Tetrahedron xxx (xxxx) xxx

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Relevant analysis to the productivity in selective synthesis of dibenzo[*g*,*p*]chrysene derivatives

Yoshino Fujii, Yuta Taguchi, Shugo Tokai, Yasuhiro Matsumoto, Naruhiro Yoshida, Tetsuo Iwasawa*

Department of Materials Chemistry, Ryukoku University, Otsu, Shiga, 520-2194, Japan

ARTICLE INFO

Article history:
Received 7 April 2021
Received in revised form
12 July 2021
Accepted 13 July 2021
Available online xxx

Keywords:
Dibenzo[g,p]chrysense
Selective synthesis
Spiroketones
Wagner-Meerwein rearrangement
Functional organic materials

ABSTRACT

In this paper we explored several issues surrounding metal-free selective synthesis of dibenzo[*g*,*p*]chrysene (DBC) by steps that consist of the dimerization of fluorenones and the carbocation 1,2-shift. We focus on structurally non-symmetric two fluorenones having a bromine atom as a reactive moiety and a *tert*-butyl group as a solubilizing agent: One is 4-bromo-2,7-di-*tert*-butyl-9-fluorenone (**1**), and the other 4,7-dibromo-2-(*tert*-butyl)-9-fluorenone (**2**). Each starting **1** and **2** undertakes the homo-coupling to give two isomeric spiroketones and the following Wagner-Meerwein rearrangement to yield two isomeric DBCs. The spiroketone intermediates have now been crystallographically characterized, which informed us of the exact structures and lead us to comprehend which aryl group predominantly migrates from one carbon to a neighboring carbon along with production of DBC skeletons. Although the construction of DBCs proved to be involved in four paths, it seems likely now that a clear demonstration of making different DBCs by different reaction conditions enables us to accomplish selective synthesis of DBCs.

1. Introduction

Dibenzo[*g*,*p*]chrysenes (DBCs), shown in Scheme 1, have constituted a class of non-planar aromatic compounds of interest from material and synthetic points of view [1–3]. However, the synthesis was often a bottleneck so far in the industrially practical deployment [4]: most of the reported methods were generally hampered by lengthy procedures from starting compounds [5]. For example, intra-molecular oxidative coupling reactions to form carbon-carbon bonds [6], palladium-mediated intra- and/or inter-molecular transformations [7,8], intra-molecular Friedel-Crafts cyclization to use a difluoroethene moiety [9], and dimerization of fluorenones mediated by large quantities of zinc [10] were worthily demonstrable but long, tedious, and expensive.

Our group has recently reported metal-free construction of the DBC frameworks in homogeneous reaction systems, which consists of the dimerization of 9-fluorenones (up to 80-g scale) and the following Wagner-Meerwein rearrangement (Scheme 1) [11]. Triethyl phosphite mediates to put two fluorenones together and the resultant spiroketone undertakes acid-assisted 1,2-shift to afford the corresponding fused rings. The most prominent feature of this procedure is in simple, speedy, and scalable operation (at least academic laboratory scale): 300 g of unsubstituted DBC were practically prepared for one week. Despite the relevant utility of this process, one shortcoming remains in a grand challenge: dimerization reactions of *non-symmetric* fluorenones give isomeric mixtures of DBCs.

Herein we present a study of gaining some insights into isomeric production processes and selective production controls in the dimerization reactions of *non-symmetric* fluorenones and the following synthesis of DBCs. To the best of our knowledge, there is no report about such dimerization of *non-symmetric* 9-fluorenones and its relevant elucidation. It would be envisaged that the analytical studies are relevant to the efficient production of solution-processable DBC derivatives.

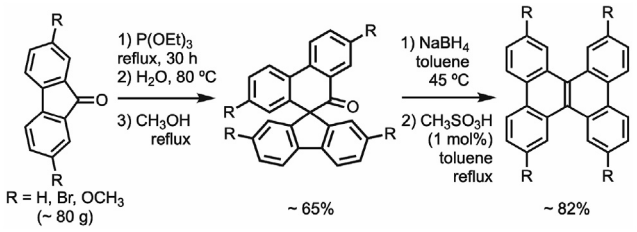
2. Results and discussion

2.1. Preparation of highly soluble fluorenones *1* and *2*

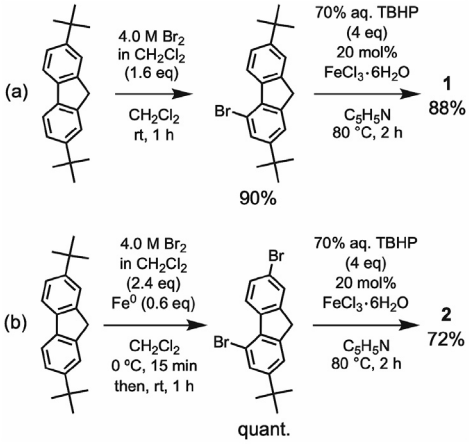
We prepared fluorenones **1** and **2**, as illustrated in Scheme 2: the *tert*-butyl groups in **1** and **2** was designed to provide good solubility to DBC derivatives in organic solvents. In part (a), upon addition of bromine to readily commercially available 2,7-di-*tert*-butyl-

* Corresponding author.
E-mail address: iwasawa@rins.ryukoku.ac.jp (T. Iwasawa).

https://doi.org/10.1016/j.tet.2021.132353
0040-4020/



Scheme 1. Metal-free dimerization of the starting symmetric 9-fluorenones to form dibenzo[*g,p*]chrysenes (DBCs) (R = H, Br, OCH_3).



Scheme 2. Synthesis of new fluorenones (a) **1**, and (b) **2**.

fluorenes, mono-bromination occurred just at 4-position in 90% yield [12]. The Bolm oxidation method effected a clean formation of **1** in 88% yield [13]. In part (b), when the bromine was fortified with zero-valent iron, the starting fluorenes quantitatively undertook double bromination at 4- and 7-positions with regio-specific manner. The resultant bis-bromide was subjected to the Bolm oxidation in 72% yield. As we expected, fluorenones **1** and **2** proved to be highly soluble.

2.2. Dimerization of *1* and *2* according to Scheme 1

During the recent course of our study, we have been involved in dimerization of non-symmetric fluorenones of **1** and **2** for diversity-oriented syntheses of new DBC platforms (Scheme 3): however, we faced the fact that isomeric mixtures of spiroketones **3**/*iso*-**3** (79% yield, 50:50 ratio) and **4**/*iso*-**4** (71% yield, 30:70 ratio) were formed and followed by transformation into the bis-bromo-DBC **5**/*iso*-**5** (93%, 46:54 ratio) and tetra-bromo-DBC **6**/*iso*-**6** (88%, 40:60 ratio). Isolation of **3**/**4** from *iso*-**3**/*iso*-**4** by silica-gel column chromatography was possible but formidably tedious action; what is worse, we were unable to separate **5** (or **6**) and *iso*-**5** (or *iso*-**6**) from each other even in small amounts.

2.3. Formation of spiroketones *3*/iso-*3* and *4*/iso-*4*

Dimerization reaction of **1** was carried out in refluxing $P(OEt)_3$ solvent: Although the prolonged reaction time of 60 h was required presumably due to the bulky *tert*-butyl groups, complete consumption of the starting **1** was observed along with 79% yield of the corresponding spiroketones **3** and *iso*-**3** in equal ratio (Scheme 3 (a)). Rf values in TLC (hexane/toluene, 1:1) are 0.57 for **3** and 0.60 for *iso*-**3**: these mixtures of maximum amount of 1.0 g were barely separable by silica-gel column chromatography, yielding **3** in 28% and *iso*-**3** in 33%. Single crystals of **3** in propionitrile was prepared by slow evaporation, and the crystallographic analysis revealed its absolute configuration as shown in Fig. 1 [14]; thus, the definite structure of *iso*-**3** was also determined as drawn in Scheme 3 (a). In a similar vein, for the starting **2**, two molecules coupled to give isomeric mixtures of **4**/*iso*-**4** in 71% yield along with the ratio of 30:70 (Scheme 3 (b)). Rf values in TLC (hexane/toluene, 2:1) are 0.55 for **4** and 0.49 for *iso*-**4**, respectively; it was difficult to isolate proper quantities of the samples by silica-gel column chromatography. We recrystallized the mixture from propionitrile (23 mL/g); only the major *iso*-**4** precipitated out as pure form in 42% yield. The resultant residue consisted of **4** and *iso*-**4** with 60:40 ratio, which underwent barely purification by silica-gel column chromatography to finally isolate 16% yield of **4** and 48% yield of *iso*-**4**. Single crystals of the major *iso*-**4** in ethyl acetate were made by slow evaporation, and the ORTEP drawing clarified its structure as shown in Fig. 2 [15]; therefore, the minor spiroketone **4** was defined as the figure depicted in Scheme 3 (b).

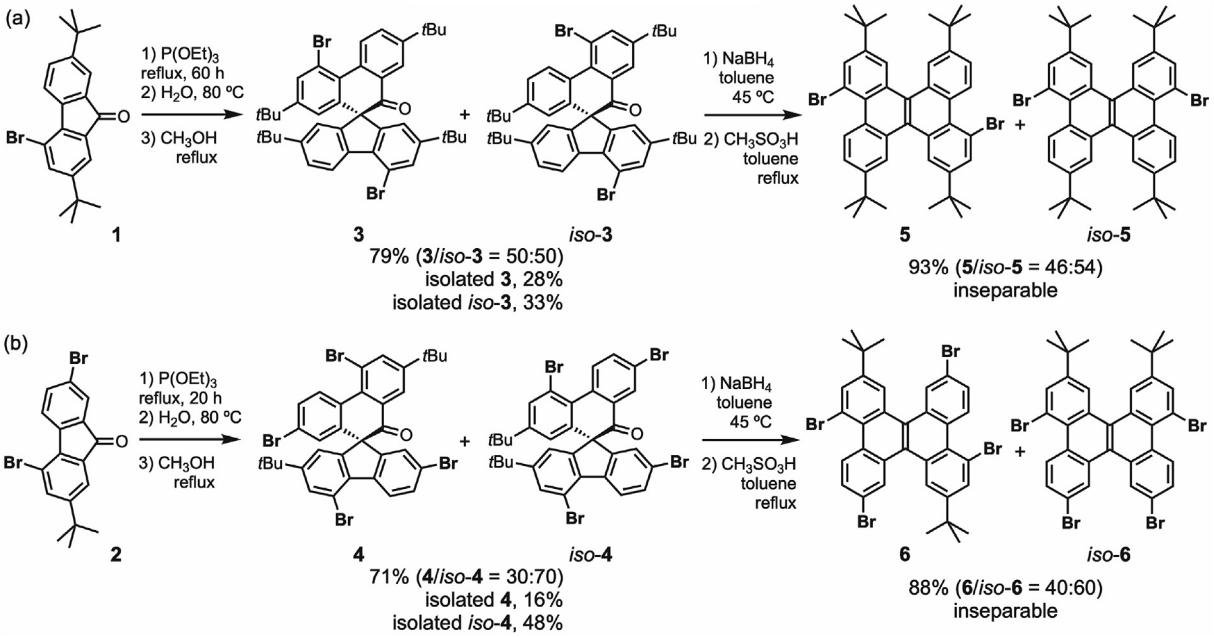
Next, we focused on a study of the effect of reaction temperature and tri-alkyl phosphite reagents on the dimerization process: For experimental convenience, the starting **1** (0.3 mmol) was diluted in 1.0 mL of phosphite solvent (Table 1). The condition at 125 °C in $P(OEt)_3$ didn't complete the reaction along with 35% unreacted **1** (entry 1). Alternative $P(Oi\text{-}Pr)_3$ consumed **1** with high 81% yield of **3**/*iso*-**3** (entry 2). Decrease of reaction temperatures to 95 °C maintained the chemical yields (entry 3), although lower 75 °C left unreacted **1** in 8% (entry 4). Finally, the highest-yielding transformation with up to 87% was achieved at 95 °C in the high concentration of **1** (entry 5). Through the whole entries, molar ratios of **3**/*iso*-**3** were not improved at all.

Table 2 summarized the effect of reaction temperature and phosphite reagents on the dimerization of **2**. When the reaction in $P(OEt)_3$ at 120 °C was carried out, unreacted **2** remained in 13% even in prolonged reaction time 40 h (entry 1). The reaction in $P(Oi\text{-}Pr)_3$ at 120 °C consumed **2**, giving 72% yield of **4**/*iso*-**4** with a good molar ratio of 18:82 (entry 2). A decrease of temperature to 95 °C didn't improve the chemical yield, although it maintained a good molar ratio (entry 3).

For the reason of the selective production of *iso*-**4** in entry 2 of Table 2, we prepared an illustration of Fig. 3 that is based on a report by Borowith and co-workers [16]. They confirmed the definite production of pentaoxyphosphoranes with careful spectroscopic analyses, in which the carbanion oxy-phosphonium betaines play important roles to construct the skeletal phosphoranes. When the betaine generated from **2** here attacks another fluorenone to cause the dimerized event, steric repulsion between two bulky *tert*-butyl groups would lead one phosphorane conformer illustrated in Fig. 3. In the phosphorane, pinacol type-migration of the electron-rich aromatic ring having a *tert*-butyl group is accompanied with side-production of tri-*iso*-propyl phosphate and followed by predominant formation of *iso*-**4** [17]. On the other hand, in the dimerized event of **1** in Table 1, there is no difference of the electron density in the corresponding two aromatic rings owing to the two *tert*-butyl groups at the same positions; hence, the molar ratios of **3** to *iso*-**3** reside in around 50:50.

2.4. Construction of DBCs *5*/iso-*5* and *6*/iso-*6*

What kind of paths do the spiroketones follow to the DBCs? First, we focused on the reaction process in the Wagner-Meerwein rearrangement of isolated **3** to form **5**/*iso*-**5** (Scheme 4(a)): Although the reduction of **3** by $NaBH_4$ smoothly gave the corresponding alcohol, the following 1,2-shift made bifurcated paths to mixture **5**/*iso*-**5** in 97% yields. We attempted to separate **5** from *iso*-



Scheme 3. Dimerization of *non-symmetric* fluorenones (a) **1** and (b) **2** to produce the isomeric spiroketones **3**/*iso*-**3** and **4**/*iso*-**4**, and DBCs **5**/*iso*-**5** and **6**/*iso*-**6**.

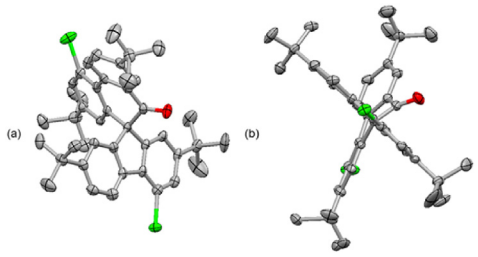


Fig. 1. Molecular structures with ORTEP drawing of **3** with thermal ellipsoids at the 50% probability level; (a) side view; (b) top view. Hydrogen atoms are omitted for clarity.

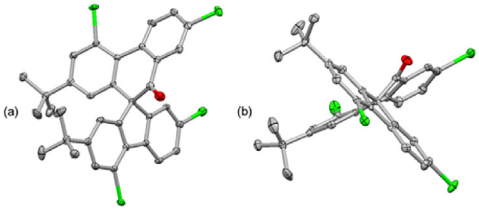
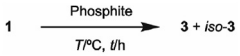


Fig. 2. Molecular structures with ORTEP drawing of *iso*-**4** with thermal ellipsoids at the 50% probability level; (a) side view; (b) top view. Hydrogen atoms are omitted for clarity.

5; however, their Rf values were too close to separate each other. To take ^{1}H NMR spectra into consideration, we noted the isomeric ratio of **5** to *iso*-**5** is 20:80. If we could isolate **8** (**7**) and *iso*-**8** (*iso*-**7**) those are derived from **5** and *iso*-**5** as shown in Scheme 4(a) and Fig. 4, the isomers should be distinguished by ^{13}C NMR spectra in aromatic regions because there are 13 peaks for **5**/**7**/**8**, and 14 peaks for *iso*-**5**/*iso*-**7**/*iso*-**8**. Thus, copper mediated-etherification of the mixture **5**/*iso*-**5** (20:80) yielded the 24:76 mixture of **7**/*iso*-**7** in 83%. Although **7** was not separable from *iso*-**7**, the further demethylation enabled to isolate **8** in 17% yield and *iso*-**8** in 63% yield. We confirmed that aromatic carbon signals in ^{13}C NMR spectra are 13 peaks for **8** and 14 peaks for *iso*-**8**, and deduced that the structures of **5** and *iso*-**5** are clarified as illustrations of Scheme 3 (a).

On the other hand, in Scheme 4(b), isolated *iso*-**3** also undertook the migration protocol to afford mixtures of **5**/*iso*-**5** in 89% yield.

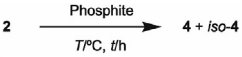
Table 1
Evaluation of reaction conditions in the dimerization of **1** for synthesis of **3**/*iso*-**3**.[a]



Entry	R in $P(OR)_3$	T/°C	t/h	Yield (%)[b]	3:*iso*-3 Ratio[c]	Unreacted 1 (%)
1	Et	125	42	54	45:55	35
2	*i*-Pr	125	45	81	50:50	0
3	*i*-Pr	95	41	80	49:51	0
4	*i*-Pr	75	47	73	49:51	8
5[d]	*i*-Pr	95	47	87	50:50	0

[a] Reactions were carried out with **1** (111 mg, 0.30 mmol) diluted in 1.0 mL of phosphite, unless otherwise stated.
[b] Isolated mixtures of **3** and *iso*-**3**.
[c] Molar ratios of **3**:*iso*-**3** were determined by ^{1}H NMR analyses.
[d] 2.2 mmol (814 mg) of **1** was employed in 4.4 mmol (1.0 mL) of $P(Oi\text{-}Pr)_3$.

Table 2
Evaluation of reaction conditions in the dimerization of **2** for synthesis of **4**/*iso*-**4**.[a]



Entry	R in $P(OR)_3$	T/°C	t/h	Yield (%)[b]	4:*iso*-4 Ratio[c]	Unreacted 2 (%)
1	Et	120	40	56	27:73	13
2[d]	*i*-Pr	120	8	72	18:82	0
3	*i*-Pr	95	8	40	17:83	35

[a] Reactions were carried out with **2** (118 mg, 0.30 mmol) diluted in 1.0 mL of phosphite, unless otherwise stated.
[b] Isolated mixtures of **4** and *iso*-**4**.
[c] Molar ratios of **4**:*iso*-**4** were determined by ^{1}H NMR analyses.
[d] 2.2 mmol (867 mg) of **2** was used in 4.4 mmol (1.0 mL) of $P(Oi\text{-}Pr)_3$.

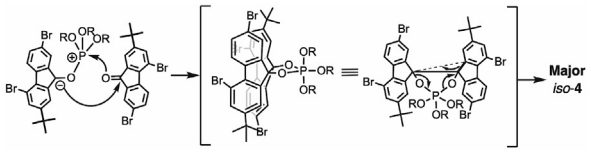
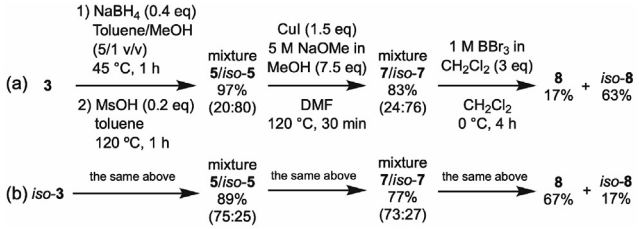


Fig. 3. Plausible path to major *iso*-**4** *via* phosphorane intermediates.



Scheme 4. Transformation of the isolated pure spiroketones (a) **3** and (b) *iso*-**3** into the DBCs **7**, *iso*-**7**, **8** and *iso*-**8**.

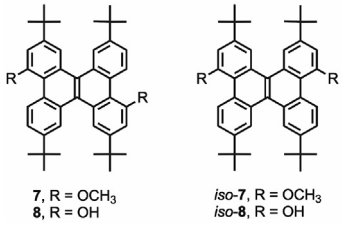
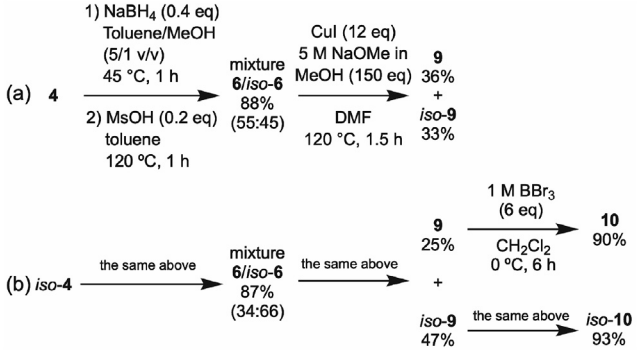


Fig. 4. DBCs **7**, *iso*-**7**, **8**, and *iso*-**8**.

The spectra of ^{1}H NMR and ^{13}C NMR explained the ratio of **5** to *iso*-**5** as 75:25, which is complementary to the output in the former Scheme 4(a). When this isomeric mixture **5**/*iso*-**5** was in use for further transformation, the next etherification proceeded in 77% yield of **7**/*iso*-**7** with 73:27 ratio and the following demethylation provided the isolated **8** in 67% yield and *iso*-**8** in 17%.

In the same vein, isolated **4** (Scheme 5(a)) and *iso*-**4** (Scheme 5(b)) underwent the rearrangement to bifurcate into **6** and *iso*-**6** with ratios of 55:45 and 33:67, respectively. The bifurcation is the reason why the isomeric ratios of 30:70 in **4**/*iso*-**4** change into 40:60 in **6**/*iso*-**6** through the rearrangement process in Scheme 3. Inseparable **6**/*iso*-**6** mixtures here were amenable to etherification, which enabled the separation of **9** from *iso*-**9** (Fig. 5). We checked



Scheme 5. Transformation of the isolated pure spiroketones (a) **4**, and (b) *iso*-**4** into the DBCs **9**, *iso*-**9**, **10** and *iso*-**10**.

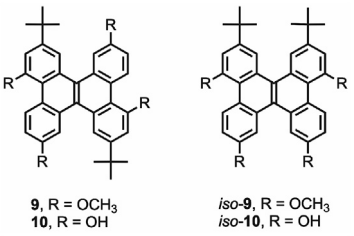
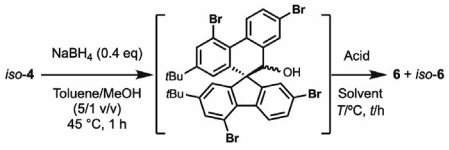


Fig. 5. DBCs 9, iso-9, 10, and iso-11.

that aromatic carbon signals in ^{13}C NMR are 13 peaks for **9** and 14 peaks for *iso*-**9**, which reasoned that structures of **6** and *iso*-**6** are elucidated as drawings of Scheme 3 (b).

We have pursued improvement of the selective Wagner-Meerwein shift of **3**/*iso*-**3** and **4**/*iso*-**4**: Does the different acid and/or solvent enable to improve the selective formation of DBCs **5**/iso-**5** and **6**/iso-**6**? [18] We optimized the reaction conditions utilizing *iso*-**4** (Table 3), because the isolated *iso*-**4** by recrystallization was more available than other three spiroketones of **4**, **3** and *iso*-**3**. A criterion for the optimization was in entry 1 where use of MsOH in refluxing toluene for 1 h gave 87% yield with 33:67 ratio of **6**/*iso*-**6**. When MsOH was used, HFIP (hexafluoro-2-propanol) solvent proved to be workable even at room temperature (entry 2) [19,20]. However, several tests of Brønsted acids didn't surpass the result of entry 1 in both chemical yields and isomeric ratios (entries 3 and 4). We changed such protic acids to a Lewis acidic $AlCl_3$ (entry 5): the desired migration seemed to progress fast at ambient temperature, but $AlCl_3$ was too strong acid to suppress disgusting side-reactions that are elimination of *tert*-butyl groups. Therefore, we had the Lewis acid altered into weaker $EtAlCl_2$ and Et_2AlCl (entries 6–10): Thus, $EtAlCl_2$ achieved the highest ratio of 18:82 with sufficient yield of 81% (entry 7). The catalytic amount of $EtAlCl_2$ was

Table 3
Evaluation of reactivities and selectivities in the transformation of *iso*-**4** into **6**/*iso*-**6**.[a]



Entry	Acid[b]	Solvent[c]	T/°C	t/h	Yield[d] (%)	Ratio[e] 6:*iso*-6
1	MsOH	Toluene	reflux	1	87	33:67
2	MsOH	HFIP	r.t.	20	70	34:66
3	TsOH	HFIP	r.t.	20	71	38:62
4	conc. HCl	HFIP	r.t.	22	63	34:66
5[f]	$AlCl_3$	Toluene	r.t.	0.5	<50	–
6	$EtAlCl_2$	Toluene	r.t.	1	83	25:75
7	$EtAlCl_2$	Toluene	0	2	81	18:82
8[g]	$EtAlCl_2$	Toluene	−78–0	4	79	19:81
9[h]	$EtAlCl_2$	Toluene	r.t.	2	22	32:68
10	Et_2AlCl	Toluene	r.t.	1	0	–

[a] For entries 2–4, conditions: single *iso*-**4** (150 mg, 0.19 mmol), acid (0.11 mmol), solvent (1.0 mL). For entries 5–10; single *iso*-**4** (100 mg, 0.13 mmol), acid (0.16 mmol), solvent (0.67 mL).
[b] MsOH, methanesulfonic acid; TsOH, *p*-toluenesulfonic acid.
[c] HFIP, hexafluoro-2-propanol.
[d] Isolated mixtures of **6** and *iso*-**6**.
[e] Determined by ^{1}H NMR analysis.
[f] The purified compounds included small amounts of impurities, and the accurate ratio was not determined.
[g] The reaction temperature started at −78 °C, and increased gradually to 0 °C.
[h] 0.5 equiv of $EtAlCl_2$ was used.

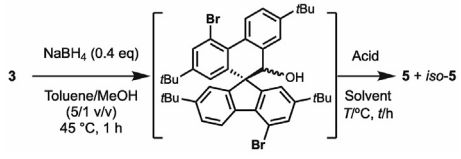
powerless (entry 9), and much weaker Et_2AlCl was unworkable (entry 10).

Next, we concentrated on searching good conditions in the transformations of **3** and *iso*-**3** into **5**/*iso*-**5** (Tables 4 and 5). For **3** in Table 4, criterion for the optimization was in entry 1 where high-yielding transformation in toluene at room temperature gave the isomeric ratios of 11:89. Although the change of the solvent to HFIP didn't improve the ratios, the major and minor products were unexpectedly yet totally replaced by each other (entry 2). And we anticipated that Lewis acid reagent of $EtAlCl_2$ would be effective; however, the isomeric ratio ended up in the non-selective 60:40 (entry 3). For *iso*-**3** in Table 5, the reaction was carried out at room temperature in the presence of conc. HCl and the toluene solvent didn't work at all (entry 1), but the HFIP drastically activated the reaction system (entry 2). The state of the alcohol generated from *iso*-**3** in HFIP solvent was white suspension, so we mixed equal volume of toluene in with the HFIP, and the reaction was conducted in a solution phase (entry 3): the most selective production in 91:9 ratio was accomplished in 91% yield.

Taken together these data in Table 3 and Scheme 5 suggest that the selective synthesis of **6**/*iso*-**6** prefers use of Lewis acid $EtAlCl_2$ (entry 7). On the other hand, the accumulated data in Tables 4 and 5 and Scheme 4 show that the catalytic amount of conc. HCl is effective for selective formation of **5**/*iso*-**5** under the mixed solvent of HFIP and toluene (Table 5, entry 3). Although some details were found through those experiments, the mechanism resulting in the high stereochemical control and product selectivity is not yet fully known: Our understanding of product distribution differs from solvent to solvent and from acid to acid still lacks consistency and finds no reasonable discussion. Whatever is reason, different spiroketones match different conditions to selectively construct the corresponding DBCs [21, 22].

Lastly, we again intensively tried to isolate **5**, *iso*-**5**, **6**, and *iso*-**6** those were inseparable in the previous procedure that is depicted in Scheme 3: this led us to demonstrate experiments in Scheme 6, where the best conditions effect a single construction or predominant formation of each **5**, *iso*-**5**, **6**, and *iso*-**6**. For part (a), **3** and *iso*-**3** were separated by silica-gel column chromatography, and each undertook the Wagner-Meerwein rearrangement in the presence of conc. HCl under the mixed solvent of toluene and HFIP. And DBC **5** and *iso*-**5** were given in high yields with 20:80 and 90:10 ratios, respectively: Perfect separation of **5** from *iso*-**5** was not achieved but recrystallization from ethyl acetate made them much more purified with 11:89 and 93:7 ratios [23]. For part (b), **2** dimerized to give **4**/*iso*-**4** with 13:87 ratio, and the following recrystallization from propionitrile yielded *iso*-**4** in 49% as a single isomer. The next migration reaction of *iso*-**4** in the presence of Lewis acidic $EtAlCl_2$ produced mixture of DBC **6**/*iso*-**6** in 25:75 ratio: The difference in the molar ratio was significant enough to isolate **6** in 12% and *iso*-**6** in 51% yields. Thus, perfect isolation of **6** and *iso*-**6** were finally achieved.

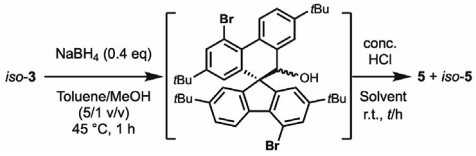
Table 4
Evaluation of reactivities and selectivities in the transformation of **3** into **5**/*iso*-**5**.[a]



Entry	Acid[b]	Solvent[c]	T/°C	t/h	Yield[d] (%)	Ratio[e] 5:*iso*-5
1	MsOH	Toluene	r.t.	4	93	11:89
2	MsOH	HFIP	r.t.	1	93	74:26
3	$EtAlCl_2$	Toluene	0	0.5	96	60:40

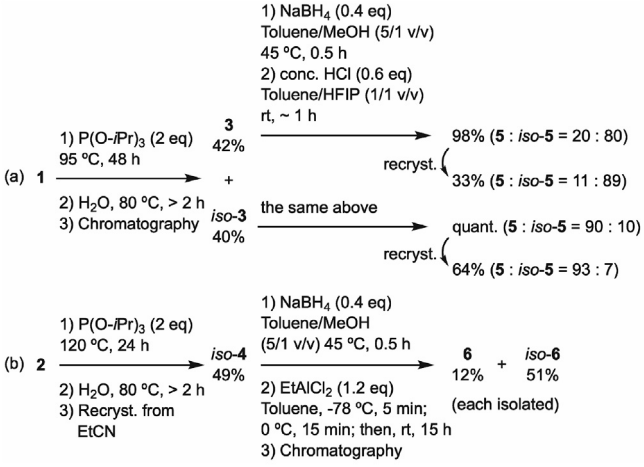
[a] Conditions: single **3** (100 mg, 0.14 mmol), acid (0.080 mmol), solvent (1.0 mL). For entries 3, 0.17 mmol of acid reagent was used.
[b] MsOH, methanesulfonic acid.
[c] HFIP, hexafluoro-2-propanol.
[d] Mixtures of **5** and *iso*-**5**.
[e] Determined by ^{1}H NMR analysis.

Table 5
Evaluation of reactivities and selectivities in the transformation of *iso*-**3** into **5**/*iso*-**5**.[a]



Entry	Solvent[b]	t/h	Yield[c] (%)	Ratio[d] 5:*iso*-5
1	Toluene	2	0	–
2[e]	HFIP	1	91	72:28
3	Toluene/HFIP (1:1 v/v)	1	91	91:9

[a] Conditions: single *iso*-**3** (100 mg, 0.14 mmol), acid (0.080 mmol), solvent (1.0 mL).
[b] HFIP, hexafluoro-2-propanol.
[c] Mixtures of **5** and *iso*-**5**.
[d] Determined by ^{1}H NMR analysis.
[e] 250 mg of **1** was employed.



Scheme 6. Predominant formation of (a) **5** and *iso*-**5**, and perfect isolation of (b) **6** and *iso*-**6**.

3. Conclusion

To conclude, we have been in the process of studying variations of the selective DBCs production in depth. Some of the most important variations will be the substituents in the non-symmetric fluorenones, the phosphite reagents, the acid sources, and the solvent effects. The results provide the following four salient features: One, the high-yielding dimerization steps were enhanced by the usage of $P(O\text{-}iPr)_3$ solvent even at relatively low temperature 95 °C and 120 °C. Two, the selective dimerization to produce spiroketones with up to 85:15 ratio might be attributed to the electron-rich aromatic ring caused by the *tert*-butyl groups in the corresponding reaction intermediate of phosphorane. Three, the crystallographic analyses of the spiroketones revealed that two

possible migratory bonds in Wagner-Meerwein rearrangement selectively shift with some different proportions. Four, the productivity in the selective Meerwein migrations is enhanced by combination of acid reagents and solvent molecules. Clearly, these four features enable us to completely isolate the structurally similar isomeric DBCs **6** and *iso*-**6** those are inseparable so far. Our progress reported herein should serve as an intellectual basis for future synthetic chemistry of selective production of functional DBCs. There are much more variations of non-symmetric 9-fluorenones to try. Further synthetic research of speedy, scalable and selective production of new DBCs is ongoing and will be reported in due course.

4. Experimental section

4.1. General

All reactions sensitive to air or moisture were carried out under an argon or a nitrogen atmosphere and anhydrous conditions unless otherwise noted. Dry solvents were purchased and used without further purification and dehydration. All reagents were purchased and used without further purification. Analytical thin layer chromatography was carried out on Merck silica $60F_{254}$. Column chromatography was carried out with silica gel 60 $_N$ (Kanto Chemical Co.). LRMS and HRMS were reported on the basis of TOF (time of flight)-MS (MALDI-TOF or LCMS-IT-TOF), and DART (Direct Analysis in Real Time)-MS. ^{1}H and ^{13}C NMR spectra were recorded with a 5 mm QNP probe at 400 MHz and 100 MHz, respectively. Chemical shifts are reported in d (ppm) with reference to residual solvent signals [^{1}H NMR: $CHCl_3$ (7.26), CH_3CN (1.94); ^{13}C NMR: $CDCl_3$ (77.0), DMSO (39.5)]. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

4.2. Synthesis of 4-bromo-2,7-di-t-butyl-9H-fluoren-9-one (1), for Scheme 2

To a solution of 4-bromo-2,7-di-*t*-butyl-9*H*-fluorene (5.72 g, 16 mmol) in pyridine (32 mL) was added $FeCl_3\cdot 6H_2O$ (864 mg, 3.2 mmol), then *tert*-butyl hydroperoxide (70% in H_2O, 6.6 mL, 48 mmol) was slowly added over 5 min. After the mixture was stirred for 1 h at 80 °C, additional *t*-butyl hydroperoxide (2.2 mL, 16 mmol) was poured over 5 min. After the reaction was conducted at 80 °C for further 1 h, the mixture was allowed to cool to room temperature. The mixture was filtered through a pad of celite and silica-gel (eluent, CH_2Cl_2), and the filtrate was thoroughly evaporated off. The resultant residue was diluted with CH_2Cl_2 (30 mL), which was transferred into a 100 mL separatory funnel, and washed with brine (30 mL), and dried over Na_2SO_4, and concentrated *in vacuo* to give crude products of yellow solid materials. Purification by recrystallization from 2-propanol (15.8−7.4 = 8.4 mL/g) afforded 5.22 g of desired molecule (88%) as yellow crystals. *Rf* value 0.37 (Hexane/EtOAc, 19:1); ^{1}H NMR (400 MHz, $CDCl_3$) 8.18 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 2.0 Hz, 1H), 7.66 (d, J = 1.7 Hz, 1H), 7.56 (d, J = 1.7 Hz, 1H), 7.55 (dd, J = 8.0, 2.0 Hz, 1H), 1.35 (s, 9H), 1.33 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 193.6, 154.2, 153.1, 141.4, 140.2, 137.3, 136.3, 134.8, 131.9, 123.1, 121.9, 120.9, 117.3, 35.33, 35.30, 31.4, 31.3 ppm; MS (DART-TOFMS) *m/z*: 371 $[MH]^+$; IR (neat): 2960, 1714 (C═O), 1606, 1475, 1360, 1148, 826, 778, 563 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{21}H_{24}BrO$: 371.1011 $[MH]^+$, Found: 371.1009; Anal. Calcd for $C_{21}H_{23}BrO$: C, 67.93; H, 6.24. Found: C, 67.73; H, 6.10.

4.3. Synthesis of 4,7-dibromo-2-t-butyl-9H-fuluoren-9-one (2), for Scheme 2

To a solution of 4,7-dibromo-2-*t*-butyl-9*H*-fluorene (6.30 g, 16.6 mmol) in pyridine (26 mL) was added $FeCl_3\cdot 6H_2O$ (897 mg, 3.3 mmol), then *t*-butyl hydroperoxide (TBHP, 70% in H_2O, 6.8 mL, 49.7 mmol) was slowly added over 5 min. After the mixture was stirred for 1 h at 80 °C, additional TBHP (2.3 mL, 16.6 mmol) was poured over 5 min. After the reaction was conducted at 80 °C for further 1 h, the mixture was allowed to cool to room temperature. The reaction was filtered through a pad of celite and silica-gel (eluent, toluene), and the filtrate was thoroughly evaporated off. The resultant residue was diluted with 40 mL of toluene, which was transferred into a 100 mL separatory funnel, and washed with brine (30 mL), and dried over Na_2SO_4, and concentrated *in vacuo* to give crude products of yellow solid materials (6.44 g). Purification by reprecipitation from CH_2Cl_2/MeOH (1/8 v/v) gave 5.22 g of yellow solid materials (79%). The following recrystallization from EtCN (5.2−2.3 = 2.9 mL/g) afforded 4.72 g of desired molecule (72%) as yellow solid materials. *Rf* value 0.35 (Hexane/EtOAc, 19:1); ^{1}H NMR (400 MHz, $CDCl_3$) 8.16 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 2.0 Hz, 1H), 7.68 (d, J = 1.7 Hz, 1H), 7.64 (dd, J = 8.2, 2.0 Hz, 1H), 7.60 (d, J = 1.7 Hz, 1H), 1.33 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 191.6, 155.2, 142.6, 139.4, 137.4, 136.8, 136.5, 136.3, 127.8, 124.6, 123.5, 121.4, 117.7, 35.5, 31.3 ppm; MS (DART-TOFMS) *m/z*: 393 $[M]^+$; IR (neat): 2952, 1713 (C═O), 1441, 1235, 1175, 1144, 780, 709 cm^{-1}, HRMS (DART-TOFMS) calcd for $C_{17}H_{14}Br_2O$ $[M]^+$: 393.9391, Found: 393.9387; Anal. Calcd for $C_{17}H_{14}Br_2O$, C, 51.81; H, 3.58. Found: C, 51.76; H, 3.66.

4.4. Synthesis of 3 and iso-3, for Scheme 3

4-bromo-2,7-di-*t*-butyl-9*H*-fluoren-9-one (6.68 g, 16 mmol) was added to $P(OEt)_3$ (6.2 mL, 36 mmol), and the resultant yellow solution was stirred at 175 °C (oil bath temp.). After stirred for 60 h, the mixture was cooled to 60 °C. To the mixture was slowly added water (6.5 mL, 360 mmol) over 3 min, and the mixture was heated to 80 °C for hydrolyzing the residual $P(OEt)_3$. After stirred for more than 2 h, the reaction mixture was filtered, and the precipitates were washed with H_2O (200 mL) and cold methanol (30 mL). The collected solid materials in methanol (53 mL) were refluxed in 30 min, and the mixture was filtered and washed again with cold methanol (50 mL). The resultant sample was dried *in vacuo* (80 °C, 1 h), giving 5.17 g of desired yellowish white solid materials in 79% yield (50:50). Purification by silica-gel column chromatography (crude 500 mg, Hexane/CH_2Cl_2 = 4:1) separated **3** from *iso*-**3** in which both are white solid materials.

4.4.1. 4,5′-dibromo-2,2′,7,7′-tetra-t-butyl-10′H-spiro[fluorene-9,9′-phenanthren]-10′-one (3)

28% yield (178 mg); *Rf* value 0.70 (hexane/toluene, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) 8.72 (d, J = 8.5 Hz, 1H), 8.42 (d, J = 8.3 Hz, 1H), 7.82 (dd, J = 8.5, 2.3 Hz, 1H), 7.72 (d, J = 2.3 Hz, 1H), 7.65 (d, J = 2.0 Hz, 1H), 7.50 (d, J = 1.6 Hz, 1H) 7.42 (dd, J = 8.3, 2.0 Hz, 1H), 6.84 (d, J = 1.6 Hz, 1H), 6.82 (d, J = 1.8 Hz, 1H), 6.66 (d, J = 1.8 Hz, 1H), 1.32 (s, 9H), 1.15 (s, 9H), 1.13 (s, 9H), 1.09 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 198.3, 152.5, 152.1, 152.0, 151.4, 148.0, 145.8, 140.7, 138.0, 137.3, 134.9, 132.9, 132.6, 130.6, 130.5, 129.7, 128.6, 125.3, 125.1, 124.9, 123.4, 122.4, 122.2, 120.7, 116.6, 70.3, 35.1, 35.0 (two peaks are overlapped), 34.9, 31.5, 31.4, 31.3, 31.1 ppm; MS (DART-TOF) *m/z*: 727 $[MH]^+$; IR (neat): 2959, 1702 (C═O), 1454, 1362, 1229, 829, 753 cm^{-1}; HRMS (DART-TOF) calcd for $C_{42}H_{47}Br_2O$: 727.1973 $[MH]^+$, Found: 727.1971; Anal. Calcd for $C_{42}H_{46}Br_2O$: C, 69.42; H, 6.38. Found: C, 69.35; H, 6.34.

4.4.2. 4,4′-dibromo-2,2′,7,7′-tetra-t-butyl-10′H-spiro[fluorene-9,9′-phenanthren]-10′-one (iso-3)

33% yield (209 mg); *Rf* value 0.74 (hexane/toluene, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) 8.55 (d, J = 8.3 Hz, 1H), 8.44 (d, J = 8.3 Hz, 1H), 8.03 (d, J = 2.0 Hz, 1H), 7.71 (d, J = 2.0 Hz, 1H), 7.52 (d, J = 1.5 Hz, 1H),

7.43 (dd, J = 8.3, 2.0 Hz, 1H), 7.41 (d, J = 8.3, 2.1 Hz, 1H), 7.04–7.03 (m, 2H), 6.82 (d, J = 2.1 Hz, 1H), 1.30 (s, 9H), 1.19 (s, 9H) 1.18 (s, 9H), 1.14 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 198.0, 152.8, 152.3, 151.9, 151.2, 147.2, 144.9, 138.1, 138.0, 137.7, 137.4, 136.1, 134.0, 130.5, 128.9, 128.8, 125.2, 125.1, 124.9, 124.4, 123.4, 122.9, 122.7, 119.5, 116.6, 69.9, 35.1 (four peaks are overlapped), 31.52, 31.45, 31.3, 31.1 ppm; MS (DART-TOF) *m/z*: 727 $[MH]^+$; IR (neat): 2959, 1699 (C═O), 1447, 1362, 1234, 1157, 830, 746, 695 cm^{-1}; HRMS (DART-TOF) calcd for $C_{42}H_{47}Br_2O$: 727.1973 $[MH]^+$, Found: 727.1988; Anal. Calcd for $C_{42}H_{46}Br_2O$: C, 69.42; H, 6.38. Found: C, 69.59; H, 6.41.

4.5. Synthesis of 4, and iso-4, for Scheme 3

2,5-di-bromo-7-*t*-butyl-9*H*-fluoren-9-one (12 g, 30 mmol) was added to $P(OEt)_3$ (10.2 mL, 60 mmol), and the resultant yellow solution was stirred at 175 °C (oil bath temp.). After stirred for 20 h, the mixture was cooled to 60 °C. To the mixture was slowly added water (10.8 mL, 600 mmol) over 10 min, and the mixture was heated to 80 °C for hydrolyzing the residual $P(OEt)_3$. After stirred for more than 2 h, the reaction mixture was filtered, and the precipitates were washed with cold methanol (60 mL). The collected solid materials in methanol (80 mL) were refluxed in 20 min, and the mixture was filtered and washed again with cold methanol (120 mL). The resultant sample was dried *in vacuo* (85 °C, 15 min), giving 8.92 g of desired yellowish white solid materials in 77% yield. Purification by short-plugged silica-gel column chromatography (Hexane/CH_2Cl_2 = 4/1) gave 8.22 g of whitish red solid materials (71%, 70:30). Purification by recrystallization from EtCN (crude 1.2 g, 70–47 = 23 mL/g) afforded *iso*-**4** of 702 mg (42%) as white crystals in pure form. The following purification of the residual mixture samples by silica-gel column chromatography (sample 250 mg, hexane/toluene, 9:1) gave *iso*-**4** of 62 mg (6%) and **4** of 152 mg (15%), in which both are white solid materials.

4.5.1. 4,4′,7,7′-tetrabromo-2,2′-di-t-butyl-10′H-spiro[fluorene-9,9′-phenanthren]-10′-one (**4**)

48% yield (764 mg); *Rf* value 0.52 (hexane/toluene, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) 8.54 (d, J = 8.6 Hz, 1H), 8.47 (d, J = 8.5 Hz, 1H), 8.06 (d, J = 2.4 Hz, 1H), 7.78 (d, J = 1.9 Hz, 1H), 7.64 (dd, J = 8.5, 2.4 Hz, 1H), 7.54 (dd, J = 8.6, 2.0 Hz, 1H), 7.46 (d, J = 1.7 Hz, 1H), 7.28 (d, J = 1.7 Hz, 1H), 6.88 (d, J = 1.9 Hz, 1H), 6.81 (d, J = 2.0 Hz, 1H), 1.32 (s, 9H), 1.08 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 195.4, 153.5, 152.8, 146.4, 146.0, 140.2, 139.3, 138.4, 135.2, 134.5, 132.9, 131.7, 130.8, 130.4, 130.0, 129.9, 129.3, 125.1, 124.8, 123.2, 122.1, 120.9, 119.5, 116.9, 34.9, 34.8, 30.9, 30.8 ppm; MS (DART-TOFMS) *m/z*: 772 $[MH]^+$; IR (neat): 2960, 1698, 1439, 1391, 1232, 1160, 822, 750, 710 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{34}H_{29}Br_4O$: 772.8911 $[MH]^+$, Found: 772.8883 $[MH]^+$; Anal. Calcd for $C_{34}H_{28}Br_4O$: C, 52.88; H, 3.65. Found: C, 52.60; H, 3.54.

4.5.2. 2′,4,5′,7-tetrabromo-2,7′-di-t-butyl-10′H-spiro[fluorene-9,9′-phenanthren]-10′-one (iso-**4**)

15% yield (152 mg); *Rf* value 0.55 (hexane/toluene, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) 8.72 (d, J = 8.6 Hz, 1H), 8.42 (d, J = 8.4 Hz, 1H), 7.92 (dd, J = 8.6, 1.9 Hz, 1H), 7.88 (d, J = 1.8 Hz, 1H), 7.68 (d, J = 1.9 Hz, 1H), 7.56 (d, J = 1.6 Hz, 1H), 7.54 (dd, J = 8.4, 1.9 Hz, 1H), 6.96 (d, J = 1.6 Hz, 1H), 6.83 (d, J = 1.8 Hz, 1H), 6.60 (d, J = 1.9 Hz, 1H), 1.17 (s, 9H), 1.10 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 195.4, 153.7, 153.4, 147.8, 147.6, 139.80, 139.79, 136.6, 136.4, 136.2, 133.8, 133.4, 131.8, 131.3, 131.0, 130.6, 128.6, 128.3, 125.4, 125.2, 123.1, 122.1, 122.0, 121.1, 117.3, 69.8, 35.3, 35.1, 31.4, 31.0 ppm; MS (DART-TOFMS) *m/z*: 772 $[MH]^+$; IR (neat): 2955, 1689 (C═O), 1441, 1389, 1243, 816, 748, 685 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{34}H_{29}Br_4O$: 772.8911 $[MH]^+$, Found: 772.8902$[MH]^+$ Anal. Calcd for $C_{34}H_{28}Br_4O$: C, 52.88; H, 3.65. Found: C, 52.80; H, 3.49.

4.6. Representative procedure for the dimerization of 1 to synthesize 3/iso-3, for Table 1, entry 5

4-Bromo-2,7-di-*t*-butyl-9*H*-fluoren-9-one (816 mg, 2.2 mmol) was added to $P(Oi\text{-}Pr)_3$ (1.0 mL, 4.4 mmol), and the resultant yellow solution was stirred at 95 °C (oil bath temp.). After stirred for 47 h, the reaction was cooled to 60 °C. To the reaction mixture at 60 °C was slowly added water (2 mL, 116 mmol) over 2 min, and the mixture was re-heated to 80 °C for hydrolyzing the residual $P(Oi\text{-}Pr)_3$. After the reaction was stirred for more than 8 h, the aqueous layer was separated and followed by extraction with toluene (10 mL x 3). The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give crude products. Purification by short-plugged silica-gel column chromatography (toluene only) yielded 695 mg of whitish yellow solid materials (87%, 50:50). The data of the obtained compounds were identified with authentic samples.

4.7. Representative procedure for the dimerization of 2 to synthesize 4/iso-4, for Table 2, entry 2

2,5-di-bromo-7-*t*-butyl-9*H*-fluoren-9-one (867 mg, 2.2 mmol) was added to $P(Oi\text{-}Pr)_3$ (1.0 mL, 4.4 mmol), and the resultant yellow solution was stirred at 120 °C. After stirred for 8 h, the reaction mixture was cooled to 60 °C. To the mixture at 60 °C was slowly added water (2.0 mL, 116 mmol) over 2 min, and the reaction system was re-heated to 80 °C for hydrolyzing the residual $P(Oi\text{-}Pr)_3$. After the reaction was stirred for more than 14 h, the aqueous layer was separated and followed by extraction with toluene (10 mL x 3). The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give crude products. Purification by short-plugged silica-gel column chromatography (toluene only) yielded 613 mg of whitish yellow solid materials (72%, **4**:*iso*-**4** = 18:82). The data of the obtained compounds were identified with authentic samples.

4.8. Synthesis of 8 and iso-8, for Scheme 4

Under an Ar atmosphere, to a suspension of di-bromo-tetra-*t*-butyl-DBC (618 mg, 0.87 mmol, **5**:*iso*-**5** = 20:80) in *N*,*N*-dimethylformamide (9.0 mL) was added CuI (249 mg, 1.3 mmol) and 28% NaOMe in MeOH (1.3 mL, 6.5 mmol). The mixture was stirred for 30 min at 120 °C, and quenched with 1 M aq. HCl (20 mL). The resultant mixture was diluted with CH_2Cl_2, and the aqueous phase was extracted with CH_2Cl_2 (10 mL x 3). Combined organic phases were washed with brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give the crude products. Purification by silica-gel column chromatography (hexane/toluene = 9/1) gave 445 mg (83%) of mixture of **7**/*iso*-**7** (24:76) as white solid materials. The isomeric mixtures were provided to the next step without separation. Under an Ar atmosphere, to a 25 mL flask was added **7**/*iso*-**7** (445 mg, 0.73 mmol, 24:76) and CH_2Cl_2 (5.0 mL). After the mixture was stirred for 10 min at 0 °C, 1 M BBr_3 in CH_2Cl_2 (2.2 mL, 2.2 mmol) was added dropwise over 5 min. The reaction mixture was stirred at 0 °C for 4 h, and quenched at 0 °C with H_2O (10 mL). The resultant mixture was diluted with CH_2Cl_2, and the aqueous phase was extracted with CH_2Cl_2 (10 mL x 3). Combined organic phases were washed with brine (30 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give 451 mg of samples as brownish white solid materials. Purification by silica-gel column chromatography (toluene/hexane, 4:1) afforded **8** as brownish white solid materials, and *iso*-**8** as whitish yellow solid materials.

4.8.1. 3,6,11,14-tetra-t-butyldibenzo[g,p]chrysene-1,9-diol (**8**)

17% yield (71 mg); *Rf* value 0.28 (toluene only); ^{1}H NMR

(400 MHz, CD_3CN) 9.15 (d, J = 8.7 Hz, 2H), 8.59 (d, J = 2.0 Hz, 2H), 8.24 (d, J = 1.7 Hz, 2H), 7.66 (dd, J = 8.8, 2.0 Hz, 2H), 7.09 (d, J = 1.7 Hz, 2H), 5.57 (s, 2H), 1.41 (s, 18H), 1.40 (s, 18H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) 153.4, 150.1, 149.0, 131.9, 130.4, 129.6, 127.5, 127.2, 124.9, 124.0, 118.3, 117.5, 111.8, 35.33, 35.28, 31.9, 31.8 ppm; MS (DART-TOFMS) *m/z*: 585 $[MH]^+$; IR (neat): 3470, 2960, 1610, 1404, 1232, 1204, 759 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{42}H_{49}O_2$: 585.3733 $[MH]^+$, Found: 585.3725.

4.8.2. 3,6,11,14-tetra-t-butyldibenzo[g,p]chrysene-1,8-diol (iso-**8**)

63% yield (270 mg); *Rf* value 0.42 (toluene only); ^{1}H NMR (400 MHz,CD_3CN) 9.16 (d, J = 8.8 Hz, 2H), 8.60 (d, J = 2.0 Hz, 2H), 8.23 (d, J = 1.8 Hz, 2H), 7.67 (dd, J = 8.8, 2.0 Hz, 2H), 7.07 (d, J = 1.8 Hz, 2H), 5.56 (s, 2H), 1.42 (s, 18H), 1.39 (s, 18H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) 152.3, 148.9, 148.0, 131.1, 129.2, 129.0, 127.9, 126.6, 126.3, 123.9, 123.1, 117.3, 116.4, 110.6, 34.3, 34.2, 30.8, 30.7 ppm; MS (DART-TOFMS) *m/z*: 585 $[MH]^+$; IR (neat): 3509, 3235, 2956, 1615, 1399, 1236, 1097, 942 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{42}H_{49}O_2$: 585.3733 $[MH]^+$, Found: 585.3737.

4.9. Synthesis of 9 and iso-9, for Scheme 5

Under an Ar atmosphere, to a solution of **6**/*iso*-**6** (615 mg, 0.80 mmol, 34:66) in *N*,*N*-dimethylformamide (50 mL) was added CuI (1.85 g, 9.72 mmol) and 28% NaOMe in MeOH (25 mL, 122 mmol). After the mixture was stirred for 1 h at 120 °C, and the reaction was filtered through a pad of celite (eluent, toluene). The filtrate was quenched with 3 M aq. HCl (70 mL), and the resultant mixture was diluted with toluene, and the aqueous phase was extracted with toluene (15 mL x 3). Combined organic phases were washed with brine (20 mL), dried over Na_2SO_3, and concentrated *in vacuo* to give the crude products. Purification by short-plugged silica-gel column chromatography (hexane/toluene = 1/1 to 1/2) afforded *iso*-**9** and **9** in which both were yellowish white solid materials.

4.9.1. 3,11-di-t-butyl-1,6,9,14-tetramethoxydibenzo[g,p]chrysene (**9**)

25% yield (100 mg); *Rf* value 0.38 (hexane/toluene, 1:2); ^{1}H NMR (400 MHz, $CDCl_3$) 9.28 (d, J = 9.2 Hz, 2H), 8.33 (d, J = 1.7 Hz, 2H), 8.07 (d, J = 2.7 Hz, 2H), 7.20 (d, J = 1.7 Hz, 2H), 7.19 (dd, J = 9.2, 2.7 Hz, 2H), 4.13 (s, 6H), 3.89 (s, 6H), 1.42 (s, 18H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 158.0, 157.8, 149.5, 132.2, 131.1, 130.6, 123.0, 124.1, 119.5, 118.2, 115.8, 110.2, 107.5, 56.6, 55.9, 35.9, 32.2 ppm; MS (DART-TOFMS) *m/z*: 561 $[MH]^+$; IR (neat): 2952, 1606, 1463, 1232, 1092, 1045, 730, 619 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{38}H_{41}O_4$: 561.3004 $[MH]^+$, Found: 561.2995 $[MH]^+$; Anal. Calcd for $C_{38}H_{40}O_4$: C, 81.40; H, 7.19. Found: C, 81.20; H, 7.27.

4.9.2. 3,6-di-t-butyl-1,8,11,14-tetramethoxydibenzo[g,p]chrysene (iso-**9**)

47% yield (184 mg); *Rf* value 0.55 (hexane/toluene, 1:2); ^{1}H NMR (400 MHz, $CDCl_3$) 9.29 (d, J = 9.4 Hz, 2H), 8.25 (d, J = 1.6 Hz, 2H), 8.13 (d, J = 2.8 Hz, 2H), 7.21 (d, J = 1.6 Hz, 2H), 7.20 (dd, J = 9.4, 2.8 Hz, 2H), 4.13 (s, 6H), 3.90 (s, 6H), 1.42 (s, 18H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 157.7, 157.4, 149.1, 131.5, 131.2, 130.5, 130.2, 129.2, 123.8, 119.3, 118.4, 114.9, 109.7, 107.3, 56.3, 55.7, 35.6, 31.9 ppm; MS (DART-TOFMS) *m/z*: 561 $[MH]^+$; IR (neat): 2948, 1606, 1455, 1387, 1224, 1017, 826, 790 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{38}H_{41}O_4$: 561.3004 $[MH]^+$, Found: 561.3005 $[MH]^+$; Anal. Calcd for $C_{38}H_{40}O_4$: C, 81.40; H, 7.19. Found: C, 81.43; H, 7.01.

4.10. Synthesis of 10 and iso-10, for Scheme 5

Under an Ar atmosphere, to a 20 mL flask was added **9** or *iso*-**9** (0.36 mmol, 200 mg) and CH_2Cl_2 (2.0 mL). After the mixture was stirred for 20 min at 0 °C, 1 M BBr_3 in CH_2Cl_2 (2.2 mmol, 2.2 mL) was added dropwise over 5 min, and the reaction mixture was stirred for 4 h. The reaction was allowed to warm to room temperature over 0.5 h, and quenched at 0 °C with H_2O (10 mL). The resultant mixture was diluted with EtOAc, and the aqueous phase was extracted with EtOAc (10 mL × 3). Combined organic phases were washed with brine (15 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give a desired tetrol molecule as whitish yellow solid.

4.10.1. 3,11-di-t-butyldibenzo[g,p]chrysene-1,6,9,14-tetrol (**10**)

90% yield (126 mg); *Rf* value 0.31 (toluene/EtOAc, 4:1); ^{1}H NMR (400 MHz, CD_3CN) 9.29 (d, J = 9.0 Hz, 2H), 8.17 (d, J = 1.8 Hz, 2H), 7.95 (d, J = 2.7 Hz, 2H), 7.69 (s, 2H), 7.20 (s, 2H), 7.19 (d, J = 1.8 Hz, 2H), 7.10 (d, J = 2.7, 9.0 Hz, 2H), 1.39 (s, 18H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) 155.1, 154.5, 147.9, 130.9, 129.7, 129.6, 128.3, 122.4, 116.8, 115.3, 115.0, 111.7, 111.0, 34.4, 31.1 ppm; MS (DART-TOFMS) *m/z*: 505 $[MH]^+$; IR (neat): 3530, 3382, 2956, 1606, 1407, 1188, 854, 774 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{34}H_{33}O_4$: 505.2378 $[MH]^+$, Found: 505.2385.

4.10.2. 3,6-di-t-butyldibenzo[g,p]chrysene-1,8,11,14-tetrol (iso-**10**)

93% yield (130 mg); *Rf* value 0.29 (Hexane/EtOAc, 1:1); ^{1}H NMR (400 MHz, CD_3CN) 9.29 (d, J = 9.0 Hz, 2H), 8.11 (d, J = 1.8 Hz, 2H), 8.06 (d, J = 2.6 Hz, 2H), 7.68 (s, 2H), 7.26 (s, 2H), 7.20 (d, J = 1.8 Hz, 2H), 7.117 (d, J = 2.6, 9.0 Hz, 2H), 1.36 (s, 18H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) 155.1, 154.5, 147.8, 130.5, 130.2, 129.8, 129.3, 127.4, 122.2, 117.0, 115.8, 115.1, 111.2, 111.0, 34.5, 31.2 ppm; MS (DART-TOFMS) *m/z*: 505 $[MH]^+$; IR (neat): 3501, 3346, 2955, 1606, 1404, 1222, 1179, 1084, 851, 791 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{34}H_{33}O_4$: 505.2378 $[MH]^+$, Found: 505.2372.

4.11. Representative procedure for the transformation of iso-4 into 6/iso-6, for Table 3, entry 8

To a solution of *iso*-**4** (576 mg, 0.75 mmol) in toluene (2.0 mL) was added MeOH (0.40 mL), and the flask was heated at 45 °C. To the flask was slowly added $NaBH_4$ (28 mg, 0.75 mmol) over 20 min (each 7.0 mg, 4 times, 5-min intervals). After stirred for 0.5 h, the reaction was quenched with acetone (1.0 mL) and treated for additional 0.5 h. The organic layer was washed with water (10 mL x 5), washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 556 mg of the corresponding alcohol as white solid materials. This crude product was provided in the next step without further purification. To a solution of the alcohol (100 mg, 0.13 mmol) in toluene (1.0 mL) at −78 °C was added $EtAlCl_2$ (0.16 mL, 1 M in hexane) dropwise over 2 min. After stirred at −78 °C for 5 min, the mixture was stirred at 0 °C for 4 h. The reaction was quenched with water (2.0 mL) at 0 °C, and the organic layer was washed with brine (10 mL), dried over Na_2SO_4, and filtered, and concentrated *in vacuo* to give white solid materials. Purification by silica-gel column chromatography (hexane only) afforded white solid materials of 77 mg (79%, **6**/*iso*-**6** 19:81).

4.12. Representative procedure for the transformation of 3 or iso-3 into 5/iso-5, for Table 5, entry 3

To a solution of *iso*-**3** (541 mg, 0.74 mmol) in toluene (3.0 mL) was added methanol (0.60 mL), and the flask was heated at 45 °C. To the flask was slowly added $NaBH_4$ (28 mg, 0.74 mmol) over 20 min (each 7.0 mg, 4 times, 5-min intervals). After stirred for 0.5 h, the reaction was quenched with acetone (1.0 mL) and conducted for additional 0.5 h. The organic layer was washed with water (10 mL x 5), washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 520 mg of the

corresponding alcohol as white solid materials. The crude sample was provided in the next step without further purification. To a solution of the alcohol (250 mg, 0.34 mmol) in toluene (2.5 mL) was added HFIP (2.5 mL) and conc. HCl (0.020 mL, 0.21 mmol, 35% in water) at room temperature. After stirred for 1 h, the reaction was quenched with saturated aqueous $NaHCO_3$ (2.0 mL) at 0 °C. And the organic layer was washed with brine (10 mL), dried over Na_2SO_4, and filtered, and concentrated *in vacuo* to give crude of white solid materials. Purification by silica-gel short column chromatography (hexane only) afforded 221 mg (91%, **5**/*iso*-**5** 91:9) of white solid materials.

4.13. Selective production of 5/iso-5, for Scheme 6 (a)

To a solution of **3** (826 mg, 1.14 mmol) in toluene (4.0 mL) was added methanol (0.80 mL), and to the mixture at 45 °C was added $NaBH_4$ (17.2 mg, 0.46 mmol). After stirred for 0.5 h, the reaction was quenched with acetone (3.2 mL, 43.5 mmol) and treated for additional 0.5 h. The organic layer was washed with water (10 mL x 5) and brine (10 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 812 mg of the corresponding alcohol as white solid materials. The crude sample was provided in the next step without further purification. To a solution of the alcohol in toluene (8.2 mL) was added HFIP (8.2 mL) and conc. HCl (0.060 mL, 0.68 mmol, 35% in water) at room temperature. After stirred for 1 h, the reaction was quenched with saturated aq. $NaHCO_3$ (10 mL) at 0 °C, and the aqueous phase was extracted with toluene (20 mL x 3). Combined organic phases were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 790 mg of **5**/*iso*-**5** (98%, 20:80) as white solid materials in pure form. Recrystallization from EtOAc (150 mg, 37 mL/g) afforded 51 mg of **5**/*iso*-**5** (33%, 11:89). As for another route from *iso*-**3**, experimental procedures are the same above. After the workup operation, white solid materials of 247 mg of **5**/*iso*-**5** (90:10) were given as a pure form in quantitative yield. Recrystallization from hexane (150 mg, 133−85 = 48 mL/g) afforded 105 mg (64%, **5**/*iso*-**5** 93:7) of white solid materials.

4.14. Isolation of 6 and iso-6, for Scheme 6 (b)

To a solution of *iso*-**4** (500 mg, 0.65 mmol) in toluene (3.0 mL) was added methanol (0.60 mL), and to the mixture at 45 °C was added $NaBH_4$ (10 mg, 0.26 mmol). After stirred for 0.5 h, the reaction was quenched with acetone (1.0 mL, 13.6 mmol) and treated for additional 0.5 h. The organic layer was washed with water (50 mL x 3) and brine (10 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 512 mg the corresponding alcohol as white solid materials. The crude sample was provided in the next step without further purification. To a solution of the alcohol in toluene (5.0 mL) at −78 °C was added $EtAlCl_2$ (0.80 mL, 1.0 M in hexane) dropwise over 3 min. After stirred at −78 °C for 5 min, the mixture was stirred for 15 min at 0 °C, and followed by conductance at room temperature for additional 15 h. The reaction was quenched with water (5.0 mL) at 0 °C, and the aqueous phase was extracted with toluene (5.0 mL x 3). Combined organic phases were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give white solid products 470 mg of **6**/*iso*-**6** (25:75) in pure form. Column chromatography by silica-gel (360 mg, hexane only) afforded **6** and *iso*-**6** in which both were white solid materials.

4.14.1. 3,11-di-t-butyl-1,6,9,14-tetrabromodibenzo[g,p]chrysene (6)

12% yield (45 mg); *Rf* value 0.43 (hexane only); ^{1}H NMR (400 MHz, $CDCl_3$) 9.28 (d, J = 8.9 Hz, 2H), 8.60 (d, J = 1.9 Hz, 2H), 8.52 (d, J = 1.8 Hz, 2H), 7.99 (d, J = 1.8 Hz, 2H), 7.68 (dd, J = 1.9, 8.9 Hz, 2H), 1.41 (s, 18H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 151.8, 132.6, 132.0, 131.2, 130.5, 130.1, 129.0, 128.7, 128.2, 127.5, 125.0, 121.7, 120.9, 35.5, 31.5 ppm; MS (DART-TOFMS) *m/z*: 756 $[MH]^+$; IR (neat): 2955, 1598, 1455, 1389, 870, 819, 752, 700 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{34}H_{28}Br_4$: 755.8883 $[MH]^+$, Found: 755.8879 $[MH]^+$.

4.14.2. 3,6-di-t-butyl-1,8,11,14-tetrabromodibenzo[g,p]chrysene (iso-6)

51% yield (191 mg); *Rf* value 0.40 (hexane only); ^{1}H NMR (400 MHz, $CDCl_3$) 9.25 (d, J = 9.0 Hz, 2H), 8.59 (d, J = 2.0 Hz, 2H), 8.44 (d, J = 1.8 Hz, 2H), 7.99 (d, J = 1.8 Hz, 2H), 7.69 (dd, J = 2.0, 9.0 Hz, 2H), 1.41 (s, 18H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2) 151.7, 132.6, 131.9, 131.7, 130.4, 130.2, 129.8, 128.6, 128.4, 127.9, 127.6, 124.9, 121.9, 121.1, 35.4, 31.4 ppm; MS (DART-TOFMS) *m/z*: 756 $[MH]^+$; IR (neat): 2959, 1590, 1444, 1384, 993, 870, 787, 676 cm^{-1}; HRMS (DART-TOFMS) calcd for $C_{34}H_{28}Br_4$: 755.8883 $[MH]^+$, Found: 755.8895 $[MH]^+$.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors thank Dr. Toshiyuki Iwai and Dr. Takatoshi Ito at ORIST for gentle assistance with HRMS. We are grateful to Prof. Dr. Kiyosei Takasu, Dr. Yosuke Yamaoka, and Dr. Naoki Ogawa at Kyoto University for helpful assistance of X-ray diffraction and scattering. Prof. Dr. Schramm, M. P. at CSULB are gratefully thanked for helpful discussion.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.132353.

References

[1] a) J.C. Fetzer, Polycyclic aromat, Compd 27 (2007) 143−162;
b) R.A. Pascal Jr., Chem. Rev. 106 (2006) 4809−4819;
c) H. Hopf, Classics in Hydrocarbon Chemistry, Wiley-VCH, Weinheim, Germany, 2000.
[2] a) F.H. Herbstein, Acta Crystallogr. B35 (1979) 1661−1670;
b) H. Tsuji, Y. Ueda, L. Ilies, E. Nakamura, J. Am. Chem. Soc. 132 (2010) 11853−11855.
[3] a) S. Wang, P. Yang, K. Chang, W. Lv, B. Mi, J. Song, X. Zhao, Z. Gao, Org. Electron. 74 (2019) 269−275;
b) S. Jeong, S.H. Kim, D.Y. Kim, C. Kim, H.W. Lee, S.E. Lee, Y.K. Kim, S.S. Yoon, Thin Solid Films 636 (2017) 8−14;
c) T. Mori, K. Fujita, M. Kimura, J. Photopolym. Sci. Technol. 23 (2010) 317−322;
d) R. Chaudhuri, M.-Y. Hsu, C.-W. Li, C.-I. Wang, C.-J. Chen, C.-K. Lai, L.-Y. Chen, S.-H. Liu, C.-C. Wu, R.S. Liu, Org. Lett. 10 (2008) 3053−3056;
e) S. Tokito, K. Noda, H. Fujikawa, Y. Taga, M. Kimura, K. Shimada, Appl. Phys. Lett. 77 (2000) 160−162.
[4] a) T. Aoki, Y. Deguchi, Jpn. Kokai Tokkyo Koho (2020) 2020−2064;
b) K. Ohta, Jpn. Kokai Tokkyo Koho (2016). JP 2016-125007 A 20160711;
c) T. Makinoshima, M. Echigo, PCT Int. Appl. (2015). WO 2015170736 A1 20151112;
d) H. Kato, M. Takatori, Jpn. Kokai Tokkyo Koho (2014). JP 2014152164 A 20140825;
e) H. Kato, M. Takatori, Jpn. Kokai Tokkyo Koho (2013). JP 2013227307 A 20131107.
[5] a) L.C. Eversloh, Z. Liu, B. Müller, M. Stangl, C. Li, K. Müllen, Org. Lett. 13 (2011) 5528−5531;
b) T. Hatakeyama, S. Hashimoto, S. Seki, M. Nakamura, J. Am. Chem. Soc. 133 (2011) 18614−18617;
c) S. Xiao, S.J. Kang, Y. Wu, S. Ahn, J.B. Kim, Y.-L. Loo, T. Siegrist, M.L. Steigerwald, H. Li, C. Nuckolls, Chem. Sci. 4 (2013) 20182−20183;
d) K. Nakamura, S. Furumi, M. Takeuchi, T. Shibuya, K. Tanaka, J. Am. Chem.

Soc. 136 (2014) 5555–5558;
e) D. Sakamaki, D. Kumano, E. Yashima, S. Seki, Angew. Chem. Int. Ed. 54 (2015) 5404–5407;
f) H. Ito, Y. Segawa, K. Murakami, K. Itami, J. Am. Chem. Soc. 141 (2019) 3–10;
g) W. Hagui, H. Doucet, J.F. Soule, Inside Chem. 5 (2019) 2006–2078.

[6] S. Yamaguchi, T.M. Swager, J. Am. Chem. Soc. 123 (2001) 12087–12088.

[7] a) A. Mukherjee, K. Pati, R.S. Liu, J. Org. Chem. 74 (2009) 6311–6314;
b) T.S. Navale, K. Thakur, R. Rathore, Org. Lett. 13 (2011) 1634–1637;
c) K. Mochida, K. Kawasumi, Y. Segawa, K. Itami, J. Am. Chem. Soc. 133 (2011) 10716–10719.

[8] a) C.-W. Li, C.-I. Wang, H.-Y. Liao, R. Chaudhuri, R.-S. Liu, J. Org. Chem. 72 (2007) 9203–9207;
b) Y. Ueda, H. Tsuji, H. Tanaka, E. Nakamura, Chem. Asian J. (2014) 1623–1628;
c) M. Shimizu, I. Nagao, Y. Tomioka, T. Hiyama, Angew. Chem. Int. Ed. 47 (2008) 8096–8099;
d) K. Ozaki, K. Kawashima, M. Shibata, H. Ito, K. Itami, Nat. Commun. 6 (2015) 6251;
e) K. Kogashi, T. Matsuno, S. Sato, H. Isobe, Angew. Chem. Int. Ed. 58 (2019) 7385–7389.

[9] N. Suzuki, T. Fujita, J. Ichikawa, Org. Lett. 17 (2015) 4984–4987.

[10] X.-Y. Liu, X. Tang, Y. Zhao, D. Zhao, J. Fan, L.-S. Liao, Dyes Pigments 146 (2017) 234–239.

[11] a) N. Yoshida, S. Kamiguchi, K. Sakao, R. Akasaka, Y. Fujii, T. Maruyama, T. Iwasawa, Tetrahedron Lett. 61 (2020) 152033;
b) N. Yoshida, S. Kamiguchi, Y. Fujii, K. Sakao, T. Maruyama, S. Tokai, Y. Taguchi, Y. Matsumoto, R. Akasaka, T. Iwasawa, Tetrahedron Lett. 61 (2020) 152406.

[12] S. Kajigaeshi, T. Kadowaki, A. Nishida, S. Fujisaki, Bull. Chem. Soc. Jpn. 59 (1986) 97–103.

[13] M. Nakanishi, C. Bolm, Adv. Synth. Catal. 349 (2007) 861–864.

[14] The single crystal of 3 was prepared by slow evaporation of CH3CH2CN (1.0 mL) solution of the sample (5 mg); CCDC-2040641 (for 3) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Monoclinic, space group P 1 21/c 1, colorless, a = 15.2175(8) Å, b = 11.9914(6) Å, c = 21.0696(10) Å, α = 90°, β = 105.619°, γ = 90°, V = 3702.8(3) Å3, Z = 4, T = 293 K, dcalcd. = 1.673 g cm−3, μ(Mo-Kα) = 5.641 mm−1, R1 = 0.0597, wR2 = 0.2633, GOF = 1.063.

[15] The single crystal of iso-4 was prepared by slow evaporation of EtOAc (0.7 mL) solution of the sample (5 mg); CCDC-2040656 (for iso-4) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Monoclinic, space group P 1 21/n 1, colorless, a = 15.2175(8) Å, b = 11.9914(6) Å, c = 21.0696(10) Å, α = 90°, β = 105.619°, γ = 90°, V = 3702.8(3) Å^3, Z = 4, T = 293 K, $d_{calcd.}$ = 1.673 g cm−3, μ(Mo-Kα) = 5.641 mm−1, R1 = 0.0863, wR2 = 0.2633, GOF = 1.091.

[16] To the best of our knowledge, there are two papers concerning some insights into the dimerization of symmetric 9-fluorenones or related molecules, see:.
a) I.J. Borowith, M. Anschel, P.D. Readio, J. Org. Chem. 36 (1971) 553–560;
b) L. Martin, Y. Zhang, K. Robeyns, B. Champagne, P. Adriaensens, L. Lusten, D. Vanderzande, D. Bevk, W. Maes, Tetrahedron Lett. 54 (2013) 526–529.

[17] M. Hoang, T. Gadosy, H. Ghazi, D.-F. Hou, A.C. Hopkinson, L.J. Johnston, E. Lee-Ruff, J. Org. Chem. 63 (1998) 7168–7171.

18 We confirmed that no reaction was observed without acid reagent.

[19] a) J.R. Hanson, Comprehensive Organic Synthesis 3 (1991) 705–719;
b) G.A. Olah, Acc. Chem. Res. 9 (1976) 41–52;
c) G.A. Olah, G.K. Surya Prakash, Carbocation Chemistry, Wiley-Interscience, The United States of America, 2004.

[20] HFIP is effective for this type of rearrangement, see: T. Fujita, I. Takahashi, M. Hayashi, J. Wang, K. Fuchibe, J. Ichikawa Eur. J. Org Chem. (2017) 262–265.

21 One referee commented that the stereochemistry around the alcohol segments will give an insight into the mechanism of the Wagner-Meerwein rearrangement. However, the alcohols were observed as diastereomeric mixtures in around 1:1 ratio, and the mixtures were too close in Rf values to separate each other.

[22] N. Ogawa, Y. Yamaoka, K. Takasu, Org. Lett. 21 (2019) 7563–7567.

23 As we were not able to isolate **5** and *iso*-**5**, it was difficult to characterize them accurately and to list the characterization in this manuscript. Alternatively, we certainly inferred their structures from isolation of their derivatives 8 and iso-8.