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The chemistry of α,β-ditosyloxyketones: new and convenient route for the synthesis of 1,4,5-trisubstituted pyrazoles from α,β-chalcone ditosylates

Om Prakash [a,*], Deepak Sharma [a], Raj Kamal [a], Rajesh Kumar [b], Reshmi R. Nair [a]

[a] Department of Chemistry, Kurukshetra University, Kurukshetra 136119, Haryana, India
[b] Post Graduate Department of Chemistry, M.L.N. College, Yamuna Nagar-135001, Haryana, India

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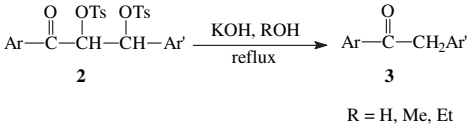
ABSTRACT

The reaction of α,β-chalcone ditosylates with various reagents such as phenylhydrazine hydrochloride, semicarbazide hydrochloride and thiosemicarbazide in suitable conditions leads to 1,2-aryl shift, thereby providing a novel route for the synthesis of 1,4,5-trisubstituted pyrazoles.

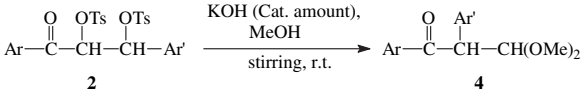
1. Introduction

α-Tosyloxyketones have been found to behave analogous to α-haloketones in most of their chemical transformations. A great deal of work from our research group and others has emphasized the advantages of α-tosyloxyketones over α-haloketones.[1,2] On the other hand while the chemistry of α,β-chalcone dibromides **1** is well explored,[3] the reactivity mode of α,β-chalcone ditosylates **2** has been studied recently in our research group for the first time. The aim of the study is to explore the potential of α,β-chalcone ditosylates **2** in organic synthesis with particular emphasis on comparison with their dibromo analogs.

In our preliminary study it has been reported that the reaction of α,β-chalcone ditosylates **2** with 2 equiv of potassium hydroxide leads to 1,2-aryl shift and carbon–carbon bond cleavage thereby providing new route for the synthesis of desoxybenzoins **3** Eq (1).[4] Using catalytic amount of potassium hydroxide at room temperature, the reaction however affords α-aryl-β-ketoaldehyde dimethylacetals **4** Eq. (2).[4] These results have shown that the reactivity pattern of α,β-chalcone ditosylates **2** is quite different from α,β-chalcone dibromides **1**, which are known to undergo elimination under the similar reaction conditions.[3b]



(1)

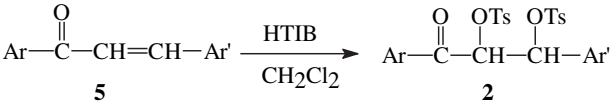


(2)

Prompted by foregoing observations coupled with our interest in the synthesis of heterocyclic compounds, we now became interested to investigate the reactivity of α,β-chalcone ditosylates **2** with phenylhydrazine hydrochloride, semicarbazide hydrochloride and thiosemicarbazide. The results obtained from this study have offered a novel convenient route for the synthesis of 1,4,5-trisubstituted pyrazoles.

2. Results and discussion

Thus, various derivatives of α,β-chalcone ditosylates **2aa–2dh** were prepared by the treatment of respective chalcone with



Scheme 1. α,β-Ditosyloxylation of chalcones using HTIB.

* Corresponding author. Tel.: +91 1744 234366; fax: +91 1744 238277.
E-mail address: dromprakash50@rediffmail.com (O. Prakash).

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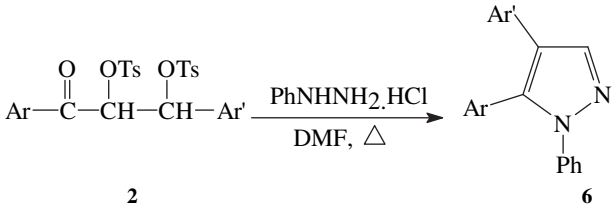
Table 1
Physical data of α,β-chalcone ditosylates **2**

Entry	2	Ar	Ar′	Mpt.	Yield[a] (%)
1	**aa**	C_6H_5	C_6H_5	134–136(136–138)[6]	65
2	**ab**	C_6H_5	4-MeC_6H_4	114–115	61
3	**ac**	C_6H_5	4-$MeOC_6H_4$	138–140	71
4	**ae**	C_6H_5	4-BrC_6H_4	110–112	62
5	**af**	C_6H_5	2-thienyl	120–122	62
6	**ag**	C_6H_5	3-methyl-2-thienyl	146–147	61
7	**bb**	4-MeC_6H_4	4-MeC_6H_4	128–129	68
8	**bf**	4-MeC_6H_4	2-thienyl	138–139	67
9	**bg**	4-MeC_6H_4	3-methyl-2-thienyl	118–120	67
10	**bh**	4-MeC_6H_4	5-methyl-2-thienyl	135–136	68
11	**ca**	4-$MeOC_6H_4$	C_6H_5	132–133	62
12	**cc**	4-$MeOC_6H_4$	4-$MeOC_6H_4$	93–94	69
13	**cf**	4-$MeOC_6H_4$	2-thienyl	154–155	65
14	**cg**	4-$MeOC_6H_4$	3-methyl-2-thienyl	110–112	64
15	**da**	4-ClC_6H_4	C_6H_5	108–110	60
16	**df**	4-ClC_6H_4	2-thienyl	128–130	57
17	**dg**	4-ClC_6H_4	3-methyl-2-thienyl	148–150	58
18	**dh**	4-ClC_6H_4	5-methyl-2-thienyl	144–145	62

[a] Yield (%) of the products was calculated with respect to the corresponding chalcones.

hydroxy(tosyloxy)iodobenzene (HTIB)[5] according to the method of Koser[6] (Scheme 1)[4](Table 1).

We first examined the reaction of α,β-chalcone ditosylates **2** with phenylhydrazine hydrochloride with a view to compare their reactivity with α,β-chalcone dibromides **1**.[7] Thus α,β-chalcone ditosylate **2aa** (0.001 mol) was refluxed with phenylhydrazine hydrochloride (0.002 mol) in dimethylformamide (25 mL) for 3 h. The usual work up of the reaction afforded single colorless product in 76% yield. The melting point and spectral data (IR, NMR) of the product matched with the structure of 1,4,5-triphenylpyrazole (**6aa**). To study the scope of reaction a wide range of substituted α,β-chalcone ditosylates (**2ab**–**2dh**) were treated with phenylhydrazine hydrochloride under similar conditions. It was observed that each of the derivatives behaves in a similar manner and affords corresponding pyrazole (**6ab**–**6dh**) in good yield (52–68%) (Scheme 2, Table 2).



2 6

Scheme 2. Synthesis of 1,4,5-triarylpyrazoles from α,β-chalcone ditosylates.

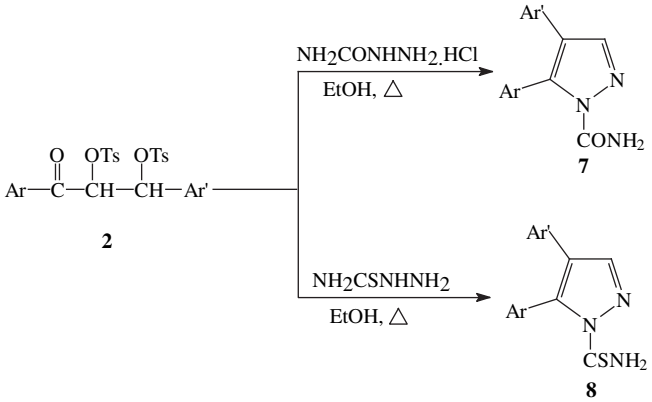
Table 2
Physical data of 1,4,5-triarylpyrazoles **6**

Entry	6	Mpt.	Yield[a] (%)
1	**aa**	209–210(210–211)[8]	76
2	**ab**	167–168(168–169)[9]	68
3	**ac**	151(150–151)[8]	65
4	**ae**	189–190	64
5	**af**	210–212	68
6	**ag**	120–122	54
7	**bb**	186–187	63
8	**bf**	175–176	62
9	**bg**	110–112	65
10	**bh**	163–164	63
11	**ca**	181–182(182–183)[8]	62
12	**cc**	172–173(173)[8]	64
13	**cf**	138–140	64
14	**cg**	88–90	62
15	**da**	202(201–202)[9]	64
16	**df**	140–142	58
17	**dg**	150–152	57
18	**dh**	144–145	52

[a] Yield (%) of the products was calculated with respect to the corresponding α,β-chalcone ditosylates.

In the light of encouraging results obtained from the studies on the reactivity of α,β-chalcone ditosylates **2** with phenylhydrazine hydrochloride, it was thought of significant interest to examine the reactivity of **2** with other nucleophilic carbonyl reagents namely, semicarbazide hydrochloride and thiosemicarbazide. Based on our previous observations, it was anticipated that the reaction of **2** with semicarbazide hydrochloride and thiosemicarbazide might afford 4,5-disubstituted pyrazole-1-carboxamides and 4,5-disubstituted pyrazole-1-thiocarboxamides, respectively.

The reaction of α,β-chalcone ditosylate **2aa** was carried out separately with semicarbazide hydrochloride and thiosemicarbazide under the conditions described in Elba's work[10] on the reaction of α,β-dibromochalcones. The reactions occurred according to our expectation and 4,5-diphenylpyrazole-1-carboxamide (**7aa**) and 4,5-diphenylpyrazole-1-thiocarboxamide (**8aa**) were obtained in good yields. Using the similar conditions, the other derivatives of α,β-chalcone ditosylate (**2ab**,**2ac**,**2ae**,**2da**) also gave the corresponding 4,5-diarylpyrazole-1-carboxamides (**7ab**,**7ac**,**7ae**,**7da**). Similarly other 4,5-diarylpyrazole-1-thiocarboxamide derivatives (**8ab**,**8ac**,**8da**) were prepared in good yield from corresponding α,β-chalcone ditosylates (**2ab**,**2ac**,**2da**) (Scheme 3, Tables 3 and 4). The results clearly indicated that α,β-chalcone ditosylates **2** behave in a similar manner with different derivatives of carbonyl reagents and provide a general approach for the synthesis of 1,4,5-trisubstituted pyrazoles (**6**–**8**).



Scheme 3. Synthesis of 4,5-diarylpyrazole-1-carboxamides and 4,5-diarylpyrazole-1-thiocarboxamides from α,β-chalcone ditosylates.

Table 3
Physical data of 4,5-diarylpyrazole-1-carboxamides **7**

Entry	7	Mpt.	Yield[a] (%)
1	**aa**	155–156	62
2	**ab**	110–112	63
3	**ac**	97–98	65
4	**ae**	140–142	53
5	**da**	139–140	58

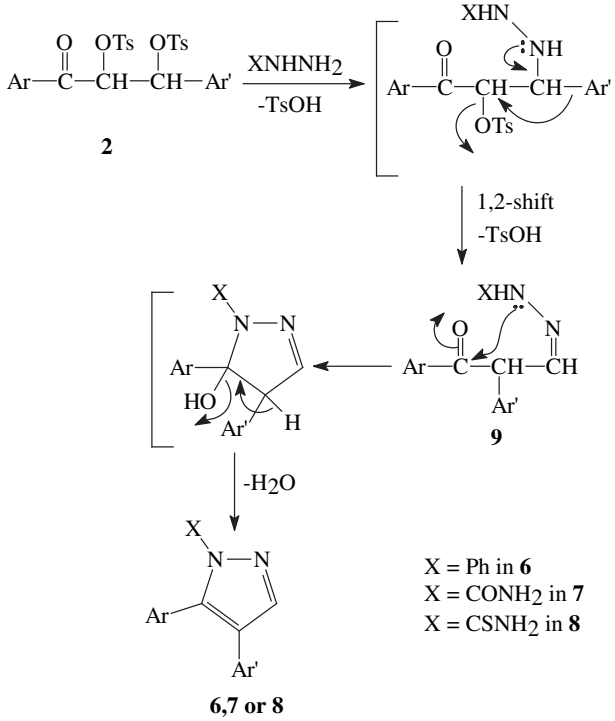
[a] Yield (%) of the products was calculated with respect to the corresponding α,β-chalcone ditosylates.

Table 4
Physical data of 4,5-diarylpyrazole-1-thiocarboxamides **8**

Entry	8	Mpt.	Yield[a] (%)
1	**aa**	160–162	61
2	**ab**	88–90	63
3	**ac**	110–112	65
4	**da**	148–149	59

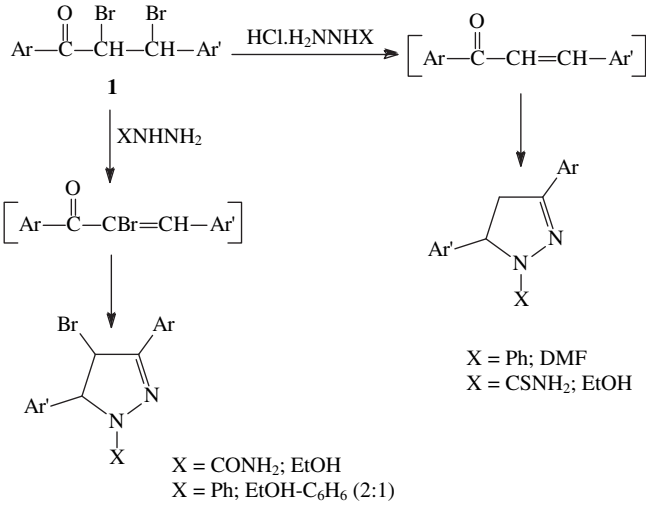
[a] Yield (%) of the products was calculated with respect to the corresponding α,β-chalcone ditosylates.

Although the mechanism of conversion **2**→**6**–**8** is not certain, the exclusive formation of 1,4,5-trisubstituted pyrazoles **6**–**8** clearly reveals that the conversion involves 1,2-aryl migrations. The mechanism of this migration is very closely related to a pinacol rearrangement and is outlined in Scheme 4. The first step of the reaction is probably the nucleophilic substitution of –OTs group, situated at position 3, by $-NH_2$ group of reagent. The substitution is followed by 1,2-aryl migration, resulting in the formation of intermediate **9**, which subsequently undergoes cyclization in usual manner to afford rearranged product. Of the various reported examples of rearrangement of this sort, two important ones are: (i) bistosyloxylation of 1,1-diphenylethylene leading to desoxybenzoin[6] (ii) copper-catalysed rearrangement of hydroxyketones.[11]



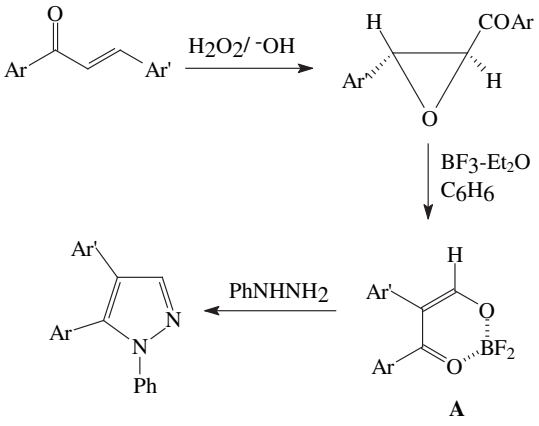
Scheme 4. Plausible mechanistic pathway for the formation of 1,4,5-trisubstituted pyrazoles **6**–**8**.

It is interesting to note that bis-brominated homologs of these substrates were never reported to undergo such rearrangement.[7,10,12,13] Instead, the reactions of α,β-chalcone dibromides **1** with phenylhydrazine hydrochloride, semicarbazide hydrochloride and thiosemicarbazide are known to give pyrazolines[7,10] or 4-bromrpyrazolines.[10,12] The reactions have been proposed to occur through in situ formation of chalcones or α-bromochalcones as intermediates depending upon the reaction conditions (Scheme 5).



Scheme 5.

It is also worthwhile to mention that synthetic and structural studies on 1,4,5-trisubstituted pyrazoles in literature are limited. One of the literature reports involves three-step synthesis of 1,4,5-triarylpyrazoles, starting from respective chalcones. Chalcones are first converted to epoxides using $H_2O_2/^-OH$, then treated with BF_3–Et_2O to get rearrangement and finally reaction with hydrazine affords desired pyrazoles (Scheme 6).[9] Considering the difficulty to access 3-oxo-2,3-diarylpropanals of the type **A**, this study provides an alternative and convenient route to 1,4,5-trisubstituted pyrazoles.



Scheme 6.

3. Conclusion

It is evident from the study that unlike α-haloketones and α-tosyloxyketones, which are analogous to each other in their chemical reactions the reactivity pattern of α,β-chalcone ditosylates **2** is quite different from α,β-chalcone dibromides **1**. The actual reason for this remarkable difference in the reactivity pattern is not known yet. Detail investigations dealing with comparative study are still going on. Finally, the noteworthy features of the report on the comparison of reactivity of α,β-chalcone ditosylates **2** and dibromo analogs **1** are:

1. It offers novel route for the synthesis of various 1,4,5-trisubstituted pyrazoles.

2. All the α,β-chalcone ditosylates behave in similar manner on their reaction with phenylhydrazine hydrochloride, semicarbazide hydrochloride and thiosemicarbazide.
3. The newly developed route involves simple experimentation with good yields.
4. There is possibility of using α,β-chalcone ditosylate derivatives to effect selective transformations, which are otherwise not possible through α,β-chalcone dibromides.

4. Experimental

4.1. General

Melting points were taken in open capillaries and are uncorrected. IR spectra were recorded on Perkin–Elmer IR1800 spectrophotometer. The ^{1}H NMR spectra were recorded on Bruker 300 MHz instrument. The chemical shifts are expressed in ppm units downfield from an internal TMS standard. Elemental analyses were carried out in Perkin–Elmer 2400 instrument. All commercially available reagents were used as-received. Chalcones **5** were synthesized according to literature procedures.[14–19]

4.2. Preparation of α,β-chalcone ditosylates 2

General procedure: To a solution of chalcone (**5aa**, 1.04 g, 0.005 mol) in dichloromethane (40 mL) was added [hydroxy (tosyloxy)iodo]benzene (HTIB) (3.92 g, 0.01 mol). The resulting mixture was allowed to stir at 40–42 °C. HTIB was highly insoluble in dichloromethane, but gradually disappeared as the reaction proceeded. The stirring was allowed to continue for about 16–18 h. Then the solvent was evaporated in vacuo. The gummy mass so obtained was triturated with pet ether (Bp. 60–80 °C) to remove iodobenzene. The colorless solid obtained was thoroughly washed with water to remove *p*-toluenesulphonic acid formed as byproduct. The solid then recrystallized with acetonitrile to give the pure chalcone ditosylate **2aa** (yield 65%, 1.78 g). Other derivatives were prepared in a similar manner. Compounds **2aa**–**ae**, **ca**, **da** were previously reported, while **2af**–**ag**, **bb**–**bh**, **cc**–**cg**, **df**–**dh** are new compounds.

*4.2.1. 1,3-Diphenyl-2,3-ditosyloxypropanone (**2aa**)*[4]. IR (ν_{max}, in KBr): 1681 cm^{-1} (CO stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.43 (s, 3H, CH_3); 2.46 (s, 3H, CH_3); 5.03 (d, 1H, CH, J=8.1 Hz); 6.96 (d, 1H, CH, J=8.1 Hz); 7.04–7.05 (m, 2H, ArH); 7.18–7.24 (m, 4H, ArH); 7.30–7.38 (m, 3H, ArH); 7.41–7.44 (m, 2H, ArH); 7.49–7.50 (m, 3H, ArH); 7.71–7.73 (m, 2H, ArH); 7.79–8.21 (m, 2H, ArH).

*4.2.2. 3-(4-Methylphenyl)-1-phenyl-2,3-ditosyloxypropanone (**2ab**)*[4]. IR (ν_{max}, in KBr): 1682 cm^{-1} (CO stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.18 (s, 3H, CH_3); 2.34 (s, 6H, CH_3); 5.03 (d, 1H, CH, J=8.1 Hz); 6.84–6.92 (m, 3H, ArH); 6.95 (d, 1H, CH, J=8.1 Hz); 7.0–7.12 (m, 4H, ArH); 7.26–7.30 (m, 3H, ArH); 7.39–7.42 (m, 3H, ArH); 7.60–7.72 (m, 4H, ArH). Elemental analysis: Calculated for $C_{30}H_{28}O_7S_2$; C 63.8, H 4.9; Found C 62.6, H 4.2.

*4.2.3. 3-(4-Methoxyphenyl)-1-phenyl-2,3-ditosyloxypropanone (**2ac**)*[4]. IR (ν_{max}, in KBr): 1683 cm^{-1} (CO stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.42 (s, 3H, CH_3); 2.43 (s, 3H, CH_3); 3.75 (s, 3H, OCH_3); 5.00 (d, 1H, CH, J=8.1 Hz); 6.65–6.68 (m, 2H, ArH); 6.98 (d, 1H, CH, J=8.1 Hz); 7.09–7.16 (m, 4H, ArH); 7.30–7.36 (m, 4H, ArH); 7.43–7.47 (m, 3H, ArH); 7.71–7.80 (m, 4H, ArH). Elemental analysis: Calculated for $C_{30}H_{28}O_8S_2$; C 62.0, H 4.8; Found C 61.8, H 4.3.

*4.2.4. 3-(4-Bromophenyl)-1-phenyl-2,3-ditosyloxypropanone (**2ae**)*[4]. IR (ν_{max}, in KBr): 1681 cm^{-1} (CO stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.43 (s, 3H, CH_3); 2.46 (s, 3H, CH_3); 5.03 (d, 1H, CH, J=8.1 Hz); 6.96 (d, 1H, CH, J=8.1 Hz); 7.04–7.05 (m, 2H, ArH); 7.18–7.24 (m, 4H, ArH); 7.30–7.38 (m, 3H, ArH); 7.41–7.44 (m, 2H, ArH); 7.49–7.50 (m, 2H, ArH); 7.71–7.73 (m, 2H, ArH); 7.79–8.21 (m, 2H, ArH). Elemental analysis: Calculated for $C_{29}H_{25}O_7S_2Br$; C 55.3, H 3.9; Found C 54.8, H 3.8.

*4.2.5. 1-Phenyl-3-(2-thienyl)-2,3-ditosyloxypropanone (**2af**)*. IR (ν_{max}, in KBr): 1678 cm^{-1} (CO stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.42 (s, 3H, CH_3); 2.44 (s, 3H, CH_3); 5.32 (d, 1H, CH, J=8.1 Hz); 6.93 (d, 1H, CH, J=8.1 Hz); 6.84 (dd, 1H, CH, J=3.6 Hz); 6.86 (d, 1H, CH, J=3.6 Hz); 7.15 (d, 1H, CH, J=3.6 Hz); 7.17–7.24 (m, 4H, ArH); 7.34–7.40 (m, 2H, ArH); 7.46–7.60 (m, 4H, ArH); 7.67–7.77 (m, 3H, ArH). Elemental analysis: Calculated for $C_{27}H_{24}O_7S_3$; C 58.27, H 4.32; Found C 59.31, H 5.27.

*4.2.6. 3-(3-Methyl-2-thienyl)-1-phenyl-2,3-ditosyloxypropanone (**2ag**)*. IR (ν_{max}, in KBr): 1678 cm^{-1} (CO stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.19 (s, 3H, CH_3); 2.43 (s, 3H, CH_3); 2.45 (s, 3H, CH_3); 5.34 (d, 1H, CH, J=8.1 Hz); 6.63 (d, 1H, CH, J=5.1 Hz); 6.92 (d, 1H, CH, J=8.1 Hz); 7.10 (d, 1H, CH, J=5.1 Hz); 7.12–7.13 (m, 3H, ArH); 7.24–7.27 (m, 4H, ArH); 7.53–7.64 (d, 4H, ArH); 7.75–7.76 (m, 2H, ArH. Elemental analysis: Calculated for $C_{28}H_{26}O_7S_3$; C 58.95, H 4.56; Found C 59.37, H 4.64).

*4.2.7. 1,3-Di(4-methylphenyl)-2,3-ditosyloxypropanone (**2bb**)*. IR (ν_{max}, in KBr): 1681 cm^{-1} (CO stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.18 (s, 3H, CH_3); 2.20 (s, 3H, CH_3); 2.34 (s, 6H, CH_3); 5.03 (d, 1H, CH, J=8.1 Hz); 6.84–6.92 (m, 3H, ArH); 6.95 (d, 1H, CH, J=8.1 Hz); 7.00–7.12 (m, 4H, ArH); 7.26–7.30 (m, 3H, ArH); 7.39–7.42 (m, 3H, ArH); 7.60–7.72 (m, 3H, ArH). Elemental analysis: Calculated for $C_{31}H_{30}O_7S_2$; C 64.3, H 5.2; Found C 63.7, H 4.7.

*4.2.8. 1-(4-Methylphenyl)-3-(2-thienyl)-2,3-ditosyloxypropanone (**2bf**)*. IR (ν_{max}, in KBr): 1681 cm^{-1} (CO stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.42 (s, 3H, CH_3); 2.43 (s, 3H, CH_3); 2.46 (s, 3H, CH_3); 5.30 (d, 1H, CH, J=8.1 Hz); 6.84 (dd, 1H, CH, J=3.6 Hz); 6.86 (d, 1H, CH, J=3.6 Hz); 7.01 (d, 1H, CH, J=8.1 Hz); 7.15 (d, 1H, CH, J=3.6 Hz); 7.17–7.27 (m, 4H, ArH); 7.46–7.60 (m, 4H, ArH); 7.67–7.77 (m, 4H, ArH). Elemental analysis: Calculated for $C_{28}H_{26}O_7S_3$; C 58.95, H 4.56; Found C 59.27, H 4.67.

*4.2.9. 1-(4-Methylphenyl)-3-(3-methyl-2-thienyl)-2,3-ditosyloxypropanone (**2bg**)*. IR (ν_{max}, in KBr): 1681 cm^{-1} (CO stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.19 (s, 3H, CH_3); 2.42 (s, 3H, CH_3); 2.44 (s, 3H, CH_3); 2.46 (s, 3H, CH_3); 5.36 (d, 1H, CH, J=8.1 Hz); 6.64 (d, 1H, CH, J=5.1 Hz); 7.01 (d, 1H, CH, J=8.1 Hz); 7.10 (d, 1H, CH, J=5.1 Hz); 7.23–7.30 (m, 4H, ArH); 7.48–7.56 (m, 4H, ArH); 7.62–7.71 (m, 4H, ArH). Elemental analysis: Calculated for $C_{29}H_{28}O_7S_3$; C 59.58, H 4.79; Found C 60.33, H 4.85.

*4.2.10. 1-(4-Methylphenyl)-3-(5-methyl-2-thienyl)-2,3-ditosyloxypropanone (**2bh**)*. IR (ν_{max}, in KBr): 1681 cm^{-1} (CO stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.32 (s, 3H, CH_3); 2.34 (s, 3H, CH_3); 2.40 (s, 3H, CH_3); 2.42 (s, 3H, CH_3); 5.12 (d, 1H, CH, J=8.1 Hz); 6.41 (d, 1H, CH, J=3.3 Hz); 6.65 (d, 1H, CH, J=3.3 Hz); 6.87 (d, 1H, CH, J=8.1 Hz); 7.13–7.21 (m, 4H, ArH); 7.55–7.61 (m, 4H, ArH); 7.62–7.71 (m, 4H, ArH). Elemental analysis: Calculated for $C_{29}H_{28}O_7S_3$; C 59.58, H 4.79; Found C 60.33, H 5.39.

*4.2.11. 1-(4-Methoxyphenyl)-3-phenyl-2,3-ditosyloxypropanone (**2ca**)*[4]. IR (ν_{max}, in KBr): 1674 cm^{-1} (CO stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.41 (s, 3H, CH_3); 2.42 (s, 3H, CH_3); 3.81 (s, 3H, OCH_3); 5.00 (d, 1H, CH, J=8.1 Hz); 6.79–6.81 (m, 2H, ArH); 7.00 (d, 1H, CH, J=8.1 Hz); 7.14–7.22 (m, 8H, ArH); 7.43–7.45 (m, 3H, ArH); 7.70–7.74 (m, 4H, ArH). Elemental analysis: Calculated for $C_{30}H_{28}O_8S_2$; C 62.0, H 4.8; Found C 61.5, H 4.2.

*4.2.12. 1,3-Di(4-methoxyphenyl)-2,3-ditosyloxypropanone (**2cc**)*. IR (ν_{max}, in KBr): 1674 cm^{-1} (CO stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ):

2.41 (s, 3H, CH_3); 2.43 (s, 3H, CH_3); 3.75 (s, 3H, OCH_3); 3.81 (s, 3H, OCH_3); 4.95 (d, 1H, CH, *J*=8.1 Hz); 6.64–6.67 (m, 2H, ArH); 6.67–6.81 (m, 2H, ArH); 6.97 (d, 1H, CH, *J*=8.1 Hz); 7.09–7.15 (m, 4H, ArH); 7.43–7.46 (m, 3H, ArH); 7.69–7.8 (m, 3H, ArH); 7.95–7.98 (m, 2H, ArH). Elemental analysis: Calculated for $C_{31}H_{30}O_9S_2$; C 60.9, H 4.9; Found C 60.5, H 4.8.

*4.2.13. 1-(4-Methoxyphenyl)-3-(2-thienyl)-2,3-ditosyloxypropanone (**2cf**).* IR (ν_{max}, in KBr): 1680 cm^{-1} (CO stretch) ^1H NMR ($CDCl_3$, 300 MHz, δ): 2.42 (s, 3H, CH_3); 2.44 (s, 3H, CH_3); 3.83 (s, 3H, OCH_3); 5.31 (d, 1H, CH, *J*=8.1 Hz); 6.83 (dd, 1H, CH, *J*=3.6 Hz); 6.85 (d, 1H, CH, *J*=3.6 Hz); 7.01 (d, 1H, CH, *J*=8.1 Hz); 7.16 (d, 1H, CH, *J*=3.6 Hz); 7.17–7.27 (m, 4H, ArH); 7.46–7.60 (m, 4H, ArH); 7.67–7.77 (m, 4H, ArH). Elemental analysis: Calculated for $C_{28}H_{26}O_8S_3$; C 57.34, H 4.44; Found C 58.27, H 5.12.

*4.2.14. 1-(4-Methoxyphenyl)-3-(3-methyl-2-thienyl)-2,3-ditosyloxypropanone (**2cg**).* IR (ν_{max}, in KBr): 1680 cm^{-1} (CO stretch) ^1H NMR ($CDCl_3$, 300 MHz, δ): 2.19 (s, 3H, CH_3); 2.43 (s, 3H, CH_3); 2.44 (s, 3H, CH_3); 3.84 (s, 3H, OCH_3); 5.36 (d, 1H, CH, *J*=8.1 Hz); 6.64 (d, 1H, CH, *J*=5.1 Hz); 7.01 (d, 1H, CH, *J*=8.1 Hz); 7.10 (d, 1H, CH, *J*=5.1 Hz); 7.21–7.31 (m, 4H, ArH); 7.45–7.56 (m, 4H, ArH); 7.69–7.72 (m, 4H, ArH). Elemental analysis: Calculated for $C_{29}H_{28}O_8S_3$; C 58.00, H 4.67; Found C 58.72, H 4.70.

*4.2.15. 1-(4-Chlorophenyl)-3-phenyl-2,3-ditosyloxypropanone (**2da**)*[4]. IR (ν_{max}, in KBr): 1682 cm^{-1} (CO stretch) ^1H NMR ($CDCl_3$, 300 MHz, δ): 2.42 (s, 3H, CH_3); 2.43 (s, 3H, CH_3); 4.9 (d, 1H, CH, *J*=8.1 Hz); 6.9 (d, 1H, CH, *J*=8.1 Hz); 7.01–7.15 (m, 6H, ArH); 7.26–7.28 (m, 5H, ArH); 7.42–7.45 (m, 2H, ArH); 7.61–7.64 (m, 2H, ArH); 7.77–7.80 (m, 2H, ArH). Elemental analysis: Calculated for $C_{29}H_{25}O_7S_2Cl$; C 59.5, H 4.2; Found C 59.4, H 4.0.

*4.2.16. 1-(4-Chlorophenyl)-3-(2-thienyl)-2,3-ditosyloxypropanone (**2df**).* IR (ν_{max}, in KBr): 1674 cm^{-1} (CO stretch) ^1H NMR ($CDCl_3$, 300 MHz, δ): 2.42 (s, 3H, CH_3); 2.46 (s, 3H, CH_3); 5.31 (d, 1H, CH, *J*=8.1 Hz); 6.83 (dd, 1H, CH, *J*=3.6 Hz); 6.85 (d, 1H, CH, *J*=3.6 Hz); 7.01 (d, 1H, CH, *J*=8.1 Hz); 7.14 (d, 1H, CH, *J*=3.6 Hz); 7.31 (d, 2H, ArH, *J*=8.4 Hz); 7.17–7.27 (m, 4H, ArH); 7.53 (d, 2H, ArH, *J*=8.4 Hz); 7.67–7.78 (m, 4H, ArH). Elemental analysis: Calculated for $C_{27}H_{23}O_7S_3Cl$; C 54.82, H 3.89; Found C 55.32, H 4.27.

*4.2.17. 1-(4-Chlorophenyl)-3-(3-methyl-2-thienyl)-2,3-ditosyloxypropanone (**2dg**).* IR (ν_{max}, in KBr): 1674 cm^{-1} (CO stretch) ^1H NMR ($CDCl_3$, 300 MHz, δ): 2.19 (s, 3H, CH_3); 2.42 (s, 3H, CH_3); 2.43 (s, 3H, CH_3); 5.36 (d, 1H, CH, *J*=8.1 Hz); 6.64 (d, 1H, CH, *J*=5.1 Hz); 7.01 (d, 1H, CH, *J*=8.1 Hz); 7.10 (d, 1H, CH, *J*=5.1 Hz); 7.23–7.31 (m, 4H, ArH); 7.33 (d, 2H, ArH, *J*=8.4 Hz); 7.57 (d, 2H, ArH, *J*=8.4 Hz); 7.72–7.73 (m, 4H, ArH). Elemental analysis: Calculated for $C_{28}H_{25}O_7S_3Cl$; C 55.62, H 4.13; Found C 56.20, H 4.39.

*4.2.18. 1-(4-Chlorophenyl)-3-(5-methyl-2-thienyl)-2,3-ditosyloxypropanone (**2dh**).* IR (ν_{max}, in KBr): 1675 cm^{-1} (CO stretch) ^1H NMR ($CDCl_3$, 300 MHz, δ): 2.35 (s, 3H, CH_3); 2.43 (s, 3H, CH_3); 2.44 (s, 3H, CH_3); 5.14 (d, 1H, CH, *J*=8.1 Hz); 6.45 (d, 1H, CH, *J*=3.3 Hz); 6.66 (d, 1H, CH, *J*=3.3 Hz); 6.88 (d, 1H, CH, *J*=8.1 Hz); 7.21–7.28 (m, 4H, ArH); 7.33 (d, 2H, ArH, *J*=8.4 Hz); 7.57 (d, 2H, ArH, *J*=8.4 Hz); 7.69–7.76 (m, 4H, ArH). Elemental analysis: Calculated for $C_{28}H_{25}O_7S_3Cl$; C 55.62, H 4.13; Found C 56.30, H 4.79.

4.3. Synthesis of 4,5-diaryl-1-phenylpyrazoles 6

General procedure: A mixture of chalcone ditosylate (**2aa**, 0.550 g, 0.001 mol) and phenylhydrazine hydrochloride (0.29 g, 0.002 mol) in dimethylformamide (25 mL) was refluxed for about 3 h. The reaction mixture was then poured onto ice-cold water. Resulting mixture was extracted with dichloromethane in three portions (3×50 mL). The organic extract was dried over anhydrous sodium sulfate and filtered. Evaporation of dichloromethane in vacuo gave the crude product, which was purified by column chromatography on silica gel (100–200 mesh) using pet ether–ethyl acetate as eluent to give pure pyrazole **6aa** (yield 76%, 0.224 g). Other derivatives were prepared in a similar manner. Compounds **6aa**–**ac**, **6ca**, **6cc**, **6da** are reported while others are new.

*4.3.1. 4-(4-Bromophenyl)-1,5-diphenylpyrazole (**6ae**).* IR (ν_{max}, in KBr): No peak in CO region ^1H NMR ($CDCl_3$, 300 MHz, δ): 7.02–7.05 (m, 2H); 7.18–7.23 (m, 4H); 7.25–7.29 (m, 5H); 7.32–7.34 (m, 3H); 7.9 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{21}H_{15}N_2Br$; C 67.0, H 3.9, N 7.4; Found C 66.8, H 3.4, N 7.1.

*4.3.2. 1,5-Diphenyl-4-(2-thienyl)pyrazole (**6af**).* IR (ν_{max}, in KBr): No peak in CO region ^1H NMR ($CDCl_3$, 300 MHz, δ): 6.87 (d, 1H, CH, *J*=3.6 Hz); 6.90 (dd, 1H, CH, *J*=3.6 Hz); 7.15 (d, 1H, CH, *J*=3.6 Hz); 7.28–7.38 (m, 10H, ArH); 7.95 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{19}H_{14}N_2S$; C 75.49, H 4.63, N 9.27; Found C 75.65, H 5.16, N 9.72.

*4.3.3. 4-(3-Methyl-2-thienyl)-1,5-diphenylpyrazole (**6ag**).* IR (ν_{max}, in KBr): No peak in CO region ^1H NMR ($CDCl_3$, 300 MHz, δ): 1.96 (s, 3H, CH_3); 6.83 (d, 1H, CH, *J*=5.1 Hz); 7.15 (d, 1H, CH, *J*=5.1 Hz); 7.23–7.33 (m, 10H, ArH); 7.84 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{20}H_{16}N_2S$; C 75.95, H 5.06, N 8.86; Found C 76.00, H 5.13, N 9.23.

*4.3.4. 4,5-Di(4-methylphenyl)-1-phenylpyrazole (**6bb**).* IR (ν_{max}, in KBr): No peak in CO region ^1H NMR ($CDCl_3$, 300 MHz, δ): 2.19 (s, 3H, CH_3); 2.20 (s, 3H, CH_3); 7.15–7.20 (m, 4H); 7.23–7.28 (m, 3H); 7.30–7.34 (m, 4H); 7.35–7.37 (m, 2H); 7.87 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{23}H_{20}N_2$; C 85.2, H 6.2, N 8.6; Found C 84.9, H 6.1, N 8.3.

*4.3.5. 5-(4-Methylphenyl)-1-phenyl-4-(2-thienyl)pyrazole (**6bf**).* IR (ν_{max}, in KBr): No peak in CO region ^1H NMR ($CDCl_3$, 300 MHz, δ): 2.37 (s, 3H, CH_3); 6.86 (d, 1H, CH, *J*=3.6 Hz); 6.88 (dd, 1H, CH, *J*=3.6 Hz); 7.11 (d, 1H, CH, *J*=3.6 Hz); 7.21–7.31 (m, 9H, ArH); 7.91 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{20}H_{16}N_2S$; C 75.95, H 5.06, N 8.86; Found C 76.02, H 5.26, N 8.92.

*4.3.6. 5-(4-Methylphenyl)-4-(3-methyl-2-thienyl)-1-phenylpyrazole (**6bg**).* IR (ν_{max}, in KBr): No peak in CO region ^1H NMR ($CDCl_3$, 300 MHz, δ): 1.97 (s, 3H, CH_3); 2.33 (s, 3H, CH_3); 6.83 (d, 1H, CH, *J*=5.1 Hz); 6.98 (d, 2H, ArH, *J*=8.1 Hz); 7.05 (d, 2H, ArH, *J*=8.1 Hz); 7.14 (d, 1H, CH, *J*=5.1 Hz); 7.30–7.37 (m, 5H, ArH); 7.82 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{21}H_{18}N_2S$; C 76.36, H 5.45, N 8.48; Found C 76.67, H 5.52, N 8.57.

*4.3.7. 5-(4-Methylphenyl)-4-(5-methyl-2-thienyl)-1-phenylpyrazole (**6bh**).* IR (ν_{max}, in KBr): No peak in CO region ^1H NMR ($CDCl_3$, 300 MHz, δ): 2.37 (s, 3H, CH_3); 2.41 (s, 3H, CH_3); 6.57 (d, 1H, CH, *J*=3.6 Hz); 6.65 (d, 1H, CH, *J*=3.6 Hz); 6.98 (d, 2H, ArH, *J*=8.1 Hz); 7.05 (d, 2H, ArH, *J*=8.1 Hz); 7.30–7.37 (m, 5H, ArH); 7.85 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{21}H_{18}N_2S$; C 76.36, H 5.45, N 8.48; Found C 76.52, H 5.54, N 8.75.

*4.3.8. 5-(4-Methoxyphenyl)-1-phenyl-4-(2-thienyl)pyrazole (**6cf**).* IR (ν_{max}, in KBr): No peak in CO region ^1H NMR ($CDCl_3$, 300 MHz, δ): 3.82 (s, 3H, OCH_3); 6.86 (d, 1H, CH, *J*=3.6 Hz); 6.88 (d, 2H, ArH, *J*=8.1 Hz); 6.89 (dd, 1H, CH, *J*=3.6 Hz); 7.13 (d, 2H, ArH, *J*=8.1 Hz); 7.15 (d, 1H, CH, *J*=3.6 Hz); 7.25–7.27 (m, 5H, ArH); 7.91 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{20}H_{16}N_2SO$; C 72.29, H 4.82, N 8.43; Found C 72.20, H 5.16, N 8.55.

*4.3.9. 5-(4-Methoxyphenyl)-4-(3-methyl-2-thienyl)-1-phenylpyrazole (**6cg**).* IR (ν_{max}, in KBr): No peak in CO region ^1H NMR

($CDCl_3$, 300 MHz, δ): 1.98 (s, 3H, CH_3); 3.81 (s, 3H, OCH_3); 6.78 (d, 2H, ArH, J=8.1 Hz); 6.83 (d, 1H, CH, J=5.1 Hz); 7.02 (d, 2H, ArH, J=8.1 Hz); 7.15 (d, 1H, CH, J=5.1 Hz); 7.31–7.38 (m, 5H, ArH); 7.82 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{21}H_{18}N_2SO$; C 72.83, H 5.20, N 8.09; Found C 73.30, H 5.21, N 8.21.

*4.3.10. 5-(4-Chlorophenyl)-1-phenyl-4-(2-thienyl)pyrazole (**6df**).* IR (ν_{max}, in KBr): No peak in CO region ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 6.88 (d, 1H, CH, J=3.6 Hz); 6.96 (dd, 1H, CH, J=3.6 Hz); 7.17 (d, 1H, CH, J=3.6 Hz); 7.19 (d, 2H, ArH, J=8.1 Hz); 7.26 (d, 2H, ArH, J=8.1 Hz); 7.27–7.28 (m, 5H, ArH); 7.94 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{19}H_{13}N_2SCl$; C 67.86, H 3.86, N 8.33; Found C 67.86, H 4.12, N 8.62.

*4.3.11. 5-(4-Chlorophenyl)-4-(3-methyl-2-thienyl)-1-phenylpyrazole (**6dg**).* IR (ν_{max}, in KBr): No peak in CO region ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 1.96 (s, 3H, CH_3); 6.84 (d, 1H, CH, J=5.1 Hz); 7.03 (d, 2H, ArH, J=8.1 Hz); 7.17 (d, 1H, CH, J=5.1 Hz); 7.23 (d, 2H, ArH, J=8.1 Hz); 7.29–7.35 (m, 5H, ArH); 7.81 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{20}H_{15}N_2SCl$; C 68.57, H 4.28, N 8.00; Found C 68.40, H 4.35, N 8.20.

*4.3.12. 5-(4-Chlorophenyl)-4-(5-methyl-2-thienyl)-1-phenylpyrazole (**6dh**).* IR (ν_{max}, in KBr): No peak in CO region ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.42 (s, 3H, CH_3); 6.58 (d, 1H, CH, J=3.6 Hz); 6.59 (d, 1H, CH, J=3.6 Hz); 7.03 (d, 2H, ArH, J=8.1 Hz); 7.23 (d, 2H, ArH, J=8.1 Hz); 7.29–7.35 (m, 5H, ArH); 7.85 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{20}H_{15}N_2SCl$; C 68.57, H 4.28, N 8.00; Found C 68.40, H 4.28, N 8.16.

4.4. Synthesis of 4,5-diarylpyrazole-1-carboxamides 7

General procedure: A mixture of chalcone ditosylate (**2aa**, 0.550 g, 0.001 mol), semicarbazide hydrochloride (0.167 g, 0.0015 mol) and sodium acetate (0.123 g, 0.0015 mol) in ethanol (30 mL) was refluxed for 2–3 h. The reaction mixture was then poured onto ice-cold water and extracted with dichloromethane in three portions (3×50 mL). The organic extract was dried over anhydrous sodium sulfate and filtered. Evaporation of dichloromethane in vacuo gave the crude product, which was purified by column chromatography on silica gel (100–200 mesh) using pet ether–ethyl acetate as eluent to afford pure pyrazole **7aa** (62%, 0.163 g). Other derivatives were prepared in similar manner.

*4.4.1. 4,5-Diphenylpyrazole-1-carboxamide (**7aa**).* IR (ν_{max}, in KBr, cm^{-1}): 1675 (CO stretch), 3390 (NH stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 6.93 (s, 2H, $CONH_2$); 7.25–7.34 (m, 4H, ArH); 7.44–7.48 (m, 6H, ArH); 7.68 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{16}H_{13}N_3O$; C 73.00, H 4.94, N 15.96; Found C 73.65, H 5.34, N 16.29.

*4.4.2. 4-(4-Methylphenyl)-5-phenylpyrazole-1-carboxamide (**7ab**).* IR (ν_{max}, in KBr, cm^{-1}): 1678 (CO stretch), 3378 (NH stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.38 (s, 3H, CH_3); 5.65 (s, 2H, $CONH_2$); 7.14 (d, 2H, ArH, J=8.1 Hz); 7.28–7.38 (m, 5H, ArH); 7.40 (d, 2H, ArH, J=8.1 Hz); 7.69 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{17}H_{15}N_3O$; C 73.65, H 5.41, N 15.16; Found C 74.28, H 5.58, N 15.92.

*4.4.3. 4-(4-Methoxyphenyl)-5-phenylpyrazole-1-carboxamide (**7ac**).* IR (ν_{max}, in KBr, cm^{-1}): 1665 (CO stretch), 3380 (NH stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 3.77 (s, 3H, OCH_3); 4.69 (s, 2H, $CONH_2$); 7.12 (d, 2H, ArH, J=8.1 Hz); 7.31–7.46 (m, 5H, ArH); 7.50 (d, 2H, ArH, J=8.1 Hz); 7.62 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{17}H_{15}N_3O_2$; C 69.62, H 5.12, N 14.33; Found C 70.14, H 6.22, N 15.12.

*4.4.4. 4-(4-Bromophenyl)-5-phenylpyrazole-1-carboxamide (**7ae**).* IR (ν_{max}, in KBr, cm^{-1}): 1671 (CO stretch), 3384 (NH stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 5.72 (s, 2H, $CONH_2$); 7.06 (d, 2H, ArH, J=8.1 Hz); 7.12 (d, 2H, ArH, J=8.1 Hz); 7.31–7.34 (m, 5H, ArH); 7.64 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{16}H_{12}N_3OBr$; C 56.14, H 3.51, N 12.28; Found C 56.78, H 4.28, N 13.28.

*4.4.5. 5-(4-Chlorophenyl)-4-phenylpyrazole-1-carboxamide (**7da**).* IR (ν_{max}, in KBr): 1675 cm^{-1} (CO stretch), 3372 cm^{-1} (NH stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 5.45 (s, 2H, $CONH_2$); 7.14 (d, 2H, ArH, J=8.1 Hz); 7.23 (d, 2H, ArH, J=8.1 Hz); 7.29–7.33 (m, 5H, ArH); 7.64 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{16}H_{12}N_3OCl$; C 64.64, H 4.04, N 14.14; Found C 65.32, H 4.84, N 14.94.

4.5. Synthesis of 4,5-diarylpyrazole-1-thiocarboxamides 8

General procedure: A mixture of chalcone ditosylate (**2aa**, 0.550 g, 0.001 mol) and thiosemicarbazide (0.136 g, 0.0015 mol) in ethanol (30 mL) was refluxed for 2–3 h. The reaction mixture was then poured onto ice-cold water. Resulting mixture was extracted with dichloromethane in three portions (3×50 mL). The organic extract was dried over anhydrous sodium sulfate and filtered. Evaporation of dichloromethane in vacuo gave the crude product, which was purified by column chromatography on silica gel (100–200 mesh) using pet ether–ethyl acetate as eluent to give pure pyrazole **8aa** (61%, 0.170 g). Other derivatives were prepared in similar manner.

*4.5.1. 4,5-Diphenylpyrazole-1-thiocarboxamide (**8aa**).* IR (ν_{max}, in KBr): 3295 cm^{-1} (NH stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 6.34 (s, 2H, $CSNH_2$); 7.24–7.28 (m, 5H, ArH); 7.34–7.38 (m, 2H, ArH); 7.55–7.59 (m, 3H, ArH); 7.78 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{16}H_{13}N_3S$; C 68.82, H 4.66, N 15.05; Found C 69.24, H 5.12, N 16.36

*4.5.2. 4-(4-Methylphenyl)-5-phenylpyrazole-1-thiocarboxamide (**8ab**).* IR (ν_{max}, in KBr): 3265 cm^{-1} (NH stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 2.38 (s, 3H, CH_3); 5.45 (s, 2H, $CSNH_2$); 7.14 (d, 2H, ArH, J=8.1 Hz); 7.26 (d, 2H, ArH, J=8.1 Hz); 7.49–7.58 (m, 5H, ArH); 7.69 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{17}H_{15}N_3S$; C 69.62, H 5.12, N 14.33; Found C 70.14, H 6.23, N 15.31

*4.5.3. 4-(4-Methoxyphenyl)-5-phenylpyrazole-1-thiocarboxamide (**8ac**).* IR (ν_{max}, in KBr): 3265 cm^{-1} (NH stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 3.84 (s, 3H, OCH_3); 5.02 (s, 2H, $CSNH_2$); 6.91 (d, 2H, ArH, J=8.1 Hz); 7.26 (d, 2H, ArH, J=8.1 Hz); 7.39–7.41 (m, 3H, ArH); 7.51–7.52 (m, 2H, ArH); 7.67 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{17}H_{15}N_3OS$; C 66.02, H 4.85, N 13.59; Found C 67.18, H 5.25, N 14.67.

*4.5.4. 5-(4-Chlorophenyl)-4-phenylpyrazole-1-thiocarboxamide (**8da**).* IR (ν_{max}, in KBr): 3271 cm^{-1} (NH stretch) ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 5.32 (s, 2H, $CSNH_2$); 7.23 (d, 2H, ArH, J=8.1 Hz); 7.32 (d, 2H, ArH, J=8.1 Hz); 7.38–7.40 (m, 3H, ArH); 7.44–7.46 (m, 2H, ArH); 7.72 (s, 1H, C_3–H). Elemental analysis: Calculated for $C_{16}H_{12}N_3SCl$; C 61.34, H 3.83, N 13.42; Found C 62.30, H 4.26, N 13.58.

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References and notes

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