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Solvent and Substituent Effects on the Photochemistry of Norbornadiene-Diarylacetylene Pauson–Khand Adducts

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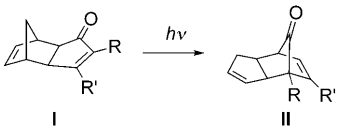
Abstract: The photochemistry of Pauson–Khand cycloadducts of norbornadiene with a series of bis-aryl alkynes has been studied. Two types of photochemical transformation take place: photorearrangement to tricyclic ketones or photochemical 6π electrocyclization. High selectivity levels have been attained for each pathway, controlled by the polarity of the solvent, irradiation wavelength, and presence (or absence) of oxygen.

Keywords: cyclopentenones · electrocyclic reactions · photochemistry · rearrangement · solvent effects

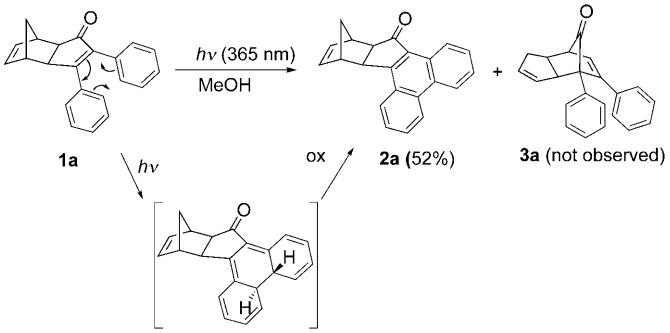
Introduction

Enones[1] are among the most synthetically useful substrates in photochemical reactions because high levels of selectivity are observed in reactions such as [2+2] cycloadditions,[2] rearrangements,[3] and conjugate additions.[4] Some years ago, we reported a novel enone photoreaction by irradiation of cyclopentenones **I** at 365 nm, which afforded the rearranged products **II** in excellent yields[5] (Scheme 1). Cyclopentenones **I** are widely available substrates; they can be obtained in one step by a Pauson–Khand (PK) reaction[6] between norbornadiene and the appropriate acetylene. Compounds **I** are also accessible in enantiomerically enriched form through an asymmetric version of the reaction developed recently by our group.[7]



Scheme 1. Photochemical rearrangement of Pauson–Khand adducts **I**.

This rearrangement is mostly general for norbornadiene PK adducts.[5] The compounds have the *exo* stereochemistry required to prevent the well-known intramolecular [2+2] cycloaddition that occurs in *endo* tricyclic alkenyl enones.[8] Although this novel photorearrangement tolerates a wide variety of functional groups and affords the rearranged products in high yields, irradiation of the PK adduct of diphenylacetylene (**1a**) gives exclusively the phenanthrene derivative **2a**, instead of the expected rearranged product **3a**[5] (Scheme 2). In this case, a stilbene fragment is suitably placed in the *cis* configuration and can undergo conrotatory electrocyclic ring closure to afford **2a** via an unstable dihydrophenanthrene intermediate. It must be pointed out that the aromatization to the thermodynamically favored derivative **2a** takes place without any extra source of oxidant; the most probable oxidative reagent is the oxygen solved in the solution. Several precedents of this 1,6-electrocyclization have been described in the photochemistry of stilbenes,[9] as well as in the synthesis of photochromic compounds.[10] More recently, this type of 6π-electrocycloreversion oxidative aromatization reaction has been reported with norbornene PK adducts of 4-(phenylethynyl)-2-pyrone.[11]



Scheme 2. Electrocyclization of the Pauson–Khand adduct of norbornene and phenylacetylene (**1a**).

Based on the absence of the rearranged product **3a** in the crude reaction mixture, we initiated an exploration of this photochemical reaction to establish the impact of the solvent and irradiation wavelength on the reaction outcome. To pursue the synthesis of the photorearranged product **3a**,

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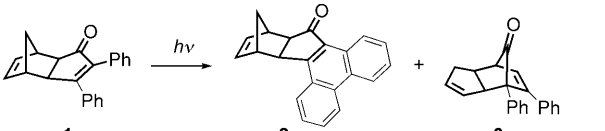
we reasoned that the two possible photochemical pathways (namely rearrangement and electrocyclization) take place through two different mechanistic pathways and, therefore, should be sensitive to the reaction conditions. Here we report a study of the scope of the photochemical transformations of aromatic PK cycloadducts and the optimized conditions that ultimately lead to the formation of either the phenanthrene or the photorearranged products with complete selectivity.

Results and Discussion

For exploratory purposes, we used diphenylacetylene as a benchmark internal symmetric alkyne. As described in our preliminary communication,[5] irradiation of **1a** at 365 nm in methanol afforded the phenanthrene product **2a** (Table 1, entry 1) in a modest 54% yield. Moreover, careful analysis identified a small amount of **3a** (4%) in the crude material. Assuming that oxygen was the oxidant, the reaction was conducted without degassing the solution. Gratifyingly, in non-degassed methanol we obtained **2a** in quantitative yield (Table 1, entry 2). Under irradiation with a shorter wavelength (300 nm) in non-degassed methanol, the same phenanthrene derivative **2a** was formed exclusively, at a higher reaction rate—the reaction time was reduced to half (Table 1, entry 3). In the absence of oxygen (Table 1, entry 4), the reaction gave a poor 30% yield, although the selectivity towards **2a** was still very high. Clearly, in methanol oxygen plays an essential role to obtain high yields but has little influence on the ratio **2a**/**3a**. The addition of benzophenone as triplet sensitizer significantly increased the amount of photorearranged product **3a**, but the selectivity could not be reversed (Table 1, entry 5). This is in agreement with our mechanistic study of the rearrangement,[12] in which we observed that the energy transfer from the benzophenone triplet was not very efficient.

Table 1. Photochemical reactions of Pauson–Khand adduct **1a**, derived from norbornadiene and diphenylacetylene



1a **2a** **3a**

Entry	Solvent	*hν* [nm]	O_2	*t* [h][a]	Conv. [%]	**2a/3a**[b]	Yield[c] [%]
1	MeOH	365	no	15	100	96:4	54
2	MeOH	365	yes	15	100	100:0	quant
3	MeOH	300	yes	7	100	100:0	quant
4	MeOH	300	no	7	100	98:2	30
5	MeOH[d]	365	no	15	100	85:15	n.m.[f]
6	CH_2Cl_2	300	no	120	81	56:44	n.m. [f]
7	CH_2Cl_2	365	no	26	100	4:96	83
8	acetone	365	no	38	100	10:90	80
9	hexane	365	no	72[e]	100	5:95	82

[a] Reactions were performed at 30–35 °C. [b] Ratio measured by ^{1}H NMR spectroscopy of the crude material. [c] Combined yield of **2** and **3**. [d] Benzophenone (1 equiv) was added. [e] Dilute solution due to low solubility of **1a**. [f] Not measured

We then proceeded to study the solvent effect. Photoirradiation of **1a** in non-degassed CH_2Cl_2 afforded mixtures of **2a** and **3a** with very low conversions and selectivities. In these reactions, the amount of solvated oxygen was critical. When we undertook the reaction at 300 nm in degassed CH_2Cl_2 a 1:1 mixture of **2a** and **3a** was obtained, in only 81% conversion after 5 days of irradiation (Table 1, entry 6). Most pleasingly, the reaction performed in degassed CH_2Cl_2 at 365 nm provided photorearranged compound **3a** as the main product (**3a**/**2a** = 96:4, 83%; Table 1, entry 7). Therefore, a strong solvent dependence of the reaction product was clearly revealed in this photochemical transformation. Thus, we concluded that irradiation at 365 nm in degassed CH_2Cl_2 were the best conditions for the photorearrangement to **3a**. Two more solvents were tested. Acetone gave the rearranged product **3a** with a slightly lower selectivity (**3a**/**2a** = 90:10; Table 1, entry 8). Hexane gave similar selectivity to CH_2Cl_2 (Table 1, entry 9), although a much longer reaction time was required because highly diluted solutions (5×10^{-3} M) of the reagent were necessary to overcome poor solubility. On the basis of the above results, we concluded that a shorter wavelength (300 nm) and non-degassed MeOH favor the pericyclic reaction, whereas a longer wavelength (365 nm) and degassed apolar solvents favor the photorearrangement.

To gain a deeper insight into these photochemical processes, we undertook a kinetic study of the photoconversion of **1a** into either **2a** or **3a**. We found that temperature is critical to the pericyclic reaction rate and is even more significant in the photorearrangement. To achieve significant conversion in short reaction times, we performed the kinetic experiments at 50 °C, which forced us to use dichloroethane (DCE) as the solvent instead of CH_2Cl_2.

The plots of the concentration of electrocyclization product **2a** versus time during the initial 3 h of the reaction are shown in Figure 1. The formation of **2a** in MeOH (both degassed and non-degassed) was much faster than in DCE.

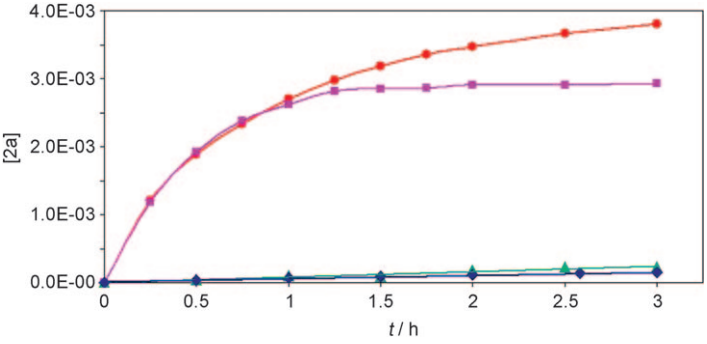


Figure 1. Reaction rates for the electrocyclization of **1a** to **2a**. (λ = 365 nm; initial concentration of **1a** = 4.2×10^{-3} M; ● MeOH non-degassed; ■ MeOH degassed; ▲ DCE non-degassed; ◆ DCE degassed).

Non-degassed MeOH proved to be more advantageous for the pericyclic transformation, not only because the oxidative photocyclized product **2a** was generated efficiently, but also because the formation of **3a** was suppressed (Figure 2). Al-

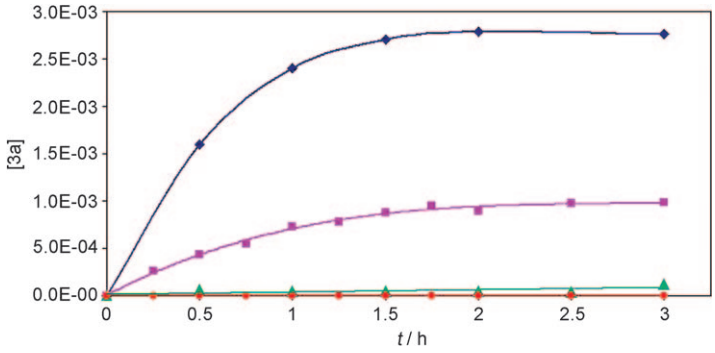


Figure 2. Reaction rates of the photochemical rearrangement of **1a** to **3a**. ($\lambda = 365$ nm; initial concentration of **1a** $= 4.2 \times 10^{-3}$ M; ● MeOH non-degassed; ■ MeOH degassed; ▲ DCE non-degassed; ◆ DCE degassed).

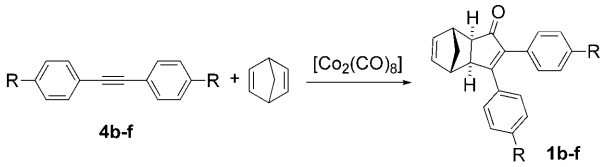
though the reaction took place initially at the same rate in degassed methanol, the reaction could not go further after 1.5 h. At this point, the formation of **3a** became significant (Figure 2). It appears that oxygen was not totally excluded from the solvent by degassing (2 h of nitrogen bubbling), which then allowed initial rapid conversion of **1a** to **2a**. The reaction stopped when all of the oxygen present in the medium was consumed. This behavior indicates that oxygen is required for the dehydrogenation step after the photocyclization.

As illustrated in Figure 2, degassed DCE was clearly the solvent of choice for the formation **3a**. In degassed MeOH, the rearrangement to **3a** was quite slow and the formation of the phenanthrene product **2a** was clearly favored. In non-degassed solvents, the rearrangement was completely inhibited, probably because oxygen acts as efficient triplet quencher.

With suitable reaction conditions identified for both reaction courses, we studied the scope of the reaction. We performed experiments to determine the influence of the substituents in the aromatic ring. First, a set of tricyclic cyclopentenones (**1b–f**) was prepared by stoichiometric intermolecular PK reactions of norbornadiene with a range of diversely substituted alkynes. Symmetrical alkynes **4b–f** were synthesized by following a reported procedure based on Sonogashira couplings between trimethylsilylacetylene and the corresponding iodobenzenes.[13] The stoichiometric PK reactions took place uneventfully to afford compounds **1b–f** in good yields (Table 2). All reactions were promoted thermally except the reaction of the electron-deficient acetylene **4d** (R = CO_2Me), which was activated with *N*-methylmorpholine *N*-oxide (NMO).

Unsymmetrical acetylene **4g** was prepared in a similar fashion, from two different aryl iodides. The thermal PK reaction of **4g** with norbornadiene afforded a mixture of re-

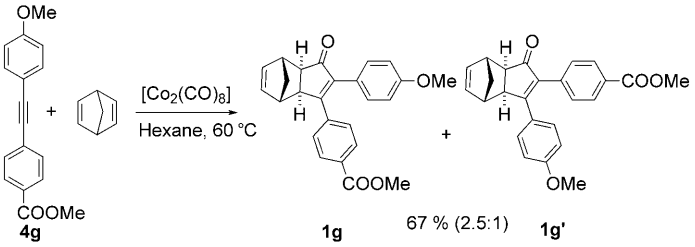
Table 2. Pauson–Khand reaction of norbornadiene with internal aromatic alkynes **1b–f**.



Entry	R	Solvent	T [°C]	t [h]	Product	Yield [%]
1	F	hexane	60	24	**1b**	99
2	Cl	toluene	75	21	**1c**	98
3	CO_2Me	CH_2Cl_2[a]	RT	72[b]	**1d**	56
4	*t*Bu	hexane	60	96	**1e**	77
5	OMe	toluene	60	96	**1f**	69

[a] Activated with NMO. [b] 89% conversion.

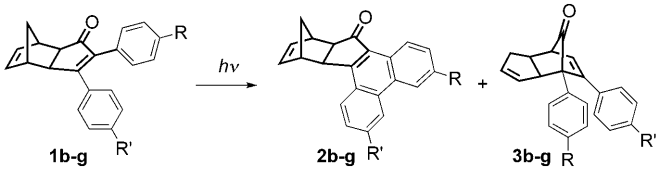
gioisomers **1g** and **1g′** (2.5:1), which were easily separable by chromatography on silica gel. As reported in the literature,[14] the regiochemistry was governed by the electronic nature of the substituents. In the major isomer, the electron-releasing group (ERG) was settled at the α-position, the electron-withdrawing group (EWG) at the β-position (Scheme 3).



Scheme 3. Pauson–Khand reaction of the unsymmetrical diarylacetylene **4g**.

With diaryl PK cycloadducts **1b–g** in hand, we performed a series of photochemical reactions with a range of solvents (CH_2Cl_2, hexane, MeOH) and irradiation wavelengths (300, 365 nm). The results are summarized in Table 3. The corresponding phenanthrene derivatives **2b**, **2c**, and **2e–g** were obtained in quantitative yields with high purity (>95%) when the substrates were irradiated in non-degassed MeOH at 300 nm (Table 3, entries 1–5). The reaction could not be performed with cycloadduct **1d** due to its low solubility in MeOH. Notably, all the products precipitated from the reaction medium and the pure products were isolated after simple filtration. Cycloadducts **1b** and **1c** (R = R' = EWG; Table 3, entries 1 and 2) reacted more slowly than PK adducts **1e** and **1f** (R = R' = ERG; Table 3, entries 3 and 4). Two days were required for the reactions of **1b** and **1c** to reach completion, whereas seven hours were sufficient in the case of **1e**. Remarkably, the reaction of cycloadduct **1f** was very fast and the compound was fully converted into **2f** after three hours of irradiation. We next considered the PK adduct **1g**, which bears an ERG and EWG. The deleterious

Table 3. Photochemical reactions of diaryl Pauson–Khand adducts **1b–g**.



Entry	R	R′	*hν* [nm]	Solvent	*t* [h]	Ratio **2/3**	Product	Yield [%]
1	F	F	300	MeOH[a]	48	100:0	**2b**	quant
2	Cl	Cl	300	MeOH[a]	48	100:0	**2c**	quant
3	*t*Bu	*t*Bu	300	MeOH[a]	7	100:0	**2e**	quant
4	OMe	OMe	300	MeOH[a]	3	100:0	**2f**	quant
5	OMe	CO_2Me	300	MeOH[a]	144	100:0	**2g**	quant
6	F	F	365	CH_2Cl_2[b]	26	0:100	**3b**	quant
7	Cl	Cl	365	CH_2Cl_2[b]	26	0:100	**3c**	quant
8	CO_2Me	CO_2Me	365	CH_2Cl_2[b]	22	0:100	**3d**	68
9	OMe	CO_2Me	365	CH_2Cl_2[b]	72	0:100	**3g**	58[c]
10	CO_2Me	CO_2Me	365	MeOH/ CH_2Cl_2[b]	72	50:50	**2d/3d**	79[d]
11	*t*Bu	*t*Bu	365	CH_2Cl_2[b]	72	40:60	**2e/3e**	47[d]
12	*t*Bu	*t*Bu	365	hexane[b]	72	16:84	**2e/3e**	66[d]
13	OMe	OMe	365	CH_2Cl_2[b]	23	n.d.[e]	**2f**	7

[a] Non-degassed solution. [b] Degassed solution. [c] 26% of starting material (**1g**) was recovered. [d] Combined yield of **2** and **3**. [e] Compound **3f** was not detected by NMR spectroscopy.

effect of the EWG appeared to predominate over the reaction rate because the reaction was slowed down dramatically relative to that of cycloadduct **1f**. The selectivity towards **2g**, however, was complete when working at 300 nm.

In addition, to achieve the most favorable conditions for the rearrangement, PK adducts **1b–g** were irradiated at 365 nm in degassed CH_2Cl_2. The reaction was completely selective for PK adducts **1b–d** and **1g** (Table 3, entries 6–9). Selectivity dropped dramatically when a mixture of solvents was used. Thus, irradiation of **1d** in degassed CH_2Cl_2/MeOH (1:1) at 365 nm gave a 1:1 mixture of **2d** and **3d** (Table 3, entry 10). This result could be attributed to the presence of MeOH. The presence of an ERG on the aryl ring lowered the rate and the selectivity of the reaction (Table 3, entries 11 and 12). For instance, a mixture of **2e** and **3e** was obtained when the cycloadduct **1e**, which bears *tert*-butyl groups at the *para* positions of the aromatic rings, was subjected to irradiation in CH_2Cl_2 at 365 nm (Table 3, entry 11). Interestingly, selectivity in favor of **3e** increased from 40:60 to 16:84 when hexane was used instead of CH_2Cl_2 (Table 3, entry 12). It became clear that ERGs do not favor the photorearrangement, which is almost completely suppressed in the case of methoxy-substituted cycloadduct **1f** (Table 3, entry 13). After 23 h of irradiation, we observed a complex mixture of products, from which only 7% of **2f** could be isolated. In the case of the unsymmetrical PK adduct **1g**, the reaction proceeded at a slow rate (26% of starting material was recovered after 3 days of irradiation), although the photorearranged compound **3g** was the only product observed (Table 3, entry 9).

To explain the experimental findings and rationalize the strong dependence of selectivity on the nature of the solvent, it is necessary to analyze both reaction mechanisms. We have recently reported a detailed theoretical and experimental study of the photorearrangement of compounds **I** into the tricyclic ketones **II**.[12] From this study, it was concluded that, although there is a non-adiabatic pathway that starts on the $^1(n\pi^*)$ potential energy surface (PES), the reaction product is formed through the $^3(\pi\pi^*)$ state, because the energy barrier involved in the initial C–C γ-bond cleavage of the enone is much lower in the $^3(\pi\pi^*)$ PES than in the $^1(n\pi^*)$ PES. The $^3(\pi\pi^*)$ PES can be easily accessed in the reactant region through intersystem crossing (ISC) from the $^1(n\pi^*)$ to the $^3(\pi\pi^*)$ state.

Although a detailed mechanistic study of the transformation of **1** into **2** has not yet been performed, several theoretical and experimental studies on related systems (hexatrienes[15] and diarylethenes[16]) have established that the conrotatory 6π electrocyclization is allowed under photochemical activation and that the reaction occurs in the singlet manifold.[17]

In both reaction pathways, the strong solvent dependence of the photochemical reactions of PK adducts **1** can be explained by the assumption that the 6π electrocyclization to **2** takes place through the $^1(n\pi^*)$ state, whereas the rearrangement to **3** occurs through the $^3(\pi\pi^*)$ state. Consequently, apolar solvents, such as hexanes or CH_2Cl_2, facilitate ISC from the $^1(n\pi^*)$ to the $^3(\pi\pi^*)$ state and strongly favor the rearrangement to **3**. It is well-documented that the ISC rate constant depends strongly on the polarity of the solvent, the rate being higher in less polar solvents.[18] Conversely, because the pericyclic reaction occurs through a singlet excited state it is more favored in polar reaction mediums, such as MeOH,[19] in which the rate of ISC is very low.

Oxygen plays two essential roles: as an enone triplet quencher and an oxidant in the tandem electrocyclization/oxidative aromatization reaction. Thus, oxygen should be present in the medium to favor the pathway to phenanthrene compounds **2**. Conversely, oxygen should be removed from the reaction medium for the photorearrangement to compounds **3** because it quenches the triplet enone through which the transformation occurs.

The effect of the aromatic ring substituents can be easily explained. We assume that ERGs stabilize the $^1(n\pi^*)$ state by acceleration of the 6π-electrocyclization, whereas EWGs displace the electron density, thus disfavoring this process. Our results fully support this interpretation.[20]

Conclusion

We have reported the diverse photochemical behavior of the PK adducts of bis-aryl alkynes **1a–g** in response to several solvents, oxygen, and irradiation wavelengths. Several trends emerge from these experimental results. For degassed CH_2Cl_2, a longer wavelength (365 nm) and an electron-releasing group favor the formation of photorearranged products **3a–g**; for non-degassed MeOH, a shorter wavelength (300 nm) and an electron-withdrawing group are the condi-

tions of choice for the preparation of phenanthrene products **2a–g**. We have recently developed the first asymmetric intermolecular PK reaction for internal symmetric alkynes and it is worth noting that both products **2** and **3** can be obtained in their optically pure form and, in most cases, in high yield and complete selectivity.

Experimental Section

General: All reactions were carried out under nitrogen atmosphere in solvents dried with a solvent purification system (SPS). Chromatographic purifications performed on a Combiflash (Teledyne Isco) automated chromatography system with silica gel Redi*Hep* columns. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded at room temperature on a Varian Mercury 400 spectrometer and were referenced to residual solvent peaks. Signal multiplicities in the ^{13}C NMR spectra have been assigned with the aid of DEPT and HSQC experiments. Melting points were measured by differential scanning calorimetry. Compounds **4b–j** were prepared by described procedures; compounds **1a–c** are known.[7]

General procedure for the photochemical reactions: The PK cycloadduct **1** was dissolved into the volume of solvent necessary to reach a 0.018 M concentration or until a totally homogeneous solution was formed. When stated, the solvent was previously degassed with a stream of bubbling nitrogen for 1 h. The solution was placed into a flask provided with magnetic stirring and irradiated at 365 or 300 nm in a Rayonet-type reactor provided with seven lamps (8 W). The temperature inside the reactor was measured to be 30–35 °C. The reaction was monitored by TLC.

Reaction products **2** precipitated from the reaction mixture. Simple filtration after cooling the solution afforded pure products. In the preparation of rearranged products **3**, the solvent was removed in vacuo and the crude product was purified by flash chromatography.

(1*S,2*S**,6*R**,7*R**)-1,9-Diphenyltricyclo[5.2.1.0^{2,6}]deca-3,8-dien-10-one (3a)**: Following the general procedure, a solution of **1a** (30 mg, 0.10 mmol) in degassed CH_2Cl_2 was irradiated at 365 nm for 26 h. Purification by flash chromatography on SiO_2 (hexanes/AcOEt, gradient elution) afforded both **2a**[5] (1 mg, 3%) and **3a** (24 mg, 80%) as white solids. M.p. 164 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30–2.40 (m, 1H; CH_2), 2.69–2.79 (m, 1H; CH and 1H; CH_2), 3.00 (d, J = 3.9 Hz, 1H; CH), 3.72–3.76 (m, 1H; CH), 5.78–5.85 (m, 2H; CH), 6.79 (d, J = 3.9 Hz, 1H; CH), 6.96–7.00 (m, 2H; CH), 7.07–7.12 (m, 3H; CH), 7.16–7.22 (m, 1H; CH), 7.26–7.31 (m, 2H; CH), 7.35–7.38 ppm (m, 2H; CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.7 (CH_2), 43.2 (CH), 53.0 (CH), 54.7 (CH), 64.0 (C), 126.9 (CH), 127.0 (2×CH), 127.5 (CH), 128.0 (2×CH), 128.2 (2×CH), 128.6 (CH), 128.9 (CH), 130.5 (2×CH), 134.3 (CH), 134.7 (C), 135.8 (C), 149.5 (C), 202.3 ppm (C=O); IR (film): $\tilde{\nu}$ = 3054, 1768, 1496, 1444, 756, 743 cm^{-1}; HRMS (ESI): m/z calcd for $C_{22}H_{19}O$: 299.1430; found: 299.1436 [M+H]$^+$; m/z calcd for $C_{22}H_{22}NO$: 316.1695; found: 316.1693 [M+NH_4]$^+$; m/z calcd for $C_{22}H_{18}ONa$: 321.1249; found: 321.1250 [M+Na]$^+$; elemental analysis calcd (%) for $C_{22}H_{18}O\cdot{}^1/_5H_2O$: C 87.50, H 6.14; found: C 87.77, H 6.14.

(9a*S,10*S**,13*R**,13a*R**)-3,6-Bis(fluoro)-10,13-methano-9a,10,13,13a-tetrahydro-[9*H*]-indeno[1,2-*l*]phenanthren-9-one (2b)**: Following the general procedure, a solution of **1b** (50 mg, 0.15 mmol) in MeOH was irradiated at 300 nm for 2 d. Filtration afforded **2b** (50 mg, quant) as a white solid. M.p. 198 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13 (d, J = 9.5 Hz, 1H; CH_2), 1.44 (d, J = 9.5 Hz, 1H; CH_2), 2.82 (d, J = 5.6 Hz, 1H; CH), 3.14 (s, 1H; CH), 3.22 (s, 1H; CH), 3.64 (d, J = 5.5 Hz, 1H; CH), 6.40 (dd, J = 5.5, 2.9 Hz, 1H; CH), 6.52 (dd, J = 5.5, 2.9 Hz, 1H; CH), 7.46 (dt, J = 8.7, 2.4 Hz, 1H; CH), 7.51 (dt, J = 8.5, 2.4 Hz, 1H; CH), 8.11 (dd, J = 10.8, 2.5 Hz, 1H; CH), 8.19 (dd, J = 10.8, 2.4 Hz, 1H; CH), 8.30 (dd, J = 8.9, 5.9 Hz, 1H; CH), 9.33 ppm (dd, J = 9.0, 6.2 Hz, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.7 (CH_2), 44.6 (CH), 45.3 (CH), 45.9 (CH), 55.1 (CH), 108.4 (d, J(C,F) = 22.5 Hz; CH), 109.6 (d, J(C,F) = 22.7 Hz; CH), 117.0 (d, J(C,F) = 23.7 Hz; CH), 117.7 (d, J(C,F) = 22.8 Hz; CH), 124.6 (d, J(C,F) = 1.7 Hz; C), 125.8 (d, J(C,F) = 1.7 Hz; C), 127.7 (d, J(C,F) = 8.6 Hz; CH), 128.5 (d, J(C,F) = 9.3 Hz; CH), 131.8 (dd, J(C,F) = 8.2, 4.0 Hz; C), 132.8 (C), 135.4 (dd, J(C,F) = 8.7, 4.0 Hz; C), 138.1 (CH), 138.6 (CH), 158.0 (C), 162.0 (d, J(C,F) = 247.5 Hz; C), 163.8 (d, J(C,F) = 251.3 Hz; C), 207.4 ppm (C=O); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −111.9 (br), −107.9 ppm (br); IR (film): $\tilde{\nu}$ = 2974, 1691, 1620, 1514, 1406, 1175 cm^{-1}; HRMS (ESI): m/z calcd for $C_{22}H_{15}F_2O$: 333.1091; found: 333.1083 [M+H]$^+$; elemental analysis calcd (%) for $C_{22}H_{14}F_2O\cdot{}^1/_3H_2O$: C 78.10, H 4.37; found: C 78.20, H 4.34.

(1*S,2*S**,6*R**,7*R**)-1,9-Bis(4-fluorophenyl)tricyclo[5.2.1.0^{2,6}]deca-3,8-dien-10-one (3b)**: Following the general procedure, a solution of **1b** (37 mg, 0.11 mmol) in CH_2Cl_2 was irradiated at 365 nm for 26 h. Purification by flash chromatography on SiO_2 (hexanes/AcOEt, gradient elution) afforded **3b** (37 mg, quant) as a white solid. M.p. 151 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.28–2.40 (m, 1H; CH_2), 2.68–2.80 (m, 1H; CH and 1H; CH_2), 3.00 (d, J = 3.9 Hz, 1H; CH), 3.65–3.73 (m, 1H; CH), 5.70–5.76 (m, 1H; CH), 5.79–5.84 (m, 1H; CH), 6.75 (d, J = 3.9 Hz, 1H; CH), 6.77–6.84 (m, 2H; CH), 6.87–6.94 (m, 2H; CH), 6.96–7.04 (m, 2H; CH), 7.29–7.35 ppm (m, 2H; CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.7 (CH_2), 43.1 (CH), 53.2 (CH), 54.6 (CH), 63.4 (C), 115.1 (d, J(C,F) = 18.8 Hz, 2×CH), 115.4 (d, J(C,F) = 18.5 Hz, 2×CH), 128.4 (CH), 128.7 (d, J(C,F) = 1.0 Hz; CH), 128.8 (d, J(C,F) = 8.1 Hz, 2×CH), 130.5 (d, J-(C,F) = 3.3 Hz; C), 131.8 (d, J(C,F) = 3.4 Hz; C), 131.9 (d, J(C,F) = 7.9 Hz, 2×CH), 134.7 (CH), 148.4 (C), 161.8 (d, J(C,F) = 246.3 Hz; C), 162.3 (d, J(C,F) = 247.7 Hz; C), 201.9 ppm (C=O); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −114.5 (br), −115.65 ppm (br); IR (film): $\tilde{\nu}$ = 2909, 1775, 1511, 1226, 1160, 813 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{16}F_2O$ (334.36): C 79.03, H 4.82; found: C 78.81, H 4.84.

(9a*S,10*S**,13*R**,13a*R**)-3,6-Dichloro-10,13-methano-9a,10,13,13a-tetrahydro-[9*H*]-indeno[1,2-*l*]phenanthren-9-one (2c)**: Following the general procedure, a solution of **1c** (50 mg, 0.14 mmol) in MeOH was irradiated at 300 nm for 2 d. Filtration afforded **2c** (50 mg, quant) as a white solid. M.p. 213 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (d, J = 9.5 Hz, 1H; CH_2), 1.44 (d, J = 9.5 Hz, 1H; CH_2), 2.83 (d, J = 5.6 Hz, 1H; CH), 3.13 (s, 1H; CH), 3.22 (s, 1H; CH), 3.63 (d, J = 5.6 Hz, 1H; CH), 6.40 (dd, J = 5.5, 2.9 Hz, 1H; CH), 6.52 (dd, J = 5.5, 3.0 Hz, 1H; CH), 7.67 (dd, J = 8.8, 2.0 Hz, 1H; CH), 7.71 (dd, J = 8.6, 1.9 Hz, 1H; CH), 8.22 (d, J = 8.6 Hz, 1H; CH), 8.50 (d, J = 1.9 Hz, 1H; CH), 8.58 (d, J = 1.8 Hz, 1H; CH), 9.25 ppm (d, J = 8.8 Hz, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.6 (CH_2), 45.4 (CH), 45.9 (CH), 55.2 (CH), 122.6 (CH), 123.8 (CH), 126.2 (C), 126.8 (CH), 127.3 (C), 127.4 (CH), 128.5 (CH), 129.4 (CH), 130.8 (C), 133.4 (C), 134.0 (C), 134.0 (C), 136.9 (C), 138.1 (CH), 138.6 (CH), 158.6 (C), 207.3 ppm (C=O); IR (film): $\tilde{\nu}$ = 2976, 1695, 1604, 1514, 1400, 1175 cm^{-1}; HRMS (ESI): m/z calcd for $C_{22}H_{15}Cl_2O$: 365.0500; found: 365.0491 [M+H]$^+$; elemental analysis calcd (%) for $C_{22}H_{14}Cl_2O\cdot{}^1/_4H_2O$: C 71.46, H 3.95; found: C 71.39, H 3.90.

(1*S,2*S**,6*R**,7*R**)-1,9-Bis(4-chlorophenyl)tricyclo[5.2.1.0^{2,6}]deca-3,8-dien-10-one (3c)**: Following the general procedure, a solution of **1c** (45 mg, 0.12 mmol) in CH_2Cl_2 was irradiated at 365 nm for 26 h. Purification by flash chromatography on SiO_2 (hexanes/AcOEt, gradient elution) afforded **3c** (45 mg, quant) as a white solid. M.p. 177 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.28–2.38 (m, 1H; CH_2), 2.68–2.79 (m, 1H; CH and 1H; CH_2), 3.01 (d, J = 3.9 Hz, 1H; CH), 3.65–3.70 (m, 1H; CH), 5.70–5.73 (m, 1H; CH), 5.79–5.83 (m, 1H; CH), 6.79 (d, J = 3.9 Hz, 1H; CH), 6.85–6.91 (m, 2H; CH), 7.07–7.13 (m, 2H; CH), 7.28 ppm (s, 4H; CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.7 (CH_2), 43.1 (CH), 53.1 (CH), 54.6 (CH), 63.4 (C), 128.3 (CH), 128.3 (2×CH), 128.5 (2×CH), 128.6 (2×CH), 129.3 (CH), 131.7 (2×CH), 133.1 (C), 133.1 (C), 133.7 (C), 134.0 (C), 134.8 (CH), 148.1 (C), 201.4 ppm (C=O); IR (film): $\tilde{\nu}$ = 2901, 1774, 1493, 1092, 1013, 802 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{16}Cl_2O$ (367.27): C 71.95, H 4.39; found: C 71.91, H 4.41.

(9a*S,10*S**,13*R**,13a*R**)-3,6-Bis(methoxycarbonyl)-10,13-methano-9a,10,13,13a-tetrahydro-[9*H*]-indeno[1,2-*l*]phenanthren-9-one (2d)**: Following the general procedure, a solution of **1d** (72 mg, 0.17 mmol) in MeOH (plus a small amount of CH_2Cl_2 to achieve a totally homogeneous solution) was irradiated at 365 nm for 3 d. Purification by flash chromatography on SiO_2 (hexanes/AcOEt, gradient elution) afforded **2d** (27 mg, 39%) as a yellow solid and **3d** (28 mg, 40%) as a white solid. M.p. 246 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (d, J = 9.5 Hz, 1H; CH_2),

1.46 (d, $J=9.6$ Hz, 1H; CH_2), 2.88 (d, $J=5.6$ Hz, 1H; CH), 3.20 (br, 1H; CH), 3.26 (br, 1H; CH), 3.73 (d, $J=5.6$ Hz, 1H; CH), 4.06 (s, 3H; CH_3), 4.09 (s, 3H; CH_3), 6.42 (dd, $J=5.5$, 3.0 Hz, 1H; CH), 6.56 (dd, $J=5.6$, 3.0 Hz, 1H; CH), 8.34 (dd, $J=8.5$, 1.6 Hz, 1H; CH), 8.35 (d, $J=0.9$ Hz, 1H; CH), 9.38 (d, $J=8.4$ Hz, 1H; CH), 9.46 (d, $J=1.5$ Hz, 1H; CH), 9.52 ppm (brs, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=42.7$ (CH_2), 44.8 (CH), 45.4 (CH), 46.2 (CH), 52.7 (CH_3), 52.9 (CH_3), 55.2 (CH), 125.1 (CH), 125.4 (CH), 126.1 (CH), 126.3 (CH), 127.8 (CH), 128.8 (CH), 129.1 (C), 130.3 (C), 130.6 (C), 131.5 (C), 131.6 (C), 133.5 (C), 134.9 (C), 138.1 (CH), 138.7 (CH), 160.4 (C), 166.9 (C=O), 167.2 (C=O), 207.4 ppm (C=O); IR (film): $\tilde{\nu}=2963$, 1691, 1614, 1409, 1263, 827 cm^{-1}; HRMS (ESI): m/z calcd for $C_{26}H_{21}O_5$: 413.1383; found: 413.1370 $[M+H]^+$, m/z calcd for $C_{52}H_{41}O_{10}$: 825.2694; found: 825.2674 $[2M+H]^+$; m/z calcd for $C_{52}H_{44}NO_{10}$: 842.2959; found: 842.2929 $[2M+NH_4]^+$.

(1*S,2*S**,6*R**,7*R**)-1,9-Bis(4-methoxycarbonylphenyl)tricyclo[5.2.1.0^{2,6}]deca-3,8-dien-10-one (3d)**: Following the general procedure, a solution of **1d** (41 mg, 0.10 mmol) in CH_2Cl_2 was irradiated for 22 h. Purification by flash chromatography on SiO_2 (hexanes/AcOEt, gradient elution) afforded **3d** (28 mg, 68%) as a white solid. M.p. 189 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=2.35$–2.45 (m, 1H; CH_2), 2.72–2.82 (m, 1H; CH and 1H; CH_2), 3.07 (d, $J=3.9$ Hz, 1H; CH), 3.75–3.80 (m, 1H; CH), 3.84 (s, 3H; CH_3), 3.89 (s, 3H; CH_3), 5.76–5.86 (m, 2H; CH), 6.92 (d, $J=3.9$ Hz, 1H; CH), 7.02 (d, $J=8.5$ Hz, 2H; CH), 7.43 (d, $J=8.5$ Hz, 2H; CH), 7.76 (d, $J=8.5$ Hz, 2H; CH), 7.96 ppm (d, $J=8.5$ Hz, 2H; CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=36.7$ (CH_2), 43.1 (CH), 52.2 (2×CH_3), 52.9 (CH), 54.8 (CH), 64.2 (C), 126.9 (2×CH), 128.3 (CH), 128.9 (C), 129.2 (C), 129.5 (2×CH), 129.6 (2×CH), 130.5 (2×CH), 130.6 (CH), 135.0 (CH), 139.8 (C), 139.9 (C), 148.3 (C), 166.8 (C=O), 167.0 (C=O), 200.9 ppm (C=O); IR (film): $\tilde{\nu}=2943$, 1779, 1722, 1610, 1435, 1281 cm^{-1}; HRMS (ESI): m/z calcd for $C_{26}H_{23}O_5$: 415.1540; found: 415.1540 $[M+H]^+$, m/z calcd for $C_{26}H_{22}O_5Na$: 437.1359; found: 437.1361 $[M+Na]^+$; m/z calcd for $C_{52}H_{45}O_{10}$: 829.3007; found: 829.3019 $[2M+H]^+$; m/z calcd for $C_{52}H_{44}O_{10}Na$: 851.2827; found: 851.2834 $[2M+Na]^+$; elemental analysis calcd (%) for $C_{26}H_{22}O_5\cdot{}^1/_4H_2O$: C 74.54, H 5.41; found: C 74.83, H 5.39.

(9a*S,10*S**,13*R**,13a*R**)-3,6-Bis(*tert*-butyl)-10,13-methano-9a,10,13,13a-tetrahydro-[9*H*]-indeno[1,2-*l*]phenanthren-9-one (2e)**: Following the general procedure, a solution of **1e** (60 mg, 0.15 mmol) in MeOH was irradiated at 300 nm for 7 h. Filtration afforded **2e** (60 mg, quant) as a yellow solid. M.p. 185 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.14$ (d, $J=9.3$ Hz, 1H; CH_2), 1.39 (d, $J=9.6$ Hz, 1H; CH_2), 1.51 (s, 9H; CH_3), 1.54 (s, 9H; CH_3), 2.86 (d, $J=5.5$ Hz, 1H; CH), 3.18 (br, 1H; CH), 3.20 (br, 1H; CH), 3.66 (d, $J=5.6$ Hz, 1H; CH), 6.38 (dd, $J=5.6$, 2.9 Hz, 1H; CH), 6.52 (dd, $J=5.5$, 3.0 Hz, 1H; CH), 7.76–7.81 (m, 2H; CH), 8.23 (d, $J=8.5$ Hz, 1H; CH), 8.66 (d, $J=1.9$ Hz, 1H; CH), 8.74 (d, $J=1.8$ Hz, 1H; CH), 9.22 ppm (d, $J=8.6$ Hz, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=31.5$ (3×CH_3), 31.6 (3×CH_3), 35.4 (C), 35.7 (C), 42.6 (CH_2), 44.5 (CH), 45.3 (CH), 45.9 (CH), 55.1 (CH), 118.1 (CH), 119.3 (CH), 124.9 (CH), 125.3 (CH), 125.6 (C), 125.8 (CH), 126.4 (CH), 126.7 (C), 130.3 (C), 133.8 (C), 134.0 (C), 138.0 (CH), 138.7 (CH), 150.0 (C), 153.1 (C), 158.6 (C), 207.9 ppm (C=O); IR (film): $\tilde{\nu}=2963$, 1691, 1614, 1409, 1263, 827 cm^{-1}; HRMS (ESI): m/z calcd for $C_{30}H_{33}O$: 409.2525; found: 409.2516 $[M+H]^+$, m/z calcd for $C_{60}H_{65}O_2$: 817.4979; found: 817.4971 $[2M+H]^+$.

(1*S,2*S**,6*R**,7*R**)-1,9-Bis(4-*tert*-butylphenyl)tricyclo[5.2.1.0^{2,6}]deca-3,8-dien-10-one (3e)**: Following the general procedure, a solution of **1e** (248 mg, 0.60 mmol) in CH_2Cl_2 was irradiated for 3 d. Purification by flash chromatography on SiO_2 (hexanes/AcOEt, gradient elution) provided **2e** (46 mg, 19%) as a yellow solid and **3e** (69 mg, 28%) as a white solid. M.p. 153 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.21$ (s, 9H; CH_3), 1.28 (s, 9H; CH_3), 2.28–2.38 (m, 1H; CH_2), 2.66–2.74 (m, 1H; CH and 1H; CH_2), 2.97 (d, $J=3.9$ Hz, 1H; CH), 3.69–3.74 (m, 1H; CH), 5.78 (dd, $J=5.8$, 1.9 Hz, 1H; CH), 5.87 (dd, $J=5.8$, 2.1 Hz, 1H; CH), 6.79 (d, $J=3.9$ Hz, 1H; CH), 6.92 (d, $J=8.4$ Hz, 2H; CH), 7.10 (d, $J=8.5$ Hz, 2H; CH), 7.27–7.33 ppm (m, 4H; CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=31.3$ (3×CH_3), 31.5 (3×CH_3), 34.6 (2×C), 36.7 (CH_2), 43.4 (CH), 52.8 (CH), 54.5 (CH), 63.6 (C), 124.9 (2×CH), 125.2 (2×CH), 126.5 (2×CH), 127.8 (CH), 129.2 (CH), 130.2 (2×CH), 131.6 (C), 132.8 (C), 134.1 (CH), 149.1 (C), 149.6 (C), 150.4 (C), 203.1 ppm (C=O); IR (film): $\tilde{\nu}=2961$, 1776, 1518, 1363, 1269, 837 cm^{-1}; HRMS (ESI): m/z calcd for $C_{30}H_{35}O$: 411.2682; found: 411.2685 $[M+H]^+$; m/z calcd for $C_{30}H_{38}NO$: 428.2947; found: 428.2951 $[M+NH_4]^+$; m/z calcd for $C_{60}H_{72}NO_2$: 838.5557; found: 838.5555 $[2M+NH_4]^+$; elemental analysis calcd (%) for $C_{30}H_{34}O\cdot H_2O$: C 84.07, H 8.47; found: C 84.15, H 8.29.

(9a*S,10*S**,13*R**,13a*R**)-3,6-Bis(methoxy)-10,13-methano-9a,10,13,13a-tetrahydro-[9*H*]-indeno[1,2-*l*]phenanthren-9-one (2f)**: Following the general procedure, a solution of **1f** (55 mg, 0.15 mmol) in MeOH was irradiated at 300 nm for 3 h. Filtration afforded **2f** (55 mg, quant) as a yellow solid. M.p. 221 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.15$ (d, $J=9.4$ Hz, 1H; CH_2), 1.40 (d, $J=9.4$ Hz, 1H; CH_2), 2.78 (d, $J=5.6$ Hz, 1H; CH), 3.13 (s, 1H; CH), 3.19 (s, 1H; CH), 3.61 (d, $J=5.6$ Hz, 1H; CH), 4.02 (s, 3H; CH_3), 4.06 (s, 3H; CH_3), 6.38 (dd, $J=5.6$, 3.0 Hz, 1H; CH), 6.50 (dd, $J=5.5$, 3.0 Hz, 1H; CH), 7.33 (dd, $J=3.9$, 2.5 Hz, 1H; CH), 7.35 (dd, $J=3.8$, 2.6 Hz, 1H; CH), 7.94 (d, $J=2.5$ Hz, 1H; CH), 7.98 (d, $J=2.4$ Hz, 1H; CH), 8.20 (d, $J=8.9$ Hz, 1H; CH), 9.24 ppm (d, $J=9.0$ Hz, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=42.7$ (CH_2), 44.4 (CH), 45.4 (CH), 45.8 (CH), 55.1 (CH), 55.7 (CH_3), 55.8 (CH_3), 105.5 (CH), 105.8 (CH), 116.9 (CH), 117.1 (CH), 122.5 (C), 123.5 (C), 126.8 (CH), 127.8 (CH), 131.5 (C), 131.7 (C), 135.3 (C), 138.0 (CH), 138.6 (CH), 157.2 (C), 158.7 (C), 161.0 (C), 207.5 ppm (C=O); IR (film): $\tilde{\nu}=2933$, 1680, 1612, 1514, 1402, 1236 cm^{-1}; HRMS (ESI): m/z calcd for $C_{24}H_{21}O_3$: 357.1485; found: 357.1486 $[M+H]^+$; m/z calcd for $C_{48}H_{41}O_6$: 713.2898; found: 713.2899 $[2M+H]^+$; elemental analysis calcd (%) for $C_{24}H_{20}O_3\cdot{}^1/_2H_2O$: C 78.88, H 5.79; found: C 78.75, H 5.67.

(9a*S,10*S**,13*R**,13a*R**)-3-Methoxycarbonyl-6-methoxy-10,13-methano-9a,10,13,13a-tetrahydro-[9*H*]-indeno[1,2-*l*]phenanthren-9-one (2g)**: Following the general procedure, a solution of **1g** (40 mg, 0.10 mmol) in MeOH was irradiated at 300 nm for 6 d. Filtration afforded **2g** (40 mg, quant) as a yellow solid. M.p. 221 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.13$ (d, $J=9.5$ Hz, 1H; CH_2), 1.42 (d, $J=9.5$ Hz, 1H; CH_2), 2.82 (d, $J=5.6$ Hz, 1H; CH), 3.15 (s, 1H; CH), 3.22 (s, 1H; CH), 3.64 (d, $J=5.6$ Hz, 1H; CH), 4.05 (s, 3H; CH_3), 4.07 (s, 3H; CH_3), 6.39 (dd, $J=5.6$, 2.9 Hz, 1H; CH), 6.53 (dd, $J=5.5$, 3.0 Hz, 1H; CH), 7.36 (dd, $J=9.0$, 2.5 Hz, 1H; CH), 8.08 (d, $J=2.5$ Hz, 1H; CH), 8.30 (br, 2H; CH), 9.23 (d, $J=9.0$ Hz, 1H; CH), 9.33 ppm (s, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=42.7$ (CH_2), 44.7 (CH), 45.2 (CH), 45.8 (CH), 52.7 (CH_3), 55.2 (CH), 55.8 (CH_3), 105.1 (CH), 118.0 (CH), 122.1 (C), 126.0 (CH), 126.1 (CH), 126.8 (CH), 127.1 (CH), 130.4 (C), 131.8 (C), 132.5 (C), 132.8 (C), 135.3 (C), 138.0 (CH), 138.8 (CH), 155.7 (C), 159.4 (C), 167.1 (C=O), 208.0 ppm (C=O); IR (film): $\tilde{\nu}=2923$, 1720, 1691, 1515, 1256, 762 cm^{-1}; HRMS (ESI): m/z calcd for $C_{25}H_{21}O_4$: 385.1440; found: 385.1435 $[M+H]^+$; m/z calcd for $C_{50}H_{40}O_8Na$: 791.2621; found: 791.2635 $[2M+Na]^+$; elemental analysis calcd (%) for $C_{25}H_{20}O_4\cdot{}^1/_3H_2O$: C 76.91, H 5.34; found: C 76.89, H 5.26.

(1*S,2*S**,6*R**,7*R**)-1-(4-Methoxyphenyl)-9-(4-methoxycarbonylphenyl)-tricyclo[5.2.1.0^{2,6}]deca-3,8-dien-10-one (3g)**: Following the general procedure, a solution of **1g** (50 mg, 0.13 mmol) in CH_2Cl_2 was irradiated for 3 d. Purification by flash chromatography on SiO_2 (hexanes/AcOEt, gradient elution) afforded **3g** (29 mg, 58%) as a white solid and **1g** (26%). M.p. 192 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=2.29$–2.40 (m, 1H; CH_2), 2.69–2.79 (m, 1H; CH and 1H; CH_2), 3.02 (d, $J=4.0$ Hz, 1H; CH), 3.70–3.73 (m, 1H; CH), 3.76 (s, 3H; CH_3), 3.85 (s, 3H; CH_3), 5.81 (s, 2H; CH), 6.84 (d, $J=8.8$ Hz, 2H; CH), 6.90 (d, $J=4.0$ Hz, 1H; CH), 7.06 (d, $J=8.5$ Hz, 2H; CH), 7.26 (d, $J=8.8$ Hz, 2H; CH), 7.78 ppm (d, $J=8.5$ Hz, 2H; CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=36.7$ (CH_2), 43.2 (CH), 52.2 (CH_3), 53.1 (CH), 54.7 (CH), 55.3 (CH_3), 63.4 (C), 113.9 (2×CH), 126.3 (C), 126.9 (2×CH), 128.8 (CH), 128.9 (C), 129.4 (2×CH), 130.3 (CH), 131.4 (2×CH), 134.4 (CH), 140.3 (C), 148.7 (C), 158.6 (C), 166.9 (C=O), 202.4 ppm (C=O); IR (film): $\tilde{\nu}=2953$, 1773, 1721, 1609, 1516, 1282 cm^{-1}; HRMS (ESI): m/z calcd for $C_{25}H_{21}O_4$: 387.1591; found: 387.1593 $[M+H]^+$; m/z calcd for $C_{55}H_{44}O_8Na$: 773.3109; found: 773.3112 $[2M+H]^+$; m/z calcd for $C_{55}H_{44}O_8Na$: 795.2928; found: 791.2933 $[2M+Na]^+$; elemental analysis calcd (%) for $C_{25}H_{22}O_4\cdot{}^1/_4H_2O$: C 76.81, H, 5.80; found: C 76.61, H 5.74.

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