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ARTICLE TYPE

Synthesis of 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4- dihydropyrano[2,3-c]pyrazoles using disulfonic acid imidazolium chloroaluminate as a dual and heterogeneous catalyst

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In this work, disulfonic acid imidazolium chloroaluminate {[Dsim]$AlCl_4$} is applied as a new acidic and heterogeneous catalyst for green, simple and efficient synthesis of 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazoles by the one-pot multi-component condensation of aryl aldehydes with ethyl acetoacetate, malononitrile and hydrazine hydrate at 80 ºC under solvent-free conditions.

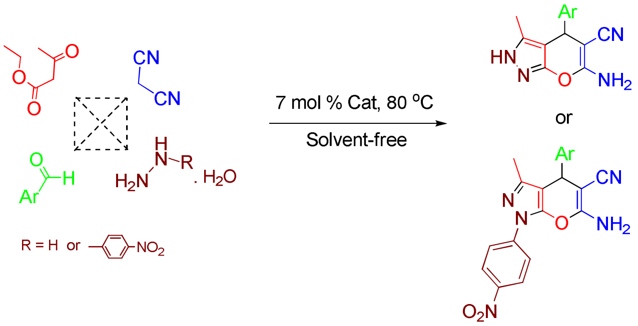
Introduction

In recent years, the use of ionic liquids and solid salts (with an organic cation) as homogeneous, heterogeneous and reusable catalysts have received massive attention in organic synthesis.[1-3] Application of these catalysts under solvent-free conditions often leads to significant decreases in reaction times, increased yields, easier workup, clean conditions and compliance with the green chemistry protocols. With this issue in mind, we have recently introduced a new category of ionic liquids and solid salts (with an organic cation), namely sulfonic acid functionalized imidazolium salts (SAFIS).[4-14] In this class of salts, S-N bond formation in imidazole ring, as five member's heterocyclic compounds, was reported for the first time. These compounds have been successfully used as catalysts or reagent to prepare bis(indolyl)methanes,[4] *N*-sulfonyl imines,[5] nitro aromatic compounds,[6,7] 1-amidoalkyl-2-naphthols,[8] benzimidazoles,[9] xanthenes,[10] 1-carbamatoalkyl-2-naphthols,[11] 4,4'-(arylmethylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5- ol)s,[12] tert-butyl aryl carbamates[13] and 1,2,4,5-tetrasubstituted imidazoles.[14] In continuation of our previous projects involving the preparation and applications of acidic ionic liquids and solid salts in organic transformations, we have introduced disulfonic acid imidazolium chloroaluminate {[Dsim]$AlCl_4$} which exhibits many interesting properties.

Pyranopyrazoles are an important class of heterocyclic compounds; they have been used as fungicidal,[15] bactericidal,[16] vasodilatory,[17] and anticancer.[18] These heterocycles have also applications as pharmaceutical ingredients and biodegradable agrochemicals.[19] Moreover, pyrano[2,3-c]pyrazoles have been shown to act as potential insecticidal[20] and molluscicidal agents.[21,22] Consequently, considerable attention has been focused on the development of new procedures for the preparation of these compounds. [23-26]

Multi-component reactions (MCRs) have a significant role in combinatorial chemistry as they can prepare target compounds with higher efficacy and atom economy by formation of structural complexity in a single step from three or more reactants. Furthermore, MCRs present some advantages compared with conventional chemical reactions, e.g. simplicity and synthetic efficiency.[27–30]

In this investigation, we report a highly efficient solvent-free method for the synthesis of 6-amino-4-(4 -methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazoles by the one-pot multi-component condensation of arylaldehydes with ethyl acetoacetate, malononitrile and hydrazine hydrate using disulfonic acid imidazolium chloroaluminate {[Dsim]$AlCl_4$} as a new acidic and heterogeneous catalyst (Scheme 1).



Scheme 1. The condensation between aromatic aldehyde, malononitrile, ethyl acetoacetate and hydrazine hydrate or (4-nitrophenyl)hydrazine hydrate using [Dsim]$AlCl_4$.

Results and discussion

Disulfonic acid imidazolium chloroaluminate was prepared in two steps. Initially, ionic liquid disulfonic acid imidazolium chloride {[Dsim]Cl} was synthesized according to our previous report,[8] by the reaction of imidazole (1 eq.) with chlorosulfonic

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acid (2 eq.). Then, [Dsim]AlCl$_4$ was prepared by the reaction of [Dsim]Cl (1 eq.) with aluminum chloride (1 eq.) with high atomic economy.[12]

XRD pattern of the catalyst {[Dsim]AlCl$_4$} was studied and exhibited a broadened pattern due to its non-crystal at 2θ = 15-35° (Figure 1).

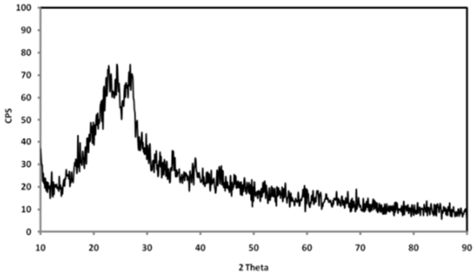

Figure 1. The XRD pattern of [Dsim]AlCl$_4$.

In another investigation, the SEM micrographs of the catalyst showed that the particles have not completely agglomerated. Some particles of the catalyst were observed in nano and micro scales [Figure 2 (a and b)].

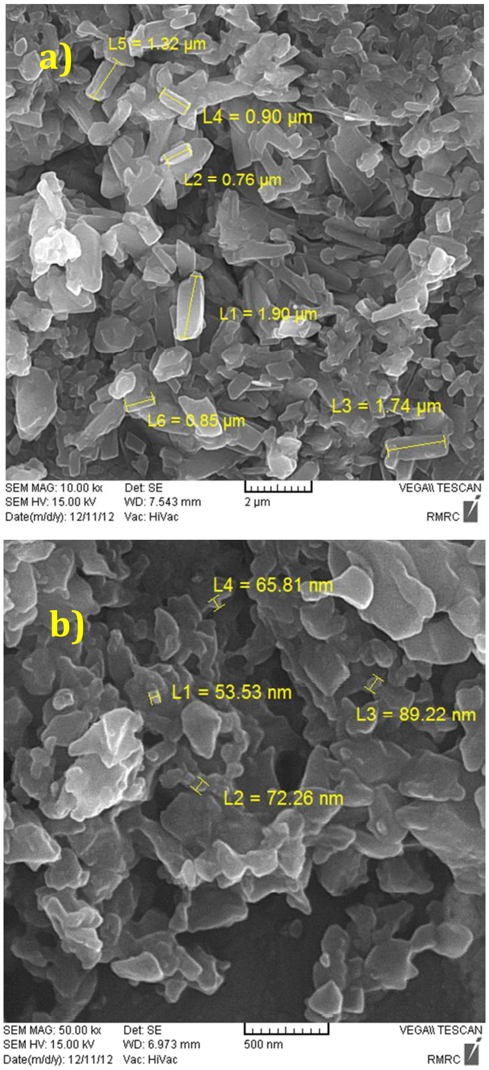

Figure 2. The SEM images of the catalyst in micro size (a) and in nano size (b)

To optimize the reaction conditions, as a model reaction, the condensation between hydrazine hydrate (2.5 mmol) ethyl acetoacetate (2 mmol), malononitrile (2 mmol) and 4-chlorobenzaldehyde (2 mmol) was studied in the presence of different amounts of [Dsim]AlCl$_4$ at range of 50-120 °C in the absence of solvent (Table 1). As it is shown in Table 1, the reaction was efficiently performed using 7 mol% of the catalyst at 80 °C to give the desired product in high yield within short reaction time (Table 1, entry 2). The reaction was also examined at 80 °C without catalyst under solvent-free conditions in which the reaction did not significantly progress even after long reaction time (Table 1, entry 5).

Table 1. Effect of different amounts of the catalyst and temperature on the reaction of hydrazine hydrate (2.5 mmol) with ethyl acetoacetate (2 mmol), malononitrile (2 mmol) and 4-chlorobenzaldehyde (2 mmol) in the absence of solvent.

Entry	Mol% of Catalyst	Temp. (°C)	Time (min)	Yield^a (%)
1	7	50	8	75
2	7	80	1	92
3	7	100	1	92
4	7	120	1	92
5	-	80	90	28
6	3	80	5	50
7	5	80	3	65
8	7	80	1	92
9	10	80	1	92

^{a}Isolated yield.

In the next step, the model reaction was examined in several solvents using 7 mol% of [Dsim]AlCl$_4$ in reflux conditions. The results are depicted in Table 2.

Table 2. The reaction of hydrazine hydrate (2.5 mmol) with ethyl acetoacetate (2 mmol), malononitrile (2 mmol) and 4-chlorobenzaldehyde (2 mmol) using [Dsim]AlCl$_4$ (7 mol%) in different solvents (5 mL) under reflux conditions.

Entry	Solvent	Time (min)	Yield^a (%)
1	EtOH	60	30
2	CH_3CN	60	40
3	CH_3OH	60	50
4	CH_2Cl_2	60	20
5	Acetone	60	40

^{a}Isolated yield.

As Table 2 indicates, solution conditions were not efficient, and afforded the product in low yields. Increasing the reaction times did not improve the yields.

To assess the efficacy and generality of [Dsim]AlCl$_4$ in the

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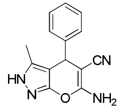
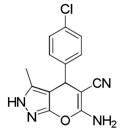
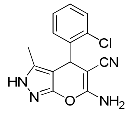
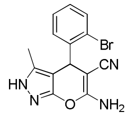
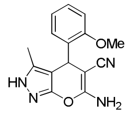
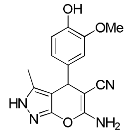
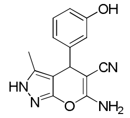
synthesis of 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazoles, various arylaldehydes (including benzaldehyde, and arylaldehydes aldehydes possessing electron-releasing substituents, electron-withdrawing substituents and halogens on their aromatic ring) were reacted with hydrazine hydrate, ethyl acetoacetate and malononitrile under the optimal reaction conditions to afford the corresponding products in high yields and in short reaction times. The results are summarized in Table 3.

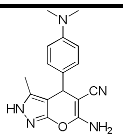
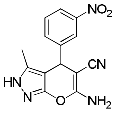
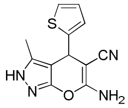
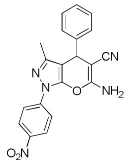
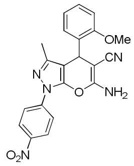
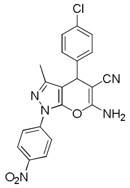
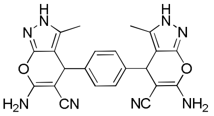
Table 3. The preparation of 6-amino-4-(4 -methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4- dihydropyrano[2,3-c]pyrazoles using [Dsim]$AlCl_4$ as catalyst at 80 ºC.

Entry	Product	Time (min)	Yield[a] (%)	Mp. ºC (Lit.)
1		1	90	264-266 (244-246[23])
2		1	92	245-247 (234-236[24])
3		3	88	261-263 (145-147[24])
4		3	85	259-261
5		5	82	260-263
6		7	80	240-242 (235-237[24])
7		3	85	262-264 (248-249[25]) tot

[a] Isolated yield.

In another investigation, the condensation of arylaldehyde with malononitrile, ethyl acetoacetate and (4-nitrophenyl)hydrazine hydrate using [Dsim]$AlCl_4$ was studied wherein the corresponding products were produced in high yields and short reaction times (Table 3, entries 11, 12 and13). Interestingly, the condensation of hydrazine hydrate (5 mmol) ethyl acetoacetate (4 mmol), malononitrile (4 mmol) and terephthaldehyde (2 mmol) at 80 °C under solvent-free conditions afforded 4,4'-(1,4-phenylene)bis(6-amino-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile) (**15**) in 78 % yield within 60 min (Table 3, entry 14). Thus, the catalyst was general and highly efficient.

Table 3. (Continued)

Entry	Product	Time (min)	Yield[a] (%)	Mp. ºC (Lit.)
8		7	85	227-229 (191[26])
9		1	90	244-246 (214-216[23])
10		5	85	246-248 (223-225[25])
11		1	85	215-217
12		5	85	206-208
13		1	88	240-242
14[b]		60	75	266[c]

[a]Isolated yield. [b]The product was produced by the reaction of hydrazine hydrate (5 mmol) with ethyl acetoacetate (4 mmol), malononitrile (4 mmol) and terephthaldehyde (2 mmol) in the absence of solvent. [c]In this temprature, the product was decomposed.

In a plausible mechanism (Scheme 2), initially, ethyl acetoacetate is activated by [Dsim]$AlCl_4$, and then hydrazine attacks to the activated carbonyl group of ethyl acetoacetate. Loss of one molecule of H_2O, and intramolecular nucleophillic attack by another NH_2 group of hydrazine to the next carbonyl group of ethyl acetoacetate (which acticted by the catalyst) affords 5-methyl-2,4-dihydro-pyrazol-3-one (**I**). Sulfonic acid groups of the catalyst cation can be deprotonated with $AlCl_4$ anion and the intermediate structure of the catalyst (in equilibrium with the first structure of the catalyst) can be produced. Meanwhile, the deprotonated cation has another sulfonic acid functional group which can be catalyzed the reaction. $AlCl_4$ anion can be produced Cl anion and $AlCl_3$ during the reaction. Malononitrile is coordinated and activated by $AlCl_3$. Cl anion and $AlCl_4$ anion react to activated form of malononitrile (**II**, **II'**, **II''**) as a base to give **III** after reaction with aldehyde and removing one molecule

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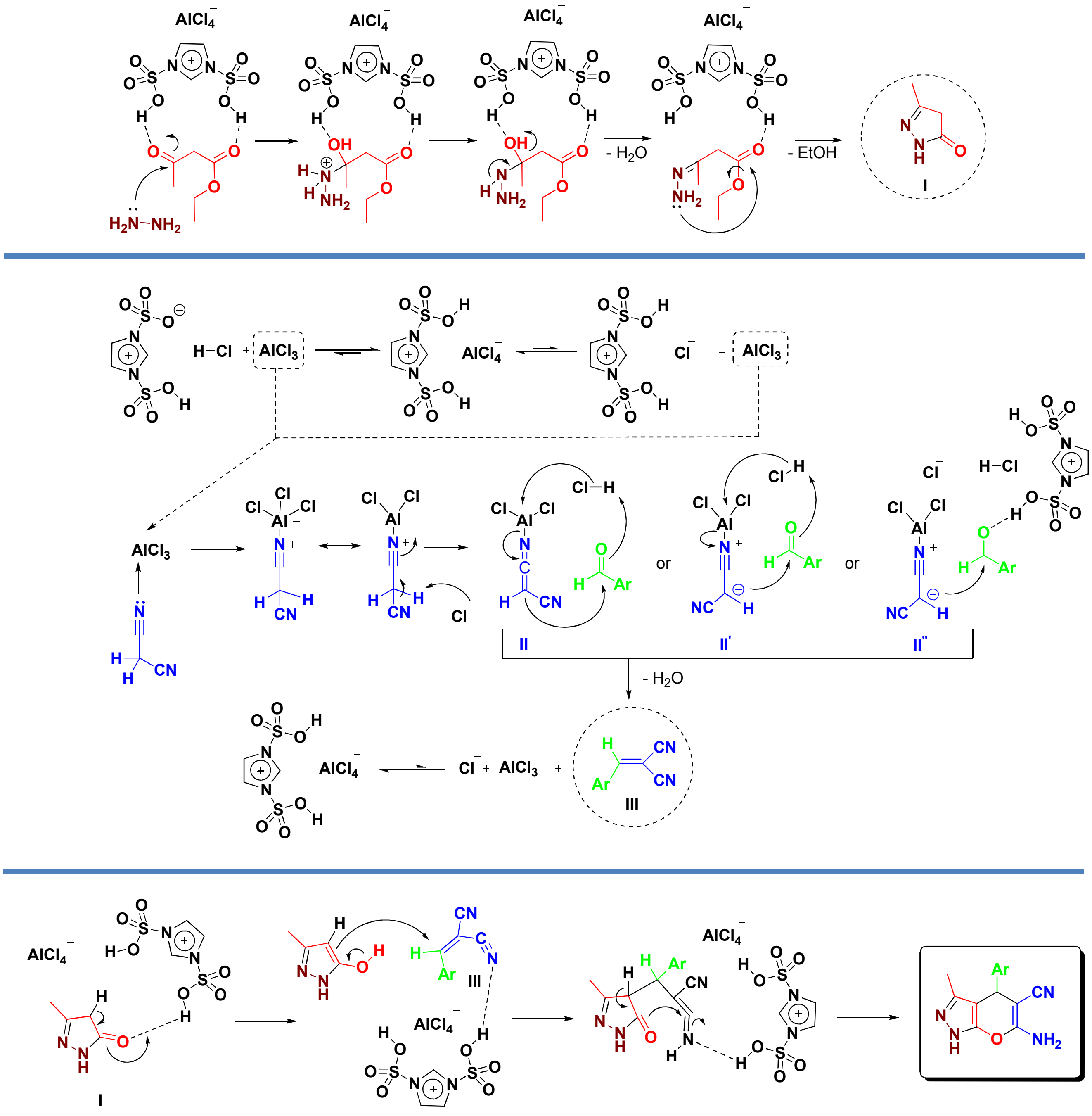
of H_2O.



Scheme 2. The proposed mechanism for the synthesis of 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazoles.

Finally, addition of I to III in the presence of [Dsim]$AlCl_4$ followed by intramolecular nucleophillic attack, can give the expected pyranopyrazole.

In another study, to confirm the dual application of [Dsim] $AlCl_4$, we studied the model reaction in the presence of some other species which can be presented in this reaction condition such as [Dsim]Cl, HCl, $AlCl_3$, [Dsim] Cl/ $AlCl_3$ (Table 4, Entries 2-5). In these cases, the results were not similar to [Dsim] $AlCl_4$. Obtained results from this study showed dual activity of [Dsim] $AlCl_4$. Also, [Msim] Cl as an acidic ionic liquid and H_2SO_4 as a traditional catalyst were tested in the reaction in order to get a direct comparison with [Dsim] $AlCl_4$ which afforded lower yields of the products in longer reaction times (Table 4, Entries 1 and 6).

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Table 4. The reaction of hydrazine hydrate (2.5 mmol) with ethyl acetoacetate (2 mmol), malononitrile (2 mmol) and 4-chlorobenzaldehyde (2 mmol) using different catalysts (7 mol%) under solvent-free conditions.

Entry	Catalyst	Time (min)	Yield^a (%)
1	[Msim]Cl	4	80
2	[Dsim]Cl	2	85
3	$AlCl_3$	6	70
4	[Dsim]Cl/$AlCl_3$ (1/1)	10	75
5	HCl	3	53
6	H_2SO_4	5	87

^{a}Isolated yield.

Recyclability of the catalyst was examined upon the condensation of hydrazine hydrate (2.5 mmol) with ethyl acetoacetate (2 mmol), malononitrile (2 mmol) and 4-chlorobenzaldehyde (2 mmol). After completion of the reaction, the reaction mixture was extracted with warm ethanol (20 mL) to separate the catalyst (the product is soluble in warm ethanol; however, the catalyst is not soluble in this solvent). Then, ethanol was evaporated and the solid residue (crude product) was triturated by a mixture of ethanol and water (9/1) to give the pure product. The recovered catalyst was washed with EtOAc (2×20 mL), dried at 90 ºC under vacuum condition, and reused for the preparation of 6-amino-4-(4 -methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazoles according to the mentioned procedure. The catalyst was recovered and reused for four times without any significant changes in the yield and the reaction time (Table 5).

Table 5. The reaction between hydrazine hydrate (2.5 mmol), ethyl acetoacetate (2 mmol), malononitrile (2 mmol) and 4-chlorobenzaldehyde (2 mmol) in the presence of reused [Dsim]$AlCl_4$ (7 mol%) at 80 ºC under solvent-free conditions.

Entry	Cycle	Time (min)	Yield^a (%)
1	1st run	1	92
2	2st run	2	90
3	3st run	4	89
4	4st run	5	87

^{a}Isolated yield.

Conclusions

In summary, we have reported the efficient synthesis of 6-amino-4-(4 -methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazoles using disulfonic acid imidazolium chloroaluminate {[Dsim]$AlCl_4$} as a dual, heterogeneous and reusable catalyst in a green media. The promising points for the presented methodology are efficiency, generality, high yield, relatively short reaction time, low cost, cleaner reaction profile, ease of product isolation, simplicity, and finally compliance with the green chemistry protocols.

Experimental

All chemicals were purchased from Merck or Fluka Chemical Companies. The known products were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates. The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were run on a Bruker Avance DPX-250 FT-NMR spectrometer (δ in ppm). Mass spectra were recorded on a Shimadzu GC MS-QP 1000 EX 85 apparatus. Infrared spectrum of products is recorded by Perkin Elmer PE-1600-FTIR. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

2.1. Preparation of 1,3-disulfonic acid imidazolium tetrachloroaluminate {[Dsim]$AlCl_4$}:

A round-bottomed flask (50 mL) was charged with 1,3-disulfonic acid imidazolium chloride (1.323 g, 5mmol), and then $AlCl_3$ (0.6667 g, 5 mmol) was added over a period of 5 min at 50 °C. Afterward, the reaction mixture was stirred for 30 min at 50 °C to give [Dsim]$AlCl_4$ as a white powder in 98% yield, 1.95 g.[12]

2.1.1. Spectral data of [Dsim]$AlCl_4$:

White powder, mp 395ºC (dec.); IR (KBr) 629, 1051, 1127, 1200, 1315, 2950-3400 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 7.66 (s, 2H), 9.06 (s, 1H), 14.37 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 119.8, 134.8; MS: m/z = 399 (M^++1), 398 (M^+).

2.2. General procedure for the synthesis of 6-amino-4-(4 -methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazoles (1-15)

A mixture of aromatic aldehyde (2 mmol), malononitrile (0.132 g, 2 mmol), ethyl acetoacetate (0.26 g, 2 mmol) hydrazine hydrate (2.5 mmol) and [Dsim]$AlCl_4$ (0.14 mmol) was added to a test tube, and stirred at 80 ºC. After the completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature, extracted with warm ethanol (20 mL) to separate the catalyst (the product is soluble in warm ethanol; however, the catalyst is not soluble in this solvent). Then, the ethanol was evaporated and the solid residue (crude product) was triturated by a mixture of ethanol and water (9/1) to give the pure product. The recovered catalyst was washed with EtOAc (2×20 mL), dried at 90 ºC under vacuum, and reused.

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Notes and references

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