# Color Tuning and Highly Efficient Blue Emitters of Finite Diphenylamino-Containing Oligo(arylenevinylene) Derivatives Using Fluoro Substituents** 

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#### Abstract

New fluoro derivatives of $\mathrm{Ph}_{2} \mathrm{~N}$-containing ( Ph : phenyl) oligo(arylenevinylene) derivatives are prepared by using double Heck-coupling reactions or Horner-Wadsworth-Emmons reactions. These oligomers are highly fluorescent (fluorescence quantum yields $\Phi=0.93-0.68$ ) with emissions in a broad wavelength region (448-579 nm ), depending on the position of the fluoro substituents. The highest occupied and lowest unoccupied molecular orbital (HOMO-LUMO) energy levels of these oligomers are characterized by electrochemistry and UV spectroscopy. The effects of the fluoro substituents on the energy levels are rationalized with HOMO-LUMO simulations. In a classical organic light emitting diode (OLED), one representative (5a) shows a remarkable external quantum efficiency value ( $\eta_{\mathrm{ext}}=4.87 \%$ ) at $J=20 \mathrm{~mA} \mathrm{~cm}^{-2}$; the maximum brightness at 10.2 V is $22506 \mathrm{~cd} \mathrm{~m}^{-2}$ ( $\lambda=458 \mathrm{~nm}$; Commission Internationale de l'Eclairage (CIE) coordinates $x=0.14, y=0.14$ ) with a full width at half-maximum of 54 nm , demonstrating the superiority of these fluoro-containing oligomers in OLED devices.


## 1. Introduction

trans-4-Diphenylaminostilbene is a highly fluorescent molecule as a result of the unusual electronic effect of the $N$-phenyl substituents. ${ }^{[1,2]}$ The introduction of an $N$-phenyl substituent onto a stilbene framework produces a nearly planar groundstate geometry around the nitrogen atom, a red shift of the absorption and fluorescence spectra, and a less distorted structure with a larger charge-transfer character for the fluorescent excited states. ${ }^{[3,4]}$ Consequently, these $N$-phenylstilbene derivatives are in general highly fluorescent because of a significant diminution of the quantum yields for cis-trans photoisomerization. Because of their outstanding fluorescence quantum yields, these molecules have served for various applications including organic light-emitting diodes (OLEDs) as well as two- and three-photon absorption fluorophores. ${ }^{[5-8]}$ Scheme 1 shows representative molecules $\mathbf{1}$ and $\mathbf{3}(\mathrm{R}=\mathrm{H})$ that have been employed as blue emitters ( $\lambda=470-480 \mathrm{~nm}$ ) in OLED devices. ${ }^{[6 a, \mathrm{~d}]}$ We attempted to introduce cyano groups at the central aryl groups, as indicated by compounds 2 and $4(\mathrm{R}=\mathrm{CN})$, to obtain long-wavelength emissions. ${ }^{[6 a]}$ This approach is based the formation on an extensive conjugation network between the donor and acceptor functionalities. The emission wavelengths of

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Scheme 1. Structures of representative $\mathrm{Ph}_{2} \mathrm{~N}$-containing ( Ph : phenyl) oligo(arylenevinylene) derivatives.
these cyano-containing species depend strongly on the positions of their cyano groups; for example, 2a emits greenyellow light ( $\lambda=541 \mathrm{~nm}$ ) whereas its regioisomer $\mathbf{2 b}$ radiates in the blue region of the spectrum $(\lambda=472 \mathrm{~nm})$. We rationalize such a varied behavior with the effects of extended conjugation. ${ }^{[9]}$ Despite successful color tuning, there are several drawbacks associated with cyano-containing derivatives 2 and 4 that hamper their applications in OLEDs: ${ }^{[6 a]}$ (i) small fluorescence quantum yields ( $0.32-0.41$ ) for most yellow and orange emitters, (ii) poor durability because of the vulnerable cyano functionality, and (iii) poor volatility for vacuum sublimation. OLED devices of blue-emitter $\mathbf{2 b}$ show only a moderate performance (Commission Internationale de l'Eclairage
(CIE) coordinates $x=0.15, y=0.18$ ) with a maximum external quantum efficiency ( $\eta_{\text {ext }}$ ) of $2.12 \%$, power and luminance efficiencies of $1.33 \mathrm{~lm} \mathrm{~W}^{-1}$ and $3.14 \mathrm{~cd} \mathrm{~A}^{-1}$, respectively, and a maximum brightness $\left(L_{\max }\right)$ of $11190 \mathrm{~cd} \mathrm{~m}^{-2}(12 \mathrm{~V})$. In the present work, we sought to achieve the color tuning of these $\mathrm{Ph}_{2} \mathrm{~N}$-containing ( Ph : phenyl) oligo(arylenevinylene)s by using chemically inert fluoro substituents. According to several precedents, introduction of a fluoro substituent onto a chromophore not only leads to color tuning ${ }^{[10]}$ but also improves the efficiency of phosphoresecent or fluorescent emission, ${ }^{[11]}$ in addition to facilitating vacuum sublimation.

## 2. Results and Discussion

### 2.1. Synthesis of Fluorine-Containing Oligomers

Scheme 2 shows our targeted fluorine-containing molecules $\mathbf{5 a}-\mathbf{h}$ and $\mathbf{6 a - d}$; the fluorine positions were determined on the basis of the location of highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs). Most of these arylenevinylene oligomers were prepared within five steps from commercially available reagents by employing routine operations, and their synthetic protocols are depicted in Schemes $3(5 a-\mathbf{h})$ and $4(\mathbf{6 a - d})$. As shown in Scheme 3 (reaction 1), we first prepared diphenylamine species 7a and 7b via Buchwald-Hartwig coupling ${ }^{[12]}$ reactions


Scheme 2. Structures of targeted fluoro-substituted oligo(arylenevinylene) derivatives.
using $\mathrm{Pd}_{2}(\mathrm{dba})_{3}, t$-BuONa, and the dppf ligand (dba: dibenzylideneacetone, $t$-Bu: tert-butyl, dppf: bis(diphenylphospho)ferrocene). These two fluorine-containing ligands were subsequently transformed into 4-(diphenylamino)benzaldehydes 7c and 7 d via a second coupling reaction using $\mathrm{Pd}(\mathrm{OAc})_{2} /$ $(t-\mathrm{Bu})_{3} \mathrm{P} / t-\mathrm{BuONa}$ (Ac: acetate). The final Horner-Wads-worth-Emmons reaction ${ }^{[13]}$ produced the desired bis(diphenylamino) arylenevinylenes 5a and $\mathbf{5 b}$ exclusively in $E$-form ${ }^{[14]}$ ( $>96 \%$ ). The procedures for the preparation of target compounds 5c-e, for which we used fluoro-substituted 4-bromobenzaldehydes $\mathbf{7 g}-\mathbf{i}$ as building blocks, are depicted in Scheme 3, reaction 2. These three intermediates were conveniently prepared through either bromination of 4-bromotoluene reagents with $N$-bromosuccinimide (NBS) or formylation of 1,4-dibromobenzenes. The aldehyde groups of species $\mathbf{7 g}-\mathbf{i}$ were further masked, and ultimately efficiently transformed into the desired oligomers $5 \mathrm{c}-\mathbf{e}$ via coupling with diphenylamine followed by olefination with bisphosphate species 8 . Reactions 3 and 4 (Scheme 3) show the procedures for preparation of oligomers $\mathbf{5 f} \mathbf{- h}$ with fluoro substituents at the central biphenyl groups. 4-Bromobenzaldehydes $\mathbf{7 i}$ and $7 \mathbf{j}$ were first converted to benzyl bromides, and subsequently to phosphates $\mathbf{7 r}$ and $7 \mathbf{s}$. Olefination of these phosphates with 4 -aminobenzaldehyde afforded 4-diphenylamino-stilbenes $7 \mathbf{t}$ and $\mathbf{7 u}$ smoothly. A $\mathrm{Ni}(\mathrm{COD})_{2}$-mediated (COD: 1,5-cyclooctadiene) coupling reaction ${ }^{[15]}$ of species $7 \mathbf{t}$ and $7 \mathbf{u}$ delivered the desired arylenevinylene species $\mathbf{5 g}$ and $\mathbf{5 h}$ in $52 \%$ and $43 \%$ yields, respectively. The remaining fluorine-containing oligomer $\mathbf{5 f}$ was prepared according to a conventional four-step procedure starting from 2-fluoro-4-bromotoluene (Scheme 3, Reaction 4); the key step is the olefination of bisphophate species 7w with 4-(diphenylamino)benzaldehyde. Synthetic methods for $\mathrm{Ph}_{2} \mathrm{~N}$-containing (arylenevinylene) compounds $\mathbf{6 a - d}$ in another class are described in Scheme 4. The key phosphates 8ac were prepared easily from the benzyl bromide $7 \mathbf{f}$ or benzaldehydes $\mathbf{7 i}$ and $\mathbf{7 j}$ using a conventional transformation protocol: benzaldehyde $\rightarrow$ benzyl bromide $\rightarrow$ benzyl phosphate. These phosphates were used to prepare 4,4'-dibromostibenes 8d-f via olefination with 4 -bromobenzaldehydes $\mathbf{7 h}-\mathbf{j}$. A final Pd-catalyzed double-Heck olefination ${ }^{[16]}$ of these species with 4-diphenylaminostyrene delivered the desired arylenevinylene oligomers $6 \mathbf{6}-\mathbf{c}$ in exclusive $E$-configuration with yields in the range of $50-79 \%$. A similar coupling reaction of species $\mathbf{8 f}$ with 4 -(biscyclohexylamino)styrene gave compound $\mathbf{6 d}$ in $42 \%$ yield.

### 2.2. Photophysical Properties

Figures 1 and 2 show the UV-vis and photoluminescence (PL) absorption spectra of representative compounds $\mathbf{5 a}, \mathbf{5 b}$, $\mathbf{5 d}, \mathbf{5 e}, \mathbf{5 f}, \mathbf{5 h}$, and $\mathbf{6 a}-\mathbf{d}$, respectively. The PL absorption bands of their corresponding unsubstituted complexes $\mathbf{1}$ and $\mathbf{3}$ (Scheme 1, reaction 2) appear at 480 and 510 nm , respectively. According to the data given in Table 1 and Figures 1 and 2, the introduction of fluoro substituents onto the various benzene groups of these fluorophores has either a hypsochromic or bathochromic effect on their fluorescent emissions. For example, species 5a and 5b, bearing 4-fluoro and 2,4-difluoro groups
(1)


X = Y = F (7b, 63\%)
$X=F, Y=H(7 c, 88 \%)$
$X=Y=F(7 d, 83 \%)$
(2)






$X=F, Y=H(7 k, 97 \%)$
$X=F, Y=H(70,99 \%)$
$\mathrm{X}=\mathrm{H}, \mathrm{Y}=\mathrm{F}(7 \mathrm{I}, 99 \%)$
$X=H, Y=F(7 p, 99 \%)$
$X=Y=F(7 m, 99 \%)$
$X=Y=F(7 q, 99 \%)$
(3)


$$
\hat{X}=\mathrm{H}, \mathrm{Y}=\mathrm{F}(7 \mathrm{~s}, 81 \%)
$$



$X=F, Y=H(7 t, 73 \%)$
$X=H, Y=F(7 u, 75 \%)$
(4)


Scheme 3. Synthetic protocol for $\mathrm{Ph}_{2} \mathrm{~N}$-containing oligo(arylenevinylene)s 5a-h. Conditions: (a) $\mathrm{Pd}_{2}(\mathrm{dba})_{3}$ ( $2 \mathrm{~mol} \%$ ), DPPF ( $4 \mathrm{~mol} \%$ ), $t$ - BuONa ( 1.1 eq ), toluene, $110^{\circ} \mathrm{C}, 12 \mathrm{~h}$; (b) $\mathrm{Pd}(\mathrm{OAc})_{2}(2 \mathrm{~mol} \%), \mathrm{P}(t-\mathrm{Bu})_{3}(4 \mathrm{~mol} \%)$, toluene, $110^{\circ} \mathrm{C}, 12 \mathrm{~h}$; (c) 1 N HCl , acetone; (d) $t$-BuONa ( 2.2 eq ), THF , 24 h ; (e) NBS (1 eq), BPO (1\%), $\mathrm{CCl}_{4}$, reflux, 5 h ; (f) $\mathrm{NaHCO}_{3}(9 \mathrm{eq}), \mathrm{DMSO}, 70^{\circ} \mathrm{C}, 1 \mathrm{~h}$; (g) n-BuLi ( 1 eq ), ethyl formate, diethyl ether, $-78^{\circ} \mathrm{C}$ to room temperature; (h) PTSA (5 \%), ethylene glycol, benzene, reflux, 24 h ; (i) NaBH 4 ( 1.5 eq ), methanol; (j) $\mathrm{PBr}_{3}, \mathrm{CH}_{2} \mathrm{Cl} \mathrm{C}_{2}$; (k) $\mathrm{P}(\mathrm{OEt}){ }_{3}, 150{ }^{\circ} \mathrm{C}, 12 \mathrm{~h}$; (l) $\mathrm{Ni}(C O D)_{2}(1.1 \mathrm{eq}), \mathrm{DMF},. 40^{\circ} \mathrm{C}, 16 \mathrm{~h}$. See the Experimental section for full details.

(a)
$X=Z=H, Y=F(7 h) \quad X=Z=H, Y=F(8 a)$
$X=Y=F, Z=H(7 i) \quad X=Y=F, Z=H(8 b)$ $X=Y=Z=F(7 j) \quad X=Y=Z=F(8 c)$


$X=Z=H, Y=F(8 d, 88 \%)$
$X=Y=F, Z=H(8 e, 83 \%)$
$X=Y=Z=F(8 f, 79 \%)$

Scheme 4. Synthetic protocol of $\mathrm{Ph}_{2} \mathrm{~N}$-containing oligo(arylenevinylene) 6a-d. Conditions: (a) $t$-BuONa, THF, 24 h ; (b) $\mathrm{Pd}(\mathrm{OAc})_{2}$ ( $4 \mathrm{mmol} \%$ ), $\mathrm{PPh}_{4} \mathrm{Br}$ ( $20 \mathrm{mmol} \%$ ), NaOAc (5 eq.), DMF, $100^{\circ} \mathrm{C}, 16 \mathrm{~h}$. See the Experimental section for full details.
at the outer diphenylamino groups, show emissions at 462 and 448 nm with hypsochromic shifts of nearly 18 and 32 nm , respectively. The fluoro groups at the central aminobenzene group, as in species $\mathbf{5 c}$ and $\mathbf{5 d}$, produce similar hypsochromic effects but the shifts are smaller, ca. $9-17 \mathrm{~nm}$. In contrast, species $\mathbf{5 f}-\mathbf{h}$, bearing fluorine groups at the inner biphenyl group, show emissions at $505-527 \mathrm{~nm}$; red-shifted ca. $25-47 \mathrm{~nm}$ relative to the unsubstituted species $\mathbf{1}$. According to this trend, we prepared species 6a-d with fluoro groups at the inner stilbene moieties to achieve emissions at longer wavelengths. These four fluorophores show emissions at 523-579 nm, giving bathochromic shifts of $13-69 \mathrm{~nm}$. On the basis of these color-tuning effects, we reasonably expect that the HOMOs of structures $\mathbf{1}$ and $\mathbf{3}$ are located mainly on the outer triphenylamine groups, whereas the LUMOs reside on the inner biphenyl and stilbene moieties.


Figure 1. a,b) UV-vis (a) and PL (b) spectra of fluoro-substituted oligo(arylenevinylene) derivatives $\mathbf{5 a}, \mathbf{b}, \mathbf{5 d} \mathbf{- f}$, and $\mathbf{5 h}$.

One notable feature associated with these fluorine-containing species is that their fluorescence emission wavelengths can be tuned by fluoro substituents while maintaining a high fluorescence quantum efficiency. ${ }^{[10,11]}$ The quantum yields of 5a-h and 6a-d in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution at $25^{\circ} \mathrm{C}$ are given in Table 1; the corresponding values for unsubstituted species $\mathbf{1}$ and $\mathbf{3}$ are 0.86 and 0.84 , respectively. Outstanding quantum yields are found for the blue emitters 5a-e ( $\Phi=0.91-0.81, \lambda=448-471 \mathrm{~nm}$ ), blue-green emitters $\mathbf{5 f}-\mathbf{h}$ and $6 \mathbf{6} \quad(\Phi=0.91-0.93, \quad \lambda=505-527 \mathrm{~nm})$, yellow emitter $\mathbf{6 b}$ $(\Phi=0.95, \lambda=555 \mathrm{~nm})$, and orange emitters $\mathbf{6 c}$ and $\mathbf{6 d}$ ( $\Phi=0.68-0.72, \quad \lambda=568-579 \mathrm{~nm}$ ). 4-Diphenylaminostilbenes generally have quantum yields in solution about ten times those of their dialkylamino analogues. ${ }^{[1 a]}$ The fluorescence efficiency of bis(cyclohexyl)amine-containing species 6d is attributed to its planar geometry around the bis-chelated nitrogen atom, which retards the photochemically induced cistrans stilbene isomerization because of a less distorted structure in the fluorescent excited states. The enhancing effects of fluoro substituents on emission quantum yields are considered to arise from an altered molecular packing and a small $\mathrm{C}-\mathrm{F}$ vibrational frequency. ${ }^{[17,18]}$


Figure 2. a,b) UV-vis (a) and PL (b) spectra of fluoro-substituted oligo(arylenevinylene) derivatives 6a-d.

### 2.3. Electrochemical Data and Energy Gaps

Table 1 shows electrochemical data obtained through cyclic voltammetry (CV) measurements using $\mathrm{Bu}_{4} \mathrm{NPF}_{6}(0.1 \mathrm{~m}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ) and $\mathrm{Bu}_{4} \mathrm{NClO}_{4}(0.1 \mathrm{~m}$ in tetrahydrofuran (THF)) as supporting electrolytes in anodic oxidation and cathodic reduction, respectively. ${ }^{[6 a]}$ Compounds 5a-h and 6a-d show quasireversible, or two quasireversible, anodic redox couples, which are closely overlapped within the conditions $-1.60<V<+1.80 \mathrm{~V}$. This process corresponds to the removal of electrons from the diphenylamino groups. No reduction behavior was observed for these fluorine-containing compounds. Figure 3 shows CV curves for representative compounds 5d and $\mathbf{6 c}$. The HOMO and LUMO energy levels of species $\mathbf{5 a - h}$ and 6a-d, obtained from the oxidation potentials and UV absorption measurements, are shown in Table 1 and Figure 4.

Table 1. Photophysical and electrochemical data of species $\mathbf{5 a - 5 h}$ and $\mathbf{6 a}$ 6d.

| Compound | $\begin{gathered} \text { Abs } \lambda_{\text {max }}[\mathrm{a}] \\ (\mathrm{nm}) \end{gathered}$ | PL $\lambda_{\text {max }}$ (nm) | $F_{f}$ | oxid $E_{1 / 2}$ <br> (V) | HOMO <br> (eV) | Bandgap <br> (eV) | LUMO <br> (eV) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 5a | 296(67569) | 462 | 0.91 | 1.26 | 5.66 | 2.93 | 2.73 |
|  | 393(176129) |  |  |  |  |  |  |
| 5b | 292(30657) | 448 | 0.83 | 1.19 | 5.59 | 2.88 | 2.71 |
|  | 383(132310) |  |  | 1.45 |  |  |  |
| 5c | 294(71162) | 471 | 0.83 | 1.12 | 5.52 | 2.80 | 2.72 |
|  | 386(152645) |  |  | 1.36 |  |  |  |
| 5d | 295 (66758) | 469 | 0.82 | 1.11 | 5.51 | 2.79 | 2.72 |
|  | 394(149709) |  |  | 1.37 |  |  |  |
| 5 e | 298 (56308) | 463 | 0.81 | 1.21 | 5.61 | 2.89 | 2.72 |
|  | 396(146774) |  |  | 1.48 |  |  |  |
| 5 f | 302(93534) | 505 | 0.93 | 1.01 | 5.41 | 2.65 | 2.76 |
|  | 406(182013) |  |  | 1.22 |  |  |  |
| 5g | 301 (108319) | 509 | 0.91 | 1.02 | 5.42 | 2.61 | 2.81 |
|  | 406(176129) |  |  |  |  |  |  |
| 5h | 301 (19415) | 527 | 0.92 | 1.03 | 5.43 | 2.57 | 2.86 |
|  | 416(179065) |  |  |  |  |  |  |
| 6a | 304(70393) | 523 | 0.92 | 1.01 | 5.41 | 2.59 | 2.82 |
|  | 424(178854) |  |  |  |  |  |  |
| 6b | 305 (87101) | 555 | 0.95 | 1.02 | 5.42 | 2.49 | 2.93 |
|  | 435(189022) |  |  | 1.16 |  |  |  |
| 6c | 331 (48578) | 573 | 0.68 | 1.02 | 5.42 | 2.42 | 3.00 |
|  | 443 (97683) |  |  | 1.19 |  |  |  |
| 6d | 327 (42310) | 579 | 0.72 | 1.04 | 5.44 | 2.39 | 3.05 |
|  | 447(111212) |  |  |  |  |  |  |

[a] Values in parentheses represent the molar extinction coefficients, expressed in $\mathrm{m}^{-1} \mathrm{~cm}^{-1}$. Data were obtained from $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solutions.


Figure 3. CV curves of fluoro-substituted oligo(arylenevinylene)s $5 \mathbf{d}$ and $\mathbf{6 c}$.

To rationalize the trends of the energy gaps of these fluorosubstituted chromophores, we performed a theoretical simulation of the HOMO and LUMO of compound $\mathbf{5 c}$ by using its X-ray crystallographic data. The resulting HOMO-LUMO maps of compound $\mathbf{5 c}$ and its ORTEP (Oak Ridge Thermal Ellipsoid Program) drawing appear in Figure 5, which reveals that its HOMO is located mainly on the two outer aminophenyl groups, but partly on the central aminophenyl moiety, whereas the LUMO is located primarily on the inner biphenyl group. For species 5a-e, introduction of one or two fluoro groups at the outer and center aminophenyl groups leads to a decreased energy level of their HOMOs, but has little effect on


Figure 4. Energy levels of $\mathbf{5 a} \mathbf{- h}, \mathbf{6 a - d}$, and unsubstituted species $\mathbf{1}$ and $\mathbf{3}$.
their LUMO levels. These results rationalize the hypsochromic effects of the fluoro substituents of species $\mathbf{5 a - c}$ and $\mathbf{5 d}, \mathbf{e}$ relative to parent species $\mathbf{1}$. Compounds $\mathbf{5 f} \mathbf{- h}$, bearing fluoro-substituents, have decreasing energy levels in their LUMOs and the same HOMO levels relative to their unsubstituted species 3. This trend can be rationalized by considering the presence of an electron-withdrawing fluoro substituent at the inner diphenyl group. The HOMO-LUMO gaps of species $\mathbf{6 a}$ and $\mathbf{6 b}$ follow the same trend as for $\mathbf{5 f} \mathbf{- h}$, because their fluoro substituents are located on the inner stilbene moiety.

### 2.4. Electroluminescence Properties

The parent species $\mathbf{1}$ and $\mathbf{3}$ show fluorescence emissions at 480 and 510 nm , respectively. Their fluoro derivatives 5a-h and 6a-d show emission wavelengths in a wide range ( $448-579 \mathrm{~nm}$ ) because of the hypso- and bachochromic effects. Our interest lies in deep-blue emitters ( $\lambda=440-470 \mathrm{~nm}$ ), because few efficient emitters have been reported for both fluorescent and phosphorescent emission. ${ }^{[19,20]}$ We selected compounds 5a, 5d, and $\mathbf{5 e}$ for electroluminescence measurements because of their large quantum yields ( $\Phi=0.91-0.81$ ) and suitable emission wavelengths. A solid film ( 30 nm ) was prepared through thermal sublimation with $3 \%$ of $\mathbf{5 a}$ embedded in various host materials. Because the quantum yield of 5 a embedded in 9,10-di(2-naphthyl)anthracene (ADN) ( $\Phi \approx 89 \%$ ) was found to


Figure 5. Crystal structure of 5 c (top), and a theoretical simulation of its HOMO and LUMO.
$\mathbf{5 a}, \mathbf{5 d}$, and $\mathbf{5 e}$ relative to that of a similar device using only AND as the emitting layer (see Fig. 7). The corresponding CIE coordinates are $x=0.14, y=0.14$ for 5a, $x=0.12, y=0.21$ for $\mathbf{5 d}$, and $x=0.16$, $y=0.25$ for $\mathbf{5 e}$.

Current density-voltage-luminance ( $J-V-L$ ) measurements were performed under ambient conditions. Figure 8 shows the $J-V-L$ characteristics of the devices, according to which the driving voltage for the device based on 5a at a given current density is less than that for devices based on 5d and 5e. For example, the voltages at $J=20 \mathrm{~mA} \mathrm{~cm}^{-2}$ for devices $\mathbf{5 a}, \mathbf{5 d}$, and $\mathbf{5 e}$ are $5.7,8.3$, and 7.5 V , respectively. Figure 7 shows the external quantum effi-ciency-current density characteristics of the devices, showing that the external quantum efficiencies decrease slowly with increasing current densities. Compounds 5a and 5e show promising EL performances in view of the maximum brightnesses and external quantum efficiencies of OLEDs based on these molecules. The maximum brightness of 5a and 5b are $22506 \mathrm{~cd} \mathrm{~m}^{-2}$ and $21423 \mathrm{~cd} \mathrm{~m}^{-2}$, respectively. The external quantum efficiency $\left(\eta_{\text {ext }}\right)$ of $\mathbf{5 a}$ was $4.48 \%$ at $J=20 \mathrm{mAcm}^{-2}$, with a luminance efficiency and a power efficiency of $5.47 \mathrm{~cd} \mathrm{~A}^{-1}$ and $3.00 \mathrm{~lm}^{-1}$, respectively. As shown in Figure 7, the $\eta_{\text {ext }}$ gradually decreased to $3.92 \%$ at $J=400 \mathrm{~mA} \mathrm{~cm}^{-2}$, for which the luminance efficiency and power efficiency were $4.79 \mathrm{~cd} \mathrm{~A}^{-1}$ and $1.63 \mathrm{~lm} \mathrm{~W}{ }^{-1}$, respectively. In comparison, the $\eta_{\text {ext }}$ value of species 5e was $3.47 \%$ at $J=20 \mathrm{~mA} \mathrm{~cm}{ }^{-2}$, with a luminance efficiency and power efficiency of $6.78 \mathrm{~cd} \mathrm{~A}^{-1}$ and $2.84 \mathrm{~lm} \mathrm{~W}^{-1}$, respectively. The EL data shown in Table 2, particularly for 5a, are excellent compared to recently reported data on blue fluorophores, ${ }^{[19]}$ most of which show a maximum $\eta_{\mathrm{ext}}$ of ca. 3-4 \% with CIE co-
be $30 \%$ greater than that of $\mathbf{5 a}$ embedded in 4,4'-bis(9-carba-zolyl)-biphenyl (CBP, $\Phi \approx 68 \%$ ), ${ }^{[21]}$ ADN served as the host material in this work. OLEDs were fabricated by high-vacuum $\left(5 \times 10^{-6}\right.$ Torr, 1 Torr $\left.=1.333 \times 10^{2} \mathrm{~Pa}\right)$ thermal evaporation onto precleaned glass substrates. The devices consisted of indium tin oxide (ITO)/copper phthalocyanine ( $\mathrm{CuPc}, 30 \mathrm{~nm}$ )/ 4,4'-bis( $N$-naphthylphenylamino)biphenyl (NPB, 40 nm )/dopant ( $3 \%$ ) in ADN ( 30 nm )/tris(8-hydroxyquinoline) aluminum (iII) (Alq, 30 nm )/ $\mathrm{Mg}: \mathrm{Ag}$, in which ITO served as the substrate, ADN acted as a host material, (CuPc) as a hole-injection material, NPB as a hole-transport material, and as an electron-transport material.

The electroluminescence (EL) spectra and corresponding data of OLEDs based on oligomers 5a, 5d, and $\mathbf{5 e}$ are summarized in Table 2. Figure 6 shows the EL spectrum of a device based only on ADN and devices prepared with 5a, 5d and 5e at $J=20 \mathrm{~mA} \mathrm{~cm}{ }^{-2}$. All three stilbene-based devices exhibited blue emissions in the region 456-462 nm with a vibrational shoulder at $482-487 \mathrm{~nm}$; these EL wavelengths were independent of the applied voltage (5-12) V. The EL spectrum was nearly superimposed on the photoluminescence (PL) spectrum of films of their authentic compounds, demonstrating light emission from the compound. The contribution of the host molecule ADN to EL emission can be excluded because of the superior EL performances of species

Table 2. Electroluminescence characteristics of OLEDs based on $\mathbf{5 a}$, $\mathbf{5 d}$, and $\mathbf{5 e}$.

| Compound | Brightness <br> $\left(\mathrm{cd} \mathrm{m}^{-2}\right)$ | $\eta_{\text {ext }}$ <br> $(\%)$ | Luminance <br> efficiency <br> $\left(\mathrm{cd} \mathrm{A}^{-1}\right)$ | Power <br> efficiency <br> $\left(\mathrm{lm} \mathrm{W}^{-1}\right)$ | Voltage (V) | CIE <br> coordinates [d] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{5 a}$ | $576[\mathrm{a}]$ | 4.48 | 5.47 | 3.00 | 5.74 | $\mathrm{x}=0.14$ |
|  | $3748[\mathrm{~b}]$ | 4.81 | 5.88 | 2.55 | 7.24 | $\mathrm{y}=0.14$ |
|  | $22506[\mathrm{c}]$ | 4.87 | 5.91 | 3.01 |  | $(456 \mathrm{~nm})$ |
| 5d | 1139 | 3.51 | 5.69 | 2.16 | 8.28 | $\mathrm{x}=0.12$ |
|  | 5602 | 3.45 | 5.60 | 1.70 | 10.38 | $\mathrm{y}=0.21$ |
| 5e | 17992 | 3.53 | 5.74 | 2.54 |  | $(462 \mathrm{~nm})$ |
|  | 1356 | 3.47 | 6.78 | 2.84 | 7.51 | $\mathrm{x}=0.16$ |
|  | 6239 | 3.19 | 6.24 | 2.04 | 9.62 | $\mathrm{y}=0.25$ |
|  | 21423 | 3.51 | 6.87 | 3.40 |  | $(458 \mathrm{~nm})$ |

For each parameter, the data in different rows correspond to those measured at different current densities: [a] $J=20 \mathrm{~mA} \mathrm{~cm}^{-2}$. [b] $J=100 \mathrm{~mA} \mathrm{~cm}^{-2}$. [c] maximum value. [d] The values in parentheses represent the maximum EL emission.


Figure 6. Electroluminescence spectra of ADN, 5a, 5d, and $\mathbf{5 e}$.


Figure 7. External quantum efficiencies of ADN, species $\mathbf{5 a}, \mathbf{5 d}$, and $\mathbf{5 e}$ as a function of current densities.


Figure 8. J-V-L characteristics of OLEDs based on ADN, species $\mathbf{5 a}, \mathbf{5 d}$, and 5 e .
ordinates $x=0.13-0.16, y=0.16-0.32$. The EL parameters for species $\mathbf{5 a}$ reflect its promising application in OLED devices.

## 3. Conclusions

We have prepared fluoro-substituted $\mathrm{Ph}_{2} \mathrm{~N}$-containing oligo(arylenevinylene) derivatives using double Heck-coupling reactions or Horner-Wadsworth-Emmons reactions. We have demonstrated that the absorption, emission, and electrochemical properties are significantly affected by the position of the fluoro substitutents, which provides an effective tool to tune the color emission from deep blue to orange. Theoretical simulations on HOMO-LUMO orbitals rationalize the hypso- and bathochromic shifts of these fluoro substituents in their emission wavelengths. With blue emitter 5a, we achieved a high luminescence efficiency, $5.91 \mathrm{~cd} \mathrm{~A}^{-1}$ at $J=53 \mathrm{~mA} \mathrm{~cm}^{-2}$, together with a high power efficiency of $3.01 \mathrm{~lm} \mathrm{~W}^{-1}$ at $J=21 \mathrm{~mA} \mathrm{~cm}^{-2}$ and CIE coordinates $x=0.14$ and $y=0.14$. The commendable electroluminescent performance of these oligomers demonstrates their promising features for OLED displays.

## 4. Experimental

### 4.1. General Procedure for the Synthesis of 7a and 7b

To a toluene ( 35 mL ) solution of 1-bromo-4-fluorobenzene $(1.57 \mathrm{~g}$, 8.99 mmol ) were added 4-fluorophenylamine ( $1.00 \mathrm{~g}, 8.99 \mathrm{mmol}$ ), sodium tert-butoxide $(1.04 \mathrm{~g}, 10.79 \mathrm{mmol}), \mathrm{Pd}_{2}(\mathrm{dba})_{3}(0.16 \mathrm{~g}, 0.18 \mathrm{mmol})$ and $1,1^{\prime}$-bis(diphenylphosphino)ferrocene (DPPF, $0.20 \mathrm{~g}, 0.36 \mathrm{mmol}$ ) under $\mathrm{N}_{2}$. The resulting suspension was heated to reflux for 12 h . The reaction mixture was extracted with ethyl acetate, washed with aqueous NaCl solution, dried with $\mathrm{MgSO}_{4}$, and concentrated to yield a brownish oil. Chromatography (hexanes: $\mathrm{EtOAc}=10: 1, R_{\mathrm{f}}=0.7$ ) afforded bis(4fluorophenyl)amine ( $\mathbf{7 a}$ ) as a white solid ( $1.31 \mathrm{~g}, 71 \%$ ).

7a: IR (Nujol): $v=3385$ (s), 1596 (s), 1499 (s), 1418 (m), 1320 (s), 1175 (m), 877 (m), 746 (s), $693 \mathrm{~cm}^{-1}$ (s); ${ }^{1} \mathrm{HNMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$, $\delta):$ 6.94-6.92 (m, 8H), $5.42(\mathrm{~s}, 1 \mathrm{H}) ;{ }^{13} \mathrm{CNMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right)$ : $159.8\left(\mathrm{~d}, J_{\mathrm{CF}}=253.2 \mathrm{~Hz}\right), 142.6,118.6,112.3\left(\mathrm{~d}, J_{\mathrm{CF}}=21.2 \mathrm{~Hz}\right)$; Highresolution mass spectromety (HRMS, $(70 \mathrm{eV}):[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{12} \mathrm{H}_{9} \mathrm{~F}_{2} \mathrm{~N}, 205.0703$; found, 205.0703. Anal. calcd for $\mathrm{C}_{15} \mathrm{H}_{11} \mathrm{~N}$ : C 70.24, H 4.42, N, 6.83; found: C 70.25, H 4.41, N 6.84.

7b: IR (Nujol): $v=3372$ (s), 1591 (s), 1489 (s), 1415 (m), 1327 (s), 1176 (m), 877 (m), 744 (s), $699 \mathrm{~cm}^{-1}$ (s); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$, $\delta): 6.59(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.57(\mathrm{~d}, J=1.6 \mathrm{~Hz}, 2 \mathrm{H}), 6.43(\mathrm{~d}, J=8.8$, $2.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.89(\mathrm{br}, 1 \mathrm{H}) ;{ }^{13} \mathrm{CNMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 163.9(\mathrm{dd}$, $\left.J_{\mathrm{CF}}=245.9,15.2 \mathrm{~Hz}\right), 144.0\left(\mathrm{t}, J_{\mathrm{CF}}=13.7 \mathrm{~Hz}\right), 101.0\left(\mathrm{dd}, J_{\mathrm{CF}}=19.9\right.$ 7.7 Hz ), $97.3\left(\mathrm{t}, J_{\mathrm{CF}}=25.9 \mathrm{~Hz}\right)$; HRMS ( 70 eV ): $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{12} \mathrm{H}_{7} \mathrm{~F}_{4} \mathrm{~N}$, 241.0515; found, 241.0516. Anal. calcd for $\mathrm{C}_{12} \mathrm{H}_{7} \mathrm{~F}_{4} \mathrm{~N}$ : C 59.76, H 2.93, N 5.81; found: C 59.77, H 2.93, N 5.81.

### 4.2. General procedure for the Synthesis of 7c, 7d, 7o, 7p, and $7 q$

To a toluene ( 35 mL ) solution of 2-(4-bromophenyl)-1,3-dioxolane $(1.12 \mathrm{~g}, 4.87 \mathrm{mmol})$ were added $7 \mathrm{a}(1.00 \mathrm{~g}, 4.87 \mathrm{mmol})$, sodium tertbutoxide $(0.52 \mathrm{~g}, 5.36 \mathrm{mmol}), \mathrm{Pd}(\mathrm{OAc})_{2}(21.9 \mathrm{mg}, 0.10 \mathrm{mmol})$ and $\mathrm{P}(t-\mathrm{Bu})_{3}(39.4 \mathrm{mg}, 0.20 \mathrm{mmol})$ under $\mathrm{N}_{2}$, and the resulting suspension was heated to reflux for 12 h . After cooling to room temperature, 1 N
$\mathrm{HCl}(10 \mathrm{~mL})$ and acetone $(20 \mathrm{~mL})$ were added, and the mixture was stirred another 1 h . The reaction mixture was extracted with ethyl acetate, washed with aqueous NaCl solution, dried with $\mathrm{MgSO}_{4}$, and concentrated to yield a brownish oil. Chromatography (hexanes:E$\mathrm{tOAc}=8: 1, R_{\mathrm{f}}=0.4$ ) afforded 4-[bis(4-fluorophenyl)amino]benzaldehyde ( $\mathbf{7 c}$ ) as a light yellow solid ( $1.33 \mathrm{~g}, 88 \%$ ).

7c: IR (Nujol): $v=1715$ (s), 1588 (s), 1493 (s), 1331 (m), 1278 (m), 1175 (s), 752 (s), 699 (s), 626 (s), $506 \mathrm{~cm}^{-1}$ (m); ${ }^{1} \mathrm{HNMR}\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$, $\delta): 9.78(\mathrm{~s}, 1 \mathrm{H}), 7.65(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.13-7.11(\mathrm{~m}, 4 \mathrm{H}), 7.03(\mathrm{t}$, $J=8.0 \mathrm{~Hz}, 4 \mathrm{H}), 6.90(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}) ;{ }^{13} \mathrm{CNMR}\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right)$ $190.3,160.1\left(\mathrm{~d}, J_{\mathrm{CF}}=244.8 \mathrm{~Hz}\right), 153.3,141.9,131.4,129.0$, $128.0(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=8.0 \mathrm{~Hz}\right), 118.3,116.7\left(\mathrm{~d}, J_{\mathrm{CF}}=22.7 \mathrm{~Hz}\right) ; \operatorname{HRMS}(70 \mathrm{eV}):[M+\mathrm{H}]^{+}$ calcd for $\mathrm{C}_{19} \mathrm{H}_{13} \mathrm{~F}_{2} \mathrm{NO}$, 309.0965; found, 309.0965. Anal. calcd for $\mathrm{C}_{19} \mathrm{H}_{13} \mathrm{~F}_{2} \mathrm{NO}: \mathrm{C} 73.78, \mathrm{H} 4.24$, N 4.53 ; found: C 73.75, H 4.25, N 4.56.

7d: IR (Nujol): $v=1718$ (s), 1591 (s), 1491 (s), 1338 (m), 1272 (m), 1171 (s), 755 (s), 693 (s), 624 (s), $505 \mathrm{~cm}^{-1}$ (m); ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\left.\mathrm{CDCl}_{3}, \delta\right): 9.91(\mathrm{~s}, 1 \mathrm{H}), 7.81(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.17(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H})$, 6.64-6.61 (m, 6H); ${ }^{13}$ CNMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): 190.4, 163.7 (dd, $\left.J_{\mathrm{CF}}=247.4,13.7 \mathrm{~Hz}\right), 151.0,147.9\left(\mathrm{t}, J_{\mathrm{CF}}=12.2 \mathrm{~Hz}\right), 132.0,131.4,123.2$, $108.1\left(\mathrm{dd}, J_{\mathrm{CF}}=19.9,7.7 \mathrm{~Hz}\right), 100.6\left(\mathrm{t}, J_{\mathrm{CF}}=25.9 \mathrm{~Hz}\right) ; \operatorname{HRMS}(70 \mathrm{eV})$ : $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{19} \mathrm{H}_{11} \mathrm{~F}_{4} \mathrm{NO}, 345.0777$; found, 345.0775. Anal. calcd for $\mathrm{C}_{19} \mathrm{H}_{11} \mathrm{~F}_{4} \mathrm{NO}: \mathrm{C} 66.09, \mathrm{H} 3.21, \mathrm{~N} 4.06$; found: C 66.11, H 3.21, N 4.09.

7o: IR (Nujol): $v=1708$ (s), 1595 (s), 1488 (s), 1335 (m), 1276 (m), 1168 (s), 758 (s), 696 (s), $621 \mathrm{~cm}^{-1}$ (s); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): $10.08(\mathrm{~s}, 1 \mathrm{H}), 7.63(\mathrm{t}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.34(\mathrm{t}, J=8.0 \mathrm{~Hz}, 4 \mathrm{H}), 7.20-7.17$ $(\mathrm{m}, 6 \mathrm{H}), 6.70(\mathrm{dd}, J=8.8,2.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.55(\mathrm{dd}, J=13.6,2.2 \mathrm{~Hz}, 1 \mathrm{H})$; ${ }^{13} \mathrm{CNMR}\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 185.1 \quad\left(\mathrm{~d}, J_{\mathrm{CF}}=5.4 \mathrm{~Hz}\right), 165.9$ (d, $\left.J_{\mathrm{CF}}=255.2 \mathrm{~Hz}\right), 154.9,145.2,129.8,129.4\left(\mathrm{~d}, J_{\mathrm{CF}}=3.3 \mathrm{~Hz}\right), 126.6,125.8$, $116.3,114.3,104.5\left(\mathrm{~d}, J_{\mathrm{CF}}=24.9 \mathrm{~Hz}\right)$; HRMS $(70 \mathrm{eV}):[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{19} \mathrm{H}_{14} \mathrm{FNO}$, 291.1059; found, 291.1058. Anal. calcd for $\mathrm{C}_{19} \mathrm{H}_{14} \mathrm{FNO}: \mathrm{C} 78.33$, H 4.84, N 4.81; found: C 78.36, H 4.84, N 4.85.

7p: IR (Nujol): $v=1716$ (s), 1595 (s), 1493 (s), 1333 (m), 1174 (s), 758 (s), 696 (s), $621(\mathrm{~s}), 509 \mathrm{~cm}^{-1}(\mathrm{~m}) ;{ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): 10.09 $(\mathrm{s}, 1 \mathrm{H}), 7.63(\mathrm{t}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.34(\mathrm{t}, J=8.4 \mathrm{~Hz}, 4 \mathrm{H}), 7.20-7.16(\mathrm{~m}$, $7 \mathrm{H}), 6.70(\mathrm{dd}, J=8.8,2.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.55(\mathrm{dd}, J=13.5,2.1 \mathrm{~Hz}, 1 \mathrm{H})$; ${ }^{13}$ CNMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): $185.1\left(\mathrm{~d}, J_{\mathrm{CF}}=5.4 \mathrm{~Hz}\right), 165.9(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=255.2 \mathrm{~Hz}\right), \quad 154.9 \quad\left(\mathrm{~d}, J_{\mathrm{CF}}=11.6 \mathrm{~Hz}\right), 145.2,129.8,129.4(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=3.2 \mathrm{~Hz}\right), 126.6,125.8,116.4\left(\mathrm{~d}, J_{\mathrm{CF}}=8.6 \mathrm{~Hz}\right), 114.3,104.5(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=24.9 \mathrm{~Hz}\right)$; HRMS ( 70 eV ): $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{19} \mathrm{H}_{14} \mathrm{FNO}$, 291.1059; found, 291.1059. Anal. calcd for $\mathrm{C}_{19} \mathrm{H}_{14} \mathrm{FNO}$ C 78.33, H 4.84, N 4.81; found: C 78.35, H 4.83, N 4.86 .

7q: IR (Nujol): $v=1711$ (s), 1586 (s), 1493 (s), 1336 (m), 1279 (m), 1173 (s), 754 (s), 695 (s), 622 (s), $501 \mathrm{~cm}^{-1}$ (m); ${ }^{1} \mathrm{H}$ NMR ( 600 MHz , $\left.\mathrm{CDCl}_{3}, \delta\right): 10.12(\mathrm{~d}, J=2.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.49(\mathrm{dd}, J=11.3,6.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.28$ $(\mathrm{t}, J=8.0 \mathrm{~Hz}, 4 \mathrm{H}), 7.12(\mathrm{t}, J=7.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.05(\mathrm{t}, J=7.9 \mathrm{~Hz}, 4 \mathrm{H}), 6.74$ (dd, $J=11.6,6.2 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{CNMR}\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta 184.5\right):(\mathrm{d}$, $\left.J_{\mathrm{CF}}=4.1 \mathrm{~Hz}\right), 161.2\left(\mathrm{~d}, J_{\mathrm{CF}}=253.4 \mathrm{~Hz}\right), 151.9\left(\mathrm{~d}, J_{\mathrm{CF}}=248.9 \mathrm{~Hz}\right), 145.9$, $142.4\left(\mathrm{t}, J_{\mathrm{CF}}=10.9 \mathrm{~Hz}\right), 129.3\left(\mathrm{~d}, J_{\mathrm{CF}}=29.8 \mathrm{~Hz}\right), 124.8,124.3,118.4(\mathrm{dd}$, $\left.J_{\mathrm{CF}}=10.2, \quad 5.6 \mathrm{~Hz}\right), \quad 115.3 \quad\left(\mathrm{dd}, \quad J_{\mathrm{CF}}=22.2, \quad 2.0 \mathrm{~Hz}\right), \quad 111.9 \quad(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=25.5 \mathrm{~Hz}\right)$; HRMS $(70 \mathrm{eV}):[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{19} \mathrm{H}_{13} \mathrm{~F}_{2} \mathrm{NO}$, 309.0965; found, 309.0966. Anal. calcd for $\mathrm{C}_{19} \mathrm{H}_{13} \mathrm{~F}_{2} \mathrm{NO}$ : C 73.78, H 4.24, N 4.53; found: C 73.75, H 4.23, N 4.56.

### 4.3. General Procedure for the Synthesis of 7e and 7f

To a $\mathrm{CCl}_{4}(50 \mathrm{~mL})$ solution of 4-bromo-3-fluorotoluene $(7.00 \mathrm{~g}$, $37.03 \mathrm{mmol})$ were added NBS ( $6.59 \mathrm{~g}, 37.03 \mathrm{mmol}$ ), benzoyl peroxide ( $\mathrm{BPO}, 0.45 \mathrm{~g}, 1.85 \mathrm{mmol}$ ), and the resulting suspension was heated to reflux for 5 h . After cooling to room temperature, the reaction mixture was extracted with ethyl acetate, washed with aqueous NaCl solution, dried with $\mathrm{MgSO}_{4}$, and concentrated to yield a colorless oil. Chromatography (pure hexanes, $R_{\mathrm{f}}=0.7$ ) afforded 4-bromo-1-bromomethyl-2fluorobenzene (7e) as a colorless oil ( $8.14 \mathrm{~g}, 82 \%$ ).

7e: IR (Nujol): $v=1586$ (s), 1491 (s), 1235 (s), 877 (m), 835 (m), 615 (s), $530 \mathrm{~cm}^{-1}$ (s); ${ }^{1} \mathrm{HNMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 7.50(\mathrm{t}, J=7.6 \mathrm{~Hz}$, $\left.{ }^{13} \mathrm{H}\right), 7.14(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.04(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.39(\mathrm{~s}, 2 \mathrm{H})$; ${ }^{13} \mathrm{CNMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 161.2\left(\mathrm{~d}, J_{\mathrm{CF}}=251.5 \mathrm{~Hz}\right), 138.8,134.1$, $133.9,125.9\left(\mathrm{~d}, J_{\mathrm{CF}}=13.1 \mathrm{~Hz}\right), 120.4\left(\mathrm{~d}, J_{\mathrm{CF}}=23.8 \mathrm{~Hz}\right), 24.8$. HRMS $(70 \mathrm{eV}):[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{Br}_{2} \mathrm{~F}, 265.8742$; found, 265.8744. Anal. calcd for $\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{Br}_{2} \mathrm{~F}$ : C 31.38, H 1.88; found, C 31.37, H, 1.86.

7f: IR (Nujol): $v=1581$ (s), 1496 (s), 1231 (s), 866 (m), 836 (m), 610 (s), $526 \mathrm{~cm}^{-1}(\mathrm{~s}) ;{ }^{1} \mathrm{HNMR}\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 7.24-7.20(\mathrm{~m}, 3 \mathrm{H})$, $4.41(\mathrm{~s}, 2 \mathrm{H}) ;{ }^{13} \mathrm{CNMR}\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 160.3\left(\mathrm{~d}, J_{\mathrm{CF}}=253.5 \mathrm{~Hz}\right)$, $132.2,127.9,124.4\left(\mathrm{~d}, J_{\mathrm{CF}}=14.3 \mathrm{~Hz}\right), 123.0\left(\mathrm{~d}, J_{\mathrm{CF}}=9.2 \mathrm{~Hz}\right), 119.5(\mathrm{~d}$, $J_{\mathrm{CF}}=24.3 \mathrm{~Hz}$ ), 24.7; HRMS ( 70 eV ): $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{Br}_{2} \mathrm{~F}$, 265.8742; found, 265.8742. Anal. calcd for $\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{Br}_{2} \mathrm{~F}$ : C 31.38, H 1.88; found: C 31.38, H 1.89 .

### 4.4. General Procedure for the Synthesis of $\mathbf{7 g}$ and $\mathbf{7 h}$

To a dimethyl sulfoxide (DMSO) ( 50 mL ) solution of $7 \mathrm{e}(1.23 \mathrm{~g}$, $4.59 \mathrm{mmol})$ was added $\mathrm{NaHCO}_{3}(3.47 \mathrm{~g}, 41.34 \mathrm{mmol})$, and the resulting suspension was heated to $70<\mathrm{Mo}<\mathrm{C}$ for 1 h . After cooling to room temperature, the reaction mixture was extracted with hexane, washed with aqueous NaCl solution, dried with $\mathrm{MgSO}_{4}$, and concentrated to yield a light yellow solid. Chromatography (hexanes: $\mathrm{EtOAc}=10: 1$, $R_{\mathrm{f}}=0.4$ ) afforded 4-bromo-3-fluorobenzaldehyde $(\mathbf{7 g})$ as a light yellow solid ( $0.68 \mathrm{~g}, 73 \%$ ).

7g: IR (Nujol): $v=1728$ (s), 1491 (s), 1230 (s), 871 (m), 839 (m), 611 (s), $541 \mathrm{~cm}^{-1}(\mathrm{~s}) ;{ }^{1} \mathrm{H}$ NMR ( $\left.400 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 9.93(\mathrm{~s}, 1 \mathrm{H}), 7.72(\mathrm{t}$, $J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.58(\mathrm{~d}, J=8.2,1 \mathrm{H}), 7.52(\mathrm{~d}, J=8.0,1 \mathrm{H}) ;{ }^{13} \mathrm{CNMR}$ ( $\left.100 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 189.3,164.1\left(\mathrm{~d}, J_{\mathrm{CF}}=244.2 \mathrm{~Hz}\right), 130.2,129.1$, $127.1,122.2\left(\mathrm{~d}, J_{\mathrm{CF}}=8.8 \mathrm{~Hz}\right), 119.2\left(\mathrm{~d}, J_{\mathrm{CF}}=21.4 \mathrm{~Hz}\right) ; \operatorname{HRMS}(70 \mathrm{eV})$ : $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{7} \mathrm{H}_{4} \mathrm{BrFO}, 201.9430$; found, 201.9435. Anal. calcd for $\mathrm{C}_{7} \mathrm{H}_{4} \mathrm{BrFO}$ : C 41.41, H 1.99; found: C 41.40, H 1.98 .

7h: IR (Nujol): $v=1732$ (s), 1581 (s), 1492 (s), 1229 (s), 872 (m), 833 (m), $611(\mathrm{~s}), 529 \mathrm{~cm}^{-1}(\mathrm{~s}) ;{ }^{1} \mathrm{H}$ NMR ( $\left.600 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 10.16(\mathrm{t}$, $J=1.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.59(\mathrm{t}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.29(\mathrm{dd}, J=8.2,2.1 \mathrm{~Hz}, 1 \mathrm{H})$, 7.23 (dd, $J=8.4,2.2 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{CNMR}\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 185.5$ (d, $\left.J_{\mathrm{CF}}=5.4 \mathrm{~Hz}\right), 163.7\left(\mathrm{~d}, J_{\mathrm{CF}}=243.1 \mathrm{~Hz}\right), 129.7\left(\mathrm{~d}, J_{\mathrm{CF}}=9.6 \mathrm{~Hz}\right), 129.3$, $128.1,122.8\left(\mathrm{~d}, J_{\mathrm{CF}}=8.1 \mathrm{~Hz}\right), 119.9\left(\mathrm{~d}, J_{\mathrm{CF}}=23.4 \mathrm{~Hz}\right) ; \operatorname{HRMS}(70 \mathrm{eV})$ : $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{7} \mathrm{H}_{4} \mathrm{BrFO}, 201.9430$; found, 201.9432. Anal. calcd for $\mathrm{C}_{7} \mathrm{H}_{4} \mathrm{BrFO}$ : C 41.41, H 1.99; found: C 41.41, H 2.00 .

### 4.5. General Procedure for the Synthesis of $7 \mathbf{i}$ and $7 \mathbf{j}$

To a diethyl ether $(40 \mathrm{~mL})$ solution of 1,4-dibromo-2,5-difluorobenzene $(3.49 \mathrm{~g}, 12.85 \mathrm{mmol})$ was added $n$-butyllithium $(5.14 \mathrm{~mL}, 2.5 \mathrm{M}$, 12.85 mmol ) dropwise at $-78^{\circ} \mathrm{C}$, and the mixture was stirred at this temperature for 10 min before ethyl formate $(1.43 \mathrm{~g}, 19.29 \mathrm{mmol})$ was added. The resulting suspension was slowly warmed to room temperature before addition of $2 \mathrm{~N} \mathrm{NH}_{4} \mathrm{Cl}(10 \mathrm{~mL})$. The reaction mixture was extracted with ethyl acetate, washed with aqueous NaCl solution, dried with $\mathrm{MgSO}_{4}$, and concentrated to yield a colorless oil. Chromatography (hexanes:EtOAc =10: 1, $R_{\mathrm{f}}=0.4$ ) afforded 4-bromo-2,5-difluorobenzaldehyde ( $\mathbf{7 i}$ ) as a white solid ( $1.68 \mathrm{~g}, 59 \%$ ).

7i: IR (Nujol): $v=1736$ (s), 1577 (s), 1482 (s), 1231 (s), 876 (m), 838 $(\mathrm{m}), 608 \mathrm{~cm}^{-1}(\mathrm{~s}) ;{ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 10.10(\mathrm{t}, J=2.5 \mathrm{~Hz}$, $1 \mathrm{H}), 7.40(\mathrm{dt}, J=6.2,2.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.34(\mathrm{dd}, J=9.0,4.2 \mathrm{~Hz}, 1 \mathrm{H})$; ${ }^{13}$ CNMR ( $\left.125 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 184.5\left(\mathrm{~d}, J_{\mathrm{CF}}=6.6 \mathrm{~Hz}\right), 159.4$ (d, $\left.J_{\mathrm{CF}}=257.3 \mathrm{~Hz}\right), \quad 155.6 \quad\left(\mathrm{~d}, \quad J_{\mathrm{CF}}=246.1 \mathrm{~Hz}\right), \quad 123.9, \quad 121.6 \quad(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=25.5 \mathrm{~Hz}\right), 116.8\left(\mathrm{dd}, J_{\mathrm{CF}}=23.3,10.0 \mathrm{~Hz}\right), 114.0\left(\mathrm{~d}, J_{\mathrm{CF}}=23.3 \mathrm{~Hz}\right)$; HRMS ( 70 eV ): $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{7} \mathrm{H}_{3} \mathrm{BrF}_{2} \mathrm{O}, 219.9335$; found, 219.9333. Anal. calcd for $\mathrm{C}_{7} \mathrm{H}_{3} \mathrm{BrF}_{2} \mathrm{O}$ : C 38.04, H 1.37; found: C 38.03, H 1.38 .

7j: IR (Nujol): $v=1725$ (s), 1580 (s), 1497 (s), 1231 (s), 875 (m), 826 $(\mathrm{m}), 603 \mathrm{~cm}^{-1}$ (s); ${ }^{1} \mathrm{HNMR}\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 10.27$ ( $\left.\mathrm{s}, 1 \mathrm{H}\right) ;$ ${ }^{13} \mathrm{CNMR}\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 181.8,146.5\left(\mathrm{dd}, J_{\mathrm{CF}}=249.3,22.5 \mathrm{~Hz}\right)$, $145.2\left(\mathrm{dd}, J_{\mathrm{CF}}=247.6,22.3 \mathrm{~Hz}\right), 114.4\left(\mathrm{t}, J_{\mathrm{CF}}=9.6 \mathrm{~Hz}\right), 107.3(\mathrm{t}$, $\left.J_{\mathrm{CF}}=21.6 \mathrm{~Hz}\right) ;$ HRMS $(70 \mathrm{eV}):[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{7} \mathrm{HBrF}_{4} \mathrm{O}$, 255.9147; found, 255.9148. Anal. calcd for $\mathrm{C}_{7} \mathrm{HBrF}_{4} \mathrm{O}$ : C 32.72; found: C 32.74.

### 4.6. General Procedure for the Synthesis of 7k, 71, and 7m

To a benzene $(80 \mathrm{~mL})$ solution of $7 \mathbf{g}(1.00 \mathrm{~g}, 4.93 \mathrm{mmol})$ were added ethylene glycol ( $1.73 \mathrm{~g}, 7.39 \mathrm{mmol}$ ), para-toluenesulfonic acid (PTSA, $0.1 \mathrm{~g}, 0.058 \mathrm{mmol}$ ), and the resulting suspension was heated under re-
flux ( 24 h ) using a Dean-Stack trap. After cooling to room temperature, $\mathrm{NaHCO}_{3}(2 \mathrm{~g})$ was added, and the solution was concentrated to yield a colorless oil. Chromatography (hexanes: $\mathrm{EtOAc}=10: 1, R_{\mathrm{f}}=0.4$ ) afforded 2-(4-bromo-3-fluorophenyl)-1,3-dioxolane (7k) as a colorless oil ( $1.20 \mathrm{~g}, 99 \%$ ).

7k: IR (Nujol): $v=2895$ ( s ), 1446 (s), 1386 (s), 1219 (s), 1113 (s), 1006 (s), 948 (s), 793 (s), $615 \mathrm{~cm}^{-1}$ (s); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): 7.54 $(\mathrm{t}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.23(\mathrm{t}, J=8.2,1 \mathrm{H}), 7.12(\mathrm{~d}, J=8.2,1 \mathrm{H}), 5.76(\mathrm{~s}, 1 \mathrm{H})$, 4.21-4.00 (m, 4H); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): 158.6 (d, $\left.J_{\mathrm{CF}}=248.8 \mathrm{~Hz}\right), 134.5,131.8,128.2,121.7,117.5\left(\mathrm{~d}, J_{\mathrm{CF}}=23.2 \mathrm{~Hz}\right), 99.6$, 65.8; HRMS $(70 \mathrm{eV}):[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{9} \mathrm{H}_{8} \mathrm{BrFO}_{2}, 245.9692$; found, 245.9696. Anal. calcd for $\mathrm{C}_{9} \mathrm{H}_{8} \mathrm{BrFO}_{2}$ : C 43.75, H 3.26; found: C 43.77, H 3.25.

71: IR (Nujol): 2887 (s), 1436 (s), 1378 (s), 1211 (s), 1102 (s), 999 (s), 945 (s), $785(\mathrm{~s}), 611 \mathrm{~cm}^{-1}(\mathrm{~s}) ;{ }^{1} \mathrm{H}$ NMR ( $\left.400 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 7.41(\mathrm{t}$, $J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.28(\mathrm{dd}, J=8.2,2.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.24(\mathrm{dd}, J=8.2,2.0 \mathrm{~Hz}$, $1 \mathrm{H}), 6.03(\mathrm{~s}, 1 \mathrm{H}), 4.13-4.09(\mathrm{~m}, 2 \mathrm{H}), 4.03-4.00(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C} N \mathrm{NR}$ $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 160.8\left(\mathrm{~d}, J_{\mathrm{CF}}=251.9 \mathrm{~Hz}\right), 128.9,127.4,124.5(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=12.2 \mathrm{~Hz}\right), 123.3\left(\mathrm{~d}, J_{\mathrm{CF}}=9.1 \mathrm{~Hz}\right), 119.2\left(\mathrm{~d}, J_{\mathrm{CF}}=22.9 \mathrm{~Hz}\right), 98.4$, 65.4; HRMS ( 70 eV ): $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{9} \mathrm{H}_{8} \mathrm{BrFO}_{2}, 245.9692$; found, 245.9692. Anal. calcd for $\mathrm{C}_{9} \mathrm{H}_{8} \mathrm{BrFO}_{2}$ : C 43.75, H 3.26; found, C 43.76, H 3.26.

7m: IR (Nujol): $v=2881$ ( s ), 1432 ( s ), 1373 ( s ), 1208 ( s$), 1096$ ( s$), 993$ (s), 940 (s), 783 (s), $603 \mathrm{~cm}^{-1}$ (s); ${ }^{1} \mathrm{HNMR}$ ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): 7.30-7.27 (m, 2H), $5.99(\mathrm{~s}, 1 \mathrm{H}), 4.13-4.01(\mathrm{~m}, 4 \mathrm{H}) ;{ }^{13} \mathrm{CNMR}(100 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}, \delta\right): 158.8\left(\mathrm{dd}, J_{\mathrm{CF}}=243.6,21.8 \mathrm{~Hz}\right), 157.6\left(\mathrm{dd}, J_{\mathrm{CF}}=242.8\right.$, 22.2 Hz ), 126.2, 122.9, 118.5, 107.2, 103.6, 65.4; HRMS (70 eV): $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{9} \mathrm{H}_{8} \mathrm{BrFO}_{2}, 263.9597$; found, 263.9595. Anal. calcd for $\mathrm{C}_{9} \mathrm{H}_{7} \mathrm{BrF}_{2} \mathrm{O}_{2}$ : C 40.78, H 2.66; found: C 40.77, H 2.66.

### 4.7. General Procedure for the Synthesis of $7 \mathbf{r}$ and 7s

To a methanol ( 25 mL ) solution of $7 \mathbf{i}(1.00 \mathrm{~g}, 4.53 \mathrm{mmol})$ was added $\mathrm{NaBH}_{4}(0.21 \mathrm{~g}, 5.43 \mathrm{mmol})$ at $0^{\circ} \mathrm{C}$ and stirred for 1 h . The reaction mixture was extracted with ethyl acetate, dried with $\mathrm{MgSO}_{4}$, and concentrated to yield a colorless oil. This oil was added into a dichloromethane solution of $\mathrm{PBr}_{3}(1.78 \mathrm{~g}, 6.59 \mathrm{mmol})$ at $0^{\circ} \mathrm{C}$ and stirred for 3 h ; The reaction mixture was poured into excess ice, and $\mathrm{NaHCO}_{3}$ was added until neutralization, then extracted with ethyl acetate, dried with $\mathrm{MgSO}_{4}$, and concentrated to yield a colorless oil. Triethyl phosphite $(1.35 \mathrm{~g}, 8.15 \mathrm{mmol})$ was added, and the reaction mixture was stirred at $150{ }^{\circ} \mathrm{C}$ for 12 h . After cooling to room temperature, the reaction mixture was purified by bulb-to-bulb distillation to afford $7 \mathbf{r}$ as a colorless oil ( $1.29 \mathrm{~g}, 83 \%$ ).

7r: IR (Nujol): $v=2983$ (m), 1496 (m), 1252 (s), 1099 (m), 1031 (s), 963 (s), 833 (m), 699 (s), $535 \mathrm{~cm}^{-}$(s); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): $7.28(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.18-7.13(\mathrm{~m}, 1 \mathrm{H}), 4.11-4.04(\mathrm{~m}, 4 \mathrm{H}), 3.12(\mathrm{~d}$, $J=22.0 \mathrm{~Hz}, 2 \mathrm{H}), 1.26(\mathrm{t}, J=7.06 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{31} \mathrm{CNMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$, $\delta): 159.8\left(\mathrm{~d}, J_{\mathrm{CF}}=251.3 \mathrm{~Hz}\right), 157.2\left(\mathrm{~d}, J_{\mathrm{CF}}=248.1 \mathrm{~Hz}\right), 123.6(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=13.5 \mathrm{~Hz}\right), 120.8\left(\mathrm{~d}, J_{\mathrm{CF}}=25.5 \mathrm{~Hz}\right), 116.8\left(\mathrm{~d}, J_{\mathrm{CF}}=23.3 \mathrm{~Hz}\right), 113.2$ $\left(\mathrm{d}, J_{\mathrm{CF}}=23.1 \mathrm{~Hz}\right), 62.3,25.8\left(\mathrm{~d}, J_{\mathrm{CP}}=139.6 \mathrm{~Hz}\right), 16.5$; HRMS $(70 \mathrm{eV})$ : $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{11} \mathrm{H}_{14} \mathrm{BrF}_{2} \mathrm{O}_{3} \mathrm{P}$, 341.9832; found, 341.9835. Anal. calcd for $\mathrm{C}_{11} \mathrm{H}_{14} \mathrm{BrF}_{2} \mathrm{O}_{3} \mathrm{P}: \mathrm{C} 38.51$, H 4.11 ; found: C 38.50 , H 4.12 .

7s: IR (Nujol): $v=2978$ (m), 1492 (m), 1245 (s), 1093 (m), 1018 (s), 955 (s), 822 (m), 691 (s), $524 \mathrm{~cm}^{-1}$ (s); ${ }^{1} \mathrm{HNMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right)$ : 4.14-4.06 (m, 4H), $3.23(\mathrm{~d}, J=21.2 \mathrm{~Hz}, 2 \mathrm{H}), 1.28(\mathrm{t}, J=7.02 \mathrm{~Hz}, 6 \mathrm{H})$; ${ }^{13} \mathrm{CNMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 146.8\left(\mathrm{dd}, J_{\mathrm{CF}}=249.3,22.5 \mathrm{~Hz}\right), 144.8$ $\left(\mathrm{dd}, \quad J_{\mathrm{CF}}=247.6, \quad 22.3 \mathrm{~Hz}\right), \quad 114.4 \quad\left(\mathrm{t}, \quad J_{\mathrm{CF}}=9.6 \mathrm{~Hz}\right), 107.1 \quad(\mathrm{t}$, $\left.J_{\mathrm{CF}}=21.6 \mathrm{~Hz}\right), 62.7,26.2\left(\mathrm{~d}, J_{\mathrm{CP}}=142.2 \mathrm{~Hz}\right), 16.6 ; \operatorname{HRMS}(70 \mathrm{eV}):$ $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{11} \mathrm{H}_{12} \mathrm{BrF}_{4} \mathrm{O}_{3} \mathrm{P}, 377.9644$; found, 377.9647. Anal. calcd for $\mathrm{C}_{11} \mathrm{H}_{12} \mathrm{BrF}_{4} \mathrm{O}_{3} \mathrm{P}$ : C 34.85, H 3.19; found: C 34.84, H 3.21.

### 4.8. General Procedure for the Synthesis of 5a-f, 7t, and 7u

To a THF solution of compound $\mathbf{8}(1.63 \mathrm{~g}, 3.58 \mathrm{mmol})$ was added sodium tert-butoxide $(0.76 \mathrm{~g}, 7.91 \mathrm{mmol})$ at $0^{\circ} \mathrm{C}$. The reaction mixture was stirred on an ice bath for 1 h , and subsequently a THF solution ( 5 mL ) of compound 7 c was added. After $24 \mathrm{~h}, 5 \mathrm{~mL}$ of $\mathrm{NH}_{4} \mathrm{Cl}$ solution was added. The reaction mixture was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, dried
with $\mathrm{MgSO}_{4}$ and evaporated in vacuo. The residue was purified by recrystallization in a mixed solution of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and hexane affording 5a $(2.14 \mathrm{~g}, 82 \%)$ as a light-green solid.

5a: IR (Nujol): $v=1661$ (m), 1584 (s), 1493 (s), 1333 (m), 1219 (s), 1168 (s), 745 (s), 692 (s), 625 (s); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): 7.59 (d, $J=8.4 \mathrm{~Hz}, 4 \mathrm{H}), 7.54$ (d, $J=8.4 \mathrm{~Hz}, 4 \mathrm{H}), 7.37$ (dd, $J=8.8,2.4 \mathrm{~Hz}$, $4 \mathrm{H}), 7.09(\mathrm{~s}, 2 \mathrm{H}), 7.06-7.03(\mathrm{~m}, 12 \mathrm{H}), 7.02(\mathrm{~s}, 2 \mathrm{H}), 6.99-6.94(\mathrm{~m}, 8 \mathrm{H})$; ${ }^{13} \mathrm{CNMR}(150 \mathrm{MHz} \mathrm{CDCl} 3, \delta): 158.9\left(\mathrm{~d}, J_{\mathrm{CF}}=241.9 \mathrm{~Hz}\right), 147.5,139.4$, $136.6,131.2,128.1,127.4,127.0,126.7,126.5,126.1\left(\mathrm{~d}, J_{\mathrm{CF}}=7.7 \mathrm{~Hz}\right)$, 122.3, $116.2\left(\mathrm{~d}, J_{\mathrm{CF}}=22.5 \mathrm{~Hz}\right)$; HRMS $(70 \mathrm{eV}):[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{52} \mathrm{H}_{36} \mathrm{~F}_{4} \mathrm{~N}_{2}, 764.2815$; found, 764.2811. Anal. calcd for $\mathrm{C}_{52} \mathrm{H}_{36} \mathrm{~F}_{4} \mathrm{~N}_{2}$ : C 81.66, H 4.74, N 3.66; found: C 81.63, H 4.74, N 3.69.

5b: IR (Nujol): $v=1668$ (m), 1585 (s), 1492 (s), 1329 (m), 1217 (s), 1172 (s), 749 (s), 696 (s), $603 \mathrm{~cm}^{-1}$ (s); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): $7.68(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 4 \mathrm{H}), 7.62(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 4 \mathrm{H}), 7.46(\mathrm{~d}, J=8.7 \mathrm{~Hz}$, $4 \mathrm{H}), 7.33-7.29(\mathrm{~m}, 4 \mathrm{H}), 7.17(\mathrm{~d}, J=16.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.08(\mathrm{~d}, J=16.2 \mathrm{~Hz}$, $2 \mathrm{H}), 7.00-6.94(\mathrm{~m}, 8 \mathrm{H}), 6.82(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 4 \mathrm{H}) ;{ }^{13} \mathrm{CNMR}(150 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}, \delta\right): 160.3\left(\mathrm{dd}, J_{\mathrm{CF}}=247.1,11.0 \mathrm{~Hz}\right), 158.3\left(\mathrm{dd}, J_{\mathrm{CF}}=252.8\right.$, $12.2 \mathrm{~Hz})$, 146.7, 139.3, 136.7, 130.4, $129.6\left(\mathrm{~d}, J_{\mathrm{CF}}=10.2 \mathrm{~Hz}\right)$, 128.1, $127.4,126.9,126.7,126.2,117.7,112.0\left(\mathrm{~d}, J_{\mathrm{CF}}=21.8 \mathrm{~Hz}\right), 105.4(\mathrm{t}$, $J_{\mathrm{CF}}=24.8 \mathrm{~Hz}$ ); HRMS (70 eV): $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{52} \mathrm{H}_{32} \mathrm{~F}_{8} \mathrm{~N}_{2}$, 836.2438; found, 836.2435. Anal. calcd for $\mathrm{C}_{52} \mathrm{H}_{32} \mathrm{~F}_{8} \mathrm{~N}_{2}$ : C 74.64, H 3.85, N 3.35; found: C 74.64, H 3.85, N 3.35.

5c: IR (Nujol): $v=1676$ (m), 1592 (s), 1496 (s), 1339 (m), 1224 (s), 1159 (s), $690(\mathrm{~s}), 623 \mathrm{~cm}^{-1}$ (s); ${ }^{1} \mathrm{HNMR}(600 \mathrm{MHz} \mathrm{CDCl} 3, \delta): 7.69(\mathrm{~d}$, $J=8.0 \mathrm{~Hz}, 4 \mathrm{H}), 7.62(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 4 \mathrm{H}), 7.34-7.31(\mathrm{~m}, 10 \mathrm{H}), 7.27(\mathrm{~d}$, $J=8.1 \mathrm{~Hz}, 2 \mathrm{H}), 7.20(\mathrm{t}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.14-7.12(\mathrm{~m}, 12 \mathrm{H}), 7.11-7.08$ $(\mathrm{m}, 4 \mathrm{H}) ;{ }^{13} \mathrm{CNMR}\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 158.0\left(\mathrm{~d}, J_{\mathrm{CF}}=249.8 \mathrm{~Hz}\right)$, 147.1, $139.8,136.1,135.3\left(\mathrm{~d}, J_{\mathrm{CF}}=6.3 \mathrm{~Hz}\right), 133.8\left(\mathrm{~d}, J_{\mathrm{CF}}=10.5 \mathrm{~Hz}\right)$, $129.1,128.8,128.6,127.1,123.2,122.6,122.5,114.3\left(\mathrm{~d}, J_{\mathrm{CF}}=19.9 \mathrm{~Hz}\right)$. HRMS (70 eV): $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{52} \mathrm{H}_{38} \mathrm{~F}_{2} \mathrm{~N}_{2}, 728.3003$; found, 728.3005. Anal. calcd for $\mathrm{C}_{52} \mathrm{H}_{38} \mathrm{~F}_{2} \mathrm{~N}_{2}$ : C 85.69, H 5.25, N 3.84; found: C 85.67; H 5.25, N 3.87.

5d: IR (Nujol): $v=1673$ (m), 1595 (s), 1499 (s), 1336 (m), 1175 (s), 745 (s), 694 (s), $618 \mathrm{~cm}^{-1}$ (s); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): 7.58 (d, $J=8.4 \mathrm{~Hz}, 4 \mathrm{H}), 7.56(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 4 \mathrm{H}), 7.43(\mathrm{t}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H})$, $7.29-7.26(\mathrm{~m}, 8 \mathrm{H}), 7.12(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 8 \mathrm{H}), 7.07(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 8 \mathrm{H}), 6.80$ (dd, $J=8.5,2.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.72$ (dd, $J=8.9,2.2 \mathrm{~Hz}, 2 \mathrm{H}) ;{ }^{13} \mathrm{CNMR}$ $\left(150 \mathrm{MHz}, \quad \mathrm{CDCl}_{3}, \quad \delta\right): \quad 160.9 \quad\left(\mathrm{~d}, \quad J_{\mathrm{CF}}=247.7 \mathrm{~Hz}\right), \quad 148.5 \quad(\mathrm{~d}$, $J_{\mathrm{CF}}=10.1 \mathrm{~Hz}$ ), 146.9, 139.6, 136.7, 129.5, 128.0, 127.2, 127.1, 127.0, 125.1, $123.8, \quad 120.8,118.5 \quad\left(\mathrm{~d}, \quad J_{\mathrm{CF}}=12.5 \mathrm{~Hz}\right), 117.9,109.1 \quad(\mathrm{~d}$, $J_{\mathrm{CF}}=25.2 \mathrm{~Hz}$ ); HRMS ( 70 eV ): $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{52} \mathrm{H}_{38} \mathrm{~F}_{2} \mathrm{~N}_{2}$, 728.3003; found, 728.3003. Anal. calcd for $\mathrm{C}_{52} \mathrm{H}_{38} \mathrm{~F}_{2} \mathrm{~N}_{2}$ : C 85.69, H 5.25, N 3.84; found: C 85.69, H 5.22, N 3.88 .

5e: IR (Nujol): $v=1670$ (m), 1588 (s), 1481 (s), 1257 (m), 1165 (s), $691(\mathrm{~s}), 629 \mathrm{~cm}^{-1}(\mathrm{~s}){ }^{1}{ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): $7.62(\mathrm{~d}, J=8.4 \mathrm{~Hz}$, $4 \mathrm{H}), 7.58(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 4 \mathrm{H}), 7.31(\mathrm{dd}, J=11.6,6.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.27-7.25$ $(\mathrm{m}, 8 \mathrm{H}), 7.19(\mathrm{~s}, 2 \mathrm{H}), 7.11(\mathrm{~s}, 2 \mathrm{H}), 7.05-7.02(\mathrm{~m}, 12 \mathrm{H}), 6.82(\mathrm{dd}$, $J=11.2, \quad 6.8 \mathrm{~Hz}, 2 \mathrm{H}) ;{ }^{13} \mathrm{CNMR}\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 156.5(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=246.2 \mathrm{~Hz}\right), 153.8\left(\mathrm{~d}, J_{\mathrm{CF}}=246.5 \mathrm{~Hz}\right), 146.8,140.1,136.2,134.6(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=11.1 \mathrm{~Hz}\right), 130.1,129.3,127.2,123.3,123.0,121.8\left(\mathrm{~d}, J_{\mathrm{CF}}=7.2 \mathrm{~Hz}\right)$, 119.7, $114.6\left(\mathrm{~d}, J_{\mathrm{CF}}=25.7 \mathrm{~Hz}\right), 113.8 \quad\left(\mathrm{~d}, J_{\mathrm{CF}}=23.3 \mathrm{~Hz}\right) ; \quad H R M S$ (70 eV): $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{52} \mathrm{H}_{36} \mathrm{~F}_{4} \mathrm{~N}_{2}, 764.2815$; found, 764.2811. Anal. calcd for $\mathrm{C}_{52} \mathrm{H}_{36} \mathrm{~F}_{4} \mathrm{~N}_{2}$ : C 81.66, H 4.74, N 3.66; found: C 81.61, H 4.74, N 3.69.

5f: IR (Nujol): $v=1659$ (m), 1581 (s), 1488 (s), 1312 (m), 1211 (s), 1152 (s), 751 (s), $679 \mathrm{~cm}^{-1}$ (s); ${ }^{1} \mathrm{HNMR}$ ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): 7.63 (t, $J=8.1 \mathrm{~Hz}, 2 \mathrm{H}), 7.40(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 4 \mathrm{H}), 7.36(\mathrm{dd}, J=8.1,1.6 \mathrm{~Hz}, 2 \mathrm{H})$, 7.29 (dd, $J=11.8,1.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.27-7.24(\mathrm{~m}, 8 \mathrm{H}), 7.15(\mathrm{~s}, 4 \mathrm{H}), 7.12-7.10$ $(\mathrm{m}, 8 \mathrm{H}), 7.05-7.02(\mathrm{~m}, 8 \mathrm{H}) ;{ }^{13} \mathrm{CNMR}\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 160.6(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=248.3 \mathrm{~Hz}\right), 147.8,147.5,139.6\left(\mathrm{~d}, J_{\mathrm{CF}}=7.4 \mathrm{~Hz}\right), 131.2,130.7,129.3$, $127.6,127.2,124.9\left(\mathrm{~d}, J_{\mathrm{CF}}=12.0 \mathrm{~Hz}\right), 124.6,123.2\left(\mathrm{~d}, J_{\mathrm{CF}}=17.9 \mathrm{~Hz}\right)$, $122.3,118.6,113.8\left(\mathrm{~d}, J_{\mathrm{CF}}=23.3 \mathrm{~Hz}\right) ;$ HRMS $(70 \mathrm{eV}):[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{52} \mathrm{H}_{38} \mathrm{~F}_{2} \mathrm{~N}_{2}$, 728.3003; found, 728.3003. Anal. calcd for $\mathrm{C}_{52} \mathrm{H}_{38} \mathrm{~F}_{2} \mathrm{~N}_{2}$ : C 85.69, H 5.25, N 3.84; found: C 85.72, H 5.22, N 3.84.

7t: IR (Nujol): $v=1655$ (m), 1571 (s), 1465 (s), 1309 (m), 1195 (s), 749 (s), 688 (s), $598 \mathrm{~cm}^{-1}$ (s); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): 7.44 (d, $J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.39-7.30(\mathrm{~m}, 6 \mathrm{H}), 7.20(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 4 \mathrm{H}), 7.16-7.12$ $(\mathrm{m}, 4 \mathrm{H}), 7.07(\mathrm{~d}, J=16.2 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{CNMR}\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right)$ : $155.6\left(\mathrm{dd}, J_{\mathrm{CF}}=241.7,21.2 \mathrm{~Hz}\right), 155.5\left(\mathrm{dd}, J_{\mathrm{CF}}=242.3,21.5 \mathrm{~Hz}\right), 148.2$,
147.2, $131.9\left(\mathrm{~d}, J_{\mathrm{CF}}=4.1 \mathrm{~Hz}\right), 130.1,129.3,129.2,127.7$, $124.6(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=14.6 \mathrm{~Hz}\right), 123.4,122.9,120.3\left(\mathrm{~d}, J_{\mathrm{CF}}=27.5 \mathrm{~Hz}\right), 116.7,112.8(\mathrm{dd}$, $\left.J_{\mathrm{CF}}=24.9,4.1 \mathrm{~Hz}\right), 106.6\left(\mathrm{dd}, J_{\mathrm{CF}}=23.9,10.2 \mathrm{~Hz}\right) ; \operatorname{HRMS}(70 \mathrm{eV})$ : $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{26} \mathrm{H}_{18} \mathrm{BrF}_{2} \mathrm{~N}, 461.0591$; found, 461.0591. Anal. calcd for $\mathrm{C}_{26} \mathrm{H}_{18} \mathrm{BrF}_{2} \mathrm{~N}$ : C 67.54, H 3.92, N 3.03; found: C $67.51, \mathrm{H}, 3.92, \mathrm{~N}$ 3.03.

7u: IR (Nujol): $v=1649$ (m), 1568 (s), 1478 (s), 1302 (m), 1187 (s), 775 (s), 677 (s), $589 \mathrm{~cm}^{-1}(\mathrm{~s}) ;{ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): 7.45 (d, $J=16.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.40(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.30(\mathrm{t}, J=8.0 \mathrm{~Hz}, 4 \mathrm{H}), 7.15$ (d, $J=7.8 \mathrm{~Hz}, 4 \mathrm{H}), 7.10-7.06(\mathrm{~m}, 4 \mathrm{H}), 6.90(\mathrm{~d}, J=16.7 \mathrm{~Hz}, 1 \mathrm{H}) ;$ ${ }^{13}$ CNMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): $148.7\left(\mathrm{~d}, J_{\mathrm{CF}}=25.5 \mathrm{~Hz}\right), 147.2(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=9.9 \mathrm{~Hz}\right), 145.0\left(\mathrm{dd}, J_{\mathrm{CF}}=245.0,15.9 \mathrm{~Hz}\right), 144.5\left(\mathrm{dd}, J_{\mathrm{CF}}=250.6\right.$, $13.4 \mathrm{~Hz}), 137.3\left(\mathrm{t}, J_{\mathrm{CF}}=8.3 \mathrm{~Hz}\right), 129.9,129.4,127.7,124.9,123.5,122.5$, $116.9\left(\mathrm{t}, J_{\mathrm{CF}}=13.4 \mathrm{~Hz}\right), 111.0,96.7\left(\mathrm{t}, J_{\mathrm{CF}}=22.7 \mathrm{~Hz}\right) ; \operatorname{HRMS}(70 \mathrm{eV})$ : $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{26} \mathrm{H}_{16} \mathrm{BrF}_{4} \mathrm{~N}, 497.0402$; found, 497.0408. Anal. calcd for $\mathrm{C}_{26} \mathrm{H}_{16} \mathrm{BrF}_{4} \mathrm{~N}$ : C 62.67, H 3.24, N 2.81; found: C 62.63, H 3.25, N 2.83.

### 4.9. General Procedure for the Synthesis of $\mathbf{5 g}, \mathbf{5 h}$, and $\mathbf{7 v}$

To a dried $N, N$-dimethylformamide (DMF) solution ( 20 mL ) of $\mathrm{Ni}(\mathrm{COD})_{2} \quad(0.65 \mathrm{~g}, 2.38 \mathrm{mmol})$ was added compound $\mathbf{5 g}(1.00 \mathrm{~g}$, 2.16 mmol ), and the reaction mixture was heated at $40^{\circ} \mathrm{C}$ for 16 h . The resulting solution was filtered and dried in vacuo. Chromatography (hexanes:EtOAc $=7: 1, R_{\mathrm{f}}=0.5$ ) afforded $\mathbf{5 g}$ as a yellow solid $(0.86 \mathrm{~g}$, $52 \%$ ).

5g: IR (Nujol): $v=1652$ (m), 1579 (s), 1481 (s), 1325 (m), 1222 (s), 1178 (s), $696 \mathrm{~cm}^{-1}(\mathrm{~s}) ;{ }^{1} \mathrm{HNMR}\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 7.41$ (d, $J=8.7 \mathrm{~Hz}, 4 \mathrm{H}), 7.38-7.36(\mathrm{~m}, 2 \mathrm{H}), 7.30-7.27(\mathrm{~m}, 8 \mathrm{H}), 7.16-7.12(\mathrm{~m}$, $14 \mathrm{H}), 7.09-7.05(\mathrm{~m}, 8 \mathrm{H}) ;{ }^{13} \mathrm{CNMR}\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 155.8(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=244.8 \mathrm{~Hz}\right), 148.1,147.3,131.9,130.4,129.3,127.8,127.1(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=8.7 \mathrm{~Hz}\right), 124.7,123.3,123.1,121.4\left(\mathrm{~d}, J_{\mathrm{CF}}=15.0 \mathrm{~Hz}\right), 117.8(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=25.5 \mathrm{~Hz}\right), \quad 117.4, \quad 112.9 \quad\left(\mathrm{~d}, \quad J_{\mathrm{CF}}=21.6 \mathrm{~Hz}\right) ; \quad \operatorname{HRMS}(70 \mathrm{eV})$ : $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{52} \mathrm{H}_{36} \mathrm{~F}_{4} \mathrm{~N}_{2}, 764.2815$; found, 764.2819. Anal. calcd for $\mathrm{C}_{52} \mathrm{H}_{36} \mathrm{~F}_{4} \mathrm{~N}_{2}$ : C 81.66, H 4.74, N 3.66; found: C 81.62, H 4.71, N 3.69.

5h: IR (Nujol): $v=1647$ (m), 1574 (s), 1476 (s), 1329 (m), 1206 (s), 1172 (s), $688 \mathrm{~cm}^{-1}(\mathrm{~s}) ;{ }^{1} \mathrm{HNMR}\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 7.51$ (d, $J=16.7 \mathrm{~Hz}, 2 \mathrm{H}), 7.42(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 4 \mathrm{H}), 7.29-7.24(\mathrm{~m}, 8 \mathrm{H}), 7.13-7.12$ $(\mathrm{m}, 8 \mathrm{H}), 7.08-7.04(\mathrm{~m}, 8 \mathrm{H}), 6.98(\mathrm{~d}, J=16.7 \mathrm{~Hz}, 2 \mathrm{H}) ;{ }^{13} \mathrm{CNMR}$ $\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 148.9,147.1,144.5\left(\mathrm{dd}, J_{\mathrm{CF}}=241.2,22.8 \mathrm{~Hz}\right)$, $144.2\left(\mathrm{dd}, J_{\mathrm{CF}}=240.1,22.5 \mathrm{~Hz}\right), 138.0\left(\mathrm{t}, J_{\mathrm{CF}}=8.5 \mathrm{~Hz}\right), 129.9,129.3$, 128.1, 124.9, 123.6, 122.3, 111.3; HRMS (70 eV): $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{52} \mathrm{H}_{32} \mathrm{~F}_{8} \mathrm{~N}_{2}, 836.2438$; found, 836.2442. Anal. calcd for $\mathrm{C}_{52} \mathrm{H}_{32} \mathrm{~F}_{8} \mathrm{~N}_{2}$ : C 74.64, H 3.85, N 3.35; found: C 74.63, H 3.85, N 3.36.

7v: IR (Nujol): $v=3021$ (s), 1502 (m), 1159 (s), 1008 (w), 803 (s), 725 (w), $509 \mathrm{~cm}^{-1}$ (w); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): 7.23 (s, 2H), 7.04 (d, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.01(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 2.08(\mathrm{~s}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C} N \mathrm{NR}$ $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 161.9\left(\mathrm{~d}, J_{\mathrm{CF}}=240.6 \mathrm{~Hz}\right), 139.2,128.8,125.6(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=19.2 \mathrm{~Hz}\right), 123.7,113.1\left(\mathrm{~d}, J_{\mathrm{CF}}=8.8 \mathrm{~Hz}\right), 14.6 ; \operatorname{HRMS}(70 \mathrm{eV})$ : $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{14} \mathrm{H}_{12} \mathrm{~F}_{2}, 218.0907$; found, 218.0907. Anal. calcd for $\mathrm{C}_{14} \mathrm{H}_{12} \mathrm{~F}_{2}$ : C 77.05, H 5.54; found: C 77.09, H 5.52.

### 4.10. Synthesis of 7w

To a $\mathrm{CCl}_{4}(35 \mathrm{~mL})$ solution of $7 \mathbf{v}(1.00 \mathrm{~g}, 4.58 \mathrm{mmol})$ were added NBS ( $1.63 \mathrm{~g}, 9.16 \mathrm{mmol}$ ), BPO ( $0.11 \mathrm{~g}, 0.46 \mathrm{mmol})$. The resulting suspension was heated to reflux for 5 h ; after cooling to room temperature, the reaction mixture was extracted with ethyl acetate, washed with aqueous NaCl solution, dried with $\mathrm{MgSO}_{4}$, and concentrated to yield a colorless oil. Chromatography (pure hexanes, $R_{\mathrm{f}}=0.3$ ) afforded a white solid. Triethyl phosphite ( $1.52 \mathrm{~g}, 9.16 \mathrm{mmol}$ ) was added, and the reaction mixture was stirred at $150^{\circ} \mathrm{C}$ for 12 h ; after cooling to room temperature, the reaction mixture was purified by bulb-to-bulb distillation to afford $\mathbf{7 w}$ as a white solid $(1.53 \mathrm{~g}, 68 \%)$.

7w: IR (Nujol): $v=2995$ (m), 1522 (m), 1161 (s), 1018 (w), 809 (s), $725 \mathrm{~cm}^{-1}$ (w); ${ }^{1} \mathrm{HNMR}\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 7.37(\mathrm{dt}, J=7.9,2.5 \mathrm{~Hz}$, $2 \mathrm{H}), 7.25(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.20(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 2 \mathrm{H}), 4.04-3.99(\mathrm{~m}$, $8 \mathrm{H}), 3.17(\mathrm{~d}, J=21.7 \mathrm{~Hz}, 4 \mathrm{H}), 1.22(\mathrm{t}, J=7.4 \mathrm{~Hz}, 12 \mathrm{H}) ;{ }^{13} \mathrm{CNMR}$ $\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 160.9\left(\mathrm{dd}, J_{\mathrm{CF}}=245.7,7.2 \mathrm{~Hz}\right), 140.3,132.1(\mathrm{~d}$,
$\left.J_{\mathrm{CF}}=4.1 \mathrm{~Hz}\right), \quad 122.4, \quad 118.5 \quad\left(\mathrm{dd}, \quad J_{\mathrm{CF}}=15.7, \quad 9.3 \mathrm{~Hz}\right), \quad 113.6 \quad(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=23.3 \mathrm{~Hz}\right), 62.2\left(\mathrm{~d}, J_{\mathrm{CF}}=6.5 \mathrm{~Hz}\right), 25.9\left(\mathrm{~d}, J_{\mathrm{CP}}=139.7 \mathrm{~Hz}\right), 16.2$; HRMS ( 70 eV ): $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{22} \mathrm{H}_{30} \mathrm{~F}_{2} \mathrm{O}_{6} \mathrm{P}_{2}, 490.1486$; found, 490.1483. Anal. calcd for $\mathrm{C}_{22} \mathrm{H}_{30} \mathrm{~F}_{2} \mathrm{O}_{6} \mathrm{P}_{2}$ : C 53.88, H 6.17; found: C 53.88, H 6.19.

### 4.11. General Procedure for the Synthesis of $\mathbf{6 a}, \mathbf{6 b}, \mathbf{6 c}$, and $\mathbf{6 d}$

To a DMF ( 35 mL ) solution of $N, N$-diphenyl-4-vinylbenzenamine $(1.59 \mathrm{~g}, 5.87 \mathrm{mmol})$ were added $\mathbf{8 d}(1.00 \mathrm{~g}, 2.67 \mathrm{mmol}), \mathrm{Pd}(\mathrm{OAc})_{2}$ ( $29.9 \mathrm{mg}, 0.13 \mathrm{mmol}$ ), $\mathrm{PPh}_{4} \mathrm{Br}(0.22 \mathrm{~g}, 0.53 \mathrm{mmol})$, and NaOAc ( $0.91 \mathrm{~g}, 13.4 \mathrm{mmol}$ ) under $\mathrm{N}_{2}$, and the resulting suspension was heated to $100^{\circ} \mathrm{C}$ for 16 h ; after cooling to room temperature, water ( 20 mL ) was added and the yellow precipitate was collected by filtration. Chromatography (hexanes: $\mathrm{EtOAc}=8: 1, R_{\mathrm{f}}=0.4$ ) afforded 6a as a yellow solid ( $1.59 \mathrm{~g}, 79 \%$ ).

6a: IR (Nujol): $v=1653$ (m), 1572 (s), 1488 (s), 1342 (m), 1178 (s), 749 (s), $598 \mathrm{~cm}^{-1}(\mathrm{~s}) ;{ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): $7.58(\mathrm{t}, J=8.0 \mathrm{~Hz}$, $2 \mathrm{H}), 7.36(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 4 \mathrm{H}), 7.32(\mathrm{~s}, 2 \mathrm{H}), 7.28-7.22(\mathrm{~m}, 10 \mathrm{H}), 7.18(\mathrm{~d}$, $J=10.1 \mathrm{~Hz}, 2 \mathrm{H}), 7.11(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 8 \mathrm{H}), 7.06-7.03(\mathrm{~m}, 10 \mathrm{H}), 6.92(\mathrm{~d}$, $J=10.5 \mathrm{~Hz}, \quad 2 \mathrm{H}) ; \quad{ }^{13} \mathrm{CNMR} \quad\left(150 \mathrm{MHz}, \quad \mathrm{CDCl}_{3}, \quad \delta\right): 160.7 \quad(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=248.4 \mathrm{~Hz}\right), 147.8,147.4,139.1\left(\mathrm{~d}, J_{\mathrm{CF}}=7.8 \mathrm{~Hz}\right), 130.8,129.4,129.3$, $127.5,126.9,125.4,124.7,124.0,123.9,123.2\left(\mathrm{~d}, J_{\mathrm{CF}}=8.7 \mathrm{~Hz}\right), 122.4$, 122.2, $112.8\left(\mathrm{~d}, J_{\mathrm{CF}}=22.7 \mathrm{~Hz}\right)$; HRMS $(70 \mathrm{eV}):[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{54} \mathrm{H}_{40} \mathrm{~F}_{2} \mathrm{~N}_{2}, 754.3160$; found, 754.3159 . Anal. calcd for $\mathrm{C}_{54} \mathrm{H}_{40} \mathrm{~F}_{2} \mathrm{~N}_{2}$ : C 85.92, H 5.34, N 3.71; found: C 85.95, H 5.34, N, 3.74.

6b: IR (Nujol): $v=1646$ (m), 1566 (s), 1479 (s), 1345 (m), 1179 (s), 751 (s), 583 (s); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): $7.38(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 4 \mathrm{H})$, $7.30-7.25(\mathrm{~m}, 12 \mathrm{H}), 7.21(\mathrm{~s}, 4 \mathrm{H}), 7.11-7.07(\mathrm{~m}, 10 \mathrm{H}), 7.05-7.02(\mathrm{~m}, 8 \mathrm{H})$; ${ }^{13} \mathrm{CNMR}\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 156.6\left(\mathrm{~d}, J_{\mathrm{CF}}=241.8 \mathrm{~Hz}\right), 156.3(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=243.5 \mathrm{~Hz}\right), 148.0\left(\mathrm{~d}, J_{\mathrm{CF}}=241.8 \mathrm{~Hz}\right), 147.3,131.5,130.5$, 129.3, $129.1,127.7,124.7,123.8,123.3,122.4,122.3\left(\mathrm{~d}, J_{\mathrm{CF}}=19.4 \mathrm{~Hz}\right), 117.6$, $113.0\left(\mathrm{~d}, J_{\mathrm{CF}}=25.1 \mathrm{~Hz}\right), 112.7\left(\mathrm{~d}, J_{\mathrm{CF}}=24.0 \mathrm{~Hz}\right) ; \operatorname{HRMS}(70 \mathrm{eV}):$ $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{54} \mathrm{H}_{38} \mathrm{~F}_{4} \mathrm{~N}_{2}, 790.2971$; found, 790.2975. Anal. calcd for $\mathrm{C}_{54} \mathrm{H}_{38} \mathrm{~F}_{4} \mathrm{~N}_{2}$ : C 82.01, H 4.84, N 3.54; found: C 82.00, H 4.82, N, 3.57.

6c: IR (Nujol): $v=1633$ (m), 1552 (s), 1463 (s), 1329 (m), 1201 (s), 1167 (s), 743 (s), $676 \mathrm{~cm}^{-1}$ (s); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): 7.45 (d, $J=16.4 \mathrm{~Hz}, 4 \mathrm{H}), 7.39(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 4 \mathrm{H}), 7.26(\mathrm{t}, J=8.1 \mathrm{~Hz}, 8 \mathrm{H}), 7.11$ $(\mathrm{d}, J=7.8 \mathrm{~Hz}, 8 \mathrm{H}), \quad 7.07-7.03(\mathrm{~m}, 8 \mathrm{H}), 6.95(\mathrm{~s}, 2 \mathrm{H}) ;{ }^{13} \mathrm{CNMR}$ $\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 148.7,147.2,144.7\left(\mathrm{dd}, J_{\mathrm{CF}}=242.3,23.5 \mathrm{~Hz}\right)$, $144.3\left(\mathrm{dd}, J_{\mathrm{CF}}=239.5,22.1 \mathrm{~Hz}\right), 137.1\left(\mathrm{t}, J_{\mathrm{CF}}=8.7 \mathrm{~Hz}\right), 130.2$, 129.4 , $127.9,125.0,123.6,122.6,122.0,116.7,113.7\left(\mathrm{t}, J_{\mathrm{CF}}=12.5 \mathrm{~Hz}\right), 111.7$; HRMS (70 eV): $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{54} \mathrm{H}_{34} \mathrm{~F}_{8} \mathrm{~N}_{2}, 862.2594$; found, 862.2594. Anal. calcd for $\mathrm{C}_{54} \mathrm{H}_{34} \mathrm{~F}_{8} \mathrm{~N}_{2}$ : C 75.17, H 3.97, N 3.25; found: C 75.19, H 3.97, N 3.26.

6d: IR (Nujol): $v=2934$ (s), 1635 (m), 1597 (s), 1546 (s), 1476 (s), 1435 (m), 1172 (s), 788 (m), $671 \mathrm{~cm}^{-1}$ (s); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$, $\delta): 7.46-7.39(\mathrm{~m}, 6 \mathrm{H}), 6.85(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.64(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 2 \mathrm{H})$, $3.43(\mathrm{t}, J=5.3 \mathrm{~Hz}, 8 \mathrm{H}), 2.29(\mathrm{t}, J=5.1 \mathrm{~Hz}, 8 \mathrm{H}), 1.75(\mathrm{~s}, 24 \mathrm{H}) ;{ }^{13} \mathrm{CNMR}$ $\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta\right): 144.2,143.1\left(\mathrm{~d}, J_{\mathrm{CF}}=249.1 \mathrm{~Hz}\right), 142.8(\mathrm{~d}$, $\left.J_{\mathrm{CF}}=243.2 \mathrm{~Hz}\right), 138.0\left(\mathrm{~d}, J_{\mathrm{CF}}=9.8 \mathrm{~Hz}\right), 135.2,128.7,127.7,123.2,121.1$, 108.5, 104.8, 49.6, 35.0, 29.7, 25.7; HRMS (70 eV): $[M+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{50} \mathrm{H}_{50} \mathrm{~F}_{8} \mathrm{~N}_{2}, 830.3846$; found, 830.3849. Anal. calcd for $\mathrm{C}_{50} \mathrm{H}_{50} \mathrm{~F}_{8} \mathrm{~N}_{2}$ : C 72.27, H 6.07, N 3.37; found: C 72.28, H 6.06, N 3.40.

### 4.12. Measurement of Quantum Yields and Photoelectron Spectra

Steady-state absorption and emission spectra were recorded with a Hitachi U-3310 spectrophotometer and an Edinburgh FS920 fluorimeter, respectively. Both the wavelength-dependent excitation and emission response of the fluorimeter were calibrated. A configuration of front-face excitation was used to measure the emission of the solid sample, in which the cell was made by assembling two edge-polished quartz plates with various Teflon spacers. A combination of appropriate filters was used to avoid interference from scattered light. For measurements of the PL quantum yields in solution, 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM, $\lambda_{\mathrm{em}}=620 \mathrm{~nm}$,

Exciton, Inc.) in methanol served as a reference, assuming a quantum yield of 0.43 with 460 nm excitation [22]. An integrating sphere was applied to measure the quantum yield in the solid state, for which the solid sample film was prepared via vapor-deposition methods and was excited by a $365 \mathrm{~nm} \mathrm{Ar}^{+}$laser line ( ca .1 mW ); an intensified chargecoupled detector served for subsequent analyses of the quantum yield of the resulting luminescence. To obtain the PL quantum yield in the solid state, we collected the emission with an integrating sphere and calculated the quantum yield according to a reported method [23].

### 4.13. OLED Fabrication and Measurements

Prepatterned ITO substrates with an effective individual device area of $3.14 \mathrm{~mm}^{2}$ were cleaned by sonication in a detergent solution for 3 min and then washed copiously with doubly distilled water. Further sonication in ethanol for 3 min was carried out before blow-drying with a stream of nitrogen. The ITO substrates were then treated with $\mathrm{O}_{2}$ plasma for 1 min before being loaded into the vacuum chamber. The organic layers were deposited thermally at a rate of $0.1-0.3 \mathrm{~nm} \mathrm{~s}^{-1}$ at a pressure of ca. $5 \times 10^{-6}$ Torr in an Ulvac Cryogenic deposition system. Typical devices were constructed with CuPc as the hole-injection layer (HIL, 30 nm ), NPB as the hole-transporting layer (HTL, 40 nm ), ADN ( 30 nm ) doped with $3 \%$ organic oligomers as the emission layer, and $\mathrm{Alq}_{3}(30 \mathrm{~nm})$ as the electron-transporting layer (ETL). An alloy of magnesium and silver (ca. 10:1, 50 nm ) was deposited as the cathode, which was capped with 100 nm of silver. The current density-voltageluminance behavior of the diodes was measured under ambient conditions with a Keithley 2400 source meter and an Newport 1835C optical meter equipped with an 818 ST silicon photodiode. The luminance is expressed as:
$\mathrm{L}^{\infty}=\int \mathrm{V}(\lambda)^{*} \mathrm{f}(\lambda) \mathrm{d} \lambda$
where $L$ represents the luminance, $V(\lambda)$ is the visual function with a 555 nm peak, decreasingly rapidly from 555 nm to the blue or red region, and $f(\lambda)$ is the relative EL intensity at each wavelength obtained on measuring the EL spectrum.

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[1] a) J.-S. Yang, S.-Y. Chiuo, K.-L. Liau, J. Am. Chem. Soc. 2002, 124, 2518. b) F. D. Lewis, R. S. Kalgutkar, J.-S. Yang, J. Am. Chem. Soc. 1999, 121, 12045 . c) U. F. W. Bunz, Chem. Rev. 2000, 100, 1605.
[2] a) M. Rumi, J. E. Ehrlich, A. A. Heikal, J. W. Perry, S. Barlow, Z. Hu, D. McCord-Maughon, T. C. Parker, H. Röckel, S. Thayumanavan, S. R. Marder, D. Beljonne, J.-L. Bredas, J. Am. Chem. Soc. 2000, 122, 9500. b) J.-F. Létard, R. Lapouyade, W. Retting, J. Am. Chem. Soc. 1993, 115, 2441.
[3] a) E. N. Bokeriya, V. S. Viktorova, L. I. Karegishvili, K. A. Kovyrzina, Y. P. Kushakevich, L. A. Radaikina, Russ. J. Org. Chem. 1979, 15, 1944. b) S. Nakatsuji, K. Matsuda, Y. Uesugi, K. Nagashima, S. Akiyama, G. Katzer, W. Fabian, J. Chem. Soc. Perkin Trans. 2 1991, 861.
$[4] \quad$ a) H. Görner, H. J. Kuhn, Adv. Photochem. 1995, 19, 1. b) D. H. Waldeck, Chem. Rev. 1991, 91, 415. c) J. Saltiel, A. S. Waller, D. F. Sears, E. A. Hoburg, D. M. Zeglinski, D. H. Waldeck, J. Phys. Chem. 1994, 98, 10 689. d) J. Saltiel, A. S. Waller, D. F. Sears, C. Z. Garrett, J. Phys. Chem. 1993, 97, 2516.
[5] a) C.-T. Chen, C.-L. Chiang, Y.-C. Lin, L.-H. Chan, C.-H. Huang, Z.-W. Tsai, C.-T. Chen, Org. Lett. 2003, 5, 1261. b) C.-W. Ko, Y.-T. Tao, A. Danel, L. Krzeminska, P. Tomasik, Chem. Mater. 2001, 13, 2441. c) C. W. Tang, S. A. Van Slyke, C. H. Chen, J. Appl. Phys. 1989, 65, 3610. d) J. R. Sheats, H. Antoniadis, M. Mueschen, W. Leonard, J. Miller, R. Moon, D. Roitman, A. Stocking, Science 1996, 273, 884.
[6] a) C.-L. Li, S.-J. Shieh, S.-C. Lin, R.-S. Liu, Org. Lett. 2003, 5, 1131. b) J. Margado, F. Cacialli, R. H. Friend, B. S. Chuah, H. Rost, A. B. Holmes, Macromolecules 2001, 34, 3094. c) S. Wang, W. J. Oldham, R. A. Hudack, G. C. Bazan, J. Am. Chem. Soc. 2000, 122, 5695. d) M.-T. Lee, H.-H. Chen, C.-H. Liao, C.-H. Tsai, C.-H. Chen, Appl. Phys. Lett. 2004, 85, 3301.
[7] a) M.-S. Wong, Z.-H. Li, Pure Appl. Chem. 2004, 76, 1409. b) M.-S. Wong, Z.-H. Li, Y. Tao, M. D'lorio, Chem. Mater. 2003, 15, 1198. c) S.-C. Jain, W. Greens, A. Mehra, V. Kumar, T. Aernouts, J. Poortmans, R. Mertens, M. Willander, J. Appl. Phys. 2001, 89, 3804. d) M.-S. Wong, Z.-H. Li, M.-F. Shek, K.-H. Chow, Y. Tao, M. D'lorio, J. Mater. Chem. 2000, 10, 1805.
[8] a) T. Goodson, W.-J. Li, A. Gharavi, L.-P. Yu, Adv. Mater. 1997, 9, 639. b) G. Cheng, Z. Xie, Y. Zhao, Y.-F. Zhang, H. Xia, Y.-G. Ma, S.-Y. Liu, Thin Solid Films 2005, 484, 54. c) M. R. Robinson, S.-J. Wang, G. C. Bazan, Y. Cao, Adv. Mater. 2000, 12, 1701.
[9] a) T. Maddux, W. Li, L. Yu, J. Am. Chem. Soc. 1997, $119,844$. b) K. D. Shrishendu, T. Maddux, L. Yu, J. Am. Chem. Soc. 1997, 119, 9079.
[10] a) I.-N. Kang, H.-K. Shim, T. Zyung, Chem. Mater. 1997, 9, 746. b) I. R. Laskar, T.-M. Chen, Chem. Mater. 2004, 16, 111. c) M. L. Renak, G. P. Bartholomew, S. Wang, P. J. Ricatto, R. J. Lachicotte, G. C. Bazan, J. Am. Chem. Soc. 1999, 121, 7787.
[11] a) O. Garcia, R. Sastre, D. del Agua, A. Costela, I. Garcia-Moreno, Chem. Mater. 2006, 18, 601. b) Y. Wang, N. Herron, V. V. Grushin, D. LeCloux, V. Petrov, Appl. Phys. Lett. 2001, 79, 449. c) T. Tsuzuki, N. Shirasawa, T. Suzuki, S. Tokito, Adv. Mater. 2003, 15, 1455. d) R. M. Gurge, A. M. Sarker, P. M. Lahti, B. Hu, F. E. Karasz, Macromolecules 1997, 30, 8286.
[12] L. F. Hartwig, M. Kawatsura, S. I. Hauck, K. H. Shaughnessy, L. M. Alcazar-Roman, J. Org. Chem. 1999, 64, 5575.
[13] J. F. Reichwein, B. L. Pagenkopf, J. Am. Chem. Soc. 2003, 125, 1821.
$[14] ~ a)$ W. Cabri, I. Candiani, A. Bedeschi, R. Santi, J. Org. Chem. 1992, 57, 3558. b) W. Cabri, I. Candiani, A. Bedeschi, R. Santi, Synlett 1992, 871.
[15] R. Barhdadi, C. Courtinard, J. Y. Nedelec, M. Troupel, Chem. Comтип. 2003, 1434.
[16] a) T. R. Manfred, L. Gunther, S. Renate, Angew. Chem. Int. Ed. 1998, 37, 481. b) S. V. Rajender, P. N. Kannan, J. L. Per, Tetrahedron Lett. 1999, 40, 2075.
[17] V. V. Grushin, A. Petrov, Y. Wang, Chem. Commun. 2001, 1494.
$[18] ~ a) ~ T . ~ S u z u k i, ~ Y . ~ T a g a, ~ J . ~ A m . ~ C h e m . ~ S o c . ~ 2000, ~ 122, ~ 1832 . ~ b) ~ T . ~ S u z u k i, ~, ~$ Y. Taga, J. Am. Chem. Soc. 2000, 122, 10240.
[19] a) B. K. Shah, D. C. Neckers, J. Shi, E. W. Forsythe, D. Morton, Chem. Mater. 2006, 18, 603. b) A. P. Kulkarni, A. P. Gifford, C. J. Tonzola, S. A. Jenekhe, Appl. Phys. Lett. 2005, 86, 061 106. c) J. Shi, C. W. Tang, Appl. Phys. Lett. 2002, 80, 3201. d) C. Hosokawa, H. Higashi, H. Nakamura, T. Kusumoto, Appl. Phys. Lett. 1995, 67, 3853. e) Y. Kan, L.-D. Wang, L. Duan, Y.-C. Hu, G.-S. Wu, Y. Qiu, Appl. Phys. Lett. 2004, 84, 1513. f) W.-J. Shen, R. Dohha, C.-C. Wu, F.-I. Wu, T.-H. Liu, H.-H. Chen, C.-H. Chen, C.-F. Shu, Chem. Mater. 2004, 16, 930. g) Y. Z. Wu, X. Y. Zheng, W. Q. Zhu, R. G. Sun, X. Y. Jiang, Z. L. Zhang, S. H. Xu, Appl. Phys. Lett. 2003, 83, 5077.
$[20] ~ a)$ C. Adachi, R. C. Kwong, P. Djurovich, V. Adamovich, M. A. Baldo, M. E. Thompson, S. R. Forrest, Appl. Phys. Lett. 2001, 79, 2082. b) R. J. Holmes, S. R. Forrest, Y.-J. Tung, R. C. Kwong, J. J. Brown, S. Garon, M. E. Thompson, Appl. Phys. Lett. 2003, 82, 2422. c) S. Tokito, T. Iijima, Y. Suzuri, H. Kita, T. Tsuzuki, F. Sato, Appl. Phys. Lett. 2003, 85, 569. d) R. J. Holmes, B. W. D'Andrade, S. R. Forrest, X. Ren, J. Li, M. E. Thompson, Appl. Phys. Lett. 2003, 83, 3818.
[21] T. Aimono, Y. Kawamura, K. Goushi, H. Yamamoto, H. Sasabe, C. Adachi, Appl. Phys. Lett. 2005, 86, 071110.
[22] J. M. Drake, M. L. Lesiecki, D. M. Camaioni, Chem. Phys. Lett. 1985, 113, 530.
[23] J. C. de Mello, H. F. Wittmann, R. H. Friend, Adv. Mater. 1997, 9, 230.


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