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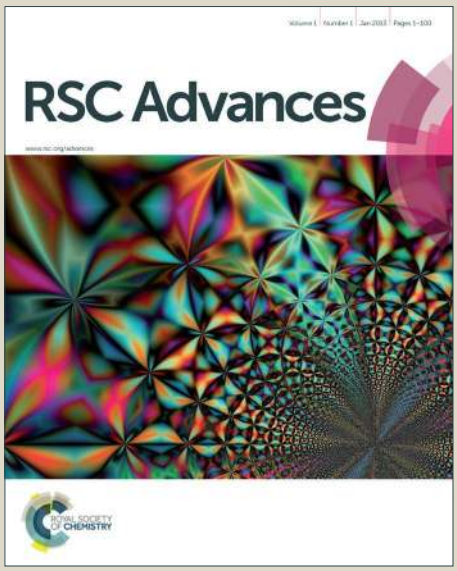

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ARTICLE

Copper Catalyzed Coupling of Protecting Group Free and Sterically Hindered 2-Bromobenzyl Tertiary Alcohols with Phenols and Anilines: Facile Synthesis of Xanthenes and Dihydroacridines

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Abstract: A simple and efficient method for the synthesis of xanthenes and dihydroacridines containing a quaternary carbon atom at 9th-position, is presented. Significantly, the protocol facilitated the smooth participation of sterically hindered and protecting group free 2-bromobenzyl tertiary alcohols in cross coupling reaction with phenols and anilines, under copper-catalysis. The Lewis acid mediated intramolecular C-C bond formation enabled the formation of quaternary carbon atom at 9th-position. Remarkably, this two-step protocol required single column purification technique.

Introduction

Xanthenes[1] and xanthones[2] are special class of tricyclic dibenzopyrans, since these skeletons constitutes pharmaceutically important compounds and natural products as well. Their other uses include dyes or fluorescent materials and chiroptical molecular switches.[3] They exhibit a variety of physicochemical and pharmacological properties (e.g. anti-oxidants, anti-bacterial, anti-tumoral, anti-neoplastics, vasodilators and anti-inflammatory activities).[4] Interestingly, their biological behaviour depends upon the nature and position of substituents on their structure.[5] Some of the notable natural and unnatural compounds are as depicted in Figure 1. Vowing to their occurrence from natural sources of biological relevance and pharmaceutical reputation of analogues compounds, prompted organic chemists to design and develop new synthetic methods to establish functionalized xanthenes. Though a good number of methods established for their synthesis, most of them either require pre-synthesized precursors or involve multi-step protocols.[6] On the other hand, one-step processes for their synthesis are very few.[7] Particularly, some of the established strategies affording 9-substituted xanthenes, have some limitations, either due to low yields or require multiple steps. Therefore, it is highly desirable to develop new and efficient methods to achieve 9-substituted xanthenes.

On the other hand, acridines are another class of important nitrogen containing heterocyclic compounds, in which the oxygen atom of xanthenes replaced with nitrogen and with complete aromatization. Acridines are also well known for their broad range of biological and medicinal properties.[8] In this regard, some important natural and unnatural products are as shown in Figure 1. Notably, dihydroacridine analogue found as selective activator of temperature- and mechano-sensitive K_{2P} channels.[9] Since it is certain that acridines are indispensable compounds, development of efficient protocols for their synthesis is very much essential. Apart from the well-established named reaction (Bernthsen acridine synthesis), recently, there are good number of approaches developed for the synthesis of acridines from eminent research groups.[10] In continuation of our on-going research interests on transition-metal mediated efficient transformations,[11] herein we disclose an efficient method for synthesis of xanthenes and dihydroacridines containing a quaternary carbon atom at 9th-position. This protocol enabled the accomplishment of xanthenes and dihydroacridines with simple to dense functionality on the aromatic ring. Significantly, this two-step process required a single column chromatographic technique.

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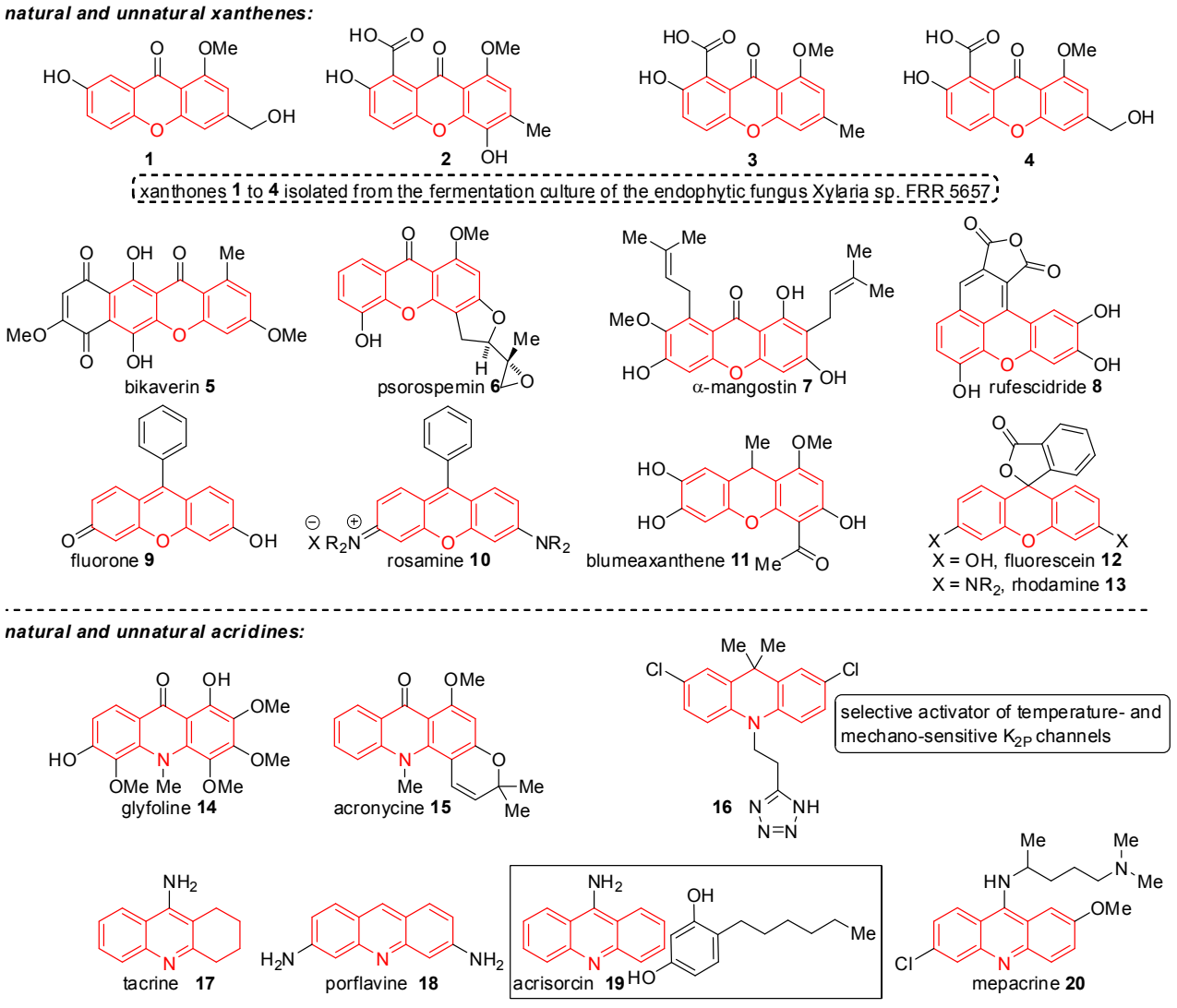

Figure 1: Some of the notable examples of natural/unnatural xanthones (**1** to **7**), xanthenes (**8** to **13**), acridones (**14** to **15**), dihydroacridine (**16**) and acridines (**17** to **20**).

Result and Discussion

Though methods were known for the synthesis of 9-substitituted xanthenes/acridines, most of them were made with the tertiary carbon atoms at 9th-position. Also, many of them were based on multistep processes or using derivatization of simple xanthenes. Whereas, most of one-pot protocols were limited to the synthesis of simple xanthenes without any substitution at 9th-carbon centre. Moreover, to the best of our knowledge, there is no report on the direct synthesis of xanthenes/acridines with a quaternary carbon atom at 9th-position. Further, 9,9-dimethylxanthene was identified as the useful synthon, for the synthesis of novel ligands (xanthphos etc.),[12] which were proved to be vital in metal-catalysis. All earlier reports for the synthesis of 9,9-dimethylxanthene accomplished using xanthone as the synthetic precursor through di-methylation with trimethylaluminium ($AlMe_3$).[13] With these observations, it was prompted us to develop new and efficient method for the synthesis

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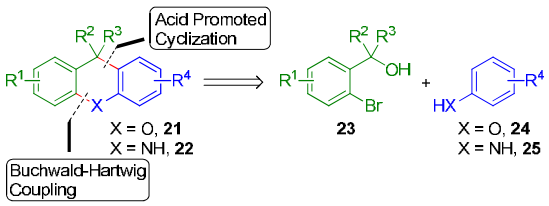
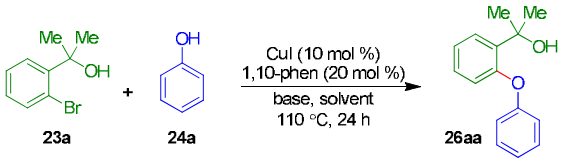
of xanthenes and acridines with a quaternary carbon atom at 9th-position, which may not only open a path for accomplishment of new compounds of biological relevance but also could further expand scope to develop new sort of ligands in-order to prepare efficient metal-catalysts. In our laboratory, recently, we have demonstrated the efficient and domino one-pot conversions of 2-bromotertiary benzyl alcohols into novel heterocyclic compounds using transition-metal catalysis. With this background, we envisioned that xanthenes **21** and dihydroacridines **22** could be obtained from sterically hindered and protecting free 2-bromotertiary benzyl alcohols **23** using copper-catalyzed Buchwald-Hartwig coupling with phenols **24**/anilines **25** and acid induced intramolecular C-C bond formation (Scheme 1).



Scheme 1: Retrosynthetic analysis to give **21**/**22** from alcohols **23** and phanols **24**/anilines **25**.

To initiate the synthetic study, first we decided to examine the coupling reaction between the simple tertiary alcohol **23a** and the phenol **24a**. Thus, the reaction was performed in the presence of catalyst CuI (10 mol %)/1,10-phen (20 mol %), base Na_2CO_3 (2 equiv) in toluene at 110 °C for 24 h. As anticipated, the product **26aa** was obtained in moderate yield along with the unreacted starting material **23a** (Table 1, entry 1). To our delight, as we presumed, the tertiary alcohol moiety was not interfered in the reaction. This may be due to the fact that though the tertiary hydroxyl group is more nucleophilic than phenolic OH, the steric hindrance around the *tert*-OH moiety might be severe and not allowed it to participate in the competitive intermolecular coupling. Also, it was well demonstrated in one of our earlier reports that this tertiary alcohol did not prefer intramolecular coupling to give oxetane derivatives. Interestingly, with bases K_2CO_3 and K_3PO_4, gave the product **26aa**, in very good yields (Table 1, entries 2 & 3). While, no progress was noted with mild base $NaHCO_3$ (Table 1, entry 4). To our delight, the reaction with the strong base Cs_2CO_3, furnished the product **26aa**, in excellent yield (Table 1, entry 5). On the other hand, the solvents DMF and DMA instead of toluene with base Cs_2CO_3, gave good yields of the product **26aa** (Table 1, entries 6 & 7). However, the reactions in other solvents such DMSO and CH_3CN were found further inferior (Table 1, entries 8 & 9).

Table 1: Optimization conditions for the formation of biaryl ether **26aa**.



Entry[a]	Base (2 equiv)	Solvent	Yield of **26aa**[b]
1	Na_2CO_3	toluene	50% + SM[c]
2	K_2CO_3	toluene	84%
3	K_3PO_4	toluene	76%
4	$NaHCO_3$	toluene	SM
5	**Cs_2CO_3**	**toluene**	**91%**
6	Cs_2CO_3	DMF	73%
7	Cs_2CO_3	DMA	72%
8	Cs_2CO_3	DMSO	65% + SM[c]
9	Cs_2CO_3	CH_3CN	53% + SM[c]

[a]All reactions were carried out on 0.5 mmol of **23a** and 1 mmol of **24a** in 0.5 mL solvent. [b]Isolated yields of chromatographically pure products. [c]Starting material also recovered along with the product.

With the optimized reaction conditions in hand (Table 1, entry 5), to check the scope of the method, we explored the reaction between 2-bromotertiary benzyl alcohols **23a**/**23e** and phenols **24a**/**24b** and aninlines **25a**/**25b**. To our delight, the reaction found amenable and furnished the biaryl ethers **26aa**/**24eb** and coupled anilines **27aa**/**27ab**, in very good to excellent yields (Table 2).

With these coupled ethers **26aa**/**26eb** and anilines **27aa**/**27ab**, we next planned for acid promoted intramolecular C-C bond formation. Thus, the reaction was carried out with the Lewis acid $BF_3{\cdot}OEt_2$ in DCM at 0 °C to rt for 30 min. Gratifyingly, the reaction was quite successful and furnished the corresponding xanthenes **21aa**/**21eb** and dihydroacridines **22aa**/**22ab**, in good to excellent yields (Table 3).

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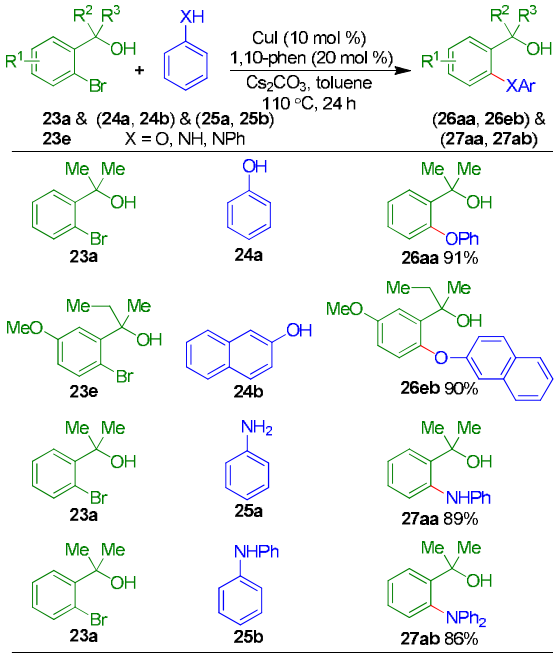
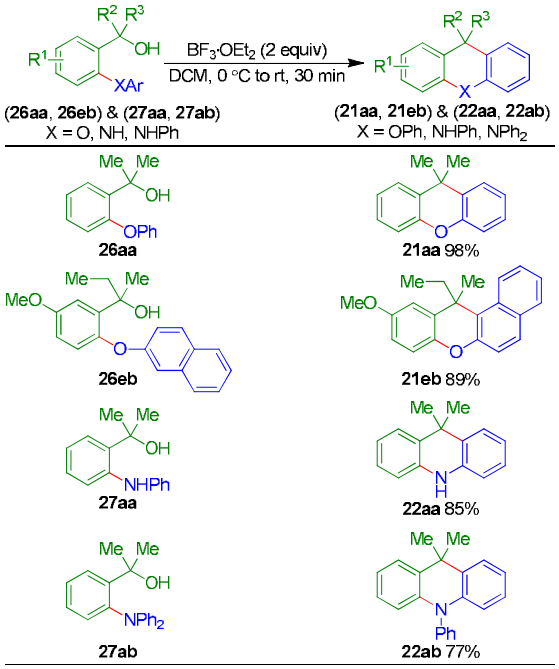
Table 2: Synthesis of biaryl ethers **26aa/26eb** and coupled anilines **27aa/27ab**.[a,b,c,d]



Reaction conditions: [a]**23a** & **23e** (0.50 mmol), **24a** & **24b** (1.00 mmol), CuI (10 mol %), 1,10-phenanthroline (20 mol %), Cs_2CO_3 (1.0 mmol), in 0.5 mL toluene, at 110 °C for 24 h. [b]Isolated yields of chromatographically pure products. [c]For final compounds **26aa** & **26eb**, the first alphabet represents from 2-bromobenzyl tertiary alcohols **23a** & **23e**, while second letter indicates the phenols **24a** & **24b**. [d]For final compounds **27aa** & **27ab** the first alphabet represents from 2-bromobenzyl tertiary alcohol **23a**, while second letter indicates the anilines **25a** & **25b**.

Table 3: Synthesis of xanthenes **21aa/21eb** and dihydroacridines **22aa/22ab**.[a,b,c,d]

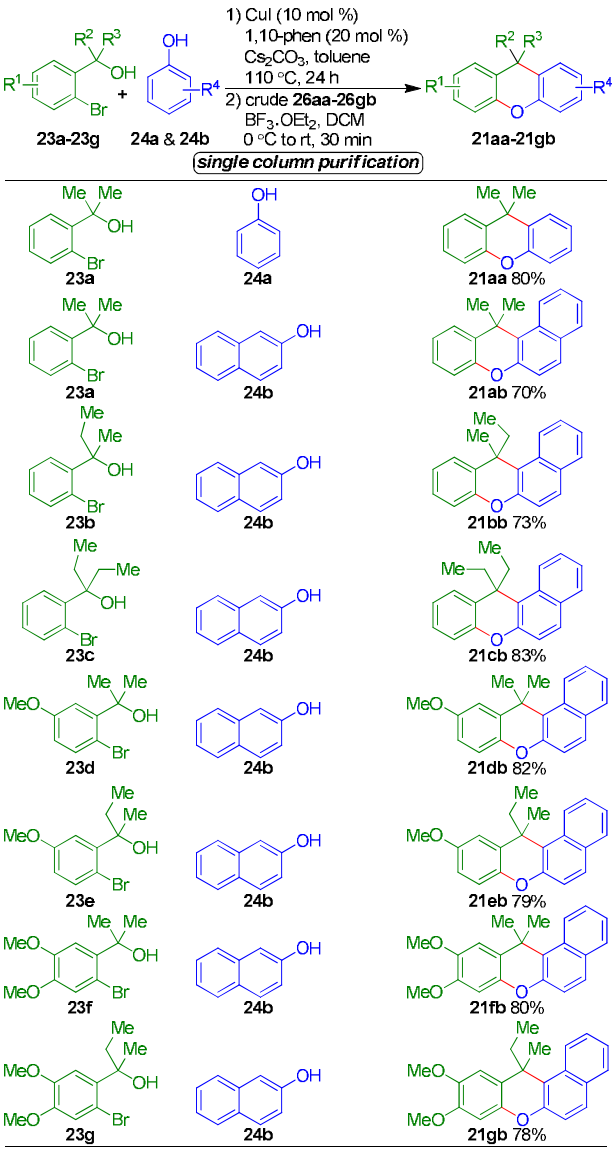


Reaction conditions: [a](**26aa**, **26eb**) & (**27aa**, **27ab**) (0.25 mmol), $BF_3{\cdot}OEt_2$ (2 equiv), in 2 mL DCM, at 0 °C to rt for 30 min. [b]Isolated yields of chromatographically pure products.

[c]For final compounds **21aa** & **21eb**, the first alphabet represents from 2-bromobenzyl tertiary alcohols **23a** & **23e**, while second letter indicates the phenols **24a** & **24b**. [d]For final compounds **22aa** & **22ab** the first alphabet represents from 2-bromobenzyl tertiary alcohol **23a**, while second letter indicates the anilines **25a** & **25b**.

After the accomplishment of xanthenes **21aa/21fa** and dihydroacridines **22aa/22ab**, we thought that protocol can be made still more efficient by conducting acid mediated cyclization directly on the concentrated crude reaction mixture of biaryl ethers **26** and coupled anilines **27** without column purification, so that we may end up in doing a single column chromatography for two-steps together. Thus, initially, we have directly treated the crude biaryl ethers **26aa-26gb** with $BF_3{\cdot}OEt_2$. To our delight, as expected, afforded the xanthenes **21aa-21gb**, in good to very good yields (Table 4), thus enable us to make the method more efficient and interesting.

Table 4: Synthesis of xanthenes **21aa-21gb**.[a,b,c]



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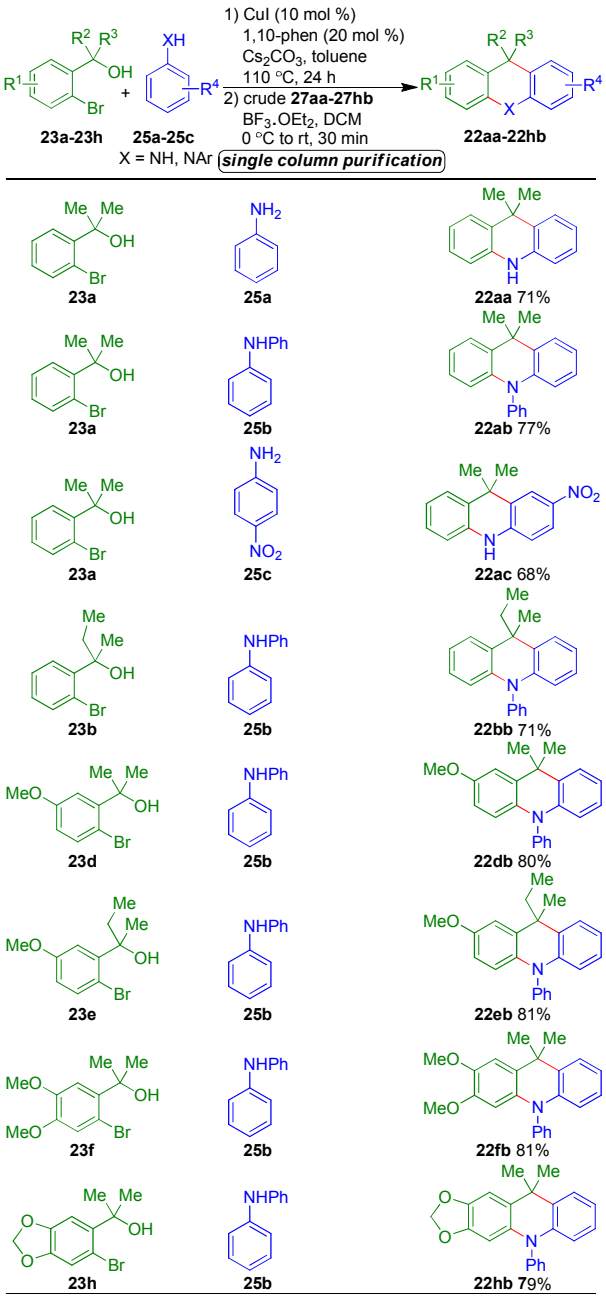
Reaction conditions: [a]**23a**-**23g** (0.50 mmol), **24a**-**24b** (1.00 mmol), CuI (10 mol %), 1,10-phenthroline (20 mol %), Cs_2CO_3 (1.0 mmol), in 0.5 mL toluene, at 110 °C for 24 h then work up and evaporated under vacuum added $BF_3{\cdot}OEt_2$ (2 equiv) in 2 mL DCM, at 0 °C to rt for 30 min. [b]isolated yields of chromatographically pure products. [c]For xanthenes **21aa**-**21gb**, the first alphabet represents from 2-bromobenzyl tertiary alcohols **23a**-**23g**, while second letter indicates the anilines **24a**-**24b**.

Similarly, the crude coupled anilines **27aa-27bh** were subjected to $BF_3{\cdot}OEt_2$ induced cyclization. Quite interestingly, as anticipated, the strategy was also proved amenable and furnished the dihydroacridines **22aa-22hb** (Table 5). Remarkably, the reaction was also successful with strong electron withdrawing nitro group (**22ac**, Table 5). Thus reveals the significance of the present strategy. It is worth noting that the reaction with 2-bromobenzyl secondary alcohols was unclear (i.e. neither starting material nor the product was isolated). This is in accordance with our earlier observations that only 2-bromobenzyl tertiary alcohols were suitable for intermolecular Sonogashira[11e] and cyanations[11f] followed by intramolecular nucleophilic attacks, under copper catalysis, whereas the reaction was unclear with the corresponding primary or secondary alcohols, under standard reaction conditions.

Table 5: Synthesis of xanthenes **22aa-22hb**.[a,b,c]



Reaction conditions: [a]**23a**-**23h** (0.50 mmol), **25a**-**25c** (1.00 mmol), CuI (10 mol %), 1,10-phenthroline (20 mol %), Cs_2CO_3 (1.0 mmol), in 0.5 mL toluene, at 110 °C for 24 h then work up and evaporated under vacuum added $BF_3{\cdot}OEt_2$ (2 equiv) in 2 mL DCM, at 0 °C to rt for 30 min. [b]isolated yields of chromatographically pure products. [c]For dihydroacridines **22aa**-**22hb**, the first alphabet represents from 2-bromobenzyl tertiary alcohols **23a**-**23h**, while second letter indicates the anilines **25a**-**25c**.

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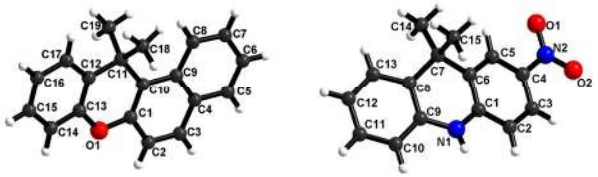
In addition to the spectroscopic evidence for the structural confirmation of xanthenes **21** and dihydroacridines **22**, the structures were confirmed by the single crystal x-ray diffraction analysis of **21ab** and **22ac** Figure 2 (see; supporting information).



21ab **22ac**

Figure 2. X-ray crystal structure of product **21ab** and **22ac**. Thermal ellipsoids are drawn at 50% probability level.

Conclusion:

In summary, we have disclosed a simple and efficient method for the synthesis of xanthenes and acridines containing a quaternary carbon atom at 9th-position. Significantly, sterically hindered and protecting group free 2-bromobenzyl tertiary alcohols were involved in smooth coupling reaction with phenols and anilines, under copper-catalysis. The Lewis acid mediated intramolecular C-C bond formation enable the formation of quaternary carbon atom at 9th-position. Remarkably, this two-step protocol required single column purification technique.

Experimental Section

General Considerations

IR spectra were recorded on a FTIR spectrophotometer. ^{1}H NMR spectra were recorded on 400 MHz spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δ_H=0.00 ppm) or $CHCl_3$ (δ_H=7.25 ppm). ^{13}C NMR spectra were recorded on 100 MHz spectrometer at RT in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CHCl_3$ [δ_C=77.00 ppm (central line of triplet)]. In the ^{13}C NMR, the nature of carbons (C, CH, CH_2, and CH_3) was determined by recording the DEPT-135 spectra and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH_2) and q = -quartet (for CH_3). In the ^{1}H NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui =quintet, m = multiplet and br s. = broad singlet. The assignment of signals was confirmed by ^{1}H, ^{13}C CPD (carbon proton decoupled), and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded using Q-TOF multimode source. Melting points were determined on an electrothermal melting point apparatus and are uncorrected. Benzaldehydes, methyl iodide, bromoethane, Mg metal and Na_2SO_4 were commercially available (local made) used without further purification. CuI, 1,10-Phenthroline and Cs_2CO_3 purchased from Sigma-Aldrich, while $BF_3{\cdot}OEt_2$ was used from local commercial sources. All dry solvents were used, diethyl ether and toluene were dried over sodium metal, DCM and DMF were dried over calcium hydride.

All the solvents (diethyl ether, DCM, DMF) are commercially available. All small scale dry reactions were carried out using standard syringe-septum technique. Reactions were monitored by TLC on silica gel using a combination of petroleum ether and ethyl acetate as eluents. Reactions were generally run under inert atmosphere. Solvents were distilled prior to use; petroleum ether with a boiling range of 40 to 60 °C was used. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

General Procedure-1 (For the synthesis of aryl ethers **26** and aryl amines **27**):

In an oven-dried Schlenk tube 2-bromobenzyl tertiary alcohols **23** (0.5 mmol), phenols **24** or anillines **25** (1.00 mmol), CuI (10 mol %), 1,10-phenthroline (20 mol %), Cs_2CO_3 (1.0 mmol) and solvent toluene (0.5 mL) were added. The resulting reaction mixture was stirred at 110 °C for 24 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was allowed to cool to room temperature, then saturated aqueous NH_4Cl was added fallowed by extraction with ethyl acetate. The organic layers were dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent furnished the aryl ethers **26** and aryl amines **27**.

General Procedure-2 (For the synthesis of xanthenes **21** and dihydroacridines **22**):

In an oven-dried Schlenk tube aryl ethers **26** or aryl amines **27** (0.25 mmol) dissolved in 2 mL dry DCM, $BF_3{\cdot}OEt_2$ (2 equiv) was added at 0 °C. The resulting reaction mixture was stirred at 0 °C to rt for 30 min. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was diluted with (10 mL) water and extracted with DCM fallowed by washed with $NaHCO_3$. The organic layers were dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent furnished the xanthenes **21** and dihydroacridines **22**.

General Procedure-3 (For the synthesis of xanthenes **21** and dihydroacridines **22** using single column purification):

In an oven-dried Schlenk tube 2-bromobenzyl tertiary alcohol **23** (0.5 mmol), phenols **24** or anilline **25** (1.00 mmol), CuI (10 mol %), 1,10-phenthroline (20 mol %), Cs_2CO_3 (1.0 mmol) and toluene (0.5 mL) were added. The resulting reaction mixture was stirred at 110 °C for 24 h. After completion of reaction, the reaction mixture was allowed to cool to room temperature, then diluted with (10 mL) ethyl acetate and water was added fallowed by extraction with ethyl acetate. The organic layers were dried

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(Na_2SO_4) and concentrated in vacuo. The crude reaction mixture of aryl ethers **26** and aryl amines **27** was dissolved in 2 mL dry DCM, $BF_3{\cdot}OEt_2$ (2 equiv) was added at 0 °C. The resulting reaction mixture was stirred at 0 °C to rt for 30 min. The progress of the reaction was monitored by TLC. After completion of reaction, the reaction mixture was diluted with (10 mL) water and extracted with DCM fallowed by washed with $NaHCO_3$. The organic layers were dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent furnished the xanthenes **21** and acridines **22**.

2-(2-phenoxyphenyl)propan-2-ol (26aa):

This compound was prepared according to the GP-1 and isolated as pale yellow color oil 91% yield (103 mg): [TLC (petroleum ether/ethyl acetate 9:1, R_f(**23a**)=0.60, R_f(**26aa**)=0.60, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3416, 2971, 1576, 1481, 1442, 1364, 1224, 1162, 1072, 854, 752, 690 cm^{-1}. ^{1}H NMR ($CDCl_3$ 400 MHz): δ=7.51 (d, 1H, *J*=7.8 Hz), 7.36 (dd, 2H, *J*=8.8 and 7.3 Hz), 7.15 (d, 2H, *J*=7.8 Hz), 7.10-7.00 (m, 3H), 6.79 (d, 1H, *J*=7.8 Hz), 1.68 (s, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=156.4 (s, C_q), 154.9 (s, C_q), 138.2 (d, CH), 129.9 (d, 2C, CH), 128.1 (d, CH), 126.3 (d, CH), 123.8 (d, CH), 123.2 (d, CH), 119.4 (d, 2C, CH), 118.7 (d, CH), 72.4 (s, C_q), 30.0 (q, 2C, CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{15}H_{15}O]^+$=$[(M+H)-H_2O]^+$: 211.117; found 211.1118.

2-(5-methoxy-2-(naphthalen-2-yloxy)phenyl)butan-2-ol (26eb):

This compound was prepared according to the GP-3 and isolated as pale yellow color viscous liquid 90% yield (144 mg): [TLC (petroleum ether/ethyl acetate 9:1, R_f(**23e**)=0.40, R_f(**26eb**)=0.40, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3447, 2964, 1598, 1461, 1251, 1194, 1037, 961, 810, 742 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.85-7.76 (m, 2H, Ar-H), 7.68 (d, 1H, *J*=7.8 Hz, Ar-H), 7.50-7.35 (m, 2H, Ar-H), 7.30-7.20 (m, 2H, Ar-H), 7.14 (d, 1H, *J*=3.4 Hz, Ar-H), 6.85 (d, 1H, *J*=8.8 Hz, Ar-H), 6.74 (dd, 1H, *J*=8.8 and 2.9 Hz, Ar-H), 3.83 (s, 3H, Ar-OCH_3), 2.15-2.00 (m, 1H, CH_2), 1.95-1.80 (m, 1H, CH_2), 1.61 (s, 3H, CH_3), 0.84 (t, 3H, *J*=7.3 Hz, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=155.6 (s, Ar-C), 155.5 (s, Ar-C), 147.3 (s, Ar-C), 139.4 (s, Ar-C), 134.3 (s, Ar-C), 129.9 (d, Ar-CH), 127.7 (d, Ar-CH), 127.0 (d, Ar-CH), 126.6 (d, Ar-CH), 124.6 (d, Ar-CH), 121.2 (d, Ar-CH), 119.3 (d, Ar-CH), 113.4 (s, Ar-CH), 113.1 (d, Ar-CH), 112.6 (d, Ar-CH), 75.1 (s, Ar-C), 55.6 (q, OCH_3), 34.8 (t, CH_2), 27.7 (q, CH_3), 8.7 (q, CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{22}NaO_3]^+$=$[M+Na]^+$: 345.1461; found 345.1457.

2-(2-(diphenylamino)phenyl)propan-2-ol (27aa):

This compound was prepared according to the GP-1 and isolated as black color semi solid 86% yield (130 mg): [TLC (petroleum ether/ethyl acetate 9:1, R_f(**23a**)=0.60, R_f(**27aa**)=0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3396, 2975, 1587, 1486, 1258, 1161, 907, 821, 728, 693 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.56-7.50 (m, 1H), 7.30-7.15 (m, 6H), 7.10-7.04 (m, 1H), 7.03-7.93 (m, 6H), 5.11 (br s, 1H), 1.36 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=148.2 (s, 2C, C_q), 146.0 (s, C_q), 143.9 (s, C_q), 132.7 (d, CH), 129.1 (d, 4C, CH), 128.3 (d, CH), 127.8 (d, CH), 127.0 (d, CH), 122.6 (d, 6C, CH), 73.6 (s, C_q), 31.2 (q, 2C, CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{22}NO]^+$=$[M+H]^+$: 304.1696; found 304.1695.

12,12-dimethyl-12*H*-benzo[*a*]xanthene (21aa):

This compound was prepared according to the GP-3 and isolated as white color solid 70% yield (90 mg): mp: 98-100 °C; [TLC (petroleum ether/ethyl acetate 9:1, R_f(**23aa**)=0.60, R_f(**21aa**)=0.80, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2930, 1625, 1575, 1491, 1336, 1245, 1142, 1036, 956, 811, 747, 666 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=8.48 (d, 1H, *J*=8.8 Hz), 7.82 (d, 1H, *J*=8.3 Hz), 7.71 (d, 1H, *J*=8.8 Hz), 7.51 (d, 2H, *J*=7.8 Hz), 7.38 (dd, 1H, *J*=6.8 and 8.3 Hz), 7.22 (dd, 2H, *J*=6.4 and 8.8 Hz), 7.13 (dd, 1H, *J*=7.3 and 7.8 Hz), 7.03 (d, 1H, J=7.8 Hz), 2.16 (s, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=147.7 (s, C_q), 147.3 (s, C_q), 132.0 (s, C_q), 131.8 (s, C_q), 131.7 (s, C_q), 129.7 (d, CH), 129.4 (d, CH), 127.7 (d, CH), 127.2 (d, CH), 126.0 (d, CH), 125.6 (d, CH), 123.3 (d, CH), 123.1 (d, CH), 119.8 (s, C_q), 118.5 (d, CH), 115.7 (d, CH), 34.6 (s, C_q), 32.5 (q, 2C, CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{19}H_{17}O]^+$=$[M+H]^+$: 261.1274; found 261.1262.

12-ethyl-12-methyl-12*H*-benzo[a]xanthene (21bb):

This compound was prepared according to the GP-3 and isolated as pale yellow color oil 73% yield (99 mg): [TLC (petroleum ether/ethyl acetate 9:1, R_f(**23b**)=0.50, R_f(**21bb**)=0.60, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2964, 1588, 1491, 1342, 1247, 1142, 1052, 957, 812, 749, 670 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=8.47 (d, 1H, *J*=8.8 Hz), 7.79 (d, 1H, *J*=8.3 Hz), 7.69 (d, 1H, *J*=8.8 Hz), 7.47 (d, 1H, *J*=6.8 Hz), 7.44 (dd, 1H, *J*=6.8 and 7.8 Hz, Ar-H), 7.36 (dd, 1H, *J*=6.8 and 7.8 Hz), 7.19 (d, 2H, *J*=8.8 Hz), 7.10 (dd, 1H, *J*=7.8 and 8.8 Hz), 6.99 (d, 1H, *J*=7.8 Hz), 2.93 - 3.06 (m, 1H, CH_2), 2.15 (s, 3H, CH_3), 1.97–2.08 (m, 1H, CH_2), 0.49 (t, 3H, *J*=7.3 Hz, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=149.5 (s, C_q), 148.9 (s, C_q), 132.0 (s, C_q), 131.8 (s, C_q), 129.7 (d, CH), 129.4 (d, CH), 129.2 (s, C_q), 127.1 (d, 2C, CH), 125.6 (d, 2C, CH), 123.3 (d, CH), 123.2 (d, CH), 118.4 (d, CH), 117.0 (s, C_q), 115.3 (d, CH), 39.9 (s, C_q), 36.0 (t, CH_2), 31.9 (q, CH_3), 10.5 (t, CH_3] ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{19}O]^+$=$[M+H]^+$: 275.1430; found 275.1428.

12,12-diethyl-12*H*-benzo[*a*]xanthene (21cb):

This compound was prepared according to the GP-3 and isolated as white color solid 83% yield (118 mg): mp: 86-88 °C; [TLC (petroleum ether/ethyl acetate 9:1, R_f(**23c**)=0.50, R_f(**21cb**)=0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2964, 1587, 1491, 1350, 1242, 1131, 1037, 961, 812, 747, 671 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=8.53 (d, 1H, *J*=8.8 Hz), 7.80 (d, 1H, *J*=7.8 Hz), 7.70 (d, 1H, *J*=8.8 Hz), 7.46 (dd, 1H, *J*=7.3 and 8.8 Hz), 7.40 (dd, 1H, *J*=7.3 and 7.8 Hz), 7.36 (dd, 1H, *J*=6.8 and 7.8 Hz), 7.20 (d, 2H, *J*=8.8 Hz), 7.10 (dd, 1H, *J*=7.3 and 8.3 Hz), 7.00 (d, 2H, *J*=8.3 Hz), 2.95–3.08 (m, 2H, CH_2), 1.98–2.11 (m, 2H, CH_2) 0.51 (t, 6H, *J*=7.3 Hz, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=151.1 (s, C_q), 150.4 (s, C_q), 132.2 (s, C_q), 131.7 (s, C_q), 129.7 (d, CH), 129.5 (d, CH), 127.1 (d, CH), 126.5 (s, C_q), 126.4 (d, CH), 125.6 (d, CH), 125.1 (d, CH), 123.3 (d, CH), 123.2 (d, CH), 118.4 (d, CH), 115.2 (d, CH), 114.3 (s, C_q), 46.0 (s, C_q), 34.8 (t, CH_2), 10.2 (q, CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{21}O]^+$=$[M+H]^+$: 289.1587; found 289.1577.

10-methoxy-12,12-dimethyl-12*H*-benzo[a]xanthene (21db):

This compound was prepared according to the GP-3 and isolated as white color solid 82% yield (118 mg): mp: 92-94 °C; [TLC (petroleum ether/ethyl acetate 9:1, R_f(**23d**)=0.40, R_f(**21db**)=0.60, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2932, 1577, 1498, 1338, 1240,

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1173, 1042, 958, 810, 730, 601 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=8.44 (d, 1H, *J*=8.8 Hz), 7.80 (d, 1H, *J*=8.3 Hz), 7.68 (d, 1H, *J*=8.8 Hz), 7.49 (dd, 1H, *J*=6.8 and 8.3 Hz), 7.36 (dd, 1H, *J*=6.8 and 7.8 Hz), 7.17 (d, 1H, *J*=8.8 Hz), 7.01 (s, 1H), 6.96 (d, 1H, *J*=8.8 Hz), 6.78 (d, 1H, *J*=8.8 Hz), 3.84 (s, 3H, CH3), 2.14 (s, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=155.4 (s, C_q), 147.4 (s, C_q), 142.0 (s, C_q), 132.5 (s, C_q), 131.8 (s, C_q), 129.6 (d, CH), 129.4 (d, CH), 125.9 (d, CH), 125.6 (d, CH), 123.1 (d, CH), 119.3 (s, C_q), 118.8 (d, CH), 118.5 (s, C_q), 116.3 (d, CH), 112.9 (d, CH), 112.7 (d, CH), 55.7 (q, CH_3), 35.0 (s, CH_3), 32.2 (q, 2C, CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{19}O_2]^+$=$[M+H]^+$: 291.1380; found 291.1376.

12-ethyl-10-methoxy-12-methyl-12*H*-benzo[a]xanthene (21eb):
This compound was prepared according to the GP-3 and isolated as pale yellow color viscous liquid 89% yield (134 mg): [TLC (petroleum ether/ethyl acetate 9:1, R_f(**23e**)=0.40, R_f(**21eb**)=0.60, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2965, 1592, 1474, 1312, 1211, 1039, 933, 879, 745, 610 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=8.46 (d, 1H, *J*=8.8 Hz), 7.79 (d, 1H, *J*=8.3 Hz), 7.69 (d, 1H, *J*=8.8 Hz), 7.47 (dd, 1H, *J*=6.8 and 8.3 Hz), 7.36 (dd, 1H, *J*=6.8 and 7.8 Hz), 7.17 (d, 1H, *J*=8.8 Hz), 6.97 (s, 1H), 6.94 (d, 1H, *J*=8.8 Hz), 6.78 (d, 1H, *J*=8.8 Hz), 3.84 (s, 3H, CH_3), 3.10-2.90 (m, 1H, CH_2), 2.10-2.95 (m, 1H, CH_2), 2.16 (s, 3H, CH_3), 0.50 (t, 3H, *J*=7.3 Hz, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=155.4 (s, C_q), 149.0 (s, C_q), 143.8 (s, C_q), 131.9 (s, C_q), 131.7 (s, C_q), 130.0 (d, CH), 129.6 (d, CH), 129.4 (d, CH), 125.5 (d, CH), 123.2 (d, CH), 118.4 (d, CH), 116.1 (s, C_q), 116.0 (d, CH), 112.8 (d, CH), 112.0 (d, CH), 55.7 (q, CH_3), 40.3 (s, C_q), 35.7 (t, CH_2), 31.6 (q, CH_3), 10.5 (q, CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{22}H_{22}N]^+$=$[M+H]^+$: 305.1536; found 305.1537.

9,10-dimethoxy-12,12-dimethyl-12*H*-benzo[a]xanthene (21fb):
This compound was prepared according to the GP-3 and isolated as brown color solid 90% yield (127 mg): mp: 68-70 °C; [TLC (petroleum ether/ethyl acetate 8:2, R_f(**23f**)=0.40, R_f(**21fb**)=0.60, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2933, 1629, 1510, 1402, 1339, 1241, 1150, 1078, 998, 815, 750, 668 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=8.42 (d, 1H, *J*=8.8 Hz), 7.78 (d, 1H, *J*=7.8 Hz), 7.67 (d, 1H, *J*=8.8 Hz), 7.48 (dd, 1H, *J*=7.3 and 8.8 Hz), 7.35 (dd, 1H, *J*=7.8 and 7.8 Hz), 7.14 (d, 1H, *J*=8.8 Hz), 6.92 (s, 1H), 6.54 (s, 1H), 3.92 (s, 3H, CH_3), 3.89 (s, 3H, CH3), 2.10 (s, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=148.4 (s, C_q), 147.5 (s, C_q), 145.2 (s, C_q), 131.9 (s, 2C, C_q), 129.6 (d, CH), 129.3 (d, CH), 126.0 (d, CH), 125.6 (d, CH), 123.2 (d, CH), 122.3 (s, C_q), 119.3 (s, C_q), 118.4 (d, CH), 110.3 (d, CH), 99.2 (d, CH), 56.6 (q, CH_3), 56.0 (q, CH_3), 34.6 (s, C_q), 32.2 [q, 2C, CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{21}O_3]^+$=$[M+H]^+$: 321.1485; found 321.1487.

12-ethyl-9,10-dimethoxy-12-methyl-12*H*-benzo[a]xanthene (21gb):
This compound was prepared according to the GP-3 and isolated as pale yellow color solid 78% yield (129 mg): mp: 93-95 °C; [TLC (petroleum ether/ethyl acetate 8:2, R_f(**23g**)=0.40, R_f(**21gb**)=0.60, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2963, 1592, 1474, 1312, 1211, 1039, 933, 879, 746, 699 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=8.44 (d, 1H, *J*=8.8 Hz), 7.78 (d, 1H, *J*=6.8 Hz), 7.67 (d, 1H, *J*=8.8 Hz), 7.46 (dd, 1H, *J*=6.8 and 8.8 Hz), 7.34 (dd, 1H, *J*=6.8 and 7.8 Hz), 7.14 (d, 1H, *J*=8.8 Hz), 6.86 (s, 1H), 6.54 (s, 1H), 3.91 (s, 3H, CH_3), 3.90 (s, 3H, CH_3), 3.05–2.85 (m, 1H, CH_2), 2.12 (s, 3H, CH_3), 2.10–1.90 (m, 1H, CH_2), 0.48 (t, 3H, *J*=7.3 Hz, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=149.1 (s, C_q), 148.3 (s, C_q), 145.2 (s, C_q), 143.6 (s, 1C, C_q), 132.0 (s, C_q), 131.8 (s, C_q), 129.6 (d, CH), 129.4 (d, CH), 125.6 (d, 2C, CH), 123.2 (d, CH), 119.6 (s, C_q), 118.3 (d, CH), 116.5 (s, C_q), 109.5 (d, CH), 99.0 (d, CH), 56.6 (q, CH_3), 55.9 (q, CH_3), 39.9 (s, CH_3), 35.4 (t, CH_2), 31.6 (q, CH_3), 10.5 (q, CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{22}H_{23}O_3]^+$=$[M+H]^+$: 349.1672; found 349.1669.

9,9-dimethyl-10-phenyl-9,10-dihydroacridine (22ab):
This compound was prepared according to the GP-2 and 3 isolated as black color solid 77% yield (109 mg): mp: 116-118 °C; [TLC (petroleum ether/ethyl acetate 9:1, R_f(**23a**)=0.50, R_f(**22ab**)=0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2965, 2923, 1584, 1473, 1450, 1331, 1263, 1061, 906, 742, 697 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.63 (dd, 2H, *J*=7.8 and 7.8 Hz), 7.51 (dd, 1H, *J*=7.3 and 7.3 Hz), 7.47 (d, 2H, *J*=7.3 Hz), 7.35 (d, 2H, *J*=7.3 Hz), 6.98 (dd, 2H, *J*=7.3 and 7.8 Hz), 6.93 (dd, 2H, *J*=7.3 and 7.3 Hz), 6.27 (d, 2H, *J*=8.3 Hz), 1.71 (s, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=141.2 (s, C_q), 140.9 (s, 2C, C_q), 131.3 (d, 2C, CH), 130.8 (d, 2C, 2 CH), 129.9 (s, 2C, C_q), 128.2 (d, 2C, CH), 126.3 (d, 2C, CH), 125.1 (d, 2C, CH), 120.5 (d, 2C, CH), 114.0 (d, 2C, CH), 35.9 (s, C_q), 31.2 (q, 2C, CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{20}N]^+$=$[M+H]^+$: 286.1590; found 286.1596.

9-ethyl-9-methyl-10-phenyl-9,10-dihydroacridine (22bb):
This compound was prepared according to the GP-3 and isolated as brown color solid 71% yield (106 mg): mp: 84-86 °C; [TLC (petroleum ether/ethyl acetate 9:1, R_f(**23b**)=0.50, R_f(**22bb**)=0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2962, 1589, 1476, 1334, 1268, 1164, 1028, 907, 743, 699 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.62 (dd, 2H, *J*=7.3 and 7.8 Hz), 7.49 (dd, 1H, *J*=7.3 and 7.8 Hz), 7.37 (d, 2H, *J*=7.8 Hz), 7.30 (d, 2H, J=8.3 Hz), 6.94 (dd, 2H, *J*=7.3 and 8.8 Hz), 6.89 (dd, 2H, *J*=7.3 and 8.8 Hz), 6.19 (d, 2H, *J*=8.3 Hz), 1.93 (q, 2H, *J*=7.3 Hz, CH_2), 1.77 (s, 3H, CH_3), 0.70 (t, 3H, *J*=7.3 Hz, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=141.5 (s, 2C, C_q), 141.3 (s, C_q), 131.3 (d, 2C, CH), 130.9 (d, 2C, CH), 128.1 (d, CH), 127.6 (s, C_q), 126.3 (d, 2C, CH), 126.1 (d, 2C, CH), 120.1 (d, 2C, CH), 113.8 (d, 2C, CH), 40.1 (s, C_q), 38.6 (t, CH_2), 30.5 (q, CH_3), 9.5 (q, CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{22}H_{22}N]^+$=$[M+H]^+$: 300.1747; found 300.1737.

2-methoxy-9,9-dimethyl-10-phenyl-9,10-dihydroacridine (22db):
This compound was prepared according to the GP-3 and isolated as pale yellow color viscous liquid 80% yield (126 mg): [TLC (petroleum ether/ethyl acetate 9:1, R_f(**23d**)=0.40, R_f(**22db**)=0.60, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2967, 1591, 1474, 1329, 1297, 1208, 1046, 872, 801, 747, 700, 639 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.62 (dd, 2H, *J*=7.8 and 7.8 Hz), 7.49 (dd, 1H, *J*=7.3 and 7.3 Hz), 7.44 (d, 1H, *J*=7.8 Hz), 7.34 (d, 2H, J=7.3 Hz), 7.04 (s, 1H), 6.96 (dd, 1H, J=7.3 and 7.8 Hz), 6.90 (dd, 1H, J=7.3 and 7.3 Hz), 6.55 (d, 1H, *J*=8.8 Hz), 6.26 (d, 1H, *J*=8.3 Hz), 6.20 (d, 1H, *J*=8.8 Hz), 3.77 (s, 3H, CH_3), 1.69 (s, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=154.1 (s, C_q), 141.6 (s, C_q), 141.3 (s, C_q), 135.5 (s, C_q), 131.5 (s, C_q), 131.4 (d,

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2C, CH), 130.8 (d, 2C, CH), 129.2 (s, C_q), 128.1 (d, CH), 126.4 (d, CH), 125.1 (d, CH), 120.1 (d, CH), 114.7 (d, CH), 113.7 (d, CH), 111.6 (d, CH), 111.0 (d, CH), 55.7 (q, CH_3), 36.3 (s, C_q), 30.9 (q, 2C, CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{22}H_{22}NO]^+$=$[M+H]^+$: 316.1696; found 316.1682.

9-ethyl-2-methoxy-9-methyl-10-phenyl-9,10-dihydroacridine (22eb): This compound was prepared according to the GP-3 and isolated as black color solid 81% yield (132 mg): mp: 112-114 °C; [TLC (petroleum ether/ethyl acetate 9:1, R_f(**23e**)=0.40, R_f(**22eb**)=0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2961, 1589, 1477, 1332, 1269, 1174, 1047, 908, 800, 746, 699 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.61 (dd, 2H, *J*=7.3 and 7.8 Hz), 7.49 (dd, 1H, *J*=6.8 and 7.8 Hz), 7.36 (d, 1H, *J*=7.8 Hz), 7.30 (d, 2H, *J*=8.3 Hz), 6.98 (s, 1H), 6.94 (dd, 1H, *J*=6.8 and 8.3 Hz), 6.87 (dd, 1H, *J*=7.3 and 7.3 Hz), 6.53 (d, 1H, *J*=7.3 Hz), 6.19 (d, 1H, *J*=8.3 Hz), 6.14 (d, 1H, *J*=7.8 Hz), 3.77 (s, 3H, CH_3), 1.94 (q, 2H, *J*=7.3 and 7.8 Hz, CH_2), 1.78 (s, 3H, CH_3), 0.72 (t, 3H, *J*=7.3 Hz, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=153.7 (s, C_q), 141.7 (s, 2C, C_q), 136.1 (s, C_q), 131.4 (d, 2C, C_q), 130.8 (d, 2C, C_q), 129.1 (d, 2C, CH), 128.0 (d, CH), 126.7 (s, C_q), 126.3 (d, CH), 126.1 (d, CH), 119.7 (d, CH), 114.5 (d, CH), 113.5 (d, CH), 112.5 (d, CH), 111.1 (d, CH), 55.6 (q, CH_3), 40.4 (s, C_q), 38.3 (t, CH_2), 30.2 (q, CH_3), 9.5 (q, CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{23}H_{24}NO]^+$=$[M+H]^+$: 330.1852; found 330.1857.

2,3-dimethoxy-9,9-dimethyl-10-phenyl-9,10-dihydroacridine (22fb): This compound was prepared according to the GP-3 and isolated as black color solid 81% yield (139 mg): mp: 80-82 °C; [TLC (petroleum ether/ethyl acetate 8:2, R_f(**23f**)=0.50, R_f(**22fb**)=0.30, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2955, 2930, 1590, 1444, 1311, 1239, 1154, 1082, 877, 747, 607 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.62 (dd, 2H, *J*=7.8 and 7.8 Hz), 7.50 (dd, 1H, *J*=7.3 and 8.8 Hz), 7.43 (d, 1H, *J*=7.3 Hz), 7.34 (d, 2H, *J*=7.3 Hz), 7.00 (s, 1H), 6.95 (dd, 1H, *J*=7.3 and 7.8 Hz), 6.89 (dd, 1H, *J*=6.8 and 7.8 Hz), 6.24 (d, 1H, *J*=7.8 Hz), 5.84 (s, 1H), 3.88 (s, 3H, CH_3), 3.53 (s, 3H, CH_3), 1.68 (s, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=147.5 (s, C_q), 143.3 (s, C_q), 141.4 (s, C_q), 141.0 (s, C_q), 135.3 (s, C_q), 131.3 (d, C_q), 130.8 (d, 3C, CH), 129.4 (s, C_q), 128.2 (d, CH), 126.2 (d, CH), 125.2 (d, CH), 121.3 (s, C_q), 120.2 (d, CH), 113.9 (d, CH), 110.1 (d, CH), 99.4 (d, CH), 56.9 (q, CH_3), 55.6 (q, CH_3), 35.7 (s, C_q), 31.5 (q, 2C, CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{23}H_{24}NO_2]^+$=$[M+H]^+$: 346.1802; found 346.1795.

10,10-dimethyl-5-phenyl-5,10-dihydro-[1,3]dioxolo[4,5-b]acridine (22hb): This compound was prepared according to the GP-3 and isolated as white color solid 79% yield (130 mg): mp: 188-190 °C; [TLC (petroleum ether/ethyl acetate 8:2, R_f(**23h**)=0.50, R_f(**22hb**)=0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2965, 2882, 1592, 1475, 1313, 1224, 1172, 1040, 934, 879, 747, 700, 610 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.59 (dd, 2H, *J*=6.6 and 8.0 Hz), 7.48 (dd, 1H, *J*=7.4 and 7.4 Hz), 7.42 (d, 1H, *J*=7.5 Hz), 7.31 (d, 2H, *J*=6.8 Hz), 6.96 (s, 1H), 6.92 (dd, 1H, *J*=8.0 and 5.4 Hz), 6.90 (dd, 1H, *J*=7.4 and 7.3 Hz), 6.25 (d, 1H, *J*=8.0 Hz), 5.87 (s, 1H), 5.81 (s, 2H, CH_2) 1.64 (s, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=145.8 (s, C_q), 141.7 (s, C_q), 141.5 (s, C_q), 141.1 (s, C_q), 136.2 (s, C_q), 131.3 (d, 2C, CH), 130.9 (d, 2C, CH), 129.3 (s, C_q), 128.3 (d, CH), 126.3 (d, CH), 125.0 (d, CH), 122.4 (s, C_q), 120.4 (d, CH), 113.9 (d, CH), 105.2 (d, CH), 100.7 (t, CH_2), 96.5 (d, CH), 36.1 (s, C_q), 31.1 (q, 2C, CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{22}H_{20}NO_2]^+$=$[M+H]^+$: 330.1489; found 330.1484.

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Copper Catalyzed Coupling of Protecting Group Free and Sterically Hindered 2-Bromobenzyl Tertiary Alcohols with Phenols and Anilines: Facile Synthesis of Xanthenes and Dihydroacridines

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