A highly stereoselective synthesis of stilbenes under solvent-free conditions

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A highly stereoselective synthesis of stilbenes (*trans*-1,2-diarylethylenes) was achieved under solvent-free conditions from aryl-aldehydes and aromatic substances bearing an activated methyl group in the presence of anhydrous K_2CO_3 and poly(ethylene glycol). This method avoided the need for completely anhydrous condition and use of a noxious organic solvent.

Keywords: *trans*-stilbenes, *trans*-1,2-diarylethylenes, stereoselectivity, Knoevenagel type condensation, solvent-free condition

Stilbenes (1,2-diarylethylenes) are very useful chemical substances which are used as liquid crystal materials,[1] fluorescence reagents[2] and anti-tumour drugs including resveratrol (3,4′,5-trihydroxystilbene)[3–5] and pterostilbene (3,5-dimethoxy-4′-hydroxystilbene).[6] They are also important building blocks with applications in materials science and synthetic chemistry since their *E*/*Z* isomerisation, cyclisation, cyclodimerisation, and statistical C–C bond formations (polymerisation, crosslinking) offer various reaction possibilities.[7] Interest in the drug synthesis and evaluation of 1,2-diaryl ethylenes as potential anticancer agents stems from the discovery of many such natural products as antimitotic and antileukemic agents.[8–10] This includes the isolation of some polymethoxylated stilbene derivatives, termed combretastatins, from the South African tree *Combretum caffrum*. Many of these combretastatins were found to be cytotoxic, with combretastatin A-4 the most potent.[11] This compound was found to cause mitotic arrest in L1210 murine leukemia cells, inhibit tubulin polymerisation, and competitively inhibit the binding of radiolabeled colchicine to tubulin.[12] Therefore, in order to obtain new 1,2-diarylethylenes with antitumour activity, we have synthesised a series of *trans*-4′-alkyloylimino-3,4,5-trimethoxystilbene[13] and 4′–*O*-substituted derivatives of *trans*-4′-hydroxy-3,4,5-trimethoxystilbene[14,15] from *trans*-3,4,5-trimethoxy-4′-nitrostilbene as a key intermediate. To the best of our knowledge, the preparation of this key intermediate and analogues, 1,2-diaryl ethylenes, requires anhydrous conditions and affords low yields. Wang's group reported a method for the synthesis of hemicyanine dyes through the condensation of activated aromatic methyl groups with aldehydes in the presence of piperidine under microwave irradiation,[16] this process was not adaptable to the preparation of these stilbenes and its analogue on a larger scale. Recently we have found a highly stereoselective synthesis for these 1,2-diaryl ethylenes which is described here.

Results and discussion

We are interested in the synthesis of stilbenes (1,2-diaryl ethylenes) with antitumour activity. Firstly, A key intermediate, *trans*-3,4,5-trimethoxy-4′-nitrostilbene, was required for our work. Cushman's group, synthesised a series of methoxylated stilbenes and related compounds for evaluation as cytotoxic agents and inhibitors of tubulin polymerisation, using the Wittig reaction of 3,4,5-trimethoxybenzyltriphenyl phosphonium bromide with *p*-nitrobenzaldehyde in the presence of sodium hydride in benzene under an argon atmosphere for 16 h. This gave a mixture of *cis*- and *trans*-3,4,5-trimethoxy-4′-nitrostilbene, which was followed by preparative TLC separation to give the corresponding *trans*-3,4,5-trimethoxy-4′-nitrostilbene in 44% yield.[11] There are three obvious drawbacks in this route: the phosphonium bromide is sensitive to moisture, thus the reaction requires anhydrous condition and an argon atmosphere; the low stereoselectivity of reaction gave a mixture of *cis*- and *trans*-3,4,5-trimethoxy-4′-nitrostilbene and there is a low reaction overall yield. To overcome these disadvantages, we attempted to find a new synthesis method for *trans*-3,4,5-trimethoxy-4′-nitrostilbene.

For the synthesis of *trans*-3,4,5-trimethoxy-4′-nitrostilbene, we used Zou's method for the synthesis of pterostilbene,[17] in which a mixture of 10 mmol 3,4,5-trimethoxybenzaldehyde and 20 mmol of the activated methyl compound, *p*-nitrotoluene, was refluxed in dry methanol in the presence of sodium methoxide for 48 h to give (*E*)-3,4,5-trimethoxy-4′-nitrostilbene in 39% yield. The base, sodium methoxide, was necessary for this reaction. This removes a proton from the activated methyl *group* of *p*-nitrotoluene to yield a nucleophilic carbanion. The double bond is formed by the nucleophilic addition of this carbanion to the carbonyl of 3,4,5-trimethoxybenzaldehyde followed by dehydration. However, this process still requires anhydrous conditions and a long time, and gave a low yield.

Some reactions can be achieved in high yield and shorter time by grinding under solvent-free condition.[18] Therefore we ground the mixture of 3,4,5-trimethoxybenzaldehyde, *p*-nitrotoluene and anhydrous K_2CO_3 to explore the solvent-free synthesis of 3,4,5-trimethoxy-4′-nitrostilbene, but the reaction did not occur, possibly because K_2CO_3 did not adequately react with the *p*-nitrotoluene to remove the proton of the methyl group in the solid. Polyethylene glycols (PEGs) have been widely used as phase transfer catalyst in many organic reactions[19,20] because of their stability, low cost, environment-friendly and easy availability. PEG can effectively catalyse the reactions of K^+ or Na^+ participation.[21] Thus Cao's group used PEG-400 and K_2CO_3 as catalysts to explore Knoevenagel condensation of aromatic aldehydes with ethyl cyanoacetate as active methylene compounds under solvent-free conditions, and successfully achieved an efficient synthesis of mono-arylidene compounds.[22] In our exploration of the synthesis of stilbenes (diarylidene compounds), when PEG-400 was added as a phase transfer catalyst to the mixture of 3,4,5-trimethoxybenzaldehyde, *p*-nitrotoluene and anhydrous K_2CO_3, the colour of the mixture changed immediately from white to yellow, which showed the reaction has occured. After adequately grinding and leaving the mixture for 24 h, 3,4,5-trimethoxy-4′-nitrostilbene was identified by TLC. The nondehydrated product, 1-(3,4,5-trimethoxyphenyl)-2-(4-nitrophenyl)ethanol, was observed from the ^{1}H NMR spectrum of the resultant mixture. The molar ratio of the dehydrated and nondehydrated products was about 1:8 based on the integral ratio between resonance

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peaks at δ 7.07 for the proton of the double bond of 3,4,5-trimethoxy-4′-nitrostilbene and at δ 4.87 of the proton at the 1-position of the methine of 1-(3,4,5-trimethoxyphenyl)-2-(4-nitrophenyl)ethanol. This was further confirmed by the ^{1}H, ^{13}C, DEPT NMR spectra of the isolated product from silica gel column chromatographic separation of the mixture eluted with a mixture of ethyl acetate and petroleum ether, v/v =1:1. This result led us to further explore this process.

Since *p*-nitrotoluene has low melting point (54.5 °C), we examined the condensation reaction of 3,4,5-trimethoxybenzaldehyde with *p*-nitrotoluene in the presence of anhydrous K_2CO_3 and PEG-400 when the mixture was heated up to the melting point of *p*-nitrotoluene, *i.e.* using *p*-nitrotoluene as both a reactant and a solvent. A good result was obtained when the mixture of 10.0 mmol 3,4,5-trimethoxybenzaldehyde, 10.0 mmol *p*-nitrotoluene, 20.0 mmol anhydrous K_2CO_3 and 1.0 mL PGE-400 was heated to 100 °C with magnetic stirring for 3 h. After the addition of water to the mixture, filtration and recrystallising from ethanol, 3,4,5-trimethoxy-4′-nitrostilbene was obtained in 85% yield (see entry 1 of Table 1). The *trans* isomer was obtained exclusively by this simple process without the need for chromatographic separation. This was confirmed by the characteristic coupling constant in the NMR spectrum of 3,4,5-trimethoxy-4′-nitrostilbene for the olefinic protons of 16.2 Hz.[23] This method has a remarkable advantage compared to the previous methods, such as its high stereoselectivity for the *trans* isomer, and completely avoiding anhydrous condition and the use of noxious organic solvent.

This procedure using solvent-free conditions was successfully applied to the stereoselective synthesis of other *trans*-1,2-diarylethylenes from aryl aldehydes and aromatic substances bearing activated methyl groups (see Table 1). The results indicated that the yields of compounds bearing electron donating groups on the aromatic ring of the aldehyde were higher than those of electron withdrawing groups on the aromatic ring. Higher yields were obtained when there were more electron donating groups on the aromatic ring of aldehyde (entries 1–5 and 7). Although there were more electron donating groups on the aromatic ring of the aldehydes in entries 8–10, lower yields were obtained because of the steric hindrance of the nitro group in the *ortho* position (entry 8) or two methyl groups in the *ortho* position of the activated methyl (entries 9 and 10).

In summary, an effective synthesis method of *trans*-1,2-diarylethylenes was achieved under solvent-free conditions from aryl-aldehydes and aromatic substances bearing an activated methyl group in the presence of anhydrous K_2CO_3 and the phase transfer catalyst PEG. This method avoided the need for completely anhydrous conditions and the use of noxious organic solvents, and it exhibited a high stereoselectivity for the *trans* configuration of the 1,2-diaryl ethylene compounds.

Experimental

All chemicals were of analytical reagent grade. The NMR spectra were recorded with a Bruker AVANCE300 spectrometer using TMS as internal standard. The IR spectra were recorded with a Nicolet 170SX FT-IR spectrometer using KBr pellets. Elemental analyses were performed on a VarioEL CHNS Elementar Analysensystem. The melting point were determined using a WRS-113 digital melting point instrument (the thermometer was not corrected).

Synthesis of trans-1,2-diaryl ethylene compounds

The aryl aldehyde (10.0 mmol) was added to the mixture of aromatic substance bearing the activated methyl (10.0 mmol), anhydrous K_2CO_3 (20.0 mmol) and PGE-400 (0.5–1.0 mL) (or 1 g PGE-600 or 1 g PEG-1000) in a 50 mL flask and the mixture was heated to 90–100 °C with magnetic stirring for 2–4.5 h. Water (10 mL) was added to the mixture and the product was filtered. The filter cake was rinsed with H_2O (5 mL × 3) and recrystallised from ethanol to give *trans*-1,2-diaryl ethylene compounds as a solid.

trans-*3,4,5-Trimethoxy-4′-nitrostilbene (entry 1 of Table 1)*: M.p. 192–194 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.89 (s, 3H, OCH_3), 3.93 (s, 6H, $2OCH_3$), 6.77 (s, 2H, 2,6-ArH), 7.07 (d, 1H, *J* = 16.2 Hz, –CH=CH–), 7.17 (d, 1H, *J* = 16.2 Hz, –CH=CH–), 7.64 (d, 2H, *J* = 8.6 Hz, 2′,6′-ArH), 8.24 (d, 2H, *J* = 8.6 Hz, 3′,5′-ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.2, 60.9, 104.4, 124.1, 125.7, 126.7, 131.8, 133.3, 139.2, 143.8, 146.7, 153.6; IR: ν_{max} 3066, 2928, 2831, 1633, 1587, 1503, 1454, 1329, 1236, 1122, 980 cm^{-1}. Anal. Calcd for $C_{17}H_{17}NO_5$: C, 64.75; H, 5.43; N, 4.44. Found: C, 64.77; H, 5.39; N, 4.43%.

trans-*3,4-Dimethoxy-4′-nitrostilbene (entry 2 of Table 1)*: M.p. 131.3–132.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.92 (s, 3H, $–OCH_3$), 3.96 (s, 3H, $–OCH_3$), 6.90 (d, 1H, *J* = 8.5 Hz, 5-ArH), 7.03 (d, 1H, *J* = 16.2 Hz, –CH=CH–), 7.09 (d, 1H, *J* = 8.5 Hz, 6-ArH), 7.09 (s, 1H, 2-ArH), 7.24 (d, 1H, *J* = 16.2 Hz, –CH=CH–), 7.61 (d, 2H, *J* = 8.7 Hz, 2′,6′-ArH), 8.22 (d, 2H, *J* = 8.7 Hz, 3′,5′-ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ 55.9, 56.0, 109.2, 111.4, 120.9, 124.1, 124.3, 126.5, 129.4, 133.2, 144.2, 149.4, 150.1; IR: ν_{max}1508, 1462, 1259, 1633, 1587, 1503, 1454, 1329, 1236, 1122, 962 cm^{-1}. Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.56; H, 5.50; N, 4.81%.

trans-*4-Methoxy-4′-nitrostilbene (entry 3 of Table 1)*: M.p. 130.0–131.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.85 (s, 3H, OCH_3), 6.93 (d, 2H, *J* = 8.6 Hz, 3,5-ArH), 7.00 (d, 1H, *J* = 16.6 Hz, –CH=CH–), 7.20 (d, 1H, *J* = 16.6 Hz, –CH=CH–), 7.49 (d, 2H, *J* = 8.6 Hz, 2,6-ArH), 7.84 (d, 2H, *J* = 7.7 Hz, 2′,6′-ArH), 8.20 (d, 2H, *J* = 7.7 Hz, 3′,5′-ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.3, 113.3, 123.1, 125.4, 127.3, 127.9, 131.9, 143.2, 145.4, 159.2; IR: ν_{max} 3026, 2917, 1584, 1505, 1331, 1248, 1171, 1102, 1023, 961 cm^{-1}. Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 71.19; H, 5.24; N, 5.33%.

trans-*4-(N,N-Dimethylamino)-4′-nitrostilbene (entry 4 of Table 1)*: M.p. 152.0–153.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.02 (s, 6H, $N(CH_3)_2$), 6.72 (d, 2H, *J* = 8.1 Hz, 2,6-ArH), 6.93 (d, 1H, *J* = 16.1 Hz, –CH=CH–), 7.16 (d, 1H, *J* = 16.1 Hz, –CH=CH–), 7.45 (d, 2H, *J* = 8.1 Hz, 3,5-ArH), 7.56 (d, 2H, *J* = 8.2 Hz, 2′,6′-ArH), 8.18 (d, 2H, *J* = 8.1 Hz, 3′,5′-ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 39.2, 111.2, 120.6, 123.1, 123.2, 125.0, 126.4, 127.3, 127.8, 129.6, 132.6; IR: ν_{max} 3031, 2914, 1586, 1507, 1331, 1177, 1112, 962 cm^{-1}. Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.58; H, 6.19; N, 10.71%.

trans-*4-nitrostilbene (entry 5 of Table 1)*: M.p. 136.0–138.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17 (m, 1H, 4′-ArH), 7.30 (d, 1H, *J* = 16.2 Hz, –CH=CH–), 7.33 (d, 1H, *J* = 16.2 Hz, –CH=CH–), 7.41 (d, 2H, *J* = 7.3 Hz, 3, 5-ArH), 7.55 (d, 2H, *J* = 7.3 Hz, 2, 6-ArH), 7.63 (d, 2H, *J*=8.2 Hz, 2′, 6′-ArH), 8.22 (d, 2H, *J*=8.2 Hz, 3′, 5′-ArH); IR: ν_{max} 2909, 1638, 1583, 1512, 1430, 1331, 1107, 964 cm^{-1}. Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.89; H, 4.78; N, 6.36%.

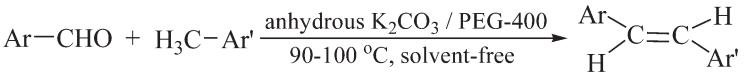
trans-*2-(4-Nitrostyryl)furan (entry 6 of Table 1)*: M.p. 129.8–131.4 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.48 (d, 2H, *J* = 2.5 Hz, 3,4-H), 7.02 (br s, 2H, –CH=CH– and 5-H), 7.46 (d, 1H, *J* = 16.1 Hz, –CH=CH–), 7.57 (d, 2H, *J* = 8.4 Hz, 2′,6′-ArH), 8.20 (d, 2H, *J* = 8.4 Hz, 3′, 5′-ArH); IR: ν_{max} 2915, 1578, 1501, 1320, 1106, 1019, 958, 854 cm^{-1}. Anal. Calcd for $C_{12}H_9NO_3$: C, 66.97; H, 4.22; N, 6.51. Found: C, 66.71; H, 4.23; N, 6.49%.

trans-*4,4′-Dinitrostilbene (entry 7 of Table 1)*: M.p. 117.2–118.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (s, 2H, –CH=CH–), 7.69 (d, 4H, *J* = 7.6 Hz, 2,2′,6,6′-ArH), 8.27 (d, 4H, *J* = 7.6 Hz, 3,3′,5,5′-ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 124.6, 128.5, 131.4, 143.5, 146.1. IR: ν_{max} 3106, 2926, 1600, 1501, 1331, 1106, 964 cm^{-1}. Anal. Calcd for $C_{14}H_{10}N_2O_4$: C, 62.22; H, 3.73; N, 10.37. Found: C, 62.39; H, 3.65; N, 10.45%.

trans-*3,4,5-Trimethoxy-2′-nitrostilbene (entry 8 of Table 1)*: M.p. 127.0–128.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H, OCH_3), 3.92 (s, 6H, 2–OCH_3), 6.76 (s, 2H, 2,6-ArH), 7.02 (d, 1H, *J* = 16.0 Hz, –CH=CH–), 7.41 (m, 1H, 4′-ArH), 7.50 (d, 1H, *J* = 16.0 Hz, –CH=CH–), 7.61 (m, 1H, 5′-ArH), 7.76 (d, 1H, *J* = 7.46 Hz, 6′-ArH), 7.97 (d, 1H, *J* = 7.93 Hz, 3′-ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.2, 60.9, 103.3, 118.9, 121.9, 122.0, 126.8, 127.0, 132.0, 132.8, 139.2, 143.8, 146.7, 153.6; IR: ν_{max} 3021, 1582, 1515, 1462, 140, 1341, 1250, 1121, 997 cm^{-1}. Anal. Calcd for $C_{17}H_{17}NO_5$: C, 64.75; H, 5.43; N, 4.44. Found: C, 64.77; H, 5.39; N, 4.43%.

trans-2-*(3,4,5-Trimethoxystyryl)-3,3-dimethyl-3H-benzo[e]indole (entry 9 of Table 1)*: M.p. 157.2–158.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.73 (s, 6H, $–CH_3$), 3.92 (s, 3H, $–OCH_3$), 3.94 (s, 6H, $–OCH_3$), 6.76 (s, 2H, ArH), 7.06 (d, 1H, *J* = 16.2 Hz, –CH=CH–), 7.49 (m, 1H, ArH), 7.58 (m, 1H, ArH), 7.75 (d, 1H, *J* = 16.2 Hz,

Table 1 Synthesis of *trans*-1,2-diaryl ethylenes under solvent-free conditions[a]



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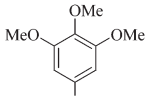
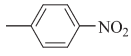
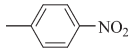
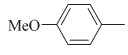
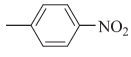
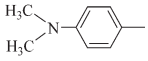
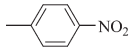
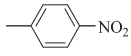
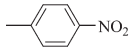
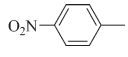
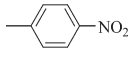
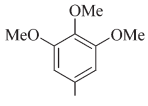
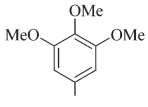
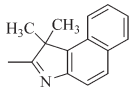
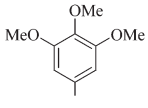
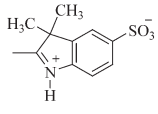
1			100	3.0	85
2			100	3.0	81
3			100	3.0	74
4			100	3.0	82
5			90	2.0	71
6			90	2.0	89
7[c]			90	2.0	50
8[d]			100	2.5	26
9			100	4.5	35
10			100	4.0	38

[a]Reactions performed with 10 mmol of aryl-aldehydes, 10 mmol of aromatic substances bearing activity methyl, 20 mmol of anhydrous K_2CO_3 and 0.5–1.0 mL of PEG-400 under solvent-free conditions.
[b]Isolated yields after recrystallisation.
[c]1.0 g PEG-1000 was used as phase transfer catalyst.
[d]1.0 g PEG-600 was used as phase transfer catalyst.

–CH=CH–), 7.88 (d, 2H, J = 3.9 Hz, ArH), 7.96 (1H, J = 7.80 Hz, ArH), 8.07 (d, 1H, J = 7.80 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.4, 54.4, 56.2, 61.0, 104.7, 118.9, 120.3, 122.8, 124.6, 126.4, 128.5, 129.2, 129.8, 131.7, 132.6, 137.7, 137.8, 153.5, 184.9; IR: ν_{max} 3057, 2920, 1572, 1506, 1452, 1413, 1342, 1238, 1117, 1001 cm^{-1}. Anal. Calcd for $C_{25}H_{25}NO_3$: C, 77.49; H, 6.50; N, 3.61. Found: C, 77.37; H, 6.58; N, 3.43%.

trans-*2-(3,4,5-Trimethoxystyryl)-3,3-dimethyl-3H-indoleninium-5-sulfonate (entry 10 of Table 1)*: M.p. >300 °C; ^{1}H NMR (300 MHz, D_2O): δ 1.06 (s, 6H, $C(CH_3)_2$), 3.38 (s, 3H, –OCH_3), 3.46 (s, 6H, –OCH_3), 6.40 (s, 2H, ArH), 6.50 (d, 1H, J = 16.5 Hz, CH=CH), 7.08–7.13 (m, 2H, ArH), 7.50 (d, 1H, J = 8.1 Hz, ArH), 7.56 (s, 1H, ArH); ^{13}C NMR (75 MHz, D_2O): δ 22.8, 52.9, 56.0, 60.9, 105.2, 118.3, 119.0, 119.4, 125.9, 131.6, 138.4, 134.0, 140.3, 147.0, 152.5, 154.3, 186.7; IR: ν_{max}1611, 1564, 1311, 1236, 1105, 1023, 975 cm^{-1}. Anal. Calcd for $C_{21}H_{23}NO_6S$: C, 60.42; H, 5.55; N, 3.36. Found: C, 60.25; H, 5.43; N, 3.42%.

Synthesis of 1-(3,4,5-trimethoxyphenyl)-2-(4-nitrophenyl)ethanol
A mixture of 3,4,5-trimethoxybenzaldehyde (1.96 g, 10.0 mmol), *p*-nitrotoluene (1.37 g, 10.0 mmol), anhydrous K_2CO_3 (2.76 g, 20.0 mmol) and PGE-400 (0.5 mL) were ground thoroughly in a porcelain mortar in room temperature. After leaving the mixture for 24 h, water (10 mL) was added to the mixture and the product was filtered. The filter cake was rinsed with H_2O (5 mL × 3). The resultant was separated by silica gel column chromatography (eluted with the mixture of ethyl acetate and petroleum ether, v/v =1:1) to give 1.9 g of 1-(3,4,5-trimethoxyphenyl)-2-(4-nitrophenyl)ethanol as a yellow solid. M.p. 122.0–123.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.11 (s, 1H, OH), 3.12 (d, 2H, J = 6.9 Hz, CH_2), 3.83 (s, 9H, OCH_3), 4.87 (t, 1H, J = 6.9 Hz, CH), 6.52 (s, 2H, 2, 6-ArH), 7.34 (d, 2H, J = 8.4 Hz, 2′, 6′-ArH), 8.12 (d, 2H, J = 8.4 Hz, 3′, 5′-ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 45.5, 56.2, 60.9, 75.0, 102.8, 123.4, 130.4, 137.7, 139.1, 146.0, 146.8, 153.4; IR: ν_{max} 3477, 2926, 2846, 1595, 1511, 1458, 1336, 1233, 1119, 964 cm^{-1}.

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