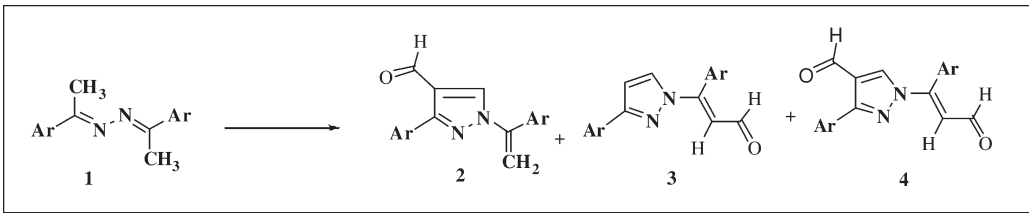
Ring and Side Chain Formylated Pyrazoles from Acetophenone Azines and Vilsmeier's Reagent

Ramaiyan Manikannan and Shanmugam Muthusubramanian*

Department of Organic Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai-625 021, India
*E-mail: muthumanian2001@yahoo.com

Received May 1, 2010
DOI 10.1002/jhet.576
Published online 29 March 2011 in Wiley Online Library (wileyonlinelibrary.com).



Differently substituted acetophenone azines on treatment with excess phosphorous oxychloride in *N,N*-dimethylformamide have found to yield three products in each case. An acceptable mechanism has been suggested for the formation of all the three products.

J. Heterocyclic Chem., **48**, 671 (2011).

INTRODUCTION

Pyrazole derivatives, which have been the basis of numerous dyes, also find a wide range of pharmacological applications as analgesic, anti-inflammatory, antipyretic, anaesthetic, antibacterial, antimicrobial [1,2], antipsychotic [3], antimalarial [4], antitumor, anticancer, antiangiogenic [5], and antianxiety activities [6,7]. Certain alkyl pyrazoles show significant bacteriostatic, bactericidal, and fungicidal acitivites [8,9]. Kira *et al*. [10] synthesized 1*H*-pyrazole-4-carbaldehyde (**2**) from acetophenone azine using Vilsmeier's reagent in 1:2 ratio.

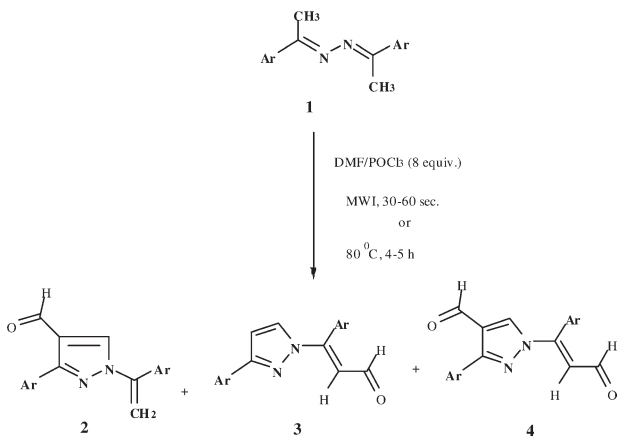
It is of interest to find out the product selectivity of the above reaction when the reaction is carried out with excess reagent or when the microwave irradiation is used as a source of energy. With this view, the reaction between differently substituted acetophenone azines and Vilsmeier's reagent taken in excess (1:8) under the influence of the microwave irradiation has been investigated in the present work. Significant product selectivity has been noticed and in addition to the reported product **2** by Kira *et al*. [10], two additional products *viz* **3** and **4** have been obtained in good yield. These interesting results are summarized in this article.

RESULTS AND DISCUSSION

Differently substituted acetophenone azines were prepared by the reaction of hydrazine and substituted acetophenone [11–16]. These azines (**1**) were then treated with phosphorous oxychloride in 1:8 ratio taken in dimethylformamide under microwave irradiation for 30 to 60 seconds. The products obtained were separated through column and it has been found that the reaction has yielded three products, **2**, **3**, and **4** in each case (Scheme 1), except in **1k**, where only two compounds–**2k** and **4k**–alone could be isolated. The physical constants and the spectral features of the respective compounds are given in the experimental section. The reaction has also been carried out under conventional method in each case—by heating the above reaction mixture at 80°C for 4 to 5 h. The yields of the different compounds **2**, **3**, and **4** in these cases are closer to those obtained under microwave condition (Scheme 1).

Compounds **2**, **3**, and **4** were obtained in pure form in all the cases and they have all been fully characterized by spectral data. Compound **2** has been found to be 3-aryl-1-(1-arylvinyl)-1*H*-pyrazole-4-carbaldehyde. The ^{1}H-NMR spectrum of **2b** has two different methyl signals at 2.42 and 2.43 ppm as singlets accounting for three hydrogens each. Two olefinic hydrogens appear as singlets at 5.31 and 5.87 ppm with zero geminal coupling. These two hydrogens have a common C,H-COSY contour with the carbon at 106.7 ppm. The presence of two aryl rings is evidenced by the signals between 7.20 to 7.80 ppm. Two singlets, one at 8.05 ppm and another at 9.98 ppm, each accounting for one hydrogen, can be assigned to C-5 hydrogen of the pyrazole ring and to the hydrogen due to the formyl group at C-4 position, respectively. The ^{13}C-NMR spectrum and DEPT 135 spectrum of **2b** is also consistent with the structure assigned. Both the vinylic hydrogens have common HMBC contours at 131.6 and 144.8 ppm, indicating the former may be the *ipso* carbon of the aryl group and the latter as the olefinic quaternary carbon. Of the signals

Scheme 1



due to two olefinic hydrogens, the one at 5.87 ppm may be due to the hydrogen *cis* to the pyrazolyl ring, as the pyrazole ring has been shown to exhibit more anisotropic deshielding than simple phenyl group. (Table 1)

It is to be noted that compound **2** has been obtained as the sole product when the reaction was carried under conventional condition in 1:2 ratio of substrate and reagent in quantitative yields (40 to 95%) as the only product [10]. However in the present investigation, this compound is not obtained as the major product, but as a minor one with very low yield in some cases. Probably, the excess formylating agent and the additional energy available in the form of microwaves would have left **2** as the minor product. Out of the 11 compounds obtained, **2a**, **2b**, and **2c** are found to be reported in literature [10].

Compound **3**, isolated as the major compound in some cases (**3a**, **3c**, **3d**, **3e**, and **3i**), exhibits a doublet around 9.44 ppm and another doublet around 7.00 ppm (J = 8.3 Hz). For **3c**, these two signals are having connecting contours in the H,H-COSY spectrum. Two doublets at 6.69 ppm (J = 2.7 Hz, 1H) and 7.32 ppm (J = 2.7 Hz, 1H) have connecting contours indicating these two hydrogens are neighbours. The presence of two *p*-anisyl rings is also evident from the signals between 6.80 and 7.90 ppm and the signals at 3.87 and 3.92 ppm. There are 14 carbons in the aromatic/olefinic region, seven of them being quaternary. Out of these, there is a formyl group as evidenced by the signal at 192.6 ppm and the formyl hydrogen has been found to be vicinal to another olefinic hydrogen. The other two coupled doublets can be assigned to the C-4 and C-5 hydrogens of the pyrazolyl ring and hence it is clear that the compound **3** is 3-aryl-3-(3-aryl-1*H*-1-pyrazolyl)-2-propenal. There can be two geometrical forms for this compound and an attempt has been made to establish the geometry through NOESY spectrum. It is expected that if the molecule assumes *Z* geometry, the formyl hydrogen can give a contour with the hydrogen of the pyrazolyl ring and if the geometry is *E*, the olefinic hydrogen at 7.00 ppm can give a contour with the later hydrogens. But unfortunately the spatial relation is not revealed in the NOESY spectrum, which shows only the dipolar coupling relationship. From the single crystal X-ray analysis of (**3b**) [17] (Fig. 1), it is found that **3** is having a geometry in which the olefinic hydrogen and the pyrazolyl ring are *cis* to each other. Thus compound **3** is (*E*)-3-aryl-3-[3-aryl-1*H*-1-pyrazolyl]-2-propenal.

Compound **4** has been obtained as the major product in some cases (**4b**, **4f**, **4g**, **4h**, **4j**, and **4k**). The initial inspection of the ^{1}H- and ^{13}C-NMR spectra of **4c** reveals the presence of two formyl groups. One of the formyl hydrogen appears as a singlet at 9.96 ppm, while the other appears as a doublet at 9.49 ppm. The latter signal has a coupling partner, which appears as a multiplet along with some other hydrogens in the region around 7.01 ppm, as evidenced by the H,H-COSY spectrum. There is a sharp singlet appearing at 7.93 ppm accounting for one hydrogen. The presence two aryl rings are also evident from the spectral pattern. These results clearly suggest that there is an additional formyl

Table 1

Pyrazole derivatives from substituted acetophenone azines.

		Yield % (MWI)			Yield % (thermal)		
Entry	Ar	**2**	**3**	**4**	**2**	**3**	**4**
a	Phenyl	25	36	35	15	40	32
b	*p*-Methylphenyl	7	34	57	10	33	45
c	*p*-Methoxy phenyl	5	40	38	7	42	36
D	*p*-Chlorophenyl	7	46	40	13	44	38
e	*p*-Nitrophenyl	12	33	30	11	40	35
f	p-Bromophenyl	15	35	40	14	33	38
g	*o*-Chlorophenyl	13	28	56	12	25	53
h	*m*-Methoxyphenyl	20	34	38	17	31	35
i	1-Naphthyl	22	43	30	16	42	29
j	2-Naphthyl	25	22	46	16	24	44
k	*o*-Methoxyphenyl	35	–	58	34	–	55

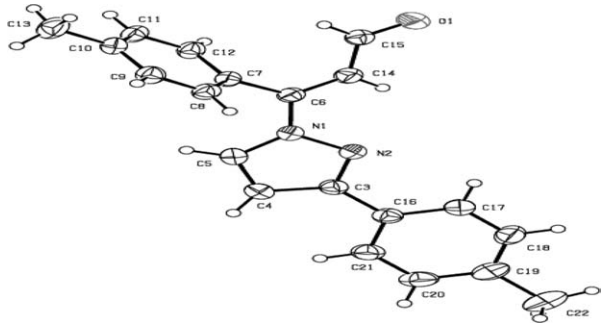


Figure 1. ORTEP diagram of compound **3b**.

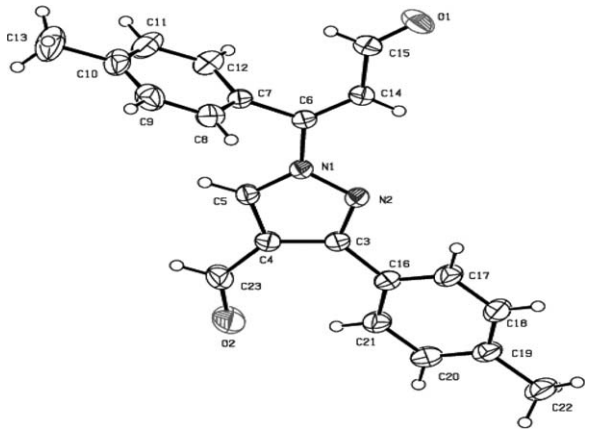


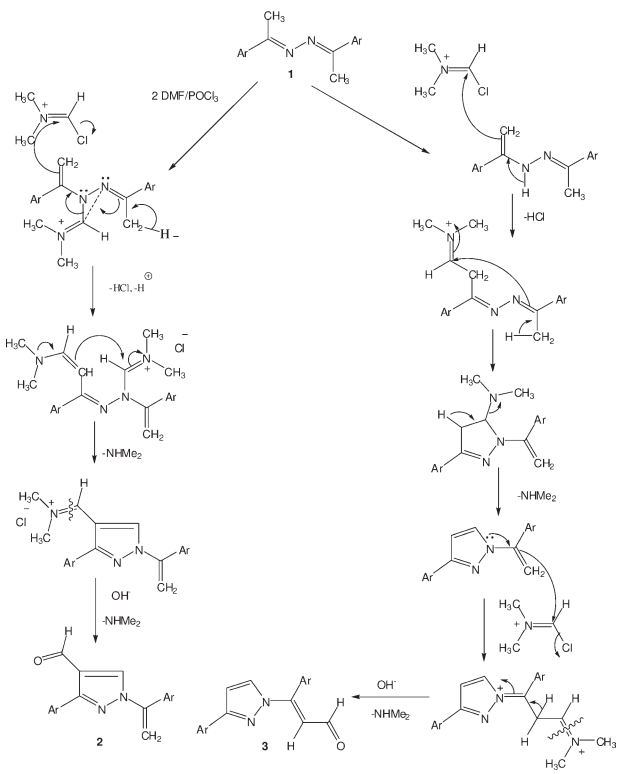
Figure 2. ORTEP diagram of compound **4b**.

group in this compound compared to compound **3**. The absence of pair of doublets due to the pyrazolyl ring hydrogens and the appearance of only one singlet for the pyrazolyl hydrogen indicates that the formylation has occurred in the pyrazolyl ring. Of the two free positions, by logic, the formyl group can be placed in 4th position. The ^{13}C-NMR spectrum also supports the assigned structure. The singlet formyl hydrogen at 9.96 ppm has HMBC contours with the carbon at 135.9 ppm and this unambiguously indicates that this carbon to be C-5 of the pyrazolyl ring. This hydrogen has another HMBC contour with the quartenary carbon at 122.9 ppm, indicating the latter carbon to C-4 of the pyrazolyl ring. The formyl hydrogen at 9.49 ppm has a HMBC contour with the methylenic carbon at 118.6 ppm and hence this carbon is α to the formyl group. The singlet at 7.93 ppm has a HMBC contour with the quaternary carbon at 155.5 ppm and hence this carbon is the C-3 carbon of the pyrazolyl ring. This hydrogen has also a HMBC contour with the C-4 carbon, already assigned. It has a C,H-COSY contour with the carbon at 135.9 ppm and hence this carbon is C-5 carbon. The chemical shift value of the terminal olefinic hydrogen is very close to that of the compound **3** and hence it can be assumed to have a similar geometry, the one in which the olefinic hydrogen and the pyrazolyl ring are *cis* to each other. The single crystal X-ray structure of **4b** [18] (Fig. 2) also confirms this assignment.

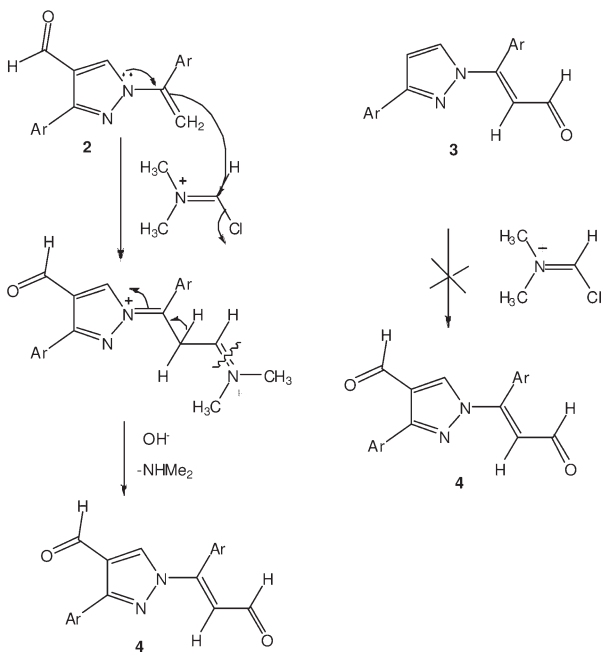
The interesting aspect of this reaction of the acetophenone azine with excess Vilsmeier's reagent is the fact that the simple formylated compound **2**, which was originally obtained as the exclusive product, has now obtained as a minor one. Two more products **3** and **4** are obtained due to formylation at a different centre and further formylation, respectively. The mechanism of the reaction and the reason for the selective formation of **3** and **4** over **2** can be explained as follows:

It has already been established that during the reaction of acetophenone azine with two moles of Vilsmeier's reagent, the reaction takes place by the initial formylation at carbon end followed by formylation at the nitrogen end to yield the product **2** and not by double formylation at the methyl end of the acetophenone [10].

Scheme 2



Scheme 3



However, under microwave condition and in presence of excess reagent, it is found that the reaction takes place not only at the nitrogen and methyl end leading to ultimate cyclisation, but also to a product in which both the methyl ends of the acetophenone entities have been formylated with subsequent cyclisation leading to **3**. Probably both **2** and **3** would have formed in equal amounts in the reaction, but due to the presence of excess reagent, **2** would have got further formylated to yield **4**, while **3** has no change of getting further formylated. The whole sequence of the reaction leading to products **2**, **3**, and **4** are depicted in the Schemes 2 and 3.

It is interesting to note that with **1e** and **1f**, apart from the indicated products **2**, **3**, and **4**, a few minor products are also obtained. With **1e**, three products, **5e**, **6e**, and **7e** are obtained in minor quantities. With **1f**, a small amount of **5f** is obtained. These compounds are identified as the products that can be obtained from the hydrazone of the respective acetophenones or the acetophenone themselves. The identified minor products from **1e** are (*E*)-3-chloro-3-(4-nitrophenyl)-2-propenal (**5e**), 3-(4-nitrophenyl)-1*H*-pyrazole (**6e**) and 3-(4-nitrophenyl)-1*H*—pyrazole-4-carbaldehyde (**7e**) and that from **1f** is (*E*)-3-(4-bromophenyl)-3-chloro-2-propenal (**5f**). These compounds would have formed by the initial hydrolysis of the azine to hydrazone and then to acetophenones by the moisture in the reaction medium.

This article summarises the effect excess reagent during the Vilsmeier reaction of acetophenone azines under thermal and microwave conditions to get differently formylated and diformylated products apart form the simple formylated product. The mechanisms for the formation of the different products have been described.

EXPERIMENTAL

All chemicals used in this investigation were of reagent grade quality and used without further purification. All melting points were recorded in open capillaries and are uncorrected. The ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker 300 MHz spectrometer at 300 and 75 MHz, respectively in $CDCl_3$/DMSO-d_6 using TMS as internal standard. The chemical shifts are presented in δ-scale. Microanalyses were carried out on a Perkin-Elmer instrument. Microwave assisted reactions were carried out in a Biotage Microwave Synthesizer. All chromatographic separations were performed on 60–120 mesh silica gel using petroleum ether-ethyl acetate as eluent, unless mentioned otherwise. Single crystal XRD data were collected on a APEX2 (BRUKER, 2004).

General procedure for the preparation of 1-aryl-1-ethanone N-[(*E*)-1-arylethylidene]hydrazones (1a-k). A mixture of substituted acetophenone (0.005 mol) and hydrazine sulfate (0.002 mol) in presence of sodium acetate (0.008 mole) in ethanol medium was refluxed for 1 to 2 h. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was poured into crushed ice then filtered the product. Crude compounds **1a-k** were recrystallised from dichloromethane. All the synthesized substituted acetopheonone azines, except **1k**, have been reported.

1-(2-Methoxyphenyl)-1-ethanone N-[(E)-1-(2-methoxyphenyl)ethylidene]hydrazone (1k). This compound was obtained as white solid (Dichloromethane), yield 95%; mp 75–76°C; time 2 h; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.23 (s, 6H), 3.89 (s, 6H), 6.93 (d, J = 8.4 Hz, 2H), 7.00 (td, J = 7.5, 0.9 Hz, 2H), 7.35 (td, J = 8.4, 1.8 Hz, 2H), 7.53 (dd, J = 7.5, 1.8 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 18.7, 55.4, 111.0, 120.6, 129.4, 129.5, 130.0, 157.4, 158.6. *Anal*. Calcd. for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45%. Found: C, 73.07; H, 6.91; N, 9.56%.

General procedure for the preparation of pyrazole derivatives 3-(aryl)-1-[1-(aryl)vinyl]-1*H*-4-pyrazole carbaldehyde (2a-k), (*E*)-3-aryl-3-(3-aryl-1*H*-1-pyrazolyl)-2-propenal (3a-j), and 3-(aryl)-1-[(*E*)-1-(aryl)-3-oxo-1-propenyl]-1*H*-4-pyrazolecarbaldehyde (4a-k). ***Microwave irradiation method.*** To a mixture of 1-aryl-1-ethanone *N*-[(*E*)-1-arylethylidene]hydrazones (**1**) (0.003 mol) and 3 mL of dimethyl formamide kept in ice bath at 0°C, phosphorous oxycholride (0.024 mole) was added dropwise for 5 to 10 minutes. The reaction mixture was then irradiated under microwaves for 30 to 60 seconds. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was poured into crushed ice and extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate. The different compounds present in the mixture were separated by column chromatography using petroleum ether and ethyl acetate mixture as eluent.

Conventional method. To a mixture of 1-aryl-1-ethanone N-[(*E*)-1-arylethylidene]hydrazones **1** (0.003 mole) and 3 mL of dimethyl formamide kept in ice bath at 0°C, phosphorous oxycholride (0.024 mole) was added dropwise for 5 to 10 minutes. The reaction mixture was then stirred with reflux for 4 to 5 h at 80°C. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was poured into crushed ice and extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate. The different compounds present in the mixture were separated by column chromatography using petroleum ether and ethyl acetate mixture as eluent.

3-Phenyl-1-(1-phenylvinyl)-1*H*-4-pyrazolecarbaldehyde (2a). This compound was obtained as white solid (Dichloromethane), mp 63–64 (62)°C [19]; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.35 (s, 1H), 5.91(s, 1H), 7.41–7.45 (m, 8H), 7.79–7.82 (m, 2H), 8.06 (s, 1H), 9.98 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 107.5, 121.6, 128.1, 128.7, 128.8, 129.0, 129.3, 129.8, 131.2, 134.0, 134.4, 144.8, 154.6, 185.1. *Anal*. Calcd. for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21%. Found: C, 78.85; H, 5.19; N, 10.27%.

3-(4-Methylphenyl)-1-[1-(4-methylphenyl) vinyl]-1*H*-4-pyrazolecarbaldehyde (2b). This compound was obtained as white solid (Dichloromethane), mp 115–116 (116)°C [19]; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.42 (s, 3H), 2.43 (s, 3H), 5.31(s, 1H), 5.87 (s, 1H), 7.24–7.34 (m, 6H), 7.71 (d, J = 7.8 Hz, 2H), 8.05 (s, 1H), 9.98 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 21.3, 21.4, 106.7, 121.5, 128.1, 128.3, 128.8, 129.4, 129.5, 131.6, 134.0, 139.3, 139.9, 144.8, 154.5, 185.2. *Anal*. Calcd. for $C_{20}H_{18}N_2O$: C, 79.44; H, 6.00; N, 9.26%. Found: C, 79.47; H, 6.06; N, 9.29%.

3-(4-Methoxyphenyl)-1-[1-(4-methoxyphenyl) vinyl]-1*H*-4-pyrazolecarbaldehyde (2c). This compound was obtained as white solid (Dichloromethane), mp 105–106 (105)°C [19]; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 3.86 (s, 3H), 3.89 (s, 3H), 5.25 (s, 1H), 5.78 (s,1H), 6.94 (d, J = 8.9, Hz, 2H), 7.00 (d, J = 8.9 Hz, 2H), 7.34 (d, J = 8.7 Hz, 2H), 7.77 (d, J = 8.7 Hz, 2H), 8.03 (s, 1H); 9.95 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 55.3, 55.4, 106.2, 114.1, 114.2, 121.3, 123.7, 126.9, 129.5, 130.3, 134.4, 144.5, 154.2, 160.5, 160.7, 185.1. *Anal*. Calcd. for $C_{20}H_{18}N_2O_3$: C, 71.84; H, 5.43; N, 8.38%. Found: C, 71.89; H, 5.47; N, 8.42%.

3-(4-Chlorophenyl)-1-[1-(4-chlorophenyl) vinyl]-1*H*-4-pyrazolecarbaldehyde (2d). This compound was obtained as viscous oil; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.37 (s, 1H), 5.85 (s, 1H), 7.35 (d, J = 8.7 Hz, 2H), 7.41–7.46 (m, 4H), 7.79 (d, J = 8.4 Hz, 2H), 8.01 (s, 1H), 9.95 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 108.2, 121.7, 128.9, 129.1, 129.3, 129.6, 130.2, 132.8, 135.1, 135.5, 136.0, 143.9, 153.0, 184.3.

3-(4-Nitrophenyl)-1-[1-(4-nitrophenyl)vinyl]-1*H*-4-pyrazolecarbaldehyde (2e). This compound was obtained as viscous oil; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.62 (d, J = 1.7 Hz, 1H), 5.98 (d, J = 1.7 Hz, 1H), 7.61 (d, J = 8.9 Hz, 2H), 8.09 (d, J = 8.9 Hz, 2H), 8.20 (s, 1H), 8.30–8.32 (m, 4H), 10.02 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 111.3, 122.5, 123.8, 124.2, 126.9, 128.9, 129.8, 132.0, 136.5, 140.2, 143.3, 148.2, 153.2, 183.4.

3-(4-Bromophenyl)-1-[1-(4-bromophenyl) vinyl]-1*H*-4-pyrazolecarbaldehyde (2f). This compound was obtained as viscous oil; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.38 (s, 1H), 5.86 (s, 1H), 7.25–7.76 (m, 8H), 8.10 (s, 1H), 10.0 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 108.2, 121.7, 123.8, 124.5, 129.6, 130.1, 130.4, 131.9, 132.1, 133.3, 135.1, 143.9, 153.1, 184.2.

3-(2-Chlorophenyl)-1-[1-(2-chlorophenyl)vinyl]-1*H*-4-pyrazolecarbaldehyde (2g). This compound was obtained as viscous oil; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.21 (s, 1H), 6.18 (s, 1H), 7.16–7.51 (m, 8H), 7.82 (s, 1H), 9.71 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 108.2, 122.5, 126.9, 127.0, 127.3, 129.9, 130.1, 130.2, 130.4, 130.6, 131.2, 132.1, 133.3, 133.7, 133.9, 141.9, 152.5, 185.1.

3-(3-Methoxyphenyl)-1-[1-(3-methoxyphenyl)vinyl]-1*H*-4-pyrazolecarbaldehyde (2h). This compound was obtained as white solid (Dichloromethane), mp 98–99°C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 3.81 (s, 3H), 3.86 (s, 3H), 5.33 (s, 1H), 5.90 (s, 1H), 6.95-7.00 (m, 4H), 7.26–7.37 (m, 4H), 8.05 (s, 1H), 9.96 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 55.27*, 107.5, 113.9, 114.1, 115.1, 115.2, 120.4, 121.4, 121.6, 129.7, 129.9, 132.4, 134.1, 135.7, 144.5, 154.3, 159.7, 158.8, 185.0 (* One carbon merged with other). *Anal*. Calcd. for $C_{20}H_{18}N_2O_3$: C, 71.84; H, 5.43; N, 8.38%. Found: C, 71.88; H, 5.50; N, 8.43%.

3-(1-Naphthyl)-1-[1-(1-naphthyl)vinyl]-1*H*-4-pyrazolecarbaldehyde (2i). This compound was obtained as viscous oil; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (s, 1H), 6.45 (s, 1H), 7.52–8.08 (m, 15H), 9.53 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 108.1, 123.1, 124.6, 125.1, 125.4, 125.5, 126.3, 126.6, 126.9*, 127.3, 128.2, 128.4, 128.7, 128.8, 129.0, 129.8, 130.5, 131.5, 131.7, 132.0, 133.7, 133.8, 142.6, 154.4, 185.6 (*One carbon merged with other).

3-(2-Naphthyl)-1-[1-(2-naphthyl)vinyl]-1*H*-4-pyrazolecarbaldehyde (2j). This compound was obtained as viscous oil; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.52 (s, 1H), 6.03 (s, 1H), 7.51–7.96 (m, 13H), 8.15 (s, 1H), 8.37(s, 1H), 10.09 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 108.2, 121.9, 125.1, 126.2, 126.5, 126.8, 126.9, 127.2, 127.7, 127.8, 128.0, 128.4, 128.4, 128.5, 128.6, 128.7*, 131.8, 133.0, 133.2, 133.6, 133.7, 134.6, 145.0, 154.4, 185.0 (*One carbon merged with other).

3-(2-Methoxyphenyl)-1-[1-(2-methoxyphenyl)vinyl]-1*H*-4-pyrazolecarbaldehyde (2k). This compound was obtained as white solid (Dichloromethane), mp 88–89°C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.12 (s, 3H), 6.14 (s, 3H), 6.97–7.14 (m, 5H), 7.36 (d, J = 7.5 Hz, 1H), 7.43–7.48 (m, 3H), 7.63 (d, J = 7.5 Hz, 1H), 7.78 (s, 1H), 9.70 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 55.4, 55.7, 106.6, 111.0, 111.1, 120.6, 120.9, 121.0, 122.2, 123.4, 130.8, 130.9, 131.4*, 131.7, 141.8, 151.8, 156.9, 157.3, 186.8 (*One carbon merged with other). *Anal*. Calcd. for $C_{20}H_{18}N_2O_3$: C, 71.84; H, 5.43; N, 8.38%. Found: C, 71.89; H, 5.48; N, 8.41%.

(*E*)-3-Phenyl-3-(3-phenyl-1*H*-1-pyrazolyl)-2-propenal (3a). This compound was obtained as white solid (Dichloromethane), mp 118–119°C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.74 (d, J = 2.7 Hz, 1H), 7.09 (d, J = 8.3 Hz, 1H), 7.27 (d, J = 2.7 Hz, 1H), 7.34–7.62 (m, 8H), 7.91 (d, J = 8.1 Hz, 2H), 9.42 (d, J = 8.3 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 106.8, 116.4, 126.2, 128.8, 128.9, 129.1, 130.6, 130.8, 131.1, 131.8, 132.1, 155.4, 155.8, 192.4. *Anal* Calcd for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21%. Found: C, 78.88; H, 5.17; N, 10.27%.

(*E*)-3-(4-Methylphenyl)-3-[3-(4-methylphenyl)-1*H*-1-pyrazolyl]-2-propenal (3b). This compound was obtained as white solid (Dichloromethane), mp 174–175°C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.41(s, 3H), 2.48 (s, 3H), 6.71 (d, J = 2.4 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H), 7.25–7.31 (m, 3H), 7.42 (d, J = 7.8 Hz, 2H), 7.80 (d, J = 8.1 Hz, 2H), 9.43 (d, J = 8.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 21.4, 21.5, 106.5, 116.2, 126.1, 127.6, 129.0, 129.4, 129.5, 130.8, 132.1, 139.0, 141.5, 155.4, 156.1, 192.6. *Anal*. Calcd. for $C_{20}H_{18}N_2O$: C, 79.44; H, 6.00; N, 9.26%. Found: C, 79.49; H, 6.09; N, 9.31%.

(*E*)-3-(4-Methoxyphenyl)-3-[3-(4-methoxyphenyl)-1*H*-1-pyrazolyl]-2-propenal (3c). This compound was obtained as white solid (Dichloromethane), mp 127–128°C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 3.87 (s, 3H), 3.92 (s, 3H), 6.69 (d, J = 2.7 Hz, 1H), 6.97 (d, J = 8.7 Hz, 2H), 7.00 (d, J = 8.3 Hz, 1H), 7.05 (d, J = 8.7 Hz, 2H), 7.32 (d, J = 2.7 Hz, 1H), 7.45 (d, J = 8.9 Hz, 2H), 7.84 (d, J = 8.9 Hz, 2H), 9.44 (d, J = 8.3 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 55.3, 55.5, 106.3, 114.2, 114.3, 116.1, 122.7, 124.6, 127.5, 132.1, 132.5, 155.2, 155.9, 160.4, 161.8, 192.6. *Anal*. Calcd. for $C_{20}H_{18}N_2O_3$: C, 71.84; H, 5.43; N, 8.38%. Found: C, 71.88; H, 5.47; N, 8.42%.

(*E*)-3-(4-Chlorophenyl)-3-[3-(4-chlorophenyl)-1*H*-1-pyrazolyl]-2-propenal (3d). This compound was obtained as white solid (Dichloromethane), mp 144–145°C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.74 (d, J = 2.7 Hz, 1H), 7.04 (d, J = 8.1 Hz, 1H), 7.31 (d, J = 2.7 Hz, 1H), 7.42 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 9.43 (d, J = 8.1 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 106.9, 116.8, 127.4, 128.8, 129.0, 129.4, 130.2, 132.0, 132.1, 135.0, 137.6, 154.3, 154.4, 191.7. *Anal*. Calcd. for $C_{18}H_{12}Cl_2N_2O$: C, 62.99; H, 3.52; N, 8.16%. Found: C, 63.02; H, 3.56; N, 8.19%.

(*E*)-3-(4-Nitrophenyl)-3-[3-(4-nitrophenyl)-1*H*-1-pyrazolyl]-2-propenal (3e). This compound was obtained as white solid (Dichloromethane), mp 170–172°C; ^{1}H-NMR ($CDCl_3$,

300 MHz): δ 6.90 (d, J = 2.7 Hz, 1H), 7.09 (d, J = 8.1 Hz, 1H), 7.41 (d, J = 2.7 Hz, 1H), 7.78 (d, J = 8.4 Hz, 2H), 8.03 (d, J = 8.7 Hz, 2H), 8.30 (d, J = 8.4 Hz, 2H), 8.47 (d, J = 8.4 Hz, 2H), 9.44 (d, J = 8.1 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 108.0, 117.9, 124.1, 124.2*, 126.8, 132.0, 136.4, 137.5, 148.0, 149.9, 152.7, 153.4, 190.5 (*One carbon merged with other). *Anal*. Calcd. for $C_{18}H_{12}N_4O_5$: C, 59.34; H, 3.32; N, 15.38%. Found: C, 59.41; H, 3.39; N, 15.38%.

(*E*)-3-(4-Bromophenyl)-3-[3-(4-bromophenyl)-1*H*-1-pyrazolyl]-2-propenal (3f). This compound was obtained as white solid (Dichloromethane), mp 146–147°C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.73 (d, J = 2.7 Hz, 1H), 7.02 (d, J = 8.3 Hz, 1H), 7.29 (d, J = 2.7 Hz, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.7 Hz, 2H), 7.71(d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 9.41 (d, J = 8.1 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 106.9, 116.9, 123.3, 125.9, 127.7, 129.3, 130.6, 132.0*, 132.2, 132.3, 154.4, 154.5, 191.6 (*One carbon merged with other). *Anal*. Calcd. for $C_{18}H_{12}Br_2N_2O$: C, 50.03; H, 2.80; N, 6.48%. Found: C, 50.08; H, 2.86; N, 6.53%.

(*E*)-3-(2-Chlorophenyl)-3-[3-(2-chlorophenyl)-1*H*-1-pyrazolyl]-2-propenal (3g). This compound was obtained as viscous oil; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.98 (d, J = 2.7 Hz, 1H), 7.14 (d, J = 8.4 Hz, 1H), 7.21 (d, J = 2.7 Hz, 1H), 7.31–7.62 (m, 7H), 7.92 (dd, J = 6.9 Hz, 1H), 9.32 (d, J = 8.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 110.8, 116.5, 127.0, 127.2, 129.5, 130.0, 130.1, 130.2*, 130.7, 130.8, 132.2, 132.5, 132.6, 134.5, 152.6, 153.5, 191.4 (*One carbon merged with other).

(*E*)-3-(3-Methoxyphenyl)-3-[3-(3-methoxyphenyl)-1*H*-1-pyrazolyl]-2-propenal (3h). This compound was obtained as viscous oil; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 3.85 (s, 3H), 3.89 (s, 3H), 6.72 (d, J = 2.7 Hz, 1H), 6.95 (d, J = 8.1 Hz, 1H), 7.04–7.49 (m, 9H), 9.44 (d, J = 8.1 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 55.3, 55.5, 106.9, 110.9, 115.2, 116.1, 116.2, 116.6, 118.7, 123.1, 129.8, 130.0, 131.6, 132.2, 133.1, 155.2, 155.5, 159.7, 159.9, 192.5.

(*E*)-3-(1-Naphthyl)-3-[3-(1-naphthyl)-1*H*-1-pyrazolyl]-2-propenal (3i). This compound was obtained as white solid (Dichloromethane), mp 117–118°C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.67 (d, J = 2.7 Hz, 1H), 7.11 (d, J = 2.7 Hz, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.53–8.13 (m, 13H), 8.79 (d, J = 9.00 Hz, 1H), 9.32 (d, J = 8.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 110.4, 117.1, 124.8, 125.0, 125.2, 126.0, 126.1, 126.9, 127.0, 127.6, 127.7, 128.0, 128.4, 128.6, 129.5, 129.6, 129.9, 130.9, 131.1, 131.4, 132.0, 133.5, 134.0, 154.6, 155.7, 192.3. *Anal*. Calcd. for $C_{26}H_{18}N_2O$: C, 83.40; H, 4.85; N, 7.48%. Found: C, 83.45; H, 4.89; N, 7.51%.

(*E*)-3-(2-Naphthyl)-3-[3-(2-naphthyl)-1*H*-1-pyrazolyl]-2-propenal (3j). This compound was obtained as white solid (Dichloromethane), mp 92–93°C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.90 (d, J = 2.7 Hz, 1H); 7.23 (d, J = 8.1 Hz, 1H), 7.36 (d, J = 2.7 Hz, 1H), 7.54–8.15 (m, 14H), 9.50 (d, J = 8.1 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 107.0, 116.9, 123.9, 125.5, 126.4, 126.5, 126.7, 127.5, 127.7, 127.8, 127.9, 128.1, 128.4, 128.5, 128.6, 128.9, 129.2, 131.7, 132.4, 132.5, 133.4, 133.7, 134.1, 155.4, 155.5, 192.5. *Anal*. Calcd. for $C_{26}H_{18}N_2O$: C, 83.40; H, 4.85; N, 7.48%. Found: C, 83.47; H, 4.88; N, 7.53%.

1-[(*E*)-3-Oxo-1-phenyl-1-propenyl]-3-phenyl-1*H*-4-pyrazolecarbaldehyde (4a). This compound was obtained as white solid (Dichloromethane), mp 152–153°C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.15 (d, J = 8 Hz, 1H), 7.52–7.84 (m, 10H), 7.89 (s, 1H), 9.47 (d, J = 8 Hz, 1H), 9.98 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 118.9, 123.3, 128.9*, 128.9, 129.4, 130.0, 130.4, 130.7, 131.6, 135.4, 154.5, 156.0, 184.6, 191.8 (*One carbon merge with other). *Anal*. Calcd. for $C_{19}H_{14}N_2O_2$: C, 75.48; H, 4.67; N, 9.27%. Found: C, 75.52; H, 4.70; N, 9.31%.

3-(4-Methylphenyl)-1-[(*E*)-1-(4-methylphenyl)-3-oxo-1-propenyl]-1*H*-4-pyrazolecarbaldehyde (4b). This compound was obtained as white solid (Dichloromethane), mp 141–142°C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.45 (s, 3H), 2.51 (s, 3H), 7.12 (d, J = 8.1 Hz, 1H), 7.34 (d, J = 7.8 Hz, 2H), 7.38–7.41 (m, 4H), 7.73 (d, J = 8.1 Hz, 2H), 7.91 (s, 1H), 9.49 (d, J = 8.1 Hz, 1H), 9.98 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 21.4, 21.5, 118.7, 123.2, 126.5, 127.6, 128.8, 129.6, 130.0, 130.7, 135.4, 140.1, 142.2, 154.8, 156.0, 184.8, 192.1. *Anal*. Calcd. for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48%. Found: C, 76.39; H, 5.52; N, 8.54%.

3-(4-Methoxyphenyl)-1-[(*E*)-1-(4-methoxyphenyl)-3-oxo-1-propenyl]-1*H*-4-pyrazolecarbaldehyde (4c). This compound was obtained as viscous oil; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 3.88 (s, 3H), 3.93 (s, 3H), 7.02–7.10 (m, 5H), 7.45 (d, J = 8.7 Hz, 2H), 7.81 (d, J = 8.7 Hz, 2H), 7.93 (s, 1H), 9.49 (d, J = 8.1 Hz, 1H), 9.96 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 55.4, 55.6, 114.3, 114.7, 118.6, 121.4, 122.9, 123.1, 130.3, 132.4, 135.9, 154.6, 155.5, 161.0, 162.2, 184.6, 192.1.

3-(4-Chlorophenyl)-1-[(*E*)-1-(4-chlorophenyl)-3-oxo-1-propenyl]-1*H*-4-pyrazolecarbaldehyde (4d). This compound was obtained as white solid (Dichloromethane), mp 150–151°C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.11 (d, J = 7.8 Hz, 1H), 7.48–7.51 (m, 4H), 7.61 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 7.89 (s, 1H), 9.48 (d, J = 7.8 Hz, 1H), 9.95 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 119.2, 123.5, 127.6, 128.7, 129.1, 129.8, 130.2, 132.0, 136.1, 136.2, 138.3, 153.0, 154.5, 183.8, 191.1. *Anal*. Calcd. for $C_{19}H_{12}Cl_2N_2O_2$: C, 61.47; H, 3.26; N, 7.55%. Found: C, 61.50; H, 3.30; N, 7.59%.

3-(4-Nitrophenyl)-1-[(*E*)-1-(4-nitrophenyl)-3-oxo-1- propenyl]-1*H*-4-pyrazolecarbaldehyde (4e). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.19 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 8.6 Hz, 2H), 7.93 (s, 1H), 8.12 (d, J = 8.6 Hz, 2H), 8.36 (d, J = 8.6 Hz, 2H), 8.51 (d, J = 8.6 Hz, 2H), 9.48 (d, J = 7.8 Hz, 1H); 10.05 (s, 1H).

3-(4-Bromophenyl)-1-[(*E*)-1-(4-bromophenyl)-3-oxo-1-propenyl]-1*H*-4-pyrazolecarbaldehyde (4f). This compound was obtained as white solid (Dichloromethane), mp 198–199°C; ^{1}H-NMR ($CDCl_3$ 300 MHz): δ 7.23 (d, J = 7.8 Hz, 1H), 7.41 (d, J = 7.8 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.51–7.78 (m, 4H), 7.89 (s, 1H), 9.48 (d, J = 7.8 Hz, 1H), 9.95 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 119.2, 123.5, 124.6, 126.6, 128.1, 129.2, 130.4, 132.1, 132.2, 132.8, 136.2, 153.1, 154.6, 183.8, 191.1. *Anal*. Calcd. for $C_{19}H_{12}Br_2N_2O_2$: C, 49.60; H, 2.63; N, 6.09%. Found: C, 49.68; H, 2.67; N, 6.17%.

3-(2-Chlorophenyl)-1-[(*E*)-1-(2-chlorophenyl)-3-oxo-1-propenyl]-1*H*-4-pyrazolecarbaldehyde (4g). This compound was obtained as viscous oil; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.19 (d, J = 8.1 Hz, 1H), 7.43–7.65 (m, 8H), 7.78 (s, 1H), 9.38 (d, J = 8.1 Hz, 1H), 9.72 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 119.2, 124.1, 127.1, 127.6, 128.5, 129.6, 130.0, 130.8, 131.1, 131.9, 132.5, 132.7, 132.8, 133.4, 134.5, 151.4, 154.1, 184.7, 190.8.

3-(3-Methoxyphenyl)-1-[(*E*)-1-(3-methoxyphenyl)-3-oxo-1-propenyl]-1*H*-4-pyrazolecarbaldehyde (4h). This compound was obtained as white solid (Dichloromethane), mp 157–158°C;

^{1}H-NMR ($CDCl_3$, 300 MHz): δ 3.87 (s, 3H), 3.89 (s, 3H), 7.02–7.18 (m, 5H), 7.36–7.52 (m, 4H), 7.90 (s, 1H), 9.48 (d, J = 8.1 Hz, 1H), 9.97 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 55.4, 55.5, 113.9, 115.9, 116.2, 116.9, 118.7, 121.4, 122.9, 123.3, 129.9, 1305, 130.6, 131.7, 135.4, 154.3, 155.8, 159.9, 160.0, 184.7, 191.9. *Anal*. Calcd. for $C_{21}H_{18}N_2O_4$: C, 69.60; H, 5.01; N, 7.73%. Found: C, 69.68; H, 5.10; N, 7.82%.

3-(1-Naphthyl)-1-[(*E*)-1-(1-naphthyl)-3-oxo-1-propenyl]-1*H*-4-pyrazolecarbaldehyde (4i). This compound was obtained as white solid (Dichloromethane), mp 85–86°C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.44 (d, J = 8 Hz, 1H), 7.57–8.18 (m, 15H), 9.35 (d, J = 8 Hz, 1H), 9.56 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 120.0, 124.2, 124.6, 125.1, 125.2*, 126.4, 126.5, 127.2, 127.3, 127.8, 128.4, 128.6, 129.0, 129.1 130.1, 130.4, 131.7, 131.8, 132.0, 133.3, 133.7, 133.8, 153.4, 155.8, 185.2, 191.7 (*one carbon merged with other). *Anal*. Calcd. for $C_{27}H_{18}N_2O_2$: C, 80.58; H, 4.51; N, 6.96%. Found: C, 80.63; H, 4.59; N, 6.99%.

3-(2-Naphthyl)-1-[(*E*)-1-(2-naphthyl)-3-oxo-1-propenyl]-1*H*-4-pyrazolecarbaldehyde (4j). This compound was obtained as white solid (Dichloromethane), mp 155–156°C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.28 (d, J = 8.1 Hz, 1H), 7.55–8.10 (m, 14 H), 8.39 (s, 1H), 9.55 (d, J = 8.1 Hz, 1H), 10.05 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 119.3, 123.6, 125.8, 126.2, 126.5, 126.7, 127.2, 127.8*, 128.0, 128.5*, 128.6, 128.7, 128.8, 129.0, 129.5, 131.8, 132.6, 133.1, 133.8, 134.3, 136.0, 154.6, 155.8, 184.5, 191.9 (*one carbon merged with other). *Anal*. Calcd. for $C_{27}H_{18}N_2O_2$: C, 80.58; H, 4.51; N, 6.96%. Found: C, 80.67; H, 4.55; N, 7.01%.

3-(2-Methoxyphenyl)-1-[(E)-1-(2-methoxyphenyl)-3-oxo-1-propenyl]-1H-4-pyrazolecarbaldehyde (4k). This compound was obtained as white solid (Dichloromethane), mp 108–109°C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 3.80 (s, 3H), 3.82 (s, 3H), 7.02–7.17 (m, 5H), 7.37 (dd, J = 7.5, 1.5 Hz, 1H), 7.48 (td, J = 8.7, 1.5 Hz, 1H), 7.59 (td, J = 8.7 Hz, 1H), 7.64 (dd, J = 7.5, 1.5 Hz, 1H), 7.78 (s, 1H), 9.38 (d, J = 8.4 Hz, 1H), 9.69 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 55.4, 55.7, 111.1, 111.6, 118.0, 118.4, 119.7, 121.0, 121.2, 123.9, 131.2, 131.4, 132.2, 132.5, 133.1, 152.1, 153.4, 156.8, 157.7, 186.4, 192.1. *Anal*. Calcd. for $C_{21}H_{18}N_2O_4$: C, 69.60; H, 5.01; N, 7.73%. Found: C, 69.64; H, 5.06; N, 7.77%.

(*E*)-3-Chloro-3-(4-nitrophenyl)-2-propenal (5e). This compound was obtained as white solid (Dichloromethane), mp 75–76°C [20]; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.75 (d, J = 6.6 Hz, 1H), 7.92 (d, J = 9 Hz, 2H), 8.33 (d, J = 9.3 Hz, 2H), 10.25 (d, J = 6.9 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 121.0, 126.8, 128.2, 141.4, 148.9, 149.4, 190.6.

3-(4-Nitrophenyl)-1*H*-pyrazole (6e). This compound was obtained as white solid (Dichloromethane), mp 108–109 (192)°C [21]; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.25 (s, 1H), 6.77 (d, J = 1.8 Hz, 1H), 7.69 (d, J = 2.1 Hz, 1H), 7.98 (d, J = 8.7 Hz, 2H), 8.28 (d, J = 8.7 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 103.7, 124.1, 126.2, 130.9, 139.2, 147.2, 149.2. *Anal*. Calcd. for $C_9H_7N_3O_2$: C, 57.14; H, 3.73; N, 22.21%. Found: C, 57.25; H, 3.81; N, 22.30%.

3-(4-Nitrophenyl)-1*H*-pyrazole-4-carbaldehyde (7e). This compound was obtained as white solid (Dichloromethane), mp 189–190 (198–200)°C [19, 21]; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.00 (d, J = 8.4 Hz, 2H), 8.26–8.29 (m, 3H), 9.98 (s, 1H).

(*E*)-3-(4-Bromophenyl)-3-chloro-2-propenal (5f). This compound was obtained as viscous liquid [22]; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.66 (d, J = 6.9 Hz, 1H), 7.62 (d, J = 8.7 Hz, 2H), 7.82 (d, J = 8.7 Hz, 2H), 10.21 (d, J = 6.9 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 124.5, 128.5, 129.8, 131.9, 132.0, 150.9, 191.2.

Acknowledgments. The authors thank DST, New Delhi for assistance under the IRHPA program for the NMR facility. One of the authors (R.M.) thanks Madurai Kamaraj University for a research fellowship.

REFERENCES AND NOTES

[1] Windholz, M., Ed. The Merck Index, 9th ed.; Merck & Co.: Rahway, New Jersey, 1976; p 291.

[2] Sridhar, R.; Perumal, P. T; Etti, S.; Shanmugam, G.; Ponnuswamy, M. N.; Prabavathy, V. R.; Mathivanan, N. Bioorg Med Chem Lett 2004, 14, 6035.

[3] Wolff, M. E. Burger's Medicinal Chemistry, 4th ed.; Wiley: New York, 1980, p 291–296, 301–303.

[4] Garg, H. G.; Singhal, A.; Mathur, J. M. L. J Pharm Sci 1973, 62, 494.

[5] Abadi, A. H.; Eissa, A. A. H.; Hassan, G. S. Chem Pharm Bul 2003, 51, 838.

[6] Haufel, J.; Breitmaier, E. Angew Chem 1974, 13, 604.

[7] Wustrow, D. J.; Capiris, T.; Rubin, R.; Knobeldorf, J. A.; Zoski, K. T.; Heffiner, T. G.; Wise, L. D. Bioorg Med Chem Lett 1998, 8, 2067.

[8] Tsutomu, I.; Toshiaki, K.; Hitoshi, S.; Yoshinori, T.; Katsutoshi, I. Jpn Kokai Tokkyo Koho JP 01,106,866 [89, 106, 866] (Cl. C07D231/14), 24 Apr 1989, Appl. 87/261, 738, 19 Oct. 1987; pp 8; Chem Abstr 1989, 111, 194759h.

[9] Tsutomu, I.; Hideo, Y.; Toshiaki, K.; Hitoshi, S.; Yoshinori, T.; Katsutoshi, I. Jpn Kokai Tokkyo Koho JP 01,113,371[89, 113, 371] (Cl. C07D231/14), 02 May 1989, Appl. 87/266, 612, 23 Oct. 1987; pp 11; Chem Abstr 1989, 111, 214479x.

[10] Kira, M. A.; Nofal, Z. M.; Gadalla, K. Z. Tetrahedron Lett 1970, 11, 4215.

[11] Nanjundaswamy, H. M.; Pasha, M. A. Synth Commun 2007, 37, 3417.

[12] Nenajdenko, V. G.; Verseev, G. N.; Shastin, A. V.; Balenkova, E. S. J Fluorine Chem 2005, 126, 907.

[13] Mira, C.; Shlomo, R. Tetraheadron Lett 2006, 47, 763.

[14] Shastin, A. V.; Korotchenko, V. N.; Varseev, G. N.; Nenajdenko, V. G.; Balenkova, E. S. Russ J Org Chem 2003, 39, 403.

[15] Miroslaw, G.; Jacek, M. Synth Commun 1999, 29, 4307.

[16] Love, B. E.; Tsai, L. Synth Commun 1992, 22, 3101.

[17] Ramesh, P.; Subbiahpandi, A.; Manikannan, R.; Muthusubramanian, S.; Ponnuswamy, M. N. Acta Cryst 2008, E64, o2243.

[18] Ramesh, P.; Subbiahpandi, A.; Manikannan, R.; Muthusubramanian, S.; Ponnuswamy, M. N. Acta Cryst 2008, E64, o1889.

[19] Cacchi, S.; Fabrizi, G.; Carangio, A. Synlett 1997, 959.

[20] Rappoport, Z.; Gazit, A. J Org Chem 1986, 51, 4112.

[21] Lebedev, A. V.; Lebedeva, A. B.; Sheludyakov, V. D.; Kovaleva, E. A.; Ustinova, O. L.; Kozhevnikov, I. B. Russ J Gen Chem 2005, 75, 782.

[22] Prim, D.; Joseph, D.; Kirsch, G. Phosphorus Sulfur Silicon Relat Elem 1994, 91, 137.