Section A -Research paper

Scaffold Divergent Synthesis of Substituted Quinoxalines *via* TBAF Catalyzed Condensation of *O*-phenylenediamine with 1,2-diketones and Bromoacetophenone

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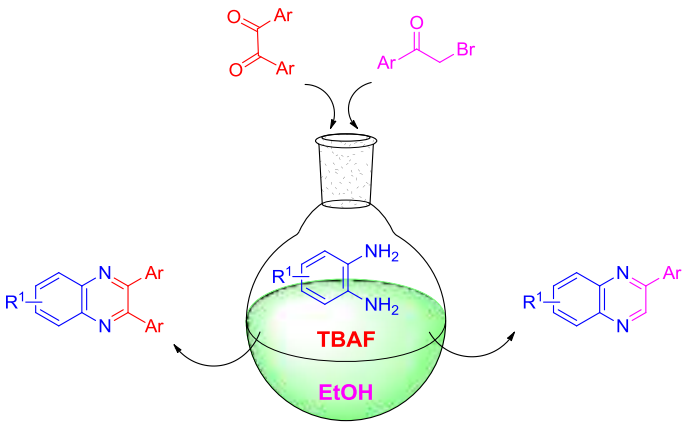
Graphical abstract



Abstract

A novel strategy for the quinoxalines derivatives have been developed by condensation of 1,2-diaminoarenes with 1,2-diketones or 2-bromo-1-arylethanone in presence of TBAF as the catalyst. This strategy seems to suitable for the construction of numerous 2-phenylquinoxalines, biquinoxalinephenazine, and tetraphenyl-biquinoxaline

analogue with high productivity. This protocol allows C-N bond formation with excellent scope and highly substituted group tolerance under mild and ease condition. The mild reaction condition, easy purification process and high reaction rate afford excellent yields it makes this methodology an ideal alternative substitute for the conventional acid/base or metal catalyzed thermal processes.

Keywords

Quinoxalines, TBAF, ocular hypertension, anti-tumor and organic semiconductors

Introduction

As many of the leads identified from high-throughput screening are nitrogen-containing heterocycles that are indispensable structural units for the organic synthesis. Benzopyrazine nitrogen-containing heterocycles serves as the units to the construction of several potent pharmacologically compounds including anti-mycobacterial, anti-depressant, anti-tumor, anti-HIV, and kinase inhibitors illustrated in **Figure 1**.[1] Quinoxalines groups are helpful for rapidly developing medicinal chemistry programs to identify useful chemical lead, and also to quickly deliver safety assessment for clinical evaluation. Moreover, quinoxaline moiety is a part of various antibiotics, such as Echinomycin (I) that are known to inhibit growth of Gram positive bacteria and active against various transplantable tumors.[2a] Varenicline (II) is a prescription medication used to treat smoking addiction.[2b] Brimonidine (III) drug used to treat open-angle glaucoma or ocular hypertension.[2c] They have been also used as building blocks for the synthesis of organic semiconductors [3a-b] and investigated as the catalyst's ligands.[3c]

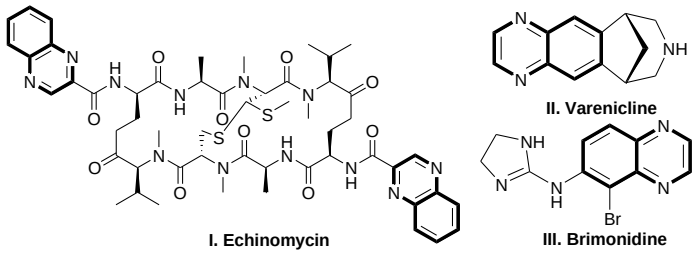


Figure 1. Structurally related biologically active compounds.

The quinoxalines having wide-range of biological activity, both naturally occurring

and synthetic, ensures that the synthesis of this important heteroatom ring system remains a topic of current interest. Motivated by these significant applications, chemists have developed various strategies in presence of acid, base and metal catalyst for the construction of important quinoxalines heterocycles.[4] Zhang and coworkers developed Gallium-catalyzed condensation reactions to synthesis of 1,2-diphenylquinoxalines.[5] Padmavathy *et.al.* reported microwave assisted two-step one-pot reaction for 1,2-disubstituted quinoxalines starting from ketones *via* their *α*-hydroxylimino ketone derivatives and followed by condensation with 1,2-diaminobenzene.[6] Madhav and coworkers described biomimetic approach for 2-phenylquinoxalines in presence of *β*-cyclodextrin (*β*-CD) by using α-bromoketones and 1,2-diamines in water medium.[7] Benzopyrazine derivatives synthesized by the liquid phase condensation reaction between various 1,2-diamines and 1,2-diketones using ZrO_2/Ga_2O_3/MCM-41 as the catalysts described by Ajaikumar *et.al.*[8] Heravi and co-worker found that $MnCl_2$ in EtOH, Zn[(L)proline] with acetic acid, cupric sulfate pentahydrate in EtOH, and *o*-iodoxybenzoic acid (IBX) in acetic acid could all work as effective catalyst for the synthesis of quinoxaline derivatives from the condensation of the *o*-phenylenediamines with 1,2-dicarbonyl compounds at room temperature.[9]

These results promoted us the necessity to develop an efficient and easy strategy to construct quinoxalines heterocycles. Previously, we report TBAF successfully used in promoting C-C bond formation reaction between Michael donors and diiminoquionid ring[10] which ultimately provides an unprecedented method for a direct-functionalization[11] of polyaniline backbone with versatile functional alkyl groups, here we check the feasibility of using the mild F anion catalyst to promote the simple and rapid condensation approach for the synthesis of 2,3-diphenylquinoxaline and 2-phenylquinoxaline *via* C-N bond formation at mild condition.

Over the past years, tetrabutylammonium fluoride (TBAF) in organic synthesis has been widely used for most fluoride-assisted reactions, particularly for desilylation,[12] and fluorination.[13] TBAF has been widely recognized as a convenient, organic soluble source of naked fluoride ion and widely used as the base of choice for the different organic transformations.[14] Owing the involvement of nucleophiles as well as electrophiles in the synthesis of quinoxalines, we believed that the unique ability of

fluoride catalyst might also enable the synthesis of various quinoxalines.

Materials and methods

All reactions were carried out under nitrogen atmosphere in oven-dried glassware using standard syringe, cannula, septa and other apparatus. Solvents were dried with calcium hydride or sodium/benzophenone and distilled before use. All NMR spectra were recorded on BRUKER-400 NMR. HRMS was recorded on a Thermo Finnigan Model: MAT 95 XL spectrometer. Unless otherwise noted, reagents were obtained from commercial sources and used without further purification.

Typical experimental procedures for quinoxalines:

(a) Synthesis of 2,3-diphenylquinoxaline (3a) *via* condensation method.

To a solution of *o*-phenylediamine **1a** (0.1081g, 1 mmol) in EtOH (10 mL) was added benzil **2a** (0.2102g, 1 mmol,) and TBAF.$3H_2O$ (0.315g, 1 mmol,) sequentially. The resulting homogenous mixture was then stirred at 30 ^oC, the reaction progress was monitored with TLC using 20 % ethyl acetate in hexane as eluent. After the reaction completion, solvent was removed on rotary evaporator to give semi-solid gummy crude reaction mixture. The crude mixture was extracted by ethyl acetate (2 X 10 mL), and dried with anhydrous $MgSO_4$. The organic solvent was removed on rotary evaporator and the obtained crude product was purified by column chromatography using 20% ethyl acetate in hexane as eluent to give 2,3-diphenylquinoxaline **3a** in excellent yield (0.2710g; 96 % yield), its structure was confirmed by ^1H NMR, ^{13}C-DEPT NMR, and HRMS. This procedure was used for the synthesis of all **3** and **5** derivatives.

(b) Synthesis of diquinoxalino[2,3-a:2',3'-c]phenazine (7) *via* condensation method

To a solution of hexaketocyclohexane octahydrate (**6**) (0.2g, 0.6406 mmol) in EtOH (20 mL) was added *o*-phenylediamine **1a** (0.2070g, 1.9218 mmol) and TBAF.$3H_2O$ (0.6053g, 1.9218 mmol) sequentially. The resulting homogenous mixture was stirred at 80 ^oC for 9 h, the reaction progress was monitored with TLC using 50% ethyl acetate in hexane. The complete disappearance of the starting materials then stopped and allowed to cool down to room temperature. The formed precipitate was collected by filtration and washed with water. The remaining products within the mother liquor were extracted by

EtOAc. The obtained precipitate and the extracted material from the mother liquor were combined and purified by column chromatography using 50% ethyl acetate in hexane as eluent to give diquinoxalino[2,3-a:2',3'-c]phenazine **7** in good yield (0.3192g; 69%).

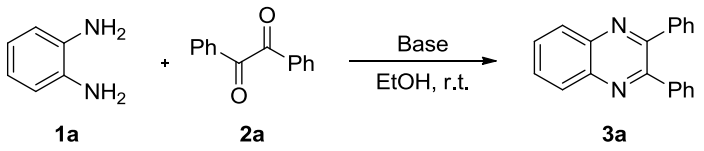
(c) Synthesis of 2,2',3,3'-tetraphenyl-6,6'-biquinoxaline (9) *via* condensation method

To an oven-dried two neck round bottom flask equipped with a condenser was charged with 3,3',4,4'-tetraamino-1,1'-biphenyl **8** (0.2142g, 1 mmol) in EtOH (10 mL), followed by the addition of benzil **2a** (0.4204g, 2 mmol,) and TBAF.$3H_2O$ (0.315g, 1 mmol,) sequentially. The resulting homogenous mixture was stirred at room temperature (80 ^oC) for 5 h, the reaction progress was monitored by TLC using 50 % ethyl acetate in hexane as eluent. After the completion of reaction the solvent was removed on rotary evaporator to give semi-solid gummy crude reaction mixture. The crude mixture was extracted by ethyl acetate and dried with anhydrous $MgSO_4$. The obtained crude product was purified by column chromatography using 20% ethyl acetate in hexane as eluent to give 2,2',3,3'-tetraphenyl-6,6'-biquinoxaline **9** as the major product (0.4758g; 85 %).

Results and discussion

Our study commenced with the investigation of several fluoride anions as promoter for the condensation of diamines (**1a**) with diketones (**2a**) in ethanol at room temperature illustrated in Scheme 1 and results are summarized in Table 1.

Scheme 1. Synthesis 2,3-diarylquinoxaline.



1a **2a** **3a**

To our delight, when the reaction was performed in presence of inorganic fluoride source such as NaF (35%, entry 2), KF (30%, entry 5), and CsF (33%, entry 6) offered the desired quinoxaline **3a** in lower yield. Entry 3 and 4 shows NaF in water at high temperatures (50 ^oC and 80 ^oC) furnished 47% and 65% yields, respectively. In an attempt to improve the yields and to check the feasibility of organic salts, the reaction was tested with various tetrabutylammonium halides. Although TBAB and TBAC

(entries 8-9) also helped to promote the synthesis of 1,2-diphenylquinoxaline *via* condensation between 1,2-diamineobenzene and benzil, they are not as effective as TBAF (entry 7) that offered the desired **3a** in excellent yield (96%). The structures of products were confirmed by spectroscopic methods. It is worth noting that, without the fluoride catalyst inferior yield was obtained at ambient temperature even after 24 h (entry 6). Hence, it is evident that fluoride anion of TBAF has indeed mediated the condensation reaction.

Table 1. Catalyst screening for the synthesis of 2,3-diphenylquinoxaline **3a**.[a]

entry	catalyst	*t* (h)	yield[b] (%)
1	0	24	15
2	NaF	10	35
3[c]	NaF	12	47
4[d]	NaF	12	65
5	KF	10	30
6	CsF	10	33
7	TBAF	15 min	96
8	TBAB	10	30
9	TBAC	10	25

[a]All reaction carried out in EtOH and used 1 equiv base; [b]Isolated yield after column chromatography; [c]Reaction carried out in H_2O at 50 ^oC; [d]Reaction carried out in H_2O at 80 ^oC.

With this encouraging result, in order to improve the yield and indentify the role of solvent and amount of catalyst loading, a wide range of conventional organic solvents were screened and the results are summarized in Table 2. It was found that reaction in THF (Table 2, entry 1) and ethyl acetate (Table 2, entry 2) required a longer time to provide the desired product **3a**. Whereas in polar solvents such as CH_3CN (Table 2, entry 3), MeOH (Table 2, entry 5), and EtOH (Table 2, entry 4) under the identical condition reaction was afford product **3a** in 92%, 90%, and 96% yields, respectively in a very short span of time (15-30 min). In even more polar solvents like water at its reflux temperature (entry 6) and the co-solvent of H_2O/EtOH (Table 2, entry 7), they offered the expected quinoxaline in good yields. Although acetonitrile, methanol, and ethanol furnished the

product **3a** in more or less similar yields, ethanol was chosen as a solvent for further reaction optimization, owing to its low toxicity, low cost, and easy availability. It was found that 1 equiv of TBAF was sufficient to catalyze the reaction and delivered **3a** in 15 min with 96 % yield. Further reduced and increased TBAF amount (Table 2, entry 8 and 9) led to longer reaction time and inferior yields. This result clearly demonstrated the effectiveness of TBAF in catalyzing the reaction.

Table 2. Solvent screening for the synthesis of substituted quinoxaline.[a]

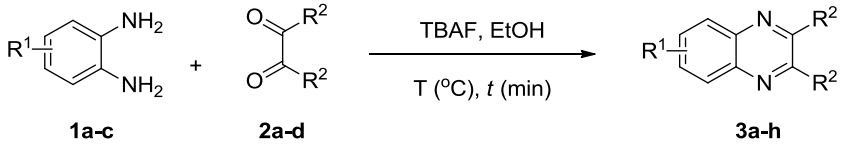
entry	solvent	*t* (min)	yield[b] (%)
1	THF	150	80
2	EA	120	85
3	CH_3CN	30	92
4	EtOH	15	96
5	MeOH	25	90
6[c]	H_2O	240	80
7[d]	H_2O:EtOH	150	88
8[e]	EtOH	60	79
9[f]	EtOH	60	85

[a]All reaction carried out at r.t. with TBAF (1 equiv); [b]After column chromatography isolated yield; [c]Reaction performed at 100 ^oC. [d]Reaction carried at 80 ^oC with 1:1 ration of H_2O:EtOH.[e]TBAF used as 0.5 equiv; [f]TBAF used as 2 equiv.

The scope of the synthesis of numerous quinoxaline *via* condensation reaction was evaluated by using various 1,2-diaminoarenes and benzils having different electron-withdrawing and electron-donating substituent groups and results are shown in Table 3. Results specify that the electron-donating groups on the benzil and phenyl ring of 1,2-diamine favored the formation of product to give quantitative yields in short time. In contrast, the moderate electron-withdrawing groups at 1,2-diamine such as bromo gave slightly lower yields (Table 3, entries 4-5). Whereas, the strong electron-withdrawing NO_2 group further reduced the yield to 86-88%, and required even longer reaction time (up to 3 h) and higher reaction temperature (up to 80 ^oC) (Table 3, entry 6-7). In another variation, aliphatic diketone such as biacetyl (2,3-diketobutane) it underwent

condensation with diamino in the presence of TBAF to give the product **3h** in good yield (Table 3, entry 8).

Table 3. Synthesis of substituted 1,2-diarylquinoxalines.[a]

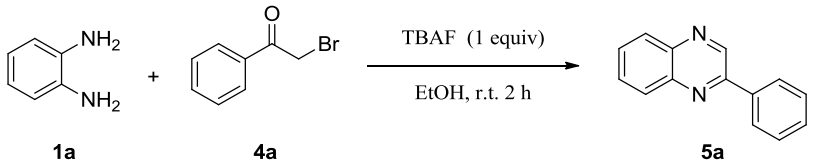


entry	R^1	R^2	Product	*t* (min)	T (^oC)	yield[b] (%)
1	H	C_6H_5	**3a**	15	30	96
2	H	4-Me-C_6H_4	**3b**	20	30	93
3	H	4-Br-C_6H_4	**3c**	30	30	90
4	4-Br	C_6H_5	**3d**	30	30	93
5	4-Br	4-Br-C_6H_4	**3e**	120	80	92
6	4-NO_2	C_6H_5	**3f**	150	80	86
7	4-NO_2	4-Br-C_6H_4	**3g**	170	80	88
8	H	Me	**3h**	20	30	89

[a]All reaction carried out in presence of TBAF (1 equiv) in EtOH at r.t.; [b]Isolated yield.

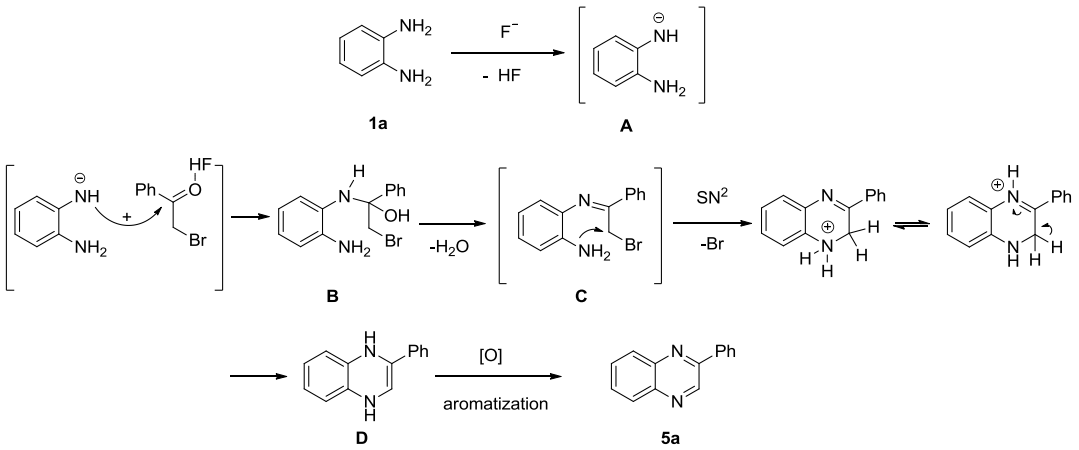
With this promising results in hand, we synthesize 2-phenyl quinoxalines by using 1,2-diamines (**1**) and phenacyl bromide (**4**) via condensation reaction under optimized condition, shown in Scheme 2. The reaction is presumed to precede condensation of diamine with 2-bromoacetophene through imine formation followed by nucleophilic substitution to furnish desired 2-quinoxalines. The reactivity of 2-bromo-1-phenylethanone is slower than diketones may be attributed to its slower S_N2 reaction or aromatization step and plausible mechanism illustrated in Scheme 3.

Scheme 2. Synthesis of 2-arylquinoxaline**.**



Though the clear mechanistic details of this condensation reaction are not yet fully understood, a feasible pathway is proposed in Scheme 3. Fluoride ion might abstract proton of amino group to convert 1,2-diaminobenzene into stronger nucleophiles (**A**). The librated HF could on the other hand activate the carbonyl to convert 2-bromoacetophene into a stronger electrophile. Both activation reactions greatly enhanced the coupling reaction rate between the amino and the carbonyl groups, forming the imine compound **C.** Then the second amino group will undergo S_N2 reaction with at the allylic bromide of **C** to form the 1,4-dihydroquinoxalines **D**, which then undergo aromatization to form **5a.**

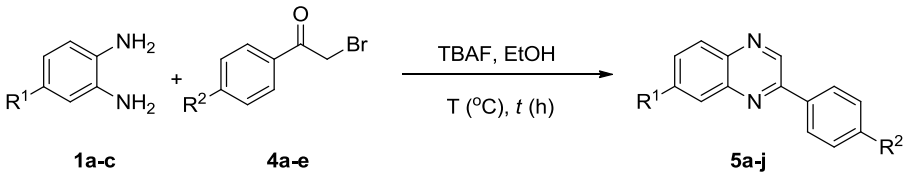
Scheme 3. Plausible mechanism for the synthesis of 2-phenylquinoxaline **5a.**



The applicable scope for the synthesis of 2-arylquinoxalines *via* condensation reaction under optimal conditions and the results are summarized in Table 4. Results show that electron-donating groups on phenyl ring of diamines and 2-bromo-1-arylethanone favored the formation of product to give excellent yields in short time. While, the electron-withdrawing groups at the phenyl ring of the bromo compounds gave slightly lower yields (Table 4, entries 6-9). Whereas, the NO_2 group at the phenyl

ring of the diamine compounds reduced the yield significantly (Table 4, entry 10).

Table 4. Synthesis of substituted 2-arylquinoxalines.[a]



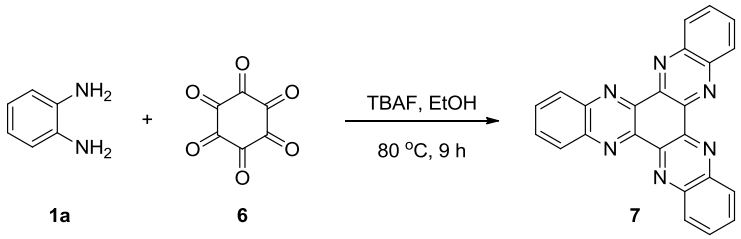
1a-c **4a-e** **5a-j**

entry	R^1	R^2	Product	*t* (h)	T (°C)	yield[b] (%)
1	H	H	**5a**	2	30	92
2	H	Br	**5b**	2.1	30	90
3	H	CH_3	**5c**	2.5	30	92
4	H	Cl	**5d**	2	30	87
5	H	CN	**5e**	2.5	30	85
6	Br	Br	**5f**	1.5	30	90
7	Br	CH_3	**5g**	1.5	30	88
8	Br	Cl	**5h**	1.5	30	94
9	Br	CN	**5i**	1.5	30	90
10	NO_2	H	**5j**	4	80	70

[a]All reaction carried out in EtOH using TBAF (1 equiv) at r.t.; [b]Isolated product.

To check the versatility of this method, TBAF was also used to catalyze the coupling reaction between 1,2-diaminobenzene and (**1a**) hexaketocyclohexane (**6**) to prepare diquinoxalino[2,3-α:2',3'-c]phenazine (**7**), shown in Scheme 4. The results indicated that when the reaction was performed at 80 °C in presence of TBAF (3 equiv), it give the desired quinoxalines **7** with a fair good yield of 69 % in 9 h.

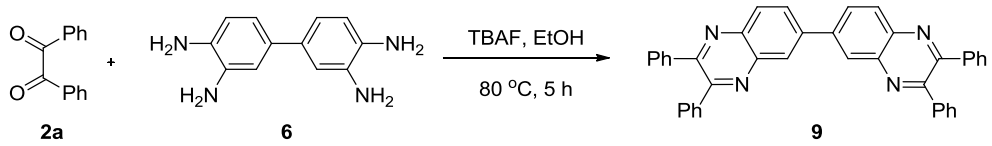
Scheme 4. Synthesis of biquinoxalinephenazine **7**.



1a **6** **7**

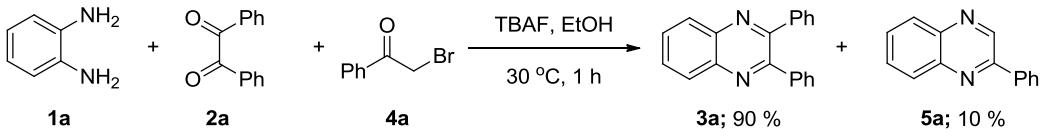
For bulkier tetraamines, such as 3,3',4,4'-tetraamino-1,1'-biphenyl **(8)**, TBAF helps to promote its condensation reaction with benzil (**2a**) to leads the corresponding quinoxaline **9** in 85 % yields at 80 ^{o}C, illustrated in Scheme 5.

Scheme 5. Synthesis of tetraphenyl-biquinoxaline **9**.



We have further examined the competition rate for the condensation reaction of benzyl (**2a**) and phenacyl bromide (**4a**) with *o*-phenylenediamine (**1a**) in one pot using a molar ratio of 1:1:1 for the three compounds, in presence of TBAF (1 equiv) showed in Scheme 6. We have found that benzil (**2a**) reacted faster with *o*-phenylenediamine (**1a**) than phenacyl bromide (**4a**), forming 90% of 2,3-diphenylquinoxalines (**3a**) and 10% of 2-phenylquinoxalines (**5a**). Hence, the control studies confirmed that the reactivity of diketones is higher than phenacyl bromide for the condensation reaction. The slower formation rate of 2-phenylquinoxaline (**5a**) may be attributed to its slower S_N2 and aromatization step.

Scheme 6. Study of reaction reactivity for synthesis quinoxaline.



Conclusion

In conclusion, we have successfully demonstrated a novel and rapid strategy for the synthesis of various substituted quinoxalines by coupling 1,2-diaminoarenes with 2-bromo-1-arylethanone or 1,2-diketones by using TBAF as the milder base catalyst. This strategy further successfully demonstrated the ability of F anion to the synthesis of

biquinoxalinephenazine and tetraphenyl-biquinoxaline analogue at mild condition. TBAF catalyzed condensation method is very rapid with excellent yields at mild condition and further feasibility of F anion for the formation of C-C, C-S and C-O bonds are progress in our research laboratory.

Acknowledgment: The authors wish to thank the Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, Maharashtra, India and the authorities of the Sir Sayyed College, Roshangate, Aurangabad, Maharashtra, India for providing the laboratory facilities.

Supporting Information Available: The spectral data of all key compounds available free of charge via the google drive link https://drive.google.com/file/d/1_GTVlQ3Uq8tmil19TdplsqAsJWActjgO/view?usp=drivesdk

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