Highly Conjugated Molecules from Dibromonaphthyl Derivatives and 4-Vinylpyridine or 4-Acetoxystyrene by the Heck Reaction

C. C. Chang, K. J. Chen, and L. J. Yu*

Department of Chemistry, Tamkang University, Tamsui, Taipei 25137, Taiwan

Received April 26, 1999

Palladium-catalyzed coupling of 1,6- and 2,6-dibromonaphthyl derivatives with 4-vinylpyridine or 4-acetoxystyrene resulted in mono- and bis-arylvinylation depending on the choice of reaction conditions. For the 1,6-dibromoarenes, the mono-arylvinylated derivative at position-6 was the sole product in the presence of (*o*-tol)$_3$P/Et$_3$N. The bis-arylvinylated derivative was the major product, accompanied by a minor product, arylvinylated at position-6 and reduced at position-1, in the presence of (*o*-tol)$_3$P/Et$_3$N/MeCN. For the 2,6-dibromoarenes, the bis-arylvinylated derivative was the sole product in the presence of either Ph$_3$P or (*o*-tol)$_3$P, if provided with a small volume of Et$_3$N/MeCN solvent, and the mono-arylvinylated derivative was the major product with larger solvent volume and higher haloarene ratio. Fluorescence intensities of 2,6-bis-arylvinylated products were 2 to 3 orders of magnitude higher than that of stilbene. Nematic phases, at relatively high temperatures, were observed for some of the rodlike molecules. Shown by ^{1}H NMR study, at the photostationary state of isomerization, smaller fractions of cis-form were obtained for molecules that exhibited larger fluorescence quantum yields. The results presented here are beneficial to the pursuit of nonlinear optical materials, fluorescent mesogens, photo- and electroactive materials.

Introduction

The palladium-catalyzed Heck reaction has been widely employed for the carbon−carbon bond formation in organic synthesis ever since its original development by Heck and co-workers.[1] Several reviews[2] and advanced studies[3] of the palladium-catalyzed reactions have appeared recently. Since the palladium-catalyzed Heck reaction is a coupling between aryl halides and olefins, it is a particularly valuable method when an extended π-system is desired. Molecules consisting of extended π-systems are of interest for the development of new dyes and nonlinear optical and photo- and electroactive materials. Stilbene and stilbazole are examples.[4] While both have been used as models for photochemical and photophysical studies, they have also led to derivatives that exhibit large solvatochromism,[5] intense fluorescence,[6] high hyperpolarizability,[7] and large cross-section for two-photon absorption.[8] Enhancements of these properties would be expected if the π-system were extended due to a longer π-conjugated chain or more aromatic rings. It is therefore interesting to study the variations in these chemical and physical properties when the phenyl rings of stilbene and stilbazole are replaced by a naphthyl moiety.

While the Heck reaction has been applied amply to the arylvinylation of halobenzene, which proceeds smoothly, the studies on polyhaloarenes are limited,[9] and similar studies of fused ring halides are rare.[10] In the present study, the palladium-catalyzed Heck reaction was employed for the arylvinylation of dibromonaphthyl derivatives. The olefins used were 4-acetoxystyrene and 4-vinylpyridine and the haloarenes were 1,6-dibromo-2-naphthol and 2,6-dibromo-1,5-naphthalenediol derivatives,

* To whom correspondence should be addressed. E-mail: ljyu@mail.tku.edu.tw.

(1) (a) Heck, R. F. *J. Am. Chem. Soc.* **1968,** *90,* 5518. (b) Heck, R. F. *Acc. Chem. Res.* **1979,** *12,* 146. (c) Heck, R. F. *Org. React.* **1982,** *27,* 345. And references therein.

(2) (a) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: London, 1985. (b) de Meijere, A.; Meyer, F. E. *Angew. Chem., Int. Ed. Engl.* **1994,** *33,* 2379. (c) Tsuji, J. *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*; John Wiley: Chichester, 1995. (d) Cabri, W.; Candiani, I. *Acc. Chem. Res.* **1995,** *28,* 2. (e) Shibasaki, M.; Boden, C. D. J.; Kojima, A. *Tetrahedron* **1997,** *53,* 7371.

(3) (a) Reetz, M. T.; Lohmer, G.; Schwickardi, R. *Angew. Chem., Int. Ed.* **1998,** *37,* 481. (b) Wagaw, S.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998,** *120,* 6621. (c) Nakamura, H.; Sekido, M.; Ito, M.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998,** *120,* 6838. (d) Buezo, N. D.; Alonso, I.; Carretero, J. C. *J. Am. Chem. Soc.* **1998,** *120,* 7129. (e) Dussault, P. H.; Eary, C. T. *J. Am. Chem. Soc.* **1998,** *120,* 7133. (f) Old, D. W.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998,** *120,* 9722. (g) Kadota, I.; Shibuya, A.; Gyoung, Y. S.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998,** *120,* 10262. (h) Loiseleur, O.; Hayashi, M.; Schmees, N.; Pfaltz, A. *Synthesis* **1997,** 1338.

(4) Görner, H.; Kuhn, H. J. In *Advances in Photochemistry*; Neckers, D. C., Volman, D. H., von Bunau, G., Eds.; John Wiley & Sons: New York, 1995; Vol. 19, pp 1−117.

(5) (a) Morley, J. O.; Morley, R. M.; Fitton, A. L. *J. Am. Chem. Soc.* **1998,** *120,* 11479, and references therein. (b) Cao, X.; Tolbert, R. W.; McHale, J. L.; Edwards, W. D. *J. Phys. Chem. A* **1998,** *102,* 2739.

(6) (a) Strehmel, B.; Seifert, H.; Rettig, W. *J. Phys. Chem. B* **1997,** *101,* 2232. (b) Turkewitsch, P.; Darling, G. D.; Powell, W. S. *J. Chem. Soc., Faraday Trans.* **1998,** *94,* 2083. (c) Peng, Z.; Galvin, M. E. *Chem. Mater.* **1998,** *10,* 1785. (d) Vanden Bout, D. A.; Yip, W. T.; Hu, D.; Fu, D. K.; Swager, T. M.; Barbara, P. F. *Science* **1997,** *277,* 1074. (e) Hide, F.; Díaz-García, M. A.; Schwartz, B. J.; Heeger, A. J. *Acc. Chem. Res.* **1997,** *30,* 430.

(7) (a) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984,** *23,* 690. (b) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994,** *94,* 195. (c) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical effects in Molecules and Polymers*; John Wiley & Sons: New York, 1991. (d) Marder, S. R.; Sohn, J. E.; Stucky, G. D. *Materials for Nonlinear Optics: Chemical Perspectives*; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991. (e) Chemla, D. S.; Zyss, J. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: New York, 1987.

(8) (a) Reinhardt, B. A.; Brott, L. L.; Clarson, S. J.; Dillard, A. G.; Bhatt, J. C.; Kannan, R.; Yuan, L.; He, G. S.; Prasad, P. N. *Chem. Mater.* **1998,** *10,* 1863. (b) Albota, M.; Beljonne, D.; Brédas, J. L.; Ehrlich, J. E.; Fu, J. Y.; Heikal, A. A.; Hess, S. E.; Kogej, T.; Levin, M. D.; Marder, S. R.; McCord-Maughon, D.; Perry, J. W.; Röckel, H.; Rumi, M.; Subramaniam, G.; Webb, W. W.; Wu, X. L.; Xu, C. *Science* **1998,** *281,* 1653.

(9) Tao, W.; Nesbitt, S.; Heck, R. F. *J. Org. Chem.* **1990,** *55,* 63, and ref 2b.

(10) Scherf, U.; Müllen, K. *Synthesis* **1992,** 23.

A and **B**, respectively. To the best of our knowledge, this is the first report of arylvinylation of 1,6-dibromo- and 2,6-dibromonaphthyl derivatives by the Heck reaction. It was found that depending upon the phosphines and solvents used, the dibromoarenes could undergo either mono- or bis-arylvinylation. These arylvinylated products exhibit intense fluorescence and mesophase behaviors, particularly the **B**-type molecules. Photoisomerization was studied by NMR spectroscopy.

Experimental Section

Compounds 1,6-dibromo-2-naphthol (**A1**) and 2,6-dibromo-1,5-naphthalenediol (**B1**) were prepared from 2-naphthol (Merck, as received) and 1,5-naphthalenediol (Aldrich and Merck, either as received or recrystallized) according to refs 11 and 12, respectively. Their ether- and ester- derivatives were synthesized by conventional methods. The catalysts palladium(II) acetate (Pd(OAc)$_2$, Strem), triphenylphosphine (Ph$_3$P, Merck), and tri(o-tolyl)phosphine ((o-tol)$_3$P, Aldrich) were used, as received. The olefin 4-acetoxystyrene (Aldrich) was used, as received, and 4-vinylpyridine (4VP, Merck) was vacuum-distilled before use.

General Procedures for Heck Reaction.[1c] The amount of phosphine used was 6−8 times (molar ratio) that of Pd(OAc)$_2$, and the latter was 1 mol % (per halo) of the haloarene (10 mmol for each run). Either triethylamine (Et$_3$N) alone or Et$_3$N/MeCN (volume ratio 1:2 to 1:9) were used as solvents. The desired amounts of reagents were placed in a thick wall Pyrex pressure bottle equipped with a cap and gasket. After thoroughly mixing and flushing with nitrogen gas, the bottle was capped and heated to 100 °C for the time indicated in Tables. After workup, the final products were separated by silica gel column chromatography with various solvents. All the results of elemental analysis, molecular mass determination, and proton NMR spectra confirmed the expected structures.

Melting points were determined without correction. Elemental analysis was carried out at the Tainan Instrumentation Center of the National Science Council. ^{1}H NMR spectra were recorded with a 300 MHz spectrometer. Chemical shifts are reported in ppm relative to residual nondeuterated solvent, and J values are in hertz. Mass spectra were recorded under electron impact at 70 eV. Absorption and emission spectra were recorded with a UV−vis spectrometer and a fluorospectrometer, respectively. Mesophases were characterized by optical polarizing microscopy in conjunction with a heating stage for temperature variation. A medium-pressure mercury lamp (450 W) was used for photochemical study.

Results and Discussion

1,6-Dibromo-2-naphthol Derivatives as the Haloarenes. After several attempts, under various conditions, the coupling of 4-vinylpyridine and 1,6-dibromo-2-naphthol resulted in no isolable products, possibly due to the instability of the naphthol in the slightly basic medium and the electron-donating property of the hydroxyl group.[1c] The ether and ester derivatives were therefore employed, Scheme 1, and the results are listed in Table 1.

The coupling of 4VP with 1,6-dibromo-2-methoxynaphthalene (**A2**) resulted in only 8% yield of 1,6-bis-arylvinylated product (**A2a**) and 41% yield of 6-arylvinylated-1-bromo-2-methoxynaphthalene (**A2b**; structure confirmation is discussed later) in Ph$_3$P/Et$_3$N condition. Replacing the Et$_3$N with Et$_3$N/MeCN solvent resulted in similar prod-

(11) Koelsch, F. In *Organic Syntheses*; Horning, E. C., Ed.; John Wiley & Sons: New York, 1960; Coll. Vol. 3, pp 132−133.

(12) Carter, A. H.; Race, E.; Rowe, F. M. *J. Chem. Soc.* **1942**, 236.

Scheme 1

	R
A1	H
A2	CH$_3$
A3	C$_3$H$_7$
A4	(S)CH$_2$CH(CH$_3$)C$_2$H$_5$
A5	C$_8$H$_{17}$
A6	CH$_2$C$_6$H$_5$
A7	OCC$_6$H$_5$

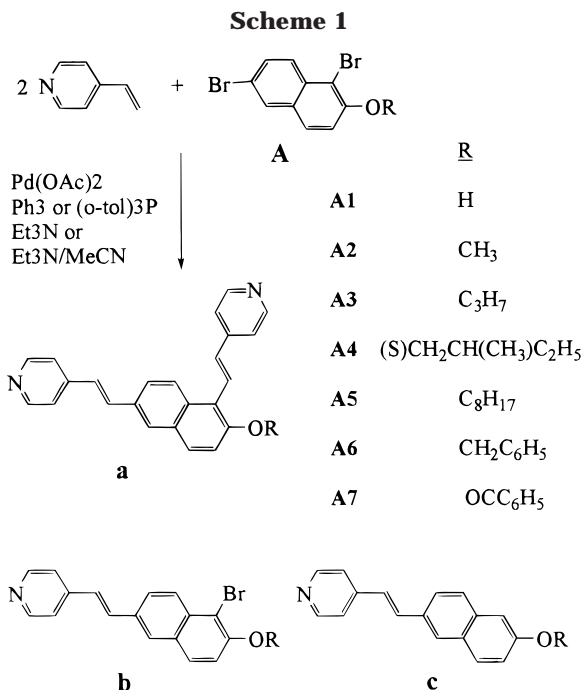**Table 1. Reaction Conditions and Yields of Products for the Heck Reaction of 1,6-Dibromo-2-naphthol Derivatives and 4-Vinylpyridine**

				yield, %		
haloarene	ligand	Et$_3$N/MeCN (mL)	reaction time (h)	a	b	c
A2	Ph$_3$P	30/0	96	8	41	
A2	Ph$_3$P	10/90	96	5	28	
A2	(o-tol)$_3$P	30/0	96		63	
A2	(o-tol)$_3$P	100/0	96		31	
A2	(o-tol)$_3$P	20/50	96	46		13
A2	(o-tol)$_3$P	10/90	96	43		11
A3	(o-tol)$_3$P	10/90	96	33		4
A4	(o-tol)$_3$P	10/90	96	37		7
A5	(o-tol)$_3$P	40/80	96	48		25
A6	Ph$_3$P	30/0	96		41	
A6	(o-tol)$_3$P	10/90	96	45		6
A7	Ph$_3$P	30/0	96	3	25	
A7	Ph$_3$P	10/90	96	7	22	
A7	(o-tol)$_3$P	30/0	96		47	
A7	(o-tol)$_3$P	10/90	96	48		14
A2b′	(o-tol)$_3$P	10/90	96	12^a		

^{a} **A2a**, but with a 4-acetoxystyryl group at position-6, **A2a″**.

ucts but in lower yields, 5% of **A2a** and 28% of **A2b**. When (o-tol)$_3$P was used instead of Ph$_3$P, in Et$_3$N alone, **A2b** was obtained as the sole product in 63% yield. When Et$_3$N/MeCN was used together with (o-tol)$_3$P, the highest yield of 1,6-bis-arylvinylated product (**A2a**) was obtained (46%) but along with a 13% yield of 6-arylvinylated-2-methoxynaphthalene (**A2c**), i.e., a product with reduction at 1-position. The ^{1}H NMR spectrum of this product is identical to that of the product obtained from 6-bromo-2-alkyloxynaphthalene reported previously.[13] This reduction during the reaction was observed also by Heck and co-workers although the situation was slightly different.[9]

Replacement of the methoxy group at position-2 with a benzoate (**A7**) resulted in the same types of products but in slightly different yields. The mono-arylvinylated product (**A7b**) was the major product in the presence of Ph$_3$P (in either Et$_3$N alone or Et$_3$N/MeCN) and was the

(13) Yu, L. J.; Chen, K. Y. *Mol. Cryst. Liq. Cryst.* **1995**, *265*, 89.

Table 2. Reaction Conditions and Yields of Products for the Heck Reaction of 1,6-Dibromo-2-naphthol Derivatives and 4-Acetoxystyrene

haloarene	ligand	Et₃N/MeCN (mL)	reaction time (h)	yield, % a′	b′	c′
A2	(*o*-tol)₃P	30/0	48		67	
A2	(*o*-tol)₃P	10/90	48	21		36
A2	(*o*-tol)₃P	10/30	48	66		3
A2b	(*o*-tol)₃P	10/30/10DMF	96	19*a*		

a **A2a**, but with 4-acetoxystyryl group at position-1, **A2a′′′**.

sole product (in 47% yield) in the (*o*-tol)₃P/Et₃N case. In the case of (*o*-tol)₃P/Et₃N/MeCN, 48% yield of 1,6-bis-arylvinylated product (**A7a**) and 14% yield of 6-arylvinylated-1-H product (**A7c**) were obtained. It was noted that 10% of the dibromoarene were recovered for the cases with Et₃N alone.

The above results indicated that the variations of products and yields were mainly due to the phosphine and solvent chosen, the ether and ester linkages played a minor role if any. Similar results were also obtained when the methoxy group at position-2 was changed to longer chains (propyloxy, **A3**, and octyloxy, **A5**), chiral ((*S*)-2-methylbutyloxy, **A4**) and bulkier (benzyloxy, **A6**) groups, as shown for the case of (*o*-tol)₃P/Et₃N/MeCN, i.e., 1,6-bis-arylvinylation was the major product and 6-arylvinylated-1-reduced product was the minor. It was noted that higher yields were obtained, in the presence of (*o*-tol)₃P, when the ratio of Et₃N/MeCN was in the range of 1/2 to 1/3. Also noted was that lower yields were obtained with larger volumes of solvents (vide infra).

When 4-acetoxystyrene was used as the olefin, as in Scheme 1 but replacing the 4VP moieties by 4-acetoxystyrene (and the corresponding products were designated by **a′**, **b′**, and **c′**), no product could be isolated for the cases with Ph₃P. For the cases with (*o*-tol)₃P, shown in Table 2, however, 67% yield of 6-arylvinylation, **A2b′**, was obtained as the sole product with Et₃N as solvent, and 21% yield of 1,6-bis-arylvinylated product, **A2a′**, and 36% yield of 6-arylvinylated-1-reduced product, **A2c′**, were obtained with Et₃N/MeCN(10 mL/90 mL) as solvent. When this ratio was changed to 10 mL/30 mL, higher yields were obtained, 66% yield of **A2a′** and 3% yield of **A2c′**. With 4-acetoxystyrene as the olefin, the reaction time was shortened to 48 h.

The mono-arylvinylated products, i.e., 1-bromo-6-arylvinylated derivatives, could be subjected to Heck reaction again, but DMF was needed in order to reach a homogeneous solution. Thereafter, 1,6-bis-arylvinylated product could be obtained along with the 6-arylvinylated-1-reduced product. The total yield was lower. Furthermore, for the second arylvinylation, a different olefin could be used. Thus, different arylvinyl groups could be attached to the 1- and 6-positions and resulted in different final products as shown for **A2b′** in Table 1 and **A2b** in Table 2. These results indicated that stepwise arylvinylation could be achieved by a proper choice of reaction conditions, and the first arylvinylation always occurred at the 6-position.

The First Arylvinylation Occurred at Position-6. The ¹H NMR spectra for the aromatic protons of **A2b**, 1D and 2D COSY, are shown in Figure 1 along with the peak assignments (confirmed by proton decoupling). The doublet signals at 8.23 ppm are of He. The signals of Hd, doublet−doublet due to He(ortho) and Hc(meta), are located at 7.80 and 7.82 ppm. The latter signal is
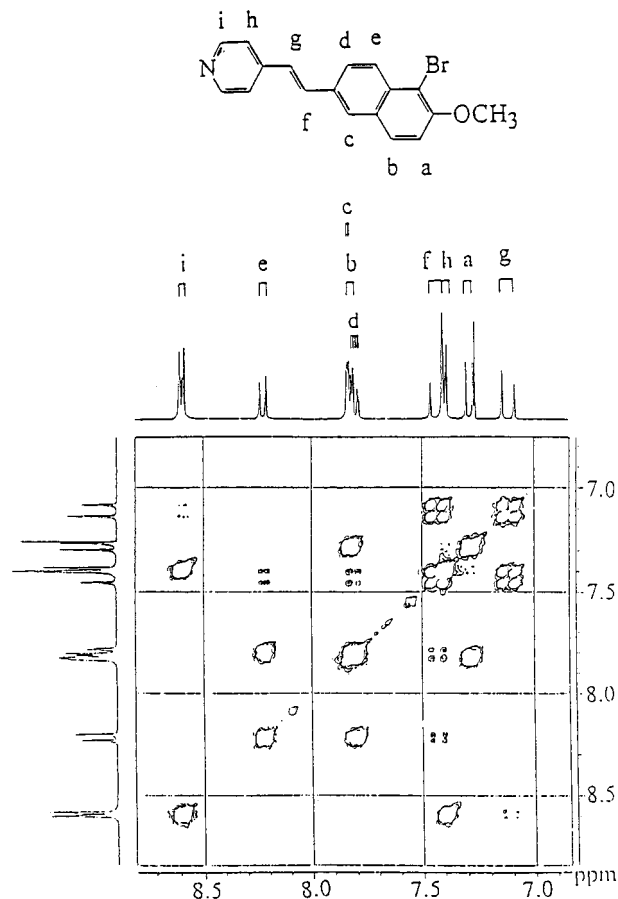

Figure 1. The structural representation and peak assignments of the ¹H NMR spectra, 1D and 2D COSY, for the aromatic protons of 1-bromo-2-methoxy-6-(2′(4′′-pyridyl)ethenyl)naphthalene (**A2b**) in CDCl₃.

overlapped with one of the Hb doublet (due to Ha). The other half of the Hb doublet is overlapped with the singlet (compounded by a smaller coupling due to Hd) of Hc. If the bromo group were located at position-6 (of naphthalene), and the pyridylvinyl group at position-1, the most downfield signals (of naphthalene protons) should be the doublet−doublet of Hd (due to He and Hc) and the singlet (compounded by a smaller coupling due to Hd) of Hc located nearby. However, these are not observed in the spectrum.

A further confirmation is obtained by analysis of the COSY spectrum. The strongest cross-peaks associated with Hf (the vinylic proton) observed are a pair of contours located at 7.83 ppm, indicating that the associated signal should be a singlet, which should be of Hc. Those of Hd are barely observed, since they are doublet−doublet in nature and should be weaker. The contours of weaker cross-peaks are observed also for Hf−He interaction. If the vinyl group were located at position-1, the strongest cross-peaks should be of two pairs of contours for He (with Hf), and also for Hd but weaker. Those of Hc, one pair of contours, would not be observable. This is not the spectrum observed.

The third confirmation is assisted by the consideration of molecular geometry. The molecular shapes of **A2b** and **A2c** are rodlike and that of the 1-substituted analogue (see next section for its preparation) is more like a T. It

Table 3. Mesophase and Transition Temperature (°C) for Mixtures of *p*-Butyloxybenzoic Acid with A2b, A2c, and 1-(2′(4″-pyridyl)ethenyl)-2-methoxynaphthalene (1-A2c) in 1:1 Molar Ratio

| compound	mp[a]	mesophase behavior[b]
A2b	162−164	$C \xrightleftharpoons[131]{161} N \xrightleftharpoons[177]{181}$ Iso
A2c	189−191	$C \xrightleftharpoons[130]{150} N \xrightleftharpoons[186]{189}$ Iso
1-A2c	109−111	$C \xrightleftharpoons[115]{129}$ Iso

[a] Melting points of **A2b**, **A2c**, and **1-A2c**. [b] C: Crystal, N: Nematic, Iso: Isotropic.

has been well-known that pyridine could act as a proton acceptor, and formation of a hydrogen bond would be expected in the presence of a proton donor. Therefore, mesophases should be observed for the hydrogen-bonded complexes of **A2b** and **A2c**, for they were more like rodlike mesogens, and not for the 1-substituted analogue. The results are listed in Table 3; the melting points of the pure components are also included. Nematic phases, with extended temperature ranges, are observed for mixtures of *p*-(butyloxy)benzoic acid (crystal 147 °C, Nematic 160 °C, isotropic) with either **A2b** or **A2c**, in 1:1 molar ratio, but not with the 1-substituted analogue. All the above results indicate that **A2b** should have the structure as shown.

Reduction Occurred at Position-1. The occurrence of reduction at position-1 required, as the above results indicated, the presence of Pd(OAc)$_2$, (*o*-tol)$_3$P, Et$_3$N, and MeCN. In a parallel run, but with 1-bromo-2-methoxy-naphthalene (obtained by methylation for 1-bromo-2-naphthol (Aldrich)) as the haloarene, the sole product obtained was the 1-arylvinylated derivative (47% yield), and no reduced product, 2-methoxynaphthalene, was detected. This result further indicates that the presence of a substituent at positon-6 would facilitate the reduction. This situation resembles to the reduction of 1,6-dibromo-2-naphthol, by tin (Sn) in the presence of acids, to 6-bromo-2-naphthol during its preparation.[11] The reducing agent would be the palladium because it changed back and forth between Pd(II)-complex and Pd(0)-complex states during the catalytic cycle;[2b,d] however, both (*o*-tol)$_3$P and MeCN were required to furnishing the reduction with proton. Further study would be helpful to reveal the mechanism.

2,6-Dibromo-1,5-naphthalenediol Derivatives as the Haloarenes. The dimethoxy and bis(4′-alkyloxyben-zoyloxy) derivatives of 2,6-dibromo-1,5-naphthalenediol were used for coupling with 4VP and 4-acetoxystyrene, Scheme 2, because the diol did not give isolable product. The results are listed in Tables 4 and 5. For the coupling of the 4VP and dimethoxy derivatives, with Et$_3$N alone as the base and also as solvent, both mono- and bis-arylvinylated products, **B2d** and **B2e**, were obtained along with 17−35% recovery of the dibromoarene. However, the bis-arylvinylated product was the predominant in the presence of Ph$_3$P and the mono-arylvinylated product was predominant in the presence of (*o*-tol)$_3$P. In either case the total yield was about 30%. When Et$_3$N was replaced by Et$_3$N/MeCN (10 mL/90 mL), the same as that for 1,6-dibromo-2-methoxynaphthalene to obtain the bis-arylvinylated product, the mono-arylvinylated product was obtained as the sole product in only 10%

Scheme 2

	R
B1	H
B2	CH$_3$
B3	COC$_6$H$_4$OC$_8$H$_{17}$
B4	COC$_6$H$_4$OC$_{12}$H$_{25}$
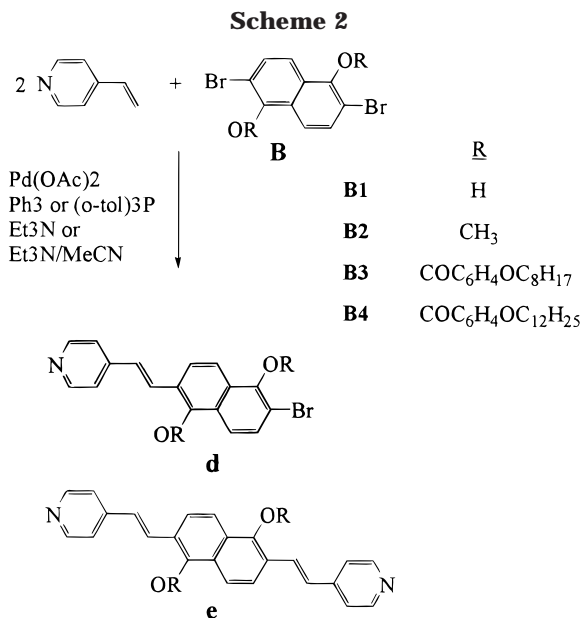
Table 4. Reaction Conditions and Yields of Products for the Heck Reaction of 2,6-Dibromo-1,5-Naphthalenediol Derivatives and 4-Vinylpyridine

				yield, %		
haloarene	ligand	Et$_3$N/MeCN (mL)	reaction time (h)	d	e	recovery, %
B2	Ph$_3$P	30/0	96	17	17.4	35
B2	Ph$_3$P	30/0	120	8.7	28.7	17
B2	(*o*-tol)$_3$P	30/0	96	30.3	2.2	17.4
B2	(*o*-tol)$_3$P	10/90	96	10		40
B2	Ph$_3$P	10/90	96	10.8		40.5
B2	Ph$_3$P	6/54	96	8	66.3	trace
B2	(*o*-tol)$_3$P	4.5/40.5	96		80.9	trace
B2	(*o*-tol)$_3$P	15/28	96		81.5	trace
B2	Ph$_3$P	15/30	96		80.3	trace
B2[a]	(*o*-tol)$_3$P	33.5/66.5	96	38.2	3	57.2
B3	(*o*-tol)$_3$P	30/30/10DMF	48		38	trace
B3	(*o*-tol)$_3$P	15/30	72		28	trace
B4	(*o*-tol)$_3$P	20/40	48		30	trace

[a] Haloarene:4-vinylpyridine = 3:1 mole ratio.

Table 5. Reaction Conditions and Yields of Products for the Heck Reaction of 2,6-Dibromo-1,5-Naphthalenediol Derivatives and 4-Acetoxystyrene

				yield, %	
haloarene	ligand	Et$_3$N/MeCN (mL)	reaction time (h)	d′	e′
B2	(*o*-tol)$_3$P	30/0	48	23	
B2	(*o*-tol)$_3$P	10/90	48	21.7	50.1
B2	(*o*-tol)$_3$P	15/30	48	8.2	62.6
B2d	(*o*-tol)$_3$P	15/30	48		70[a]

[a] **B2e**, but with 4-acetoxystyryl group at position-2, **B2e″**.

yield, along with 40% recovery of the dibromoarene, regardless of the phosphines used. When the solvent volume was reduced, 6 mL/54 mL of Et$_3$N/MeCN, higher yields were obtained, 8% of **B2d** and 66.3% of **B2e**. A further reduction of solvent volume resulted in 80.9% yield of **B2e** as the sole product. When the solvent ratio was changed to 15 mL/28 mL (and a further reduction of volume), 81.5% yield of **B2e** was obtained as the sole product. A similar result was obtained when Ph$_3$P was used. For the case of 33.5 mL/66.5 mL of Et$_3$N/MeCN, with molar ratio of haloarene/4VP = 3/1, mono-arylvi-nylation was the major product (38.2% of **B2d**), and a large amount of haloarene was recovered (57.2%). Under the condition of Et$_3$N/MeCN = 1:2, the diester derivatives
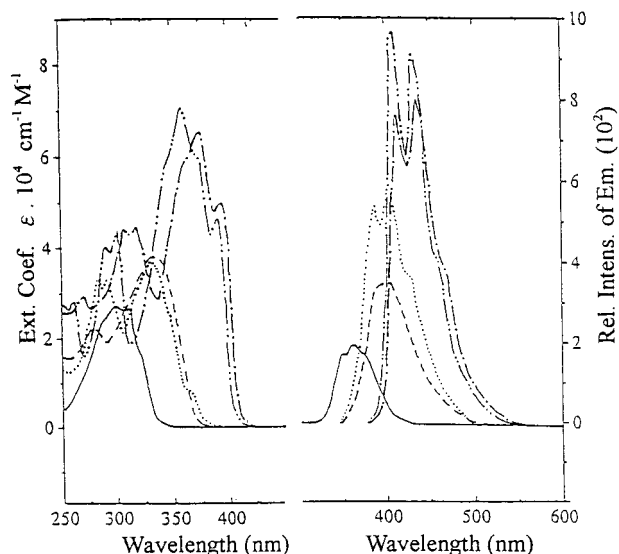
Figure 2. The absorption (left) and fluorescence (right) spectra of stilbene analogues in chloroform. Concentration for absorption, 4.4×10^{-5} M. Concentration ($\times 10^{-7}$ M, in parentheses) for fluorescence, **B2e′** ··—··— (0.65); **B2e′** † ·—·— (1.0); **B2d′** ···· (8.0); **A2c′** † − − − (2.0); stilbene — (30.0).

(bis(4′-octyloxybenzoyloxy) and bis(4′-dodecyloxybenzoyloxy)) gave the bis-arylvinylation as the sole products in 30−40% yields.

With 4-acetoxystyrene as the olefin (as in Scheme 2 but replacing 4VP with 4-acetoxystyrene, and the corresponding products were designated by **d′** and **e′**) and employing $(o\text{-tol})_3$P, the dimethoxy derivative resulted in bis-arylvinylation as the sole product (**B2e′**) in 23% yield in Et_3N. However, in Et_3N/MeCN (10 mL/90 mL) mixed solvent, the mono- and bis-arylvinylation (**B2d′** and **B2e′**) were obtained in 21.7% and 50.1% yields, respectively. These yields were changed to 8.2% and 62.6%, respectively, in Et_3N/MeCN (15/30 mL) mixed solvent. When this olefin was used for the second coupling with 2-bromo-1,5-dimethoxy-6-(2′(4″-pyridyl)ethenyl)naphthalene (**B2d**), a dissymmetrical bis-arylvinylated product (**B2e″**) was obtained in 70% yield in Et_3N/MeCN (15 mL/30 mL). It was found that the 1,5-diester derivatives resulted in only recovery of p-(alkyloxy)benzoic acids, side products due to dissociation of the ester linkages, with the above various conditions.

The above results indicated that mono- or bis-arylvinylation for derivatives of 2,6-dibromo-1,5-naphthalenediol could be obtained by a proper choice of reaction conditions. It was noted that under all of the above conditions there was no product found with Br replaced by H for the mono-arylvinylation, the case observed for the 1,6-dibromoarenes.

Absorption and Emission. The UV−vis absorption and emission spectra for some of these highly conjugated molecules, in chloroform, are shown in Figures 2 (stilbene analogues) and 3 (stilbazole analogues). Also included are those of stilbene and stilbazole for comparison. It can be seen clearly that the absorption bands are wider and red-shifted by about 60−100 nm, and extinction coefficients are about two times larger for the bis-arylvinylated products. These spectra display vibronic structures spaced by energies of ~1300, ~1200, and ~1100 cm^{-1} from the long wavelength side. The wavelengths of maximum emission of these bis-arylvinylated products are also red-

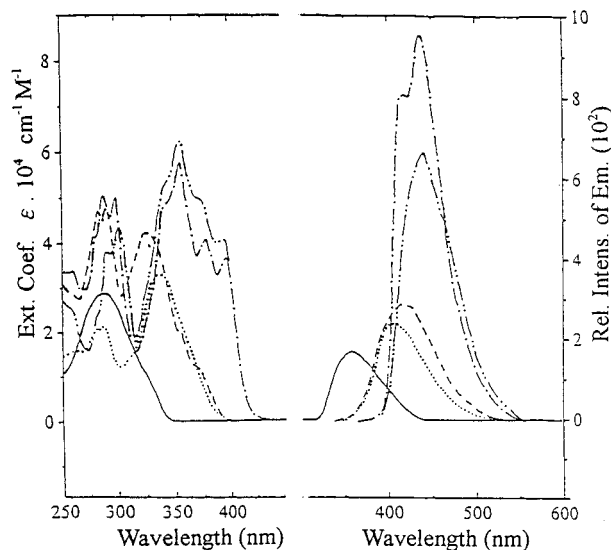**Figure 3.** The absorption (left) and fluorescence (right) spectra of stilbazole analogues in chloroform. Concentration for absorption, 4.4×10^{-5} M. Concentration ($\times 10^{-7}$ M, in parentheses) for fluorescence, **B2e** ·—·— (1.0); **B2e″** ··—··— (0.8); **B2d** − − − (4.0); **A2c** ···· (10.0); stilbazole — (28.0).

Table 6. The Parameters of Absorption, Fluorescence, and Photoisomerization Products for Stilbene and Stilbazole Analogues in Chloroform

compound	absorption ext coef ϵ, 10^4 cm^{-1} M^{-1} (λ_{max}, nm)	fluorescence[a] Φ_f[b] ($\lambda_{max,em}$, nm)[c]	photoisomerization cis/trans (%, ss)[d]
B2e′	7.0 (357)	0.982 (405)	11.2/88.8
B2e	5.8 (357)	0.716 (440)	14.5/85.5
B2e″ [e]	6.2 (360)	0.607 (441)	40.7/59.3
B2e′ † [f]	6.7 (373)	0.564 (408)	
B2e″ † [f]	5.1 (363)	0.358 (460)	
A2a′ † [f]	5.6 (337)	0.195 (430)	
B2d′	3.7 (330)	0.070 (395)	63.5/36.5
B2d	4.3 (330)	0.040 (411)	80.1/19.9
A2c	3.3 (337)	0.033 (408)	87.4/22.6
A2c′ † [f]	3.8 (333)	0.020 (397)	
A2a	3.3 (330)	0.015 (435)	
stilbazole	3.0 (300)	0.016 (355)	90.4/9.6
stilbene	2.7 (295)	0.040 (353)	77.2/22.8

[a] Concentration was 1.0×10^{-7} M for recording the fluorescence spectrum. [b] The fluorescence quantum yield, quinine sulfate ($\Phi_f = 0.55$) used as standard (ref 14). [c] The wavelength of the maximum fluorescence intensity, excited at the λ_{max} of excitation spectrum (uncorrected). [d] Percentages evaluated from the ^{1}H NMR (CDCl$_3$) spectra at the photostationary state of isomerization. [e] **B2e** but with 4-acetoxystyryl group at position-2, see footnote of Table 5. [f] The superscript † indicates that the acetoxyl group was replaced by hydroxyl group.

shifted by about 60−100 nm, and emission intensities are about 2 to 3 orders of magnitude higher than that of stilbene (compared with same concentration, 1.0×10^{-6} M). These emission spectra also display vibronic structures but with energy spacings different from those of absorption. Smaller red shifts of wavelength (both absorption and emission) and smaller increments of extinction coefficient and fluorescence intensity are observed for the mono-arylvinylated products. The results are summarized in Table 6 for some of the molecules synthesized.

Considering the fluorescent quantum yield, listed in Table 6, the bis-arylvinylated products exhibit much larger values than the mono-arylvinylated products. The exception is **A2a** as compared to **A2c**. Both molecules

have the same values of extinction coefficient. Apparently, the second pyridylethenyl group in **A2a** played a mysterious role, which did not help for photon absorption but dissipated the excited-state energy. A further study would help to elucidate this. For the same type of chromophore attached, the fluorescent quantum yields for the **B** type products are higher than **A** type products (**B2e** vs **A2a** and **B2e'**[†] vs **A2a'**[†]). This enhancement is attributed to the resonance effect for chromophores located at positions-2 and -6 (of naphthalene). It is worth noting that the stilbenoid derivatives exhibit fluorescent quantum yields larger than the stilbazolyl derivatives, **B2e'** vs **B2e** and **A2a'**[†] vs **A2a**. Moreover, for the stilbenoid derivatives, the existence of acetyl group results in a larger enhancement (**B2e'** vs **B2e'**[†], and **B2e''** vs **B2e''**[†]). These variations in fluorescent quantum yield might have something to do with the characteristics of electron-donating and -withdrawing properties of the functional groups.[8b] It is also worth noting that the enhancement of **B2e''** is the smallest among the **B2e**'s. The **B2e''** molecule possesses different chromophores at positions-2 and -6. These results are consistent with that reported by Albota et al.,[8b] that the symmetrical chromophores result in larger enhancements. The molecules synthesized in the present study exhibit two-photon absorption behavior. The details of these properties will be reported later.

Photoisomerization. The photoisomerizations of these compounds, 0.008 M in CDCl$_3$, were monitored spectroscopically by ^{1}H NMR spectrametry up to the photostationary states, and the ratios of cis/trans isomers are also included in Table 6. Further photochemical processes were observed for prolong irradiation and not included here. The proton spectra at different irradiation stages for **B2d** are shown in Figure 4 along with the schematic representations of molecular conformations and the corresponding peak assignments. Upon irradiation of UV light for 2 min, a doublet at 6.7 ppm with coupling constant of 12.4 cps is clear evidence for the cis-conformation of the ethenylic protons, and a doublet at 8.45 ppm is clearly due to the protons next to the nitrogen atom of the pyridyl ring. The signals of cis-isomer grew at the expenses of the trans-isomer with irradiation time. At the photostationary state (12 min), the signals of the cis-isomer dominate the spectrum, and the assignments of remaining peaks are apparent and supported further by the 2D COSY spectrum, as shown in Figure 5. The cross-peaks at 6.68−8.46 ppm confirm the assignments for Hg' and Hi'. Stronger interaction should be expected for Hg'−Hh', but only half of the cross-peaks is observed, at 6.7−7.14 ppm, the other half is buried under the Hg' and Hf' cross-peaks. The cross-peaks at 7.1−7.2 and 7.1−7.7 ppm are apparently due to interactions of Hf' with Hd' and He', respectively. It is interesting to note that nearly equally intense cross-peaks are observed for the Hf'−He' interaction (through five chemical bonds). The fact that the assignments for Hd' and He' are not interchanged can be accounted for considering the cis-conformation.

All the aromatic proton signals of the cis-conformation are upfield shifted except those of Ha and Hb, which are the farthest away from the ethenyl group and retain their chemical shifts. The largest shift is observed for the doublet of Hd, from 7.92 to 7.2 ppm, suggesting a shielding effect due to the π-electrons of the pyridyl moiety in the cis-conformation and the pyridyl ring plane
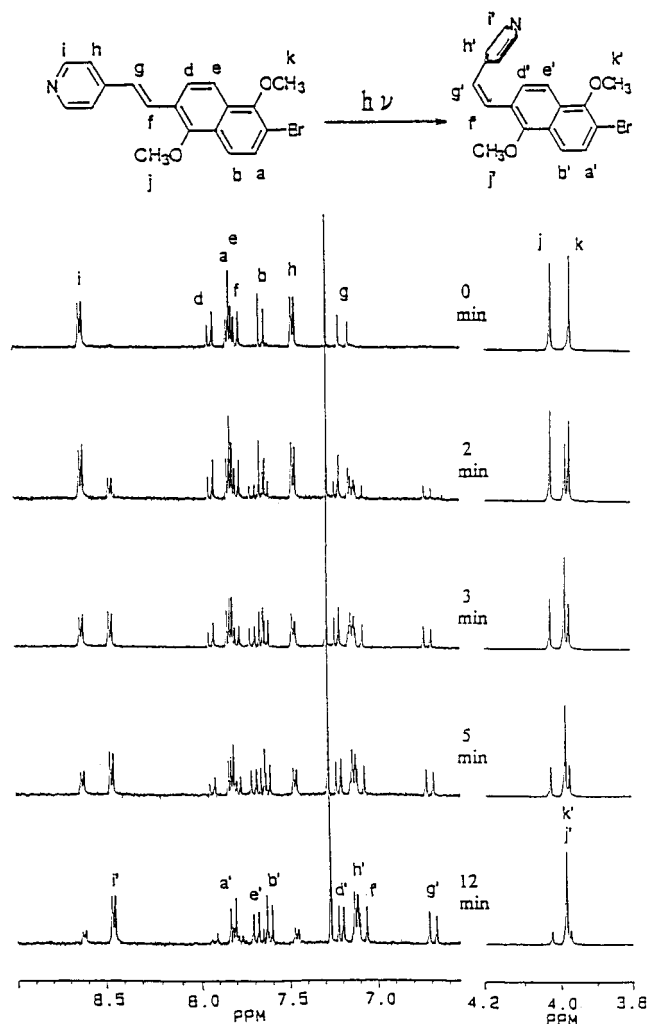

Figure 4. The ^{1}H NMR spectra as a function of irradiation time for **B2d** in CDCl$_3$ (0.008 M). The schematic representations of trans- and cis-isomers and the corresponding peak assignments.

facing the edge of naphthalene. In the cis-conformation the naphthalene plane is slightly rotated counterclockwise (viewing along the Br−C bond) with respect to the ethenylic plane resulting in upfield shifts for both ethenylic protons due to the shielding effects from either rings. In this conformation, the adjacent methoxy group is swung to a position having a better shielding from the ethenylic π-electrons. These analyses are consistent with those discussed by Steiner et al. in the study of isomerization of *N*-methylated stilbazolium dye.[15]

The variation in compositions of cis- and trans-isomers, obtained from the ^{1}H NMR spectra, for **B2d** and **B2e** during the irradiation and up to the isomerization photostationary states are shown in Figure 6. The proton spectra of **B2e** consisted of two sets of signals correlated to the all-trans and all-cis conformations, thus only the all-cis photoproduct was included for analysis. Also shown in Figure 6 are the curves obtained with the fitted rate constants ($R = 0.995$ and 0.992 for **B2d** and **B2e**, respectively). The ratio of k_{t-c}/k_{c-t} ($= K$, the equilibrium constant at the photostationary state) is 4 for **B2d** and

(14) Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; Wiley: New York, 1966.

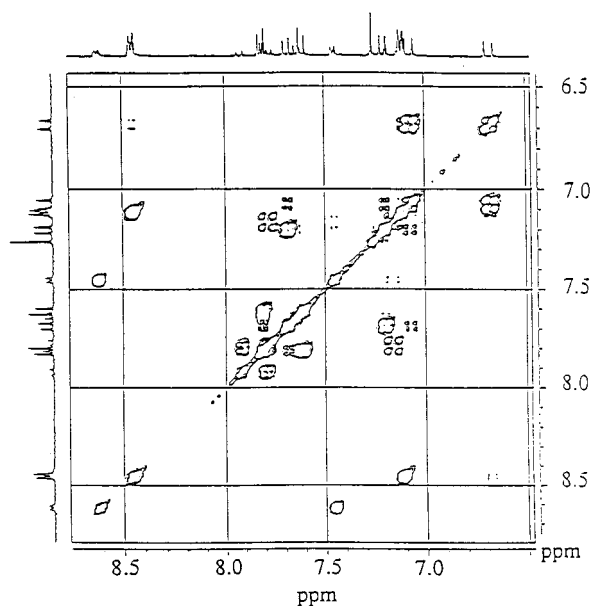(15) Steiner, U.; Abdel-Kader, M. H.; Fischer, P.; Kramer, M. E. A. *J. Am. Chem. Soc.* **1978**, *100*, 3190.

Figure 5. The ^{1}H NMR 2D COSY spectrum of **B2d** in CDCl$_3$ (0.06 M) at the photostationary state of isomerization (45 min of irradiation). See Figure 4 for peak assignments.
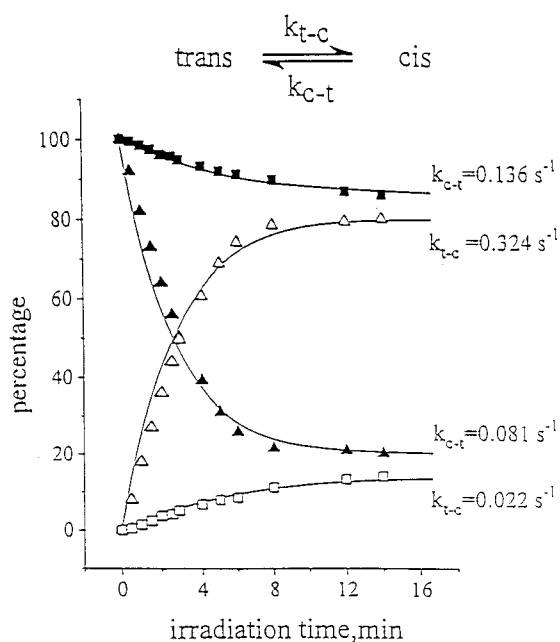

Figure 6. The percentages of trans- and cis-isomers of **B2d** (▲ and △) and **B2e** (■ and □), evaluated from the ^{1}H NMR spectra, as a function of irradiation time. The theoretical curves are obtained with the fitted k values with R values of 0.995 and 0.992 for **B2d** and **B2e**, respectively.

Table 7. Mesophase and Transition Temperature (°C) for the Synthesized Molecules

compound	mesophase behavior^c
A7c	$C \underset{190}{\overset{212}{\rightleftharpoons}} N \underset{}{\overset{202}{\rightleftharpoons}} Iso$
A2b'	$C \underset{152}{\overset{193}{\rightleftharpoons}} N \underset{}{\overset{191}{\rightleftharpoons}} Iso$
A2c'$^{\dagger a}$	$C \xrightarrow{229} N \xrightarrow{237} Iso(dec)^b$
B2e'	$C \xrightarrow{235} N \xrightarrow{336} Iso(dec)$
B2e'$^{\dagger a}$	$C \xrightarrow{278} N \xrightarrow{306} Iso(dec)$
B2e''	$C \xrightarrow{197} N \xrightarrow{252} Iso(dec)$
B2e''$^{\dagger a}$	$C \xrightarrow{247} N \xrightarrow{261} Iso(dec)$

^{a} The superscript † indicates that the acetoxyl group was replaced by hydroxyl group. ^{b} dec: decomposed. ^{c} C: crystal, N: nematic, Iso: isotropic.

considerable amount of shorter wavelengths (<330 nm) and the filtering was apparently not complete.

Mesophases. Considering the shape of molecular geometry of these highly conjugated molecules, the existences of liquid crystal behavior would be expected, particularly for the bis-arylvinylated products of 2,6-dibromo-1,5-dimethoxynaphthalene (**B**'s). The results are listed in Table 7. Either monotropic or enantiotropic nematic phases were observed for the mono-arylvinylated **A** type products. Enantiotropic nematic phases, at relative high temperatures with wide ranges and up to decomposition, were observed for the **B** type products. The conjugated moieties studied here could serve as the cores of rod like mesogens, and a large variety of new mesogens could be synthesized.

Conclusion

Palladium-catalyzed coupling of dibromonaphthyl derivatives with 4-vinylpyridine or 4-acetoxystyrene underwent mono- and bis-arylvinylation dependent on the choice of reaction conditions. For the 1,6-dibromoarenes, the mono-arylvinylated derivative, shown to occur at position-6, was the sole product in the presence of (*o*-tol)$_3$P/Et$_3$N, and the bis-arylvinylated derivative was the major product and accompanied by a minor product, 6-arylvinylated-1-reduced, in the presence of (*o*-tol)$_3$P/Et$_3$N/MeCN. For the 2,6-dibromoarenes, the bis-arylvinylated derivative was the sole product in the presence

0.16 for **B2e**. This variation in rate constant ratios correlates well with the fluorescent quantum yields as shown in Table 6, the larger the fluorescent quantum yield the smaller the fraction of cis-isomer at the photoisomerization stationary state. This is quite reasonable since a larger fraction of energy of the excited state is radiated out as fluorescence a smaller fraction is left for the chemical processes. It should be noted here that a sample of *trans*-stilbene was next to the others during the irradiation, the occurrence of *cis*-stilbene indicated that the UV light, after filtering, was composed of a

of either Ph_3P or (o-tol)$_3$P provided with a small volume of Et_3N/MeCN solvent and the mono-arylvinylated derivative was the major product with larger solvent volume and higher haloarene ratio.

These molecules exhibit intense fluorescence, mesogenic behaviors, and photochemical properties. In view of the current interests in the development of nonlinear optical materials, two-photon dyes, and photo- and electroactive materials, the results presented here are beneficial to the pursuit of such materials.

Supporting Information Available: Tables of results of elemental analysis, melting point, molecular mass, and ^{1}H NMR peak assignments for molecules synthesized. This material is available free of charge via the Internet at http://pubs.acs.org.

JO990697A