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A Sc(OTf)$_3$ catalyzed dehydrogenative reaction of electron-rich (hetero)aryl nucleophiles with 9-aryl-fluoren-9-ols†

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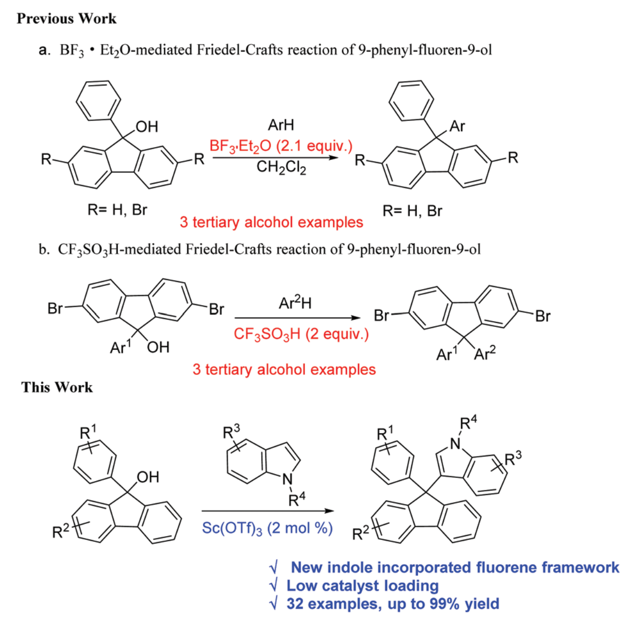
A highly efficient dehydrogenative reaction of a series of nucleophiles with 9-aryl-fluoren-9-ols has been realized by using only 2 mol% of Sc(OTf)$_3$ as a catalyst. The corresponding indole-containing 9,9-diarylfluorenes were obtained in up to 99% yield as well as other electron-rich (hetero)arene adducts. The protocol exhibits high selectivity, mild reaction conditions and good substrate compatibility (32 examples). This protocol is further highlighted by its applications in the construction of potential electroluminescent materials.

Introduction

Fluorene-based small molecules have been comprehensively used in organic electronics,[1] exhibiting a broad range of advantages compared to fluorene-based polymers,[2] such as high fluorescence quantum efficiency, high luminescent brightness and ease of purification.[3] Among fluorene-based small molecules, 9,9-diarylfluorenes especially have demonstrated significance in electroluminescent devices and other applications.[4] For instance, ter(9,9-diarylmethylfluorene) can be applied in optoelectronic materials due to high quantum efficiencies and carrier transport properties.[5] Furthermore, carbazole/fluorine hybrids with thermal and morphological stabilities play a crucial role as host materials for OLED construction.[6] In 2008, the elegant work of the Zhang group indicated that different substituents at the C9 and C2,7 positions influence the optical and thermal properties of 9,9-diarylfluorenes.[7] As a result, to improve the comprehensive optoelectronic performance, the main modification of fluorene-based small molecules is concentrated on the highly reactive C9 position.[8] In this vein, the dehydrogenative reaction of alcohol[9] is a promising route to polysubstituted fluorenes.[4a,10,11] For example, in 2006, the dehydrogenation coupling of 9-phenyl-fluoren-9-ol with electron-rich aromatic substrates was disclosed by Huang and co-workers in the presence of $BF_3{\cdot}Et_2O$ (Scheme 1a).[10b] The Wong group developed a triflic acid promoted dehydrogenative reaction to introduce 9,9-diaryl-2,7-dibromofluorenes (Scheme 1b).[3a] However, limited scope (only 3 alcohol derivatives) and excessive catalyst loading may impede their further applications in multiple fields of chemical science.

The functionalized indoles represent a significant class of aromatic heterocycles in natural products, agrochemicals and pharmaceuticals.[12] Moreover, indoles are extensively distributed in electroluminescent materials on account of their electron-donating properties.[13] Indoles with nucleophilic properties can serve as N-, C2- and C3-nucleophiles which have



Scheme 1 The routes for the synthesis of 9,9-diarylfluorenes.

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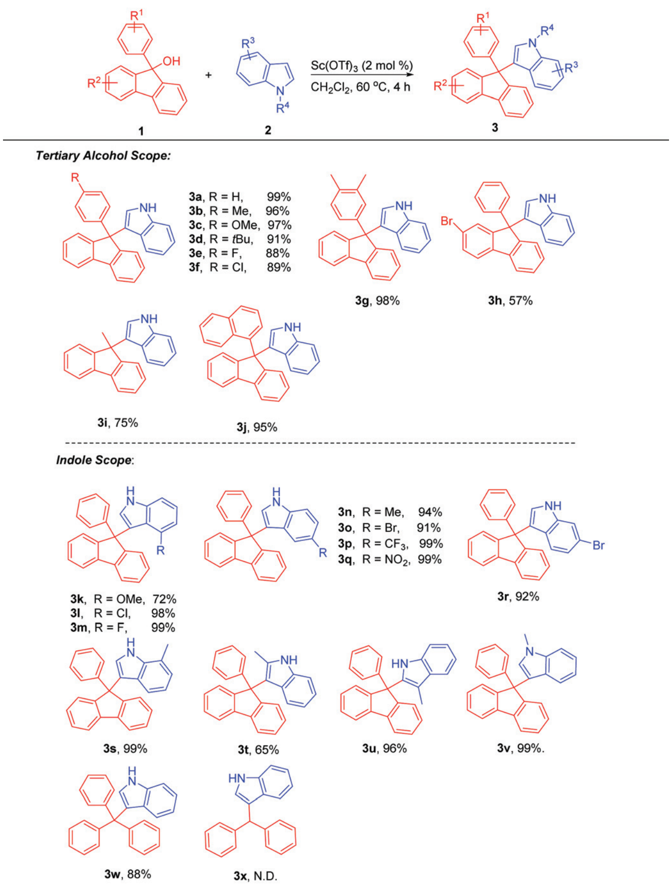
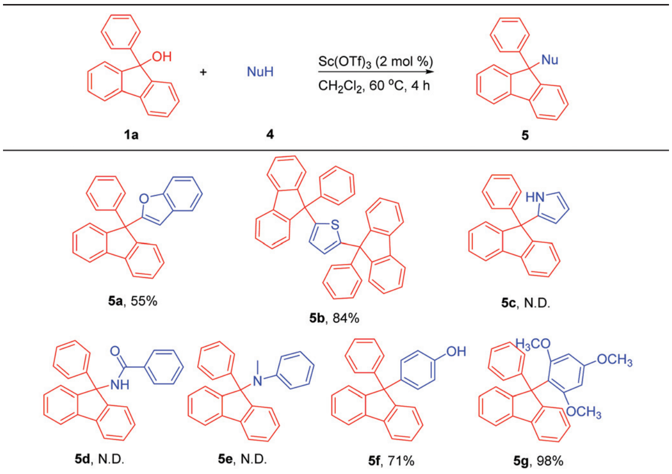
been widely researched, illustrating the diverse reactivity of indoles.[14] For example, the alkylation of indoles using tertiary alcohol has been widely reported before.[15] Meanwhile, scandium triflate, as a strong Lewis acid, is an important catalyst which aroused great attention.[16] Within the framework of our ongoing program committed to the development of rare earth chemistry[17] and the construction of a new fluorene framework,[18] we disclosed a direct dehydrogenative reaction of 9-phenyl-fluoren-9-ols with indole derivatives enabling multiple novel polysubstituted fluorenes. In addition, the practicability of this approach was further manifested in the synthesis of 2-pyrenyl-9,9-diarylfluorene, which has potential applications in the construction of organic photoelectric materials.

Table 1 Substrate scope[a]



[a] Reaction conditions: **1** (0.25 mmol), **2** (0.3 mmol), $Sc(OTf)_3$ (2 mol%) and CH_2Cl_2 (2 mL), at 60 °C. Isolated yield.

Table 2 Other nucleophiles examined[a]



[a] Reaction conditions: **1a** (0.25 mmol), **4** (0.3 mmol), $Sc(OTf)_3$ (2 mol%) and CH_2Cl_2 (2 mL), at 60 °C. Isolated yield.

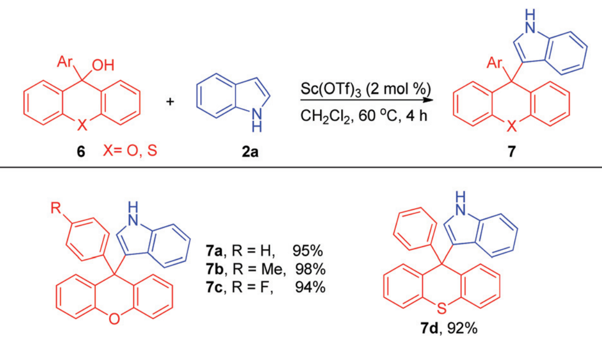
Results and discussion

After carefully evaluating the reaction condition parameters including catalyst, solvent, temperature and reaction time, we found the optimized conditions to be 2 mol% $Sc(OTf)_3$ CH_2Cl_2 as a solvent, 60 °C for 4 h (see the detailed discussion in Table S1†). With the optimized reaction conditions in hand, the scope of diverse 9-phenyl-fluoren-9-ols and indoles was scrutinized (Table 1). Firstly, a number of 9-phenyl-fluoren-9-ols **1** were reacted with indole **2a** and the corresponding products were produced in good to excellent yields (top of Table 1). Tertiary alcohols with electron-deficient or electron-rich aryls all afforded the corresponding products in high yields (**3a–3g**). The decrease of the yield was observed (57%) for fluorene with bromo in the framework (**3h**). Remarkably, 9-methyl-fluoren-9-ol gave **3i** in 75% yield. Steric hindrance exhibited negligible influence on the reactivity of tertiary alcohol (**3j**).

Next, the scope of the dehydrogenative coupling reactions was examined by employing various indoles with 9-phenyl-fluoren-9-ols (bottom of Table 1). Interrogation of indoles bearing a library of different position substitutions (OMe, Me, F, Cl, Br, CF_3, NO_2) suggested that electronic effects are inconsequential (**3k–3t**). It should be noted that the indoles bearing methyl performed well with a yield of 96% (**3u**). Moreover, *N*-methyl indole was also perfectly accommodated, affording **3v** in 99% yield. Notably, an appreciable yield (88%) was obtained when triphenylmethanol was employed (**3w**). However, diphenylmethanol failed to provide the target product, due to the decreased reactivity of the *in situ* generated carbocation (**3x**). Overall, the successful incorporation of the indole skeleton into fluorene is remarkable in consideration of the significant importance of heterocyclic moieties as pharmacophores.

To further exemplify the synthetic utility of this methodology, we were interested in the reactivity of other potential nucleophiles with 9-phenyl-fluoren-9-ol (Table 2). Product **5a** was smoothly afforded in 55% yield. Notably, the efficiency of our catalytic system was further highlighted by the formation of **5b** in 84% yield, where two molecules of **1a** were incorporated into thiophene. Unfortunately, amine compounds such as benzamide (**4d**) and *N*-methylaniline (**4e**) failed to react with 9-phenyl-fluoren-9-ol probably on account of the strong coordinating effect. To our delight, the desired targets **5f** and **5g** were

Table 3 The scope of xanthen-9-ols[a]



[a] Reaction conditions: **6** (0.25 mmol), **2a** (0.3 mmol), $Sc(OTf)_3$ (2 mol%) and CH_2Cl_2 (2 mL), at 60 °C. Isolated yield.

obtained in 71% and 98% yields respectively when phenol and trimethoxybenzene were employed.

We next turned to evaluate the scope with respect to xanthen-9-ols (Table 3). The multifaceted applications of the xanthene skeleton in perovskite solar cells and dyes[19] render xanthene a heavily pursued synthetic target. Xanthen-9-ols including 9-phenyl-9-hydroxythioxanthene performed smoothly delivering the corresponding products in high yields (**7a–7d**), which further demonstrated the compatibility of the current catalytic system.

Furthermore, a range of prepared products with different functional groups were tested to explore the corresponding optical properties. The absorption spectra and fluorescence spectra of the selected products in DCM (0.1 mM) are shown in Fig. 1. The absorption maxima ($\lambda_{\max}^{\text{abs}}$) of these selected products peaked around 260 nm (Fig. 1a). Their molar extinction coefficient increased slightly with the increase of the electron-donating ability on the indole ring (Table 4). Also, the fluorescence quantum yields (Φ_{PL}) of selected products measured in dichloromethane using 9,10-diphenylanthracene in cyclohexane as a standard are listed in Table 4. The Φ_{PL} values of indole with the electron-withdrawing group (**3p**, **3m**) are higher than that with the electron-donating group (**3k**). On the other hand, the electronic effect on the benzene ring has negligible influence on the emission peaks of substrates. However, the increasing electron-withdrawing ability of the substituent on the indole ring led to a gradual blue-shift of the emission maxima. Also, compared to other heterocycle substituted 9,9-diarylfluorenes like **5a** and **5b**, the emission peaks of indole substituted 9,9-diarylfluorenes were red-shifted.

Subsequently, a yield of 37% was obtained when the reaction for the preparation of **3h** was scaled up to 5 mmol. Then, an elemental conversion of product **3h** was performed by employing Suzuki coupling, which produced the final product **8** in 83% yield (Scheme 2).

The product **8** was soluble in dichloromethane and the optical spectra of **8** in dichloromethane are shown in Fig. 2. As we can see from the absorption spectrum of product **8**, compound **8** exhibited a strong π–π* absorption with $\lambda_{\max}$ at 354 nm ($\varepsilon = 3.8 \times 10^4\ M^{-1}\ cm^{-1}$) and an emission peak centered at 404 nm (Fig. 2). In particular, the fluorescence quantum yield of compound **8** in CH_2Cl_2 was found to be 0.74 using quinine sulfate ($\Phi = 0.55$ in 0.1 M H_2SO_4) as a calibration

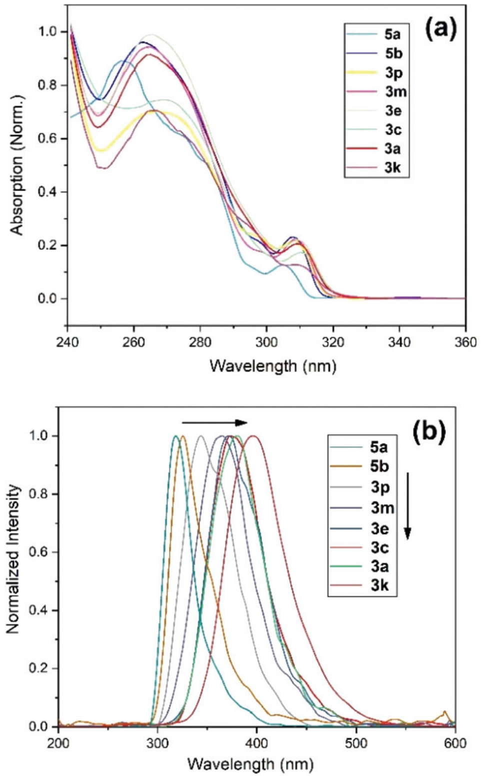
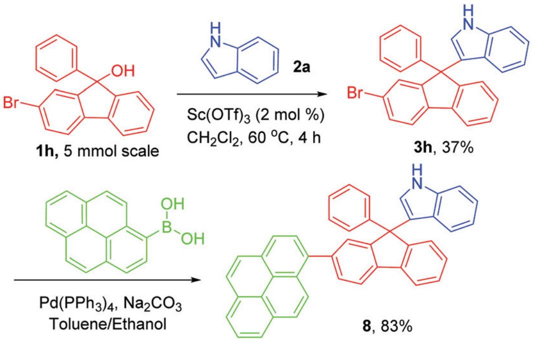


Fig. 1 (a) Absorption spectra of selected products in DCM; (b) emission spectra of selected products in DCM.

Table 4 Optical properties of selected products

	5a	5b	3p	3m	3e	3c	3a	3k
$\varepsilon \times 10^4\ (M^{-1}\ cm^{-1})^a$	3.09	1.68	1.59	1.79	1.68	1.74	2.06	2.82
$\Phi^{a,b}$	0.12	0.06	0.22	0.13	0.10	0.14	0.14	0.04

[a] Measured in CH_2Cl_2. [b] Using 9,10-diphenylanthracene ($\Phi_F = 0.90$) in cyclohexane as a standard.



Scheme 2 Further product transformation and application.

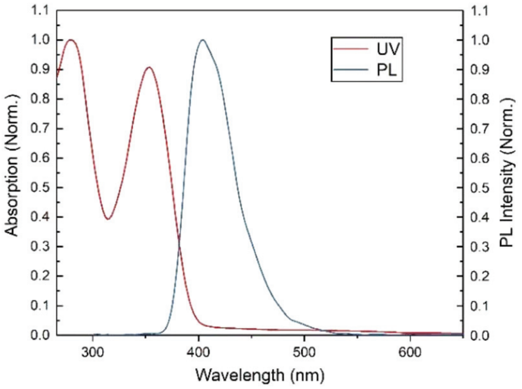


Fig. 2 UV and PL spectra of product **8** in CH_2Cl_2 solution.

standard (see the details in the ESI†). Besides, the thermal property of product **8** was examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The glass transition temperature (T_g) of product **8** was found to be 100 °C while the decomposition temperature (T_d) was up to 379 °C (Fig. S1†), which indicated excellent thermal and morphological stability of **8**.

In addition, the UV and PL spectra of pyrene and compound **8** were also tested and compared, indicating the importance of conjugated structures between pyrene and fluorene units (Fig. S2†).

Conclusions

In conclusion, a library of indole-containing 9,9-diarylfluorenes and other electron-rich (hetero)arene adducts were synthesized in the presence of scandium triflate. This new strategy exhibited high yield, mild reaction conditions and good substrate compatibility. Preliminary exploration of the optical property and morphological stability of some products and new pyrenyl substituted 9,9-diarylfluorene with nonplanar conformations may likely foreshadow their further applications in electroluminescent materials such as OLED.

Conflicts of interest

There are no conflicts to declare.

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