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$PhI(OAc)_2$–BF_3–OEt_2 mediated domino imine activation, intramolecular C–C bond formation and β-elimination: new approach for the synthesis of fluorenones, xanthones and phenanthridines†

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$PhI(OAc)_2$–BF_3–OEt_2 mediated domino synthesis of biologically important fluorenones, xanthones and phenanthridines has been developed. The reaction proceeds through imine activation, intramolecular C–C bond formation and β-elimination.

The construction of carbon–carbon bonds is the prime art in organic synthesis. For this reason, carbon–carbon bond forming reactions are enormous and the development of new methodologies is a subject of constant interest. Over the last decade, palladium, copper, iron and nickel-catalyzed cross coupling reactions have become fundamental methodologies in organic synthesis for C–C bond formation.[1] The discovery of metal free efficient processes for C–C bond formation will also be of great significance because such procedures prevent the need for disposing the metal catalysts from the reaction residues and eliminating traces of metals from the final compounds. Among metal free reagents, hypervalent iodines have received great attention from synthetic organic chemists for C–C bond forming reactions, leading to the synthesis of carbocyclic and heterocyclic molecules.[2] The immense interest in hypervalent iodines is because of easy availability, mild Lewis acidity and their strong oxidizing properties. The hypervalent iodine and Lewis acid combination was highly employed in various organic transformations, such as oxidation of alcohols,[3] Michael reactions,[4] C2-acyloxy glycosylation,[5] C–H iodination,[6] oxidative coupling of aromatic substrates,[7] C–H amidation,[8] α-acetoxylation of ketones,[9] allylic amination of allylsilanes and allylstannanes,[10] α-halogenation of dicarbonyl compounds,[11] oxidation of sillyl ether in alcohol or water,[12] heterocyclic sulfides,[13] and ligand exchange.[3] As a part of our ongoing synthetic programme on the carbocyclic and heterocyclic scaffolds,[14] we intended on developing a new method for the synthesis of fluorenones, xanthones and phenanthridines *via* a hypervalent iodine-Lewis acid mediated C–C bond forming process.

Fluorenones are an important structural moiety found in various natural products exhibiting promising biological activities.[15] These compounds also show optical and electrical properties.[16] There are several methods for the synthesis of fluorenones, *e.g.* oxidation of fluorenes,[17] Friedel–Crafts ring closure of biarylcarboxylic acids and its derivatives,[18] palladium catalyzed cyclo carbonylation of *o*-halobiaryls,[19] remote metalation of 2-biphenylcarboxamides and 2-biphenyloxazolines,[20] imidoyl palladium migration involving C–H bond activation,[21] decarboxylation of *o*-carboxyarylketones,[22] palladium catalyzed C–H functionalization of arylaldoxime ethers with arenes,[23] palladium catalyzed annulation of arynes with 2-haloarenecarboxaldehydes,[24] and metal[25] or metal free[26] intramolecular cyclization of biaryl-2-carbaldehydes. Recently, Pd catalyzed dehydrogenative cyclization,[27] nitrile directed dual C–H bond activation,[28] cross dehydrogenative coupling *via* base-promoted homolytic aromatic substitution (BHAS),[29] radical cyclizations of arylboronic acids and trifluoroborates,[30] and quaternary ammonium salt-promoted intramolecular dehydrogenative arylation of aldehydes[31] have been applied for the synthesis of fluorenones.

Xanthones are naturally occurring molecules, which exhibit excellent pharmaceutical properties.[32] Jackson *et al.* synthesized xanthones from functionalized diaryl ethers *via* Friedel–Crafts reaction.[33] Snieckus reported LDA-mediated conversion of 2-carbamoyl diaryl ethers to xanthone derivatives *via* an anionic Friedel–Crafts process.[34] Frahm presented a series of substituted xanthones synthesized from 2-aryloxybenzoic acids in the presence of PPA.[35] Larock *et al.* reported a synthesis of xanthones *via* tandem coupling of arynes with salicylates and also developed a synthesis of xanthones *via* aryl to imidoyl palladium migration involving C–H bond activation.[21,36] Recently, copper(II)-catalyzed aza-Friedel–Crafts reaction of *o*-phenoxyl-*N*-tosyl-benzaldimine,[37] rhodium catalyzed dehydrogenative cross coupling of 2-aryloxybenzaldehydes,[38] copper-

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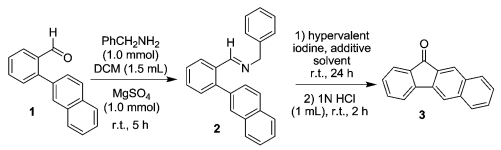
Table 1 Optimization of reaction conditions[a] for the formation of fluorenone, **3**



Entry	Hypervalent iodine	Additive	Solvent	Yield[b] (%)
1	PhIO	—	DCM	—
2	$PhI(OAc)_2$	—	DCM	—
3	$PhI(OTf)_2$	—	DCM	—
4	PhI(OH)(OTs)	—	DCM	—
5	—	HFIP	DCM	—
6	—	BF_3–OEt_2	DCM	—
7	$PhI(OAc)_2$	HFIP	DCM	—
8[c]	$PhI(OAc)_2$	BF_3–OEt_2	DCM	20
9[c]	$PhI(OAc)_2$	BF_3–OEt_2	DCE	32
10[d]	$PhI(OAc)_2$	BF_3–OEt_2	DCE	52
11[e]	$PhI(OAc)_2$	BF_3–OEt_2	DCE	61
12[f]	$PhI(OAc)_2$	BF_3–OEt_2	DCE	62
13[g]	$PhI(OAc)_2$	BF_3–OEt_2	DCE	65
14[h]	$PhI(OAc)_2$	BF_3–OEt_2	MeCN	41

[a] 0.25 mmol **2** was dissolved in a solvent (1.0 mL) and added in the same solvent (3 mL) containing 0.275 mmol hypervalent iodine and 0.275 mmol additive, unless otherwise noted. [b] Isolated yield of the product, **3** with respect to **1**. [c] 1N HCl (2 mL) was added and run for 4 h. [d] The reaction was conducted at 80 °C and 1N HCl (2 mL) was added and run for 5 h. [e] 0.375 mmol $PhI(OAC)_2$ and 0.375 mmol BF_3–OEt_2 were employed and the reaction was performed at 80 °C and 1N HCl (3 mL) was added and run for 6 h. [f] 0.5 mmol $PhI(OAC)_2$ and 0.5 mmol BF_3–OEt_2 were employed and the reaction was performed at 80 °C and 1N HCl (3 mL) was added and run for 6 h. [g] 0.75 mmol $PhI(OAC)_2$ and 0.75 mmol BF_3–OEt_2 were employed and the reaction was performed at 80 °C for 36 h and 1N HCl (2 mL) was added and run for 6 h. [h] 0.75 mmol $PhI(OAC)_2$ and 0.75 mmol BF_3–OEt_2 were employed and the reaction was performed at 80 °C for 36 h and 1N HCl (2 mL) was added and run for 5 h.

catalyzed *ortho*-acylation of phenols with aryl aldehydes,[39] and cross dehydrogenative coupling *via* base-promoted homolytic aromatic substitution (BHAS),[29] have been employed for the synthesis of xanthones.

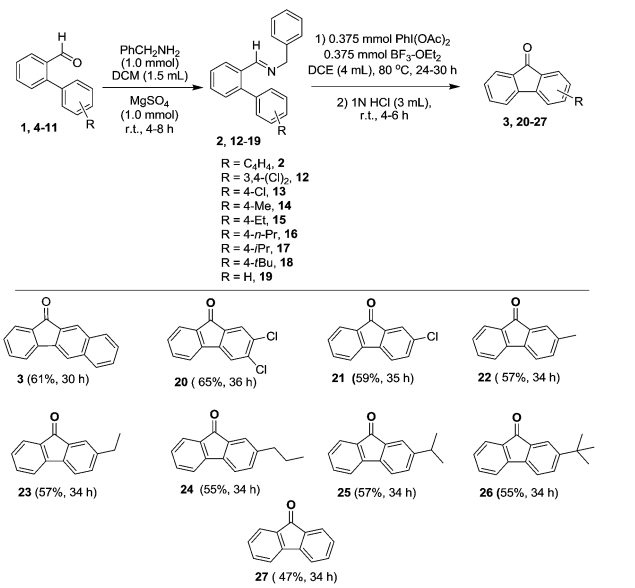
Phenanthridine core containing molecules such as ethidium,[40] trispheridine,[41] bicolorine,[42] and decarine[43] are found in nature and are biologically important.[44] Microwave assisted [2 + 2 + 2] cyclotrimerisation,[45] photolysis,[46] benzyne mediated cyclization,[47] radical cyclization,[48] TFA catalyzed C–C and C–N bond formation,[49] Pd catalyzed oxidative C–H bond activation,[50] hypervalent iodine mediated process[51] and transition metal free intramolecular direct C–H bond arylation[52] have been utilized for the synthesis of phenanthridines.

In order to synthesize fluorenones, we initiated our work with the synthesis of 2-(naphthalen-2-yl)benzaldehyde **1** using a Suzuki coupling reaction between 2-bromobenzaldehyde and 2-naphthylboronic acid and consequently **1** was converted into key intermediate aldimine **2** by treating with benzyl amine (Table 1).[53] We anticipated that hypervalent iodine in presence of a Lewis acid could recognize and coordinate through the imine group of **2**, and their combination might assist the C–C bond formation and β-elimination to give ketimine. The hydrolysis of the resultant ketimine might produce fluorenone **3** (Table 1).[21] The coordination of the hypervalent iodine to the imine moiety is the key step for this hypervalent iodine-Lewis acid mediated C–C bond forming reaction or domino process. To explore the idea, we have selected **2** as a model substrate for the screening of experimental conditions for the formation of fluorenone **3** with various hypervalent iodines, additives (HFIP and Lewis acid BF_3–OEt_2), and solvents, and the results are summarized in Table 1.

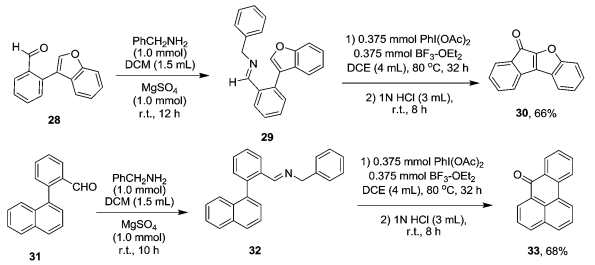
It was observed that 0.375 mmol $PhI(OAc)_2$ and 0.375 mmol boron trifluoride diethyl ether complex in dry DCE at 80 °C in 24 h followed by hydrolysis afforded **3** in good yield (entry 11, Table 1). No significant improvement was observed in the formation of **3** while increasing the quantity of $PhI(OAc)_2$ and boron trifluoride diethyl ether complex (entry 12). Major increment was not observed in the formation of **3** by increasing the time or the concentrations of $PhI(OAc)_2$ or boron trifluoride diethyl ether complex (entry 13). Further, 0.375 mmol $PhI(OAc)_2$ and 0.375 mmol boron trifluoride diethyl ether complex in dry acetonitrile at 80 °C in 36 h, followed by hydrolysis, also did not furnish **3** in good yield (entry 14). It is noteworthy to mention here that the domino process was not feasible with other aldimine, which was prepared from 2-(naphthalen-2-yl) benzaldehyde **1** and aniline at room temperature in 2 h (ref. 53) under the same reaction conditions.

With the above optimized conditions (entry 11, Table 1) the metal free domino process was explored with various aldimines **12–19**. The structures of the fluorenones **20–27** obtained through domino process, reaction times and isolated yields are presented in Scheme 1.

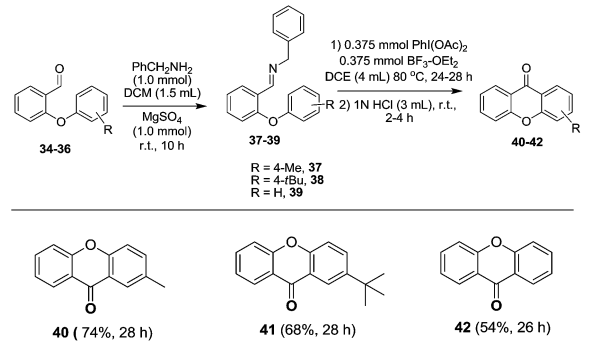
Better yields were observed in the formation of fluorenones **3** and **20** because of the rich electronic nature of **2** and **12**. The



Scheme 1 Synthesis of fluorenones **3** and **20–27**, reaction times and isolated yields are given in parenthesis.



Scheme 2 Synthesis of heterocycle based fluorenone (**30**) and anthranone (**33**), reaction times and isolated yields are given in parenthesis.



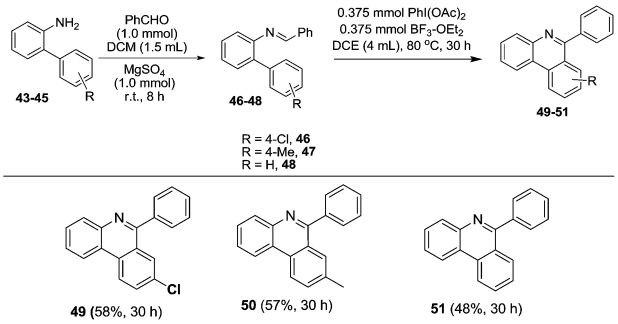
Scheme 3 Synthesis of Xanthones **40–42**, reaction times and isolated yields are given in parenthesis.

generality and versatility of this process was proved by pursuing the synthesis of fluorenones **21–26** from aldimines **13–18**. The isolated yield of product **27** was low because of the aldimine **19** having the unreactive or electronically weak phenyl ring.

Applicability of this method was proved with the synthesis of heterocycle based fluorenone (**30**) and anthranone (**33**) Scheme 2.

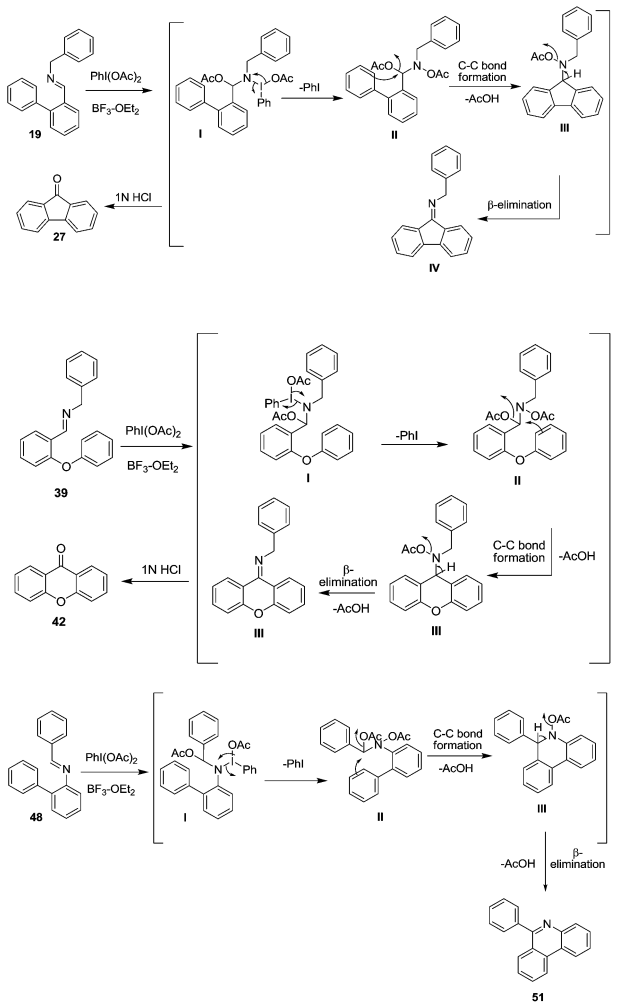
After the successful synthesis of fluorenones, we explored the synthesis of various xanthones using the optimized conditions (entry 11, Table 1). 2-(*p*-tolyloxy)benzaldehyde[54] **34** was prepared using aromatic nucleophilic substitution reaction and converted into aldimine (**37**, Scheme 3) by treating with benzyl amine.[53] The domino process was carried out on **37** (entry 11, Table 1), which resulted in the formation of xanthone **40**. After getting these successful results the domino process was employed on other aldimines **38** and **39**, which gave the respective xanthones **41** and **42** in reasonable yields (Scheme 3).

The applicability of this domino process was further proved with the synthesis of phenanthridines. To synthesize phenanthridines **49–51**, 4′-chlorobiphenyl-2-amine[8] **43** was synthesized using Suzuki coupling and converted into aldimine (**46**, Scheme 4) by treating with benzaldehyde.[53] The domino process was applied on **46** under the above optimized experimental conditions (entry 11, Table 1), which provided phenanthridine **49**. Encouraged by these results the domino process was employed with other aldimines **47** and **48** to produce xanthones **50** and **51** (Scheme 4).



Scheme 4 Synthesis of phenanthridines **49–51**, reaction times and isolated yields are given in parenthesis.

The plausible reaction mechanism for the formation of fluorenones (**3**, **20–27** and **30**), xanthones (**40–42**) and phenanthridines (**49–51**) is described in Scheme 5. The first step appears to be the coordination of iodosobenzene diacetate with aldimine and nucleophilic attack of the acetate ion to the polarized imine carbon to provide intermediate (**I**).[5] In the



Scheme 5 Plausible reaction mechanism for the formation of fluorenones, xanthones and phenanthridines.

second step the transfer of the acetate group to the nitrogen of (**I**) might have afforded (**II**) in which I^{+3} readily converted to I^{+1}.[5] In the third step C–C bond formation and cleavage of C–OAc bond in the presence of BF_3–OEt_2, might have taken place to give intermediate (**III**).[55] In the final step BF_3–OEt_2 might have induced β-2 elimination to furnish intermediate (**IV**). The reaction mechanism for the formation of **27**, **42** and **51** is presented in Scheme 4 as representative examples from each class of compounds. Anthranone (**30**) follows the similar mechanism corresponding to fluorenone (**27**).

In conclusion, we have developed a new method for the synthesis of biologically important fluorenones, xanthones and phenanthridines using the combination of a hypervalent iodine and a Lewis acid. The formation of the fluorenones, xanthones and phenanthridines appears to be through hypervalent iodine-Lewis acid mediated domino sequence, *i.e.* imine activation, intramolecular C–C bond formation and β-elimination. To the best of our knowledge, we are the first group to report a hypervalent iodine-Lewis acid mediated domino process for the synthesis of fluorenones, xanthones and phenanthridines.

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