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Graphical Abstract

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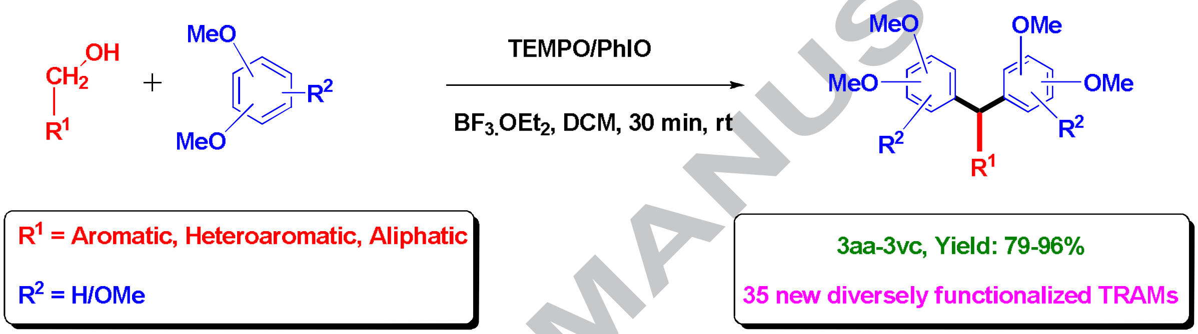

Novel and highly efficient one pot protocol for the synthesis of diversely functionalized triarylmethanes

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Abstract— An efficient, convenient and novel one pot approach is described for the synthesis of triarylmethanes by in situ oxidation of benzylalcohols followed by the Friedel–Crafts alkylation of di/trimethoxybenzenes in the presence of $BF_3.OEt_2$. The generality of the present method is strengthened by screening a variety of aromatic, aliphatic, heteroaromatic alcohols with methoxy arenes. Shorter reaction time, mild reaction condition, good yields and wide scope of substrates are the significant features of this protocol.

Keywords: Triarylmethanes; Friedel–Crafts reaction; Oxidation; $BF_3.OEt_2$, Lewis acid.

Triarylmethanes (TRAMs) are valuable scaffolds which possess promising pharmacological properties such as antiviral,[1] antitumor,[2] antifungal,[3] anti-inflammatory,[3] antitubercular,[4] antioxidant[5] as well as anti-diabetic[6] (Fig. 1). Some of the triarylmethane also constitute the core structure in natural products such as cassigarol B.[7] In addition to this, triarylmethanes are used as a protective groups,[8] leuco dyes,[9] photochromic agents,[10] building blocks for dendrimers,[11] and in material science.[12] Due to such widespread applications of TRAMs, there is a continuous research interest to develop an efficient and convenient protocol for the synthesis of these molecules in mild condition.

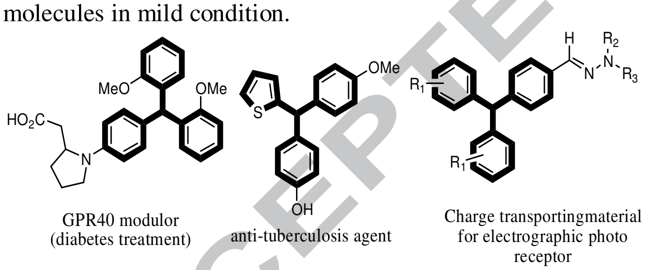
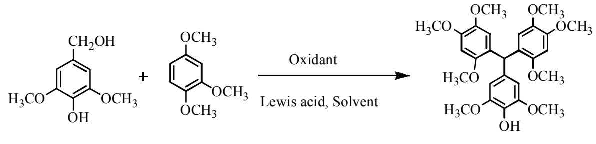


Fig. 1: Representative examples of biologically active triarylmethane derivatives.

Various protocols for the synthesis of triarylmethanes have been reported so far which include the Friedel–Crafts reaction of electron-rich arene on aldehyde using various Lewis or Bronsted acids.[13] Inorganic solid supported montmorillonite K-10,[14] organolithium,[15] organotin,[16] microwave assisted[17] and acidic zeolites[18] have also been employed to accomplish this transformation. Olah[19] and coworkers are reported the hydroxyalkylation of weakly deactivated aromatics by aromatic mono- and dicarboxaldehydes under super electrophilic activation using BF_3–H_2O in good yields. Friedel-Crafts alkylation has been also accomplished with a catalytic amount of iodine which required longer reaction times (72 h).[20] Recently, palladium catalyzed arylation of methyl phenyl sulfone was reported to yield triarylmethanes.[21] Although these reported methods are satisfactory, some of these methods also suffer from certain disadvantages such as harsh reaction conditions,[13p,16,17,21] longer reaction time,[13o,20] and unsatisfactory yield[13a] of the desired products. Moreover, a few of methods involves the catalyst which required multi-step synthesis.[13b] Therefore, there is a scope to develop a general, convenient and high yield method by addressing the shortcomings of reported methods to afford triarylmethanes.

During our extensive literature survey it was found that, most of the reported methods for the synthesis of triarylmethanes were achieved from aldehydes and methoxy arenes. As we are involved in the development of new methodologies, we envision the synthesis of triarylmethane from alcohol and arenes by one pot oxidation and Friedel–Crafts reaction using Lewis acid with suitable oxidizing reagent (Scheme 1). In this regard, we focused our attention on the use of TEMPO for synthesis of triarylmethanes from alcohol and arenes. TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxyl) has been effectively used as an oxidizing reagent for oxidation of alcohols with suitable co-oxidant in organic synthesis.[22] Recently, we have reported a new series of diversely functionalized triarylmethane derivatives using $BF_3.OEt_2$ as a catalyst.[23b] To the best of our knowledge, there is no report for the direct synthesis of triarylmethanes starting from alcohol. In the continuation of our work,[23] in the development of useful methodology for the synthesis of biologically active molecules, herein we wish to report an operationally simple, novel and an efficient one pot protocol for the direct synthesis of triarylmethanes by the reaction of activated aromatic compounds with substituted benzyl alcohols using TEMPO/PhIO and $BF_3.OEt_2$ catalyst system.



Scheme 1: Optimization of the reaction conditions.

Initially, the reaction of 4-(hydroxymethyl)-2,6-dimethoxyphenol **1a** (1 mmol) with 1,2,4-trimethoxybenzene **2a** (2 mmol) was performed using $BF_3.OEt_2$ (2 equiv) and PhIO (1.2 equiv) in the presence of catalytic amount of TEMPO in 5mL DCM(CH_2Cl_2) at room temperature. The progress of the reaction was monitored by TLC. After work-up, triarylmethane was obtained as a sole product in high isolated yield (94%) (Table 1, entry 2). The structure of obtained triarylmethane **3aa** was confirmed by means of ^{1}H NMR, ^{13}C NMR, IR and Mass spectrometry analysis. We presumed that the reaction might have proceeded by the in situ formation of aldehydes which undergoes Friedel–Crafts alkylation reaction with arene to afford triarylmethane (Scheme 1). To support our assumption, an independent experiment was performed. When we performed the reaction of alcohol **1a** with catalytic amounts of TEMPO in combination with a stoichiometric amount of reoxidant iodosylbenzene (PhIO) in 5mL DCM at rt, we observed the formation of the corresponding aldehyde in good yield in 24 hours. The formed aldehydes in the reaction vessel, was subjected to undergo Friedel–Crafts alkylation with 1,2,4-trimethoxybenzene in conjugation with $BF_3.OEt_2$ which afforded triarylmethane **3aa** in 88% yield (Table 1, entry 1).

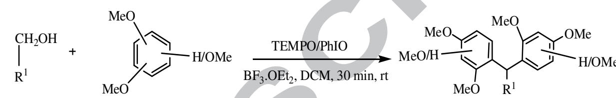
Table 1: Optimization of the reaction conditions.[a]

Entry	Oxidant (0.13equiv)/ Co-oxidant (1.2equiv)	Lewis acid (equiv)	Solvent	Time	Yield[b] (%)
1	TEMPO/PhIO	$BF_3.OEt_2$ (1.0)	DCM	24 h	88[c]
2	**TEMPO/PhIO**	**$BF_3.OEt_2$ (1.0)**	**DCM**	**30 min**	**94**
3	TEMPO/PhIO	$Sc(OTf)_3$ (2.0)	DCM	5 h	10
4	TEMPO/PhIO	$Bi(OTf)_3$ (2.0)	DCM	5 h	18
5	TEMPO/PhIO	$Bi(OTf)_3$ (2.0)	Toluene	30 min	68
6	TEMPO/PhIO	$BF_3.OEt_2$ (2.0)	THF	30 min	78
7	TEMPO/PhIO	$BF_3.OEt_2$ (2.0)	DCM	30 min	51
8	TEMPO/PhI(OAc)$_2$	TfOH (2.0)	EtOH	30 min	19
9	TEMPO/I_2	$Yb(OTf)_3$ (2.0)	DCE	30 min	37
10	TEMPO/NaOCl	$FeCl_3$ (2.0)	MeCN	30 min	21
11	-	$BF_3.OEt_2$ (2.0)	DCM	24 h	-

[a] All the reactions were conducted one pot with 4-(hydroxymethyl)-2,6-dimethoxyphenol **1a** (1 equiv) and 1,2,4-trimethoxybenzene **2a** (2 equiv) in the presence of PhIO (1.2 equiv), TEMPO (0.13 equiv) with $BF_3.OEt_2$ (2.0 equiv) in 5 mL DCM at room temperature. [b] Isolated yield. [c] in the sequential oxidation and Friedel–Crafts reaction.

Although we observed the formation of triarylmethane **3aa** in good yield by this sequential oxidation and Friedel–Crafts reaction process the longer reaction time was taken to complete both reactions. Conversely drastic reduction in reaction time was observed when we performed the reaction of alcohol **1a** and arenes **2a** in one pot in the presence of PhIO, TEMPO and $BF_3.OEt_2$. The reaction proceeded efficiently using **1a** (1 mmol) and **2a** (2 mmol) in the presence of PhIO (1.2 equiv), TEMPO (0.13 equiv) with $BF_3.OEt_2$ (2 equiv) and resulted in high yields (94 %) of the desired product in 30 min. (Table 1, entry 2). It is worthy to

Table 2: Synthesis of new substituted triarylmethanes.[a]



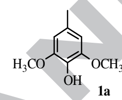
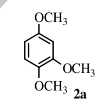
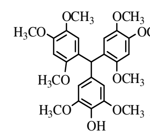
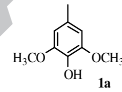
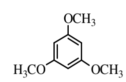
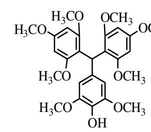
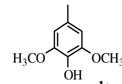
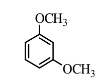
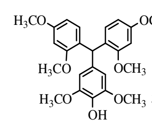
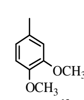
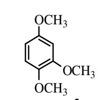
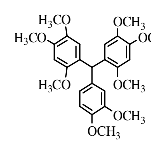
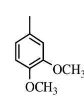
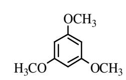
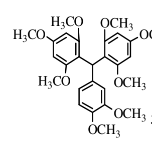
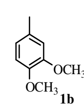
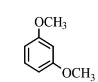
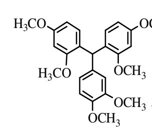
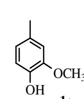
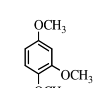
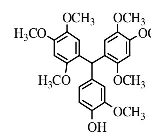
Entry	R[1]	Arene	Product	Yield[b](%)
1	 1a	 2a	 3aa	94
2	 1a	 2b	 3ab	94
3	 1a	 2c	 3ac	96
4	 1b	 2a	 3ba	95
5	 1b	 2b	 3bb	93
6	 1b	 2c	 3bc	96
7	 1c	 2a	 3ca	92

Table 2 cont.

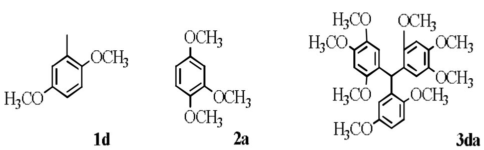
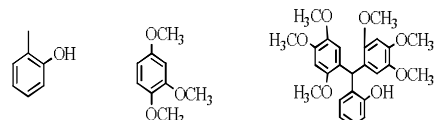
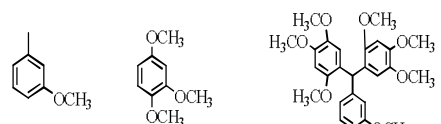
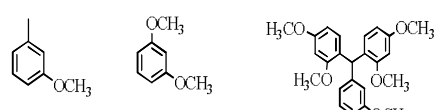
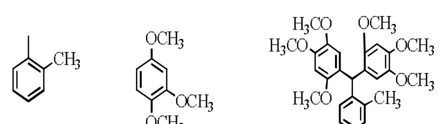
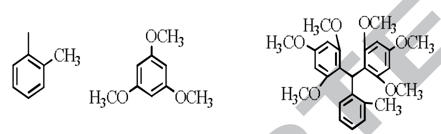
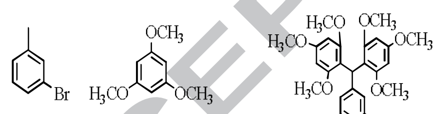
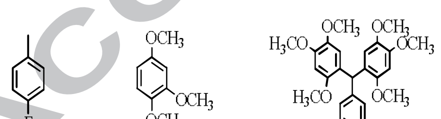
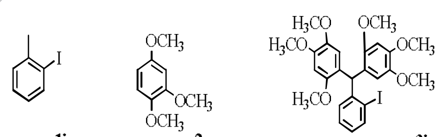
Entry	R1	Arene	Product	Yield[b](%)
8	 **1d**	**2a**	**3da**	96
9	 **1e**	**2a**	**3ea**	93
10	 **1f**	**2a**	**3fa**	94
11	 **1f**	**2c**	**3fc**	95
12	 **1g**	**2a**	**3ga**	92
13	 **1g**	**2b**	**3gb**	92
14	 **1h**	**2b**	**3hb**	86
15	 **1i**	**2a**	**3ia**	84
16	 **1j**	**2a**	**3ja**	86

Table 2 cont.

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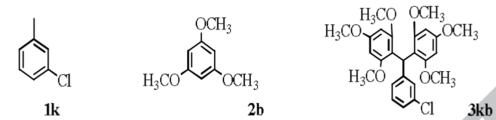
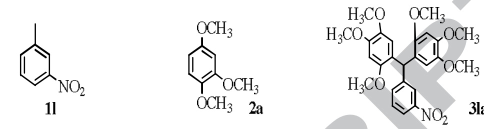
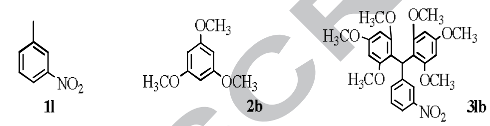
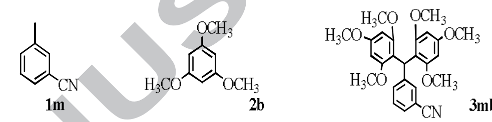
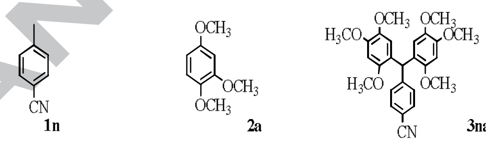
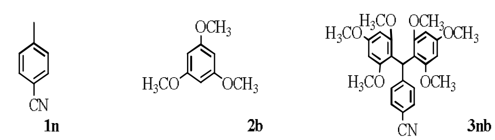
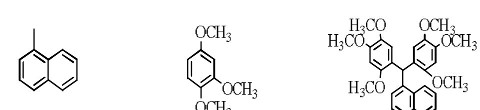
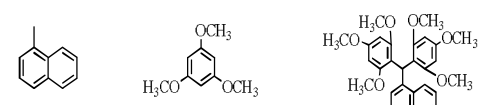
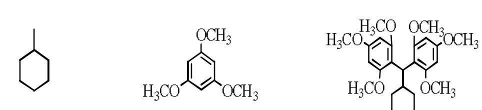
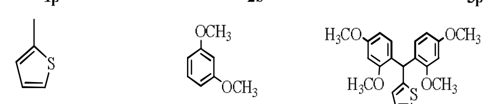
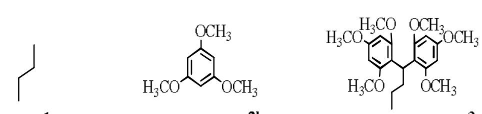
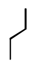
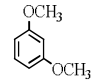
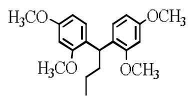
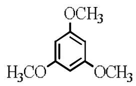
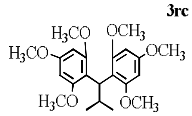
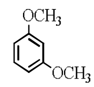
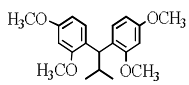
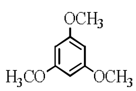
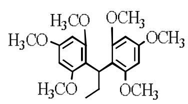
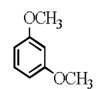
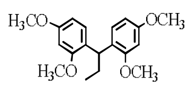
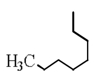
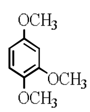
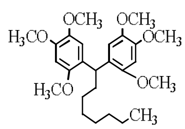
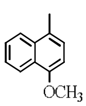
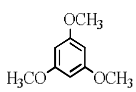
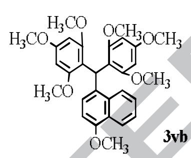
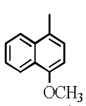
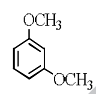
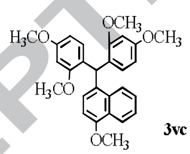
17	 **1k**	**2b**	**3kb**	85
18	 **1l**	**2a**	**3la**	82
19	 **1l**	**2b**	**3lb**	84
20	 **1m**	**2b**	**3mb**	87
21	 **1n**	**2a**	**3na**	84
22	 **1n**	**2b**	**3nb**	84
23	 **1o**	**2a**	**3oa**	92
24	 **1o**	**2b**	**3ob**	93
25	 **1p**	**2b**	**3pb**	79
26	 **1q**	**2c**	**3qc**	95
27	 **1r**	**2b**	**3rb**	81

Table 2 cond.

Entry	R^1	Arene	Product	Yield[b](%)
28	 **1r**	 **2c**	 **3rc**	83
29	 **1s**	 **2b**	 **3sb**	78
30	 **1s**	 **2c**	 **3sc**	84
31	 **1t**	 **2b**	 **3tb**	77
32	 **1t**	 **2c**	 **3tc**	80
33	 **1u**	 **2a**	 **3ua**	87
34	 **1v**	 **2b**	 **3vb**	92
35	 **1v**	 **2c**	 **3vc**	94

[a] All the reactions were conducted one pot with alcohol **1a-1v** (1 equiv) and methoxybenzene **2a-2c** (2 equiv) in the presence of PhIO (1.2 equiv), TEMPO (0.13 equiv) with $BF_3.OEt_2$ (2.0 equiv) in 5 mL DCM at room temperature. [b] Isolated yield.

note that, under our condition two processes, oxidation and Friedel–Crafts reactions were taking place rapidly in one pot which resulted into the high isolated yield of triarylmethane in short reaction time without isolation of the intermediates.

We then examined the catalytic activity of several Lewis acids such as $BF_3.OEt_2$, $Sc(OTf)_3$ (entry 3), $Bi(OTf)_3$ (entry 4), TfOH (entry 8), $Yb(OTf)_3$ (entry 9), $FeCl_3$ (entry 10) with co-oxidants like PhIO, $PhI(OAc)_2$, $FeCl_3$, NaOCl, I_2, tBuOCl and the results are incorporated in Table 1. These preliminary results indicated that $BF_3.OEt_2$ was the catalyst of choice for the oxidation as well as Friedel–Crafts reactions of alcohols with the TEMPO/PhIO in terms of yields and mildness.

Next the effect of solvent is also tested by screening various solvents like THF, toluene, DCM, CH_3CN, EtOH, DCE and the results are incorporated in Table 1. The study showed that DCM is the best choice of solvent for model reaction. The model reaction was also performed in the absence of TEMPO/PhIO but formation of the desired product was not observed even after stretching the reaction time up to 24 hours (Table 1, entry 11). With this study, we selected reaction of **1a** (1 mmol) and **2a** (2 mmol) in the presence of PhIO (1.2 equiv), TEMPO (0.13 equiv) with $BF_3.OEt_2$ (2 equiv) in DCM at rt as an optimized reaction condition to afford **3aa** (Table 1, entry 2).

With this established optimum condition, we were keen to explore the generality of the reaction with respect to various electron-rich arenes and substituted aromatic or aliphatic alcohols for the synthesis of the corresponding TRAMs and the results are outlined in the Table 2. We have studied the electronic effects of the substituents on the rate of the reaction and the mode of formation of triarylmethanes. To our delight, we found that, an electron-rich substituents (OH, OMe and Me) on the benzylalcohol proceeded smoothly with arenes to afford desired products **3aa-3gb** in excellent yields under optimized reaction condition (Table 2, entries 1-13). For example, the reaction of 2-hydroxybenzylalcohol with 1,2,4-trimethoxybenzene gave desired triarylmethane **3ea** in 93% isolated yield (Table 2, entry 9). Analogously 2-methylbenzylalcohol also reacted with 1,2,4-trimethoxybenzene and 1,3,5- trimethoxybenzene in the same fashion under standard reaction condition to give corresponding triarylmethanes **3ga, 3gb** in very good yields (Table 2, entries 12 and 13 respectively). Whereas the presence of electron-withdrawing substituents such as halides, cyano, nitro on the benzylalcohol ring decreases the yield of the corresponding products. For example the reaction of halogenated benzylalcohols with arenes also proceeded same way and afforded the corresponding products **3hb-3kb** in good yields (Table 2, entries 14-17). Other substituted benzylalcohols like 3-nitro, 3-cyano and 4-cyanobezylalcohols also participated under same reaction conditions to furnish corresponding products **3la-3nb** in good to moderate yields (Table 2, entries 18-22).

The efficiency of the reaction was further strengthened by the participation of hindered alcohol like naphthalen-1-ylmethanol **1o** and 4-methoxynaphthalen-1-ylmethanol **1v** which also underwent smooth reaction with arenes and resulted in high yield of corresponding products **3oa, 3ob, 3vb and 3vc** (Table 2, entry 23, 24, 34 and 35). The synthesis of heteroaryldiarylmethane was also explored. As can be seen in Table 2, the 2-(bis(2,4-dimethoxyphenyl)methyl)thiophene **3qc** was obtained in excellent yields on treatment of thiophen-2-ylmethanol **1q** with 1,3-dimethoxybenzene **2c** (Table 2, entry 26). To further extend the scope of the reaction, we intended to study the reaction of cyclic alcohols with arenes. In this regard, we treated cyclohexylmethanol with 1,3,5- trimethoxybenzene to afford the diarylalkanes **3pb** in acceptable yield (Table 2, entry 25). It was found that even butan-1-ol **1r**, 2-methylpropan-1-ol **1s**, propan-1-ol **1t** and Octan-1-ol **1u** as fairly sterically demanding precursors reacted with corresponding arenes in similar fashion to afford the respective diarylalkanes in acceptable yields (Table 2, entries 27-33). It is important to note that, the developed method is amenable for the synthesis of different functionalized triarylmethanes and all the compounds synthesized in this work are not prepared earlier. We believe that this protocol may be useful for the rapid preparation of library of new compounds desirable in drug discovery program and material sciences.

In conclusion, we have demonstrated efficient synthesis of new diversely functionalized triarylmethanes from alcohol by one pot oxidation, Friedel–Crafts reactions process using PhIO-TEMPO with $BF_3.OEt_2$ in DCM at rt under mild reaction conditions. The developed protocol is a novel and operationally simple which provide direct access for the synthesis of triarylmethane scaffolds from alcohol and arene. Moreover the developed method is applicable for variety of aromatic, aliphatic, heteroaromatic and cyclic alcohols and arenes. Shorter reaction time, mild reaction condition, good yields and wide scope of substrates are the significant features of this protocol. Further investigations on the scope, applications and limitations of this method are in progress in our laboratory and results will be published elsewhere in due course.

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