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Suzuki–Miyaura coupling of aryl fluorosulfates in water: a modified approach for the synthesis of novel coumarin derivatives under mild conditions

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ABSTRACT

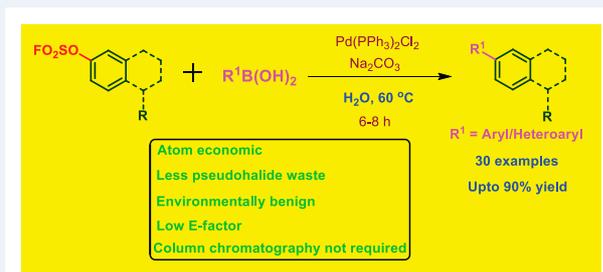
We herein report a modified, eco-friendly and atom-economical approach for the synthesis of a series of novel coumarin analogues via Suzuki–Miyaura cross-coupling methodology under mild conditions. The utilization of coumarin fluorosulfate as an atom-economical pseudohalide based electrophilic coupling partner was the key for success of our modified methodology. In addition, the use of water as a solvent, exceptionally milder reaction conditions and traditional catalytic systems further demonstrates the synthetic utility of the developed protocol. A comparative study of different pseudohalide leaving groups has been carried out in the later stage to understand the efficiency of aryl fluorosulfate. From this study, the increased hydrophilic nature of the fluorosulfate electrophilic coupling partner when compared to the other electrophiles has been realized. This allowed the increased solubility of the fluorosulfate electrophile in water under milder temperature conditions thereby furnishing the desired products in good to excellent yields.

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Coumarin; Suzuki–Miyaura coupling; pseudohalide; aryl fluorosulfate



1. Introduction

The current area of organic research is majorly focused on developing greener synthetic methodologies that allows waste minimization [1]. The need for developing greener protocols with low E-factors is highly important in organic synthesis owing to the diverse range of waste materials generated after complex organic reactions [2]. To address these issues, the adoption of greener techniques like use of catalytic reaction conditions, utilization of water as solvent media for performing organic reactions, development of energy efficient processes and employing atom-economical electrophiles are of immense potential [3]. The raising environmental

concerns nowadays can be minimized to some extent by implementing these methods.

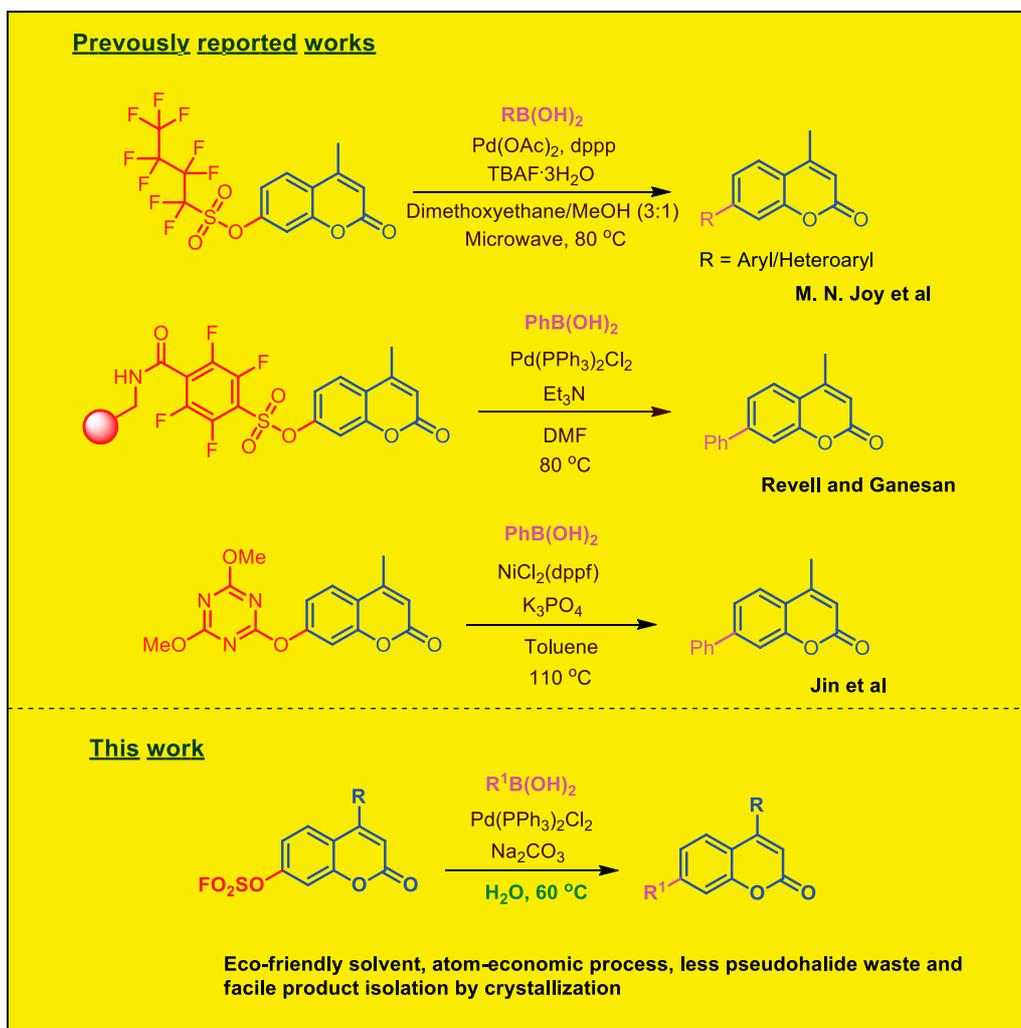
Coumarins are important heterocyclic compounds that occur in green plants and many natural products in free or combined state [4]. They exhibit a broad spectrum of biological and photo physical activities. The various applications of coumarins and their derivatives in medicinal chemistry and other related fields have encouraged the synthetic chemists around the globe to produce them in the laboratory. The pharmacological importance of coumarin derivatives have been underlined by their various therapeutic applications like photo chemotherapy, anti-tumor therapy

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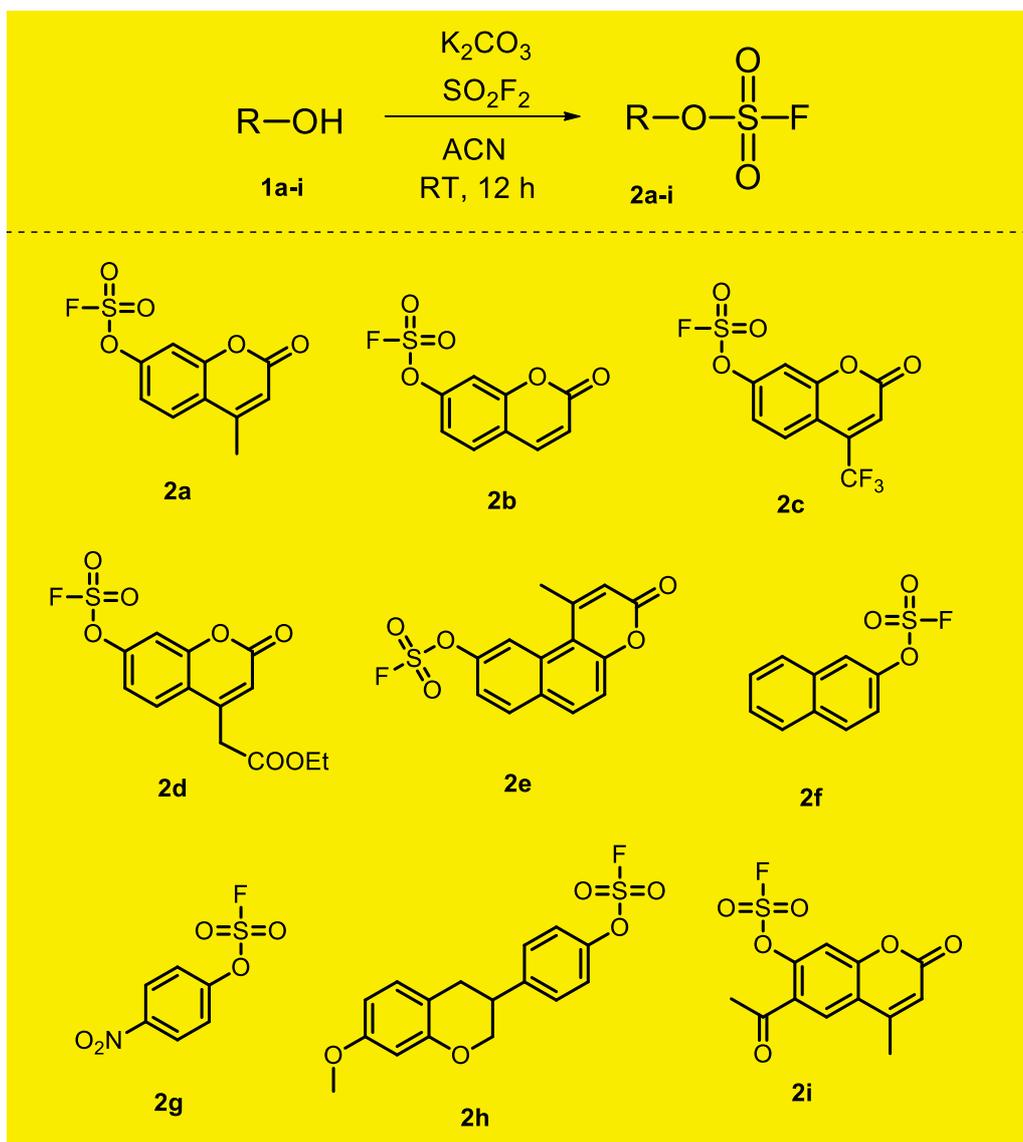
Scheme 1. Previously reported works on synthesis of 4-methyl-7-aryl/phenyl-coumarins and present work.

and anti-HIV therapy [5]. Moreover, the coumarin analogues are also reported to possess anti-bacterial, anti-inflammatory and anti-coagulating activities. The presence of coumarin motif in many marketed drugs also emphasizes its importance in medicinal chemistry.

The transition metal catalyzed cross-coupling reactions have served as an excellent tool in the last three decades for synthesizing novel compounds with various applications [6–9]. Among the diverse transition metal catalyzed cross-coupling reactions discovered hitherto, the palladium-catalyzed cross-coupling reactions of aryl halides or pseudohalides with different boronic acids initially reported by Suzuki et al (commonly called as Suzuki–Miyaura coupling) is an important reaction used by synthetic chemists throughout the world for new C–C bond formation [10]. Over the past decades, the application of Suzuki cross-coupling has gained tremendous significance in various fields of research. The development of different palladium catalysts and electron-rich ligands further advanced the scope of this methodology in academic and industrial research [11]. However, considerable

efforts are still made around the globe to make this reaction more facile and eco-friendly by decreasing the halide/pseudohalide waste and avoiding organic solvents containing hydrocarbons. In addition to this, the tedious purification processes for isolating the product also emphasize the need for developing more efficient, environmentally benign and facile approach for Suzuki–Miyaura coupling reactions. Recently, the utilization of supported palladium catalysts, environmentally benign solvents and non-conventional energy sources for these reactions have been reported by various research groups for circumventing these issues to some extent [12].

Among the various coumarin derivatives synthesized so far, 4-methyl-7-substituted coumarins have been found to demonstrate profound applications in fluorescent studies and medicinal chemistry [13]. In 2004, Revell and Ganesan reported the synthesis of polystyrene-tetrafluorosulfonate linker of 4-methyl-7-hydroxy coumarin and utilized it for Suzuki–Miyaura coupling with phenyl boronic acid for synthesizing 4-methyl-7-phenyl coumarin in DMF as the solvent



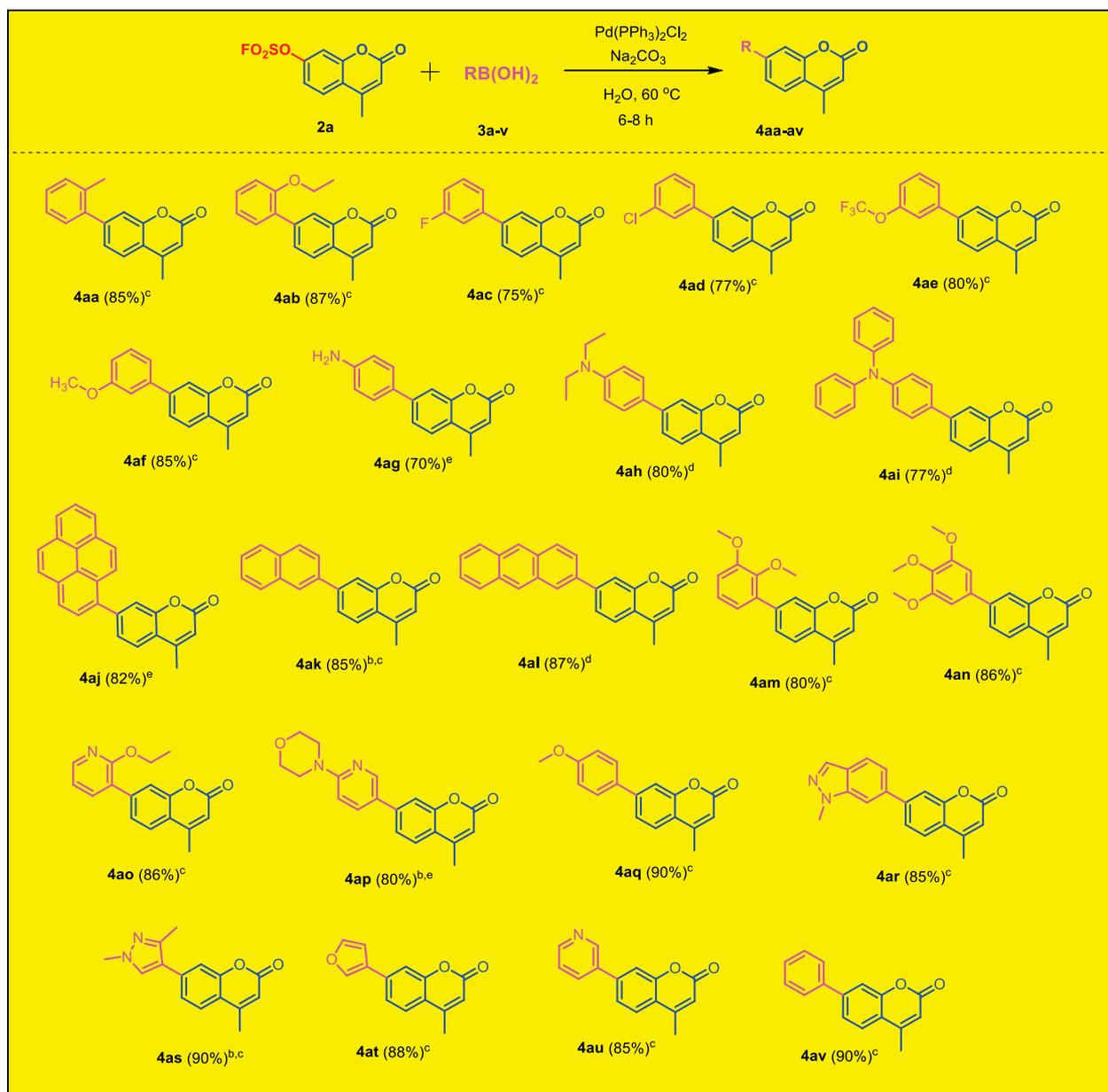
Scheme 2. Synthesis of fluorosulfate intermediates 2a-i.

[14]. Jin et al reported the synthesis of 4-methyl-7-phenyl coumarin by nickel-catalyzed reaction of corresponding heteroaryl ether and phenyl boronic acid in toluene as solvent [15]. The need for organic solvents and the generation of bulky pseudohalide wastes as byproducts are the major limitations of these protocols. Recently, we reported the synthesis of a series of 4-methyl-7-(hetero)aryl coumarins [16] by Suzuki–Miyaura cross-coupling of 4-methyl-7-nonafluorobutylsulfonyloxy coumarin with different boronic acids under microwave irradiation (Scheme 1). We utilized a combination of two organic solvents (Dimethoxyethane–MeOH) and Pd(OAc)₂/dppp catalytic system in that optimized methodology along with TBAF·3H₂O as base. Although the reaction was successful in synthesizing an array of coumarin derivatives, the high amount of pseudohalide wastes generated and the need for organic solvents were certainly the limitations.

The aforementioned observations encouraged us to develop a modified, eco-friendly and facile approach for synthesizing a variety of novel coumarin derivatives under mild conditions. In our successful trials, we have employed coumarin fluorosulfate as the electrophilic coupling partner in water using traditional palladium catalyst to synthesize the desired coumarin analogues. In this letter, we report our modified methodology for accessing some novel coumarin derivatives in good yields. A comparative study of various pseudohalide leaving groups have also been carried out to understand the efficiency of fluorosulfate over other electrophilic coupling partners.

2. Results and discussion

As depicted in Scheme 2, we started our synthetic route by synthesizing the fluorosulfate intermediates 2a-i from corresponding phenols 1a-i by treating them

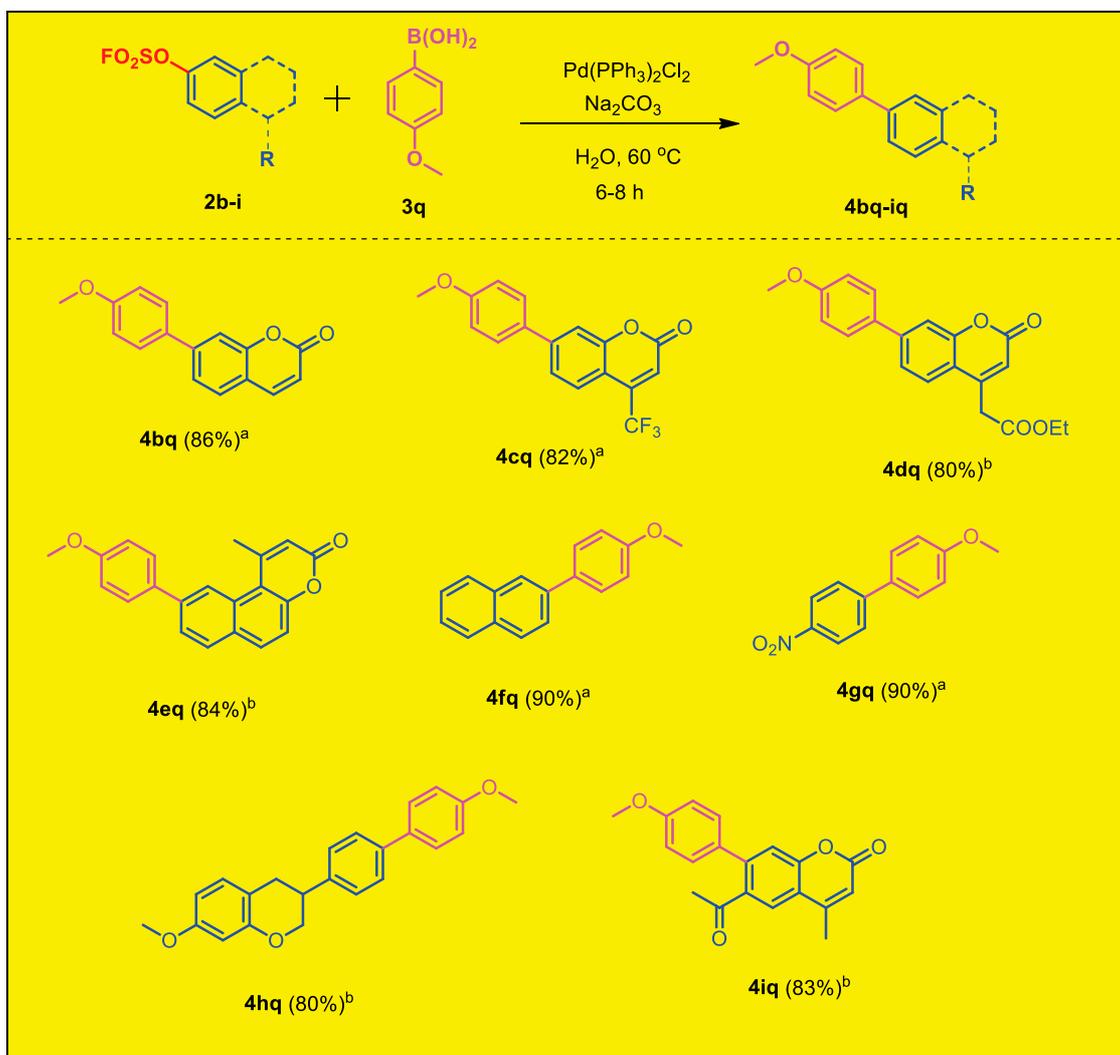


Scheme 3. Scope of boronic acids in the synthesis of 4-methyl-7-(hetero)aryl coumarins. Reaction conditions: 2a (1 mmol), 3a-v (1 mmol), Pd(PPh₃)₂Cl₂ (5 mol%), Na₂CO₃ (2 mmol), 2 mL H₂O, 60 °C for 6-8 h. Isolated yield after crystallization in parenthesis. ^b Corresponding boronic acid pinacol ester used for the reaction. ^c Reaction carried out for 6 hours. ^d Reaction carried out for 7 hours. ^e Reaction carried out for 8 hours.

with SO₂F₂ gas at room temperature. The generation of SO₂F₂ gas was achieved by performing a slight modification in the previously reported procedure (See Supporting Information) [17]. The fluorosulfate substrates 2a-i was then treated with various aryl boronic acids in view of synthesizing an array of novel coumarin analogues.

As a model reaction, we employed *o*-tolylboronic acid 3a as the coupling partner for Suzuki coupling with coumarin fluorosulfate 2a. Recently, Sharpless and coworkers reported the ligand-free Suzuki coupling of aryl fluorosulfates and boronic acids in water at room temperature by utilizing Pd(OAc)₂ as catalyst and triethylamine (Et₃N) as base [18]. Our initial efforts for reaction optimization were based on the results of Sharpless

under mild conditions. Accordingly, we screened different reaction parameters (catalyst, base, solvent and temperature) in view of obtaining the expected product 4aa in appreciably high yield. Unfortunately, we couldn't obtain the desired product in good yield when the reaction was carried out in water at ambient temperature by employing Pd(OAc)₂ as catalyst and Et₃N as base under ligand-free conditions (Table 1, entry 1). The utilization of additional ligands did not help in improving the yield of the expected product 4aa (Table 1, entries 2-4). Increasing the reaction temperature to 60°C slightly improved the yield of the desired product (Table 1, entries 7,8). After a series of optimization studies, we obtained the desired product in reasonable yield when the reaction was carried out at 60°C



Scheme 4. Scope of aryl fluorosulfates in Suzuki coupling. Reaction conditions: 2b-i (1 mmol), 3q (1 mmol), Pd(PPh₃)₂Cl₂ (5 mol%), Na₂CO₃ (2 mmol), 2 mL H₂O, 60 °C for 6-8 h. Isolated yield after crystallization in parenthesis. ^a Reaction carried out for 6 hours. ^b Reaction carried out for 8 hours.

and 30°C by employing Pd(PPh₃)₂Cl₂ as the catalyst, Na₂CO₃ as base and dioxane-H₂O (1:1) as the solvents (Table 1, entries 12,13). To our delight, we obtained the desired product in excellent yield when the reaction was carried out in water at 60°C (Table 1, entry 14). It is worth noting that the reaction was sluggish when dioxane and DMF was employed as solvents at 60°C (Table 1, entries 16,17). However, the desired product was obtained in 70% yield when the reaction was carried out at 100°C in DMF solvent (Table 1, entry 18). Moreover, decreasing the stoichiometry of the catalyst and base significantly decreased the yield of the expected product (Table 1, entries 19,20). Increasing the equivalents of base also afforded the desired product in slightly lower yield (Table 1, entry 21). Finally, the optimized reaction conditions were affixed as detailed in entry 14 of Table 1. The isolation of pure product was carried out by crystallization in ethanol without using column chromatography.

After optimizing the suitable reaction conditions for obtaining the desired product 4aa in excellent

yield, we decided to evaluate the generality of the developed protocol. Accordingly, we treated 2a with a series of boronic acids 3a-v in water at 60 °C by employing the catalyst Pd(PPh₃)₂Cl₂ and Na₂CO₃ base (Scheme 3). To our delight, we obtained the desired products 4aa-av in good to excellent yields. The boronic acids containing polyaromatic hydrocarbons like naphthalene, anthracene and pyrene furnished the corresponding products in excellent yields. However, the boronic acid with *p*-amino substituent afforded the desired product in satisfactory yield (70% isolated yield). The heteroaryl boronic acids also rendered the expected products in good to excellent yields. It is worth noting that the isolation of all the final products was successfully achieved by crystallization in ethanol.

Our next attention was to evaluate the substrate scope of various coumarin/aryl fluorosulfates in our modified methodology. Accordingly, we treated different fluorosulfates 2b-i with 4-methoxyphenylboronic acid 3q in our optimized reaction conditions (Scheme 4).

Table 1. Optimization of reaction conditions^a

Entry	Catalyst	Ligand	Base	Solvent	Temperature	Yield ^b 4aa (%)
1	Pd(OAc) ₂	—	Et ₃ N	H ₂ O	RT	10
2	Pd(OAc) ₂	PPh ₃	Et ₃ N	H ₂ O	RT	15
3	Pd(OAc) ₂	BINAP	Et ₃ N	H ₂ O	RT	0
4	Pd(OAc) ₂	Xantphos	Et ₃ N	H ₂ O	RT	0
5	Pd(PPh ₃) ₄	—	Et ₃ N	H ₂ O	RT	0
6	Pd(PPh ₃) ₂ Cl ₂	—	Et ₃ N	H ₂ O	RT	10
7	Pd(OAc) ₂	—	Et ₃ N	H ₂ O	60°C	25
8	Pd(OAc) ₂	PPh ₃	Et ₃ N	H ₂ O	60°C	35
9	Pd(PPh ₃) ₂ Cl ₂	—	Na ₂ CO ₃	H ₂ O	RT	20
10	Pd(PPh ₃) ₂ Cl ₂	—	Na ₂ CO ₃	Dioxane	RT	0
11	Pd(PPh ₃) ₂ Cl ₂	—	Na ₂ CO ₃	Dioxane-H ₂ O (1:1)	RT	25
12	Pd(PPh ₃) ₂ Cl ₂	—	Na ₂ CO ₃	Dioxane-H ₂ O (1:1)	60°C	70
13	Pd(PPh ₃) ₂ Cl ₂	—	Na ₂ CO ₃	Dioxane-H ₂ O (1:1)	30°C	60
14 ^c	Pd(PPh ₃) ₂ Cl ₂	—	Na ₂ CO ₃	H ₂ O	60°C	90 (85)
15	Pd(PPh ₃) ₂ Cl ₂	—	Cs ₂ CO ₃	H ₂ O	60°C	80
16	Pd(PPh ₃) ₂ Cl ₂	—	Na ₂ CO ₃	Dioxane	60°C	20
17	Pd(PPh ₃) ₂ Cl ₂	—	Na ₂ CO ₃	DMF	60°C	25
18	Pd(PPh ₃) ₂ Cl ₂	—	Na ₂ CO ₃	DMF	100°C	70
19 ^d	Pd(PPh ₃) ₂ Cl ₂	—	Na ₂ CO ₃	H ₂ O	60°C	60
20 ^e	Pd(PPh ₃) ₂ Cl ₂	—	Na ₂ CO ₃	H ₂ O	60°C	75
21 ^{c,f}	Pd(PPh ₃) ₂ Cl ₂	—	Na ₂ CO ₃	H ₂ O	60°C	85 (77)

^aReaction conditions: 2a (1 mmol), 3a (1 mmol), catalyst (5 mol%), ligand (10 mol%), base (2 mmol), 2 mL solvent at given temperature for 6 h.

^b¹H NMR yield using terephthalaldehyde as internal standard.

^cIsolated yield after crystallization in parenthesis.

^d1 mol% of catalyst used.

^e1 mmol of base used.

^f3 mmol of base used.

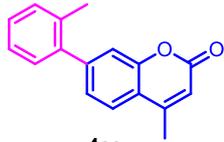
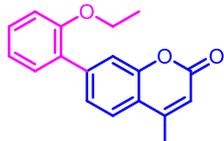
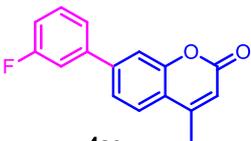
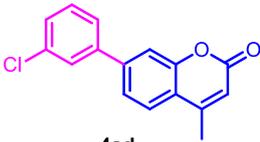
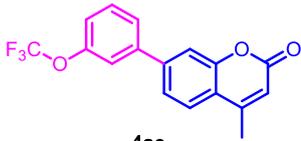
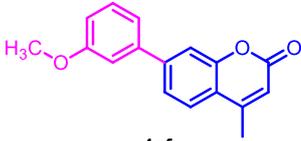
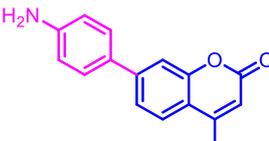
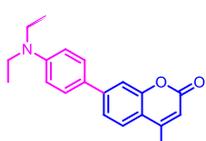
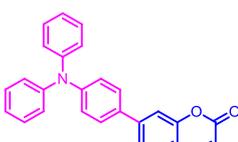
Table 2. Screening of different leaving groups for Suzuki coupling^a.

Entry	Compound	R	Yield ^b 4aa (%)
1	2a	F	85
2	2ab	CH ₃	0
3	2ac	CF ₃	0
4	2ad		0
5	2ae		30
6	2af		40
7	2ag		35

^aReaction conditions: 2a-ag (1 mmol), 3a (1 mmol), Pd(PPh₃)₂Cl₂ (5 mol%), Na₂CO₃ (2 mmol), 2 mL H₂O, 60 °C for 6 h.

^bIsolated yield after crystallization.

Table 3. Evaluation of E-factor for the synthesized compounds^a.

Entry	Product	Isolated yield (%)	E-factor
1	 4aa	85	2.01
2	 4ab	87	1.75
3	 4ac	75	2.37
4	 4ad	77	2.18
5	 4ae	80	1.77
6	 4af	85	1.90
7	 4ag	70	2.65
8	 4ah	80	1.84
9	 4ai	77	1.56

Gratifyingly, we obtained the desired products 4bq-iq in satisfactory to excellent yields. The coumarins containing electron-withdrawing substituents like COCH₃,

CF₃ and COOEt procured the expected products in satisfactory yields whereas the fluorosulfate derived from β -naphthol and 4-nitrophenol afforded the

Table 3. Continued.

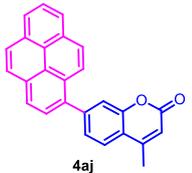
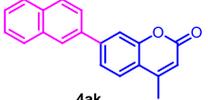
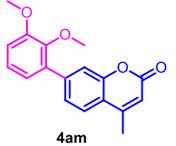
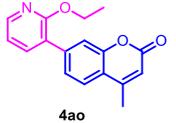
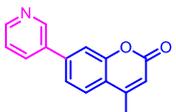
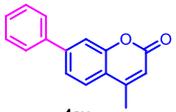
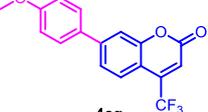
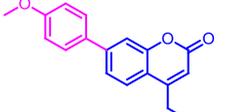
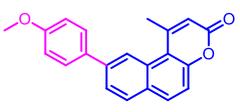
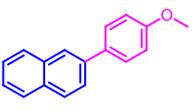
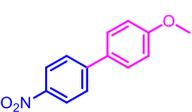
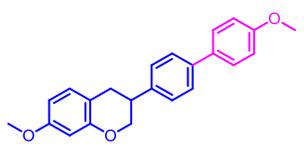
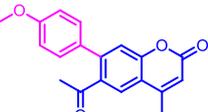
Entry	Product	Isolated yield (%)	E-factor
10	 4aj	82	1.54
11	 4ak	85	2.12
12	 4al	87	1.49
13	 4am	80	1.90
14	 4an	86	1.56
15	 4ao	86	1.78
16	 4ap	80	2.09
17	 4aq	90	1.74
18	 4ar	85	1.76
19	 4as	90	2.17
20	 4at	88	2.10

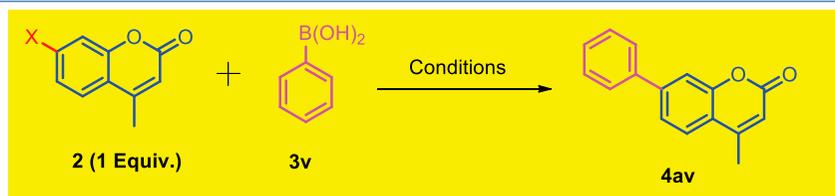
Table 3. Continued.

Entry	Product	Isolated yield (%)	E-factor
21	 4au	85	2.10
22	 4av	90	1.94
23	 4bq	86	1.96
24	 4cq	82	1.70
25	 4dq	80	1.69
26	 4eq	84	1.66
27	 4fq	90	1.96
28	 4gq	90	2.01
29	 4hq	80	1.66
30	 4iq	83	1.73

^aThe calculation is given in Supporting Information.

corresponding products 4fq and 4gq in excellent yield. However, the fluorosulfate obtained from equol furnished the expected product 4hq in satisfactory yield only.

After the successful synthesis of a variety of final products, we directed our immediate attention to study the efficiency of aryl fluorosulfate as a leaving group when compared to other pseudohalide leaving

Table 4. A comparative study of previously reported works and present work

Entry	X =	Ph-B(OH) ₂ Equiv.	Catalyst Equiv.	Ligand Equiv.	Base Equiv.	Solvent	Temperature	Yield ^a 4av (%)
This work	OSO ₂ F	1	0.05	—	2	H ₂ O	60°C	90
Revell et al [14]		3	0.1	—	3	DMF	80°C	76
Jin et al [15]		4	0.05	—	7	Toluene	110°C	84
M.N. Joy et al [16]		1.5	0.05	0.1	3	DME-MeOH (3:1)	80°C	93

^aIsolated yield.

groups. Accordingly, we synthesized different pseudohalide leaving groups like triflate, nonaflate, mesylate etc. of corresponding 4-methyl-7-hydroxy coumarin and subjected them for our optimized Suzuki coupling conditions (Table 2). Among the different leaving groups screened, fluorosulfate was found to be superior to corresponding pentafluorobenzenesulfonates, imidazylates and nonaflates. It is noteworthy that the traditional leaving groups like mesylate, tosylate and triflate did not give the desired product in our optimized protocol.

The utilization of aryl fluorosulfates 2a-i as the key electrophilic coupling partner has indeed reduced the generation of bulky pseudohalide wastes in our developed protocol. Our experiments clearly indicated the superior reactivity of fluorosulfate based electrophile in aqueous medium, highlighting its increased hydrophilicity when compared to the other pseudohalide coupling partners. The superior polarity of this electrophilic coupling partner when compared to the other electrophiles could be the possible reason for its enhanced aqueous solubility which eventually led to the higher yields of the final products [18,19]. The utilization of water as solvent also contributed to the overall efficiency and eco-friendliness of our reactions. To understand the environmental friendliness of our methodology, we decided to calculate the E-factor for the formation of desired products in our reactions (Table 3). Taking this into account, the E-factor for the formation of 4aa-av and 4bq-iq was calculated using the known mathematical formula (See Supporting Information for more details) [20]. To our delight, the E-factor of most of the reactions has been found to be between 1 and 3 which underlines the eco-friendliness of our reactions developed.

Our next attention was to compare the efficiency of our optimized protocol with previously reported methodologies (Table 4). Taking this into consideration, we selected the synthesis of 4av and compared our results with previously reported ones. To our delight, our optimized reaction conditions afforded the required product in better yield at lower temperature. Moreover, our reaction conditions were found to be milder in terms of catalyst loading, utilization of eco-friendly solvent (H₂O) and the stoichiometry of boronic acid and base employed.

3. Conclusion

In summary, we have developed a modified approach for accessing some novel coumarins 4aa-av and 4bq-iq in good to excellent yields under mild conditions. The utilization of aryl fluorosulfate as the electrophilic coupling partner and the use of traditional Pd(PPh₃)₂Cl₂ catalyst in water as solvent are the main highlights of our developed protocol. The screening of different pseudohalide leaving groups emphasized the importance of fluorosulfate to be employed as the substrate

for obtaining the desired products under exceptionally milder conditions. The generation of less bulky pseudohalide byproduct and lower E-factor for the formation of desired products also highlights eco-friendliness of this developed methodology. This methodology can be utilized for the Suzuki cross-coupling reactions of more complex heterocycles containing hydroxyl groups in future.

Conflicts of interest statement

No potential conflict of interest was reported by the author(s).

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