JOC The Journal of Organic Chemistry

Note

pubs.acs.org/joc

Palladium-Catalyzed Iodine-Mediated Electrophilic Annulation of 2-(1-Alkynyl)biphenyls with Disulfides

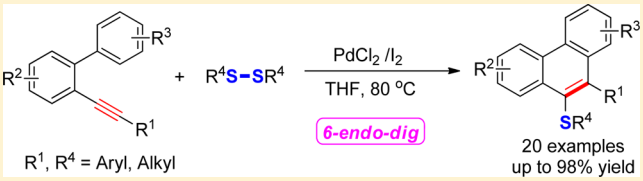
Bo-Lun Hu,[†] Sha-Sha Pi,[†] Peng-Cheng Qian,*[,†] Jin-Heng Li,[‡] and Xing-Guo Zhang*[,†]

[†]College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, China

[‡]State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China

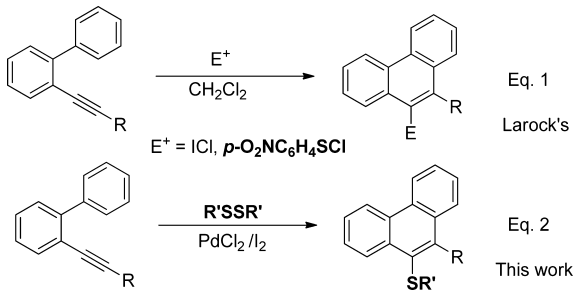
Supporting Information

ABSTRACT: A palladium-catalyzed, iodine-mediated electrophilic annulation between 2-(1-alkynyl)biphenyl and disulfide has been developed. With the combination of $PdCl_2$ and I_2, a variety of 2-(1-alkynyl)biphenyls underwent electrophilic annulations with various disulfides successfully to afford the corresponding 9-sulfenyl phenanthrenes in moderate to excellent yields.



Phenanthrenes are an important class of polycyclic aromatic compounds and widely represented in many natural products[1] and biologically active molecules due to their diverse biological activities such as anticancer,[2] anti-HIV,[3] and antimicrobial activity.[4] Moreover, phenanthrenes also have a wide range of applications in materials science owing to their optical and electronic properties.[5] Consequently, extensive efforts have been focused on the development of methods for the construction of the phenanthrene ring.[6] The carbocyclization of alkynylated biaryl derivatives is a frequently utilized strategy because of the atom-economical advantage.[7] For example, Jana et al.[8] developed an iron-catalyzed intramolecular alkyne carbonyl metathesis of 2′-alkynylbiphenyl-2-carbaldehydes for the preparation of functionalized phenanthrenes. Larock and co-workers also reported the electrophilic cyclization of 2-(arylethynyl)biphenyls with ICl, NBS, or arylsulfenyl chloride for the synthesis of phenanthrene derivatives (Scheme 1, eq 1).[9] In our former study, we reported some transition-metal-catalyzed electrophilic cyclization of arylethynyl derivatives using disulfides as electrophilic reagent.[10] As a continual interest in the synthetic utility of disulfides, we herein wish to report a simple and efficient protocol for the synthesis of 9-sulfenylphenanthrenes by palladium-catalyzed electrophilic annulation of 2-(1-alkynyl)-biphenyls with disulfides in the presence of iodine (eq 2).

Scheme 1



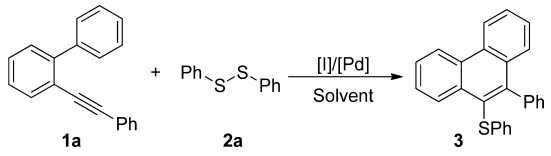
We began our study by examining the reaction between 2-(phenylethynyl)biphenyl **1a** and 1,2-diphenyldisulfane **2a** to obtain the optimal reaction conditions. As shown in Table 1, several iodine sources, including iodine, ICl, NIS, and $PhI(OAc)_2$, were investigated first (entries 1−4). As expected, all iodides could promote the electrophilic annulations but provide the desired product **3** only in moderate yields (44−54%, entries 1−4). Further investigation found that a 32% yield was obtained using Larock's $I_2/NaHCO_3$ system (entry 5).[9b] After a series of trials, we found that palladium catalysts could facilitate the reaction (entries 6−9). We observed that $PdCl_2$ was more effective than $Pd(OAc)_2$, $Pd(PPh_3)_2Cl_2$, and $Pd(PPh_3)_4$. The reaction yield increased sharply to 95% when substrate **1a** was treated with 1,2-diphenyldisulfane, 2 equiv of I_2, and 10 mol % of $PdCl_2$ in THF at 80 °C (entry 6). It is worth noting that $PdCl_2$ could not catalyze the annulation reaction in the absence of I_2, which suggested that iodine played a key role in this transformation (entry 10). Subsequently, the effect of solvents was examined (entries 11−14). The results showed that various solvents, including toluene, DMSO, CH_3NO_2, and MeCN, were less effective than THF. Lower yield was found when the loading of iodine was reduced to 1 equiv (entry 15) or when the loading of $PdCl_2$ was reduced to 5 mol % (entry 16). The obvious decrease of reaction yield was observed using 0.5 equiv of disulfide in this reaction, although 0.5 equiv of disulfides was enough for the electrophilic annulations in our reported works[10] (entry 17). The reaction yield decreased to 19% when benzenethiol was used as electrophile instead of 1,2-diphenyldisulfane (entry 18).

With the optimal reaction conditions in hand, we explored the substrate scope of 2-(1-alkynyl)biphenyls and disulfides for

Received: December 6, 2012
Published: January 10, 2013

dx.doi.org/10.1021/jo302634n | J. Org. Chem. 2013, 78, 1300−1305

Table 1. Screening Conditions[a]



entry	[I] (equiv)	[Pd] (mol %)	solvent	yield (%)
1	I_2 (2)		THF	54
2	ICl (2)		THF	53
3	NIS (2)		THF	44
4	$PhI(OAc)_2$ (2)		THF	51
5[b]	I_2 (2)		THF	32
6	I_2 (2)	$PdCl_2$ (10)	THF	95
7	I_2 (2)	$Pd(OAc)_2$ (10)	THF	62
8	I_2 (2)	$Pd(PPh_3)_2Cl_2$ (10)	THF	69
9	I_2 (2)	$Pd(PPh_3)_4$ (10)	THF	65
10		$PdCl_2$ (10)	THF	0
11	I_2 (2)	$PdCl_2$ (10)	toluene	39
12	I_2 (2)	$PdCl_2$ (10)	DMSO	trace
13	I_2 (2)	$PdCl_2$ (10)	CH_3NO_2	42
14	I_2 (2)	$PdCl_2$ (10)	MeCN	54
15	I_2 (1)	$PdCl_2$ (10)	THF	28
16	I_2 (2)	$PdCl_2$ (5)	THF	68
17[c]	I_2 (2)	$PdCl_2$ (10)	THF	50
18[d]	I_2 (2)	$PdCl_2$ (10)	THF	19

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), [I] source, and Pd catalyst in solvent (2 mL) under N_2 atmosphere at 80 °C for 24 h. [b]3 equiv of $NaHCO_3$ was added. [c]0.1 mmol of **2a** was used. [d]0.2 mmol of PhSH was used instead of PhSSPh.

the electrophilic annulations (Table 2). First, the reaction between 2-(phenylethynyl)biphenyl **1a** and various disulfides **2b**–**2i** was investigated under the standard conditions. The results disclosed that a variety of aryl disulfides and aliphatic alkyl disulfides are suitable substrates, and the electrophilic annulations provide the corresponding products in moderate to good yields (entries 1–8). In general, electron-rich phenyl disulfide afforded a higher yield than electron-deficient phenyl disulfide. For example, substrates **2b** and **2f**, bearing a *p*-tolyl or 4-nitrophenyl group, reacted with substrate **1a** to give the corresponding products in 92 and 61% yields, respectively (entries 1 and 5). The transformation of substrate **1a** with 1,2-dimethyldisulfane **2g** or 1,2-dibenzyldisulfane **2h** also proceeded successfully to provide product in good yields (entries 6 and 7), but a lower yield was observed when 1,2-dicyclohexyldisulfane **2i** was used as coupling partner (entry 8). Subsequently, various 2-(1-alkynyl)biphenyls **1b**–**1g**, which bear different substituents at the terminal alkyne moiety, were evaluated (entries 9–14). The results showed that different functional groups, including *p*-tolyl, *o*-tolyl, *p*-ClC_6H_4, *m*-$CF_3C_6H_4$, thiophen-2-yl, and *n*-hexyl, were tolerated well under standard conditions. For example, substrates **1b** and **1c** bearing a *p*-tolyl or a bulky *o*-tolyl group afforded the corresponding products in 93 and 90% yield, respectively (entries 9 and 10). Moderate yields were observed when substrates **1d** and **1e** bearing an electron-deficient phenyl group were used as substrate (entries 11 and 12). Gratifyingly, substrate **1f** bearing a heteroaryl group furnished the desired product in a moderate yield (60%, entry 13). Substrate **1g** bearing an aliphatic alkyl group also underwent the reaction smoothly to afford the target product in quantitative yield (entry 14). Finally, the substituents on the biphenyl moiety were examined (entries 15–19). Methyl-substituted substrates **1h**, **1i**, and **1k** were treated with disulfide **2a** under standard conditions to afford the corresponding products in 58–64% yields (entries 15, 16, and 18). Substrates **1j** and **1l** bearing a chloro or fluoro group on the biphenyl ring were also successfully converted to the desired products in 31 and 81% yields, respectively (entries 17 and 19).

To elucidate the mechanism, a control reaction of 2-(phenylethynyl)biphenyl **1a**, I_2, and $PdCl_2$ was carried out under the standard conditions in the absence of disulfide (Scheme 2). However, the expected product **23** could not be detected, and almost 90% of reactant **1a** was recovered. The results revealed that the electrophilic annulation of 2-(1-alkynyl)biphenyls with disulfides did not proceed through an iodocyclization process.

On the basis of the present results and other mechanisms reported in the literature,[8,9] a possible mechanism was proposed as outlined in Scheme 3. Iodine could promote the electrophilic annulations without $PdCl_2$ (entry 1 in Table 1), and iodocyclization product could not be detected (Scheme 2). These results imply that the reaction of disulfide **2** with iodine in situ may yield active RSI. In the absence of $PdCl_2$ (Path 1),[8] the electrophilic addition of RSI to the triple bond of substrate **1** affords intermediate **A**. The intramolecular electrophilic attack on the neighboring benzene ring provides intermediate **B**, and subsequent deprotonation yields the desired products **3**–**22**. In the presence of $PdCl_2$ (Path 2), RSI could undergo ligand exchange with $PdCl_2$ to afford RSPdX and subsequently inserts into alkyne **1** to produce a vinylpalladium(II) complex **C**. The electrophilic aromatic palladation through a C–H activation step provides seven-membered palladacycle **D**.[11] The following reductive elimination produces the desired products **3**–**22** and Pd(0) species, which could be reoxidized to Pd(II) by I_2 or RSI. Study of the detailed mechanism is in progress.

In summary, we have developed a practical palladium-catalyzed iodine-mediated electrophilic annulation method for the synthesis of 9-sulfenylphenanthrenes using commercially available disulfides as electrophiles. In the presence of $PdCl_2$ and I_2, a variety of 2-(1-alkynyl)biphenyls underwent the electrophilic annulations successfully with various disulfides to afford the corresponding 9-sulfenylphenanthrenes in moderate to excellent yields. This methodology might provide a new strategy for constructing polycyclic aromatic hydrocarbons and also for the synthesis of sulfenyl phenanthrenes.

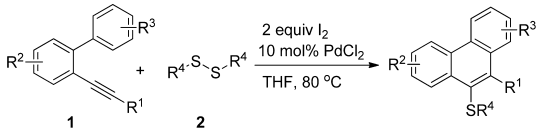
EXPERIMENTAL SECTION

General Information. Chemicals were either purchased or purified by standard techniques. ^1H NMR and ^{13}C NMR spectra were measured on a 500 MHz spectrometer (^1H at 500 MHz, ^{13}C at 125 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in δ relative to TMS, and the coupling constants J are given in hertz. ^{19}F NMR spectra were recorded on a 500 MHz spectrometer (^{19}F at 470 MHz) and are reported relative to $CFCl_3$ as the internal standard. High-resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometer. All reactions under nitrogen atmosphere were conducted using standard Schlenk techniques. Column chromatography was performed using EM silica gel 60 (300–400 mesh).

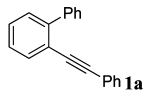
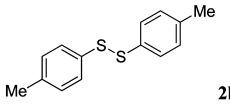
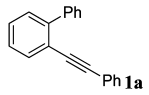
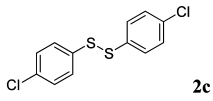
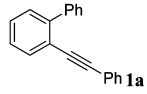
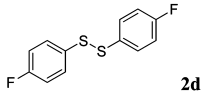
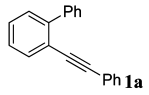
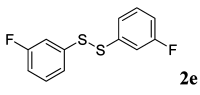
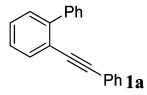
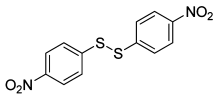
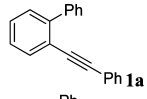
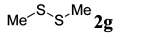
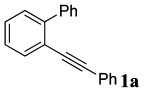
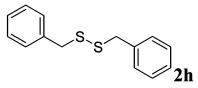
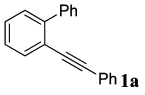
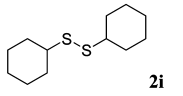
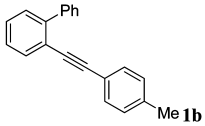
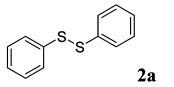
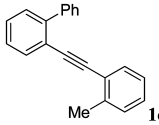
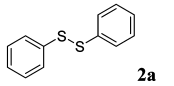
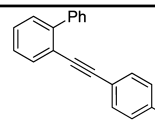
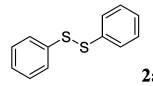
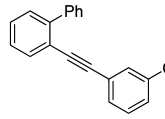
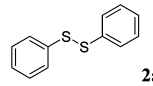
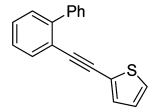
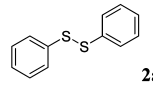
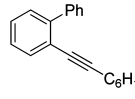
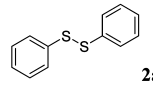
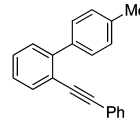
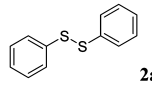
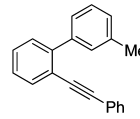
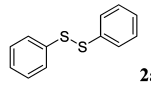
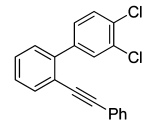
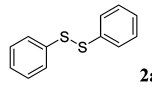
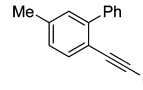
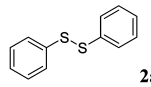
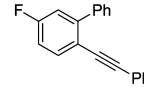
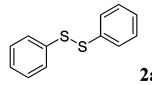
General Procedure for the Synthesis of 9-Sulfenyl Phenanthrenes. To a flame-dried Schlenk tube with a magnetic stirring bar were charged 2-(1-alkynyl)biphenyls **1** (0.2 mmol), disulfide (0.2 mmol), $PdCl_2$ (3.5 mg, 0.02 mmol), I_2 (101.6 mg, 0.4 mmol), and THF (anhydrous solvent, 2 mL) under N_2 atmosphere. The reaction mixture was stirred at 80 °C for 24 h. After the reaction equilibrium, the mixture was poured into ethyl acetate, which was washed with

dx.doi.org/10.1021/jo302634n | J. Org. Chem. 2013, 78, 1300–1305

Table 2. Electrophilic Annulation of 2-(1-Alkynyl)biphenyls with Disulfides[a]

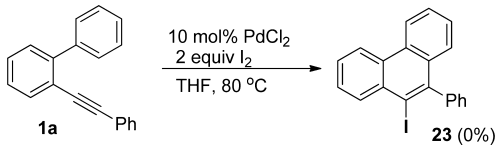


1 2

Entry	Substrate 1	Disulfide 2	Yield[%]
1	 **1a**	 **2b**	92 (**4**)
2	 **1a**	 **2c**	75 (**5**)
3	 **1a**	 **2d**	77 (**6**)
4	 **1a**	 **2e**	72 (**7**)
5	 **1a**	 **2f**	61 (**8**)
6	 **1a**	 **2g**	82 (**9**)
7	 **1a**	 **2h**	84 (**10**)
8	 **1a**	 **2i**	45 (**11**)
9	 **1b**	 **2a**	93 (**12**)
10[c]	 **1c**	 **2a**	90 (**13**)
11[c]	 **1d**	 **2a**	56 (**14**)
12	 **1e**	 **2a**	42 (**15**)
13	 **1f**	 **2a**	60 (**16**)
14	 **1g**	 **2a**	99 (**17**)
15	 **1h**	 **2a**	64 (**18**)
16	 **1i**	 **2a**	60 (**19**)
17	 **1j**	 **2a**	31 (**20**)
18	 **1k**	 **2a**	58 (**21**)
19	 **1l**	 **2a**	81 (**22**)

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.2 mmol), I_2 (2 equiv), and $PdCl_2$ (10 mol %) in THF (2 mL) under N_2 atmosphere at 80 °C for 24 h.

Scheme 2. Control Experiment



90% of **1a** was recovered

Scheme 3. Possible Mechanism

saturated NaS_2O_3 (2 × 10 mL) and then brine (1 × 10 mL). After the aqueous layer was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the desired products **3**–**22**.

*Phenyl(10-phenylphenanthren-9-yl)sulfane (**3**):* yellow solid (69.0 mg, 95% yield), mp 122–124 °C; IR (KBr, cm^{-1}) 3054, 2917, 1594, 1565, 1547, 746; ^1H NMR (300 MHz, $CDCl_3$) δ 8.78 (d, J = 8.4 Hz, 2H), 8.61 (d, J = 8.4 Hz, 1H), 7.65–7.71 (m, 2H), 7.55–7.60 (m, 1H), 7.47–7.48 (m, 2H), 7.40–7.44 (m, 3H), 7.23–7.26 (m, 2H), 6.91–7.06 (m, 3H), 6.89–6.91 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 140.2, 139.0, 132.2, 132.1, 131.1, 130.9, 129.5, 128.7, 128.6, 128.0, 127.9, 127.6, 127.6, 127.3, 127.2, 127.0, 126.7, 126.4, 124.6, 122.7, 122.6; LRMS (EI, 70 eV) m/z (%) 362 (M^+, 100), 284

dx.doi.org/10.1021/jo302634n | J. Org. Chem. 2013, 78, 1300–1305

(34), 252 (39); HRMS (ESI) calcd for $C_{26}H_{19}S^+$ ([M + H]$^+$) 363.1202, found 363.1205.

(10-Phenylphenanthren-9-yl)(p-tolyl)sulfane (**4**): yellow solid (69.5 mg, 92% yield), mp 133−135 °C; IR (KBr, cm^{-1}) 2963, 1566, 1528, 741; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72−8.76 (m, 2H), 8.61 (d, J = 8.0 Hz, 1H), 7.62−7.69 (m, 2H), 7.52−7.58 (m, 1H), 7.45−7.47 (m, 2H), 7.40−7.42 (m, 3H), 7.24−7.27 (m, 2H), 6.79−6.88 (m, 4H), 2.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 140.2, 135.3, 134.4, 132.8, 132.2, 132.0, 131.0, 130.9, 129.8, 129.5, 129.4, 128.7, 128.1, 128.0, 127.5, 127.3, 127.0, 126.7, 126.4, 122.7, 122.5, 20.8; LRMS (EI, 70 eV) m/z (%) 376 (M$^+$, 100), 343 (14), 284 (31), 252 (23); HRMS (ESI) calcd for $C_{27}H_{21}S^+$ ([M + H]$^+$) 377.1358, found 377.1358.

(4-Chlorophenyl)(10-phenylphenanthren-9-yl)sulfane (**5**): yellow solid (59.1 mg, 75% yield), mp 135−136 °C; IR (KBr, cm^{-1}) 2923, 1669, 1566, 1544, 1277, 938, 826; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.76 (d, J = 8.2 Hz, 2H), 8.56 (d, J = 8.2 Hz, 1H), 7.67−7.70 (m, 2H), 7.55−7.60 (m, 1H), 7.46−7.48 (m, 2H), 7.41−7.43 (m, 3H), 7.21−7.23 (m, 2H), 7.00−7.03 (m, 2H), 6.79−6.81 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.0, 140.0, 137.5, 132.2, 131.8, 131.2, 131.0, 130.5, 129.4, 128.8(2C), 128.0, 127.8 (2C), 127.7, 127.6, 127.5, 127.2, 126.8, 126.7, 122.9, 122.6; LRMS (EI, 70 eV) m/z (%) 396 (M$^+$, 100), 328 (23), 284 (48), 252 (60); HRMS (ESI) calcd for $C_{26}H_{18}ClS^+$ ([M + H]$^+$) 397.0812, found 397.0808.

(4-Fluorophenyl)(10-phenylphenanthren-9-yl)sulfane (**6**): yellow solid (58.6 mg, 77% yield), mp 43−44 °C; IR (KBr, cm^{-1}) 1717, 1684, 1541, 1507, 1097; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.76 (d, J = 8.4 Hz, 2H), 8.62 (d, J = 8.4 Hz, 1H), 7.65−7.71 (m, 2H), 7.56−7.62 (m, 1H), 7.46−7.47 (m, 2H), 7.41−7.43 (m, 3H), 7.20−7.23 (m, 2H), 6.83−6.88 (m, 2H), 6.73−6.79 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.8 (d, J_{C-F} = 243.0 Hz), 146.7, 140.1, 133.9 (2C), 132.2, 132.0, 131.1, 131.0, 129.6, 128.7, 128.4, 128.3, 128.0, 127.9, 127.7, 127.6, 127.4, 127.1, 126.8, 122.7 (d, J_{C-F} = 31.9 Hz), 115.7 (d, J_{C-F} = 22.9 Hz); ^{19}F NMR (470 MHz) δ −117.90; LRMS (EI, 70 eV) m/z (%) 380 (M$^+$, 88), 328 (54), 284 (64), 252 (100); HRMS (ESI) calcd for $C_{26}H_{18}FS^+$ ([M + H]$^+$) 381.1108, found 381.1112.

(3-Fluorophenyl)(10-phenylphenanthren-9-yl)sulfane (**7**): yellow solid (54.4 mg, 72% yield), mp 88−90 °C; IR (KBr, cm^{-1}) 1688, 1524, 1493, 1005; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.78 (d, J = 8.2 Hz, 2H), 8.57 (d, J = 8.1 Hz, 1H), 7.67−7.72 (m, 2H), 7.56−7.61 (m, 1H), 7.47−7.49 (m, 2H), 7.41−7.43 (m, 3H), 7.23−7.25 (m, 2H), 6.98−7.05 (m, 1H), 6.67−6.70 (m, 2H), 6.55−6.58 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9 (d, J_{C-F} = 245.0 Hz), 147.2, 141.4 (d, J_{C-F} = 7.8 Hz), 140.0, 132.2, 131.9, 131.3, 131.0, 129.9 (d, J_{C-F} = 8.5 Hz), 129.4, 128.8, 128.0, 127.9, 127.8, 127.7, 127.5, 127.2, 126.8, 126.4, 122.9, 122.6, 122.0 (d, J_{C-F} = 2.5 Hz), 113.2 (d, J_{C-F} = 23.8 Hz), 111.7 (d, J_{C-F} = 21.3 Hz); LRMS (EI, 70 eV) m/z (%) 380 (M$^+$, 100), 328 (24), 284 (43), 252 (62); HRMS (ESI) calcd for $C_{26}H_{18}FS^+$ ([M + H]$^+$) 381.1108, found 381.1103.

(4-Nitrophenyl)(10-phenylphenanthren-9-yl)sulfane (**8**):[9b] white solid (50.0 mg, 61% yield), mp 185−187 °C; IR (KBr, cm^{-1}) 2916, 1704, 1496, 1359, 1036, 744; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80 (d, J = 8.2 Hz, 2H), 8.44 (d, J = 8.2 Hz, 1H), 7.91 (d, J = 8.7 Hz, 2H), 7.69−7.75 (m, 2H), 7.57−7.62 (m, 1H), 7.47−7.51 (m, 2H), 7.41−7.43 (m, 3H), 7.19−7.23 (m, 2H), 6.95 (d, J = 8.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.9, 147.7, 144.7, 139.6, 132.0, 131.3, 131.2, 131.0, 129.1, 128.9, 128.3, 128.1, 128.0, 127.8, 127.5, 127.1, 127.0, 125.5, 124.6, 123.8, 123.1, 122.7; LRMS (EI, 70 eV) m/z (%) 407 (M$^+$, 23), 322 (35), 252 (100), 207 (44).

Methyl(10-phenylphenanthren-9-yl)sulfane (**9**): white solid (49.4 mg, 82% yield), mp 137−139 °C; IR (KBr, cm^{-1}) 1364, 1223, 772, 733; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85−8.88 (m, 1H), 8.70−8.77 (m, 2H), 7.69−7.73 (m, 2H), 7.59−7.64 (m, 1H), 7.50−7.53 (m, 3H), 7.41−7.43 (m, 2H), 7.31−7.33 (m, 2H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2, 140.8, 132.1, 132.0, 131.6, 130.8, 130.5, 129.9, 128.4, 128.0, 127.7, 127.4, 127.2, 127.1, 126.8, 126.6, 123.0, 122.4, 20.0; LRMS (EI, 70 eV) m/z (%) 300 (M$^+$, 100), 285 (86), 284 (67), 252 (39); HRMS (ESI) calcd for $C_{21}H_{17}S^+$ ([M + H]$^+$) 301.1045, found 301.1051.

Benzyl(10-phenylphenanthren-9-yl)sulfane (**10**): white solid (63.0 mg, 84% yield), mp 186−188 °C; IR (KBr, cm^{-1}) 2921, 1362, 1220, 783, 727; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.88−8.91 (m, 1H), 8.73−8.76 (m, 2H), 7.71−7.74 (m, 2H), 7.62−7.65 (m, 1H), 7.35−7.45 (m, 5H), 7.09−7.13 (m, 3H), 6.95−6.98 (m, 2H), 6.79−6.82 (m, 2H), 3.82 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2, 140.3, 137.7, 132.2, 132.1, 130.7, 130.6, 130.1, 129.2, 128.9, 128.5, 128.2, 127.8, 127.7, 127.4, 127.2, 127.0, 126.8, 126.8, 126.6, 123.0, 122.4, 40.8; LRMS (EI, 70 eV) m/z (%) 376 (M$^+$, 100), 284 (30), 252 (36); HRMS (ESI) calcd for $C_{27}H_{21}S^+$ ([M + H]$^+$) 377.1358, found 377.1357.

Cyclohexyl(10-phenylphenanthren-9-yl)sulfane (**11**): white solid (33.0 mg, 45% yield), mp 131−133 °C; IR (KBr, cm^{-1}) 2917, 2850, 1713, 1364, 1223 784; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87−8.90 (m, 1H), 8.67−8.73 (m, 2H), 7.67−7.70 (m, 2H), 7.60−7.64 (m, 1H), 7.46−7.49 (m, 3H), 7.41−7.42 (m, 2H), 7.28−7.31 (m, 2H), 2.78−2.85 (m, 1H), 1.83−1.88 (m, 4H), 1.60−1.69 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5, 140.6, 133.2, 132.2, 130.7, 130.6, 130.5, 129.9, 128.4, 128.3, 127.8, 127.1, 126.9, 126.7, 126.6 (2C), 122.8, 122.4, 48.6, 33.5, 26.0, 25.7; LRMS (EI, 70 eV) m/z (%) 368 (M$^+$, 100), 286 (100), 252 (26); HRMS (ESI) calcd for $C_{26}H_{25}S^+$ ([M + H]$^+$) 369.1671, found 369.1674.

Phenyl(10-p-tolylphenanthren-9-yl)sulfane (**12**): yellow solid (70.1 mg, 93% yield), mp 109−111 °C; IR (KBr, cm^{-1}) 2913, 1570, 1541, 1412, 1279, 935; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73−8.76 (m, 2H), 8.59 (d, J = 8.0 Hz, 1H), 7.62−7.69 (m, 2H), 7.43−7.54 (m, 3H), 7.20−7.23 (m, 2H), 7.13−7.15 (m, 2H), 7.03−7.06 (m, 2H), 6.90−6.99 (m, 3H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9, 139.1, 137.2, 136.9, 132.4, 132.1, 131.1, 130.9, 129.4, 128.8, 128.7, 128.6, 128.1, 127.6, 127.5, 127.1, 127.0, 126.7, 126.3, 124.6, 122.7, 122.5, 21.4; LRMS (EI, 70 eV) m/z (%) 376 (M$^+$, 100), 284 (34), 252 (26); HRMS (ESI) calcd for $C_{27}H_{21}S^+$ ([M + H]$^+$) 377.1359, found 377.1357.

Phenyl(10-o-tolylphenanthren-9-yl)sulfane (**13**): yellow solid (68.0 mg, 90% yield), mp 51−53 °C; IR (KBr, cm^{-1}) 2913, 1610, 1567, 1541, 1445, 1137; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (d, J = 8.2 Hz, 2H), 8.59 (d, J = 8.2 Hz, 1H), 7.66−7.72 (m, 2H), 7.55−7.60 (m, 1H), 7.44−7.49 (m, 1H), 7.32−7.37 (m, 3H), 7.17−7.23 (m, 1H), 6.91−7.07 (m, 4H), 6.88−6.91 (m, 2H), 1.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 139.6, 138.5, 136.6, 132.1, 131.7, 131.1, 130.9, 129.7, 129.3, 128.6 (2C), 128.1, 128.0, 127.7 (2C), 127.5, 127.2, 127.0, 126.6, 125.5, 124.7, 122.8, 122.7, 19.9; LRMS (EI, 70 eV) m/z (%) 376 (M$^+$, 100), 284 (29), 252 (22); HRMS (ESI) calcd for $C_{27}H_{21}S^+$ ([M + H]$^+$) 377.1359, found 377.1359.

(10-(4-Chlorophenyl)phenanthren-9-yl)(phenyl)sulfane (**14**): yellow solid (48.1 mg, 56% yield), mp 131−133 °C; IR (KBr, cm^{-1}) 3005, 1698, 1653, 1528; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.76−8.79 (m, 2H), 8.62 (d, J = 8.3 Hz, 1H), 7.67−7.71 (m, 2H), 7.57−7.60 (m, 1H), 7.44−7.50 (m, 2H), 7.37−7.38 (m, 2H), 7.15−7.16 (m, 2H), 7.05−7.08 (m, 2H), 6.98−7.01 (m, 1H), 6.86−6.88 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5, 138.7, 138.5, 133.4, 132.0 (2C), 131.1, 130.9, 129.5, 128.7, 128.4, 128.2, 128.0, 127.8, 127.7, 127.5, 127.3, 126.9, 126.3, 124.8, 122.8, 122.7; LRMS (EI, 70 eV) m/z (%) 396 (M$^+$, 100), 284 (31), 252 (22); HRMS (ESI) calcd for $C_{26}H_{18}ClS^+$ ([M + H]$^+$) 397.0812, found 397.0811.

Phenyl(10-(3-(trifluoromethyl)phenyl)phenanthren-9-yl)sulfane (**15**): yellow solid (36.4 mg, 42% yield), mp 116−118 °C; IR (KBr, cm^{-1}) 2884, 1664, 1528, 1184; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.81 (d, J = 8.4 Hz, 2H), 8.71 (d, J = 8.4 Hz, 1H), 7.71−7.76 (m, 4H), 7.39−7.64 (m, 6H), 7.04−7.07 (m, 2H), 6.84−6.86 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 140.7, 138.5, 133.0, 132.2, 131.8, 131.1, 130.9, 130.3 (q, J_{C-F} = 32 Hz), 129.5, 128.8, 128.4, 128.1, 128.0, 127.9, 127.8, 127.5, 126.6, 126.5 125.1, 124.2 (2C), 124.1 (q, J_{C-F} = 270.6 Hz), 122.8 (2C); ^{19}F NMR (470 MHz) δ −62.49; LRMS (EI, 70 eV) m/z (%) 430 (M$^+$, 16), 322 (100), 252 (84), 207 (56); HRMS (ESI) calcd for $C_{27}H_{18}F_3S^+$ ([M + H]$^+$) 431.1076, found 431.1069.

2-(10-(Phenylthio)phenanthren-9-yl)thiophene (**16**): yellow solid (43.6 mg, 60% yield), mp 150−152 °C; IR (KBr, cm^{-1}) 2913, 1573, 1337, 1097, 882; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.76 (d, J = 7.4 Hz, 2H), 8.60 (d, J = 7.4 Hz, 1H), 7.66−7.74 (m, 3H), 7.52−7.59 (m,

dx.doi.org/10.1021/jo302634n | J. Org. Chem. 2013, 78, 1300−1305

2H), 7.45 (d, J = 8.5 Hz, 1H), 7.07−7.15 (m, 3H), 7.02 (d, J = 6.9 Hz, 1H), 6.94−6.98 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 139.4, 138.9, 132.8, 131.8, 131.3, 130.9, 130.4, 128.7, 128.4, 128.3, 128.1, 127.8, 127.6, 127.5, 127.0, 126.7, 126.4, 125.8, 124.8, 122.8, 122.5; LRMS (EI, 70 eV) m/z (%)368 (M^+, 100), 252 (54), 207 (64); HRMS (ESI) calcd for $C_{24}H_{17}S_2^+$ ([M + H]$^+$) 369.0766, found 369.0765.

(10-Hexylphenanthren-9-yl)(phenyl)sulfane ***(17)****:* yellow oil (72.9 mg, 99% yield); IR (KBr, cm^{-1}) 2919, 1598, 1557, 1541, 1421, 811; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51−7.52 (m, 1H), 7.49−7.50 (m, 1H), 7.37−7.41 (m, 3H), 7.29−7.34 (m, 3H), 7.17−7.21 (m, 3H), 6.94−6.97 (m, 2H), 2.23−2.43 (m, 2H), 1.32−1.37 (m, 2H), 1.11−1.25 (m, 6H), 0.83 (t, J = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 140.9, 140.5, 140.1, 134.5, 131.1, 130.4, 130.2, 129.4, 129.3, 129.2, 128.7, 128.4, 128.0, 127.9, 127.3, 127.1, 127.0, 39.8, 31.4, 28.5, 27.2, 22.4, 14.1; LRMS (EI, 70 eV) m/z (%) 370 (M^+, 88), 322 (100), 252 (34); HRMS (ESI) calcd for $C_{26}H_{27}S^+$ ([M + H]$^+$) 371.1828, found 371.1824.

(2-Methyl-10-phenylphenanthren-9-yl)(phenyl)sulfane ***(18)****:* yellow solid (48.3 mg, 64% yield), mp 123−125 °C; IR (KBr, cm^{-1}) 2920, 1605, 1529, 1514, 1339, 803, 739; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, J = 8.2 Hz, 1H), 8.66 (d, J = 8.2 Hz, 1H), 8.58 (d, J = 8.2 Hz, 1H), 7.62−7.67 (m, 1H), 7.50−7.55 (m, 2H), 7.40−7.42 (m, 3H), 7.21−7.24 (m, 3H), 6.97−7.07 (m, 3H), 6.87−6.90 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 140.3, 139.1, 136.6, 132.3, 131.7, 130.9, 129.9, 129.5, 129.4, 129.0, 128.6, 128.2, 128.0, 127.9, 127.3, 127.1, 127.0 (2C), 126.3, 124.6, 122.5, 21.6; LRMS (EI, 70 eV) m/z (%) 376 (M^+, 100), 284 (32), 252 (25); HRMS (ESI) calcd for $C_{27}H_{21}S^+$ ([M + H]$^+$) 377.1358, found 377.1358.

(3-Methyl-10-phenylphenanthren-9-yl)(phenyl)sulfane ***(19)****:* yellow solid (45.4 mg, 60% yield), mp 127−129 °C; IR (KBr, cm^{-1}) 3077, 2923, 1609, 1557, 1502, 1425, 1317, 1121; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (d, J = 8.5 Hz, 1H), 8.69 (d, J = 7.8 Hz, 1H), 7.62−7.65 (m, 1H), 7.55−7.58 (m, 2H), 7.39−7.41 (m, 3H), 7.36−7.37 (m, 2H), 7.21−7.23 (m, 2H), 7.05−7.08 (m, 2H), 6.97−7.08 (m, 1H), 6.90 (d, J = 7.5 Hz, 2H), 3.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2, 140.9, 138.9, 135.0, 133.7, 133.0, 132.2, 132.1, 131.4, 129.5, 129.1, 128.6, 127.9, 127.7, 127.3, 127.2, 127.1, 126.9, 126.4, 125.8, 125.7, 124.6, 29.7; LRMS (EI, 70 eV) m/z (%) 376 (M^+, 100), 284 (30), 252 (23); HRMS (ESI) calcd for $C_{27}H_{21}S^+$ ([M + H]$^+$) 377.1358, found 377.1362.

(2,3-Dichloro-10-phenylphenanthren-9-yl)(phenyl)sulfane ***(20)****:* white solid (26.9 mg, 31% yield), mp 183−184 °C; IR (KBr, cm^{-1}) 2946, 1623, 1522, 1218; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66−8.70 (m, 2H), 8.60 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 9.0 Hz, 1H), 7.66−7.71 (m, 1H), 7.56−7.61 (m, 1H), 7.29−7.37 (m, 3H), 7.18−7.21 (m, 2H), 7.00−7.10 (m, 3H), 6.84−6.87 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 142.2, 138.8, 134.5, 132.5, 132.1, 131.7, 131.0, 130.4,, 130.3, 129.9, 128.9, 128.7, 128.6, 128.4, 127.8, 127.3, 127.2, 126.5, 124.9, 123.0, 122.3; LRMS (EI, 70 eV) m/z (%) 430 (M^+, 3), 376 (100), 284 (31), 265 (25); HRMS (ESI) calcd for $C_{26}H_{17}Cl_2S^+$ ([M + H]$^+$) 431.0423, found 431.0420.

(7-Methyl-10-phenylphenanthren-9-yl)(phenyl)sulfane ***(21)****:* yellow solid (43.3 mg, 58% yield), mp 125−127 °C; IR (KBr, cm^{-1}) 2963, 1694, 1503, 1278, 941; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (d, J = 8.0 Hz, 1H), 8.54 (s, 1H), 8.48 (d, J = 8.0 Hz, 1H), 7.63−7.69 (m, 1H), 7.43−7.45 (m, 2H), 7.37−7.40 (m, 4H), 7.22−7.24 (m, 2H), 7.02−7.06 (m, 2H), 6.95−6.98 (m, 1H), 6.88−6.90 (m, 2H), 2.59 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 140.3, 139.1, 136.8, 132.6, 132.4, 130.9, 130.8, 130.0, 129.6, 129.3, 128.7, 128.6, 127.9 (2C), 127.4, 127.3, 126.6, 126.3, 124.6, 122.6, 122.5, 21.9; LRMS (EI, 70 eV) m/z (%) 376 (M^+, 100), 284 (33), 252 (25); HRMS (ESI) calcd for $C_{27}H_{21}S^+$ ([M + H]$^+$) 377.1358, found 377.1359.

(7-Fluoro-10-phenylphenanthren-9-yl)(phenyl)sulfane ***(22)****:* yellow solid (59.1 mg, 81% yield), mp 113−115 °C; IR (KBr, cm^{-1}) 2967, 1528, 1441, 1366, 1275; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58−8.62 (m, 2H), 8.35 (d, J = 8.5 Hz, 1H), 7.67−7.70 (m, 1H), 7.46−7.51 (m, 2H), 7.41−7.42 (m, 3H), 7.27−7.31 (m, 1H), 7.23−7.24 (m, 2H), 7.05−7.08 (m, 2H), 6.98−7.01 (m, 1H), 6.87−6.89 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.8 (d, J_{C-F} = 245.5 Hz), 146.0 (d, J_{C-F} = 2.3 Hz), 139.9, 138.7, 132.6, 132.5, 130.7, 130.6, 130.5, 129.5, 128.8, 128.7, 128.0, 127.7, 127.5, 127.4, 126.8, 126.4, 124.8, 122.8, 116.4 (d, J_{C-F} = 23.0 Hz), 107.9 (d, J_{C-F} = 22.4 Hz); ^{19}F NMR (470 MHz) δ −117.60; LRMS (EI, 70 eV) m/z (%) 380 (M^+, 100), 302 (35), 270 (38); HRMS (ESI) calcd for $C_{26}H_{18}FS^+$ ([M + H]$^+$) 381.1108, found 381.1110.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray data of compound **3** and characterization data for all new and known compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: zxg@wzu.edu.cn, pcq@wzu.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (Nos. 21002070 and 21102104) and Zhejiang Provincial Natural Science Foundation of China (No. Y4100307) for financial support.

■ REFERENCES

(1) (a) Floyd, A. J.; Dyke, S. F.; Ward, S. E. *Chem. Rev.* **1976**, *76*, 509. (b) Wang, K.; Hu, Y.; Liu, Y.; Mi, N.; Fan, Z.; Liu, Y.; Wang, Q. *J. Agric. Food. Chem.* **2010**, *48*, 12337.

(2) (a) Wilson, S.; Ruenitz, P. C. *J. Pharm. Sci.* **1993**, *82*, 571. (b) Wei, L.-Y.; Shi, Q.; Bastow, K. F.; Brossi, A.; Morris-Natschke, S. L.; Nakagawa-Goto, K.; Wu, T.-S.; Pan, S.-L.; Teng, C.-M.; Lee, K.-H. *J. Med. Chem.* **2007**, *50*, 3674.

(3) (a) Tanabe, A.; Nakashima, H.; Yoshida, O.; Yamamoto, N.; Tenmyo, O.; Oki, T. *J. Antibiot.* **1988**, *41*, 1708. (b) Hoshino, H.; Seki, J.-I.; Takeuchi, T. *J. Antibiot.* **1989**, *42*, 344.

(4) (a) Boger, D. L.; Mullican, M. D. *J. Org. Chem.* **1984**, *49*, 4045. (b) Hattori, T.; Shimazumi, Y.; Goto, H.; Yamabe, O.; Morohashi, N.; Kawai, W.; Miyano, S. *J. Org. Chem.* **2003**, *68*, 2099.

(5) (a) Wu, J.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718. (b) Murphy, A. R.; Frechet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066. (c) Yamamoto, T.; Koizumi, T.-A. *Polymer* **2007**, *48*, 5449. (d) Grisorio, R.; Suranna, G. P.; Mastrorilli, P.; Nobile, C. F. *Org. Lett.* **2007**, *9*, 3149. (e) He, B.; Tian, H.-K.; Geng, Y.-H.; Wang, F.-S.; Müllen, K. *Org. Lett.* **2008**, *10*, 773.

(6) For selected examples, see: (a) Gies, A.-E.; Pfeffer, M. *J. Org. Chem.* **1999**, *64*, 3650. (b) Mandal, A. B.; Lee, G.-H.; Liu, Y.-H.; Peng, S.-M.; Leung, M.-K. *J. Org. Chem.* **2000**, *65*, 332. (c) Yoshikawa, E.; Radhakrishnan, K. V.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7280. (d) Yoshikawa, E.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 173. (e) Catellani, M.; Motti, E.; Baratta, S. *Org. Lett.* **2001**, *3*, 3611. (f) Almeida, J. F.; Castedo, L.; Fernández, D.; Neo, A. G.; Romero, V.; Tojo, G. *Org. Lett.* **2003**, *5*, 4939. (g) Luliano, A.; Piccioli, P.; Fabbri, D. *Org. Lett.* **2004**, *6*, 3711. (h) Kanno, K.-i.; Liu, Y.-H.; Lesato, A.; Nakajima, K.; Takahashi, T. *Org. Lett.* **2005**, *7*, 5453. (i) Shen, H.-C.; Tang, J.-M.; Chang, H.-K.; Yang, C.-W.; Liu, R.-S. *J. Org. Chem.* **2005**, *70*, 10113. (j) Wang, Y.; Xu, J.-J.; Burton, D. J. *J. Org. Chem.* **2006**, *71*, 7780. (k) Lin, Y.-D.; Cho, C.-L.; Ko, C.-W.; Pulte, A.; Wu, Y.-T. *J. Org. Chem.* **2012**, *77*, 9979.

(7) (a) Fürstner, A.; Mamane, V. *J. Org. Chem.* **2002**, *67*, 6264. (b) Mamane, V.; Hannen, P.; Fürstner, A. *Chem.—Eur. J.* **2004**, *10*, 4556. (c) Bandini, M.; Emer, E.; Tommasi, S.; Umani-Ronchi, A. *Eur. J. Org. Chem.* **2006**, 3527. (d) Chernyak, N.; Gevorgyan, V. *Adv. Synth. Catal.* **2009**, *351*, 1101. (e) Komeyama, K.; Igawa, R.; Takaki, K. *Chem. Commun.* **2010**, *46*, 1748.

(8) Bera, K.; Sarkar, S.; Jalal, S.; Jana, U. *J. Org. Chem.* **2012**, *77*, 8780.

(9) (a) Yao, T.-L.; Campo, M. A.; Larock, R. C. *Org. Lett.* **2004**, *6*, 2677. (b) Yao, T.-L.; Campo, M. A.; Larock, R. C. *J. Org. Chem.* **2005**, *70*, 3511.
(10) (a) Guo, Y.-J.; Tang, R.-Y.; Li, J.-H.; Zhong, P.; Zhang, X.-G. *Adv. Synth. Catal.* **2009**, *351*, 2615. (b) Du, H.-A.; Zhang, X.-G; Tang, R.-Y.; Li, J.-H. *J. Org. Chem.* **2009**, *74*, 7844. (c) Du, H.-A.; Tang, R.-Y.; Deng, C.-L.; Liu, Y.; Li, J.-H.; Zhang, X.-G. *Adv. Synth. Catal.* **2011**, *353*, 2739.
(11) (a) Wu, Y.-T.; Kuo, M.-Y.; Chang, Y.-T.; Shin, C.-C.; Wu, T.-C.; Tai, C.-C.; Cheng, T.-H.; Liu, W.-S. *Angew. Chem., Int. Ed.* **2008**, *47*, 9891. (b) Shi, Z.-Z.; Ding, S.-T.; Cui, Y.-X.; Jiao, N. *Angew. Chem., Int. Ed.* **2009**, *48*, 7895. (c) Wang, C.; Rakshit, S.; Glorius, F. *J. Am. Chem. Soc.* **2010**, *132*, 14006.

dx.doi.org/10.1021/jo302634n | *J. Org. Chem.* 2013, 78, 1300−1305