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A general and efficient synthesis of substituted fluorenes and heterocycle-fused indenes containing thiophene or indole rings utilizing a Suzuki–Miyaura coupling and acid-catalyzed Friedel–Crafts reactions as key steps

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ABSTRACT

A general and efficient synthesis of fluorenes or heterocycle-fused indenes including 3-thia-cyclopenta[*a*]indenes, 9-thia-indeno[1,2-*a*]indenes, 5,6-dihydroindeno[2,1-*b*]indoles has been developed. This methodology is realized by a multistep protocol involving first preparation of *ortho*-formylbiaryls through Suzuki–Miyaura coupling of *o*-bromobenzaldehydes with arylboronic acids or the coupling of aryl halides with 2-formylbenzene boronic acid, this is followed by Grignard addition and Friedel–Crafts cyclization reactions catalyzed by Brønsted or Lewis acid to form the desired fluorene or indene rings. The method offers several advantages such as high yields, high selectivities, mild reaction conditions, easily accessible starting materials, and so on.

1. Introduction

π-Conjugated molecules such as fluorenes and its polymeric derivatives have attracted much attention in recent years due to their wide applications as advanced materials with unique electronic and photonic properties including organic light-emitting diodes (OLEDs), thin film transistors, photovoltaic cells, etc.[1] The most useful syntheses of fluorenes include addition of organometals to 9-fluorenones,[2] Friedel–Crafts ring closures of biaryl-2-yl-methanols utilizing a large excess of strong Brønsted acids such as HCl/HOAc[1k,l] or PPA at refluxing temperatures,[3] or an equal or excess amount of $BF_3 \cdot Et_2O$,[1b,j] Friedel–Crafts alkylation of fluorenes,[4] metal-catalyzed or mediated reactions including Pd-catalyzed rearrangement reactions,[5] Pd-catalyzed annulative reaction of dihalobenzenes with hindered Grignard reagents,[6] activation of C–F/C–H bonds of *o*-arylated α,α,α-trifluorotoluene derivatives,[7] etc. Although these methods are effective for the synthesis of fluorenes, they have certain drawbacks, more or less, for example, a strong acid medium or a stoichiometric amount of a Lewis acid sometimes required (catalytic formation of fluorine derivatives is quite rare), effective strategies relying on a structural modification of simple fluorenes were less explored, etc. Recently, we have developed a convenient and catalytic protocol for the synthesis of aryl-substituted anthracenes or heteroacenes with the advantages of high selectivities, high yields, and easily accessible starting materials under mild reaction conditions.[8] The reactions were suggested to be initiated through the facile formation of a benzylic cation intermediate from aromatic diols or diacetates promoted by TfOH. Especially, the use of diacetates significantly decreases the reaction temperature to room temperature. Based on this work, we envisioned that the fluorenes and its analogues might be readily constructed through a three-step protocol wherein biaryl-2-carbaldehydes are first prepared using Suzuki–Miyaura coupling of arylboronic acids with aryl bromides, this will be followed by Grignard addition and Friedel–Crafts cyclizations catalyzed by Brønsted or Lewis acid to form the desired polycyclic aromatic rings (Scheme 1). As we known, Suzuki–Miyaura coupling reaction represents one of the most powerful methods for C–C bond formations, which permits the highly efficient synthesis of a wide variety of biaryl compounds.[9] Therefore, the above-mentioned methodology would serve as an attractive route for the synthesis of substituted fluorenes. Although similar method has been precedent in the preparation of specific fluoreneacene oligomers, however, a large excess of Lewis acid of $BF_3 \cdot Et_2O$ was usually required in the

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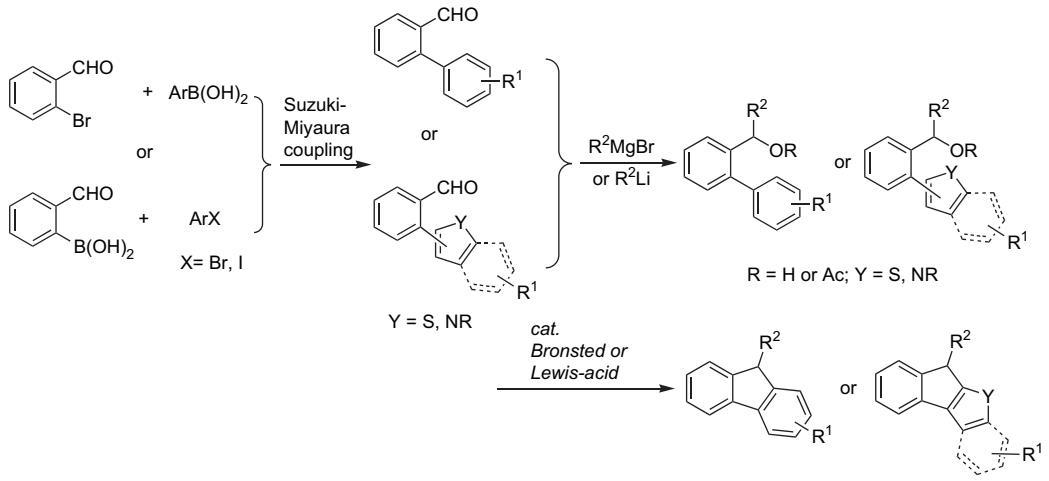


Scheme 1.

procedure,[1a] and this methodology has never been studied systematically. Herein, we report the full details of this fluorene synthesis.

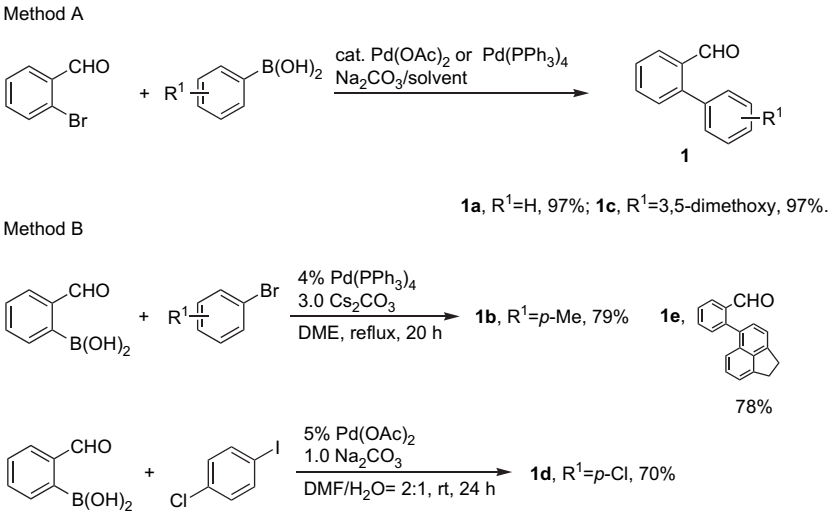
2. Results and discussion

2.1. Preparation of biaryl-2-yl-methanols and its derivatives

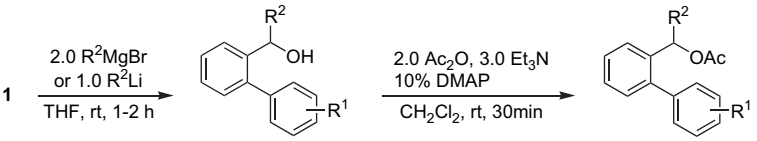
As shown in Scheme 2, the *ortho*-formyl biaryl derivatives **1** were conveniently synthesized through Suzuki–Miyaura coupling reactions according to published procedures.[10] Two methods were utilized for preparing *ortho*-formylbiaryls **1a**–**1e**. Method A is the Pd-catalyzed coupling reactions of 2-bromobenzaldehyde with arylboronic acids (for substrates **1a** and **1c**), while the method B is the Pd-catalyzed coupling of the parent aryl halides with 2-formylbenzene boronic acid (for substrates **1b**, **1d**, and **1e**). The requisite substrates of biaryl alcohols **2** and its ester derivatives **3** can be easily prepared in general good to high yields through Grignard addition (or using organolithiums) to biaryl derivatives **1** (Scheme 3). Similarly, the thienyl-containing biaryl aldehydes **4** were prepared through Pd-catalyzed coupling of heteroaryl bromides with 2-formylbenzene boronic acid (Scheme 4). Grignard addition of these aldehydes afforded high yields of alcohol **5** or its ester **6** through acylation (Scheme 5). Next, we chose the following route for the preparation of indole-based substrates **10** and its ester **11** (Scheme 6): first, lithiation of *N*-benzyl-3-bromo-1*H*-indole **7** by halogen-metal exchange reaction with *n*-BuLi at −78 °C followed by the transmetalation with $B(O^iPr)_3$ and hydrolysis afforded the indol-3-ylboronic acid **8**. Suzuki coupling of **8** with 2-bromobenzaldehyde in the presence of 5% $Pd(PPh_3)_4$, 5.0 equiv of Na_2CO_3 in a mixed solvent of DME and H_2O afforded the aldehyde **9** in 45% yield (overall yield from **7**). Grignard addition of **9** yielded the alcohol **10** in 82–88% yield. Acylation of **10** by Ac_2O afforded the acetate **11** in 84–97% yields.

2.2. Optimization studies of intramolecular Friedel–Crafts reaction

With the desired biaryl alcohols and its acetates in hand, we were interested in exploring the feasibility of using these substrates in fluorene syntheses. We began our investigation with the substrates of **2a** and **3a**. In view of the high catalytic activity in our work on TfOH-catalyzed anthracene formation reactions,[8] we first examined the cyclization of alcohol **2a** in the presence of TfOH (Table 1). Treatment of **2a** with 10% TfOH at room temperature for 1 min afforded the fluorene **12a** and the dimeric ether **13a** (derived from the intermolecular dehydration reaction) in 29 and 70% yields, respectively (Table 1, entry 1). However, it was found that **13a** could be exclusively transformed to fluorene **12a** (91% yield) by extending the reaction time to 3 h (Table 1, entry 2). The use of $TsOH\cdot H_2O$ or

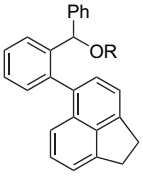


Scheme 2.



2a or **3a**: R^1 = H, R^2 = Ph,
2b or **3b**: R^1 = H, R^2 = *p*-MeC_6H_4
2c or **3c**: R^1 = H, R^2 = *p*-$MeOC_6H_4$
2d or **3d**:R^1 = H, R^2 = *p*-phenylC_6H_4
2e or **3e**: R^1 = H, R^2 = *p*-ClC_6H_4
2f or **3f**:R^1 = H, R^2 =1-naphthyl
2g or **3g**: R^1 = H, R^2 = 9-phenanthryl

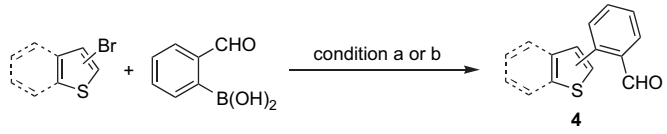
2h or **3h**: R^1 = *p*-Me, R^2= Ph
2i or **3i**: R^1 = 3,5-dimethoxy, R^2 = Ph
2j or **3j**: R^1 = *p*-Cl, R^2 = Ph
2l or **3l**: R^1 = 3,5-dimethoxy, R^2 = n-Bu
2m[a] or **3m**: R^1 = 3,5-dimethoxy, R^2 = H
2n or **3n**: R^1 = 3,5-dimethoxy, R^2 = ethynyl



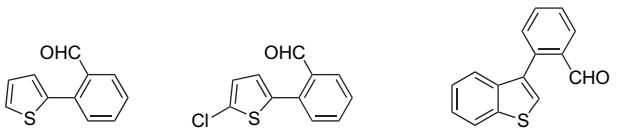
2k R = H
3k R = OAc

[a]**2m** was synthesized directly by the Pd-catalyzed coupling of (2-bromophenyl)methanol and 3,5-dimethoxyphenylboronic acid.

Scheme 3.



condition a: 4% $Pd(PPh_3)_4$, 3.0 Cs_2CO_3, in DME, reflux
condition b: 5% $Pd(PPh_3)_4$, 5.0 K_3PO_4, in DME, reflux

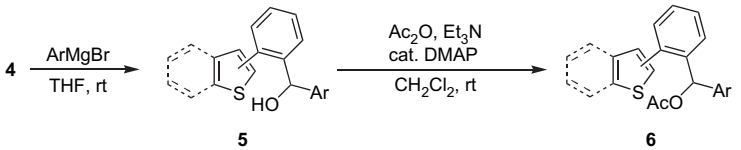


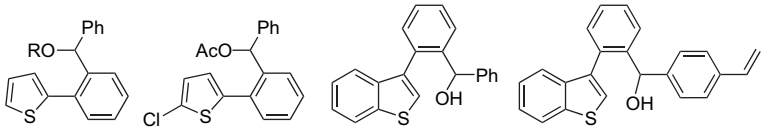
4a, 84% (condition a) **4b**, 61% (condition a) **4c**, 69% (condition b)

Scheme 4.

H_2SO_4 could afford some amount of the desired product, however, the results were not good (Table 1, entries 3–4). $BF_3\cdot Et_2O$ could also catalyze the cyclization, in which **12a** and **13a** were formed in 67 and 25% yields, respectively (Table 1, entry 8). According to our original work, we envisioned that a catalytic cycle could be readily initiated through the formation of benzylic cation by using the ester **3a**. As we expected, in the presence of 10% of TfOH, **3a** cyclized smoothly at room temperature for 1 min to give **12a** in 98% yield (Table 1, entry 11). The dimeric ether was not observed in this case. This is in contrast to the above result of biaryl alcohol **2a**, in which the kinetic product of **13a** was obtained predominantly in a short time of 1 min. Further investigations revealed that 10% H_2SO_4 could also afford high yield (93%) of **12a**, albeit in a longer reaction time (0.5 h, entry 13). The use of $BF_3\cdot Et_2O$ afforded the similar results as TfOH (Table 1, entry 16).

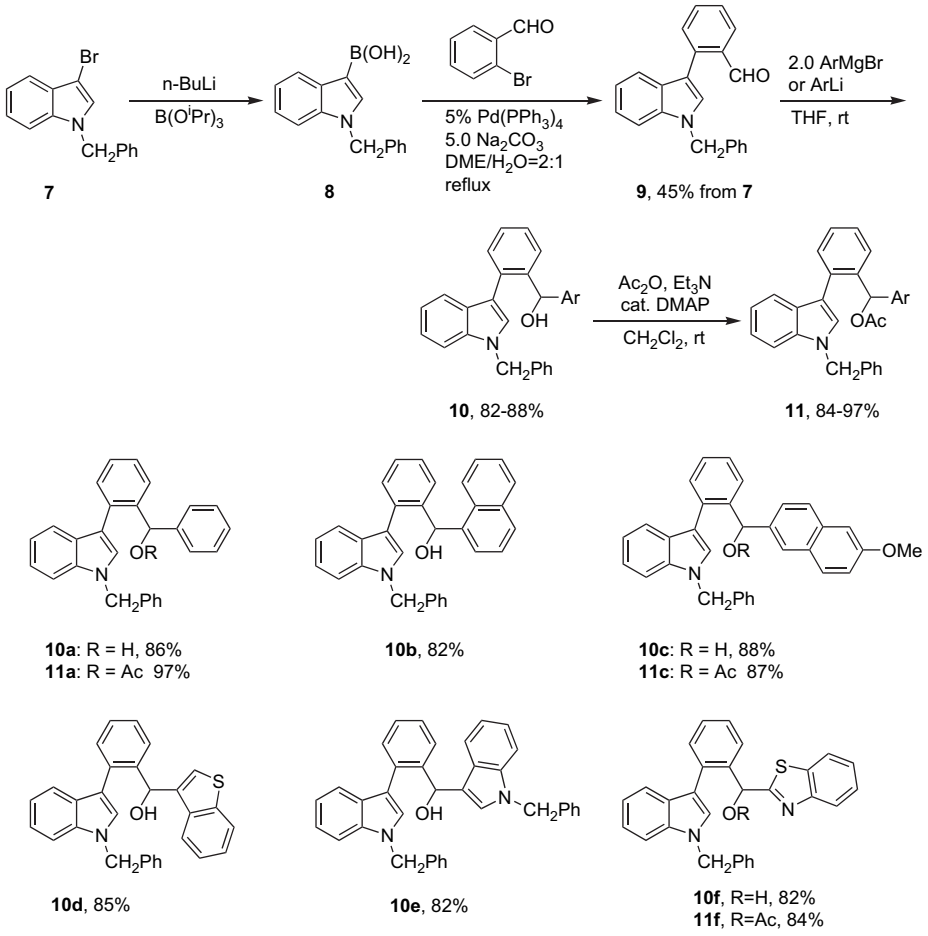
Based on the above optimization results, we chose both biarylmethanols and its acetates in most of the cases as cyclization precursors and TfOH and/or $BF_3\cdot Et_2O$ as catalysts for the investigation of the scope of this fluorene synthesis. As shown in Table 2, this procedure has been applied to a wide range of biarylmethanols or its esters, and all of the reactions proceeded well in CH_2Cl_2 in the presence of a catalytic amount of Brønsted acid to afford the corresponding fluorenes in high yields. The substituents of the –Me, –MeO, –Ph, –Cl on the aromatic ring of the R^2 group or –Cl substituent of R^1 were well tolerated during the reaction to afford **12b**–**12e** and **12j** in 68 to >99% yields (Table 2, entries 1–8, 19). Introducing bulky groups such as 1-naphthyl or 9-phenanthryl groups to the biaryl substrates **2f**, **2g** or **3f**, **3g** resulted in the formation of a mixture of rotamers **12f** and **12g** due to the slow rotation around the bond between the aryl group and the central carbon atom (Table 2, entries 9–12).[11] When the substrate **2k** containing a dihydroacenaphthylene ring was subjected to the reaction conditions, the cyclization readily occurred to afford a polycyclic fluorene **12k** in 74–93% yields (Table 2, entries 20–22). It should be noted that within the tested substrates, all the cyclizations could be completed to generate the desired fluorenes in 1 min using acetate **3**. However, when biarylmethanols **2** were employed, the reaction rate was highly dependent on the nature of the aromatic substituents (R^1 or substituents on R^2 group). For example, when alcoholic substrate **2e** bearing an electron-withdrawing group (Cl) on the aromatic ring, a complete conversion to fluorene **12e** was observed after 12 h (Table 2, entry 7), possibly due to the less stabilization of the benzyl cation intermediate formed in the reaction.





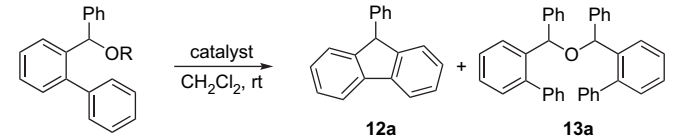
5a, R= H, 94%
6a, R= Ac, 97%
6b, 79% (overall yield from **4b**)
5c, 90%
5d, 100%

Scheme 5.



Scheme 6.

Table 1
Optimization studies for the Brønsted or Lewis acid-catalyzed cyclization reactions



2a, R = H; **3a**, R = Ac

Entry	Substrate	Catalyst	Time	Yield (%) of **12a**[a]	Yield (%) of **13a**[a]
1	**2a**	10% TfOH	1 min	29	70[b]
2	**2a**	10% TfOH	3 h	91[c]	—[d]
3	**2a**	10% $TsOH\cdot H_2O$	2 h	70	24
4	**2a**	10% H_2SO_4	32 h	14	44
5	**2a**	10% CF_3COOH	40 h	NR[e]	
6	**2a**	10% H_3PO_4	40 h	NR[e]	
7	**2a**	10% AcOH	12 h	NR[e]	
8	**2a**	10% $BF_3\cdot Et_2O$	1.5 h	67	25
9	**2a**	5% $AuCl_3$	24 h	15	69
10	**2a**	10% $La(OTf)_3$	6 h	NR[e]	
11	**3a**	10% TfOH	1 min	98[c]	—[d]
12	**3a**	10% $TsOH\cdot H_2O$	20 h	35	33
13	**3a**	10% H_2SO_4	30 min	93[c]	—[d]
14	**3a**	10% H_3PO_4	8 h	NR[e]	
15	**3a**	10% AcOH	12 h	NR[e]	
16	**3a**	10% $BF_3\cdot Et_2O$	1 min	98[c]	—[d]

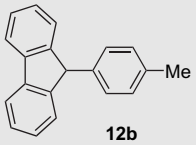
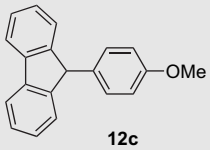
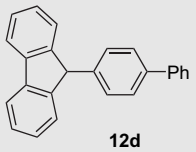
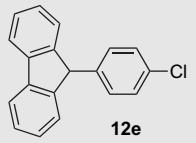
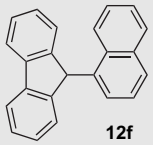
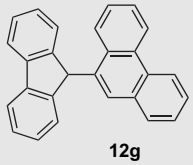
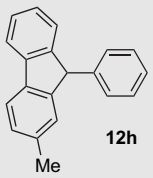
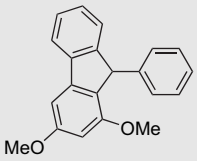
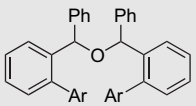
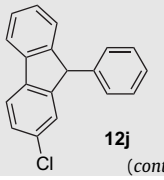
[a] NMR yields.
[b] Isolated yield. Two diastereomers were obtained in a ratio of 60:40 as determined by ^1H NMR.
[c] Isolated yields.
[d] Compound **13a** was not observed.
[e] NR=no reaction.

Similarly, a *p*-chlorophenyl-substituted **2j** resulted only in the formation of the ether **13j** in 73% yield in 10 min, while the use of ester **3j** afforded the desired fluorene **12j** in >99% yield in 1 min (Table 2, entries 18–19). In the cases of alcohols **2f** and **2g**, while R^2 is a 1-naphthyl or 9-phenanthryl group, the cyclization also require a longer reaction time of 2 h, perhaps due to the steric hindrance caused by these groups (Table 2, entries 9 and 11). It is interesting to note that this strategy offers the flexibility in the creation of regiospecific patterns around the fluorene nucleus by choosing the appropriate arylboronic acids or aryl halides when preparing the starting materials. For example, 2-methyl-, 1, 3-dimethoxy- or 2-Cl-substituted 9-phenylfluorenes could be efficiently constructed by this method (Table 2, entries 13–17, 19).

This methodology is not limited to secondary alcohols bearing two aryl substituents at the alcoholic carbon, as shown in Table 3, the biaryl alcohol **2l** bearing *n*-butyl substituent could also afford the fluorene **12l** in 74% NMR yield (Table 3, entry 1, in this case, the product could not be separated from the byproducts upon isolation by column chromatography), while the use of acetate **3l** readily generated the pure fluorene **12l** in 95% yield (Table 3, entry 2). When R^1 is a hydrogen, the use of alcohol **2m** did not produce any product due to the less stability of the carbon cationic intermediate, however, employing acetate **3m** could afford the cyclized product **12m**, although the yield is moderate (49%, Table 3, entry 5). An ethynyl-substituted **2n** or **3n** afforded the 9-alkynylfluorene **12n** in 45 and 42% yields, respectively (Table 3, entries 6 and 7).

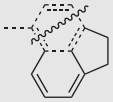
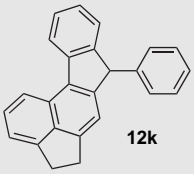
This highly efficient and versatile strategy can also be applied to the synthesis of 9,9-disubstituted fluorenes. For example, in the presence of 10% TfOH, **14** readily cyclized to generate **15** in 86% isolated yield (Scheme 7).

Table 2
Formation of 9-substituted fluorene derivatives

Entry	Substrate	R[a]	R^1	R^2	Catalyst (10 mol %)	Time	Product	Yield[b] (%)
1	**2b**	H	H	*p*-MeC_6H_4	TfOH	10 min	 **12b**	86
2	**3b**	Ac	H	*p*-MeC_6H_4	TfOH	1 min		96
3	**2c**	H	H	*p*-$MeOC_6H_4$	TfOH	5 min	 **12c**	68
4	**3c**	Ac	H	*p*-$MeOC_6H_4$	TfOH	1 min		95
5	**2d**	H	H	*p*-PhC_6H_4	TfOH	20 min	 **12d**	88
6	**3d**	Ac	H	*p*-PhC_6H_4	TfOH	1 min		94
7	**2e**	H	H	*p*-ClC_6H_4	TfOH	12 h	 **12e**	77
8	**3e**	Ac	H	*p*-ClC_6H_4	TfOH	1 min		90
9	**2f**	H	H	1-Naphthyl	TfOH	2 h	 **12f**	88[c]
10	**3f**	Ac	H	1-Naphthyl	TfOH	1 min		99[d]
11	**2g**	H	H	9-Phenanthryl	TfOH	2 h	 **12g**	89[e]
12	**3g**	Ac	H	9-Phenanthryl	TfOH	1 min		83[f]
13	**2h**	H	4-Me	Ph	TfOH	10 min	 **12h**	90
14	**3h**	Ac	4-Me	Ph	TfOH	1 min		98
15	**2i**	H	3,5-Di-OMe	Ph	TfOH	10 min	 **12i**	95
16	**3i**	Ac	3,5-Di-OMe	Ph	TfOH	1 min		98
17	**3i**	Ac	3,5-Di-OMe	Ph	$BF_3 \cdot Et_2O$	1 min		98
18	**2j**	H	4-Cl	Ph	TfOH	10 min	 Ar=*p*-ClC_6H_4 **13j**	73[g]
19	**3j**	Ac	4-Cl	Ph	TfOH	1 min	 **12j**	>99

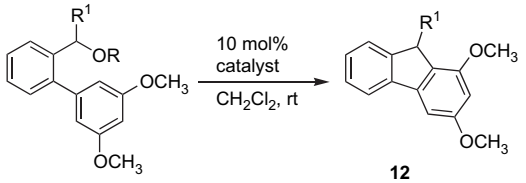
(*continued on next page*)

Table 2 (*continued*)

Entry	Substrate	R[a]	R^1	R^2	Catalyst (10 mol %)	Time	Product	Yield[b] (%)
20	**2k**	H		Ph	TfOH	5 min		86
21	**3k**	Ac		Ph	TfOH	1 min		74
22	**3k**	Ac		Ph	$BF_3\cdot Et_2O$	1 min	 **12k**	93

[a] R=H means substrate **2**, R=Ac means substrate **3**.
[b] Isolated yields.
[c] Two rotamers were obtained in a ratio of 68:32 as determined by ^{1}H NMR.
[d] The ratio of two rotamers is 68:32.
[e] The ratio of two rotamers is 57:43.
[f] The ratio of two rotamers is 58:42.
[g] Two diastereomers were obtained in a ratio of 60:40 as determined by ^{1}H NMR.

Table 3
Formation of non-aryl-substituted 9-fluorene derivatives



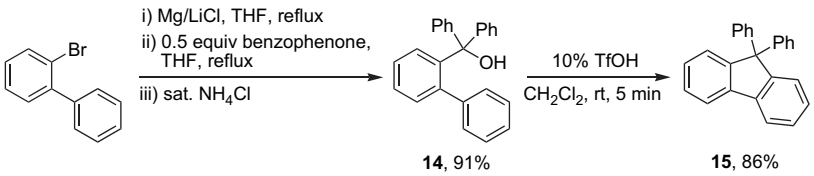
2 or **3** **12**

Entry	Substrate	R	R^1	Catalyst	Time	Product	Yield[a] (%)
1	**2l**	H	*n*-Bu	10% TfOH	1 h	**12l**	74[b]
2	**3l**	Ac	*n*-Bu	10% TfOH	1 min	**12l**	95
3	**3l**	Ac	*n*-Bu	10% $BF_3\cdot Et_2O$	40 min	**12l**	90
4	**2m**	H	H	10% TfOH	3 h		NR[c]
5	**3m**	Ac	H	100% $BF_3\cdot Et_2O$	1 h	**12m**	49[d]
6	**2n**	H	≡	10% TfOH	2 h	**12n**	45
7	**3n**	Ac	≡	10% TfOH	1 h	**12n**	42

[a] Isolated yields.
[b] NMR yield, in this case, the product could not be separated from the byproducts upon isolation by column chromatography.
[c] NR=no reaction.
[d] The reaction was carried out in $Cl(CH_2)_2Cl$ at 60 °C.

So far we have demonstrated that the facile F–C cyclization from biarylmethanols and its acetates bearing six-membered aromatic rings such as benzene or dihydroacenaphthylenes smoothly occurred under the catalytic conditions, we next extended this method for the preparation of heterocycle-fused indenes from biarylmethanols or its acetates containing a thiophene, benzothiophene or an indole ring. Recent studies have shown that thiophene-containing fluorenes exhibit highly efficient photoluminescence and high thermal and morphological stability.[1j,l,12] On the other hand, indoles fused with five-membered carbocycles are present in many biologically active natural products such as in antitumor indenoindole,[13a] acetylcholinesterase inhibitors,[13b] yuehchukene,[13c,d] (−)-12-*epi*-fischerindole,[13e] fischerindole I and G,[13f] or U,[13g] etc.[13] Thus the development of a new method for the synthesis of these heterocycles is highly attractive. Treatment of phenyl-(2-thiophen-2-yl-phenyl)methanol **5a** with 10% TfOH afforded 8-phenyl-8*H*-3-thia-cyclopenta[*a*]indene **16a** in 84% NMR yield (Table 4, entry 1, in this case, the product could not be separated from the byproducts upon isolation by column chromatography), while the use of acetate **6a** resulted in 69% yield of pure **16a**. Chloro-substituted **6b** produced a chlorinated heterofluorene **16b** in 82% yield (Table 4, entry 3). Benzothiophene rings could be also easily incorporated into the sequence, in which the corresponding products **16c** and **16d** were formed in 87–90% yields (Table 4, entries 4–5). It is interesting to note that an acid-sensitive vinyl-substituent is well tolerated during the reaction, as exampled in **16d** (Table 4, entry 5). For *N*-benzyl-substituted indole biaryl substrates, the cyclization smoothly occurred to produce the 5-benzyl-6-phenyl-5,6-dihydroindeno[2,1-*b*]indole **17a** in high yields of 83–91% whenever using an alcoholic substrate **10a** or its acetate **11a** (Table 4, entries 6–8). Similarly, 1-naphthyl-, 6-methoxy-naphthyl-, 3-benzo[*b*]thienyl-, 3-indolyl, 2-benzothiazolyl groups could also be conveniently introduced to the final products, in which the cyclized products **17b**–**17f** were formed in 47–99% yields (Table 4, entries 9–15). In the case of benzothiazolyl-substituted biaryl alcohol **10f**, an excess amount of TfOH (4 equiv) and longer reaction time (6 h) were needed to achieve the reasonable yields (47%, Table 4, entry 14). This result suggested that the protonation of nitrogen atom on the benzothiazole ring might occur, which tended to inhibition of the catalysis. In this case, the use of acetate **11f** is superior to alcohol **10f** due to the fact that a short reaction time of 5 min and higher yield of 77% were observed (Table 4, entry 15). The structures of these heterocycle-fused indenes were further confirmed by X-ray crystal analysis of **16c** and **17d**.[14]

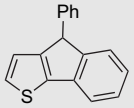
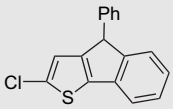
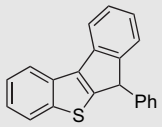
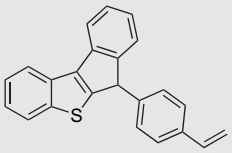
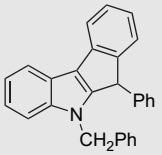
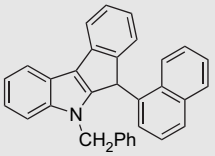
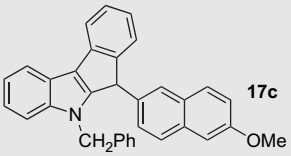
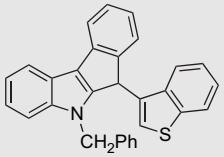
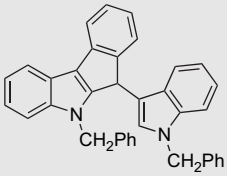
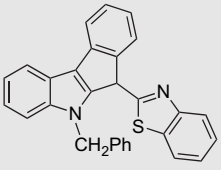
We propose the following mechanism for the cyclization of the indole-containing biaryls (Scheme 8). First, protonation followed by elimination of a leaving group in **10** or **11** generates a benzylic cation intermediate **18**, second, an electrophilic aromatic substitution reaction occurs on the indole ring in a Friedel–Crafts type manner to yield the dihydro-indeno[2,1-*b*]indole products **17**. The ring closure is accompanied by loss of a proton, making the reaction catalytic. Notably, both C-2 and C-3 on the indole ring are nucleophilic, therefore, after carbon cation formation, the cyclization can proceed either by attack of C-2 to directly yield the five-membered ring intermediate **19** (path A) or by attack of C-3 to yield a spiro



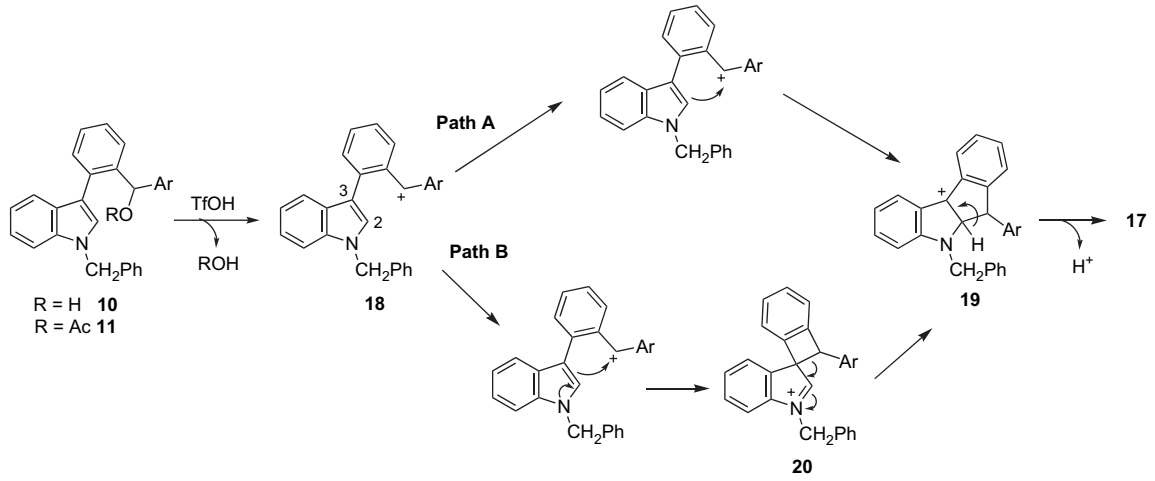
14, 91% **15**, 86%

Scheme 7.

Table 4
Formation of heterocycle-fused indenes containing thiophene or indole rings

Entry	Substrate	Catalyst (10 mol %)	Time	Product	Yield[a] (%)
1	**5a**	TfOH	5 min	 **16a**	84[b]
2	**6a**	TfOH	1 min		69
3	**6b**	TfOH		 **16b**	82
4	**5c**	TfOH	5 min	 **16c**	90
5	**5d**	TfOH	5 min	 **16d**	87
6	**10a**	TfOH	1 min	 **17a**	83
7	**11a**	TfOH	1 min		91
8	**11a**	$BF_3 \cdot Et_2O$	1 min		90
9	**10b**	TfOH	1 min	 **17b**	96[c]
10	**10c**	TfOH	1 min		73
11	**11c**	$BF_3 \cdot Et_2O$	1 min	 **17c**	89
12	**10d**	TfOH	1 min	 **17d**	99
13	**10e**	TfOH	1 min	 **17e**	88
14	**10f**	TfOH[d]	6 h		47
15	**11f**	TfOH[d]	5 min	 **17f**	77

[a] All of the reactions were carried out at room temperature. Unless noted, all the yields are isolated yields.
[b] NMR yield, in this case, the product could not be separated from the byproducts upon isolation by column chromatography.
[c] Two rotamers were obtained in a ratio of 44:56 as determined by ^1H NMR.
[d] TfOH was used in an excess amount of 4 equiv.



Scheme 8.

indolenine **20**,[15] then followed by a 1,2-shift and deprotonation to give the products **17** (path B).

In summary, we have developed a convenient and catalytic protocol for the synthesis of fluorenes or heterocycle-fused indenes including 3-thia-cyclopenta[*a*]indenes, 9-thia-indeno[1,2-*a*]indenes, 5,6-dihydroindeno[2,1-*b*]indoles, etc. utilizing a Suzuki–Miyaura coupling and acid-catalyzed Friedel–Crafts reactions as key steps. This method offers several advantages such as high selectivities, mild reaction conditions, and easily accessible starting materials. The fluorenes and its analogues are potentially useful in pharmaceutical and material science. We are currently exploring the synthetic potential of this cyclization reaction for the synthesis of polycyclic aromatic compounds.

3. Experimental section

3.1. A typical procedure for the synthesis of 1,3-dimethoxy-9-phenyl-9*H*-fluorene (12i) (Table 2, entry 16)

To a solution of acetic acid (3′,5′-dimethoxy-biphenyl-2-yl)-phenyl-methyl ester **3i** (0.2 mmol, 72.5 mg) in 4 mL of dry CH_2Cl_2 was added TfOH (0.02 mmol, 1.78 μL) under N_2 atmosphere. The resulting solution was stirred at room temperature for 1 min. An appropriate amount of silica gel was added to the mixture and the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate=3:1) to afford the desired product **12i** as a white solid in 98% yield. Mp 165 °C; ^{1}H NMR ($CDCl_3$, Me_4Si): δ 3.64 (s, 3H), 3.91 (s, 1H), 5.03 (s, 1H), 6.39 (d, J=1.8 Hz, 1H), 6.96 (d, J=1.8 Hz, 1H), 7.06–7.08 (m, 2H), 7.16–7.33 (m, 6H), 7.72 (d, J=7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 51.9, 55.2, 55.5, 96.2, 98.1, 119.7, 125.1, 126.2, 126.97, 126.9, 127.3, 127.8, 128.1, 140.6, 141.4, 143.4, 149.2, 157.2, 161.4; IR (KBr): 3059, 3027, 3004, 2943, 2833, 1611, 1592, 1586, 1493, 1453, 1343, 1199, 1156, 1146, 1046, 823, 765 cm^{-1}; HRMS (EI) for $C_{21}H_{18}O_2$: calcd 302.1307, found 302.1305. Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.49; H, 6.08.

The spectroscopic data of **12a**[16] and **12b**[16,17] are in agreement with that previously reported.

3.1.1. 2,2′-Oxybis(phenylmethylene)dibiphenyl (*13a*)

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the title compound as two diastereoisomers with a ratio of 60:40 as a colorless solid in 70% yield (from the alcohol **2a** with TfOH as catalyst). ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers: δ 5.49 (s, 2H), 5.61 (s, 2H), 6.71–6.74 (m), 6.78–6.81 (m), 6.89–6.94 (m), 6.96–6.99 (m), 7.01–7.41 (m), 7.75 (dd, J=7.8, 1.5 Hz, 2H), 7.90 (dd, J=7.8, 1.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers: δ 76.1, 76.7, 126.7, 126.7, 126.9, 127.0, 127.1, 127.3, 127.4, 127.8, 127.8, 127.9, 127.9, 128.0, 129.1, 129.2, 129.5, 129.9, 139.4, 139.9, 140.6, 140.7, 141.0, 141.3, 142.1, 142.4; IR (KBr): 3059, 3026, 1597, 1492, 1476, 1451, 1437, 1181, 1047, 1028, 1008, 753, 699 cm^{-1}; HRMS (MALDI/DHB) for $C_{38}H_{30}ONa$ $[M+Na]^+$: calcd 525.2194, found 525.2201.

3.1.2. 9-(4-Methoxyphenyl)-9H-fluorene (*12c*)

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the title compound as a colorless solid in 68% yield (from the alcohol **2c**) or 95% yield (from the ester **3c**). ^{1}H NMR ($CDCl_3$, Me_4Si): δ 3.72 (s, 3H), 4.97 (s, 1H), 6.76–6.81 (m, 2H), 6.96–7.01 (m, 2H), 7.18–7.37 (m, 6H), 7.77 (d, J=7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 53.6, 55.1, 114.0, 119.8, 125.2, 127.2, 127.2, 129.2, 133.5, 140.8, 148.1, 158.4; HRMS (EI) for $C_{20}H_{16}O$ $[M]^+$: calcd 272.1201, found 272.1193. The ^{1}H NMR data is in agreement with that previously reported.[18]

3.1.3. 9-(Biphenyl-4-yl)-9H-fluorene (*12d*)

Purification of the crude product by flash chromatography on silica gel (eluent: chloroform) afforded the title compound as a colorless solid in 88% yield (from the alcohol **2d**) or 94% yield (from the ester **3d**). ^{1}H NMR ($CDCl_3$, Me_4Si): δ 5.09 (s, 1H), 7.15 (d, J=7.8 Hz, 2H), 7.23–7.43 (m, 9H), 7.47–7.57 (m, 4H), 7.82 (d, J=7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 54.0, 119.9, 125.3, 127.0, 127.1, 127.4, 127.4, 128.7, 139.7, 140.7, 140.8, 141.0, 147.8; HRMS (EI) for $C_{25}H_{18}$ $[M]^+$: calcd 318.1409, found 318.1405.

3.1.4. 9-(4-Chlorophenyl)-9H-fluorene (*12e*)

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the title compound as a white solid in 77% yield (from the alcohol **2e**) or 90% yield (from the ester **3e**). Mp 147–149 °C (lit.[15] 148–149 °C); ^{1}H NMR ($CDCl_3$, Me_4Si): δ 4.97 (s, 1H), 6.98 (d, J=8.7 Hz, 2H), 7.18–7.26 (m, 6H), 7.35–73.39 (m, 2H), 7.77 (d, J=7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 53.6, 119.9, 125.2, 127.4, 127.5, 128.8, 129.6, 132.5, 140.1, 140.9, 147.4. The ^{1}H NMR data is in agreement with that previously reported.[19]

3.1.5. 9-(Naphthalen-1-yl)-9H-fluorene (*12f*)

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the title compound as a mixture of two rotamers as a colorless sticky liquid in 88% yield (from the alcohol **2f**, the ratio of rotamers is 68:32) or 99% yield (from the ester **3f**, the ratio of rotamers is

68:32). ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers: δ 5.24 (s, 1H), 5.96 (s, 1H), 6.48 (d, J=8.7 Hz, 1H), 6.74 (d, J=7.2 Hz, 1H), 6.80 (t, J=7.2 Hz, 1H), 7.09–7.17 (m), 7.26–7.37 (m), 7.45–7.55 (m), 7.60–7.80 (m), 7.86–7.90 (m), 8.56 (d, J=8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers: δ 48.9, 56.4, 120.0, 120.2, 123.7, 124.4, 124.6, 124.9, 125.1, 125.2, 125.3, 125.6, 125.6, 125.9, 126.3, 127.2, 127.2, 127.3, 127.3, 128.4, 128.5, 129.1, 130.2, 131.0, 132.8, 134.1, 134.5, 136.0, 138.0, 140.2, 141.1, 147.9, 148.0; HRMS (EI) for $C_{23}H_{16}$: calcd 292.1252, found 292.1259. The ^{1}H NMR data is in agreement with that previously reported.[20]

*3.1.6. 9-(9H-Fluoren-9-yl)phenanthrene (**12g**)*

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the title compound as a mixture of two rotamers as a white solid in 89% (from the alcohol **2g**, the ratio of rotamers is 57:43) or 83% yield (from the ester **3g**, the ratio of rotamers is 58:42). ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers: δ 5.39 (s, 1H), 6.07 (s, 1H), 6.52 (d, J=8.7 Hz, 1H), 6.95 (t, J=8.1 Hz, 1H), 7.08 (s, 1H), 7.17–7.28 (m), 7.36–7.69 (m), 7.77–8.03 (m), 8.12 (s, 1H), 8.61–8.69 (m), 8.75 (d, J=8.4 Hz, 1H), 8.85 (d, J=8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers: δ 49.0, 56.7, 120.0, 120.3, 122.3, 122.3, 122.8, 123.5, 124.5, 124.6, 124.9, 125.2, 125.8, 126.0, 126.2, 126.3, 126.5, 126.6, 126.7, 126.7, 126.9, 127.3, 127.3, 127.4, 128.2, 128.4, 129.7, 129.9, 130.5, 131.1, 131.3, 131.6, 131.7, 132.0, 134.4, 136.2, 140.2, 141.2, 147.6, 147.7; HRMS (EI) for $C_{27}H_{18}$: calcd 342.1409, found 342.1415. Anal. Calcd for $C_{27}H_{18}$: C, 94.70; H, 5.30. Found: C, 94.87; H, 5.37.

*3.1.7. 2-Methyl-9-phenyl-9H-fluorene (**12h**)*

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the title compound as a white solid in 90% yield (from the alcohol **2h**) or 98% (from the ester **3h**). Mp 122–123 °C; ^{1}H NMR ($CDCl_3$, Me_4Si): δ 2.29 (s, 3H), 4.95 (s, 1H), 7.04–7.08 (m, 3H), 7.12–7.25 (m, 6H), 7.31 (t, J=7.8 Hz, 1H), 7.64 (d, J=7.8 Hz, 1H), 7.71 (d, J=7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 21.6, 54.2, 119.48, 119.54, 125.2, 125.9, 126.7, 126.8, 127.2, 128.1, 128.3, 128.6, 137.1, 138.3, 141.0, 141.8, 147.7, 148.1; IR (KBr): 3063, 3021, 2916, 1600, 1495, 1451, 1294, 1283, 1073, 1028, 950, 821, 764, 753, 742, 697 cm^{-1}; HRMS (EI) for $C_{20}H_{16}$: calcd 256.1252, found 256.1252. Anal. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.54; H, 6.38.

*3.1.8. 2-Chloro-9-phenyl-9H-fluorene (**12j**)*

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the title compound as a white solid in quantitative yield. Mp 116–118 °C; ^{1}H NMR ($CDCl_3$, Me_4Si): δ 4.94 (s, 1H), 7.02–7.04 (m, 2H), 7.22–7.34 (m, 8H), 7.64 (d, J=7.8 Hz, 1H), 7.71 (d, J=6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 54.2, 119.9, 120.8, 125.3, 125.6, 127.1, 127.5, 127.5, 127.6, 128.2, 128.8, 132.9, 139.5, 139.9, 140.6, 147.6, 149.5; IR (KBr): 3061, 3022, 2924, 1597, 1493, 1452, 1445, 1410, 1167, 1073, 826, 751, 738, 696 cm^{-1}; HRMS (EI) for $C_{19}H_{13}Cl$: calcd 276.0706, found 276.0706. Anal. Calcd for $C_{19}H_{13}Cl$: C, 82.46; H, 4.73. Found: C, 82.21; H, 4.97.

*3.1.9. 2′,2″-Oxybis(phenylmethylene)bis(4-chlorobiphenyl) (**13j**)*

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=20:1) afforded the title compound as two isomers with a ratio of 60:40 as a colorless liquid in 73% yield (from the alcohol **2j** with TfOH as catalyst). ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers: δ 5.40 (s, 2H), 5.52 (s, 2H), 6.60–6.63 (m), 6.71–6.74 (m), 6.91–7.20 (m), 7.26–7.43 (m), 7.69–7.73 (m, 2H), 7.85–7.88 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers: δ 76.1, 76.7, 126.9, 127.1, 127.2, 127.4, 128.0, 128.1, 128.2, 129.5, 129.9, 130.4, 130.5, 132.8, 132.9, 139.1, 139.3, 139.6, 139.7, 140.1, 141.6, 141.9; IR (neat): 3061, 3027, 2926, 1714, 1600, 1493, 1474, 1447, 1361, 1219, 1182, 1089, 1046, 1020, 1005, 910, 832, 763, 734, 699 cm^{-1}; HRMS (MALDI/DHB) for $C_{38}H_{28}OCl_2Na$ $[M+Na]^+$: calcd 593.1415, found 593.1423.

*3.1.10. 7-Phenyl-5,7-dihydro-4H-indeno[1,7-bc]fluorene (**12k**)*

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the title compound as a yellow solid in 86% yield (from the alcohol **2k** with TfOH as catalyst), or 74% yield (from the ester **3k** with TfOH as catalyst), or 93% yield (from the ester **3k** with $BF_3\cdot Et_2O$ as catalyst). Mp=182–183 °C; ^{1}H NMR ($CDCl_3$, Me_4Si): δ 3.25–3.27 (m, 2H), 3.34–3.36 (m, 2H), 4.97 (s, 1H), 7.06 (dd, J=7.5, 1.5 Hz, 2H), 7.17–7.32 (m, 7H), 7.43 (t, J=7.5 Hz, 1H), 7.58 (t, J=7.5 Hz, 1H), 8.25 (d, J=7.5 Hz, 1H), 8.32 (d, J=9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 29.9, 30.8, 54.9, 117.1, 119.1, 119.5, 121.9, 124.9, 125.6, 126.8, 127.1, 127.3, 128.49, 128.51, 128.6, 131.8, 139.4, 141.5, 142.3, 146.5, 146.8, 148.7, 149.3; IR (KBr): 3079, 3022, 2931, 2907, 2886, 2832, 1599, 1492, 1470, 1454, 1441, 1398, 1382, 1291, 1167, 1072, 857, 781, 769, 747, 730, 695 cm^{-1}. Anal. Calcd for $C_{25}H_{18}$: C, 94.30; H, 5.70. Found: C, 94.26; H, 5.58.

*3.1.11. 9-Butyl-1,3-dimethoxy-9H-fluorene (**12l**)*

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the title compound as a colorless sticky liquid in 74% NMR yield (from the alcohol **2l** with TfOH as catalyst), or 95% (from the ester **3l** with TfOH as catalyst), or 90% yield (from the ester **3l** with $BF_3\cdot Et_2O$ as catalyst). ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.74 (t, J=3.9 Hz, 3H), 0.77–0.95 (m, 2H), 1.12–1.22 (m, 2H), 2.10–2.17 (m, 2H), 3.85 (s, 3H), 3.86 (s, 3H), 6.41 (d, J=1.8 Hz, 1H), 6.89 (d, J=1.8 Hz, 1H), 7.25–7.35 (m, 2H), 7.46–7.49 (m, 1H), 7.67 (dd, J=6.6, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.9, 22.9, 26.8, 30.2, 45.9, 55.2, 55.5, 96.0, 97.6, 119.6, 124.1, 126.5, 126.7, 126.7, 141.3, 143.1, 148.6, 157.2, 160.8; IR (neat): 3050, 2998, 2955, 2932, 2858, 2836, 1609, 1589, 1494, 1453, 1432, 1347, 1315, 1279, 1204, 1156, 1133, 1095, 1048, 1035, 1020, 935, 828, 767, 740 cm^{-1}; HRMS (EI) for $C_{19}H_{22}O_2$: calcd 282.1620, found 282.1621.

*3.1.12. 1,3-Dimethoxy-9H-fluorene (**12m**)*

The reaction was carried out in $ClCH_2CH_2Cl$ at 60 °C. Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=20:1) afforded the title compound as a white solid in 49% yield (from the ester **3m** with $BF_3\cdot Et_2O$ as catalyst). Mp=66–68 °C; ^{1}H NMR ($CDCl_3$, Me_4Si): δ=3.75 (s, 2H), 3.88 (s, 3H), 3.89 (s, 3H), 6.43 (d, J=2.1 Hz, 1H), 6.93 (d, J=1.8 Hz, 1H), 7.23–7.38 (m, 2H), 7.53 (d, J=7.2 Hz, 1H), 7.72 (d, J=7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ=33.7, 55.3, 55.6, 96.2, 97.4, 119.8, 123.1, 125.0, 126.4, 126.7, 141.7, 143.5, 144.0, 156.7, 160.9; IR (KBr): 2996, 2932, 2835, 1592, 1497, 1453, 1433, 1349, 1307, 1281, 1207, 1155, 1129, 1092, 1048, 1035, 1019, 934, 821, 764, 728 cm^{-1}; HRMS (EI) for $C_{14}H_{11}O_2$ $[M-CH_3]^+$: calcd 211.0759, found 211.0767.

*3.1.13. 9-Ethynyl-1,3-dimethoxy-9H-fluorene (**12n**)*

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=20:1) afforded the title compound as a yellow sticky liquid in 45% yield (from the alcohol **2n** with TfOH as catalyst) or 42% yield (from the ester **3n** with TfOH as catalyst). ^{1}H NMR ($CDCl_3$, Me_4Si): δ 2.18 (d, J=2.7 Hz, 1H), 3.89 (s, 3H), 3.94 (s, 3H), 4.72 (d, J=2.7 Hz, 1H), 6.46 (d, J=2.1 Hz, 1H), 6.88 (d, J=2.1 Hz, 1H), 7.35–7.42 (m, 2H), 7.66–7.69 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 36.2, 55.7, 68.8, 96.5, 98.3, 120.0, 122.2, 124.9, 127.7, 140.4, 142.7, 144.4, 157.1, 161.8; IR (neat): 3286, 3002, 2936, 2838, 2113, 1710, 1608, 1593, 1497, 1451, 1432, 1350, 1206, 1155, 828, 766, 740 cm^{-1}; HRMS (EI) for $C_{17}H_{14}O_2$: calcd 250.0994, found 250.1002.

*3.1.14. 9,9-Diphenyl-9H-fluorene (**15**)*

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the title compound as a white solid in 86% yield. Mp 223–225 °C (lit.[21] 224 °C); ^{1}H NMR ($CDCl_3$, Me_4Si): δ 7.16–7.25 (m, 12H), 7.32 (td, J=6.9, 1.5 Hz, 2H), 7.40 (d, J=7.2 Hz, 2H), 7.73 (d, J=7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 65.4, 120.1, 126.1, 126.6, 127.4, 127.7, 128.1, 128.2, 140.1, 145.9, 151.1; IR (KBr): 3051, 3017, 2926, 1594, 1489, 1447, 1031, 912, 755, 741, 728, 627 cm^{-1}.

*3.1.15. 8-Phenyl-8H-3-thia-cyclopenta[a]indene (**16a**)*

Purification of the crude product by preparative TLC (solution: petroleum ether/ethyl acetate=20:1) afforded the title compound as a white solid in 84% NMR yield (from the alcohol **5a**) or 69% yield (from the ester **6a**). Mp 136 °C; ^{1}H NMR ($CDCl_3$, Me_4Si): δ 4.84 (s, 1H), 6.90 (d, J=5.1 Hz, 2H), 7.07–7.12 (m, 3H), 7.18–7.28 (m, 6H), 7.45 (d, J=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 51.6, 118.8, 122.5, 125.1, 125.3, 126.9, 127.3, 127.6, 127.8, 128.7, 137.9, 140.2, 142.7, 150.7, 151.8; IR (KBr): 3096, 3075, 3018, 2918, 1602, 1493, 1452, 1341, 1283, 1290, 1072, 823, 752, 699 cm^{-1}; HRMS (EI) for $C_{17}H_{12}S$: calcd 248.0660, found 248.0662. Anal. Calcd for $C_{17}H_{12}S$: C, 82.22; H, 4.87. Found: C, 82.39; H, 5.00.

*3.1.16. 2-Chloro-8-phenyl-8H-3-thia-cyclopenta[a]indene (**16b**)*

Purification of the crude product by preparative TLC (solution: petroleum ether/ethyl acetate=20:1) afforded the title compound as a brown solid in 82%. Mp 106 °C; ^{1}H NMR ($CDCl_3$, Me_4Si): δ 4.78 (s, 1H), 6.78 (s, 1H), 7.04–7.15 (m, 3H), 7.20–7.28 (m, 5H), 7.36 (d, J=7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 52.5, 118.6, 122.2, 125.0, 125.5, 127.1, 127.4, 127.7, 128.8, 131.3, 137.6, 139.4, 139.9, 149.2, 149.5; IR (KBr): 3084, 3062, 3020, 2915, 1601, 1510, 1494, 1458, 1451, 1341, 1018, 953, 819, 755, 713, 698 cm^{-1}; HRMS (EI) for $C_{17}H_{11}ClS$: calcd 282.0270, found 282.0260.

*3.1.17. 10-Phenyl-10H-9-thia-indeno[1,2-a]indene (**16c**)*

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the title compound as a white solid in 90% yield. Mp 136–138 °C; ^{1}H NMR ($CDCl_3$, Me_4Si): δ 5.11 (s, 1H), 7.13–7.40 (m, 9H), 7.48 (td, J=7.8, 1.2 Hz, 1H), 7.84 (d, J=7.8 Hz, 2H), 8.19 (d, J=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 52.8, 119.1, 122.1, 123.8, 124.0, 124.7, 124.8, 1245.9, 127.2, 127.3, 127.8, 128.8, 132.8, 138.5, 139.9, 140.1, 145.1, 150.9, 151.2; IR (KBr): 3060, 3025, 2897, 1602, 1494, 1479, 1452, 1423, 1389, 1176, 1055, 1012, 934, 770, 729 cm^{-1}. Anal. Calcd for $C_{21}H_{14}S$: C, 84.53; H, 4.73. Found: C, 84.52; H, 4.78.

*3.1.18. 10-(4-Vinyl-phenyl)-10H-9-thia-indeno[1,2-a]indene (**16d**)*

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the title compound as a white solid in 87% yield. Mp 149–151 °C; ^{1}H NMR ($CDCl_3$, Me_4Si): δ 5.05 (s, 1H), 5.18 (d, J=10.8 Hz, 1H), 5.67 (d, J=17.7 Hz, 1H), 6.64 (dd, J=17.4, 10.8 Hz, 1H), 7.06–7.16 (m, 3H), 7.24–7.38 (m, 5H), 7.46 (t, J=7.8 Hz, 1H), 7.82 (d, J=7.8 Hz, 2H), 8.16 (d, J=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 52.5, 113.7, 119.1, 122.1, 123.8, 124.1, 124.7, 124.9, 126.7, 127.3, 128.0, 132.8, 136.3, 136.6, 138.5, 139.5, 140.1, 145.1, 150.8, 151.2; IR (KBr): 3062, 1629, 1600, 1508, 1482, 1427, 1405, 1200, 1177, 1016, 992, 913, 852, 805, 766, 724 cm^{-1}; HRMS (EI) for $C_{23}H_{16}S$: calcd 324.0973, found 324.0974. Anal. Calcd for $C_{23}H_{16}S$: C, 85.15; H, 4.97. Found: C, 85.42; H, 4.74.

*3.1.19. 5-Benzyl-6-phenyl-5,6-dihydro-indeno[2,1-b]indole (**17a**)*

Purification by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded the title compound as a light yellow solid in 83% (from the alcohol **10a** with TfOH as catalyst), or 91% (from the ester **11a** with TfOH as catalyst), or 90% yield (from the ester **11a** with $BF_3\cdot Et_2O$ as catalyst). Mp 194–196 °C; ^{1}H NMR ($CDCl_3$, Me_4Si): δ 4.75 (s, 1H), 4.89 (ABq, J=16.2 Hz, 1H), 5.24 (ABq, J=15.9 Hz, 1H), 6.88–6.91 (m, 2H), 6.97–7.11 (m, 4H), 7.19–7.33 (m, 10H), 7.66 (d, J=7.5 Hz, 1H), 7.94 (d, J=8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 47.9, 49.0, 110.5, 118.4, 119.7, 120.3, 120.6, 121.5, 121.9, 123.0, 124.6, 126.5, 127.2, 127.4, 128.1, 128.6, 128.8, 136.7, 138.5, 139.0, 141.2, 148.7, 151.1; IR (KBr): 3056, 3030, 2923, 2852, 1604, 1525, 1495, 1470, 1454, 1445, 1432, 1342, 746, 727, 696 cm^{-1}. Anal. Calcd for $C_{28}H_{21}N$: C, 90.53; H, 5.70; N, 3.77. Found: C, 90.50; H, 5.84; N, 3.74.

*3.1.20. 5-Benzyl-6-naphthalen-1-yl-5,6-dihydro-indeno[2,1-b]-indole (**17b**)*

Purification by flash chromatography on silica gel (eluent: dichloromethane) afforded the title compound as a white solid as a mixture of two rotamers with a ratio of 44:56 by ^{1}H NMR in 96% yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 4.65 (ABq, J=16.5 Hz, 1H), 4.71 (ABq, J=16.2 Hz, 1H), 4.97 (ABq, J=16.5 Hz, 1H), 5.02 (s, 1H), 5.10 (ABq, J=16.2 Hz, 1H), 5.58 (s, 1H), 6.61 (d, J=7.2 Hz), 6.67 (d, J=7.2 Hz), 6.81–7.43 (m), 7.51–7.59 (m), 7.64–7.73 (m), 7.78 (d, J=7.2 Hz, 1H), 7.86–7.89 (m), 7.97 (d, J=7.5 Hz, 1H), 8.01 (d, J=7.5 Hz, 1H), 8.28 (d, J=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 43.5, 47.7, 48.2, 50.8, 110.5, 110.6, 118.6, 118.7, 119.57, 119.63, 119.8, 120.3, 120.4, 121.3, 121.4, 121.5, 122.0, 122.1, 122.9, 123.0, 123.5, 124.0, 124.1, 124.2, 124.4, 125.1, 125.6, 125.7, 125.8, 126.2, 126.3, 126.3, 126.6, 127.1, 127.4, 127.4, 127.5, 127.6, 128.2, 128.3, 128.4, 128.8, 129.1, 129.9, 131.4, 132.3, 133.4, 134.1, 134.2, 134.7, 136.4, 136.5, 138.4, 138.8, 141.3, 141.4, 147.7, 148.8, 151.0, 151.4; IR (KBr): 3.57, 3041, 3004, 2924, 1599, 1528, 1492, 1478, 1448, 1461, 1392, 1339, 1145, 800, 774, 748, 732, 720 cm^{-1}; HRMS (EI) for $C_{32}H_{23}N$: calcd 421.1830, found 421.1833. Anal. Calcd for $C_{32}H_{23}N$: C, 91.18; H, 5.50; N, 3.32. Found: C, 90.92; H, 5.23; N, 3.07.

*3.1.21. 5-Benzyl-6-(6-methoxy-naphthalen-2-yl)-5,6-dihydro-indeno[2,1-b]indole (**17c**)*

Purification by flash chromatography on silica gel (eluent: dichloromethane) afforded the title compound as a white solid in 73% yield (from the alcohol **10c** with TfOH as catalyst) or 89% yield (from the ester **11c** with $BF_3\cdot Et_2O$ as catalyst). Mp 222–224 °C; ^{1}H NMR ($CDCl_3$, Me_4Si): δ 3.86 (s, 3H), 4.84 (ABq, J=15.9 Hz, 1H), 4.85 (s, 1H), 5.16 (ABq, J=16.5 Hz, 1H), 6.83–6.88 (m, 3H), 6.96 (t, J=8.4 Hz, 1H), 7.04–7.32 (m, 10H), 7.50 (d, J=8.4 Hz, 1H), 7.58 (s, 1H), 7.61 (d, J=9.0 Hz, 1H), 7.68 (d, J=7.5 Hz, 1H), 7.96 (d, J=7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 47.9, 49.0, 55.3, 105.7, 110.5, 118.4, 118.9, 119.7, 120.4, 120.7, 121.5, 121.9, 123.0, 124.7, 126.2, 126.5, 127.1, 127.4, 127.5, 127.6, 128.5, 129.0, 133.6, 133.9, 136.7, 139.1, 141.2, 148.7, 151.2, 157.6; IR (KBr): 3056, 3028, 2962, 2935, 1634, 1606, 1519, 1493, 1470, 1459, 1448, 1256, 1208, 1163, 1209, 859, 839, 812, 738 cm^{-1}; HRMS (EI) for $C_{33}H_{25}NO$: calcd 451.1936, found 451.1925. Anal. Calcd for $C_{33}H_{25}NO$: C, 87.77; H, 5.58; N, 3.10. Found: C, 87.95; H, 5.79; N, 3.24.

*3.1.22. 6-Benzo[b]thien-3-yl-5-benzyl-5,6-dihydro-indeno[2,1-b]-indole (**17d**)*

Purification by flash chromatography on silica gel (eluent: dichloromethane) afforded the title compound as a white solid in 99% yield. Mp 184–185 °C; ^{1}H NMR ($CDCl_3$, Me_4Si): δ 4.79 (ABq, J=16.2 Hz, 1H), 5.05 (s, 1H), 5.08 (ABq, J=17.7 Hz, 1H), 6.62–7.33 (m, 15H), 7.71 (d, J=6.6 Hz, 2H), 7.98 (d, J=8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 44.7 (br), 47.7 (br), 110.5, 118.5, 119.7, 120.4, 1120.6 (br), 121.6, 121.9, 122.5 (br), 123.0, 124.2, 124.3, 125.6 (br), 126.2, 127.2, 127.5 (br), 127.7, 128.3, 131.6 (br), 136.4, 136.7 (br), 138.9 (br), 140.7, 141.3, 145.8 (br), 149.1 (br); IR (KBr): 3060, 2925, 2875, 1604, 1521, 1495, 1459, 1440, 1425, 1263, 1162, 740, 723, 702 cm^{-1}; HRMS (EI) for $C_{30}H_{21}NS$: calcd 427.1395, found 427.1386. Anal. Calcd for $C_{30}H_{21}NS$: C, 84.27; H, 4.95; N, 3.28. Found: C, 84.03; H, 5.04; N, 3.04.

*3.1.23. 5-Benzyl-6-(1-benzyl-1H-indol-3-yl)-5,6-dihydro-indeno[2,1-b]indole (**17e**)*

Purification by flash chromatography on silica gel (eluent: dichloromethane) afforded the title compound as a white solid in 88% yield. Mp 142–144 °C; ^{1}H NMR ($CDCl_3$, Me_4Si): δ 4.87 (ABq, J=15.9 Hz, 1H), 4.97–5.13 (m, 4H), 6.67–7.30 (m, 21H), 7.68 (d, J=7.8 Hz, 1H), 7.95 (d, J=7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 40.6, 47.6, 49.6, 109.6, 110.5, 111.0, 118.3, 119.4, 119.6, 119.9, 120.2, 121.2, 121.95, 122.03, 122.9, 124.4, 126.3, 126.6, 126.9, 127.1, 127.2, 127.5, 128.3, 128.7, 136.8, 136.9, 137.4, 138.9, 141.1, 148.0, 150.7; IR (KBr): 3056, 2919, 2874, 1604, 1523, 494, 1465, 1453, 1354, 1337, 1309, 1257, 1174, 1164, 1014, 763, 744, 729, 699 cm^{-1}; HRMS (MALDI/DHB) for [M+H$^+$] $C_{37}H_{29}N_2$: calcd 501.2331, found 501.2322.

*3.1.24. 6-Benzothiazol-2-yl-5-benzyl-5,6-dihydro-indeno[2,1-b]-indole (**17f**)*

Purification by flash chromatography on silica gel (eluent: dichloromethane) afforded the title compound as a white solid in 47% yield (from the alcohol **10f** with TfOH as catalyst) or 77% (from the ester **11f** with TfOH as catalyst). Mp 171–172 °C; ^{1}H NMR ($CDCl_3$, Me_4Si): δ 5.25 (ABq, J=15.9 Hz, 1H), 5.37 (ABq, J=16.5 Hz, 1H), 5.44 (s, 1H), 6.87–6.91 (m, 2H), 6.97–7.07 (m, 4H), 7.17–7.43 (m, 7H), 7.59 (dt, J=7.2, 0.6 Hz, 1H), 7.67 (d, J=7.5 Hz, 1H), 7.92–7.96 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ 47.5, 48.4, 110.8, 118.9, 120.0, 120.6, 121.3, 121.5, 121.7, 122.2, 122.7, 123.4, 125.0, 125.2, 125.8, 126.4, 127.3, 128.4, 128.6, 135.2, 136.4, 139.1, 141.3, 144.7, 147.5, 152.8, 169.6; IR (KBr): 3056, 3031, 2933, 2905, 1606, 1524, 1510, 1496, 1467, 1443, 1435, 1398, 1333, 1310, 1183, 1012, 935, 762, 744, 730, 701 cm^{-1}; HRMS (EI) for $C_{29}H_{20}N_2S$: calcd 428.1347, found 428.1359. Anal. Calcd for $C_{29}H_{20}N_2S$: C, 81.28; H, 4.70; N, 6.54. Found: C, 81.41; H, 4.77; N, 6.45.

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Supplementary data

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References and notes

1. (a) Reisch, H.; Wiester, U.; Scherf, U.; Tuytuylkov, N. *Macromolecules* **1996**, *29*, 8204; (b) Xia, C.; Advincula, R. C. *Macromolecules* **2001**, *34*, 6922; (c) Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* **2002**, *35*, 2426; (d) Merlet, S.; Birau, M.; Wang, Z. Y. *Org. Lett.* **2002**, *4*, 2157; (e) Scherf, U.; List, E. J. W. *Adv. Mater.* **2002**, *14*, 477; (f) Katsis, D.; Geng, Y. H.; Ou, J. J.; Culligan, S. W.; Trajkovska, A.; Chen, S. H.; Rothberg, L. J. *Chem. Mater.* **2002**, *14*, 1332; (g) Cao, X.; Zhang, W.; Wang, J.; Zhou, X.; Lu, H.; Pei, J. *J. Am. Chem. Soc.* **2003**, *125*, 12430; (h) Hadizad, T.; Zhang, J.; Wang, Z. Y.; Gorjanc, T. C.; Py, C. *Org. Lett.* **2005**, *7*, 795; (i) Jaramillo-Isaza, F.; Turner, M. L. J. *Mater. Chem.* **2006**, *16*, 83; (j) Xie, L.; Fu, T.; Hou, X.; Tang, C.; Hua, Y.; Wang, R.; Fan, Q.; Peng, B.; Wei, W.; Huang, W. *Tetrahedron Lett.* **2006**, *47*, 6421; (k) Wong, K.; Chi, L.; Huang, S.; Liao, Y.; Liu, Y.; Wang, Y. *Org. Lett.* **2006**, *8*, 5029; (l) Wong, K.; Hwu, T.; Balaiah, A.; Chao, T.; Fang, F.; Lee, C.; Peng, Y. *Org. Lett.* **2006**, *8*, 1415.
2. (a) Orfanopoulos, M.; Smonou, I. *Synth. Commun.* **1988**, *18*, 833; (b) Vougioukalakis, G. C.; Orfanopoulos, M. *Tetrahedron Lett.* **2003**, *44*, 8649; (c) Schmid, M. A.; Alt, H. G.; Milius, W. *J. Organomet. Chem.* **1996**, *525*, 15.
3. Iihama, T.; Fu, J.-M.; Bourguignon, M.; Sniekus, V. *Synthesis* **1989**, 184.
4. (a) Bruch, M.; Groβe, M.; Rewicki, D. *Liebigs Ann. Chem.* **1976**, 74; (b) Cairns, J. F.; Hickinbottom, W. J. *J. Chem. Soc.* **1962**, 867.
5. Tian, Q.; Larock, R. C. *Org. Lett.* **2000**, *2*, 3329.
6. (a) Dong, C.-G.; Hu, Q.-S. *Angew. Chem., Int. Ed.* **2006**, *45*, 2289; (b) Hu, Q. *Synlett* **2007**, 1331.
7. Fuchibe, K.; Akiyama, T. *J. Am. Chem. Soc.* **2006**, *128*, 1434.
8. Li, G.; Zhou, S.; Su, G.; Liu, Y.; Wang, P. *J. Org. Chem.* **2007**, *72*, 9830.
9. (a) Miyaura, N. *Top. Curr. Chem.* **2002**, *219*, 11; (b) Suzuki, A.; Brown, H. C. *Organic Synthesis via Boranes*; Aldrich: Milwaukee, WI, 2003; Vol. 3; (c) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
10. (a) Zhao, J.; Yue, D.; Campo, M. A.; Larock, R. C. *J. Am. Chem. Soc.* **2007**, *129*, 5288; (b) Barluenga, J.; Trincado, M.; Rubio, E.; González, J. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3140; (c) Mito, T.; Shirae, Y.; Sakamoto, M.; Fujita, T. *J. Org. Chem.* **2005**, *70*, 2191; (d) Furstner, A.; Mamane, V. *J. Org. Chem.* **2002**, *67*, 6264.
11. Siddall, T. H., III; Stewart, W. E. *J. Org. Chem.* **1969**, *34*, 233.
12. Xie, L.; Hou, X.; Hua, Y.; Tang, C.; Liu, F.; Fan, Q.; Huang, W. *Org. Lett.* **2006**, *8*, 3701.
13. (a) Bal, C.; Baldeyrou, B.; Moz, F.; Lansiaux, A.; Colson, P.; Berthier, L. K.; Léonce, S.; Pierré, A.; Boussard, M. F.; Rousseau, A.; Wierzbicki, M.; Bailly, C. *Biochem. Pharmacol.* **2004**, *68*, 1911; (b) Shao, D.; Zou, C.; Luo, C.; Tang, X.; Li, Y. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 4639; (c) Chang, K.-F.; Kong, Y.-C.; Chan, T.-Y. *J. Chem. Soc., Chem. Commun.* **1985**, 48; (d) Bergman, J.; Venematm, L. *Tetrahedron Lett.* **1988**, *29*, 2993; (e) Baran, P. S.; Richter, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 7450; (f) Baran, P. S.; Richter, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 15394; (g) Baran, P. S.; Maimone, T.; Richter, J. M. *Nature* **2007**, *446*, 404.
14. See Supplementary data.
15. Wilkins, D. J.; Jackson, A. H.; Shannon, P. V. R. *J. Chem. Soc., Perkin Trans. 1* **1994**, 299.
16. See Ref. 2c.
17. Mathew, P. D. M.; Kandategе, W. *J. Org. Chem.* **1998**, *63*, 2858.
18. Bartle, K. D.; Jones, D. W. *J. Chem. Soc. B* **1971**, 388.
19. Robert, C.; Sever, S. *Aust. J. Chem.* **1987**, *40*, 1499.
20. Bartle, K. D.; Bavin, P. M. G.; Jones, D. W.; Lamie, R. *Tetrahedron* **1970**, *26*, 911.
21. Hori, M.; Kataoka, T.; Shimizu, H.; Ikemori, M.; Aoyama, Y. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1209.