Synthesis of Functionalized Organic Second-Order Nonlinear Optical Chromophores for Electrooptic Applications

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Received August 21, 1998

The design and syntheses of functionalized second-order nonlinear optical chromophores, suitable for covalent incorporation into functionalized high-performance polymers, are described. The chromophores with hydroxy alkyl functionality have diarylamino groups as the donor moiety and a styryl thiophene moiety as the conjugated bridge. The triarylamine parts of the molecules were synthesized using palladium-catalyzed C−N bond forming reactions. The conjugated bridge was assembled using the Wittig reaction. The acceptor groups were installed in the last steps of the syntheses.

Electrooptic materials, whose index of refraction can be changed by the application of an electric field, are of interest due to their potential for use in applications including optical data transmission and optical information processing.[1,2] One of the important components of these materials is nonlinear optical (NLO) chromophores.[3−5] The NLO chromophores can be incorporated into polymer hosts as guests or they can be covalently attached to the polymer backbone. Covalent incorporation of the NLO chromophores is preferred over the host−guest system, since: (i) sublimation of the NLO chromophores under poling conditions is obviated when they are covalently incorporated into the polymeric system and (ii) processibility problems due to phase separation at high loading is less likely with covalently incorporated systems.

Covalent incorporation can be achieved by using functionalized NLO chromophores as comonomers in the polymerization reaction or by attaching the chromophores to a prefunctionalized polymer under mild reaction conditions.[6] In the former process, the chromophore can either be a part of the polymer backbone or a side-chain appendage.[7−10] Both of these procedures involve survival of the NLO chromophores under the often harsh polymerization reaction conditions. Therefore, incorporation of chromophores into a prefunctionalized polymer as a side-chain appendage using the latter procedure is preferable

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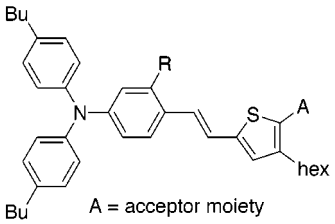
10.1021/jo981707v CCC: $18.00
Published on Web 05/25/1999

in many cases.[11] This process commonly involves incorporation of hydroxy functionalized chromophores into polymers with phenolic functionalities under Mitsunobu reaction conditions.[12]

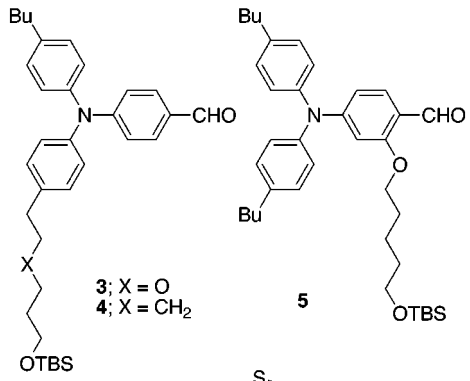


1 (R = -H)
2 (R = -OMe)

The required noncentrosymmetric alignment of chromophores in organic electrooptic materials is achieved by electric poling at temperatures near the glass transition temperature (T_g) of the host polymer. Therefore, it is imperative that the NLO chromophores possess high thermal stabilities. It has been recently shown that substitution of the diarylamino group as the donor in place of the dialkylamino group improves the thermal stabilities of the chromophores without a major compromise in optical nonlinearities.[13−15] Using this design principle, we have recently demonstrated that chromophores represented by structure **1** exhibit enhanced photochemical stabilities in addition to high optical nonlinearities and thermal stabilities when compared to the corresponding dialkylamino donor-based chromophores.[16] We also observed that the incorporation of an additional methoxy group on the bridging phenyl ring (represented by **2**) further enhances the optical nonlinearity without any major effect on the thermal and photochemical stabilities. Therefore, we chose to incorporate hydroxy alkyl functionality on the aryl rings in the chromophores of the types represented by **1** and **2**. In this paper, we describe the syntheses of these hydroxy-functionalized chromophores with tricyanovinyl, dicyanovinyl, or 3-phenylisoxazolone moieties as acceptors.

Results and Discussion

The syntheses of these chromophores were approached in a convergent fashion. The functionalized triarylamine parts of the chromophores were synthesized as *tert*-butyldimethylsilyl (TBS)-protected hydroxyalkyl terminated (diarylamino)aryl carboxaldehydes **3**−**5**.[17] The main skeletons of the chromophores were then assembled by Wittig reactions with a thiophene phosphonium salt **6**. The acceptor moieties were installed in the last or the penultimate step of the synthesis.



The triarylamines were assembled using the palladium-catalyzed aryl carbon−nitrogen bond-forming reaction reported in the literature recently.[18] We realized that this methodology can be used to rapidly assemble unsymmetrically substituted triarylamines by a sequential addition of aryl bromides to the anilines.[19] To synthesize **3**, aniline was treated sequentially with the aryl bromides **7** and **8** in the presence of sodium *tert*-butoxide and catalytic amounts of tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$) and 1,1′-bis(diphenylphosphino)ferrocene (DPPF) to afford the triarylamine product **9** in 72% yield.[19] The allylic double bond in the compound **9** was hydroborated using 9-BBN, which after oxidative workup afforded the corresponding alcohol. The alcohol was then protected as the TBS ether to afford the compound **10** in 66% overall yield. Compound **10** was then treated with *N*-bromosuccinimide in DMF to brominate the only available para position of the triarylamine. Bromine−lithium exchange followed by treatment with DMF provided the aldehyde **3** in 75% yield.[20] The synthetic approach is outlined in Scheme 1.

To synthesize the triarylaminecarboxaldehyde **4**, we utilized the one-pot triarylamine synthetic strategy with 4-butylaniline, bromobenzene, and 1,4-dibromobenzene to obtain the brominated triarylamine **11** in 75% yield. Treatment of the compound **11** with *tert*-butyllithium followed by 6-bromohex-1-ene afforded the triarylamine **12** in 73% yield. Hydroboration followed by oxidation afforded the corresponding primarily alcohol, which was then protected as a TBS ether **13** as shown in Scheme 2.[21]

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(16) Thayumanavan, S. et al. Manuscript in preparation.

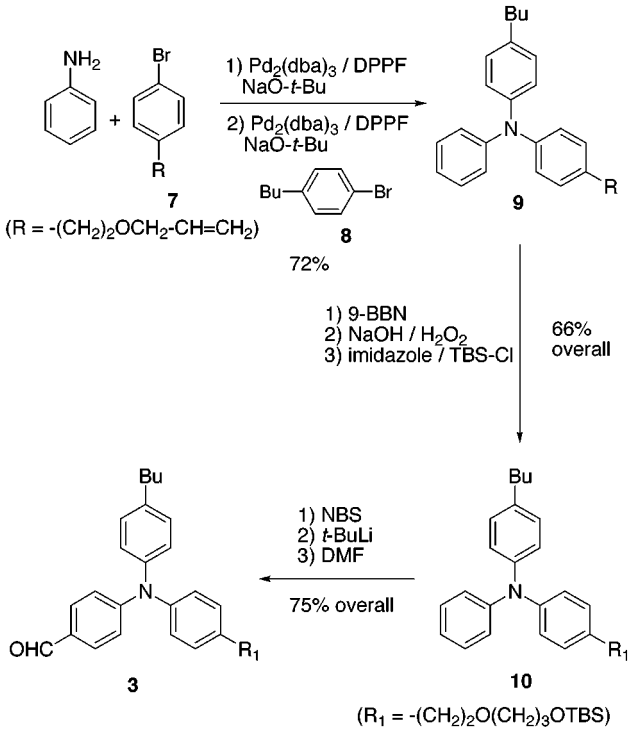
(17) We are interested in analyzing the effect of the additional ethereal linkage, such as in **5**, on the stability of the chromophores. Therefore, we targeted both **3** and **4** to analyze the effect of an additional ethereal linkage in the absence of other variables.

(18) (a) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217. (c) Wolfe, J. P.; Wagaw, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 7215. For a recent review, see: (c) Hartwig, J. F. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2046.

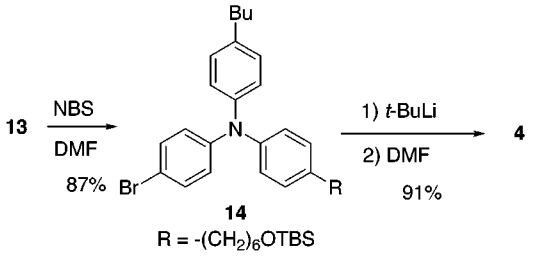
(19) Thayumanavan, S.; Barlow, S.; Marder, S. R. *Chem. Mater.* **1997**, *9*, 3231.

(20) Application of Vilsmeier-type reaction conditions to synthesize **3** from **10** resulted in the conversion of the −OTBS group to the −Cl group.

Scheme 1



Bromination of the available para position in the triarylamine ring using *N*-bromosuccinimide in DMF provided the brominated triarylamine **14**. Bromine−lithium exchange and the subsequent treatment of the organolithium intermediate with DMF afforded the triarylamine carboxaldehyde **4** in 91% yield as depicted below.

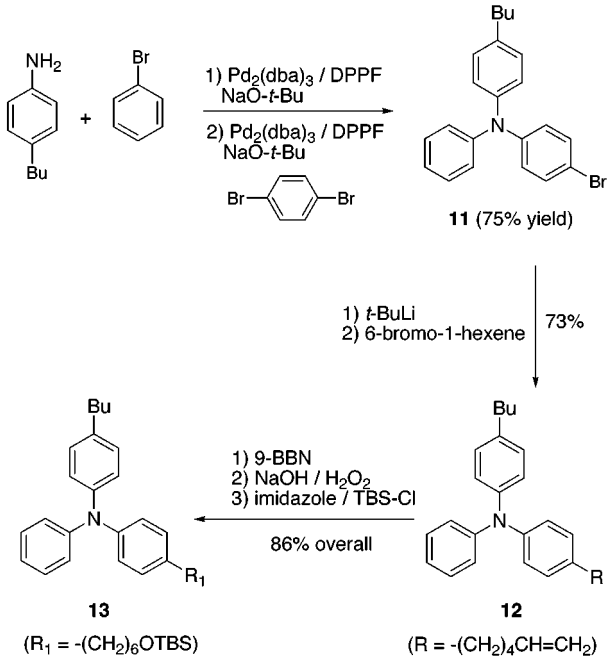


The alkoxy-functionalized triarylaminecarboxaldehyde **5** was synthesized from the triarylamine **15**, which was assembled in 84% yield from *m*-anisidine and **8** under palladium catalysis conditions. The methoxy-substituted triarylamine **15** was converted to the phenol **16** by reaction with BBr_3 in 66% yield. Treatment of **16** with monoprotected pentane-1,5-diol **17** under Mitsunobu reaction conditions affords the product **18**. The synthetic sequence is shown in Scheme 3.

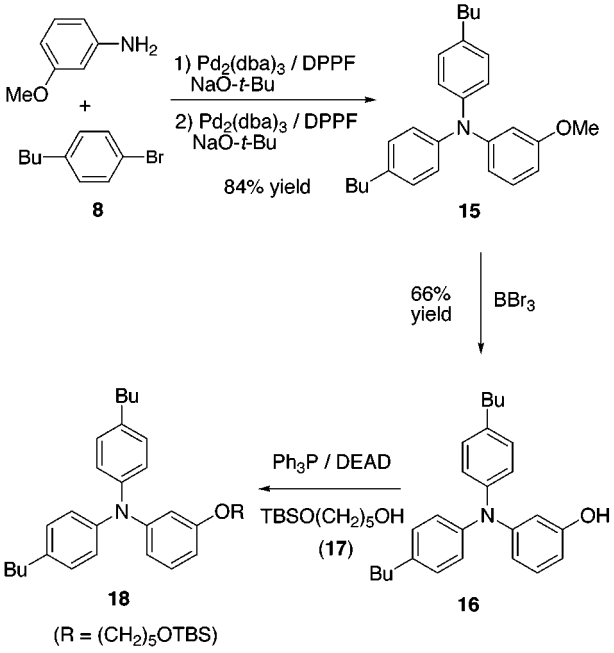
Bromination of the open para position in the triarylamine ring in **18** using *N*-bromosuccinimide in DMF provided the brominated triarylamine **19** in low yield. Bromine−lithium exchange and the subsequent treatment of the organolithium intermediate with DMF afforded the triarylamine carboxaldehyde **5** in 14% overall yield from **16**.[22]

(21) We also attempted to synthesize **13** directly from **11** by treating the lithiated intermediate with the TBS ether of 6-bromo-1-hexanol. However, the product had an inseparable impurity that was carried over from the preparation of the TBS ether of 6-bromo-1-hexanol. The origin of the impurity is ascribed to an inseparable impurity in the commercially available starting material.

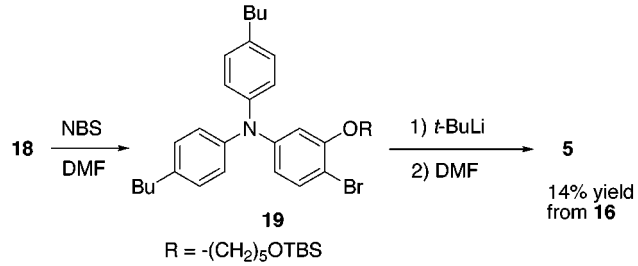
Scheme 2



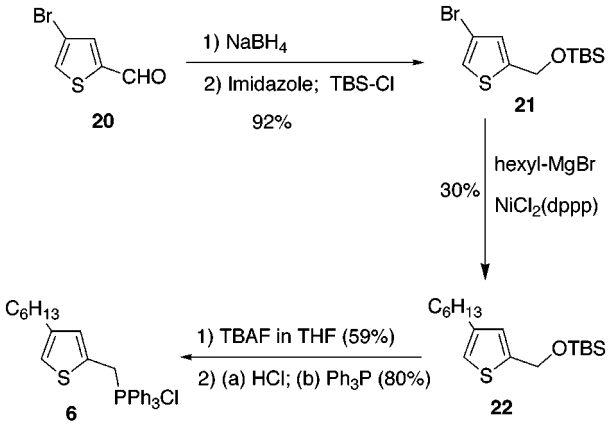
Scheme 3



For the synthesis of 4-hexylthiophene-2-methylenetriphenylphosphonium chloride (**6**), we utilized the com-

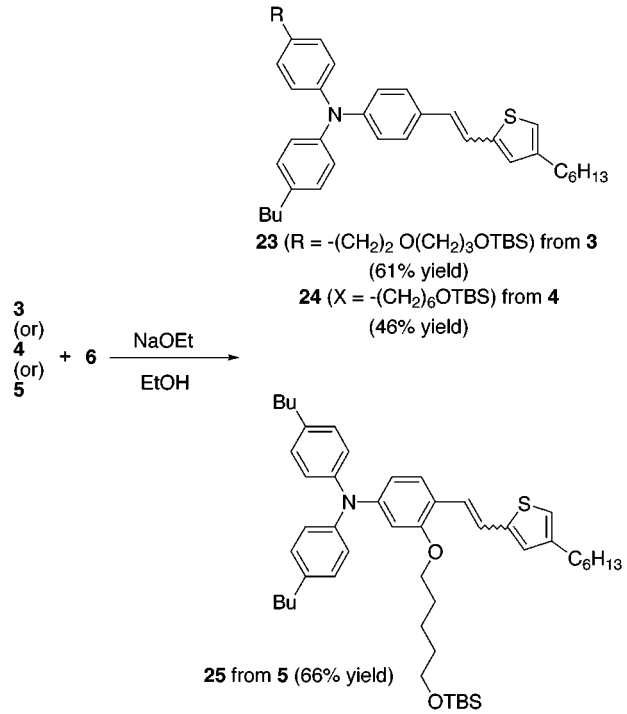


Scheme 4



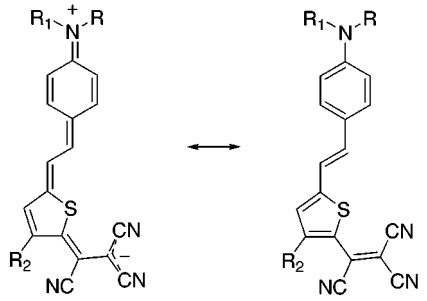
mercially available 4-bromothiophene-2-carboxaldehyde (**20**) as the starting material. Reduction of the aldehyde to the corresponding alcohol followed by protection of the hydroxy group provided the 4-bromothiophenemethylene ether (**21**). At this juncture, the hexyl group was installed by a nickel-catalyzed coupling reaction to afford **22**.[23] The methylene ether was then converted to the phosphonium salt **6** through the corresponding alcohol and chloride. The synthetic sequence is outlined in Scheme 4.[24]

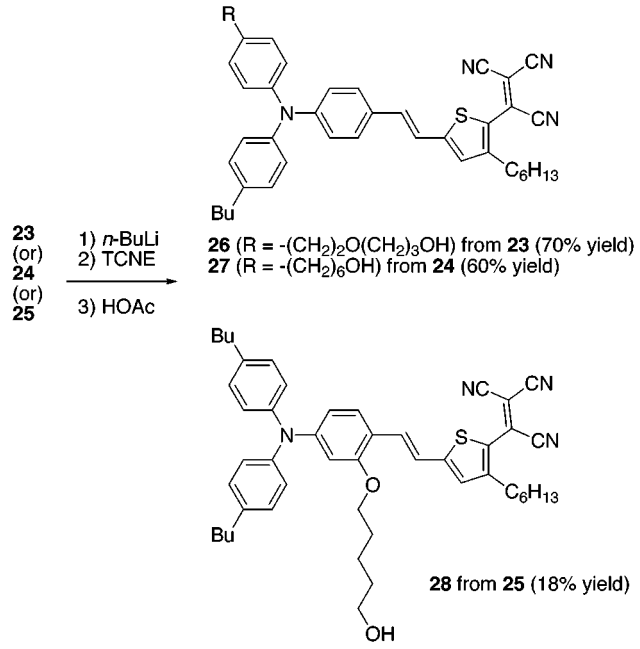
Treatment of the aldehydes **3**−**5** with the phosphonium salt **6** under Wittig reaction conditions using sodium ethoxide as the base in ethanol afforded the thiophenyl stilbene compounds **23**−**25** as outlined below. The compounds were obtained as a mixture of cis and trans isomers which were not separated before performing the next step of the reaction sequence.



Treatment of the compound **23**−**25** with *n*-butyllithium, followed by reaction with tetracyanoethylene, afforded the corresponding tricyanovinyl-substituted chromophores. Deprotection of the TBS ether at this juncture, using acetic acid, afforded the hydroxy-functionalized tricyanovinylated chromophores **26**−**28**.[25] When we attempted to synthesize these chromophores by heating tetracyanoethylene in DMF with **23**, the product **26** was directly obtained in only 12% yield. In all these reactions, the chromophores were obtained exclusively as the trans isomer after the installation of the tricyanovinyl moiety in the structure. This result is attributed to the strength of the tricyanovinyl group as an acceptor that favors significant contribution from the charge-transfer structure. This reduces the double-bond character of the formal C=C bond, thus lowering the barrier for isomerization to the thermodynamically more stable trans isomer (Scheme 5).

Scheme 5





We are also interested in NLO chromophores that absorb in different regions of the visible spectrum (see Table 1). Therefore, we targeted functionalized chromophores with dicyanovinyl and 3-phenylisoxazolone groups as acceptor moieties. For this purpose, we treated

(22) We suggest that the low-yielding step in the reaction is the bromination reaction. During an independent effort to brominate **15**, we realized that longer reaction times are needed for this type of substrate.

(23) Tamo, K. In *Comprehensive Organic Synthesis*: *Selectivity, Strategy, and Efficiency in Modern Organic Chemistry*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 3, Chapter 2.2.

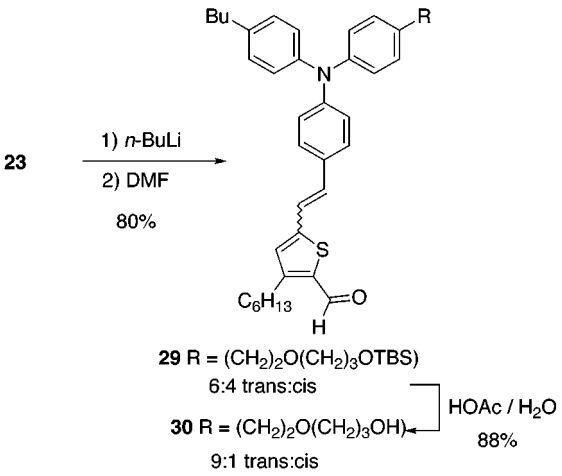
(24) We have used an alternate route to synthesize **6**.[16] However, the route reported here is useful since it allows for flexibility to introduce groups other than the hexyl at the 4-position.

(25) The reason for the low yield in the synthesis of **28** under the current unoptimized reaction conditions is not clear.

Table 1. Linear Optical Data of the NLO Chromophores

compd	λ_{max} (CH_2Cl_2) (nm)	ϵ (CH_2Cl_2) ($L \cdot mol^{-1} \cdot cm^{-1}$)	peak width at half-height (cm^{-1})
26	670	38000	3250
28	696	45000	3500
31	539	41000	3830
34	558	41000	4170
32	570	41000	3830

the compound **23** with *n*-butyllithium followed by DMF to afford the aldehyde product **29** in 80% yield as a 6:4 mixture of trans and cis isomers. This mixture was then treated with aqueous acetic acid in THF for 12 h at room temperature and for another 12 h at 45 °C. At this time, in addition to the deprotection of the hydroxy group there was a partial isomerization to afford the hydroxy-functionalized aldehyde product **30** in 88% yield as a 9:1 mixture of trans and cis isomers.

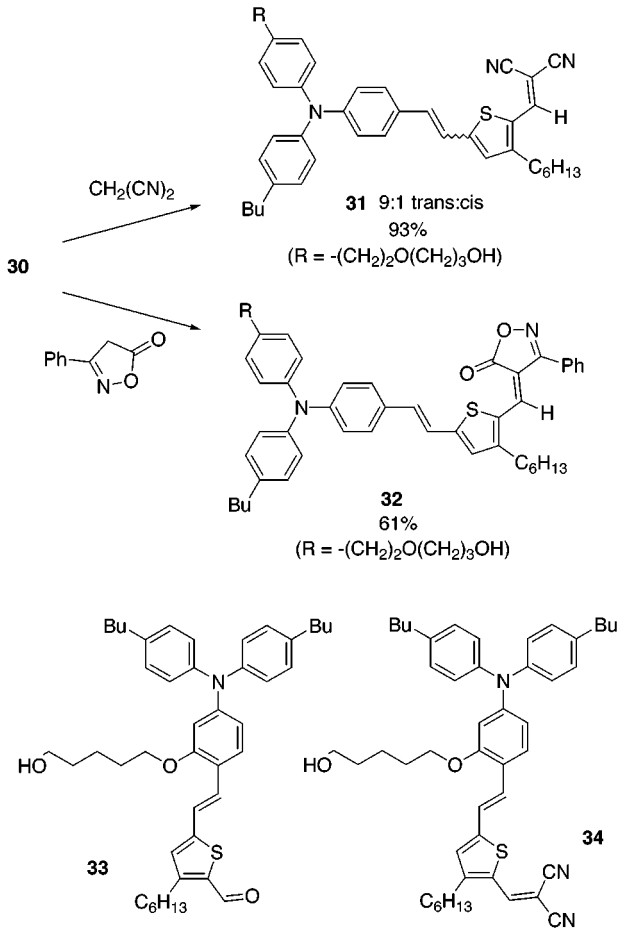


The aldehyde **30** was subjected to Knoevenagel reaction conditions with malononitrile and 3-phenylisoxazolone to afford the chromophores **31** and **32**, respectively. The aldehyde was treated with malononitrile in methylene chloride for 5 h at room temperature in the presence of catalytic amount of triethylamine to obtain the chromophore **31** in 93% yield. However, the reaction with 3-phenylisoxazolone required 12 h at reflux in ethanol to afford the chromophore **32** in only 61% yield (Scheme 6). The chromophore **31** remained as a 9:1 mixture of trans and cis isomers while only the trans isomer of the chromophore **32** could be isolated.[26] Chromophore **34** was also synthesized through a similar route from **25** through the aldehyde **33**.

In summary, we designed and synthesized hydroxy alkyl-functionalized chromophores with second-order nonlinear optical properties. Since the corresponding unfunctionalized chromophores have been demonstrated to show high optical nonlinearities, along with enhanced thermal and photochemical stabilities, we expect these chromophores to have similar properties associated with them.[16] Work is in progress to study the properties of bulk electrooptic materials following incorporation of these chromophores into functionalized high-performance polymers.

(26) This result is attributed to the difference in the strength of the dicyanovinyl and the 3-phenylisoxazolone acceptor. The stronger acceptor would have more attenuated bond length alternation and thus reduce the barrier to isomerization to the thermodynamically more stable trans isomer.

Scheme 6



Experimental Section

^1H NMR and ^{13}C NMR spectra were recorded on a 300 MHz FT NMR spectrometer. ^{13}C NMR spectra were recorded as proton-decoupled spectra or as attached proton test (APT) spectra. Fast atom bombardment (FAB) mass spectra were performed at the University of California, Riverside, or at the University of California, Los Angeles, Mass Spectrometry Facilities. The high-resolution mass spectra were obtained within an uncertainty of +3.2 ppm. Elemental analyses were performed by the Atlantic Microlab, Inc., Norcross, GA. Where microanalyses are not reported, the purity of the compounds was judged to be >95% by NMR. All the reported yields are isolated yields unless otherwise indicated. Melting points are reported for all solids isolated and are uncorrected. Toluene was distilled over Na/Ph_2CO ketyl. Aniline was used as obtained from the commercial sources, and *m*-anisidine was distilled under reduced pressure prior to use. All the other solvents and reagents were used as obtained from the commercial sources unless otherwise mentioned. Flash chromatography was performed with 37−75 μm silica gel. Analytical thin-layer chromatography was performed on silica gel plates with F-254 indicator, and the visualization was accomplished by UV lamp or using the molybdic acid stain mixture. Synthesis of the compound **9** has been reported elsewhere.[19]

Synthesis of the TBS Ether 10 from 9 by Hydroboration Followed by Protection. To the neat allyl ether **9** (1.51 g, 3.91 mmol) in a round-bottom flask was added 9-BBN (20.63 mL, 0.50 M solution in THF, 10.32 mmol), and the mixture was stirred for 24 h at room temperature. At this time, water (3.0 mL) was added, and the solution was stirred for 5 min. Then a 3 M aqueous NaOH (3.5 mL) solution followed by 30% hydrogen peroxide solution (3.5 mL) was added, and the resulting solution was stirred at 50 °C for 2 h. The solution was cooled to room temperature and poured into ether (2 × 100 mL) and water (100 mL). The combined organic layer was

dried over Na_2SO_4, filtered, concentrated in vacuo, and purified by flash column chromatography using 1:1 hexanes/ethyl acetate mixture as the mobile phase to afford 1.20 g (76%) of the alcohol product as an yellow oil. ^{1}H NMR (C_6D_6, 300 MHz) δ: 7.14−7.01 (m, 8H); 6.92 (d, 4H, J = 8.0 Hz); 6.81 (t, 1H, J = 7.1 Hz); 3.59 (bt, 2H); 3.36 (t, 2H, J = 6.9 Hz); 3.29 (t, 2H, J = 5.9 Hz); 2.65 (t, 2H, J = 6.9 Hz); 2.42 (t, 2H, J = 7.7 Hz); 2.15 (s, 1H); 1.60 (m, 2H); 1.46 (m, 2H); 1.23 (m, 2H); 0.84 (t, 3H, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 148.1, 146.2, 145.3, 137.5, 132.7, 129.5, 129.1, 129.0, 124.4, 124.0, 123.3, 121.9, 72.1, 70.2, 62.0, 35.6, 35.0, 33.6, 31.9, 22.4, 14.0. HRMS: calcd for $C_{27}H_{33}NO_2$ 403.2511, found 403.2502.

The alcohol from the last step (1.03 g, 2.55 mmol), imidazole (0.38 g, 5.6 mmol), and *tert*-butyldimethylsilyl chloride (0.42 g, 2.8 mmol) were taken in a round-bottom flask with 20 mL of DMF/dry CH_2Cl_2 (1:1) and stirred for 90 min at room temperature. The resultant solution was poured into water (100 mL) and extracted with methylene chloride (2 × 100 mL). The combined organic layer was washed with water (4 × 150 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resultant residue was purified by flash column chromatography using 9:1 hexanes/ethyl acetate mixture as the mobile phase to obtain 1.15 g (87%) of the product **10** as a yellow oil. ^{1}H NMR (C_6D_6, 300 MHz) δ: 7.17 (bd, 6H, J = 8.3 Hz); 7.06 (d, 2H, J = 7.3 Hz); 7.01 (d, 2H, J = 7.2 Hz); 6.95 (t, 2H); 6.81 (t, 1H, J = 7.2 Hz); 3.66 (t, 2H, J = 6.1 Hz); 3.45 (t, 2H, J = 7.0 Hz); 3.41 (t, 2H, J = 6.0 Hz); 2.74 (t, 2H, J = 6.5 Hz); 2.42 (t, 2H, J = 7.7 Hz); 1.75 (m, 2H); 1.47 (m, 2H); 1.23 (m, 2H); 0.97 (s, 9H); 0.84 (t, 3H, J = 7.3 Hz); 0.05 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 148.1, 146.1, 145.4, 137.5, 133.1, 129.6, 129.1, 129.0, 124.4, 124.0, 123.3, 121.9, 71.9, 67.5, 60.0, 35.7, 35.0, 33.7, 32.9, 26.0, 22.4, 18.3, 14.0, −5.3. HRMS: calcd for $C_{33}H_{47}NO_2Si$ 517.3376, found: 517.3371.

Synthesis of the Triarylamine 3 from 10. To a solution of NBS (2.69 g, 15.09 mmol) in DMF (15 mL) was added a solution of **10** (7.82 g, 15.1 mmol) in DMF (15 mL), and the resulting solution was stirred overnight at ambient temperature. The reaction mixture was then poured into water (100 mL) and ether (2 × 150 mL). The combined ether layer was washed with water (4×), dried over Na_2SO_4, decanted, concentrated in vacuo, and purified by flash column chromatography using 19:1 hexanes/ethyl acetate mixture as the mobile phase to afford 8.50 g (94%) of bromo compound as a yellow oil. This product was carried over to the next step without further characterization.

To a solution of the TBS ether from the previous step (8.40 g, 14.1 mmol) in THF (150 mL) at −78 °C was added *t*-BuLi (20.4 mL, 1.45 M solution in pentane, 29.6 mmol), and the resultant mixture was stirred for 10 min at this temperature. To this solution was added DMF (3.30 mL, 42.2 mmol), and the resultant mixture was stirred at −78 °C for 15 min and at ambient temperature for over 2 h. The solution was poured into water (300 mL) and extracted with ether (2 × 250 mL). The combined ether layer was washed with water (300 mL), dried over $MgSO_4$, filtered, concentrated in vacuo, and purified by flash column chromatography using 9:1 hexanes/ethyl acetate mixture as the mobile phase to afford 6.14 g (80%) of the product **3** as a viscous oil. ^{1}H NMR (acetone-d_6, 300 MHz) δ: 9.82 (s, 1H); 7.71 (d, 2H, J = 8.7 Hz); 7.32 (d, 2H, J = 8.3 Hz); 7.27 (d, 2H, J = 8.2 Hz); 7.15 (d, 4H, J = 8.1 Hz); 6.92 (d, 2H, J = 8.7 Hz); 3.72 (t, 2H, J = 6.2 Hz); 3.66 (t, 2H, J = 6.8 Hz); 3.55 (t, 2H, J = 6.1 Hz); 2.89 (t, 2H, J = 6.8 Hz); 2.65 (t, 2H, J = 7.6 Hz); 1.75 (m, 2H); 1.64 (m, 2H); 1.39 (m, 2H); 0.96 (t, 3H, J = 7.4 Hz); 0.91 (s, 9H); 0.06 (s, 6H). ^{13}C NMR (acetone-d_6, 75 MHz) δ: 190.4, 154.3, 145.0, 144.6, 141.0, 137.7, 131.8, 131.2, 130.6, 129.7, 127.4, 127.2, 118.7, 72.1, 67.7, 60.4, 36.4, 35.6, 34.4, 33.8, 26.2, 23.0, 18.9, 14.2, −5.2. HRMS: Calcd for $C_{34}H_{47}NO_3Si$ 545.3325, found 545.3311.

Synthesis of 11 from 4-Butylaniline, Bromobenzene, and 1,4-Dibromobenzene. To a solution of tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$) (2.17 g, 2.38 mmol) and 1,1′-bis(diphenylphosphino)ferrocene (DPPF) (1.98 g, 3.56 mmol) in toluene (400 mL) under nitrogen atmosphere was added bromobenzene (16.7 mL, 0.160 mol) at room temperature, and the resultant mixture was stirred at that temperature for 10 min. Then, sodium *tert*-butoxide (19.8 g, 0.206 mmol) and 4-butylaniline (25 mL, 0.16 mol) were added, and the resulting solution was stirred at 90 °C for 6 h. After the completion of the reaction was confirmed by thin-layer chromatography, 1,4-dibromobenzene (112 g, 0.470 mol) and sodium *tert*-butoxide (19.8 g, 0.210 mmol) were added, and the mixture was stirred for another 12 h. Following workup using water and ether, the reaction mixture was purified by flash column chromatography using 30:1 hexanes/ethyl acetate mixture as the mobile phase to afford 45.2 g (75%) of the product as a colorless oil. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 7.35−7.22 (m, 4H); 7.12−6.98 (m, 7H); 6.91 (d, 2H, J = 7.0 Hz); 2.59 (t, 2H, J = 7.7 Hz); 1.61 (m, 2H); 1.40 (m, 2H); 0.95 (t, 3H, J = 7.3 Hz); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 147.9, 147.7, 145.2, 139.0, 132.3, 129.7, 129.6, 125.4, 124.8, 124.4, 123.3, 114.3, 35.4, 34.1, 22.8, 14.2.

Synthesis of 12 from 11. To a solution of **11** (2.53 g, 6.64 mmol) in THF (50 mL) at −78 °C was added *tert*-butyllithium (8.20 mL, 1.70 M solution in pentane, 13.9 mmol), and the resultant mixture was stirred at this temperature for 15 min. Then 6-bromo-1-hexene (over 2 equivalent) was added to this solution, and the resultant mixture was stirred at −78 °C for 1 h and at ambient temperature for 3 h. Following workup using water and ether, flash column chromatography with hexanes as the mobile phase provided 1.86 g (73%) of **12** as a colorless oil. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 7.20 (t, 2H, J = 8.3 Hz); 7.07 (d, 4H, J = 8.1 Hz); 6.94 (bm, 7H); 5.80 (m, 1H); 4.99 (d, 1H, J = 17.1 Hz); 4.90 (d, 1H, J = 10.1 Hz); 2.56 (t, 4H, J = 7.7 Hz); 2.08 (m, 2H); 1.63−1.35 (m, 8H); 0.93 (t, 3H, J = 7.4 Hz). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 148.8, 146.1, 146.0, 139.4, 138.1, 137.8, 129.6, 129.5, 124.8, 124.7, 123.5, 122.2, 114.1, 35.6, 35.4, 34.2, 34.1, 31.5, 29.1, 22.9, 14.2. One overlapping aromatic ^{13}C signal is assumed. HRMS: calcd for $C_{28}H_{33}N$ 388.2613, found 388.2615.

Synthesis of 13 from 12. To the neat triarylamine **12** (1.85 g, 4.82 mmol) in a round-bottomed flask was added 9-BBN (24.10 mL, 0.50 M solution in THF, 12.05 mmol), and the resulting solution was stirred for 24 h at room temperature. At this time, water (5 mL) was added, and the solution was stirred for 5 min. Then to this solution was added 3 M aqueous NaOH (6 mL) followed by 30% hydrogen peroxide solution (6 mL), and the resulting mixture was stirred at 50 °C for 2 h. The solution was cooled to room temperature and poured into ether (2 × 100 mL) and water (100 mL). The combined organic layer was dried over Na_2SO_4, concentrated in vacuo, and purified by flash column chromatography using 1:1 hexanes/ethyl acetate mixture as the mobile phase to afford 1.74 g (90%) of the product as an oil. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 7.20 (t, 2H, J = 7.8 Hz); 7.05 (d, 4H, J = 8.2 Hz); 6.97 (bm, 7H); 3.60 (m, 2H); 2.55 (t, 4H, J = 7.7 Hz); 1.63−1.53 (m, 6H); 1.42−1.32 (m, 6H); 1.22 (bm, 1H); 0.93 (t, 3H, J = 7.3 Hz). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 148.8, 146.1, 146.0, 138.0, 137.9, 129.5, 129.4, 124.8, 124.7, 123.4, 122.2, 63.2, 35.7, 35.4, 34.7, 33.3, 32.0, 29.6, 26.1, 22.9, 14.2. One overlapping aromatic ^{13}C signal is assumed. HRMS: calcd for $C_{28}H_{35}NO$ 401.2719, found 401.2715.

The alcohol from the last step (1.61 g, 4.01 mmol), imidazole (0.55 g, 8.0 mmol), and *tert*-butyldimethylsilyl chloride (0.73 g, 4.8 mmol) were taken in a round-bottomed flask with 20 mL of DMF/dry CH_2Cl_2 (1:1) and stirred for 90 min at room temperature. The resultant solution was poured into water (100 mL) and extracted with methylene chloride (2 × 100 mL). The combined organic layer was washed with water (4 × 150 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The resultant residue was purified by flash column chromatography using 9:1 hexanes/ethyl acetate mixture as the mobile phase to obtain 1.98 g (96%) of the product **13** as a yellow oil. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 7.20 (t, 2H, J = 7.8 Hz); 7.06 (d, 4H, J = 8.3 Hz); 6.94 (bm, 7H); 3.60 (t, 2H, J = 6.4 Hz); 2.55 (t, 4H, J = 7.6 Hz); 1.63−1.33 (m, 12H); 0.93 (t, 3H, J = 7.3 Hz); 0.88 (s, 9H); 0.04 (s, 6H). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 148.8, 146.1, 138.1, 138.0, 129.6, 129.4, 124.8, 123.4, 122.2, 63.6, 35.7, 35.4, 34.2, 33.3, 32.0, 29.6, 26.2, 26.1, 22.9, 18.7, 14.2, −5.1. Three overlapping aromatic ^{13}C signals

are assumed due to the similarities in the aliphatic side chains. HRMS: calcd for $C_{34}H_{49}NOS$ 515.3583, found 515.3576.

Synthesis of the Triarylamine 4 from 13. The open para position of the aromatic ring was brominated in 87% yield using the same procedure adapted for the bromination of **10**. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 7.27 (d, 2H, J = 8.8 Hz); 7.07 (d, 4H, J = 8.3 Hz); 6.96 (d, 4H, J = 8.3 Hz); 6.85 (d, 2H, J = 8.8 Hz); 3.59 (t, 2H, J = 6.4 Hz); 2.56 (t, 4H, J = 7.5 Hz); 1.60−1.32 (m, 12H); 0.93 (t, 3H, J = 7.4 Hz); 0.88 (s, 9H); 0.03 (s, 6H). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 148.1, 145.5, 138.7, 132.3, 129.7, 125.1, 124.2, 113.8, 63.6, 35.7, 35.4, 34.2, 33.3, 32.0, 29.6, 26.2, 26.1, 22.9, 18.7, 14.2, −5.1. HRMS: calcd for $C_{34}H_{48}$-NOBrSi 593.2689, found 593.2691.

The procedure for bromine lithium exchange used in the synthesis of **3** was adapted here to afford **4** as a viscous oil in 91% yield. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 9.74 (s, 1H); 7.61 (d, 2H, J = 8.7 Hz); 7.17 (d, 4H, J = 8.3 Hz); 7.08 (d, 4H, J = 8.3 Hz); 6.91 (d, 2H, J = 8.7 Hz); 3.59 (t, 2H, J = 6.4 Hz); 2.60 (t, 4H, J = 7.6 Hz); 1.65−1.32 (m, 12H); 0.94 (t, 3H, J = 7.3 Hz); 0.88 (s, 9H); 0.03 (s, 6H). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 190.3, 154.1, 144.1, 140.7, 131.4, 130.1, 128.9, 126.9, 118.4, 63.5, 35.8, 35.5, 34.1, 33.2, 31.9, 29.5, 26.2, 26.1, 22.8, 18.6, 14.1, −2.6. HRMS: calcd for $C_{35}H_{49}NO_2Si$ 543.3533, found 543.3539.

Synthesis of 4′,4″-Dibutyl-3-methoxytriphenylamine (15). To a solution of $Pd_2(dba)_3$ (0.90 g, 0.98 mmol) and DPPF (0.81 g, 1.5 mmol) in toluene (120 mL) under nitrogen atmosphere was added 1-bromo-4-butylbenzene (20.90 g, 97.89 mmol) at room temperature, and the resultant mixture was stirred at that temperature for 10 min. Then, sodium *tert*-butoxide (10.69 g, 110 mmol) and *m*-anisidine (5.48 g, 44.5 mmol) were added to this solution and stirred at 90 °C for 24 h. Following workup, the reaction mixture was purified by flash column chromatography using 20:1 hexanes/ethyl acetate mixture as the mobile phase to afford 14.4 g (84%) of **15** as an oil. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 7.19−7.10 (bt, 5H); 7.05 (d, 4H, J = 8.4 Hz); 6.65−6.50 (m, 3H); 3.75 (s, 3H); 2.64 (t, 4H, J = 7.7 Hz); 1.66 (m, 4H); 1.46 (m, 4H); 1.02 (t, 6H, J = 7.3 Hz). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 160.8, 150.0, 145.8, 138.1, 129.9, 129.5, 124.9, 115.5, 109.0, 107.1, 55.4, 35.4, 34.2, 22.8, 14.2. HRMS: calcd for $C_{27}H_{33}NO$ 387.2562, found 387.2549.

Synthesis of 16 from 15. To the round-bottom flask containing **15** (31.90 g, 82.31 mmol) in CH_2Cl_2 (400 mL) under nitrogen atmosphere at −78 °C was added BBr_3 (8.97 mL, 98.8 mmol). The resultant solution was stirred at −78 °C for 5 min, the cold bath was removed, and the solution was stirred for 3 h at ambient temperature. The reaction mixture was then poured in 150 mL of ice−water slush and stirred for another 90 min. The solution was poured in a separatory funnel and separated between methylene chloride and water. The organic layer was concentrated in vacuo and purified by flash column chromatography using 10:1 hexanes/ethyl acetate mixture as the mobile phase to afford 20.4 g (66%) of the product **16** as an oil. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 7.13 (d, 4H, J = 8.4 Hz); 7.08 (d, 1H, J = 8.2 Hz); 7.03 (d, 4H, J = 8.4 Hz); 6.58 (dd, 1H, J = 1.4 Hz; J = 8.1 Hz); 6.48 (t, 1H, J = 1.4 Hz); 6.43 (dd, 1H, J = 2.0 Hz, J = 7.5 Hz); 4.80 (s, 1H); 2.62 (t, 4H, J = 1.2 Hz); 1.64 (m, 4H, J = 8.0 Hz); 1.43 (m, 4H, J = 7.6 Hz); 0.99 (t, 6H, J =7.3 Hz). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 156.7, 150.2, 145.6, 138.4, 130.1, 129.5, 125.2, 114.9, 109.2, 108.5, 35.3, 34.1, 22.8, 14.1. HRMS: calcd for $C_{26}H_{31}NO$ 373.2421, found 373.2406.

Synthesis of 17. To a solution of pentane-1,5-diol (47.7 g, 0.460 mol) in DMF (800 mL) were added imidazole (23.4 g, 0.340 mol) and *tert*-butyldimethylsilyl chloride (34.5 g, 0.230 mol), and the resultant solution was stirred at ambient temperature for 2 h. The reaction mixture was partitioned between ether and water and the organic layer was washed with water (4×). The resultant organic mixture was concentrated in vacuo. The reaction mixture was purified by flash column chromatography using 9:1 followed by 3:1 hexanes/ethyl acetate mixture as the mobile phases to afford 31.11 g (62%) of **17** as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.61 (t, 4H, J = 6.33 Hz), 2.09 (br, 1H), 1.52 (m, 4H), 1.39 (m, 2H), 0.89 (s, 9H), 0.04 (s, 6H). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 63.6, 62.9, 33.1, 33.0, 26.3, 22.6, 18.7, −5.1.

Synthesis of 5 from 16. To a solution of **16** (0.96 g, 4.3 mmol), triphenylphosphine (1.39 g, 5.32 mmol), and 5-*tert*-butyldimethylsilyloxypentanol (**17**) (0.77 g, 3.5 mmol) in THF (50 mL) at 0 °C was added diethyl azodicarboxylate (DEAD) (0.74 g, 4.3 mmol) dropwise with stirring. The resultant solution was allowed to stir for 18 h while warming to room temperature. Separation of the reaction mixture between water and ether layers and concentration of the organic layer in vacuo followed by purification by flash column chromatography provided 0.83 g of a colorless oil that was a mixture of product and triphenylphosphine. Since this mixture could not be easily separated to afford the pure product **18**, this mixture was taken to the next step without further purification.

The mixture from the previous reaction (0.78 g) in DMF (2 mL) was mixed with a solution of *N*-bromosuccinimide (0.33 g, 1.8 mmol) in DMF (3 mL), and the resultant mixture was stirred at room temperature overnight. The reaction mixture was separated between ether and water, and then the organic layer was washed with water. Concentration of the organic layer followed by purification using silica gel flash column chromatography afforded 0.51 g of colorless oil. This reaction mixture contained small amounts of triphenylphosphine and the product from the previous step along with the desired brominated product. This mixture was taken to the next step without further purification.

To a solution of the crude product from the previous reaction (0.48 g) in THF (10 mL) at −78 °C under nitrogen atmosphere was added *t*-BuLi (1.37 mL, 1.45 M solution in pentane, 1.99 mmol), and the resultant solution was stirred at this temperature for 10 min. Then, DMF (0.22 mL, 2.9 mmol) was added to this solution and the resultant mixture was stirred at −78 °C for 1 h and at ambient temperature for 3 h. Separation of the reaction mixture between water and ether and concentration of the organic layer in vacuo followed by purification by flash column chromatography using 10:1 hexanes/ethyl acetate mixture as the mobile phase afforded 0.20 g of the product **5** as a yellow oil. The overall yield of the reaction was 14%. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 10.3 (s, 1H); 7.63 (d, 1H, J = 8.7 Hz); 7.23 (d, 4H, J = 8.2 Hz); 7.15 (d, 4H, J = 8.3 Hz); 6.48 (d, 1H, J = 8.7 Hz); 6.44 (s, 1H); 3.87 (t, 2H, J = 6.2 Hz); 3.68 (t, 2H, J = 6.0 Hz); 2.67 (t, 4H, J = 7.6 Hz); 1.81−1.41 (m, 14H); 1.01 (t, 6H, J = 7.3 Hz); 0.96 (s, 9H); 0.11 (s, 6H). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 187.5, 163.2, 155.5, 144.0, 140.6, 129.9, 129.3, 126.9, 118.0, 111.3, 101.6, 68.5, 63.3, 35.5, 34.0, 32.9, 29.2, 29.0, 26.1, 22.8, 18.6, 14.2, −5.2. HRMS: calcd for $C_{38}H_{56}$-NO_3Si 602.4030, found 602.4026.

Synthesis of 21 from 20. To a solution of the commercially available aldehyde **20** (49 g, 0.26 mol) in absolute ethanol (500 mL) at room temperature was added sodium borohydride (27.4 g, 0.720 mol), and the resultant solution was stirred for 4 h at ambient temperature. The reaction mixture was separated between CH_2Cl_2 and water, and the organic layer was concentrated in vacuo. The resultant product mixture was passed through a plug of silica gel and taken to the next step after drying in vacuo without further purification or characterization.

The product from the previous reaction was dissolved in a mixture of methylene chloride (200 mL) and DMF (300 mL) along with imidazole (34.9 g, 0.510 mol) and *tert*-butyldimethylsilyl chloride (42.5 g, 0.280 mol). The resultant mixture was stirred at room temperature for 90 min and then separated between methylene chloride and water. The organic layer was washed with water (4×), concentrated in vacuo, and passed through a silica gel plug to afford 72.1 g (92%) of the product **21** as a colorless oil. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 7.16 (s, 1H); 6.85 (s, 1H); 4.84 (s, 2H); 0.94 (s, 9H); 0.12 (s, 6H). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 147.5, 126.1, 122.1, 109.1, 60.8, 28.0, 18.6, −5.2.

Synthesis of 22 from 21. A cold solution (−10 °C) of hexylmagnesium bromide (141 mL, 2 M solution in THF, 0.282 mol) was added to a cold round-bottomed flask (−10 °C) containing 1,3-bis(diphenylphosphino)propanedichloronickel (1.53 g, 2.82 mmol), and the resultant solution was stirred at

this temperature for 10 min. Then the bromothiophene compound **21** (72.1 g, 0.240 mol) was added dropwise over a period of 1 h to this reaction mixture. The resultant solution was stirred for 24 h while the solution warmed to room temperature. The worked-up reaction mixture was purified by flash column chromatography using 30:1 hexanes/ethyl acetate mixture as the mobile phase to afford 30.6 g (42%) of the product **22** as a colorless oil. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 6.81 (s, 1H); 6.76 (s, 1H); 4.79 (s, 2H); 2.54 (t, 2H, J = 7.4 Hz); 1.55 (m, 2H); 1.30 (bs, 6H); 0.90 (bm, 12H); 0.09 (s, 6H). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 145.2, 143.3, 125.8, 119.4, 61.1, 32.1, 30.9, 30.8, 29.4, 26.0, 23.0, 19.2, 14.3, −5.2.

Synthesis of 6 from 22. To a solution of **22** (27.4 g, 87.7 mmol) in THF (100 mL) was added tetrabutylammonium fluoride (105 mL, 1 M solution in THF, 105 mmol), and the resulting solution was stirred at ambient temperature for 24 h. Following workup with water and ether, the mixture was purified by flash column chromatography using 10:1 hexanes/ethyl acetate mixture as the mobile phase to afford 10.5 g (60%) of the alcohol product was isolated as a colorless oil. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 6.86 (s, 1H); 6.85 (s, 1H); 4.73 (d, 2H, J = 5.7 Hz); 2.56 (t, 2H, J = 7.6 Hz); 2.0 (bs, 1H); 1.59 (bm, 2H); 1.31 (bm, 6H); 0.89 (t, 3H, J = 6.1 Hz). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 144.3, 143.6, 127.1, 120.2, 60.3, 32.0, 30.8, 30.7, 29.3, 23.0, 14.2.

The alcohol product from the previous step (8.21 g, 41.4 mmol) was cooled to −78 °C, and concentrated hydrochloric acid (25.0 mL, 298 mmol) was added slowly to result in an inhomogeneous mixture. After 15 min, this mixture was warmed to room temperature and stirred for 4 h. The reaction mixture was separated between water and ether. The resultant organic layer was dried over anhydrous sodium sulfate, decanted, and concentrated in vacuo. The resultant product was characterized by thin-layer chromatography and carried over to the next step without further characterization.

To a solution of the product from the above reaction in xylene (50 mL) was added triphenylphosphine (11.94 g, 45.50 mmol), and the resultant mixture was heated to reflux overnight. Then, the reaction mixture was allowed to cool to room temperature and filtered. The solid obtained was washed with benzene and dried in vacuo to afford 15.9 g (80%) of **6** as a white solid. Mp: 220−222 °C. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 7.87−7.63 (m, 15H); 6.78 (s, 1H); 6.77 (s, 1H); 5.70 (d, 2H, J = 13.4 Hz); 2.44 (t, 2H, J = 7.6 Hz); 1.42 (bm, 2H); 1.27 (bm, 6H); 0.87 (bt, 3H). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 143.5 (d, J = 3.4 Hz); 134.9 (d, J = 2.4 Hz); 134.4 (d, J = 9.9 Hz); 132.7 (d, J = 7.9 Hz); 130.0 (d, J = 12.5 Hz); 127.9 (d, J = 10.2 Hz); 121.4 (d, J = 4.5 Hz); 118.0 (d, J = 85.8 Hz); 31.0 (d, J = 86.0 Hz); 30.1, 28.8, 26.9, 26.3, 22.6, 13.9. ^{31}P NMR (CD_2Cl_2, 400 MHz) δ: 22.90.

General Procedure for the Wittig Reaction of the Aldehydes 3, 4, or 5 with 6. To a 1:1 mixture of the aldehyde and the phosphonium salt **6** in ethanol was added a freshly prepared solution of sodium ethoxide (1.5 equiv) in ethanol. The resultant mixture was stirred at reflux for 5 h. Following workup with ether and water, the product **23**, **24**, or **25** was obtained as a mixture of trans and cis isomers. These products were carried over to the next step without further characterization.

General Procedure for the Synthesis of the Chromophores 26−28 from 23−25. To a solution of the styryl thiophene **23**, **24**, or **25** in THF at −78 °C was added *n*-butyllithium (1.2 equiv), and the resultant mixture was stirred at −78 °C for 45 min. Then tetracyanoethylene was added as a solid to this solution, and the mixture was stirred for 1 h at −78 °C and for 3 h at ambient temperature. Following workup with ethyl acetate and water, flash column chromatography was performed to afford the TBS-protected chromophores.

To a solution of the TBS-protected chromophore from the above reaction in THF (3 mL for 1 mmol substrate) were added acetic acid (10 mL) and water (3 mL). The resultant mixture was stirred at ambient temperature for 12 h and at 45 °C for 12 h. Following workup with ethyl acetate and water, flash column chromatography was performed to afford the chromophore **26**, **27**, or **28**.

Chromophore 26. Characterizing data for the TBS protected precursor follow: ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 7.36 (d, 2H, J = 8.7 Hz); 7.26−7.04 (m, 11H); 6.93 (d, 2H, J = 8.7 Hz); 3.67 (t, 2H, J = 6.2 Hz); 3.60 (t, 2H, J = 6.9 Hz); 3.51 (t, 2H, J = 6.3 Hz); 3.04 (t, 2H, J = 7.6 Hz); 2.84 (t, 2H, J = 6.8 Hz); 2.60 (t, 2H, J = 7.6 Hz); 1.76−1.32 (m, 14H); 0.95−0.90 (m, 6H); 0.89 (s, 9H); 0.04 (s, 6H). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 158.6, 155.4, 150.5, 145.0, 144.4, 139.9, 137.4, 136.1, 130.7, 130.3, 130.1, 129.8, 129.1, 127.7, 126.4, 126.2, 125.9, 120.6, 116.6, 113.9, 71.9, 67.7, 60.2, 36.0, 35.4, 34.1, 33.3, 31.9, 31.6, 31.2, 29.5, 26.1, 22.9, 22.8, 14.2, 14.1, 9.0, −5.3. Overlap of three aromatic ^{13}C signals are assumed. The overlapping peaks can be identified by comparison with the ^{13}C NMR spectrum of **26**. HRMS: calcd for $C_{50}H_{62}N_4O_2SSi$ 810.4363, found 810.4380.

Characterizing data for the chromophore **26** follow. Mp: 100−103 °C. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 7.37 (d, 2H, J = 8.7 Hz); 7.30−7.03 (m, 11H); 6.93 (d, 2H, J = 8.7 Hz); 3.65 (m, 6H); 3.04 (t, 2H, J = 7.7 Hz); 2.85 (t, 2H, J = 6.8 Hz); 2.60 (t, 2H, J = 7.7 Hz); 2.04 (t, 1H, J = 5.5 Hz); 1.81−1.32 (m, 14H); 0.90 (m, 6H). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 158.6, 155.4, 150.4, 145.1, 144.4, 139.9, 137.4, 135.7, 130.7, 130.6, 130.5, 130.3, 130.0, 129.8, 129.1, 127.7, 126.6, 126.4, 126.2, 125.9, 120.6, 116.6, 113.9, 72.1, 70.4, 62.0, 36.0, 35.4, 34.0, 32.5, 31.8, 31.6, 31.1, 29.4, 22.9, 22.8, 14.2, 14.1. HRMS: calcd for $C_{44}H_{48}N_4O_2S$ 696.3498, found 696.3507.

Chromophore 27. Characterizing data for the TBS-protected precursor follow. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 7.36 (d, 2H, J = 8.8 Hz); 7.22 (d, 1H, J = 16.0 Hz); 7.13 (d, 4H, J = 8.3 Hz); 7.08−7.03 (bt, 6H); 6.91 (t, 2H, J = 8.8 Hz); 3.60 (t, 2H, J = 6.3 Hz); 3.04 (t, 2H, J = 7.7 Hz); 2.59(t, 4H, J = 7.7 Hz); 1.64−1.32 (m, 20H); 0.94 (t, 3H, J = 7.3 Hz); 0.88 (bs, 12H); 0.04 (s, 6H). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 158.5, 155.5, 150.8, 144.6, 144.5, 139.9, 137.6, 130.7, 130.1, 129.9, 129.3, 127.5, 126.3, 126.0, 120.4, 116.6, 113.9, 113.8, 68.2, 63.5, 35.8, 35.5, 34.1, 33.3, 32.1, 32.0, 31.7, 31.3, 29.6, 26.3, 26.2, 23.0, 22.9, 18.7, 14.3, 14.2, −5.0. Overlap of one aromatic ^{13}C signal is assumed. The overlapping peak can be identified by comparison with the ^{13}C NMR spectrum of **27**. HRMS: calcd for $C_{51}H_{64}N_4OSSi$ 808.4570, found 808.4591.

Characterizing data for the chromophore **27** follow. Mp: 95−97 °C. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 7.40 (d, 2H, J = 8.8 Hz); 7.26 (d, 1H, J = 16.0 Hz); 7.17 (d, 4H, J = 8.3 Hz); 7.12−7.06 (t, 6H); 6.95 (d, 2H, J = 8.8 Hz); 3.63 (q, 2H, J = 6.3 Hz); 3.08 (t, 2H, J = 7.7 Hz); 2.63 (t, 4H, J = 7.5 Hz); 1.75−1.21 (m, 21H); 0.97 (t, 3H, J = 7.3 Hz); 0.91 (t, 3H). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 158.6, 155.5, 150.7, 144.5, 144.4, 139.9, 139.8, 137.5, 130.7, 130.0, 129.8, 129.2, 127.5, 126.2, 125.9, 120.4, 116.6, 113.9, 113.8, 63.1, 35.7, 35.5, 34.0, 33.2, 31.9, 31.8, 31.6, 31.2, 29.5, 29.4, 26.0, 22.9, 22.8, 14.2, 14.1. HRMS: calcd for $C_{45}H_{50}N_4OS$ 694.3705, found 694.3764. Anal. Calcd for $C_{45}H_{50}N_4OS$: C, 77.77; H, 7.25; N, 8.06, found C, 77.70; H, 7.28; N, 7.97.

Chromophore 28. Characterizing data for the TBS-protected precursor follow. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 7.50 (d, 1H, J = 16.0 Hz); 7.30 (d, 1H, J = 8.3 Hz); 7.23 (d, 1H, J = 16.0 Hz); 7.14 (d, 4H, J = 8.3 Hz); 7.08 (m, 5H); 6.48 (m, 2H); 3.83 (t, 2H, J = 6.4 Hz); 3.61 (t, 2H, J = 6.7 Hz); 3.04 (t, 2H, J = 6.7 Hz); 2.59 (t, 4H, J = 7.6 Hz); 1.81−1.26 (m, 22H); 0.94 (m, 9H); 0.86 (s, 9H); 0.02 (s, 6H). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 159.4, 158.6, 157.3, 152.3, 144.5, 140.1, 134.0, 130.0, 129.9, 129.6, 129.3, 126.5, 126.0, 125.7, 117.1, 117.0, 114.2, 114.1, 114.0, 113.1, 103.8, 68.8, 63.4, 35.5, 34.1, 33.0, 32.0, 31.7, 31.3, 29.6, 29.3, 26.2, 23.0, 22.9, 22.8, 18.6, 14.3, 14.2, −5.1. HRMS: calcd for $C_{54}H_{70}N_4O_2SSi$ 866.4989, found 866.4979.

Characterizing data for chromophore **28** follow. Mp: 112−114 °C. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 7.53 (d, 1H, J = 16.0 Hz); 7.32 (d, 1H, J = 8.6 Hz); 7.21 (d, 1H, J = 16.0 Hz); 7.14 (d, 4H, J = 8.3 Hz); 7.05 (m, 5H); 6.45 (m, 2H); 3.82 (t, 2H, J = 6.1 Hz); 3.61 (q, 2H, J = 5.6 Hz); 3.04 (t, 2H, J = 7.8 Hz); 2.59 (t, 4H, J = 7.6 Hz); 1.82−1.30 (m, 23H); 0.90 (m, 9H). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 159.3, 158.9, 157,4, 152.3, 144.4, 140.1, 133.9, 130.3, 129.8, 129.7, 129.4, 126.4, 126.0, 125.7, 117.0, 116.9, 114.2, 114.1, 114.0, 113.0, 103.6, 68.7, 62.8, 35.5,

34.0, 32.9, 31.9, 31.7, 31.2, 29.5, 29.2, 23.1, 22.9, 22.8, 14.2, 14.1. HRMS: calcd for $C_{48}H_{56}N_4O_2S$ 752.4124, found 752.4118. Anal. Calcd for $C_{48}H_{56}N_4O_2S$: C, 76.56; H, 7.50; N, 7.44. Found C, 76.48; H, 7.50; N, 7.41.

General Procedure for the Synthesis of 30 or 33 from 23 or 25. To a solution of the styryl thiophene **23** or **25** at −78 °C in THF was added *n*-butyllithium (1.2 equiv). The resultant mixture was stirred at −78 °C for 45 min, and then DMF (2 equiv) was added to the reaction. The reaction mixture was stirred at −78 °C for 1 h and at room temperature for 3 h. Following workup and purification by column chromatography, the product **29** or TBS-protected **33** was obtained as a mixture of cis and trans isomers. These products were carried over to the next step without further characterization.

The product from the above reaction was subjected to deprotection using acetic acid using the procedure adapted in the synthesis of the chromophores **26**−**28**.

The trans isomers of **30** and **33** were isolated by column chromatography and characterized. Characterizing data for *trans*-**30** follow. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 9.95 (s, 1H); 7.35 (d, 2H, J = 8.7 Hz); 7.15−6.94 (m, 13H); 3.67−3.58 (m, 6H); 2.92−2.81 (m, 4H); 2.58 (t, 2H, J = 7.7 Hz); 2.06 (bs, 1H); 1.78 (m, 2H); 1.69−1.54 (m, 4H); 1.41−1.22 (m, 8H); 0.96−0.86 (m, 6H). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 181.7, 154.3, 152.1, 149.2, 145.9, 145.1, 139.2, 135.6, 134.9, 132.8, 130.2, 129.7, 129.2, 128.8, 128.2, 125.7, 125.4, 122.0, 118.8, 72.3, 70.3, 62.0, 36.0, 35.4, 34.1, 32.7, 32.0, 31.7, 29.4, 28.8, 23.0, 22.8, 14.2, 14.1. HRMS: calcd for $C_{40}H_{49}NO_3S$ 623.3433, found 623.3461.

Characterizing data for *trans*-**33** follow. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 9.93 (s, 1H); 7.40 (d, 1H, J = 16.2 Hz); 7.32 (d, 1H, J = 8.7 Hz); 7.12 (m, 5H); 7.02 (d, 4H, J = 8.2 Hz); 6.91 (s, 1H); 6.50 (bm, 2H); 3.82 (t, 2H, J = 6.3 Hz); 3.63 (q, 2H, J = 5.6 Hz); 2.89 (t, 2H, J = 7.6 Hz); 2.58 (t, 4H, J = 7.6 Hz); 1.81−1.23 (m, 23H); 0.91 (m, 9H). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 181.6, 158.2, 154.5, 153.5, 150.5, 145.1, 139.1, 135.1, 129.7, 128.6, 128.4, 128.2, 125.7, 118.9, 118.4, 114.2, 105.6, 68.8, 62.9, 35.4, 34.1, 33.0, 32.0, 31.8, 29.4, 28.8, 23.0, 22.9, 22.8, 14.3, 14.2. Overlap of one aliphatic ^{13}C signal is assumed. HRMS: calcd for $C_{44}H_{57}NO_3S$ 679.4059, found 679.4058.

General Procedure for the Knoevenagel Reaction with Malononitrile To Synthesize 31 and 34. To a solution of the aldehyde **30** or **33** in methylene chloride were added malononitrile (5 equiv), triethylamine (cat.), and 4 Å molecular sieves. The resultant solution was stirred at ambient temperature for 5 h. Following workup with water and methylene chloride, the crude reaction mixture was purified by flash column chromatography to afford **31** or **34**. The major trans isomer was isolated in pure form by column chromatography and characterized.

Characterizing data for *trans*-**31** follow. Mp: 77−79 °C. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 7.83 (s, 1H); 7.35 (d, 2H, J = 8.7 Hz); 7.23−7.01 (m, 11H); 6.93 (d, 2H, J = 8.7 Hz); 3.67 (m, 6H); 2.84 (t, 2H, J = 6.8 Hz); 2.70 (t, 2H, J = 6.9 Hz); 2.58 (t, 2H, J = 7.9 Hz); 2.06 (t, 1H, J = 5.5 Hz); 1.79 (m, 2H); 1.61 (m, 4H); 1.41−1.28 (m, 8H); 0.90 (m, 6H). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 157.8, 154.5, 149.8, 147.7, 145.5, 144.8, 139.5, 135.3, 135.1, 130.2, 129.8, 128.7, 128.6, 128.3, 125.9, 125.7, 121.3, 117.7, 115.8, 114.7, 73.2, 72.2, 70.1, 61.8, 36.0, 35.4, 34.0, 32.7, 31.9, 31.5, 29.5, 29.4, 22.9, 22.8, 14.2, 14.1. Overlap of one aromatic ^{13}C signal is assumed. HRMS: calcd for $C_{43}H_{49}N_3O_2S$: 671.3546. Found: 671.3560. Anal. Calcd for $C_{43}H_{49}N_3O_2S$: C, 76.86; H, 7.35; N, 6.25. Found: C, 76.60; H, 7.38; N, 6.51.

Characterizing data for *trans*-**34** follow. Mp: 104−105 °C. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 7.81 (s, 1H); 7.47 (d, 1H, J = 16.1 Hz); 7.32 (d, 1H, J = 9.0 Hz); 7.20 (d, 1H, J = 16.1 Hz); 7.12 (d, 4H, J = 8.3 Hz); 7.05 (m, 5H); 6.48 (m, 2H); 3.82 (t, 2H, J = 6.0 Hz); 3.62 (q, 2H, J = 5.6 Hz); 2.71 (t, 2H, J = 7.6 Hz); 2.59 (t, 4H, J = 7.6 Hz); 1.82−1.26 (m, 23H); 0.90 (m, 9H). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 158.7, 158.1, 156.2, 151.3, 147.7, 144.8, 139.5, 131.1, 129.7, 128.8, 128.4, 127.8, 126.0, 118.0, 117.7, 116.0, 115.0, 113.6, 104.6, 72.2, 68.7, 62.8, 35.4, 34.1, 32.9, 32.0, 31.6, 29.5, 29.4, 29.3, 23.1, 23.0, 22.8, 14.2, 14.1. HRMS: calcd for $C_{47}H_{57}N_3O_2S$ 727.4172, found 727.4180. Anal. Calcd for $C_{47}H_{57}N_3O_2S$: C, 77.54; H, 7.89; N, 5.77. Found: C, 77.54; H, 7.88; N, 5.79.

Synthesis of the Chromophore 32 by Knoevenagel Reaction. To a mixture of 3-phenylisoxazolone (1.47 g, 9.20 mmol), **30** (4.05 g, 6.13 mmol), and 4 Å molecular sieves in ethanol (120 mL) was added few drops of piperidine (cat.). The resultant mixture was stirred at reflux overnight. The solution was concentrated and purified by flash column chromatography to afford 3.00 g (61%) of **32** as a purple solid. Mp: 118−121 °C. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 7.81 (s, 1H); 7.59 (bd, 4H); 7.38 (d, 2H, J = 8.6 Hz); 7.30 (d, 1H, J = 16.0 Hz); 7.17−7.02 (m, 11H); 6.95 (d, 2H, J = 8.6 Hz); 3.68 (m, 6H); 2.85 (t, 2H, J = 6.8 Hz); 2.65 (t, 2H, J = 7.5 Hz); 2.59 (t, 2H, J = 7.5 Hz); 2.05 (t, 1H, J = 5.5 Hz); 1.78 (m, 2H); 1.63−1.53 (m, 4H); 1.42−1.24 (m, 8H); 0.94 (t, 3H, J = 7.3 Hz); 0.86 (t, 3H, J = 6.8 Hz). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 170.2, 164.4, 159.7, 157.6, 149.9, 145.8, 145.1, 139.6, 138.1, 135.5, 135.1, 131.1, 130.5, 130.3, 129.9, 129.6, 129.1, 129.0, 128.7, 128.6, 126.0, 125.8, 121.6, 118.6, 109.5, 72.3, 70.2, 62.0, 36.2, 35.5, 34.1, 32.9, 32.0, 31.9, 30.0, 29.5, 23.0, 22.9, 14.2, 14.1. Overlap of one aromatic ^{13}C signal is assumed. HRMS: calcd for $C_{49}H_{54}N_2O_4S$ 767.3883, found 767.3881. Anal. Calcd for $C_{49}H_{54}N_2O_4S$: C, 76.73; H, 7.10; N, 3.65. Found: C, 76.48; H, 7.15; N, 3.59.

Acknowledgment. Support from the US Air Force Office of Scientific Research (AFOSR grants AFS5X F496209610387 and AFS 5 F496209610295) and US Office of Naval Research (ONR grant N00014-95-1-1319) are acknowledged. The research described in this paper was performed in part by the Jet Propulsion Laboratory, (JPL) California Institute of Technology, as part of its Center for Space Microelectronics Technology and was supported by the Ballistic Missile Defense Initiative Organization, Innovative Science and Technology Office, and AFOSR through an agreement with the National Aeronautics and Space Administration (NASA). Support from Lockheed-Martin Corp. and Lightwave Microsystems is also acknowledged. J.M. thanks the Summer Undergraduate Research Fellowship Program at Caltech for support. We thank Galina Levina for helpful discussions and technical assistance. We are also thankful to the reviewers for helpful comments.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of new compounds **3**−**6**, unprotected alcohol **10**, **10**−**12**, unprotected alcohol **13**, **13**−**17**, **21**, **22**, deprotected **22**, TBS-protected **26**, **26**, TBS-protected **27**, TBS-protected **28**, **30**, and **33**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO981707V