Brønsted Acid-Catalyzed Cationic Cyclizations in Fluoroalcohols toward Facile Syntheses of Polycyclic Aromatic Hydrocarbons

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Doctoral Program in Chemistry

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CHAPTER 1

General Introduction

1.1. Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are comprised of poly-fused aromatic rings and have subclasses such as linear-shaped acenes, zigzag-shaped phenacenes, and helical-shaped helicenes (Figure 1).[1] Generally, PAHs often exhibit semi-conducting properties owing to narrow HOMO−LUMO gaps derived from their extended π-conjugated systems. Therefore, PAHs have been widely studied, directed toward applications to electronic devices, such as organic field-effect transistors (OFETs),[2] organic light-emitting diodes (OLEDs),[3] and organic photovoltaic cells (OPVs).[4]

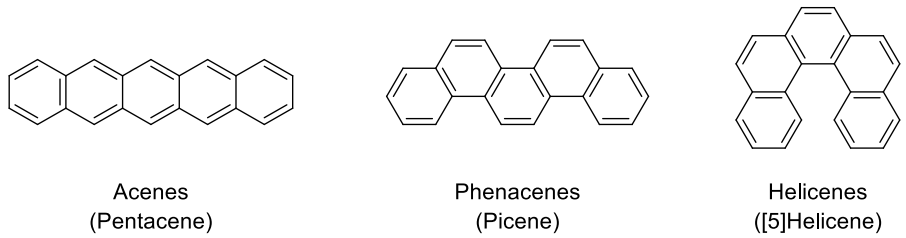
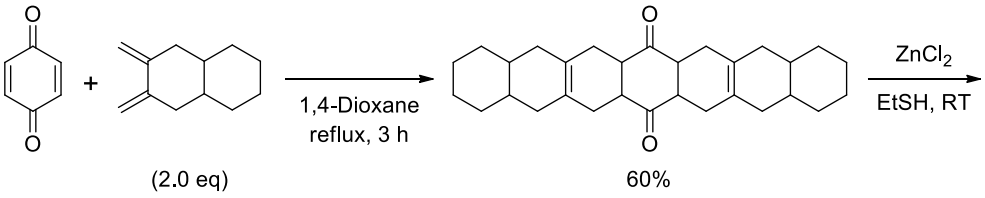
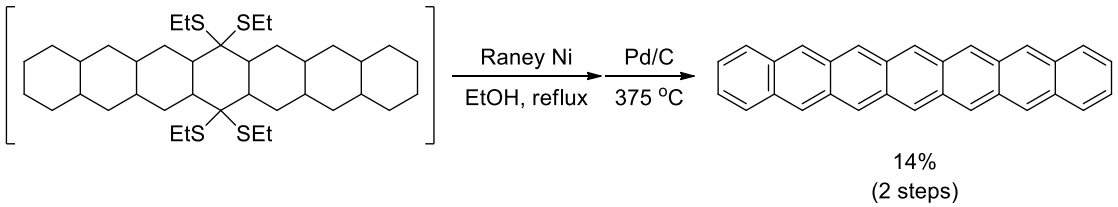


Figure 1. Subclasses of polycyclic aromatic hydrocarbons.

In the past century, PAHs were synthesized by several methods. For example, PAHs are generally synthesized by Diels−Alder reaction (eqs 1, 2),[5] aldol condensation (eq 3),[6] photochemical oxidative cyclization (Mallory reaction, eq 4),[7] and intramolecular McMurry coupling (eq 5).[8] Then, rare metal-catalyzed reactions for PAH synthesis have been recently reported (eqs 6, 7).[9] However, these synthetic methods for PAHs still have several drawbacks: (i) high dilution conditions, (ii) excessive reagents, and/or (iii) expensive metal catalysts are required. In addition, controlling regioselectivities in cyclization for PAH synthesis has been troublesome.

Therefore, the development of more facile and selective methods for the synthesis of PAHs by using more inexpensive reagents is highly desired for large-scale synthesis directed toward applied research of PAHs.





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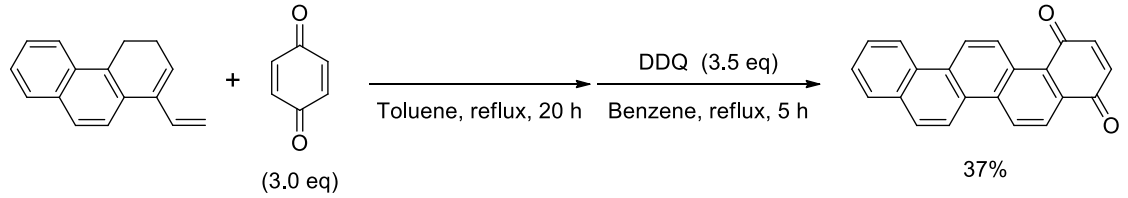

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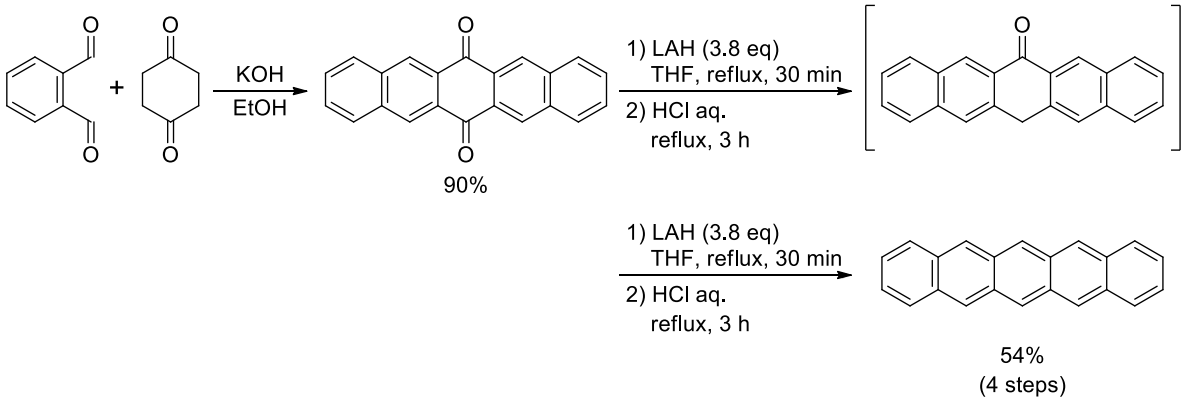

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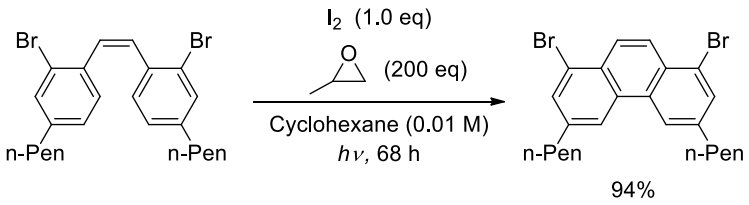

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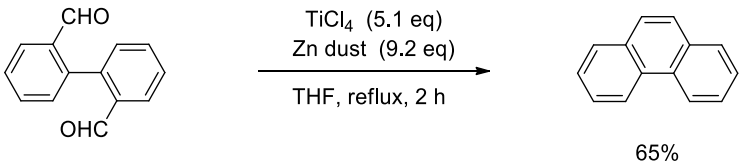

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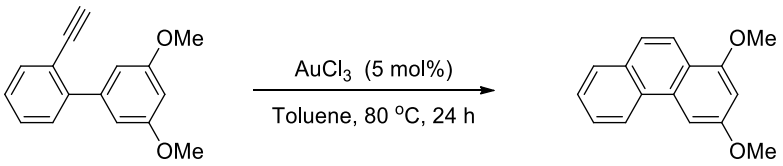

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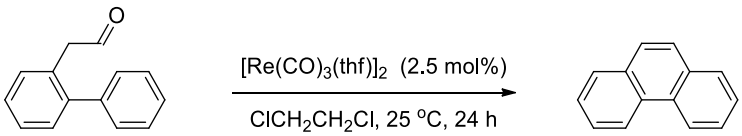

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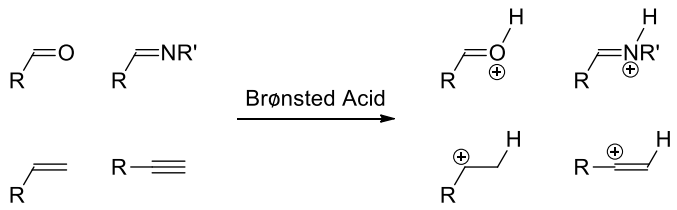
1.2. Brønsted Acid-Catalyzed Reaction

Brønsted acids serve as strong proton donors. Compared to Lewis acids such as $AlCl_3$, $SnCl_4$, $TiCl_4$, $BF_3{\cdot}Et_2O$, and Me_3SiOTf, Brønsted acids are more usable because of their stability toward dioxygen and water. In terms of reactivity, for example, Brønsted acids enable protonation of carbonyl compounds, imines, alkenes, and alkynes, leading to the generation of the corresponding cations, such as oxonium ions, iminium ions, alkyl cations, and vinyl cations, respectively (Scheme 1).[10] These cationic intermediates generated by Brønsted acids in situ are available for reactions with nucleophilic partners.

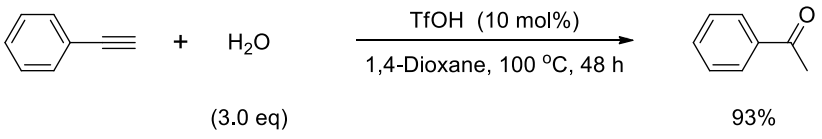


Scheme 1. Protonation of various organic molecules.

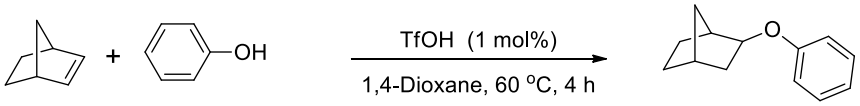
Table 1. pK_a values of Brønsted acids.

	CH_3COOH	CF_3COOH	H_2SO_4	HCl	TfOH	Tf_2NH
pK_a value in H_2O (AcOH)	4.76	–0.25	–3.0	–8.0	–14 (7.8)	(4.2)

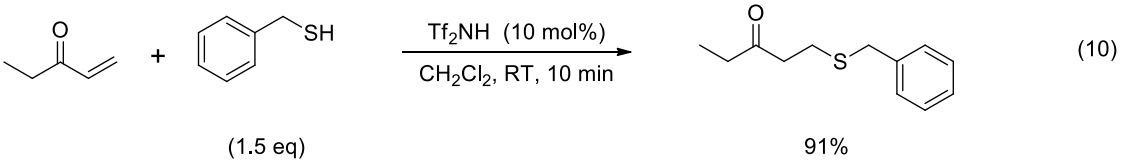
Remarkable progress has been achieved in chemistry of Brønsted acid-catalyzed reactions via cationic intermediates since stronger Brønsted acids, such as trifluoromethansulfonic acid (TfOH) and bis(trifluoromethanesulfonyl)imide (Tf_2NH), were developed (Table 1).[10] Strong Brønsted acid-catalyzed addition of heteroatom nucleophiles to cationic intermediates has been widely developed since 2000. Kawakami *et al*. developed TfOH-catalyzed hydration of alkynes via protonation of alkynes (eq 8).[11a] In addition, intermolecular nucleophilic addition of alcohols to carbocations generated in situ by Brønsted acid catalyst was smoothly proceeded (eq 9).[11b] As for C–S bond formation, Spencer *et al.* reported Tf_2NH-catalyzed Michael addition of thiols (eq 10).[11c] It is noted that this reaction was completed within 10 min, which proved that Brønsted acids serve as powerful mediators. Hartwig *et al*. achieved TfOH-catalyzed intramolecular hydroamination of sulfonylamides toward the synthesis of pyrrolidines and piperidines (eq 11).[11d] As shown above, strong Brønsted acids effectively catalyzed C–O, C–S, and C–N bond formations.



(3.0 eq) 93% (8)



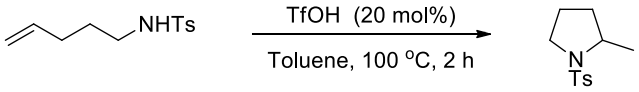
(1.5 eq) 94% (9)



(1.5 eq)

91%

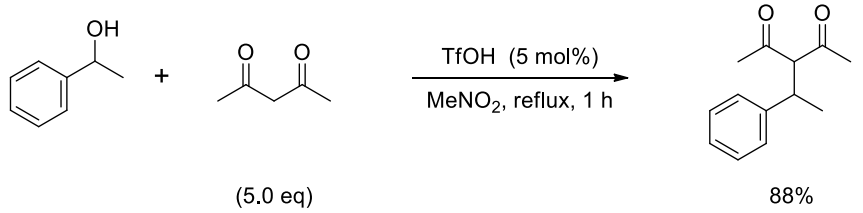
(10)



95%

(11)

Furthermore, Brønsted acid-catalyzed cationic reactions involving C–C bond formation have been developed recently. The key to success in such reactions was the choice of nucleophilic partners that have substantial nucleophilicity. For example, Sanz *et al*. reported Brønsted acid-catalyzed benzylation of 1,3-dicarbonyl derivatives (eq 12).[12a] In this reaction, using 1,3-dicarbonyl compounds as nucleophilic partners successfully allowed C–C bond formation. Yamamoto *et al*. developed Tf_2NH-catalyzed Mukaiyama cross-aldol reaction of aldehydes with tris(trimethylsilyl)silyl enol ethers (eq 13).[12b] Furthermore, Yamamoto *et al*. achieved Brønsted acid-catalyzed Sakurai–Hosomi allylation of carbonyl compounds with simple allylsilane in high yields (eq 14).[12c] As illustrated in eqs 13 and 14, silylated nucleophiles possessing substantial nucleophilicity enable Brønsted acid-catalyzed C–C bond formations. In contrast, Brønsted acid-catalyzed carbocylizations with weak nucleophilic moieties such as a benzene ring were rarely achieved to date. Kozmin et al. reported the first Brønsted acid-catalyzed carbocyclization of silyl ynol ethers with arene and alkene moieties to afford tetralone and cyclohexenone derivatives (eq 15).[12d] In a similar manner, Hsung *et al*. reported Brønsted acid-catalyzed ynamide–arene carbocyclization via keteniminium intermedates (eq 16).[12e]



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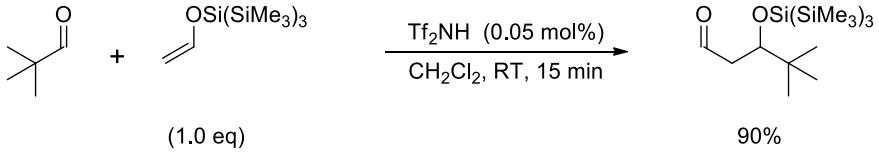

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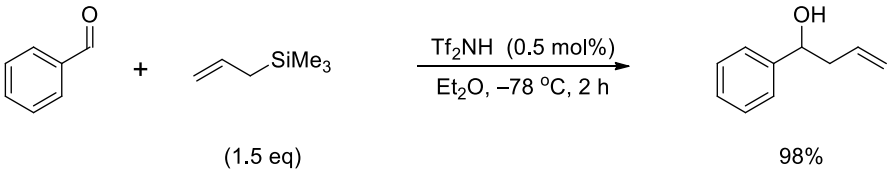

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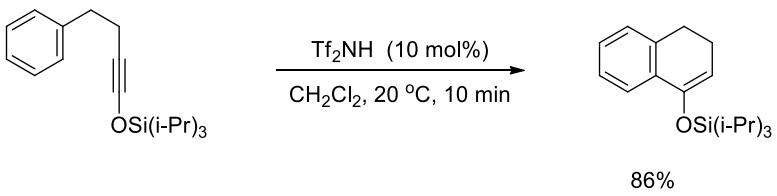

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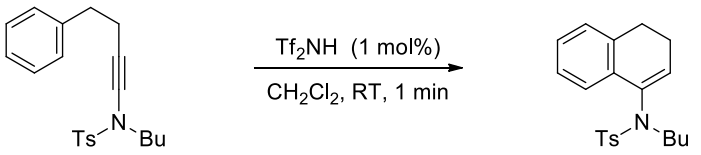

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As described in this section, Brønsted acid-catalyzed reactions require careful choice of nucleophilicities of nucleophiles. Especially, carbocyclization involving addition of aromatic rings is still a challenging topic. Since the carbocyclization has potential to provide PAHs, development of Brønsted acid-catalyzed carbocyclization is seriously desired.

1.3. Fluorinated Alcohol

Fluorinated alcohols such as 1,1,1,3,3,3-hexafluoropeopan-2-ol (HFIP) and 2,2,2-trifluoroethanol (TFE) possess strong ionizing power derived from their high polarity.[13] Moreover, the electron-withdrawing inductive effect and the steric hindrance derived from fluorine substituents significantly weaken nucleophilicity in comparison with fluorine-free alcohols (Figure 2). Thus, the combination with high ionizing power and low nucleophilicity results in a powerful cation-stabilizing effect. This effect strongly promotes protonation, leading to generation of cationic intermediates, and stabilizes the formed cationic intermediates without nucleophilic attack by fluorinated alcohols themselves.

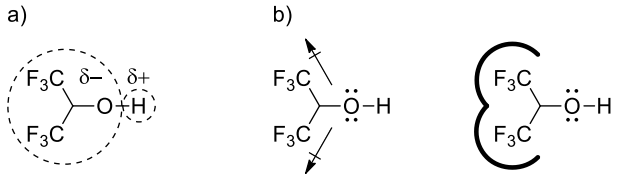


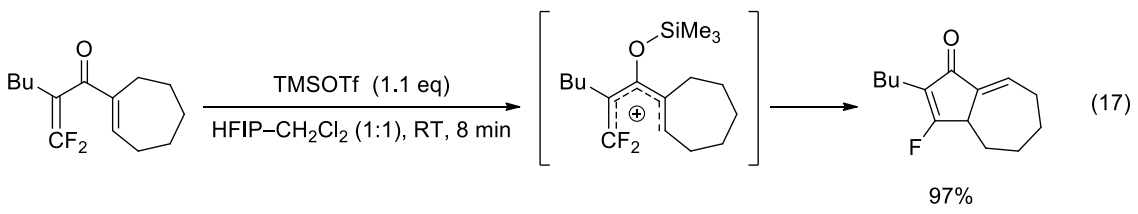
Figure 2. Properties of HFIP, (a) high ionizing power, (b) low nucleophilicity.

Fujio *et al*. reported the experimental estimation of ionizing powers and nucleophilicities of several solvents using solvolysis of 2-adamantyl tosylate and benzyl tosylate, respectively. (Table 2).[14] As described in Table 2, fluorinated alcohols exhibited higher ionizing powers compared to fluorine-free alcohols such as *i*-PrOH and EtOH. Although water shows high ionizing power (Y_{OTs} = 4.1), its nucleophilicity cannot be ignored (N_{OTs} = −0.44). Therefore, water would attack the cationic intermediates to inhibit their reactions with other nucleophilies. In contrast, fluorinated alcohols such as TFE and HFIP possess high ionizing power (Y_{OTs} = 1.80, 3.61) and low nucleophilicity (N_{OTs} = −3.0, −4.27). Particularly reflecting this trend, HFIP would acts as an effective solvent in organic reactions via cationic intermediates.

Table 2. Ionizing power and nucleophilicity of alcoholic solvents.

	i-PrOH	EtOH	80% EtOH/H_2O	TFE	97w% HFIP/H_2O	H_2O
Ionizing Power (Y_{OTs})	–2.23	–1.75	0.0	1.80	3.61	4.1
Nucleophilicty (N_{OTs})	0.12	0.0	0.0	–3.0	–4.27	–0.44

Our laboratory has been developing acid-catalyzed or -mediated cationic cyclizations by combining the α-carbocation stabilizing effect of fluorine substituents and the cation-stabilizing effect of HFIP solvent. We have first reported application of HFIP as solvent to synthetic reactions involving C–C bond formation via carbocations in 1995.[15a] In the Nazarov cyclization, HFIP solvent drastically accelerated the cyclization and enabled the fluorine-directed reaction (eq 17). In the presence of magic acid ($FSO_3H{\cdot}SbF_5$), protonation of 1,1-difluoro-1-alkenes bearing phenethyl group readily proceeded in HFIP to generate the carbocation intermediates, which stabilized by HFIP and the fluorine substituents. The cationic species thus formed induced tandem Friedel–Crafts cyclization and subsequent HF elimination to afford helical carbocyclic compounds (eq 18).[16b] In other methods for activating 1,1-difluoro-1-alkenes, cationic palladium(II)- or silver(I)-catalyzed intramolecular cationic cyclizations have been also achieved in HFIP solvent, leading to the synthesis of pinpoint-fluorinated phenacenes or indoles, respectively (eq 19, 20).[17b,18] Since HFIP solvent was essential to these reactions, HFIP serves as a powerful solvent in organic reactions via cationic intermediates generated by protonation or metalation.



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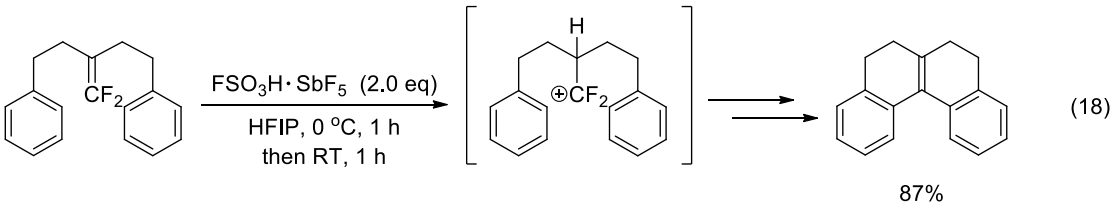

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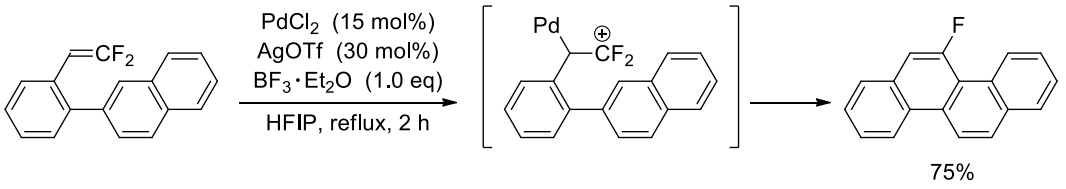

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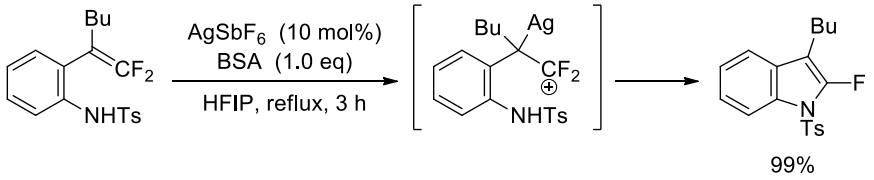

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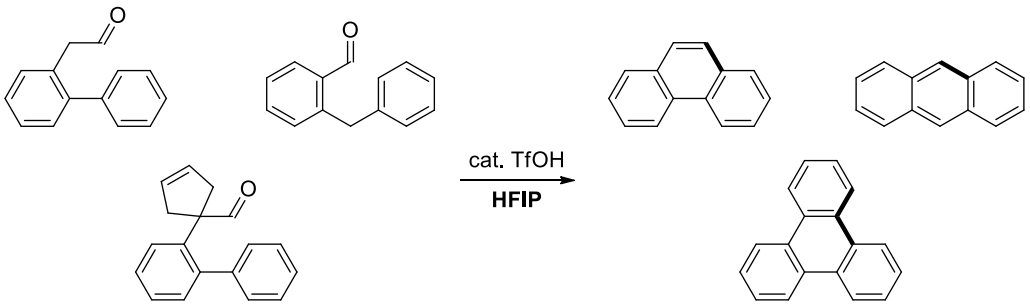
1.4. Survey of This Thesis

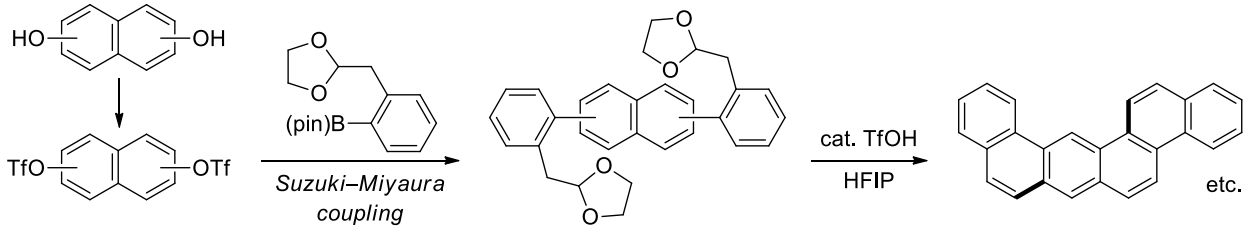
As mentioned above, HFIP exhibits promising potential in acid-catalyzed reactions via cationic intermediates. Considering such properties of HFIP throughout this thesis, I challenged to develop Brønsted acid-catalyzed intramolecular cationic cyclizations for facile synthesis of PAHs in order to provide practical mass-synthesis in the field of organic electronic devices.

Chapter 2 described Brønsted acid-catalyzed dehydrative cycloaromatization (Bradsher reaction). In this chapter, I archived facile synthesis of phenacenes, acenes, and triphenylenes from carbonyl compounds and their analogues in high yields (Scheme 2). Since the preparation of precursors for Bradsher reaction such as (biaryl-2-yl)acetaldehydes has been troublesome in literatures, I also achieved an efficient and rapid synthesis of (biaryl-2-yl)acetaldehydes via Suzuki–Miyaura coupling with 2-(2-bromophenyl)acetaldehyde, prepared by hydrolysis from vinyl ether in two steps.



Scheme 2. TfOH-catalyzed synthesis of phenacenes, acenes, and triphenylenes.

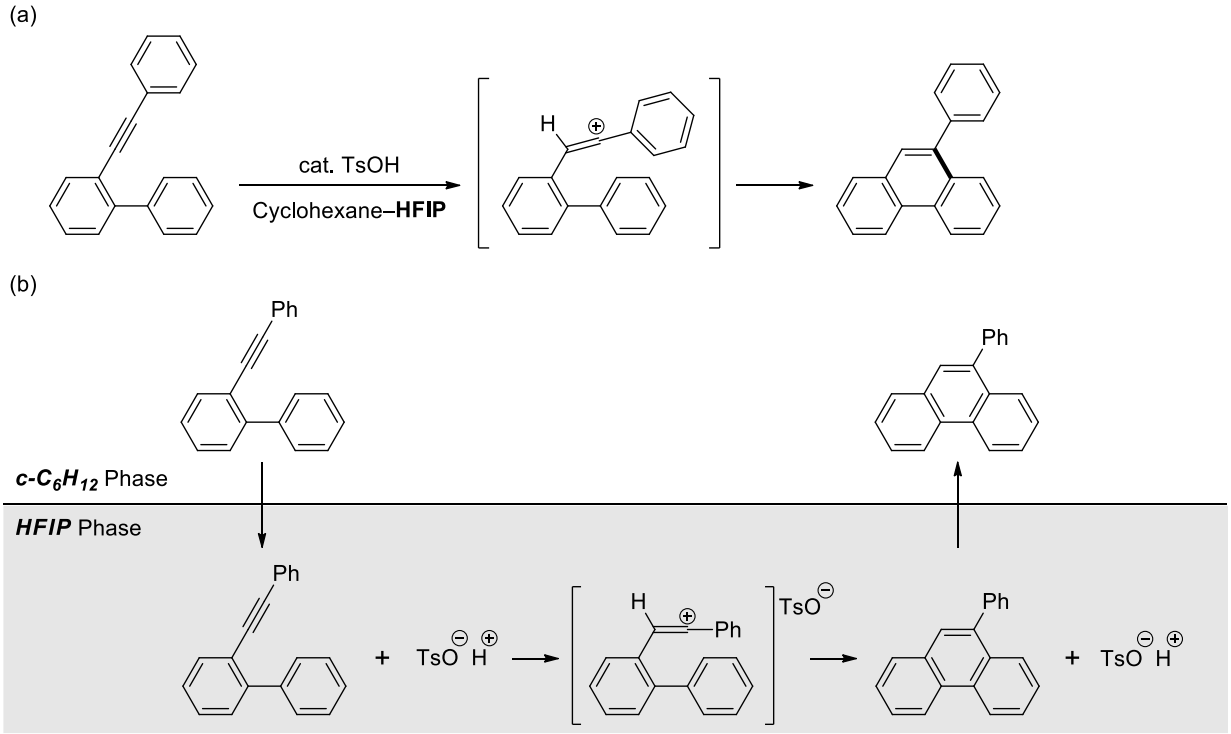
In Chapter 3, I accomplished Brønsted acid-catalyzed cycloaromatization via tandem fashion, which leads to the synthesis of higher order PAHs. Naphthalenes bearing two acetal moieties connected by a methylene-2,1-phenylene group underwent regioselective tandem cycloraromatization in the presence of a catalytic amount of TfOH in HFIP. Five substrates, easily prepared from commercially available naphthalenediols in 2 steps, were successfully employed in this protocol to afford *ortho*-fused six-hexagon benzenoids in excellent yields and with high selectivities (Scheme 3).



Scheme 3. Preparation of bisacetals and their tandem cycloaromatization leading to *ortho*-fused six-hexagon benzenoids.

In Chapter 4, I succeeded in Brønsted acid-catalyzed intramolecular hydroarylation via vinyl cations generated by protonation of unactivated alkynes. As reported previously, Brønsted acid-mediated or -catalyzed carbocyclizations of alkynes required so far activating groups, such as alkoxy or siloxy groups, on the alkyne carbons to stabilize the generated vinyl cations.[12d,e,19] By using HFIP as solvent, however, Brønsted acid-catalyzed protonation of non-activated alkynes

proceeded smoothly, followed by high-yielding carbocyclization (Scheme 4a). In this protocol, I adopted a two-phase HFIP/cyclohexane solvent system to avoid undesirable side reactions by separating the in-situ generated vinyl cations and the other organic compounds into two phases (Scheme 4b).



Scheme 4. TsOH-catalyzed synthesis of phenanthrenes in two-phase HFIP/cyclohexane system.

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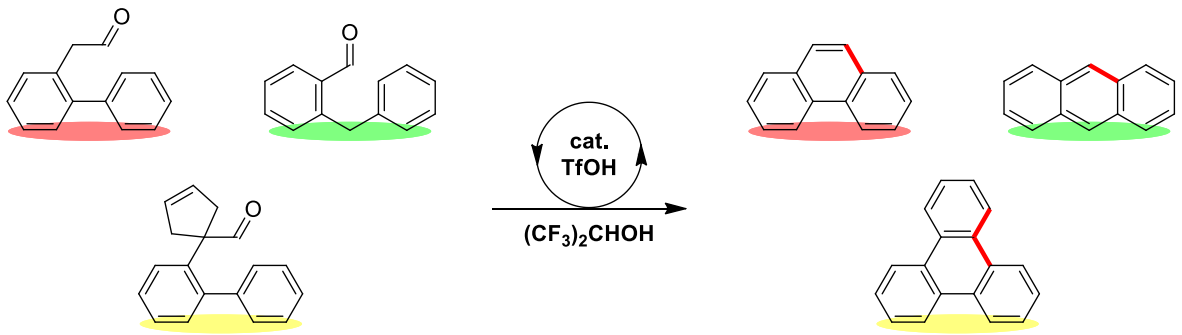
CHAPTER 2

Brønsted Acid-Catalyzed Dehydrative Cycloaromatization of Carbonyl Compounds

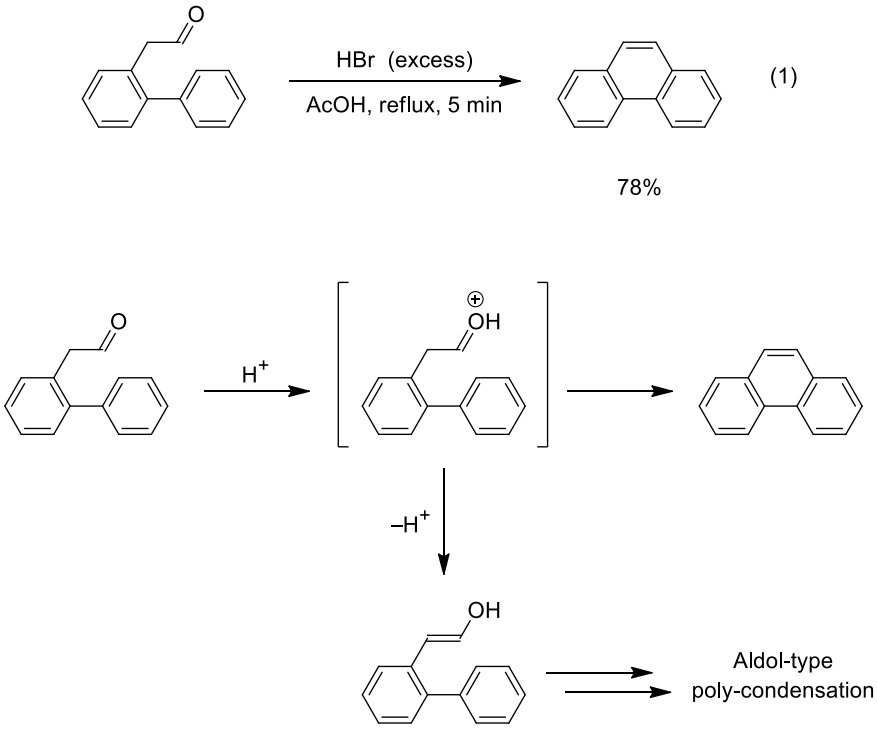
Abstract

Cycloaromatization of aromatic aldehydes and ketones was readily achieved by using a Brønsted acid catalyst in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP). In the presence of a catalytic amount of trifluoromethanesulfonic acid, biaryl-2-ylacetaldehydes and 2-benzylbenzaldehydes underwent sequential intramolecular cationic cyclization and dehydration to afford phenacenes and acenes, respectively. Furthermore, biaryl-2-ylacetaldehydes bearing a cyclopentene moiety at the α-position underwent unprecedented cycloaromatization including ring expansion to afford triphenylenes. HFIP effectively promoted the cyclizations by suppressing side reactions presumably as a result of stabilization of the cationic intermediates.



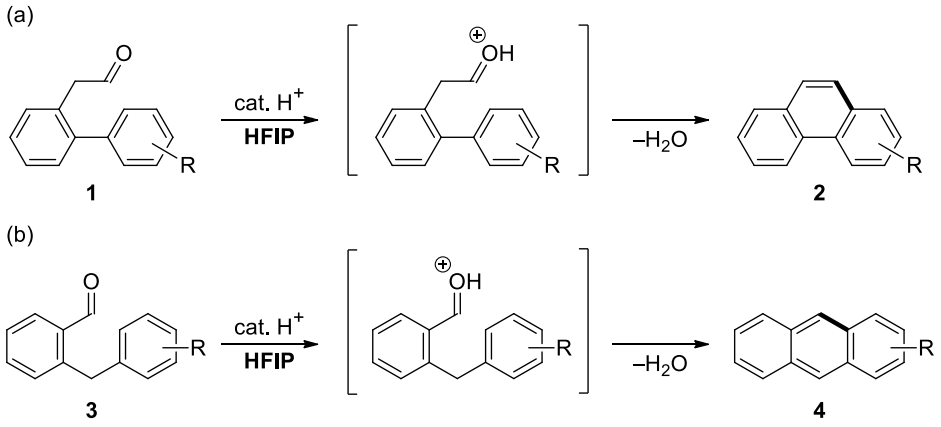
2.1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and their electronic properties, which are based on extended π-systems, have been intensively studied.[1] Among PAHs, linear-shaped acenes and zigzag-shaped phenacenes have especially been found to have practical applications in electronic devices, such as organic field-effect transistors (OFETs).[2] Among conventional methods for the preparations of acenes and phenacenes,[3–8] Brønsted acid-mediated dehydrative cycloaromatization of carbonyl compounds is one of the most versatile approaches common to both acenes and phenacenes (eq 1).[7,8] In this type of reaction, however, there is a drawback: an excess amount of acid is generally essential, even though the entire reaction could, in theory, be mediated by a catalytic amount of acid. An excess amount of acid is used, presumably because the desired reaction is otherwise sluggish. Particularly for phenacene synthesis, a catalytic amount of acid promotes both protonation and deprotonation to increase the population of the enol form, which might induce unwanted side reactions, such as aldol-type polymerizations (Scheme 1).[9]



Scheme 1. Bradsher reaction and side reation via oxocarbenium ion.

The solvent 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) exhibits a strong cation-stabilizing effect owing to its high ionizing power with low nucleophilicity. Thus, we[10] and other groups[11,12] have utilized HFIP as a solvent in reactions involving cationic intermediates. I envisaged that HFIP would serve as an effective medium in the Brønsted acid-mediated cycloaromatization of carbonyl compounds to overcome the above-mentioned drawback. Stabilizing the intermediary oxonium ions (protonated carbonyl compounds) should allow the use of a catalytic amount of acid. I demonstrate that the Brønsted acid-catalyzed cycloaromatization of (biaryl-2-yl)acetaldehydes **1** and 2-benzylbenzaldehydes **3** readily proceeds in HFIP to provide phenacenes **2** and acenes **4**, respectively (Scheme 2).

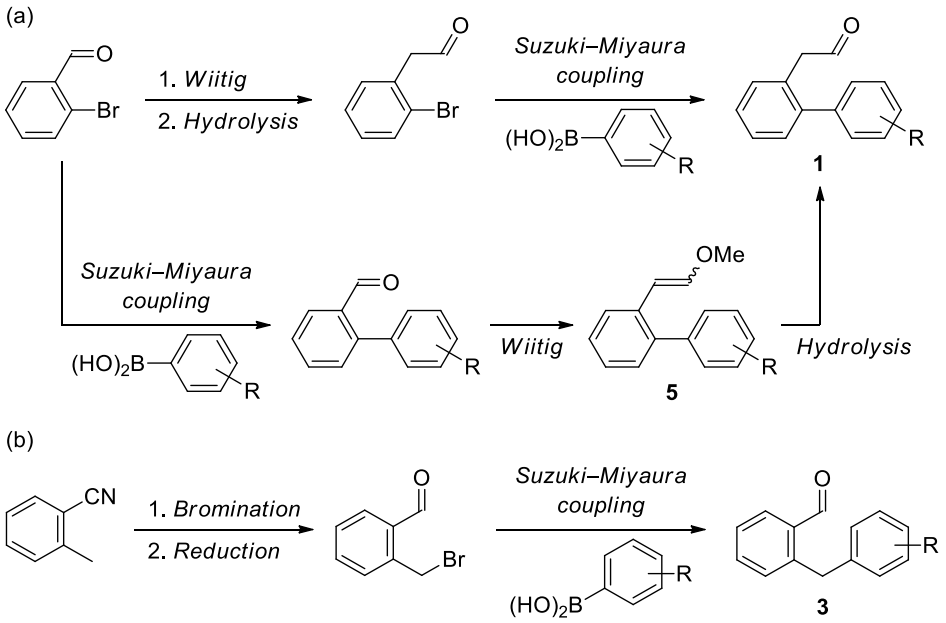


Scheme 2. Brønsted acid-catalyzed syntheses of (a) phenacenec **2** from (biaryl-2-yl)acetaldehydes **1** and (b) acenes **4** from 2-benzylbenzaldehydes **3.**

2.2. Preparation of Precursors

The cyclization precursors, (biaryl-2-yl)acetaldehydes **1** and 2-benzylbenzaldehydes **3**, were both readily available, as shown in Scheme 2. Aldehydes **1**, the precursors of phenacenes **2**, were prepared by the Suzuki–Miyaura cross-coupling of 2-(2-bromophenyl)acetaldehyde with arylboronic acids (Scheme 2a). Alternatively, aldehydes **1** were also prepared by Wittig reaction/hydrolysis of 2-arylbenzaldehydes (Scheme 2a). Both aldehyde intermediates were obtained from the same substrate, 2-bromobenzaldehyde, through a Wittig reaction/hydrolysis sequence and Suzuki–Miyaura coupling, respectively (Scheme 2a). On the other hand, aldehydes **3**,

the precursors of acenes **4**, were prepared by the Suzuki–Miyaura cross-coupling of 2-(bromomethyl)benzaldehyde, formed through a bromination/reduction sequence starting from 2-methylbenzonitrile, with arylboronic acids (Scheme 2b).[13]



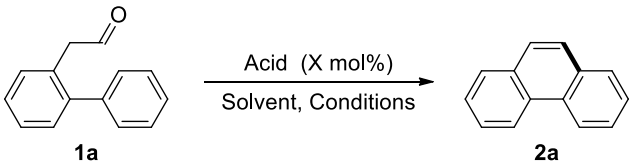
Scheme 2. Preparation of (a) (biaryl-2-yl)acetaldehydes **1** and (b) 2-benzylbenzaldehydes **3**.

2.3. Synthesis of Phenacenes, Acenes, and Triphenylenes via Brønsted Acid-Catalyzed Dehydrative Cycloaromatization

To establish a versatile catalytic system, I sought suitable conditions for the dehydrative cycloaromatization of (biphenyl-2-yl)acetaldehyde (**1a**) as a model substrate (Table 1). First, the solvent effects in the reaction of **1a** were examined in the presence of a stoichiometric amount of trifluoroacetic acid (Table 1, Entries 1–5). Whereas almost no cyclized product was obtained in toluene, dichloromethane, or acetonitrile (Table 1, Entries 1–3), nitromethane afforded the cyclized product, phenanthrene (**2a**), albeit in low yield (Table 1, Entry 4). Among the solvents examined, HFIP was by far found to be the most effective and afforded **2a** in 92% yield (Table 1, Entry 5). Upon using 10 mol% of trifluoroacetic acid, the reaction proceeded catalytically (Table 1, Entry 6). The choice of acid was also critical. The use of 10 mol% trifluoromethanesulfonic acid (TfOH),

which is a stronger acid than trifluoroacetic acid, quantitatively afforded **2a** (Table 1, Entry 7). Finally, only 4 mol% of TfOH in HFIP was found to be sufficient to complete the reaction at 0 °C in 20 min, leading to a 93% yield of **2a** (Table 1, Entry 8).

Table 1. Effects of solvents and acids on the dehydrative cycloaromatization of aldehyde **1a**.



1a **2a**

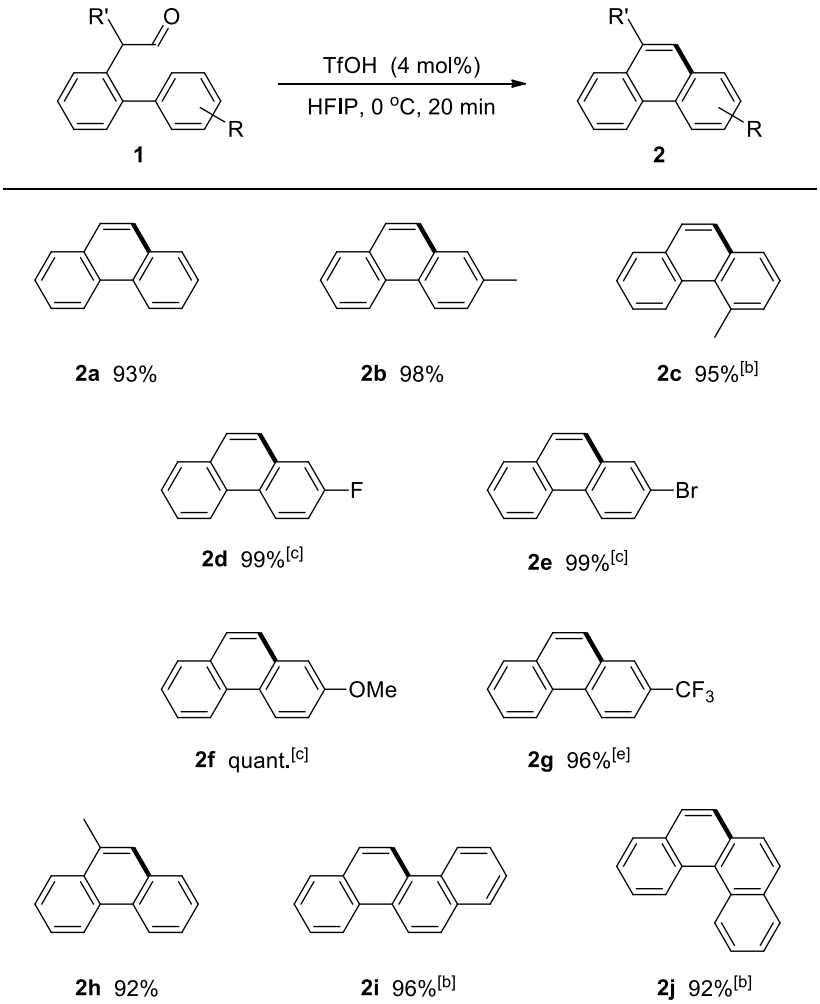
Entry	Acid	X (mol%)	Solvent	Conditions	Yield (%)[a]
1	CF_3CO_2H	100	Toluene	RT, 16 h	1
2	CF_3CO_2H	100	CH_2Cl_2	RT, 16 h	1
3	CF_3CO_2H	100	CH_3CN	RT, 16 h	N.D.[b]
4	CF_3CO_2H	100	CH_3NO_2	RT, 16 h	13
5	CF_3CO_2H	100	HFIP	RT, 16 h	92
6	CF_3CO_2H	10	HFIP	RT, 16 h	41
7	TfOH	10	HFIP	0 °C, 20 min	98[c]
8	TfOH	4	HFIP	0 °C, 20 min	93[c]

[a] Yield was determined by ^{1}H NMR measurement using CH_2Br_2 as an internal standard. [b] N.D. = Not detected. [c] Isolated yield.

The optimal conditions obtained above for **1a** were then successfully applied to the cycloaromatization of other (biaryl-2-yl)acetaldehydes **1** with a variety of substituents on the nucleophilic aryl groups (Table 2). The reaction of *p*-tolyl- and *o*-tolylsubstituted phenylacetaldehydes **1b** and **1c** readily proceeded to afford 2-methylphenanthrene (**2b**) and 4-methylphenanthrene (**2c**), respectively, in excellent yields. Although the reactions of aldehydes **1d**–**g** bearing electron-deficient nucleophilic moieties were sluggish under the same conditions, higher catalyst loadings and/or longer reaction times dramatically improved the yields of the corresponding phenanthrenes **2d**–**g**. In particular, it is noted that aldehyde **1g** successfully underwent intramolecular cationic cyclization despite its reduced reactivity owing to the strong

electron-withdrawing CF_3 substituent on the nucleophilic benzene ring.[14] In addition, α-substituted aldehyde **1h** also participated in the cycloaromatization to afford 9-methylphenanthrene (**2h**) in high yield. Aldehyde **1i** underwent regioselective cyclization at the α-position of the 2-naphthyl group, which led to chrysene ([4]phenacene, **2i**) exclusively in 96% yield.[15] Cyclization at the β-position of the 1-naphthyl group also proceeded effectively with substrate **1j** to produce [4]helicene (**2j**) in 92% yield.

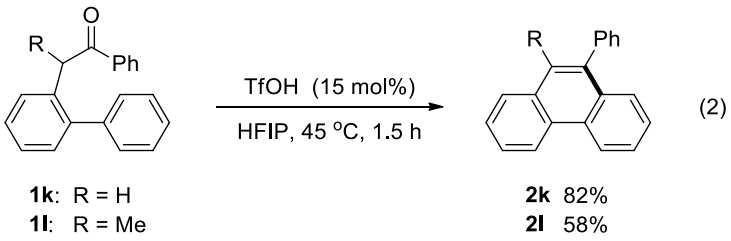
Table 2. TfOH-catalyzed synthesis of substituted phenacenes **2** in HFIP.[a]



[a] Isolated yield. [b] TfOH (10 mol%). [c] TfOH (14 mol%). [d] 2 g scale.
[e] TfOH (35 mol%), 80 min.

Furthermore, ketone substrates were employed in the TfOH-catalyzed dehydrative cyclization, despite steric hindrance around the carbonyl carbon atom (eq 2). Heating of

biphenyl-2-ylmethyl phenyl ketone (**1k**) at 45 °C in the presence of TfOH (15 mol%) afforded 9-phenylphenanthrene (**2k**) in 82% yield. Under the same conditions, α-substituted ketone **1l** gave 9,10-disubstituted phenanthrene **2l** in 58% yield.

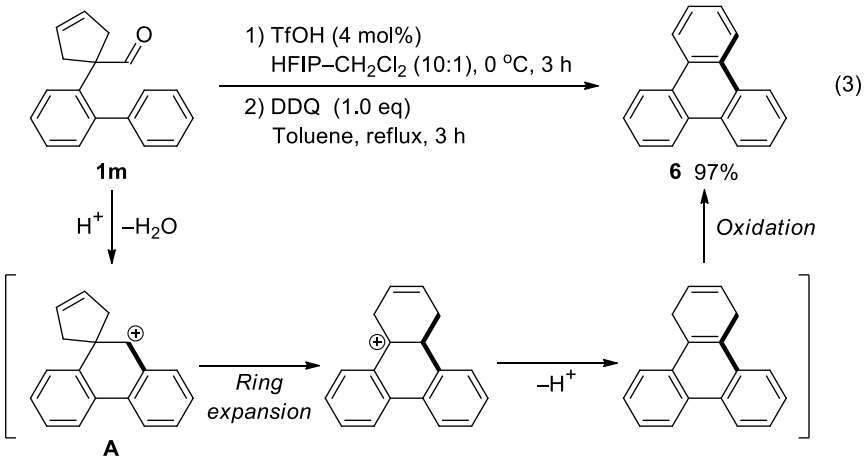


1k: R = H
1l: R = Me

2k 82%
2l 58%

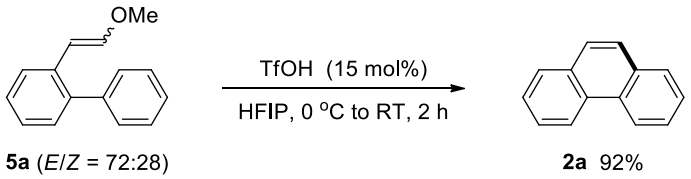
(2)

Intriguingly, the construction of two benzene rings was accomplished by conducting the above-mentioned cyclization in combination with ring expansion during the dehydration step. Thus, α,α-disubstituted biphenyl-2-ylacetaldehydes underwent the acid-catalyzed cyclization followed by 1,2-migration of the α-substituent.[16] In particular, aldehydes bearing a carbocyclic structure at the α-position caused ring expansion as a result of 1,2-migration. Aldehyde **1m** bearing a cyclopentene moiety underwent the cyclization/ring expansion sequence followed by dehydrogenation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to afford triphenylene (**6**) in 97% yield (eq 3). In this reaction, cationic intermediate **A** generated by dehydrative cyclization of **1m** underwent ring expansion to form a six-membered ring. This protocol can be a facile method for the synthesis of triphenylenes.[17]



(3)

In addition, biphenyl-2-ylvinyl ether **5a**, the hydrolysis of which leads to **1a** (Scheme 2a), directly underwent a similar cyclization in the presence of the acid catalyst (eq 4).[18,19] On treatment with TfOH (15 mol%), cyclization of **5a** (*E*/*Z* = 72:28) proceeded by elimination of methanol to afford phenanthrene (**2a**) in 92% yield. Despite a higher catalyst loading (15 mol%) and a longer reaction time (2 h), cyclization of **5a** provided an effective approach to **2a** because of saving the hydrolysis step.

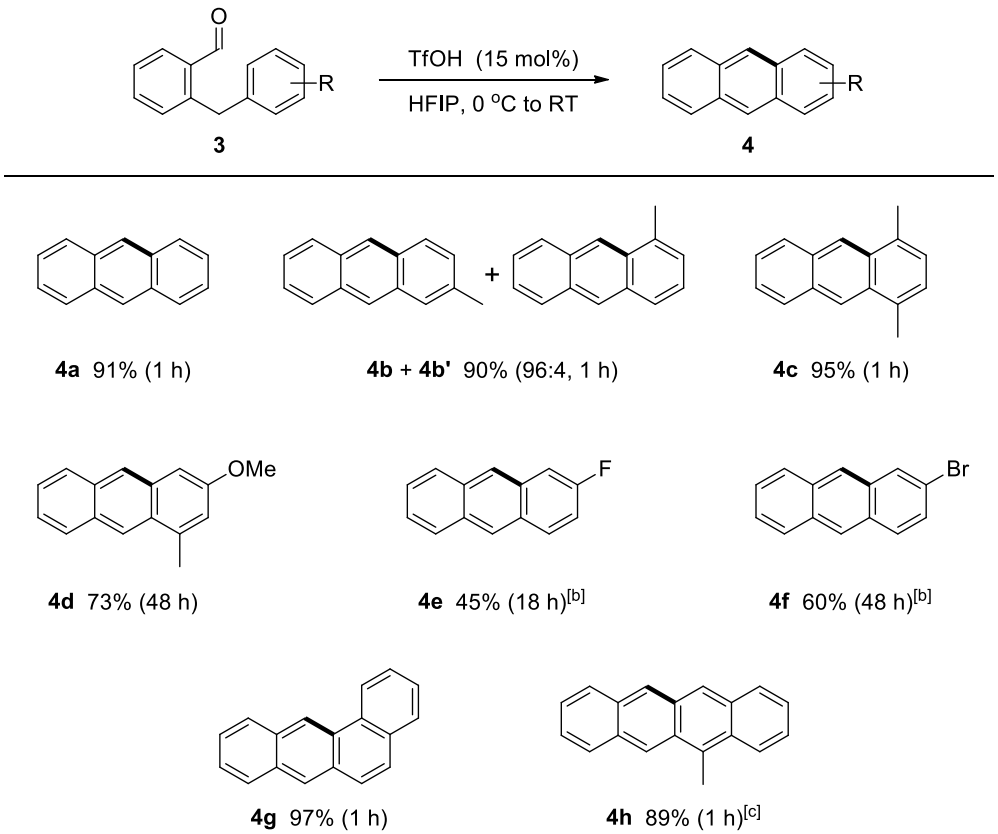


(4)

Next, the efficient synthesis of acenes **4** starting from 2-benzylbenzaldehydes **3** was examined by a similar dehydrative cycloaromatization (Table 3). On treatment of 2-benzylbenzaldehyde (**3a**) with TfOH (15 mol%), the expected anthracene (**4a**) was obtained in 91% yield. Cyclization of both electron-rich substrates **3b**–**d** and electron-deficient substrates **3e** and **3f** readily proceeded under similar conditions to afford the corresponding anthracenes **4b**–**f** in good to high yields, although cyclization of halogen-bearing substrates **4e** and **4f** required heating. As with the cyclization of acetaldehyde **1i** (Table 2), the cyclization of aldehyde **3g** proceeded

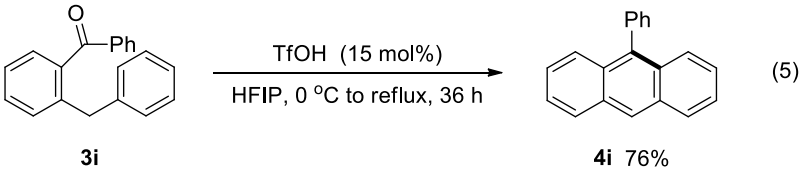
exclusively at the α-position of the 2-naphthyl group to afford tetraphene (**4g**).[15] In contrast, substrate **3h** bearing an 1-methyl-substituted naphth-2-yl group underwent cyclization at its β-position, which led to the formation of 5-methyl-substituted tetracene **4h**.

Table 3. TfOH-catalyzed synthesis of substituted acenes **4** in HFIP.[a]

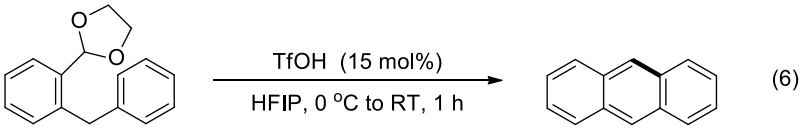


[a] Isolated yield. [b] Reflux. [c] Reaction was conducted in the dark.

2-Benzylbenzaldehyde analogues also participated in the cyclization. The synthesis of a 9-substituted anthracene was successfully achieved through the cyclization of a ketone substrate (eq 5). The TfOH-catalyzed cyclization of phenyl ketone **3i** proceeded to afford 9-phenylanthracene (**4i**) in 76% yield. Furthermore, an acetal derived from 2-benzylbenzaldehyde underwent a TfOH-catalyzed deacetalization/cycloaromatization sequence (eq 6).[20] Treatment of 2-(2-benzylphenyl)-1,3-dioxolane (**7a**) with a catalytic amount of TfOH afforded anthracene (**4a**) in 97% yield.



3i **4i** 76% (5)



7a **4a** 97% (6)

2.4. Conclusion

In summary, I developed an efficient, atom-economical approach common to phenacenes, acenes, and triphenylenes through the dehydrative cycloaromatization of aldehydes and ketones. In this process, only a catalytic amount of a Brønsted acid (TfOH) was required for the formation of additional aromatic rings. The catalytic dehydrative cycloaromatization involving cationic cyclization was obviously promoted in HFIP. This methodology can be applied to the synthesis of a wide variety of PAHs, which may serve as next-generation electronic materials.

2.5. References and Notes

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2.6. Experimental Section

General Statements

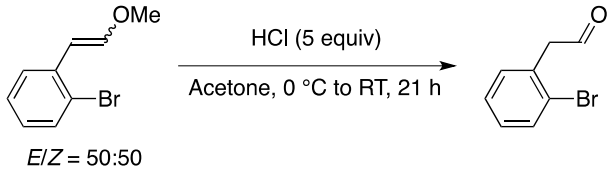
^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker Avance 500 spectrometer at 500 MHz (^{1}H NMR), 126 MHz (^{13}C NMR), and 470 MHz (^{19}F NMR). Chemical shift values are given in ppm relative to internal Me_4Si (for ^{1}H NMR: δ = 0.00 ppm), $CDCl_3$ (for ^{13}C NMR: δ = 77.0 ppm), and C_6F_6 (for ^{19}F NMR: δ = 0.00 ppm). IR spectra were recorded on a Horiba FT-300S spectrometer by the attenuated total reflectance (ATR) method. Mass spectra were measured on a JEOL JMS-T100GCV spectrometer.

Column chromatography was conducted on silica gel (Silica Gel 60 N, Kanto Chemical Co., Inc. for column chromatography). All the reactions were conducted under argon. Tetrahydrofuran (THF), diethyl ether (Et_2O), *N*,*N*-dimethylformamide (DMF), and dichloromethane (CH_2Cl_2) were purified by a solvent-purification system (GlassContour) equipped with columns of activated alumina and supported-copper catalyst (Q-5) before use. 1,1,1,3,3,3-Hexafluoropropan-2-ol (HFIP) and chlorobenzene were distilled from CaH_2 and stored over activated molecular sieves 4A. Trifluoromethanesulfonic acid was distilled from $MgSO_4$. 1-Bromo-2-(2-methoxyvinyl)benzene (*E*/*Z* = 50:50),[1] 2-bromobenzyl cyanide,[2] 2-(bromomethyl)benzaldehyde,[3] 2-(biphenyl-2-yl)-1-phenylethan-1-one (**1k**),[4] (2-benzylphenyl)(phenyl)methanone (**3i**),[5] and 2-(2-methoxyvinyl)biphenyl (**5a**, *E*/*Z* = 72:28)[6] were prepared according to the literature procedures. Unless otherwise noted, materials were obtained from commercial sources and used directly without further purifications.

2.6.2. Preparation of Substrates

2.6.2.1. Preparation of (Biaryl-2-yl)acetaldehydes and acetophenones 1

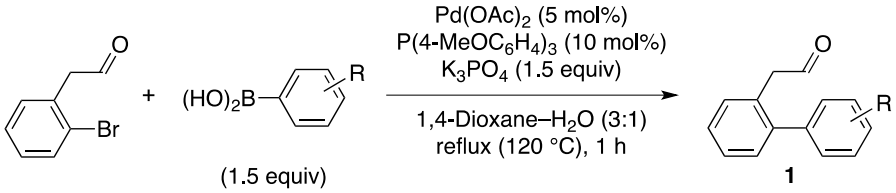
2-(2-Bromophenyl)acetaldehyde[1]



E/*Z* = 50:50

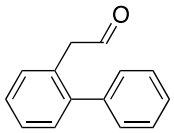
To an acetone (11 mL) solution of 2-(2-methoxyvinyl)bromobenzene (*E*/*Z* = 50:50, 962 mg, 4.51 mmol) was slowly added aqueous HCl (6 M, 3.8 mL) at 0 °C. After stirring at room temperature for 21 h, the reaction mixture was diluted with H_2O, and organic materials were extracted with Et_2O three times. The combined extracts were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure gave a crude mixture (908 mg) including 2-(2-bromophenyl)acetaldehyde as a pale yellow liquid.

[General Procedure A]



The obtained crude mixture (300 mg) of 2-(2-bromophenyl)acetaldehyde was dissolved in 1,4-dioxane (23 mL) and H_2O (8 mL). To the solution were added $Pd(OAc)_2$ (5 mol%), $P(4\text{-}MeOC_6H_4)_3$ (10 mol%), an arylboronic acid (1.5 equiv), and K_3PO_4 (1.5 equiv). After stirring at 120 °C for 1 h, the reaction was quenched with H_2O, and organic materials were extracted with Et_2O three times. The combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography to give the corresponding (biaryl-2-yl)acetaldehyde **1**. The yields of **1** was determined based on 2-(2-methoxyvinyl)bromobenzene.

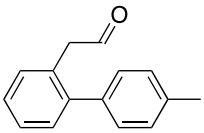
(Biphenyl-2-yl)acetaldehyde (1a)



Compound **1a** was prepared according to General Procedure A using the crude mixture (300 mg) including 2-(2-bromophenyl)acetaldehyde, $Pd(OAc)_2$ (17 mg, 78 μmol), $P(4\text{-}MeOC_6H_4)_3$ (54 mg, 0.15 mmol), phenylboronic acid (281 mg, 2.31 mmol), and K_3PO_4 (488 mg, 2.30 mmol). Purification by silica gel column chromatography (hexane/EtOAc = 30:1) gave **1a** (153 mg, 52%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.69 (d, *J* = 2.0 Hz, 2H), 7.24–7.28 (m, 3H), 7.32–7.38 (m, 4H), 7.40–7.43 (m, 2H), 9.63 (t, *J* = 2.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 48.3, 127.4, 127.5, 127.8, 128.4, 129.1, 129.8, 130.4, 130.6, 140.8, 142.9, 199.6. IR (neat): ν 3059, 2922, 1724, 1481, 771, 704 cm^{-1}. HRMS (EI) *m*/*z* Calcd. for $C_{14}H_{12}O$ $[M]^+$: 196.0883; Found: 196.0884.

(4'-Methylbiphenyl-2-yl)acetaldehyde (1b)

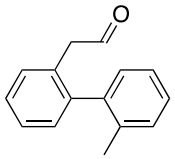


Compound **1b** was prepared according to General Procedure A using the crude mixture (301 mg) including 2-(2-bromophenyl)acetaldehyde, $Pd(OAc)_2$ (17 mg, 76 μmol), $P(4\text{-}MeOC_6H_4)_3$ (54 mg, 0.15 mmol), 4-methylphenylboronic acid (317 mg, 2.33 mmol), and K_3PO_4 (488 mg, 2.30 mmol). Purification by silica gel column chromatography (hexane/EtOAc = 30:1) gave **1b** (184 mg, 58%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.40 (s, 3H), 3.69 (d, *J* = 2.0 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.22 (dd, *J* = 7.3, 0.6 Hz, 2H), 7.26 (dd, *J* = 4.4, 4.4 Hz, 1H), 7.30–7.32 (m, 1H), 7.34–7.36 (m, 2H), 9.62–9.63 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.1, 48.3, 127.5, 127.7, 129.0, 129.1, 129.9, 130.5, 130.6, 137.1, 137.9, 142.9, 199.8. IR (neat): ν 3022, 2920, 2817, 2723, 1720, 1483, 1444, 1109, 1034, 1007, 820, 758 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{15}H_{14}O$ $[M]^+$: 210.1039; Found:

210.1034.

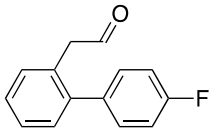
(2'-Methylbiphenyl-2-yl)acetaldehyde (1c)



Compound **1c** was prepared according to General Procedure A using the crude mixture (306 mg) including 2-(2-bromophenyl)acetaldehyde, $Pd(OAc)_2$ (18 mg, 82 μmol), $P(4\text{-}MeOC_6H_4)_3$ (55 mg, 0.16 mmol), 2-methylphenylboronic acid (313 mg, 2.30 mmol), and K_3PO_4 (485 mg, 2.28 mmol). Purification by silica gel column chromatography (hexane/EtOAc = 30:1) gave **1c** (146 mg, 45%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.04 (s, 3H), 3.44 (dd, *J* = 16.7, 1.9 Hz, 1H), 3.53 (dd, *J* = 16.7, 2.2 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 7.20–7.23 (m, 2H), 7.27–7.30 (m, 3H), 7.34–7.39 (m, 2H), 9.54 (dd, *J* = 2.2, 1.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 19.9, 48.1, 125.7, 127.4, 127.77, 127.77, 129.5, 130.08, 130.13, 130.3, 130.4, 135.8, 140.2, 142.2, 199.3. IR (neat): ν 3059, 3018, 2920, 2821, 2723, 1720, 1477, 1444, 1034, 1009, 752, 729 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{15}H_{14}O$ $[M]^+$: 210.1039; Found: 210.1038.

(4'-Fluorobiphenyl-2-yl)acetaldehyde (1d)

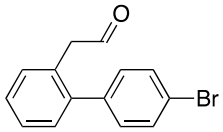


Compound **1d** was prepared according to General Procedure A using the crude mixture (302 mg) including 2-(2-bromophenyl)acetaldehyde, $Pd(OAc)_2$ (18 mg, 82 μmol), $P(4\text{-}MeOC_6H_4)_3$ (53 mg, 0.15 mmol), 4-fluorophenylboronic acid (320 mg, 2.29 mmol), and K_3PO_4 (484 mg, 2.28 mmol). Purification by silica gel column chromatography (hexane/EtOAc = 30:1) gave **1d** (165 mg, 51%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.67 (d, *J* = 1.8 Hz, 2H), 7.08–7.12 (m, 2H), 7.19–7.23 (m, 2H),

7.27–7.30 (m, 2H), 7.34–7.40 (m, 2H), 9.63 (t, J = 1.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 48.3, 115.3 (d, J_{CF} = 21 Hz), 127.5, 128.0, 130.0, 130.5, 130.7 (d, J_{CF} = 4 Hz), 130.8, 136.8 (d, J_{CF} = 3 Hz), 141.8, 162.2 (d, J_{CF} = 247 Hz), 199.3. ^{19}F NMR (470 MHz, $CDCl_3$): δ 47.8–47.9 (m). IR (neat): ν 3066, 2924, 2854, 1722, 1512, 1483, 1219, 1157, 837, 760 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{14}H_{11}FO$ $[M]^+$: 214.0788; Found: 214.0785.

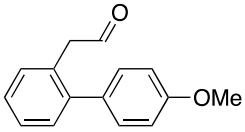
(4'-Bromobiphenyl-2-yl)acetaldehyde (1e)



Compound **1e** was prepared according to General Procedure A using the crude mixture (322 mg) including 2-(2-bromophenyl)acetaldehyde, $Pd(OAc)_2$ (18 mg, 78 μmol), $P(4\text{-}MeOC_6H_4)_3$ (53 mg, 0.15 mmol), 4-bromophenylboronic acid (456 mg, 2.27 mmol), and K_3PO_4 (479 mg, 2.26 mmol). Purification by silica gel column chromatography (hexane/EtOAc = 30:1) gave **1e** (88 mg, 20%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.67 (d, J = 1.8 Hz, 2H), 7.11–7.13 (m, 2H), 7.25–7.29 (m, 2H), 7.34–7.40 (m, 2H), 7.53–7.55 (m, 2H), 9.64 (t, J = 1.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 48.2, 121.7, 127.6, 128.2, 129.7, 130.3, 130.7, 130.8, 131.5, 139.7, 141.6, 199.2. IR (neat): ν 3065, 2923, 2821, 1720, 1475, 1390, 1070, 1003, 827, 756, cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{14}H_{11}{}^{79}BrO$ $[M]^+$: 273.9988; Found: 273.9992.

(4'-Methoxybiphenyl-2-yl)acetaldehyde (1f)

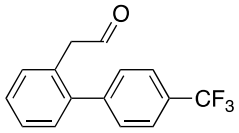


Compound **1f** was prepared according to General Procedure A using the crude mixture (303 mg) including 2-(2-bromophenyl)acetaldehyde, $Pd(OAc)_2$ (19 mg, 84 μmol), $P(4\text{-}MeOC_6H_4)_3$ (55 mg, 0.16 mmol), 4-methoxyphenylboronic acid (349 mg, 2.30 mmol), and K_3PO_4 (483 mg, 2.28

mmol). Purification by silica gel column chromatography (hexane/EtOAc = 30:1) gave **1f** (186 mg, 54%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.70 (d, *J* = 2.0 Hz, 2H), 3.85 (s, 3H), 6.93–6.96 (m, 2H), 7.16–7.19 (m, 2H), 7.24–7.27 (m, 1H), 7.30–7.37 (m, 3H), 9.63 (t, *J* = 2.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 48.4, 55.3, 113.8, 127.5, 127.6, 130.1, 130.2, 130.57, 130.62, 133.1, 142.5, 158.9, 199.8. IR (neat): ν 3018, 2935, 2835, 2723, 1718, 1610, 1514, 1483, 1242, 1174, 1034, 833, 762 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{15}H_{14}O_2$ $[M]^+$: 226.0988; Found: 226.0981.

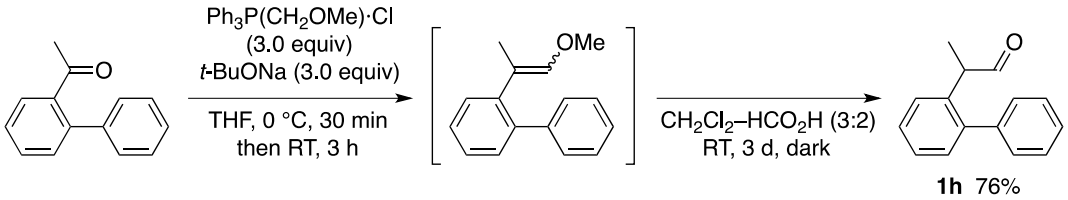
[4'-(Trifluoromethyl)biphenyl-2-yl]acetaldehyde (1g)



Compound **1g** was prepared according to General Procedure A using the crude mixture (298 mg) including 2-(2-bromophenyl)acetaldehyde, $Pd(OAc)_2$ (19 mg, 82 μmol), $P(4\text{-}MeOC_6H_4)_3$ (56 mg, 0.16 mmol), 4-(trifluoromethyl)phenylboronic acid (431 mg, 2.27 mmol), and K_3PO_4 (484 mg, 2.28 mmol). Purification by silica gel column chromatography (hexane/EtOAc = 30:1) gave **1g** (127 mg, 32%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.68 (d, *J* = 1.8 Hz, 2H), 7.28–7.31 (m, 2H), 7.37–7.44 (m, 4H), 7.68 (d, *J* = 8.0 Hz, 2H), 9.66 (t, *J* = 1.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 48.2, 124.1 (q, J_{CF} = 273 Hz), 125.4 (q, J_{CF} = 4 Hz), 127.7, 128.5, 129.51, 129.53 (q, J_{CF} = 65 Hz), 129.7, 130.2, 130.8, 141.4, 144.5, 199.0. ^{19}F NMR (470 MHz, $CDCl_3$): δ 99.3 (s). IR (neat): ν 3020, 2827, 2733, 1724, 1323, 1120, 1068, 847, 769 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{15}H_{11}F_3O$ $[M]^+$: 264.0757; Found: 264.0756.

2-(Biphenyl-2-yl)propanal (1h)

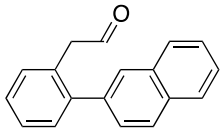


A mixture of $Ph_3P(CH_2OMe)\cdot Cl$ (10.8 g, 31.5 mmol) and *t*-BuONa (3.18 g, 33.1 mmol) was dissolved in THF (25 mL) at 0 °C. After stirring at 0 °C for 30 min, a THF (10 mL) solution of 2-acetylbiphenyl (1.93 g, 9.84 mmol) was added. After stirring at room temperature for 3 h, the reaction was quenched with aqueous NH_4Cl, and organic materials were extracted with Et_2O two times. The combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to give 2-(1-methoxyprop-1-en-2-yl)biphenyl as a pale yellow oil.

To a CH_2Cl_2 (15 mL) solution of the obtained 2-(1-methoxyprop-1-en-2-yl)biphenyl was added formic acid (10 mL). After stirring at room temperature for 3 days in the dark, the reaction was quenched with H_2O, and organic materials were extracted with CH_2Cl_2 three times. The combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/EtOAc = 100:1) to give **1h** (1.58 g, 76% from 2-acetylbiphenyl) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.43 (d, *J* = 7.0 Hz, 3H), 3.89 (q, *J* = 7.0 Hz, 1H), 7.15 (d, *J* = 7.6, 1H), 7.29–7.41 (m, 6H), 7.42–7.45 (m, 2H), 9.65 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 15.6, 49.1, 127.2, 127.4, 128.0, 128.1, 128.4, 129.2, 130.6, 135.8, 140.9, 142.9, 201.1. IR (neat): ν 3060, 2976, 2933, 2814, 2717, 1716, 1479, 1450, 1018, 866, 756, 746, 700 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{15}H_{14}O$ $[M]^+$: 210.1039; Found: 210.1040.

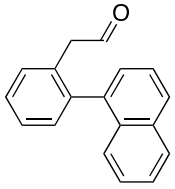
2-(Naphthalen-2-yl)phenylacetaldehyde (1i)



Compound **1i** was prepared according to General Procedure A using the crude mixture (301 mg) including 2-(2-bromophenyl)acetaldehyde, $Pd(OAc)_2$ (19 mg, 83 μmol), $P(4\text{-}MeOC_6H_4)_3$ (54 mg, 0.15 mmol), (naphthalen-2-yl)boronic acid (390 mg, 2.27 mmol), and K_3PO_4 (486 mg, 2.29 mmol). Purification by silica gel column chromatography (hexane/EtOAc = 30:1) gave **1i** (238 mg, 64%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.69 (d, *J* = 1.9 Hz, 2H), 7.29–7.31 (m, 1H), 7.37–7.42 (m, 4H), 7.50–7.54 (m, 2H), 7.72 (d, *J* = 0.8 Hz, 1H), 7.83–7.85 (m, 1H), 7.88–7.89 (m, 2H), 9.65 (t, *J* = 1.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 48.3, 126.2, 126.5, 127.3, 127.5, 127.7, 127.9, 127.95, 128.00, 128.01, 130.1, 130.63, 130.63, 132.4, 133.2, 138.3, 142.8, 199.5. IR (neat): ν 3053, 2821, 2723, 1722, 1491, 823, 758 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{18}H_{14}O$ $[M]^+$: 246.1039; Found: 246.1044.

2-(Naphthalen-1-yl)phenylacetaldehyde (1j)

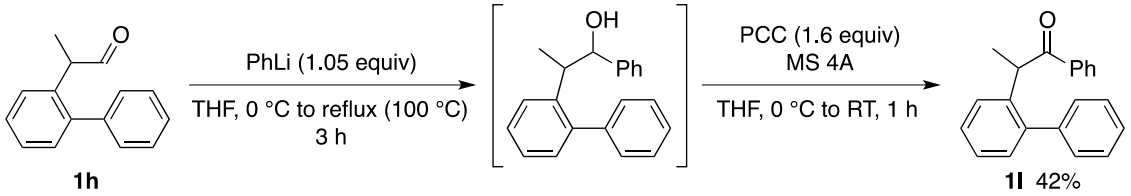


Compound **1j** was prepared according to General Procedure A using the crude mixture (304 mg) including 2-(2-bromophenyl)acetaldehyde, $Pd(OAc)_2$ (19 mg, 83 μmol), $P(4\text{-}MeOC_6H_4)_3$ (54 mg, 0.15 mmol), (naphthalen-1-yl)boronic acid (389 mg, 2.26 mmol), and K_3PO_4 (482 mg, 2.27 mmol). Purification by silica gel column chromatography (hexane/EtOAc = 30:1) gave **1j** (224 mg, 60%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.36 (dd, *J* = 16.8, 2.0 Hz, 1H), 3.46 (dd, *J* = 16.8, 1.9 Hz, 1H), 7.29–7.50 (m, 9H), 7.85–7.89 (m, 2H), 9.43 (dd, *J* = 2.0, 1.9 Hz, 1H). ^{13}C NMR (126 MHz,

$CDCl_3$): δ 48.3, 125.3, 125.7, 126.0, 126.4, 127.1, 127.4, 128.1, 128.2, 128.3, 130.4, 131.1, 131.4, 132.0, 133.5, 138.2, 140.9, 199.3. IR (neat): ν 3059, 3016, 2823, 2727, 1720, 1215, 746 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{18}H_{14}O$ $[M]^+$: 246.1039; Found: 246.1029.

2-(Biphenyl-2-yl)-1-phenylpropan-1-one (1l)



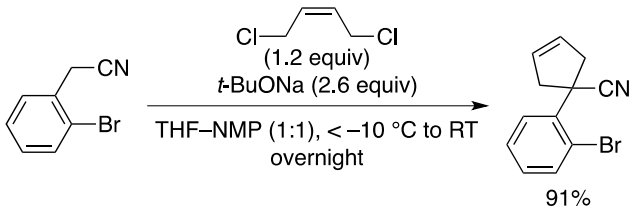
1h **1l** 42%

To a THF (30 mL) solution of 2-(biphenyl-2-yl)propanal (**1h**, 1.00 g, 4.76 mmol) was slowly added PhLi (1.8 M in cyclohexane and Et_2O, 2.8 mL, 5.0 mmol) at 0 °C. After stirring at 100 °C for 3 h, the reaction was quenched with aqueous NH_4Cl, and organic materials were extracted with EtOAc three times. The combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to give 2-(biphenyl-2-yl)-1-phenylpropan-1-ol.

To a suspension of pyridinium chlorochromate (PCC, 898 mg, 4.17 mmol) and molecular sieves 4A (772 mg) in CH_2Cl_2 (5 mL) was added a CH_2Cl_2 (3.5 mL) solution of 2-(biphenyl-2-yl)-1-phenylpropan-1-ol at 0 °C. After stirring at room temperature for 1 h, the reaction mixture was filtered through a pad of Celite (CH_2Cl_2). After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/EtOAc = 30:1) to give **1l** (566 mg, 42% from **1h**) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.56 (d, *J* = 6.8 Hz, 3H), 4.72 (q, *J* = 6.8 Hz, 1H), 7.21–7.31 (m, 6H), 7.37–7.45 (m, 4H), 7.49 (dd, *J* = 8.1, 7.4 Hz, 2H), 7.56 (dd, *J* = 8.4, 1.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 19.6, 43.7, 126.8, 127.4, 127.5, 128.0, 128.2, 128.4, 128.5, 129.3, 130.5, 132.5, 136.3, 138.6, 141.2, 141.3, 200.9. IR (neat): ν 3059, 2976, 2931, 1682, 1477, 1446, 1217, 949, 750, 688 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{21}H_{18}O$ $[M]^+$: 286.1352; Found: 286.1350.

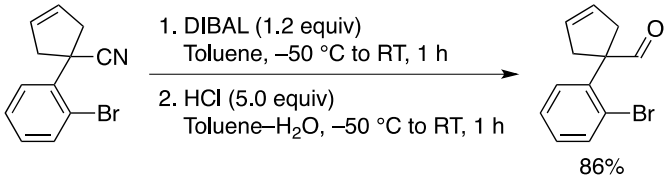
1-(2-Bromophenyl)cyclopent-3-ene-1-carbonitrile



2-Bromobenzyl cyanide (4.90 g, 25.0 mmol) and *t*-BuONa (6.28 g, 65.4 mmol) were dissolved in THF (25 mL) and *N*-methyl-2-pyrrolidone (NMP, 25 mL). To the solution was slowly added *cis*-1,4-dichloro-2-butene (3.15 mL, 29.9 mmol) under –10 °C. After stirring at room temperature overnight, the reaction was quenched with aqueous HCl (2 M), and organic materials were extracted with EtOAc three times. The combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/EtOAc = 10:1) to give 1-(2-bromophenyl)cyclopent-3-ene-1-carbonitrile (5.66 g, 91%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.25–3.33 (m, 4H), 5.82 (s, 2H), 7.19 (ddd, *J* = 7.8, 7.8, 1.6 Hz, 1H), 7.34 (ddd, *J* = 7.8, 7.8, 1.4 Hz, 1H), 7.60 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.66 (dd, *J* = 7.8, 1.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 45.3, 46.8, 122.5, 124.1, 127.6, 128.2, 128.9, 129.6, 135.5, 136.6. IR (neat): ν 3066, 2929, 2862, 2233, 1469, 1427, 1022, 742 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{12}H_{10}{}^{79}BrN$ $[M]^+$: 246.9991; Found: 246.9988.

1-(2-Bromophenyl)cyclopent-3-ene-1-carbaldehyde

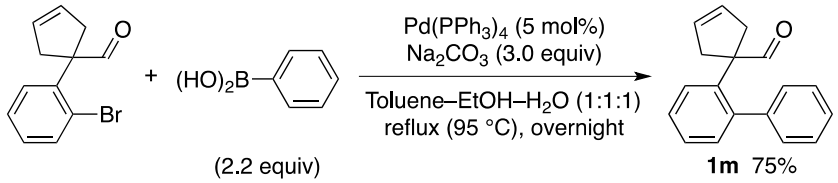


To a toluene (14 mL) solution of 1-(2-bromophenyl)cyclopent-3-ene-1-carbonitrile (3.33 g, 13.4 mmol) was slowly added diisobutylaluminium hydride (DIBAL, 1.0 M in toluene, 16 mL, 16 mmol) at –50 °C. After stirring at room temperature for 2 h, aqueous HCl (6 M, 11.2 mL) was added at –50 °C. The reaction mixture was allowed to warm to room temperature, and stirred for

another 30 min. To the reaction mixture was added H_2O, and organic materials were extracted with EtOAc three times. The combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/EtOAc = 10:1) to give 1-(2-bromophenyl)cyclopent-3-ene-1-carbaldehyde (2.92 g, 86%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.85 (d, *J* = 15.1 Hz, 2H), 3.20 (d, *J* = 15.1 Hz, 2H), 5.72 (s, 2H), 7.14–7.18 (m, 1H), 7.31–7.35 (m, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 9.79 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 40.5, 62.9, 123.8, 127.5, 128.2, 128.9, 129.3, 134.5, 140.8, 200.6. IR (neat): ν 3059, 2906, 2848, 2710, 1718, 1468, 1011 cm^{-1}. HRMS (EI): *m/z* Calcd. for $C_{12}H_{11}{}^{79}BrO$ $[M]^+$: 249.9988; Found: 249.9985.

1-(Biphenyl-2-yl)cyclopent-3-ene-1-carbaldehyde (1m)



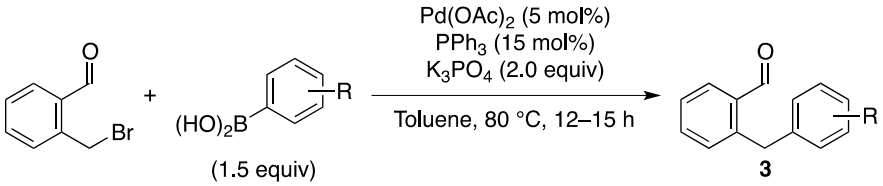
1-(2-Bromophenyl)cyclopent-3-ene-1-carbaldehyde (136 mg, 0.54 mmol) was dissolved in toluene (0.3 mL), EtOH (0.3 mL), and H_2O (0.3 mL). To the solution were added $Pd(PPh_3)_4$ (33 mg, 29 μmol), phenylboronic acid (146 mg, 1.2 mmol), and Na_2CO_3 (182 mg, 1.7 mmol). After stirring at 95 °C overnight, the reaction was quenched with H_2O, and organic materials were extracted with EtOAc three times. The combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/EtOAc = 60:1) to give **1m** (101 mg, 75%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.62 (d, *J* = 15.1 Hz, 2H), 2.72 (d, *J* = 15.1 Hz, 2H), 5.59 (s, 2H), 7.16–7.20 (m, 3H), 7.29–7.33 (m, 1H), 7.34–7.38 (m, 3H), 7.39–7.42 (m, 2H), 9.38 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 41.5, 62.1, 126.7, 127.6, 127.8, 127.9, 128.5, 128.8, 129.7, 131.7, 139.2, 142.4, 142.5, 199.0. IR (neat): ν 3057, 2952, 2912, 2798, 2708, 1722, 1475, 1340, 754, 688

cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{18}H_{16}O$ $[M]^+$: 248.1196; Found: 248.1192.

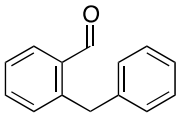
2.6.2.2. Preparation of 2-Benzylbenzaldehydes 3

[General Procedure B]



To a toluene (6 mL) solution of 2-(bromomethyl)benzaldehyde (3.0 mmol) were added $Pd(OAc)_2$ 5 mol%), PPh_3 (15 mol%), an arylboronic acid (1.5 equiv), and K_3PO_4 (2.0 equiv). After stirring at 80 °C for 12–15 h, the reaction mixture was filtered through a pad of silica gel (EtOAc). After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography to give the corresponding 2-benzylbenzaldehyde **3**.

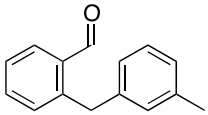
2-Benzylbenzaldehyde (3a)



Compound **3a** was prepared according to General Procedure B using 2-(bromomethyl)benzaldehyde (604 mg, 3.03 mmol), $Pd(OAc)_2$ (36 mg, 0.16 mmol), PPh_3 (122 mg, 0.47 mmol), phenylboronic acid (553 mg, 4.54 mmol), and K_3PO_4 (1.34 g, 6.31 mmol) at 80 °C for 15 h. Purification by silica gel column chromatography (hexane/EtOAc = 50:1) gave **3a** (593 mg, quant.) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.45 (s, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.19 (tt, *J* = 7.4, 1.5 Hz, 1H), 7.26–7.29 (m, 3H), 7.42 (ddd, *J* = 7.6, 7.5, 1.0 Hz, 1H), 7.53 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.86 (dd, *J* = 7.6, 1.5 Hz, 1H), 10.25 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): 38.0, 126.3, 127.0, 128.6, 128.8, 131.6, 132.0, 133.91, 133.91, 140.3, 143.0, 192.4. IR (neat): ν 3026, 2738, 1695, 1597, 1495, 1452, 1209, 727, 694 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{14}H_{12}O$ $[M]^+$: 196.0883; Found: 196.0882.

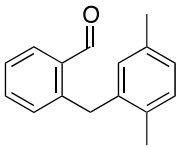
2-(3-Methylbenzyl)benzaldehyde (3b)



Compound **3b** was prepared according to General Procedure B using 2-(bromomethyl)benzaldehyde (603 mg, 3.03 mmol), $Pd(OAc)_2$ (35 mg, 0.16 mmol), PPh_3 (124 mg, 0.47 mmol), 3-methylphenylboronic acid (623 mg, 4.58 mmol), and K_3PO_4 (1.28 g, 6.03 mmol) at 80 °C for 12 h. Purification by silica gel column chromatography (hexane/EtOAc = 30:1) gave **3b** (534 mg, 84%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.29 (s, 3H), 4.41 (s, 2H), 6.92–6.96 (m, 2H), 7.01 (d, *J* = 7.6 Hz, 1H), 7.16 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.41 (ddd, *J* = 7.6, 7.6, 1.0 Hz, 1H), 7.53 (ddd, *J* = 7.6, 7.6, 1.5 Hz, 1H), 7.87 (dd, *J* = 7.6, 1.5 Hz, 1H), 10.27 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): 21.4, 37.9, 125.8, 126.9, 127.0, 128.5, 129.5, 131.6, 131.7, 133.91, 133.91, 138.2, 140.2, 143.1, 192.4. IR (neat): ν 3020, 2920, 2860, 2731, 1691, 1597, 1194, 742, 694 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{15}H_{14}O$ $[M]^+$: 210.1039; Found: 210.1040.

2-(2,5-Dimethylbenzyl)benzaldehyde (3c)

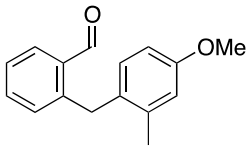


Compound **3c** was prepared according to General Procedure B using 2-(bromomethyl)benzaldehyde (802 mg, 4.03 mmol), $Pd(OAc)_2$ (45 mg, 0.20 mmol), PPh_3 (152 mg, 0.58 mmol), 2,5-dimethylphenylboronic acid (902 mg, 6.01 mmol), K_3PO_4 (1.74 g, 8.20 mmol), and toluene (8 mL) at 80 °C for 12 h. Purification by silica gel column chromatography (hexane/EtOAc = 30:1) gave **3c** (669 mg, 74%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.21 (s, 3H), 2.23 (s, 3H), 4.39 (s, 2H), 6.70 (s, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.41 (dd, *J* = 7.6, 7.5 Hz, 1H), 7.48 (7.6, 7.5, 1.5 Hz, 1H), 7.88 (dd, *J* = 7.6, 1.5 Hz, 1H), 10.25 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): 19.1,

21.0, 35.6, 126.7, 127.2, 130.1, 130.3, 130.7, 132.1, 133.3, 133.9, 134.0, 135.6, 137.9, 142.8, 192.6. IR (neat): ν 2922, 2862, 2735, 1691, 1599, 1196, 810, 750 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{16}H_{16}O$ $[M]^+$: 224.1196; Found: 224.1190.

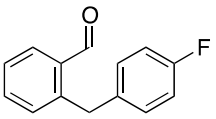
2-(4-Methoxy-2-methylbenzyl)benzaldehyde (3d)



Compound **3d** was prepared according to General Procedure B using 2-(bromomethyl)benzaldehyde (601 mg, 3.02 mmol), $Pd(OAc)_2$ (36 mg, 0.16 mmol), PPh_3 (119 mg, 0.46 mmol), 4-methoxy-2-methylphenylboronic acid (754 mg, 4.54 mmol), and K_3PO_4 (1.32 g, 6.22 mmol) at 80 °C for 15 h. Purification by silica gel column chromatography (hexane/EtOAc = 50:1) gave **3d** (372 mg, 51%) as a pale yellow oil.

^1H NMR (500 MHz, $CDCl_3$): δ 2.23 (s, 3H), 3.78 (s, 3H), 4.36 (s, 2H), 6.66 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.77 (d, *J* = 2.6 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 7.40 (dd, *J* = 7.6, 7.4 Hz, 1H), 7.48 (dd, *J* = 7.5, 7.4 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 10.24 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): 19.9, 34.9, 55.2, 111.1, 116.1, 126.7, 130.3, 130.4, 130.6, 132.2, 133.9, 134.0, 137.8, 143.2, 158.2, 192.6. IR (neat): ν 2949, 2835, 2733, 1691, 1599, 1500, 1288, 1252, 1198, 1045, 750 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{16}H_{16}O_2$ $[M]^+$: 240.1145; Found: 240.1140.

2-(4-Fluorobenzyl)benzaldehyde (3e)

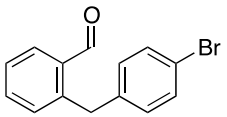


Compound **3e** was prepared according to General Procedure B using 2-(bromomethyl)benzaldehyde (598 mg, 3.01 mmol), $Pd(OAc)_2$ (35 mg, 0.15 mmol), PPh_3 (123 mg, 0.47 mmol), 4-fluorophenylboronic acid (711 mg, 5.08 mmol), and K_3PO_4 (1.35 g, 6.36 mmol) at 80 °C for 15 h. Purification by silica gel column chromatography (hexane/EtOAc = 50:1) gave **3e**

(315 mg, 49%) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.42 (s, 2H), 6.96 (dd, J_{HF} = 8.7 Hz, J = 8.6 Hz, 2H), 7.10 (dd, J = 8.6 Hz, J_{HF} = 5.5 Hz, 2H), 7.25 (d, J = 7.5 Hz, 1H), 7.43 (ddd, J = 7.6, 7.5, 0.9 Hz, 1H), 7.54 (ddd, J = 7.5, 7.5, 1.4 Hz, 1H), 7.85 (dd, J = 7.6, 1.4 Hz, 1H), 10.21 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): 37.3, 115.3 (d, J_{CF} = 21 Hz), 127.1, 130.2 (d, J_{CF} = 8 Hz), 131.6, 132.8, 133.8, 133.9, 135.9 (d, J_{CF} = 3 Hz), 142.7, 161.4 (d, J_{CF} = 245 Hz), 192.5. ^{19}F NMR (470 MHz, $CDCl_3$): δ 44.7–44.8 (m). IR (neat): ν 3020, 2742, 1693, 1599, 1508, 1217, 1157, 746 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{14}H_{11}FO$ $[M]^+$: 214.0788; Found: 214.0784.

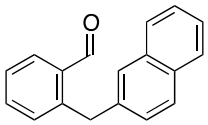
2-(4-Bromobenzyl)benzaldehyde (3f)



Compound **3f** was prepared according to General Procedure B using 2-(bromomethyl)benzaldehyde (600 mg, 3.02 mmol), $Pd(OAc)_2$ (35 mg, 0.16 mmol), PPh_3 (121 mg, 0.46 mmol), 4-bromophenylboronic acid (921 mg, 4.59 mmol), and K_3PO_4 (1.27 g, 5.98 mmol) at 80 °C for 15 h. Purification by silica gel column chromatography (hexane/EtOAc = 100:1) gave **3f** (221 mg, 27%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.40 (s, 2H), 7.02 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 8.3 Hz, 2H), 7.44 (dd, J =7.6, 7.4 Hz, 1H), 7.54 (ddd, J = 7.6, 7.4, 1.2 Hz, 1H), 7.85 (dd, J = 7.6, 1.2 Hz, 1H), 10.18 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): 37.6, 120.1, 127.2, 130.5, 131.55, 131.61, 133.2, 133.8, 133.9, 139.3, 142.1, 192.5. IR (neat): ν 3022, 2858, 2742, 1695, 1599, 1485, 1194, 1070, 1011, 748 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{14}H_{11}{}^{79}BrO_2$ $[M]^+$: 273.9988; Found: 273.9976.

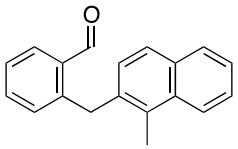
2-[(Naphthalen-2-yl)methyl]benzaldehyde (3g)



Compound **3g** was prepared according to General Procedure B using 2-(bromomethyl)benzaldehyde (600 mg, 3.02 mmol), $Pd(OAc)_2$ (35 mg, 0.15 mmol), PPh_3 (121 mg, 0.46 mmol), (naphthalen-2-yl)boronic acid (781 mg, 4.54 mmol), and K_3PO_4 (1.30 g, 6.12 mmol) at 80 °C for 12 h. Purification by silica gel column chromatography (hexane/EtOAc = 100:1) gave **3g** (363 mg, 49%) as an orange oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.61 (s, 2H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.31 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.40–7.45 (m, 3H), 7.52–7.55 (m, 2H), 7.72–7.74 (m, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.78–7.80 (m, 1H), 7.88 (dd, *J* = 7.6, 1.4 Hz, 1H), 10.28 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): 38.2, 125.5, 126.1, 127.06, 127.13, 127.3, 127.58, 127.60, 128.2, 131.7, 132.1, 132.3, 133.6, 133.9, 134.0, 137.8, 142.8, 192.4. IR (neat): ν 3053, 2854, 2735, 1689, 1597, 1194, 814, 739 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{18}H_{14}O$ $[M]^+$: 246.1039; Found: 246.1048.

2-[(1-Methylnaphthalen-2-yl)methyl]benzaldehyde (3h)



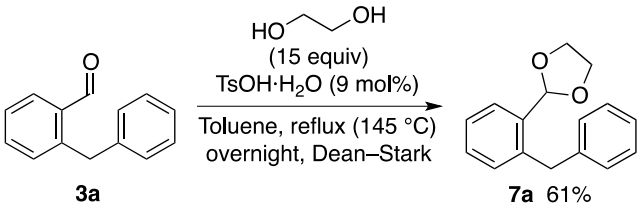
Compound **3h** was prepared according to General Procedure B using 2-(bromomethyl)benzaldehyde (604 mg, 3.04 mmol), $Pd(OAc)_2$ (36 mg, 0.16 mmol), PPh_3 (119 mg, 0.45 mmol), (1-methylnaphthalen-2-yl)boronic acid (845 mg, 4.54 mmol), and K_3PO_4 (1.29 g, 6.08 mmol) at 80 °C for 12 h. Purification by silica gel column chromatography (hexane/EtOAc = 100:1) gave **3h** (380 mg, 48%) as an orange oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.66 (s, 3H), 4.85 (s, 2H), 6.93 (d, *J* = 7.2 Hz, 1H), 7.01–7.02 (m, 1H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.36–7.40 (m, 2H), 7.44–7.47 (m, 1H), 7.50–7.53 (m, 1H), 7.88–7.90 (m, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 10.25 (s, 1H). ^{13}C NMR (126 MHz,

$CDCl_3$): 19.2, 34.8, 124.1, 124.6, 125.4, 125.6, 126.1, 126.5, 126.6, 130.8, 131.8, 131.9, 132.7, 133.1, 133.6, 133.8, 134.0, 142.6, 192.3. IR (neat): ν 3070, 2860, 2735, 1689, 1597, 1572, 1194, 744 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{19}H_{16}O$ $[M]^+$: 260.1196; Found: 260.1191.

2.6.2.3. Preparation of Dioxolane 7

2-(2-Benzylphenyl)-1,3-dioxolane (7a)



3a **7a** 61%

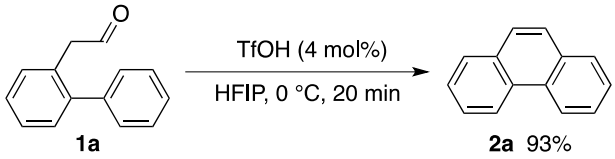
To a toluene (20 mL) solution of 2-benzylbenzaldehyde (**3a**, 381 mg, 1.94 mmol) and ethylene glycol (1.7 mL, 30 mmol) was added $TsOH·H_2O$ (32 mg, 0.17 mmol) was added. The mixture was heated at 145 °C overnight, cooled to room temperature, and dried over Na_2SO_4. The mixture was concentrated under reduced pressure and filtered with Et_2O. After removal of the solvent, the residue was purified by silica gel column chromatography (hexane/NEt_3/EtOAc = 100:3:2) gave **7a** (284 mg, 61%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.97–4.03 (m, 2H), 4.09–4.16 (m, 2H), 4.17 (s, 2H), 5.94 (s, 1H), 7.10 (dd, *J* = 7.0, 1.6 Hz, 1H), 7.14–7.20 (m, 3H), 7.26–7.30 (m, 4H), 7.61 (dd, *J* = 7.2, 1.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 37.8, 65.2, 101.7, 126.0, 126.1, 126.4, 128.4, 128.9, 129.2, 130.6, 135.5, 139.1, 140.5. IR (neat): ν 3026, 2885, 1495, 1452, 1111, 1066, 943, 729, 696 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{16}H_{16}O_2$ $[M]^+$: 240.1145; Found: 240.1144.

2.6.3. Synthesis of Polycyclic Aromatic Hydrocarbons

2.6.3.1. Synthesis of Phenacenes 2

Phenanthrene (2a)

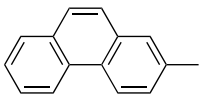


To an HFIP (3 mL) solution of (biphenyl-2-yl)acetaldehyde (**1a**, 63 mg, 0.32 mmol) was added trifluoromethanesulfonic acid (1.1 μL, 12 μmol) at 0 °C. After stirring at the same temperature for 20 min, the reaction was quenched with phosphate buffer (pH 7). Organic materials were extracted with CH_2Cl_2 three times, and the combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 30:1) to give phenanthrene (**2a**, 54 mg, 93%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (ddd, *J* = 7.8, 7.0, 1.2 Hz, 2H), 7.65 (ddd, *J* = 8.2, 7.0, 1.5 Hz, 2H), 7.73 (s, 2H), 7.89 (ddd, *J* = 7.8, 1.5, 0.5 Hz, 2H), 8.68 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 122.6, 126.54, 126.54, 126.9, 128.6, 130.3, 132.0.

Spectral data for this compound showed good agreement with the literature data.[7]

2-Methylphenanthrene (2b)



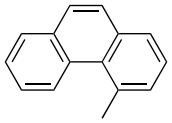
Phenanthrene **2b** was synthesized by the method described for **2a** using (4'-methylbiphenyl-2-yl)acetaldehyde (**1b**, 66 mg, 0.31 mmol), trifluoromethanesulfonic acid (1.1 μL, 12 μmol), and HFIP (3 mL). Purification by silica gel column chromatography (hexane/CH_2Cl_2 = 5:1) gave phenanthrene **2b** (59 mg, 98%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.56 (s, 3H), 7.48 (d, 8.4 Hz, 1H), 7.56 (dd, 7.7, 7.4 Hz, 1H), 7.63 (dd, 8.1, 7.4 Hz, 1H), 7.66–7.71 (m, 3H), 7.86 (d, *J* = 7.8 Hz, 1H), 8.57 (d, *J* = 8.4 Hz, 1H), 8.64 (d,

J = 8.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.4, 122.4, 122.5, 126.1, 126.5, 126.7, 126.9, 128.11, 128.14, 128.3, 128.5, 130.3, 131.7, 132.2, 136.3.

Spectral data for this compound showed good agreement with the literature data.[6]

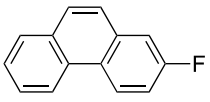
4-Methylphenanthrene (2c)



Phenanthrene **2c** was synthesized by the method described for **2a** using (2'-methylbiphenyl-2-yl)acetaldehyde (**1c**, 63 mg, 0.30 mmol), trifluoromethanesulfonic acid (2.6 μL, 30 μmol), and HFIP (3 mL). Purification by silica gel column chromatography (hexane) gave phenanthrene **2c** (54 mg, 95%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.09 (s, 3H), 7.43–7.44 (m, 2H), 7.53–7.59 (m, 2H), 7.64–7.68 (m, 2H), 7.70–7.73 (m, 1H), 7.86 (dd, J = 7.7, 1.6 Hz, 1H), 8.87 (d, J = 8.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 27.3, 125.5, 125.7, 125.8, 127.0, 127.4, 127.5, 128.0, 128.7, 130.0, 131.2, 131.6, 133.4, 133.7, 135.5. IR (neat): ν 3049, 2962, 2875, 1439, 1215, 1165, 1132, 1103, 820, 735, 708 cm^{-1}. HRMS (EI): m/z Calcd. for $C_{15}H_{12}$ $[M]^+$: 192.0934; Found: 192.0938.

2-Fluorophenanthrene (2d)



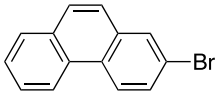
Phenanthrene **2d** was synthesized by the method described for **2a** using (4'-fluorobiphenyl-2-yl)acetaldehyde (**1d**, 65 mg, 0.30 mmol), trifluoromethanesulfonic acid (3.7 μL, 42 μmol), and HFIP (3 mL). Purification by silica gel column chromatography (hexane/CH_2Cl_2 = 20:1) gave phenanthrene **2d** (59 mg, 99%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (ddd, J = 8.9 Hz, J_{HF} = 8.7 Hz, J = 2.7 Hz, 1H), 7.51 (dd, J_{HF} = 9.4 Hz, J = 2.7 Hz, 1H), 7.58 (dd, J = 7.6, 7.4 Hz, 1H), 7.63–7.66 (m, 2H), 7.76 (d, J = 8.8 Hz, 1H),

7.88 (d, J = 7.6 Hz, 1H), 8.59 (d, J = 8.2 Hz, 1H), 8.64 (dd, J = 8.9 Hz, J_{HF} = 5.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 112.5 (d, J_{CF} = 20 Hz), 115.4 (d, J_{CF} = 24 Hz), 122.4, 125.0 (d, J_{CF} = 9 Hz), 126.1 (d, J_{CF} = 4 Hz), 126.4, 126.9 (d, J_{CF} = 2 Hz), 127.0, 128.2, 128.7, 130.1, 131.5, 133.4 (d, J_{CF} = 9 Hz), 161.3 (d, J_{CF} = 247 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 46.49–46.54 (m).

Spectral data for this compound showed good agreement with the literature data.[8]

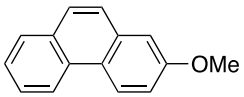
2-Bromophenanthrene (2e)



Phenanthrene **2e** was synthesized by the method described for **2a** using (4'-bromobiphenyl-2-yl)acetaldehyde (**1e**, 1.97 g, 7.16 mmol), trifluoromethanesulfonic acid (90 μL, 1.0 mmol), and HFIP (72 mL). Purification by silica gel column chromatography (hexane/CH_2Cl_2 = 5:1) gave phenanthrene **2e** (1.83 g, 99%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56–7.64 (m, 3H), 7.67 (dd, J = 8.8, 2.1 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.98 (d, J = 2.1 Hz, 1H), 8.45 (d, J = 8.8 Hz, 1H), 8.55 (d, J = 8.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 120.5, 122.5, 124.4, 125.7, 126.9, 127.0, 128.1, 128.7, 128.9, 129.6, 129.9, 130.6, 131.8, 133.4. IR (neat): ν 3014, 1593, 1454, 1215, 1078, 883, 849, 808, 741, 667 cm^{-1}. HRMS (EI): m/z Calcd. for $C_{14}H_9{}^{79}Br$ $[M]^+$: 255.9882; Found: 255.9874.

2-Methoxyphenanthrene (2f)

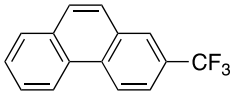


Phenanthrene **2f** was synthesized by the method described for **2a** using (4'-methoxybiphenyl-2-yl)acetaldehyde (**1f**, 68 mg, 0.30 mmol), trifluoromethanesulfonic acid (3.7 μL, 42 μmol), and HFIP (3 mL). Purification by silica gel column chromatography (hexane/CH_2Cl_2 = 20:1) gave phenanthrene **2f** (63 mg, quant.) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.96 (s, 3H), 7.25–7.30 (m, 2H), 7.53 (ddd, *J* = 7.5, 7.4, 0.7 Hz, 1H), 7.62 (ddd, *J* = 7.8, 7.5, 1.2 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.86 (dd, *J* = 7.8, 0.7 Hz, 1H), 8.58–8.59 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 55.4, 108.6, 117.1, 122.1, 124.2, 124.6, 125.6, 126.4, 126.6, 127.5, 128.5, 130.4, 131.0, 133.4, 158.3.

Spectral data for this compound showed good agreement with the literature data.[6]

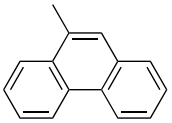
2-(Trifluoromethyl)phenanthrene (2g)



Phenanthrene **2g** was synthesized by the method described for **2a** using [4'-(trifluoromethyl)biphenyl-2-yl]acetaldehyde (**1g**, 80 mg, 0.30 mmol), trifluoromethanesulfonic acid (9.3 μL, 0.11 mmol), and HFIP (3 mL) at 0 °C for 80 min. Purification by silica gel column chromatography (hexane/CH_2Cl_2 = 20:1) gave phenanthrene **2g** (71 mg, 96%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (ddd, *J* = 7.5, 7.4, 1.35 Hz, 1H), 7.70 (ddd, *J* = 7.8, 7.4, 1.6 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.82 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.91 (dd, *J* = 7.5, 1.6 Hz, 1H), 8.15 (s, 1H), 8.67 (d, *J* = 7.8 Hz, 1H), 8.74 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 122.4 (q, J_{CF} = 3 Hz), 123.0, 123.5, 124.4 (q, J_{CF} = 273 Hz), 125.8 (q, J_{CF} = 4 Hz), 126.6, 127.1, 127.7, 128.3 (q, J_{CF} = 33 Hz), 128.4, 128.7, 129.6, 131.3, 132.3, 132.7. ^{19}F NMR (470 MHz, $CDCl_3$): δ 99.7 (s). IR (neat): ν 3018, 1329, 1292, 1215, 1113, 1076, 903, 818, 750 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{15}H_9F_3$ $[M]^+$: 246.0651; Found: 246.0641.

9-Methylphenanthrene (2h)



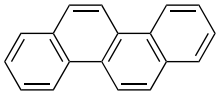
Phenanthrene **2h** was synthesized by the method described for **2a** using 2-(biphenyl-2-yl)propanal (**1h**, 67 mg, 0.32 mmol), trifluoromethanesulfonic acid (1.1 μL, 12 μmol),

and HFIP (3 mL) . Purification by silica gel column chromatography (hexane/CH_2Cl_2 = 20:1) gave phenanthrene **2h** (57 mg, 92%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.67 (s, 3H), 7.50–7.56 (m, 3H), 7.58–7.62 (m, 2H), 7.75 (d, *J* = 7.4 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 8.59 (d, *J* = 7.5 Hz, 1H), 8.66 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 20.0, 122.4, 123.0, 124.6, 125.8, 126.2, 126.46, 126.52, 126.7, 127.8, 129.6, 130.3, 131.98, 132.04, 132.4.

Spectral data for this compound showed good agreement with the literature data.[6]

Chrysene (2i)

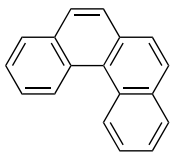


Chrysene (**2i**) was synthesized by the method described for **2a** using 2-(naphthalen-2-yl)phenylacetaldehyde (**1i**, 74 mg, 0.30 mmol), trifluoromethanesulfonic acid (2.6 μL, 30 μmol), and HFIP (3 mL) at 0 °C for 80 min. Purification by silica gel column chromatography (hexane/CH_2Cl_2 = 20:1) gave chrysene (**2i**, 66 mg, 96%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62–7.65 (m, 2H), 7.69–7.72 (m, 2H), 7.98–8.01 (m, 4H), 8.72 (d, *J* = 9.0 Hz, 2H), 8.78 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 121.2, 123.1, 126.4, 126.7, 127.3, 128.2, 128.5, 130.6, 132.2.

Spectral data for this compound showed good agreement with the literature data.[8]

[4]Helicene (2j)



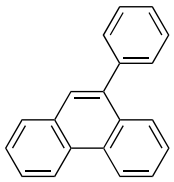
Helicene **2j** was synthesized by the method described for **2a** using 2-(naphthalen-1-yl)phenylacetaldehyde (**1j**, 75 mg, 0.30 mmol), trifluoromethanesulfonic acid (2.6 μL, 30 μmol), and HFIP (3 mL) at 0 °C for 80 min. Purification by silica gel column

chromatography (hexane/EtOAc = 100:1) gave helicene **2j** (64 mg, 92%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (dd, *J* = 7.8, 7.2 Hz, 2H), 7.77 (dd, *J* = 8.4, 7.2 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 8.10 (d, *J* = 7.8 Hz, 2H), 9.25 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 125.8, 126.0, 126.8, 127.3, 127.4, 127.8, 128.5, 130.2, 130.9, 133.4.

Spectral data for this compound showed good agreement with the literature data.[6]

9-Phenylphenanthrene (2k)

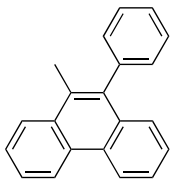


Phenanthrene **2k** was synthesized by the method described for **2a** using 2-(biphenyl-2-yl)-1-phenylethan-1-one (**1k**, 67 mg, 0.25 mmol), trifluoromethanesulfonic acid (3.3 μL, 37 μmol), and HFIP (3 mL) at 45 °C for 1.5 h. Purification by silica gel column chromatography (hexane) gave phenanthrene **2k** (52 mg, 82%) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.47 (m, 1H), 7.50–7.56 (m, 5H), 7.60–7.69 (m, 3H), 7.69 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 8.72 (d, *J* = 8.2 Hz, 1H) 8.78 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 122.5, 122.9, 126.4, 126.5, 126.6, 126.8, 126.9, 127.3, 127.5, 128.3, 128.6, 129.9, 130.0, 130.6, 131.1, 131.5, 138.8, 140.8.

Spectral data for this compound showed good agreement with the literature data.[9]

9-Methyl-10-phenylphenanthrene (2l)



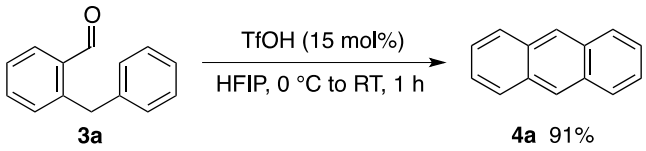
Phenanthrene **2l** was synthesized by the method described for **2a** using 2-(biphenyl-2-yl)-1-phenylpropan-1-one (**1l**, 86 mg, 0.30 mmol), trifluoromethanesulfonic acid (3.9 μL, 45 μmol), and HFIP (3 mL) at 45 °C for 1.5 h. Purification by silica gel column

chromatography (hexane/EtOAc = 100:1) gave phenanthrene **2l** (47 mg, 58%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 3H), 7.27–7.29 (m, 2H), 7.35–7.45 (m, 3H), 7.48–7.51 (m, 2H), 7.53–7.56 (m, 1H), 7.62–7.67 (m, 2H), 8.11–8.14 (m, 1H), 8.70 (dd, *J* = 8.2, 0.4 Hz, 1H), 8.73–8.76 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 17.3, 122.3, 122.8, 125.1, 125.6, 126.2, 126.3, 126.8, 127.0, 127.4, 128.4, 129.3, 129.8, 129.9, 130.3, 131.9, 132.3, 137.0, 140.7.

Spectral data for this compound showed good agreement with the literature data.[10]

2.6.3.2. Synthesis of Acenes 4

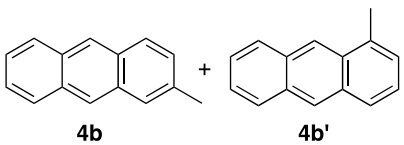
Anthracene (4a)



To an HFIP (3 mL) solution of 2-benzylbenzaldehyde (**3a**, 59 mg, 0.30 mmol) was added trifluoromethanesulfonic acid (4.0 μL, 45 μmol) at 0 °C. After stirring at room temperature for 1 h, the reaction was quenched with phosphate buffer (pH 7). Organic materials were extracted with CH_2Cl_2 three times, and the combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 20:1) to give anthracene (**4a**, 49 mg, 91%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.47 (m, 4H), 7.98–8.01 (m, 4H), 8.41 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 125.3, 126.2, 128.1, 131.7.

Spectral data for this compound showed good agreement with the literature data.[11]

2-Methylanthracene (4b) and 1-Methylanthracene (4b')



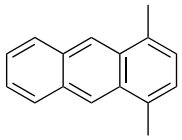
A mixture of anthracenes **4b** and **4b'** was synthesized by the method described for **4a** using

2-(3-methylbenzyl)benzaldehyde (**3b**, 64 mg, 0.30 mmol), trifluoromethanesulfonic acid (4.0 μL, 45 μmol), and HFIP (3 mL). Purification by silica gel column chromatography (hexane/CH_2Cl_2 = 20:1) gave a mixture of anthracenes **4b** and **4b'** (52 mg, 90%, **4b**/**4b'** = 96:4) as a pale yellow solid.

4b: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.52 (s, 3H), 7.28 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.39–7.44 (m, 2H), 7.72 (s, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.94–7.96 (m, 2H), 8.28 (s, 1H), 8.35 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 22.0, 124.9, 125.1, 125.2, 125.9, 126.3, 127.9, 128.0, 128.16, 128.23, 130.3, 131.2, 131.8, 132.0, 134.9.

Spectral data for this compound showed good agreement with the literature data.[11]

1,4-Dimethylanthracene (4c)

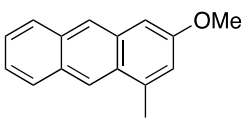


Anthracene **4c** was synthesized by the method described for **4a** using 2-(2,5-dimethylbenzyl)benzaldehyde (**3c**, 68 mg, 0.30 mmol), trifluoromethanesulfonic acid (4.0 μL, 45 μmol), and HFIP (3 mL). Purification by silica gel column chromatography (hexane/CH_2Cl_2 = 20:1) gave anthracene **4c** (59 mg, 95%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.72 (s, 6H), 7.13 (s, 2H), 7.41–7.44 (m, 2H), 7.96–7.99 (m, 2H), 8.47 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 19.7, 123.2, 125.25, 125.34, 128.2, 131.1, 131.5, 132.3.

Spectral data for this compound showed good agreement with the literature data.[12]

3-Methoxy-1-methylanthracene (4d)

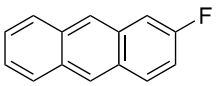


Anthracene **4d** was synthesized by the method described for **4a** using 2-(4-methoxy-2-methylbenzyl)benzaldehyde (**3d**, 72 mg, 0.30 mmol), trifluoromethanesulfonic acid

(4.0 μL, 45 μmol), and HFIP (3 mL) at room temperature for 48 h. Purification by silica gel column chromatography (hexane/CH_2Cl_2 = 20:1) gave anthracene **4d** (49 mg, 73%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.71 (s, 3H), 3.88 (s, 3H), 6.98 (s, 1H), 7.00 (s, 1H), 7.36–7.43 (m, 2H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 8.19 (s, 1H), 8.38 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 19.5, 55.0, 101.9, 120.6, 122.8, 124.3, 124.7, 125.5, 127.3, 128.1, 128.5, 130.1, 131.9, 133.1, 136.2, 156.7. IR (neat): ν 2924, 1628, 1462, 1410, 1203, 1163, 877, 742, 735 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{16}H_{14}O$ $[M]^+$: 222.1039; Found: 222.1037.

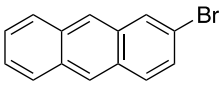
2-Fluoroanthracene (4e)



Anthracene **4e** was synthesized by the method described for **4a** using 2-(4-fluorobenzyl)benzaldehyde (**3e**, 64 mg, 0.30 mmol), trifluoromethanesulfonic acid (4.0 μL, 45 μmol), and HFIP (3 mL) at reflux for 18 h. Purification by silica gel column chromatography (hexane/CH_2Cl_2 = 20:1) gave anthracene **4e** (26 mg, 45%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (ddd, J_{HF} = 8.8 Hz, *J* = 8.8, 2.3 Hz, 1H), 7.43–7.49 (m, 2H), 7.56 (dd, J_{HF} = 10.1 Hz, *J* = 2.1 Hz, 1H), 7.94–7.99 (m, 3H), 8.32 (s, 1H), 8.40 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 109.7 (d, J_{CF} = 20 Hz), 117.2 (d, J_{CF} = 28 Hz), 125.2, 125.4 (d, J_{CF} = 7 Hz), 126.0, 126.6 (d, J_{CF} = 1 Hz), 127.7, 128.2, 129.0, 130.9 (d, J_{CF} = 9 Hz), 131.1 (d, J_{CF} = 3 Hz), 131.7 (d, J_{CF} = 9 Hz), 132.2, 160.1 (d, J_{CF} = 248 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 47.4–47.5 (m). IR (neat): ν 3018, 1215, 750, 669 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{14}H_9O$ $[M]^+$: 196.0683; Found: 196.0685.

2-Bromoanthracene (4f)



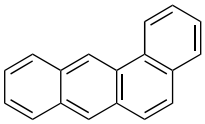
Anthracene **4f** was synthesized by the method described for **4a** using 2-(4-bromobenzyl)benzaldehyde (**3f**, 82 mg, 0.30 mmol), trifluoromethanesulfonic acid (4.0 μL, 45

μmol), and HFIP (3 mL) at reflux for 48 h. Purification by silica gel column chromatography (hexane/CH_2Cl_2 = 20:1) gave anthracene **4f** (46 mg, 60%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47–7.51 (m, 3H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.96–8.00 (m, 2H), 8.16 (s, 1H), 8.31 (s, 1H), 8.38 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 119.4, 125.3, 125.8, 126.0, 126.6, 128.1, 128.2, 128.8, 129.76, 129.81, 129.9, 131.8, 132.1, 132.3.

Spectral data for this compound showed good agreement with the literature data.[12]

Tetraphene (4g)

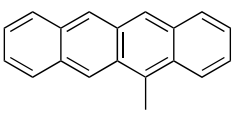


Tetraphene (**4g**) was synthesized by the method described for **4a** using 2-[(naphthalen-2-yl)methyl]benzaldehyde (**3g**, 74 mg, 0.30 mmol), trifluoromethanesulfonic acid (4.0 μL, 45 μmol), and HFIP (3 mL). Purification by silica gel column chromatography (hexane/CH_2Cl_2 = 20:1) gave tetraphene (**4g**, 66 mg, 97%) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48–7.53 (m, 2H), 7.55–7.58 (m, 2H), 7.63 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.79 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.97–7.99 (m, 1H), 8.05–8.07 (m, 1H), 8.29 (s, 1H), 8.76 (d, *J* = 8.1 Hz, 1H), 9.09 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 121.5, 122.9, 125.6, 125.7, 126.7, 126.8, 127.02, 127.02, 127.3, 127.7, 128.4, 128.6, 128.8, 130.5, 130.6, 131.88, 131.92, 131.92.

Spectral data for this compound showed good agreement with the literature data.[11]

5-Methyltetracene (4h)

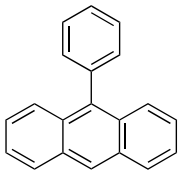


Tetracene **4h** was synthesized by the method described for **4a** using 2-[(1-methylnaphthalen-2-yl)methyl]benzaldehyde (**3h**, 78 mg, 0.30 mmol),

trifluoromethanesulfonic acid (4.0 μL, 45 μmol), and HFIP (3 mL) in the dark. Purification by silica gel column chromatography (hexane/CH_2Cl_2 = 20:1) gave tetracene **4h** (65 mg, 89%) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.62 (s, 3H), 7.45–7.50 (m, 2H), 7.53 (s, 1H), 7.59–7.65 (m, 2H), 7.94–7.96 (m, 2H), 8.02–8.05 (m, 1H), 8.16 (s, 1H), 8.79 (dd, *J* = 7.6, 1.7 Hz, 1H), 9.04 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 20.1, 121.3, 123.1, 124.7, 125.2, 125.62, 125.63, 126.5, 126.7, 127.0, 127.6, 128.4, 128.5, 130.6, 130.7, 131.5, 132.1, 132.3, 132.4. IR (neat): ν 2922, 2856, 1030, 899, 883 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{19}H_{14}$ $[M]^+$: 242.1090; Found: 242.1097.

9-Phenylanthracene (4i)



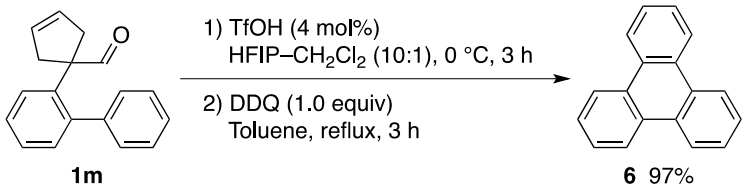
Anthracene **4i** was synthesized by the method described for **4a** using (2-benzylphenyl)(phenyl)methanone (**3i**, 83 mg, 0.30 mmol), trifluoromethanesulfonic acid (4.0 μL, 45 μmol), and HFIP (3 mL) at reflux for 36 h. Purification by silica gel column chromatography (hexane) gave anthracene **4i** (58 mg, 76%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (dd, *J* = 8.6, 6.7 Hz, 2H), 7.41–7.44 (m, 4H), 7.48–7.52 (m, 1H), 7.53–7.57 (m, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 2H), 8.46 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 125.1, 125.3, 126.5, 126.8, 127.4, 128.30, 128.32, 130.2, 131.2, 131.3, 137.0, 138.8.

Spectral data for this compound showed good agreement with the literature data.[11]

2.6.3.3. Synthesis of Triphenylene (6)

Triphenylene (6)



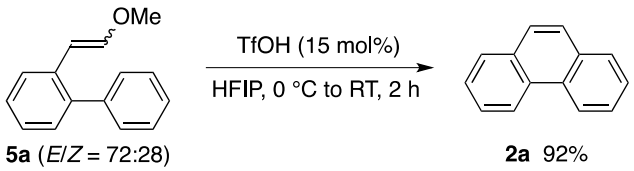
After 1-(biphenyl-2-yl)cyclopent-3-ene-1-carbaldehyde (**1m**, 75 mg, 0.30 mmol) was dissolved in HFIP (2.0 mL) and CH_2Cl_2 (0.2 mL), trifluoromethanesulfonic acid (1.1 μL, 12 μL) was added at 0 °C. After stirring at the same temperature for 3 h, the solvent was removed under reduced pressure. The residue was dissolved in toluene (3 mL), and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 70 mg, 0.31 mmol) was added to the mixture. After being heated to reflux for 3 h, the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (hexane) to give triphenylene (**6**, 67 mg, 97%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (dd, *J* = 6.2, 3.3 Hz, 6H), 8.63 (dd, *J* = 6.2, 3.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 123.3, 127.2, 129.8.

Spectral data for this compound showed good agreement with the literature data.[13]

2.6.3.4. Cyclization of Aldehyde Analogues 5 and 7

Cyclization of (Biphenyl-2-yl)vinyl Ether 5a

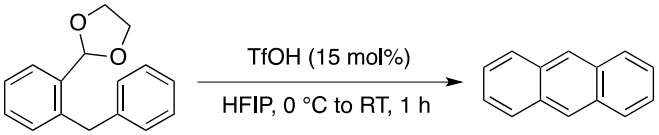


To an HFIP (3 mL) solution of 2-(2-methoxyvinyl)biphenyl (**5a**, 63 mg, 0.30 mmol) was added trifluoromethanesulfonic acid (4.0 μL, 45 μmol) at 0 °C. After stirring at the room temperature for 2 h, the reaction was quenched with phosphate buffer (pH 7). Organic materials were extracted with CH_2Cl_2 three times, and the combined extracts were washed with brine and

dried over Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 50:1) to give phenanthrene (**2a**, 49 mg, 92%) as a white solid.

Spectral data for this compound showed good agreement with the data of **2a** synthesized from **1a**.

Cyclization of (2-Benzylphenyl)dioxolane 7a



7a **4a** 97%

To an HFIP (3 mL) solution of 2-(2-benzylphenyl)-1,3-dioxolane (**7a**, 72 mg, 0.30 mmol) was added trifluoromethanesulfonic acid (4.0 μL, 45 μmol) at 0 °C. After stirring at the room temperature for 1 h, the reaction was quenched with phosphate buffer (pH 7). Organic materials were extracted with CH_2Cl_2 three times, and the combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 20:1) gave anthracene (**4a**, 52 mg, 97%) as a white solid.

Spectral data for this compound showed good agreement with the data of **4a** synthesized from **3a**.

2.6.4. References

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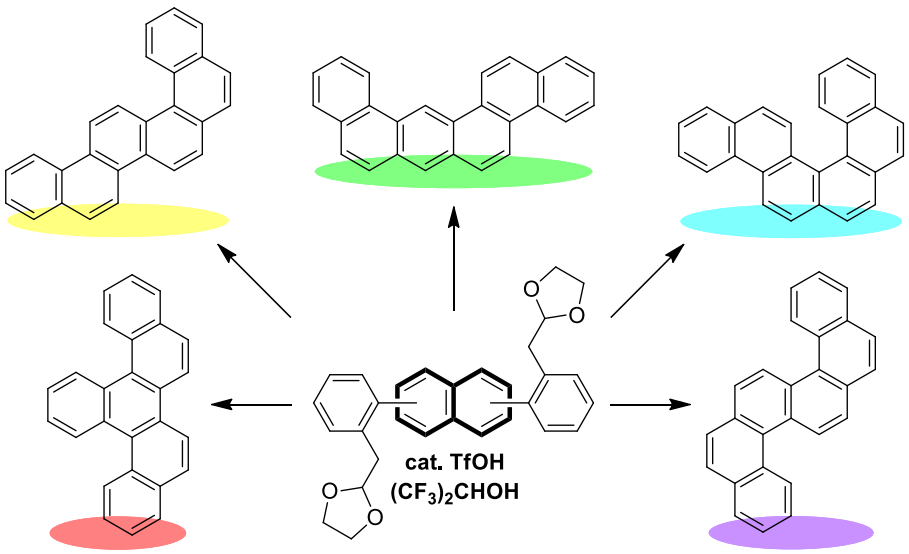
Chapter 3

Brønsted Acid-catalyzed Tandem Cycloaromatization of Naphthalene-Based Bisacetals

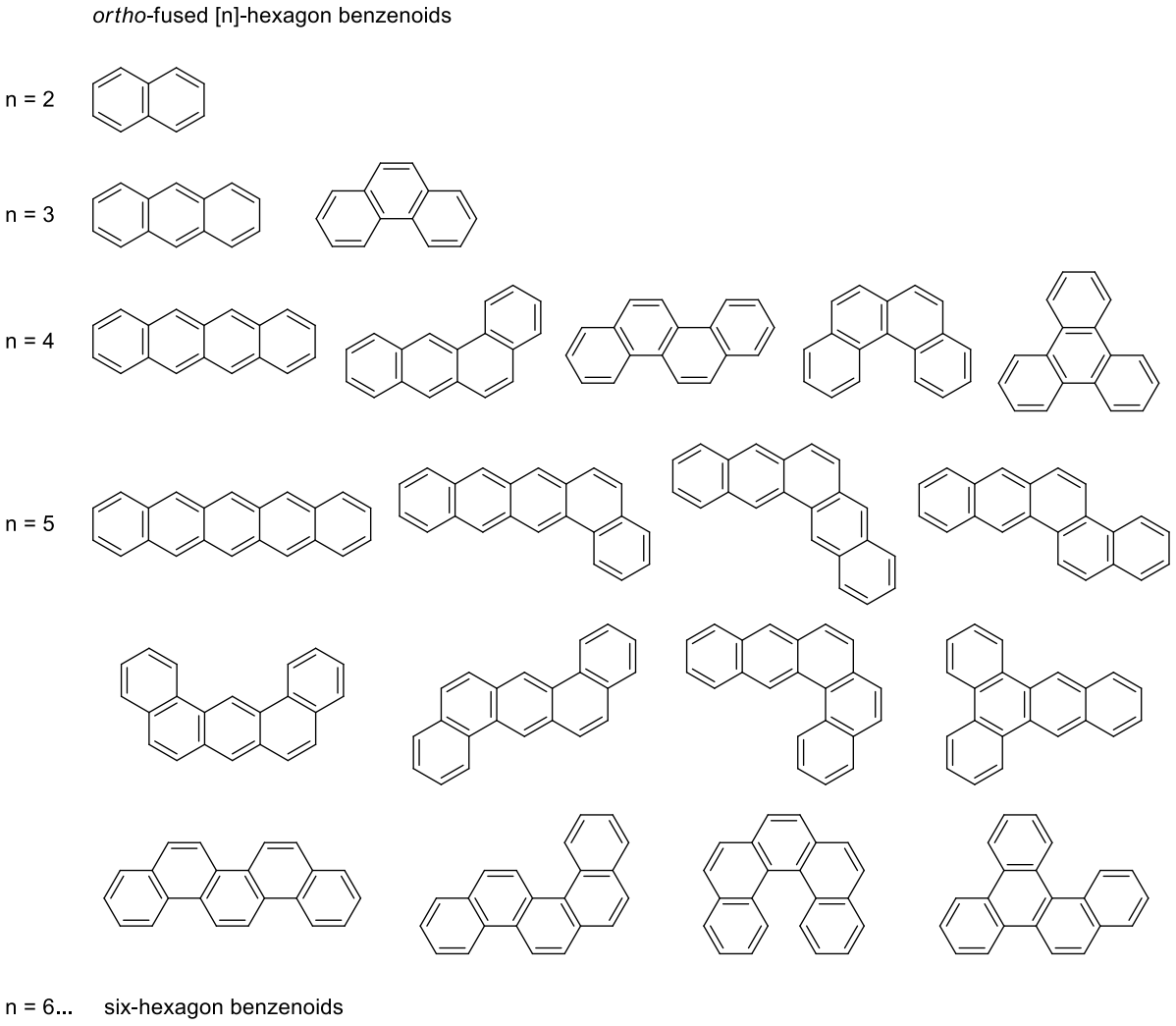
Abstract

Naphthalenes bearing two acetal moieties connected by a methylene-2,1-phenylene group underwent regioselective tandem cycloaromatization using a catalytic amount of trifluoromethanesulfonic acid in 1,1,1,3,3,3-hexafluoropropan-2-ol. Five substrates were successfully employed in this protocol to afford ortho-fused six-hexagon benzenoids with high selectivities and in excellent yields.



3.1. Introduction

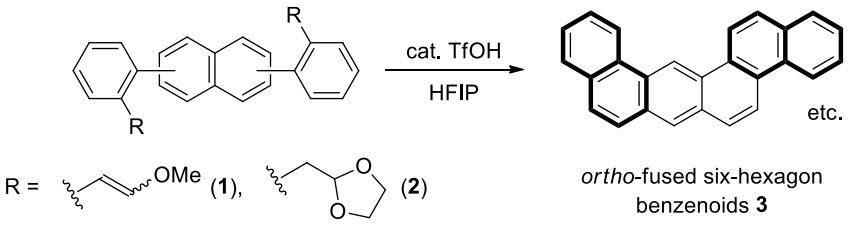
Polycyclic aromatic hydrocarbons (PAHs) have polyform structures comprising benzene rings, and are considered to be promising candidates for functional materials such as electronic devices.[1] As the number of benzene rings in PAHs increases, the number of structural isomers exponentially increases (Figure 1). Although PAHs of substantial sizes have numerous isomers, research has typically focused on isomers of specific families such as acenes,[1b–d,2] phenacenes,[1d,e,3] and helicenes,[1f,4] and not on other *ortho*-fused isomers despite their great potential.[5]



Fugure 1. Number of structual isomers of *ortho*-fused benzenoids.

In Chapter 2, I developed a Brønsted acid-catalyzed cycloaromatization of carbonyl compounds, resulting in the synthesis of phenanthrene and anthracene derivatives.[6] Since the method served as a powerful tool for benzene-ring construction, I embarked on the synthesis of PAHs in a variety of shapes via double cycloaromatization of substrates bearing two reactive sites.[7] This protocol would enable rapid access to higher-order PAHs by simultaneous construction of multiple fused benzene rings.

I selected naphthalenes **1** and **2** bearing two phenylacetaldehyde-related moieties as cyclization precursors (Scheme 1). Their tandem cycloaromatization afforded *ortho*-fused benzenoids, with the structure depending on the substitution pattern on the naphthalene ring. As a result, five predicted isomers of the *ortho*-fused benzenoids bearing six benzene rings were selectively synthesized in excellent yields from readily available cyclization precursors.

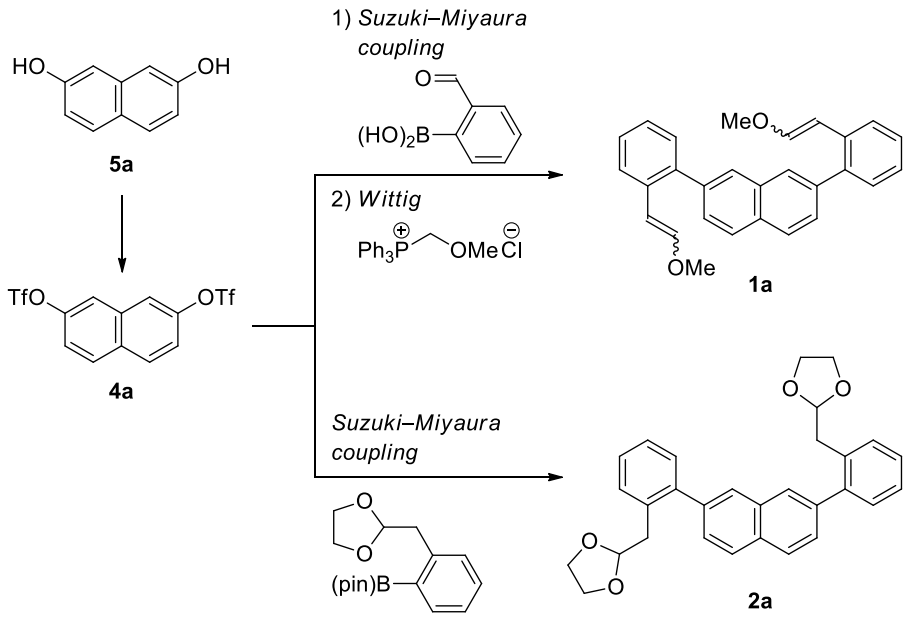


Scheme 1. Synthesis of *ortho*-fused six-hexagon benzenoids via TfOH-catalyzed tandem cycloaromatization

3.2. Preparation of Precursors for Tandem Cycloaromatization

The cyclization precursors **1a** and **2a** bearing two phenylacetaldehyde-related moieties on the 2- and 7-positions of the naphthalene ring were readily available starting from naphthalene-2,7-diyl bis(trifluoromethanesulfonate) (**4a**), which was obtained via double *O*-sulfonylation of naphthalene-2,7-diol (**5a**). Bis(vinyl ether) **1a** was prepared via the Suzuki–Miyaura cross-coupling of **4a** with (2-formylphenyl)boronic acid, followed by a Wittig reaction with (methoxymethyl)triphenylphosphonium chloride. Although hydrolysis of **1a** afforded the corresponding dial, it was unstable for use in the subsequent cycloaromatization. In contrast, bisacetal **2a** was directly prepared via the Suzuki–Miyaura cross-coupling of **4a** with

2-[(1,3-dioxolan-2-yl)methyl]phenylboronic acid pinacolate. Other bisacetal precursors **2b**–**e** were also prepared similarly.



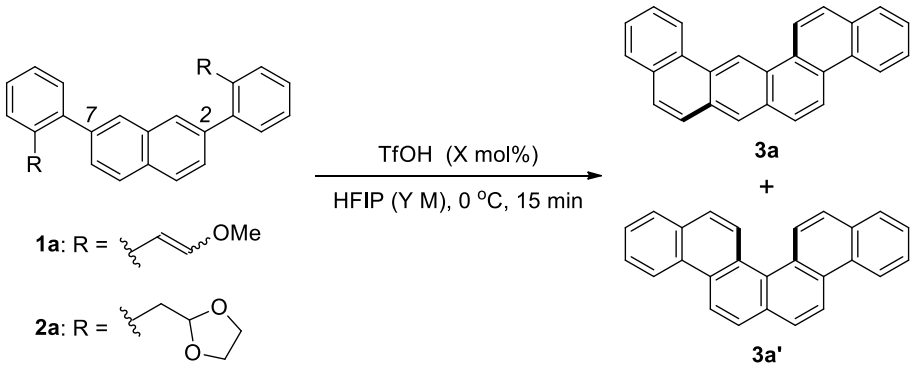
Scheme 2. Preparation of bis(vinyl ether) **1a** and bisacetal **2a**.

3.3. Synthesis of *ortho*-Fused Benzenoids via Brønsted Acid-Catalyzed Tandem Cycloaromatization

I sought suitable conditions for tandem cycloaromatization of bis(vinyl ether) **1a**[7k,8] and bisacetal **2a**[9] as model substrates (Table 1). First, the reaction of **1a** was investigated using a catalytic amount of trifluoromethansulfonic acid (TfOH) and 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) as a solvent.[10] On treatment with 15 mol% of TfOH at 0.05 M in HFIP, bis(vinyl ether) **1a** underwent tandem cycloaromatization to afford dibenzo[*c*,*m*]tetraphene (**3a**)[11] and naphtho[1,2-*c*]chrysene (**3a'**) in 79% total yield and in a 75:25 ratio (Entry 1).[12] Neither more concentrated nor more diluted conditions improved the total yield of **3a** and **3a'** (Entries 2 and 3). In contrast, when bisacetal **2a** at 0.1 or 0.3 M in HFIP was treated with 15 mol% of TfOH, the product yield and ratio significantly improved to afford **3a** exclusively in almost quantitative yields (Entries 4 and 5). The efficiency and selectivity remained excellent even when the amount of TfOH was

reduced to 10 mol% (Entry 7). The selective formation of **3a** is attributed to the following factors: (i) the first cycloaromatization would proceed at the α-position of the naphthalene core in accordance with the regioselectivity observed in normal electrophilic aromatic substitution reactions and (ii) the second cycloaromatization might proceed avoiding steric hindrance, which explains the better selectivity of bisacetal **2a**.

Table 1. Screening of conditions for tandem cycloaromatization of **1a** and **2a**.



Entry	**1a** or **2a**	X (mol %)	Y (M)	Total yield (%)[a]	**3a**/**3a'**[b]
1	**1a**[c]	15	0.05	79	75:25
2	**1a**[c]	15	0.03	80	75:25
3	**1a**[c]	15	0.1	71	70:30
4	**2a**	15	0.1	quant.	>99:<1
5	**2a**	15	0.3	quant.	>99:<1
6	**2a**	15	1.0	86	97:7
7	**2a**	10	0.3	quant. (97)	>99:<1
8	**2a**	3	0.3	77	>99:<1

[a] Yield was determined by ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard. Isolated yield was shown in parentheses. [b] Isomer ratio was determined by ^{1}H NMR spectroscopy. [c] *EE*/*EZ*/*ZZ* = 37:55:8.

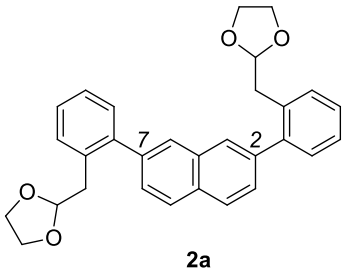
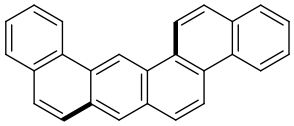
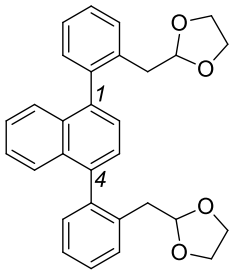
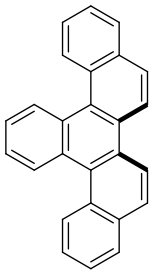
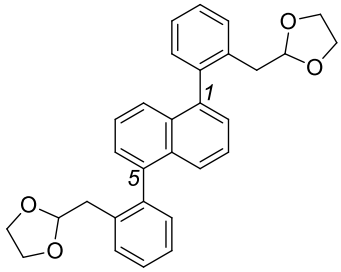
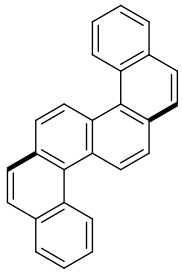
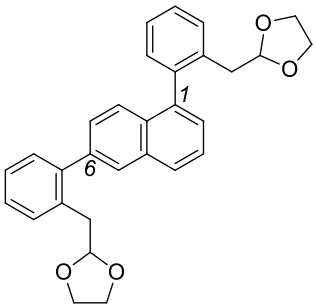
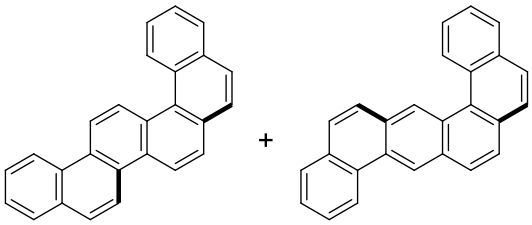
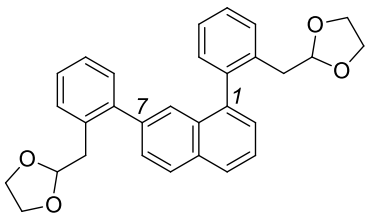
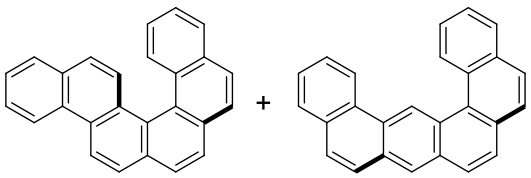
Not only bisacetal **2a** but also bisacetals **2b**–**e** participated in the tandem cycloaromatization under the above-mentioned optimal conditions (Table 2). Naphthalenes **1b** and **1c**, bearing two phenylacetaldehyde acetal moieties on the 1,4- and 1,5-positions, respectively, successfully underwent tandem cycloaromatization to afford benzo[*s*]picene (**3b**)[13] and dibenzo[*c*,*l*]chrysene (**3c**)[14] as the only products in 84% and 99% yields, respectively (Entries 4

and 5). Although the reactions of **1b** and **1c** required cycloaromatization on the less reactive β-positions of the naphthalene core in the first cyclization, benzenoids **3b** and **3c** were obtained in high to excellent yields. Tandem cycloaromatization of 1,6- and 1,7-disubstituted naphthalenes **2d** and **2e** also proceeded to afford benzo[*a*]picene (**3d**)[11] and naphtho[2,1-*c*]chrysene (**3e**),[15] respectively, as major products (Entries 4 and 5). In each case, one of two possible products was selectively formed, presumably because regioselective cycloaromatization proceeded preferably on the α-position of the naphthalene core in the first cyclization.

3.4. Conclusion

In summary, I achieved a systematic synthesis of a series of rarely offered *ortho*-fused six-hexagon benzenoids via TfOH-catalyzed tandem cycloaromatization of naphthalene-based bisacetals. With a similar protocol, the use of benzenoids larger than naphthalene as platforms will enable the synthesis of more extensive *ortho*-fused benzenoids.

Table 2. Synthesis of *ortho*-fused six-hexagon benzenoids **3**.[a]

Entry	Bisacetal **2**	Product **3**
1	 **2a**	 **3a** 97%
2	 **2b**	 **3b** 84%
3	 **2c**	 **3c** 99%
4	 **2d**	 **3d** + **3d'** 95% (98:2)[b]
5	 **2e**	 **3e** + **3e'** 87% (93:7)[b]

[a] Isolated yield. [b] Product ratio was determined by ^{1}H NMR sectroscopy.

3.5. References and Notes

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[3] For selected reports on phenacene synthesis, see: (a) Mallory, F. B.; Butler, K. E.; Evans, A. C.; Brondyke, E. J.; Mallory, C. W.; Yang, C.; Ellenstein, A. *J. Am. Chem. Soc.* **1997**, *119*, 2119–2114. (b) Gies, A.-E.; Pfeffer, M. *J. Org. Chem.* **1999**, *64*, 3650–3654. (c) Mamane, V.; Hannen, P.; Fürstner, A. *Chem.—Eur. J.* **2004**, *10*, 4556–4575. (d) Some, S.; Dutta, B.; Ray, J. K. *Tetrahedron Lett.* **2006**, *47*, 1221–1224. (e) Okamoto, H.; Yamaji, M.; Gohda, S.; Kubozono, Y.; Komura, N.; Sato, K.; Sugino, H.; Satake, K. *Org. Lett.* **2011**, *13*, 2758–2761.

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[7] For selected reports on PAH synthesis via tandem cyclization, see: (a) Goldfinger, M. B.; Crawford, K. B.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 4578–4593. (b) Bonifacio, M. C.; Robertson, C. R.; Jung, J.-Y.; King, B. T. *J. Org. Chem.* **2005**, *70*, 8522–8526. (c) Shen, H.-C.;

Tang, J.-M.; Chang, H.-K.; Yang, C.-W.; Liu, R.-S. *J. Org. Chem.* **2005**, *70*, 10113–10116. (d) Kamikawa, K.; Takemoto, I.; Takemoto, S.; Matsuzaka, H. *J. Org. Chem.* **2007**, *72*, 7406–7408. (e) Chen, T.-A.; Lee, T.-J.; Lin, M.-Y.; Sohel, S. M. A.; Diau, E. W.-G.; Lush, S.-F.; Liu, R.-S. *Chem.—Eur. J.* **2010**, *16*, 1826–1833. (f) Matsuda, T.; Moriya, T.; Goya, T.; Murakami, M. *Chem. Lett.* **2011**, *40*, 40–41. (g) Kitazawa, K.; Kochi, T.; Nitani, M.; Ie, Y.; Aso, Y.; Kakiuchi, F. *Chem. Lett.* **2011**, *40*, 300–302. (h) Nakae, T.; Ohnishi, R.; Kitahata, Y.; Soukawa, T.; Sato, H.; Mori, S.; Okujima, T.; Uno, H.; Sakaguchi, H. *Tetrahedron Lett.* **2012**, *53*, 1617–1619. (i) Umeda, R.; Miyake, S.; Nishiyama, Y. *Chem. Lett.* **2012**, *41*, 215–217. (j) Little, M.; Lan, H.; Raftery, J.; Morrison, J. J.; McDouall, J. J. W.; Yeates, S. G.; Quayle, P. *Eur. J. Org. Chem.* **2013**, 6038–6041. (k) Murai, M.; Maekawa, H.; Hamao, S.; Kubozono, Y.; Roy, D.; Takai, K. *Org. Lett.* **2015**, *17*, 708–711. (l) Ozaki, K.; Kawasumi, K.; Shibata, M.; Ito, H.; Itami, K. *Nat. Commun.* **2015**, *6*, 6251–6258. (m) Mori, K.; Murase, T.; Fujita, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 6847–6851.

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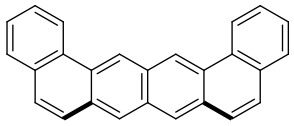
S. *J. Fluorine Chem.* **2015**, *172*, 51–61. See also ref. 6 and references cited therein.

[11] No synthetic method is known in the literatures.

[12] Although dibenzo[*a*,*l*]tetracene (**3a''**) is considered to be another possible product, its formation is not detected at all under conditions I screened.



3a"

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[15] Compound **3e** was synthesized as a minor product. See ref. 14.

3.6. Experimental Section

General Statement

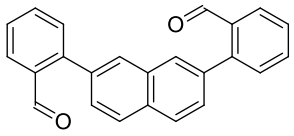
^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker Avance 500 spectrometer at 500 MHz (^{1}H NMR) and 126 MHz (^{13}C NMR). Chemical shift values are given in ppm relative to internal Me_4Si (for ^{1}H NMR: δ = 0.00 ppm) and $CDCl_3$ (for ^{13}C NMR: δ = 77.0 ppm). IR spectra were recorded on a Horiba FT-300S spectrometer by the attenuated total reflectance (ATR) method. Mass spectra were measured on a JEOL JMS-T100GCV or a JEOL JMS-T100CS spectrometer. X-ray diffraction study was performed on a Bruker APEXII ULTRA instrument equipped with a CCD diffractometer using Mo Kα (graphite monochromated, λ = 0.71069 Å) radiation. The structure was solved by direct methods (SIR97). The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares method using SHELXS-97. Hydrogen atoms were placed at calculated positions and refined with the riding mode on their corresponding carbon atoms. The CCDC deposition number of compound **3c** is 1523810.

Column chromatography was conducted on silica gel (Silica Gel 60 N, Kanto Chemical Co., Inc. for column chromatography). All the reactions were conducted under argon. Tetrahydrofuran (THF) was purified by a solvent-purification system (GlassContour) equipped with columns of activated alumina and supported-copper catalyst (Q-5) before use. 1,1,1,3,3,3-Hexafluoropropan-2-ol (HFIP) and chlorobenzene were distilled from CaH_2 and stored over activated molecular sieves 4A. Trifluoromethanesulfonic acid was distilled from $MgSO_4$. Naphthalene-2,7-diyl bis(trifluoromethanesulfonate) (**4a**),[1] naphthalene-1,4-diyl bis(trifluoromethanesulfonate) (**4b**),[2] naphthalene-1,5-diyl bis(trifluoromethanesulfonate) (**4c**),[3] naphthalene-1,6-diyl bis(trifluoromethanesulfonate) (**4d**),[4] naphthalene-1,7-diyl bis(trifluoromethanesulfonate) (**4e**),[4] and 1-bromo-2-(2-methoxyethenyl)benzene (*E*/*Z* = 50:50),[5] were prepared according to the literature procedures. Unless otherwise noted, materials were obtained from commercial sources and used directly without further purifications.

3.6.2. Preparation of Substrates

3.6.2.1. Preparation of Bis(vinyl ether) 1a

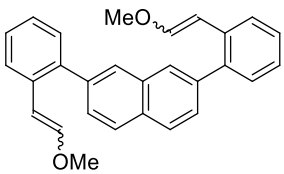
2,2'-(Naphthalene-2,7-diyl)dibenzaldehyde



A 1,4-dioxane (16.7 mL) and H_2O (8.4 mL) solution of naphthalene-2,7-diyl bis(trifluoromethanesulfonate) (**4a**, 2.13 g, 5.02 mmol), 2-formylphenylboronic acid (1.91 g, 12.7 mmol), $Pd(OAc)_2$ (10 mg, 46 μmol), PPh_3 (56 mg, 0.22 mmol), and Na_2CO_3 (3.18 g, 30.0 mmol) was degassed by using the freeze-pump-thaw method three times. After stirring at 120 °C for 1 h, organic materials were extracted with EtOAc three times. The combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 1:1) to give 2,2'-(naphthalene-2,7-diyl)dibenzaldehyde (1.58 g, 94%) as an orange solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54–7.57 (m, 4H), 7.59 (dd, *J* = 8.4, 1.7 Hz, 2H), 7.70 (ddd, *J* = 7.4, 7.4, 1.4 Hz, 2H), 7.88 (s, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 8.08 (d, *J* = 7.4 Hz, 2H), 10.05 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 127.8, 127.98, 128.04, 128.6, 129.4, 131.0, 132.0, 132.6, 133.6, 133.8, 136.3, 145.5, 192.1. IR (neat): ν 3059, 2846, 2748, 1685, 1595, 1196, 850, 760, 731 cm^{-1}. HRMS (ESI+) *m*/*z* Calcd. for $C_{24}H_{16}NaO_2$ $[M+Na]^+$: 359.1043; Found: 359.1052.

2,7-Bis[2-(2-methoxyethenyl)phenyl]naphthalene (1a)



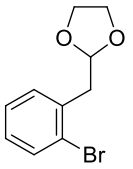
To a THF (12.4 mL) solution of $Ph_3P^+CH_2OMeCl^-$ (6.46 g, 18.8 mmol) was added *t*-BuONa (2.27 g, 23.6 mmol) at 0 °C. After stirring at 0 °C for 30 min, a THF (17.6 mL) solution of 2,2'-(naphthalene-2,7-diyl)dibenzaldehyde (1.58 g, 4.70 mmol) was added. After stirring at 0 °C for another 10 min, the reaction was quenched with H_2O, and organic materials were extracted with

EtOAc three times. The combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 1:1) to give 2,7-bis[2-(2-methoxyethenyl)phenyl]naphthalene (**1a**, 1.25 g, 68%, *EE*/*EZ*/*ZZ* = 37:55:8) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.50 (s, 1.65H), 3.51 (s, 2.22H), 3.75 (s, 1.65H), 3.75 (s, 0.48H), 5.22 (d, *J* = 7.2 Hz, 0.16H), 5.23 (d, *J* = 7.2 Hz, 0.55H), 5.82 (d, *J* = 12.8 Hz, 0.55H), 5.83 (d, *J* = 12.8 Hz, 0.74H), 6.06 (d, *J* = 7.2 Hz, 0.16H), 6.06 (d, *J* = 7.2 Hz, 0.55H), 6.98 (d, *J* = 12.8 Hz, 0.55H), 6.98 (d, *J* = 12.8 Hz, 0.74H), 7.24–7.56 (m, 8H), 7.82–7.90 (m, 5.29H), 8.15 (d, *J* = 7.8 Hz, 0.16H), 8.15 (d, *J* = 7.8 Hz, 0.55H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 56.38, 56.44, 60.6, 103.8, 104.29, 104.34, 125.0, 125.1, 125.8, 125.9, 126.01, 126.03, 127.08, 127.11, 127.14, 127.29, 127.31, 127.6, 127.7, 128.2, 128.3, 128.4, 128.5, 129.27, 129.30, 130.0, 130.4, 131.1, 131.2, 133.1, 133.2, 133.4, 134.3, 139.3, 139.4, 139.66, 139.68, 139.72, 140.09, 140.14, 148.0, 149.06, 149.10. IR (neat): ν 3055, 3018, 2954, 2931, 2831, 1637, 1230, 1157, 1107, 1090, 945, 937, 849, 754 cm^{-1}. HRMS (ESI+) *m*/*z* Calcd. for $C_{28}H_{24}NaO_2$ $[M+Na]^+$: 415.1669; Found: 415.1672.

3.6.2.2. Preparation of Bisacetals 2

2-(2-Bromophenylmethyl)-1,3-dioxolane



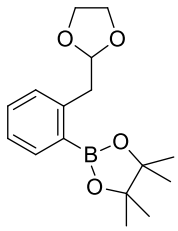
To an acetone (123 mL) solution of 1-bromo-2-(2-methoxyethenyl)benzene (*E*/*Z* = 50:50, 4.91 g, 23.0 mmol) was slowly added aqueous HCl (11 M, 20.4 mL) at 0 °C. After stirring at room temperature for 12 h, the reaction mixture was diluted with H_2O, and organic materials were extracted with Et_2O three times. The combined extracts were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure gave a crude mixture (4.65 g) including 2-(2-bromophenyl)acetaldehyde as a pale yellow liquid.

To a toluene (46 mL) solution of the obtained crude mixture and ethylene glycol (3.76 mL,

67.4 mmol) was added $TsOH \cdot H_2O$ (445 mg, 2.34 mmol). After stirring at 140 °C for 1 day and then 150 °C for 11 h in a reaction vessel equipped with a Dean–Stark apparatus, aqueous $NaHCO_3$ was added to the reaction mixture. The organic layer was separated and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/EtOAc = 10:1) to give 2-(2-bromophenylmethyl)-1,3-dioxolane (4.35 g, 78%) as an orange oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.12 (d, *J* = 5.0 Hz, 2H), 3.79–3.85 (m, 2H), 3.92–3.98 (m, 2H), 5.14 (t, *J* = 5.0 Hz, 1H), 7.07 (ddd, *J* = 7.6, 7.6, 1.5 Hz, 1H), 7.23 (ddd, *J* = 7.6, 7.6, 1.0 Hz, 1H), 7.33 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.52 (dd, *J* = 7.6, 1.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 40.5, 64.8, 103.1, 124.8, 127.2, 128.2, 131.7, 132.5, 135.7. IR (neat): ν 2968, 2883, 1473, 1117, 1026, 985, 748, 660 cm^{-1}. HRMS (EI+) *m*/*z* Calcd. for $C_{10}H_{11}{}^{79}BrO_2$ $[M]^+$: 241.9937; Found: 241.9942.

2-{2-[(1,3-Dioxolan-2-yl)methyl]phenyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

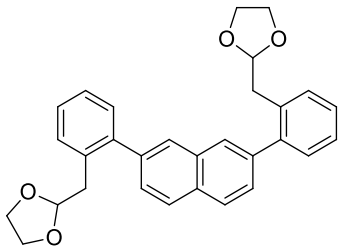


A 1,4-dioxane (75.8 mL) solution of 2-(2-bromophenylmethyl)-1,3-dioxolane (6.00 g, 24.7 mmol), $B_2(pin)_2$ (6.97 g, 27.5 mmol), potassium acetate (14.0 g, 150 mmol), and $PdCl_2(dppf) \cdot CH_2Cl_2$ (212 mg, 0.260 mmol) was degassed by using the freeze-pump-thaw method three times. After stirring at 100 °C for 5 h, the reaction mixture was filtered through a pad of silica gel (CH_2Cl_2). After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (toluene/EtOAc = 10:1) to give 2-{2-[(1,3-dioxolan-2-yl)methyl]phenyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.76 g, 80%) as an orange oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.34 (s, 12H), 3.30 (d, *J* = 4.9 Hz, 2H), 3.78–3.90 (m, 4H), 5.08 (t, *J* = 4.9 Hz, 1H), 7.22 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.37 (ddd, *J* = 7.5, 7.5, 1.2

Hz, 1H), 7.78 (dd. J = 7.5, 1.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 24.8, 40.1, 64.8, 83.5, 105.3, 125.8, 130.6, 130.7, 135.7, 142.4 (the signal for the carbon which is attached to the boron atom was omitted). IR (neat): ν 2978, 2931, 2885, 1383, 1348, 1313, 1146, 1119, 1072, 661 cm^{-1}. HRMS (EI+) *m*/*z* Calcd. for $C_{16}H_{23}BO_4$ $[M]^+$: 290.1684; Found: 290.1694.

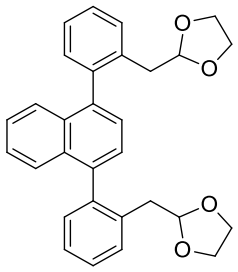
2,7-Bis{2-[(1,3-dioxolan-2-yl)methyl]phenyl}naphthalene (2a)



A 1,4-dioxane (10 mL) and H_2O (5 mL) solution of naphthalene-2,7-diyl bis(trifluoromethanesulfonate) (**4a**, 1.28 g, 3.02 mmol), 2-{2-[(1,3-dioxolan-2-yl)methyl]phenyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.61 g, 5.55 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (120 mg, 0.15 mmol), and K_3PO_4 (3.82 g, 18.0 mmol) was degassed by using the freeze-pump-thaw method three times. After stirring at 120 °C for 2 h, organic materials were extracted with EtOAc three times. The combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (CH_2Cl_2) gave **2a** (881 mg, 65%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.03 (d, J = 4.7 Hz, 4H), 3.74–3.86 (m, 8H), 5.01 (t, J = 4.7 Hz, 2H), 7.28–7.37 (m, 6H), 7.48–7.51 (m, 4H), 7.80 (s, 2H), 7.89 (d, J = 8.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 37.5, 64.7, 104.4, 126.5, 127.3, 127.4, 127.9, 128.2, 130.3, 130.4, 131.1, 133.0, 133.8, 139.5, 142.5. IR (neat): ν 2960, 2883, 1485, 1396, 1130, 1038, 985, 945, 908, 849, 756, 729 cm^{-1}. HRMS (ESI+) *m*/*z* Calcd. for $C_{30}H_{28}NaO_4$ $[M+Na]^+$: 475.1880; Found: 475.1885.

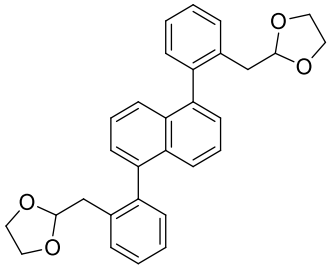
1,4-Bis{2-[(1,3-dioxolan-2-yl)methyl]phenyl}naphthalene (2b)



Compound **2b** was prepared by the method described for **2a** using naphthalene-1,4-diyl bis(trifluoromethanesulfonate) (**4b**, 426 mg, 1.00 mmol), 2-{2-[(1,3-dioxolan-2-yl)methyl]phenyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (544 mg, 1.87 mmol), $Pd(PPh_3)_4$ (62 mg, 53 μmol), and K_3PO_4 (1.25 g, 5.89 mmol) at 120 °C for 1 h. Purification by silica gel column chromatography (hexane/EtOAc = 30:1) and washing with EtOAc gave **2b** (62 mg, 14%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.72–2.83 (m, 4H), 3.71–3.85 (m, 8H), 4.89 (dd, *J* = 5.2, 5.2 Hz, 2H), 7.32–7.37 (m, 6H), 7.39 (s, 2H), 7.42–7.48 (m, 4H), 7.56 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 37.9, 64.6, 64.7, 104.2, 125.7, 126.35, 126.43, 126.5, 127.6, 130.2, 130.9, 132.4, 135.1, 138.6, 140.6. IR (neat): ν 2956, 2883, 1387, 1132, 1036, 976, 943, 760 cm^{-1}. HRMS (ESI+) *m*/*z* Calcd. for $C_{30}H_{28}NaO_4$ $[M+Na]^+$: 475.1880; Found: 475.1867.

1,5-Bis{2-[(1,3-dioxolan-2-yl)methyl]phenyl}naphthalene (2c)

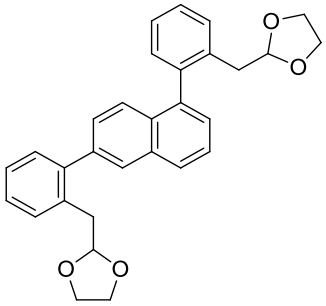


Compound **2c** was prepared by the method described for **2a** using naphthalene-1,5-diyl bis(trifluoromethanesulfonate) (**4c**, 416 mg, 0.980 mmol), 2-{2-[(1,3-dioxolan-2-yl)methyl]phenyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (545 mg, 1.88 mmol), $Pd(PPh_3)_4$ (54 mg, 47 μmol), and K_3PO_4 (1.28 g, 6.03 mmol) at 120 °C for 1 h. Purification

by washing with EtOAc gave **2c** (207 mg, 47%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.68–2.80 (m, 4H), 3.70–3.82 (m, 8H), 4.86 (dd, *J* = 5.2, 5.1 Hz, 2H), 7.32–7.39 (m, 8H), 7.41–7.44 (m, 4H), 7.54 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 37.9, 64.6, 64.7, 104.2, 125.2, 125.8, 126.4, 127.1, 127.6, 130.2, 130.8, 132.3, 135.0, 139.1, 140.8. IR (neat): ν 2964, 2887, 1489, 1406, 1130, 1049, 976, 796, 762 cm^{-1}. HRMS (ESI+) *m/z* Calcd. for $C_{30}H_{28}NaO_4$ $[M+Na]^+$: 475.1880; Found: 475.1864.

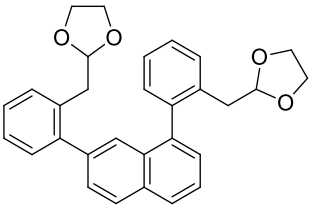
1,6-Bis{2-[(1,3-dioxolan-2-yl)methyl]phenyl}naphthalene (2d)



Compound **2d** was prepared by the method described for **2a** using naphthalene-1,6-diyl bis(trifluoromethanesulfonate) (**4d**, 432 mg, 1.02 mmol), 2-{2-[(1,3-dioxolan-2-yl)methyl]phenyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (638 mg, 2.20 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (40 mg, 49 μmol), and K_3PO_4 (1.28 g, 6.03 mmol) at 120 °C for 2 h. Purification by silica gel column chromatography (hexane/EtOAc = 2:1) gave **2d** (446 mg, 97%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.72 (d, *J* = 14.2, 4.9 Hz, 1H), 2.80 (d, *J* = 14.2, 5.0 Hz, 1H), 3.00 (d, *J* = 5.1 Hz, 2H), 3.69–3.87 (m, 8H), 4.87 (t, *J* = 5.1 Hz, 1H), 4.99 (dd, *J* = 5.0, 4.9 Hz, 1H), 7.28–7.38 (m, 7H), 7.42 (ddd, *J* = 7.4, 7.4, 1.4 Hz, 1H), 7.45–7.48 (m, 2H), 7.51–7.54 (m, 2H), 7.84–7.86 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 37.4, 37.9, 64.58, 64.62, 64.7, 104.2, 104.5, 125.5, 125.8, 126.4, 126.5, 127.1, 127.4, 127.6, 127.7, 128.0, 128.4, 130.26, 130.34, 130.4, 130.7, 131.1, 133.3, 133.8, 135.0, 138.9, 139.0, 140.5, 142.4. IR (neat): ν 2966, 2883, 1489, 1396, 1124, 1036, 985, 760, 729 cm^{-1}. HRMS (ESI+) *m/z* Calcd. for $C_{30}H_{28}NaO_4$ $[M+Na]^+$: 475.1880; Found: 475.1885.

1,7-Bis{2-[(1,3-dioxolan-2-yl)methyl]phenyl}naphthalene (2e)

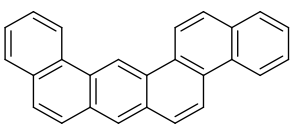


Compound **2e** was prepared by the method described for **2a** using naphthalene-1,7-diyl bis(trifluoromethanesulfonate) (**4e**, 427 mg, 1.01 mmol), 2-{2-[(1,3-dioxolan-2-yl)methyl]phenyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (639 mg, 2.20 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (40 mg, 49 μmol), and K_3PO_4 (1.29 g, 6.08 mmol) at 120 °C for 2 h. Purification by silica gel column chromatography (hexane/EtOAc = 2:1) gave **2e** (433 mg, 95%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.69 (d, *J* = 14.1, 4.9 Hz, 1H), 2.77 (d, *J* = 14.1, 5.0 Hz, 1H), 2.89 (d, *J* = 5.0 Hz, 2H), 3.67–3.79 (m, 8H), 4.81 (dd, *J* = 4.9, 5.0 Hz, 1H), 4.83 (d, *J* = 5.0 Hz, 1H), 7.18–7.30 (m, 5H), 7.35 (ddd, *J* = 7.6, 7.6, 1.8 Hz, 1H), 7.38–7.41 (m, 3H), 7.45–7.47 (m, 2H), 7.52 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 37.4, 37.8, 64.5, 64.61, 64.64, 104.22, 104.24, 125.2, 126.2, 126.41, 126.42, 127.2, 127.4, 127.6, 127.7, 127.8, 127.9, 130.28, 130.31, 130.5, 130.6, 132.0, 132.3, 133.7, 135.0, 139.2, 139.3, 140.5, 142.6. IR (neat): ν 2970, 2881, 1485, 1396, 1124, 1036, 984, 837, 752 cm^{-1}. HRMS (ESI+) *m*/*z* Calcd. for $C_{30}H_{28}NaO_4$ $[M+Na]^+$: 475.1880; Found: 475.1869.

3.6.3. Synthesis of *ortho*-Fused Six-Hexagon Benzenoids 3

Dibenzo[*c*,*m*]tetraphene (3a)

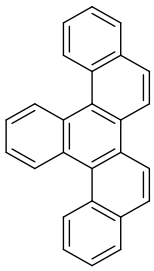


To an HFIP (1.44 mL) solution of bisacetal **2a** (195 mg, 0.43 mmol) was added trifluoromethanesulfonic acid (6.5 mg, 43 μmol) at 0 °C. After stirring at the same temperature for

15 min, the reaction was quenched with phosphate buffer (pH 7). Organic materials were extracted with CH_2Cl_2 three times, and the combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified by silica gel column chromatography (EtOAc) to give dibenzo[*c*,*m*]tetraphene (**3a**, 137 mg, 97%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64–7.68 (m, 2H), 7.71–7.78 (m, 3H), 7.88 (d, *J* = 8.9 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 8.04 (d, *J* = 7.7 Hz, 1H), 8.11 (d, *J* = 9.0 Hz, 1H), 8.14 (d, *J* = 9.2 Hz, 1H), 8.45 (s, 1H), 8.72 (d, *J* = 9.1 Hz, 1H), 8.79 (d, *J* = 8.4 Hz, 1H), 9.03–9.05 (m, 2H), 10.1 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 116.9, 121.3, 121.5, 122.9, 123.2, 126.4, 126.8, 126.89, 126.91, 127.0, 127.3, 127.36, 127.45, 127.5, 128.1, 128.5, 128.6, 128.8, 129.0, 129.1, 130.68, 130.72, 130.73, 130.8, 132.1, 132.4. IR (neat): ν 3055, 1647, 1558, 895, 829, 806, 748 cm^{-1}. HRMS (APCI+): *m*/*z* Calcd. for $C_{26}H_{17}$ $[M+H]^+$: 329.1330; Found: 329.1316.

Benzo[*s*]picene (3b)

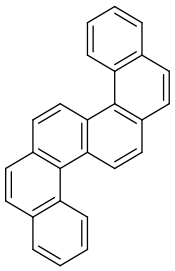


Benzo[*s*]picene (**3b**) was synthesized by the method described for **3a** using bisacetal **2b** (62 mg, 0.14 mmol), trifluoromethanesulfonic acid (2.2 mg, 15 μmol), and HFIP (0.46 mL). Purification by silica gel column chromatography (hexane/CH_2Cl_2 = 2:1) gave **3b** (38 mg, 84%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61–7.65 (m, 4H), 7.68 (ddd, *J* = 6.9, 6.9, 1.4 Hz, 2H), 8.01 (d, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 7.6 Hz, 2H), 8.59 (d, *J* = 8.9 Hz, 2H), 8.94–8.98 (m, 2H), 9.02 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 120.6, 125.9, 126.09, 126.15, 127.4, 127.66, 127.72, 128.1, 128.3, 129.1, 129.7, 130.2, 133.4.

Spectral data for this compound showed good agreement with the literature data.[6]

Dibenzo[*c*,*l*]chrysene (3c)



Dibenzo[*c*,*l*]chrysene (**3c**) was synthesized by the method described for **3a** using bisacetal **2c** (92 mg, 0.20 mmol), trifluoromethanesulfonic acid (3.1 mg, 21 μmol), and HFIP (0.67 mL). Purification by silica gel column chromatography (hexane/CH_2Cl_2 = 2:1) gave **3c** (66 mg, 99%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (ddd, *J* = 6.9, 6.9, 1.1 Hz, 2H), 7.67 (ddd, *J* = 8.1, 8.1, 1.3 Hz, 2H), 7.85–7.92 (m, 6H), 8.03 (dd, *J* = 8.1, 1.1 Hz, 2H), 9.02 (d, *J* = 8.3 Hz, 2H), 9.10 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 126.05, 126.05, 126.2, 126.3, 127.4, 127.61, 127.61, 128.4, 128.6, 130.1, 130.2, 130.7, 133.4. IR (neat): ν 3045, 2920, 1475, 1425, 1230, 874, 843, 812, 746, 606 cm^{-1}. HRMS (APCI+): *m*/*z* Calcd. for $C_{26}H_{17}$ $[M+H]^+$: 329.1330; Found: 329.1337. The structure of **3c** was also confirmed by X-ray diffraction analysis (Figure S1 and Table S1).

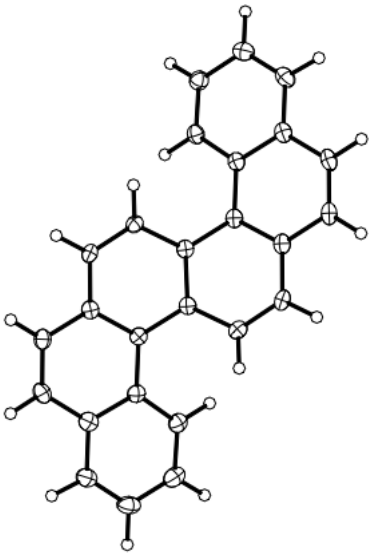
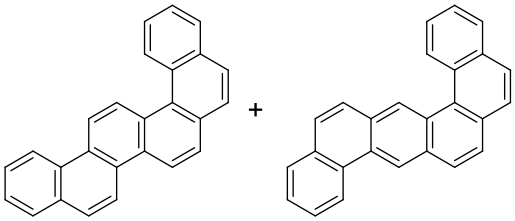


Figure S1. ORTEP drawing of **3c** with 50% ellipsoid probability.

Table S1. Crystal Data Collection Parameters for **3c**

compound	**3c**
formula	$C_{26}H_{16}$
crystal system	monoclinic
space group	$P2_1/c$
R, R_w ($I > 2\sigma(I)$)	0.0441, 0.0615
$R1$, $wR2$ (all data)	0.0977, 0.1065
GOF on F^2	1.059
a (Å)	7.957(2)
b (Å)	12.949(4)
c (Å)	15.791(4)
α (deg)	90
β (deg)	92.586(4)
γ (deg)	90
V (Å^3)	1529.0(7)
Z	4
T (K)	120(2)
crystal size (mm)	0.30, 0.13, 0.06
D_{calcd} (g/cm^3)	1.342
$2\theta_{min}$, $2\theta_{max}$ (deg)	4.06, 55.00

Benzo[*a*]picene (3d)

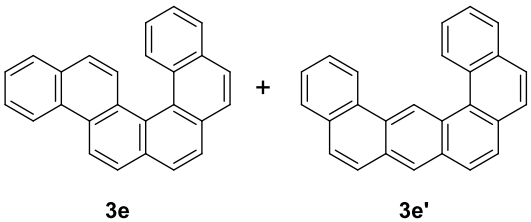


3d **3d'**

Benzo[*a*]picene (**3d**) was synthesized by the method described for **3a** using bisacetal **2d** (91 mg, 0.20 mmol), trifluoromethanesulfonic acid (2.8 mg, 19 μmol), and HFIP (0.67 mL). Purification by silica gel column chromatography (hexane/CH_2Cl_2 = 2:1 and then hexane/toluene = 2:1) gave **3d** including a small amount of **3d'** (**3d**/**3d'** = 98:2, 63 mg, 95%) as a white solid.

3d: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (ddd, *J* = 7.7, 7.7, 1.2 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.98–8.03 (m, 4H), 8.76 (d, *J* = 9.1 Hz, 1H), 8.81–8.83 (m, 3H), 9.13 (d, *J* = 8.3 Hz, 1H), 9.23 (d, *J* = 9.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 120.7, 121.8, 122.2, 123.2, 126.06, 126.07, 126.5, 126.6, 126.8, 126.9, 127.2, 127.4, 127.6, 127.8, 128.0, 128.39, 128.43, 128.49, 128.54, 128.8, 130.2, 130.32, 130.32, 130.8, 132.0, 133.6. IR (neat): ν 3049, 1604, 1475, 1433, 1257, 867, 827, 796, 754, 737 cm^{-1}. HRMS (APCI+): *m*/*z* Calcd. for $C_{26}H_{17}$ $[M+H]^+$: 329.1330; Found: 329.1334.

Naphtho[2,1-*c*]chrysene (3e)



3e **3e'**

Naphtho[2,1-*c*]chrysene (**3e**) was synthesized by the method described for **3a** using bisacetal **2e** (94 mg, 0.21 mmol), trifluoromethanesulfonic acid (3.1 mg, 21 μmol), and HFIP (0.70 mL). Purification by silica gel column chromatography (hexane/CH_2Cl_2 = 2:1) gave **3e** including a small amount of **3e'** (**3e**/**3e'** = 93:7, 60 mg, 87%) as a white solid.

3e: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.50–7.54 (m, 2H), 7.62 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.70 (dd, *J* = 8.1, 8.1 Hz, 1H), 7.87–7.97 (m, 6H), 8.09 (d, *J* = 8.7 Hz, 1H), 8.23 (d, *J* = 9.2 Hz, 1H), 8.33 (d, *J* = 8.5 Hz, 1H), 8.81 (d, *J* = 8.1 Hz, 1H), 8.82 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 122.0, 123.4, 124.4, 124.7, 126.1, 126.3, 126.51, 126.54, 126.6, 126.8, 127.0, 127.21, 127.24, 127.67, 127.69, 127.74, 128.0, 128.2, 129.1, 129.2, 130.4, 130.9, 132.06, 132.06, 132.3, 132.5. IR (neat): ν 3047, 1601, 1485, 1423, 1255, 1226, 906, 839, 804, 746, 690, 627 cm^{-1}. HRMS (APCI+): *m*/*z* Calcd. for $C_{26}H_{17}$ $[M+H]^+$: 329.1330; Found: 329.1343.

3.6.4. References

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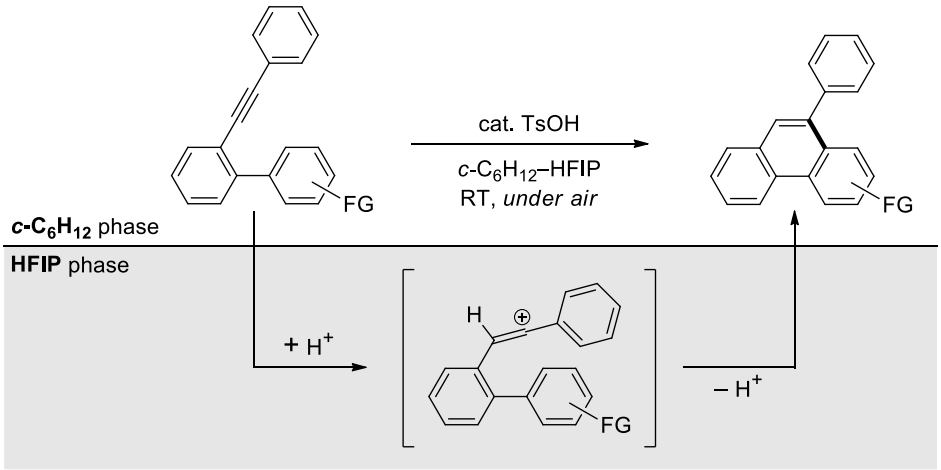
Chapter 4

Brønsted Acid-Catalyzed Intramolecular Hydroarylation of Unactivated Alkynes

Abstract

Brønsted acid-catalyzed intramolecular hydroarylation of unactivated alkynes proceeded via the vinylic carbocations to provide substituted phenacenes. The reaction was promoted by TsOH in 1,1,1,3,3,3-hexafluoropropan-2-ol/cyclohexane two-phase system. This protocol is applicable to a wide variety of arylethynyl-bearing biaryls with electron-donating or electron-withdrawing groups.

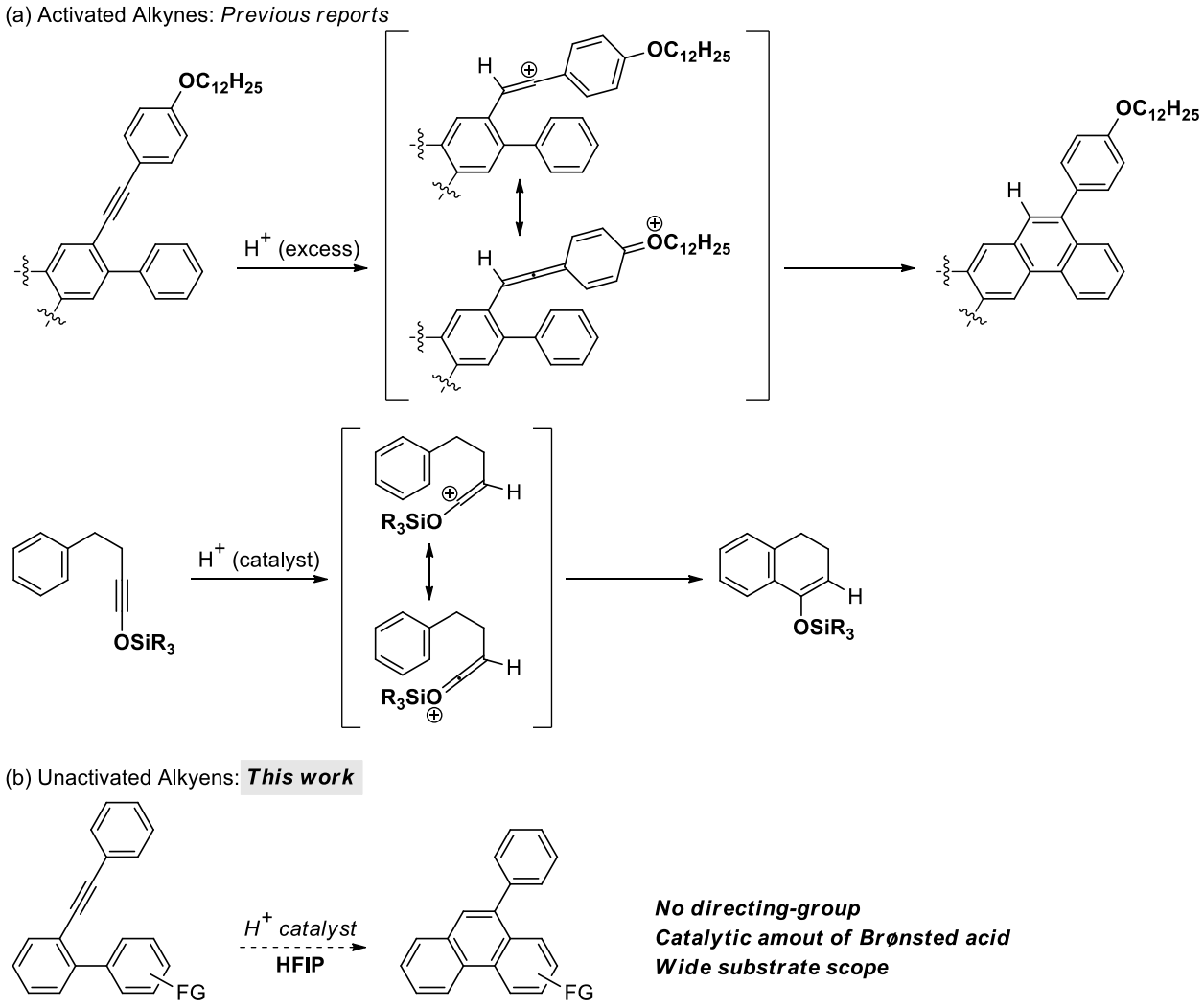


4.1. Introduction

Phenacenes have *ortho*-fused aromatic rings in zigzag configuration and constitute a subclass of polycyclic aromatic carbons (PAHs).[1] They attract much attention because of unique electronic and optical properties derived from their extended π-conjugated systems and high stability toward oxidation. Thus, they have been widely studied on organic semiconducting devices such as organic field-effect transistors (OFETs)[2] and light-emitting diodes (OLEDs).[3] Phenacenes have been generally synthesiszed via photochemical oxidative cyclization of stilbene derivatives (Mallory reaction),[4] McMurry coupling,[5] dehydrative cycloaromatization of carbonyl compounds (Bradsher reation),[6] and metal-catalyzed annulation.[7]

Among synthetic method for phenacenes, the hydroarylation of 2-alkynyl biaryls is a particularly straightforward and atom-economical synthetic method. Since Fürstner *et al*. have reported the synthesis of phenacenes via Pt(II)- or In(III)-catalyzed hydroarylaiton of alkynes,[8] various similar studies have emerged.[9] Swager *et al*. have achieved a pioneering work on Brønsted acid-mediated hydroarylation of alkynes utilizing an excess amount of a Brønsted acid (Scheme 1a).[10,11] Subsequently Kozmin *et al*. achieved Brønsted acid-catalyzed carbocyclization of alkynes (Scheme 1a).[12] However, both protocols required alkyne-activating groups such as *p*-alkoxy phenyl group or a siloxy group, respectively. This limitation was due to extremely unstable vinylic carbocation intermediates, which need electron donation from the activating groups.

To overcome the limitation, I envisaged that the vinyl cation intermediates might be stabilized by the effect of 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) to broaden the scope of alkyne substrates.[13,14] Eventually, I achieved the TsOH-catalyzed hydroarylation of phenylethynyl biaryls by conducting in HFIP, which led to the synthesis of functionalized phenacenes (Scheme 1b).



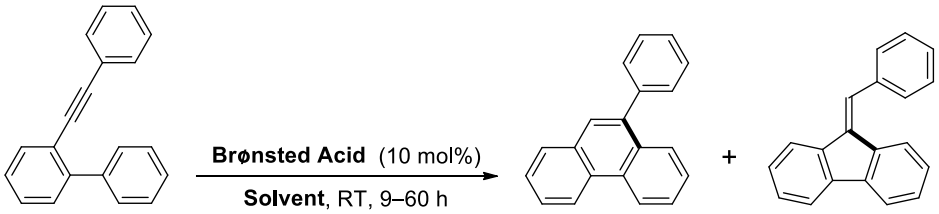
Scheme 1. Brønsted acid-mediated hydroarylation of (a) activated and (b) unactivated alkynes

4.2. Synthesis of Substituted Phenacenes via Brønsted Acid-Catalyzed Intramolecular Hydroarylation

First, I applied the combination of trifluoromethanesulfonic acid (TfOH) as a catalyst and HFIP as a solvent, which was the most effective for dehydrative cycloaromatization of carbonyl compounds,[15] to intramolecular hydroarylation of 2-(phenylethynyl)biphenyl (**1a**). The desired reaction proceeded, leading to the formation of the corresponding 6-*endo* cyclized product **2a** and 5-*exo* cyclized product **3a** in 53% and 7% yields, respectively (Table 1, Entry 1). In order to improve the yield of **2a**, various weaker Brønsted acids, such as *p*-toluenesulfonic acid

monohydrate ($TsOH \cdot H_2O$), methansulfonic acid (MsOH), tetrafluoroboric acid (HBF_4), and 10-camphorsulfonic acid (CSA), were examined as catalysts to afford **2a** in 44–54% yields (Entries 2–5). Since cheap and easy-handling $TsOH \cdot H_2O$ gave the best result, various solvents were screened in the presence of a catalytic amount of $TsOH \cdot H_2O$ (Entries 6–9). As expected, HFIP was found to be the most effective among solvents examined. To improve the yield of **2a** by suppressing side reactions, I employed a two-phase co-solvent of HFIP and aliphatic solvents, such as hexane, cyclohexane, and decaline (decahydronaphthalene), in this hydroarylation (Entries 10–12, vide infra). In the case where cyclohexane was used as a co-solvent, the desired product **2a** was obtained in 85% yield with good selectivity (Entry 11). Consequently, this reaction proceeded even under air without any problem (Entry 13).

Table 1. Screening of conditions.[a]



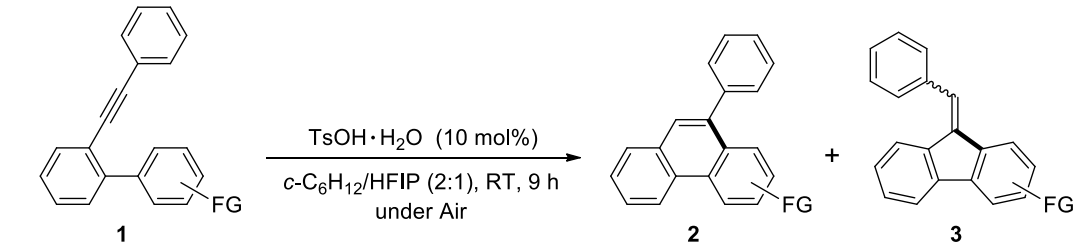
1a **2a** **3a**

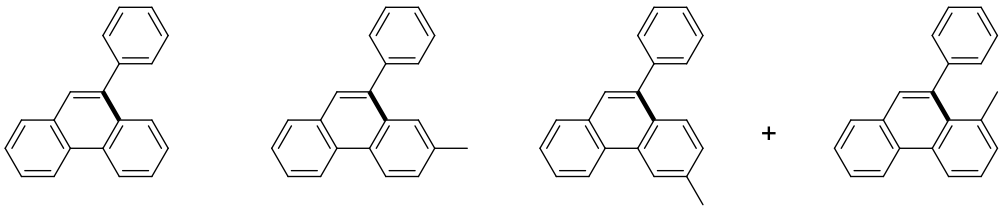
Entry	Brønsted Acid	Solvent	**2a** (%)[b]	**3a** (%)[b]
1	TfOH	HFIP	53	7
2	$TsOH \cdot H_2O$	HFIP	54	5
3	MsOH	HFIP	47	7
4	HBF_4	HFIP	48	9
5	CSA	HFIP	44	5
6	$TsOH \cdot H_2O$	Hexane	N.D.[c]	N.D.[c]
7	$TsOH \cdot H_2O$	CH_2Cl_2	trace	N.D.[c]
8	$TsOH \cdot H_2O$	$MeNO_2$	1	N.D.[c]
9	$TsOH \cdot H_2O$	*i*-PrOH	N.D.[c]	N.D.[c]
10	$TsOH \cdot H_2O$	HFIP/Hexane (1:2)	78	9
11	$TsOH \cdot H_2O$	HFIP/Cyclohexane (1:2)	85	13
12	$TsOH \cdot H_2O$	HFIP/Decaline (1:2)	67	11
13[d]	$TsOH \cdot H_2O$	HFIP/Cyclohexane (1:2)	85	11

[a] 0.3 mmol scale. [b] Yield was determined by ^1H NMR measurement using CH_2Br_2 as an internal standard. [c] N.D. = Not detected. [d] Reaction under air atmosphere.

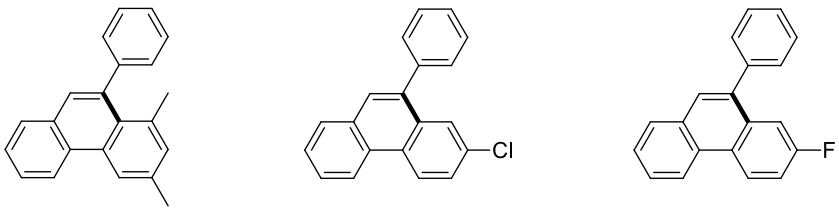
The optimal conditions obtained above for the synthesis of **2a** from **1a** were then successfully applied to the hydroarylation of phenylethynyl biaryls **1** with a variety of substituents on the nucleophilic aryl groups (Table 2). Hydroarylation of phenylethynyl biaryls **1b**–**d** bearing electron-donating methyl groups smoothly proceeded to afford the corresponding substituted phenanthrenes **2b**–**d** in high yields. Phenylethynyl biaryls **1e** and **f** bearing electron-withdrawing chlorine and fluorine groups also underwent hydroarylation successfully.

Table 2. TsOH-catalyzed synthesis of substituted phenacenes **2** in *c*-C_6H_{12}/HFIP co-solvent.[a]





96% (**2a**/**3a** = 90:10) | 93% (**2b**/**3b** = 93:7) | 81% (**2c**/**3c** = 50:45:3:2)



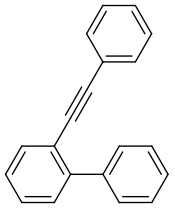
88% (**2d**/**3d** = 97:3) | 89% (**2e**/**3e** = 94:6) | 91% (**2f**/**3f** = 90:10)

[a] Total isolated yield of **2** and **3**. Product ratio (**2**/**3**) was determined by ^{1}H NMR spectroscopy.

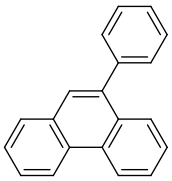
4.3. Mechanistic Studies on Hydroarylation in Two-Phase Systems

In order to elucidate the effect of the two-phase solvent system, the following experiments were conducted. First, distribution ratios of 2-(phenylethynyl)biphenyl (**1a**), 9-phenylphenanthrene (**2a**), and TsOH in cyclohexane and HFIP were determined (Table 4). As listed in Table 4, the 88% of the starting alkyne **1a** was dissolved in cyclohexane, while 12% of **1a** was dissolved in HFIP (in *c*-C_6H_{12}/HFIP = 88:12). The product phenanthrene (**2a**) and TsOH were completely separated to be located in the cyclohexane layer and in the HFIP layer, respectively.

Table 4. Distribusion ratios of **1a**, **2a**, and TsOH.



1a



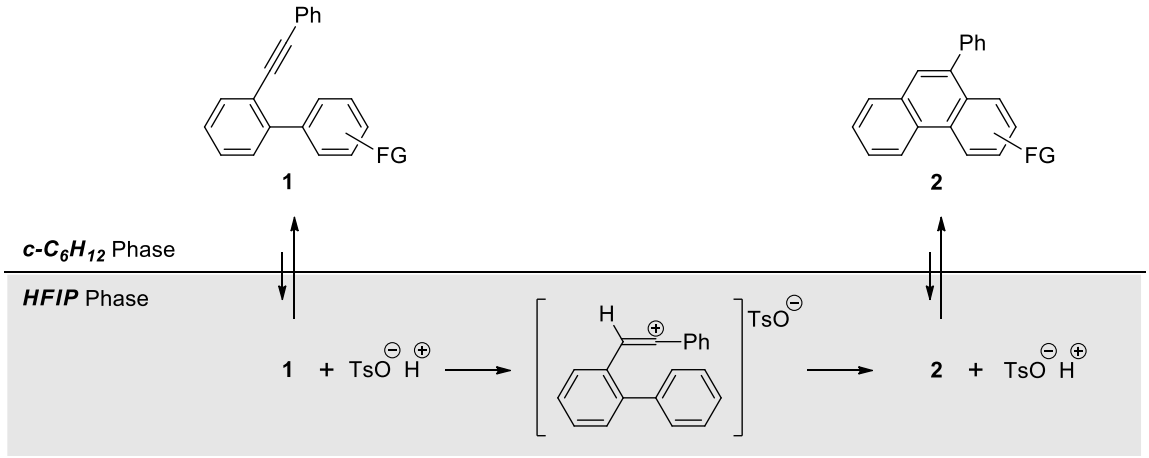
2a

TsOH

	1a (%)	**2a** (%)	TsOH (%)
c-C_6H_{12} layer	88[a]	quant[a]	N.D.[a,c]
HFIP layer	12[b]	0[b]	quant[b]

[a] Determined by ^{1}H NMR spectroscopy using CH_2Br_2 as internal standard. [b] Calculated value. [c] N.D. = Not detected.

Plausible behaviors of alkynes **1**, phenacenes **2**, and TsOH in the cyclohexane/HFIP two-phase system of the hydroarylation are shown in Scheme 2. Alkynes **1** and phenacenes **2** were mainly dissolved in the cyclohexane layer, while TsOH was dissolved in the HFIP layer. A part of alkynes **1** was protonated by TsOH in the HFIP layer to generate the intermediary vinyl cations. Subsequent intramolecular Friedel–Crafts-type cyclization proceeded in the HFIP layer to afford phenacenes **2**, which moved from the HFIP layer into the cyclohexane layer. Thus, the two-phase system separates the vinyl cations from alkynes **1** and phenacenes **2**, which can suppress undesirable reactions of the reactive vinyl cations with **2** and **1**.



Scheme 2. Proposed behavior of organic compounds in cyclohexane/HFIP two-phase system.

In addition, I succeeded in recycling the HFIP solution of $TsOH \cdot H_2O$. After the reaction, the cyclohexane layer including **2** and **3** was separated from the HFIP layer including $TsOH \cdot H_2O$, which was reused repeatedly by adding a new cyclohexane solution of **1a**. After the reaction with stirring under the same conditions, the corresponding phenanthrene **2a** and fulvens **3a** were obtained in 95% (**2a**/**3a** = 88:12; 1st cycle), 97% (**2a**/**3a** = 89:11; 2nd cycle), 93% (**2a**/**3a** = 88:12; 3rd cycle), and 94% (**2a**/**3a** = 88:12; 4th cycle) of total yields. Thus, the reactivity of HFIP solution of $TsOH \cdot H_2O$ was found to be maintained over four cycles, which showed the practicality of this procedure.[16]

4.4. Conclusion

In summary, I have developed an efficient and atom-economical method for the synthesis of phenacenes via TsOH-catalyzed intramolecular hydroarylation of unactivated alkynes with a wide variety of substituents. The two-phase HFIP/cyclohexane solvent system promoted the catalytic reaction and suppressed side reactions. Therefore, I demonstrated great potential of the two-phase solvent system including HFIP.

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4.6. Experimental Section

4.6.1. General Statement

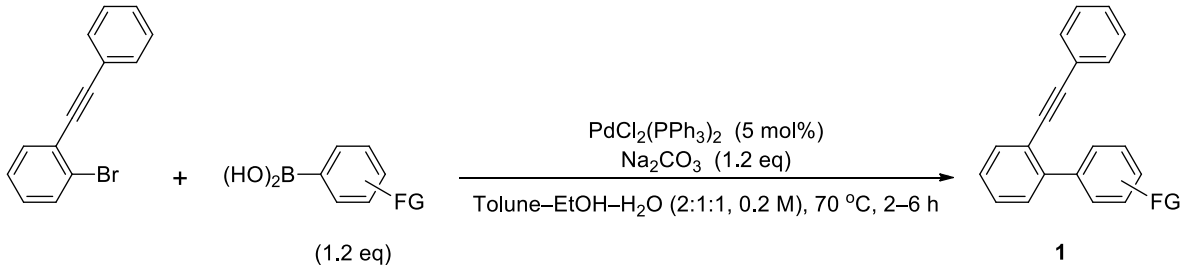
^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker Avance 500 spectrometer at 500 MHz (^{1}H NMR), at 126 MHz (^{13}C NMR), and 470 MHz (^{19}F NMR). Chemical shift values are given in ppm relative to internal Me_4Si (for ^{1}H NMR: δ = 0.00 ppm), $CDCl_3$ (for ^{13}C NMR: δ = 77.0 ppm), and C_6F_6 (for ^{19}F NMR: δ = 0.00 ppm). IR spectra were recorded on a Horiba FT-300S spectrometer by the attenuated total reflectance (ATR) method. Mass spectra were measured on a JEOL JMS-T100GCV spectrometer.

Column chromatography was conducted on silica gel (Silica Gel 60 N, Kanto Chemical Co., Inc. for column chromatography). All the reactions for substrate preparation were conducted under argon. All the reactions for phenacene synthesis were conducted under air. Toluene and dichloromethane (CH_2Cl_2) were purified by a solvent-purification system (GlassContour) equipped with columns of activated alumina and supported-copper catalyst (Q-5) before use. 1,1,1,3,3,3-Hexafluoropropan-2-ol (HFIP) was distilled from CaH_2 and stored over activated molecular sieves 4A. Cyclohexane was distilled from $MgSO_4$ and stored over activated molecular sieves 4A. 1-Bromo-2-(2-phenylethynyl)benzene was prepared according to the literature procedures.[1)] Unless otherwise noted, materials were obtained from commercial sources and used directly without further purifications.

4.6.2. Preparation of Substrates

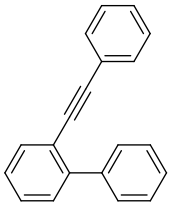
4.6.2.1. Preparation of 2-(Phenylethnyl)biaryls[2)]

[*Precedure A*]



After 1-bromo-2-(phenylethynyl)benzene (1.2 mmol) was dissolved in toluene (3.0 mL), EtOH (1.5 mL), and H_2O (1.5 mL), the solution was degassed by using the freeze-pump-thaw method three times. To a solution were added $PdCl_2(PPh_3)_2$ (5 mol%), Na_2CO_3 (1.2 equiv), and arylboronic acid (1.2 equiv). After stirring at 70 ^oC for 2–6 h, the reaction was quenched with aquenous NH_4Cl, and organic materials were extracted with EtOAc three times. The combined extracts were washed with brine and dried over Na_2SO_4 After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography to give the corresponding 2-(phenylethynyl)biaryls **1**.

2-(Phenylethynyl)biphenyl (1a)



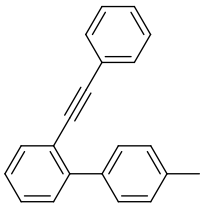
Compound **1a** was prepared according to *Procedure A* using 1-bromo-2-(phenylethynyl)benzene (316 mg, 1.23 mmol), $PdCl_2(PPh_3)_2$ (43 mg, 61 μmol), Na_2CO_3 (162 mg, 1.5 mmol), and phenylboronic acid (176 mg, 1.44 mmol) at 70 ^oC for 2 h. Purification by silica gel column chromatography (hexane) gave **1a** (235 mg, 75%) as a pale yellow oil.

^1H NMR (500 MHz, $CDCl_3$): δ 7.27–7.29 (m, 3H), 7.32–7.35 (m, 3H), 7.38–7.48 (m, 5H), 7.64–7.68 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 89.7, 92.6, 121.9, 123.8, 127.4, 127.8, 128.2,

128.4, 128.6, 128.9, 129.7, 129.8, 131.7, 133.2, 140.9, 144.3.

Spectral data for this compound showed good agreement with literature data.[2)]

4'-Methyl-2-(phenylethynyl)biphenyl (1b)

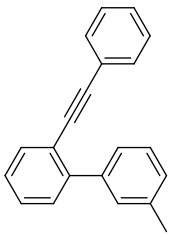


Compound **1b** was prepared according to *Procedure A* using 1-bromo-2-(phenylethynyl)benzene (312 mg, 1.21 mmol), $PdCl_2(PPh_3)_2$ (43 mg, 61 μmol), Na_2CO_3 (163 mg, 1.54 mmol), and 4-methylphenylboronic acid (210 mg, 1.54 mmol) at 70 ^oC for 6 h. Purification by silica gel column chromatography (hexane) gave **1b** (232 mg, 71%) as a pale yellow oil.

^1H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 3H), 7.25–7.32 (m, 6H), 7.35–7.42 (m, 4H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.63–7.65 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.2, 89.5, 92.1, 121.4, 123.5, 126.8, 128.0, 128.2, 128.5, 128.6, 129.2, 129.4, 131.3, 133.0, 137.2, 137.6, 143.7.

Spectral data for this compound showed good agreement with the literature data.[3)]

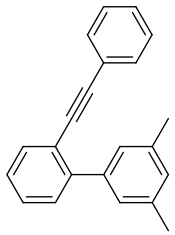
3'-Methyl-2-(phenylethynyl)biphenyl (1c)



Compound **1c** was prepared according to *Procedure A* using 1-bromo-2-(phenylethynyl)benzene (314 mg, 1.21 mmol), $PdCl_2(PPh_3)_2$ (50 mg, 71 μmol), Na_2CO_3 (188 mg, 1.8 mmol), and 3-methylphenylboronic acid (202 mg, 1.49 mmol) at 70 ^oC for 6 h. Purification by silica gel column chromatography (hexane) gave **1c** (232 mg, 71%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.38 (s, 3H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.20–7.26 (m, 4H), 7.29–7.33 (m, 4H), 7.38 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.45–7.7.47 (m, 2H), 7.61 (dd, *J* = 7.6, 0.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.5, 89.5, 92.2, 121.5, 123.5, 126.5, 126.9, 127.7, 128.0, 128.1, 128.2, 128.4, 129.4, 130.1, 131.3, 132.8, 137.3, 140.4, 143.9. IR (neat): ν 3057, 3030, 3020, 1599, 1489, 1441, 750, 702, 687 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{21}H_{16}$ $[M]^+$: 268.1247; Found: 268.1244.

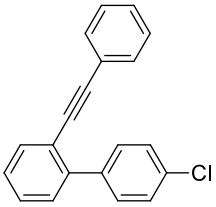
3',5'-Dimethtyl-2-(phenylethynyl)biphenyl (1d)



Compound **1d** was prepared according to *Procedure A* using 1-bromo-2-(phenylethynyl)benzene (312 mg, 1.21 mmol), $PdCl_2(PPh_3)_2$ (47 mg, 66 μmol), Na_2CO_3 (177 mg, 1.7 mmol), and 3,5-dimethylphenylboronic acid (228 mg, 1.52 mmol) at 70 ^{o}C for 6 h. Purification by silica gel column chromatography (hexane) gave **1d** (219 mg, 64%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.39 (s, 6H), 7.04 (s, 1H), 7.28–7.39 (m, 3H), 7.30–7.31 (m, 3H), 7.32–7.35 (m, 2H), 7.38 (ddd, *J* = 7.5, 7.5, 1.2 Hz, 1H), 7.42 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.63 (dd, *J* = 7.5, 0.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.4, 89.6, 92.2, 121.4, 123.6, 126.8, 127.2, 128.0, 128.2, 128.4, 129.1, 129.4, 131.3, 132.8, 137.3, 140.4, 144.0. IR (neat): ν 3059, 3032, 3022, 2916, 1603, 1493, 850, 750, 687 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{22}H_{18}$ $[M]^+$: 282.1403; Found: 282.1411.

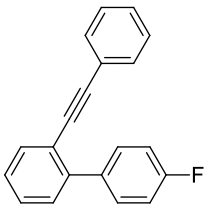
4'-Chloro-2-(phenylethynyl)biphenyl (1e)



Compound **1e** was prepared according to *Procedure A* using 1-bromo-2-(phenylethynyl)benzene (313 mg, 1.22 mmol), $PdCl_2(PPh_3)_2$ (44 mg, 63 μmol), Na_2CO_3 (164 mg, 1.5 mmol), and 4-chlorophenylboronic acid (231 mg, 1.48 mmol) at 70 ^oC for 6 h. Purification by silica gel column chromatography (hexane) gave **1e** (256 mg, 73%) as a pale yellow solid.

^1H NMR (500 MHz, $CDCl_3$): δ 7.23–7.29 (m, 4H), 7.31–7.33 (m, 4H), 7.38 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 7.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 89.0, 92.5, 121.4, 123.1, 127.3, 128.0, 128.2, 128.3, 128.5, 129.2, 130.6, 131.3, 133.0, 133.5, 138.9, 142.4. IR (neat): ν 3059, 1489, 1471, 1088, 827, 750, 687 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{20}H_{13}Cl$ $[M]^+$: 288.0700; Found: 288.0695.

4'-Fluoro-2-(phenylethynyl)biphenyl (1f)



Compound **1f** was prepared according to *Procedure A* using 1-bromo-2-(phenylethynyl)benzene (315 mg, 1.22 mmol), $PdCl_2(PPh_3)_2$ (57 mg, 80 μmol), Na_2CO_3 (178 mg, 1.7 mmol), and 4-fluorophenylboronic acid (213 mg, 1.52 mmol) at 70 ^oC for 6 h. Purification by silica gel column chromatography (hexane) gave **1f** (244 mg, 73%) as a pale yellow oil.

^1H NMR (500 MHz, $CDCl_3$): δ 7.12–7.17 (m, 2H), 7.28–7.32 (m, 3H), 7.32–7.36 (m, 3H), 7.38–7.40 (m, 2H), 7.61–7.65 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 89.1, 92.4, 114.8 (d, J_{CF} =

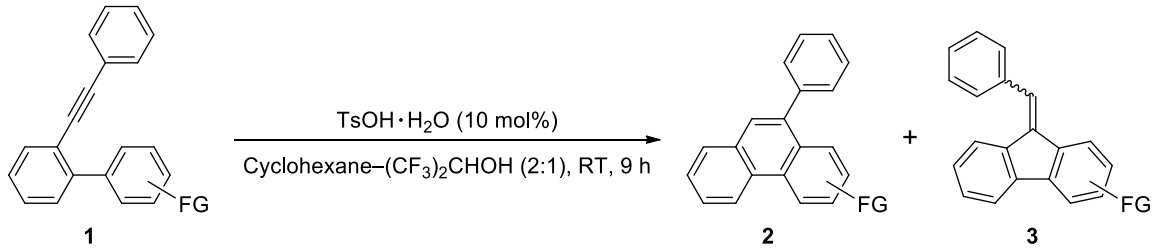
21 Hz), 121.6, 123.3, 127.2, 128.2, 128.3, 128.6, 129.4, 131.0 (d, J_{CF} = 8 Hz), 131.3, 132.9, 136.6 (d, J_{CF} = 3 Hz), 142.8, 162.4 (d, J_{CF} = 247 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 46.5–46.6 (m).

Spectral data for this compound showed good agreement with literature data.[3)]

4.6.3. Synthesis of Polycyclic Aromatic Hydrocarbons

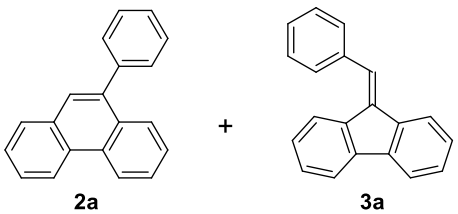
4.6.3.1. Synthesis of Phenacenes

[*Procedure B*]



After 2-(phenylethynyl)biaryl (**1**, 0.3 mmol) was dissolved in cyclohexane (3 mL). HFIP (0.8 mL) was added to mixture. To the reaction mixture was added a HFIP (0.7 mL) solution of TsOH·H_2O (5.7 mg, 30 μmol). After stirring vigorously for 9 h under air, CH_2Cl_2 (5 mL) was added, and the reaction mixture was filtered through a pad of $NaHCO_3$ (CH_2Cl_2). After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography to give the corresponding phenathrenes **2** including a small of dibenzofulvenes **3**.

9-Phenylphenanthrene (2a)



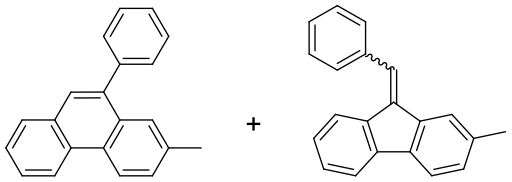
Phenacene **2a** was synthesized according to *Procedure B* using 2-(phenylethynyl)biphenyl (**1a**, 76 mg, 0.30 mmol), TsOH·H_2O (6.1 mg, 32 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/$CHCl_3$ = 20:1) gave phenanthrene **2a**

including a small amount of dibenzofluvene **3a** (73 mg, 96%, **2a**/**3a** = 90:10) as a white solid.

2a: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.44 (m, 1H), 7.46–7.53 (m, 5H), 7.55–7.58 (m, 1H), 7.60–7.63 (m, 2H), 7.65 (s, 1H), 7.84 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.90 (dd, *J* = 8.2, 0.9 Hz, 1H), 8.67 (d, *J* = 8.2 Hz, 1H), 8.72 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 122.5, 122.9, 126.4, 126.46, 126.54, 126.8, 126.9, 127.3, 127.5, 128.3, 128.6, 129.9, 130.0, 130.6, 131.1, 131.5, 138.7, 140.8.

Spectral data for this compound showed good agreement with literature data.[4)]

2-Methyl-10-phenylphenanthrene (2b)



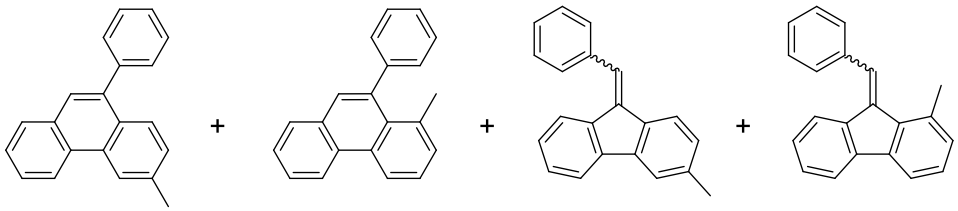
Phenacene **2b** was synthesized according to *Procedure B* using 4'-methyl-2-(phenylethynyl)biphenyl (**1b**, 82 mg, 0.30 mmol), $TsOH·H_2O$ (6.1 mg, 32 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/$CHCl_3$ = 20:1) gave phenanthrene **2b** including a small amout of dibenzofluvene **3b** (76 mg, 93%, **2b**/**3b** = 93:7) as a pale yellow oil.

2b: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 3H), 7.43–7.55 (m, 7H), 7.58–7.61 (m, 1H), 7.62 (s, 1H), 7.67 (s, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 8.61 (d, *J* = 8.7 Hz, 1H), 8.62 (d, *J* = 9.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 21.7, 122.3, 122.8, 126.36, 126.36, 126.5, 127.3, 127.6, 128.2, 128.3, 128.4, 128.6, 129.98, 130.02, 131.16, 131.19, 136.2, 138.5, 141.0.

Spectral data for this compound showed good agreement with literature data.[3)]

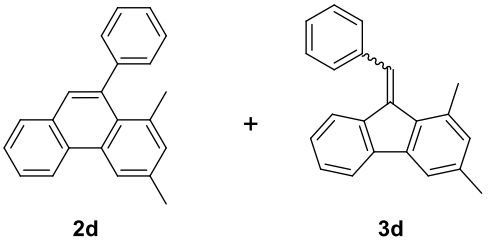
3-Methyl-10-phenylphenanthrene (2c)



Phenacene **2c** was synthesized according to *Procedure B* using 3'-methyl-2-(phenylethynyl)biphenyl (**1c**, 81 mg, 0.30 mmol), $TsOH·H_2O$ (5.8 mg, 30 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/$CHCl_3$ = 20:1) gave phenanthrene **2c** including a small amout of dibenzofulvene **3c** (66 mg, 81%, **2c**/**2c'**/**3c**/**3c'** = 50:45:3:2) as a pale yellow oil.

(**2c**/**2c'** =53:47): ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.02 (s, 3H×0.47 = 1.41H), 2.57 (s, 3H×0.53 = 1.59H), 7.30 (m, 8H×0.53 + 11H×0.47 = 9.94H), 7.76–7.80 (m, 2H×0.53 = 1.06H **2c**), 7.82 (d, *J* = 7.1 Hz, 1H×0.53H), 8.52 (s, 1×0.53 = 0.53H), 8.64–8.67 (m, 1H×0.53 + 2H×0.47 = 1.47H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.9, 25.4, 121.3,122.5, 122.7, 122.9, 126.1, 126.3, 126.5, 126.6, 126.66, 126.70,126.72, 126.8, 127.2, 127.8, 128.16, 128.18, 128.22, 128.6, 129.0, 129.3, 129.7, 130.00, 130.02, 130.1, 130.4, 130.68, 130.71, 130.73, 131.72, 131.75, 136.10, 136.15, 138.6, 138.7, 140.9, 145.3. IR (neat): ν 3076, 3057, 3020, 1595, 1491, 1452, 1442, 1215, 891, 822, 760, 744, 731, 700 cm^{-1}. HRMS (EI+): *m*/*z* Calcd. for $C_{21}H_{16}$ $[M]^+$: 268.1247; Found: 268.1247.

1,3-Dimethtyl-10-phenylphenanthrene (2d)



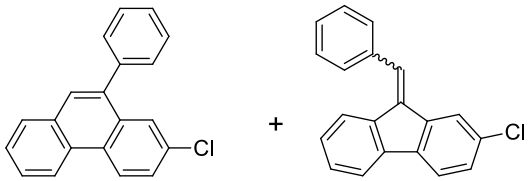
Phenacene **2d** was synthesized according to *Procedure B* using 3',5'-dimethyl-2-(phenylethynyl)biphenyl (**1d**, 86 mg, 0.30 mmol), $TsOH·H_2O$ (6.1 mg, 32 μmol),

cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/$CHCl_3$ = 20:1) gave phenanthrene **2d** including a small amount of dibenzofluvene **3d** (69 mg, 80%, **2d**/**3d** = 97:3) as a white solid.

2d: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.93 (s, 3H), 2.47 (s, 3H), 7.10 (s, 1H), 7.28–7.31 (m, 5H), 7.43 (s, 1H), 7.44–7.47 (m, 1H), 7.49–7.53 (m, 1H), 7.70 (dd, *J* = 7.8, 1.1 Hz, 1H), 8.40 (s, 1H), 8.60 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.6, 25.2, 121.1, 122.9, 126.3, 126.6, 126.7, 127.7, 128.0, 128.1, 129.1, 129.3, 130.1, 130.9, 131.9, 132.5, 135.6, 135.9, 138.6, 145.4.

Spectral data for this compound showed good agreement with literature data.[5)]

2-Chloro-10-phenylphenanthrene (2e)



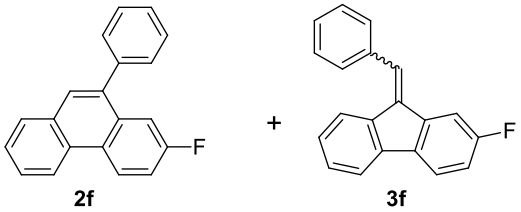
2e **3e**

Phenacene **2e** was synthesized according to *Procedure B* using 4'-chloro-2-(phenylethynyl)biphenyl (**1e**, 87 mg, 0.30 mmol), $TsOH·H_2O$ (6.0 mg, 32 μmol), cyclohexane (3.0 mL), and HFIP (1.5 mL). Purification by silica gel column chromatography (hexane/$CHCl_3$ = 20:1) gave phenanthrene **2g** including a small amouto of dibenzofluvene **3e** (77 mg, 96%, **2e**/**3e** = 94:6) as a pale yellow solid.

2e: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41–7.50 (m, 5H), 7.52 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.54–7.61 (m, 2H), 7.64 (s, 1H), 7.81 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.85 (d, *J* = 2.2 Hz, 1H), 8.54 (d, *J* = 8.1 Hz, 1H), 8.57 (d, *J* = 8.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 122.4, 124.5, 125.9, 126.8, 126.9, 127.1, 127.6, 128.5, 128.6, 128.7, 128.9, 129.4, 129.9, 131.3, 132.2, 132.5, 137.8, 140.0.

Spectral data for this compound showed good agreement with literature data.[6)]

2-Fluoro-10-phenylphenanthrene (2f)



2f **3f**

Phenacene **2f** was synthesized according to *Procedure B* using 4'-fluoro-2-(phenylethynyl)biphenyl (**1f**, 82 mg, 0.30 mmol), $TsOH \cdot H_2O$ (5.7 mg, 30 μmol), cyclohexane (3.0 mL), and HFIP (0.8, 0.7 mL). Purification by silica gel column chromatography (hexane/$CHCl_3$ = 20:1) gave phenanthrene **2f** including a small sount of dibenzofluvene **3f** (74 mg, 91%, **2f**/**3f** = 90:10) as a white solid.

2f: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33–7.37 (m, 1H), 7.42–7.46 (m, 1H), 7.48–7.49 (m, 4H), 7.53–7.58 (m, 2H), 7.60–7.64 (m, 1H), 7.68 (s, 1H), 7.84 (dd, *J* = 7.8, 1.1 Hz, 1H), 8.57 (d, *J* = 8.3 Hz, 1H), 8.66–8.69 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 111.3 (d, J_{CF} = 22 Hz), 115.3 (d, J_{CF} = 24 Hz), 122.3, 125.2 (d, J_{CF} = 9 Hz), 126.6, 126.9, 127.21, 127.22, 128.5, 128.6, 128.8, 129.6, 129.9, 131.0, 132.7 (d, J_{CF} = 8 Hz), 138.1 (d, J_{CF} = 4 Hz), 140.2, 161.4 (d, J_{CF} = 246 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 47.57–47.62 (m).

Spectral data for this compound showed good agreement with literature data.[3)]

4. Reference

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Chapter 5

Conclusion

I demonstrated facile syntheses of polycyclic aromatic hydrocabons (PAHs) via Brønsted-catalyzed cationic cyclization of (i) carbonyl compounds including their analogues and (ii) unactivated alkynes bearing biaryls, both reactions of which are rigorously promoted in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP).

In Chapter 2, I achieved Brønsted acid-catalyzed dehydrative cycloaromatization (Bradsher reaction) via intermediary oxocarbenium ions, leading to the synthesis of various PAHs such as phenacenes, acenes, and triphenylenes. These reactions were effectively promoted by the cation-stabilizing effect of HFIP solvent and applied to carbonyl compounds, vinyl ethers, and acetals.

In Chapter 3, I synthesized rarely reported *ortho*-fused six-hexagon benzenoids via Brønsted acid-catalyzed tandem cycloaromatization of easily accessible naphthalene-based bisacetals. This methodology will enable the regioselective synthesis of more extensive *ortho*-fused benzenoids.

In Chapter 4, I developed unprecedented Brønsted acid-catalyzed intramolecular hydroarylation of unactivated alkynes to afford substituted phenacenes. The key to success in this reaction was a two-phase HFIP/cyclohexane solvent system, which promoted the protonation of alkynes to generate the vinyl cation intermediates, and suppressed side reactions.

Through these studies, I accomplished Brønsted acid-catalyzed cationic cyclizations involving formation of additional benzene rings. These protocols require only a catalytic amount of Brønsted acid, and thus will enable a large-scale synthesis of PAHs and accelerate research on their applications as electronic materials.

List of Publications

1. “Facile Synthesis of Polycyclic Aromatic Hydrocarbons: Brønsted Acid Catalyzed Dehydrative Cycloaromatization of Carbonyl Compounds in 1,1,1,3,3,3-Hexafluoropropan-2-ol”

   Takeshi Fujita, Ikko Takahashi, Masaki Hayashi, Jingchen Wang, Kohei Fuchibe, Junji Ichikawa

   European Journal of Organic Chemistry **2017**, 262–265.

2. “Brønsted Acid-catalyzed Tandem Cycloaromatization of Naphthalene-besed Bisacetals: Selective Synthesis of *ortho*-Fused Six-hexagon Benzenoids”

   Ikko Takahashi, Masaki Hayashi, Takeshi Fujita, Junji Ichikawa

   Chemistry Letters **2017**, *46*, 392–394.

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