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Graphical Abstract

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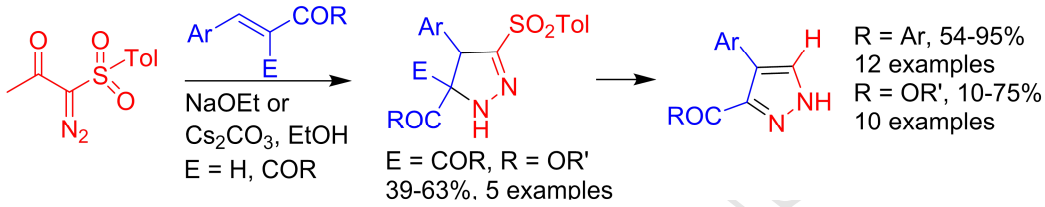

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ABSTRACT

A convenient method for the synthesis of 3-acylpyrazoles and pyrazole-3-carboxylates using diazosulfone as a reactive 1,3-dipole and a diazomethane equivalent is reported here. Chalcones, arylidenemalonates and other arylidene-1,3-dicarbonyls performed well as the dipolarophiles in the reaction with the diazosulfone which took place under simple base mediated conditions (Cs_2CO_3 or NaOEt in EtOH). In few cases, the initial cycloadducts, the intermediate pyrazoline derivatives, could also be isolated and characterized. The pyrazoline derivatives undergo an alkoxide mediated 1,4-elimination, viz. decarboxylation-detosylation to afford the pyrazole derivatives.

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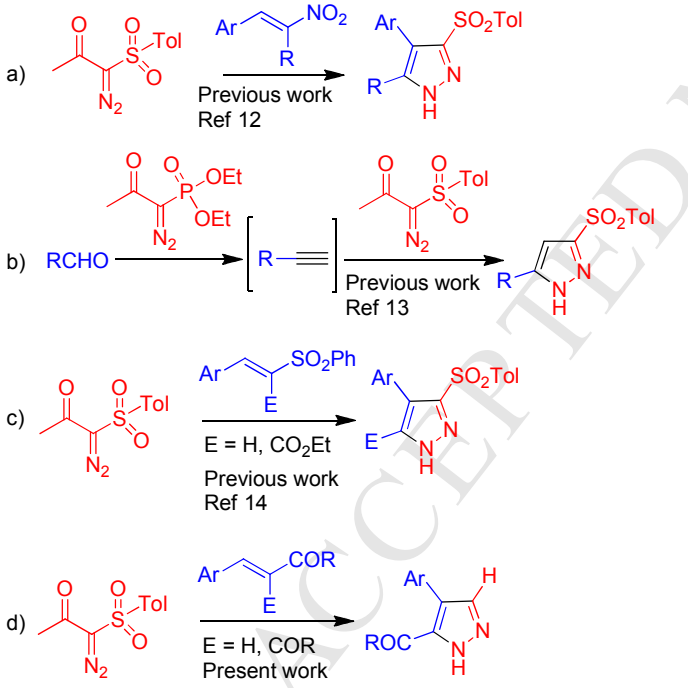
1. Introduction

Pyrazole is one of the most important N-heterocycles due to its wide occurrence, various applications and ease of synthesis.[1] Pyrazole moiety is present in several natural products and designed drug molecules.[2] Natural products such as withasomnine, pyrazofurin, formycin, fluviol etc and drug molecules such as Celecoxib, Lonazolac, Rimonabant, Viagra etc contain a pyrazole moiety.[2] Possible applications of other pyrazole derivatives in medicinal chemistry,[3] for instance, as anticancer, antitubercular, anti-obesity, anti-mycobacterial, anti-metabolite, anti-inflammatory and anti-microbial agents are highlighted in the recent literature.[4] Pyrazole derivatives are also employed in crop protection,[5] as ligands in synthesis[6] and as N-heterocyclic carbene precursors.[7]

General methods for the synthesis of pyrazoles[8] include 1,3-dipolar cycloaddition of diazo compounds with electron deficient alkenes/alkynes[9] and condensation of 1,3-difunctional compounds with hydrazines.[10] As for the synthesis of functionalized pyrazoles, we and others have demonstrated the application of α-diazo-β-ketophosphonate (Bestmann-Ohira reagent),[11] its corresponding sulfone[12-14] and carboxylate[15] analogs for the regioselective synthesis of pyrazoles bearing, respectively, phosphonate, sulfone and carboxylate functionalities.[16]

Although α-diazo-β-ketosulfone has been employed as a carbene precursor under metal catalysed conditions,[17] its application as a diazoalkane equivalent for cycloaddition with various electron deficient substrates such as nitroalkenes,[12] acetylenes,[13] vinyl sulfones and vinyl sulfonylcarboxylates[14] has been investigated only recently. These cycloadditions led to regioselective synthesis of sulfonylpyrazoles. However, similar reactions of diazosulfone with chalcone and alkylidenemalonate remain unreported.

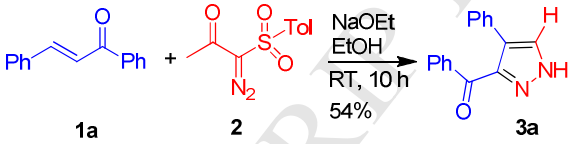


Scheme 1. Reaction of diazosulfone in the synthesis of pyrazoles

Interestingly, the sulfonyl group is retained in the products formed from α-diazo-β-ketosulfone and substrates such as nitroalkenes, acetylenes, vinyl sulfones and vinyl sulfonylcarboxylates (Schemes 1a-c).[12-14] This is because of the better leaving group ability of the dipolarophile derived electron withdrawing group (nitro or sulfonyl) in the intermediate pyrazoline. We envisioned that in the absence of a dipolarophile derived leaving group in the intermediate pyrazoline, the dipole derived sulfonyl group would undergo elimination (Scheme 1d). Therefore, substrates such as chalcones and alkylidenemalonates which do not have good leaving group were chosen for reaction with α-diazo-β-ketosulfone and demonstrate the above possibility. This would also be a novel application of α-diazo-β-ketosulfone as a safe diazomethane equivalent.

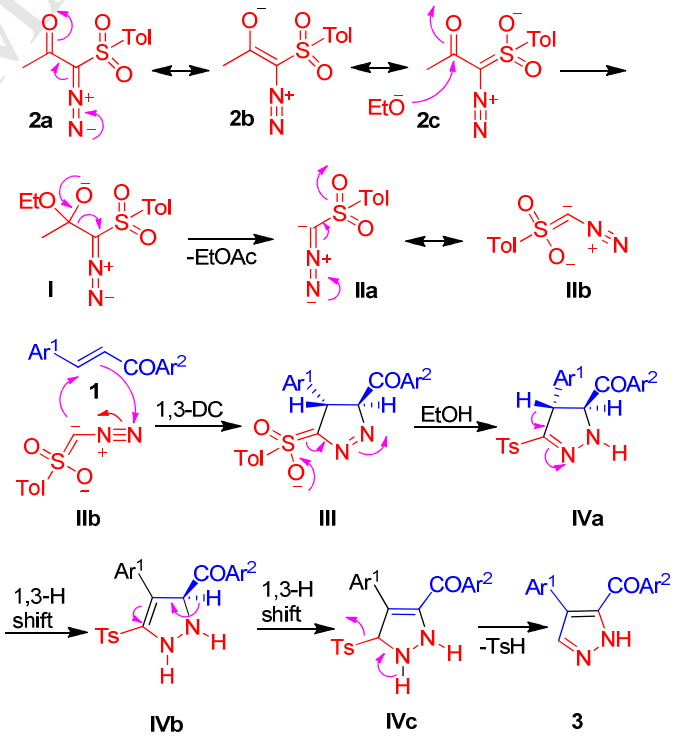
2. Results and discussion

At the outset, we treated a representative chalcone **1a** with sulfone **2** under the previously optimized conditions, i.e. NaOEt in EtOH,[12] at room temperature and we were pleased to note that the reaction proceeded smoothly to afford 3-aroyl pyrazole **3a** as the exclusive product (Scheme 2). Moreover, smooth elimination of sulfonyl group was achieved in a one pot manner without employing harsh reaction conditions.



Scheme 2. Reaction of diazosulfone with chalcone

A mechanism proposed for the above reaction is outlined in Scheme 3. The diazosulfone **2** could exist as a resonance hybrid of **2a-c**. An initial deacylation of the intermediate diazo compound **I** results in the formation of diazo anion **IIa** which is stabilized due to the presence of an electron withdrawing group in the vicinity and is in resonance with **IIb**. A 1,3-dipolar cycloaddition of the in situ generated 1,3-dipole **IIb** with chalcone **1** ensues and the cycloadduct **III** thus formed gets protonated by the solvent EtOH to form intermediate **IVa**. Two successive 1,3-proton shifts, **IVa** to **IVb** and **IVb** to **IVc**, followed by aromatization via elimination of toluenesulfinic acid delivers pyrazole **3**.



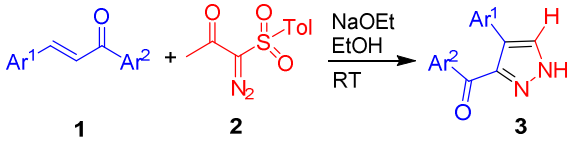
Scheme 3. Proposed mechanism for the formation of pyrazole from diazosulfone and chalcone

Delighted with this result, diversely substituted chalcones were subjected to cycloaddition with sulfone **2** and the corresponding products **3** were obtained in moderate to excellent yields (54-94%, Table 1). Besides parent chalcone **1a**, which afforded pyrazole **3a** in moderate yield (54%, entry 1), chalcones **1b-c**, possessing a weakly electron donating substituent at the para position and a weakly electron withdrawing substituent at the meta position, respectively, on

the β-aryl group, afforded the corresponding pyrazoles **3b-c** in identical yields (62%, entries 2-3). The reactivity improved when stronger electron withdrawing substituents such as chloro, fluoro, cyano and nitro were present on the β-aryl group (**1d-i**) and the corresponding pyrazoles **3d-i** were obtained in excellent yields (86-91%) in shorter reaction times (10 min-3 h, entries 4-9). A representative substituent such as chloro at the para position of the aroyl ring in conjunction with Ph and substituted aryl group at the β position as in chalcones **1j-l** also afforded the corresponding products **3j-l**, though in wider range of yields (70-88%, 3-4 h, entries 10-12).

Subsequently, arylidenemalonates **4** were utilized as efficient dipolarophiles for reaction with diazosulfone **2** (Tables 2-5). To begin with, we employed benzylidenemalonate **4a** as the model dipolarophile which reacted with sulfone **2** in the presence of NaOEt in EtOH in 30 min and afforded a mixture of products, pyrazole-3-carboxylate **5a** and pyrazoline dicarboxylate **6a** in 30% and 20% yields, respectively (entry 1). However, Cs_2CO_3 turned out to be superior to NaOEt providing product **5a** with complete selectivity in 56% yield (entry 2). While other carbonate bases such as Na_2CO_3 and K_2CO_3 proved less effective both in terms of reaction time and product yield (entries 3-4), hydroxide bases such as NaOH and KOH were not found suitable for our reaction (entries 5-6). Lowering the temperature of the NaOEt mediated reaction to 0^oC led to improvement in the total yield of **5a** and **6a** (65%, entry 7). At the same temperature (0^oC), Cs_2CO_3 delivered the product **5a** exclusively in substantially higher yield (70%, entry 8). Lowering the quantity of Cs_2CO_3 to 1.2 equiv adversely affected the yield of **5a** (50%, entry 9). On the other hand, gradually lowering the quantity of NaOEt to 1.2 equiv and then to 1.0 equiv tilted the ratio in favor of the intermediate pyrazoline dicarboxylate **6a** (entries 10-11).

Table 1. 1,3-Dipolar cycloaddition of α-diazo-β-ketosulfone with chalcones[a]

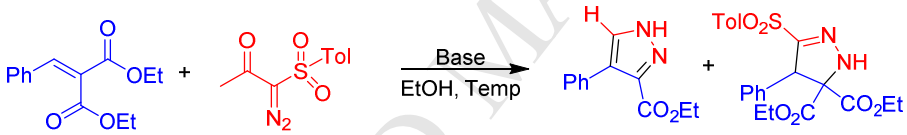


1 2 3

Entry	1	Ar^1	Ar^2	3	Time	%Yield[b]
1	**1a**	C_6H_5	C_6H_5	**3a**	10 h	54
2	**1b**	4-MeC_6H_4	C_6H_5	**3b**	10 h	62
3	**1c**	3-BrC_6H_4	C_6H_5	**3c**	3 h	62
4	**1d**	4-ClC_6H_4	C_6H_5	**3d**	3 h	86
5	**1e**	2-ClC_6H_4	C_6H_5	**3e**	30 min	94
6	**1f**	4-FC_6H_4	C_6H_5	**3f**	10 min	95
7	**1g**	4-CNC_6H_4	C_6H_5	**3g**	30 min	93
8	**1h**	4-$NO_2C_6H_4$	C_6H_5	**3h**	30 min	94
9	**1i**	3-$NO_2C_6H_4$	C_6H_5	**3i**	3 h	91
10	**1j**	C_6H_5	4-ClC_6H_4	**3j**	4 h	77
11	**1k**	4-ClC_6H_4	4-ClC_6H_4	**3k**	4 h	70
12	**1l**	3-$NO_2C_6H_4$	4-ClC_6H_4	**3l**	3 h	88

[a] Reaction scale: chalcone **1** (0.5 mmol), diazosulfone **2** (1 mmol, 2 equiv) and NaOEt (1 mmol, 2 equiv) in EtOH (7 mL).
[b] After silica gel column chromatography.

Table 2. Screening of bases



4a 2 5a 6a

Entry	Base (equiv)	Temp	Time/h	% Yield **5a**[b]	% Yield **6a**[b]
1	NaOEt (1.5)	RT	30 min	30	20[c]
2	Cs_2CO_3 (1.5)	RT	1	56	-[d]
3	Na_2CO_3 (1.5)	RT	6	48	-[d]
4	K_2CO_3 (1.5)	RT	6	52	-[d]
5	NaOH (1.5)	RT	3	42	-[d]
6	KOH (1.5)	RT	2	-[e]	-[e]
7	NaOEt (1.5)	0^oC	1	35	30[c]
8	**Cs_2CO_3 (1.5)**	**0^oC**	**4**	**70**	-[d]
9	Cs_2CO_3 (1.2)	0^oC	4	50	-[d]
10	NaOEt (1.2)	0^oC	2.5	34	38[c]
11	NaOEt (1.0)	0^oC	5	18	58[c]

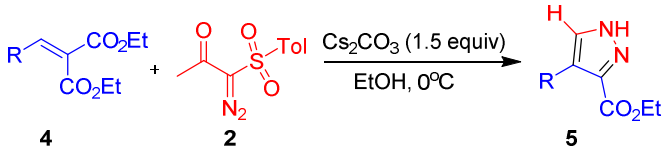
[a] Reaction scale: Arylidenemalonate **1** (0.5 mmol), diazosulfone **2** (0.6, 1.2 equiv), EtOH (5 mL).
[b] After silica gel column chromatography.
[c] Could not be isolated in pure form as it decomposed during attempted purification.
[d] Not observed.
[e] Complex mixture.

Since the Cs_2CO_3 mediated reaction (Table 2, entry 8) was highly selective for pyrazole carboxylate **5a**, the scope of arylidenemalonates **4** was investigated under these conditions (Table 3). Thus, besides benzylidenemalonate **4a** which delivered the corresponding pyrazole carboxylate **5a** in very good yield (70%, entry 1), various other arylidenemalonates **4b-j** were subjected to 1,3-dipolar cycloaddition with diazosulfone **2** (entries 2-10). Arylidenemalonate **4b**, bearing a weakly electron donating substituent such as Me at the para position, afforded the corresponding product **5b** in 58% yield (entry 2). On the other hand, a strongly electron donating substitutent such as OMe as in **4c** adversely affected the yield of the corresponding pyrazole **5c** (40%, entry 3). Surprisingly, the intermediate cycloadduct **6d**, formed from malonate **4d**, bearing a para-chlorophenyl group, did not undergo decarboxylation and detosylation and was isolated in 63% yield (entry 4). On the other hand, malonates bearing stronger deactivating substituents such as fluoro and cyano at the para position as in **4e** and **4f** furnished the corresponding pyrazoles **5e** and **5f** in 60% and 56% yields, respectively (entries 5 and 6). A strongly

electron withdrawing group such as NO_2 on the aromatic ring did not favor the reaction as almost 70% of the starting material **4g** was recovered (entry 7). In the case of a fused arylidenemalonate such as **4h**, the corresponding pyrazole **5h** was isolated in low yield (32%, entry 8). The heteroaryl substituted malonate **4i** afforded a complex mixture when Cs_2CO_3 was used as base. Therefore, the reaction was carried out in the presence of 1.5 equiv of NaOEt which fortunately furnished pyrazole **5i** in 58% yield as the only product (entry 9). It appears that extended conjugation makes the double bond less reactive as a dipolarophile such as the cinnamaldehyde derived malonate **4j** does not react under our experimental conditions (entry 10).

As for the mechanism of the reaction, the first part of which is similar to that described in Scheme 2, the cycloaddition of the in situ generated 1,3-dipole **IIb** with the arylidenemalonate **4** results in the formation of the initial cycloadduct **Va** which undergoes protonation by EtOH to form **Vb** (Scheme 4). Tautomerization of **Vb** generates reasonably stable pyrazoline dicarboxylate intermediate **6'**. However, excess ethoxide, when present in the medium, acts as a nucleophile and causes decarboxylation and detosylation of **6** furnishing **5'** which readily tautomerizes to **5** *via* a 1,3-proton shift.

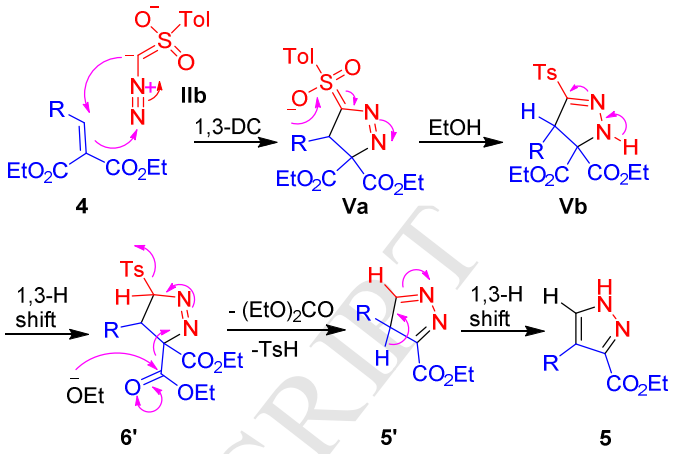
Table 3. Scope of arylidenemalonates with Cs_2CO_3 as base[a]



4 2 5

Entry	4	R	Time/h	5	% Yield[b]
1	**4a**	C_6H_5	4	**5a**	70
2	**4b**	4-MeC_6H_4	4	**5b**	58
3	**4c**	4-$OMeC_6H_4$	3	**5c**	40[c]
4	**4d**	4-ClC_6H_4	2	**5d**	-[d]
5	**4e**	4-FC_6H_4	2	**5e**	60
6	**4f**	4-CNC_6H_4	1.5	**5f**	56
7	**4g**	4-$NO_2C_6H_4$	4	**5g**	-[e]
8	**4h**	1-naphthyl	1.5	**5h**	32[c]
9	**4i**	2-furyl	12	**5i**	58[f]
10	**4j**	C_6H_5-CH=CH	16	**5j**	-[g]

[a] Reaction scale: arylidenemalonate **4** (0.5 mmol), diazosulfone **2** (0.6 mmol, 1.2 equiv), Cs_2CO_3 (0.75 mmol, 1.5 equiv), EtOH (5 mL).
[b] After silica gel column chromatography.
[c] No characterizable side products were observed in these reactions.
[d] **6d** was isolated in 63% yield.
[e] 68% of **4g** was recovered.
[f] NaOEt (1.5 equiv) was used as base as complex mixture was formed in the presence of Cs_2CO_3.
[g] No reaction.

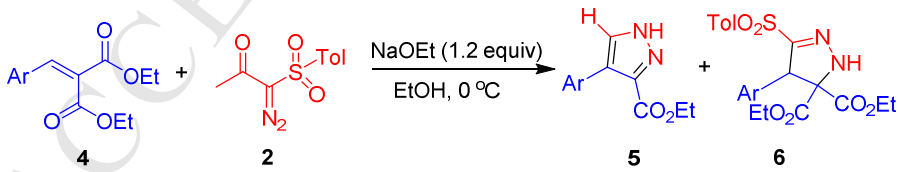


Scheme 4. Proposed mechanism for the formation of pyrazole from diazosulfone and arylidenemalonates

After investigating the scope of Cs_2CO_3 mediated synthesis of pyrazole carboxylates **5**, we subjected various arylidenemalonates **4** to study the effect of substituents on the ratio of the products **5** and **6** when sodium ethoxide was used as the base (Table 4). Arylidenemalonate **4b**, bearing a weakly electron donating substituent such as methyl at the para position, afforded a mixture of pyrazole **5b** in 50% yield and pyrazoline **6b** in 39% yield (entry 2). However, a strongly electron rich aryl derivative **4c** furnished only the pyrazoline dicarboxylate **6c**, that too in moderate yield (40%, entry 3). In the case of deactivated aryl derivatives **4d** and **4f**, pyrazolines **6d** and **6f**, respectively, were the only products which were formed in comparable yields (62-63%, entries 4-5). Finally, naphthylidenemalonate **4h** provided a mixture of pyrazole **5h** (10% yield) and pyrazoline **6h** (52% yield, entry 6).

The structures of pyrazole carboxylate **5** and the intermediate pyrazoline dicarboxylate **6** were unambiguously confirmed by single crystal X-Ray diffraction analysis of representative compounds **5a** and **6h**.

Table 4. Scope of arylidenemalonates **4** with NaOEt as base[a]



4 2 5 6

Entry	4	Ar	Time/h	5	% Yield/5[b]	6	% Yield/ 6[b]
1	**4a**	C_6H_5	2.5	**5a**	34	**6a**	38[c]
2	**4b**	4-MeC_6H_4	3.5	**5b**	50	**6b**	39
3	**4c**	4-$OMeC_6H_4$	4	**5c**	-[d]	**6c**	40[e]
4	**4d**	4-ClC_6H_4	1.5	**5d**	-[d]	**6d**	63
5	**4f**	4-CNC_6H_4	1.5	**5f**	-[d]	**6f**	62
6	**4h**	1-naphthyl	1.5	**5h**	10	**6h**	52

[a] Reaction scale: arylidenemalonate **4** (0.5 mmol), diazosulfone **2** (0.6 mmol, 1.2 equiv), NaOEt (0.6 mmol, 1.2 equiv), EtOH (5 mL).
[b] After silica gel column chromatography.
[c] Could not be isolated in pure form as it decomposed during attempted purification.
[d] Not observed.
[e] No characterizable side products were observed in this reaction.

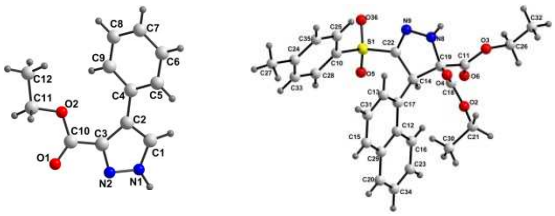
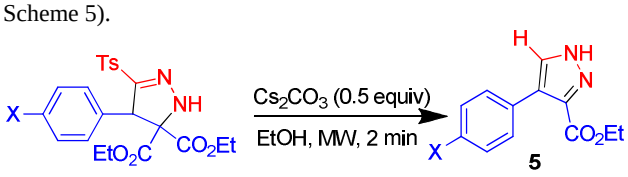


Figure 1. X-ray structures of **5a** and **6h**

It may be noted that pyrazoline dicarboxylates **6c**, **6d** and **6f** were formed as the only products and could be isolated in pure form before they underwent elimination to the corresponding pyrazole carboxylates **5c**, **5d** and **5f** (Table 4). Subsequently, these pyrazoline dicarboxylates (**6c**, **6d** and **6f**) and crude **6a** were subjected to microwave irradiation under mild basic conditions (0.5 equiv Cs_2CO_3) to achieve their complete conversion to the respective pyrazole carboxylates **5a**, **5c**, **5d** and **5f** in nearly quantitative yield (96-97%, Scheme 5).



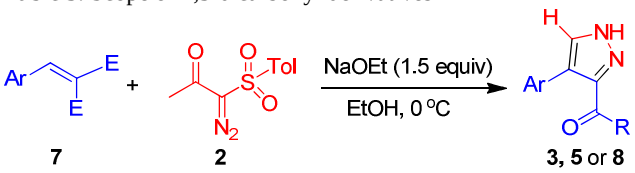
Scheme 5. Conversion of pyrazoline dicarboxylates to pyrazole carboxylates

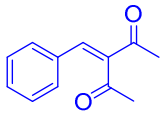
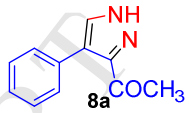
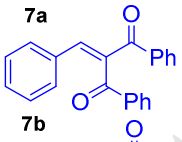
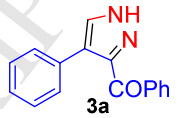
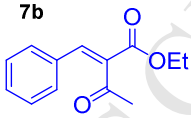
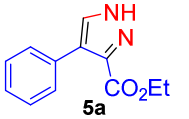
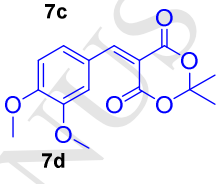
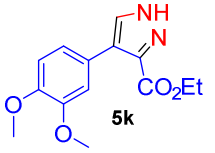
To further extend the scope of our diazosulfone cycloaddition, other benzylidene-1,3-dicarbonyls **7a-d** were prepared and their cycloaddition with diazosulfone **2** was investigated (Table 5). Although the optimized conditions (Cs_2CO_3, EtOH, 0° C) worked reasonably well for malonates **4** for the selective synthesis of pyrazole carboxylates **5**, these conditions were not suitable for arylidene-1,3-dicarbonyls **7a-d** as intractable mixtures of pyrazoline and pyrazole were often formed. Therefore, NaOEt (1.5 equiv) was used as the base to achieve best results. Benzylidenediketones **7a** and **7b** afforded acylated pyrazoles **8a** and **3a**, respectively, in 62% and 75% yields (entries 1-2). Ketoester **7c**, the condensation product of benzaldehyde and ethylacetoacetate, reacted with sulfone **2** and provided pyrazole carboxylate **5a** as the only product in 70% yield (entry 3). The above observations confirmed that deacylation could also take place under our experimental conditions (entries 2-3) and it is in fact preferred over decarboxylation (entry 3). A cyclic malonate equivalent **7d**, the condensation product of Meldrum's acid and an aromatic aldehyde, afforded pyrazole carboxylate **5k** in 50% yield (entry 4).

3. Conclusions

Synthesis of 3-acyl and 3-carboxyl substituted pyrazoles via 1,3-dipolar cycloaddition of chalcones, arylidenemalonates and other arylidene-1,3-dicarbonyls with a diazosulfone, generated in situ from α-diazo-β-ketosulfone, has been carried out. The diazosulfonyl anion intermediate was generated from α-diazo-β-ketosulfone in the presence of Cs_2CO_3 or NaOEt in EtOH. While in the case of chalcones, cycloaddition followed by detosylation takes place to provide 3-aroyl pyrazoles,[18] a decarboxylation or deacylation takes place prior to detosylation in the initial cycloadduct arising from arylidene-1,3-dicarbonyls. This protocol also highlights the role of diazosulfone as a safe and easy-to-handle diazomethane equivalent in the synthesis of pyrazole derivatives. The dual role of NaOEt as a nucleophile and as a base is also reflected in our reaction.

Table 5. Scope of 1,3-dicarbonyl derivatives[a]



Entry	7	Time (h)	Product	% Yield[b]
1	 7a	4	 8a	62
2	 7b	2	 3a	75
3	 7c	1.5	 5a	70
4	 7d	2.5	 5k	50

[a] Reaction scale: **7** (0.5 mmol), diazosulfone **2** (0.6 mmol, 1.2 equiv), NaOEt (0.75 mmol, 1.5 equiv), EtOH (5 mL); intractable mixtures of pyrazoline and pyrazole derivatives were often formed in the presence of Cs_2CO_3 in EtOH at 0° C.

[b] After silica gel column chromatography.

4. Experimental section

4.1 General Experimental Details

The melting points recorded are uncorrected. NMR spectra (^{1}H, ^{1}H decoupled ^{13}C) were recorded with TMS as the internal standard. The coupling constants (*J* values) are given in Hz. High resolution mass spectra were recorded under ESI Q-TOF conditions. X-ray data were collected on a diffractometer equipped with graphite monochromated Mo Kα radiation. The structure was solved by direct methods shelxs97 and refined by full-matrix least squares against F^2 using shelxl97 software. Chalcones,[19] arylidenemalonates,[20] *α-diazo-β*-ketosulfone[21] and compounds **7a-d**[22] were prepared following the literature procedures.

*4.2 General procedure for synthesis of pyrazoles **3** from chalcones **1** and sulfone **2** (see Table 1)*

To a solution of chalcone **1** (0.5 mmol) in dry EtOH (5 mL), was added diazosulfone **2** (238 mg, 1 mmol, 2 equiv) at RT under N_2. The reaction mixture was stirred and NaOEt (68 mg, 1 mmol, 2 equiv) in dry EtOH (2 mL) was added. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated in *vacuo* and the residue was purified by silica gel column chromatography (EtOAc/pet ether, 2/8) to afford pure pyrazole **3**.

*4.2.1 Phenyl(4-phenyl)-1H-pyrazol-3-yl)(phenyl)methanone (**3a**)*
White solid; Yield 54% (67 mg); mp 182-184 °C; IR (KBr, cm^{-1}) 3411 (s), 2926 (s), 2852 (m), 1654 (s), 1449 (m), 1416 (m), 1344 (m), 1262 (s), 1158 (w), 911 (m), 736 (s); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.24 (t, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.44 (d, *J* = 7.3 Hz, 2H),

7.51 (t, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.97 (d, *J* = 7.2 Hz, 2H), 8.19 (s, 1H), 13.62 (brs, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 123.8, 126.7, 128.2, 128.3, 128.4, 129.4, 130.2, 132.3, 132.9, 137.8, 145.8, 189.9; MS (ES+) m/z (rel intensity) 250 (MH^+, 19), 249 (M^+, 100), 171 (8); HRMS (ES+) calcd for $C_{16}H_{13}N_2O$ (MH^+) 249.1028, found 249.1033.

*4.2.2 Phenyl(4-p-tolyl-1H-pyrazol-3-yl)methanone (**3b**)*
Colorless solid; Yield 62% (81 mg); mp 170-172 °C; IR (KBr, cm^{-1}) 3400 (br vs), 3187 (s), 2962 (w), 1629 (s), 1449 (w), 1284 (w), 1251 (w), 1161 (w), 907 (m), 812 (m), 743 (m); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.31 (s, 3H), 7.05 (d, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.61 (s, 1H), 7.85 (d, *J* = 7.5 Hz, 2H), 11.92 (brs, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 20.7, 123.8, 128.2, 128.8, 129.1, 129.3, 130.2, 132.8, 135.8, 137.8, 145.8, 189.9; MS (ES+) m/z (rel intensity) 264 (MH^+, 20), 263 (M^+, 100), 185 (3); HRMS (ES+) calcd for $C_{17}H_{15}N_2O(MH^+)$ 263.1184, found 263.1184.

*4.2.3 (4-(3-Bromophenyl)-1H-pyrazol-3-yl)(phenyl)methanone (**3c**)*
White solid; Yield 62% (101 mg); mp 166-167 °C; IR (KBr, cm^{-1}) 3271 (brm), 2930 (m), 1656 (vs), 1598 (w), 1451 (s), 1322 (s), 1248 (s), 1162 (vs), 1085 (m), 905 (s), 761 (s), 696 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.14-7.19 (m, 2H), 7.21-7.25 (m, 1H), 7.29-7.35 (m, 3H), 7.42-7.49 (m, 2H), 7.87 (d, *J* = 7.1 Hz, 2H), 13.08 (brs, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 121.7, 126.7, 128.3, 128.9, 129.7, 130.3, 131.3, 132.0, 133.1, 133.5, 137.3, 189.4; MS (ES+) m/z (rel intensity) 330 ($[M+4]^+$, 20), 329 ($[M+3]^+$, 100), 328 ($[M+2]^+$, 18), 327 (MH^+, 96), 248 (5); HRMS (ES+) calcd for $C_{16}H_{11}BrN_2O(MH^+)$ 327.0133, found 327.0128.

*4.2.4 (4-(4-Chlorophenyl)-1H-pyrazol-3-yl)(phenyl)methanone (**3d**)*
White solid; Yield 86% (121 mg); mp 195-196 °C; IR (KBr, cm^{-1}) 3374 (br m), 2924 (s), 2857 (m), 1651 (vs), 1095 (m), 916 (s), 820 (vs), 739 (m), 693 (m); ^{1}H NMR (DMSO-d_6, 400 MHz) 7.36 (d, *J* = 7.4 Hz, 2H), 7.44-7.50 (m, 4H), 7.60 (t, *J* = 6.8 Hz, 1H), 7.96 (d, *J* = 7.4 Hz, 2H), 8.18 (s, 1H), 13.69 (brs, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 122.9, 125.8, 128.3, 128.3, 129.8, 130.3, 130.4, 131.5, 133.0, 137.8, 145.9, 189.8; MS (ES+) m/z (rel intensity) 286 ($[M+4]^+$, 7), 285 ($[M+3]^+$, 40), 284 ($[M+2]^+$, 22), 283 (MH^+, 100), 252 (6); HRMS (ES+) calcd for $C_{16}H_{12}ClN_2O$ (MH^+) 283.0638, found 283.0642.

*4.2.5 (4-(2-Chlorophenyl)-1H-pyrazol-3-yl)(phenyl)methanone (**3e**)*
Light yellow solid; Yield 94% (133 mg); mp 167-168 °C; IR (KBr, cm^{-1}) 3122 (br s), 2915 (s), 1655 (vs), 1597 (m), 1345 (m), 1273 (m), 740 (m), 693 (m); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.11 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.33-7.39 (m, 3H), 7.45 (s, 1H), 7.51-7.56 (m, 2H), 7.87 (d, *J* = 7.5Hz, 2H), 12.06 (brs, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.4, 123.8, 127.7, 128.4, 128.6, 129.9, 130.3, 130.4, 131.1, 131.8, 133.4, 133.8, 137.5, 189.8; MS (ES+) m/z (rel intensity) 286 ($[M+4]^+$, 7), 285 ($[M+3]^+$, 40), 284 ($[M+2]^+$, 22), 283 (MH^+, 100); HRMS (ES+) calcd for $C_{16}H_{11}ClN_2O(MNa^+)$ 305.0452, found 305.0453.

*4.2.6 (4-(4-Fluorophenyl)-1H-pyrazol-3-yl)(phenyl)methanone (**3f**)*
White solid; Yield 95% (126 mg); mp 140-141 °C;IR (KBr, cm^{-1}) 3394 (br vs), 2891 (w), 1652 (vs), 1551 (w), 1398 (w), 1342 (m), 1158 (m), 914 (m), 821 (s), 740 (s); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.13-7.17 (m, 2H), 7.45-7.65 (m, 5H), 7.96 (d, *J* = 6.6 Hz, 2H), 8.17 (s, 1H), 13.62 (brs, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 114.9 (d, J_{C-F} = 22.0 Hz), 123.0, 128.2, 128.7, 129.5, 130.3, 130.4 (d, *J* = 8.0 Hz), 132.8, 137.8, 145.7, 161.2 (d, J_{C-F} = 241.0 Hz), 189.6; MS (ES+) m/z (rel intensity) 268 ($[M+2]^+$, 24), 267 (MH^+, 100); ^{19}F NMR ($CDCl_3$, 470 MHz) δ -114.81; HRMS (ES+) calcd for $C_{16}H_{12}FN_2O(MH^+)$ 267.0934, found 267.0948.

*4.2.7 4-(3-Benzoyl-1H-pyrazol-4-yl)benzonitrile (**3g**)*
White solid; Yield 93% (127 mg); mp 143-145 °C; IR (KBr, cm^{-1}) 3445 (br m), 2923 (s), 2225 (m), 1654 (vs), 1611 (m), 125 (m), 1093 (s), 1013 (s), 829 (m); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38-7.42 (m, 4H), 7.51-7.58 (m, 4H), 7.90 (d, *J* = 6.9 Hz, 2H), 12.75 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 110.8, 118.9, 123.6, 128.6, 129.4, 130.5, 132.2, 133.7, 136.6, 137.2, 189.5; MS (ES+) m/z (rel intensity) 296 (MNa^+, 24), 251 (12), 235 (100); HRMS (ES+) calcd for $C_{17}H_{11}N_3ONa$ (MNa^+) 296.0794, found 296.0794.

*4.2.8 (4-(4-Nitrophenyl)-1H-pyrazol-3-yl)(phenyl)methanone (**3h**)*
Off-white solid; Yield 94% (138 mg); mp 168-170 °C; IR (KBr, cm^{-1}) 3402 (br vs), 2919 (w), 1653 (m), 1509 (w), 1336 (m), 1265 (m), 823 (w), 739 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41 (t, *J* = 7.4 Hz, 2H), 7.51-7.59 (m, 3H), 7.79 (s, 1H), 7.91-7.97 (br m, 2H), 8.15 (d, *J* = 8.5 Hz, 2H), 11.16 (brs, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 121.9, 123.4, 128.3, 129.2, 130.3, 130.7, 133.1, 137.4, 139.5, 145.9, 146.1, 189.5; MS (ES+) m/z (rel intensity) 295 ($[M+2]^+$, 21), 294 (MH^+, 100), 216 (7); HRMS (ES+) calcd for $C_{16}H_{12}N_3O_3(MH^+)$ 294.0879, found 294.0878.

*4.2.9 (4-(3-Nitrophenyl)-1H-pyrazol-3-yl)(phenyl) methanone (**3i**)*
Light yellow solid; Yield 91% (133 mg); mp 155-157 °C; IR (KBr, cm^{-1}) 3400 (br vs), 2923 (vw), 1652 (vs), 1524 (w), 1450 (w), 1349 (m), 1254 (w), 1150 (w), 1021 (w), 910 (w), 807 (m), 735 (s); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.50 (t, *J* = 7.0 Hz, 2H), 7.62 (t, *J* = 7.1 Hz, 2H), 7.92 (d, *J* = 7.1 Hz, 1H), 7.99 (d, *J* = 7.0 Hz, 2H), 8.11 (d, *J* = 7.1 Hz, 1H), 8.36 (s, 1H), 8.39 (s,1H), 13.8 (brs, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 121.5, 122.0, 122.9, 128.2, 129.6, 130.3, 132.9, 134.1, 135.1, 137.6, 145.8, 147.7, 189.5; MS (ES+) m/z (rel intensity) 295 (MH^+, 14), 294 (M^+, 100), 263 (42), 216 (19); HRMS (ES+) calcd for $C_{16}H_{12}N_3O_3$ (MH^+) 294.0879, found 294.0878.

*4.2.10 (4-Chlorophenyl)(4-phenyl-1H-pyrazol-3-yl)methanone (**3j**)*
White solid; Yield 77% (109 mg); mp 155-157 °C; IR (KBr, cm^{-1}) 3393 (vs), 2924 (vs), 2857 (m), 1655 (vs), 1446 (w), 1262 (m), 1152 (w), 1094 (w), 1015 (w), 820 (w), 757 (m); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.20-7.26 (m, 1H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.99 (d, *J* = 8.5 Hz, 2H), 8.17 (s, 1H), 13.66 (brs, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 124.2, 126.8, 128.2, 128.4, 128.5, 129.6, 132.1, 132.2, 136.5, 137.8, 145.5, 188.4; MS (ES+) m/z (rel intensity) 286 ($[M+4]^+$, 7), 285 ($[M+3]^+$, 42), 284 ($[M+2]^+$, 21), 283 (MH^+, 100), 263 (19), 171 (18); HRMS (ES+) calcd for $C_{16}H_{11}ClN_2O(MH^+)$ 283.0638, found 283.0635.

*4.2.11 (4-Chlorophenyl)(4-(4-chlorophenyl)-1H-pyrazol-3-yl)methanone (**3k**)*
White solid; Yield 70% (111 mg); mp 165-167 °C; IR (KBr, cm^{-1}) 3110 (s), 2912 (s), 1654 (vs), 1588 (m), 1427 (s), 1342 (m), 1095 (s), 918 (m), 817 (m); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.35 (d, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 7.7 Hz, 2H), 7.54 (d, *J* = 7.9 Hz, 2H), 7.98 (d, *J* = 7.7 Hz, 2H), 8.17 (s, 1H), 13.74 (brs, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 123.1, 128.2, 128.5, 130.0, 130.4, 131.2, 131.6, 132.2, 136.4, 138.0, 145.5, 188.3; MS (ES+) m/z (rel intensity) 321 ($[M+5]^+$, 12), 319 ($[M+3]^+$, 65), 317 (MH^+, 100), 282 (8); HRMS (ES+) calcd for $C_{16}H_{11}Cl_2N_2O(MH^+)$ 317.0248, found 317.0238.

*4.2.12 (4-Chlorophenyl)(4-(3-nitrophenyl)-1H-pyrazol-3-yl)methanone (**3l**)*
Light yellow solid; Yield 88% (144 mg); mp 171-173 °C; IR (KBr, cm^{-1}) 3075 (m), 2802 (w), 1658 (w), 1516 (m), 1554 (w), 1517 (m), 1405 (m), 1350 (vs), 1083 (m), 741 (vs); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 8.12 (d, *J* = 7.5 Hz, 1H), 8.38 (s, 1H), 8.39 (s, 1H), 13.86 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 121.7, 122.2, 123.1, 128.4, 129.7, 130.8, 132.3, 134.1, 135.3, 136.3, 137.9, 145.5, 147.8, 188.0; MS (ES+) m/z (rel intensity) 350 (MNa^+, 100), 328 (MH^+, 20), 235 (13); HRMS (ES+) calcd for $C_{16}H_{10}ClN_3O_3Na$ (MNa^+) 350.0303, found 350.0304.

*4.3 General procedure for the synthesis of pyrazoles **5** from arylidenemalonates **4** and sulfone **2** (see Table 3)*

To a stirred solution of arylidenemalonate **4** (0.5 mmol) and *α*-diazo-*β*-ketosulfone **2** (143 mg, 0.6 mmol, 1.2 equiv) in dry EtOH (5 mL) was added Cs_2CO_3 (245 mg, 0.75 mmol, 1.5 equiv) at 0 ^oC and the resulting mixture was stirred until the reaction was complete (monitored by TLC). Then the reaction mixture was concentrated in *vacuo* and the crude residue was directly subjected to silica gel column chromatography (pet ether/ethyl acetate: 8/2) to afford pure pyrazole carboxylate **5**.

*4.3.1 Ethyl 4-phenyl-1H-pyrazole-3-carboxylate (**5a**)*
White solid, Yield 50% (54 mg); mp 156 ^oC; IR (KBr, cm^{-1}) 3230 (br vs), 2986 (w), 2926 (w), 1685 (vs), 1434 (m), 1289 (m), 1269 (m), 1174 (m), 759 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.1 Hz, 3H), 4.36 (q, *J* = 7.1 Hz, 2H), 7.32-7.45 (m, 3H), 7.52-7.54 (m, 2H), 7.86 (s, 1H), 9.47 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 61.3, 125.5, 127.6, 128.1, 129.7, 131.9, 134.9, 135.6, 161.7; MS (ES+) m/z (rel intensity) 239 (MNa^+, 100); HRMS (ES+) calcd for $C_{12}H_{12}N_2O_2Na$ (MNa^+) 239.0791, found 239.0790 Selected crystallographic parameters for $C_{12}H_{12}N_2O_2$, M = 216.24, Monoclinic, space group P2(1)/n, a = 12.343(9) Å, b = 7.749(5) Å, c = 12.3545(10) Å, α = 90°, β = 114.9500°, γ = 90°, V = 1071.4(10) $Å^3$, Dc = 1.341 Mg/m^3, Z = 4, F(000) = 456, λ = 0.71073 Å, μ = 0.093 mm^{-1}, Total unique reflections = 8004 / 1955 [R(int) = 0.0921], T = 100(2) K, θ range = 3.07 to 25.33°, Final R indices [I>2σ(I)] : R1 = 0.0447, wR2 = 0.0893, R(all data) : R1 = 0.0667, wR2 = 0.0981.

*4.3.2 Ethyl 4-p-tolyl-1H-pyrazole-3-carboxylate (**5b**)*
White solid, Yield 58% (67 mg); mp 208 ^oC; IR (KBr, cm^{-1}) 3235 (br m), 3128 (w), 2930 (w), 1687 (vs), 1436 (m), 1296 (s), 1280 (s), 1248 (m), 1178 (m), 1171 (m), 1020 (m), 832 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.2 Hz, 3H), 2.38 (s, 3H), 4.36 (q, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 21.4, 61.4, 127.5, 128.3, 128.5, 129.0, 129.4, 129.9, 137.6, 160.8; MS (ES+) m/z (rel intensity) 253 (MNa^+, 100); HRMS (ES+) calcd for $C_{13}H_{14}N_2O_2Na$ (MNa^+) 253.0947, found 253.0944.

*4.3.3 Ethyl 4-(4-methoxyphenyl)-1H-pyrazole-3-carboxylate (**5c**)*
White solid, Yield 40% (49 mg); mp 162 ^oC; IR (KBr, cm^{-1}) 3246 (br s), 3128 (w), 2985 (m), 2836 (w), 1722 (m), 1688 (m), 1442 (m), 1273 (s), 1249 (vs), 1179 (vs), 1162 (vs), 1020 (m), 832 (m), 816 (m); ^1H NMR (500 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.2 Hz, 3H), 3.85 (s, 3H), 4.36 (q, *J* = 7.2 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 55.5, 61.3, 113.6, 124.1, 125.5, 129.1, 130.8, 135.1, 159.3, 161.5; MS (ES+) m/z (rel intensity) 269 (MNa^+, 100), 247 (MH^+, 3); HRMS (ES+) calcd for $C_{13}H_{14}N_2O_3Na$ (MNa^+) 269.0897, found 269.0896.

*4.3.4 Ethyl 4-(4-fluorophenyl)-1H-pyrazole-3-carboxylate (**5e**)*
White solid, Yield 60% (70 mg); mp 176 ^oC; IR (KBr, cm^{-1}) 3223 (br s), 2923 (m), 1686 (vs), 1436 (s), 1289 (s), 1267 (m), 1173 (m), 1015 (m), 831 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, *J* = 7.1 Hz, 3H), 4.22 (q, *J* = 7.1 Hz, 2H), 7.02 (t, *J* = 8.7 Hz, 2H), 7.37-7.42 (m, 2H), 7.61 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 61.4, 115.1 (d, $J_{C\text{-}F}$ = 24.5 Hz), 124.9, 127.7, 131.3 (d, $J_{C\text{-}F}$ = 7.5 Hz), 134.1, 136.4, 161.2 (d, *J* = 245.0 Hz), 163.8; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -114.75; MS (ES+) m/z (rel intensity) 257 (MNa^+, 100), 244 (10); HRMS (ES+) calcd for $C_{12}H_{11}FN_2O_2Na$ (MNa^+) 257.0697, found 257.0686.

*4.3.5 Ethyl 4-(4-cyanophenyl)-1H-pyrazole-3-carboxylate (**5f**)*
White solid, Yield 56% (67 mg); mp 144 ^oC; IR (KBr, cm^{-1}) 3419 (br vs), 2991 (w), 2225 (m), 1719 (s), 1691 (s), 1607 (s), 1441 (m), 1355 (m), 1285 (s), 1161 (m), 828 (s); ^1H NMR (500 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.2 Hz, 3H), 4.35 (q, *J* = 7.2 Hz, 2H), 7.66, 7.69 (ABq, *J* = 8.4 Hz, 4H), 7.77 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 61.7, 111.4, 119.0, 123.9, 130.3, 132.0, 135.6, 136.8, 161.0; MS (ES+) m/z (rel intensity) 264 (MNa^+, 100), 161 (6); HRMS (ES+) calcd for $C_{13}H_{11}N_3O_2Na$ (MNa^+) 264.0743, found 264.0744.

*4.3.6 Ethyl 4-(naphthalen-1-yl)-1H-pyrazole-5-carboxylate (**5h**)*
White solid, Yield 32% (42 mg); mp 142 ^oC; IR (KBr, cm^{-1}) 3407 (br vs), 3230 (br vs), 2986 (w), 1689 (vs), 1475 (m), 1430 (m), 1353 (m), 1283 (s), 1182 (m), 1013 (m), 775 (m); ^1H NMR (500 MHz, $CDCl_3$) δ 0.70 (t, *J* = 7.1 Hz, 3H), 4.01 (q, *J* = 7.1 Hz, 2H), 7.39-7.51 (m, 4H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.88 (t, *J* = 8.4 Hz, 2H), 7.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 60.8, 122.7, 125.1, 125.8, 126.0, 126.2, 128.1, 128.2, 128.3, 128.6, 129.6, 130.5, 133.1, 133.6, 162.2; MS (ES+) m/z (rel intensity) 305 (MK^+, 100), 289 (MNa^+, 55); HRMS (ES+) calcd for $C_{16}H_{14}N_2O_2K$ (MK^+) 305.0687, found 305.0689.

*4.3.7 Ethyl 4-(furan-2-yl)-1H-pyrazole-3-carboxylate (**5i**)*
White solid, Yield 58% (60 mg); mp 142 ^oC; IR (KBr, cm^{-1}) 3122 (w), 2981 (w), 2923 (m), 1718 (vs), 1446 (m), 1356 (w), 1286 (s), 1171 (m), 1033 (m), 743 (w); ^1H NMR (500 MHz, $CDCl_3$) δ 1.45 (t, *J* = 7.2 Hz, 3H), 4.50 (q, *J* = 7.2 Hz, 2H), 6.49 (dd, *J* = 3.3, 1.7 Hz, 1H), 7.09 (d, *J* = 3.3 Hz, 1H), 7.45 (t, *J* = 1.7 Hz, 1H), 8.12 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.5, 61.5, 109.5, 111.6, 115.9, 127.3, 129.8, 132.2, 135.0, 141.6, 146.4, 161.6; MS (ES+) m/z (rel intensity) 229 (MNa^+, 100); HRMS (ES+) calcd for $C_{10}H_{10}N_2O_3Na$ (MNa^+) 229.0584, found 229.0584.

*4.4 General procedure for the synthesis of pyrazolines **6** from arylidenemalonates **4** and sulfone **2** (see Table 4)*

To a stirred solution of arylidenemalonate **4** (0.5 mmol, 1 equiv) and α-diazo-β-ketosulfone **2** (143 mg, 0.6 mmol, 1.2 equiv) in dry EtOH (5 mL) was added NaOEt (41 mg, 0.6 mmol, 1.2 equiv) at 0 ^oC and the resulting mixture was stirred until the reaction was complete (monitored by TLC) keeping the temperature maintained at 0 ^oC. Then the reaction mixture was concentrated in *vacuo* and the crude residue was directly subjected to silica gel column chromatography (pet ether/ethyl acetate: 8/2) to afford pure pyrazolines **6**.

*4.4.1 Diethyl 4-(p-tolyl)-3-tosyl-1H-pyrazole-5,5(4H)-dicarboxylate (**6b**)*
White solid; Yield 39% (90 mg); mp 102 ^oC IR (KBr, cm^{-1}) 3336 (s), 2983 (m), 1741 (s), 1515 (w), 1447 (w), 1329 (m), 1274 (s), 1220 (m), 1113 (m), 812 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 0.74 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 2.25 (s, 3H), 2.36 (s, 3H), 3.62- 3.67 (m, 1H), 3.72- 3.79 (m, 1H), 4.18- 4.36 (m, 2H), 5.23 (s, 1H), 6.89 (bs, 2H), 7.04 (d, *J* = 7.3 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.17 (s, 1H), 7.45 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4, 14.1, 21.3, 21.8, 56.1, 62.6, 63.5, 81.3, 128.5, 129.2, 129.6, 136.8, 138.4, 144.8, 153.8, 165.5, 167.2; MS (ES+) m/z (rel intensity) 481 (MNa^+, 100); HRMS (ES+) calcd for $C_{23}H_{26}N2O_6S$ (MNa^+) 481.1404, found 481.1407.

*4.4.2 Diethyl 4-(4-methoxyphenyl)-3-tosyl-1H-pyrazole-5,5(4H)-dicarboxylate (**6c**)*
Viscous liquid; Yield 40% (97 mg); IR (KBr, cm^{-1}) 3330 (m), 2982 (m), 1741 (vs), 1610 (m), 1596 (w), 1514 (s), 1329 (s), 1253 (vs), 1220 (m), 1147 (m), 1114 (m), 1033 (m), 755 (m), 670 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 0.77 (t, *J* = 7.2 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 2.36 (s, 3H), 3.59-3.67 (m, 1H), 3.73 (s, 3H), 3.74-3.83 (m, 1H), 4.19-4.34 (m, 2H), 5.25 (s, 1H), 6.61 (d, *J* = 8.4 Hz, 2H), 6.88-6.90 (unresolved m, 2H), 7.04 (s, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 14.1, 21.7, 55.4, 55.8, 62.6, 63.5, 81.2, 113.9, 124.6, 128.5, 129.6, 130.5, 136.8, 144.8, 153.7, 159.8, 165.5, 167.2; HRMS (ES+) calcd for $C_{23}H_{26}N_2O_7SNa$ (MNa^+) 497.1353, found 497.1358.

*4.4.3 Diethyl 4-(4-chlorophenyl)-3-tosyl-1H-pyrazole-5,5(4H)-dicarboxylate (**6d**)*
White solid; Yield 63% (150 mg); mp 110 ^oC; IR (KBr, cm^{-1}) 3338 (w), 2982 (w), 1742 (vs), 1683 (m), 1491 (m), 1331 (m), 1303 (m),

1281 (s), 1148 (m), 1091 (s), 1016 (m), 814 (m), 666 (m), 592 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 2.36 (s, 3H), 3.60-3.67 (m, 1H), 3.73- 3.79 (m, 1H), 4.18-4.30 (m, 2H), 5.23 (s, 1H), 6.87-6.92 (br unresolved d, 2H), 7.03 (d, *J* = 7.3 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.17 (brs, 1H), 7.44 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4, 13.9, 21.7, 55.5, 62.7, 63.6, 81.1, 128.3, 128.6, 129.7, 130.5, 131.2, 134.6, 136.4, 145.1, 152.1, 165.1, 166.8; MS (ES+) m/z (rel intensity) 503 ([M+2]Na^+, 40), 501 (MNa^+, 100); HRMS (ES+) calcd for $C_{22}H_{23}ClN_2O_6SNa$ (MNa^+) 501.0858, found 501.0862.

*4.4.4 Diethyl 4-(4-cyanophenyl)-3-tosyl-1H-pyrazole-5,5(4H)-dicarboxylate (**6f**)*

White solid; Yield 62% (164 mg); mp 110 °C ; IR (KBr, cm^{-1}) 3317 (m), 2985 (m), 2230 (s), 1742 (s), 1596 (w), 1447 (w), 1330 (m), 1275 (m), 1149 (m), 669 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.73 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 2.35 (s, 3H), 3.56- 3.63 (m, 1H), 3.71- 3.78 (m, 1H), 4.18- 4.31 (m, 2H), 5.27 (s, 1H), 7.13 (d, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 3H), 7.46 (d, 8.1 Hz, 2H), 7.62 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4, 13.8, 21.6, 55.7, 62.7, 63.7, 81.2, 112.2, 118.1, 128.2, 129.7, 129.9, 130.0, 131.8, 132.1, 136.1, 138.2, 145.4, 151.7, 164.8, 166.4; MS (ES+) m/z (rel intensity) 492 (MNa^+, 100); HRMS (ES+) calcd for $C_{23}H_{23}N_3O_6S$ (MNa^+) 492.1200, found 492.1196.

*4.4.5 Diethyl 4-(naphthalen-1-yl)-3-tosyl-1H-pyrazole-5,5(4H)-dicarboxylate (**6h**)*

White solid; Yield 52% (137 mg); mp 140 °C; IR (KBr, cm^{-1}) 3338 (m), 1739 (s), 1596 (w), 1329 (s), 1272 (s), 1148 (m), 799 (m), 672 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.14 (t, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 2.36 (s, 3H), 3.12- 3.17 (m, 1H), 3.38- 3.44 (m, 1H), 4.27- 4.36 (m, 2H), 6.27 (s, 1H), 6.76-6.78 (dd, *J* = 1.1 Hz, 7.2 Hz, 1H),7.00- 7.04 (m, 2H), 7.05 (s, 1H) 7.37-7.39 (dd *J* = 1.6 Hz, 6.9 Hz, 2H), 7.48-7.52 (td, *J* = 0.9, 7.0 Hz, 1H); 7.58-7.62 (td, *J* = 1.3, 6.9 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 8.3 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.7, 14.1, 21.7, 62.4, 63.6, 81.5, 123.9, 125.0, 126.1, 127.0, 127.5, 128.1, 128.5, 128.7, 128.8, 128.9, 129.0, 129.6, 132.0, 133.8, 136.6, 145.0, 154.0, 165.5, 167.5; HRMS (ES+) calcd for $C_{26}H_{26}N_2O_6S$ (MNa^+) 517.1404, found 517.1397. Selected crystallographic parameters for $C_{26}H_{26}N_2O_6S$, M = 494.56, Monoclinic, space group P 1 21/c 1, a = 11.140(4) Å, b = 13.845(5) Å, c = 15.887(5) Å, α = 90°, β = 95.476°, γ = 90°, V = 2439.1(15) $Å^3$, Dc = 1.347Mg/m^3, Z = 4, F(000) = 1040, λ = 0.71070 Å, μ = 0.177 mm^{-1}, Total unique reflections = 32157 / 6542 [R(int) = 0.1780], T = 100(2) K, θ range = 3.21 to 29.16°, Final R indices [I>2σ(I)] : R1 = 0.0711, wR2 = 0.1531, R(all data) : R1 = 0.1225, wR2 = 0.1863.

*4.5 General procedure for the synthesis of pyrazole carboxylate **5** from pyrazoline **6** under MW irradiation (see Scheme 5)*

In a 10 mL microwave glass vial containing EtOH (1 mL), was added pyrazoline **6** (0.1 mmol) followed by Cs_2CO_3 (16.5 mg, 0.05 mmol, 0.5 equiv) and the resulting mixture was subjected to microwave irradiation for 10-15 min at 80 °C until the completion of reaction (monitored by TLC). After removal of EtOH in vacuo, the residue was treated with water (10 mL) and the aqueous layer was extracted with EtOAc (2 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the filtrate was then concentrated in vacuo. The residue was recrystallized from EtOAc/hexane (1:1) to obtain pure **5** in quantitative yields.

*4.5.1 Ethyl 4-phenyl-1H-pyrazole-3-carboxylate (**5a**)*

White solid, Yield 96% (21 mg); mp, IR, ^{1}H, ^{13}C and Mass data are consistent with those of **5a** obtained from **4a** (Table 3).

*4.5.2 Ethyl 4-(4-methoxyphenyl)-1H-pyrazole-3-carboxylate (**5c**)*

White solid, Yield 97% (24 mg); mp, IR, ^{1}H, ^{13}C and Mass data are consistent with those of **5c** obtained from **4c** (Table 3).

*4.5.3 Ethyl 4-(4-chlorophenyl)-1H-pyrazole-3-carboxylate (**5d**)*

White solid, Yield 97% (24 mg); mp 142 °C; IR (KBr, cm^{-1}) 3339 (br m), 2988 (w), 1742 (vs), 1492 (m), 1445 (m), 1332 (m), 1274 (s), 1219 (m), 1149 (m), 1091 (s), 1017 (m), 737 (m), 665 (s); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.37 (t, *J* = 7.1 Hz, 3H), 4.41 (q, *J* = 7.1 Hz, 2H), 7.40-7.42 (m, 2H), 7.44-7.51 (m, 2H), 7.90 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 60.3, 122.7, 125.5, 127.9, 128.1, 130.8, 131.7, 140.1, 162.6; MS (ES+) m/z (rel intensity) 275 ([M+2]Na^+, 30), 273 (MNa^+, 100), 251 (MH^+, 10), 235 (35); HRMS (ES+) calcd for $C_{12}H_{11}ClN_2O_2Na$ (MNa^+) 273.0401, found 273.0403.

*4.5.4 Ethyl 4-(4-cyanophenyl)-1H-pyrazole-3-carboxylate (**5f**)*

White solid, Yield 96% (23 mg); mp, IR, ^{1}H, ^{13}C and Mass data are consistent with those of **5f** obtained from **4f** (Table 3).

*4.6 General procedure for the reaction of arylidene-1,3-dicarbonyls **7** with sulfone **2** (see Table 5)*

To a stirred solution of **7** (0.5 mmol, 1 equiv) and *α*-diazo-*β*-ketosulfone **2** (143 mg, 0.6 mmol, 1.2 equiv) in dry EtOH (5 mL) was added NaOEt (51 mg, 0.75 mmol, 1.5 equiv) at 0 °C and the resulting mixture was stirred at the same temperature until the reaction was complete (monitored by TLC). Then the reaction mixture was concentrated in *vacuo* and the crude residue was directly subjected to silica gel column chromatography (pet ether/ethyl acetate: 8/2) to afford pure **3, 5** or **8**.

*4.6.1 Phenyl(4-phenyl-1H-pyrazol-3-yl)methanone (**3a**)*

White solid; Yield 75% (117 mg); mp, IR, ^{1}H, ^{13}C and Mass data are consistent with those of **3a** obtained from **1a** (Table 1).

*4.6.2 Ethyl 4-phenyl-1H-pyrazole-3-carboxylate (**5a**)*

White solid, Yield 70% (76 mg); mp, IR, ^{1}H, ^{13}C and Mass data are consistent with those of **5a** obtained from **4a** (Table 3).

*4.6.3 Ethyl 4-(3,4-dimethoxyphenyl)-1H-pyrazole-3-carboxylate (**5k**)*

White solid; Yield 50% (69 mg); mp 157 °C; IR (KBr, cm^{-1}) 3214 (brs), 2960 (w), 1685 (vs), 1513 (m), 1465 (s), 1438 (m), 1327 (m), 1253 (s), 1182 (m), 1146 (s), 1027 (m), 851 (m); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.2 Hz, 3H), 3.91 (s, 6H), 4.36 (q, *J* = 7.2 Hz, 2H), 6.90 (d, *J* = 8.2 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 7.14 (s, 1H), 7.76 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 56.1 (× 2), 61.3, 110.9, 113.2, 122.0, 124.5, 125.6, 134.6, 135.8, 148.5, 148.8, 161.4; MS (ES+) m/z (rel intensity) 299 (MNa^+, 40), 277 (MH^+, 42), 232 (15), 231 (100); HRMS (ES+) calcd for $C_{14}H_{16}N_2O_4Na$ (MNa^+) 299.1008, found 299.0997.

*4.6.4 1-(4-Phenyl-1H-pyrazol-3-yl)ethanone (**8a**)*

White solid; Yield 62% (58 mg); mp 151 °C; IR (KBr, cm^{-1}) 3228 (s), 2998 (w), 2343 (w), 1673 (s), 1454 (m), 1424 (m), 1115 (m), 1095 (m), 950 (m); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.44 (s, 3H), 7.34-7.39 (m, 2H), 7.41-7.45 (m, 3H), 7.66 (s, 1H), 9.47 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.5, 125.3, 128.0, 128.1, 128.5, 129.7, 132.1, 135.4, 192.6; MS (ES+) m/z (rel intensity) 371 ([2M-1]$^+$, 28), 355 ([2M-17]$^+$, 100), 333 (10); HRMS (ES+) calcd for $C_{11}H_{10}N_2O$ (MNa^+) 209.0685, found 209.0682.

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