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An organocatalytic method for the synthesis of some novel xanthene derivatives by the intramolecular Friedel–Crafts reaction†

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An efficient organocatalytic method for the synthesis of new substituted 9-arylxanthenes (**2a–2u**) starting from diarylcarbinol compounds with an arenoxy group (**1a–1u**) has been developed using the intramolecular Friedel–Crafts reaction. The substrates were prepared in two steps by Ullmann-type coupling and then Grignard reaction. Some organic Brønsted acids were studied as catalysts (**3a–3g**) in the intramolecular Friedel–Crafts alkylation reaction for the first time. *N*-triflylphosphoramide (**3g**) provided the synthesis of some novel substituted 9-arylxanthenes with excellent yields at room temperature within 15 minutes.

Introduction

Xanthenes and their derivatives have biological characteristics; they are used against inflammatory diseases and to treat illnesses caused by viruses and bacteria.[1] Thus, xanthenes are pharmaceutically active and used in photodynamic therapy.[2] They are used also as fluorescent materials or dyes and molecular switches, which occur in natural products.[3] The structure of xanthenes being straight and strict is advantageous; they are used as linkers in peptide syntheses and in the synthesis of unnatural amino acids.[4] The HIV-1 nucleocapsid protein has around 2000 small molecules (the NCI Diversity Set), in which 26 of them are active inhibitors and five of them were reported to have a xanthenyl ring.[5]

Many synthetic routes to obtain xanthene derivatives have been reported.[6] The most important examples are the iron-catalysed cascade benzylation–cyclisation of phenols,[7] Pd-catalyzed cyclisation of polycyclic aryltriflate esters,[8] Lewis acid-catalysed cyclisation of salicylaldehydes and cyclohexenones or tetralones,[9] and the condensation of 2-naphthol and numerous aryl aldehydes.[10] The synthesis of substituted 9-arylxanthenes using the tandem arylation/Friedel–Crafts reaction of *O*-hydroxy bisbenzylic alcohols with diaryliodonium salts was recently reported by Wang *et al.*[11] Another study concerning the synthesis of substituted 9-arylxanthenes reported an $Sc(OTf)_3$-catalyzed domino reaction.[12] Additionally some nitrogen or sulphur-containing xanthene derivatives, which may be used especially as antitumor agents, were synthesized in previous works.[13]

We have determined that the most suitable method to obtain 9-arylxanthenes is the intramolecular Friedel–Crafts alkylation (FCA) of proper alcohols because the literature on arylation using an FCA protocol has recently started to see new developments. In particular, arylation that does not use any metals has became a very popular topic for avoiding the disadvantages of organometallic chemistry, which poses high cost, uses toxic materials, and poses difficulties during purification.[14] These new methods have opened new doors using mild reaction conditions and employing cheap and less toxic catalysts.[15]

In this field, the development of new π-activated alcohols has increasing importance over the development of organohalides, which are more toxic and require harsh conditions.[16] Thus, Lautens *et al.* reported an efficient synthesis of the targeted *cis*-hexahydrobenzophenanthridines from tetralins, which are very easy to obtain. The reaction included π-activated alcohols produced using intramolecular FCA in the presence of Lewis acids.[17] An important work which realised cyclization of π-activated alcohols by $Bi(OTf)_3$-catalyzed intramolecular FCA was reported by Rueping *et al.*[18] To synthesise substituted 9-arylxanthenes, another Lewis acid-catalysed intramolecular FCA procedure was carried out by Panda and co-workers in 2009.[19] In this study, they used well-known FCA catalysts and some Lewis acids like conc. H_2SO_4, anhyd. $AlCl_3$, $FeCl_3$, $Sc(OTf)_3$ and TfOH. Among the catalysts studied, $FeCl_3$ gave the best result with 91% yield in dry CH_2Cl_2 at room temperature.

According to the literature, although there are reports of hydroarylation reactions of activated alkenes using FCA with Brønsted acids such as diphenyl hydrogen phosphate as the catalysts,[20] there are no reports of intramolecular FCA using organic Brønsted acids as the catalysts instead of Lewis acids. Considering the recent reports, non-chiral, organic Brønsted "super-acids" are comparable or even better than Lewis or inorganic Brønsted acids.[21] Furthermore, the organic Brønsted acids are similar to Lewis acids as they are usually stable against

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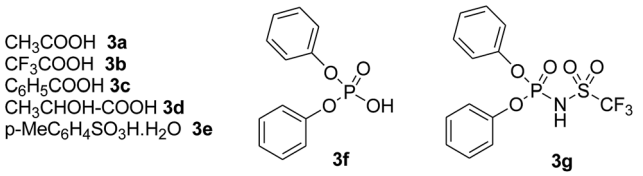


Fig. 1 Structures of used organic Brønsted acids.

oxidizing ambience or humidity, and they can be easily handled and are stable over a long period of time.[22] Recently, in order to create new types of super acids or super acid catalysts, new Brønsted acids including $=NSO_2CF_3$ or $=NSO_2F$ groups were synthesized because these groups increase the acidity substantially.[23] It is understood that triflate groups in particular, among all acidic compounds, increase the acidity significantly. Due to *N*-triflate groups having lower pK_a values than normal organic acids,[24] the more acidic *N*-triflate groups can catalyze the reactions with generally better yields and in less time. As an example of an organic Brønsted acid, *N*-triflylphosphoramide (**3g**) (Fig. 1) was used in some previous reports. A study on this subject includes the preparation of 1,3-dioxolane-4-ones starting from α-hydroxy acids and aldehydes with the use of **3g**.[25] Another example reports a transformation, which has merged the Ugi reaction and Houben–Hoesch cyclisation in the presence of **3g**.[26] In that report, after several Brønsted and Lewis acids were examined, they found that the acid-promoted reaction is effective in the synthesis of many 3-aminoindole molecules using **3g** with high yields and under mild conditions.

In this study, to develop an effective and economic organocatalytic FCA protocol to synthesize some novel substituted arylxanthenes under mild conditions, we explored some organic Brønsted acids as catalysts (**3a–3g**) in the intramolecular FCA reaction for the first time.

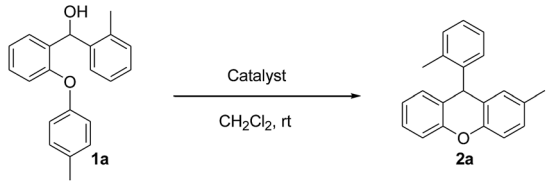
We obtained arylxanthenes with excellent yields using *N*-triflylphosphoramide (**3g**). Among all synthesised substituted arylxanthenes, seventeen of the compounds are novel, and the others, **2i**,[27] **2j**,[27] and **2k**,[19] have been synthesised previously with different methods.

Results and discussion

Our starting materials were synthesised in two steps involving metal-free Ullmann coupling[28] and then Grignard reaction. Finally, we obtained diarylcarbinol compounds including an arenoxy group as the starting material with very high yields (95–100%). All starting compounds (diarylcarbinols) are novel except **1k**.[19]

We have chosen carbinol **1a** in order to examine the catalysts and carry out initial optimisation experiments of the intramolecular FCA. Therefore, we explored the different organic Brønsted acids as catalysts for the intramolecular FCA reaction (Table 1). The catalysts we used were acetic acid (**3a**), trifluoroacetic acid (**3b**), benzoic acid (**3c**), L-lactic acid (**3d**), *p*-toluenesulfonic acid (**3e**), diphenyl hydrogen phosphate (**3f**), and *N*-triflylphosphoramide (**3g**). Firstly, the solution of **1a** and acid catalyst (**3a–3g**) in dichloromethane was stirred at 25 °C until the starting material was consumed. In this way, the different Brønsted acids were compared against each other for the intramolecular FCA reaction.

Table 1 Screening of catalysts for intramolecular FCA of **1a**[a]



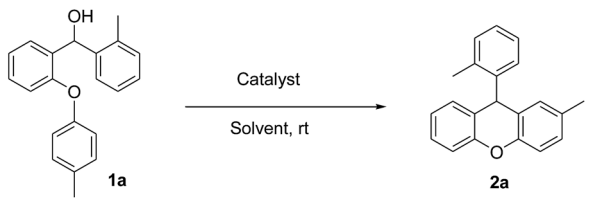
Entry	Catalyst (10% equiv.)	Time	Yield[b] (%)
1	None	24 h	nr
2	**3a**	24 h	2
3	**3b**	2 h	65
4	**3c**	24 h	nr
5	**3d**	24 h	nr
6	**3e**	2 h	70
7	**3f**	24 h	5
8	**3g**	2 h	78

[a] Condition: **1a** (0.1 mmol) and catalyst (10% equiv.) in CH_2Cl_2 (2.5 mL) were stirred at room temperature. [b] Yield of isolated product.

Moderate yields were obtained using **3b** and **3e** catalysts (Table 1, entries 3 and 6). **3a** and **3f** gave very low yields (Table 1, entries 2 and 7) despite the long reaction times. Benzoic acid (**3c**) and L-lactic acid (**3d**) did not react at all (Table 1, entries 4 and 5). As expected, no conversion was observed in the absence of the catalyst (Table 1, entry 1). Interestingly, the best result was achieved when 10 mol% of **3g** was used to obtain the desired product **2a** in 78% yield within 2 hours (Table 1, entry 8).

In the second phase, we examined the effect of the solvent on the intramolecular FCA reaction **1a** using the best catalyst **3g**

Table 2 Screening of solvents for intramolecular FCA of **1a**[a]



Entry	Catalyst	Solvent	Cat. amount (mol%)	Time	Yield[b] (%)
1	**3g**	CH_2Cl_2	10	2 h	78
2	**3g**	Benzene	10	2 h	13
3	**3g**	Toluene	10	2 h	17
4	**3g**	$CHCl_3$	10	2 h	91
5	**3g**	THF	10	2 h	11
6	**3g**	CH_3CN	10	15 min	>99
7	**3g**	CH_3CN	5	15 min	85
8	**3b**	CH_3CN	10	15 min	85
9	**3e**	CH_3CN	10	15 min	87

[a] Condition: **1a** (0.1 mmol) and catalyst (10% mmol) in solvent (2.5 mL) were stirred at room temperature. [b] Yield of isolated product.

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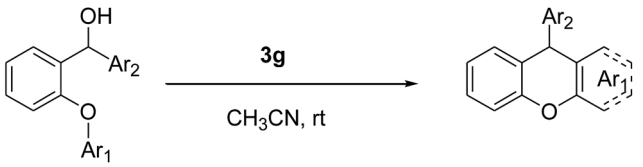
(Table 2). Performing the reaction in several solvents gave interesting results. The intramolecular FCA reaction of **1a** with CH_2Cl_2 and $CHCl_3$ showed good yields with side products. While THF, benzene and toluene gave very low yields, CH_3CN provided the best result with 99% yield and no side reaction when using 10 mol% of **3g** (Table 2, entry 6). Also we observed a lower yield when using 5 mol% of the catalyst (Table 2, entry 7). Additionally, the other best catalysts **3b** and **3e** were also tested in CH_3CN. However, lower yields of 85 and 87% were obtained in these reactions (Table 2, entries 8 and 9).

In parallel to our work, it was shown in previous studies that CH_3CN is a good discriminating solvent for strong acids, because of its weak basicity and weak solvating power to anions.[23] Therefore we found that performing the cyclisation by intramolecular FCA with 10 mol% **3g** in CH_3CN at room temperature for 15 min showed excellent results for obtaining substituted 9-arylxanthene derivatives. After these optimisation reactions, we looked at the differences when we used different aromatic hydroxy compounds (Ar_1) in the Ullmann coupling reaction. We used different substituent aryl groups including Me, Br, Cl, F, CN, NO_2 *etc.* (Ar_1) during this reaction step and synthesized diaryl compounds that have these substituents on the arenoxy group in order to investigate the effect of the different functional groups on the intramolecular FCA. The other aryl group *p*-methoxy phenyl (Ar_2) was chosen for use in all substrates for these experiments. The effect of the functional groups on Ar_1 screening reactions are summarized in Table 3.

As can be seen in Table 3, electron donating groups like methyl and naphthyl groups (entries 1 and 2) increase the rate of the electrophilic substitution. Therefore, their yields are excellent during intramolecular FCA. When we look at halogen containing electron withdrawing groups, although they are weakly deactivating, their yields are very good, especially for the 3-Br substituent (Table 3, entry 3). As expected, the other electron withdrawing groups nitro and cyano gave very low yields

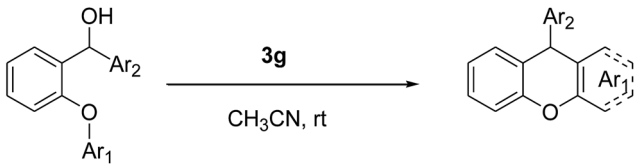
Table 3 The effect of the functional groups on Ar_1 for intramolecular FCA[a]



Entry	Product	Ar_1	Ar_2	Yield[b] (%)
1	**2e**	2-MeC_6H_4	4-$MeOC_6H_4$	96
2	**2k**	2-Np	4-$MeOC_6H_4$	>99
3	**2p**	3-BrC_6H_4	4-$MeOC_6H_4$	98
4	**2r**	4-ClC_6H_4	4-$MeOC_6H_4$	95
5	**2s**	4-FC_6H_4	4-$MeOC_6H_4$	75
6	**2t**	4-CNC_6H_4	4-$MeOC_6H_4$	5
7	**2u**	4-$NO_2C_6H_4$	4-$MeOC_6H_4$	4

[a] Condition: carbinol (0.1 mmol) and **3g** in CH_3CN (2.5 mL) were stirred at room temperature. [b] Yield of isolated product.

Table 4 The effect of the functional groups on Ar_2 for intramolecular FCA[a]



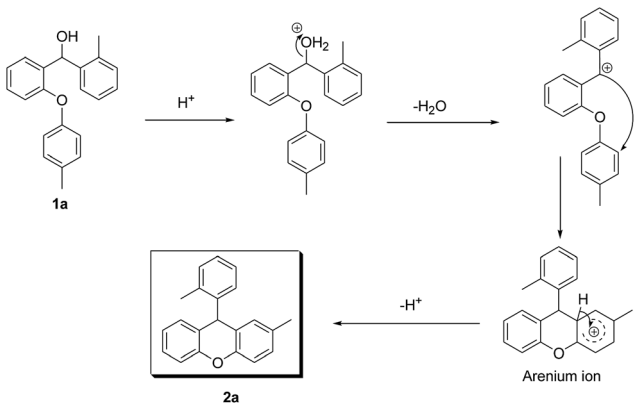
Entry	Product	Ar_1	Ar_2 (or R)	Yield[b] (%)
1	**2a**	4-MeC_6H_4	2-MeC_6H_4	>99
2	**2b**	3-MeC_6H_4	4-MeC_6H_4	>99
3	**2c**	2-MeC_6H_4	2-MeC_6H_4	95
4	**2d**	2-MeC_6H_4	4-MeC_6H_4	96
5	**2e**	2-MeC_6H_4	4-$MeOC_6H_4$	96
6	**2f**	2-MeC_6H_4	2-Np	88
7	**2m**	3-MeC_6H_4	$C_{15}H_{31}$	73
8	**2n**	4-MeC_6H_4	2-Thienyl	79

[a] Condition: carbinol (0.1 mmol) and **3g** (10% mmol) in CH_3CN (2.5 mL) were stirred at room temperature. [b] Yield of isolated product.

(Table 3, entries 6 and 7), because of their strongly deactivating effect in the electrophilic aromatic substitution reactions.

Following this, various arylmagnesium bromides (Ar_2) were used in the Grignard reaction step. When Ar_1 was kept as an Me group with different positions and Ar_2 (or R) was changed with different groups and positions (Table 4), we observed that CH_3 and CH_3O groups showed almost the same yield with 99–95% (entries 1–5). In addition, the position of the Me group on the Ar_1 did not significantly affect the reaction. The naphthyl and thienyl groups resulted in slightly lower yields of 88 and 79% (Table 4, entries 6 and 8). When a long chain alkyl group was used instead of Ar_2, the yield was only 73% (Table 4, entry 7). Consequently, the Ar_1 group is more effective than the Ar_2 group in this reaction (FCA) because the Ar_1 group is part of the mechanism of the reaction.

The well known SN1 type intramolecular Friedel–Crafts alkylation mechanism can be shown for our compounds (Scheme 1).



Scheme 1 Proposed Brønsted acid-mediated intramolecular Friedel–Crafts alkylation mechanism of **1a**.

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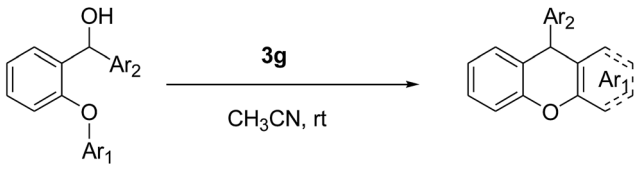
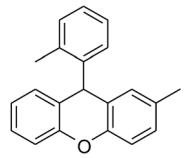
In the proposed mechanism, after protonation of the starting material **1a**, a water molecule leaves and the carbocation anion is formed. Following this, the carbocation anion attacks the other aryl functional group and the arenium ion is produced. Finally, a proton is lost from the arenium ion and the cyclisation is completed to give the desired product **2a**. The new ring formed is very stable because it is six membered.

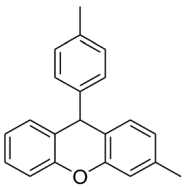
In addition, although the mechanism that we have proposed is an SN1 type Friedel–Crafts mechanism, an *ortho*-quinone-methide (*o*-QM) intermediate may also be composed in the presence of the acidic media. Recently, Rueping *et al.* studied

Table 5 Scope of substrates for intramolecular FCA of **1a–1u** and their yields[ab]



1a-1u **2a-2u**


2a >99%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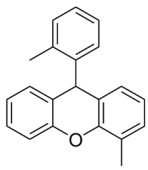
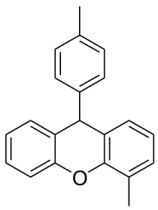

2c 95%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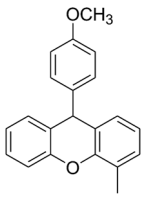

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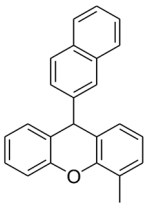
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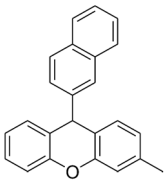
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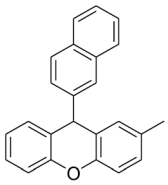
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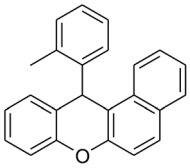
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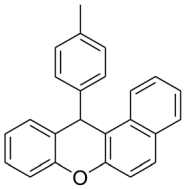
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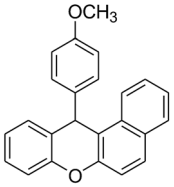

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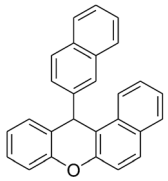
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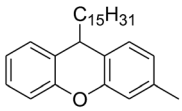

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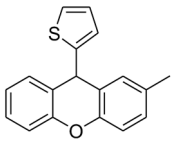

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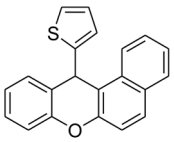

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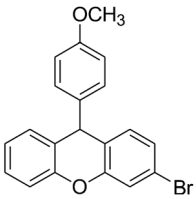

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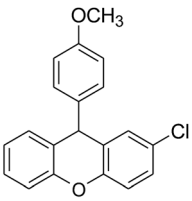

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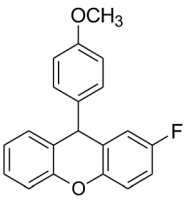
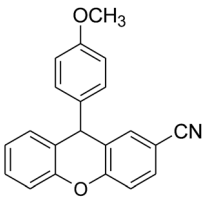
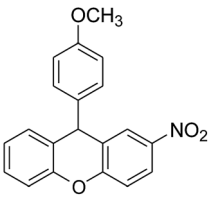


2s 75%



2t 5%



2u 4%

[a] Condition: **1a–1u** (0.1 mmol) and **3g** (10% equiv.) in CH_3CN (2.5 mL) were stirred at room temperature for 15–60 min. [b] Yield of isolated product.

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this mechanism with asymmetric Brønsted acids.[29] In these works, a possible transition-state model was proposed in order to describe the mechanism of some Brønsted acid catalysed reactions *via* multiple hydrogen-bond interplay between the chiral catalyst and substrate.

Experimental

General information

The majority of the chemicals used in this work were commercially available from Merck or Aldrich. CH_3CN was purchased from Merck with catalog number 114291. It has 99.8% purity and was not additionally dried. The starting carbinols **1a–1u** were prepared by Ullmann coupling of 2-fluorobenzaldehyde and substituted phenols, and then by the Grignard reaction of 2-arenoxybenzaldehydes and some arylmagnesium bromides. All substrates were purified by crystallization or column chromatography and characterized by IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy, elemental analysis and GC-MS. All novel products were characterized by IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy, elemental analysis and GC-MS. The reactions were monitored by TLC using silica gel plates and the products were purified by flash column chromatography on silica gel (Merck; 230–400 mesh), eluting with hexane–ethyl acetate (v/v 9 : 1). The NMR spectra were recorded at 500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR using Me_4Si as the internal standard in $CDCl_3$. The GC-MS were recorded on a Shimadzu/QP2010 Plus. The IR spectra were recorded on a Mattson 1000 spectrometer. The melting points were determined with a Büchi Melting Point B-540.

General procedure for intramolecular Friedel–Crafts cyclization

Under room temperature conditions, *N*-triflylphosphoramide (**3g**) (10 mol%) was added to a stirred solution of a starting alcohol compound (**1a–1m**) (0.1 mmol) in CH_3CN (2.5 mL), and the reaction was stirred for 15 min. After the completion of the reaction, as observed with TLC, the mixture was concentrated in a vacuum and extracted with ethylacetate. After the usual reaction workup and concentration, the product was charged on silica gel.

Conclusions

In conclusion, an efficient synthetic method was developed for the synthesis of new substituted 9-arylxanthenes *via* intramolecular Friedel–Crafts cyclisation, using non-transition metal organocatalysis, and starting from diarylcarbinol compounds. In this work, we looked for an optimisation of the reaction conditions to yield highly efficient 9-arylxanthene synthesis. Thus, we examined some organic Brønsted-acids as catalysts and determined the best catalyst for intramolecular FCA. We found that *N*-triflylphosphoramide (**3g**) as a catalyst is highly effective, inexpensive and non-toxic for the rapid synthesis of xanthenes in CH_3CN at room temperature, when compared to previous intramolecular FCA reactions and the synthesis of 9-arylxanthenes.

Finally, we determined a new organocatalytic FCA protocol, which does not require inert reaction conditions or any protection, to synthesise some novel substituted arylxanthenes using **3g** with excellent yields. The twenty newly synthesised substituted 9-arylxanthenes **2a–2u** (Table 5) may be used as natural and bio-active compounds, dyes or fluorescent materials, and their biochemical properties and activities will be investigated in the future.

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