with loss of water rather than elimination of hydrogen chloride. The structure of the product was assigned as 5,7-dimethylpyrazolo[1,5-*a*]pyrimidine **6** based on the elemental analysis and spectral data. Its <sup>1</sup>H NMR spectrum revealed the presence of singlet signal at  $\delta$  2.23 ppm assignable to the 2Me protons attached to pyrimidine ring. The mass spectrum of **6** showed the molecular ion at  $m/z$  359 (M<sup>+</sup>+2) and at 357 (M<sup>+</sup>).

Similarly, compound **3** reacted with ethyl 2-chloro-3-oxobutanoate to give 5-methylpyrazolo[1,5-*a*]pyrimidin-7(6*H*)-one **7** via intermediate, which readily undergoes heterocyclization with loss of ethanol rather than elimination of hydrogen chloride. The structure product **7** was assigned based on the elemental analysis and spectral data which in agreement with this structure. Its IR spectrum showed absorption band in the region 1689 cm<sup>-1</sup> assignable to carbonyl function and Its <sup>1</sup>H NMR spectrum revealed the presence of singlet signal at  $\delta$  3.81 ppm assignable to the C-6 proton. The mass spectrum of **7** showed the molecular ion at  $m/z$  361 (M<sup>+</sup>+2) and 359 (M<sup>+</sup>). Furthermore, the <sup>13</sup>C NMR spectrum also revealed a signal at 186.3 ppm and 46.2 ppm due to carbonyl carbon and sp<sup>3</sup> C-6 bearing the chlorine atom, respectively (Scheme 2).

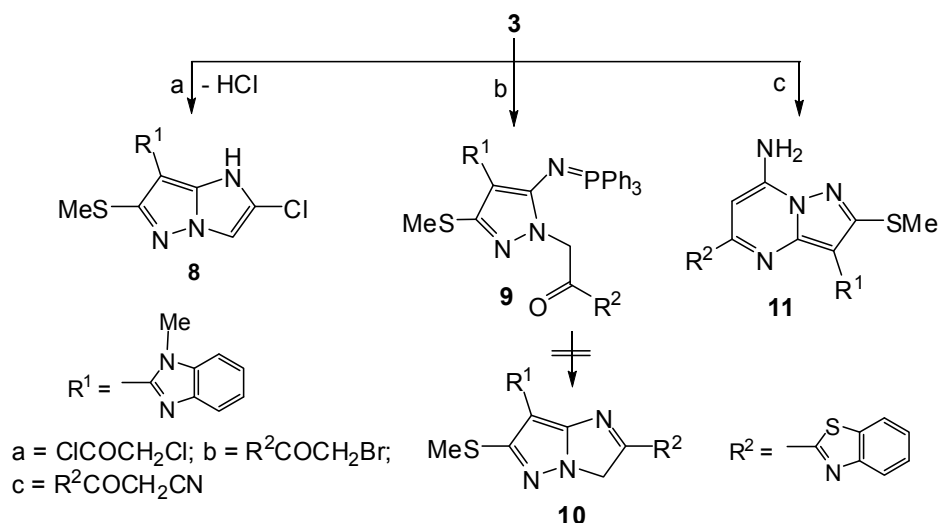


Scheme 2

Reaction of compound **3** with 2-chloroacetyl chloride gave the corresponding imidazo[1,2-*b*]pyrazole derivative **8**. The formation of **8** proceed via an initial aza-Wittig reaction between compound **3** with 2-chloroacetyl chloride to give the intermediate, which readily undergoes heterocyclization via elimination of hydrogen chloride. The structure product was assigned as 1*H*-imidazo[1,2-*b*]pyrazole **8** based on the elemental analysis and spectral data which in agreement with this structure. Its <sup>1</sup>H NMR spectrum revealed the presence of singlet signal at δ 11.2 ppm assignable to the NH proton and disappearance of CH<sub>2</sub>, so that we ruled out the tautomer 3*H*-imidazo[1,2-*b*]pyrazole.<sup>40</sup> The mass spectrum of **8** showed the molecular ion at *m/z* 319 (M<sup>++</sup>) and 317 (M<sup>+</sup>).

In contrast, it was expected that the reaction of compound **3** with 1-(benzothiazol-2-yl)-2-bromoethanone would afforded the imidazo[1,2-*b*]pyrazole derivative **10**. However, based on the spectral data this assumption had to be ruled out. The IR spectrum showed absorption band in the region 1712 cm<sup>-1</sup> assignable to acyclic carbonyl function. Its <sup>1</sup>H NMR spectrum revealed the presence of singlet signal at δ 4.74 ppm assignable to the methylene protons, in addition to multiplets signals at δ 7.21-8.14 ppm due to aryl protons. Its mass spectrum showed *m/z* at 694 (M<sup>+</sup>). Thus, structure **9** was suggested as the reaction product, which seemed thermodynamically stable. All attempts to cyclize **9** failed and it recovered without change, this may be due to the steric hindrance.

Also, the pyrazolo[1,5-*a*]pyrimidine derivative **11** was obtained through the reaction of compound **3** reacted with 3-(benzothiazol-2-yl)-3-oxopropanenitrile. The structure product was assigned as 7-amino-pyrazolo[1,5-*a*]pyrimidine **11** based on the elemental analysis and spectral data which in agreement with this structure. Its IR spectrum showed absorption band in the region 3335 cm<sup>-1</sup> assignable to amino function and exhibited the lack of cyano group absorption. Its <sup>1</sup>H NMR spectrum revealed the presence of singlet signal at δ 5.45 ppm (*D*<sub>2</sub>*O*-exchangeable) assignable to the amino protons. The mass spectrum of **11** showed the molecular ion at *m/z* 443 (M<sup>+</sup>).

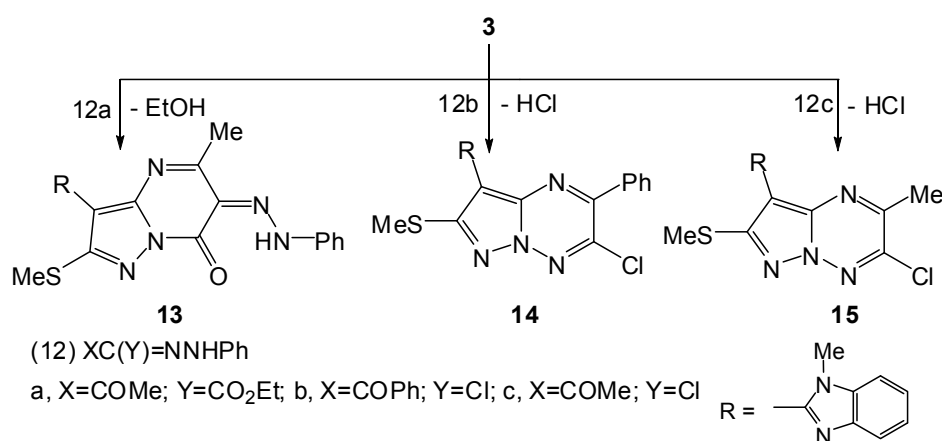


**Scheme 3**

Thus, reaction of compound **3** with ethyl 2-(2-phenylhydrazono)-3-oxobutanoate **12a** in refluxing toluene solution containing triethylamine as basic catalyst afforded solely the corresponding pyrazolo[1,5-*a*]-pyrimidin-7(6*H*)-one **13**. Formation of the latter structure is assumed proceed via an initial aza-Wittig reaction between **3** with **12a**. The structure product **13** was assigned based on the elemental analysis and spectral data which in agreement with this structure. The IR spectrum showed absorption bands at 3235  $\text{cm}^{-1}$  due to NH and at 1672  $\text{cm}^{-1}$  due to carbonyl function. Its  $^1\text{H}$  NMR spectrum showed a new signal at  $\delta$  11.83 ppm for hydrazo proton. Its mass spectrum showed a molecular ion at  $m/z$  430 ( $M^++1$ ) and at 429 ( $M^+$ ) corresponding to a molecular formula  $\text{C}_{22}\text{H}_{19}\text{N}_7\text{OS}$ .

In contrast, compound **3** reacted with equimolar amounts of 2-(2-phenylhydrazono)-2-chloro-1-phenylethanone **12b** in refluxing toluene solution containing triethylamine as basic catalyst afforded solely the corresponding 2-phenylpyrazolo[1,5-*b*][1,2,4]triazine **14**. Formation of the latter structure is assumed proceed via an initial aza-Wittig reaction between **3** with **12b** to give the intermediate, which readily undergoes heterocyclization with loss of aniline. The structure product **14** was assigned based on the elemental analysis and spectral data which in agreement with this structure. Its  $^1\text{H}$  NMR spectrum showed lack of signal due to NH proton. Its mass spectrum showed a molecular ion at  $m/z$  407 ( $M^++1$ ) corresponding to a molecular formula  $\text{C}_{20}\text{H}_{15}\text{N}_6\text{SCl}$ .

In similar manner compound **3** reacted with equimolar amounts of 1-(2-phenylhydrazono)-1-chloropropan-2-one **12c** furnished one isolable product (as tested by TLC analyses) which have the pyrazolo[1,5-*b*][1,2,4]triazine derivative **15** based on their elemental and spectral analyses (Scheme 4).



**Scheme 4**

## CONCLUSIONS

In the present work, iminophosphoranes used in heterocyclic synthesis of pyrazolopyrimidine, imidazopyrazole and pyrazolotriazine derivatives incorporating benzimidazole moiety via intermolecular aza-Wittig reactions.

## EXPERIMENTAL

Melting points were determined on a Gallenkamp apparatus and are uncorrected. The IR spectra were recorded on Shimadzu FT-IR 8101 PC infrared spectrophotometer. The  $^1\text{H}$  NMR spectra were determined in  $\text{DMSO-}d_6$  at 300 MHz on a Varian Mercury VX 300 NMR spectrometer using TMS as an internal standard. Mass spectra were measured on a GCMS-QP1000 EX spectrometer at 70 eV. Elemental analyses were carried out at the Microanalytical Center of Cairo University. 5-aminopyrazole<sup>35</sup> (**1**) and hydrazonyl halides<sup>41,42</sup> (**12b,c**) were prepared according to the reported literature.

**Synthesis of 4-(1-Methylbenzimidazol-2-yl)-3-(methylthio)-5-(triphenylphosphoranylideneamino)-1H-pyrazole (3).** *Method A:* pyrazol-5-amine **1** (10 mmol), hexachloroethane (10 mmol) and triphenylphosphine (10 mmol) were dissolved in (25 mL) anhydrous benzene and stirred for 30 min. Triethylamine (13 mmol) was added dropwise over 5 min with stirring and the reaction mixture was kept at reflux for 3 h. After cooling, the solid was filtered off and the mother liquor was concentrated under vacuum and the residue was triturated with EtOAc to afford the iminophosphorane **3**.

*Method B:* Pyrazol-5-amine **1** (10 mmol) was dissolved in mixture of water (10 mL) and conc.  $\text{H}_2\text{SO}_4$  (2 mL), cooled to 0 °C. A cooled solution of  $\text{NaNO}_2$  (15 mmol) in water (10 mL) was added dropwise and the reaction mixture was stirred at 0 °C for 2 h. then a cooled solution of  $\text{NaN}_3$  (17 mmol) in water (5 mL) was added with stirring and the reaction mixture was kept in a refrigerator for 24 h. The solid formed was separated by filtration to give the azide **2** which was crystallized from  $\text{CH}_2\text{Cl}_2$  to give pale yellow crystals mp 183 °C. The azide **2** (5 mmol) was dissolved in dry  $\text{CH}_2\text{Cl}_2$  (15 mL) and then added dropwise to a solution of dry  $\text{CH}_2\text{Cl}_2$  (15 mL) containing (5 mmol) of  $\text{Ph}_3\text{P}$  at room temperature under nitrogen and the reaction mixture was stirred for 3 h. The solid product was collected by filtration and crystallized from EtOAc as colorless crystals (63%), mp 215-217 °C, IR  $\nu_{\text{max}}/\text{cm}^{-1}$  (KBr) 3187 (NH), 1630 (C=N);  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ )  $\delta$  2.61 (3H, s,  $\text{SCH}_3$ ), 3.86 (3H, s,  $\text{NCH}_3$ ), 7.28-7.79 (19H, m, Ar-H), 9.63 (1H, s, NH),  $m/z$  519 ( $\text{M}^+$ , 82), 365 (12), 318 (32), 141 (100). Anal. Calcd for  $\text{C}_{30}\text{H}_{26}\text{N}_5\text{PS}$ : C, 69.35; H, 5.04; N, 13.48; S, 6.17. Found: C, 69.41; H, 5.11; N, 13.54; S, 6.21.

**Reaction of 3 with carbonyl compounds and hydrazonyl halides. (General Procedure).** To a solution of the iminophosphorane **3** (2 mmol) in dry toluene (50 mL), the appropriate ketone (2 mmol) and  $\text{Et}_3\text{N}$  (0.4 mL) was added and the reaction mixture was refluxed for 6 h. The precipitate obtained was filtered off, dried and recrystallized from the appropriate solvent until TLC revealed that no triphenylphosphine oxide remained.

**3-(1-Methylbenzimidazol-2-yl)-2-(methylthio)-5-phenylpyrazolo[1,5-a]pyrimidin-7(6H)-one (4).**

Recrystallized from DMF, pale yellow crystals (65%), mp >300 °C, IR  $\nu_{\text{max}}/\text{cm}^{-1}$  (KBr) 1693 (CO), 1628 (C=N);  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ )  $\delta$  2.45 (2H, s,  $\text{CH}_2$ ), 2.66 (3H, s,  $\text{SCH}_3$ ), 3.86 (3H, s,  $\text{NCH}_3$ ), 7.28-7.84 (9H,

m, Ar-H),  $^{13}\text{C}$  NMR 188.8 (C=O), 156.4 (C-5), 151.6 (C-2 imidazole), 137.3 (C-3a), 135.2 (C-2), 119 (C-3), 33.6 (C-6), 31.3 (CH<sub>3</sub>), 15.2 (CH<sub>3</sub>), 116.7-139.4 (C-phenyl and imidazole);  $m/z$  (%) 387 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>21</sub>H<sub>17</sub>N<sub>5</sub>OS: C, 65.10; H, 4.42; N, 18.08; S, 8.28. Found: C, 65.41; H, 4.48; N, 18.12; S, 8.15.

**5-Methyl-3-(1-methylbenzimidazol-2-yl)-2-(methylthio)pyrazolo[1,5-*a*]pyrimidin-7(6*H*)-one (5).**

Recrystallized from dioxane/DMF (1:2) pale yellow crystals (76%), mp >300 °C, IR  $\nu_{\text{max}}/\text{cm}^{-1}$  (KBr) 1695 (CO), 1630 (C=N);  $^1\text{H}$  NMR (DMSO-*d*<sub>6</sub>)  $\delta$  2.35 (3H, s, CH<sub>3</sub>), 2.42 (2H, s, CH<sub>2</sub>), 2.67 (3H, s, SCH<sub>3</sub>), 3.88 (3H, s, NCH<sub>3</sub>), 7.28-7.71 (4H, m, Ar-H);  $m/z$  325 (M<sup>+</sup>, 64). Anal. Calcd for C<sub>16</sub>H<sub>15</sub>N<sub>5</sub>OS: C, 59.06; H, 4.65; N, 21.52; S, 9.85. Found: C, 59.32; H, 4.69; N, 21.58; S, 9.91.

**6-Chloro-5,7-dimethyl-3-(1-methylbenzimidazol-2-yl)-2-(methylthio)pyrazolo[1,5-*a*]pyrimidine (6).**

Recrystallized from MeOH yellow crystals (70%), mp >300 °C, IR  $\nu_{\text{max}}/\text{cm}^{-1}$  (KBr) 1635 (C=N);  $^1\text{H}$  NMR (DMSO-*d*<sub>6</sub>)  $\delta$  2.23 (6H, s, 2CH<sub>3</sub>), 2.62 (3H, s, SCH<sub>3</sub>), 3.87 (3H, s, NCH<sub>3</sub>), 7.28-8.12 (4H, m, Ar-H),  $m/z$  (%) 359 (M<sup>+</sup>+2, 26), 357 (M<sup>+</sup>, 72). Anal. Calcd for C<sub>17</sub>H<sub>16</sub>N<sub>5</sub>SCl: C, 57.06; H, 4.51; N, 19.57; S, 8.96; Cl, 9.91%. Found: C, 57.24; H, 4.62; N, 19.64; S, 9.05; Cl, 9.96.

**6-Chloro-5-methyl-3-(1-methylbenzimidazol-2-yl)-2-(methylthio)pyrazolo[1,5-*a*]pyrimidin-7(6*H*)-one (7).**

Recrystallized from dioxane, pale yellow crystals (63%), mp >300 °C, IR  $\nu_{\text{max}}/\text{cm}^{-1}$  (KBr) 1689 (CO), 1635 (C=N);  $^1\text{H}$  NMR (DMSO-*d*<sub>6</sub>)  $\delta$  2.19 (3H, s, CH<sub>3</sub>), 2.64 (3H, s, SCH<sub>3</sub>), 3.81 (1H, s, CH), 3.86 (3H, s, NCH<sub>3</sub>), 7.28-7.73 (4H, m, Ar-H),  $^{13}\text{C}$  NMR 186.3 (C=O), 156.4 (C-5), 151.6 (C-2 imidazole), 139.1 (C-3a), 137.3 (C-2), 121 (C-3), 46.2 (C-6), 31.8 (CH<sub>3</sub>), 15.7 (CH<sub>3</sub>), 115.4-136.5 (C-phenyl and imidazole),  $m/z$  (%) 361 (M<sup>+</sup>+2, 31), 359 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>16</sub>H<sub>14</sub>N<sub>5</sub>OSCl: C, 53.41; H, 3.92; N, 19.46; S, 8.91, Cl, 9.85. Found: C, 53.48; H, 4.02; N, 19.53; S, 8.94, Cl, 9.91.

**2-(2-Chloro-6-(methylthio)-1*H*-imidazo[1,2-*b*]pyrazol-7-yl)-1-methylbenzimidazole (8).**

Recrystallized from EtOAc/EtOH (2:1), yellow crystals (66%), mp 289 °C, IR  $\nu_{\text{max}}/\text{cm}^{-1}$  (KBr) 1632 (C=N);  $^1\text{H}$  NMR (DMSO-*d*<sub>6</sub>)  $\delta$  2.65 (3H, s, SCH<sub>3</sub>), 3.85 (3H, s, NCH<sub>3</sub>), 7.22-7.78 (5H, m, CH and Ar-H), 11.2 (1H, s, NH),  $m/z$  (%) 319 (M<sup>+</sup>+2, 8), 317 (M<sup>+</sup>, 23). Anal. Calcd for C<sub>14</sub>H<sub>12</sub>N<sub>5</sub>SCl: C, 52.91; H, 3.81; N, 22.04; S, 10.09, Cl, 11. Found: C, 53.07; H, 4.02; N, 22.35; S, 10.26, Cl, 11.32.

**4-(1-Methylbenzimidazol-2-yl)-3-(methylthio)-1-(2-oxo-2-(benzothiazol-2-yl)ethyl)-5-(triphenylphosphorylideneamino)pyrazole (9).**

Recrystallized from DMF, yellow crystals (56%), mp 295-296 °C, IR  $\nu_{\text{max}}/\text{cm}^{-1}$  (KBr) 1711 (CO), 1635 (C=N);  $^1\text{H}$  NMR (DMSO-*d*<sub>6</sub>)  $\delta$  2.68 (3H, s, SCH<sub>3</sub>), 3.88 (3H, s, NCH<sub>3</sub>), 4.74 (2H, s, CH<sub>2</sub>), 7.21-8.14 (23H, m, Ar-H),  $m/z$  (%) 694 (M<sup>+</sup>, 4). Anal. Calcd for C<sub>39</sub>H<sub>31</sub>N<sub>6</sub>OS<sub>2</sub>P: C, 67.42.41; H, 4.50; N, 12.10; S, 9.23. Found: C, 67.48; H, 4.54; N, 12.34; S, 9.34.

**5-(Benzothiazol-2-yl)-3-(1-methylbenzimidazol-2-yl)-2-(methylthio)pyrazolo[1,5-*a*]pyrimidin-7-amine (11).**

Recrystallized from dioxane, yellow crystals (45%), mp 269 °C, IR  $\nu_{\text{max}}/\text{cm}^{-1}$  (KBr) 3335 (NH<sub>2</sub>),

1635 (C=N);  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ , 2.65 (3H, s, SCH<sub>3</sub>), 3.86 (3H, s, NCH<sub>3</sub>), 5.45 (2H, s, NH<sub>2</sub>), 7.21-8.19 (8H, m, Ar-H), 8.45 (1H, s, CH),  $m/z$  (%) 443 ( $\text{M}^+$ , 19). Anal. Calcd for C<sub>22</sub>H<sub>17</sub>N<sub>6</sub>S<sub>2</sub>: C, 59.57; H, 3.86; N, 22.11; S, 14.46. Found: C, 59.58; H, 4.02; N, 22.31; S, 14.54.

**6-(2-Phenylhydrazono)-5-methyl-3-(1-methylbenzimidazol-2-yl)-2-(methylthio)pyrazolo[1,5-*a*]-pyrimidin-7(6*H*)-one (13).** Recrystallized from dioxane, pale brown crystals (43%), mp >300 °C, IR  $\nu_{\text{max}}/\text{cm}^{-1}$  (KBr) 3235 (NH), 1672 (CO), 1628 (C=N);  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  2.35 (3H, s, CH<sub>3</sub>), 2.67 (3H, s, SCH<sub>3</sub>), 3.86 (3H, s, NCH<sub>3</sub>), 7.09-7.75 (9H, m, Ar-H), 11.83 (1H, s, NH),  $m/z$  (%) 430 ( $\text{M}^++1$ , 12), 429 ( $\text{M}^+$ , 35). Anal. Calcd for C<sub>22</sub>H<sub>19</sub>N<sub>7</sub>OS: C, 61.52; H, 4.46; N, 22.83; S, 7.47. Found: C, 61.59; H, 4.49; N, 22.88; S, 7.51.

**3-Chloro-8-(1-methylbenzimidazol-2-yl)-7-(methylthio)-2-phenyl-pyrazolo[1,5-*b*][1,2,4]triazine (14).** Recrystallized from DMF/EtOH (2:1), yellow crystals (42%), mp >300 °C, IR  $\nu_{\text{max}}/\text{cm}^{-1}$  (KBr) 1630 (C=N);  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  2.66 (3H, s, SCH<sub>3</sub>), 3.86 (3H, s, NSCH<sub>3</sub>), 7.19-7.71 (9H, m, Ar-H),  $m/z$  (%) 407 ( $\text{M}^++1$ , 6). Anal. Calcd for C<sub>20</sub>H<sub>15</sub>N<sub>6</sub>SCl: C, 59.04; H, 3.72; N, 20.65; S, 7.88; Cl, 8.71. Found: C, 59.17; H, 4.04; N, 20.68; S, 7.91, Cl, 8.78.

**3-Chloro-2-methyl-8-(1-methylbenzimidazol-2-yl)-7-(methylthio)pyrazolo[1,5-*b*][1,2,4]triazine (15).** Recrystallized from dioxane, yellow crystals (41%), mp >300 °C, IR  $\nu_{\text{max}}/\text{cm}^{-1}$  (KBr) 1635 (C=N);  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  2.26 (3H, s, CH<sub>3</sub>), 2.65 (3H, s, SCH<sub>3</sub>), 3.87 (3H, s, NCH<sub>3</sub>), 7.28-7.73 (4H, m, Ar-H),  $m/z$  (%) 346 ( $\text{M}^++2$ , 11), 344 ( $\text{M}^+$ , 51). Anal. Calcd for C<sub>15</sub>H<sub>13</sub>N<sub>6</sub>SCl: C, 52.25; H, 3.80; N, 24.37; S, 9.30; Cl, 10.28. Found: C, 52.55; H, 4.04; N, 24.42; S, 9.45, Cl, 10.32.

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