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Ultrasound-assisted synthesis of *Z* and *E* stilbenes by Suzuki cross-coupling reactions of organotellurides with potassium organotrifluoroborate salts

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Abstract—Palladium (0)-catalyzed cross-coupling reactions between potassium aryl- and vinyltrifluoroborate salts and aryl- and vinylic tellurides proceeds readily to afford the desired stilbenes in good to excellent yields. Stilbenes containing a variety of functional groups can be prepared.

1. Introduction

The palladium-catalyzed cross-coupling reaction of an organometallic (R^1M) with an organic electrophile (R^2X) has emerged over the past 30 years as one of the most general and selective methods for carbon–carbon bond formation. Currently, it appears to be generally superior to related methods involving the use of Ni, Cu, or Fe catalysts in its scope and stereo-, regio-, and chemoselectivities.[1] The R^1 group of R^1M can be aryl, alkenyl, alkynyl, allyl, benzyl, propargyl, alkyl, cyano, or enoxy; while the R^2 group of R^2X can be aryl, alkenyl, alkynyl, allyl, benzyl, propargyl, alkyl, or acyl. The use of other related carbon groups as R^1 and/or R^2 is not only conceivable, but also known in the literature. The direct cross-coupling of alkenes with aryl and alkenyl halides is the most widely used and well known cross-coupling procedure.[2]

Boronic acids and boronate esters are the most commonly used derivatives in Suzuki cross-coupling reactions. Recently, Molander et al.[3] have explored the use of potassium organotrifluoroborate salts as an alternative to these boron reagents in Suzuki cross-coupling reactions. These salts are readily prepared from organoboronic acids or esters by the treatment with an aqueous solution of inexpensive and widely available KHF_2.[4] The potassium organotrifluoroborates are monomeric solids and indefinitely stable in the air.

The interest for chemistry of organotellurium compounds has increased and has been extensively explored in the last 20 years. As a consequence of these studies, many methods employing tellurium compounds have been developed.[5] Some metal-catalyzed cross-coupling reactions employing organotellurium reagents as the electrophilic reagent[6] have been successfully demonstrated, among this cross-coupling reactions we can mention the Sonogashira,[7] Negishi,[8] Heck,[9] and Suzuki–Miyaura.[10]

Ultrasound has been utilized recently to accelerate a number of synthetically useful reactions.[11] The use of ultrasound in chemistry is called sonochemistry and the ultrasound effects observed on organic reactions are due to cavitation, a physical process that create, enlarge, and implode gaseous and vaporous cavities in an irradiated liquid. Cavitation induces very high local temperatures and pressure inside the bubbles (cavities), leading to a turbulent flow in the liquid and enhanced mass transfer.

Although stilbene itself (1,2-diphenylethene) is not a natural product, a large number of its derivatives has been isolated from various plant species. Among these naturally occurring stilbenoid compounds, polyhydroxystilbenes, and their glucosides are currently attracting considerable attention, because of their wide range of biological activities and potential therapeutic value.[12] Stilbenes, the target of this paper, exhibit some activities such as antineoplastic, antimicrobial, multi-drug-resistant, antiangiogenesis, cytotoxic, and inhibit cell proliferation.[13]

Since these early days, several catalytic approaches have been proposed and investigated for the synthesis of

Keywords: Stilbenes; Suzuki; Tellurium compounds; Potassium organotrifluoroborate salt.
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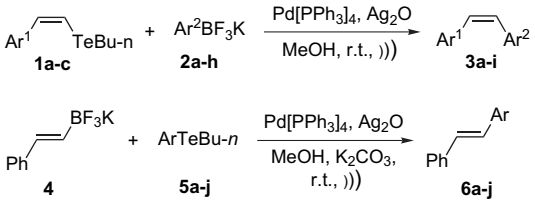
stilbenoid compounds. Among them, methods based on the Heck and Suzuki reactions stand out for their synthetic versatility and efficiency.[14]

By taking advantage of the attractive features of sonochemistry and of potassium organotrifluoroborate salts and the organotellurium compounds in cross-coupling reactions, we report herein an efficient ultrasound-assisted method for the synthesis of *Z* and *E* stilbene compounds by the palladium-catalyzed cross-coupling reaction of aryl- and vinyl tellurides and potassium aryl- and vinyltrifluoroborate salts (Scheme 1).



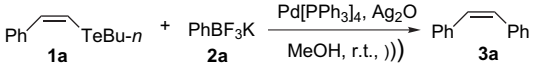
Scheme 1. Cross-coupling reaction between potassium organotrifluoroborate salts and the organotellurium compounds.

2. Results and discussion

The ultrasound-assisted cross-coupling reaction between the *Z*-styryl *n*-butyltellurides (**1a**) and potassium phenyltrifluoroborate (**2a**) in presence of silver oxide was chosen as the model reaction and a variety of conditions were screened (Table 1). Palladium (II) and (0) species were employed in the cross-coupling reaction, and the best results were reached with the catalysts of palladium (0) (Table 1, entries 3 and 6). $Pd(PPh_3)_4$ was chosen as the source of palladium. When the reaction was performed without the silver oxide, no reaction was observed (Table 1, entry 7). Other additives were used in the reaction, like AgOAc and CuI (Table 1, entries 9 and 10), however the results were worse. A base, triethylamine was also used in combination of $Pd(PPh_3)_4$ (Table 1, entry 8), but the yield decreased.

The catalyst loadings were analyzed (Table 1, entries 11–13), and the reaction yield decreased as the catalyst loadings were lowered. The best result was achieved when 8 mol % of catalyst was used. Thus, the careful analysis of the optimized reactions revealed that the optimum conditions for the coupling was found to be the use of *Z*-styryl *n*-butyltelluride (**1a**, 1 mmol), potassium organotrifluoroborate (**2a**, 1.2 equiv), $Pd(PPh_3)_4$ (8 mol %), and silver oxide (2 equiv) diluted in methanol (4 mL), under irradiation of ultrasound waves for 40 min at room temperature. Using this reaction condition we were able to prepare the *Z*-stilbene (**3a**) in 82% yield. The homocoupling reaction of phenyltrifluoroborate **2a** under these conditions was observed on a small scale. Because of this, the phenyltrifluoroborate **2a** is used in a little excess.

Table 1. Study of catalyst effect on cross-coupling reaction using vinylic telluride **1a** and potassium phenyltrifluoroborate salt **2a**



Entry	Catalyst	Additive	Base	Yield (%)
1	$Pd(acac)_2$ 10%	Ag_2O (2 equiv)	—	10
2	$PdCl_2$ 10%	Ag_2O (2 equiv)	—	60
3	$Pd_2(dba)_3$ 10%	Ag_2O (2 equiv)	—	72
4	$PdCl_2(BnCN)_2$ 10%	Ag_2O (2 equiv)	—	64
5	$Pd(dppf)Cl_2$ 10%	Ag_2O (2 equiv)	—	68
6	$Pd(PPh_3)_4$ 10%	Ag_2O (2 equiv)	—	79
7	$Pd(PPh_3)_4$ 10%	—	—	Nr
8	$Pd(PPh_3)_4$ 10%	Ag_2O (2 equiv)	TEA	50
9	$Pd(PPh_3)_4$ 10%	CuI (2 equiv)	—	Nr
10	$Pd(PPh_3)_4$ 10%	AcOAg (2 equiv)	—	15
11	$Pd(PPh_3)_4$ 8%	Ag_2O (2 equiv)	—	82
12	$Pd(PPh_3)_4$ 5%	Ag_2O (2 equiv)	—	73
13	$Pd(PPh_3)_4$ 1%	Ag_2O (2 equiv)	—	60

This optimal condition was employed under conventional reaction (magnetic stirring), but it was necessary a prolonged time reaction (18 h) at reflux temperature. The product *Z*-stilbene (**3a**) was obtained in medium yield, 63%. When the reaction was carried out at room temperature after 24 h, it remained many starting materials.

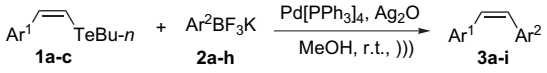
With the optimized cross-coupling conditions at hand, we examined the *Z*-stilbene derivates (**3**) formation with a range of potassium aryltrifluoroborate salts and *Z*-styryl tellurides, as shown in Table 2. The Pd (0)-catalyzed Suzuki reaction proved to be active. It is clear that this is a general method that tolerates the presence of functional groups. In addition, even an *ortho*-substituted aryltrifluoroborate salt afforded the corresponding stilbene compound in medium yield (Table 2; entry 5). However, when the potassium heteroaryltrifluoroborate was used as a nucleophilic partner no reaction was observed (Table 2, entries 9 and 10) and all of the starting material was recovered.

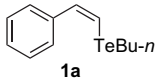
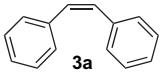
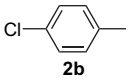
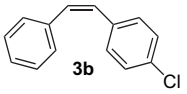
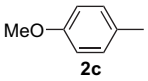
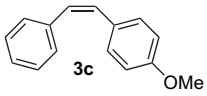
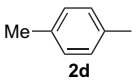
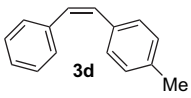
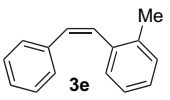
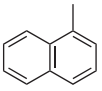
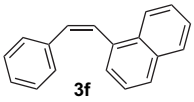
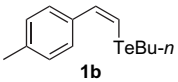
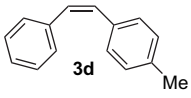
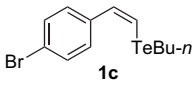
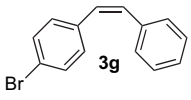
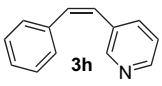
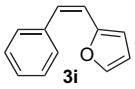
In a next step of this report, we synthesized *E*-stilbenes from the palladium (0)-catalyzed Suzuki–Miayura cross-coupling reaction between the potassium *E*-styryltrifluoroborate (**4**) and *n*-butyl(aryl)tellurides (**5**). Initially, we used the protocol above, which describe the synthesis of *Z*-stilbenes. However, the protocol described before to prepare Z-stilbenes did not demonstrate to be efficient for this case, remaining many starting material, under this condition. Using the *E*-styrylfluoroborate **4** and the aryl telluride **5a** we observed that just by addition of 1 equiv of potassium carbonate all starting material was consumed and the stilbene **6a** (Table 3, entry 1) was obtained in 90% yield.

As shown in Table 3, a variety of aryl tellurides (**5**) were subjected to the optimized palladium-catalyzed cross-coupling reaction conditions with the *E*-styryltrifluoroborate (**4**). When heteroaryl tellurides were employed, the products were obtained in moderate yields (Table 3, entries 10 and 11), while in the other case (Table 2, entries 9 and 10), the starting materials were unreactive.

When aryl tellurides (**5**) containing halides attached to the ring were used under the optimal conditions for Suzuki cross-coupling, the reaction demonstrated high chemoselectivity, with the substitution occurring only in the tellurium group leaving the halide moiety intact. The *E*-1-chloro-4-styryl-benzene (**6g**) (Table 3, entry 7), *E*-1-bromo-4-styryl-benzene (**6h**) (Table 3, entry 8), and *E*-1-iodo-4-styryl-benzene (**6i**) (Table 3, entry 9) were obtained in good yields. We described similar results in a previous report,[10a] but

Table 2. Reaction of *Z*-vinylic tellurides with potassium aryltrifluoroborate salts



Entry	Ar^1	Ar^2	Product	Yield (%)[a]
1	 **1a**	 **2a**	 **3a**	82
2	**1a**	 **2b**	 **3b**	70
3	**1a**	 **2c**	 **3c**	60
4	**1a**	 **2d**	 **3d**	78
5	**1a**	 **2e**	 **3e**	62
6	**1a**	 **2f**	 **3f**	70
7	 **1b**	 **2a**	 **3d**	76
8	 **1c**	 **2a**	 **3g**	78
9	**1a**	 **2g**	 **3h**	Nr
10	**1a**	 **2h**	 **3i**	Nr

[a] Isolated product yield.

here in this report we did not observe reaction when the aryl telluride containing iodo (Table 3, entry 9) was used. With these results at hand, we can rule that the general order of reactivity for Suzuki cross-coupling is as follows: BuTe>I>Br≥OTf≫Cl.

3. Conclusion

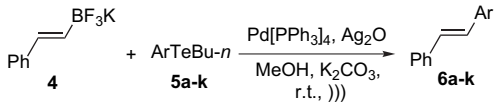
In summary, we have developed general and good yielding methods for accomplishing Suzuki cross-coupling reactions between aryl- and vinylic tellurides and potassium aryl- and vinyltrifluoroborate salts. The use of potassium organotrifluoroborate salts, as well as the use of ultrasound energy makes this method useful, fast and attractive for the synthesis of stilbenes and derivative compounds. One feature of this method was the tolerance of functional groups in both substrates. The Suzuki–Miyaura cross-coupling reaction was highly chemoselective, and we have demonstrated that aryl tellurides are more reactive than aryl halides under these conditions.

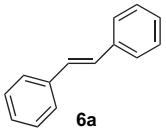
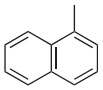
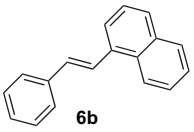
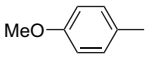
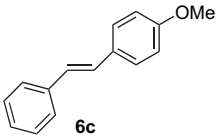
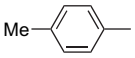
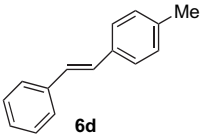
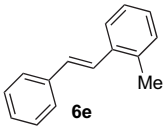
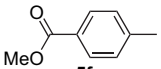
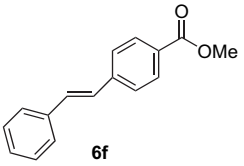
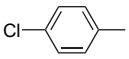
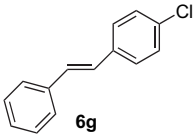
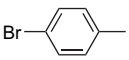
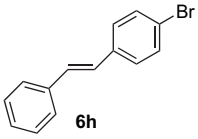
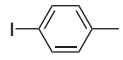
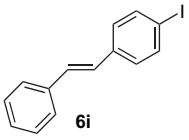
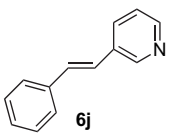
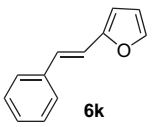
4. Experimental

4.1. General

IR spectra were recorded on Varian 3100 FTIR (ν in cm^{-1}). NMR spectra were performed on a Bruker DPX 300, chemical shifts δ in parts per million, the following abbreviations are used: singlet (s), doublet (d), multiplet (m). Low-resolution mass spectra were determined on a Shimadzu GCMS-QP5050A. Chromatographic purifications were performed by flash silica gel Merck. Palladium catalyst, potassium carbonate and silver (I) oxide were obtained from commercial sources. The methanol was distilled from sodium methoxide and kept over molecular sieves. THF was distilled from sodium benzophenone. Vinylic tellurides (**1**),[15] aryl tellurides

Table 3. Reaction of potassium *E*-vinylic trifluoroborates with aryl tellurides



Entry	Ar	Product	Yield (%)[a]
1	 **5a**	 **6a**	90
2	 **5b**	 **6b**	87
3	 **5c**	 **6c**	75
4	 **5d**	 **6d**	83
5	 **5e**	 **6e**	91
6	 **5f**	 **6f**	72
7	 **5g**	 **6g**	77
8	 **5h**	 **6h**	91
9	 **5i**	 **6i**	71
10	 **5j**	 **6j**	69
11	 **5k**	 **6k**	59

[a] Isolated product yield.

(**5**),[10a,b] aryltrifluoroborate (**2**), and vinyltrifluoroborate (**4**)[3,4] were prepared according to literature procedures.

4.2. Representative procedure of *Z*-stilbenes (3a–g) synthesis by Suzuki–Miyaura cross-coupling reaction

A suspension of *Z*-(2-butyltellanyl-vinyl)-benzene (**1a**) (0.144 g, 0.5 mmol), potassium phenyltrifluoroborate (**2a**) (0.110 g, 0.6 mmol), $Pd(PPh_3)_4$ (0.046 g, 0.04 mmol) and silver (I) oxide (0.232 g, 1 mmol) in 4 mL of methanol was irradiated in a water bath of an ultrasonic cleaner for 40 min. Then, the reaction was diluted with ethyl acetate (30 mL). The organic layer was washed with saturated solution of NH_4Cl (2×10 mL) and water (2×10 mL), dried over $MgSO_4$ and concentrated under vacuum. Purification by silica gel chromatography (eluting with hexane/ethyl acetate 9.5:0.5) yielded *Z*-stilbene (**3a**).[16] This product was obtained in 82% yield with data identical to a commercial sample.

4.2.1. *Z*-1-Chloro-4-styryl-benzene (3b).[17] This product was obtained as a colorless oil in 70% yield from **1a** and **2b** by the general method. ^1H NMR (300 MHz, $CDCl_3$) δ ppm 7.18–7.10 (m, 9H), 6.58 (d, J=12.2 Hz, 1H), 6.48 (d, J=12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 137.0; 135.8; 131.1; 130.3; 129.1; 128.9; 128.6; 128.5; 128.4; 127.47. MS: *m*/*z* (%) 216 (21); 214 (65); 179 (91); 178 (100); 76 (41). IR (neat): 3099, 1268, 937, 749 cm^{-1}.

4.2.2. *Z*-1-Methoxy-4-styryl-benzene (3c).[17] This product was obtained as a colorless oil in 60% yield from **1a** and **2c** by the general method. ^1H NMR (300 MHz, $CDCl_3$) δ ppm 7.27–7.15 (m, 7H), 7.72 (d, J=9.7 Hz, 2H), 6.50 (s, 2H), 3.74 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 158.8; 137.8; 130.3; 129.9; 129.0; 128.9; 128.4; 127.9; 127.0; 113.7; 55.4. MS: *m*/*z* (%) 210 (100); 209 (18); 195 (18); 179 (15); 76 (8). IR (neat): 3016, 1512, 1267, 925, 747 cm^{-1}.

4.2.3. *Z*-1-Methyl-4-styryl-benzene (3d).[17] This product was obtained as a colorless oil in 78% and 76% yield from **1a** and **2d** or from **1b** and **2a**, respectively, by the general method. ^1H NMR (300 MHz, $CDCl_3$) δ ppm 7.37–7.10 (m, 7H), 7.00–6.98 (m, 2H), 6.52 (s, 2H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 137.7; 137.1; 134.5; 130.4; 129.8; 129.2; 129.1; 129.0; 128.4; 127.2; 21.5. MS: *m*/*z* (%) 194 (100); 193 (32); 179 (99); 76 (13). IR (neat): 2982, 1453, 820, 668 cm^{-1}.

4.2.4. *Z*-1-Methyl-2-styryl-benzene (3e).[17] This product was obtained as a colorless oil in 62% yield from **1a** and **2e** by the general method. ^1H NMR (300 MHz, $CDCl_3$) δ ppm 7.19–7.08 (m, 8H), 7.05–7.00 (m, 1H), 6.64 (d, J=12.4 Hz, 1H), 6.59 (d, J=12.1 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 137.1; 137.0; 136.1; 130.5; 130.0; 129.5; 128.9; 128.8; 128.0; 127.2; 127.0; 125.5; 19.8. MS: *m*/*z* (%) 194 (83); 193 (14); 179 (100); 178 (70). IR (neat): 3059, 2989, 1324, 816, 666 cm^{-1}.

4.2.5. *Z*-1-Styryl-naphthalene (3f).[18] This product was obtained as a colorless oil in 70% yield from **1a** and **2f** by the general method. ^1H NMR (300 MHz, $CDCl_3$) δ ppm 8.11–8.08 (m, 1H), 7.90–7.86 (m, 1H), 7.77 (d, J=8.4 Hz, 1H), 7.53–7.47 (m, 2H), 7.40–7.28 (m, 4H), 7.10–7.04 (m, 4H), 6.84 (d, J=12.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 132.0; 129.0; 128.6; 128.5; 128.4; 128.3; 128.0; 127.5; 127.0; 126.6; 126.5; 126.4; 126.0; 125.9; 125.6; 124.9. MS: *m*/*z* (%) 230 (90); 229 (100); 152 (27); 128 (7); 101 (25). IR (neat): 3062, 1383, 987, 790, 672 cm^{-1}.

4.2.6. *Z*-1-Bromo-4-styryl-benzene (3g).[19] This product was obtained as a colorless oil in 78% yield from **1c** and **2a** by the general method. ^1H NMR (300 MHz, $CDCl_3$) δ ppm 7.40 (d, J=9.8 Hz, 2H), 7.20–7.13 (m, 5H), 7.07 (d, J=6.4 Hz, 2H), 6.60 (d, J=12.2 Hz, 1H), 6.46 (d, J=13.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 137.0; 136.3; 131.6; 131.3; 130.8; 129.2; 129.0; 128.6; 127.6; 121.2. MS: *m*/*z* (%) 259 (10); 258 (59); 179 (79); 178 (100); 76 (48). IR (neat): 2986, 1479, 1266, 1064, 751 cm^{-1}.

4.3. Representative procedure of *E*-stilbenes (6a–k) synthesis by Suzuki–Miyaura cross-coupling reaction

A suspension of potassium *E*-styryltrifluoroborate (**4**) (0.126 g, 0.5 mmol), butyl(phenyl)tellane (**5a**) (0.131 g, 0.5 mmol), $Pd(Ph_3P)_4$ (0.046 g, 0.04 mmol), potassium carbonate (0.138 g, 1 mmol), and silver (I) oxide (0.232 g, 1 mmol) in 4 mL of methanol was irradiated in a water bath of an ultrasonic cleaner for 40 min. Then the reaction was diluted with ethyl acetate (30 mL). The organic layer was washed with saturated solution of NH_4Cl (2×10 mL) and water (2×10 mL), dried over $MgSO_4$ and concentrated under vacuum. Purification by silica gel chromatography (eluting with hexane/ethyl acetate 9.5:0.5) yielded *E*-stilbene (**6a**).[20] This product was obtained in 90% yield with data identical to a commercial sample.

4.3.1. *E*-1-Styryl-naphthalene (6b).[21] This product was obtained as a white solid in 87% yield from **4** and **5b** by the general method. Mp 68–72 °C (lit., 70 °C). ^1H NMR (300 MHz, $CDCl_3$) δ ppm 8.19 (d, J=8.3 Hz, 1H), 7.88–7.69 (m, 4H), 7.58–7.32 (m, 7H), 7.25 (q, J=7.6 Hz, 1H), 7.07 (d, J=10.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 137.6; 135.0; 133.7; 131.7; 131.4; 129.2; 128.7; 128.6; 128.0; 127.7; 127.5; 126.7; 126.4; 126.0; 125.8; 125.7; 123.8; 123.6. MS: *m*/*z* (%) 230 (100); 229 (40); 152 (24); 101 (29). IR (neat): 3070, 1368, 967, 863, 651 cm^{-1}.

4.3.2. *E*-1-Methoxy-4-styryl-benzene (6c).[20] This product was obtained as a white solid in 75% yield from **4** and **5c** by the general method. Mp 133–136 °C (lit., 135 °C). ^1H NMR (300 MHz, $CDCl_3$) δ ppm 7.46–7.39 (m, 4H), 7.3 (t, J=7.9 Hz, 2H), 7.21–7.16 (m, 1H), 7.06–6.95 (m, 2H), 6.90–6.84 (m, 2H), 3.75 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 159.6; 137.9; 130.4; 128.9; 128.5; 128.0; 127.5; 126.9; 126.5; 114.4; 55.5. MS: *m*/*z* (%) 210 (100); 209 (22); 195 (21); 179 (15); 89 (15). IR (neat): 3067, 1416, 1046, 879, 649 cm^{-1}.

4.3.3. *E*-1-Methyl-4-styryl-benzene (6d).[20] This product was obtained as a white solid in 83% yield from **4** and **5d** by the general method. Mp 119–122 °C (lit., 120 °C). ^1H NMR (300 MHz, $CDCl_3$) δ ppm 7.49 (d, J=7.6 Hz, 2H), 7.41–7.31 (m, 4H), 7.26–7.21 (m, 1H), 7.16 (d, J=8.3 Hz, 2H); 7.06 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 137.6; 134.6; 129.5; 129.3; 128.7; 127.8;

127.6; 127.5; 126.8; 126.5; 21.3. MS: *m/z* (%) 194 (100); 193 (32); 179 (99); 178 (96); 89 (20). IR (neat): 2991, 1421, 899, 753 cm^{-1}.

4.3.4. *E*-1-Methyl-2-styryl-benzene (6e).[20] This product was obtained as a colorless oil in 91% yield from **4** and **5e** by the general method. ^1H NMR (300 MHz, $CDCl_3$) δ ppm 7.67 (d, J=7.8 Hz, 1H), 7.59 (d, J=8.5 Hz, 1H), 7.49–7.39 (m, 3H), 7.36–7.25 (m, 4H), 7.08 (d, J=16.1 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 138.0; 136.7; 136.1; 130.8; 130.4; 129.0; 127.9; 126.9; 126.7; 126.6; 125.7; 20.2. MS: *m/z* (%) 194 (85); 193 (15); 179 (100); 178 (66); 89 (18). IR (neat): 3027, 1268, 923, 748 cm^{-1}.

4.3.5. *E*-4-Styryl-benzoic acid methyl ester (6f).[22] This product was obtained as a white solid in 72% yield from **4** and **5f** by the general method. ^1H NMR (300 MHz, $CDCl_3$) δ ppm 8.20 (d, J=9.2 Hz, 2H), 7.56–7.51 (m, 4H), 7.39–7.24 (m, 3H), 7.20 (d, J=15.6 Hz, 1H), 7.10 (d, J=15.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 167.0; 141.9; 136.9; 131.4; 130.2; 129.0; 128.9; 128.4; 127.7; 126.9; 126.4; 52.2. MS: *m/z* (%) 238 (92); 207 (44); 179 (89); 178 (100); 89 (72); 76 (34). IR (neat): 2977, 1714, 1406, 1273, 1060, 713 cm^{-1}.

4.3.6. *E*-1-Chloro-4-styryl-benzene (6g).[20] This product was obtained as a white solid in 77% yield from **4** and **5g** by the general method. Mp 127–130 °C (lit., 128 °C). ^1H NMR (300 MHz, $CDCl_3$) δ ppm 7.45–7.20 (m, 9H), 6.99 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 137.2; 136.0; 133.4; 129.5; 129.0; 128.9; 128.1; 127.9; 127.5; 126.8. MS: *m/z* (%) 216 (25); 214 (82); 179 (87); 178 (100); 89 (45); 76 (45). IR (neat): 3072, 1399, 1055 cm^{-1}.

4.3.7. *E*-1-Bromo-4-styryl-benzene (6h).[22] This product was obtained as a white solid in 91% yield from **4** and **5h** by the general method. ^1H NMR (300 MHz, $CDCl_3$) δ ppm 7.52–7.38 (m, 4H), 7.33–7.17 (m, 5H), 7.04 (d, J=16.2 Hz, 1H); 6.96 (d, J=16.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 137.2; 136.5; 132.0; 129.6; 129.0; 128.2; 128.1; 127.6; 126.8; 121.5. MS: *m/z* (%) 260 (48); 258 (49); 179 (69); 178 (100); 89 (68); 76 (45). IR (neat): 3010, 1267, 912, 746 cm^{-1}.

4.3.8. *E*-1-Iodo-4-styryl-benzene (6i).[23] This product was obtained as a white solid in 71% yield from **4** and **5i** by the general method. ^1H NMR (300 MHz, $CDCl_3$) δ ppm 7.64 (d, J=8.3 Hz, 2H), 7.47 (d, J=8.4 Hz, 2H), 7.40–7.19 (m, 5H), 7.08 (d, J=16.1 Hz, 1H), 6.97 (d, J=16.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 137.9; 137.1; 137.0; 129.6; 128.9; 128.4; 128.1; 127.6; 126.8; 92.9. MS: *m/z* (%) 306 (100); 179 (52); 178 (91); 89 (63); 76 (28). IR (neat): 3068, 1415, 879 cm^{-1}.

4.3.9. *E*-3-Styryl-pyridine (6j).[24] This product was obtained as a white solid in 69% yield from **4** and **5j** by the general method. ^1H NMR (300 MHz, $CDCl_3$) δ ppm 8.70 (s, 1H), 8.47 (d, J=6.7 Hz, 1H), 7.79 (d, J=6.7 Hz, 1H), 7.50 (d, J=9.3 Hz, 2H), 7.39–7.23 (m, 4H), 7.14 (d, J=17.1 Hz, 1H), 7.07 (d, J=15.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 148.7; 136.8; 133.2; 132.8; 131.0; 129.0 (2C); 128.4; 126.9; 125.0; 123.7. MS: *m/z* (%) 181 (14); 180 (100); 89 (23); 76 (22). IR (neat): 3068, 1400, 662 cm^{-1}.

4.3.10. *E*-2-Styryl-furan (6k).[25] This product was obtained as a white solid in 59% yield from **4** and **5k** by the general method. ^1H NMR (300 MHz, $CDCl_3$) δ ppm 7.45–7.19 (m, 6H), 7.02 (d, J=15.3 Hz, 1H), 6.86 (d, J=15.0 Hz, 1H), 6.40–6.38 (m, 1H), 6.31 (d, J=3.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 153.5; 142.3; 137.2; 128.9; 127.8; 127.4; 126.5; 116.8; 111.8; 108.8. MS: *m/z* (%) 170 (100); 169 (64); 89 (10). IR (neat): 3072, 1369, 968, 651 cm^{-1}.

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