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Palladium-Catalyzed Arylation of Methylene-Bridged Polyarenes: Synthesis and Structures of 9-Arylfluorene Derivatives

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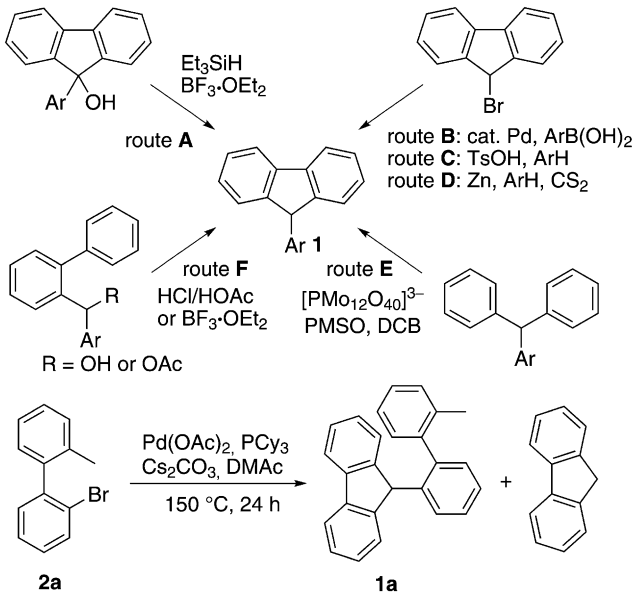
Abstract: In the presence of a catalytic system comprised of palladium(II) acetate and tricyclohexylphosphine, the reaction of fluorene with haloarenes generated 9-arylfluorenes in good to excellent yields. The scope and limitations of the coupling reaction were investigated. This synthetic protocol is more efficient than conventional methods. A wide range of functional groups, including alkyl, alkoxy, ester, and nitrile, can tolerate the reaction conditions herein. Sterically congested haloarenes also gave satisfactory results. Furthermore, this synthetic method is utilized to prepare 9,9-diarylfluorenes and tetraarylindenofluorene. Depending on the reaction conditions, the arylation of bowl-shaped sumanene gave monoarylated sumanene either as the sole product or with another diaryl-substituted product.

Keywords: arylation; fluorenes; indenofluorenes; palladium; polyarenes; sumanene

Introduction

Fluorene is the simplest methylene-bridged arene and it is an important building block for various organic materials, including those used in optoelectronics,[1] semiconductors,[2] and solar cells.[3] Unlike benzenoids, fluorene and other methylene-bridged polyarenes are classified as non-alternant aromatic hydrocarbons because their additional methylene carbons cannot present aromaticity associated with the Kekulé structure.[4] Moreover, the methylene protons exhibit high acidity,[5] which allows fluorene to be easily converted to 9,9-dialkylfluorenes. Molecules of this type are more stable and soluble than the parent compound. However, for use in optoelectronics, 9,9-diarylfluorenes are superior to 9,9-dialkylfluorenes because the alkyl pendant group of the latter can be photochemically or electrooxidatively cleaved,[6] resulting in poor color purity. The high strength of the bond between the pendant aryl groups and the C-9 carbon of fluorene in 9,9-diarylfluorenes gives them excellent morphological and thermal stability.[7] In addition to their use in organic materials, 9-arylfluorenes are useful precursors for the formation of chiral ligands,[8] which are used in polymer catalysts.[8d] Accordingly, efficient preparations of 9-arylfluorenes **1** and 9,9-diarylfluorenes are important, and conventional methods for synthesizing **1** are summarized in Scheme 1. The reac-



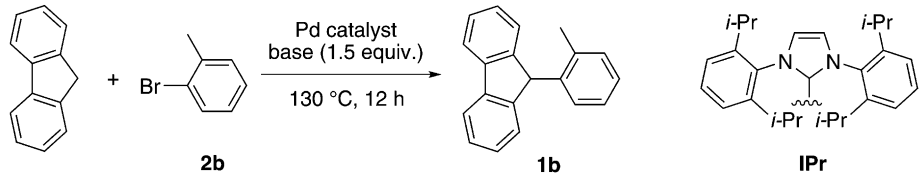
Scheme 1. Synthetic methods for preparing 9-arylfluorenes.

tion of 9-fluorenone with aryllithium or aryl-Grignard reagents yields the corresponding carbinols, which are subsequently transformed into **1** by treatment with reductants, such as $Et_2O{\cdot}BF_3/Et_3SiH$ system (route **A**).[9] Additionally, **1** can be formed from 9-bromofluorene through many reaction mechanisms (routes **B**–**D**). Organostannoxane-supported palladium nanoparticles efficiently catalyze the Suzuki reaction of 9-bromofluorene with phenylboronic acid (route **B**).[10] In the presence of *p*-toluenesulfonic acid, 9-bromofluorene in toluene is transformed into a regioisomeric mixture of 9-(2-tolyl)fluorene and 9-(4-tolyl)fluorene (route **C**), with the latter as the major product. In this reaction, the fluorenyl cation is believed to be the key intermediate.[11] The zinc-mediated radical reaction of 9-bromofluorene with anthracene in CS_2 yields 9-(9-anthryl)fluorene (route **D**).[12] Alternatively, the formation of the central five-membered ring can be adopted as the key step in the synthesis of **1**.[13] For example, using a catalytic system consisting of phenyl methyl sulfoxide (PMSO) and the oxidized Keggin-type polyoxomolybdate $[PMo_{12}O_{40}]^{3-}$ in dichlorobenzene (DCB), triphenylmethane furnishes 9-phenylfluorene *via* the triphenylmethane cation (route **E**).[14] Alternatively, Friedel–Crafts cyclizations of biaryl alcohols or acetates catalyzed by a Brønsted or Lewis acid, such as HCl/HOAc, polyphosphoric acid or $BF_3{\cdot}Et_2O$, can also furnish **1** (route **F**).[15] As in route **A**, the biphenyl derivatives that are used in route **F** are formed by the reaction of 2-biphenylcarbaldehyde with aryllithium or aryl-Grignard reagents. Of these synthetic methods, routes **A** and **F** are the most extensively used, but functional group tolerance is a major limitation. Routes **B**–**E** have not been comprehensively investigated (with only one example of each reaction), and their scope and limitations are unclear. Therefore, the direct preparation of 9-arylfluorenes by the metal-catalyzed coupling reaction of fluorene with haloarenes has great potential.[16] The synthetic method proposed herein should not only mitigate the drawbacks of routes **A**–**F**, but also efficiently reduce the number of reaction steps. In our earlier study of the synthesis of fluorene by the palladium-catalyzed cyclization of 2-bromo-2′-methylbiphenyl (**2a**), 9-(2-biphenyl)fluorene (**1a**) was obtained as a by-product in low yield (Scheme 1).[17a] Compound **1a** should be obtained by the cross-coupling reaction of fluorene with **2a**.[18] Accordingly, this investigation concerns the arylation of fluorene and methylene-bridged polyarenes.

Results and Discussion

The reaction conditions for synthesizing 9-(2-tolyl)-fluorene (**1b**) from fluorene and 2-bromotoluene (**2b**) were systematically studied (Table 1). The palladium catalyst, base, and solvent all have crucial roles. The

Table 1. Optimization of reaction conditions for the preparation of **1b**.[a]

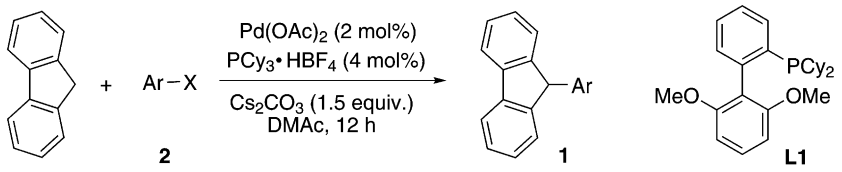


2b **1b** **IPr**

Entry	Catalyst (mol%)	Ligand (mol%)	Base	Solvent	Fluorene:**1b**[b]	Isolated yield [%]
1	$PdCl_2(PCy_3)_2$ (5)	–	Cs_2CO_3	DMAc	9:91	–
2	$Pd(OAc)_2$ (5)	$PCy_3{\cdot}HBF_4$ (10)	Cs_2CO_3	DMAc	0:100	94
3	$Pd(OAc)_2$ (2)	$PCy_3{\cdot}HBF_4$ (4)	Cs_2CO_3	DMAc	0:100	95
4	$Pd(OAc)_2$ (1)	$PCy_3{\cdot}HBF_4$ (2)	Cs_2CO_3	DMAc	0:100	90
5	$Pd(OAc)_2$ (5)	$PCy_3{\cdot}HBF_4$ (10)	Cs_2CO_3	NMP	34:66	55
6	$Pd(OAc)_2$ (5)	$PCy_3{\cdot}HBF_4$ (10)	K_2CO_3	NMP	85:5	–
7	$Pd(OAc)_2$ (5)	$PCy_3{\cdot}HBF_4$ (10)	Na_2CO_3	NMP	100:0	–
8	$Pd(OAc)_2$ (5)	$PCy_3{\cdot}HBF_4$ (10)	KOAc	NMP	100:0	–
9	$Pd(OAc)_2$ (5)	$PCy_3{\cdot}HBF_4$ (10)	Cs_2CO_3	1,4-dioxane	6:94	87
10	$Pd(OAc)_2$ (5)	$PCy_3{\cdot}HBF_4$ (10)	Cs_2CO_3	DMF	0:100	95
11	$Pd(OAc)_2$ (5)	$P(t\text{-}Bu)_3{\cdot}HBF_4$ (10)	Cs_2CO_3	DMAc	66:34	–
12	$Pd(OAc)_2$ (5)	PPh_3 (10)	Cs_2CO_3	DMAc	73:27	–
13	$Pd(OAc)_2$ (5)	dppm (5)	Cs_2CO_3	DMAc	14:86	–
14	$Pd(OAc)_2$ (5)	dppe (5)	Cs_2CO_3	DMAc	70:30	–
15	$Pd(OAc)_2$ (5)	IPr·HCl (10)	Cs_2CO_3	DMAc	20:80	–

[a] The reaction was performed with fluorene (0.50 mmol), **2** (0.60 mmol) and base (0.75 mmol) in a thick-walled sealed tube at 130 °C for 12 h.
[b] Determination by GC MS.

Table 2. Preparation of 9-arylfluorenes.[a]



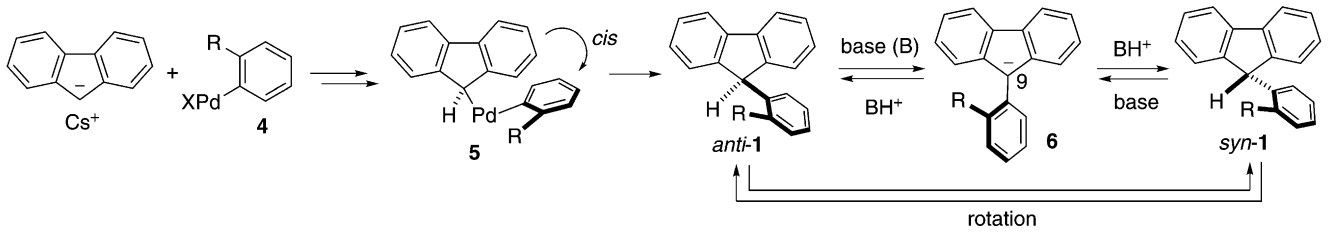
Entry	Ar–X	Ratio (fluorene/**2**)	Temp. [°C]	Product	Isolated yield [%]
1	2-CH_3-C_6H_4Br (**2b**)	1/1.2	130	**1b**	95[b]
2	C_6H_5Cl (**2c**)	1/1.2	130	**1c**	95
3	C_6H_5Br (**2d**)	1/1.2	130	**1c**	95
4	2-Ph-C_6H_4Br (**2e**)	1/1.2	130	**1e**	75[c]
5	2-CO_2CH_3-C_6H_4Cl (**2f**)	1.3/1	110	**1f**	79[c]
6	4-CHO-C_6H_4Br (**2g**)	1/1.2	130	**1g**	0
7	4-CO_2CH_3-C_6H_4Br (**2h**)	1/1.5	130	**1h**	75
8	4-Ac-C_6H_4Br (**2i**)	1/1.2	110	**1i**	57
9	4-Ac-C_6H_4Br (**2i**)	1/1.2	110	**1i**	85[d]
10	4-CF_3-C_6H_4Br (**2j**)	1/1.2	130	**1j**	51
11	4-CF_3-C_6H_4Br (**2j**)	1/1.2	110	**1j**	82
12	4-CN-C_6H_4Br (**2k**)	1/1.2	130	**1k**	70
13	4-OCH_3-C_6H_4Br (**2l**)	1.2/1	130	**1l**	0
14	4-OCH_3-C_6H_4Br (**2l**)	1.2/1	130	**1l**	95[e]
15	2,6-$(CH_3)_2$-C_6H_3Br (**2m**)	1/1.2	130	**1m**	94
16	9-bromophenanthrene (**2n**)	1/1.2	130	**1n**	83[f]
17	1-bromo-2-methylnaphthalene (**2o**)	1/1.2	130	**1o**	84 [g]

[a] The reaction was conducted with fluorene and **2** (0.50 mmol) in a thick-walled sealed tube.
[b] The ratio (*syn/anti* = 63/37) was determined by ^{1}H NMR.
[c] The rotamers of **1e** and **1f** cannot be easily distinguished by ^{1}H NMR. For details, see: ref.[26]
[d] The reaction was conducted with Cs_2CO_3 (3.0 equiv.).
[e] The reaction was conducted with ligand **L1**.
[f] The ratio (*syn/anti* = 57/43) was determined by ^{1}H NMR.
[g] The ratio (*syn/anti* = 60/40) was determined based on the ^{1}H NMR spectrum of the crude product. Both *syn*-**1o** and *anti*-**1o** were obtained in their pure forms.

combination of $Pd(OAc)_2$ and PCy_3 was found to drastically outperform $PdCl_2(PCy_3)_2$ and other catalytic systems that are shown in Table 1. The fluorenyl anion is the key intermediate in this reaction. The use of Cs_2CO_3 was preferred over the use of Na_2CO_3, K_2CO_3 or KOAc due to its greater basicity (entries 3 and 6–8 in Table 1). Unlike other solvents, such as *N*-methylpyrrolidinone (NMP) and 1,4-dioxane, dimethylacetamide (DMAc) and DMF yielded excellent results (entries 2, 5, 9 and 10 in Table 1). Under the optimal conditions herein, the desired **1b** was obtained in 95% yield (entry 3 in Table 1).

The reactivity of haloarenes **2** was tested under the optimal conditions and on most occasions, the desired products **1** were obtained in good to excellent yields (Table 2). This procedure is compatible with many functional groups, such as alkyl, alkoxy, ester, nitrile, and others. 4-Bromobenzaldehyde (**2g**) cannot be used in this reaction because the aldol condensation is much faster than the coupling reaction, according to GC-MS analysis (entry 6 in Table 2). Chlorobenzene (**2c**) and bromobenzene (**2d**) produced 9-phenylfluorene (**1c**) in the same yield (entries 2 and 3 in Table 2). Sterically congested haloarenes, including 2-bromobiphenyl (**1e**), 2-bromo-1,3-dimethylbenzene (**2m**) and 1-bromo-2-methylnaphthalene (**2o**) furnished the corresponding products in good yields (entries 4, 15 and 17 in Table 2).

The electronic properties of haloarenes strongly influence the reaction efficiency. The reaction with electron-deficient arenes, such as methyl 2-chlorobenzoate (**2f**), 4-bromoacetophenone (**2i**), and 4-bromo-1-(trifluoromethyl)benzene (**2j**), must be conducted at a lower temperature (110 °C) to inhibit the formation of the biphenyl by-product by self-dimerization (entries 5, 8–11 in Table 2). Due to the presence of acidic protons, excess base is required to form 4-(9-fluorenyl)acetophenone (**1i**) efficiently (entries 8 and 9 in Table 2). Unlike in other examples, 4-bromoanisole (**2l**) did not yield the coupling product **1l** under the regular conditions in Table 2, but the yield of the latter compound was dramatically improved when ligand PCy_3 was replaced by **L1** (entries 13 and 14 in Table 2). It is noteworthy that the protocol herein for synthesizing alkyl 2-(9-fluorenyl)benzoates is simpler to implement than the coupling reaction of 2-(trime-



Scheme 2. Formation mechanism and stereochemistry of **1**.

thylsilyl)phenyl triflate with alkyl fluorene-9-carboxylate.[19]

With compounds **1** in hand, the stereochemistry of 9-(2-substituted phenyl)fluorene derivatives such as **1b**, **1e**, **1f**, **1n** and **1o** was investigated because their bulky aryl substituents inhibit their rotation.[20] For example, the rotation barriers of **1b** and **1n**, measured in tetrachloroethene, were determined to be 14.3 and 29.8 kcal mol^{-1}, respectively.[21] These high values allow their rotamers to be observed. The stereochemistry of **1** was initially analyzed by considering the mechanism of formation proposed in Scheme 2. The reaction of arylpalladium **4** with fluorenyl anion followed by rearrangement yields complex *cis*-**5**, whose steric repulsion is low when the substituent R is located far from the fluorenyl backbone. Then, the reductive elimination of *cis*-**5** yields *anti*-**1** (with the substituent R *anti* to the fluorene 9-H). The *anti*/*syn* isomerization has been extensively examined.[22] Depending on the bulkiness of the substituent R, *anti*-**1** may directly convert into *syn*-**1**, which is thermodynamically more stable. Under basic conditions, 9-arylfluorenyl anion **6** is also responsible for *anti*/*syn* isomerization through inversion of the 9-position[23] or rotation of the aryl substituent.[22a] As expected, *syn*-**1** was obtained as the major rotamer in several of the cases in Table 2. However, the observed products **1e** and **1f** were first believed to be a single rotamer, based on their NMR spectra. Other similar derivatives, such as alkyl 1-(9-fluorenyl)-naphthalene-2-carboxylates,[8c] ethyl 2-(9-fluorenyl)benzoates[19] and 1,4-di(9-fluorenyl)-2,5-diphenylbenzene,[24] prepared by different synthetic routes have the same stereochemistry. Indeed, X-ray crystallographic analysis revealed that **1e** is the single *syn*-rotamer.[25] Unlike the X-ray crystallographic study, the chemical shift of the fluorenyl 9-H in the ^{1}H NMR spectrum is not always a suitable indicator for identifying the configuration of rotamers, because its value is strongly influenced by the substituents and/or is almost identical for both rotamers in some cases. For example, an attempt was made to observe and identify *syn*- and *anti*-conformers of **1e** and **1f** based on variable-temperature NMR experiments. However, their rotamers, according to the chemical shift of 9-H, cannot be easily distinguished at either low or high temperature.[26,27]

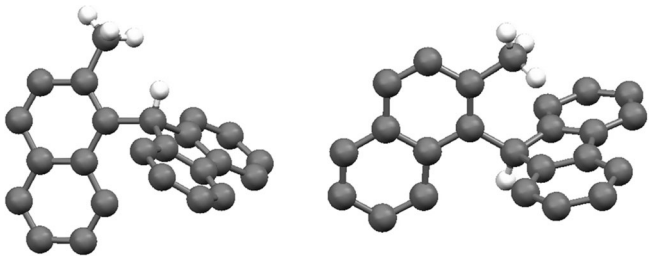


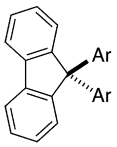
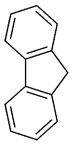
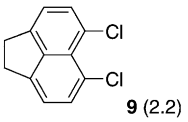
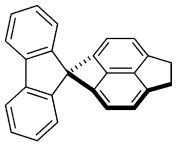
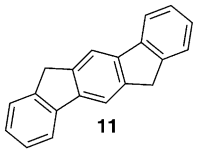
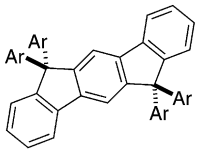
Figure 1. The molecular structure of *syn*-**1o** (*left*) and *anti*-**1o** (*right*). The aryl hydrogen atoms are omitted for clarity.

The ^{1}H NMR signals of the protons in one methyl group in **1m** and the methyl protons in *anti*-**1b** and *anti*-**1o** exhibit high-field shifts.[28] For example, the chemical shifts of the methyl protons in *syn*-**1o** and *anti*-**1o** are approximately 2.88 and 1.35 ppm, respectively, but a proton in a normal benzylic methyl group resonates at around 2.3 ppm. This finding is caused by the ring current because the methyl hydrogen is located over the fluorene ring with substantial shielding. Fortunately, the *syn*- and *anti*-rotamers of **1o** can be separated and analyzed by X-ray crystallography (Figure 1).[25] The distance between the methyl carbon and the fluorenyl plane in *anti*-**1o** is estimated to be 2.93 Å. The crystallographic data recorded herein are useful for a theoretical study of the correlation between the ring current effect and the distance between a proton and the aromatic plane.[29]

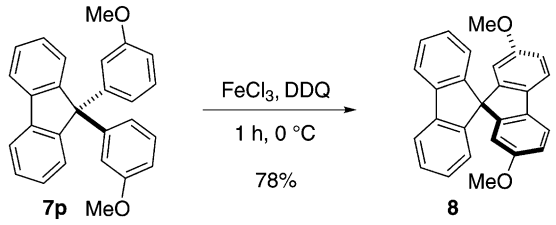
The synthetic method herein was also adopted to prepare 9,9-diarylfluorenes **7** (Table 3). Both electron-rich and electron-deficient haloarenes gave the corresponding products in good yields. 9,9-Di(3-anisyl)-fluorene (**7p**) was efficiently generated in a reaction with the ligand dppe in dioxane for a longer reaction time. It is noteworthy that a recently developed protocol enabled the conversion of **7p** into spirobifluorene **8** in good yield (Scheme 3).[30]

An attempt was made to synthesize **10** by the reaction of fluorene with excess 5,6-dichloroacenaphthene (**9**) (entry 4 in Table 3). Perhaps because of the steric effect, the reaction gave only 5-(9-fluorenyl)acenaphthene, which was formed through the mono-coupling reaction and subsequent dechlorination. The reaction of 6,12-dihydroindeno[1,2-*b*]fluorene (**11**) with excess 4-bromo-4-*n*-butylbenzene (**1q**) furnished 6,6,12,12-

Table 3. Multiarylations methylene-bridged arenes.[a]

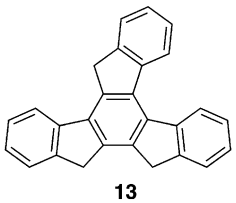
Entry	Ar–X (equiv.)	Conditions (amount)	Solvent	Time [days]	Product (isolated yield [%])
1	C_6H_5Cl (2.4)	**I** (4/8 mol%)	DMAc	0.5	 **7c** (75)
2	4-CF_3-C_6H_4Br (3.0)	**I** (4/8 mol%)	dioxane	0.5	**7j** (85)
3	3-OMe-C_6H_4Br (2.5)	**II** (5/10 mol%)	dioxane	3	**7p** (81)
4	  **9** (2.2)	**I** (6/12 mol%)	DMF	1	 **10** (0)[b]
5	 **11** 4-*n*-Bu-C_6H_4Br (6.0)	**II** (15/15 mol%)	dioxane	4	 **12** (58)[c]

[a] The reaction was conducted with fluorene or **11** (0.50 mmol), haloarene and Cs_2CO_3 (3 equiv.) in a thick-walled sealed tube at 130 °C. *Conditions **I**:* $Pd(OAc)_2/PCy_3{\cdot}HBF_4$. *Conditions **II**:* $Pd(OAc)_2$/dppe.
[b] An inseparable mixture of two rotamers of 5-(9-fluorenyl)acenaphthene was isolated (72%, *syn/anti* = 55/45).
[c] Cs_2CO_3 (8 equiv.) was used.



Scheme 3. Formation of spirobifluorene **8**.

tetraaryl-6,12-dihydroindeno[1,2-*b*]fluorene **12** in 58% yield as the sole product (entry 5 in Table 3). In this reaction, the use of dppe and dioxane reduced the amount of triaryl-substituted by-product. Unfortunately, isotruxene (**13**) and truxene (**14**) were not as reactive as indenofluorene **11** in multiarylation reactions.[31] The reaction did not give the corresponding hexaaryl-substituted arenes, but rather a mixture of complex products. Isotruxene (**13**) was easily prepared by palladium-catalyzed cyclization of 1,2,4-tris(2-chlorophenyl)-3,5,6-trimethylbenzene (see Supporting Information).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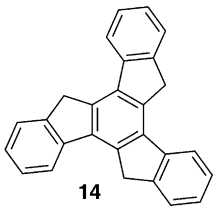
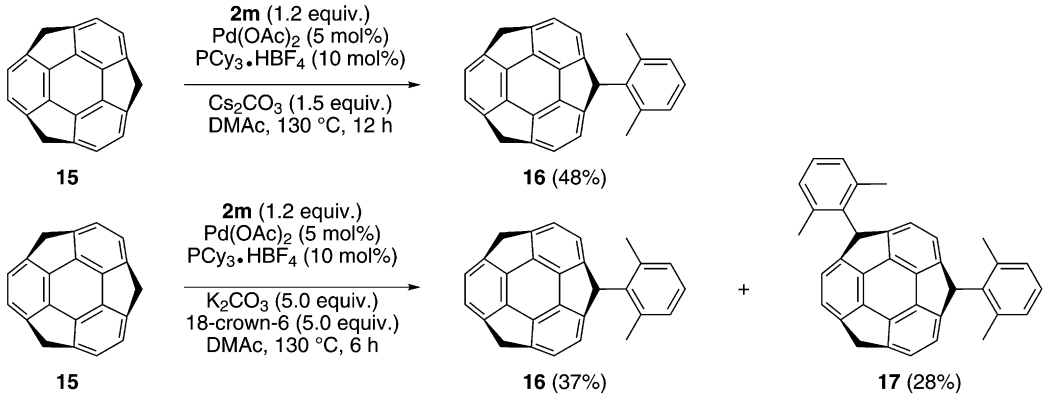

14

Sumanene (**15**) is an elementary subunit of buckminsterfullerene.[32] Its curvature[33] and bowl-to-bowl inversion barrier (*ca.* 20 kcal mol^{-1})[34] have been determined. Although the silylation, alkylation, and condensation through the anion generated at the benzylic positions have been reported,[33–35] the arylation has not been developed yet. Since aryl-substituted sumanenes provide the possibility for expansion of the backbone of sumanene (**15**),[36] our developed Pd-catalyzed arylation was applied to the coupling reaction between sumanene (**15**) and bromoxylene **2m** (Scheme 4). The desired xylylsumanene **16** was successfully obtained in 48% yield by employing the optimized conditions for the arylfluorene [$Pd(OAc)_2$ (5 mol%), $PCy_3{\cdot}HBF_4$ (10 mol%), Cs_2CO_3 (1.5 equiv.) in DMAc at 130 °C]. After screening the bases, a combination of K_2CO_3 (5.0 equiv.) and 18-crown-6 (5.0 equiv.) was found to give the dixylylsumanene **17** in 28% yield and **16** in 37% yield. Interestingly, the ^{1}H NMR of **16** shows two kinds of conformers of **16** in a 5:1 ratio. The conformers derive from the bowl-to-bowl inversion of the sumanene skeleton, where the xylyl group is directed to the *endo*-orientation or *exo*-orientation to the bowl structure (Figure 2). The ^{1}H NMR of **17** also shows one major set of signals accompanying minor signals. In this case, the configurations of two xylyl groups of **17** could be *endo-endo*, *exo-exo*, and *endo-exo*. While the *endo-endo* and *exo-exo* correspond to the interconvertible conformers through bowl-to-bowl inversion, the *endo-exo* conformer is a stereoisomer of the other two. The assignment of configurations of xylyl groups in **16** and **17** and more detailed investigations of their dynamics are now under investigation.



Scheme 4. Synthesis of xylylsumanenes.

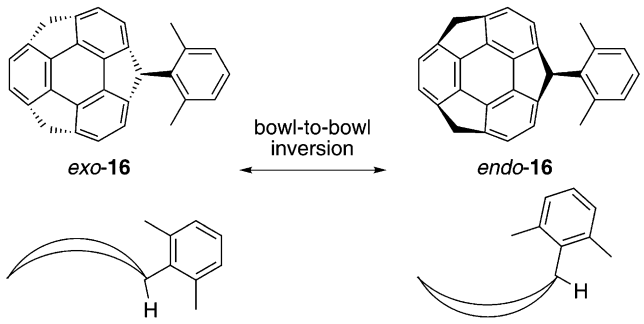


Figure 2. The bowl-to-bowl inversion of the sumanene skeleton.

Conclusions

This work has developed a simple and efficient procedure for the mono- and multiarylations of methylene-bridged arenes. Applications of our protocol to the construction of extended π-bowls and organic materials, as well as studies of their physical properties are currently underway.

Experimental Section

General Procedure for Synthesis of 9-Arylfluorenes (GP1)

A mixture of fluorene (0.50 mmol), haloarene (0.63 mmol), $Pd(OAc)_2$ (2.25 mg, 10.0 μmol), $PCy_3{\cdot}HBF_4$ (8.50 mg, 20.0 μmol), Cs_2CO_3 (247 mg, 0.75 mmol) and DMAc (2.5 mL) in a thick-walled Pyrex tube was purged with nitrogen for 5 min. The sealed tube was kept in an oil bath at 130 °C for 12 h. After cooling to room temperature, the solution was extracted with Et_2O or EA (2×10 mL) and washed with water. The organic phase was dried over $MgSO_4$ and filtered. The solvents of the filtrate were removed under reduced pressure. The residue was subjected to chromatography on silica gel. A crystal can be obtained by crystallization from CH_2Cl_2/CH_3OH.

General Procedure for Preparation of 9,9-Diarylfluorenes (GP2)

A mixture of fluorene (0.50 mmol), haloarene (1.20 mmol), $Pd(OAc)_2$ (4.48 mg, 20.0 μmol), $PCy_3{\cdot}HBF_4$ (14.7 mg, 40.0 μmol), Cs_2CO_3 (529 mg, 1.50 mmol) and DMAc (3.0 mL) in a thick-walled Pyrex tube was purged with nitrogen for 5 min. The sealed tube was kept in an oil bath at 130 °C for 12 h. After cooling to room temperature, the solution was extracted with EA (3×15 mL) and washed with water. The organic phase was dried over $MgSO_4$ and filtered. The solvents of the filtrate were removed under reduced pressure. The residue was subjected to chromatography on silica gel. A crystal can be obtained by crystallization from CH_2Cl_2/CH_3OH.

Procedure for the Arylation of Sumanene (15)

A mixture of sumanene **15** (20.0 mg, 0.0757 mmol), 2,6-dimethyl-1-bromobenzene (11 μL, 0.091 mmol), $Pd(OAc)_2$ (0.8 mg, 3.8 μmol), $PCy_3{\cdot}HBF_4$ (2.8 mg, 7.6 μmol), K_2CO_3 (78.5 mg, 0.379 mmol), 18-crown-6 (100.0 mg, 0.379 mmol) and DMAc (379 μL) in a thick-walled Pyrex tube was purged with nitrogen. The sealed tube was kept in an oil bath at 130 °C for 12 h. After cooling to room temperature, 1 M HCl solution (1 mL) was added and the solution was extracted with hexane/toluene (1:1, 3×5 mL) and washed with water. The organic phase was dried over Na_2SO_4 and filtered. The solvents of the filtrate are removed under reduced pressure. Purification by PTLC (*n*-hexane/dichloromethane = 7:3) then GPC gave **19** (yield: 10.3 mg, 37%) as a colorless solid, **20** (yield: 10.0 mg, 28%) as a colorless solid and recovered **15** (yield: 6.6 mg, 13%).

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