Review Article

Rapid Methods of Synthesis of Stilbene and Phenylethynylstilbene Arms

ABSTRACT

Stilbene and phenylethynylstilbene units are excellent candidates for fluorescent sensor synthesis. In this paper we show a fast and efficient method for the preparation of fluorophores based on biphenyl nuclei with phenylene-vinylene units functionalized by donor groups. Using pallado catalysed coupling reactions of Sonogashira types and Wittig or Wittig-Horner reaction, the stylbene and phenylethylsylbene arms functionalized with O-alkyl and N-alkyl donor groups were synthesized.

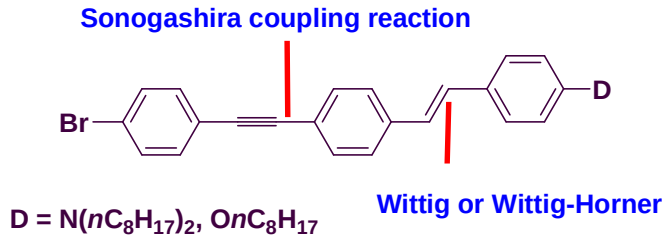


Figure 1

KEYWORDS

Stilbene, Phenylethynylstilbene, photophysical and photochemical properties

1. Introduction

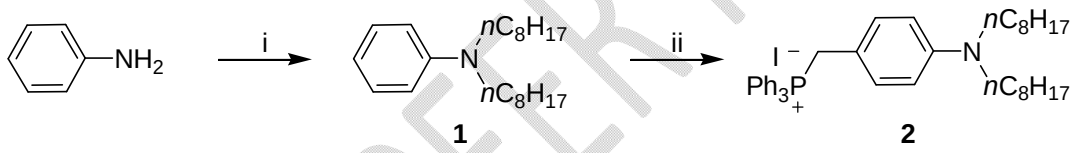
Phenylethynylstilbenes have been extensively studied during the last 30 years.[1-2] Their interest arises from the wide variety of properties of those systems, such as efficient charge and electron transfer and high fluorescence.[3-4] The origin of these photophysical and photochemical properties can be directly attributed to the conjugation π which extends along the main molecular axis. For

these reasons, that we have been interested in these compounds in this work. Today, there is a growing demand for fluorescent polymers in a wide range of sectors. For instance, in the field of safety, fluorescent marking is of interest in combating counterfeiting. In the field of forensics, it is implemented in police investigations. Fluorescent polymers are also used in chemical sensors to detect pollutants such as toxic heavy metals.[5-8]

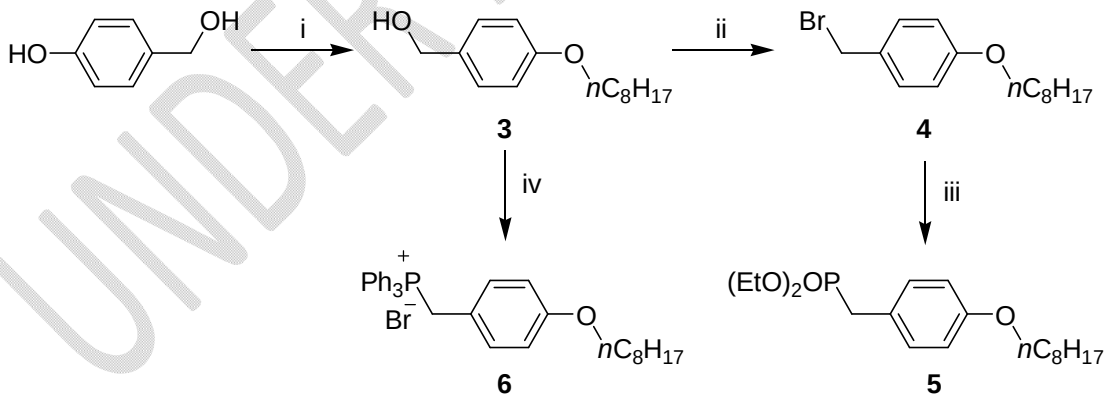
2. Experimental

2.1. Synthesis of Wittig and Wittig-Horner reagents

For the preparation of the halogenated arms, aniline and 4-hydroxybenzyl alcohol were used as starting materials. In the first step, by a dialkylation reaction on the amine, *N*,*N*-dioctylbenzenamine **1** was obtained in an excellent yield of 95%. From this, we prepared phosphonium **2** with a yield of 90%. The action of cesium carbonate in presence of 1-bromooctane on 4-(hydroxymethyl)phenol allowed the selective alkylation of the alcohol in the 4 position, leading to the derivative **3** with 56% yield.



i) K_2CO_3, NaI, $nC_8H_{17}Br$, DMF at ebb, 95% ; ii) paraformaldehyde, PPh_3, NaI, CH_3COOH, H_2O, $CHCl_3$ at ebb, 75%.



i) Cs_2CO_3, $nC_8H_{17}Br$, acetone, 56% ; ii) CBr_4, PPh_3, Et_2O ; iii) $P(OEt)_3$ at ebb ;
iv) PPh_3.HBr, refluxing toluene

Scheme 1

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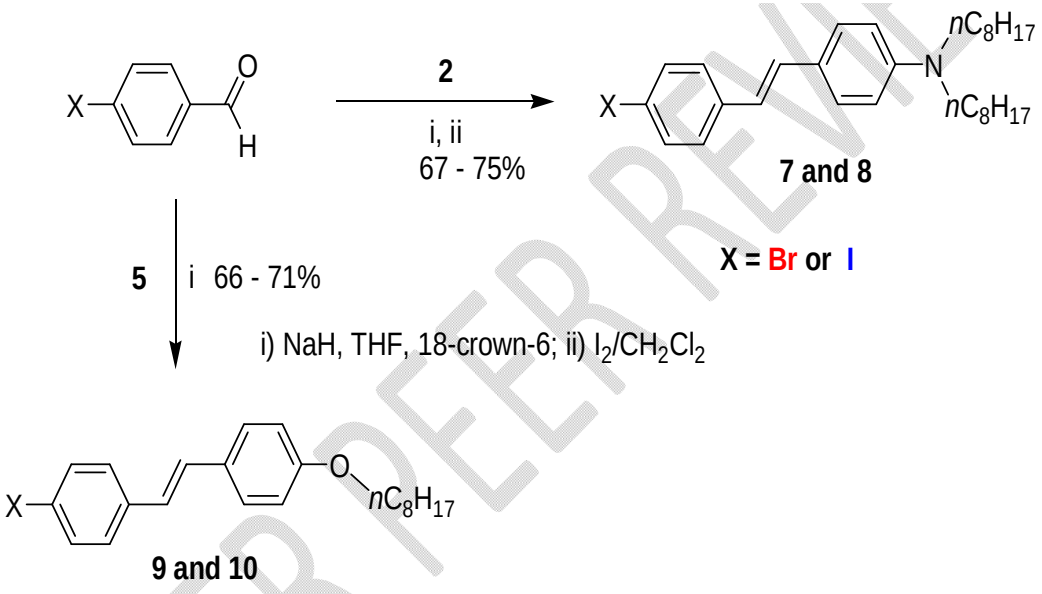
A bromination reaction in presence of perbromomethane (CBr_4) on the primary alcohol of compound **3** made it possible to isolate the compound **4** functionalized with a bromine. The phosphonate **5** was synthesized with 62% in both steps. Compound **3** in presence of triphenylphosphine hydrobromide at reflux in toluene yielded phosphonium **6** quantitatively.[9-14]

3. Results and discussion

3.1. Obtaining halogenated arms of stilbene type.

After obtaining the phosphonium and phosphanate derivatives, we synthesized two stilbene halogenated arms by Wittig and Wittig-Horner reaction by using 4-bromobenzaldehyde and 4-iodobenzaldehyde as a partner. Derivatives **7, 8, 9** and **10** were isolated with good yields.



Scheme 2

In order to anchor the final compounds in ionic liquids, another iodinated arm, compound **14**, has also been prepared. Starting from 4-hydroxybenzaldehyde, compound **12** was prepared by alkylation with 1,4-dibromobutane in presence of potassium carbonate. The latter with the presence of dimethylamine hydrochloride and potassium carbonate in ethanol at 100°C under pressure for 2 hours is converted to the desired compound **13**. Compound **13** is engaged in a Wittig-Horner reaction with as a partner the diethyl 4-iodobenzylphosphonate **11** which has been prepared from 1-(bromomethyl)-4-iodobenzene in order to obtain the iodized arm **14** in a good yield of 86%.

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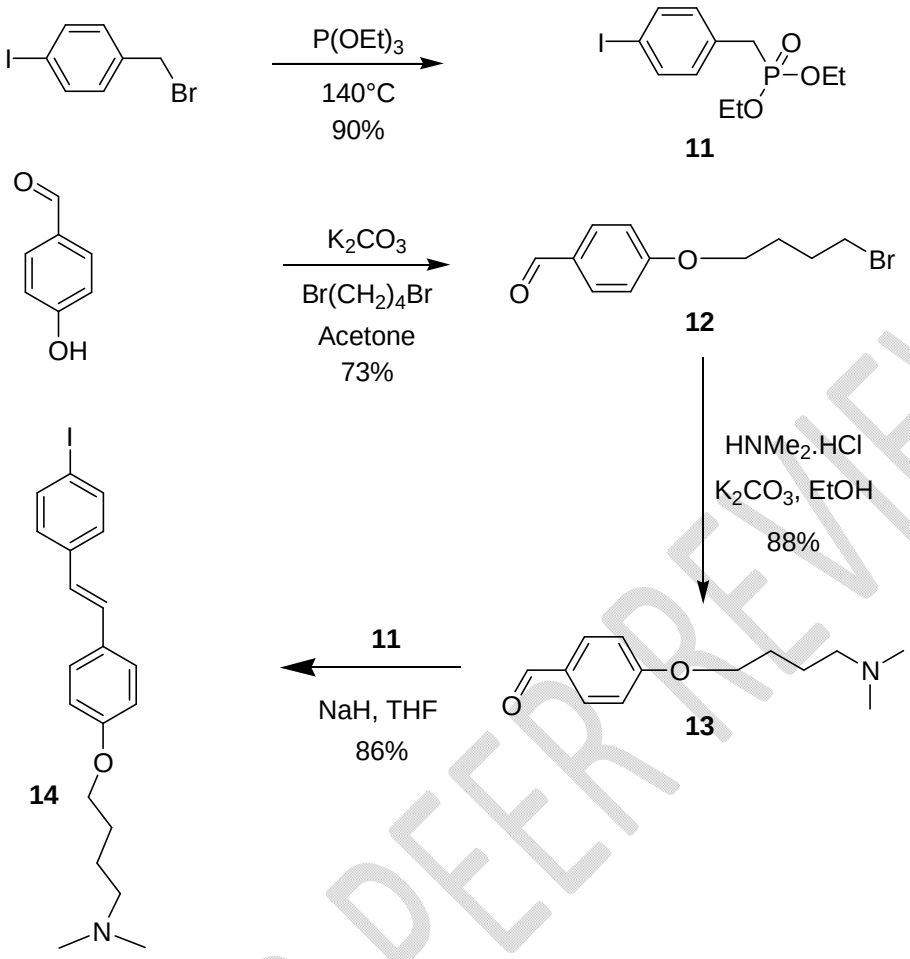

Scheme 3

3.2. Synthesis of phenylethynylstilbene arms

Two brominated phenylethynylstilbene arms functionalized with donor groups N($n$$C_8H_{17}$)$_2$ and O$n$$C_8H_{17}$ were also synthesized. From commercial 2-(4-bromophenyl)ethynyl)trimethylsilane, trimethylsilane was deprotected by the action of potassium carbonate in a mixture of dichloromethane / methanol and the true alkyne (compound **15**) was obtained quantitatively. The latter is put into Sonogashira coupling reaction with 4-bromobenzaldehyde in order to obtain compound **16** with a good yield of 88%.

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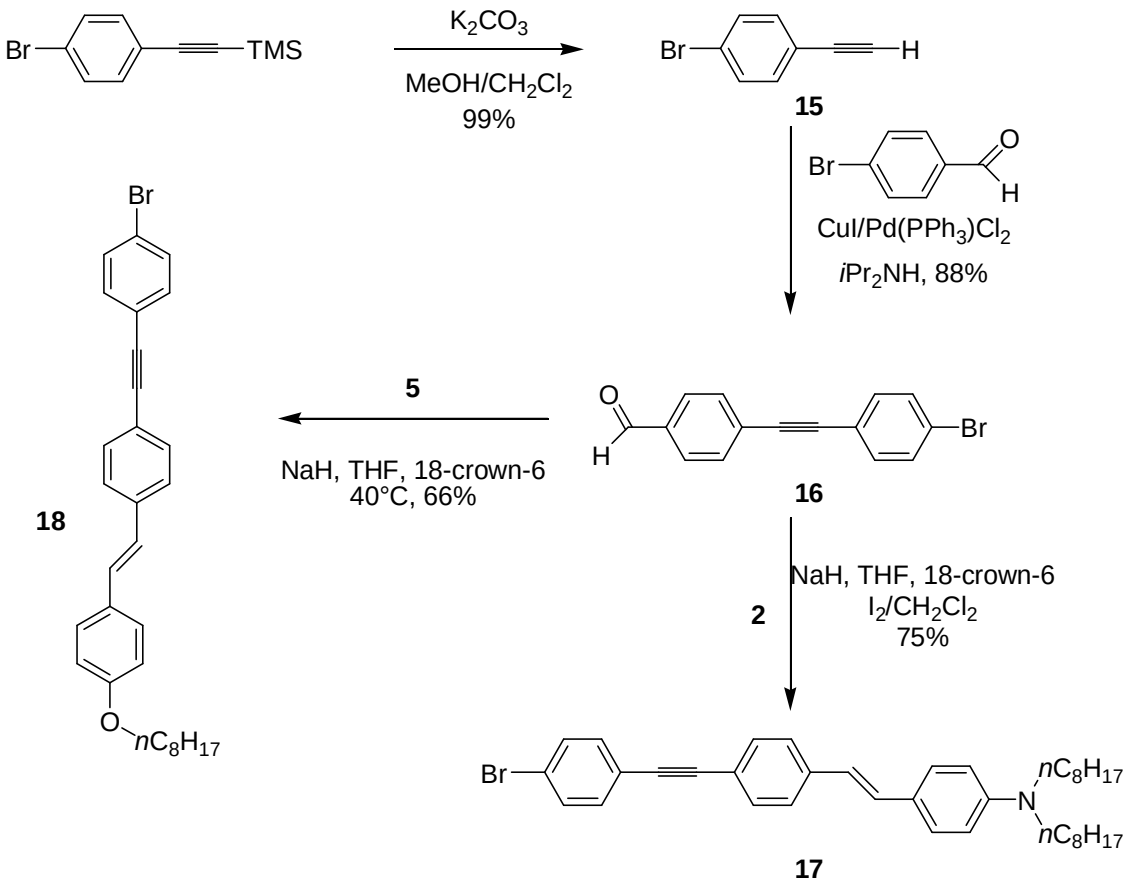

Scheme 4

Compound **16** is subjected to a Wittig and Wittig-Horner reaction with phosphonium 2 and phosphonate **5** as a partner, the desired compounds **17** and **18** have been obtained in good yields. In the case of the Wittig reaction, the E / Z mixture was isomerized to the E derivative (compound **17**) by the action of iodine in ambient light.

4. General procedure for the synthesis

4.1. Procedure of Sonogashira coupling

CuI and [$PdCl_2(PPh_3)_2$] were added to a solution of 4-bromobenzaldehyde, compound 15 in a mixture of toluene (10 mL), and diisopropylamine. The resulting mixture was stirred for 15h at 50

°C, then cooled to room temperature and concentrated under vacuum. The residue was purified by silica gel chromatography (cyclohexane / ethyl acetate 80/20) to give the product.

Compound 16: 4-(2-(4-bromophenyl) ethynyl) benzaldehyde

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.41 (d, 2H, *J* = 8.7Hz), 7.51 (d, 2H, *J* = 8.7Hz), 7.67 (d, 2H, *J* = 8.1Hz), 7.86 (d, 2H, *J* = 8.5Hz), 10.02 (s, 1H).

4.2. Procedure of Wittig or Wittig-Horner reactions

To a solution of phosphonate (or phosphonium) and aldehyde in tetrahydrofuran (10 mL) at 0 °C were added 60% w/w NaH in mineral oil and 18-crown-6. The resulting mixture was stirred at room temperature for 2 hours, then quenched with water and extracted with dichloromethane (2 X 10 mL). The organic phase was dried over $MgSO_4$ and the volatiles removed under vacuum. The crude product was redissolved in dichloromethane (5 mL) and a catalytic amount of iodine was added. The solution was stirred at room temperature for 3h under light exposure then washed with saturated aqueous $Na_2S_2O_3$ and dried over $MgSO_4$. The residue was purified by flash silica gel chromatography (cyclohexane / ethyl acetate 80/20 then 70/30) to give the product

Compound 7: **(E)-4-(4-bromostyryl)-*N, N*-dioctylbenzenamine**

^{1}H NMR (200 MHz, $CDCl_3$): δ(ppm) = 0.91 (t, 6H, *J* = 6.9Hz), 1.31-1.40 (m, 20H), 1.55-1.65 (m, 4H), 3.29 (t, 4H, *J* = 7.8 Hz), 6.62 (d, 2H, *J* = 8.7Hz), 6.80 (d, 1H, *J* = 16.2Hz), 7.02 (d, 2H, *J* = 16.2Hz), 7.32-7.45 (m, 10H).

^{13}C NMR (50 MHz, CDCl3): δ (ppm) = 14.2, 22.8, 27.0, 27.2, 29.4, 29.6, 30.3, 31.9, 51.2, 111.7, 122.2, 124.0, 127.5, 128.0, 129.8, 131.4, 131.7, 137.4, 148.1.

Compound 14: (E)-4-(4-(4-iodostyryl) phenoxy)-*N,N*-dimethylbutan-1-amine

^{1}H NMR (300MHz, $CDCl_3$), δ (ppm) = 7.57 (2H, dd, J =8.4Hz), 7.35 (2H, dd, J = 8.4Hz), 7.15 (2H, d, J = 8.4Hz), 6.98 (1H, d, J = 19.2Hz), 6.89-6.85 (3H, m), 3.94 (2H, t, J = 6Hz), 2.36 (2H, t, J = 7.2Hz), 2.25 (6H, s), 1.81-1.72(2H, m), 1.69-1.61 (2H, m).

^{13}C NMR (75.48 MHz, $CDCl_3$), δ (ppm) = 24.1, 27.1, 45.3, 59.2, 67.7, 92.1, 114.7, 125.2, 127.7, 127.9, 129.1, 129.6, 137.2, 137.6, 158.9.

Compound 17: (E)-4-(4-(2-(4-bromophenyl) ethynyl) styryl)-*N, N*-dioctylbenzenamine

^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) = 0.89 (t, 6H, *J* = 6.7Hz), 1.20-1.40 (m, 20H), 1.55-1.70 (m, 4H), 3.28 (t, 4H, *J* = 7.6 Hz), 6.62 (d, 2H, *J* = 8.6Hz), 6.84 (d, 1H, *J* = 16.2Hz), 7.07 (d, 2H, *J* = 16.2Hz), 7.32-7.50 (m, 10H).

^{13}C NMR (50 MHz, CDCl3): δ (ppm) = 14.2, 22.8, 27.3, 27.4, 29.5, 29.6, 31.9, 51.2, 111.6, 125.9, 127.5, 127.9, 131.7, 131.9, 133.0, 148.0.

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5. Conclusion

This work describes an efficient method for the preparation of organic ligands exhibiting electron transfer properties and significant fluorescence due to the π conjugation which extends along the main molecular axis. These stylbene and phenylethynylstilbene derivatives with very interesting photophysical and photochemical properties have been synthesized by the Sonogashira coupling reaction and the Wittig or Wittig-Horner reactions**.**

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