JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Manganese(III) Acetate-Mediated Cyclization of Diarylmethylenecyclopropa[*b*]naphthalenes: A Method for the Synthesis of 1,2-Benzanthracene Derivatives

Jian Cao,[†] Maozhong Miao,[†] Wanli Chen,[‡] Luling Wu,*[,†] and Xian Huang[†,§,⊥]

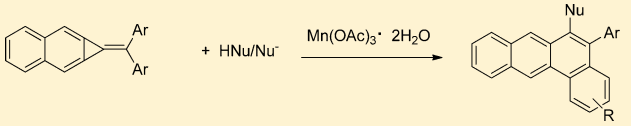
[†]Department of Chemistry, Zhejiang University, Xi-xi Campus, Hangzhou 310028, People's Republic of China

[‡]Zhejiang University of Technology, Chaowang Road, Hangzhou, People's Republic of China

[§]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China

Supporting Information

ABSTRACT: The manganese(III) acetate-mediated free radical cyclization of diarylmethylenecyclopropa[*b*]naphthalenes with nucleophiles such as carboxylic acid and sulfonic acid provides an efficient method for the synthesis of 1,2-benzanthracenes in moderate to good yields under mild conditions. In addition, after several steps of simple and routine operations, the obtained 1,2-benzanthracenes bearing an acetoxy group could be easily converted to structurally more sophisticated 1,2-benzanthracene derivatives, which are not easily accessible yet potentially useful candidates for materials science.



INTRODUCTION

The chemistry of polycyclic aromatic hydrocarbons (PAHs) has become a field of increasing interest during the past decades, particularly in materials science because of their unique electrical and optical properties.[1−5] The charge transport properties exhibited by some PAHs, for example, make them potential candidates for organic optoelectronic devices such as light-emitting diodes, field-effect transistors, and photovoltaics.[6−12] PAHs with 1,2-benzanthracene skeletons are also of considerable importance due to their applications as carcinogenic activity compounds in medical chemistry as well as valuable synthetic intermediates in organic synthesis.[13] Therefore, much attention has been paid to the synthesis of 1,2-benzanthracene derivatives. Many known methods have provided reliable routes; however, most of them require multiple steps or harsh conditions.[14−21] Thus, it remains highly desired to develop facile and efficient protocols for their synthesis.

On the other hand, the Mn(III)-mediated radical cyclization has become a valuable method for the synthesis of cyclic compounds during the past 30 years.[22−25] The previous investigations have shown that $Mn(OAc)_3{\cdot}2H_2O$ is a useful reagent for oxidative single-electron transfer processes leading to a large number of novel carbon−carbon and carbon−heteroatom bond-forming reactions. Numerous chemo-, regio-, and stereoselective synthetic methods have been developed in both inter- and intramolecular manners, and their applicability to the construction of natural and biologically active molecules has been demonstrated, as well.[26−37]

We have been engaged in the synthetic application of methylenecyclopropanes (MCPs) for years, and a variety of useful reactions for the synthesis of various compounds were developed based on these structurally interesting molecules.[38−44] Recently, we were interested in the chemistry of its analogues, diarylmethylenecyclopropa[*b*]naphthalenes **1**, which can be prepared from naphthalene according to the known procedure (Scheme 1).[45] Due to their unusual structure, which contains a triafulvene, a [3]radialene, and a cycloproparene unit, diarylmethylenecyclopropa[*b*]naphthalenes **1** are of considerable importance for physical and theoretical study.[46−49] Recently, they also have attracted much attention from synthetic viewpoints and have been used as building blocks for the synthesis of otherwise inaccessible compounds. In this regard, we have reported a highly regioselective Pd(0)-catalyzed [3 + 2] cycloaddition reaction of diarylmethylenecyclopropa[*b*]naphthalenes with alkenes, alkynes, or arynes to produce 1(3)-alkylidene-2,3-dihydro-1*H*-cyclopenta-[*b*]naphthalene, 1-alkylidene-1*H*-cyclopenta[*b*]naphthalene, and 11-diarylmethylene-11*H*-benzo[*b*]fluorine derivatives.[43,44] As a continuing exploration on the synthetic utility of these interesting compounds, in this paper, we wish to disclose a manganese(III) acetate-mediated radical cyclization reaction of **1** with nucleophiles such as carboxylic acid, sulfonic acid, and hydrazoic acid, affording an efficient synthesis of 1,2-benzanthracenes **2**. Meanwhile, we also demonstrate that compounds **2** could be easily converted to 1,2-benzanthracene derivatives with more advanced structures after several simple and routine operations (Scheme 2).

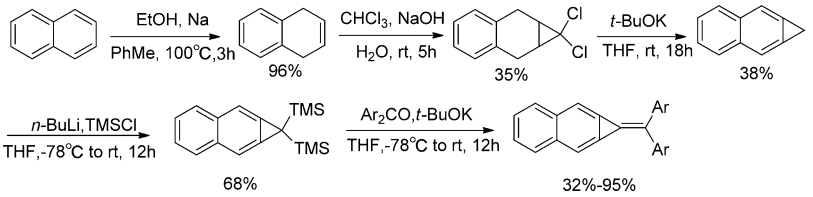
RESULTS AND DISCUSSION

As an initial examination on the reaction of 1-(diphenylmethylene)-1*H*-cyclopropa[*b*]naphthalene **1a** with 3.0 equiv of manganese(III) acetate dihydrate ($Mn(OAc)_3{\cdot}2H_2O$) in HOAc at 25 °C, fortunately, we found that 5-phenyl-1,2-benzanthracene-6-yl acetate **2a** was produced in 80% yield after 24 h (Table 1, entry 1). The structure of **2a** was unambiguously

Received: July 30, 2011
Published: October 12, 2011

   dx.doi.org/10.1021/jo2015906 | J. Org. Chem. 2011, 76, 9329−9337

Scheme 1



Scheme 2

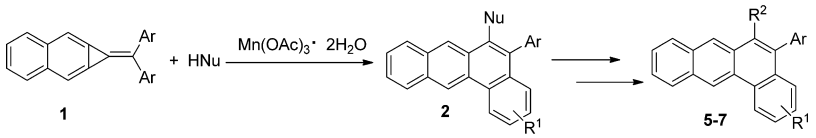
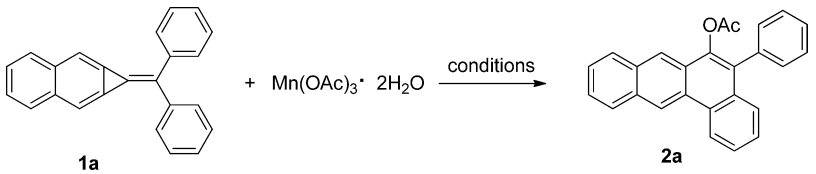


Table 1. Optimization on the Reaction of 1-(Diphenylmethylene)-1*H*-cyclopropa[*b*]naphthalene 1a with Oxidants under Various Conditions[a]



entry	$Mn(OAc)_3{\cdot}2H_2O$ (equiv)	solvent	temp (°C)	time (h)	yield of **2a** (%)[b]
1	3.0	HOAc	25	24	80
2	3.0	HOAc	40	4	93
3	3.0	HOAc	60	0.5	86
4	**2.4**	**HOAc**	**40**	**4**	**93**
5	2.4	THF	60	24	trace[c]
6	2.4	$CHCl_3$	60	24	trace[c]
7	2.4	CH_3OH	60	24	20[d]
8	2.4[e]	HOAc	40	24	trace
9	2.4[f]	HOAc	40	0.5	trace

[a]The reactions were conducted with 0.2 mmol of **1a** in 2 mL of solvent. [b]Isolated yield. [c]90% of **1a** was recovered. [d]70% of **1a** was recovered. [e]$Cu(OAc)_2$ was used instead of $Mn(OAc)_3{\cdot}2H_2O$. [f]$(NH_4)_2Ce(NO_3)_6$ was used instead of $Mn(OAc)_3{\cdot}2H_2O$.

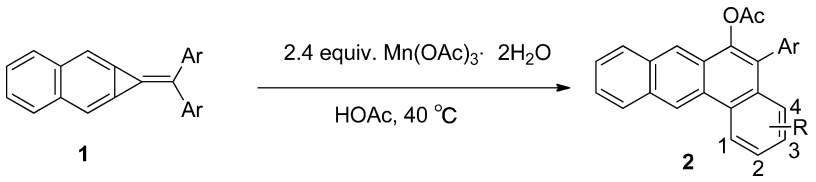
confirmed by X-ray diffraction analysis.[50] Several reaction parameters were subsequently investigated to optimize the reaction conditions. The results are summarized in Table 1. It was found that the reaction proceeded much more efficiently at 40 °C, therefore producing **2a** in 93% yield within 4 h (Table 1, entry 2). However, the yield dropped to 86% at 60 °C, although the reaction could complete within 0.5 h (Table 1, entry 3). The amount of $Mn(OAc)_3{\cdot}2H_2O$ could be reduced from 3.0 equiv to 2.4 equiv with a similar yield of **2a** (Table 1, entry 4). The reaction conducted in other solvents such as THF, $CHCl_3$, or CH_3OH gave **2a** in very low yields (entries 5−7). For example, in THF and $CHCl_3$, only trace amount of **2a** was obtained, and in CH_3OH, the yield of **2a** was limited to 20%. In addition, other oxidants such as ammonium cerium(IV) nitrate (CAN) and copper(II) acetate ($Cu(OAc)_2$) were also examined, but only a trace amount of **2a** was formed (Table 1, entries 8 and 9). Overall, the optimized reaction condition is defined as follows: 1.0 equiv of **1** reacted with 2.4 equiv of $Mn(OAc)_3{\cdot}2H_2O$ in HOAc at 40 °C(Table 1, entry 4).

With the optimized reaction conditions in hand, a variety of diarylmethylenecyclopropa[*b*]naphthalenes **1**, which bear substituted phenyl rings as the Ar group, were synthesized and treated with $Mn(OAc)_3{\cdot}2H_2O$ and HOAc to examine the scope of the reaction. As shown in Table 2, diarylmethylenecyclopropa[*b*]naphthalenes **1** with electron-withdrawing aryl groups such as *p*-FC_6H_4, *p*-Cl C_6H_4, and *p*-Br C_6H_4 all gave the corresponding products in good yields (Table 2, entries 2−4). Substrate **1e** bearing electron-donating aryl groups (Ar = 3,5-dimethoxyphenyl) also reacted smoothly to produce the expected product **2e** in 84% yield (Table 2, entry 5). Treatment of diarylmethylenecyclopropa[*b*]naphthalene bearing *p*-tolyl groups (**1f**) with $Mn(OAc)_3{\cdot}2H_2O$ efficiently gave a 90% yield of desired compound **2f**. Comparatively, the reaction of diarylmethylenecyclopropa[*b*]naphthalene with a *m*-tolyl group (**1g**) gave the corresponding compounds **2g** and **2g′** as a 1:1 mixture of inseparable isomers in an 85% overall yield (Table 2, entries 6 vs 7). In addition, an interesting result was observed when we employed the substrate **1h** which bears a phenyl and methyl group; the desired compound **2h** was produced in 35% yield together with 1-(naphthalen-2-yl)-2-phenylprop-2-en-1-one (**2h′**) in 33% yield (Scheme 3).

We also examined the reaction of diarylmethylenecyclopropa[*b*]naphthalenes **1** with other carboxylic acids. The corresponding 1,2-benzanthracenes were also successfully obtained. For example, the reaction of **1a** with $Mn(OAc)_3{\cdot}2H_2O$ in hexanoic acid produced 5-phenyl-1,2-benzanthracene-6-yl hexanoate (**2i**) in 86% yield (eq 1, Scheme 4), and treatment of **1a** with excessive benzoic acid using THF as solvent also selectively led to the formation of

dx.doi.org/10.1021/jo2015906 | *J. Org. Chem.* 2011, 76, 9329−9337

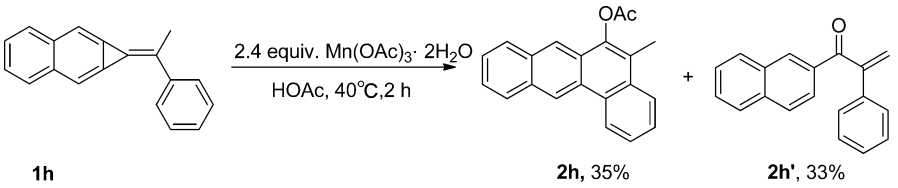
Table 2. Reactions of Diarylmethylenecyclopropa[*b*]naphthalenes 1 with $Mn(OAc)_3 \cdot 2H_2O$ To Produce 5-Aryltetraphen-6-yl Acetate 2[a]



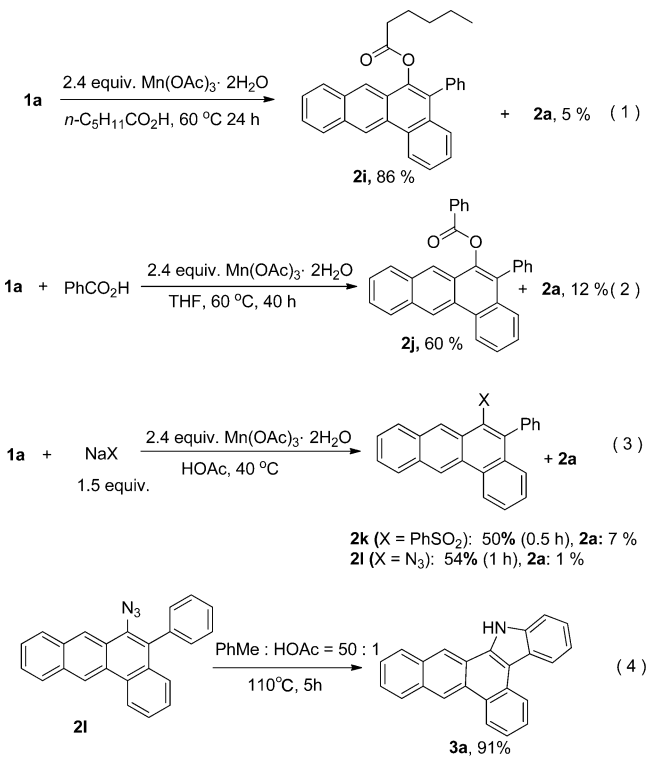
entry	Ar (1)	R (2)	time (h)	yield (%)[b]
1	C_6H_5 (**1a**)	2-H (**2a**)	4	93
2	4-FC_6H_4 (**1b**)	2-F (**2b**)	8	85
3	4-ClC_6H_4 (**1c**)	2-Cl (**2c**)	20	82
4	4-BrC_6H_4 (**1d**)	2-Br (**2d**)	24	86
5	3,5-$MeOC_6H_4$ (**1e**)	1,3-MeO (**2e**)	12	84
6	4-MeC_6H_4 (**1f**)	2-Me (**2f**)	2	90
7	3-MeC_6H_4 (**1g**)	3-Me (**2g**)/1-Me (**2g′**)	4	85 (1:1)[c]

[a]The reactions were conducted with 0.2 mmol of **1** and 0.48 mmol of $Mn(OAc)_3 \cdot 2H_2O$ in 2 mL of HOAc at 40 °C. [b]Isolated yield. [c]The ratio of products was determined by ^1H NMR spectral analysis

Scheme 3. Reactions of 1h with $Mn(OAc)_3 \cdot 2H_2O$



Scheme 4. Reactions of 1-(Diphenylmethylene)-1*H*-cyclopropa[*b*]naphthalene 1a with Nucleophiles and $Mn(OAc)_3 \cdot 2H_2O$ and the Synthetic Utilities of 2l



5-phenyl-1,2-benzanthracene-6-yl benzoate (**2j**) in 60% yield (eq 2, Scheme 4). Interestingly, when diarylmethylenecyclopropa[*b*]-naphthalene **1a** was treated with $PhSO_2H$ or HN_3, which were generated in situ from a mixture of $PhSO_2Na$ or NaN_3 with HOAc, we also observed the formation of 5-phenyl-6-(phenylsulfonyl)-1,2-benzanthracene (**2k**) and 6-azido-5-phenyl-1,2-benzanthracene (**2l**), albeit in a relatively low yield. Herein, it should also be mentioned that 6-azido-5-phenyl-1,2-benzanthracene (**2l**) may be quite useful for the synthesis of polycyclic aromatic hydrocarbons with heterocycles due to the versatile transformation of the azido group.[51−53] As exemplified in eq 4, by direct heating a solution of **2l** in toluene and HOAc for 5 h, a new polycyclic compound, 11*H*-benzo[*c*]naphtho[2,3-*a*]carbazole (**3a**), could be obtained in 91% yield via an unprecedented oxidative cyclization reaction.

On the basis of the above results and the known chemistry of the manganese(III) acetate-mediated reaction,[22−25] the current reaction can be rationalized as follows (Scheme 5). The single-electron oxidation of **1** by $Mn(OAc)_3$ may furnish radical cation **A**,[54,55] which subsequently accepts the nucleophilic attack of Nu^-, with high regioselectivity to give the radical intermediate **B**. Then the ring opening occurs with the highly strained three-membered ring of intermediate **B** giving radical intermediate **C** or **D**.[41] The intramolecular cyclization of intermediate **C**, in which the phenyl group and the free radical is on the same side, produces **2** with the loss of a proton and oxidation by another molecule of $Mn(OAc)_3$ (Scheme 5, path a); when R is a methyl group and it is on the same side with the free radical (Scheme 5, path b), the 1,5-H shift of radical intermediate **D** produces the allylic radical intermediate **E**. In the presence of another molecule of $Mn(OAc)_3$, **E** can be further converted to the allylic cation **F**. Then the migration of the C═C of **F** gives the intermediate **G**, which can be attacked by OH^- to furnish **H**. At last, **2h′** is obtained by the elimination of a molecule of HOAc from **H**.

Transition-metal-catalyzed coupling reaction of aryl esters with organometallic reagents is a very useful method to synthesize aryl−aryl products with extended π system.[56−58] Considering the readily available 1,2-benzanthracenes **2** bearing ester functionality with the current protocol, our further experiments applying the nickel-catalyzed Suzuki coupling reaction of **2a** with arylboronic acids demonstrated that a

dx.doi.org/10.1021/jo2015906 | J. Org. Chem. 2011, 76, 9329−9337

variety of 1,2-benzanthracene derivatives could be successfully obtained. As shown in Table 3, arylboronic acids both with electron-donating and electron-withdrawing substituents coupled smoothly with **2a** to give the corresponding products in good yields. Nevertheless, alkylboronic acids unfortunately cannot be applied in these reactions. Thus, we developed an alternative route by using 5-aryltetraphen-6-yl triflates **7** as the cross-coupling precursors. Aryl triflates could be easily generated from arylols with Tf_2O. They have higher reactivity than their acetate counterparts and consequently wider application in the transition-metal-catalyzed coupling reactions. As shown in Scheme 6, treatment of **2a** with NaOH in MeOH followed by esterification with triflic anhydride afforded 5-phenyltetraphen-6-yl triflate (**7a**) in 82% yield (two steps). In the presence of 5 mol % of $Pd(PPh_3)_4$ and 3.0 equiv of K_3PO_4, **7a** successfully coupled with (*E*)-styrylboronic acid and butylboronic acid to give the coupled products **5f** and **5g** in 73 and 74% yields, respectively. In addition, the reaction of **7a** with terminal alkynes catalyzed by a combination of 5 mol % of $Pd(PPh_3)_4$ and 5 mol % of $AuClPPh_3$[59] also proceeded smoothly to afford **5h** and **5i** in good yields.

Scheme 5. Proposed Mechanism

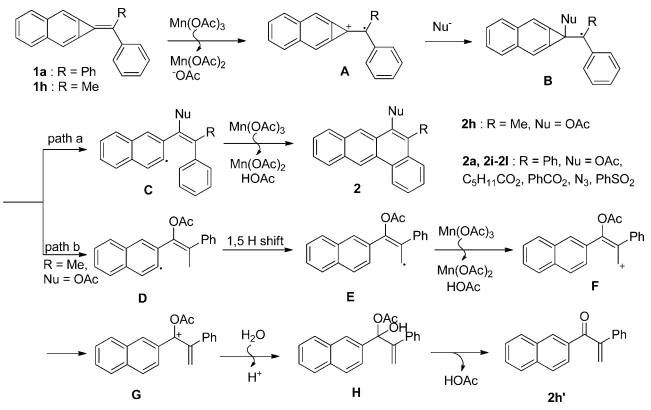
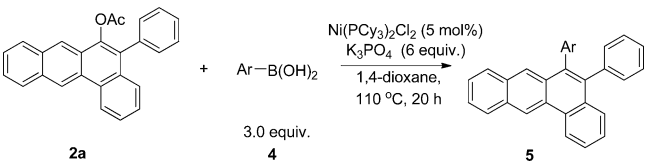


Table 3. Suzuki Coupling Reaction of 5-Phenyl-1,2-benzanthracene-6-yl Acetate 2a with Arylboronic Acids[a]



entry	Ar (**4**)	product **5**	yield (%)[b]
1	C_6H_5 (**4a**)	**5a**	66
2	4-FC_6H_4 (**4b**)	**5b**	75
3	4-MeC_6H_4 (**4c**)	**5c**	74
4	4-$MeOC_6H_4$ (**4d**)	**5d**	66
5	3-$MeOC_6H_4$ (**4e**)	**5e**	61

[a]The reactions were conducted with 0.1 mmol of **2a**, 0.3 mmol of boroxine **4**, 0.005 mmol of $Ni(PCy_3)_2Cl_2$, and 0.6 mmol of K_3PO_4 in 1 mL of 1,4-dioxane at 110 °C for 20 h. [b]Isolated yield.

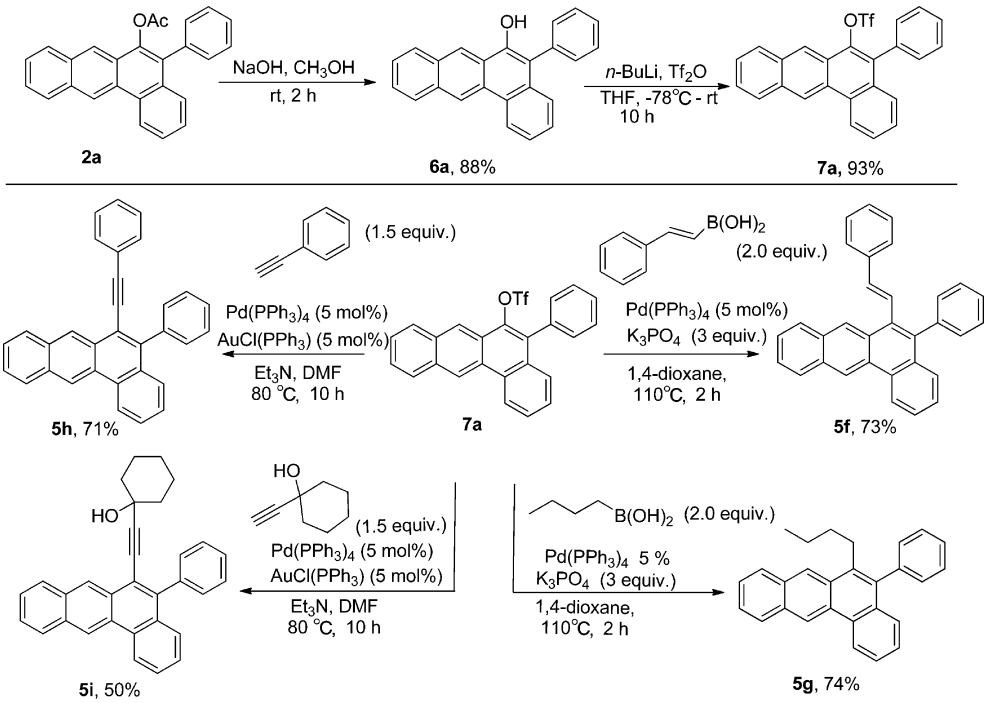
CONCLUSIONS

In conclusion, we have disclosed a manganese(III) acetate-mediated oxidative annulation of diarylmethylenecyclopropa[*b*]-naphthalenes with nucleophiles such as carboxylic acid and sulfonic acid under mild conditions, providing an efficient method for the preparation of 1,2-benzanthracenes. We also demonstrated that the obtained 1,2-benzanthracenes **2** could be easily converted to 1,2-benzanthracene derivatives with more advanced structures with several simple and routine operations. Further studies in this area are being conducted in our laboratory.

EXPERIMENTAL SECTION

Materials. 1,4-Dioxane and THF were distilled from Na/benzophenone immediately prior to use. Petroleum ether refers to the fraction with the boiling point in the range of 60−90 °C. DMF was distilled from $MgSO_4$. All ^1H NMR (400 MHz) and ^{13}C NMR (100

Scheme 6. Synthetic Utilities of 2a



dx.doi.org/10.1021/jo2015906 | J. Org. Chem. 2011, 76, 9329–9337

MHz) spectra were measured in $CDCl_3$ with TMS as the internal standard unless noted otherwise. Chemical shifts are expressed in parts per million, and J values are given in hertz. The other commercially available chemicals were purchased and used without further purification unless noted otherwise.

General Experimental Procedures. *Synthesis of 5-Phenyl-1,2-benzanthracene-6-yl Acetate (**2a**). Representative General Procedure for the Preparation of 1,2-Benzanthracene-6-yl Acetates **2a**–**2l**.* A rubber-capped Schlenk vessel containing $Mn(OAc)_3{\cdot}2H_2O$ (85 mg, 0.48 mmol) and 1-(diphenylmethylene)-1*H*-cyclopropa[*b*]-naphthalene (**1a**) (61 mg, 0.2 mmol) was degassed and backfilled with nitrogen three times, then HOAc (2 mL) was added to the Schlenk vessel. The resulting mixture was then allowed to stir at 40 °C. After 4 h, the reaction was complete as monitored by TLC. The reaction solution was diluted with ether (20 mL) and washed with a saturated aqueous $NaHCO_3$ solution (20 mL × 3). The combined oganic layer was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography (petroleum ether/CH_2Cl_2 = 10:1) to afford **2a** (67 mg, 93%) as a white solid: mp 157–158 °C (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.19 (s, 1H), 8.83 (d, J = 8.4 Hz, 1H), 8.33 (s, 1H), 8.11–8.07 (m,1H), 8.03–87.99 (m, 1H), 7.64 (m, 1H), 7.56–7.40 (m, 9H), 2.11 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 169.4, 142.4, 135.6, 132.1, 132.0, 130.2, 129.5, 129.2, 129.1, 128.4, 128.3, 128.1, 127.7, 127.3, 127.2, 126.6 126.2, 125.2, 122.9, 122.0, 121.0, 20.5 ppm; MS m/z (%) = 362 (M^+, 14.16), 320(100); IR (neat) 3054, 1761, 1497, 1438, 1367, 1195, 1059, 1008, 873, 757, 734, 703 cm^{-1}; HRMS calcd for $C_{26}H_{18}O_2$ (M^+) 362.1307, found 362.1315.

The following compounds were prepared according to this procedure.

*2-Fluoro-5-(4-fluorophenyl)-1,2-benzanthracene-6-yl acetate (**2b**).* The reaction of $Mn(OAc)_3{\cdot}2H_2O$ (85 mg, 0.48 mmol) and **1b** (68 mg, 0.2 mmol) in HOAc (2 mL) afforded **2b** (68 mg, 85%) as a white solid (eluent, petroleum ether/CH_2Cl_2 = 10:1) mp 216–217 °C (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.99 (s, 1H), 8.42–8.39 (m, 1H), 8.28 (s, 1H), 8.07–7.97 (m, 2H), 7.55–7.52 (m, 2H), 7.44–7.34 (m, 3H), 7.24–7.17 (m, 3H), 2.16 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 169.2, 162.4 (d, J = 245.4 Hz), 161.7 (d, J = 254.4 Hz), 142.0 (d, J = 3.1 Hz), 132.3, 132.0, 131.9, 131.9, 131.3 (d, J = 8.1 Hz), 131.2 (d, J = 3.0 Hz), 129.1 (d. J = 8.8 Hz), 128.3, 128.0, 127.6, 126.6, 126.4, 125.1, 122.4, 121.1, 115.6, 115.5, 115.3, 108.7(d, J = 22.6 Hz), 20.4 ppm; MS m/z (%) = 398 (M^+, 14.40), 356(100); IR (neat) 2923, 1760, 1710, 1608, 1511, 1433, 1368, 1266, 1187, 1108, 1057, 1017, 838 cm^{-1}; HRMS calcd for $C_{26}H_{16}O_2F_2$ (M^+) 398.1118, found 398.1115.

*2-Chloro-5-(4-chlorophenyl)-1,2-benzanthracene-6-yl Acetate (**2c**).* The reaction of $Mn(OAc)_3{\cdot}2H_2O$ (85 mg, 0.48 mmol) and **1c** (75 mg, 0.2 mmol) in HOAc (2 mL) afforded **2c** (71 mg, 82%) as a white solid (eluent, petroleum ether/CH_2Cl_2 = 10:1) mp 243–245 °C (petroleum ether);^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.13 (s, 1H), 8.80 (s, 1H), 8.33 (s, 1H), 8.15–8.10 (m, 1H), 8.05–8.03 (m, 1H), 7.60–7.57 (m, 2H), 7.53–7.47 (m, 2H), 7.46–7.24 (m, 4H), 2.19(s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 169.2, 142.7, 134.1, 133.6, 133.1, 132.3, 132.2, 131.6, 130.9, 130.1, 128.8, 128.5, 128.1, 127.6, 127.4, 126.7, 126.6, 125.1, 122.8, 122.4, 121.3, 20.6 ppm; MS m/z (%) = 434 ([M^+(^{37,37}Cl)], 1.99), 432 (M^+(^{35,37}Cl), 10.16), 430 (M^+(^{35,35}Cl),14.25), 388 (100); IR (neat) 3053, 1758, 1596, 1540, 1494, 1435, 1372, 1320, 1197, 1123, 1093, 874, 824, 777, 739 cm^{-1}; HRMS calcd for $C_{26}H_{16}O_2{}^{35}Cl_2$($M^+$) 430.0527, found 430.0531.

*2-Bromo-5-(4-bromophenyl)-1,2-benzanthracene-6-yl Acetate (**2d**).* The reaction of $Mn(OAc)_3{\cdot}2H_2O$ (85 mg, 0.48 mmol) and **1d** (92 mg, 0.2 mmol) in HOAc (2 mL) afforded **2d** (89 mg, 86%) as a white solid (eluent, petroleum ether/CH_2Cl_2 = 10:1) mp 270–272 °C (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.07 (s, 1H), 8.92 (s, 1H), 8.30 (s, 1H), 8.10 (d, J = 7.6 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.68–7.64 (m, 2H), 7.58–7.54 (m, 3H), 7.30–7.25 (m, 3H), 2.19(s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 169.1, 142.7, 134.0, 132.3, 132.2, 131.9, 131.7, 131.1, 130.3, 128.5, 128.4, 128.1, 128.0, 127.4, 126.7, 126.6, 125.9, 124.9, 122.4, 122.2, 121.3, 121.3, 20.5 ppm; MS m/z (%) = 522 (M^+(^{81,81}Br), 4.20), 520 (M^+(^{79,81}Br), 7.95), 518 (M^+(^{79,79}Br), 4.05), 49(100); IR (neat) 2982, 1761, 1592, 1491, 1369, 1194, 1059, 1012, 939, 875, 823, 7465, 705 cm^{-1}; HRMS calcd for $C_{26}H_{16}O_2{}^{79}Br_2$ (M^+) 517.9517, found 517.9513.

*5-(3,5-Dimethoxyphenyl)-1,3-dimethoxy-1,2-benzanthracene-6-yl Acetate (**2e**).* The reaction of $Mn(OAc)_3{\cdot}2H_2O$ (85 mg, 0.48 mmol) and **1e** (85 mg, 0.2 mmol) in HOAc (2 mL) afforded **2e** (81 mg, 84%) as a white solid (eluent, petroleum ether/AcOEt = 10:1) mp 160–162 °C (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 10.14 (s, 1H), 8.30 (s, 1H), 8.12–8.10 (m, 1H), 8.00–7.98 (m, 1H), 7.53–7.49 (m, 2H), 6.80 (s, 1H), 6.68 (s, 1H), 6.58–6.56 (m, 3H), 4.14 (s, 3H), 3.80 (s, 6H), 3.72, 3H), 2.19 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 169.4, 160.6, 160.1, 158.3, 143.3, 138.2, 135.1, 132.4, 130.5, 129.0, 128.8, 128.7, 127.7, 127.4, 125.7, 125.7, 124.8, 120.1, 113.9, 107.8, 102.4, 100.2, 98.7, 55.9, 55.4, 55.2, 20.7 ppm; MS m/z (%) = 483 (M + 1$^+$, 16.14), 441(100); IR (neat) 2969, 1759, 1603, 1456, 1422, 1373, 1319, 1294, 1200, 1157, 1067, 1018, 837 cm^{-1}; HRMS calcd for $C_{30}H_{26}O_6$ (M^+) 482.1729, found 482.1744.

*2-Methyl-5-p-tolyl-1,2-benzanthracene-6-yl acetate (**2f**).* The reaction of $Mn(OAc)_3{\cdot}2H_2O$ (85 mg, 0.48 mmol) and **1f** (66 mg, 0.2 mmol) in HOAc (2 mL) afforded **2f** (70 mg, 90%) as a white solid (eluent, petroleum ether/CH_2Cl_2 = 10:1) mp 198–199 °C (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.17 (s, 1H), 8.63 (s, 1H), 8.30 (s, 1H), 8.11–8.08 (m, 1H), 8.01–7.98 (m, 1H), 7.55–7.49 (m, 2H), 7.43 (d, J = 8.4 Hz, 1H), 7.30–7.27 (m, 5H), 2.60 (s, 3H), 2.45 (s, 3H), 2.14 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 169.5, 141.6, 137.2, 136.3, 132.7, 132.0, 132.0, 130.0, 129.9, 129.5, 129.1, 119.1, 129.0, 128.6, 128.3, 128.0, 127.3, 126.0, 126.0, 125.4, 123.0, 121.9, 120.8, 21.8, 21.3, 20.6 ppm; MS m/z (%) = 390 (M^+, 14.47), 348 (100); IR (neat) 2982, 1760, 1621, 1511, 1369, 1302, 1203, 1124, 1061, 952, 874, 822, 744 cm^{-1}; HRMS calcd for $C_{28}H_{22}O_2$ (M^+) 390.1620, found 390.1615.

*3-Methyl-5-m-toly-1,2-benzanthracene-6-yl Acetate (**2g**) and 1-Methyl-5-m-tolyl-1,2-benzanthracene-6-yl Acetate (**2g′**).* The reaction of $Mn(OAc)_3{\cdot}2H_2O$ (85 mg, 0.48 mmol) and **1g** (66 mg, 0.2 mmol) in HOAc (2 mL) afforded a mixture of **2g** and **2g′** (1:1) (66 mg, 85%) as a white solid (eluent, petroleum ether/CH_2Cl_2 = 10:1): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.33 (s, 1H), 9.13 (s, 1H), 8.71 (d, J = 8.4 Hz, 1H), 8.34 (s, 1H), 8.30 (s, 1H), 8.09–8.06 (m, 2H), 8.02–7.99 (m, 2H), 7.56–7.18 (m, 17H), 3.223 (s, 3H),2.44–2.38 (m, 9H), 2.13–2.10 (m, 6H) pm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 169.5, 142.4, 142.1, 137.8, 137.1, 136.2, 135.7, 135.6, 135.5, 132.1, 131.8, 131.4, 131.3, 131.1, 130.7, 130.7, 130.2, 129.6, 129.4, 129.3, 129.2, 128.7, 128.4, 128.3, 128,2, 128.1, 128.1, 127.7, 127.7 127.2, 126.3, 126.2, 126.1, 126.1, 126.0, 125.9, 125.0, 122.8, 121.6, 120.9, 120.2, 27.4, 21.6, 21.5, 21.5, 20.5 ppm; MS m/z (%) = 390 (M^+, 14.16), 348(100); IR (neat) 3053, 1759, 1603, 1499, 1439, 1305, 1265, 1195, 1601, 874, 735, 703 cm^{-1}; HRMS calcd for $C_{28}H_{22}O_2$ (M^+) 390.1620, found 390.1617.

*5-Methyl-1,2-benzanthracene-6-yl Acetate (**2h**) and 1-(Naphthalen-2-yl)-2-phenylprop-2-en-1-one (**2h′**).* The reaction of $Mn(OAc)_3{\cdot}2H_2O$ (85 mg, 0.48 mmol) and **1h** (48 mg, 0.2 mmol) in HOAc (2 mL) afforded **2h** (21 mg, 35%) and **2h′** (17 mg, 33%) both as white solid (eluent, petroleum ether/CH_2Cl_2 = 10:1). **2h**: mp 135–137 °C (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.17 (s, 1H), 8.87–8.83 (m, 1H), 8.27 (s, 1H), 8.13–8.10 (m, 1H), 8.05–8.02 (m, 2H), 7.69–7.65 (m, 2H), 7.56–7.53 (m, 2H), 2.61 (s, 3H), 2.54 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 169.1, 142.6, 132.0, 132.0, 131.8, 129.4, 128.9, 128.4, 128.1, 127.4, 126.5, 126.1, 125.9, 125.5, 125.0, 123.2, 122.8, 121.9, 120.2, 20.8, 12.7 ppm; MS m/z (%) = 300 (M^+, 38.70), 258 (100); IR (neat) 2987, 2901, 1759, 1630, 1503, 1406, 1394, 1201, 1142, 1066, 1056, 872, 753 cm^{-1}; HRMS calcd for $C_{21}H_{16}O_2$ (M^+) 300.1150, found 300.1151.

2h′: mp 80–82 °C (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.41 (s, 1H), 8.04–8.00 (m, 1H), 7.91–7.85 (m, 3H), 7.62–7.46 (m, 4H), 7.37–7.31 (m, 3H), 6.13 (s, 1H), 5.70 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 197.6, 148.3, 137.1, 135.6, 134.4, 132.4, 132.3, 129.6, 128.7, 128.6, 128.5, 128.4, 127.8, 127.0, 126.7, 125.1, 120.6 ppm; MS m/z (%) = 258 (M^+, 34.21), 155

dx.doi.org/10.1021/jo2015906 | J. Org. Chem. 2011, 76, 9329–9337

(100); IR (neat) 2981, 2901, 1661, 1626, 1597, 1495, 1465, 1403, 1324, 1249, 1179, 1069, 830, 793,700 cm^{-1}; HRMS calcd for $C_{19}H_{14}O$ (M^+) 258.1045, found 258.1049.

*5-Phenyl-1,2-benzanthracene-6-yl Hexanoate (**2i**).* The reaction of $Mn(OAc)_3{\cdot}2H_2O$ (85 mg, 0.48 mmol) and **1a** (61 mg, 0.2 mmol) in hexanoic acid (2 mL) afforded **2a**(4 mg, 5%) and **2i** (72 mg, 86%) as a white solid (eluent, petroleum ether/CH_2Cl_2 = 10:1): mp 98−99 °C (petroleum ether); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.23 (s, 1H), 8.87 (d, J = 8.0 Hz, 1H), 8.33 (s, 1H), 8.15−8.11 (m, 1H), 8.04−8.00 (m, 1H), 7.68−7.63 (m, 1H), 7.57−7.40 (m, 9H), 2.42(t, J = 8.0 Hz, 2H), 1.51−1.45 (m, 2H),1.31−1.18 (m, 4H), 0.90(t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 172.1, 142.3, 135.7, 132.2, 132.1, 132.0, 130.3, 129.5, 129.3, 129.2, 128.4, 128.3, 128.1, 127.7, 127.3, 127.2, 126.6, 126.2, 126.1, 125.4, 1222.9, 122.0, 121.1, 34.1, 31.2, 24.5, 22.3, 13.9 ppm; MS m/z (%) = 418 (M^+, 8.57), 320 (100); IR (neat) 2957, 2930, 1758, 1624, 1500, 1457, 1378, 1302, 1139, 1095, 978, 952, 877, 760, 705 cm^{-1}; HRMS calcd for $C_{30}H_{26}O_2$ (M^+) 418.1933, found 418.1941.

*5-Phenyl-1,2-benzanthracene-6-yl Benzoate (**2j**).* The reaction of $Mn(OAc)_3{\cdot}2H_2O$ (85 mg, 0.48 mmol), **1a** (61 mg, 0.2 mmol), and benzoic acid (1 g, 8.2 mmol) in THF (1 mL) afforded **2a** (9 mg, 12%) and **2j** (51 mg, 60%) as a white solid (eluent, petroleum ether/CH_2Cl_2 = 10:1): mp 200−202 °C (petroleum ether); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.22 (s, 1H), 8.88 (d, J = 8.4 Hz, 1H), 8.37 (s, 1H), 8.10 (d, J = 8.4 Hz, 1H), 8.06−8.02 (m, 2H), 7.93 (d, J = 8.4 Hz, 1H), 7.67−7.63(m, 1H), 7.59−7.29 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 165.2, 142.6, 135.5, 133.4, 132.1, 132.0, 130.2, 130.1, 129.6, 129.4, 129.3, 129.2, 128.5, 128.3, 128.2, 128.2, 127.6, 127.4, 127.2, 126.6, 126.2, 126.1, 125.4, 123.0, 122.0, 121.2 ppm; MS m/z (%) = 425 (M + 1^+, 10.37),105 (100); IR (neat) 2982, 1736, 1600, 1497, 1448, 1247, 1180, 1114, 1082, 1022, 882, 736, 703, cm^{-1}; HRMS calcd for $C_{31}H_{20}O_2$ (M^+) 424.1463, found 424.1460.

*Phenyl-6-(phenylsulfonyl)-1,2-benzanthracene (**2k**).* The reaction of $Mn(OAc)_3{\cdot}2H_2O$ (85 mg, 0.48 mmol), **1a** (61 mg, 0.2 mmol), and $PhSO_2Na$ (49 mg, 0.3 mmol) in HOAc (2 mL) afforded **2a** (5 mg, 7%) an **2k** (44 mg, 50%) as a white solid (eluent, petroleum ether/AcOEt = 10:1): mp 196−197 °C (petroleum ether); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.56 (s, 1H), 9.19 (s, 1H), 8.84 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.77−7.72 (m, 3H), 7.60−7.54 (m, 2H), 7.49−7.28 (m, 10H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 144.5, 143.6, 137.4, 132.5, 132.4, 131.8, 131.5, 131.5, 130.0, 130.0, 129.8, 128.9, 128.7, 128.6, 127.7, 127.6, 127.4, 127.0, 127.0, 126.4, 126.3, 124.4, 122.6, 121.8 ppm; MS m/z (%) = 445 (M + 1^+, 24.08), 303 (100); IR (neat) 2983, 2903, 1736, 1491, 1445, 1400, 1319, 1251, 1149, 1079, 882, 840, 754, 725, 703 cm^{-1}; HRMS calcd for $C_{30}H_{20}O_2S$ (M^+) 444.1184, found 444.1166.

*5-Phenyl-6-(phenylsulfonyl)-1,2-benzanthracene (**2l**).* The reaction of $Mn(OAc)_3{\cdot}2H_2O$ (85 mg, 0.48 mmol), **1a** (61 mg, 0.2 mmol), and Na N_3 (20 mg, 0.3 mmol) in HOAc (2 mL) afforded **2a** (1 mg, 1%) and **2l** (37 mg, 54%) as a white solid (eluent, petroleum ether): mp 236−238 °C (petroleum ether); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.15 (s, 1H), 8.85 (s, 1H), 8.80 (d, J = 8.0 Hz, 1H), 8.13−8.05 (m, 2H), 7.63−7.41 (m, 10H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 135.4, 132.3, 132.1, 132.0, 131.6, 131.2, 129.9, 128.9, 128.8, 128.7, 128.5, 128.4, 128.2, 127.3, 126.4, 126.4, 126.2, 125.8, 123.3, 122.8, 121.6 ppm; MS m/z (%) = 345 (M^+, 14.21), 317 (100); IR (neat) 3055, 2923, 2853, 2114, 1601, 1498, 1450, 1350, 1312, 1279, 883, 760, 701 cm^{-1}; HRMS calcd for $C_{24}H_{15}N_3$ (M^+) 345.1266, found 345.1253.

Synthetic Utilities of 2l. *Synthesis of 11H-Benzo[c]naphtho-[2,3-a]carbazole (**3a**).* A rubber-capped Schlenk vessel containing 5-phenyl-6-(phenylsulfonyl)-1,2-benzanthracene (**2l**) (69 mg, 0.2 mmol) was degassed and backfilled with nitrogen three times, then toluene (5 mL) and HOAc (0.1 mL) were added to the Schlenk vessel. The resulting mixture was then allowed to stir at 110 °C. After 5 h, the reaction was complete as monitored by TLC. The reaction solution was diluted with ether (20 mL) and washed with a saturated aqueous $NaHCO_3$ solution (20 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography (petroleum ether/AcOEt = 5:1) to afford **3a** (58 mg, 91%) as a white solid: mp 250−252 °C (petroleum ether); ^1H NMR (400 MHz, CD_3COCD_3, 25 °C) δ = 11.57 (s, 1H), 9.40 (s, 1H), 9.01−8.96 (m, 2H), 8.80 (d, J = 8.0 Hz, 1H), 8.55 (d, J = 8.0 Hz, 1H), 8.22−8.19 (m, 1H), 8.09−8.05 (m, 1H), 7.79−7.70 (m, 2H), 7.61−7.54 (m, 3H), 7.45−7.33 (m, 2H) ppm; ^{13}C NMR (100 MHz, CD_3COCD_3, 25 °C) δ = 139.8, 135.0, 132.8, 132.7, 131.6, 129.5, 128.7, 128.3, 127.1, 126.5, 125.5, 124.9, 124.7, 124.6, 124.4, 123.8, 123.2, 122.2, 121.2, 120.7, 112.6 ppm; MS m/z (%) = 317 (M^+, 100); IR (neat) 3439, 3405, 3051, 1606, 1526, 1428, 1309, 871, 749 cm^{-1}; HRMS calcd for $C_{24}H_{15}N$ (M^+) 317.1204, found 317.1210.

Synthetic Utilities of 2a. *Synthesis of 5,6-Diphenyl-1,2-benzanthracene (**5a**). Representative General Procedure for the Preparation of 6-(Aryl)-5-phenyltetraphenes **5a**−**5e**.* A rubber-capped Schlenk vessel containing 5-phenyl-1,2-benzanthracene-6-yl acetate (**2a**) (36 mg, 0.1 mmol), phenylboronic acid (**4a**) (37 mg, 0.3 mmol), K_3PO_4 (127 mg, 0.6 mmol), and $Ni(PCy_3)_2Cl_2$ (3 mg, 0.005 mmol) was degassed and backfilled with nitrogen for three times, then 1,4-dioxane (1 mL) was added to the Schlenk vessel. The resulting mixture was then allowed to stir at 110 °C. After 20 h, the reaction was complete as monitored by TLC, the reaction mixture was filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/CH_2Cl_2 = 10:1) to afford **5a** (25 mg, 66%) as a white solid: mp 206−208 °C (petroleum ether); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.26 (s, 1H), 8.93 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.00 (s, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.69−7.64 (m, 1H), 7.55−7.42 (m, 4H), 7.30−7.15 (m, 10H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 139.6, 139.5, 137.1, 132.2, 131.8, 131.6, 131.1, 131.0, 130.9, 130.2, 128.6, 128.2, 128.1, 128.0, 127.7, 127.6, 127.0, 126.8, 126.7, 126.6, 126.5, 125.9, 125.7, 122.8, 121.3 ppm; MS m/z (%) = 380 (M^+, 11.65), 43 (100); IR (neat) 3054, 1599, 1491, 1470, 1071, 1029, 953, 908, 787, 701 cm^{-1}; HRMS calcd for $C_{30}H_{20}$ (M^+) 380.1565, found 380.1567.

The following compounds were prepared according to this procedure.

*6-(4-Fluorophenyl)-5-phenyl-1,2-benzanthracene (**5b**).* The reaction of **2a** (36 mg, 0.1 mmol), 4-fluorophenylboronic acid (**4b**) (42 mg, 0.3 mmol), K_3PO_4 (127 mg, 0.6 mmol), and $Ni(PCy_3)_2Cl_2$ (3 mg, 0.005 mmol) in 1,4-dioxane (1 mL) afforded **5b** (30 mg, 75%) as a white solid (eluent, petroleum ether/CH_2Cl_2 = 10:1): mp 212−214 °C (petroleum ether); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.26 (s, 1H), 8.92 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 8.8 Hz, 1H), 7.96 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.69−7.65 (m, 1H), 7.55−7.44 (m, 4H), 7.28−7.12 (m, 7H), 6.97(t, J = 8.4 Hz, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 161.6 (d, J = 244.0 Hz), 139.4, 137.5, 136.1, 135.4 (d, J = 2.3 Hz), 132.7, 132.6, 132.1, 131.9, 131.6, 130.9, 130.3, 128.6, 128.2, 128.1, 128.1, 127.8, 127.1, 126.8, 126.5 (d, J = 8.0 Hz), 126.0, 125.8, 122.8, 121.5, 114.8 (d, J = 21.1 Hz) ppm; MS m/z (%) = 398 (M^+, 9.78), 69 (100); IR (neat) 3053, 1601, 1548, 1505, 1219, 1155, 953, 863, 767, 702 cm^{-1}; HRMS calcd for $C_{30}H_{19}F$ (M^+) 398.1471, found 398.1478.

*5-Phenyl-6-p-tolyl-1,2-benzanthracene (**5c**).* The reaction of **2a** (36 mg, 0.1 mmol), *p*-tolylboronic acid (**4c**) (41 mg, 0.3 mmol), K_3PO_4 (127 mg, 0.6 mmol), and $Ni(PCy_3)_2Cl_2$ (3 mg, 0.005 mmol) in 1,4-dioxane (1 mL) afforded **5c** (29 mg, 74%) as a white solid (eluent, petroleum ether/CH_2Cl_2 = 10:1): mp 240−242 °C (petroleum ether); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.25 (s, 1H), 8.92 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.03 (s, 1H), 7.82 (d, J = 8.8 Hz, 1H), 7.67−7.63 (m, 1H), 7.52−7.43 (m, 4H), 7.25−7.16 (m, 5H), 7.08−7.05 (m, 4H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 139.7, 137.2, 137.0, 136.5, 135.9, 132.3, 131.9, 131.6, 131.1, 131.0, 130.9, 130.2, 128.7, 128.4, 128.2, 128.1, 128.0, 127.6, 126.9, 126.8, 126.6, 126.4, 125.8, 125.6, 122.7, 121.3, 21.3 ppm; MS m/z (%) = 394 (M^+, 24.46), 43 (100); IR (neat) 3053, 2985, 1512, 1503, 1120, 1106, 986, 865, 778 cm^{-1}; HRMS calcd for $C_{31}H_{22}$ (M^+) 394.1722, found 394.1720.

*6-(4-Methoxyphenyl)-5-phenyl-1,2-benzanthracene (**5d**).* The reaction of **2a** (36 mg, 0.1 mmol), 4-methoxyphenylboronic acid

(**4d**) (46 mg, 0.3 mmol), K_3PO_4 (127 mg, 0.6 mmol), and $Ni(PCy_3)_2Cl_2$ (3 mg, 0.005 mmol) in 1,4-dioxane (1 mL) afforded **5d** (27 mg, 66%) as a white solid (eluent, petroleum ether/CH_2Cl_2 = 10:1): mp 250−252 °C (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.27 (s, 1H), 8.94 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 8.04 (s, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.55−7.51 (m, 1H), 7.54−7.44 (m, 4H), 7.28−7.10 (m, 7H), 6.81 (d, J = 8.8 Hz, 2 H), 3.80 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 158.1, 139.8, 137.3, 136.9, 132.3, 132.1, 131.9, 131.8, 131.6, 131.3, 130.9, 130.2, 128.7, 128.2, 128.1, 128.0, 127.7, 127.0, 126.8, 126.6, 126.4, 125.9, 125.6, 122.8, 121.3, 113.2, 55.1 ppm; MS m/z (%) = 410 (M^+, 9.23), 43 (100); IR (neat) 3055, 1607, 1507, 1441, 1285, 1244, 1179, 1106, 1076, 1029, 758 cm^{-1}; HRMS calcd for $C_{31}H_{22}O$ (M^+) 410.1671, found 410.1670.

*6-(3-Methoxyphenyl)-5-phenyl-1,2-benzanthracene (**5e**).* The reaction of **2a** (36 mg, 0.1 mmol), 4-methoxyphenylboronic acid (**4e**) (46 mg, 0.3 mmol), K_3PO_4 (127 mg, 0.6 mmol), and $Ni(PCy_3)_2Cl_2$ (3 mg, 0.005 mmol) in 1,4-dioxane (1 mL) afforded **5e** (25 mg, 61%) as a white solid (eluent, petroleum ether/CH_2Cl_2 = 10:1): mp 175−176 °C (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.25 (s, 1H), 8.921 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.07 (s, 1H), 7.84 (d, J = 8.8 Hz, 1H), 7.69−7.63 (m, 1H), 7.55−7.42 (m, 4H), 7.28−7.14 (m, 6H), 6.85−6.75 (m, 3H), 3.68 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 159.0,140.9, 139.5, 137.0, 136.9, 132.2, 131.9, 131.6, 130.9, 130.8, 130.7, 130.2, 128.6, 128.6, 128.2, 128.1, 128.0, 127.7, 127.6, 127.0, 126.8, 126.7, 126.5, 125.9, 125.7, 123.8, 122.8, 121.3, 116.6, 112.5, 55.1 ppm; MS m/z (%) = 410 (M^+, 3.73), 84 (100); IR (neat) 3054, 1598, 1577, 1489, 1313, 1250, 1178, 1408, 908, 732, 704 cm^{-1}; HRMS calcd for $C_{31}H_{22}O$ (M^+) 410.1671, found 410.1675.

Hydrolysis of 2a. *Synthesis of 5-Phenyl-1,2-benzanthracene-6-ol (**6a**).* A rubber-capped Schlenk vessel containing 5-phenyl-1,2-benzanthracene-6-yl acetate (**2a**) (72 mg, 0.2 mmol) and NaOH (80 mg, 2.0 mmol) was degassed and backfilled with nitrogen three times, then methanol (2 mL) was added to the Schlenk vessel. The resulting mixture was then allowed to stir at 25 °C. After 2 h, the reaction was complete as monitored by TLC, and the reaction mixture was filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/CH_2Cl_2 = 10:1) to afford **6a** (56 mg, 88%) as a white solid: mp 120−121 °C (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.16 (s, 1H), 8.87 (s, 1H), 8.79 (d, J = 8.0 Hz, 1H), 8.13−8.07 (m, 2H), 7.63−7.32 (m, 8H), 7.43−7.34(m, 1H), 7.33−7.31(m, 1H), 5.51 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 145.9, 134.4, 132.7, 132.2, 131.9, 131.4, 129.8, 129.2,128.6, 128.4, 128.3, 127.2, 126.9, 126.1, 125.9, 125.5, 124.3, 124.0, 122.8, 122.0, 121.54, 116.5 ppm; MS m/z (%) = 320 (M^+, 42.81), 57 (100); IR (neat) 3529, 3054, 1623, 1503, 1314, 1254, 1114, 1068, 884, 754 cm^{-1}; HRMS calcd for $C_{24}H_{16}O$ (M^+) 320.1201, found 320.1194.

Esterification of 6a. *Synthesis of 5-Phenyl-1,2-benzanthracene-6-yl trifluoromethanesulfonate (**7a**).* A rubber-capped Schlenk vessel containing **6a** (64 mg, 0.2 mmol) was degassed and backfilled with nitrogen three times, then THF (2 mL) was added to the Schlenk vessel. After being stirred for 0.5 h at −78 °C, n-BuLi (0.18 mL, 0.4 mmol, 2.25 M in hexane) was added. Then after another 0.5 h, Tf_2O (113 mg, 0.4 mmol, 0.067 mL) was added. The resulting mixture was then allowed to stir from −78 °C to room temperature for 10 h. After the reaction was complete as monitored by TLC, the reaction solution was diluted with ether (20 mL) and washed with a saturated aqueous $NaHCO_3$ solution (20 mL × 3). The organic layers were dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography (petroleum ether/CH_2Cl_2 = 10:1) to afford **7a** (84 mg, 93%) as a white solid: mp 188−189 °C (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.20 (s, 1H), 8.85 (d, J = 8.0 Hz, 1H), 8.75 (s, 1H), 8.15−8.09 (m, 2H), 7.73−7.69 (m, 1H), 7.65−7.48 (m, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 141.3, 133.4, 132.3, 132.1, 131.7, 131.4, 131.1, 130.0, 129.2, 128.7, 128.5, 128.2, 127.9, 127.6, 127.0, 126.8, 124.3, 123.0, 122.1, 122.1, 118.2 ppm; MS m/z (%) = 452 (M^+, 16.19), 319 (100); IR (neat) 3975, 2903, 1451, 1415, 1208, 1135, 1070, 942, 905, 820 cm^{-1}; HRMS calcd for $C_{25}H_{15}O_3F_3S$ (M^+) 452.0694, found 452.0702.

Synthetic Utilities of 7a. *(E)-5-Phenyl-6-styryl-1,2-benzanthracene (**5f**).* A rubber-capped Schlenk vessel containing 5-phenyl-1,2-benzanthracene-6-yl trifluoromethanesulfonate (**7a**) (45 mg, 0.1 mmol), (*E*)-styrylboronic acid (30 mg, 0.2 mmol), K_3PO_4 (64 mg, 0.3 mmol), and $Pd(PPh_3)_4$ (6 mg, 0.005 mmol) was degassed and backfilled with nitrogen three times. Then 1,4-dioxane (1 mL) was added to the Schlenk vessel. The resulting mixture was then allowed to stir at 110 °C. After 20 h, the reaction was complete as monitored by TLC. The reaction mixture was filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/CH_2Cl_2 = 10:1) to afford **5f** (30 mg, 73%) as a white solid: mp 165−167 °C (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.22 (s, 1H), 8.86 (d, J = 8.0 Hz, 1H), 8.80 (s, 1H), 8.11 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.62−7.20 (m, 15H), 7.16 (d, J = 16.8 Hz, 1H), 6.67 (d, J = 16.8 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 139.7, 137.6, 136.5, 135.8, 132.4, 132.1, 132.0, 131.6, 130.8, 130.0, 129.5, 128.8, 128.6, 128.2, 128.1, 127.8, 127.5, 127.0, 126.9, 126.8, 126.6, 126.3, 125.9, 125.8, 125.6, 122.7, 121.7 ppm; MS m/z (%) = 406 (M^+, 22.11), 84 (100); IR (neat) 3055, 1599, 1490, 1442, 1072, 908, 880, 729, 692, 669 cm^{-1}; HRMS calcd for $C_{32}H_{22}$ (M^+) 406.1722, found 406.1726.

The following compounds were prepared according to this procedure.

*6-Pentyl-5-phenyl-1,2-benzanthracene (**5g**).* A rubber-capped Schlenk vessel containing 5-phenyl-1,2-benzanthracene-6-yl trifluoromethanesulfonate (**7a**) (45 mg, 0.1 mmol), butylboronic acid (20 mg, 0.2 mmol), K_3PO_4 (64 mg, 0.3 mmol), and $Pd(PPh_3)_4$ (6 mg, 0.005 mmol) was degassed and backfilled with nitrogen three times, then 1,4-dioxane (1 mL) was added to the Schlenk vessel. The resulting mixture was then allowed to stir at 110 °C. After 20 h, the reaction was complete as monitored by TLC, the reaction mixture was filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/CH_2Cl_2 = 10:1) to afford **5g** (27 mg, 74%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.25 (s, 1H), 8.86 (d, J = 8.4 Hz, 1H), 8.60 (s, 1H), 8.15−8.05 (m, 2H), 7.61−7.34 (m, 7H), 7.33−7.26(m, 2H), 7.25 (d, J = 8.4 Hz, 1H), 2.95−2.89 (m, 2H), 1.69−1.64 (m, 2H), 1.39−1.31 (m, 2H), 0.84(t, J = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 140.5, 136.6, 134.7, 132.7, 132.0, 131.4, 130.1, 129.6, 129.0, 128.4, 128.2, 128.1, 127.7, 127.0, 126.8, 125.9, 125.7, 125.7, 123.8, 122.6, 121.8, 32.8, 30.3, 23.19, 13.78 ppm; MS m/z (%) 360 (M^+, 31.36), 84 (100); IR (neat) 3054, 2955, 1599, 1492, 1440, 951, 907, 877, 766, 733, 689 cm^{-1}; HRMS calcd for $C_{28}H_{24}$(M^+) 360.1878, found 360.1874.

*5-Phenyl-6-(phenylethynyl)-1,2-benzanthracene (**5h**).* A rubber-capped Schlenk vessel containing **7a** (45 mg, 0.1 mmol), $Pd(PPh_3)_4$ (6 mg, 0.005 mmol), and $AuCl(PPh_3)$ (2 mg, 0.005 mmol) was degassed and backfilled with nitrogen three times. Then ethynylbenzene (15 mg, 0.15 mmol), Et_3N (30 mg, 0.3 mmol), and DMF (2 mL) were added to the Schlenk vessel. The resulting mixture was then allowed to stir at 80 °C for 10 h. After the reaction was complete as monitored by TLC. The reaction solution was diluted with ether (20 mL) and washed with a saturated aqueous $NaHCO_3$ solution (20 mL × 3). The combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography (petroleum ether/CH_2Cl_2 = 10:1) to afford **5h** (29 mg, 71%) as a white solid: mp 140−142 °C (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.21 (s, 1H), 9.08 (s, 1H), 8.87 (d, J = 8.4 Hz, 1H), 8.16−8.13 (m, 2H), 7.70−7.7.64 (m, 1H), 7.62−7.49 (m, 9H), 7.32−7.28 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 143.2, 139.8, 132.2, 132.0, 131.6, 131.5, 130.6, 130.5, 129.0, 128.3, 128.2, 128.1, 128.0, 127.5, 127.4, 127.1, 126.1, 126.1, 126.0, 123.5, 122.9, 121.6, 119.1, 98.3, 87.9 ppm; MS m/z (%) = 404 (M^+, 32.09), 43 (100); IR (neat) 3055, 1598, 1492, 1442, 1323, 1279, 1073, 908, 882, 753, 694 cm^{-1}; HRMS calcd for $C_{32}H_{20}$ (M^+) 404.1565, found 404.1563.

1-((5-Phenyl-1,2-benzanthracene-6-yl)ethynyl)cyclohexanol (5i). A rubber-capped Schlenk vessel containing **7a** (45 mg, 0.1 mmol), $Pd(PPh_3)_4$ (6 mg, 0.005 mmol), and $AuCl(PPh_3)$ (2 mg, 0.005 mmol) was degassed and backfilled with nitrogen three times, then 1-ethynylcyclohexanol (19 mg, 0.15 mmol), Et_3N (30 mg, 0.3 mmol), and DMF (2 mL) were added to the Schlenk vessel. The resulting mixture was then allowed to stir at 80 °C for 10 h. After the reaction was complete as monitored by TLC, the reaction solution was diluted with ether (20 mL) and washed with a saturated aqueous $NaHCO_3$ solution (20 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography (petroleum ether/CH_2Cl_2 = 10:1) to afford **5i** (21 mg, 50%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.19 (s, 1H), 8.95 (s, 1H), 8.86 (d, J = 8.0 Hz, 1H), 8.16−8.08 (m, 2H), 7.70−7.63 (m, 1H), 7.60−7.44 (m, 9H), 1.90−1.84 (m, 3H), 1.62−1.43 (m, 5H), 1.36−1.24 (m, 2H), 1.21−1.12 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 143.1, 139.9, 132.2, 132.0, 131.5, 130.3, 130.2, 129.0, 128.3, 128.2, 128.0, 127.9, 127.5, 127.4, 127.1, 126.1, 126.0, 122.9, 121.6, 118.6, 101.8, 82.3, 69.6, 39.9, 25.1, 23.3 ppm; MS m/z (%) = 426 (M^+, 34.61), 43 (100); IR (neat) 3398, 2932, 1494, 1445, 1400, 1339, 1256, 1058, 961, 908, 882, 753 cm^{-1}; HRMS calcd for $C_{32}H_{26}O$ (M^+) 426.1984, found 426.1985.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for **2**, **3**, **5**−**7**, X-ray crystallographic data (CIF file) for **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: wululing@zju.edu.cn.

Notes

[⊥]Professor Huang passed away on March 6, 2010. He was fully in charge of this project. Professor Luling Wu is helping to finish all the projects with assistance from Professor Shengming Ma.

■ ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China (Project Nos. 20872127, 20732005, and J0830431) and National Basic Research Program of China (973 Program, 2009CB825300) and CAS Academician Foundation of Zhejiang Province and the Fundamental Research Funds for the Central Universities for financial support.

■ REFERENCES

(1) Watson, M. D.; Fethtenkotter, A.; Mullen, K. *Chem. Rev.* **2001**, *101*, 1267−1300.
(2) Chandrasekhar, S. *Liq. Cryst.* **1993**, *14*, 3−14.
(3) Pérez, D.; Guitián, E. *Chem. Soc. Rev.* **2004**, *33*, 274−283.
(4) Buess, C. M.; Lawson, D. D. *Chem. Rev.* **1960**, *60*, 313−330.
(5) Sergeyev, S.; Pisula, W.; Geerts, Y. H. *Chem. Soc. Rev.* **2007**, *36*, 1902−1929.
(6) Freundenmann, R.; Behnisch, B.; Hanack, M. *J. Mater. Chem.* **2001**, *11*, 1618−1624.
(7) Schmidt-Mende, L.; Fechtenkötter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119−1122.
(8) van de Craats, A. M.; Stutzmann, N.; Bunk, O.; Nielsen, M. M.; Watson, M.; Müllen, K.; Chanzy, H. D.; Sirringhaus, H.; Friend, R. H. *Adv. Mater.* **2003**, *15*, 495−499.
(9) Anthony, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 452−483.
(10) Pisula, W.; Feng, X.; Müllen, K. *Chem. Rev.* **2011**, *111*, 554−567.
(11) Wu, J.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718−747.
(12) Kaafarani, B. R. *Chem. Mater.* **2011**, *23*, 378−396.
(13) Harvey, R. G.; Cortez, C.; Sawyer, T. W.; DiGiovannit, J. *J. Med. Chem.* **1988**, *31*, 1308−1312.
(14) Chan, J. M. W.; Tischler, J. R.; Kooi, S. E.; Bulović, V.; Swager, T. M. *J. Am. Chem. Soc.* **2009**, *131*, 5659−5666.
(15) Newman, M. S.; Hussain, N. S. *J. Org. Chem.* **1982**, *47*, 2837−2840.
(16) Sangaiah, R.; Gold, A.; Toney, G. E. *J. Org. Chem.* **1983**, *48*, 1632−1638.
(17) Manning, W. B.; Muschik, G. M.; Tomaszewski, J. E. *J. Org. Chem.* **1979**, *34*, 699−702.
(18) Muschik, G. M.; Tomaszewski, J. E.; Sato, R. I.; Manning, W. B. *J. Org. Chem.* **1979**, *44*, 2250−2153.
(19) Bonifacio, M. C.; Robertson, C. R.; Jung, J.; King, B. T. *J. Org. Chem.* **2005**, *70*, 8522−8526.
(20) Saino, N.; Kawaji, T.; Ito, T.; Matsushita, Y.; Okamoto, S. *Tetrahedron Lett.* **2010**, *51*, 1313−1316.
(21) Gribble, G. W.; LeHoullier, C. S.; Sibi, M. P.; Allen, R. W. *J. Org. Chem.* **1985**, *50*, 1611−1616.
(22) Curran, D. P. *Synthesis* **1988**, *417*, 489.
(23) Jasperse, C. P.; Curran, D. P. *Chem. Rev.* **1991**, *91*, 1237−1286.
(24) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon−Carbon Bonds*; Pergamon Press: Oxford, 1986.
(25) Radikale, C. In *Houben−Weyl Methoden der Organischen Chimie*; Regitz, M., Giese, B., Eds.; Thieme: Stuttgart, 1989; Vol. *E*, p 19A.
(26) de Klein, W. J. In *Organic Syntheses by Oxidation and Metal Compound*; Mijs, W. J., de Jonge; C. R. H. I., Eds.; Plenum: New York, 1986; Chapter 4.
(27) Snider, B. B. *Chemtracts−Org. Chem.* **1991**, *4*, 403−419.
(28) (a) Demir, A. S.; Jeganathan, A. *Synthesis* **1992**, 235−247. (b) Melikyan, G. G. *Synthesis* **1993**, 833−850.
(29) Melikyan, G. G. *Org. React.* **1997**, *49*, 427−670.
(30) Fristad, W. E.; Peterson, J. R.; Ernst, A. B. *Tetrahedron* **1986**, *42*, 3429−3442.
(31) Snider, B. B.; Patricia, J. J.; Kates, S. A. *J. Org. Chem.* **1988**, *53*, 2137−2143.
(32) Corey, E. J.; Gross, A. W. *Tetrahedron Lett.* **1985**, *26*, 4291−4294.
(33) Snider, B. B. *Chem. Rev.* **1996**, *96*, 339−363.
(34) Wang, Y.; Chiba, S. *J. Am. Chem. Soc.* **2009**, *131*, 12570−12572.
(35) Wang, Y.; Toh, K. K.; Chiba, S.; Narasaka, K. *Org. Lett.* **2008**, *10*, 5019−5022.
(36) Wang, Y.; Toh, K. K.; Ng, E. P. J.; Chiba, S. *J. Am. Chem. Soc.* **2011**, *133*, 6411−6421.
(37) Huang, J.; Shi, M. *J. Org. Chem.* **2005**, *70*, 3859−3863.
(38) Yang, Y.; Huang, X. *J. Org. Chem.* **2008**, *73*, 4702−4704.
(39) Chen, W.; Su, C.; Huang, X. *Synlett* **2006**, 1446−1448.
(40) Huang, X.; Zhou, H.; Chen, W. *J. Org. Chem.* **2004**, *69*, 839−842.
(41) Zhou, H.; Huang, X.; Chen, W. *J. Org. Chem.* **2004**, *69*, 5471−5472.
(42) Chen, W.; Huang, X.; Zhou, H.; Ren, L. *Synthesis* **2006**, 609−614.
(43) Chen, W.; Cao, J.; Huang, X. *Org. Lett.* **2008**, *10*, 5537−5540.
(44) Lin, Y.; Wu, L.; Huang, X. *Eur. J. Org. Chem.* **2011**, 2993−3000.
(45) Halton, B.; Randall, C. J.; Gainsford, G. J.; Stang, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 5949−5956.
(46) Halton, B.; Stang, P. J. *Acc. Chem. Res.* **1987**, *20*, 443−448.
(47) Billups, W. E.; Rodin, W. A.; Haley, M. M. *Tetrahedron* **1988**, *44*, 1305−1307.
(48) Halton, B. *Tetrahedron Lett.* **2006**, *47*, 1077−1079.
(49) Halton, B. *Chem. Rev.* **2003**, *103*, 1327−1370.
(50) X-ray crystal data for **2a**: $C_{26}H_{18}O_2$; M = 362.40; crystal system, monoclinic; space group, $C2/c$; final R indices ($I > 2\sigma(I)$), $R1$ = 0.0516, $wR2$ = 0.1421, R indices (all data), $R1$ = 0.0675, $wR2$ = 0.1600; a = 31.808(2) Å, b = 5.6746(3) Å, c = 20.9233(12) Å; α = 90.00, β = 98.100(6), γ = 90.00, V = 3738.9(4) Å^3, T = 293(2) K, Z = 8; reflections collected/unique 10054/3171 (R(int) = 0.0755); number

of observations (>2σ(I)) 2322; parameters, 255. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, CCDC 833667 .
(51) Shou, W. G.; Li, J.; Guo, T.; Lin, Z.; Jia, G. *Organometallics* **2009**, *28*, 6847−6854.
(52) Sun, K.; Sachwani, R.; Richert, K. J.; Driver, T. G. *Org. Lett.* **2009**, *11*, 3598−3601.
(53) Stokes, B. J.; Richert, K. J.; Driver, T. G. *J. Org. Chem.* **2009**, *74*, 6442−6451.
(54) Nair, V.; Mathew, J.; Kanakamma, P. P.; Panicker, S. B.; Sheeba, V.; Zeena, S.; Eigendorf, G. K. *Tetrahedron Lett.* **1997**, *38*, 2191−2194.
(55) Nair, V.; Sheeba, V.; Panicker, S. B.; George, T. G.; Rajan, R.; Balagopal, L.; Vairamoni, M.; Prabhakar, S. *Tetrahedron* **2000**, *56*, 2461−2467.
(56) Li, Z.; Zhang, S.; Fu, Y.; Guo, Q.; Liu, L. *J. Am. Chem. Soc.* **2009**, *131*, 8815−8823.
(57) Quasdorf, K. W.; Tian, X.; Garg, N. K. *J. Am. Chem. Soc.* **2008**, *130*, 14422−14423.
(58) Guan, B.; Wang, Y.; Li, B.; Yu, D.; Shi, Z. *J. Am. Chem. Soc.* **2008**, *130*, 14468−14470.
(59) Panda, B.; Sarkar, T. K. *Tetrahedron Lett.* **2010**, *51*, 301−305.