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Mechanistic Insight into Transition Metal-Catalyzed Reaction of Enynal/Enynone with Alkenes: Metal-Dependent Reaction Pathway

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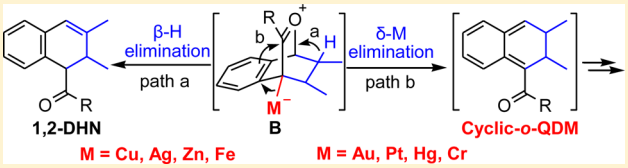
Supporting Information

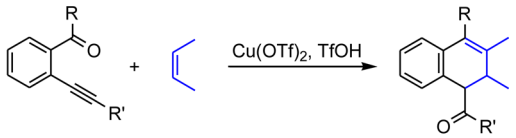
ABSTRACT: A systematic study of the transition metal-catalyzed reaction of enynal/enynone with alkenes has been reported. It was found that the reaction has two metal-dependent reaction pathways. One led to the formation of 1,2-DHN, while another led to cyclic-*o*-QDM.



INTRODUCTION

Enynal/enynone is a versatile building block for the construction of the benzannulated system. Among the different methods, the transition metal-catalyzed reaction of enynal/enynone with alkenes is one of the most efficient and straightforward ways to construct aphthalene derivatives.[1] For example, Asao and Yamamoto synthesized a series of functionalized 1,2-dihydronaphthalene through $Cu(OTf)_2$-catalyzed [4 + 2] cycloaddition of enynal with alkenes (Scheme 1).[1b]

Scheme 1. Copper-Catalyzed Reaction of Enynals/Enynones with Alkenes



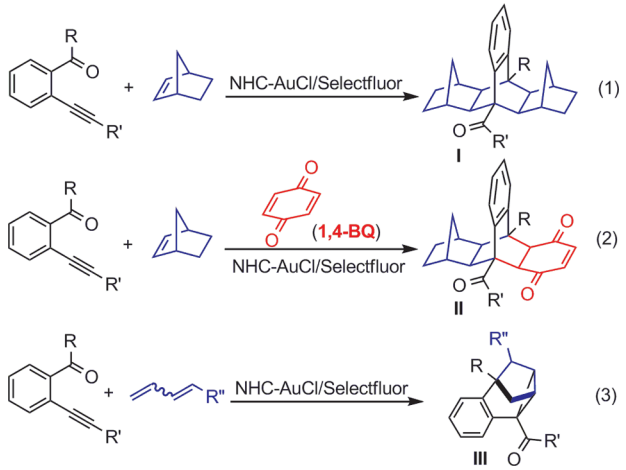
Asao, Yamamoto

Recently, we reported a gold-catalyzed reaction of enynal/enynone with different alkenes to synthesize different structurally unique polycyclic structures **I**–**III** (Scheme 2).[2] However, the reactions worked efficiently only when high-reactive alkenes, norborenes, and 1,3-dienes were used as the substrates (Scheme 2).

The reaction was believed to proceed through the gold-catalyzed tandem Diels–Alder reactions via trapping of the key intermediate cyclic *o*-quinodimethane[3,4] (cyclic-*o*-QDM), a highly reactive species (Scheme 3).

When styrene was tested as the substrate, however, the expected propeller-like molecule **I** was not formed. 1,2-Dihydronaphthalene (1,2-DHN) **4** was formed as the product instead (Scheme 4, eq 4). It seems that the reaction is identical to the $Cu(OTf)_2$-catalyzed system reported by Asao and Yamamoto (Scheme 1).[1b] Trying to trap the proposed cyclic-*o*-QDM intermediate by addition of 1,4-benzoquinone (1,4-BQ) as the more reactive dienophile also failed. Naphthalene **5**, not

Scheme 2. Our Previous Work



the desired propeller-like molecule **II**, was isolated as the only product (eq 5). Interestingly, 1,2-DHN **4** could not be oxidized into naphthalene **5** with 1,4-BQ as the oxidant (eq 6). It indicated that naphthalene **5** may not simply come from the oxidation of 1,2-DHN **4**.

Through carefully controlling the reaction conditions, it was found that the desired propeller-like product **6a** was actually generated during the reaction course. However, this molecule was unstable and would aromatize into naphthalene **5a** immediately after treatment with silica gel/air (Scheme 5). The propeller-like structure of **6a** was confirmed by the X-ray diffraction analysis of its single crystal (see the SI).

The $Cu(OTf)_2$-catalyzed reaction of **1a**, **2a**, and **3a** under similar conditions resulted in a complex system. Both adducts of **5a** and **6a** were not detected in the reaction system (Scheme 6). It indicated that copper-catalyzed and gold-catalyzed

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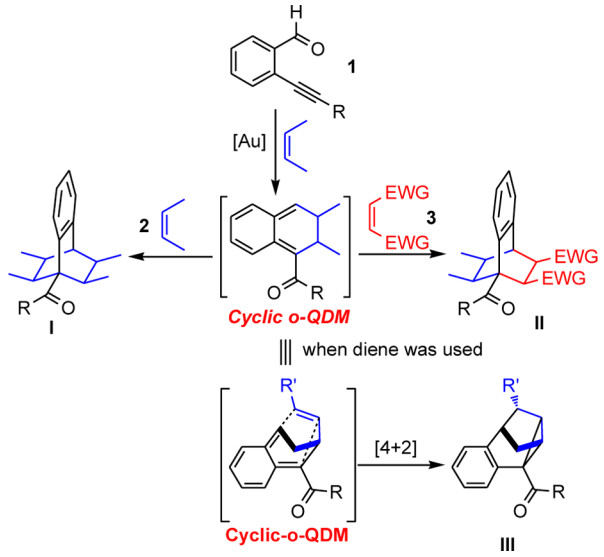
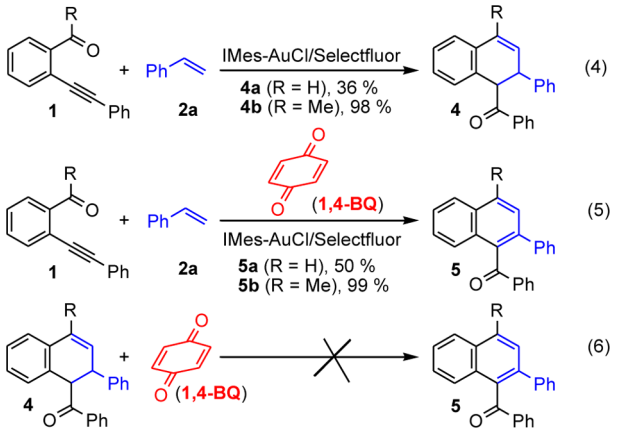
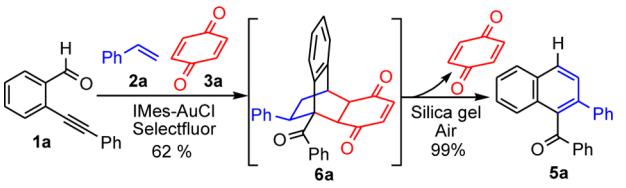
Scheme 3. Possible Reaction Mechanism



Scheme 4



Scheme 5. Gold-Catalyzed Reaction of Enynal with Styrene and 1,4-BQ

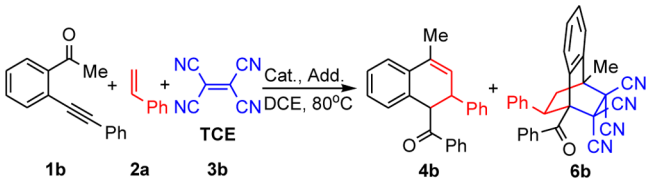


reactions of enynal with alkenes might experience different reaction mechanisms.

RESULTS AND DISCUSSION

To figure out the underlying reaction mechanism, a systematic study was then carried out. Initially, different metal catalysts were investigated. Styrene **2a** and tetracyanoethylene (TCE) **3b** were chosen as the dienophiles for the model reactions (Table 1). Among the different metal salts being tested, silver, copper, zinc, and iron salts furnished 1,2-DHN **4b** in 13−72% yields (entries 1−8). Silver and copper salts functioned better than zinc and iron. The yield is up to 72% when $Cu(OTf)_2$ was used as catalyst, which is consistent with the literature results.[1b] $CdCl_2$, $MnCl_2$, $NiCl_2$, and $CoCl_2$ were inefficient for this transformation (entries 9−12). $InCl_3$ gave the mixture of **4b** and **6b**, with the yields being 15% and 40%, respectively (entry 13). The desired product **6b** could be obtained as the sole product when chromium ($CrCl_2$), platinum ($PtCl_2$), mercury (HgI_2), and gold ($KAuCl_4$*$2H_2O$) salts were used as catalysts, albeit in modest yields (24−32%, entries 14−17). Comparing with the inorganic gold salts, the organic gold-complex gave superior results (entries 18−20). For instance, 2-picolinate and N-heterocyclic carbene (NHC) supported gold complexes, $PicAuCl_2$, $IMes\text{-}AuCl_3$, and IMes-AuCl, could catalyze the

Table 1. Screen Different Catalytic Conditions[a]



entry	cat. (5 mol %)	add. (10 mol %)	yield (**4b**)	yield (**6b**)
1	$AgSbF_6$		69%	
2	AgOTf		55%	
3	$AgNTf_2$		44%	
4	$Cu(OTf)_2$		72%	
5	$CuCl_2$•$2H_2O$		13%	
6	$ZnCl_2$		32%	
7	ZnI_2		33%	
8	$FeCl_3$		19%	
9[b]	$CdCl_2$			
10[b]	$MnCl_2$			
11[b]	$NiCl_2$			
12[b]	$CoCl_2$			
13	$InCl_3$		15%	40%
14	$CrCl_2$			24%
15	$PtCl_2$			28%
16	HgI_2			32%
17	$KAuCl_4$•$2H_2O$			32%
18	$PicAuCl_2$			41%
19	$IMes\text{-}AuCl_3$			57%
20	IMes-AuCl			52%
21	IMes-AuCl	Selectfluor		81%
22	SIMes-AuCl	Selectfluor		67%
23	IPr-AuCl	Selectfluor		46%
24	SIPr-AuCl	Selectfluor		42%
25[c]	**IMes-AuCl**	**Selectfluor**		**93%**[d]
26		Selectfluor		

[a]Unless otherwise noted, the reactions were performed in DCE at 80 °C for 24 h using 5 mol % catalyst and 10 mol % additive under N_2, **1**/**2**/**3** = 1:5:1. [**1**] = 0.1 M. The yield was determined by ^1H NMR with $MeNO_2$ as internal standard. **Pic**: 2-picolinate, **IMes**: 1,3-dimesitylimidazol-2-ylidene; **SIMes**: 1,3-dimesitylimidazolin-2-ylidene; **IPr**: 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene; **SIPr**: 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene. [b]No reaction. [c]**1**/**2**/**3** = 1:5:2. [d]Isolated yield.

Scheme 6. Copper-Catalyzed Reaction of Enynal with Styrene and 1,4-BQ

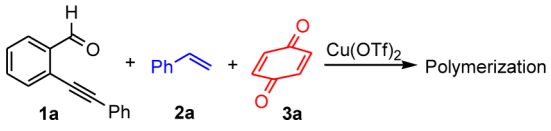


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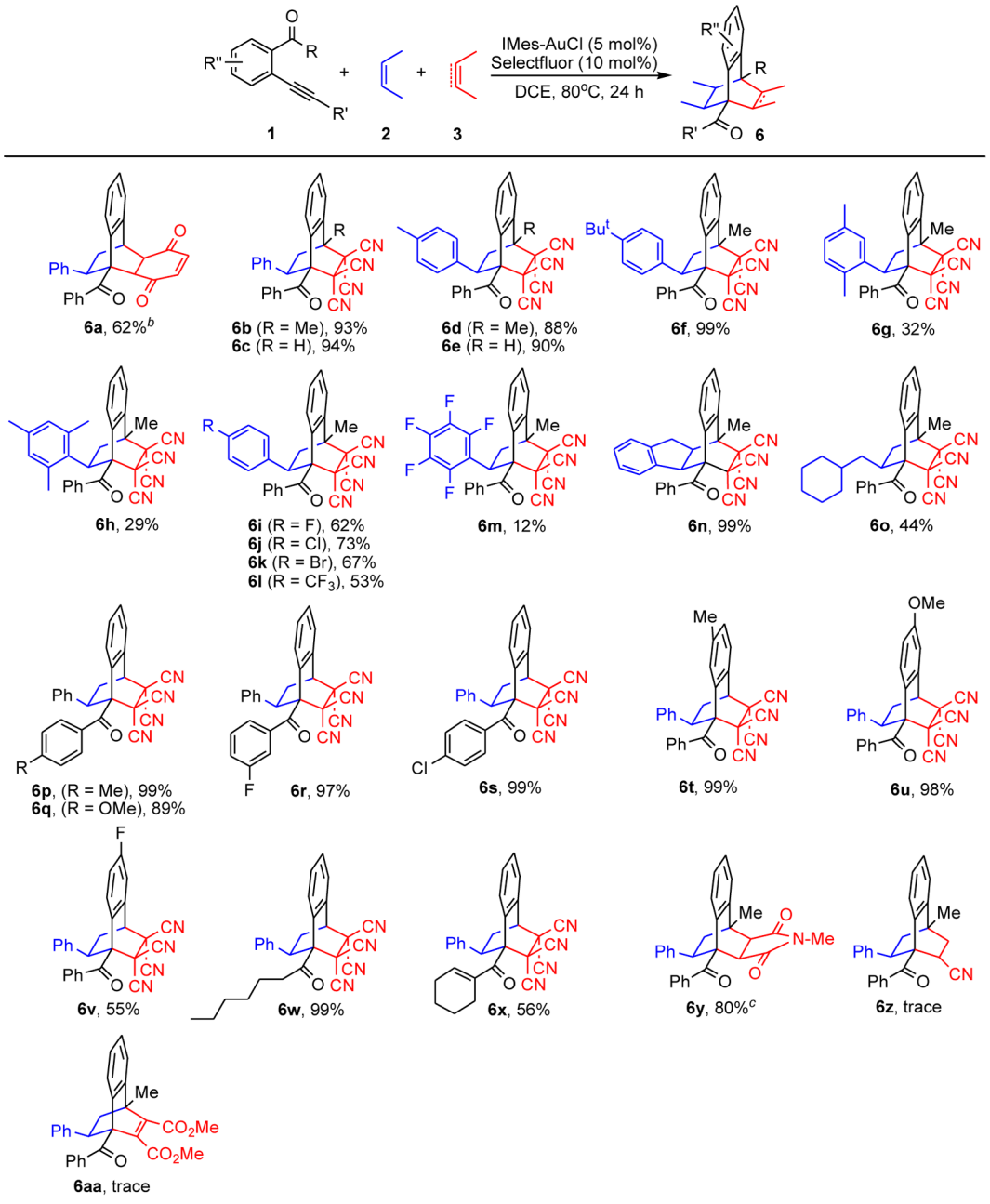
Table 2. Substrate Scopes[a]



[a]The reaction was performed at 80 °C for 24 h using 5 mol % cat and 10 mol % add under N_2; **1**:**2**:**3** = 1:5:2, [**1**] = 0.1 M, isolated yield. [b]Purified by crystallization. [c]The stereochemistry was determined by its NOE spectrum (see the SI).

reaction smoothly to furnish the corresponding product **6b**, with the yields ranging from 41% to 57% (entries 18−20). The NHC-Au(III) complex proved to be better than $PicAuCl_2$ and NHC-Au(I). In our previous work, it was found that the combination of NHC-Au(I)/Selectfluor was a more reliable and efficient system than the NHC-Au(III) one for the reaction of enynal/enynone with alkenes.[2,5] It was proposed that Selectfluor severed as a mild organic oxidant to oxidize NHC-Au(I) into NHC-Au(III)$^+$, which is the real catalyst for the reaction. Inspired by these facts, four different NHC-AuCl/Selectfluor (1:2) combinations was then tested (entries 21−24). As expected, a significant positive effect was observed when the combination of NHC-AuCl/Selectfluor (1:2) was applied. Among four different NHC-complexes, IMes-AuCl functioned better than the other three. The yield of **6b** was improved to 81% for the combination of IMes-AuCl/Selectfluor (entry 21). Increasing the amount of TCE **3b** could improve the yield further (93%, entry 25). The reaction did not occur without NHC-AuCl (entry 26).

With the optimized reaction conditions (Table 1, entry 25) in hand, the substrate scope was then examined. As summarized in Table 2, the catalytic process could be successfully applied to a variety of enynals/enynones **1** and alkenes **2**. For example, in addition to styrene **2a**, various styrene derivatives could be effectively reacted with enynal/enynone **1** as well (Table 2, **6a**-**6n**). The reaction was sensitive to the steric hindrance of the alkenes. For example, bulky 2,5-dimethylstyrene and 2,4,6-trimethylstyrene gave the products **6g** and **6h** only in 32% and

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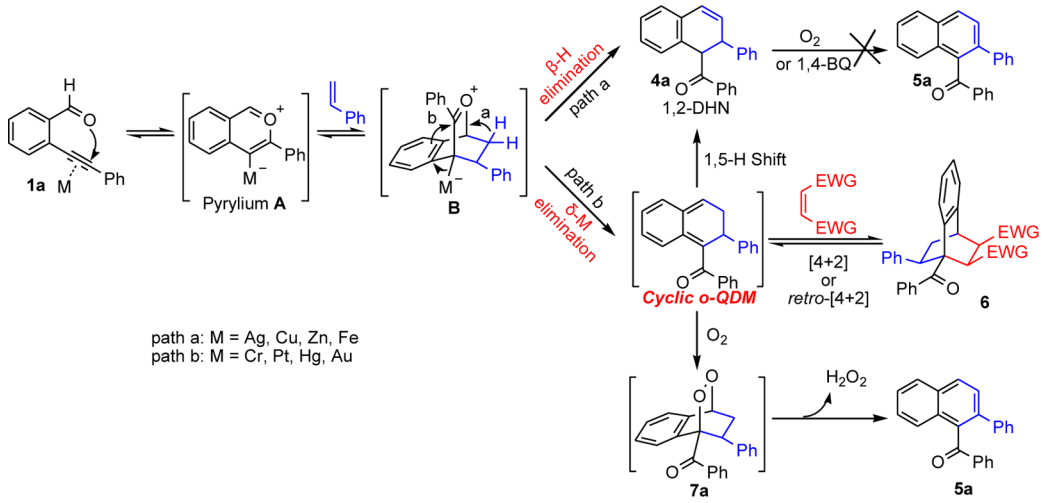
Scheme 7. Possible Pathways of Metal-Catalyzed Reaction of Enynal with Styrenes



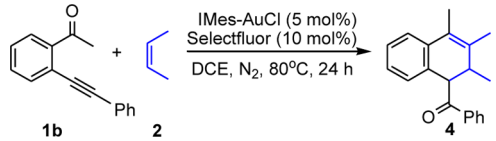
29% yields, respectively. Electron-rich alkenes were better substrates than the electron-poor ones (electron-rich: **6a-6f**; electron-poor: **6i-6m**).

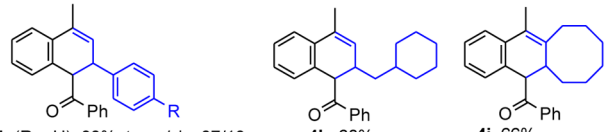
For the extremely electron-deficient 2,3,4,5,6-pentafluorostyrene, the yield was only 12% (**6m**). Indene, a cyclic alkene, was an efficient substrate for this transformation, with the yield being almost quantitative (**6n**). In addition to styrene derivatives, the aliphatic alkene could be used as the substrate as well, giving the desired product **6o** in 44% yield. Comparing with the styrene derivatives **2**, the reaction was less sensitive to the properties of enynals/enynones **1** (**6p-6x**). For example, both the enynals substituted with electron-donating and electron-withdrawing groups furnished the desired products in good to excellent yields (**6p-6v**). For enynal bearing the alkyl group, the reactions proceed smoothly as well, giving the product **6w** in 99% yield. For the enynal with a cyclohexenyl group, the product **6x** could be obtained in 56% yield. In addition to 1,4-BQ and TCE, *N*-methyl maleimide could be used as a good dienophile as well (**6y**). However, acrylonitrile and dimethyl acetylene-dicarboxylate were not efficient dienophiles for this reaction (**6z**, **6aa**). For all the products **6** in Table 2, only the endoadduct isomers were detected.

Based on the above results, the reaction mechanism was then proposed (Scheme 7). The coordination of the triple bond of enynal **1a** to [M] 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 styrene and pyrylium **A** then occurred to furnish the key intermediate **B**. Two different possible reaction pathways would then follow. Path a): *β*-H elimination of intermediate **B** led to the formation of 1,2-DHN **4a**; Path b): *δ*-metal elimination of intermediate **B** led to the formation of the cyclic-*o*-QDM. In the absence of dienophile or dioxygen, the 1,5-H shift would happen to furnish 1,2-DHN **4a**. While in the presence of dienophile or dioxygen, the cyclic-*o*-QDM could be trapped through the second Diels–Alder reaction to form the adducts **6** and **7a**. Among them, the unstable peroxide **7a** would decompose into naphthalene **5a**. Based on the results shown in Tables 1 and 2, the reaction pathway is metal-dependent. When silver, copper, zinc, and iron salts were used as the catalysts, reaction path a was followed. While chromium, platinum, mercury, and gold salts were applied as the catalysts, reaction path b was followed.

To further prove the above reaction mechanism, especially the reaction pathway of the cyclic-*o*-QDM, two control reactions were then carried out. As shown in Scheme 7, 1,2-DHN **4a** would be formed when the reactions were set without the dienophile or dioxygen. Therefore, the first set control reactions without addition of the electron-deficient olefins were then conducted under the N_2 atmosphere. As shown in Table 3, a variety of 1,2-DHNs **4** could be generated in good to excellent yields as expected.

Table 3. Control Reaction[a]





4b (R = H), 98%, trans/cis: 87/13
4c (R = OMe), 87%, trans/cis: 90/10
4d (R = ^{t}Bu), 94%, trans/cis: 88/12
4e (R = F), 87%, trans/cis: 96/04
4f (R = Cl), 88%, trans/cis: 93/07
4g (R = Br), 94%, trans/cis: 95/05

4h, 68%
trans/cis: 91/09

4i, 66%
trans/cis: 98/02

[a]The reaction was performed at 80 °C for 24 h using 5 mol % cat., 10 mol % Selectfluor, and 1.0 equiv of H_2O under N_2; **1**:**2** = 1:5; [**1**] = 0.05 M, isolated yield; the stereochemistry was determined by ^{1}H NMR.

As shown in Scheme 7, a peroxide **7a** would be generated if the cyclic-*o*-QDM was trapped by the dioxygen. Therefore, another control reaction was then performed under the oxygen atmosphere. As expected, the aromatization product naphthalene **5b** was isolated in 71% yield when enynone **1b** reacted with styrene **2a** (Scheme 8). Furthermore, the key intermediate **7b**, an unstable peroxide, could be detected by the ^{1}H NMR spectrum and HRMS analysis of the crude reaction mixture (see the SI).

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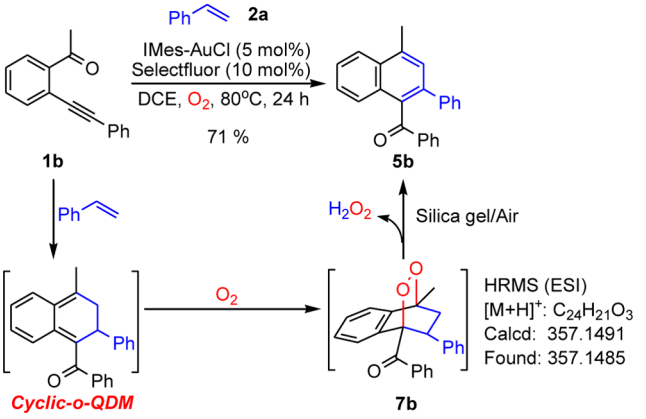
Scheme 8. Control Reaction under Oxygen Atmosphere



CONCLUSIONS

In conclusion, we have conducted a systematic study of the transition metal-catalyzed reaction of enynals/enynones with alkenes. It was found that the reactions have two metal-dependent reaction pathways. The reactions started with the nucleophilic attack of the carbonyl oxygen to the alkyne, which was activated by the coordination of metal catalysts, forming the intermediate pyrylium **A**. It subsequently reacted with alkenes through the Diels–Alder reactions to form the bridge intermediate **B**. When silver, copper, zinc, and iron salts were used as the catalysts, a β-H elimination of the intermediate **B** led to the formation of 1,2-DHN **4**. When chromium, platinum, mercury, and gold salts were applied as the catalysts, the δ-metal elimination of the intermediate **B** led to the formation of the cyclic-*o*-QDM. The highly reactive transient species could rearrange to 1,2-DHN **4** through the 1,5-H shift. Furthermore, the cyclic-*o*-QDM was also a good diene which could be trapped by the dienophiles (electron deficient alkenes/alkynes or dioxygen molecules) through the Diels–Alder reactions. We believe such metal-dependent reaction mechanisms would render useful information to the organometallic chemists in understanding the catalytic behavior of different transition metals.

EXPERIMENTAL SECTION

General Information. All reactions were carried out under an inert atmosphere of dry N_2 in a Schlenk tube, and solvents were purified by standard methods. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on 400 MHz, 100 MHz, and 376 MHz spectrometers, respectively. ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0, and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as external standard. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. The mass analyzer type used for the HRMS is Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature.

General Procedure for the Preparation of ***1a–k.*** $PdCl_2(PPh_3)_2$ (3% mmol) and CuI (5% mmol) were added to a solution of 2-bromobenzaldehyde or 2-iodoacetophenone (1.0 mmol), phenylacetylene (1.2 mmol), and NEt_3 (2 mmol) in THF (1.2 mL). The mixture was heated under reflux or RT overnight under N_2. The system was filtered by short silica, then the solvent was evaporated under reduced pressure, and the residue was purified by flash chromatography with petroleum to afford the desired products **1**.[7]

*2-(Phenylethynyl)benzaldehyde (**1a**).*[7a] Eluent petroleum ether/ethyl acetate (20/1), yellow oil, yield (198 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.65 (s, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 7.7 Hz, 1H), 7.60–7.54 (m, 3H), 7.44 (t, J = 7.5 Hz, 1H), 7.40–7.34 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 135.9, 133.8, 133.2, 131.7, 129.1, 128.6, 128.5, 127.3, 126.9, 122.4, 96.4, 85.0.

*1-[2-(Phenylethynyl)phenyl]ethanone (**1b**).*[7b] Eluent petroleum ether/ethyl acetate (20/1), yellow oil, yield (210 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 7.8, 1.1 Hz, 1H), 7.63 (dd, J = 7.7, 0.8 Hz, 1H), 7.55 (ddd, J = 8.2, 4.0, 2.3 Hz, 2H), 7.48 (td, J = 7.6, 1.2 Hz, 1H), 7.43–7.39 (m, 1H), 7.39–7.34 (m, 3H), 2.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 140.8, 133.9, 131.5, 131.3, 128.8, 128.7, 128.5, 128.3, 122.9, 121.7, 95.1, 88.5, 30.0.

*2-(p-Tolylethynyl)benzaldehyde (**1c**).*[7a] Eluent petroleum ether/ethyl acetate (20/1), yellow solid, yield (202 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.62 (s, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.42 (d, J = 7.2 Hz, 2H), 7.35 (t, J = 7.5 Hz, 1H), 7.13 (d, J = 7.6 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 139.4, 135.8, 133.8, 133.2, 131.7, 129.4, 128.4, 127.2 (2C), 119.4, 96.8, 84.5, 21.6.

*2-[(4-Methoxyphenyl)ethynyl]benzaldehyde (**1d**).*[7a] Eluent petroleum ether/ethyl acetate (20/1), yellow solid, yield (233 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.64 (s, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 7.4 Hz, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.50 (d, J = 7.8 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 6.90 (d, J = 7.8 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 160.3, 135.7, 133.8, 133.3, 133.1, 128.2, 127.4, 127.2, 114.4, 114.2, 96.6, 83.8, 55.4.

*2-[(3-Fluorophenyl)ethynyl]benzaldehyde (**1e**).*[7a] Eluent petroleum ether/ethyl acetate (20/1), yellow oil, yield (194 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.50 (s, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.54–7.45 (m, 2H), 7.35 (t, J = 7.5 Hz, 1H), 7.23 (dd, J = 5.3, 4.6 Hz, 2H), 7.14 (dd, J = 8.7, 1.8 Hz, 1H), 7.01–6.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 162.4 (d, J = =247.2 Hz), 136.0, 133.8, 133.3, 130.2 (d, J = 8.6 Hz), 129.0, 127.6 (d, J = 3.1 Hz), 127.5, 126.2, 124.2 (d, J = 9.4 Hz), 118.5 (d, J = 22.9 Hz), 116.4 (d, J = 21.2 Hz), 94.8 (d, J = 3.4 Hz), 85.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ −112.4.

*2-[(4-Chlorophenyl)ethynyl]benzaldehyde (**1f**).*[7a] Eluent petroleum ether/ethyl acetate (20/1), yellow solid, yield (218 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 7.94 (d, J = 7.5 Hz, 1H), 7.59 (ddd, J = 14.9, 7.7, 4.1 Hz, 2H), 7.47 (dd, J = 14.2, 7.9 Hz, 3H), 7.35 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 135.9, 135.2, 133.8, 133.3, 132.9, 128.9 (2C), 127.5, 126.4, 120.8, 95.1, 85.9.

*4-Methyl-2-(phenylethynyl)benzaldehyde (**1g**).*[7a,c] Eluent petroleum ether/ethyl acetate (20/1), yellow solid, yield (196 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.58 (s, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.56 (dd, J = 3.9, 1.6 Hz, 2H), 7.45 (s, 1H), 7.38 (d, J = 1.8 Hz, 3H), 7.25 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 144.9, 133.7, 133.6, 131.7, 129.7, 129.0, 128.5, 127.4, 126.9, 122.5, 95.9, 85.1, 21.6.

*5-Methoxy-2-(phenylethynyl)benzaldehyde (**1h**).*[7c] Eluent petroleum ether/ethyl acetate (20/1), yellow solid, yield (223 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.59 (s, 1H), 7.53 (d, J = 7.4 Hz, 3H), 7.40 (s, 1H), 7.34 (s, 3H), 7.11 (d, J = 8.5 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 159.8, 137.2, 134.6, 131.5, 128.8, 128.5, 122.7, 121.7, 119.6, 109.9, 94.9, 84.9, 55.6.

*5-Fluoro-2-(phenylethynyl)benzaldehyde (**1i**).*[7c] Eluent petroleum ether/ethyl acetate (20/1), yellow solid, yield (211 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.56 (s, 1H), 7.58 (t, J = 6.9 Hz, 2H), 7.54–7.50 (m, 2H), 7.35 (d, J = 4.9 Hz, 3H), 7.24 (dd, J = 10.9, 5.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 162.4 (d, J = 252.6 Hz), 137.8 (d, J = 6.6 Hz), 135.3 (d, J = 7.6 Hz), 131.7, 129.2, 128.6, 123.0 (d, J = 3.4 Hz), 122.2, 121.3 (d, J = 22.8 Hz), 113.7 (d, J = 23.0 Hz), 96.1, 83.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ −108.9.

*2-(Cyclohex-1-en-1-ylethynyl)benzaldehyde (**1j**).*[7d] Eluent petroleum ether/ethyl acetate (20/1), yellow oil, yield (201 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.56 (s, 1H), 7.92 (d, J = 7.9 Hz, 1H), 7.56–7.53 (m, 2H), 7.44–7.38 (m, 1H), 6.35–6.30 (m, 1H), 2.31–2.25 (m, 2H), 2.20 (dd, J = 6.0, 2.3 Hz, 2H), 1.76–1.70 (m, 2H), 1.68–1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 136.9,

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135.6, 133.7, 133.0, 128.0, 127.6, 127.1, 120.3, 98.5, 82.4, 29.0, 25.8, 22.2, 21.4.

*2-(Oct-1-yn-1-yl)benzaldehyde (**1k**).*[7a] Eluent petroleum ether/ethyl acetate (20/1), yellow oil, yield (199 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.54 (s, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.49 (s, 2H), 7.36 (s, 1H), 2.47 (dd, J = 9.4, 4.4 Hz, 2H), 1.66−1.60 (m, 2H), 1.47 (d, J = 5.3 Hz, 2H), 1.32 (s, 4H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 136.0, 133.6, 133.3, 128.0, 127.8, 126.9, 98.2, 76.3, 31.3, 28.6, 28.5, 22.5, 19.6, 14.0.

*General Procedure for the Preparation of Product **4a**−**i**.* The corresponding enynals/enynones (1.0 equiv, 0.2 mmol) and styrene (5.0 equiv) were added to a solution of the catalyst combination of [AuCl(IMes)] (5% equiv) and Selectfluor (10% equiv) in DCE (4.0 mL) and H_2O (1.0 equiv). The reaction mixture was stirred under a nitrogen atmosphere at 80 °C for 24 h. After the reaction was finished, the mixture 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 desired products **4**.[1b]

*Phenyl(2-phenyl-1,2-dihydronaphthalen-1-yl)methanone (**4a**).* Eluent petroleum ether/ethyl acetate (20/1), yellow oil, yield (22 mg, 36%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.6 Hz, 2H), 7.45 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.7 Hz, 2H), 7.18−7.12 (m, 5H), 7.09 (d, J = 6.2 Hz, 2H), 7.00 (t, J = 7.3 Hz, 1H), 6.77 (d, J = 7.5 Hz, 1H), 6.56 (d, J = 9.6 Hz, 1H), 5.90 (dd, J = 9.6, 4.1 Hz, 1H), 4.94 (d, J = 7.8 Hz, 1H), 4.20−4.02 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 142.9, 137.2, 133.7, 133.1, 131.9, 130.3, 128.7, 128.6, 128.0, 127.9, 127.8, 127.7, 127.4, 127.0, 126.7, 53.4, 44.0.

*(4-Methyl-2-phenyl-1,2-dihydronaphthalen-1-yl)(phenyl)-methanone (**4b**).* Eluent petroleum ether/ethyl acetate (20/1), yellow oil, yield (64 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.4 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.40 (dd, J = 16.4, 8.3 Hz, 3H), 7.30−7.22 (m, 2H), 7.20 (d, J = 4.1 Hz, 4H), 7.10 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 7.5 Hz, 1H), 5.88−5.72 (m, 1H), 4.99 (d, J = 8.2 Hz, 1H), 4.22−4.05 (m, 1H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 143.3, 137.3, 135.4, 133.0, 132.8, 132.0, 129.6, 128.7, 128.6, 128.5, 128.0, 127.9, 127.6, 127.4, 126.9, 123.4, 53.9, 44.0, 19.4. IR (KBr) ν_{max} 3060.6, 2923.6, 1680.3, 1597.0, 1491.3, 1448.5, 1028.8, 759.5, 697.6 cm^{-1}.

*[2-(4-Methoxyphenyl)-4-methyl-1,2-dihydronaphthalen-1-yl]-(phenyl)methanone (**4c**).* Eluent petroleum ether/ethyl acetate (20/1), yellow oil, yield (62 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.49−7.39 (m, 3H), 7.31 (dd, J = 8.1, 3.5 Hz, 1H), 7.14 (t, J = 8.7 Hz, 3H), 6.90 (d, J = 7.5 Hz, 1H), 6.78 (d, J = 8.5 Hz, 2H), 5.81 (d, J = 2.8 Hz, 1H), 4.99 (d, J = 8.1 Hz, 1H), 4.18−4.06 (m, 1H), 3.76 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 158.5, 137.3, 135.4, 133.0, 131.8, 130.6, 129.6, 128.9, 128.7, 128.6, 127.9, 127.7, 127.5, 123.3, 114.0, 113.7, 55.2, 54.2, 43.1, 19.4. IR (KBr) ν_{max} 3503.5, 2934.6, 2837.3, 1680.8, 1607.4, 1512.4, 1448.9, 1374.2, 1178.5, 1109.4, 1035.0, 895.3, 830.2, 760.9, 694.9, 560.1 cm^{-1}. MS (EI): m/z 368, 352, 275, 249, 234, 202, 105, 77, 43. HRMS (EI) calcd for $C_{25}H_{22}O_2$ [M]: 354.1620; Found: 354.1618.

*[2-(4-(tert-Butyl)phenyl)-4-methyl-1,2-dihydronaphthalen-1-yl]-(phenyl)methanone (**4d**).* Eluent petroleum ether/ethyl acetate (20/1), yellow oil, yield (72 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.4 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.44−7.36 (m, 3H), 7.27 (t, J = 7.5 Hz, 1H), 7.22 (d, J = 8.4 Hz, 2H), 7.10 (dd, J = 7.7, 5.8 Hz, 3H), 6.89 (d, J = 7.5 Hz, 1H), 5.78 (d, J = 3.3 Hz, 1H), 4.97 (d, J = 7.1 Hz, 1H), 4.11−4.02 (m, 1H), 2.15 (s, 3H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 149.7, 140.2, 137.2, 135.6, 132.9, 132.7, 131.7, 128.6 (2C), 128.1, 127.5 (2C), 127.3, 125.5, 123.4, 53.8, 43.4, 34.4, 31.3, 19.4. IR (KBr) ν_{max} 3061.3, 2962.5, 2921.1, 1682.4, 1597.7, 1511.2, 1449.0, 1368.7, 1045.9, 828.9, 759.7, 694.3, 579.3 cm^{-1}. MS (EI): m/z 394, 378, 275, 259, 219, 105, 77, 57, 41. HRMS (EI) calcd for $C_{28}H_{28}O$ [M]: 380.2140; Found: 380.2139.

*[2-(4-Fluorophenyl)-4-methyl-1,2-dihydronaphthalen-1-yl]-(phenyl)methanone (**4e**).* Eluent petroleum ether/ethyl acetate (20/1), yellow oil, yield (59 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.3 Hz, 2H), 7.46 (t, J = 7.4 Hz, 1H), 7.37−7.29 (m, 3H), 7.21 (d, J = 7.3 Hz, 1H), 7.12−7.06 (m, 2H), 7.03 (dd, J = 7.5, 6.6 Hz, 1H), 6.84−6.77 (m, 3H), 5.69 (d, J = 2.5 Hz, 1H), 4.87 (d, J = 8.7 Hz, 1H), 4.12−4.02 (m, 1H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 161.8 (d, J = 245.0 Hz), 139.0 (d, J = 3.2 Hz), 137.4, 135.3, 133.1, 132.8, 132.3, 129.5, 129.4, 128.7, 128.5, 127.7 (d, J = 3.1 Hz), 127.6, 127.4, 123.4, 115.4 (d, J = 21.2 Hz), 54.1, 43.3, 19.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ −116.0. IR (KBr) ν_{max} 3062.3, 2924.4, 1680.7, 1599.7, 1509.2, 1448.2, 1374.6, 1046.2, 833.0, 760.8, 694.4, 554.9 cm^{-1}. MS (EI): m/z 340, 263, 236, 220, 202, 122, 105, 77, 61, 43. HRMS (EI) calcd for $C_{24}H_{19}FO$ [M]: 342.1420; Found: 342.1418.

*[2-(4-Chlorophenyl)-4-methyl-1,2-dihydronaphthalen-1-yl]-(phenyl)methanone (**4f**).* Eluent petroleum ether/ethyl acetate (20/1), yellow solid (mp 140−141 °C), yield (63 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.5 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.46−7.35 (m, 3H), 7.28 (d, J = 7.5 Hz, 1H), 7.19−7.07 (m, 5H), 6.86 (d, J = 7.5 Hz, 1H), 5.75 (d, J = 2.6 Hz, 1H), 4.94 (d, J = 8.6 Hz, 1H), 4.17−4.07 (m, 1H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 141.9, 137.3, 135.2, 133.2, 132.6 (2C), 132.4, 129.4, 128.8, 128.7, 128.5, 127.8, 127.7 (2C), 127.0, 123.4, 53.9, 43.3, 19.3. IR (KBr) ν_{max} 3061.6, 2920.9, 1682.2, 1595.8, 1488.8, 1446.9, 1090.5, 1015.0, 860.0, 821.1, 758.7, 697.7, 551.8 cm^{-1}. MS (EI): m/z 358, 253, 238, 218, 202, 141, 105, 77, 55. HRMS (EI) calcd for $C_{24}H_{19}ClO$ [M]: 358.1118; Found: 358.1119.

*[2-(4-Bromophenyl)-4-methyl-1,2-dihydronaphthalen-1-yl]-(phenyl)methanone (**4g**).* Eluent petroleum ether/ethyl acetate (20/1), yellow oil, yield (75 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.6 Hz, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.37 (d, J = 7.8 Hz, 1H), 7.30 (dd, J = 15.4, 7.9 Hz, 3H), 7.09 (dd, J = 11.4, 8.1 Hz, 3H), 6.86 (d, J = 7.5 Hz, 1H), 5.74 (d, J = 2.3 Hz, 1H), 4.93 (d, J = 8.5 Hz, 1H), 4.12 (d, J = 5.9 Hz, 1H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 142.4, 137.2, 135.2, 133.2, 132.6, 132.5, 131.7, 129.8, 128.8, 128.6, 127.8, 127.7 (2C), 126.9, 123.5, 120.7, 53.7, 43.3, 19.4. IR (KBr) ν_{max} 3064.4, 2927.3, 1681.4, 1596.4, 1487.7, 1447.3, 1374.5, 1046.1, 1008.8, 895.9, 820.3, 759.8, 695.3, 551.5 cm^{-1}. MS (EI): m/z 402, 296, 244, 218, 202, 122, 105, 77, 43. HRMS (EI) calcd for $C_{24}H_{19}BrO$ [M]: 402.0619; Found: 402.0620.

*[2-(Cyclohexylmethyl)-4-methyl-1,2-dihydronaphthalen-1-yl]-(phenyl)methanone (**4h**).* Eluent petroleum ether/ethyl acetate (20/1), yellow oil, yield (47 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.5 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.31 (d, J = 7.4 Hz, 1H), 7.27 (s, 1H), 7.11 (t, J = 7.4 Hz, 1H), 6.94 (d, J = 7.5 Hz, 1H), 5.68 (d, J = 3.9 Hz, 1H), 4.52 (d, J = 5.9 Hz, 1H), 2.99−2.85 (m, 1H), 2.09 (s, 3H), 1.72−1.61 (m, 4H), 1.48−1.33 (m, 2H), 1.30−1.09 (m, 5H), 0.90−0.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 137.1, 135.7, 133.1, 132.9, 131.3, 128.7, 128.6, 128.3, 127.4, 127.2, 127.1, 123.2, 52.5, 42.0, 34.6, 34.2, 34.1, 32.7, 26.6, 26.3, 26.2, 19.4. IR (KBr) ν_{max} 3061.5, 2922.6, 2850.3, 1684.9, 1596.7, 1489.4, 1447.9, 1044.3, 756.8, 696.4 cm^{-1}. MS (EI): m/z 344, 239, 157, 143, 115, 97, 77, 55, 41. HRMS (EI) calcd for $C_{25}H_{28}O$ [M]: 344.2140; Found: 344.2142.

*(12-Methyl-5,5a,6,7,8,9,10,11-octahydrocycloocta[b]-naphthalen-5-yl)(phenyl)methanone (**4i**).* Eluent petroleum ether/ethyl acetate (20/1), yellow oil, yield (44 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.74 (m, 2H), 7.46 (t, J = 7.3 Hz, 1H), 7.37 (t, J = 7.5 Hz, 2H), 7.23 (d, J = 7.2 Hz, 1H), 7.19−7.16 (m, 1H), 6.98 (dd, J = 7.3, 1.1 Hz, 1H), 6.93 (d, J = 7.3 Hz, 1H), 4.28 (d, J = 2.6 Hz, 1H), 2.78 (d, J = 10.8 Hz, 1H), 2.55 (ddd, J = 14.9, 9.0, 3.4 Hz, 1H), 1.95 (s, 3H), 1.66−1.56 (m, 2H), 1.54−1.43 (m, 4H), 1.42−1.27 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 137.7, 137.1, 136.9, 132.5, 132.0, 128.7, 128.6, 128.3, 127.5, 125.9, 125.0, 123.2, 54.2, 40.7, 34.1, 33.3, 28.7, 26.2, 25.5, 24.2, 14.4. IR (KBr) ν_{max} 3061.4, 2924.9, 1685.4, 1597.9, 1449.5, 1373.0, 1045.9, 760.5, 695.8 cm^{-1}. MS (EI): m/z 330, 224, 181, 155, 141, 122, 105, 77, 61, 43. HRMS (EI) calcd for $C_{24}H_{26}O$ [M]: 330.1984; Found: 330.1981.

*General Procedure for the Preparation of Product **5a** and **5b**.* The corresponding enynals/enynones (1.0 equiv, 0.25 mmol) and styrene (5.0 equiv) were added to a solution of 1,4-benzoquinone (2.0 equiv) and the catalyst combination of [AuCl(IMes)] (5% equiv) and Selectfluor (10% equiv) in DCE (5.0 mL). The reaction mixture was stirred under a nitrogen atmosphere at 80 °C for 24 h. After the

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reaction was finished, the mixture 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 desired products **5**.[8]

*Phenyl(2-phenylnaphthalen-1-yl)methanone (**5a**).* Eluent petroleum ether/ethyl acetate (20/1), yellow oil, yield (39 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.5 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.54 (d, J = 7.9 Hz, 2H), 7.50 (d, J = 8.5 Hz, 1H), 7.45 (t, J = 7.4 Hz, 1H), 7.41−7.35 (m, 1H), 7.31 (dd, J = 14.2, 7.0 Hz, 3H), 7.19−7.12 (m, 4H), 7.12−7.06 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 140.2, 138.0, 137.5, 135.7, 133.2, 132.4, 130.7, 129.6, 129.5, 128.3, 128.2, 127.6, 127.4, 127.2, 126.3, 125.6.

*(4-Methyl-2-phenylnaphthalen-1-yl)(phenyl)methanone (**5b**).* Eluent petroleum ether/ethyl acetate (20/1), yellow solid (mp 145−146 °C), yield (80 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 7.3 Hz, 2H), 7.48−7.43 (m, 1H), 7.36 (dd, J = 12.5, 5.3 Hz, 2H), 7.30−7.22 (m, 3H), 7.15−7.09 (m, 4H), 7.08−7.03 (m, 1H), 2.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 140.4, 138.2, 137.2, 136.1, 134.2, 133.1, 131.7, 130.9, 129.6, 129.5, 128.4, 128.3, 128.2, 127.4, 126.9, 126.2 (2C), 124.3, 19.7.

*General Procedure for the Preparation of Product **6a**−**y**.* The corresponding enynals/enynones (1.0 equiv, 0.25 mmol) and styrene (5.0 equiv) were added to a solution of olefins (2.0 equiv) (one of these olefins, including 1,4-benzoquinone, tetracyanoethlene, etc.) and the catalyst combination of [AuCl(IMes)] (5% equiv) and Selectfluor (10% equiv) in DCE (2.5 mL). The reaction mixture was stirred under a nitrogen atmosphere at 80 °C for 24 h. After the reaction was finished, the mixture 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 desired products **6** (except **6a**, by crystallization).

*9-Benzoyl-12-phenyl-4a,9,9a,10-tetrahydro-9,10-ethanoanthracene-1,4-dione (**6a**).* By crystallization (petroleum ether/ethyl acetate), yellow solid (mp 175−176 °C), yield (65 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.8 Hz, 1H), 7.29 (t, J = 7.4 Hz, 1H), 7.18−6.97 (m, 10H), 6.58 (d, J = 7.0 Hz, 2H), 6.36 (d, J = 10.3 Hz, 1H), 6.22 (d, J = 10.3 Hz, 1H), 4.54 (d, J = 10.1 Hz, 1H), 3.81−3.71 (m, 2H), 3.45 (d, J = 10.0 Hz, 1H), 2.72−2.63 (m, 1H), 1.88−1.80 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 197.7, 196.1, 142.4, 141.9, 141.3, 140.6, 139.6, 136.3, 130.1, 129.2, 128.5, 128.3, 127.8, 127.6, 127.3, 127.2, 127.0, 124.8, 59.7, 55.1, 49.2, 46.4, 40.9, 38.6. IR (KBr) ν_{max} 2926.6, 2853.5, 1597.0, 1596.9, 1595.3, 1235.7, 1088.3, 893.1, 754.2, 650.1 cm^{-1}. MS (MALDI/DHB): m/z 860.2, 859.2, 441.0, 420.0, 419.0. HRMS (MALDI/DHB) calcd for $C_{29}H_{22}O_3Na$ [M + Na]: 441.1471; Found: 441.1472.

*1-Benzoyl-4-methyl-10-phenyl-1,4-ethanonaphthalene-2,2,3,3-(1H,4H)-tetracarbonitrile (**6b**).* Eluent petroleum ether/ethyl acetate (8/1), purple solid (mp 230−232 °C), yield (105 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.60 (m, 2H), 7.36 (ddd, J = 18.8, 10.2, 4.7 Hz, 2H), 7.19 (dd, J = 9.7, 5.0 Hz, 1H), 7.09 (d, J = 7.6 Hz, 2H), 6.94 (t, J = 7.4 Hz, 1H), 6.83 (dt, J = 22.0, 7.7 Hz, 4H), 6.44 (d, J = 7.6 Hz, 2H), 3.94 (dd, J = 10.4, 5.5 Hz, 1H), 2.92 (dd, J = 15.3, 10.5 Hz, 1H), 2.24 (dd, J = 15.3, 5.6 Hz, 1H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 139.9, 137.1, 136.0, 132.9, 131.3, 130.8, 130.7, 130.6, 129.6, 129.5, 128.7, 128.6, 127.4, 124.9, 112.1, 111.2, 111.1, 110.4, 67.8, 52.8, 50.1, 45.3, 43.7, 37.6, 20.2. IR (KBr) ν_{max} 2924.0, 2852.4, 2025.8, 1655.9, 1385.0, 1134.3, 1098.6, 736.2, 698.0, 639.1, 618.5 cm^{-1}. MS (MALDI/DHB): m/z 475.9, 475.0, 471.0, 470.1, 318.1, 274.0. HRMS (MALDI/DHB) calcd for $C_{30}H_{20}N_4ONa$ [M + Na]: 475.1542; Found: 475.1543.

*1-Benzoyl-10-phenyl-1,4-ethanonaphthalene-2,2,3,3(1H,4H)-tetracarbonitrile (**6c**).* Eluent petroleum ether/ethyl acetate (8/1), orange solid (mp 226−227 °C), yield (103 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.56 (m, 2H), 7.40−7.35 (m, 1H), 7.30 (d, J = 7.8 Hz, 1H), 7.20 (dd, J = 12.1, 4.6 Hz, 1H), 7.08 (d, J = 7.5 Hz, 2H), 6.96 (t, J = 7.4 Hz, 1H), 6.85 (dt, J = 15.6, 7.6 Hz, 4H), 6.48 (d, J = 7.5 Hz, 2H), 4.09 (t, J = 2.9 Hz, 1H), 3.93 (dd, J = 10.5, 5.6 Hz, 1H), 3.07 (ddd, J = 15.2, 10.5, 2.3 Hz, 1H), 2.46 (ddd, J = 15.3, 5.5, 3.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 139.8, 136.0, 134.8, 133.0, 131.5, 130.9, 130.7, 130.3, 130.0, 129.7, 128.8, 128.7, 127.6, 127.5, 112.0, 111.6, 111.1, 110.9, 68.2, 49.2, 47.1, 45.1, 42.8, 30.7. IR (KBr) ν_{max} 2926.3, 2853.5, 2027.3, 1659.2, 1592.5, 1492.7, 1452.4, 1269.2, 1087.0, 1016.7, 886.9, 770.4, 731.8, 697.5, 639.6, 558.4 cm^{-1}. MS (ESI): m/z 462.0, 461.0, 457.0, 456.1, 439.0. HRMS (ESI) calcd for $C_{29}H_{18}N_4ONa$ [M + Na]: 461.1378; Found: 461.1373.

*1-Benzoyl-4-methyl-10-(p-tolyl)-1,4-ethanonaphthalene-2,2,3,3-(1H,4H)-tetracarbonitrile (**6d**).* Eluent petroleum ether/ethyl acetate (8/1), purple solid (mp 199−200 °C), yield (103 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78−7.70 (m, 2H), 7.49−7.41 (m, 2H), 7.32 (d, J = 7.4 Hz, 1H), 7.18 (d, J = 7.6 Hz, 2H), 6.96 (t, J = 7.9 Hz, 2H), 6.69 (d, J = 8.0 Hz, 2H), 6.40 (d, J = 8.1 Hz, 2H), 4.02 (dd, J = 10.5, 5.6 Hz, 1H), 3.01 (dd, J = 15.3, 10.5 Hz, 1H), 2.31 (dd, J = 15.3, 5.6 Hz, 1H), 2.15 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 138.6, 137.1, 136.6, 136.1, 132.6, 131.3, 130.9, 130.7, 130.6, 129.5, 129.4, 129.3, 127.3, 124.9, 112.2, 111.3, 111.1, 110.4, 67.9, 52.8, 50.1, 45.4, 43.3, 37.6, 20.8, 20.3. IR (KBr) ν_{max} 2923.9, 2851.6, 2025.4, 1656.7, 1515.2, 1385.4, 1235.5, 1099.6, 821.0, 787.0, 759.6, 737.8, 701.1, 639.4, 618.3, 550.5, 479.7 cm^{-1}. MS (MALDI/DHB): m/z 486.0, 485.0, 484.1, 467.0. HRMS (MALDI/DHB) calcd for $C_{31}H_{22}N_4ONa$ [M + Na]: 489.1683; Found: 489.1683.

*1-Benzoyl-10-(p-tolyl)-1,4-ethanonaphthalene-2,2,3,3(1H,4H)-tetracarbonitrile (**6e**).* Eluent petroleum ether/ethyl acetate (8/1), orange solid (mp 222−223 °C), yield (102 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.57 (m, 2H), 7.40−7.34 (m, 1H), 7.30 (d, J = 7.8 Hz, 1H), 7.23 (dt, J = 8.5, 1.1 Hz, 1H), 7.07 (dd, J = 8.5, 1.1 Hz, 2H), 6.87 (t, J = 8.0 Hz, 2H), 6.62 (d, J = 8.0 Hz, 2H), 6.35 (d, J = 8.2 Hz, 2H), 4.09−4.04 (m, 1H), 3.91 (dd, J = 10.5, 5.6 Hz, 1H), 3.06 (ddd, J = 15.2, 10.5, 2.4 Hz, 1H), 2.43 (ddd, J = 15.3, 5.6, 3.7 Hz, 1H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 138.7, 136.6, 136.1, 134.9, 132.6, 131.3, 130.9, 130.8, 130.5 129.9, 129.5, 129.4, 127.5, 127.3, 111.9, 111.6, 111.0, 110.8, 68.3, 49.1, 47.1, 45.3, 42.5, 30.6, 20.8. IR (KBr) ν_{max} 2927.5, 2854.6, 2026.9, 1660.6, 1596.7, 1267.5, 1089.3, 1017.5, 735.4, 696.3, 560.3 cm^{-1}. MS (MALDI/DHB): m/z 474.9, 471.0, 470.1, 453.1, 382.0. HRMS (MALDI/DHB) calcd for $C_{30}H_{21}N_4O$ [M + H]: 453.1724; Found: 453.1723.

*1-Benzoyl-10-[4-(tert-butyl)phenyl]-4-methyl-1,4-ethanonaphthalene-2,2,3,3(1H,4H)-tetracarbonitrile (**6f**).* Eluent petroleum ether/ethyl acetate (8/1), purple solid (mp 232−233 °C), yield (126 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (q, J = 7.2 Hz, 2H), 7.40−7.31 (m, 2H), 7.16 (d, J = 7.4 Hz, 1H), 7.09 (d, J = 7.8 Hz, 2H), 6.83 (dd, J = 14.7, 7.8 Hz, 4H), 6.36 (d, J = 8.2 Hz, 2H), 3.93 (dd, J = 10.3, 5.6 Hz, 1H), 2.90 (dd, J = 15.2, 10.6 Hz, 1H), 2.23 (dd, J = 15.2, 5.5 Hz, 1H), 2.00 (s, 3H), 1.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 151.8, 137.1, 136.7, 136.1, 132.8, 131.3, 130.9, 130.7, 129.5, 129.2, 127.3, 125.7, 124.9, 112.2, 111.2, 111.1, 110.4, 67.8, 52.8, 50.1, 45.4, 43.2, 37.6, 34.4, 31.1, 20.3. IR (KBr) ν_{max} 2962.9, 2867.7, 2027.5, 1660.7, 1596.6, 1444.9, 1259.3, 1113.5, 834.1, 700.2, 573.9 cm^{-1}. MS (MALDI/DHB): m/z 531.1, 527.2, 526.2, 509.0. HRMS (MALDI/DHB) calcd for $C_{34}H_{28}N_4ONa$ [M + Na]: 531.2167; Found: 531.2166.

*1-Benzoyl-10-(2,5-dimethylphenyl)-4-methyl-1,4-ethanonaphthalene-2,2,3,3(1H,4H)-tetracarbonitrile (**6g**).* Eluent petroleum ether/ethyl acetate (8/1), purple solid (mp 279−280 °C), yield (38 mg, 32%). ^{1}H NMR (400 MHz, DMSO) δ 7.96−7.72 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.1 Hz, 2H), 7.24 (d, J = 7.8 Hz, 2H), 7.03 (t, J = 7.7 Hz, 2H), 6.67 (d, J = 7.6 Hz, 1H), 6.36 (d, J = 7.7 Hz, 1H), 6.27 (s, 1H), 4.22 (dd, J = 10.0, 6.7 Hz, 1H), 2.88 (dd, J = 15.2, 10.6 Hz, 1H), 2.41 (dd, J = 15.2, 6.5 Hz, 1H), 2.04 (d, J = 9.9 Hz, 6H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 196.7, 138.2, 137.0, 135.6, 134.6, 134.0, 133.1, 131.0, 130.6, 130.4, 129.8, 129.7, 129.2, 128.9, 128.6, 126.9, 125.5, 112.3, 111.7, 111.6, 111.1, 67.7, 52.4, 50.3, 45.4, 37.1, 36.8, 20.6, 19.5, 18.9. IR (KBr) ν_{max} 2923.6, 2851.7, 2026.5, 1659.5, 1596.9, 1451.9, 1296.7, 1070.9, 732.6, 696.9 cm^{-1}. MS (MALDI/DHB): m/z 503.0, 499.1, 498.0, 481.0. HRMS (MALDI/DHB) calcd for $C_{32}H_{24}N_4ONa$ [M + Na]: 503.1856; Found: 503.1856.

*1-Benzoyl-10-mesityl-4-methyl-1,4-ethanonaphthalene-2,2,3,3-(1H,4H)-tetracarbonitrile (**6h**).* Eluent petroleum ether/ethyl acetate

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(8/1), purple solid (mp 192−193 °C), yield (36 mg, 29%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.62 (m, 1H), 7.59 (d, J = 7.7 Hz, 1H), 7.47−7.41 (m, 4H), 7.17 (d, J = 7.4 Hz, 1H), 6.89 (t, J = 7.8 Hz, 2H), 6.45 (s, 1H), 6.13 (s, 1H), 4.37 (dd, J = 10.7, 8.5 Hz, 1H), 2.69 (dd, J = 15.1, 10.9 Hz, 1H), 2.46 (dd, J = 15.0, 8.3 Hz, 1H), 1.99 (s, 3H), 1.97 (s, 3H), 1.88 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4 139.3 137.8, 136.4, 136.1, 133.2, 132.7, 132.3, 131.4, 130.5, 130.0, 129.9, 128.7, 126.9, 125.2, 112.3, 111.4, 111.2, 110.6, 68.1, 52.0, 45.3, 37.7, 34.2, 22.4, 22.2, 20.3, 20.2. IR (KBr) ν_{max} 2924.8, 2853.3, 2024.9, 1660.6, 1597.0, 1452.5, 1245.7, 1095.5, 769.5, 645.7, 620.2 cm^{-1}. MS (MALDI/DHB): m/z 517.0, 513.2, 512.2, 495.0. HRMS (MALDI/DHB) calcd for $C_{33}H_{26}N_4ONa$ [M + Na]: 517.2001; Found: 517.1999.

*1-Benzoyl-10-(4-fluorophenyl)-4-methyl-1,4-ethanonaphthalene-2,2,3,3(1H,4H)-tetracarbonitrile (**6i**).* Eluent petroleum ether/ethyl acetate (8/1), purple solid (mp 227−228 °C), yield (73 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75−7.56 (m, 2H), 7.41 (dt, J = 15.1, 4.8 Hz, 2H), 7.26 (t, J = 7.4 Hz, 1H), 7.13 (d, J = 7.5 Hz, 2H), 6.94 (t, J = 7.9 Hz, 2H), 6.50 (t, J = 8.5 Hz, 2H), 6.39 (dd, J = 8.7, 5.2 Hz, 2H), 3.94 (dd, J = 10.5, 5.7 Hz, 1H), 2.94 (dd, J = 15.4, 10.5 Hz, 1H), 2.16 (dd, J = 15.4, 5.7 Hz, 1H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 162.6 (d, J = 249.4 Hz), 137.0, 136.0, 135.7, 133.1, 131.5, 131.2 (d, J = 8.3 Hz), 130.8, 130.7, 129.7, 127.5, 125.0, 115.6 (d, J = 22.5 Hz), 112.0, 111.1, 110.3 (2C), 67.8, 52.7, 50.1, 45.3, 42.7, 37.9, 20.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −112.7. IR (KBr) ν_{max} 2924.7, 2853.5, 2026.3, 1660.6, 1596.5, 1512.0, 1232.6, 1152.2, 760.7, 759.0, 645.3, 620.1, 560.5 cm^{-1}. MS (MALDI/DHB): m/z 493.0, 489.1, 488.0, 471.0. HRMS (MALDI/DHB) calcd for $C_{30}H_{19}FN_4ONa$ [M + Na]: 493.1454; Found: 493.1459.

*1-Benzoyl-10-(4-chlorophenyl)-4-methyl-1,4-ethanonaphthalene-2,2,3,3(1H,4H)-tetracarbonitrile (**6j**).* Eluent petroleum ether/ethyl acetate (8/1), purple solid (mp 258−259 °C), yield (88 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.62 (m, 2H), 7.41 (q, J = 7.3 Hz, 2H), 7.28 (t, J = 7.4 Hz, 1H), 7.13 (d, J = 7.6 Hz, 2H), 6.93 (t, J = 7.9 Hz, 2H), 6.75 (d, J = 8.5 Hz, 2H), 6.33 (d, J = 8.4 Hz, 2H), 3.91 (dd, J = 10.4, 5.6 Hz, 1H), 2.94 (dd, J = 15.4, 10.5 Hz, 1H), 2.14 (dd, J = 15.4, 5.6 Hz, 1H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 138.4, 136.9, 136.0, 134.7, 133.0, 131.5, 130.8 (2C), 130.7, 130.4, 129.7, 128.8, 127.6, 125.0, 112.0, 111.0 (2C), 110.2, 67.8, 52.7, 50.0, 45.2, 42.8, 37.7, 20.2. IR (KBr) ν_{max} 2925.6, 2854.3, 2026.7, 1661.2, 1596.8, 1384.7, 1098.9, 825.3, 749.8, 630.5, 570.6 cm^{-1}. MS (MALDI/DHB): m/z 507.0, 505.1, 504.0. HRMS (MALDI/DHB) calcd for $C_{30}H_{19}ClN_4ONa$ [M + Na]: 509.1155; Found: 509.1153.

*1-Benzoyl-10-(4-bromophenyl)-4-methyl-1,4-ethanonaphthalene-2,2,3,3(1H,4H)-tetracarbonitrile (**6k**).* Eluent petroleum ether/ethyl acetate (8/1), purple solid (mp 238−239 °C), yield (89 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82−7.70 (m, 2H), 7.56−7.48 (m, 2H), 7.39 (t, J = 7.0 Hz, 1H), 7.22 (d, J = 7.3 Hz, 2H), 7.02 (dd, J = 15.6, 7.4 Hz, 4H), 6.36 (d, J = 6.7 Hz, 2H), 3.99 (dd, J = 10.0, 5.3 Hz, 1H), 3.08−2.96 (m, 1H), 2.28−2.18 (m, 1H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 138.9, 136.9, 136.0, 133.0, 131.7, 131.5, 131.1, 130.7, 130.6, 130.4, 129.8, 127.6, 125.0, 122.8, 112.0, 111.0 (2C), 110.2, 67.8, 52.7, 50.0, 45.2, 42.9, 37.7, 20.2. IR (KBr) ν_{max} 2924.9, 2853.4, 2026.9, 1660.4, 1596.5, 1240.1, 1151.4, 1011.5, 825.7, 771.8, 733.4, 697.9, 603.4 cm^{-1}. MS (MALDI/DHB): m/z 571.0, 552.9, 550.0, 549.0, 548.0. HRMS (MALDI/DHB) calcd for $C_{30}H_{19}BrN_4ONa$ [M + Na]: 553.0654; Found: 553.0659.

*1-Benzoyl-4-methyl-10-[4-(trifluoromethyl)phenyl]-1,4-ethanonaphthalene-2,2,3,3(1H,4H)-tetracarbonitrile (**6l**).* Eluent petroleum ether/ethyl acetate (8/1), purple solid (mp 244−245 °C), yield (69 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (ddd, J = 13.6, 9.9, 4.2 Hz, 2H), 7.45 (dt, J = 15.0, 4.7 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.06 (dd, J = 26.5, 7.9 Hz, 4H), 6.86 (t, J = 7.9 Hz, 2H), 6.51 (d, J = 8.2 Hz, 2H), 3.97 (dd, J = 10.5, 5.5 Hz, 1H), 2.97 (dd, J = 15.4, 10.5 Hz, 1H), 2.18 (dd, J = 15.4, 5.5 Hz, 1H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 144.0, 136.9, 136.1, 133.2, 131.7, 130.6, 130.5, 130.3, 130.0, 129.9, 127.6, 125.5 (q, J = 3.8 Hz), 125.1, 111.9, 111.0, 110.9, 110.2, 67.8, 52.8, 50.0, 45.2, 43.0, 37.7, 20.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −63.1. IR (KBr) ν_{max} 2926.5, 2854.6, 2026.6, 1660.7, 1594.4, 1457.8, 1325.2, 1238.3, 1171.4, 1128.3, 1067.8, 1012.5, 842.9, 772.8, 733.7, 697.4 cm^{-1}. MS (MALDI/DHB): m/z 543.0, 540.0, 539.1, 538.1. HRMS (MALDI/DHB) calcd for $C_{31}H_{19}F_3N_4ONa$ [M + Na]: 543.1406; Found: 543.1405.

*1-Benzoyl-4-methyl-10-(perfluorophenyl)-1,4-ethanonaphthalene-2,2,3,3(1H,4H)-tetracarbonitrile (**6m**).* Eluent petroleum ether/ethyl acetate (8/1), yellow solid (mp 261−262 °C), yield (16 mg, 12%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83−7.76 (m, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.67−7.58 (m, 4H), 7.47 (t, J = 7.3 Hz, 1H), 7.21 (t, J = 7.5 Hz, 2H), 4.39−4.30 (m, 1H), 2.92 (dd, J = 14.4, 11.1 Hz, 1H), 2.38 (dd, J = 14.8, 7.6 Hz, 1H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 136.4 (d, J = 23.2 Hz), 133.8, 131.9, 130.5, 130.0 (d, J = 6.3 Hz), 129.0, 127.7, 125.0, 111.2, 111.0, 110.5, 110.1, 66.4, 52.0, 50.7, 45.4, 34.4, 31.7, 20.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −136.8 (dd, J = 105.5, 22.5 Hz, 2H), −151.8 (t, J = 21.0 Hz, 1H), −160.8 (m, 2H). IR (KBr) ν_{max} 2923.7, 2025.6, 1638.8, 1522.4, 1384.8, 1096.9, 954.6, 700.7, 639.1, 618.1, 569.3 cm^{-1}. MS (MALDI/DHB): m/z 565.9, 564.9, 561.0, 560.0. HRMS (MALDI/DHB) calcd for $C_{30}H_{15}F_5N_4ONa$ [M + Na]: 565.1050; Found: 565.1049.

*10-Benzoyl-5-methyl-5,10,10a,11-tetrahydro-4bH-5,10-ethanobenzo[b]fluorene-12,12,13,13-tetracarbonitrile (**6n**).* Eluent petroleum ether/ethyl acetate (8/1), purple solid (mp 240−241 °C), yield (115 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.48 (m, 2H), 7.32 (t, J = 7.4 Hz, 1H), 7.27 (d, J = 7.0 Hz, 2H), 7.21 (t, J = 6.3 Hz, 2H), 6.95 (dt, J = 15.1, 7.5 Hz, 4H), 6.40 (t, J = 7.4 Hz, 1H), 6.19 (d, J = 7.7 Hz, 1H), 4.09 (d, J = 9.3 Hz, 1H), 3.59 (q, J = 9.1 Hz, 1H), 3.01 (dd, J = 16.1, 8.9 Hz, 1H), 2.55 (dd, J = 16.1, 9.1 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 141.6, 138.8, 135.1, 134.8, 134.2, 132.5, 132.1, 131.4, 131.3, 129.2, 128.9 (2C), 127.4, 125.9, 124.9, 112.2, 111.3, 110.8, 110.5, 66.1, 52.2, 51.6, 48.9, 48.0, 45.8, 35.6, 19.2. IR (KBr) ν_{max} 2925.3, 2852.2, 2026.0, 1660.9, 1596.5, 1389.4, 1242.6, 1149.4, 745.6, 697.5 cm^{-1}. MS (MALDI/DHB): m/z 487.1, 483.1, 482.1. HRMS (MALDI/DHB) calcd for $C_{31}H_{20}N_4ONa$ [M + Na]: 487.1546; Found: 487.1543.

*1-Benzoyl-10-(cyclohexylmethyl)-4-methyl-1,4-ethanonaphthalene-2,2,3,3(1H,4H)-tetracarbonitrile (**6o**).* Eluent petroleum ether/ethyl acetate (8/1), brown solid (mp 222−224 °C), yield (52 mg, 44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.1 Hz, 2H), 7.60−7.51 (m, 2H), 7.48−7.36 (m, 5H), 2.88 (dd, J = 17.6, 8.8 Hz, 1H), 2.58 (dd, J = 14.2, 9.2 Hz, 1H), 1.91 (s, 3H), 1.52−1.39 (m, 5H), 1.24 (d, J = 19.3 Hz, 2H), 1.01 (t, J = 12.1 Hz, 3H), 0.81 (t, J = 6.9 Hz, 1H), 0.70 (t, J = 10.6 Hz, 1H), 0.46 (ddd, J = 31.9, 21.9, 10.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 137.2, 136.8, 134.1, 131.5, 131.1, 130.8, 130.3, 129.3, 128.2, 124.3, 112.1, 111.2, 110.8, 110.4, 65.5, 51.7, 50.5, 44.6, 44.3, 36.9, 34.5, 34.4, 33.6, 31.0, 26.2, 26.0, 25.8, 20.3. IR (KBr) ν_{max} 2924.0, 2852.1, 1661.4, 1448.4, 1402.1, 1384.6, 1239.1, 1184.9, 1105.3, 764.6, 736.2, 710.0, 660.8, 619.5, 479.8 cm^{-1}. MS (MALDI/DHB): m/z 495.0, 491.1, 490.1. HRMS (MALDI/DHB) calcd for $C_{31}H_{28}N_4ONa$ [M + Na]: 495.2150; Found: 495.2153.

*1-(4-Methylbenzoyl)-10-phenyl-1,4-ethanonaphthalene-2,2,3,3-(1H,4H)-tetracarbonitrile (**6p**).* Eluent petroleum ether/ethyl acetate (8/1), orange solid (mp 199−200 °C), yield (112 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 4.1 Hz, 2H), 7.34 (dt, J = 8.7, 4.4 Hz, 1H), 7.28 (d, J = 7.8 Hz, 1H), 6.96 (t, J = 8.7 Hz, 3H), 6.83 (t, J = 7.7 Hz, 2H), 6.65 (d, J = 8.2 Hz, 2H), 6.47 (d, J = 7.6 Hz, 2H), 4.08 (t, J = 2.7 Hz, 1H), 3.91 (dd, J = 10.4, 5.5 Hz, 1H), 3.04 (ddd, J = 15.2, 10.5, 2.2 Hz, 1H), 2.46 (ddd, J = 15.3, 5.1, 3.9 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 144.4, 139.9, 134.9, 133.3, 131.4, 131.0 (2C), 130.4, 129.9, 129.8, 128.8, 128.5, 128.1, 127.5, 112.1, 111.7, 111.2, 110.9, 68.2, 49.2, 47.2, 45.1, 43.0, 30.5, 21.6. IR (KBr) ν_{max} 2926.5, 2853.6, 2025.5, 1658.6, 1598.0, 1240.8, 1179.2, 1021.1, 887.1, 770.3, 731.0, 703.5, 650.6 cm^{-1}. MS (MALDI/DHB): m/z 476.0, 475.0, 470.0, 454.0, 453.0. HRMS (MALDI/DHB) calcd for $C_{30}H_{20}N_4ONa$ [M + Na]: 475.1539; Found: 475.1540.

*1-(4-Methoxybenzoyl)-10-phenyl-1,4-ethanonaphthalene-2,2,3,3(1H,4H)-tetracarbonitrile (**6q**).* Eluent petroleum ether/ethyl acetate (8/1), purple solid (mp 258−259 °C), yield (104 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 4.0 Hz, 2H), 7.39−7.29 (m, 2H), 7.08 (d, J = 8.6 Hz, 2H), 6.98 (t, J = 7.3 Hz, 1H), 6.86 (t, J = 7.6 Hz, 2H), 6.50 (d, J = 7.7 Hz, 2H), 6.32 (d, J = 8.7 Hz, 2H), 4.09 (s,

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1H), 3.92 (dd, J = 10.4, 5.3 Hz, 1H), 3.69 (s, 3H), 3.05 (dd, J = 14.3, 11.6 Hz, 1H), 2.48 (dt, J = 15.3, 4.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 163.4, 140.1, 134.9, 133.6, 131.3, 131.0, 129.9, 129.8, 128.8, 128.6, 128.3, 127.5, 112.7, 112.2, 111.7, 111.2, 110.9, 68.2, 55.5, 49.2, 47.2, 45.2, 43.0, 30.3. IR (KBr) ν_{max} 2924.7, 2853.8, 2026.1, 1598.2, 1506.9, 1311.9, 1259.0, 1174.1, 1020.9, 840.2, 770.1 cm^{-1}. MS (MALDI/DHB): m/z 491.0, 471.0, 470.0, 469.0. HRMS (MALDI/DHB) calcd for $C_{30}H_{21}N_4O_2$ [M + H]: 469.1677; Found: 469.1673.

*1-(3-Fluorobenzoyl)-10-phenyl-1,4-ethanonaphthalene-2,2,3,3-(1H,4H)-tetracarbonitrile (**6r**).* Eluent petroleum ether/ethyl acetate (8/1), orange solid (mp 235−236 °C), yield (111 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71−7.57 (m, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.28 (d, J = 7.8 Hz, 1H), 6.93 (ddt, J = 21.9, 15.0, 7.5 Hz, 6H), 6.70 (d, J = 10.0 Hz, 1H), 6.49 (d, J = 7.7 Hz, 2H), 4.10 (s, 1H), 3.91 (dd, J = 10.4, 5.6 Hz, 1H), 3.13−3.02 (m, 1H), 2.50−2.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 161.2 (d, J = 247.4 Hz), 139.5, 137.9, 134.8, 131.7, 130.6, 130.2, 130.0, 129.6, 129.1 (d, J = 7.6 Hz), 128.9, 127.7, 126.5 (d, J = 2.9 Hz), 120.3 (d, J = 21.2 Hz), 117.5 (d, J = 24.3 Hz), 111.8, 111.5, 110.9, 110.8, 68.3, 49.2, 47.1, 45.1, 42.7, 30.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ −111.9. IR (KBr) ν_{max} 2924.3, 2852.7, 2025.9, 1661.5, 1596.8, 1230.4, 1159.3, 767.9, 754.2, 650.1, 623.0 cm^{-1}. MS (MALDI/DHB): m/z 480.0, 479.0, 475.0, 474.0. HRMS (MALDI/DHB) calcd for $C_{29}H_{17}FN_4ONa$ [M + Na]: 479.1298; Found: 479.1303.

*1-(4-Chlorobenzoyl)-10-phenyl-1,4-ethanonaphthalene-2,2,3,3-(1H,4H)-tetracarbonitrile (**6s**).* Eluent petroleum ether/ethyl acetate (8/1), orange solid (mp 228−229 °C), yield (117 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.59 (m, 2H), 7.37 (td, J = 8.1, 4.2 Hz, 1H), 7.24 (d, J = 7.8 Hz, 1H), 7.02 (d, J = 8.2 Hz, 3H), 6.85 (dd, J = 13.2, 7.8 Hz, 4H), 6.47 (d, J = 7.8 Hz, 2H), 4.10 (s, 1H), 3.90 (dd, J = 10.3, 5.5 Hz, 1H), 3.10−3.00 (m, 1H), 2.50−2.37 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 139.9, 139.7, 134.9, 134.2, 132.1, 131.7, 130.6, 130.1, 129.8, 129.0, 128.8, 127.8, 127.7, 111.9, 111.6, 111.0, 110.8, 68.2, 49.1, 47.1, 45.0, 42.8, 30.5. IR (KBr) ν_{max} 2927.7, 2856.3, 2033.8, 1660.8, 1595.9, 1578.9, 1233.3, 1089.0, 1017.2, 899.2, 735.2, 696.8, 555.8 cm^{-1}. MS (ESI): m/z 495.0, 493.0, 492.0, 490.0, 473.0, 358.9, 354.0, 274.2. HRMS (ESI) calcd for $C_{29}H_{17}ClN_4ONa$ [M + Na]: 495.0989; Found: 495.0983.

*1-Benzoyl-7-methyl-10-phenyl-1,4-ethanonaphthalene-2,2,3,3-(1H,4H)-tetracarbonitrile (**6t**).* Eluent petroleum ether/ethyl acetate (8/1), orange solid (mp 211−212 °C), yield (112 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.7 Hz, 1H), 7.40 (d, J = 7.7 Hz, 1H), 7.20 (t, J = 7.3 Hz, 1H), 7.09 (d, J = 6.7 Hz, 3H), 6.94 (t, J = 7.3 Hz, 1H), 6.84 (dt, J = 18.4, 7.5 Hz, 4H), 6.46 (d, J = 7.7 Hz, 2H), 4.06 (s, 1H), 3.88 (dd, J = 10.3, 5.4 Hz, 1H), 3.09−2.96 (m, 1H), 2.42 (dt, J = 15.2, 4.0 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 140.3, 139.9, 136.0, 133.0, 132.1, 131.7, 131.4, 130.7, 130.1, 129.8, 128.8, 128.6, 127.4 (2C), 112.1, 111.8, 111.2, 111.0, 68.3, 49.2, 47.3, 44.8, 42.8, 30.8, 21.7. IR (KBr) ν_{max} 2927.9, 2855.3, 2033.4, 1660.6, 1596.4, 1128.0, 1100.6, 989.5, 831.6, 743.1, 693.7, 621.4 cm^{-1}. MS (MALDI/DHB): m/z 475.1, 474.9, 471.1, 470.1, 453.0. HRMS (MALDI/DHB) calcd for $C_{30}H_{21}N_4O$ [M + H]: 453.1726; Found: 453.1723.

*1-Benzoyl-6-methoxy-10-phenyl-1,4-ethanonaphthalene-2,2,3,3-(1H,4H)-tetracarbonitrile (**6u**).* Eluent petroleum ether/ethyl acetate (8/1), orange solid (mp 211−212 °C), yield (115 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 7.4 Hz, 1H), 7.15 (d, J = 8.7 Hz, 1H), 7.10 (d, J = 1.6 Hz, 1H), 7.06 (d, J = 8.0 Hz, 2H), 6.96 (t, J = 7.3 Hz, 1H), 6.93−6.69 (m, 5H), 6.51 (d, J = 7.7 Hz, 2H), 4.03 (s, 1H), 3.90 (dd, J = 10.3, 5.5 Hz, 1H), 3.84 (s, 3H), 3.10−2.94 (m, 1H), 2.53−2.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 161.6, 139.8, 136.3, 135.9, 133.0, 132.2, 130.7, 129.8, 128.8, 128.6, 127.4, 121.3, 115.1, 113.1, 112.1, 111.7, 111.3, 110.9, 68.0, 55.8, 49.4, 47.1, 45.4, 43.1, 30.5. IR (KBr) ν_{max} 2926.5, 2854.5, 2030.3, 1660.2, 1605.9, 1498.2, 1459.8, 1269.5, 1128.7, 1099.7, 989.5, 827.0, 743.8, 696.2, 624.2, 611.7, 552.1 cm^{-1}. MS (MALDI/DHB): m/z 491.0, 488.0, 487.0, 486.0, 470.0, 469.0. HRMS (MALDI/DHB) calcd for $C_{30}H_{21}N_4O_2$ [M + H]: 469.1663; Found: 469.1659.

*1-Benzoyl-6-fluoro-10-phenyl-1,4-ethanonaphthalene-2,2,3,3-(1H,4H)-tetracarbonitrile (**6v**).* Eluent petroleum ether/ethyl acetate (8/1), orange solid (mp 180−181 °C), yield (63 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, J = 7.2, 1.5 Hz, 1H), 7.31−7.21 (m, 2H), 7.10−6.97 (m, 4H), 6.88 (q, J = 7.6 Hz, 4H), 6.51 (d, J = 7.8 Hz, 2H), 4.08 (s, 1H), 3.96 (dd, J = 10.4, 5.5 Hz, 1H), 3.14−3.02 (m, 1H), 2.51−2.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 163.8 (d, J = 255.5 Hz), 139.4, 137.2 (d, J = 8.4 Hz), 135.8, 133.1 (d, J = 8.7 Hz), 133.0, 130.6, 129.7, 128.9, 127.6, 126.1 (d, J = 3.6 Hz), 117.3 (d, J = 22.0 Hz), 115.1 (d, J = 23.0 Hz), 111.8, 111.3, 111.0, 110.6, 67.7, 49.2, 46.9, 45.2, 42.9, 30.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −106.1. IR (KBr) ν_{max} 2927.7, 2856.3, 2033.5, 1660.9, 1598.2, 1491.8, 1128.4, 1101.1, 989.6, 878.6, 744.6, 696.0, 623.9, 612.2, 550.5 cm^{-1}. MS (MALDI/DHB): m/z 480.0, 475.0, 474.0, 457.0. HRMS (MALDI/DHB) calcd for $C_{29}H_{17}FN_4ONa$ [M + Na]: 479.1289; Found: 479.1289.

*1-Heptanoyl-10-phenyl-1,4-ethanonaphthalene-2,2,3,3(1H,4H)-tetracarbonitrile (**6w**).* Eluent petroleum ether/ethyl acetate (8/1), yellow solid (mp 170−171 °C), yield (110 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (t, J = 7.5 Hz, 1H), 7.55 (dd, J = 18.0, 7.6 Hz, 2H), 7.20 (t, J = 7.9 Hz, 2H), 7.13 (t, J = 7.5 Hz, 2H), 6.52 (d, J = 7.4 Hz, 2H), 3.99 (s, 1H), 3.64 (dd, J = 10.2, 5.9 Hz, 1H), 3.14−2.99 (m, 1H), 1.98 (td, J = 15.2, 4.9 Hz, 2H), 1.47−1.31 (m, 3H), 1.12 (dt, J = 14.1, 7.0 Hz, 2H), 0.97 (m, 3H), 0.86 (dd, J = 8.7, 6.1 Hz, 1H), 0.76 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.0, 140.5, 134.5, 131.4, 130.8, 130.5, 129.3, 128.9, 128.7, 127.9, 127.7, 111.5 (2C), 111.1, 110.7, 67.2, 47.4, 46.2, 44.6, 43.5, 41.5, 33.4, 31.1, 28.5, 24.2, 22.3, 14.0. IR (KBr) ν_{max} 3065.8, 3033.2, 2958.6, 2929.9, 2872.5, 2854.9, 2251.3, 2026.1, 1702.1, 1603.1, 1494.4, 1461.8, 1381.8, 1214.7, 1088.7, 910.5, 765.7, 702.0, 618.6, 548.2, 525.7, 477.4, 427.7 cm^{-1}. MS (MALDI/DHB): m/z 470.1, 469.0, 465.1, 464.1. HRMS (MALDI/DHB) calcd for $C_{29}H_{26}N_4ONa$ [M + Na]: 469.2009; Found: 469.2010.

*1-(Cyclohex-1-enecarbonyl)-10-phenyl-1,4-ethanonaphthalene-2,2,3,3(1H,4H)-tetracarbonitrile (**6x**).* Eluent petroleum ether/ethyl acetate (8/1), orange solid (mp 215−216 °C), yield (62 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63−7.51 (m, 2H), 7.49−7.39 (m, 2H), 7.12 (d, J = 5.6 Hz, 3H), 6.73−6.50 (m, 2H), 5.69 (s, 1H), 4.02 (d, J = 2.8 Hz, 1H), 3.78 (dd, J = 10.2, 6.4 Hz, 1H), 3.08−2.96 (m, 1H), 2.39 (ddd, J = 15.2, 6.3, 3.4 Hz, 1H), 2.28 (d, J = 17.1 Hz, 1H), 1.98 (d, J = 17.5 Hz, 1H), 1.72 (d, J = 18.6 Hz, 1H), 1.40 (d, J = 4.8 Hz, 1H), 1.36−1.23 (m, 2H), 1.17−1.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 150.3, 141.1, 137.3, 134.9, 131.2, 130.9, 129.9, 129.7, 129.1, 128.6, 127.3, 112.1, 111.7, 111.1, 110.9, 68.6, 49.6, 46.8, 45.1, 42.6, 30.8, 26.5, 24.2, 21.8, 20.4. IR (KBr) ν_{max} 2926.4, 2855.1, 2026.1, 1623.0, 1460.3, 1384.6, 1269.5, 1095.4, 765.3, 737.0, 700.5, 639.3, 618.5, 560.1 cm^{-1}. MS (MALDI/DHB): m/z 465.0, 460.0, 451.0, 444.0, 443.0. HRMS (MALDI/DHB) calcd for $C_{29}H_{23}N_4O$ [M + H]: 443.1877; Found: 443.1880.

*4-Benzoyl-2,9-dimethyl-11-phenyl-3a,4,9,9a-tetrahydro-1H-4,9-ethanobenzo[f]isoindole-1,3(2H)-dione (**6y**).* Eluent petroleum ether/ethyl acetate (8/1), yellow solid (mp 179−180 °C), yield (87 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, J = 7.4 Hz, 2H), 7.24−7.11 (m, 5H), 7.10−6.95 (m, 5H), 6.51 (d, J = 7.3 Hz, 2H), 4.31 (d, J = 8.6 Hz, 1H), 3.72 (dd, J = 10.7, 6.0 Hz, 1H), 2.94 (d, J = 8.6 Hz, 1H), 2.42 (dd, J = 13.5, 10.8 Hz, 1H), 2.32 (s, 3H), 1.74 (s, 3H), 1.65 (dd, J = 13.5, 5.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.6, 176.6, 176.4, 142.4, 142.2, 140.5, 133.8, 130.2, 129.5, 128.9, 128.6, 127.8, 127.7, 127.6, 127.4, 126.9, 122.4, 58.3, 50.2, 48.9, 47.8, 45.1, 39.1, 24.1, 20.7. IR (KBr) ν_{max} 2928.9, 2854.3, 2030.0, 1769.9, 1699.1, 1441.9, 1379.4, 1291.6, 1233.6, 1125.6, 957.9, 843.5, 761.6, 700.3 cm^{-1}. MS (MALDI/DHB): m/z 894.2, 893.3, 458.0, 437.0, 436.1. HRMS (MALDI/DHB) calcd for $C_{29}H_{26}NO_3$ [M + H]: 436.1908; Found: 436.1907.

■ ASSOCIATED CONTENT

Supporting Information

The copies of NMR spectral data, the crystallographic data (CIF file) of **6a**, and the copy of HRMS spectrum of compound **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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