Oxidative Cross-Coupling of Vinylsilanes in Water

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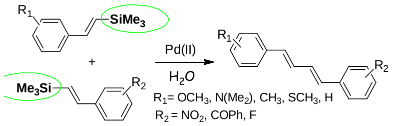
R1
SiMe3
+
Me3Si
R2
Pd(II)
H2O
R1
R2
R1= OCH3, N(Me2), CH3, SCH3, H
R2 = NO2, COPh, F

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Keywords: Cross-coupling; Oxidative Cross-coupling; Vinylsilanes; Reactions in Water; Palladium

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Abstract: Palladium-promoted cross-dimerization reaction of alkenylsilanes is reported for the first time, which is also one of the very first studies on oxidative cross-coupling between vinylic organometallic reagents. The reaction occurs at room temperature in aqueous micelles and represents a convenient access to all-trans push-pull butadienes.

The first investigation of palladium-catalyzed oxidative cross-coupling reaction of vinylsilanes bearing substituents with complementary electronic effects is reported. Besides being the first example on oxidative cross-coupling of vinylic organosilicon reagents, the protocol is a convenient access to *push-pull* butadienes.

1. Introduction

Transition metal catalyzed cross-coupling reactions of C-sp2-organometallic reagents with unsaturated electrophiles have been widely investigated as an effective tool for C-C bond formation[1] and are commonly used to build extended polyconjugated systems of interest in materials science.[2] Conversely, the study of oxidative cross-coupling processes between organometallic reagents is still at an early stage, in spite of their great potential in organic synthesis.[3] In particular, reports on Csp2-Csp2 bond formation by this class of reaction are mainly limited to the synthesis of biaryl compounds,[4] stimulated by their applications in materials science and medicinal chemistry.[5]

To the best of our knowledge, no systematic investigation on transition metal-catalyzed oxidative cross-coupling between vinyl organometallic reagents has been reported so far, although the occurrence of products of cross-dimerization was mentioned in a study by Stefani *et al.* on the relative reaction rates in palladium-catalyzed homocoupling of potassium alkenyltrifluoroborates.[6]

As a part of our research efforts on the development of efficient organometallic methods for the synthesis of conjugated oligomers and polymers for photonics and electronics,[2,7] and, in particular, of protocols based on the use of alkenylsilanes,[8] we reported a $PdCl_2/CuCl_2/LiCl$-promoted homocoupling reaction of vinylsilanes, useful to build extended polyenic systems.[9] More recently, we have described a micellar version of the same process with significantly improved outcome for the synthesis of symmetric 1,4-diarylbutadienes.[10]

Starting from these previous reports, we decided to investigate the coupling of different vinylsilanes, and herein we describe the results of our study demonstrating the first oxidative cross-coupling reaction between two vinylic organosilicon reagents, which also turns out to be one of the very first reports on oxidative cross-coupling between alkenyl organometallic reagents.

2. Results and Discussion

In a previous paper,[9] we had systematically studied a reaction protocol which delivers satisfactory yields in the highly stereoselective homocoupling reaction of vinylsilanes promoted by Pd(II). The presence of a large excess of $CuCl_2$ and LiCl is required to reoxidize the Pd(0) generated in the reductive elimination step leading to the butadienic system formation. Notably, the reactions can also be carried out in water in the presence of the non ionic surfactant TRITON X-100 (15% wt) (Figure 1) with improved outcomes.[10]

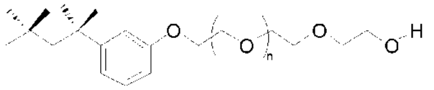
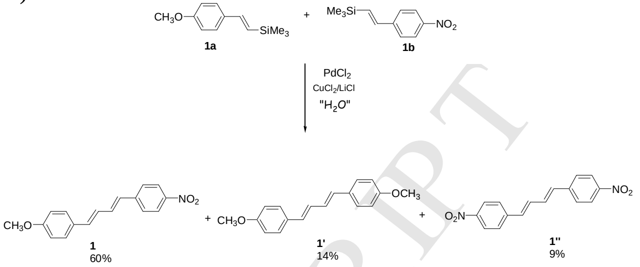


Fig. 1. Structure of Triton X-100

Therefore, we adopted the same reaction protocol[10] for the first experiments of cross-dimerization between two different styryl silanes **1a** and **1b** bearing the electron-donating methoxy group and the electron-withdrawing nitro group, respectively (Scheme 1).

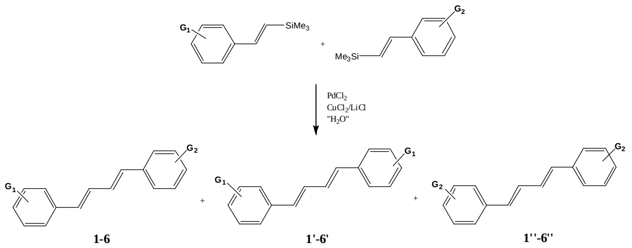


Scheme 1. Pd-catalyzed oxidative cross-coupling reaction of **1a** and **1b**.

Compound **1**, resulting from the cross-coupling process, was obtained as the major product (60% yield) (Table 1, entry 1) together with lower amounts of the two homocoupling products (14 % **1'** and 9% **1''**). The (*E*,*E*)-dienes were obtained as pure isomers as demonstrated by ^{1}H NMR spectroscopy.

The result of this first experiment clearly shows a remarkable selectivity for the oxidative coupling in favor of the cross-coupling product. The same reaction carried out in MeOH afforded a lower yield of the cross-coupling compound **1** (45%) as well as of the homocoupling reaction products (10% **1'** and 7% **1''**), but the same ratio between the three compounds was maintained, confirming the selectivity and also the advantage of the micellar environment over the MeOH reaction medium. In fact, according to our previous report,[10] the micellar system prevents the formations of protodesilylation byproducts thus leading to higher yields of the 1,4-disubstituted 1,3-butadienes.

Encouraged by these interesting results, we decided to extend the study to other styrylsilanes bearing substituents with different electronic effects on the phenyl rings. The general equation of the reaction is shown in the Scheme 2.



Scheme 2. Pd-catalyzed oxidative cross-coupling of styryl silanes in water.

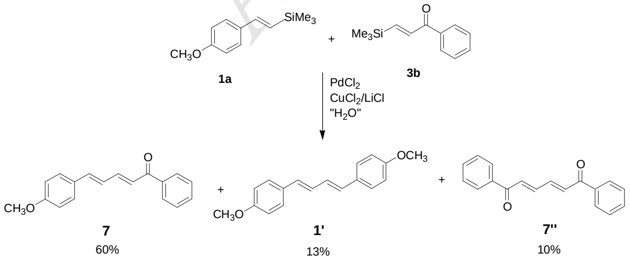
Table 1. Oxidative cross coupling reaction of G_1-substituted styryl silanes with G_2-substituted styryl silanes

Entry[a]	G_1	G_2	Product	Yield[b]	Ratio[c]	T(h)
1	OCH_3 **(1a)**	NO_2 **(1b)**	**1**	60	72:17:11	12
2	$N(Me)_2$ **(2a)**	NO_2 **(1b)**	**2**	65	74:16:10	12
3	SCH_3 **(3a)**	NO_2 **(1b)**	**3**	-	-	-
4	CH_3 **(4a)**	NO_2 **(1b)**	**4**	58	70:18:12	24
5	H **(5a)**	NO_2 **(1b)**	**5**	55	67:19:14	24
6	OCH_3 **(1a)**	3,5-diF **(2b)**	**6**	50	68:18:14	24

[a] Reactions carried out at room temperature in 15% wt Triton X-100/H_2O; the catalytic system consists of $PdCl_2$/LiCl/$CuCl_2$ with a molar ratio 1:3:8 optimized in previous studies.[9,10] [b] Based on isolated materials. [c] This value indicates the cross-coupling G_1-G_2: self-coupling G_1-G_1: self-coupling G_2-G_2 products ratio.

The results summarized in Table 1 show similar chemoselectivity in all the reactions investigated, which is only slightly affected by the nature of the electron-donating and electron-withdrawing substituents. The cross-coupling compounds were always obtained as the main reaction products in fair to good yields (50-65%) and the ratio of the unsymmetrical butadienes *vs* the two symmetrical products was similar in all cases. The only exception is represented by compound **3a** substituted with the SCH_3 group (entry 3). In this case no reaction was observed, which is likely to be due to the poisoning effect of the sulfur atom on the catalytic system. The reaction of the substrates functionalized with the strongly electron-donating (**1a**, **2a**) and electron-withdrawing (**1b**) substituents went to completion in 12 hours, while a rate retarding effect was observed by decreasing the electron-donating strength of the substituent (**4a)** or removing it (**5a**). Similarly, a 24 hours reaction time was necessary to lead to completion the reaction involving the difluorosubstituted styrylsilane (**2b**).

Cross-coupling product **7** (Scheme 3) was obtained from the reaction of the 2-ketovinyltrimethyl silane **3b** with **1a**, with a selectivity similar to that observed in the case of the styrylsilanes, in 24 hours reaction time.



Scheme 3. Cross-coupling reaction with the ketosilane **3b**

The unsymmetrical substituted 1,3-butadienes **1-2** and **4-7** obtained are listed in Figure 2. In fact, the method disclosed here offers convenient synthetic access to stereodefined all *trans* push-pull butadienes, a class of molecules widely employed as active materials in organic photonics.[11]

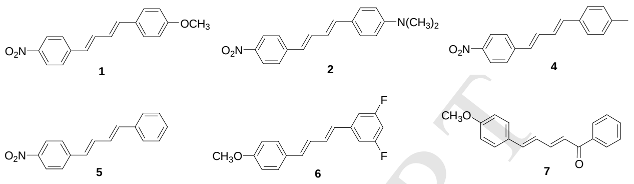


Fig. 2. 1,4-Disubstitued-1,3-butadienes **1-7** synthesized

Starting from the mechanistic path postulated for the homocoupling process of vinylsilanes,[12] we can speculate that the initial electrophilic addition of $PdCl_2$ occurs preferentially on the more electron-rich double bond, thus generating the β-styrylpalladium chloride intermediate of the electron-donor substituted olefin as the most abundant intermediate. Such intermediate would then undergo electrophilic addition to the electron-poor residual vinylsilane, remaining as the most abundant in the reaction mixture, thus generating preferentially the asymmetric butadienes upon the last reductive elimination step with Pd(0) release.

The substituted styryl silanes **1a-5a** and **1b-3b** used as starting materials were prepared with various organometallic methods, as shown in the Experimental Section.

3. Conclusions

In summary, we have reported the first systematic investigation on oxidative cross-coupling of vinylsilanes functionalized with substituents with complementary electronic effects. Besides being the first report on the oxidative cross-coupling of vinyl organosilicon reagents, this is one of the very first investigations on oxidative cross-coupling between alkenyl organometallic reagents. Moreover, this procedure turns out to be a convenient synthesis of *all-trans* unsymmetrical 1,4-disubstituted-1,3-butadienes carried out in water at room temperature, affording *push-pull* butadienic systems, with the distinctive advantages of operational simplicity and low toxicity starting materials.

Experimental

All chemicals were purchased from Aldrich, Alfa Aesar and Acros and used without further purification. (*E*)-1-(tributylstannyl)-2-(trimethylsilyl)ethene **8**[13] and (*E*)-trimethyl-(4-methylstyryl)silane[10] **4a** were prepared as reported in the literature.

Column chromatography was performed by using silica gel 60 (0.04-0.063 mm) from Merck. Petroleum ether was the 40-70 °C boiling fraction. Thin-layer-cromatography analysis was conducted using Merck Silica gel 60 F254 aluminium sheets. GC analysis was performed with Varian 3900 (dimethylpolysiloxane 30 m x 25 mm x 0.25 μm). MS spectra were acquired on a Shimadzu GCMS-QP 5000 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AM 500 spectrometer at 500 MHz and 125 MHz, respectively. The residual $CHCl_3$ signal at δ=7.24 ppm and the $CDCl_3$ signal at δ=77.0 ppm were used as standards for ^{1}H NMR and ^{13}C NMR spectra, respectively. ^{19}F NMR spectra were recorded in $CDCl_3$ on a Varian Inova 400 spectrometer at 376 MHz, using $CFCl_3$ as internal standard. FT-IR spectra were measured on a Perkin-Elmer 1710 spectrofotometer using dry KBr pellets. Elemental analyses were done by a Carlo Erba CHNS-O EA1108-Elemental Analyzer. Melting points were determined on a Gallenkamp capillary melting points apparatus.

$CHCl_3$ was distilled from P_2O_5 under a nitrogen atmosphere; THF, Et_2O and toluene were distilled over sodium and benzophenone under a nitrogen atmosphere, immediately prior to use. Methanol was degassed by bubbling nitrogen for 30 minutes, prior to use.

(E)-(4-Methoxystyryl)trimethylsilane **(1a)**. A three neck 250 ml round bottom flask equipped with a magnetic stir bar and 100 ml dropping funnel was charged with (*E*)-(2-bromovinyl)trimethylsilane (4.9 g, 27.35 mmol), $NiCl_2$(dppe) (0.84 g, 1.37 mmol) and 100 ml of freshly distilled THF. The solution was cooled to 0°C and *p*-methoxyphenylmagnesium bromide (0.32 N in THF, 100 ml, 32 mmol) was added dropwise. The solution was maintained at 0°C during the addition and then warmed to room temperature overnight. The reaction mixture was then quenched with water and extracted twice with diethyl ether. The organic layer was dried by using anhydrous Na_2SO_4, filtered and concentrated at reduced pressure. The pure product was isolated as a white solid after purification by column chromatography on silica gel using petroleum ether/ethyl acetate (9.6:0.4) as eluent (4.84 g, 86 %).

The characterization of the product **1a** is in agreement with the data reported in the literature.[14] M.p.= 50-52°C (Methanol). MS (EI, 70 eV) *m/z* (%)= 206 [M$^+$], 191 (100), 175 (43), 165 (30), 145 (7), 131 (6), 73 (5). FTIR (KBr): 2955, 1606, 1249, 1033, 992, 835, 801 cm^{-1}. ^{1}H NMR: δ 7.4 (d, J=8.5 Hz, 2H), 6.88 (d, J= 8.5 Hz, 2H), 6.84 (d, J= 19.1 Hz, 1H), 6.33 (d, J=19.1 Hz, 1H), 3.82 (s, 3H), 0.12 (s, 9H) ppm. ^{13}C NMR: δ = 159.4, 142.9, 131.2, 127.5, 126.6, 113.8, 55.2, 1.1 ppm.

(E)-[4-(N,N-Dimethylamino)styryl]trimethylsilane **(2a)**. Following the same procedure used to prepare **1a**, the silane **2a** was prepared starting from (*E*)-(2-bromovinyl)trimethylsilane (3.0 g, 16.8 mmol), $NiCl_2$(dppe) (0.44 g, 0.84 mmol) and 4-*N,N* dimethylaminophenylmagnesium bromide (0.33 N in THF, 60 ml, 20 mmol). The pure product was isolated as a white solid after purification by column chromatography using petroleum ether/ethyl acetate (9:1) as eluent (2.85 g, 78 %). M.p.= 48-50°C (Methanol).

MS (EI, 70 eV) *m/z* (%)= 219 [M$^+$] (100), 204 (99), 188 (16), 178 (23), 144 (7). FTIR (KBr): 2953, 1607, 1520, 1360, 1259, 1244, 1182, 1096, 1065, 1022, 986, 791, 727 cm^{-1}. ^{1}H NMR: δ 7.32-7.37 (m, 2H), 6.81 (d, J=19.1 Hz, 1H), 6.64-6.73 (m, 2H), 6.22 (d, J=19.1 Hz, 1H), 2.97 (s, 6H), 0.151 (s, 9H) ppm. ^{13}C NMR: δ = 150.2, 143.4, 136.5, 127.3, 127.1, 112.3, 40.5, 1.0 ppm. Anal. Calcd. for $C_{13}H_{21}NSi$ (219.40): C 71.70, H 9.64, N 6.38. Found: C 71. 81, H 9.78, N 6.43.

(E)-(Styryl)trimethylsilane **(5a)**. Following the same procedure used to prepare **1a**, the silane **5a** was prepared starting from (*E*)-(2-bromovinyl)trimethylsilane (3.0 g, 16.8 mmol), $NiCl_2$(dppe) (0.44 g, 0.84 mmol) and 4-phenylmagnesium bromide (N=0.54 in THF, 37 ml, 20 mmol). The pure product was isolated as a colourless oil after purification by column chromatography by using petroleum ether as eluent (2.6 g, 87 %).

The characterization of the product **5a** is in agreement with the data reported in the literature.[14]

MS (EI, 70 eV) *m/z* (%): 176 [M$^+$], 161 (100), 145 (61), 135 (13), 73 (8). FTIR (KBr): 2956, 1606, 1466, 1248, 988, 866, 843, 756, 723, 691 cm^{-1}. ^{1}H NMR: δ 7.47-7.52 (m, 2H), 7.33-7.41 (m, 2H), 7.22-7.33 (m, 1H), 6.95 (d, J=19.1 Hz, 1H), 6,55 (d, J=19.1 Hz, 1H), 0.18 (s, 9H) ppm. ^{13}C NMR: δ = 143.7, 138.4, 129.5, 128.6, 128.0, 126.4, 1.1 ppm.

(E)-(4-Nitrostyryl)trimethylsilane **(1b)**. A three neck 100 mL round bottom flask equipped with a magnetic stir bar was charged with dry toluene (60 ml), (*E*)-1-(tributylstannyl)-2-(trimethylsilyl)ethene **8** (2 g, 5.14 mmol), 1-iodo-4-nitrobenzene (1.28 g, 5.14 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.29 g, 0.25 mol), under a nitrogen atmosphere. The resulting mixture was refluxed overnight. The reaction mixture was quenched with water and extracted with ethyl acetate (3 x 50 mL). The organic layers were combined and dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using petroleum ether/ethyl acetate 9:1 as eluent, to give the pure product a pale yellow solid (0.97 g, 85 %). The characterization of the product **1b** is in agreement with the data reported in the literature.[15] M. p.= 37-39 °C (Water).

MS (EI, 70 eV) *m/z* (%): 221 [M$^+$], 206 (67), 160 (58), 147 (100), 145 (75), 117 (17), 115 (20), 75 (3). FTIR (KBr): 2956, 1591, 1521, 1341, 1240, 1109, 993, 861, 839, 750 cm^{-1}. ^{1}H NMR: δ 8.16-8.21 (m, 2H), 7.53-7.57 (m, 2H), 6.91 (d, J=19.1 Hz, 1H), 6.71 (d, J=19.1 Hz, 1H), 0.18 (s, 9H) ppm. ^{13}C NMR: δ = 147.1, 144.4, 141.2, 136.2, 126.9, 124.0, 1.2 ppm.

(E)-[4-(Methylthio)styryl]trimethylsilane **(3a)**. Following the same procedure used to prepare 1b, the silane **3a** was prepared starting from (*E*)-1-(tributylstannyl)-2-(trimethylsilyl)ethene **8** (1.5 g, 3.86 mmol), 4-bromo-1-methylthiobenzene (0.78 g, 3.85 mmol) tetrakis(triphenylphosphine)palladium(0) (0.22 g, 0.19 mmol) and dry THF (30 mL). The reaction mixture was quenched with water and extracted with ethyl acetate (3 x 30 mL). The organic layers were combined and dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using petroleum ether as eluent, to give the pure product as a colourless oil (0.45 g, 53 %). MS (EI, 70 eV) *m/z* (%): 222 [M$^+$], 207 (100), 177 (52), 145 (9), 115 (10), 73 (5). FTIR(KBr): 2956, 2922, 1602, 1490, 1247, 985, 866, 834, 790 cm^{-1}. ^{1}H NMR: δ 7.18-7.22 (m, 4H), 6.81 (d, J= 19.1 Hz, 1H), 6.41 (d, J= 19.1 Hz, 1H), 2.48 (s, 3H), 0.09 (s, 9H) ppm. ^{13}C NMR: δ = 142.9, 138.2, 136.2, 134.6, 128.9, 126.6, 15.9, 1.2 ppm. Anal. Calcd. for $C_{12}H_{18}SSi$ (222.42): C 64.80, H 8.16, S 14.42. Found: C 65.11, H 8.93, S 14.77.

(E)-1-Phenyl-3-(trimethylsilyl)-propen-1-one **(3b)**. To 50 mL of previously degassed chloroform was added $PdCl_2$(dppf) (0.21g,

0.25 g, 0,25 mmol), benzoylchloride (1.0 g, 5.07 mmol) and (*E*)-1-(tributylstannyl)-2-(trimethylsilyl)ethene (2.15 g, 5.5 mmol). The mixture was stirred under a nitrogen atmosphere for 2 days at room temperature. The reaction mixture was quenched with water and extracted with dichloromethane (3x 30 mL). The organic layer was washed with water (3 x 50 mL) and dried over anhydrous Na_2SO_4, and the solvent evaporated at reduced pressure. The residue was purified by column chromatography using petroleum ether/ethyl acetate (9:1) as eluent to yield the pure product as a pale yellow oil (0.83 g, 80%).

The characterization of the product **3b** is in agreement with the data reported in the literature.[16]

MS (EI, 70 eV) *m/z* (%): 204 [M$^+$], 189 (100), 161 (10), 105 (16), 73 (16). FTIR (KBr): 3062, 3032, 2955, 2893, 1665, 1608, 1577, 1450, 1244, 1180, 1010, 873, 855, 750, 690 cm^{-1}. ^{1}H NMR: δ = 7.95-7.91 (m, 2H), 7.57-7.51 (m, 1H), 7.48-7.43 (m, 2H), 7.33-7.21 (m, 2H), 0.19 (s, 9H) ppm. ^{13}C NMR: δ = 193.4, 149.6, 138.1, 137.5, 132.7, 128.9, 128.6, 0.9 ppm.

(E)-(3,5-Difluorostyryl)trimethylsilane **(2b)**. A three-neck 100 ml round bottom flask containing a magnetic stirrer was charged under a nitrogen atmosphere with 3,5-difluorophenyl boronic acid (0.88 g, 5.54 mmol), (*E*)-(2-bromovinyl)trimethylsilane (0.83 g, 4.64 mmol), tetrakis(triphenylphosphine)palladium(0) (0.16 g, 0.14 mmol), dry toluene (40 mL), methanol (10 mL) and sodium carbonate 2M (30 mL). The resulting mixture was stirred at 110 °C and the reaction was monitored by GC-MS until the disappearance of (*E*)-(2-bromovinyl)trimethylsilane. The reaction mixture was quenched with water, extracted with ethyl acetate (2 x 100 mL) and the organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent evaporated at reduced pressure. The residue was purified by column chromatography using petroleum ether as eluent to yield the pure product as a colourless liquid (0,73 g, yield 74%).

MS (EI, 70 eV) *m/z* (%) : 212 [M$^+$], 197 (98), 181 (100), 115(53), 75 (12). FTIR (KBr): 2956, 1617, 1584, 1319, 1249, 1119, 983, 866, 838 cm^{-1}. ^{1}H NMR: δ= 6.90–6.96 (m, 2H), 6.76 (d, J= 19.1 Hz, 1H), 6.71-6.66 (m, 1H), 6.51 (d, J = 19.1 Hz, 1H), 0.17 (s, 9H) ppm. ^{13}C NMR: δ =163.3 (dd, J= 247.6, 13.2 Hz), 141.9 (t, J= 9.0 Hz), 141.3 (t, J = 2.7 Hz), 133.1, 109.0 (dd, J = 19.3, 5.7 Hz), 103.0 (t, J = 25.7 Hz), 1.1 ppm. ^{19}F NMR (CF_3Cl): δ= -(110.93-111.00) (m, 2F) ppm.

Anal. Calcd. for $C_{11}H_{14}F_2Si$ (212.31): C 62.23, H 6.65. Found: C 62.34, H 6.88.

(1E,3E)-1-(4-Methoxyphenyl)-4-(4'-nitrophenyl)-1,3-butadiene **(1)**. A 50 ml round bottom flask was charged with (*E*)-(4-methoxystyryl)trimethylsilane **1a** (0.19 g, 0.91 mmol), (*E*)-(4-nitrostyryl)trimethylsilane **1b** (0.20 g, 0.91 mmol), $PdCl_2$ (0.08 g, 0.45 mmol), $CuCl_2$ (0.49 g, 3.65 mmol), and LiCl (0.06 g, 1.36 mmol) in 20 ml of surfactant solution (15% wt Triton X-100 in H_2O) and the mixture was stirred at room temperature. The reaction was monitored by TLC and GC-MS until the disappearance of the starting reagents. The reaction mixture was quenched with a saturated aqueous NaCl and then extracted with ethyl acetate (3 x 50 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. After filtration the solvent was evaporated under a reduced pressure and the residue was purified by column chromatography using petroleum ether and ethyl acetate 9:1 as eluent to give the pure product **1** as an orange solid (0.15 g, 60%).

MS (EI, 70 eV) *m/z* (%): 281 [M$^+$] (100), 250 (31), 234 (25), 219 (22), 204(24), 189 (27), 115 (10). FTIR (KBr): 2956, 2834, 1585, 1504, 1463, 1325, 1250, 1171, 1106, 1036, 980, 853, 806, 746 cm^{-1}. ^{1}H NMR: δ= 8.21-8.10 (m, 2H), 7.55-7.51 (m, 2H), 7.38-7.34 (m, 2H), 7.19-7.15 (m, 2H), 7.15-7.05 (m, 1H), 6.96-6.89 (m, 1H), 6.77 (d, J= 15.5 Hz, 1H), 6,67 (d, J= 15.5 Hz, 1H), 2.36 (3H, s) ppm. ^{13}C NMR: δ= 147.2, 144.9, 136.8, 136.5, 133.8, 130.4, 129.0, 128.4, 128.2, 126.6, 126.5, 123.3, 56.5 ppm. M.p.= 176-177 °C (Methanol). Anal. Calcd. for $C_{17}H_{15}NO_3$ (281.31): C 72.58, H 5.37, N 4.98. Found: C 72.81, H 5.41, N 5.16.

The self-coupling product (*1E*,*3E*)-1,4-di(4-methoxyphenyl)-1,3-butadiene (**1'**)[6] was recovered as a white solid (0.03g, 14%). MS (70 eV) *m/z* (%): 266 [M$^+$], 251 (22), 236 (16), 220 (19), 209 (26), 207 (100), 191(28). FTIR (KBr): 2923, 2852, 1600, 1508, 1462, 1256, 1176, 1110, 1028, 985, 847, 800 cm^{-1}. ^{1}H NMR: δ= 7.36 (d, J= 8.7 Hz, 4H), 6.87 (d, J= 8.7 Hz, 4H), 6.81 (dd, J= 11.9, 2,8 Hz, 2H), 6.58 (dd, J= 11.9, 2.8 Hz, 2H), 3,82 (s, 6H) ppm. ^{13}C NMR: δ=159.1, 131.3, 130,4, 127.5, 127.4, 114.1, 55.3 ppm. M.p.= 221-223 °C (Ethanol).

The self-coupling product (*1E*,*3E*)-1,4-di(4-nitrophenyl)-1,3-butadiene (**1''**) was recovered as a yellowish solid (0.02 g, 9%) MS (70 eV) *m/z* (%): 296 [M$^+$], 281 (29), 279 (21), 249 (49), 207 (100), 202 (51), 191 (38). FTIR (KBr): 2918, 2850, 1592, 1505, 1377, 1109, 984, 861 cm^{-1}. ^{1}H NMR: δ= 8.22 (d, J= 8.9 Hz, 4H), 7,59 (d, J= 8.8 Hz, 4H), 7.11 (dd, J= 11.9, 2.9 Hz, 2H), 6.83 (dd, J= 11.6, 2.7 Hz, 2H) ppm. ^{13}C NMR: δ= 147.1, 143.1, 133.1, 132.5, 127.1, 124.2 ppm. M.p.= 272-273°C (Water).

Anal. Calcd. for $C_{16}H_{12}N_2O_4$ (296.28): C 64.86, H 4.08, N 9.46. Found: C 65.01, H 4.21, N 9.86.

(1E,3E)-1-(4-N,N-Dimethylaminophenyl)-4-(4'-nitrophenyl)-1,3-butadiene **(2)**. A 50 mL round bottom flask was charged with (*E*)-[4-(*N*,*N*-dimethylaminostyryl)trimethylsilane **2a** (0.2 g, 0.90 mmol), (*E*)-trimethyl(4-nitrostyryl)silane **1b** (0.2 g, 0.90 mmol), $PdCl_2$ (0.08 g, 0.45 mmol), $CuCl_2$ (0.49 g, 3.66 mmol), and LiCl (0.06 g, 1.36 mmol) in 20 mL of surfactant solution (15% wt Triton X-100 in H_2O) and the mixture was stirred at room temperature. The reaction was monitored by TLC and GC-MS until the disappearance of the starting reagents. The reaction mixture was quenched with a saturated aqueous NaCl and then extracted with ethyl acetate (3 x 50 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. After filtration the solvent was evaporated under a reduced pressure and the residue was purified by column chromatography using petroleum ether and acetone 9:1 as eluent to give the pure product as a red solid (0.17 g, 65%).

FTIR (KBr): 2896, 2814, 1599, 1575, 1505, 1442, 1329, 1178, 1107, 987, 856, 804, 749 cm^{-1}. ^{1}H NMR: δ= 8.19-8.14 (m, 2H), 7.53-7.48 (m, 2H), 7.35-7.44 (m, 2H), 7.14-7.03 (m, 1H), 6.56-6.09 (m, 5H), 3.02 (s, 6H) ppm. ^{13}C NMR: δ = 146.5, 144.1, 138.5, 137.4, 136.2, 134.0, 129.6, 129.4, 127.4, 126.7, 126.6, 124.2, 21.4 ppm. M.p.= 300°C (dec.) (Methanol).

Anal.Calcd. for $C_{18}H_{18}N_2O_2$ (294.35): C 73.45, H 6.16, N 9.52. Found: C 73.71, H 6.48, N 9.80.

The self-coupling product (*E*,*E*)-1,4-di(*p*-*N*,*N*-dimethylaminophenyl)-1,3-butadiene (**2'**)[17], was recovered as a yellow solid (0.04 g, 13%).

MS (EI, 70 eV) *m/z* (%): 292 [M$^+$] (100), 277 (10), 248 (18), 202 (36), 172 (52), 158 (66), 77 (4). FTIR (KBr): 2803, 1612, 15240, 992, 817 cm^{-1}. ^{1}H NMR: δ= 7.32 (d, J= 8.8 Hz, 4H), 6.77 (dd, J= 12.0, 2,5 Hz, 2H), 6.71 (d, J= 7,5 Hz, 4 H), 6.52 (dd, J= 11.9, 2.6 Hz, 2H), 2.97 (s, 12H); ^{13}C NMR: δ = 133.7, 129.1, 128.9, 127.2, 114.3, 114.2, 41.5 ppm. M.p.= 245-246 °C (Methanol).

0.02 g, (8%) of the self-coupling product (*1E,3E*)-1,4-di(4-nitrophenyl)-1,3-butadiene (1'') were recovered.

(1E,3E)-1-(4-Nitrophenyl)-4-(4'-tolyl)-1,3-butadiene **(4)**. A 50 mL round bottom flask was charged with (*E*)-trimethyl(4-nitrostyryl)silane **1b** (0.23 g, 1.05 mmol), (*E*)-trimethyl(4-methylstyryl)silane **4a** (0.20 g 1.05 mmol) $PdCl_2$ (0.09 g, 0.52 mmol), $CuCl_2$ (0.57 g, 4.2 mmol), and LiCl (0.07 g, 1.58 mmol) in 20 mL of surfactant solution (15% wt Triton X-100 in H_2O) and the mixture was stirred at room temperature. The reaction was monitored by TLC and GC-MS until the disappearance of the starting reagents. The reaction mixture was quenched with a saturated aqueous NaCl and then extracted with ethyl acetate (3 x 50 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. After filtration the solvent was evaporated under a reduced pressure and the residue was purified by column chromatography (petroleum ether/ethyl acetate 9:1 as eluent) to give the pure product as a pale orange solid (0.16 g, 58%).

MS (EI, 70 eV) *m/z* (%): 265 [M^+] (100), 250 (65), 218 (2), 204 (63), 202 (49), 191 (16), 128 (15). FTIR (KBr): 2918, 2849, 1587, 1512, 1344, 1109, 993, 862, 803, 746 cm^{-1}.

^{1}H NMR: δ = 8.18 (d, J=8.7 Hz, 2H), 7.53 (d, J=8.7 Hz, 2H), 7.36 (d, J=8.0 Hz, 2H), 7.16 (d, J= 8.0 Hz, 2H), 7.05-7.11 (m, 1H), 6.96-6.88 (m, 1H), 6.77 (d, J=15.4 Hz, 1H), 6.66 (d, J=15.4 Hz, 1H), 2.36 (s, 3H) ppm.

^{13}C NMR: δ = 146.5, 144.1, 138.5, 136.2, 134.0, 129.6, 129.5, 128.6, 127.4, 126.7, 126.6, 124.2, 21.4 ppm. Mp: 172-174 °C (Methanol). Anal. Calcd. for $C_{17}H_{15}NO_2$ (265.31): C 76.96, H 5.70, N 5.28. Found: C 77.31, H 6.01, N 5.64.

The (*1E,3E*)-1,4-di(*p*-tolyl)-1,3-butadiene (**4'**)[10] (0.04 g, 14%) was recovered as a white solid. MS (70eV): 234 [M^+], 229 (18), 219 (100), 218 (17), 204 (40), 203 (25), 202 (21), 105 (10) ppm. FTIR (KBr): 2922, 2851, 1506, 1456, 985, 850, 798 cm^{-1}. ^{1}H NMR: δ = 7.29-7.39 (m, 4H), 7.10-7.20 (m, 4H), 6.85-6.98 (m, 2H), 6.56-6.69 (m, 2H), 2.35 (s, 6H) ppm. ^{13}C NMR: δ = 137.2, 134.5, 132.1, 129.2, 128.3, 126.1, 21.3 ppm.

0.03 g (9%) of the self-coupling product product (*1E,3E*)-1,4-di(4-nitrophenyl)-1,3-butadiene (**1''**) were recovered.

(1E,3E)-1-(4-Nitrophenyl)-4-(phenyl)-1,3-butadiene **(5)**. A 25 mL round bottom flask was charged with (*E*)-trimethyl(4-nitrostyryl)silane **1b** (0.13 g, 0.57 mmol), (*E*)-trimethyl(styryl)silane **5a** (0.10 g 0.57 mmol), $PdCl_2$ (0.05 g, 0.28 mmol), $CuCl_2$ (0.31 g, 2.28 mmol), and LiCl (0.04 g, 0.94 mmol) in 15 mL of surfactant solution (15% wt Triton X-100 in H_2O) and the mixture was stirred at room temperature. The reaction was monitored by TLC and GC-MS until the disappearance of the starting reagents. The reaction mixture was quenched with a saturated aqueous NaCl and then extracted with ethyl acetate (3 x 50 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. After filtration the solvent was evaporated under a reduced pressure and the residue was purified by column chromatography using petroleum ether and ethyl acetate 9.4:0.6 as eluent, to give the pure product as a yellow solid (0.08 g, 55%).

MS (EI, 70 eV) *m/z* (%): 251 [M^+] (100), 205 (25), 202 (51), 189 (24), 178 (23), 165 (22), 129 (28), 115 (89). FTIR (KBr): 2920, 2850, 1587, 1512, 1341, 1108, 992, 857, 760, 743, 688 cm^{-1}. ^{1}H NMR: δ = 8.21-8.17 (m, 2H), 7.57-7.52 (m, 2H), 7.49-7.44 (m, 2H), 7.38-7.32 (m, 2H), 7.31-7.26 (m, 1H), 7.14-7.06 (m, 1H), 7.01-6.93 (m, 1H), 6.80 (d, J=15.4 Hz, 1H), 6.70 (d, J=15.4 Hz, 1H) ppm. ^{13}C NMR: δ = 146.6, 143.9, 136.7, 136.1, 133.8, 130.1, 128.8, 128.4, 128.3, 126.8, 126.7, 124.2 ppm. M.p.= 137-139 °C (Methanol). Anal. Calcd. for $C_{16}H_{13}NO_2$ (251.28): C 76.48, H 5.21, N 5.57. Found: C 76.71, H 5.58, N 5.82.

The self-coupling product (*1E,3E*)-1,4-diphenyl-1,3-butadiene **(5')** was recovered as a white solid (0.021 g, 15%)[6]. MS (70eV) *m/z* (%): 206 [M^+](100), 205 (51), 203 (30), 202 (21), 191 (48), 190 (20), 128 (34), 91 (38). FTIR (KBr): 2918, 1490, 1412, 991, 738, 689, 491 cm^{-1}. ^{1}H NMR: δ= 7.48 (dd, J= 8.6, 1.4 Hz, 4H), 7.35-7.40 (m, 4H), 7.25-7.30 (m, 2H), 7.00 (dd, J= 11.9, 2.8 Hz, 2H), 6.71 (dd, J= 11.9, 2.8 Hz, 2H). ^{13}C NMR: δ = 137.3, 132.8, 129.2, 128.6, 127.5, 126.4 ppm.

0.019 g (11%) of the self-coupling product (*1E,3E*)-1,4-di(4-nitrophenyl)-1,3-butadiene (**1''**) were recovered.

(1E,3E)-1-(4-Methoxyphenyl)-4-(3,5-difluorophenyl)-1,3-butadiene **(6)**. A 50 mL round bottom flask was charged with (*E*)-(4-methoxystyryl)trimethylsilane **1a** (0.20 g, 0.97 mmol), (*E*)-(3,5-difluorostyryl)trimethylsilane **2b** (0.21 g, 0.97 mmol), $PdCl_2$ (0.09 g, 0.49 mmol), $CuCl_2$ (0.52 g, 3.88 mmol), and LiCl (0.06 g, 1.45 mmol) in 20 mL of surfactant solution (15% wt Triton X-100 in H_2O) and the mixture was stirred at room temperature. The reaction was monitored by TLC and GC-MS until the disappearance of the starting reagents. The reaction mixture was quenched with a saturated aqueous NaCl and then extracted with ethyl acetate (3 x 50 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. After filtration the solvent was evaporated under a reduced pressure and the residue was purified by column chromatography using petroleum ether and ethyl acetate 9:1 as eluent, to give the pure product as a white solid (0.13 g, 50%).

MS (EI, 70 eV) *m/z* (%): 272 [M^+] (100), 256 (37), 241 (50), 214 (26), 159 (26), 145 (29). FTIR (KBr): 2924, 2850, 1622, 1594, 1511, 1442, 1250, 1173, 1117, 1031, 984, 834 cm^{-1}. ^{1}H NMR: δ = 7.41 (m, 2H), 6.93 - 6.86 (m, 4H), 6.83 - 6.76 (m, 1H), 6.70 - 6.62 (m, 3H), 6.50 (d, J=15.35 Hz, 1H), 3.83 (s, 3H) ppm. ^{13}C NMR: δ = 163.3 (dd, J=13.19, 247.50 Hz), 159.1, 141.1 (t, J= 9.7 Hz), 134.5, 132.1, 129.2 (t, J=3.2 Hz), 127.9, 127.4, 126.2, 114.3, 108.7 (dd, J= 19.7, 5.8 Hz), 102.3 (t, J= 25.7 Hz), 55.3 ppm. M.p.= 97-99 °C (Methanol). ^{19}F NMR (CF_3Cl): δ= −(110.49−110.58) (m, 2F) ppm.

Anal. Calcd. for $C_{17}H_{14}F_2O$ (272.29): C 74.99, H 5.18. Found: C 75.31, H 5.28.

0.03 g (13 %) of the (*1E,3E*)-1,4-di(4-methoxyphenyl)-1,3-butadiene (**1'**) were recovered.

The homocoupling product (*1E,3E*)-bis(3,5-difluorophenyl)-1,3-butadiene (**6''**) was recovered as a white solid (0.02 g, 10%)

MS (EI, 70eV) *m/z* (%): 278 [M^+], 257 (18), 256 (19), 165 (37), 151 (100), 127 (73), 119 (18). FTIR (KBr): 2924, 2848, 1622, 1586, 1443, 1260, 1115, 977, 864, 855 825 cm^{-1}. ^{1}H NMR: δ = 6.91-6.96 (m, 4H), 6.89 (dd, J= 11.9, 2.8 Hz, 2H), 6.70 (tt, J= 8.0, 2.3 Hz, 2H), 6.61 (dd, J= 11.9, 2.8 Hz, 2Hz) ppm. ^{13}C NMR : δ = 163.1 (dd, J= 247.9, 13.1 Hz), 140.3 (t, J= 9.6 Hz), 132.2 (t, J=3.1 Hz), 131.4, 109.0 (dd, J= 19.5, 5.9 Hz), 103.1 (t, J=.25.7 Hz) ppm. ^{19}F NMR (CF_3Cl): δ= −(110.97÷ −111.04) (m, 4F). M.p.= 168-170°C (Methanol).

Anal.Calcd. for $C_{16}H_{10}F_4$ (278.24): C 69.07, H 3.62. Found: C 69.34, H 3.95.

(2E,4E)-5-(4-Methoxyphenyl)-1-phenylpenta-2,4-dien-1-one **(7)**. A 50 mL round bottom flask was charged with (*E*)-(4-methoxystyryl)trimethylsilane **1a** (0.17 g, 0.84 mmol), (*E*)-1-phenyl-3-(trimethylsilyl)propen-1-one **3b** (0.17 g, 0.84 mmol), $PdCl_2$ (0.07 g, 0.42 mmol), $CuCl_2$ (0.45 g, 3.36 mmol), and LiCl

(0.05 g, 1.18 mmol) in 25 mL of surfactant solution (15% wt Triton X-100 in H_2O) and the mixture was stirred at room temperature. The reaction was monitored by TLC and GC-MS until the disappearance of the starting reagents. The reaction mixture was quenched with a saturated aqueous NaCl and then extracted with ethyl acetate (3 x 50 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. After filtration the solvent was evaporated under a reduced pressure and the residue was purified by column chromatography using petroleum ether and ethyl acetate 9:1 as eluent, to give the pure product as a yellow solid (0.13 g, 60%).

MS (EI, 70 eV) *m/z* (%): 264 [M^+] (100), 233 (19), 159 (31), 144 (26), 115 (16). FTIR (KBr): 2919, 2850, 1672, 1598, 1511, 1251, 1175, 1033, 837, 816 cm^{-1}. ^1H NMR: δ = 7.98-7.95 (m, 2H), 7.63-7.58 (m, 1H), 7.58-7.50 (m, 2H), 7.50-7.42 (m, 5H), 7.07-7.01 (m, 1H), 6.91-6.88 (m, 2H), 3.84 (s, 3H) ppm. ^{13}C NMR: δ = 160.6, 145.5, 141.9, 138.4, 132.5, 128.9, 128.8, 128.6, 128.5, 128.4, 124.9, 124.3, 114.4, 55.4 ppm. M.p.= 176-178°C (Hexane).

Anal. Calcd. for $C_{18}H_{16}O_2$ (264.32): C 81.79, H 6.10. Found: C 81.92, H 6.32.

0.03 g (13%) of the self-coupling product (*1E,3E*)-1,4-di(4-methoxyphenyl)-1,3-butadiene (**1’**) were recovered.

The homo-coupling product (*2E,4E*)-1,6-diphenyl-2,4-butadiene-1,6-dione (**7’’**) was recovered as a white solid (0.02 g, 10%) MS (EI, 70eV) *m/z* (%): 262 [M^+], 157 (73), 128 (31), 105 (71), 77 (100), 51 (47). FTIR (KBr): 2921, 2852, 1647, 1578, 1445, 1260, 1192, 1176, 1008, 764, 689, 651 cm^{-1}. ^1H NMR: δ = 7.98-8.00 (m, 4H), 7.56-7.63 (m, 4H), 7.49-7.54 (m, 4H), 7.38 (dd, J= 11.3, 3.0 Hz, 2H) ppm. ^{13}C NMR: δ = 189.9, 141.1, 137.4, 133.3, 132.5, 128.8, 126.6 ppm. M.p.= 180-181°C (Methanol). Anal. Calcd for $C_{18}H_{14}O_2$ (262.30): C 82.42, H 5.38. Found: C 82.63, H 5.57.

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- one of the very first examples of oxidative cross-coupling between vinyl organometallic reagents
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- a suitable approach to the synthesis of unsymmetrically substituted push-pull butadienes,