Parallel Synthesis of Unsymmetrical *trans*-Stilbenes

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New unsymmetrical *trans*-stilbenes have been prepared by the sequential coupling reactions of bromobenzenesulfonate with formylarylboronic acids, benzylphosphonates and arylmagnesium bromides and characterized. The nickel-catalyzed reactions of stilbenesulfonates with aryl Grignard reagents produced the corresponding stilbenes *via* the nucleophilic aromatic substitution of the neopentyloxysulfonyl group by aryl nucleophiles. The great chemoselectivity of the alkyloxysulfonyl group allows the stepwise construction of unsymmetrical *trans*-stilbenes possessing terphenyl moieties. This procedure appears to be a promising and conceptually straightforward route for the parallel synthesis of various unsymmetrical stilbenes as well as other highly conjugated hydrocarbons.

Key Words : Unsymmetrical *trans*-stilbenes, Stilbenesulfonates, Nickel-catalyst, Cross-coupling

Introduction

Stilbene and oligostilbene derivatives, which are frequently found in nature, have become of particular interest owing to their wide range of biological activities including anti-cancer,[1] antifungal,[2] antioxidant,[3] anti-HIV[4] and anti-inflammatory[5] activities. Resveratrol, a hydroxylated *trans*-stilbene compound isolated from various plant species, is especially attracting much attention due to its interesting pharmacological properties.[6] The stilbene skeleton has often been chosen as a central chromophore for the construction of bulky photoresponsive materials.[7] Accordingly, the photochemical and photophysical properties of stilbene derivatives have been extensively studied as they are the prototype of the photochemical *cis-trans* isomerization of 1,2-disubstituted olefins.[8] Stilbene derivatives are also attractive for technological applications in optical data storage[9] and NLO.[10]

Stilbene derivatives have recently attracted great interest in the area of organic flexible displays. Since the first emitting conjugated poly(*p*-phenylenevinylene) (PPV) was reported in 1990,[11] PPV derivatives have been important as the emissive layer of organic light-emitting diodes (OLEDs).[12] Stilbenes as well as the π-conjugated oligomers with alternating phenyl and vinyl units, short subunits of PPV compounds, have been of wide interest in research to gain an understanding of the light emission mechanisms and to predict the influence of substitution on the emitted light.[13] Also, stilbene derivatives are known to exhibit blue photo-luminescence by themselves.[14] Aminostilbene compounds have been described as showing the fluorescence[15] as well as the hole transport[16] property. Stilbene dendrimers have recently attracted considerable attention as novel luminescent materials for applications in OLEDs.[17]

The most familiar synthetic pathways for unsymmetrical stilbenes[18] have adapted the Wittig[19] and Horner-Wadsworth-Emmons (HWE) reactions[20] of substituted benzaldehydes with benzyl phosphonium ylides or phosphonates. Stilbenes are often elaborated from styrene derivatives *via* the Heck reaction.[21] Two sequential Heck reactions of haloarenes with ethene have been described for the preparation of stilbenes and PPVs.[22] The combined use of the Heck and Wittig reactions[23] or the Heck and HWE reactions[24] has also been employed to construct the alternating phenyl and vinyl units. The Perkins reaction has also recently been applied for the synthesis of stilbene derivatives.[25] Symmetrical stilbenes are often formed *via* dimerization reactions. Oxidative dimerization of methylarenes,[26] eliminative dimerization of benzyl halides[27] and reductive dimerization of benzaldehydes[28] have been reported for the efficient preparation of symmetrical stilbene compounds. However, there has been difficulty isolating the synthetic strategy appropriate for the rapid preparation of highly conjugated stilbenes possessing oligophenyl moieties.

In a program directed at the development of organic fluorescent materials, we have investigated an efficient synthetic pathway for the preparation of various highly conjugated stilbene and distyrylarylene derivatives. Recently, the neopentyloxysulfonyl groups, directly attached onto arenes, have been discovered to act as excellent leaving groups in the nickel-catalyzed reactions with aryl- and alkylmagnesium halides by our group.[29] In this paper, our efforts in applying this new coupling reaction to the parallel synthesis of a unsymmetrical stilbene library are reported. Unsymmetrical *trans*-stilbene derivatives **8** could be prepared by the nickel(0)-catalyzed cross-coupling reaction of *trans*-stilbenesulfonates **6**, which were prepared by the consecutive Suzuki-Miyaura coupling and HWE olefination of 4-bromobenzenesulfonate **2**, with aryl Grignard reagents **7** (Scheme 1). All the stilbenesulfonates **6** and stilbenes **8** except **8a** prepared for this study, to our knowledge, have not been reported before. The results of this study are presented and discussed below.

Results and Discussion

Formylbiphenylsulfonates **4** were prepared by employing
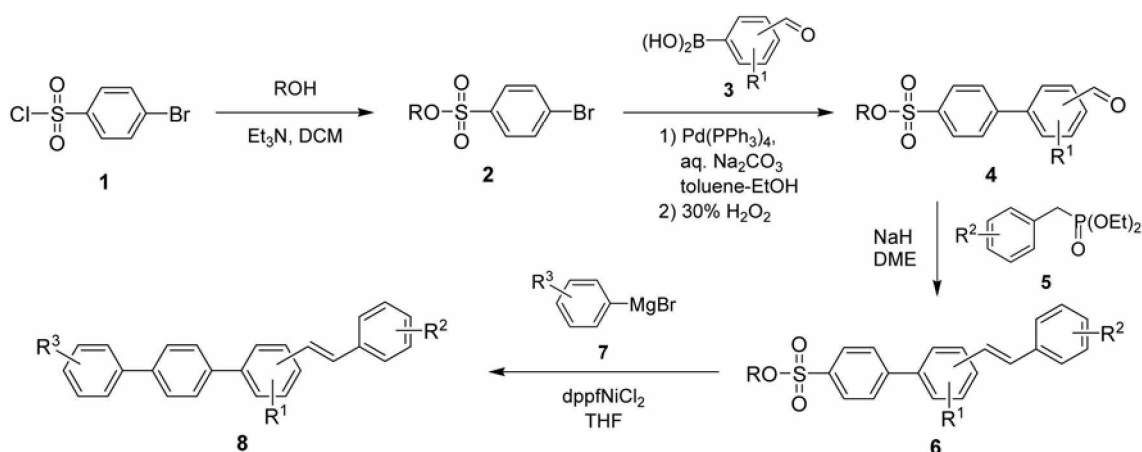
Scheme 1

a modification of literature procedure.[30] The Suzuki-Miyaura coupling of bromobenzenesulfonate **2**. which was prepared by the reaction of neopentyl alcohol with 4-bromobenzene-

sulfonyl chloride (**1**), with formylarylboronic acids **3** proceeded efficiently in the presence of a Pd(PPh₃)₄ catalyst. The neopentyl moiety, 2.2-dimethyl-3-phenyl-1-propyl. was

Table 1. Preparation of *trans*-stilbenesulfonates **6**[a]

	4	+	5	NaH / DME →	6	

entry	4	5	stilbenesulfonate 6	yield (%)[b]
1	**4a**	**5a**	**6a**	78
2	**4a**	**5b**	**6b**	76
3	**4a**	**5c**	**6c**	73
4	**4a**	**5d**	**6d**	76
5	**4b**	**5a**	**6e**	55
6	**4b**	**5b**	**6f**	43
7	**4b**	**5c**	**6g**	41

[a]Reactions of **4** (2.80 mmol) with **5** (3.08 mmol) were carried out in the presence of NaH (3.10 mmol) at the refluxing temperature of DME (30 mL) for 1016 h. [b] Isolated yields based on **4**.

selected as the alkyl group of the sulfonates to avoid the competitive substitution or elimination of arenesulfonate anions in the subsequent reactions with strong nucleophiles. Both the coupling reactions of 4-formylphenylboronic acid (**3a**) and 3-formyl-4-methoxyphenylboronic acid (**3b**) proceeded well to produce the desired sulfonates **4a** and **4b**, which were purified by simple recrystallization, in 68 and 71% yields respectively.

The formylbiphenylsulfonates **4a** and **4b** reacted with four benzylphosphonates **5** to form stilbenesulfonates **6** by constructing the central vinyl moiety of the stilbene structure (Table 1). 4'-Formyl-1,1'-biphenyl-4-sulfonate **4a** reacted with phosphonates **5a-5d** to generate the stilbenesulfonates **6a-6d** in good yields (entries 1-4). 3'-Formyl-4'-methoxy-1,1'-biphenyl-4-sulfonate **4b** was also reactive towards **5a-5c** rapidly generating the corresponding stilbenesulfonates **6e-6g** (entries 5-7), even though the yields of **6e-6g** were slightly lower than those of **6a-6d**. All products, **6a-6g**, were purified by recrystallization from either *i*-PrOH or *i*-PrOH:*n*-hexane (90:10).

All reactions showed great stereoselectivity in producing only the *trans*-stilbenesulfonates within the limits of the NMR and GC detection, as expected from the literature.[31] The coupling constants between the two vinylic protons of stilbenes **6** were 16-17 Hz, the typical coupling constants between the *trans* vicinal vinylic protons, in the ^{1}H-NMR spectra.

Cross-coupling reactions of the stilbenesulfonates **6** with the aryl Grignard reagents **7** were carried out in the presence of a nickel(0) catalyst, and the results of which are summarized in Table 2. Treatment of a mixture of sulfonates **6** and dppfNiCl$_2$ (5 mol% based on **6**) with the aryl Grignard reagents **7** in THF effectively produced unsymmetrical *trans*-stilbene derivatives **8** via the nucleophilic aromatic substitution of the neopentyloxysulfonyl group by aryl nucleophiles. The optimized process discovered in our previous study,[20d] which used the 3 + 2 equivalents of **7** to the sulfonates **6**, was adapted. Although the stilbenesulfonates **6** dissolve poorly in THF at room temperature, they adequately dissolve by refluxing in THF to undergo the coupling reaction.

All the coupling reactions proceeded rapidly, regardless of the stilbene structure, and were finished within 12 h. A faster reaction of the more conjugated arenesulfonates has been consistently observed in previous work.[29] While no significant levels of byproducts originating from the sulfonates **6** were obtained, a large amount of biphenyls derived by the dimerization of **7** were produced in these reactions. However, the biphenyls were easily removed by washing the crude solid products with methanol. Despite the efficient reaction, the poor solubility of the products in organic solvents seemed to decrease the final yields by making the purification difficult. Accordingly, the stilbenes that showed better solubility due to a greater number of alkyl or methoxy substituents were obtained in relatively higher yields (entries 5, 6, 8, 9, 12, and 13).

While all the ^{1}H NMR spectra of **8** were clear enough to

Table 2. Preparation of unsymmetrical *trans*-stilbenes **8**[a]

entry	6	7	product 8	yield (%)[b]
1	6a	7a	8a	41
2	6a	7b	8b	56
3	6a	7c	8c	51
4	6b	7a	8d	63
5	6b	7b	8e	69
6	6b	7c	8f	67
7	6c	7a	8g	61
8	6c	7b	8h	74
9	6c	7c	8i	74
10	6d	7b	8j	53
11	6e	7b	8k	64
12	6f	7b	8l	72
13	6g	7b	8m	76

[a]Reactions of **6** (0.100 mmol) with **7** (0.50 mmol) were carried out at the refluxing temperature of THF (20 mL) using dppfNiCl$_2$ (0.00500 mmol). [b]Isolated yields based on **6**.

characterize their full chemical structures, it was extremely difficult to obtain good ^{13}C NMR spectra for most stilbenes **8** due to their poor solubility. Only **8k-8m**, which show relatively better solubilities in CDCl$_3$, allowed reasonably good ^{13}C NMR spectra to be obtained. A substituent of the phenyl ring, directly attached on the vinyl moiety, has an interesting influence on the chemical shift of the vinylic protons. Both of the vinylic protons of **8a**, **8b** and **8c**, which contain no substituent on that phenyl group, are equivalent, and form a singlet in ^{1}H NMR spectra. However, each vinylic proton of the stilbenes possessing a methyl (**8d-8f**) or a *tert*-butyl (**8g-8i**) group on the phenyl ring is different and generates a doublet in different positions of ^{1}H NMR spectra. A similar phenomenon was found in the ^{1}H NMR spectra of the stilbenesulfonates **6**. The two vinylic protons

of stilbenes **8j-8m** are also different, and form a pair of doublets. The coupling constants of those doublets in the ¹H NMR spectra of **8d-8m** are 16-17 ppm. which clearly indicate that the stilbenes **8** are *trans*-isomers.

Conclusions

Unsymmetrical *trans*-stilbenes are prepared *via* the sequential coupling reactions of bromobenzenesulfonate. The great chemoselectivity of the neopenyloxysulfonyl group, which is an excellent leaving group in the presence of a nickel catalyst while not reactive toward phosphonate carbanions or palladium catalyst at all. allows the stepwise construction of highly conjugated unsymmetrical stilbenes in good overall yields. Only *trans*-stilbenes are produced as a result of the stereoselectivity of the HWE reaction. To our knowledge, this is the first general preparation of unsymmetrical stilbenes possessing oligophenyl moieties, which would be useful as novel luminescent materials. The procedure described in this paper appears to be a promising and conceptually straightforward route for the parallel synthesis of various unfunctionalized hydrocarbons with phenyl and vinyl units. The synthesis and characterization of other highly conjugated compounds using this method are under investigation. and will be reported in due course.

Experimental Section

General. Solvents were distilled from appropriate drying agents prior to use: THF and DME from sodium-benzophenone ketyl: toluene from CaH_2. Commercially available reagents were used without further purification unless otherwise stated. ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) were registered in $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in δ units (ppm) by assigning TMS resonance in the ¹H and ¹³C spectrum as 0.00 ppm. All coupling constants, *J*. are reported in hertz (Hz). Column chromatography was performed on silica gel 60. 70-230 mesh. Analytical thin-layer chromatography (TLC) was performed using Merck Kieselgel 60 F_{254} precoated plates (0.25 mm) with a fluorescent indicator and visualized with UV light (254 and 365 nm) or by iodine vapor staining. GC analysis was performed on a bonded 5% phenylpolysiloxane BPX 5 capillary column (SGE. 30 m. 0.32 mm i.d.). Electron impact (EI. 70 eV) was used as the ionization method for the mass spectrometry.

General Procedure for the Preparation of Stilbenesulfonates 6. To the mixture of benzyl phosphonates **5** (3.08 mmol) and sodium hydride (124 mg of 60% oil dispersion. 3.10 mmol) in DME (15 mL) was added formylbiphenylsulfonates **4** (2.80 mmol) in DME (15 mL) dropwise at room temperature under Ar atmosphere. The brown mixture was heated at reflux for 10-16 h until TLC analysis showed the complete disappearance of **4**. The reaction mixture was cooled to room temperature and diluted with CH_2Cl_2. The resulting mixture was washed with 1% aqueous HCl. water.

and brine: dried over $MgSO_4$: and concentrated in vacuo. The crude product **6** was purified by recrystallization from *i*-PrOH or *i*-PrOH:*n*-hexane (90:10).

(*E*)-2,2-Dimethyl-3-phenyl-1-propyl   4'-styryl-1,1'-biphenyl-4-sulfonate (6a) was prepared by the reaction of **5a** (0.660 g. 3.08 mmol), NaH (124 mg of 60% oil dispersion, 3.10 mmol). and **4a** (1.14 g. 2.80 mmol). The crude product was purified by recrystallization from *i*-PrOH to afford **6a** (1.05 g. 78%) as a pale yellowish solid: mp 134-135 °C (uncorrected): TLC R_f 0.16 (CH_2Cl_2:*n*-hexane = 1:1): ¹H NMR (500 MHz, $CDCl_3$) δ 0.90 (s. 6H), 2.57 (s. 2H), 3.72 (s. 2H). 7.02 (dd. *J* = 7.80, 1.91 Hz. 2H). 7.18-7.21 (m, 3H). 7.19 (s, 2H). 7.29 (t. *J* = 7.68 Hz. 1H). 7.39 (t. *J* = 7.63 Hz. 2H). 7.55 (d. *J* = 8.44 Hz. 2H). 7.64 (s. 4H), 7.79 (d. *J* = 8.51 Hz. 2H). 7.99 (d. *J* = 8.51 Hz. 2H); ¹³C NMR (125 MHz, $CDCl_3$) δ 24.1 (×2), 35.3. 44.3, 77.2, 126.3, 126.7 (×2), 127.2 (×2). 127.5 (×2), 127.6 (×2), 127.7. 128.0 (×2). 128.0, 128.5 (×2). 128.8 (×2), 129.8. 130.4 (×2), 134.4. 137.0, 137.4, 137.9, 138.0, 146.1: HRMS (EI, 70 eV) calcd for $C_{31}H_{30}O_3S$ (M⁺) 482.1916. found 482.1838.

(*E*)-2,2-Dimethyl-3-phenyl-1-propyl 4'-[2-(4-tolyl)vinyl]-1,1'-biphenyl-4-sulfonate (6b) was prepared by the reaction of **5b** (0.703 g. 3.08 mmol). NaH (124 mg of 60% oil dispersion, 3.10 mmol), and **4a** (1.14 g. 2.80 mmol). The crude product was purified by recrystallization from *i*-PrOH to afford **6b** (1.06 g. 76%) as a bright yellow solid: mp 198-199 °C (uncorrected): TLC R_f 0.16 (CH_2Cl_2:*n*-hexane = 1:1): ¹H NMR (500 MHz, $CDCl_3$) δ 0.90 (s. 6H). 2.38 (s. 3H), 2.57 (s. 2H), 3.72 (s. 2H). 7.02 (dd. *J* = 7.80. 1.91 Hz. 2H), 7.11 (d. *J* = 16.31 Hz, 1H). 7.167.21 (m, 6H). 7.45 (d. *J* = 8.06 Hz. 2H), 7.63 (s. 4H), 7.79 (d. *J* = 8.52 Hz, 2H), 7.99 (d. *J* = 8.52 Hz, 2H); ¹³C NMR (125 MHz. $CDCl_3$) δ 21.3, 24.1 (×2), 35.3. 44.3. 77.2, 126.3. 126.6 (×2). 126.7, 127.1 (×2). 127.5 (×2). 127.6 (×2), 128.0 (×2), 128.5 (×2), 129.5 (×2). 129.8, 130.4 (×2). 134.3, 134.4, 137.4. 137.7, 138.0, 138.2, 146.2: HRMS (EI, 70 eV) calcd for $C_{32}H_{32}O_3S$ (M⁻) 496.2072, found 496.2008.

(*E*)-2,2-Dimethyl-3-phenyl-1-propyl 4'-[2-(4-*tert*-butyl-phenyl)vinyl]-1,1'-biphenyl-4-sulfonate (6c) was prepared by the reaction of **5c** (0.833 g. 3.08 mmol). NaH (124 mg of 60% oil dispersion. 3.10 mmol). and **4a** (1.14 g. 2.80 mmol). The crude product was purified by recrystallization from *i*-PrOH to afford **6c** (1.10 g. 73%) as a fluffy white solid: mp 158-159 °C (uncorrected): TLC R_f 0.19 (CH_2Cl_2:*n*-hexane = 1:1): ¹H NMR (500 MHz. $CDCl_3$) δ 0.90 (s, 6H). 1.35 (s. 9H). 2.57 (s, 2H). 3.72 (s. 2H). 7.02 (dd, *J* = 7.80, 1.93 Hz, 2H). 7.12 (d. *J* = 16.30 Hz. 1H). 7.167.21 (m. 4H). 7.41 (d. *J* = 8.41 Hz. 2H). 7.49 (d. *J* = 8.41 Hz. 2H). 7.63 (s. 4H). 7.79 (d. *J* = 8.51 Hz. 2H). 7.99 (d. *J* = 8.51 Hz. 2H): ¹³C NMR (125 MHz. $CDCl_3$) δ 24.1 (×2), 31.3 (×3), 34.7, 35.3, 44.3, 77.2, 125.7 (×2). 126.3. 126.4 (×2). 126.9, 127.1 (×2), 127.5 (×2). 127.6 (×2). 127.9 (×2). 128.5 (×2). 129.7, 130.4 (×2). 134.3. 134.4. 137.4. 137.7, 138.2, 146.2, 151.2: HRMS (EI. 70 eV) calcd for $C_{35}H_{38}O_3S$ (M⁺) 538.2542, found 538.2527.

(*E*)-2,2-Dimethyl-3-phenyl-1-propyl 4'-[2-(2-methyl-biphenyl-3-yl)vinyl]-1,1'-biphenyl-4-sulfonate (6d) was prepared by the reaction of **5d** (0.536 g. 1.76 mmol). NaH

(72.0 mg of 60% oil dispersion. 1.80 mmol), and **4a** (0.654 g, 1.60 mmol). The crude product was purified by recrystallization to from *i*-PrOH afford **6d** (0.70 g, 76%) as a yellow solid: mp 143-145 °C (uncorrected): ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.90 (s, 6H), 2.33 (s, 3H), 2.57 (s, 2H), 3.72 (s, 2H), 7.02 (dd, J = 7.74, 1.95 Hz, 2H), 7.07 (d, J = 16.08 Hz, 1H), 7.16-7.21 (m, 4H), 7.28 (t, J = 7.64 Hz, 1H), 7.32 (d, J = 7.53 Hz, 2H), 7.36 (t, J = 7.44 Hz, 1H), 7.43 (t, J = 7.37 Hz, 2H), 7.52 (d, J = 16.08 Hz, 1H), 7.62 (d, J = 7.28 Hz, 1H), 7.65 (d, J = 8.76 Hz, 2H), 7.67 (d, J = 8.76 Hz, 2H), 7.79 (d, J = 8.42 Hz, 2H), 7.99 (d, J = 8.42 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 17.2, 24.1 (×2), 35.3, 44.3, 77.2, 125.0, 125.8, 126.3, 126.9, 127.3 (×2), 127.5 (×2), 127.7 (×2), 128.0 (×2), 128.1 (×2), 128.5, 128.5 (×2), 129.4 (×2), 129.7, 129.8, 130.4 (×2), 133.4, 134.5, 137.1, 137.4, 138.0, 138.3, 142.2, 143.0, 146.1; HRMS (EI, 70 eV) calcd for C$_{38}$H$_{36}$O$_3$S (M$^+$) 572.2385, found 572.2335.

(*E*)-2,2-Dimethyl-3-phenyl-1-propyl 4'-methoxy-3'-styryl-1,1'-biphenyl-4-sulfonate (6e) was prepared by the reaction of **5a** (0.259 g, 1.21 mmol). NaH (50.0 mg of 60% oil dispersion, 1.25 mmol), and **4b** (0.482 g, 1.10 mmol). The crude product was purified by recrystallization from *i*-PrOH:*n*-hexane (9:1) to afford **6e** (0.31 g, 55%) as a pale yellowish solid: mp 124-126 °C (uncorrected): TLC R_f 0.25 (CH$_2$Cl$_2$:*n*-hexane = 1:1): ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.90 (s, 6H), 2.57 (s, 2H), 3.72 (s, 2H), 3.96 (s, 3H), 7.02 (d, J = 8.59 Hz, 1H), 7.03 (dd, J = 7.86, 1.82 Hz, 2H), 7.16-7.20 (m, 3H), 7.20 (d, J = 16.45 Hz, 1H), 7.27 (t, J = 7.34 H, 1H), 7.37 (t, J = 7.66 Hz, 2H), 7.51 (d, J = 16.45 Hz, 1H), 7.51 (dd, J = 8.59, 2.35 Hz, 1H), 7.56 (d, J = 7.34 Hz, 2H), 7.78 (d, J = 8.50 Hz, 2H), 7.84 (d, J = 2.35 Hz, 1H), 7.98 (d, J = 8.50 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 24.1 (×2), 35.3, 44.3, 55.8, 77.2, 111.5, 123.0, 125.4, 126.3, 126.7 (×2), 127.2, 127.3 (×2), 127.5, 127.7, 128.0 (×2), 128.5 (×2), 128.7 (×2), 130.1, 130.5 (×2), 131.5, 133.9, 137.4, 137.6, 146.4, 157.6; HRMS (EI, 70 eV) calcd for C$_{32}$H$_{32}$O$_4$S (M+) 512.2021, found 512.2033.

(*E*)-2,2-Dimethyl-3-phenyl-1-propyl 4'-methoxy-3'-[2-(4-tolyl)vinyl]-1,1'-biphenyl-4-sulfonate (6f) was prepared by the reaction of **5b** (0.276 g, 1.21 mmol). NaH (50.0 mg of 60% oil dispersion, 1.25 mmol), and **4b** (0.428 g, 1.10 mmol). The crude product was purified by recrystallization to from *i*-PrOH:*n*-hexane (9:1) afford **6f** (0.250 g, 43%) as a white solid: mp 96-97 °C (uncorrected); TLC R_f 0.26 (CH$_2$Cl$_2$:*n*-hexane = 1:1): ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.90 (s, 6H), 2.37 (s, 3H), 2.57 (s, 2H), 3.72 (s, 2H), 3.95 (s, 3H), 7.00-7.03 (m, 3H), 7.16-7.20 (m, 6H), 7.46 (d, J = 16.46 Hz, 1H), 7.46 (d, J = 8.07 Hz, 2H), 7.50 (dd, J = 8.50, 2.31 Hz, 1H), 7.78 (d, J = 8.49 Hz, 2H), 7.84 (d, J = 2.31 Hz, 1H), 7.98 (d, J = 8.49 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 21.3, 24.1 (×2), 35.3, 44.3, 55.8, 77.2, 111.4, 121.9, 125.3, 126.3, 126.6 (×2), 127.3, 127.3 (×2), 127.4, 128.0 (×2), 128.5 (×2), 129.4 (×2), 130.0, 130.4 (×2), 131.5, 133.8, 134.8, 137.4, 137.6, 146.4, 157.5; HRMS (EI, 70 eV) calcd for C$_{33}$H$_{34}$O$_4$S (M+) 526.2178, found 526.2162.

(*E*)-2,2-Dimethyl-3-phenyl-1-propyl 3'-[2-(4-*tert*-butyl-phenyl)vinyl]-4'-methoxy-1,1'-biphenyl-4-sulfonate (6g)

was prepared by the reaction of **5c** (0.327 g, 1.21 mmol), NaH (50.0 mg of 60% oil dispersion, 1.25 mmol), and **4b** (0.482 g, 1.10 mmol). The crude product was purified by recrystallization to from *i*-PrOH:*n*-hexane (9:1) afford **6g** (0.260 g, 41%) as a fluffy white solid: mp 117-118 °C (uncorrected): TLC R_f 0.30 (CH$_2$Cl$_2$:*n*-hexane = 1:1): ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.90 (s, 6H), 1.34 (s, 9H), 2.57 (s, 2H), 3.72 (s, 2H), 3.95 (s, 3H), 7.00-7.04 (m, 3H), 7.16-7.21 (m, 4H), 7.40 (d, J = 8.40 Hz, 2H), 7.47 (d, J = 16.93 Hz, 1H), 7.49-7.51 (m, 3H), 7.78 (d, J = 8.49 Hz, 2H), 7.84 (d, J = 2.28 Hz, 1H), 7.98 (d, J = 8.49 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 24.1 (×2), 31.3 (×3), 34.7, 35.3, 44.3, 55.8, 77.2, 111.5, 122.2, 125.3, 125.6 (×2), 126.3, 126.4 (×2), 127.3, 127.3 (×2), 127.4, 128.0 (×2), 128.5 (×2), 129.8, 130.5 (×2), 131.5, 133.8, 134.9, 137.4, 146.5, 150.9, 157.5; HRMS (EI, 70 eV) calcd for C$_{36}$H$_{40}$O$_4$S (M$^-$) 568.2647, found 568.2636.

General Procedure for the Preparation of Unsymmetrical Stilbenes 8. To a stirred solution of **6** (0.100 mmol) and dppfNiCl$_2$ (3.42 mg, 0.00500 mmol) in dry THF (20 mL) were added the aryl Grignard reagents **7** (0.30 mmol) *via* a syringe at room temperature. This resulted in a color change from dark green to dark brown. The reaction mixture was heated under reflux for 6 h and then cooled to room temperature, and an additional 0.20 mmol of **7** was added. The reaction mixture was stirred under reflux for a further 6 h. The reaction mixture was poured into a separatory funnel containing CH$_2$Cl$_2$ and 1% aqueous HCl. The combined organic layer was washed with water and brine, dried over MgSO$_4$, and concentrated *in vacuo*. To the concentrated mixture was added MeOH to precipitate the product **8**. The suspension was filtered through a small pad of silica gel in a sintered glass filter. The solid remaining on the silica gel was washed with MeOH, collected by elution with CH$_2$Cl$_2$, and concentrated under reduced pressure. The resulting crude product was purified by column chromatography.

(*E*)-4-Styryl-[1,1';4',1"]terphenyl (8a) was prepared by the reaction of **6a** (48.3 mg, 0.100 mmol) with **7a** (1.0 M in THF, 0.30 mL, 0.30 mmol + 0.20 mL, 0.20 mmol) in the presence of dppfNiCl$_2$. The crude compound was purified by column chromatography (CH$_2$Cl$_2$) to give **8a** (13.6 mg, 41%) as a pale ivory solid: mp 315-317 °C (uncorrected): TLC R_f 0.57 (CH$_2$Cl$_2$:*n*-hexane = 1:1): ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.17 (s, 2H), 7.28 (t, J = 7.39 Hz, 1H), 7.35-7.39 (m, 3H), 7.47 (t, J = 7.57 Hz, 2H), 7.55 (d, J = 7.47 Hz, 2H), 7.61 (d, J = 8.21 Hz, 2H), 7.65 (d, J = 7.57 Hz, 2H), 7.66 (d, J = 8.21 Hz, 2H), 7.69 (d, J = 8.37 Hz, 2H), 7.72 (d, J = 8.37 Hz, 2H); HRMS (EI, 70 eV) calcd for C$_{26}$H$_{20}$ (M$^+$) 332.1565, found 332.1520.

(*E*)-4"-Methyl-4-styryl-[1,1';4',1"]terphenyl (8b) was prepared by the reaction of **6a** (48.3 mg, 0.100 mmol) with **7b** (1.0 M in Et$_2$O, 0.30 mL, 0.30 mmol + 0.20 mL, 0.20 mmol) in the presence of dppfNiCl$_2$. The crude compound was purified by column chromatography (CH$_2$Cl$_2$) to give **8b** (19.4 mg, 56%) as an ivory solid: mp 326-328 °C (uncorrected); TLC R_f 0.57 (CH$_2$Cl$_2$:*n*-hexane = 1:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.41 (s, 3H), 7.17 (s, 2H), 7.26-

7.29 (m, 3H), 7.38 (t, J = 7.65 Hz, 2H), 7.55 (d, J = 8.33 Hz, 2H), 7.55 (d, J = 8.06 Hz, 2H), 7.61 (d, J = 8.28 Hz, 2H), 7.66 (d, J = 8.28 Hz, 2H), 7.67 (d, J = 8.34 Hz, 2H), 7.70 (d, J = 8.34 Hz, 2H); HRMS (EI, 70 eV) calcd for $C_{27}H_{22}$ (M^+) 346.1721, found 346.1755.

(E)-4"-*tert*-Butyl-4-styryl-[1,1';4',1"]terphenyl (8c) was prepared by the reaction of **6a** (48.3 mg, 0.100 mmol) with **7c** (2.0 M in Et₂O, 0.15 mL, 0.30 mmol + 0.10 mL, 0.20 mmol) in the presence of dppfNiCl₂. The crude compound was purified by column chromatography (CH₂Cl₂) to give **8c** (19.8 mg, 51%) as a pale yellow solid: mp 279-283 °C (uncorrected); TLC R_f 0.61 (CH₂Cl₂:*n*-hexane = 1:1); ¹H NMR (500 MHz, CDCl₃) δ 1.38 (s, 9H), 7.17 (s, 2H), 7.28 (t, J = 7.45 Hz, 1H), 7.38 (t, J = 7.63 Hz, 2H), 7.49 (d, J = 8.38 Hz, 2H), 7.55 (d, J = 7.30 Hz, 2H), 7.60 (d, J = 8.38 Hz, 2H), 7.61 (d, J = 8.49 Hz, 2H), 7.66 (d, J = 8.49 Hz, 2H), 7.68 (d, J = 8.48 Hz, 2H), 7.70 (d, J = 8.48 Hz, 2H); HRMS (EI, 70 eV) calcd for $C_{30}H_{28}$ (M^+) 388.2191, found 388.2146.

(E)-4-[2-(4-Tolyl)vinyl]-[1,1';4',1"]terphenyl (8d) was prepared by the reaction of **6b** (49.7 mg, 0.100 mmol) with **7a** (1.0 M in THF, 0.30 mL, 0.30 mmol + 0.20 mL, 0.20 mmol) in the presence of dppfNiCl₂. The crude compound was purified by column chromatography (CH₂Cl₂) to give **8d** (21.8 mg, 63%) as a pale yellow solid: mp 313-316 °C (uncorrected); TLC R_f 0.58 (CH₂Cl₂:*n*-hexane = 1:1); ¹H NMR (500 MHz, CDCl₃) δ 2.37 (s, 3H), 7.11 (d, J = 16.38 Hz, 1H), 7.15 (d, J = 16.38 Hz, 1H), 7.19 (d, J = 7.81 Hz, 2H), 7.37 (t, J = 7.38 1H), 7.44 (d, J = 7.81 Hz, 2H), 7.47 (t, J = 7.45 Hz, 2H), 7.60 (d, J = 8.21 Hz, 2H), 7.65 (d, J = 7.91 Hz, 4H), 7.68 (d, J = 8.27 Hz, 2H), 7.71 (d, J = 8.27 Hz, 2H); HRMS (EI, 70 eV) calcd for $C_{27}H_{22}$ (M^+) 346.1712, found 346.1724.

(E)-4"-Methyl-4-[2-(4-tolyl)vinyl]-[1,1';4',1"]terphenyl (8e) was prepared by the reaction of **6b** (49.7 mg, 0.100 mmol) with **7b** (1.0 M in Et₂O, 0.30 mL, 0.30 mmol + 0.20 mL, 0.20 mmol) in the presence of dppfNiCl₂. The crude compound was purified by column chromatography (CH₂Cl₂) to give **8e** (24.9 mg, 69%) as a pale ivory solid: mp 326-330 °C (uncorrected); TLC R_f 0.59 (CH₂Cl₂:*n*-hexane = 1:1); ¹H NMR (500 MHz, CDCl₃) δ 2.36 (s, 3H), 2.37 (s, 3H), 7.11 (d, J = 16.41 Hz, 1H), 7.15 (d, J = 16.41 Hz, 1H), 7.19 (d, J = 7.94 Hz, 2H), 7.28 (d, J = 8.11 Hz, 2H), 7.44 (d, J = 7.94 Hz, 2H), 7.55 (d, J = 8.11 Hz, 2H), 7.59 (d, J = 8.17 Hz, 2H), 7.65 (d, J = 8.17 Hz, 2H), 7.67 (d, J = 8.59 Hz, 2H), 7.70 (d, J = 8.59 Hz, 2H); HRMS (EI, 70 eV) calcd for $C_{28}H_{24}$ (M^+) 360.1878, found 360.1840.

(E)-4"-*tert*-Butyl-4-[2-(4-tolyl)vinyl]-[1,1';4',1"]terphenyl (8f) was prepared by the reaction of **6b** (49.7 mg, 0.100 mmol) with **7c** (2.0 M in Et₂O, 0.15 mL, 0.30 mmol + 0.10 mL, 0.20 mmol) in the presence of dppfNiCl₂. The crude compound was purified by column chromatography (CH₂Cl₂) to give **8f** (27.0 mg, 67%) as a pale yellow solid: mp 299-301 °C (uncorrected); TLC R_f 0.61 (CH₂Cl₂:*n*-hexane = 1:1); ¹H NMR (500 MHz, CDCl₃) δ 1.38 (s, 9H), 2.37 (s, 3H), 7.11 (d, J = 16.48 Hz, 1H), 7.15 (d, J = 16.48 Hz, 1H), 7.19 (d, J = 7.79 Hz, 2H), 7.44 (d, J = 7.79 Hz, 2H), 7.49 (d, J = 8.17 Hz, 2H), 7.59 (d, J = 7.70 Hz, 4H), 7.65 (d, J = 8.11 Hz,

2H), 7.67 (d, J = 8.58 Hz, 2H), 7.70 (d, J = 8.58 Hz, 2H); HRMS (EI, 70 eV) calcd for $C_{31}H_{30}$ (M^+) 402.2348, found 402.2319.

(E)-4-[2-(4-*tert*-Butylphenyl)vinyl]-[1,1';4',1"]terphenyl (8g) was prepared by the reaction of **6c** (53.9 mg, 0.100 mmol) with **7a** (1.0 M in THF, 0.30 mL, 0.30 mmol + 0.20 mL, 0.20 mmol) in the presence of dppfNiCl₂. The crude compound was purified by column chromatography (CH₂Cl₂) to give **8g** (23.7 mg, 61%) as an ivory solid: mp 293-294 °C (uncorrected); TLC R_f 0.60 (CH₂Cl₂:*n*-hexane = 1:1); ¹H NMR (500 MHz, CDCl₃) δ 1.35 (s, 9H), 7.12 (d, J = 16.37 Hz, 1H), 7.17 (d, J = 16.37 Hz, 1H), 7.37 (t, J = 7.40 Hz, 1H), 7.40 (d, J = 8.27 Hz, 2H), 7.47 (t, J = 7.82 Hz, 2H), 7.49 (d, J = 8.27 Hz, 2H), 7.60 (d, J = 8.28 Hz, 2H), 7.65 (d, J = 8.25 Hz, 4H), 7.68 (d, J = 8.49 Hz, 2H), 7.71 (d, J = 8.49 Hz, 2H); HRMS (EI, 70 eV) calcd for $C_{30}H_{28}$ (M^-) 388.2191, found 388.2103.

(E)-4-[2-(4-*tert*-Butylphenyl)vinyl]-4"-methyl-[1,1';4',1"]-terphenyl (8h) was prepared by the reaction of **6c** (53.9 mg, 0.100 mmol) with **7b** (1.0 M in Et₂O, 0.30 mL, 0.30 mmol + 0.20 mL, 0.20 mmol) in the presence of dppfNiCl₂. The crude compound was purified by column chromatography (CH₂Cl₂) to give **8h** (29.8 mg, 74%) as a pale yellow solid: mp 310-315 °C (uncorrected); TLC R_f 0.64 (CH₂Cl₂:*n*-hexane = 1:1); ¹H NMR (500 MHz, CDCl₃) δ 1.35 (s, 9H), 2.41 (s, 3H), 7.12 (d, J = 16.31 Hz, 1H), 7.16 (d, J = 16.31 Hz, 1H), 7.27 (d, J = 8.08 Hz, 2H), 7.40 (d, J = 8.37 Hz, 2H), 7.49 (d, J = 8.37 Hz, 2H), 7.55 (d, J = 8.08 Hz, 2H), 7.60 (d, J = 8.31 Hz, 2H), 7.65 (d, J = 8.31 Hz, 2H), 7.66 (d, J = 8.60 Hz, 2H), 7.69 (d, J = 8.60 Hz, 2H); HRMS (EI, 70 eV) calcd for $C_{31}H_{30}$ (M^+) 402.2348, found 402.2371.

(E)-4-[2-(4-*tert*-Butylphenyl)vinyl]-4"-*tert*-butyl-[1,1';4', 1"]terphenyl (8i) was prepared by the reaction of **6c** (53.9 mg, 0.100 mmol) with **7c** (2.0 M in Et₂O, 0.15 mL, 0.30 mmol + 0.10 mL, 0.20 mmol) in the presence of dppfNiCl₂. The crude compound was purified by column chromatography (CH₂Cl₂) to give **8i** (32.9 mg, 0.0740 mmol, 74%) as a white solid: mp 307-310 °C (uncorrected); TLC R_f 0.62 (CH₂Cl₂:*n*-hexane = 1:1); ¹H NMR (500 MHz, CDCl₃) δ 1.35 (s, 9H), 1.38 (s, 9H), 7.12 (d, J = 16.34 Hz, 1H), 7.16 (d, J = 16.34 Hz, 1H), 7.40 (d, J = 8.41 Hz, 2H), 7.49 (d, J = 8.41 Hz, 2H), 7.49 (d, J = 8.45 Hz, 2H), 7.60 (d, J = 8.45 Hz, 2H), 7.60 (d, J = 8.40 Hz, 2H), 7.65 (d, J = 8.40 Hz, 2H), 7.67 (d, J = 8.43 Hz, 2H), 7.70 (d, J = 8.43 Hz, 2H); HRMS (EI, 70 eV) calcd for $C_{34}H_{36}$ (M^-) 444.2817, found 444.2829.

(E)-4-[2-(2-Methylbiphenyl-3-yl)vinyl]-4"-methyl-[1,1'; 4',1"]terphenyl (8j) was prepared by the reaction of **6d** (57.3 mg, 0.100 mmol) with **7b** (1.0 M in Et₂O, 0.30 mL, 0.30 mmol + 0.20 mL, 0.20 mmol) in the presence of dppfNiCl₂. The crude compound was purified by column chromatography (CH₂Cl₂) to give **8j** (23.2 mg, 53%) as a pale yellow solid: mp 307-310 °C (uncorrected); ¹H NMR (500 MHz, CDCl₃) δ 2.33 (s, 3H), 2.41 (s, 3H), 7.07 (d, J = 16.20 Hz, 1H), 7.19 (d, J = 7.50 Hz, 1H), 7.28 (d, J = 8.09 Hz, 2H), 7.28 (t, J = 7.51 Hz, 1H), 7.33 (dd, J = 8.24, 1.44 Hz, 2H), 7.36 (t, J = 7.42 Hz, 1H), 7.43 (t, J = 7.57 Hz, 2H), 7.48 (d, J = 16.20 Hz, 1H), 7.55 (d, J = 8.09 Hz, 2H), 7.63

(d, J = 8.20 Hz, 1H), 7.63 (d, J = 8.52 Hz, 2H), 7.67 (d, J = 8.52 Hz, 2H), 7.67 (d, J = 8.69 Hz, 2H), 7.70 (d, J = 8.69 Hz, 2H); HRMS (EI, 70 eV) calcd for $C_{34}H_{28}$ (M$^+$) 436.2191, found 436.2189.

(*E*)-4-Methoxy-4''-methyl-3-styryl-[1,1';4',1'']terphenyl (8k) was prepared by the reaction of **6e** (51.3 mg, 0.100 mmol) with **7b** (1.0 M in Et$_2$O, 0.30 mL, 0.30 mmol + 0.20 mL, 0.20 mmol) in the presence of dppfNiCl$_2$. The crude compound was purified by column chromatography (CH$_2$Cl$_2$) to give **8k** (24.1 mg, 64%) as a pale yellow solid: mp 211-214 °C (uncorrected); ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.41 (s, 3H), 3.95 (s, 3H), 6.99 (d, J = 8.51 Hz, 1H), 7.20 (d, J = 16.47 Hz, 1H), 7.24-7.28 (m, 3H), 7.36 (t, J = 7.62 Hz, 2H), 7.52 (dd, J = 8.51, 2.25 Hz, 1H), 7.53 (d, J = 16.47 Hz, 1H), 7.55 (d, J = 7.91 Hz, 2H), 7.57 (d, J = 7.13 Hz, 2H), 7.67 (s, 4H), 7.86 (d, J = 2.25 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 21.1, 55.8, 111.3, 123.5, 125.1, 126.6 (×2), 126.8, 126.9 (×2), 127.1 (×2), 127.2, 127.3 (×2), 127.5, 128.6 (×2), 129.5 (×2), 129.5, 133.4, 137.1, 137.9, 137.9, 137.9, 139.6, 156.6; HRMS (EI, 70 eV) calcd for $C_{28}H_{24}O$ (M$^+$) 376.1827, found 376.1815.

(*E*)-4-Methoxy-4''-methyl-3-[2-(4-tolyl)vinyl]-[1,1';4',1'']-terphenyl (8l) was prepared by the reaction of **6f** (52.7 mg, 0.100 mmol) with **7b** (1.0 M in Et$_2$O, 0.30 mL, 0.30 mmol + 0.20 mL, 0.20 mmol) in the presence of dppfNiCl$_2$. The crude compound was purified by column chromatography (CH$_2$Cl$_2$) to give **8l** (28.1 mg, 72%) as a pale yellow solid: mp 266-268 °C (uncorrected); ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.36 (s, 3H), 2.41 (s, 3H), 3.94 (s, 3H), 6.99 (d, J = 8.52 Hz, 1H), 7.17 (d, J = 8.00 Hz, 2H), 7.18 (d, J = 16.48 Hz, 1H), 7.27 (d, J = 8.07 Hz, 2H), 7.46 (d, J = 8.00 Hz, 2H), 7.48 (d, J = 16.48 Hz, 1H), 7.50 (dd, J = 8.52, 2.26 Hz, 1H), 7.55 (d, J = 8.07 Hz, 2H), 7.66 (s, 4H), 7.85 (d, J = 2.26 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 21.1, 21.3, 55.7, 111.3, 122.4, 125.0, 126.6 (×2), 126.9, 126.9 (×2), 127.0, 127.1 (×2), 127.3 (×2), 129.3 (×2), 129.5, 129.5 (×2), 133.4, 135.1, 137.1, 137.3, 137.9, 139.6, 139.6, 156.5; HRMS (EI, 70 eV) calcd for $C_{29}H_{26}O$ (M$^-$) 390.1984, found 390.2012.

(*E*)-4-Methoxy-4''-methyl-3-[2-(4-*tert*-butylphenyl)vinyl]-[1,1';4',1'']terphenyl (8m) was prepared by the reaction of **6g** (56.9 mg, 0.100 mmol) with **7b** (2.0 M in Et$_2$O, 0.15 mL, 0.30 mmol + 0.10 mL, 0.20 mmol) in the presence of dppfNiCl$_2$. The crude compound was purified by column chromatography (CH$_2$Cl$_2$) to give **8m** (32.9 mg, 76%) as a pale yellow solid: mp 239-241 °C (uncorrected); ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.34 (s, 9H), 2.41 (s, 3H), 3.93 (s, 3H), 6.98 (d, J = 8.54 Hz, 1H), 7.19 (d, J = 16.45 Hz, 1H), 7.27 (d, J = 8.08 Hz, 2H), 7.39 (d, J = 8.40 Hz, 2H), 7.49 (d, J = 16.45 Hz, 1H), 7.50 (d, J = 8.40 Hz, 2H), 7.50 (dd, J = 8.54, 2.25 Hz, 1H), 7.55 (d, J = 8.08 Hz, 2H), 7.67 (s, 4H), 7.85 (d, J = 2.25 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 21.1, 31.3 (×3), 34.6, 55.8, 111.3, 122.7, 125.0, 125.5 (×2), 126.4 (×2), 126.9 (×2), 127.0, 127.0, 127.1 (×2), 127.3 (×2), 129.3, 129.5 (×2), 133.4, 135.2, 137.1, 137.9, 139.6, 139.6, 150.6, 156.5; HRMS (EI, 70 eV) calcd for $C_{32}H_{32}O$ (M$^+$) 432.2453, found 432.2461.

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