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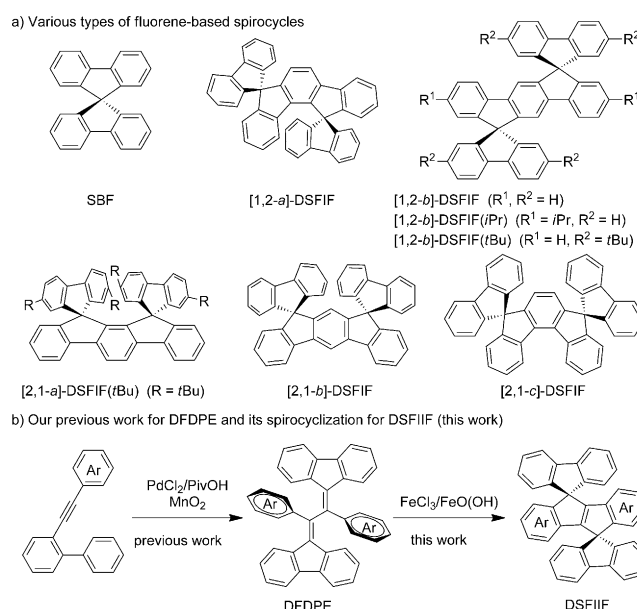
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FeCl₃-Mediated Oxidative Spirocyclization of Difluorenylidene Diarylethanes Leading to Dispiro[fluorene-9,5'-indeno[2,1-*a*]indene-10',9''-fluorene]s

Jian Zhao, Zhanqiang Xu, Kazuaki Oniwa, Naoki Asao, Yoshinori Yamamoto, and Tienan Jin*

Abstract: A novel FeCl₃-mediated oxidative spirocyclization for construction of a new class of di-spirolinked π -conjugated molecules, dispiro[fluorene-9,5'-indeno[2,1-*a*]indene-10',9''-fluorene]s (DSFIIFs), has been reported. The combination of FeCl₃ with FeO(OH) triggered an unprecedented double one-electron oxidation of difluorenylidene diarylethanes to afford the corresponding dispirocycles in high yields. The highest fluorescence quantum yield was up to 0.94 in solution. This protocol is also applicable to the synthesis of the non-spirolinked dihydroindenoindenes.

Fluorene-based π -conjugated spirocycles have attracted attention as important optoelectronic materials in various fields of organic electronics because of their unique structural features.^[1–14] As common features of π -conjugated spirocycles, the high rigidity of spiro molecules efficiently minimizes the electronic interactions between the π -systems and offers high solubility, high thermal and morphological stability, and intense fluorescence properties, without significantly changing their absorption and fluorescence spectra compared with the corresponding non-spirolinked parent compounds. In this context, many structural modifications have been made based on the spirobifluorene (SBF) unit in attempts to study the hole-transporting and light-emitting performances in various electronics (Scheme 1a).^[1–10] In addition, several positional isomers of di-spirofluorene indenofluorenes (DSFIIFs), combining both di-hydroindenofluorene and fluorene units, have also been reported for high-performance organic light-emitting diodes (OLEDs).^[11–16] For example, the [1,2-*a*], [1,2-*b*], and [2,1-*c*] isomers were used as hosts in blue and green phosphorescent OLEDs, the [2,1-*b*] and [1,2-*a*] isomers were used as efficient blue fluorophores, and the [2,1-*a*] isomer was used as an emitting layer for an excimer-based OLED (Scheme 1a). Taking into consideration the prominent role of the spirolinked π -systems in organic electronics, the discovery of a novel class of spirocycles is highly



Scheme 1. Reported fluorene-based spirocycles and our novel method for constructing a new class of dispirocycle DSFIIFs.

challenging from the perspective of the structural diversity and the future of organic electronics.

Very recently, we developed an interesting synthetic approach for constructing 9,9-bifluorenylidene (9,9'BF) and 1,2-di(9*H*-fluorene-9-ylidene)-1,2-diphenylethane (DFDPE; Scheme 1b) units from the corresponding bis(biaryl) alkynes or biaryl alkynes through a novel palladium-catalyzed dual C(sp²)-H bond activation.^[17] The facile synthetic method and the structurally intriguing DFDPE, having all sp²-hybridized carbon atoms, led us to explore a new C-H oxidation reaction for constructing new π -conjugated fused systems. Recently, the 5,10-dihydro-[2,1-*a*]-indenoindene (DII) core, having aromatic 14 π electrons, has been reported as a new class of chromophores in OLEDs to show high hole mobility and high sky-blue fluorescence.^[18–21] However, to the best of our knowledge, the di-spirolinked indenofluorenes, such as dispiro[fluorene-9,5'-indeno[2,1-*a*]indene-10',9''-fluorene] (DSFIIF; Scheme 1b), have not yet been reported, presumably owing to synthetic difficulties. Herein, we report a novel and highly efficient FeCl₃-mediated oxidative spirocyclization of DFDPEs towards the synthesis of a new class of di-spirolinked π -systems, that is, DSFIIFs (Scheme 1b).

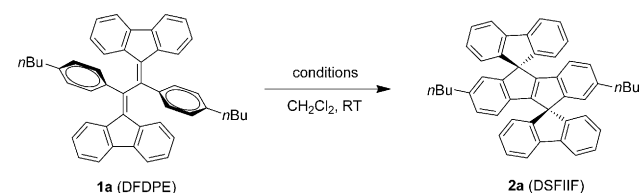
As stated in Scheme 1b, DFDPEs were synthesized efficiently through our previously reported palladium-catalyzed C-H activation of biaryl alkynes.^[17] In the presence of

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PdCl_2 (10 mol %), PivOH (10 mol %), and MnO_2 (3 equiv), various biaryl alkynes afforded the corresponding DFDPEs having a variety of functional groups on either the diphenyl or difluorenylidene moiety in good to high yields (see the Supporting Information). With these structurally intriguing molecules in hand, we examined many different oxidants and acids using the DFDPE **1a** as a substrate in dichloromethane at room temperature (Table 1). Interestingly, when the Lewis-

Table 1: Investigation of reaction conditions of spirocyclization of DFDPE **1a**.^[a]



Entry	Oxidant or acid	Additive	t [h]	Yield [%] ^[b]	
				2a	1a
1	FeCl_3	—	1	58	0
2	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	—	2	78	5
3	$\text{K}_3[\text{Fe}(\text{CN})_6]$	—	12	0	99
4	MoCl_5	—	12	0	0
5	CuCl_2	—	20	14	60
6	I_2	—	12	12	36
7 ^[c]	DDQ	$\text{CF}_3\text{CO}_2\text{H}$	12	75	0
8	AlCl_3	—	12	0	0
9	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	Fe_2O_3	24	99	0
10 ^[d]	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	$\text{FeO}(\text{OH})$	12	99 ^[e]	0
11 ^[d]	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	K_2CO_3 ^[f]	24	26	73

[a] Reaction conditions: **1a** (0.1 mmol), acid or oxidant (3 equiv), additive, CH_2Cl_2 (0.05 M), under dark conditions at room temperature.

[b] Both yields were determined by ^1H NMR spectroscopy using CH_2Br_2 as an internal standard. [c] DDQ (2 equiv) and $\text{CF}_3\text{CO}_2\text{H}$ (5 equiv) were used. [d] $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.5 equiv) and Fe_2O_3 (0.5 equiv) or $\text{FeO}(\text{OH})$ (1 equiv) were used. [e] Yield of isolated product is shown after silica gel chromatography. [f] K_2CO_3 (4 equiv) was used.

acidic oxidant of anhydrous FeCl_3 (3 equiv) was used, a novel dispirocyclic (**2a**) was formed in 58% yield along with decomposition of **1a** (entry 1). The structure of **2a** was confirmed unambiguously by X-ray crystallography analysis (Figure 1). In the crystal structure, the central indeno[2,1-*a*]-indene core is perfectly flat, and is nearly perpendicular to the

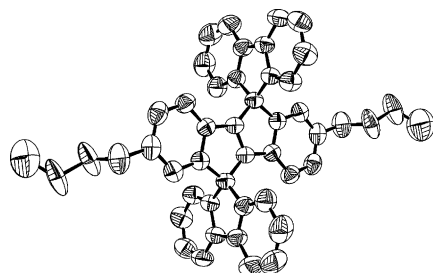


Figure 1. ORTEP drawing of the dispirocyclic **2a**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.^[25]

two parallel two fluorene moieties having a dihedral angle of 89.98° . $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ proved to be more effective for achieving a higher yield of **2a** (entry 2). The non-acidic $\text{K}_3[\text{Fe}(\text{CN})_6]$ oxidant was ineffective (entry 3). The strong acidic oxidant of MoCl_5 resulted in complete decomposition of **1a** (entry 4). The reaction in the presence of other oxidants, such as CuCl_2 and I_2 , afforded **2a** in very poor yields (entries 5 and 6). The classical oxidant systems of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and $\text{CF}_3\text{CO}_2\text{H}$ (TFA) produced **2a** in a reasonable yield of 75% with partial decomposition of **1a** (entry 7), and the use of either DDQ or TFA alone did not promote the present spirocyclization. It was worth noting that the reaction with the non-oxidizing Lewis acid AlCl_3 led to decomposition of **1a** (entry 8). The distinct reactivity difference between FeCl_3 and AlCl_3 implies that the present spirocyclization seems to undergo a well-known one-electron oxidation.^[22] After screening various additives, **2a** was achieved in an excellent 99% yield when $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.5 equiv) was combined with either Fe_2O_3 (0.5 equiv) or $\text{FeO}(\text{OH})$ (1 equiv); the combination with $\text{FeO}(\text{OH})$ was more reactive (entries 9 and 10). In contrast, the use of bases, such as K_2CO_3 suppressed the effective spirocyclization (entry 11). We assumed that the effect of ferric oxide should be to regenerate the active FeCl_3 oxidant by the reaction with HCl generated in situ. It was noted that although $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ could serve as the catalyst in this reaction, the catalytic reproducibility was not satisfactory. Consequently, the most effective oxidant systems of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.5 equiv) and $\text{FeO}(\text{OH})$ (1 equiv) were chosen as optimal reaction conditions for investigating the substrate scope of various DFDPEs.

A variety of DFDPEs (**1**) having versatile functional groups were investigated under the optimized reaction conditions (Table 2). It was found that the electronic property of the phenyl ring significantly affected the reactivity of **1**. The reactions with **1a** and **1b**, having an electron-donating *n*-butyl and *tert*-butyl group, respectively, on the phenyl ring proceeded smoothly at room temperature to give the corresponding dispirocyclics **2a** and **2b** in nearly quantitative yields. However, the reaction with **1c**, having a strong electron-donating methoxy group, required a higher temperature of 80°C , thus affording the corresponding product **2c** in 95% yield. Interestingly, **1d** with an electron-donating functional group, also underwent the present spirocyclization at room temperature to give the highly π -extended dispirocyclic **2d** in 95% yield. Both the unsubstituted **1e** and **1f** were active at 40°C , thus affording the corresponding dispirocyclics **2e** and **2f** in high yields within 12 hours, without being influenced by the protonated or deuterated phenyl group. The presence of the electron-donating groups on the fluorenyl moiety did not affect the reactivity of the DFDPEs. For example, **1g** and **1h**, having four methyl and four *tert*-butyl groups, respectively, on the fluorenyl moieties underwent the present spirocyclization at 40°C , thus leading to the formation of the dispirocyclics **2g** and **2h**, respectively, in high yields. We found that the introduction of the electron-withdrawing groups, such as an ester (**1i**), CF_3 (**1j**), or Br (**1k** and **1l**), to the phenyl moiety of DFDPEs lowered the reaction efficiency at low temperatures, while the reaction at the elevated temperature of 80°C gave

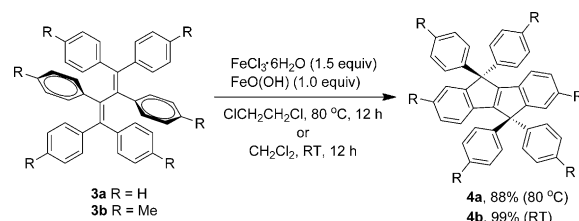
Table 2: FeCl₃-mediated spirocyclization of various DFDPEs (**1**).^[a]

Entry	1	2
1		
2	1a , R = <i>n</i> Bu	2a , 99 % (RT)
3	1b , R = <i>t</i> Bu	2b , 98 % (RT)
4	1c , R = OMe	2c , 95 % (80 °C)
5		
6	1d	2d , 95 % (RT)
7		
8	1e , R = H	2e , 95 % (40 °C)
9		
10	1f , R = D	2f , 90 % (40 °C)
11		
12	1g , R = Me	2g , 97 % (40 °C)
13		
14	1h , R = <i>t</i> Bu	2h , 99 % (40 °C)
15		
16	1i , R ¹ = CO ₂ Et, R ² = H	2i , 99 % (80 °C)
17		
18	1j , R ¹ = CF ₃ , R ² = H	2j , 82 % (80 °C)
19		
20	1k , R ¹ = Br, R ² = H	2k , 99 % (80 °C)
21		
22	1l , R ¹ = Br, R ² = Cl	2l , 97 % (80 °C)

[a] Standard reaction conditions: **1** (0.1 mmol), FeCl₃·6H₂O (1.5 equiv), FeO(OH) (1.0 equiv), under dark conditions in CH₂Cl₂ at either RT or 40 °C, or in ClCH₂CH₂Cl at 80 °C. Yields are those of the isolated products.

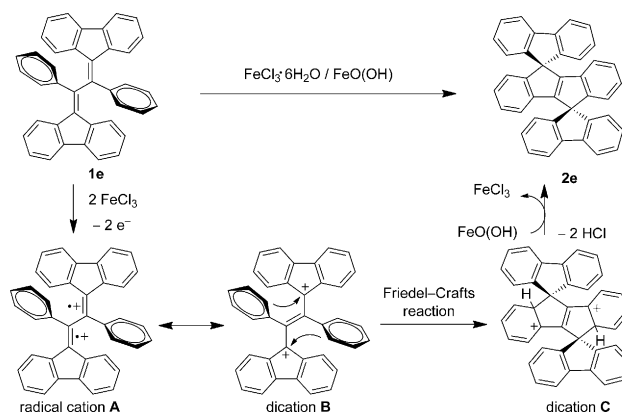
rise to the corresponding dispirocycles **2h–l** in good to excellent yields.

The present FeCl₃-mediated conditions have also proven effective for the non-fluorenyl-incorporated buta-1,3-dienes (Scheme 2). For example, the reaction of the multisubstituted diene **3a** led to the formation of the tetraphenyl-substituted 5,10-dihydroindeno[2,1-*a*]indene (DII) **4a** in 88 % yield at 80 °C, and was synthesized previously by multistep methods in low yields.^[18,19] Similarly, the reaction of the multisubstituted diene **3b**, having electron-donating *p*-tolyl groups, reacted at room temperature to give the corresponding product **4b** in 99 % yield.


Scheme 2. Synthesis of 5,10-dihydroindeno[2,1-*a*]indene.

Recently it has become clear that in the most oxidative aromatic couplings (Scholl type reaction) mediated by one-electron oxidants, such as FeCl₃ or DDQ, the oxidation could preferentially occur at the most electron-rich position to form radical cations.^[22] Interestingly, the density functional theory (DFT) computational studies of the frontier molecular orbitals revealed that the highest occupied molecular orbitals (HOMOs) of the substrates **1a** and **3a** are more localized on the C=C bonds of the conjugated diene moiety rather than on the phenyl and fluorenyl moieties, thus indicating the highest electron density is on the diene moiety (see Figure S1 in the Supporting Information). These studies suggested that in the present spirocyclization, the C=C bond of the diene in DFDPEs should be oxidized preferably to form the radical cation species. In addition, the intermolecular competing reactions of the protonated **1e** and the deuterated **1f** under the standard reaction conditions for 2 hours, revealed that the kinetic isotope effect (KIE) was 1.14 (see Scheme S1), thus indicating that the C–H bond cleavage of the phenyl group was not the rate-determining step.

On the basis of the distinct activity of FeCl₃, electronic effects of substrates, and electron density distribution, we proposed a mechanism involving a one-electron oxidation reaction as shown in Scheme 3. FeCl₃ induces double one-electron oxidations of the two more-electron-rich C=C bonds of the diene moiety in **1e** to give the radical cation species **A**, which can exist as the dication intermediate **B**. It should be noted that the analogous dication having an I₃[−] counteranion has been isolated and characterized by X-ray crystallography.^[23] Subsequently, the double Friedel–Crafts reactions take place to form an arenium dication (**C**), which undergoes the rapid deprotonation by chloride anions to give the dispiro-


Scheme 3. Proposed reaction mechanism.

cycle **2e** and HCl. The DFT calculation shows that the HOMO of **B** is mainly localized in the central stilbene moiety, thus indicating the electron-donating nature of the phenyl rings, which are favorable for reacting with the cation electrophiles (see Figure S1). Either the FeO(OH) or Fe₂O₃ additive may react with HCl to supply the fresh FeCl₃ oxidant, thus suppressing the partial decomposition of **1e** by HCl, and it is crucial for achieving high yields of the dispirocycles.

The optical and electrochemical properties of the selected dispirocycles **2** are summarized in Table 3 and Figure 2 (see also Figures S2 and S3). The UV-vis absorption spectra of the

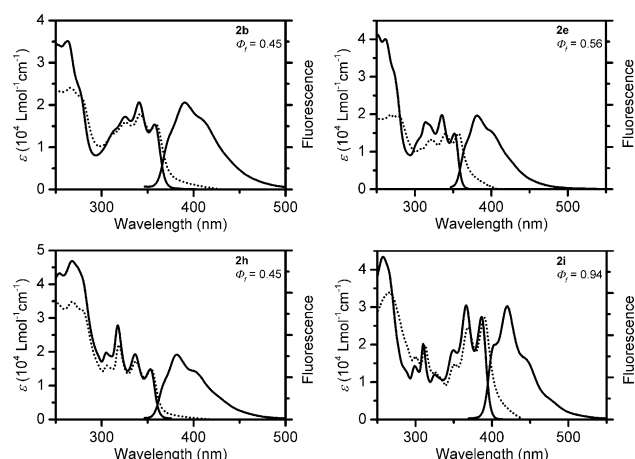


Figure 2. UV-vis spectra (left; solid line) and fluorescence spectra (right; solid line) of **2b**, **2e**, **2h**, and **2i** in chloroform solution. Normalized UV-vis absorption of spin-coated thin films on the quartz plates (dashed line) at room temperature. Φ_f = quantum yield.

nonsubstituted (**2e**) and *t*Bu-substituted (**2b** and **2h**) DSFIIFs exhibit bands of the central indeno[2,1-*a*]indene moiety in the range of $\lambda = 300$ –360 nm in chloroform, and they are very similar to the [1,2-*b*]DSFIFs having similar substituents at the central dihydroindeno[1,2-*b*]fluorene moiety as reported by Poriel, Rault-Berthelot et al. (Scheme 1a).^[15,24] Thin-film absorption maxima of **2b**, **2e**, and **2h**, recorded on spin-coated films on the quartz plates, are slightly red-shifted compared to the corresponding solution absorption maxima, thus implying very weak intermolecular interactions in solid state. The photoluminescence spectra of the present DSFIIFs show Stock shifts of 15–17 nm, which are larger than that of [1,2-*b*]DSFIF analogues (2–3 nm),^[15,24] thus indicating the

reduced structural rigidity of the former. DSFIIFs exhibit the absolute fluorescence quantum yields of 0.45 for **2b**, 0.56 for **2e**, and 0.45 for **2h**, and are lower than the reported results of [1,2-*b*]DSFIFs (Scheme 1a, 0.62–0.70). It is worth noting that the DSFIIF **2i**, having two electron-withdrawing ester groups at the central indeno[2,1-*a*]indene moiety, exhibits a red-shifted absorption and emission maxima compared to other DSFIIF derivatives. Interestingly, **2i** is highly fluorescent with the absolute quantum yield of 0.94 in CHCl₃, thus implying the distinct substituent effect of the ester group on the π -conjugated indeno[2,1-*a*]indene moiety. The HOMO energy levels of DSFIIFs were calculated from the oxidation potentials by cyclic voltammetry (CV) in CH₂Cl₂, and the lowest unoccupied molecular orbital (LUMO) energy levels were estimated from the optical bandgap and HOMOs. The HOMO energy levels of **2b**, having two electron-donating *tert*-butyl groups at the indeno[2,1-*a*]indene moiety is –5.49 eV, similar to the reported [2,1-*a*]DSFIF(*t*Bu) (–5.48 eV, Scheme 1a).^[24] The nonsubstituted **2e** (–5.68 eV) and **2h** (–5.62 eV), having four *tert*-butyl substituents at the fluorene moieties, exhibited slightly lower HOMOs than that of **2b**, and are similar to the reported values (–5.76 eV, –5.66 eV, 5.61 eV) of the three [1,2-*b*]DSFIF isomers (Scheme 1a).^[15,24] The LUMO energy levels of **2b**, **2e**, and **2h**, estimated to be in the range of –2.10 to –2.23 eV, are very near to the reported DSFIF series. **2i** shows both low HOMO and LUMO energy levels of –5.95 eV and –2.80 eV with a narrow energy bandgap of 3.15 eV resulting from the two electron-withdrawing ester groups at the indeno[2,1-*a*]indene moiety.

In conclusion, we have developed a novel and highly efficient FeCl₃-mediated oxidative spirocyclization of 1,2-di(9*H*-fluoren-9-ylidene)-1,2-diphenylethanes under mild reaction conditions. A new class of di-spirolinked indeno[2,1-*a*]indene π -conjugated systems having a wide range of functional groups have been synthesized in very high yields with the highest fluorescence quantum yield of 0.94 for the ester-substituted dispirocycle. The results led to the conclusion that the present mechanism involved two one-electron oxidations and a dication-induced Friedel–Crafts spirocyclization pathway. This protocol also can be applicable for the construction of non-spirolinked dihydroindenoindenes. The present method provides not only a novel and valuable spirocycle synthetic tool, but also a new type of spirolinked π -conjugated system which is expected to be highly applicable in the field of optoelectronics.

Table 3: Selected optical and electrochemical properties of DSFIIFs

DSFIIF	λ_{abs} [nm] ^[a]	λ_{abs} [nm] ^[b]	λ_{em} (λ_{exc}) [nm] ^[c]	Φ_f ^[d]	E^{ox} [V] ^[e]	ΔE^{opt} [eV] ^[f]	HOMO [eV] ^[g]	LUMO [eV] ^[h]
2b	358, 341, 326, 263	359	390 (340)	0.45	0.91	–3.39	–5.49	–2.10
2e	352, 336, 315, 261	356	382 (320)	0.56	1.11	–3.45	–5.68	–2.23
2h	353, 336, 318, 305, 268, 254	353	382 (340)	0.45	1.04	–3.44	–5.62	–2.18
2i	386, 366, 350, 325, 310, 299	390	420 (340)	0.94	1.29	–3.15	–5.95	–2.80

[a] UV-vis absorptions were measured in chloroform. [b] UV-vis absorptions were measured using as-spun thin films on the quartz plates.

[c] Fluorescence maxima were measured in chloroform. [d] Absolute fluorescence quantum yield (Φ_f) was measured by a photon-counting method using an integration sphere. [e] Oxidation potential (vs Ag/AgCl) was measured by cyclic voltammetry in CH₂Cl₂. [f] Optical bandgap (ΔE^{opt}) was estimated from the contact between the UV-vis absorption and the fluorescence spectra. [g] HOMO was calculated from the oxidation potential.

[h] LUMO was calculated from the HOMO energy and the optical bandgap.

Experimental Section

General procedure of FeCl_3 -mediated oxidative spirocyclization of **1a**. **1a** (0.1 mmol, 62 mg), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.15 mmol, 40 mg), and $\text{FeO}(\text{OH})$ (0.1 mmol, 9 mg) were added to an anhydrous CH_2Cl_2 (2 mL, 0.05 M) solution. The reaction vial was capped. The reaction mixture was stirred vigorously at room temperature for 12 h. After monitoring by TLC, the reaction mixture was passed through a short silica (Merck) pad using CH_2Cl_2 /hexanes as an eluent. After concentration, the residue was purified by silica gel (Merck) chromatography using a mixture of hexanes and CH_2Cl_2 [10:1 to 3:1 (v/v)] as the eluent to afford the product **2a** as a white solid (99%, 61 mg).

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Keywords: conjugation · fluorescence · materials science · oxidation · spirocompounds

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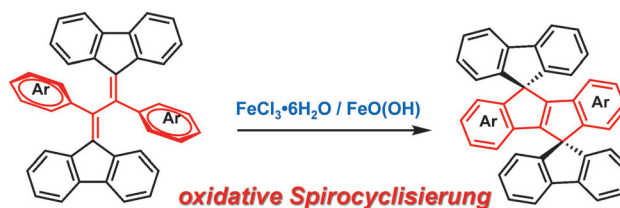
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Konjugation

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FeCl₃-Mediated Oxidative
Spirocyclization of Difluorenylidene
Diarylethanes Leading to
Dispiro[fluorene-9,5'-indeno[2,1-
a]indene-10',9''-fluorene]s



Dispiro-Gerüste: Die Titelreaktion ebnet
den Weg zu einer neuen Klasse von π -
konjugierten Verbindungen. Die höchste
Fluoreszenzquantenausbeute unter

diesen Dispiro[fluoren-9,5'-indeno[2,1-
a]inden-10',9''-fluorenen] in Lösung
betrug 0.94.