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Design, Synthesis and Optical Response of Pyridine-Cored V-Shaped Stilbenoid Dendrimers

Debabrata Jana and Binay K. Ghorai*

Department of Chemistry, Bengal Engineering and Science University, Shibpur, Howrah 711 103, India

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Abstract: Design, synthesis and characterization of new series of first-generation V-shaped dendrimers bearing phenylenevinylene dendritic branches in periphery and pyridine as a core is described. A preliminary study of the optical properties of the resulting compounds was conducted by UV/vis and fluorescence spectroscopy.

Keywords: Stilbenoid dendrimer, two-fold Heck reaction, fluorosolvatochromism.

INTRODUCTION

The interest in dendrimers was mainly focused on discovering synthetic routes toward novel members of unique family of macromolecule. Today, however, scientists working in this field have increasingly shifted their attention to the modification of existing dendrimers in order to explore the material properties of these regular highly branched molecules. Such modifications of the core molecule of dendrimers can tune the photophysical properties. Recently, conjugated oligomers are subjected to important investigations from both academic and industrial laboratories [1] due to their promising applications, such as organic light emitting diodes (OLEDs) [2], solar cell [3], field-effect transistors (FETs) [4], and models [5] to understand the fundamental properties of their analogous polydiverse polymers. Among these oligomers, molecules with a D-π-A or D-π-A-π-D structure (where D is an electron-donating group, A an electron accepting group, and π a conjugating moiety) are of high interest due to their fluorescence properties with internal charge transfer (ICT) and as chromophores for second and third-order nonlinear optics (NLO) [6].

The pyridine ring is an excellent candidate to be incorporated in such structures. Indeed, this heterocyclic moiety has a moderate electron-withdrawing character, significant aromaticity that can lead to highly conjugated molecules, as well as basic and potential ligand properties that can also be used to modulate the optoelectronic properties of molecules. On the other hand, dendritic poly(phenylenevinylenes) [7], also called stilbenoid dendrimers, represent an important group within this class of material. Several studies have been published to date concerning the synthesis and properties of these materials [8]. For example, such compounds have been used successfully as charge transporting [9], light-emitting [10], and electron transfer materials [11]. It has also been demonstrated that phenylenevinylene dendrite arms can function as light-harvesting antennae [10b].

While the photophysical properties of several dendrimers with electron deficient cores have been investigated and well characterized [12], stilbenoid dendrimers with pyridine as a core is not well known. Our interest is in the synthesis of novel conjugated V-shaped 1st generation dendrimer with pyridine core for optoelectronic applications. In this paper, we wish to present a convergent synthesis of stilbenoid dendrimers *via* the strategic use of multifold Heck reactions and the influence of the length and orientation of linkage in phenylenevinylene skeleton on the optical absorption and emission properties with the fluorosolvatochromism and pH sensitivity.

Wittig or Horner-Emmons reactions have been mostly used for the synthesis of stilbenoid dendrimers [13]. For such strategies, special bifunctional synthons are usually required, both for dendron preparation as well as for the core-coupling reactions. Syntheses of stilbenoid dendrimers *via* a sequential Heck reaction (for dendron propagation) and Horner–Emmons condensation (for core-coupling) have also been reported. However, stilbene synthesis *via* Wittig or Horner–Emmons reactions usually gives rise to a *cis*-*trans* mixture of products, necessitating an extra isomerization step to produce the desired *trans*-stilbene linkages. It must be mentioned that lack of stereochemical homogeneity in the dendrimer structure can severely affect its optoelectronic property. We decided to use the Heck arylation reaction to construct all the stilbenoid linkages (both at the core and in the periphery).

RESULTS AND DISCUSSION

Requisite 1-vinyl(4-*tert*-butylstyrene)benzene (**1**) [14] required for our study was synthesized from the readily available methyl 4-bromobenzoate (**2**) in good yield as outlined in Scheme **1**. At first Heck reaction on **2** with 4-*t*-butylstyrene under Jeffery's conditions [15] provided **3** (76%), and subsequent treatment of **3** with lithium aluminium hydride in THF gave the alcohol **4** (79%) and the later was oxidized (PDC, CH_2Cl_2, rt) to produce the styryl-benzaldehyde **5** (86%). Wittig reaction of **5** ($Ph_3P^+MeI^-$, *n*-BuLi, THF) at -20 °C afforded compound **1** in 72% yield.

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*Address correspondence to this author at the Department of Chemistry, Bengal Engineering and Science University, Shibpur, Howrah 711 103, India; Tel: +913326684561; Fax: +913326682916;
E-mail: bkghorai@yahoo.co.in

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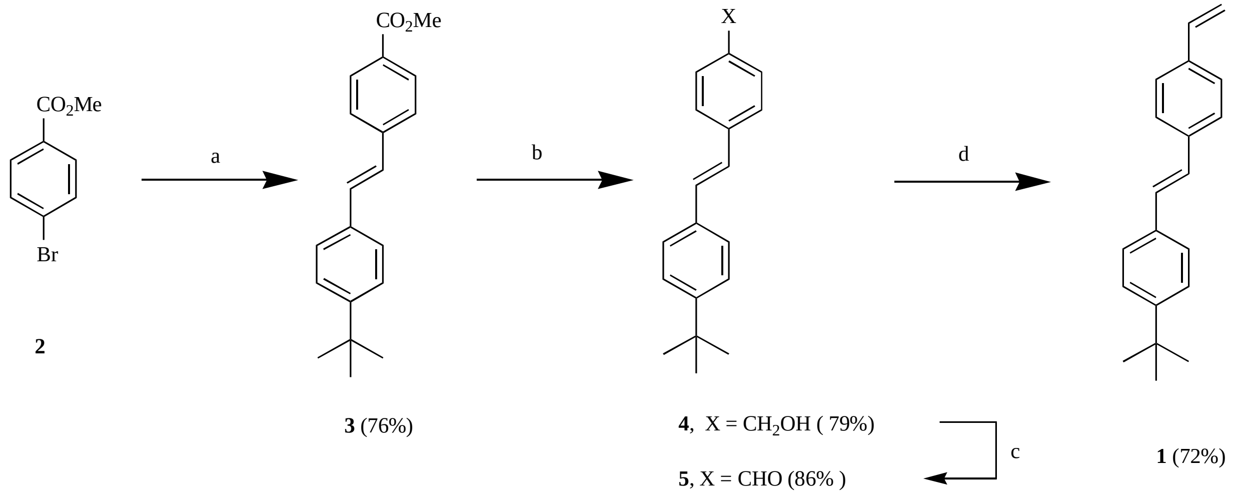
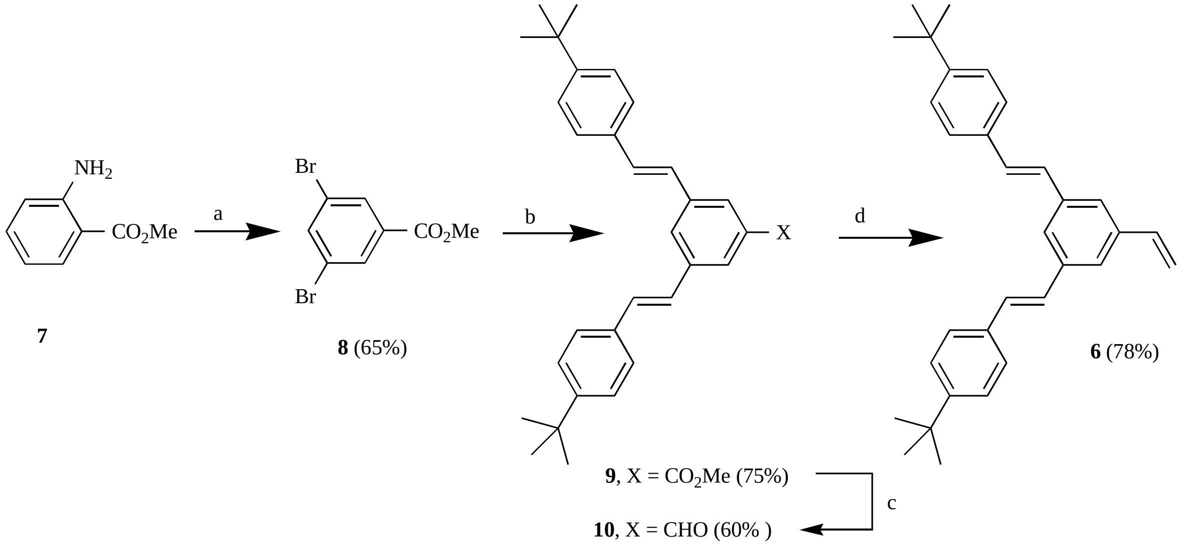


Scheme 1. Reagents and conditions: (**a**) 4-*t*-Butylstyrene, Pd(OAc)$_2$, n-Bu$_4$NBr, KOAc, DMF, 90 °C, 24 h; (**b**) LiAlH$_4$, THF, rt; (**c**) PDC, CH$_2$Cl$_2$, rt; (**d**) Ph$_3$P$^+$MeI$^-$, n-BuLi, THF, -20 °C.



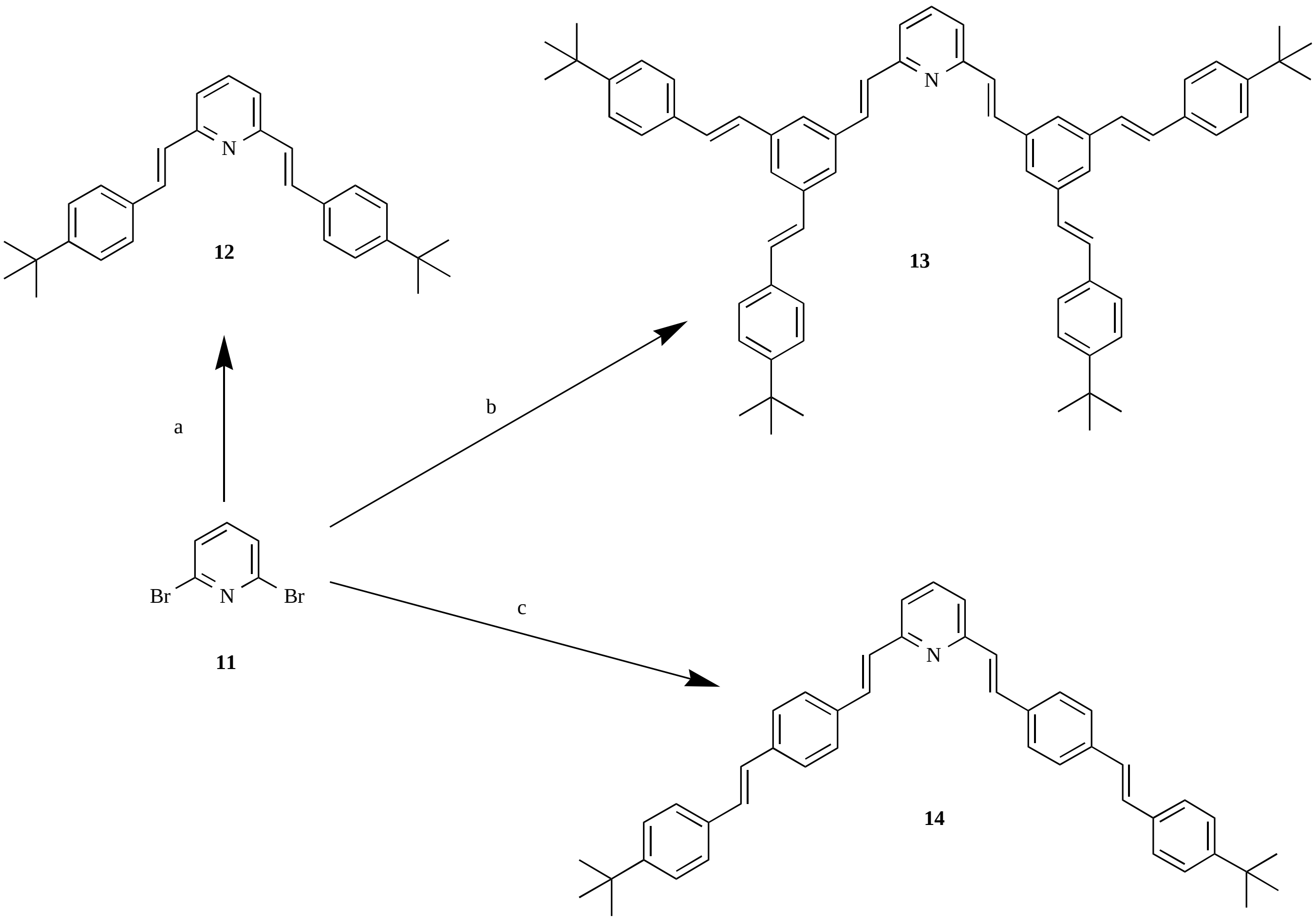
Scheme 2. Reagents and conditions: (**a**) (i) Br$_2$, HOAc; (ii) ^{t}BuONO, DMF, 60 °C; (**b**) 4-*t*-Butylstyrene (2.5 equiv.), Pd(OAc)$_2$, n-Bu$_4$NBr, KOAc, DMF, 90 °C, 36 h; (**c**) LiAlH$_4$, THF, rt; (**d**) (i) PDC, CH$_2$Cl$_2$, rt; (ii) Ph$_3$P$^+$MeI$^-$, n-BuLi, THF, -20 °C.

Dendron **6** was synthesized from methyl anthranilate (**7**) according to the literature method depicted in Scheme **2** [8c]. Dibromination of methyl anthranilate (**7**) followed by deamination (^{t}BuONO, DMF) gave methyl 3,5-dibromobenzoate (**8**) in 65% yield [16]. Two-fold Heck reaction on **8** with 4-*t*-butylstyrene under Jeffery's conditions gave **9**, which on treatment with lithium aluminium hydride in THF afforded the alcohol **10**. PDC oxidation of **10** followed by Wittig reaction yielded the desired dendron **6**.

Generally, multifold Heck coupling reaction for stilbenoid dendrimer preparation afforded low yields due to the insolubility of partially coupled intermediates, which were observed to precipitate from solution during early reaction times [14]. We have chosen 2,6-dibromopyridine as a core molecule to prepare stilbenoid dendrimer because it has a π-acceptor property, which control the absorption and emission spectra in different solvents and also the nitrogen atom of pyridine ring enhances the solubility of the *mono*- and *bis*-coupled products, which lead to the complete conversions with a considerable easy isolation and purification process.

Thus, two-fold Heck reaction of 2,6-dibromopyridine (**11**) with 4-*tert*-butylvinyl styrene derivative under Jeffery's phase transfer conditions [10% Pd(OAc)$_2$, n-Bu$_4$NBr, KOAc, DMF, 90 °C] give rise to the first generation dendrimer **12** [17] in 45% yield (Scheme **3**). Under the same conditions, two-fold Heck reaction of **11** with excess of styrene derivative **6** led to the fluorescent meta-branched V-shaped pyridine-cored dendrimer **13** [18] was formed in 30% yield. An additional example using the same two-fold Heck reaction strategy with dendron **1** led to the formation of a highly fluorescent compound **14** [19] in low yield (15%).

We investigated the absorption and emission behaviors of **12, 13** and **14** in different solvents. The results of these investigations are summarized in Table **1**. The absorption



Scheme 3. Synthesis of stilbenoid dendritic molecules. Reagents and conditions: (**a**) 4-*t*-Butylstyrene, Pd(OAc)$_2$, n-Bu$_4$NBr, KOAc, DMF, 90 °C, 24 h, 45%; (**b**) **6** (4.0 equiv), Pd(OAc)$_2$, n-Bu$_4$NBr, KOAc, DMF, 90 °C, 48 h, 30%; (**c**) **1** (4.0 equiv), Pd(OAc)$_2$, n-Bu$_4$NBr, KOAc, DMF, 90 °C, 48 h, 15%.

Table 1. Spectroscopic Data of 12-14

Compd	Solvent	UV/Vis λ_{max} [nm]	Excitation λ_{max} [nm]	Fluorescence λ_{max} [nm]
12	Toluene	313	338	399
	Chloroform	316,339	341	415
	Tetrahydrofuran	318,340	342	409
	Methanol	-	342	465
13	Toluene	313,335	338	392
	Chloroform	318	344	400
	Tetrahydrofuran	317	342	397
	Methanol	317	342	409
14	Toluene	348	372	421
	Chloroform	351	375	445
	Tetrahydrofuran	350	375	437
	Methanol	350	375	492

All spectra were recorded at room temperature at C = (1.0 x 10^{-6} M to 1.2 x 10^{-6} M).

spectra are nearly independent of solvent polarity, except for a slight, insignificant red shift indicates a negligible intramolecular interaction between solvent molecule and pyridine system in the ground state. In contrast, the emission spectra exhibit distinct solvent dependence behavior. Broad structure less emission and large maximum fluorescence wave length shifts were observed on increasing the solvent polarity along with a successive decrease in the fluorescence intensity. This solvatochromic behavior, which results from the stabilization of the highly polar emitting state by polar solvents, is typical for compounds that undergo an internal charge transfer upon excitation and has been fully documented for numerous fluorophores or cores containing donor-acceptor units [6a]. As an example, the photoluminescence (PL) spectra of compound **12** (Fig. **1**) shows broad and strong red shift in more polar solvent (e.g. methanol) with a λ_{max} of 465 nm, compare to the λ_{max} of 399 nm in less polar solvent (e.g. toluene).

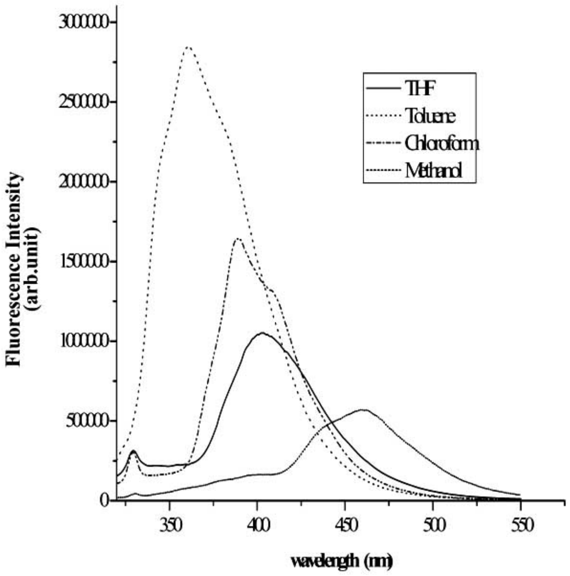


Fig. (**1**). Emission spectra of compound **12** (1.2 x 10^{-6} M) in various solvents.

It is well known that *meta*-substituted systems are weaker light emitters than the corresponding *para* isomers; exactly same phenomenon is observed for our V-shaped pyridine-cored dendrimer. The emission spectra of compound **13** shows lower λ_{max} than that of compound **14** which implies that extended conjugation in *para* position is more efficient for red shift than in *meta* position. The PL (λ_{max}) of compound **13** in chloroform appears in 400 nm where as for compound **14** in same solvent appears in 445 nm.

The PL spectrum of compound **12** in toluene (excitation at 338 nm) showed an emission band at 399 nm whereas for compound **14** in same solvent (excited at 372 nm) showed at 421 nm, this change probably attributed to the length of the peripheral vinylphenylene arms.

The nitrogen atoms of all prepared pyridines are basic centers that can be protonated. Thus, the effect of protonation on the UV-vis absorption spectra of $CHCl_3$ solutions of compound **12** is illustrated in Fig. (**2**). The spectra show a new similar intensity red-shifted band at 402 nm corresponding to the protonated species **15**. It may be noted that the absorption band for the neutral compound on increasing the concentration of TFA from 10^{-5} to 10^{-2} M remains more or less same [12b].

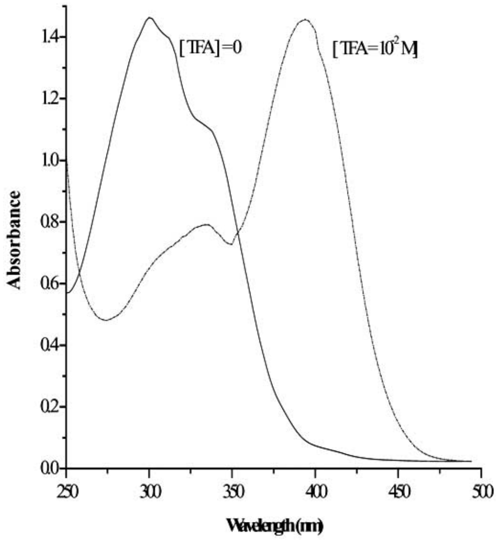
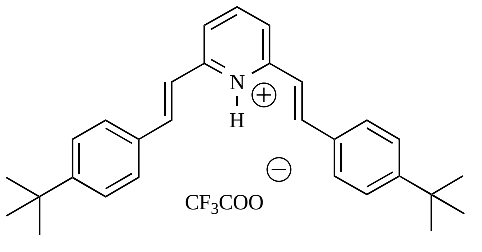


Fig. (**2**). UV/vis absorption changes of **12** (1.05 x 10^{-5} M) in $CHCl_3$ with TFA (10^{-2} M) addition.



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In conclusion, we have successfully synthesized and characterized a series of new 2,6-bis(arylvinyl)pyridines in a straightforward manner by two-fold Heck coupling reaction between 2,6-dibromopyridine and appropriate vinylphenylene moiety. This well known protocol permits highly stereoselective *trans* coupling. The material exhibits moderate emission solvatochromism and red shifted broad structureless bands are obtained in polar solvents, an observation characteristic of intramolecular charge transfer at excited state. The pH sensing properties of absorption spectra were also studied particularly. Further work in this area is currently underway in this laboratory.

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[16] Dibromination of **7** followed by protodiazoniation can also be carried out *via* a literature procedure (ref. 8c).

[17] *Typical experimental procedure for preparation of V-shaped pyridine cored stilbenoid dendrimers*: A mixture of dried KOAc (124 mg, 1.266 mmol), *n*-Bu_4NBr (299 mg, 19.4 mmol) in DMF (6 mL) was stirred for 15 min in a double necked round-bottomed flask in argon atmosphere at room temperature. To the reaction mixture **11** (100 mg, 0.422 mmol), PPh_3 (22 mg, 0.084 mmol), 4-*tert*-butylstyrene (169 mg, 1.055 mmol) were added simultaneously and stirred for another 15 min. Catalytic amount of $Pd(OAc)_2$ was added and heated for 24 h at 90 °C. The mixture was cooled to room temperature and extracted with hexane and ether mixture (1:1) (30 mL). The organic layer was washed with water (3x5 mL) and brine (5 mL), and dried over anhydrous Na_2SO_4. Solvent was removed in a rotary evaporator and the crude product was purified using column chromatography (silica gel/ethyl acetate:petroleum ether 1:99) to yield the compound **12** (76 mg, 45 %) as white solids. *Data for* ***12***: Mp 172 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, 2H, J = 16.0 Hz), 7.64 (t, 1H, J = 7.5 Hz), 7.56 (d, 4H, J = 8.3 Hz), 7.41 (d, 4H, J = 8.3 Hz), 7.27 (d, 2H, J = 7.5 Hz), 7.19 (d, 2H, J = 16.0 Hz), 1.35 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.6, 151.4, 136.7, 134.0, 132.6, 127.6, 126.9, 125.6, 120.0, 34.7, 31.2; MALDI-TOF MS: m/e : 396.0 (MH^+).

[18] *Data for* ***13*****:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (t, 1H, J = 7.5 Hz), 7.85 (d, 2H, J = 16.0 Hz), 7.68 (s, 4H), 7.59 (br s, 2H), 7.52 (d, 8H, J = 8.3 Hz), 7.48 (d, 2H, J = 7.5 Hz), 7.43 (d, 8H, J = 8.3 Hz), 7.37 (d, 2H, J = 16.0 Hz), 7.23 (d, 4H, J = 16.0 Hz), 7.15 (d, 4H, J = 16.0 Hz), 1.35 (s, 36H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.4, 150.9, 138.3, 137.4, 134.4, 132.5, 129.1, 128.8, 127.5, 126.3, 125.6, 124.6, 124.2, 122.1, 120.4, 34.6, 31.3; MALDI-TOF MS: m/e : 916.7 (MH^+).

[19] *Data for* ***14*****:** ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86 (d, 4H, J = 8.1 Hz), 7.65 (d, 4H, J = 8.1 Hz), 7.49 (m, 5H), 7.41 (m, 6H), 7.26 (d, 4H, J = 16.2 Hz), 7.10 (d, 4H, J = 16.2 Hz), 1.34 (s, 18H); MALDI-TOF MS: m/e : 600.0 (MH^+).