JOC The Journal of Organic Chemistry
Article
pubs.acs.org/joc

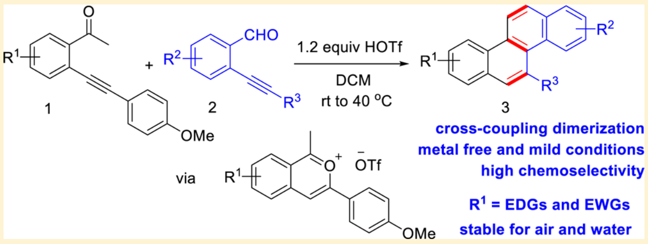
Brønsted Acid-Promoted One-Pot Synthesis of Chrysene Derivatives via Isochromenylium Intermediate Formed in Situ

Biao Guo, Yiming Zhou, Lei Zhang, and Ruimao Hua*

Department of Chemistry, Tsinghua University, Key Laboratory of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Beijing 100084, China

S *Supporting Information*

ABSTRACT: Trifluoromethanesulfonic acid (HOTf) promoted cross-coupling of *ortho*-[2-(4-methoxylphenyl)-alkynyl]acetophenones with *ortho*-alkynylbenzaldehydes affording chrysene derivatives has been developed. The present cascade reaction provides a facile one-pot synthesis of multisubstituted chrysenes as well as naked chrysene under mild conditions. The mechanism experimental results demonstrate isochromenylium is a key intermediate for this transformation.



■ INTRODUCTION

Isochromenyliums are reactive and versatile structures in construction of complicated frameworks, and they have been reported as important intermediates or starting materials in many cascade reactions in the past decades.[1−7] By treating *o*-alkynylcarbonylbenzene precursors with transition metal catalysts or other electrophiles (Au,[1] Cu(II),[2] Pd(II),[3] W,[4] Pt(II),[5] IPy_2BF_4,[6] I_2,[7] etc.), isochromenyliums can be formed in situ as inseparable intermediates which are high reactive toward the unsaturated carbon−carbon bonds. For example, isochromenyliums undergo [4 + 2] cycloaddition with alkynes to provide multisubstituted naphthyl ketones, which are usually called Asao−Yamamoto benzannulation.[1,2] Multisubstituted naphthalenes can also be obtained via the departure of carbonyl group in the presence of Brønsted acid except for metal catalyst. Besides, isochromenyliums can also be used as 1,3-dipolar species to react with dipolarophiles via intramolecular [3 + 2] cycloaddition to afford oxa-bridged ring compounds.[8] In the presence of strong Brønsted acid with bulky anion (HOTf,[9] HBF_4,[10] etc.), isochromenylium salts can be isolated with good yield, and the presence of a large amount of anion is considered to be of benefit to stabilize isochromenylium cation. In this respect, Swager[9a] and Yao[10] have done elegant pioneering work to get stable isochromenylium salts and apply them in the organic synthesis, but their approaches need large excess amount of Brønsted acid and limit to the reactants, which must bear electron-donating groups (EDGs) on the benzene ring.

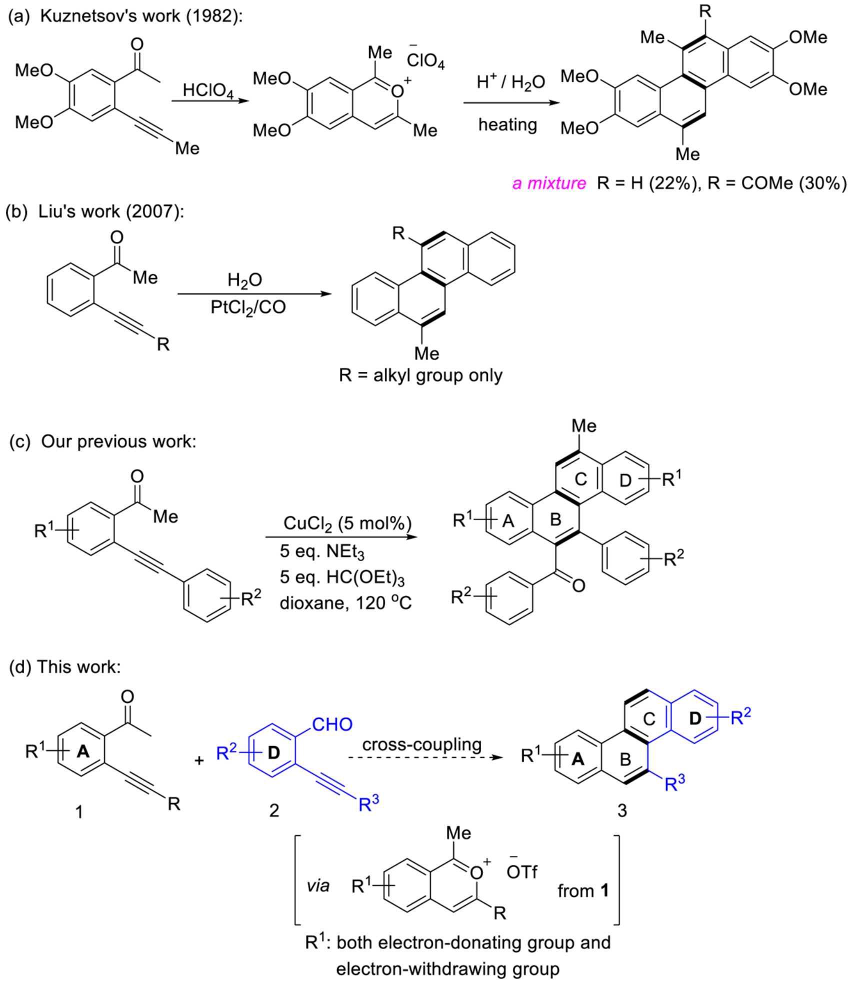
On the other hand, chrysene derivatives have attracted growing attention due to their potential applications in the fields of electronic devices such as field-effect transistors (FETs) and organic light-emitting diodes (OLEDs).[11,12] Therefore, it is significant and interesting to develop the different synthetic methods to access multisubstituted chrysenes having substituents in requisite positions. Although there have several kinds of synthetic routes to chrysene derivatives, including photocyclization of naphthylstyrenes or their analogues,[13] 1,5-naphthodiyne synthon formed in situ[14] and the homocyclodimerization of 2-alkynyl-1-acetylbenzenes.[15,16] The synthetic method by the homocyclodimerization of 2-alkynyl-1-acetylbenzenes is considered to be much more attractive due to the readily available starting materials and easily introducing versatile substituents. Therefore, Kuznetsov et al. reported an acid-promoted homocyclodimerization of 2-alkynyl-1-acetylbenzenes bearing electron-donating groups OMe on benzene ring to obtain chrysene derivatives with low chemoselectivity via isochromenylium intermediate (Scheme 1a),[15] and Liu et al. recently developed a Pt(II)-catalyzed hydrative homodimerization of 2-alkynyl-1-acetylbenzenes having R group to be an alkyl substituent (Scheme 1b).[16a]

In continuation of our studies on the application of *o*-alkynyl aromatic carbonyl compounds in the synthesis of cyclic compounds,[17] very recently, we also reported a copper-catalyzed homocyclodimerization of *o*-alkynylacetophenones affording chrysene derivatives (Scheme 1c).[16b] However, it could only construct the chrysene ring with the same substituents on the benzene rings of A and D. With the purpose of developing an another method to form the chrysene ring with easy introduction of different substituents, we designed a cross-coupling of *o*-alkynylacetophenones (**1**) and *o*-alkynylbenzaldehydes (**2**) with controllable formation of isochromenylium from *o*-alkynylacetophenones (**1**) as intermediate, which further undergoes [4 + 2] cycloaddition with *o*-alkynylbenzaldehydes (**2**) selectively followed by intramolecular dehydration to construct chrysene skeletons (Scheme 1d).

Received: May 30, 2015
Published: July 16, 2015

DOI: 10.1021/acs.joc.5b01219
J. Org. Chem. 2015, 80, 7635−7641

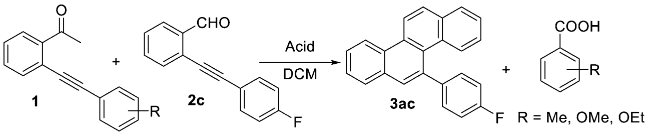
Scheme 1. Synthesis of Chrysene Derivatives via 2-Alkynyl-1-acetylbenzenes



■ RESULTS AND DISCUSSION

The initial investigation was carried out by treating *o*-(2-arylalkynyl)acetophenone **1** with *o*-(2-arylalkynyl)benzaldehyde **2c** by dropping HOTf (1.6 equiv based on **2c**) in DCM at 5 °C for 10 min, then the reaction temperature was increased to 30 °C, and the reaction mixture was further stirred for 18 h. It was found that the use of *o*-(2-phenylalkynyl)acetophenone afforded trace amount of **3ac** (Table 1, entry 1), and its structure was confirmed to be a chrysene derivative by X-ray crystallography (see Supporting Information). However, the reactions of **1** bearing an electron-poor alkynyl group (4-F-, 4-Cl- and 4-MeCO-phenylalkynyl) gave no desired chrysene derivatives at all (Table 1, entries 2−4). Fortunately, **1** having an electron-rich alkynyl group reacted with **2c** to afford **3ac** as exclusive chrysene derivative in low to moderate yields, depending on the property of the electron donating groups (EDGs) (Table 1, entries 5−7), and in the cases of *o*-[2-(*para*-methoxyphenyl)alkynyl]-acetophenone and *o*-[2-(*para*-ethoxyphenyl)alkynyl]-acetophenone used, **3ac** could be isolated in 68 and 62% yields, respectively. These results obviously indicated that the effect of substituent group showed very important role to stabilize the isochromenylium cation forming from **1** in situ, and the presence of electron-rich group of *para*-methoxyphenyl bonded to carbon−carbon triple bond is the key factor to stabilize the isochromenylium cation, which further react with **2c** to construct chrysene ring. It should be also noted that the formation of the relative isochromenylium as orange precipitation was observed by adding HOTf, when the substrates of **1** having R groups to be OMe and OEt were used (vide Scheme 4). A higher temperature

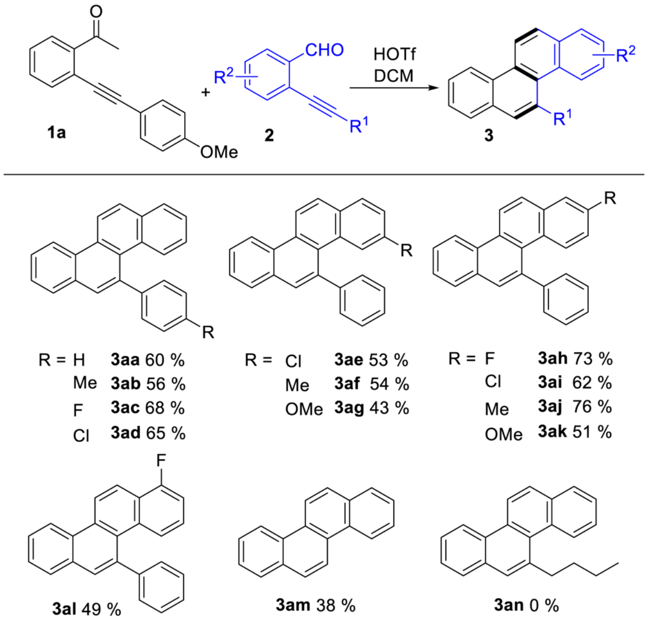
Table 1. Reaction Optimization for the Synthesis of 3ac[a]



entry	R	acid (equiv)	T (°C)	yield[b] (%)
1	H	HOTf (1.6)	30	trace
2	4-F	HOTf (1.6)	30	0
3	4-Cl	HOTf (1.6)	30	0
4	4-COMe	HOTf (1.6)	30	0
5	4-Me	HOTf (1.6)	30	8
6	4-OMe	HOTf (1.6)	30	68
7	4-OEt	HOTf (1.6)	30	62
8	4-OMe	HOTf (1.6)	40	52
9	4-OMe	HOTf (1.0)	30	37
10	4-OMe	HOTf (2.0)	30	60
11	4-OMe	TFA (1.6)	30	0
12	4-OMe	CH_3SO_3H (1.6)	30	0
13	4-OMe	HBF_4 (1.6)	30	29

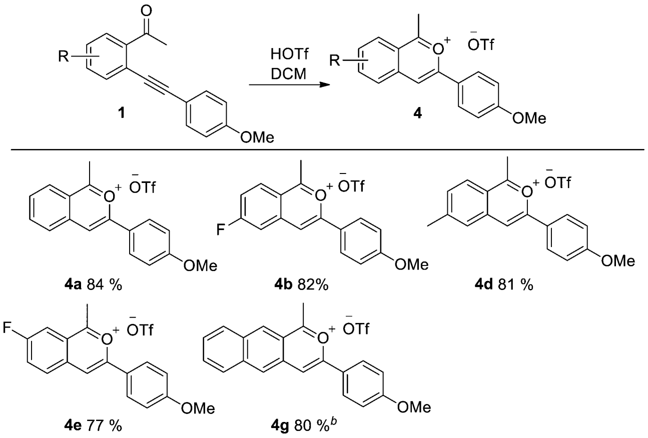
[a]Reaction conditions: **1** (0.3 mmol), **2c** (0.2 mmol), DCM (3.0 mL), 18 h. [b]Isolated yield of **3ac**.

Scheme 2. Scope of *o*-Alkynebenzaldehydes for the Synthesis of Chrysenes[a]



[a]Reaction conditions: **1a** (0.6 mmol), **2** (0.4 mmol), HOTf (0.64 mmol), DCM (5 mL), 10−30 °C, 18 h, isolated yield of **3**.

Scheme 4. Synthesis of Isochromenylium Salts[a]



[a]Reaction conditions: **1** (1 mmol), HOTf (1.2 mmol), DCM (3 mL), 5 °C, 30 min. [b]HOTf (2 mmol).

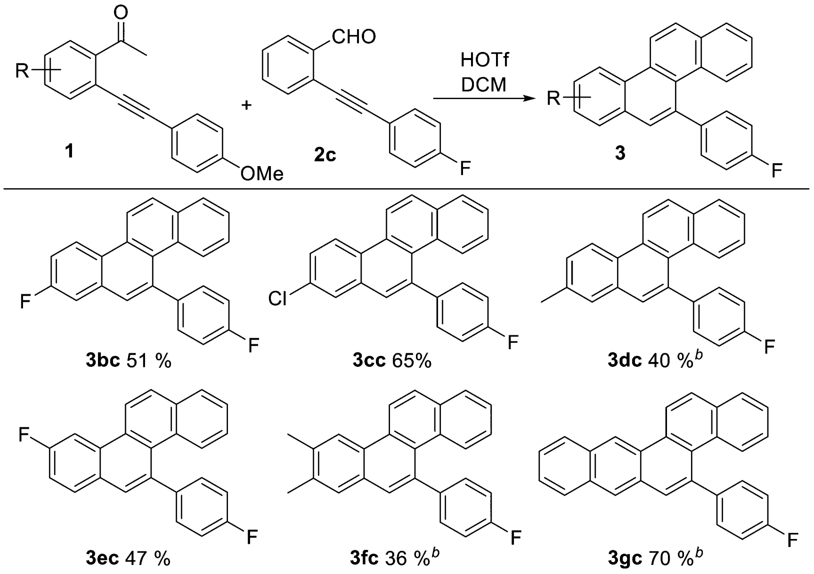
resulted in decline of yield (Table 1, entry 8). In addition, the changes of the amount of HOTf led to slight decrease of yields (Table 1, entries 9−10). Although the use of HBF_4 also gave a fair yield of **3ac** (Table 1, entry 13), TFA and $MeSO_3H$ are inappropriate for the present transformation, indicating that both acid strength and anion volume are crucial to effect the formation of **3ac** (Table 1, entries 11−12).

More importantly, in the cases of **3ac** formed, a compatible amount of 4-methoxylbenzoic acid could be obtained from the reaction mixture as byproduct, which is an important result to propose the mechanism for the formation of chrysene ring as shown in Scheme 5.

Under the optimized conditions as indicated in entry 6 of Table 1, the scope of the cross-coulping was investigated by using a variety of *o*-alkynylbenzaldehydes **2** with *o*-[2-(*para*-methoxyphenyl)alkynyl]acetophenone **1a**. As concluded in Scheme 2, substrate 2 bearing a terminal electron-rich substituent (e.g., R^1 = *p*-tolyl) or electron-withdrawing substituent (e.g., R^1 = Ph, *p*-FC_6H_4 or *p*-ClC_6H_4) underwent the cross-co with **1a** giving the corresponding chrysenes in moderate to good yields (Scheme 2, **3aa−ad**). Alternatively, the investigation on the effect of substituent (R^2) on the central phenyl ring disclosed that substrates **2** bearing the functional group at 5-position of the central phenyl ring afforded the corresponding chrysenes in a higher yield (Scheme 2, **3ah** vs **3al**, **3ai−ak** vs **3ae−ag**). In addition, the electron effect trend of substituents on the central phenyl ring of **2** was not observed.

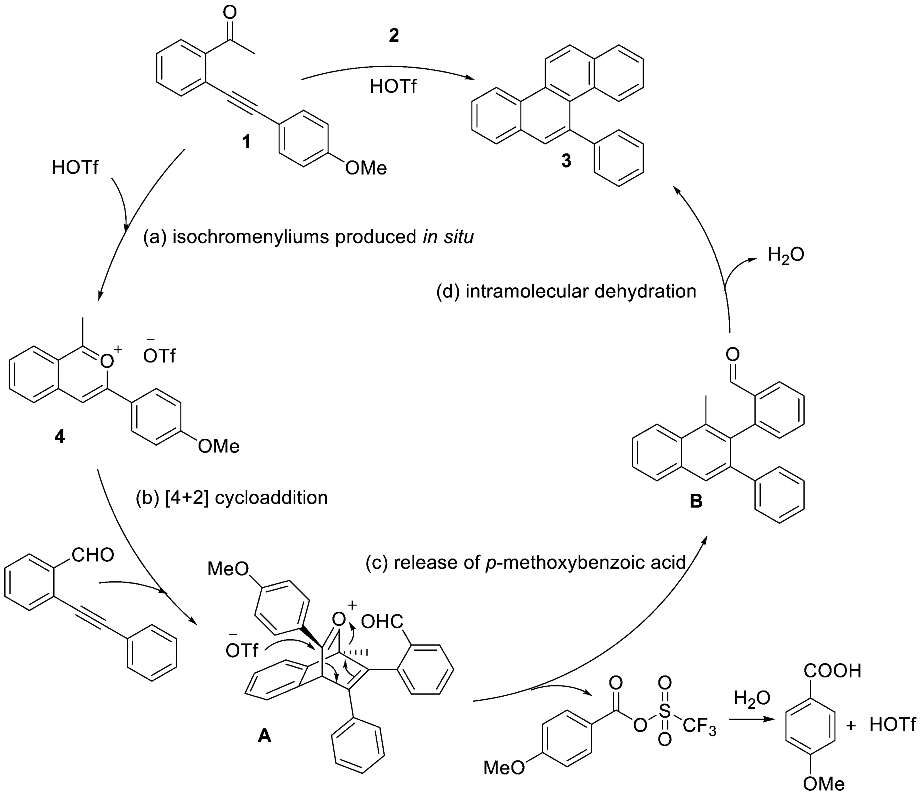
To our delight, 2- ethynylbenzaldehyde (**2m**) also performed the present cross-coupling with **1a** to form the naked chrysene

Scheme 3. Scope of *o*-Alkyneacetophenone for the Synthesis of Chrysenes[a]



[a]Reaction conditions: **1** (0.6 mmol), **2** (0.4 mmol), HOTf (0.64 mmol), DCM (5 mL), 30 °C. 18 h. [b]40 °C. 28 h.

Scheme 5. Proposed Mechanism

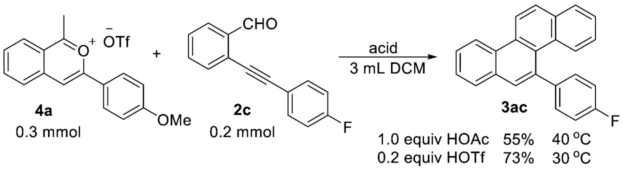


ring **3am** in 38% isolated yield under the similar reaction conditions. However, unfortunately, the reaction of **2** bearing a terminal alkyl substituent (e.g., $R^1 = n\text{-}C_4H_9$, **2n**) underwent side reaction, and the desired chrysene derivative was not obtained at all. Therefore, the present reaction system could not be extended to alkyl-substituted (R^1) 2-alkynylbenzaldehydes.

We also examined the scope of the cross-coulping of **1** having various R groups with **2c**. As summarized in Scheme 3, the reactions of substrates **1** bearing not only electron-withdrawing groups (e.g., R = F (**1b**, **1e**), Cl (**1c**) at 4- or 5-position), but also electron-donating groups (e.g., R = Me (**1d**, **1f**) at 4-position or at both 4- and 5-positions) on the central phenyl ring afforded the corresponding chrysene derivatives in moderate yields. Interestingly, the present transformation could be applied to *o*-alkynylacetonaphthone and the expected benzo[*b*]chrysene derivative (**3gc**) was obtained in 70% yield, when the reaction was performed with a higher temperature (40 °C) and in a prolonged time (28 h).

In order to confirm the present transformation occurring via the intermediate of isochromenylium, the reaction of **1a** with HOTf in DCM at 5 °C was examined, and the expected isochromenylium triflate **4a** was isolated as orange solid in 84% yield. The ^{1}H NMR and ^{13}C NMR spectroscopic data unambiguously indicated an identical isochromenylium structure with OTf^- anion confirmed by its ^{19}F NMR showing a typical signal at −79.7 ppm. In addition, we performed the reactions of **4a** with **2c** in the presence of HOTf or HOAc, and the expected **3ac** was obtained in 73% and 55% respectively eq 1. These results obviously demonstrated that isochromenylium **4a** was the key intermediate for the formation of chrysene ring.

In addition to the synthesis of **4a**, we also investigated the generality of other isochromenylium formation. It showed *p*-alkoxyphenyl was a good substituent to stabilize the isochromenylium. Not only substrates bearing alkyl was compatible for the formation of isochromenylium, but also substrates bearing an electron-withdrawing group fluorine could afford satisfactory yield (Scheme 4).



(1)

On the basis of the known isochromenylium chemistry and our experimental results, a plausible mechanism was proposed for the formation of chrysene ring as depicted in Scheme 5. It involves the formation of isochromenylium **4** promoted by HOTf, and the Asao−Yamamoto type [4 + 2] cycloaddition of **4** with o-alkynylbenzaldehydes **2** to give intermediate A, which undergoes the rearrangement reaction to give intermediate B with the release of *p*-methoxybenzoic acid, the final intramolecular dehydration constructs the chrysene ring.

In addition, it is interesting to know the optical properties of the synthesized chrysene derivatives **3** and isochromenylium triflates **4**. Therefore, some selected chrysene derivatives **3** and isochromenylium triflates **4** were analyzed by UV−vis and photoluminescence (PL) spectroscopy in solution. As shown in Figure 1, compared to naked chrysene **3m**, substituted chrysenes **3aa**, **3ak** and **3gc** have bathochromic shifts in both absorption and emission spectra to some extent. Their absorption maxima are observed within the range 260−326 nm, and their emission bands are within 360−450 nm. The UV−vis spectra of isochromenylium triflate **4a** and **4b** have high-intensity absorption between 330 and 350 nm and lower-intensity bands

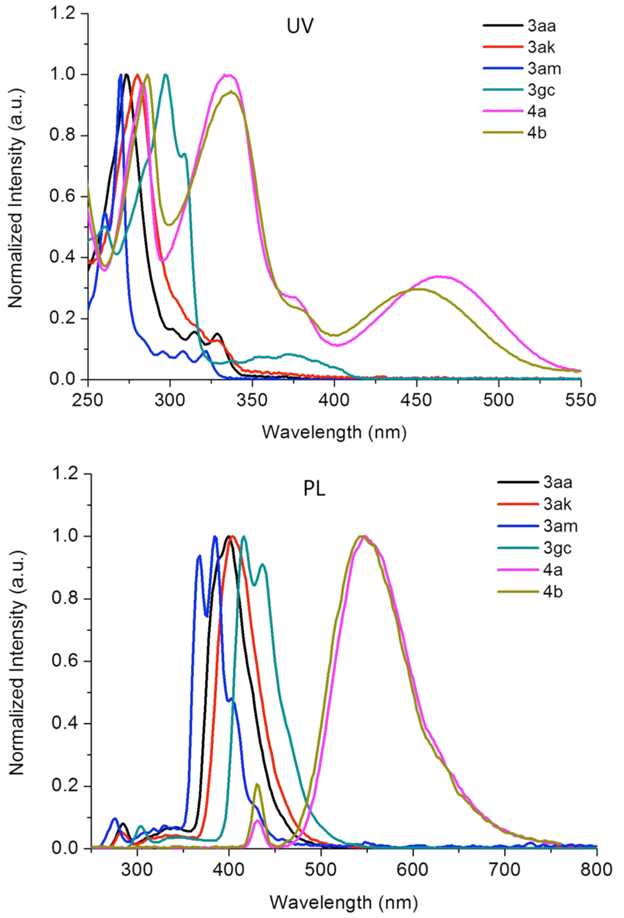


Figure 1. Normalized UV−vis and photoluminescence (PL) spectra of selected chrysene derivatives **3** and isochromenylium triflate **4** in DCM (1.0×10^{-5} M).

between 420 and 500 nm, and their emission maxima are observed within the range 540−560 nm.

■ CONCLUSION

In conclusion, we have developed a new synthetic method access to chrysene derivatives in moderate to good yields by a simple one-pot cross-coulping of *o*-alkynylacetophenones and *o*-alkynylbenzaldehydes in the presence of TfOH with high chemoselectivity. On the basis of the controlled experimental results, the formation of chrysene ring is proposed including the formation of isochromenylium triflate as the key intermediates.

■ EXPERIMENTAL SECTION

General Methods. All commercial reagents are analytically pure and used without further purification. Nuclear magnetic resonance (NMR) spectra were recorded using $CDCl_3$ as solvent at 298 K. ^{1}H NMR (400 MHz) chemical shifts (δ) were referenced to internal standard TMS (for ^{1}H, δ = 0.00 ppm). ^{13}C NMR (101 MHz) chemical shifts were referenced to internal solvent $CDCl_3$ (for ^{13}C, δ = 77.16 ppm). HRMS experiments were performed on a high resolution magnetic sector mass spectrometer. The melting points are uncorrected.

*Typical Experimental Procedure for Synthesis of **1a**.* To a 50 mL tube equipped with a magnetic stirrer, 2-bromoacetophenone (1990.0 mg, 10.0 mmol), $Pd(PPh_3)_2Cl_2$ (70.1 mg, 0.1 mmol), CuI (38.1 mg, 0.2 mmol), NEt_3 (20 mL), THF (10 mL), and 4-methoxyphenylacetylene (1980.0 mg, 15 mmol) were added sequentially under N_2 atmosphere. The tube was sealed and stirred at 90 °C in an oil bath for 24 h. After removal of the solvent under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 100:0 to 98:5) as eluent to afford 2-(4-methoxyphenylethynyl)acetophenone **1a** in 80% yield (2000.0 mg).

o-Alkynylbenzaldehydes were prepared under the similar procedure by the cross-coupling reactions of 2-bromobenzaldehydes with terminal aryl acetylenes.

*Typical Experimental Procedure for Synthesis of **3ac**.* To a 25 mL tube equipped with a magnetic stirrer, **1a** (150.0 mg, 0.6 mmol), DCM (3 mL) and **2c** (90.0 mg, 0.4 mmol) were added sequentially at 0−5 °C in an ice bath, and then HOTf (0.056 mL, 0.64 mmol) was slowly added with a pipet. Kept the reaction mixture at 5 °C and stirred for 20 min. The tube was then sealed and stirred at 30 °C in an oil bath for 18 h. After removal of the solvent under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/DCM (gradient mixture ratio from 100:0 to 98:2) as eluent to afford 5-(4-fluorophenyl)chrysene **3ac** in 90% yield (87.0 mg).

*Typical Experimental Procedure for Synthesis of **4a**.* To a solution of **1a** (250.0 mg, 1.0 mmol) in DCM (3 mL) was added HOTf (0.105 mL, 1.2 mmol) at 0−5 °C in an ice bath. The solution was stirred at 0−5 °C for 30 min. The solids were collected by simple filtration, washed with ether and dried under a vacuum, affording the pure orange solid 3-(4-methoxyphenyl)-1-methylisochromenylium trifluoromethanesulfonate **4a** in 84% yield (336.0 mg).

Characterization Data of the Chrysene Derivatives. *5-Phenylchrysene (**3aa**).* White solid (60%, 73.0 mg); mp 182−184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, J = 8.8 Hz, 2H), 8.04 (d, J = 8.9 Hz, 1H), 7.98−7.96 (m, 2H), 7.89 (s, 1H), 7.87 (d, J = 8.9 Hz, 1H), 7.73 (dd ≈ t, J = 7.3 Hz, 1H), 7.67 (dd ≈ t, J = 7.3 Hz, 1H), 7.50 (m, 6H), 7.18 (dd ≈ t, J = 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 138.5, 133.5, 131.6, 131.0, 130.7, 130.2, 130.1, 129.1, 129.0, 128.9, 128.5, 128.3, 128.2, 127.5, 127.1, 126.9, 126.8, 125.9, 124.7, 123.2, 121.4; HRMS (APPI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{24}H_{17}$ 305.1325, found 305.1315.

*5-(p-Tolyl)chrysene (**3ab**).* White solid (56%, 71.0 mg); mp 156−158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 8.9 Hz, 2H), 7.96−7.83 (m, 4H), 7.82−7.77 (m, 1H), 7.61 (m, 2H), 7.43 (m, 1H), 7.33 (m, 2H), 7.25 (d, J = 7.8 Hz, 2H), 7.14 (m, 1H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 138.5, 136.7, 133.4, 131.6, 131.0, 130.8, 130.1, 130.0, 129.7, 129.0, 128.4, 128.2, 128.1, 127.6, 126.8, 126.7, 125.8, 124.6, 123.2, 121.3, 21.4; HRMS (APPI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{25}H_{19}$ 319.1481, found 319.1472.

*5-(4-Fluorophenyl)chrysene (**3ac**).* White solid (68%, 87.0 mg); mp 198−200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, J = 8.9 Hz, 2H), 8.02 (d, J = 8.8 Hz, 1H), 7.97−7.92 (m, 2H), 7.81 (s, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.72 (m, 1H), 7.66 (m, 1H), 7.51−7.41 (m, 3H), 7.22−7.14 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, $J\,^1{}_{C-F}$ = 246.0 Hz), 141.6 (d, $J\,^4{}_{C-F}$ = 3.4 Hz), 137.4, 133.5, 131.5, 131.1, 130.7 (d, $J\,^3{}_{C-F}$ = 7.8 Hz), 130.6, 130.2, 130.1, 128.7, 128.48, 128.4, 128.3, 127.5, 127.0, 126.9, 126.0, 124.8, 123.3, 121.4, 116.0 (d, $J\,^2{}_{C-F}$ = 21.5 Hz); HRMS (APPI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{24}H_{16}F$ 323.1230, found 323.1237.

*5-(4-Chlorophenyl)chrysene (**3ad**).* White solid (65%, 88.0 mg); mp 154−156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 8.8 Hz, 2H), 8.01 (d, J = 8.8 Hz, 1H), 7.95 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.8 Hz, 1H), 7.80 (s, 1H), 7.72 (t, J = 7.2 Hz, 1H), 7.66 (m, 1H), 7.52 (d, J = 7.2 Hz, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.23 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 137.1, 133.5, 133.1, 131.4, 131.0, 130.4, 130.39, 130.2, 130.2, 129.2, 128.8, 128.5, 128.4, 128.3, 127.2, 127.0, 126.96, 126.0, 124.8, 123.2, 121.3; HRMS (APPI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{24}H_{16}Cl$ 339.0935, found 339.0925.

*3-Chloro-5-phenylchrysene (**3ae**).* White solid (53%, 72.0 mg); mp 172−176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 7.8 Hz, 1H), 8.72 (d, J = 8.9 Hz, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.92 (d, J = 8.9 Hz, 1H), 7.86 (s, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.75−7.64 (m, 3H), 7.55−7.53 (m, 2H), 7.47−7.44 (m, 1H), 7.41 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 138.3, 131.7, 131.6, 131.5, 131.0, 130.6, 130.5, 130.0, 129.5, 129.2, 129.0, 128.5, 128.4, 127.5, 127.48, 127.2, 127.0, 126.6, 126.4, 123.3, 121.6; HRMS (APPI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{24}H_{16}Cl$ 339.0935, found 339.0927.

*3-Methyl-5-phenylchrysene (**3af**).* White solid (54%, 68.0 mg); mp 160−162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, J = 8.2 Hz, 1H), 8.61 (d, J = 8.9 Hz, 1H), 7.90−7.85 (m, 2H), 7.78 (s, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.61 (dd, J = 7.0, 1.5 Hz, 1H), 7.55 (dd, J = 7.0, 1.5 Hz, 1H), 7.45 (s, 1H), 7.42 (m, 5H), 7.23 (dd, J = 8.1, 1.2 Hz, 1H), 2.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 138.6, 134.1, 131.5, 131.5, 130.7, 130.5, 130.2, 130.2, 129.2, 129.0, 128.9, 128.4, 128.0, 127.9, 127.6, 127.2, 127.0, 126.8, 126.7, 123.3, 120.4, 22.1; HRMS (APPI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{25}H_{19}$ 319.1481, found 319.1470.

*3-Methoxy-5-phenylchrysene (**3ag**).* White solid (43%, 57.0 mg); mp 192−196 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 8.3 Hz, 1H), 8.66 (d, J = 8.8 Hz, 1H), 7.98−7.93 (m, 2H), 7.82 (d, J = 8.8 Hz, 1H), 7.80 (s, 1H), 7.74−7.68 (m, 1H), 7.66−7.62 (m, 1H), 7.55−7.48 (m, 4H), 7.42 (m, 1H), 7.37 (d, J = 2.3 Hz, 1H), 7.11 (dd, J = 8.7, 2.5 Hz, 1H), 3.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 146.1, 138.5, 131.9, 131.5, 130.6, 130.3, 129.6, 129.4, 129.2, 128.5, 128.3, 127.8, 127.0, 126.9, 126.8, 126.7, 123.4, 119.1, 117.9, 109.2, 54.4; HRMS (APPI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{25}H_{19}O$ 335.1430, found 335.1421.

*2-Fluoro-5-phenylchrysene (**3ah**).* White solid (73%, 94.0 mg); mp 178−180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, J = 9.1 Hz, 1H), 8.74 (d, J = 8.4 Hz, 1H), 7.96 (m, 1H), 7.92 (d, J = 9.1 Hz, 1H), 7.86 (s, 1H), 7.80 (m, 1H), 7.73−7.69 (m, 1H), 7.69−7.63 (m, 1H), 7.54 (m, 1H), 7.52−7.43 (m, 5H), 6.90 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4 (d, $J\,^{1}{}_{C-F}$ = 247.4 Hz), 145.4, 138.1, 134.9 (d, $J\,^{3}{}_{C-F}$ = 8.7 Hz), 131.3 (d, $J\,^{3}{}_{C-F}$ = 8.8 Hz), 131.2, 130.1, 129.5, 129.2, 129.1, 128.5, 127.6, 127.4 (d, $J\,^{4}{}_{C-F}$ = 3.5 Hz), 127.3, 127.0, 126.9, 123.1, 122.6, 114.1, 113.8, 113.9 (d, $J\,^{2}{}_{C-F}$ = 23.2 Hz), 111.7 (d, $J\,^{2}{}_{C-F}$ = 20.0 Hz); HRMS (APPI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{24}H_{16}F$ 323.123, found 323.1235.

*2-Chloro-5-phenylchrysene(**3ai**).* White solid (62%, 84.0 mg); mp 164−166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 9.2 Hz, 1H), 8.73 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 7.5 Hz, 1H), 7.88 (m, 1H), 7.86 (d, J = 9.5 Hz, 2H), 7.74−7.62 (m, 3H), 7.53−7.42 (m, 5H), 7.07 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 138.2, 134.5, 131.6, 131.6, 131.3, 130.4, 130.0, 129.2, 129.1, 129.0, 128.5, 137.4, 127.3, 127.1, 127.0, 126.9, 125.2, 123.2, 122.6; HRMS (APPI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{24}H_{16}Cl$ 339.0935, found 339.0924.

*2-Methyl-5-phenylchrysene (**3aj**).* White solid (76%, 96.0 mg); mp 142−144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (m, 2H), 7.83 (t, J = 9.2 Hz, 2H), 7.75 (s, 1H), 7.65−7.57 (m, 3H), 7.53 (t, J = 7.3 Hz, 1H), 7.39 (m, 5H), 6.91 (d, J = 8.8 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 138.4, 135.5, 133.7, 131.4, 130.8, 130.2, 129.6, 129.1, 129.0, 128.7, 128.6, 128.5, 127.8, 127.7, 127.5, 127.0, 126.7, 126.68, 126.6, 123.1, 121.3, 21.3; HRMS (APPI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{25}H_{19}$ 319.1481, found 319.1473.

*2-Methoxy-5-phenylchrysene (**3ak**).* White solid (51%, 68.0 mg); mp 192−196 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 9.2 Hz, 2H), 7.96−7.91 (m, 2H), 7.83 (s, 1H), 7.73−7.67 (m, 2H), 7.66−7.60 (m, 1H), 7.53−7.43 (m, 5H), 7.28 (d, J = 2.8 Hz, 1H), 6.80 (dd, J = 9.5, 2.8 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 145.7, 138.2, 135.1, 131.2, 131.0, 130.4, 130.3, 129.1, 129.0, 128.7, 128., 49 127.8, 127.6, 127.1, 126.8, 126.5, 125.3, 123.0, 121.9, 115.7, 107.6, 55.4; HRMS (APPI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{25}H_{19}O$ 335.1430, found 335.1418.

*1-Fluoro-5-phenylchrysene (**3al**).* White solid (49%, 63.0 mg); mp 124−126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, J = 9.3 Hz, 1H), 8.78 (d, J = 8.3 Hz, 1H), 8.34 (d, J = 9.3 Hz, 1H), 7.96 (dd, J = 7.9, 1.1 Hz, 1H), 7.87 (s, 1H), 7.74−7.70 (m, 1H), 7.70−7.63 (m, 1H), 7.58 (d, J = 8.7 Hz, 1H), 7.54−7.43 (m, 5H), 7.18−7.12 (m, 1H), 7.09−7.02 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8 (d, $J\,^{1}{}_{C-F}$ = 249.1 Hz), 145.4, 138.4, 132.3 (d, $J\,^{4}{}_{C-F}$ = 3.6 Hz), 131.7, 131.4, 130.4, 130.0, 129.1, 129.0, 128.5, 127.2, 127.0, 124.82, 124.78, 124.4 (d, $J\,^{3}{}_{C-F}$ = 8.6 Hz), 123.3, 123.2 (d, $J\,^{2}{}_{C-F}$ = 15.5 Hz), 121.9, 119.8 (d, $J\,^{3}{}_{C-F}$ = 7.9 Hz), 109.90 (d, $J\,^{2}{}_{C-F}$ = 19.9 Hz); HRMS (APPI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{24}H_{16}F$ 323.123, found 323.1237.

*Chrysene (**3am**).* White solid (38%, 35.0 mg); mp 140−144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, J = 8.4 Hz, 2H), 8.74 (d, J = 8.8 Hz, 2H), 8.02 (d, J = 8.8 Hz, 2H), 8.01 (d, J = 8.4 Hz, 2H), 7.75−7.69 (m, 2H), 7.67−7.62 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.3, 130.7, 128.7, 128.4, 127.5, 126.8, 126.5, 123.3, 121.4; HRMS (APPI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{18}H_{13}$ 229.1012, found 229.1003.

*2-Fluoro-11-(4-fluorophenyl)chrysene (**3bc**).* White solid (51%, 69.0 mg); mp 146−148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 9.2 Hz, 1H), 8.68 (d, J = 9.2 Hz, 1H), 8.63 (d, J = 9.1 Hz, 1H), 7.99 (d, J = 9.1 Hz, 1H), 7.93(dd ≈ t, J = 7.3 Hz, 1H), 7.74 (dd ≈ t, J = 8.7 Hz, 1H), 7.69 (s, 1H), 7.54−7.36 (m, 5H), 7.22−7.14 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ162.4 (d, $J\,^{1}{}_{C-F}$= 246.5 Hz), 161.5 (d, $J\,^{1}{}_{C-F}$ = 247.2 Hz), 141.2 (d, $J\,^{4}{}_{C-F}$ = 3.3 Hz), 138.7, 133.3, 132.7 (d, $J\,^{3}{}_{C-F}$ = 8.8 Hz), 130.6, 130.5, 130.5, 130.2, 130.1 (d, $J\,^{4}{}_{C-F}$ = 3.9 Hz), 128.7, 128.6, 128.4, 126.9 (d, $J\,^{3}{}_{C-F}$ = 8.7 Hz), 126.0, 125.8 (d, $J\,^{3}{}_{C-F}$ = 8.8 Hz), 125.0, 121.1, 116.3 (d, $J\,^{2}{}_{C-F}$ = 25.2 Hz), 116.0 (d, $J\,^{2}{}_{C-F}$ = 21.8 Hz), 111.9 (d, $J\,^{2}{}_{C-F}$ = 20.2 Hz); HRMS (APPI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{24}H_{15}F_2$ 341.1136, found 341.1144.

*2-Chloro-11-(4-fluorophenyl)chrysene (**3cc**).* White solid (65%, 92.0 mg); mp 186−188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 9.0 Hz, 1H), 8.51 (d, J = 9.0 Hz, 1H), 7.91 (d, J = 9.0 Hz, 1H), 7.88−7.83 (m, 1H), 7.78 (d, J = 2.2 Hz, 1H), 7.67 (d, J = 8.7 Hz, 1H), 7.56 (s, 1H), 7.52 (dd, J = 9.0, 2.2 Hz, 1H), 7.46−7.40 (m, 1H), 7.33−7.27 (m, 2H), 7.16−7.07 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (d, $J\,^{1}{}_{C-F}$ = 246.6 Hz), 141.1 (d, $J\,^{4}{}_{C-F}$ = 3.5 Hz), 138.6, 133.5, 132.7, 132.3, 130.6 (d, $J\,^{3}{}_{C-F}$ = 7.9 Hz), 130.4, 129.9, 129.8, 128.7, 128.5, 128.4, 127.4, 127.1, 126.1, 126.0, 125.0, 121.0, 116.0 (d, $J\,^{2}{}_{C-F}$ = 21.5 Hz); HRMS (APPI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{24}H_{15}ClF$ 357.0840, found 357.0829.

*2-Methyl-11-(4-fluorophenyl)chrysene (**3dc**).* White solid (40%, 54.0 mg); mp 192−194 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 9.0 Hz, 1H), 8.61 (d, J = 8.6 Hz, 1H), 7.96 (d, J = 9.0 Hz, 1H), 7.89 (d, J = 7.9 Hz, 1H), 7.72 (d, J = 8.7 Hz, 1H), 7.68 (d, J = 5.9 Hz, 2H), 7.50 (dd, J = 8.6, 1.5 Hz, 1H), 7.45−7.35 (m, 3H), 7.18−7.08 (m, 3H), 2.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, $J\,^{1}{}_{C-F}$ = 246.0 Hz), 141.7 (d, $J\,^{4}{}_{C-F}$ = 3.3 Hz), 137.4, 136.8, 133.4, 131.7, 130.8, 130.7 (d, $J\,^{3}{}_{C-F}$ = 7.7 Hz), 130.6, 130.2, 129.0, 128.7, 128.4, 128.23, 128.19, 127.8, 126.9, 125.7, 124.7, 123.2, 121.4, 116.0 (d, $J\,^{2}{}_{C-F}$ = 21.2 Hz). 21.6; HRMS (APPI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{25}H_{18}F$ 337.1387, found 337.1390.

*3-Fluoro-11-(4-fluorophenyl)chrysene (**3ec**).* White solid (47%, 64.0 mg); mp 186−188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 9.0 Hz, 1H), 8.34 (m, 1H), 7.99 (d, J = 9.0 Hz, 1H), 7.93 (t, J = 8.4 Hz, 1H), 7.89 (d, J = 6.0 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.76 (s, 1H), 7.49 (dd ≈ t, J = 7.4 Hz, 1H), 7.39 (m, 3H), 7.18 m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, $J\,^{1}{}_{C-F}$ = 246.4 Hz), 161.8 (d, $J\,^{1}{}_{C-F}$ = 245.5 Hz), 141.4 (d, $J\,^{4}{}_{C-F}$ = 3.3 Hz), 136.7, 133.7, 131.5 (d, $J\,^{3}{}_{C-F}$ = 8.5 Hz), 130.6 (d, $J\,^{3}{}_{C-F}$ = 8.1 Hz), 130.5, 130.4, 129.5 (d, $J\,^{4}{}_{C-F}$ = 4.7 Hz), 128.8, 128.4 (d, $J\,^{3}{}_{C-F}$ = 7.4 Hz), 128.3, 128.0, 126.3, 124.9, 121.3, 116.5 (d, $J\,^{2}{}_{C-F}$ = 24.4 Hz), 116.0 (d, $J\,^{2}{}_{C-F}$ = 21.4 Hz), 108.0 (d, $J\,^{2}{}_{C-F}$ = 22.5 Hz); HRMS (APPI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{24}H_{15}F_2$ 341.1136, found 341.1142.

*11-(4-Fluorophenyl)-2,3-dimethylchrysene (**3 fc**).* White solid (36%, 50.0 mg); mp 200−202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, J = 9.1 Hz, 1H), 8.51 (s, 1H), 7.98 (d, J = 9.1 Hz, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.70 (s, 1H), 7.68 (s, 1H), 7.50−7.39 (m, 3H), 7.49−7.38 (m, 3H), 7.22−7.13 (m, 3H), 7.22−7.13 (m, 3H), 2.59 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, J = 245.7 Hz), 141.9 (d, J = 3.5 Hz), 136.6, 136.5, 133.3, 130.7 (d, J = 7.6 Hz), 130.6, 130.5, 130.2, 129.7, 128.8, 128.7, 128.4, 128.3, 127.9, 126.9, 125.6, 124.6, 123.3, 121.4, 115.9 (d, J = 21.2 Hz), 21.0, 20.1; HRMS (APPI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{26}H_{20}F$ 351.1543, found 351.1534.

*5-(4-Fluorophenyl)benzo[c]tetraphene (**3gc**).* White solid (70%, 1040.0 mg); mp 198−200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.83 (d, J = 9.0 Hz, 1H), 8.33 (s, 1H), 8.12−8.07 (m, 1H), 7.99 (dd, J = 9.3, 2.7 Hz, 2H), 7.90 (d, J = 7.6 Hz, 1H), 7.77 (s, 1H), 7.69 (d, J = 8.7 Hz, 1H), 7.55−7.48 (m, 2H), 7.46−7.41 (m, 1H), 7.40−7.33 (m, 2H), 7.18−7.08 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, $J\,^{1}{}_{C-F}$ = 246.1 Hz), 141.5 (d, $J\,^{4}{}_{C-F}$ = 3.1 Hz), 137.1, 133.7, 132.2, 131.3, 130.5, 130.5 (d, $J\,^{3}{}_{C-F}$ = 7.5 Hz), 130.3, 130.0, 128.83, 128.8, 128.7, 128.4, 127.8, 127.3, 126.7, 126.1, 125.9, 125.8, 124.7, 122.3, 121.5, 115.9 (d, $J\,^{2}{}_{C-F}$ = 21.4 Hz); HRMS (APPI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{28}H_{18}F$ 373.1387, found 373.1375.

*3-(4-Methoxyphenyl)-1-methylisochromenylium trifluoromethanesulfonate (**4a**).* Orange solid (84%, 336.0 mg); mp 150−154 °C; ^{1}H

NMR (400 MHz, $CDCl_3$, a drop of CF_3COOH) δ 8.48 (d, $J = 8.6$ Hz, 1H), 8.37 (s, 1H), 8.29−8.23 (m, 1H), 8.12 (d, $J = 8.3$ Hz, 1H), 8.04 (d, $J = 8.9$ Hz, 2H), 7.96−7.89 (m, 1H), 7.07 (d, $J = 8.9$ Hz, 2H), 3.89 (s, 3H), 3.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, a drop of CF_3COOH) δ 185.4, 164.2, 162.4, 143.54, 143.1, 132.3, 130.4, 128.9, 128.3, 123.4, 120.7, δ 119.9 (q, $J\,^{1}{}_{C-F} = 318.2$ Hz), 115.6, 113.5, 55.8, 20.7; ^{19}F NMR (565 MHz, $CDCl_3$, a drop of CF_3COOH as internal standard) δ −79.7. HRMS (ESI-TOF) m/z $[M - OTf]^+$ calcd for $C_{17}H_{15}O_2$ 251.1067, found 251.1068.

*6-Fluoro-3-(4-methoxyphenyl)-1-methylisochromenylium trifluoromethanesulfonate (**4b**).* Orange solid (82%, 343.0 mg); mp 160−164 °C; ^1H NMR (400 MHz, $CDCl_3$, a drop of CF_3COOH) δ 8.60 (m, 1H), 8.30 (s, 1H), 8.02 (d, $J = 8.9$ Hz, 2H), 7.69 (dd, $J = 8.3$, 2.2 Hz, 1H), 7.63 (m, 1H), 7.06 (d, $J = 8.9$ Hz, 2H), 3.89 (s, 3H), 3.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, a drop of CF_3COOH) δ 184.7, 171.4 (d, $J\,^{1}{}_{C-F} = 276.0$ Hz), 164.4, 162.6, 146.4 (d, $J\,^{3}{}_{C-F} = 15.1$ Hz), 135.4 (d, $J\,^{3}{}_{C-F} = 12.9$ Hz), 129.1, 123.3 (d, $J\,^{2}{}_{C-F} = 26.2$ Hz), 120.9, 120.3, 119.8 (q, $J\,^{1}{}_{C-F} = 318.2$ Hz), 115.6, 112.6, 112.5 (d, $J\,^{2}{}_{C-F} = 19.6$ Hz), 55.8, 20.7; HRMS (ESI-TOF) m/z $[M - OTf]^+$ calcd for $C_{17}H_{14}FO_2$ 269.0972, found 269.0976.

*3-(4-Methoxyphenyl)-1,6-dimethylisochromenylium trifluoromethanesulfonate (**4d**).* Orange solid (81%, 335.0 mg); mp 150−154 °C; ^1H NMR (400 MHz, $CDCl_3$, a drop of CF_3COOH) δ 8.37 (d, $J = 8.8$ Hz, 1H), 8.21 (s, 1H), 8.02 (d, $J = 8.9$ Hz, 2H), 7.89 (s, 1H), 7.77 (d, $J = 8.8$ Hz, 1H), 7.10 (d, $J = 8.9$ Hz, 2H), 3.91 (s, 3H), 3.44 (s, 3H), 2.71 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, a drop of CF_3COOH) δ 183.7, 164.1, 162.2, 158.3, 143.2, 134.8, 130.1, 128.7, 127.2, 121.8, 120.9, 119.8 (q, $J\,^{1}{}_{C-F} = 317.9$ Hz), 115.6, 112.4, 55.8, 23.5, 20.3; HRMS (ESI-TOF) m/z $[M - OTf]^+$ calcd for $C_{18}H_{17}O_2$ 265.1223, found 265.1224.

*7-Fluoro-3-(4-methoxyphenyl)-1-methylisochromenylium trifluoromethanesulfonate (**4e**).* Orange solid (77%, 322.0 mg); mp 154−156 °C; ^1H NMR (400 MHz, $CDCl_3$, a drop of CF_3COOH) δ 8.44 (s, 1H), 8.23−8.15 (m, 1H), 8.07−7.95 (m, 4H), 7.07 (d, $J = 8.9$ Hz, 2H), 3.89 (s, 3H), 3.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, a drop of CF_3COOH) δ 184.4 (d, $J\,^{4}{}_{C-F} = 6.8$ Hz), 164.4, 162.9, 162.8 (d, $J\,^{1}{}_{C-F} = 260.3$ Hz), 141.0, 134.1 (d, $J\,^{2}{}_{C-F} = 26.3$ Hz), 131.7 (d, $J\,^{3}{}_{C-F} = 8.9$ Hz), 129.0, 124.6 (d, $J\,^{3}{}_{C-F} = 10.1$ Hz), 120.5, 119.8 (d, $J\,^{1}{}_{C-F} = 318.2$ Hz), 115.7, 113.8, 112.7 (d, $J\,^{2}{}_{C-F} = 23.8$ Hz), 55.8, 20.9; HRMS (ESI-TOF) m/z $[M - OTf]^+$ calcd for $C_{17}H_{14}FO_2$ 269.0972, found 269.0976.

*3-(4-Methoxyphenyl)-1-methylbenzo[g]isochromen-2-ium trifluoromethanesulfonate (**4g**).* Atropurpureus solid (80%, 360.0 mg); mp 132−134 °C; ^1H NMR (400 MHz, $CDCl_3$, a drop of CF_3COOH) δ 9.38 (s, 1H), 8.49 (s, 1H), 8.24 (m, 2H), 8.07 (d, $J = 8.6$ Hz, 1H), 7.95 (d, $J = 8.9$ Hz, 2H), 7.92−7.84 (m, 1H), 7.76−7.68 (m, 1H), 7.06 (d, $J = 8.9$ Hz, 2H), 3.87 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, a drop of CF_3COOH) δ 190.4, 163.1, 157.7, 142.1, 136.6, 135.6, 134.3, 133.2, 131.5, 129.8, 128.6, 127.9, 126.7, 121.1, 120.4, 119.8 (d, $J\,^{1}{}_{C-F} = 317.8$ Hz), 115.5, 111.7, 55.7, 21.6; HRMS (ESI-TOF) m/z $[M - OTf]^+$ calcd for $C_{21}H_{17}O_2$ 301.1223, found 301.1225.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^1H and ^{13}C NMR charts of all products and X-ray structural details of **3ac**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01219.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ruimao@mail.tsinghua.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This project was supported by National Natural Science Foundation of China (21473097, 21273125).

■ REFERENCES

(1) (a) Asao, N.; Takahashi, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **2002**, *124*, 12650. (b) Asao, N.; Nogami, T.; Lee, S.; Yamamoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 10921. (c) Asao, N.; Aikawa, H.; Yamamoto, Y. *J. Am. Chem. Soc.* **2004**, *126*, 7458. (d) Dyker, G.; Hildebrandt, D.; Liu, J. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4399. (e) Kim, N.; Kim, Y.; Park, W.; Sung, D.; Gupta, A. K.; Oh, C. H. *Org. Lett.* **2005**, *7*, 5289.

(2) (a) Asao, N.; Takahashi, K.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2003**, *42*, 3504. (b) Patil, N. T.; Yamamoto, Y. *J. Org. Chem.* **2004**, *69*, 5139.

(3) (a) Asao, N.; Nogami, T.; Takahashi, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **2002**, *124*, 764. (b) Nakamura, H.; Ohtaka, M.; Yamamoto, Y. *Tetrahedron Lett.* **2002**, *43*, 7631. (c) Mondal, S.; Nogami, T.; Asao, N.; Yamamoto, Y. *J. Org. Chem.* **2003**, *68*, 9496.

(4) (a) Maeyama, K.; Iwasawa, N. *J. Am. Chem. Soc.* **1998**, *120*, 1928. (b) Iwasawa, N.; Shido, M.; Maeyama, K.; Kusama, H. *J. Am. Chem. Soc.* **2000**, *122*, 10226. (c) Iwasawa, N.; Shido, M.; Kusama, H. *J. Am. Chem. Soc.* **2001**, *123*, 5814. (d) Kusama, H.; Funami, H.; Shido, M.; Iwasawa, N. *J. Am. Chem. Soc.* **2005**, *127*, 2709.

(5) (a) Kusama, H.; Funami, H.; Takaya, J.; Iwasawa, N. *Org. Lett.* **2004**, *6*, 605. (b) Bruneau, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 2328. (c) Hildebrandt, D.; Hüggenberg, W.; Kanthak, M.; Dyker, G. *Chem. Commun.* **2006**, 2260. (d) Kusama, H.; Ishida, K.; Funami, H.; Iwasawa, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 4903.

(6) (a) Barluenga, J.; Vázquez-Villa, H.; Ballesteros, A.; González, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 9028. (b) Barluenga, J.; Vázquez-Villa, H.; Ballesteros, A.; González, J. M. *Adv. Synth. Catal.* **2005**, *347*, 526. (c) Barluenga, J.; Vázquez-Villa, H.; Merino, I.; Ballesteros, A.; González, J. M. *Chem. - Eur. J.* **2006**, *12*, 5790.

(7) (a) Yue, D.; Cá, N. D.; Larock, R. C. *Org. Lett.* **2004**, *6*, 1581. (b) Yue, D.; Cá, N. D.; Larock, R. C. *J. Org. Chem.* **2006**, *71*, 3381.

(8) Kim, J. H.; Ray, D.; Hong, C. S.; Hana, J. W.; Oh, C. H. *Chem. Commun.* **2013**, *49*, 5690.

(9) (a) Tovar, J. D.; Swager, T. M. *J. Org. Chem.* **1999**, *64*, 6499. (b) Sato, K.; Menggenbateer; Kubota, T.; Asao, N. *Tetrahedron* **2008**, *64*, 787.

(10) (a) Hu, Z.-L.; Qian, W.-J.; Wang, S.; Yao, Z.-J. *J. Org. Chem.* **2009**, *74*, 8787. (b) Hu, Z.-L.; Qian, W.-J.; Wang, S.; Yao, Z.-J. *Org. Lett.* **2009**, *11*, 4676. (c) Hu, Z.-L.; Yang, Z.-Y.; Wang, S.; Yao, Z.-J. *Chem. - Eur. J.* **2011**, *17*, 1268. (d) Zhang, H.; Cui, W.-C.; Hu, Z.-L.; Yang, Z.-Y.; Wang, S.; Yao, Z.-J. *RSC Adv.* **2012**, *2*, 5101.

(11) (a) Okamoto, H.; Kawasaki, N.; Kaji, Y.; Kubozono, Y.; Fujiwara, A.; Yamaji, M. *J. Am. Chem. Soc.* **2008**, *130*, 10470. (b) Kunugi, Y.; Ikari, M.; Okamoto, K. *ECS Trans.* **2010**, *25*, 11. (c) Shinamura, S.; Osaka, I.; Miyazaki, E.; Nakao, A.; Yamagishi, M.; Takeya, J.; Takimiya, K. *J. Am. Chem. Soc.* **2011**, *133*, 5024. (d) Kunugi, Y.; Arai, T.; Kobayashi, N.; Otsuki, H.; Nishinaga, T.; Okamoto, K. J. *J. Photopolym. Sci. Technol.* **2011**, *24*, 345.

(12) (a) Ionkin, A. S.; Marshall, W. J.; Fish, B. M.; Bryman, L. M.; Wang, Y. *Chem. Commun.* **2008**, 2319. (b) Wu, T.-L.; Chou, H.-H.; Huang, P.-Y.; Cheng, C.-H.; Liu, R.-S. *J. Org. Chem.* **2014**, *79*, 267.

(13) (a) Leznoff, C. C.; Hayward, R. J. *Can. J. Chem.* **1972**, *50*, 528. (b) Nagel, D. L.; Kupper, R.; Antonson, K.; Wallcave, L. *J. Org. Chem.* **1977**, *42*, 3626. (c) Hamza, K.; Abu-Reziq, R.; Avnir, D.; Blum, J. *Org. Lett.* **2004**, *6*, 925. (d) Okamoto, H.; Yamaji, M.; Gohda, S.; Kubozono, Y.; Komura, N.; Sato, K.; Sugino, H.; Satake, K. *Org. Lett.* **2011**, *13*, 2758.

(14) LeHoullier, C. S.; Gribble, G. W. *J. Org. Chem.* **1983**, *48*, 1682.

(15) (a) Korobka, I. V.; Kuznetsov, E. V. *Khim. Geterotsikl. Soedin.* **1982**, 1184. (b) Korobka, I. V.; Voloshina, A. I.; Kuznetsov, E. V. *Khim. Geterotsikl. Soedin.* **1984**, 1472. (c) Korobka, I. V.; Revinskii, Yu. V.; Kuznetsov, E. V. *Khim. Geterotsikl. Soedin.* **1985**, 910.

(16) (a) Das, A.; Liao, H.-H.; Liu, R.-S. *J. Org. Chem.* **2007**, *72*, 9214. (b) Guo, B.; Zheng, L.; Yang, L.; Hua, R. *J. Org. Chem.* **2014**, *79*, 4352.

(17) Ju, J.; Hua, R. *Curr. Org. Synth.* **2013**, *10*, 328.