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The diaza-Nazarov cyclization involving a 2,3-diaza-pentadienyl cation for the synthesis of polysubstituted pyrazoles†

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An unprecedented iodine-mediated diaza-Nazarov (DAN) type cyclization for the construction of substituted pyrazoles from easily available starting materials *via* an enamine–iminium ion intermediate is described. The oxidative cyclization worked under green conditions with remarkable regioselectivity. This one-pot, efficient and operationally simple three-component intramolecular regioselective DAN cyclization displayed a wide range of substrate scope. The dichotomy of reaction pathways has been explored with density functional theory in the gas phase and solution phase. Of the possible 1,5-, 1,6-, and 1,7-electrocyclizations, the DAN cyclization, *i.e.*, the 1,5-pathway offers the lowest activation energy barrier supporting our experimental observations.

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Introduction

The pyrazole moiety belongs to an important class of heteroaromatic compounds owing to its frequent occurrence in many natural products and biologically active compounds.[1] Pyrazole ring containing compounds exhibit antidiabetic,[2] anticancer,[3] antiinflammatory,[4] and analgesic[5] activities. These are also important building blocks in the agrochemical industry.[6] On account of their great biological importance, diverse approaches were established for the synthesis of pyrazoles. Traditionally, these pyrazoles can be synthesized by the reaction of 1,3-diketones/α,β-unsaturated carbonyls with hydrazine derivatives[7] and the 1,3-dipolar cycloaddition of hydrazines with alkenes/alkynes.[8] With the growing interest in the synthesis of pyrazoles, many transition metal[9] and metal-free[10] approaches have been reported in the past few years. In 2014, Chang and co-workers established the iodine mediated synthesis of pyrazoles from α,β-unsaturated aldehydes/ketones and hydrazones.[11] In 2015, Singh *et al.* reported the sulphur-promoted synthesis of pyrazoles through cross dehydrogenative cyclisation of acetophenone hydrazones with aldehydes.[12] Herein, for the first time we describe the iodine-mediated diaza-Nazarov reaction for the synthesis of substituted pyrazoles from benzaldehyde hydrazone and acetophenone.

In recent years, Lewis acid mediated Nazarov-type cyclization has emerged as an important tool for the synthesis of five-membered carbocyclic compounds from dienones.[13] In general, the key step for the Nazarov reaction is the 4π-electrocyclization of a pentadienyl cation. A heteroatom involved Nazarov-type approach has attracted incredibly wide attention in the present research scenario owing to its remarkable ability to facilitate cationic 4π-electrocyclization of a pentadienyl system bearing an imino group instead of the classical ketone functionality. So far, only a few reports are known describing the imino-Nazarov reaction. In 2007, the Klumpp research group developed the aza-Nazarov cyclization reaction of *N*-acyliminium salts with CF_3SO_3H.[14a] Later in 2010, Tius and co-workers revealed the enamine–iminium ion Nazarov cyclization of α-ketoenones *via* diamine salt catalyzed enamine–iminium ion formation.[14b,c] It is a big challenge to develop the Nazarov-type reaction since the cyclization event of a stable acyclic imino diene is not favourable in comparison to conventional Nazarov-type reactions. Subsequently Hsung,[15a] West,[15b] and Liu,[15c] explored the interrupted imino-Nazarov electrocyclization. Recently, the Liao group reported the aza-Nazarov reaction for the synthesis of *N*-hydroxy oxyindoles where they described the involvement of an azaoxyallyl cation as an intermediate.[16] In 2009, the Würthwein group disclosed the synthesis of dihydrospiroindenepyrazoles and dihydroindenodiazepine derivatives by 1,5- and 1,7-cascade electrocyclizations under the superelectrophilic solvation conditions, with the involvement of an iminium cation intermediate. To support the mechanism, they calculated the relative energies

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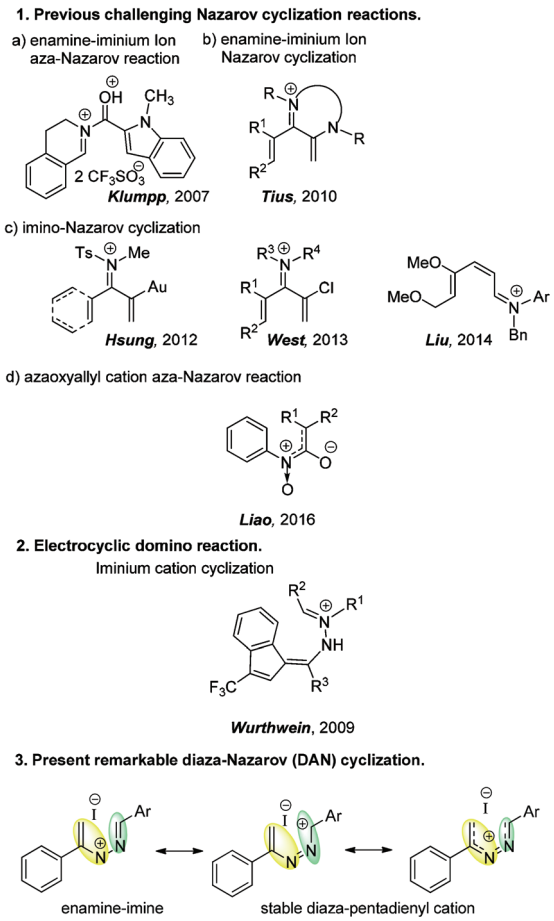


Scheme 1 Nazarov-type cyclizations.

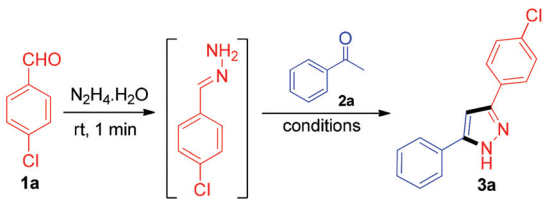
of Hückel- and Möbius-type transition states of both the cyclizations.[17]

To the best of our knowledge, diaza-Nazarov-type 4π-electrocyclization is not reported for the synthesis of pyrazoles. Herein, we describe an iodine-mediated metal-free one-pot approach for the synthesis of substituted pyrazoles *via* diaza-Nazarov-type cyclization of the enamine–imino ion (Scheme 1) under mild conditions by employing *in situ* generated aldehyde hydrazones and acetophenone derivatives as starting materials.

Results and discussion

We envisaged that diaza-Nazarov type cyclization with a 1,3-diene embedded with two nitrogen atoms would lead to the generation of pyrazoles. As a prelude to our objective, we started our investigation by choosing 4-chlorobenzaldehyde (**1a**) and acetophenone (**2a**) as model substrates. At the beginning, we performed a straightforward condensation of benzaldehyde and hydrazine hydrate under solvent-free conditions for the *in situ* generation of the corresponding hydrazone within a minute. The *in situ* generated hydrazone was then treated with acetophenone in the presence of various promoters. To our delight, when the reaction was carried out in MeOH using iodine (1.2 equiv.), the pyrazole derivative **3a** was obtained in 65% yield in 24 h (Table 1, entry 1). To evaluate the effect of the solvent in the reaction, we screened various solvents such as THF, CH_3CN, 1,4-dioxane, H_2O and EtOH. The former solvents provided pyrazole **3a** in 44, 56, 44, and 33% yield, respectively (entries 2–5). The reaction in EtOH afforded the pyrazole **3a** in a maximum yield of 70% (entry 6). The reaction, when performed under solvent-free conditions, afforded the desired product **3a** in 42% yield in 24 h (entry 7). By choosing EtOH as an optimum solvent, reagents such as NCS, NBS, NIS, KI and $PhI(OAc)_2$ were screened. No improvement was observed in the yield of the product with NCS and NBS-mediated reactions (entries 8 and 9). When the reaction was performed with NIS, the starting material was recovered along with traces of the product (entry 10). The reaction was inefficient in the presence of KI and $PhI(OAc)_2$ (entries 11 and 12). The yield was diminished by reducing the amount of iodine to 0.5 equiv. (entry 13). We observed lower yield when the amount of iodine was increased to 1.5 equiv. (entry 14). To further improve the efficiency of the reaction, we evaluated the effect of temperature. For that we performed the reaction at 50 °C, which afforded the product **3a** in 69% yield (entry 15). An increase in the yield of the product was observed when we performed the model reaction at 70 °C (entry 16). The reaction at 90 °C led to the formation of the product in a marginally lower yield (entry 17). We further studied the effect of different

Table 1 Optimization of reaction conditions[a]



Entry	Reagent	Solvent	Temp.	Time	Yield[b] (%)
1	I_2	MeOH	rt	24 h	65
2	I_2	THF	rt	24 h	44
3	I_2	ACN	rt	24 h	56
4	I_2	1,4-Dioxane	rt	24 h	44
5	I_2	H_2O	rt	24 h	33
6	I_2	EtOH	rt	24 h	70
7	I_2	Neat	rt	24 h	42
8	NCS	EtOH	rt	24 h	54
9	NBS	EtOH	rt	24 h	57
10	NIS	EtOH	rt	24 h	Traces
11	KI	EtOH	rt	24 h	nr
12	DIB	EtOH	rt	24 h	nr
13[c]	I_2	EtOH	rt	24 h	52
14[d]	I_2	EtOH	rt	24 h	60
15	I_2	EtOH	50 °C	12 h	69
16	I_2	EtOH	70 °C	12 h	76
17	I_2	EtOH	90 °C	12 h	72
18	$BF_3{\cdot}OEt_2$	EtOH	70 °C	12 h	nr
19	$ZrCl_4$	EtOH	70 °C	12 h	nr
20	$ZnCl_2$	EtOH	70 °C	12 h	nr

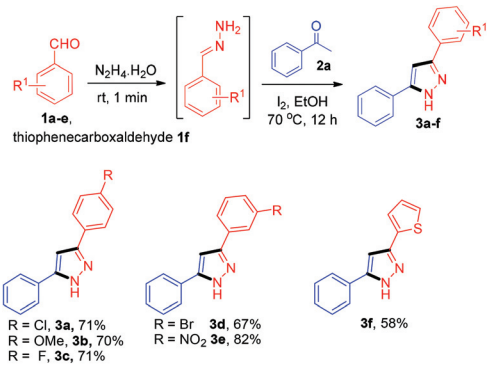
[a] Reaction conditions: **1a** (0.6 mmol), hydrazine hydrate 80% (1 mmol), **2a** (0.50 mmol), reagent (0.6 mmol). [b] Isolated yield. nr = no reaction. [c] I_2: 0.5 equiv., 24 h. [d] I_2: 1.5 equiv.

reagents such as $BF_3{\cdot}OEt_2$, $ZrCl_4$ and $ZnCl_2$ on the reaction, but no product was formed (entries 18–20). Thus these studies identified EtOH as the optimum solvent at 70 °C and iodine as the promoter for the reaction (entry 16).

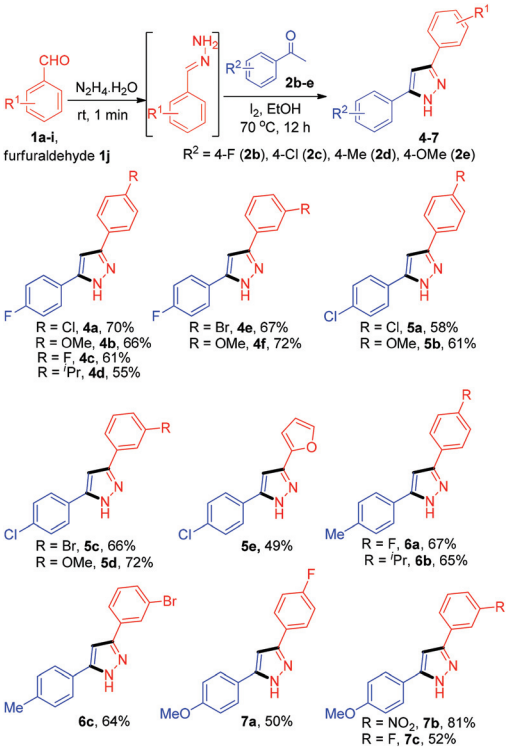
With the optimized reaction conditions in hand, we explored the scope of the present one-pot, three-component diaza-Nazarov-type cyclization. Thus various substituted aldehydes **1a–e** having electron-withdrawing as well as electron-donating groups were selected and were reacted with acetophenone (**2a**) under optimized reaction conditions. In all cases, the reactions proceeded cleanly to furnish the corresponding pyrazole derivatives **3a–e** in good to high yields of 67–82% (Scheme 2). The reaction of thiophene aldehyde **1f** with acetophenone (**2a**) under a similar set of conditions furnished the product **3f** in moderate yield.

On the basis of the successful results obtained from the aldehydes **1a–f** and acetophenone **2a**, we further tested the scope of the reaction with a series of acetophenones **2b–e**. The reactions are well tolerant of both electron-withdrawing and electron-releasing groups. In all cases, the corresponding pyrazole derivatives **4–7** were isolated in good to high yields (49–81%, Scheme 3). We further extended the scope of the reaction by using α-substituted acetophenone **2f** with aldehydes **1b,c** at 80 °C. To our delight, the cyclized products **8a** and **8b** were obtained in 52 and 47% yield in 24 h, respectively (Scheme 4). It is noteworthy to mention here that about 10–15% of aryl aldehydes **1a–j** were recovered in these reactions from the decomposition of the corresponding hydrazones presumably due to the presence of the HI by-product. The products were characterized on the basis of spectroscopic data and the structure of the pyrazole **5a** was further confirmed from its single crystal X-ray analysis (see ESI, Fig. S2†).[18]

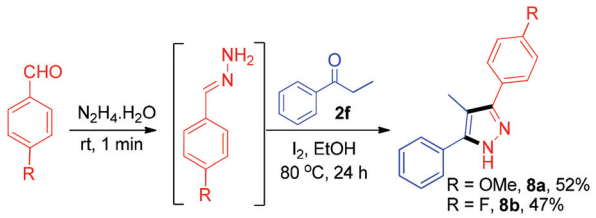
To verify the radical pathway of the reaction, a radical trapping agent TEMPO was used in varied amounts. However, the reaction was not inhibited, albeit the product **3a** was obtained in a relatively lower yield. Based on the above results and the previous reports,[14–17] a plausible mechanism for the formation of **3a** is depicted in Scheme 8. The hydrazone, generated from aldehyde **1a** and hydrazine hydrate, undergoes condensation



Scheme 2 Scope of benzaldehyde derivatives in DAN cyclization. Reaction conditions: **1a** (0.6 mmol), hydrazine hydrate 80% (1.0 mmol), **2a** (0.5 mmol), iodine (0.6 mmol), EtOH (3 mL).

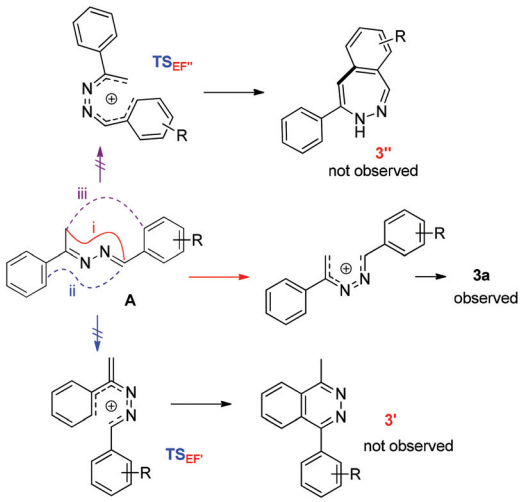


Scheme 3 Scope of different acetophenone and benzaldehyde derivatives. Reaction conditions: **1a** (0.6 mmol), hydrazine hydrate 80% (1.0 mmol), **2** (0.5 mmol), iodine (0.6 mmol), EtOH (3 mL).

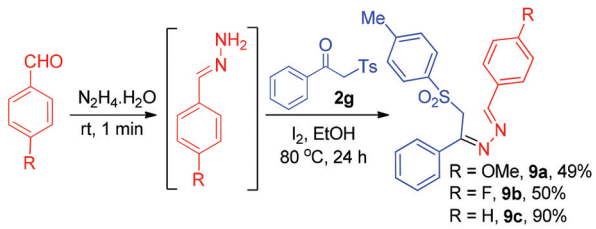


Scheme 4 DAN approach with propiophenone (**2f**).

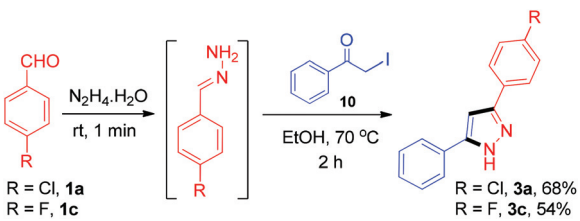
with acetophenone **2a** to generate intermediate **A.** α-Iodination of tautomer **B** with molecular iodine provides alkyl iodide **C** with the concomitant removal of HI. The conformational change of s-*trans* diimine **C** to s-*cis* diimine **D** followed by de-iodination leads to 2,3-diaza-pentadienyl cation **E**, which is stabilized by the delocalization of positive charge. This enamine–iminium ion undergoes 4π-electrocyclization ring closure to generate diaza-allyl cation **F**, which upon dehydrohalogenation and aromatization furnishes exclusively five-membered heterocycle **3**. The other possible nitrogen-embedded regioisomers from 6π-electron-6-atom and 6π-electron-7-atom oxidative electro-cyclizations[19] were not formed in this reaction (Scheme 5, also see the ESI†). To gain insights into the mechanism, we performed the reaction of tosyl substituted acetophenone **2g** with **1b,c**. In both cases, noncyclized 2,3-diaza-1,3-dienes **9a** and **9b** were isolated in 50% yield in 24 h. The



Scheme 5 Possible regioisomers during cyclization.



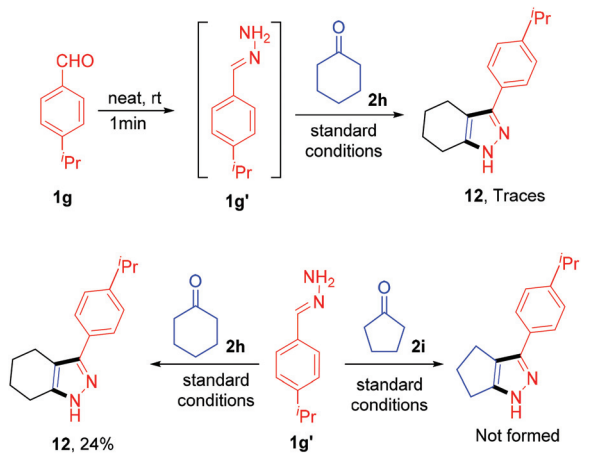
Scheme 6 Reaction of α-tosyl acetophenone (**2g**).



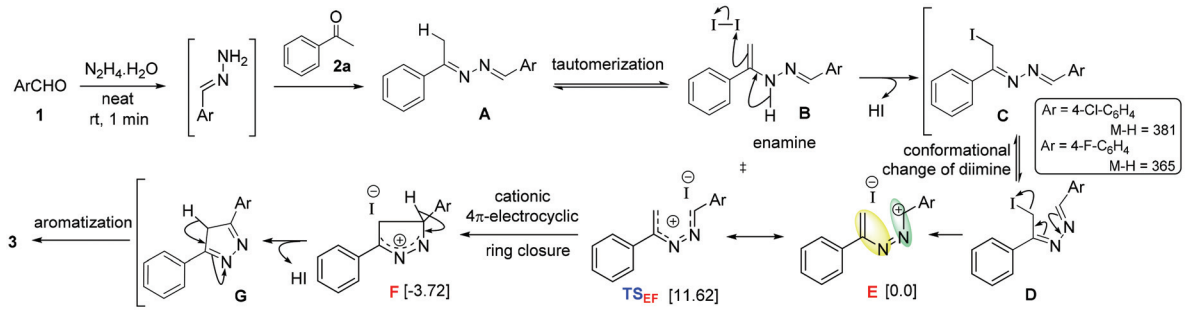
Scheme 7 DAN approach with α-iodoacetophenone (**10**).

parent benzaldehyde hydrazone also reacted with **2g** to afford acyclic heterodiene **9c**. This clearly indicates that the formation of the 2,3-diaza-pentadienyl cation does not occur and hence no diaza-Nazarov reaction product (Scheme 6). Our efforts to cyclise **9** in the presence of reagents such as I_2/TFA, $SnCl_4$ and $FeCl_3$ did not result in success (see the ESI†). Since the α-position of aza-diene was blocked with the tosyl group, α-iodination did not take place. Thus it is indirectly proving that α-iodination (as in intermediates **C** and **D**) is essential for the success of the DAN cyclization (Scheme 8).

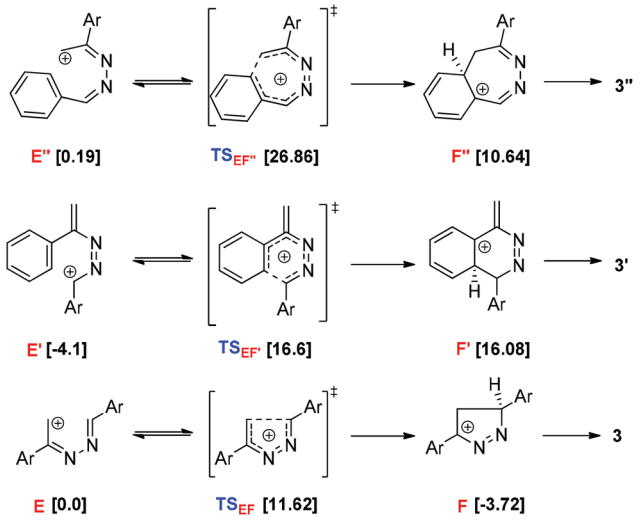
The obtained mass spectral evidence for the intermediate **C** (Ar = Ph, 4-Cl-C_6H_4, 4-F-C_6H_4) also supports the proposed mechanism (see the ESI†). The reaction of α-iodoacetophenone (**10**) with aldehydes **1a** and **1c** and hydrazine provided pyrazoles **3a** and **3c**, which also confirms the generation of intermediate **C** (Ar = 4-Cl-C_6H_4 and 4-F-C_6H_4) (Schemes 7 and 8) (see the ESI†). The *in situ* generated 4-iso-propylbenzaldehyde hydrazone did not undergo cyclization with ketones such as cyclohexanone and cyclopentanone under standard conditions. However, the isolated 4-iso-propylbenzaldehyde hydrazone reacted with cyclohexanone to furnish the corresponding DAN product in 24% yield (Scheme 9). Valeraldehyde failed to produce the product with **2a** under the optimized conditions.



Scheme 9 Substrate scope of DAN reaction.



Scheme 8 Plausible reaction mechanism.



Scheme 10 Calculated electronic energies (E_{rel}) in kcal mol^{-1} relative to 2,3-diaza-pentadienyl cation (*E*) for the 1,5-, 1,6- and 1,7-cyclization pathways of electrocyclization step of the diaza-Nazarov reaction at the B3LYP/6-311G** level of theory in the gas phase.

Computational study

In order to pay attention to a better understanding of the plausible mechanism of the electrocyclization step (**E** to **F**) of the diaza-Nazarov reaction and to validate the results found experimentally, we performed quantum chemical calculations using hybrid B3LYP functional[20,21] with a 6-311G** basis set[22] in the gas phase. All DFT calculations were performed using a G09, revision A.02, program package.[23] All structures of 1,5-, 1,6- and 1,7-electrocyclization pathways were optimized. Frequency calculations were also performed to confirm that the structures are minima with all positive frequencies and transition states (TSs) with one imaginary frequency. Intrinsic reaction coordinate (IRC) calculations were also run to confirm the nature of TSs.

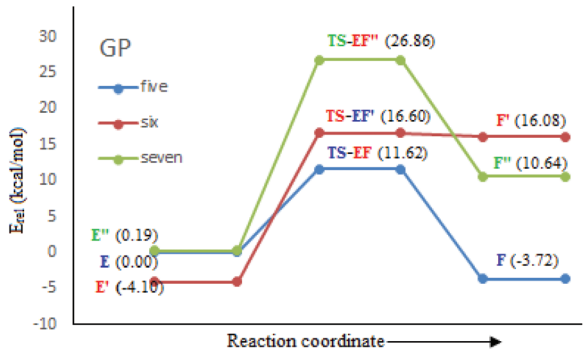


Fig. 1 A comparative energy profile diagram for the 1,5-, 1,6- and 1,7-cyclization pathways of electro-cyclization step of the diaza-Nazarov reaction at the B3LYP/6-311G** level of theory in the gas phase.

The electrocyclic step begins with three different conformations of the diaza-pentadienyl (DAP) cation for DFT calculations of 1,5-, 1,6- and 1,7-electrocyclization pathways. The conformations were obtained from IRC calculations starting from the transition structures and the lowest energy conformer (1,5-) differ in energy by about −4.10 (1,6-) and 0.19 (1,7-) kcal mol^{-1} (Scheme 10). From our results, two important things were observed for DAN cyclization reaction using DFT calculations: (i) a comparative DFT study of 1,5-, 1,6- and 1,7-DAN electrocyclization pathways, and (ii) a DFT calculation preferred 4π-1,5-electrocyclization pathway with the lowest activation energy barrier (11.62 kcal mol^{-1}) supporting our experimentally observed 1,5-DAP. As shown in Fig. 1, the 1,6- (20.70 kcal mol^{-1}) and 1,7- (26.67 kcal mol^{-1}) electrocyclization pathways lead to higher activation energy barriers by 9.08 and 15.05 kcal mol^{-1}, respectively, than that of the 4π-1,5-electrocyclization pathway. DFT calculations show that the cyclization of the 1,5-DAP cation can be considered as a process with a low activation barrier and exothermicity (ΔH, −3.11 kcal mol^{-1}), while the unfavourable 1,6- and 1,7-cyclization products formed *via* higher activation barriers and predicted to be highly endothermic with 19.89 and 11.05 kcal mol^{-1}, respectively. Negative Gibbs free energy (ΔG) results show that the 1,5-cyclization pathway (−1.49 kcal mol^{-1}) is the most favourable compared to the six- (22.15 kcal mol^{-1}) and seven- (14.36 kcal mol^{-1}) cyclization pathways (see ESI, Table S4†). To evaluate the effect of the solvent on activation barriers of electronic energy, we performed B3LYP/6-311G** calculations using the CPCM model with ethanol solvent. The activation energy barriers in the gas phase and solution phase are very close (less than 1 kcal mol^{-1}) and there is no significant change (see the ESI†).

We generated HOMO and LUMO plots using B3LYP/6-311G** optimized geometries of TSs by using Gauss view visu-

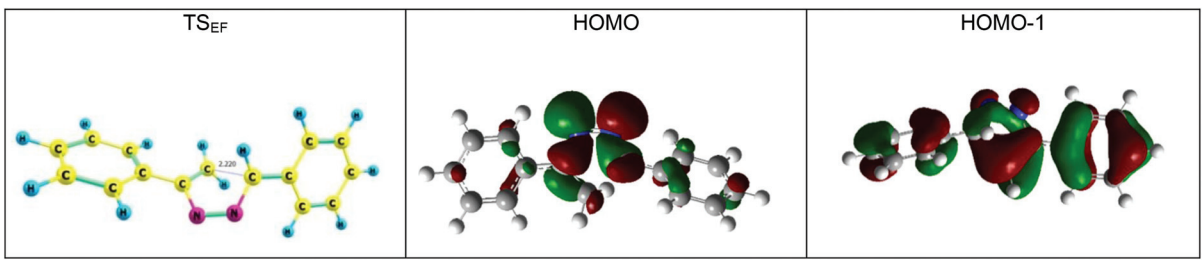


Fig. 2 Optimised structures of TS with HOMO and HOMO−1 molecular diagrams of the 1,5-cyclization pathway of electrocyclization step of the diaza-Nazarov reaction at the B3LYP/6-311G** level of theory in the gas phase (the bond forming distances between terminal atoms of TS are in Å).

alization software.[24] The binding interaction in TS_{EF} is dominated by HOMO−1 as shown in Fig. 2, while HOMO is localized at the heterocyclic part.

Conclusion

In conclusion, we have described the first examples of diaza-Nazarov cyclization employing *in situ* generated hydrazones and acetophenones. This iodine-mediated expedient process furnished functionally-rich pyrazoles in ethanol under aerobic conditions. The cascade reaction for the pyrazole formation proceeds through enamine–imino diaza-Nazarov 4π-electrocyclization. The title five-membered heterocycles are accessed in good to high yields from a one-pot three-component protocol under mild conditions. The simplicity of the experimental procedure and the ready accessibility of starting materials thus make this an experimentally attractive method for the preparation of the nitrogenous heterocycles. Computational studies predicted that the cyclization of the 1,5-DAP cation is the most favourable pathway compared to 1,6- and 1,7-cyclizations supporting the experimentally obtained DAN products.

Experimental section

General information

Unless otherwise noted, chemicals were purchased from commercial suppliers at the highest purity grade available and were used without further purification. Thin layer chromatography was performed on 0.25 mm silica gel plates (60F-254) using UV light as the visualizing agent. Silica gel (100–200 mesh) was used for column chromatography. Melting points were determined on a capillary point apparatus equipped with a digital thermometer and are uncorrected. Nuclear magnetic resonance spectra were recorded on 400 and 500 MHz spectrometers, and chemical shifts are reported in δ units, parts per million (ppm), relative to residual chloroform (7.26 ppm) or DMSO (2.5 ppm) in the deuterated solvent or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak) and DMSO-d_6 (δ 39.5 ppm, the middle peak). Coupling constants are expressed in Hz. The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, sp = septet, and brs = broad singlet. High resolution mass spectra were recorded with a micro TOF-Q analyzer spectrometer by using the electrospray mode.

General procedure for the synthesis of substituted pyrazoles

To a benzaldehyde derivative **1** (0.6 mmol) was added hydrazine hydrate (80% in water, 1.0 mmol) under solvent-free conditions. After the addition of hydrazine hydrate, a yellow solid was formed within a minute which indicated the formation of the hydrazone derivative. To the thus formed hydrazone derivative was added acetophenone derivative **2** (0.5 mmol) in EtOH (3 mL) followed by iodine (0.154 g, 1.2 mmol). Then the reaction mixture was refluxed at 70 °C on a pre-heated oil bath for 12 h. After completion of the reaction, as checked by TLC, the reaction was quenched with a saturated sodium thiosulfate solution and extracted twice with ethyl acetate (2 × 15 mL). The organic layer was washed with water and dried over anhyd. sodium sulfate. The solvent was evaporated under reduced pressure, and the residue was subjected to silica gel column chromatography using ethyl acetate in hexanes as the eluent to afford a pure pyrazole derivative.

Characterization data

3-(4-Chlorophenyl)-5-phenyl-1*H*-pyrazole (3a). Yield: 0.090 g (71%) as a brown solid; mp: 218–219 °C; IR (KBr): ν_{max} 3443, 1636, 1489, 1386, 1309, 1259, 1180, 1088, 1021, 968, 826 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.86 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 7.2 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.35 (d, J = 7.6 Hz, 1H), 7.23 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 128.8, 126.8, 125.1, 99.9 ppm; HRMS: m/z calculated for $C_{15}H_{12}ClN_2$ $(M + H)^+$: 255.0689, found: 255.0686.

3-(4-Methoxyphenyl)-5-phenyl-1*H*-pyrazole (3b). Yield: 0.087 g (70%) as a brown solid; mp: 155–156 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 6.8 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.36 (t, J = 7.2 Hz, 2H), 7.32–7.30 (m, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.73 (s, 1H) 3.81 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 131.4, 128.7, 128.0, 126.8, 125.5, 123.8, 114.1, 99.4, 55.2 ppm; HRMS: m/z calculated for $C_{16}H_{15}N_2O$ $(M + H)^+$: 251.1179, found: 251.1178.

3-(4-Fluorophenyl)-5-phenyl-1*H*-pyrazole (3c). Yield: 0.084 g (71%) as a brown solid; mp: 189–190 °C; IR (KBr): ν_{max} 3443, 1620, 1510, 1467, 1444, 1304, 1253, 1181, 1029, 987, 865 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.89 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 7.2 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.25 (t, J = 7.6 Hz, 1H), 6.85 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ 146.7 (d, $^1J_{C,F}$ = 113 Hz), 135.3, 130.0, 128.5, 128.1, 127.4, 124.9, 124.8, 122.2, 99.3 ppm; HRMS: m/z calculated for $C_{15}H_{12}FN_2$ $(M + H)^+$: 239.0979, found: 239.0950.

3-(3-Bromophenyl)-5-phenyl-1*H*-pyrazole (3d). Yield: 0.099 g (67%) as a brown solid; mp: 165–166 °C; IR (KBr): ν_{max} 3456, 2360, 1637, 1503, 1442, 1371, 1312, 1079, 976 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.47 (brs, 1H, N*H*), 8.06 (s, 1H), 7.83 (d, J = 17.5 Hz, 3H), 7.50–7.35 (m, 5H), 7.29 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ 146.8, 146.2, 133.6, 130.0, 129.6, 129.5, 128.0, 127.4, 127.2, 124.6, 123.3, 121.8, 98.8 ppm; HRMS: m/z calculated for $C_{15}H_{12}BrN_2$ $(M + H)^+$: 299.0178, found: 299.0163.

3-(3-Nitrophenyl)-5-phenyl-1*H*-pyrazole (3e). Yield: 0.108 g (82%) as a brown solid; mp: 207–209 °C; IR (KBr): ν_{max} 3440, 1572, 1533, 1506, 1446 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.63 (brs, 1H, N*H*), 8.67 (s, 1H), 8.30 (d, J = 7.5 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 7.0 Hz, 2H), 7.74 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.0 Hz, 2H), 7.43 (s, 1H) 7.37 (t, J = 7.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ 147.0, 133.1,

129.9, 128.9, 128.4, 127.4, 126.7, 124.0, 123.7, 120.5, 118.4, 98.6 ppm; HRMS: *m*/*z* calculated for $C_{15}H_{12}N_3O_2$ (M + H)$^+$: 266.0924, found: 266.0921.

5-Phenyl-3-(thiophen-2-yl)-1*H*-pyrazole (3f). Yield: 0.065 g (58%) as a brown solid; mp: 185–184 °C; IR (KBr): ν_{max} 3415, 1577, 1487, 1404, 1174, 844, 755 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.72 (d, J = 7.6 Hz, 2H), 7.37 (t, J = 7.6 Hz, 3H), 7.26 (dd, J = 5.6 Hz, 7.6 Hz, 2H), 7.01 (t, J = 4.4 Hz, 1H), 6.74 (t, J = 4.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ 129.1, 127.4, 126.6, 126.2, 124.0, 123.1, 122.3, 122.1, 98.0 ppm; HRMS: *m*/*z* calculated for $C_{13}H_{11}N_2S$ (M + H)$^+$: 227.0637, found: 227.0619.

3-(4-Chlorophenyl)-5-(4-fluorophenyl)-1*H*-pyrazole (4a). Yield: 0.096 g (70%) as a brown solid; mp: 209–210 °C; IR (KBr): ν_{max} 3468, 1618, 1508, 1306, 1247, 1174, 1035, 912 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.44 (brs, 1H, N*H*), 7.84 (s. 4H), 7.50 (s, 2H), 7.28 (s, 2H), 7.17 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ 161.8 (d, $^1J_{C,F}$ = 245 Hz), 132.7, 128.2, 126.7, 126.6, 126.2, 115.2, 114.9, 98.8 ppm; HRMS: *m*/*z* calculated for $C_{15}H_{11}ClFN_2$ (M + H)$^+$: 273.0589, found: 273.0589.

5-(4-Fluorophenyl)-3-(4-methoxyphenyl)-1*H*-pyrazole (4b). Yield: 0.088 g (66%) as a brown solid; mp: 205–206 °C; IR (KBr): ν_{max} 3470, 1627, 1503, 1450, 1256, 1177, 965 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (q, J = 5.5 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H), 6.92 (t, J = 8.5 Hz, 2H), 6.75 (d, J = 8.5 Hz, 2H), 6.57 (s, 1H), 3.77 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7 (d, $^1J_{C,F}$ = 245 Hz), 159.3, 148.0 (d, $^2J_{C,F}$ = 104), 127.9, 127.1, 123.1, 115.5, 115.4, 114.0, 98.7, 55.0 ppm; HRMS: *m*/*z* calculated for $C_{16}H_{14}FN_2O$ (M + H)$^+$: 269.1085, found: 269.1087.

3,5-Bis(4-fluorophenyl)-1*H*-pyrazole (4c). Yield: 0.078 g (61%) as a brown solid; mp: 168–169 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.41 (brs, 1H, N*H*), 7.87 (s, 4H), 7.27 (s, 4H), 7.11 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.8 (d, $^1J_{C,F}$ = 243 Hz), 127.1, 127.1, 115.8, 115.5, 99.5 ppm; HRMS: *m*/*z* calculated for $C_{15}H_{11}F_2N_2$ (M + H)$^+$: 257.0885, found: 257.0862.

5-(4-Fluorophenyl)-3-(4-isopropylphenyl)-1*H*-pyrazole (4d). Yield: 0.077 g (55%) as a brown solid; mp: 179–181 °C; IR (KBr): ν_{max} 3414, 1624, 1450, 1321, 1177, 1024, 832 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.13 (brs, 1H, N*H*), 7.57 (q, J = 6.5 Hz, 2H), 7.53 (d, J = 10.5 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.87 (t, J = 11.0 Hz, 2H), 6.61 (s, 1H), 2.88 (sp, J = 8.5 Hz, 1H), 1.26 (d, J = 9.0 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3 (d, $^1J_{C,F}$ = 246 Hz), 148.7, 148.1 (d, $^2J_{C,F}$ = 35 Hz), 128.1, 127.7, 127.1, 126.7, 125.4, 115.5, 115.3, 99.2, 33.7, 23.7 ppm; HRMS: *m*/*z* calculated for $C_{18}H_{18}FN_2$ (M + H)$^+$: 281.1449, found: 281.1448.

3-(3-Bromophenyl)-5-(4-fluorophenyl)-1*H*-pyrazole (4e). Yield: 0.106 g (67%) as a brown solid; mp: 150–151 °C; IR (KBr): ν_{max} 3415, 1621, 1495, 1233, 1165, 1091, 968, 826, 773 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.50 (brs, 1H, N*H*), 7.86 (s, 4H), 7.48–7.13 (m, 5H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.8 (d, $^1J_{C,F}$ = 244 Hz), 15.6, 143.0, 132.3, 128.8, 127.2, 127.1, 126.4, 115.8, 115.6, 99.8 ppm; HRMS: *m*/*z* calculated for $C_{15}H_{10}BrFN_2Na^+$ (M + Na)$^+$: 338.9904, found: 338.9912.

5-(4-Fluorophenyl)-3-(3-methoxyphenyl)-1*H*-pyrazole (4f). Yield: 0.096 g (72%) as a brown solid; mp: 162–163 °C; IR (KBr): ν_{max} 3415, 1628, 1468, 1165, 1035, 985, 762 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.92 (t, J = 5.6 Hz, 2H), 7.46–7.43 (m, 2H), 7.36 (t, J = 8.0 Hz, 1H), 7.27 (t, J = 7.6 Hz, 2H), 7.18 (s, 1H), 6.91 (d, J = 8.0 Hz, 1H), 3.82 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.8 (d, $^1J_{C,F}$ = 243 Hz), 159.7, 129.9, 127.2, 127.1, 117.6, 115.7, 115.5, 113.4, 110.6, 99.8, 55.1 ppm; HRMS: *m*/*z* calculated for $C_{16}H_{14}FN_2O$ (M + H)$^+$: 269.1085, found: 269.1088.

3,5-Bis(4-chlorophenyl)-1*H*-pyrazole (5a). Yield: 0.084 g (58%) as a brown solid; mp: 240–241 °C; IR (KBr): ν_{max} 3448, 1638, 1506, 1025, 994, 829 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.75 (d, J = 8.4 Hz, 4H), 7.35 (d, J = 8.4 Hz, 4H), 6.93 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ 144.8, 131.1, 128.5, 127.0, 125.0, 98.0 ppm; HRMS: *m*/*z* calculated for $C_{15}H_{11}Cl_2N_2$ (M + H)$^+$: 289.0294, found: 289.0298.

5-(4-Chlorophenyl)-3-(4-methoxyphenyl)-1*H*-pyrazole (5b). Yield: 0.086 g (61%) as a brown solid; mp: 157–159 °C; IR (KBr): ν_{max} 3425, 2911, 1615, 1508, 1450, 1254, 1074, 821 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.27 (brs, 1H, N*H*), 7.85 (d, J = 5.5 Hz, 2H), 7.74 (d, J = 6.5 Hz, 2H), 7.49 (s, 2H), 7.09 (s, 1H), 7.02 (d, J = 6.5 Hz, 2H), 3.79 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.1, 128.9, 128.7, 126.7, 126.5, 114.3, 99.0, 55.1 ppm; HRMS: *m*/*z* calculated for $C_{16}H_{14}ClN_2O$ (M + H)$^+$: 285.0789, found: 285.0789.

3-(3-Bromophenyl)-5-(4-chlorophenyl)-1*H*-pyrazole (5c). Yield: 0.109 g (66%) as a brown solid; mp: 202–203 °C; IR (KBr): ν_{max} 3478, 3413, 1625, 1490, 1365, 629 cm^{-1}; ^{1}H NMR (500 MHz): δ 13.52 (brs, 1H, N*H*), 8.05 (s, 1H), 7.85 (s, 3H), 7.52–7.41 (m, 4H), 7.32 (d, J = 3.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 131.0, 128.9, 127.5, 126.7, 124.0, 100.6 ppm; HRMS: *m*/*z* calculated for $C_{15}H_{11}{}^{81}BrClN_2$ (M + H)$^+$: 334.9769, found: 334.9770.

5-(4-Chlorophenyl)-3-(3-methoxyphenyl)-1*H*-pyrazole (5d). Yield: 0.102 g (72%) as a brown solid; mp: 165–166 °C; IR (KBr): ν_{max} 3418, 2925, 1621, 1491, 1453, 1300, 1232, 1159, 1062, 994, 885, 758 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.42 (brs, 1H, N*H*), 7.87 (s, 2H), 7.50–7.36 (m, 5H), 7.23 (s, 1H), 6.92 (s, 1H), 3.82 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.6, 129.9, 128.8, 127.7, 125.1, 117.5, 113.4, 110.4, 99.9, 54.9 (O*C*H$_3$) ppm; HRMS: *m*/*z* calculated for $C_{16}H_{14}ClN_2$ (M + H)$^+$: 285.0789, found: 285.0772.

5-(4-Chlorophenyl)-3-(furan-2-yl)-1*H*-pyrazole (5e). Yield: 0.052 g (49%) as a brown solid; mp: 180–181 °C; IR (KBr): ν_{max} 3415, 1624, 1471, 1230, 1156, 1094, 611 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, J = 8.5 Hz, 2H), 7.42 (s, 1H), 7.32 (d, J = 8.0 Hz, 2H), 6.69 (s, 1H), 6.60 (d, J = 3.5 Hz, 1H), 6.45 (d, J = 1.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 142.5, 139.4, 134.2, 129.5, 129.0, 128.9, 126.9, 115.5, 107.0, 99.3 ppm; HRMS: *m*/*z* calculated for $C_{13}H_9ClN_2NaO$ (M + Na)$^+$: 267.0296, found: 267.0271.

3-(4-Fluorophenyl)-5-*p*-tolyl-1*H*-pyrazole (6a). Yield: 0.084 g (67%) as a brown solid; mp: 162–163 °C; IR (KBr): ν_{max} 3417, 2984, 1629, 1506, 1447, 1177, 959, 785 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.31 (brs, 1H, N*H*), 7.88–7.70 (m, 4H),

7.26 (s, 4H), 7.11 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.7 (d, $^1J_{C,F}$ = 243 Hz), 129.3, 127.0, 127.0, 125.0, 115.5, 99.1, 20.7 ppm; HRMS: *m*/*z* calculated for $C_{16}H_{14}FN_2$ (M + H)$^+$: 253.1136, found: 253.1110.

3-(4-Isopropylphenyl)-5-*p*-tolyl-1*H*-pyrazole (6b). Yield: 0.086 g (65%) as a brown solid; mp: 182–183 °C; IR (KBr): ν_{max} 3417, 2985, 1629, 1506, 1447, 1177, 959, 785 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.5 Hz, 2H), 6.73 (s, 1H), 2.91 (septet, *J* = 6.5 Hz, 1H), 2.35 (s, 3H), 1.27 (d, *J* = 7.0 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.8, 148.7, 148.5, 137.8, 129.4, 128.8, 128.5, 126.8, 125.6, 125.5, 99.4, 33.8, 23.8, 21.3 ppm; HRMS: *m*/*z* calculated for $C_{19}H_{21}N_2$ (M + H)$^+$: 277.1699, found: 277.1670.

3-(3-Bromophenyl)-5-*p*-tolyl-1*H*-pyrazole (6c). Yield: 0.100 g (64%) as a brown solid; mp: 149–151 °C; IR (KBr): ν_{max} 3479, 2947, 1629, 1315, 1180, 1024, 991 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.42 (brs, 1H, N*H*), 8.06 (s, 1H), 7.85 (d, *J* = 6.5 Hz, 1H), 7.72 (d, *J* = 6.0 Hz, 2H), 7.51 (d, *J* = 6.0 Hz, 1H), 7.40 (t, *J* = 6.5 Hz, 1H), 7.26 (d, *J* = 6.0 Hz, 2H), 7.23 (s, 1H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 137.3, 130.9, 130.2, 129.4, 127.5, 125.0, 124.0, 122.2, 99.8, 20.8 ppm; HRMS: *m*/*z* calculated for $C_{16}H_{14}BrN_2$ (M + H)$^+$: 313.0335, found: 313.0335.

3-(4-Fluorophenyl)-5-(4-methoxyphenyl)-1*H*-pyrazole (7a). Yield: 0.067 g (50%) as a brown solid; mp: 128–129 °C; IR (KBr): ν_{max} 3416, 2935, 1625, 1515, 1450, 1241, 1306, 1174, 1032 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.28 (brs, 1H, N*H*), 7.89 (t, *J* = 6.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 4.0 Hz, 2H), 7.01 (s, 1H), 3.78 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.7 (d, $^1J_{C,F}$ = 243 Hz), 159.1 127.1, 127.0, 126.5, 115.7, 115.6, 114.9, 114.3, 114.2, 98.5, 55.1 ppm; HRMS: *m*/*z* calculated for $C_{16}H_{14}FN_2O$ (M + H)$^+$: 269.1085, found: 269.1087.

5-(4-Methoxyphenyl)-3-(3-nitrophenyl)-1*H*-pyrazole (7b). Yield: 0.119 g (81%) as a brown solid; mp: 209–210 °C; IR (KBr): ν_{max} 415, 2945, 1165, 1098, 1052, 964, 835 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.46 (brs, 1H, N*H*), 8.65 (s, 1H), 8.27 (d, *J* = 7.5 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.28 (s, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.79 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.1, 132.1, 128.7, 126.7, 126.5, 114.3, 99.0, 55.1 ppm; HRMS: *m*/*z* calculated for $C_{16}H_{14}N_3O_3$ (M + H)$^+$: 296.1031, found: 296.1030.

3-(3-Fluorophenyl)-5-(4-methoxyphenyl)-1*H*-pyrazole (7c). Yield: 0.069 g (52%) as a brown solid; mp: 131–132 °C; IR (KBr): ν_{max} 463, 2920, 1620, 1510, 1467, 1444, 1304, 1253, 1181, 1029, 987, 865 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.39 (brs, 1H, N*H*), 7.77 (d, *J* = 8.5 Hz, 2H), 7.70 (t, *J* = 6.5 Hz, 2H), 7.46 (q, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 7.0 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 3.78 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.6 (d, $^1J_{C,F}$ = 241 Hz), 159.1, 134.9, 130.7, 126.5, 123.5, 121.1, 114.2, 114.1, 111.7, 111.5, 99.3, 55.1 ppm; HRMS: *m*/*z* calculated for $C_{16}H_{14}FN_2O$ (M + H)$^+$: 269.1085, found: 269.1082.

3-(4-Methoxyphenyl)-4-methyl-5-phenyl-1*H*-pyrazole (8a). Yield: 0.069 g (52%) as a brown solid; mp: 196–197 °C; IR (KBr): ν_{max} 3429, 2852, 2357, 1638, 1403, 1023, 994 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 2.23 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ 159.0, 128.7, 128.3, 127.5, 127.3, 124.6, 113.8, 109.6, 55.1, 10.0 ppm; HRMS: *m*/*z* calculated for $C_{17}H_{17}N_2O$ (M + H)$^+$: 265.1335, found: 265.1342.

3-(4-Fluorophenyl)-4-methyl-5-phenyl-1*H*-pyrazole (8b). Yield: 0.059 g (47%) as a brown solid; mp: 199–200 °C; IR (KBr): ν_{max} 3432, 2926, 1608, 1505, 1441, 1403, 1250, 835 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): δ 7.56–7.52 (m, 4H), 7.38 (t, *J* = 8.8 Hz, 2H), 7.29 (t, *J* = 5.6 Hz, 1H), 7.06 (t, *J* = 7.2 Hz, 2H), 2.23 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ 162.1 (d, $^1J_{C,F}$ = 245 Hz), 129.2, 128.8, 128.4, 127.6, 127.5, 115.4, 115.2, 110.0, 10.0 ppm; HRMS: *m*/*z* calculated for $C_{16}H_{14}FN_2$ (M + H)$^+$: 253.1136, found: 253.1140.

1-(4-Methoxybenzylidene)-2-(1-phenyl-2-*p*-tosylethylidene) hydrazine (9a). Yield: 0.099 g (49%) as a yellow solid; mp: 155–156 °C; IR (KBr): ν_{max} 3463, 2910, 1545, 1485, 1042, 839 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (m, 3H), 7.60 (d, *J* = 6.8 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.48 (m, 3H), 6.97 (d, *J* = 7.2 Hz, 2H), 6.93 (d, *J* = 7.2 Hz, 2H), 5.13 (s, 2H), 3.86 (s, 3H), 2.10 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1, 159.1, 155.8, 144.5, 135.8, 135.5, 130.6, 130.4, 129.3, 128.4, 128.3, 127.6, 126.6, 113.9, 55.3, 54.8, 21.3 ppm; HRMS: *m*/*z* calculated for $C_{23}H_{22}N_2NaO_3S$ (M + Na)$^+$: 429.1243, found: 429.1259.

1-(4-Fluorobenzylidene)-2-(1-phenyl-2-*p*-tosylethylidene)hydrazine (9b). Yield: 0.098 g (50%) as a brown solid; mp: 151–152 °C; IR (KBr): ν_{max} 432, 2922, 1585, 1508, 1459, 1405, 1301, 1253, 1075, 1033, 969, 830, 763 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.2 Hz, 2H), 7.70 (t, *J* = 9.2 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 3H), 7.10 (d, *J* = 8.8 Hz, 1H), 7.06 (t, *J* = 4.8 Hz, 2H), 6.79 (s, 1H), 4.87 (s, 2H), 2.28 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8–161.4 (d, $^1J_{C,F}$ = 247 Hz), 155.6, 144.7, 136.7, 135.2, 131.1, 129.5, 128.9, 128.3, 128.0, 127.3, 125.5, 115.8–115.6 (d, $^1J_{C,F}$ = 21 Hz), 99.9, 55.0, 21.5 ppm; HRMS: *m*/*z* calculated for $C_{22}H_{20}FN_2O_2S$ (M + H)$^+$: 395.1224, found: 395.1232.

1-Benzylidene-2-(1-phenyl-2-tosylethylidene)hydrazine (9c). Yield: 0.122 g (65%) as a yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–8.06 (m, 3H), 7.59 (t, *J* = 6.8 Hz, 2H), 7.48 (d, *J* = 6.8 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 4H), 7.48–7.45 (m, 3H), 7.43–7.39 (m, *J* = 7.2 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 5.14 (s, 2H), 2.09 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 156.5, 144.6, 135.7, 135.4, 133.7, 131.3, 130.9, 129.4, 128.6, 128.4, 128.4, 128.3, 128.2, 127.7, 55.0, 21.2 ppm; HRMS: *m*/*z* calculated for $C_{22}H_{20}N_2NaO_2S$ (M + H)$^+$: 399.1138, found: 399.1125.

3,5-Diphenyl-1*H*-pyrazole (11). Yield: 0.091 g (82%) as a brown solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.50 (m, 4H), 7.46–7.07 (m, 4H), 7.04–7.01 (m, 2H), 6.58 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ 130.9, 127.9, 127.0, 124.6, 98.5 ppm.

3-(4-Isopropylphenyl)-4,5,6,7-tetrahydro-1*H*-indazole (12). Yield: 0.029 g (24%) as a brown solid; mp: 197–198 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.6 Hz, 2H), 2.92 (sp, J = 7.4 Hz, 1H), 2.70 (t, J = 6.0 Hz, 2H), 2.59 (t, J = 6.0 Hz, 2H), 1.87–1.85 (m, 2H), 1.76–1.73 (m, 2H), 1.27 (s, 3H), 1.25 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ 147.4, 139.5, 131.9, 126.5, 126.4, 113.4, 35.4, 33.8, 23.9, 23.2, 22.3, 21.6 ppm. HRMS: m/z calculated for $C_{16}H_{21}N_2$ $(M + H)^+$: 241.1699, found: 241.1682.

Conflicts of interest

There are no conflicts of interest to declare.

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