Large Electro-optic Activity and Enhanced Thermal Stability from Diarylaminophenyl-Containing High-β Nonlinear Optical Chromophores

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Two series of highly efficient and thermally stable nonlinear optical chromophores based on the (4-diarylamino)phenyl electron donors have been synthesized and systematically investigated. A modular approach has been employed to synthesize these electron donors with tunable size, shape, and electron-donating abilities. Efficient conjugated bridges were extended from these donors and coupled with very strong CF_3−TCF electron acceptors to afford chromophores with very high β values (up to 7077 × 10^{-30} esu at 1.907 μm). These chromophores possess much higher thermal stability (with their onset decomposition temperatures all above 220 °C) than those substituted with (4-dialkylamino)phenyl donors. Most importantly, the high molecular hyperpolarizability of these chromophores can be effectively translated into very large electro-optic (E-O) coefficients (r_{33}) in poled polymers through suitable shape engineering. Exemplified by the chromophore **B4**, which has a fluorinated aromatic substituent anchored at its donor end, it showed a very large r_{33} (169 pm/V) at 1.31 μm. This value is almost 1 order higher than the E-O activities usually reported for (4-diarylamino)phenyl-substituted NLO chromophores.

Introduction

Over the past decade, considerable progress has been made on developing organic and polymeric electro-optic (E-O) materials for applications in high-speed and broadband information technology.[1] One of the often encountered challenges in making highly efficient E-O materials is to develop nonlinear optical (NLO) chromophores with large hyperpolarizabilities (β), good optical transparency, and excellent thermal and chemical stabilities.[2] These properties need to be optimized simultaneously to facilitate the fabrication of high-performance integrated optical devices. Among all the materials studied, the dipolar chromophores with 4-(diarylamino)phenyl donor have demonstrated significantly enhanced thermo- and photostabilities compared to their 4-(dialkylamino)phenyl analogues.[3] It has been shown from both theoretical and experimental analysis that the linear and nonlinear optical properties of aryl D-π-A chromophores are strongly dependent on the strength of 4-(diphenylamino)-phenyl donors. These properties could also be tuned through the structural variation of two terminal phenyl rings.[4] This provides an effective mechanism to adjust the polarization of aryl D-π-A chromophores to achieve high-β values and good stabilities.

However, up to now, the promise of aryl D-π-A chromophores has never been realized, especially in the area of translating high-β into large E-O coefficients (r_{33}) in poled polymers. The r_{33} values derived from aryl D-π-A chromophores remained ∼10−20 pm/V (at 1.3 or 1.55 μm),

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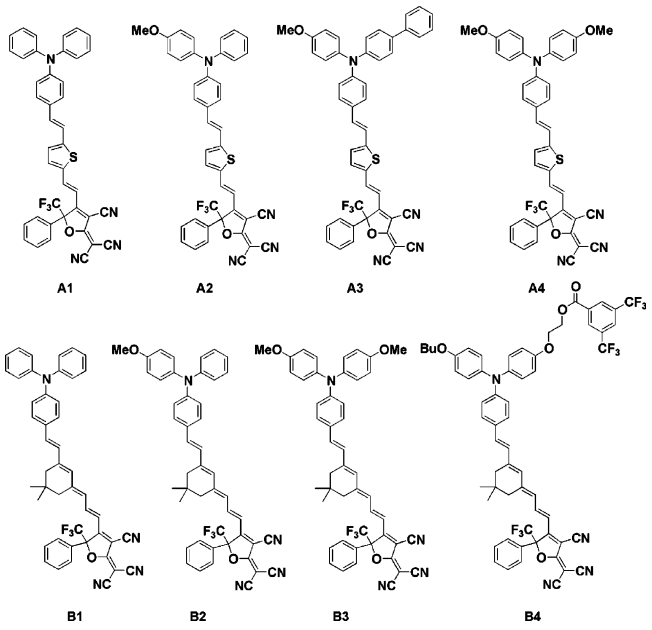
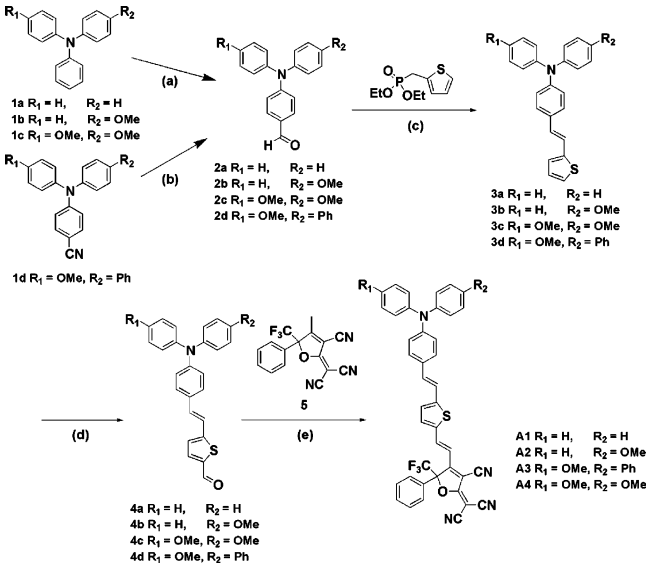
Chart 1. Structures of A1−A4 and B1−B4



which are much lower than those obtained from their alkyl D-π-A counterparts.[5] This may be due to the poling efficiency of these materials being strongly attenuated by large dipole−dipole and $\pi-\pi$ stacking interactions,[6] and charge transporting[7] between their triarylamino moieties under high poling electric fields.

To alleviate these problems, we have designed and synthesized two series of aryl D-π-A chromophores (**A1**−**A4** and **B1**−**B4** in Chart 1) for conducting a systematic study of their structure/property relationships. We have employed a modular approach to synthesize these 4-(diarylamino)-phenyl donors with tunable size, shape, and electron-donating abilities. Efficient conjugation of the π bridges were further extended from these donors, followed by coupling them with very strong CF_3−TCF acceptors[8] to afford chromophores with very large β values (up to 7077×10^{-30} esu at 1.907 μm). These chromophores also possess much higher thermal stability (with their onset decomposition temperatures all above 220 °C) than those 4-(dialkylamino)phenyl-substituted chromophores. Most importantly, the high β of these chromophores can be effectively translated into very large r_{33} values in poled polymers by suitable shape engineering. Exemplified by the chromophore **B4**, which has a fluorinated aromatic substituent anchored at its donor end, it showed a very large r_{33} value (169 pm/V) at the wavelength of 1.31 μm. This value is almost 1 order higher than the best E-O performance reported from 4-(diarylamino)phenyl-substituted NLO chromophores.

Scheme 1. Synthesis of Chromophores A[a]



[a] Reagents and conditions: (a) 1 equiv of $POCl_3$ and DMF, 1,2-dichloroethane, rt 24 h, then H_2O; (b) DIBAL-H, THF, −78 °C, 2h; (c) phosphonate, 1.2 equiv of *t*-BuOK, THF, 0 °C to reflux, 24 h; (d) *n*-BuLi, THF, −78 °C, 1 h then DMF, −78 °C to rt; (e) aldehyde and 1.1 equiv of acceptor **5**, ethanol, 50 °C, 2 h.

Results and Discussion

Synthesis of A-Series Chromophores. Synthesis of chromophores **A1**−**A4** is depicted in Scheme 1. Triarylamine **1a**−**1c** were reacted with 1 equiv of phosphorus oxachloride and DMF followed by hydrolyzing the intermediates to furnish products **2a**−**2c,** respectively, whereas **2d** was obtained by reducing the nitrile group on **1d** with diisobutylaluminum hydride (DIBAL-H). Reacting compound **2** with diethyl (2-thienyl)methanephosphonate[9] using potassium *tert*-butoxide as base under a Horner-Emmons reaction condition afforded (*E*)-alkene **3** exclusively. Lithiation of **3** with *n*-butyl lithium followed by the addition of DMF yielded the corresponding aldehyde **4**.

Acceptor **5**, 2-dicyanomethylen-3-cyano-4-methyl-5-phenyl-5-trifluoro-methyl-2,5-dihydrofuran (CF_3−TCF), possesses not only very strong electron-withdrawing power but also a 3-D shape which can prevent close packing of chromophores.[8] The target chromophores **A1** (without methoxy), **A2** (with one methoxy), **A3** (with one methoxy and one phenyl), and **A4** (with two methoxy groups) on the terminal phenyl rings of 4-(diarylamino)phenyl donors were successfully obtained by condensing aldehydes **4a**−**4d** with acceptor **5** in ethanol without using any base.

Synthesis of B-Series Chromophores. The donor-substituted aldehyde **2e** with a MOM-protected hydroxy group that can be used for making **B4** was prepared as shown in Scheme 2. In a sequential Hartwig-Buchwald Pd-catalyzed amination, **10** was first treated with 4-butoxy-aniline to yield **11**, which was then allowed to react with 4-bromobenzonitrile

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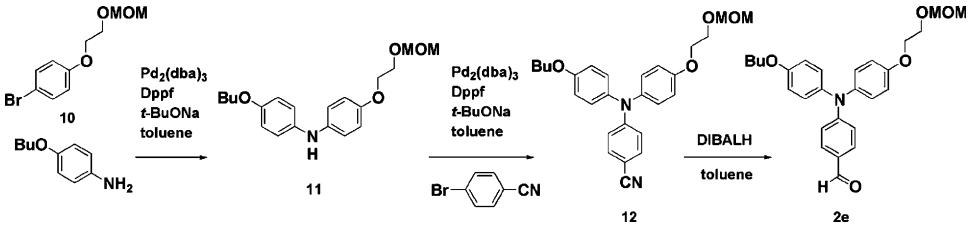
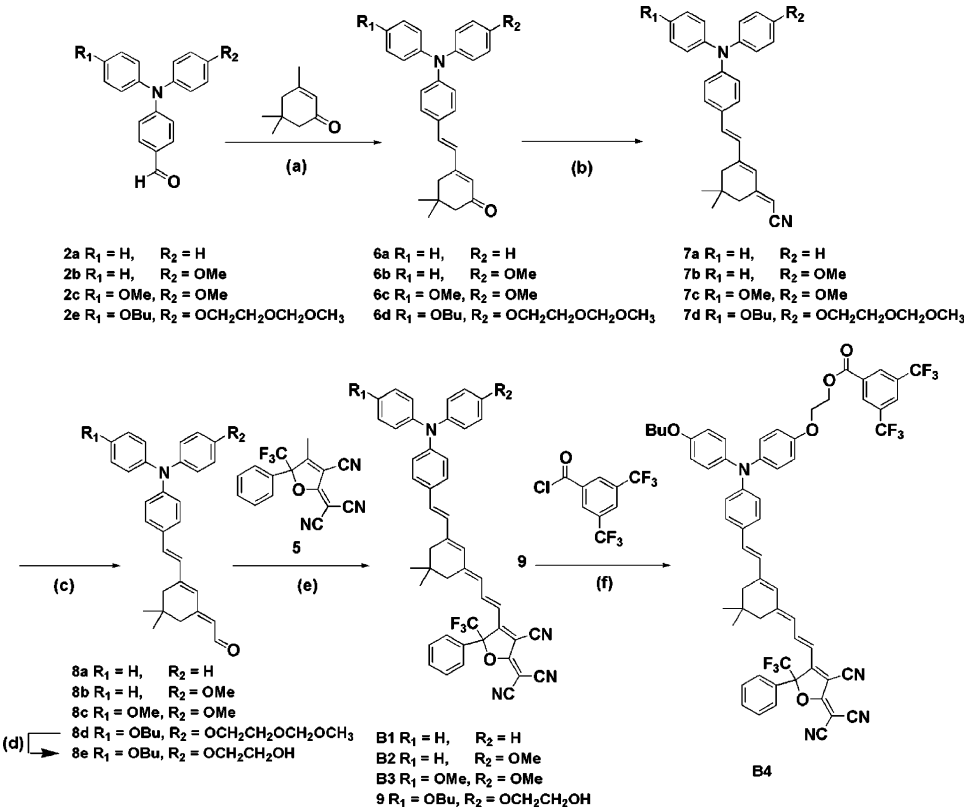
Scheme 2. Synthesis of Donor 2e



Scheme 3. Synthesis of Chromophores B1−B4[a]



[a] Reagents and conditions: (a) 1 equiv of Na in ethanol, then isophorone, and aldehyde **2**, THF, 60 °C, 24 h; (b) 2.5 equiv of NaH and 2.5 equiv of $(C_3H_7O)_2(CH_2CN)P{=}O$ in THF and then **6**, reflux, 18 h. (c) 1.5 equiv of DIBAL-H, toluene, −78 °C, 2 h and then $HCl_{(aq)}$; (d) 6 M HCl, THF, reflux, 8 h; (e) aldehyde **8** and 1.1 equiv of acceptor **5**, ethanol, 50 °C, 2 h; (f) 10 equiv of 3,5-bis(trifluoromethyl)-benzoyl chloride in THF, reflux, 12 h.

to afford **12**. Similarly, the reduction of **12** by DIBAL-H followed by hydrolysis resulted in the formation of **2e**.

Synthesis of chromophores **B1**−**B4** is shown in Scheme 3. The CLD-type polyene chromophores are one of the most highly polarizable organic NLO materials.[10] Incorporation of isophorone unit to rigidify and protect the central olefinic linkage not only provides efficient charge transfer and improved thermal and photochemical stability but also renders suitable steric hindrance to prevent intermolecular chromophore aggregation. The aldehyde **2** was condensed with isophorone by Knoevenagel reaction in which the proper base plays a key role in determining the yield. We found that by replacing the commonly used potassium hydroxide or potassium *tert*-butoxide with sodium ethoxide, which was freshly generated by reacting sodium with ethanol, produces **6** with a much improved yield (75%). The second crucial reaction involves the creation of an additional double bond and a functional group on **6** for later conversion to aldehyde. The reaction of **6** with diisopropyl (cynaomethyl)-phosphonate using sodium hydride as base resulted in **7** with 82% yield. The ratio between the *E* and *Z* isomers is 3:2. The reduction with DIBAL-H followed by acid hydrolysis converts the nitrile group on **7** into the corresponding aldehyde **8** in 78% yield. As previously described, the aldehyde-containing bridges **8a**−**8c** were condensed with acceptor **5** to furnish chromophores **B1**−**B3** in high yield without using any base. This means that the methyl group on acceptor **5** is acidic enough to couple with aldehydes under neutral conditions. Furthermore, the content of *E*-form isomer in the final chromophores has been improved to around 85−87%, indicating that *Z*-form chromophores were partially isomerized to the thermodynamically more favorable *E*-form during the condensation. The higher ratio of *E*-form

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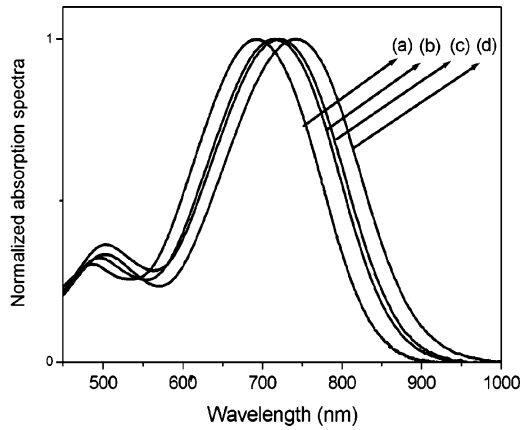

Figure 1. Normalized absorption spectra of chromophores A in chloroform: **A1** (a); **A2** (b); **A3** (C); **A4** (d).

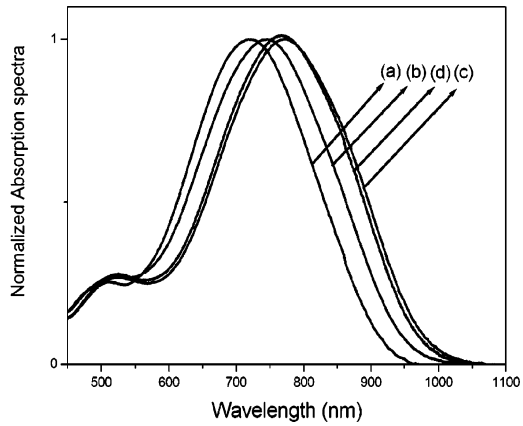

Figure 2. Normalized absorption spectra of chromophores B in chloroform: **B1** (a); **B2** (b); **B3** (c); **B4** (d).

isomers usually contributes to higher β values because of better conjugation. A relatively high overall yield (35%) was obtained for chromophore **B3** after four reaction steps.

The bridge of **B4** was constructed in a similar way. The methoxymethyl (MOM) protecting group on **8d** was first cleaved by 6 M HCl to yield **8e**, which was then condensed with acceptor **5** to afford **9** with a free hydroxyl group. To modify the shape of the chromophore to avoid close packing, chromophore **9** was reacted with an excess amount of 3,5-bis(trifluoromethyl)-benzoyl chloride to afford the chromophore **B4** with a bulky fluorinated substituent anchored at one arm of the aromatic donor. Again, this step was carried out without using any base to avoid the possible decomposition of chromophore. All of the chromophores were fully characterized by ^{1}H NMR, ^{13}C NMR, and HRMS. They also possess good solubility in common organic solvents, such as dichloromethane, tetrahydrofuran, and ethyl acetate.

Optical Properties. The absorption characteristics of chromophore series **A** and **B** were measured in chloroform (Figures 1 and 2). **A1** shows a λ_{max} of 694 nm. With an additional methoxy group on the donor, the λ_{max} of **A2** red-shifted by 23 nm to 717 nm. With two additional methoxy groups on the donor, the λ_{max} of **A4** further red-shifted to 745 nm. It is worthy to note that **A3** with an additional phenyl ring on the donor has a λ_{max} of 721 nm, which is slightly red-shifted compared to **A2**. Likewise, the λ_{max} of **B1**, **B2**, and **B3** are 722, 746, and 770 nm, respectively. The same trend of λ_{max} shifting in both chromophore series **A** and **B** clearly shows that the methoxy groups provide extra donating strength to the π-conjugated bridge, shifting the charge-transfer absorption of the chromophore to lower energy. Owing to the weak electron-withdrawing effect from the ester group on the donor of **B4**, the λ_{max} of **B4** is slightly blue-shifted to 767 nm compared to that of **B3**.

Table 1. Summary of Thermal and Optical Properties and E-O Coefficients of Chromophores A and B

	T_g (°C)	T_d[a] (°C)	λ_{max}[b] (nm)	E (M^{-1} cm^{-1})	β[c] (10^{-30} esu)	r_{33}[d] (pm/V)
A1	90	259	694	44800	1770 ± 89	19
A2	103	257	717	42600	2150 ± 259	27
A3	84	263	721	38100	2700 ± 147*	37
A4	98	260	745	51000	3456 ± 128*	60
B1	89	220	722	37300	3395 ± 126*	47
B2	104	222	746	55700	4794 ± 127*	60
B3	114	221	770	57000	7077 ± 706*	106
B4	75	237	767	64000	6296 ± 221*	169

[a] T_d was determined by an onset point, measured by DSC under nitrogen at a heating rate of 10 °C/min. [b] λ_{max} was measured in $CHCl_3$. [c] β values were measured by Hyper-Rayleigh scattering at 1.9 μm. The values were determined with that of $CHCl_3$ (0.49×10^{-30} esu). EZ-FTC was used as an external standard. Error reported is ±1 standard deviation of the mean. * These values are resonantly enhanced. [d] r_{33} values were measured at the wavelength of 1.31 μm. Chromophores A and B were poled under the poling field of 100 and 125 V/μm, respectively.

HRS Measurement. As shown in Table 1, the first molecular hyperpoloarizability of the chromophore series **A** and **B** were determined by using the Hyper-Rayleigh scattering (HRS) technique at 1.907 μm. A standardized chromophore, EZ-FTC, was used as an external standard.[11] The influence of methoxy groups on the absorption charge-transfer band (λ_{max}: **A4** > **A3** > **A2** > **A1** and **B3** > **B2** > **B1**) totally reflects the result of β values (β : **A4** > **A3** > **A2** > **A1** and **B3** > **B2** > **B1**). The trend of increasing λ_{max} is in good agreement with the trend of increasing β value in both series of chromophores. Apparently, the more powerful the donor, the easier the charge separation, leading to larger β in these chromophores. The chromophore **B3** exhibits a very high β value (7077×10^{-30} esu), which is one of the highest hyperpolarizabilities measured in aryl D-π-A chromophores.

Thermal Analysis. Thermal properties of chromophores **A1**−**A4** and **B1**−**B4** were measured by differential scanning calorimetry (DSC) (Figures 3 and 4). **A1** containing a triphenylamino donor shows a clear glass transition at 90 °C followed by the crystallization at 158 °C and a melting point at 234 °C. However, **A2**−**A4** and **B1**−**B4** only exhibit glass transition temperatures (T_g), suggesting that these chromophores with aromatic amino donors tend to form amorphous glasses. Furthermore, the glass transition behavior of these chromophores can be reproduced by multiple heating cycles without the need of fast cooling or any special sample treatments, indicating excellent thermodynamic stabilities of their amorphous state. This is highly unusual compared to

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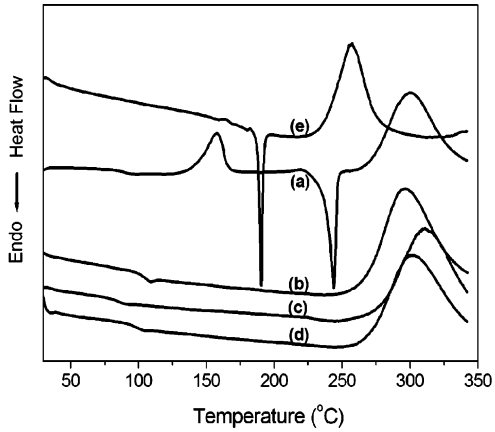

Figure 3. DSC of chromophores **A1** (a), **A2** (b), **A3** (C), **A4** (d), and **AJL8** (e).

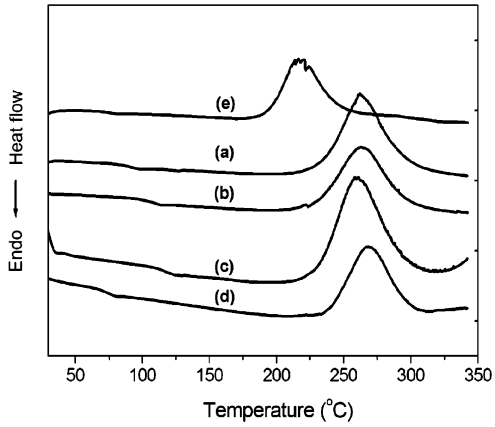

Figure 4. DSC of chromophores **B1** (a), **B2** (b), **B3** (c), **B4** (d), and **AJC146** (e).

some of the meta-stable organic glasses reported by Twieg and co-workers for photorefractive studies.[12] The unique organization state of these large dipole-moment chromophores can be rationalized by the fact that the triphenylamino donors possess nonplanar structures which can prevent close packing of molecules and hence crystallization.[4,13] This is necessary but not sufficient for their glass-forming abilities, given the fact that similar chromophores with bulky or shape-modified dialkylaminophenyl donors are mostly crystalline compounds instead. Alternatively, primary dipole−dipole electrostatic interaction between these chromophores could be interfered by their dipole−quadrupole interactions due to their structures of enriched aromatic rings.[14] Therefore, extended intermolecular interaction can be built up from such enhanced but finely balanced interactive forces, which makes these small organic molecules behaving like higher molecular-weight compounds. Full interpretation of this interesting property is beyond the scope of this report but deserves more systematic studies, theoretically and experimentally.

The decomposition temperature (T_d) of chromophores **A1**−**A4** are around 260 °C, which is almost 40 °C higher than that of chromophore **AJL8**, a commonly employed chromophore that has a 4-(dialkylamino)phenyl donor.[15] By addition of another phenyl ring on the aromatic donor, the chromophore **A3** exhibits an even higher T_d (∼263 °C). Furthermore, the T_d values of **B1**−**B3** are ∼220 °C, which show quite significant enhancement compared to that of their dialkylamino analogue, **AJC146**, which has a T_d of 185 °C.[15]

More importantly, by incorporating a fluorinated aromatic substituent at the donor side, the T_d of **B4** further increased to 237 °C. It should be pointed out that the stronger donor strength provided by adding the methoxy groups did not compromise the thermal stability of the resulting chromophores. The enhanced thermal stability of these aromatic amino donor-substituted chromophores might be ascribed to the absence of α-hydrogen adjacent to the nitrogen atom.

Electric Field Poling and E-O Property Measurements. For studying E-O property derived from these chromophores, a series of guest−host polymers were generated by formulating chromophores **A1**−**A4** or **B1**−**B3** (25 wt %) into amorphous polycarbonate (APC) using cyclopentanone as solvent. The resulting solutions (with the solid content of 12 wt %) were filtered through a 0.2-μm PTFE filter and spin-coated onto indium tin oxide (ITO) glass substrates. Films of doped polymers were baked in a vacuum oven at 80 °C overnight to ensure the removal of the residual solvent. Then, a thin layer of gold was sputtered onto the films as a top electrode for contact poling. The r_{33} values were measured using the Teng-Man simple reflection technique at the wavelength of 1.31 μm.[16] The optical transmission of ITO glass substrate was >85% at 1.31 μm. The accuracy of r_{33} measurements has been proved to be consistent with the results obtained from using other transparent electrodes such as ZnO or In_2O_3.[17] The E-O coefficients obtained from the optimal poling conditions are summarized in Table 1. In chromophore series **A**, the r_{33} values were gradually improved from 19 to 60 pm/V. The similar trend of enhancement was also observed for **B1**−**B3**, whose r_{33} values increase from 47 to 106 pm/V, illustrating that the increased donor strength of the chromophores significantly increase their macroscopic E-O activities. Interestingly, the r_{33} value of **A3** is 37 pm/V, which is 10 pm/V higher than that of **A2**. This indicates that the phenyl group on **A3** may slightly strengthen the electron-donating power of the donor, leading to higher λ_{max}, β, and r_{33} values than those of **A2**.

Site-Isolation Effect. B4 with two alkoxy groups on the aromatic amino donor was designed to optimize the shape of the chromophore. The butoxy group was also used to increase the solubility of the chromophore. The fluorinated aromatic substituent linked at the donor was intended to

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prevent the strong electrostatic interactions between chromophores. The undesired antiparallel packing between chromophores is expected to decrease during the poling process.[18] A guest−host polymer with 25 wt % of the shape-modified chromophore **B4** in poly(methyl methacrylate) (PMMA) was shown to have an exceptional r_{33} of 169 pm/V at 1.31 μm. This value is much higher than those reported (70−110 pm/V) for guest−host polymers that were doped with dialkylamino-substituted polyene-type chromophores.[15] To the best of our knowledge, this is also the highest value obtained for the polymers using the 4-(diarylamino)phenyl-substituted chromophores. It should be noted that higher loading than 25 wt % is highly achievable for these very soluble chromophores, and the r_{33} values reported in this paper have not been optimized with the concentration of chromophores. Our main concern at this point is to have large r_{33} values, with the combination of good optical transparency and high temporal stability.

Conclusion

Two series of nonlinear optical chromophores based on the 4-(diarylamino)phenyl donors have been synthesized and systematically investigated. The size, shape, and electron-donating abilities of these electron donors could be easily tuned via a modular synthetic approach. The derived chromophores exhibit good thermal stability and large molecular hyperpolarizabilities, which can be effectively translated into very large electro-optic coefficients in poled polymers. We believe that these new chromophores can be used in exploring high-performance organic E-O and photorefractive materials where both thermal stability and optical nonlinearity are of equal importance.

Experimental Section

General Procedures. All chemicals were purchased from Aldrich and used as received unless otherwise specified. ^{1}H and ^{13}C NMR spectra were measured using a Bruker 500 instrument spectrometer. High-resolution mass spectrometry (HRMS) was performed by UW Bio-Mass Spectrometry Lab. Thermal transitions were measured on a TA Instruments differential scanning calorimeter (DSC) 2010 with a heating rate of 10 °C min^{-1}. Details of the HRS spectrometer have been provided elsewhere.[11] The sample concentrations from 1 to 80 μM in chloroform (Fisher ACS Spectranalyzed) were investigated. The sample was circulated through a low-volume flow cell and filtered using an in-line 0.1 μm PTFE filter to minimize chromophore photodecomposition and scattering from particulate matter. UV−vis absorption measurements (Shimadzu UV-1601) were obtained for each sample before and after each experiment check for chromophore photodegradation. No evidence of photodegradation was observed. Data analysis entailed fitting the HRS intensity to a Gaussian function after subtraction of the multiphoton-excited fluorescence background. The internal reference method was used to determine β for EZ-FTC relative to chloroform, and the external reference method was used to determine β for the chromophores of interest relative to EZ-FTC. Several of the chromophores (**A3**, **A4**, **B1**, **B2**, **B3**, and **B4**) absorb at the second harmonic (953.5 nm); therefore, the values for these chromophores presumably reflect resonance enhancement.

Synthesis of Compound 1d. A solution of 4-(4-methoxyphenylamino)benzonitrile (1.14 g, 5 mmol), 4-bromobiphenyl (1.16 g, 5 mmol), $Pd_2(dba)_3$ (56 mg, 0.06 mmol), 1,1′-bis(diphenylphosphino)-ferrocene (46 mg, 0.08 mmol), and *t*-BuONa (0.61 g, 6.3 mmol) in toluene (50 mL) was stirred at 110 °C for 24 h. Solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 4/1) to give a white solid (1.6 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.86 (s, 3 H), 6.95 (d, J = 8.5 Hz, 2 H), 7.00 (d, J = 9 Hz, 2 H), 7.18 (d, J = 9 Hz, 2 H), 7.23 (d, J = 8 Hz, 2 H), 7.38 (t, J = 7 Hz, 1 H), 7.45 (d, J = 7.5 Hz, 2 H), 7.48 (d, J = 7.5 Hz, 2 H), 7.57 (d, J = 8.5 Hz, 2 H), 7.61 (d, J = 8 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.5, 101.6, 115.1, 118.7, 120.0, 125.5, 126.8, 127.2, 128.2, 128.4, 128.8, 133.1, 137.3, 138.4, 140.1, 145.1, 151.6, 157.3.

Synthesis of Compound 2d. To a solution of **1d** (1.6 g, 4.25 mmol) in dry THF (50 mL) was added 1 M solution of diisobutylaluminum hydride in hexanes (8.5 mL, 8.5 mmol) dropwise by syringe at −78 °C. The reaction was stirred at −78 °C for 30 min and at 0 °C for 4 h. After the mixture was warmed up to room temperature, the mixture was diluted by ethyl acetate (30 mL) and then 6 M HCl solution (10 mL) was added to quench the reaction. The mixture was stirred for 30 min for complete hydrolysis. The organic solvent was collected and removed in vacuo. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 4/1) to yield a light yellow solid (1.15 g, 72%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.87 (s, 3 H), 6.97 (d, J = 9 Hz, 2 H), 7.06 (d, J = 8.5 Hz, 2 H), 7.21 (d, J = 9 Hz, 2 H), 7.27 (d, J = 8.5 Hz, 2 H), 7.39 (t, J = 7.5 Hz, 1 H), 7.48 (t, J = 7.5 Hz, 2 H), 7.59 (d, J = 8 Hz, 2 H), 7.62 (d, J = 8 Hz, 2 H), 7.72 (d, J = 9 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.4, 115.0, 118.3, 125.6, 126.7, 127.2, 128.1, 128.4, 128.8, 131.3, 137.2, 138.5, 140.1, 145.2, 153.3, 157.4, 190.5.

Synthesis of Compound 3a. Under N_2, to a solution of **2a** (1 g, 3.7 mmol) and diethyl (2-methylthiophene)-phosphonate (0.37 g, 3.7 mmol) in dry THF (20 mL) at 0 °C was added a 1 M solution of *t*-BuOK in 2-methyl-2-propanol (4.4 mL, 4.4 mmol) dropwise. The mixture was warmed up to room temperature and heated to 60 °C for 24 h. After removal of the organic solvent in vacuo, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 4/1) to obtain a yellow solid (0.9 g, 69%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.96 (d, J = 16 Hz, 1 H), 7.04−7.08 (m, 2 H), 7.08−7.14 (m, 5 H), 7.16−7.24 (m, 5 H), 7.31 (d, J = 8.5 Hz, 2 H), 7.34 (d, J = 8 Hz, 2 H), 7.40 (d, J = 8.5 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 120.1, 123.0, 123.5, 123.8, 124.5, 125.5, 127.1, 127.5, 127.9, 129.2, 131.0, 143.2, 147.3, 147.5.

Synthesis of Compound 3b. In a similar manner described above, **3b** was synthesized from **2b** as a yellow solid (82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.87 (s, 6 H), 6.92 (d, J = 9 Hz, 2 H), 6.94 (d, J = 15.5 Hz, 1 H), 7.03−7.10 (m, 5 H), 7.13−7.22 (m, 6 H), 7.28−7.33 (m, 2 H), 7.32 (d, J = 8.5 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.4, 114.8, 119.7, 122.2, 122.3, 123.4, 123.7, 125.3, 127.0, 127.4, 127.5, 128.0, 129.1, 130.2, 140.3, 143.3, 147.6, 147.7, 156.3.

Synthesis of Compound 3d. In a similar manner described above, **3d** was synthesized from **2d** as a yellow solid (81%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.87 (s, 3 H), 6.93 (d, J = 9 Hz, 2 H), 6.93 (d, J = 15.5 Hz, 1 H), 7.02−7.05 (m, 1 H), 7.07 (d, J = 3.5 Hz, 1 H), 7.09 (d, J = 8.5 Hz, 2 H), 7.15−7.22 (m, 6 H), 7.38 (d, J = 8.5 Hz, 3 H, overlap), 7.47 (t, J = 7.7 Hz, 2 H) 7.52 (d, J

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= 8.5 Hz, 2 H), 7.65 (d, J = 7.5 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.4, 114.7, 119.8, 122.4, 123.1, 123.7, 125.5, 126.6, 126.7, 127.0, 127.5, 127.6, 127.7, 127.8, 128.7, 130.3, 134.6, 140.0, 140.5, 143.3, 146.9, 147.3, 156.3.

Synthesis of Compound 3c. In a similar manner described above, **3c** was synthesized from **2c** as a yellow solid (85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.84 (s, 6 H), 6.87 (d, J = 8.5 Hz, 4 H), 6.9−6.95 (m, 3 H), 6.99−7.05 (m, 3 H), 7.10 (d, J = 8.5 Hz, 4 H), 7.17 (d, J = 4.5 Hz, 1 H), 7.30 (d, J = 9 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.5, 114.7, 119.2, 120.4, 123.5, 125.1, 126.6, 127.0, 127.5, 128.2, 129.1, 140.7, 143.5, 148.3, 156.0.

Synthesis of Compound 4a. To a solution of **3a** (0.8 g, 1.93 mmol) in dry THF (15 mL) was added a 2.5 M solution of *n*-BuLi in hexane (1.2 mL, 3 mmol) dropwise at −78 °C. After this mixture was stirred at this temperature for 1 h, dry DMF (0.19 mL, 2.4 mmol) was introduced. The resulting solution was stirred for 30 min at −78 °C and then allowed to warm up to room temperature. The reaction was quenched by water. THF was removed by evaporation. The residue was extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 4/1) to obtain a red solid (0.65 g, 88%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.05 (d, J = 8.5 Hz, 2 H), 7.07−7.12 (m, 5 H), 7.14 (d, J = 8 Hz, 4 H), 7.29 (d, J = 8 Hz, 2 H), 7.31 (d, J = 7.5 Hz, 2 H), 7.37 (d, J = 8.5 Hz, 2 H), 7.65 (d, J = 3.5 Hz, 1 H), 9.85 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 118.6, 122.5, 123.5, 124.7, 124.9, 125.8, 127.8, 129.3, 132.5, 137.3, 140.9, 147.1, 148.4, 153.0, 182.3.

Synthesis of Compound 4b. In a similar manner described above, **4b** was synthesized from **3b** as a red solid (82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.85 (s, 3 H), 6.90 (d, J = 9 Hz, 2 H), 7.01 (d, J = 8.5 Hz, 2 H), 7.04−7.14 (m, 8 H), 7.29 (t, J = 8 Hz, 2 H), 7.36 (d, J = 8.5 Hz, 2 H), 7.67 (d, J = 3.5 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.4, 114.4, 118.2, 121.3, 123.0, 124.0, 125.7, 127.7, 127.8, 128.5, 129.2, 132.7, 137.3, 139.9, 140.8, 147.3, 148.8, 153.3, 156.6, 182.4.

Synthesis of Compound 4d. In a similar manner described above, **4d** was synthesized from **3d** as a red solid (83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.86 (s, 3 H), 6.93 (d, J = 8.5 Hz, 2 H), 7.07 (d, J = 8.5 Hz, 2 H), 7.12 (s, 3 H), 7.15 (d, J = 8.5 Hz, 2 H), 7.18 (d, J = 8.5 Hz, 2 H), 7.35 (d, J = 7 Hz, 1 H), 7.39 (d, J = 8.5 Hz, 2 H), 7.47 (t, J = 7.5 Hz, 2 H), 7.52 (d, J = 8 Hz, 2 H), 7.61 (d, J = 8 Hz, 2 H), 7.68 (s, 1 H), 9.87 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.4, 114.8, 118.3, 121.5, 123.8, 125.9, 126.6, 126.9, 127.7, 127.76, 127.84, 128.6, 128.7, 132.6, 135.2, 137.7, 139.7, 140.3, 140.6, 146.5, 148.5, 153.2, 156.6, 182.6.

Synthesis of Compound 4c. In a similar manner described above, **4c** was synthesized from **3c** as a red solid (75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.84 (s, 3 H), 6.88 (d, J = 9 Hz, 4 H), 6.91 (d, J = 8.5 Hz, 2 H), 7.05 (d, J = 16 Hz, 1 H), 7.11 (d, J = 9 Hz, 6 H, overlap), 7.33 (d, J = 8.5 Hz, 2 H), 7.66 (d, J = 4 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.5, 114.8, 117.7, 119.5, 125.5, 127.0, 127.4, 127.8, 132.9, 137.4, 140.1, 140.6, 149.4, 153.5, 156.3, 182.3.

Synthesis of Compound A1. A mixture of aldehydic bridge **4a** (110 mg, 0.29 mmol) and acceptor **5** (110 mg, 0.35 mmol) in ethanol (3 mL) was stirred at 50 °C for 2 h. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 4:1). The product was redissolved in a minimum amount of dichloromethane. The solution was added to methanol to precipitate. After filtration, a dark solid was obtained (130 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.69 (d, J = 15.5 Hz, 1 H), 7.05 (d, J = 8.5 Hz, 2 H), 7.07−7.15 (m, 5 H), 7.17 (d, J = 8 Hz, 4 H), 7.30−7.36 (m, 5 H), 7.38 (d, J = 8.5 Hz, 2 H), 7.52−7.62 (m, 5 H), 7.82 (d, J = 8.5 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 59.1, 96.4, 97.7, 110.3, 110.5, 110.7, 112.3, 118.2, 121.9, 124.0, 125.3, 126.8, 128.2, 128.3, 128.7, 129.3, 129.5, 129.8, 131.7, 134.7, 138.5, 138.9, 141.8, 146.8, 149.3, 155.1, 156.9, 162.3, 175.0. HRMS (ESI) (M^+, $C_{41}H_{25}F_3N_4OS$): calcd, 678.1701; found, 678.1702.

Synthesis of Compound A2. In a similar manner described above, **A2** was synthesized from **4b** as a dark solid (66%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.85 (s, 3 H), 6.68 (d, J = 15.5 Hz, 1 H), 6.91 (d, J = 9 Hz, 2 H), 6.99 (d, J = 8.5 Hz, 2 H), 7.05−7.18 (m, 7 H), 7.28−7.38 (m, 6 H), 7.52−7.63 (m, 5 H), 7.82 (d, J = 15.5 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.5, 59.1, 96.4, 96.5, 97.8, 110.3, 110.6, 110.8, 112.2, 115.0, 117.8, 120.6, 123.6, 124.6, 126.8, 127.8, 127.9, 128.1, 128.4, 129.3, 129.4, 129.8, 131.6, 134.9, 138.4, 139.0, 139.5, 141.8, 146.9, 149.6, 155.5, 156.9, 162.3, 175.1. HRMS (ESI) (M^+, $C_{42}H_{27}F_3N_4O_2S$): calcd, 708.1807; found, 708.1805.

Synthesis of Compound A3. In a similar manner described above, **A3** was synthesized from **4c** as a dark solid (69%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.87 (s, 3 H), 6.69 (d, J = 15.3 Hz, 1 H), 6.94 (d, J = 9 Hz, 2 H), 7.06 (d, J = 9 Hz, 2 H), 7.07−7.10 (m, 1 H), 7.12 (d, J = 12 Hz, 2 H), 7.17 (d, J = 8.5 Hz, 2 H), 7.21 (d, J = 9 Hz, 2 H), 7.33−7.37 (m, 2 H), 7.39 (d, J = 8.5 Hz, 2 H), 7.53−7.63 (m, 9 H), 7.47 (dd, J_1= 7 Hz, J_2 = 7 Hz, 2 H) 7.83 (d, J = 15.5 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.5, 59.1, 96.2, 97.9, 110.3, 110.6, 110.8, 112.2, 115.0, 117.9, 121.0, 124.4, 126.7, 126.8, 127.0, 127.90, 127.94, 128.10, 128.14, 128.4, 128.8, 129.3, 129.8, 130.9, 131.6, 134.8, 136.1, 138.5, 139.0, 139.4, 140.4, 141.7, 146.2, 149.4, 155.4, 157.0, 162.3, 175.1. HRMS (ESI) (M^+, $C_{48}H_{31}F_3N_4O_2S$): calcd, 784.2120; found, 784.2105.

Synthesis of Compound A4. In a similar manner described above, **A4** was synthesized from **4d** as a dark solid (71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.84 (s, 6 H), 6.66 (d, J = 15 Hz, 1 H), 6.90 (d, J = 8.5 Hz, 6 H),7.00−7.20 (m, 7 H), 7.25−7.40 (m, 3 H), 7.50−7.65 (m, 5 H), 7.82 (d, J = 15 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.5, 59.1, 96.2, 96.4, 110.3, 110.4, 110.6, 112.0, 114.9, 117.2, 118.9, 122.5, 126.76, 126.82, 127.4, 128.0, 128.5, 129.4, 129.8, 131.6, 135.3, 138.3, 139.2, 139.6, 141.8, 150.2, 156.0, 156.7, 162.2, 175.2. HRMS (ESI) (M^+, $C_{43}H_{29}F_3N_4O_3S$): calcd, 738.1912; found, 738.1893.

Synthesis of Compound 6a. Under N_2, to a flask charged with ethanol (10 mL) were added small pieces of sodium (0.46 g, 20 mmol). The mixture was stirred at room temperature until the sodium disappeared and the evolution of hydrogen stopped. Isophorone (2.76 g, 20 mmol) and **2a** (5.47 g, 20 mmol) in dry THF (20 mL) were added into the solution by syringe. The mixture was stirred at 60 °C for 24 h. The solvent was removed by rotary evaporator. Ethyl acetate (30 mL) was added and the organic layer was extracted with water and brine. After removal of the solvent in vacuo, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 4/1) to obtain a yellow solid (5.9 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.14 (s, 6 H), 2.35 (s, 2 H), 2.5 (s, 2 H), 6.07 (s, 1 H), 6.83 (d, J = 16 Hz, 1 H), 6.98 (d, J = 16 Hz, 2 H), 7.06 (d, J = 9 Hz, 2 H), 7.11 (t, J = 7.5 Hz, 2 H), 7.15 (d, J = 7.5 Hz, 4 H), 7.29−7.34 (m, 4 H), 7.39 (d, J = 9 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.5, 33.3, 38.9, 51.3, 122.3, 123.6, 125.0, 126.1, 127.2, 128.2, 129.2, 129.4, 134.7, 146.9, 148.6, 155.3, 200.4.

Synthesis of Compound 6b. In a similar manner described above, **6b** was synthesized from **2b** as a yellow solid (71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.14 (s, 6 H), 2.34 (s, 2 H), 2.5 (s, 2 H), 3.84 (s, 3 H), 6.06 (s, 1 H), 6.81 (d, J = 16 Hz, 1 H), 6.89 (d, J = 9 Hz, 2 H), 6.95 (s, 1 H), 7.00 (d, J = 9 Hz, 2 H), 7.06 (t, J = 7 Hz, 2 H), 7.10−7.14 (m, 4 H), 7.28 (d, J = 7.5 Hz, 1 H), 7.29

(d, $J = 8$ Hz, 1 H), 7.36 (d, $J = 9$ Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.4, 33.2, 38.8, 51.3, 55.4, 114.7, 120.9, 123.0, 124.0, 125.9, 126.7, 127.6, 128.1, 128.3, 129.2, 134.8, 139.7, 147.0, 148.9, 155.4, 156.5, 200.3.

Synthesis of Compound 6c. In a similar manner described above, **6c** was synthesized from **2c** as a solid (75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.13 (s, 6 H), 2.32 (s, 2 H), 2.49 (s, 2 H), 3.83 (s, 6 H), 6.05 (s, 1 H), 6.77 (d, $J = 16$ Hz, 1 H), 6.85−6.91 (m, 6 H), 6.95 (d, $J = 16$ Hz, 2 H), 7.10 (d, $J = 8.5$ Hz, 4 H), 7.32 (d, $J = 8.5$ Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.5, 33.3, 39.1, 51.4, 55.4, 114.8, 119.3, 125.7, 126.3, 127.1, 127.5, 128.2, 134.9, 140.0, 149.6, 155.4, 156.4, 200.0.

Synthesis of Compound 7a. A 50 mL three-necked flask was charged with NaH (0.1 g, 4.45 mmol) in dry THF (10 mL) under N_2 atmosphere. Disiopropyl (cyanomethyl)-phosphonate (0.88 mL, 4.45 mmol) was introduced to the mixture dropwise by syringe at 0 °C with an ice bath. After the solution became clear, **6a** (0.7 g, 1.78 mmol) in THF (10 mL) was added. The mixture was refluxed for 18 h. After removal of THF in vacuo, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 5/1) to obtain a yellow solid (0.59 g, 79%). The ratio of the geometric isomers is 38:62% *Z*:*E* calculated by the integration of respective protons. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.04 (s, 3.72 H, *E*), 1.07 (s, 2.28 H, *Z*), 2.27 (s, 1.24 H, *E*), 2.34 (s, 2 H), 2.51 (s, 0.76 H, *Z*), 4.99 (s, 0.62 H, *E*), 5.15 (s, 0.38 H, *Z*), 6.29 (s, 0.38 H, *Z*), 6.7−7.4 (m, 16.62 H).

Synthesis of Compound 7b. In a similar manner described above, **7b** was synthesized from **6b** as a yellow solid (80%). The ratio of the geometric isomers is 38:62% *Z*:*E* calculated by the integration of respective protons. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.04 (s, 3.72 H, *E*), 1.07 (s, 2.28 H, *Z*), 2.27 (s, 1.24 H, *E*), 2.34 (s, 2 H), 2.51 (s, 0.76 H, *Z*), 3.85 (s, 3 H), 4.98 (s, 0.62 H, *E*), 5.14 (s, 0.38 H, *Z*), 6.28 (s, 0.38 H, *Z*), 6.7−7.4 (m, 15.62 H).

Synthesis of Compound 7c. In a similar manner described above, **7c** was synthesized from **6c** as a yellow solid (82%). The ratio of the geometric isomers is 38:62% *Z*:*E* calculated by the integration of respective protons. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.03 (s, 3.72 H, *E*), 1.06 (s, 2.28 H, *Z*), 2.26 (s, 1.24 H, *E*), 2.33 (s, 2 H), 2.50 (s, 0.76 H, *Z*), 3.84 (s, 6 H), 4.96 (s, 0.62 H, *E*), 5.13 (s, 0.38 H, *Z*), 6.27 (s, 0.38 H, *Z*), 6.72−7.32 (m, 14.62 H).

Synthesis of Compound 8a. To a solution of **7a** (0.5 g, 1.2 mmol) in dry toluene (10 mL) was added a 1 M solution of diisobutylaluminum hydride in hexanes (1.8 mL, 1.8 mmol) by syringe at −78 °C with a dry ice/acetone bath. The reaction was stirred at −78 °C for 2 h. After the mixture was warmed to room temperature, $NH_4Cl_{(sat)}$ solution was added to quench the reaction. The mixture was stirred for 30 min to complete the hydrolysis. The organic solvent was collected and removed in vacuo. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 4/1) to yield a red solid (0.4 g, 80%). The ratio of the geometric isomers is 37:63% *Z*:*E* calculated by the integration of respective aldehydic protons. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.08 (s, 2.22 H, *Z*), 1.10 (s, 3.78 H, *E*), 2.24 (s, 1.24 H, *Z*), 2.34 (s, 1.24 H, *Z*), 2.39 (s, 1.26 H, *E*), 2.73 (s, 1.26 H, *E*), 5.78 (d, $J = 7.8$ Hz, 0.37 H, *Z*), 5.97 (d, $J = 8.3$ Hz, 0.63 H, *E*), 6.35 (s, 0.63 H, *E*), 6.76−7.42 (m, 16.37 H), 10.10 (d, $J = 8.3$ Hz, 0.63 H, *E*), 10.25 (d, $J = 7.8$ Hz, 0.37 H, *Z*). HRMS (ESI) (M^+, $C_{30}H_{29}NO$): calcd, 419.2249; found, 419.2254.

Synthesis of Compound 8b. In a similar manner described above, **8b** was synthesized from **7b** as a red oil (79%). The ratio of the geometric isomers is 28:72% *Z*:*E* calculated by the integration of respective aldehydic protons. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.07 (s, 1.68 H, *Z*), 1.10 (s, 4.32 H, *E*), 2.33 (s, 0.56 H, *Z*), 2.39 (s, 2 H), 2.72 (s, 1.44 H, *E*), 3.85 (s, 3 H), 5.77 (d, $J = 7.5$ Hz, 0.28 H, *Z*), 5.96 (d, $J = 8$ Hz, 0.72 H, *E*), 6.34 (s, 0.72 H, *E*), 6.74−7.42 (m, 15.28 H), 10.10 (d, $J = 8$ Hz, 0.72 H, *E*), 10.25 (d, $J = 7.5$ Hz, 0.28 H, *Z*). HRMS (ESI) (M^+, $C_{31}H_{31}NO_2$): calcd, 449.2355; found, 449.2348.

Synthesis of Compound 8c. In a similar manner described above, **8c** was synthesized for **7c** as a red solid (78%). The ratio of the geometric isomers is 30:70% *Z*:*E* calculated by the integration of respective aldehydic protons. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.06 (s, 1.8 H, *Z*), 1.09 (s, 4.2 H, *E*), 2.32 (s, 0.6 H, *Z*), 2.37 (s, 0.6 H, *Z*), 2.38 (s, 1.4 H, *E*), 2.72 (s, 1.4 H, *E*), 3.84 (s, 6 H), 5.76 (d, $J = 8$ Hz, 0.3 H, *Z*), 5.95 (d, $J = 8$ Hz, 0.7 H, *E*), 6.32 (s, 0.7 H, *E*), 6.75−7.35 (m, 14.3 H), 10.09 (d, $J = 8$ Hz, 0.7 H, *E*), 10.24 (d, $J = 8$ Hz, 0.3 H, *Z*). HRMS (ESI) (M^+, $C_{32}H_{33}NO_3$): calcd, 479.2460; found, 479.2458.

Synthesis of Compound B1. A mixture of **8a** (120 mg, 0.29 mmol) and acceptor **5** (110 mg, 0.35 mmol) in ethanol (3 mL) was stirred at 50 °C for 2 h. After the removal of solvent, the residue was directly purified by column chromatography on silica gel (hexane/EtOAc, v/v, 4/1). The product was redissolved in a minimum amount of dichloromethane. The solution was added to methanol to precipitate. After filtration, a dark solid was obtained (0.13 g, 65%). The ratio of the geometric isomers is 13:87% *Z*:*E* calculated by the integration of respective protons. ^{1}H NMR of *E* isomer (500 MHz, $CDCl_3$): δ 0.95 (s, 3 H), 1.05 (s, 3 H), 2.24 (d, $J = 15.5$ Hz, 1 H), 2.34 (d, $J = 15.5$ Hz, 1 H), 2.43 (s, 2 H), 6.30−6.45 (m, 3 H), 6.80−7.05 (m, 6 H), 7.05−7.20 (m, 5 H), 7.25−7.40 (m, 4 H), 7.50−7.65 (m, 5 H), 7.95−8.10 (m, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.0, 28.5, 31.5, 39.4, 39.7, 57.8, 110.7, 111.2, 116.2, 122.0, 122.1, 123.85, 123.90, 125.16, 125.2, 126.7, 128.2, 128.4, 129.0, 129.4, 129.58, 129.6, 129.9, 130.8, 131.3, 134.3, 146.5, 146.83, 146.87, 149.0, 150.2, 157.9, 162.5, 175.6. HRMS (ESI) (M^+, $C_{46}H_{35}F_3N_4O$): calcd, 716.2763; found, 716.2767.

Synthesis of Compound B2. In a similar manner described above, **B2** was synthesized from **8b** as a dark solid (73%). The ratio of the geometric isomers is 14:86% *Z*:*E* calculated by the integration of respective protons. ^{1}H NMR of *E* isomer (500 MHz, $CDCl_3$): δ 0.99 (s, 3 H), 1.05 (s, 3 H), 2.24 (d, $J = 16.3$ Hz, 1 H), 2.34 (d, $J = 16.3$ Hz, 1 H), 2.43 (s, 2 H), 3.85 (s, 3 H), 6.30−6.45 (m, 3 H), 6.80−7.05 (m, 6 H), 7.05−7.20 (m, 5 H), 7.25−7.40 (m, 4 H), 7.50−7.65 (m 5 H), 7.95−8.10 (m, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.0, 28.5, 31.5, 39.4, 39.7, 55.5, 57.7, 110.7, 111.2, 111.5, 114.9, 116.0, 120.7, 120.8, 123.5, 124.4, 124.5, 126.7, 127.78, 127.81, 128.5, 128.8, 128.9, 129.3, 129.59, 129.61, 130.0, 130.7, 131.3, 134.6, 139.6, 146.5, 146.9, 149.4, 150.5, 156.9, 158.0, 162.4, 175.6. HRMS (ESI) (M^+, $C_{47}H_{37}F_3N_4O_2$): calcd, 746.2869; found, 746.2871.

Synthesis of Compound B3. In a similar manner described above, **B3** was synthesized from **8c** as a dark solid (72%). The ratio of the geometric isomers is 15:85% *Z*:*E* calculated by the integration of respective protons. ^{1}H NMR of *E* isomer (500 MHz, $CDCl_3$): δ 0.99 (s, 3 H), 1.05 (s, 3 H), 2.24 (d, $J = 16.3$ Hz, 1 H), 2.34 (d, $J = 16.3$ Hz, 1 H), 2.42 (s, 2 H), 3.84 (s, 6 H), 6.30−6.45 (m, 3 H), 6.75−6.95 (m, 8 H), 7.05−7.20 (m, 4 H), 7.25−7.40 (2 H), 7.45−7.65 (m 5 H), 7.95−8.15 (m, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.0, 28.5, 31.5, 39.4, 39.7, 55.4, 57.4, 110.8, 111.3, 111.6, 114.81, 115.8, 119.0, 126.7, 127.2, 127.3, 127.8, 128.5, 128.6, 128.8, 129.55, 129.57, 130.0, 130.5, 131.2, 135.1, 139.7, 146.5, 150.0, 151.0, 156.6, 158.3, 162.3, 175.7. HRMS (ESI) (M^+, $C_{48}H_{39}F_3N_4O_3$): calcd, 776.2974; found, 776.2971.

Synthesis of Compound 11. A mixture of 4-butoxy-aniline (6 g, 36.3 mmol), 1-[2-(methoxy−methoxy)]ethoxy-4-bromo-benzene **10** (8 g, 30.6 mmol), $Pd_2(dba)_3$ (0.53 g, 0.57 mmol), 1,1′-bis-(diphenylphosphino)-ferrocene (0.5 g, 0.9 mmol), and *t*-BuONa (5

g, 50 mmol) in toluene (130 mL) was stirred at 110 °C for 24 h. Toluene was removed in vacuo and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 3/1 and then 4/1) to give an oil (8 g, 76%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.98 (t, J = 7 Hz, 3 H), 1.45−1.55 (m, 2 H), 1.71−1.80 (m, 2 H), 3.41 (s, 3 H), 3.88 (t, J = 5 Hz, 2 H), 3.92 (t, J = 6.5 Hz, 2 H), 4.11 (t, J = 5 Hz, 2 H), 4.72 (s, 2 H), 6.82 (d, J = 9 Hz, 2 H), 6.84 (d, J = 9 Hz, 2 H), 6.91 (d, J = 8.5 Hz, 2 H), 6.93 (d, J = 8.5 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.8, 19.2, 31.4, 55.2, 66.0, 67.8, 68.1, 96.5, 115.3, 115.4, 119.0, 119.7, 137.5, 138.3, 153.1, 153.8.

Synthesis of Compound 12. A mixture of **11** (7.4 g, 21.5 mmol), 4-bromobenzonitrile (4.7 g, 25.8 mmol), $Pd_2(dba)_3$ (0.35 g, 0.38 mmol), 1,1′-bis(diphenylphosphino)-ferrocene (0.34 g, 0.6 mmol), and *t*-BuONa (3.4 g, 35 mmol) in toluene (100 mL) was stirred at 110 °C for 24 h. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 4/1) to give an oil (7.7 g, 80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.98 (t, J = 7.5 Hz, 3 H), 1.4−1.6 (m, 2 H), 1.7−1.8 (m, 2 H), 3.40 (s, 3 H), 3.90 (t, J = 4.5 Hz, 2 H), 3.95 (t, J = 6.5 Hz, 2 H), 4.14 (t, J = 4.5 Hz, 2 H), 4.72 (s, 2 H), 6.78 (d, J = 9 Hz, 2 H), 6.86 (d, J = 9 Hz, 2 H), 6.90 (d, J = 9 Hz, 2 H), 7.07 (d, J = 9 Hz, 2 H), 7.09 (d, J = 9 Hz, 2 H), 7.35 (d, J = 9 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 13.8, 19.2, 31.3, 55.3, 65.9, 67.6, 67.9, 96.6, 100.5, 115.6, 115.8, 117.1, 120.1, 127.8, 127.9, 133.1, 138.3, 138.9, 152.2, 156.4, 156.9.

Synthesis of Compound 2e. To a solution of compound **12** (7.6 g, 17.1 mmol) in toluene (100 mL) was added a 1 M solution of DIBAL-H in hexanes (25.6 mL, 15.6 mmol) by syringe at −78 °C. The reaction was stirred at this temperature for 2 h. After the mixture was warmed to room temperature, $NH_4Cl_{(sat)}$ solution was added to quench the reaction and the mixture was stirred for 30 min for hydrolysis. Organic solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 3/1) to give an oil (7 g, 91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.98 (t, J = 7 Hz, 3 H), 1.4−1.6 (m, 2 H), 1.7−1.9 (m, 2 H), 3.40 (s, 3 H), 3.90 (t, J = 4.5 Hz, 2 H), 3.95 (t, J = 6.5 Hz, 2 H), 4.15 (t, J = 4.5 Hz, 2 H), 4.72 (s, 2 H), 6.84 (d, J = 9 Hz, 2 H), 6.88 (d, J = 9 Hz, 2 H), 6.91 (d, J = 9 Hz, 2 H), 7.10 (d, J = 9 Hz, 2 H), 7.12 (d, J = 9 Hz, 2 H), 7.62 (d, J = 9 Hz, 2 H), 9.75 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.8, 19.2, 31.3, 55.3, 65.9, 67.6, 67.9, 96.6, 115.5, 115.7, 116.8, 127.8, 127.9, 128.0, 131.4, 138.5, 139.1, 154.0, 156.4, 156.9, 190.2.

Synthesis of Compound 6d. In a similar manner described above, **6d** was obtained from **2e** as an oil (75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.98 (t, J = 7 Hz, 3 H), 1.09 (s, 6 H), 1.4−1.6 (m, 2 H), 1.7−1.9 (m, 2 H), 2.29 (s, 2 H), 2.45 (s, 2 H), 3.40 (s, 3 H), 3.90 (t, J = 5 Hz, 2 H), 3.94 (t, J = 6.5 Hz, 2 H), 4.13 (t, J = 5 Hz, 2 H), 4.72 (s, 2 H), 6.74 (d, J = 16 Hz, 1 H), 6.8−6.9 (m, 6 H), 6.91 (d, J = 16 Hz, 1 H), 7.04 (d, J = 6 Hz, 2 H), 7.06 (d, J = 6 Hz, 2 H), 7.28 (d, J = 9 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.8, 19.2, 28.5, 31.3, 33.3, 39.1, 51.4, 55.3, 65.9, 67.6, 67.9, 96.6, 115.3, 115.5, 119.4, 125.7, 126.3, 126.9, 127.1, 127.5, 128.2, 134.9, 140.3, 149.6, 155.4, 155.5, 156.0, 200.1.

Synthesis of Compound 7d. In a similar manner described above, **7d** was obtained from **6d** as an oil (85%). The ratio of the geometric isomers is 40:60% *Z*:*E* calculated by the integration of respective protons. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.02 (t, J = 7.5 Hz, 3 H), 1.03 (s, 0.4 H, *Z*), 1.06 (s, 0.6 H, *E*), 1.45−1.6 (m, 2 H), 1.75−1.85 (m, 2 H), 2.21 (s, 1.2 H, *E*), 2.26 (s, 0.8 H, *Z*), 2.33 (s, 1.2 H, *E*), 2.49 (s, 0.8 H, *Z*), 3.44 (s, 3 H), 3.93 (t, J = 5 Hz, 2 H), 3.98 (t, J = 6 Hz, 2 H), 4.17 (t, J = 5 Hz, 2 H), 4.76 (s, 2 H), 4.96 (s, 0.6 H), 5.12 (s, 0.4 H), 6.26 (s, 0.4 H), 6.71−6.84 (m, 2 H), 6.85−6.93 (m, 6 H), 7.05−7.12 (m, 4 H), 7.27 (s, 0.4 H, *Z*), 7.28−7.31 (m, 2 H).

Synthesis of Compound 8d. In a similar manner described above, **8d** was obtained from **7d** as a red oil (75%). The ratio of the geometric isomers is 30:70% *Z*:*E* calculated by the integration of respective protons. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.02 (t, J = 7.5 Hz, 3 H), 1.06 (s, 1.8 H, *Z*), 1.09 (s, 4.2 H, *E*), 1.4−1.6 (m, 2 H), 1.7−1.9 (m, 2 H), 2.32 (s, 0.6 H, *Z*), 2.37 (s, 0.6 H, *Z*), 2.38 (s, 1.4 H, *E*), 2.71 (s, 1.4 H, *E*), 3.44 (s, 3 H), 3.93 (t, J = 4.5 Hz, 2 H), 3.98 (t, J = 6 Hz, 2 H), 4.17 (t, J = 4.5 Hz, 2 H), 4.76 (s, 2 H), 5.76 (d, J = 8 Hz, 0.3 H, *Z*), 5.95 (d, J = 8 Hz, 0.7 H, *E*), 6.32 (s, 0.7 H, *E*), 6.75−6.95 (m, 8 H), 7.08 (d, J = 5.5 Hz, 2 H), 7.09 (d, J = 5.5 Hz, 2 H), 7.23 (s, 0.3 H, *Z*), 7.28−7.33 (m, 2 H), 10.09 (d, J = 8 Hz, 0.7 H, *E*), 10.24 (d, J = 8 Hz, 0.3 H, *Z*). HRMS (ESI) (M^+, $C_{38}H_{45}NO_5$): calcd, 595.3298; found, 595.3288.

Synthesis of Compound 8e. To a solution of **8d** (0.4 g, 0.67 mmol) in THF (12 mL) was added 6 M HCl (1.5 mL). The reaction was refluxed for 8 h. The solution was diluted with ethyl acetate (30 mL) and extracted with 5% $NaHCO_3$ (20 mL × 2) and brine. After removal of organic solvent, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 1/1) to give a red oil (0.29 g, 78%). The ratio of the geometric isomers is 33:67% *Z*:*E* calculated by the integration of respective protons. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.02 (t, J = 7.5 Hz, 3 H), 1.06 (s, 1.98 H, *Z*), 1.09 (s, 4.02 H, *E*), 1.45−1.60 (m, 2 H), 1.7−1.9 (m, 2 H), 2.32 (s, 0.66 H, *Z*), 2.37 (s, 0.66 H, *Z*), 2.38 (s, 1.34 H, *E*), 2.71 (s, 1.34 H, *E*), 3.98 (t, J = 6.5 Hz, 2 H), 3.99 (t, J = 4.5 Hz, 2 H), 4.10 (t, J = 4.5 Hz, 2 H), 5.76 (d, J = 8 Hz, 0.33 H, *Z*), 5.95 (d, J = 8.5 Hz, 0.66 H, *E*), 6.32 (s, 0.66 H, *E*), 6.75−6.95 (m, 8 H), 7.05−7.14 (m, 4 H), 7.23 (s, 0.33 H, *Z*), 7.27−7.33 (m, 2 H), 10.08 (d, J = 8 Hz, 0.67 H, *E*), 10.23 (d, J = 8.5 Hz, 0.33 H, *Z*). HRMS (ESI) (M^+, $C_{36}H_{41}NO_4$): calcd, 551.3036; found, 551.3048.

Synthesis of Compound 9. In a similar manner described above, **9** was obtained from **8e** as a dark solid (61%). The ratio of the geometric isomers is 15:85% *Z*:*E* calculated by the integration of respective protons. ^{1}H NMR of *E* isomer (500 MHz, $CDCl_3$): δ 0.99 (s, 3 H), 1.02 (t, J = 7.5 Hz, 3 H), 1.04 (s, 3 H), 1.49−1.58 (m, 2 H), 1.77−1.85 (m, 2 H), 2.24 (d, J = 16 Hz, 1 H), 2.33 (d, J = 16 Hz, 1 H), 2.42 (s, 2 H), 3.95−4.05 (m, 4 H), 4.11 (t, J = 4 Hz, 2 H), 6.35 (d, J = 13.5 Hz, 1 H), 6.38 (d, J = 16 Hz, 1 H), 6.40 (s, 1 H), 6.82 (d, J = 16 Hz, 1 H), 6.86−6.96 (m, 7 H), 7.06−7.16 (m, 4 H), 7.28−7.36 (m, 2 H), 7.50−7.60 (m, 5 H), 7.98−8.12 (dd, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 13.8, 19.2, 28.0, 28.5, 31.3, 31.5, 39.5, 39.8, 57.6, 61.5, 67.9, 69.5, 110.8, 111.3, 111.6, 115.4, 115.5, 115.9, 119.2, 126.7, 127.2, 127.3, 127.9, 128.6, 128.8, 129.6, 130.1, 130.5, 131.3, 134.9, 139.4, 140.2, 146.5, 149.9, 150.9, 155.5, 156.3, 158.2, 162.3, 175.7. HRMS (ESI) (M^+, $C_{52}H_{47}F_3N_4O_4$): calcd, 848.3549; found, 848.3541.

Synthesis of Compound B4. To a solution of **9** (0.1 g, 0.12 mmol) in THF (10 mL) was added a solution of 3,5-bis-(trifluoromethyl)-benzoyl chloride (0.2 g, 0.72 mmol) in THF (2 mL). The reaction was refluxed for 12 h. After being cooled to ambient temperature, the mixture was diluted with ethyl acetate (20 mL) and washed with 5% aqueous $NaHCO_3$ (2 × 20 mL). The organic layer was dried ($MgSO_4$) and concentrated in vacuo to obtain a residue which was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 4/1 and then 3/1). The product was redissolved in a minimum amount of dichloromethane. The solution was added to methanol to precipitate. After filtration, a dark solid was obtained (80 mg, 61%). The ratio of the geometric isomers is 13:87% *Z*:*E* calculated by the integration of respective protons. ^{1}H NMR of *E* isomer (500 MHz, $CDCl_3$): δ 0.99 (s, 3 H), 1.02 (t, J = 7.5 Hz, 3 H), 1.05 (s, 3 H), 1.49−1.59 (m, 2 H),

1.77−1.85 (m, 2 H), 2.24 (d, $J = 16$ Hz, 1 H), 2.34 (d, $J = 16$ Hz, 1 H), 2.42 (s, 2 H), 3.98 (t, $J = 6.5$ Hz, 2 H), 4.37 (t, $J = 4.5$ Hz, 2 H), 4.79 (t, $J = 4.5$ Hz, 2 H), 6.35 (d, $J = 14$ Hz, 1 H), 6.38 (d, $J = 16$ Hz, 1 H), 6.41 (s, 1 H), 6.82 (d, $J = 16$ Hz, 1 H), 6.86−6.96 (m, 7 H), 7.06−7.18 (m, 4 H), 7.28−7.38 (m, 2 H), 7.50−7.62 (m, 5 H), 7.98−8.10 (dd, 1 H), 8.12 (s, 1 H), 8.56 (s, 2 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 13.8, 19.2, 28.0, 28.5, 31.3, 31.5, 39.5, 39.8, 57.6, 64.4, 65.9, 67.9, 110.8, 111.3, 111.6, 115.4, 115.6, 115.9, 119.3, 121.7, 123.9, 126.5, 126.7, 127.0, 127.1, 127.4, 128.0, 128.5, 128.8, 129.59, 129.61, 129.9, 130.4, 130.5, 131.3, 132.0, 132.1, 132.4, 134.9, 139.4, 140.5, 146.5, 149.8, 150.8, 155.1, 156.4, 158.2, 162.3, 163.9, 175.7. HRMS (ESI) (M^+, $C_{61}H_{49}F_9N_4O_5$): calcd, 1088.3559; found, 1088.3575.

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