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In situ generation and conversion of a half-zirconocene catalyst for the synthesis of *N*-acylpyrazoles†

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Pyrazoles are an important class of five-membered nitrogen heterocyclic compounds that have been widely used in agriculture and medicine. Exploring their synthesis methods under mild conditions has always been a hot research topic. Herein, a new strategy was developed to enhance the activity of a zirconium metal centre for the synthesis of *N*-acylpyrazole derivatives using Cp₂ZrCl₂ as a pre-catalyst. Cp₂ZrCl₂ was activated *in situ* within the catalytic system through cyclopentadienyl ring dissociation, leading to the formation of an activated species, [CpZrCl(acac)₂]. The new approach demonstrates broad substrate scope under mild reaction conditions, leading to formation of (3,5-dimethyl-1*H*-pyrazol-1-yl)(phenyl)methanones with yields of up to 97%.

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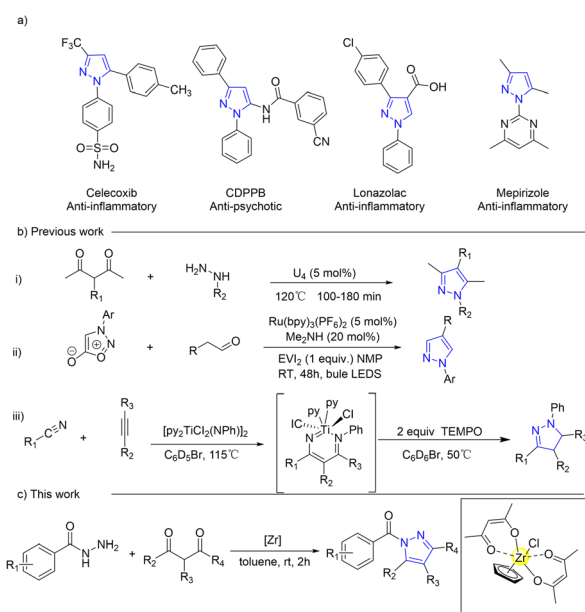
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Introduction

Pyrazoles, a significant class of five-membered nitrogen heterocyclic compounds, serve as versatile building blocks^{1–3} and crucial intermediates^{4,5} in organic synthesis. They exhibit a wide range of pharmaceutical activities and are extensively studied in medical research^{6–9} for their anti-tubercular, anti-cancer,¹⁰ anti-depressant, anti-bacterial,^{11,12} and anti-parkinsonism activities (Scheme 1a). Several methods, such as cyclocondensation of hydrazine and its derivatives with carbonyl systems,^{13–18} dipolar cycloadditions,^{19–23} and multi-component reactions,^{24,25} have been employed in the development of pyrazoles (Scheme 1b). However, certain existing synthetic approaches for pyrazole synthesis necessitate expensive metal catalysts, harsh reaction conditions, and inconvenient operations as well as yield low product quantities. These limitations impose constraints on the practicality of these reactions, thereby necessitating the establishment of convenient, mild, high-yielding methods that employ cost-effective and less toxic reagents for *N*-acylpyrazole synthesis.

The use of tetravalent IVB Lewis acid catalysts coordinated with cyclopentadienyl (Cp), such as titanocene^{26–32} and

zirconocene,^{33–37} has been demonstrated to be more diverse, efficient, and practical for C–C^{38–43} and C–N^{44–47} formation reactions. This is attributed to their cost-effectiveness,⁴⁸ low toxicity,⁴⁹ high stability,⁵⁰ tunable Lewis acidity,^{51,52} and high coordination number.^{53–57} By incorporating the Cp ligand into the catalyst system, the requirement for stringent anhydrous conditions can also be eliminated due to its less electron deficiency and steric hindrance, which provides a hydrophobic



Scheme 1 Structures of significant pyrazoles and novel synthetic routes for *N*-acylpyrazole.

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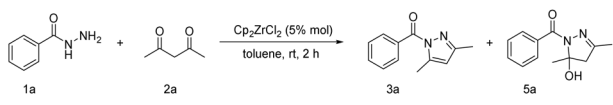
domain for protecting the Lewis acid centre against water.^{58–60} However, increased catalyst stability comes at the expense of catalytic activity. The development of a titanocene or zirconocene catalyst with a single Cp ligand is advisable in order to maintain the original catalytic stability and further enhance its catalytic performance.^{61,62} Nowadays, the synthesis of these catalysts typically involves the use of precursors such as CpZrCl₃^{63,64} and CpTiCl₃,^{65–68} which require intricate procedures and a stringent anhydrous and oxygen-free environment, in addition to being costly. The establishment of an *in situ*, convenient, and mild conversion method for a half-zirconocene catalyst is therefore imperative to enable its direct application in catalytic reactions. Additionally, these diverse coordination modes between zirconium and both the ligand^{69–71} and substrate^{72–74} facilitate facile capture of adduct products and thereby enable comprehensive investigation into catalyst–substrate interaction.

Herein, we present an *in situ* acetylacetonate-coordinated half-zirconocene complex and its catalytic role in the synthesis of *N*-acylpyrazoles, as depicted in Scheme 1c. The evidence from *in situ* ESI(+)-MS and ¹H NMR experiments elucidated the interaction between the zirconium centre and substrates. The catalyst effectively facilitated the synthesis of pyrazoles, achieving a remarkable yield of 97% under mild, low catalyst loading, non-anhydrous and non-anaerobic conditions.

Results and discussion

Our experimental optimization for *N*-acylpyrazole synthesis commenced with benzoyl hydrazine (**1a**) and acetylacetonate (acac) (**2a**), resulting in the formation of two products, namely, *N*-acylpyrazole (**3a**) and 5-hydroxy-dihydropyrazole (**5a**). The reaction was conducted at room temperature for 2 hours in toluene solvent using 5 mol% of Cp₂ZrCl₂ as a pre-catalyst, leading to the desired *N*-acylpyrazole **3a** ((3,5-dimethyl-1*H*-pyrazol-1-yl)(phenyl)methanone) with a high yield of 97% (Table 1, entry 1). The control experiment confirmed the essential role of zirconium catalyst in preventing the undesirable generation of compound **5a** (entry 2). Initially, various solvents were evaluated employing Cp₂ZrCl₂ as a pre-catalyst; their results are presented in entries 3–8 of Table 1. DMSO provided a yield of only 47% while THF, DMF, acetonitrile, EtOH and CH₂Cl₂ exhibited similar yields, ranging from 80% to 90%. Consequently, toluene was identified as the optimal choice due to its superior yield up to 97%. Subsequently, several catalysts were examined (entries 9–18). Considering that oxygen within acetylacetonate readily interacts with the zirconium metal centre, ZrCl₄ was initially assessed due to its easily breakable Zr–Cl bonds, resulting in an 88% yield. However, the presence of Zr(OH)₄ failed to produce desired product **3a** while yielding only 22% of compound **5a**, possibly due to the inability of stable Zr–OH ligand to be replaced by acetylacetonate. Zr(OAc)₂ yielded only 83% of compound **5a** without any desired product formation. Acetylacetonate zirconium was introduced as a contrasting catalyst to the *in situ* coordinating complex, resulting in only 22% yield of **5a**. CpZrCl₃ was employed as a formed half-zirconocene catalyst, giving 90% yield, consistent with

Table 1 Solvent and catalyst effect in the reaction of benzoyl hydrazine and acetylacetonate^a



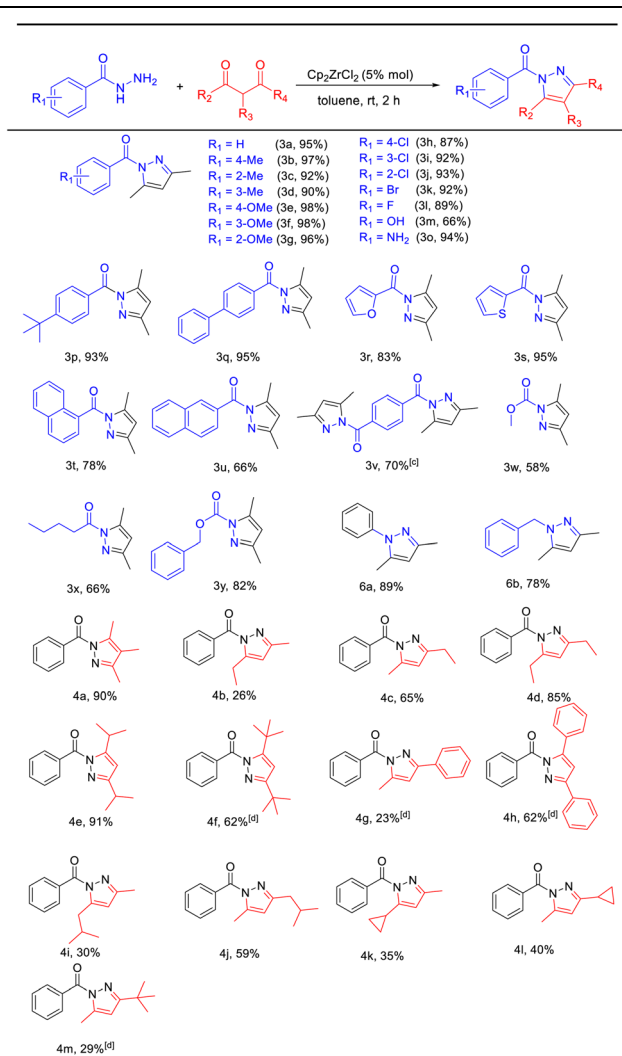
Entry	Catalyst	Solvent	Yield ^b (%)	
			Product 3a	Product 5a
1	Cp ₂ ZrCl ₂	Toluene	97	—
2	—	Toluene	—	76
3	Cp ₂ ZrCl ₂	DMSO	47	—
4	Cp ₂ ZrCl ₂	THF	82	—
5	Cp ₂ ZrCl ₂	DMF	80	—
6	Cp ₂ ZrCl ₂	CH ₃ CN	81	—
7	Cp ₂ ZrCl ₂	CH ₂ Cl ₂	87	—
8	Cp ₂ ZrCl ₂	EtOH	90	—
9	ZrCl ₄	Toluene	88	—
10	Zr(OH) ₄	Toluene	—	22
11	Zr(OAc) ₂	Toluene	—	83
12	Zr(O ₂ C ₅ H ₇) ₄	Toluene	—	22
13	CpZrCl ₃	Toluene	90	—
14	FeCl ₃ ·6H ₂ O	Toluene	74	—
15	CuCl ₂ ·2H ₂ O	Toluene	36	—
16	PTSA	Toluene	—	—
17	Sulfamic acid	Toluene	32	—
18	Camphor sulfonic acid	Toluene	79	—

^a 0.5 mmol of benzoyl hydrazine, 0.5 mmol of acetylacetonate and 5% of the catalyst in 0.5 mL solvent at room temperature for 2 h. ^b Yield of ¹H NMR.

Cp₂ZrCl₂. When FeCl₃·6H₂O and CuCl₂·2H₂O were used as Lewis acid catalysts, the desired products were obtained with yields of 74% and 36%, respectively. Several mild acids, including PTSA, sulfamic acid and camphor sulfonic acid, were introduced as alternatives to the Zr catalyst. Consequently, the yields of the target product were 0%, 32% and 79%, respectively.

With the optimized conditions established, the substrate scope was explored by reacting various benzoyl hydrazines with acetylacetonate. The reactivity of various substituted benzoyl hydrazines was examined and is summarized in Table 2. Electron-donating groups such as –Me and –OMe gave *N*-acylpyrazole yields in the range of 90–98% (**3b–3g**), while electron-withdrawing halogen groups (–F, –Cl, –Br) produced the desired products with 87–93% yields (**3h–3l**). 66% yield (**3m**) for the benzoyl hydrazine with –OH substitution was obtained, which can be attributed to the facile coordination of the oxygen atom in the hydroxyl group with the zirconium metal centre, thereby causing catalyst poisoning and rendering it inactive. The amino-substituted benzoyl hydrazine underwent a reaction with acetylacetonate, leading to the formation of two distinct products. One of these products was the desired compound **3o**, while the other product **3n** exhibited an imine structure resulting from subsequent interaction between compound **3o** and another molecule of acetylacetonate. The reaction between *p*-*tert*-butyl and *p*-phenyl-substituted benzoyl hydrazine resulted in a product yield of 93% for compound **3p** and 95% for



Table 2 Cyclization of benzoyl hydrazine and acetylacetone.^{a,b}

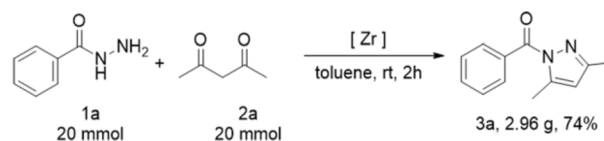
^a 0.5 mmol of benzoyl hydrazine, 0.5 mmol of acetylacetone, 5% of Cp_2ZrCl_2 in 0.5 mL solvent at room temperature for 2 h. ^b Yield of the isolated product. ^c 1.0 mmol acetylacetone was used. ^d 120 °C for 12 h.

compound **3q**, respectively. Heterocyclic substituted substrates including furyl-, thienyl-, 1-naphthyl-, and 2-naphthyl- exhibited favorable yields of 83%, 95%, 78%, and 66%, respectively (**3r–3u**). Upon the introduction of terephthalic dihydrazide, each of the two hydrazide groups underwent a reaction with one molecule of acetylacetone. Consequently, we increased the amount of acetylacetone to 2 equivalents in order to obtain a product featuring two pyrazole rings, yielding 70% (**3v**). In the absence of aromatic ring influence (**3w–3y**), the corresponding *N*-acylpyrazoles were obtained with moderate yields ranging from 58% to 82%. Simple hydrazine examples, including phenylhydrazine and benzylhydrazine, were also evaluated under the optimized conditions. The reactions gave 89% yield for compound **6a** and 78% for compound **6b**. The impact of changes in β -diketone derivatives on the reaction was subsequently investigated, resulting in excellent yields ranging from

85% to 91% (**4a, 4d, 4e**). The introduction of 2,4-hexanedione led to the formation of two distinct structures, namely, **4b** and **4c**, due to variations in the order of reaction between the 2-carbonyl and 4-carbonyl groups. These findings suggest that the generation of structure **4c** is more favorable. Similarly, 6-methylheptane-2,4-dione resulted in the formation of compounds **4i** and **4j** with yields of 30% and 59%, respectively. Additionally, 1-cyclopropyl-1,3-butandione produced the corresponding *N*-acylpyrazoles **4k** and **4l**, yielding 35% and 40%, respectively. When the substituent of β -diketone is changed to *tert*-butyl or phenyl, the conversion of enone may be hindered by site-blocking effects, necessitating an increase in reaction temperature and time to achieve moderate yields of the target products (**4f–4h**). Dipivaloylmethane affords the product with a yield of 62% (**4f**). Benzoylacetone only yields 23% of the desired product (**4g**). Dibenzoylmethane provides the corresponding *N*-acylpyrazole with a yield of 62% (**4h**). The reaction of 5,5-dimethylhexane-2,4-dione results in the formation of compound **4m** with a yield of 29%.

The scalability of this half-zirconocene catalytic system was assessed by conducting a 20 mmol scale reaction in a reaction tube under standard conditions (Scheme 2). The reaction between **1a** and **2a** yielded the desired product (3,5-dimethyl-1*H*-pyrazol-1-yl)-(phenyl)methanone with a yield of 74%.

To elucidate the activation mechanism of the reaction between acetylacetone and benzoyl hydrazine in the presence of Cp_2ZrCl_2 , ¹H NMR titration experiments were conducted (Fig. 1a). The gradual addition of acetylacetone and benzoyl hydrazine to a solution of Cp_2ZrCl_2 resulted in changes in the Cp signal, as detected in the ¹H NMR spectra, which can be attributed to the transformation of zirconocene species. The addition of acetylacetone alone induced a minor new signal at δ 6.29 ppm (●), indicating coordination between Cp_2Zr and acetylacetone. Upon further addition of benzoyl hydrazine, the peak corresponding to Cp_2ZrCl_2 rapidly vanished, while the immediate appearance of a new signal at δ 6.44 ppm (▲) suggested that conversion had occurred from Cp_2ZrCl_2 to a novel zirconium species inconsistent with direct coordination between Cp_2ZrCl_2 and acetylacetone. The chemical conversion of Cp_2ZrCl_2 might be attributed to the induced effect of benzoyl hydrazine, which not only served as the reaction substrate but also played a crucial role in removing one Cp ligand. In addition to the change in the characteristic hydrogen of Cp ligand, the newly generated peak at δ 6.13 ppm (✦) gradually increased during the progression of the reaction. This peak is assigned to the alkene hydrogen in the enol structure after acetylacetone coordinates with zirconium. As shown in Fig. 1b, there is a proton number ratio of 2 : 5 for acetylacetone (H_b) and Cp



Scheme 2 Reaction scale-up.



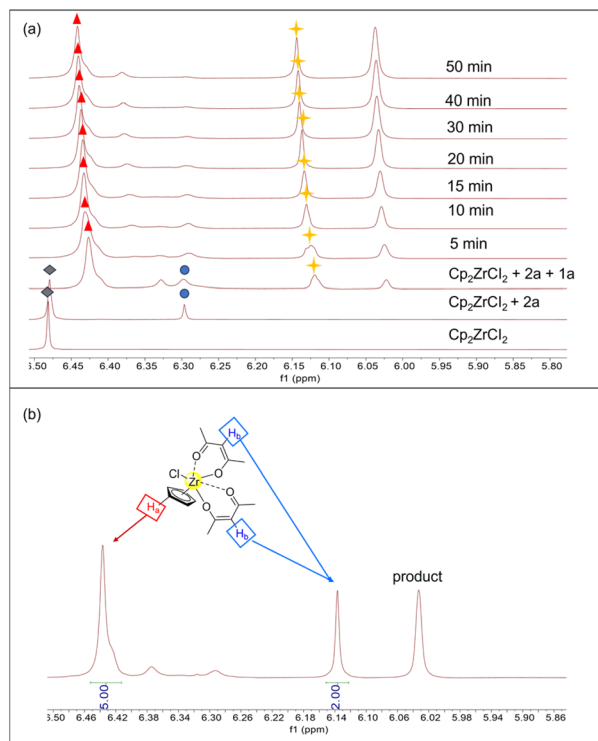


Fig. 1 (a) 400 MHz ^1H NMR titration experiments. 6.48 ppm [$\text{Cp}_2\text{-ZrCl}_2$]; 6.29 ppm [$\text{Cp}_2\text{ZrCl}(\text{acac})$]; 6.44 ppm and 6.13 ppm [$\text{CpZrCl}(\text{acac})_2$]. (b) Proton number ratio for acetylacetonate (H_b) and the Cp ligand (H_a).

ligand (H_a), indicating that the ligand ratio for acetylacetonate and Cp is 2:1 in zirconocene catalytic species (more proton number ratio shown in Fig. S8†). The experimental results indicate that the structure of the catalyst possesses a zirconium metal centre coordinated with two acetylacetonate molecules, as depicted in Fig. 1b.

The structure of the real catalytic species was further determined through *in situ* ESI(+)-MS experiments, providing insights into potential reaction mechanisms by capturing

several reaction intermediates in the ESI-MS spectra (Fig. 2). The dominant signal at an m/z value of 353.0321 is attributed to **Int-II**, where two acetylacetonate ligands and one Cp ligand are coordinated to the zirconium metal centre. The other major peak, with an m/z value of 471.0852, corresponds to the compound formed by the coordination of a zirconium centre with an acetylacetonate, a Cp ligand, and an imide structure, resulting from the reaction of acetylacetonate and imine (**Int-IV**). This peak also arises from a product where the zirconium centre is coordinated with an acetylacetonate, a Cp ligand, and an undehydrated intermediate (**Int-V**). The signal at an m/z value of 489.0962 corresponds to the intermediate structure **Int-III**, which is formed through the coordination of a half-zirconocene with an acetylacetonate and the nucleophilic addition of acetylacetonate to benzoyl hydrazine. The analysis of these three main peaks reveals that the initial step involves the reaction between acetylacetonate and the catalyst, followed by the subsequent reaction between benzoyl hydrazine and acetylacetonate. The overall reaction occurs with the participation of the catalytic species. Fig. 2 also illustrates additional peaks that can be identified, facilitating speculation on the catalytic process. The m/z value of 437.0799 corresponds to **Int-VII**, which consists of two Cp ligands and an imide intermediate structure connected to the zirconium centre. The presence of **Int-VII** indicates that the process of Cp ligand removal has not been completed, which corresponds to the gradual disappearance of the signal at δ 6.29 ppm (●) in the ^1H NMR titration experiments. **Int-VIII**, with a mass-charge ratio of m/z 589.1395, comprises one Cp ligand and two undehydrated intermediates connected to zirconium. The peak at m/z 689.1917 corresponds to the intermediate structure **Int-IX**, which bears two undehydrated hydroxy-dihydropyrazole and an acetylacetonate. The structures **Int-VIII** and **Int-IX** illustrate that the catalyst possesses the ability to incorporate multiple substrates at a single half-zirconocene catalytic centre, thereby enabling simultaneous catalysis of two or even three molecular reactions during the catalytic process. ESI-MS analysis reveals that Cp_2ZrCl_2 undergoes Cp ligand dissociation during catalysis, while the presence of acetylacetonate in a coordinated form^{69,70} significantly enhances the reaction rate.

After carefully considering the aforementioned ^1H NMR titration experiments, control experiment results, and ESI-MS analysis collectively, a plausible mechanism for the synthesis of (3,5-dimethyl-1*H*-pyrazol-1-yl)(phenyl)methanone derivatives is proposed (Scheme 3). Initially, benzoyl hydrazine promotes the pre-catalyst Cp_2ZrCl_2 to remove Cp ligand and coordinate with two acetylacetonate ligands, forming the catalytic species [$\text{CpZrCl}(\text{acac})_2$]. Then, the primary amine on benzoyl hydrazine undergoes nucleophilic addition to attack acetylacetonate and generate intermediate **III**. This intermediate then proceeds to eliminate a molecule of water and form imine intermediate **IV**. Subsequently, the enol carbon in the imine intermediate **IV** undergoes nucleophilic attack by the secondary amine of benzoyl hydrazine, resulting in the formation of *N,O*-acetal intermediate **V**. Finally, under the facilitation of the half-zirconocene centre, ligand dissociation occurs to release *N,O*-acetal and facilitate its dehydration, enabling the formation of target compound (3,5-

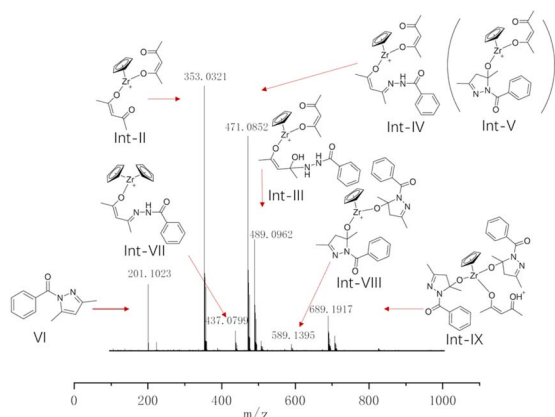
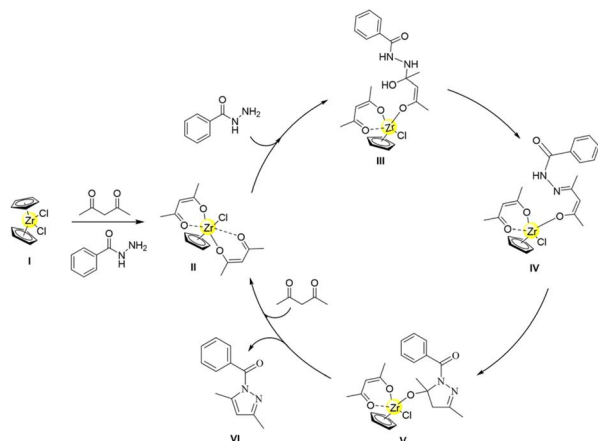


Fig. 2 ESI-MS analysis for the synthesis of *N*-acylpyrazole under standard conditions.





Scheme 3 Plausible mechanism for the synthesis of (3,5-dimethyl-1H-pyrazol-1-yl)(phenyl)methanone catalyzed by *in situ* formed half-zirconocene.

dimethyl-1H-pyrazol-1-yl)(phenyl)methanone while regenerating the catalyst species.

Experimental

General procedure for synthesis of compound 3a

A representative example of the preparation of (3,5-dimethyl-1H-pyrazol-1-yl)(phenyl)methanone (3a) is described as follows. The reactants, acetylacetone (50.06 mg, 0.5 mmol), benzoyl hydrazine (68.08 mg, 0.5 mmol), Cp₂ZrCl₂ (7.45 mg, 0.025 mmol), and toluene (0.5 mL), were combined in a reactor to establish the reaction system. The reaction was carried out under magnetic stirring at room temperature for 2 hours. Upon completion of the reaction, as confirmed by TLC analysis, the reaction mixture was subjected to silica gel flash column chromatography using an eluent mixture of petroleum ether and EtOAc in a ratio of 10 : 1 to yield the desired product 3a (97 mg) as a yellow liquid with a yield of 97%.

Conclusions

In conclusion, the development of an efficient catalytic system that facilitates the condensation and cyclization reaction between benzoyl hydrazine and acetylacetone has been achieved. This system involved the *in situ* formation of half-zirconocene using Cp₂ZrCl₂ as a pre-catalyst. Under mild conditions, high yields of *N*-acylpyrazoles were obtained with as low as 5% Cp₂ZrCl₂ catalyst loading. Mechanistic studies, including ¹H NMR, ESI(+)-MS analyses, and control experiments, revealed that the coordination of Cp₂ZrCl₂ during the reaction led to the generation of the catalytically active species. The detection of half-zirconocene-based catalyst–substrate adducts by ESI-MS elucidated the process of catalyst–substrate interaction.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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Paper

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