基于 C—C 键断裂碱促进扩环构建环庚酮化合物

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摘要 报道了通过 C—C 键断裂开环构建环庚酮化合物的有效策略。反应在碳酸铯存在下进行, 无需使用任何金属和氧化剂, 具有原料易得、底物适用性良好、反应条件温和的优点。这种无金属催化炔插入 C—C σ -键, 通过分子内亲核加成/开环反应构建环庚酮化合物的方法, 在有机合成化学中有着广泛的应用前景。

关键词 C—C 键断裂; 碱促进; 扩环; 环庚酮化合物

Base-Promoted Ring Expansion Reactions for the Construction of Cycloheptanones through C—C Bond Cleavage

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Abstract An efficient ring expansion strategy has been developed for the construction of cycloheptanones through C—C bond cleavage. The reactions take place with easily accessible starting materials, good functional group tolerance, and mild reaction conditions in the presence of Cs₂CO₃ without any metal or oxidant reagent. The transition-metal free insertions of alkynes into carbon-carbon σ -bonds of acenaphthenone initialized through intramolecular nucleophilic addition/ring-opening to furnish multifarious cycloheptanones, which has the potential to be widely utilized in organic synthetic chemistry.

Keywords C—C bond cleavage; ring expansion; base-promoted; cycloheptanone compounds

1 Introduction

The chemical transformation involving cleavage of C—C bonds has attracted great attention due to its potential utility in chemical industries and academic settings.^[1] Generally, the C—C bond cleavage is studied extensively in highly strained molecules with three- or four-membered rings.^[2] For unstrained systems, the reactions initiated by the C—C bond cleavage usually need the participation of transition metals such as rhenium, nickel, palladium and rhodium.^[3] Transition-metal-catalyzed C—C bond cleavage can be divided into two mechanistic pathways including oxidative addition and β -carbon elimination (Scheme 1a).^[4] However, the cleavage of unstrained C—C bonds under transition-

metal-free conditions still remains a major challenge because of its inherent inert nature and stable property. Particularly, beside the highly reactive arynes^[5] or cyclohexynes,^[6] the reports involving insertions of unsaturated bonds into C—C σ -bonds are rare. Recently, Li's group have disclosed the insertion of alkynes into C—C σ -bonds of indene-1,3-diones,^[7] indolin-2-ones,^[8] 3-oxopropanenitriles,^[9] ethanones,^[10] and dicarbonyl compounds^[11] under transition-metal-free conditions, which offer efficient routes towards benzoannulated seven-membered ring compounds, seven-membered ring benzolactams, conjugated dienones, hydroxydienones, xanthenes and medium-sized ring compounds, respectively (Scheme 1b). To our best knowledge, cycloheptanone is a privileged seven-membered-ring struc-

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tural scaffold for drug discovery owing to its significant biological activities, which widely occurs in natural products such as purpurogallin, sinularia A, pavidolide B as shown in Figure 1.^[12] However, the efficient synthetic strategies to build cycloheptanone scaffolds are often inhibited due to entropic factors and transannular interactions within these molecules. Accordingly, the synthesis of cycloheptanones is still a challenging task and more facile procedure for such purpose is highly desirable. Herein, we envision that acenaphthenone could be served as a platform involving the insertion of alkynes into carbon-carbon σ -bonds under transition-metal free conditions, which results in the cyclization of seven-membered-ring cycloheptanones (Scheme 1c).

2 Results and discussion

We began our investigation by the cycloaddition reaction

Figure 1 Selected cycloheptanone-containing natural compounds

of 1,3-diphenylprop-2-yn-1-one (**1a**) and acenaphthylen-1(2*H*)-one (**2**) in dimethyl sulfoxide (DMSO) in the presence of K_2CO_3 at room temperature for 12 h (Table 1). The preliminary result was encouraging, and the thin-layer chromatography (TLC) analysis showed that starting material **1a** was completely consumed and the desired product **3a** was isolated in 28% yield (Table 1, Entry 1). The yield was improved to 78% when the transformation was conducted

Scheme 1 Ring expansion reactions on the synthesis of multifarious compounds

with Cs_2CO_3 instead of K_2CO_3 (Table 1, Entry 2). Further studies focused on screening of versatile base, whereas product **3a** was provided in acceptable yields by switching Cs_2CO_3 to other strong bases such as NaOH, KOH, NaH, NaO^tBu and KO^tBu (Table 1, Entries 3~7). Additionally, an interesting solvent effect was also observed, whereby the reactions proceeded more quickly and cleanly when conducted in *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMAC) (Table 1, Entries 8~9). However, other solvents such as CH_3CN , THF, H_2O , toluene, EtOH, 1,4-dioxane and CH_2Cl_2 , gave only a trace amount of the desired product **3a** (Table 1, Entries 10~16). Finally, decreasing the loading of Cs_2CO_3 lowered the yield, while no obvious deviation was observed when the amount of Cs_2CO_3 was increased (Table 1, Entries 17~19).

Table 1 Optimization of the reaction conditions^a

Entry	Base	Solvent	Time/h	Yield ^b /%
1	K_2CO_3	DMSO	12	28
2	Cs_2CO_3	DMSO	2	78
3	NaOH	DMSO	2	51
4	KOH	DMSO	2	58
5	NaH	DMSO	2	45
6	NaO ^t Bu	DMSO	2	68
7	KO ^t Bu	DMSO	2	62
8	Cs_2CO_3	DMF	2	82
9	Cs_2CO_3	DMAC	2	82
10	Cs_2CO_3	CH_3CN	12	Trace
11	Cs_2CO_3	THF	12	Trace
12	Cs_2CO_3	H_2O	12	Trace
13	Cs_2CO_3	Toluene	12	Trace
14	Cs_2CO_3	EtOH	12	Trace
15	Cs_2CO_3	1,4-Dioxane	12	Trace
16	Cs_2CO_3	CH_2Cl_2	12	Trace
17 ^c	Cs_2CO_3	DMF	2	72
18 ^d	Cs_2CO_3	DMF	2	78
19 ^e	Cs_2CO_3	DMF	2	83

^a Reaction conditions: **1a** (0.5 mmol), **2** (0.6 mmol), and base (1.0 mmol) in 3.0 mL of solvent at room temperature given time under N_2 . ^b Isolated yield based on **1a**. ^c 1.0 equiv. of Cs_2CO_3 . ^d 1.5 equiv. of Cs_2CO_3 . ^e 2.5 equiv. of Cs_2CO_3 . DMSO = dimethyl-sulfoxide, DMF = *N,N*-dimethylformamide, DMAC = *N,N*-dimethylacetamide, THF = tetrahydrofuran.

With the optimal reaction conditions in hand, the substrate scope of the ring-expansion reaction was explored as listed in Scheme 2. In general, acenaphthenone **2** was reacted smoothly with ynones **1a**~**1u** under the base-promoted conditions, and most of the reactions gave the desired products in moderate to good yields. Notably, ynones with electron-withdrawing substituents (F, Cl, Br, COOMe) (**3d**~**3g**) provided the corresponding products in higher yields than those bearing electron-donating groups (^{*n*}Bu,

OMe) (**3b**, **3c**). Particularly, both of thiophene- and alkyl-based ynones were smoothly employed in the reaction and provide the cycloheptanones in satisfactory yield (**3h**, **3i**). For the substituents R^1 on the aryl ring to the carbonyl carbon, electron-donating groups such as Me and OMe afforded the desired products in higher yields than those bearing electron-withdrawing groups such as F, Cl, Br and CN (**3j**~**3r**). Compared to the yield of **3n** with **3o**, **3p** and **3q** (75% vs 64%, 62% and 69%), it is worth noting that the steric hindrance influenced this reaction obviously. Interestingly, 2-naphthyl-substituted substrate could also be subjected to the reaction, and the desired product **3s** was formed in 75% yield. Subsequently, the heteroaryl substituent 2-thiophene gave the desired product **3t** in 65% yield, whereas the alkyl substituent cyclopropyl furnished cycloheptanone **3u** in 49% yield. Finally, the desired product **3v** was furnished in 42% yield when 1,3-dihydro-2*H*-inden-2-one was involved in the reaction, whereby the acenaphthylen-1(2*H*)-one **3w** was provided in 86% yield when the substrate was switched to 3-phenylpropionaldehyde **3v**. As for 1-phenylprop-2-yn-1-one, it was failed to afford any cycloheptanone product (**3x**).

To explore the application of cycloheptanone compounds, two experiments were carried out as shown in Scheme 3. When ynone **1o** was employed in the reaction at 100 °C for 6 h, no chromone product was observed, whereas the intermediate cycloheptanone **3o** was isolated in 64% yield (Scheme 3a). However, the intermediate **3o** was performed with Cs_2CO_3 at even 140 °C within 2 h, and no desired product chromone was furnished, probably due to the inherent inert of cycloheptanone, which resulted in non-tautomerism of enol-keto (Scheme 3b).

On the basis of the aforementioned observations and previous reports,^[7-11] a possible reaction mechanism was proposed as outlined in Scheme 4. Initially, the intermediate **A** could be generated from the ynone **1a** attacked by acenaphthenone **2** in the presence of Cs_2CO_3 . Then, the intermediate **B** was formed via the nucleophilic addition of **A**. Subsequently, ring opening of **B** afforded the intermediate **C**. Finally, the target product **3a** was provided by the hydrolysis of **C**.

3 Conclusions

In conclusion, we have developed an effective protocol for the synthesis of cycloheptanones from ynones and acenaphthenone under mild conditions. The ring expansion and C—C σ -bond cleavage were involved in this base-promoted procedure. With advantages such as easily accessible starting materials, good functional group tolerance, and mild reaction conditions, it has the potential to be widely applied in organic synthetic chemistry.

4 Experimental section

4.1 Instruments and reagents

Unless otherwise stated, all reagents were used directly without further purification. Silica gel was purchased from

Table 2 Scope of the method

^a 1,3-dihydro-2H-inden-2-one as substrate, ^b 3-phenylpropiolaldehyde as substrate, ^c 1-phenylprop-2-yn-1-one as substrate.

Qing Dao Hai Yang Chemical Industry Co. All melting points were determined on a Beijing Science Instrument Dianguang Instrument Factory XT4B melting point apparatus and uncorrected. ¹H NMR and ¹³C NMR spectra were measured on a 400 MHz Bruker spectrometer (¹H NMR 400 MHz, ¹³C NMR 100 MHz), using CDCl₃ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. HRMS-ESI spectra were equipped with an ESI

source and a TOF detector. PE is petroleum ether (60~90 °C).

4.2 Synthesis of compounds 3

A typical procedure for the synthesis of 8-benzoyl-9-phenylcyclohepta[de]naphthalen-7(10H)-one (**3a**). A suspension of 1,3-diphenylprop-2-yn-1-one (**1a**) (0.5 mmol, 103.0 mg), acenaphthylene-1(2H)-one (**2**) (0.6 mmol, 100.8

mg) and Cs_2CO_3 (1.0 mmol, 326.0 mg) in DMF (3 mL) was stirred at room temperature for 2 h. After **1a** was exhausted completely (monitored by TLC), saturated aqueous brine (20 mL) was added. The mixture was stirred for 10 min and then was extracted by EtOAc (3×10 mL). The combined organic layers were dried over Na_2SO_4 . Removal of the solvent gave a residue, which was purified by a column

chromatography (silica gel, PE/EtOAc, $V/V=10/1$) to afford **3a** as yellow solid. m.p. $173 \sim 174$ °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.06 (d, $J=8.0$ Hz, 2H), 8.03 (d, $J=8.0$ Hz, 1H), 7.96 (d, $J=8.0$ Hz, 1H), 7.73 (d, $J=8.0$ Hz, 1H), 7.68 (t, $J=8.0$ Hz, 1H), 7.57 (t, $J=8.0$ Hz, 1H), 7.51~7.42 (m, 7H), 7.29 (d, $J=4.0$ Hz, 1H), 6.48 (d, $J=8.0$ Hz, 1H), 5.06 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 196.2, 193.9, 147.2, 142.0, 139.0, 137.2, 133.9, 133.2, 133.0, 132.6, 131.2, 130.3, 129.0 (2C), 128.5 (2C), 128.4, 128.1 (2C), 128.0, 127.6, 127.3 (2C), 125.0, 121.2, 120.8, 45.8. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{19}\text{O}_2$ ($\text{M} + \text{H}$) $^+$ 375.1380, found 375.1381.

The similar procedure was used for the preparation of products **3b**~**3w**.

8-Benzoyl-9-(4-butylphenyl)cyclohepta[de]naphthalen-7(10H)-one (**3b**): Yellow solid, m.p. $86 \sim 87$ °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.04 (d, $J=8.0$ Hz, 2H), 7.98 (d, $J=8.0$ Hz, 1H), 7.91 (d, $J=8.0$ Hz, 1H), 7.68 (d, $J=8.0$ Hz, 1H), 7.62 (t, $J=8.0$ Hz, 1H), 7.53 (t, $J=8.0$ Hz, 1H), 7.44 (t, $J=8.0$ Hz, 2H), 7.36 (d, $J=8.0$ Hz, 2H), 7.28~7.22 (m, 3H), 6.54 (d, $J=8.0$ Hz, 1H), 5.03 (s, 2H), 2.68 (t, $J=8.0$ Hz, 2H), 1.70~1.62 (m, 2H), 1.44~1.35 (m, 2H), 0.96 (t, $J=8.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 196.2, 193.9, 147.7, 143.3, 139.3, 138.9, 137.2, 134.1, 133.3, 132.9, 132.5, 131.1, 130.3, 128.9 (2C), 128.5 (2C), 128.1 (2C), 128.0, 127.6, 127.2 (2C), 124.8, 121.1, 120.7, 45.9, 35.4, 33.4, 22.3, 13.9. HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{27}\text{O}_2$ ($\text{M} + \text{H}$) $^+$ 431.2006, found 431.2008.

8-Benzoyl-9-(4-methoxyphenyl)cyclohepta[de]naphthalen-7(10H)-one (**3c**): Yellow solid, m.p. $146 \sim 147$ °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.06 (d, $J=8.0$ Hz, 2H), 8.01 (d, $J=8.0$ Hz, 1H), 7.95 (d, $J=8.0$ Hz, 1H), 7.72 (d, $J=8.0$ Hz, 1H), 7.65 (t, $J=8.0$ Hz, 1H), 7.56 (t, $J=8.0$ Hz, 1H), 7.49~7.40 (m, 4H), 7.30 (t, $J=8.0$ Hz, 1H), 7.02 (d, $J=8.0$ Hz, 2H), 6.69 (d, $J=8.0$ Hz, 1H), 5.06 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 196.4, 193.8, 159.7, 147.4, 138.8, 137.2, 134.2, 134.1, 133.3, 132.9, 132.5, 131.1, 130.3, 129.0 (2C), 128.5 (2C), 128.1 (2C), 128.0, 127.6, 124.8, 121.1, 120.6, 114.2 (2C), 55.2, 45.9. HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{21}\text{O}_3$ ($\text{M} + \text{H}$) $^+$ 405.1485, found 405.1488.

8-Benzoyl-9-(4-fluorophenyl)cyclohepta[de]naphthalen-7(10H)-one (**3d**): Yellow solid, m.p. $163 \sim 164$ °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.04 (d, $J=8.0$ Hz, 2H), 7.98 (d, $J=8.0$ Hz, 1H), 7.91 (d, $J=8.0$ Hz, 1H), 7.70 (d, $J=8.0$ Hz, 1H), 7.62 (t, $J=8.0$ Hz, 1H), 7.54 (t, $J=8.0$ Hz, 1H), 7.44 (t, $J=8.0$ Hz, 4H), 7.25 (t, $J=8.0$ Hz, 1H), 7.16 (t, $J=8.0$ Hz, 2H), 6.48 (d, $J=8.0$ Hz, 1H), 5.01 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 196.2, 193.7, 162.6 ($J=247$ Hz), 146.1, 139.0, 137.9 ($J=3$ Hz), 137.1, 133.7, 133.08, 133.06, 133.0, 131.2, 130.3, 129.4 ($J=8$ Hz, 2C), 128.6 (2C), 128.1 (2C), 127.8 ($J=27$ Hz, 2C), 125.1, 121.2, 120.6, 116.1, 115.9, 45.7. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{18}\text{FO}_2$ ($\text{M} + \text{H}$) $^+$ 393.1285, found 393.1286.

8-Benzoyl-9-(4-chlorophenyl)cyclohepta[de]naphthalen-7(10H)-one (**3e**): Yellow solid, m.p. $169 \sim 170$ °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.06 (d, $J=8.0$ Hz, 2H), 8.03 (d, $J=8.0$ Hz, 1H), 7.95 (d, $J=8.0$ Hz, 1H), 7.75 (d, $J=8.0$

Hz, 1H), 7.67 (t, $J=8.0$ Hz, 1H), 7.58 (t, $J=8.0$ Hz, 1H), 7.50~7.42 (m, 6H), 7.32 (t, $J=8.0$ Hz, 1H), 6.56 (d, $J=4.0$ Hz, 1H), 5.03 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 196.2, 193.7, 145.7, 140.3, 139.1, 137.0, 134.4, 133.6, 133.12, 133.08, 132.9, 131.3, 130.4, 129.3 (2C), 129.0 (2C), 128.6 (2C), 128.1 (2C), 128.0, 127.7, 125.2, 121.3, 120.7, 45.5. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{18}\text{ClO}_2$ ($\text{M} + \text{H}$) $^+$ 409.0990, found 409.0991.

8-Benzoyl-9-(4-bromophenyl)cyclohepta[de]naphthalen-7(10*H*)-one (**3f**): Yellow solid, m.p. 152~153 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.05 (t, $J=8.0$ Hz, 3H), 7.95 (d, $J=8.0$ Hz, 1H), 7.76 (d, $J=8.0$ Hz, 1H), 7.68 (t, $J=8.0$ Hz, 2H), 7.63 (t, $J=8.0$ Hz, 1H), 7.57 (d, $J=8.0$ Hz, 1H), 7.48 (d, $J=8.0$ Hz, 2H), 7.38 (d, $J=12.0$ Hz, 2H), 7.33 (t, $J=8.0$ Hz, 1H), 6.57 (d, $J=4.0$ Hz, 1H), 5.03 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 196.1, 193.7, 145.6, 140.8, 139.1, 137.0, 133.6, 133.13, 133.08, 132.9, 132.2 (2C), 131.3, 130.4, 129.3 (2C), 128.6 (2C), 128.2 (2C), 128.0, 127.8, 125.3, 122.6, 121.3, 120.7, 45.5. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{18}\text{BrO}_2$ ($\text{M} + \text{H}$) $^+$ 453.0485, found 453.0487.

Methyl 4-(9-benzoyl-10-oxo-7,10-dihydrocyclohepta[de]naphthalen-8-yl)benzoate (**3g**): Yellow solid, m.p. 192~193 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.17 (d, $J=8.0$ Hz, 2H), 8.07~8.05 (m, 3H), 7.97 (d, $J=8.0$ Hz, 1H), 7.75 (d, $J=8.0$ Hz, 1H), 7.70 (t, $J=8.0$ Hz, 1H), 7.57 (t, $J=8.0$ Hz, 3H), 7.48 (t, $J=8.0$ Hz, 2H), 7.29 (d, $J=8.0$ Hz, 1H), 6.44 (d, $J=8.0$ Hz, 1H), 5.05 (s, 2H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 196.1, 193.7, 166.7, 146.6, 145.7, 139.2, 137.0, 136.9, 133.5, 133.2, 133.1, 132.9, 131.4, 130.4 (2C), 130.1, 128.7 (2C), 128.2 (2C), 128.1, 127.8, 127.6 (2C), 125.3, 121.4, 120.8, 52.3, 45.3. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{21}\text{O}_4$ ($\text{M} + \text{H}$) $^+$ 433.1434, found 433.1432.

8-Benzoyl-9-(thiophen-3-yl)cyclohepta[de]naphthalen-7(10*H*)-one (**3h**): Yellow solid, m.p. 149~150 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.07 (d, $J=8.0$ Hz, 2H), 8.02 (d, $J=8.0$ Hz, 1H), 7.94 (d, $J=8.0$ Hz, 1H), 7.74 (d, $J=12.0$ Hz, 1H), 7.66 (t, $J=8.0$ Hz, 1H), 7.57 (t, $J=8.0$ Hz, 1H), 7.49~7.42 (m, 4H), 7.36 (t, $J=8.0$ Hz, 1H), 7.21 (d, $J=4.0$ Hz, 1H), 6.76 (d, $J=8.0$ Hz, 1H), 5.06 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 196.4, 193.6, 142.5, 142.1, 138.9, 137.1, 133.9, 133.21, 133.19, 133.0, 131.2, 130.3, 128.5 (2C), 128.12 (2C), 128.09, 127.6, 127.4, 126.5, 125.1, 123.6, 121.2, 120.6, 45.5. HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{17}\text{O}_2\text{S}$ ($\text{M} + \text{H}$) $^+$ 381.0944, found 381.0945.

8-Benzoyl-9-hexylcyclohepta[de]naphthalen-7(10*H*)-one (**3i**): Yellow solid, m.p. 131~132 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.13 (d, $J=8.0$ Hz, 2H), 8.00 (d, $J=8.0$ Hz, 1H), 7.89 (d, $J=4.0$ Hz, 1H), 7.78 (d, $J=8.0$ Hz, 1H), 7.74 (d, $J=8.0$ Hz, 1H), 7.64~7.56 (m, 3H), 7.50 (t, $J=8.0$ Hz, 2H), 4.86 (s, 2H), 2.84 (t, $J=8.0$ Hz, 2H), 1.76~1.68 (m, 2H), 1.56~1.49 (m, 2H), 1.40~1.33 (m, 4H), 0.93 (t, $J=8.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 196.8, 193.5, 151.8, 138.5, 137.3, 134.6, 133.5, 132.9, 131.5, 131.0, 130.4, 128.5 (2C), 128.2, 128.1 (2C), 127.6, 124.7, 121.0, 120.8, 44.0, 37.4, 31.6, 29.7, 26.8, 22.5, 14.0. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{27}\text{O}_2$ ($\text{M} + \text{H}$) $^+$ 383.2006, found 383.2008.

8-(4-Methylbenzoyl)-9-phenylcyclohepta[de]naphthalen-7(10*H*)-one (**3j**): Yellow solid, m.p. 166~167 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.02~7.94 (m, 4H), 7.71 (d, $J=8.0$ Hz, 1H), 7.66 (t, $J=8.0$ Hz, 1H), 7.52~7.43 (m, 5H), 7.28 (d, $J=8.0$ Hz, 2H), 6.48 (d, $J=8.0$ Hz, 1H), 5.06 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.8, 193.9, 147.5, 143.7, 142.0, 138.9, 134.7, 133.9, 133.2, 132.5, 131.1, 130.3, 129.2 (2C), 128.9 (2C), 128.3, 128.2 (2C), 128.0, 127.6, 127.3 (2C), 124.9, 121.1, 120.7, 45.6, 21.6. HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{21}\text{O}_2$ ($\text{M} + \text{H}$) $^+$ 389.1536, found 389.1539.

8-(4-Methylbenzoyl)-9-phenylcyclohepta[de]naphthalen-7(10*H*)-one (**3k**): Yellow solid, m.p. 168~169 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.05 (d, $J=8.0$ Hz, 2H), 8.01 (d, $J=8.0$ Hz, 1H), 7.95 (d, $J=8.0$ Hz, 1H), 7.71 (d, $J=8.0$ Hz, 1H), 7.66 (t, $J=8.0$ Hz, 1H), 7.51~7.43 (m, 5H), 7.26 (d, $J=8.0$ Hz, 1H), 6.94 (d, $J=8.0$ Hz, 2H), 6.47 (d, $J=4.0$ Hz, 1H), 5.04 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 194.7, 193.9, 163.4, 147.7, 142.0, 138.9, 134.0, 133.3, 132.5, 131.1, 130.4 (2C), 130.31, 130.27, 128.9 (2C), 128.3, 128.0, 127.6, 127.3 (2C), 124.9, 121.1, 120.7, 113.7 (2C), 55.4, 45.4. HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{21}\text{O}_3$ ($\text{M} + \text{H}$) $^+$ 405.1485, found 405.1488.

8-(4-Fluorobenzoyl)-9-phenylcyclohepta[de]naphthalen-7(10*H*)-one (**3l**): Yellow solid, m.p. 176~177 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.06 (d, $J=8.0$ Hz, 2H), 7.98 (d, $J=8.0$ Hz, 1H), 7.92 (d, $J=8.0$ Hz, 1H), 7.69 (d, $J=8.0$ Hz, 1H), 7.62 (t, $J=8.0$ Hz, 1H), 7.50~7.41 (m, 5H), 7.23 (t, $J=8.0$ Hz, 1H), 7.11 (t, $J=8.0$ Hz, 2H), 6.47 (d, $J=8.0$ Hz, 1H), 4.99 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 194.6, 193.9, 165.6 ($J=253$ Hz), 146.9, 141.9, 139.0, 133.8, 133.5 ($J=3$ Hz), 133.1, 132.6, 131.2, 130.8 ($J=9$ Hz, 2C), 130.3, 129.0 (2C), 128.4, 128.0, 127.6, 127.3 (2C), 125.0, 121.2, 120.7, 115.5 ($J=22$ Hz, 2C), 45.6. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{18}\text{FO}_2$ ($\text{M} + \text{H}$) $^+$ 393.1285, found 393.1288.

8-(3-Chlorobenzoyl)-9-phenylcyclohepta[de]naphthalen-7(10*H*)-one (**3m**): Yellow solid, m.p. 150~151 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.06 (d, $J=8.0$ Hz, 2H), 8.02 (d, $J=8.0$ Hz, 2H), 7.95 (d, $J=8.0$ Hz, 2H), 7.73 (d, $J=8.0$ Hz, 1H), 7.67 (t, $J=8.0$ Hz, 1H), 7.55~7.39 (m, 6H), 7.41 (t, $J=8.0$ Hz, 1H), 7.29 (d, $J=8.0$ Hz, 1H), 6.52 (d, $J=4.0$ Hz, 1H), 4.99 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 194.9, 193.9, 146.4, 141.9, 139.0, 138.7, 134.8, 133.7, 133.1, 132.9, 132.7, 131.3, 130.3, 129.9, 129.0 (2C), 128.5, 128.2, 128.0, 127.7, 127.3 (2C), 126.2, 125.1, 121.3, 120.8, 45.9. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{18}\text{ClO}_2$ ($\text{M} + \text{H}$) $^+$ 409.0990, found 409.0992.

8-(4-Bromobenzoyl)-9-phenylcyclohepta[de]naphthalen-7(10*H*)-one (**3n**): Yellow solid, m.p. 182~183 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.04 (d, $J=8.0$ Hz, 1H), 7.96 (d, $J=8.0$ Hz, 1H), 7.93 (d, $J=8.0$ Hz, 2H), 7.73 (d, $J=8.0$ Hz, 1H), 7.68 (t, $J=8.0$ Hz, 1H), 7.62 (d, $J=8.0$ Hz, 2H), 7.52~7.44 (m, 5H), 7.29 (d, $J=8.0$ Hz, 1H), 6.50 (d, $J=4.0$ Hz, 1H), 4.99 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.3, 194.0, 146.7, 141.9, 139.1, 136.0, 133.8, 133.2, 132.7, 131.9 (2C), 131.3, 130.4, 129.7 (2C), 129.0 (2C),

128.5, 128.14, 128.06, 127.7, 127.3 (2C), 125.1, 121.3, 120.9, 45.7. HRMS (ESI) calcd for $C_{27}H_{18}BrO_2$ ($M+H$)⁺ 453.0485, found 453.0486.

8-(2-Bromobenzoyl)-9-phenylcyclohepta[de]naphthalen-7(10*H*)-one (**3o**): Yellow solid, m.p. 121~122 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.98 (d, *J*=8.0 Hz, 1H), 7.95 (d, *J*=8.0 Hz, 1H), 7.82 (d, *J*=8.0 Hz, 1H), 7.68 (d, *J*=12.0 Hz, 1H), 7.63 (t, *J*=8.0 Hz, 1H), 7.55 (d, *J*=8.0 Hz, 1H), 7.51~7.42 (m, 5H), 7.38 (t, *J*=8.0 Hz, 1H), 7.26~7.22 (m, 2H), 6.51 (d, *J*=8.0 Hz, 1H), 4.92 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 199.3, 193.9, 145.7, 141.6, 141.5, 138.9, 133.6, 133.4, 133.1, 132.8, 131.4, 131.2, 130.3, 129.0 (2C), 128.7, 128.5, 128.0, 127.6, 127.4, 127.3 (2C), 125.1, 121.2, 120.8, 118.5, 49.4. HRMS (ESI) calcd for $C_{27}H_{18}BrO_2$ ($M+H$)⁺ 453.0485, found 453.0487.

8-(2-Bromobenzoyl)-9-(*p*-tolyl)cyclohepta[de]naphthalen-7(10*H*)-one (**3p**): Yellow solid, m.p. 150~151 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.00 (d, *J*=8.0 Hz, 1H), 7.97 (d, *J*=8.0 Hz, 1H), 7.83 (d, *J*=8.0 Hz, 1H), 7.70 (d, *J*=8.0 Hz, 1H), 7.66 (t, *J*=8.0 Hz, 1H), 7.56 (d, *J*=8.0 Hz, 1H), 7.42~7.35 (m, 3H), 7.30~7.24 (m, 4H), 6.64 (d, *J*=8.0 Hz, 1H), 4.92 (s, 2H), 2.45 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 199.4, 193.9, 146.1, 141.6, 138.9, 138.7, 138.4, 133.9, 133.4, 133.2, 132.7, 131.4, 131.2, 130.3, 129.6 (2C), 128.8, 128.0, 127.6, 127.4, 127.3 (2C), 125.0, 121.2, 120.9, 118.6, 49.6, 21.4. HRMS (ESI) calcd for $C_{28}H_{20}BrO_2$ ($M+H$)⁺ 467.0641, found 467.0638.

8-(2-Bromobenzoyl)-9-(4-fluorophenyl)cyclohepta[de]naphthalen-7(10*H*)-one (**3q**): Yellow solid, m.p. 128~129 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.03 (d, *J*=8.0 Hz, 1H), 7.99 (d, *J*=8.0 Hz, 1H), 7.83 (d, *J*=8.0 Hz, 1H), 7.74 (d, *J*=8.0 Hz, 1H), 7.68 (t, *J*=8.0 Hz, 1H), 7.59 (d, *J*=8.0 Hz, 1H), 7.49~7.41 (m, 3H), 7.33~7.27 (m, 2H), 7.21 (t, *J*=8.0 Hz, 2H), 6.56 (d, *J*=8.0 Hz, 1H), 4.93 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 199.4, 193.7, 162.70 (*J*=247 Hz), 144.6, 141.4, 139.1, 137.5 (*J*=3 Hz), 133.54, 133.46, 133.3, 133.0, 131.5, 131.4, 130.4, 129.4 (*J*=8 Hz, 2C), 128.7, 128.0, 127.7, 127.5, 125.3, 121.3, 120.7, 118.5, 116.1 (*J*=21 Hz, 2C), 49.4. HRMS (ESI) calcd for $C_{27}H_{17}BrFO_2$ ($M+H$)⁺ 471.0930, found 471.0929.

4-(7-oxo-9-phenyl-7,10-dihydrocyclohepta[de]naphthalene-8-carbonyl)benzonitrile (**3r**): Yellow solid, m.p. 166~167 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.15 (d, *J*=8.0 Hz, 2H), 8.06 (d, *J*=8.0 Hz, 1H), 7.96 (d, *J*=8.0 Hz, 1H), 7.79 (d, *J*=8.0 Hz, 2H), 7.75 (d, *J*=8.0 Hz, 1H), 7.70 (t, *J*=8.0 Hz, 1H), 7.53~7.45 (m, 5H), 7.30 (t, *J*=8.0 Hz, 1H), 6.53 (d, *J*=8.0 Hz, 1H), 4.99 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 195.1, 194.0, 145.9, 141.7, 140.3, 139.2, 133.5, 133.0, 132.8, 132.5 (2C), 131.5, 130.4, 129.1 (2C), 128.7, 128.6 (2C), 128.1, 127.8, 127.3 (2C), 125.3, 121.4, 120.9, 118.0, 116.2, 46.0. HRMS (ESI) calcd for $C_{28}H_{18}NO_2$ ($M+H$)⁺ 400.1332, found 400.1329.

8-(1-Naphthoyl)-9-phenylcyclohepta[de]naphthalen-7(10*H*)-one (**3s**): Yellow solid, m.p. 172~173 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.64 (s, 1H), 8.11 (d, *J*=8.0 Hz, 1H), 8.03 (d, *J*=8.0 Hz, 1H), 7.97 (d, *J*=8.0 Hz, 2H), 7.90 (d, *J*=8.0 Hz, 1H), 7.87 (d, *J*=8.0 Hz, 1H), 7.73 (d,

J=8.0 Hz, 1H), 7.67 (d, *J*=8.0 Hz, 1H), 7.60~7.44 (m, 7H), 7.28 (t, *J*=8.0 Hz, 1H), 6.51 (d, *J*=8.0 Hz, 1H), 5.22 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 196.1, 194.0, 147.3, 142.0, 139.0, 135.6, 134.5, 134.0, 133.3, 132.7, 132.5, 131.2, 130.4, 129.8, 129.6, 129.0 (2C), 128.41, 128.36, 128.3, 128.0, 127.7, 127.6, 127.3 (2C), 126.6, 125.0, 124.0, 121.2, 120.8, 45.9. HRMS (ESI) calcd for $C_{31}H_{21}O_2$ ($M+H$)⁺ 425.1536, found 425.1538.

9-Phenyl-8-(thiophene-2-carbonyl)cyclohepta[de]naphthalen-7(10*H*)-one (**3t**): Yellow solid, m.p. 186~187 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.03 (d, *J*=8.0 Hz, 1H), 7.97 (d, *J*=8.0 Hz, 1H), 7.90 (d, *J*=4.0 Hz, 1H), 7.73 (d, *J*=8.0 Hz, 1H), 7.68 (t, *J*=8.0 Hz, 1H), 7.62 (d, *J*=8.0 Hz, 1H), 7.52~7.43 (m, 5H), 7.27 (t, *J*=8.0 Hz, 1H), 7.14 (t, *J*=4.0 Hz, 1H), 6.46 (d, *J*=8.0 Hz, 1H), 5.03 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 194.0, 188.9, 146.4, 144.0, 141.7, 139.0, 133.9, 133.4, 133.2, 132.8, 132.1, 131.3, 130.4, 129.0, 128.5 (2C), 128.06 (2C), 128.03, 127.7, 127.3, 125.0, 121.3, 120.9, 46.0. HRMS (ESI) calcd for $C_{25}H_{17}O_2S$ ($M+H$)⁺ 381.0944, found 381.0946.

8-(Cyclopropanecarbonyl)-9-phenylcyclohepta[de]naphthalen-7(10*H*)-one (**3u**): Yellow solid, m.p. 100~101 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.03 (t, *J*=8.0 Hz, 2H), 7.91 (m, 2H), 7.56~7.43 (m, 5H), 7.29 (d, *J*=8.0 Hz, 1H), 6.46 (d, *J*=4.0 Hz, 1H), 4.68 (s, 2H), 2.25~2.19 (m, 1H), 1.16~1.12 (m, 2H), 0.99~0.94 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 206.1, 193.9, 146.8, 141.8, 138.8, 133.9, 133.2, 132.4, 131.1, 130.3, 128.9 (2C), 128.3, 128.0, 127.6, 127.2 (2C), 124.9, 121.1, 120.7, 50.0, 20.8, 10.9. HRMS (ESI) calcd for $C_{24}H_{19}O_2$ ($M+H$)⁺ 339.1380, found 339.1382.

7-(4-Methoxybenzoyl)-8-phenyl-5,9-dihydro-6*H*-benzo[7]annulen-6-one (**3v**): Light purple solid, m.p. 103~104 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.10 (d, *J*=8.0 Hz, 2H), 7.58~7.37 (m, 7H), 7.04 (t, *J*=8.0 Hz, 3H), 6.48 (d, *J*=8.0 Hz, 1H), 4.91 (s, 2H), 3.98 (s, 3H), 3.68 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 205.5, 194.7, 163.4, 146.2, 142.2, 139.3, 137.4, 133.5, 130.4 (2C), 130.3, 129.2 (2C), 128.3 (2C), 126.9 (2C), 126.7, 124.9, 124.2, 113.7 (2C), 55.4, 45.9, 42.5. HRMS (ESI) calcd for $C_{25}H_{21}O_3$ ($M+H$)⁺ 369.1485, found 369.1486.

(*E*)-2-(3-Phenylprop-2-yn-1-ylidene)acenaphthylen-1(2*H*)-one (**3w**): White solid, m.p. 68~69 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.37 (d, *J*=8.0 Hz, 1H), 8.08 (d, *J*=8.0 Hz, 1H), 8.02 (d, *J*=8.0 Hz, 1H), 7.90 (d, *J*=8.0 Hz, 1H), 7.74~7.63 (m, 4H), 7.44 (t, *J*=4.0 Hz, 3H), 7.03 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 191.5, 141.2, 140.4, 132.9, 132.0 (2C), 131.4, 130.4, 129.5, 128.7 (2C), 128.4, 128.0, 126.3, 122.6, 121.7, 120.8, 111.4, 104.1, 87.9. HRMS (ESI) calcd for $C_{21}H_{13}O$ ($M+H$)⁺ 281.0961, found 281.0960.

Supporting Information Copies of ¹H NMR and ¹³C NMR spectra for all products **3a**~**3w**. The Supporting Information is available free of charge via the Internet at <http://sioc-journal.cn>.

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