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Organic high-spin and mixed-valence systems; synthesis, electrochemical and spectroscopic studies of asymmetric and symmetric tetraaryl-*m*-phenylenediamines

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Abstract

An asymmetric tetraaryl-1,3-phenylenediamine was designed and synthesized as a model for positively charged high-spin systems as well as for organic mixed-valence molecular systems, and their electrochemical and spectroscopic properties were examined.

Keywords: Oligoarylamines; Coupling reactions; Electrochemical methods; UV–Vis absorption; Charged high-spin systems; Organic mixed-valence system

1. Introduction

Among the recent topics in chemistry and materials science, positively charged high-spin molecular systems generated by hole doping have attracted much attention as models for studying an interplay between pluricharge fluctuation and spin polarization in π-electron networks [1]. Particularly, π-conjugated oligoarylamines recently have been widely used as model precursors for positively charged organic high-spin systems [1b,1c,1d,1e,1f,1g]. They are suitable for models for purely organic mixed-valence systems [2]. As *p*-substituted triarylamines give extremely stable aminium radicals upon chemical or electrochemical oxidation, π-conjugated oligoarylamine systems are considered to be promising candidates. Previously, we have reported that *N*,*N*,*N*′,*N*′-tetrakis(*p*-anisyl)-4,6-dimethyl-1,3-phenylenediamine (**1**) and *N*,*N*,*N*′,*N*′,*N*″,*N*″-hexakis(*p*-anisyl)-1,3,5-phenylenetriamine (**2**) exhibit triplet and quartet ground states upon multi-step electron oxidation, respectively [1b,1c]. Furthermore, Ito et al., have recently reported that all-*para*-brominated di- and tri-arylamine systems give triplet ground states upon two electron oxidation [1h].

Many documented π-conjugated oligoarylamines as precursors of positively charged high-spin molecular systems, however, have all equivalent nitrogen sites in terms of their topological structures. As represented by ‘captodative effect’, combinations of electrodonating and withdrawing groups are a promising approach for manipulation of properties of open-shell organic molecules in a controlled manner. We have recently reported electrochemical and spectroscopic studies of a series of asymmetric *N*,*N*,*N*′,*N*′-tetraaryl-1,4-phenylenediamines, in which two different electrodonating and/or electrowithdrawing groups are asymmetrically connected at four peripheral phenyl rings [3]. However, in contrast to corresponding symmetric derivatives no remarkable feature has been observed. These results suggest that the electrochemical and spectroscopic properties of *N*,*N*,*N*′,*N*′-tetraaryl-1,4-phenylenediamines are strongly governed by their π-topological features rather than by electronic modifications such as by the adjacent substitutions. A strong electronic couplings for *N*,*N*,*N*′,*N*′-tetraaryl-1,4-phenylenedia-

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mines can also be suggested by an extremely large ΔE value (a difference between the first and second redox potential) of about 0.41 V.

In this study, we have chosen *N*,*N*,*N*′,*N*′-tetraaryl-1,3-phenylenediamines, which can be considered as the topological isomers of the 1,4-phenylenediamines. The smaller ΔE values for 1,3-isomers (for compound **1**, ΔE is reported to be 0.158 V [1c]) suggest a smaller electronic coupling than the corresponding 1,4-isomers; namely, the electrochemical and spectroscopic properties of 1,3-isomers would be affected more remarkably by the electronic nature of the substituents.

In order to examine how a set of electrodonating and withdrawing groups affect the electrochemical and spectroscopic properties of π-conjugated molecules, we have studied *N*,*N*-bis(*p*-chlorophenyl)-*N*′,*N*′-bis(*p*-tolyl)-4,6-dimethyl-1,3-phenylenediamine (**3**), where two different substituents are asymmetrically connected at four peripheral phenyl rings (Fig. 1). This type of asymmetric 1,3-diamines can be regarded as precursors for charge-inclined, positively charged organic high-spin systems.

2. Results and discussion

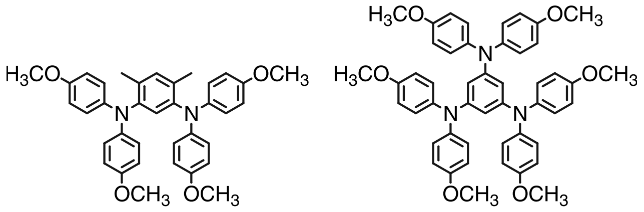
2.1. Molecular design and synthesis of asymmetric tetraaryl-1,3-phenylenediamine

In order to manipulate the electronic state of the π-conjugated tetraaryl-1,3-phenylenediamine system in a controlled manner, we introduce both strong electrodonating groups into one diphenylamino group and strong electrowithdrawing groups into another diphenylamino groups. In this respect, *N*,*N*-bis(*p*-anisyl)-*N*′,*N*′-bis(*p*-chlorophenyl)-4,6-dimethyl-1,3-phenylenediamine (**4**), where very strong electrodonating methoxy groups and very strong electrowithdrawing chloro groups are substituted, will be a promising model. However, at present, we have not succeeded in isolating the compound because of some instability. Instead, we have designed *N*,*N*-bis(*p*-chlorophenyl)-*N*′,*N*′-bis(*p*-tolyl)-4,6-dimethyl-1,3-phenylenediamine (**3**), where relatively strong electrodonating methyl groups and very strong electrowithdrawing chloro groups are substituted (Fig. 2). The compound **3** was prepared in three steps by the similar method reported previously [1b,1c] as shown in Fig. 3.

5-Nitro-2,4-xylidine was reacted with *p*-iodotoluene under Ullmann coupling condition to give nitrotriarylamine (**5**), which was reduced by tin dichloride/hydrochloric acid to give aminotriarylamine (**6**) (yield 25% for two steps). The second Ullmann reaction of the resulting **6** with *p*-chloroiodobenzene gave **3**, which was purified by column chromatography ($CHCl_3$/ethyl acetate = 1/1) in 31% isolated yield. The structure of **3** was confirmed by ordinary NMR and MS analyses. At the second Ullmann reaction, symmetric compound, *N*,*N*,*N*′,*N*′-tetrakis(4-chlorophenyl)-4,6-dimethyl-1,3-phenylenediamine (**7**) was not formed, indicating the absence of the scrambling reaction (aryl exchange).

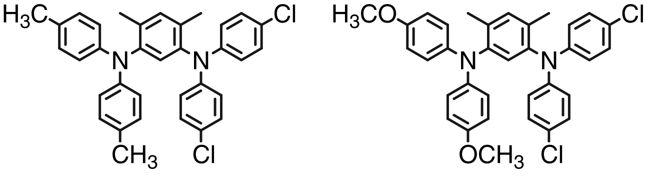
2.2. UV and cyclic voltammetry measurements

The UV spectra of **1** and **3** in chloroform exhibited broad absorption maxima around 300 nm, which are characteristic of triarylamine chromophores, and no significant difference was observed between them, indicating their similar electronic structures. To investigate electrochemical behaviours of mono- and dicationic states of **3**, cyclic voltammetry measurements were made in *n*-butyronitrile at ambient temperature and −78 °C. The cyclic voltammogram of **3** at ambient temperature is shown in Fig. 4, in which the voltammogram of **1** observed at the same condition is also given for comparison. The first and second redox potentials (E_1° and E_2°) were observed at 0.441 and 0.774 V (vs. ferrocene/ferrocenium (Fc/Fc^+)), which are assigned to be a two-step one electron transfer process corresponding to the removal of an electron from each triphenylamine system. No oxidation peak was observed upon further anodic sweeping. While the first redox couple was reversible, the second one was slightly irreversible, suggesting the thermodynamic instability of the corresponding dicationic state under this condition. Although the parent monomeric triarylamines, tris(*p*-tolyl)amine and tris(*p*-chlorophenyl)amine were reported to give a very stable monocationic state [4a,4b], the generated



1 **2**

Fig. 1. Structures of *N*,*N*,*N*′,*N*′-tetrakis(*p*-anisyl)-4,6-dimethyl-1,3-phenylenediamine (**1**) and *N*,*N*,*N*′,*N*′,*N*″,*N*″-hexakis(*p*-anisyl)-1,3,5-phenylenetriamine (**2**).



3 **4**

Fig. 2. Structures of *N*,*N*-bis(*p*-chlorophenyl)-*N*′,*N*′-bis(*p*-tolyl)-4,6-dimethyl-1,3-phenylenediamine (**3**) and *N*,*N*-bis(*p*-anisyl)-*N*′,*N*′-bis(*p*-chlorophenyl)-4,6-dimethyl-1,3-phenylenediamine (**4**).

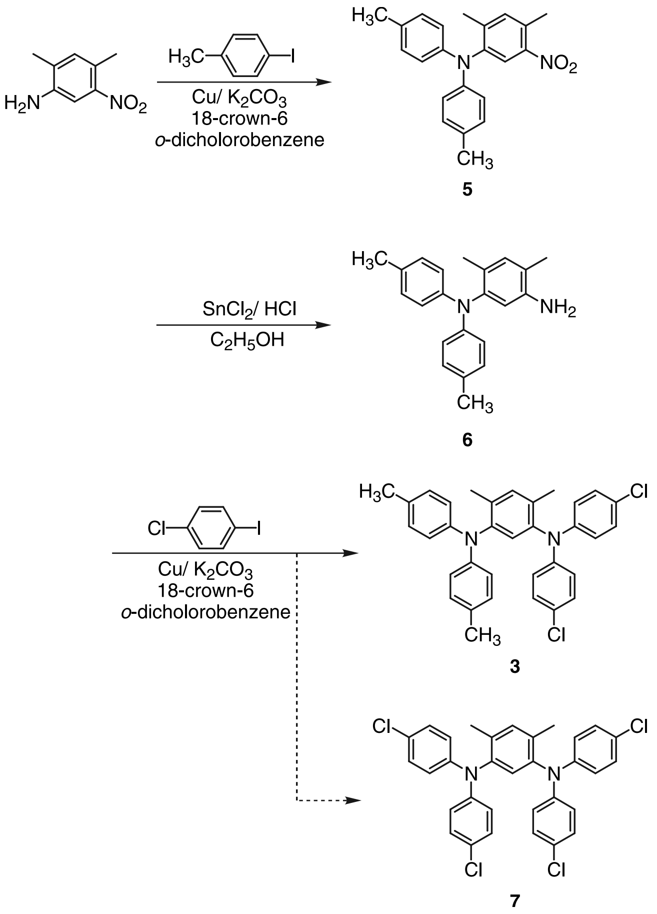


Fig. 3. Synthetic route for **3**.

dicationic state of **3** might be decomposed via some follow-up reactions, such as chloro group elimination and dimerization. Previously, Stickley and Blackstock have investigated a series of hexaaryl-1,3,5-phenylenetriamine with various substituents at their *para*-positions of the peripheral aryl rings, reporting that only six methoxy groups substituted compound, **2**, afforded a stable tricationic state at −78 °C [1e]. In this context, introduction of one or more methoxy groups may be required to stabilize oligocationic states of *meta*-connected oligoarylamine systems, such as **1** and **2**, effectively.

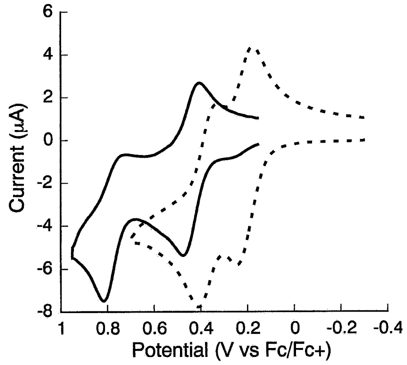


Fig. 4. Cyclic voltammogram of **1** (broken) and **3** (solid) in *n*-butyronitrile at ambient temperature.

At low temperatures, the stability of the dicationic state was remarkably improved. The cyclic voltammogram of **3** at −78 °C exhibited two reversible redox couples at 0.525 and 0.868 V (vs. Fc/Fc$^+$). Even at 20 mV s^{-1}, the dicationic state was extremely stable, indicating the surprising long life time-in-solution ($\tau >$ 30 s) as for dicationic species.

Interestingly, the ΔE (difference between E_2° and E_1°) of **3** (0.343 V) at −78 °C was larger than that of **1** (0.158 V), contrasting with the results for the topologically isomeric *N*,*N*,*N*′,*N*′-tetraaryl-1,4-phenylenediamines, where the ΔE values are not affected by the electronic perturbation of the substituents on the four peripheral aryl rings; the values are nearly constant ($\approx$0.41 V). Judging from the obtained large ΔE value for **3**, it seems apparent that a strong electronic coupling occurs between the two nitrogen atoms. However, another reason for this large ΔE value should be taken into account. The feasible mechanism is that there is no significant interaction between the two nitrogen atoms, that is, each diphenylamine unit behaves as an electrochemically independent group. In order to distinguish the two cases, a molecular orbital of **3** was calculated at the AM1 level. Fig. 5(a) shows the shape of the HOMO and next HOMO of **3**. At the HOMO level, two electrons are localized in the 2,4,4′,4″-tetramethyl triphenylamine site. Similarly, at the next HOMO level, two electrons are localized in the 4,4′-dichlorodiphenylamine site. These results contrast with that of the symmetrically substituted **1**, where electrons are delocalized over the whole π-electron network at both HOMO and next HOMO levels, respectively (Fig. 5(b)).

It is suggested from the MO calculations that the interaction between the two nitrogen cores is very weak, that is, each diphenylamine unit would behave as an electrochemically independent group. Furthermore, tris(*p*-tolyl)amine and tris(*p*-chlorophenyl)amine were reported to be oxidized at 0.75 and 1.04 V ($E_{p/2}$ vs. SCE in CH_3CN), respectively [4a], and the difference ($1.04-0.75=0.29$ V) can be regarded to be equal to the ΔE value for **3** (0.343 V), also supporting the above discussion.

2.3. Spectroelectrochemistry

The UV–Vis spectra of **3** upon electrochemical oxidation to mono- and di-cationic states were investigated in *n*-butyronitrile by using a spectroelectrochemical quartz cuvett at ambient temperature. The applied potential for the electrolytic formation of the mono- and di-cationic states of **3** were 0.637 V versus Fc/Fc$^+$, the midpoint between the first and second redox potentials, and 1.013 V, respectively. Upon oxidation to the monocationic state, a broad peak at 687 nm gradually

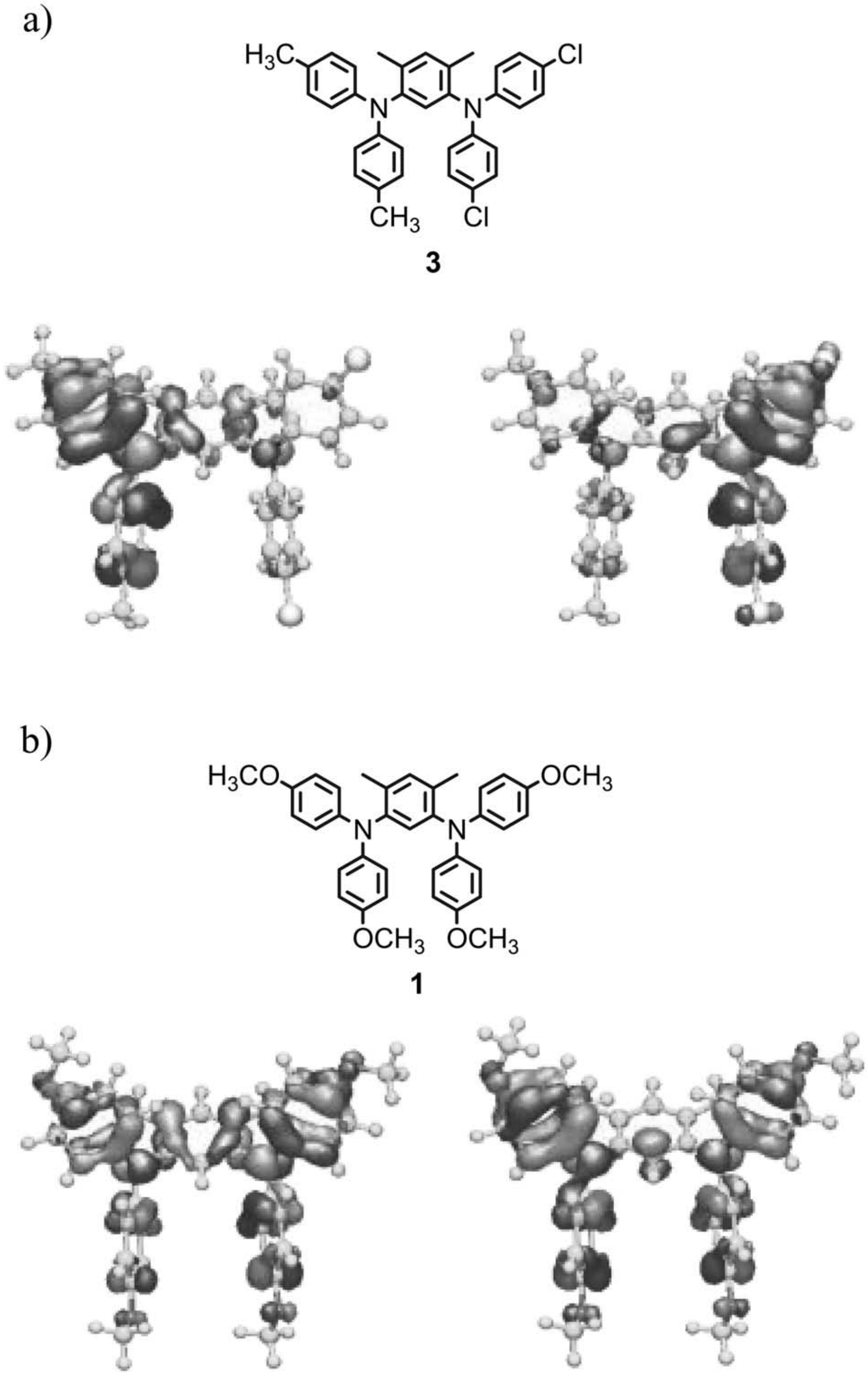


Fig. 5. (a) Shapes of the HOMO (left) and next HOMO (right) of **3**; (b) the shapes of the HOMO (left) and next HOMO (right) of **1**.

increased, which is characteristic of triarylaminium radicals [5] (Fig. 6). The absorption maximum was blue-shifted by about 60 nm than that of **1** ($\lambda_{\max} = 750$ nm) [6]. However, the monocationic state of **3** was slightly unstable under this condition, and slowly decomposed into a product, which exhibited an absorption peak at 501 nm. This product was electrochemically inert in the surveyed potential range. This is in contrast with the compound **1**, which gave a very stable monocationic state under the same condition [6]. The unstableness would originate from the lack of thermodynamic stabilization. Upon oxidation to the dicationic state, no peak derived from the dicationic state was observed, and the absorption peak at 501 nm

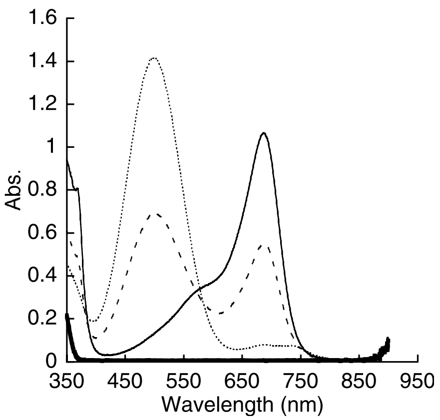


Fig. 6. UV–Vis spectra of **3**; neutral (bold), oxidized at 0.637 V (vs. Fc/Fc$^+$) for 30 s (solid), 2 min (broken), 10 min (dot).

rapidly increased, indicating the occurrence of the fast follow-up reactions. At present, we have not detected the dicationic state of **3** spectrometrically, however, expecting that the state will be detectable at low temperature, as suggested by the electrochemical measurements described above. Elaborate spectroelectrochemical measurements of **3** and its various asymmetric derivatives at −78 °C are now in progress.

3. Summary

In conclusion, we have designed and successfully synthesized asymmetric tetraaryl-1,3-phenylenediamine (**3**). The oxidized dicationic state was found to be enough stable in solution at −78 °C. Cyclic voltammetry measurements and molecular orbital calculation suggested that each diphenylamine unit may behave as an independent group, despite the two nitrogen sites are close and are connected via π-electron network. These results serve for establishing guidelines for molecular designing of charged high-spin molecular systems and organic mixed-valence ones as well. The ESR and the spectroelectrochemical measurements of **3** are in progress.

4. Experimental

4.1. Materials and measurements

^{1}H NMR spectra were recorded with JEOL JNM-GSX400 (400 MHz). UV–Vis spectra were recorded with Shimadzu UV-2550. Cyclic voltammograms were recorded with ALS/chi Electrochemical Analyzer Model 600A using a platinum disk working electrode, a platinum wire counter electrode, an Ag/Ag$^+$ or a platinum wire reference electrode, tetrabutylammonium hexafluorophosphate (0.1 M) as a supporting electrode, and *n*-butyronitrile as a solvent. Spectroelectrochemical measurements were conducted by using a spectroelectrochemical quartz cuvett with a Nichia NP-IR1000 potentio/galvanostat, a Pt gauze working electrode, a Pt counter electrode and Ag/Ag$^+$ reference electrode at ambient temperature under nitrogen atmosphere. *n*-Butyronitrile was distilled from CaH_2. Other reagents (analytical grade) were used without further purification. Semiempirical calculations of **1** and **3** were carried out at the AM1 level using the MOPAC97 program (WinMOPAC, Fujitsu Inc., Japan 1997).

4.2. Synthesis of N,N-di-4-tolyl-5-nitro-2,4-xylidine (5)

A mixture of 1 g (0.006 mol) of 5-nitro-2,4-xylidine, 6.34 g (0.027 mol) of *p*-iodotoluene, 1.4 g of copper powder, 6.8 g of potassium carbonate and 0.5 g of 18-crown-6 ether in *o*-dichlorobenzene (50 ml) was heated under reflux in argon atmosphere for 8 h. The mixture was filtered off, washed with water (100 ml × 2), and dried over sodium sulfate. The solvent was distilled off under reduced pressure. The obtained black oil was decolorized with active charcoal to give yellow oil, which was purified by column chromatography (chloroform/*n*-hexane = 1/1), giving 0.60 g (29%) of **5** as yellow oil. ^{1}H NMR (CDCl3); δ 2.03 (s, 3H), 2.29 (s, 6H), 2.57 (s, 3H), 6.81 (d, 4H, $J = 8.4$ Hz), 7.03 (d, 4H, $J = 8.4$ Hz), 7.15 (s, 1H), 7.74 (s, 1H).

4.3. Synthesis of N,N-di-4-tolyl-2,4-dimethyl-1,3-phenylenediamine (6)

A mixture of 1.05 g of **1**, 2.0 g of tin dichloride and 10 ml of hydrochloric acid in ethanol (40 ml) was heated under reflux for 5 h. The mixture was poured onto ice-water containing potassium carbonate and extracted ethyl acetate. The organic phase was washed with water and dried over sodium sulfate. The solvent was distilled off under reduced pressure. The obtained crude oil was purified by column chromatography (chloroform/ethyl acetate = 2/1) to give 0.83 g (86%) of **6** as yellow oil. ^{1}H NMR ($CDCl_3$); δ 1.89 (s, 3H), 2.15 (s, 3H), 2.27 (s, 6H), 3.42 (br, 2H), 6.45 (s, 1H), 6.86 (d, 4H, $J = 8.4$ Hz), 6.89 (s, 1H), 6.98 (d, 4H, $J = 8.4$ Hz).

4.4. Synthesis of N,N-bis(p-chlorophenyl)-N′,N′-bis(p-tolyl)-4,6-dimethyl-1,3-phenylene-diamine (3)

A mixture of 0.83 g (0.0026 mol) of **6**, 3.11 g (0.013 mol) of *p*-chloroiodobenzene, 1.4 g of copper powder, 6.8 g of potassium carbonate and 0.5 g of 18-crown-6 ether in *o*-dichlorobenzene (50 ml) was heated under reflux in an argon atmosphere for 16 h. The mixture was filtered off, washed with water (100 ml × 2), and dried over sodium sulfate. The solvent was distilled off under reduced pressure. The obtained crude oil was decolorized with active charcoal and purified by column chromatography (chloroform/ethyl acetate = 1/1), giving 0.43 g (31%) of **3** as white powder. ^{1}H NMR ($CDCl_3$); δ 1.96 (s, 3H), 1.98 (s, 3H), 2.26 (s, 6H), 6.80 (d, 4H, $J = 8.4$ Hz), 6.85 (d, 4H, $J = 8.8$ Hz), 6.88 (s, 1H), 6.98 (d, 4H, $J = 8.4$ Hz), 7.09 (s, 1H), 7.13 (d, 4H, $J = 8.8$ Hz). MS: *m*/*e* 536.

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