# Synthesis, Isolation and Crystal Structure Characterization of (*Z*)-4'-(1-Phenyl-2-*p*-tolylvinyl)biphenyl-4-carbaldehyde

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Fluorescent organic materials are used in a range of applications including bio-sensors,[1] optical storage devices,[2] and organic solar cells.[3] They have recently gained particular interest as efficient light emitters and charge transporters in organic light-emitting diodes (OLEDs) due to their significant advantages in energy consumption and flexible applications.[4] The improved efficiency and stability of blue emitting materials is especially important in the area of OLEDs, because efficient blue emitters are rare due to the intrinsic wide band-gap.[5] Blue fluorescent materials include oligophenylenes,[6] diarylanthracenes,[7] and poly(phenylene vinylene)s.[8] Recently, organometallic phosphorescent materials including iridium (III) complexes have been studied due to their high efficiency.[9]

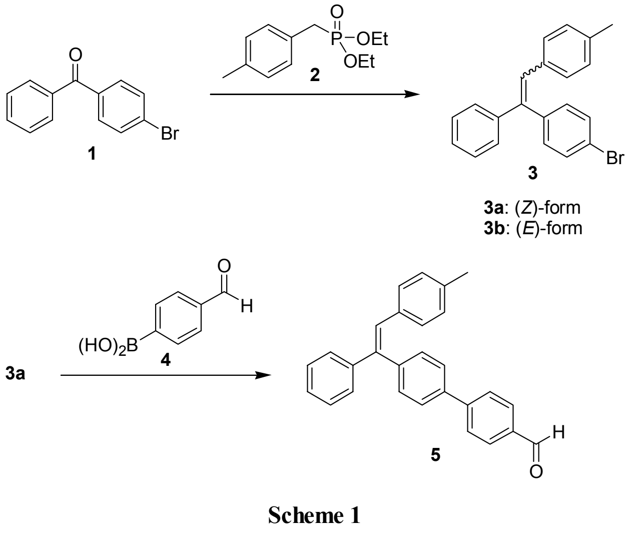
Since Hosokawa's pioneering work with 4,4'-bis(2,2-diphenylvinyl)-1,1'-biphenyl (DPVBi) in the 1990s,[10] various distyrylarylenes (DSAs) have been investigated as representative blue fluorescent materials in OLEDs.[11] However, their low quantum efficiency, low glass transition temperature and crystallizing tendency have limited their applications in OLEDs.[12] The tendency for crystallization eventually degrades the lifetime of the corresponding devices by destroying the film homogeneity and crystal boundary.[13] Structural modifications have been investigated to decrease the crystallizing tendency of DSAs, typically by constructing spiro-DSAs[14] and tetrahedral DSAs.[15]

The Horner-Wadsworth-Emmons reaction[16] has been frequently used to prepare π-conjugated hydrocarbons for OLEDs and organic field-effect transistors. While (*E*)-isomers are predominantly produced by reactions of aldehydes with benzyl phosphonates,[17] reactions of ketones generate mixtures of (*E*)- and (*Z*)-geometric isomers that are difficult to be resolved.[11(b),18] Significant problems in understanding the relationship between chemical structures and physical properties of emitting materials have been encountered because each isomer shows different optical properties.[19] Therefore, an efficient separating process for two geometric isomers has been explored for the systematic development of functional π-conjugated hydrocarbons.

In a program for the development of blue fluorescent materials in our laboratory, 1-(4-bromophenyl)-2-(4-methylphenyl)-1-phenylethylene (**3**), an important intermediate for unsymmetrical DSAs, was prepared by the reaction of 4-bromobenzophenone (**1**) with diethyl (4-methylbenzyl)phosphonate (**2**) (Scheme 1). However, the crude product **3** was obtained as a 60 : 40 mixture of geometric isomers that were not separable by common chromatographic methods. Fortunately, we observed that a careful recrystallizing process in 2-propanol facilitated the selective isolation of both isomers. Nuclear magnetic resonance (NMR) study showed that the initially recrystallized major product was (*Z*)-isomer, **3a**. (*Z*)-4'-(1- Phenyl-2-*p*-tolylvinyl)biphenyl-4-carbaldehyde (**5**) was prepared by Suzuki-Miyaura reaction of **3a** with 4-formylphenylboronic acid (**4**), and recrystallized in *n*-hexane : $Et_2O$ (8 : 1) to give a single crystal that was characterized by X-ray structure analysis. The results of this study are presented and discussed below.

The reaction of **1** with **2** in the presence of potassium *tert*-butoxide produced a 60 : 40 mixture of geometric isomers of bromotriphenylethylene **3** at the refluxing temperature of THF. While conventional chromatographic methods were not able to resolve those isomers, the recrystallization process in 2-propanol facilitated the selective isolation of each isomer in a crystalline form. The major product **3a** was initially obtained as a clear crystalline solid, which was purified by a double recrystallizing process, in 31% isolated yield with 98% purity. The other isomer **3b** was obtained by the consecutive recrystallization process of the remaining mother liquor.

The crystalline solids of both isomers were not uniform enough for single-crystal X-ray crystallography. Although various spectroscopic analyses were performed to distinguish the configuration of both isomers, their configuration could not be easily identified. Among $^1$H-NMR, $^{13}$C-NMR, correla-



**Scheme 1**

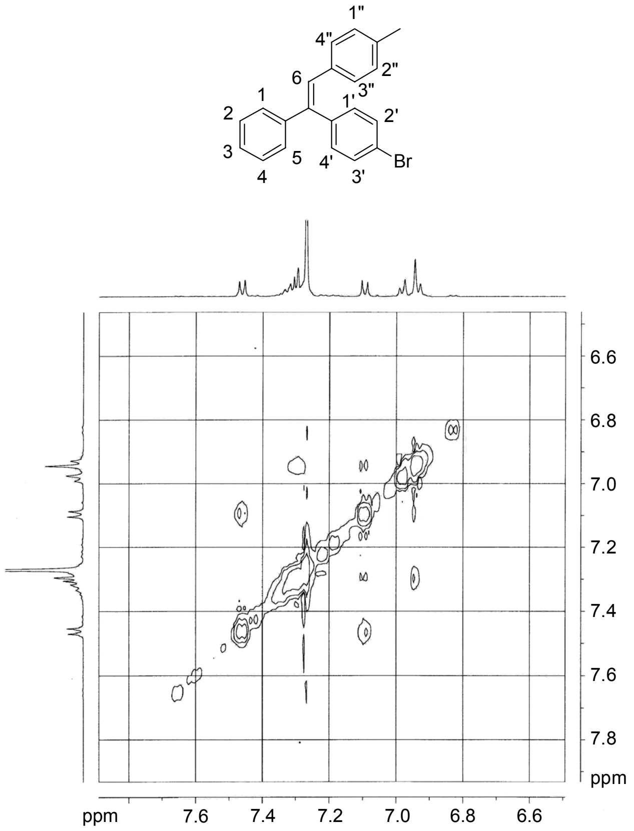


**Figure 1.** NOESY spectra of **3a**.

**Table 1.** Crystal data and structure refinement for **5**.

| | |
|---|---|
| Empirical formula | $C_{28}H_{22}O$ |
| Formula weight | 374.46 |
| Temperature | 296(2)K |
| Crystal system, space group | Monoclinic, $P2(1)/c$ |
| Unit cell dimension | a = 11.684 (2) Å<br>b = 15.626 (2) Å<br>c = 11.325 (2) Å<br>β = 92.66 (1)° |
| Volume | 2065.4 (5) $Å^3$ |
| Z | 4 |
| Absorption coefficient | 0.07 $mm^{-1}$ |
| F(000) | 792 |
| Theta range for data collection | 2.18 to 28.61 deg. |
| Index range | $-15 \leq h \leq 15$<br>$-21 \leq k \leq 20$<br>$-13 \leq l \leq 15$ |
| Independent reflections | 5192 [R (int) = 0.069] |
| Goodness-of-fit on $F^2$ | 1.051 |
| Final R indices [I > 2σ(I)] | $R = 0.1303$,<br>$R_w = 0.3223$ |
| Largest diff. peak and hole | 0.33 and −0.42 e/ $Å^3$ |

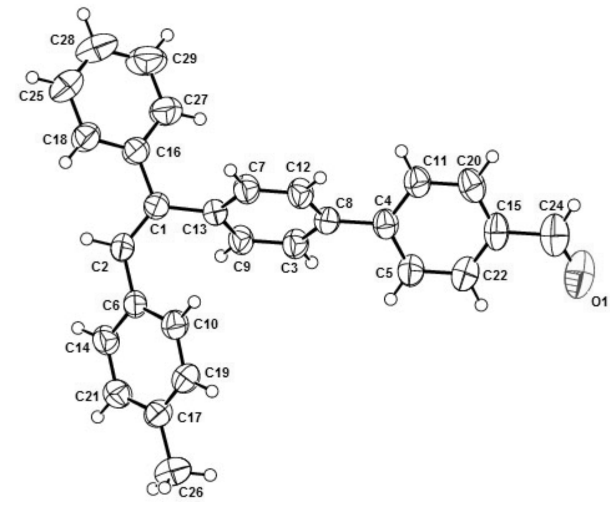


**Figure 2.** Molecular structure of **5**, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

tion spectroscopy (COSY), nuclear Overhauser effect spectroscopy (NOESY) and heteronuclear single quantum coherence (HSQC) analyses analyses, the NOESY spectra of **3a** presented a vague clue (Figure 1). The correlations between H-6 at δ 7.05 and H-1 δ 7.30 and between H-3" at δ 7.05 and H-1' at δ 6.94 suggested that **3a** may have the *Z*-configuration.

The configuration of **3a** could be clearly determined after the synthesis of **5**. Stilbene **5** was prepared by the palladium-catalyzed cross-coupling reaction of **3a** with **4** in the presence of sodium carbonate. The crude product was purified by column chromatography to give **5** in 85% isolated yield. A single crystal of **5** was obtained by recrystallization of the purified product in *n*-hexane : $Et_2O$ (8 : 1). The single-crystal X-ray crystallography of **5** has not been disclosed before. The structural information of the crystalline **5** is presented in Table 1.

The molecular structure of compound **5** illustrated in Figure 2 clearly shows the configuration and non-planar conformation of **5**. The torsion angles C2−C1−C16−C18, C2−C1−C13−C9, and C1−C2−C6−C10 in **5** were 29.4 (4), 57.8 (4), and 38.4 (4)°, respectively. The bond length of C1=C2 was 1.353 (4) Å, which is longer than the reported C=C bond lengths of *trans*-[20] and *cis*-stilbenes.[21]

The steric hindrance between rings **a** and **c** created a significant distortion around the ethylene group, and especially broadened the angle C7−C14−C15 to 127.9 (2)°. The dihedral angles between rings **a** and **b**, rings **a** and **c** and rings **a** and **d** were 36.6 (2), 57.0 (2), and 76.1 (2)°, respectively (Figure 3). Among the six angles in phenyl rings, the angles involving C4, C6, C8, C13, and C16, which are directly connected to outside the $sp^2$ carbon of the ring, were generally smaller than the others.

In summary, bromotriphenylethylene **3** was prepared as a 60 : 40 mixture of geometric isomers and efficiently separated to give both pure (*Z*)- and (*E*)-isomers by a careful recrystallizing process in 2-propanol. NMR study revealed the initially recrystallized major product to be the (*Z*)-isomer, **3a**. The configuration of **3a** was confirmed by the first single crystal X-ray structure analysis of (*Z*)-4'-(1-phenyl-2-*p*-tolylvinyl)biphenyl-4-carbaldehyde (**5**) that was prepared by Suzuki-Miyaura reaction of **3a** with **4** and recrystallized in *n*-hexane : $Et_2O$ (8 : 1). The procedure described in this paper is a promising synthetic route for preparing important intermediates of unsymmetrical DSAs. It is also expected to facilitate the systematic develop-

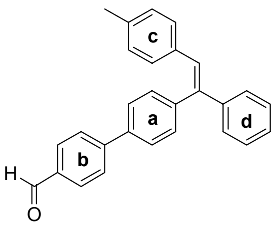


**Figure 3.** Molecular structure of **5**.

ment of functional π-conjugated hydrocarbons, such as organic fluorescent materials.

## Experimental Section

**Preparation of 1-(4-bromophenyl)-2-(4-methylphenyl)-1-phenylethylene (3).** To the mixture of **2** (35.1 mmol, 8.51 g) and potassium *tert*-butoxide (54.0 mmol, 6.06 g) in THF (54 mL) was added a solution of **1** (27.0 mmol, 5.00 g) in THF (200 mL) at room temperature under an Ar atmosphere. The mixture was stirred at refluxing temperature for 3 h. The reaction mixture was cooled to room temperature; diluted with ethyl acetate (300 mL); washed with 1% aqueous HCl (200 mL), water (300 mL) and brine; dried over $MgSO_4$; and concentrated in vacuo. When the crude product was purified by column chromatography, **3** was obtained as a white powder (8.83 g, 94%) that was a 60 : 40 mixture of **3a** and **3b** by GC analysis. When the mixture was recrystallized from 2-propanol, a crystalline product was generated as a 91 : 9 mixture of **3a** and **3b**. This crystalline mixture was purified further by the second recrystallization from 2-propanol to give **3a** as a needle crystal with 98% purity (2.91 g, 31%): TLC $R_f$ 0.73 (*n*-hexane : $Et_2O$ = 1 : 1), mp 119 - 121 °C. $^1$H NMR spectrum (500 MHz, $CDCl_3$) δ 2.28 (s, 3H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.93 (s, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 7.27-7.31 (m, 5H), 7.45 (d, *J* = 8.3 Hz, 2H); $^{13}$C NMR spectrum (125 MHz, $CDCl_3$) δ 21.4, 121.6, 127.8 (×3), 128.5 (×2), 128.9, 129.1 (×2), 129.7 (×2), 132.1 (×2), 132.5 (×2), 134.4, 137.1, 139.8, 140.7, 143.3: HRMS (EI, 70 eV) calcd for $C_{21}H_{17}Br$ ($M^+$), 348.0514, found 348. 0495.

The (*E*)-isomer **3b** was obtained by the consecutive recrystallizing process of the remaining mother liquor. Recrystallization of the white solid that was obtained by concentrating the remaining solution produced a pure crystalline **3b** (0.281 g, 3%): TLC $R_f$ 0.73 (*n*-hexane : $Et_2O$ = 1 : 1), mp 69 - 70 °C. $^1$H NMR spectrum (500 MHz, $CDCl_3$) δ 2.26 (s, 3H), 6.89-6.91 (m, 3H), 6.94 (d, *J* = 8.1 Hz, 2H), 7.16-7.19 (m, 4H), 7.33-7.34 (m, 3H), 7.41 (d, *J* = 8.5 Hz, 2H); $^{13}$C NMR spectrum (75 MHz, $CDCl_3$) δ 21.3, 121.6, 127.8, 128.8, 129.0 (×4), 129.4 (×2), 129.7 (×2), 130.6 (×2), 131.5 (×2), 134.5, 137.2, 140.3, 140.8, 142.8: HRMS (EI, 70 eV) calcd for $C_{21}H_{17}Br$ ($M^+$), 348.0514, found 348. 0540.

**Preparation of 4'-(1-phenyl-2-*p*-tolyl-vinyl)-biphenyl-4-cabaldehyde (5).** To a solution of **3a** (1.4 mmol, 0.50 g) and $Pd(PPh_3)_4$ (0.072 mmol, 0.083 g) in DMF (60 mL) was added 2.0 M aqueous $Na_2CO_3$ (1.5 mL). To the resulting mixture was added **4** (1.7 mmol, 0.25 g), which was dissolved in MeOH (1 mL). The mixture was stirred at refluxing temperature for 7 h. The reaction mixture was cooled to room temperature; diluted with ethyl acetate (150 mL); washed with 1% aqueous HCl (100 mL); water (300 mL) and brine; dried over $MgSO_4$; and concentrated in vacuo. The crude compound was purified by column chromatography (*n*-hexane : $Et_2O$ = 4 : 1) to generate **5** (0.445 g, 85%) as a white solid: TLC $R_f$ 0.63 (*n*-hexane : $Et_2O$ = 1 : 1), mp 207 - 208 °C. $^1$H NMR spectrum (500 MHz, $CDCl_3$) δ 2.28 (s, 3H), 6.96-6.99 (m, 5H), 7.32-7.35 (m, 7H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.97 (d, *J* = 8.2 Hz, 2H), 10.07 (s, 1H); $^{13}$C NMR spectrum (75 MHz, $CDCl_3$) δ 21.2, 127.7 (×4), 127.9 (×2), 128.5 (×2), 129.1, 129.1 (×2), 129.7 (×2), 130.6 (×3), 131.5 (×2), 134.6, 135.5, 137.1, 138.6, 141.3, 141.3, 143.6, 146.9, 192.3: HRMS (EI, 70 eV) calcd for $C_{28}H_{22}O$ ($M^+$), 374.1671, found 374.1670. The product was recrystallized from *n*-hexane : $Et_2O$ (8 : 1) to give a single crystal of **5** that was analyzed by X-ray crystallography.

**X-ray crystallographic analysis for 5.** A single crystal of **5** was mounted on a glass fiber. The diffraction data for **5** were collected on a Bruker 1K SMART CCD-based diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å) at 296 K. The reflection data were collected as φ and ω scans. Cell parameters were determined and refined by the *SMART* program.[22] Data reduction and empirical absorption correction were performed using *SAINT* software[23] and the *SADABS* program,[24] repectively.

**Supplementary Data.** Christallographic data for the structure **5** reported here have been deposited with the Cambridge Crystallographic Data Centre (Deporsition No. CCDC-734302). That data can be obtained free of charge *via http://www.ccdc.cam.ac.uk/data_request/cif* (or from The CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033: e-mail: *deposit@ccdc.cam.ac.uk*).

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