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# An efficient combination of Zr-MOF and microwave irradiation in catalytic Lewis acid Friedel–Crafts benzoylation†

Tan L. H. Doan, Thong Q. Dao, Hai N. Tran, Phuong H. Tran and Thach N. Le\*

A zirconium-based metal–organic framework, an effective heterogeneous catalyst, has been developed for the Friedel–Crafts benzoylation of aromatic compounds under microwave irradiation. Constructed by a Zr(IV) cluster and a linker 1,4-bis(2-[4-carboxyphenyl]ethynyl)benzene (H<sub>2</sub>CPEB), the MOF, possessing large pores and high chemical stability, was appropriate for the enhancement of Lewis acid activity under microwave irradiation. The reaction studies demonstrated that the material could give high yields for a few minutes and maintain its reactivity and structure over several cycles.

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## Introduction

Friedel–Crafts acylation is the most important method for functionalizing aromatic compounds, which are useful precursors in the pharmaceutical and agrochemical industries.<sup>1</sup> Unfortunately, the traditional Lewis acid-catalyzed Friedel–Crafts acylation has its environmental drawbacks, including requiring more than stoichiometric amounts, strictly anhydrous conditions, and produces corrosive acid wastes. Moreover, Lewis acids are not recovered and reused after aqueous work-up.<sup>2</sup> Therefore, research seeking efficient and green catalysts for the reaction has attracted much attention over the past two decades.<sup>2</sup> Several greener methods involving homogeneous (Brønsted acids<sup>3</sup> and metal triflates<sup>4</sup>) and heterogeneous (zeolites,<sup>5</sup> montmorillonite,<sup>6</sup> metal oxides,<sup>7</sup> sulfate zirconia<sup>8</sup>) catalysts have been developed extensively. However, in spite of their potential utility, the catalysts are normally used in stoichiometric amounts along with dangerous additives under harsh conditions, strongly acidic conditions, or involve tedious work-up and long reaction times. Consequently, the search to find efficient and green catalysts for Friedel–Crafts acylation is still in progress.

Metal–organic frameworks (MOFs), a new class of highly ordered and porous materials, possessing high surface areas, low framework densities, and large pore volumes are considered to be interesting materials for many applications, including gas storage<sup>9</sup> and separation,<sup>10</sup> heterogeneous cataly-

sis,<sup>11</sup> chemical sensing,<sup>12</sup> and biotechnology applications.<sup>13</sup> These materials are built from organic linkers and inorganic clusters, which are joined together through covalent bonds to form crystalline structures.<sup>14</sup> Among the reported MOFs, Zr(IV)-MOFs, with extremely good chemical and water stability in comparison to other MOFs due to the highly oxophilic character of Zr(IV), have recently attracted the attention of researchers for many applications in environmental treatment<sup>15</sup> and photocatalysis.<sup>16</sup> However, there are few studies of catalytic activity based on Lewis acids of the Zr-MOFs due to the saturated sites on the Zr(IV) clusters although their high stability as well as large pore sizes suggests these MOFs would be efficient for recycling and suitable for use under severe reaction conditions. Recently, some methods have been applied to overcome this low activity of Zr-MOFs, such as the use of functionalized linkers containing electron-withdrawing groups<sup>17</sup> or an azobenzene backbone,<sup>18</sup> a modulation approach in synthesis to generate open metal sites after thermal activation,<sup>19</sup> or by sulfonation on defect sites of the cluster to generate superacid material.<sup>20</sup> However, these have drawbacks in regards to the reduction of pore space,<sup>16e</sup> an increase in moisture sensitivity,<sup>19,20</sup> or long reaction times<sup>17–20</sup> leading to a limit in their use under practical conditions. Therefore, new methods that can take advantage of the Zr-MOFs' characteristics for Lewis acid catalysis effectively are still being studied and developed.

Microwave-assisted organic syntheses have attracted much attention due to them offering the shortest and most efficient routes to carry out many reactions. Moreover, zirconium(IV) compounds have been demonstrated to be good catalysts for many organic transformations of carbamates,<sup>21</sup> coumarins,<sup>22</sup> biodiesel,<sup>23</sup> and 5-HMF<sup>24</sup> under microwave irradiation. Microwave irradiation has been applied for Friedel–Crafts acylation with great success. It has been demonstrated that the short

Department of Organic Chemistry, Faculty of Chemistry, University of Science, Vietnam National University, Hochiminh City 721337, Vietnam.

E-mail: lenthach@yahoo.com

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reaction time associated with microwave irradiation restricts the decomposition of the reagents or products, increases the chemo- and regio-selectivity of isomers, and prevents the diacylation or dimethylation.<sup>25</sup>

In the present paper, we integrated the advantages of the microwave method and the characteristics of Zr-MOFs toward the benzoylation reaction. Although Friedel–Crafts acylation has been reported using Zn-MOF,<sup>26</sup> Cu-MOF,<sup>27</sup> and sulfonated UiO-66<sup>28</sup> as the catalysts, the application of microwave irradiation for the reaction has not been studied in literature due to their poor stability to moisture.<sup>26–28</sup> We reported the use of a long, slim dicarboxylate linker-based Zr(IV)-MOF, named VNU-1<sup>16d</sup> ( $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CPEB})_6$ ,  $\text{H}_2\text{CPEB}$ : 1,4-bis(2-[4-carboxyphenyl]ethynyl)benzene). The material possessed a large pore space, providing appropriate space for bulky substrates, and had extremely high chemical stability, leading to retaining its structure, together with high reactivity in a highly acidic environment due to HCl generation in the reaction. The results exhibited that the material was an efficient catalyst in the benzoylation of aromatic compounds with benzoyl chloride under microwave irradiation without a loss of reactivity for five cycles. It is noteworthy that the reactions catalyzed by VNU-1 gave a significantly higher yield than other Zr-MOFs and traditional zirconium Lewis acid catalysts.

## Experimental

### General methods

Powder X-ray diffraction (PXRD) patterns were recorded using a Bruker D8 Advance operated at 40 kV and 40 mA with a Ni filtered Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) source. Thermal gravimetric analyses (TGA) were performed on a TA Q500 Thermal Analysis System under an airflow. Nitrogen adsorption isotherms at 77 K were collected on a Quantachrome Autosorb-iQ2. Helium (99.999% purity) was used for estimation of the dead space. Ultra-high purity grade N<sub>2</sub> (99.999% purity) was used throughout the adsorption experiments. Microwave irradiation was performed on a CEM Discover BenchMate apparatus, which offered microwave synthesis with safe pressure regulation using a 10 mL pressurized glass tube with a Teflon-coated septum and vertically focused IR temperature sensor to control reaction temperature. Melting point was performed on Büchi B-545. GC-MS analyses were performed on an Agilent GC System 7890 equipped with a mass selective detector Agilent 5973N and a capillary DB-5MS column (30 m  $\times$  250  $\mu\text{m}$   $\times$  0.25  $\mu\text{m}$ ). The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Advance 500 and Varian Mercury 300 instruments using CDCl<sub>3</sub> as the solvent and solvent peaks or TMS as the internal standards. FT-IR spectra were analyzed from KBr pellets by a Bruker Vertex 70.

### Preparation of 1,4-bis(2-[4-carboxyphenyl]ethynyl)benzene (H<sub>2</sub>CPEB)

1,4-Bis(2-[4-carboxyphenyl]ethynyl)benzene was prepared following a literature procedure.<sup>1</sup> The Sonogashira coupling of

methyl 4-iodobenzoate (0.524 g, 2.00 mmol) and 1,4-diethynylbenzene (0.126 g, 1.00 mmol) was catalyzed by bis(triphenylphosphine)palladium dichloride (35.2 mg, 0.0500 mmol) and copper(I) iodide (2.0 mg, 10  $\mu\text{mol}$ ) in a 10 mL mixture of triethylamine and toluene ( $v/v = 1:1$ ) under a nitrogen atmosphere. The solution was stirred at room temperature for 24 h. After the reaction, the solid was filtered, thoroughly washed with hexane, a saturated solution of NH<sub>4</sub>Cl, and a saturated solution of NaCl, and dried under vacuum to afford a pink product. Then, the precursor (0.985 g, 0.250 mmol) was hydrolyzed by potassium hydroxide (0.420 g, 7.50 mmol) in a mixture of methanol (3 mL), THF (3 mL), and water (1.5 mL) at room temperature for 12 h. After 12 h, the solvents were evaporated under reduced pressure and the remaining solution was added dropwise to HCl (37% w/w in water) till the pH = 1. The final product was recovered as a yellow powder, which was thoroughly washed with water and dried at 80 °C under vacuum overnight. Yield: 0.0780 g (72%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, TMS):  $\delta = 7.66$  (s, 4H), 7.68 (d, 4H,  $J = 8.5$  Hz), 7.98 (d, 4H,  $J = 8.5$  Hz) ppm. <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>, TMS):  $\delta = 166.61, 131.88, 131.59, 130.79, 129.55, 126.22, 122.37, 91.34, 90.73$  ppm. HRMS (ESI) calculated for C<sub>24</sub>H<sub>14</sub>O<sub>4</sub>:  $m/z = 366.09$  (M – H<sup>−</sup>); Found  $m/z = 365.09$ .

### Synthesis of VNU-1

Microcrystalline VNU-1 was prepared using a slightly modified published procedure in a 100 mL capped bottle. ZrOCl<sub>2</sub>·8H<sub>2</sub>O (109 mg, 0.340 mmol) and H<sub>2</sub>CPEB (124 mg, 0.340 mmol) were dissolved in a 40 mL solvent mixture of DMF and acetic acid ( $v/v = 39:1$ ) by using ultrasound to give a clear solution. The solution was heated in an isothermal oven at 120 °C under static conditions for 24 h. A yellow precipitate was collected by filtration and washed three times with 100 mL of fresh DMF. As-synthesized VNU-1 was suspended in 100 mL DMF for three days, during which time the DMF was replaced three times per day. After that, the material was immersed in 100 mL chloroform for 1 day. The chloroform-exchanged sample was then activated at 120 °C for 24 h to remove guest molecules.

### Procedure for the VNU-1 catalyzed Friedel–Crafts acylation of aromatic compounds

A mixture of VNU-1 (21.3 mg, 7.50  $\mu\text{mol}$ ), arene (1.00 mmol), nitrobenzene (1 mL), and benzoyl chloride (140 mg, 1.00 mmol) was heated under microwave irradiation at 120 °C for 5 min in a CEM Discover apparatus. After being cooled, the catalyst was filtered from the reaction mixture. The filtrate was diluted with ethyl acetate (50 mL), washed with H<sub>2</sub>O (3  $\times$  20 mL), aqueous NaHCO<sub>3</sub> (2  $\times$  20 mL), and brine (20 mL), and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed on a rotary evaporator. The crude product was purified by flash chromatography (*n*-hexane, then 10% ethyl acetate in *n*-hexane) to give the corresponding product. The purity and identity of the products were confirmed by GC-MS spectra, which were compared with the spectra in the NIST library, and by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

## Results and discussion

VNU-1 was synthesized from zirconium(IV) chloride and the slim, linear linker, H<sub>2</sub>CPEB, by the solvothermal method. The structure of the synthesized sample was confirmed by PXRD measurements, in which the experimental pattern corresponded to the pattern simulated from the reported structure (Fig. S3†).<sup>16d</sup> Similar to the structure of the first MOFs based on Zr(IV) clusters, UiO-66, and UiO-67, VNU-1 is composed of 12-coordinated cuboctahedral Zr<sub>6</sub> clusters, Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(CO<sub>2</sub>)<sub>12</sub>, which are connected together by twelve carboxylate groups of the CPEB linker (Fig. 1).<sup>16d</sup> However, due to the length of the linker, the VNU-1 structure is an interpenetrated framework containing one large tetrahedral pore (25 Å) and one smaller octahedral pore (9 Å).<sup>16d,29</sup> The tetrahedral pore is significantly higher in comparison to the pores of UiO-66 and UiO-67 (8.5 and 15 Å, respectively).<sup>30</sup> Therefore, the large pore can be an efficient space for large substrates to go inside the pore and react in the highly chemical- and water-stable framework of VNU-1.

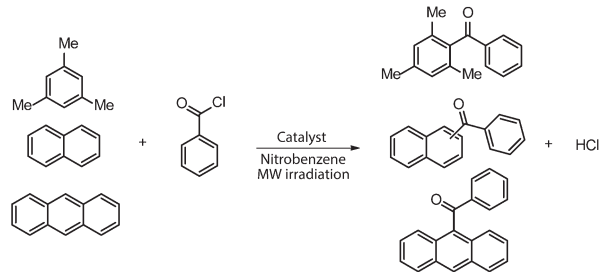
Friedel–Crafts acylation is industrially applied to the synthesis of aromatic ketones. Environmental pollution is a major problem for most traditional Lewis acids, and new catalysts are under ongoing research. The highly active, recyclable, and leaching catalyst is negligible. The reports of Friedel–Crafts alkylation catalyzed by metal–organic framework under mild conditions led us to investigate Friedel–Crafts acylation using a zirconium MOF.<sup>31</sup>

The benzoylation of mesitylene with benzoyl chloride was selected as the model reaction, and VNU-1 was tested as the catalyst under microwave irradiation. In this method, 0.75% mol catalytic loading of VNU-1 was used for the Friedel–Crafts benzoylation of mesitylene in nitrobenzene as the solvent. The reaction did not take place in the absence of catalyst. After screening the reaction conditions, we found the optimal

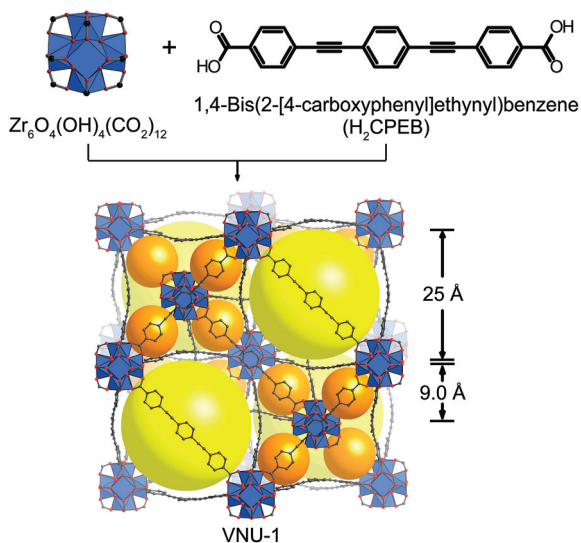
condition of this reaction and the best result was obtained in a 94% yield at 120 °C for 5 min (Table S1,† entry 3). An equally good result could be obtained at 120 °C in 10 min (Table S1,† entry 4). All the attempts increasing the reaction temperature led to diminished yields (Table S1, entries 7 and 8†).

The scope with respect to the catalyst is presented in Table S1.† Both the Zr-MOFs and zirconium salts were also tested for catalytic activity in the benzoylation of mesitylene, naphthalene, and anthracene under microwave irradiation and conventional heating. Although microwave irradiation has been extensively studied in a wide range of organic transformations, the use of MOF as a catalyst for Friedel–Crafts acylation under monomode microwave irradiation has not been reported in the previous literature. In this method, microwave irradiation demonstrated that it was a powerful tool to use in combination with zirconium-based MOF. Microwave-assisted Friedel–Crafts benzoylation catalyzed by MOF results in high yields with short reaction times. In comparison to microwave irradiation, the strongly decreased yields in the Friedel–Crafts benzoylation of mesitylene and naphthalene were obtained under conventional heating, despite increasing the reaction times (Table 1, entries 1–3 and 7–9). However, equally good

**Table 1** Friedel–Crafts benzoylation in the presence of zirconium catalysts



Entry	Substrate	Catalyst	Yield <sup>a</sup> (%)	
			MW <sup>b</sup>	Δ <sup>c</sup>
1	Mesitylene	VNU-1	94	58
2	Mesitylene	UiO-66	89	62
3	Mesitylene	UiO-67	90	70
4	Mesitylene	ZrCl <sub>4</sub>	12	35
5	Mesitylene	ZrOCl <sub>2</sub> ·8H <sub>2</sub> O	9	30
6	Mesitylene	Blank	0	0
7	Naphthalene	VNU-1	68	5
8	Naphthalene	UiO-66	37	3
9	Naphthalene	UiO-67	50	0
10	Naphthalene	ZrCl <sub>4</sub>	0	0
11	Naphthalene	ZrOCl <sub>2</sub> ·8H <sub>2</sub> O	0	0
12	Naphthalene	Blank	0	0
13	Anthracene	VNU-1	86	85
14	Anthracene	UiO-66	65	66
15	Anthracene	UiO-67	70	72
16	Anthracene	ZrCl <sub>4</sub>	28	14
17	Anthracene	ZrOCl <sub>2</sub> ·8H <sub>2</sub> O	18	11
18	Anthracene	Blank	0	0



**Fig. 1** VNU-1 structure constructed from CPEB<sup>2-</sup> and cuboctahedron Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(CO<sub>2</sub>)<sub>12</sub>. Atom color: Zr, blue polyhedra; O, red; C, black; H atoms are omitted for clarity. The yellow and orange colored balls represent the free pores.

<sup>a</sup> Yields are isolated yields. <sup>b</sup> Microwave irradiation (80 W) was carried out at 120 °C for 5 min (exception for naphthalene in 15 min). <sup>c</sup> Conventional heating was carried out at 120 °C for 60 min.

results could be obtained in the Friedel–Crafts benzylation of anthracene for 60 min under conventional heating (Table 1, entries 13–15). In general, microwave irradiation afforded the higher yields within short reaction times in the reaction.

We found that the activity of the Zr-MOFs is significantly accelerated when using microwave irradiation. For example, only 5 min was required for the benzylation of anthracene to afford the ketone product in 86% (VNU-1), 65% (UiO-66), and 70% (UiO-67) yields at 120 °C under microwave irradiation, whereas 60 min was needed to obtain the same yield under conventional heating at the same temperature (Table 1, entries 13–15). Moreover, it is noted that the catalytic activity of VNU-1 was higher in comparison to UiO-66 and UiO-67 in the benzoylations of naphthalene and anthracene (Table 1, entries 1–3, 7–9 and 13–15). We assume that the large pore size of 25 Å of VNU-1 provides efficient space for the molecules of naphthalene (size: 6.74 × 4.98 Å<sup>2</sup>) and anthracene (size: 9.09 × 4.98 Å<sup>2</sup>) to react.

Zirconium salts, such as ZrCl<sub>4</sub> and ZrOCl<sub>2</sub>·8H<sub>2</sub>O, were also investigated for their catalytic activity. These traditional Lewis acids are not very reactive either with microwave irradiation or conventional heating. Mesitylene can be benzoylated in 12% and 9% yields under microwave irradiation. A slightly better yield was obtained under conventional heating for 60 min at 120 °C (Table 1, entries 4 and 5). In addition, the amount of zirconium salts was unable to be recycled after the aqueous work-up. Naphthalene was unreactive in this method (Table 1, entries 10 and 11). Anthracene was found to have low reactivity, and yields of 11% to 28% were obtained using zirconium salts under both microwave irradiation and conventional heating.

In order to highlight the role of Zr(IV)-based Lewis acid sites in the benzoylations, control experiments were performed without any catalyst present. From the results, it was clear that the benzoylations were not able to be effected by microwave irradiation alone (Table 1, entries 6, 12 and 18).

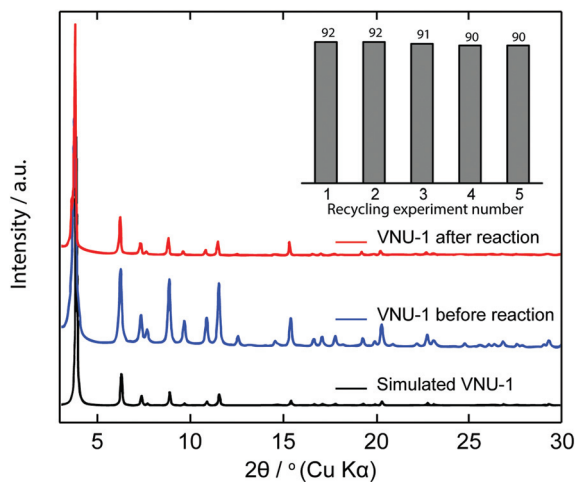
The scope with respect to the substrates is presented in Table 2. Anisole was benzoylated in a 95% yield, with only 1% of the *ortho* benzoylated product (Table 2, entry 1). Veratrole could be benzoylated in an 85% yield (Table 2, entry 2). 1,3-Dimethoxybenzene was also benzoylated in good yield (Table 2, entry 3). However, 1,4-dimethoxybenzene, in which the aromatic ring employs a counteracting orientation of two methoxy substituents, was also less reactive (Table 2, entry 4). Trimethoxybenzene was benzoylated in a 78% yield, without other benzoylated isomers (Table 2, entry 5). Phenetole was benzoylated in an excellent yield (Table 2, entry 6). However, *p*-fluoroanisole was benzoylated in only a 25% yield due to the stronger electron-withdrawing inductive effect of fluorine making the *o*-position to the methoxy substituent of the ring more electron-poor (Table 2, entry 7). Thioanisole was also reactive under these conditions without giving an *o*-benzoylated product. Interestingly, weak electron-donating alkylbenzenes were benzoylated in good to excellent yields (Table 2, entries 9–11). The rings without electron-donating substituent were also investigated. Naphthalene was benzoylated in a moderate yield, with  $\alpha/\beta = 52/48$  selectivity of the isomers.

**Table 2** Friedel–Crafts benzylation of aromatic compounds using VNU-1 under microwave irradiation at 80 W

Entry	Substrate <sup>a</sup>	Condition	Product	Yield <sup>b</sup> (%)
1		120 °C, 5 min		95
2		120 °C, 5 min		85
3		140 °C, 5 min		86
4		140 °C, 10 min		48
5		120 °C, 10 min		78
6		120 °C, 5 min		96
7		120 °C, 20 min		25 <sup>c</sup>
8		120 °C, 5 min		87
9		120 °C, 5 min		82
10		120 °C, 5 min		92
11		120 °C, 5 min		94
12		120 °C, 15 min		68 <sup>d</sup>
13		140 °C, 30 min		47
14		120 °C, 5 min		86

<sup>a</sup> Low boiling substrates, such as benzene, toluene and substrates containing an electron-poor substituent, are not suitable under these conditions. <sup>b</sup> Yields are isolated yields, the other isomers are usually less than 5% yield, unless otherwise noted. <sup>c</sup> Yield is calculated by GC-MS. <sup>d</sup> Yields are isolated yields of a mixture of isomers ( $\alpha/\beta = 52/48$ ).

Fluorene could be benzoylated in an acceptable yield, with major regioselectivity in position 2, although the reaction was carried out in a longer reaction time (Table 2, entry 13). Inter-



**Fig. 2** PXRD analysis of VNU-1 before (blue) and after (red) the benzoylation reaction of mesitylene in comparison to the simulated pattern. Inset: The recycling experiments of the reaction over five cycles (the numbers on the top represent the yield of reaction).

estingly, anthracene was benzoylated in good yield under this method, although the benzoylation of anthracene was not convenient under microwave irradiation.<sup>25c</sup>

The recycling of VNU-1 was confirmed for the Friedel-Crafts benzoylation of mesitylene under microwave irradiation. Due to its high stability in these reaction media, VNU-1 was easily recovered in a quantitative yield. After washing many times with ethyl acetate and methanol, the material was dried under vacuum at 120 °C for 24 h and reused. The benzoylation of mesitylene was run for five consecutive cycles at 120 °C for 5 min under microwave irradiation. The VNU-1 structure was retained and the yield of product decreased slightly after each run but with the same selectivity (Fig. 2). The high activity and easy recycling of VNU-1 are promising for its application on a large scale.

## Conclusion

Microwave irradiation was used as an efficient method to enhance the Lewis acid catalytic activity of highly porous VNU-1 in the heterogeneous benzoylation of aromatic compounds. The method allows synthesizing aromatic ketones in high yields within a few minutes. Furthermore, the easy handling and recycling of VNU-1 are promising for its application on a large scale. VNU-1 is a significant replacement for the traditional catalysts currently used on an industrial scale for Friedel-Crafts acylation.

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