EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201200042

A Facile Synthesis of 2*H*-Chromenes and 9-Functionalized Phenanthrenes through Reactions between α,β-Unsaturated Compounds and Arynes

Tiexin Zhang,[a] Xian Huang,[a,b][‡] and Luling Wu*[a]

Keywords: Arynes / Cyclization / Domino reactions / Chromenes / Phenanthrenes

Facile syntheses of 2*H*-chromenes or 9-functionalized phenanthrenes under mild conditions in moderate to good yields have been developed. They each involve annulations of arynes with α,β-unsaturated compounds bearing different electron-withdrawing groups (EWGs). Depending on the natures of the different EWGs, the reactions proceed by different pathways: enals react with arynes through a tandem [2+2] cycloaddition/thermal electrocyclic ring-opening/6e-electrocyclization sequence to afford 2*H*-chromenes, whereas acyl-/ethoxycarbonyl-/cyano-substituted styrenes undergo Diels–Alder reactions with arynes followed by aromatization to afford 9-functionalized phenanthrenes. The scope, limitations, regioselectivities and mechanisms have been studied and are discussed in detail.

Introduction

2*H*-Chromenes and their analogues constitute a significant family of scaffolds found in naturally existing and artificial molecules and exhibit unique biological/pharmacological activities[1] and outstanding photochromic properties.[2] Ageratochromenes I and II (Figure 1a), for example, initially isolated from *Ageratum houstonianum*, are important because of their insecticidal activities, including the abilities to induce precocious metamorphosis.[1c] Although 2*H*-chromenes have attracted much synthetic interest,[3] new efficient routes are still highly desirable.

Phenanthrenes, on the other hand, are the fundamental building blocks of many organic compounds.[4] PBT-1 (Figure 1b), well-known for its inhibition of the growth of cancer cells, is difficult to obtain because of the multi-step synthesis of 9-carbonylphenanthrenes en route (Figure 1c).[5] New, concise constructions of 9-carbonylphenanthrenes were thus essential for the rapid assembly of PBT-1 and its analogues.

The reactions of highly reactive arynes[6,7] have been extensively developed as powerful tools in organic synthesis. The innovation of fluoride-induced in-situ generation of arynes from silylaryl triflates under mild conditions has naturally resulted in rapid progress in aryne chemistry in recent years.[8] [2+2] Cycloadditions[9,10] of arynes can provide highly strained benzannulated four-membered rings,[11] which tend to undergo ring-opening to afford the important intermediates **A** [Figure 2, Equation (a)] for further transformations. In Suzuki's pioneering contribution,[6a,6f,9d] [2+2] cycloadditions between arynes and alkenes afforded stable benzocyclobutenes that were found to be hard to isomerize to *ortho*-quinodimethanes[12] [Figure 2, Equation (a), X = C] by thermal electrocyclic ring-opening without heating. [2+2] Cycloadditions between carbon–heteroatom double bonds and arynes have been much less widely studied and are still challenging in relation to those between alkenes and arynes. The heteroatom-containing [2+2] adducts tend, however, to undergo ring-opening at lower temperatures, owing to their high ring strain, and can then be trapped with subsequent reagents, which resulted in a tandem strategy for facile construction of benzoheterocycles [Figure 2, Equation (a), X = heteroatom]:[10,13] trapping of

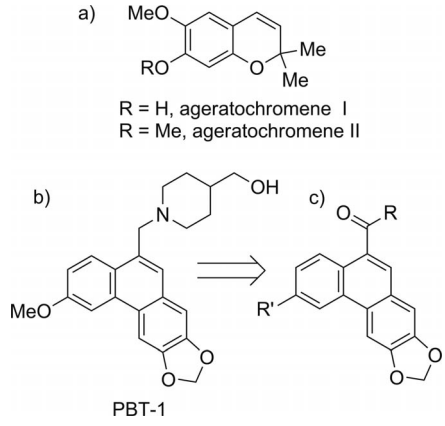


Figure 1. 2*H*-Chromenes and 9-functionalized phenanthrenes with biological/pharmacological acivities.

[a] Department of Chemistry, Zhejiang University (Xixi Campus), Hangzhou 310028, People's Republic of China
Fax: +86-571-88807077
E-mail: wululing@zju.edu.cn
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China
[‡] Prof. Huang passed away on March 6, 2010. He had been fully in charge of this project. At this moment, Prof. Luling Wu is helping in finishing all the projects with the assistance of Prof. Shengming Ma
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201200042.

the aryne–aldehyde [2+2] adduct with an additional aryne was reported by Yoshida [Figure 2, Equation (b)],[13g] dialkylzinc reagents have been shown to be effective in trapping the [2+2] adducts of formamide with arynes[13c] [Figure 2, Equation (c)], and enolates of esters[13a] and ketenimine anions[13b] have very recently also been successfully utilized in [4+2] cycloadditions with the intermediates **A**.

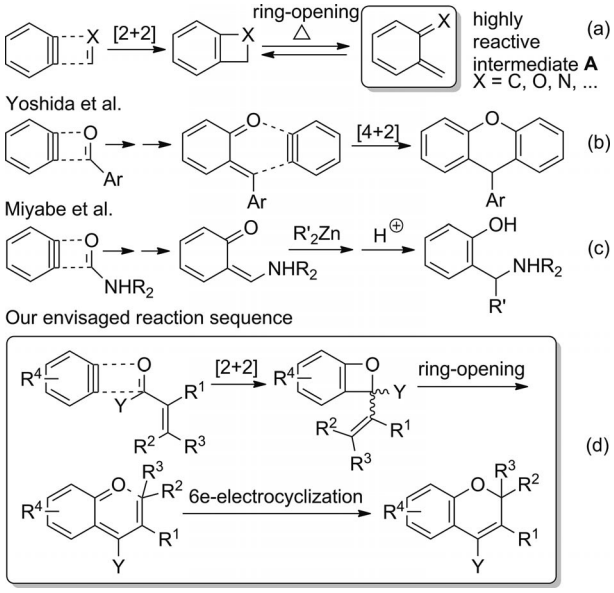


Figure 2. [2+2] Cycloadditions of C=X with arynes and further trapping reactions.

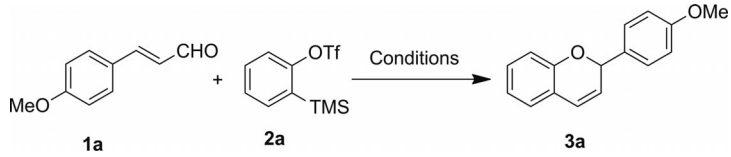
In view of these impressive results, we considered it worthwhile to examine the feasibility of trapping formal aryne/C=O [2+2] adducts intramolecularly with alkenes to furnish a tandem aryne [2+2] cycloaddition/ring-opening/6e-electrocyclization sequence [Figure 2, Equation (d)]. In the pioneering work of Heaney, tetrachlorobenzenediazonium-2-carboxylate was employed as the aryne precursor in reactions with cinnamaldehydes (40 equiv.), giving 2*H*-chromenes in 4–58% yields.[14a] Here we report a facile synthesis of 2*H*-chromenes by the tandem protocol described above with use of α,β-unsaturated enals and arynes generated from silylaryl triflates under very mild conditions. Interestingly, when the aldehyde functionality was changed to ketone, ester or nitrile, the reactions proceeded through a totally different aryne Diels–Alder/aromatization sequence to afford 9-functionalized phenanthrenes.

Results and Discussion

Synthesis of 2*H*-Chromenes 3 by a Formal [2+2] Cycloaddition/Thermal Electrocyclic Ring-Opening/6e-Electrocyclization Sequence with Enals 1 and Arynes Produced from *o*-(Trimethylsilyl)aryl Triflates 2

A preliminary experiment was conducted in acetonitrile at 75 °C, with 3-(4-methoxyphenyl)propenal (**1a**, Table 1), *o*-(trimethylsilyl)phenyl triflate (**2a**) and CsF in a ratio of 1:1.5:3. The reaction went to completion within 24 h (Table 1, Entry 1) to afford the expected product 2-(4-methoxyphenyl)-2*H*-chromene (**3a**, 40% yield), together with recovered **1a** (25%). Efforts to optimize the reaction conditions to improve the yield of **3a** were then made. Mixed solvents with different ratios of acetonitrile and toluene were tested to control the rate of in-situ generation of aryne from **2a** (Entries 2–6). It was found that the reaction in MeCN/PhMe (1:4, v/v) afforded **3a** in an improved yield of 51% with a 20% yield of **1a** being recovered (Entry 5). The yield of **3a** was not improved with more equivalents of

Table 1. Optimization of reaction conditions for the synthesis of 2-(4-methoxyphenyl)-2*H*-chromene (**3a**).[a]



Entry	**2a** [equiv.]	CsF [equiv.]	MeCN/PhMe [v/v]	*T* [°C]	Addition time of **2a**[b] [h]	Time of reaction[c] [h]	Yield of **3a**[d] [%]	Recovery of **1a**[d] [%]
1	1.5	3	1:0	75	–	24	40	25
2	1.5	3	1:1	75	–	48	43	17
3	1.5	3	1:2	75	–	48	48	18
4	1.5	3	1:3	75	–	48	50	30
5	1.5	3	1:4	75	–	48	51	20
6	1.5	3	1:9	75	–	96	29	26
7	2.0	4	1:4	75	–	48	40	17
8	2.5	5	1:4	75	–	48	43	9
9	2.5	5	1:4	75	10.5	24	53	7
10	***3.0***	***6***	***1:4***	***75***	***12.5***	***24***	***59***	***0***
11	3.0	6	1:4	45	12.5	72	55	0
12	3.0	3.5	1:4	75	12.5	48	56	7

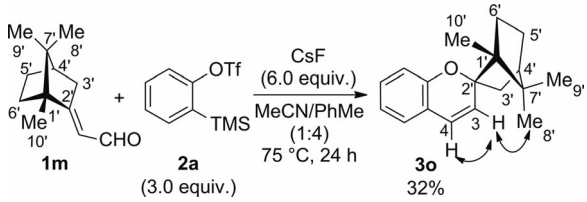
[a] The reaction was conducted with **1a** (0.5 mmol), the specified amount of CsF and **2a** in anhydrous solvent (5.0 mL). [b] When **2a** was added by microinfusion syringe pump, the addition rate of **2a** was approximately 0.12 mmol h^{-1}. [c] Reaction times after addition of **2a**. [d] Isolated yields.

aryne (Entries 7, 8). Interestingly, though, when a solution of aryne precursor **2a** (2.5 equiv.) in MeCN/PhMe (1:4, v/v, 2.5 mL) was added slowly by microinfusion syringe pump to a stirred mixture of **1a** and CsF in MeCN/PhMe (1:4, v/v, 2.5 mL) over 10.5 h, 93% of **1a** could be converted to afford **3a** (53% yield) after additional stirring for 24 h (Entry 9). In order to consume all **2a**, slow addition of **2a** (3 equiv.) in MeCN/PhMe (1:4, v/v, 2.5 mL) by microinfusion syringe pump over 12.5 h was used, and the yield of **3a** was improved to 59%. If the reaction was conducted at a lower temperature or with a reduced amount of CsF, lower yields of **3a** and longer reaction times were observed (Entries 11, 12).

With the optimized conditions to hand, the scope and limitations of this process were then examined with various enals **1** and aryne precursors **2**. Typical results are summarized in Table 2. Firstly, when β-aryl enals **1b**–**1f** were employed, lower to good yields of the corresponding 2-aryl-2*H*-chromenes **3b**–**3f** could be obtained, indicating the remarkable electronic effect of the substituents. Enals bearing electron-donating groups on the β-aryl substituents gave higher yields of products, probably due to the enhancement of the nucleophilicities of the aldehyde groups by the electron-donating groups (Table 1, Entry 10 and Table 2, Entries 1, 2).[13g] When α-methyl enal **1g** was used, 3-methyl-2*H*-chromene **3g** was afforded in a lower yield (relative to that of Table 1, Entry 10) of 33%, which implied considerable steric hindrance by the α-methyl group of **1g** in the reaction. Secondly, β,β-disubstituted enals **1h**–**1l** were found also to participate smoothly in the reactions to afford the corresponding 2,2-disubstituted 2*H*-chromenes in moderate to good yields (Entries 7–11).

We next investigated the tandem reactions of substituted arynes. Reactions utilizing **1i** and symmetrical arynes (from **2b** and **2c**) proceeded efficiently to give polysubstituted 2*H*-chromenes in yields of 77% and 98%, respectively (Table 2, Entries 12, 13).

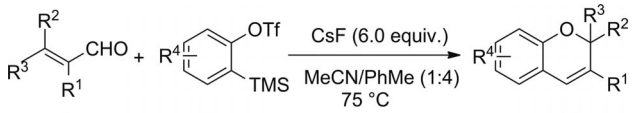
It should be noted that when (2-bornyliden)acetaldehyde (**1m**) was employed, the unsymmetrical bornylidene moiety could be successfully introduced into the C2 position of the 2*H*-chromene scaffold stereoselectively, with the structure of the resulting product **3o** being determined by a 2D NOE experiment [Equation (1)].



(1)

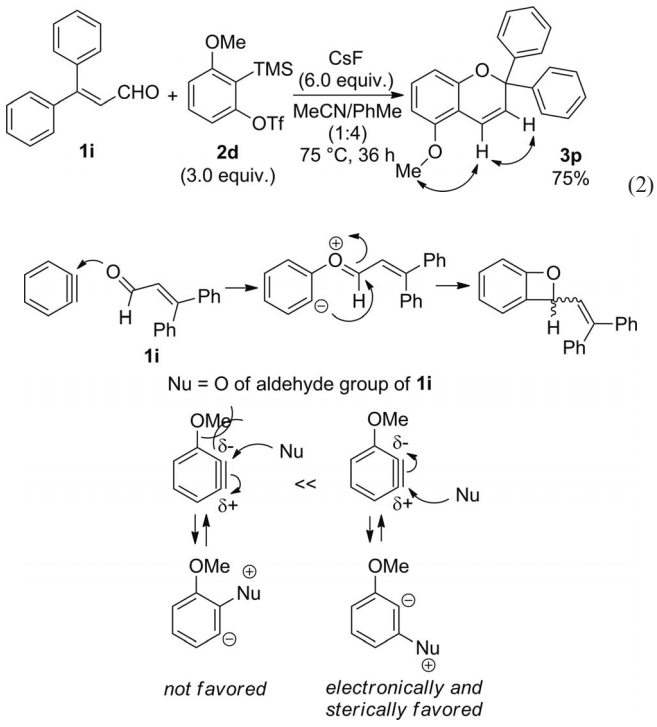
To establish the regiochemistry of this protocol, the unsymmetrical 3-methoxy-substituted aryne (from **2d**) was employed in the reaction with **1i**, leading to the formation of only one regioisomer – **3p** – in 75% yield, as determined by a 2D NOE experiment [Equation (2)]. The regioselectivity could be explained in terms of the electronic and steric factors during the initial step of this reaction (Scheme 1).[12a]

Table 2. Synthesis of 2*H*-chromenes through the reactions between enals **1** and symmetrical arynes.[a]



Entry	$R^1/R^2/R^3$ (**1**)	R^4 (**2**)/equiv. of **2**	Time[b] [h]	Yield of **3**[c] [%]
1	H/H/2-$MeOC_6H_4$ (**1b**)	H (**2a**)/3.0	24	70 (**3b**)
2	H/H/4-MeC_6H_4 (**1c**)	H (**2a**)/4.0	36	66 (**3c**)
3	H/H/C_6H_5 (**1d**)	H (**2a**)/4.5	36	45 (**3d**)
4	H/H/4-BrC_6H_4 (**1e**)	H (**2a**)/4.5	60	34 (**3e**)
5	H/H/4-FC_6H_4 (**1f**)	H (**2a**)/4.5	120	22 (**3f**)[d]
6	Me/H/4-$MeOC_6H_4$ (**1g**)	H (**2a**)/3.0	48	33 (**3g**)
7	H/4-$MeOC_6H_4$/4-$MeOC_6H_4$ (**1h**)	H (**2a**)/3.0	24	61 (**3h**)
8	H/C_6H_5/C_6H_5 (**1i**)	H (**2a**)/3.7	24	80 (**3i**)
9	H/C_6H_5/4-$MeOC_6H_4$ (**1j**)	H (**2a**)/3.0	24	61 (**3j**)
10	H/Me/3-$MeOC_6H_4$ (**1k**)	H (**2a**)/3.0	24	52 (**3k**)
11	H/Me/*i*Bu (**1l**)	H (**2a**)/3.0	24	31 (**3l**)[e]
12	H/C_6H_5/C_6H_5 (**1i**)	4,5-Me_2 (**2b**)/3.0	36	77 (**3m**)
13	H/C_6H_5/C_6H_5 (**1i**)	4,5-F_2 (**2c**)/3.0	24	98 (**3n**)[f]

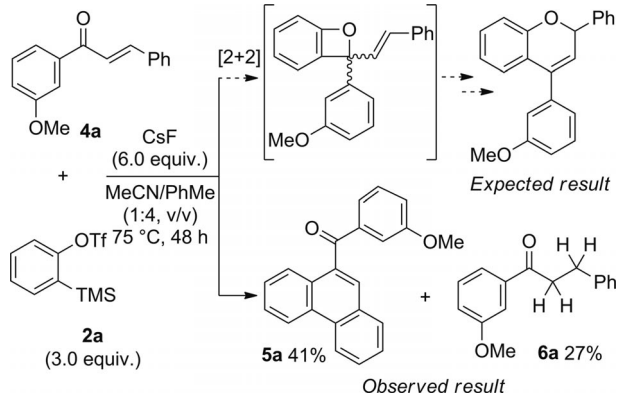
[a] Reaction conditions: a solution of **2** (1.5 mmol) in MeCN/PhMe (1:4, v/v, 2.5 mL) was added by microinfusion syringe pump at 75 °C to a stirred mixture of **1** (0.5 mmol) and CsF (3.0 mmol) in MeCN/PhMe (1:4, v/v, 2.5 mL) over 12.5 h. The reaction mixture was then stirred for a specified time until the completion of the reaction. [b] Subsequent stirring time needed after slow addition of the solution of **2** until completion of reaction. [c] Isolated yields. [d] The reaction was conducted at 85 °C. [e] A solution of **1l** (0.5 mmol) in MeCN/PhMe (1:4, v/v, 2.5 mL) was added by microinfusion syringe pump under N_2 to a stirred mixture of **2a** (1.5 mmol) and CsF (3.0 mmol) in MeCN/PhMe (1:4, v/v, 2.5 mL) over 5 h and the stirring was then continued until the completion of reaction. [f] Conducted on a 0.3 mmol scale.



Scheme 1. Steric and electronic factors in the initial formal [2+2] cycloadditions between **1i** and 3-methoxybenzyne (from **2d**).

Synthesis of 9-Functionalized Phenanthrenes 5 by a Diels–Alder/Aromatization Sequence with α,β-Unsaturated Ketones/Esters/Nitriles 4 and Arynes Produced from *o*-(Trimethylsilyl)aryl Triflates 2

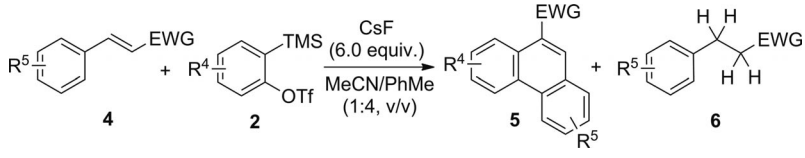
On the basis of the reactions between the enals and the arynes, we naturally sought to expand the scope of the reaction to the synthesis of 4-substituted-2*H*-chromenes from arynes and other α,β-unsaturated carbonyl compounds. Firstly, under the same reaction conditions as in Entry 10 in Table 1, 1-(3-methoxyphenyl)-3-phenylpropenone (**4a**) was employed to react with benzyne (from **2a**). The expected tandem reaction triggered by the formal aryne/C=O [2+2] cycloaddition did not take place, however, probably due to the increased steric hindrance of the ketone functionality in **4a** relative to the aldehyde functionality of **1**. Interestingly, though, a sequential aryne Diels–Alder/aromatization reaction with the styrene moiety of **4a** was observed, providing 9-aroylphenanthrene **5a** (41% yield) as the main product, along with a 27% isolated yield of the byproduct **6a**, presumably formed from the hydrogenation of **4a** (Scheme 2). Although aryne Diels–Alder reactions with cyclic dienes have been extensively studied,[15] sequential aryne Diels–Alder/aromatization reactions with acyclic dienes are still not well developed.[16]



Scheme 2. Reaction between **4a** and aryne (from **2a**).

To the best of our knowledge, sequential Diels–Alder/dehydrogenation reactions between α,β-unsaturated compounds and arynes derived from silylaryl triflates have not

Table 3. Synthesis of 9-functionalized phenanthrenes **5** through the reactions between α,β-unsaturated ketones/ester/nitrile **4** and arynes.[a]



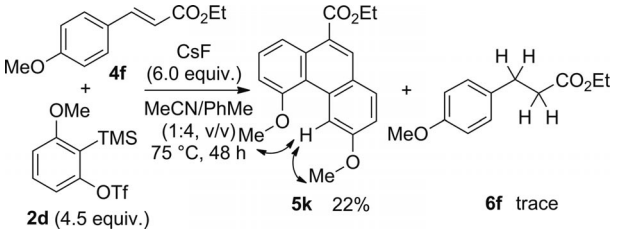
Entry	EWG/R^5 (**4**)	R^4 (**2**)/equiv. of **2**	Time [h][b]	Yield [%][c]	
				5	**6**
1	3-$MeOC_6H_4CO$/4-MeO (**4b**)	H (**2a**)/3.0	48	49 (**5b**)	44 (**6b**)
2	3-$MeOC_6H_4CO$/4-Me (**4c**)	H (**2a**)/3.0	48	38 (**5c**)	37 (**6c**)[d]
3	2-$MeOC_6H_4CO$/4-Br (**4d**)	H (**2a**)/3.0	48	35 (**5d**)	32 (**6d**)[e]
4	MeCO/4-MeO (**4e**)	H (**2a**)/3.0	48	51 (**5e**)	41 (**6e**)
5	EtOCO/4-MeO (**4f**)	H (**2a**)/4.5	48	52 (**5f**)	12 (**6f**)
6	CN/4-MeO (**4g**)	H (**2a**)/4.5	48	53 (**5g**)	16 (**6g**)
7	NO_2/4-MeO(**4h**)	H (**2a**)/3.0	24	0 (**5h**)	0 (**6h**)[d,f]
8	EtOCO/4-MeO (**4f**)	4,5-Me_2 (**2b**)/4.5	36	50 (**5i**)	trace (**6f**)[d,g]
9	EtOCO/4-MeO (**4f**)	4,5-F_2 (**2c**)/4.5	36	55 (**5j**)	23 (**6f**)

[a] Reactions were carried out on a 1.0 mmol scale under conditions similar to those of Entry 10 in Table 1. [b] Subsequent stirring time after slow addition of the solution of **2** until completion of the reaction. [c] Isolated yields. [d] Conducted on a 0.5 mmol scale. [e] Conducted on a 0.3 mmol scale. [f] Unknown mixtures were formed. [g] Formation of **6f** was detected by ^1H NMR examination of the crude reaction mixture.

been researched, but might supply an efficient and mild means of access to 9-functionalized phenanthrenes en route to PBT-1 derivatives.

To test the scope and limitations of the sequential course, interactions between arynes and α,β-unsaturated compounds bearing various electron-withdrawing groups (EWGs) were examined. Some typical examples are listed in Table 3. When the EWGs were aroyl groups, compounds **4** reacted smoothly with **2a** to afford 9-aroylphenanthrenes **5** in moderate yields, together with the corresponding compounds **6** in slightly lower yields (Table 3, Entries 1–3). A similar result was obtained with **4e**, bearing an acetyl group (Entry 4). Not only keto groups, but also ester and nitrile groups were tolerated in the reactions, producing modest yields of the corresponding 9-functionalized phenanthrenes **5** and much smaller amounts of compounds **6** (Entries 5, 6). However, the reaction between **2a** and **4h**, containing a nitro group, was not effective, resulting only in unknown mixtures (Entry 7). After screening of a number of α,β-unsaturated compounds, we turned our attention to substituted arynes. 4,5-Dimethyl- and 4,5-difluoro-substituted arynes (from **2b** and **2c**) performed well in the reactions to afford **5i** and **5j** in moderate yields (Table 3, Entries 8, 9).

When the unsymmetrical 3-methoxy-substituted aryne generated from **2d** was employed to react with **4f**, the regioisomer **5k** was formed exclusively in 22% yield [Equation (3)]. On the other hand, only trace amounts of **6f** were detected by ^{1}H NMR spectroscopy of the crude products of the reaction. The lower yield of **5k** might be attributable to steric hindrance caused by the 3-methoxy group of the aryne during the reaction. The regiochemistry of the reaction relating to the formation of **5k** was determined by a 2D NOE experiment.

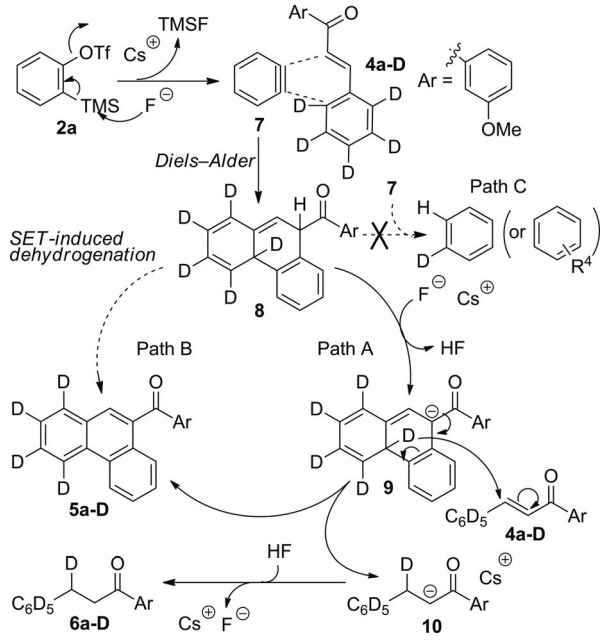


(3)

Mechanistic Studies

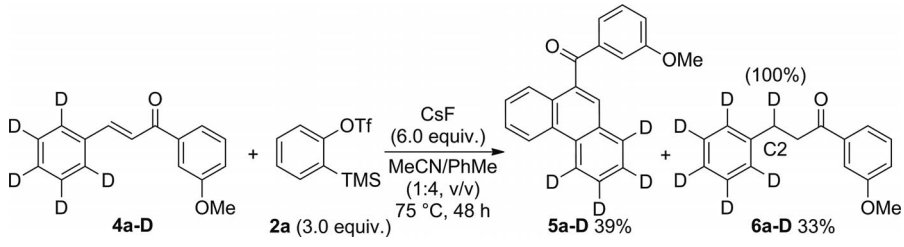
In order to study the mechanism of this reaction, based on the formation of **5** and **6**, deuterium-labelled substrate **4a-D** (Scheme 3) was prepared according to a literature method.[17] We then performed the reaction between **4a-D** and the aryne produced from **2a**. The products **5a-D** and **6a-D** were obtained in yields of 39% and 33%, respectively, and the corresponding ^{1}H NMR results showed that deuterium incorporation at the C2 position of **6a-D** was nearly 100% (Scheme 3; see the Experimental Section and the Supporting Information for details).

With the evidence of the deuterium incorporation shown in Scheme 3 to hand, the mechanism of this reaction, especially of the formation of **5** and **6**, could be explained (Scheme 4). After the fluoride-induced 1,2-elimination in **2a**, the aryne **7** could be generated in situ. It could then undergo a Diels–Alder reaction with **4a-D** to form the intermediate **8**. Through the subsequent path A, the α proton of the carbonyl group of **8** could be abstracted by the fluoride anion, which would afford the anionic intermediate **9**.



Scheme 4. Proposed mechanism for the formation of **5a-D** and **6a-D**.

A Michael addition could then occur between the deuterium anion generated from **9** and a second **4a-D** molecule to give the aromatization product **5a-D** and anionic intermediate **10**,[18] which might be driven by the aromatization and the migration of the negatively charged centre of **9**. After protonation of **10**, **6a-D** would be formed. However,



Scheme 3. Isotopic distribution reaction between **4a-D** and aryne (from **2a**).

path B, by which the intermediate **8** might be dehydrogenized directly, probably by a single-electron transfer process, to afford **5a-D**, cannot be ruled out completely.[19]

The fact that the yields of **5** are higher than those of **6** was consistent with this hypothesis. In some cases, compounds **6** are produced only in trace amounts [Table 3, Entry 8 and Equation (3)]. In view of the possibility of arynes acting as the dehydrogenation reagents of intermediate **8**, GC-MS experiments were performed on the supernatants of the reaction mixtures of Scheme 3 and Table 3, but path C was not supported, because no signals of the corresponding deuteriobenzene/benzene/*o*-xylene/*o*-F_2-benzene products could be observed.[20] This can be viewed as circumstantial evidence for path B.

Conclusions

We have developed facile and mild syntheses of 2*H*-chromenes and 9-functionalized phenanthrenes starting from commercially available or easily prepared α,β-unsaturated compounds and aryne precursors in the presence of CsF. The reaction pathways largely depend on the nature of the EWGs of the α,β-unsaturated compounds: enals and arynes undergo a tandem [2+2] cycloaddition/thermal electrocyclic ring-opening/6e-electrocyclization course, whereas α,β-unsaturated ketones/esters/nitriles react with arynes through a Diels–Alder/aromatization sequence, as is supported by the result of the isotopic distribution experiment. The electronic effects of these reactions are remarkable; in general, substrates bearing electron-donating groups on the β-aryl substituents afforded higher yields of products. The regiochemistry of the reaction with unsymmetrical arynes has been examined, and the results could be explained by electronic and/or steric factors. Further studies in this area are being conducted in this laboratory.

Experimental Section

General Remarks: All ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ or [D_6]acetone with a 400 MHz spectrometer and with TMS as the internal standard. Chemical shifts are expressed in ppm, and *J* values are given in Hz. Anhydrous solvents were distilled prior to use: PhMe was distilled from sodium/benzophenone, and CH_3CN was distilled from CaH_2. Reagents in the solid state were used as received without further purification. Petroleum ether refers to the fraction with boiling point in the 60–90 °C range. Melting points are uncorrected.

General Methods for Preparation of Starting Materials: The starting materials **1a**–**1g**,[17] **4a**–**4e**,[17] **4a-D**,[17] **4g**,[21a] **4h**,[21b] **1h**–**1j**,[22a–22c] **1m**,[22d] **1k**–**1l**,[23] **4f**[23a] and **2a**–**2d**[24] were prepared according to literature procedures.

General Procedure for the Synthesis of 2*H*-Chromenes 3 (Except for 3l and 3o): A solution of **2** (1.5 mmol) in MeCN/PhMe [1:4 (v/v), 2.5 mL, anhydrous] was added by microinfusion syringe pump at 75 °C over 12.5 h to a mixture of **1** (0.5 mmol) and CsF (3.0 mmol) in MeCN/PhMe [1:4 (v/v), 2.5 mL, anhydrous] in a dry Schlenk tube. The resulting mixture was then stirred until completion of the reaction (monitored by TLC). The reaction mixture was then diluted with acetone (20 mL) and filtered through a short pad of silica gel to remove insoluble substances. After concentration of the filtrates under vacuum, the residue was purified by flash chromatography on silica gel to afford **3**.

2-(4-Methoxyphenyl)-2*H*-chromene (3a): The General Procedure with **1a** (0.082 g, 0.50 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL), **2a** (0.449 g, 1.51 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL) and CsF (0.464 g, 3.05 mmol) afforded **3a**[25] (0.070 g, 59%) as a clear oil {purified by flash chromatography [gradient eluents: petroleum ether/dichloromethane (20:1, v/v) containing triethylamine (3‰), then petroleum ether/ethyl acetate (80:1, v/v) containing triethylamine (3‰)]; R_f = 0.47 [TLC eluent: petroleum ether/ethyl acetate (40:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, J = 8.8 Hz, 2 H), 7.08 (td, J_1 = 8.8, J_2 = 1.6 Hz, 1 H), 7.00 (dd, J_1 = 7.2, J_2 = 1.2 Hz, 1 H), 6.89–6.82 (m, 3 H), 6.75 (d, J = 8.0 Hz, 1 H), 6.54 (dd, J_1 = 9.6, J_2 = 0.8 Hz, 1 H), 5.86–5.85 (m, 1 H), 5.77 (dd, J_1 = 9.6, J_2 = 3.4 Hz, 1 H), 3.78 (s, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 55.2, 76.7, 113.9, 116.0, 121.0, 121.3, 124.0, 124.9, 126.5, 128.6, 129.4, 132.8, 153.0, 159.7 ppm. IR (neat): $\tilde{\nu}$ = 2933, 2835, 1606, 1511, 1484, 1456, 1303, 1247, 1204, 1173, 1109, 1033, 955, 830, 801, 754, 692 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 238 (100.0) $[M]^+$. HRMS (EI): calcd. for $C_{16}H_{14}O_2$ $[M]^+$ 238.0994; found 238.0997.

2-(2-Methoxyphenyl)-2*H*-chromene (3b): The General Procedure with **1b** (0.081 g, 0.50 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL), **2a** (0.444 g, 1.48 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL) and CsF (0.462 g, 3.04 mmol) afforded **3b**[26] (0.083 g, 70%) as a clear oil {purified by flash chromatography [gradient eluents: petroleum ether/dichloromethane (20:1, v/v) containing triethylamine (3‰), then petroleum ether/ethyl acetate (80:1, v/v) containing triethylamine (3‰)]; R_f = 0.52 [TLC eluent: petroleum ether/ethyl acetate (40:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, J = 8.0 Hz, 1 H), 7.29–7.22 (m, 1 H), 7.10 (t, J = 7.8 Hz, 1 H), 6.98–6.80 (m, 5 H), 6.46 (d, J = 9.6 Hz, 1 H), 6.35–6.34 (m, 1 H), 5.78 (dd, J_1 = 10.0, J_2 = 3.6 Hz, 1 H), 3.84 (s, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 55.5, 71.6, 110.6, 115.8, 120.8, 121.0, 121.3, 123.3, 125.0, 126.5, 127.7, 129.1, 129.2, 129.3, 153.6, 155.8 ppm. IR (neat): $\tilde{\nu}$ = 2937, 1598, 1486, 1457, 1353, 1228, 1160, 1107, 1029, 955, 833, 749, 697, 633 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 238 (100.0) $[M]^+$. HRMS (EI): calcd. for $C_{16}H_{14}O_2$ $[M]^+$ 238.0994; found 238.0995.

2-(4-Methylphenyl)-2*H*-chromene (3c): The General Procedure with **1c** (0.074 g, 0.51 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL), **2a** (0.599 g, 2.01 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL) and CsF (0.464 g, 3.05 mmol) afforded **3c**[26a] (0.073 g, 66%) as a clear oil {purified by flash chromatography [eluent: petroleum ether/dichloromethane (20:1, v/v) containing triethylamine (3‰)]; R_f = 0.48 [TLC eluent: petroleum ether/ethyl acetate (40:1, v/v)]}. ^{1}H NMR (400 MHz, [D_6]acetone): δ = 7.33 (d, J = 8.0 Hz, 2 H), 7.17 (d, J = 7.2 Hz, 2 H), 7.12–7.05 (m, 2 H), 6.84 (td, J_1 = 7.6, J_2 = 1.0 Hz, 1 H), 6.71 (d, J = 8.0 Hz, 1 H), 6.60 (dd, J_1 = 11.0, J_2 = 3.2 Hz, 1 H), 5.89–5.87 (m, 2 H), 2.30 (s, 3 H) ppm. ^{13}C NMR (90 MHz, [D_6]acetone): δ = 21.0, 77.2, 116.5, 121.8, 122.3, 124.3, 126.0, 127.3, 127.7, 129.8, 130.0, 138.6, 138.9, 154.0 ppm. IR (neat): $\tilde{\nu}$ = 2922, 2853, 1638, 1484, 1456, 1228, 1204, 1111, 1041, 786, 755 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 222 (100.0) $[M]^+$. HRMS (EI): calcd. for $C_{16}H_{14}O$ $[M]^+$ 222.1045; found 222.1049.

2-Phenyl-2*H*-chromene (3d): The General Procedure with **1d** (0.067 g, 0.51 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL), **2a** (0.668 g, 2.24 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL) and CsF (0.467 g, 3.07 mmol) afforded **3d**[27] (0.047 g, 45%) as a clear oil {purified by flash chromatography [gradient eluents: petroleum ether/dichlo-

romethane (20:1, v/v) containing triethylamine (3‰), then petroleum ether/ethyl acetate (80:1, v/v) containing triethylamine (3‰)]; R_f = 0.71 [TLC eluent: petroleum ether/ethyl acetate (40:1, v/v)]}. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 7.48–7.46 (m, 2 H), 7.39–7.30 (m, 3 H), 7.11 (td, J_1 = 7.6, J_2 = 1.2 Hz, 1 H), 7.07 (dd, J_1 = 7.4, J_2 = 1.4 Hz, 1 H), 6.86 (td, J_1 = 7.2, J_2 = 1.2 Hz, 1 H), 6.74 (d, J = 8.0 Hz, 1 H), 6.61 (d, J = 9.6 Hz, 1 H), 5.96–5.94 (m, 1 H), 5.92 (dd, J_1 = 9.6, J_2 = 3.6 Hz, 1 H) ppm. ^{13}C NMR (90 MHz, [D$_6$]acetone): δ = 77.4, 116.4, 121.8, 122.3, 124.3, 125.9, 127.4, 127.6, 128.9, 129.2, 130.1, 141.9, 154.0 ppm. IR (neat): $\tilde{\nu}$ = 2980, 2902, 1404, 1251, 1056, 893 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 208 (100.0) [M]$^+$. HRMS (EI): calcd. for $C_{15}H_{12}O$ [M]$^+$ 208.0888; found 208.0885.

2-(4-Bromophenyl)-2*H*-chromene (3e): The General Procedure with **1e** (0.105 g, 0.50 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL), **2a** (0.673 g, 2.26 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL) and CsF (0.460 g, 3.03 mmol) afforded **3e** (0.050 g, 34%) as a clear oil {purified by flash chromatography [gradient eluents: petroleum ether/dichloromethane (20:1, v/v) containing triethylamine (3‰), then petroleum ether/dichloromethane (10:1, v/v) containing triethylamine (3‰)]; R_f = 0.68 [TLC eluent: petroleum ether/ethyl acetate (40:1, v/v)]}. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 7.56 (dd, J_1 = 6.4, J_2 = 1.6 Hz, 2 H), 7.43 (d, J = 8.0 Hz, 2 H), 7.12 (td, J_1 = 7.8, J_2 = 1.6 Hz, 1 H), 7.08 (dd, J_1 = 7.6, J_2 = 1.2 Hz, 1 H), 6.87 (td, J_1 = 7.4, J_2 = 1.0 Hz, 1 H), 6.75 (d, J = 8.0 Hz, 1 H), 6.64 (d, J = 9.2 Hz, 1 H), 5.96–5.92 (m, 2 H) ppm. ^{13}C NMR (90 MHz, [D$_6$]acetone): δ = 76.5, 116.5, 122.0, 122.2, 122.4, 124.6, 125.4, 127.5, 129.6, 130.2, 132.3, 141.3, 153.7 ppm. IR (neat): $\tilde{\nu}$ = 2981, 2902, 1631, 1404, 1250, 1069, 893 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 286 (9.6) [M(^{79}Br)]$^+$, 288 (7.4) [M(^{81}Br)]$^+$, 208 (100.0). HRMS (EI): calcd. for $C_{15}H_{11}O^{79}Br$ [M]$^+$ 285.9993; found 285.9996.

2-(4-Fluorophenyl)-2*H*-chromene (3f): The General Procedure with **1f** (0.074 g, 0.49 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL), **2a** (0.677 g, 2.27 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL) and CsF (0.455 g, 2.99 mmol) afforded **3f** (0.025 g, 22%) as a clear oil {purified by flash chromatography [eluent: petroleum ether/dichloromethane (10:1, v/v) containing triethylamine (3‰)]; R_f = 0.49 [TLC eluent: petroleum ether/ethyl acetate (40:1, v/v)]}. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 7.53–7.49 (m, 2 H), 7.16–7.07 (m, 4 H), 6.86 (td, J_1 = 7.4, J_2 = 1.0 Hz, 1 H), 6.73 (d, J = 8.0 Hz, 1 H), 6.64 (dd, J_1 = 9.8, J_2 = 0.6 Hz, 1 H), 5.97–5.96 (m, 1 H), 5.91 (dd, J_1 = 10.2, J_2 = 3.8 Hz, 1 H) ppm. ^{13}C NMR (90 MHz, [D$_6$]acetone): δ = 76.6, 116.0 (d, J = 19.5 Hz), 116.6, 122.0, 122.3, 124.6, 125.7, 127.5, 129.8 (d, J = 6.9 Hz), 130.2, 138.1 (d, J = 2.8 Hz), 153.8, 163.4 (d, J = 219.4 Hz) ppm. IR (neat): $\tilde{\nu}$ = 2982, 2903, 1738, 1602, 1508, 1456, 1409, 1232, 1157, 1063, 839, 758 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 226 (93.8) [M]$^+$, 225 (100.0) [M – 1]$^+$. HRMS (EI): calcd. for $C_{15}H_{11}OF$ [M]$^+$ 226.0794; found 226.0797.

2-(4-Methoxyphenyl)-3-methyl-2*H*-benzopyran (3 g): The General Procedure with **1g** (0.088 g, 0.50 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL), **2a** (0.449 g, 1.51 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL) and CsF (0.469 g, 3.08 mmol) afforded **3g** (0.041 g, 33%) as a clear oil {purified by flash chromatography [gradient eluents: petroleum ether/dichloromethane (10:1, v/v) containing triethylamine (3‰), then petroleum ether/dichloromethane (7:1, v/v) containing triethylamine (3‰)]; R_f = 0.39 [TLC eluent: petroleum ether/ethyl acetate (40:1, v/v)]}. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 7.31 (dd, J_1 = 6.6, J_2 = 2.7 Hz, 2 H), 7.02–6.98 (m, 2 H), 6.90–6.87 (m, 2 H), 6.81 (td, J_1 = 7.2, J_2 = 1.0 Hz, 1 H), 6.60 (dd, J_1 = 8.0, J_2 = 0.4 Hz, 1 H), 6.44 (s, 1 H), 5.67 (s, 1 H), 3.77 (s, 3 H), 1.71 (s, 3 H) ppm. ^{13}C NMR (90 MHz, [D$_6$]acetone): δ = 19.8, 55.3, 80.8, 114.5, 116.1, 120.3, 121.5, 123.0, 126.3, 128.9, 129.6, 132.1, 133.8, 152.3, 160.8 ppm. IR (neat): $\tilde{\nu}$ = 2980, 2902, 1608, 1511, 1485, 1404, 1247, 1176, 1052, 877, 755 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 252 (33.9) [M]$^+$, 237 (100.0). HRMS (EI): calcd. for $C_{17}H_{16}O_2$ [M]$^+$ 252.1150; found 252.1147.

2,2-Bis(4-methoxyphenyl)-2*H*-benzopyran (3h): The General Procedure with **1h** (0.134 g, 0.50 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL), **2a** (0.449 g, 1.51 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL) and CsF (0.469 g, 3.08 mmol) afforded **3h**[28] (0.105 g, 61%) as a pale white solid; m.p. 92–94 °C {recrystallized from petroleum ether/ethyl acetate (40:1, v/v) after purification by flash chromatography [eluent: petroleum ether/ethyl acetate (40:1, v/v)]; R_f = 0.32 [TLC eluent: petroleum ether/ethyl acetate (40:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, J = 9.2 Hz, 4 H), 7.09 (t, J = 7.8 Hz, 1 H), 6.97 (d, J = 7.6 Hz, 1 H), 6.88–6.79 (m, 6 H), 6.56 (d, J = 10.0 Hz, 1 H), 6.08 (d, J = 10.0 Hz, 1 H), 3.75 (s, 6 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 55.2, 82.1, 113.4, 116.4, 121.0, 121.1, 122.9, 126.4, 128.3, 129.2, 129.4, 137.3, 152.5, 158.8 ppm. IR (neat): $\tilde{\nu}$ = 2955, 2835, 1607, 1508, 1484, 1454, 1303, 1248, 1173, 1112, 1059, 1031, 984, 946, 827, 768, 754 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 344 (84.7) [M]$^+$, 237 (100.0). HRMS (EI): calcd. for $C_{23}H_{20}O_3$ [M]$^+$ 344.1412; found 344.1418.

2,2-Diphenyl-2*H*-benzopyran (3i): The General Procedure with **1i** (0.104 g, 0.50 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL), **2a** (0.548 g, 1.84 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL) and CsF (0.459 g, 3.02 mmol) afforded **3i**[29] (0.113 g, 80%) as a white solid; m.p. 84–86 °C (ref.[29] 85–87 °C) {recrystallized from petroleum ether/ethyl acetate (40:1, v/v) after purification by flash chromatography [eluent: petroleum ether/ethyl acetate (20:1, v/v) containing triethylamine (1‰)]}; R_f = 0.67 [TLC eluent: petroleum ether/ethyl acetate (40:1, v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 7.6 Hz, 4 H), 7.32–7.21 (m, 6 H), 7.10 (t, J = 7.8 Hz, 1 H), 6.98 (d, J = 7.2 Hz, 1 H), 6.91 (d, J = 8.0 Hz, 1 H), 6.82 (t, J = 7.4 Hz, 1 H), 6.59 (d, J = 10.0 Hz, 1 H), 6.15 (d, J = 10.0 Hz, 1 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 82.6, 116.5, 121.1, 121.2, 123.3, 126.6, 127.0, 127.4, 128.1, 128.8, 129.5, 145.0, 152.5 ppm. IR (neat): $\tilde{\nu}$ = 3059, 1637, 1604, 1486, 1450, 1238, 1112, 1054, 988, 942, 755, 698 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 284 (39.0) [M]$^+$, 207 (100.0). HRMS (EI): calcd. for $C_{21}H_{16}O$ [M]$^+$ 284.1201; found 284.1204.

2-(4-Methoxyphenyl)-2-phenyl-2*H*-benzopyran (3j): The General Procedure with **1j** (0.119 g, 0.50 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL), **2a** (0.449 g, 1.51 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL) and CsF (0.464 g, 3.05 mmol) afforded **3j** (0.095 g, 61%) as a white solid; m.p. 80–82 °C {recrystallized from petroleum ether/ethyl acetate (10:1, v/v) after purification by flash chromatography [eluent: petroleum ether/ethyl acetate (10:1, v/v)]; R_f = 0.70 [TLC eluent: petroleum ether/ethyl acetate (10:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 7.6 Hz, 2 H), 7.34–7.28 (m, 4 H), 7.23 (t, J = 7.6 Hz, 1 H), 7.09 (t, J = 7.6 Hz, 1 H), 6.98 (d, J = 7.2 Hz, 1 H), 6.89 (d, J = 7.6 Hz, 1 H), 6.83–6.79 (m, 3 H), 6.57 (d, J = 10.0 Hz, 1 H), 6.11 (d, J = 10.0 Hz, 1 H), 3.74 (s, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 55.2, 82.3, 113.4, 116.4, 121.1, 123.1, 126.5, 126.8, 127.3, 128.0, 128.4, 129.0, 129.4, 137.0, 145.2, 152.5, 158.9 ppm. IR (neat): $\tilde{\nu}$ = 2957, 1607, 1509, 1485, 1452, 1304, 1242, 1174, 1112, 1057, 1033, 986, 943, 830, 756, 700 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 314 (78.1) [M]$^+$, 237 (100.0). HRMS (EI): calcd. for $C_{22}H_{18}O_2$ [M]$^+$ 314.1307; found 314.1315.

2-(3-Methoxyphenyl)-2-methyl-2*H*-chromene (3k): The General Procedure with **1k** (0.091 g, 0.51 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL), **2a** (0.456 g, 1.53 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL) and CsF (0.483 g, 3.17 mmol) afforded **3k** (0.066 g, 52%) as an oil {purification by flash chromatography [gradient eluents: petroleum ether/dichloromethane (20:1, v/v) containing triethylamine (1‰),

then petroleum ether/dichloromethane (10:1, v/v) containing triethylamine (1‰)]; R_f = 0.49 [TLC eluent: petroleum ether/ethyl acetate (40:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (t, J = 8.0 Hz, 1 H), 7.13–7.15 (m, 3 H), 6.96 (d, J = 7.6 Hz, 1 H), 6.88 (d, J = 8.4 Hz, 1 H), 6.82 (t, J = 7.6 Hz, 1 H), 6.76 (dd, J_1 = 8.6, J_2 = 1.8 Hz, 1 H), 6.43 (d, J = 9.6 Hz, 1 H), 5.91 (d, J = 9.6 Hz, 1 H), 3.77 (s, 3 H), 1.76 (s, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 29.3, 55.2, 78.6, 111.4, 112.3, 116.3, 117.5, 121.0, 121.2, 122.8, 126.5, 129.2, 129.3, 129.5, 147.6, 152.9, 159.4 ppm. IR (neat): $\tilde{\nu}$ = 2987, 2901, 1730, 1605, 1511, 1453, 1406, 1394, 1252, 1167, 1066, 892, 758 cm^{-1}. MS (70 eV, EI): m/z (%) = 252 (61.8) [M]$^+$, 237 (100.0). HRMS (EI): calcd. for $C_{17}H_{16}O_2$ [M]$^+$ 252.1150; found 252.1149.

6,7-Dimethyl-2,2-diphenyl-2*H*-chromene (3m): The General Procedure with **1i** (0.104 g, 0.50 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL), **2b** (0.491 g, 1.51 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL) and CsF (0.469 g, 3.08 mmol) afforded **3m** (0.119 g, 77%) as a white solid; m.p. 140–142 °C {recrystallized from petroleum ether/ethyl acetate (40:1, v/v) after purification by flash chromatography [eluent: petroleum ether/ethyl acetate (10:1, v/v)]; R_f = 0.68 [TLC eluent: petroleum ether/ethyl acetate (40:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 7.6 Hz, 4 H), 7.30 (t, J = 7.6 Hz, 4 H), 7.24–7.23 (m. 2 H), 6.75 (s, 1 H), 6.72 (s, 1 H), 6.55 (d, J = 9.6 Hz, 1 H), 6.07 (d, J = 9.6 Hz, 1 H), 2.16 (s, 3 H), 2.11 (s, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 18.8, 19.9, 82.4, 117.5, 118.6, 123.2, 127.0, 127.3, 127.4, 127.8, 128.0, 128.9, 138.1, 145.2, 150.4 ppm. IR (neat): $\tilde{\nu}$ = 3060, 2971, 2919, 1619, 1493, 1448, 1411, 1259, 1224, 1178, 1099, 1052, 943, 890, 758, 698 cm^{-1}. MS (70 eV, EI): m/z (%) = 312 (76.6) [M]$^+$, 235 (100.0). HRMS (EI): calcd. for $C_{23}H_{20}O$ [M]$^+$ 312.1514; found 312,1511.

6,7-Difluoro-2,2-diphenyl-2*H*-chromene (3n): The General Procedure with **1i** (0.061 g, 0.29 mmol)/MeCN (0.3 mL)/PhMe (1.2 mL), **2c** (0.303 g, 0.91 mmol)/MeCN (0.3 mL)/PhMe (1.2 mL) and CsF (0.286 g, 1.88 mmol) afforded **3n** (0.091 g, 98%) as a white solid; m.p. 100–102 °C {recrystallized from petroleum ether/ethyl acetate (40:1, v/v) after purification by flash chromatography [eluent: petroleum ether/ dichloromethane (10:1, v/v)]; R_f = 0.48 [TLC eluent: petroleum ether/ethyl acetate (40:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, J = 7.2 Hz, 4 H), 7.33–7.22 (m, 6 H), 6.81–6.70 (m, 2 H), 6.50 (d, J = 9.6 Hz, 1 H), 6.16 (d, J = 10.0 Hz, 1 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 82.9, 106.1 (d, J = 18.4 Hz), 114.2 (dd, J_1 = 17.2, J_2 = 1.4 Hz), 117.3 (dd, J_1 = 6.0, J_2 = 3.2 Hz), 122.0, 126.9, 127.7, 128.2, 129.3 (d, J = 3.3 Hz), 144.1, 145.2 (dd, J_1 = 215.2, J_2 = 11.8 Hz), 148.5 (dd, J_1 = 8.9, J_2 = 2.2 Hz), 150.3 (dd, J_1 = 222.2, J_2 = 11.2 Hz) ppm. IR (neat): $\tilde{\nu}$ = 2973, 2919, 1598, 1502, 1440, 1371, 1321, 1237, 1156, 1120, 1052, 976, 872, 810, 753, 697 cm^{-1}. MS (70 eV, EI): m/z (%) = 320 (69.3) [M]$^+$, 243 (100.0). HRMS (EI): calcd. for $C_{21}H_{14}OF_2$ [M]$^+$ 320.1013; found 320.1010.

5-Methoxy-2,2-diphenyl-2*H*-chromene (3p): The General Procedure with **1i** (0.104 g, 0.50 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL), **2e** (0.662 g, 2.02 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL) and CsF (0.468 g, 3.08 mmol) afforded **3p** (0.118 g, 75%) as an oil {purified by flash chromatography [eluent: petroleum ether/dichloromethane (10:1, v/v)]; R_f = 0.52 [TLC eluent: petroleum ether/ethyl acetate (40:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.40 (m, 4 H), 7.28–7.24 (m, 4 H), 7.19 (tt, J_1 = 7.4, J_2 = 1.2 Hz, 2 H), 7.00 (t, J = 8.2 Hz, 1 H), 6.94 (d, J = 10.4 Hz, 1 H), 6.57 (d, J = 8.4 Hz, 1 H), 6.32 (d, J = 8.0 Hz, 1 H), 6.07 (d, J = 9.6 Hz, 1 H), 3.70 (s, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 55.4, 82.1, 103.3, 109.5, 110.6, 118.08, 118.11, 127.0, 127.3, 128.0, 129.3, 145.0, 153.2, 155.3 ppm. IR (neat): $\tilde{\nu}$ = 2938, 1602, 1576, 1464, 1446, 1275, 1251, 1212, 1096, 1006, 750, 698 cm^{-1}. MS (70 eV, EI): m/z (%) = 314 (39.9) [M]$^+$, 237 (100.0). HRMS (EI): calcd. for $C_{22}H_{18}O_2$ [M]$^+$ 314.1307; found 314.1315.

General Procedure. Synthesis of 3l: A solution of **1l** (0.062 g, 0.49 mmol) in MeCN/PhMe [1:4 (v/v), 2.5 mL, anhydrous] was added by microinfusion syringe pump under dry nitrogen at 75 °C over 5.0 h to a mixture of **2a** (0.448 g, 1.50 mmol) and CsF (0.466 g, 3.06 mmol) in MeCN/PhMe [1:4 (v/v), 2.5 mL, anhydrous] in a dry Schlenk tube. The resulting mixture was then stirred for 24 h until completion of the reaction (monitored by TLC). The reaction mixture was then diluted with acetone (20 mL) and filtered through a short pad of silica gel to remove insoluble substances. After concentration of the filtrates under vacuum, the residue was dissolved in EtOH (5 mL). KF (0.061 g, 1.05 mmol), 18-crown-6 (0.533 g, 2.02 mmol) and KOH (water solution, 1 M, 1 mL) were added to the solution. The mixture was stirred under reflux for 20 h to consume the TMS-containing compounds in the residue to facilitate the following purification. The reaction mixture was poured into brine (20 mL) and then extracted with diethyl ether (3 × 20 mL). The organic layers were combined, dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford **3l**[30] (0.031 g, 31%).

2-Methyl-2-(2-methylpropyl)-2*H*-chromene (3l): Clear oil [purified by flash chromatography (eluent: petroleum ether); R_f = 0.47 (TLC eluent: petroleum ether)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (td, J_1 = 8.0, J_2 = 1.2 Hz, 1 H), 6.94 (d, J = 7.2 Hz, 1 H), 6.80 (t, J = 7.6 Hz, 1 H), 6.73 (d, J = 8.0 Hz, 1 H), 6.31 (d, J = 9.6 Hz, 1 H), 5.54 (d, J = 10.0 Hz, 1 H), 1.98–1.88 (m, 1 H), 1.65–1.54 (m, 2 H), 1.39 (s, 3 H), 0.96 (d, J = 6.8 Hz, 3 H), 0.93 (d, J = 6.4 Hz, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 24.1, 24.4, 24.5, 27.2, 49.5, 78.9, 116.2, 120.4, 121.0, 122.3, 126.3, 129.0, 130.4, 153.0 ppm. IR (neat): $\tilde{\nu}$ = 3041, 2955, 2926, 2869, 1640, 1606, 1576, 1486, 1458, 1367, 1275, 1243, 1182, 1126, 1041, 946, 772, 751 cm^{-1}. GC-MS (70 eV, EI): m/z (%) = 202 (9.6) [M]$^+$, 145 (100.0). HRMS (EI): calcd. for $C_{14}H_{18}O$ [M]$^+$ 202.1358; found 202.1360.

(1′*R*,2′*R*,4′*R*)-1′,7′,7′-Trimethylspiro[bicyclo[2.2.1]heptane-2,2′-2*H*-chromene] (3o): Compound **3o** was prepared similarly to **3l**. The General Procedure with **1m** (0.091 g, 0.51 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL), **2a** (0.452 g, 1.52 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL) and CsF (0.461 g, 3.03 mmol) afforded **3m** (0.041 g, 32%) as a clear oil [purified by flash chromatography (eluent: petroleum ether); R_f = 0.75 (TLC eluent: petroleum ether)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07 (td, J_1 = 7.8, J_2 = 1.4 Hz, 1 H), 6.94 (dd, J_1 = 7.4, J_2 = 1.4 Hz, 1 H), 6.81 (t, J = 8.2 Hz, 2 H), 6.35 (d, J = 10.4 Hz, 1 H), 5.75 (d, J = 10.4 Hz, 1 H), 2.39–2.32 (m, 1 H, $C_{6'}$-H_{endo}), 2.10 (dt, J_1 = 14.0, J_2 = 3.6 Hz, 1 H, $C_{3'}$-H_{exo}), 1.79–1.71 (m, 3 H, $C_{5'}$-H_{exo}, $C_{3'}$-H_{endo}, C_4-H), 1.46–1.39 (m, 1 H, $C_{5'}$-H_{endo}), 1.32 (td, J_1 = 12.0, J_2 = 5.2 Hz, 1 H, $C_{6'}$-H_{exo}), 0.98 (s, 3 H, $C_{8'}$-CH_3), 0.90 (s, 3 H, $C_{9'}$-CH_3), 0.81 (s, 3 H, $C_{10'}$-CH_3) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 12.2, 21.29, 21.35, 27.0, 29.1, 44.8, 46.1, 49.4, 55.3, 86.2, 116.1, 120.6, 122.5, 122.7, 125.8, 128.8, 130.9, 154.2 ppm. IR (neat): $\tilde{\nu}$ = 2989, 2952, 2926, 2869, 1634, 1606, 1572, 1483, 1454, 1389, 1309, 1273, 1250, 1206, 1179, 1152, 1114, 1082, 1035, 1003, 983, 924, 862, 838, 804, 768, 754, 742, 708 cm^{-1}. GC-MS (70 eV, EI): m/z (%) = 254 (14.8) [M]$^+$, 144 (100.0). HRMS (EI): calcd. for $C_{18}H_{22}O$ [M]$^+$ 254.1671; found 254.1668.

Compounds **5** and **6** were prepared similarly to **3a**.

(3-Methoxyphenyl)(9-phenanthrenyl)methanone (5a) and 1-(3-Methoxyphenyl)-3-phenylpropan-1-one (6a): The General Procedure with **4a** (0.072 g, 0.30 mmol)/MeCN (0.3 mL)/PhMe (1.2 mL), **2a** (0.270 g, 0.91 mmol)/MeCN (0.3 mL)/PhMe (1.2 mL) and CsF

(0.277 g, 1.82 mmol) afforded **5a** (0.038 g, 41%) and **6a** (0.019 g, 27%).

Compound 5a: White solid; m.p. 147–149 °C {recrystallized from petroleum ether/ethyl acetate (10:1, v/v) after purification by flash chromatography [eluent: petroleum ether/dichloromethane (7:1, v/v), then petroleum ether/ethyl acetate (40:1, v/v)]; R_f = 0.48 [TLC eluent: petroleum ether/ethyl acetate (10:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (d, J = 8.4 Hz, 1 H), 8.72 (d, J = 8.4 Hz, 1 H), 8.11 (d, J = 8.8 Hz, 1 H), 7.88 (d, J = 7.6 Hz, 1 H), 7.85 (s, 1 H), 7.76–7.72 (m, 1 H), 7.69 (t, J = 7.8 Hz, 1 H), 7.63 (t, J = 7.4 Hz, 1 H), 7.60–7.56 (m, 2 H), 7.42 (d, J = 7.6 Hz, 1 H), 7.33 (t, J = 8.0 Hz, 1 H), 7.16 (dd, J_1 = 8.2, J_2 = 2.6 Hz, 1 H), 3.84 (s, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 55.5, 114.0, 120.0, 122.7, 122.9, 123.6, 126.6, 127.1, 127.15, 127.19, 128.3, 129.1, 129.3, 129.46, 129.50, 130.0, 130.6, 131.3, 135.4, 139.6, 159.8, 197.6 ppm. IR (neat): $\tilde{\nu}$ = 2983, 2903, 1658, 1583, 1449, 1401, 1261, 1051, 895, 769 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 312 (100.0) $[M]^+$. HRMS (EI): calcd. for $C_{22}H_{16}O_2$ $[M]^+$ 312.1150; found 312.1158.

Compound 6a:[31] Oil {purified by flash chromatography [gradient eluents: petroleum ether/dichloromethane (7:1, v/v), then petroleum ether/ethyl acetate (40:1, v/v)]; R_f = 0.50 [TLC eluent: petroleum ether/ethyl acetate (10:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, J = 7.6 Hz, 1 H), 7.49–7.48 (m, 1 H), 7.36 (t, J = 8.2 Hz, 1 H), 7.32–7.25 (m, 4 H), 7.23–7.19 (m, 1 H), 7.10 (dd, J_1 = 8.4, J_2 = 2.0 Hz, 1 H), 3.85 (s, 3 H), 3.29 (t, J = 7.8 Hz, 2 H), 3.07 (t, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 30.2, 40.6, 55.4, 112.3, 119.6, 120.7, 126.1, 128.4, 128.5, 129.6, 138.3, 141.3, 159.9, 199.0 ppm. IR (neat): $\tilde{\nu}$ = 3028, 2943, 2836, 1685, 1595, 1489, 1455, 1431, 1290, 1256, 1194, 1167, 1041, 993, 771, 746, 698, 619 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 240 (96.4) $[M]^+$, 135 (100.0). HRMS (EI): calcd. for $C_{16}H_{16}O_2$ $[M]^+$ 240.1150; found 240.1155.

(3-Methoxy-9-phenanthrenyl)(3-methoxyphenyl)methanone (5b) and 1-(3-Methoxyphenyl)-3-(4-methoxyphenyl)propan-1-one (6b): The General Procedure with **4b** (0.268 g, 1.0 mmol)/MeCN (1.0 mL)/PhMe (4.0 mL), **2a** (0.898 g, 3.01 mmol)/MeCN (1.0 mL)/PhMe (4.0 mL) and CsF (0.921 g, 6.06 mmol) afforded **5b** (0.167 g, 49%) and **6b** (0.119 g, 44%).

Compound 5b: Oil {purified by flash chromatography [gradient eluents: petroleum ether/dichloromethane (7:1, v/v), then petroleum ether/ethyl acetate (15:1, v/v)]; R_f = 0.25 [TLC eluent: petroleum ether/ethyl acetate (10:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.67 (d, J = 8.4 Hz, 1 H), 8.21 (d, J = 8.0 Hz, 1 H), 8.07 (d, J = 2.0 Hz, 1 H), 7.83 (s, 1 H), 7.80 (d, J = 8.8 Hz, 1 H), 7.67 (td, J_1 = 7.6, J_2 = 1.0 Hz, 1 H), 7.59 (td, J_1 = 7.8, J_2 = 0.8 Hz, 1 H), 7.54 (dd, J_1 = 2.2, J_2 = 1.4 Hz, 1 H), 7.42 (d, J = 7.6 Hz, 1 H), 7.34 (t, J = 7.8 Hz, 1 H), 7.27 (dd, J_1 = 8.8, J_2 = 2.8 Hz, 1 H), 7.17–7.14 (m, 1 H), 4.05 (s, 3 H), 3.85 (s, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 55.4, 55.5, 104.0, 114.0, 117.3, 119.7, 122.9, 123.5, 124.5, 126.67, 126.70, 127.3, 129.4, 129.7, 130.0, 131.1, 132.6, 133.0, 140.0, 159.7, 160.0, 197.6 ppm. IR (neat): $\tilde{\nu}$ = 2921, 1654, 1616, 1505, 1455, 1373, 1296, 1248, 1218, 1176, 1041, 889, 838, 770, 684, 624 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 342 (19.4) $[M]^+$, 57 (100.0). HRMS (EI): calcd. for $C_{23}H_{18}O_3$ $[M]^+$ 342.1256; found 342.1254.

Compound 6b:[32] Oil {purified by flash chromatography [gradient eluents: petroleum ether/dichloromethane (7:1, v/v), then petroleum ether/ethyl acetate (15:1, v/v)]; R_f = 0.28 [TLC eluent: petroleum ether/ethyl acetate (10:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, J = 7.6 Hz, 1 H), 7.47 (s, 1 H), 7.32 (t, J = 7.8 Hz, 1 H), 7.15 (d, J = 8.4 Hz, 2 H), 7.07 (dd, J_1 = 8.2, J_2 = 2.6 Hz, 1 H), 6.82 (d, J = 8.4 Hz, 2 H), 3.81 (s, 3 H), 3.75 (s, 3 H), 3.22 (t, J = 7.6 Hz, 2 H), 2.99 (t, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 29.2, 40.6, 55.1, 55.2, 112.2, 113.8, 119.3, 120.5, 129.2, 129.4, 133.1, 138.2, 157.9, 159.7, 199.0 ppm. IR (neat): $\tilde{\nu}$ = 2935, 2835, 1683, 1584, 1511, 1457, 1430, 1291, 1244, 1176, 1035, 994, 909, 876, 826, 776, 730, 685 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 270 (97.2) $[M]^+$, 121 (100.0).

(3-Methoxyphenyl)(3-methyl-9-phenanthrenyl)methanone (5c) and 1-(3-Methoxyphenyl)-3-(4-methylphenyl)propan-1-one (6c): The General Procedure with **4c** (0.127 g, 0.50 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL), **2a** (0.444 g, 1.49 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL) and CsF (0.462 g, 3.04 mmol) afforded **5c** (0.062 g, 38%) and **6c** (0.047 g, 37%).

Compound 5c: Oil {purified by flash chromatography [eluent: petroleum ether/ethyl acetate (40:1, v/v)]; R_f = 0.34 [TLC eluent: petroleum ether/ethyl acetate (10:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (d, J = 8.4 Hz, 1 H), 8.49 (s, 1 H), 8.14 (d, J = 8.4 Hz, 1 H), 7.82 (s, 1 H), 7.76 (d, J = 8.0 Hz, 1 H), 7.68–7.64 (m, 1 H), 7.58–7.54 (m, 2 H), 7.43 (t, J = 9.2 Hz, 2 H), 7.32 (t, J = 7.8 Hz, 1 H), 7.16–7.13 (m, 1 H), 3.83 (s, 3 H), 2.63 (s, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 22.3, 55.4, 114.0, 119.9, 122.4, 122.8, 123.5, 126.5, 126.9, 127.0, 127.9, 128.8, 129.4, 129.5, 130.2, 130.3, 131.4, 134.2, 138.4, 139.7, 159.7, 197.7 ppm. IR (neat): $\tilde{\nu}$ = 2942, 1657, 1583, 1451, 1429, 1365, 1302, 1264, 1208, 1117, 1039, 877, 808, 772, 699 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 326 (26.6) $[M]^+$, 302 (100.0). HRMS (EI): calcd. for $C_{23}H_{18}O_2$ $[M]^+$ 326.1307; found 326.1302.

Compound 6c: Oil {purified by flash chromatography [eluent: petroleum ether/ethyl acetate (40:1, v/v)]; R_f = 0.36 [TLC eluent: petroleum ether/ethyl acetate (10:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, J = 7.6 Hz, 1 H), 7.48 (s, 1 H), 7.34 (t, J = 8.2 Hz, 1 H), 7.15–7.08 (m, 5 H), 3.84 (s, 3 H), 3.26 (t, J = 7.8 Hz, 2 H), 3.02 (t, J = 7.6 Hz, 2 H), 2.32 (s, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 21.0, 29.7, 40.7, 55.4, 112.2, 119.5, 120.6, 128.3, 129.2, 129.5, 135.6, 138.1, 138.2, 159.8, 199.1 ppm. IR (neat): $\tilde{\nu}$ = 2924, 1684, 1584, 1515, 1485, 1453, 1430, 1359, 1289, 1254, 1191, 1166, 1110, 1041, 997, 876, 839, 811, 779, 719, 686, 648 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 254 (76.8) $[M]^+$, 135 (100.0). HRMS (EI): calcd. for $C_{17}H_{18}O_2$ $[M]^+$ 254.1307; found 254.1303.

(3-Bromo-9-phenanthrenyl)(2-methoxyphenyl)methanone (5d) and 3-(4-Bromophenyl)-1-(2-methoxyphenyl)propan-1-one (6d): The General Procedure with **4d** (0.094 g, 0.30 mmol)/MeCN (0.3 mL)/PhMe (1.2 mL), **2a** (0.272 g, 0.91 mmol)/MeCN (0.3 mL)/PhMe (1.2 mL) and CsF (0.282 g, 1.85 mmol) afforded **5d** (0.041 g, 35%) and **6d** (0.031 g, 32%).

Compound 5d: Oil {purified by flash chromatography [gradient eluents: petroleum ether/dichloromethane (10:1, v/v), then petroleum ether/ethyl acetate (40:1, v/v)]; R_f = 0.17 [TLC eluent: petroleum ether/ethyl acetate (40:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (s, 1 H), 8.63 (d, J = 7.6 Hz, 1 H), 8.51 (d, J = 8.6 Hz, 1 H), 7.78 (s, 1 H), 7.72–7.62 (m, 5 H), 7.55–7.51 (m, 1 H), 7.06 (t, J = 7.4 Hz, 1 H), 6.97 (d, J = 8.4 Hz, 1 H), 3.54 (s, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 55.7, 112.0, 120.6, 122.8, 123.0, 125.7, 126.7, 127.2, 127.9, 128.8, 129.4, 129.50, 129.53, 129.6, 130.1, 131.1, 133.0, 133.4, 137.1, 158.6, 197.4 ppm. IR (neat): $\tilde{\nu}$ = 3010, 2937, 1657, 1596, 1485, 1461, 1405, 1298, 1246, 1164, 1117, 1059, 1019, 882, 858, 809, 755, 670 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 390 (27.0) $[M(^{79}Br)]^+$, 392 (28.3) $[M(^{81}Br)]^+$, 135 (100.0). HRMS (EI): calcd. for $C_{22}H_{15}O_2{}^{79}Br$ $[M]^+$ 390.0255; found 390.0252.

Compound 6d: Oil {purified by flash chromatography [gradient eluents: petroleum ether/dichloromethane (10:1, v/v), then petroleum

ether/ethyl acetate (40:1, v/v)]; R_f = 0.21 [TLC eluent: petroleum ether/ethyl acetate (40:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (dd, J_1 = 7.6, J_2 = 1.2 Hz, 1 H), 7.47–7.43 (m, 1 H), 7.39 (d, J = 8.4 Hz, 2 H), 7.10 (d, J = 8.0 Hz, 2 H), 6.99 (t, J = 7.4 Hz, 1 H), 6.95 (d, J = 8.4 Hz, 1 H), 3.87 (s, 3 H), 3.27 (t, J = 7.6 Hz, 2 H), 2.97 (t, J = 7.8 Hz, 2 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 29.8, 45.1, 55.5, 111.5, 119.6, 120.7, 128.1, 130.2, 130.3, 131.4, 133.5, 140.7, 158.5, 201.1 ppm. IR (neat): $\tilde{\nu}$ = 3019, 2924, 2845, 1662, 1592, 1481, 1431, 1398, 1358, 1296, 1272, 1243, 1181, 1111, 1068, 1018, 981, 810, 759, 654 cm^{-1}. MS (70 eV, EI): m/z (%) = 318 (8.8) [M(^{79}Br)]$^+$, 320 (8.8) [M(^{81}Br)]$^+$, 135 (100.0). HRMS (EI): calcd. for $C_{16}H_{15}O_2{}^{79}Br$ [M]$^+$ 318.0255; found 318.0258.

1-(3-Methoxy-9-phenanthrenyl)ethanone (5e) and 4-(4-Methoxyphenyl)butan-2-one (6e): The General Procedure with **4e** (0.177 g, 1.00 mmol)/MeCN (1.0 mL)/PhMe (4.0 mL), **2a** (0.892 g, 2.99 mmol)/MeCN (1.0 mL)/PhMe (4.0 mL) and CsF (0.934 g, 6.14 mmol) afforded **5e** (0.128 g, 51%) and **6e** (0.074 g, 41%).

Compound 5e:[33] Light yellow solid; m.p. 66–68 °C {recrystallized from petroleum ether/ethyl acetate (10:1, v/v) after purification by flash chromatography [gradient eluents: petroleum ether/dichloromethane (10:1, v/v), then petroleum ether/ethyl acetate (40:1, v/v)]; R_f = 0.32 [TLC eluent: petroleum ether/ethyl acetate (10:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.85–8.83 (m, 1 H), 8.59–8.57 (m, 1 H), 8.16 (s, 1 H), 7.97 (d, J = 2.0 Hz, 1 H), 7.82 (d, J = 8.8 Hz, 1 H), 7.65–7.63 (m, 2 H), 7.24 (dd, J_1 = 8.4, J_2 = 2.4 Hz, 1 H), 4.01 (s, 3 H), 2.78 (s, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 29.6, 55.5, 104.0, 117.3, 122.7, 124.4, 126.6, 127.0, 127.7, 128.8, 130.1, 131.3, 131.4, 131.8, 133.8, 160.4, 201.3 ppm. IR (neat): $\tilde{\nu}$ = 2924, 1667, 1614, 1523, 1504, 1453, 1439, 1374, 1293, 1218, 1176, 1158, 1036, 1020, 895, 817, 763, 620 cm^{-1}. MS (70 eV, EI): m/z (%) = 250 (61.8) [M]$^+$, 235 (100.0). HRMS (EI): calcd. for $C_{17}H_{14}O_2$ [M]$^+$ 250.0994; found 250.1000.

Compound 6e:[34] Oil {purified by flash chromatography [gradient eluents: petroleum ether/dichloromethane (10:1, v/v), then petroleum ether/ethyl acetate (40:1, v/v)]; R_f = 0.36 [TLC eluent: petroleum ether/ethyl acetate (10:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09 (d, J = 8.4 Hz, 2 H), 6.81 (d, J = 8.4 Hz, 2 H), 3.76 (s, 3 H), 2.83 (t, J = 7.6 Hz, 2 H), 2.71 (t, J = 7.4 Hz, 2 H), 2.11 (s, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 28.8, 29.9, 45.3, 55.1, 113.8, 129.1, 132.9, 157.8, 208.0 ppm. IR (neat): $\tilde{\nu}$ = 2935, 1712, 1611, 1583, 1511, 1443, 1361, 1299, 1243, 1178, 1159, 1109, 1034, 817, 742, 698 cm^{-1}. GC-MS (70 eV, EI): m/z (%) = 178 (48.1) [M]$^+$, 121 (100.0).

Ethyl 3-Methoxy-9-phenanthrenecarboxylate (5f) and Ethyl 3-(4-Methoxyphenyl)propanoate (6f): The General Procedure with **4f** (0.207 g, 1.00 mmol)/MeCN (1.0 mL)/PhMe (4.0 mL), **2a** (1.345 g, 4.51 mmol)/MeCN (1.0 mL)/PhMe (4.0 mL) and CsF (0.915 g, 6.02 mmol) afforded **5f** (0.146 g, 52%) and **6f** (0.025 g, 12%).

Compound 5f: Oil {purified by flash chromatography [gradient eluents: petroleum ether/dichloromethane (10:1 to 7:1, v/v), then petroleum ether/ethyl acetate (40:1, v/v)]; R_f = 0.37 [TLC eluent: petroleum ether/ethyl acetate (40:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.99–8.97 (m, 1 H), 8.64–8.62 (m, 1 H), 8.44 (s, 1 H), 8.02 (d, J = 1.6 Hz, 1 H), 7.88 (d, J = 8.4 Hz, 1 H), 7.69–7.64 (m, 2 H), 7.26 (dd, J_1 = 8.6, J_2 = 2.2 Hz, 1 H), 4.50 (q, J = 7.2 Hz, 2 H), 4.04 (s, 3 H), 1.49 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 14.4, 55.5, 61.0, 104.0, 117.3, 122.8, 123.9, 124.8, 126.4, 126.7, 127.4, 129.6, 130.1, 131.5, 132.2, 133.9, 160.4, 167.7 ppm. IR (neat): $\tilde{\nu}$ = 2921, 2854, 1709, 1617, 1507, 1453, 1375, 1293, 1219, 1183, 1161, 1121, 1036, 959, 878, 812, 782, 624 cm^{-1}. MS (70 eV, EI): m/z (%) = 280 (100.0) [M]$^+$. HRMS (EI): calcd. for $C_{18}H_{16}O_3$ [M]$^+$ 280.1099; found 280.1097.

Compound 6f:[35] Oil {purified by flash chromatography [gradient eluents: petroleum ether/dichloromethane (10:1 to 7:1, v/v)]; R_f = 0.38 [TLC eluent: petroleum ether/ethyl acetate (40:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11 (d, J = 8.4 Hz, 2 H), 6.82 (d, J = 8.8 Hz, 2 H), 4.12 (q, J = 7.0 Hz, 2 H), 3.78 (s, 3 H), 2.89 (t, J = 7.8 Hz, 2 H), 2.58 (t, J = 8.0 Hz, 2 H), 1.23 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 14.2, 30.1, 36.2, 55.2, 60.3, 113.8, 129.2, 132.6, 158.0, 172.9 ppm. IR (neat): $\tilde{\nu}$ = 2981, 1730, 1612, 1512, 1461, 1372, 1297, 1244, 1176, 1106, 1035, 824, 705 cm^{-1}. MS (70 eV, EI): m/z (%) = 208 (100.0) [M]$^+$.

3-Methoxy-9-phenanthrenecarbonitrile (5g) and 3-(4-Methoxyphenyl)propanenitrile (6g): The General Procedure with **4g** (0.159 g, 1.00 mmol)/MeCN (1.0 mL)/PhMe (4.0 mL), **2a** (1.344 g, 4.51 mmol)/MeCN (1.0 mL)/PhMe (4.0 mL) and CsF (0.913 g, 6.01 mmol) afforded **5g** (0.123 g, 53%) and **6g** (0.025 g, 16%).

Compound 5g:[36] Pale white solid; m.p. 116–118 °C {recrystallized from petroleum ether/ethyl acetate (10:1, v/v) after purification by flash chromatography [gradient eluents: petroleum ether/dichloromethane (7:1, v/v), then petroleum ether/ethyl acetate (40:1, v/v)]; R_f = 0.32 [TLC eluent: petroleum ether/ethyl acetate (10:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59–8.57 (m, 1 H), 8.26–8.24 (m, 1 H), 8.14 (s, 1 H), 7.97 (d, J = 2.0 Hz, 1 H), 7.81 (d, J = 8.8 Hz, 1 H), 7.73–7.71 (m, 2 H), 7.28 (dd, J_1 = 8.8, J_2 = 2.8 Hz, 1 H), 4.04 (s, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 55.6, 104.1, 106.5, 117.8, 118.3, 123.0, 124.5, 126.1, 127.6, 128.1, 129.31, 129.34, 131.1, 133.6, 135.2, 160.9 ppm. IR (neat): $\tilde{\nu}$ = 3675, 2987, 2901, 1616, 1506, 1454, 1406, 1394, 1251, 1233, 1145, 1066, 897, 759 cm^{-1}. MS (70 eV, EI): m/z (%) = 233 (100.0) [M]$^+$. HRMS (EI): calcd. for $C_{16}H_{11}NO$ [M]$^+$ 233.0841; found 233.0838.

Compound 6g:[37] Oil {purified by flash chromatography [gradient eluents: petroleum ether/dichloromethane (7:1, v/v), then petroleum ether/ethyl acetate (40:1, v/v)]; R_f = 0.38 [TLC eluent: petroleum ether/ethyl acetate (10:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14 (d, J = 8.4 Hz, 2 H), 6.86 (d, J = 8.4 Hz, 2 H), 3.78 (s, 3 H), 2.88 (t, J = 7.4 Hz, 2 H), 2.56 (t, J = 7.4 Hz, 2 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 19.6, 30.6, 55.2, 114.2, 119.2, 129.2, 130.1, 158.7 ppm. IR (neat): $\tilde{\nu}$ = 2935, 2247, 1612, 1512, 1462, 1300, 1246, 1179, 1110, 1032, 913, 832, 808, 731, 700, 647 cm^{-1}. GC-MS (70 eV, EI): m/z (%) = 161 (19.0) [M]$^+$, 121 (100.0).

Ethyl 3-Methoxy-6,7-dimethyl-9-phenanthrenecarboxylate (5i): The General Procedure with **4f** (0.102 g, 0.49 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL), **2b** (0.491 g, 1.51 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL) and CsF (0.461 g, 3.03 mmol) afforded **5i** (0.075 g, 50%) as a white solid; m.p. 116–118 °C recrystallized from petroleum ether/ethyl acetate (40:1, v/v) after purification by flash chromatography [eluent: petroleum ether/ethyl acetate (40:1, v/v)]; R_f = 0.31 [TLC eluent: petroleum ether/ethyl acetate (40:1, v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (s, 1 H), 8.35 (s, 1 H), 8.33 (s, 1 H), 7.96 (d, J = 2.0 Hz, 1 H), 7.83 (d, J = 8.8 Hz, 1 H), 7.21 (dd, J_1 = 8.8, J_2 = 2.4 Hz, 1 H), 4.49 (q, J = 7.0 Hz, 2 H), 4.03 (s, 3 H), 2.52 (s, 3 H), 2.49 (s, 3 H), 1.49 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 14.4, 20.37, 20.38, 55.5, 60.8, 103.6, 116.7, 123.0, 123.3, 124.5, 126.6, 128.0, 128.5, 131.3, 131.4, 133.5, 135.6, 136.9, 160.1, 167.9 ppm. IR (neat): $\tilde{\nu}$ = 2922, 1709, 1617, 1508, 1455, 1363, 1296, 1220, 1177, 1102, 1041, 840 cm^{-1}. MS (70 eV, EI): m/z (%) = 308 (100.0) [M]$^+$. HRMS (EI): calcd. for $C_{20}H_{20}O_3$ [M]$^+$ 308.1412; found 308.1411.

Ethyl 6,7-Difluoro-3-methoxy-9-phenanthrenecarboxylate (5j) and Ethyl 3-(4-Methoxyphenyl)propanoate (6f): The General Procedure with **4f** (0.206 g, 1.00 mmol)/MeCN (1.0 mL)/PhMe (4.0 mL), **2c** (1.510 g, 4.52 mmol)/MeCN (1.0 mL)/PhMe (4.0 mL) and CsF

(0.921 g, 6.06 mmol) afforded **5j** (0.174 g, 55%) and **6f** (0.048 g, 23%).

Compound 5j: White solid; m.p. 139–142 °C {recrystallized from chloroform after purification by flash chromatography [gradient eluents: petroleum ether/dichloromethane (7:1, v/v), then petroleum ether/ethyl acetate (40:1, v/v)]; R_f = 0.35 [TLC eluent: petroleum ether/ethyl acetate (40:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.97 (dd, J_1 = 13.6, J_2 = 8.8 Hz, 1 H), 8.48 (s, 1 H), 8.26 (dd, J_1 = 12.6, J_2 = 8.2 Hz, 1 H), 7.87 (d, J = 8.8 Hz, 1 H), 7.72 (s, 1 H), 7.27 (dd, J_1 = 8.8, J_2 = 2.4 Hz, 1 H), 4.48 (q, J = 7.2 Hz, 2 H), 4.03 (s, 3 H), 1.49 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 14.4, 55.5, 61.2, 103.7, 110.1 (d, J = 15.9 Hz), 114.4 (d, J = 17.8 Hz), 117.8, 122.0, 124.5, 126.9 (dd, J_1 = 7.5, J_2 = 1.4 Hz), 127.4 (dd, J_1 = 5.6, J_2 = 1.2 Hz), 131.8, 133.0 (d, J = 2.6 Hz), 133.1 (d, J = 1.3 Hz), 149.6 (dd, J_1 = 222.6, J_2 = 13.0 Hz), 150.2 (dd, J_1 = 222.0, J_2 = 12.4 Hz), 160.6, 167.0 ppm. IR (neat): $\tilde{\nu}$ = 2920, 1706, 1616, 1541, 1509, 1456, 1428, 1362, 1294, 1213, 1134, 1103, 1043, 897, 844, 806 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 316 (100.0) $[M]^+$. HRMS (EI): calcd. for $C_{18}H_{14}O_3F_2$ $[M]^+$ 316.0911; found 316.0909.

Compound 6f: Oil {purified by flash chromatography [gradient eluents: petroleum ether/dichloromethane (7:1, v/v), then petroleum ether/ethyl acetate (40:1, v/v)]}; R_f = 0.38 [TLC eluent: petroleum ether/ethyl acetate (40:1, v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11 (d, J = 8.4 Hz, 2 H), 6.82 (d, J = 8.8 Hz, 2 H), 4.12 (q, J = 7.0 Hz, 2 H), 3.78 (s, 3 H), 2.89 (t, J = 7.8 Hz, 2 H), 2.58 (t, J = 8.0 Hz, 2 H), 1.23 (t, J = 7.2 Hz, 3 H) ppm.

Ethyl 3,5-Dimethoxy-9-phenanthrenecarboxylate (5k): The General Procedure with **4f** (0.103 g, 0.50 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL), **2e** (0.739 g, 2.25 mmol)/MeCN (0.5 mL)/PhMe (2.0 mL) and CsF (0.461 g, 3.03 mmol) afforded **5k** (0.034 g, 22%) as a white solid; m.p. 89–91 °C {recrystallized from petroleum ether/ethyl acetate (20:1, v/v) after purification by flash chromatography [gradient eluents: petroleum ether/ethyl acetate (40:1 to 20:1, v/v)]; R_f = 0.37 [TLC eluent: petroleum ether/ethyl acetate (20:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.21 (d, J = 2.4 Hz, 1 H), 8.52 (dd, J_1 = 8.4, J_2 = 0.8 Hz, 1 H), 8.36 (s, 1 H), 7.86 (d, J = 8.4 Hz, 1 H), 7.59 (t, J = 8.0 Hz, 1 H), 7.26 (dd, J_1 = 8.8, J_2 = 2.4 Hz, 1 H), 7.17 (d, J = 7.2 Hz, 1 H), 4.49 (q, J = 7.2 Hz, 2 H), 4.13 (s, 3 H), 4.01 (s, 3 H), 1.48 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 14.4, 55.3, 55.9, 61.0, 108.5, 110.6, 116.1, 119.1, 121.1, 124.4, 125.4, 127.3, 130.9, 131.9, 132.9, 133.4, 158.8, 159.8, 168.2 ppm. IR (neat): $\tilde{\nu}$ = 2982, 1710, 1613, 1572, 1457, 1434, 1408, 1362, 1255, 1217, 1193, 1142, 1036, 866, 808, 760 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 310 (100.0) $[M]^+$. HRMS (EI): calcd. for $C_{19}H_{18}O_4$ $[M]^+$ 310.1205; found 310.1209.

Synthesis of 1-(3-Methoxyphenyl)-3-(2,3,4,5,6-pentadeuteriophenyl)-prop-2-en-1-one (4a-D): Sodium hydroxide solution (10%, 2.1 mL) was added dropwise to a cooled (0 °C), stirred solution of 2,3,4,5,6-pentadeuteriobenzaldehyde (1.415 g, 12.73 mmol) and 1-(3-methoxyphenyl)ethanone (1.912 g, 12.73 mmol) in ethanol (6.4 mL). The reaction mixture was brought to room temperature and further stirred overnight and was then neutralized by addition of dilute hydrochloric acid and extracted with diethyl ether (3 × 20 mL). The combined extracts were washed with brine, followed by drying with anhydrous magnesium sulfate. Filtration, concentration and column chromatography {gradient eluents: petroleum ether/ethyl acetate (15:1 to 10:1, v/v); R_f = 0.34 [TLC eluent: petroleum ether/ethyl acetate (10:1, v/v)]} afforded **4a-D** (1.983 g, 64%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, J = 16.0 Hz, 1 H), 7.60 (d, J = 7.2 Hz, 1 H), 7.55 (d, J = 1.6 Hz, 1 H), 7.51 (d, J = 15.6 Hz, 1 H), 7.40 (t, J = 7.8 Hz, 1 H), 7.12 (dd, J_1 = 8.0, J_2 = 2.4 Hz, 1 H), 3.87 (s, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 55.3, 112.7, 119.1, 120.9, 121.9, 127.9 (t, J = 21.4 Hz), 128.3 (t, J = 21.4 Hz), 129.4, 129.9 (t, J = 21.9 Hz), 134.6, 139.4, 144.6, 159.8, 190.0 ppm. IR (neat): $\tilde{\nu}$ = 2939, 1661, 1584, 1485, 1454, 1429, 1344, 1303, 1272, 1247, 1195, 1157, 1021, 979, 859, 790, 765, 738, 717, 682 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 243 (100.0) $[M]^+$. HRMS (EI): calcd. for $C_{16}H_9D_5O_2$ $[M]^+$ 243.1308; found 243.1309.

Compounds **5a-D** and **6a-D** were prepared similarly to **5a** and **6a**.

(3-Methoxyphenyl)(1,2,3,4-tetradeuteriophenanthren-9-yl)methanone (5a-D) and 3-Deuterio-1-(3-methoxyphenyl)-3-(2,3,4,5,6-pentadeuteriophenyl)propan-1-one (6a-D): The General Procedure with **4a-D** (0.192 g, 0.79 mmol)/MeCN (0.8 mL)/PhMe (3.2 mL), **2a** (0.718 g, 2.41 mmol)/MeCN (0.8 mL)/PhMe (3.2 mL) and CsF (0.728 g, 4.79 mmol) afforded **5a-D** (0.098 g, 39%) and **6a-D** (0.065 g, 33%).

Compound 5a-D: White solid; m.p. 149–151 °C {recrystallized from petroleum ether/ethyl acetate (40:1, v/v) after purification by flash chromatography [gradient eluents: petroleum ether/dichloromethane (15:1 to 10:1, v/v), then petroleum ether/ethyl acetate (40:1, v/v)]; R_f = 0.41 [TLC eluent: petroleum ether/ethyl acetate (20:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (d, J = 8.0 Hz, 1 H), 8.11 (d, J = 8.4 Hz, 1 H), 7.85 (s, 1 H), 7.68 (t, J = 7.6 Hz, 1 H), 7.59–7.55 (m, 2 H), 7.42 (d, J = 7.6 Hz, 1 H), 7.32 (t, J = 7.8 Hz, 1 H), 7.15 (dd, J_1 = 8.4, J_2 = 2.4 Hz, 1 H), 3.83 (s, 3 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 55.4, 113.9, 120.0, 122.3 (t, J = 21.2 Hz), 122.9, 123.6, 126.6, 126.6 (overlapped with previous peak, t, J = 21.3 Hz), 127.1, 127.2, 127.5–128.2 (m), 128.8, 129.1, 129.3, 129.4, 129.9, 130.5, 131.2, 135.3, 139.5, 159.8, 197.7 ppm. IR (neat): $\tilde{\nu}$ = 2972, 2903, 1658, 1584, 1484, 1430, 1387, 1265, 1175, 1044, 894, 767, 685 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 316 (100.0) $[M]^+$. HRMS (EI): calcd. for $C_{22}H_{12}D_4O_2$ $[M]^+$ 316.1401; found 314.1404.

Compound 6a-D: Oil {purified by flash chromatography [gradient eluents: petroleum ether/dichloromethane (15:1 to 10:1, v/v)]; R_f = 0.43 [TLC eluent: petroleum ether/ethyl acetate (10:1, v/v)]}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, J = 7.6 Hz, 1 H), 7.48 (d, J = 2.4 Hz, 1 H), 7.35 (t, J = 8.0 Hz, 1 H), 7.09 (dd, J_1 = 8.2, J_2 = 2.0 Hz, 1 H), 3.84 (s, 3 H), 3.28 (d, J = 7.6 Hz, 2 H), 3.05 (t, J = 7.6 Hz, 1 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 29.7 (t, J = 18.0 Hz), 40.4, 55.4, 112.2, 119.5, 120.6, 125.6 (t, J = 21.2 Hz), 128.0 (t, J = 21.6 Hz), 129.6, 138.2, 141.0, 159.8, 199.0 ppm. IR (neat): $\tilde{\nu}$ = 2937, 2836, 2361, 2273, 1684, 1592, 1486, 1457, 1430, 1334, 1253, 1198, 1168, 1042, 873, 788, 686 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 246 (94.1) $[M]^+$, 135 (100.0). HRMS (EI): calcd. for $C_{16}H_{10}D_6O_2$ $[M]^+$ 246.1527; found 246.1524.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of all the products.

Acknowledgments

We are grateful to the National Natural Science Foundation of China (Project Nos. 20872127, 20732005 and J0830431), the National Basic Research Program of China (973 Program, 2009CB825300), the CAS Academician Foundation of Zhejiang Province, and the Fundamental Research Funds for the Central Universities for financial support.

[1] For book chapters on the biological and pharmacological activities of 2*H*-chromenes, see: a) E. E. Schweizer, O. Meeder-Nycz, in *Chromenes, Chromanes, Chromones* (Ed.: G. P. Ellis),

Wiley-Interscience, New York, **1977**, pp. 11–139; b) J. Hepworth, in *Comprehensive Heterocyclic Chemistry*, vol. 3 (Eds.: A. R. Katritzky, C. W. Rees), Pergamon, Oxford, UK, **1984**, pp. 737–883. For selected examples, see: c) G. E. Pratt, R. C. Jennings, A. F. Hamnett, G. T. Brooks, *Nature* **1980**, *284*, 320–323; d) W. S. Bowers, T. Ohta, J. S. Cleere, P. A. Marsella, *Science* **1976**, *193*, 542–547.

[2] For reviews on the photochromic properties of 2*H*-chromenes, see: a) V. I. Minkin, *Chem. Rev.* **2004**, *104*, 2751–2776. For selected examples, see: b) J. N. Moorthy, P. Venkatakrishnan, S. Samanta, D. K. Kumar, *Org. Lett.* **2007**, *9*, 919–922; c) M.-J. R. P. Queiroz, A. S. Abreu, P. M. T. Ferreira, M. M. Oliveira, R. Dubest, J. Aubard, A. Samat, *Org. Lett.* **2005**, *7*, 4811–4814.

[3] For typical procedures to prepare 2*H*-chromenes, see: a) R.-J. Li, S.-F. Pi, Y. Liang, Z.-Q. Wang, R.-J. Song, G.-X. Chen, J.-H. Li, *Chem. Commun.* **2010**, *46*, 8183–8185; b) G. B. Bajracharya, O. Daugulis, *Org. Lett.* **2008**, *10*, 4625–4628; c) R. Sanz, Y. Fernández, M. P. Castroviejo, A. Pérez, F. J. Fañanás, *Eur. J. Org. Chem.* **2007**, 62–69; d) L.-W. Ye, X.-L. Sun, C.-Y. Zhu, Y. Tang, *Org. Lett.* **2006**, *8*, 3853–3856; e) T. Eguchi, Y. Hoshino, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 967–970; f) K. C. Nicolaou, J. A. Pfefferkorn, F. Schuler, A. J. Roecker, G.-Q. Cao, J. E. Casida, *Chem. Biol.* **2000**, *7*, 979–992; g) D. W. Knight, P. B. Little, *J. Chem. Soc. Perkin Trans. 1* **2000**, 2343–2355; h) S. Chang, R. H. Grubbs, *J. Org. Chem.* **1998**, *63*, 864–866; i) R. C. Larock, L. Wei, T. R. Hightower, *Synlett* **1998**, 522–524; j) D. W. Knight, P. B. Little, *Tetrahedron Lett.* **1998**, *39*, 5105–5108.

[4] For recent reviews on phenanthrenes in organic synthesis, see: a) X. Feng, W. Pisula, K. Müllen, *Pure Appl. Chem.* **2009**, *81*, 2203–2224; b) C. K. Bradsher, *Chem. Rev.* **1987**, *87*, 1277–1297; c) A. J. Floyd, S. F. Dyke, S. E. Ward, *Chem. Rev.* **1976**, *76*, 509–562. For selected examples, see: d) S. A. Worlikar, R. C. Larock, *J. Org. Chem.* **2009**, *74*, 9132–9139; e) N. Saito, K. Shiotani, A. Kinbara, Y. Sato, *Chem. Commun.* **2009**, 4284–4286.

[5] For selected examples of bioactivities and synthesis of PBT-1, see: X. Yang, Q. Shi, Y.-N. Liu, G. Zhao, K. F. Bastow, J.-C. Lin, S.-C. Yang, P.-C. Yang, K.-H. Lee, *J. Med. Chem.* **2009**, *52*, 5262–5268.

[6] For reviews and book chapters on progress in aryne chemistry, see: a) C. Wentrup, *Aust. J. Chem.* **2010**, *63*, 979–986; b) T. Kitamura, *Aust. J. Chem.* **2010**, *63*, 987–1001; c) R. Sanz, *Org. Prep. Proced. Int.* **2008**, *40*, 215–291; d) K. Rathwell, M. A. Brimble, *Synthesis* **2007**, 643–662; e) D. Peña, D. Pérez, E. Guitián, *Angew. Chem.* **2006**, *118*, 3659; *Angew. Chem. Int. Ed.* **2006**, *45*, 3579–3581; f) A. M. Dyke, A. J. Hester, G. C. Lloyd-Jones, *Synthesis* **2006**, 4093–4112; g) H. H. Wenk, M. Winkler, W. Sander, *Angew. Chem.* **2003**, *115*, 518; *Angew. Chem. Int. Ed.* **2003**, *42*, 502–528; h) H. Pellissier, M. Santelli, *Tetrahedron* **2003**, *59*, 701–730; i) S. V. Kessar, in *Comprehensive Organic Synthesis*, vol. 4 (Eds.: B. M. Trost, I. Fleming), Pergamon, New York, **1991**, pp. 483–515; j) E. R. Biehl, S. P. Khanapure, *Acc. Chem. Res.* **1989**, *22*, 275–281; k) M. R. Bryce, J. M. Vernon, in *Advances in Heterocyclic Chemistry*, vol. 28 (Eds.: A. R. Katritsky, A. J. Boulton), Academic, New York, **1981**, pp. 183–229; l) S. V. Kessar, *Acc. Chem. Res.* **1978**, *11*, 283–288; m) H. Heaney, *Chem. Rev.* **1962**, *62*, 81–97.

[7] For selective reports on aryne chemistry in our group in recent years, see: a) X. Huang, T. Zhang, *J. Org. Chem.* **2010**, *75*, 506–509; b) T. Zhang, X. Huang, J. Xue, S. Sun, *Tetrahedron Lett.* **2009**, *50*, 1290–1294; c) X. Huang, T. Zhang, *Tetrahedron Lett.* **2009**, *50*, 208–211; d) X. Huang, J. Xue, *J. Org. Chem.* **2007**, *72*, 3965–3968.

[8] For Y. Himeshima, T. Sonoda, H. Kobayashi, *Chem. Lett.* **1983**, 1211–1214.

[9] For selected examples of [2+2] cycloaddition of C=C with arynes in recent years, see: a) X. Lu, H. Nikawa, T. Tsuchiya, T. Akasaka, M. Toki, H. Sawa, N. Mizorogi, S. Nagase, *Angew. Chem.* **2010**, *122*, 604; *Angew. Chem. Int. Ed.* **2010**, *49*, 594–597; b) A. Criado, M. J. Gómez-Escalonilla, J. L. Garcia-Fierro, A. Urbina, D. Peña, E. Guitián, F. Langa, *Chem. Commun.* **2010**, *46*, 7028–7030; c) T. Blackburn, Y. K. Ramtohul, *Synlett* **2008**, 1159–1164; d) T. Suzuki, T. Hamura, K. Suzuki, *Angew. Chem.* **2008**, *120*, 2280; *Angew. Chem. Int. Ed.* **2008**, *47*, 2248–2252. For reviews, see ref.[6b,6c,6e,6f,6h,6k] and references cited therein.

[10] For selected examples relating to [2+2] cycloadditions of carbon–heteroatom double bonds with arynes, see: a) K. Biswas, M. F. Greaney, *Org. Lett.* **2011**, *13*, 4946–4949; b) A. A. Aly, N. K. Mohamed, A. A. Hassan, A.-F. E. Mourad, *Tetrahedron* **1999**, *55*, 1111–1118. For reviews, see ref.[6c,6e,6f,6h] and references cited therein.

[11] For recent reviews relating to benzocyclobutenes (X = C), see: a) W. Adam, C. R. Saha-Möller, C.-G. Zhao, *Org. React.* **2002**, *61*, 219–516; b) G. Mehta, S. Cota, *Tetrahedron* **2001**, *57*, 625–659. For selected reports relating to benzoxetenes (X = O), see: c) S. Arumugam, V. V. Popik, *J. Am. Chem. Soc.* **2009**, *131*, 11892–11899. For selected reports relating to benzazetidines (X = N), see: d) K. Kobayashi, K. Miyamoto, T. Yamase, D. Nakamura, O. Morikawa, H. Konishi, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1580–1584.

[12] For recent reviews relating to *ortho*-quinodimethanes (X = C), see: a) H. Yoshida, J. Ohshita, A. Kunai, *Bull. Chem. Soc. Jpn.* **2010**, *83*, 199–219; b) H. Butenschön, *Pure Appl. Chem.* **2002**, *74*, 57–62. For book chapters and reviews relating to *ortho*-quinone methides (X = O), see: c) J. L. Bolton, J. A. Thompson, *Reactive Intermediates in Chemistry and Biology: Quinone Methides*, vol. 1 (Ed.: S. E. Rokita), Wiley, Hoboken, NJ, **2009**, p. 329; d) H. Amouri, J. Le Bras, *Acc. Chem. Res.* **2002**, *35*, 501–510. For recent reports relating to *ortho*-quinone methide imines (X = N), see: e) A. S. Caillé, L. Trimble, C. Berthelette, C. K. Lau, *Synlett* **1996**, 669–671; f) J. M. Wiebe, A. S. Caille, L. Trimble, C. K. Lau, *Tetrahedron* **1996**, *52*, 11705–11724. For other kinds of *ortho*-quinoids, see review: g) V. Nair, R. Dhanya, C. Rajesh, S. Devipriya, *Synlett* **2005**, 2407–2419.

[13] For recent researches applying this cascade strategy, see: a) E. Yoshioka, S. Kohtani, H. Miyabe, *Angew. Chem.* **2011**, *123*, 6768; *Angew. Chem. Int. Ed.* **2011**, *50*, 6638–6642; b) H. Yoshida, Y. Ito, J. Ohshita, *Chem. Commun.* **2011**, *47*, 8512–8514; c) E. Yoshioka, S. Kohtani, H. Miyabe, *Org. Lett.* **2010**, *12*, 1956–1959; d) G. A. Kraus, T. Wu, *Tetrahedron* **2010**, *66*, 569–572; e) J. B. Feltenberger, R. Hayashi, Y. Tang, E. S. C. Babiash, R. P. Hsung, *Org. Lett.* **2009**, *11*, 3666–3669; f) K. R. Buszek, D. L. Bixby, Abstracts of Papers, *231st ACS National Meeting*, Atlanta, GA, US, **2006**, ORGN-524; g) H. Yoshida, M. Watanabe, H. Fukushima, J. Ohshita, A. Kunai, *Org. Lett.* **2004**, *6*, 4049–4051. See also ref.[10]

[14] For reactions of cinnamaldehydes with arynes produced from tetrachlorobenzenediazonium-2-carboxylate, see: a) H. Heaney, J. M. Jablonski, C. T. McCarty, *J. Chem. Soc. Perkin Trans. 1* **1972**, 2903–2910. For reactions employing ketones, see: b) H. Heaney, C. T. McCarty, *J. Chem. Soc. D* **1970**, 123–124.

[15] For selected recent examples relating to aryne Diels–Alder reactions with cyclic dienes, see: a) A. Criado, D. Peña, A. Cobas, E. Guitián, *Chem. Eur. J.* **2010**, *16*, 9736–9740; b) D. Rodríguez-Lojo, D. Peña, D. Pérez, E. Guitián, *Org. Biomol. Chem.* **2010**, *8*, 3386–3388; c) G.-Y. J. Im, S. M. Bronner, A. E. Goetz, R. S. Paton, P. H.-Y. Cheong, K. N. Houk, N. K. Garg, *J. Am. Chem. Soc.* **2010**, *132*, 17933–17944; d) K. J. Procko, H. Li, S. F. Martin, *Org. Lett.* **2010**, *12*, 5632–5635; e) A. N. Garr, D. Luo, N. Brown, C. J. Cramer, K. R. Buszek, D. VanderVelde, *Org. Lett.* **2010**, *12*, 96–99; f) T. Ikawa, A. Takagi, Y. Kurita, K. Saito, K. Azechi, M. Egi, K. Kakiguchi, Y. Kita, S. Akai, *Angew. Chem.* **2010**, *122*, 5695; *Angew. Chem. Int. Ed.* **2010**, *49*, 5563–5566; g) R. Webster, M. Lautens, *Org. Lett.* **2009**, *11*, 4688–4691; h) S. Akai, T. Ikawa, S.-i. Takayanagi, Y. Morikawa, S. Mohri, M. Tsubakiyama, M. Egi, Y. Wada, Y. Kita, *Angew. Chem.* **2008**, *120*, 7787; *Angew. Chem. Int. Ed.* **2008**, *47*, 7673–7676. For reviews, see also ref.[6c,6e,6f,6h,6i]

[16] For reviews, see ref.[6c,6h] For selected recent examples of aryne Diels–Alder reactions with acyclic dienes, see: a) K. Nikitin, H. Müller-Bunz, Y. Ortin, M. J. McGlinchey, *Org. Biomol. Chem.* **2007**, *5*, 1952–1960; b) C. Dockendorff, S. Sahli, M. Olsen, L. Milhau, M. Lautens, *J. Am. Chem. Soc.* **2005**, *127*, 15028–15029; c) L. Minuti, A. Taticchi, E. Gacs-Baitz, A. Marrocchi, *Tetrahedron* **1998**, *54*, 10891–10898; d) J. C. Estévez, R. J. Estévez, L. Castedo, *Tetrahedron* **1995**, *51*, 10801–10810; e) N. Atanes, L. Castedo, E. Guitián, C. Saá, J. M. Saá, R. Suau, *J. Org. Chem.* **1991**, *56*, 2984–2988; f) N. Atanes, L. Castedo, A. Cobas, E. Guitián, C. Saá, J. M. Saá, *Tetrahedron* **1989**, *45*, 7947–7956; g) J. C. Estévez, R. J. Estévez, E. Guitián, M. C. Villaverde, L. Castedo, *Tetrahedron Lett.* **1989**, *30*, 5785–5786; h) Y. Ittah, I. Shahak, J. Blum, J. Klein, *Synthesis* **1977**, 678–679; i) R. Harrison, H. Heaney, J. M. Jablonski, K. G. Mason, J. M. Sketchley, *J. Chem. Soc. C* **1969**, 1684–1689; j) E. Wolthuis, W. Cady, *Angew. Chem.* **1967**, *79*, 575; *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 555–556; k) W. L. Dilling, *Tetrahedron Lett.* **1966**, *7*, 939; l) S. F. Dyke, A. R. Marshall, J. P. Watson, *Tetrahedron* **1966**, *22*, 2515–2521; m) W. Davies, J. R. Wilmshurst, *J. Chem. Soc.* **1961**, 4079–4082. For selected examples of aryne Diels–Alder reactions with enynes and their derivatives, see: n) T. T. Jayanth, M. Jeganmohan, M.-J. Cheng, S.-Y. Chu, C.-H. Cheng, *J. Am. Chem. Soc.* **2006**, *128*, 2232–2233; o) M. E. Hayes, H. Shinokubo, R. L. Danheiser, *Org. Lett.* **2005**, *7*, 3917–3920.

[17] R. L. Nongkhlaw, R. Nongrum, B. Myrboh, *J. Chem. Soc. Perkin Trans. 1* **2001**, 1300–1303.

[18] For reviews on hydride transfer reactions, see: a) N. C. Deno, H. J. Peterson, G. S. Saines, *Chem. Rev.* **1960**, *60*, 7–14. For reports relating to hydride transfer induced aromatization, see: b) E. Dorrestijn, M. Kranenburg, M. V. Ciriano, P. Mulder, *J. Org. Chem.* **1999**, *64*, 3012–3018; c) D. H. Reid, W. Bonthrone, *J. Chem. Soc.* **1965**, 5920–5926. For reports relating to hydride transfer reactions with Michael acceptors, see: d) K. M. McQuaid, D. Sames, *J. Am. Chem. Soc.* **2009**, *131*, 402–403; e) K. M. McQuaid, J. Z. Long, D. Sames, *Org. Lett.* **2009**, *11*, 2972–2975. This hydride Michael addition/protonation process might be also responsible for the formation of small amounts of ethylbenzene when 2-benzenediazonium-2-carboxylate was employed as the aryne source to react with styrene, although the author did not clarify this; see ref.[16i]

[19] For single-electron-transfer-induced aromatizations and dehydrogenations, see: a) P. S. Sadhua, M. Ravindera, P. A. Kumara, V. J. Rao, *Photochem. Photobiol. Sci.* **2009**, *8*, 513–515; b) M. Stratakis, M. Stavroulakis, *Tetrahedron Lett.* **2001**, *42*, 6409–6411; c) G. Giese, A. Heesing, *Chem. Ber.* **1991**, *124*, 2623–2628.

[20] After the reactions were complete, the reactors were cooled to room temp. and then shaken vigorously to wash down the residuals on the inner walls of the reactors and to redissolve possibly evaporated volatiles, followed by standing for a few minutes. GC-MS samples were then collected from the supernatants of the reaction mixtures.

[21] For the aldol condensation methods, see: a) H. Dong, M. Shen, J. E. Redford, B. J. Stokes, A. L. Pumphrey, T. G. Driver, *Org. Lett.* **2007**, *9*, 5191–5194; b) D. M. Mampreian, A. H. Hoveyda, *Org. Lett.* **2004**, *6*, 2829–2832.

[22] For the synthesis of the corresponding propargyl alcohols, see: a) J.-P. R. Hermet, D. W. Porter, M. J. Dearden, J. R. Harrison, T. Koplin, P. O'Brien, J. Parmene, V. Tyurin, A. C. Whitwood, J. Gilday, N. M. Smith, *Org. Biomol. Chem.* **2003**, *1*, 3977–3988. For the synthesis of α,β-unsaturated aldehydes from the propargylic alcohols through Meyer–Schuster rearrangements, see: b) K. H. Meyer, K. Schuster, *Ber. Dtsch. Chem. Ges.* **1922**, *55*, 819–823; c) S. Swaminathan, K. V. Narayanan, *Chem. Rev.* **1971**, *71*, 429–438; d) S. S. Koval'skaya, N. G. Kozlov, E. A. Dikusar, *Russ. J. Org. Chem.* **2009**, *45*, 185–199, and references therein.

[23] For the synthesis of the allylic alcohols as the starting materials, see: a) Z. Bourhani, A. V. Malkov, *Chem. Commun.* **2005**, 4592–4594. For the synthesis of the α,β-unsaturated aldehydes through oxidation of the corresponding allylic alcohols, see: b) E. J. Leopold, *Org. Synth. Coll. Vol.* **1990**, *VII*, 258–263; *Org. Synth.* **1986**, *64*, 164–172.

[24] D. Peña, D. Pérez, E. Guitián, L. Castedo, *J. Am. Chem. Soc.* **1999**, *121*, 5827–5828. See also ref.[8]

[25] A. H. L. Machado, M. A. de Sousa, D. C. S. Patto, L. F. S. Azevedo, F. I. Bombonato, C. R. D. Correia, *Tetrahedron Lett.* **2009**, *50*, 1222–1225.

[26] a) N. A. R. Hatam, W. G. Nacy, *Tetrahedron Lett.* **1983**, *24*, 4455–4456; b) T. G. C. Bird, B. R. Brown, I. A. Stuart, A. W. R. Tyrrell, *J. Chem. Soc. Perkin Trans. 1* **1983**, 1831–1846.

[27] K. Freudenberg, K. Weinges, *Justus Liebigs Ann. Chem. Ann. Chem.* **1954**, *590*, 140–154.

[28] a) D. Abson, K. D. Bartle, J. Bryant, R. Livingstone, R. B. Watson, *J. Chem. Soc.* **1965**, 2978–2982; b) R. Wizinger, H. Wenning, *Helv. Chim. Acta* **1940**, *23*, 247–271.

[29] C. S. Barnes, M. I. Strong, J. L. Occolowitz, *Tetrahedron* **1963**, *19*, 839–847.

[30] S. L. Vander Velde, E. N. Jacobsen, *J. Org. Chem.* **1995**, *60*, 5380–5381.

[31] P. Colbon, J. Ruan, M. Purdie, J. Xiao, *Org. Lett.* **2010**, *12*, 3670–3673.

[32] H. M. Smith, A. J. S. Knox, D. M. Zisterer, D. G. Lloyd, M. J. Meegan, *Medicinal Chemistry* **2007**, *3*, 135–155.

[33] E. L. May, E. Mosettig, *J. Org. Chem.* **1946**, *11*, 15–20.

[34] J. A. Murphy, A. G. J. Commeureuc, T. N. Snaddon, T. M. McGuire, T. A. Khan, K. Hisler, M. L. Dewis, R. Carling, *Org. Lett.* **2005**, *7*, 1427–1429.

[35] S. P. Morcillo, L. Alvarez de Cienfuegos, A. J. Mota, J. Justicia, R. Robles, *J. Org. Chem.* **2011**, *76*, 2277–2281.

[36] F. B. Mallory, C. W. Mallory, *Org. React.* **1984**, *30*, 1–456.

[37] S. Iida, H. Togo, *Tetrahedron* **2007**, *63*, 8274–8281.

Received: January 12, 2012
Published Online: May 11, 2012

