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

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New fluoro derivatives of Ph<sub>2</sub>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 ( $\eta_{ext} = 4.87\%$ ) at J = 20 mA cm<sup>-2</sup>; the maximum brightness at 10.2 V is 22 506 cd m<sup>-2</sup> ( $\lambda = 458$  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.<sup>[1,2]</sup> 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.<sup>[3,4]</sup> 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.<sup>[5-8]</sup> Scheme 1 shows representative molecules 1 and 3 (R = H) that have been employed as blue emitters ( $\lambda = 470-480$  nm) in OLED devices.<sup>[6a,d]</sup> We attempted to introduce cyano groups at the central aryl groups, as indicated by compounds 2 and 4 (R = CN), to obtain long-wavelength emissions.<sup>[6a]</sup> 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  $Ph_2N$ -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 ( $\lambda = 541$  nm) whereas its regioisomer **2b** radiates in the blue region of the spectrum ( $\lambda = 472$  nm). We rationalize such a varied behavior with the effects of extended conjugation.<sup>[9]</sup> Despite successful color tuning, there are several drawbacks associated with cyano-containing derivatives **2** and **4** that hamper their applications in OLEDs:<sup>[6a]</sup> (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 **2b** show only a moderate performance (Commission Internationale de l'Eclairage

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(CIE) coordinates x = 0.15, y = 0.18) with a maximum external quantum efficiency ( $\eta_{ext}$ ) of 2.12 %, power and luminance efficiencies of 1.33 lm W<sup>-1</sup> and 3.14 cd A<sup>-1</sup>, respectively, and a maximum brightness ( $L_{max}$ ) of 11 190 cd m<sup>-2</sup> (12 V). In the present work, we sought to achieve the color tuning of these Ph<sub>2</sub>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<sup>[10]</sup> but also improves the efficiency of phosphoresecent or fluorescent emission,<sup>[11]</sup> 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 **5a–h** and **6a–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 (**5a–h**) and 4 (**6a–d**). As shown in Scheme 3 (reaction 1), we first prepared diphenylamine species **7a** and **7b** via Buchwald–Hartwig coupling<sup>[12]</sup> reactions



Scheme 2. Structures of targeted fluoro-substituted oligo(arylenevinylene) derivatives.

using Pd<sub>2</sub>(dba)<sub>3</sub>, 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 **7d** via a second coupling reaction using  $Pd(OAc)_2/$ (t-Bu)<sub>3</sub>P/t-BuONa (Ac: acetate). The final Horner-Wadsworth-Emmons reaction<sup>[13]</sup> produced the desired bis(diphenylamino)arylenevinylenes 5a and 5b exclusively in E-form<sup>[14]</sup> (>96%). The procedures for the preparation of target compounds 5c-e, for which we used fluoro-substituted 4-bromobenzaldehydes 7g-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 7g-i were further masked, and ultimately efficiently transformed into the desired oligomers 5c-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 5f-h with fluoro substituents at the central biphenyl groups. 4-Bromobenzaldehydes 7i and 7j were first converted to benzyl bromides, and subsequently to phosphates 7r and 7s. Olefination of these phosphates with 4-aminobenzaldehyde afforded 4-diphenylamino-stilbenes 7t and 7u smoothly. A Ni(COD)<sub>2</sub>-mediated (COD: 1,5-cyclooctadiene) coupling reaction<sup>[15]</sup> of species 7t and 7u delivered the desired arylenevinylene species 5g and 5h in 52% and 43% yields, respectively. The remaining fluorine-containing oligomer 5f 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 Ph<sub>2</sub>N-containing (arylenevinylene) compounds 6a-d in another class are described in Scheme 4. The key phosphates 8ac were prepared easily from the benzyl bromide 7f or benzaldehydes 7i and 7j 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 7h-j. A final Pd-catalyzed double-Heck olefination<sup>[16]</sup> of these species with 4-diphenylaminostyrene delivered the desired arylenevinylene oligomers **6a–c** in exclusive *E*-configuration with yields in the range of 50-79%. A similar coupling reaction of species 8f with 4-(biscyclohexylamino)styrene gave compound 6d in 42 % yield.

# 2.2. Photophysical Properties

Figures 1 and 2 show the UV-vis and photoluminescence (PL) absorption spectra of representative compounds **5a**, **5b**, **5d**, **5e**, **5f**, **5h**, and **6a**–**d**, respectively. The PL absorption bands of their corresponding unsubstituted complexes 1 and 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





**Scheme 3.** Synthetic protocol for  $Ph_2N$ -containing oligo(arylenevinylene)s **5a–h**. Conditions: (a)  $Pd_2(dba)_3$  (2 mol%), DPPF (4 mol%), t-BuONa (1.1 eq), toluene, 110 °C, 12 h; (b)  $Pd(OAc)_2$  (2 mol%),  $P(t-Bu)_3$  (4 mol%), toluene, 110 °C, 12 h; (c)  $1 \times HCl$ , acetone; (d) t-BuONa (2.2 eq), THF, 24 h; (e) NBS (1 eq), BPO (1%),  $CCl_4$ , reflux, 5 h; (f) NaHCO<sub>3</sub> (9 eq), DMSO, 70 °C, 1 h; (g) *n*-BuLi (1 eq), ethyl formate, diethyl ether, -78 °C to room temperature; (h) PTSA (5%), ethylene glycol, benzene, reflux, 24 h; (i) NaBH4 (1.5 eq), methanol; (j) PBr<sub>3</sub>,  $CH_2Cl_2$ ; (k)  $P(OEt)_3$ , 150 °C, 12 h; (l) Ni(COD)<sub>2</sub> (1.1 eq.), DMF, 40 °C, 16 h. See the Experimental section for full details.



**Scheme 4.** Synthetic protocol of Ph<sub>2</sub>N-containing oligo(arylenevinylene) **6a**–d. Conditions: (a) *t*-BuONa, THF, 24 h; (b) Pd(OAc)<sub>2</sub> (4 mmol%), PPh<sub>4</sub>Br (20 mmol%), NaOAc (5 eq.), DMF, 100 °C, 16 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 5c and 5d, produce similar hypsochromic effects but the shifts are smaller, ca. 9-17 nm. In contrast, species 5f-h, bearing fluorine groups at the inner biphenyl group, emissions at 505–527 nm; red-shifted show ca. 25-47 nm relative to the unsubstituted species 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 nm. On the basis of these color-tuning effects, we reasonably expect that the HOMOs of structures 1 and 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 **5a,b**, **5d–f**,and **5h**.

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.<sup>[10,11]</sup> The quantum yields of 5a-h and 6a-d in CH<sub>2</sub>Cl<sub>2</sub> solution at 25 °C are given in Table 1; the corresponding values for unsubstituted species 1 and 3 are 0.86 and 0.84, respectively. Outstanding quantum yields are found for the blue emitters 5a-e  $(\Phi = 0.91 - 0.81, \lambda = 448 - 471 \text{ nm})$ , blue-green emitters **5f-h** and **6a** ( $\phi = 0.91 - 0.93$ ,  $\lambda = 505 - 527$  nm), yellow emitter **6b**  $(\Phi = 0.95, \lambda = 555 \text{ nm})$ , and orange emitters **6c** and **6d**  $(\Phi = 0.68 - 0.72, \lambda = 568 - 579 \text{ nm}).$  4-Diphenylaminostilbenes generally have quantum yields in solution about ten times those of their dialkylamino analogues.<sup>[1a]</sup> 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 C-F vibrational frequency.<sup>[17,18]</sup>



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

# 2.3. Electrochemical Data and Energy Gaps

Table 1 shows electrochemical data obtained through cyclic voltammetry (CV) measurements using  $Bu_4NPF_6$  (0.1 M in  $CH_2Cl_2$ ) and  $Bu_4NClO_4$  (0.1 M in tetrahydrofuran (THF)) as supporting electrolytes in anodic oxidation and cathodic reduction, respectively.<sup>[6a]</sup> 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 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 **6c**. The HOMO and LUMO energy levels of species **5a–h** and **6a–d**, obtained from the oxidation potentials and UV absorption measurements, are shown in Table 1 and Figure 4.



Compound	Abs λ <sub>max</sub> [a] (nm)	PL λ <sub>max</sub> (nm)	F <sub>f</sub>	oxid E <sub>1/2</sub> (V)	HOMO (eV)	Bandgap (eV)	LUMO (eV)
5a	296(67569) 393(176129)	462	0.91	1.26	5.66	2.93	2.73
5b	292(30657) 383(132310)	448	0.83	1.19 1.45	5.59	2.88	2.71
5c	294(71162) 386(152645)	471	0.83	1.12 1.36	5.52	2.80	2.72
5d	295 (66758) 394 (149709)	469	0.82	1.11 1.37	5.51	2.79	2.72
5e	298(56308) 396(146774)	463	0.81	1.21 1.48	5.61	2.89	2.72
5f	302(93534) 406(182013)	505	0.93	1.01 1.22	5.41	2.65	2.76
5g	301 (108319) 406 (176129)	509	0.91	1.02	5.42	2.61	2.81
5h	301 (119415) 416 (179065)	527	0.92	1.03	5.43	2.57	2.86
6a	304(70393) 424(178854)	523	0.92	1.01	5.41	2.59	2.82
6b	305(87101) 435(189022)	555	0.95	1.02 1.16	5.42	2.49	2.93
6с	331 (48578) 443 (97683)	573	0.68	1.02 1.19	5.42	2.42	3.00
6d	327(42310) 447(111212)	579	0.72	1.04	5.44	2.39	3.05

 
 Table 1. Photophysical and electrochemical data of species 5a-5h and 6a-6d.

[a] Values in parentheses represent the molar extinction coefficients, expressed in  $M^{-1}$  cm<sup>-1</sup>. Data were obtained from CH<sub>2</sub>Cl<sub>2</sub> solutions.



Figure 3. CV curves of fluoro-substituted oligo (arylenevinylene)s 5d and 6c.

To rationalize the trends of the energy gaps of these fluorosubstituted chromophores, we performed a theoretical simulation of the HOMO and LUMO of compound **5c** by using its X-ray crystallographic data. The resulting HOMO–LUMO maps of compound **5c** 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 5a-h, 6a-d, and unsubstituted species 1 and 3.

their LUMO levels. These results rationalize the hypsochromic effects of the fluoro substituents of species **5a–c** and **5d,e** relative to parent species **1**. Compounds **5f–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 **6a** and **6b** follow the same trend as for **5f–h**, because their fluoro substituents are located on the inner stilbene moiety.

# 2.4. Electroluminescence Properties

The parent species 1 and 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 nm) because of the hypso- and bachochromic effects. Our interest lies in deep-blue emitters ( $\lambda = 440-470$  nm), because few efficient emitters have been reported for both fluorescent and phosphorescent emission.<sup>[19,20]</sup> We selected compounds **5a**, **5d**, and **5e** 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 **5a** embedded in various host materials. Because the quantum yield of **5a** embedded in 9,10-di(2-naphthyl)anthracene (ADN) ( $\Phi \approx 89\%$ ) was found to





Figure 5. Crystal structure of 5c (top), and a theoretical simulation of its HOMO and LUMO.

be 30 % greater than that of **5a** embedded in 4,4'-bis(9-carbazolyl)-biphenyl (CBP,  $\Phi \approx 68$  %),<sup>[21]</sup> ADN served as the host material in this work. OLEDs were fabricated by high-vacuum (5 × 10<sup>-6</sup> Torr, 1 Torr = 1.333 × 10<sup>2</sup> Pa) thermal evaporation onto precleaned glass substrates. The devices consisted of indium tin oxide (ITO)/copper phthalocyanine (CuPc, 30 nm)/ 4,4'-bis(*N*-naphthylphenylamino)biphenyl (NPB, 40 nm)/dopant (3 %) in ADN (30 nm)/tris(8-hydroxyquinoline)aluminum(III) (Alq, 30 nm)/Mg: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 **5e** 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 mA cm<sup>-2</sup>. All three stilbene-based devices exhibited blue emissions in the region 456–462 nm with a vibrational shoulder at 482–487 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 **5a**, **5d**, and **5e** 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 **5d**, and x = 0.16, y = 0.25 for **5e**.

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  $J = 20 \text{ mA cm}^{-2}$  for devices 5a, 5d, and 5e are 5.7, 8.3, and 7.5 V, respectively. Figure 7 shows the external quantum efficiency-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  $22\,506 \text{ cd m}^{-2}$  and  $21\,423 \text{ cd m}^{-2}$ , respectively. The external quantum efficiency  $(\eta_{\text{ext}})$  of **5a** was 4.48 % at  $J = 20 \text{ mA cm}^{-2}$ , with a luminance efficiency and a power

efficiency of 5.47 cd A<sup>-1</sup> and 3.00 lm W<sup>-1</sup>, respectively. As shown in Figure 7, the  $\eta_{\text{ext}}$  gradually decreased to 3.92 % at  $J = 400 \text{ mA cm}^{-2}$ , for which the luminance efficiency and power efficiency were 4.79 cd A<sup>-1</sup> and 1.63 lm W<sup>-1</sup>, respectively. In comparison, the  $\eta_{\text{ext}}$  value of species **5e** was 3.47 % at  $J = 20 \text{ mA cm}^{-2}$ , with a luminance efficiency and power efficiency of 6.78 cd A<sup>-1</sup> and 2.84 lm W<sup>-1</sup>, respectively. The EL data shown in Table 2, particularly for **5a**, are excellent compared to recently reported data on blue fluorophores,<sup>[19]</sup> most of which show a maximum  $\eta_{\text{ext}}$  of ca. 3–4 % with CIE co-

Table 2. Electroluminescence characteristics of OLEDs based on 5a, 5d, and 5e.

Compound	Brightness (cd m <sup>-2</sup> )	η <sub>ext</sub> (%)	Luminance efficiency (cd A <sup>-1</sup> )	Power efficiency (Im W <sup>-1</sup> )	Voltage (V)	CIE coordinates [d]
	576 [a]	4.48	5.47	3.00	5.74	x = 0.14
5a	3748 [b]	4.81	5.88	2.55	7.24	y = 0.14
	22506 [c]	4.87	5.91	3.01		(456 nm)
	1139	3.51	5.69	2.16	8.28	x = 0.12
5d	5602	3.45	5.60	1.70	10.38	y = 0.21
	17992	3.53	5.74	2.54		(462 nm)
5e	1356	3.47	6.78	2.84	7.51	x = 0.16
	6239	3.19	6.24	2.04	9.62	y = 0.25
	21423	3.51	6.87	3.40		(458 nm)

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





Figure 6. Electroluminescence spectra of ADN, 5a, 5d, and 5e.



Figure 7. External quantum efficiencies of ADN, species 5a, 5d, and 5e as a function of current densities.



Figure 8. J–V–L characteristics of OLEDs based on ADN, species 5a, 5d, and 5e.

ordinates x = 0.13-0.16, y = 0.16-0.32. The EL parameters for species **5a** reflect its promising application in OLED devices.

# 3. Conclusions

We have prepared fluoro-substituted Ph<sub>2</sub>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 cd A<sup>-1</sup> at J = 53 mA cm<sup>-2</sup>, together with a high power efficiency of 3.01 lm W<sup>-1</sup> at J = 21 mA cm<sup>-2</sup> 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 g, 8.99 mmol) were added 4-fluorophenylamine (1.00 g, 8.99 mmol), sodium *tert*-butoxide (1.04 g, 10.79 mmol),  $Pd_2(dba)_3$  (0.16 g, 0.18 mmol) and 1,1'-bis(diphenylphosphino)ferrocene (DPPF, 0.20 g, 0.36 mmol) under N<sub>2</sub>. 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 MgSO<sub>4</sub>, and concentrated to yield a brownish oil. Chromatography (hexanes:EtOAc=10:1,  $R_f$ =0.7) afforded bis(4-fluorophenyl)amine (**7a**) as a white solid (1.31 g, 71 %).

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

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

To a toluene (35 mL) solution of 2-(4-bromophenyl)-1,3-dioxolane (1.12 g, 4.87 mmol) were added **7a** (1.00 g, 4.87 mmol), sodium *tert*butoxide (0.52 g, 5.36 mmol), Pd(OAc)<sub>2</sub> (21.9 mg, 0.10 mmol) and P(*t*-Bu)<sub>3</sub> (39.4 mg, 0.20 mmol) under N<sub>2</sub>, and the resulting suspension was heated to reflux for 12 h. After cooling to room temperature, 1 N



HCl (10 mL) and acetone (20 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 MgSO<sub>4</sub>, and concentrated to yield a brownish oil. Chromatography (hexanes:EtOAc = 8:1,  $R_f$  = 0.4) afforded 4-[bis(4-fluorophenyl)amino]benzaldehyde (**7c**) as a light yellow solid (1.33 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 cm<sup>-1</sup> (m); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 9.78 (s, 1H), 7.65 (d, J = 8.2 Hz, 2H), 7.13–7.11 (m, 4H), 7.03 (t, J = 8.0 Hz, 4H), 6.90 (d, J = 8.2 Hz, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>,  $\delta$ ) 190.3, 160.1 (d,  $J_{CF} = 244.8$  Hz), 153.3, 141.9, 131.4, 129.0, 128.0 (d,  $J_{CF} = 8.0$  Hz), 118.3, 116.7 (d,  $J_{CF} = 22.7$  Hz); HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>19</sub>H<sub>13</sub>F<sub>2</sub>NO; C73.78, H 4.24, N 4.53; found: C 73.75, H 4.25, N 4.56.

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

**70**: IR (Nujol): v = 1708 (s), 1595 (s), 1488 (s), 1335 (m), 1276 (m), 1168 (s), 758 (s), 696 (s), 621 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 10.08 (s, 1H), 7.63 (t, J = 8.4 Hz, 1H), 7.34 (t, J = 8.0 Hz, 4H), 7.20–7.17 (m, 6H), 6.70 (dd, J = 8.8, 2.1 Hz, 1H), 6.55 (dd, J = 13.6, 2.2 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>,  $\delta$ ): 185.1 (d,  $J_{CF} = 5.4$  Hz), 165.9 (d,  $J_{CF} = 255.2$  Hz), 154.9, 145.2, 129.8, 129.4 (d,  $J_{CF} = 3.3$  Hz), 126.6, 125.8, 116.3, 114.3, 104.5 (d,  $J_{CF} = 24.9$  Hz); HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>19</sub>H<sub>14</sub>FNO, 291.1059; found, 291.1058. Anal. calcd for C<sub>19</sub>H<sub>14</sub>FNO: 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 (s), 509 cm<sup>-1</sup> (m); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 10.09 (s, 1H), 7.63 (t, J = 8.3 Hz, 1H), 7.34 (t, J = 8.4 Hz, 4H), 7.20–7.16 (m, 7H), 6.70 (dd, J = 8.8, 2.1 Hz, 1H), 6.55 (dd, J = 13.5, 2.1 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>,  $\delta$ ): 185.1 (d,  $J_{CF} = 5.4$  Hz), 165.9 (d,  $J_{CF} = 255.2$  Hz), 154.9 (d,  $J_{CF} = 11.6$  Hz), 145.2, 129.8, 129.4 (d,  $J_{CF} = 24.9$  Hz); 126.6, 125.8, 116.4 (d,  $J_{CF} = 8.6$  Hz), 114.3, 104.5 (d,  $J_{CF} = 24.9$  Hz); HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>19</sub>H<sub>14</sub>FNO; C78.33, H 4.84, N 4.81; found: C 78.35, H 4.83, N 4.86.

**7q:** IR (Nujol):  $\nu$ =1711 (s), 1586 (s), 1493 (s), 1336 (m), 1279 (m), 1173 (s), 754 (s), 695 (s), 622 (s), 501 cm<sup>-1</sup> (m); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 10.12 (d, *J*=2.5 Hz, 1H), 7.49 (dd, *J*=11.3, 6.2 Hz, 1H), 7.28 (t, *J*=8.0 Hz, 4H), 7.12 (t, *J*=7.4 Hz, 2H), 7.05 (t, *J*=7.9 Hz, 4H), 6.74 (dd, *J*=11.6, 6.2 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>,  $\delta$ 184.5): (d, *J*<sub>CF</sub>=4.1 Hz), 161.2 (d, *J*<sub>CF</sub>=25.4 Hz), 151.9 (d, *J*<sub>CF</sub>=248.9 Hz), 145.9, 142.4 (t, *J*<sub>CF</sub>=10.9 Hz), 129.3 (d, *J*<sub>CF</sub>=29.8 Hz), 124.8, 124.3, 118.4 (dd, *J*<sub>CF</sub>=25.5 Hz); HRMS (70 eV): [*M*+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>13</sub>F<sub>2</sub>NO, 309.0965; found, 309.0966. Anal. calcd for C<sub>19</sub>H<sub>13</sub>F<sub>2</sub>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 CCl<sub>4</sub> (50 mL) solution of 4-bromo-3-fluorotoluene (7.00 g, 37.03 mmol) were added NBS (6.59 g, 37.03 mmol), benzoyl peroxide (BPO, 0.45 g, 1.85 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 MgSO<sub>4</sub>, and concentrated to yield a colorless oil. Chromatography (pure hexanes,  $R_f$ =0.7) afforded 4-bromo-1-bromomethyl-2-fluorobenzene (**7e**) as a colorless oil (8.14 g, 82%).

**7e**: IR (Nujol): v = 1586 (s), 1491 (s), 1235 (s), 877 (m), 835 (m), 615 (s), 530 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.50 (t, J = 7.6 Hz, 1H), 7.14 (d, J = 7.2 Hz, 1H), 7.04 (d, J = 7.2 Hz, 1H), 4.39 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 161.2 (d,  $J_{CF} = 251.5$  Hz), 138.8, 134.1, 133.9, 125.9 (d,  $J_{CF} = 13.1$  Hz), 120.4 (d,  $J_{CF} = 23.8$  Hz), 24.8. HRMS (70 eV):  $[M + H]^+$  calcd for  $C_7H_5Br_2F$ , 265.8742; found, 265.8744. Anal. calcd for  $C_7H_5Br_2F$ : 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 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.24–7.20 (m, 3H), 4.41 (s, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>,  $\delta$ ): 160.3 (d,  $J_{CF} = 253.5$  Hz), 132.2, 127.9, 124.4 (d,  $J_{CF} = 14.3$  Hz), 123.0 (d,  $J_{CF} = 9.2$  Hz), 119.5 (d,  $J_{CF} = 24.3$  Hz), 24.7; HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>7</sub>H<sub>5</sub>Br<sub>2</sub>F; 265.8742; found, 265.8742. Anal. calcd for C<sub>7</sub>H<sub>5</sub>Br<sub>2</sub>F: C 31.38, H 1.88; found: C 31.38, H 1.89.

#### 4.4. General Procedure for the Synthesis of 7g and 7h

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

**7g**: IR (Nujol): v = 1728 (s), 1491 (s), 1230 (s), 871 (m), 839 (m), 611 (s), 541 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 9.93 (s, 1H), 7.72 (t, J = 8.0 Hz, 1H), 7.58 (d, J = 8.2, 1H), 7.52 (d, J = 8.0, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 189.3, 164.1 (d,  $J_{CF} = 244.2$  Hz), 130.2, 129.1, 127.1, 122.2 (d,  $J_{CF} = 8.8$  Hz), 119.2 (d,  $J_{CF} = 21.4$  Hz); HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>7</sub>H<sub>4</sub>BrFO, 201.9430; found, 201.9435. Anal. calcd for C<sub>7</sub>H<sub>4</sub>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 (s), 529 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 10.16 (t, J = 1.5 Hz, 1H), 7.59 (t, J = 8.3 Hz, 1H), 7.29 (dd, J = 8.2, 2.1 Hz, 1H), 7.23 (dd, J = 8.4, 2.2 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>,  $\delta$ ): 185.5 (d,  $J_{CF} = 5.4$  Hz), 163.7 (d,  $J_{CF} = 243.1$  Hz), 129.7 (d,  $J_{CF} = 9.6$  Hz), 129.3, 128.1, 122.8 (d,  $J_{CF} = 8.1$  Hz), 119.9 (d,  $J_{CF} = 23.4$  Hz); HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>7</sub>H<sub>4</sub>BrFO, 201.9430; found, 201.9432. Anal. calcd for C<sub>7</sub>H<sub>4</sub>BrFO: C 41.41, H 1.99; found: C 41.41, H 2.00.

#### 4.5. General Procedure for the Synthesis of 7i and 7j

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

**7i**: IR (Nujol): v = 1736 (s), 1577 (s), 1482 (s), 1231 (s), 876 (m), 838 (m), 608 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 10.10 (t, J = 2.5 Hz, 1H), 7.40 (dt, J = 6.2, 2.0 Hz, 1H), 7.34 (dd, J = 9.0, 4.2 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$ ): 184.5 (d,  $J_{CF} = 6.6$  Hz), 159.4 (d,  $J_{CF} = 257.3$  Hz), 155.6 (d,  $J_{CF} = 246.1$  Hz), 123.9, 121.6 (d,  $J_{CF} = 25.5$  Hz), 116.8 (dd,  $J_{CF} = 23.3$ , 10.0 Hz), 114.0 (d,  $J_{CF} = 23.3$  Hz); HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>7</sub>H<sub>3</sub>BrF<sub>2</sub>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 (m), 603 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 10.27 (s, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>,  $\delta$ ): 181.8, 146.5 (dd,  $J_{CF} = 249.3$ , 22.5 Hz), 145.2 (dd,  $J_{CF} = 247.6$ , 22.3 Hz), 114.4 (t,  $J_{CF} = 9.6$  Hz), 107.3 (t,  $J_{CF} = 21.6$  Hz); HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>7</sub>HBrF<sub>4</sub>O, 255.9147; found, 255.9148. Anal. calcd for C<sub>7</sub>HBrF<sub>4</sub>O: C 32.72; found: C 32.74.

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

To a benzene (80 mL) solution of 7g (1.00 g, 4.93 mmol) were added ethylene glycol (1.73 g, 7.39 mmol), *para*-toluenesulfonic acid (PTSA, 0.1 g, 0.058 mmol), and the resulting suspension was heated under reflux (24 h) using a Dean–Stack trap. After cooling to room temperature, NaHCO<sub>3</sub> (2 g) was added, and the solution was concentrated to yield a colorless oil. Chromatography (hexanes:EtOAc=10:1,  $R_f$ =0.4) afforded 2-(4-bromo-3-fluorophenyl)-1,3-dioxolane (**7k**) as a colorless oil (1.20 g, 99 %).

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

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

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

### 4.7. General Procedure for the Synthesis of 7r and 7s

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

**7r**: IR (Nujol): v = 2983 (m), 1496 (m), 1252 (s), 1099 (m), 1031 (s), 963 (s), 833 (m), 699 (s), 535 cm<sup>-</sup> (s); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.28 (d, J = 8.2 Hz, 1H), 7.18–7.13 (m, 1H), 4.11–4.04 (m, 4H), 3.12 (d, J = 22.0 Hz, 2H), 1.26 (t, J = 7.06 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 159.8 (d,  $J_{CF} = 251.3$  Hz), 157.2 (d,  $J_{CF} = 248.1$  Hz), 123.6 (d,  $J_{CF} = 13.5$  Hz), 120.8 (d,  $J_{CF} = 25.5$  Hz), 116.8 (d,  $J_{CF} = 23.3$  Hz), 113.2 (d,  $J_{CF} = 23.1$  Hz), 62.3, 25.8 (d,  $J_{CP} = 139.6$  Hz), 16.5; HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>11</sub>H<sub>14</sub>BrF<sub>2</sub>O<sub>3</sub>P, 241.9832; found, 341.9835. Anal. calcd for C<sub>11</sub>H<sub>14</sub>BrF<sub>2</sub>O<sub>3</sub>P: 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 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 4.14–4.06 (m, 4H), 3.23 (d, J = 21.2 Hz, 2H), 1.28 (t, J = 7.02 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 146.8 (dd,  $J_{CF} = 249.3$ , 22.5 Hz), 144.8 (dd,  $J_{CF} = 247.6$ , 22.3 Hz), 114.4 (t,  $J_{CF} = 9.6$  Hz), 107.1 (t,  $J_{CF} = 21.6$  Hz), 62.7, 26.2 (d,  $J_{CP} = 142.2$  Hz), 16.6; HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>11</sub>H<sub>12</sub>BrF<sub>4</sub>O<sub>3</sub>P, 377.9644; found, 377.9647. Anal. calcd for C<sub>11</sub>H<sub>12</sub>BrF<sub>4</sub>O<sub>3</sub>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 **8** (1.63 g, 3.58 mmol) was added sodium *tert*-butoxide (0.76 g, 7.91 mmol) at 0 °C. The reaction mixture was stirred on an ice bath for 1 h, and subsequently a THF solution (5 mL) of compound **7c** was added. After 24 h, 5 mL of NH<sub>4</sub>Cl solution was added. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried with MgSO<sub>4</sub> and evaporated in vacuo. The residue was purified by recrystallization in a mixed solution of  $CH_2Cl_2$  and hexane affording **5a** (2.14 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); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.59 (d, J = 8.4 Hz, 4H), 7.54 (d, J = 8.4 Hz, 4H), 7.37 (dd, J = 8.8, 2.4 Hz, 4H), 7.09 (s, 2H), 7.06–7.03 (m, 12H), 7.02 (s, 2H), 6.99–6.94 (m, 8H); <sup>13</sup>C NMR (150 MHz CDCl<sub>3</sub>,  $\delta$ ): 158.9 (d,  $J_{CF} = 241.9$  Hz), 147.5, 139.4, 136.6, 131.2, 128.1, 127.4, 127.0, 126.7, 126.5, 126.1 (d,  $J_{CF} = 7.7$  Hz), 122.3, 116.2 (d,  $J_{CF} = 22.5$  Hz); HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>52</sub>H<sub>36</sub>F<sub>4</sub>N<sub>2</sub>, 764.2815; found, 764.2811. Anal. calcd for C<sub>52</sub>H<sub>36</sub>F<sub>4</sub>N<sub>2</sub>: 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 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.68 (d, J = 8.3 Hz, 4H), 7.62 (d, J = 8.2 Hz, 4H), 7.46 (d, J = 8.7 Hz, 4H), 7.33–7.29 (m, 4H), 7.17 (d, J = 16.2 Hz, 2H), 7.08 (d, J = 16.2 Hz, 2H), 7.00–6.94 (m, 8H), 6.82 (d, J = 8.6 Hz, 4H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>,  $\delta$ ): 160.3 (dd,  $J_{CF} = 247.1$ , 11.0 Hz), 158.3 (dd,  $J_{CF} = 252.8$ , 12.2 Hz), 146.7, 139.3, 136.7, 130.4, 129.6 (d,  $J_{CF} = 10.2$  Hz), 128.1, 127.4, 126.9, 126.7, 126.2, 117.7, 112.0 (d,  $J_{CF} = 21.8$  Hz); 105.4 (t,  $J_{CF} = 24.8$  Hz); HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>52</sub>H<sub>32</sub>F<sub>8</sub>N<sub>2</sub>, N3.632438; found, 836.2435. Anal. calcd for C<sub>52</sub>H<sub>32</sub>F<sub>8</sub>N<sub>2</sub>: C 74.64, H 3.85, N 3.35; found: C 74.64, H 3.85, N 3.35.

**5c:** IR (Nujol):  $\nu = 1676$  (m), 1592 (s), 1496 (s), 1339 (m), 1224 (s), 1159 (s), 690 (s), 623 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (600 MHz CDCl<sub>3</sub>,  $\delta$ ): 7.69 (d, J = 8.0 Hz, 4H), 7.62 (d, J = 8.1 Hz, 4H), 7.34–7.31 (m, 10H), 7.27 (d, J = 8.1 Hz, 2H), 7.20 (t, J = 8.2 Hz, 2H), 7.14–7.12 (m, 12H), 7.11–7.08 (m, 4H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>,  $\delta$ ): 158.0 (d,  $J_{CF} = 249.8$  Hz), 147.1, 139.8, 136.1, 135.3 (d,  $J_{CF} = 6.3$  Hz), 133.8 (d,  $J_{CF} = 10.5$  Hz), 129.1, 128.8, 128.6, 127.1, 123.2, 122.6, 122.5, 114.3 (d,  $J_{CF} = 19.9$  Hz). HRMS (70 eV):  $[M + H]^+$  calcd for  $C_{52}H_{38}F_2N_2$ , 728.3003; found, 728.3005. Anal. calcd for  $C_{52}H_{38}F_2N_2$ : 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 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.58 (d, J = 8.4 Hz, 4H), 7.56 (d, J = 8.4 Hz, 4H), 7.43 (t, J = 8.6 Hz, 2H), 7.29–7.26 (m, 8H), 7.12 (d, J = 8.2 Hz, 8H), 7.07 (d, J = 7.8 Hz, 8H), 6.80 (dd, J = 8.5, 2.2 Hz, 2H), 6.72 (dd, J = 8.9, 2.2 Hz, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>,  $\delta$ ): 160.9 (d,  $J_{CF} = 247.7$  Hz), 148.5 (d,  $J_{CF} = 10.1$  Hz), 146.9, 139.6, 136.7, 129.5, 128.0, 127.2, 127.1, 127.0, 125.1, 123.8, 120.8, 118.5 (d,  $J_{CF} = 12.5$  Hz), 117.9, 109.1 (d,  $J_{CF} = 25.2$  Hz); HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>52</sub>H<sub>38</sub>F<sub>2</sub>N<sub>2</sub>, 728.3003; found, 728.3003. Anal. calcd for C<sub>52</sub>H<sub>38</sub>F<sub>2</sub>N<sub>2</sub>: C 85.69, H 5.25, N 3.84; found: C 85.69, H 5.22, N 3.88.

**5e**: IR (Nujol):  $\nu = 1670$  (m), 1588 (s), 1481 (s), 1257 (m), 1165 (s), 691 (s), 629 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.62 (d, J = 8.4 Hz, 4H), 7.58 (d, J = 8.4 Hz, 4H), 7.31 (dd, J = 11.6, 6.8 Hz, 2H), 7.27–7.25 (m, 8H), 7.19 (s, 2H), 7.11 (s, 2H), 7.05–7.02 (m, 12H), 6.82 (dd, J = 11.2, 6.8 Hz, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>,  $\delta$ ): 156.5 (d,  $J_{CF} = 246.2$  Hz), 153.8 (d,  $J_{CF} = 246.5$  Hz), 146.8, 140.1, 136.2, 134.6 (d,  $J_{CF} = 11.1$  Hz), 130.1, 129.3, 127.2, 123.3, 123.0, 121.8 (d,  $J_{CF} = 7.2$  Hz), 119.7, 114.6 (d,  $J_{CF} = 25.7$  Hz), 113.8 (d,  $J_{CF} = 23.3$  Hz); HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>52</sub>H<sub>36</sub>F<sub>4</sub>N<sub>2</sub>, 764.2815; found, 764.2811. Anal. calcd for C<sub>52</sub>H<sub>36</sub>F<sub>4</sub>N<sub>2</sub>: 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 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.63 (t, J = 8.1 Hz, 2H), 7.40 (d, J = 8.6 Hz, 4H), 7.36 (dd, J = 8.1, 1.6 Hz, 2H), 7.29 (dd, J = 11.8, 1.5 Hz, 2H), 7.27–7.24 (m, 8H), 7.15 (s, 4H), 7.12–7.10 (m, 8H), 7.05–7.02 (m, 8H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>,  $\delta$ ): 160.6 (d,  $J_{CF} = 248.3$  Hz), 147.8, 147.5, 139.6 (d,  $J_{CF} = 7.4$  Hz), 131.2, 130.7, 129.3, 127.6, 127.2, 124.9 (d,  $J_{CF} = 12.0$  Hz), 124.6, 123.2 (d,  $J_{CF} = 17.9$  Hz), 122.3, 118.6, 113.8 (d,  $J_{CF} = 23.3$  Hz); HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>52</sub>H<sub>38</sub>F<sub>2</sub>N<sub>2</sub>: 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 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.44 (d, J = 8.8 Hz, 2H), 7.39–7.30 (m, 6H), 7.20 (d, J = 8.4 Hz, 4H), 7.16–7.12 (m, 4H), 7.07 (d, J = 16.2 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>,  $\delta$ ): 155.6 (dd,  $J_{CF} = 241.7$ , 21.2 Hz), 155.5 (dd,  $J_{CF} = 242.3$ , 21.5 Hz), 148.2,



147.2, 131.9 (d,  $J_{CF}$ =4.1 Hz), 130.1, 129.3, 129.2, 127.7, 124.6 (d,  $J_{CF}$ =  $J_{CF}$ =14.6 Hz), 123.4, 122.9, 120.3 (d,  $J_{CF}$ =27.5 Hz), 116.7, 112.8 (dd,  $J_{CF}$ =  $J_{CF}$ =24.9, 4.1 Hz), 106.6 (dd,  $J_{CF}$ =23.9, 10.2 Hz); HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>26</sub>H<sub>18</sub>BrF<sub>2</sub>N, 461.0591; found, 461.0591. Anal. calcd for C<sub>26</sub>H<sub>18</sub>BrF<sub>2</sub>N: C 67.54, H 3.92, N 3.03; found: C 67.51, H, 3.92, N 53.88

**7u**: IR (Nujol):  $\nu = 1649$  (m), 1568 (s), 1478 (s), 1302 (m), 1187 (s), 775 (s), 677 (s), 589 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.45 (d, J = 16.7 Hz, 1H), 7.40 (d, J = 8.5 Hz, 2H), 7.30 (t, J = 8.0 Hz, 4H), 7.15 (d, J = 7.8 Hz, 4H), 7.10–7.06 (m, 4H), 6.90 (d, J = 16.7 Hz, 1H); <sup>13</sup>CNMR (150 MHz, CDCl<sub>3</sub>,  $\delta$ ): 148.7 (d,  $J_{CF} = 25.5$  Hz), 147.2 (d,  $J_{CF} = 9.9$  Hz), 145.0 (dd,  $J_{CF} = 245.0$ , 15.9 Hz), 144.5 (dd,  $J_{CF} = 25.6$ , 13.4 Hz), 137.3 (t,  $J_{CF} = 8.3$  Hz), 129.9, 129.4, 127.7, 124.9, 123.5, 122.5, 116.9 (t,  $J_{CF} = 13.4$  Hz), 111.0, 96.7 (t,  $J_{CF} = 22.7$  Hz); HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>26</sub>H<sub>16</sub>BrF<sub>4</sub>N, 497.0402; found, 497.0408. Anal. calcd for C<sub>26</sub>H<sub>16</sub>BrF<sub>4</sub>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 5g, 5h, and 7v

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

**5g**: IR (Nujol):  $\nu = 1652$  (m), 1579 (s), 1481 (s), 1325 (m), 1222 (s), 1178 (s), 696 cm<sup>-1</sup> (s); <sup>1</sup>HNMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.41 (d, J = 8.7 Hz, 4H), 7.38–7.36 (m, 2H), 7.30–7.27 (m, 8H), 7.16–7.12 (m, 14H), 7.09–7.05 (m, 8H); <sup>13</sup>CNMR (150 MHz, CDCl<sub>3</sub>,  $\delta$ ): 155.8 (d,  $J_{CF} = 244.8$  Hz), 148.1, 147.3, 131.9, 130.4, 129.3, 127.8, 127.1 (d,  $J_{CF} = 8.7$  Hz), 124.7, 123.3, 123.1, 121.4 (d,  $J_{CF} = 15.0$  Hz), 117.8 (d,  $J_{CF} = 25.5$  Hz), 117.4, 112.9 (d,  $J_{CF} = 21.6$  Hz); HRMS (70 eV):  $[M + H]^+$  calcd for  $C_{52}H_{36}F_4N_2$ , 764.2815; found, 764.2819. Anal. calcd for  $C_{52}H_{36}F_4N_2$ : C 81.66, H 4.74, N 3.66; found: C 81.62, H 4.71, N 3.69.

**5h**: IR (Nujol):  $\nu = 1647$  (m), 1574 (s), 1476 (s), 1329 (m), 1206 (s), 1172 (s), 688 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.51 (d, J = 16.7 Hz, 2H), 7.42 (d, J = 7.8 Hz, 4H), 7.29–7.24 (m, 8H), 7.13–7.12 (m, 8H), 7.08–7.04 (m, 8H), 6.98 (d, J = 16.7 Hz, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>,  $\delta$ ): 148.9, 147.1, 144.5 (dd,  $J_{CF} = 241.2$ , 22.8 Hz), 144.2 (dd,  $J_{CF} = 240.1$ , 22.5 Hz), 138.0 (t,  $J_{CF} = 8.5$  Hz), 129.9, 129.3, 128.1, 124.9, 123.6, 122.3, 111.3; HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>52</sub>H<sub>32</sub>F<sub>8</sub>N<sub>2</sub>, 836.2438; found, 836.2442. Anal. calcd for C<sub>52</sub>H<sub>32</sub>F<sub>8</sub>N<sub>2</sub>: 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 cm<sup>-1</sup> (w); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.23 (s, 2H), 7.04 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 7.8 Hz, 2H), 2.08 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 161.9 (d,  $J_{CF} = 240.6$  Hz), 139.2, 128.8, 125.6 (d,  $J_{CF} = 19.2$  Hz), 123.7, 113.1 (d,  $J_{CF} = 8.8$  Hz), 14.6; HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>14</sub>H<sub>12</sub>F<sub>2</sub>, 218.0907; found, 218.0907. Anal. calcd for C<sub>14</sub>H<sub>12</sub>F<sub>2</sub>: C 77.05, H 5.54; found: C 77.09, H 5.52.

# 4.10. Synthesis of 7w

To a CCl<sub>4</sub> (35 mL) solution of **7v** (1.00 g, 4.58 mmol) were added NBS (1.63 g, 9.16 mmol), BPO (0.11 g, 0.46 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 MgSO<sub>4</sub>, and concentrated to yield a colorless oil. Chromatography (pure hexanes,  $R_f = 0.3$ ) afforded a white solid. Triethyl phosphite (1.52 g, 9.16 mmol) was added, and the reaction mixture was stirred at 150 °C for 12 h; after cooling to room temperature, the reaction mixture was purified by bulb-to-bulb distillation to afford **7w** as a white solid (1.53 g, 68 %).

**7w**: IR (Nujol): v=2995 (m), 1522 (m), 1161 (s), 1018 (w), 809 (s), 725 cm<sup>-1</sup> (w); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.37 (dt, J=7.9, 2.5 Hz, 2H), 7.25 (d, J=8.0 Hz, 2H), 7.20 (d, J=9.2 Hz, 2H), 4.04–3.99 (m, 8H), 3.17 (d, J=21.7 Hz, 4H), 1.22 (t, J=7.4 Hz, 12H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>,  $\delta$ ): 160.9 (dd,  $J_{CF}=245.7$ , 7.2 Hz), 140.3, 132.1 (d, 

### 4.11. General Procedure for the Synthesis of 6a, 6b, 6c, and 6d

To a DMF (35 mL) solution of *N*,*N*-diphenyl-4-vinylbenzenamine (1.59 g, 5.87 mmol) were added **8d** (1.00 g, 2.67 mmol),  $Pd(OAc)_2$  (29.9 mg, 0.13 mmol),  $PPh_4Br$  (0.22 g, 0.53 mmol), and NaOAc (0.91 g, 13.4 mmol) under N<sub>2</sub>, and the resulting suspension was heated to 100 °C for 16 h; after cooling to room temperature, water (20 mL) was added and the yellow precipitate was collected by filtration. Chromatography (hexanes:EtOAc=8: 1,  $R_f$ =0.4) afforded **6a** as a yellow solid (1.59 g, 79%).

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

**6b**: IR (Nujol):  $\nu = 1646$  (m), 1566 (s), 1479 (s), 1345 (m), 1179 (s), 751 (s), 583 (s); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.38 (d, J = 8.7 Hz, 4H), 7.30–7.25 (m, 12H), 7.21 (s, 4H), 7.11–7.07 (m, 10H), 7.05–7.02 (m, 8H); <sup>13</sup>CNMR (150 MHz, CDCl<sub>3</sub>,  $\delta$ ): 156.6 (d,  $J_{CF} = 241.8$  Hz), 156.3 (d,  $J_{CF} = 243.5$  Hz), 148.0 (d,  $J_{CF} = 241.8$  Hz), 147.3, 131.5, 130.5, 129.3, 129.1, 127.7, 124.7, 123.8, 123.3, 122.4, 122.3 (d,  $J_{CF} = 19.4$  Hz), 117.6, 113.0 (d,  $J_{CF} = 25.1$  Hz), 112.7 (d,  $J_{CF} = 24.0$  Hz); HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>54</sub>H<sub>38</sub>F<sub>4</sub>N<sub>2</sub>, 790.2971; found, 790.2975. Anal. calcd for C<sub>54</sub>H<sub>38</sub>F<sub>4</sub>N<sub>2</sub>: 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 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.45 (d, J = 16.4 Hz, 4H), 7.39 (d, J = 8.6 Hz, 4H), 7.26 (t, J = 8.1 Hz, 8H), 7.11 (d, J = 7.8 Hz, 8H), 7.07–7.03 (m, 8H), 6.95 (s, 2H); <sup>13</sup>CNMR (150 MHz, CDCl<sub>3</sub>,  $\delta$ ): 148.7, 147.2, 144.7 (dd,  $J_{CF} = 242.3$ , 23.5 Hz), 144.3 (dd,  $J_{CF} = 239.5$ , 22.1 Hz), 137.1 (t,  $J_{CF} = 8.7$  Hz), 130.2, 129.4, 127.9, 125.0, 123.6, 122.6, 122.0, 116.7, 113.7 (t,  $J_{CF} = 12.5$  Hz), 111.7; HRMS (70 eV):  $[M + H]^+$  calcd for C<sub>54</sub>H<sub>34</sub>F<sub>8</sub>N<sub>2</sub>, 862.2594; found, 862.2594. Anal. calcd for C<sub>54</sub>H<sub>34</sub>F<sub>8</sub>N<sub>2</sub>: 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 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.46–7.39 (m, 6H), 6.85 (d, J = 8.2 Hz, 2H), 6.64 (d, J = 8.7 Hz, 2H), 3.43 (t, J = 5.3 Hz, 8H), 2.29 (t, J = 5.1 Hz, 8H), 1.75 (s, 24H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>,  $\delta$ ): 144.2, 143.1 (d,  $J_{CF} = 249.1$  Hz), 142.8 (d,  $J_{CF} = 243.2$  Hz), 138.0 (d,  $J_{CF} = 9.8$  Hz), 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):  $[M + H]^+$  calcd for C<sub>50</sub>H<sub>50</sub>F<sub>8</sub>N<sub>2</sub>, 830.3846; found, 830.3849. Anal. calcd for C<sub>50</sub>H<sub>50</sub>F<sub>8</sub>N<sub>2</sub>: 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,  $\lambda_{em} = 620$  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 nm  $Ar^+$  laser line (ca. 1 mW); an intensified charge-coupled 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 mm<sup>2</sup> 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 O2 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 nm s<sup>-1</sup> 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 Alq<sub>3</sub> (30 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 818ST silicon photodiode. The luminance is expressed as:

$$L^{\infty} = \int V(\lambda)^* f(\lambda) d\lambda$$

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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