Stereoselective Hydroboration of Diynes and Triyne to **Give Products Containing Multiple Vinylene Bridges: A Versatile Application to Fluorescent Dyes and Light-Emitting Copolymers**

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The Rh(I)-catalyzed hydroboration of a variety of aromatic diynes and a triyne afforded bis(boryl)- and tris(boryl)vinyl products. The hydroboration products underwent Suzuki crosscoupling reactions with a variety of substrates containing chromophore units to give fluorescent dye-substituted products. The hydroboration product also reacted with dibromoarenes to afford an oligomer with a vinylene unit along the oligomer backbone.

Introduction

Organic molecules bearing extended π -conjugated systems have received considerable attention due to their applications in molecular electronics¹ and photonics.² In particular, oligophenylenevinylene derivatives have been investigated extensively for applications in the fields of photo- and electroluminescence,³ photovoltaics,⁴ or nonlinear optics.⁵ Although 1-alkenylboron derivatives are useful intermediates in organic synthesis on the basis of their applications in the Pd-catalyzed cross-coupling reaction with a variety of organic electrophiles,⁶ little is known about the synthetic applications of such boron derivatives to the preparation of polymers or oligomers containing alternate vinylene units.⁷ Although various polymerization methods for the synthesis of such polymers have been developed that include the Wittig reaction,8 Heck reaction,9 Gilch

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polymerization,¹⁰ and Suzuki coupling reaction,¹¹ starting boranes such as 4 and 5 should be useful in the synthesis of fluorescent dyes and light-emitting copolymers using this methodology.



Hydroboration provides a useful entry for the synthesis of vinylic boron compounds.¹² Although there has been significant progress using a variety of metalcatalyzed reactions to provide vinylboron derivatives of type **1**, **2**, or **3**,¹³ aromatic compounds containing two¹⁴ or three vinylborane substituents have received only little attention. We report here the preparation of a number of such compounds and their use in Suzuki cross-coupling reactions to prepare fluorescent dyes and light-emitting polymers.

Results and Discussion

Our initial experiment on the hydroboration of 1,3,5triethynylbenzene with pinacolborane in the presence of Wilkinson's catalyst resulted in (E)-1,3,5-tris(borylvinyl)benzene 6 in very low yield (Table 1). Significant improvement in yield was achieved using Rh(CO)-

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^a To a solution of catalyst and 1,3,5-triethynylbenzene was added pinacolborane. The mixture was stirred at room temperature for 8 h. ^b Isolated yield.

(PPh₃)₂Cl as the catalyst (entry 2). The catalyst generated in situ from [Rh(cod)Cl]₂ and P'Pr₃ (4 equiv) gave 6 in excellent yield (entry 3). The use of Et₃N was found to be essential to achieve good yields and trans-selectivity in the case of some substrates. Use of different amines such as piperidine, pyrrolidine, Et₂NH, and Pr₂-NH resulted in unsatisfactory yields and gave a mixture of E- and Z-isomers. Screening a number of phosphine ligands during the hydroboration of 1,3,5-triethynylbenzene showed $P'Pr_3$ to be superior in terms of yield and reaction rate (entries 4-7). An iridium catalyst, [Ir-(cod)Cl]₂-4PⁱPr₃, was also effective, but led to a lower yield. The solvent is crucial in order to obtain a high yield and stereoselectivity, and cyclohexane was found to be the best solvent.

A variety of diynes and triynes were investigated. The data for the hydroboration in Table 2 were obtained with the Rh(I)-P¹Pr₃ catalyst under the optimum reaction conditions. The Rh-catalyzed hydroboration of 1,4diethynylbenzene afforded (E)-bis(borylvinyl)benzene in high yield (entry 2). There is no great difference in transselectivity for the diynes and triyne studied (entries 1–4). Hydroboration of terminal alkynes using the same catalyst has been reported to give cis-1-alkenylboronates.¹⁵ However, the hydroboration of 3,6-diethynyl-9-hexylcarbazole and 9,10-diethynylanthracene resulted in a mixture of products, E- and Z-isomers (entries 5, 6). Moreover, the 1,3-diethynylazulene underwent a hydroboration to form only the Z-isomer (entry 7). Although it has been well documented that the hydroboration of terminal or internal alkynes affords a variable product distribution depending on the nature of the catalyst and substrate,¹⁶ it is quite remarkable that some of the diynes used in the present study

reacted to give 100% trans product. The trans configuration was assigned on the basis of the characteristic large coupling constant of the vinylene unit $({}^{3}J_{H-H} =$ 18.6-18.9 Hz).

To demonstrate the synthetic application of the obtained bis(borylvinyl) and tris(borylvinyl) products, compound 6 was chosen for a study of the Suzuki crosscoupling reaction with aryl bromides containing a chromophore unit. As expected, tris(borylvinyl)benzene is an efficient precursor for the cross-coupling reaction under mild conditions (Scheme 1). The Suzuki reaction of 6 with 9-bromoanthracene in the presence of Pd-(PPh₃)₄ and aqueous K₂CO₃ afforded the trianthrylsubstituted vinyl compound 13 in 55% yield. Compound 13 was obtained in 50% yield using a PdCl₂(PPh₃)₂-dppf, K₃PO₄ base, and DMF solvent system developed by Miyaura et al.¹⁷ Compound **6** also reacted readily with 1-bromopyrene to afford 14. The structures of compounds 13 and 14 were readily assigned by a combination of MS and ¹H and ¹³C NMR spectroscopies and by comparison with analogous compounds.¹⁸ A parent ion in the mass spectrum of 13 and 14 was observed at m/z684 and 756, respectively. Two doublets and large coupling constants (16.8-17.4 Hz) in the ¹H NMR spectra of 13 and 14 are consistent with trans-vinylic hydrogens. The ¹³C NMR spectra of 13 and 14 also exhibited the expected resonances. The amorphous N,Nbis(9,9-dimethylfluoren-2-yl)-4-bromoaniline¹⁹ underwent the Suzuki cross-coupling reaction with 6 to give 15. The compound was purified by silica gel column chromatography and identified by NMR spectroscopy and elemental analysis. Furthermore, we found that 6 reacted with 2-(4-bromophenyl)-5-(4-tert-butylphenyl)-1.3.4-oxadiazole²⁰ to provide the starburst product **16**. whose structure was confirmed by NMR spectroscopy and elemental analysis. Such π -electron starburst molecules have been extensively explored as either lightemitting materials or host materials in organic LEDs due to their good film-forming properties.²¹ The absorption and emission spectra of 13-15 taken in methylene chloride, depicted in Figure 1, reveal the varying geometrical differences between the electronic ground state and the fluorescent singlet excited state (Table 3). The absorption spectra of 13 and 14 exhibit intense absorption bands at 390 and 384 nm, indicating that the electronic transitions are mostly $\pi \rightarrow \pi^*$, originating from the π -conjugation chain extending from the anthryl and pyrenyl units. Compounds 13 and 14 exhibit fluorescence emission in the blue (478 and 457 nm) wavelength region. Since the vinylene groups and the chromophore units are planar, their fluorescence spectra are characterized by a small Stokes shift (88 and 73 nm). The

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entry	alkyne	product	$(hr, yield)^a$
1		$\begin{cases} & & \\ & $	4 h, 85%
2	-	to ^B ↓ bot	4 h, 88%
3		ton to the set of the	24 h, 45%
4		X ^o B X ^o B X ^o B	6 h, 74%
5	N C ₆ H ₁₃	$\begin{array}{c} & & & & & & \\ & & & & & & \\ & & & & & $	8 h, 84%
6	-&-	$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array}\\ \end{array}\\ \end{array}\\ \end{array}\\ \end{array} \begin{array}{c} \end{array} \begin{array}{c} \end{array}\\ \end{array} \begin{array}{c} \end{array} \begin{array}{c} \end{array}\\ \end{array} \begin{array}{c} \end{array} \end{array} \begin{array}{c} \end{array} \begin{array}{c} \end{array} \end{array} \begin{array}{c} \end{array} \end{array} \begin{array}{c} \end{array} \begin{array}{c} \end{array} \end{array} \begin{array}{c} \end{array} \begin{array}{c} \end{array} \end{array} \begin{array}{c} \end{array} \end{array} $	8 h, 78%
7	R		8 h, 38%

Table 2. Hydroboration of Diynes and a Triyne Catalyzed by Rh(I)

 a hr = reaction time; yield = isolated yield.

absorption and emission spectroscopic properties of **15** and **16** are basically similar to those of **13** and **14**, suggesting that the loss of fine structures results from the conjugation of the phenyl groups with the vinylene chromophore units. The somewhat large Stokes shift (120 nm) of **15** most likely stems from the excited-state-

induced coplanarity of the amorphous chromophore substituents.

Another synthetic utility of the hydroboration product was demonstrated by transformation of 2,2'-diethoxy-6,6'-bis(borylvinyl)-1,1'-binaphthalene **9** to chiral ditopic ligands. Compound **17** was prepared by Suzuki coupling



^a Reaction conditions: (i) 9-bromoanthracene, 55% yield; (ii) 1-bromopyrene, 61% yield; (iii) N,N-bis(9,9-dimethylfluorene-2yl)-4-bromoaniline, 47% yield; (iv) 2-(4-bromophenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole, 48% yield. All the reactions were carried out in the presence of $Pd(PPh_3)_4$ and K_2CO_3 in THF.



Figure 1. UV-visible spectra and PL spectra of 13–15.

Table 3. Photophysical Data for 13-16 in CH₂Cl₂ at Room Temperature^a

	UV-vis		emission	
compound	λ_{\max} (nm)	$\epsilon (\mathrm{dm^3 mol^{-1} cm^{-1}})$	$\overline{E_{\mathrm{em}}}$ (nm)	$\Phi_{\rm em}{}^b$
13	390	6240	478	0.12
14	384	12 420	457	0.22
15	376	19 240	496	0.26
16	349	18 840	406	0.34

^{*a*} Concentration of compounds is in the range 10^{-4} - 10^{-5} mol dm⁻³. ^b Quinine sulfate in 1 M H₂SO₄ ($\Phi_{f1} = 0.55$) was used as quantum yield standard.

reaction between 9 and 4-bromopyridine hydrochloride in 32% yield. The compound had been synthesized earlier by Heck coupling reaction between 4-vinylpyridine and 6,6'-dibromo-2,2'-diethoxy-1,1'-binaphthalene by Lin.²² Also the bis(borylvinyl)binaphthalene ligand 9 readily reacted with 5-bromo-2,2'-bipyridine to give 18 (Scheme 2). Many binuclear Ru(II) and Os(II) complexes containing two bipyridine units connected by various bridges have been reported.²³

Preliminary results with the well-established synthesis of alternating copolymers using the Suzuki coupling reaction²⁴ encouraged us to extend the new synthetic methodology to copolymers containing vinylene units along the polymer backbone. Most remarkably, the Suzuki coupling reaction of 2,2'-diethoxy-6,6'-bis(borylvinyl)-1,1'-binaphthalene 9 with 9,10-dibromoanthracene afforded the fully conjugated oligomer 19 in 35% yield (Scheme 3). The molecular weight and the polydispersity of the oligomer, determined by gel-permeation chromatography using a polystyrene standard, were in the ranges 2450-2550 and 1.9, respectively. The oligomer was soluble in common solvents such as CHCl₃, CH₂-Cl₂, and THF. The ¹H NMR spectrum of **19** shows a resonance at 6.18 ppm with a large coupling constant $(J_{\rm H-H} = 18.6 \text{ ppm})$ due to a vinylic hydrogen. The ¹³C NMR spectrum of the oligomer shows the expected resonances in the aromatic region. Such multiple C-C bond formation by the stepwise Suzuki cross-coupling reaction, providing a route to PPV-based molecular wires, was recently reported by Anderson and coworkers.²⁵

In summary, the first hydroboration of a variety of diynes and a triyne to afford bis- and trisborylsubstituted vinyl compounds with high stereoselectivity

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Scheme 2^a



^a Reaction conditions: (i) 4-bromopyridine, Pd(PPh₃)₄, K₂CO₃, toluene, reflux, 24 h, 32% yield; (ii) 5-bromo-2,2'-pyridine, Pd(PPh₃)₄, K₂CO₃, toluene, reflux, 24 h, 19% yield.

Scheme 3



is presented. The hydroboration products underwent the Suzuki cross-coupling reaction with a variety of substrates containing chromophore units to give trischromophore-substituted products. The mild and easy access of the isomerically distinct hydroboration protocol opens access to a host of potential subsequent transformations toward the construction of a large number of emitting copolymers. Additional investigations into the photophysical properties and novel synthesis of a variety of copolymers are now being undertaken in this laboratory.

Experimental Section

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques. Toluene, THF, and cyclohexane were freshly distilled from sodium benzophenone. The ¹H, ¹³C, and ¹¹B NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.00, 75.44, and 96.00 MHz, respectively. The absorption and photoluminescence spectra were recorded on a Perkin-Elmer Lambda 25 UV-visible spectrophotometer and a Perkin-Elmer LS fluorescence spectrometer, respectively. Pinacolborane, P'Pr₃, 1-bromopyrene, 9-bromoanthracene, 9,10-dibromoanthracene, and 4-bromopyridine hydrochloride were purchased from Aldrich Chemical Co. [Rh(cod)Cl]₂,²⁶ 1,4-diethynylbenzene,²⁷ 1,3,5-triethynylbenzene,²⁸ 2,7-diethynyl-9,9-dimethylfluorene,²⁹ 3,6-diethynyl-9hexylcarbazole,³⁰ 2,2'-diethynyl-9,9'-spirobifluorene,³¹ 1,3diethynylazulene,³² 9,10-diethynylanthracene,³³ 2,2'-diethoxy-6,6'-diethynyl-1,1'-binaphthalene,³⁴ N,N-bis(9,9-dimethylfluorene-2-yl)-4-bromoaniline,¹⁹ 2-(4-bromophenyl)-5-(4-*tert*-butylphenyl)-

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1,3,4-oxadi-azole,²⁰ and 5-bromo-2,2'-bipyridine³⁵ were prepared according to procedures reported in the literature.

General Procedure for Hydroboration of Diynes and a Triyne. To a stirred cyclohexane solution (10 mL) of [Rh-(cod)Cl]₂ (0.022 g, 0.045 mmol), NEt₃ (0.7 mL, 5 mmol), P'Pr₃ (0.035 mL, 0.18 mmol), and pinacolborane (0.44 mL, 3 mmol) was added 1,3,5-triethynylbenzene (0.15 g, 1 mmol) dissolved in cyclohexane (10 mL) at room temperature. The solution was stirred for 8 h at that temperature. The solvent was removed in vacuo. The pure product **6** was obtained by silica gel column chromatography (eluent: methylene chloride/hexane, 2:1) as a white solid in 88% yield.

1,3,5-Tris[2-(pinacolboryl)vinyl]benzene (6). Mp: 225 °C. ¹H NMR (CDCl₃): δ 7.53 (s, 3H, Ph-*H*), 7.37 (d, 3H, J = 18.9 Hz, *CH*=), 6.16 (d, 3H, J = 18.9 Hz, =*CH*-B), 1.32 (s, 36H, *CH*₃). ¹³C{¹H} NMR (CDCl₃): δ 148.7, 138.2, 126.1, 116.9, 83.5, 24.8. ¹¹B NMR (CDCl₃): δ 15.8. MS: *m*/*z* 534 [M⁺]. Anal. Calcd for C₃₀H₄₅O₆B₃: C, 67.46; H, 8.49. Found: C, 67.18; H, 8.24.

1,4-Bis[2-(pinacolboryl)vinyl]benzene (7). Mp: 195 °C. ¹H NMR (CDCl₃): δ 7.45 (s, 4H, Ph-*H*), 7.36 (d, 2H, J = 18.6 Hz, *CH*=), 6.17 (d, 2H, J = 18.6 Hz, =*CH*-B), 1.31 (s, 24H, *CH*₃). ¹³C{¹H} NMR (CDCl₃): δ 148.4, 138.3, 128.4, 119.6, 83.6, 24.9. ¹¹B NMR (CDCl₃): δ 16.4. MS: *m/z* 382 [M⁺]. Anal. Calcd for C₂₂H₃₂O₄B₂: C, 69.15; H, 8.44. Found: C, 68.97; H, 8.26.

2,7-Bis[2-(pinacolboryl)vinyl]-9,9'-spirobifluorene (8). Mp: 208 °C. ¹H NMR (CDCl₃): δ 7.83 (d, 2H, J = 7.8 Hz), 7.76 (d, 2H, J = 7.2 Hz), 7.50 (d, 2H, J = 7.8 Hz), 7.34 (t, 2H, J = 7.5 Hz), 7.24 (d, 2H, J = 18.9 Hz, CH=), 7.08 (t, 2H, J = 7.5 Hz), 6.86 (s, 2H), 6.71 (t, 2H, J = 7.2 Hz), 5.96 (d, 2H, J = 18.9 Hz, =CH-B), 1.22 (s, 24H, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 149.8, 149.2, 148.8, 142.0, 141.7, 137.4, 128.4, 128.1, 127.1, 125.0, 124.4, 123.4, 120.1, 119.8, 83.1, 26.8. ¹¹B NMR (CDCl₃): δ 16.0. MS: m/z 620 [M⁺]. Anal. Calcd for C₄₁H₄₂-O₄B₂: C, 79.38; H, 6.82. Found: C, 79.19; H, 6.65.

2,2'-Diethoxy-6,6'-bis[2-(pinacolboryl)vinyl]-1,1'-binaphthalene (9). Mp: 198 °C. ¹H NMR (CDCl₃): δ 7.91 (d, 2H, J = 9.0 Hz), 7.85 (s, 2H), 7.53 (d, 2H, J = 18.6 Hz, CH=), 7.48 (d, 2H, J = 9.0 Hz), 7.39 (s, 2H), 7.08 (d, 2H, J = 9.0 Hz), 6.15 (d, 2H, J = 18.6 Hz, =CH-B), 4.04 (m, 4H, OCH₂), 1.31 (s, 24H, CH₃), 1.05 (t, 6H, J = 6.9 Hz, OCH₂CH₃). ¹³C{¹H} NMR (CDCl₃): δ 154.7, 148.9, 137.8, 136.4, 134.0, 132.9, 129.4, 126.5, 126.2, 125.3, 123.8, 120.7, 83.2, 65.3, 25.3, 15.1. ¹¹B NMR (CDCl₃): δ 15.8. MS: *m*/*z* 646 [M⁺]. Anal. Calcd for C₄₀H₄₈-B₂O₆: C, 74.32; H, 7.48. Found: C, 74.12; H, 7.35.

3,6-Bis[2-(**pinacolbory**])**viny**]-9-hexylcarbazole (10). Mp: 167 °C. ¹H NMR (CDCl₃): δ 8.12 (s, 2H, Ph-*H*), 7.60 (d, 2H, J = 8.4 Hz), 7.34 (d, 2H, J = 18.9 Hz, CH=), 7.27 (d, 2H, J = 8.4 Hz), 6.14 (d, 2H, J = 18.9 Hz, =CH-B) {*cis*-10, 6.02 (d, J = 15.0 Hz, =CH-B)}, 4.18 (t, 2H, J = 6.6 Hz, NC*H*₂), 1.49–0.85 (m, 11H), 1.23 (s, 24H, C*H*₃). ¹³C{¹H} NMR (CDCl₃): δ 150.5, 141.3, 140.8, 130.0, 129.1, 125.0, 123.0, 119.8, 82.8, 45.8, 31.4, 28.9, 24.6, 23.3, 22.4, 16.2. ¹¹B NMR (CDCl₃): δ 16.8. MS: m/z 555 [M⁺]. Anal. Calcd for C₃₄H₄₇O₄NB₂: C, 73.53; H, 8.53. Found: C, 73.26; H, 8.40.

9,10-Bis[2-(pinacolboryl)vinyl]anthracene (11). Mp: 201 °C. ¹H NMR (CDCl₃): δ 8.35 (m, 4H, *anthryl*), 7.47 (m, 4H, *anthryl*), 7.45 (d, 2H, J = 18.6 Hz, CH=), 5.61 (d, 2H, J = 18.6 Hz, =CH-B) {*cis*-**11**, 6.02 (d, J = 14.1 Hz, =CH-B)}, 1.28 (s, 24H, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 140.7, 133.9, 131.7, 129.0, 126.3, 125.4, 83.7, 25.3. ¹¹B NMR (CDCl₃): δ 16.0. MS: *m*/*z* 482 [M⁺]. Anal. Calcd for C₃₀H₃₆O₄B₂: C, 74.72; H, 7.52. Found: C, 74.53; H, 7.37.

1,3-Bis[2-(pinacolboryl)vinyl]azulene (12). Mp: 175 °C. ¹H NMR (CDCl₃): δ 8.70 (s, 1H, Ph-*H*), 8.31 (d, 2H, J = 10.2 Hz), 7.77 (d, 2H, J = 15.0 Hz, CH=), 7.53 (t, 1H, J = 9.6 Hz), 7.11 (dd, 2H, J = 10.2 Hz, J = 9.6 Hz), 5.65 (d, 2H, J = 15.0 Hz, = CH-B), 1.23 (s, 24H, CH_3). ¹³C{¹H} NMR (CDCl₃): δ 140.9, 139.2, 138.5, 135.1, 134.0, 133.7, 127.9, 124.5, 83.1, 24.7. ^{11}B NMR (CDCl_3): δ 18.4. MS: m/z 432 [M+]. Anal. Calcd for C_{26}H_{34}O_4B_2: C, 72.26; H, 7.93. Found: C, 72.08; H, 7.80.

1,3,5-Tris[2-(anthryl)vinyl]benzene (13). To a stirred THF solution (25 mL) of 6 (0.15 g, 0.28 mmol), 9-bromoanthracene (0.24 g, 0.93 mmol), and Pd(PPh₃)₄ (0.05 g, 0.043 mmol) was added degassed K₂CO₃(aq) (2 M, 2.1 mL, 4.2 mmol). The solution was heated at reflux for 24 h. After cooling the solution, H₂O (10 mL) was added. The organic layer was separated and dried with MgSO₄. The solvent was removed in vacuo. The pure product 13 was obtained by silica gel chromatography (eluent: methylene chloride/hexane, 1:5) as a white solid in 55% yield. Mp: 262 °C dec. ¹H NMR (CDCl₃): δ 8.48–8.44 (m, 6H, *anthryl*), 8.13 (d, 3H, J = 17.4 Hz, CH=), 8.07-8.03 (m, 9H, anthryl), 7.98 (s, 3H, Ph), 7.54-7.50 (m, 12H, anthryl), 7.13 (d, 3H, J = 17.4 Hz, =CH). ¹³C{¹H} NMR (CDCl₃): δ 138.4, 134.2, 133.6, 132.6, 131.6, 129.8, 128.8, 127.5, 127.2, 125.9, 125.5. MS: m/z 684 [M⁺]. Anal. Calcd for C₅₄H₃₆: C, 94.70; H, 5.30. Found: C, 94.46; H, 5.21.

1,3,5-Tris[2-(pyrenyl)vinyl]benzene (14). Compound **14** was prepared using the same procedure as that described for **13** except that 1-bromopyrene was used instead of 9-bromoan-thracene. The pure product **14** was isolated by silica gel chromatography (eluent: ethyl acetate/hexane, 1:1) as a white solid in 61% yield. Mp: 238 °C dec. ¹H NMR (CDCl₃): δ 8.57 (d, 3H, *J* = 8.7 Hz, *pyrenyl*), 8.38 (d, 3H, *J* = 8.7 Hz, *pyrenyl*), 8.32 (d, 3H, *J* = 16.8 Hz, *CH*=), 8.22–8.02 (m, 21H, *pyrenyl*), 7.70 (s, 3H, *Ph*), 7.45 (d, 3H, *J* = 16.8 Hz, *CH*=). ¹³C{¹H} NMR (CDCl₃): δ 157.9, 157.1, 148.1, 138.6, 132.0, 131.8, 131.6, 131.2, 131.0, 128.6, 127.9, 127.6, 127.2, 126.5, 126.2, 125.3, 125.1, 124.4, 124.1, 122.3. MS: *m*/*z* 756 [M⁺]. Anal. Calcd for C₆₀H₃₆: C, 95.21; H, 4.79. Found: C, 94.88; H, 4.67.

1,3,5,-Tris{**2**-[*N*,*N*-bis(9,9-dimethylfluoren-2-yl)-4anilinyl]vinyl}benzene (15). Compound 15 was prepared using the same procedure as that described for **13** except that *N*,*N*-bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline was used instead of 9-bromoanthracene. The pure product **15** was isolated by silica gel chromatography (eluent: methylene chloride/hexane, 1:3) as a pale yellow solid in 47% yield. Mp: 230 °C. ¹H NMR (CDCl₃): δ 7.65–7.16 (m, 60H), 7.14 (d, 3H, *J* = 16.8 Hz, =*CH*), 1.43 (s, 36H, C–*CH*₃). ¹³C{¹H} NMR (CDCl₃): δ 155.2, 153.6, 147.7, 147.2, 139.0, 138.5, 138.1, 134.4, 131.5, 127.8, 127.4, 127.1, 126.7, 126.1, 123.8, 123.2, 122.9, 120.9, 120.6, 119.4, 46.9, 27.1. Anal. Calcd for C₁₂₀H₉₉N₃: C, 91.04; H, 6.30. Found: C, 90.83; H, 6.21.

1,3,5-Tris{**2-[phenyl-5-(4-***tert***-butylphenyl)-1,3,4-oxadiazolyl]vinyl}benzene (16).** Compound **16** was prepared using the same procedure as that described for **13** except 2-(4-bromophenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole was used instead of 9-bromoanthracene. The pure product **16** was isolated by silica gel chromatography (eluent: ethyl acetate/hexane, 1:3) as a white solid in 48% yield. Mp: 195 °C. ¹H NMR (CDCl₃): δ 8.12 (d, 6H, J = 8.1 Hz), 8.02 (d, 3H, J = 16.8 Hz, CH=), 7.96 (d, 6H, J = 8.1 Hz), 7.67 (d, 6H, J = 8.1 Hz), 7.59 (s, 3H, *Ph*), 7.52 (d, 6H, J = 7.5 Hz), 7.53 (d, 6H, J = 7.5 Hz), 7.12 (d, 3H, J = 16.8 Hz, =CH), 1.37 (s, 27H, ^{*i*}Bu). ¹³C{¹H} NMR (CDCl₃): δ 164.7, 164.4, 155.5, 145.5, 140.7, 137.2, 134.5, 127.5, 127.0, 126.8, 126.3, 126.0, 122.9, 121.2. 31.3, 25.0 MS: m/z 985 [M⁺]. Anal. Calcd for C₆₆H₆₀N₆O₃: C, 80.46; H, 6.14. Found: C, 80.22; H, 6.02.

2,2'-Diethoxy-1,1'-binaphthalene-6,6'-bis(4-vinylpyridine) (17). Compound **17** was prepared using the same procedure as that described for **13** except that compound **9** and 2 equiv of 4-bromopyridine hydrochloride were used instead of compound **6** and 3 equiv of 9-bromoanthracene. The pure product **17** was isolated by silica gel chromatography (eluent: ethyl acetate/hexane, 2:1 ($R_f = 0.1$)) in 32% yield. The spectroscopic data of **17** were identical to those of Lin.²¹

2,2'-Diethoxy-1,1'-binaphthalene-6,6'-bis(5-vinyl-2,2'bipyridine) (18). Compound 18 was prepared using the same procedure as that described for 17 except that 5-bromo-2,2'-

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bipyridine was used instead of 4-bromopyridine hydrochloride. The pure product 18 was isolated by silica gel chromatography (eluent: ethyl acetate/hexane, 2:1 ($R_f = 0.1$)) as a pale yellow solid in 19% yield. Mp: 253 °C. ¹H NMR (CDCl₃): δ 8.78 (s, 2H), 8.68 (d, 2H, J=3.6 Hz), 8.40 (d, 2H, J=8.4 Hz), 8.39 (d, 2H, J = 8.4 Hz), 8.00 (d, 2H, J = 8.4 Hz), 7.86 (d, 2H, J = 9.0 Hz), 7.94 (s, 2H), 7.81 (dd, 2H, J = 8.4 Hz, J = 1.8 Hz), 7.50 (d, 2H, J = 9.0 Hz), 7.44 (d, 2H, J = 9.0 Hz), 7.38 (d, 2H, J =17.1 Hz, vinyl), 7.32 (dd, 2H, J = 3.6 Hz, J = 1.8 Hz), 7.17 (d, 2H, J = 9.0 Hz), 7.15 (d, 2H, J = 17.1 Hz, vinyl), 4.08 (m, 4H, OCH₂), 1.09 (t, 6H, J = 6.9 Hz, OCH₂CH₃). ¹³C{¹H} NMR (CDCl₃): δ 156.1, 155.0, 154.9, 149.5, 148.1, 137.0, 134.2, 133.5, 132.08, 129.7, 129.43, 128.5, 127.5, 126.0, 124.0, 123.5, 122.4, 121.3, 121.0, 120.7, 116.3, 115.9, 65.3, 15.0. MS: m/z702 [M⁺]. Anal. Calcd for C48H38N4O2: C, 82.03; H, 5.45. Found: C, 81.87; H, 5.32.

Oligo(2,2'-diethoxy-6,6'-divinyl-1,1'-binaphthalenyl-9,10-anthracene) (19). 2,2'-Diethoxy-6,6'-bis(borylvinyl)-1,1'binaphthalene (0.24 g, 0.37 mmol) and 9,10-dibromoanthracene (0.12 g, 0.37 mmol) were dissolved in THF (20 mL). The palladium complex $Pd(PPh_3)_4$ (0.03 g) and degassed K_2 - CO_3 (5.25 mL, 1 M) were added to the mixture. The reaction mixture was heated at reflux for 48 h. An excess of bromobenzene (0.040 g, 0.25 mmol) was added as an end-capper. After it was refluxed for 10 h, the reaction mixture was cooled to about 40 °C and added to a stirred mixture of MeOH (100 mL) and 6 mL of 1 N aqueous HCl. The oligomer was collected by filtration and reprecipitated from MeOH and acetone. The oligomer was extracted by a Soxhlet in acetone for 1 day. The extract was dried in vacuo. The final product 19 was obtained as a yellow solid in 35% yield. Mp: 277 °C. ¹H NMR (CDCl₃): δ 7.92–7.06 (m, 20H, aromatic and vinyl), 6.18 (d, 2H, J = 18.6 Hz, vinyl), 4.12 (m, 4H, OCH₂), 1.05 (m, 6H, OCH₂CH₃). ¹³C{¹H} NMR (CDCl₃): δ 155.0, 137.3, 134.1, 132.7, 132.3, 131.6, 130.6, 129.5, 128.3, 127.4, 126.8, 126.4, 126.0, 125.2, 124.6, 122.7, 120.8, 117.2, 115.2, 65.2, 16.1. Anal. Calcd for (C₄₂H₃₂O₂)_n: C, 88.51; H, 5.71. Found: C, 88.17; H, 5.58. The number-average molecular weights (M_n) was determined by gel permeation chromatography (GPC) with an HPLC Waters 510 using a series of monodisperse polystyrenes as standard in THF. The number-average molecular weight (Mn) was 2500 $(M_{\rm w}/M_{\rm n} = 1.9).$

Acknowledgment. This work was supported by a Korea Research Foundation Grant (KRF-2002-070-C00055). OM049832M