

Synthesis of naphthalene derivatives through inexpensive $\text{BF}_3 \cdot \text{Et}_2\text{O}$ -catalyzed annulation reaction of arylacetaldehydes with arylalkynes

XIANG ShiKai^{1*}, HU Hao¹, MA Jing¹, LI YuanZhuo¹, WANG BiQin^{1*}, FENG Chun¹, ZHAO KeQing¹, HU Ping¹ & CHEN XiaoZhen²

¹College of Chemistry and Materials Science, Sichuan Normal University, Chengdu 610066, China

²Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu 610041, China

Received November 11, 2012; accepted December 26, 2012; published online February 21, 2013

An inexpensive $\text{BF}_3 \cdot \text{Et}_2\text{O}$ -catalyzed annulation reaction of arylacetaldehydes with arylalkynes has been developed. Various substituted phenylacetaldehydes and phenylacetylenes can undergo this reaction, producing corresponding α -aryl substituted naphthalene derivatives. Use of inexpensive and readily available $\text{BF}_3 \cdot \text{Et}_2\text{O}$ catalyst constitutes the most attractive advantage of this transformation.

naphthalene derivatives, $\text{BF}_3 \cdot \text{Et}_2\text{O}$, arylacetaldehydes, arylalkynes, annulation reaction

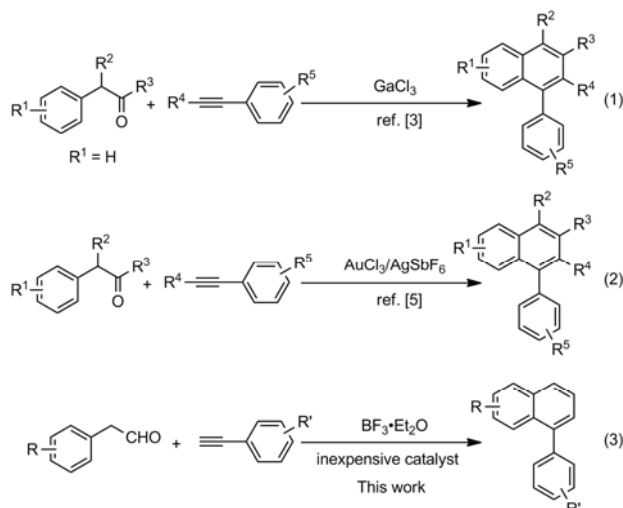
1 Introduction

The naphthalene unit is a ubiquitous skeleton in chemical and pharmaceutical industries as well as optical and electronic materials [1]. In the past decades, the development of some new and efficient methodologies for the synthesis of polysubstituted naphthalene derivatives has aroused great interest of organic chemists [2–5]. Among these methodologies, the acid-catalyzed annulation reaction of α -aryl-substituted carbonyl compounds with alkynes is quite an efficient approach for the synthesis of naphthalene derivatives. In 2002, Li and co-workers [3] realized a highly regioselective synthesis of polysubstituted naphthalene derivatives through GaCl_3 -catalyzed annulation reaction of phenylacetaldehydes (and ketones) with alkynes (Eq. (1)). In spite of the moderate yields and the application of expensive GaCl_3 catalyst, this annulation reaction was discovered by them for the first time. Next year, Kabalka and co-

workers [4] reported a TiCl_4 -mediated annulation reaction of α -aryl-substituted carbonyl compounds with alkynes. Kabalka's method greatly improved the yields of naphthalene derivatives, but required the use of quantitative TiCl_4 for this transformation. In 2009, the catalytic system of $\text{AuCl}_3/\text{AgSbF}_6$ was utilized by Balamurugan group to achieve the similar transformation to synthesize polysubstituted naphthalene derivatives (Eq. (2)) [5]. This approach is very effective, however, use of expensive $\text{AuCl}_3/\text{AgSbF}_6$ catalyst limited its broad application.

Inexpensive $\text{BF}_3 \cdot \text{Et}_2\text{O}$ is widely used as a Lewis acid catalyst in organic synthesis [6]. Recently, we developed a $\text{BF}_3 \cdot \text{Et}_2\text{O}$ /ammonium salt cocatalyzed alkenylation reaction of indoles with α, β -unsaturated ketones [7]. The combination of inexpensive and readily available $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and an ammonium salt as the efficient cocatalyst constitutes the attractive advantage of the reaction. Herein, we wish to report a new annulation reaction of arylacetaldehydes with arylalkynes catalyzed by inexpensive $\text{BF}_3 \cdot \text{Et}_2\text{O}$ to give naphthalene derivatives (Eq. (3)).

*Corresponding authors (email: xiangsk@hotmail.com; wangbiqin1964@126.com)



2 Results and discussion

Initially, we investigated the annulation reaction of phenylacetaldehyde **1a** and phenylacetylene **2a** in the presence of 5 mol% of FeCl_3 . Gratifyingly, 58% of 1-phenylnaphthalene **3aa** was obtained when dichloroethane (DCE) was used as the solvent (entry 1, Table 1). Although other Lewis acid catalysts or Brønsted acid catalysts such as $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$, AgOTf , and $\text{CH}_3\text{SO}_3\text{H}$ also promoted this transformation, their efficiencies were lower than FeCl_3 (entries 2–4, Table 1). TsOH hardly led to any desired product (entry 5, Table 1). Notably, the yield was improved to 74% when $\text{BF}_3\cdot\text{Et}_2\text{O}$ was used as a catalyst (entry 6, Table 1).

Table 1 Annulation reaction of phenylacetaldehyde (**1a**) with phenylacetylene (**2a**) under different conditions^{a)}

1a		2a		3aa	
Entry	Catalyst (mmol%)	Solvent (mL)	T (°C)	Yield (%) ^{b)}	
1	FeCl_3 (5)	DCE	80	58	
2	$\text{FeCl}_2\cdot\text{H}_2\text{O}$ (5)	DCE	80	27	
3	AgOTf (5)	DCE	80	27	
4	$\text{CH}_3\text{SO}_3\text{H}$ (5)	DCE	80	28	
5	TsOH (5)	DCE	80	trace	
6	$\text{BF}_3\cdot\text{Et}_2\text{O}$ (5)	DCE	80	74	
7	$\text{BF}_3\cdot\text{Et}_2\text{O}$ (5)	PhCl	80	42	
8	$\text{BF}_3\cdot\text{Et}_2\text{O}$ (5)	toluene	80	26	
9	$\text{BF}_3\cdot\text{Et}_2\text{O}$ (5)	MeCN	80	38	
10	$\text{BF}_3\cdot\text{Et}_2\text{O}$ (5)	MeNO_2	80	37	
11	$\text{BF}_3\cdot\text{Et}_2\text{O}$ (5)	DMF	80	ND ^{c)}	
12	$\text{BF}_3\cdot\text{Et}_2\text{O}$ (5)	DCE	50	30	
13	$\text{BF}_3\cdot\text{Et}_2\text{O}$ (5)	DCE	rt	ND ^{c)}	
14 ^{d)}	$\text{BF}_3\cdot\text{Et}_2\text{O}$ (5)	DCE	80	82	

a) All the reactions were carried out in the scale of 0.3 mmol **1a**, 0.3 mmol **2a**, 5 mmol% catalyst in 1.0 mL solvent if without further note; b) the yields were isolated yields; c) ND = not detected; d) 0.36 mmol **2a** was used.

Different solvents were then screened, indicating DCE as the best reaction medium (entries 6–11, Table 1). In addition, the reaction temperature was also critical for this annulation reaction (cf. entries 6, 12 and 13, Table 1). Finally, the best result of 82% yield was achieved by increasing the amount of phenylacetylene to 1.2 equivalents (entry 14, Table 1).

The scope of annulation reaction was expanded to a variety of substituted phenylacetaldehydes **1** and phenylacetylenes **2** (Tables 2 and 3). Phenylacetaldehydes **1** with both electron-donating groups and electron-withdrawing groups in the benzene ring smoothly underwent this kind of transformation, generating naphthalene derivatives **3** in moderate

Table 2 Annulation reaction of substituted phenylacetaldehydes (**1**) with phenylacetylene (**2a**)^{a)}

1		2a		3	
entry	1	2a	3	yield (%)	
1		1a		3aa	82
2		1b		3ba	58
3		1c		3ca	60
4 ^{b)}		1d		3da	30
5		1e		3ea	53
6		1f		3fa	64

a) All the reactions were carried out in the scale of 0.3 mmol **1**, 0.36 mmol **2a**, 5 mmol% $\text{BF}_3\cdot\text{Et}_2\text{O}$ in 1.0 mL DCE at 80 °C if without further note. The yields were isolated yields; b) the reactions were carried out at 90 °C. 10 mmol% $\text{BF}_3\cdot\text{Et}_2\text{O}$ was used.

Table 3 Annulation reaction of phenylacetaldehydes (**1a**) with various phenylacetylenes (**2**)^{a)}

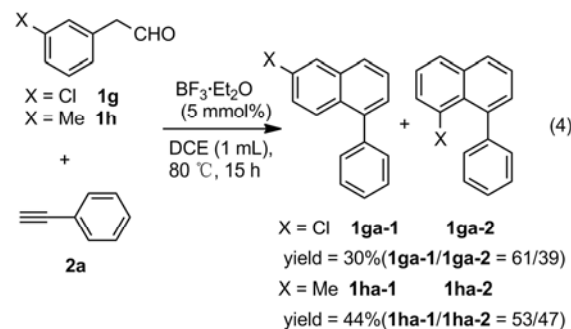
entry	2	3		yield (%)	
1			2a	3aa	82
2			2b	3ab	73
3			2c	3ac	78
4 ^{b)}			2d	3ad	55
5 ^{b)}			2e	3ae	61
6			2f	3af	0
7			2g	3ag	0
8			2h	3ah	trace

a) All the reactions were carried out in the scale of 0.3 mmol **1a**, 0.36 mmol **2**, 5 mmol% $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in 1.0 mL DCE at 80 °C if without further note. The yields were isolated yields; b) the reactions were carried out in PhCl (1 mL) instead of DCE at 110 °C. 20 mmol% $\text{BF}_3 \cdot \text{Et}_2\text{O}$ was used.

to excellent yields 30–82% (entries 1–6, Table 2). It is noteworthy that electronic effect of the arylacetaldehydes component had some influence on the reaction, but the regularity was not obvious (entries 1–6, Table 2). The substituents Cl and Br were compatible under these conditions, which could be further transformed into other functionalities (entries 5 and 6, Table 2).

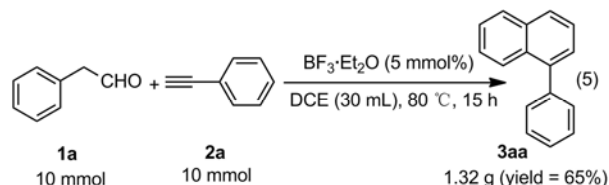
In addition, both electron-rich and electron-deficient arylacetylenes were tolerable as the annulation reaction partners with the yields of 55–82% (entries 1–5, Table 3). Notably, the electron-rich arylacetylenes gave the desired

products in higher yields than the electron-deficient ones (entries 2–5, Table 3). It is regretful that both (trimethylsilyl)acetylene and internal alkyne can not undergo this transformation to give the desired product (entries 6 and 7, Table 3). The internal alkynes failed to undergo the reaction possibly due to the following two reasons: i) The diphenylacetylene has a weaker nucleophilicity than phenylacetaldehyde; ii) The Lewis acidity of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ is lower than GaCl_3 or $\text{AuCl}_3/\text{AgSbF}_6$. Furthermore, the 1-hexyne **2h** was examined and gave only trace amount of product (entry 8, Table 3).



Two meta-substituted arylacetaldehydes (**1g**, **1h**) was employed to study the selectivity of the reaction (Eq. (4)). The results showed that the selectivity is terrible.

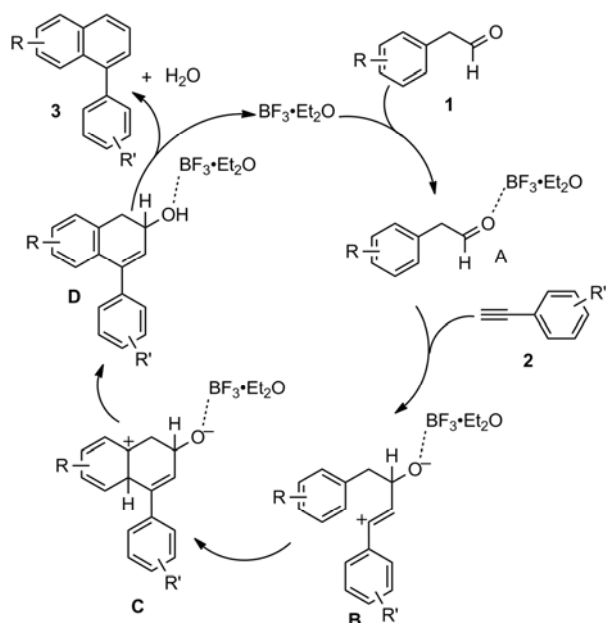
To explore the application of such transformations, this annulation reaction was scaled up to 10 mmol (Eq. (5)). When 10 mmol of phenylacetaldehyde **1a** and phenylacetylene **2a** were used as substrates, 1.32 g of 1-phenylnaphthalene **3aa** was obtained with the good yield of 65%. The result indicated that the catalytic method was very efficient.



A possible mechanism for this catalytic transformation is illustrated in Scheme 1. Initially, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ coordinates with the carbonyl oxygen to form the aldehyde-Lewis acid complex **A** [3, 5, 6]. Electrophilic attack of the carbonyl carbon in complex **A** on the arylalkyne **2** takes place to generate complex **B** with a vinyl carbocation stabilized by the aryl group. Intramolecular electrophilic attack of the formed vinyl carbocation to the aromatic ring followed by elimination of a proton generates the cyclization product **D**. Finally, the complex **D** can aromatize by dehydration to form the corresponding naphthalene derivative **3**, releasing the catalyst at the completion of catalytic cycle.

3 Conclusions

In summary, we developed an inexpensive $\text{BF}_3 \cdot \text{Et}_2\text{O}$ -catalyzed annulation reaction of arylacetaldehydes with arylalkynes.



Scheme 1 Proposed mechanism for this catalytic transformation.

Various substituted phenylacetaldehydes and phenylacetylenes can undergo this reaction, providing an alternative approach for the synthesis of naphthalene derivatives. Use of inexpensive and readily available $\text{BF}_3 \cdot \text{Et}_2\text{O}$ catalyst constitutes the most attractive advantage of this transformation. Development of other methodologies for the synthesis of naphthalene derivatives is ongoing in our laboratory.

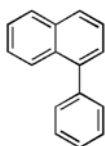
4 Experimental

4.1 General experimental section

All manipulations were conducted with Schlenk tube. ^1H NMR spectra were recorded on the Varian 400 MHz WB spectrometers. Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in CDCl_3 as an internal standard. ^{13}C NMR spectra were obtained by the same NMR spectrometers and were calibrated with CDCl_3 ($\delta = 77.00$ ppm). Mass spectra were obtained using Electron Impact (EI) mass spectrometer. Arylacetaldehydes **1b–f** were synthesized according to literature method [8]. Unless otherwise noted, materials and solvents from commercial suppliers were used without further purification.

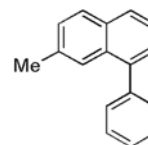
4.2 Experimental procedures and characterization of products

1-Phenylnaphthalene (**3aa**)



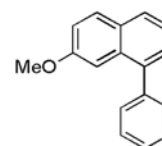
Typical procedure: phenylacetaldehyde (36.0 mg, 0.3 mmol) and phenylacetylene (36.7 mg, 0.36 mmol), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (2.1 mg, 0.015 mmol) and DCE (1 mL) were mixed in a Schlenk tube. The reaction mixture was stirred for 15 h at 80°C . The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, $v/v = 70:1$) to afford 50.2 mg (82%) of **3aa**. IR (KBr): ν_{max} 3056, 2921, 2851 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.91–7.88 (m, 2H), 7.85–7.82 (m, 1H), 7.48–7.40 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 140.7, 140.2, 133.7, 131.6, 130.0, 128.2, 127.6, 127.2, 126.9, 126.0, 125.7, 125.4; MS (70 eV), m/z (%): 204.4 (72) $[\text{M}]^+$, 203.2 (100).

7-Methyl-1-phenylnaphthalene (**3ba**)



2-*p*-Tolylacetaldehyde (40.2 mg, 0.3 mmol) and phenylacetylene (36.7 mg, 0.36 mmol), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (2.1 mg, 0.015 mmol) and DCE (1 mL) were mixed in a Schlenk tube. The reaction mixture was stirred for 15 h at 80°C . The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, $v/v = 70:1$) to afford 37.9 mg (58%) of **3ba**. IR (KBr): ν_{max} 3052, 2917, 2855, 2732 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.79 (d, $J = 8.0$ Hz, 2H), 7.66 (s, 1H), 7.50–7.45 (m, 4H), 7.44–7.41 (m, 2H), 7.38–7.36 (m, 1H), 7.33–7.30 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 141.0, 139.5, 135.7, 132.0, 131.7, 130.0, 128.2, 128.1, 128.0, 127.4, 127.1, 127.0, 124.8, 124.5, 21.9; MS (70 eV), m/z (%): 218.0 (100) $[\text{M}]^+$.

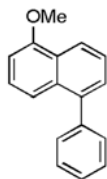
7-Methoxy-1-phenylnaphthalene (**3ca**)



2-(4-Methoxyphenyl)acetaldehyde (45.0 mg, 0.3 mmol) and phenylacetylene (36.7 mg, 0.36 mmol), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (2.1 mg, 0.015 mmol) and DCE (1 mL) were mixed in a Schlenk tube. The reaction mixture was stirred for 15 h at 80°C . The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, $v/v = 5:1$) to afford 42.1 mg (60%) of **3ca** with two isomers in 92:8 ratio. IR (KBr) ν_{max} 3054, 3022, 2956, 2936, 2878, 2831 cm^{-1} ; ^1H NMR of major product (400 MHz, CDCl_3 , ppm) δ 7.81–7.79 (m, 2H), 7.52–7.46 (m, 4H), 7.43–7.41 (m, 1H), 7.39–7.36 (m, 2H),

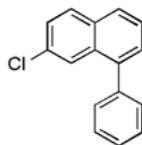
7.23 (s, 1H), 7.16 (d, $J = 8.8$ Hz, 1H), 3.75 (s, 3H); MS (70 eV), m/z (%): 234.1 (100) $[M]^+$.

1-Methoxy-5-phenylnaphthalene (3da)



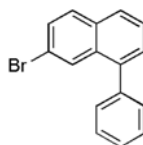
2-(2-Methoxyphenyl)acetaldehyde (45.0 mg, 0.3 mmol) and phenylacetylene (36.7 mg, 0.36 mmol), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (4.2 mg, 0.03 mmol) and DCE (1 mL) were mixed in a Schlenk tube. The reaction mixture was stirred for 15 h at 90 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, $v/v = 5:1$) to afford 21.1 mg (30%) of **3da**. IR(KBr) ν_{max} 3031, 3006, 2966, 2934, 2853, 2833 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 8.33–8.29 (m, 1H), 7.53–7.41 (m, 8H), 7.33–7.28 (m, 1H), 6.81 (d, $J = 7.2$ Hz, 1H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 155.5, 141.1, 139.8, 132.6, 130.1, 128.1, 127.5, 127.1, 125.9, 125.8, 124.7, 121.5, 118.3, 103.6, 55.6; MS (70 eV), m/z (%): 234.2 (100) $[M]^+$.

7-Chloro-1-phenylnaphthalene (3ea)



2-(4-Chlorophenyl)acetaldehyde (46.4 mg, 0.3 mmol) and phenylacetylene (36.7 mg, 0.36 mmol), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (2.1 mg, 0.015 mmol) and DCE (1 mL) were mixed in a Schlenk tube. The reaction mixture was stirred for 15 h at 80 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, $v/v = 70:1$) to afford 41.6 mg (58%) of **3ea**. IR(KBr) ν_{max} 3056, 2924, 2853 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.87–7.81 (m, 3H), 7.51–7.44 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 140.0, 139.6, 132.3, 132.01, 131.99, 129.93, 129.86, 128.4, 127.9, 127.5, 127.4, 126.7, 125.6, 124.9; MS (70 eV), m/z (%): 238.0 (100) $[M]^+$.

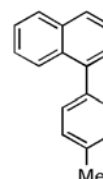
7-Bromo-1-phenylnaphthalene (3fa)



2-(4-Bromophenyl)acetaldehyde (59.7 mg, 0.3 mmol) and phenylacetylene (36.7 mg, 0.36 mmol), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (2.1 mg,

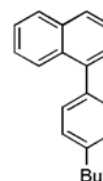
0.015 mmol) and DCE (1 mL) were mixed in a Schlenk tube. The reaction mixture was stirred for 15 h at 80 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, $v/v = 70:1$) to afford 54.0 mg (64%) of **3fa**. IR(KBr) ν_{max} 3056, 2922, 2851 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 8.04 (s, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.75 (d, $J = 8.4$ Hz, 1H), 7.57–7.43 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 140.0, 139.5, 132.7, 132.2, 129.9, 129.2, 128.5, 128.1, 127.9, 127.53, 127.48, 125.8, 120.4; MS (70 eV), m/z (%): 282.0 (100) $[M]^+$.

1-p-Tolynaphthalene (3ab)



Phenylacetaldehyde (36.0 mg, 0.3 mmol) and 1-ethynyl-4-methylbenzene (41.8 mg, 0.36 mmol), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (2.1 mg, 0.015 mmol) and DCE (1 mL) were mixed in a Schlenk tube. The reaction mixture was stirred for 15 h at 80 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, $v/v = 70:1$) to afford 47.7 mg (73%) of **3ab**. IR(KBr) ν_{max} 3037, 2963, 2918, 2857 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.92–7.85 (m, 3H), 7.51–7.41 (m, 6H), 7.31 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.2, 137.8, 136.9, 133.8, 131.7, 130.0, 129.0, 128.3, 127.4, 126.9, 126.1, 125.9, 125.7, 125.4, 21.3; MS (70 eV), m/z (%): 218.2 (100) $[M]^+$.

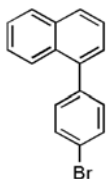
1-(4-Tert-butylphenyl)naphthalene (3ac)



Phenylacetaldehyde (36.0 mg, 0.3 mmol) and 1-tert-butyl-4-ethynylbenzene (57.0 mg, 0.36 mmol), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (2.1 mg, 0.015 mmol) and DCE (1 mL) were mixed in a Schlenk tube. The reaction mixture was stirred for 15 h at 80 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, $v/v = 70:1$) to afford 60.9 mg (78%) of **3ac**. IR(KBr) ν_{max} 3063, 3039, 2958, 2900, 2863 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.96 (d, $J = 8.8$ Hz, 1H), 7.90 (d, $J = 8.4$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.53–7.48 (m, 4H), 7.47–7.40 (m, 4H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 150.1, 140.2, 137.7, 133.8,

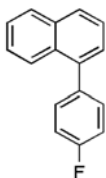
131.7, 129.7, 128.2, 127.4, 126.9, 126.2, 125.9, 125.7, 125.4, 125.2, 34.6, 31.5; MS (70 eV), m/z (%): 260.0 (100) $[M]^+$.

1-(4-Bromophenyl)naphthalene (3ad)



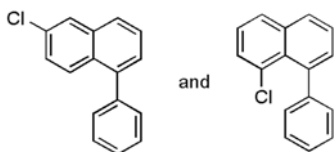
Phenylacetaldehyde (36.0 mg, 0.3 mmol) and 1-bromo-4-ethynylbenzene (65.2 mg, 0.36 mmol), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (8.2 mg, 0.06 mmol) and PhCl (1 mL) were mixed in a Schlenk tube. The reaction mixture was stirred for 15 h at 110 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, $v/v = 70:1$) to afford 46.7 mg (55%) of **3ad**. IR(KBr) ν_{max} 3058, 2924 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.90–7.81 (m, 3H), 7.61–7.58 (m, 2H), 7.49–7.47 (m, 2H), 7.44–7.41 (m, 1H), 7.35–7.33 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 139.6, 138.9, 133.7, 131.7, 131.4, 131.3, 128.3, 128.0, 126.8, 126.2, 125.9, 125.6, 125.3, 121.4; MS (70 eV), m/z (%): 282.2 (100) $[M]^+$.

1-(4-Fluorophenyl)naphthalene (3ae)



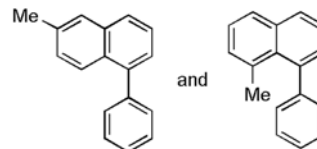
Phenylacetaldehyde (36.0 mg, 0.3 mmol) and 1-ethynyl-4-fluorobenzene (43.2 mg, 0.36 mmol), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (8.4 mg, 0.06 mmol) and PhCl (1 mL) were mixed in a Schlenk tube. The reaction mixture was stirred for 15 h at 110 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, $v/v = 70:1$) to afford 40.6 mg (61%) of **3ae**. IR(KBr) ν_{max} 3042, 2929, 2850 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.91–7.84 (m, 3H), 7.52–7.36 (m, 6H), 7.19–7.14 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.2 (d, $J = 244.4$ Hz), 139.1, 136.63, 136.59, 133.7, 131.6, 131.5, 128.3, 127.8, 127.0, 126.1, 125.8, 125.7, 125.3, 115.3, 115.0; MS (70 eV), m/z (%): 222.4 (74) $[M]^+$, 221.1 (100).

6-Chloro-1-phenylnaphthalene (3ga-1) and 1-chloro-8-phenylnaphthalene (3ga-2)



2-(3-Chlorophenyl)acetaldehyde (46.4 mg, 0.3 mmol) and phenylacetylene (36.7 mg, 0.36 mmol), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (2.1 mg, 0.015 mmol) and DCE (1 mL) were mixed in a Schlenk tube. The reaction mixture was stirred for 15 h at 80 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, $v/v = 70:1$) to afford 21.4 mg (30%) of **3ga** (**3ga-1/3ga-2** = 61/39). **3ga-1**: ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.867 (d, $J = 2.0$ Hz, 1H), 7.82 (d, $J = 8.8$ Hz, 1H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.55–7.39 (m, 7H), 7.34 (dd, $J_1 = 9.6$ Hz, $J_2 = 2.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 140.4, 140.2, 134.5, 131.6, 129.93, 129.0, 128.3, 127.8, 127.5, 127.1, 126.8, 126.7, 126.5; MS (70 eV), m/z (%): 237.7 (100) $[M]^+$. **3ga-2**: ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.88–7.82 (m, 2H), 7.52–7.47 (m, 2H), 7.41–7.32 (m, 7H); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 143.5, 139.5, 136.0, 131.4, 131.0, 129.6, 129.4, 128.7, 128.6, 128.2, 127.2, 126.7, 125.6, 125.4; MS (70 eV), m/z (%): 238.7 (100) $[M]^+$.

6-Methyl-1-phenylnaphthalene (3ha-1) and 1-methyl-8-phenylnaphthalene (3ha-2)



2-*m*-Tolylacetaldehyde (40.2 mg, 0.3 mmol) and phenylacetylene (36.7 mg, 0.36 mmol), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (2.1 mg, 0.015 mmol) and DCE (1 mL) were mixed in a Schlenk tube. The reaction mixture was stirred for 15 h at 80 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, $v/v = 70:1$) to afford 28.8 mg (44%) of **3ha** (**3ha-1/3ha-2** = 53/47). ^1H NMR (400 MHz, CDCl_3 , ppm) δ 7.66 (s, 1H); MS (70 eV), m/z (%): 218.2 (100) $[M]^+$.

We are grateful for the financial supports from Sichuan Provincial Department of Education (11ZA108), National Natural Science Foundation of China (21202109 and 21072140), Special Funds of Sichuan Normal University for Sharing the Large Precision Equipments (DJ2012-07, DJ2011-16) and Sichuan Normal University.

- (a) Medarde M, Maya ABS, Pérez-Melero CJ. Naphthalene combretastatin analogues: Synthesis, cytotoxicity and antitubulin activity. *Enzyme Inhib Med Chem*, 2004, 19: 521–540; (b) Xie X, Kozłowski MC. Synthesis of the naphthalene portion of the rubromycins. *Org Lett*, 2001, 3: 2661–2663; (c) Ukita T, Nakamura Y, Kubo A, Yamamoto Y, Takahashi M, Kotera J, Ikeo T. 1-Arylnaphthalene lignan: A novel scaffold for type 5 phosphodiesterase inhibitor. *J Med Chem*, 1999, 42: 1293–1305; (d) Ward RS. Lignans, neolignans, and related compounds. *Nat Prod Rep*, 1995, 12: 183–205; (e) Trujillo JM, Jorge RE, Navarro E, Boada J. Lignans from *Justicia hysopifolia*. *Phytochemistry*, 1990, 29: 2991–2993; (f) Seong BL, Han

- MH. A facile preparation of rifamycin derivatives by use of manganese dioxide. *Chem Lett*, 1982, 627–628; (g) Georgiou PE, Li Z, Ashram M, Chowdhury S, Mizyed S, Tran AH, Al-Saraierh H, Miller DO. Calixnaphthalenes: Deep, electron-rich naphthalene ring-containing calixarenes. the first decade. *Synlett*, 2005, 879–891; (h) Watson MD, Fechtenkötter A, Müllen K. Big is beautiful—“aromaticity” revisited from the viewpoint of macromolecular and supramolecular benzene chemistry. *Chem Rev*, 2001, 101: 1267–1300; (i) Zeng F, Su YS, Chen CF. Li⁺-templated complexation of cylindrical macrotricyclic host with naphthalene diimide: Cation-controlled switchable complexation processes. *Sci China Chem*, 2012, 10: 2069–2074
- 2 For some reviews, see: (a) Koning CB, Rousseau AL, Otterlo WAL. Modern methods for the synthesis of substituted naphthalenes. *Tetrahedron*, 2003, 59: 7–36; (b) Saito S, Yamamoto Y. Recent advances in the transition-metal-catalyzed regioselective approaches to polysubstituted benzene derivatives. *Chem Rev*, 2000, 100: 2901–2916; (c) Bradsher CK. Formation of six-membered aromatic rings by cycloalkylation of some aldehydes and ketones. *Chem Rev*, 1987, 87: 1277–1297; (d) Asao N. Gold- and copper-catalyzed [4+2] benzanulations between enynal or enynone units and 2 π -systems. *synlett*, 2006, 1645–1656.
- 3 (a) Viswanathan GS, Wang M, Li CJ. A highly regioselective synthesis of polysubstituted naphthalene derivatives through Gallium trichloride catalyzed alkyne–aldehyde coupling. *Angew Chem Int Ed*, 2002, 41: 2138–2141; (b) Viswanathan GS, Li CJ. Synthesis of naphthalene derivatives via a novel Gallium trichloride catalyzed cross-coupling of epoxides with alkynes. *synlett*, 2002, 1553–1555
- 4 Kabalka GW, Ju Y, Wu Z. A new Titanium tetrachloride mediated annulation of α -aryl-substituted carbonyl compounds with alkynes: A simple and highly efficient method for the regioselective synthesis of polysubstituted naphthalene derivatives. *J Org Chem*, 2003, 68: 7915–7917
- 5 Balamurugan R, Gudla V. Gold-catalyzed electrophilic addition to arylalkynes. A facile method for the regioselective synthesis of substituted naphthalenes. *Org Lett*, 2009, 11: 3116–3119; For the intramolecular reaction, see: Balamurugan R, Gudla V. Synthesis of aryl naphthalene lignan scaffold by Gold-catalyzed intramolecular sequential electrophilic addition and benzannulation. *J Org Chem*, 2011, 76: 9919–9933
- 6 For the review, see: Yamamoto H, *Lewis Acids in Organic Synthesis*, John Wiley & Sons: New York, 2000, 96–113; For some other examples, see: (a) Pastine SJ, McQuaid KM, Sames D. Room temperature hydroalkylation of electron-deficient olefins: sp³ C–H Functionalization via a Lewis acid-catalyzed intramolecular redox event. *J Am Chem Soc*, 2005, 127: 12180–12181; (b) McQuaid KM, Sames D. C–H bond functionalization via hydride transfer: Lewis acid catalyzed alkylation reactions by direct intramolecular coupling of sp³ C–H bonds and reactive alkenyl oxocarbenium intermediates. *J Am Chem Soc*, 2009, 131: 402–403; (c) Pastine SJ, Sames D. Room temperature intramolecular hydro-O-alkylation of aldehydes: sp³ C–H functionalization via a Lewis acid catalyzed tandem 1,5-hydride transfer/cyclization. *Org Lett*, 2005, 7: 5429–5431
- 7 Xiang SK, Wu G, Zhang B, Cui Y, Jiao N. Csp²–Csp² bond formation via Lewis acid/ammonium salt cocatalyzed tandem addition and oxidative dehydrogenation strategy: alkenylation of indoles with α,β -unsaturated ketones. *Tetrahedron Lett*, 2012, 53(29): 3802–3804
- 8 Jia SX, Wang ML. Synthetic method of 3,4-dimethoxybenzene acetaldehyde. *Chem Indus Times*, 2006, 20(2): 21–22 (in Chinese)