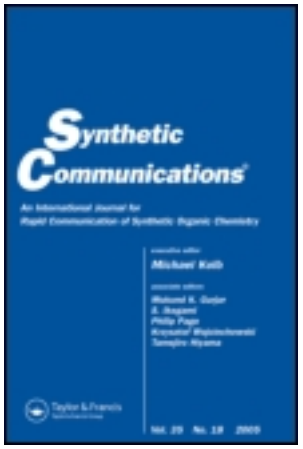

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H_2SO_4-Promoted Synthesis of (E)-Stilbenes from Substituted Phenylacetones and Substituted Benzaldehydes Through Tandem Aldol-Grob Reaction

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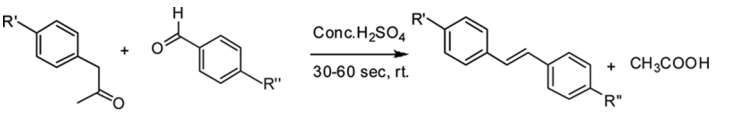
H_2SO_4-PROMOTED SYNTHESIS OF (*E*)-STILBENES FROM SUBSTITUTED PHENYLACETONES AND SUBSTITUTED BENZALDEHYDES THROUGH TANDEM ALDOL–GROB REACTION

T. Narender, K. Papi Reddy, and Sriniwas Tiwari
Medicinal and Process Chemistry Division, Central Drug Research Institute, Lucknow, India

GRAPHICAL ABSTRACT



Abstract *Stilbene derivates (stilbenoids) are present in plants and show a wide range of biological activities and potential therapeutic value. In continuation of our natural product synthesis program, an efficient, simple, and practical method has been developed to regioselectively synthesize* (E)*-stilbenes using* H_2SO_4 *as a catalyst in a short time (30–60 s) at room temperature in good to excellent yields.*

Keywords (*E*)-Stilbenes; H_2SO_4; phenylacetones; 1-phenylpropan-2-one

INTRODUCTION

Stilbene derivates (stilbenoids) are present in plants and show a wide range of biological activities and potential therapeutic value (Fig. 1).[1] For example, resveratrol exhibits a variety of useful bioactivities including cancer chemopreventive, antiplatelet aggregation, antioxidative, antibacterial, anti-inflammatory, and antidyslipidemic activities.[2] Pterostilbene acts as an effective PPAR-α agonist[2b] and hypolipidemic agent, and in vivo studies demonstrated that it also possesses lipid- and glucose-lowering effects. Pinosylvin is a constituent of heartwood of pine and exhibits antifungal and antibacterial activity.[3] Piceatannol is found in red wine and shows anti-inflammatory, immunomodulatory, and antiproliferative activities.[4] The *cis* and *trans* isomers of combretastain A4 are reported to have antitumor

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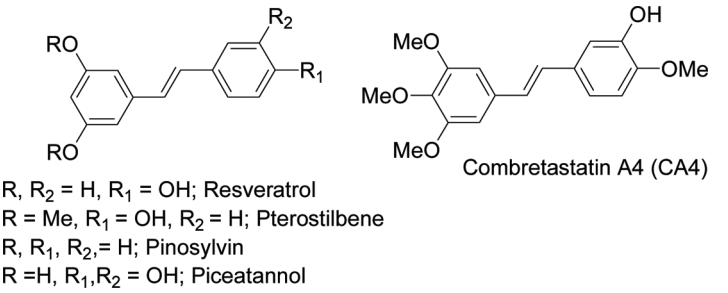
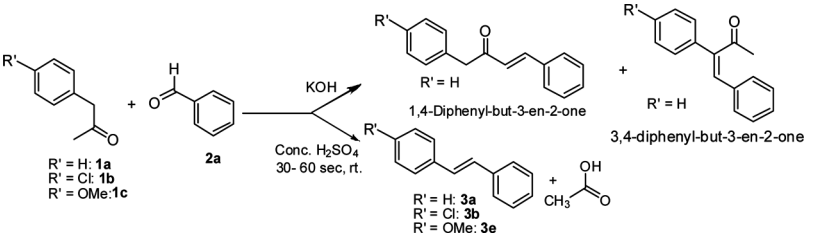


Figure 1. Biologically active stilbene derivatives.

activity[5] (Fig. 1). Some of the synthetic stilbenes are used as optical brighteners,[6] phosphors,[7] and scintillators.[8]

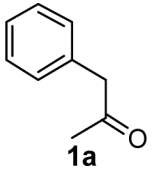
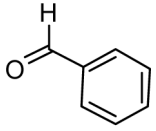
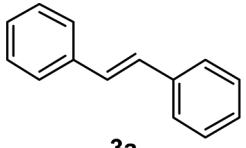
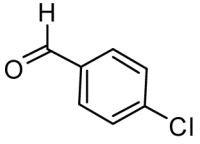
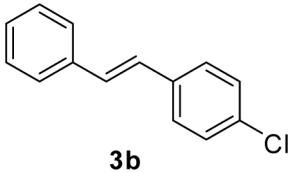
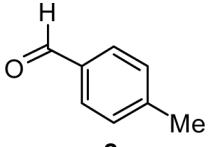
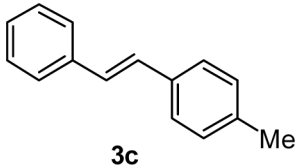
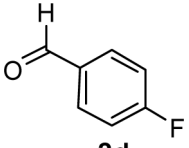
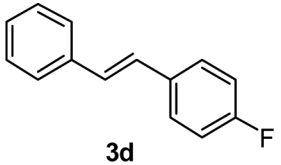
Several methods are available for the synthesis of stilbenes.[9–27] The currently available methods for the synthesis of stilbenes have some limitations, such as (i) the need for multistep synthesis,[27] (ii) the use of toxic metal complexes such as Pd-NHC complexes,[15] $[Pd(O_2CCF_3]$, $[PdCl_2(PPh_3)]_2$, and $[NiCl_2\ (PPh_3)]$,[20] (iii) the requirement to prepare special synthons such as organozinc arylhalides,[20] aromatic boronic acids, aryl or vinyl tellurides, aryl or vinyl trifluoroborate salts,[16] (iv) the lack of stereoselectivity (*cis* and *trans* isomers),[27] (v) long reaction times,[15,20,21] and (vi) harsh reaction conditions.[10,16] The development of new and simple methods to form such bonds by procedures devoid of these disadvantages is still a challenge for organic chemists.[28] Herein we show that (*E*)-stilbenes can be easily synthesized by the reaction of 1-phenylpropan-2-one (**1a**), its derivative 1-*p*-chlorophenylpropan-2-one (**1b**), and 1-*p*-methoxyphenylpropan-2-one (**1c**) with aryl aldehydes **2a–2h** in the presence of H_2SO_4 (Scheme 1, Table 1).

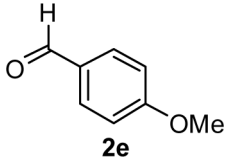
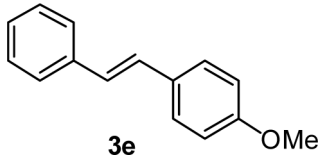
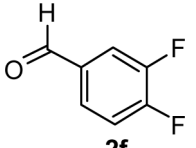
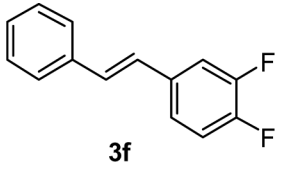
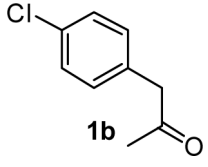
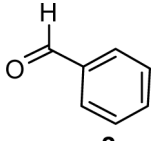
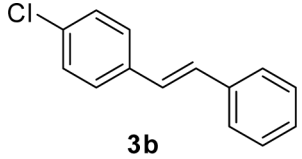
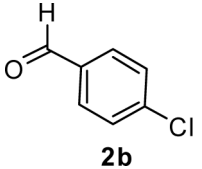
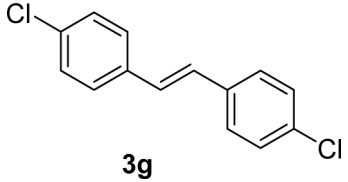
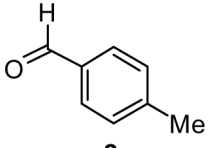
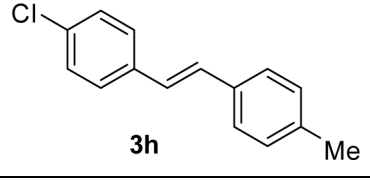
In 1890, Miller and Rohde described a reaction between 1-phenylpropan-2-one (**1a**) and benzaldehyde (**2a**) using sulfuric acid and water (H_2SO_4-H_2O, 3:1).[29] However, so far the synthetic potential and the generalizability with respect to the aldehyde and ketone in the synthesis of stilbenes has never been explored. To investigate the scope and limitations of H_2SO_4 as a catalyst for the synthesis of (*E*)-stilbenes, various aromatic aldehydes **2a–2h**, on the one hand, and 1-phenylpropan-2-one (**1a**), 1-*p*-chlorophenyl propan-2-one (**1b**), and 1-*p*-methoxyphenylpropan-2-one (**1c**), on the other hand, were utilized as substrates (Scheme 1). The results are summarized in Table 1.



Scheme 1. Synthesis of (*E*)-stilbene derivatives **3a, 3b,** and **3e** using H_2SO_4.

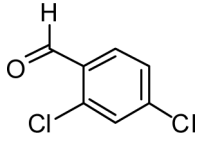
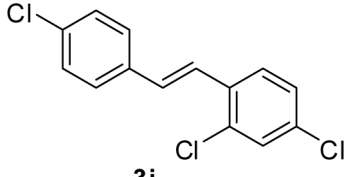
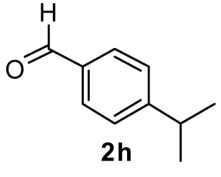
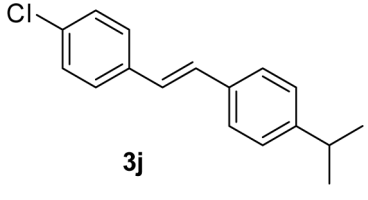
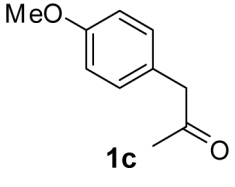
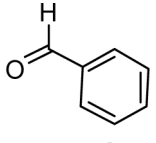
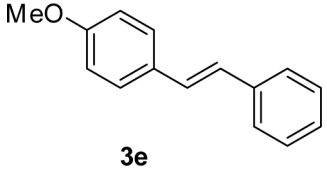
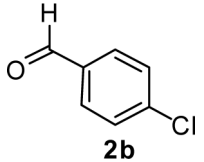
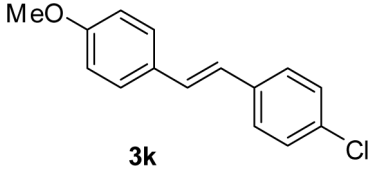
Table 1. Synthesis of (*E*)-stilbene derivatives **3a–3n** using H_2SO_4

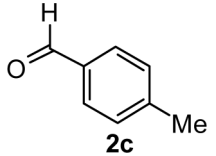
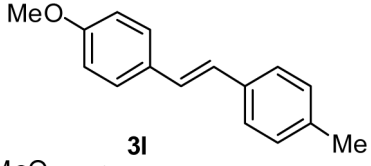
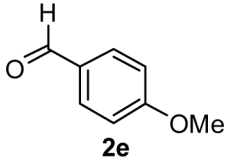
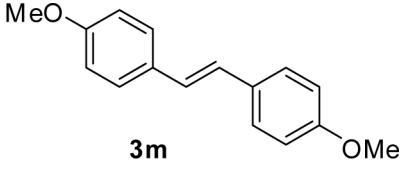
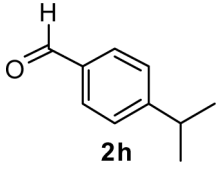
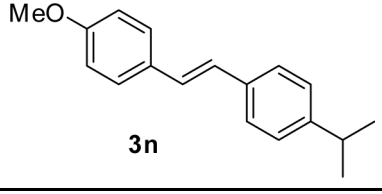
Entry	Ketone	Aldehyde	Product	Yields[a] (%)
1	 **1a**	 **2a**	 **3a**	58
2	**1a**	 **2b**	 **3b**	89
3	**1a**	 **2c**	 **3c**	62
4	**1a**	 **2d**	 **3d**	76

5	**1a**	 **2e**	 **3e**	32
6	**1a**	 **2f**	 **3f**	72
7	 **1b**	 **2a**	 **3b**	86
8	**1b**	 **2b**	 **3g**	96
9	**1b**	 **2c**	 **3h**	89

(*Continued*)

Table 1. Continued

Entry	Ketone	Aldehyde	Product	Yields[a] (%)
10	**1b**	 **2g**	 **3i**	67
11	**1b**	 **2h**	 **3j**	87
12	 **1c**	 **2a**	 **3e**	26
13	**1c**	 **2b**	 **3k**	35

14	**1c**	 **2c**	 **3l**	48
15	**1c**	 **2e**	 **3m**	10
16	**1c**	 **2h**	 **3n**	49

[a]Isolated yields.

RESULTS AND DISCUSSION

The regioselective reaction between 1-phenylpropan-2-one (**1a**) and benzaldehyde (**2a**) in the presence of H_2SO_4 resulted in the formation of (*E*)-stilbene (**3a**) stereoselectively in a short time (30–60 s). Further exploration with various substituted aromatic aldehydes **2b–2f** also provided the (*E*)-stilbenes **3b–3f**. To study the reaction conditions, we carried out the reaction between 1-*p*-chlorophenylpropan-2-one (**1b**) and substituted benzaldehydes **2a–2c** and **2 g–2h**, which provided the (*E*)-stilbenes **3b** and **3g–3j** in excellent yields. To demonstrate the wider applicability of this reaction, we carried out reactions between 1-*p*-methoxyphenylpropan-2-one (**1c**) and substituted benzaldehydes **2a–2c, 2e,** and **2h**, which also afforded the (*E*)-stilbenes **3e** and **3k–3n** exclusively in poor yields (Table 1). It is important to note that in the presence of an activating group (OMe) on ketone, yields were poor, whereas in the presence of a deactivating group (Cl) on ketone, yields were excellent. The *trans* nature of the double bond of synthesized stilbenes was confirmed by their coupling constants ($J = \sim 16$ Hz) in the ^{1}H NMR spectra,[30] and we did not observe their respective *cis* isomers (*cis*-stilbenes) during our isolation process.

It is noteworthy to mention here that under basic conditions (KOH) the reaction between 1-phenylpropan-2-one (**1a**) and benzaldehyde (**2a**) resulted in the synthesis of a mixture of 1,4-diphenyl-but-3-en-2-one and 3,4-diphenyl-but-3-en-2-one in our own studies as described by Southwick and coworkers[30] (Scheme 1). The reaction mechanism appears to be tandem aldol–Grob reaction sequence (Fig. 2).[31] The rapid reaction at room temperature with a catalytic amount of H_2SO_4 in our studies might be due to presence of benzylic hydrogens adjacent to ketones **1a–1c**.

In summary, we described an efficient, simple, and practical method for the synthesis of (*E*)-stilbenes from 1-phenylpropan-2-one (**1a**), its derivatives 1-*p*-chlorophenylpropan-2-one (**1b**), and 1-*p*-methoxyphenylpropan-2-one (**1c**) with aromatic aldehydes **2a–2h** in the presence of H_2SO_4 in good to excellent yields. The advantages of this method are the following: the reaction proceeds regioselectively to provide stereoselective (*E*)-stilbenes, it uses a simple experimental procedure

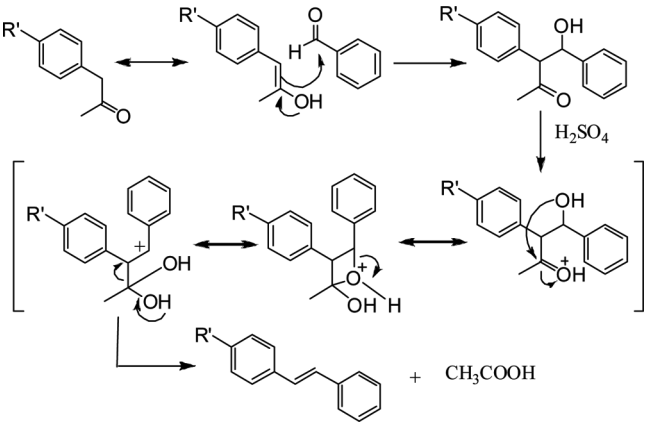


Figure 2. Tandem aldol–Grob reaction sequence in the formation of stilbenes.

within a short reaction time (30–60 s) using mild reaction conditions (room temperature), it is a solvent-free reaction in the case of at least one liquid reactant, and catalyst is inexpensive. This method might also be useful for the synthesis of diphenyl-substituted polyenes. Our reaction avoids the use of toxic metal complexes, multistep synthesis, preparation of special synthons, long reaction times and harsh reaction conditions.

EXPERIMENTAL

Infrared (IR) spectra were recorded on a Perkin-Elmer AC-1 spectrometer. ^{1}H NMR spectra were run on Bruker Advance DPX 200 and 300 MHz in $CDCl_3$; ^{13}C NMR spectra were recorded at 75 MHz and 50 MHz in $CDCl_3$. Chemical shifts are reported as values in parts per million (ppm) relative to $CHCl_3$ (7.26) in $CDCl_3$, and tetramethylsilane (TMS) was used as internal standard. Electrospray ionization (ESI) mass spectra were recorded on a Jeol SX 102/DA-6000 instrument. Chromatography was executed with silica gel (60–120 mesh) using mixtures of ethyl acetate and hexane as eluants. Ethyl acetate and hexane were dried and purified by distillation prior to use.

Representative Procedure for the Preparation of (E)-1-Chloro-4-(4-isopropylstyryl)benzene (3j)

Concentrated H_2SO_4 (three drops by syringe) was added gradually to a stirred solution of 1-*p*-chlorophenylpropan-2-one (**1b**) (200 mg, 1.5 mmol) and isopropylbenzaldehyde (**2h**) (210 mg, 1.4 mmol) at room temperature. The resultant solution was stirred for 30–60 s. After dilution with ethyl acetate (100 mL), the solution was washed with water (3×30 mL) to decompose the H_2SO_4 complex. The organic solution obtained after extraction was dried over anhydrous Na_2SO_4 and filtered, and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica-gel column chromatography using hexane–ethyl acetate to afford the desired (*E*)-1-chloro-4-(4-isopropylstyryl)benzene (**3j**) (264 mg, 87%).

Data

(*E*)-1-Chloro-4-(4-isopropylstyryl)benzene (3j). IR (KBr) 2925, 2857, 1460, 1216, 965, 763 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, $J = 8.3$ Hz 2H), 7.46 (d, $J = 8.5$ Hz 2H), 7.35 (d, $J = 8.5$ Hz, 2H), 7.28 (d, $J = 8.3$ Hz, 2H), 7.12 (d, $J = 16.4$ Hz, 1H), 7.04 (d, $J = 16.4$ Hz, 1H), 2.97 (m, 1H), 1.32 (d, $J = 6.9$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8, 136.0, 134.6, 132.9, 129.4, 128.9 (2C), 127.7 (2C), 126.9 (2C), 126.7 (2C), 126.6, 34.1, 23.9.

(*E*)-1,2-Diphenylethene (3a). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.62–7.58 (m, 4H), 7.48–7.3 (m, 6H), 7.20 (brs, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.4, 128.8, 128.7 (2C), 127.6, 126.5.

(*E*)-1-Chloro-4-styrylbenzene (3b). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.55–7.45 (m, 5H), 7.43–7.25 (m, 4H), 7.08 (brs, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2, 136.3, 133.6, 129.7, 129.3 (2C), 129.2 (2C), 128.3, 128.1 (2C), 127.8, 126.9 (2C).

(*E*)-1-Methyl-4-styrylbenzene (3c). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.56–7.53 (m, 2H), 7.48–7.39 (m, 5H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.12 (brs, 2H), 2.40 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.8, 137.7, 134.8, 129.6 (2C), 128.9 (3C), 127.9, 127.6, 126.7 (2C), 126.6 (2C), 22.4 (3H).

(*E*)-1-Fluoro-4-styrylbenzene (3d). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.58–7.50 (m, 4H), 7.50–7.41 (m, 2H), 7.38–7.32 (m, 1H), 7.18–7.00 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$), 165.3 (C-1),* 160.4 (C-1),* 137.6, 134.0 (C-4),* 133.9 (C-4),* 129.2 (2C), 129.0 (C-7),* 128.9 (C-7),* 128.5 (C-3/5),* 128.4 (C-3/5),* 128.1 (C-2/6),* 127.9 (C-2/6),* 126.9 (2C), 116.3, 115.9. Asterisks (*) denote splitting due to long-range coupling with fluorine substitution on the phenyl ring (F).

(*E*)-1-Methyl-4-styrylbenzene (3e). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.53–7.47 (m, 4H), 7.40–7.35 (m, Hz, 2H), 7.26 (m, 1H), 7.10 (d, $J = 16.3$ Hz, 1H), 7.00 (d, $J = 16.3$ Hz, 1H) 6.93 (d, $J = 7.8$ Hz, 2H), 3.85 (s, 3H); ^{13}C (75 MHz, $CDCl_3$) δ 159.3, 137.6, 130.1, 128.6 (2C), 128.2, 127.7 (2C), 126.2, 126.6, 126.2 (2C), 114.1 (2C), 55.3.

(*E*)-1,2-Difluoro-4-styrylbenzene (3f). IR (KBr) 2924, 1596, 1510, 1431, 1271, 1112, 959 cm^{-1}; ^{1}H NMR (300 MH_Z, $CDCl_3$) δ 7.55–7.49 (m, 2H), 7.44–7.27 (m, 4H), 7.23–7.10 (m, 2H), 7.02 (brs, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 153.6 (C-2),* 153.4 (C-2),* 152.8 (C-1),* 152.6 (C-1),* 148.7 (C-2),* 148.4 (C-2),* 147.9 (C-1),* 147.6 (C-1),* 137.1, 135.2–135.0 (q, C-4), 130.3–130.2 (d, C-7),* 129.2 (2C), 128.5, 127.0 (2C), 126.9 (d, C-8),* 123.3–123.1 (q, C-5),* 118.0–117.6 (C-6),* 115.2–114.9 (C-3).* Asterisks denote splitting due to long-range coupling of fluorine (F) substitution on the phenyl ring.

(*E*)-1,2-Bis(4-chlorophenyl)ethene (3g). IR (KBr) 2923, 1588, 1487, 1406, 1090, 828 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, $J = 8.5$ Hz, 4H), 7.33 (d, $J = 8.5$ Hz, 4H), 7.03 (s, 2H); ^{13}C (75 MHz, $CDCl_3$) δ 135.5 (2c), 133.4 (2C), 128.9 (4C), 127.9 (2C), 127.7 (4C).

(*E*)-1-Chloro-4-(4-methylstyryl)benzene (3h). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, $J = 8.4$ Hz, 2H), 7.42 (d, $J = 7.8$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 7.20 (d, $J = 7.8$ Hz, 2H), 7.09 (d, $J = 16.3$ Hz, 1H), 7.01 (d, $J = 16.3$ Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 136.0, 134.2, 132.9, 129.4 (2C), 129.2, 128.8 (2C), 127.5 (2C), 126.5 (2C), 126.3, 21.3 (3H).

(*E*)-2,4-Dichloro-1-(4-chlorostyryl)benzene (3i). IR (KBr) 3021, 2925, 1588, 1491, 1216, 1095, 761 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, $J = 8.6$ Hz, Hz, 1H), 7.48–7.34 (m, 6H), 7.25 (dd, $J = 8.6$, 1.9 Hz, 1H), 7.0 (d, $J = 16.3$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.2, 134.0, 133.9, 133.7, 130.4, 129.6, 128.9 (2C), 128.0 (2C), 127.3, 127.1, 124.2.

(*E*)-4-(4-Chlorostyryl)phenol (3k). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.48–7.38 (m, 4H), 7.32–7.26 (m, 2H), 7.04 (d, $J = 16.4$ Hz, 2H), 6.94–6.86 (m, 3H), 3.83 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 159.9, 136.6, 133.1, 130.2, 129.3, 129.2 (2C), 128.2 (2C), 127.8 (2C), 125.7, 114.6 (2C), 55.7.

(*E*)-1-Methoxy-4-(4-methylstyryl)benzene (3l). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.43–7.34 (m, 4H), 7.12 (d, $J = 8.2$ Hz, 2H), 7.05–6.94 (m, 2H), 6.86 (d,

$J = 8.6$ Hz, 2H), 3.79 (s, 3H), 2.32 (s, 3H); ^{13}C (75 MHz, $CDCl_3$) δ 159.4, 137.3, 135.1, 130.6, 129.6 (2C), 127.8 (2C), 127.5, 126.8, 126.4 (2C), 114.3 (2C), 55.5, 21.4.

(*E*)-1,2-Bis(4-methoxyphenyl)ethene (3m). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.43 (d, $J = 8.8$ Hz, 4H), 6.93 (s, 2H), 6.89 (d, $J = 8.8$ Hz, 4H), 3.83 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 139.4, 127.6 (4C), 126.3 (2C), 114.2 (4C), 55.5.

(*E*)-1-Isopropyl-4-(4-methoxystyryl)benzene (3n). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.48–7.42 (m, 4H), 7.24–7.20 (d, $J = 8.2$ Hz, 2H), 7.09–6.99 (m, 2H), 6.90 (d, $J = 8.8$ Hz, 2H), 3.83 (s, 3H), 2.92 (m, 1H), 1.27 (d, $J = 6.9$ Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 159.4, 148.3, 135.5, 130.6, 127.8 (2C), 126.9 (2C), 126.8, 126.4 (2C), 114.3 (2C), 55.5, 34.1, 24.1 (2C).

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