Supporting Information for

Novel and Rapid Approach for Benzanthrones: BBr3 -Promoted

Annulation of 8- Aryl-1- Naphthoic Acid Derivatives

Xinkun An, Haoyun Ma, Guoen Cui, Tingting Zhang, Leichuan Xu, Mingan Wang *

Innovation Center of Pesticide Research, Department of Applied Chemistry, College of Science,

China Agricultural University, Beijing 100193, China;

Correspondence: Mingan Wang, Ph.D. & Professor College of Science China Agricultural University Beijing 100193 P. R. China TEL: 86-010-62734093 E-mail: wangma@cau.edu.cn

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Part 1. General information

As for the preparation of substrate 3, all manipulations of Suzuki-Miyaura coupling were performed under N₂ by standard Schlenk techniques unless otherwise noted.

Nuclear magnetic resonance spectra were measured at 500 MHz (¹H NMR), and at 126 MHz (¹³C NMR). ¹H NMR chemical shifts were reported in δ relative to the resonance of TMS (δ 0.00) and the residual solvent signals at δ 7.26 for CDCl₃. ¹³C NMR chemical shifts were reported in δ relative to the residual solvent signals at δ 77.16 for CDCl₃. High resolution mass spectra (HRMS) were recorded by Bruker APEX II mass spectrometer (Varian, Palo Alto, CA). The crystal structure was recorded by Agilent Gemini E X-ray single-crystal diffractometer. The melting points were determined by WRX-4 melting-point apparatus with a microscope (Shanghai Yice Apparatus & Equipment Co. Ltd., Shanghai, China). Fluorescence absorption and emission of representative compounds were detected by Shimadzu RF-6000 spectro fluorophotometer.

Scheme S1. Preparation of methyl 8-bromo-5-methoxy-1-naphthoate 1a



Methyl 5-methoxy-1-naphthoate (5.0 mmol, 1.0 eq) and NBS (5.25 mmol, 1.05 eq) were placed in a 250 mL round-bottom flask equipped with a magnetic stirrer. 50 mL DCM was added into the flask and the mixture was stirred for 8 h at room temperature. The mixture was washed with brine, and the organic layer was dried over by Na₂SO₄, and concentrated in vacuo. The resulting crude material was subjected to column chromatography (silica gel, 200–300 mesh, PE/EtOAc = 80/1) to give methyl 8-bromo-5-methoxy-1-naphthoate (**1a**) as white crystal (1.36 g, 92% yield).

¹H NMR (500 MHz, CDCl₃) δ 8.43 (dd, J = 8.4, 1.4 Hz, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.65 (dd, J = 7.1, 1.4 Hz, 1H), 7.49 (dd, J = 8.4, 7.1 Hz, 1H), 6.72 (d, J = 8.3 Hz, 1H), 3.99 (s, 3H), 3.98 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 170.95, 155.35, 132.90, 131.67, 128.93, 128.79, 127.69, 125.14, 124.64, 109.65, 105.30, 55.86, 52.81.

Optimization towards Suzuki-Miyaura coupling

In consideration of the steric hindrance of ester group in the 1-position of aryl bromide substrate **1**, Suzuki-Miyaura Coupling may be difficult to proceed. In the first step of reaction, methyl 8-bromo-5-methoxy-1-naphthoate (**1a**), phenylboronic acid (**2a**) and $Pd(PPh_3)_2Cl_2$ were selected as substrates to explore the applicability of financially available Pd catalyst containing phosphorus to carry out this reaction. The reaction was firstly performed in the presence of 1.2 equiv. of **2a**, 2.0 equiv. of K₂CO₃ and 5 mol% Pd(PPh_3)₂Cl₂ in the 1:1 mixed solvent of dioxane and water at a temperature of 80°C, in which the desired product **3aa** was obtained in 21% yield (**Table S1**, entry 1). We suspected that the large steric hindrance PPh₃ ligand of Pd might prevent oxidative addition of Suzuki-Miyaura coupling. Thus, we chose Pd(OAc)₂ to replace Pd(PPh_3)₂Cl₂, which has smaller steric effect of ligands. To our delight, the yield of **3aa** was dramatically improved to 55% (**Table S1**, entry 2). We also screened Pd(PPh_3)₄ as catalyst, investigating whether Pd(0) could successfully catalyze the reaction. Unfortunately, only 5% yield of **3aa** could be isolated (**Table S1**,

entry 3). Then, we replaced dioxane with THF in the solvent due to the weak solubility of 1a in dioxane, and the yield of **3aa** was smoothly enhanced to 60% (Table S1, entry 4). In this reaction, we analyzed that the main by-product of the reaction was the debromination product of 1a. Considering that the exorbitant temperature resulting in the undesired debromination reaction, the reaction temperature was reduced to 60 °C and the yield of **3aa** was improved to 68% (**Table S1**, entry 5). Nevertheless, more lowered reaction temperature led Suzuki-Miyaura coupling difficult to process (Table S1, entry 6). Next, a various of base (Cs₂CO₃, NEt₃, pyridine) were screened (Table 1, entry 7-9). The moderate alkaline strength of Cs_2CO_3 mildly promoted the yield of **3aa** to 77% without hydrolyzing the ester group of **1a**. While organic base (NEt₃, pyridine) was used, the reaction would be hard to proceed. Whether prolonging reaction time of 48 h nor increase the catalytic loading of 10 mol % Pd(OAc)₂ could result in obviously higher yield of 81% and 78% (Table S1, entry 10-11). Ultimately, increasing phenylboronic acid (2a) loading gave no better results (Table S1, entry 12), it may due to the large excess of 2a aggravated the self-coupling reaction of 2a. Consequently, the optimal reaction conditions were 1.2 equiv of 2a, 2.0 equiv of Cs₂CO₃ and 5 mol% of Pd(OAc)₂ in the mixture of 1:1 of dioxane and water as a solvent at 60 °C for 24 h.

 Table S1. Reaction Optimization towards Suzuki-Miyaura Coupling of methyl 8-bromo-5methoxy-1-naphthoate (1a) and phenylboronic acid (2a) ^a

OMe Br (+ COOMe	B(OH) ₂ cata solvent, '	ılyst, base Temp. , N ₂ , tin	ne (COOMe
1a	eatalvet	2a	hase	T(°C)	3aa
entry	catalyst	solvent	base	1(0)	1 Ieiu (70)
1	Pd (PPh ₃) ₂ Cl ₂	dioxane : $H_2O = 1$: 1	K ₂ CO ₃	80	21
2	Pd (OAc) ₂	dioxane : $H_2O = 1 : 1$	K ₂ CO ₃	80	55
3	Pd (PPh ₃) ₄	dioxane : $H_2O = 1 : 1$	K ₂ CO ₃	80	5
4	Pd (OAc) ₂	$THF:H_2O=1:1$	K ₂ CO ₃	80	60
5	Pd (OAc) ₂	$THF:H_2O=1:1$	K ₂ CO ₃	60	68
6	Pd (OAc) ₂	$THF:H_2O=1:1$	K ₂ CO ₃	40	Trace
7	Pd (OAc) ₂	$THF:H_2O=1:1$	Cs ₂ CO ₃	60	77
8	Pd (OAc) ₂	$THF:H_2O=1:1$	NEt ₃	60	Trace
9	Pd (OAc) ₂	$THF:H_2O=1:1$	pyridine	60	Trace
10 ^c	Pd (OAc) ₂	$THF:H_2O=1:1$	Cs ₂ CO ₃	60	81
11 ^{<i>d</i>}	Pd (OAc) ₂	$THF:H_2O=1:1$	Cs ₂ CO ₃	60	78
12 ^e	Pd (OAc) ₂	$THF: H_2O = 1:1$	Cs ₂ CO ₃	60	75

^a Reactions were performed under a N₂ atmosphere, reaction conditions: 1a (0.5 mmol),

2a (0.6 mmol, 1.2 equiv.), base (1.0 mmol, 2.0 equiv.), catalyst (0.025 mmol, 5 mol %).

^b Yield of isolated products. ^c Reaction was prolonged to 48 h.

^d 0.05 mmol Pd (OAc)₂ (10 mol %) was added. ^e 0.75 mmol (1.5 equiv.) 2a was added.

With the optimal reaction conditions identified, utilizing phenylboronic acid (2) with different

substituents, the scope of intermediate products **3** was investigated. As shown in **Scheme S2**, various electron-neutral, donating, and with-drawing substituents or different steric effects of phenylboronic acid (**2**) could be well tolerated, and most reactions proceeded smoothly with moderate to high yields (70%-92%) (**3aa-3ae**, **3ag-3ak**, **3ap-3au**'). But unexpectedly, it is worth mentioning that the reaction of (4-vinylphenyl)-boronic acid (**2**) with **1a** could only afford a low yield of **3al** (24%), on account of that the vinyl group of **2l** was easy to coordinate with Pd(2), causing the formation of self-coupling product directly from two molecules of **2l**. Subsequently, we investigated the reaction in the presence of steric hindrance groups on arylboric acid (**2**). The reaction could also work smoothly, affording moderate yields of 30%-74% (**3am-3ao**, **3ar-3as**, **3ax**).

To better understand whether olefins could be used as electron donors for subsequent Friedel-Crafts acylation reaction. Alkenyl substituted aryl products need to be synthesized. Surprisingly, with the alkenyl substituted boric acid reacting with **1a**, the reaction yields remained moderate of 66% and 50% (**3av**, **3aw**).



Scheme S2. Scope of intermediate products: methyl 5-methoxy-8-aryl-1-naphthoate (3)^{*a,b*}

^{*a*} Reaction conditions: Reactions were equipped under a N₂ atmosphere, **1a** (0.5 mmol), **2** (0.6 mmol), Cs₂CO₃ (1.0 mmol) and Pd(OAc)₂ (5 mol %) in 5 mL of THF and 5 mL of H₂O at 60 °C for 24 h. ^{*b*} Isolated yield

Scheme S3. Preparation of methyl 5-methoxy-8-aryl-1-naphthoate 3



To an oven-dried Schlenk tube was added methyl 8-bromo-5-methoxy-1-naphthoate (1a) (0.5 mmol, 1.0 equiv.), various substituted arylboronic acids (2) (0.6 mmol, 1.2 equiv.), Cs_2CO_3 (1.0 mmol, 2.0 equiv.), and Pd(OAc)₂ (5 mol %). THF (5 mL) and H₂O (5 mL) was added via a syringe, and the reaction was protected under a N₂ atmosphere. The mixture was stirred at 60 °C in an oil bath for 12- 48 h. The mixture was cooled and transferred into a separating funnel, extracted by EtOAc for 3 times. The organic phase was washed with brine and concentrated in vacuo and the crude product was purified by silica gel column chromatography (silica gel, 200–300 mesh, PE/EtOAc 150/1 to 100/1) to give compounds **3**. Most reactions could be completed within 12 h, for arylboronic acids with substituents in the ortho position, the reaction rate and yield would be substantially reduced due to the steric hindrance.

Scheme S4. Preparation of benzanthrone derivatives 4



To an oven-dried round-bottom flask was added 5-methoxy-8-aryl-1-naphthoate (3) (0.3 mmol, 1.0 equiv.), BBr₃ (0.6 mmol, 2.0 equiv.) and DCM (10 mL) at room temperature. After 0.5 h, the reaction was quenched by 3 mL MeOH, and the mixture was transferred into a separating funnel and extracted by DCM for 3 times. The combined organic phase was washed with brine and concentrated in vacuo and the crude product was purified by silica gel column chromatography (silica gel, 200–300 mesh, PE/EtOAc 50/1 to 25/1) to give compounds 4.

Scheme S5. One step synthesis of 1,2-dihydro-5H-indeno[6,7,1-def]indolo[2,1-a]isoquinolin-5-one 4cz



To an oven-dried Schlenk tube was added methyl 6-bromo-1,2-dihydroacenaphthylene-5-carboxylate (1c) (0.5 mmol, 1.0 equiv.), (1-(tert-butoxycarbonyl)-1H-indol-2-yl)boronic acid (2z) (0.6 mmol, 1.2 equiv.), Cs_2CO_3 (1.0 mmol, 2.0 equiv.), and Pd(OAc)₂ (5 mol %). THF (5 mL) and H₂O (5 mL) was added via a syringe, and the reaction was protected under a N₂ atmosphere. The mixture was stirred at 60 °C in an

oil bath for 24 h. The mixture was cooled and transferred into a separating funnel, extracted by EtOAc for 3 times. The organic phase was washed with brine and concentrated in vacuo and the crude product was purified by silica gel column chromatography (silica gel, 200–300 mesh, PE/EtOAc 75/1) to give compounds **4cz** as yellow solid powder (105 mg, 71% yield).

Scheme S6. Preparation of 9-fluoro-3-hydroxy-7H-benzo[de]anthracen-7-one 5ad



To an oven-dried round-bottom flask was added 9-fluoro-3-methoxy-7H-benzo[de]anthracen-7-one (**4ad**), (0.1 mmol, 1.0 equiv.), BBr₃ (0.2 mmol, 2.0 equiv.) and DCM (5 mL) at room temperature. After 72 h, the reaction was quenched by 1 mL MeOH, and the mixture was transferred into a separating funnel and extracted by DCM for 3 times. The combined organic phase was washed with brine and concentrated in vacuo and the crude product was purified by silica gel column chromatography (silica gel, 200–300 mesh, PE/EtOAc 20/1 to 10/1) to give compounds **5ad** as orange solid (24 mg, 90% yield). 9-fluoro-3-hydroxy-7H-benzo[de]anthracen-7-one (**5ad**) could also be synthesized by methyl 8-(4-fluorophenyl)-5-methoxy-1-naphthoate (**3ad**), using 4.0 equiv BBr₃ as an one-pot reaction. While the reaction time was extended to 72 h, the product **5ad** would be obtained instead of **4ad**.

Scheme S7. Preparation of 9-acetyl-2-bromo-3-methoxy-7H-benzo[de]anthracen-7-one 7ak



To an oven-dried round-bottom flask was added 9-acetyl-3-methoxy-7H-benzo[de]anthracen-7-one (**4ak**), (0.1 mmol, 1.0 equiv.), NBS (0.12 mmol, 1.2 equiv.) and DCM (5 mL) at room temperature. After 48 h, the mixture was washed with brine and concentrated in vacuo and the crude product was purified by silica gel column chromatography (silica gel, 200–300 mesh, PE/EtOAc 50/1) to give compounds **7ak** as yellow solid (26 mg, 68% yield).

Scheme S8. Preparation of methyl 8-(3,4-dimethoxyphenyl)-6,7-dimethoxyisoquinoline-1carboxylate 9



To an oven-dried Schlenk tube was added methyl 8-bromo-6,7-dimethoxyisoquinoline-1-carboxylate (8) (0.5 mmol, 1.0 equiv.), (3,4-dimethoxyphenyl)-boronic acid (0.6 mmol, 1.2 equiv.), Cs_2CO_3 (1.0 mmol, 2.0 equiv.), and $Pd(OAc)_2$ (5 mol %). dioxane (5 mL) and H_2O (5 mL) was added via a syringe, and the reaction was protected under a N_2 atmosphere. The mixture was stirred at 80 °C in an oil bath for 48 h. The mixture was cooled and transferred into a separating funnel, extracted by EtOAc for 3 times. The organic phase was washed with brine and concentrated in vacuo and the crude product was purified by silica gel column chromatography (silica gel, 200–300 mesh, DCM/ MeOH 50/1) to give compounds **9** as white solid (153 mg, 80% yield).

Scheme S9. Preparation of 1,2,9,10-tetramethoxy-7H-dibenzo[de,g]quinolin-7-one 10



To an oven-dried Schlenk tube was added **9** (0.1 mmol, 1.0 equiv.), BBr₃ (0.2 mmol, 2.0 equiv.) and DCM (5 mL) at room temperature. After 0.5 h, the reaction was quenched by 2 mL MeOH. Then 1.0 mol/L NaHCO₃ solution was added and the mixture was stirred for 10 minutes. Subsequently, the mixture was transferred into a separating funnel and extracted by DCM for 3 times. The combined organic phase was washed with brine and concentrated in vacuo and the crude product was purified by silica gel column chromatography (silica gel, 200–300 mesh, DCM/MeOH 35:1) to give compounds **10** as yellow solid (31 mg, 88% yield).

Part 2. Previous Synthetic Methodologies of Benzanthrones





Part 3. The crystal structure parameters for compound 4ac



adi	able S2: Crystal data and structure refinement for exp_8094 (CCDC 2183633)						
	Identification code	exp_8094					
	Empirical formula	$C_{19}H_{14}O_2$					
	Formula weight	274.30					
	Temperature / K	124.3(3)					
	Crystal system	orthorhombic					
	Space group	P212121					
	a / Å, b / Å, c / Å	4.2162(5), 14.4562(15), 21.1593(16)					
	$\alpha/^{\circ},\beta/^{\circ},\gamma/^{\circ}$	90.00, 90.00, 90.00					
	Volume / Å ³	1289.7(2)					
	Z	4					
	$ ho_{calc}$ / mg mm ⁻³	1.413					
	μ / mm^{-1}	0.091					
	F(000)	576					
	Crystal size / mm ³	$0.45 \times 0.04 \times 0.03$					
	2Θ range for data collection	6.42 to 52°					
	Index ranges	$-5 \le h \le 3, -17 \le k \le 16, -24 \le l \le 26$					
	Reflections collected	5130					
	Independent reflections	2482[R(int) = 0.0524 (inf-0.9Å)]					
	Data/restraints/parameters	2482/0/192					
	Goodness-of-fit on F ²	1.013					
	Final R indexes [I> 2σ (I) i.e. F _o > 4σ (F _o)]	$R_1 = 0.0602, wR_2 = 0.1067$					
	Final R indexes [all data]	$R_1 = 0.1026, wR_2 = 0.1339$					
	Largest diff. peak/hole / e Å ⁻³	0.214/-0.211					
	Completeness	0.9943					

Table S2 1 L 2004 (CCDC 2192622)

Atom	x	У	z	U(eq)
O2	-6705(6)	-3801.1(16)	-1053.7(9)	30.9(6)
C10	-10087(8)	-3816(2)	-2919.4(13)	22.0(8)
С9	-8123(8)	-4543(2)	-2689.1(13)	21.7(8)
01	-8130(6)	-6114.5(17)	-4029.3(9)	35.3(7)
C11	-11299(8)	-3876(2)	-3572.1(13)	23.0(8)
C4	-6959(8)	-4515(2)	-2051.2(13)	22.9(8)
C1	-10810(9)	-3100(2)	-2516.0(12)	26.3(8)
C6	-4124(9)	-5951(2)	-2218.0(14)	28.4(9)
C12	-10622(9)	-4653(2)	-3949.1(14)	23.2(8)
C16	-14399(9)	-3251(3)	-4437.6(13)	29.2(9)
C13	-8617(9)	-5415(2)	-3712.1(14)	27.5(9)
C15	-13793(8)	-4025(2)	-4809.1(13)	25.8(8)
C3	-7851(8)	-3754(2)	-1656.3(13)	23.5(8)
C17	-13194(8)	-3169(3)	-3834.4(13)	27.8(9)
C8	-7302(8)	-5318(2)	-3063.9(13)	23.2(8)
C14	-11910(8)	-4723(2)	-4560.3(13)	26.4(8)
C2	-9749(8)	-3063(3)	-1887.1(13)	26.2(9)
C18	-15174(9)	-4105(3)	-5469.9(13)	35.7(10)
C7	-5315(9)	-5998(3)	-2836.6(13)	27.9(9)
C5	-4989(9)	-5229(3)	-1833.8(14)	28.4(9)
C19	-7725(11)	-3089(3)	-618.6(13)	40.8(11)

Table S3 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for exp_8094. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Table S4 Anisotropic Displacement Parameters (Å2×103) for exp_8094. The Anisotropic displacementfactor exponent takes the form: $-2\pi 2[h2a*2U11+...+2hka×b×U12]$

Atom	U11	U ₂₂	U33	U ₂₃	U ₁₃	U ₁₂
O2	39.4(16)	32.3(14)	21(1)	-3(1)	-1.4(11)	3.3(14)
C10	19.9(18)	23(2)	23.2(15)	2.8(15)	5.6(15)	-4.9(18)
С9	19.9(19)	22.8(18)	22.5(15)	-1.1(14)	6.7(15)	-5.4(19)
01	49.3(18)	29.4(14)	27.3(11)	-5.8(11)	2.1(12)	-0.4(16)
C11	22.6(19)	25.3(19)	21.0(14)	1.9(15)	5.2(15)	-5.1(19)
C4	20.8(19)	25.1(19)	22.8(15)	1.3(15)	0.5(16)	-4.3(19)
C1	30(2)	24.7(19)	24.7(16)	3.2(15)	3.2(17)	0(2)
C6	25.1(19)	28(2)	32.2(17)	5.0(16)	5.4(17)	3(2)
C12	27(2)	21.7(19)	20.7(15)	-1.6(14)	7.5(16)	-3.5(18)
C16	29(2)	32(2)	26.0(17)	0.4(16)	4.8(17)	1(2)
C13	33(2)	25(2)	24.8(16)	1.3(15)	10.7(17)	-5(2)

C15	24.5(19)	33(2)	19.6(15)	0.4(15)	5.9(15)	-8.1(19)
C3	24.3(19)	27(2)	19.4(14)	-0.2(15)	2.5(15)	-6.7(19)
C17	32(2)	30(2)	21.7(15)	-1.5(16)	6.2(16)	0(2)
C8	24(2)	23.2(19)	22.4(15)	0.7(14)	9.0(16)	-1.5(18)
C14	30(2)	25.9(19)	22.8(16)	-3.3(15)	6.5(17)	-4(2)
C2	31(2)	23.4(19)	24.2(15)	-4.3(15)	4.0(17)	-1.7(19)
C18	36(2)	43(2)	28.5(17)	-3.3(18)	2.6(18)	-4(2)
C7	28(2)	25(2)	31.1(17)	1.3(16)	6.4(17)	1(2)
C5	25(2)	34(2)	26.3(17)	4.7(16)	3.5(16)	-4(2)
C19	60(3)	41(2)	22.2(15)	-8.1(17)	-1.1(19)	5(3)

Table S5 Bond Lengths for exp_8094.

Atom	Atom	Length/Å	Atom	Length/Å
O2	C3	1.365(3)	C1	1.405(4)
O2	C19	1.446(4)	C6	1.404(4)
C10	С9	1.425(4)	C6	1.373(4)
C10	C11	1.475(4)	C12	1.476(5)
C10	C1	1.376(4)	C12	1.406(4)
С9	C4	1.437(4)	C16	1.391(4)
С9	C8	1.416(4)	C16	1.379(4)
01	C13	1.231(4)	C13	1.486(4)
C11	C12	1.407(4)	C15	1.387(4)
C11	C17	1.411(4)	C15	1.519(4)
C4	C3	1.432(4)	C3	1.370(4)
C4	C5	1.402(5)	C8	1.377(4)

Table S6 Bond Angles for exp_8094.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	O2	C19	117.0(3)	C17	C16	C15	121.7(3)
С9	C10	C11	118.6(3)	01	C13	C12	121.5(3)
C1	C10	C9	118.2(3)	01	C13	C8	121.2(3)
C1	C10	C11	123.2(3)	C12	C13	C8	117.2(3)
C10	C9	C4	119.9(3)	C16	C15	C18	120.7(3)
C8	C9	C10	122.3(3)	C14	C15	C16	118.4(3)
C8	C9	C4	117.7(3)	C14	C15	C18	120.9(3)
C12	C11	C10	120.5(3)	O2	C3	C4	114.4(3)
C12	C11	C17	118.0(3)	O2	C3	C2	125.2(3)
C17	C11	C10	121.5(3)	C2	C3	C4	120.4(3)
C3	C4	C9	118.7(3)	C16	C17	C11	120.7(3)
C5	C4	C9	119.3(3)	С9	C8	C13	120.0(3)

C5	C4	C3	122.0(3)	C7	C8	С9	121.2(3)
C10	C1	C2	123.0(3)	C7	C8	C13	118.8(3)
C5	C6	C7	119.6(3)	C15	C14	C12	121.2(3)
C11	C12	C13	121.3(3)	C3	C2	C1	119.8(3)
C14	C12	C11	120.0(3)	C8	C7	C6	120.6(3)
C14	C12	C13	118.7(3)	C6	C5	C4	121.5(3)

Table S7 Torsion Angles for exp_8094.

Α	В	С	D	Angle/°
O2	C3	C2	C1	-179.2(3)
C10	С9	C4	C3	0.9(4)
C10	С9	C4	C5	-179.0(3)
C10	С9	C8	C13	-2.8(5)
C10	С9	C8	C7	177.9(3)
C10	C11	C12	C13	-1.8(5)
C10	C11	C12	C14	177.1(3)
C10	C11	C17	C16	-177.7(3)
C10	C1	C2	C3	1.4(5)
С9	C10	C11	C12	2.4(4)
C9	C10	C11	C17	-178.5(3)
С9	C10	C1	C2	-1.2(5)
С9	C4	C3	O2	178.2(3)
C9	C4	C3	C2	-0.7(5)
C9	C4	C5	C6	0.5(5)
C9	C8	C7	C6	1.9(5)
O1	C13	C8	C9	-174.5(3)
O1	C13	C8	C7	4.8(5)
C11	C10	С9	C4	-178.7(3)
C11	C10	С9	C8	0.0(4)
C11	C10	C1	C2	177.5(3)
C11	C12	C13	O1	176.8(3)
C11	C12	C13	C8	-1.0(5)
C11	C12	C14	C15	1.6(5)
C4	С9	C8	C13	175.9(3)
C4	С9	C8	C7	-3.4(5)
C4	C3	C2	C1	-0.4(5)
C1	C10	С9	C4	0.0(4)
C1	C10	С9	C8	178.7(3)

C1	C10	C11	C12	-176.3(3)
C1	C10	C11	C17	2.9(5)
C12	C11	C17	C16	1.4(5)
C12	C13	C8	С9	3.3(4)
C12	C13	C8	C7	-177.4(3)
C16	C15	C14	C12	-0.3(5)
C13	C12	C14	C15	-179.5(3)
C13	C8	C7	C6	-177.5(3)
C15	C16	C17	C11	-0.2(5)
C3	C4	C5	C6	-179.4(3)
C17	C11	C12	C13	179.0(3)
C17	C11	C12	C14	-2.1(5)
C17	C16	C15	C14	-0.3(5)
C17	C16	C15	C18	179.4(3)
C8	С9	C4	C3	-177.8(3)
C8	С9	C4	C5	2.2(4)
C14	C12	C13	01	-2.1(5)
C14	C12	C13	C8	-179.9(3)
C18	C15	C14	C12	180.0(3)
C7	C6	C5	C4	-2.1(5)
C5	C4	C3	O2	-1.9(5)
C5	C4	C3	C2	179.2(3)
C5	C6	C7	C8	1.0(5)
C19	O2	C3	C4	-175.4(3)
C19	O2	C3	C2	3.5(5)



Part 4. Copies of ¹H and ¹³C NMR Spectra of Products

Figure S2 ¹³C NMR of compound **1a** (126 MHz, CDCl₃)



190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)

Figure S4¹³C NMR of compound **3aa** (126 MHz, CDCl₃)



Figure S5 ¹H NMR of compound **3ab** (500 MHz, CDCl₃)



200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 fl (ppm)

Figure S6¹³C NMR of compound **3ab** (126 MHz, CDCl₃)



Figure S8¹³C NMR of compound **3ac** (126 MHz, CDCl₃)



Figure S9¹H NMR of compound **3ad** (500 MHz, CDCl₃)



Figure S10¹³C NMR of compound **3ad** (126 MHz, CDCl₃)



Figure S11 ¹H NMR of compound **3ae** (500 MHz, CDCl₃)



Figure S12 ¹³C NMR of compound **3ae** (126 MHz, CDCl₃)



Figure S13 ¹H NMR of compound **3af** (500 MHz, CDCl₃)



Figure S14 ¹³C NMR of compound **3af** (126 MHz, CDCl₃)



Figure S15 ¹H NMR of compound **3ag** (500 MHz, CDCl₃)



Figure S16¹³C NMR of compound **3ag** (126 MHz, CDCl₃)



Figure S17 ¹H NMR of compound **3ah** (500 MHz, CDCl₃)



fl (ppm)

Figure S18¹³C NMR of compound **3ah** (126 MHz, CDCl₃)



Figure S20¹³C NMR of compound **3ai** (126 MHz, CDCl₃)



Figure S21¹H NMR of compound **3aj** (500 MHz, CDCl₃)



00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 fl (ppm)





Figure S23¹H NMR of compound **3ak** (500 MHz, CDCl₃)



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 fl (ppm)





Figure S25 ¹H NMR of compound **3al** (500 MHz, CDCl₃)



Figure S26¹³C NMR of compound **3al** (126 MHz, CDCl₃)



Figure S27 ¹H NMR of compound **3am** (500 MHz, CDCl₃)



Figure S28¹³C NMR of compound **3am** (126 MHz, CDCl₃)



Figure S30¹³C NMR of compound **3an** (126 MHz, CDCl₃)







Figure S32 ¹³C NMR of compound **3ao** (126 MHz, CDCl₃)







Figure S34 ¹³C NMR of compound **3ap** (126 MHz, CDCl₃)



Figure S35 ¹H NMR of compound **3aq** (500 MHz, CDCl₃)



fl (ppm)

Figure S36¹³C NMR of compound **3aq** (126 MHz, CDCl₃)







Figure S38 ¹³C NMR of compound **3ar** (126 MHz, CDCl₃)



Figure S40¹³C NMR of compound **3as** (126 MHz, CDCl₃)







210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)

Figure S42 ¹³C NMR of compound **3at** (126 MHz, CDCl₃)



Figure S44 ¹³C NMR of compound **3au** (126 MHz, CDCl₃)






Figure S46¹³C NMR of compound **3au'** (126 MHz, CDCl₃)







Figure S48 ¹³C NMR of compound **3av** (126 MHz, CDCl₃)

$\begin{bmatrix} 8.4110 \\ 8.3939 \\ 8.3911 \\ 7.6162 \\ 7.6162 \\ 7.6163 \\ 7.6022 \\ 7.6022 \\ 7.4527 \\ 7.4527 \\ 7.4527 \\ 7.4528 \\ 7.45216 \\ 7.4121 \\ 7.4121 \\ 7.4121 \\ 7.4121 \\ 7.4123 \\ 6.8048 \\ 6.8048 \\ 6.8033 \\ 6.8210 \\ 6.8033 \\ 6.8210 \\ 6.8233 \\ 6.8210 \\ 6.8233 \\ 7.4121 \\ 7.4121 \\ 7.4121 \\ 7.4121 \\ 7.4121 \\ 7.4121 \\ 7.4226 \\ 7.4238 \\ 6.8233 \\ 6.8233 \\ 8.926 \\ 6.8048 \\ 6.8233 \\ 6.8233 \\ 6.8233 \\ 6.8233 \\ 6.8233 \\ 6.8233 \\ 6.8233 \\ 6.8233 \\ 6.8233 \\ 6.8233 \\ 6.8233 \\ 6.8233 \\ 6.9233 \\ 7.1930 \\ 1.5152 \\ 1.5004 \\ 1.5152 \\ 1.5004 \\ 1.5003 \\$



Figure S49 ¹H NMR of compound **3aw** (500 MHz, CDCl₃) (Contains 10% cis isomer)



Figure S50 ¹³C NMR of compound **3aw** (126 MHz, CDCl₃) (Contains 10% cis isomer)







Figure S52 ¹³C NMR of compound **3ax** (126 MHz, CDCl₃)



Figure S54 ¹³C NMR of compound **3aa-d5** (126 MHz, CDCl₃)



Figure S56¹³C NMR of compound **3ba** (126 MHz, CDCl₃)



Figure S57 ¹H NMR of compound 4aa (500 MHz, CDCl₃)



Figure S58 ¹³C NMR of compound 4aa (126 MHz, CDCl₃)







Figure S60 ¹³C NMR of compound **4ab** (126 MHz, CDCl₃)







Figure S62 ¹³C NMR of compound 4ac (126 MHz, CDCl₃)







Figure S64 ¹³C NMR of compound 4ad (126 MHz, CDCl₃)







Figure S66 ¹³C NMR of compound 4ae (126 MHz, CDCl₃)







Figure S68 ¹³C NMR of compound **4af** (126 MHz, CDCl₃)







Figure S70¹³C NMR of compound 4ag (126 MHz, CDCl₃)







Figure S72 ¹³C NMR of compound 4aia (126 MHz, CDCl₃)







Figure S74¹³C NMR of compound 4aic (126 MHz, CDCl₃)



Figure S76 ¹³C NMR of compound 4aja (126 MHz, CDCl₃)



Figure S78 ¹³C NMR of compound **4ajb** (126 MHz, CDCl₃)







Figure S80¹³C NMR of compound 4ak (126 MHz, CDCl₃)





Figure S82 ¹³C NMR of compound 4alb (126 MHz, CDCl₃)



Figure S84 ¹³C NMR of compound **4am** (126 MHz, CDCl₃)



Figure S85 ¹H NMR of compound **4an** (500 MHz, CDCl₃)



Figure S86¹³C NMR of compound 4an (126 MHz, CDCl₃)



Figure S87 ¹H NMR of compound 4aoa (500 MHz, CDCl₃)



Figure S88 ¹³C NMR of compound 4aoa (126 MHz, CDCl₃)





Figure S90 ¹³C NMR of compound 4aob (126 MHz, CDCl₃)



Figure S91 ¹H NMR of compound **4ap** (500 MHz, DMSO-*d*6)



Figure S92 ¹³C NMR of compound 4ap (126 MHz, DMSO-d6)

8.8252 8.7695 8.7668 8.7550 8.7550 8.6482 8.64855 8.64555 8.64555 8.64555 8.64555 8.64555 8.64555 8.64555 8.64751 8.6487 8.6317 8.6290 8.6317 8.633796 8.3534 8.0517 8.0354 8.03566 8.03566 8.03566 8.03566 8.03566 8.03566 8.03566 8.03566 8.03566 8.035666 8.035666 8.035666 8.00







Figure S94 ¹³C NMR of compound 4aqa (126 MHz, CDCl₃)







Figure S96 ¹³C NMR of compound 4ar (126 MHz, CDCl₃)



Figure S97 ¹H NMR of compound **4as** (500 MHz, CDCl₃)



Figure S98 ¹³C NMR of compound 4ar (126 MHz, CDCl₃)

8.8227 8.8220 8.8200 8.87548 8.875491 8.77491 8.7342 8.7342 8.7342 8.7342 8.7342 8.7342 8.7342 8.7342 8.7342 8.7342 8.2973 8.2073 8.2075 8.2075 8.7073 8.7075 8.7075 8.7075 7.7075 8.7075 7.707



Figure S99 ¹H NMR of compound 4at (500 MHz, CDCl₃)



Figure S100¹³C NMR of compound 4at (126 MHz, CDCl₃)







Figure S102 ¹³C NMR of compound 4au (126 MHz, CDCl₃)



Figure S103 ¹H NMR of compound 4au' (500 MHz, CDCl₃)



Figure S104 ¹³C NMR of compound 4au' (126 MHz, CDCl₃)



Figure S105 ¹H NMR of compound 4ava (500 MHz, CDCl₃)



Figure S106¹³C NMR of compound 4ava (126 MHz, CDCl₃)



Figure S107 ¹H NMR of compound **4avb** (500 MHz, CDCl₃)



Figure S108 ¹³C NMR of compound **4avb** (126 MHz, CDCl₃)



Figure S109 ¹H NMR of compound 4awa (500 MHz, CDCl₃)



200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)

Figure S110 ¹³C NMR of compound 4awa (126 MHz, CDCl₃)



Figure S111 ¹H NMR of compound **4awb** (500 MHz, CDCl₃)



Figure S112 ¹³C NMR of compound 4awb (126 MHz, CDCl₃)



Figure S113 ¹H NMR of compound 4axa (500 MHz, CDCl₃)



Figure S114¹³C NMR of compound 4axa (126 MHz, CDCl₃)



Figure S115 ¹H NMR of compound 4axb (500 MHz, CDCl₃)



Figure S116¹³C NMR of compound **4axb** (126 MHz, CDCl₃)






Figure S118 ¹³C NMR of compound 4ay (126 MHz, CDCl₃)



Figure S119 ¹H NMR of compound 4aa-d4 (500 MHz, CDCl₃)



Figure S120¹³C NMR of compound 4aa-d4 (126 MHz, CDCl₃)

8.6844 8.6698 8.4555 8.45365 8.45365 8.45365 8.45365 8.4378 8.4378 8.4378 8.4378 8.4378 8.4378 8.4378 8.4378 8.4378 8.4378 8.4378 8.2912 8.2912 8.2029 8.1867 8.1089 8.1089 8.1089 8.1089 8.1080 7.6570 <t



4ba











200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)

Figure S123 ¹³C NMR of compound 4ca (126 MHz, CDCl₃)







Figure S125 ¹³C NMR of compound 4cz (126 MHz, CDCl₃)



Figure S126 ¹H NMR of compound **5aa** (500 MHz, DMSO-*d*6)



Figure S127 ¹³C NMR of compound **5aa** (126 MHz, DMSO-d6)

$\begin{array}{c} 11.2604\\ 8.7145\\ 8.7145\\ 8.6979\\ 8.6952\\ 8.6952\\ 8.6985\\ 8.6985\\ 8.6985\\ 8.6963\\ 8.5361\\ 8.5361\\ 8.5361\\ 8.5361\\ 8.5363\\ 8.5363\\ 8.5361\\ 7.9479\\ 7.9351\\ 7.9351\\ 7.9351\\ 7.9351\\ 7.9351\\ 7.9352\\ 7.9351\\ 7.9351\\ 7.9352\\ 7.9351\\ 7.9351\\ 7.9351\\ 7.9351\\ 7.9352\\ 7.9352\\ 7.9351\\ 7.9352$



Figure S128 ¹H NMR of compound **5ad** (500 MHz, DMSO-*d*6)



Figure S129 ¹³C NMR of compound **5ad** (126 MHz, DMSO-*d*6)







Figure S131 ¹³C NMR of compound 6ac (126 MHz, CDCl₃)



Figure S132 ¹H NMR of compound **7ak** (500 MHz, CDCl₃)



Figure S133 ¹³C NMR of compound 7ak (126 MHz, CDCl₃)



Figure S135 ¹³C NMR of compound 8 (126 MHz, CDCl₃)



Figure S136 ¹H NMR of compound 9 (500 MHz, CDCl₃)



Figure S137 ¹³C NMR of compound 9 (126 MHz, CDCl₃)



Figure S138 ¹H NMR of compound **10** (500 MHz, CDCl₃)



Figure S139 ¹³C NMR of compound **10** (126 MHz, CDCl₃)

Part 5. Deuterium-Labelling experiments

KIE determined from two parallel reactions

To get further insight into the mechanism of these Friedel-crafts acylation reactions promoted by Lewis acids. A deuterium-labeling experiment was designed to determine the values of the kinetic isotope effects (KIEs). As shown in **Scheme S11**, two parallel reactions, one with the hydrogenated substrate **3aa** (1.0 equiv.) and the other with the deuterated substrate **3aa-d5** (1.0 equiv.), were conducted separately within 20 min under ice salt bath. Their relative ratio of **4aa** and **4aa-d4** gave a sketchy KIE value of $k_{H/D} = 0.70$, indicating that the C-H bond cleavage process was not the speedlimiting step of the reaction. The reaction rate of hydrogenated reagent **3aa** was lower than that of deuterated substrate **3aa-d5**, which showed that the reaction conforms to the secondary kinetic isotope effect (SKIE).





In consideration of the inapparent values of SKIE, reaction solutions at a series of time (5, 10, 15, 20, 30, 50, 120 min) were carried out to determine NMR yield at each time (shown as **Scheme S12**), to demonstrate a more accurate SKIE value of parallel deuterium-labeling experiment.

Scheme S12. Deuterium-Labelling experiments in various times



The results were shown in Scheme S13. It is obvious that each reaction time, deuterated

substrate **3aa-***d***5** converted much faster than hydrogenated substrate **3aa** (**Scheme S13, I**), and the changes of each species over time roughly satisfied the relationship of logarithm. Thus, we conjectured that the reaction was a first-order reaction, which had a linear relationship between logarithm of reciprocal of species concentration and reaction time. We rearranged the data according to the logarithmic model shown as **Scheme S12, II**. We chose the formation rate of the products **4aa** and **4aa-***d***4** to define the rate of the reactions. From the slope of the two lines, we concluded that the reaction rate of hydrogenated substrate **3aa** (*k*_H) and deuterated substrate **3aa-***d***5** (*k*_D) were determined to be 0.02177 min⁻¹ and 0.06454 min⁻¹, respectively, Hence, we obtained a more accurate SKIE value of $k_{H/D} = 0.3373$. The reason for this phenomenon was that the hybridization mode of isotopic bonded carbon atoms changes from sp² to sp³ when the substrates converted to the transition states (σ -complex), and the energy required for bending vibration was lower for C-D bond. Hence, deuterated substrate **3aa-***d***5** showed the lower activation energy and the faster reaction rate.

Consequently, we identified the significant secondary kinetic isotope effect (SKIE) of the deuterium experiments, which indicated the formation of σ -complex is the speed-limiting step of the reaction, the same with Friedel-Crafts acylation.



Scheme S12. Data obtained from Deuterium-Labelling experiments

One dried Schlenk flask was charged with methyl 5-methoxy-8-phenyl-1-naphthoate **3aa** (20.5 mg, 0.07 mmol), and DCM (4.86 mL) added by pipette gun under ice salt bath. Then 0.14 mL DCM solution of BBr₃ (1M, 0.14 mmol) was quickly added into the Schlenk flask by pipette gun. The reaction mixture was stirred under ice salt bath. Then, take 50 μ L reaction solution at 5, 10, 15, 20, 30, 50, 120 min, the taken solution were immediately quenched with MeOH (50 μ L).

The other dried Schlenk flask was charged with methyl 5-methoxy-8-(phenyl-d5)-1-naphthoate **3aa**-d5 (20.8 mg, 0.07 mmol), and DCM (4.86 mL) added by pipette gun under ice salt bath. Then 0.14 mL DCM solution of BBr₃ (1M, 0.14 mmol) was quickly added into the Schlenk flask by pipette gun. The reaction mixture was stirred under ice salt bath. Then, take 50 µL reaction solution at 5, 10, 15, 20, 30, 50, 120 min, the taken solution were immediately quenched with MeOH (50 µL).

50 μ L internal standard solution (0.158 mol/L DCM solution of 1,3,5-trimethoxybenzene) was added into each mixture, and each combined mixture was detected by NMR with the solvent of CDCl₃.

¹H NMR of crude samples at each moment are shown as follows:



Figure S140 ¹H NMR at 5 min of Reaction I



Figure S141 ¹H NMR at 10 min of Reaction I







Figure S143 ¹H NMR at 20 min of Reaction I



Figure S144 ¹H NMR at 30 min of Reaction I



Figure S145 ¹H NMR at 50 min of Reaction I



Figure S146 ¹H NMR at 120 min of Reaction I



Figure S147 ¹H NMR at 5 min of Reaction II



Figure S148 ¹H NMR at 10 min of Reaction II



Figure S149 ¹H NMR at 15 min of Reaction II



Figure S151 ¹H NMR at 30 min of Reaction II



Figure S153 ¹H NMR at 120 min of Reaction II

Calculate the concentration of each species at 5, 10, 15, 20, 30, 50, 120 min from the crude ¹H NMR. (shown as in **Table S8**)

 Table S8: Concentration of various species at each time and calculation of rate equation of first-order reaction. x represents the concentration of 4aa or 4aa-d4 at each reaction moment

		Reaction I				Reactio	n II	
Reaction time (min)	4aa (mol/L)	3aa (mol/L)	Internal standard (mol/L)	n (1/ (0.014-x)) x = c(4aa)	4aa-d4 (mol/L)	3aa-d5 (mol/L)	Internal standard (mol/L)	ln (1/ (0.014-x) x = c(4aa-d4)
0	0	0.014		4.268698	0	0.014		4.268698
5	0.004012	0.004052	0.158	4.60639	0.004069	0.003296	0.158	4.612096
10	0.007928	0.003171	0.158	5.104026	0.010077	0.002217	0.158	5.540779
15	0.008373	0.002093	0.158	5.180193	0.012173	0	0.158	6.304846
20	0.00917	0.001559	0.158	5.33292	0.013058	0	0.158	6.967347
30	0.007556	0.001058	0.158	5.044636	0.013322	0	0.158	7.296498
50	0.009438	0.001227	0.158	5.390097	0.013888	0	0.158	9.097012
120	0.013356	0	0.158	7.347618	0.013989	0	0.158	11.41762

The concentration of each species was plotted as a function of time. It could be seen intuitively that the reaction had the characteristics of a first-order reaction. The reaction was regarded as the first order reaction, and $\ln(1/(0.014-x))$ was plotted against the reaction time, so the rate constant ($k_{\rm H}$ and $k_{\rm D}$) of the reaction could be obtained from the slope of the curves (**Scheme S12, II**).

 $k_{\rm H} = 0.02177 \text{ min}^{-1}$ $k_{\rm D} = 0.06454 \text{ min}^{-1}$

Part 6. Absorption and fluorescent spectra

Absorption and fluorescence spectra were measured as CHCl₃ solution (1.0×10⁻⁴ mol/L for **4aa**, **4ab**, **4ac**, **4ad**, **4ae**, **4ag**, **4aia**, **4ak**, **4am**, **4an**, **4aoa**, **4aob**, **4awa** and **6ac**).



Figure S154 Absorption and fluorescence spectra of 4aa.



Figure S155 Absorption and fluorescence spectra of 4ab.



Figure S156 Absorption and fluorescence spectra of 4ac.



Figure S157 Absorption and fluorescence spectra of 4ad.



Figure S158 Absorption and fluorescence spectra of 4ae.



Figure S159 Absorption and fluorescence spectra of 4ag.



Figure S160 Absorption and fluorescence spectra of 4aia.



Figure S161 Absorption and fluorescence spectra of 4ak.



Figure S162 Absorption and fluorescence spectra of 4an.



Figure S163 Absorption and fluorescence spectra of 4aob.



Figure S164 Absorption and fluorescence spectra of 6ac.

Compound **5ad** and **4ap** exhibited different characteristic absorption in buffer solutions with various pH values. The buffer solution was composed of aqueous solution of H₃PO₄, H₃BO₃ and HOAc in a certain proportion, and the pH values was calibrated with NaOH under the monitor of pH meter. Fluorescence emission was detected in the range $\lambda = 390-600$ nm upon the excitation at 365 nm in H₂O (1 × 10⁻⁵ mol/L) for compound **5ad**, and in the range $\lambda = 400-680$ nm upon the excitation at the same conditions for compound **4ap**. **5ad** exhibited optimal fluorescence intensity at pH = 5, and exhibited multiple characteristic absorption peaks under alkaline conditions. **4ap** showed optimal fluorescence intensity at pH = 3, but fluorescence was quenched under alkaline conditions.



Figure S165 Fluorescence characteristic absorption changes with pH values of compound **5ad**. (pH = 2-7)



Figure S166 Fluorescence characteristic absorption changes with pH values of compound **4ap**. (pH = 2-7)



Figure S167 Fluorescence characteristic absorption changes with pH values of compound **4ap**. (pH = 7-12)

Part 7. Thermodynamics, proposed mechanism and cartesian coordinates for all optimized species

Species	Free energy	SCF Done	G (DCM)		
BBr ₃	-0.024968	-7746.992166	-7747.017134		
MeBr	0.013576	-2613.905341	-2613.891765		
HBr	-0.013335	-2574.620306	-2574.633641		
B(OH) ₃	0.021534	-252.4670804	-252.4455464		
MeOH	0.028755	-115.6928674	-115.6641124		
B(OH)(OMe) ₂	0.072565	-331.0065581	-330.9339931		
3aa	0.230429	-958.9142639	-958.6838349		
Α	0.254506	-8705.925239	-8705.670733		
В	0.217062	-6092.018533	-6091.801471		
С	0.220807	-6091.991255	-6091.770448		
D	0.221187	-6092.033759	-6091.812572		
4aa	0.209258	-843.2243295	-843.0150715		
Ε	0.253523	-8705.920772	-8705.667249		
F	0.216969	-6092.029732	-6091.812763		
G	0.230815	-919.6408697	-919.4100547		
3 aa'	0.181165	-727.9849221	-727.8037571		
A'	0.179158	-8474.996784	-8474.817626		
В,	0.142378	-5861.098139	-5860.955761		
Н	0.156625	-688.7174212	-688.5607962		
Е'	0.178697	-8474.998469	-8474.819772		
F'	0.141684	-5861.107409	-5860.965725		
G'	0.153807	-688.713648	-688.559841		

 Table S9 Free energy for all optimized species.

Scheme S14. Proposed reaction mechanism via density functional calculations. Pathway I: Proposed mechanism of BBr₃-promoted annulation of **3aa**. Pathway II: Proposed mechanism of BBr₃-catalyzed ether cleavage of **3aa**. Pathway III: Proposed mechanism of BBr₃-catalyzed ester cleavage of **3aa**'. Pathway IV: Proposed mechanism of BBr₃-catalyzed ether cleavage of **3aa**'. Gibbs energies are in kcal/mol.

Pathway I



Pathway II



Pathway III



Pathway IV



Our computations showed that initial formation of the BBr₃–**3aa** adducts A and E were thermodynamically unfavorable (19.0 kcal/mol vs. 21.1 kcal/mol) but still easily accessible under the experimental conditions. Intramolecular elimination of methyl bromide was happened for both of complex A and E to form neutral intermediate B and F (-14.1 kcal/mol vs. -23.4 kcal/mol). Subsequently, an intramolecular Friedel-Crafts acylation reaction occurred for intermediate **B** to form σ -complex **C**, which was the speed-limiting step of **Pathway I** ($\Delta G^{\ddagger} = 19.5$ kcal/mol). The activation free energies for Pathway I were always very low (<20 kcal/mol), which interpreted the reaction rate of Pathway I was very fast, usually completing the reaction within 0.5 h. With the energy barrier overcome, an intramolecular proton exchange took place and benzene group aromatization accomplished to form intermediate **D** ($\Delta G = -26.4$ kcal/mol). Finally, the reaction was quenched by methanol, B(OH)₃ and two molecules of MeBr were eliminated for intermediate **D** to obtain the desired product 4aa ($\Delta G = -64.8$ kcal/mol), while B(OMe)3 and two molecules of HBr were eliminated for intermediate **F** to obtain the ether cleavage product **G** ($\Delta G = -33.6$ kcal/mol). Thus, the computations results revealed that the production of 4aa was both thermodynamic and dynamically controlled, explaining this reaction could access to 4aa with high yield rather than ether cleavage product G. And only 5aa, the ether cleavage products of 4aa, could be obtained when the reaction time was extended. And for the ether and ester cleavage reactions of 3aa' (Pathway III & IV), the computational calculations indicated that the produce of G' instead of H was still thermodynamically controlled. The formation of the BBr₃-3aa' adducts A' and E' were only slightly uphill in Gibbs energy (2.0 kcal/mol vs. 0.7 kcal/mol). While eliminating a portion of MeBr, intermediate F' had a more drastic energy reduction compared to B' (-23.7 kcal/mol vs. -18.8 kcal/mol). It resulted in a high selectivity of the reaction towards G' instead of H.

	BBı	3		Н	0.879006	0.000000	1.771185
В	0.000000	0.000000	0.000000	0	-1.221576	-0.000397	-0.610891
Br	0.000000	0.000000	1.902480	0	1.129665	-0.000275	-0.798561
Br	1.647596	0.000000	-0.951240	Н	-1.116937	-0.000619	-1.572311
Br	-1.647596	0.000000	-0.951240	Н	1.967112	-0.000247	-0.318067
	MeH	Br			MeOH	[
С	0.000000	0.000000	0.000000	0	0.000000	0.000000	0.000000
Н	0.000000	0.000000	1.088577	С	0.000000	0.000000	1.418491
Н	1.015166	0.000000	-0.392983	Н	1.047372	0.000000	1.732495
Н	-0.573529	-0.837632	-0.392983	Н	-0.484021	0.893251	1.843587
Br	-0.872909	1.655605	-0.598118	Н	-0.484025	-0.893254	1.843581
	HB	r		Н	-0.923067	0.000355	-0.294046
Н	0.000000	0.000000	0.000000		B(OH)(ON	Ale)2	
Br	0.000000	0.000000	1.437830	В	0.000000	0.000000	0.000000
	B(OI	H)3		0	0.000000	0.000000	1.373818
В	0.000000	0.000000	0.000000	Н	0.886186	0.000000	1.756516
0	0.000000	0.000000	1.373506	0	-1.218740	-0.000021	-0.607026

 Table S10 Cartesian coordinates (in Å) for all optimized species.

0	1.137222	-0.000088	-0.780181	Н	-2.595782	-2.141513	4.192397
С	-1.322573	-0.000178	-2.022947	Н	-3.032726	-0.409233	4.028089
Н	-2.387405	-0.001055	-2.271691	С	1.348884	0.195864	3.544273
Н	-0.853089	0.888823	-2.460648	С	0.245964	0.680583	4.421995
Н	-0.851609	-0.888413	-2.460600		Α		
С	2.431847	0.000001	-0.209948	С	0.000000	0.000000	0.000000
Н	3.159585	0.000986	-1.025820	С	0.000000	0.000000	1.393886
Н	2.607580	0.894092	0.405796	С	1.236326	0.000000	2.141231
Н	2.608278	-0.894906	0.404377	С	2.430326	-0.240781	1.379781
	3 aa			С	2.379837	-0.310466	-0.036236
С	0.000000	0.000000	0.000000	С	1.196899	-0.139015	-0.719119
С	0.000000	0.000000	1.385356	Н	-0.945854	0.064321	-0.529675
С	1.234837	0.000000	2.120157	С	3.689204	-0.383656	2.050203
С	2.437674	-0.183359	1.352507	Н	3.306130	-0.481132	-0.572325
С	2.389989	-0.228722	-0.064200	Н	1.174397	-0.157512	-1.803894
С	1.195941	-0.098598	-0.733645	С	3.760678	-0.241376	3.420582
Н	-0.955277	0.036683	-0.513983	С	2.603665	0.119335	4.134617
С	3.697616	-0.318442	2.023347	Н	4.699768	-0.341788	3.951117
Н	3.319071	-0.358173	-0.606543	Н	2.704542	0.338383	5.193535
Н	1.167162	-0.110047	-1.819328	0	4.750240	-0.645613	1.242865
С	3.764785	-0.240745	3.397088	С	6.037486	-0.768900	1.834564
С	2.594398	0.044288	4.128754	Н	6.725252	-0.964443	1.010725
Н	4.705885	-0.340605	3.924603	Н	6.330713	0.156635	2.345473
Н	2.686810	0.204507	5.199076	Н	6.070852	-1.604736	2.544309
0	4.771457	-0.517517	1.207051	С	-0.448282	1.981886	3.970347
С	6.053431	-0.644019	1.802132	С	0.008097	0.332504	5.669952
Н	6.752804	-0.789746	0.977070	С	-1.408076	2.566776	4.796971
Н	6.328118	0.261621	2.358272	Н	-0.241073	2.420791	2.998288
Н	6.098984	-1.509682	2.475518	С	-0.944139	0.924417	6.500862
С	-0.477812	1.841411	4.102476	Н	0.548708	-0.547687	6.008131
С	-0.021415	0.048251	5.648139	С	-1.659915	2.041639	6.065923
С	-1.442694	2.345756	4.975659	Н	-1.952136	3.440985	4.450556
Н	-0.274607	2.360385	3.170335	Н	-1.130104	0.507885	7.487518
С	-0.981043	0.554965	6.523268	Н	-2.405335	2.499871	6.709668
Н	0.520111	-0.858516	5.903849	С	-1.330074	-0.211130	1.974682
С	-1.697805	1.706906	6.190223	0	-2.341202	0.331244	1.424989
Н	-1.988713	3.246200	4.707273	0	-1.385998	-0.995276	3.006331
Н	-1.173222	0.046241	7.464675	С	-2.608094	-1.214893	3.771970
Н	-2.446419	2.103009	6.871192	Н	-3.041061	-2.153683	3.430642
С	-1.369643	-0.123798	1.983493	Н	-2.275300	-1.266273	4.807090
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С	-2.722472	-1.311895	3.496419	С	0.270479	0.848785	4.389938
Н	-3.467256	-1.556863	2.734534	В	-3.659245	-0.122305	0.789302

Br	-3.650139	-2.144092	0.668769	С	1.227594	0.000000	2.116646
Br	-3.658525	0.673995	-1.057997	С	2.448044	0.072856	1.376369
Br	-5.175178	0.573148	1.904473	С	2.410267	0.082944	-0.039511
	В	1		С	1.208065	0.029910	-0.716981
С	0.000000	0.000000	0.000000	Н	-0.957588	-0.000432	-0.511272
С	0.000000	0.000000	1.387005	С	3.690405	0.130109	2.090210
С	1.233646	0.000000	2.126511	Н	3.347779	0.130510	-0.581814
С	2.434535	-0.203235	1.364167	Н	1.194113	0.031891	-1.802964
С	2.388427	-0.250732	-0.052924	С	3.696664	0.105504	3.469884
С	1.198642	-0.106464	-0.728033	С	2.481927	-0.015940	4.181218
Н	-0.953303	0.028853	-0.518055	Н	4.624462	0.155231	4.026677
С	3.688866	-0.350159	2.042193	Н	2.542586	-0.068344	5.261055
Н	3.317243	-0.392758	-0.592783	0	4.800548	0.210154	1.311436
Н	1.173721	-0.119155	-1.813470	С	6.072557	0.242217	1.945428
С	3.747893	-0.260343	3.416597	Н	6.805788	0.288302	1.138869
С	2.579578	0.053602	4.139112	Н	6.176845	1.127574	2.585124
Н	4.684445	-0.371372	3.949871	Н	6.241487	-0.661797	2.543548
Н	2.667254	0.224699	5.208137	С	-0.073462	-0.079326	5.759460
0	4.762477	-0.571275	1.233561	С	-2.500245	0.375625	4.326924
С	6.040586	-0.715177	1.835646	С	-1.236192	0.181256	6.385881
Н	6.740632	-0.876680	1.014340	Н	0.834683	-0.210299	6.332286
Н	6.326516	0.189249	2.387586	С	-2.502055	0.282170	5.665107
Н	6.068135	-1.578031	2.513228	Н	-3.406971	0.451495	3.736539
С	-0.453117	1.913428	4.034765	Н	-1.243835	0.297457	7.467293
С	-0.091738	0.125622	5.614549	Н	-3.430359	0.284194	6.229690
С	-1.437465	2.448470	4.866274	С	1.259738	-0.080985	3.546832
Н	-0.200850	2.418411	3.106465	С	-0.051075	-0.336974	4.271273
С	-1.073959	0.661680	6.445520	С	-1.296032	0.102175	2.103831
Н	0.407156	-0.798205	5.892319	С	-1.191830	0.443364	3.591981
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Н	-1.954140	3.357315	4.569865	0	-2.374092	0.026726	1.537787
Н	-1.318883	0.162112	7.379053	0	-0.420372	-1.771805	4.007829
Н	-2.519728	2.240818	6.721158	В	0.083948	-2.908527	4.467070
С	-1.359416	-0.159459	1.973803	Br	-0.690357	-4.552726	3.823681
0	-2.360967	0.396246	1.612295	Br	1.545189	-3.052658	5.737200
0	-1.371443	-1.154777	2.954697		D		
С	1.339832	0.218208	3.545037	С	0.000000	0.000000	0.000000
С	0.231293	0.739910	4.393486	С	0.000000	0.000000	1.382968
В	-2.370483	-1.981951	3.333078	С	1.217380	0.000000	2.111579
Br	-3.953324	-2.300570	2.307159	С	2.442164	-0.010004	1.370370
Br	-2.097159	-2.945056	4.971868	С	2.411446	-0.022687	-0.044444
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С	0.000000	0.000000	0.000000	Н	-0.947174	0.016585	-0.529455
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Н	3.350760	-0.032495	-0.585023	0	4.808502	-0.000105	1.302412
Н	1.190465	-0.024218	-1.804516	С	6.078824	0.000725	1.939220
С	3.690565	0.021596	3.462075	Н	6.815387	0.001607	1.134279
С	2.473527	0.025561	4.172562	Н	6.213176	0.895969	2.559210
Н	4.619809	0.033090	4.019026	Н	6.214670	-0.894747	2.558572
Н	2.537586	0.039206	5.254925	С	-1.257918	0.000218	3.583875
0	4.800978	-0.011445	1.303644	С	-0.086067	0.000734	5.694878
С	6.069338	-0.009938	1.942396	С	-2.479018	0.000519	4.275796
Н	6.807860	-0.026548	1.139294	С	-1.300321	0.001185	6.369573
Н	6.209951	0.893488	2.549425	Н	0.827977	0.000913	6.278862
Н	6.197972	-0.896686	2.575986	С	-2.509255	0.001224	5.661985
С	-1.263517	-0.037688	3.610498	Н	-3.389716	0.000803	3.685847
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С	-1.277589	-0.100613	6.399936	С	1.245226	0.000051	3.545477
Н	0.846050	-0.038545	6.274454	С	-0.029114	0.000314	4.286807
С	-2.490136	-0.134109	5.706425	С	-1.302529	-0.000125	2.100482
Н	-3.409138	-0.157627	3.767215	0	-2.370041	-0.000259	1.486678
Н	-1.267740	-0.125125	7.486201		Ε		
Н	-3.433683	-0.190532	6.241193	С	0.000000	0.000000	0.000000
С	1.238763	0.009690	3.546991	С	0.000000	0.000000	1.402707
С	-0.033075	-0.016065	4.296168	С	1.198587	0.000000	2.113527
С	-1.326779	0.084430	2.100491	С	2.418803	-0.009809	1.434072
0	-1.907378	1.296567	1.708664	С	2.430741	-0.020388	0.038152
0	-2.250110	-0.952219	1.580916	С	1.230940	-0.015598	-0.674759
В	-2.133948	-2.279328	1.620748	Н	-0.947016	0.027850	1.934149
Br	-0.642407	-3.219837	2.397407	Н	1.179731	0.013154	3.199963
Br	-3.569650	-3.310894	0.849741	Н	3.353070	-0.013965	1.989013
Н	-2.702167	1.437837	2.251354	Н	3.374652	-0.044679	-0.500013
	4a a	a		Н	1.247907	-0.041439	-1.760558
С	0.000000	0.000000	0.000000	С	-1.278329	-0.080594	-0.762123
С	0.000000	0.000000	1.388079	С	-1.629689	0.831210	-1.820489
С	1.226517	0.000000	2.112513	С	-2.102789	-1.164849	-0.498566
С	2.449229	-0.000073	1.370372	С	-0.923297	2.044745	-2.123806
С	2.410831	-0.000121	-0.044101	С	-2.745645	0.506139	-2.667077
С	1.204834	-0.000097	-0.719162	С	-3.259483	-1.434532	-1.256103
Н	-0.959894	-0.000037	-0.506697	Н	-1.819548	-1.858062	0.286939
С	3.693883	-0.000137	2.079920	С	-1.211030	2.753342	-3.276669
Н	3.348286	-0.000144	-0.588718	С	-3.027508	1.270248	-3.832003
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С	3.698831	-0.000285	3.461976	Н	-3.878788	-2.303752	-1.061582
С	2.482631	-0.000190	4.172074	С	-2.247690	2.355217	-4.146895
Н	4.628505	-0.000613	4.018338	Н	-0.646836	3.654826	-3.491602
Н	2.544789	-0.000370	5.254916	Н	-3.842062	0.962284	-4.479073
Н	-2.442831	2.925684	-5.049919	С	-0.039567	2.708984	-1.171931
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0	-4.701230	-0.850631	-3.106135	0	-0.331324	2.929748	-0.016819
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С	2.011370	3.882943	-0.857066	Н	1.461058	4.765671	-0.474797
Н	2.345638	3.243488	-0.036165	Н	2.812431	4.199197	-1.514025
Н	1.510595	4.763424	-0.446398	Ο	1.098580	3.151173	-1.754663
Н	2.853039	4.175788	-1.485382	Ο	-4.576399	-1.001105	-3.203095
0	1.124400	3.151372	-1.722119	В	-5.889759	-1.098398	-2.942978
С	-5.946510	-0.371212	-2.486409	Br	-7.028165	-1.616810	-4.395143
Н	-6.691720	-0.374967	-3.278633	Br	-6.650413	-0.728226	-1.217277
Н	-5.748755	0.638642	-2.129541		G	r	
Н	-6.220834	-1.046111	-1.676176	С	0.000000	0.000000	0.000000
В	-4.792217	-2.039272	-4.216533	С	0.000000	0.000000	1.385145
Br	-2.942033	-2.448402	-4.767479	С	1.235393	0.000000	2.119828
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Br	-5.874326	-1.222079	-5.688940	С	2.389291	-0.232980	-0.069247
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С	0.000000	0.000000	0.000000	Н	-0.955768	0.036699	-0.513063
С	0.000000	0.000000	1.403006	С	3.690123	-0.320508	2.017120
С	1.197484	0.000000	2.115850	Н	3.318466	-0.365160	-0.611662
С	2.419007	-0.005502	1.438805	Н	1.163723	-0.111214	-1.822183
С	2.432358	-0.012606	0.042829	С	3.762585	-0.241151	3.388986
С	1.233309	-0.011605	-0.671398	С	2.599997	0.046306	4.127659
Н	-0.947709	0.027184	1.933195	Н	4.718818	-0.343919	3.898289
Н	1.176789	0.011233	3.202379	Н	2.694648	0.207357	5.197458
Н	3.352679	-0.008204	1.994928	0	4.786204	-0.523560	1.225290
Н	3.377212	-0.032128	-0.494232	С	-0.477635	1.840063	4.100715
Н	1.252189	-0.035263	-1.757328	С	-0.010757	0.053876	5.651176
С	-1.277724	-0.088494	-0.762072	С	-1.442007	2.343955	4.974782
С	-1.628109	0.795871	-1.841733	Н	-0.279002	2.356282	3.166038
С	-2.110562	-1.160035	-0.481029	С	-0.969603	0.560283	6.527209
С	-0.933406	2.013483	-2.155307	Н	0.534738	-0.850031	5.908958
С	-2.735501	0.445176	-2.690747	С	-1.691546	1.708431	6.192225
С	-3.256155	-1.452627	-1.245555	Н	-1.991753	3.241640	4.704801
Н	-1.839791	-1.832559	0.327123	Н	-1.156975	0.054225	7.471019
С	-1.222402	2.710866	-3.315107	Н	-2.439570	2.104191	6.874004
С	-3.021580	1.205924	-3.855601	С	-1.368828	-0.126851	1.984227
С	-3.535694	-0.675838	-2.339871	0	-2.341441	0.498597	1.612198
Н	-3.879333	-2.306018	-1.002457	0	-1.425805	-1.116001	2.900033
С	-2.255259	2.298052	-4.181515	С	-2.714752	-1.314553	3.503472
Н	-0.667936	3.617650	-3.533363	Н	-3.453160	-1.589844	2.745604
Н	-3.847193	0.899875	-4.488165	Н	-2.577851	-2.124827	4.219913
Н	-2.464189	2.867415	-5.082381	Н	-3.041028	-0.403964	4.011318

С	1.352328	0.197437	3.542676	Н	5.572780	-0.574566	1.790176
С	0.250920	0.682810	4.422001				
	3 a	a'		Н	0.664313	3.738967	-0.291039
С	0.000000	0.000000	0.000000	Н	4.719660	2.324622	-0.304473
С	0.000000	0.000000	1.442477	Н	3.091345	4.192072	-0.447289
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С	-1.174787	0.168651	2.249689	С	-0.617603	1.416460	0.029093
С	1.245108	-0.198629	2.143620	0	-1.167809	0.342874	0.175222
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С	2.407329	-0.211710	1.345698	0	-1.397522	2.803354	-0.095279
Н	3.380528	-0.101720	-0.564349	С	6.477427	-0.936034	-0.008608
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