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Efficient microwave-assisted direct *C*-benzoylation of phenols and naphthols with benzoic acid catalyzed by bismuth triflate under solvent-free or ionic liquid conditions.

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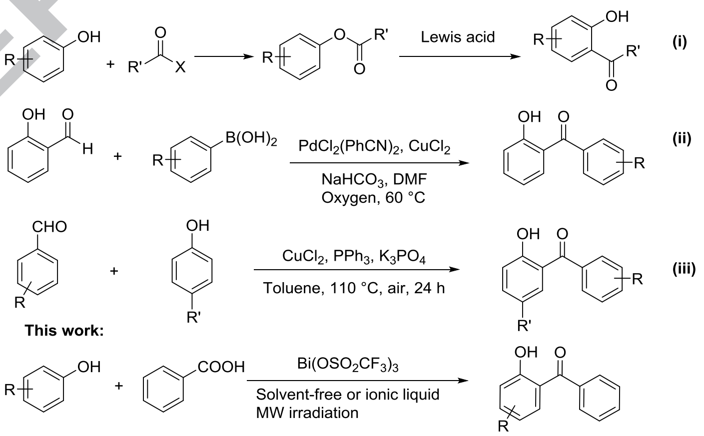
Abstract: An efficient and simple route for the synthesis of *ortho*-hydroxyaryl ketones has been developed. The microwave-assisted direct *C*-benzoylation of phenols and naphthols in the presence of metal triflates afforded the corresponding *ortho*-hydroxyaryl ketones in moderate to excellent yields. Bismuth triflate showed the best catalytic performance compared to other metal triflates. The protocol has advantages including short reaction times, high chemoselectivity towards *C*-acylation, and simple work-up. Additionally, bismuth triflate can be easily recovered and reused several times without significant loss of catalytic performance.

Keywords: Friedel–Crafts acylation, *ortho*-hydroxyaryl ketones, green chemistry, metal triflates, microwave chemistry.

Ortho-hydroxyaryl ketones are important precursors in the production of 4-hydroxycoumarin derivatives which have received significant interest due to their pervasiveness in pharmaceutical products, dyes, and pesticides.[1-12] Until now, only a few examples for the synthesis of these compounds have been developed. Three major synthetic methods have been described for the synthesis of *ortho*-hydroxyaryl ketones (Scheme 1) including: (i) the Fries rearrangement of phenolic esters,[13-17] (ii) the arylation of 2-hydroxybenzaldehyde with arylboronic acids or aryl iodides,[18-20] and (iii) the acylation of phenols with aryl aldehydes.[21,22] However, the most frequently used Fries rearrangement requires more than a stoichiometric amount of a Lewis acid (e.g. $AlCl_3$, BF_3, $TiCl_4$), strict exclusion of moisture, and long reaction times. Existing pathways also often involve uncommon acylating reagents and/or harsh reaction conditions.[2,7,12,18,23] Therefore, an efficient and operationally simple *C*-acylation of phenols is highly desired.



Scheme 1. Synthesis of *ortho*-hydroxyaryl ketones.

In past decade, metal triflates have been reported as green and efficient catalysts for the *O*-acylation of phenols,[24-27] attracting attention from the groups of Khosropour,[28] Taghavi,[29] and others.[26,30] While metal triflates are commonly known as efficient catalysts to promote the *O*-acylation of phenols and naphthols, their application in the *C*-acylation of phenols and naphthols has been only studied by the groups of Kobayashi and Jin. However, their research was limited by a narrow substrate scope.[31,32] Additionally, the requirement for an expensive catalyst $Hf(OTf)_4$, large amounts of volatile organic solvents, and prolonged reaction times were drawbacks.

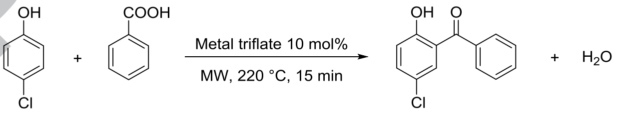
As part of our interest in the application of metal triflates for microwave-assisted Friedel–Crafts acylation reactions, herein we report the bismuth triflate catalysed, direct *C*-acylation of phenols and naphthols using benzoic acid as an acylating agent under solvent-free microwave irradiation conditions. Microwave-assisted organic synthesis has been demonstrated as a green activation method, which promotes much cleaner, faster and more selective reactions than conventional heating.[33,23,34-38] Interestingly, we found that the acylation of phenols and naphthols under microwave irradiation afforded *ortho*-hydroxyaryl ketones in good to excellent yields. Previously, the *ortho*-directed *C*-acylation of electron-rich phenols and naphthols with carboxylic acids using hafnium triflate (20 mol%) reported by Kobayashi and co-workers gave *ortho*-hydroxyaryl ketones in 50-80% yield.[31] However, this method required an expensive catalyst, a mixture of volatile organic solvents (toluene–nitromethane) and extended reaction times.

The emphasis of our research is the use of microwave heating in the bismuth triflate catalyzed acylation of electron-rich as well as electron-poor phenols and naphthols under solvent-free condition or in ionic liquids. In comparison with previous work,[31] the substrate scope has been extensively studied and bismuth triflate is used in lower amounts (10 mol%) without any co-catalysts or volatile organic solvents. Under microwave irradiation, chemoselective *C*-benzoylation of phenols and naphthols in the presence of bismuth triflate formed the corresponding *ortho*-hydroxyaryl ketones in high yields within a few minutes.

The acylation of electron-poor phenols did not generate *ortho*-acylation products in the previous literature because electron-withdrawing substituents increase the acidity of the phenols. As a result, undesired *O*-acylation predominated, furnishing *O*-acylation products which required an additional step to give *ortho*-hydroxyaryl ketones.[6,32] In the present work, the challenging benzoylation of 4-chlorophenol was selected as the model reaction to study the optimization of reaction conditions, including the effect of metal triflates, reaction temperature, and reaction time.

Initially, fourteen metal triflates were tested for their catalytic activity (Table 1). No reaction between 4-chlorophenol and benzoic acid was observed in the absence of catalyst. Most metal triflates afforded the direct *ortho*-benzoylation product in moderate yield under microwave irradiation. Among these catalysts, bismuth triflate was considered the best catalyst and gave the *C*-acylation product in 54% isolated yield (Entry 14). It has been reported that the direct *ortho*-acylation of 4-chlorophenol using $ZnCl_2/Al_2O_3$ as a catalyst produced the corresponding product in low yield[6] and did not proceed in the presence of $Yb(OTf)_3$.[32] In contrast to the microwave-enhanced Friedel-Crafts benzoylation, conventional heating was unsuccessful for the direct *ortho*-benzoylation of 4-chlorophenol (Entry 15).

Table 1. Effect of different metal triflates on the Friedel–Crafts benzoylation of 4-chlorophenol using benzoic acid under solvent-free microwave irradiation.[a]

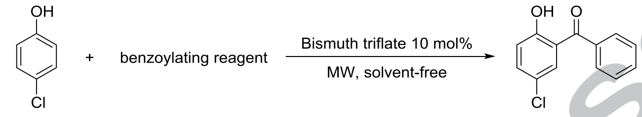


Entry	Metal triflate	Yield[b] (%)
1	$La(OTf)_3$	30
2	$Ce(OTf)_3$	44
3	$Pr(OTf)_3$	32
4	$Nd(OTf)_3$	30
5	$Gd(OTf)_3$	44
6	$Tb(OTf)_3$	43
7	$Dy(OTf)_3$	35
8	$Ho(OTf)_3$	39
9	$Er(OTf)_3$	42
10	$Tm(OTf)_3$	35
11	$Yb(OTf)_3$	45
12	$Cu(OTf)_2$	39
13	$Y(OTf)_3$	40
14	$Bi(OTf)_3$	54
15	$Bi(OTf)_3$	0[c]

[a] Reagents and conditions: 4-chlorophenol (1 mmol), benzoic acid (1 mmol), metal triflate (0.1 mmol). [b] Isolated yield. [c] Conventional heating.

Next, experiments where the temperature and reaction time were in turn varied from 120 °C to 240 °C and 5 min to 30 min, respectively, were conducted to study the effect of these parameters on the reaction. From the results presented in Table 2, it was shown that increasing the temperature led to a steady improvement in the *C*-benzoylation yield, and the best result was obtained at 220 °C for 15 min (Entry 6). Further prolonging the reaction time to 20 min and 30 min resulted in negligible increases to the yield (Entries 10 and 11). In order to establish the reaction scope, different benzoylating reagents including benzoyl chloride and benzoic anhydride were used, where the best yield for the direct *C*-benzoylation of 4-chlorophenol was achieved with benzoic acid. The fact that water is generated as the sole by-product in the reactions using benzoic acid makes this protocol more favorable from the viewpoint of green chemistry than reactions using benzoyl chloride where HCl is released.

Table 2. Effect of reaction conditions on the Friedel–Crafts benzoylation of 4-chlorophenol under solvent-free microwave irradiation.[a]

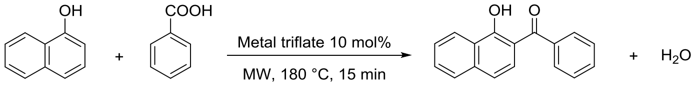


Entry	Temp. (°C)	Time (min)	Benzoylating reagent	Yield[b] (%)
1	120	15	C_6H_5COOH	5
2	140	15	C_6H_5COOH	12
3	160	15	C_6H_5COOH	25
4	180	15	C_6H_5COOH	30
5	200	15	C_6H_5COOH	43
6	220	15	C_6H_5COOH	54
7	240	15	C_6H_5COOH	55
8	220	5	C_6H_5COOH	39
9	220	10	C_6H_5COOH	40
10	220	20	C_6H_5COOH	57
11	220	30	C_6H_5COOH	58
12	220	15	C_6H_5COCl	39
13	220	15	$(C_6H_5CO)_2O$	37

[a]Reagents and conditions: 4-chlorophenol (1 mmol), benzoylating reagent (1 mmol), bismuth triflate (0.1 mmol). [b]Isolated yield.

The direct *C*-benzoylation of 1-naphthol with benzoic acid was also performed under solvent-free microwave irradiation in the presence of various metal triflates (Table 3). In the absence of metal triflate, the reaction did not proceed. The highest isolated yield of 84% was again observed in the presence of bismuth triflate (Entry 14).

Table 3. Effect of different metal triflates on the Friedel–Crafts benzoylation of 1-naphthol using benzoic acid under microwave irradiation.[a]



Entry	Metal triflate	Yield[b] (%)
1	$La(OTf)_3$	57
2	$Ce(OTf)_3$	68
3	$Pr(OTf)_3$	59
4	$Nd(OTf)_3$	64
5	$Gd(OTf)_3$	54
6	$Tb(OTf)_3$	66
7	$Dy(OTf)_3$	64
8	$Ho(OTf)_3$	55
9	$Er(OTf)_3$	70
10	$Tm(OTf)_3$	60
11	$Yb(OTf)_3$	58
12	$Cu(OTf)_2$	67

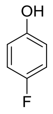
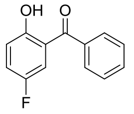
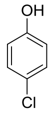
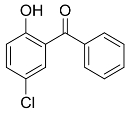
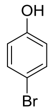
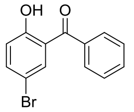
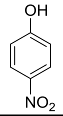
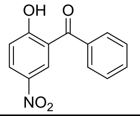
13	$Y(OTf)_3$	62
14	$Bi(OTf)_3$	84

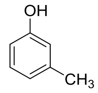
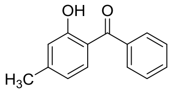
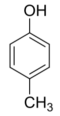
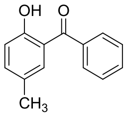
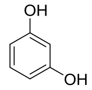
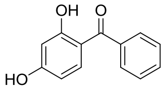
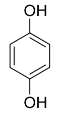
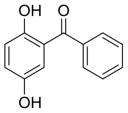
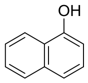
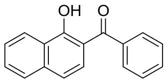
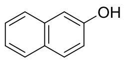
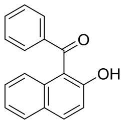
[a]Reagents and conditions: 1-naphthol (1 mmol), benzoic acid (1 mmol), metal triflate (0.1 mmol). [b]Isolated yield.

To the best of our knowledge, this represents the first time that bismuth triflate has been used to catalyze the direct Friedel–Crafts *C*-benzoylation of phenols and naphthols under solvent-free microwave irradiation conditions. However, the fact that there were examples where bismuth triflate proved to be a suitable catalyst for the Fries rearrangement of phenyl esters in toluene under conventional heating raised a concern about our postulate that the overall conversion is merely a direct Friedel-Crafts *C*-acylation, rather than a consecutive two-step process of *O*-acylation and subsequent Fries rearrangement.[15,39,40] Therefore, the benzoyl ester of 4-chlorophenol was prepared and treated with bismuth triflate to examine the Fries rearrangement under the optimized conditions (220 °C, 15 min). No reaction took place in the presence of bismuth triflate using the current method, clarifying that the phenolic substrates can be directly converted to *ortho*-hydroxyaryl ketones *via* Friedel-Crafts *C*-acylation.

The treatment of various phenols and naphthols with benzoic acid under the optimized condition provided the corresponding products in moderate to excellent yields (Table 4). As expected, the electronic effects of substituents on the reactivity of phenolic substrates were straightforward. Substrates bearing inductive electron-withdrawing halogen groups only gave the corresponding *C*-benzoylation products in moderate yields (Entries 1-3). For instance, the presence of a typical strongly electronegative fluorine substituent significantly reduced the reactivity of 4-fluorophenol, furnishing 5-fluoro-2-hydroxybenzophenone in only 39% yield, even upon prolonged microwave irradiation. In a more dramatic manner, 4-nitrophenol was completely unreactive under all conditions (Entries 4-6). In contrast, substrates containing electron-donating substituents such as methyl and methoxy can easily undergo benzoylation under milder conditions (lower temperatures within shorter times) to afford the desired products in high isolated yields (up to 86%). However, the counteracting orientation of two electron-donating groups in 4-methylphenol and hydroquinone were responsible for slightly decreased yields of the *C*-benzoylation products (Entries 8 and 10). Interestingly, 1-naphthol could be *C*-benzoylated in an excellent yield of 89% (entry 11) which was significant better than the 70% yield of the analogous 2-acetyl-1-naphthol obtained from 1-naphthol and acetic acid catalyzed by $ZnCl_2$ under microwave irradiation.[4] Furthermore, in comparison to other work where the direct *C*-acylation of 1-naphthol was performed with acetic acid and propionic acid in the presence of $Hf(OTf)_4$ in $LiClO_4$-$MeNO_2$ for 6 h under conventional heating (80-81%),[31] our method shows considerable advantages of short reaction times, use of a cheaper catalyst, and avoiding volatile solvents. 2-Naphthol afforded only 35% yield of the direct *ortho*-benzoylation product due to the steric hindrance with the hydrogen in the other ring. It has been previously reported that the direct *ortho*-acetylation of 2-naphthol afforded 1-acetyl-2-hydroxynaphthalene in low yield.[10]

Table 4. Benzoylation of phenols and naphthols with benzoic acid using bismuth triflate under solvent-free microwave irradiation.[a]

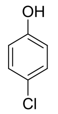
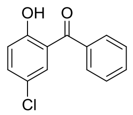
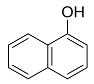
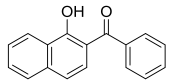
Entry	Substrate	Product	Temp. (°C)	Time (min)	Yield[b] (%)
1			220	30	39
2			220	15	54
3			220	30	52
4			160	30	0
5			180	30	0
6			220	30	0

7			180	15	86
8			160	15	72
9			180	30	85
10			180	15	77
11			180	20	89
12			180	30	35

[a]Reagents and conditions: substrate (1 mmol), benzoic acid (1 mmol), bismuth triflate (0.1 mmol). [b]Isolated yield.

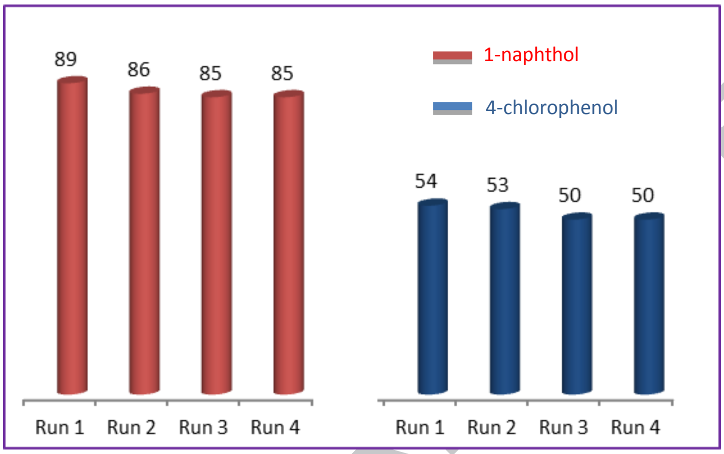
Being persuaded that better performance of metal triflates could be achieved when dissolved in ionic liquids,[41-45] we also studied the direct *C*-benzoylation of 4-chlorophenol and 1-naphthol using bismuth triflate in various ionic liquid media under microwave irradiation (Table 5). The best results were obtained using bismuth triflate dissolved in [BMI]OTf (Entries 5 and 11), furnishing the corresponding products in higher yields and lower temperatures compared to under solvent-free microwave irradiation. To the best of our knowledge this is the first time a metal triflate in ionic liquid has been applied to the direct *C*-benzoylation of phenols and naphthols.

Table 5. Benzoylation of 4-chlorophenol and 1-naphthol with benzoic acid using bismuth triflate in various ionic liquids under microwave irradiation.[a]

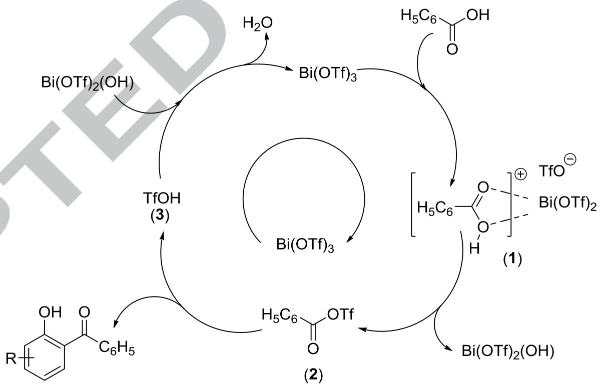
Entry	Substrate	Product	Ionic liquid[b]	Temp. (°C)	Yield[c] (%)
1			[EMI]Cl	220	30
2			[BMI]Br	220	34
3			[BMI]BF_4	180	53
4			[BMI]PF_6	180	67
5			[BMI]OTf	180	72
6			[BPy]OTf	180	68
7			[EMI]Cl	180	78
8			[BMI]Br	180	80
9			[BMI]BF_4	160	88
10			[BMI]PF_6	160	90
11			[BMI]OTf	160	93
12			[BPy]OTf	160	89

[a]Reagents and conditions: substrate (1 mmol), benzoic acid (1 mmol), bismuth triflate (0.1 mmol), ionic liquid (0.1 g). [b][EMI]: 1-ethyl-3-methylimidazolium, [BMI]: 1-butyl-3-methylimidazolium, [BPy]: *N*-butylpyridinium. [c]Isolated yield.

The great concern for green catalysis is the ease of separation and reusability without significant loss of catalytic activity. Thus, bismuth triflate was also investigated for its recoverability and reusability in the benzoylation of 4-chlorophenol and 1-naphthol using bismuth triflate (10 mol%) under the optimal solvent-free microwave irradiation conditions (Scheme 2). After reaction completion, bismuth triflate was recovered by the removal of water under reduced pressure.[44] The resulted bismuth triflate was further dried under vacuum at 80 °C overnight; then reused in four consecutive reactions without significant loss of catalytic activity.



Scheme 2. Recycling of bismuth triflate over four consecutive reactions in the benzoylation of 1-naphthol and 4-chlorophenol under optimal conditions.



Scheme 3. Proposed mechanism.

In the classical Friedel-Crafts reaction, an excess of Lewis acid is required to react with the acylating reagent to ensure quantitative generation of the corresponding reactive electrophile ($R\text{-}CO^+$), which is the effective ionic intermediate in the Friedel-Crafts acylation. Metal triflates are well known as more efficient and greener catalysts which can be used in only catalytic amounts with the same reactivity. To verify the necessity of the bismuth species, we conducted a control experiment where TfOH instead of $Bi(OTf)_3$ was used as the catalyst for the *C*-benzoylation of 4-chlorophenol. The desired product could still be obtained, but in a poor yield of 21%. From the outcome of the control reaction as well as work reported in the literature,[46-49] we were able to propose a plausible mechanism for the $Bi(OTf)_3$-mediated Friedel-Crafts *C*-acylation of phenolic subtrates as depicted in Scheme 3. In this mechanism, the carboxylic acid is converted *in situ* to the more reactive acylating reagent benzoyl triflate (**2**) *via* the intermediate bismuth complex (**1**). Subsequent benzoylation with the phenolic compound affords the *ortho*-hydroxyaryl ketones and triflic acid. Bismuth triflate can be regenerated to start a new catalytic cycle.

In conclusion, we have developed an efficient bismuth triflate-catalyzed direct *C*-benzoylation of phenols and naphthols. Phenols containing both electron-poor and electron-rich substituents were efficiently functionalized. Bismuth triflate possesses several advantages such as low toxicity, easy handling, low cost (25 times cheaper than hafnium triflate), and easy recycling which are expected to contribute to the development of the direct *ortho*-benzoylation of phenols and naphthols with benzoic acid. Additionally, $Bi(OTf)_3$ in [BMI]OTf showed slightly higher catalytic activity than under solvent-free conditions. The procedure is simple and potentially applicable to industrial scale synthesis.

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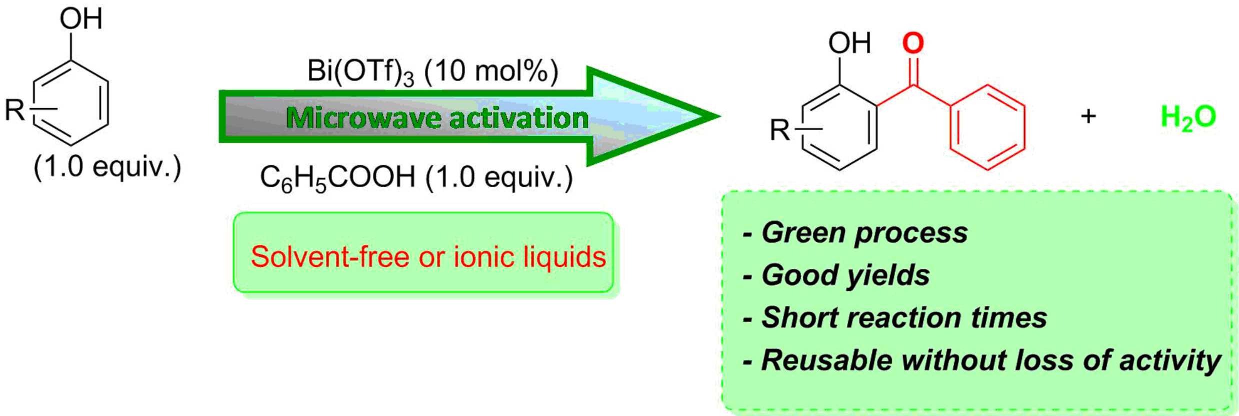

- ***Green process***
- ***Good yields***
- ***Short reaction times***
- ***Reusable without loss of activity***

- Microwave-assisted, direct *ortho*-benzoylation of phenols and naphthols catalyzed by bismuth triflate.
- Simple, straightforward and efficient method.
- O*rtho*-hydroxyaryl ketones were obtained in high yields in short reaction times.
- Bismuth triflate can be easily recovered and reused without loss of catalytic activity.