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Synthesis of Partially Reduced Imidazo[1,2-*a*]pyridines through an Unprecedented Base-Mediated (4+2) Cyclization

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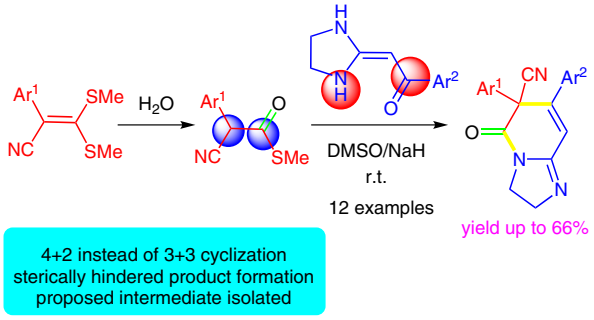

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Abstract A water-mediated regioselective synthesis of 6,7-diaryl-5-oxo-2,3,5,6-tetrahydroimidazo[1,2-*a*]pyridine-6-carbonitriles was performed by the reaction of 2-[1-cyano-2,2-bis(methylsulfanyl)vinyl]benzonitrile with 1-aryl-2-(imidazolidin-2-ylidene)ethanones under basic conditions. This reaction involves an unprecedented (4+2) annulation.

Key words imidazopyridines, ketene aminals, ketene dithioacetals, cyclizations

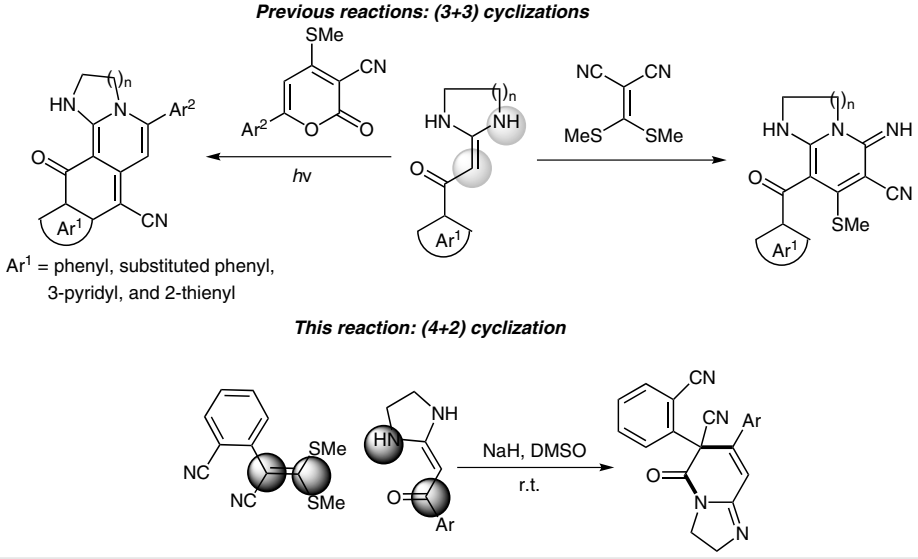
Ketene dithioacetals are widely used as precursors of aromatic and nonaromatic nuclei.[1–3] 1-Aryl-2-(imidazolidin-2-ylidene)ethanones, obtained by the reaction of ethane-1,2-diamine with the corresponding ketene dithioacetals, can also act as useful synthetic precursors. Various polycyclic heterocycles have been synthesized by using heterocyclic ketene aminals.[4] Structurally, these molecules are interesting as they contain a double bond with an electron-donating group at one end and an electron-withdrawing group at the other. Various reactions of aminals with azides,[5] nitrile oxides,[6] or nitrile imines[7] have been reported. Heterocyclic ketene aminals can also behave as bisnucleophiles through the nitrogen atom and the vinylic carbon atom in the position α to the carbonyl group.[8] They can react with various biselectrophilic precursors, such as unsaturated carboxylic acid esters,[9] enones,[10] ethyl bromoacetate,[11] keto esters, diethyl oxomalonate, glyoxylic esters,[12] or 1,3-dibromopropane.[13]

Recently, Ram and co-workers have used 1-aryl-2-(imidazolidin-2-ylidene)ethanones as precursors to perform ring transformations of 2-pyranone, annelated azaanthracenones, and thieno[3,2-*g*]aza-naphthalenones.[14,15] Liao and co-workers reported the synthesis of highly functionalized pyridine-fused 1,3-diazaheterocycles by the reaction of heterocyclic ketene aminals with ketene dithioacetals in refluxing xylene.[16]

From these earlier reports, it was evident that ketene aminals utilize the nitrogen and vinylic carbon atoms for [3+3] cyclization. In the expectation of achieving a [3+3] cyclization, we performed the reaction of 2-[1-cyano-2,2-bis(methylsulfanyl)vinyl]benzonitrile, a biselectrophile, with ketene hemiaminals, and we isolated unexpected products, characterized as 7-aryl-6-(2-cyanophenyl)-5-oxo-2,3,5,6-tetrahydroimidazo[1,2-*a*]pyridine-6-carbonitriles (Scheme 1).

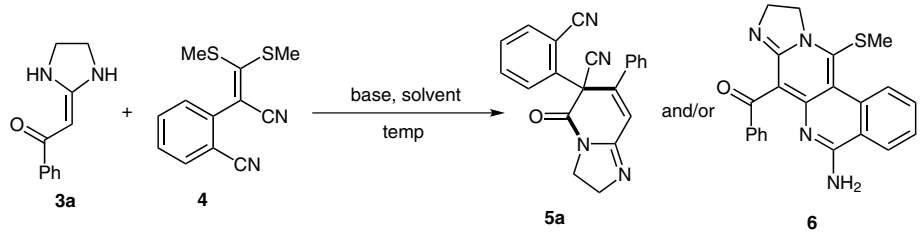
We synthesized the required precursors by a previously reported procedure. 2-[1-Cyano-2,2-bis(methylsulfanyl)vinyl]benzonitrile[17] was synthesized by the reaction of 2-(cyanomethyl)benzonitrile, carbon disulfide, and methyl iodide under basic conditions. Other 2-(imidazolidin-2-ylidene)-1-arylethanone precursors **3**[14,15,17] were synthesized in two steps (Scheme 2). The first step involved the synthesis of the corresponding 1-aryl-3,3-bis(methylsulfanyl)prop-2-en-1-ones **2** by reaction of a range of acetophenones **1** with carbon disulfide and methyl iodide. These, on reaction with ethane-1,2-diamine, afforded the desired precursors **3**.

Because of the possibility of forming [5-amino-12-(methylsulfanyl)-9,10-dihydrobenzo[*c*]imidazo[1,2-*g*]-1,6-naphthyridin-7-yl](phenyl)methanone (**6**), we screened various reaction conditions (Table 1). We chose 2-imidazolidin-2-ylidene-1-phenylethanone (**3a**) and 2-[1-cyano-2,2-bis(methylsulfanyl)vinyl]benzonitrile (**4**) as model substrates, and we examined their reaction in DMSO with sodium hydride as a base at room temperature. After workup and purification, the unexpected product 6-(2-cyanophenyl)-5-oxo-7-phenyl-2,3,5,6-tetrahydroimidazo[1,2-*a*]pyridine-6-carbonitrile (**5a**) was isolated in 56% yield, instead of the expected product **6**. Because sodium hydride appeared to work well, we examined other solvents and we per-



Scheme 1 Comparison of reported reactions and the current reaction

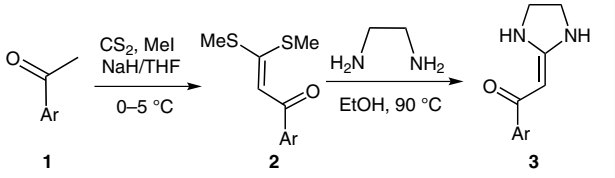
Table 1 Effect of the Base and Solvent on the Synthesis of **5a** and **6**[a]



Entry	Base	Solvent	Temp (°C)	Time (h)	Yield[b] of **5a** (%)
1	NaH	DMSO	r.t.[c]	8	56
2	NaH	DMSO	60	10	CM[d]
3	NaH	THF	r.t.[c]	12	34
4	NaH	DMF	r.t.[c]	12	CM[d]
5	NaH	DMF	90	12	CM[d]
6	–	xylene	reflux	12	CM[d]
7	$NaNH_2$	DMSO	r.t.[c]	12	CM[d]
8	KOH	DMSO	r.t.[c]	15	CM[d]
9	*t*-BuOK	DMSO	r.t.[c]	24	44
10	KOH	DMF	r.t.[c]	12	CM[d]
11	NaH	xylene	reflux	12	CM[d]
12	$NaNH_2$	THF	r.t.[c]	12	CM[d]
13	**NaH**	**DMSO**	**r.t.**[c]	**8**	**66**[e]

[a] Reaction conditions: **3a** (0.5 mmol), **4** (0.6 mmol), base (1.0 mmol), solvent (3.0 mL).
[b] Isolated yield.
[c] CM = complex mixture; starting material recovered.
[d] r.t. = 25–30 °C.
[e] H_2O (1.2 equiv) was added.

formed the reaction at various temperatures. At 60 °C, a complex mixture was obtained, containing a small amount of product **5a** and the recovered starting material **3a** (entry 2). The lower stability of compound **4** is responsible for the complexity of the reaction, as **4** undergoes decomposition at 60 °C.

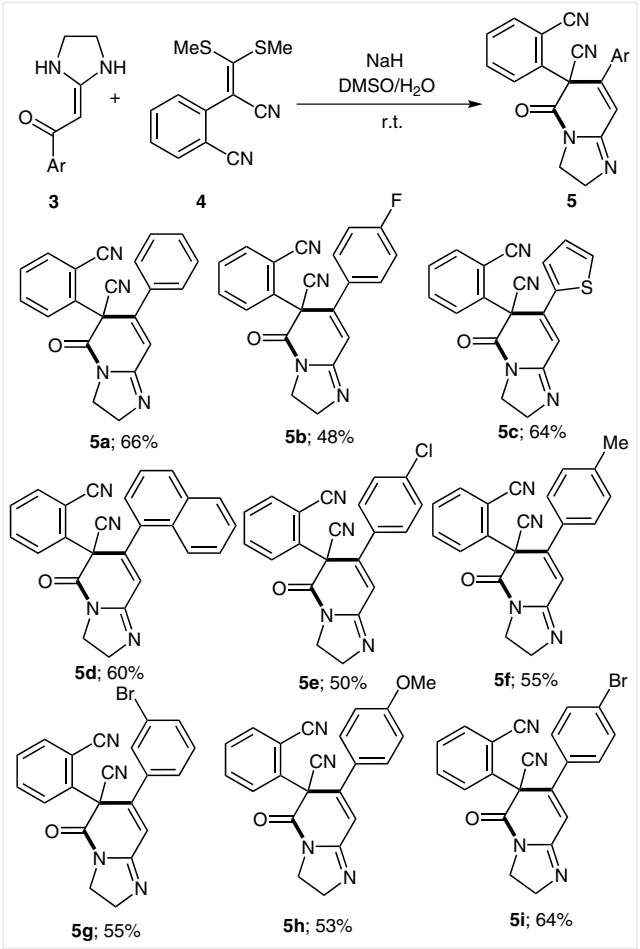


Scheme 2 Synthesis of 2-(imidazolidin-2-ylidene)-1-arylethanones **3**

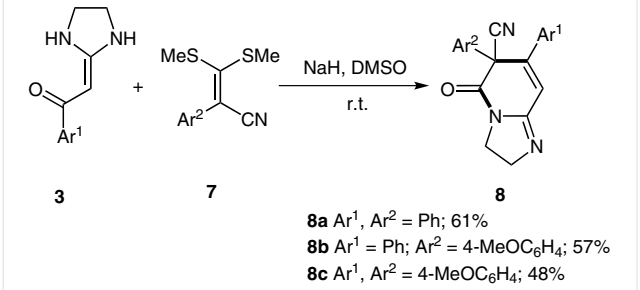
We then performed the reaction in THF with sodium hydride as a base, and we obtained a 34% yield of the desired product **5a** (Table 1, entry 3). In other trials, when we used sodium hydride in DMF at room temperature or at an elevated temperature, we obtained complex mixtures containing unreacted starting material (entries 4 and 5). Following a previous report,[16] we heated the reaction mixture to reflux in xylene for 12 hours, and again we obtained a complex mixture containing recovered starting material (entry 6). From this, we concluded that DMSO is the most suitable solvent for the reaction. Next, we screened various bases in DMSO. The use of sodamide or potassium hydroxide was ineffective, but potassium *tert*-butoxide afforded a 44% yield of **5** (entries 7–9). The use of KOH in DMF was also ineffective (entry 10). We also screened sodium hydride in xylene and sodamide in THF, but complex mixtures were formed (entries 11 and 12). In another trial, the reaction of **3a** and **4** in DMSO with sodium hydride as base in the presence of 1.2 equivalents of water gave 66% yield of the desired product (entry 13). Because we had not used dried solvents for the reaction, the presence of adventitious water presumably led to the formation of product **5a**, and the introduction of an additional equivalent of water probably facilitates the hydrolysis of the ketene dithioacetal to provide a better yield.

Next, by using the optimized conditions of sodium hydride and 1.2 equivalent of water in DMSO, we examined the reaction of 2-[1-cyano-2,2-bis(methylsulfanyl)vinyl]benzonitrile (**4**) with various functionalized 1-aryl-2-(imidazolidin-2-ylidene)ethanones **3** (Scheme 3), and we observed that functional groups on the phenyl ring of **3** affected the yield of product **5**, although the results did not follow any specific trend.

The scope of reaction was further examined by using a series of 2-aryl-3,3-bis(methylsulfanyl)acrylonitriles (**7**) as substrates (Scheme 4). Stirring a mixture of nitrile **7** with a 1-aryl-2-(imidazolidin-2-ylidene)ethanone **3** under the optimized reaction conditions gave the expected 6,7-diaryl-5-oxo-2,3,5,6-tetrahydroimidazo[1,2-*a*]pyridine-6-carbonitriles **8a–c** in good yields. All the synthesized compounds were characterized by spectroscopic analysis (see Supporting Information).[18]



Scheme 3 Synthesis of 7-aryl-6-(2-cyanophenyl)-5-oxo-2,3,5,6-tetrahydroimidazo[1,2-*a*]pyridine-6-carbonitriles **5**. *Reagents and conditions*: **3** (0.5 mmol), **4** (0.6 mmol), H_2O (0.6 mmol), NaH (1.0 mmol), DMSO (3.0 mL), stirring, r.t.

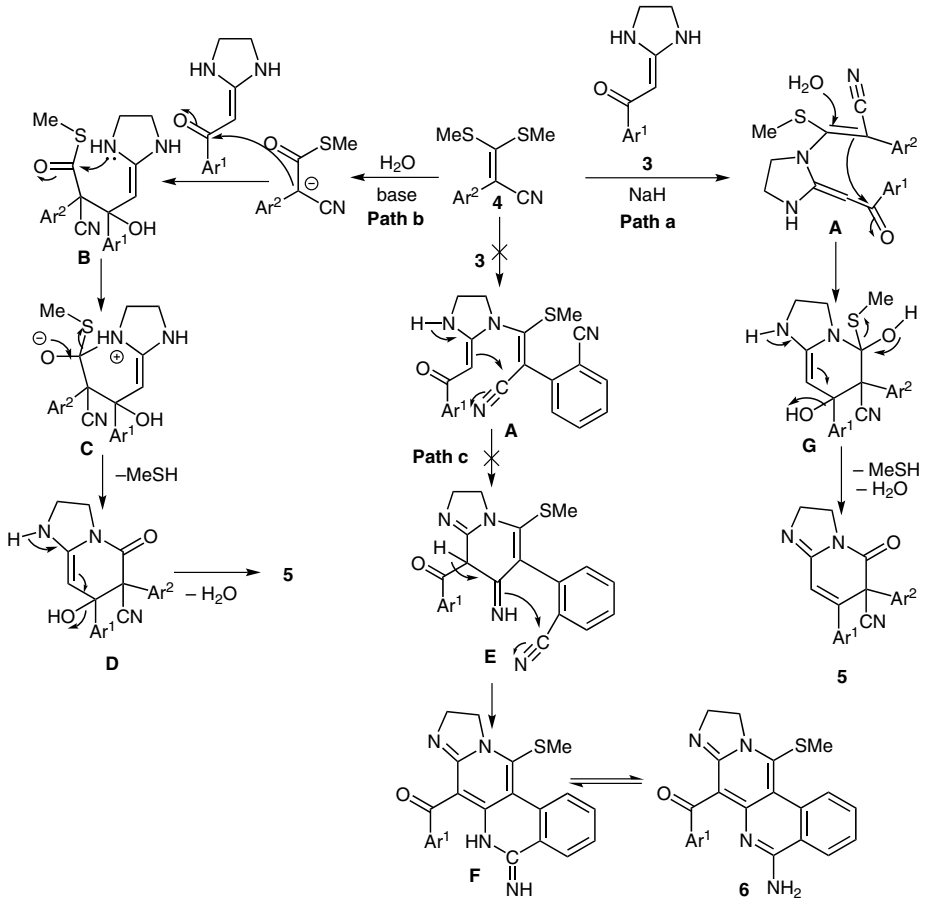


Scheme 4 Synthesis of 6,7-diaryl-5-oxo-2,3,5,6-tetrahydroimidazo[1,2-*a*]pyridine-6-carbonitriles **8a–c**

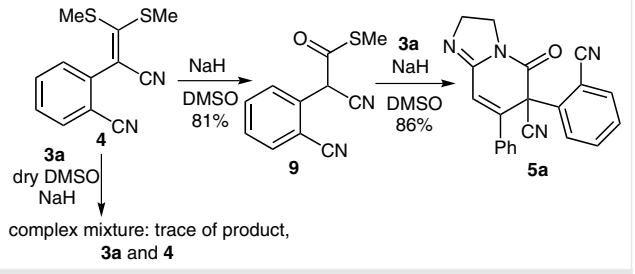
In an attempt to extend the scope of the reaction further, we examined the reaction of 2-[cyano(imidazolidin-2-ylidene)methyl]benzonitrile with 3,3-bis(methylsulfanyl)-1-phenylprop-2-en-1-one under basic conditions, with the aim of preparing [8-amino-5-(methylsulfanyl)-2,3-dihydrobenzo[*c*]imidazo[2,1-*f*]-1,6-naphthyridin-6-yl](phenyl)methanone, but this reaction failed.

Mechanistically, the reaction might follow either Path a or Path b (Scheme 5) to give the desired product, or Path c to give the alternative product **6**. Mechanistically, in Path b, the reaction is initiated by hydrolysis of **4** to produce a highly activated and stable carbanion that can undergo 1,2-addition to the carbonyl group of **3** to yield intermediate **B**. Cyclization can then occur by preferential intramolecular nucleophilic attack of nitrogen onto the thioester to generate intermediate **C**, which subsequently loses methanethiol to yield **D**. Intermediate **D** then undergoes loss of water to produce the desired product. The same product can also be formed by following Path a, which is initiated by Michael addition of the nitrogen onto 2-[1-cyano-2,2-bis(methylsulfanyl)vinyl]benzonitrile, followed by loss of methanethiol with formation of intermediate **A**. Intermediate **A** can undergo addition of water followed by nucleophilic attack on the aryl carbonyl to generate an intermediate **G**, which loses water and methanethiol to yield product **5**. In the alternative Path c, intermediate **A** cyclizes by nucleophilic attack of the carbon α to the aromatic carbonyl group on the aliphatic nitrile to generate intermediate **E**. The in situ generated imine group of intermediate **E** can further cyclize with the aromatic nitrile group and generate the intermediate **F**, which undergoes tautomerization to afford product **6**.

In an attempt to ascertain the probable route for the formation of **5**, we stirred compound **4** in DMSO containing NaH and 1.2 equivalents of water, and we isolated thioester **9** in good yield (Scheme 6). We then performed an independent reaction of **9** with **3a** using sodium hydride in DMSO, and we isolated the desired product **5a** in 86% yield. This result strongly supports the view that the reaction follows Path b (Scheme 5). This seems feasible, because intermediate **A** is sterically less hindered than intermediate **B**, and should cyclize more readily. We also performed the same reaction in dry DMSO and we observed the formation of a complex product mixture containing only traces of the



Scheme 5 Plausible mechanisms for the synthesis of 7-aryl-6-(phenyl/2-cyanophenyl)-5-oxo-2,3,5,6-tetrahydroimidazo[1,2-*a*]pyridine-6-carbonitriles



Scheme 6 Control experiments: isolation of a proposed intermediate **9** and its reaction with ketene aminal **3a**

product along with recovered starting material, which confirmed the central role of water in the reaction pathway.

Single-crystal X-ray analyses for **5b** and **8b** are presented as ORTEP plots with the atom-numbering scheme in Figure 1.[19] In the case of **5b**, the compound crystallizes in the triclinic system with two molecules in the unit cell. The two aromatic rings containing fluoro and cyano groups are essentially planar, whereas the six-membered ring of the imidazo[1,2-*a*]pyridine-6-carbonitrile fragment is almost planar, with the carbonyl carbon slightly deviating from the plane by 0.076 Å. The dihedral angle between the fluorobenzene and imidazo[1,2-*a*]pyridine-6-carbonitrile ring is 29.96°, whereas the imidazo[1,2-*a*]pyridine-6-carbonitrile and cyanophenyl rings are almost perpendicular to one another, with a dihedral angle of 85.80°. In the case of **8b**, there are four molecules in the monoclinic unit cell. The anisyl and phenyl rings are essentially planar, whereas the six-membered ring of the imidazo[1,2-*a*]pyridine-6-carbonitrile fragment is almost planar, with the carbonyl carbon deviating from the plane by 0.089 Å. The dihedral angle between the anisyl and imidazo[1,2-*a*]pyridine-6-carbonitrile rings is significantly larger than the corresponding angle in **5b** at 69.80°, whereas the imidazo[1,2-*a*]pyridine-6-carbonitrile and cyanophenyl rings are almost perpendicular to one another, with a dihedral angle of 87.49°.

The supramolecular architecture in **5b** is stabilized by N···H, O···H, π···π, and F···C interactions (see Supporting Information; Figure S1). A pair of N···H interactions operates between the cyano nitrogen N3 of the imidazo[1,2-*a*]pyridine-6-carbonitrile fragment and the ethylene hydrogens H10A and H11B of the imidazole moiety, with interaction distances N3···H10A = 2.57 Å and N3···H11B = 2.67 Å. An O···H interaction is evident between the carbonyl oxygen O1 and the ethylene hydrogen H11A of the imidazole fragment, with an intramolecular distance of 2.50 Å. The most important feature in the supramolecular framework of **5b** is the existence of a π···π interaction between the two fluorophenyl fragments. This π···π interaction is not of the face-to-face type, but rather has a sideways nature in which the two *ortho* C5 carbon atoms of the two rings interact with each other with an interaction distance of 3.38 Å. In addition to these interactions, another weak F···C interaction ap-

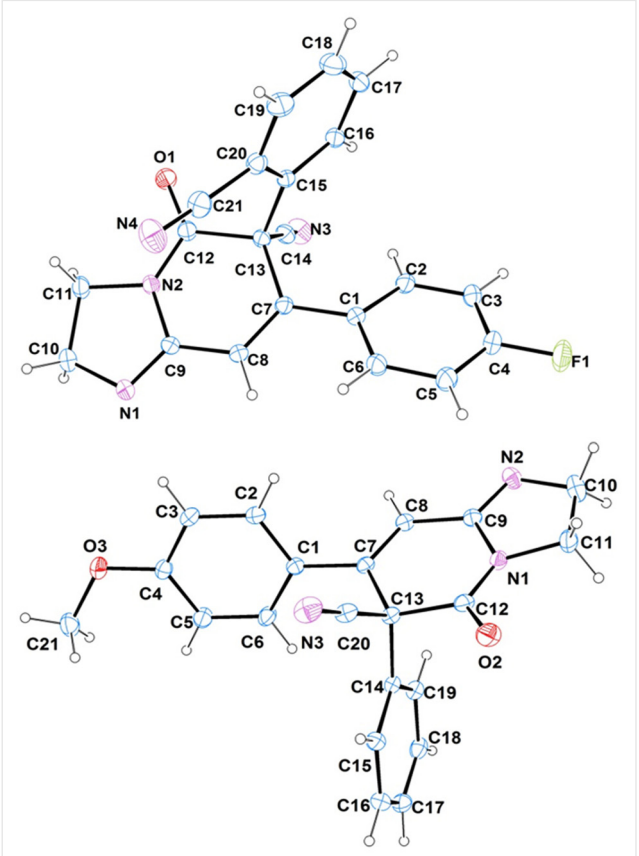


Figure 1 ORTEP diagrams of **5b** and **8b** at 30% probability with the atom-numbering scheme. Only one of the two molecules of the asymmetric unit is shown.

pears to be operating between the fluoro group and the cyano carbon of the cyanophenyl fragment, with an interaction distance of 3.07 Å. As in the case of **5b**, the supramolecular architecture of **8b** is also stabilized by weak O···H and C–H···π interactions (see Supporting Information, Figure S2). However, unlike the case of **5b**, no π···π interaction exists in **8b**. A pair of weak O···H interactions operate between the methoxy oxygen O3 and the phenyl hydrogen H18 and the methoxy proton H21C, with dimensions of 2.69 Å and 2.59 Å. A C–H···π interaction occurs between the *ortho*-carbon C5 of the anisole group and the methoxy hydrogen H21B, with an interaction distance of 2.82 Å.

The crystal structures of **5b** and **8b**, as discussed above, are good examples of the interplay of different molecular interactions that lead to interesting supramolecular aggregates in the solid state (see Supporting Information; Figures S1 and S2). It is obvious that C≡N···H, O···H, π···π, and C–H···π noncovalent interactions play an important role, if the structure is to be rationalized in terms of interactions between the molecular fragments.

In summary, we have established an economical, simple, efficient, and regioselective approach to the synthesis of 6,7-diaryl-5-oxo-2,3,5,6-tetrahydro-imidazo[1,2-*a*]pyri-

dine-6-carbonitriles in moderate to good yields. Interestingly, we have also demonstrated that 2-(imidazolidin-2-ylidene)-1-arylethanones can act as nucleophiles as well as electrophiles, depending on the counter-precursor used, and [3+3] annulation can be replaced by [4+2] annulation. We have also investigated the mechanistic pathway and have found experimental evidence, in the form of isolated intermediates, to support the proposed path of the reaction.

Acknowledgment

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1588943.

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(18) **7-Aryl-6-(2-cyanophenyl)-5-oxo-2,3,5,6-tetrahydroimidazo[1,2-*a*]pyridine-6-carbonitriles 5a–i; General Procedure**
A mixture of the appropriate 1-aryl-2-(imidazolidin-2-ylidene)ethanone **3** (0.5 mmol), 2-[1-cyano-2,2-bis(methylsulfanyl)vinyl]benzonitrile (**4**; 0.6 mmol), H_2O (0.6 mmol), and NaH (1.0 mmol) in DMSO (3.0 mL) was stirred at r.t. for 8 h. When the reaction was complete, the crude mixture was poured slowly onto ice–water with constant stirring. The mixture was then neutralized with 10% aq HCl. The resulting precipitate was collected by filtration, washed with H_2O, and dried. Products were purified by column chromatography (silica gel, EtOAc).
6-(2-Cyanophenyl)-5-oxo-7-phenyl-2,3,5,6-tetrahydroimidazo[1,2-*a*]pyridine-6-carbonitrile (5a)
Brown solid; yield: 112 mg (66%); mp 130–132 °C. IR (KBr): 2924, 2225, 1606 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.05–3.90 (m, 2 H, CH_2), 4.10–4.27 (m, 2 H, CH_2), 6.83 (s, 1 H, ArH), 7.13–7.22 (m, 5 H, ArH), 7.33 (t, *J* = 7.6 Hz, 1 H, ArH), 7.50–7.55 (m, 2 H, ArH), 7.81 (d, *J* = 7.6 Hz, 1 H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.5, 54.2, 54.8, 110.1, 115.3, 115.6, 120.1, 127.8, 128.5, 129.4, 129.7, 130.8, 133.3, 134.8, 134.9, 136.5, 144.2, 152.4, 158.7. HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{21}H_{15}N_4O$: 339.1240; found: 339.1238.
(19) CCDC 1501042 and 1501043 contain the supplementary crystallographic data for compounds **5b** and **8b**, respectively. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.
5b: $C_{21}H_{13}FN_4O$, *M* = 356.35, triclinic, *P-1*, *a* = 8.1557(9) Å, *b* = 8.6242(8) Å, *c* = 13.0701(13) Å, α = 109.147(9)°, β= 95.496(8)°, γ = 100.594(8)°, *V* = 841.50(16) Å^3, *Z* = 2, D_{calc} = 1.406 mg/m^3, F(000) = 368, crystal size 0.p220 × 0.200 × 0.180 mm, reflections collected 6662, independent reflections 3844 [$R_{(int)}$ = 0.0198], Final indices [*I*> 2σ(*I*)] *R*1 = 0.0519, *wR2* = 0.0997, *R* indices (all data) *R*1 = 0.0854, *wR2* = 0.1188, *GoF* 1.038, Largest difference peak and hole 0.168 and –0.220 e Å–3.
8b: $C_{21}H_{17}N_3O_2$, *M* = 343.38, monoclinic, $P2_{1/c}$, *a* = 9.9517(10) Å, *b* = 23.171(2) Å, *c* = 7.5232(7) Å, β = 105.529(10)°, *V* = 1671.4(3) Å^3, Z = 4, D_{calc} = 1.365 mg/m^3, F(000) = 720, crystal size 0.210 × 0.200 × 0.170 mm, reflections collected 13503, independent reflections 3912 [$R_{(int)}$ = 0.0663], Final indices [I> 2σ(I)] *R*1 = 0.0668, *wR2* = 0.1530, *R* indices (all data) *R*1 = 0.0924, *wR2* = 0.1741, *GoF* 1.078, Largest difference peak and hole 0.368 and –0.248 e Å–3.