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COMMUNICATION

Tritylium assisted iodine catalysis for the synthesis of unsymmetrical triarylmethanes

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The combined Lewis acid catalytic system, generated from molecular iodine and tritylium tetrafluoroborate effectively catalyzed the Friedel–Crafts (FC) arylation of diarylmethyl sulfides providing an efficient access to various unsymmetrical triarylmethanes. The addition of tritylium and iodine created a more active catalytic system to promote the cleavage of sulfidic C–S bonds.

Unsymmetrical triarylmethanes¹ represent an important class of organic molecules due to their occurrence in bioactive natural products (such as muchimangin G–J,^{1f} melanervin^{1k}) and pharmaceuticals^{1g–i} (Figure 1).

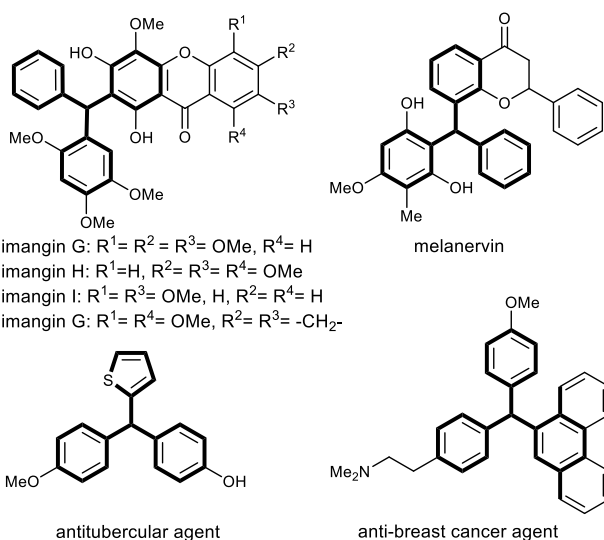


Figure 1 Representative examples containing triarylated methanes.

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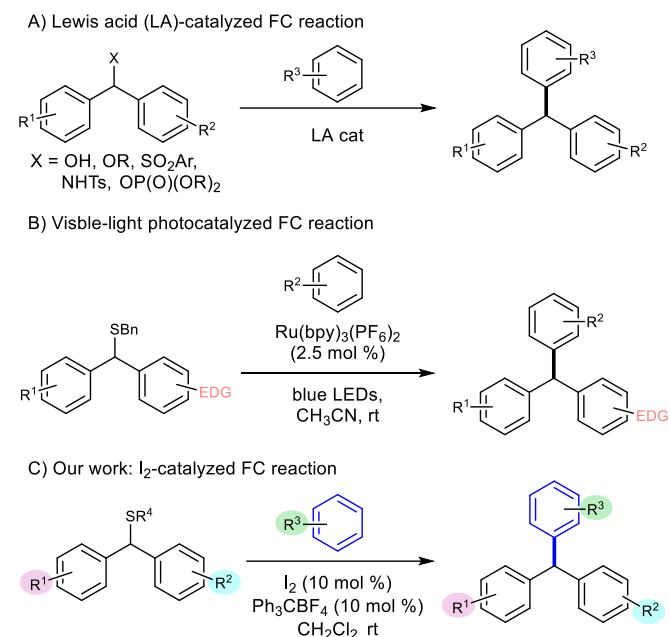
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Moreover, the molecules containing a triarylmethane motif exhibit interesting photophysical properties and have also found numerous applications mainly in dyes, fluorescent probes and optoelectronic devices.^{1a,e} Accordingly, a number of efforts have been conducted to develop efficient catalytic methods for their preparation. The most frequently employed approach relies on Friedel–Crafts (FC) arylation of unsymmetrical diarylmethanol, diarylmethyl ethers, diarylmethyl sulfones, diarylmethyl sulfonamides, diarylmethyl carbamates or diarylmethyl phosphates in the presence of Brønsted or Lewis acids (A, Scheme 1).^{2,3} Although this traditional method is straightforward and convergent, it suffers from limitations such as harsh reaction conditions that include high acidity and/or temperature. In this regard, we have recently disclosed an efficient visible-light photoredox catalyzed FC reaction of readily accessible diarylmethyl benzylsulfides⁴ leading to various triarylalkanes under mild condition (B, Scheme 1).^{5–7} However, this photocatalyzed desulfurative arylation was severely restricted to electron-rich diarylmethyl benzylsulfides. Even the neutral diphenylmethyl alkylsulfides produce only trace of triarylated products (15% yield). The presence of at least one electron-donating group on one of aromatic rings of **1** was essential for the C–S bonds cleavage reaction to occur. In this context, we became interested in developing an alternative catalytic approach that could overcome these limitations regarding C–S cleavage of electron neutral and electron-deficient diarylmethyl alkylsulfides.

Over the past decade, molecular iodine has emerged as a cheap and non-toxic catalyst in various metal-free organic transformations.^{2g,8} Among them, iodine-promoted functionalization of sulfenic C–S bonds is an efficient method for constructing C–C and C–heteroatom bonds. For instance, iodine has been widely used for the anomeric activation of thioglycosides.⁹ In 2014, our group has developed iodonium-catalyzed chemoselective C–S bond cleavage of α -carbamoylsulfides to generate an *N*-acyliminium ion intermediates which can undergo addition of various nucleophiles to form α,α -disubstituted amines.⁷ In light of this

work, we wondered whether iodine could be an effective catalyst to perform the desulfurative arylation of diarylmethyl sulfides. Herein, we report an efficient process for the synthesis of various triarylmethanes based on a catalyst combination of iodine and trityl salt. Noteworthy, the presence of electron donating group is not required and weakly electron withdrawing are tolerated on diarylmethyl sulfides, broadening the applicability of the FC reaction (C, Scheme 1).

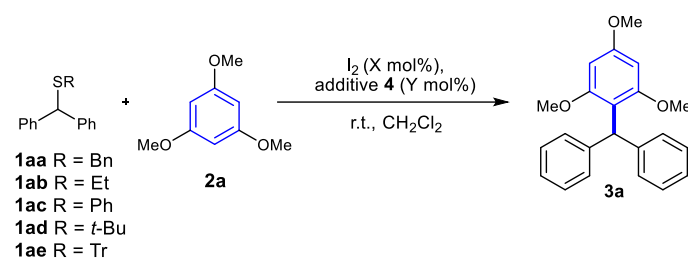
contrast, *S*-phenyl (**1ab**, entry 13) and *S*-ethyl (**1ac**, entry 14) derivatives gave similar results, with 87% yield of **3a**. Slightly better yields were observed with the *S*-*tert*-butyl (**1ad**, entry 15). Further studies revealed that the Lewis acidity of triaryl salt affected significantly the yield, with **4c** being optimal. When I₂ along with cyclic salts **4f** and **4g** were employed as a dual catalyst, **3a** was isolated in lower yield (entries 19 and 20). Electron rich salts either reduced the yield of **3a** or completely inhibited the reaction (entries 17 and 18).



Scheme 1 Syntheses of triarylmethanes via FC-reaction.

To test the feasibility of this hypothesis, we carried out the FC reaction of 1-benzylthio(methylene)dibenzene (**1aa**) with 1,3,5-trimethoxybenzene (**2a**) in the presence of I₂ in dichloromethane at room temperature (Table 1). As a result, the desired FC product **3a** was formed in moderate yield (32% yield, Table 1, entry 1). Modification of the catalyst loading did not really improve the result due to partial iodination of **2a**. The use of a base (such as Na₂HPO₄ or Na₂CO₃) in order to accelerate the rearomatization step did not lead to any improvement of the reaction (entries 3-4). In an attempt to improve the catalytic efficiency, we then turned our attention to the concept of combined Lewis acids introduced by Yamamoto.^{10,11} Addition of a Lewis acid may enhance the Lewis acid character of I₂ and thus favoring the overall process.^{9g,h} To our delight, a significant improvement was found when the reaction was conducted in the presence of 10 mol% of tritylium tetrafluoroborate and gave the desired product in 87% yield (entry 5).¹² Decreasing the amount of I₂ as well as **4c** led to a diminished yield (entries 6-9). The use of other solvents such as acetonitrile, and toluene resulted in slightly lower yields (entries 10-11). When *i*-PrOH was used as solvent, the undesired *O*-alkylated product was formed as major product (entry 12). It was observed that the nature of the substituent on the *S* atom played an important role in the present transformation. No reaction occurred when sterically hindered *S*-trityl **1ae** was used (entry 16). In sharp

Table 1 Optimization of reaction conditions

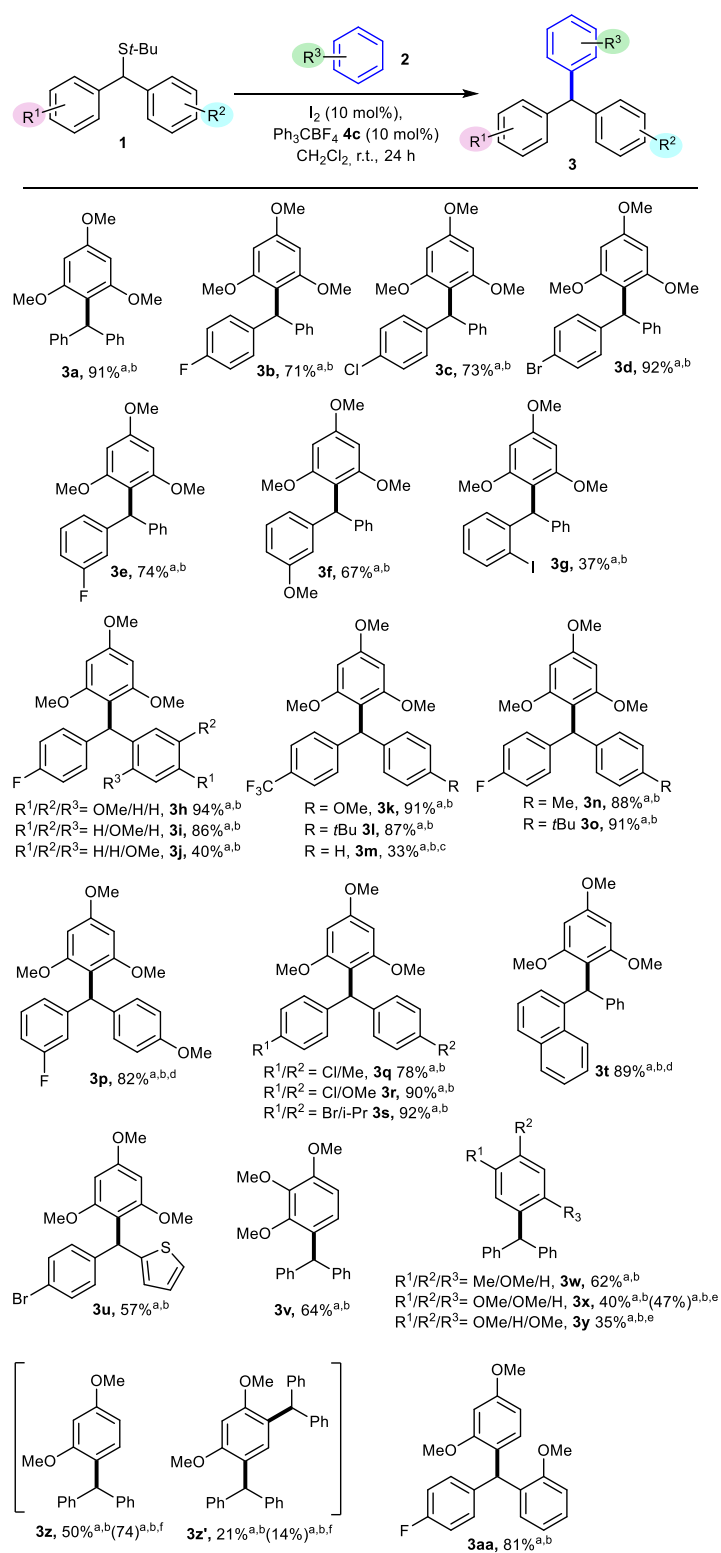


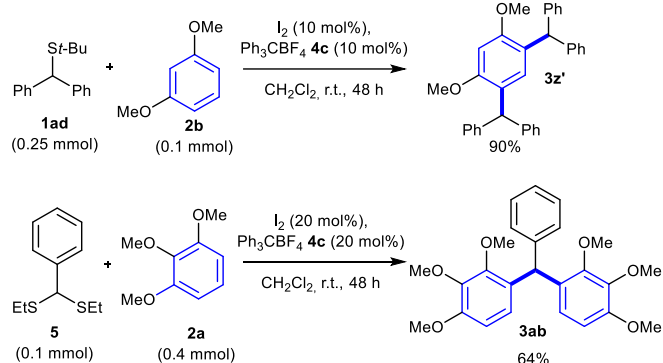
Entry	1	X	Additive	Y	Yield (%) ^b
1 ^a	1aa	10	–	–	32
2 ^a	1aa	100	–	–	51
3 ^{a,c}	1aa	10	Na ₂ HPO ₄ (4a)	10	16
4 ^{a,c}	1aa	10	Na ₂ CO ₃ (4b)	10	34
5 ^d	1aa	10	Ph ₃ CBF ₄ (4c)	10	87
6 ^d	1aa	5	4c	5	59
7 ^d	1aa	10	4c	7.5	65
8 ^d	1aa	10	4c	5	58
9 ^d	1aa	10	4c	2.5	35
10 ^{d,e}	1aa	10	4c	10	78
11 ^{d,f}	1aa	10	4c	10	75
12 ^{d,g}	1aa	10	4c	10	18
13 ^d	1ab	10	4c	10	87
14 ^d	1ac	10	4c	10	87
15 ^d	1ad	10	4c	10	91
16 ^d	1ae	10	4c	10	0
17 ^d	1ac	10	<i>p</i> -MeOC ₆ H ₄ Ph ₂ CBF ₄ (4d)	10	<10
18 ^d	1ac	10	(<i>p</i> -MeOC ₆ H ₄) ₃ CBF ₄ (4e)	10	0
19 ^d	1ac	10		10	9
20 ^d	1ac	10		10	55

^a Reaction conditions: **1** (0.1 mmol) and 1,3,5-trimethoxybenzene **2a** (0.15 mmol), I₂ (X x 0.01 mmol) in 1 mL of CH₂Cl₂ at r.t. for 24 hours. ^b Isolated yield after column chromatography. ^c With 1 equiv. of base. ^d Reaction conditions: **1** (0.1 mmol) and 1,3,5-trimethoxybenzene **2a** (0.15 mmol), I₂ (X x 0.01 mmol) and additive (Y x 0.01 mmol) in 1 mL of CH₂Cl₂ at r.t. for 24 hours. ^e Reaction in CH₃CN. ^f Reaction in toluene. ^g Reaction in isopropanol.

With the optimized conditions set, the substrate scope of this FC reaction was investigated. A range of diarylmethyl sulfides was tested with 1,3,5-trimethoxybenzene (**2a**). Diarylmethanes with electron-withdrawing substituents (such as F, Cl, and Br) at the *para*-position of the benzene ring gave the desired triarylmethanes **3b-3d** in excellent yields. Remarkably, this catalytic system proved to be efficient for diarylmethanes bearing substituents at the meta position (such as F, **3e** or OMe, **3f**), which were totally unreactive in our previous photocatalyzed protocol.^{5a} A lower yield **3g** was obtained in the case of *ortho*-substituted sulfide, most likely due to unfavorable steric factors. We also found that, contrary to our previous studies,^{5a} substrate combining an electron rich arene with electron poor one participated smoothly in this reaction. For instance, the presence of F, Cl, Br and CF₃ substituents at the *meta*- and *para* position led to the formation of triarylmethane products **3h-3l** and **3n-3s** in excellent yields. The reaction with diarylmethyl sulfides bearing only a CF₃ group gave only trace of product. However, we were pleased to find that when the reaction was carried out with 1 equiv of I₂, the desired product **3m** was isolated in 33% yield. A sterically more demanding 1-naphthyl group afforded the desired product **3t** in 89% yield. The presence of heteroaromatic group such as thiophene was also compatible, providing an efficient access to antitubercular agents.¹⁸ Then, other electron-rich arenes **2** were evaluated. 1,2,3-Trimethoxybenzene underwent nucleophilic addition to **1ad** affording **3v** in 64% yield. To our satisfaction, this condition was also applicable to the less-electron-rich arenes. For instance, 2-methylanisole and 1,2-dimethoxybenzene successfully produced the corresponding triarylmethane **3w** and **3x** in descent yield. 1,4-Dimethoxybenzene was also a competent reaction partner requiring nevertheless to heat the reaction at 50 °C to get adduct **3y** in low but significant yields. 1,3-Dimethoxybenzene proved to be more reactive. However, depending on the structure of **1**, the mono-arylation product or a mixture of mono- and bis-arylation products were formed. Selective monoarylated product **3aa** was formed from *ortho*-substituted aryl tert-butyl sulfide, while a separable mixture of mono- and diarylated products **3z** and **3z'** was obtained from **1ad**. Pleasingly, increasing the amount of **1ac** to 3 equiv. resulted in the predominant formation of mono-arylated product **3z**, isolated in 74% yield. Interestingly, clean double FC could also be achieved (Scheme 3). As such, when arene **2b** was used as limiting reagent (0.4 equiv) and opposed to thioether **1ad** under otherwise identical conditions, compound **3z'** was exclusively formed and could be isolated in 90% yields. Reaction with other less nucleophilic arenes such as anisole and toluene, even an excess failed to produce the corresponding triarylmethanes.

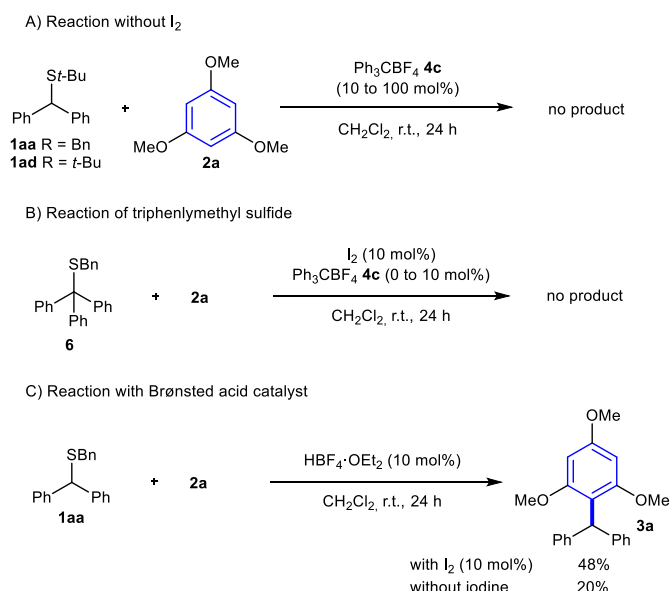
To our delight, the dithioacetals **5** were also competent reaction partners under the developed conditions allowing for double thioether displacement. Indeed, 2,2'-(phenylmethylene)bis(1,3,5-trimethoxybenzene) **3ab** was easily synthesized in 64% yield from phenylbis(ethylthio)methane.¹³ However in this case, full conversion was only achieved by adding a second batch of combined catalyst (I₂ and **4c**, 10 mol%, respectively) after 24 hours.





Scheme 3 Syntheses of triarylmethanes via double FC-reaction.

To gain an insight into the reaction mechanism, control experiments were performed. The use of I_2 catalyst appeared to be critical for the C-S bond cleavage reaction. Indeed, when the reaction was performed without I_2 , there was no formation of the desired FC product, even if a stoichiometric amount of the trityl salt was added (A, Scheme 4). Thus, this result indicates that the Lewis acid carbocation only assists I_2 to promote the C-S bond cleavage. In addition, arylation of trityl benzylsulfide **6** did not proceed with I_2 catalyst or combined $I_2/4c$ catalysts (B, Scheme 4).

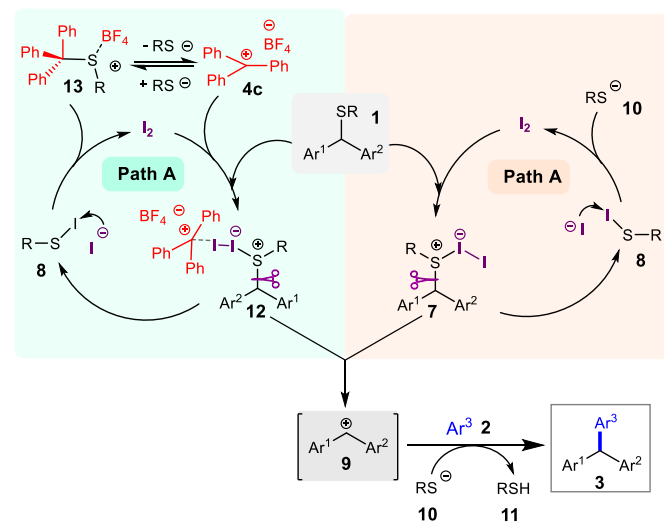


Scheme 4 Control experiments.

On the basis of the results described above and previous works,^{7,8,9} two plausible mechanisms are proposed as outlined in Scheme 5. In absence of trityl cation, the sulfur atom of **1** is initially attacked by the iodine, leading to the formation of cationic iodosulfonium intermediate **7**. Subsequently, the salt **7** undergoes an elimination to form the sulfenyl iodide **8** and

carbocation **9**. The sulfenyl iodide **8** can then undergo nucleophilic addition of iodine to regenerate iodine catalyst and produce thiolate **10**. The carbocation **9** can react with electron rich arene **2**, followed by hydrogen atom abstraction mediated by thiolate, furnishing the desired FC products **3** and thiol **11**. On the other hand, when tritylium tetrafluoroborate **4c** is added in the reaction, the cation may activate the iodosulfonium ion through a possible Lewis acid assisted Lewis acid model **12**, thus facilitating the cleavage of C-S bond. Then, based on Yoshida's work,¹⁴ the triphenylmethyl thiolate **13** generated during this step can be in equilibrium with thiolate **10** and tritylium tetrafluoroborate **4c**, and thus allowing the regeneration of co-catalyst. It is also conceivable that electrophilic sulfonium ion **12** may directly act as a Lewis acid to promote the formation of carbocation **9**.

The observation of characteristic odor of thiol at the end of the reaction in both catalytic conditions seems to support our proposed catalytic cycle.¹⁵ In addition, results from table 1 (entries 16 to 19) definitively established that the nature of the cation plays an important role in the reaction. Nevertheless, at the present stage, we cannot exclude the pathway involving Brønsted acid catalysis (HBF_4). However, when $HBF_4 \cdot OEt_2$ was used instead of **4c**, the triarylated product was isolated in lower yield (C, Scheme 3). For the control experiment, in absence of iodine, lower amount of product **3a** was found. This supports the possibility of Lewis-acid assisted iodine catalysis.



Scheme 5 Proposed Mechanism.

Conclusions

In summary, we have developed an efficient synthesis of unsymmetrical triarylmethanes using a Lewis acid assisted Lewis acid catalyst system under mild conditions. We have demonstrated that iodine in the presence of catalytic amount of trityl cation was efficient catalyst for the FC arylation of diarylmethyl sulfides. This novel catalytic protocol provides a

simple and efficient entry to unsymmetrical triarylmethanes in high yields. The substitution patterns readily achievable by this Lewis acid-assisted-Lewis acid approach complement our previous photocatalyzed method.^{5a}

Conflicts of interest

There are no conflicts to declare.

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