Prayogik Rasayan

Approaches to benzanthrones *via* anthrone-derived Morita−Baylis−Hillman adducts of nitroalkenes

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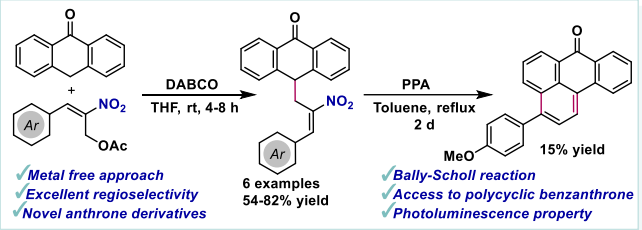
Abstract



Herein, we report the synthesis of novel anthrone-derived Morita−Baylis−Hillman (MBH) adducts of nitroalkenes. The reaction proceeds through two consecutive S_N2' additions of anthrone to MBH acetates of nitroalkenes, leading to the formation of allyl arylated anthrones. Further, we attempted a subsequent Friedel-Crafts type cyclization (Bally-Scholl reaction) to synthesize substituted benzanthrones, though with limited success.

Keywords: Morita−Baylis−Hillman reaction, nitroalkene, anthrone, benzanthrone

1. Introduction

Anthrone **1**, a cyclic ketone, is well-known for its ability to detect carbohydrates.[1,2] Chemically, it exists in a tautomeric mixture of keto and enol forms, where the keto form is prevalent as it has a greater number of π-aromatic sextet and is attributed to Clar's rule (Figure 1).[3]

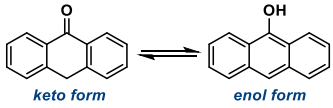


Figure 1. Keto-enol equilibrium of anthrone

The anthrone skeleton is present in various biologically relevant compounds, such as barbaloin, rheinosides A–D, palmidin A-C *etc* (Figure 2) and it exhibits important pharmacological properties *viz.* antioxidant, anti-tumour, anti-inflammatory, anti-viral, anti-diabetic, anti-microbial, *etc.*[4,5]

Anthrone **1** has been used in Lewis acid catalyzed coupling reactions,[6] Michael additions,[7,8] as diene in the Diels-Alder reactions[9] and as a precursor for simple unsubstituted benzanthrone synthesis.[10] But, surprisingly, its reaction with the Morita−Baylis−Hillman (MBH) adducts remains unexplored. In 2004, our group pioneered the MBH reaction of conjugated nitroalkenes.[11] In subsequent years, we and others have been actively engaged in the development of diverse MBH reactions of nitroalkenes and have exploited those newly synthesized MBH adducts to prepare value-added building blocks.[12-15] Recently, we introduced CTAB as a surfactant that successfully shortened the reaction time of the MBH reaction of dicyclopentadienone with formaldehyde.[16] It is worth noting that nucleophilic bases such as DABCO, imidazole *etc* are frequently used as catalysts for synthesizing the MBH adducts, but we have recently reported a base and catalyst-free MBH reaction of enaminonitroalkenes taking advantage of their push-pull effect.[17]

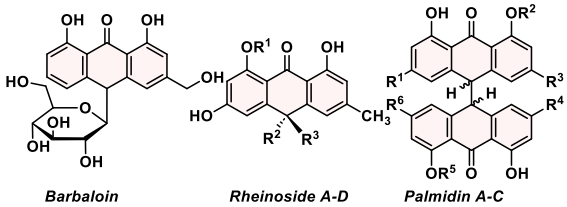


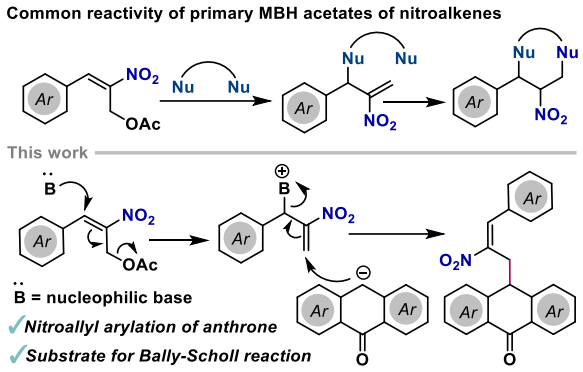
Figure 2. Biologically active compounds containing anthrone

In our previous studies on primary MBH acetates of nitroalkenes, we observed that an external binucleophile displaces the acetate group first, and in the next step, the second nucleophilic moiety targets the newly formed olefinic moiety, resulting in the formation of a carbocycle or heterocycle (Scheme 1).[12-15]

We envisioned that anthrone **1** would function as a potential binucleophile involving its active methylene carbon and the oxygen of the carbonyl group, leading to an allylic arylation *via* two consecutive S_N2' displacement.

2. Results and discussion

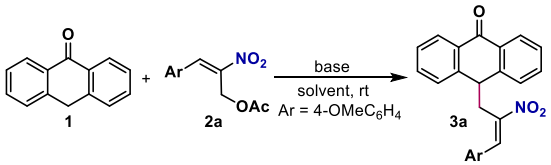
At the outset, we performed a model reaction between anthrone **1** and MBH acetate of nitroalkene **2a** in the presence of a mild base, *viz.* DABCO (1.0 equiv) in THF as solvent at room temperature. We isolated the product **3a** in excellent yield (82%, Table 1, entry 1). The product **3a** was



Scheme 1. General reactivity of MBH acetates vs. this work

characterized as a single regioisomeric allylic arylated product of anthrone **1**, which was formed presumably *via* two consecutive S_N2' additions on the bi-electrophilic MBH acetate **2a**. This result prompted us to screen different conditions to improve the result. We isolated 78% of the product **3a** in comparatively lesser reaction time (4 h) when K_2CO_3 was employed instead of DABCO, whereas Cs_2CO_3 took more than 24 h to complete the reaction, and the yield dropped considerably to 65% (entries 2-3). The stronger bases, such as TMG, piperidine, and NaOH, provided only complex mixtures (entries 4-6). To examine the role of solvent, we attempted the reaction using DABCO in different solvents. In the case of dichloromethane (DCM) as solvent, we observed

Table 1. Optimization of the reaction conditions[a]



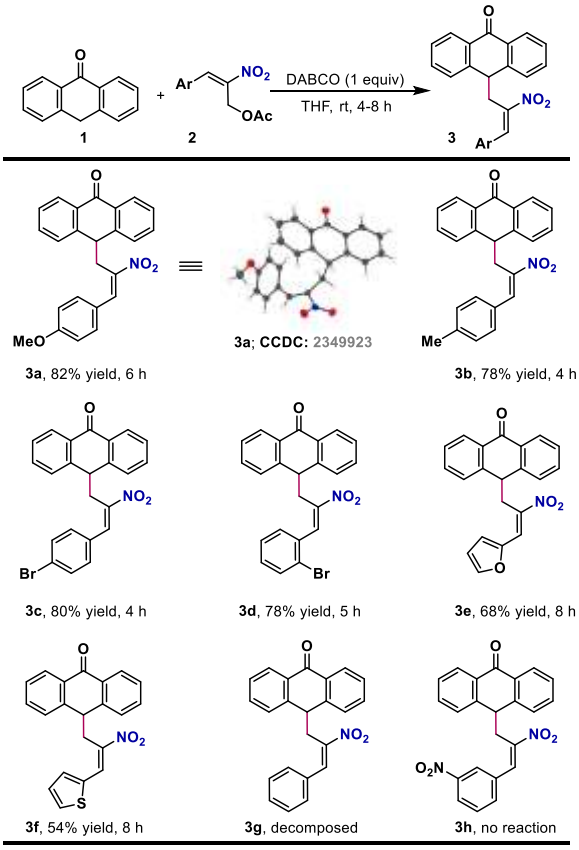
Entry	Base (1 equiv)	Solvent	Time (h)	Yield (%)[b]
1	**DABCO**	**THF**	**5**	**82**
2	K_2CO_3	THF	4	78
3	Cs_2CO_3	THF	24	65
4	TMG	THF	8	Complex mixture
5	Piperidine	THF	10	Complex mixture
6	NaOH	THF	8	Complex mixture
7	DABCO	DCM	8	63
8	DABCO	toluene	10	57
9	DABCO	CH_3CN	2.5	80
10	DABCO	MeOH	6.5	75

[a]Reaction scale: anthrone **1** (0.1 mmol), MBH acetate **2a** (0.12 mmol), solvent (2 mL). [b]After silica-gel column chromatography.

63% product, whereas the yield dropped further to 57% when toluene was used (entries 7-8). However, a yield comparable to that of entry 1 was achieved when acetonitrile was opted as solvent (80%, entry 9). Good yield of the product was obtained in a protic solvent MeOH as well (75%, entry 10). Finally, DABCO in THF was chosen as the optimum condition for the reaction in terms of reaction time and product yield (entry 1).

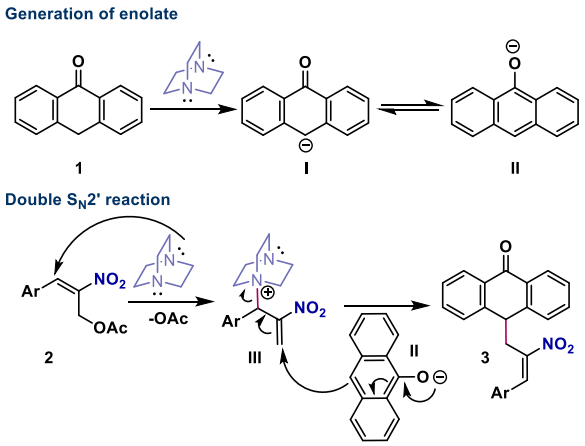
After establishing the reaction conditions, we demonstrated the generality of the reaction using different MBH acetates (Table 2). The methodology worked efficiently when mild electron-donating (methyl) or electron-withdrawing (bromo) substituents were introduced at the *para*-position of the aryl ring in MBH acetate (**2b** and **2c**), leading to corresponding products **3b** and **3c** in excellent yields (78% and 80%, respectively). The *ortho* bromo substituted MBH acetate **2d** delivered the product **3d** in excellent yield (78%). Even heteroaryl-derived MBH acetates, *viz.* **2e** and **2f**, were compatible with our methodology and afforded the corresponding products **3e** and **3f** in a fair yield of 68% and 54%, respectively. Unfortunately, the reaction mixture decomposed in the case of unsubstituted MBH acetate **2g** and the reaction did not progress in the case of *meta*-substituted MBH acetate **2h**. This is attributable to the fact that electron withdrawing aryl group competes with the nitro group of nitroalkene leading to greater concentration of electron density at the benzylic position thus making the substrate less reactive or unreactive.

Table 2. Scope of MBH acetates of nitroalkenes



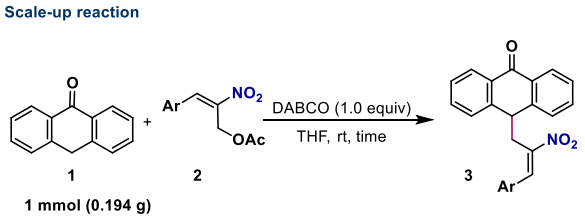
[a]Reaction scale: anthrone **1** (0.5 mmol), MBH acetate **2a** (0.6 mmol), solvent (5 mL). [b]Yields after silica-gel column chromatography.

A plausible mechanism for the formation of product **3** is presented in Scheme 2. Initially, the base deprotonates anthrone **1** to form the intermediate **I**, which remains in equilibrium with enolate **II**. In the next step, DABCO attacks the benzylic position of primary MBH acetate **2** in an S_N2' fashion and eliminates the acetate group, forming intermediate **III**. Then, enolate **II** behaves as a potential nucleophile and adds to intermediate **III** in a Michael fashion, facilitating the second S_N2' reaction with the elimination of DABCO to deliver the final product **3**.



Scheme 2. Proposed mechanism for the formation of anthrone-derived MBH adducts of nitroalkenes

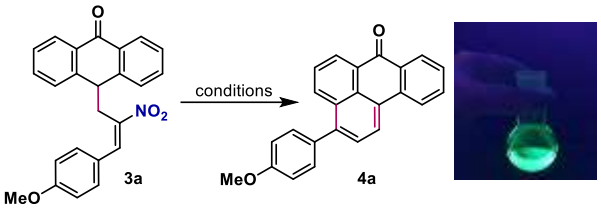
To determine the synthetic applicability of this methodology, we performed the reaction on a 1 mmol scale and isolated the desired products **3a** and **3e** in 80% and 60% yields, respectively (Scheme 3).



Scheme 3. Scale-up reaction: (a) Ar = 4-OMeC$_6$H$_4$ (**2a**, 1.2 mmol, 0.301 g), **3a:** 80% yield (0.308 g), 7 h; (b) Ar = 2-furfuryl (**2e**,1.2 mmol, 0.253 g), **3e:** 60% yield (0.207 g), 8.5 h.

Further cyclization of anthrone-derived MBH adduct **3a** was attempted under acidic conditions in a Friedel-Crafts fashion (Bally-Scholl reaction). Initially, we performed the reaction with Brønsted and Lewis acids *viz.* $BF_3.OEt_2$, TfOH, $Cu(OAc)_2$, LiCl, *p*-TSA and dil H_2SO_4 in DCM at room temperature, but no product formation was observed (Table 3, entries 1-6). Then, the reaction mixture was refluxed, keeping the solvent constant, *i.e.* DCM, but unfortunately, the result was not promising (entries 7-10). The solvent was changed from DCM to toluene to get a higher reflux temperature, keeping other parameters unchanged (entry 11). To our delight, formation of a new product was noted on TLC, though in very small quantity. To improve the yield of the product, TFA was used instead of *p*-TSA at room temperature and at higher temperatures, including reflux, but none of the conditions appeared useful (entries 12-14). Even a strong Lewis acid, *viz*. $TiCl_4$, was unsuitable in delivering product **4a**. Finally, the yield improved slightly when polyphosphoric acid (PPA) was used (entry 16). The product **4a** was isolated and characterized with the help of ^{1}H NMR, ^{13}C NMR, ^{1}H-^{13}C HSQC, HRMS (m/z calcd 337.1223, found 337.1224), IR and single crystal x-ray analysis (Figure 3). Interestingly, compound **4a** displays luminescence in organic solvent (chloroform as a solvent in the picture), which is attributed to its extensive conjugation. Due to the very low product yield, it is necessary to further refine the reaction conditions to achieve a substantial yield. Attempted Bally-Scholl reaction of MBH adducts **3b** and **3e** under the above conditions (PPA, toluene, reflux) were unsuccessful due to lack of reactivity of the former (4-tolyl analog **3b**) and formation of a complex mixture in the case of the latter (furyl analog **3e**).

Table 3. Optimization of reaction conditions for the Friedel-Crafts reaction[a]



Entry	Reagent (1 equiv)	Solvent	Temperature	Time	Yield (%)[b]
1	$BF_3.OEt_2$	DCM	rt	3 d	-
2	TfOH	DCM	rt	3 d	-
3	$Cu(OAc)_2$	DCM	rt	3 d	-
4	LiCl	DCM	rt	3 d	-
5	*p*-TSA	DCM	rt	3 d	-
6	dil. H_2SO_4	DCM	rt	3 d	-
7	TfOH	DCM	reflux	24 h	-
8	$Cu(OAc)_2$	DCM	reflux	24 h	-
9	LiCl	DCM	reflux	24 h	-
10	*p*-TSA	DCM	reflux	24 h	-
11	*p*-TSA	Toluene	reflux	24 h	10
12	TFA	Toluene	rt	3 d	-
13[c]	TFA	Toluene	80 ºC	24 h	traces
14[c]	TFA	Toluene	reflux	24 h	traces
15	$TiCl_4$	Toluene	rt	2 d	-
16	PPA	Toluene	reflux	2 d	15

[a]Reaction scale: anthrone-derived MBH adduct of nitroalkene **3a** (0.5 mmol), solvent (5 mL). [b]After silica-gel column chromatography.[c]1.5 equiv reagent was used instead of 1 equiv.

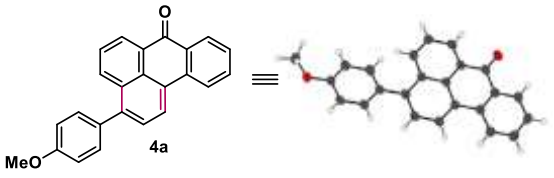
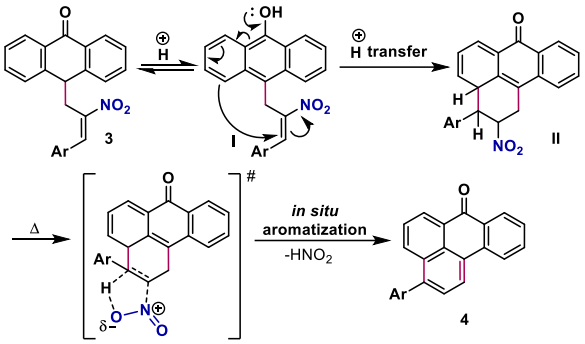


Figure 3. X-ray structure of **4a** (**CCDC:** 2406319)

The proposed reaction mechanism begins with the protonation of the anthrone carbonyl group in **3** followed by a simultaneous *π*-electron flow from the *meta* position to the benzylic carbon of nitroolefin, leading to the construction of a new aromatic ring fused to anthrone moiety in an overall benzannulation of anthrone. Then, a thermal *syn* HNO_2 elimination and *in situ* aromatization results in the substituted benzanthrone **4a** *via* a cyclic transition state (Scheme 4).



Scheme 4. Proposed mechanism for the Bally-Scholl reaction of anthrone-derived MBH adduct of nitroalkenes

3. Conclusions

In summary, we have developed a method for the synthesis of novel anthrone-derived MBH adducts of nitroalkenes *via* a double S_N2' reaction facilitated by the nucleophilic base DABCO. Further, the Bally-Scholl reaction of a representative anthrone-derived MBH adduct afforded substituted benzanthrone, though in very low yield. The synthesized benzanthrone is highly luminescent, presumably due to close-lying singlet-triplet excited states and favorable solvent interaction. Such benzanthrones are potential candidates for applications in biosensors, optoelectronic devices, and photosensitizers.[18,19]

4. Acknowledgements

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5. Experimental section

General information

The melting points are uncorrected. All the NMR spectra were recorded with TMS as the internal standard. The coupling constants (*J* values) are expressed in Hz. The HRMS spectra were recorded under ESI Q-TOF conditions. X-ray data were collected on a diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was determined by direct methods shelxt and refined by full-matrix least-squares against F2 using olex2 software. The MBH acetates of nitroalkenes were prepared according to the literature procedure,[11,20] and anthrone was commercially available.

General procedure for the synthesis of anthrone-derived MBH adducts 3

To a stirred solution of anthrone **1** (0.5 mmol, 1.0 equiv) and primary MBH acetate **2** (0.6 mmol, 1.2 equiv) in THF (5.0 mL), DABCO (1.0 equiv) was added at room temperature. After completion of the reaction (monitored by TLC), the solvent was evaporated in *vacuo*, the residue was diluted with water (10 mL) and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by silica gel column chromatography by eluting with petroleum ether/ethyl acetate (98:02 to 90:10) to isolate pure anthrone-derived MBH adducts **3**.

(*E*)-10-(3-(4-Methoxyphenyl)-2-nitroallyl) anthracen-9(10*H*)-one (3a). Light green solid; Yield 82% (158 mg); petroleum ether:ethyl acetate (90:10), mp 176-178 °C; IR (KBr, cm^{-1}) 2925 (s), 1662 (vs), 1603 (vs), 1511 (vs), 1462 (s), 1314 (vs), 1258 (vs), 1176 (vs), 1029 (s), 930 (m), 827 (m), 761 (m), 690 (m); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ* 3.19 (d, *J* = 6.9 Hz, 2H), 3.74 (s, 3H), 4.59 (t, *J* = 6.9 Hz, 1H), 6.53, 6.62 (ABq, *J* = 8.1 Hz, 4H), 7.43-7.45 (unresolved m, 4H), 7.53 (t, *J* = 7.3 Hz, 2H), 8.12 (s, 1H), 8.29 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ* 41.3, 41.5, 55.6, 114.4, 123.5, 127.9, 128.0, 128.7, 131.4, 132.0, 133.3, 137.7, 143.6, 146.6, 161.6, 184.6; HRMS (ES+) m/z: $[M+H]^+$ calcd for $C_{24}H_{20}NO_4$, 386.1387; found 386.1385; Selected X-ray Data (CCDC 2349923): $C_{24}H_{19}NO_4$, M 385.40, Monoclinic, space group C2/c, a = 17.9007(10) Å, b = 7.7061(4) Å, c = 27.2658(14) Å, *α* = 90°, *β* = 97.625(5)°, *γ* = 90°, V = 3727.9(3) Å^3, ρ_{calc} = 1.373 g/cm^3, Z = 8, F(000) = 1616.0, λ = 0.71073 Å, μ = 0.094 mm^{-1}, R(int) = 0.0902, T = 150.00 (10) K, 2Θ range = 4.592 to 66.998°, Final R [I>2σ(I)]: R_1 = 0.0622, wR_2 = 0.1192, R (all data): R_1 = 0.1193, wR_2 = 0.1461

(*E*)-10-(2-Nitro-3-(*p*-tolyl)allyl)anthracen-9(10*H*)-one (3b). Light green solid; Yield 78% (144 mg); petroleum ether:ethyl acetate (98:2), mp 158-160 °C; IR (Neat, cm^{-1}) 2923 (w), 1664 (s), 1599 (m), 1514 (s), 1312 (vs), 693 (m); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* 2.25 (s, 3H), 3.17 (d, *J* = 7.4 Hz, 2H), 4.59 (t, *J* = 7.4 Hz, 1H), 6.42 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 8.1 Hz, 2H), 7.44 (overlapped d and t, *J* = 7.7 Hz, 4H), 7.54 (t, *J* = 7.7 Hz, 2H), 8.12 (s, 1H), 8.29 (d, *J* = 7.7 Hz, 2H); Confirmed by ^{1}H-^{1}H COSY and ^{1}H-^{13}C HSQC; ^{13}C NMR ($CDCl_3$, 100 MHz) *δ* 21.4, 41.3 (× 2), 127.9 (× 2), 128.3, 128.6, 129.1, 129.6, 132.0, 133.3, 137.8, 141.1, 143.5, 147.9, 184.4; HRMS (ES+) m/z: $[M+H]^+$ calcd for $C_{24}H_{20}NO_3$, 370.1433; found 370.1433.

(*E*)-10-(3-(4-bromophenyl)-2-nitroallyl)anthracen-9(10*H*)-one (3c). Light green solid; Yield 80% (173 mg); petroleum ether:ethyl acetate (98:2), mp 278-280 °C; IR (Neat, cm^{-1}) 2924 (w), 1664 (s), 1595 (s), 1518 (vs), 1314 (vs), 1218 (m); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* 3.11 (d, *J* = 7.3 Hz, 2H), 4.55 (t, *J* = 7.3 Hz, 1H), 6.31 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 2H), 8.02 (s, 1H), 8.27 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ* 41.2, 41.3, 128.0, 128.1, 128.6, 130.1, 130.3, 132.0, 132.1, 133.4, 133.6, 136.2, 143.2, 149.1, 184.2;

HRMS (ES+) m/z: $[M+H]^+$ calcd for $C_{23}H_{17}Br^{79}NO_3$, 434.0384; found 434.0384.

(*E*)-10-(3-(2-Bromophenyl)-2-nitroallyl)anthracen-9(10*H*)-one (3d). Light green solid; Yield 78% (169 mg); petroleum ether:ethyl acetate (90:10), mp 188-190 °C; IR (KBr, cm^{-1}) 1662 (vs), 1600 (s), 1523 (s), 1331 (s), 1315 (vs), 1027 (m), 762 (m), 693 (m); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.03 (d, J = 7.5 Hz, 2H), 4.56 (t, J = 7.5 Hz, 1H), 5.71 (d, J = 7.6 Hz, 1H), 6.94 (t, J = 7.6 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 7.40 (d, J = 7.7 Hz, 2H), 7.44 (d, J = 7.6 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.59 (t, J = 7.7 Hz, 2H), 8.12 (s, 1H), 8.25 (d, J = 7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 41.1, 41.2, 124.3, 127.6, 128.0 (x 2), 128.6, 129.1, 131.2, 132.0, 133.1, 133.5, 136.5, 143.3 (x 2), 150.1, 184.3; HRMS (ES+) m/z: $[M+H]^+$ calcd for $C_{23}H_{17}Br^{79}NO_3$, 434.0386; found 434.0381.

(*E*)-10-(3-(Furan-2-yl)-2-nitroallyl)anthracen-9(10*H*)-one (3e). Yellow solid; Yield 68% (117 mg); petroleum ether:ethyl acetate (90:10), mp 177-179 °C; IR (KBr, cm^{-1}) 2925 (w), 1660 (s), 1641 (s), 1599 (m), 1504 (m), 1308 (vs), 1021 (m), 926 (m), 756 (m); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.42 (d, J = 7.7 Hz, 2H), 4.53 (t, J = 7.7 Hz, 1H), 6.30 (dd, J = 3.4, 1.6 Hz, 1H), 6.51 (d, J = 3.4 Hz, 1H), 7.23 (unresolved d, J = 1.6 Hz, 1H), 7.36-7.40 (m, 4H), 7.44-7.48 (m, 2H), 7.79 (s, 1H), 8.21 (d, J = 7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 41.5, 42.4, 112.6, 121.1, 123.3, 127.6, 127.7, 128.2, 132.3, 132.7, 143.9, 144.5, 147.1, 147.2, 185.2; HRMS (ES+) m/z: $[M+H]^+$ calcd for $C_{21}H_{16}NO_4$, 346.1078; found 346.1074.

(*E*)-10-(2-Nitro-3-(thiophen-2-yl)allyl)anthracen-9(10*H*)-one (3f). Yellow solid; Yield 54% (97 mg); petroleum ether:ethyl acetate (93:07), mp 147-149 °C; IR (KBr, cm^{-1}) 2924 (w), 1659 (s), 1642 (s), 1600 (s), 1508 (m), 1363 (vs), 711 (m); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.31 (d, J = 7.6 Hz, 2H), 4.57 (t, J = 7.6 Hz, 1H), 6.94 (dd, J = 5.0, 3.7 Hz, 1H), 7.08 (d, J = 3.7 Hz, 1H), 7.36-7.43 (m, 5H), 7.47-7.51 (m, 2H), 8.26 (d, J = 7.7 Hz, 2H), 8.35 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) 41.4, 41.9, 127.8, 127.9, 128.5, 130.7, 132.1, 132.6, 133.1 (× 2), 134.0, 136.2, 143.4, 144.8, 184.7; HRMS (ES+) m/z: $[M+H]^+$ calcd for $C_{21}H_{16}NSO_3$, 362.0843; found 362.0845.

Procedure for the synthesis of benzanthrone 4a

To a stirred solution of anthrone-derived MBH adduct **3** (193 mg, 0.5 mmol) in anhydrous toluene (5.0 mL), polyphosphoric acid (PPA, 90 µL, 0.5 mmol, 1.0 equiv) was added at room temperature, and the reaction mixture was stirred under reflux for 2 d. After completion of the reaction (monitored by TLC), the solvent was evaporated *in vacuo*, the residue was diluted with water (10 mL) and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by silica gel column chromatography by eluting with petroleum ether/ethyl acetate (99:01) to isolate pure benzanthrone **4a**.

3-(4-Methoxyphenyl)-7H-benzo[*de*]anthracen-7-one (4a). Yellow solid; Yield 15% (26 mg); petroleum ether:ethyl acetate (99:01), mp 186-188 °C; IR (Neat, cm^{-1}) 2921 (vs), 2854 (s), 1660 (s), 1459 (m), 1305 (s), 1253 (vs), 1174 (m), 1027 (m); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.92 (s, 3H), 7.08 (d, J = 8.6 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.58 (t, J = 7.8 Hz, 1H), 7.64 (d, J = 7.9 Hz, 1H), 7.75 (t, J = 8.2 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 8.36 (d, J = 8.2 Hz, 1H), 8.40 (d, J = 8.2 Hz, 1H), 8.52 (overlapped t, J = 7.9 Hz, 1H), 8.54 (d, J = 7.9 Hz, 1H), 8.82 (d, J = 8.2 Hz, 1H); Confirmed by ^{1}H-^{1}H COSY; ^{13}C NMR ($CDCl_3$, 125 MHz) 55.6, 114.2, 123.2, 124.1, 126.0, 126.7, 127.7, 128.3, 128.4, 129.0, 129.8, 130.0, 131.1, 131.6, 131.8, 132.3, 133.6, 133.9, 136.5, 142.8, 159.7, 184.3; HRMS (ES+) m/z: $[M+H]^+$ calcd for $C_{24}H_{17}O_2$, 337.1223; found 337.1224; Selected X-ray Data (CCDC 2406319): $C_{24}H_{16}O_2$, M 336.37, triclinic, space group P-1, a = 9.7254(11) Å, b = 9.8063(12) Å, c = 10.5482(15) Å, α = 116.148(13)°, β = 111.372(12)°, γ = 92.896(9)°, V = 813.7(2) Å^3, ρ_{calc} = 1.373 g/cm^3, Z = 2, F(000) = 352.0, λ = 0.71073 Å, µ = 0.086 mm^{-1}, R(int) = 0.1195, T = 150.00 (10) K, 2Θ range = 4.648 to 50°, Final R [I>2σ(I)]: R_1 = 0.0909, wR_2 = 0.2482, R (all data): R_1 = 0.1092, wR_2 = 0.2633.

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