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ARTICLE

Rhodium-Catalyzed Cyclization of Acceptor-Substituted Biphenyl α-Diazoketones: A Study of Substitution Effect on Chemoselectivity†

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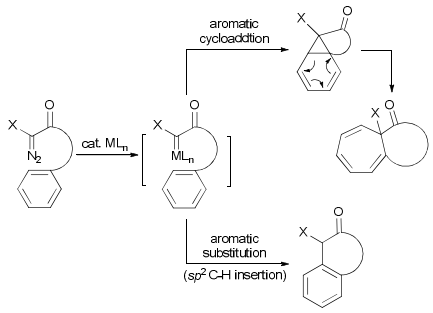
A range of biphenyl α-diazoketones containing various electron-withdrawing groups (EWG = $COCH_3$, CN, CO_2Et, COPh, SO_2CH_3, SO_2Ph) on diazo carbon has been investigated for the rhodium(II)-catalyzed intramolecular cyclization. Among which, the α-acetyl, carboxylate and cyano substituted substrates show markedly different selectivity between aromatic substitution and aromatic cycloaddition processes, to afford phenanthrol and/or benz[α]azulenone products in varying ratios. The selectivity is mainly directed by α-substitutions, and also possibly influenced by the substituents on the biphenyl ring. Moreover, high chemoselectivity for aromatic substitution over cycloaddition is observed for the α-benzoyl and sulfonyl substituted substrates. But in addition to phenanthrols, these reactions produce aromatic ketone and/or 1,2-diketones as unprecedented products obtained from diazo precursors. Mechanistic rationales are given in the report.

Introduction

Transition-metal-catalyzed intramolecular cyclization reactions of aryl α-diazocarbonyl compounds are widely employed for the construction of unsaturated polycycles.[1] Such reactions typically proceed in either an aromatic cycloaddition (the Büchner reaction)[2] or an aromatic substitution[3] pathway, depending on the pattern of carbenoids to react with aryl components (Scheme 1). The norcaradiene products generated by aromatic cycloaddition occasionally undergo a spontaneous ring expansion to give cycloheptatriene isomers.[1,2b,c] Moreover, the aromatic substitution, sometimes also referred as sp^2 C-H insertion, has been proved to involve a zwitterionic intermediate resulting from electrophilic addition, and therefore differs mechanistically from aliphatic C(sp^3)-H insertion process.[4] These reactions are traditionally conducted with rhodium(II) or copper catalysts,[1] while in recent years, Rh(III)[5] or some other transition metals[6] have become more widespread as substitutes for the catalysis.

However, when the aforementioned two processes are potentially competitive with each other, chemoselectivity issue arises. According to literature reports, high selectivity for the desired reaction pathway can be possibly achieved with a given diazo substrate, by selecting appropriate dirhodium(II) ligand,[2b,7] catalytic metal[6a,8] or even solvent.[9] Besides, earlier studies in this area have revealed that a subtle change in diazo substrates may dramatically affect the distribution of products. In this context, the substituent on diazo carbon (X, Scheme 1) is considered as key structural component in directing the chemo- and/or regioselectivity.[10] For electronic reasons, it is believed that α-substituents with different electron-withdrawing (or donating) abilities can profoundly influence the electrophilicity of metal carbenes, the most important factor[7a,10c] determining the selectivity. Additionally, some steric features related to an α-substituent, such as the size,[10a] geometry[11c] and/or conformation,[11a,b] may also need to be taken into account when evaluating its influence on the selectivity. So far, the α-substitution strategy has been used in a few reported studies for controlling the chemoselectivity of the processes in Scheme 1.[12] Under same catalytic conditions, these protocols allow the deliberate generation of different kinds of products (*e.g.*, cycloheptapyrrolones/isoquinolinones[12a]) from similar diazo substrates by simply varying their α-substitutions.



Scheme 1 Transition-metal-catalyzed aromatic cycloaddition and aromatic substitution (sp^2 C-H insertion).

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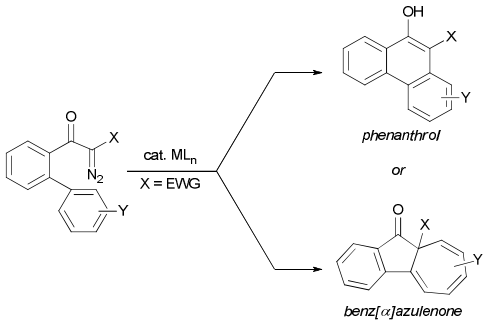
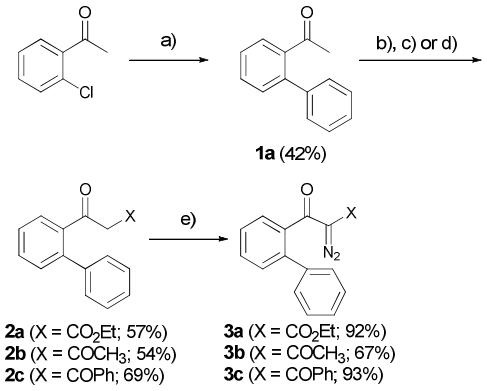


Scheme 2 Concept of selective generation of phenanthrol or benz[α]azulenone derivatives.



Scheme 3 Preparation of substrates **3a**-**c**. a) PhMgBr, $MnCl_2$, LiCl, THF, -10 °C. b) $(EtO)_2CO$, NaH, toluene, reflux. c) LiHMDS, CH_3COCl, toluene, 0 °C. d) LiHMDS, PhCOCl, toluene, 0 °C. e) *p*-ABSA, Et_3N, CH_3CN, rt.

To further explore the utility of such intriguing substitution-controlled strategy, we initiated a program aimed at investigating the transition metal-catalyzed cyclization of biphenyl α-diazoketones. Through the variation of substituents on diazo carbon, we anticipated to find the candidate(s) that could selectively undergo either aromatic substitution or cyclopropanation reaction (Scheme 2). Endowed with the *in-situ* enolization, the former process would lead to the assembly of 9-phenanthrol scaffold, a structural motif that presents in a large number of natural products.[13] It also serves as an important pharmacophore in the drug discovery process,[14] as well as a useful synthon in coordination[15] and material[16] chemistry. Accordingly, the development of methods for its construction has attracted considerable attention in the synthetic community,[17] with many recent works highlighting transition-metal catalysis.[17c-e,g-l] On the other hand, the cycloaddition reaction was supposed to provide benz[α]azulenones after the ring-opening of the cyclopropanes. This type of compounds and their derivatives have also found wide applications in many fields,[18] especially in optoelectronic science[18b,c,f,g] and physical organic chemistry.[18h] In our studies, a range of electron-withdrawing groups[19] was introduced to the α-carbon (Scheme 2, X), and the resulting acceptor/acceptor (A/A)-substituted diazo compounds indeed showed divergent chemoselectivity upon exposure to rhodium catalysts. On this basis, the influence of the substitutions on the biphenyl ring (Y) was also briefly examined. Herein, we wish to disclose the results from these investigations.

Results and discussion

Reactivity of the substrates containing carbonyl-related groups

Our initial efforts focused on studying the effect of the carbonyl-related -CO_2Et, -$COCH_3$ and –COPh groups. The parent substrates **3a**-**c** were easily prepared in three steps from 2-chloroacetophenone by cross coupling with the Grignard reagent,[20] base-induced esterification or acylation, and diazo transfer reaction (Scheme 3). In the current investigation, this sequence allows facile access to a variety of arene substitution pattern from commercially available starting material and organomagnesium reagents.

The reactivity of **3a**-**c** was subsequently examined by using $Rh_2(OAc)_4$, $Rh_2(oct)_4$ or $Rh_2(esp)_2$ as the catalysts (1 mol%), which were demonstrated to favor either aromatic substitution[3a] or aromatic cycloaddition[2a] in many documented cases. With $Rh_2(OAc)_4$ or $Rh_2(oct)_4$ in CH_2Cl_2, the reactions of **3a** exhibited no selective bias between the two competing processes, delivering phenanthrol **4a** and benz[α]azulenone **5a** in almost equal amounts (Table 1, entries 1 and 2). Although use of $Rh_2(esp)_2$ improved the selectivity for the aromatic substitution, significant amount of **5a** was still formed (entry 3). Unlike **3a**, substrate **3b** displayed a strong propensity to undergo aromatic substitution upon exposure to $Rh_2(OAc)_4$ or $Rh_2(oct)_4$, to afford 10-acyl-9-phenanthrol (**4b**)[17g] in good yield with no trace of cycloaddition product (entries 4 and 5). Only when using $Rh_2(esp)_2$ did we isolate the cycloaddition product **5b** in detectable quantity (entry 6; **4b**: 40%, **5b**: 18%). Taken together, these findings suggest that the α-acetyl group should be more effective in inducing aromatic substation than the carboxylate group. Furthermore, high chemoselectivity for substitution over cycloaddition was observed for benzoyl-substituted precursor **3c**. Surprisingly, in addition to offering phenanthrol **4c**, the reactions also produced large amounts of 2-(biphenyl-2-yl)-1-phenyl-ethan-1-one (**6**) and 1-([1,1'-biphenyl]2-yl)-2-phenylethane-1,2-dione (**7**) (entries 7-9). The NMR spectroscopic date of **6** were in agreement with those reported in the literature,[21] and the structure of **7** was confirmed by X-ray crystallographic analysis. Notably, both products were formed by losing one carbon unit from **3c**.

Regarding the stronger electron-withdrawing ability of the benzoyl group, we originally expected that the carbenoid of **3c** would be more reactive for a nucleophilic addition[12a,11c] than the one derived from **3b**. However, the uniformly lower yields of **4c** than **4b,** combined with the formation of **6/7**, apparently do not accommodate this expectation. We therefore propose that these results are possibly attributed to a steric hindrance caused by the bulky benzoyl group, which can impede the access of the phenyl ring to the carbene center. Under such circumstance, the carbenoid may alternatively undergo a Wolff rearrangement[22] or an O-H insertion reaction[23] (Scheme 4). The ketene intermediate resulting from the former process

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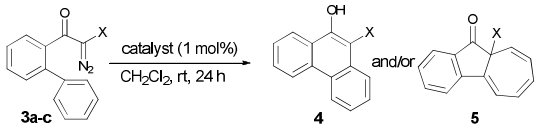
Table 1 Screening for reactivity of **3a-c** under rhodium(II) catalysis

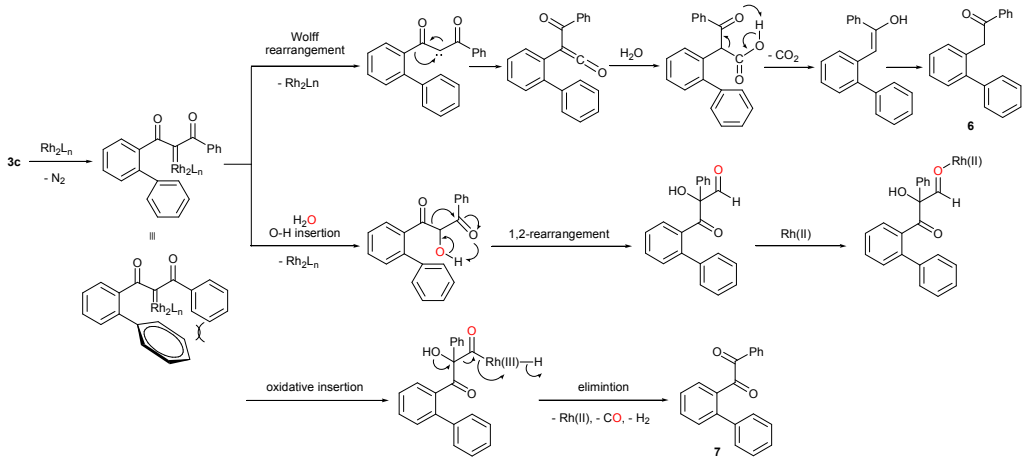


Entry[a]	Substrate	Catalyst	**4** (yield %)[b]	**5** (yield %)[b]
1	**3a**	$Rh_2(OAc)_4$	**4a** (X= CO_2Et) (35%)	**5a** (X = CO_2Et) (31%)
2	**3a**	$Rh_2(oct)_4$	**4a** (47%)	**5a** (41%)
3	**3a**	$Rh_2(esp)_2$	**4a** (39%)	**5a** (24%)
4	**3b**	$Rh_2(OAc)_4$	**4b** (X= $COCH_3$) (74%)	-
5	**3b**	$Rh_2(oct)_4$	**4b** (74%)	-
6	**3b**	$Rh_2(esp)_2$	**4b** (40%)	**5b** (X= $COCH_3$) (18%)
7[c]	**3c**	$Rh_2(OAc)_4$	**4c** (X= COPh) (26%)	-
8[d]	**3c**	$Rh_2(oct)_4$	**4c** (11%)	-
9[e]	**3c**	$Rh_2(esp)_2$	**4c** (10%)	-

[a] Conducted in a 0.01 M solution of **3**. [b] Isolated yield. [c] Yield of **6**: 35%; yield of **7**: 33%. [d] Yield of **6**: 38%; yield of **7**: 36%. [e] Yield of **6**: 25%; yield of **7**: 24%.

can be converted into a *β*-keto acid via hydrolysis, and subsequent decarboxylation leads to the formation of compound **6**. On the other hand, the hydroxylketone product generated by the O-H insertion may further undergo a 1,2-rearrangement with the 2-phenylbenzoyl group, yielding a formyl intermediate. In the presence of rhodium catalyst, this intermediate then participates in a tandem oxidative insertion/elimination sequence,[24] to produce the decarbonylation product **7**. To our knowledge, the formation of **7** represents an unprecedented example of producing biologically[25] and synthetically[26] important aromatic 1,2-diketones from diazo compounds. Currently, a detailed mechanistic investigation is under our active pursuit.

Having established the reactivity of **3a** and **3b**, we also briefly examined the effect of the substitution on the phenyl ring intercepted by the carbene species. Thus, a few analogues bearing electron-withdrawing or donating groups at the *meta*- or *para*-position were similarly prepared as **3a/b** (Scheme 5) and evaluated under the same catalytic conditions [$Rh_2(OAc)_4$ or $Rh_2(oct)_4/CH_2Cl_2$] (Scheme 6). Similar to what observed for **3a**, treatment of carboxylate substrate **3d-f** containing *p*-methyl, *p*-fluoro or *p*-methoxy group with catalytic $Rh_2(oct)_4$ also produced a mixture of two functional isomers (**4d/5d**, **4e/5e** or **4f/5f**). But unlike **3a** offering the low chemoselectivity, all of these substrates demonstrated the preference for cycloaddition, in particular of **3f**. As compared with **3d/e**, acetyl substrates **3g** and **3h** with the same aryl substituents only afforded phenanthrols **4g** and **4h** after chromatographic purification. In these cases, no benz[*α*]azulenones or cyclopropanes[2a] were detected in the crude reaction mixtures and the modest yields of the products were probably due to competing dimerization process. Besides, the aromatic substitution of *m*-Me and *m*-Cl substituted acetyl substrates **3j/k** also proceeded smoothly to give products **4j/k**. For both substrates, the reactions occurred regioselectively at the less hindered site of the phenyl ring, and $Rh_2(OAc)_4$ was shown to be more efficient than $Rh_2(oct)_4$ in giving better yields of the products. As such, it can be seen that a weak electron-donating or withdrawing group at the *meta* or *para* position does not exert a significant influence on the chemoselectivity regulated by the α-acetyl substituent. Nevertheless, introducing a strong electron-donating methoxy group in the



Scheme 4 Proposed mechanisms for the formation of **6** and **7**.

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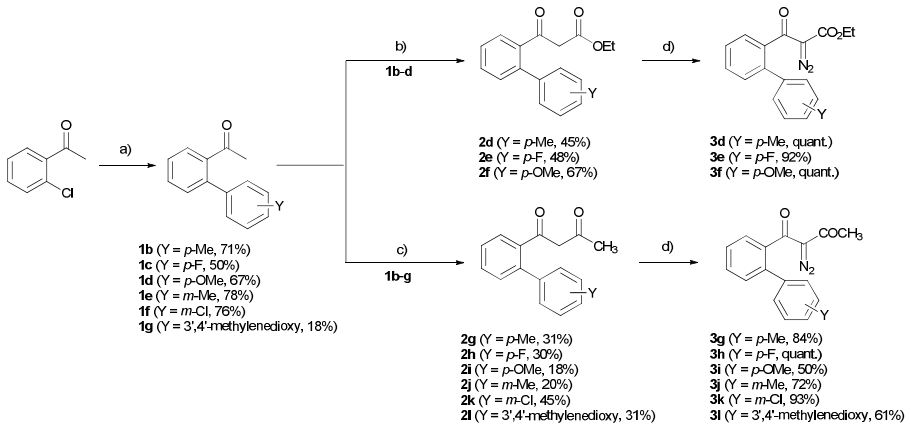
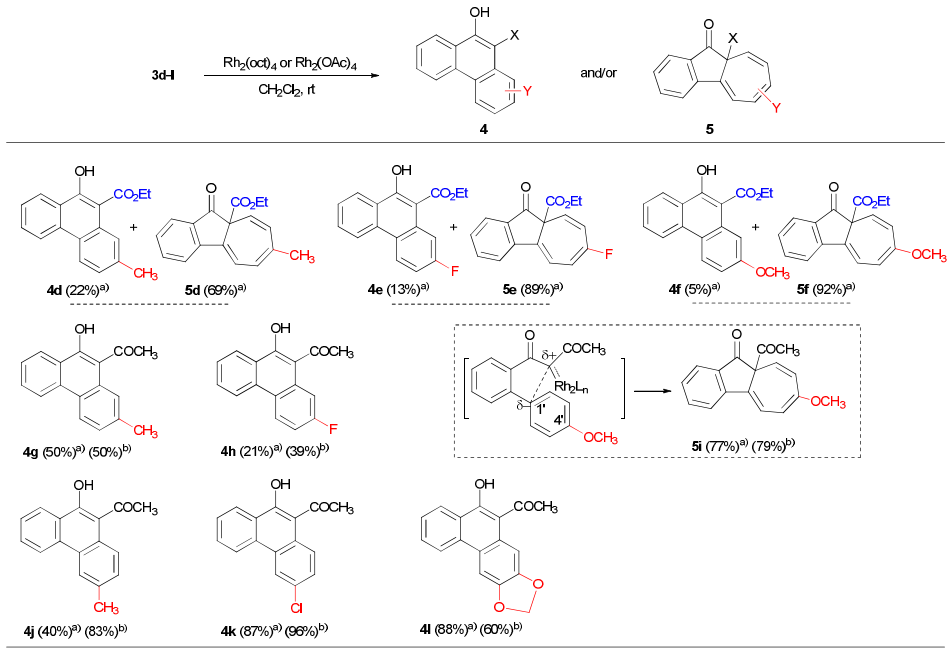


Scheme 5 Preparation of substrates **3d-l**. a) ArMgX, $MnCl_2$, LiCl, THF, -10 °C. b) $(EtO)_2CO$, NaH, toluene, reflux. c) LiHMDS, CH_3COCl, toluene, 0 °C. d) *p*-ABSA, Et_3N, CH_3CN, rt.

para-position drastically affected the chemoselectivity, with the reaction of **3i** now favouring cycloaddition to yield benz[*α*]azulenone **5i**. We attribute this dichotomy in the reactivity to an enormously increased electron density at the C-1' position, which can promote the nucleophilic addition of the C-1' carbon to the electron-deficient carbenoid. Despite of this, we found that aromatic substitution could be renewed with the concomitant incorporation of the oxygen atoms into the 3', 4'-positions, as showcased by the exclusive generation of **4l** from **3l**.

Reactivity of the α-cyano substituted substrates

We further evaluated the cyclization of α-cyano biphenyl diazoketones **3m**-**s**, which were synthesized from intermediates **1a**-**g** via based-induced cyanation followed by diazo transfer reaction (Scheme 7). Under the catalysis of $Rh_2(oct)_4$, the parent and *para*-substituted substrates **3m**-**p** were found to cleanly undergo cycloaddition to produce benz[*α*]azulenones **5m**-**p** in high to quantitative yields. In contrast, substrates **3q**-**s** with the *m*-substituents tended to favour aromatic substitution, affording the phenanthrols either exclusively (**4q**/**4q'**, **4s**) or as the major products (**4r**) (Scheme 8). Besides, TLC analysis of the reactions of **3q**-**s**, together with the non-conversion of **5r** to **4r**, suggest that these phenanthrol products were derived from the aromatic substitution rather than the *in-situ* aromatisation of corresponding benz[*α*]azulenone intermediates.



[a] Conducted with 1 mol% of $Rh_2(oct)_4$. [b] Conducted with 1 mol% of $Rh_2(OAc)_4$.

Scheme 6 Rhodium-catalyzed cyclization reactions of substrates **3d-l**.

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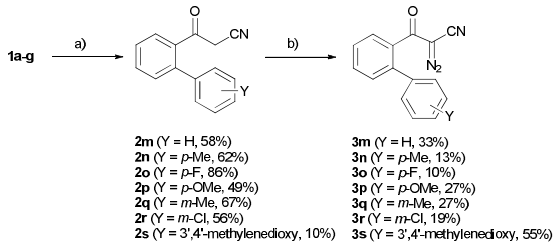
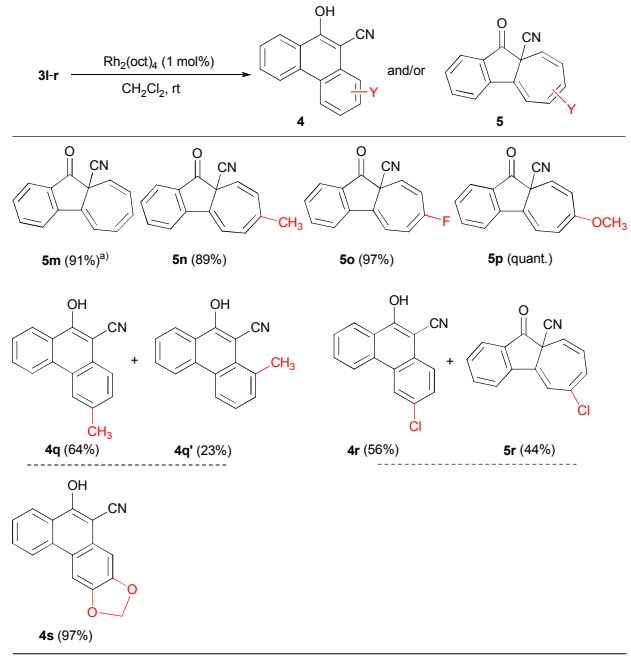


Scheme 7 Preparation of 3m-s. a) LDA, p-TsCN, THF, -78 °C to rt. b) p-ABSA, NaH, THF, 0 °C.

Previous studies by Charetter et al.[11c] have led to the proposal that the Rh-carbenoids derived from α-diazonitriles inherently adopt a coplanar conformation with the linear nitrile group lying in the plane of carbene π-bond. As compared with the out-of-plane conformation proposed for other A-A substituted carbenoids (*e.g.*, ester or ketone carbenoids), the unique steric feature of nitrile carbenoids is considered to be particularly suited for the cycloaddition owing to the increased electrophilicity[11c] through in-plane conjugation, and the minimized non-bonding interactions with alkenes[27]/arenes[2a] in the transition state. Regarding the biphenyl ketone system, these steric and electronic factors may explain the strong propensity of substrates **3l**-**o** to undergo aromatic cycloaddition. In the transition structure, the requisite *p*-orbital interaction can occur efficiently between the parallel phenyl ring and Rh=C bond, with or without the presence of *p*-substitution (Fig. 1, a). However, when a substitutent is introduced in the *meta*-position, its steric repulsion with the carbenoid unit may force the two planes to deviate from the parallel orientation (b). Such deviation can presumably weaken the orbital interaction required for the cycloaddition, and consequently impel the carbenoids to engage in the aromatic substitution.



[a] Same yield was obtained with $Rh_2(OAc)_4$.

Scheme 8 $Rh_2(oct)_4$-catalyzed cyclization of the cyano-substituted substrates **3m**-**s.**

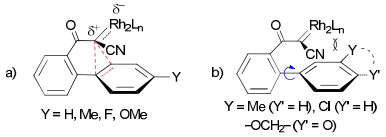
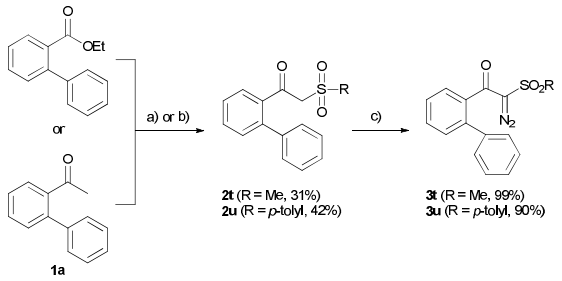


Fig. 1 a) Nitrile and carbenoid are coplanar/the planes of phenyl ring and carbenoid are parallel. b) Planes of phenyl ring and carbenoid are non-parallel.

Reactivity of the α-sulfonyl substituted substrates

Finally, we sought to investigate the effect of α-sulfonyl moiety on the chemoselectivity. To the end, the mesyl and tosyl substrates **3t** and **3u** were respectively prepared from ethyl biphenyl-2-carboxylate[28] and **1a** in a two-step sequence (Scheme 9). Treatment of **3t** with 1 mol% of $Rh_2(OAc)_4$ or $Rh_2(oct)_4$ in CH_2Cl_2 for 24 hours only produced 20% of phenanthrol **4t**. To our surprise, the reactions also gave phenanthrene-9,10-dione (**8**)[29] along with large amounts of recovered **3t** after chromatographic purification (Scheme 10, a and b). When proceeding, the color of the reaction mixtures was found to change from green to yellow in a period of 10 hours, implying a possible decomposition of the catalysts. In this respect, we further conducted a reaction by increasing the amount of $Rh_2(oct)_4$ (5, 15, 20, 25 mol%), and discovered that a full consumption of **3t** could be attended when the loading was raised up to 25 mol% (c). Similarly, the reaction of **3u** with $Rh_2(oct)_4$ (5 mol%) also gave the formation of compound **8**, phenanthrol **4u** and the recovered starting material (d). After screening a few catalytic systems, we found that the yields of **4t/u** could be improved to 60% and 56%, respectively, by employing a Rh(III)-catalyzed protocol [$(Cp^*RhCl_2)_2$/$AgSbF_6$] (e).[30] Notably, there is no precedence of producing 10-sulfonyl-phenanthren-9-ol compounds in literature, and the structure of **4t** has been unambiguously confirmed by the x-ray crystal diffraction. Furthermore, we speculated that compound **8** might be derived from **4t/u** at the expense of rhodium catalysts, and this assumption has been validated by the conversion of **4t** into **8** under the $Rh_2(oct)_4$-mediated reaction conditions (f).



Scheme 9 Preparation of **3t** and **3u**. a) *n*-BuLi, $(Me)_2SO_2$, THF, 0 °C to rt. b) $TsNa{\cdot}4H_2O$, I_2, MeOH, rt. c) K_2CO_3, *p*-ABSA, CH_3CN, rt.

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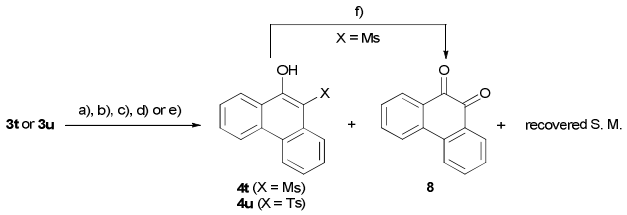
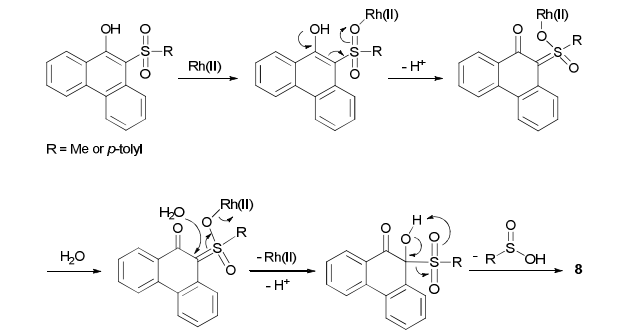


Scheme 10 Rhodium-catalyzed reactions of **3t/u** and conversion of **4t** into **8**. a) $Rh_2(OAc)_4$ (1 mol%), CH_2Cl_2, 24 h, rt; **4t**: 20%; **8**: 5%; recovered **3t**: 37%. b) $Rh_2(oct)_4$ (1 mol%), CH_2Cl_2, 24 h, rt; **4t**: 20%; **8**: 16%; recovered **3t**: 52%. c) $Rh_2(oct)_4$ (25 mol%), CH_2Cl_2, 40 h, rt; **4t**: 40%; **8**: 6%; recovered **3t**: 0%. d) $Rh_2(oct)_4$ (5 mol%), CH_2Cl_2, 24 h, rt; **4u**: 11%; **8**: 17%; recovered **3u**: 15%. e) $(Cp^*RhCl_2)_2$ (2.5 mol%), $AgSbF_6$ (2 equiv.), 1,2-dichloroethane, reflux, 5 h; **4t**: 60%; **4u**: 56%. f) $Rh_2(oct)_4$ (50 mol%), CH_2Cl_2, rt, 25 h, 41%.



Scheme 11 Plausible mechanism for the generation of **8**.

A mechanism for producing **8** is tentatively proposed in Scheme 11. Once **4t** or **4u** is formed, the sulfonyl oxygen atom may coordinate with the rhodium catalyst, to thus trigger a migration of the electrons[31] and produce a keto sulfonyl complex. Through the attack by H_2O at the double bond, this complex can be decomposed into a hydroxysulfone intermediate with losing Rh(II) ion. Subsequently, desulfination of the intermediate via a proton transfer process results in the formation of **8**. In term of the catalytic activity, we postulate that the rhodium species released from this sequence is less active as the initially introduced $Rh_2(oct)_4$ or $Rh_2(oct)_4$, accounting for the incomplete consumption of **3t/u** in some cases (Scheme 10, a, b and d). Since the conversion of a β-sulfonyl enol fragment into a 1,2-diketone moiety has not yet been known in literature, a thorough investigation is being undertaken in order to gain a full understanding of this newly discovered process.

Conclusions

In the biphenyl α-diazoketone system, the substitution effect on the chemoselectivity of the rhodium(II)-catalyzed cyclization has been investigated. The studies reveal that most of the α-acetyl substrates can exclusively undergo aromatic substitution, except for that bearing a strong electron-donating group at the *para*-position of the phenyl ring as it showing a complete selectivity for aromatic cycloaddition. Besides, all of the carboxylate substrates give the mixtures of two functional isomers from both processes, and mostly in favor of the cycloaddition products. For the α-cyano series, the non- or *para*-substituted substrates show a strong preference for aromatic cycloaddition, while the *meta*-substituted analogues instead favour aromatic substitution. Predictably, these established patterns should provide the guidelines for the selective generation of important phenanthrol or benz[*α*]azulenone derivatives with extended functional diversity. Furthermore, high chemoselectivity for aromatic substitution over cycloaddition is observed for the benzyl and sulfonyl substituted substrates. Interestingly, these reactions not only give phenanthrols but also produce **6**-**8**, with compounds **7**/**8** (or analogues) having never been reported for diazo precursors. The latter findings have offered an opportunity for developing new synthetic strategies to prepare useful aromatic 1,2-diketone derivatives.

Experimental Section

General

The reagents and catalysts were purchased from commercial suppliers and used without further purification. Some solvents were properly dried (THF/Na, toluene and CH_2Cl_2/CaH_2) and freshly distilled before each use, while others were directly used as HPLC grade without pre-treatment (acetonitrile, 1,2-dichloroethane and methanol). The reactions were monitored by TLC on 0.25 mm silica plates (60F-254) and visualized by UV light, ethanolic solution of vanillin (5%) or aqueous $KMnO_4$ solution (10%). The chromatographic purifications were performed with silica gel (70-230 mesh). The NMR spectra (^1H, ^{13}C and ^{19}F) were recorded on 400 or 300 MHz spectrometer using chloroform-d, methanol-d4 or dimethyl sulfoxide-d6 as solvents. The ^1H NMR data are reported as the chemical shift in parts per million, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constants (*J*) in Hertz, and number of protons. The resonances of infrared (IR) spectra are reported in wave numbers (cm^{-1}). High resolution mass spectrometry (HRMS) was determined in electron-impact ionization (EI) or electrospray ionization (ESI) mode with a magnetic sector analyzer. The melting points were measured with a capillary apparatus and uncorrected. Crystal crystallographic data of compounds **7** and **4t** have been deposited in the Cambridge Crystallographic Data Center with the deposition numbers as CCDC 1813583 and CCDC 1836777.

General Procedure for Rh(II)-Catalyzed Cyclization of Diazo Precursors

A dry round-bottom flask containing biphenyl α-diazoketone **3** (1.00 equiv.) and equipped with a stir bar was flushed with N_2, followed by charging with CH_2Cl_2 (0.01 M of **3**) and the rhodium(II) catalyst (0.01 equiv.). Under a N_2 atmosphere, the reaction mixture was stirred at room temperature until TLC analysis showed full consumption of the starting material. The solution was then concentrated under reduced pressure, and the crude residue was purified by flash chromatography on silica gel (ethyl acetate/hexane) to afford the product(s).

Ethyl 10-hydroxyphenanthrene-9-carboxylate (4a) and ethyl 10-oxo-9a,10-dihydrobenzo[*α*]azulene-9a-carboxylate (5a).

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The titled compounds were prepared from **3a** by using $Rh_2(oct)_4$ as the catalyst (Table 1, entry 2). Chromatographic purification (hexane-EtOAc 50:1, 40:1, 20:1) afforded **4a** (47%) followed by **5a** (41%). **4a**:[32] ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.3 (s, 1 H), 8.81 (dd, *J* = 8.5, 1.2 Hz, 1 H), 8.58-8.55 (m, 3 H), 7.77 (ddd, *J* = 8.3, 7.1, 1.4 Hz, 1 H), 7.64 (ddd, *J* = 8.1, 7.1, 1.4 Hz, 1 H), 7.58 (ddd, *J* = 8.5, 7.0, 1.4 Hz, 1 H), 7.49 (ddd, *J* = 8.1, 7.0, 1.4 Hz, 1 H), 4.62 (q, *J* = 7.1 Hz, 2 H), 1.56 (t, *J* = 7.1 Hz, 3 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 162.7, 133.7, 130.4, 129.5, 127.6, 126.8, 126.1, 126.0, 125.3, 125.0, 124.2, 122.9, 122.4, 101.6, 62.0, 14.4 ppm. **5a** (yellow oil): IR (neat) 3019, 1745, 1714, 1598, 1209, 765, 703 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2 H), 7.64 (t, *J* = 7.5 Hz, 1 H), 7.41 (t, *J* = 7.5 Hz, 1 H), 6.93 (d, *J* = 6.0 Hz, 1 H), 6.60-6.43 (m, 3 H), 5.91 (d, *J* = 9.7 Hz, 1 H), 4.04 (q, *J* = 7.1 Hz, 2 H), 1.09 (t, *J* = 7.1 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 167.0, 149.0, 135.9, 134.1, 133.5, 131.7, 129.3, 129.2, 129.2, 125.9, 125.0, 122.1, 118.3, 64.2, 61.9, 13.9 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{17}H_{14}O_3$: 266.0943; found: 266.0950.

1-(10-Hydroxyphenanthren-9-yl)ethanone (4b). The titled compound was prepared from **3b** by using $Rh_2(OAc)_4$ (Table 1, entry 4) or $Rh_2(oct)_4$ (Table 1, entry 5) as the catalyst. Chromatographic purification (hexane-EtOAc 30:1, 15:1) afforded **4b**[17g] in 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.72 (br s, 1 H), 8.57-8.51 (m, 3 H), 7.98 (d, *J* = 8.1 Hz, 1 H), 7.77 (ddd, *J* = 8.4, 7.0, 1.1 Hz, 1 H), 7.63 (dd, *J* = 7.6, 7.1 Hz, 1 H), 7.56 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1 H), 7.49 (dd, *J* = 8.4, 7.2 Hz, 1 H), 2.83 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 163.2, 134.2, 131.0, 129.8, 127.2, 127.1, 126.2, 125.6, 125.5, 125.4, 124.6, 123.4, 122.5, 112.3, 31.7 ppm.

9a-Acetylbenzo[*a*]azulen-10(9*a*H)-one (5b). The titled compound was obtained from **3b** by using $Rh_2(esp)_2$ as the catalyst (Table 1, entry 6). Chromatographic purification (hexane-EtOAc 20:1, 10:1) afforded **5b** (18%) as a yellow oil along with 40% of **4b**. **5b**: IR (neat) 3017, 1710, 1703, 1598, 762, 707 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 1 H), 7.75 (d, *J* = 7.7 Hz, 1 H), 7.65 (dd, *J* = 7.8, 7.4 Hz, 1 H), 7.42 (dd, *J* = 7.7, 7.4 Hz, 1 H), 7.01 (d, *J* = 6.5 Hz, 1 H), 6.59-6.55 (m, 1 H), 6.46-6.39 (m, 2 H), 6.12 (d, *J* = 9.8 Hz, 1 H), 2.20 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 198.0, 149.0, 135.9, 134.8, 133.8, 130.5, 130.2, 129.4, 128.7, 127.0, 124.9, 122.0, 118.7, 72.9, 26.4 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{16}H_{12}O_2$: 236.0837; found: 236.0833.

(10-Hydroxyphenanthren-9-yl)-phenylmethanone (4c), 2-([1,1'-biphenyl]-2-yl)-1-phenylethanone (6), and 1-([1,1'-biphenyl]-2-yl)-2-phenylethane-1,2-dione (7). The titled compounds were obtained from **3c** by using $Rh_2(OAc)_4$ as the catalyst (Table 1, entry 7). Chromatographic purification (hexane-EtOAc 50:1, 30:1) afforded **4c** (26%) along with compounds **6** (35%) and **7** (33%). **4c**:[17h] ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.73 (br s, 1 H), 8.61 (dd, *J* = 9.2, 9.0 Hz, 2 H), 8.54 (d, *J* = 8.24, 1 H), 7.84 dd, *J* = 8.2, 7.2 Hz, 1 H), 7.69 (dd, *J* = 7.8, 7.4 Hz, 1 H), 7.63 (d, *J* = 7.4 Hz, 2 H), 7.56 (dd, *J* = 7.6, 7.5 Hz, 1 H), 7.42-7.34 (m, 4 H), 7.17 (dd, *J* = 7.4, 7.8 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 160.6, 140.4, 134.0, 132.4, 130.6, 130.3, 129.4, 128.5, 127.7, 127.1, 126.1, 125.9, 125.3, 125.1, 124.4, 122.8, 122.6, 111.0 ppm. **6**:[21] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.40 Hz, 2 H), 7.51 (t, *J* = 7.40 Hz, 1 H), 7.40 (m, 11 H), 4.25 (s, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 142.4, 141.3, 136.7, 133.0, 132.4, 130.7, 130.2, 129.2, 128.5, 128.3, 128.3, 127.6, 127.2, 127.0, 43.3 ppm. **7**:[33] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.68 Hz, 1 H), 7.78 (d, *J* = 7.60 Hz, 2 H), 7.64 (dd, *J* = 7.56, 7.36 Hz, 1 H), 7.53 (dd, *J* = 7.68, 7.36 Hz, 2 H), 7.41 (d, *J* = 7.56 Hz, 1 H), 7.35 (dd, *J* = 7.72, 7.64 Hz, 2 H), 7.21-7.19 (m, 2 H), 7.05-7.04 (m, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 191.3, 143.6, 139.7, 135.1, 133.9, 132.8, 130.6, 130.4, 129.8, 128.3, 128.1, 128.0, 127.7 ppm.

Ethyl 10-hydroxy-7-methylphenanthrene-9-carboxylate (4d) and ethyl 7-methyl-10-oxo-9a,10-dihydrobenzo[*a*]azulene-9a-carboxylate (5d). The titled compounds were prepared from **3d** by using $Rh_2(oct)_4$ as the catalyst. The reaction proceeded for 20 hours at rt. Chromatographic purification (hexane-EtOAc 50:1, 20:1, 5:1) afforded **4d** (22%) as a white solid followed by **5d** (69%) as a yellow oil. **4d**: m.p. 119-120 °C; IR (neat) 3210, 3079, 1717, 1633, 1615, 1590, 766, 722 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.26 (s, 1 H), 8.60 (s, 1 H), 8.55-8.51 (m, 2 H), 8.44 (d, *J* = 8.4 Hz, 1 H), 7.73 (ddd, *J* = 8.4, 7.0, 1.2 Hz, 1 H), 7.60 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1 H), 7.31 (dd, *J* = 8.3, 1.4 Hz, 1 H), 4.61 (q, *J* = 7.2 Hz, 2 H), 2.54 (s, 3 H), 1.57 (t, *J* = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 162.7, 137.2, 133.7, 130.3, 129.6, 126.4, 126.0, 125.7, 124.9, 124.9, 123.9, 122.7, 122.2, 101.4, 61.9, 22.2, 14.3 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{18}H_{16}O_3$: 280.1099; found: 280.1097. **5d**: IR (neat) 3020, 1746, 1714, 1623, 1470, 1212, 765, 739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.68 (m, 2 H), 7.57 (dd, *J* = 7.7, 7.4 Hz, 1 H), 7.33 (dd, *J* = 7.4, 7.4 Hz, 1 H), 6.77 (d, *J* = 6.5 Hz, 1 H), 6.33 (d, *J* = 6.5 Hz, 1 H), 6.26 (d, *J* = 10.0 Hz, 1 H), 5.82 (d, *J* = 10.0 Hz, 1 H), 4.00 (q, *J* = 7.08 Hz, 2 H), 2.02 (s, 3 H), 1.05 (t, *J* = 7.08 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 167.2, 149.3, 141.4, 135.8, 133.9, 132.7, 131.7, 128.9, 126.2, 124.8, 124.8, 121.8, 118.2, 63.8, 61.7, 24.8, 13.9 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{18}H_{16}O_3$: 280.1099; found: 280.1092.

Ethyl 7-fluoro-10-hydroxyphenanthrene-9-carboxylate (4e) and ethyl 7-fluoro-10-oxo-9a,10-dihydrobenzo[*a*]azulene-9a-carboxylate (5e). The titled compounds were prepared from **3e** by using $Rh_2(oct)_4$ as the catalyst. The reactions was carried out for 18 hours at rt. Chromatographic purification (hexane-EtOAc 40:1, 20:1, 10:1) afforded **4e** (13%) as a white solid followed by **5e** (89%) as a yellow solid. **4e**: m.p. 133-135 °C; IR (neat) 3013, 1631, 1618, 1579, 1319, 1313, 1236, 808, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.50 (s, 1 H), 8.50-8.39 (m, 4 H), 7.72 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1 H), 7.59 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1 H), 7.19 (m, 1 H), 4.60 (q, *J* = 7.1 Hz, 2 H), 1.57 (t, *J* = 7.1 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 164.0, 162.2 (d, $J_{C\text{-}F}$ = 242.4 Hz), 133.3, 131.3, 131.2, 130.8, 126.6, 125.1, 124.8 (d, $J_{C\text{-}F}$ = 9.5 Hz), 122.6 (d, $J_{C\text{-}F}$ = 2.0 Hz), 122.2, 122.5 (d, $J_{C\text{-}F}$ = 23.4 Hz), 111.5 (d, $J_{C\text{-}F}$ = 25.3 Hz), 101.0 (d, $J_{C\text{-}F}$ = 2.4 Hz), 62.3, 14.3 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.8 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{17}H_{13}FO_3$: 284.0849; found: 284.0852. **5e**: m.p. 88-90 °C; IR (neat) 3040, 1746, 1717, 1645, 1599, 1226, 764, 744 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.75 (m, 2 H), 7.66 (dd, *J* = 7.6, 7.5 Hz, 1 H), 7.42 (dd, *J* = 7.5, 7.40 Hz, 1 H), 6.85 (dd, *J* = 7.2, $J_{H\text{-}F}$ = 6.0 Hz, 1 H), 6.44 (ddd, *J* = 10.5, $J_{H\text{-}F}$ = 8.74, *J* = 1.64 Hz, 1 H), 6.32 (ddd, $J_{H\text{-}F}$ = 17.0, *J* = 7.8, *J*

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= 1.1 Hz, 1 H), 6.08 (dd, J = 10.5, $J_{H\text{-}F}$ = 5.0 Hz, 1 H), 4.07 (q, J = 7.0 Hz, 2 H), 1.12 (t, J = 7.0 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 165.1 (d, $J_{C\text{-}F}$ = 290.2 Hz), 161.2, 148.9, 136.1, 133.7, 130.6 (d, $J_{C\text{-}F}$ = 3.4 Hz), 129.3, 128.1 (d, $J_{C\text{-}F}$ = 13.3 Hz), 125.1, 124.2 (d, $J_{C\text{-}F}$ = 36.6 Hz), 122.0, 115.3 (d, $J_{C\text{-}F}$ = 11.6 Hz), 110.2 (d, $J_{C\text{-}F}$ = 28.6 Hz), 64.0, 62.2, 13.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -95.3 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{17}H_{13}FO_3$: 284.0849; found: 284.0847.

Ethyl 10-hydroxy-7-methoxyphenanthrene-9-carboxylate (4f) and ethyl 7-methoxy-10-oxo-9a,10-dihydrobenzo[*a*]azulene-9a-carboxylate (5f). The titled compounds were prepared from **3f** by using $Rh_2(oct)_4$ as the catalyst. The reaction proceeded for 24 hours at rt. Chromatographic purification (hexane-EtOAc 20:1, 10:1, 5:1) afforded trace amount of **4f** (～5%) followed by **5f** (92%) as a yellow oil. **4f**: IR (neat) 3001, 2923, 1634, 1615, 1319, 1243, 853 761 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.43 (s, 1 H), 8.53-8.47 (m, 3 H), 8.36 (d, J = 2.4 Hz, 1 H), 7.74 (dd, J = 7.16, 7.16 Hz, 1 H), 7.57 (dd, J = 7.3, 7.3 Hz, 1 H), 7.13 (dd, J = 9.0 2.4 Hz, 1 H), 4.61 (q, J = 7.1 Hz, 2 H), 3.95 (s, 3 H), 1.58 (t, J = 7.1 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 163.7 159.1, 133.9, 131.0, 130.6, 125.8, 125.0, 124.3, 124.2, 121.9, 120.2, 133.6, 108.1, 101.2, 62.0, 55.2, 14.4 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{18}H_{16}O_4$: 296.1049; found: 296.1053. **5f**: IR (neat) 3071, 1742, 1712, 1221, 1194, 820, 763 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.7 Hz, 1 H), 7.71 (d, J = 7.9 Hz, 1 H), 7.61 (dd, J_1 = 7.7, J_2= 7.3 Hz, 1 H), 7.34 (dd, J_1 = 7.9, J_2= 7.3 Hz, 1 H), 6.86 (d, J = 7.5 Hz, 1 H), 6.33 (dd, J_1 = 10.5, J_2 = 1.8 Hz, 1 H), 6.02 (d, J = 10.5 Hz, 1 H), 5.78 (br d, J = 7.5 Hz, 1 H), 4.12-4.01 (m, 2 H), 3.66 (s, 3 H), 1.09 (t, J = 7.1 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 167.1, 160.9, 149.7, 135.8, 133.4, 128.2, 128.1, 127.6, 126.9, 124.9, 121.4, 117.2, 102.1, 63.6, 61.8, 54.9, 13.9 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{18}H_{16}O_4$: 296.1049; found: 296.1049.

1-(10-Hydroxy-7-methylphenanthren-9-yl)ethanone (4g). The titled compound was prepared from **3g** by using $Rh_2(OAc)_4$ as the catalyst. The reaction proceeded for 24 hours at rt. Chromatographic purification (hexane-EtOAc 60:1, 30:1) afforded **4g** (50%) as a yellow solid. M.p. 88-90 °C; IR (neat) 3060, 1615, 1593, 1574, 1236, 765, 725 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.63 (s, 1 H), 8.53 (d, J = 8.2 Hz, 1 H), 8.49 (d, J = 8.3 Hz, 1 H), 8.42 (d, J = 8.4 Hz, 1 H), 7.76 (br s, 1 H), 7.75 (dd, J = 7.4 Hz, 1 H), 7.60 (dd, J = 8.2, 7.6 Hz, 1 H), 7.32 (d, J = 8.3 Hz, 1 H), 2.83 (s, 3 H), 2.55 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.9, 162.9, 137.0, 134.2, 130.9, 129.9, 126.6, 126.0, 125.6, 125.4, 125.1, 124.0, 123.2, 122.2, 112.1, 31.7, 21.9 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{17}H_{14}O_2$: 250.0994; found: 250.0986.

1-(7-Fluoro-10-hydroxyphenanthren-9-yl)ethanone (4h). The titled compound was prepared from **3h** by using $Rh_2(OAc)_4$ as the catalyst. The reaction proceeded for 18 hours at rt. Chromatographic purification (hexane-EtOAc 30:1) afforded **4h** (39%) as a pale yellow solid. M.p. 131-133 °C; IR (neat) 3015, 1616, 1595, 1579, 1227, 1192, 990, 871, 765 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.96 (s, 1 H), 8.51 (dd, J = 8.3, 0.7 Hz, 1 H), 8.47 (dd, J = 9.0, $J_{H\text{-}F}$ = 6.1 Hz, 1 H), 8.40 (d, J = 8.3 Hz, 1 H), 7.76 (ddd, J = 8.3, 7.2, 1.2 Hz, 1 H), 7.63-7.58 (m, 2 H), 7.23-7.18 (m, 1 H), 2.81 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 164.3, 161.7 (d, $J_{C\text{-}F}$ = 244.6 Hz), 133.7, 131.5, 131.4, 126.9, 125.6 (d, $J_{C\text{-}F}$ = 9.2 Hz), 125.5, 125.0, 122.6 (d, $J_{C\text{-}F}$ = 1.7 Hz), 122.3, 112.7 (d, $J_{C\text{-}F}$ = 22.8 Hz), 111.5 (d, $J_{C\text{-}F}$ = 2.8 Hz), 110.8 (d, $J_{C\text{-}F}$ = 23.5 Hz), 31.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.4 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{16}H_{11}FO_2$: 254.0743; found: 254.0733.

9a-Acetyl-7-methoxybenzo[*a*]azulen-10(9aH)-one (5i). The titled compound was prepared from **3i** by using $Rh_2(OAc)_4$ as the catalyst. The reaction proceeded for 15 hours at rt. Chromatographic purification (hexane-EtOAc 50:1, 20:1, 10:1) afforded **5i** (79%) as a yellow oil. IR (neat) 3011, 1728, 1704, 1625, 1219, 759, 726 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (m, 2 H), 7.61 (dd, J = 7.8, 7.4 Hz, 1 H), 7.33 (dd, J = 7.5, 7.4 Hz, 1 H), 6.93 (d, J = 7.6 Hz, 1 H), 6.29 (d, J = 10.6 Hz, 1 H), 6.19 (d, J = 10.6 Hz, 1 H), 5.75 (d, J = 7.6 Hz, 1 H), 3.64 (s, 3 H), 2.17 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 198.1, 160.1, 149.8, 135.9, 133.1, 129.0, 128.4, 127.9, 127.3, 124.9, 121.4, 117.6, 102.6, 72.3, 54.9, 26.3 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{17}H_{14}O_3$: 266.0943; found: 266.0951.

1-(10-Hydroxy-6-methylphenanthren-9-yl)ethanone (4j). The titled compound was prepared from **3j** by using $Rh_2(OAc)_4$ as the catalyst. The reaction proceeded for 24 hours at rt. Chromatographic purification (hexane-EtOAc 30:1) afforded **4j** (83%) as a pale yellow solid. M.p. 81-83 °C; IR (neat) 3060, 3016, 1600, 1574, 1224, 812, 772 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.66 (s, 1 H), 8.54 (d, J = 8.2 Hz, 2 H), 8.34 (s, 1 H), 7.89 (d, J = 8.4 Hz, 1 H), 7.76 (dd, J = 8.2, 7.7 Hz, 1 H), 7.62 (dd, J = 8.2, 7.7 Hz, 1 H), 7.39 (d, J = 8.4 Hz, 1 H), 2.82 (s, 3 H), 2.57 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.0, 162.4, 134.1, 134.0, 130.9, 128.7, 127.4, 127.0, 126.2, 125.6, 125.4, 125.4, 123.3, 122.5, 112.1, 31.8, 21.5 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{17}H_{14}O_2$: 250.0994; found: 250.1020.

1-(6-Chloro-10-hydroxyphenanthren-9-yl)ethanone (4k). The titled compound was prepared from **3k** by using $Rh_2(OAc)_4$ as the catalyst. The reaction proceeded for 24 hours at rt. Chromatographic purification (hexane-EtOAc 40:1) afforded **4k** (96%) as a yellow solid. M.p. 133-135 °C; IR (neat) 3087, 3038, 1593, 1568, 1246, 807, 769 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.74 (s, 1 H), 8.44 (d, J = 8.0 Hz, 1 H), 8.30 (d, J = 2.0 Hz, 1 H), 8.27 (d, J = 8.3 Hz, 1 H), 7.78 (d, J = 8.9 Hz, 1 H), 7.70 (ddd, J = 8.3, 7.1, 1.1 Hz, 1 H), 7.59 (ddd, J = 8.0, 7.1, 1.1 Hz, 1 H), 7.41 (dd, J = 8.9, 2.1 Hz, 1 H), 2.73 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.5, 163.1, 132.8, 131.1, 130.4, 128.0, 127.9, 127.7, 127.3, 126.5, 125.7, 125.4, 122.9, 122.4, 111.4, 31.8 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{16}H_{11}ClO_2$: 270.0448; found: 270.0439.

1-(5-Hydroxyphenanthro[2,3-*d*][1,3]dioxol-6-yl)ethanone (4l). The titled compound was prepared from **3l** by using $Rh_2(oct)_4$ as the catalyst. The reaction proceeded for 24 hours at rt. Chromatographic purification (hexane-EtOAc 10:1, 5:1) afforded **4l** (88%) as a yellow solid. M.p. 170-172 °C; IR (neat) 3074, 1621, 1597, 1575, 1252, 1236, 1204, 1039, 862, 777 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.21 (s, 1 H), 8.49 (d, J = 8.0 Hz, 1 H), 8.28 (d, J = 8.3 Hz, 1 H), 7.86 (s, 1 H), 7.71 (ddd, J = 8.3, 7.1, 1.0 Hz, 1 H), 7.56 (ddd, J = 8.0, 7.1, 1.0 Hz, 1 H), 7.32 (s, 1 H), 6.09 (s, 2 H), 2.77 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.9, 161.2, 148.0, 146.0, 133.8, 130.7, 126.2, 125.6, 125.4,

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124.5, 122.2, 121.7, 112.9, 104.2, 101.9, 101.6, 31.7 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{17}H_{12}O_4$: 280.0736; found: 280.0729.

10-Oxo-9a,10-dihydrobenzo[*a*]azulene-9a-carbonitrile (5m). The titled compound was prepared from **3m** by using $Rh_2(oct)_4$ as the catalyst. The reaction proceeded for 24 hours at rt. Chromatographic purification (hexane-EtOAc 10:1, 5:1) afforded **5m** (91%) as a yellow oil. IR (neat) 3236, 2226, 1729, 1596, 761, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.7 Hz, 1 H), 7.77-7.70 (m, 2 H), 7.50 (ddd, *J* = 7.7, 6.2, 1.5 Hz, 1 H), 6.99 (d, *J* = 6.3 Hz, 1 H), 6.87 (dd, *J* = 11.3, 6.3 Hz, 1 H), 6.78 (dd, *J* = 11.3, 6.2 Hz, 1 H), 6.51 (dd, *J* = 9.5, 6.2 Hz, 1 H), 5.73 (d, *J* = 9.5 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 147.1, 137.0, 133.2, 132.4, 131.3, 130.7, 130.3, 128.7, 125.7, 122.5, 121.4, 119.7, 114.7, 49.0 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{15}H_9NO$: 219.0684; found: 219.0678.

7-Methyl-10-oxo-9a,10-dihydrobenzo[*a*]azulene-9a-carbonitrile (5n). The titled compound was prepared from **3n** by using $Rh_2(oct)_4$ as the catalyst. The reaction proceeded for 24 hours at rt. Chromatographic purification (hexane-EtOAc 12:1, 5:1) afforded **5n** (89%) as a yellow solid. M.p. 221-224 °C; IR (neat) 3013, 2233, 1723, 1596, 762, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.8 Hz, 1 H), 7.74-7.67 (m, 2 H), 7.46 (ddd, *J* = 7.8, 5.6, 2.2 Hz, 1 H), 6.89 (d, *J* = 6.6 Hz, 1 H), 6.66 (d, *J* = 6.6 Hz, 1 H), 6.36 (d, *J* = 9.6 Hz, 1 H), 5.68 (d, *J* = 9.6 Hz, 1 H), 2.21 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 147.4, 142.4, 136.9, 134.6, 133.0, 129.8, 127.7, 126.8, 125.6, 122.2, 120.4, 119.7, 115.1, 48.6, 24.9 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{16}H_{11}NO$: 233.0841; found: 233.0845.

7-Fluoro-10-oxo-9a,10-dihydrobenzo[*a*]azulene-9a-carbonitrile (5o). The titled compound was prepared from **3o** by using $Rh_2(oct)_4$ as the catalyst. The reaction proceeded for 24 hours at rt. Chromatographic purification (hexane-EtOAc 10:1, 5:1) afforded **5o** (97%) as a yellow solid. M.p. 153-155 °C; IR (neat) 3045, 2236, 1729, 1627, 841, 762 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.8 Hz, 1 H), 7.77-7.71 (m, 2 H), 7.55-7.47 (m, 1 H), 6.95 (dd, *J* = 7.5, J_{H-F} = 5.7 Hz, 1 H), 6.62 (ddd, J_{H-F} = 16.5, *J* = 7.5, 1.7 Hz, 1 H), 6.53 (ddd, *J* = 10.1, J_{H-F} = 8.4, *J* = 1.7 Hz, 1 H), 5.90 (dd, *J* = 10.1, J_{H-F} = 5.0 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 162.2 (d, J_{C-F} = 250.4 Hz), 147.0, 137.2, 132.8, 130.3, 126.4 (d, J_{C-F} = 36.9 Hz), 125.8, 125.8, 123.4 (d, J_{C-F} = 13.0 Hz), 122.4, 117.1 (d, J_{C-F} = 11.4 Hz), 114.4, 112.2 (d, J_{C-F} = 28.9 Hz), 48.6 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -92.7 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{15}H_8FNO$: 237.0590; found: 237.0596.

7-Methoxy-10-oxo-9a,10-dihydrobenzo[*a*]azulene-9a-carbonitrile (5p). The titled compound was prepared from **3p** by using $Rh_2(oct)_4$ as the catalyst. The reaction proceeded for 24 hours at rt. Chromatographic purification (hexane-EtOAc 10:1, 5:1) afforded **5p** (quant.) as a yellow oil. IR (neat) 3010, 2234, 1721, 1630, 1596, 1234, 759, 725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.8 Hz, 1 H), 7.72-7.64 (m, 2 H), 7.46-7.38 (m, 1 H), 6.94 (d, *J* = 7.6 Hz, 1 H), 6.39 (dd, *J* = 10.2, 1.8 Hz, 1 H), 6.03 (dd, *J* =7.6, 1.8 Hz, 1 H), 5.84 (d, *J* = 10.2 Hz, 1 H), 3.78 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 161.1, 148.0, 137.0, 132.4, 129.9, 129.2, 125.6, 123.1, 122.5, 121.8, 119.1, 115.1, 103.4, 55.3, 48.4 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{16}H_{11}NO_2$: 249.0790; found: 249.0787.

10-Hydroxy-6-methylphenanthrene-9-carbonitrile (4q) and 10-hydroxy-8-methylphenanthrene-9-carbonitrile (4q'). The titled compounds were prepared from **3q** by using $Rh_2(oct)_4$ as the catalyst. The reaction proceeded for 22 hours at rt. Chromatographic purification (hexane-EtOAc 8:1, 5:1; then EtOAc-MeOH 30:1) afforded **4q** and **4q'** as a regioisomeric mixture (87%; **4q**/**4q'** = 74/26; white solid). M.p. 198-215 °C (mixture); IR (neat) 3262, 2224, 2223, 1614, 1592, 1258, 1228, 763, 751 cm^{-1}; ^1H NMR (400 MHz, DMSO-d6) **4q**: δ 11.64 (br s, 1 H), 8.82 (d, *J* = 8.3 Hz, 1 H), 8.56 (s, 1 H), 8.41 (d, *J* = 8.1 Hz, 1 H), 7.87-7.80 (m, 2 H), 7.77-7.71 (m, 1 H), 7.53 (d, *J* = 8.2 Hz, 1 H), 2.53 (s, 3 H) ppm; **4q'**: δ 11.64 (br s, 1 H), 8.82 (d, *J* = 8.3 Hz, 1 H), 8.66-8.62 (m, 1 H), 8.41 (d, *J* = 8.1 Hz, 1 H), 7.87-7.80 (m, 1 H), 7.77-7.71 (m, 1 H), 7.46-7.44 (m, 2 H), 2.95 (s, 3 H) ppm; ^{13}C NMR (100 MHz, DMSO-d6) **4q**: δ 158.4, 135.4, 132.7, 130.6, 130.6, 127.8, 127.5, 125.8, 125.3, 124.1, 124.0, 123.9, 123.6, 117.1, 90.6, 21.7 ppm; **4q'**: δ 161.4, 133.3, 133.0, 131.9, 130.9, 128.3, 127.9, 126.6, 125.6, 124.6, 124.3, 123.9, 122.4, 119.4, 89.9, 23.3 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{16}H_{11}NO$: 233.0841; found: 233.0836.

6-Chloro-10-hydroxyphenanthrene-9-carbonitrile (4r) and 6-chloro-10-oxo-9a,10-dihydrobenzo[*a*]azulene-9a-carbonitrile (5r). The titled compounds were prepared from **3r** by using $Rh_2(oct)_4$ as the catalyst. The reaction proceeded for 2.5 hours at rt. Chromatographic purification (hexane-EtOAc 10:1, 5:1; then EtOAc-MeOH 30:1, 20:1, 5:1) afforded **4r** (56%) followed by **5r** (44%) as white solids. **4r**: m.p. 307-309 °C; IR (neat) 3229, 2226, 1615, 1589, 813, 767 cm^{-1}; ^1H NMR (400 MHz, DMSO-d6) δ 12.02 (br s, 1 H), 8.89 (d, *J* = 8.3 Hz, 1 H), 8.84 (s, 1 H), 8.44 (d, *J* = 8.0 Hz, 1 H), 7.93-7.84 (m, 2 H), 7.83-7.76 (m, 1 H), 7.74 (d, *J* = 8.7 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, DMSO-d6) δ159.8, 131.9, 131.1, 130.8, 129.2, 128.6, 128.6, 127.0, 126.0, 125.7, 124.5, 124.3, 123.5, 116.8, 90.0 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{15}H_8ClNO$: 253.0294; found: 253.0293. **5r**: m.p. 314-316 °C; IR (neat) 3066, 2238, 1731, 790, 765, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ7.88 (d, *J* = 7.8 Hz, 1 H), 7.80-7.75 (m, 2 H), 7.61-7.53 (m, 1 H), 6.97 (s, 1 H), 6.93 (dd, *J* = 7.0, 0.6 Hz, 1 H), 6.44 (dd, *J* = 9.4, 7.0 Hz, 1 H), 5.73 (d, *J* = 9.4 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 145.8, 137.3, 135.9, 133.5, 131.3, 130.5, 130.0, 129.7, 125.9, 122.9, 121.3, 121.0, 114.3, 48.5 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{15}H_8ClNO$: 253.0294; found: 253.0297.

5-Hydroxyphenanthro[2,3-*d*][1,3]dioxole-6-carbonitrile (4s). The titled compound was prepared from **3s** by using $Rh_2(oct)_4$ as the catalyst. The reaction proceeded for 2.5 hours at rt. Chromatographic purification (hexane-EtOAc 8:1; then EtOAc-MeOH 10:1, 5:1) afforded **4s** (97%) as a white solid. M.p. 287-289 °C; IR (neat) 3269, 2913, 2225, 1592, 1238, 1039, 859, 758 cm^{-1}; ^1H NMR (400 MHz, DMSO-d6) δ 11.51 (br s, 1 H), 8.67 (d, *J* = 8.4 Hz, 1 H), 8.38 (d, *J* = 8.2 Hz, 1 H), 8.23 (s, 1 H), 7.76 (dd, *J* = 8.4, 7.1 Hz, 1 H), 7.65 (dd, *J* = 8.2, 7.1 Hz, 1 H), 7.24 (s, 1 H), 6.20 (s, 2 H) ppm; ^{13}C NMR (100 MHz, DMSO-d6) δ 157.9, 149.3, 147.5, 132.7, 130.4, 126.8, 126.2, 124.2, 124.1, 124.0, 121.3, 117.2, 102.4, 102.4, 101.7, 91.3 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{16}H_9NO_3$: 263.0582; found: 263.0584.

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10-(Methylsulfonyl)phenanthren-9-ol (4t) and phenanthrene-9,10-dione (8). In the typical procedure, the titled compounds were obtained from **3t** by using $Rh_2(oct)_4$ as the catalyst (1 mol%, Scheme 10, b). The reaction mixture was stirred at rt for 24 hours till no consumption of **3s** was shown by TLC analysis. Flash chromatography (hexane-EtOAc 8:1, 6:1) gave **4t** as a pale yellow solid (20%), plus the known[29] compound **8** (16%) and recovered **3t** (52%). **4t**: m.p. 153-155 °C; IR (neat) 3143, 2925, 1612, 1586, 1575, 1289, 1254, 770, 753, 725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.70 (br s, 1 H), 8.66-8.57 (m, 3 H), 8.55 (d, *J* = 8.1 Hz, 1 H), 7.83 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1 H), 7.72-7,63 (m, 2 H), 7.58 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1 H), 3.36 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 133.7, 131.0, 128.4, 127.5, 127.2, 126.4, 125.3, 125.2, 125.1, 123.4, 123.3, 122.5, 108.7, 44.9 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{15}H_{12}O_3S$: 272.0507; found: 272.0509. **8**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 7.6, 1.3 Hz, 2 H), 8.01 (d, *J* = 8.0 Hz, 2 H), 7.71 (ddd, *J* = 8.0, 7.6, 1.3 Hz, 2 H), 7.47 (dd, *J* = 7.6, 7.6 Hz, 2 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 136.0, 135.9, 131.1, 130.5, 129.6, 124.0 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{14}H_8O_2$: 208.0524; found: 208.0519.

10-Tosylphenanthren-9-ol (4u). In the typical procedure, the titled compound was obtained from **3u** by using $Rh_2(oct)_4$ as the catalyst (5 mol%, Scheme 10, d). The reaction mixture was stirred at rt for 24 hours till no consumption of **3u** was shown by TLC analysis. Flash chromatography (hexane-EtOAc 16:1, 10:1, 8:1) gave **4u** as a white solid (11%), along with **8** (17%) and recovered **3u** (15%). **4u**: m.p. 139-142 °C; IR (neat) 3132, 2923, 1611, 1585, 1255, 1123, 760, 724, 594 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.06 (br s, 1 H), 8.62 (d, *J* = 8.3 Hz, 1 H), 8.57 (d, *J* = 8.4 Hz, 1 H), 8.55-8.51 (m, 1 H), 8.41-8.36 (m, 1 H), 7.86 (d, *J* = 8.2 Hz, 2 H), 7.81 (ddd, *J* = 8.4, 7.3, 1.1 Hz, 1 H), 7.69 (ddd, *J* = 8.3, 7.2, 1.1 Hz, 1 H), 7.49-7.42 (m, 2 H), 7.27-7.23 (m, 2 H), 2.35 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 144.6, 139.2, 133.8, 130.9, 130.2, 129.8, 127.8, 127.3, 126.9, 126.7, 126.2, 125.3, 124.9, 123.9, 123.0, 122.5, 108.5, 21.5 ppm; HRMS-EI: *m/z* $[M]^+$ calcd. for $C_{21}H_{16}O_3S$: 348.0820; found: 348.0813.

Procedure for Rh(III)-Catalyzed Reaction of Sulfonyl Diazo Precursors

To a stirred solution of **3t** (44 mg, 0.147 mmol) in 1,2-dichloroethane (15 mL) under N_2 protection, $[Cp^*RhCl_2]_2$ (99%, 2.3 mg, 0.0037 mmol) and $AgSbF_6$ (98%, 5.1 mg, 0.015 mmol) were successively added. The mixture was then stirred for 5 hours at reflux, cooled to rt, and concentrated under reduced pressure. Chromatographic purification of the crude mixture (hexane-EtOAc 12:1, 8:1, 4:1) afforded **4t** in 60% yield (24 mg). The application of the same procedure to **3u** led to the formation of **4u** (56%) and **8** (7%).

Conversion of 4t into 8

$Rh_2(oct)_4$ (24 mg, 0.031 mmol) was added to a stirred solution of **4t** (17 mg, 0.062 mmol) in CH_2Cl_2 (7 mL). The reaction mixture was stirred at rt for 25 hours, and concentrated under vacuo. The residue was subjected to chromatography (hexane-EtOAc 8:1, 4:1) to provide 5.33 mg of **8** (41%).

Conflicts of interest

There are no conflicts to declare.

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