JOC The Journal of Organic Chemistry

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A Tandem Reaction of Benzyne with Functionalized Benzylidenephthalan To Afford Phenanthro[10,1-*bc*]furan

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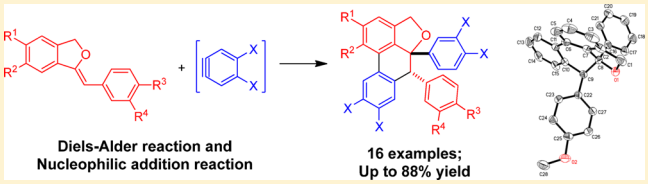
Supporting Information

ABSTRACT: A tandem reaction of benzyne with functionalized benzylidenephthalan for the synthesis of a variety of phenanthro[10,1-*bc*]furans has been achieved for the first time in moderate to good yields. The reaction mechanism involves a Diels–Alder reaction and an intermolecular nucleophilic addition reaction as the key steps.

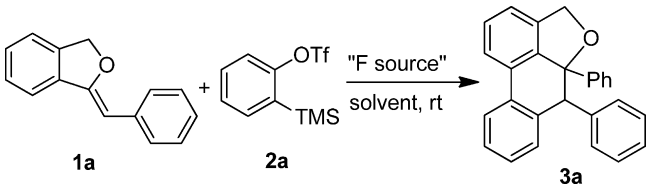


Aryne, as one of the most interesting and useful reactive intermediates,[1] has offered numerous applications in organic synthesis.[2] Since the mild approach to highly reactive aryne from fluoride-induced 1,2-elimination of 2-(trimethylsilyl)aryl triflates was first reported by Kobayashi in 1983,[3] the efficient use of this method has undergone unprecedented revival.[4] More recently, *ortho*-(trimethylsilyl)aryl triflate has been applied to a variety of reactions, such as electrophilic,[5] nucleophilic,[6] and cycloaddition reactions.[7] Because of the pronounced electrophilic character, arynes render as excellent dienophiles in pericyclic reactions, which have been extensively exploited in transition-metal-free reactions, particularly in the aryne Diels–Alder (ADA) reaction.[8] While the ADA reaction is well-known, few examples about intermolecular tandem processes involving ADA reaction were available[9] to synthesize molecules that are otherwise difficult to accomplish.

On the other hand, phthalans (1,3-dihydroisobenzofurans), as useful building blocks[10] as well as key structural units in several natural products[11] and biologically active compounds,[12] have drawn much attention in organic chemistry. As a result, much effort has focused on the synthesis of the phthalan derivatives, especially in functionalized benzylidenephthalans.[13] Meanwhile, following with these advances, several examples have been shown to the construction of natural products using functionalized benzylidenephthalans as precursors.[14] However, functionalized benzylidenephthalans have not been applied to aryne chemistry, yet. Upon our own work with benzylidenephthalans to the construction of heterocycles,[15] we envisage to investigate the functionalized benzylidenephthalan with benzyne as attractive candidates. Here, we report a novel tandem reaction of functionalized benzylidenephthalans involving [4 + 2] cycloaddition with benzyne generated in situ and 9,10-diphenyl-9,10-dihydrophenanthrene containing a phthalan moiety was constructed. This method provides an efficient transition-metal-free access to phenanthro[10,1-*bc*]furans under mild conditions.

In our investigations, we examined the reaction of benzylidenephthalan (**1a**, 0.25 mmol) with 2-(trimethylsilyl)-phenyl trifluoromethanesulfonate (**2a**, 0.75 mmol) in the presence of CsF (3.0 mmol), and the results are listed in Table 1. Initially, we tried the reaction of **1a** and **2a** in THF, toluene, or dichloromethane, but no product **3a** was observed (Table 1, entries 1–3). Gratifyingly, when the reaction of **1a** and **2a** was carried out in CH_3CN (10 mL) in the presence of CsF, the product **3a** was isolated in excellent 88% yield after 16 h at room temperature (Table 1, entry 4). As the volume of the solvent in the reaction of **1a** and **2a** was reduced to 5, 2, or 1

Table 1. Conditions Optimization for the Reaction of 1a and 2a[a]



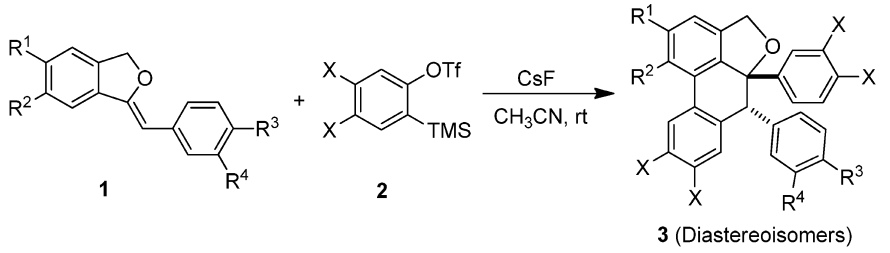
entry	fluoride	solvent	volume (mL)	time (h)	**3a** (%)[b]
1	CsF	THF	10	48	trace
2	CsF	toluene	10	48	trace
3	CsF	DCM	10	48	trace
4	CsF	CH_3CN	10	16	88
5	CsF	CH_3CN	5	22	78
6	CsF	CH_3CN	2	70	68
7	CsF	CH_3CN	1	72	39
8[c]	CsF	CH_3CN	10	22	62
9[d]	CsF	CH_3CN	10	18	55
10[e]	KF	CH_3CN	10	48	10
11	TBAF	CH_3CN	10	48	trace

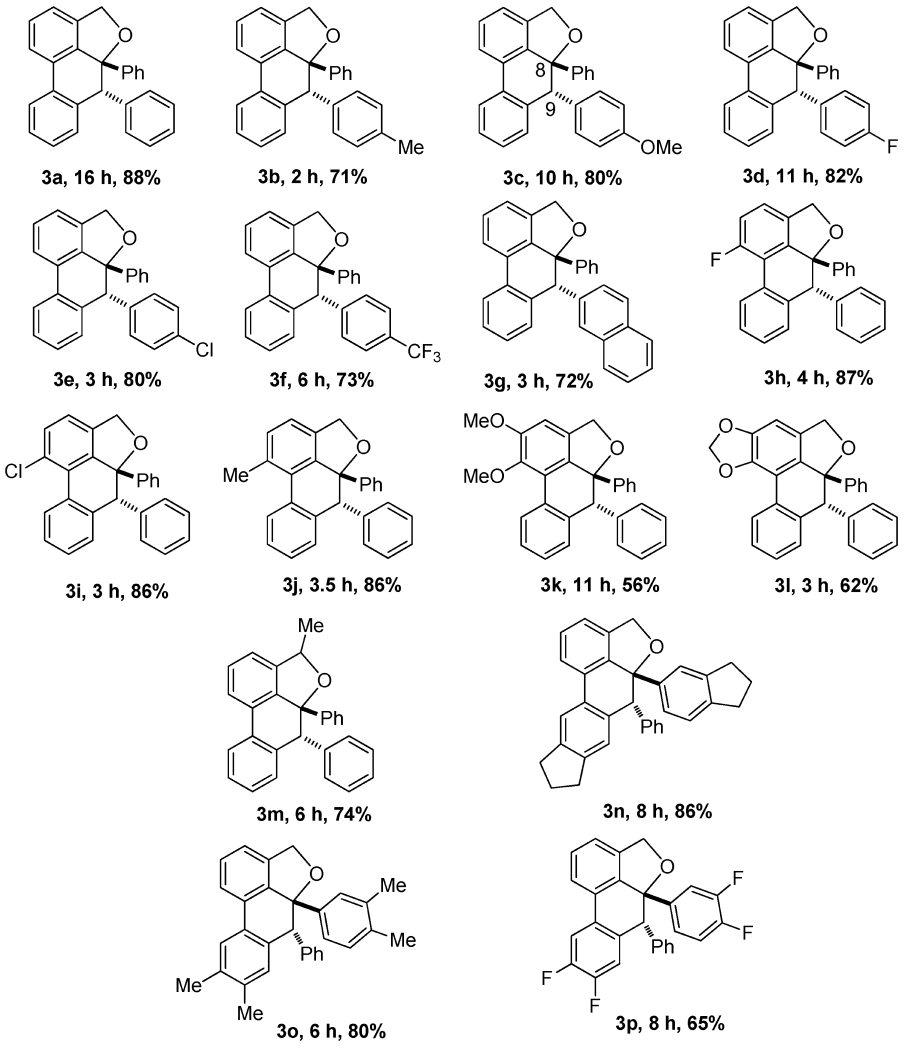
[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.75 mmol), fluoride (3.0 mmol), room temperature, unless noted. [b]Isolated yield. [c]CsF (1.5 mmol) was used. [d]**2a** (0.60 mmol) was used. [e]18-Crown-6 (3.0 mmol) was added.

Received: December 5, 2013
Published: January 17, 2014

dx.doi.org/10.1021/jo402701q | *J. Org. Chem.* 2014, 79, 1505–1510

Table 2. Reactions of Benzylidenephthalans (1) and Benzyne (2) To Afford Phenanthro[10,1-*bc*]furan Derivatives[a]





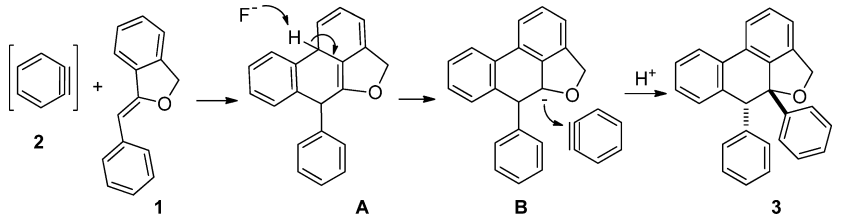
[a]Reaction conditions: **1** (0.25 mmol), **2** (0.75 mmol), CsF (3.0 mmol), CH_3CN (10 mL), room temperature under N_2. The yields reported are isolated yields.

mL, the yields of **3a** decreased gradually to 78% or 68% and even 39% with prolonged reaction time (Table 1, entries 5–7). The results illustrate that the concentration of the reaction has a remarkable influence on the yield of the product and dilution of aryne is beneficial for the reaction. When the amount of CsF was reduced from 12 equiv of **1a** to 6 equiv (1.5 mmol), the reaction of **1a** and **2a** only afforded the product **3a** in 62% yield (Table 1, entry 8). Moreover, the excess of **2a** to **1a** is crucial for the reaction, and substantial decrease of the yield to 55% was observed when the ratio of **1a**/**2a** was decreased from 1:3 to 1:2.4 (Table 1, entry 9). Finally, when the fluoride source of the reaction was replaced by KF/18-crown-6 or tetrabutylammonium fluoride (TBAF), the product **3a** was generated only in 10% yield or a traceable amount (Table 1, entries 10 and 11).

For an evaluation of substrate scope of the tandem reaction, reactions of a series of benzylidenephthalans **1** prepared via $Cu(OTf)_2$-catalyzed intramolecular hydroalkoxylation of alkynols[13f] were carried out with various arynes **2**. Under the optimized conditions, **1** (0.25 mmol) and **2** (0.75 mmol) were mixed at room temperature with CsF (3.0 mmol) in CH_3CN (10 mL). After the indicated reaction time, a variety of products **3** were obtained in moderate to good yields, as depicted in Table 2. All products were characterized by ^1H, ^{13}C NMR, and

dx.doi.org/10.1021/jo402701q | J. Org. Chem. 2014, 79, 1505–1510

Scheme 1. Proposed Mechanism for the Reaction of 1 and 2 To Afford 3



HRMS spectra. The structure of compound **3c** was further confirmed as diastereoisomers by the single-crystal X-ray analysis, which disclosed the *trans*-configuration of two substitutes on C8 and C9 (see the Supporting Information). Interestingly, the *trans*-diastereoselectivity of **3c** before recrystallization was 100% and no *cis*-diastereoisomers were detected. On the basis of the comparison of ^{1}H NMR of other products with **3c**, *trans*-diastereoselectivity of all products was proved as 100%.

In the examination of benzylidenephthalan **1**, for the substrates containing the electron-donating Me and MeO groups or the electron-withdrawing F, Cl, and CF_3 groups at the R^3 position, their reactions with **2a** proceeded smoothly to afford the products **3b**−**3f** in 71−82% yields. The results illustrate that the reaction is not sensitive to the electronic property of the substituents on the benzene ring of **1**. As the benzene ring was replaced by the naphthyl group, its reaction with **2a** afforded **3g** in 72% yield. If the 2,3-dihydrobenzofuran moiety of benzylidenephthalan **1** was substituted by F, Cl, or Me groups at the R^2 position, the reactions of the corresponding benzylidenephthalans with **2a** gave the products **3h**−**3j** in 86−87% yields. As the R^1 and R^2 positions were substituted by OMe or $-OCH_2O-$ groups, the reactions of the corresponding benzylidenephthalans with **2a** generated the products **3k** and **3l** in a little decreased 56% and 62% yields, respectively. It is noteworthy that the products **3k** and **3l** might attract potential pharmacological interest as derivatives of the natural product aristololide, which possesses strong antiplatelet activity and other bioactivity.[16] If the benzylic methylene of the 2,3-dihydrobenzofuran moiety in benzylidenephthalan **1** was substituted by a methyl group, the product **3m** was also afforded by the reaction in 74% yield.

We also tested the substrate scope on the aryne component. Symmetrical arynes with the electron-donating $-CH_2CH_2CH_2-$ group or two methyl groups reacted smoothly with **1a** to afford the products **3n** and **3o** in 86% and 80% isolated yields, respectively. Although all other products are solid, the product **3o** is a pale yellow viscous liquid and a similar compound as a viscous liquid has also been reported.[17] When the aryne was substituted by two electron-withdrawing fluoric groups, the product **3p** could also be obtained in moderate 65% yield.

On the basis of previous work,[8e] a tentative mechanism for the reaction of **1** and **2** to afford the product **3** is outlined in Scheme 1. At first, benzyne generated in situ by Kobayashi's method[3] undergoes Diels−Alder reaction with substrate **1** to give intermediate **A**. Subsequently, a fluoride anion acts as a base to abstract hydrogen from intermediate **A** to initiate the thermodynamically favored aromatization to afford the anion intermediate **B**. Then, the intermolecular addition of **B** to the benzyne and the following protonation leads to the *trans*-diastereoselective product **3** due to the steric effect.

In summary, we have developed a novel tandem reaction to generate phenanthro[10,1-*bc*]furans with benzyne and functionalized benzylidenephthalans under mild and transion-metal-free conditions. A variety of phenanthro[10,1-*bc*]furan derivatives are generated in moderate to good yields after the tandem Diels−Alder reaction and intermolecular nucleophilic addition. This protocol provides highly concise and effective routes to the related complex compounds including natural product derivatives.

EXPERIMENTAL SECTION

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium-benzophenone (THF, toluene) or calcium hydride (CH_3CN, DCM). Chemical shifts (δ, ppm) in the ^{1}H NMR spectra were recorded using TMS as internal standard. Chemical shifts in $^{13}C\{^1H\}$ NMR spectra were internally referenced to $CDCl_3$ (δ = 77.1 ppm).

Typical Procedure for the Tandem Reaction of Benzyne with Functionalized Benzylidenephthalan. To a mixture of benzylidenephthalan **1** (0.25 mmol) and CsF (3.0 mmol) in acetonitrile (10 mL) was added the benzyne precursor **2** (0.75 mmol). The reaction mixture was stirred at room temperature for several hours, and the progress was monitored using TLC detection. After completion of the present reaction, the solvent was evaporated under reduced pressure and the residue was passed through flash column chromatography on silica gel to afford the desired products **3**.

*5a,6-Diphenyl-5a,6-dihydro-4H-phenanthro[10,1-bc]furan (**3a**).* The compound was prepared from **1a** (0.052 g, 0.25 mmol), CsF (0.456 g, 3.0 mmol), and **2a** (0.224 g, 0.75 mmol) following the typical procedure: 0.079 g (88% yield) of product was obtained after column chromatography (eluent = petroleum ether/ethyl acetate 100:1 v/v); mp 186.7−189.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.93 (d, J = 7.6 Hz, 1H), 7.71 (d, J = 7.7 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.30−7.34 (m, 3H), 7.15−7.20 (m, 3H), 7.06−7.10 (m, 6H), 6.82−6.84 (m, 2H), 4.82 (d, J = 12.2 Hz, 1H), 4.64 (s, 1H), 4.62 (d, J = 12.3 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 143.6, 140.1, 139.7, 138.8, 138.5, 133.7, 131.8, 131.5, 129.5, 129.2, 128.8, 128.0, 128.0, 127.8, 127.3, 126.4, 126.3, 123.3, 120.9, 120.8, 88.2, 71.9, 58.6; HRMS (EI, TOF) calcd for $C_{27}H_{20}O$ $[M]^+$ 360.1514, found 360.1515.

*5a-Phenyl-6-(p-tolyl)-5a,6-dihydro-4H-phenanthro[10,1-bc]furan (**3b**).* The compound was prepared from **1b** (0.056 g, 0.25 mmol), CsF (0.456 g, 3.0 mmol), and **2a** (0.224 g, 0.75 mmol) following the typical procedure: 0.066 g (71% yield) of product was obtained after column chromatography (eluent = petroleum ether/ethyl acetate 100:1 v/v); mp 175.4−177.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.91 (d, J = 7.7 Hz, 1H), 7.71 (d, J = 7.7 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.28−7.32 (m, 3H), 7.07−7.20 (m, 5H), 7.03 (d, J = 7.5 Hz, 1H), 6.88 (d, J = 7.8 Hz, 2H), 6.71 (d, J = 7.1 Hz, 2H), 4.81 (d, J = 12.2 Hz, 1H), 4.63 (d, J = 12.2 Hz, 1H), 4.60 (s, 1H), 2.19 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 143.7, 140.1, 138.9, 138.7, 136.8, 135.9, 133.7, 131.9, 131.5, 129.4, 129.1, 128.9, 128.6, 128.0, 127.9, 127.3, 126.4, 123.3, 121.0, 120.8, 88.3, 71.9, 58.3, 21.1; HRMS (ESI, TOF) calcd for $C_{28}H_{23}O$ $[M + H]^+$ 375.1749, found 375.1750.

*6-(4-Methoxyphenyl)-5a-phenyl-5a,6-dihydro-4H-phenanthro-[10,1-bc]furan (**3c**).* The compound was prepared from **1c** (0.060 g, 0.25 mmol), CsF (0.456 g, 3.0 mmol), and **2a** (0.224 g, 0.75 mmol) following the typical procedure: 0.078 g (80% yield) of product was

dx.doi.org/10.1021/jo402701q | J. Org. Chem. 2014, 79, 1505−1510

obtained after column chromatography (eluent = petroleum ether/ethyl acetate 50:1 v/v); mp 154.7−156.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.91 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.30−7.32 (m, 3H), 7.08−7.19 (m, 5H), 7.04 (d, J = 7.3 Hz, 1H), 6.74 (d, J = 8.7 Hz, 2H), 6.62 (d, J = 8.7 Hz, 2H), 4.82 (d, J = 12.2 Hz, 1H), 4.64 (d, J = 12.2 Hz, 1H), 4.59 (s, 1H), 3.68 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 158.1, 143.6, 140.1, 138.9, 138.8, 133.7, 131.9, 131.5, 130.2, 129.5, 128.9, 128.0, 127.9, 127.3, 126.4, 126.3, 123.3, 120.9, 120.8, 113.2, 88.4, 72.0, 57.8, 55.1; HRMS (ESI, TOF) calcd for $C_{28}H_{23}O_2$ $[M + H]^+$ 391.1698, found 391.1698.

*6-(4-Fluorophenyl)-5a-phenyl-5a,6-dihydro-4H-phenanthro-[10,1-bc]furan (**3d**).* The compound was prepared from **1d** (0.057 g, 0.25 mmol), CsF (0.456 g, 3.0 mmol), and **2a** (0.224 g, 0.75 mmol) following the typical procedure: 0.078 g (82% yield) of product was obtained after column chromatography (eluent = petroleum ether/ethyl acetate 100:1 v/v); mp 193.7−194.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.92 (d, J = 7.7 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 7.5 Hz, 1H), 7.29−7.31 (m, 2H), 7.14−7.20 (m, 3H), 7.10 (t, J = 6.9 Hz, 2H), 7.03 (d, J = 7.5 Hz, 1H), 6.73−6.80 (m, 4H), 4.83 (d, J = 12.2 Hz, 1H), 4.62 (d, J = 12.2 Hz, 1H), 4.62 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 143.4, 140.1, 138.6, 138.3, 135.3, 133.8, 131.8, 131.5, 130.8, 130.7, 129.6, 128.9, 128.2, 128.1, 127.4, 126.4, 123.4, 121.0 (d, J_{CF}= 15.4 Hz), 114.6 (d, J_{CF} = 21.2 Hz), 88.2, 72.0, 57.7; HRMS (EI, TOF) calcd for $C_{27}H_{19}FO$ $[M]^+$ 378.1420, found 378.1422.

*6-(4-Chlorophenyl)-5a-phenyl-5a,6-dihydro-4H-phenanthro-[10,1-bc]furan (**3e**).* The compound was prepared from **1e** (0.061 g, 0.25 mmol), CsF (0.456 g, 3.0 mmol), and **2a** (0.224 g, 0.75 mmol) following the typical procedure: 0.079 g (80% yield) of product was obtained after column chromatography (eluent = petroleum ether/ethyl acetate 100:1 v/v); mp 186.5−188.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.92 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.28−7.34 (m, 3H), 7.14−7.20 (m, 3H), 7.07−7.11 (m, 2H), 7.01−7.05 (m, 3H), 6.75 (d, J = 8.4 Hz, 2H), 4.82 (d, J = 12.2 Hz, 1H), 4.62 (s, 1H), 4.61 (d, J = 12.2 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 143.3, 140.1, 138.5, 138.1, 137.9, 133.8, 132.2, 131.7, 131.4, 130.7, 129.6, 129.0, 128.3, 128.1, 127.9, 127.4, 126.3, 123.5, 121.1, 120.9, 88.2, 72.0, 57.8; HRMS (EI, TOF) calcd for $C_{27}H_{19}ClO$ $[M]^+$ 394.1124, found 394.1126.

*5a-Phenyl-6-(4-(trifluoromethyl)phenyl)-5a,6-dihydro-4H-phenanthro[10,1-bc]furan (**3f**).* The compound was prepared from **1f** (0.069 g, 0.25 mmol), CsF (0.456 g, 3.0 mmol), and **2a** (0.224 g, 0.75 mmol) following the typical procedure: 0.078 g (73% yield) of product was obtained after column chromatography (eluent = petroleum ether/ethyl acetate 50:1 v/v); mp 174.5−176.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.95 (d, J = 7.6 Hz, 1H), 7.73 (d, J = 7.7 Hz, 1H), 7.44 (t, J = 7.1 Hz, 1H), 7.30−7.37 (m, 5H), 7.10−7.20 (m, 5H), 7.03 (d, J = 7.6 Hz, 1H), 6.94 (d, J = 8.0 Hz, 2H), 4.82 (d, J = 12.2 Hz, 1H), 4.69 (s, 1H), 4.61 (d, J = 12.3 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 143.7, 143.1, 140.1, 138.4, 137.6, 133.8, 131.7, 131.5, 129.8, 129.6, 129.0, 128.5, 128.2, 127.5, 126.4, 124.7, 123.6, 121.2, 121.0, 88.1, 72.0, 58.3; HRMS (EI, TOF) calcd for $C_{28}H_{19}F_3O$ $[M]^+$ 428.1388, found 428.1389.

*6-(Naphthalen-2-yl)-5a-phenyl-5a,6-dihydro-4H-phenanthro-[10,1-bc]furan (**3g**).* The compound was prepared from **1g** (0.065 g, 0.25 mmol), CsF (0.456 g, 3.0 mmol), and **2a** (0.224 g, 0.75 mmol) following the typical procedure: 0.074 g (72% yield) of product was obtained after column chromatography (eluent = petroleum ether/ethyl acetate 100:1 v/v); mp 166.4−168.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.96 (d, J = 7.7 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.66−7.68 (m, 1H), 7.55−7.59 (m, 2H), 7.31−7.43 (m, 6H), 7.16−7.24 (m, 4H), 7.01−7.10 (m, 4H), 4.81 (s, 1H),4.80 (d, J = 12.3 Hz, 1H), 4.54 (d, J = 12.2 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 143.6, 140.1, 138.8, 138.4, 137.5, 133.9, 133.2, 132.3, 131.9, 131.7, 129.6, 128.9, 128.1, 128.1, 128.0, 127.9, 127.4, 127.1, 126.4, 125.5, 125.4, 123.4, 121.1, 120.9, 88.5, 71.9, 58.7; HRMS (EI, TOF) calcd for $C_{31}H_{22}O$ $[M]^+$ 410.1671, found 410.1672.

*1-Fluoro-5a,6-diphenyl-5a,6-dihydro-4H-phenanthro[10,1-bc]-furan (**3h**).* The compound was prepared from **1h** (0.057 g, 0.25 mmol), CsF (0.456 g, 3.0 mmol), and **2a** (0.224 g, 0.75 mmol) following the typical procedure: 0.082 g (87% yield) of product was obtained after column chromatography (eluent = petroleum ether/ethyl acetate 100:1 v/v); mp 184.2−186.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.19 (d, J = 7.8 Hz, 1H), 7.30−7.35 (m, 3H), 7.16−7.19 (m, 3H), 7.05−7.15 (m, 6H), 6.99 (m, 1H), 6.87−6.89 (m, 2H), 4.77 (d, J = 11.9 Hz, 1H), 4.65 (s, 1H), 4.56 (d, J = 11.9 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 142.9, 139.1, 138.5, 135.3, 131.4, 130.6, 129.4, 129.1, 128.1, 127.9, 127.8, 127.6, 127.5, 126.5, 126.3, 122.1,122.1, 117.2, 116.9, 88.4, 71.6, 58.6; HRMS (EI, TOF) calcd for $C_{27}H_{19}FO$ $[M]^+$ 378.1420, found 378.1421.

*1-Chloro-5a,6-diphenyl-5a,6-dihydro-4H-phenanthro[10,1-bc]-furan (**3i**).* The compound was prepared from **1i** (0.061 g, 0.25 mmol), CsF (0.456 g, 3.0 mmol), and **2a** (0.224 g, 0.75 mmol) following the typical procedure: 0.085 g (86% yield) of product was obtained after column chromatography (eluent = petroleum ether/ethyl acetate 100:1 v/v); mp 193.2−195.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.62 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 7.9 Hz, 1H), 7.26−7.35 (m, 3H), 7.05−7.19 (m, 8H), 6.97 (d, J = 8.0 Hz, 1H), 6.88−6.90 (m, 2H), 4.80 (d, J = 12.2 Hz, 1H), 4.65 (s, 1H), 4.55 (d, J = 12.2 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 142.5, 142.1, 139.1, 138.7, 138.5, 132.8, 132.0, 131.2, 129.7, 129.5, 129.3, 128.9, 128.1, 127.8, 127.7, 127.5, 127.5, 126.5, 126.5, 121.9, 89.3, 71.8, 58.4; HRMS (EI, TOF) calcd for $C_{27}H_{19}ClO$ $[M]^+$ 394.1124, found 394.1125.

*1-Methyl-5a,6-diphenyl-5a,6-dihydro-4H-phenanthro[10,1-bc]-furan (**3j**).* The compound was prepared from **1j** (0.056 g, 0.25 mmol), CsF (0.456 g, 3.0 mmol), and **2a** (0.224 g, 0.75 mmol) following the typical procedure: 0.080 g (86% yield) of product was obtained after column chromatography (eluent = petroleum ether/ethyl acetate 50:1 v/v); mp 179.2−181.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.94 (d, J = 7.8 Hz, 1H), 7.29−7.32 (m, 3H), 7.68 (d, J = 7.7 Hz, 1H), 7.12−7.17 (m, 3H), 7.06−7.07 (m, 5H), 6.97 (d, J = 7.6 Hz, 1H), 6.82−6.85 (m, 2H), 4.82 (d, J = 11.8 Hz, 1H), 4.62 (s, 1H), 4.55 (d, J = 11.9 Hz, 1H), 2.79 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 143.3, 140.2, 139.5, 139.2, 137.8, 135.2, 132.8, 132.5, 131.3, 130.9, 129.6, 128.1, 127.9, 127.7, 127.4, 127.3, 127.3, 126.6, 126.3, 120.8, 89.3, 72.0, 58.7, 22.3; HRMS (EI, TOF) calcd for $C_{28}H_{22}O$ $[M]^+$ 374.1671, found 374.1668.

*1,2-Dimethoxy-5a,6-diphenyl-5a,6-dihydro-4H-phenanthro-[10,1-bc]furan (**3k**).* The compound was prepared from **1k** (0.067 g, 0.25 mmol), CsF (0.456 g, 3.0 mmol), and **2a** (0.224 g, 0.75 mmol) following the typical procedure: 0.059 g (56% yield) of product was obtained after column chromatography (eluent = petroleum ether/ethyl acetate 50:1 v/v); mp 165.8−168.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.50 (d, J = 7.8 Hz, 1H), 7.29−7.30 (m, 3H), 7.01−7.16 (m, 8H), 6.89 (br, 2H), 6.67 (br, 1H), 4.78 (d, J = 11.6 Hz, 1H), 4.61 (s, 1H), 4.51 (d, J = 11.8 Hz, 1H), 3,90 (s, 3H), 3,89 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 154.6, 145.5, 143.7, 139.6, 138.9, 134.7, 132.7, 131.7, 131.2, 129.5, 128.7, 128.0, 128.0, 127.7, 127.3, 126.5, 126.3, 124.8, 105.5, 88.9, 72.0, 60.2, 58.9, 56.4; HRMS (EI, TOF) calcd for $C_{29}H_{24}O_3$ $[M]^+$ 420.1725, found 420.1728.

*6a,7-Diphenyl-6a,7-dihydro-5H-furo[2′,3′,4′:10,1]phenanthro-[3,4-d][1,3]dioxole (**3l**).* The compound was prepared from **1l** (0.063 g, 0.25 mmol), CsF (0.456 g, 3.0 mmol), and **2a** (0.224 g, 0.75 mmol) following the typical procedure: 0.063 g (62% yield) of product was obtained after column chromatography (eluent = petroleum ether/ethyl acetate 50:1 v/v); as a foamed pale yellow solid, mp 173.2−175.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.09 (d, J = 7.7 Hz, 1H), 7.28−7.35 (m, 3H), 7.04−7.22 (m, 8H), 6.88−6.90 (m, 2H), 6.56 (s, 1H), 6.19−6.22 (m, 2H), 4.71 (d, J = 11.7 Hz, 1H), 4.63 (s, 1H), 4.51 (d, J = 11.8 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 143.9, 139.7, 138.5, 132.2, 131.3, 129.2, 128.7, 127.9, 127.8, 127.2, 126.8, 126.4, 126.2, 114.6, 102.0, 88.2, 71.7, 58.7; HRMS (EI, TOF) calcd for $C_{28}H_{20}O_3$ $[M]^+$ 404.1407, found 404.1414.

*4-Methyl-5a,6-diphenyl-5a,6-dihydro-4H-phenanthro[10,1-bc]-furan (**3m**).* The compound was prepared from **1m** (0.056 g, 0.25 mmol), CsF (0.456 g, 3.0 mmol), and **2a** (0.224 g, 0.75 mmol) following the typical procedure: 0.069 g (74% yield) of product was obtained after column chromatography (eluent = petroleum ether/

dx.doi.org/10.1021/jo402701q | J. Org. Chem. 2014, 79, 1505−1510

ethyl acetate 50:1 v/v); mp 160.8−162.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.91 (d, J = 7.6 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.30−7.34 (m, 3H), 7.04−7.19 (m, 8H), 6.98 (d, J = 7.4 Hz, 1H), 6.77−6.80 (m, 2H), 5.10 (q, J = 6.4 Hz, 1H), 4.65 (s, 1H), 0.86 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 144.3, 144.2, 139.6, 138.7, 134.1, 131.9, 131.5, 129.7, 129.6, 128.8, 128.0, 128.0, 127.5, 127.2, 126.3, 123.3, 121.2, 120.5, 87.7, 78.9, 58.6, 20.4; HRMS (EI, TOF) calcd for $C_{28}H_{22}O$ $[M]^+$ 374.1671, found 374.1673.

*5a-(2,3-Dihydro-1H-inden-5-yl)-6-phenyl-4,5a,6,8,9,10-hexahydrocyclopenta[6,7]phenanthro[10,1-bc]furan (**3n**).* The compound was prepared from **1a** (0.052 g, 0.25 mmol), CsF (0.456 g, 3.0 mmol), and 6-(trimethylsilyl)-2,3-dihydro-1*H*-inden-5-yl trifluoromethanesulfonate **2b** (0.254 g, 0.75 mmol) following the typical procedure: 0.095 g (86% yield) of product was obtained after column chromatography (eluent = petroleum ether/ethyl acetate 100:1 v/v) as a foamed white solid, mp 153.4−156.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.76 (s, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.00−7.07 (m, 7H), 6.91 (s, 1H), 6.81−6.84 (m, 2H), 4.79 (d, J = 12.2 Hz, 1H), 4.63 (s, 1H), 4.56 (d, J = 12.2 Hz, 1H), 2.92 (t, J = 7.3 Hz, 2H), 2.78−2.83 (m, 4H), 2.73 (t, J = 7.4 Hz, 2H), 1.96−2.05 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 145.2, 144.0, 144.0, 143.2, 141.8, 140.5, 140.1, 138.9, 136.7, 132.5, 131.8, 129.2, 129.2, 127.8, 127.4, 126.2, 124.4, 123.7, 122.4, 120.5, 120.2, 119.1, 88.6, 71.8, 58.8, 33.0, 32.7, 32.7, 32.6, 25.4, 25.4; HRMS (EI, TOF) calcd for $C_{33}H_{28}O$ $[M]^+$ 440.2140, found 440.2139 .

*5a-(3,4-Dimethylphenyl)-8,9-dimethyl-6-phenyl-5a,6-dihydro-4H-phenanthro[10,1-bc]furan (**3o**).* The compound was prepared from **1a** (0.052 g, 0.25 mmol), CsF (0.456 g, 3.0 mmol), and 4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2c** (0.24 g, 0.75 mmol) following the typical procedure: 0.083 g (86% yield) of product was obtained after column chromatography (eluent = petroleum ether/ethyl acetate 50:1 v/v) as a pale yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.65−7.67 (m, 2H), 7.38 (t, J = 7.5 Hz, 1H), 7.23 (s, 1H), 7.02−7.07 (m, 4H), 6.89 (s, 2H), 6.82−6.83 (m, 3H), 4.78 (d, J = 12.2 Hz, 1H), 4.58 (s, 1H), 4.56 (d, J = 12.8 Hz, 1H), 2.28 (s, 3H), 2.18 (s, 3H), 2.15 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 141.2, 140.3, 139.9, 138.7, 137.2, 136.1, 135.9, 135.4, 132.7, 132.0, 131.1, 129.1, 129.0, 127.7, 127.5, 126.1, 124.3, 123.8, 120.3, 120.2, 88.2, 71.7, 58.0, 20.0, 19.7, 19.6, 19.4; HRMS (EI, TOF) calcd for $C_{31}H_{28}O$ $[M]^+$ 416.2135, found 416.2139.

*5a-(3,4-Difluorophenyl)-8,9-difluoro-6-phenyl-5a,6-dihydro-4H-phenanthro[10,1-bc]furan (**3p**).* The compound was prepared from **1a** (0.052 g, 0.25 mmol), CsF (0.456 g, 3.0 mmol), and 4,5-difluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2d** (0.251 g, 0.75 mmol) following the typical procedure: 0.070 g (65% yield) of product was obtained after column chromatography (eluent = petroleum ether/ethyl acetate 100:1 v/v) as a foamed white solid, mp 180.3−183.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.68−7.73 (m, 1H), 7.61 (d, J = 7.7 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.08−7.17 (m, 5H), 6.96−6.99 (m, 2H), 6.87−6.91 (m, 1H), 6.74−6.77 (m, 2H), 4.81 (d, J = 12.4 Hz, 1H), 4.62 (d, J = 12.4 Hz, 1H), 4.48 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 140.4, 140.1, 138.1, 137.7, 130.2, 130.0, 129.0, 128.0, 127.0, 122.4, 121.7, 121.0, 120.3, 120.2, 117.0, 116.8, 115.7, 115.6, 112.6, 112.4, 87.4, 72.2, 58.0; HRMS (EI, TOF) calcd for $C_{27}H_{16}F_4O$ $[M]^+$ 432.1132, found 432.1136.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The X-ray crystallographic data of **3c**, the copies of ^{1}H and ^{13}C NMR spectra for products **3a**−**3p**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Project Nos. 21172069, 21190033, and 21372072), the Innovation Program of the Shanghai Municipal Education Commission (Project No. 12ZZ050), the Basic Research Program of the Shanghai Committee of Science and Technology (Project No. 13NM1400802), and the Fundamental Research Funds for the Central Universities.

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