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# Pd-Catalyzed Tandem Homocupling-Adol-Dehydration of *ortho*-Acylphenyl Iodides

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A Pd-catalyzed cascade Ullmann coupling/Aldol/dehydration reaction of *ortho*-acylphenyl iodides has been explored. This transformation provides a concise access to colchino analogues in moderate to good yields with wide functional group tolerance.

## Introduction

Transition-metal catalyzed homocoupling of aryl halides, as a powerful tool to construct aryl carbon ($sp^2$)–aryl carbon ($sp^2$) bonds, provides an efficient access to biaryl motifs which are frequently encountered in the fields of optical materials,[1] molecular devices [2] and natural products.[3] Since the Ullmann coupling was first reported one century ago, [4] much significant progress on various transition- metal catalyzed homocoupling of aryl halides has already been achieved. [5] In contrast, there have been rare reports about the transition-metal catalyzed cascade Ullmann coupling reaction of aryl halides, which possibly provides a concise approach to construct complex organic compounds.[6]

On the other hand, rapid assembly of dibenzo-seven-memebered-ring system has attracted growing interesting in synthetic and medicinal field due to that this macrocyclic system belongs to an important core strucutre of many biologically active molecules such colchicine derivatives.[7] Therefore, various methodologies including the ring expansion of phenanthrene derivatives,[8] Diels-Alder reactions,[9] direct arylations [10] and Nicholas reactions, [11] Suzuki-Miyaura coupling/Aldol condensation reaction [12] were successively developed to make these compounds. Nevertheless, the number and range of examples disclosed in the above-mentioned methods to date is still limitted. Moreover, Leonard ever reported an elegant synthetic process to construct dibenzo-cycloheptenone core *via* a six-step protocol including Ullmann coupling and aldol condensation, etc. [13] However, this procedure suffered from tedious reaction steps and harsh reaction conditions. Considering that colchicine derivatives possesses potent anti-tumour properties, the development of a concise approach to these compounds therefore is desirable. In order to further richen the colchinol libray, herein we described a Pd-catalyzed tandem Ullmann homocoupling/aldol/ dehydration of *ortho*-acylphenyl iodides [14] to rapidly construct colchinol analogues.

## Results and discussion

The $Pd(OAc)_2$-catalyzed cascade cyclization of *ortho*-bromoacetophenone **1b** (0.20 mmol) in the presence of $NaHCO_3$ (1.5 equiv) and $PPh_3$ (10 mol %) was first investigated in DMF (1.0 mL) at 150 ˚C for 3 h (Table 1, entry 1), and we quickly found that this transformation could provide us the 7-membered-ring product **2a** (23% yield) and the by product **3a** (16% yield) which was derived from the further C-H functionalization reaction of **2a**, and the chemical structure of **3a** was also unambiguously confirmed by its single crystal X-ray analysis (see Figure 1 and ESI† for more details).

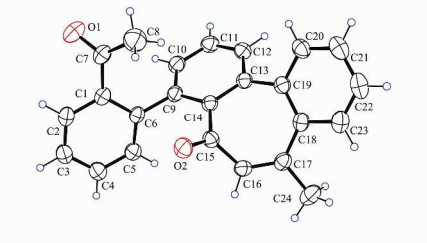


**Figure 1**. Single Crystal Structure of **3a**

Although the competitive C-H arylation led to lower yield of the desired dibenzo-cycloheptenone **2a**, this positive result still encouraged us to conduct further optimization of the reaction conditions for achieving excellent selectivity. Then, we investigated the $PdCl_2/PPh_3/K_2CO_3$ system could afford **2a** and **3a** in 78% overall yield, but the reaction specification is still very poor (**2a**/**3a**≈1, entry 7). Subsequently, we had to switch our focus to the substrate and ligand screening for improving the reaction selectivity (entries 8-17). To our delight, *ortho*-iodo-substituted acetophenone (**1c**) could high-specifically give the desired product **2a** in 80% yield using 1, 3-bis (diphenylphosphino) propane (DPPP) ($\mathbf{L_3}$) as ligand, and only trace amounts of **3a** (<5 % yield) was observed (entry 17). Notably, the Pd-catalyzed cascade cyclization of *ortho*-chloro-substituted acetophenone (**1a**) could not furnish **2a** or **3a** under $PdCl_2/\mathbf{L_3}/K_2CO_3$ conditions, and the starting material **1a** was recovered completely (entry 14). Further optimization of this reaction conditions demonstrated that lowering the reaction temperature or reducing the Pd catalyst loading led to poorer yield of **2a** (compare entries 17 with 19 and 20) (see SI for more

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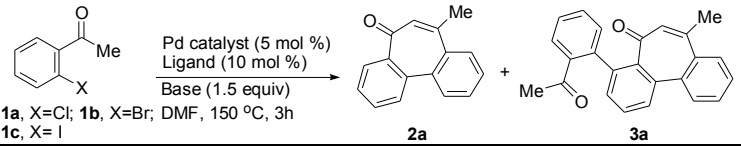
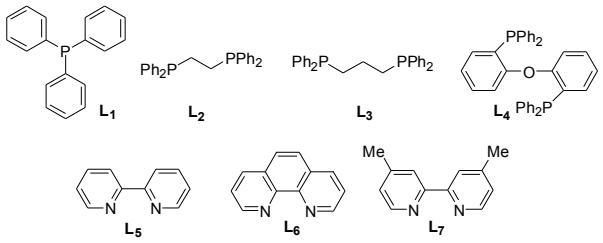
details).

**Table 1.** Optimisation of the Pd-catalyzed cascade cyclization of *ortho*-haloacetophenone



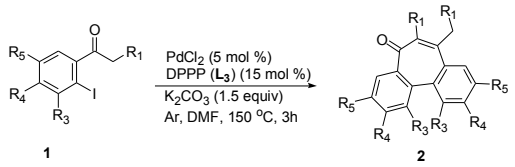

| entry | X | Pd salts | L | base | 2a/3a yield (%) [b] |
|---|---|---|---|---|---|
| 1 | Br | $Pd(OAc)_2$ | $L_1$ | $NaHCO_3$ | 23/16 |
| 2 | Br | $Pd(OAc)_2$ | $L_1$ | $K_2CO_3$ | 32/32 |
| 3 | Br | $Pd(OAc)_2$ | $L_1$ | $Cs_2CO_3$ | 14/10 |
| 4 | Br | $Pd(OAc)_2$ | $L_1$ | $NEt_3$ | 0/16 |
| 5 | Br | $Pd(TFA)_2$ | $L_1$ | $K_2CO_3$ | 28/37 |
| 6 | Br | $Pd(MeCN)_2Cl_2$ | $L_1$ | $K_2CO_3$ | 32/32 |
| 7 | Br | $PdCl_2$ | $L_1$ | $K_2CO_3$ | 41/37 |
| 8 | Br | $PdCl_2$ | $L_2$ | $K_2CO_3$ | 41/42 |
| 9 | Br | $PdCl_2$ | $L_3$ | $K_2CO_3$ | 42/39 |
| 10 | Br | $PdCl_2$ | $L_4$ | $K_2CO_3$ | 32/18 |
| 11 | Br | $PdCl_2$ | $L_5$ | $K_2CO_3$ | 0/22 |
| 12 | Br | $PdCl_2$ | $L_6$ | $K_2CO_3$ | 0/0 |
| 13 | Br | $PdCl_2$ | $L_7$ | $K_2CO_3$ | 0/0 |
| 14 | Cl | $PdCl_2$ | $L_3$ | $K_2CO_3$ | 0/0 |
| 15 | I | $PdCl_2$ | $L_1$ | $K_2CO_3$ | 14/28 |
| 16 | I | $PdCl_2$ | $L_2$ | $K_2CO_3$ | 60/4 |
| 17 | **I** | **$PdCl_2$** | $L_3$ | **$K_2CO_3$** | **80/<5** |
| 18 | I | $PdCl_2$ | $L_4$ | $K_2CO_3$ | 46/18 |
| 19 | I | $PdCl_2$ | $L_3$ | $K_2CO_3$ | 71/4[c] |
| 20 | I | $PdCl_2$ | $L_3$ | $K_2CO_3$ | 68/<5[d] |

[a] Unless otherwise noted, *ortho*-haloacetophenone (0.20 mmol) was treated with Pd catalyst (5 mol %) in the presence of ligand (**L**) (10 mol %) and base (1.5 equiv) in DMF (1.0 mL) at 150 °C for 3 h under Ar condition in a sealed tube, followed by flash chromatography on $SiO_2$. [b] Isolated yield. [c] The reaction temperature was 140 °C. [d] 2.5 mol % of $PdCl_2$ was used.

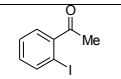
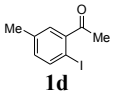
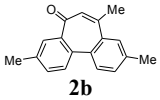
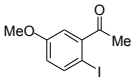
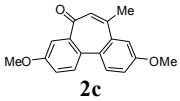
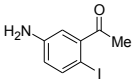
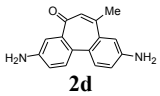
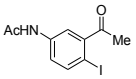
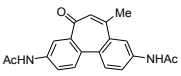
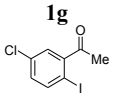
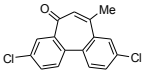
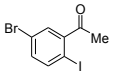
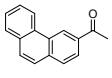
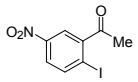
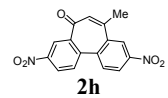
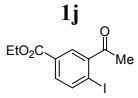
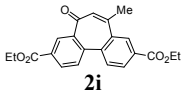
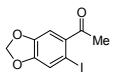
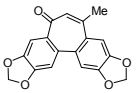
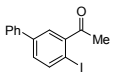
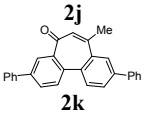
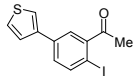
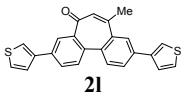
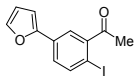
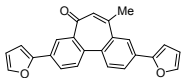
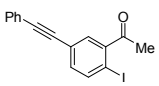
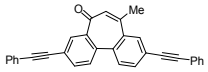
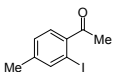
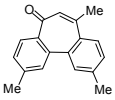
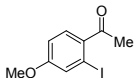
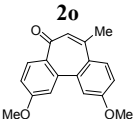
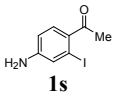
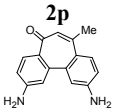
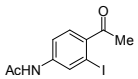
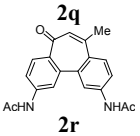
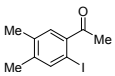
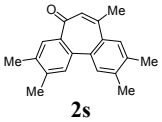
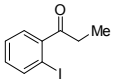


Having established an efficient reaction protocol that enables the smooth cascade homocoupling cyclization of *ortho*-iodoacetophenone, we next investigated the effect of substituents on this tandem reaction. As shown in Table 2, although the various functional group-substituted phenylketones (**1**) could smoothly homocouple and cyclize to furnish dibenzo-cycloheptenone **2** under the optimized conditions, the substituted group on the benzene ring showed significant electronic effects. The electron donating group including 5-MeO, 5-Me, 5-$NH_2$, 5-NHAc, 5-aryl, 5-alkynyl, 4-Me, 4-MeO, 4-$NH_2$ and 4-AcNH on the phenyl ring afforded the dibenzo-7-membered-ring compounds in moderate to excellent yields (48-80%) (entries 1-5, 10-19).[15] On the contrary, the electron withdrawing group such as 5-Cl and 5-$CO_2$Et on the phenyl ring gave the desired product in poorer yields (30-46%) (entries 6 and 9). It is worth noting that the 5-bromo-substituted phenylketone **1i** led to the formation of 3-acetylphenanthrene instead of 7-membered ring product (entry 7). Moreover, no cascade homocoupling/cyclization product from the electon-poor 5-nitro-substituted phenylketone **1j** was observed (entry 8). To further explore the substrate scope, we also investigated the effect of the acyl substitutent ($R_1CH_2CO$-) on this cascade reaction, and found the *ortho*-propionyl phenyliodide (**1v**) and *ortho*-phenyl acetyl phenyliodide (**1w**) could also provide the expected polysubstituted dibenzo-cycloheptenone **2t** and **2u** (entries 20 and 21). Unfortunately, *ortho*-bromoactyl phenyl iodide (**1x**) only led to the formation of **2a** in which bromo group was reductively removed. In addition, we tried to use the 1-(2-iodo-3-methyl-phenyl)-ethanone (**1y**) as a substrate, but no desired product **2v** was obtained possibly due to the "*ortho*-substitutent" effect (entry 23).

**Table 2.** Pd-catalyzed cascade cyclization of *ortho*-acylphenyl iodides[a]




1 2

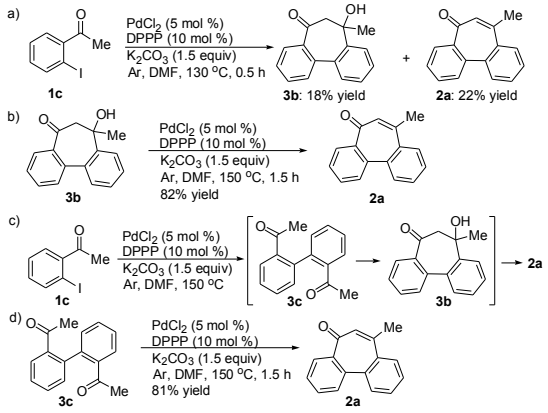
| entry | substrate | product | yield (%)[b] |
|---|---|---|---|
| 1 |  **1c** |  **2a** | 80 |
| 2 |  **1d** |  **2b** | 72 |
| 3 |  **1e** |  **2c** | 80 |
| 4 |  **1f** |  **2d** | 64 |
| 5 |  **1g** |  **2e** | 72 |
| 6 |  **1h** |  **2f** | 35 |
| 7 |  |  | 30 |
| 8 |  **1j** |  **2h** | 0 |
| 9 |  **1k** |  **2i** | 46 |
| 10 |  **1l** |  **2j** | 62 |
| 11 |  **1m** |  **2k** | 66 |
| 12 |  **1n** |  **2l** | 80 |
| 13 |  **1o** |  **2m** | 61 |
| 14 |  **1p** |  **2n** | 48 |
| 15 |  **1q** |  **2o** | 74 |
| 16 |  **1r** |  **2p** | 75 |
| 17 |  **1s** |  **2q** | 72 |
| 18 |  **1t** |  **2r** | 68 |
| 19 |  **1u** |  **2s** | 78 |
| 20 |  **1v** |  **2t** | 34 |
| 21 |  **1w** |  **2u** | 40 |
| 22 |  **1x** |  **2a** | 48 |
| 23 |  **1y** |  **2v** | 0 |

[a]Unless otherwise noted, *ortho*-acylphenyl iodides **1** (0.20 mmol) was treated with $PdCl_2$ (5 mol %) in the presence of ligand (DPPP)

(10 mol %) and $K_2CO_3$ (1.5 equiv) in DMF (1.0 mL) at 150 °C for 3 h under Ar condition in a sealed tube, followed by flash chromatography on $SiO_2$. [b]Isolated yield.

To further investigate the reaction mechanism, we conducted the Pd(II)-catalyzed cascade cyclization of *ortho*-iodoacetophone (**1c**) at lower reaction temperature (130 °C) in order to trap some possible byproducts and intermediates (Scheme 1a). After the reaction was carried out for 0.5 h, we observed the formation of alcohol intermediate **3b** (18% isolated yield) which could be further converted into the desired product **2a** in 82% yield under our standard conditions (Scheme 1b). Considering that aryl halides (**1c**) could easily convert to symmetric biaryl ketone (**3c**) using palladium catalysts *via* a Ullmann process,[5d, 16] and the alcohol intermediate **3b** is also possibly derived from the ketone **3c** *via* an intramolecular aldol reaction (Scheme 1c), we tried to use **3c** as a substrate under our standard conditions. As expected, we also obtained the 7-membered-ring product **2a** in 81% yield (Scheme 1d).

**Scheme 1.** Control Reactions




Although the exact reaction mechanism about Pd-catalyzed homocoupling of aryl halides is not still clear,[17] on the basis of the above-mentioned control experimental results, we proposed two plausible reaction pathways (see Figure 2). At first, the organic phosphine ligand (DPPP) or DMF [18] reduces Pd(II) to Pd(0), followed by the oxidative addition with Ar-I (**1c**) to form Pd(II) i-

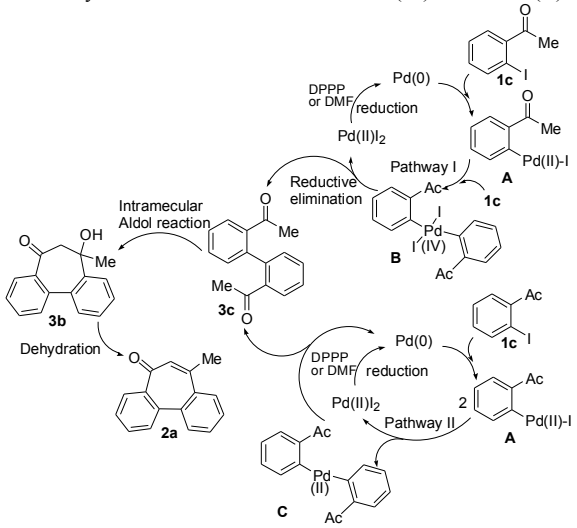



**Figure 2**. The Proposed Reaction Mechanism

ntermediate **A**.[15] Then the second oxidative addition of Pd(II) intermediate **A** with another *ortho*-iodoacetophenone molecule (**1c**) *via* Pathway I leads to the formation of the Pd(IV) intermediate **B**,[15, 19] and subsequent reductive elimination affords homocoupling product **3c** which can further lead to the formation of the final dibenzo-cycloheptenone **2a** *via* cascade intramolecular aldol/dehydration process;[20] In addition to Pathway I, an alternative reaction Pathway II can not be ruled out in the absence of strong oxidizing agents, in which the disproportionation between two Ar-Pd(II)-I (**A**) molecules can lead to Ar-Pd(II)-Ar (**C**) and $Pd(II)I_2$.[21] The resulting bisarylpalladium (II) **C** will be subjected to reductive elimination to afford the corresponding coupling product **3c** and Pd(0).

## Conclusions

In summary, we have developed an efficient Pd-catalyzed cascade homocoupling-adol-dehydration reaction of *ortho*-acylphenyl iodides to rapidly construct colchinol analogues in moderate to good yields, and the further biological activity evaluation for these compounds is currently underway in our laboratory.

## Experimental

### General information

Unless otherwise noted, all reagents including **1a**, **1b** and **1c** were purchased from commercial suppliers and used without purification, and all reactions were carried out under argon atmosphere in flame-dried sealed tubes with magnetic stirring. Solvents were treated with 4 Å molecular sieves or sodium and distilled prior to use. Flash chromatography was performed on silica gel (40~63 mm) by standard technique. $^1H$ and $^{13}C$ NMR spectra were recorded on a 400 MHz spectrometer at room temperature with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). High resolution exact mass measurements (HR-MS) were performed on a TOF spectrometer (Micromass). Infrared spectra (IR) were reported as wavelength numbers ($cm^{-1}$). Infrared spectra were recorded by preparing a KBr pellet containing the title compound. Crystal data were obtained by employing graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293 (2) K and operating in the φ-ωscan mode. The structure was solved by direct methods SHELXS-97; 1-(2-amino-5-methylphenyl)ethanone, [20] 1-(2-amino-5-chlorophenyl)ethanone, [22] 2-amino-5-nitroacetophenone, [23] 1-(2-amino-5-bromophenyl)ethanone, [24] 1-(4-amino-[1, 1'-biphenyl]-3-yl)ethanone, [24] 1-(2-amino-5-(thiophen-3-yl)phenyl)ethanone, [24] 1-(2-amino-5-(furan-2-yl)phenyl)ethanone, [24] 1-(2-amino-5-(phenylethynyl)phenyl)ethanone, [24] ethyl-3-acetyl-4-aminobenzoate, [25] 1-(2-amino-4, 5-dimethylphenyl)ethanone, [26] 1-(2-amino-3-methylphenyl)ethanone [27] and 1, 1'-([1,1'-biphenyl]-2,2'-diyl)diethanone, [28] 1-(2-iodo-5-methoxyphenyl)ethanone (**1e**) [29], 1-(2-iodo-4-methylphenyl)ethanone (**1q**), [30] 1-(2-iodo-4-methoxyphenyl)ethanone (**1r**), [30] 1-(2-iodophenyl)propan-1-one (**1v**), [29] 1-(2-iodophenyl)-2-phenyl-1-ethanone (**1w**) , [31] 2-bromo-1-(2-iodophenyl)ethanone (**1x**) [32] and 2-iodo-3-methylacetophenone (**1y**) [33] were prepared using the previous reported procedure. Procedures for the preparation of *ortho*-acylphenyl Iodides.

**Procedure A: General procedure for the preparation of 1d, 1f, 1h-1p and 1u.**

To a stirred solution of *p*-toluenesulfonic acid monohydrate (3.8 g, 20.1 mol) in acetonitrile (24 mL) was added corresponding 4-or 5-substituted-2-acyl-anilines (6.7 mmol). The resulting suspension of protonated amine was cooled to 10 ˚C. To this mixture was carefully added an aqueous solution (4 mL) of potassium iodide (2.78 g, 16.75 mmol) and sodium nitrite (0.92 g, 13.4 mmol). The resulting brown solution was warmed to room temperature after $N_2$ gas evolution ceased. After 4.5 hours, 55 mL of water was added, the mixture was brought to pH = 9 by saturated sodium bicarbonate solution and adding 6 mL of a saturated aqueous solution of sodium thiosulfate. The resulting light yellow solution was extracted with ether (3 × 50 mL) and washed with brine, dried over anhydrous magnesium sulphate, and concentrated under reduced pressure to afford the aryl iodide*s* after purification *via* flash column chromatography.

**1-(2-Iodo-5-methylphenyl)ethanone** (**1d**): Yellow oil; 48% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 7.9, 3.2 Hz, 1H), 7.26 (s, 1H), 6.93 (d, *J* = 7.9 Hz, 1H), 2.59 (s, 3H), 2.33 (s, 3H)*;* $^{13}$C NMR (101 MHz, $CDCl_3$) δ 202.0, 143.9, 140.5, 138.2, 132.8, 129.1, 86.8, 29.5, 20.9; IR (KBr): 3680, 2979, 2924, 1699, 1562, 1467, 1268, 1175, 1120, 1014, 756 cm$^{-1}$*;* HRMS (EI) calcd for $[M]^+$: $C_9H_9IO$ 259.9693, found 259.9692.

**1-(5-Amino-2-iodophenyl)ethanone** (**1f**): Yellow solid; 52% yield; mp 276–278 ˚C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 1H), 6.75 (d, *J* = 2.5 Hz, 1H), 6.48 (dd, *J* = 8.4, 2.5 Hz, 1H), 3.86 (s, 2H), 2.57 (s, 3H)*;* $^{13}$C NMR (101 MHz, $CDCl_3$) δ 202.4, 146.6, 145.0, 141.0, 118.6, 114.7, 75.3, 29.5; IR (KBr): 3541, 2955, 1631, 1528, 1484, 1242, 1125, 1010, 754, 536 cm$^{-1}$. HRMS (EI) calcd for $[M]^+$: $C_8H_8INO$ 260.9645, found 260.9646.

**Procedure B: General procedure for the preparation of 1g and 1t.**

A solution of 1-(5-amino-2-iodophenyl)ethanone (**1f**) or 1-(4-amino-2-iodophenyl)ethanone (**1s**) (3.7 mmol) in dichloromethane (15 mL) at room temperature was treated with triethylamine (4 mmol) and acetyl chloride (4.5 mmol). The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with EtOAc and washed with water. The aqueous layer was extracted with ethyl acetate. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated to provide the desired product **1g or 1t** after purification *via* flash column chromatography.

***N*-(3-acetyl-4-iodophenyl)acetamide** (**1g**): Yellow solid; 82% yield; mp 223–225 ˚C; 1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 18.9 Hz, 1H), 7.84 – 7.76 (m, 2H), 7.27 (d, *J* = 9.2 Hz, 1H), 2.60 (s, 3H), 2.18 (s, 3H)*;* $^{13}$C NMR (101 MHz, $CDCl_3$) δ 202.6, 169.6, 144.2, 140.9, 138.7, 123.2, 119.7, 83.4, 29.6, 24.4; IR (KBr): 3601, 2999, 1718, 1588, 1268, 1115, 1024, 755, 561 cm$^{-1}$*;* HRMS (EI) calcd for $[M + Na]^+$: $C_{10}H_{10}INO_2Na$ 325.9648, found 325.9655.

**1-(5-Chloro-2-iodophenyl)ethanone** (**1h**): Yellow oil; 40% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 2.4 Hz, 1H), 7.11 (dd, *J* = 8.4, 2.4 Hz, 1H), 2.60 (s, 3H)*;* $^{13}$C NMR (101 MHz, $CDCl_3$) δ 200.3, 145.4, 141.9, 134.7, 131.8, 128.3, 88.0, 29.4; IR (KBr): 3618, 2936, 1700, 1548, 1447, 1270, 1229, 1011, 814, 754, 670 cm$^{-1}$. HRMS (EI) calcd for $[M]^+$: $C_8H_6ICIO$ 279.9146, found 279.9147.

**1-(5-Bromo-2-iodophenyl)ethanone** (**1i**): Yellow oil; 53% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 2.3 Hz, 1H), 7.25 (dd, *J* = 8.4, 2.4 Hz, 1H), 2.60 (s, 3H)*;* $^{13}$C NMR (101 MHz, $CDCl_3$) δ 200.2, 145.6, 142.1, 134.8, 131.2, 122.5, 88.9, 29.4; IR (KBr): 3542, 2987, 1695, 1447, 1338, 1142, 1019, 754, 548 cm$^{-1}$; HRMS (EI) calcd for $[M]^+$: $C_8H_6IBrO$ 323.8641, found 323.8640.

**1-(2-Iodo-5-nitrophenyl)ethanone** (**1j**): Yellow solid; 36% yield; mp 145–147 ˚C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 2.4 Hz, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 7.96 (dd, *J* = 8.6, 2.5 Hz, 1H), 2.69 (s, 3H)*;* $^{13}$C NMR (101 MHz, $CDCl_3$) δ 199.5, 147.8, 145.0, 142.3, 125.6, 122.6, 99.3, 29.3; IR (KBr): 3779, 3538, 3082, 2916, 1704, 1567, 1415, 1264, 1113, 1014, 752, 494 cm$^{-1}$; HRMS (EI) calcd for $[M]^+$: $C_8H_6INO_3$ 290.9387, found 290.9388.

**Ethyl-3-acetyl-4-iodobenzoate** (**1k**): Yellow oil; 54% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 2.0 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.76 (dd, *J* = 8.2, 2.0 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 2.67 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 200.9, 165.3, 144.0, 141.3, 132.1, 130.6, 128.9, 97.0, 61.6, 29.4, 14.2; IR (KBr): 3782, 3542, 1695, 1447, 1338, 1142, 1019, 754, 548 cm$^{-1}$; HRMS (EI) calcd for $[M]^+$: $C_{11}H_{11}IO_3$ 317.9747, found 317.9749.

**1-(6-Iodobenzo[d][1,3]dioxol-5-yl)ethanone** (**1l**): Yellow solid; 65% yield; mp 93–94 ˚C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.06 (s, 1H), 6.05 (s, 2H), 2.58 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 199.5, 150.3, 148.2, 136.6, 120.6, 109.1, 102.3, 81.3, 29.2; IR (KBr): 2992, 2906, 1690, 1607, 1482, 1375, 1239, 1128, 1034, 930, 863, 754 cm$^{-1}$; HRMS (EI) calcd for $[M]^+$: $C_9H_7IO_3$ 289.9434, found 289.9435.

**1-(4-Iodo-[1,1'-biphenyl]-3-yl)ethanone** (**1m**): Yellow solid; 61% yield; mp 87–89 ˚C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 2.1 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.32 (dd, *J* = 8.2, 2.0 Hz, 1H), 2.65 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 201.9, 144.7, 141.4, 141.2, 139.1, 130.4, 129.1, 128.2, 126.9, 126.9, 89.5, 29.6; IR (KBr): 3120, 2920, 2767, 1692, 1452, 1355, 1224, 1010, 755, 690 cm$^{-1}$; HRMS (EI) calcd for $[M]^+$: $C_{14}H_{11}IO$ 321.9849, found 321.9848.

**1-(2-Iodo-5-(thiophen-3-yl)phenyl)ethanone** (**1n**): Yellow solid; 57% yield; mp 67–68 ˚C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 1.9 Hz, 1H), 7.49 (d, *J* = 1.4 Hz, 1H), 7.42 (dd, *J* = 4.7, 3.1 Hz, 1H), 7.33 (dd, *J* = 12.1, 3.7 Hz, 2H), 2.65 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 202.0, 144.9, 141.1, 140.2, 136.0, 129.5, 127.0, 126.1, 125.9, 121.4, 88.7, 29.6; IR (KBr): 3463, 2922, 2889, 1701, 1625, 1458, 1352, 1256, 1014, 780, 691 cm$^{-1}$; HRMS (EI) calcd for $[M]^+$: $C_{12}H_9IOS$ 327.9413, found 327.9412.

**1-(5-(Furan-2-yl)-2- iodophenyl)ethanone** (**1o**): Yellow solid; 52% yield; mp 94–96 ˚C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 2.0 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.37 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.71 (d, *J* = 3.3 Hz, 1H), 6.49 (dd, *J* = 3.3, 1.7 Hz, 1H), 2.65 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 201.7, 151.9, 144.5, 142.9, 141.1, 130.9, 126.6, 123.3, 112.0, 106.6, 88.7, 29.5; IR (KBr): 3119, 2922, 2855, 1766, 1695, 1555, 1356, 1293, 1090, 961, 820 cm$^{-1}$; HRMS (EI) calcd for $[M]^+$: $C_{12}H_9IO_2$ 311.9642, found 311.9644.

**1-(2-Iodo-5-(phenylethynyl)phenyl)ethanone** (**1p**): Yellow solid; 63% yield; mp 82–84 ˚C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 2.0 Hz, 1H), 7.46–7.39 (m, 2H), 7.27–7.20 (m, 3H), 7.11 (dd, *J* = 8.2, 2.0 Hz, 1H), 2.50 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 200.8, 143.9, 141.0, 134.3, 131.7, 131.1, 128.8, 128.5, 123.6, 122.5, 91.8, 90.7, 87.6, 29.4; IR (KBr): 3120, 2957, 2764, 1695, 1447, 1356, 1131, 1009, 754, 685 cm$^{-1}$; HRMS (EI) calcd for $[M]^+$: $C_{16}H_{11}IO$ 345.9849, found 345.9850.

**1-(4-Amino-2-iodophenyl)ethanone** (**1s**): 3-Iodo-phenylamine (6.4 mmol), $AlCl_3$ (1.07 g, 8.0 mmol), and anhydrous $CS_2$ (15 mL) were added to a 50-mL flask under argon atmosphere. To the mixture was dropwise added a solution of

acetyl chloride (0.628 g, 8.05 mmol) in anhydrous $CS_2$ (2.5 mL) at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred for 1 h. Then the mixture was heated to reflux for 12 h. After being cooled to room temperature, the resulting mixture was poured out to ice water and extracted with $CH_2Cl_2$ (3 × 30 mL). The organic layer was washed with saturated aqueous $Na_2CO_3$ (20 mL) and brine (20 mL) and then dried over $Na_2SO_4$. After evaporation of the solvent under *vacuum*, the residue was purified by column chromatography on silica gel to give the desired compounds **1s**. Yellow solid; 32% yield; mp 143–145 ˚C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.29 (s, 1H), 6.64-6.61 (m, 1H), 4.07 (br, 2H), 2.56 (s, 3H); $^{13}$C NMR (101 MHz, CDCl3) δ 197.6, 150.2, 132.1, 130.0, 127.5, 113.2, 94.2, 28.3; IR (KBr): 3700, 2917, 2849, 1674, 1581, 1370, 1264, 754, 538 cm $^{-1}$; HRMS (EI) calcd for $[M]^+$: $C_8H_8INO$ 260.9645, found 260.9646.

***N*-(4-Acetyl-3-iodophenyl)acetamide (1t)**: A solution of 1-(4-amino-2-iodophenyl)ethanone (**1s**) (3.7 mmol) in dichloromethane (15 mL) at room temperature was treated with triethylamine (4 mmol) and acetyl chloride (4.5 mmol). The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with EtOAc and washed with water. The aqueous layer was extracted with ethyl acetate. The combined extracts were rinsed with brine, dried over $MgSO_4$, and concentrated to provide the desired product **1t** after purification via flash column chromatography. Yellow solid; 76% yield; mp 168–170 ˚C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.04 (s, 1H), 7.65 (d, *J* = 8.0Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 2.51 (s, 3H), 2.13 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 200.35, 169.7, 141.5, 137.2, 131.9, 130.1, 118.9, 92.0, 29.1, 24.6; IR (KBr): 3652, 2934, 1719, 1584, 1356, 1238, 1013, 754, 542 cm$^{-1}$. HRMS (EI) calcd for $[M + H]^+$: $C_{10}H_{11}INO_2$ 302.3053, found 302.3077.

**1-(2-Iodo-4, 5-dimethylphenyl)ethanone (1u)**: Yellow oil; 60% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.28 (s, 1H), 2.60 (s, 3H), 2.24 (s, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 201.0, 141.8, 141.7, 140.8, 136.8, 130.2, 87.8, 29.2, 19.3, 19.2; IR (KBr): 3662, 3006, 2919, 2849, 1690, 1590, 1354, 1267, 754, 537 cm $^{-1}$; HRMS (EI) calcd for $[M]^+$: $C_{10}H_{11}IO$ 273.9849, found 273.9850.

**General procedure for the Pd-catalyzed tandem homocupling-Adol-dehydration of *ortho*-acylphenyl iodides**

To the solution of *ortho*-acylphenyl iodides 1 (0.2 mmol) in DMF (1.0 mL) were added $PdCl_2$ (5 mol %), $K_2CO_3$ (1.5 equiv) and DPPP (10 mol %) in a sealed tube under Ar atmosphere. The reaction mixture was stirred at 150 ˚C for 3 h, then cooled down to room temperature and filtered, and the corresponding filtrate was concentrated under *vacuum* and further purified by flash column chromatography on silica gel to furnish the target products 2.

**7-Methyl-5H-dibenzo[a,c][7]annulen-5-one (2a)**: Yellow oil; 80% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 6.7, 5.0 Hz, 2H), 7.69 – 7.61 (m, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.49 – 7.33 (m, 3H), 6.53 (s, 1H), 2.36 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 194.0, 144.8, 142.0, 137.5, 137.3, 135.7, 133.2, 131.9, 131.2, 130.0, 128.6, 128.1, 127.8, 127.3, 127.1, 24.4; IR (KBr): 3067, 2983, 2890, 1724, 1636, 1595, 1445, 1222, 1147, 1104, 989, 881, 750 cm$^{-1}$. HRMS (EI) calcd for $[M]^+$: $C_{16}H_{12}O$ 220.0883, found 220.0883.

**3, 7, 9-Trimethyl-5H-dibenzo[a,c][7]annulen-5-one (2b)**: Yellow oil; 72% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.52 (s, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 6.61 (s, 1H), 2.46 (s, 6H), 2.44 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.0, 143.8, 140.4, 136.9, 136.2, 134.2, 133.8, 133.8, 131.9, 131.1, 130.5, 128.8, 128.5, 126.4, 126.4, 23.5, 20.2, 19.8; IR (KBr): 3635, 2997, 2951, 1731, 1643, 1445, 1268, 1191, 1150, 986, 840, 752 cm$^{-1}$. HRMS (EI) calcd for $[M + H]^+$: $C_{18}H_{17}O$ 249.1273, found 249.1274.

**3, 9-Dimethoxy-7-methyl-5H-dibenzo[a,c][7]annulen-5-one (2c)**: Yellow oil; 80% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 10.9, 8.9 Hz, 2H), 7.30 (d, *J* = 2.8 Hz, 1H), 7.23 – 7.16 (m, 2H), 7.04 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.62 (s, 1H), 3.90 (d, *J* = 2.5 Hz, 6H), 2.44 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 193.5, 159.0, 158.4, 144.7, 142.3, 136.3, 132.9, 132.8, 131.2, 130.5, 130.4, 119.4, 114.5, 112.2, 109.8, 55.5, 55.4, 24.6; IR (KBr): 3547, 3002, 2839, 1702, 1602, 1483, 1271, 1001, 755 cm $^{-1}$. HRMS (EI) calcd for $[M + H]^+$: C18H17O3 281.1172, found 281.1172.

**3, 9-Diamino-7-methyl-5H-dibenzo[a,c][7]annulen-5-one (2d)**: Yellow solid; 64% yield; mp 155–156 ˚C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.5 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.00 (d, *J* = 2.2 Hz, 1H), 6.88 (d, *J* = 1.9 Hz, 1H), 6.85 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.75–6.71 (m, 1H), 6.49 (s, 1H), 3.79 (s, 4H), 2.31 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.9, 145.7, 145.0, 144.8, 141.8, 135.9, 132.4, 132.3, 130.8, 128.9, 118.7, 116.2, 112.5, 112.0, 24.7; IR (KBr): 3781, 3662, 3005, 2919, 1666, 1485, 1267, 1018, 754 cm$^{-1}$. HRMS (EI) calcd for $[M + H]^+$: $C_{16}H_{15}N_2O$ 251.1178, found 251.1179.

***N*, *N*'-(7-Methyl-5-oxo-5H-dibenzo[a,c][7]annulene-3,9-diyl)diacetamide (2e)**: Yellow solid; 72% yield; mp 129–131 ˚C; $^1$H NMR (400 MHz, DMSO) δ 10.26 (d, *J* = 19.1 Hz, 2H), 8.04 (s, 1H), 7.94 (d, *J* = 10.4 Hz, 2H), 7.84 (d, *J* = 7.0 Hz, 2H), 7.77 (d, *J* = 8.7 Hz, 1H), 6.65 (s, 1H), 2.40 (s, 3H), 2.11 (s, 6H). $^{13}$C NMR (101 MHz, DMSO) δ 192.6, 168.7, 144.5, 141.2, 139.0, 138.7, 135.0, 132.4, 131.9, 131.2, 130.5, 122.1, 119.6, 116.9, 116.0, 24.0, 24.0, 23.9; IR (KBr): 3700, 3462, 3008, 2922, 1662, 1268, 1022, 999, 825, 755 cm$^{-1}$. HRMS (EI) calcd for $[M + Na]^+$: $C_{20}H_{19}N_2O_3Na$ 357.1209, found 357.1204.

**3, 9-Dichloro-7-methyl-5H-dibenzo[a,c][7]annulen-5-one (2f)**: Yellow solid; 35% yield; mp 141–142 ˚C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 2.2 Hz, 1H), 7.70 (dd, *J* = 5.3, 3.2 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.60 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.46 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.63 (s, 1H), 2.44 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 191.0, 143.10, 141.7, 136.0, 134.0, 133.9, 133.7, 133.3, 132.7, 132.0, 130.4, 130.2, 127.8, 126.2, 23.3; IR (KBr): 3680, 2921, 2854, 1730, 1647, 1460, 1260, 1091, 1023, 804 cm$^{-1}$. HRMS (EI) calcd for $[M + H]^+$: $C_{16}H_{11}Cl_2O$ 289.0181, found 289.0181.

**1-Phenanthren-3-yl-ethanone (2g)**: Yellow oil; 35% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 2.59 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.1, 140.7, 139.1, 136.6, 130.7, 128.0, 127.9, 126.8, 126.1, 126.1, 125.9, 25.7; IR (KBr): 3009, 2947, 2852, 1680, 1622, 1501, 1324, 1233, 1009, 870, 765 cm$^{-1}$. MS (EI, 70eV): m/z= 220.09 $[M]^+$

**Diethyl 7-methyl-5-oxo-5H dibenzo[a,c][7]annulene-3,9-dicarboxylate (2i)**: Yellow solid; 46% yield; mp 122–124 ˚C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 1.6 Hz, 2H), 8.30 (dd, *J* = 8.3, 1.9 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 6.66 (d, *J* = 1.0 Hz, 1H), 4.45 (dd, *J* = 14.1, 7.0 Hz, 4H), 2.52 (d, *J* = 1.0 Hz, 3H), 1.44 (td, *J* = 7.1, 6.0 Hz, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 192.8, 165.7, 165.5, 144.6, 142.2, 140.4, 140.1, 136.1, 133.7, 132.2, 131.8, 130.8, 130.4, 129.1, 128.9, 128.7, 61.5, 24.4, 14.3; IR (KBr): 3462, 2923, 2855, 1718, 1650, 1285, 1252, 1196, 1115, 754, 685

cm$^{-1}$. HRMS (EI) calcd for [M + Na]$^+$: $C_{22}H_{20}O_5Na$ 387.1202, found 387.1219.

**2, 3, 9, 10-Bis (di-1, 3-benzodioxol)- 7-methyl-5H-dibenzo[a,c][7]annulen-5-one (2j)**: Yellow solid; 62% yield; mp 222–224 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 3.8 Hz, 1H), 7.14 (d, *J* = 5.4 Hz, 3H), 6.54 (s, 1H), 6.06 (d, *J* = 7.2 Hz, 4H), 2.38 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 191.8, 150.5, 148.0, 147.9, 147.2, 143.6, 137.0, 133.7, 132.7, 131.6, 130.3, 110.9, 109.2, 106.8, 106.4, 102.0, 101.8, 24.9; IR (KBr): 3838, 3581, 3008, 2923, 1668, 1591, 1482, 1267, 1037, 754, 537 cm$^{-1}$. HRMS (EI) calcd for [M]$^+$: $C_{18}H_{12}O_5$ 308.0679, found 308.0680.

**7-Methyl-3, 9-diphenyl-5H-dibenzo[a,c][7]annulen-5-one (2k)**: Yellow solid; 66% yield; mp 164–166 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.98 – 7.82 (m, 4H), 7.69 (d, *J* = 8.1 Hz, 3H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.47 (dd, *J* = 15.5, 7.7 Hz, 4H), 7.38 (dt, *J* = 12.3, 6.3 Hz, 2H), 6.68 (s, 1H), 2.51 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.8, 144.9, 142.2, 140.9, 140.7, 140.1, 139.4, 136.1, 136.1, 136.0, 133.4, 132.3, 130.6, 129.8, 129.0, 129.0, 127.9, 127.9, 127.4, 127.2, 127.1, 125.9, 125.8, 24.6. IR (KBr): 3638, 3005, 2919, 2848, 1722, 1665, 1455, 1268, 754, 696 cm$^{-1}$. HRMS (EI) calcd for [M]$^+$: $C_{28}H_{20}O$ 372.1509, found 372.1507.

**7-Methyl-3, 9-di(thiophen-3-yl)-5H dibenzo[a,c][7]annulen-5-one (2l)**: Yellow solid; 80% yield; mp 226–227 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.82 (s, 1H), 7.76 – 7.70 (m, 2H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.49 (d, *J* = 1.1 Hz, 1H), 7.43 (s, 1H), 7.38 (d, *J* = 4.9 Hz, 1H), 7.32 (dd, *J* = 9.0, 5.9 Hz, 3H), 6.57 (s, 1H), 2.39 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.7, 144.8, 142.1, 141.2, 140.7, 136.0, 135.9, 135.8, 135.6, 135.3, 133.3, 132.2, 130.5, 129.1, 126.7, 126.7, 126.6, 126.2, 126.1, 125.0, 124.9, 121.3, 121.2, 24.6. IR (KBr): 3464, 2901, 2778, 1640, 1425, 1358, 1147, 1036, 780, 664 cm$^{-1}$. HRMS (EI) calcd for [M + H]$^+$: $C_{24}H_{17}OS_2$ 385.0715, found 385.0740.

**3,9-Di(furan-2-yl)-7-methyl-5H dibenzo[a,c][7]annulen-5-one (2m)**: Yellow solid; 61% yield; mp 188–189 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.04 (s, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.76 (q, *J* = 8.6 Hz, 2H), 7.55 (s, 2H), 6.80 (d, *J* = 15.9 Hz, 2H), 6.68 (s, 1H), 6.54 (s, 2H), 2.53 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.5, 152.9, 152.7, 144.9, 142.8, 142.7, 142.0, 136.0, 136.0, 135.8, 133.2, 132.0, 130.7, 130.3, 130.2, 126.3, 123.9, 122.4, 122.2, 111.9, 111.9, 106.5, 106.2, 24.6. IR (KBr): 3546, 3402, 2922, 1642, 1428, 1359, 1054, 742 cm$^{-1}$. HRMS (EI) calcd for [M + Na]$^+$: $C_{24}H_{16}O_3Na$ 375.0991, found 375.1001.

**7-Methyl-3, 9-bis(phenylethynyl)-5H-dibenzo[a,c][7]annulen-5-one (2n)**: Yellow solid; 48% yield; mp 174–175 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 1.2 Hz, 1H), 7.89 (d, *J* = 1.4 Hz, 1H), 7.78 (dd, *J* = 8.7, 4.9 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.63 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.57 (ddd, *J* = 9.2, 6.6, 3.0 Hz, 4H), 7.42 – 7.34 (m, 6H), 6.65 (d, *J* = 0.7 Hz, 1H), 2.48 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 192.9, 144.4, 141.8, 136.6, 136.3, 135.9, 133.8, 133.5, 131.8, 131.7, 131.7, 131.4, 130.6, 130.5, 130.0, 128.7, 128.6, 128.4, 128.4, 123.8, 123.3, 122.8, 122.8, 91.8, 91.2, 88.5, 88.2, 24.5. IR (KBr): 3480, 3120, 2922, 2780, 1750, 1690, 1510, 1440, 1358, 1120, 864, 687 cm$^{-1}$. HRMS (EI) calcd for [M]$^+$: $C_{32}H_{20}O$ 420.1509, found 420.1509.

**2, 7, 10-Trimethyl-5H-dibenzo[a,c][7]annulen-5-one (2o)**: Yellow oil; 74% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.59 (s, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 6.60 (s, 1H), 2.53 (s, 3H), 2.49 (s, 3H), 2.45 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.6, 144.7, 141.5, 139.7, 138.5, 137.5, 137.4, 133.2, 132.7, 132.3, 130.5, 129.1, 128.6, 127.6, 127.1, 24.5, 21.6, 21.3; IR (KBr): 3441, 2921, 2855, 1644, 1577, 1445, 1358, 1301, 1035, 823, 743 cm$^{-1}$. HRMS (EI) calcd for [M + Na]$^+$: $C_{18}H_{16}ONa$ 271.1093, found 271.1093.

**2, 10-Dimethoxy-7-methyl-5H-dibenzo[a,c][7]annulen-5-one (2p)**: Yellow oil; 75% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.7 Hz, 1H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.17 (s, 2H), 6.99 (d, *J* = 8.7 Hz, 1H), 6.94 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.44 (s, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 2.32 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 192.4, 161.7, 159.2, 144.1, 139.3, 139.2, 135.5, 131.9, 130.1, 129.0, 116.8, 114.9, 114.2, 113.7, 55.5, 55.4, 24.6; IR (KBr): 3454, 2936, 2854, 1637, 1594, 1454, 1359, 1298, 1237, 1028, 857, 820 cm$^{-1}$. HRMS (EI) calcd for [M + H]$^+$: $C_{18}H_{17}O_3$ 281.1172, found 281.1174.

**2, 10-Diamino-7-methyl-5H-dibenzo[a,c][7]annulen-5-one (2q)**: Yellow solid; 72% yield; mp 202–204 °C; $^1$H NMR (400 MHz, DMSO) δ 7.47 (dd, *J* = 10.0, 8.6 Hz, 2H), 6.95 (d, *J* = 2.3 Hz, 1H), 6.89 (d, *J* = 2.0 Hz, 1H), 6.73 (ddd, *J* = 8.4, 4.3, 2.3 Hz, 2H), 6.25 (s, 1H), 5.87 (s, 4H), 2.30 (s, 3H). $^{13}$C NMR (101 MHz, DMSO) δ 190.0, 151.7, 149.1, 143.5, 139.6, 139.2, 130.3, 129.5, 128.7, 123.8, 115.4, 113.9, 113.6, 113.2, 24.3; IR (KBr): 3781, 3636, 2922, 1665, 1590, 1315, 1117, 995, 754 cm$^{-1}$. HRMS (EI) calcd for [M + H]$^+$: $C_{16}H_{15}N_2O$ 251.1178, found 251.1178.

***N*, *N*'-(7-methyl-5-oxo-5H-dibenzo[a,c][7]annulene-2, 10-diyl)diacetamide (2r)**: Yellow solid; 68% yield; mp 132–134 °C; $^1$H NMR (400 MHz, DMSO) δ 10.42 (s, 1H), 10.32 (s, 1H), 8.15 (s, 1H), 8.07 (s, 1H), 7.89–7.73 (m, 3H), 7.65 (d, *J* = 8.5 Hz, 1H), 6.53 (s, 1H), 2.40 (s, 3H), 2.12 (d, *J* = 9.2 Hz, 6H). $^{13}$C NMR (101 MHz, DMSO) δ 191.4, 169.0, 168.8, 144.3, 142.1, 139.6, 137.6, 137.4, 136.5, 131.8, 130.1, 128.4, 128.2, 120.9, 119.1, 118.8, 118.7, 24.1, 24.0, 23.9; IR (KBr): 3636, 2923, 1722, 1667, 1489, 1324, 1268, 1021, 755, 537 cm$^{-1}$. HRMS (EI) calcd for [M + Na]$^+$: $C_{20}H_{18}N_2O_3Na$ 357.1209, found 357.1215.

**2, 3, 7, 9, 10-Pentamethyl-5H-dibenzo[a,c][7]annulen-5-one (2s)**: Yellow oil; 78% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.1 Hz, 2H), 7.54 (s, 1H), 7.47 (s, 1H), 6.57 (d, *J* = 0.9 Hz, 1H), 2.42 (d, *J* = 1.0 Hz, 3H), 2.41 (s, 3H), 2.38 (s, 3H), 2.36 (d, *J* = 2.3 Hz, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.6, 144.7, 140.4, 139.5, 137.4, 136.8, 136.1, 135.3, 135.1, 133.3, 132.6, 132.6, 130.9, 128.3, 128.1, 24.6, 20.0, 19.7, 19.6, 19.2; IR (KBr): 3436, 2920, 2854, 1640, 1587, 1452, 1360, 1054, 742 cm$^{-1}$. HRMS (EI) calcd for [M + Na]$^+$: $C_{20}H_{20}ONa$ 299.1406, found 299.1423.

**7-Ethyl-6-methyl-5H-dibenzo[a,c][7]annulen-5-one (2t)**: Yellow oil; 34% yield; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.9 Hz, 1H), 7.68–7.65 (m, 1H), 7.64–7.57 (m, 2H), 7.53–7.45 (m, 2H), 7.39 (ddt, *J* = 14.9, 7.3, 3.7 Hz, 2H), 2.76 (q, *J* = 7.5 Hz, 2H), 2.18 (s, 3H), 1.08 (t, *J* = 7.5 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 201.3, 143.5, 142.2, 138.5, 136.9, 136.8, 136.7, 130.9, 130.7, 128.3, 127.7, 127.5, 127.3, 127.0, 125.8, 27.0, 17.3, 13.1; IR (KBr): 3439, 2919, 2852, 1649, 1457, 1359, 1054, 987, 741 cm$^{-1}$. HRMS (EI) calcd for [M + Na]$^+$: $C_{18}H_{16}ONa$ 271.1093, found 271.1103.

**7-Benzyl-6-phenyl-5H-dibenzo[a,c][7]annulen-5-one (2u)**: Yellow solid; 40% yield; mp 75–77 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.8 Hz, 1H), 7.64 (dt, *J* = 8.7, 3.8 Hz, 1H), 7.60–7.51 (m, 2H), 7.44 (dd, *J* = 13.7, 5.4 Hz, 1H), 7.37 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.29–7.19 (m, 7H), 7.02–6.91 (m, 3H), 6.76 (d, *J* = 6.9 Hz, 2H), 3.96 (s, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 199.1, 145.9, 144.8, 139.3, 138.6, 137.6, 137.5, 136.5, 135.5, 131.1, 130.9, 129.1, 128.5, 128.4, 128.2, 128.0, 128.0, 127.7, 127.7, 127.5, 125.8, 125.2, 39.1. IR (KBr): 3572, 2441, 2922, 2853, 1644, 1434, 1359, 1067, 737, 696 cm$^{-1}$. HRMS (EI) calcd for [M + Na]$^+$: $C_{28}H_{20}ONa$ 395.1465, found 395.1438.

**Mechanistic studies about this transformation**

**4-(2-Acetylphenyl)-7-methyl-5H-dibenzo[a,c] [7] annulen-5-one (3a)**: To the solution of *ortho*-acylphenyl bromide 1 (0.2 mmol) in DMF (1.0 mL) were added $PdCl_2$ (5 mol %), $K_2CO_3$ (1.5 equiv) and DPPP (10 mol %) in a sealed tube under Ar atmosphere. The reaction mixture was stirred at 150 ˚C for 3 h, then cooled down to room temperature and filtered, and the corresponding filtrate was concentrated under *vacuum* and further purified by flash column chromatography on silica gel to furnish the target products **3a**.Yellow solid; 39% yield; mp 125–126 ˚**C**; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.73–7.63 (m, 3H), 7.58 (dd, *J* = 5.9, 3.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.39 (ddd, *J* = 9.3, 4.2, 1.6 Hz, 3H), 7.37–7.32 (m, 1H), 7.21 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.15–7.13 (m, 1H), 6.30 (d, *J* = 1.0 Hz, 1H), 2.29 (d, *J* = 1.0 Hz, 3H), 2.19 (s, 3H; $^{13}$CNMR (101 MHz, $CDCl_3$) δ 202.1, 195.6, 141.7, 140.7, 140.0, 138.5, 137.2, 137.1, 136.1, 133.4, 132.0, 130.6, 130.2, 129.7, 129.4, 128.2, 128.1, 127.9, 127.4, 126.5, 29.5, 23.3; HRMS (EI) calcd for $[M + Na]^+$: $C_{24}H_{18}O_2Na$ 361.1199, found 361.1207; IR (KBr): 3700, 2918, 2846, 1758, 1669, 1481, 1385, 1266, 1128, 755 $cm^{-1}$.

**7-Hydroxy-7-methyl-6, 7-dihydro-5H-dibenzo[a,c]|[7]annulen-5-one (3b)**: To the solution of *ortho*-acylphenyl iodide (**1c**) (0.2 mmol) in DMF (1.0 mL) were added $PdCl_2$ (5 mol %), $K_2CO_3$ (1.5 equiv) and DPPP (10 mol %) in a sealed tube under Ar atmosphere. The reaction mixture was stirred at 150 ˚C for 1.5 h, then cooled down to room temperature and filtered, and the corresponding filtrate was concentrated under *vacuum* and further purified by flash column chromatography on silica gel to furnish the target products **3b**. Yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 6.2, 1.9 Hz, 2H), 7.59 (td, *J* = 7.7, 1.3 Hz, 1H), 7.46–7.32 (m, 5H), 3.17 (q, *J* = 19.1 Hz, 2H), 2.80 (s, 1H), 1.54 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 202.6, 143.9, 140.2, 137.7, 136.4, 132.9, 131.8, 129.7, 128.5, 128.3, 128.3, 127.8, 71.0, 61.2, 28.2; HRMS (EI) calcd for $[M]^+$: $C_{16}H_{14}O_2$ 238.0988, found 238.0989; IR (KBr): 3686, 2975, 2865, 1722, 1669, 1543, 1458, 1269, 1052, 754 $cm^{-1}$.

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## Notes and references

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