An Efficient Route to 2,6-Disubstituted Styrenes via the Palladium-Catalyzed [4 + 2] Cyclodimerization of Conjugated Enynes

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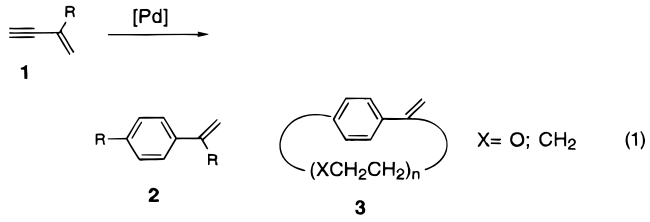
An efficient and general method for the synthesis of 2,6-disubstituted styrenes **5** via the palladium-catalyzed [4+2] homobenzannulation of conjugated enynes **4** was developed. In all cases, the reactions proceeded in *regiospecific* manner, affording the disubstituted styrenes, bearing various functional groups at the 2 and 6 positions of the benzene ring, as a single reaction product in good to excellent yields. Initial attempts at cross-cycloaddition of two different enynes indicated low degrees of *chemoselectivity* of this process. Accordingly, the cross-dimerization products **6** in all cases were accompanied with notable amounts of the *chemoisomeric* homodimers **5**.

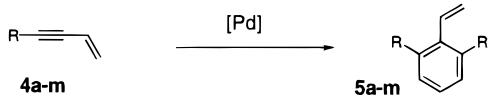
Styrene derivatives are of great importance for polymeric industry[1] and for synthetic organic chemistry.[2] Despite obvious potential significance of 2,6-disubstituted styrenes as monomers[3] and as substrates for various types of organic transformations,[4] only 2,6-dimethyl- and 2,6-dimethoxystyrene have been reported to date.[5] Furthermore, the methods for their preparation are lengthy, cumbersome, and not general in character.[5] Accordingly, an efficient and general method for the preparation of 2,6-disubstituted styrenes is exceedingly desired.[6] We recently reported effective methods for the preparation of α,para-disubstituted styrenes **2** and *exo*-methylene *p*-cyclophanes **3** via the *inter*-[7] and *intramolecular*[8] palladium-catalyzed homodimerization of 2-substituted conjugated enynes of type **1** (eq 1). Encouraged by the



(1)

successful preparation of styrene derivatives **2** via cycloaddition pathway[7,8] and motivated by the practical importance of 2,6-disubstituted styrenes, we attempted to apply the novel [4 + 2] benzannulation motif[9] for the synthesis of the title compounds.

We now wish to report a general, practically simple, and *regiospecific* method for the synthesis of a wide range of 2,6-disubstituted styrenes **5** via the palladium-catalyzed [4 + 2] cycloaddition reaction of 4-substituted enynes **4** (eq 2).



(2)

Results and Discussion

Homodimerization of 4-Substituted Enynes. During our study on dimerization of 1-substituted enyne **1**,[7]

(1) For a review, see: (a) *Styrene Polymers* in *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Moore, E. R., Ed.; Wiley-Interscience: New York, 1989; Vol. 16 and references therein. See also: (b) *Cationic Polymerizations: Mechanisms, Synthesis, and Applications*; Matyajaszewski, K., Ed.; Marcel Dekker: New York, 1996. For an earlier review, see: (c) Boundy, R. H.; Boyer, R. F. *Styrene, Its Polymers, Copolymers, and Derivatives*; Reinhold: New York, 1952. For an example of recent work, see: (d) Stranix, B. R.; Gao, J. P.; Barghi, R.; Salha, J. *J. Org. Chem.* **1997**, *62*, 8987 and references therein.

(2) See, for example: (a) Nomura, N.; Jin, J.; Park, H.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1998**, *120*, 459. (b) Kolis, S. P.; Chordia, M. D.; Liu, R.; Kopach, M. E.; Harman, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 2218. (c) Deb, S. K.; Maddux, T. M.; Yu, L. *J. Am. Chem. Soc.* **1997**, *119*, 9079. (d) Nzeru, A.; Ebdon, J. R.; Rimmer, S. *J. Am. Chem. Soc.* **1997**, *119*, 8928. (e) Galardon, E.; Roue, S.; Maux, P.; Simonneaux, G. *Tetrahedron Lett.* **1998**, *39*, 2333. (f) Bruckner, R.; Huisgen, R.; Schmid, J. *Tetrahedron Lett.* **1990**, *31*, 7129.

(3) For a review, see: (a) Boyer, R. F. In *Encyclopedia of Polymer Science and Technology*; Mark, H. F., Gaylord, N. G., Bikales, N. M., Eds.; Wiley-Interscience: New York, 1970; Vol. 13. (b) Ravve, A. *Principles of Polymer Chemistry*; Plenum Press: New York, 1995; and references therein. For earlier examples, see: (c) Lau, W. Y.; Burns, C. M. *Can. J. Chem.* **1969**, *47*, 2057. (d) Hopf, H.; Lochner, F. *Macromol. Chem.* **1965**, *84*, 261. (e) Korshak, V. V.; Matveeva, N. G. *Bull. Acad. Sci. USSR, Div. Chem. Sci. Engl. Transl.* **1953**, 547.

(4) (a) Hardinger, S. A.; Bayne, C.; Kantorowski, E.; McClellan, R.; Larres, L.; Nuesse, M.-A. *J. Org. Chem.* **1995**, *60*, 1104. (b) Kwok, T. J.; Wink, D. J. *Organometallics* **1993**, *12*, 1954. (c) Srinivasan, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2309. (d) Chisholm, M. H.; Hammond, C. E.; Ho, D.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7860. (e) Collman, J. P.; Hampton, P. D.; Brauman, J. I. *J. Am. Chem. Soc.* **1990**, *112*, 2986. (f) Crabtree, R. H.; Mellea, M. F.; Quirk, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 2913. (g) Lyons, A. L.; Turro, N. J. *J. Am. Chem. Soc.* **1978**, *100*, 3177. (h) Coutelle, H.; Huttel, R. *J. Organomet. Chem.* **1978**, *153*, 359.

(5) (a) Saa, J. M.; Martorell, G.; Garsia-Raso, A. *J. Org. Chem.* **1992**, *57*, 678. (b) Martorell, G.; Garsia-Raso, A.; Saa, J. M. *Tetrahedron Lett.* **1990**, *31*, 2357. (c) Schwartzman, L. H.; Corson, B. B. *J. Am. Chem. Soc.* **1954**, *76*, 781. (d) See also ref 4f.

(6) Very recently, an elegant method for the preparation of 2,6-disubstituted styrenes was reported; however, this method was restricted to the preparation of styrenes, which neccessarily possess an additional substituent at the β-position. Catelani, M.; Frignani, F.; Rangoni, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 119.

(7) Saito, S.; Salter, M. M.; Gevorgyan, V.; Tsuboya, N.; Tando, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3970.

(8) (a) Saito, S.; Tsuboya, N.; Yamamoto, Y. *J. Org. Chem.* **1997**, *62*, 5042. (b) Weibel, D.; Gevorgyan, V.; Yamamoto, Y. *J. Org. Chem.* **1998**, *63*, 1217.

(9) The preparation of substituted ethynylbenzenes via the palladium-catalyzed enyne−diyne cycloaddition reaction has been recently reported: (a) Gevorgyan, V.; Takeda, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 11313. (b) Gevorgyan, V.; Sadayori, N.; Yamamoto, Y. *Tetrahedron Lett.* **1997**, *38*, 8603. (c) Gevorgyan, V.; Quan, L. G.; Yamamoto, Y. *J. Org. Chem.* **1998**, *63*, 1244.

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Table 1. Optimization of the Catalyst System for Cyclodimerization of 4a[a]

entry	catalyst (mol %)	ligand (mol %)	method	time (h)	yield[b] (%)
1	$Pd(PPh_3)_4$ (5)	none	A	24	87
2	$Pd(PPh_3)_4$ (2)	none		24	traces
3	$Pd(PPh_3)_4$ (2)	$(o\text{-Tol})_3P$ (20)		15	51
4	$Pd(PPh_3)_4$ (1)	$(o\text{-Tol})_3P$ (10)	B	15	72
5	$Pd(PPh_3)_4$ (1)	COD (10)	C	8	80

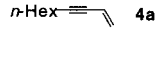
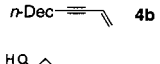
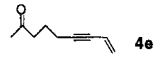
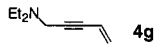
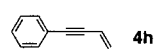
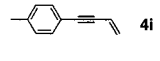
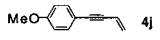
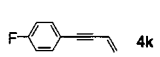
[a] All rections were conducted in Wheaton microreactors in THF (0.5 M) at 100 °C. [b] NMR yield using anisole as an internal standard.

we found that even prolonged heating of **4a** at 60 °C in toluene in the presence of 2 mol % of $Pd(PPh_3)_4$ (the best conditions that were found for dimerization of **1**) did not cause any notable transformation of the starting material. However, we found that in THF[10] at 100 °C in the presence of 5 mol % of $Pd(PPh_3)_4$ hexyl-substituted **4a** smoothly underwent a cyclodimerization reaction affording the desired 2,6-dialkylstyrene **5a** in 87% NMR yield (method A, Table 1, entry 1). Next, we attempted to decrease the amount of palladium catalyst. Thus, employment of 2 mol % of the catalyst produced only traces of **5a** (Table 1, entry 2), whereas combination of 2 mol % $Pd(PPh_3)_4$ with 20 mol % of additional $(o\text{-Tol})_3P$ ligand produced **5a** in moderate yield (Table 1, entry 3). Further diminishing of the quantity of palladium catalyst in combination with additional ligands gave even better results. Indeed, cylodimerization reactions of **4a** in the presence of 1 mol % of $Pd(PPh_3)_4$ (5-fold decrease vs ligand-free catalyst system) with 10 mol % of $(o\text{-Tol})_3P$ (method B, Table 1, entry 4) or with 10 mol % of COD (method C, Table 1, entry 5) afforded **5a** in 72 and 80% yields, respectively.

Encouraged by the successful cyclodimerization of **4a**, we attempted to generalize this methodology with other 4-substituted enynes under the conditions of optimized methods A−C (Table 2). Thus, among alkyl chain substituted enynes, the hexyl- (**4a**), decyl- (**4b**), (hydroxypropyl)- (**4c**), (methoxymethyl)- (**4f**), and (diethylamino)-methyl-substituted enynes (**4g**) reacted smoothly, producing the corresponding 2,6-dialkyl-substituted styrenes **5a**,**b**,**c**,**f**, and **g**, respectively, in excellent to quantitative yields (Table 2, entries 1−3, 6, and 7). Exceptionally low yields in the cases of enynes bearing chloro (**4d**) and keto (**4e**) functionalities in the side chain are not clearly understood. Among aryl- and heteroaryl-substituted enynes (**4h**−**m**), only the *p*-methoxyphenyl derivative (**4j**) gave a low yield of the corresponding styrene **5j** (entry 10). In all other cases, the reaction proceeded well to give phenyl- (**5h**), *p*-tolyl- (**5i**), *p*-fluorophenyl- (**5k**), 2-furyl- (**5l**), and 2-thienyl-substituted (**5m**) styrenes in good yields (Table 2, entries 8, 9, and 11−13). It should be mentioned that enynes bearing bulky substituents, such as *tert*-butyl- (**4n**), TMS- (**4o**), and naphthyl- (**4p**), did not undergo the cyclodimerization reaction at all, perhaps due to steric reasons.

Cross-Dimerization of 4-Substituted Enynes. Finally, we would like to disclose our initial attempts on cross-dimerization of enynes **4**. We investigated the cyclodimerization of hexyl-substituted **4a** in the presence of the second enynes **4h**,**f**,**n**,**o**, and **p** (Scheme 1, Table 3). Statistically, three combinations of enyne with enynophile are possible, which could produce the first homodimer **5a**, cross-dimer **6**, and the second homodimer

Table 2. Preparation of 2,6-Disubstituted Styrenes 5 via Cyclodimerization of 4-Substituted Enynes 4

entry	enyne **4**	catalyst system	time (h)	styrene **5**	yield (%)[a]
1	 **4a**	C	24	**5a**	86
2	 **4b**	C	10	**5b**	92
3	 **4c**	B	66	**5c**	81
4	**4d**	C	22	**5d**	30
5	 **4e**	A	72	**5e**	51
6	 **4f**	B	24	**5f**	100
7	 **4g**	B	24	**5g**	100
8	 **4h**	A	48	**5h**	71
9	**4i**	C	84	**5i**	71
10	 **4j**	B	96	**5j**	40
11	 **4k**	B	48	**5k**	80[b]
12	 **4l**	B	24	**5l**	69
13	**4m**	B	48	**5m**	81

[a] Isolated yield. [b] NMR yield using dibromomethane as an internal standard.

5 (Scheme 1). If we could find the matched combination of enyne−enynophile, employing two different enynes, we would be able to synthesize the cross-dimer **6** selectively (Scheme 1). Experiments demonstrated that, indeed, the cross-dimers **6a** and **6b** could be obtained through the mixed dimerization of **4a** with **4h** and **4f** (Table 3). However, the cross-dimers **6a**,**b** were contaminated with comparable amounts of the first homodimer (**5a**) (13 and 5%) and equal (23%) or even overwhelming amounts (80%) of the second homodimers (**5h**,**f**) (Table 3, entries 1 and 2). Bulky enynes **4n** and **4o** did not participate in the cross-dimerization at all (Table 3, entries 3 and 4). It was rather surprising to find that naphthyl enyne **4p**, which was nonreactive in the homodimerization reaction, produced 23% of cross-dimer **6e**, along with 25% of the first homodimer **5a** (Table 3, entry 5).

(10) Analogous *homodimerization* of **4** proceeded at 100 °C in toluene as well; however, the yields of **5** in these cases were somewhat lower.

Scheme 1

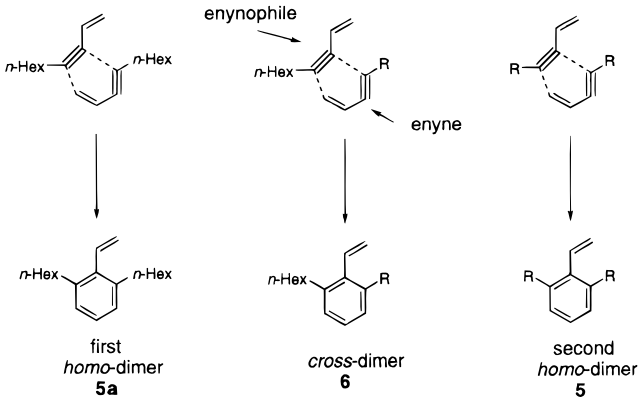
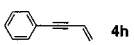
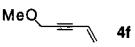
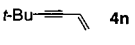
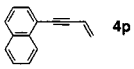


Table 3. Cross-Dimerization of 4a with Second Enyne 4[a]

entry	second enyne **4**	yield (%)[b] first *homo*-dimer **5a**	*cross*-dimer **6**	second *homo*-dimer **5**
1	 **4h**	13	19 (**6a**)	23 (**5b**)
2[c]	 **4f**	5	15 (**6b**)	80 (**5f**)
3[c]	 **4n**	36	0 (**6c**)	0 (**5n**)
4	 **4o**	0	0 (**6d**)	0 (**5o**)
5	 **4p**	25	23 (**6e**)	0 (**5p**)

[a] Method B was employed. [b] Isolated yield. [c] NMR yield using dibromomethane as an internal standard.

Conclusion

A novel efficient and general methodology for the preparation of 2,6-disubstituted styrenes **5** via palladium-catalyzed enyne−enyne cyclodimerization methodology was developed. Accordingly, we are now in a position to synthesize a wide variety of potentially attractive and scarce 2,6-disubstituted styrenes **5** in one step from easily available and cheap conjugated enynes **4**.

Experimental Section

General Information. All solvents were purified and dried before use according to the standard procedures. Reactions were performed under an argon atmosphere in oven-dried glassware. All starting materials were prepared according to the described methods.[11]

Preparation of 2,6-Disubstituted Styrenes 5 (General Procedure). Enynes **4** (1.0 mmol) were added at room temperature to a solution of $Pd(PPh_3)_4$ and ligand (according to methods A−C, see text) in THF (2.0 mL) in a 5 mL Wheaton microreactor under an argon atmosphere. After being stirred at 100 °C for the time indicated in the Table 2, THF was evaporated off, hexane was added, and the resulting mixture was filtered through silica gel. Purification by silica gel column chromatography using hexanes−ethyl acetate as an eluent gave styrenes **5** in 30−100% yields.

5a: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.13−7.00 (m, 3H), 6.74 (dd, J = 17.8,11.5 Hz, 1H), 5.49 (dd, J = 11.5, 2.4 Hz, 1H), 5.20 (dd, J = 18.0, 2.4 Hz, 1H), 2.60 (m, 4H), 1.55−1.47 (m, 4H), 1.29 (m, 12H), 0.88 (m, 6H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 140.7, 137.5, 135.0, 126.7, 126.5, 119.2, 33.8, 31.7, 31.1, 29.4, 22.6, 14.1; IR (neat) 1632, 1578, 760 cm^{-1}; HRMS calcd for $C_{20}H_{32}$ 272.2501, found 272.2500. Anal. Calcd for $C_{20}H_{32}$: C, 88.16; H, 11.84. Found: C, 88.44; H, 11.67.

5b: ^{1}H NMR (270 MHz, CDCl3) δ 7.18−7.05 (m, 3H), 6.79 (dd, J = 17.8, 11.5 Hz, 1H), 5.53 (dd, J = 11.7, 2.2 Hz, 1H), 5.26 (dd, J = 17.9, 2.2 Hz, 1H), 2.65 (m, 4H), 1.57 (m, 4H), 1.31 (m, 28H), 0.93 (t, J = 6.8 Hz, 6H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 140.7, 137.5, 135.0, 126.7, 126.5, 119.2, 33.8, 31.9, 31.2, 29.8, 29.7, 29.6, 29.5, 29.4, 22.7, 14.1; IR (KBr) 1655, 1560, 764 cm^{-1}; HRMS calcd for $C_{28}H_{48}$ 384.3756, found 384.3753. Anal. Calcd for $C_{28}H_{48}$: C, 87.42; H, 12.58. Found: C, 87.77; H, 12.53.

5c: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.17−7.05 (m, 3H), 6.78 (dd, J = 18.0, 11.4 Hz, 1H), 5.54 (dd, J = 11.4, 2.2 Hz, 1H), 5.25 (dd, J = 18.0, 2.2 Hz, 1H), 3.66 (t, J =6.4 Hz, 4H), 2.72 (m, 4H), 1.82 (m, 4H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 139.7, 137.7, 134.9, 127.0, 126.8, 119.8, 62.5, 33.8, 29.9; IR (neat) 3170, 1632, 1593, 1578, 760 cm^{-1}; HRMS calcd for $C_{14}H_{20}O_2$ 220.1461, found 220.1449. Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.11; H, 8.98.

5d: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.18−7.05 (m, 3H), 6.75 (dd, J = 17.9, 11.4 Hz, 1H), 5.56 (dd, J = 11.4, 2.0 Hz, 1H), 5.24 (dd, J = 17.9, 2.0 Hz, 1H), 3.52 (t, J =6.5 Hz, 4H), 2.79 (m, 4H), 2.05−1.95 (m, 4H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 138.8, 137.9, 134.4, 127.2, 127.1, 120.2, 44.6, 33.5, 30.8; IR (neat) 1632, 1578, 1541, 1508, 762 cm^{-1}; HRMS calcd for $C_{14}H_{18}Cl_2$ 256.0785, found 256.0786. Anal. Calcd for $C_{14}H_{18}Cl_2$: C, 65.38; H, 7.05. Found: C, 65.653; H, 7.234.

5e: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.15−7.01 (m, 3H), 6.74 (dd, J = 17.9, 11.4 Hz, 1H), 5.52 (dd, J = 11.4, 2.0 Hz, 1H), 5.22 (dd, J = 17.9, 2.0 Hz, 1H), 2.63 (m, 4H), 2.43 (t, J = 7.4 Hz, 4H), 2.11 (s, 6H), 1.82 (quint, J = 7.6 Hz, 4H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 208.5, 139.3, 137.5, 134.5, 126.7 (×2), 119.6, 43.0, 32.6, 29.6, 24.6; IR (neat) 1713, 1632, 1576, 764 cm^{-1}; HRMS calcd for $C_{18}H_{24}O_2$ 272.1774, found 272.1767.

5f: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39−7.24 (m, 3H), 6.82 (dd, J = 17.8, 11.6 Hz, 1H), 5.57 (dd, J = 11.5, 2.0 Hz, 1H), 5.37 (dd, J = 17.8, 2.1 Hz, 1H), 4.46 (s, 4H), 3.39 (s, 6H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 137.6, 135.7, 132.8, 128.2, 126.9, 120.6, 120.6, 72.7, 58.0; IR (neat) 1632, 1450, 768 cm^{-1}; HRMS calcd for $C_{12}H_{16}O_2$ 192.1149, found 192.1150.

5g: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39−7.16 (m, 3H), 6.92 (dd, J = 17.9, 11.5 Hz, 1H), 5.49 (dd, J = 11.5, 2.2 Hz, 1H), 5.21 (dd, J = 17.9, 2.2 Hz, 1H), 3.55 (s, 4H), 2.49 (q, J = 7.1 Hz, 8H), 1.00 (t, J = 7.1 Hz, 12H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 138.7, 137.6, 134.7, 127.7, 126.2, 119.3, 55.4, 46.8, 11.8; IR (neat) 1630, 1454, 768 cm^{-1}.

5h: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.41−7.25 (m, 13H), 6.46 (dd, J = 17.9, 11.7 Hz, 1H), 5.04 (dd, J = 11.5, 1.6 Hz, 1H), 4.69 (dd, J = 17.9, 1.6 Hz, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 142.2, 141.5, 134.8, 134.6, 129.8, 129.7, 127.9, 126.7, 126.6, 121.4; IR (KBr) 1628, 1599, 1495, 1456, 1441, 761 cm^{-1}; HRMS calcd for $C_{20}H_{16}$ 256.1251, found 256.1253. Anal. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.62; H, 6.21.

5i: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.32−7.15 (m, 11H), 6.47 (dd, J = 18.0, 11.4 Hz, 1H), 5.04 (dd, J = 11.7, 1.8 Hz, 1H), 4.72 (dd, J = 18.0, 1.8 Hz, 1H), 2.37 (s, 6H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 141.5, 139.3, 136.2, 134.9, 134.8, 129.7, 129.6, 128.6, 126.6, 121.1, 21.1; IR (KBr) 1626, 1560, 1514, 766 cm^{-1}; HRMS calcd for $C_{22}H_{20}$ 284.1564, found 248.158. Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.90; H, 7.19.

5j: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.30−6.86 (m, 11H), 6.47 (dd, J = 17.9, 11.6 Hz, 1H), 5.05 (dd, J = 11.6, 1.8 Hz, 1H), 4.72 (dd, J = 17.9, 1.8 Hz, 1H), 3.80 (s, 6H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 158.4, 141.1, 134.9, 134.8, 134.5, 130.8, 129.4, 126.6, 120.9, 113.3, 55.1; IR (KBr) 1630, 1609, 1576, 1512, 781 cm^{-1}; HRMS calcd for $C_{22}H_{20}O_2$ 316.1462, found 316.1484. Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.81; H, 6.46.

5k: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.35−7.01 (m, 11H), 6.40 (dd, J = 17.9,11.5 Hz, 1H), 5.08 (dd, J = 11.5, 1.6 Hz, 1H), 4.69 (dd, J = 17.9, 1.6 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 162.1, 140.8, 138.1, 135.3, 134.6, 131.6, 130.0, 127.0, 121.9, 115.0; IR (KBr) 1605, 1508, 772 cm^{-1}; HRMS calcd for $C_{20}H_{14}F_2$

(11) Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, 1988.

292.1062, found 292.1061. Anal. Calcd for $C_{20}H_{14}F_2$: C, 82.17; H, 4.83. Found: C, 82.09; H, 5.03.

5l: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.63−7.31 (m, 5H), 6.92 (dd, J = 17.9, 11.5 Hz, 1H), 6.57−6.42 (m, 4H), 5.37 (dd, J = 11.5, 1.6 Hz, 1H), 5.09 (dd, J = 17.9, 1.6 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 153.0, 141.6, 135.4, 134.5, 130.5, 127.7, 127.1, 119.9, 111.1, 109.8; IR (neat) 1632, 1499, 735 cm^{-1}; HRMS calcd for $C_{16}H_{12}O_2$ 236.0836, found 236.0839. Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.18; H, 5.30.

5m: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.43−7.02 (m, 9H), 6.71 (dd, J = 17.9, 11.5 Hz, 1H), 5.25 (dd, J = 11.5, 1.6 Hz, 1H), 5.06 (dd, J = 17.9, 1.6 Hz, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 142.9, 136.7, 134.4, 134.1, 130.8, 127.4, 126.9, 126.7, 125.4, 121.6; IR (neat) 1628, 1458, 760 cm^{-1}; HRMS calcd for $C_{16}H_{12}S_2$ 268.0380, found 268.0380. Anal. Calcd for $C_{16}H_{12}S_2$: C, 71.60; H, 4.50; S, 23.89. Found: C, 71.47; H, 4.75; S, 23.98.

6a: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.37−7.10 (m, 8H), 6.63 (dd, J = 17.9, 11.5 Hz, 1H), 5.27 (dd, J = 11.5, 2.0 Hz, 1H), 4.98 (dd, J = 17.8, 1.9 Hz, 1H), 2.71 (m, 2H), 1.63−1.27 (m, 8H), 0.89 (m, 3H); HRMS calcd for $C_{20}H_{24}$ 264.1877, found 64.1881.

6b: ^{1}H NMR (500 MHz, acetone-d_6) δ 7.26−7.13 (m, 3H), 6.86 (dd, J = 17.9, 11.5 Hz, 1H), 5.52 (dd, J = 11.5, 2.2 Hz, 1H), 5.30 (dd, J = 17.9, 2.9 Hz, 1H), 4.39 (s, 2H), 3.32 (s, 3H), 2.63 (m, 2H), 1.55−1.29 (m, 8H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125.8 MHz, acetone-d_6) δ 141.4, 138.1, 136.9, 134.9, 129.2, 127.5, 127.2, 120.2, 73.6, 58.0, 34.1, 32.4, 31.7, 29.7, 23.2, 14.3; HRMS calcd for $C_{16}H_{24}O$ 232.1826, found 232.1801.

6e: ^{1}H NMR (270 MHz, CDCl3) δ 7.88−7.10 (m, 10H), 6.48 (dd, J = 17.9, 11.5 Hz, 1H), 4.93 (dd, J = 11.5, 1.8 Hz, 1H), 4.83 (dd, J = 17.8, 1.9 Hz, 1H), 2.75 (m, 2H), 1.68−1.29 (m, 8H), 0.90 (t, J = 6.9 Hz, 3H).

Supporting Information Available: ^{1}H NMR spectra of stryrenes **5e**−**g** and **6a,b,e** (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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