Synthesis of substituted styrenes and stilbenes mediated by palladium on zirconia

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Palladium on zirconia has been found to be an effective catalyst for the synthesis of various substituted styrenes and stilbenes, including biologically active natural products, by reaction of aryl halides with olefins.

Keywords: stilbenes, styrenes, heterogeneous catalyst, palladium on zirconia

Substituted stilbenes constitute an important group of biologically active compounds exhibiting significant anticancer activity.[1-6] Some of the stilbenes exhibit antifungal activity[7] while some are used as intermediates in the synthesis of, for example, fluorescent brighteners,[8] dyes,[8] antibiotics,[9] cyclooxygenase-2 inhibitors.[10] The significant biological activity exhibited by stilbenes keeps on attracting the synthetic organic chemistry community to explore alternative methods for their synthesis to make these compounds available in larger quantities for biological studies. Methods for the preparation of stilbenes include the Wittig reaction,[1,2,6,11-12] the Heck reaction,[13] reaction of benzyl sodium and benzaldehyde,[8] reductive metalation of benzaldehyde dimethyl acetal,[9] LDA-mediated condensation of benzyl bromides,[14] condensation of benzaldehydes and nitrotoluenes,[15] and Knoevenagel condensation.[16]

The Heck reaction is an important reaction for forming the C–C bond and is accomplished by employing various homogeneous and heterogeneous catalysts containing different metals. The heterogeneous catalysts offer advantages including mild reaction conditions, ease of work-up and reusability of catalyst, which are important in view of environmental concerns and the overall efficiency of the processes. There are a number of reports about the use of heterogeneous catalysts for the Heck reaction including recent examples such as LDH-supported nanoplatinum,[17] chitosan-based heterogeneous catalysts,[18] Pd-SAPO-31,[19] Pd-zeolites,[20] Pd supported on metal oxides and zeolites,[21] silica supported palladium catalysts[22] and Ni, Co, Cu and Mn heterogeneous catalysts.[23]

Zirconia-supported palladium catalysts have been studied extensively for removing volatile organic compounds from industrial processes and automobile exhaust emissions by catalytic oxidation to harmless products like water and carbon dioxide.[24-28] They are also studied for various other purposes including hydrodechlorination wherein polychlorinated organic substances, which are pollutants, can be converted into useful products.[29-30] In continuation of our research interest in the synthesis of heterogeneous catalysts and their use in organic transformations,[31-36] we have found that a heterogeneous catalyst containing palladium on zirconia[37] is effective in catalysing the reaction between aryl halides and olefins to afford styrenes and stilbenes in good yields and the results are reported here.

Initially, acrylamide was reacted with 4-iodoanisole in the presence of a palladium on zirconia catalyst and various bases in different solvents at a range of temperatures in an attempt to form the desired substituted styrene.

Dimethyl formamide was found to be the best solvent; *N*-methyl pyrrolidone and xylene gave 5–20% conversion of starting materials while there was no reaction in toluene, ethanol or water (Table 1).

Table 1 Influence of solvent used during arylation of CH_2=CH–$CONH_2$ with 4-iodoanisole in presence of the catalyst (Pd/ZrO_2) and K_2CO_3 at reflux

Solvent	Reaction time/h	Yield of 4-methoxy-*trans*-cinnamic amide (%)
DMF	4	80
H_2O	10	No reaction
1,4 -Dioxan	12	No reaction
NMP	12	20
Xylene	12	5
Ethanol	12	No reaction
Toluene	12	No reaction

The work-up involved filtration from catalyst, dilution of the organic layer with water, extraction with ethyl acetate, concentration and purification by column chromatography.

Among the bases tried (sodium acetate, sodium carbonate, triethylamine, pyridine and potassium carbonate), potassium carbonate was found to be most effective and convenient to use. The reaction was found to be temperature dependent (Table 2) and stirring under reflux was found to give the best results.

The catalyst was washed with acetone, dried and reused without significant decrease in the yield (Table 3). The observed increase in the reaction time for the successive reuse of the catalysts is expected because of a small loss of the catalyst during its processing (i.e. filtration and drying).

The study of leaching of palladium by the reported method[38] showed that leaching was not observed (*i.e.* <0.1 ppm Pd) from the catalyst in the reaction. Palladium leaching (if any) from the palladium catalyst in the reaction medium, after the reaction, was determined by adding an aqueous ethanolic dimethylglyoxime (1%) solution to the reaction mixture (after separating the catalyst) and observing a yellow-orange precipitate of palladium dimethylglyoximate which indicates

Table 2 Influence of temperature during the arylation of CH_2 =CH–$CONH_2$ with 4-iodoanisole in presence of the catalyst (Pd/ZrO_2) and K_2CO_3 in DMF

Temperature/°C	Reaction time/h	Product yield%
0	20	No reaction
50	20	No reaction
100	10	50
140	4	80

Table 3 Influence of reuse of the catalyst during the arylation of CH_2 =CH–$CONH_2$ with 4-iodoanisole in presence of the catalyst (Pd/ZrO_2) and K_2CO_3 in DMF

Reuse of catalyst	Reaction time/h	Yield/%
Reuse I	4	79
Reuse II	4	78
Reuse III	5	77
Reuse IV	5.5	76

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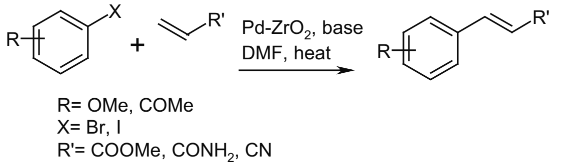
the presence of palladium (in trace amounts) in the reaction mixture. In all the experiments, no yellow orange precipitate was observed. This indicated the absence of Pd leaching from the catalyst in the reaction.

When various aryl halides were reacted with acrylamide, alkyl acrylate or acrylonitrile in dimethyl formamide in presence of palladium on zirconia catalyst (10% by weight of aryl halide) and K_2CO_3 at 140 °C under a nitrogen atmosphere (Scheme 1), the corresponding styrenes were obtained in good yields (Table 4).

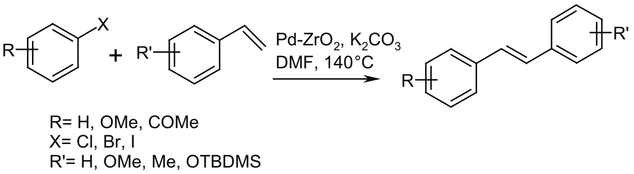
Aryl iodides gave the best yields, bromides gave reasonable yields while chlorides afforded negligible yields. A number of substituted styrenes were prepared to generalise the method. The encouraging results obtained in the preparation of styrenes were explored further to synthesise substituted stilbenes which exhibit a wide variety of biological activity (Scheme 2). The substituted styrenes, used as starting materials for these reactions, were prepared[39] by Wittig reaction of the corresponding aldehydes and subjected to the reaction with aryl halides as described before to afford the desired stilbenes in good yields.

Comparison of the spectroscopic data with reported values showed that the products obtained had *trans* geometry. The probable mechanism of this reaction is shown in Scheme 3.

In conclusion, we have found that palladium on a zirconia catalyst is useful for the synthesis of various styrenes and stilbenes. The reaction conditions are amenable to scale up making the present method suitable to make available the substituted stilbenes in larger quantities for detailed biological activity studies. Also, the present work employs a heterogeneous catalyst that is easily removed from the product simply by filtration and can be recovered and reused.



Scheme 1

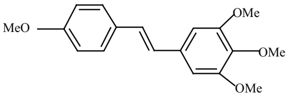
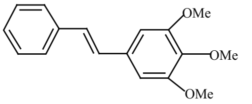
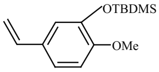
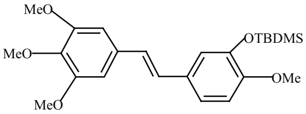
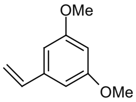
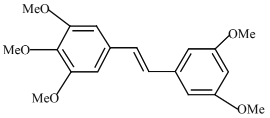
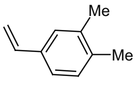
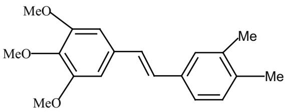


Scheme 2

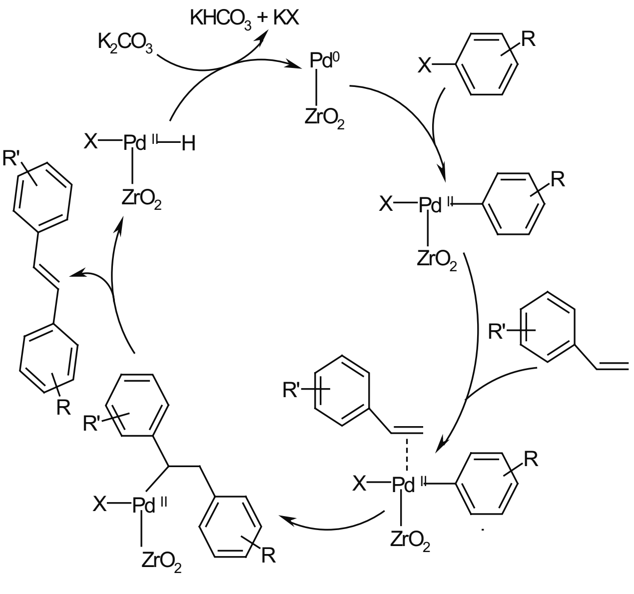
Experimental

All chemicals were reagent grade and purchased from Aldrich or Lancaster Synthesis. All reactions were performed under an

Table 4 Preparation of styrenes and stilbenes

Entry no.	Substrates used		Time/h	Product[a]	Yield/%
	Aryl halide	Olefin			
1	4-Iodoanisole	Acrylamide	4	4-Methoxy-*trans*-cinnamic amide	80
2	4-Iodoanisole	Methyl acrylate	4	Methyl 4-methoxy-*trans*-cinnamate	75
3	4-Iodoanisole	Acrylonitrile	3.5	4-Methoxycinnamonitrile	70
4	4-Bromoacetophenone	Methyl acrylate	5	Methyl 4-acetyl-*trans*-cinnamate	75
5	4-Iodoanisole	Methyl 3-(4-methoxy-phenyl)-acrylate	6	Methyl 3,3-bis-(4-methoxy-phenyl)-acrylate	70
6	Iodobenzene	Styrene	7	*trans*-Stilbene	82
7	Bromobenzene	Styrene	15	*trans*-Stilbene	65
8	Chlorobenzene	Styrene	30	*trans*-Stilbene	5
9	3-Bromoacetophenone	Styrene	9	3-Acetyl-*trans*-stilbene	65
10	4-Bromoacetophenone	Styrene	7	4-Acetyl-*trans*-stilbene	68
11	4-Iodoanisole	Styrene	4	4-Methoxy-*trans*-stilbene	80
12	4-Iodoanisole	4-Methoxystyrene	5	4,4′-Dimethoxy-*trans*-stilbene	55
13	4-Iodoanisole	3,5-Dimethoxystyrene	5	3,4′,5-Trimethoxy- *trans*-stilbene	60
14	4-Iodoanisole	3,4,5-Trimethoxystyrene	4		50
15	3,4,5-Trimethoxyiodobenzene	Styrene	7		70
16	3,4,5-Trimethoxyiodobenzene		7		49
17	3,4,5-Trimethoxyiodobenzene		7		55
18	3,4,5-Trimethoxyiodobenzene		5		45

[a]The products were characterised by ^1H NMR, ^{13}C NMR, IR and mass spectroscopy.



Scheme 3

inert atmosphere of nitrogen. Reactions were monitored by TLC. For the structural determination of the Heck reaction products, ^1H NMR spectra were determined on a Bruker AC-200, 300, 400 or 500 spectrometer (200, 300, 400 or 500 MHz) with TMS as the internal standard. For *para* substituted benzene rings, which form an AA'XX', system, $J^* = J_{23} = J_{56}$. IR spectra were recorded on an ATI MATTSON RS-1- FT-IR spectrometer. MS spectra were determined on API-QSTAR Pulsar Mass Spectrometer. Melting points are uncorrected. Elemental analysis was done on FLASH EA 1112 SERIES-CHNS Analyser in the microanalysis section of the National Chemical Laboratory.

Synthesis and characterisation of the catalyst [Pd (2.5 wt%)/ZrO$_2$]

Pd/ZrO_2 was prepared[37] by impregnating $PdCl_2$ from its aqueous solution on zirconia [prepared from zirconium nitrate by its hydrolysis with ammonium hydroxide, followed by washing and drying the zirconium hydroxide and then calcining it at 500 °C for 3 h] support by the incipient wetness impregnation technique. In a typical procedure, aq. $PdCl_2$ (2.08 ml from the stock solution made by dissolving 0.083 g $PdCl_2$ in 250 ml water) was taken in a 100 ml crucible. The crucible was kept on a boiling water bath. Zirconia (2 g) was added slowly into that solution. After impregnation, the wet catalyst mass was dried at 100 °C for 4 h and then calcined in static air in a muffle furnace at 500 °C for 3 h. The resulting catalyst mass was further treated with an ammoniacal solution of hydrazine on a water bath to transform the PdO (from the catalyst) to metallic Pd. The presence of a metallic Pd phase in the reduced catalyst was confirmed by X-ray diffraction. The TEM picture of these particles indicated the presence of metallic Pd with particle size $d = 15.9 \pm 0.5$ nm.

The characterisation of the catalyst was performed by means of X-ray diffraction (XRD) [using a Phillips Diffractometer (1730 series) with CuKα radiations], and transmission electron microscopy (TEM) (at 200 kV in a JEOL 1200 EX using a CCD camera).

General procedure for preparation of stilbenes

To 5 ml of DMF, were added 2.5 mmol of aryl halide, 6.8 mmol of alkene, 10% by weight (of aryl halide) of palladium on zirconia catalyst and 7.23 mmol of K_2CO_3. The mixture was stirred at 140 °C under a nitrogen atmosphere for an appropriate time and the reaction was monitored by TLC. After completion of reaction, the catalyst was separated by filtration and washed with DMF (3 × 3 ml). Then the filtrate was diluted with water followed by extraction with ethyl acetate to give the crude product, which was subsequently purified by column chromatography on silica gel with petroleum ether/ethyl acetate as eluent.

General procedure for preparation of substituted styrenes used as starting materials

Ph_3P^+–Me–Br^- (1.2 equiv, 10.9 g, 30 mmol) was taken in a two-neck round bottom flask. Dry tetrahydrofuran (100 ml) was added under a nitrogen atmosphere, the mixture was stirred for five minutes, *n*-butyllithium (1.2 equiv, 2.88 ml, 30.5 mmol) was added dropwise at –78 °C (dry ice + acetone) over 15 minutes and the reaction mixture was stirred at 25 °C for 3 h. Then the substituted benzaldehyde (1 equiv, 5 g, 25.5 mmol) in dry tetrahydrofuran (50 ml) was added dropwise and stirred at 25 °C for 20 min. The reaction mixture was heated at 60 °C for 10 h and the reaction was monitored by TLC. After completion of reaction, the reaction mixture was quenched with methanol and the mixture was allowed to cool to room temperature. Methanol was removed under reduced pressure and the residue was extracted with ethyl acetate. The organic layer was washed with water followed by brine, dried over sodium sulfate and concentrated to dryness under reduced pressure using a rotary evaporator, The crude residue was purified by column chromatography using silica gel (petroleum ether: ethyl acetate as eluent) to collect the pure product.

Spectroscopic and analytical data

trans-*Stilbene*:[40,41] White crystalline solid; m.p. 123 °C (Lit.,[42] 124 °C); ^1H NMR ($CDCl_3 + CCl_4$, 200 MHz): δ 7.57 (d, J = 8 Hz, 4H), 7.47–7.25 (m, 6H), 7.16 (s, 2H); ^{13}C NMR ($CDCl_3 + CCl_4$, 200 MHz): δ 137.3 (2C), 128.7 (4C), 127.6 (2C), 126.5 (4C); IR (chloroform,): 3019, 1600, 1497, 1452, 961, 758 cm^{-1}.

4-Methoxy-trans-*cinnamic amide*:[43] Off-white powder; m.p. 199–200 °C (Lit.,[43] 199–201 °C); ^1H NMR (DMSO-d_6, 300 MHz): δ 7.33 (m, J^* = 8 Hz, 2H), 7.29 (br s, 1H), 7.20 (d, J = 15 Hz, 1H), 6.84 (br s, 1H), 6.80 (m, J^* = 8 Hz, 2H), 6.30 (d, J = 15 Hz, 1H), 3.61 (s, 3H); ^{13}C NMR (DMSO-d_6, 300 MHz): δ 167.3, 160.5, 139.1, 129.2 (2C), 127.6, 119.9, 114.5 (2C), 55.4; mass (+ TOF): 178.11 [M + 1], 200.04 [M + Na]; Found: C, 67.70; H, 6.24; N, 7.80. Calc. for $C_{10}H_{11}O_2N$: C, 67.78; H, 6.20; N, 7.90%**;** IR (chloroform): 3461, 3358, 3020, 1662, 1602, 1513, 1425 cm^{-1}.

Methyl 4-methoxy-trans-*cinnamate*:[40] White solid; m.p. 86–87 °C (Lit.,[44] 87–89 °C); ^1H NMR ($CDCl_3 + CCl_4$, 300 MHz): δ 7.64 (d, J = 15 Hz, 1H), 7.47 (m, J^* = 9 Hz, 2H), 6.89 (m, J^* = 9 Hz, 2H), 6.30 (d, J = 15 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H); ^{13}C NMR ($CDCl_3 + CCl_4$, 200 MHz): δ 167.3, 161.2, 144.3, 129.6 (2C), 127.0, 115.2, 114.2 (2C), 55.0, 51.3; mass (+ TOF): 192.78 [M^+], 214.67 [M + Na]; IR (chloroform): 2963, 1714, 1635, 1604, 1513, 1330, 1288, 1256, 1174, 1026, 984, 836, 755 cm^{-1}.

4-Methoxycinnamonitrile:[45] Faint yellow semisolid (Lit.,[45] m.p. 61–62 °C); ^1H NMR ($CDCl_3 + CCl_4$, 200 MHz) for (E) isomer: δ 7.27 (m, J^* = 9 Hz, 2H), 7.19 (d, J = 16 Hz, 1H), 6.80 (m, J^* = 9 Hz, 2H), 5.59 (d, J = 16 Hz, 1H), 3.73 (s, 3H); ^1H NMR ($CDCl_3 + CCl_4$, 200 MHz) for (Z) isomer: δ 7.67 (d, J = 9 Hz, 2H), 6.92 (d, J = 12 Hz, 1H), 6.81 (d, J = 9 Hz, 2H), 5.17 (d, J = 12 Hz, 1H), 3.73 (s, 3H); Found: C, 75.48; H, 5.60; N, 8.74%. Calc. for $C_{10}H_9ON$: C, 75.46; H, 5.69; N, 8.79%; IR (chloroform): 2213 cm^{-1}.

Methyl 3,3-bis(4-methoxyphenyl)-acrylate:[44] Semisolid (Lit.,[46] oil); ^1H NMR ($CDCl_3 + CCl_4$, 200 MHz): δ 7.29 (m, J^* = 9 Hz, 2H), 7.20 (m, J^* = 9 Hz, 2H), 6.96 (m, J^* = 9 Hz, 2H), 6.88 (m, J^* = 9 Hz, 2H), 6.27 (s, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.68 (s, 3H); ^{13}C NMR ($CDCl_3 + CCl_4$, 300 MHz): δ 165.9, 160.3, 159.2, 156.1, 133.4, 130.6, 130.4 (2C), 129.4 (2C), 113.8, 113.2 (2C), 112.7 (2C), 54.6, 54.5, 50.3; Found: C, 72.40; H, 6.00%. Calc. for $C_{18}H_{18}O_4$: C, 72.48; H, 6.04%; IR (chloroform): 3019, 1710, 1633, 1512, 1249, 116 cm^{-1}.

4-Acetyl-trans-*stilbene*:[41,47] White solid; m.p. 131 °C (Lit.,[47] 132 °C); ^1H NMR ($CDCl_3 + CCl_4$, 200 MHz): δ 8.02 (m, J^* = 9 Hz, 2H), 7.66 (m, J^* = 9 Hz, 2H), 7.61(m, J^* = 9 Hz, 2H), 7.51–7.32 (m, 3H), 7.26 (d, J = 15 Hz, 1H), 7.19 (d, J = 15 Hz, 1H), 2.69 (s, 3H); ^{13}C NMR ($CDCl_3 + CCl_4$, 200 MHz): δ 196.9, 141.9, 136.7, 135.9, 131.4, 128.8 (2C), 128.7 (2C), 128.3, 127.4, 126.7 (2C), 126.4 (2C), 26.4; mass (+ TOF): 223.872 [M + 1], 245.810 [M + Na]; Found: C, 86.53; H, 6.30%. Calc. for $C_{16}H_{14}O$: C, 86.45; H, 6.34%; IR (chloroform): 3019, 1676, 1601, 1267, 964, 755 cm^{-1}.

Methyl 4-acetyl-trans-*cinnamate*:[48] Off-white solid; m.p. 104 °C (Lit.,[49] 105–106 °C); ^1H NMR ($CDCl_3 + CCl_4$, 200 MHz): δ 7.97 (m, J^* = 9 Hz, 2H), 7.70 (d, J = 16 Hz, 1H), 7.61 (m, J^* = 9 Hz, 2H), 6.52 (d, J = 16 Hz, 1H), 3.83 (s, 3H), 2.62 (s, 3H); ^{13}C NMR ($CDCl_3 + CCl_4$, 200 MHz): δ 196.3, 166.2, 142.7, 138.2, 137.6, 128.4 (2C), 127.7(2C), 119.9, 51.3, 26.1; Found: C, 70.47; H, 5.80%. Calc. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92%; IR (chloroform): 3020, 1717, 1684, 1266, 758 cm^{-1}.

3-Acetyl-trans-*stilbene*:[50] Off-white solid; m.p. 78 °C (Lit.,[51] 79–80 °C); ^1H NMR ($CDCl_3 + CCl_4$, 200 MHz): δ 8.05 (t, J = 2 Hz, 1H), 7.83–7.62 (m, 2H), 7.52–7.20 (m, 6H), 7.16 (d, J = 16 Hz, 1H), 7.07 (d, J = 16 Hz, 1H), 2.60 (s, 3H); ^{13}C NMR ($CDCl_3 + CCl_4$, 400 MHz): δ 197.7, 137.9, 137.6, 136.9, 130.8, 130.0, 128.9, 128.7 (2C), 128.0, 127.5, 127.4, 126.6 (2C), 126.2, 26.6; mass (+ TOF): 223.872 [M + 1], 245.810 [M + Na]; Found: C, 86.53; H, 6.30%. Calc. for $C_{16}H_{14}O$: C, 86.45; H, 6.34%; IR (chloroform): 3019, 1678, 1602, 1560, 1360, 1267, 963, 757 cm^{-1}.

4-Methoxy-trans-*stilbene*:[41] Off-white solid; m.p. 137 °C (Lit.,[42] 136 °C); ^{1}H NMR (CDCl$_3$ + CCl$_4$, 200 MHz): δ 7.57–7.46 (m, 4H), 7.39 (t, J = 8 Hz, 2H), 7.31–7.22 (m, 1H), 7.12 (d, J = 16 Hz, 1H), 7.00 (d, J = 16 Hz, 1H), 6.94 (m, J^* = 8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (CDCl$_3$ + CCl$_4$, 400 MHz): 159.4, 137.8, 130.3, 128.7(2C), 128.3, 127.7 (2C), 127.2, 126.7, 126.3 (2C), 114.2 (2C), 55.2; GCMS: 210; Found: C, 85.57; H, 6.70%. Calc. for $C_{15}H_{14}O$: C, 85.68; H, 6.71%; IR (chloroform): 3019, 1602, 1512, 929, 758 cm^{-1}.

trans-*1-Phenyl-2-(3,4,5-trimethoxyphenyl)ethene*:[52] White solid; m.p. 105 °C (Lit.,[52] 105–106 °C); ^{1}H NMR (CDCl$_3$ + CCl$_4$, 200 MHz): δ 7.45–7.38 (m, 2H), 7.32–7.15 (m, 3H), 6.96 (d, J = 16 Hz, 1H), 7.88 (d, J = 16 Hz, 1H), 6.64 (s, 2H), 3.84 (s, 6H), 3.79 (s, 3H); ^{13}C NMR (CDCl$_3$ + CCl$_4$, 400 MHz): 153.4 (2C), 138.2, 137.2, 133.1, 128.8, 128.7 (2C), 128.2, 127.6, 126.4 (2C), 103.8 (2C), 60.9, 56.1 (2C); mass (+ TOF): 271.739 [M + 1], 293.765 [M + Na]; Found C, 75.44; H, 6.62%. Calc. for $C_{17}H_{18}O_3$: C, 75.55; H, 6.66%; IR (chloroform): 3019, 1584, 1420, 758 cm^{-1}.

trans-*1-(4-Methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)ethene*:[52] White solid; m.p. 154 °C (Lit.,[52] 152–155 °C); ^{1}H NMR (CDCl$_3$ + CCl$_4$, 200 MHz): δ 7.43 (m, J^* = 9 Hz, 2H), 6.97 (d, J = 16 Hz, 1H), 6.89 (m, J^* = 9 Hz, 2H), 6.87 (d, J = 16 Hz, 1H), 6.70 (s, 2H), 3.93 (s, 6H), 3.87 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (CDCl$_3$ + CCl$_4$, 400 MHz): 159.4, 153.5 (2C), 137.9, 133.5, 130.1, 127.8, 127.7 (2C), 126.7, 114.2 (2C), 103.6 (2C), 60.9, 56.2 (2C), 55.3; mass (+ TOF): 301.581 [M + 1], 323.590 [M + Na]; Found: C, 71.80; H, 6.60%. Calc. for $C_{18}H_{20}O_4$: C, 72.00; H, 6.66%; IR (chloroform): 3019, 1599, 1578, 1496, 1451, 961 cm^{-1}.

4,4'-Dimethoxy-trans-*stilbene*:[53] White solid; m.p. 210 °C (Lit.,[53] 208–209 °C); ^{1}H NMR (CDCl$_3$ + CCl$_4$, 200 MHz): δ 7.41 (m, J^* = 10 Hz, 4H), 6.92 (s, 2H), 6.87 (m, J^* = 10 Hz, 4H), 3.84 (s, 6H); ^{13}C NMR (CDCl$_3$ + CCl$_4$, 200 MHz): 159.0 (2C), 130.5 (2C), 127.4 (4C), 126.2 (2C), 114.1 (4C), 55.2 (2C); mass (+ TOF): 241.697[M + 1], 263.546 [M + Na]; Found: C, 80.0; H, 6.60%. Calc. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.66%; IR (chloroform): 3020, 1665, 1608, 1514 cm^{-1}.

trans-*1-(3*-tert-*Butyldimethylsilanyloxy-4-methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)ethene*: Semisolid; ^{1}H NMR (CDCl$_3$ + CCl$_4$, 200 MHz): δ 7.07–6.79 (m, 5H), 6.70 (s, 2H), 3.92 (s, 6H), 3.86 (s, 3H), 3.83 (s, 3H), 1.04 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (CDCl$_3$ + CCl$_4$, 500 MHz): 153.4 (2C), 150.8, 145.2, 137.8, 133.4, 130.5, 127.9, 126.7, 120.5, 118.6, 112.0, 103.4 (2C), 60.9, 56.1 (2C), 55.4, 25.8 (3C), 18.5, 4.5 (2C).

trans-*1-(3-Hydroxy-4-methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)-ethene*:[54] Off-white solid; m.p. 104 °C(Lit.,[54] 102–104 °C); ^{1}H NMR (CDCl$_3$ + CCl$_4$, 200 MHz): δ 7.12 (d, J = 2 Hz, 1H), 6.95 (dd, J = 8 Hz, 2 Hz, 1H), 6.91 (d, J = 16 Hz, 1H), 6.84 (d, J = 16 Hz, 1H), 6.82 (d, J = 8 Hz, 1H), 6.69 (s, 2H), 3.92 (s, 9H), 3.86 (s, 3H); ^{13}C NMR (CDCl$_3$ + CCl$_4$, 500 MHz): 153.1 (2C), 146.1, 145.6, 137.5, 133.0, 130.8, 127.5, 126.8, 118.8, 111.5, 110.3, 103.2 (2C), 60.6, 55.7 (2C), 55.6; mass (+ TOF): 317.565[M + 1], 339.581 [M + Na]; Found: C, 68.30; H, 6.39%. Calc. for $C_{18}H_{20}O_5$: C, 68.35; H, 6.32%.

3,4',5-Trimethoxy-trans-*stilbene*:[55] White solid; m.p. 57 °C (Lit.,[55] 55–57 °C); ^{1}H NMR (CDCl$_3$ + CCl$_4$, 200 MHz): δ 7.44 (m, J^* = 8 Hz, 2H), 7.04 (d, J = 16 Hz, 1H), 6.90 (d, J = 16 Hz, 1H), 6.89 (m, J^* = 8 Hz, 2H), 6.63 (d, J = 2 Hz, 2H), 6.36 (t, J = 2 Hz, 1H), 3.84 (s, 9H); ^{13}C NMR (CDCl$_3$ + CCl$_4$, 400 MHz): 161.0 (2C), 159.4, 139.7, 130.0, 128.7, 127.8 (2C), 126.7, 114.1 (2C), 104.4 (2C), 99.7, 55.2 (3C); mass (+ TOF): 271.409 [M + 1], 293.426 [M + Na]; Found: C, 75.55; H, 6.71%. Calc. for $C_{17}H_{18}O_3$: C, 75.56; H, 6.67%; IR (chloroform): 3019, 1599, 758 cm^{-1}.

trans-*1-(3,5-Dimethoxyphenyl)-2-(3,4,5-trimethoxyphenyl)ethene*:[55] White solid; m.p. 138 °C (Lit.,[55] 136–138 °C); ^{1}H NMR (CDCl$_3$ + CCl$_4$, 200 MHz): δ 7.01 (d, J = 16 Hz, 1H), 6.90 (d, J = 16 Hz, 1H), 6.72 (s, 2H), 6.65 (d, J = 2 Hz, 2H), 6.38 (t, J = 2 Hz, 1H), 3.93 (s, 6H), 3.87 (s, 3H), 3.84 (s, 6H); ^{13}C NMR (CDCl$_3$ + CCl$_4$, 500 MHz): 161.1 (2C), 153.5 (2C), 139.2, 132.9 (2C), 129.2, 128.2, 104.6 (2C), 103.8 (2C), 100.1, 60.9, 56.1 (2C), 55.3 (2C); mass (+ TOF): 331.538 [M + 1], 353.536 [M + Na]; Found: C, 69.07; H, 6.70%. Calc. for $C_{19}H_{22}O_5$: C, 69.09; H, 6.67%.

trans-*1-(3, 4-Dimethylphenyl)-2-(3,4,5-trimethoxyphenyl)-ethene*:[56] Off-white solid; ^{1}H NMR (CDCl$_3$ + CCl$_4$, 200 MHz): δ 7.29 (d, J = 2 Hz, 1H), 7.24 (dd, J = 8 Hz, 2 Hz, 1H), 7.12 (d, J = 8 Hz, 1H), 7.01 (d, J = 16 Hz, 1H), 6.93 (d, J = 16 Hz, 1H), 6.72 (s, 2H), 3.93 (s, 6H), 3.88 (s, 3H), 2.31 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (CDCl$_3$ + CCl$_4$, 400 MHz): 153.4 (2C), 137.9, 136.6, 136.1, 134.9, 133.4, 129.9, 128.2, 127.7, 127.5, 124.0, 103.6 (2C), 60.8, 56.1 (2C), 19.9, 19.6; mass (+ TOF): 299.890 [M + 1], 321.825 [M + Na], 337.756 [M + K]; Found: C, 76.46; H, 7.41%. Calc. for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43%; IR (chloroform): 3020, 1653, 758 cm^{-1}.

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