Methylarene-Based PAH Synthesis via Domino Cyclization of 1,1-Difluoro-1-Alkenes

Kohei Fuchibe,[1] Go Takao,[1] Hiroki Takahashi,[1] Shiori Ijima,[1] and Junji Ichikawa*

[1] Division of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba, 1–1–1, Tennodai, Tsukuba, Ibaraki 305–8571, Japan.

E-mail: junji@chem.tsukuba.ac.jp

Kohei Fuchibe
Kohei Fuchibe was born in Fukui, Japan in 1974. He received his B.Sc. in 1999 and Ph.D. in 2002 from the University of Tokyo (Prof. K. Narasaka). He joined Gakushuin University as a Research Associate in 2002 and was shifted to an Assistant Professor in 2007. He moved to University of Tsukuba as a Lecturer in 2007 and was promoted to an Associate Professor in 2011. His research interests involve synthetic reactions catalyzed by transition metals or organic small molecules.

Go Takao
Go Takao was born in Hiroshima, Japan in 1991. He received his B.Sc. in 2015 and M.Sc. in 2017 from Yamaguchi University (Prof. T. Murafuji). He enrolled in University of Tsukuba (Doctor's Program in Chemistry, Prof. J. Ichikawa) in 2017. He is now focusing on studies of oxidative generation of fluorinated carbocations, directed toward organic synthesis.

Hiroki Takahashi
Hiroki Takahashi was born in Tochigi, Japan in 1986. He received his B.Sc. in 2009 and M.Sc. in 2011 from University of Tsukuba (Prof. J. Ichikawa). After he worked on synthetic reactions that proceed through fluorinated carbocations at University of Tsukuba, he joined Midori Kagaku Co., Ltd. in 2011.

Shiori Ijima
Shiori Ijima was born in Tochigi, Japan in 1991. She received her B.Sc. in 2014 from Tokyo University of Science (Prof. T. Satoh) and M.Sc. in 2016 from University of Tsukuba (Prof. J. Ichikawa). After she worked on domino cyclization of fluoroalkenes at University of Tsukuba, she joined Teikoku Printing Inks Mfg. Co., Ltd. in 2016.

Junji Ichikawa
Junji Ichikawa was born in Tokyo, Japan in 1958. He received his B.Sc. in 1981 and Ph.D. in 1986 from the University of Tokyo (Prof. T. Mukaiyama). He joined Kyushu University as an Assistant Professor in 1985. In 1989, he was a research associate at Harvard University (Prof. E. J. Corey) and then worked at Kyushu Institute of Technology as a Lecturer and an Associate Professor. In 1999, he moved to the University of Tokyo as an Associate Professor. He was appointed Professor at University of Tsukuba in 2007. His research interests lie in the area of synthetic methodology based on the properties of metals and fluorine.

Abstract

Polycyclic aromatic hydrocarbons (PAHs) containing 4–7 benzene rings were synthesized via a methylarene-based protocol. Trimethyl[2-(trifluoromethyl)allyl]silane was electrophilically benzylated with Ar^1CH_2Br (prepared from Ar^1CH_3) to afford 2-trifluoromethyl-1-alkenes that were in turn nucleophilically benzylated with Ar^2CH_2Li (prepared from Ar^2CH_3) through an S_N2'-type reaction to produce 1,1-difluoroethylenes, which are cyclization precursors bearing two 2-arylethyl groups. Magic acid efficiently promoted the domino Friedel–Crafts-type cyclization of these precursors, followed by dehydrogenation that enabled the connection among two aryl groups (Ar^1 and Ar^2) by forming two benzene rings between them, facilitating the synthesis of the desired higher-order PAHs. With the proposed protocol, the combination of even a limited number of methylarenes can yield a variety of PAHs in diverse configurations.

Keywords: Carbocation, Fluorine, PAHs

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) consist of fused benzene rings in various configurations;[1] for example, acenes, phenacenes, and helicenes exhibit linear, zig-zag, and helical arrangements with chirality (number of benzene rings n $\geq$ 5), respectively, of the benzene rings.

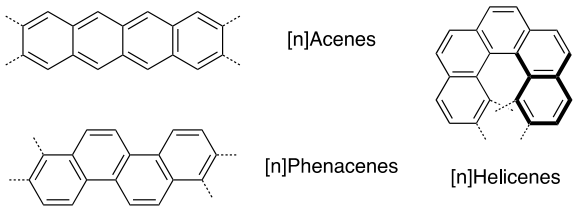
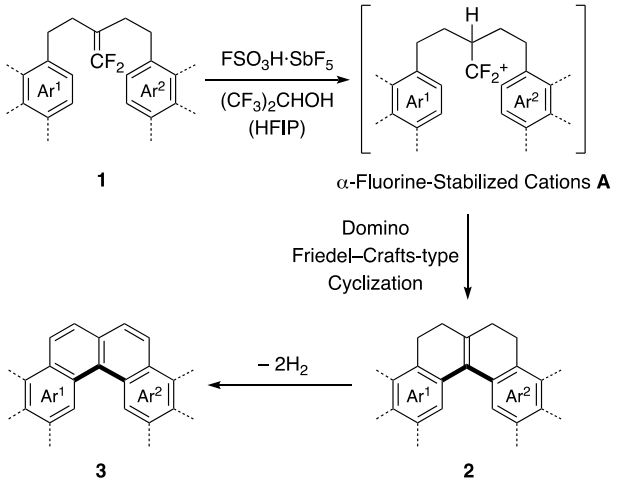


Figure 1. Major families of polycyclic aromatic hydrocarbons (n represents the number of benzene rings).

During the past decades, PAHs have attracted considerable attention, mainly because of their viability as materials for organic electronic devices.[2] Acenes are already known as one of the most representative organic semiconducting materials.[3] Moreover, phenacenes are emerging as a new semiconducting PAH subfamily, partly due to their oxidation resistance and O_2 sensing behavior;[4] thus, the synthesis and physical properties of higher-order phenacenes have been extensively investigated.[5] Helicenes also appeared quite recently as organic semiconductors[6] with unique chirality-derived characteristics.[7]

These advances have made PAHs fascinating synthetic targets. Besides the frequently used oxidative photocyclization of *cis*-stilbene derivatives,[8] many powerful methods such as oxidative aromatic coupling (Scholl reaction),[9] alkynylbiaryl cyclization,[10,11] and alkyne trimerization[12] have been developed.[13] However, given the wide diversity of the PAH structures, a systematic approach to their synthesis is still highly required.[14,15]



Scheme 1. Domino cyclization of 1,1-difluoroalkenes.

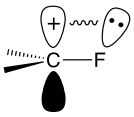


Figure 2. The α-cation stabilizing effect of fluorine substituents.

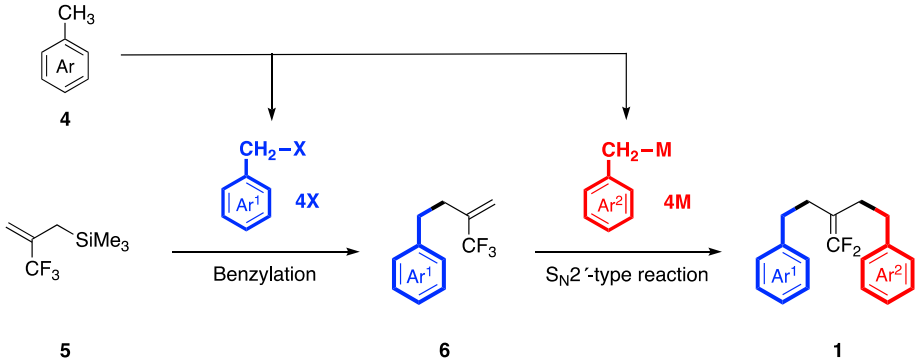
We have reported the domino Friedel–Crafts-type cyclization of 1,1-difluoro-1-alkenes **1** (Scheme 1), which efficiently yielded a [4]helicene structure by forming two benzene rings between two aryl groups (Ar^1 and Ar^2).[16] In this process, the fluorine substituents play crucial roles:[17] (i) stabilizing the α-carbocations by donating their unshared electron pair to the vacant p-orbital of the cationic center (Figure 2) and (ii) acting as leaving groups because of their high electronegativity. Upon the treatment of **1** bearing two 2-arylethyl groups [CF_2=C($CH_2CH_2Ar^1$)($CH_2CH_2Ar^2$)] with magic acid (FSO_3H·SbF_5) in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP),[18] the protonation proceeded regioselectively, generating α-fluorine-stabilized cations **A**. These, in turn, underwent the domino Friedel–Crafts-type cyclization followed by dehydrogenation of the resulting tetracyclic products **2**, forming [4]helicenes and their π-extended variants **3**.[19,20]

Despite the utility of the domino cyclization, the preparation of the starting **1** has been less examined. Bromine-mediated coupling was employed for the symmetrical difluoroalkenes [CF_2=C(CH_2CH_2Ar)$_2$],[21] while the S_N2'-type reaction of 2-trifluoromethyl-1-alkenes was adopted (not shown) for the unsymmetrical ones [CF_2=C($CH_2CH_2Ar^1$)($CH_2CH_2Ar^2$)].[22] For the systematic synthesis of PAHs, we based the preparation of **1** on methylarenes **4** as starting materials (Scheme 2). Allylsilane **5**, originally developed as a (trifluoromethyl)allylating agent for aldehydes or ketones,[23] would react with the benzyl halides **4X** (Ar^1CH_2X) derived from **4** (Ar^1CH_3). Then, the resulting (trifluoromethyl)alkenes **6** would undergo an S_N2'-type reaction with the benzyl metals **4M** (Ar^2CH_2M) derived from **4** (Ar^2CH_3), forming the desired unsymmetrical **1**. Thus, the combination of even a limited number of **4** could facilitate the production of a variety of **1**, whose domino cyclization might lead to the corresponding PAHs.[24]

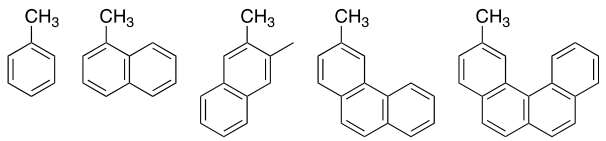
2. Results and Discussion

Preparation of Methylarene 4. Five methylarenes (Figure 3) were selected for this study. Toluene (**4a**) and methylnaphthalenes **4b**,**c** are commercially available, while methylphenanthrene **4d**[20] and methyl[4]helicene **4e**[16] were prepared by our cation cyclization methods as follows.

For the preparation of **4d**, commercially available 2-bromotoluidine was subjected to Suzuki–Miyaura coupling with phenylboronic acid (Scheme 3). The subsequent diazotization and iodination resulted in the corresponding biphenyl iodide in a 94% yield (two steps); the formylation of this iodide with dimethylformamide (DMF, 74% yield) followed by methoxymethylidenation gave the corresponding vinyl ether (94% yield, *cis*/*trans* = 34:66). Upon treatment with trifluoromethanesulfonic acid (TfOH, 1.2 equiv), the vinyl ether underwent Friedel–Crafts-type cyclization via the in situ generated oxocarbenium ion, forming the desired **4d** in a 68% yield.



Scheme 2. Concept of methylarene-based approach to 1,1-difluoroalkenes.



4a **4b** **4c** **4d** **4e**

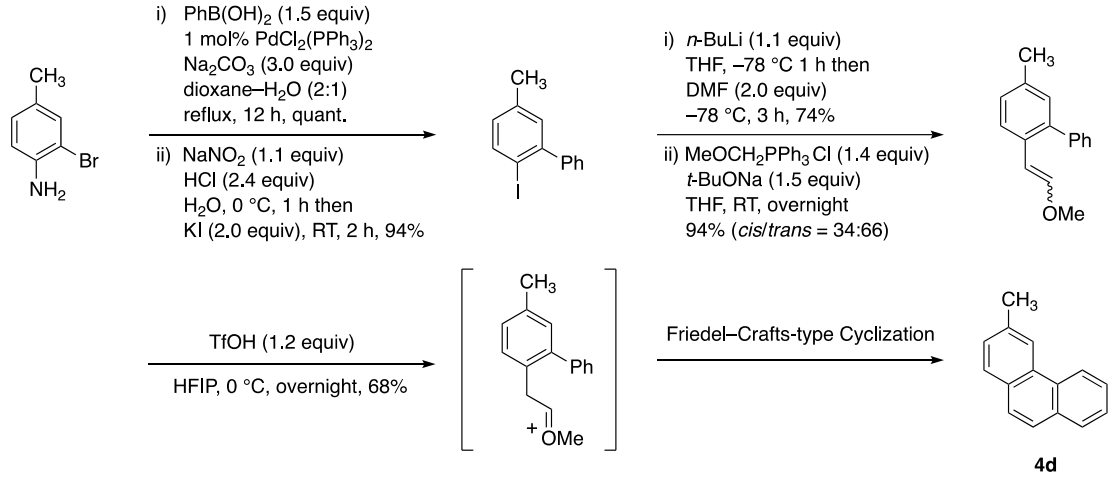
Methylarene	Aryl Group	# of Benzene Ring(s)
4a	Phenyl	1
4b	Naphthalen-1-yl	2
4c	3-Methylnaphthalen-2-yl	2
4d	Phenanthren-3-yl	3
4e	[4]Helicen-2-yl	4

Figure 3. List of Starting Methylarenes **4**

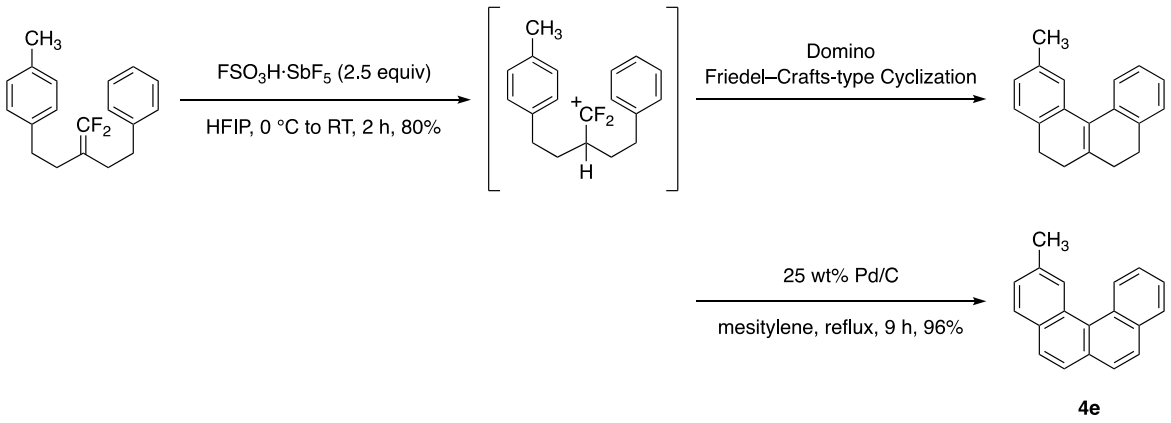
4e was prepared through the method as shown in Scheme 4. Thus, **1** bearing a phenyl group and a *p*-tolyl group was treated with magic acid (2.5 equiv) in HFIP (80% yield for domino cyclization); the subsequent dehydrogenation of the product with Pd/C gave **4e** (96% yield).

Preparation of Benzyl Bromides 4X and 2-Trifluoromethyl-1-alkenes 6 (Benzylation). The electrophilic benzyl components ($ArCH_2Br$ **4X**) were prepared by the bromination of **4** (Table 1). The bromination of **4b** and **4c** with *N*-bromosuccinimide (NBS)/benzoyl peroxide (BPO) in refluxing tetrachloromethane (77 °C) gave the corresponding benzyl bromides **4Xb** and **4Xc** in 78% and 72% yields, respectively (Entries 1 and 2). However, **4d** formed the corresponding bromide **4Xd** only in a 56% yield under similar conditions (Entry 3) partly because of the formation of (dibromomethyl)phenanthrene; to suppress such dibromination, the process was examined at a lower temperature. Unlike BPO and azobis(isobutyronitrile) that operate at 80 and 70 °C, respectively, 2,2′-azobis(2,4-dimethyl-4-methoxy)valeronitrile (V-70) acts as a radical initiator at 25 °C.[25] Thus, **4d** was treated with NBS/V-70 in refluxing dichloromethane (40 °C) to undergo monobromination and the desired **4Xd** was obtained in an 80% yield (Entry 4); NBS/V-70 also allowed a good yield (84%) of (bromomethyl)[4]helicene **4Xe** (Entry 5).

With benzyl bromide ($PhCH_2Br$, **4Xa**) and the prepared bromides **4Xb–e**, the benzylation of trimethyl[2-(trifluoromethyl)allyl)silane (**5**) was examined. The allylsilane was prepared from the commercially available ethyl trifluoroacetate via the reported procedure.[23] **5** readily reacted with the benzyl bromides in the presence of a stoichiometric amount of cesium fluoride (Table 2). α-Bromo-*p*-xylene (**4Xf**) was adopted as a model compound and treated with **5** (1.1 equiv) and cesium fluoride (1.1 equiv; Kanto Chemical Co., Inc., cesium fluoride 4N) in DMF at 60 °C (Entry 1); the desired CF_3-allylation product (2-trifluoromethyl-1-alkene **6f**) was obtained in a 56% yield. Attempts to perform the reaction in dimethyl sulfoxide (DMSO) or with sodium fluoride as the fluoride ion source failed (Entries 2 and 3). Among the other fluoride ion sources examined, namely, *n*-Bu_4NF,

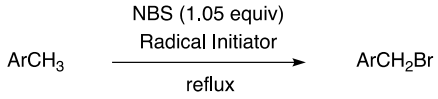


Scheme 3. Preparation of methylphenanthrene **4d**.



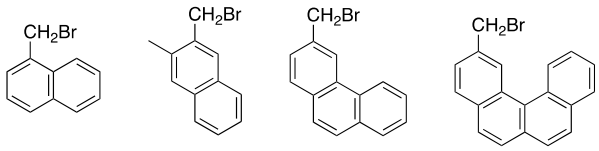
Scheme 4. Preparation of methyl[4]helicene **4e**.

Table 1. Preparation of benzyl bromides **4Xb–e**.



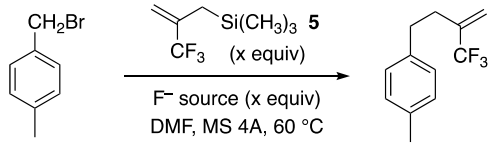
Entry	**4**	Solvent, Initiator (mol%)	*t* (h)	**4X**	Yield (%)
1	**4b**	CCl_4, BPO (3)	3	**4Xb**	78
2	**4c**	CCl_4, BPO (3)	3	**4Xc**	72 [a]
3	**4d**	CCl_4, BPO (3)	13	**4Xd**	56
4	**4d**	CH_2Cl_2, V-70 (5)	3	**4Xd**	80
5 [b]	**4e**	CH_2Cl_2, V-70 (5)	2	**4Xe**	84 [a]

a) ^{1}H NMR yield based on an internal standard CH_2Br_2. b) NBS (1.5 equiv). BPO = Dibenzoyl peroxide; V-70 = 2,2´-azobis(2,4-dimethyl-4-methoxy)valeronitrile.



4Xb **4Xc** **4Xd** **4Xe**

Table 2. Benzylation of [(trifluoromethyl)allyl]silane **5**.



4Xf **6f**

Entry	F⁻ Source	x	*t* (h)	Yield (%)
1	CsF	1.1	5	56
2 [a]	CsF	1.1	7	11
3	NaF	1.1	7	–
4	*n*-Bu_4N F [b]	1.1	1	Trace
5	$(Me_2N)_3S$ SiF_2Me_3 [c]	1.1	4	57
6	*n*-Bu_4N SnF_2Ph_3	1.1	4	–
7	CsF	2.1	4	67

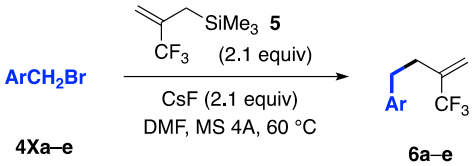
a) The reaction was conducted in DMSO. b) TBAF. c) TASF.

$(Me_2N)_3S$ SiF_2Me_3 (TASF), and *n*-Bu_4N SnF_2Ph_3, TASF formed **6f** in a 57% yield (Entries 4–6). The use of 2.1 equiv of **5** and 2.1 equiv of cesium fluoride improved this yield up to 67% (Entry 7).

Various (trifluoromethyl)alkenes **6** were synthesized by the CsF-promoted benzylation of **5** (Table 3). When using **4Xa** (1.1 equiv relative to **5**), phenylated (trifluoromethyl)alkene **6a** was obtained in a quantitative yield (Entry 1); the benzylation with the other bromides (**4Xb–e**) were effected under the optimized conditions as summarized in Table 2, leading to the corresponding **6b–e** in 46–89% yields (Entries 2–5).[26]

Generation of Benzyllithiums 4M and Preparation of 1,1-Difluoroalkenes 1 ($S_N2´$-Type Reaction). The synthesized **6** were subjected to an $S_N2´$-type reaction to afford **1**, the domino cyclization precursor. The required benzyllithiums **4Ma–c** were generated by the deprotonation of **4a–c** (Scheme 5, Method A). **4a** was treated with an equimolar amount of butyllithium in the presence of *N*,*N*,*N*´,*N*´-tetramethylethylenediamine (1 equiv) to give **4Ma**,

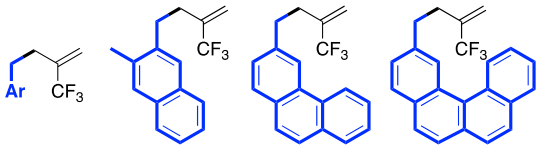
Table 3. Preparation of 2-trifluoromethyl-1-alkenes **6** with benzyl bromides **4X**.



4Xa–e **6a–e**

Entry	**4X**	*t* (h)	**6**	Yield (%)
1 [a]	**4Xa**	7	**6a**	Quant [b]
2	**4Xb**	1	**6b**	84
3 [c]	**4Xc**	7	**6c**	47
4	**4Xd**	1	**6d**	89
5	**4Xe**	5	**6e**	46

a) $PhCH_2Br$ (**4Xa**, 1.1 equiv), **5**, CsF (1.1 equiv). b) Yield based on **5**. c) **5** (1.1 equiv), CsF (1.1 equiv), 90 °C.

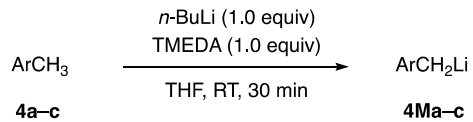


6a Ar = Ph
6b Ar = 1-Naph
6c **6d** **6e**

which in turn reacted with **6a**, producing the desired difluoroalkene **1a** as an $S_N2´$-type product in an 80% yield (Table 4, Entry 1).[16] The naphthylated difluoroalkenes **1b** and **1c** were similarly prepared using **4Mb** and **4Mc**, correspondingly generated from **4b** and **4c** via Method A, in 80% and 96% yields, respectively (Table 4, Entries 2 and 3).

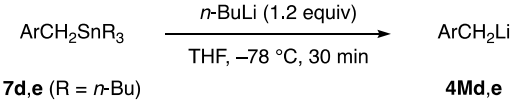
The generation of **4Md** and **4Me** bearing an extended π-system (a phenanthrene or a [4]helicene moiety) was not simple; when **6a** was treated with a solution prepared from **4d** via Method A, the desired product **1d** was obtained only in a 12% yield (Table 4, Entry 4). Replacing butyllithium with *sec*-butyllithium resulted in no change (12% yield; Table 4, Entry 5). Attempts to generate **4Md** through lithium–halogen exchange were also fruitless (not shown); **4Xd** was treated with butyllithium (1.0 equiv) in THF at –78 °C, followed by **6a**

Method A (Deprotonation)



4a–c **4Ma–c**

Method B (Sn–Li Exchange)

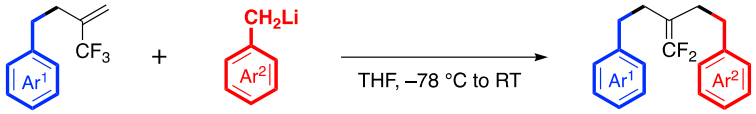


7d,**e** (R = *n*-Bu) **4Md**,**e**

Benzyllithium	Aryl Group	# of Benzene Ring(s)
4Ma	Phenyl	1
4Mb	Naphthalen-1-yl	2
4Mc	3-Methylnaphthalen-2-yl	2
4Md	Phenanthren-3-yl	3
4Me	[4]Helicen-2-yl	4

Scheme 5. Generation of benzyllithiums **4Ma–e**.

Table 4. Preparation of 1,1-difluoro-1-alkenes **1** from (trifluoromethyl)alkenes **6** and benzyllithiums **4M**.



6a,b,d **4Ma–e** **1a–h**

Entry	**6**	**4M**	Generation of **4M**	*t* (h)	**1**	Yield (%)
1	**6a**	**4Ma**	A	2	**1a**	80
2	**6a**	**4Mb**	A	2	**1b**	80
3	**6a**	**4Mc**	A	1	**1c**	96
4	**6a**	**4Md**	A [a]	2	**1d**	12
5	**6a**	**4Md**	A [b]	2	**1d**	12
6	**6a**	**4Md**	B [c]	1	**1d**	81
7	**6a**	**4Me**	B	2	**1e**	58
8	**6b**	**4Mb**	A	2	**1f**	61
9	**6b**	**4Mc**	A	2	**1g**	76
10	**6d**	**4Mc**	A	9	**1h**	84

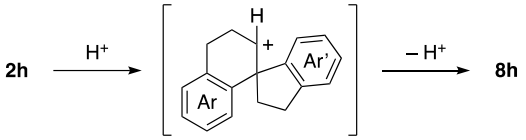
Generation of **4M**: Method A) **4a**–**c** (1.5 equiv vs. **6**), *n*-BuLi (1.5 equiv), TMEDA (1.5 equiv), THF, RT, 30 min; Method B) **7d**,**e** (1.2 equiv vs. **6**), *n*-BuLi (1.2 equiv), THF, –78 °C, 30 min. a) **4d** (0.9 equiv vs. **6a**), *n*-BuLi (0.9 equiv), TMEDA (0.9 equiv). b) **4d** (0.9 equiv vs. **6a**), *sec*-BuLi (0.9 equiv), TMEDA (0.9 equiv). c) The S_N2'-type reaction was carried out at –78 °C.

addition, to afford the undesired dimerization product [1,2-di(phenanthren-3-yl)ethane] in a quantitative yield. The treatment of (chloromethyl)phenanthrene, corresponding to **4Xd**, with lithium metal in THF at 0 °C to room temperature gave a complex mixture not containing **1d**.

Next, we tried lithiation by Sn–Li exchange (Scheme 5, Method B). The required benzylstannanes **7d** and **7e** were prepared according to the procedure reported for benzyl bromides, with some modifications.[27] Although the sterically demanding **4Xd** did not form the desired **7d** with hexabutyldistannane and a $PdCl_2(MeCN)_2$ catalyst (Table 5, Entry 1), adding lithium chloride (5 equiv) probably promoted the transmetallation step, giving **7d** in 54% and 40% yields with a $PdCl_2(MeCN)_2$ and a $PdCl_2(PPh_3)_2$ catalyst, respectively (Table 5, Entries 2 and 3). The use of a benzonitrile complex [$PdCl_2(PhCN)_2$] and distannane (2 equiv) further increased this yield to 77% (Entries 4 and 5). Under the modified conditions, **7e** bearing a [4]helicenyl group was obtained in a 56% yield (Entry 6). The Sn–Li exchange of **7d** and **7e** proceeded smoothly on treatment with butyllithium to generate (phenanthrylmethyl)lithium **4Md** and ([4]helicenylmethyl)lithium **4Me**, respectively, which were in turn subjected to the S_N2'-type reaction with (trifluoromethyl)alkene **6a** to afford difluoroalkenes **1d** and **1e** in 81% and 58% yields, respectively (Table 4, Entries 6 and 7). Thus, generation of benzyllithiums bearing an extended π system was achieved by the Migita–Kosugi–Stille coupling, followed by Sn–Li exchange.

A series of difluoroalkenes **1a**–**e** (domino cyclization precursors), consisting of toluene (**4a**) as an electrophilic benzyl component, were synthesized. Other 1,1-difluoro-1-alkenes (**1f**–**h**) were also similarly obtained. **6b** underwent an S_N2'-type reaction with **4Mb** and **4Mc** to form the corresponding precursors **1f** and **1g** in 61% and 76% yields, respectively (Table 4, Entries 8 and 9), while **6d** reacted with **4Mc** to give **1h** in an 84% yield (Table 4, Entry 10).[28]

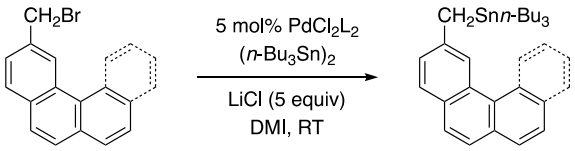
Domino Cyclization of 1 and Dehydrogenation (Synthesis of PAHs 3). Having **1** in hand, the domino cyclization and dehydrogenation were performed (Figure 4). **1a** was treated with magic acid ($FSO_3H{\cdot}SbF_5$, 2.5 equiv) in HFIP at 0 °C to room temperature; the sequential cyclization proceeded smoothly and the tetracyclic product **2a** was obtained in an 87% yield. The cyclization of **1b** gave **2b** via cyclization on the *ortho* position (not *peri*-position) in an 81% yield. When the difluoroalkenes with extended π-systems such as **1b** were hardly dissolved in HFIP, the difluoroalkenes were dissolved in a minimum amount of dichloromethane and added to an HFIP solution of magic acid. The reaction of **1c** produced **2c** in an 85% yield. The cyclization of **1d** and **1e**, respectively bearing a phenanthrene and a [4]helicene moiety, gave the corresponding products in 52% (**2d**) and 30% (**2e**) yields; in these cases, the C–C bonds were formed at the less hindered positions. The difluoroalkenes **1f** and **1g**, consisting of methylnaphthalenes **4b** and **4c**, produced **2f** and **2g** in 42% and 58% yields, respectively. In case of **1h**, consisting of methylnaphthalene **4c** and methylphenanthrene **4d**, the skeletal rearrangement previously described in our domino cyclization[16b] was observed to afford a chrysene ([4]phenacene) substructure (**8h**, 36% yield; Scheme 6) through spiro intermediates, probably due to the steric congestion in **2h**.



Scheme 6. Skeletal rearrangement to **8h**.

As shown in Scheme 4 (last step), the dehydrogenation of the cyclization products **2** with Pd/C required harsh reaction conditions (mesitylene, reflux, 9 h). The low reactivity of Pd/C might be attributed to the twisted structure of the [4]helicene moiety, which could have prevented the substrates **2** from being absorbed on the palladium surface. Thus, the dehydrogenation (aromatization) of **2** was conducted using Ph_3CBF_4.[29] **2a**, obtained from **1a**, was treated with Ph_3CBF_4 in refluxing 1,2-dichloroethane (85 °C); after chromatographic purification, the desired fully aromatized [4]helicene **3a**, consisting of the electrophilic benzyl component **4a**, CF_3-allylsilane **5**, and the nucleophilic benzyl component **4a** (i.e., **4a** + **5** + **4a**), was obtained in an 80% yield (Figure 4). The domino cyclization products **2b**–**g** and **8h**, produced from **1b**–**h**, underwent dehydrogenation with Ph_3CBF_4, forming the desired PAHs **3b**–**g** and **9h** with various benzene ring configurations in good to excellent yields.[30]

Table 5. Preparation of benzylstannanes **7d**,**e**.



4Xd,**e**

7d (phenanthren-3-yl)
7e ([4]helicen-2-yl)

Entry	**4X**	L	$(R_3Sn)_2$ (equiv)	*t* (h)	**7**	Yield (%)
1 [a]	**4Xd**	MeCN	1.2	1.5	**7d**	–
2	**4Xd**	MeCN	1.2	0.5	**7d**	54
3 [b]	**4Xd**	PPh_3	1.2	2.3	**7d**	40
4	**4Xd**	PhCN	1.2	0.5	**7d**	64
5	**4Xd**	PhCN	2.0	0.5	**7d**	77
6	**4Xe**	PhCN	2.0	0.5	**7e**	56

a) No LiCl was used. b) Room temperature to 85 °C. DMI = 1,3-Dimethylimidazolidinone. R = Butyl.

3. Conclusion

The synthesis of PAHs, consisting of [(trifluoromethyl)allyl]silane and two methylarenes, was described. Trimethyl[2-(trifluoromethyl)allyl]silane was reacted with benzyl bromides (Ar^1CH_2X) derived from Ar^1CH_3 to afford 2-trifluoromethyl-1-alkenes, which successively underwent S_N2'-type reactions with benzyllithiums (Ar^2CH_2Li) derived from Ar^2CH_3, forming 1,1-difluoro-1-alkenes, the precursors for the domino cyclization via α-fluoro carbocations. This methylarene-based preparation of difluoroalkenes and their domino cyclization followed by dehydrogenation allowed the synthesis of a wide variety of PAHs containing 4–7 benzene

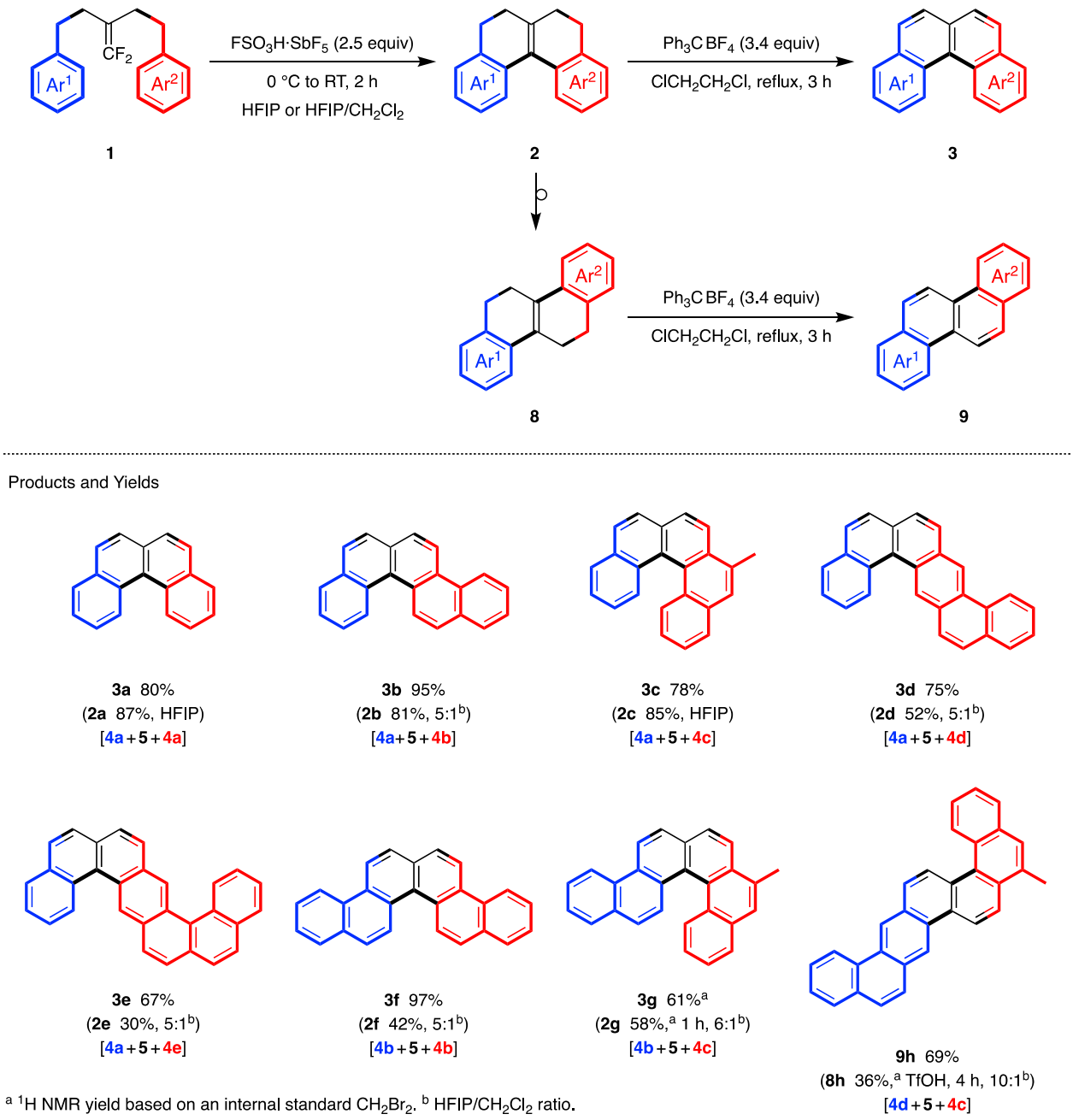


Figure 4. Synthesis of PAHs **3** and **9** by domino cyclization of 1,1-difluoroalkenes **1** and dehydrogenation.

rings in moderate to high yields. The proposed protocol connects the two aryl groups by forming two benzene rings to build the [4]helicene and [4]phenacene frameworks.

4. Experimental

General. 1,1,1,3,3,3-Hexafluoropropan-2-ol (HFIP) was distilled from activated molecular sieves 4A and stored over activated molecular sieves 4A. Dichloromethane, THF, and DMF were dried by passing through a column of activated alumina followed by a column of Q-5 scavenger (Engelhard).

Magic acid was purchased from Merck KGaA and used as received. V-70 was purchased from Wako Pure Chemical Industries, Ltd. and used as received. CsF was purchased from Kanto Chemical Co., Inc. (Cesium fluoride 4N) and activated before use (*vide infra*). Molecular sieves 4A (powder) was purchased from Merck KGaA and activated before use (*vide infra*). [(Trifluoromethyl)allyl]silane **5** was prepared by the reported procedure.[23] HFIP can be purchased from commercial suppliers such as Merck KGaA.

Column chromatography and preparative thin layer chromatography (PTLC) were conducted on silica gel (Silica Gel 60 N, Kanto Chemical Co., Inc. for column chromatography and Wakogel B-5F, Wako Pure Chemical Industries, Ltd. for PTLC). Purification of PAH **3g** was also performed by preparative HPLC (GPC), using a JAI LC-908 instrument (Jaigel-2H, $CHCl_3$).

IR spectra were recorded on a Horiba FT-300S spectrometer by the attenuated total reflectance (ATR method). NMR spectra were recorded on Bruker Avance 500 or Jeol JNM ECS-400 spectrometers in $CDCl_3$ at 500 or 400 MHz (^{1}H

NMR), at 126 or 101 MHz (^{13}C NMR), and at 470 or 376 MHz (^{19}F NMR). Chemical shifts were given in ppm relative to internal Me_4Si (for ^{1}H NMR: δ = 0.00), $CDCl_3$ (for ^{13}C NMR: δ = 77.0), and C_6F_6 (for ^{19}F NMR: δ = 0.0).[31] High-resolution mass spectroscopy (HRMS) was conducted with a Jeol JMS-T100GCV spectrometer (EI, TOF) or a Jeol JMS-T100CS spectrometer (ESI^+, TOF or $APCI^+$, TOF). Elemental analysis was performed with a Yanako MT-3 CHN Corder apparatus. Single crystal X-ray structure analysis was performed on a Bruker APEXII ULTRA instrument equipped with a CCD diffractometer using Mo Kα (graphite monochromated, λ = 0.71069 Å) radiation.

Benzylation of [(trifluoromethyl)allyl]silane 5 [preparation of 2-trifluoromethyl-1-alkene 6b]. Molecular sieves 4A (99 mg) and CsF (314 mg, 2.06 mmol) were heated under vacuum (160 °C, 2 h, 0.5 Torr). To the activated MS 4A and CsF were added a DMF solution (10 mL) of benzyl bromide **4Xb** (215 mg, 0.973 mmol) and [(trifluoromethyl)allyl]silane **5** (0.38 mL, 2.0 mmol). The reaction mixture was heated for 1 h at 60 °C. Phosphate buffer (pH 7, 10 mL) was added to quench the reaction at room temperature. Organic materials were extracted with AcOEt three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give (trifluoromethyl)alkene **6b** (206 mg, 84% yield) as a colorless liquid.

S_N2'-type reaction of 2-trifluoromethyl-1-alkenes 6 (preparation of 1,1-difluoro-1-alkene 1b, Method A). To a THF solution (4 mL) of TMEDA (0.21 mL, 1.4 mmol) and methylarene **4b** (201 mg, 1.42 mmol) was added butyllithium (1.0 mL, 1.4 mol/L in hexane, 1.4 mmol) at room temperature. The reaction mixture was stirred for 30 min at room temperature and cooled to –78 °C. To the THF solution of benzyllithium **4Mb** was added a THF solution (3 mL) of (trifluoromethyl)alkene **6a** (187 mg, 0.934 mmol). After stirring for 1 h at –78 °C, the reaction mixture was allowed to warm to room temperature and stirred for 30 min. Aqueous NH_4Cl (5 mL) was added to quench the reaction at room temperature. Organic materials were extracted with AcOEt three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/AcOEt = 50:1) to give difluoroalkene **1b** as a colorless liquid (240 mg, 80% yield).

S_N2'-type reaction of 2-trifluoromethyl-1-alkenes 6 (preparation of 1,1-difluoro-1-alkene 1d, Method B). To a THF solution (4 mL) of benzylstannane **7d** (108 mg, 0.224 mmol) was added butyllithium (0.16 mL, 1.4 mol/L in hexane, 0.22 mmol) at –78 °C. The reaction mixture was stirred for 30 min at –78 °C. To the THF solution of benzyllithium **4Md** was added a THF solution (0.7 mL) of (trifluoromethyl)alkene **6a** (37 mg, 0.19 mmol). The reaction mixture was stirred for 1 h at –78 °C. Phosphate buffer (pH 7, 5 mL) was added to quench the reaction at –78 °C. Organic materials were extracted with AcOEt three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/AcOEt = 10:1) to give difluoroalkene **1d** as a colorless liquid (57 mg, 81% yield).

Domino cyclization of 1,1-difluoro-1-alkenes 1 (preparation of tetracyclic product 2b). To an HFIP solution (3 mL) of magic acid ($FSO_3H{\cdot}SbF_5$, 387 mg, 1.22 mmol) was added an HFIP solution (3 mL) of difluoroalkene **1b** (152 mg, 0.471 mmol) at 0 °C. After stirring for 1 h at 0 °C, the reaction mixture was allowed to warm to room temperature and stirred for 30 min. Aqueous $NaHCO_3$ was added to quench the reaction at room temperature. Organic materials were extracted with $CHCl_3$ three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/AcOEt = 20:1) to give tetracyclic product **2b** as a colorless liquid (108 mg, 81% yield).

Dehydrogenation of tetracyclic products 2 (Synthesis of PAH 3b). To a 1,2-dichloroethane solution (2 mL) of Ph_3CBF_4 (161 mg, 0.488 mmol) was added a 1,2-dichloroethane solution (2 mL) of tetracyclic product **2b** (40 mg, 0.14 mmol). The reaction mixture was refluxed for 3 h. After removal of the solvent under reduced pressure, the residue was passed through a short plug of silica gel (hexane/AcOEt = 10:1). The resulting crude mixture was purified by column chromatography on silica gel (hexane/AcOEt = 10:1) to give PAH **3b** as colorless crystals (38 mg, 95% yield).

Spectral data of difluoroalkenes **1a** and **1c**, tetracyclic product **2a**, and PAHs **3a** and **3c** were described in our previous paper.[16] Spectral data of **3b** were in complete agreement with those reported in literature.[32] Spectral data of methylarene **4d** were in complete agreement with those reported in literature.[33] Spectral data of methylarene **4e** and (trifluoromethyl)alkene **6a** were described in our previous paper.[16]

1-[3-Difluoromethylidene-5-phenylpent-1-yl]naphthalene (1b): ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.34 (tdd, J = 8.0 Hz, J_{HF} = 2.0, 2.0 Hz, 2H), 2.41 (tdd, J = 8.0 Hz, J_{HF} = 2.0, 2.0 Hz, 2H), 2.72 (t, J = 8.0 Hz, 2H), 3.16 (t, J = 8.0 Hz, 2H), 7.16 (d, J = 7.0 Hz, 2H), 7.20 (dd, J = 7.5, 7.5 Hz, 1H), 7.27–7.32 (m, 3H), 7.40 (dd, J = 8.0, 7.0 Hz, 1H), 7.49 (ddd, J = 8.1, 6.9, 1.5 Hz, 1H), 7.54 (ddd, J = 8.1, 6.9, 1.5 Hz, 1H), 7.73 (d, J = 8.5 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 27.7 (d, J_{CF} = 2 Hz), 28.5 (d, J_{CF} = 2 Hz), 31.4 (dd, J_{CF} = 3, 3 Hz), 34.0 (dd, J_{CF} = 3, 3 Hz), 88.4 (dd, J_{CF} = 17, 17 Hz), 123.4, 125.52, 125.54, 125.97, 125.99, 126.1, 126.9, 128.3, 128.4, 128.9, 131.6, 133.9, 137.3, 141.1, 153.7 (dd, J_{CF} = 283, 283 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ 66.9 (br d, J = 54 Hz, 1F), 67.2 (br d, J = 54 Hz, 1F); IR (neat): ν 3026, 2956, 1745, 1263, 1215, 775, 748 cm^{-1}; EA: calcd for $C_{22}H_{20}F_2$: C, 81.96; H 6.25%, found: C, 81.8; H 6.41%.

3-[3-Difluoromethylidene-5-phenylpent-1-yl]phenanthrene (1d): ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.34 (tdd, J = 8.0 Hz, J_{HF} = 2.0, 2.0 Hz, 2H), 2.43 (tdd, J = 8.0 Hz, J_{HF} = 2.0, 2.0 Hz, 2H), 2.75 (t, J = 8.0 Hz, 2H), 2.97 (t, J = 8.0 Hz, 2H), 7.18–7.23 (m, 3H), 7.29 (dd, J = 7.5, 7.5 Hz, 2H), 7.43 (dd, J = 8.0, 1.3 Hz, 1H), 7.59 (ddd, J = 7.5, 7.5, 1.0 Hz, 1H), 7.66 (ddd, J = 7.5, 7.5, 1.0 Hz, 1H), 7.70 (d, J = 9.3 Hz, 1H), 7.72 (d, J = 9.3 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.89 (dd, J = 7.5, 1.0 Hz, 1H), 8.46 (s, 1H), 8.69 (d, J = 8.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 28.2, 28.4, 34.0 (dd, J_{CF} = 3, 3 Hz), 34.6 (dd, J_{CF} = 3, 3 Hz), 88.1 (dd, J_{CF} = 17, 17 Hz), 121.7, 122.6, 126.1, 126.3, 126.4, 126.5, 126.7, 127.3, 128.3, 128.4, 128.6, 128.7, 130.1, 130.4, 130.5, 132.2, 139.6, 141.2, 153.8 (dd, J_{CF} = 283, 283 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ 67.1 (br d, J = 53 Hz, 1F), 67.2 (br d, J = 53 Hz, 1F); IR (neat): ν 3064, 2927, 1747, 1603, 1219, 771 cm^{-1}; EA: calcd for $C_{26}H_{22}F_2$: C, 83.84; H, 5.95%, found: C, 83.44; H, 6.10%.

2-[3-Difluoromethylidene-5-phenylpent-1-yl][4]helicene (1e): ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.36 (tdd, J = 8.2 Hz,

J_{HF} = 2.0, 2.0 Hz, 2H), 2.46 (tdd, J = 7.8 Hz, J_{HF} = 2.0, 2.0 Hz, 2H), 2.75 (t, J = 8.2 Hz, 2H), 3.00 (t, J = 7.8 Hz, 2H), 7.17 (d, J = 7 Hz, 2H), 7.20 (t, J = 7.5 Hz, 1H), 7.26–7.28 (m, 2H), 7.46 (dd, J = 7.0, 1.5 Hz, 1H), 7.63 (ddd, J = 7.3, 7.3, 1.2 Hz, 1H), 7.68 (ddd, J = 7.7, 7.7, 1.7 Hz, 1H), 7.79 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 8.5 Hz, 1H), 8.03 (dd, J = 7.5, 1.5 Hz, 1H), 8.91 (s, 1H), 9.10 (d, J = 8.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 28.3 (d, J_{CF} = 2 Hz), 28.4 (d, J_{CF} = 3 Hz), 34.0 (dd, J_{CF} = 3, 3 Hz), 34.5 (dd, J_{CF} = 3, 3 Hz), 88.0 (dd, J_{CF} = 13, 13 Hz), 125.8, 126.07, 126.11, 126.3, 126.7, 126.9, 127.05, 127.11, 127.2, 127.4, 127.7, 128.3, 128.4, 128.60, 128.63, 130.3, 130.4, 131.1, 132.0, 133.5, 139.0, 141.1, 153.8 (dd, J_{CF} = 284, 284 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ 67.2 (br d, J= 55 Hz, 1F), 67.3 (br d, J= 55 Hz, 1F); IR (neat): ν 3049, 2954, 2925, 2860, 1747, 1603, 1454, 1219, 843, 771 cm^{-1}; HRMS (EI, TOF, 60 eV) m/z: calcd for $C_{30}H_{24}F_2$ ([M]$^+$): 422.1853, found: 422.1846.

1-[3-Difluoromethylidene-5-(naphthalen-1-yl)pent-1-yl]-naphthalene (1f): ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.47 (tdd, J = 8.3 Hz, J_{HF} = 2.5, 2.5 Hz, 4H), 3.17 (t, J = 8.3 Hz, 4H), 7.30 (d, J = 6.5 Hz, 2H), 7.40 (dd, J = 7.5, 7.5 Hz, 2H), 7.46–7.54 (m, 4H), 7.73 (d, J = 8.0 Hz, 2H), 7.87 (dd, J = 8.0, 1.0 Hz, 2H), 7.99 (d, J = 8.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 28.0, 31.5 (t, J_{CF} = 3 Hz), 88.8 (t, J_{CF} = 17 Hz), 123.4, 125.5, 125.6, 126.0, 126.1, 127.0, 128.9, 131.6, 133.9, 137.3, 153.8 (t, J_{CF} = 284 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ 67.3 (br s); IR (neat): ν 3055, 2960, 1747, 1512, 1217, 775 cm^{-1}; EA: calcd for $C_{26}H_{22}F_2$: C, 83.84, H, 5.95%; found: C, 83.57; H, 6.10%.

2-[3-Difluoromethylidene-5-(naphthalen-1-yl)pent-1-yl]-3-methylnaphthalene (1g): ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.35 (tdd, J = 8.4 Hz, J_{HF} = 2.0 Hz, 2.0 Hz, 2H), 2.45 (s, 3H), 2.48 (tdd, J = 8.4 Hz, J_{HF} = 2.0, 2.0 Hz, 2H), 2.82–2.87 (m, 2H), 3.17–3.23 (m, 2H), 7.32 (d, J = 9.0 Hz, 1H), 7.38–7.41 (m, 3H), 7.47–7.54 (m, 2H), 7.54 (s, 1H), 7.60 (s, 1H), 7.72–7.76 (m, 3H), 7.85–7.89 (m, 1H), 8.02 (d, J = 8.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 19.6, 27.6 (d, J_{CF} = 3 Hz), 27.9 (d, J_{CF} = 3 Hz), 31.5 (dd, J_{CF} = 3, 3 Hz), 31.9 (dd, J_{CF} = 3, 3 Hz), 88.7 (dd, J_{CF} = 17, 17 Hz), 123.4, 125.1, 125.3, 125.55, 125.56, 126.0, 126.1, 126.9, 126.9, 127.0, 127.1, 128.2, 128.9, 131.7, 132.3, 132.4, 133.9, 134.5, 137.3, 138.2, 153.8 (dd, J_{CF} = 283, 283 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ 67.1 (br d, J = 54 Hz, 1F), 67.3 (br d, J = 54 Hz, 1F); IR (neat): ν 3055, 2954, 1745, 1597, 1261, 1215, 775, 746 cm^{-1}; EA: calcd for $C_{27}H_{24}F_2$: C, 83.91; H, 6.26%, found: C, 83.58; H, 6.44%.

3-[3-Difluoromethylidene-5-(3-methylnaphthalen-2-yl) pent-1-yl]phenanthrene (1h): ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.40 (tdd, J = 8.2 Hz, J_{HF} = 2.0, 2.0 Hz, 2H), 2.50 (s, 3H), 2.53 (t, J = 8.0 Hz, J_{HF} = 2.0, 2.0 Hz, 2H), 2.90 (t, J = 8.2 Hz, 2H), 3.04 (t, J = 8.0 Hz, 2H), 7.42 (t, J = 4.5 Hz, 2H), 7.46 (dd, J = 8.1, 1.5 Hz, 1H), 7.58 (s, 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.63 (s, 1H), 7.68 (td, J = 8.3, 1.3 Hz, 1H), 7.70–7.78 (m, 2H), 7.730 (s, 1H), 7.734 (s, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 7.9 Hz, 1H), 8.50 (s, 1H), 8.70 (d, J = 8.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 19.5, 27.2, 28.5, 31.7, 34.6, 88.4 (t, J_{CF} = 17 Hz), 121.8, 122.5, 125.1, 125.3, 126.3, 126.4, 126.5, 126.6, 126.7, 126.8, 127.0, 127.3, 128.2, 128.5, 128.6, 130.0, 130.3, 130.5 132.2, 132.3, 132.4 134.5, 138.2, 139.4, 153.7 (t, J_{CF} = 283 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ 67.3 (s); IR (neat): ν 3053, 2929, 1747, 1454, 1207, 839, 744 cm^{-1}; HRMS (ESI$^+$, TOF) m/z: calcd for $C_{31}H_{26}F_2Na$ ([M+Na]$^+$): 459.1900, found: 459.1894.

Benzo[*a*]naphtho[1,2-*h*]anthracene (3d): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, J = 7.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.73–7.80 (m, 3H), 7.87 (d, J = 8.5 Hz, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 7.5 Hz, 1H), 7.96–7.99 (m, 2H), 8.08 (d, J = 7.0 Hz, 1H), 8.15 (d, J = 8.5 Hz, 1H), 8.92 (d, J = 8.0 Hz, 1H), 9.28 (s, 1H), 9.34 (d, J = 9.0 Hz, 1H), 9.64 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 122.1, 123.1, 125.8, 126.5, 126.8, 127.0, 127.11, 127.14, 127.2, 127.62, 127.65, 127.7, 127.8, 128.0, 128.5, 128.6, 128.7, 129.0, 130.3, 130.5, 130.6, 131.0, 132.13, 132.15, 133.6; IR (neat): ν 1510, 1223, 906, 831, 746 cm^{-1}; HRMS (ESI$^+$, TOF) m/z: calcd for $C_{26}H_{17}$ ([M+H]$^+$): 329.1330, found: 329.1335.

Dinaphtho[1,2-*a*:1',2'-*h*]anthracene (3e): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (ddd, J = 8.5, 6.8, 1.4 Hz, 2H), 7.80 (ddd, J = 8.5, 6.8, 1.4 Hz, 2H), 7.87 (d, J = 8.5 Hz, 2H), 7.91 (d, J = 8.5 Hz, 2H), 8.01 (d, J = 8.0 Hz, 2H), 8.10 (dd, J = 7.0, 1.4 Hz, 2H), 8.11 (d, J = 9.0 Hz, 2H), 9.40 (d, J = 8.0 Hz, 2H), 9.67 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 125.8, 126.7, 126.8, 127.14, 127.19, 127.5, 127.7, 127.9, 128.2, 128.6, 128.7, 130.4, 130.9, 131.7, 133.5.; IR (neat): ν 904, 829, 750, 733, 521 cm^{-1}; HRMS (ESI$^+$, TOF) m/z: calcd for $C_{30}H_{19}$ ([M+H]$^+$): 379.1487, found: 379.1469.

Naphtho[1,2-*c*]chrysene (3f): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (ddd, J = 8.0, 7.0, 1.4 Hz, 2H), 7.76 (ddd, J = 7.0, 7.0, 1.4 Hz, 2H), 7.99 (d, J = 9.8 Hz, 2H), 8.04 (d, J = 7.0 Hz, 2H), 8.14 (d, J = 6.3 Hz, 2H), 8.865 (d, J = 8.2 Hz, 2H), 8.87 (d, J = 6.3 Hz, 2H), 9.01 (d, J = 9.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 121.9, 123.4, 125.9, 126.59, 126.61, 126.9, 126.9, 128.2, 128.3, 128.6, 130.1, 130.5, 130.9, 131.7; IR (neat): ν 1595, 1259, 831, 737, 688 cm^{-1}; HRMS (ESI$^+$, TOF) m/z: calcd for $C_{26}H_{17}$ ([M+H]$^+$): 329.1330, found: 329.1343.

9-Methylnaphtho[2,1-*c*]chrysene (3g): ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.90 (s, 3H), 7.19 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.49 (dd, J = 7.1, 7.1 Hz, 1H), 7.53 (d, J = 9.2 Hz, 1H), 7.64 (dd, J = 7.0, 7.0 Hz, 1H), 7.72 (ddd, J = 7.6, 7.6, 1.1 Hz, 1H), 7.82 (s, 1H), 7.89 (d, J = 7.6 Hz, 1H), 7.91 (d, J = 7.6 Hz, 1H), 8.00 (d, J = 8.5 Hz, 1H), 8.12 (d, J = 4.4 Hz, 1H), 8.14 (d, J = 4.6 Hz, 1H), 8.20 (d, J = 9.2 Hz, 1H), 8.24 (d, J = 8.5 Hz, 1H), 8.85 (d, J = 7.9 Hz, 1H), 8.87 (d, J = 8.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 20.3, 122.0, 123.1, 123.4, 124.0, 124.4, 126.2, 126.4, 126.50, 126.52, 126.92, 126.93, 127.2, 127.3, 127.6, 128.2, 128.4, 129.0, 129.3, 129.4, 130.1, 130.4, 131.6, 131.9, 132.0, 132.1, 132.3; IR (neat): ν 2922, 1255, 1034, 835, 750, 733 cm^{-1}; HRMS (ESI$^+$, TOF) m/z: calcd for $C_{27}H_{19}$ ([M+H]$^+$): 343.1487, found: 343.1485; CCDC 1948090.

Benzylstannanes **7d** and **7e** were prepared according to the reported procedure,[27] using a $PdCl_2(PhCN)_2$ catalyst, LiCl (5 equiv), and (n-$Bu_3Sn)_2$ (2 equiv).

3-[(Tributylstannyl)methyl]phenanthrene (7d): ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.80–0.89 (m, 15H), 1.21–1.29 (m, 6H), 1.41–1.48 (m, 6H), 2.59 (s, 2H*0.84), 2.59 (d, J_{HSn} = 55.0 Hz, 2H*0.16), 7.26 (dd, J = 8.5, 1.4 Hz, 1H), 7.56 (ddd, J = 8.5, 6.8, 1.4 Hz, 1H), 7.59 (d, J = 8.5 Hz, 1H), 7.61 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.85 (dd, J = 7.8, 1.4, 1H), 8.28 (s, 1H), 8.62 (d, J = 8.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 10.2, 14.4, 19.9, 28.0, 29.8, 120.2, 123.2, 125.4, 126.7, 126.9, 127.5, 127.7, 129.08, 129.12, 129.12, 130.6, 131.3, 133.0, 143.2; IR (neat): ν 2966, 1427, 1205, 881, 758 cm^{-1}; EA: calcd for $C_{27}H_{38}Sn$: C, 67.38; H, 7.96%, found: C, 67.41; H 7.88%.

2-[(Tributylstannyl)methyl][4]helicene (7e): ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.82 (t, J = 7.3 Hz, 9H), 0.86–0.91 (m, 6H), 1.21–1.29 (m, 6H), 1.42–1.50 (m, 6H), 2.60 (s, 2H*0.86), 2.60 (d, J_{HSn} = 55.0 Hz, 2H*0.16), 7.29 (dd, J = 8.0, 1.5 Hz, 1H), 7.60 (dd, J = 7.5, 7.5 Hz, 1H), 7.65 (dd, J = 7.5, 7.5 Hz,

1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 9.3 Hz, 1H), 7.81 (d, *J* = 9.3 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 7.5 Hz, 1H), 8.75 (s, 1H), 9.14 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 9.53, 13.6, 19.3, 27.3, 29.0, 124.4, 124.8, 125.5, 125.7, 126.5, 126.6, 127.0, 127.1, 127.3, 127.8, 128.4, 128.5, 130.2, 130.5, 130.8, 131.2, 133.6, 142.2; IR (neat): *ν* 2954, 2922, 1606, 1456, 839, 742 cm^{-1}; EA: calcd for $C_{31}H_{40}Sn$: C, 70.07; H, 7.59%, found: C, 70.04; H 7.56%.

1-Methylbenzo[*l*]naphtho[1,2-*b*]chrysene (9h) ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.86 (s, 3H), 7.05 (dd, *J* = 7.1, 7.1 Hz, 1H), 7.42 (d, *J* = 9.0 Hz, 1H), 7.46 (dd, *J* = 7.0, 7.0 Hz, 1H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.62 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.70 (dd, *J* = 7.0, 7.0 Hz, 1H), 7.77 (s, 1H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.88 (d, *J* = 8.6 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.6 Hz, 1H), 8.49 (d, *J* = 8.5 Hz, 1H), 8.87 (d, *J* = 8.1 Hz, 1H), 9.04 (s, 1H), 9.17 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 20.3, 121.2, 122.9, 123.4, 123.5, 126.5, 126.6, 126.7, 126.8, 126.9, 127.01, 127.04, 127.1, 127.4, 127.6, 127.7, 128.0, 128.5, 128.7, 128.8, 128.9, 129.2, 129.6, 130.0, 130.2, 131.4, 131.8, 131.9, 132.2, 132.48, 132.50; IR (neat): *ν* 2922, 1437, 1095, 1032, 906, 731 cm^{-1}; HRMS (APCI$^+$, TOF) *m/z*: calcd for $C_{31}H_{21}$ ([M+H]$^+$): 393.1643, found: 393.1648; CCDC 1945281.

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Graphical Abstract

<Title>
Methylarene-Based PAH Synthesis via Domino Cyclization of 1,1-Difluoro-1-Alkenes

<Authors' names>
Kohei Fuchibe, Go Takao, Hiroki Takahashi, Shiori Ijima, and Junji Ichikawa*

<Summary>
Polycyclic aromatic hydrocarbons (PAHs) were synthesized from two methylarene molecules. Trimethyl[2-(trifluoromethyl)allyl]silane was treated with Ar^1CH_2Br derived from Ar^1CH_3 to afford 2-trifluoromethyl-1-alkenes, which underwent an S_N2'-type reaction with Ar^2CH_2Li generated from Ar^2CH_3 to produce 1,1-difluoro-1-alkenes (cyclization precursors); their $FSO_3H{\cdot}SbF_5$-promoted domino cyclization followed by dehydrogenation yielded PAHs. The combination of even a limited number of methylarenes resulted in various higher order PAHs.

<Diagram>