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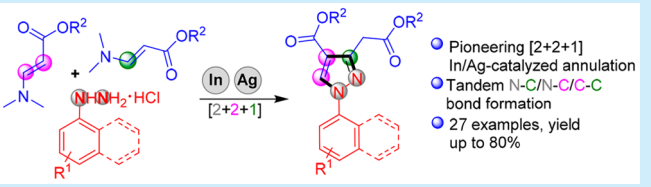
Synergistic Indium and Silver Dual Catalysis: A Regioselective [2 + 2 + 1]-Oxidative *N*-Annulation Approach for the Diverse and Polyfunctionalized *N*-Arylpyrazoles

Raju S. Thombal and Yong Rok Lee*

School of Chemical Engineering, Yeungnam University, Gyeongsan 38541, Republic of Korea

Supporting Information

ABSTRACT: Indium(III)/silver(I)-catalyzed [2 + 2 + 1] annulation of arylhydrazine hydrochlorides with β-enamino esters via multicomponent reactions for the construction of diverse and multisubstituted *N*-arylpyrazoles has been demonstrated. The oxidative cycloaddition proceeds via a cascade triple Michael addition/elimination/air oxidation. This novel protocol provides a rapid and efficient synthetic route to various 3,4-diester-substituted *N*-arylpyrazoles. The synthesized compounds are further utilized for various synthetic transformations.



Pyrazoles are among the most significant heteroaromatic compounds widely found in biologically and pharmacologically active molecules.[1] They exhibit a variety of biological properties, including anti-inflammatory,[2] antibacterial,[3] analgesic,[4] antifungal,[5] antipyretic,[6] antiviral,[7] anticancer,[8] antidiabetic,[9] antiobesity,[10] and plant growth regulating activities,[11] as well as protein kinase,[12] Cox-2,[13] and HIV-1 reverse transcriptase inhibitory functions.[14] They have been used as valuable building blocks and structural motifs in the synthesis of natural products, agrochemicals, dyes, and medicines.[15] Moreover, pyrazoles are employed as ligands, cosmetic colorings, and UV stabilizers.[16] To date, a number of substituted *N*-arylpyrazoles, including difenamizole (**1**), celecoxib (**2**), rimonabant (**3**), and fipronil (**4**), have been commercialized as pharmaceuticals and insecticides (Figure 1).[17]

Owing to the importance and usefulness of *N*-arylpyrazoles, a number of methods for their preparation have been developed (Scheme 1). Typical approaches are based on the [3 + 2]cycloaddition of hydrazines with the corresponding substrates through condensation or multistep reactions.[18−21]

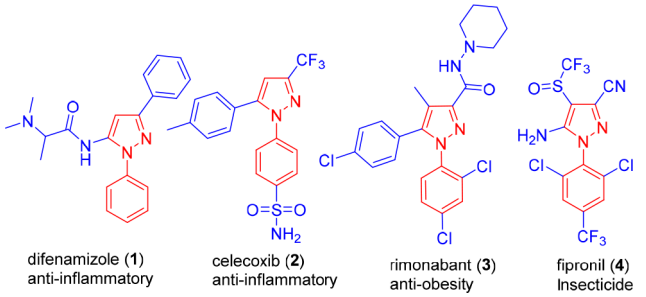
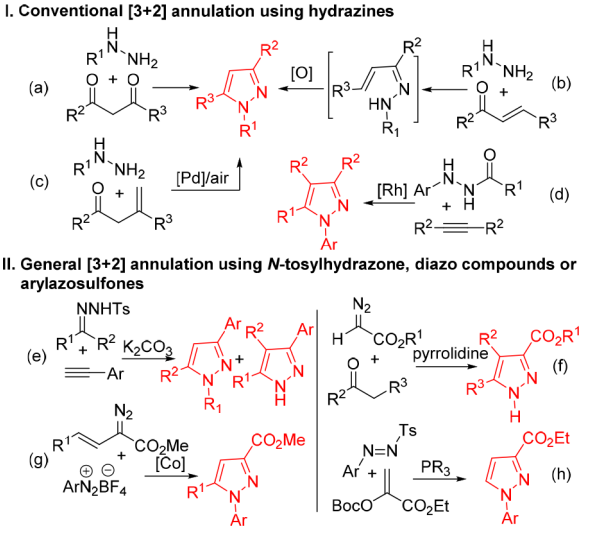


Figure 1. Selected bioactive molecules containing *N*-arylpyrazoles.

Scheme 1. Reported [3 + 2] Annulation Strategies for the Synthesis of Substituted Pyrazoles



Common strategies include the condensation of hydrazines with 1,3-dicarbonyl compounds (method a);[18] hydrazone formation, followed by Ru- or V-catalyzed intramolecular aerobic oxidative C−N coupling (method b);[19] allylic hydrazone formation and Pd-catalyzed aminohydroxylation in air (method c),[20] and Rh-catalyzed cyclization of hydrazines with alkynes (method d).[21] Other facile [3 + 2] annulation approaches to form substituted pyrazoles have also been demonstrated, including K_2CO_3-mediated reaction/[1,5] sigmatropic rearrangement (method e),[22] pyrrolidine-catalyzed

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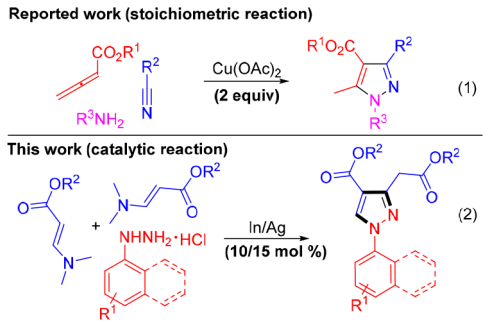
reaction of diazoacetates with carbonyl compounds (method f),[23] Co-catalyzed cycloaddition of diazoacetates with diazonium salts through C−N bond formation (method g),[24] and Bu_3P-catalyzed desulfonylative cycloaddition of arylazosulfones with allylic carbonates (method h).[25] Recently, formal [4 + 1] annulation of hydrazones with 2-bromo-1,3-dicarbonyl compounds via visible-light mediated photoredox catalysis[26a] as well as the reactions of hydrazine with Michael acceptors under visible light[26b] has been demonstrated for the synthesis of pyrazoles.

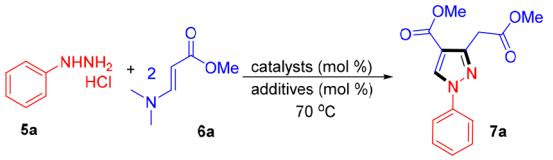
Scheme 2. Synthetic [2 + 2 + 1] Annulation Strategies for Substituted Pyrazoles through Multicomponent Reactions



Although a number of methods have been demonstrated for the construction of substituted pyrazoles via [3 + 2] cycloaddition or visible-light-mediated photoredox catalysis, most of the reported strategies have limited scope due to high catalyst loading, the use of expensive catalysts, and prefunctionalization of substrates through multistep procedure. In this regard, more facile and efficient multicomponent protocols using relatively lower loading of cost-effective catalysts are highly desirable. Recently, a very interesting Cu-mediated pyrazole formation through the multicomponent reaction of 2,3-allenoates with amines and nitriles has been described. However, it is a stoichiometric reaction, and 2.0 equiv of $Cu(OAc)_2$ is needed (eq 1, Scheme 2).[27] To the best of our knowledge, there is no report on the synthesis of diverse and polysubstituted *N*-arylpyrazoles by oxidative [2 + 2 + 1] cycloaddition of readily available arylhydrazine hydrochlorides with *β*-enamino esters employing a catalytic reaction. Recently, we demonstrated the construction of azopyrazoles by a Ag-catalyzed cascade reaction of diazo compounds with arylhydrazines.[28] We also reported the synthesis of multifunctionalized 2-hydroxybenzophenones through the benzannulation of 3-formylchromones and *β*-enamino esters.[29] As part of an ongoing study of the reactions of arylhydrazines and *β*-enamino esters, this paper describes a novel and efficient In/Ag-catalyzed oxidative [2 + 2 + 1] cycloaddition of arylhydrazine hydrochlorides with *β*-enamino esters for the construction of various multisubstituted *N*-arylpyrazoles (eq 2, Scheme 2).

To obtain the optimized conditions, the reaction of phenylhydrazine hydrochloride (**5a**) and methyl (*E*)-3-(dimethylamino)acrylate (**6a**) was carried out in an open air condition using various catalysts and solvents (Table 1). The initial attempts using 10 mol % of $Cu(OTf)_2$, $Y(OTf)_3$, and $Yb(OTf)_3$ in dichloroethane at 70 °C for 12 h provided product **7a** in 31, 17, and 27% yields, respectively (entries 1−3, Table 1). Encouraged by these results, other catalysts were

Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst (mol %)	additives (mol %)	solvent	time (h)	yield[b] (%)
1	$Cu(OTf)_2$ (10)		dichloroethane	12	31
2	$Y(OTf)_3$ (10)		dichloroethane	12	17
3	$Yb(OTf)_3$ (10)		dichloroethane	12	27
4	$InCl_3$ (10)		dichloroethane	12	43
5	$In(OTf)_3$ (10)		dichloroethane	12	48
6[c]	$In(OTf)_3$ (10)		dichloroethane	12	58
7	$In(OTf)_3$ (10)	$AgNO_3$ (15)	dichloroethane	24	52
8	$In(OTf)_3$ (10)	Ag_2O (15)	dichloroethane	24	55
9	**$In(OTf)_3$ (10)**	**$AgSbF_6$ (15)**	**dichloroethane**	**12**	**71**
10	$In(OTf)_3$ (5)	$AgSbF_6$ (15)	dichloroethane	12	38
11	$In(OTf)_3$ (20)	$AgSbF_6$ (15)	dichloroethane	12	68
12	$In(OTf)_3$ (10)	$AgSbF_6$ (10)	dichloroethane	12	61
13	$In(OTf)_3$ (10)	$AgSbF_6$ (20)	dichloroethane	12	63
14		$AgSbF_6$ (15)	dichloroethane	24	0
15	$In(OTf)_3$ (10)	$AgSbF_6$ (15)	toluene	12	10
16	$In(OTf)_3$ (10)	$AgSbF_6$ (15)	EtOH	12	40
17	$In(OTf)_3$ (10)	$AgSbF_6$ (15)	DMF	24	21
18[d]	$In(OTf)_3$ (10)	$AgSbF_6$ (15)	dichloroethane	12	32
19[e]	$In(OTf)_3$ (10)	$AgSbF_6$ (15)	dichloroethane	12	60

[a]Reaction conditions: **5a** (0.5 mmol) and **6a** (1.1 mmol) in solvent (5.0 mL) at 70 °C under air. [b]Isolated yield. [c]Reaction was performed under O_2 atmosphere. [d]Reaction was performed under N_2 atmosphere. [e]Reaction condition: phenylhydrazine (0.5 mmol) and **6a** (1.1 mmol) in DCE (5.0 mL) at 70 °C under air.

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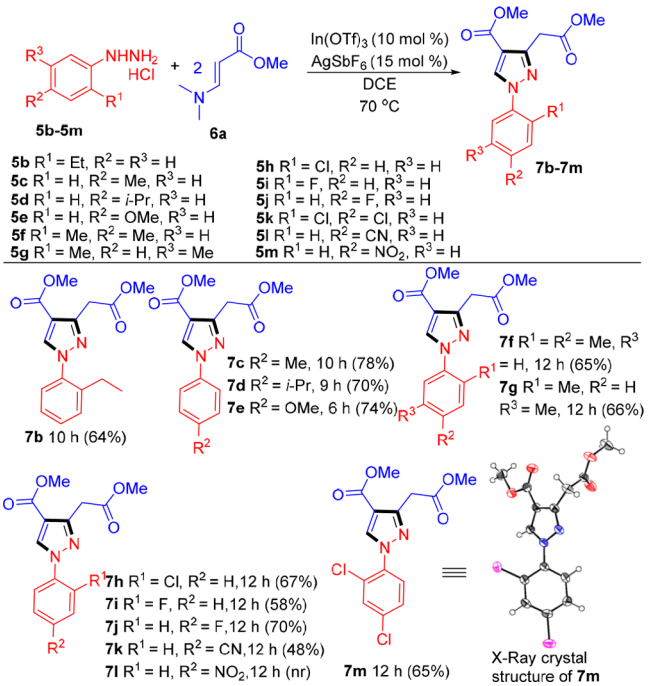
screened. Using 10 mol % $InCl_3$ and $In(OTf)_3$, the yields of **7a** increased to 43% and 48%, respectively (entries 4 and 5). When the reaction was carried out under O_2 atmosphere, the yield of **7a** slightly increased to 58% (entry 6). Interestingly, additives also provided a higher yield for the product; when $In(OTf)_3$ (10 mol %) was used as the catalyst with the addition of $AgNO_3$ (15 mol %) or Ag_2O (15 mol %) resulted in slightly increased yields of 52 and 55%, respectively (entries 7 and 8). The best yield (71%) was achieved when 10 mol % of $In(OTf)_3$ was used with $AgSbF_6$ (15 mol %) in dichloroethane at 70 °C for 12 h, forming a dual catalytic system (entry 9). Decreasing the $In(OTf)_3$ loading to 5 mol % (entry 10) or increasing it to 20 mol % (entry 11) did not improve the yield of **7a**. In addition, changing the quantity of the additive failed to improve the yield (entries 12 and 13). When the additive $AgSbF_6$ (15 mol %) was used in the absence of the $In(OTf)_3$ catalyst, the desired product was not obtained (entry 14). On the other hand, when other nonpolar or polar solvents such as toluene, EtOH, and DMF were used, **7a** was produced in 10, 40, and 21% yields, respectively (entries 15–17). When the reaction was carried out under nitrogen atmosphere, the yield of **7a** dramatically decreased to 32% (entry 18). Further reaction of hydrochloride salt-free phenylhydrazine with **6a** for 12 h provided the desired product **7a** in slightly lower yield (60%, entry 19). The structure of **7a** was determined by the analysis of its spectral data. The ^1H NMR spectrum of **7a** showed a characteristic signal of the vinyl proton on the pyrazole ring at δ 8.35 ppm as a singlet and a methylene proton signal at δ 4.00 ppm as a singlet. The structure was further confirmed by X-ray crystallographic analysis of the structurally related compound **7m**.

To explore the generality of the reaction, reactions of different arylhydrazine hydrochlorides **5b–m** with **6a** were next examined (Scheme 3). Treatment of arylhydrazine hydrochlorides **5b–g** bearing electron-donating groups on their benzene rings, such as 2-ethyl, 4-methyl, 4-isopropyl, 4-methoxy, 2,4-dimethyl, and 2,5-dimethyl groups, with **6a** for 6–12 h provided the desired products **7b–g** in 64–78% yields. Similarly, reactions of **6a** with **5h–l** bearing the electron-withdrawing groups of 2-chloro, 2-fluoro, 4-fluoro, 4-cyano, and 2,4-dichloro on the benzene ring for 12 h afforded products **7h–k**, **m** in slightly lower yields (48–70%). However, reaction of **6a** with **5m** bearing a strong electron-withdrawing group of 4-nitro on the benzene ring, did not afford product **7l**. Moreover, the reactions of 2-hydrazinopyridine dihydrochloride (heterocyclic hydrazine) or cyclohexylhydrazine hydrochloride (alkyl hydrazine) with (*E*)-3-(dimethylamino)acrylate (**6a**) were unsuccessful. These reactions provide a rapid synthetic route to diverse 4,5-disubstituted *N*-arylpyrazoles bearing various substituents on the benzene rings.

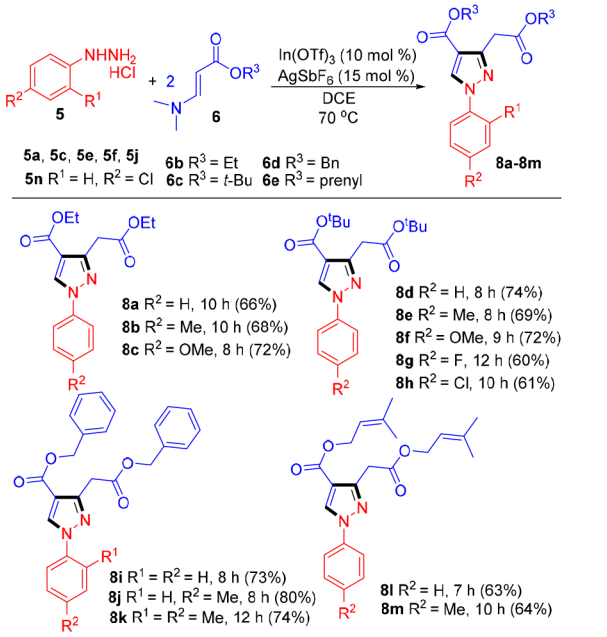
Next, the scope of this reaction was explored using other *β*-enamino esters **6b–e** bearing ethoxy, *tert*-butoxy, benzyloxy, and prenyloxy groups (Scheme 4). Reactions of ethyl (*E*)-3-(dimethylamino)acrylate (**6b**) with **5a**, **5c**, and **5e** provided the expected products **8a–c** in 66, 68, and 72% yields, respectively. A combination of *tert*-butyl (*E*)-3-(dimethylamino)acrylate (**6c**) with **5a**, **5c**, **5e**, **5j**, or **5n** afforded products **8d–h** in 60–74% yields. Moreover, treatment of benzyl (*E*)-3-(dimethylamino)acrylate (**6d**) with **5a**, **5c**, or **5f** provided products **8i–k** in 73, 80, and 74% yields, respectively, whereas the reaction of 3-methylbut-2-en-1-yl-(*E*)-3-(dimethylamino)acrylate (**6e**) with **5a** or **5c** afforded products **8l** and **8m** in 63 and 64% yields, respectively. In addition, the reaction of *β*-substituted enamino ester [methyl (*E*)-3-(dimethylamino)but-2-enoate] with phenylhydrazine hydrochloride (**5a**) under the standard reaction conditions did not produce the desired product, probably due to the direct involvement of *α* and *β* carbons in the pyrazole ring.

Having demonstrated the general applicability of this cycloaddition, we investigated the possibility of using 1-naphthalenylhydrazine hydrochloride (**9**), which will lead to the formation of a new type of *N*-arylpyrazole derivative

Scheme 3. Substrate Scope of Aryl Hydrazine Hydrochlorides



Scheme 4. Substrate Scope of Different *β*-Enamino Esters



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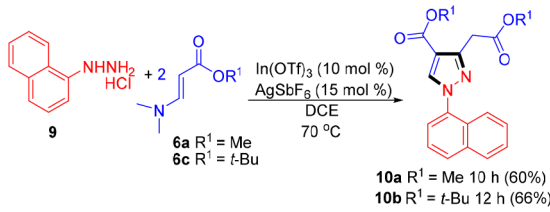
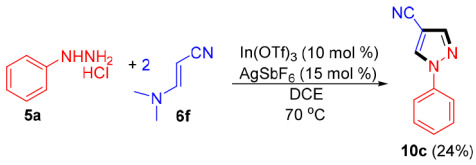
(Scheme 5). The reaction of **9** with **6a** or **6c** led to the formation of **10a** and **10b** in 60 and 66% yields, respectively.

Scheme 5. Reactions of 1-Naphthalenylhydrazine Hydrochloride (9) with 6a or 6c



Moreover, we explored the reaction of phenylhydrazine hydrochloride (**5a**) with (*E*)-3-(dimethylamino)acrylonitrile (**6f**) (Scheme 6). Interestingly, treatment of **5a** with **6f** led to

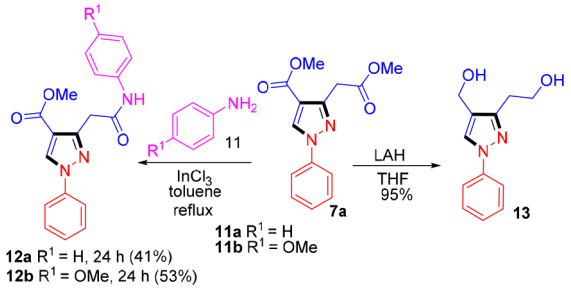
Scheme 6. Reactions of Phenylhydrazine Hydrochloride (5a) with 6f



unexpected 4-cyano-substituted pyrazole **10c** in lower yield (24%) together with the recovery of starting material **6f** (39%). However, the reaction of (*E*)-*N*,*N*-dimethyl-2-phenylethen-1-amine with phenylhydrazine hydrochloride (**5a**) did not produce any products. This result reveals that the absence of the electron-withdrawing group deactivates the ability of enamino substrates to act as Michael acceptors.

To investigate the application of the novel protocol described herein, the conversion of the prepared compound **7a** (for gram-scale synthesis of **7a**, see the Supporting Information (SI)) into new molecules was attempted (Scheme 7). The reaction of **7a** with aniline (**11a**) in the presence of 20

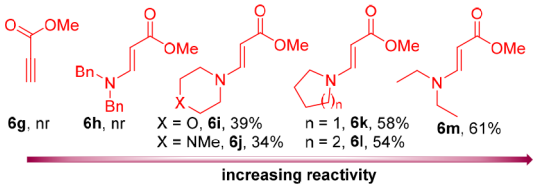
Scheme 7. Conversion of the Synthesized Compound 7a into New Molecules 12a, 12b, and 13



mol % of $InCl_3$ in refluxing toluene for 24 h chemoselectively provided **12a** in 41% yield, and the same reaction with 4-methoxyaniline (**11b**) afforded **12b** in 53% yield. Also, further LAH reduction of **7a** provided the diol product **13** in 95% yield.

To understand the reactivity of Michael acceptors toward phenyl hydrazine hydrochloride (**5a**), different reaction partners **6g**−**m** were treated under the standard reaction conditions (Scheme 8). The results indicate that the esters

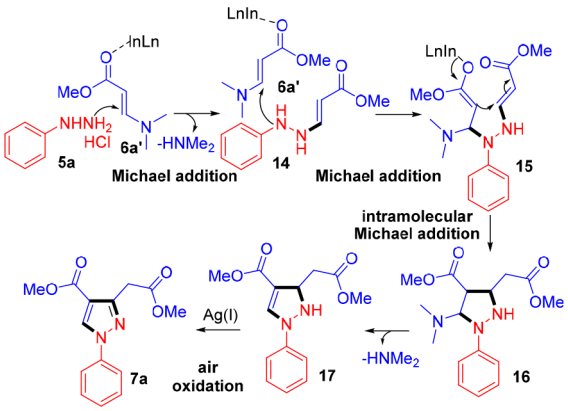
Scheme 8. Reactivity of Various Michael Acceptors 6g−m toward Phenylhydrazine Hydrochloride (5a)



bearing less bulky groups reacted smoothly with **5a**, while substrates **6g** and **6h** remained to be unreactive substrates. Due to the presence of an extra heteroatom, O or N, on enamino esters **6i** and **6j**, the lower reactivity was observed compared to the enamino ester **6l** bearing pyrrolidine ring.

On the basis of the above results, a mechanism was proposed for the formation of **7a**, as shown in Scheme 9. In the

Scheme 9. Proposed Reaction Mechanism for the Formation of 7a



presence of $In(OTf)_3$, methyl (*E*)-3-(dimethylamino)acrylate (**6a**) first forms complex **6a′**, which then reacts with phenylhydrazine hydrochloride (**5a**) to form the intermediate **14** through a Michael-type addition followed by the elimination of dimethylamine. Subsequently, further Michael addition of **14** to another complex **6a′** forms intermediate **15**, which undergoes an intramolecular Michael addition to furnish **16**. Then, further elimination of dimethylamine affords intermediate **17** followed by aerobic oxidation in the presence of a silver catalyst, leading to the final product **7a**. To elucidate the elimination of amine in the proposed reaction mechanism, a control experiment was carried out between **5a** and **6l** under the standard reaction condition (see the SI). Importantly, piperidine was detected in the crude reaction mixture by GC−MS analysis (see Figures S1−S3). The oxidation of dihydropyrazoles to pyrazoles in the presence of metal catalysis has been previously reported.[30] On the other hand, the formation of **10c** as shown in Scheme 6 might proceed via a cascade triple Michael addition followed by elimination of CH_3CN and dimethyl amine rather than the oxidation process (for the mechanism, see the SI). Through GC−MS analysis, CH_3CN was detected in the crude reaction mixture as an evidence of this reaction pathway (see Figure S4).

In summary, a facile and efficient methodology for the construction of diverse and multifunctionalized *N*-arylpyrazoles was developed, featuring a one-pot procedure by In(III)-catalyzed regioselective [2 + 2 + 1] annulation

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reactions of arylhydrazine hydrochlorides with β-enamino esters. Both In(III) and Ag(I) played distinct catalytic roles in a synergistic manner, producing *N*-arylpyrazoles with high regioselectively. This cascade protocol afforded a rapid synthetic route to highly functionalized pyrazole derivatives, which can be widely used for the synthesis of dyes, natural products, and pharmaceuticals. Further transformation of the synthesized compound was carried out to obtain biologically relevant amidopyrazole derivatives.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02008.

Detailed experimental procedures, characterization data, and ^{1}H NMR and ^{13}C NMR spectra of final products; X-ray data for compound **7m** (PDF)

Accession Codes

CCDC 1832571 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yrlee@yu.ac.kr. Fax: +82-53-810-4631. Tel: +82-53-810-2529.

ORCID

Raju S. Thombal: 0000-0003-3760-8856

Yong Rok Lee: 0000-0002-4048-8341

Notes

The authors declare no competing financial interest.

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