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Synthesis of Chrysene Derivatives via Copper-Catalyzed One-Pot Dimerization of 2-Alkynyl-1-acetylbenzenes

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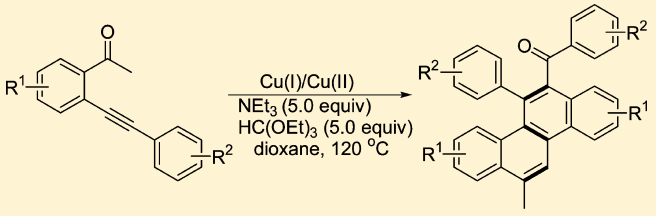
Supporting Information

ABSTRACT: An efficient route for highly substituted chrysene derivatives via operationally simple copper-catalyzed one-pot dimerization of 2-alkynyl-1-acetylbenzenes is described.



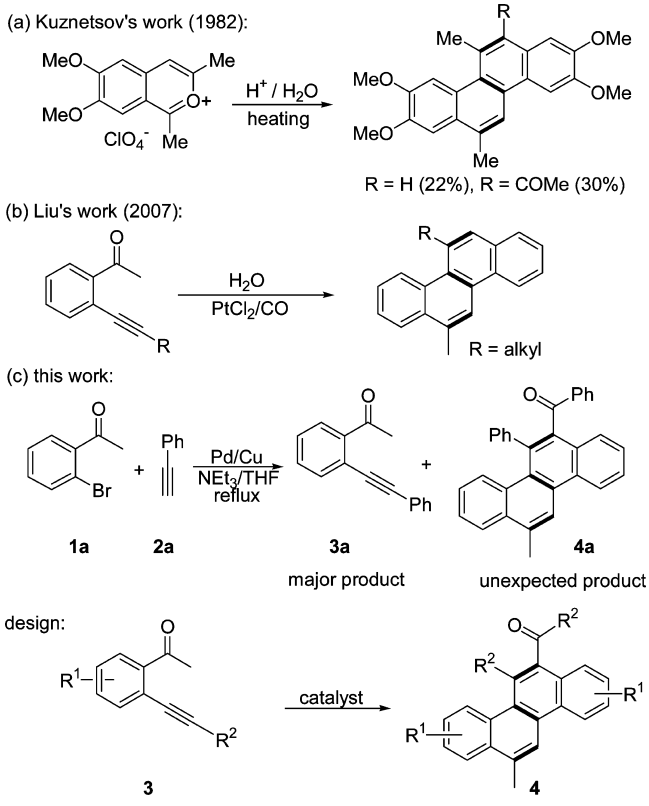
INTRODUCTION

As an important class of polycyclic aromatic hydrocarbons (PAHs),[1] chrysene derivatives are attracting renewed attention due to their unique electron properties.[2,3] With good hole- and electron-transport capabilities, these compounds can be used as base molecules for electronic devices such as field-effect transistors (FETs).[4] In addition, they are new candidates for blue emitters in organic light-emitting diodes (OLEDs) because of their high fluorescence quantum efficiency.[5,6]

Traditional procedures for chrysene derivatives usually required complex starting materials or tedious multistep reactions but with low yield.[3,6−9] Consequently, it is crucial to find practical and atom-economical synthetic methods for chrysene derivatives from simple starting materials in materials chemistry and fine chemical industries. In 1982, Kuznetsov et al. reported a unique method for chrysene derivatives synthesis via acid-promoted dimerization of benzopyrylium salts (Scheme 1a).[8] However, this procedure was not synthetically useful because of its poor chemoselectivity and the difficulty in preparing benzopyrylium salts.[9] In 2007, Liu and co-workers reported a one-pot approach to synthesize chrysenes via Pt(II)-catalyzed hydrative dimerization of 2-alkynyl-1-acetylbenzenes (Scheme 1b).[10] Although Liu's synthetic method is much more efficient than traditional methods, its substituent scope is limited (only substrates with R = alkyl are investigated). In addition, application of the procedure would be impeded by the costly platinum catalyst.

2-Alkynyl-1-acetylbenzenes are a widely investigated class of bifunctional substrates[11,12] for their convenient synthesis via the Sonogashira reaction[13] and diverse transformations to cyclic compounds.[12] During synthesis of 2-phenylethynyl-1-acetylbenzene (**3a**) from 1-(2-bromophenyl)ethanone (**1a**) and ethynylbenzene (**2a**) under the classical Sonogashira cross-coupling reaction conditions, we found unexpectedly a small amount of chrysene derivative (**4a**), which obviously derived from dimerization of **3a** (Scheme 1c). In view of the promising applications of chrysene derivatives and our continuing interest in transition-metal-catalyzed cascade alkyne annulations,[14] we embarked on developing this side reaction as an efficient method for chrysene derivative synthesis.

Scheme 1. Synthesis of Chrysene Derivatives via 2-Alkynyl-1-acetylbenzenes



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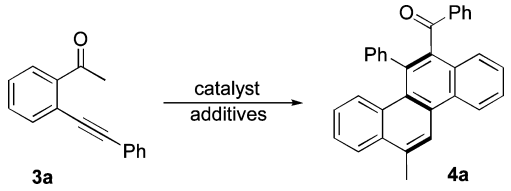
RESULTS AND DISCUSSION

We employed 2-phenylethynyl-1-acetylbenzene (**3a**) as the substrate to optimize the reaction conditions. The results are outlined in Table 1. We initially tried the transformation of **3a**

Table 1. Optimization of Reaction Conditions[a]



3a **4a**

entry	catalyst (%)	additives (equiv)	yield[b] (%)
1	$Pd(OAc)_2$ (**2**), CuI (**4**)	NEt_3 (5.0), PPh_3 (0.04)	9[c]
2	$Pd(OAc)_2$ (**2**), CuI (**4**)	NEt_3 (5.0), PPh_3 (0.04)	45
3	$Pd(OAc)_2$ (**2**)	PPh_3 (0.04)	0
4	$Pd(OAc)_2$ (**2**)	NEt_3 (5.0)	0
5	CuI (**4**)	PPh_3 (0.04)	0
6	CuI (**4**)	NEt_3 (5.0)	60
7	CuI (**4**)	none	trace
8	CuCl (**4**)	NEt_3 (5.0)	58
9	CuBr (**4**)	NEt_3 (5.0)	59
10	$CuCl_2$ (**4**)	NEt_3 (5.0)	62
11	$CuCl_2$ (**4**)	Cs_2CO_3 (1.0)	5
12	$CuCl_2$ (**4**)	KOH (1.0)	trace
13	$CuCl_2$ (**4**)	TMEDA (5.0)	53
14[d]	**$CuCl_2$ (4)**	**NEt_3 (5.0), $HC(OEt)_3$ (5.0)**	**88**
15	$CuCl_2$ (**4**)	NEt_3 (5.0), $MgSO_4$ (2.0)	71
16	$CuCl_2$ (**4**)	NEt_3 (5.0), MS (100 mg)	76
17[d]	CuI (**4**)	NEt_3 (5.0), $HC(OEt)_3$ (5.0)	83

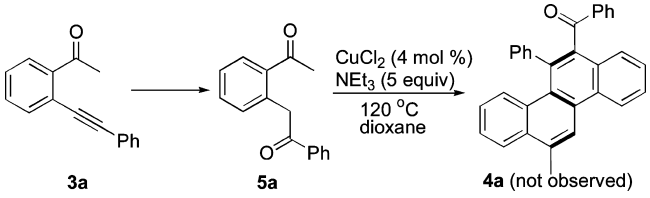
[a]Unless otherwise noted, the reactions were carried out with 0.5 mmol of **1a** in 1.0 mL of dioxane at 120 °C for 12 h. Abbreviations: TMEDA, *N,N,N′,N′*-tetramethylethane-1,2-diamine; MS, 4 Å molecular sieves. [b]Isolated yield. [c]In 1.0 mL of THF at 90 °C for 24 h. [d]Almost the same results were obtained under N_2 or air atmosphere.

under the classical Sonogashira cross-coupling conditions with the use of 2 mol % of $Pd(OAc)_2$ and 4 mol % of CuI as catalysts, 4 mol % of PPh_3 as ligand, NEt_3 as base, and THF as solvent at 90 °C under N_2 atmosphere; unfortunately, the conversion of **3a** was very sluggish even with a prolonged reaction time (24 h), and the desired **4a** was obtained in 9% yield only (Table 1, entry 1). To our delight, reaction in dioxane at an elevated temperature (120 °C) gave an increased yield (45%, entry 2).

In order to figure out which species were catalytic active in the transformation, we used either $Pd(OAc)_2$ (entries 3 and 4) or CuI (entries 5 and 6) as catalyst with PPh_3 or NEt_3 as additive. It was found that the CuI/NEt_3 catalytic system could catalyze the formation of **4a** in good yield (60%), and in the absence of NEt_3, only a trace amount of **4a** formed (entry 7). Other cuprous halides such as CuCl and CuBr, as well as $CuCl_2$, showed similar catalytic activities in the presence of Et_3N (entries 8−10). Therefore, with the use of $CuCl_2$ as catalyst, the role of some bases was examined. It was disclosed that inorganic bases such as Cs_2CO_3 (entry 11) and KOH (entry 12) failed to promote the transformation, and TMEDA was less efficient than NEt_3 (entry 13).

Inspired by Liu's work,[10] we considered that the formation of **4a** might occur via a hydrolysis/dehydration mechanism with diketone **5a** as intermediate (Scheme 2), although the reactivity

Scheme 2. Synthesis of Chrysene Derivatives via 2-(2-Acetylphenyl)-1-phenylethanone



3a **5a** **4a** (not observed)

of (arylalkynyl)acetophenones like **3a** was not reported in their catalytic system. However, no desired product **4a** was detected by using diketone **5a** as starting material under a $CuCl_2$/NEt_3 catalytic system (conditions of entry 10). These results indicated that diketone **5a** is not the crucial intermediate for the formation of **4a**, and the hydrolysis of **3a** to **5a** in situ may be a side reaction resulting in the low yield of **4a**. Therefore, we repeated the reaction with the addition of 5.0 equiv of $HC(OEt)_3$ as dehydrating agent to consume in situ generated water. Gratifyingly, the yield of **4a** was greatly improved (88%, entry 14), and under either N_2 or air atmosphere, the catalytic system showed almost the same catalytic activity. Other dehydrating agents such as anhydrous $MgSO_4$ (entry 15) and 4 Å molecular sieves (entry 16) were also examined, and both of them could improve the yield of **4a** under air atmosphere but showed less efficiency than $HC(OEt)_3$. In addition, CuI also showed the high catalytic activity in the presence of $HC(OEt)_3$ under either N_2 or air atmosphere (entry 17).

With the optimal reaction conditions in hand, we employed various 2-alkynyl-1-acetylbenzenes to explore the generality of the dimerization reaction under air atmosphere (Table 2). The reactions proceeded smoothly by using various substrates **3** having electron-donating groups (EDGs, entries 2−5) or electron-withdraw groups (EWGs, entries 6−11) at the *para*-position of the phenylethynyl group. Entries 2−11 show the suitability of the reaction with alternation of R^2 group. When the R^2 group was an alkyl group such as Me (**3b**, 42%), *n*-Pr (**3c**, 39%), and *t*-Bu (**3d**, 62%), respectively, the reactions gave the desired product in moderate yields. When R^2 was a MeO group, the corresponding product **4e** was obtained in good yield (70%). The reactions of substrate **3** with EWGs in phenylethynyl groups such as 4-F-Ph (**3f**, 53%), 4-Cl-Ph (**3g**, 57%), 4-Br-Ph (**3h**, 60%), 4-MeC(O)-Ph (**3i**, 55%), 4-NC-Ph (**3j**, 41%), and 4-phenyl-Ph (**3k**, 58%) also gave moderate to good yields. In addition, the desired products could be obtained in moderate yields even when the substituents bonded to the *meta*-position of the benzene ring (**4l**, 59%; **4m**, 54%; **3n**, 50%). The molecular structure of **4l** was confirmed by an X-ray diffraction study.[15]

When R^1 was fluorine atom and R^2 was H (**3o**), Cl (**3p**), or MeO (**3q**), the corresponding chrysene derivatives formed in moderate yields (entries 15−17). Furthermore, when thienyl- (**3r**, entry 18) and naphthyl-substituted (**3s**, entry 19) were used, the reactions also occurred to afford chrysene derivatives in 28% and 67% yield, respectively.

Furthermore, when 2′-(trimethylsilylethynyl)acetophenone (**3t**) was used, an unexpected desilicated product **4t** was isolated in 34% yield (eq 1). It was worth noting that the catalytic system could be applied to synthesize the hetero-aromatic analogue **4u** with a satisfactory yield (64%, eq 2).

However, unfortunately, when an (alkylalkynyl)aceto-phenone (a favorable substrate in the catalytic system of $PtCl_2$/CO[10]) such as 2′-(1-octynyl)acetophenone was either

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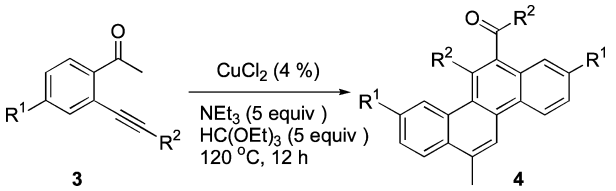
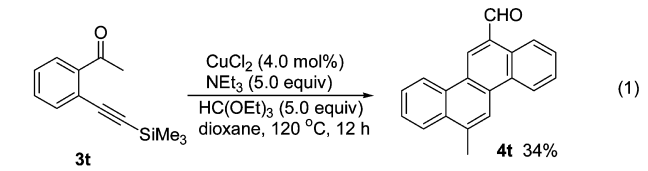
Table 2. Study of Substrate Scope[a]



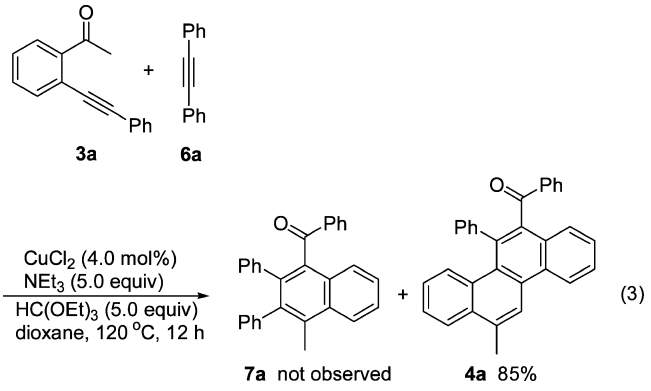
entry		substrate		yield[b] (%)
1	**3a**	R^1 = H, R^2 = Ph	**4a**	88
2	**3b**	R^1 = H, R^2 = 4-MeC_6H_4	**4b**	42
3	**3c**	R^1 = H, R^2 = 4-*n*-PrC_6H_4	**4c**	39
4	**3d**	R^1 = H, R^2 = 4-*t*-BuC_6H_4	**4d**	62
5	**3e**	R^1 = H, R^2 = 4-MeOC_6H_4	**4e**	70
6	**3f**	R^1 = H, R^2 = 4-FC_6H_4	**4f**	53
7	**3g**	R^1 = H, R^2 = 4-ClC_6H_4	**4g**	57
8	**3h**	R^1 = H, R^2 = 4-BrC_6H_4	**4h**	60
9	**3i**	R^1 = H, R^2 = 4-MeC(O)C_6H_4	**4i**	55
10	**3j**	R^1 = H, R^2 = 4-NCC_6H_4	**4j**	41
11	**3k**	R^1 = H, R^2 = 4-PhC_6H_4	**4k**	58
12	**3l**	R^1 = H, R^2 = 3-MeC_6H_4	**4l**	59
13	**3m**	R^1 = H, R^2 = 3-MeOC_6H_4	**4m**	54
14	**3n**	R^1 = H, R^2 = 3,4,5-tri-MeOC_6H_2	**4n**	50
15	**3o**	R^1 = F, R^2 = Ph	**4o**	51
16	**3p**	R^1 = F, R^2 = 4-ClC_6H_4	**4p**	62
17	**3q**	R^1 = F, R^2 = 4-MeOC_6H_4	**4q**	45
18	**3r**	R^1 = H, R^2 = thiophene-2-yl	**4r**	28
19	**3s**	R^1 = H, R^2 = naphthalen-2-yl	**4s**	67

[a]Reaction conditions: **3** (0.5 mmol), $CuCl_2$ (4 mol %), NEt_3 (5.0 equiv), $HC(OEt)_3$ (5.0 equiv), dioxane (1.0 mL), 12 h. [b]Isolated yield.



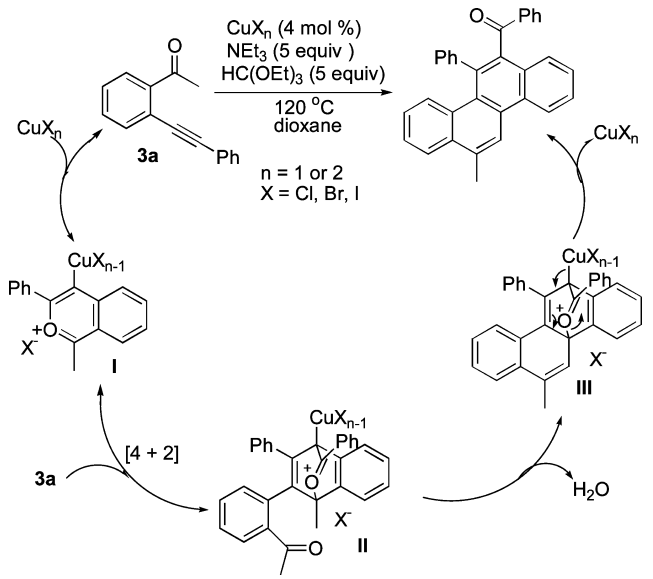
subjected to the optimized conditions (indicated in entry 14 of Table 1) or used in the absence of $HC(OEt)_3$ or in the presence of water (5.0 equiv), the corresponding chrysene did not form at all. Instead, in the former case, two products having the same molecular weight (m/z = 228) as the starting substrate were determined by GC–MS, and their possible structures might result from the intramolecular cyclization of the starting substrate. In the latter case, a considerable amount of hydrolysis compound (m/z = 246) of the starting substrate was found in the reaction mixture.[16]

In addition, as shown in Scheme 2, diketone compound **5a** could not afford the desired chrysene **4a**, indicating that the hydrolysis–dehydration mechanism does not correspond to the present transformation. In order to gain more information to understand the mechanism formation of **4**, the reaction of **3a** with diphenylacetylene (**6a**) was investigated (eq 3). It was found that the cross-adduct product **7a** did not form at all, and



we can conclude that the dehydration reaction was a crucial and irreversible step in the formation of **4a** as shown in Scheme 3.

Scheme 3. Proposed Mechanism



Therefore, on the basis of previous studies of 2-phenylethynyl-1-acetylbenzene[11,17] and our experimental results, we propose a plausible mechanism for the formation of chrysene **4a** as shown in Scheme 3. First, active intermediate isobenzopyrylium **I** is generated reversibly with the aid of copper salt from 2-phenylethynyl-1-acetylbenzene **3a**, and then intermolecular Diels–Alder reaction occurs between isobenzopyrylium **I** and **3a** to afford intermediate **II**, which subsequently undergoes the intramolecular dehydration reaction to give intermediate **III** irreversibly, and finally, the transformation of **III** occurs to construct the chrysene ring **4a**.

CONCLUSION

In conclusion, we have developed an alternative copper-catalyzed dimerization of 2-alkynyl-1-acetylbenzene to synthesize chrysene derivatives, which are promising π-extended molecules for functional materials. The present procedure provides a one-pot route to obtain polycyclic aromatic hydrocarbon from readily available substrates.

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EXPERIMENTAL SECTION

General Methods. All commercial reagents were analytically pure and used without further purification. Nuclear magnetic resonance (NMR) spectra were recorded using $CDCl_3$ as solvent at 298 K. ^1H NMR (300 MHz) chemical shifts (δ) were referenced to internal standard TMS (for ^1H, δ = 0.00 ppm). ^{13}C NMR (75 and 100 MHz) chemical shifts were referenced to internal solvent $CDCl_3$ (for ^{13}C, δ = 77.16 ppm). HRMS experiments were performed on a high-resolution magnetic sector mass spectrometer. The melting points are uncorrected.

Typical Experimental Procedure for the Synthesis of ***3a****.* A mixture of 1-(2-bromophenyl)ethanone (1990.4 mg, 10.0 mmol), $Pd(PPh_3)_2Cl_2$ (70.1 mg, 0.1 mmol), CuI (38.1 mg, 0.2 mmol), NEt_3 (15 mL), phenylacetylene (1630.0 mg, 15 mmol), and THF (15 mL) was heated at 90 °C (oil bath temperature) with stirring in a 50 mL screw-capped thick-walled Pyrex tube under N_2 atmosphere for 24 h. After removal of the solvent under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 100:0 to 98:2) as eluent to afford 2-(phenylethynyl)-1-acetylbenzene (**3a**) in 82% yield (1804.0 mg).

Typical Experimental Procedure for Synthesis of ***4a****.* A mixture of 2-(phenylethynyl)-1-acetylbenzene (**3a**, 110.0 mg, 0.5 mmol), $CuCl_2$ (2.7 mg, 0.02 mmol), NEt_3 (253.0 mg, 2.5 mmol), $HC(OEt)_3$ (371.0 mg, 2.5 mmol), and dioxane (1.0 mL) was heated at 120 °C (oil bath temperature) with stirring in a 50 mL screw-capped thick-walled Pyrex tube under air atmosphere for 12 h. After removal of the solvent under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 100:0 to 96:4) as eluent to give 12-methyl-5-phenyl-6-benzoylchrysene **4a** in 88% yield (93.0 mg).

Characterization Data of the Chrysene Derivatives. *12–Methyl-5-phenyl-6-benzoylchrysene (****4a****):* white solid (88%, 93.0 mg); mp 208–211 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.90 (d, J = 8.5 Hz, 1H), 8.69 (s, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.86–7.62 (m, 4H), 7.60–7.31 (m, 6H), 7.20–7.16 (m, 3H), 7.14–7.06 (m, 1H), 6.95 (t, J = 7.5 Hz, 1H), 6.80 (d, J = 7.5 Hz, 1H), 2.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.2, 141.7, 138.1, 137.2, 135.0, 134.7, 133.3, 133.0, 131.6, 131.2, 130.5, 130.2, 129.5, 129.4, 129.1, 128.9, 128.3, 128.2, 127.4, 127.4, 127.1, 126.2, 126.1, 126.0, 124.6, 124.3, 123.7, 121.6, 20.8; HRMS (ESI) calcd for $C_{32}H_{22}O$ $[M + H]^+$ 423.1743, found 423.1744.

*12-Methyl-5-(4-methylphenyl)-6-(4-methylbenzoyl)chrysene (****4b****):* yellow solid (42%, 47.4 mg); mp 218–220 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.87 (d, J = 8.5 Hz, 1H), 8.67 (s, 1H), 8.10 (dd, J = 8.3, 1.0 Hz, 1H), 7.87–7.65 (m, 3H), 7.57–7.41 (m, 5H), 7.26 (s, 1H), 7.15–7.06 (m, 1H), 7.01 (d, J = 8.0 Hz, 2H), 7.00–6.71 (m, 2H), 2.93 (s, 3H), 2.31 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.7, 143.9, 138.7, 137.4, 136.9, 135.8, 135.0, 134.5, 133.3, 131.3, 130.1, 129.7, 129.5, 129.5, 129.2, 129.0, 127.2, 126.9, 126.4, 126.1, 125.9, 124.6, 124.2, 123.6, 121.6, 21.8, 21.4, 20.8; HRMS (ESI) calcd for $C_{34}H_{26}O$ $[M + H]^+$ 451.2056, found 451.2057.

*12–Methyl-5-(4-propylphenyl)-6-(4-propylbenzoyl)chrysene (****4c****):* white solid (39%, 49.5 mg); mp 157–158 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.84 (d, J = 8.5 Hz, 1H), 8.64 (s, 1 H), 8.05 (d, J = 8.1 Hz, 1H), 7.78 (dd, J = 8.1, 5.7 Hz, 2H), 7.67 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.5 Hz, 2H), 7.44 (t, J = 7.5 Hz, 1H), 7.33 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 7.5 Hz, 1H), 7.02 (t, J = 7.7 Hz, 1H), 6.90 (d, J = 8.1 Hz, 2H), 6.70–6.61 (m, 2H). 2.89 (s, 3H), 2.49 (t, J = 7.6 Hz, 2H), 2.47 (t, J = 7.6 Hz, 2H), 1.53–1.48 (m, 4H), 0.82 (t, J = 7.1 Hz, 3H), 0.80 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.0, 148.3, 141.6, 139.0, 137.4, 136.1, 135.0, 134.5, 133.3, 131.3, 130.4, 130.1, 129.6, 129.5, 129.3, 129.0, 128.5, 128.2, 127.2, 126.9, 126.3, 126.1, 125.9, 124.5, 124.2, 123.6, 121.6, 38.0, 37.6, 24.4, 24.1, 20.8, 13.7, 13.4; HRMS (ESI) calcd for $C_{40}H_{38}O$ $[M + H]^+$ 535.29954, found 535.29926; HRMS (ESI) calcd for $C_{38}H_{34}O$ $[M + H]^+$ 507.2682, found 507.2687.

*12–Methyl-5-(4-tert-butylphenyl)-6-(4-tert-butylbenzoyl)-chrysene (****4d****):* white solid (62%, 78.6 mg); mp 206–208 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.85 (d, J = 8.5 Hz, 1H), 8.65 (s, 1H), 8.05 (d, J = 8.2 Hz, 1H), 7.90–7.79 (m, 2H), 7.68 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.4 Hz, 2H), 7.47–7.35 (m, 2H), 7.28–7.22 (m, 2H), 7.09–7.00 (m, 3H), 6.82 (d, J = 7.9 Hz, 1H), 6.58 (d, J = 7.9 Hz, 1H), 2.89 (s, 3H), 1.21 (s, 9H), 1.18 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.2, 156.3, 150.2, 138.8, 137.7, 136.0, 135.1, 134.5, 133.3, 131.3, 131.1, 130.4, 130.2, 129.5, 129.3, 129.2, 129.0, 127.3, 126.9, 126.3, 126.1, 125.9, 125.5, 125.0, 124.8, 124.6, 124.2, 123.6, 121.7, 35.1, 34.5, 31.4, 31.1, 20.8; HRMS (ESI) calcd for $C_{40}H_{38}O$ $[M + H]^+$ 535.2995, found 535.2993.

*12-Methyl-5-(4-methoxyphenyl)-6-(4-methoxybenzoyl)chrysene (****4e****):* white solid (70%, 84.6 mg); mp 258–260 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.85 (d, J = 8.5 Hz, 1H), 8.66 (s, 1H), 8.14–8.04 (m, 1H), 7.85–7.64 (m, 3H), 7.58–7.41 (m, 5H), 7.10 (m, 1H), 6.95 (dd, J = 8.4, 2.7 Hz, 1H), 6.73 (dd, J = 8.5, 2.1 Hz, 1H), 6.67 (d, J = 8.9 Hz, 2H), 6.54 (dd, J = 8.5, 2.7 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 2.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.6, 163.5, 158.8, 137.6, 134.5, 134.1, 133.4, 132.5, 132.0, 131.5, 131.4, 130.1, 129.5, 129.1, 129.0, 127.2, 126.9, 126.6, 126.2, 125.9, 124.7, 124.2, 123.6, 121.6, 114.5, 113.7, 113.5, 55.5, 55.3, 20.8; HRMS (ESI) calcd for $C_{34}H_{26}O_3$ $[M + H]^+$ 483.1955, found 483.1955.

*12-Methyl-5-(4-fluorophenyl)-6-(4-fluorobenzoyl)chrysene (****4f****):* white solid (53%, 60.8 mg); mp 228–230 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.88 (d, J = 8.5 Hz, 1H), 8.66 (s, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.82–7.41 (m, 8H), 7.14–7.09 (m, 2H), 6.86 (t, J = 8.6 Hz, 2H), 6.79–6.64 (m, 2H), 2.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.4, 165.6 (d, J^1_{C-F} = 268.5 Hz), 162.29 (d, J^1_{C-F} = 260.7 Hz), 137.6 (d, J^4_{C-F} = 3.5 Hz), 137.1, 135.0, 134.5 (d, J^4_{C-F} = 2.7 Hz), 133.9, 133.4, 133.2 (d, J^3_{C-F} = 7.7 Hz), 132.2 (d, J^3_{C-F} = 8.1 Hz), 132.0 (d, J^3_{C-F} = 9.5 Hz), 131.0, 130.4, 129.6, 128.9, 128.6, 127.5, 127.3, 126.1, 126.0, 125.9, 124.8, 124.4, 123.8, 121.6, 115.8 (d, J^2_{C-F} = 24.8 Hz), 115.7 (d, J^2_{C-F} = 21.6 Hz), 115.5 (d, J^2_{C-F} = 22.1 Hz), 20.8; HRMS (ESI) calcd for $C_{32}H_{20}F_2O$ $[M + H]^+$ 459.1555, found 459.1556.

*12-Methyl-5-(4-chlorophenyl)-6-(4-chlorobenzoyl)chrysene (****4g****):* white solid (57%, 70.0 mg); mp 239–240 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.87 (d, J = 8.6 Hz, 1H), 8.65 (s, 1H), 8.11 (d, J = 8.1 Hz, 1H), 7.80–7.65 (m, 3H), 7.63–7.35 (m, 6H), 7.26–7.13 (m, 3H), 6.98 (d, J = 8.0 Hz, 1H), 6.71 (d, J = 7.9 Hz, 1H), 2.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.6, 140.1, 139.8, 136.8, 136.4, 135.1, 133.7, 133.4, 132.9, 131.8, 130.9, 130.8, 130.4, 129.6, 129.2, 128.9, 128.8, 128.6, 127.6, 127.4, 126.2, 125.9, 125.8, 124.9, 124.4, 123.8, 121.6, 20.8; HRMS (ESI) calcd for $C_{32}H_{20}Cl_2O$ $[M + H]^+$ 491.0964, found 491.0963.

*12-Methyl-5-(4-bromophenyl)-6-(4-bromobenzoyl)chrysene (****4h****):* white solid (60%, 86.9 mg); mp 262–264 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.87 (d, J = 8.5 Hz, 1H), 8.65 (s, 1H), 8.11 (d, J = 8.1 Hz, 1H), 7.80–7.64 (m, 4H), 7.61–7.46 (m, 5H), 7.39–7.27 (m, 5H), 7.19–7.08 (m, 2H), 6.65 (d, J = 8.0 Hz, 1H), 2.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.8, 140.6, 136.8, 135.2, 133.7, 133.4, 133.2, 132.2, 132.0, 131. 8, 130.9, 130.4, 129.7, 129.0, 128.7, 128.6, 127.6, 127.5, 126.2, 125.9, 125.8, 125.0, 124.5, 123.8, 123.0, 121.6, 20.8; HRMS (ESI) calcd for $C_{32}H_{20}Br_2O$ $[M + H]^+$ 578.9954, found 578.9953.

*12-Methyl-5-(4-acetylphenyl)-6-(4-acetylbenzoyl)chrysene (****4i****):* white solid (55%, 69.7 mg); mp 266–268 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.89 (d, J = 8.5 Hz, 1H), 8.67 (s, 1H), 8.11 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 7.3 Hz, 1H), 7.78–7.67 (m, 5H), 7.61–7.46 (m, 7H), 7.10–7.01 (m, 1H), 6.89 (d, J = 7.0 Hz, 1H), 2.93 (s, 3H), 2.55 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.2, 197.7, 197.4, 146.7, 140.8, 140.2, 136.5, 135.9, 135.4, 133.9, 133.4, 131.9, 130.7, 130.5, 129.7, 129.5, 129.0, 128.5, 128.3, 127.6, 126.3, 125.9, 125.6, 124.9, 124.5, 123.9, 121.6, 26.9, 26.8, 20.8; HRMS (ESI) calcd for $C_{36}H_{26}O_3$ $[M + H]^+$ 507.1955, found 507.1951.

*12-Methyl-5-(4-cyanophenyl)-6-(4-cyanobenzoyl)chrysene (****4j****):* white solid (41%, 48.5 mg); mp >300 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.89 (d, J = 8.5 Hz, 1H), 8.64 (s, 1H), 8.12 (d, J = 8.2 Hz, 1H), 7.83–7.65 (m, 4H), 7.62–7.44 (m, 7H), 7.25 (d, J = 8.4 Hz, 1H), 7.10 (t, J = 7.8 Hz, 1H), 6.84 (d, J = 6.1 Hz, 1H), 2.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.2, 146.5, 140.4, 135.9, 135.8, 133.4, 133.2, 132.8, 132.4, 132.0, 131.3, 130.7, 130.2, 129.7, 129.4, 128.7, 128.1, 128.0, 127.9, 126.5, 125.7, 125.1, 124.7, 124.0, 121.5, 118.5,

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117.7, 116.6, 111.5, 20.8; HRMS (ESI) calcd for $C_{34}H_{20}N_2O$ $[M + H]^+$ 473.1648, found 473.1646.

*12-Methyl-5-(4-phenylphenyl)-6-(4-phenylbenzoyl)chrysene (**4k**):* white solid (58%, 83.4 mg); mp 298−300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.78 (d, J = 8.5 Hz, 1H), 8.57 (s, 1H), 7.98 (d, J = 8.2 Hz, 1H), 7.78−7.70 (m, 2H), 7.63−7.55 (m, 3H), 7.49−7.18 (m, 17H), 7.11−7.04 (m, 1H), 6.96 (t, J = 7.8 Hz, 1H), 6.76 (d, J = 7.9 Hz, 1H), 2.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.7, 145.6, 140.8, 140.6, 139.9, 137.4, 137.1, 134.8, 134.7, 133.4, 132.0, 131.2, 131.0, 130.3, 130.1, 129.6, 129.2, 128.9, 128.8, 128.2, 127.5, 127.4, 127.3, 127.2, 127.1, 127.0, 126.8, 126.2, 126.1, 124.8, 124.3, 123.7, 121.7, 20.8; HRMS (ESI) calcd for $C_{44}H_{30}O_1$ $[M + H]^+$ 575.2369, found 575.2369.

*12-Methyl-5-(3-methylphenyl)-6-(3-methylbenzoyl)chrysene (**4l**, a mixture of atropisomers):* white solid (59%, 66.5 mg); mp 177−180 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.91 (d, J = 8.5 Hz, 1H), 8.71 (s, 1H), 8.12 (d, J = 8.2 Hz, 1H), 7.95−7.81 (m, 2H), 7.73 (t, J = 7.6 Hz, 1H), 7.62−7.54 (m, 1H), 7.53−7.45 (m, 2H), 7.36−7.07 (m, 5H), 7.02 (d, J = 7.1 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 6.68 (m, 1H), 2.94 (s, 3H), 2.43 (s, 1.5H), 2.23 (s, 3H), 1.96 (s, 1.5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.3, 141.7, 138.4, 137.8, 137.7, 137.5, 137.3, 135.1, 134.6, 133.7, 133.6, 133.3, 132.1, 131.3, 131.2, 130.2, 129.7, 129.7, 129.5, 129.2, 129.0, 128.7, 128.6, 128.1, 128.0, 127.4, 127.2, 126.9, 126.8, 126.1, 125.9, 124.7, 124.2, 123.6, 121.6, 21.6, 21.2, 21.0, 20.8; HRMS (ESI) calcd for $C_{34}H_{26}O$ $[M + H]^+$ 451.2056, found 451.2056.

*12-Methyl-5-(3-methoxyphenyl)-6-(3-methoxybenzoyl)chrysene (**4m**, a mixture of atropisomers):* white solid (54%, 65.2 mg); mp 156−158 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.89 (d, J = 8.5 Hz, 1H), 8.69 (s, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.89−7.80 (m, 2H), 7.72 (t, J = 7.7 Hz, 1H), 7.61−7.46 (m, 2H), 7.35 (t, J = 7.8 Hz, 1H), 7.25−7.02 (m, 5H), 7.00−6.89 (m, 1H), 6.79 (t, J = 8.1 Hz, 1H), 6.51−6.41 (m, 1H), 3.86 (s, 1.5H), 3.72 (s, 3H), 3.34 (s, 1.5H), 2.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.9, 199.8, 159.9, 159.5, 142.9, 140.0, 139.6, 137.1, 134.8, 134.7, 133.2, 131.1, 130.2, 130.0, 129.6, 129.4, 129.2, 129.0, 128.8, 127.3, 127.1, 126.0, 124.8, 124.7, 124.2, 123.6, 123.1, 122.8, 121.6, 119.6, 116.7, 115.0, 114.5, 113.7, 113.0, 112.9, 55.4, 55.0, 20.7; HRMS (ESI) calcd for $C_{34}H_{26}O_3$ $[M + H]^+$ 483.1955, found 483.1951.

*12-Methyl-5-(3,4,5-trimethoxyphenyl)-6-(3,4,5-trimethoxybenzoyl)chrysene (**4n**):* white solid (50%, 75.4 mg); mp 196−198 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.88 (d, J = 8.5 Hz, 1H), 8.68 (s, 1H), 8.10 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 8.7 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.76−7.68 (m, 1H), 7.62−7.46 (m, 2H), 7.17 (t, J = 7.8 Hz, 1H), 6.85 (s, 2H), 6.78 (s, 1H), 6.09 (s, 1H), 3.84 (s, 6H), 3.82 (s, 3H), 3.66 (s, 6H), 3.29 (s, 3H), 2.93 (s, 32H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.0, 153.6, 153.2, 152., 142.8, 137.5, 137.1, 137., 134.9, 134.9, 134.0, 133.2, 131.1, 130.2, 129.6, 129.0, 127.4, 127.2, 126.2, 126.0, 125.8, 125.0, 124.2, 123.7, 121.6, 109.2, 108.0, 107.2, 61.1, 60.9, 56.4, 56.3, 55.8, 20.8; HRMS (ESI) calcd for $C_{38}H_{34}O_7$ $[M + H]^+$ 603.2377, found 603.2376.

*3,8-Difluoro-12-methyl-5-phenyl-6-benzoylchrysene (**4o**):* white solid (51%, 58.5 mg); mp 236−238 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (m, 1H), 8.42 (s, 1H), 7.95 (m, 1H), 7.52 (d, J = 7.0 Hz, 1H), 7.43−7.27 (m, 6H), 7.13 (m, 5H), 6.89 (t, J = 7.2 Hz, 1H), 6.69 (d, J = 7.3 Hz, 1H), 2.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.4, δ 161.8 (d, J^1_{C-F}= 248.33 Hz), 159.8 (d, J^1_{C-F} = 243.73 Hz), 140.6, 137.9, 136.5 (d, J^4_{C-F} = 4.2 Hz), 135.0, 133.3, 132.7 (d, J^3_{C-F} = 9.4 Hz), 131.3, 130.9, 130.3, 130.2 (d, J^3_{C-F} = 9.3 Hz), 130.0, 129.4, 129.2, 128.6, 128.3, 128.0, 126.4 (d, J^3_{C-F} = 8.62 Hz), 126.3 (d, J^3_{C-F} = 9.07 Hz), 125.0 (d, J^4_{C-F} = 3.3 Hz), 120.9, 116.7 (d, J^2_{C-F} = 24.0 Hz), 115.2 (d, J^2_{C-F} = 24.0 Hz), 113.9 (d, J^2_{C-F} = 25.3 Hz), 110.2 (d, J^2_{C-F} = 21.9 Hz), 20.9; HRMS (ESI) calcd for $C_{32}H_{20}F_2O$ $[M + H]^+$ 459.1555, found 459.1555.

*3,8-Difluoro-12-methyl-5-(4-chlorophenyl)-6-(4-chlorobenzoyl)-chrysene (**4p**):* white solid (62%, 81.7 mg); mp >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.84 (m, 1H), 8.51 (s, 1H), 8.07 (m, 1H), 7.54−7.42 (m, 2H), 7.38 (m, 1H), 7.36−7.32 (m, 2H), 7.29 (m, 1H), 7.26−7.21 (m, 2H), 7.21−7.16 (m, 2H), 7.01 (d, J = 7.7 Hz, 1H), 6.69 (d, J = 7.8 Hz, 1H), 2.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.9, 161.9 (d, J^1_{C-F} = 249.3 Hz), 159.9 (d, J^1_{C-F} = 244.7 Hz), 140.1, 139.0, 136.2 (d, J^4_{C-F} = 4.1 Hz), 136.0, 135.4, 135.0, 134.4, 132.8, 132.7, 132.5, 131.5, 131.1, 130.7, 130.0, 130.0 (d, J^3_{C-F} = 9.3 Hz), 129.5, 129.0 (d, J^3_{C-F} = 10.5 Hz), 128.9, 126.6 (d, J^3_{C-F} = 9.2 Hz), 126.6 (d, J^3_{C-F} = 8.8 Hz), 124.7 (d, J^4_{C-F} = 4.1 Hz), 120.9, 117.1 (d, J^2_{C-F} = 24.3 Hz), 115.5 (d, J^2_{C-F} = 23.8 Hz), 113.7 (d, J^2_{C-F} = 25.0 Hz), 110.2 (d, J^2_{C-F} = 22.0 Hz), 21.0; HRMS (ESI) calcd for $C_{32}H_{18}Cl_2F_2O$ $[M + H]^+$ 527.0776, found 527.0775.

*3,8-Difluoro-12-methyl-5-(4-methoxyphenyl)-6-(4-methoxybenzoyl)chrysene (**4q**):* white solid (45%, 58.4 mg); mp 285−288 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.81 (m, 1H), 8.50 (s, 1H), 8.04 (m, 1H), 7.52−7.41 (m, 3H), 7.39−7.32 (m, 2H), 7.31−7.25 (m, 1H), 7.24−7.17 (m, 1H), 6.96 (m, 1H), 6.76−6.65 (m, 3H), 6.57 (m, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 2.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 163.7, 161.7 (d, J^1_{C-F} = 248.2 Hz), 159.8 (d, J^1_{C-F} = 243.5 Hz), 159.3, 137.0 (d, J^4_{C-F} = 4.4 Hz), 135.8, 134.8, 132.9, 132.9 (d, J^3_{C-F} = 9.5 Hz), 132.3, 132.0, 131.3, 131.0, 130.8, 130.4 (d, J^3_{C-F} = 8.9 Hz), 130.0, 126.33 (d, J^3_{C-F} = 8.9 Hz), 126.31 (d, J^3_{C-F} = 9.0 Hz), 125.4 (d, J^4 = 4.7 Hz), 120.89, 120.87, 116.5 (d, J^2_{C-F} = 24.1 Hz), 115.2 (d, J^2_{C-F} = 24.1 Hz), 114.8, 114.0, 113.9 (d, J^2_{C-F} = 26.7 Hz), 113.6, 110.3 (d, J^2_{C-F} = 21.7 Hz), 55.5, 55.4, 20.9; HRMS (ESI) calcd for $C_{34}H_{24}F_2O_3$ $[M + H]^+$ 519.1766, found 519.1768.

*12-Methyl-5-(thiophene-2-yl)-6-(thiophene-2-carbonyl)chrysene (**4r**):* yellow solid (28%, 30.5 mg); mp 212−214 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.82 (d, J = 8.6 Hz, 1H), 8.60 (s, 1H), 8.09 (dd, J = 8.3, 1.1 Hz, 1H), 7.94 (d, J = 8.7 Hz, 1H), 7.85 (d, J = 8.2 Hz, 1H), 7.71 (m, 1H), 7.58−7.50 (m, 3H), 7.26 (d, J = 5.0 Hz, 1H), 7.22−7.15 (m, 2H), 6.98 (m, 2H), 6.85−6.80 (m, 1H), 2.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.5, 143.1, 138.4, 135.4, 135.2, 134.8, 133.3, 131.1, 130.2, 130.0, 128.6, 128.4, 128.0, 127.9, 127.5, 127.5, 127.3, 127.2, 126.8, 126.3, 126.3, 124.9, 124.2, 123.7, 121.4, 20.8; HRMS (ESI) calcd for $C_{28}H_{18}S_2O$ $[M + H]^+$ 435.0872, found 435.0871.

*12-Methyl-5-(naphthalen-2-yl)-6-(naphthalene-2-carbonyl)-chrysene (**4s**):* white solid (67%, 87.6 mg); mp 215−217 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.91 (d, J = 8.5 Hz, 1H), 8.72 (s, 1H), 8.21−8.05 (m, 2H), 7.90 (m, 8.1 Hz, 2H), 7.74 (m, 4H), 7.67−7.59 (m, 2H), 7.56−7.45 (m, 5H), 7.45−7.37 (m, 3H), 7.32−7.25 (m, 1H), 7.20−7.04 (m, 1H), 6.94−6.83 (m, 1H), 2.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.0, 139.4, 137.8, 136.2, 135.5, 135.4, 134.9, 133.5, 133.3, 132.4, 132.2, 132.1, 131.5, 131.3, 130.7, 130.4, 129.7, 129.5, 129.4, 129.2, 128.8, 128.6, 128.5, 128.3, 128.0, 127.8, 127.7, 127.5, 127.4, 127.3, 126.6, 126.3, 126.1, 124.9, 124.5, 124.2, 124.2, 123.7, 121.7, 20.9; HRMS (ESI) calcd for $C_{40}H_{26}O$ $[M + H]^+$ 523.2056, found 523.2054.

*12-Methyl-6-formylchrysene (**2t**):* white solid (34%, 23.4 mg); mp 223−225 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.40 (s, 1H), 9.41−9.34 (m, 1H), 8.93 (s, 1H), 8.74−8.64 (m, 2H), 8.35 (s, 1H), 8.12−8.07 (m, 1H), 7.79−7.66 (m, 4H), 2.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 137.8, 134.3, 131.9, 130.7, 130.6, 129.4, 128.9, 128.4, 127.5, 127.5, 127.1, 125.7, 125.6, 125.0, 123.3, 123.2, 121.4, 21.0; HRMS (ESI) calcd for $C_{20}H_{14}O$ $[M + H]^+$ 271.1117, found 271.1117.

*(4-Methoxyphenyl)(9-(4-methoxyphenyl)-5-methylnaphtho[1,2-b:6,5-b′]dithiophene-10-yl)methanone (**4u**):* yellow solid (64%, 79.2 mg); mp 248−250 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.60 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 5.4 Hz, 1H), 7.20 (d, J = 5.7 Hz, 2H), 7.12 (d, J = 5.4 Hz, 2H), 6.82 (d, J = 4.4 Hz, 2H), 6.74 (d, J = 8.9 Hz, 3H), 6.34 (d, J = 5.6 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 2.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.0, 163.7, 159.2, 141.3, 138.1, 136.3, 134.2, 133.6, 133.0, 132.2, 132.1, 131.2, 128.2, 126.9, 126.0, 124.7, 124.4, 123.9, 120.7, 114.0, 113.6, 55.5, 55.3, 20.9; HRMS (ESI) calcd for $C_{30}H_{22}S_2O_3$ $[M + H]^+$ 495.1083, found 495.1084.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of all products and X-ray structural details of **4l**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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(15) The detailed X-ray diffraction data of **4l** are reported in the Supporting Information.

(16) The reaction and results of (alkylalkynyl)acetophenones under the optimized reaction conditions were reported in our original manuscript. On the basis of one reviewer's comments, the reaction was repeated in the absence of dehydrating agent or in the presence of water, and no corresponding chrysenes formed at all. As required by the reviewer, the reactions of (arylalkynyl)acetophenone of **3a** using $PtCl_2$/CO catalytic system reported by Liu's group[10] were also examined in the presence of water or absence of water, and both of the reactions did not afford **4a**. In the absence of water, the reaction gave a considerable amount of product having a molecular weight the same as that of the starting material (m/z = 220), possibly due to the intramolecular cyclization reaction. In the presence of water, the reaction produced a considerable amount of hydrolysis compound (m/z = 246) as confirmed by GC−MS.

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