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Fluoradenes *via* palladium-catalyzed intramolecular arylation†

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A novel approach towards 7*b*-aryl-indeno[1,2,3-*jk*]fluorene based on a nitrogen-containing core is reported. The acid-promoted Friedel–Crafts reaction of 9-(2-bromophenyl)-9-fluorenol with carbazole, triphenylamine or triindole afforded 9-(2-bromophenyl)fluorenyl-carbazole, -triphenylamine and -triindole derivatives, which were subsequently converted to 7*b*-aryl-fluoradenes *via* palladium-catalyzed intramolecular C–H direct arylation as a key step.

Highly strained aromatic molecules such as fenestranes are theoretically interesting but experimentally challenging targets for synthetic organic chemists. It is worthwhile pursuing well-defined methods to synthesize highly strained molecules especially those bearing benzo nuclei fused across the bridgehead positions.[1] Fluoradene, namely 7*b*-*H*-indeno-[1,2,3-*jk*]fluorene (**a**)], is an example of highly acidic curved hydrocarbon with a bridgehead carbon shared by an indane and a fluorene, which can also be considered as a product of C–C bond opening of aromatic rings from the unknown hydrocarbon $C_{19}H_{10}$ (**b**) and is also a unique indenofluorene.[2] Only a few reports on fluoradene chemistry have been published because of their difficult synthesis.[3] The distinct *endo* and *exo* faces of **a** make it a suitable ligand to coordinate with metal centers to form sterically coordinated complexes.[4] However, the chemistry of 7*b*-substituted derivatives of fluoradene has seldom been explored and only two examples, 7*b*-triisopropylsilylfluoradene and 7*b*-(2,4-dinitrophenyl)fluoradene, have been reported, and these reports lack synthetic details.[5] Other aryl derivatives of fluoradene such as phenylfluoradene (**c**) and its derivatives, which could allow access to tetrabenzo[5.5.5.5]fenestrane (**d**), remain unknown (Fig. 1).

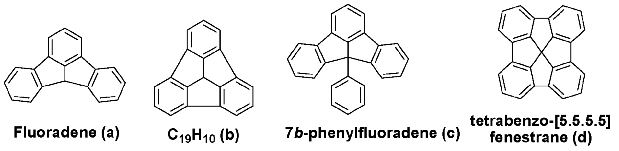
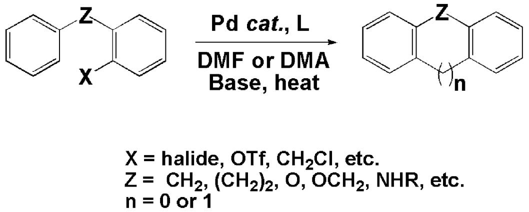


Fig. 1 Several strained polycyclic hydrocarbons.



Scheme 1 Palladium-catalyzed intramolecular arylation towards arenes and hetero-arenes.

Palladium-catalyzed direct C–H arylation of arenes is one of the simplest and most efficient methods for the synthesis of carbo- and hetero-cycles from aryl precursors (Scheme 1).[6] Generally this reaction is carried out with a palladium catalyst such as $Pd(OAc)_2$ or $Pd(PPh_3)_2Cl_2$ in polar solvents (DMF or DMA) with a base to trap HX. Several groups have conducted elegant studies on constructing interesting and/or strained poly- and hetero-arenes by using this methodology.[7]

As a continuation of the construction of polyarenes *via* palladium-catalyzed arylation,[7q] we investigated the arylation of 9-(2-bromoaryl)-9-arylfluorene, because it might undergo unconventional intramolecular arylation in the presence of catalytic palladium species to afford benzoannelated products. Considering the effect of substituents on the reactivity of arenes, nitrogen-containing activating groups are always *ortho–para* directors, so carbazole, triphenylamine, and triindole derivatives were employed. Such derivatives have been incorporated in fluorene-based derivatives to improve the hole injection and transport abilities and the resulting OLEDs show enhanced efficiency and stability.[8] Here, we wish to demonstrate the formation of structurally interesting compounds using palladium-catalyzed arylation as a prelude to the synthesis of more complex polycyclic aromatic hydrocarbons. The successful application of palladium-catalyzed arylation for the construction of highly strained 7*b*-arylfluoradene derivatives is reported.

9-(2-Bromophenyl)-9-fluorenol (**2**) was chosen as a key intermediate for the strategy described above because it has been used as a subunit to synthesize heterocycle-fused dispiro organic compounds.[9] **2** could easily be prepared by metal–halogen exchange of 2-bromo-iodobenzene with *i*PrMgBr at −40 °C or 1,2-dibromobenzene with BuLi at −120 °C and subsequently quenched with fluorenone following literature methods.[10] The synthetic route towards different fluoradenes is outlined in Scheme 2. Initially the reaction of **2** with different arenes or aryl ether was performed under acidic conditions.

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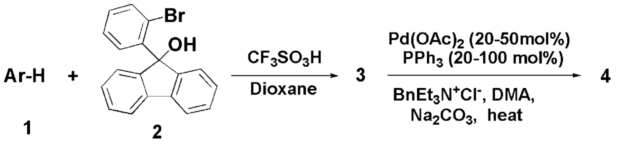
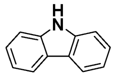
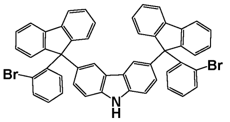
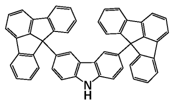
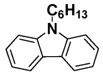
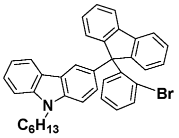
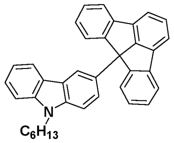
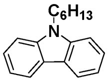
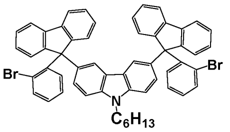
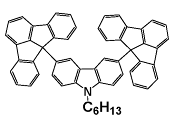
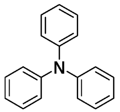
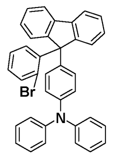
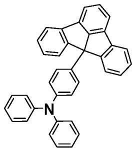
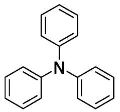
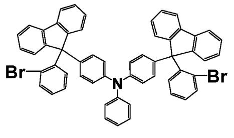
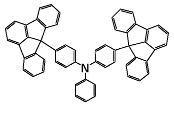
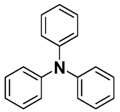
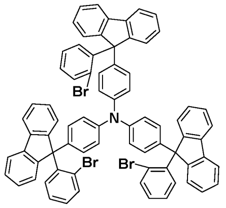
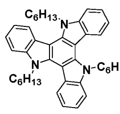
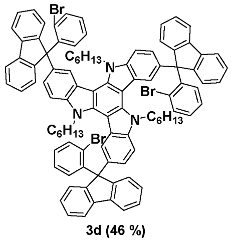
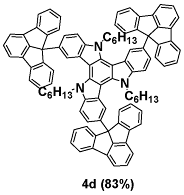


Scheme 2 Synthetic route to substituted fluoradenes.

Table 1 Synthetic conditions used to produce fluoradenes

Entry	Ar–H (**1**)	Product **3**	Product **4**
1	 1a	 3a (15%)	 4a (55 %)
2	 1b	 3ba (51 %)	 4ba (82 %)
3	 1b	 3bb (43 %)	 4bb (71 %)
4	 1c	 3ca (61 %)	 4ca (37 %)
5	 1c	 3cb (34 %)	 4cb (71 %)
6	 1c	 3cc (83 %)	**4cc** insoluble materials
7	 1d	 3d (46 %)	 4d (83%)

However, in most cases, it failed to afford target bromide, 9-(2-bromophenyl)fluorene was isolated instead. An acid-promoted Friedel–Crafts reaction[10] was then employed to react compound **2** with triphenylamine, carbazole, 9-hexylcarbazole, and 5,10,15-trihexyltriindole to afford **3a–3d** successfully. The initial reaction was conducted in a ratio of 1 : 2 (**1a** to **2**); however, the resulting yield was low (15%) and the solubility of **3a** is limited. Ring closure was then conducted using $Pd(OAc)_2/PPh_3/BnEt_3NCl/DMA/Na_2CO_3$ to form product **4a** (55%) (Table 1, entry 1). Surprisingly, the X-ray structure of **4a** revealed that C–H activation occurred at the C-1 position of the fluorenyl group. Although C–H activation of fluorene to form six-membered carbocycles and heterocycles has been reported several times,[7k,l] activation to form highly strained five-membered carbocycles related to aromatic compounds such as fluoradenes has never been reported.

To improve solubility, *N*-hexylcarbazole (**1b**) was then reacted with **2** in different ratios; monobromide **3ba** and dibromide **3bb** were isolated in moderate yield (51% and 43%, respectively) (entries 2 and 3). Ring closures of **3ba** and **3bb** under the conditions described for **4a** gave compounds **4ba** and **4bb** in excellent yield (82% and 71%). As for **1c**, the desired bromide intermediates **3ca**, **3cb** and **3cc** were isolated with yields of 61%, 34% and 83%, respectively, compounds **3ca** and **3cb** were successfully converted into **4ca** (37%) and **4cb** (71%). However in the case of **3cc**, an insoluble material **4cc** was obtained which might be crosslinked compounds or polymers. The insolubility of **4cc** prevented its characterization (entry 6). Compound **4d** was obtained by reaction of **2** with 5,10,15-trihexyl-triindole (**1d**), followed by ring closure of **3d** under the conditions described above with an overall yield of 38% for the two steps. Remarkably, the isolated yields of the C–H arylation steps are good to excellent (from 37% (**4ca**) to 83% (**4d**)). In the case of **4d**, the three C–H arylation steps occur with 94% each (entry 7).

The compounds described above were characterized by UV-vis and NMR spectroscopy, fluorimetry, mass spectrometry, and elemental analysis. The ^{13}C NMR reveal that the chemical shifts of bridge-head carbon appear between 65 ppm and 67 ppm. In addition, the structures of **4a**, **4ba**, **4bb**, **4ca**, **4cb** were confirmed by X-ray structure determination (Fig. 2) (see also ESI†). UV-Vis spectra of compounds **4a**, **4ba**, **4bb**, **4ca**, **4cb** and **4d** exhibited maxima between 270–340 nm, which were assigned to $\pi \rightarrow \pi^*$ transitions. The emission maxima of **4a**, **4ba**, **4bb**, **4ca** and **4cb** in solution appeared in the visible region at 388, 396, 446, 449 and 406 nm, respectively. In contrast, **4d** was not emissive, which might be caused by its triindole core.

The thermal properties of these compounds were investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). They all exhibited high thermal stabilities. The decomposition temperatures (T_d) with 5% weight loss under N_2 atmosphere of **4a**, **4ba**, **4bb**, **4ca**, **4cb** and **4d** ranged from 359 °C (**4ca**) to 458 °C (**4bb**). The DSC curves of the above compounds **4a**, **4ba**, **4bb**, **4ca**, **4cb** and **4d** showed obviously crystalline melting temperatures ranging from 208 °C (**4ba**) to 358 °C (**4a**). However, no melting peak for

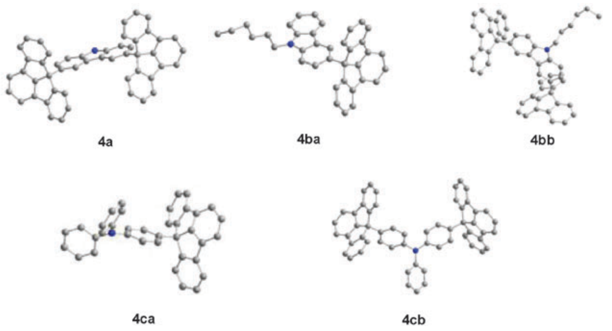


Fig. 2 Crystal structures of **4a**, **4ba**, **4bb**, **4ca** and **4cb**.

compound **4d** was detected under the same condition, which indicates that **4d** might have lower crystallized ability than **4a**, **4ba**, **4bb**, **4ca** and **4cb**.

In conclusion, the first 7*b*-aryl-indeno[1,2,3-*jk*]fluorenes containing carbazole, triphenylamine or triindole cores were successfully synthesized. This research demonstrates that palladium-catalyzed intramolecular C–H activation can be applied as an efficient and straightforward synthetic method for the formation of highly strained arenes using well-defined synthetic routes. The reaction proceeds readily using aryl bromides based on carbazole, triphenylamine and triindole functionalities. The ready construction of fluoradene derivatives should allow for the synthesis of more complex polycyclic aromatic hydrocarbons with highly strained structures. Studies are underway to establish the scope and generality of this strategy for the synthesis of more complex products.

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