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On the synthesis of dimethoxybenzyl cinnamates, monomers for electron transfer polymers

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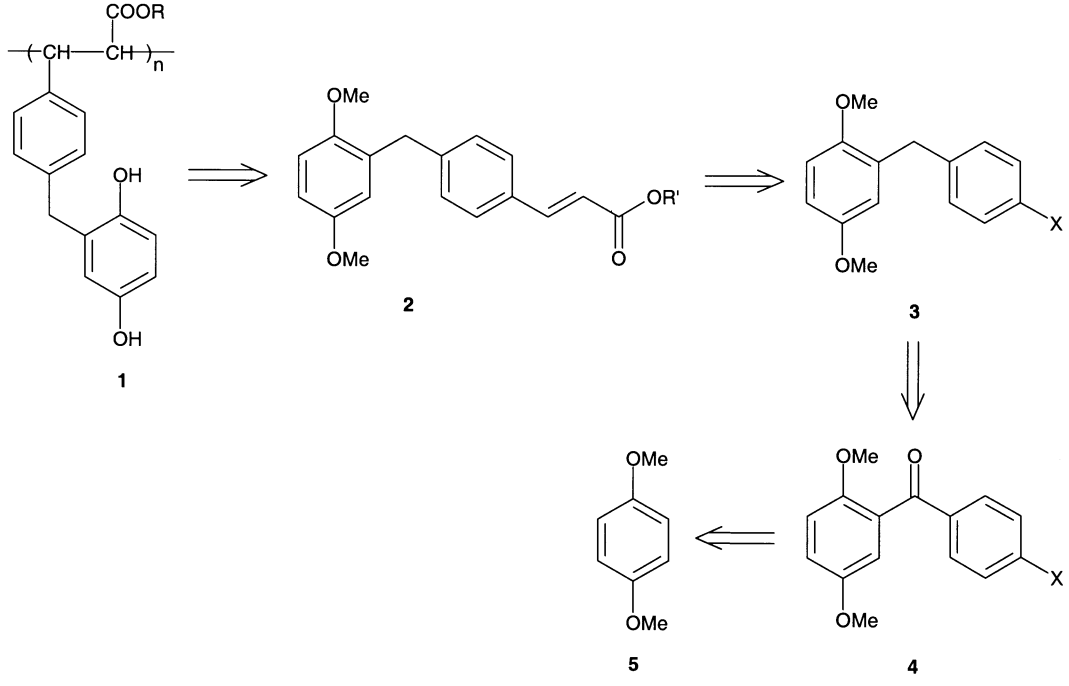
Abstract—An economical way to obtain new monomers, precursors of electron transfer polymers, is described. These monomers were obtained by a Heck reaction between amino or halogeno-2,5-dimethoxydiarylmethane and methylacrylate. Different routes for the ionic reduction of various acetophenones to the corresponding diarylmethanes were studied. The yields and the nature of the by-products was stongly dependent upon the reaction conditions. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Insoluble polymers are an important class of reagents developed for the halogenation,[1] oxidation,[2] hydrogenation[3] or reduction[4] of organic compounds. Their usefulness arises from the ability to recycle the spent polymer[3] and from an easy reaction workup[2,5] since the products of reaction can be isolated by filtration of the resin. These polymeric reagents always require the preparation of macromolecular backbone[6] or tedious modification of a commercial one.[1,5,7] Particularly, electron transfer polymers (ETP) were obtained by addition of redox functionalities to a preformed



Scheme 1.

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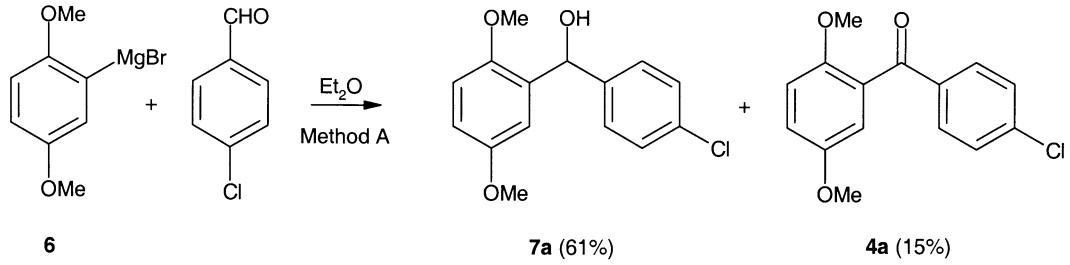
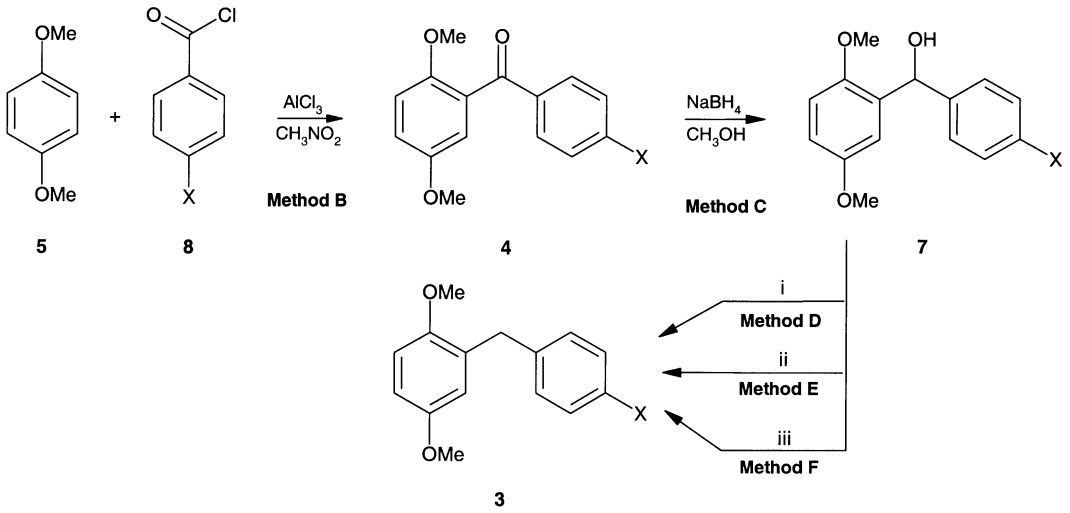


Scheme 2.



Scheme 3. Reagents and conditions: (i) $NaBH_4$, CF_3CO_2H, CH_2Cl_2, 25°C; (ii) Et_3SiH, CF_3CO_2H, CCl_4, 55°C; (iii) Et_3SiH, CF_3SO_3H, CH_2Cl_2, 25°C.

chloromethylated resin.[8] It was observed that the results obtained with these resins are closely related to the number of redox functions on the polymer matrix.[9]

On the other hand, starting from the polymer backbone, four steps are necessary to synthesize the new material with only 60–80% of grafted redox functions.[8,9] Therefore, there is a need for new methods giving maximal density of redox functionalities. We prepared polymers **1** with one hydroquinone group per monomeric unit.[10] In this paper, the preparation of monomers **2** and of their precursors **3** as well as the structure of some by-products obtained during these syntheses are described (Scheme 1).

2. Results and discussion

2.1. Preliminary reactions

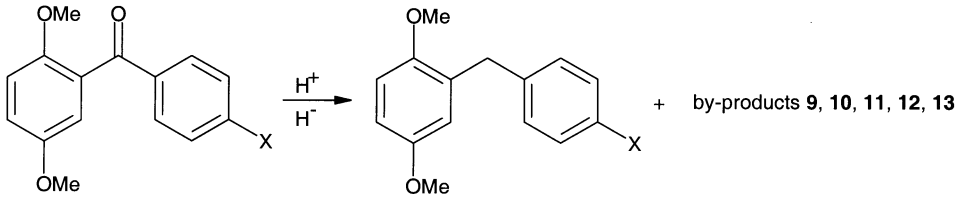
The Friedel–Crafts alkylation of 1,4-dimethoxybenzene **5** with chloromethyl substituted benzenes or chloromethylstyrene was first studied as a way to diarylmethanes **2** or **3**. Under these conditions ($ZnCl_2/CH_2Cl_2$[8a] or montmorillonite $K_{10}/ZnCl_2/CCl_4$[11]), a mixture of compounds was obtained. Other reactions leading to diarylmethanes were then investigated.

Reduction of diarylcarbinols **7** can yield such compounds.

Table 1. Acylation then reduction of *p*-dimethoxybenzene **5**

Entry	X	Method B $AlCl_3/MeNO_2$ **4** (%)[a]	Method C $NaBH_4$/MeOH **7** (%)[a]	Method D $NaBH_4/CF_3CO_2$ **3** (%)[a,b]	Method E Et_3SiH/CF_3CO_2H **3** (%)[a,c]	Method F Et_3SiH/CF_3SO_3H **3** (%)[a,d]
1	Cl	90	93	47	80	84
2	Br	85	92	53	80	90
3	I	86	88		89	92
4	CH_3	85	89		89	93
5	NO_2	85	90		89	

[a] Isolated yields.
[b] The ratio alcohol/$NaBH_4/CF_3CO_2H$ was 1/5/35.
[c] The ratio alcohol/Et_3SiH/CF_3CO_2H was 1/2/10.
[d] The ratio alcohol/Et_3SiH/CF_3SO_3H was 1/1.2/0.3.



4 3

Scheme 4.

We tried to obtain these carbinols via Grignard reaction. In that way, the reaction of 4-chlorobenzaldehyde, chosen as a model compound, with Grignard reagent **6** gives a mixture of **7a** (61%) and of ketone **4a** (15%)[12–14] (Scheme 2).

2.2. Three steps synthesis of diarylmethanes 3

Since the previous methods cannot lead to diarylmethanes **2**, **3** with good yields, a multisteps sequence (Scheme 3) starting from acid chlorides **8** was used. Substituents of **8** (X=Cl, Br, I, CH_3, NO_2) were chosen because their modifications can lead to ethylenic compounds **2**. Friedel–Crafts reaction of 1,4-dimethoxybenzene **5**[15] with yttrium triflate as catalyst[16] gives 67% of **4b** (X=Br) but yields of benzophenones **4** higher than 85% were always obtained with $AlCl_3$ in nitromethane[17] (Table 1, method B). Reduction of ketones **4** by $NaBH_4$ in methanol gives benzhydrols **7** in very good yields (Table 1, method C). Three methods for the ionic reduction[18] of diarylcarbinols **7** were tried. Reaction with $NaBH_4$ and trifluoroacetic acid[19] provide a complex mixture whose main product **3** (X=Cl, Br) was isolated only in average yields (Table 1, method D). On the other hand, triethylsilane and trifluoroacetic acid[20] or triflic acid[21] produce compounds **3** in good yield (Scheme 3, Table 1, methods E and F).

2.3. Two steps synthesis of diarylmethanes 3

The route described above was interesting because of the high yields obtained, but had the drawback of three separated steps for going from dimethoxybenzene **5** to diarylmethane **3**. Thus the one-step ionic reduction of ketones **4** to compound **3** was examined (Scheme 4, Table 2). Reaction of benzophenone with $NaBH_4/CF_3CO_2H$ has been described[19] but, when this method was used with compound **4**, the diarylmethanes formed **3** were not stable in the reaction medium, giving by-products **10** and **12** (Fig. 1) in a time dependent amount (compare Table 2, entries 1 and 2 or 3

Table 2. Reduction of benzophenones **4** to diphenylmethanes **3**

Entry	Method	X	Ratio[a]	Hydride	Acid	Solvent	Temp (°C)	Time (h)	X	**3** (%)[b]	**9** (%)[b]	**10** (%)[b]	**11** (%)[b]	**12** (%)[b]
1	G	Cl	1:10:70	$NaBH_4$	CF_3CO_2H	CH_2Cl_2	25	12	Cl	61			39	
2	G	Cl	1:10:70	$NaBH_4$	CF_3CO_2H	CH_2Cl_2	25	44	Cl	31[c]	10[c]		40[c]	
3	G	Br	1:10:70	$NaBH_4$	CF_3CO_2H	CH_2Cl_2	25	12	Br	63			17	
4	G	Br	1:10:70	$NaBH_4$	CF_3CO_2H	CH_2Cl_2	25	18	Br	47[c]			38[c]	
5	H	Cl	1:3:10	Et_3SiH	CF_3CO_2H	CCl_4	55	6	Cl	83				
6	H	Br	1:3:10	Et_3SiH	CF_3CO_2H	CCl_4	55	6	Br	82				
7	H	Cl	1:2:15	Et_3SiH	CF_3CO_2H	CCl_4	55	6	Cl	100				
8	H	Br	1:2:15	Et_3SiH	CF_3CO_2H	CCl_4	55	6	Br	100				
9	H	CH_3	1:2:15	Et_3SiH	CF_3CO_2H	CCl_4	55	6	CH_3	84[c]				
10	H	NO_2	1:2:15	Et_3SiH	CF_3CO_2H	CCl_4	55	6	NO_2	90[c]				
11	I	Cl	1:10:6	Et_3SiH	CF_3SO_3H	CH_2Cl_2	25	1	Cl	81	2			17
12	I	Cl	1:10:6	Et_3SiH	CF_3SO_3H	CH_2Cl_2	25	1.5	Cl	56	15	11		18
13	I	Br	1:10:6	Et_3SiH	CF_3SO_3H	CH_2Cl_2	25	1.5	Br	56	22			21
14	I	Cl	1:2.2:0.3	Et_3SiH	CF_3SO_3H	CH_2Cl_2	25	0.75	Cl	84[c]				
15	I	Br	1:2.2:0.3	Et_3SiH	CF_3SO_3H	CH_2Cl_2	25	0.75	Br	83[c]				
16	I	I	1:2.2:0.3	Et_3SiH	CF_3SO_3H	CH_2Cl_2	25	0.75	I	95[c]				
17	I	CH_3	1:2.2:0.3	Et_3SiH	CF_3SO_3H	CH_2Cl_2	25	0.75	CH_3	89[c]				
18	J	Cl	1:2.2:1	Et_3SiH	$AlCl_3$	CH_3NO_2	25	6	Cl	92[c]				
19	J	Br	1:2.2:1	Et_3SiH	$AlCl_3$	CH_3NO_2	25	6	Br	92[c]				
20	J	NO_2	1:2.2:1.1	Et_3SiH	$AlCl_3$	CH_3NO_2	25	6	NO_2	43[c]	15[c]			15[c]
21	K	Cl	1:3.5:15	PMHS	CF_3SO_3H	CH_3NO_2	25	200	Cl	53[d]				
22	K	Cl	1:3.5:15	PMHS	CF_3SO_3H	CH_2Cl_2	25	48	Cl	70[c]	7			7
23	K	Cl	1:3:0.3	PMHS	CF_3SO_3H	CH_2Cl_2	25	7	Cl	89[c]				
24	K	Br	1:3:0.3	PMHS	CF_3SO_3H	CH_2Cl_2	25	7	Br	85[c]				
25	K	I	1:3:0.3	PMHS	CF_3SO_3H	CH_2Cl_2	25	7	I	85[c]				
26	L	Cl	1:3:1.1	PMHS	$AlCl_3$	CH_3NO_2	25	480	Cl	9[c,e]				
27	L	Cl	1:3:1.1	PMHS	$AlCl_3$	CH_2Cl_2	25	40	Cl	75[c]				
28	L	NO_2	1:3:1.1	PMHS	$AlCl_3$	CH_2Cl_2	25	6	NO_2	79[c]				

[a] Refers to the ratio ketone **4**/hydride/acid.
[b] Yields were determined by ^1H NMR or HPLC.
[c] Isolated yields.
[d] 47% of recovered ketone.
[e] 20% of recovered ketone and 71% of compound **13** (Fig. 1) was isolated.

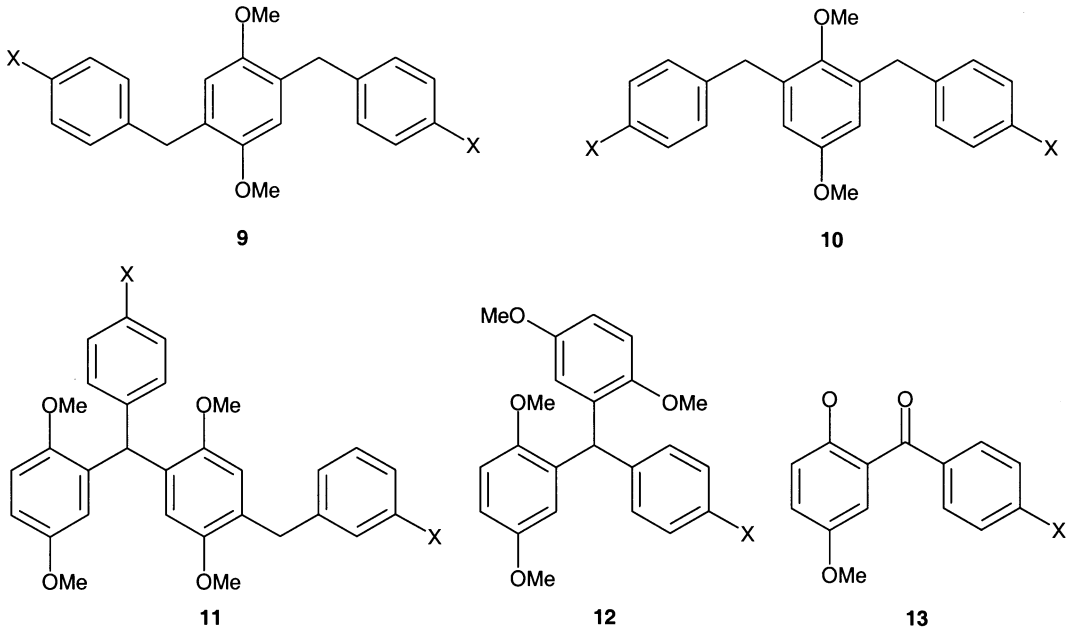
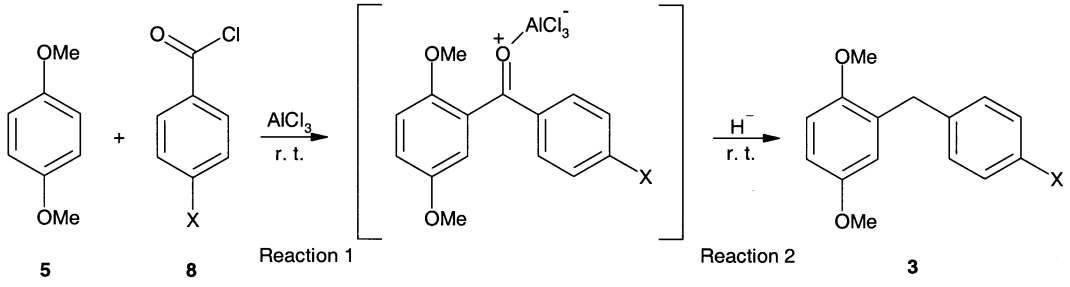


Figure 1.

and 4). Other conditions for the ionic reduction of ketones **4** were then tried; triethylsilane, in the presence of trifluoroacetic acid[18,22] gave the best yield of diphenylmethanes **3** when the ratio ketone/Et_3SiH/CF_3CO_2H was changed from 1/3/10 to 1/2/5 (compare Table 2, entries 5 and 7 or 6 and 8).

Other acids were also tested for these ionic reductions. By using triethylsilane with triflic acid,[21] the formation of by-products **9**, **10**, **12** was time dependent (compare Table 2, entries 11 and 12) and was suppressed when the reaction was performed for 45 min while the ratio ketone/hydride/acid was varied from 1/10/6[21] to 1/2.2/0.3. Almost quantitative yields of **3a** and **3b** (X=Cl, Br, Table 2, entries 18 and 19) were also obtained by using $AlCl_3$ as the acid,[23] but for

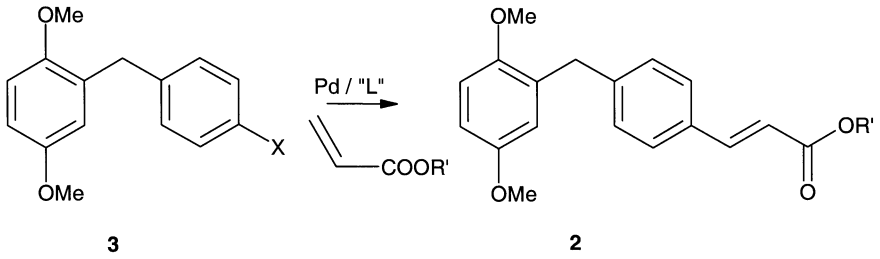


Scheme 5.

Table 3. Acylation/reduction of *p*-dimethoxybenzene **5**

Entry	Method	X	Hydride	Solvent	Ratio[a]	Time (h) Reaction 1	Time (h) Reaction 2	**3** Isolated (%)
1	M	Cl	Et_3SiH	CH_3NO_2	1:3	1	2	90
2	M	Br	Et_3SiH	CH_3NO_2	1:3	1	2	92
3	M	NO_2	Et_3SiH	CH_3NO_2	1:2.2	1	2	43[b]
4	N	Cl	Et_3SiH	CH_2Cl_2	1:3	1.5	12	75
5	O	Cl	PMHS	CH_2Cl_2	1:3.5	1.5	40	70[c]
6	O	Cl	PMHS	CH_2Cl_2	1:3.5	1.5	12	75
7	O	Br	PMHS	CH_2Cl_2	1:3.5	1.5	12	77
8	O	I	PMHS	CH_2Cl_2	1:3.5	1.5	12	77
9	O	CH_3	PMHS	CH_2Cl_2	1:3.5	1.5	12	70
10	O	NO_2	PMHS	CH_2Cl_2	1:3	1.5	6	70
11	P	Cl	PMHS	$C_6H_5NO_2$	1:3	1	960	7[d]

[a] Refers to the ratio of the hydride vs benzophenones **4**.
[b] Compounds **9** (15%) and **12** (15%) were isolated.
[c] 10% of by-product **9** was isolated.
[d] 50% of ketone **4** and 34% of **13** were also isolated.



Scheme 6.

Table 4. Synthesis of monomer **2**

Entry	Method	X	R′	Catalyst/'L'	Solvent	**2** (%) Isolated
1	Q	Cl	Et	$Pd(OAc)_2/PPh_3$	nBu_3N	0
2	Q	Br	Et	$Pd(OAc)_2/PPh_3$	nBu_3N	27
3	R	Br	Et	$Pd(OAc)_2/PPh_3$	nBu_3N	37
4	R	I	Et	$Pd(OAc)_2/PPh_3$	nBu_3N	73
5	R	I	Me	$Pd(OAc)_2/PPh_3$	nBu_3N	75
6	S	Br	Me	MK_{10}–Pd–Cu	nBu_3N	16
7	T	I	Me	MK_{10}–Pd–Cu	DMF	93
8	T	I	Et	MK_{10}–Pd–Cu	DMF	85
9	U	NH_2	Me	MK_{10}–Pd–Cu	CH_3CO_2H	70

3e (X=NO_2, Table 2, entry 20) by products **9** and **12** (Fig. 1) were also formed and the yield of **3e** was only 43%.

Analogs results were observed when polymethylhydrosiloxane (PMHS)[24] was used as the hydride, best yields being obtained by reducing the amount of triflic acid (compare Table 2, entries 22 and 23). With this acid, as well as with $AlCl_3$, best yields were obtained using methylene chloride as the solvent (compare Table 2, entries 21 and 22 or 26 and 27). Noteworthy also is the demethylation observed in the PMHS/$AlCl_3$/CH_3NO_2 reaction, giving phenol **13** (71%) (Table 2, entry 26). Not surprisingly, the reaction time was greater by using PMHS instead of Et_3SiH.

2.4. One pot synthesis of diarylmethanes 3

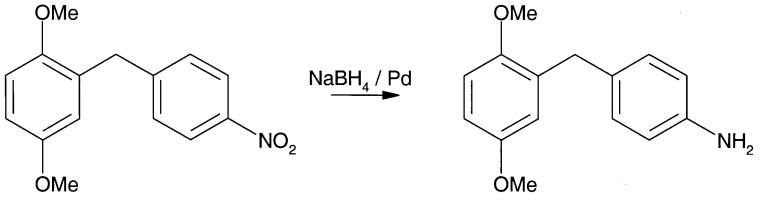
Given the good results obtained by using $AlCl_3$ as well for the acylation of *p*-dimethoxybenzene **5** (Table 1, method A) as for the reduction of benzophenones **4** (Table 2, entries 18–20 and 26–27), this acid was chosen for one-pot acylation/reduction[23] of compound **5** (Scheme 5). The best yields of diarylmethanes **3** (X=Cl, Br) were obtained by performing the reaction in nitromethane and using triethylsilane as the reducing agent (Table 3, entries 1 and 2). The formation of by-products **9** and **12** observed in these conditions for X=NO_2 was suppressed when PMHS[24] was used in dichloromethane (Table 3, entries 3 and 10), and medium yields were obtained for all the substituents tested. With nitrobenzene as solvent, even after a very long reaction time, benzophenone **4** and demethylated ketone **13** (Table 3, entry 11, Fig. 1) were mainly obtained.

2.5. Synthesis of monomers 2

The next step of the work was the synthesis of acrylates **2** by using a Heck reaction (Scheme 6). No condensation occurred between acrylic esters and diphenylmethanes **3** substituted by a Cl atom (Table 4, entry 1). Whatever the catalyst used, the yields were low when a Br was the leaving group (Table 4, entries 2, 3 and 6). The best results were obtained by using **3** (X=I) with $Pd(OAc)_2$[25] or Pd/Cu[26] modified montmorillonite K10 (MK10–Pd–Cu). Noteworthy, the newly described[27] reaction of an arylamino compound and acrylic ester with MK10–Pd–Cu as the catalyst, led to a good yield of monomer **2** (Table 4, entry 9). As for **3** (X=NH_2), it was obtained by reduction of **3** (X=NO_2) by $NaBH_4$/Pd (Scheme 7).

2.6. Structure and synthesis of by-products

Formation of by-products during Friedel–Crafts reaction[28,29] or during the ionic reduction of ketones[18,30] or benzhydrols[19,31] frequently occurred. In our work, by-products **9**–**12** were obtained (Fig. 1). Their structure were determined by elemental analysis, mass spectra and from the symmetry of their NMR spectra for compounds **9**, **10**, **12**. The structure of dimer **11a** was obtained from the NOESY and HETCOR correlations (Fig. 2).



Scheme 7.

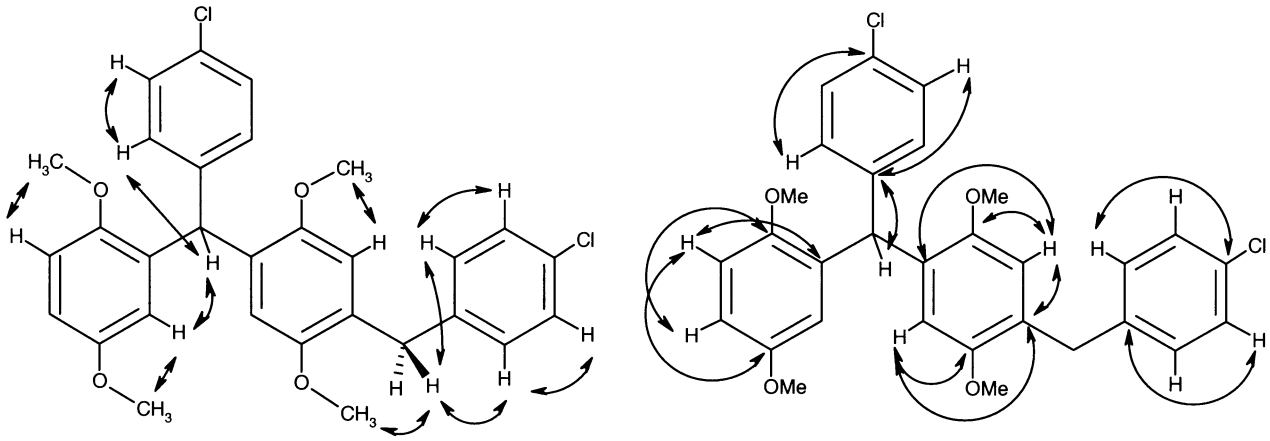
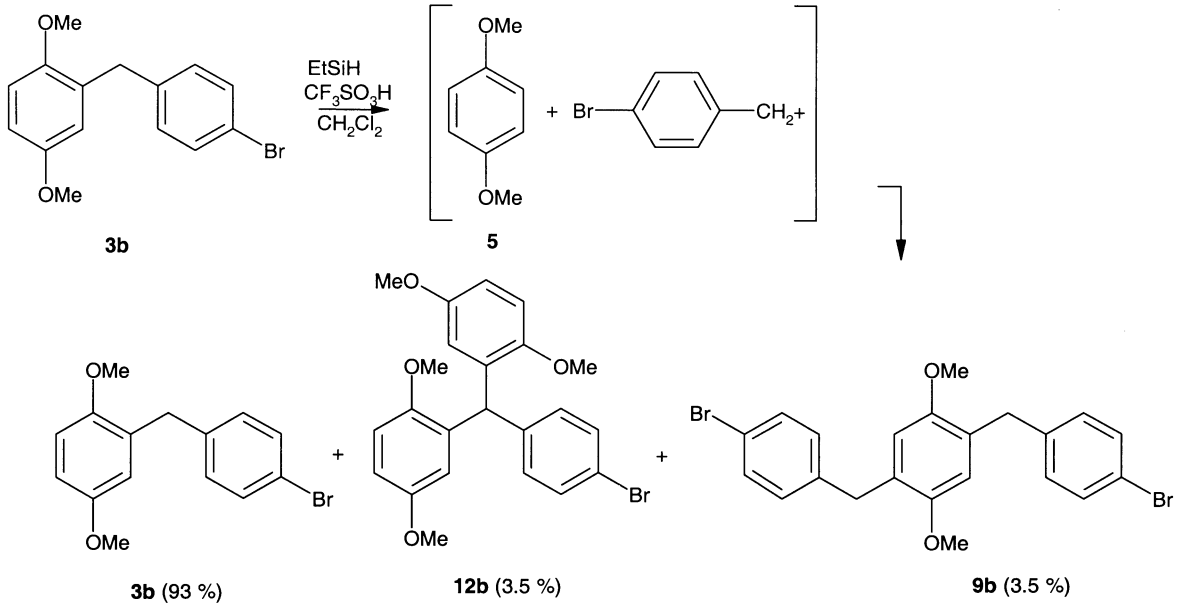
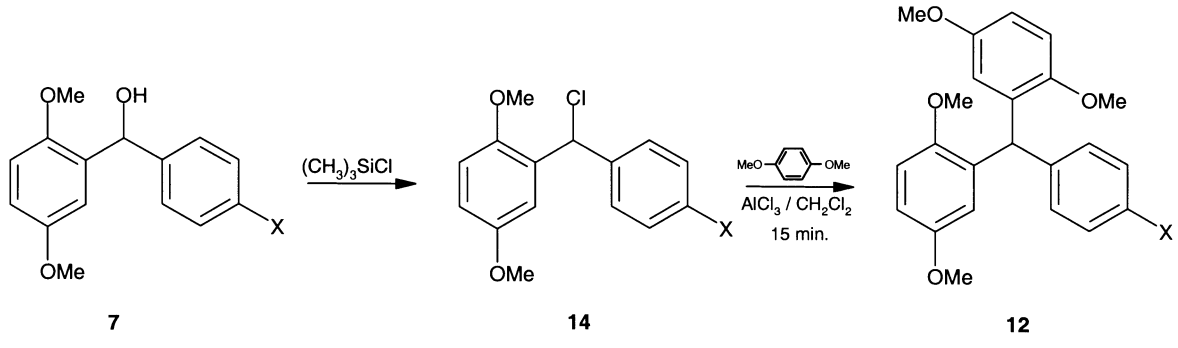


Figure 2. Main NOESY and long-range HETCOR correlations for compound **11a**.



Scheme 8.



Scheme 9.

Table 5. Synthesis of by-products **12**

Entry	X	**14** (%)	**12** (%)
1	Cl	90	68
2	Br	85	67
3	NO_2	93	63

Treatment of diarylmethane **3b** in the same conditions as for the ionic reductions (CF_3SO_3H, Et_3SiH, CH_2Cl_2) lead to the formation of 3.5% of products **9b** and **12b** (Scheme 8). This result allowed to know that the by-products are formed from the decomposition of the diarylmethanes as well as from the dimerization of diarylmethanols. Synthesis of triarylmethanes

12 from chloride **14** yields another proof of their structure: treatment of diarylcarbinols **7** with chlorotrimethylsilane lead to benzhydryl chlorides **14**[32] whose the Friedel–Crafts reaction with *p*-dimethoxybenzene **5** yields compounds **12** (Scheme 9, Table 5).

3. Conclusion

Various diarylmethanes are synthesized by reduction of the corresponding benzophenones with hydrides and acids, leading precursor **2** of electron transfer polymers in good global yield. From an economic point of view, the syntheses of diarylmethanes **3** by one-step reactions performed with $AlCl_3$ then PMHS in CH_2Cl_2 are particularly inexpensive and are very interesting for an industrial use.

4. Experimental

4.1. Materials

Melting points were determined with a Metler FP1 apparatus and are uncorrected. All reactions were monitored by HPLC using acetonitrile–water (60:40) as a mobile phase under reversed phase conditions. Thin-layer chromatographies were carried out on Merck F-254 silica glass plates. Column chromatographies were performed on silica gel (Merck, 70–230 mesh). Mass spectra were obtained on a Nermag R-10-10H spectrometer. Data are reported in the form *m*/*z*. Infrared spectra were recorded in KBr on a Brücker IFS48 Fourier transform spectrophotometer. NMR spectra were run on a Brücker AC300 spectrometer, at 300 MHz for ^1H and 75 MHz for ^{13}C, using $CDCl_3$ as the solvent and TMS as an internal reference. Chemical shifts (δ) are given in ppm; mutiplicities are indicated by s (singlet), d (doublet), dd (double–doublet), m (multiplet). Elemental analyses were performed by the 'Service Central de Microanalyses' of CNRS, in Vernaison, France.

4.2. Preparation of substituted benzophenones 4

4.2.1. 2,5-Dimethoxy-1-(4′-methylbenzoyl)benzene 4d (X=CH_3) (Method B). A mixture of 1,4-dimethoxybenzene (5 g, 36.2 mmol) and aluminum chloride (6.8 g, 50 mmol) in nitromethane (20 mL) was stirred at 10°C until complete dissolution of the Lewis acid. A solution of 4-methylbenzoyl chloride (5.6 g, 36.2 mmol) in nitromethane (10 mL) was added dropwise and the reaction mixture was stirred at room temperature for 60 min. The mixture was diluted with 0.5 M HCl (50 mL) and extracted with dichloromethane (2×20 mL). The organic layer was dried and concentrated under vacuum to give **4d** (9.3 g, 83%) as a white solid, mp 63°C; IR (KBr): 2995, 2955, 2830, 1665, 1610, 1585, 1495, 1465, 1450, 1225, 1050, 805 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.39 (s, 3H), 3.65 (s, 3H), 3.76 (s, 3H), 6.85 (m, 3H), 7.22 (d, *J*=7.2 Hz, 2H), 7.72 (d, *J*=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 21.7, 55.8, 56.3, 113.1, 114.4, 117.0, 129.0, 129.8, 130.0, 135.0, 143.9, 151.3, 153.4, 195.8.

4.2.2. 2-(4′-Bromobenzoyl)-1,4-dimethoxybenzene 4b (X=Br). This compound was obtained in the same way as compound **4d**, using 4-bromobenzoyl chloride. Yield 90%, mp 81°C; IR (KBr): 3085, 2835, 1665, 1580, 1490, 1220, 1030, 845, 715 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.63 (s, 3H), 3.76 (s, 3H), 6.90 (m, 3H), 7.00 (d, *J*=9.0 Hz, 2H), 7.65 (d, *J*=9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 55.8, 56.2, 113.0, 114.4, 117.8, 128.1, 128.8, 131.3, 131.5, 136.5, 151.4, 153.5, 195.1.

4.2.3. 2-(4′-Chlorobenzoyl)-1,4-dimethoxybenzene 4a (X=Cl). This compound was obtained in the same way as compound **4d**, using 4-chlorobenzoyl chloride. Yield 85%, mp 65°C; IR (KBr): 3090, 2830, 1665, 1580, 1495, 1220, 1050, 845, 715 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.65 (s, 3H), 3.77 (s, 3H), 6.90 (d, *J*=8.8 Hz, 1H), 6.92 (d, *J*=2.6 Hz, 1H), 7.00 (dd, *J*=8.8, 2.6 Hz, 1H), 7.39 (d, *J*=8.5 Hz, 2H), 7.75 (d, *J*=8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 55.8, 56.2, 113.0, 114.5, 117.8, 128.5, 128.8, 131.1, 136.1, 139.3, 151.4, 153.6, 194.9.

4.2.4. 2,5-Dimethoxy-1-(4′-iodobenzoyl)benzene 4c (X=I). This compound was obtained in the same way as compound **4d**, using 4-iodobenzoyl chloride. Yield 86%, mp 90°C; IR (KBr): 3080, 2835, 1665, 1580, 1495, 1220, 1045, 845, 460 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.64 (s, 3H), 3.77 (s, 3H), 6.90 (m, 2H), 7.00 (dd, *J*=9.0, 3.0 Hz, 1H), 7.50 (d, *J*=8.3 Hz, 2H), 7.60 (d, *J*=8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 55.9, 56.2, 101.0, 113.0, 114.5, 117.8, 128.7, 131.1, 137.0, 137.5, 151.5, 153.5, 195.5.

4.2.5. 2,5-Dimethoxy-1-(4′-nitrobenzoyl)benzene 4e (X=NO_2). This compound was obtained in the same way as compound **4d**, using 4-nitrobenzoyl chloride. Yield 85%, mp 136°C; IR (KBr): 2985, 2840, 1660, 1605, 1525, 1495, 1450, 1350, 1220, 1045, 835 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.60 (s, 3H), 3.79 (s, 3H), 6.92 (d, *J*=8.9 Hz, 1H), 7.00 (d, *J*=3.1 Hz, 1H), 7.07 (dd, *J*=8.9, 3.1 Hz, 1H), 7.90 (d, *J*=8.9 Hz, 2H), 8.20 (d, *J*=8.9 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 55.9, 56.0, 113.1, 114.7, 119.1, 123.4, 127.7, 130.2, 143.0, 150.2, 151.8, 153.7, 194.5.

4.3. Preparation of substituted benzhydrols 7

4.3.1. 4′-Chloro-2,5-dimethoxybenzhydrol 7a (X=Cl) (Method A). Magnesium turnings (7 g, 39 mmol) in dry THF (10 mL) were activated by a small piece of iodine, with stirring and heating until the color of iodine disappeared. 1-Bromo-2,5-dimethoxybenzene (1 g, 4.6 mmol) was added to the suspension of activated magnesium and the mixture was heated to 50°C. Next, a solution of 1-bromo-2,5-dimethoxybenzene (4 g, 18.4 mmol) in dry THF (20 mL) was added dropwise to the stirred mixture over 15 min while keeping under reflux condition. The stirring at reflux was further continued for 4 h. A solution of 4-chlorobenzaldehyde (3.2 g, 23 mmol) in THF (10 mL) was added at 0°C. The temperature was gradually allowed to warm to 55°C for 4 h. The reaction mixture was poured into aqueous NH_4Cl (200 mL) and extracted with diethyl ether (2×30 mL). The organic phases were dried over Na_2SO_4 and concentrated to give a crude product (5.1 g, 80%), which was crystallized form petroleum ether to give the 2,5-dimethoxy-1-(4′-chlorobenzoyl)benzene **4a** (X=Cl) (15%) and **7a** (3.9 g, 61%) as a colorless oil: IR (KBr pellets): 3420, 3005, 2835, 1590, 1500, 1450, 1275,

1215, 1045, 710 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.24 (s, 1H), 3.73 (s, 6H), 5.95 (s, 1H), 6.80 (m, 3H), 7,27 (m, 4H); ^{13}H NMR ($CDCl_3$): δ 55.7, 55.9, 71.6, 111.9, 112.9, 114.0, 127.9, 128.3, 132.6, 132.9, 141.7, 150.7, 153.8.

4.3.2. 2,5-Dimethoxy-4′-nitrobenzhydrol 7e (X=NO_2) (Method C). Sodium borohydride (0.48 g, 12.5 mol) was added at 25°C, over a period of 10 min, to a solution of compound **4e** (3 g, 10.4 mmol) in methanol (20 mL). The reaction mixture was stirred for 90 min at room temperature. After removing the methanol, diethyl ether (10 mL) was added and the organic phase was washed with a solution of 1 M HCl. The aqueous phases were extracted with diethyl ether (3×10 mL). After drying the organic phases over $CaCl_2$ and evaporating the solvents, the benzhydrol was obtained as an oil which crystallized in a petroleum ether and diethyl ether mixture to give **7e** (2.7 g, 90%) as a white solid, mp 88°C (petroleum ether/diethyl ether); IR (KBr): 3515, 3005, 2830, 1595, 1510, 1450, 1345, 1280, 1225, 1045, 815 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.52 (s, 1H), 3.71 (s, 3H), 3.72 (s, 3H), 6.02 (s, 1H), 6.77 (m, 2H), 6.84 (d, J=2.4 Hz, 1H), 7.51 (d, J=8.4 Hz, 2H), 8.09 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 55.6, 55.8, 70.8, 111.8, 113.2, 113.7, 123.3, 127.1, 131.9, 147.1, 150.5, 151.0, 153.8.

4.3.3. 4′-Chloro-2,5-dimethoxybenzhydrol 7a (X=Cl). This compound was obtained in the same way as compound **7e**, using 2-(4′-chlorobenzoyl)-1,4-dimethoxybenzene. The compound **7a** was isolated as a white solid (93%), mp 65°C, with the same physical properties as the compound obtained following the method A.

4.3.4. 4′-Bromo-2,5-dimethoxybenzhydrol 7b (X=Br). This compound was obtained in the same way as compound **7e**, using 2-(4′-bromobenzoyl)-1,4-dimethoxybenzene. Yield 92%, mp 70°C; IR (KBr): 3300, 3000, 2830, 1585, 1500, 1455, 1270, 1235, 1040, 700 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.12 (s, 1H), 3.71 (s, 3H), 3.72 (s, 3H), 5.93 (s, 1H), 6.78 (m, 2H), 6.85 (d, J=2.3 Hz, 1H), 7.24 (d, J=8.4 Hz, 2H), 7.41 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 55.7, 55.9, 71.6, 111.9, 112.9, 113.9, 121.0, 128.3, 131.2, 132.6, 142.3, 150.7, 153.7.

4.3.5. 2,5-Dimethoxy-4′-iodobenzhydrol 7c (X=I). This compound was obtained following the method B, using 2,5-dimethoxy-1-(4′-iodobenzoyl)benzene. Yield 88%, IR (KBr): 3305, 2995, 2835, 1580, 1500, 1450, 1270, 1230, 1045, 525 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.15 (s, 1H), 3.63 (s, 6H), 5.83 (s, 1H), 6.68 (m, 2H), 6.75 (d, J=2.3 Hz, 1H), 7.13 (d, J=7.6 Hz, 2H), 7.54 (d, J=7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 55.7, 55.9, 71.6, 92.7, 111.8, 112.9, 113.9, 121.0, 128.6, 132.5, 137.2, 143.0, 150.7, 153.7.

4.3.6. 2,5-Dimethoxy-4′-methylbenzhydrol 7d (X=CH_3). This compound was obtained following the method B, using 2,5-dimethoxy-1-(4′-methylbenzoyl)benzene. Yield 89%, mp 45°C; IR (KBr): 3470, 3005, 2940, 2830, 1605, 1495, 1460, 1280, 1210, 1030 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.37 (s, 3H), 3.45 (s, 1H), 3.74 (s, 3H), 3.76 (s, 3H), 6.02 (s, 1H), 6.80 (m, 2H), 6.98 (d, J=2.3 Hz, 1H), 7.16 (d, J=8.4 Hz, 2H), 7.32 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 21.2, 55.7, 56.0, 71.7, 111.9, 112.7, 113.9, 126.6, 128.9, 133.5, 136.8, 140.5, 150.9, 153.8.

4.4. Preparation of the substituted diarylmethanes 3 from benzhydrols 7

4.4.1. 2,5-Dimethoxy-1-(4′-methylbenzyl)benzene 3d (X=CH_3) (Method E). Triethylsilane (4.9 mL, 31.0 mmol) was added (syringe) at room temperature, to a stirred solution of compound **7d** (4 g, 15.5 mmol) and trifluoroacetic acid (11.9 mL, 155 mmol) in carbon tetrachloride (30 mL). The reaction was then stirred at 55°C for 5 h. After washing the mixture with a solution of 1 M NaOH (50 mL), the organic layer was dried over Na_2SO_4 and concentrated under vacuum to give **3d** (3.4 g, 89%) as a white solid, mp 38°C; IR (KBr): 3005, 2955, 2830, 1605, 1505,1460, 1440, 1220, 1045, 805 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.38 (s, 3H), 3.77 (s, 3H), 3.83 (s, 3H), 3.99 (s, 2H), 6.74 (dd, J=8.6, 3.0 Hz, 1H), 6.78 (d, J=3.0 Hz, 1H), 6.85 (d, J=8.6 Hz, 1H), 7.13 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 21.1, 35.6, 55.6, 56.1, 111.2, 111.4, 116.9, 128.9, 129.1, 131.4, 135.7, 137.7, 151.7, 153.6.

4.4.2. 2-(4′-Bromobenzyl)-1,4-dimethoxybenzene 3b (X=Br) (Method F). Triflic acid (1.4 g, 9.34 mmol) was added (syringe) to a stirred solution of compound **7b** (10 g, 31.1 mmol) in dichloromethane (80 mL). A solution of triethylsilane (9.02 g, 77.9 mmol) in dry dichloromethane (20 mL) was added dropwise. After 45 min, the mixture was poured into cold (5°C) saturated sodium hydrogen carbonate solution (100 mL) and extracted with dichloromethane (3×30 mL). The organic layer was dried with magnesium sulfate, and evaporated to give **3b** (8.5 g, 90%) as a white solid, mp 49°C (petroleum ether/diethyl ether); IR (KBr): 2995, 2940, 1830, 1595, 1495, 1450, 1430, 1225, 1045, 800, 710 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.75 (s, 3H), 3.77 (s, 3H), 3.91 (s, 2H), 6.68 (d, J=2.9 Hz, 1H), 6.76 (dd, J=8.8, 2.9 Hz, 1H), 6.82 (d, J=8.8 Hz, 1H), 7.11 (d, J=8.3 Hz, 2H), 7.40 (d, J=8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 35.6, 55.7, 56.0, 111.4, 116.9, 119.7, 130.2, 130.7, 131.3, 139.9, 151.6, 153.3; Anal. Calcd for $C_{15}H_{15}BrO_2$: C, 58.65; H, 4.92; O, 10.42. Found: C, 58.57; H, 4.93; O, 10.45.

4.5. Preparation of the substituted diarylmethanes 3 from benzophenones 4

4.5.1. 2-(4′-Bromobenzyl)-1,4-dimethoxybenzene 3b (X=Br) (Method I). Triflic acid (1.4 g, 9.34 mmol) was added (syringe) to a stirred solution of compound **4b** (10 g, 31.1 mmol) in dichloromethane (80 mL). A solution of triethylsilane (9.02 g, 77.9 mmol) in dry dichloromethane (20 mL) was added dropwise. An exothermic reaction took place while the temperature was maintained at 20°C in a water bath. After 45 min, the mixture was poured into cold (5°C) saturated sodium hydrogen carbonate solution (100 mL) and extracted with dichloromethane (3×30 mL). The organic layer was dried with magnesium sulfate, and evaporated to give **3b** (7.9 g, 83%) as a white solid with the same physical properties than the product obtained following the method F.

4.5.2. 2-(4′-Chlorobenzyl)-1,4-dimethoxybenzene 3a (X=Cl). This compound was obtained following the method E, using 2-(4′chlorobenzoyl)-1,4-dimethoxybenzene. Yield 84%, mp 41°C; IR (KBr): 3000, 2945, 2830, 1590, 1495, 1460, 1435, 1220, 1045, 805, 710 cm^{-1}; ^1H NMR ($CDCl_3$):

δ 3.74 (s, 3H), 3.76 (s, 3H), 3.91 (s, 2H), 6.66 (d, *J*=3.0 Hz, 1H), 6.73 (dd, *J*=8.8, 3.0 Hz, 1H), 6.80 (d, *J*=8.8 Hz, 1H), 7.14 (d, *J*=8.5 Hz, 2H), 7.20 (d, *J*=8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 35.5, 55.6, 56.0, 111.4, 116.8, 128.3, 130.2, 130.3, 131.6, 139.1, 151.6, 153.5; Anal. Calcd for $C_{15}H_{15}ClO_2$: C, 68.57; H, 5.75; O, 12.18. Found: C, 68.60; H, 5.71; O, 12.20.

4.5.3. 2,5-Dimethoxy-1-(4′-iodobenzyl)benzene 3c (X=I). This compound was obtained in the same way as compound **3b**, using 2,5-dimethoxy-1-(4′-iodobenzoyl)benzene. Yield 95%, mp 60°C; IR (KBr): 2995, 2935, 2825, 1585, 1500, 1450, 1430, 1225, 1050, 795, 525 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.74 (s, 3H), 3.76 (s, 3H), 3.89 (s, 2H), 6.66 (d, *J*=2.8 Hz, 1H), 6.74 (d, *J*=8.8, 2.8 Hz, 1H), 6.80 (d, *J*=8.8 Hz, 1H), 6.98 (d, *J*=8.2 Hz, 2H), 7.60 (d, *J*=8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 35.7, 55.7, 56.0, 91.4, 111.4, 116.9, 130.5, 131.0, 137.3, 140.9, 152.1, 153.8.

4.5.4. 2-(4′-Bromobenzyl)-1,4-dimethoxybenzene 3b (X=Br) (Method G). To a stirred solution of 2-(4′-bromobenzoyl)-1,4-dimethoxybenzene (4.0 g, 12.5 mmol) and trifluoroacetic acid (67 mL, 872 mmol) in dichloromethane (80 mL) was slowly added sodium borohydride pellets (4.74 g, 125 mmol). The reaction mixture was stirred at room temperature for 18 h. After washing the mixture with a solution of 1 M NaOH (100 mL), the organic layer was dried over $CaCl_2$ and concentrated under vacuum to give **3b** and **11b** (X=Br). The crude mixture was crystallized from petroleum ether and diethyl ether giving first **3b** (1.8 g, 47%) with the same physical properties that the product obtained following the method F and **11b** (2.91 g, 38%) as a white solid, mp 84°C (petroleum ether/diethyl ether); IR (KBr): 2995, 2945, 2830, 1590, 1500, 1450, 1215, 1045, 795, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.53 (s, 3H), 3.57 (s, 3H), 3.63 (s, 3H), 3.67 (s, 3H), 3.87 (s, 2H), 6.01 (s, 1H), 6.31 (s, 1H), 6.41 (d, *J*=3.0 Hz, 1H), 6.59 (s, 1H), 6.72 (dd, *J*=8.8, 3.0 Hz, 1H), 6.79 (d, *J*=8.8 Hz, 1H), 6.93 (d, *J*=8.3 Hz, 2H), 7.09 (d, *J*=8.8 Hz, 2H), 7.34 (d, *J*=8.8 Hz, 2H), 7.37 (d, *J*=8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 35.4, 43.1, 55.5, 56.1, 56.4, 56.6, 110.7, 111.9, 113.5, 114.0, 117.1, 119.6, 119.7, 127.7, 130.6, 130.9, 131.0, 131.3, 133.4, 140.1, 142.8, 151.1, 151.2, 151.6, 153.3; *m/z* 615 (for ^{81}Br, ^{79}Br, MH^+, 15.5%), 614 (for ^{81}Br, ^{79}Br, M^+, 51.6%), 613 (for ^{79}Br, MH^+, 41.0%), 612 (for ^{79}Br, M^+, 100%); Anal. Calcd for $C_{30}H_{28}Br_2O_2$: C, 58.84; H, 4.61; O, 10.45. Found: C, 58.64; H, 4.76; O, 10.26.

4.5.5. 2-(4′-Chlorobenzyl)-1,4-dimethoxybenzene 3a (X=Cl). This compound was obtained following the same procedure in the same way as **3b**, using 2-(4′-chlorobenzoyl)-1,4-dimethoxybenzene and stirring the reaction mixture for 44 h instead of 18 h. After recrystallization from petroleum ether and diethyl ether, three compounds were isolated: **3a** (1.0 g, 31%) with the same physical properties that the product obtained following the method I, **11a** (2.6 g, 40%) and **9a** (X=Cl) (0.5 g, 10%). Compound **11a** was obtained as a white solid, mp 90°C (petroleum ether/diethyl ether); IR (KBr): 3005, 2945, 2830, 1590, 1500, 1215, 1045, 795, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.54 (s, 3H), 3.57 (s, 3H), 3.64 (s, 3H), 3.67 (s, 3H), 3.89 (s, 2H), 6.07 (s, 1H), 6.35 (s, 1H), 6.42 (d, *J*=3.0 Hz, 1H), 6.59 (s, 1H), 6.72 (dd, *J*=8.8, 3.0 Hz, 1H), 6.80 (d, *J*=8.8 Hz, 1H), 6.99 (d, *J*=8.3 Hz, 2H), 7.14 (d, *J*=8.3 Hz, 2H), 7.20 (d, *J*=8.3 Hz, 2H), 7.23 (d, *J*=8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 35.4, 43.0, 55.6, 56.1, 56.5, 56.6, 110.8, 111.9, 113.5, 114.1, 117.2, 127.8, 128.1, 128.3, 130.3, 130.5, 130.8, 131.6, 133.5, 139.6, 142.3, 151.1, 151.2, 151.7, 153.3; *m/z* 526 (for ^{37}Cl, ^{35}Cl, MH^+, 9.3), 525 (for ^{37}Cl, ^{35}Cl, M^+, 22.8), 524 (for ^{35}Cl, MH^+, 65.9), 523 (for ^{35}Cl, M^+, 29.0), 522 (for ^{35}Cl, $M^{+\cdot}$, 100); Anal. Calcd for $C_{30}H_{28}Cl_2O_2$: C, 68.84; H, 5.39; O, 12.23. Found: C, 68.69; H, 5.41; O, 12.40. Compound **9a** was obtained as a white solid, mp 140°C (heptane/diethyl ether); IR (KBr): 2985, 2935, 2830, 1590, 1500, 1465, 1410, 1220, 1040, 870, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.70 (s, 6H), 3.90 (s, 4H), 6.55 (s, 2H), 7.13 (d, *J*=8.3 Hz, 4H), 7.21 (d, *J*=8.3 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ 35.4, 56.1, 113.1, 127.8, 128.4, 130.1, 131.6, 139.5, 151.2; *m/z* 390 (for ^{37}Cl, M^+, 11.2), 389 (for ^{37}Cl, ^{35}Cl, MH^+, 15.3), 388 (for ^{37}Cl, ^{35}Cl, M^+, 66.4), 387 (for ^{35}Cl, MH^+, 24.1), 386 (for ^{35}Cl, M^+, 100); Anal. Calcd for $C_{22}H_{20}Cl_2O_2$: C, 68.23; H, 5.20; O, 8.26. Found: C, 68.44; H, 5.29; O, 8.42.

4.5.6. 2,5-Dimethoxy-1-(4′-methylbenzyl)benzene 3d (X=CH_3) (Method H). Triethylsilane (6.2 mL, 39.0 mmol) was added (syringe) at room temperature, to a stirred solution of compound **4d** (5 g, 19.5 mmol) and trifluoroacetic acid (22.5 mL, 0.29 mol) in carbon tetrachloride (40 mL). The reaction was then stirred at 55°C for 6 h. After washing the mixture with a solution of 1 M NaOH (50 mL), the organic layer was dried over $CaCl_2$ and concentrated under vacuum to give **3d** (4.0 g, 84%) with the same physical properties that the product obtained following the method E.

4.5.7. 2,5-Dimethoxy-1-(4′-nitrobenzyl)benzene 3e (X=NO_2). This compound was obtained following the same procedure in the same way as **3d**, using 2,5-dimethoxy-1-(4′-nitrobenzoyl)benzene. Yield 90%, mp 70°C; IR (KBr): 3005, 2935, 2835, 1600, 1510, 1465, 1440, 1345, 1215, 1035, 810 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.73 (s, 3H), 3.74 (s, 3H), 4.00 (s, 2H), 6.68 (d, *J*=2.9 Hz, 1H), 6.75 (dd, *J*=8.8, 2.9 Hz, 1H), 6.80 (d, *J*=8.8 Hz, 1H), 7.33 (d, *J*=8.7 Hz, 2H), 8.08 (d, *J*=8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 36.3, 55.7, 55.9, 111.5, 111.9, 117.0, 123.5, 128.8, 129.5, 146.4, 148.9, 151.5, 153.6.

4.5.8. 2,5-Dimethoxy-1-(4′-nitrobenzyl)benzene 3e (X=NO_2) (Method J). Triethylsilane (6.1 mL, 38.5 mmol) was added (syringe) at room temperature, to a stirred solution of compound **4e** (5 g, 17.4 mmol) and aluminum chloride (2.6 g, 19.2 mmol) in nitromethane (40 mL). The reaction mixture was stirred at room temperature for 90 min. After washing the mixture with a solution of 1 M HCl (50 mL), the organic layer was dried over $CaCl_2$ and concentrated under vacuum. The crude mixture was washed in a first time with petroleum ether to give **9e** (X=NO_2) (0.5 g, 15%) as a brown solid, mp 194–195°C; IR (KBr): 2995, 2935, 2835, 1595, 1515, 1460, 1345, 1220, 1035, 835 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.64 (s, 6H), 3.97 (s, 4H), 6.61 (s, 2H), 7.28 (d, *J*=8.6 Hz, 4H), 8.05 (d, *J*=8.6 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ 36.2, 55.9, 113.7, 123.6, 126.9, 139.4, 146.3, 148.8, 151.5; Anal. Calcd for $C_{22}H_{20}N_2O_6$: C, 64.70; H, 4.94; N, 6.86. Found: C, 64.82; H, 5.21; N, 6.55. The first residue was washed with acetone to give **12e** (X=NO_2) (0.53 g, 15%) as a yellow solid, mp 59°C; IR (KBr): 2995, 2940, 2840, 1595, 1510, 1495, 1345, 1215,

1050, 825 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.64 (s, 6H), 3.66 (s, 6H), 6.18 (s, 1H), 6.36 (d, J=2.9 Hz, 2H), 6.74 (dd, J=8.8, 2.9 Hz, 2H), 6.81 (d, J=8.8 Hz, 2H), 7.20 (d, J=8.5 Hz, 2H), 8.09 (d, J=8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 43.8, 55.6, 56.3, 111.3, 111.8, 117.3, 123.3, 129.9, 132.0, 146.2, 151.5, 152.0, 153.5; Anal. Calcd for $C_{23}H_{23}NO_6$: C, 67.47; H, 5.66; N, 3.42. Found: C, 67.14; H, 5.51; N, 3.57. The second residue was concentrated under vacuum yielding **3e** with the same physical properties that the product obtained following the method I.

4.5.9. 2-(4′-Bromobenzyl)-1,4-dimethoxybenzene 3b (X=Br). This compound was obtained following the method J, using 2-(4′-bromobenzoyl)-1,4-dimethoxybenzene. The compound **3b** was isolated as a white solid (85%) with the same physical properties that the product obtained following the method F.

4.5.10. 2-(4′-Bromobenzyl)-1,4-dimethoxybenzene 3b (X=Br) (Method K). Triflic acid (0.27 mL, 4.8 mmol) was added dropwise (syringe) to a stirred solution of compound **4b** (5.1 g, 16 mmol) and polymethylhydrosiloxane (2.9 mL, 48 mmol) in dichloromethane (20 mL). The reaction mixture was stirred at room temperature for 7 h. After filtering the mixture on silica gel and washing the residue with a solution of 1 M NaOH (50 mL), the aqueous layer was extracted with dichloromethane (2×20 mL), dried over $CaCl_2$ and concentrated under vacuum. The residue was washed with a mixture of diethyl ether/heptane (7/3) yielding **3b** (4.2 g, 85%) as a white solid with the same physical properties that the product obtained following the method F.

4.5.11. 2-(4′-Chlorobenzyl)-1,4-dimethoxybenzene 3a (X=Cl). This compound was obtained following the same procedure, using 2-(4′-chlorobenzoyl)-1,4-dimethoxybenzene. The compound **3a** was isolated as a white solid (89%) with the same physical properties than the product obtained following the method I.

4.5.12. 2,5-Dimethoxy-1-(4′-iodobenzyl)benzene 3c (X=I). This compound was obtained following the same procedure, using 2,5-dimethoxy-1-(4′-iodobenzoyl)benzene. The compound **3c** was isolated as a white solid (85%) with the same physical properties than the product obtained following the method I.

4.5.13. 2-(4′-Chlorobenzyl)-1,4-dimethoxybenzene 3a (X=Cl) (Method L). Polymethylhydrosiloxane (3.2 mL, 54 mmol) was added (syringe) at room temperature, to a stirred solution of compound **4a** (5 g, 18 mmol) and aluminum chloride (2.8 g, 21 mmol) in nitromethane (10 mL). The reaction mixture was stirred at room temperature for 20 days. After filtering the mixture on silica gel and washing the residue with a solution of 1 M HCl (50 mL), the organic layer was extracted with dichloromethane (2×20 mL), dried over $CaCl_2$ and concentrated under vacuum. The crude was washed with a mixture of diethyl ether/heptane (7/3) yielding **3a** (0.4 g, 9%) as a white solid with the same physical properties that the compound obtained following the method I and **13a** (X=Cl) purified by column chromatography (petroleum ether/diethyl ether=7/3) (3.4 g, 71%) as a yellow solid, mp 82°C; IR (KBr): 3426, 3005, 2940, 2840, 1675, 1590, 1490, 1225, 1040, 825, 710 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.70 (s, 3H), 7.00 (d, J=3.1 Hz, 1H), 7.16 (dd, J=8.4, 3.1 Hz, 1H), 6.81 (d, J=8.4 Hz, 1H), 7.48 (d, J=8.6 Hz, 2H), 7.66 (d, J=8.6 Hz, 2H), 11.4 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 55.9, 115.8, 118.5, 119.4, 128.7, 130.1, 137.3, 138.4, 151.5, 157.4, 199.8.

When the reaction mixture was performed in dichloromethane (10 mL) for 40 h, compound **3a** was obtained (3.6 g, 75%) without any side products.

4.5.14. 2,5-Dimethoxy-1-(4′-nitrobenzyl)benzene 3e (X=NO_2). This compound was obtained following the same procedure, using 2,5-dimethoxy-1-(4′-nitrobenzoyl)benzene. The compound **3e** was isolated as a yellow solid (79%) with the same physical properties than the product obtained following the method I.

4.6. One step synthesis of diarylmethanes

4.6.1. 2-(4′-Chlorobenzyl)-1,4-dimethoxybenzene 3a (X=Cl) (Method M). A mixture of 1,4-dimethoxybenzene (3 g, 21.7 mmol) and aluminum chloride (4.1 g, 30.4 mmol) in nitromethane (30 mL) was stirred at 10°C for 5 min. A solution of *p*-chlorobenzoyl chloride (2.76 mL g, 21.7 mmol) in dichloromethane (10 mL) was added dropwise (5 min) and the reaction mixture was stirred at room temperature for 90 min. A solution of triethylsilane (6.5 mL, 65.1 mmol) in dichloromethane (10 mL) was then added and the mixture was stirred at room temperature for 2 h. After washing the mixture with a solution of 1 M HCl (50 mL), the organic layer was extracted with dichloromethane (2×20 mL), dried over $CaCl_2$ and concentrated under vacuum giving **3a** (5.2 g, 90%) as a white solid with the same physical properties than the product obtained following the method I.

4.6.2. 2-(4′-Chlorobenzyl)-1,4-dimethoxybenzene 3a (X=Cl) (Method O). A mixture of 1,4-dimethoxybenzene (3 g, 22.0 mmol) and aluminum chloride (4.1 g, 30.0 mmol) in dichloromethane (30 mL) was stirred at 10°C for 10 min. A solution of *p*-chlorobenzoyl chloride (2.80 mL, 22.0 mmol) in dichloromethane (10 mL) was added dropwise and the reaction mixture was stirred at room temperature for 90 min. The mixture was cooled down 10°C and a solution of polymethylhydrosiloxane (4.0 mL, 65.0 mmol) in dichloromethane (10 mL) was slowly added (5 min). The mixture was stirred at room temperature for 12 h, then filtered on silica gel and washed with a solution of 1 M HCl (50 mL). The organic layer was extracted with dichloromethane (2×20 mL), dried over $CaCl_2$ and concentrated under vacuum to give an oil which was crystallized from a mixture of diethyl ether/petroleum ether yielding **3a** (4.3 g, 75%) as a white solid with the same physical properties than the product obtained following the method I.

4.6.3. 2-(4′-Aminobenzyl)-1,4-dimethoxybenzene 3f (X=NH_2). Under N_2 atmosphere, a solution of 2,5-dimethoxy-1-(4′-nitrobenzyl)benzene **3e** (5 g, 19.3 mmol) in methanol (30 mL) was poured into a suspension of 10% palladium on charcoal (0.2 g) in methanol (20 mL). Sodium borohydride (1.5 g, 40.5 mmol) was slowly added and the mixture was stirred at room temperature for 60 min. The

reaction mixture was acidified by 2 M HCl (50 mL), neutralized by 1 M NaOH (25 mL). Methanol was removed under reduced pressure and the aqueous phase was extracted by dichloromethane (2×20 mL). The combined organic layers were dried over $MgSO_4$ then evaporated. The resulting solid was recristallized from a mixture of water and ethanol (7:3, 70 mL) yielding compound **3f** (4.2 g, 90%) as a white solid; IR (KBr): 3440, 3385, 3220, 2925, 2835, 1625, 1505, 1445, 1280 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.55 (s, 2H), 3.73 (s, 3H), 3.78 (s, 3H), 3.87 (s, 2H), 6.61 (d, J=8.7 Hz, 2H), 6.69 (dd, J=8.9, 3.0 Hz, 1H), 6.73 (d, J=3.0 Hz, 1H), 6.80 (d, J=8.9 Hz, 1H), 7.03 (d, J=8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 35.1, 55.6, 56.1, 111.0, 111.4, 115.3, 111.7, 129.8, 130.7, 141.8, 144.3, 151.7, 153.5.

4.7. Preparation of monomer 2

4.7.1. Ethyl 4-(2,5-dimethoxybenzyl)cinnamate 2 (R′=Et) (Method R). A solution of ethyl acrylate (2.8 g, 28.2 mmol) in *n*-tributylamine (2 mL) was slowly added to a mixture of compound **3c** (5 g, 14.1 mmol), triphenylphosphine (0.07 g, 0.28 mmol) and palladium diacetate (0.03 g, 0.14 mmol) in *n*-tributylamine (3 mL). The mixture was heated at 105°C for 2 h. After cooling the reaction mixture, the catalyst was collected and the organic phase was stirred with 50 mL of water for 15 min. The aqueous layer was extracted with dichloromethane (30 mL), dried over $CaCl_2$ and concentrated under vacuum. The brown solid was recrystallized from a mixture of petroleum ether/diethyl ether to give the monomer **2** (3.4 g, 73%) as a white solid; IR (KBr): 2995, 2835, 1710, 1600, 1505, 1425, 1320, 1230, 1165, 1015 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.17 (t, 3H), 3.67 (s, 3H), 3.71 (s, 3H), 3.90 (s, 2H), 4.20 (q, 2H), 6.34 (d, J=16.0 Hz, 1H), 6.62 (d, J=2.9 Hz, 1H), 6.68 (dd, J=8.8, 3.0 Hz, 1H), 6.75 (d, J=8,8 Hz, 1H), 7.18 (d, J=8.1 Hz, 2H), 7.38 (d, J=8.1 Hz, 2H), 7.61 (d, J=16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.2, 35.8, 55.5, 55.8, 60.2, 111.2, 111.3, 116.7, 117.1, 128.0, 129.2, 130.0, 132.0, 143.4, 144.4, 151.5, 153.4, 167.0.

4.7.2. Methyl 4-(2,5-dimethoxybenzyl)cinnamate 2 (R′=Me) (Method T). A solution of methyl acrylate (7.4 g, 84.7 mmol) in dimethylformamide (50 mL) was slowly added to a mixture of compound **3c** (15 g, 42.4 mmol), potassium carbonate (15.8 g, 114.3 mmol) and catalyst K_{10}–Pd–Cu[26] (1.5 g) in dimethylformamide (50 mL). The mixture was refluxed for 2 h. The catalyst was collected and the cooled reaction mixture was stirred with 100 mL of water for 15 min. The aqueous layer was extracted with dichloromethane (50 mL), dried over $CaCl_2$ and concentrated under vacuum. The brown solid was recrystallized from a mixture of petroleum ether/diethyl ether to give the monomer **2** (12.3 g, 93%) as a white solid, mp 83°C; IR (KBr): 2995, 2835, 1710, 1600, 1500, 1430, 1320, 1230, 1170, 1020 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.72 (s, 3H), 3.76 (s, 3H), 3.79 (s, 3H), 3.95 (s, 2H), 6.38 (d, J=16.1 Hz, 1H), 6.66 (d, J=3.0 Hz, 1H), 6.72 (dd, J=8.8 Hz, J=3.0 Hz, 1H), 6.79 (d, J=8.8 Hz, 1H), 7.22 (d, J=8.1 Hz, 2H), 7.42 (d, J=8.1 Hz, 2H), 7.66 (d, J=16.1 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 36.1, 51.7, 55.7, 56.0, 111.5, 116.9, 128.2, 128.4, 130.2, 132.1, 143.7, 144.9, 151.7, 153.6, 167.7; *m/z* 312 (M^+, 100); Anal. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 72.92; H, 6.29.

4.8. Preparation of benzhydryl chlorides 14

4.8.1. 4′-Chloro-2,5-dimethoxybenzhydryl chloride 14a (X=Cl). Chlorotrimethylsilane (6.6 mL, 36.9 mmol) was added (syringe) to a solution of 4′-chloro-2,5-dimethoxybenzhydrol (**7a**) (5 g, 18.0 mmol) in dichloromethane (10 mL). The mixture was stirred at 5°C for 25 min, then concentrated under vacuum. The crude product was diluted with dichloromethane (20 mL), then washed with a aqueous 1 M Na_2CO_3. The organic layer was dried over $CaCl_2$ and concentrated to give **14a** (5.2 g, 97%) as a brown oil; IR (KBr pellets): 3000, 2940, 2835, 1585, 1500, 1465, 1225, 1050, 830 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.59 (s, 3H), 3.61 (s, 3H), 6.43 (s, 1H), 6.66 (m, 2H), 7.02 (d, J=2.6 Hz, 1H), 7.14 (d, J=8.9 Hz, 2H), 7.25 (d, J=8.9 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 55.7, 56.2, 57.4, 111.9, 113.9, 115.0, 128.5, 129.1, 130.0, 133.8, 140.0, 150.0, 153.6. Anal. Calcd for $C_{15}H_{14}Cl_2O_2$: C, 60.62; H, 4.75; O, 10.77. Found: C, 60.45; H, 4.78; O, 10.82.

4.8.2. 4′-Bromo-2,5-dimethoxybenzhydryl chloride 14b (X=Br). This compound was obtained following the same procedure in the same way as **14a**, using 4′-bromo-2,5-dimethoxybenzhydrol (**7b**). Yield 97%, mp 55°C; IR (KBr): 3000, 2940, 2835, 1585, 1500, 1465, 1225, 1050, 830, 700 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.77 (s, 6H), 6.53 (s, 1H), 6.97 (m, 2H), 7.12 (d, J=2.2 Hz, 1H), 7.32 (d, J=8.5 Hz, 2H), 7.46 (d, J=8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 55.8, 56.2, 57.4, 111.9, 113.9, 115.0, 121.8, 129.4, 131.1, 139.9, 140.2, 150.1, 153.7. Anal. Calcd for $C_{15}H_{14}BrClO_2$: C, 52.74; H, 4.13; Cl, 10.38; O, 9.37. Found: C, 52.65; H, 4.15; Cl, 10.45; O, 9.20.

4.8.3. 2,5-Dimethoxy-4′-nitrobenzhydryl chloride 14e (X=NO_2). This compound was obtained following the same procedure in the same way as **14a**, using 2,5-dimethoxy-4′-nitrobenzhydrol (**7e**). Yield 93%; IR (KBr): 3090, 2940, 2835, 1610, 1595, 1450, 1460, 1350, 1210, 1110, 1035, 820 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.69 (s, 3H), 3.70 (s, 3H), 6.49 (s, 1H), 6.75 (m, 2H), 7.00 (d, J=2.2 Hz, 1H), 7.51 (d, J=8.8 Hz, 2H), 8.08 (d, J=8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 55.8, 56.1, 56.8, 111.9, 114.2, 114.9, 123.6, 128.5, 129.5, 147.6, 148.2, 150.0, 153.9. Anal. Calcd for $C_{15}H_{14}ClNO_4$: C, 58.55; H, 4.59; N, 4.55; O, 20.80. Found: C, 58.42; H, 4.61; N, 4.49; O, 20.75.

4.9. Preparation of triarylmethanes 12

4.9.1. 1-[4′-Chlorobenzyl)(2,5-dimethoxyphenyl)]-2,5-dimethoxybenzene 12a (X=Cl). To a stirred solution of *p*-dimethoxybenzene (9.2 g, 67.3 mmol) and aluminum chloride (0.9 g, 6.73 mmol) in dichloromethane (180 mL) was added a solution of chloride **14a** (X=Cl) (2 g, 6.73 mmol) in dichloromethane (20 mL). The mixture was stirred at room temperature for 15 min and washed with a solution of 0.5 M HCl (100 mL). The organic layer was dried over $CaCl_2$ and concentrated under vacuum. The residue was washed with petroleum ether, then purified by column chromatography (silica gel 100 g, petroleum ether/diethyl ether=9/1) to give **12a** (1.8 g, 67%) as a white solid. R_f: 0.20, mp 82°C; IR (KBr): 3000, 2950, 2835, 1595, 1495, 1455, 1220, 1110, 1045, 715 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.64 (s, 6H), 3.68 (s, 6H), 6.12 (s, 1H), 6.42 (d, J=3.0 Hz,

2H), 6.73 (dd, J=8.8, 3.0 Hz, 2H), 6.81 (d, J=8.8 Hz, 2H), 7.02 (d, J=8.4 Hz, 2H), 7.22 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 43.0, 55.5, 56.4, 110.8, 111.9, 117.2, 128.2, 130.6, 131.6, 133.2, 142.1, 151.6, 153.3; *m/z* 400 (for ^{37}Cl, M^+, 37.3), 398 (for ^{35}Cl, M^+, 100); Anal. Calcd for $C_{23}H_{23}ClO_4$: C, 69.26; H, 5.81; O, 16.04. Found: C, 69.17; H, 5.82; O, 15.79.

4.9.2. 1-[4′-Bromobenzyl)(2,5-dimethoxyphenyl)]-2,5-dimethoxybenzene 12b (X=Br). This compound was obtained following the same procedure in the same way as **12a**, using 4′-bromo-2,5-dimethoxybenzydryl chloride. Yield 68%, R_f: 0.13, mp 89°C; IR (KBr): 2995, 2945, 2830, 1590, 1495, 1450, 1215, 1100, 1045, 725 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.63 (s, 6H), 3.66 (s, 6H), 6.07 (s, 1H), 6.38 (d, J=3.0 Hz, 2H), 6.71 (dd, J=8.8, 3.0 Hz, 2H), 6.79 (d, J=8.8 Hz, 2H), 6.94 (d, J=8.3 Hz, 2H), 7.35 (d, J=8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 43.2, 55.6, 56.5, 110.9, 111.9, 117.2, 119.8, 131.0, 131.1, 133.3, 142.7, 151.6, 153.4; *m/z* 445 (for ^{81}Br, MH^+, 24.7), 444 (for ^{81}Br, M^+, 94.3), 443 (for ^{79}Br, MH^+, 25.9), 442 (for ^{79}Br, M^+, 100) 364 (for ^{81}Br, MH^+-Br, 100); Anal. Calcd for $C_{23}H_{23}BrO_4$: C, 62.31; H, 5.23; O, 14.44. Found: C, 62.22; H, 5.24; O, 14.36.

4.9.3. 2,5-Dimethoxy-1-[(2,5-dimethoxyphenyl)(4′-nitrobenzyl)]benzene 12e (X=NO$_2$). This compound was obtained following the same procedure in the same way as **12a**, using 4′-nitro-2,5-dimethoxybenzydryl chloride. Yield 63%, R_f: 0.11, mp 59°C; IR (KBr): 2995, 2940, 2840, 1595, 1510, 1495, 1345, 1215, 1050, 825 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.64 (s, 6H), 3.66 (s, 6H), 6.18 (s, 1H), 6.36 (d, J=2.9 Hz, 2H), 6.74 (dd, J=8.8, 2.9 Hz, 2H), 6.81 (d, J=8.8 Hz, 2H), 7.20 (d, J=8.5 Hz, 2H), 8.09 (d, J=8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 43.8, 55.6, 56.3, 111.3, 111.8, 117.3, 123.3, 129.9, 132.0, 146.2, 151.5, 152.0, 153.5; *m/z* 410 (MH^+, 27.0), 409 (M^+, 100); Anal. Calcd for $C_{23}H_{23}NO_6$: C, 67.47; H, 5.66; N, 3.42. Found: C, 67.14; H, 5.51; N, 3.57.

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