



A new disc-shaped mesogenic compound with olefinic linkage derived from triphenylamine: synthesis, mesogenic behavior and fluorescence properties

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ABSTRACT

A new disc-like triphenylamine containing mesogenic compound has been synthesized by the implementation of the Heck and ring-closing metathesis-based reactions in good yield. The designed and synthesized compound showed rectangular columnar mesophase and this is the first report of liquid crystalline phase of the triphenylamine-based compound with an olefinic linkage. The disc-shaped compound exhibited excellent fluorescence properties.

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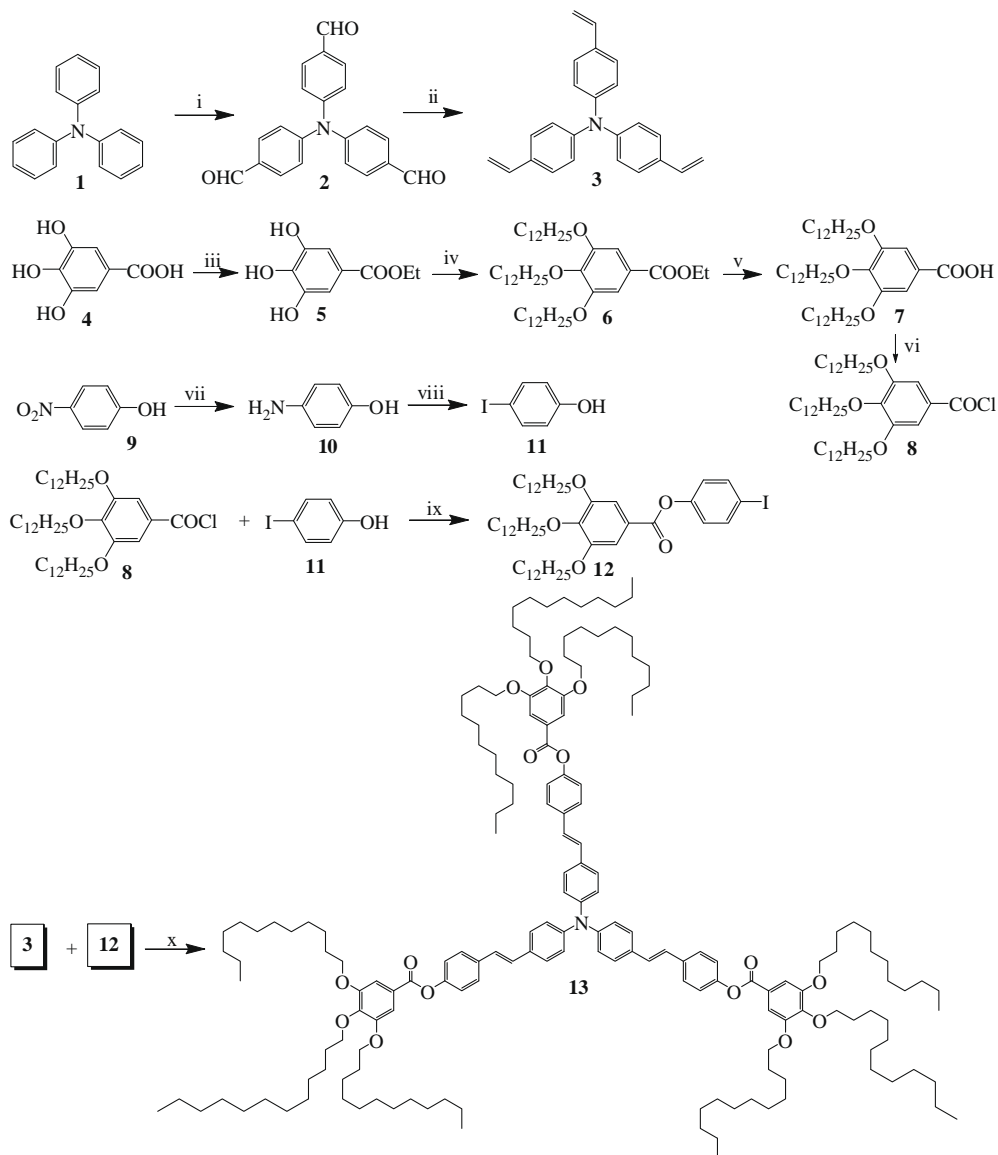
Liquid crystalline (LC) phases represent a fascinating state of soft matter, combining order and mobility on a molecular and supramolecular level. Molecular shape determines to a large extent the type of mesophase observed for thermotropic liquid crystals. For example, in general, disc-like molecules self-organize to give columnar mesophases. The first well-defined examples of disc-shaped (discotic) liquid crystals, hexa-substituted benzenes, were reported in 1977 by Chadrsekhar.^{1,2} The mesophases of these compounds usually have a columnar structure in which the discs are stacked one on top of the other to form columns. Attractive intermolecular interactions between the aromatic cores are primarily responsible for the stacking of cores. Columnar phases are also observed when a flat core is replaced by a pyramid- or cone-shaped unit³ or even when the central core is absent.⁴ These types of materials are promising for potential applications³ such as one-dimensional conductors,⁴ photoconductors,⁵ molecular wires and fibers,⁶ light emitting diodes⁷ and photovoltaic cells.⁸ Triphenylamine moiety has been widely exploited for its physical and electronic properties in display applications.⁹ Oligomeric and polymeric materials based on triphenylamine have attracted much attention because of their stability and useful properties such as electrical conductivity and electroluminescence.^{10–12} Triphenylamine is characterized by a high hole-transporting ability and a bulky volume.

Recently, we have reported¹³ a columnar mesophase from a disc-like molecule derived from triphenylamine. To the best of our knowledge, there is only one more report¹⁴ of triphenylamine-bearing discotic liquid crystal. The aforesaid liquid crystalline materials possess triphenylamine core, and are Schiff bases. In order to study the structure–property relationship we have synthesized a triphenylamine-based compound with ethylenic linkage. Herein we report the results in *Scheme 1*.

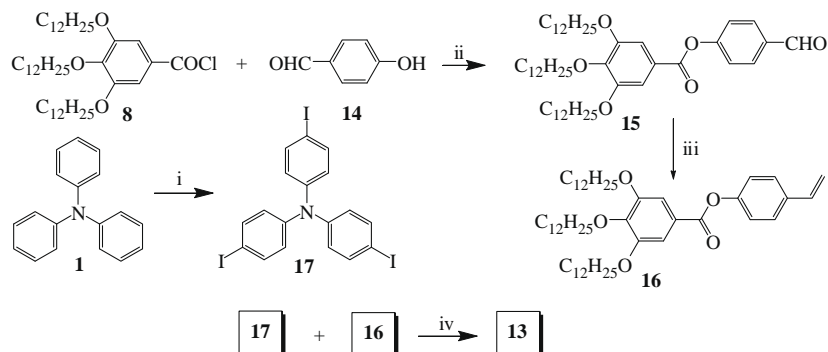
The synthetic protocols for the compound **13** are summarized in *Schemes 1–3*. The disc-shaped compound **13** was synthesized by three different methodologies. The starting material, triphenylamine trialdehyde **2** was prepared according to our earlier published procedure.¹³ Compound **2** was then subjected to Wittig olefination reaction to give the corresponding trivinyl derivative **3** in excellent yield (~100%).

The second partner (**12**) of this coupling reaction was prepared from ethyl gallate (**5**). Alkylation of (**5**) with dodecyl bromide in dry ethyl methyl ketone–K₂CO₃ under reflux afforded the corresponding ester derivative (**6**). The ester group was hydrolyzed to give (**7**) which was esterified with *p*-iodo phenol in the presence of triethylamine and DMAP (cat.) to give compound (**12**). The final product **13** was synthesized by the utilization of the intermolecular threefold Heck reaction. Initially, we attempted the Heck reaction by the application of Jeffery's two-phase protocol¹⁵ and obtained the final compound **13** in only 11% yield. Therefore, the protocol was modified¹⁶ with a view to increase the yield of the desired compound. When the cross-coupling reaction was conducted using *tri-*o*-tolyl phosphine* as a ligand in conjunction with the previous

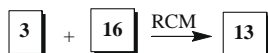
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Scheme 1. Reagents and conditions: (i) POCl_3 , DMF, 0°C for 1 h and then heated at 100°C for 7 h; (ii) Ph_3PMeI , $n\text{BuLi}$, THF, 0°C for 15 min, then 100°C for 1 h; (iii) EtOH, H_2SO_4 (cat.), reflux, 15 h; (iv) 1-bromododecane, EMK, K_2CO_3 , NaI, reflux, 6 day; (v) EtOH, KOH, reflux, 4 h; (vi) SOCl_2 , reflux, 1 h; (vii) EtOAc, Pd-C (10%), H_2 , 4 h; (viii) NaNO_2 -HCl, NaI, 0°C , 2 h; (ix) DCM- Et_3N , DMAP, 0°C for 30 min, then rt overnight; (x) Heck reaction, 30 mol % $\text{Pd}(\text{OAc})_2$, KOAc (2.75 equiv), TBAB (6 equiv), DMF (20 ml), 100°C , 72 h./ 30 mol % $\text{Pd}(\text{OAc})_2$, KOAc (2.75 equiv), TBAB (6 equiv), P(o-tol)₃, DMF (10 ml), 100°C , 72 h.



Scheme 2. Reagents and conditions: (i) HgO , I_2 , EtOH, overnight; (ii) DCM- Et_3N , DMAP, 0°C for 30 min, then rt overnight; (iii) Ph_3PMeI , $n\text{BuLi}$, THF, 0°C for 15 min, then 100°C for 1 h; (iv) Heck reaction.



Scheme 3. Reagents and conditions: Grubbs' 1st-generation catalyst, yield 7%; Grubbs' 2nd-generation catalyst, yield 16%.

protocol we obtained the desired product **13** in an improved yield (~28%).

The Heck cross-coupling strategy was next altered by replacing the coupling partners with **16** and **17**. Compound **17** was prepared from triphenylamine by treatment with HgO and molecular iodine in almost quantitative yield. The other partner **16** was synthesized by Wittig olefination of compound **15**. Compound **15** was in turn prepared by the esterification of *p*-hydroxy benzaldehyde **14** with 3,4,5-tridodecyloxy benzoyl chloride. When these two partners are allowed to react by the phosphine-free and phosphine-assisted intermolecular Heck cross-coupling, the corresponding cross-Heck product **13** was obtained in 23% yield. The lower yield of product **13** in this type of reactions is due to the possibility of formation of competitive side products along with the desired tri-Heck product (**13**) (Scheme 2).

Next, we attempted the synthesis of a disc-like molecule by the implementation of the cross-ring-closing metathesis approach.¹⁷ To this end, when the cross metathesis was conducted with the two partners **3** and **16** in dry dichloromethane in the presence of Grubbs' 1st-generation catalyst (Fig. 1) under nitrogen atmosphere for three days, the desired product **13** was obtained in only 7% yield. However, when the reaction was carried out with Grubbs' 2nd-generation catalyst (Fig. 2) the yield of the product **13**¹⁸ improved to 16% (Scheme 3).

The fluorescence property of the discotic molecule **13** was measured in different solvent systems at different concentrations to get the information regarding absorption and emission maxima, Stokes shift of fluorescence and the 'on-off' fluorescence properties. Two peaks at 380 nm and 282 nm were found in the UV–vis absorption spectra. Usually, the highest peak at 380 nm is due to the π – π^* transition of the highly conjugated system with the triphenylamine moiety at the core system. Moreover, we studied the fluorescence spectra of the compound **13** to examine the excited state characteristics of the compound.

When we studied the fluorescence spectrum in a less polar solvent (benzene) (Fig. 3), emissions at 321 and 437 nm (concentration) were observed on excitation at 282 nm. The emission peak

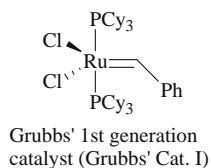


Figure 1.

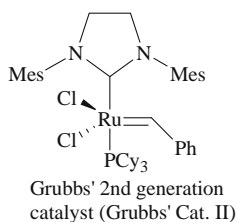


Figure 2.

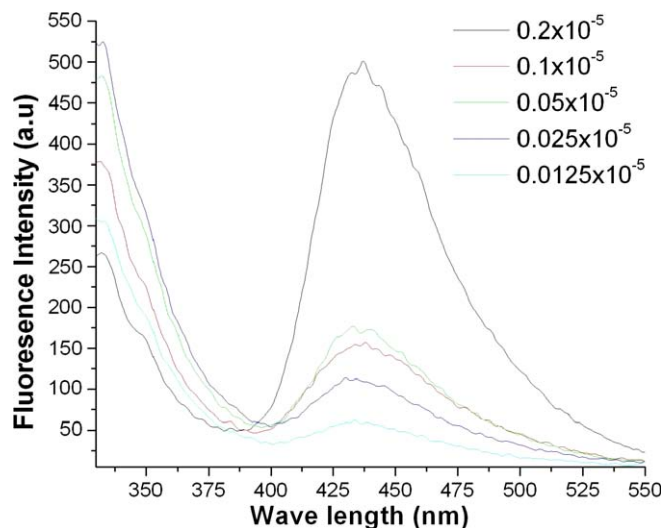


Figure 3. Fluorescence spectra of compound **13** in benzene solution at different concentrations (excitation: 282 nm).

at 437 nm with a Stokes shift of the order of 57 nm was attributed to energy transfer at the excited state.

We have studied the fluorescence spectra of this designed mesogenic compound in different solvents such as CHCl₃, THF, CH₃CN and H₂O at the same concentration and the corresponding plot is presented in Figure 4. From the plot it is seen that on gradual change from less polar solvent to more polar solvent, the emission peak is drastically shifted to longer wavelength resulting in a significant quenching in fluorescence intensity. The shifted emission peak is shown in Table 1.

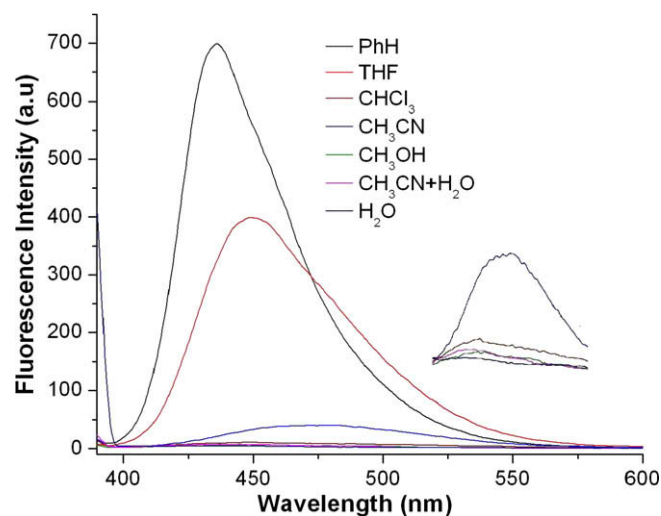


Figure 4. Fluorescence spectra of compound **13** in different solvents at the same concentration, [2×10^{-6}] (excitation: 380 nm).

Table 1
Wavelength at different solvents of **13**

Entry	Solvent	λ_{\max}	concn
1	PhH	435	10^{-5}
2	CHCl ₃	446	10^{-5}
3	THF	450	10^{-5}
4	CH ₃ CN	474	10^{-5}

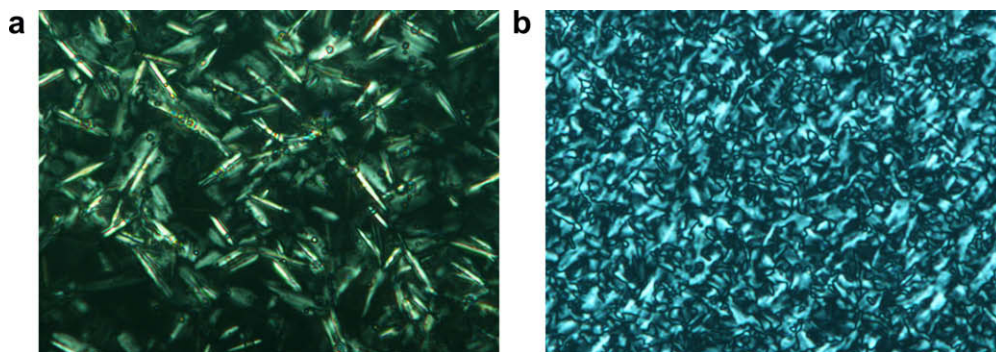


Figure 5. (a) POM texture at 79.5 °C; (b) POM texture at 74 °C.

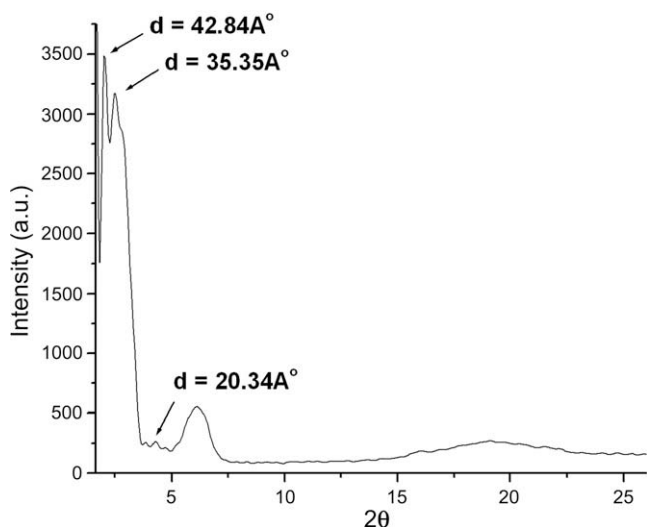


Figure 6. X-ray profile of compound **13**.

It should be mentioned here that the emission peak shifted maximum with maximum fluorescence quenching in the case of acetonitrile (474 nm). With $\text{CH}_3\text{CN}/\text{H}_2\text{O} = 1:1$ ratio the fluorescence quenching is maximum, that is, in the presence of water there is no fluorescence property (totally off).

The thermotropic properties of the compound **13** were investigated using polarizing optical microscopy (POM), differential scanning calorimeter (DSC) and X-ray diffraction (XRD). DSC analysis of the compound **13** shows monotropic mesophase. Compound **13** shows a crystal to crystal transition at 64.6 °C with $\Delta H = 28.96$ kJ/mol and crystal to mesophase transition at 72.3 °C with small but noticeable change in enthalpy. Isotropic transition occurred at 90.5 °C (0.03 kJ/mol) in the heating cycle. In the cooling cycle, an isotropic to liquid crystalline phase transition occurred at about 91.5 °C with small enthalpy change (0.06 kJ/mol) but surprisingly, transition to crystal phase was not observed. The observed enthalpy changes for the transition liquid crystal-isotropic are low. Examples of low-enthalpy transition are available in the literature.^{19,20} On slow cooling from the isotropic phase, pseudo focal-conic texture or fan-like texture (Fig. 5) of typical columnar phase appeared with large amount of homeotropy which grows slowly and fills up all field of view. No other phase was observed during the cooling cycle.

The mesophase structure was established by X-ray diffraction studies. Figure 6 shows the intensity versus 2θ plot derived from diffraction pattern of compound **13** at 80 °C. In the small angle region, three peaks were observed, taken in the ascending order of diffraction angle, the d -spacing of the first reflection (lowest angle and highest intensity) to the other two was in the ratio of $1:(1/2)^{1/2}:1/2$. These values correspond to those expected from a rectangular columnar phase. In the wide angle region there are two diffuse peaks: a broad one at $d = 4.5$ Å and another relatively

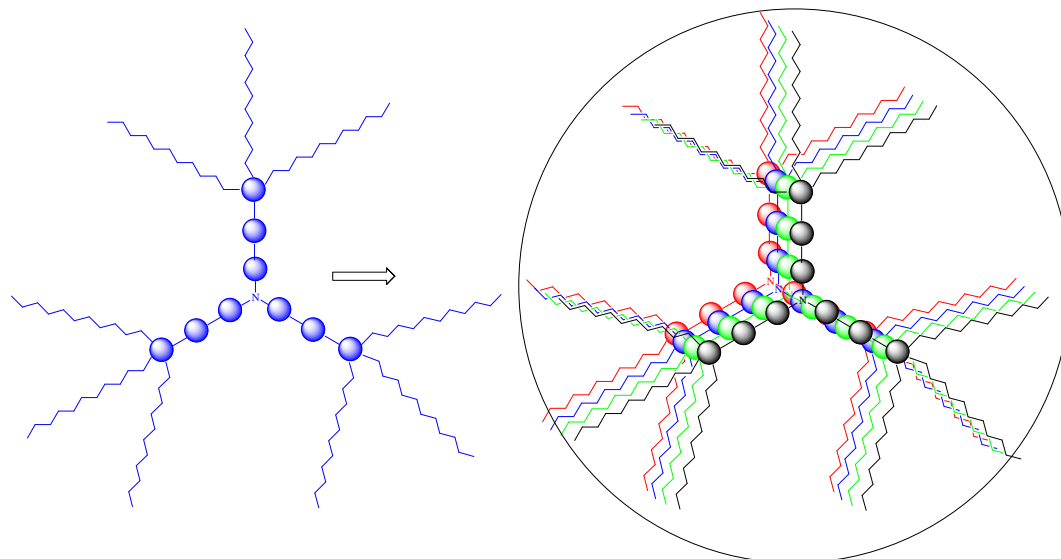


Figure 7. The schematic drawings of the molecules packed in a columnar phase formed by compound **13**.

narrow peak at $d = 3.3\text{--}3.5 \text{ \AA}$. (We also observed a diffuse peak in the low angle region in between $2\theta = 5\text{--}7.5$ due to fluctuation of the holder, which was confirmed by taking the X-ray at the same temperature in the absence of any samples.) The broad peak with d -spacing of 4.5 \AA was due to liquid-like packing of the aliphatic chains. The relatively narrow peak at higher angle region is due to core to core (intracolumnar separation) interaction.

The liquid crystalline behavior may be explained by considering the driving force for the self-organization of two types of segments viz., the promesogenic part of triphenylamine group and the non-polar hydrophobic terminal alkyl chain. In the self-assembly, the polar and non-polar parts may segregate into separate micro-domains to promote the organization of individual molecules into columns with a polar column which are assembled in the centre. Each molecule is surrounded by nine hydrophobic dodecyl alkyl units which are large enough to efficiently assemble to surround the polar parts and allow separation of the polar and non-polar parts, generating a weak force which makes them to stack into a column. The molecular stacking is shown in Figure 7.

In conclusion, we have designed and synthesized the first example of discotic liquid crystalline material based on triphenylamine as the core moiety possessing a rigid sp^2 -hybridized olefinic linkage with a permanent dipole moment. The mesogenic behavior of the compound was studied by the POM and DSC study. The rectangular columnar structure of the mesophase was established from X-ray diffraction studies. The compound exhibited excellent solvent dependent fluorescence properties. Our result is significant in view of a recent report by Wang et al. in which it was claimed that a triphenylamine-based compound possessing ethylenic linkages did not show any mesomorphic behaviour. Interestingly, we have successfully demonstrated that triphenylamine possessing an olefinic linkage can exhibit mesogenic behaviour, a rectangular columnar mesophase.

Acknowledgements

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- Procedure for the preparation of compound 13:**
Procedure 1: To a mixture of the substrates **3** (42 mg, 0.13 mmol) and **16** (300 mg, 0.386 mmol) in dry degassed dichloromethane (40 ml) under nitrogen atmosphere, either Grubbs 1st-generation catalyst (10 mol %, 32 mg) or Grubbs 2nd-generation catalyst (10 mol %, 33 mg) was added and the reaction was stirred at rt for 3 days. The solvent was distilled off and the residue was purified by flash column chromatography on silica gel using 3% ethyl acetate–petroleum ether to afford the compound **13**.
Procedure 2: A mixture of **3** (30 mg, 0.09 mmol), **12** (322 mg, 0.37 mmol), anhydrous potassium acetate (25 mg, 0.26 mmol), tetrabutylammonium bromide (180 mg, 0.56 mmol) and tri-*o*-tolyl phosphine (17 mg, 60 mol %) was taken in dry *N,N*-dimethylformamide (10 ml) under nitrogen atmosphere. Pd(OAc)₂ (6.2 mg, 30 mol %) was added and the mixture was stirred on an oil bath at 100 °C for 72 h. The reaction mixture was cooled, water (10 ml) was added and extracted with DCM (3 × 30 ml) and washed with water (2 × 40 ml), followed by brine (30 ml) and then dried (Na₂SO₄). The solvent was distilled off to furnish the viscous mass, which was purified by column chromatography over silica gel. Elution of the column with 2% ethyl acetate–petroleum ether afforded the product **13**.
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- Compound 13:** Yield: 28%; solid, IR (KBr, cm⁻¹): 2922, 2852, 1735, 1587; ¹H NMR (CDCl₃, 400 MHz): $\delta_H = 0.88\text{--}1.83$ (m, 207H, aliphatic hydrogen's of alkyl chains), 4.03–4.07 (m, 18H, –OCH₂), 7.05 (s, 6H, CH=CH), 7.11 (d, 6H, $J = 8.8$ Hz), 7.17 (d, 6H, $J = 8.8$ Hz, ArH), 7.41 (s, 6H, ArH), 7.42 (d, 6H, $J = 8.4$ Hz, ArH), 7.54 (d, 6H, $J = 8.8$ Hz, ArH) ppm; ¹³C NMR (CDCl₃, 75 MHz): $\delta_C = 14.1, 22.7, 26.0, 29.3, 29.3, 29.4, 29.6, 29.6, 29.7, 29.7, 30.3, 31.9, 69.2, 73.6, 108.5, 122.0, 122.1, 123.8, 124.1, 127.2, 128.2, 153.3, 136.1, 138.1, 143.0, 146.8, 150.5, 152.9, 165.0$ ppm; MALDI MS (m/z): 2570.676. Anal. Calcd for C₁₇₁H₂₆₁NO₁₅: C, 79.89; H, 10.23; N, 0.54. Found: C, 78.85; H, 10.56; N, 0.58.
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