EurJOC
European Journal of Organic Chemistry

A Journal of
ChemPubSoc Europe

# Accepted Article

**Title:** An efficient Benzannulation protocol for the synthesis of 9,9-diphenyl-9H-fluorenols using Intramolecular-Allene-Friedel-Crafts Annulation

**Authors:** SRINIVASARAO YARAGORLA and P. Rajesh

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

**To be cited as:** *Eur. J. Org. Chem.* 10.1002/ejoc.201900895

**Link to VoR:** http://dx.doi.org/10.1002/ejoc.201900895

Supported by
ACES Asian Chemical Editorial Society

WILEY-VCH

FULL PAPER WILEY-VCH

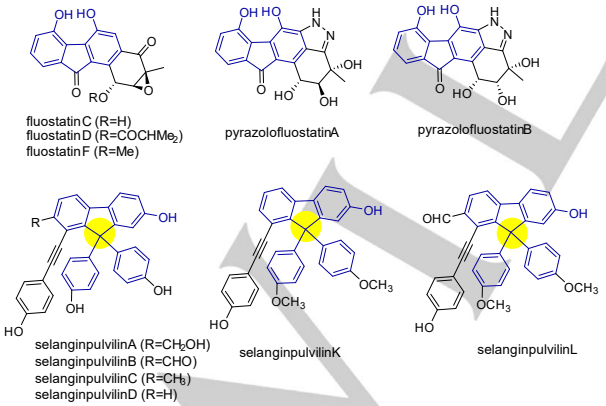
# An efficient Benzannulation protocol for the synthesis of 9,9-diphenyl-9H-fluorenols using Intramolecular-Allene-Friedel-Crafts Annulation

Srinivasarao Yaragorla*[a] and P. Rajesh[a]

**Abstract:** Herein we report a one-pot cascade benzannulation protocol for the synthesis 9,9-diaryl-9H-fluorenol, a key structure of many important natural products which exhibit the significant biological activities particularly phosphodiesterase-4 (PDE4) inhibitory activity.This approach proceeds through the annulation of *tert*-propargyl alcohols with 2-methyl acetylacetone through an Intramolecular-Allene-Friedel-Crafts reaction using $Ca(OTf)_2$ as the environmentally benign catalyst. Synthetic transformations of these compounds to useful materials are also presented here with the aid of cross-coupling and RCM reactions.

## Introduction

9,9-diphenyl-9H-fluorenol is an important structural motif with a 6-5-6 tricyclic framework presented in biologically active natural products. Generally, these structures represent a common name, fluorene which is a well-established privileged structure owing to its applications in the fields of material science and the pharmaceutical industry.[1,2] In material science, molecules bearing a core structure of fluorene are used as dyes sensitized solar cells and light emitting diodes due to their unique properties such as good charge transporters with high chemical stability.[1] As mentioned above, their abundance in natural products is also witnessed by the isolation of fluostatins and pyrazolofluostatins (Figure 1).[3,4] The fluostatin family of natural products was reported to have diverse bioactivities including dipeptidyl peptidases inhibition and antibacterial and antitumor activities.[3] Very recently, pyrazolofluostatins were isolated from south China sea-derived*micromonospora rosaria*SCSIO N160.[4]




[a] Dr. Srinivasarao Yaragorla (corresponding author)
Mr. P. Rajesh
School of Chemistry, Gurbaksh Building, W-16, 17, University of Hyderabad, P.O. Central University, Gachibowli, Hyderabad, 5000046, Telangana State, India.
E-mail: srinivas.yaragorla@uohyd.ac.in
Home page: https://sites.google.com/view/srinivasarao-yaragorla

**Figure 1.** Representative examples of biologically active natural products with the core structure of fluorenol(first row) and 9,9-diaryl-9H-fluorenol (second row).

Selanginpulvilins are another group of natural products with 9,9-diphenyl-9H-fluorenol structure (Figure 1) were isolated, and interestingl these molecules showed significant phosphodiesterase-4 (PDE4) inhibitory activity.[5,6] Owing to the unique structural framework and the biological activities associated with these molecules, the 9,9-diaryl-9H-fluorenolcorestructure becomes a promising lead for further exploration of biological properties. In this regard, a few reports on the total syntheses and a synthetic approach have been disclosed by various research groups.[6-9] Past few years, our research group was engaged in discovering novel synthetic methods for the annulations reactions.[10] Owing to the synthetic demand of 9,9-diaryl-9H-fluorenols, herein we report a single step synthesis of 9,9-diphenyl-9H-fluorenols using a benzannulation protocol. Based on our recent observation that *tert*-propargyl alcohols react with 3-methylpentane-2,4-dione through $S_N2'$ mechanism to yield tetra-substituted allene intermediates,[10a,10b] we assume that if the aryl group of allene (as highlighted in Figure 2), can react with $sp^2$ carbon of allene through an intramolecular-Friedel-Crafts annulation(IFCA) in the presence of a suitable Lewis acid conditions, that can lead to the benzannulation.

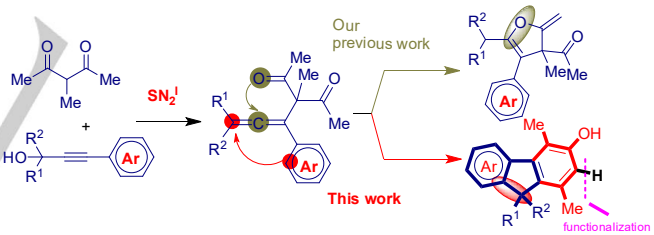



**Figure 2.**Synthetic strategies from in situ generated homo-allenylketone(previous and current)

## Results and Discussion

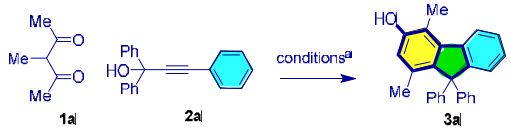
The quest for discovering the suitable reaction conditions for the synthesis of proposed 9,9-diaryl-9H-fluorenol was commenced by selecting 3-methylpentane-2,4-dione (**1a**) and propargyl alcohol (**2a**) as the reacting partners to achieve the synthesis of (**3a**) via the benzannulation protocol. Initially,**1a** (1.3equiv.) and **2a** (1 equiv.) were heated directly (neat condition) with $Ca(OTf)_2/Bu_4NPF_6$ (10/5 mol%)[10-11] at 90 °C, as expected 9,9-diphenyl-9H-fluorenol **3a** was formed in 47% yield after 3 h (entry 1, Table 1).To increase the reaction yield,we thought that a solvent medium could help and hence refluxed the reaction in acetonitrile (polar aprotic) for 2.5 h, and the reaction proceeded to yield 55% of **3a**, then the solvent was switched to ethanol (polar protic solvent) but there was no reaction in ethanol. Toluene (nonpolar solvent), gave 45% yield of **3a** (entries 2-4, table 1).1,2-dichloroethane as the solvent medium gave 85% yield of **3a** (entry 5, Table 1). Further attempts to improve the

Accepted Manuscript

This article is protected by copyright. All rights reserved.

yield of **3a** by an increase or decrease of the catalyst loadingswere unsuccessful. Alternative catalysts were also explored like TsOH (10 mol%), $FeCl_3$ (10 mol%), and TfOH (10 mol%), but all of them yielded moderate to poor yields (entries 8-10). Therefore entry 5 (Table 1) was considered as the optimum reaction condition for the synthesis of **3a** (85% yield) from **1a** and **2a**.

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

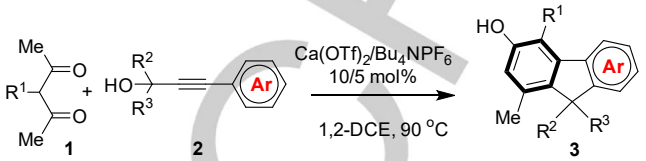


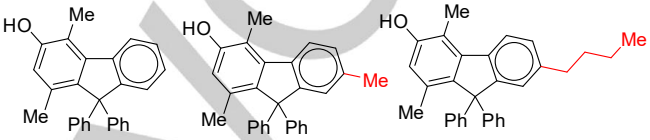

| Entry | Reaction conditions. | Yield (%)[b] |
|---|---|---|
| 1 | $Ca(OTf)_2/Bu_4NPF_6$ (10/5 mol%), neat, 90 °C, 3 h | 47 |
| 2 | $Ca(OTf)_2/Bu_4NPF_6$ (10/5 mol%), MeCN, 90°C, 2.5 h | 55 |
| 3 | $Ca(OTf)_2/Bu_4NPF_6$ (10/5 mol%), EtOH,90°C,2.5 h | nr |
| 4 | $Ca(OTf)_2/Bu_4NPF_6$ (10/5 mol%), toluene, 100 °C, 2.5 h | 45 |
| 5[c] | $Ca(OTf)_2/Bu_4NPF_6$ (10/5 mol%) DCE, 90 °C, 2.5 h | 85 |
| 6 | $Ca(OTf)_2/Bu_4NPF_6$ (10/10 mol%), DCE, 90 °C, 2.5 h | 85 |
| 7 | $Ca(OTf)_2/Bu_4NPF_6$ (5/10 mol%), DCE, 90 °C, 3 h | 67 |
| 8 | $Ca(OTf)_2/KPF_6$ (10/5 mol%), DCE, 90 °C, 6 h | 20 |
| 9 | TsOH (10 mol%) DCE, 90 °C, 3.5 h | 69 |
| 10 | TfOH (10 mol%) DCE, 90 °C, 10 h | 10 |
| 11 | $FeCl_3$ (10 mol%) DCE, 90 °C, 10 h | 28 |

[a]Mixture of **1a** (1.3 equiv.), **2a** (1 equiv.) were used;[b]Isolated yields; [c]Optimum conditions; DCE: 1,2-dichloroethane; rt: room temperature; TsOH:p-toluenesulfonic acid; TfOH: triflic acid; nr: no reaction

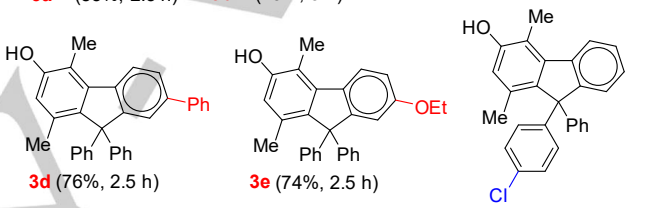
After establishing the optimum reaction conditions for the synthesis of **3a**, we aimed to generalize this protocol to check the viability of various substituents on the reactants (Table 2). Therefore we subjected **1a** with various propargyl alcohols (**2**) bearing alkyl substitutions on aryl ring under the optimized reaction conditions and obtained the corresponding fluorenols **3b** (7-methyl) and **3c**(7-butyl$^n$) in good yields. Similarly, fluorenol **3d** was made with C7-phenyl substitution and **3e** with C7-ethoxy substitution.This protocol was also tolerated the propargylic-phenyl substitutions (on substrate **2**) and gave the fluorenols **3f, 3h** and **3j** with *p*-chloro, *p*-fluoro and *p*-methoxy groups in good yields. Fluorenol **3l** was made which is bearing both the phenyl groups with *p*-fluoro substitutions at the quaternary centre. Products **3g**, **3i**, **3k** indicate that the protocol offers to have more than one substitution on reactant **2**. When the aryl moiety of propargyl alcohol **2** was taken as phenanthrenyl, it has given the product **3m** in good yield. Next, we thought to change the methyl substitution on diketone (**1a**) and hence synthesized the diketone bearing a benzyl group[12] on active methylene carbon (**1b**) and treated with propargyl alcohols under standard conditions to obtain the respective fluorenols **3n** and **3o** in moderate yields (Table 2). When we treated **1a** with propargyl alcohol **2** bearing a 3-methyl on the aryl group (*meta* substitution) under the same conditions, the reaction yielded a mixture of two regioisomers **3p**:**3p**$^l$ in 1:0.2 ratio with a 76% combined yield (Scheme 1).[13] Similarly, the reaction yielded the mixture of regioisomers **3q-3t** with the meta-substituted aryl ring of **2** (Scheme 1). The rationale for the formation of regioisomers can be explained by careful observation of these annulated products obtained in Table 2 and Scheme 1.

**Table 2.** Synthesis of 9,9-diphenyl-9H-fluorenols through a Ca(II)-catalyzed Intramolecular-Allene-Friedel-Crafts Annulation

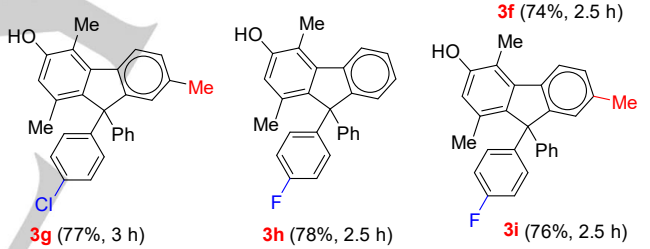


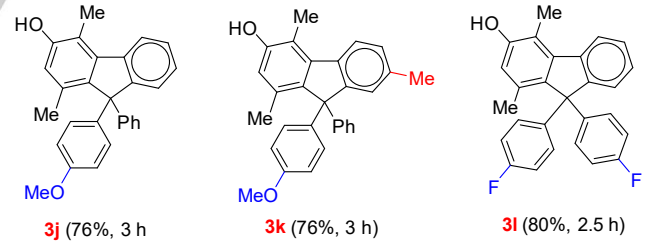

**3a**[7] (85%, 2.5 h) **3b**[7] (75%, 3 h) **3c** (75%, 2.5 h)



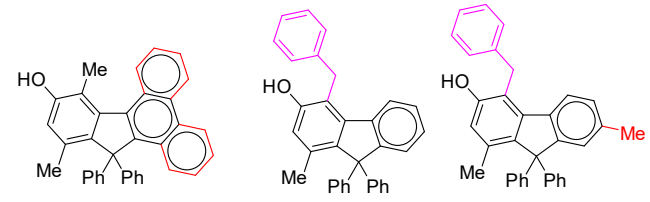

**3d** (76%, 2.5 h) **3e** (74%, 2.5 h) **3f** (74%, 2.5 h)




**3g** (77%, 3 h) **3h** (78%, 2.5 h) **3i** (76%, 2.5 h)




**3j** (76%, 3 h **3k** (76%, 3 h) **3l** (80%, 2.5 h)



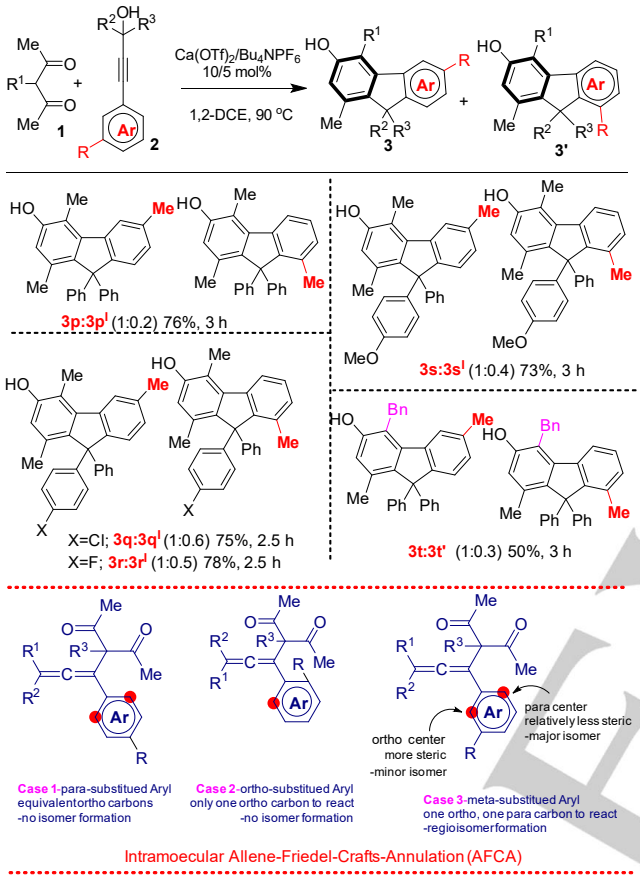

**3m** (75%, 3 h) **3n**[7] (48%, 3 h) **3o** (55%, 3 h)

Since Friedel-Crafts annulation proceeds through the C-C bond formation from ortho carbon, we will have three situations for this benzannulation reaction, based on the substitutions of the aryl ring (*ortho*, *para* and *meta*). For instance, consider the case-1, of the *para*-substituted aryl ring, it has two equivalent *ortho* carbons, so it doesn't matter which carbon will form the ring, thus a single product will be obtained (Case 1, Scheme 1) and it

Accepted Manuscript

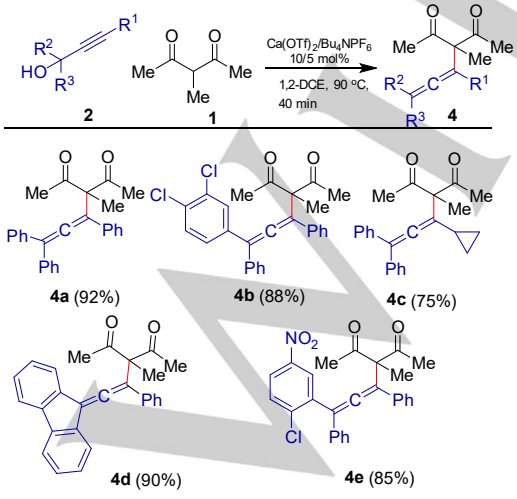
This article is protected by copyright. All rights reserved.

is evidenced by the synthesis of **3b-3e**, **3g**, **3i**, **3k** and **3o**. On the otherhand, when we have an *ortho*-substitution on aryl ring (case 2), there is only one carbon to undergo IFCA reaction, and hence we got a single product (**3m**). The third case is that a *meta*-substitution on the aryl group of **2**, where we will have two reactive carbons (ortho and para) to give two regio-isomeric products through IFCA (**3p-3t**, Scheme 1). Ofcourse, the reason for the unequal isomeric distribution can be explained based on the steric hindrance.

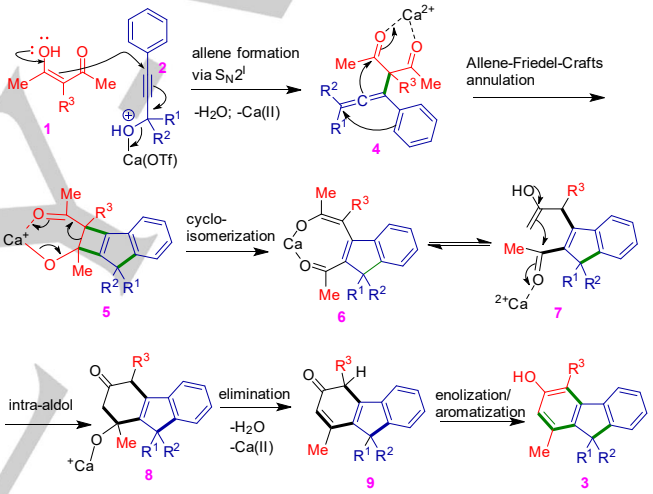



**Scheme 1.** The schematic explanation for the formation of regioisomeric fluorenols

**Table 3.** Synthesis of tetrasubstituted allenes using $Ca(OTf)_2$

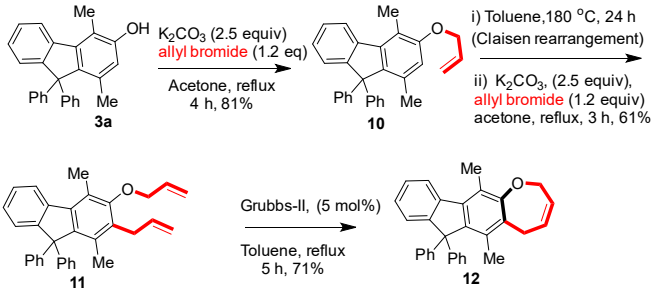



Our attempts to isolate the in situ generated homo-allenyl ketone, which we believed as the key intermediate in this benzannulation reaction, were successful. We were able to isolate allenes **4a-4e** in excellent yields in a short reaction time (Table 3). To support that the allene **4a** is the intermediate for the synthesis of **3a**, we refluxed a mixture of **4a** and $Ca(OTf)_2/Bu_4NPF_6$(under optimum conditions) for 1 h and obtained **3a** in 85% yield. Noteworthy, allene **4c** did not react as expected, because the cyclopropyl ring cannot offer IFCA reaction. Based on these observations we proposed the reaction mechanism as depicted in Scheme 2. Initially, the enol of diketone (**1**) reacts with activated *tert*-propargyl alcohol **2** through $S_N2^I$ mechanism to yield the allenyl ketone **4** (isolated and confirmed). Next, allene **4** undergoes an intramolecular-Friedel-Crafts annulation (IFCA) to give the tricarbocyclic compound **5**. Owing to the ring strain of fused cyclobutane, compound **5** further cycloisomerizes to furnish indene derivative **6**. Diketone **6** readily underwent an intramolecular-aldol annulation and gives the $\beta$-hydroxy ketone **8**. Finally, elimination followed by aromatization of aldol adduct **8** gives the fluorenol **3**.




**Scheme 2.** Mechanism

Further, we have emphasized on few important synthetic transformations of these fluorenols, for which we selected **3a** as the precursor. Initially, **3a** was subjected to o-allylation with allyl bromide and $K_2CO_3$ to give olefin **10**, which was then undergone a [3,3] Claisen rearrangementat 180 °C gave the *ortho*-allylation of **3a**, the crude compound was further allylated to get diene intermediate[14]**11**. Ring-closing metathesis (RCM) of diene **11** with Grubbs 2nd generation catalyst gave the benzoxepine[15] fused indene **12** in 71% yield (Scheme 3).

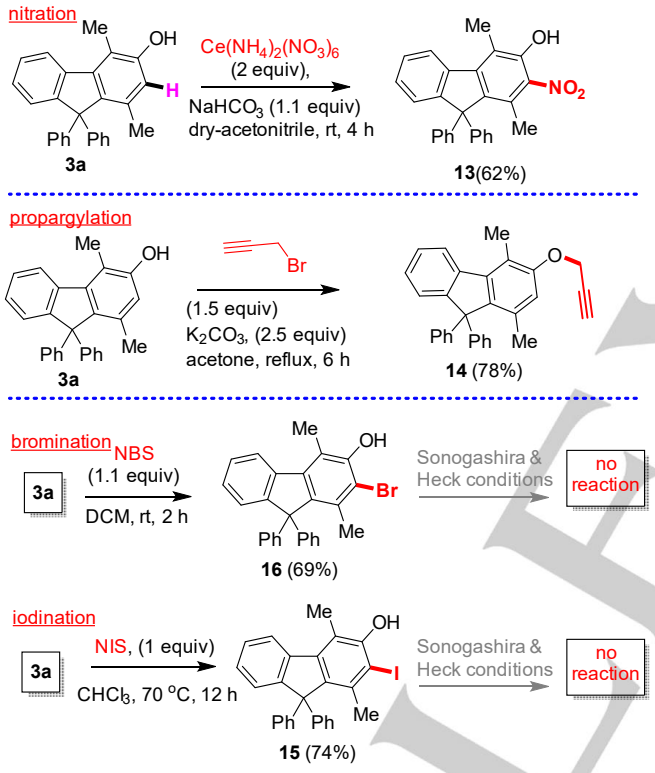



**Scheme 3.** Synthesis of flrouenoxepine (**12**)

Accepted Manuscript

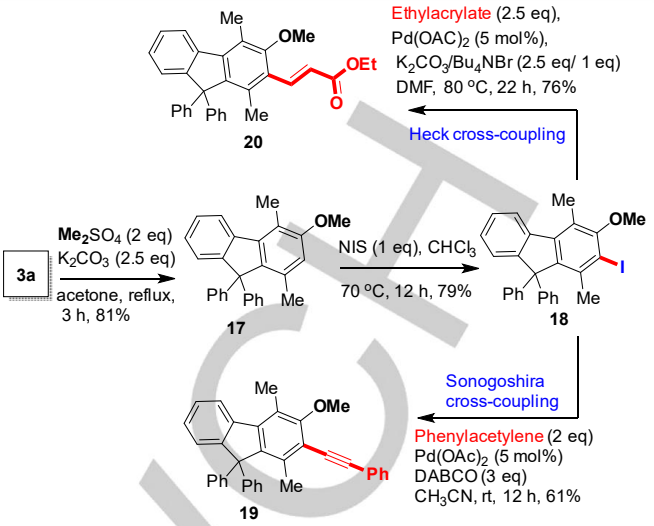
This article is protected by copyright. All rights reserved.

Fluorenol **3a** was also subjected to *o*-nitration with cericammonium nitrate to get *o*-nitro-fluorenol **13** in 62% yield; it is noteworthy that the aryl ring is now fully substituted in **13**. Propargylation of **3a** was also achieved with propargyl bromide and $K_2CO_3$ to furnish compound **14** in 78% yield (Scheme 4). Next, we planned a sequence of reactions on **3a**, that is bromination followed by Heck or Sonogashira cross-coupling reactions. Accordingly, **3a** was brominated with NBS and obtained *o*-bromo phenol **16** in 69% yield. Encouraged by this result, we attempted a Heck coupling with ethyl acrylate. Unfortunately, we found that the reaction did not proceed, then we tried a Sonogashira coupling with phenyl acetylene, which also did not proceed. Therefore we tried to install an *ortho*-iodide functionality on **3a** by treating with NIS and thus obtained *o*-iodophenol **15** in 74% yield. However, the cross-coupling reactions of iodide **15** were also failed to react under Heck and Sonogashira conditions (Scheme 4).




**Scheme 4.** Synthetic transformations of **3a** (propargylation, nitration, bromination and iodination). Conditions: **Heck** (ethyl acrylate (2.5 equiv.), $Pd(OAc)_2$ (5 mol%), $Bu_4NBr$ (1 equiv.), $K_2CO_3$ (2.5 equiv.), DMF, 80 °C, 24 h; **Sonogashira**(Phenylacetylene (2 equiv.), $Pd(OAc)_2$ (5 mol%), DABCO (3 equiv), acetonitrile, rt, 24 h)

We presume that free hydroxyl group of **3a** might be playing a role to inhibit the cross-coupling reaction, therefore we made a methyl ether of **3a** by treating with dimethyl sulfate (**17**),[14] and then subjected to iodination with NIS and obtained iodide **18**[16] in good yield. Though we are not sure of the exact reason at the moment, as presumed the iodide **18** underwent a smooth cross-coupling reaction under Heck conditions and gave the desired product **20**[17] in 76% yield. Sonogashira coupling of **18** with phenylacetylene was also successfully yielded **19** (Scheme 5).[18]




**Scheme 5.** Cross-coupling reactions of **3a**

## Conclusion

In conclusion, we have developed a simple one-pot benzannulation protocol for the synthesis of privileged structure, 9,9-diphenyl-9H-fluorenols from simple starting materials. Besides, this protocol offers to synthesize tetracyclic allenes. The reaction is catalyzed by eco-friendly catalyst $Ca(OTf)_2$ and yielded the products in good to excellent yields. Synthetic transformations of the fluorenols such as nitration, propargylation, bromination, iodination and fluorenoxepine synthesis have been developped. Further developments on this intramolecular-allene-Friedel Crafts annulation are currently ongoing in our laboratory.

## Experimental Section

**General information:** Unless otherwise noted, all reagents were used as received from commercial suppliers. $Ca(OTf)_2$ and $Bu_4NPF_6$ were obtained from Sigma-Aldrich and used without further purification. Reactions were performed in flame-dried or oven-dried glassware with magnetic stirring. Reactions were monitored using thin-layer chromatography (TLC) with aluminium sheets silica gel 60 $F_{254}$ from Merck. TLC plates were visualized with UV light (254 nm), iodine treatment. Column chromatography was carried out using silica gel 60-120 mesh as the stationary phase. NMR spectra were recorded at 500 MHz and 400 MHz (H) and 125 MHz and 100 MHz (C), respectively on Avance Bruker spectrometer. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (H: $\delta$ = 7.26 and C: $\delta$ = 77.0 ppm) as an internal standard, and coupling constants (*J*) are given in Hz. Melting points were measured with LABINDIA mepa melting apparatus.

**Experimental procedure for the synthesis of 1,4-dimethyl-9,9-diphenyl-9H-fluoren-3-ol (3a):**To a mixture of **1** (0.35mmol) and 1,3-dicarbonyl compound **2** (0.45mmol) in DCE (2 mL), $Ca(OTf)_2/Bu_4NPF_6$ (10/5 mol%) was added. The reaction was stirred at 90 °C, and the completion of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure,and the residue was purified by silica gel column chromatography using EA/PE (10:90, v/v) to obtain the desired product **3a** in 85% yield.Compounds **3a, 3b** and **3n** are reported earlier.[7]

**Experimental procedure for the synthesis of 3-methyl-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)pentane-2,4-dione(4a):** To amixture of **1**

Accepted Manuscript

This article is protected by copyright. All rights reserved.

(0.35mmol) and 1,3-dicarbonyl compound **2** (0.45mmol) in DCE (2 mL), $Ca(OTf)_2/Bu_4NPF_6$ (10/5 mol%) was added. The reaction was stirred at 90 °C, for 30-40 min and was stopped after formation of allene (monitor by TLC), solvent was removed under reduced pressure, and the resultant residue was purified by silica gel column chromatography using EA/PE (10:90, v/v) to obtain the desired product **4a** in 92% yield.

**General experimental procedure for the synthesis of 2-allyl-3-(allyloxy)-1,4-dimethyl-9,9-diphenyl-9H-fluorene (11)** To a stirring solution of 1,4-dimethyl-9,9-diphenyl-9H-fluoren-3-ol (100 mg, 0.27 mmol) in anhydrous acetone (5.0 mL) were added $K_2CO_3$ (87 mg, 0.633mmol) and allylbromide (26 µL, 0.33 mmol), the resulting reaction mixture was heated at 80 °C for 3 h. After completion of the reaction, it was filtered through a short plug of celite and the filtrate was concentrated under reduced pressure to give crude compound which was purified by silica gel column chromatography to afford the allyl ether. The above obtained above allyl etherwas dissolved in toluene (2 mL) and placed in a sealed pressure tube and heated at 180 °C for 24 h. The reaction mixture was directly purified by silica gel column chromatography to afford the rearranged allyl compound.

**General experimental procedure for the synthesis of 6,12-dimethyl-7,7-diphenyl-5,7-dihydro-2H-fluoreno[3,2-b]oxepine (12)** 2-allyl-3-(allyloxy)-1,4-dimethyl-9,9-diphenyl-9H-fluorene (**11**, 100 mg, 0.22 mmol) was dissolved in dry toluene (4 mL) and heated to reflux before adding 2nd generation Grubbs catalyst (9 mg, 5 mol%). Reaction was stirred at 100 °C for 6 h. After completion of the reaction, it was cooled to room temperature, and passed through a silica gel (20% EtOAc/Hexanes) and concentrated. The residual oil was further purified by flash chromatography (silica gel, gradient elution, 3-4% EtOAc/Hexanes) to afford the desired product **12** in 71% yield.

**General experimental procedure for the synthesis of 2-iodo-1,4-dimethyl-9,9-diphenyl-9H-fluoren-3-ol (15)** To a solution of compound 1,4-dimethyl-9,9-diphenyl-9H-fluoren-3-ol (100 mg, 0.27 mmol) in $CHCl_3$ (6 mL) was added catalytic TsOH followed by the addition of N-iodosuccinimide (61 mg, 0.22 mmol). The reaction mixture was heated at 55 °C for 16 h. After completion of the reaction, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (25 mL) and extracted with $CH_2Cl_2$ (20 mL x 3). The collected organic fractions were dried over anhydrous $Na_2SO_4$ and concentrated under vacuum to afford a white solid compound which was forwarded to the next step without further purificationand characterization.

**General experimental procedure for the synthesis of 3-methoxy-1,4-dimethyl-9,9-diphenyl-9H-fluorene (17)** To a stirring solution of 1,4-dimethyl-9,9-diphenyl-9H-fluoren-3-ol (100 mg, 0.27 mmol) in anhydrous acetone (10.0 mL) were added $K_2CO_3$ (76.0 mg, 0.55 mmol) and $Me_2SO_4$ (58 µL, 0.55 mmol).The resulting reaction mixture was heated at 80 °C for 3 h. After completion of the reaction, it was filtered through a short plug of celite,and the filtrate was concentrated in rotavapor and purified by silica gel column chromatography to afford the methoxy protected compound as white solid.

**Experimental procedure for Sonogashira cross-coupling of 18 to 19:** $Pd(OAc)_2$ (2 mol%) was dissolved in MeCN (1 mL), and was added to a mixture of phenylacetylene (45 mg, 0.45 mmol),9 (100 mg, 0.19 mmol), DABCO (3 equiv.), and MeCN (4 mL). Then the mixture was stirred under $N_2$ at room temperature for 12 h. The resulting mixture was filtered off, washed andthe filtrate was extracted with diethyl ether. The combined organic layers were washed with brine and dried over anhydrous $Na_2SO_4$. The solvent was evaporated under reduced pressure,and the residue was purified by columnchromatography (2–4%, EtOAc in pet ether) with silica gel to give product **14**in 61% yield.

**Experimental procedure for Heck reaction of 18 to 20:**Ethyl acrylate (49.8 mg, 0.49 mmol), was added to a solution of (100 mg, 0.19 mmol) in DMF (1.8 mL) containing $K_2CO_3$ (2.5 equiv.) and $Bu_4NBr$ (1 equiv.) and stirred at room temperature for 5 min. $Pd(OAc)_2$ (5 mol %) was then added, and the flask was flushed with $N_2$, sealed and allowed to stir at 80 °C for 22 h. The resulting mixture was filtered off, washed and the filtrate was extracted with diethyl ether. The combined organic layers were washed with brine and dried over anhydrous $Na_2SO_4$. The solvent was evaporated under reduced pressure, and the residue was purified by columnchromatography (6–8%, EtOAc in pet ether) with silica gel to give product in 76% yield.

**1,4-dimethyl-9,9-diphenyl-9H-fluoren-3-ol (3a**) Yield: 108 mg (85%) white solid; mp 205-206°C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.97 (d, *J* =8Hz, 1H), 7.38 (d, *J* =7.5Hz, 1H), 7.32-7.24(m, 5H), 7.23-7.20 (m, 7H), 6.50 (s, 1H), 4.92 (s, 1H), 2.69 ( s, 3H), 1.89 (s, 3H) ;ppm; $^{13}$ C NMR(125 MHz, $CDCl_3$): δ 155.7, 153.4, 142.7, 142.4, 141.0, 140.5, 133.8, 129.1, 127.9, 127.3, 127.1, 126.4, 125.4, 123.2, 116.9, 64.5, 20.0, 12.3 ppm; IR (film):$\nu_{max}$3524, 3022, 2923, 1589, 1491, 1298, 1246, 1183, 1073, 912 $cm^{-1}$; HRMS (ESI-TOF): m/z calcd for $C_{27}H_{22}O$ [M+H]+ : 363.1751, found: 363.1750.

**1,4,7-trimethyl-9,9-diphenyl-9H-fluoren-3-ol (3b)**Yield: 93 mg (75%) white solid; mp 252-254°C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.80 (d, *J*=8Hz, 1H), 7.28-7.24 (m, 4H), 7.22-7.17 (m, 8H), 7.13-7.08 (m, 2H), 6.43 (s, 1H), 4.73 (s, 1H), 2.62 (s, 3H), 2.26 (s, 3H), 1.82 (s, 3H) ppm; $^{13}$ C NMR(125 MHz, $CDCl_3$): δ 155.9, 153.4, 142.9, 142.4, 140.1, 138.5, 137.2, 133.7, 129.2, 128.1, 127.9, 126.4, 126.1, 122.9, 116.7, 116.4, 64.4, 21.7, 19.9, 12.3 ppm; IR (film): $\nu_{max}$ 3531, 2921, 2851, 1736, 1587, 1446, 1309, 850 $cm^{-1}$; (LCMS): *m/z* [M+H]+ : 377.

**7-butyl-1,4-dimethyl-9,9-diphenyl-9H-fluoren-3-ol (3c)** Yield: 92 mg (75%) white solid; mp 248-249 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.81 (d, *J*=7.0 Hz, 1H), 7.25 (m, 5H), 7.18 (m, 5H), 7.11 (m, 2H), 6.44 (s, 1H), 4.68 (s, 1H), 2.62 (s, 3H),2.52 (t, *J*=8.0 Hz, 2H), 1.83 (s, 3H), 1.48 (m, 2H), 1.25 (m, 2H), 0.85 (t, *J*=7.0 Hz, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): 155.9, 153.4, 143.0, 142.4, 142.3, 140.7, 138.6, 133.8, 129.2, 127.9, 127.3, 126.4, 125.6, 122.9, 116.7, 116.4, 64.5, 35.8, 33.7, 22.4, 20.0, 14.0, 12.3 ppm; IR (film): $\nu_{max}$ 3531, 2920, 2852, 1736, 1587, 1446, 1310 $cm^{-1}$; HRMS (ESI-TOF): m/z calcd for$C_{31}H_{30}O$[M+H]+ :419.5772, found: 419.5769.

**1,4-dimethyl-7,9,9-triphenyl-9H-fluoren-3-ol (3d)** Yield: 92 mg (76%) white solid; mp 250-251 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.98 (d, *J*=6.5 Hz, 1H), 7.49 (m, 4H), 7.37 (t, *J*=7.5 Hz, 2H), 7.30 (m, 5H), 7.23 (m, 6H), 6.48 (s, 1H), 4.73 (s, 1H), 2.67 (s, 3H), 1.86 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): 156.5, 142.8, 142.7, 141.3, 140.3, 140.2, 133.9, 129.2, 128.8, 128.0, 127.3, 127.2, 126.5, 126.2, 124.2, 123.4, 117.1, 117, 64.7, 20, 12.4 ppm; IR (film): $\nu_{max}$ 3397, 3056, 2923, 2851, 1733, 1598, 1490, 1385, 1075, 1031 $cm^{-1}$; HRMS (ESI-TOF): m/z calcd for$C_{33}H_{26}O$ [M+H]+ : 439.2064, found: 439.2060.

**7-ethoxy-1,4-dimethyl-9,9-diphenyl-9H-fluoren-3-ol (3e)** Yield: 91 mg (74%) white solid; mp 246-247 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.81 (d, *J*=8.5 Hz, 1H), 7.26 (d, *J*=7.5 Hz, 5H),7.19 (m, 5H), 6.83 (m, 2H), 6.40 (s, 1H), 4.72 (s, 1H), 3.94 (m, 2H), 2.60 (s, 3H), 1.82 (s, 3H) 1.32 (t, *J*=7.0 Hz, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): 158.7, 157.6, 153.4, 142.9, 142.1, 140.5, 134.0, 129.2, 128.0, 126.4, 123.9, 116.1, 115.8, 113.1, 112.1, 64.5, 63.6, 20.0, 14.9, 12.3 ppm; IR (film):$\nu_{max}$3551, 3517, 2975, 1603,1490,1291,1091, 854, 754cm$^{-1}$; HRMS (ESI-TOF): m/z calcd for$C_{29}H_{26}O_2$[M+H]+ : 407.2013, found: 407.2010.

**9-(4-chlorophenyl)-1,4-dimethyl-9-phenyl-9H-fluoren-3-ol (3f)** Yield: 92 mg (74%) white solid; mp 179-180 °C;$^1$H NMR ($CDCl_3$, 500 MHz): δ 7.92 (d, *J*=7.5 Hz, 1H), 7.30 (t, *J*=7.5 Hz, 2H), 7.20 (m, 10H), 6.47 (s, 1H), 4.75 (s, 1H), 2.64 (s, 3H), 1.83 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$,125 MHz): 155.3, 153.6, 142.2, 142.1, 141.5, 141.0, 133.7, 132.3, 130.6, 129.0, 127.5, 127.3, 126.3, 126.7, 125.3, 117.4, 117.0, 64.1, 20.0, 12.3 ppm; IR (film):$\nu_{max}$3386, 2923, 2358, 1693, 1487, 1353, 1295, 1090 $cm^{-1}$; HRMS (ESI-TOF): m/z calcd for $C_{27}H_{21}ClO$ [M+H]+ : 397.1361,found: 397.1362.

**9-(4-chlorophenyl)-1,4,7-trimethyl-9-phenyl-9H-fluoren-3-ol (3g)** Yield: 95 mg (77%) white solid; mp 180-181 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.79 (d, *J*=6.5 Hz, 1H), 7.20 (m, 9H), 7.09 (d, *J*=9.0 Hz, 2H), 6.42 (s, 1H), 4.81 (s, 1H), 2.60 (s, 3H), 2.26 (s, 3H), 1.81 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): 155.5, 153.6, 142.4, 142.0, 141.7, 140.6, 138.4, 137.4, 133.6, 132.2, 130.6, 129.0, 128.2, 128.0, 126.6, 126.0, 123.0, 117.0, 116.6, 64, 21.7, 20, 12.3 ppm; HRMS (ESI-TOF): m/z calcd for$C_{28}H_{23}ClO$ [M+Na]+ : 433.1334,found: 433.1333.

**9-(4-fluorophenyl)-1,4-dimethyl-9-phenyl-9H-fluoren-3-ol (3h)** Yield: 98 mg (78%) white solid; mp 193-194°C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.92 (d, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 2 Hz, 2H), 7.24-7.15 (m, 8H), 6.88 (t, *J* = 9 Hz, 2H), 6.46 (s, 1H), 4.83 (s, 1H) 2.63 (s, 3H), 1.83 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): δ 162.5, 160.6, 155.6, 153.5, 142.5, 140.5, 140.4, 138.5, 138.5, 133.7, 130.7, 129.1, 128.1, 127.4, 127.2, 126.6, 125.3, 123.3, 117.3, 117.1, 114.8, 114.6, 63.9, 19.9, 12.3 ppm; IR (film):$\nu_{max}$3398, 3057, 2925, 1705, 1503, 1297, 1226, 1077, 831 $cm^{-1}$; HRMS (ESI-TOF): m/z calcd for $C_{27}H_{21}FO$ [M+H]+ : 381.1656,found: 381.1655.

Accepted Manuscript

This article is protected by copyright. All rights reserved.

**9-(4-fluorophenyl)-1,4,7-trimethyl-9-phenyl-9H-fluoren-3-ol(3i)** Yield: 94 mg (76%) white solid; mp 202-203 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.79 (d, *J*=7.0 Hz, 1H), 7.23 (m, 5H), 7.18 (m, 2H), 7.00 (d, *J*=5 Hz, 2H), 6.88 (m, 2H), 6.42 (s, 1H), 4.78 (s, 1H), 2.61 (s, 3H), 2.26 (s, 3H), 1.81 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): 162.5, 160.6, 155.8, 153.5, 142.7, 142.2, 140.5, 138.7, 138.6, 138.3, 137.3, 133.6, 130.8, 130.7, 129.0, 128.2, 128.0, 126.5, 126.0, 123.0, 116.9, 116.5, 114.7, 114.6, 63.8, 21.7, 19.9, 12.3 ppm; (LCMS): *m/z* [M+H]+ : 395.

**9-(4-methoxyphenyl)-1,4-dimethyl-9-phenyl-9H-fluoren-3-ol (3j)** Yield: 94 mg (76%) white solid; mp 208-209 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.90 (d, *J*=7.5 Hz, 1H), 7.27 (m, 4H), 7.18 (m, 6H), 6.75 (m,2H), 6.46 (s, 1H), 4.82 (s, 1H), 3.74 (s, 3H), 2.63 (s, 3H), 1.84 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$,125 MHz): 158.1, 156.0, 153.4, 143.0, 142.6, 140.9, 140.4, 134.5, 133.7, 130.2, 129.0, 127.9, 127.3, 127.0, 126.4, 125.3, 123.2, 117.1, 117.0, 63.9, 55.3, 20.0, 12.3 ppm; IR (film):$\nu_{max}$3370, 2947, 2359, 1736, 1603, 1505, 1233, 1146, 1098, 1022, 827 cm$^{-1}$; HRMS (ESI-TOF): m/z calcd for $C_{28}H_{24}O_2$ [M+H]+ : 393.1856,found: 393.1858.

**9-(4-methoxyphenyl)-1,4,7-trimethyl-9-phenyl-9H-fluoren-3-ol (3k)** Yield: 92 mg (75%) white solid; mp 210-211 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.82 (d, *J*=8.0 Hz, 1H), 7.51 (m, 1H), 7.20 (m, 11H), 6.78 (m, 2H), 6.46 (s, 1H), 4.77 (s, 1H),3.78 (s, 3H), 2.64 (s, 3H), 2.30 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): 158.1, 156.2, 153.4, 143.2, 142.6, 140.5, 138.3, 137.2, 134.8, 133.7, 130.3, 129.1, 128.8, 128.7, 127.9, 126.3, 126.0, 124.4, 123.0, 119.8, 116.7, 116.4, 114.9, 113.2, 63.7, 55.3, 21.7, 12.3, 10.9 ppm; HRMS (ESI-TOF): m/z calcd for$C_{29}H_{26}O_2$[M+H]+: 407.2013,found:407.2013.

**9,9-bis(4-fluorophenyl)-1,4-dimethyl-9H-fluoren-3-ol (3l)** Yield: 99 mg (80%) white solid; mp 236-237 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.93 (d, *J* =7.5 Hz, 1H), 7.31-7.25 (m, 3H), 7.21-7.19 (m, 5H), 6.91-6.87 (m, 3H), 6.49 (s, 1H), 4.77 (s, 1H), 2.64 (s, 3H), 1.83 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): δ 162.8, 161.7, 155.4, 153.6, 142.1, 140.8, 140.3, 138.2, 133.5, 130.6, 130.5, 127.5, 127.4, 125.2, 123.4, 117.4, 117.1, 114.9, 114.7, 63.3, 20.1, 12.3 1 ppm; HRMS (ESI-TOF): m/z calcd for$C_{27}H_{20}F_2O$ [M+H]+ : 399. 4518, found: 399. 4516

**9,12-dimethyl-13,13-diphenyl-13H-indeno[1,2-l]phenanthren-10-ol (3m)** Yield: 90 mg (75%) white solid; mp237-238 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 8.68-8.33 (m, 3H), 7.67-7.57 (m, 7H), 7.39-7.18 (m, 8H), 6.54 (s, 1H), 4.93 (s, 1H), 2.59 (s, 3H), 2.07 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): δ 154.8, 149.5, 145.4, 140.4, 135.7, 132.8, 131.6, 131.5, 129.7, 128.4, 128.1, 127.7, 126.9, 126.7, 126.1, 126.1, 126.1, 125.7, 125.2, 123.3, 123.3, 123.1, 116.1, 60.5, 19.9, 17.2 ppm; HRMS (ESI-TOF): m/z calcd for $C_{35}H_{26}O$ [M+H]+ : 463.2064, found: 463.2063.

**4-benzyl-1-methyl-9,9-diphenyl-9H-fluoren-3-ol (3n)** Yield: 74 mg (48%) white solid; mp150-152°C; $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.24-7.20 (m, 7H), 7.18-7.12 (m, 10H), 7.05-6.93 (m, 3H), 6.46 (s, 1H), 4.79 (s, 1H), 4.49 (s, 2H), 3.20 (s, 3H) ppm;$^{13}$ C NMR(125 MHz, $CDCl_3$): δ 155.8,154.2, 142.8, 142.6, 140.9, 140.2, 139.2, 136.2, 135.1, 129.8, 129.7, 129.1, 129.1, 128.8, 128.6, 128.4, 128.2, 128.1, 127.6, 127.3, 127.1, 126.5, 125.4, 123.9, 119.2, 117.4, 64.5, 37.5, 28.5 ppm; IR (film): $\nu_{max}$ 3523, 3021, 2924, 1590, 1489, 1378, 1225, 1136, 868 cm$^{-1}$; (LCMS): *m/z* [M+H]+ : 439.

**4-benzyl-1,7-dimethyl-9,9-diphenyl-9H-fluoren-3-ol (3o)** Yield: 83 mg (55%) white solid; mp 137-138 °C; $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.56 (d, *J* = 8 Hz, 1H), 7.31 (d, *J* = 1.6 Hz, 1H) 7.29 (t, *J* = 8 Hz, 2H), 7.27-7.25 (m, 4H), 7.23-7.19 (m, 8H), 7.11 (s, 1H), 6.94 (t, *J* = 8 Hz, 1H), 6.48 (s, 1H), 4.72 (s, 1H), 4.54 (s, 2H), 2.20 (s, 3H), 1.87 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 156.1, 154.2, 142.8, 141.1, 139.3, 137.5, 137.5, 135.1, 129.2, 128.8, 128.2, 128.2, 128.1, 126.4, 126.2, 126.1, 122.7, 118.8, 116.9, 64.3, 31.7, 21.6, 20.1 ppm; IR (film): $\nu_{max}$ 3528, 3028, 2360, 1489, 1378, 1225, 1029, 802 cm$^{-1}$; HRMS (ESI-TOF): m/z calcd for$C_{34}H_{28}O$ [M+H]+ : 453. 2218,found:453. 2218.

**1,4,6-trimethyl-9,9-diphenyl-9H-fluoren-3-ol (3p)** Yield: 95 mg (76%) white solid; mp 140-143 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.73 (s, 1H), 7.25 (m, 3H), 7.18 (m, 8H), 6.99 (d, *J*=8.0 Hz, 1H), 6.46 (s, 1H), 4.70 (s, 1H), 2.65 (s, 3H), 2.39 (s, 3H), 1.84 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): 153.4, 153.1, 143.0, 141.2, 140.6, 136.6, 133.8, 129.3, 129.1, 128.3, 127.9, 127.8, 126.4, 125.1, 123.9, 117.1, 116.8, 64.2, 21.8, 20.0, 12.4 ppm; HRMS (ESI-TOF): m/z calcd for $C_{28}H_{24}O$ [M+H]+ : 377.1827,found:377.1828.

**9-(4-chlorophenyl)-1,4,6-trimethyl-9-phenyl-9H-fluoren-3-ol (3q)** Yield: 92 mg (75%) white solid; mp 161-164 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.73 (s, 1H), 7.22 (m, 3H), 7.19 (m, 6H), 7.16 (m, 1H), 7.00 (m, 1H), 6.47 (s, 1H), 4.72 (s, 1H), 2.64 (s, 3H), 2.40 (s, 3H), 1.83 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): 153.6, 152.7, 142.5, 142.4, 141.7, 141.1, 140.6, 136.9, 133.7, 132.2, 130.7, 129.0, 128.4, 128.0, 127.9, 126.6, 125.0, 124.0, 117.3, 117.0, 63.7, 21.8, 20.0, 12.4 ppm; (LCMS): *m/z* [M+H]+ : 411.

**9-(4-fluorophenyl)-1,4,6-trimethyl-9-phenyl-9H-fluoren-3-ol (3r)** Yield: 97 mg (78%) white solid; mp 177-179 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.73 (s, 1H), 7.20 (m, 9H), 6.99 (d, *J*=7.0 Hz, 1H),6.87 (d, *J*=6.5 Hz, 1H), 6.45 (s, 1H), 4.80 (s, 1H), 2.64 (s, 3H), 2.39 (s, 3H), 1.82 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): 156.5, 142.8, 142.7, 141.3, 140.3, 140.2, 133.9, 129.2, 128.8, 128.0, 127.3, 127.2, 126.5, 126.2, 124.2, 123.4, 117.1, 117.0, 64.7, 20.0, 12.4 ppm;HRMS (ESI-TOF): *m/z* calcd for$C_{28}H_{23}FO$ [M+H]+ : 395.1813,found:395.1813.

**9-(4-methoxyphenyl)-1,4,6-trimethyl-9-phenyl-9H-fluoren-3-ol (3s)**Yield: 90 mg (73%) as white solid; mp 137-138 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.26-7.24 (m, 3H), 7.22-7.14 (m, 6H), 6.99-6.97 (m, 1H), 6.75-6.73 (m, 2H), 6.43 (s, 1H), 4.90 (s, 1H), 3.73 (s, 3H), 2.63 (s, 3H), 2.38 (s, 3H), 1.83 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): δ 158.1, 153.3, 153.3, 143.2, 142.9, 141.1, 140.4, 136.5, 134.8, 133.7, 130.3, 130.2, 129.1, 129.1, 128.2, 127.9, 127.7, 126.3, 124.9, 123.9, 117.1, 116.7, 113.2, 113.1, 63.5, 53.3, 21.8, 19.9, 12.4 ppm; IR (film): $\nu_{max}$ 3371, 2947, 2359, 1736, 1603, 1505, 1233, 1098, 1022 cm$^{-1}$; HRMS (ESI-TOF): *m/z* calcd for$C_{29}H_{26}O_2$ [M+H]+ : 407. 2013,found:407. 2015.

**4-benzyl-1,6-dimethyl-9,9-diphenyl-9H-fluoren-3-ol (3t)** Yield: 76 mg (50%) white solid; mp 188-190 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.43-7.41 (m, 1H), 7.32-7.30 (m, 7H), 7.27-7.20 (m, 9H), 7.05-7.03 (m, 1H), 6.55 (s, 1H), 4.83 (s, 1H), 4.58 (s, 2H), 3.30 (s, 3H), 2.25 (s, 3H) ) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): δ 155.8, 154.2, 142.9, 142.6, 141.1, 140.2, 139.2, 135.2, 129.8, 129.1, 128.8, 128.6, 128.2, 128.1, 127.6, 127.3, 126.5, 126.3, 125.4, 123.1, 119.2, 117.4, 64.5, 37.5, 31.7, 20.1 ppm; IR (film):$\nu_{max}$3526, 3021, 2923, 1598, 1449, 1377, 1069, 743 cm$^{-1}$; HRMS (ESI-TOF): *m/z* calcd for $C_{34}H_{28}O$ [M+H]+: 453. 2218, found:453. 2218.

**3-methyl-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)pentane-2,4-dione (4a)**Yield: 123 mg (92%) white solid; mp 121-123 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.43-7.38 (m, 8H), 7.35-7.33 (m, 6H), 7.29-7-26 (m, 1H), 2.20 (s, 6H), 1.68 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): δ 207.3, 207.1, 135.4, 134.1, 128.7, 128.7, 128.3, 127.9, 127.7, 127.5, 114.1, 109.9, 68.7, 27.9, 20.2 ppm; IR (film): $\nu_{max}$ 3081, 1987, 1955, 1697, 1443, 1202, 722 cm$^{-1}$; HRMS (ESI-TOF): *m/z* calcd for$C_{27}H_{24}O_2$ [M+H]+ : 380.1776, found:380.1780.

**3-(3-(3,4-dichlorophenyl)-1,3-diphenylpropa-1,2-dien-1-yl)-3-methylpentane-2,4-dione (4b)** Yield: 111 mg (88%) white solid; mp 125-127 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.46 (t, *J* = 2 Hz, 1H), 7.39 (d, *J* = 6.5 Hz, 2H), 7.35-7.33 (m, 3H), 7.32-7.27 (m, 3H), 7.26-7.24 (m, 4H), 2.16 (s, 6H), 1.64 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): δ 207.2, 206.9, 135.9, 134.6, 133.8, 133.1, 133.1, 130.7, 130.1, 129.1, 128.9, 128.4, 128.3, 128.2, 127.7, 127.6, 112.3, 110.8, 69.1, 27.9, 20.4 ppm; HRMS (ESI-TOF): *m/z* calcd for$C_{27}H_{22}Cl_2O_2$ [M+H]+ : 448.0997,found:448.0998.

**3-(1-cyclopropyl-3,3-diphenylpropa-1,2-dien-1-yl)-3-methylpentane-2,4-dione (4c)**Yield: 104 mg (75%) white solid; mp 123-125 °C; $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.35-7.31 (m, 5H), 7.29-7.25 (m, 5H), 2.15 (s, 6H), 1.62 (s, 3H), 1.12 (d, *J* = 5.2 Hz, 1H), 0.82 (t, *J* = 2.4 Hz, 2H), 0.56 (t, *J* = 2 Hz, 2H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 207.1, 201.5, 136.1, 128.5, 128.1, 127.6, 115.1, 111.8, 69.8, 27.5, 19.2, 10.5, 8.4 ppm; IR (film): $\nu_{max}$ 3052, 2086, 2044, 1713, 1372, 1086, 740 cm$^{-1}$; HRMS (ESI-TOF): *m/z* calcd for$C_{24}H_{24}O_2$[M+H]+ : 344.1776, found:344.1780.

**3-(2-(9H-fluoren-9-ylidene)-1-phenylvinyl)-3-methylpentane-2,4-dione(4d)**Yield: 120 mg (90%) white solid; mp 121-124 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.77 (d, *J* = 8 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.41-7.38 (m, 2H), 7.33-7.30 (m, 2H), 7.29-7.25 (m, 5H), 2.38 (s, 6H), 1.67 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): δ 206.6, 204.9, 139.3, 137.1, 133.7, 128.9, 128.7, 128.4, 128.1, 127.5, 123.4, 120.5, 115.1, 109.8, 69.3, 27.8, 20.6 ppm; HRMS (ESI-TOF): *m/z* calcd for$C_{27}H_{22}O_2$[M+H]+ :378.1620, found: 378.1621.

Accepted Manuscript

This article is protected by copyright. All rights reserved.

**3-(3-(2-chloro-5-nitrophenyl)-1,3-diphenylpropa-1,2-dien-1-yl)-3-methylpentane-2,4-dione (4e)** Yield: 107 mg (85%) white solid; mp 128-130 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 8.26 (d, *J* = 3 Hz, 1H), 8.21-8.19 (m, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.38-7.31 (m, 3H), 7.30-7.24 (m, 5H), 2.2 (s, 3H), 2.18 (s, 3H), 1.67 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): δ 206.6, 206.5, 146.8, 141.3, 136.2, 133.4, 133.4, 131.1, 129.2, 128.9, 128.4, 127.9, 126.5, 124.3, 112.2, 109.9, 69.1, 28.1, 27.5, 20.5 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{27}H_{22}ClNO_4$[M+H]+ :459.1237, found:459.1228.

**3-(allyloxy)-1,4-dimethyl-9,9-diphenyl-9H-fluorene (10)** Yield: 87 mg (79%) yellow sticky compound; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.34-7.29 (m, 3H), 7.27-7.25 (m, 4H), 7.22-7.15 (m, 7H), 6.55 (s, 1H), 6.15-6.09 (m, 1H), 5.49-5.47 (m, 1H), 5.30-5.28 (m, 1H), 4.56-4.55 (m, 2H), 2.67 (s, 3H), 1.90 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): δ 156.6, 155.7, 142.8, 142.3, 141.2, 140.2, 134.1, 133.4, 129.2, 127.9, 127.3, 127.1, 126.4, 125.5, 123.4, 120.1, 117.1, 114.1, 69.8, 64.6, 20.4, 12.4 ppm; IR (film): $\nu_{max}$ 2923, 1649, 1597, 1450, 1350, 1169, 1032, 906 cm$^{-1}$; (LCMS): *m/z* [M+H]+ : 403.

**2-allyl-3-(allyloxy)-1,4-dimethyl-9,9-diphenyl-9H-fluorene (11)** Yield: 66 mg (61%) white solid; mp 226-228 °C; $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.33-7.28 (m, 4H), 7.27-7.21 (m, 5H), 7.20-7.14 (m, 4H), 6.18-6.11 (m, 2H), 5.96-5.89 (m, 1H), 5.51-5.47 (m, 1H), 5.30-5.27 (m, 1H), 4.97-4.94 (m, 1H), 4.93-4.78 (m, 1H), 4.33 (d, *J* = 5.2 Hz, 1H), 3.44-3.42 (m, 2H), 2.69 (s, 3H), 1.83 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 156.1, 155.5, 146.1, 142.7, 141.1, 138.5, 137.1, 134.2, 133.4, 131.1, 129.2, 129.1, 127.9, 127.5, 127.1, 127.1, 126.4, 125.4, 124.1, 122.9, 116.9, 114.8, 65.1, 31.4, 16.6, 13.9 ppm; HRMS (ESI-TOF): m/z calcd for $C_{33}H_{30}O$ [M+Na]+ : 465.2195, found: 465.2194.

**6,12-dimethyl-7,7-diphenyl-5,7-dihydro-2H-fluoreno[3,2-b]oxepine (12)** Yield: 71 mg (66%) white solid; mp 178-179 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.87 (d, *J* = 8 Hz, 1H), 7.30-7.18 (m, 6H), 7.17-7.14 (m, 6H), 7.11 (d, *J* = 1 Hz, 1H), 5.83-5.81 (m, 1H), 5.43-5.41 (m, 1H), 4.62 (t, *J* = 2.5 Hz, 2H), 3.44-3.42 (m, 2H), 2.68 (s, 3H), 1.88 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): δ 156.5, 155.4, 145.9, 142.8, 141.1, 137.9, 136.2, 129.1, 127.9, 127.1, 126.9, 126.4, 126.2, 125.3, 123.4, 122.7, 70.6, 65.2, 25.8, 16.9, 12.8 ppm; IR (film): $\nu_{max}$ 3020, 2922, 1595, 1491, 1156, 1023, 803 cm$^{-1}$; HRMS (ESI-TOF): m/z calcd for $C_{31}H_{26}O$ [M+H]+ : calcd 414.1984 found: 414.1983.

**1,4-dimethyl-2-nitro-9,9-diphenyl-9H-fluoren-3-ol (13)** Yield: 69 mg (62%) yellow solid; mp 158-160 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 10.47 (s, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.36-7.34 (m, 2H), 7.30-7.25 (m, 7H), 7.25-7.23 (m, 4H), 2.75 (s, 3H), 2.12 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): δ 157.1, 153.3, 145.9, 142.4, 141.8, 138.6, 135.5, 130.6, 129.8, 128.8, 128.2, 127.9, 127.6, 127.1, 125.8, 124.9, 120.6, 65.2, 29.8, 18.7 ppm; (LCMS): *m/z* [M+H]+ : 406.

**1,4-dimethyl-9,9-diphenyl-3-(prop-2-yn-1-yloxy)-9H-fluorene (14)** Yield: 85.8 mg (78%) white solid; mp 192-193 °C; $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, *J* = 7.6 Hz, 1H), 7.34-7.30 (m, 1H), 7.29-7.24 (m, 5H), 7.22-7.15 (m, 7H), 6.65 (s, 1H), 4.71 (d, *J* = 2.4 Hz, 2H), 2.65 (s, 3H), 2.52 (t, *J* = 2.4 Hz, 1H), 1.92 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 155.8, 155.6, 142.1, 142.7, 141.1, 140.4, 133.5, 129.2, 127.9, 127.4, 127.1, 126.5, 125.5, 123.4, 120.5, 114.4, 79.3, 75.3, 64.6, 57.1, 20.4, 12.5 ppm; IR (film): $\nu_{max}$ 3060, 2859, 2128, 1596, 1491, 1367, 1156, 1102 cm$^{-1}$; HRMS (ESI-TOF): m/z calcd for $C_{30}H_{24}O$ [M+H]+ : 401.1907 found: 401.1905.

**2-iodo-1,4-dimethyl-9,9-diphenyl-9H-fluoren-3-ol (15)** Yield: 99.7 mg (74%) white solid; mp 215-216 °C; $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, *J* = 7.6 Hz, 1H), 7.32-7.26 (m, 7H), 7.22-7.19 (m, 6H), 5.5 (s, 1H), 2.76 (s, 3H), 2.0 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 155.5, 152.6, 142.9, 142.4, 140.5, 140.4, 135.8, 129.1, 128.7, 128.1, 127.9, 127.3, 126.6, 125.5, 123.5, 117.3, 95.9, 65.3, 26.7, 14.1 ppm; HRMS (ESI-TOF): m/z calcd for $C_{27}H_{21}IO$ [M+H]+ : 488.0637 found: 488.0636

**2-bromo-1,4-dimethyl-9,9-diphenyl-9H-fluoren-3-ol (16)** Yield: 83 mg (69%) yellow solid; mp 188-190 °C; $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.28-7.25 (m, 6H), 7.22-7.19 (m, 6H), 5.80 (s, 1H), 2.74 (s, 3H), 2.01 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): δ 155.5, 150.2, 142.9, 142.4, 140.3, 139.9, 132.3, 129.1, 128.1, 127.8, 127.3, 126.6, 125.5, 123.4, 118.2, 114.4, 65.3, 20.8, 13.6 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{27}H_{21}BrO$ [M-H]+ : 439.0756,found:439.0755.

**3-methoxy-1,4-dimethyl-9,9-diphenyl-9H-fluorene (17)** Yield: 83 mg (81%) white solid; mp 229-230 °C; $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.29-7.26 (m, 5H), 7.21-7.13 (m, 7H), 6.54 (s, 1H), 3.84 (s, 3H), 2.63 (s, 3H), 1.91 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 157.5, 155.6, 142.8, 141.9, 141.2, 140.1, 133.4, 129.1, 127.9, 127.3, 127.1, 126.4, 125.4, 123.4, 119.6, 112.5, 64.5, 56.1, 20.5, 12.2 ppm; IR (film): $\nu_{max}$ 2923, 1597, 1491, 1349, 1168, 743, 644 cm$^{-1}$; HRMS (ESI-TOF): m/z calcd for $C_{28}H_{24}O$ [M+H]+ : 377.4975 found: 377.4973.

**2-iodo-3-methoxy-1,4-dimethyl-9,9-diphenyl-9H-fluorene (18)** Yield: 105 mg (79%) white solid; mp 224-225 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.90 (d, *J* = 8 Hz, 1H), 7.32-7.29 (m, 2H), 7.27-7.25 (m, 4H), 7.24-7.17 (m, 7H), 3.82 (s, 3H), 2.76 (s, 3H), 2.1 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 158.1, 155.4, 146.5, 142.1, 140.8, 140.1, 137.5, 129.1, 128.1, 127.9, 127.3, 126.7, 125.6, 124.4, 123.4, 101.4, 65.6, 60.7, 26.8, 14.6 ppm; IR (film): $\nu_{max}$ 2923, 2852, 2096, 1492, 1445, 1374, 1033, 745 cm$^{-1}$; HRMS (ESI-TOF): m/z calcd for $C_{28}H_{23}IO$ [M+H]+ : 502.0794 found: 502. 0793.

**3-methoxy-1,4-dimethyl-9,9-diphenyl-2-(phenylethynyl)-9H-fluorene (19)** Yield: 57 mg (61%) white solid; mp 216-218 °C; $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.90 (d, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 6.5 Hz, 1H), 7.36-7.31 (m, 5H), 7.29-7.25 (m, 5H), 7.24-7.20 (m, 7H), 3.82 (s, 3H), 2.77 (s, 3H), 2.08 (s, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 125 MHz): δ 158.1,155.4, 146.5, 142.1, 140.8, 140.1, 137.5, 132.6, 129.3, 129.1, 128.5, 128.1, 127.9, 127.3, 126.7, 125.6, 124.4, 123.4, 101.4, 65.6, 60.7, 26.8, 14.6 6 ppm; HRMS (ESI-TOF): m/z calcd for $C_{36}H_{28}O$ [M+H]+ : 477.2220 found: 477.2219.

**(E)-ethyl3-(3-methoxy-1,4-dimethyl-9,9-diphenyl-9H-fluoren-2-yl)acrylate (20)** Yield: 71.4 mg (76%) white solid; mp 230-231 °C; $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.95-7.88 (m, 2H), 7.37-7.33 (m, 6H), 7.32-7.20 (m, 7H), 6.52 (d, *J* = 16.4 Hz, 1H), 4.29-4.24 (m, 2H), 3.74 (s, 3H), 2.74 (s, 3H), 2.19 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 207.1, 167.6, 158.1, 155.9, 146.3, 142.2, 141.5, 140.3, 140.1, 133.8, 129.1, 128.1, 127.9, 127.2, 127.1, 126.6, 125.5, 124.6, 123.5, 123.2, 65.2, 60.6, 60.4, 31.1, 18.1, 14.4, 13.3 ppm; IR (film): $\nu_{max}$ 2984, 2921, 2850, 1708, 1621, 1567, 1443, 1416, 1297, 1003 cm$^{-1}$; HRMS (ESI-TOF): m/z calcd for $C_{33}H_{30}O_3$ [M+H]+ : 475.2275 found: 475. 2275.

## Acknowledgements

The authors acknowledge the funding from SERB-India project no-EMR/2016/4812. Mr. Ankit Kumar is acknowledgedfor the technical help

**Keywords:**Allene-Friedel-Crafts annulation, Cycloisomerization, Fluorenols, propargyl alcohols, Calcium catalysis.

## References

1. a) M. Zeng, T. E. Ballard, A. Tkachenko, V. Burns, D. Feldheim, C. Melander, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 5148-5151; b) Y. Han, A. Bisello, C. Nakamoto, M. Rosenblatt, M. Chorev, *J. Pept. Res.* **2000**, *55*, 230-239; c) P. Perry, M. Read, R. Davies, S. Gowan, A. Reszka, A. Wood, L. Kelland, S. Neidle, *J. Med. Chem.***1999**, *42*, 2679-2684.
2. (a) J. Tan, Z. Wang, J. Yuan, Y. Peng, Z. Chen, *Adv. Synth. Catal.* **2019**, *361*, 1295-1300. b) T. Hadizad, J. Zhang, Z. Y. Wang, T. C. Gorjanc and C. Py, *Org. Lett.,* **2005**, *7*, 795–797; c) S. Merlet, M. Birau, Z. Y. Wang, *Org. Lett.,* **2002**, *4*, 2157–2159; d) D. Thirion, J. I. Rault-Berthelot, L. Vignau and C. Poriel, *Org. Lett.,* **2011**, *13*, 4418–4421; e) K.-T. Wong, L.-C. Chi, S.-C. Huang, Y.-L. Liao, Y.-H. Liu and Y. Wang, *Org. Lett.,* **2006**, *8*, 5029–5032; f) K.-T. Wong, T.-Y. Hwu, A. Balaiah, T.-C. Chao, F.-C. Fang, C.-T. Lee and Y.-C. Peng, *Org. Lett.,* **2006**, *8*, 1415–1418.
3. a) T. Akiyama, K. T. Nakamura, Y. Takahashi, H. Naganawa, Y. Muraoka, T. Aoyagi, T.J. Takeuchi, *Antibiot.* **1998**, *51*, 586-588; b) Z. Feng, J. H. Kim, S. F. Brady,*J. Am. Chem. Soc.* **2010**, *132*, 11902-11903; c) C. Yang, C. Huang, W. Zhang, Y. Zhu, C. Zhang, *Org. Lett.* **2015**, *17*, 5324-5327.

Accepted Manuscript

This article is protected by copyright. All rights reserved.

4. a) W. Zhang, C. Yang, C. Huang, L. Zhang, H. Zhang, Q. Zhang, C. Yuan, Y. Zhu, *Org. Lett.* ***2017****, 19,* 592-595; b) W. Zhang, Z. Liu, S. Li, Y. Lu, Y. Chen, H. Zhang, G. Zhang, Y. Zhu, G. Zhang, W. Zhang, J. Liu, C. Zhang*, J. Nat. Prod*. **2012**, *75*, 1937-1943; c) M. Yu, S. J. Danishefsky, *J. Am. Chem. Soc***. 2008**, *130*, 2783-2785.
5. a) J.-S. Zhang, X. Liu, J. Weng, Y.-Q. Guo, Q.-J. Li, A. Ahmad, G.-H. Tang , S. Yin, *Org. Chem. Front.,* **2017**, *4*, 170-177;b)S. Sengupta, G. Mehta, *Org. Biomol. Chem.,* **2018**, *16*, 6372-6390.
6. a) B. S. Chinta , B. Baire, *Org. Biomol. Chem.,* **2017**, *15*, 5908–5911;b) R. Karmakar, D. Lee, *Org. Lett.* **2016**, *18*, 6105- 6107; c) M. J. Sowden, M. S. Sherburn, *Org. Lett.* **2017**, *19*, 636- 637.
7. L.-F. Yao, D. Tan, X. Miao, K.-W. Huang, *RSC Adv***.2012**, *2*, 7594- 7598.
8. a) A. C. Grimsdale, K. Leok Chan, R. E. Martin, P. G. Jokisz and A. B. Holmes, *Chem. Rev.,***2009**, *109*, 897–1091; b) L. Luo, S. H. Choi and C. D. Frisbie, *Chem. Mater.,***2010**, *23*, 631–645.
9. a) A. Facchetti, *Chem. Mater.,* **2010**, *23*, 733–758; b) B. Satpathi, Siddhant, V. Wagulde, S. S. V. Ramasastry *Chem. Commun.,* **2017**, *53*, 8042-8045.
10. a) S.Yaragorla, P. Rajesh, *Org. Biomol. Chem.,* **2019**, 17, 1924-1928; b) S. Yaragorla, P. Rajesh, A. Pareek, A. Kumar, *Adv. Synth. Catal.* **2018**, *360*, 4422-4428; c) S. Yaragorla, A. Pareek, *Tetrahedron Lett.* **2018**, *59*, 909-913; d) S. Yaragorla, A. Pareek, R. Dada, *Tetrahedron Lett.* **2017**, *58*, 4642-4647; e) G. Singh, S. Yaragorla, *RSC Adv.* **2017**, *7*, 18874-18882; f) M. Presset, B. Michelet, R. Guillot, C. Bour, S. B.-Lafolle, V. Gandon, *Chem. Commun.,* **2015**, *51*, 5318-5321; g) S. P. Morcillo, D. Leboeuf, C. Bour, V. Gandon, *Chem. Eur. J.* **2016**, *22*, 16974- 16978; h) S. P. Morcillo, M. Presset, S. Floquet, V. Coeffard, C. Greck, C. Bour, V. Gandon, *Eur. J. Org. Chem.* **2016**, 2688-2694.
11. For recent reviews on calcium catalysis see:a) J.-M. Begouin, M. Niggemann, *Chem. Eur. J.* **2013**, *19,* 8030–8041; b) S. Harder, Topics in *Organometallic Chemistry*, Springer, Berlin, 2013; (c) D. Lebœuf, V. Gandon, *Synthesis* **2017**, *49*, 1500–1508.
12. G. Kishor, Thorat, P. Kamble, A. K. Ray , N. Sekar*Phys. Chem. Chem. Phys.,* **2015**, *17*, 17221-17236.
13. Regioisomeric ratio was determined by the $^{1}$H NMR spectra of the crude product.
14. S. Singh, R. Samineni, S. Pabbaraja, G. Mehta *Angew. Chem.* **2018**, *130*, 17089-7093; b) K. Tanaka, H. Aoki, H. Hosomi, S. Ohba, *Org. Lett.* **2000**, *2,* 2133-2134.
15. S. Mondal, S. Debnath, *Synthesis,* **2014**, *46*, 368–374.
16. P. Das, Y. Mankada , D. S. Reddy, *Tetrahedron Lett.* **2019**, *60*, 831-833.
17. R. F. Heck, J. P. Nolley, *J. Org. Chem.* **1972**, *37*, 2320-2322.
18. K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, *16*, 4467- 4470.

WILEY-VCH

Accepted Manuscript

This article is protected by copyright. All rights reserved.

10.1002/ejoc.201900895


WILEY-VCH

**Entry for the Table of Contents** (Please choose one layout)

FULL PAPER

**Benzannulation of allenyl ketones***

Srinivasarao Yaragorla* and P. Rajesh

*Page No. – Page No.*

**An efficent Benzannulation protocol for the synthesis of 9,9-diphenyl-9H-fluorenols using Intramolecular-Allene-Friedel-Crafts Annulation**

A one-pot synthesis of 9,9-diphenyl-9H-fluorenols is developped from tert-propargyl alcohols and substituted-acetylacetones using Ca(II) salt in good to excellent yields. This benzannulation reaction involves the formation of allenyl-ketone and a subseqent Allene-Friedel-Crafts Annulation.

WILEY-VCH

Accepted Manuscript

This article is protected by copyright. All rights reserved.