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Palladium(0)/Copper(I)-Catalyzed Tandem Cyclization of Aryl 1-Cyanoalk-5-ynyl Ketone System: Rapid Assembly of Cyclopenta[*b*]naphthalene and Benzo[*b*]fluorene Derivatives

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Abstract: We have developed a new and general approach to construct a variety of benzo[*b*]fluorene and cyclopenta-[*b*]naphthalene derivatives *via* the palladium(0)/copper(I)-catalyzed tandem cyclization of aryl 1-cyanoalk-5-ynyl ketone systems in an extremely efficient manner. The key operation lies in the copper(I)-catalyzed aerobic oxidation, which allows for activation of two successive intramolecular cycloadditions immediately after the Sonogashira coupling reaction has occurred.

Keywords: arylnaphthalenes; benzo[*b*]fluorenes; copper; cyclopenta[*b*]naphthalenes; palladium; radical cyclization; Sonogashira reaction; tandem reactions

Introduction

Benzo[*b*]fluorene and arylnaphthalene nuclei, as typified in Figure 1, are present in many naturally occurring products exhibiting either a broad spectrum of antibiotic properties or potent antimitotic activities.[1,2] Many effective synthetic methods have been developed to construct these polycyclic frameworks, mainly making use of metal-catalyzed annulation or dehydro-Diels–Alder (DDA) cycloaddition as a key operation.[3,4] Recently we have successfully developed a variety of annulation protocols to establish highly functionalized polycyclic rings on the basis of α-activated cross-conjugated cycloalkenone systems.[5] In one approach, when substrates **1** and **2** were individually

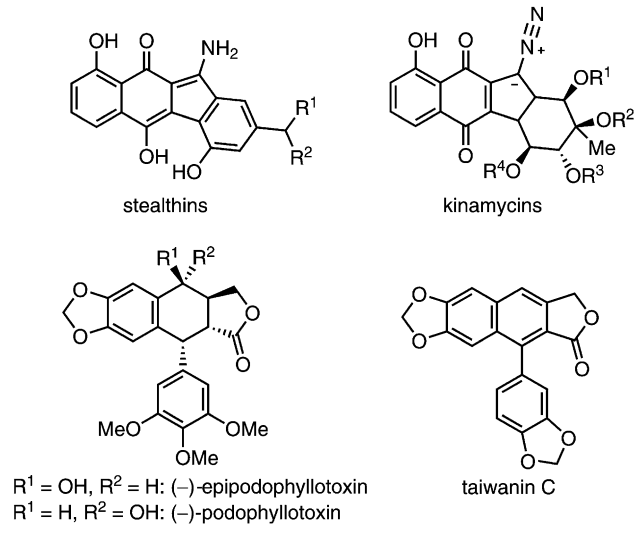
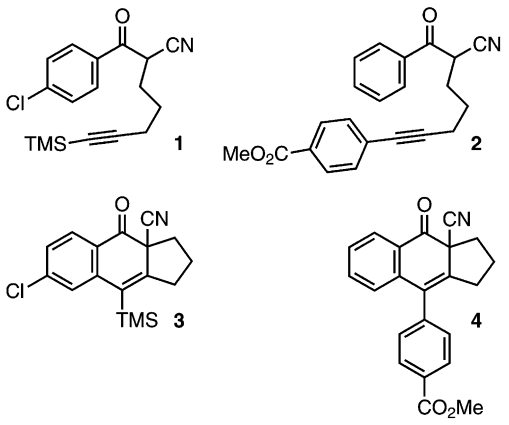
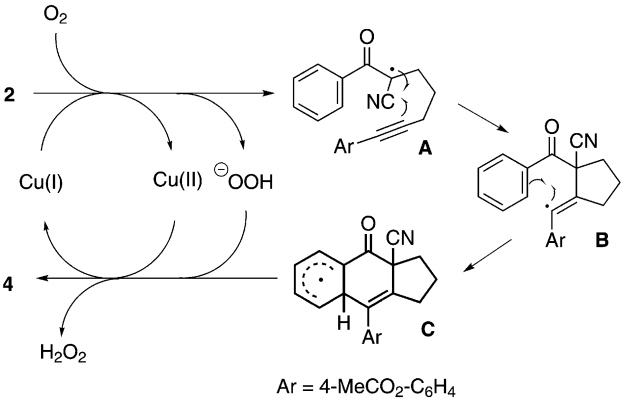


Figure 1. Natural products containing either benzo[*b*]fluorene or arylnaphthalene skeletons.



treated with oxidants *tert*-butyl hydroperoxide (TBHP) and tetrabutylammonium iodide (TBAI) under reflux in benzene, the corresponding tricyclic compounds **3** and **4**, containing a cyclopenta[*b*]naphthalene nucleus, could be synthesized effectively.[6]

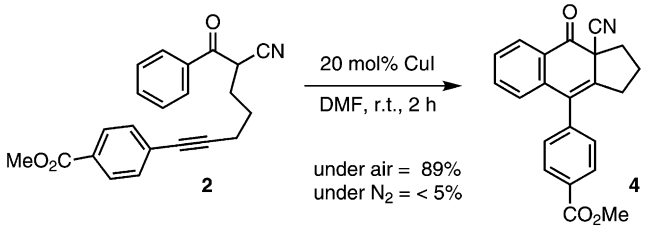
Although the methodology described above is synthetically useful, however, harsh reaction conditions are necessary to drive the reaction to completion. Herein, we wish to report that a mild Pd/Cu-catalyzed radical cascade, proceeding *via* a sequence of Sonogashira coupling followed by [4+1] and [4+2]cycloadditions,[7,8] has been developed to rapidly assemble cyclopenta[*b*]naphthalene and benzo[*b*]fluorene derivatives, for which the synthetic scope is tremendously broadened and extended as compared to the prior version indicated above.[6]



Scheme 2. Proposed mechanism for an intramolecular Cu(I)-catalyzed radical cascade under air.

Results and Discussion

That the Cu(I)-catalyzed aerobic oxidation could convert α-cyano esters to the corresponding α-keto esters has been reported by Kim et al.[9] Accordingly, the initial radical species was generated by abstracting hydrogen α to cyano with molecular oxygen mediated by Cu(I) at ambient temperature. Given that α-cyano esters bear a high similarity to α-cyano ketones in many facets of chemistry, such as Diels–Alder reaction,[10] Conia-ene reaction,[11] reductive alkylation,[12] and metal-mediated annulations,[13] the reaction system described above appears to be one of the potential alternatives to meet our purpose for seeking a radical initiator allowing us to work under mild conditions. This concept was tested and validated by the use of **2** as a model compound. As illustrated in Scheme 1, when substrate **2** was reacted under catalysis with CuI (20 mol%) in DMF under air at room temperature, it was found to undergo an intramolecular cycloaddition efficiently to afford the expected product **4** in high yield (89%), the structure of which was unambiguously confirmed by the X-ray crystallographic analysis.[14] In contrast, when the same reaction was carried out under a nitrogen atmosphere, product **4** was formed in less than 5% yield as determined by ^{1}H NMR analysis, indicating that CuI associated with O_2 should play a critical role in promoting

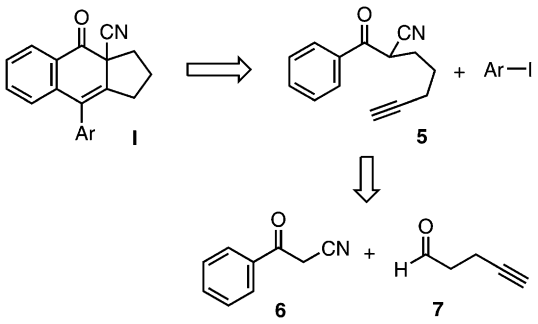


Scheme 1. CuI-catalyzed aerobic cycloaddition.

the observed radical cyclization cascade. More importantly, the results also strongly suggest that the [4+2]intramolecular cycloaddition is not the result of a Diels–Alder process. Upon exposure to air, similar experiments with an incremental addition of CuI in DMF have been intensively studied, leading to findings that the most appropriate catalytic amount of CuI is 20 mol% (Scheme 1). Moreover, it was noticed that, in the absence of CuI under air, substrate **2** could spontaneously transform into product **4** in 5–13% yield in 24 h when dissolved in commonly used solvents including CH_3COOEt, CH_2Cl_2, and DMF. However, we found that the conversion rate was constantly maintained at this level even if the reaction time was prolonged for more than two days under either air or oxygen.

As illustrated in Scheme 2, a plausible mechanism of the observed CuI-catalyzed aerobic cycloaddition is proposed using α-cyano ketone **2** as an example. The cyclization cascade is initiated by abstracting hydrogen, α to both cyano and carbonyl groups, with molecular oxygen mediated by Cu(I) to generate radical intermediate **A** and hydroperoxide anion, wherein Cu(I) is simultaneously oxidized into Cu(II). Intermediate **A** thus formed might undergo the first intramolecular 5-*exo*-*dig* cyclization to produce vinyl radical **B**, by which the ensuing [4+2]radical cycloaddition could take place to afford the corresponding cyclic pentadienyl radical **C**. Finally, rearomatization should occur through aromatic homolytic substitution (AHS) to furnish product **4** with concomitant formation of hydrogen peroxide.[15] Meanwhile, Cu(II) is reduced to Cu(I) *via* an electron transfer from hydroperoxide anion to enter the next catalytic cycle.[16]

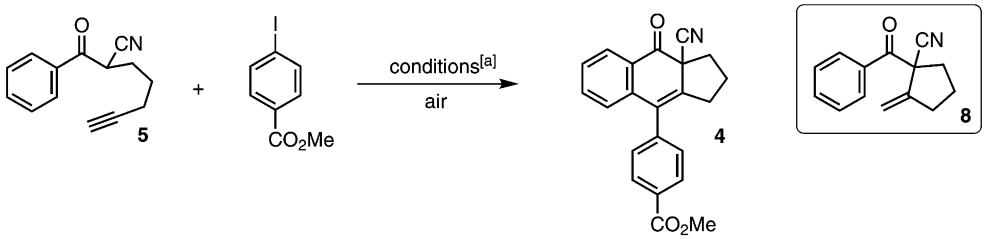
Although it can be converted into product **4** efficiently under mild reaction conditions as indicated above, substrate **2** and structurally related analogues must be prepared *via* a three-step synthetic sequence, involving Dess–Martin oxidation,[17] Knoevenagel condensation,[18] and Sonogashira coupling,[7] starting



Scheme 3. Retrosynthetic analysis of cyclopenta[*b*]naphthalene derivatives.

from commercially available 4-pentyn-1-ol and benzoylacetonitrile. Attempts to simplify this linear approach and further broaden the synthetic scope were then made. According to the retrosynthetic analysis shown in Scheme 3, it was envisioned that a general approach toward cyclopenta[*b*]naphthalene derivatives **I** might be achievable by reacting a common intermediate **5** with various aryl iodides, respectively, in a Pd(0)/Cu(I)-catalyzed system to direct both alkynylation and subsequent cycloaddition in one pot, wherein Cu(I) is expected to have dual independent functions, one for facilitating Sonogashira coupling and one for triggering cycloaddition. The key intermediate **5** was readily prepared *via* a modified procedure of Knoevenagel condensation, in which benzoylacetonitrile (**6**) was first condensed with 4-pentyn-1-al (**7**) to form the corresponding α,β-unsaturated enone *in situ* followed by reduction with Hantzsch ester.[19] Using **5** as a substrate, screening of reaction conditions *via* combining the palladium and copper source as catalyst with various parameters, including solvent, temperature and base, was then extensively carried out. Results are compiled in Table 1 and discussed as follows. As indicated in entry 1, a reaction catalyzed with $PdCl_2(PPh_3)_2$ (2 mol%) and CuI (20 mol%) in DMF using NEt_3 as base at elevated temperature under air was first examined. Unfortunately, this combination failed to induce Sonogashira coupling, but a Conia-ene reaction occurred instead, leading to product **8** in 45% yield. As such, under similar reaction conditions an increase of $PdCl_2(PPh_3)_2$ up to 10 mol% was then tried to effect the coupling. To our delight, the desired product **4** was obtained in 59% yield through this minor modification (entry 2). Thus, a primary concept that Pd(II) and Cu(I) metal might work as cocatalyst to promote independently both al-

Table 1. Optimization of reaction conditions.



Entry	Catalyst	Base	Solvent	Temp. [°C]	Yield [%][b]
1[c]	2% $PdCl_2(PPh_3)_2$/20% CuI	NEt_3	DMF	80	–
2[c]	10% $PdCl_2(PPh_3)_2$/20% CuI	NEt_3	DMF	80	59
3[c]	10% $Pd(PPh_3)_4$/20% CuI	NEt_3	DMF	80	68
4[c]	10% $Pd(PPh_3)_4$/30% CuI	NEt_3	DMF	80	75
5[c]	10% $Pd(PPh_3)_4$/40% CuI	NEt_3	DMF	80	72
6[d]	10% $Pd(PPh_3)_4$/30% CuI	NEt_3	DMF	r.t.	76
7[d]	10% $Pd(PPh_3)_4$/30% CuI	NEt_3	THF	r.t.	63
8[d]	10% $Pd(PPh_3)_4$/30% CuI	NEt_3	MeCN	r.t.	59
9[d]	10% $Pd(PPh_3)_4$/30% CuI	NEt_3	toluene	r.t.	55
10[d]	10% $Pd(PPh_3)_4$/30% CuI	NEt_3	dioxane	r.t.	63
11[d]	10% $Pd(PPh_3)_4$/30% CuI	NEt_3	CH_2Cl_2	r.t.	80
12[d]	10% $Pd(PPh_3)_4$/30% CuI	pyridine	CH_2Cl_2	r.t.	50
13[d]	10% $Pd(PPh_3)_4$/30% CuI	DIEA	CH_2Cl_2	r.t.	75
14[d]	**10% $Pd(PPh_3)_4$/30% CuI**	**pyrrolidine**	**CH_2Cl_2**	**r.t.**	**90**
15[d]	10% $Pd(PPh_3)_4$/30% CuI	Cs_2CO_3	CH_2Cl_2	r.t.	<5
16[d]	10% $Pd(PPh_3)_4$/30% CuI	Na_2CO_3	CH_2Cl_2	r.t.	<5

[a] All reactions were performed using substrate **5** (100 mg, 0.47 mmol), methyl-4-iodobenzoate (136 mg, 0.52 mmol) and base (0.94 mmol) in the presence of catalyst, as indicated above, in 3 mL of solvent.
[b] Isolated yields.
[c] Reaction was complete in 1.5 h.
[d] Reaction was complete in 3.5 h.

kynylation and subsequent cyclization was experimentally validated. Encouraged with these findings, a conventional Pd(0) coupling agent $Pd(PPh_3)_4$ instead of $PdCl_2(PPh_3)_2$ was then applied as shown in entry 3. The operation resulted in product **4** in a higher yield (68% *vs.* entry 2; 59%), implying that Pd(0) might be a better surrogate for Pd(II) to catalyze Sonogashira coupling in the presence of CuI. Along this line, an incremental addition of $Pd(PPh_3)_4$ starting with 2 mol% up to 15 mol% has been investigated, leading to findings that upon exposure to air, an amount of at least 10 mol% of $Pd(PPh_3)_4$ was required to induce the alkynylation effectively. As such, using 10 mol% of Pd(0) as a fixed theme, the amount of CuI was further adapted. When CuI was increased up to 30 mol% (entry 4), a slight increase in yield (75% *vs.* entry 3; 68%) was obtained, but it was found to be a ceiling amount in that the reaction yield dropped immediately to 72% when 40 mol% of CuI was used (entry 5). Later, we came to realize that when the reaction conditions in entry 4, in fact, were allowed to work at room temperature instead, affording product **4** in almost an equal yield, but a longer reaction time was necessary for completing the conversion (entry 6; 76%, 3.5 h *vs.* entry 4; 75%, 1.5 h). Accordingly, screening of different solvents, including THF, MeCN, toluene, dioxane and CH_2Cl_2 at ambient temperature rather than at 80 °C was then conducted to check solvent effects (entries 7–11). Consequently, we found that CH_2Cl_2 is superior to all solvents examined in terms of reaction yields (entry 11; 80%).

Replacing triethylamine with other organic bases using CH_2Cl_2 as a fixed solvent was then studied, resulting in findings that pyrrolidine could further increase the reaction yield by ~10% (entry 14; 90%). In parallel, inorganic bases such as Cs_2CO_3 and Na_2CO_3 were also tested, but they appeared to be extremely incompatible with the current catalyst to promote the desired reaction (entries 15 and 16; <5%). An explanation for this could be that organic bases might help the catalyst to dissolve more homogeneously, thus enhancing reaction yield more significantly. The reaction system [10 mol% $Pd(PPh_3)_4$/30 mol% CuI/pyrrolidine/CH_2Cl_2/room temperature) exhibited in entry 14 was considered as the optimum and adopted as a typical procedure for the following reactions. To examine the generality of this newly developed protocol, many structurally diverse substrates **5a–j** (Figure 2) were readily prepared in good to excellent yields *via* a modified procedure of Knoevenagel condensation as previously applied to the synthesis of intermediate **5** (see Experimental Section for synthetic details).

As listed in Table 2, treating **5a–j** with various monosubstituted aryl iodides under optimized conditions gave the corresponding cyclopenta[*b*]naphthalene derivatives **9aa–au** and **9ba–bl** in good to excellent

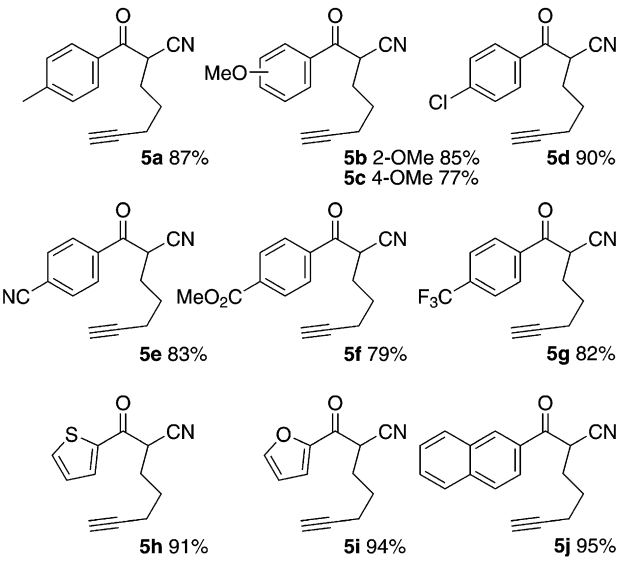
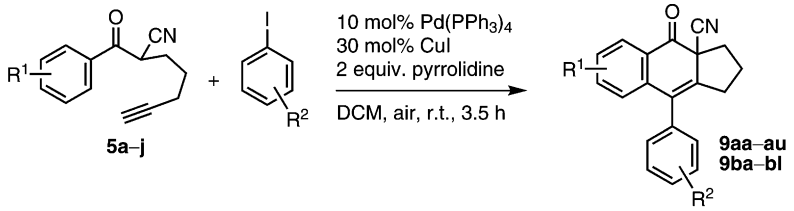
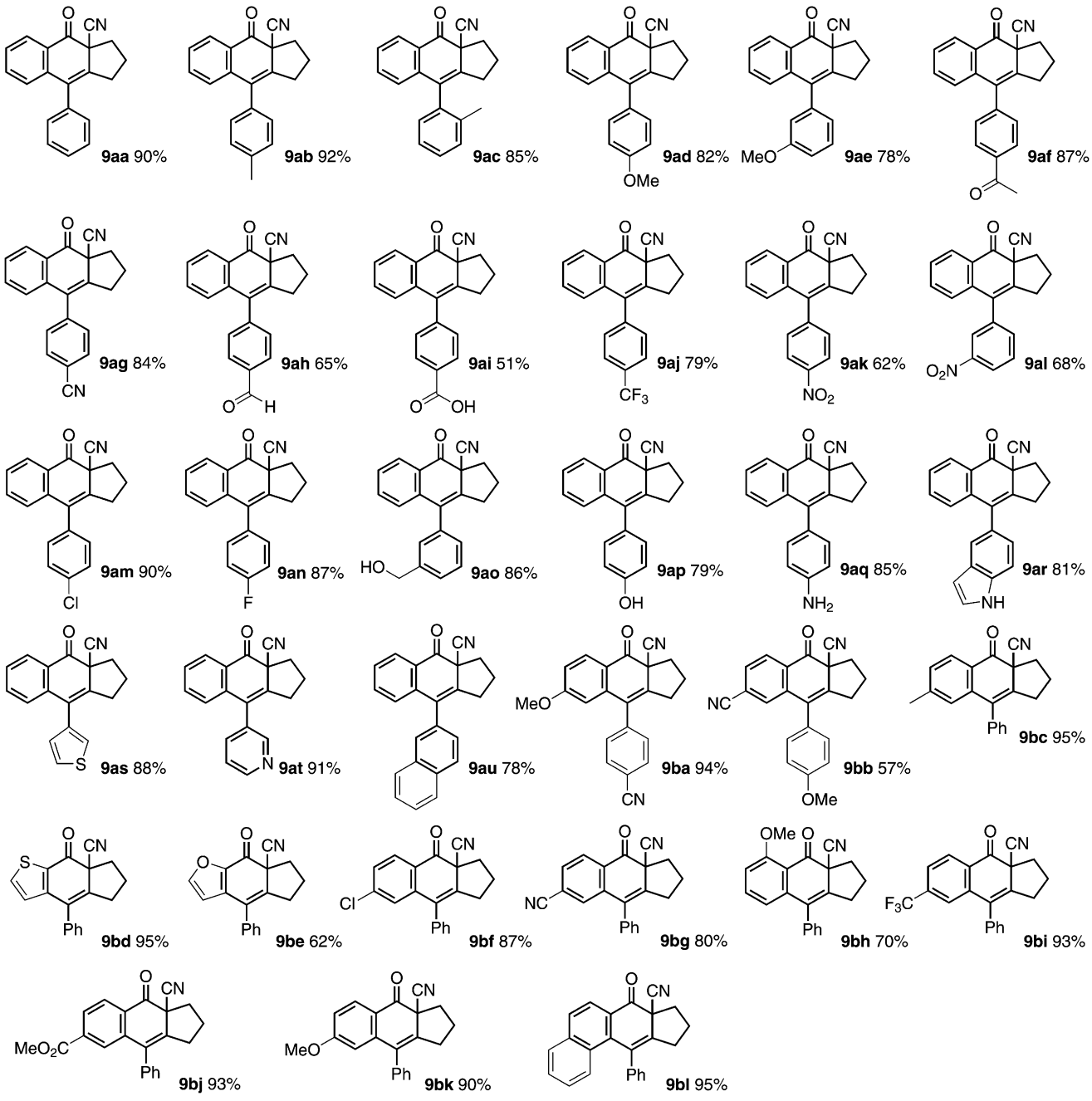


Figure 2. Preparation of aryl 1-cyanoalk-5-ynyl ketones **5a–j**.

yields (51–95%). Thus, not only is the generality of the methodology attested but also a novel series of compounds containing a linear [6,6,5] tricyclic framework has become accessible. It must be emphasized that the above isolated yields are obtained at least in a three-step chemical transformation, so that even the lowest yield (51%) might be considered to be synthetically significant and useful. Although all reactions took place in a predictable and efficient manner, in general, aryl iodides with an electron-donating group gave products [e.g., **9ab** (92%), **9ad** (82%), **9ap** (79%) and **9aq** (85%)] in higher yields than those containing an electron-withdrawing group [e.g., **9ah** (65%), **9ai** (51%), **9ak** (62%) and **9al** (68%)]. However, halogenated aryl and heteroaryl iodides contributed to the corresponding products **9am** (90%), **9an** (87%), **9as** (88%) and **9at** (91%) in excellent yields though they belong to electron-deficient chemical entities in nature. These outcomes might be attributed to a compromise between Sonogashira reaction and the subsequent [4+2]cycloaddition during the reaction course in that aryl iodides containing electron-withdrawing groups could facilitate the former by enhancing oxidative addition of the Pd(0) metal to the carbon-halogen bond, but deactivate the latter *via* inductive stabilization of the vinyl radical intermediate **B**, which is thought to assume a bent σ-type structure (Scheme 2).[20] By inference, a maximum yield might be attainable once these two opposing effects could reach a subtle balance as seen with products **9ab** (92%), **9at** (91%), **9bc** (95%) and **9bd** (95%). Compound **9bl** formed with complete regioselectivity in 95% yield is apparently the result of a beneficial effect of ambient temperature in that the same reaction performed at 80 °C in DMF resulted in the formation of a complex isomeric mixture.[21]

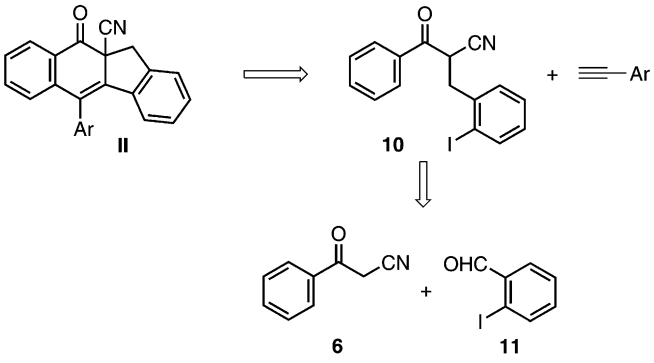
Table 2. Tandem annulation of aryl 1-cyanoalk-5-ynyl ketones under catalysis with Pd(0)/Cu(I) metal.



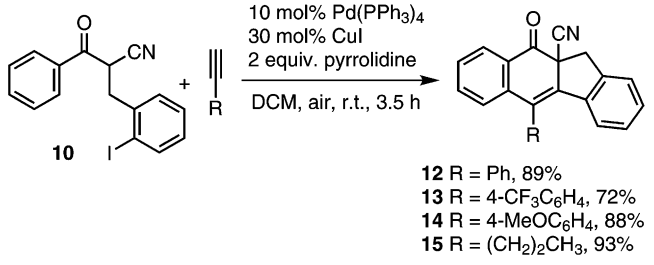


In addition, as evidenced by ^{1}H NMR data with two distinct methyl singlets, compound **9ac** must be present in two atropisomers due to the rotational energy barrier imposed with the 2-methyl group on the phenyl ring. This explanation could be justified by its isomer **9ab** in which only a singlet is observed for

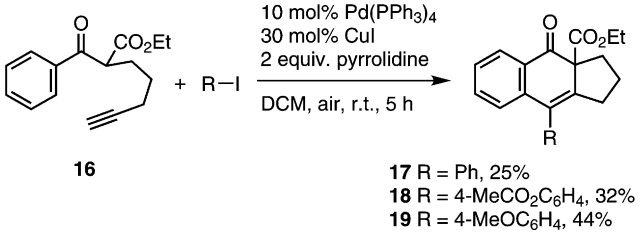
the 4-methyl group allowing for free rotation. The stereoelectronic feature of the substituent on the benzoyl portion might not dominate the yield of reaction as demonstrated by products, such as **9bc** (95%; *p*-CH_3), **9bi** (93%; *p*-CF_3), **9bj** (93%; *p*-CO_2Me), **9bk** (90%; *p*-OCH_3), and **9bl** (95%; *m*,*p*-fused phenyl), containing either an electron-withdrawing or electron-donating group but resulting in almost an equal yield, presumably due to rearomatization occurring rapidly after intermediate **C** is formed (Scheme 2). Theoretically, the methodology can be further extended to the construction of various tetracyclic benzo[*b*]fluorene derivatives **II** after minor modifications as depicted in the retrosynthetic analysis (Scheme 4). It is highly conceivable that the common intermediate **10** could be prepared through reagents **6** and **11** by the modified Knoevenagel condensation as described previously. Compound **10** thus obtained should be able to couple with a variety of arylacetylenes to provide the corresponding products in one pot. According to this synthetic design, substrate **10** was experimentally realized in 78% yield and benzo[*b*]fluorene derivatives **12**–**15** were obtained in good to excellent yields (72–93%) as displayed in Scheme 5. By this approach, not only did benzo[*b*]fluorene derivatives become available, but also the appended functionality, referred to as R, could be extended to various alkyl groups (e.g., **15**) in addition to the regular aryl moieties.



Scheme 4. Retrosynthetic analysis of the formation of benzo[*b*]fluorene derivatives.



Scheme 5. One-pot synthesis of benzo[*b*]fluorene derivatives.



Scheme 6. One-pot synthesis of α-ester cyclopenta[*b*]naphthalene derivatives.

To broaden the synthetic utility, our above optimal reaction conditions for the title compounds were further applied to the corresponding α-ester compounds as typified by substrate **16** in Scheme 6, synthetic procedures of which are detailed in the Experimental Section. It was found that upon coupling with aryl iodides, α-ester ketone **16** was allowed to take the same reaction mode, respectively, to afford the corresponding products **17**–**19** in moderate yields (25–44%). Similar results were obtained even when reaction time was prolonged to overnight. Compared to their α-cyano counterparts **4**, **9aa** and **9ad** formed in much higher yields in shorter reaction times (82–90%; 3.5 h), such a distinct difference in the reaction outcome suggests that there might be a considerable discrepancy in the homolytic bond-dissociation energy between these two analogous systems in the initially formed radical species (e.g., intermediate **A** in Scheme 2).

However, as the same reaction was carried out under a nitrogen atmosphere, Sonogashira coupling products **20**–**22**, precursors of compounds **17**–**19**, were obtained instead in excellent yields and stayed stable even if the reaction time was extended overnight (Figure 3), again supporting that the proposed [4+2] intramolecular cyclization is not the result of a Diels–Alder process.

For comparison, as the current reaction system (Table 1, entry 14) was initially performed in the absence of air, it was found that at least 5 mol% of Pd(0) was necessary to effect the Sonogashira coupling (stage I) to afford intermediate **2** (~90%, 1.5 h) as determined by crude ^{1}H NMR data. Once coupling reaction was complete, air was then introduced to facilitate the radical cyclization (stage II) to afford product **4** (92%, 3.5 h). Although the one-pot reaction

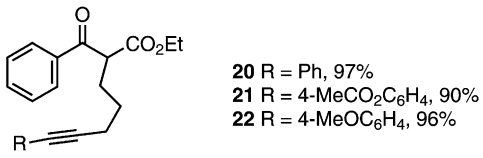


Figure 3. Formation of Sonogashira coupling products under a nitrogen atmosphere.

carried out in this manner could reduce the catalyst loading to half the original amount, however, it would result in a lower overall yield (83% *vs.* 90%) and longer reaction time (5 h *vs.* 3.5 h).

Conclusions

We have developed a new and general approach to achieve a facile access to benzo[*b*]fluorene and cyclopenta[*b*]naphthalene derivatives *via* sequential Pd(0)/Cu(I)-catalyzed radical cyclization of the aryl 1-cyanoalk-5-ynyl ketone system. Accordingly, a library of diverse arylnaphthalene lignan- and kinamycin-mimicking molecules can be rapidly established for the purpose of screening new chemical entities with potential antibacterial and/or anticancer activity. In addition, for further synthetic elaboration, polycyclic compounds thus formed could increase the degree of functionalization *via* reductive decyanation substitution below ambient temperature as demonstrated in many historical cases.[5d,10d,11a,12]

Experimental Section

General Remarks

All reactions were performed under an atmosphere of nitrogen unless otherwise stated. All solvents were dried prior to use and reagents were employed as received. Analytical thin layer chromatography was performed on SiO_2 60 F-254 plates and flash column chromatography was carried out using SiO_2 60 (particle size 0.040–0.055 mm, 230–400 mesh), both of which are available from E. Merck. Visualization was performed under UV irradiation at 254 nm followed by staining with aqueous potassium permanganate [$KMnO_4$ (3 g) and K_2CO_3 (20 g) in 300 mL of H_2O containing 5 mL of an aqueous solution of NaOH (5%, w/v)] and charring by heat gun. Fourier transform infrared spectra (IR) were recorded on a Perkin–Elmer spectrum RX I FT-IR system and expressed in cm^{-1}. ^1H and ^{13}C NMR spectra were recorded on a Varian Agilent 400 FT NMR spectrometer. Chloroform-*d* and methanol-*d* were used as the solvent and TMS ($\delta = 0.00$ ppm) as an internal standard. Chemical shifts are reported as δ values in ppm as referenced to TMS. Multiplicities are recorded as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet), dd (doublet of doublets), dt (doublet of triplets), br (broad), m (multiplet). Coupling constants (*J*) are expressed in Hz. HR-MS were measured on a JEOL JMS-HX110 spectrometer and spectral data are recorded as *m/z* values. Melting points were measured using an Electrothermal instrument.

Preparation of Substrates

The general procedure for the synthesis of substrates **5** and **5a–j** is demonstrated as follows using **5** as a typical example.

2-Benzoylhept-6-ynenitrile (5)

To a stirred solution of benzoylacetonitrile **6** (1.0 g, 6.8 mmol) and pent-4-ynal **7** (686 mg, 8.2 mmol) in EtOH (100 mL) was added L-proline (312 mg, 2.7 mmol) and Hantzsch ester (1.7 g, 6.8 mmol) sequentially in one portion. The resulting mixture was stirred at 25 °C for 16 h. The reaction solution was concentrated under reduced pressure, the residue was purified by flash chromatography on silical gel (33% CH_2Cl_2 in *n*-hexane) to afford intermediate **5** as a colorless oil; yield: 1.3 g (94%). IR (CH_2Cl_2): $\nu_{max} = 3294$, 2937, 2250, 2117, 1694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.97$ (d, $J = 8.0$ Hz, 2H), 7.64 (t, $J = 7.6$ Hz, 1H), 7.51 (dd, $J = 8.0$, 7.6 Hz, 2H), 4.40 (dd, $J = 8.8$, 5.6 Hz, 1H), 2.30 (td, $J = 6.8$, 2.8 Hz, 2H), 2.24–2.05 (m, 2H), 1.97 (t, $J = 2.8$ Hz, 1H), 1.86–1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 190.5$ (CO), 134.5 (CH), 133.7 (C), 129.0 (CH), 128.7 (CH), 117.0 (CN), 82.7 (C≡C), 69.6 (C≡CH), 39.3 (CH), 28.5 (CH_2), 25.4 (CH_2), 17.6 (CH_2); HR-MS (FAB): $m/z = 212.1076$, calcd. for $C_{14}H_{13}NO$ $[M+H]^+$: 212.1075.

2-(4-Methylbenzoyl)hept-6-ynenitrile (5a): colorless oil; yield: 87%. IR (CH_2Cl_2): $\nu_{max} = 3293$, 3035, 2936, 2249, 1689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.85$ (d, $J =$ 7.6 Hz, 2H), 7.29 (d, $J = 7.6$ Hz, 2H), 4.37 (dd, $J = 8.8$, 5.6 Hz, 1H), 2.41 (s, 3H), 2.28 (td, $J = 6.4$, 2.8 Hz, 2H), 2.21–2.03 (m, 2H), 1.96 (t, $J = 2.4$ Hz, 1H), 1.85–1.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 190.0$ (C), 145.5 (C), 131.1 (C), 129.6 (CH), 128.7 (CH), 117.2 (CN), 82.6 (C≡C), 69.5 (C≡CH), 39.1 (CH), 28.5 (CH_2), 25.3 (CH_2), 21.5 (CH_3), 17.5 (CH_2); HR-MS (EI): $m/z = 225.1145$, calcd. for $C_{15}H_{15}NO$ $[M]^+$: 225.1154.

2-(2-Methoxybenzoyl)hept-6-ynenitrile (5b): white solid; yield: 85%; mp 40–42 °C. IR (CH_2Cl_2): $\nu_{max} = 3291$, 2944, 2246, 1678 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.74$ (dd, $J = 8.0$, 1.6 Hz, 1H), 7.53 (td, $J = 8.0$, 1.6 Hz, 1H), 7.04 (td, $J = 8.0$, 1.2 Hz, 1H), 6.99 (d, $J = 8.0$ Hz, 1H), 4.55 (dd, $J =$ 8.8, 5.2 Hz, 1H), 3.95 (s, 3H), 2.25 (tt, $J = 6.8$, 2.8 Hz, 2H), 2.17–2.08 (m, 1H), 2.02–1.94 (m, 1H), 1.93 (t, $J = 2.8$ Hz, 1H), 1.84–1.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 192.1 (CO), 158.4 (C), 135.2 (CH), 131.3 (CH), 124.5 (C), 121.1 (CH), 117.6 (CN), 111.6 (CH), 82.9 (C≡C), 69.2 (C≡ CH), 55.7 (CH_3), 44.1 (CH), 28.0 (CH_2), 25.7 (CH_2), 17.8 (CH_2); HR-MS (EI): $m/z = 241.1099$, calcd. for $C_{15}H_{15}NO_2$ $[M]^+$: 241.1103.

2-(4-Methoxybenzoyl)hept-6-ynenitrile (5c): white solid; yield: 77%; mp 67–69 °C. IR (CH_2Cl_2): $\nu_{max} = 3291$, 2938, 2248, 1682 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$ (d, $J = 8.8$ Hz, 2H), 6.95 (d, $J = 8.8$ Hz, 2H), 4.33 (dd, $J = 8.8$, 6.0 Hz, 1H), 3.87 (s, 3H), 2.28 (td, $J = 6.8$, 2.4 Hz, 2H), 2.21–2.07 (m, 2H), 1.96 (t, $J = 2.8$ Hz, 1H), 1.82–1.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 188.7$ (CO), 164.5 (C), 131.1 (CH), 126.6 (C), 117.3 (CN), 114.2 (CH), 82.7 (C≡C), 69.5 (C≡CH), 55.6 (CH_3), 38.9 (CH), 28.6 (CH_2), 25.4 (CH_2), 17.6 (CH_2); HR-MS (EI): $m/z = 241.1105$, calcd. for $C_{15}H_{15}NO_2$ $[M]^+$: 241.1103.

2-(4-Chlorobenzoyl)hept-6-ynenitrile (5d): colorless oil; yield: 90%. IR (CH_2Cl_2): $\nu_{max} = 3297$, 3092, 2938, 2250, 1693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.93$ (dd, $J = 8.4$, 1.2 Hz, 2H), 7.51 (dd, $J = 8.4$, 1.2 Hz, 2H), 4.36 (dd, $J = 8.8$, 5.6 Hz, 1H), 2.30 (td, $J = 6.4$, 2.8 Hz, 2H), 2.22–2.04 (m, 2H), 1.97 (td, $J = 2.8$, 1.2 Hz, 1H), 1.85–1.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 189.4$ (C), 141.1 (C), 132.0 (C), 130.1 (CH), 129.4 (CH), 116.8 (CN), 82.6 (C≡C), 69.7

(C≡CH), 39.3 (CH), 28.3 (CH_2), 25.3 (CH_2), 17.6 (CH_2); HR-MS (EI): m/z = 245.0430, calcd. for $C_{14}H_{12}ClNO$ $[M]^+$: 245.0607.

4-(2-Cyanohept-6-ynoyl)benzonitrile (5e): white solid; yield: 83%; mp 61–63 °C. IR (CH_2Cl_2): ν_{max} = 3290, 3096, 2930, 2232, 1701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 4.35 (dd, J = 8.4, 5.6 Hz, 1H), 2.31 (td, J = 6.8, 2.8 Hz, 2H), 2.22–2.05 (m, 2H), 1.97 (t, J = 2.8 Hz, 1H), 1.86–1.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.7 (CO), 136.5 (C), 132.7 (CH), 129.0 (CH), 117.29 (CN), 117.26 (CN), 116.4 (C), 82.5 (C≡C), 69.71 (C≡CH), 39.7 (CH), 28.0 (CH_2), 25.1 (CH_2), 17.4 (CH_2); HR-MS (EI): m/z = 236.0913, calcd. for $C_{15}H_{12}N_2O$ $[M]^+$: 263.0950.

Methyl 4-(2-cyanohept-6-ynoyl)benzoate (5f): white solid; yield: 79%; mp 62–64 °C. IR (CH_2Cl_2): ν_{max} = 3289, 2953, 2250, 1725, 1702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, J = 8.8 Hz, 2H), 7.99 (d, J = 8.8 Hz, 2H), 4.43 (dd, J = 8.8, 5.6 Hz, 1H), 3.94 (s, 3H), 2.28 (td, J = 6.8, 2.4 Hz, 2H), 2.22–2.02 (m, 2H), 1.96 (t, J = 2.4 Hz, 1H), 1.84–1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.1 (CO), 165.7 (CO_2Me), 136.9 (C), 135.0 (C), 130.1 (CH), 128.7 (CH), 116.6 (CN), 82.6 (C≡C), 69.8 (C≡CH), 52.6 (CH_3), 39.7 (CH), 28.3 (CH_2), 25.3 (CH_2), 17.6 (CH_2); HR-MS (EI): m/z = 269.1034, calcd. for $C_{16}H_{15}NO_3$ $[M]^+$: 269.1052.

2-(4-(Trifluoromethyl)benzoyl)hept-6-ynenitrile (5g): white solid; yield: 82%; mp 38–40 °C. IR (CH_2Cl_2): ν_{max} = 3297, 2939, 2251, 1702, 1326 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 4.39 (dd, J = 8.8, 5.6 Hz, 1H), 2.32 (td, J = 6.4, 2.4 Hz, 2H), 2.25–2.07 (m, 2H), 1.98 (t, J = 2.4 Hz, 1H), 1.87–1.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.8 (CO), 136.5 (C), 135.5 (q, $^2J_{C,F}$ = 32.7 Hz, C), 129.1 (CH), 126.1 (CH), 123.2 (q, $^1J_{C,F}$ = 271.4 Hz, C), 116.6 (CN), 82.6 (C≡C), 69.8 (C≡CH), 39.8 (CH), 28.2 (CH_2), 25.3 (CH_2), 17.6 (CH_2); HR-MS (EI): m/z = 279.0867, calcd. for $C_{15}H_{12}F_3NO$ $[M]^+$: 279.0871.

2-(Thiophene-2-carbonyl)hept-6-ynenitrile (5h): white solid; yield: 91%; mp 46–48 °C. IR (CH_2Cl_2): ν_{max} = 3293, 2937, 2249, 1668, 1412 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.84 (dd, J = 4.0, 1.2 Hz, 1H), 7.75 (dd, J = 5.2, 1.2 Hz, 1H), 7.16 (dd, J = 5.2, 4.0 Hz, 1H), 4.26 (dd, J = 8.4, 6.0 Hz, 1H), 2.25 (td, J = 6.8, 2.8 Hz, 2H), 2.21–2.04 (m, 2H), 1.96 (t, J = 2.8 Hz, 1H), 1.82–1.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.1 (CO), 140.5 (C), 136.2 (CH), 133.7 (CH), 128.6 (CH), 116.9 (CN), 82.6 (C≡C), 69.6 (C≡CH), 40.1 (CH), 29.0 (CH_2), 25.3 (CH_2), 17.5 (CH_2); HR-MS (EI): m/z = 217.0555, calcd. for $C_{12}H_{11}NOS$ $[M]^+$: 217.0561.

2-(Furan-2-carbonyl)hept-6-ynenitrile (5i): white solid; yield: 94%; mp 40–42 °C. IR (CH_2Cl_2): ν_{max} = 3292, 2938, 2249, 1679, 1463 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.65 (dd, J = 2.0, 1.2 Hz, 1H), 7.39 (dd, J = 4.0, 1.2 Hz, 1H), 6.61 (dd, J = 4.0, 2.0 Hz, 1H), 4.21 (dd, J = 8.4, 6.0 Hz, 1H), 2.27 (td, J = 6.8, 2.8 Hz, 2H), 2.20–2.04 (m, 2H), 1.95 (t, J = 2.8 Hz, 1H), 1.84–1.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.0 (CO), 149.9 (C), 147.8 (CH), 119.9 (CH), 116.6 (CN), 113.2 (CH), 82.6 (C≡C), 69.5 (C≡CH), 39.5 (CH), 28.3 (CH_2), 25.3 (CH_2), 17.6 (CH_2); HR-MS (EI): m/z = 201.0784, calcd. for $C_{12}H_{11}NO_2$ $[M]^+$: 201.0790.

2-(2-Naphthoyl)hept-6-ynenitrile (5j): yellow solid; yield: 95%; mp 54–56 °C. IR (CH_2Cl_2): ν_{max} = 3294, 3058, 2936, 2247, 1686 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.46 (s, 1H), 7.98–7.94 (m, 2H), 7.89 (d, J = 8.8 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.62 (td, J = 8.0, 1.2 Hz, 1H), 7.56 (td, J = 8.0, 1.2 Hz, 1H), 4.57 (dd, J = 8.8, 5.6 Hz, 1H), 2.30 (td, J = 6.8, 2.8 Hz, 2H), 2.27–2.08 (m, 2H), 1.98 (t, J = 2.8 Hz, 1H), 1.89–1.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.4 (CO), 135.9 (C), 132.2 (C), 131.0 (C), 130.8 (CH), 129.7 (CH), 129.3 (CH), 129.0 (CH), 127.8 (CH), 127.2 (CH), 123.7 (CH), 117.2 (CN), 82.7 (C≡C), 69.7 (C≡CH), 39.3 (CH), 28.7 (CH_2), 25.4 (CH_2), 17.6 (CH_2); HR-MS (EI): m/z = 261.1148, calcd. for $C_{18}H_{15}NO$ $[M]^+$: 261.1154.

1-Benzoyl-2-methylenecyclopentanecarbonitrile (8): colorless oil; yield: 45%. IR (CH_2Cl_2): ν_{max} = 2962, 2236, 1689, 1231 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 7.6 Hz, 2H), 7.59 (t, J = 7.2 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 5.37 (s, 2H), 2.67–2.43 (m, 4H), 2.02–1.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.2 (CO), 148.6 (C), 133.7 (C), 133.6 (CH), 129.6 (CH), 128.5 (CH), 120.8 (CN), 113.5 (CH_2), 55.8 (C), 38.6 (CH_2), 32.1 (CH_2), 23.6 (CH_2); HR-MS (EI): m/z = 211.1001, calcd. for $C_{14}H_{13}NO$ $[M]^+$: 211.0997.

Synthesis of Products

The general procedure for the synthesis of products **4**, **9aa–au** and **9ba–bl** is demonstrated as follows using **4** as a typical example.

Methyl 4-(9α-Cyano-9-oxo-2,3,9,9α-tetrahydro-1*H*-cyclopenta[*b*]naphthalen-4-yl)benzoate (4)

A mixture of 2-benzoylhept-6-ynenitrile **5** (100 mg, 0.47 mmol), methyl 4-iodobenzoate (135 mg, 0.52 mmol), CuI (27 mg, 0.14 mmol), $Pd(PPh_3)_4$ (54 mg, 0.047 mmol) and pyrrolidine (78 μL, 0.94 mmol) in dichloromethane (3 mL) was stirred under air at room temperature for 3.5 h. The mixture was filtered through a pad of Celite and slica gel and washed with CH_2Cl_2 (50 mL). The organic layer was concentrated under reduced pressure to give the residue, which was subjected to purification by flash chromatography on silica gel (20% EtOAc in *n*-hexane) to afford compound **4** as a white solid; yield: 143 mg (90%); mp 181–183 °C. IR (CH_2Cl_2): ν_{max} = 2952, 2228, 1723, 1608, 1596, 1284 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, J = 6.4 Hz, 2H), 7.95 (dd, J = 7.6, 1.2 Hz, 1H), 7.48 (td, J = 7.6, 1.2 Hz, 1H), 7.37 (td, J = 7.6, 1.2 Hz, 1H), 7.35 (br, 2H), 6.83 (d, J = 7.6 Hz, 1H), 3.94 (s, 3H), 2.83–2.75 (m, 1H), 2.71–2.64 (m, 1H), 2.25–2.05 (m, 3H), 2.03–1.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.1 (CO), 166.5 (CO_2Me), 141.4 (C), 140.7 (C), 139.4 (C), 135.2 (CH), 132.5 (C), 130.0 (br, CH), 129.9 (C), 128.5 (C), 128.4 (CH), 127.8 (CH), 126.8 (CH), 117.2 (CN), 52.2 (CH_3), 51.4 (C), 33.2 (CH_2), 29.5 (CH_2), 22.4 (CH_2); HR-MS (EI): m/z = 343.1211, calcd. for $C_{22}H_{17}NO_3$ $[M]^+$: 343.1208.

4-Oxo-9-phenyl-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]-naphthalene-3α-carbonitrile (9aa): white solid; yield: 90%; mp 160–162 °C. IR (CH_2Cl_2): ν_{max} = 2951, 2227, 1702, 1592, 1282 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (dd, J = 7.6, 1.2 Hz, 1H), 7.48 (td, J = 7.6, 1.2 Hz, 1H), 7.44–7.39 (m, 3H), 7.34 (t, J = 7.6 Hz, 1H), 7.33–7.10 (m, 2H), 6.91 (d, J = 7.6 Hz, 1H), 2.84–2.75 (m, 1H), 2.68–2.62 (m, 1H), 2.28–2.20 (m, 1H), 2.18–2.04 (m, 2H), 2.03–1.90 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5 (CO), 140.1 (C), 139.9 (C), 136.6 (C), 135.1 (CH), 133.2 (C), 128.7 (br, CH),

128.6 (C), 128.1 (CH), 127.7 (CH), 127.1 (CH), 117.5 (CN), 51.3 (C), 33.3 (CH_2), 29.5 (CH_2), 22.4 (CH_2); HR-MS (EI): m/z = 285.1158, calcd. for $C_{20}H_{15}NO$ $[M]^+$: 285.1154.

4-Oxo-9-*p*-tolyl-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]-naphthalene-3α-carbonitrile (9ab): white solid; yield: 92%; mp 147–149 °C. IR (CH_2Cl_2): ν_{max} = 2974, 2227, 1704, 1592, 1285 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): δ = 7.93 (dd, J = 7.6, 1.2 Hz, 1H), 7.58 (td, J = 7.6, 1.2 Hz, 1H), 7.42 (td, J = 7.6, 1.2 Hz, 1H), 7.30 (d, J = 7.6 Hz, 2H), 7.14 (brm, 2H), 6.95 (d, J = 7.6 Hz, 1H), 2.80 (ddd, J = 18.4, 8.8 and 4.0 Hz, 1H), 2.61–2.55 (m, 1H), 2.40 (s, 3H), 2.34–2.11 (m, 2H), 2.09–1.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5 (CO), 140.2 (C), 139.5 (C), 137.8 (C), 135.0 (CH), 133.4 (C), 133.0 (C), 129.3 (br, CH), 128.5 (C), 127.9 (CH), 127.4 (CH), 127.0 (CH), 117.5 (CN), 51.2 (C), 33.2 (CH_2), 29.5 (CH_2), 22.3 (CH_2), 21.1 (CH_3); HR-MS (EI): m/z = 299.1314, calcd. for $C_{21}H_{17}NO$ $[M]^+$: 299.1310.

4-Oxo-9-*o*-tolyl-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]-naphthalene-3α-carbonitrile (9ac): white solid; yield: 85%; mp 144–146 °C. IR (CH_2Cl_2): ν_{max} = 2949, 2227, 1705, 1593, 1282 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, J = 7.6 Hz, 2H), 7.46 (tt, J = 7.6, 1.2 Hz, 2H), 7.36–7.28 (m, 7H), 7.26–7.19 (m, 2H), 6.88 (d, J = 7.6 Hz, 1H), 6.71 (d, J = 7.6 Hz, 1H), 6.68 (d, J = 7.6 Hz, 1H), 2.72–2.61 (m, 3H), 2.50–2.42 (m, 1H), 2.30 (s, 3H), 2.27–1.96 (m, 8H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.49 (CO), 193.46 (CO), 140.4 (C), 140.1 (C), 139.9 (C), 139.5 (C), 137.3 (C), 135.7 (C), 135.6 (C), 135.4 (CH), 135.3 (CH), 135.2 (C), 132.8 (C), 132.4 (C), 130.44 (CH), 130.41 (CH), 130.1 (CH), 128.4 (C), 128.3 (CH), 128.2 (CH), 128.1 (C), 128.05 (CH), 128.03 (CH), 128.0 (CH), 127.8 (CH), 127.6 (CH), 126.5 (CH), 126.4 (CH), 126.3 (CH), 126.1 (CH), 117.4 (CN), 117.3 (CN), 51.4 (C), 51.1 (C), 33.5 (CH_2), 33.2 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 22.2 (CH_2), 22.1 (CH_2), 19.3 (CH_3), 18.9 (CH_3); HR-MS (EI): m/z = 299.1309, calcd. for $C_{21}H_{17}NO$ $[M]^+$: 299.1310.

9-(4-Methoxyphenyl)-4-oxo-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9ad): white solid; yield: 82%; mp 97–99 °C. IR (CH_2Cl_2): ν_{max} = 2969, 2227, 1706, 1608, 1513, 1248 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.93 (dd, J = 7.6, 1.2 Hz, 1H), 7.48 (td, J = 7.6, 2.4 Hz, 1H), 7.34 (td, J = 7.6, 1.2 Hz, 1H), 7.17 (brm, 2H), 6.97 (d, J = 7.6 Hz, 1H), 6.96 (d, J = 7.2 Hz, 2H), 3.84 (s, 3H), 2.86–2.78 (m, 1H), 2.67–2.63 (m, 1H), 2.31–2.28 (m, 1H), 2.17–2.05 (m, 2H), 1.99–1.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.4 (CO), 159.1 (C), 140.2 (C), 139.4 (C), 135.0 (CH), 132.6 (C), 130.4 (br, CH), 128.5 (C), 128.4 (C), 127.8 (CH), 127.4 (CH), 126.9 (CH), 117.4 (CN), 113.9 (CH), 55.0 (OCH_3), 51.1 (C), 33.1 (CH_2), 29.5 (CH_2), 22.2 (CH_2); HR-MS (EI): m/z = 315.1255, calcd. for $C_{21}H_{17}NO_2$ $[M]^+$: 315.1259.

9-(3-Methoxyphenyl)-4-oxo-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9ae): white solid; yield: 78%; mp 117–119 °C. IR (CH_2Cl_2): ν_{max} = 2961, 2227, 1700, 1594, 1284 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.96 (dd, J = 7.6, 1.2 Hz, 1H), 7.51 (td, J = 7.6, 1.2 Hz, 1H), 7.37 (t, J = 7.6, 1.2 Hz, 2H), 6.95 (d, J = 7.6 Hz, 3H), 6.62 (brm, 1H), 3.83 (s, 3H), 2.83–2.75 (m, 1H), 2.69–2.63 (m, 1H), 2.31–2.22 (m, 1H), 2.17–2.05 (m, 2H), 1.99–1.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5 (CO), 159.8 (C), 140.0 (C), 139.9 (C), 138.0 (C), 135.2 (CH), 133.1 (C), 129.8 (br, CH), 128.5 (C), 128.1 (CH), 127.6 (CH), 127.1 (CH), 117.5 (CN), 113.6 (CH), 55.2 (OCH_3), 51.3 (C), 33.3 (CH_2), 29.5 (CH_2), 22.4 (CH_2); HR-MS (EI): m/z = 315.1266, calcd. for $C_{21}H_{17}NO_2$ $[M]^+$: 315.1259.

9-(4-Acetylphenyl)-4-oxo-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9af): white solid; yield: 87%; mp 169–171 °C. IR (CH_2Cl_2): ν_{max} = 2974, 2227, 1685, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 7.2 Hz, 2H), 7.96 (dd, J = 7.6, 1.2 Hz, 1H), 7.50 (td, J = 7.6, 1.2 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.26 (brm, 2H), 6.84 (d, J = 7.6 Hz, 1H), 2.83–2.76 (m, 1H), 2.72–2.62 (m, 1H), 2.64 (s, 3H), 2.26–2.07 (m, 3H), 2.01–1.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.5 (CO), 193.1 (CO), 141.7 (C), 140.7 (C), 139.4 (C), 136.8 (C), 135.3 (CH), 132.5 (C), 130.3 (br, CH), 128.8 (br, CH), 128.6 (C), 128.5 (CH), 127.9 (CH), 126.9 (CH), 117.3 (CN), 51.4 (C), 33.3 (CH_2), 29.6 (CH_2), 26.7 (CH_3), 22.5 (CH_2); HR-MS (EI): m/z = 327.1261, calcd. for $C_{22}H_{17}NO_2$ $[M]^+$: 327.1259.

9-(4-Cyanophenyl)-4-oxo-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9ag): white solid; yield: 84%; mp 170–172 °C. IR (CH_2Cl_2): ν_{max} = 2973, 2228, 1705, 1283 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.97 (dd, J = 7.6, 1.6 Hz, 1H), 7.75 (d, J = 7. 2 Hz, 2H), 7.51 (td, J = 7.6, 1.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.39 (br, 2H), 6.78 (d, J = 7.6 Hz, 1H), 2.82–2.75 (m, 1H), 2.71–2.65 (m, 1H), 2.24–2.05 (m, 3H), 2.03–1.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.8 (CO), 141.6 (C), 141.4 (C), 138.9 (C), 135.3 (CH), 132.6 (CH), 131.9 (C), 130.1 (br, CH), 128.7 (CH), 128.5 (C), 128.0 (CH), 126.6 (CH), 118.3 (CN), 117.0 (CN), 112.2 (C), 51.4 (C), 33.2 (CH_2), 29.6 (CH_2), 22.4 (CH_2); HR-MS (EI): m/z = 310.1100, calcd. for $C_{21}H_{14}N_2O$ $[M]^+$: 310.1106.

9-(4-Formylphenyl)-4-oxo-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9ah): white solid; yield: 65%; mp 206–208 °C. IR (CH_2Cl_2): ν_{max} = 2973, 2836, 2227, 1702, 1605, 1283 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 10.06 (s, 1H), 7.96 (dd, J = 7.6, 1.6 Hz, 3H), 7.50 (td, J = 7.6, 1.6 Hz, 1H), 7.37 (td, J = 7.6, 1.2 Hz, 1H), 7.28 (brm, 2H), 6.82 (d, J = 7.6 Hz, 1H), 2.84–2.77 (m, 1H), 2.72–2.67 (m, 1H), 2.26–2.06 (m, 3H), 2.03–1.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.0 (CO), 191.5 (CHO), 143.1 (C), 141.0 (C), 139.2 (C), 136.0 (C), 135.3 (CH), 132.3 (C), 130.1 (br, CH), 128.5 (CH), 127.9 (CH), 126.8 (CH), 117.2 (CN), 51.4 (C), 33.2 (CH_2), 29.6 (CH_2), 22.4 (CH_2); HR-MS (EI): m/z = 313.1096, calcd. for $C_{21}H_{15}NO_2$ $[M]^+$: 313.1103.

4-(9α-Cyano-9-oxo-2,3,9,9α-tetrahydro-1*H*-cyclopenta[*b*]-naphthalen-4-yl)benzoic acid (9ai): white solid; yield: 51%; mp 202–203 °C. IR (CH_2Cl_2): ν_{max} = 3441, 2228, 1691, 1609, 1285 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, J = 5.2 Hz, 2H), 7.97 (dd, J = 7.6, 1.2 Hz, 1H), 7.51 (td, J = 7.6, 1.2 Hz, 1H), 7.39 (td, J = 7.6, 1.2 Hz, 1H), 7.26 (brm, 2H), 6.85 (d, J = 7.6 Hz, 1H), 2.85–2.73 (m, 1H), 2.71–2.65 (m, 1H), 2.28–2.08 (m, 3H), 2.04–1.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.1 (CO), 171.7 (CO_2H), 142.5 (C), 140.8 (C), 139.3 (C), 135.3 (CH), 132.4 (C), 130.7 (br, CH), 129.1 (C), 128.54 (C), 128.49 (CH), 127.9 (CH), 126.9 (CH), 117.2 (CN), 51.4 (C), 33.3 (CH_2), 29.6 (CH_2), 22.4 (CH_2); HR-MS (EI): m/z = 329.1061, calcd. for $C_{21}H_{15}NO_3$ $[M]^+$: 329.1052.

4-Oxo-9-[4-(trifluoromethyl)phenyl]-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9aj): brown solid; yield: 79%; mp 150–152 °C. IR (CH_2Cl_2): ν_{max} = 2974, 2228, 1703, 1596, 1324, 1284 cm^{-1}; ^1H NMR (400 MHz,

$CDCl_3$): $\delta = 7.97$ (dd, $J = 7.6$, 1.6 Hz, 1H), 7.72 (d, $J = 5.6$ Hz, 2H), 7.51 (td, $J = 7.6$, 1.2 Hz, 1H), 7.48 (br, 2H), 7.39 (td, $J = 7.6$, 1.2 Hz, 1H), 6.83 (d, $J = 7.6$ Hz, 1H), 2.83–2.75 (m, 1H), 2.72–2.64 (m, 1H), 2.26–2.07 (m, 3H), 2.04–1.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 193.0$ (CO), 141.0 (C), 140.5 (C), 139.4 (C), 135.3 (CH), 132.2 (C), 130.4 (q, $^2J_{C-F} = 32.0$ Hz, C), 128.6 (C), 128.5 (CH), 128.0 (CH), 126.8 (CH), 125.8 (br, CH), 123.9 (q, $^1J_{C-F} = 270.7$ Hz, C), 117.2 (CN), 51.4 (C), 33.3 (CH_2), 29.6 (CH_2), 22.4 (CH_2); HR-MS (EI): $m/z = 353.1022$, calcd. for $C_{21}H_{14}F_3NO$ $[M]^+$: 353.1027.

9-(4-Nitrophenyl)-4-oxo-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9ak): yellow solid; yield: 62%; mp 171–173 °C. IR (CH_2Cl_2): $\nu_{max} = 2953$, 2228, 1703, 1597, 1519, 1347, 1284 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.31$ (d, $J = 7.2$ Hz, 2H), 7.98 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.52 (td, $J = 7.6$, 1.6 Hz, 1H), 7.47 (brm, 2H), 7.41 (t, $J = 7.6$ Hz, 1H), 6.78 (d, $J = 7.6$ Hz, 1H), 2.83–2.76 (m, 1H), 2.72–2.65 (m, 1H), 2.24–2.08 (m, 3H), 2.04–1.96 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 192.7$ (CO), 147.6 (C), 143.6 (C), 141.6 (C), 138.8 (C), 135.4 (CH), 131.6 (C), 130.4 (br, CH), 128.7 (CH), 128.5 (C), 128.0 (CH), 126.6 (CH), 124.0 (CH), 117.0 (CN), 51.4 (C), 33.2 (CH_2), 29.6 (CH_2), 22.4 (CH_2); HR-MS (EI): $m/z = 330.1008$, calcd. for $C_{20}H_{14}N_2O_3[M]^+$: 330.1004.

9-(3-Nitrophenyl)-4-oxo-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9al): white solid; yield: 68%; mp 155–157 °C. IR (CH_2Cl_2): $\nu_{max} = 2953$, 2227, 1702, 1529, 1349, 1282 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.27$ (dd, $J = 8.8$, 2.0 Hz, 1H), 7.98 (d, $J = 7.6$, 1.2 Hz, 1H), 7.65 (brm, 3H), 7.52 (td, $J = 7.6$, 1.2 Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 1H), 6.79 (d, $J = 7.6$ Hz, 1H), 2.83–2.80 (m, 1H), 2.74–2.66 (m, 1H), 2.26–2.09 (m, 3H), 2.05–1.96 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 192.6$ (CO), 148.5 (C), 141.8 (C), 138.9 (C), 138.3 (C), 135.4 (CH), 131.3 (C), 130.0 (br, CH), 128.7 (CH), 128.5 (C), 128.0 (CH), 126.5 (CH), 123.2 (CH), 117.0 (CN), 51.4 (C), 33.2 (CH_2), 29.6 (CH_2), 22.4 (CH_2); HR-MS (EI): $m/z = 330.1009$, calcd. for $C_{20}H_{14}N_2O_3$ $[M]^+$: 330.1004.

9-(4-Chlorophenyl)-4-oxo-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9am): brown solid; yield: 90%; mp 158–159 °C: IR (CH_2Cl_2): $\nu_{max} = 2974$, 2227, 1706, 1594, 1285 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.95$ (dd, $J = 7.6$, 1.6 Hz, 1H), 7.50 (td, $J = 7.6$, 1.6 Hz, 1H), 7.42 (d, $J = 6.4$ Hz, 2H), 7.37 (td, $J = 7.6$, 1.2 Hz, 1H), 7.09 (brm, 2H), 6.88 (d, $J = 7.6$ Hz, 1H), 2.83–2.75 (m, 1H), 2.71–2.63 (m, 1H), 2.27–2.05 (m, 3H), 2.02–1.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 193.2$ (CO), 140.5 (C), 139.7 (C), 135.3 (CH), 135.0 (C), 134.2 (C), 132.2 (C), 130.9 (br, CH), 129.1 (br, CH), 128.6 (C), 128.4 (CH), 127.8 (CH), 126.9 (CH), 117.3 (CN), 51.4 (C), 33.3 (CH_2), 29.6 (CH_2), 22.4 (CH_2); HR-MS (EI): $m/z = 319.0761$, calcd. for $C_{20}H_{14}ClNO$ $[M]^+$: 319.0764.

9-(4-Fluorophenyl)-4-oxo-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9an): brown solid; yield: 87%; mp 110–112 °C. IR (CH_2Cl_2): $\nu_{max} = 2969$, 2228, 1705, 1601, 1284, 1223 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$ (dd, $J = 7.6$, 1.6 Hz, 1H), 7.50 (td, $J = 7.6$, 1.6 Hz, 1H), 7.36 (t, $J = 7.6$, Hz, 1H), 7.20 (brm, 2H), 7.13 (brm, 2H), 6.87 (d, $J = 7.6$ Hz, 1H), 2.82–2.63 (m, 1H), 2.72–2.63 (m, 1H), 2.27–2.06 (m, 3H), 2.03–1.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 193.3$ (CO), 162.4 (d, $^1J_{C-F} = 246.3$ Hz, C), 140.4 (C), 139.9 (C), 135.2 (CH), 132.4 (C), 132.2 (C), 131.4 (br, CH), 128.6 (C), 128.2 (CH), 127.7 (CH), 126.8 (CH), 117.3 (CN), 115.8 (d, $^2J_{C,F} = 21.4$ Hz, CH), 51.3 (C), 33.3 (CH_2), 29.5 (CH_2), 22.4 (CH_2); HR-MS (EI): $m/z = 303.1065$, calcd. for $C_{20}H_{14}FNO$ $[M]^+$: 303.1059.

9-[3-(Hydroxymethyl)phenyl]-4-oxo-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9ao): yellow oil; yield: 86%; IR (CH_2Cl_2): $\nu_{max} = 3391$, 2925, 2228, 1699, 1592, 1285 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$ (dd, $J = 7.6$, 1.2 Hz, 1H), 7.48 (td, $J = 7.6$, 1.2 Hz, 1H), 7.39 (brm, 3H), 7.35 (td, $J = 7.6$, 1.2 Hz, 1H), 7.04 (brm, 1H), 6.88 (d, $J = 7.6$ Hz, 1H), 4.70 (brs, 2H), 2.81–2.74 (m, 1H), 2.67–2.60 (m, 1H), 2.30 (brs, OH), 2.27–2.18 (m, 1H), 2.14–2.01 (m, 2H), 1.99–1.89 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 193.5$ (CO), 141.5 (C), 140.01 (C), 139.97 (C), 136.8 (C), 135.2 (CH), 133.1 (C), 128.9 (CH), 128.5 (C), 128.1 (CH), 127.6 (CH), 127.1 (CH), 126.6 (CH), 117.5 (CN), 64.7 (CH_2), 51.3 (C), 33.3 (CH_2), 29.5 (CH_2), 22.3 (CH_2); HR-MS (EI): $m/z = 315.1266$, calcd. for $C_{21}H_{17}NO_2$ $[M]^+$: 315.1259.

9-(4-Hydroxyphenyl)-4-oxo-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9ap): yellow oil; yield: 79%. IR (CH_2Cl_2): $\nu_{max} = 3401$, 2953, 2229, 1695, 1590, 1285 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$ (d, $J = 7.6$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.34 (t, $J = 7.6$ Hz, 1H), 7.08 (brm, 2H), 6.97 (d, $J = 7.6$ Hz, 1H), 6.91 (d, $J = 8.0$ Hz, 2H), 6.28 (brm, OH), 2.80 (ddd, $J = 18.8$, 9.6 and 4.0 Hz, 1H), 2.69–2.64 (m, 1H), 2.30–2.22 (m, 1H), 2.17–2.03 (m, 2H), 2.00–1.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 194.0$ (CO), 155.8 (C), 140.4 (C), 139.4 (C), 135.3 (CH), 132.9 (C), 130.6 (br, CH), 128.5 (C), 128.3 (C), 128.1 (CH), 127.6 (CH), 127.2 (CH), 117.6 (CN), 115.6 (CH), 51.2 (C), 33.3 (CH_2), 29.6 (CH_2), 22.4 (CH_2); HR-MS (EI): $m/z = 301.1109$, calcd. for $C_{20}H_{15}NO_2$ $[M]^+$: 301.1103.

9-(4-Aminophenyl)-4-oxo-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9aq): yellow solid; yield: 85%; mp 163–165 °C. IR (CH_2Cl_2): $\nu_{max} = 3466$, 3378, 2953, 2227, 1694, 1517, 1284 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.91$ (dd, $J = 7.6$, 1.2 Hz, 1H), 7.48 (td, $J = 7.6$, 1.2 Hz, 1H), 7.32 (t, $J = 7.6$ Hz, 1H), 7.01 (d, $J = 8.0$ Hz, 3H), 6.72 (d, $J = 7.6$ Hz, 2H), 3.77 (s, 2H), 2.81 (ddd, $J = 18.8$, 8.8 and 4.0 Hz, 1H), 2.67–2.60 (m, 1H), 2.32–2.23 (m, 1H), 2.16–1.90 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 193.9$ (CO), 146.3 (C), 140.6 (C), 139.0 (C), 135.1 (CH), 133.1 (C), 130.5 (br, CH), 128.8 (C), 127.9 (CH), 127.5 (CH), 127.2 (CH), 126.2 (C), 117.7 (CN), 114.9 (CH), 51.2 (C), 33.3 (CH_2), 29.7 (CH_2), 22.4 (CH_2); HR-MS (EI): $m/z = 300.1264$, calcd. for $C_{20}H_{16}N_2O$ $[M]^+$: 300.1263.

9-(1*H*-indol-5-yl)-4-oxo-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9ar): yellow solid; yield: 81%; mp 206–208 °C. IR (CH_2Cl_2): $\nu_{max} = 3408$, 2952, 2227, 1696, 1591, 1286 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.27$ (brm, 1H), 7.94 (d, $J = 7.6$ Hz, 1H), 7.69 (brm, 1H), 7.46 (brm, 1H), 7.45 (t, $J = 7.6$ Hz, 1H), 7.33 (t, $J = 7.6$ Hz, 1H), 7.27 (brm, 1H), 6.97 (d, $J = 7.6$ Hz, 1H), 6.83 (brm, 1H), 6.56 (brm, 1H), 2.83 (brm, 1H), 2.71–2.63 (m, 1H), 2.31–2.22 (m, 1H), 2.18–2.02 (m, 2H), 1.99–1.89 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 194.1$ (CO), 141.1 (C), 139.4 (C), 135.3 (C), 135.2 (CH), 134.1 (C), 128.7 (C), 128.0 (C), 127.9 (CH), 127.6 (CH), 127.5 (CH), 125.1 (CH), 124.2 (br, CH), 122.4 (br, CH), 120.5 (br, C), 117.9 (CN), 111.4 (CH), 102.8 (CH), 51.3 (C), 33.4 (CH_2), 29.7 (CH_2), 22.4 (CH_2); HR-MS (EI): $m/z = 324.1260$, calcd. for $C_{22}H_{16}N_2O$ $[M]^+$: 324.1263.

4-Oxo-9-(thiophen-3-yl)-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9as): white solid; yield: 88%; mp 157–159 °C. IR (CH_2Cl_2): ν_{max} = 2952, 2227, 1700, 1593, 1285 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.93 (dd, J = 7.6, 1.6 Hz, 1H), 7.52 (td, J = 7.6, 1.6 Hz, 1H), 7.40 (dd, J = 4.8, 3.2 Hz, 1H), 7.36 (td, J = 7.6, 1.2 Hz, 1H), 7.26 (dd, J = 3.2, 1.2 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 6.95 (dd, J = 4.8, 1.2 Hz, 1H), 2.92–2.84 (m, 1H), 2.71–2.64 (m, 1H), 2.42–2.33 (m, 1H), 2.17–1.95 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.3 (CO), 140.3 (C), 139.9 (C), 136.5 (C), 135.2 (CH), 128.6 (C), 128.4 (C), 128.2 (CH), 127.7 (CH), 126.9 (CH), 125.9 (CH), 125.2 (CH), 117.4 (CN), 114.9 (CH), 51.3 (C), 33.3 (CH_2), 29.8 (CH_2), 22.4 (CH_2); HR-MS (EI): m/z = 291.0712, calcd. for $C_{18}H_{13}NOS$ $[M]^+$: 291.0718.

4-Oxo-9-(pyridin-3-yl)-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9at): white solid; yield: 91%; mp 143–145 °C. IR (CH_2Cl_2): ν_{max} = 2975, 2227, 1703, 1592, 1283 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.68 (br, 1H), 8.53 (brm, 1H), 7.98 (dd, J = 7.6, 1.6 Hz, 1H), 7.67 (brm, 1H), 7.53 (td, J = 7.6, 1.6 Hz, 1H), 7.45 (brm, 1H), 7.41 (t, J = 7.6 Hz, 1H), 6.84 (d, J = 7.6 Hz, 1H), 2.84–2.79 (m, 1H), 2.72–2.66 (m, 1H), 2.28–2.09 (m, 3H), 2.06–1.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.8 (CO), 150.1 (br, CH), 149.4 (CH), 141.8 (C), 139.2 (C), 137.1 (br, CH), 135.3 (CH), 132.5 (C), 129.9 (C), 128.52 (CH), 128.47 (C), 127.9 (CH), 126.5 (CH), 123.5 (CH), 117.1 (CN), 51.3 (C), 33.2 (CH_2), 29.6 (CH_2), 22.4 (CH_2); HR-MS (EI): m/z = 286.1099, calcd. for $C_{19}H_{14}N_2O$ $[M]^+$: 286.1106.

9-(Naphthalen-2-yl)-4-oxo-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9au): brown solid; yield: 78%; mp 167–169 °C. IR (CH_2Cl_2): ν_{max} = 2963, 2227, 1699, 1596, 1284 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.99 (dd, J = 7.6, 1.6 Hz, 1H), 7.91–7.89 (m, 3H), 7.55–7.46 (m, 3H), 7.47 (td, J = 7.6, 1.6 Hz, 1H), 7.36 (td, J = 7.6, 0.8 Hz, 1H), 7.14 (brm, 1H), 6.93 (d, J = 7.6 Hz, 1H), 2.86 (brm, 1H), 2.74–2.66 (m, 1H), 2.31–2.07 (m, 3H), 2.02–1.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5 (CO), 140.4 (C), 140.1 (br, CH), 135.2 (CH), 134.0 (C), 133.3 (C), 133.1 (C), 132.8 (C), 129.6 (br, CH), 128.6 (C), 128.4 (CH), 128.2 (CH), 127.9 (CH), 127.7 (CH), 127.6 (CH), 127.2 (CH), 126.5 (CH), 126.4 (CH), 126.1 (C), 117.5 (CN), 51.4 (C), 33.3 (CH_2), 29.6 (CH_2), 22.4 (CH_2); HR-MS (EI): m/z = 335.1306, calcd. for $C_{24}H_{17}NO$ $[M]^+$: 335.1310.

9-(4-Cyanophenyl)-7-methoxy-4-oxo-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9ba): white solid; yield: 94%; mp 182–184 °C. IR (CH_2Cl_2): ν_{max} = 2945, 2228, 1690, 1592, 1262 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, J = 8.4 Hz, 1H), 7.74 (br, 2H), 7.52 (br, 1H), 7.24 (br, 1H), 6.87 (dd, J = 8.4, 2.4 Hz, 1H), 6.22 (d, J = 2.4 Hz, 1H), 3.75 (s, 3H), 2.80–2.64 (m, 2H), 2.22–1.93 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.8 (CO), 165.4 (C), 142.6 (C), 141.6 (C), 141.3 (C), 132.6 (CH), 131.6 (C), 131.1 (br, CH), 130.8 (CH), 129.5 (br, CH), 121.7 (C), 118.3 (CN), 117.4 (CN), 113.0 (CH), 112.2 (C), 55.6 (OCH_3), 51.3 (C), 33.4 (CH_2), 29.6 (CH_2), 22.3 (CH_2); HR-MS (EI): m/z = 340.1210, calcd. for $C_{22}H_{16}N_2O_2$ $[M]^+$: 340.1212.

9-(4-Methoxyphenyl)-4-oxo-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α,7-dicarbonitrile (9bb): yellow solid; yield: 57%; mp 157–159 °C. IR (CH_2Cl_2): ν_{max} = 2956, 2837, 2231, 1710, 1608, 1248 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, J = 7.6 Hz, 1H), 7.61 (dd, J = 7.6, 1.2 Hz, 1H), 7.24 (brm, 1H), 7.23 (d, J = 1.2 Hz, 1H), 6.99 (d, J = 7.6 Hz, 3H), 3.86 (s, 3H), 2.87–2.79 (m, 1H), 2.69–2.63 (m, 1H), 2.33–2.24 (m, 1H), 2.20–1.94 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.4 (CO), 159.8 (C), 142.2 (C), 141.1 (C), 131.6 (C), 131.3 (C), 131.1 (CH), 130.5 (CH), 130.2 (br, CH), 128.1 (CH), 127.1 (C), 118.3 (CN), 117.5 (CN), 116.6 (C), 114.6 (CH), 55.3 (OCH_3), 51.5 (C), 33.1 (CH_2), 29.9 (CH_2), 22.4 (CH_2); HR-MS (EI): m/z = 340.1220, calcd. for $C_{22}H_{16}N_2O_2$ $[M]^+$: 340.1212.

7-Methyl-4-oxo-9-phenyl-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9bc): white solid; yield: 95%; mp 92–94 °C. IR (CH_2Cl_2): ν_{max} = 2963, 2227, 1698, 1600, 1281 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 7.6 Hz, 1H), 7.40–7.38 (m, 4H), 7.16 (brm, 1H), 7.15 (d, J = 7.6 Hz, 1H), 6.67 (s, 1H), 2.80–2.73 (m, 1H), 2.66–2.63 (m, 1H), 2.27 (s, 3H), 2.25–2.03 (m, 3H), 1.97–1.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.0 (CO), 146.4 (C), 140.1 (C), 140.6 (C), 136.7 (C), 133.1 (C), 129.9 (br, CH), 128.8 (CH), 128.6 (CH), 128.0 (CH), 127.7 (CH), 127.6 (CH), 126.2 (C), 117.6 (CN), 51.2 (C), 33.3 (CH_2), 29.5 (CH_2), 22.3 (CH_2), 21.9 (CH_3); HR-MS (EI): m/z = 299.1305, calcd. for $C_{21}H_{17}NO$ $[M]^+$: 299.1310.

8-Oxo-4-phenyl-6,7,7α,8-tetrahydro-5*H*-indeno[5,6-*b*]thiophene-7α-carbonitrile (9bd): brown solid; yield: 95%; mp 141–143 °C. IR (CH_2Cl_2): ν_{max} = 2951, 2228, 1669, 1411 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, J = 5.2 Hz, 1H), 7.47–7.39 (m, 3H), 7.30–7.27 (m, 2H), 6.79 (d, J = 5.2 Hz, 1H), 2.86 (ddd, J = 18.8, 10.4 and 3.2 Hz, 1H), 2.72 (dd, J = 11.6, 6.4 Hz, 1H), 2.34–2.13 (m, 2H), 2.06–1.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 185.6 (CO), 150.9 (C), 144.0 (C), 137.3 (CH), 136.1 (C), 131.9 (C), 129.8 (C), 128.7 (br, CH), 128.6 (CH), 128.4 (CH), 127.3 (CH), 117.4 (CN), 53.5 (C), 33.5 (CH_2), 28.5 (CH_2), 22.3 (CH_2); HR-MS (EI): m/z = 291.0717, calcd. for $C_{18}H_{13}NOS$ $[M]^+$: 291.0718.

8-Oxo-4-phenyl-6,7,7α,8-tetrahydro-5*H*-indeno[5,6-*b*]-furan-7α-carbonitrile (9be): white solid; yield: 62%; mp 156–158 °C. IR (CH_2Cl_2): ν_{max} = 2953, 2229, 1677, 1428 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, J = 1.6 Hz, 1H), 7.46–7.37 (m, 3H), 7.32–7.30 (m, 2H), 6.37 (d, J = 1.6 Hz, 1H), 2.93 (ddd, J = 18.4, 10.4 and 3.6 Hz, 1H), 2.71 (dd, J = 12.8, 6.4 Hz, 1H), 2.41–2.32 (m, 1H), 2.29–2.17 (m, 1H), 2.08–1.99 (m, 1H), 1.95–1.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.6 (CO), 150.9 (CH), 144.8 (C), 144.6 (C), 140.9 (C), 135.0 (C), 128.7 (br, CH), 128.6 (2 x CH), 127.1 (C), 117.1 (CN), 110.2 (CH), 55.1 (C), 33.1 (CH_2), 28.3 (CH_2), 22.4 (CH_2); HR-MS (EI): m/z = 275.0937, calcd. for $C_{18}H_{13}NO_2$ $[M]^+$: 275.0946.

7-Chloro-4-oxo-9-phenyl-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9bf): white solid; yield: 87%; mp 126–128 °C. IR (CH_2Cl_2): ν_{max} = 2973, 2228, 1702, 1586, 1267 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, J = 7.6 Hz, 1H), 7.46–7.40 (m, 3H), 7.32 (dd, J = 7.6, 2.0 Hz, 1H), 7.08 (br, 2H), 6.87 (d, J = 2.0 Hz, 1H), 2.85–2.78 (m, 1H), 2.73–2.65 (m, 1H), 2.31–2.22 (m, 1H), 2.18–1.94 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.1 (CO), 141.9 (C), 141.6 (C), 135.8 (C), 132.2 (C), 130.0 (br, C), 129.1 (CH), 128.9 (CH), 128.4 (CH), 128.2 (CH), 127.8 (br, CH), 127.0 (CH), 126.8 (C), 117.0 (CN), 51.3 (C), 33.2 (CH_2), 29.7 (CH_2), 22.2 (CH_2); HR-MS (EI): m/z = 319.0761, calcd. for $C_{20}H_{14}ClNO$ $[M]^+$: 319.0764.

4-Oxo-9-phenyl-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]-naphthalene-3α,7-dicarbonitrile (9bg): brown solid; yield: 80%; mp 207–209 °C. IR (CH_2Cl_2): ν_{max} = 2972, 2231, 1711,

1598, 1273 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.00$ (d, $J = 8.0$ Hz, 1H), 7.63 (dd, $J = 8.0$, 1.6 Hz, 1H), 7.50–7.43 (m, 3H), 7.18 (d, $J = 1.6$ Hz, 1H), 7.14 (br, 2H), 2.82 (ddd, $J = 18.8$, 9.2 and 3.6 Hz, 1H), 2.71–2.65 (m, 1H), 2.32–1.95 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 192.3$ (CO), 142.6 (C), 140.8 (C), 135.2 (C), 132.0 (C), 131.2 (CH), 130.5 (CH), 130.2 (br, C), 129.3 (CH), 128.8 (CH), 128.2 (CH), 118.4 (C), 117.5 (CN), 116.5 (CN), 51.5 (C), 33.1 (CH_2), 29.8 (CH_2), 22.4 (CH_2); HR-MS (EI): $m/z = 310.1112$, calcd. for $C_{21}H_{14}N_2O$ $[M]^+$: 310.1106.

5-Methoxy-4-oxo-9-phenyl-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9bh): white solid; yield: 70%; mp 153–155 °C. IR (CH_2Cl_2): $\nu_{max} = 2968$, 2840, 2226, 1708, 1586, 1573, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.42$–7.34 (m, 5H), 7.20 (brm, 1H), 6.88 (d, $J = 8.4$ Hz, 1H), 6.43 (d, $J = 7.6$ Hz, 1H), 3.93 (s, 3H), 2.75 (ddd, $J = 18.0$, 8.8 and 3.6 Hz, 1H), 2.49 (ddd, $J = 13.2$, 6.0 and 2.8 Hz, 1H), 2.33–2.16 (m, 2H), 2.08–1.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 192.0$ (CO), 159.3 (C), 142.2 (C), 140.3 (C), 137.1 (C), 135.3 (CH), 133.7 (C), 129.4 (br, CH), 128.6 (CH), 128.0 (CH), 119.8 (CH), 118.0 (C), 117.7 (CN), 111.7 (CH), 56.2 (OCH_3), 52.8 (C), 32.3 (CH_2), 29.9 (CH_2), 23.1 (CH_2); HR-MS (EI): $m/z = 315.1258$, calcd. for $C_{21}H_{17}NO_2$ $[M]^+$: 315.1259.

4-Oxo-9-phenyl-7-(trifluoromethyl)-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9bi): white solid; yield: 93%; mp 64–66 °C. IR (CH_2Cl_2): $\nu_{max} = 2969$, 2229, 1713, 1574, 1340, 1280 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.03$ (d, $J = 8.0$ Hz, 1H), 7.60 (d, $J = 8.0$ Hz, 1H), 7.44–7.40 (m, 3H), 7.14 (s, 1H), 7.11 (brm, 2H), 2.82 (ddd, $J = 18.8$, 9.6 and 4.0 Hz, 1H), 2.70–2.63 (m, 1H), 2.31–1.93 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 192.7$ (CO), 141.9 (C), 140.8 (C), 136.3 (q, $^2J_{C-F} = 32.8$ Hz, C), 135.6 (C), 132.5 (C), 131.0 (C), 129.0 (br, 2 x CH), 128.7 (CH), 128.3 (CH), 126.9 (q, $^3J_{C,F} = 3.8$ Hz, CH), 124.0 (q, $^3J_{C,F} = 3.8$ Hz, CH), 123.1 (q, $^1J_{C,F} = 272.2$ Hz, C), 116.8 (CN), 51.5 (C), 33.1 (CH_2), 29.8 (CH_2), 22.4 (CH_2); HR-MS (EI): $m/z = 353.1030$, calcd. for $C_{21}H_{14}F_3NO$ $[M]^+$: 353.1027.

Methyl 9α-cyano-9-oxo-4-phenyl-2,3,9,9α-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-6-carboxylate (9bj): white solid; yield: 93%; mp 152–154 °C. IR (CH_2Cl_2): $\nu_{max} = 2952$, 2228, 1725, 1603, 1278 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.99$ (s, 2H), 7.56 (s, 1H), 7.46–7.39 (m, 3H), 7.28 (brm, 2H), 3.83 (s, 3H), 2.82 (ddd, $J = 18.8$, 9.2 and 4.0 Hz, 1H), 2.69–2.64 (m, 1H), 2.30–1.93 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 193.2$ (CO), 165.7 (CO_2Me), 140.9 (C), 140.3 (C), 136.0 (C), 135.9 (C), 132.9 (C), 131.6 (C), 128.9 (2 x CH), 128.5 (br, CH), 128.4 (CH), 128.0 (CH), 127.8 (CH), 117.0 (CN), 52.5 (OCH_3), 51.5 (C), 33.2 (CH_2), 29.8 (CH_2), 22.5 (CH_2); HR-MS (EI): $m/z = 343.1209$, calcd. for $C_{22}H_{17}NO_3$ $[M]^+$: 343.1208.

7-Methoxy-4-oxo-9-phenyl-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carbonitrile (9bk): white solid; yield: 90%; mp 185–187 °C. IR (CH_2Cl_2): $\nu_{max} = 2968$, 2840, 2227, 1690, 1593, 1261 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.96$ (d, $J = 8.4$ Hz, 1H), 7.42–7.36 (m, 4H), 7.05 (m, 1H), 6.83 (dd, $J = 8.4$, 2.4 Hz, 1H), 6.36 (d, $J = 2.4$ Hz, 1H), 3.72 (s, 3H), 2.81–2.74 (m, 1H), 2.71–2.63 (m, 1H), 2.27–2.18 (m, 1H), 2.14–2.02 (m, 2H), 1.99–1.90 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 191.3$ (CO), 165.2 (C), 142.5 (C), 141.0 (C), 136.4 (C), 132.8 (C), 130.3 (CH), 130.29 (br, CH), 128.6 (CH), 128.0 (CH), 121.8 (C), 117.8 (CN), 112.9 (CH), 112.8 (CH), 55.4 (OCH_3), 51.0 (C), 33.5 (CH_2), 29.5 (CH_2), 22.1 (CH_2); HR-MS (EI): $m/z = 315.1259$, calcd. for $C_{21}H_{17}NO_2$ $[M]^+$: 315.1259.

7-Oxo-11-phenyl-7α,8,9,10-tetrahydro-7*H*-cyclopenta[*b*]-phenanthrene-7α-carbonitrile (9bl): yellow solid; yield: 95%; mp 176–178 °C. IR (CH_2Cl_2): $\nu_{max} = 3056$, 2969, 2228, 1698, 1590, 1268 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.93$ (d, $J = 8.8$ Hz, 1H), 7.86 (d, $J = 8.8$ Hz, 1H), 7.79 (d, $J = 8.0$ Hz, 1H), 7.72 (brm, 1H), 7.52 (brm, 1H), 7.42 (t, $J = 8.0$ Hz, 1H), 7.34–7.30 (m, 2H), 7.13 (brm, 1H), 7.07 (t, $J = 8.0$ Hz, 1H), 6.56 (brm, 1H), 3.03 (ddd, $J = 18.4$, 8.8 and 4.8 Hz, 1H), 2.63–2.57 (m, 1H), 2.43–2.27 (m, 2H), 2.15–2.03 (m, 1H), 1.97–1.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 194.7$ (CO), 141.2 (C), 140.2 (C), 138.6 (C), 138.0 (C), 133.5 (C), 129.8 (C), 129.7 (CH), 128.6 (br, 2 x CH), 128.4 (CH), 128.2 (CH), 128.1 (br, CH), 127.7 (CH), 127.4 (C), 125.8 (CH), 122.3 (CH), 117.9 (CN), 51.0 (C), 32.7 (CH_2), 31.2 (CH_2), 23.7 (CH_2); HR-MS (EI): $m/z = 335.1316$, calcd. for $C_{24}H_{17}NO$ $[M]^+$: 335.1310.

2-(2-Iodobenzyl)-3-oxo-3-phenylpropanenitrile (10)

To a stirred solution of benzoylacetonitrile **6** (0.5 g, 3.6 mmol) and 2-iodobenzaldehyde **11** (1.0 g, 4.3 mmol) in EtOH (20 mL) were added L-proline (83 mg, 0.72 mmol) and Hantzsch ester (0.9 g, 3.6 mmol) sequentially in one portion. The resulting mixture was stirred at 25 °C for 8 h. The reaction solution was concentrated under reduced pressure, the residue was purified by flash chromatography on silical gel (33% CH_2Cl_2 in *n*-hexane) to afford product **10** as a white solid; yield: 1.0 g (78%); mp 54–56 °C. IR (CH_2Cl_2): $\nu_{max} = 3058$, 2242, 1695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.01$ (dd, $J = 7.6$, 1.2 Hz, 2H), 7.83 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.64 (tt, $J = 8.0$, 1.2 Hz, 1H), 7.50 (dd, $J = 8.0$, 7.6 Hz, 2H), 7.39 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.31 (td, $J = 7.6$, 2.4 Hz, 1H), 6.97 (td, $J = 7.6$, 2.4 Hz, 1H), 4.76 (dd, $J = 9.6$, 6.0 Hz, 1H), 3.47 (dd, $J = 14.0$, 6.0 Hz, 1H), 3.28 (dd, $J = 14.0$, 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 189.7$ (CO), 139.6 (CH), 138.2 (C), 134.5 (CH), 133.8 (C), 131.3 (CH), 129.4 (CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 116.4 (CN), 100.0 (C), 39.9 (CH_2), 39.2 (CH); HR-MS (EI): $m/z = 360.9965$, calcd. for $C_{16}H_{12}INO$ $[M]^+$: 360.9964.

The general procedure for the synthesis of products **12**, **13**, **14** and **15** is demonstrated as follows using **12** as a typical example.

10-Oxo-5-phenyl-10α,11-dihydro-10*H*-benzo[*b*]-fluorene-10α-carbonitrile (12)

A mixture of 2-(2-iodobenzyl)-3-oxo-3-phenylpropanenitrile **10** (170 mg, 0.47 mmol), phenylacetylene (58 mg, 0.52 mmol), CuI (27 mg, 0.14 mmol), $Pd(PPh_3)_4$ (54 mg, 0.047 mmol) and pyrrolidine (78 μL, 0.94 mmol) in dichloromethane (3 mL) was stirred open to air at room temperature for 3 h. The mixture was filtered through a pad of celite and silica gel and washed with CH_2Cl_2 (50 mL). The organic layers were concentrated under vacuum to give the residue, which was subjected to purification by flash chromatography on silica gel (20% EtOAc in *n*-hexane) to afford the compound **12** as a yellow solid; yield: 139 mg (89%); mp 232–234 °C; IR (CH_2Cl_2): $\nu_{max} = 3063$, 2226, 1702, 1591, 1283 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.03$ (dd, $J = 7.6$, 1.2 Hz, 1H), 7.64–7.62 (m, 2H), 7.54–7.45 (m, 3H), 7.40 (dd,

$J=7.6$, 1.2 Hz, 1H), 7.34 (t, $J=7.6$ Hz, 1H), 7.22 (t, $J=7.6$ Hz, 1H), 6.97 (t, $J=8.0$ Hz, 1H), 6.95 (t, $J=8.0$ Hz, 1H), 6.91 (d, $J=7.6$ Hz, 1H), 6.32 (d, $J=8.0$ Hz, 1H), 3.67 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=192.6$ (CO), 143.2 (C), 140.7 (C), 138.0 (C), 136.4 (C), 135.9 (C), 135.4 (CH), 132.5 (C), 130.5 (CH), 129.8 (CH), 129.6 (CH), 129.2 (CH), 128.6 (CH), 128.4 (CH), 128.25 (C), 128.23 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 125.6 (CH), 124.7 (CH), 118.4 (CN), 51.5 (C), 37.3 (CH_2); HR-MS (EI): $m/z=$ 333.1154, calcd. for $C_{24}H_{15}NO$ $[M]^+$: 333.1154.

10-Oxo-5-[4-(trifluoromethyl)phenyl]-10α,11-dihydro-10*H*-benzo[*b*]fluorene-10α-carbonitrile (13): yellow solid; yield: 72%; mp 231–233 °C. IR (CH_2Cl_2): $\nu_{max}=2924$, 2225, 1693, 1587, 1323, 1284 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.06$ (dd, $J=7.6$, 1.6 Hz, 1H), 7.93 (d, $J=7.6$ Hz, 1H), 7.79–7.75 (m, 2H), 7.55 (td, $J=7.6$, 1.6 Hz, 1H), 7.45–7.39 (m, 2H), 7.27 (td, $J=7.6$, 1.2 Hz, 1H), 7.16 (d, $J=7.6$ Hz, 1H), 7.04 (t, $J=7.6$ Hz, 1H), 6.81 (d, $J=7.6$ Hz, 1H), 6.29 (d, $J=7.6$ Hz, 1H), 3.69 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=192.2$ (CO), 143.5 (C), 139.98 (C), 139.96 (C), 138.6 (C), 135.9 (C), 135.5 (CH), 131.2 (CH), 131.0 (C), 130.9 (q, $^2J_{C-F}=32.8$ Hz, C), 130.1 (CH), 129.1 (CH), 128.7 (CH), 128.2 (C), 128.0 (CH), 127.8 (CH), 127.5 (CH), 126.9 (CH), 126.2 (CH), 125.8 (CH), 124.4 (CH), 123.9 (q, $^1J_{C,F}=$ 270.6 Hz, C), 118.1 (CN), 51.6 (C), 37.3 (CH_2); HR-MS (EI): $m/z=401.1023$, calcd. for $C_{25}H_{14}F_3NO$ $[M]^+$: 401.1027.

5-(4-Methoxyphenyl)-10-oxo-10α,11-dihydro-10*H*-benzo[*b*]fluorene-10α-carbonitrile (14): yellow solid; yield: 88%; mp 196–198 °C. IR (CH_2Cl_2): $\nu_{max}=2956$, 2226, 1701, 1510, 1283 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.02$ (d, $J=7.6$ Hz, 1H), 7.53 (t, $J=7.6$ Hz, 2H), 7.41–7.36 (m, 2H), 7.23 (t, $J=7.6$ Hz, 1H), 7.16 (d, $J=6.8$ Hz, 1H), 7.02–6.88 (m, 4H), 6.45 (d, $J=7.6$ Hz, 1H), 3.92 (s, 3H), 3.67 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=192.8$ (CO), 159.7 (C), 143.1 (C), 141.1 (C), 138.2 (C), 136.6 (C), 135.3 (CH), 132.4 (C), 131.8 (CH), 129.6 (CH), 129.5 (CH), 128.3 (CH), 128.29 (C), 127.9 (C), 127.8 (CH), 127.7 (CH), 127.6 (CH), 125.5 (CH), 124.7 (CH), 118.5 (CN), 115.3 (CH), 114.5 (CH), 55.3 (CH_3), 51.6 (C), 37.3 (CH_2); HR-MS (EI): $m/z=363.1249$, calcd. for $C_{25}H_{17}NO_2$ $[M]^+$: 363.1259.

10-Oxo-5-propyl-10α,11-dihydro-10*H*-benzo[*b*]fluorene-10α-carbonitrile (15): yellow solid; yield: 93%; mp 151–153 °C. IR (CH_2Cl_2): $\nu_{max}=2965$, 2223, 1700, 1593, 1286 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.99$ (dd, $J=7.6$, 1.6 Hz, 1H), 7.72 (td, $J=7.6$, 1.6 Hz, 1H), 7.64 (d, $J=$ 7.6 Hz, 1H), 7.59 (d, $J=7.6$ Hz, 1H), 7.46–7.33 (m, 4H), 3.62, 3.56 (ABq, $J=16.8$ Hz, 1H each), 2.92 (ddd, $J=14.0$, 11.6 and 5.6 Hz, 1H), 2.76 (ddd, $J=14.0$, 11.6 and 5.6 Hz, 1H) 1.90–1.73 (m, 2H), 1.17 (t, $J=7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=192.9$ (CO), 143.2 (C), 140.2 (C), 136.8 (C), 136.2 (C), 135.6 (CH), 131.9 (C), 129.3 (CH), 128.7 (C), 128.3 (CH), 128.0 (CH), 127.9 (CH), 125.9 (CH), 125.2 (CH), 125.0 (CH), 118.4 (CN), 51.7 (C), 37.3 (CH_2), 30.8 (CH_2), 22.3 (CH_2), 14.2 (CH_3); HR-MS (EI): $m/z=$ 299.1315, calcd. for $C_{21}H_{17}NO$ $[M]^+$: 299.1310.

Ethyl 2-Benzoylhept-6-ynoate (16)

To a stirred solution of ethyl 3-oxo-3-phenylpropanoate (0.50 g, 2.60 mmol) and potassium carbonate (0.54 g, 3.90 mmol) in acetonitrile (13 mL) was added 5-iodopent-1-ynyltrimethylsilane (0.83 g, 3.12 mmol) in one portion. The resulting mixture was heated to 80 °C for 16 h, and then cooled to room temperature and quenched with water. The aqueous phase was extracted with ethyl acetate (2×20 mL). The combined organic extracts were washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give crude residue. The crude trimethylsilane residue, without purification, was further treated with TBAF (5.72 mL, 1M in THF) in THF (50 mL) at −10 °C for 1 h and then cooled to room temperature and quenched with water. The aqueous phase was extracted with ethyl acetate (2×30 mL). The combined organic extracts were washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give crude residue, which was subjected to purification by flash chromatography on silica gel with *n*-hexane/ethyl acetate (8:1) to afford the desired product **16** as a colorless oil; yield: 0.49 g (73% over two steps). IR (CH_2Cl_2): $\nu_{max}=3294$, 3062, 2981, 2938, 2117, 1735, 1686, 1597, 1448, 1221, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 7.98 (dd, $J=8.4$, 1.2 Hz, 2H), 7.58 (tt, $J=8.8$, 1.2 Hz, 1H), 7.47 (dd, $J=8.8$, 8.4 Hz, 2H), 4.32 (t, $J=7.2$ Hz, 1H), 4.14 (qd, $J=7.2$, 1.2 Hz, 2H), 2.24 (td, $J=7.2$, 2.4 Hz, 2H), 2.12 (ddd, $J=11.2$, 7.2, 5.2 Hz, 2H), 1.95 (t, $J=2.4$ Hz, 1H), 1.65–1.56 (m, 2H), 1.16 (td, $J=7.2$, 0.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=194.7$ (CO), 169.6 (CO_2Et), 135.9 (C), 133.4 (CH), 128.6 (CH), 128.4 (CH), 83.4 (C≡C), 68.8 (C≡CH), 61.2 (CH_2), 53.5 (CH), 27.7 (CH_2), 26.1(CH_2), 18.1 (CH_2), 13.8 (CH_3); HR-MS (EI): $m/z=258.1251$, calcd. for $C_{16}H_{18}O_3$ $[M]^+$: 258.1256

The general procedure for the synthesis of products **17**, **18** and **19** is demonstrated as follows using **17** as a typical example.

Ethyl 4-Oxo-9-phenyl-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carboxylate (17)

A mixture of ethyl 2-benzoylhept-6-ynoate **16** (120 mg, 0.47 mmol), iodobenzene (105 mg, 0.52 mmol), CuI (27 mg, 0.14 mmol), $Pd(PPh_3)_4$ (54 mg, 0.047 mmol) and pyrrolidine (78 μL, 0.94 mmol) in dichloromethane (3 mL) was stirred under air at room temperature for 5 h. After reaction was complete, the mixture was filtered through a pad of Celite and slica gel, and washed with CH_2Cl_2 (50 mL). The organic layer was concentrated under reduced pressure to give the residue, which was subjected to purification by flash chromatography on silica gel (20% EtOAc in *n*-hexane) to afford compound **17** as a colorless oil; yield: 25%; IR (CH_2Cl_2): $\nu_{max}=3061$, 2963, 1738, 1704, 1594, 1444, 1287, 1204, 1019, 775, 705 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 7.88 (dd, $J=1.2$, 7.6 Hz, 1H), 7.49–7.34 (m, 5H), 7.26 (t, $J=$ 7.6 Hz, 2H), 6.86 (d, $J=7.6$ Hz, 1H), 4.13–4.03 (m, 2H), 2.74–2.62 (m, 2H), 2.25–2.14 (m, 2H), 1.98–1.90 (m, 1H), 1.84–1.75 (m, 1H), 1.10 (t, $J=7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=198.8$ (CO), 169.3 (CO_2Et), 144.1 (C), 140.7 (C), 137.9 (C), 133.9 (CH), 131.5 (C), 130.1 (C), 128.5 (CH), 127.6 (CH), 127.1 (CH), 126.7 (CH), 126.3 (CH), 66.0 (C), 61.9 (CH_2), 31.8 (CH_2), 30.5 (CH_2), 22.6 (CH_2), 13.8 (CH_3); HR-MS (EI): $m/z=332.1408$, calcd. for $C_{22}H_{20}O_3$ $[M]^+$: 332.1412.

Ethyl 9-[4-(methoxycarbonyl)phenyl]-4-oxo-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carboxylate (18): pale yellow oil; yield: 32%: IR (CH_2Cl_2): $\nu_{max}=3063$, 2953,

1721, 1608, 1434, 1282, 1114, 1019, 776 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.09$ (d, $J = 6.4$ Hz, 2H), 7.88 (dd, $J = 1.6$, 7.6 Hz, 1H), 7.40 (td, $J = 7.6$, 1.6 Hz, 1H), 7.28 (td, $J = 7.6$, 1.2 Hz, 1H), 7.35 (br, 2H), 6.79 (d, $J = 7.6$ Hz, 1H), 4.14–4.02 (m, 2H), 3.94 (s, 3H), 2.74–2.61 (m, 2H), 2.21–2.13 (m, 2H), 1.99–1.87 (m, 1H), 1.85–1.76 (m, 1H), 1.09 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 198.1$ (CO), 168.8 (CO_2Et), 166.6 (CO_2Me), 144.7 (C), 142.8 (C), 139.8 (C), 133.9 (CH), 130.7 (C), 129.9 (C), 129.7 (CH), 129.3 (C), 127.3 (CH), 126.7 (CH), 125.9 (CH), 66.0 (C), 61.9 (CH_2), 52.0 (CH_3), 31.6 (CH_2), 30.4 (CH_2), 22.4 (CH_2), 13.7 (CH_3); HR-MS (EI): $m/z = 390.1460$, calcd. for $C_{24}H_{22}O_5$ $[M]^+$: 390.1467.

Ethyl 9-(4-methoxyphenyl)-4-oxo-2,3,3α,4-tetrahydro-1*H*-cyclopenta[*b*]naphthalene-3α-carboxylate (19): pale yellow solid; yield: 44%; mp 91–93 °C. IR (CH_2Cl_2): $\nu_{max} = 3064$, 2962, 1738, 1694, 1608, 1514, 1454, 1287, 1248, 1033, 774 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.87$ (dd, $J = 1.2$, 8.0 Hz, 1H), 7.40 (td, $J = 8.0$, 1.2 Hz, 1H), 7.26 (td, $J = 8.0$, 1.2 Hz, 1H), 7.24 (br, 2H), 6.95 (d, $J = 8.0$ Hz, 2H), 6.90 (d, $J = 8.0$ Hz, 1H), 4.12–4.04 (m, 2H), 3.86 (s, 3H), 2.75–2.60 (m, 2H), 2.25–2.13 (m, 2H), 1.97–1.90 (m, 1H), 1.83–1.77 (m, 1H), 1.10 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 198.8$ (CO), 169.3 (CO_2Et), 159.8 (C), 143.7 (C), 140.8 (C), 133.8 (CH), 131.0 (C), 130.1 (C), 129.3 (C), 127.0 (CH), 126.6 (CH), 126.2 (CH), 113.8 (CH), 65.8 (C), 61.8 (CH_2), 55.2 (CH_3), 31.7 (CH_2), 30.5 (CH_2), 22.5 (CH_2), 13.7 (CH_3); HR-MS (EI): $m/z = 362.1521$, calcd. for $C_{23}H_{22}O_4$ $[M]^+$: 362.1518.

Products **20**, **21** and **22** are synthesized in a similar manner as with **17**, except that instead of exposure to air, the reaction system is carried out under nitrogen.

Ethyl 2-benzoyl-7-phenylhept-6-ynoate (20): colorless oil; yield: 97%: IR (CH_2Cl_2): $\nu_{max} = 3060$, 2980, 2936, 2360, 1738, 1688, 1598, 1448, 1222, 758, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.00$ (dd, $J = 7.6$, 1.2 Hz, 2H), 7.57 (tt, $J = 7.6$, 1.2 Hz, 1H), 7.45 (dd, $J = 7.6$, 7.2 Hz, 2H), 7.37–7.34 (m, 2H), 7.27–7.25 (m, 3H), 4.39 (t, $J = 7.2$ Hz, 1H), 4.16 (qd, $J = 7.2$, 1.2 Hz, 2H), 2.47 (t, $J = 7.2$ Hz, 2H), 2.22–2.16 (m, 2H), 1.73–1.59 (m, 2H), 1.17 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 194.9$ (CO), 169.7 (CO_2Et), 136.0 (C), 133.4 (CH), 131.4 (CH), 128.6 (CH), 128.5 (CH), 128.1 (CH), 127.5 (CH), 123.6 (C), 89.1 (C≡C), 81.2 (C≡C), 61.3 (CH_2), 53.6 (CH), 28.0 (CH_2), 26.4 (CH_2), 19.1 (CH_2), 13.9 (CH_3); HR-MS (EI): $m/z = 334.1572$, calcd. for $C_{22}H_{22}O_3$ $[M]^+$: 334.1569.

Methyl 4-(6-benzoyl-7-ethoxy-7-oxohept-1-ynyl)benzoate (21): colorless oil; yield: 90%. IR (CH_2Cl_2): $\nu_{max} = 3061$, 2952, 2229, 1725, 1688, 1606, 1448, 1276, 770, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.00$ (d, $J = 10.4$ Hz, 2H), 7.93 (d, $J = 10.4$ Hz, 2H), 7.57 (tt, $J = 7.6$, 1.2 Hz, 1H), 7.48–7.38 (m, 4H), 4.37 (t, $J = 9.6$ Hz, 1H), 4.15 (qd, $J = 9.2$, 1.2 Hz, 2H), 3.90 (s, 3H), 2.49 (t, $J = 9.2$ Hz, 2H), 2.22–2.15 (m, 2H), 1.70 (quint, $J = 9.2$ Hz, 2H), 1.16 (td, $J = 9.2$, 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 194.9$ (CO), 169.8 (C), 166.6 (C), 136.0 (C), 133.5 (CH), 131.4 (CH), 129.3 (CH), 128.9 (C), 128.7 (CH), 128.6 (CH), 128.5 (C), 92.6 (C≡C), 80.7 (C≡C), 61.4 (CH_2), 53.7 (CH), 52.1 (CH_3), 28.1 (CH_2), 26.3 (CH_2), 19.3 (CH_2), 13.9 (CH_3); HR-MS (EI): $m/z = 392.1627$, calcd. for $C_{24}H_{24}O_5$ $[M]^+$: 392.1624.

Ethyl 2-benzoyl-7-(4-methoxyphenyl)hept-6-ynoate (22): colorless oil; yield: 96%. IR (CH_2Cl_2): $\nu_{max} = 3060$, 2935, 2230, 1738, 1683, 1606, 1510, 1448, 1289, 1032, 833, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.00$ (dd, $J = 7.6$, 1.2 Hz, 2H), 7.56 (tt, $J = 7.6$, 1.2 Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.31–7.26 (m, 2H), 6.81–6.77 (m, 2H), 4.39 (t, $J = 7.2$ Hz, 1H), 4.15 (qd, $J = 7.2$, 1.6 Hz, 2H), 3.78 (s, 3H), 2.45 (t, $J = 7.2$ Hz, 2H), 2.21–2.15 (m, 2H), 1.72–1.64 (m, 2H), 1.17 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 195.0$ (CO), 169.8 (CO_2Et), 159.0 (C), 136.1 (C), 133.4 (CH), 132.8 (CH), 128.7 (CH), 128.5 (CH), 115.8 (C), 113.7 (CH), 87.5 (C≡C), 80.9 (C≡C), 61.3 (CH_2), 55.2 (CH_3), 53.7 (CH), 28.1 (CH_2), 26.6 (CH_2), 19.1 (CH_2), 13.9 (CH_3); HR-MS (EI): $m/z = 364.1677$, calcd. for $C_{23}H_{24}O_4$ $[M]^+$: 364.1675.

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