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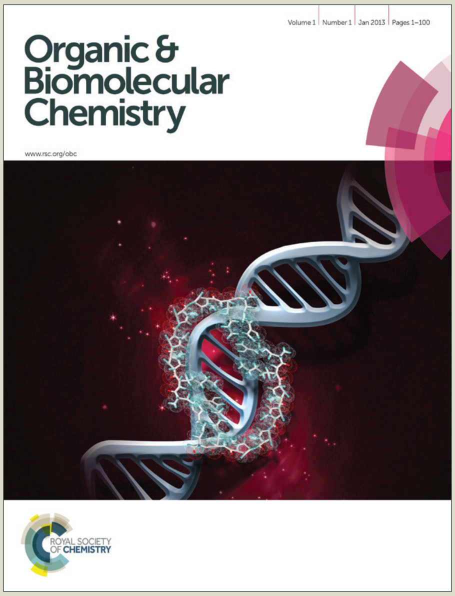

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Gold-Catalyzed Tandem Diels-Alder Reactions of Enynals/Enynones with Alkenes: Generation and Trapping of Cyclic *o*-QDMs

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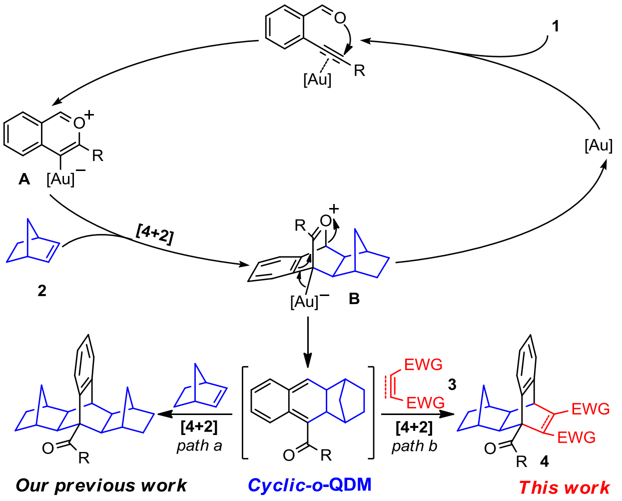
An efficient gold-catalyzed method to generate the highly reactive cyclic *o*-QDM species from the enynal/enynone and alkene was reported. This method allowed rapid access to a variety of structurally unique propeller-like products through the tandem Diels-Alder reactions.

Introduction

Recently, we reported an efficient gold-catalyzed reaction of enyal/enynone with norbornenes to synthesize of a variety of structurally symmetrical propeller-like molecules (Scheme 1, path a).[1] This reaction was believed to proceed through the gold-catalyzed tandem Diels-Alder reactions *via* trapping of the key intermediate cyclic *o*-quinodimethane (cyclic-*o*-QDM),[1,2] a highly reactive species. However, this two-component reaction occurred only with the norbornene derivatives as the substrates, which severe limited the applications.

Mechanically speaking, the cyclic-*o*-QDM intermediate is an electronic-rich diene. It would react with electron-deficient dienophile easier than norborene. Therefore, if an electron-deficient alkene or alkyne was added as the dienophile for the cyclic-*o*-QDM intermediate, a three-component reaction may be realized. Thus, the structure-nonsymmetrical propeller-like product would be formed (Scheme 1, path b). In this paper, we would like to report the results of our investigations.

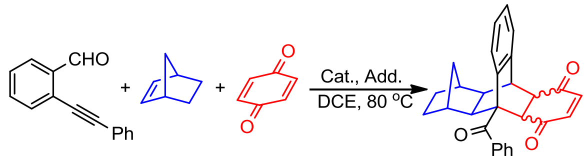


Scheme 1 Proposed reaction mechanism.

Results and discussion

Initial efforts were made to systematically investigate various catalytic reaction conditions for the reaction of enynal **1a**, norbornen **2a** and 1,4-benzoquinone **3a** (electron-deficient dienophile). By following the conditions reported in our previous work, different metal salts were then tested (Table 1, entries 1-8). No desired product **4a** was detected when AgOTf and $FeCl_3$ were used as catalysts (entries 1-2). Gratifyingly, the desired product **4a** could be obtained in low yields when $InCl_3$, $ZnCl_2$ and $CuCl_2$•$2H_2O$ were used as catalysts (entries 3-5). In these cases, the product **4a** was formed in endo-/exo-mixture. Further screening of the catalysts revealed that $KAuCl_4$•$2H_2O$ can catalyze this reaction leading to **3a** as well, although in only 12% yield (entry 6). N-heterocyclic carbene (NHC)-supported gold(I) complex (IMes-AuCl) was inefficient for this transformation (entry 7). Interestingly, a significant positve effect was observed when 15 mol% Selectfluor® was added as additive.[1,3] The yield of **4a** was improved to 92% (entry 8). Such positive effect was consistent with our previous work,[1] and it was assumed that

Table 1. Optimization of Reaction Conditions.[a]



1a **2a** **3a** **4a**

Entry	Catalyst	Additive	Yield (**4a**)[b]	endo/exo[c]
1	AgOTf	-	ND	ND
2	$FeCl_3$	-	ND	ND
3	$InCl_3$	-	22%	2.7/1.0
4	ZnI_2	-	51%	4.6/1.0
5	$CuCl_2$*$2H_2O$	-	35%	5.9/1.0
6	$KAuCl_4$*$2H_2O$	-	12%	ND
7	IMes-AuCl	-	ND	ND
8	IMes-AuCl	Selectfluor®	92%	3.1/1.0
9	**SIMes-AuCl**	**Selectfluor®**	**97%**	**3.7/1.0**
10	IPr-AuCl	Selectfluor®	74%	8.3/1.0
11	SIPr-AuCl	Selectfluor®	43%	5.6/1.0
12[d]	SIMes-AuCl	Selectfluor®	15%	1.9/1.0
13[e]	SIMes-AuCl	Selectfluor®	73%	8.3/1.0
14[f]	SIMes-AuCl	Selectfluor®	71%	3.1/1.0
15	Ph_3P-AuCl	Selectfluor®	35%	6.1/1.0
16	-	Selectfluor®	ND	ND

[a] Without other noted, the reaction was performed at 80 °C for 24 h using 5 mol % catalyst and 15% additive under N_2, **1a**:**2a**:**3a** = 1:5:2 [**1a**] = 0.25 M, **IMes**: 1,3-dimesitylimidazol-2-ylidene; **SIMes**:1,3-dimesityl-imidazolin-2-ylidene; **IPr**: 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene; **SIPr**: 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene; [b] NMR yield, [c] Determined by ^{1}HNMR, [d] Room Temp., [e] 100°C, [f] **1a**:**2a**:**3a** = 1:5:1.

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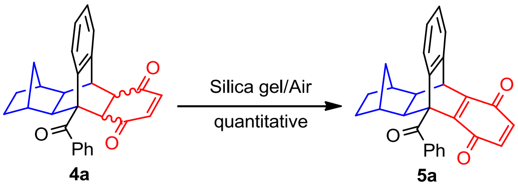
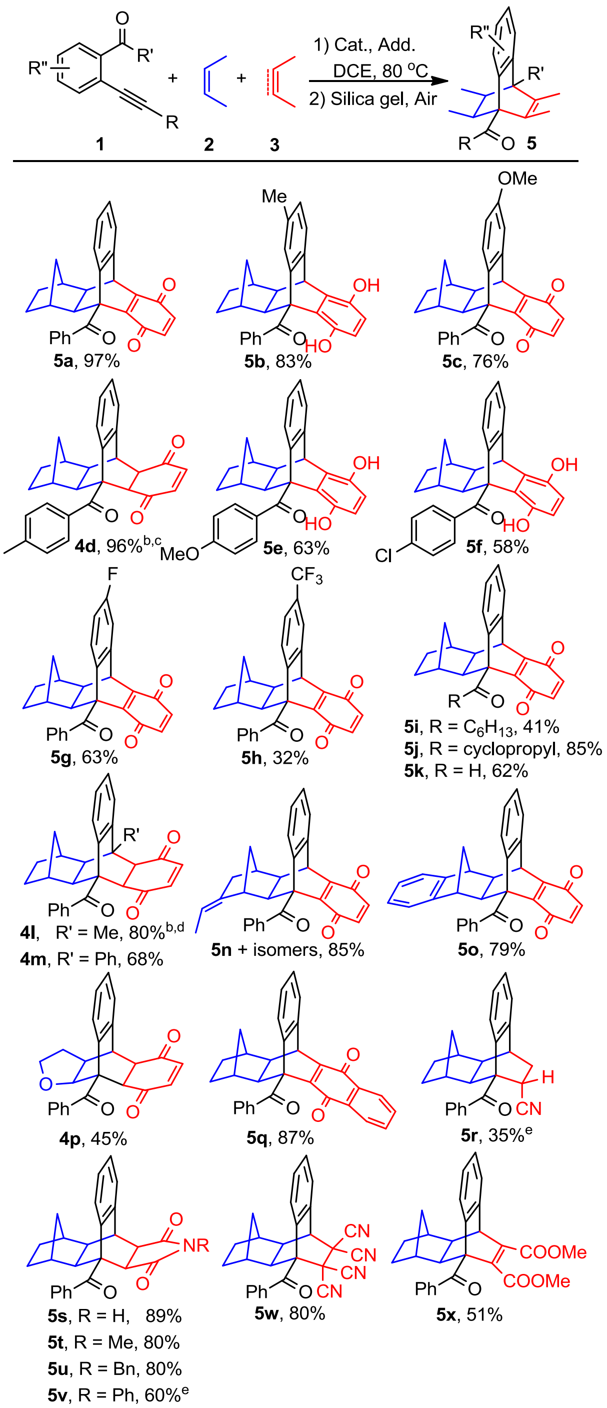
IMes-AuCl was oxidized into IMes-Au^{III} *in situ*. Based on the results above, three other NHC-AuCl/Selectfluor® combinations were then investigated as well (entries 9-11). Among four different NHC-AuCl complexes being tested, SIMes-AuCl functioned better than the other three (entries 8-11). The yield of **4a** was enhanced to 97% for the combination of SIMes-AuCl/Selectfluor® (entry 9). Lower temperature (entry 12: room temp.) or higher temperature (entry 13: 100 °C) resulted into inferior results. The yield of **4a** dropped to 71% when the amount of 1,4-benzoquinone **3a** was decreased to 1.0 equivalent (entry 14). Furthermore, the yield was only 35% when Ph$_3$P-AuCl was used as catalyst instead (entry 15). The reaction did not occur without the gold catalyst (entry 16). It is worth noting that in all cases, the product **4a** was obtained in mixtures of endo-/exo-isomers. Interestingly, the cyclohexene-1,4-dione **4a** could be oxidized into 1,4-benzoquinone **5a** quickly upon purification on silica gel (Scheme 2). Both **4a** and **5a** were confirmed by the X-ray diffraction analysis.



Scheme 2. Oxidation of 1,4-dione **4a** to 1,4-benzoquinone **5a**.

With the optimized reaction conditions (Table 1, entry 9) in hand, the substrate scope was then examined in detail. As summarized in Table 2, the catalytic process could be successfully applied to a variety of enynals/enynones **1**, alkenes **2** and **3**. For example, in addition to enynal **1a**, a variety of enynal or enynone derivatives could be effectively reacted with norbornene **2a** and 1,4-benzoquinone **3a** as well (Table 2, **5a-4m**). The enynals substituted with electron-donating groups gave higher yields (**5a-5e**: 63%-97%) than those with electron-withdrawing groups (**5f-5h**: 32%-63%). For example, CF$_3$-substituted enynal gave the corresponding prodcut **5e** only in 32% yield. It is worth mentioning that hydroquinones were obtained instead in the cases of **5b**, **5e**, and **5f**. For the enynals bearing alkyl alkyne or cyclopropyl alkyne, the reactions proceed smoothly as well (**5i**, **5j**). The reaction functioned particularly efficiently for the cyclopropyl-substituted enynal, giving the corresponding product **5j** in 85% yield. Furthermore, the 1,4-benzoquinone **5k** with a free formyl group could be obtained in 62% yield when the enynal with a terminal alkyne was used as the substrate. In addition to the enynals, enynonoes can serve as efficient substrates as well (**4l**, **4m**). For example, both the methyl ketone and phenyl ketone successfully furnished the corresponding products **4l** and **4m** in 80% and 68% yields, respectively. In addition to the simple norbornene **2a**, the norbornene containing an extra exocyclic double bond or benzonorbornene could be used as the potential substrates as well, furnishing the desired products **5n** and **5o** in 85% and 79% yields. When 1,2-dihydrofuran was used as electron-rich alkene, the cyclohexene-1,4-dione **4p** was obtained directly, and no 1,4-benzoquinone was detected. More interestingly, only the endo-adduct isomer was formed. Styrene derivatives and aliphatic olefins failed to give the desired products. As for the electron-deficient olefins, the reaction has better substrate scopes. For example, 1,4-naphthoquinone can be used to replace 1,4-benzoquinone, and it gave the corresponding product **5q** in 87% yield. Furthermore, a variety of mono-, di-, tetra-substituted electron-deficient alkenes can also be used to trap the cyclic-*o*-QDM intermediate (**5r**-**5w**).

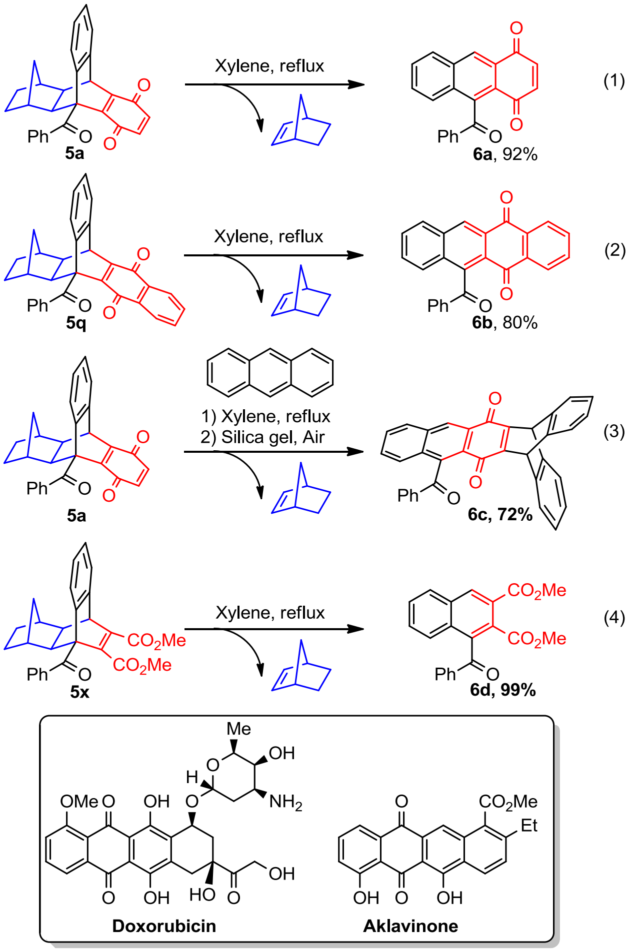
Table 2. Substrate scope^{a}



^{a} The reaction was performed at 80 °C for 24 h using 5 mol % cat and 15% add under N$_2$; **1**:**2**:**3** = 1:5:2; [**1**] = 0.25 M, isolated yield; ^{b} purified by crystallization, ^{c} endo/exo = 7.7/1.^{d} endo/exo > 20/1; ^{e} the stereochemistry was determined by noe.

As summarized in Table 2, the alkenes disubstituted or tetra-substituted with the electron-withdrawing groups served as better dienophiles than the mono-substituted one in trapping the *o*-QDM. For example, acrylonitrile gave the product **5r** only in 35% yield. While the free maleimide and its N-protected derivatives smoothly furnished the desired adducts **5s-5v** in good to excellent yields. Even the tetracyanoethylene can be successfully applied to produce the product **5w** in 80% yield. It is noteworthy that product **5r-5w** were obtained as single isomer. Dimethyl acetylenedicarboxylate can also be used as the dienophile, giving the product **5x** in 51% yield.

With the nonsymmetrical propeller-like molecules **5** in hand, especially for those 1,4-benzoquinone derivatives with the bicyclo[2.2.1]heptane moiety, we then proceeded to study their potential further chemical transformations (Scheme 3). Upon simply refluxing the xylene solvent of **5a** or **5q** resulted in the occurrence of the *retro*-Diels-Alder reaction, it furnished the anthraquinones **6a** and **6b** in 92% and 80% yields, respectively. Interestingly, when heating the mixture of **5a** and anthracene, another propeller-like molecule **6c** was formed in 72% yield. The resulting anthraquinone is the core structure of many naturally occurring and biologically active substances, such as Doxorubicin[4] and Aklavinone[5]. Similarly, heating the diester **5x** under the same reaction conditions led to the trisubstituted naphthalene **6d** in quantitative yield.



Scheme 3. Further chemical transformation of **5**.

A plausible mechanism was proposed based on our previous work (Scheme 1, path b).[1] The coordination of the triple bond of enynal **1** to [Au] enhanced the electrophilicity of alkyne, and the subsequent nucleophilic attack of the carbonyl oxygen to the electron-deficient alkyne would form the intermediate pyrylium **A.**[6] A Diels-Alder reaction between pyrylium **A** and norborene **2** followed to furnish the intermediate **B**. Then elimination of the catalyst [Au] led to the key intermediate, cyclic-*o*-QDM, which was then trapped by the electron-deficient alkene or alkyne to furnish the product **4** *via* a second Diels-Alder reaction.

Conclusions

In summary, we have developed an efficient gold-catalyzed method to synthesize a variety of structurally unique propeller-like molecules. The reaction proceeded through tandem Diels-Alder reactions *via* trapping of the cyclic-*o*-QDM. For those propeller-like products containing 1,4-benzoquinone moiety, a *retro*-Diels-Alder reaction could occur smoothly in the refluxing xylene, forming the anthraquinone derivatives. Owing to the mild reaction conditions and high functional group tolerance, this system holds considerable potential in the synthesis of structurally interesting propeller-like molecules and bioactive anthraquinone molecules.

Experimental

General Information

Unless specified, all reactions were carried out under an inert atmosphere of nitrogen in Schlenk tubes with dry solvents, using anhydrous conditions unless otherwise stated. 1,2-Dichloroethane (DCE) was distilled over calcium hydride under nitrogen prior to use. Acetonitrile (CH_3CN), dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), toluene, and triethylamine (NEt_3), were distilled under nitrogen prior to use by standard methods respectively. NHC-Au catalysts were prepared as described in the literature.[1] Unless otherwise stated, other reagents were used as received from commercial sources.

Melting points were recorded on a BUCHI Melting Point B-545 apparatus and were uncorrected. NMR spectra were recorded on a Bruker Avance III 400MHz spectrometer in deuterated chloroform ($CDCl_3$) solutions, with residual chloroform (δ 7.26 ppm for ^1H NMR and δ 77.00 ppm for ^{13}C NMR) taken as the internal standard, and were reported in parts per million (ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d =doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (IR) spectra are recorded on a Nicolet 210 spectrophotometer.

Typical procedure for Gold-catalyzed tandem reaction of enynals/enynones with norbornene (NB) and benzoquinone

To a solution of the catalyst combination of SIMes-AuCl (2.70 mg, 0.005 mmol) and Selectfluor® (5.30 mg, 0.015 mmol) in DCE (1 mL, 0.1 M) was added the corresponding enynals/enynones (0.1 mmol) with norbornene (NB, 47.10 mg, 0.5 mmol) and benzoquinone (21.60 mg, 0.2 mmol). The reaction mixture was stirred under nitrogen atmosphere at 80 ℃ for 24 hours. The reaction afforded the crude unstable 1,4-dione **4**, which could be purified by recrystallization. The crude mixture of the initially-formed unstable 1,4-dione **4** was filtered by short silica, then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the product **5**.

9-Benzoyl-decahydro-9,10-[2]bicycloanthracene-1,4-dione (4a): Yellow solid; mp 162 ℃; NMR ($MeNO_2$) yield: 99.0 %; IR (KBr): 3688, 3062, 2949, 2880, 2360, 1647, 1470, 1271, 1093, 767, 699, 645, 520, 438; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.8 Hz, 1H), 7.74 – 7.60 (m, 1H), 7.47 – 7.33 (m, 2H), 7.17 (td, J = 7.7, 1.3 Hz, 1H), 7.10 (dt, J = 7.4, 6.0 Hz, 1H), 6.94 (d, J = 7.2 Hz, 1H), 6.32 (d, J = 10.3 Hz, 1H), 6.24 (d, J = 10.3 Hz, 1H), 4.07 (d, J = 9.8 Hz, 1H), 3.60 (s, 1H), 3.24 (dd, J = 9.8, 1.4 Hz, 1H), 2.35 (d, J = 9.0 Hz, 1H), 2.19 – 2.05 (m, 1H), 1.96 (s, 1H), 1.38 (d, J = 12.7 Hz, 1H), 1.30 (d, J = 6.7 Hz, 1H), 1.15 (d, J = 10.7 Hz, 1H), 0.42 (d, J = 10.1 Hz, 1H), 0.39 (d, J = 10.7 Hz, 1H), -0.01 (d, J = 10.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.7, 197.5, 196.9, 141.24, 141.1, 140.8, 137.2, 137.2, 130.1, 128.1, 127.8, 127.3, 127.2, 127.0, 125.5, 57.0, 52.2, 50.9, 49.1, 48.6, 44.6, 41.2, 38.8, 33.5, 31.1, 30.2; HRMS (MALDI-FTMS): calcd for $C_{28}H_{24}O_3Na^+$ [M+Na$^+$] = 431.1618; found = 431.1622.

9-Benzoyl-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5a): Yellow solid; mp 221 ℃; NMR ($MeNO_2$) yield: 99.0 %; IR (KBr): 3681, 2944, 2879, 1688, 1656, 1583, 1463, 1305, 1241, 833, 767, 734, 693, 473; ^1H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.49 (s, 1H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.26 (d, *J* = 7.3 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 2H), 6.95 (t, *J* = 7.5 Hz, 3H), 6.68 (d, *J* = 7.7 Hz, 1H), 6.60 (d, *J* = 10.1 Hz, 1H), 6.41 (d, *J* = 10.1 Hz, 1H), 4.66 (d, *J* = 2.3 Hz, 1H), 2.35 (s, 1H), 2.22 (d, *J* = 8.5 Hz, 1H), 1.88 (s, 1H), 1.66 (d, *J* = 6.8 Hz, 1H), 1.39 – 1.30 (m, 2H), 1.14 (d, *J* = 6.4 Hz, 1H), 0.95 (d, *J* = 7.4 Hz, 1H), 0.15 (d, *J* = 10.8 Hz, 1H), -1.23 (d, *J* = 10.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 183.3, 183.2, 148.9, 148.9, 139.3, 137.8, 137.0, 136.4, 135.1, 132.3, 127.2, 126.4, 126.3, 124.8, 77.3, 77.0, 76.7, 59.1, 51.0, 49.6, 42.2, 39.5, 38.5, 32.3, 31.1, 30.7, 29.7. HRMS (MALDI-FTMS): calcd for $C_{28}H_{22}O_3Na^+$ [M+Na$^+$] = 429.1461; found = 429.1472.

1,4-Dihydroxy-7-methyl-octahydro-9,10-[2]bicycloanthracen-9-yl)(phenyl)methanone (5b): Yellow solid; mp 164.8 ℃; NMR ($MeNO_2$) yield: 83.5 %; IR (KBr): 3873, 2949, 2875, 2359, 1744, 1662, 1492, 1252, 1081, 1031, 869, 807, 694, 575, 478; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.17 (d, J = 10.7 Hz, 2H), 7.08 (d, J = 7.5 Hz, 1H), 6.84 (t, J = 6.8 Hz, 1H), 6.50 (d, J = 8.5 Hz, 1H), 6.34 (s, 1H), 6.24 (d, J = 8.5 Hz, 1H), 5.14 (s, 1H), 4.59 (dd, J = 11.7, 2.4 Hz, 1H), 2.29 (d, J = 8.5 Hz, 1H), 2.10 (s, 1H), 1.94 (s, 1H), 1.81 (s, 1H), 1.66 – 1.57 (m, 1H), 1.26 (dd, J = 11.7, 8.6 Hz, 1H), 1.10 (d, J = 10.7 Hz, 1H), 0.90 (t, J = 7.8 Hz, 1H), 0.11 (d, J = 10.6 Hz, 1H), -1.07 (d, J = 10.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.31, 143.27, 142.47, 139.24, 138.35, 136.72, 133.72, 131.30, 130.82, 130.26, 127.96, 127.32, 126.58, 125.86, 123.26, 115.18, 113.61, 113.53, 59.50, 58.29, 50.10, 48.81, 40.87, 38.77, 37.50, 31.59, 30.17, 20.34, 20.00, 13.16. HRMS (MALDI-FTMS): calcd for $C_{29}H_{26}O_3Na^+$ [M+Na$^+$] = 445.1774; found = 445.1786.

9-Benzoyl-6-methoxy-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5c): Yellow solid; mp 200.8 ℃; NMR ($MeNO_2$) yield: 76.0 %; IR (KBr): 2880, 2359, 1734, 1689, 1655, 1585, 1488, 1303, 1249, 1144, 1037, 832, 695; ^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.45 (s, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.00 (s, 2H), 6.82 (d, *J* = 2.4 Hz, 1H), 6.60 (d, *J* = 10.1 Hz, 1H), 6.54 (d, *J* = 8.5 Hz, 1H), 6.47 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.41 (d, *J* = 10.1 Hz, 1H), 4.65 (s, 1H), 4.59 (d, *J* = 2.4 Hz, 1H), 3.70 (s, 3H), 2.35 (s, 1H), 2.19 (d, *J* = 8.5 Hz, 1H), 1.89 (s, 1H), 1.65 (d, *J* = 8.3 Hz, 1H), 1.35 (d, *J* = 3.2 Hz, 1H), 1.14 (d, *J* = 6.1 Hz, 1H), 0.93 (t, *J* = 8.5 Hz, 1H), 0.20 (d, *J* = 10.9 Hz, 1H), -1.05 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.40, 183.41, 183.29, 159.00, 149.48, 148.68, 139.33, 136.96, 136.41, 135.07, 132.27, 131.40, 127.14, 111.38, 110.87, 58.59, 55.40, 51.06, 49.65, 42.42, 39.45, 38.49, 32.56, 30.99, 30.69, 29.70. HRMS (MALDI-FTMS): calcd for $C_{29}H_{24}$O4Na$^+$ [M+Na$^+$] = 459.1569; found = 459.1576.

9-(4-Methylbenzoyl)-decahydro-9,10-[2]bicycloanthracene-1,4-dione (4d): Brown solid; mp 189 ℃; NMR ($MeNO_2$) yield: 96.0 %; IR (KBr): 3683, 3620, 2949, 2877, 2358, 1658, 1601, 1464, 1303, 1246, 1183, 1036, 836, 734, 480; 1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.7 Hz, 1H), 7.58 (d, J = 7.9 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 7.7 Hz, 1H), 7.06 (t, J = 7.3 Hz, 1H), 6.91 (d, J = 7.2 Hz, 1H), 6.28 (d, J = 10.3 Hz, 1H), 6.20 (d, J = 10.3 Hz, 1H), 4.12 (d, J = 9.8 Hz, 1H), 3.58 (s, 1H), 3.23 (d, J = 9.8 Hz, 1H), 2.35 (s, 1H), 2.34 (s, 3H), 2.13 (d, J = 8.9 Hz, 1H), 2.07 (s, 1H), 1.94 (s, 1H), 1.33 (t, J = 10.7 Hz, 2H), 1.11 (t, J = 8.8 Hz, 1H), 0.96 (t, J = 9.5 Hz, 1H), 0.38 (d, J = 10.6 Hz, 1H), -0.01 (d, J = 10.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.25, 197.63, 196.89, 141.28, 140.73, 140.53, 138.23, 137.42, 137.25, 128.73, 128.04, 127.23, 126.97, 125.47, 57.03, 52.34, 50.98, 49.06, 48.82, 44.57, 41.20, 38.80, 33.55, 31.13, 30.24, 21.42.

9-(4-Methoxybenzoyl)-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5e): Yellow solid; mp 201.8 ℃; NMR ($MeNO_2$) yield: 63.7 %; IR (KBr): 3336, 3064, 2944, 2878, 2359, 1662, 1598, 1498, 1457, 1304, 1252, 1174, 1032, 819, 737, 609; ^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 7.4 Hz, 1H), 7.25 (d, J = 7.3 Hz, 1H), 7.15 (t, J = 7.3 Hz, 1H), 6.97 (t, J = 7.3 Hz, 2H), 6.88 (d, J = 7.2 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 6.60 (d, J = 10.0 Hz, 1H), 6.43 (t, J = 10.3 Hz, 2H), 4.65 (s, 1H), 3.74 (s, 3H), 2.34 (s, 1H), 2.21 (d, J = 8.5 Hz, 1H), 1.87 (s, 1H), 1.65 (d, J = 8.5 Hz, 1H), 1.33 (t, J = 9.1 Hz, 2H), 1.17 (d, J = 6.3 Hz, 1H), 1.13 (d, J = 6.8 Hz, 1H), 0.93 (t, J = 8.9 Hz, 1H), 0.13 (d, J = 10.8 Hz, 1H), -1.24 (d, J = 10.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.97, 183.41, 183.31, 162.59, 148.91, 148.86, 139.45, 137.89, 136.50, 134.98, 131.91, 130.61, 130.24, 127.16, 126.48, 126.37, 124.80, 59.03, 55.36, 50.97, 49.60, 42.18, 39.45, 38.57, 32.35, 31.08, 30.68.

(4-Chlorophenyl)(1,4-dihydroxy-octahydro-9,10-[2]bicycloanthracen-9-yl)methanone (5f): Brown solid; mp 219.3-221 ℃; NMR ($MeNO_2$) yield: 58.3 %; IR (KBr): 3856, 2932, 2878, 2360, 1690, 1656, 1584, 1475, 1304, 1240, 1095, 1013, 827, 738, 482; ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.45 (s, 1H), 7.26 (d, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 2H), 6.63 (dd, *J* = 13.3, 8.9 Hz, 2H), 6.43 (d, *J* = 10.1 Hz, 1H), 4.67 (s, 1H), 2.33 (s, 1H), 2.21 (d, *J* = 8.4 Hz, 1H), 1.88 (s, 1H), 1.67 (s, 2H), 1.35 (s, 2H), 0.95 (d, *J* = 6.2 Hz, 1H), 0.15 (d, *J* = 10.9 Hz, 1H), -1.24 (d, *J* = 10.6 Hz, 1H; ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.07, 183.18, 149.19, 148.47, 138.97, 138.55, 137.89, 136.38, 135.50, 135.20, 127.37, 126.46, 126.26, 124.98, 59.09, 51.05, 49.59, 42.24, 39.45, 38.50, 32.31, 31.04, 30.65, 29.68. HRMS (MALDI-FTMS): calcd for $C_{28}H_{23}O_3ClNa^+$ [M+Na$^+$] = 465.1228; found = 465.1245.

9-Benzoyl-6-fluoro-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5g): Yellow solid; mp 220.8 ℃; NMR ($MeNO_2$) yield: 63.7 %; IR (KBr): 3660, 2937, 2878, 2358, 1687,1586, 1485, 1385, 1241, 1144, 1118, 868, 828, 741, 650; ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.50 (s, 1H), 7.39 (d, J = 7.0 Hz, 1H), 7.00 (d, J = 7.9 Hz, 2H), 6.92 (s, 1H), 6.70 – 6.58 (m, 3H), 6.44 (d, J = 9.5 Hz, 1H), 4.64 (s, 1H), 2.35 (s, 1H), 2.21 (d, J = 8.2 Hz, 1H), 1.91 (s, 1H), 1.68 (d, J = 8.4 Hz, 1H), 1.36 (s, 2H), 0.93 (d, J = 11.4 Hz, 1H), 0.22 (d, J = 10.6 Hz, 1H), -1.13 (d, J = 10.5 Hz, 1H) ; ^{13}C NMR (101 MHz, CDCl3) δ 196.81, 183.16, 183.14, 148.96, 148.22, 136.77, 136.44, 135.12, 135.01, 132.44, 127.64, 127.56, 113.18, 112.96, 112.42, 112.20, 58.68, 50.96, 49.60, 42.19, 39.40, 38.51, 32.52, 30.98, 30.66; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.82. HRMS (MALDI-FTMS): calcd for $C_{28}H_{21}O_3F^+$ [M+H$^+$] = 425.1548; found = 425.1556.

9-Benzoyl-6-(trifluoromethyl)-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5h): Yellow solid; mp 130.3-131.4 ℃; NMR ($MeNO_2$) yield: 32.3 %; IR (KBr): 3328, 2934, 2879, 2358, 1666, 1588, 1500, 1445, 1325, 1245, 1127, 1077, 827, 743, 696; ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.52 (s, 2H), 7.40 (t, J = 7.0 Hz, 1H), 7.23 (d, J = 7.9 Hz, 1H), 7.00 (s, 1H), 6.82 (t, J = 15.1 Hz, 2H), 6.64 (d, J = 10.0 Hz, 1H), 6.45 (d, J = 10.2 Hz, 1H), 4.75 (s, 1H), 2.38 – 2.25 (m, 2H), 1.94 (s, 1H), 1.72 (d, J = 8.4 Hz, 1H), 1.37 (s, 2H), 1.16 (s, 1H), 0.95 (d, J = 10.8 Hz, 1H), 0.19 (d, J = 11.0 Hz, 1H), -1.25 (d, J = 10.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.30, 181.98, 181.94, 147.12, 147.06, 142.18, 137.93, 135.55, 135.45, 134.14, 131.60, 125.61, 122.31, 122.28, 120.51, 120.48, 58.03, 49.90, 48.43, 41.12, 38.36, 37.48, 31.48, 30.04, 29.57; ^{19}F NMR (376 MHz, CDCl3) δ -62.08 (s), -62.16. HRMS (ESI-MS): calcd for $C_{29}H_{21}O_3F_3Na^+$ [M+Na$^+$] = 497.1335; found = 497.1352.

9-Hexanoyl-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5i): Brown solid; mp 134.1 ℃; NMR ($MeNO_2$) yield: 41.7 %; IR (KBr): 3328, 2945, 2867, 2357, 1705, 1656, 1462, 1383, 1303, 1025, 830, 763, 664, 470; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.26 – 7.07 (m, 4H), 6.58 (d, *J* = 10.1 Hz, 1H), 6.52 (d, *J* = 10.1 Hz, 1H), 4.52 (d, *J* = 2.3 Hz, 1H), 2.92 – 2.72 (m, 1H), 2.63 – 2.48 (m, 1H), 2.22 (s, 1H), 1.97 (s, 1H), 1.91 (s, 3H), 1.80 (s, 1H), 1.54 (d, *J* = 6.4 Hz, 2H), 1.05 (t, *J* = 8.3 Hz, 1H), 0.98 (d, *J* = 6.8 Hz, 1H), 0.85 (t, *J* = 6.7 Hz, 3H), 0.21 (d, *J* = 10.4 Hz, 1H), -0.98 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.38, 183.49, 183.28, 151.41, 139.18, 138.15, 136.57, 134.89, 126.90, 126.71, 125.10, 50.51, 50.43, 41.89, 39.50, 38.83, 32.63, 31.83, 30.94, 30.65, 29.70, 29.13, 24.14, 22.62, 14.12. HRMS (MALDI-FTMS): calcd for $C_{28}H_{30}O_3H^+$ [M+H$^+$] = 415.2268; found = 415.2286.

9-(Cyclopropanecarbonyl)-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5j): Yellow solid; mp 164.8-166 ℃; NMR ($MeNO_2$=) yield: 85.8 %; IR (KBr): 3692, 2950, 2358, 1702, 1657, 1577, 1467, 1377, 1304, 1034, 987, 830, 740, 473; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 5.2, 3.4 Hz, 1H), 7.30 – 7.14 (m, 4H), 6.59 (q, *J* = 10.1 Hz, 2H), 4.57 (d, *J* = 2.5 Hz, 1H), 2.12 (s, 2H), 1.96 (s, 1H), 1.87 (s, 1H), 1.71 (d, *J* = 8.1 Hz, 1H), 1.57 (s, 1H), 1.34 (d, *J* = 6.6 Hz, 2H), 1.29 (dd, *J* = 8.7, 3.0 Hz, 2H), 1.13 – 0.96 (m, 4H), 0.91 (t, *J* = 8.7 Hz, 1H), 0.14 (d, *J* = 10.8 Hz, 1H), -1.08 (d, *J* = 9.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.84, 183.30, 183.05, 151.14, 139.43, 138.23, 136.56, 134.97, 127.11, 126.69, 125.22, 125.07, 50.27, 50.11, 42.08, 39.49, 38.34, 32.34, 30.90, 30.60, 29.71, 14.01. HRMS (MALDI-FTMS): calcd for $C_{25}H_{22}O_3H^+$ [M+H$^+$] = 371.1642; found = 371.1653.

9-Carbaldehyde-decahydro-9,10-[2]bicycloanthracene-1,4-dione (5k): Yellow solid; mp 167.1 ℃; NMR ($MeNO_2$) yield: 27.6 %; IR (KBr): 3432, 2928, 2877, 2358, 1714, 1653, 1587, 1465, 1385, 1308, 833, 760, 556, 511, 471; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.58 (s, 1H), 7.59 – 7.35 (m, 2H), 7.29 – 7.07 (m, 5H), 6.72 (s, 1H), 6.59 (q, *J* = 10.1 Hz, 2H), 4.57 (d, *J* = 2.5 Hz, 1H), 2.16 (d, *J* = 8.7 Hz, 1H), 2.04 (s, 1H), 1.93 (s, 1H), 1.83 – 1.76 (m, 2H), 1.33 (d, *J* = 7.0 Hz, 2H), 1.18 (s, 2H), 1.05 (t, *J* = 8.3 Hz, 1H), 1.00 – 0.92 (m, 1H), 0.23 (d, *J* = 10.8 Hz, 1H), -0.83 (d, *J* = 10.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.44, 183.57, 183.23, 151.40, 149.14, 139.51, 137.75, 136.56, 135.79, 135.43, 127.24, 126.89, 125.52, 123.53, 58.78, 48.71, 48.68, 41.93, 39.51, 37.88, 32.52, 30.79, 30.62. HRMS (ESI-MS): calcd for $C_{22}H_{18}O_3Na^+$ [M+Na$^+$] = 353.1148; found = 353.1160.

9-Benzoyl-10-methyl--decahydro--9,10-[2]bicycloanthracene-1,4-dione (4l): Yellow solid; mp 140-141 ℃; NMR ($MeNO_2$) yield: 80.0 %; IR (KBr): 3659, 2959, 2878, 2358, 1673, 1458, 1382, 1259, 1097, 863, 766, 700, 657; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.8 Hz, 1H), 7.78 – 7.65 (m, 2H), 7.43 (d, *J* = 7.2 Hz, 3H), 7.22 (dd, *J* = 6.6, 3.9 Hz, 3H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.24 (d, *J* = 10.3 Hz, 1H), 6.03 (d, *J* = 10.3 Hz, 1H), 4.10 (d, *J* = 8.8 Hz, 1H), 3.08 (d, *J* = 8.8 Hz, 1H), 2.43 (d, *J* = 8.9 Hz, 1H), 2.14 (s, 1H), 2.07 (s, 1H), 1.88 (d, *J* = 8.9 Hz, 1H), 1.47 (s, 3H), 1.41 (dd, *J* = 10.6, 7.2 Hz, 2H), 1.10 (d, *J* = 10.8 Hz, 1H), 1.04 (d, *J* = 10.4 Hz, 1H), 0.40 (d, *J* = 10.7 Hz, 1H), -0.01 (d, *J* = 10.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.42, 197.61, 197.61, 141.54, 141.27, 140.61, 139.33, 136.97, 129.92, 128.17, 127.73, 127.12, 127.06, 127.01, 123.24, 57.38, 57.11, 56.89, 52.41, 47.99, 41.63, 39.42, 38.32, 33.80, 31.41 , 19.45. HRMS (MALDI-FTMS): calcd for $C_{29}H_{26}O_3H^+$ [M+H$^+$] = 423.1955; found = 423.1957.

9-Benzoyl-10-phenyl-octahydro-9,10-[2]bicycloanthracene-1,4-dione (4m): Colorless solid; mp 204.7 ℃; NMR ($MeNO_2$) yield: 68.1 %; IR (KBr): 3683, 3291, 3065, 2931, 2338, 1692, 1658, 1554, 1296, 1050, 838, 767, 695, 474; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.52 (s, 3H), 7.40 (d, *J* = 6.5 Hz, 4H), 7.21 (d, *J* = 7.8 Hz, 3H), 7.11 (t, *J* = 7.6 Hz, 2H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.33 (d, *J* = 10.0 Hz, 1H), 6.29 (d, *J* = 10.0 Hz, 1H), 2.60 (s, 1H), 2.37 (s, 2H), 2.17 (s, 1H), 1.44 – 1.34 (m, 2H), 1.19 (s, 1H), 0.05 (d, *J* = 10.9 Hz, 1H), -1.58 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.27, 183.67, 183.19, 151.06, 147.85, 139.68, 139.09, 138.10, 137.34, 137.06, 134.05, 132.11, 127.04, 126.79, 126.63, 126.39, 125.83, 58.22, 56.27, 54.21, 51.98, 38.63, 38.16, 32.02, 31.02, 30.87. HRMS (MALDI-FTMS): calcd for $C_{34}H_{27}O_3Na^+$ [M+H$^+$+Na$^+$] = 506.1852; found = 506.1866.

9-Benzoyl-16-ethylidene-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5n): Yellow solid; mp 115-116 ℃; NMR ($MeNO_2$) yield: 85.3 %; IR (KBr): 3131, 2925, 2359, 1732, 1689, 1655, 1560, 1305, 1240, 1025, 834, 688, 474, 452; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.47 (s, 1H), 7.36 (s, 1H), 7.26 (d, *J* = 7.3 Hz, 1H), 7.16 (dd, *J* = 13.9, 6.3 Hz, 2H), 6.95 (t, *J* = 7.4 Hz, 2H), 6.74 – 6.63 (m, 1H), 6.59 (d, *J* = 10.0 Hz, 1H), 6.39 (d, *J* = 10.0 Hz, 1H), 5.46 (d, *J* = 6.4 Hz, 1H), 4.69 (s, 1H), 2.84 (s, 1H), 2.32 (dd, *J* = 15.2, 6.6 Hz, 1H), 2.02 (s, 1H), 1.92 – 1.82 (m, 1H), 1.77 (d, *J* = 7.4 Hz, 1H), 1.58 (d, *J* = 15.6 Hz, 1H), 1.37 (t, *J* = 6.5 Hz, 3H), 0.29 (d, *J* = 10.7 Hz, 1H), -1.15 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.02, 183.33, 183.13, 149.05, 148.86, 145.06, 139.34, 137.76, 136.94, 136.40, 135.07, 132.31, 127.32, 126.51, 126.45, 124.89, 113.09, 59.08, 50.50, 49.06, 46.82, 42.15, 39.69, 36.88, 32.76, 13.81; HRMS (MALDI-FTMS): calcd for $C_{30}H_{25}O_3^+$ [M+H$^+$] = 433.1789; found = 433.1810.

5-Benzoyl-tetrahydro-5,12-[1,2]benzeno-6,11-methanotetracene-15,18-dione (5o): Yellow solid; mp 175.8-176 ℃; NMR ($MeNO_2$) yield: 79 %; IR (KBr): 3308, 30668, 2933, 2357, 1608, 1589, 1386, 1241, 1081, 977, 843, 761, 694, 480; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.1 Hz, 2H), 7.12 (s, 1H), 7.05 – 7.00 (m, 2H), 6.98 (d, *J* = 7.0 Hz, 2H), 6.94 (d, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 4.2 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 10.0 Hz, 1H), 6.37 (d, *J* = 10.1 Hz, 1H), 4.72 (s, 1H), 3.43 (s, 1H), 2.86 (s, 1H), 2.50 (d, *J* = 8.3 Hz, 1H), 2.01 (d, *J* = 8.5 Hz, 1H), 0.91 (d, *J* = 10.3 Hz, 1H), -0.67 (d, *J* = 10.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.95, 183.34, 183.07, 150.77, 150.34, 150.21, 139.67, 138.09, 136.84, 136.37, 135.03, 132.45, 128.99, 128.41, 128.12, 127.63, 127.30, 127.12, 127.02, 126.80, 125.79, 125.49, 125.36, 125.22, 124.17, 121.18, 120.54, 120.28, 58.83, 51.93, 50.21, 46.30, 45.38, 41.69, 41.26; HRMS (MALDI-FTMS): calcd for $C_{32}H_{23}O_3^+$ [M+H$^+$] = 455.1642; found = 455.1640.

9-Benzoyl-hexahydro-9,10-[2,3]furanoanthracene-1,4-dione (4p): Green solid; mp 235-236 ℃; NMR ($MeNO_2$) yield: 45.6 %;

IR (KBr): 3308, 30668, 2933, 2357, 1608, 1589, 1386, 1241, 1081, 977, 843, 761, 694, 480; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.50 (s, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 14.8 Hz, 2H), 7.00 (t, *J* = 7.2 Hz, 2H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.66 (d, *J* = 10.1 Hz, 1H), 6.48 (d, *J* = 10.1 Hz, 1H), 5.04 (d, *J* = 7.7 Hz, 1H), 4.62 (d, *J* = 2.6 Hz, 1H), 3.44 (td, *J* = 8.4, 4.4 Hz, 1H), 2.67 – 2.57 (m, 1H), 2.05 – 1.99 (m, 1H), 1.92 – 1.84 (m, 1H), 1.54 (d, *J* = 6.8 Hz, 1H), 1.31 – 1.22 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.50, 183.14, 183.01, 150.39, 146.67, 138.11, 136.80, 136.66, 136.35, 135.17, 132.48, 128.33, 127.16, 126.74, 125.25, 83.61, 70.40, 61.82, 45.15, 42.46, 29.70, 29.42. HRMS (ESI-MS): calcd for $C_{25}H_{20}O_4Na^+$ [M+Na$^+$] = 407.1254; found = 407.1241.

5-Benzoyl-hexahydro-5,12-[2]bicyclotetracene-6,11-dione (5q): Yellow solid; mp 272.6 ℃; NMR ($MeNO_2$) yield: 86.6 %; IR (KBr): 3068, 2934, 2358, 1732, 1667, 1590, 1462, 1291, 1241, 960, 691, 702, 623, 568; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.3 Hz, 1H), 7.50 (d, *J* = 11.8 Hz, 1H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.16 (dd, *J* = 15.7, 8.4 Hz, 2H), 6.94 (t, *J* = 7.4 Hz, 2H), 6.67 (d, *J* = 7.7 Hz, 1H), 4.87 (d, *J* = 2.1 Hz, 1H), 2.40 (s, 1H), 2.33 (d, *J* = 8.4 Hz, 1H), 1.92 (s, 1H), 1.75 (s, 1H), 1.35 (s, 2H), 1.13 (d, *J* = 14.3 Hz, 1H), 0.94 (t, *J* = 9.2 Hz, 1H), 0.17 (d, *J* = 10.8 Hz, 1H), -1.18 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.43, 181.40, 181.32, 151.37, 151.02, 139.33, 138.01, 137.24, 133.85, 133.56, 132.52, 132.13, 131.78, 127.16, 126.72, 126.50, 126.30, 126.27, 124.86, 59.44, 51.05, 49.58, 42.58, 39.55, 38.64, 32.40, 31.12, 30.71, 29.70. HRMS (MALDI-FTMS): calcd for $C_{32}H_{24}O_3H^+$ [M+H$^+$] = 457.1798; found = 457.1811.

10-Benzoyl-octahydro-9,10-ethano-1,4-methanoanthracene-11-carbonitrile (5r): Yellow solid; mp 77-79 ℃; NMR ($MeNO_2$) yield: 35.8 %; IR (KBr): 2964, 2880, 2358, 1729, 1678, 1587, 1475, 1251, 939, 910, 762, 702, 604, 424; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 6.6 Hz, 2H), 7.06 (d, *J* = 7.4 Hz, 1H), 3.28 (dd, *J* = 11.2, 4.9 Hz, 1H), 3.07 (s, 1H), 2.64 (d, *J* = 8.6 Hz, 1H), 2.29 (s, 1H), 2.06 (d, *J* = 2.6 Hz, 1H), 2.02 (s, 1H), 1.99 (d, *J* = 9.3 Hz, 1H), 1.79 (s, 1H), 1.31 (s, 2H), 1.12 (s, 1H), 0.16 (d, *J* = 10.7 Hz, 1H), -0.95 (d, *J* = 10.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.83, 141.62, 136.90, 132.68, 129.88, 129.57, 128.46, 128.22, 126.73, 126.29, 125.38, 120.95, 56.22, 47.99, 47.25, 40.78, 39.31, 38.60, 33.46, 32.46, 32.40, 31.34, 30.53. HRMS (ESI-MS): calcd for $C_{29}H_{24}O_3Na^+$ [M+Na$^+$] = 443.1774; found = 443.1784.

9-Benzoyl-octahydro-9,10-[3,4]epipyrrolo-1,4-methanoanthracene-12,14-dione (5s): Colorless solid; mp 126-128 ℃; NMR ($MeNO_2$) yield: 89.3 %; IR (KBr): 3181, 2949, 2426, 1774, 1712, 1470, 1347, 1235, 1177, 975, 765, 706, 642, 480; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 6.8 Hz, 2H), 7.64 (s, 1H), 7.49 – 7.37 (m, 3H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 7.0 Hz, 1H), 3.81 (d, *J* = 8.6 Hz, 1H), 3.49 (s, 1H), 3.04 (dd, *J* = 8.6, 2.5 Hz, 1H), 2.22 (d, *J* = 8.8 Hz, 1H), 2.11 (s, 1H), 1.99 (d, *J* = 7.7 Hz, 2H), 1.50 – 1.33 (m, 2H), 1.14 (t, *J* = 9.8 Hz, 1H), 1.10 – 0.99 (m, 1H), 0.45 (d, *J* = 10.7 Hz, 1H), -0.01 (d, *J* = 10.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.55, 177.21, 176.92, 140.74, 136.17, 134.71, 130.06, 128.19, 127.75, 127.69, 127.53, 126.96, 125.94, 55.28, 49.18, 47.80, 47.73, 46.98, 41.41, 41.13, 38.53, 33.64, 30.92, 30.27. HRMS (MALDI-FTMS): calcd for $C_{26}H_{23}NO_3H^+$ [M+H$^+$] = 398.1751; found = 398.1754.

9-Benzoyl-13-methyl-octahydro-9,10-[3,4]epipyrrolo-1,4-methanoanthracene-12,14-dione (5t): Colorless solid; mp 262.4 ℃; NMR ($MeNO_2$) yield: 80.1 %; IR (KBr): 3068, 2749, 2358, 1772, 1698, 1540, 1439, 1381, 1269, 1234, 973, 762, 653, 462; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 1H), 7.68 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 3H), 7.17 (td, *J* = 7.6, 1.5 Hz, 1H), 7.11 (td, *J* = 7.4, 1.2 Hz, 1H), 6.96 (dd, *J* = 7.3, 1.1 Hz, 1H), 3.73 (d, *J* = 8.4 Hz, 1H), 3.46 (t, *J* = 2.5 Hz, 1H), 2.99 (dd, *J* = 8.4, 2.7 Hz, 1H), 2.33 (s, 3H), 2.21 (d, *J* = 8.9 Hz, 1H), 2.06 (d, *J* = 3.5 Hz, 1H), 1.98 (dd, *J* = 11.4, 2.5 Hz, 2H), 1.37 (dtdd, *J* = 27.2, 11.6, 7.8, 3.9 Hz, 2H), 1.10 (t, *J* = 9.9 Hz, 1H), 1.04 – 0.96 (m, 1H), 0.40 (d, *J* = 10.7 Hz, 1H), -0.01 (d, *J* = 10.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.62, 177.26, 177.01, 140.90, 136.17, 134.68, 130.05, 128.17, 127.63, 127.57, 126.79, 125.71, 55.57, 49.29, 47.77, 46.68, 45.83, 41.69, 41.19, 38.56, 33.71, 30.93, 30.30, 24.13. HRMS (MALDI-FTMS): calcd for C27H25NO3H+ [M+H+] = 412.1907; found = 412.1910.

9-Benzoyl-13-benzyl-octahydro-9,10-[3,4]epipyrrolo-1,4-methanoanthracene-12,14-dione (5u): Red solid; mp 140.1-143.4 ^{o}C; NMR ($MeNO_2$) yield: 80 %; IR (KBr): 3063, 2948, 2357, 1772, 1700, 1577, 1399, 1346, 1234, 1171, 1068, 930, 743, 702, 469. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 6.4 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 3H), 7.12 – 6.95 (m, 5H), 6.88 (d, *J* = 7.2 Hz, 1H), 6.55 (d, *J* = 7.2 Hz, 2H), 4.11 (d, *J* = 5.0 Hz, 2H), 3.74 (d, *J* = 8.6 Hz, 1H), 3.46 (s, 1H), 2.99 (dd, *J* = 8.6, 2.4 Hz, 1H), 2.21 (d, *J* = 8.9 Hz, 1H), 2.04 (d, *J* = 3.0 Hz, 1H), 1.95 (d, *J* = 11.6 Hz, 2H), 1.42 – 1.30 (m, 2H), 1.09 (t, *J* = 9.9 Hz, 1H), 1.05 – 0.95 (m, 1H), 0.37 (d, *J* = 10.6 Hz, 1H), -0.14 (d, *J* = 10.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.71, 176.91, 176.63, 140.91, 136.02, 134.77, 134.57, 129.99, 128.34, 128.18, 127.80, 127.74, 127.70, 127.55, 127.29, 126.79, 125.75, 55.31, 49.35, 47.98, 46.56, 45.66, 42.04, 41.50, 41.13, 38.53, 33.64, 30.93, 30.29. HRMS (MALDI-FTMS): calcd for $C_{33}H_{29}NO_3H^+$ [M+H$^+$] = 488.2220; found = 488.2229.

9-Benzoyl-13-phenyl-octahydro-9,10-[3,4]epipyrrolo-1,4-methanoanthracene-12,14-dione (5v): White solid; mp 167.1 ℃; NMR ($MeNO_2$) yield: 60.3 %; IR (KBr): 3064, 2950, 2357, 1776, 1708, 1495, 1386, 1231, 1185, 1025, 913, 863, 747, 649, 471; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.5 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 4.7 Hz, 1H), 7.05 – 6.99 (m, 3H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.27 – 6.13 (m, 2H), 3.79 (d, *J* = 8.5 Hz, 1H), 3.45 (s, 1H), 3.04 (dd, *J* = 8.5, 2.6 Hz, 1H), 2.19 (d, *J* = 8.9 Hz, 1H), 2.00 (d, *J* = 3.1 Hz, 1H), 1.97 – 1.86 (m, 2H), 1.34 – 1.22 (m, 2H), 1.01 (d, *J* = 11.6 Hz, 1H), 0.94 (d, *J* = 10.3 Hz, 1H), 0.33 (d, *J* = 10.7 Hz, 1H), -0.01 (d, *J* = 10.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.47, 176.48, 176.29, 140.88, 136.52, 135.08, 131.21, 130.10, 129.02, 128.72, 128.20, 127.77, 127.72, 127.64, 127.11, 126.39, 125.96, 55.94, 49.24, 47.68, 46.86, 45.95, 42.08, 41.29, 38.66, 33.87, 30.98, 30.34. HRMS (MALDI-FTMS): calcd for $C_{32}H_{27}NO_3H^+$ [M+H$^+$] = 474.2064; found = 474.2066.

9-Benzoyl-octahydro-9,10-ethano-1,4-methanoanthracene-11,11,12,12-tetracarbonitrile (5w): Red solid; mp 194.2 ℃; NMR ($MeNO_2$) yield: 80.4 %; IR (KBr): 3720, 3665, 3070, 2956, 2924, 2359, 1716, 1664, 1551, 1456, 1247, 968, 672, 474; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.9 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.48 – 7.32 (m, 5H), 3.91 (s, 1H), 2.58 (dd, *J* = 21.6, 9.0 Hz, 2H), 2.26 (d, *J* = 18.3 Hz, 2H), 1.37 (dd, *J* = 19.5, 8.9 Hz, 3H), 1.06 (d, *J* = 10.7 Hz, 1H), 0.75 (d, *J* = 10.8 Hz, 1H), 0.59 (d, *J* = 10.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.86, 135.89, 134.68, 133.45, 131.78, 131.24, 131.12, 129.88, 129.74, 128.27, 128.01, 111.75, 111.59, 110.92, 110.70, 65.87, 48.71, 48.53, 47.40, 46.41, 41.78, 41.18, 40.83, 33.73, 30.74, 29.99; HRMS (ESI-MS): calcd for $C_{28}H_{20}N_4ONa^+$ [M+Na$^+$] = 451.1529; found = 451.1528.

Dimethyl-9-benzoyl-octahydro-9,10-etheno-1,4-methanoanthracene-11,12-dicarboxylate (5x): Yellow solid; mp 175.7-177.3 ℃; NMR ($MeNO_2$) yield: 40.1 %; IR (KBr): 3825, 3807, 3069, 2956, 2358, 2234, 1717, 1667, 1527, 1389, 1203, 950, 673, 612, 461; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.24 (dd, *J* = 11.0, 8.6 Hz, 3H), 7.16 (dd, *J* = 13.3, 5.9 Hz, 1H), 7.01 – 6.96 (m, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 4.32 (d, *J* = 2.5 Hz, 1H), 3.73 (s, 3H), 3.08 (s, 3H), 2.42 (s, 1H), 2.35 (d, *J* = 8.5 Hz, 1H), 2.23 (d, *J* = 3.5 Hz, 1H), 2.19 (s, 1H), 1.86 – 1.78 (m, 2H), 1.33 (s, 1H), 0.98 (t, *J* = 9.2 Hz, 1H), 0.13 (d, *J* = 10.8 Hz, 1H), -1.22 (d, *J* = 10.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.74, 166.18, 165.48, 143.32, 142.30, 139.40, 138.60, 135.58, 132.96, 129.95, 128.02, 127.19, 126.29, 125.46, 124.41, 62.12, 52.50, 51.56, 50.86, 49.57, 47.02, 39.21, 38.72, 32.20, 31.04, 30.64. HRMS (MALDI-FTMS): calcd for $C_{28}H_{26}O_5Na^+$ [M+Na$^+$] = 465.1673; found = 465.1684.

Typical procedure for transformation from 5 to 7.

To a solution of xylene (0.5 mL, 0.088 M) was added **5** (18.0 mg, 0.044 mmol). The reaction was stirred under nitrogen atmosphere at 170 ℃ for 6 hours.the solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel to afford the desired product **7** (12.7 mg, 92 %).

9-Benzoylanthracene-1,4-dione (7a): Yellow solid; mp 268.9-269.2 °C; Isolated yield: 92.0 %; IR (KBr): 2921, 2852, 2393, 2287, 1667, 1602, 1419, 1230, 1076, 911, 786, 701, 479; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 5.2 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 10.3 Hz, 1H), 6.88 (d, *J* = 10.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.53, 184.15, 184.08, 141.23, 140.04, 139.73, 137.13, 134.71, 133.58, 132.61, 130.68, 130.51, 130.17, 130.01, 128.82, 128.71, 128.12, 127.62, 125.74; HRMS (MALDI-FTMS): calcd for $C_{21}H_{14}O_3^+$ [M $^+$] = 314.0938; found = 314.0942.

6-Benzoyltetracene-5,12-dione (7b): Yellow solid; mp 256.0-256.1°C; Isolated yield: 80.0%; IR (KBr): 3056, 2972, 2392, 2286, 1661, 1312, 1459, 1296, 70, 722; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.32 (d, *J* = 7.6 Hz, 1H), 8.15 – 8.07 (m, 2H), 7.79 (d, *J* = 7.3 Hz, 2H), 7.74 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.49 (d, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.82, 182.59, 182.55, 141.85, 137.36, 135.03, 134.50, 134.39, 133.96, 133.42, 132.91, 130.88, 130.59, 130.38, 129.86, 129.58, 128.85, 128.71, 127.93, 127.53, 127.50; HRMS (MALDI-FTMS): calcd for $C_{25}H_{16}O_3^+$ [M $^+$] = 364.1094; found = 364.1099.

7-Benzoyl-5,14-[1,2]benzenopentacene-6,13-dione (7c): Yellow solid; mp 302.7 °C; Isolated yield: 72%; IR: 3304, 2920, 2851, 2393, 2286, 1731, 1672, 1579, 1424, 1284, 1162, 985, 791, 718; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 7.0 Hz, 2H), 7.43 (d, *J* = 6.9 Hz, 1H), 7.40 (d, *J* = 7.1 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.33 – 7.26 (m, 3H), 7.02 – 6.89 (m, 4H), 6.00 (s, 1H), 5.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.73, 180.40, 180.31, 155.55, 155.38, 143.62, 143.55, 143.38, 143.30, 141.26, 137.11, 134.59, 133.57, 132.53, 130.60, 130.24, 129.96, 129.78, 128.91, 128.79, 128.59, 127.60, 125.73, 125.70, 125.64, 125.60, 124.66, 124.60, 124.48, 47.96, 47.89; HRMS (MALDI-FTMS): calcd for $C_{35}H_{22}O_3^+$ [M $^+$] = 490.1564; found = 490.1568.

Dimethyl-1-benzoylnaphthalene-2,3-dicarboxylate (7d): White solid; mp 124.8 °C; Isolated yield: 98%; IR: 3053, 2980, 1727, 1668, 1581, 1445, 1297, 1164, 1070, 944, 782, 640; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.55 (dd, *J* = 12.9, 5.7 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 3.88 (s, 3H), 3.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.67, 167.41, 166.90, 138.59, 137.27, 133.91, 132.89, 132.20, 131.31, 129.72, 129.57, 129.38, 128.71, 128.57, 128.16, 126.98, 126.30, 52.80, 52.55.

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