Design and investigation of calamitic liquid crystals with low aspect-ratios: rigid y-shaped 1,2,4-tris(4-alkoxyphenylethynyl)benzenes

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The synthesis and characterization of triynylbenzenes, 1-iodo-2,4,5-tri(4-alkoxyphenylethynyl)benzenes (**1**), are reported, and their structure–mesomorphism relationship is investigated. These compounds possess a y-shaped geometry with rigid linear spacers and a stable nematic phase that was achieved by lengthening the alkoxy chains or replacing the iodo group with a smaller atom. The low aspect ratios and identified calamitic nature of these rigid y-shaped liquid crystals make them suitable as potential candidates to be used in the liquid crystal layer of liquid crystal display devices for improving viewing angles. In addition, the geometry of **1** was modified stepwise from a rigid y-geometry to a rigid rectangle for realization of the unstable nematic behaviors of the previously reported board-like 1,2,4,5-tetrakis(4-tridecyloxyphenylethynyl)benzene that was expected to potentially show biaxial nematic phases. The sizes of the fourth side-arm and hence the aspect ratios of these tetra-substituted benzenes are ascribed to the less liquid crystallinity.

Introduction

Liquid crystal displays (LCDs) have played a dominating role among various display devices in recent years. The liquid crystal layer in LCDs is composed of a mixture of exclusively calamitic liquid crystals. The major drawback of devices using these calamitic materials is that the contrast varies with different viewing angles. Various methods have been proposed to improve the viewing angle characteristics of LCDs.[1–5] Among these methods, adding compensation films made of discotic nematic compounds to the devices is understood as one of the simplest way to widen the viewing angle, and it is widely used for LCDs.[2] In short, this approach is to solve the light leakage perpendicular to the molecule's longitudinal direction by using the small length-to-breadth ratio (aspect ratio) of discotic molecules. With a similar principle, Kumar *et al*. has reported a novel approach to replace the calamitic liquid crystals in the LC layer with discotic liquid crystals, and hence, the compensating films were eliminated.[5] In Kumar's approach, the intrinsically higher viscosity from the disc-like hexaynylbenzene compounds could impede its practical usage as materials in the LC layer of LCDs. In both methods, the characteristic of low aspect ratios of discogens is utilized for improving the viewing angles.

Molecular shapes play an important role for the formation as well as the types of liquid crystalline phases formed. As for nematogens, they are consisted of mainly two categories, calamitic and discotic cores with the former being predominant.[6] In between these two systems, laterally substituted calamitic mesogens[7] have also been reported. When non-rigid spacers were used, the spacers used provide enough freedom to allow the lateral segment to be in the orientation of the molecular axis to give an effective rod-like shape. In some cases, more rigid spacers were used and the molecular geometries are of y-shape. However, the aspect ratios of these mesogens may not be effectively decreased due to various possible orientations of the lateral group by rotating the relatively rigid non-linear spacer.

As a result, the challenge is to attain calamitic nematogens with low aspect ratios. Thus, laterally substituted calamitic nematogens can come into play if rigid spacers are incorporated to provide effective geometrical change for effectively decreasing the aspect ratio. In this way, the molecular geometry is kept towards calamitic to exhibit lower viscosities than those of discotic nematogens. Nonetheless, such design is against the general rule that significant reduction or even loss of liquid crystallinity is very likely to occur if the molecular geometry deviates from the rod-like or disc-like geometry. Recently, we have accidentally discovered new nematogens of the y-shaped geometry with rigid linear spacers, 2,3,5-tris(4-alkoxyphenylethynyl)-4-iodothiophenes (**T**).[8] These compounds do fulfil the characteristics of low aspect ratios and their molecular geometry is towards being rod-like; however, the nematic phase could only be observed upon cooling. Attempts to modify the lateral iodide group into a cyano for tweaking molecular dipoles or a thienyl group for increasing the core size failed to stabilize the nematic phase. The large size of the sulfur atom may have prevented higher density packing and therefore destabilized the liquid crystalline phase. Nonetheless, better design of rigid y-shaped mesogens showing superior liquid crystallinity is needed. Herein, we report the results of newly designed rigid y-shaped mesogens with a central benzene ring where enantiotropic nematic phase is observed for the first time for rigid y-shaped liquid crystals. The synthesis of y-shaped 1-iodo-2,4,5-tris(4-alkoxyphenylethynyl)benzenes (**1**)

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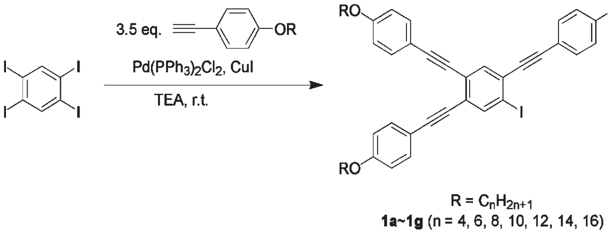


Scheme 1 Synthesis of the rigid y-shaped 1-iodo-2,4,5-tris(4-alkoxyphenylethynyl)benzenes (**1**).

are described and their mesogenic properties were investigated. The role of the iodo group on mesogenic properties of **1** is comprehended by substituting with a Br (**2**), a Cl (**3**), and a H (**4**) atom. In addition, taking advantage of the available bromo group in **2**, the geometry of **1** was modified stepwise from a rigid y-shape to a rigid rectangle, from compounds **4** to **7**, **8** and **9**, for realization of the unstable nematic behaviors of the Goodby *et al.* reported board-like 1,2,4,5-tetrakis(4-tridecyloxyphenylethynyl)benzene[9] that was expected to potentially show the biaxial nematic phase.

Results and discussion

The synthesis of the 1-iodo-2,4,5-tris(4-alkoxyphenylethynyl)benzenes, compounds **1a–1g**, is shown in Scheme 1. The best yields, ~25%, of the triynyl compounds were achieved by palladium catalyzed Sonogashira cross-coupling[10] of tetraiodobenzene[11] with 3.5 equivalents of 1-alkoxy-4-ethynylbenzene.

Table 1 summarizes the data of **1a–1g** obtained from polarizing optical microscopy (POM) and differential scanning calorimetry (DSC) studies. Under polarizing microscope, all compounds showed schlieren or marbled textures typical for a nematic phase. In accord with the suppression of lamellar mesophases observed for other laterally substituted mesogens, series **1** compounds exclusively exhibited a nematic phase. It is worth noting that the nematic phase was still the only mesophase detected even with very long hexadecyloxy chains. With shorter alkoxy chains ($n \leqslant 12$), the mesophase was observed only upon cooling. For the compounds with longer chain lengths, **1f** ($n = 14$) and **1g** ($n = 16$), an enantiotropic nematic phase was obtained for the first time for rigid y-shaped mesogens. The clearing point first decreases as the chain length increases ($n = 4, 6$) and then converge to ~60 °C for derivatives with longer chain lengths ($n = 8$–12). Interestingly, the $T_{\mathrm{I–N}}$ temperatures do not show dependence on the chain lengths and stay at ~55 °C. The crystallization temperatures of compounds **1a–1g** are all below 21 °C and severe supercooling was found for the shorter chain analogues. In summary, the phase transition temperatures for **1a–1g** with an irregular molecular geometry do not show a clear chain-length-dependence that was usually observed for mesogens with a same core.

The calamitic nature of the nematic phase from these y-shaped molecules was verified by contact studies. As shown in Fig. 1, the nematic phase of compound **1c** ($n = 8$) is completely miscible with the calamitic nematic phase of 3-cyano-8-hexyloxy-biphenylene (6OCB) suggesting the nematic phase of **1c** to be calamitic.

Table 1 Phase behaviours of compounds **1a–1g**[a]

Compound	*n*	Phase behaviors
1a	4	$\mathrm{K} \xrightarrow{110.5\ (38.28)} \mathrm{I}$ $\mathrm{K} \xleftarrow[*]{} \mathrm{N} \xleftarrow[51.8\ (-0.49)]{} \mathrm{I}$
1b	6	$\mathrm{K1} \xrightarrow{86.0\ (39.22)} \mathrm{I}$ $\mathrm{K1} \xleftarrow[-3.8\ (-5.24)]{} \mathrm{N} \xleftarrow[53.7\ (-0.53)]{} \mathrm{I}$
1c	8	$\mathrm{K1} \xrightarrow{44.7\ (8.91)} \mathrm{K2} \xrightarrow{55.6\ (3.02)} \mathrm{K3} \xrightarrow{60.3\ (38.69)} \mathrm{I}$ $\mathrm{K1} \xleftarrow[-10.5\ (-2.75)]{} \mathrm{N} \xleftarrow[54.7\ (-0.97)]{} \mathrm{I}$
1d	10	$\mathrm{K1} \xrightarrow{48.7^{b}} \mathrm{K2} \xrightarrow{53.4\ (45.65^{c})} \mathrm{I}$ $\mathrm{K1} \xleftarrow[-3.0\ (-17.64)]{} \mathrm{N} \xleftarrow[50.3\ (-0.86)]{} \mathrm{I}$
1e	12	$\mathrm{K1} \xrightarrow{63.9\ (62.31)} \mathrm{I}$ $\mathrm{K1} \xleftarrow[1.5\ (-15.26)]{} \mathrm{N} \xleftarrow[56.4\ (-1.43)]{} \mathrm{I}$
1f	14	$\mathrm{K} \underset{4.9\ (-30.79)}{\overset{47.7\ (60.49)}{\rightleftharpoons}} \mathrm{N} \underset{57.7\ (-1.20)}{\overset{59.0\ (1.30)}{\rightleftharpoons}} \mathrm{I}$
1g	16	$\mathrm{K1} \xrightarrow{20.6\ (7.94)} \mathrm{K2} \xrightarrow{51.5\ (55.23)} \mathrm{N} \xrightarrow{58.9\ (1.26)} \mathrm{I}$ $\mathrm{K1} \xleftarrow[20.3\ (-44.92)]{} \mathrm{N} \xleftarrow[58.2\ (-1.19)]{} \mathrm{I}$

[a] The transition temperatures (°C) and enthalpies (in parentheses/kJ mol^{-1}) were determined by DSC at 10 °C min^{-1}. K, K1, K2, and K3, crystalline phases; N, nematic mesophase; I, isotropic liquid. *n* denotes the length of the alkoxy chains. [b] Overlapped with the peak at 53.4 °C. [c] ΔH of the overlapped peaks at 48.7 and 53.4 °C. *Not observed.

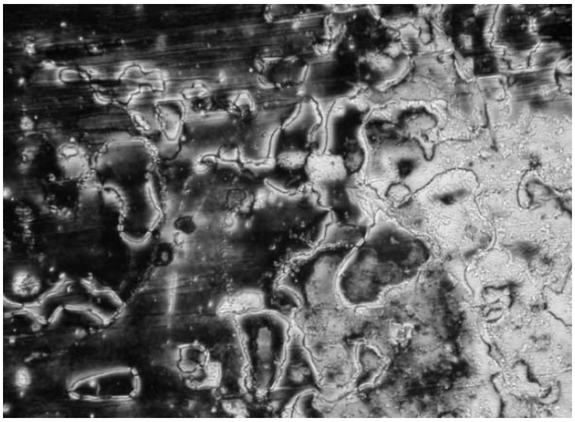
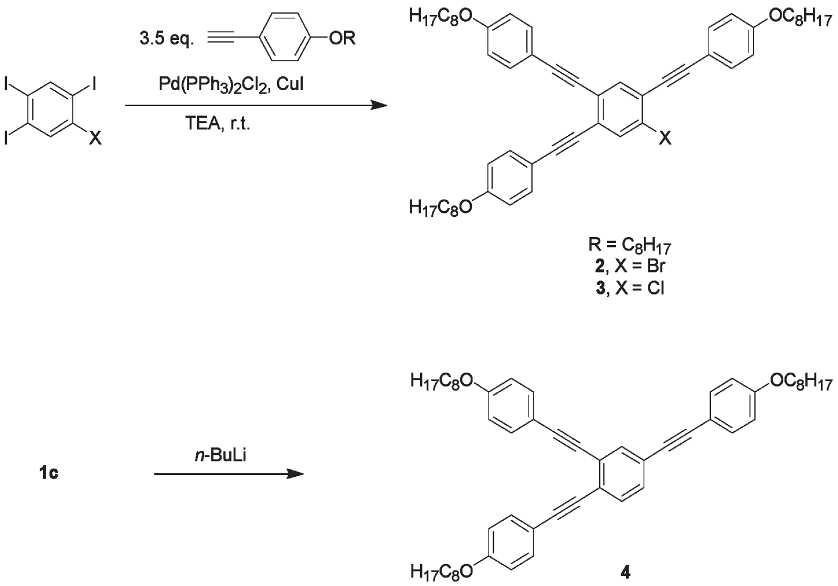


Fig. 1 A micrograph showing the contact preparation of **1c** (right) with 3-cyano-8-hexyloxy-biphenylene (left) at 50 °C on cooling.

Comparison of the mesogenic properties of **1c** and its analogue[8] with a central thienyl ring, compound **T** with octyloxy chains, will reveal the effect of the central arene on liquid crystallinity. With the same chain length, both showed a monotropic nematic phase. The melting, isotropic-to-nematic, and crystallization points of **1c** are of 32, 15, and 67 °C lower than those of its thienyl analogue. Since only a monotropic nematic phase was observed for both compounds, the comparison of the mesophase ranges is made on cooling runs. The range of **1c** is 66 °C and that of its thienyl analogue is only 12 °C. Hence, an expansion of 54 °C was achieved by simply replacing the central thiophene with a benzene ring. Since the calculated molecular dipoles for these two cores are similar, 1.6 D for **1** with no alkoxy chains and 1.5 D for the analogous thienyl derivative,[12] the dipole interactions cannot account for their very different thermal behavior. The larger central ring size as well as the smaller carbon atom with respect to the larger sulfur atom is ascribed to the wider mesophase range on cooling in **1c** than in its thienyl analogue **T** since both factors should result in higher packing density and stronger intermolecular interaction for better liquid crystallinity. For the analogous compounds **T** with a central thiophene ring, the best mesophase behavior was found for the compound with octyloxy chains, which showed monotropic nematic phase, and further lengthening of the alkoxy chains resulted in shrunk mesophase ranges. The enantiotropic mesophase behaviors of **1** with longer alkoxy chains further demonstrates better liquid crystallinity for rigid y-shaped mesogens with a central benzene ring than with a central thiophene ring.

For the mesogenic behaviors of **1**, the role of the iodo group, *e.g.*, its steric and/or the resulting molecular dipole, at the central benzene ring is yet to be clarified. In order to look into the influence of the lateral atom on the liquid crystallinity of these rigid y-shaped mesogens, the iodine atom of **1c** was replaced with a bromine, a chlorine, and a hydrogen atom. The bromo analogue (**2**, 64%) was prepared by coupling of 3.5 units of 1-ethynyl-4-octyloxybenzene with 1-bromo-2,4,5-triiodobenzene[13] (Scheme 2). Similarly, the chloro analogue (**3**, 93%) was also obtained by the coupling of 1-chloro-2,4,5-triiodobenzene[13] with the ethynyl sidearm. Compound **4** was obtained by treating **1c** with *n*-BuLi in 84% yield. Interestingly, as shown in Table 2, compounds **2**, **3**, and **4** all exhibited an enantiotropic nematic phase as opposed to the monotropic behavior of **1c**. The thermal parameters, transition temperatures, and mesophase ranges were found to be independent of the molecular dipole. On the other hand, the clearing points, $T_{\mathrm{I-N}}$, crystallization temperatures, and mesophase ranges were found to increase with decreasing size of the atom at the 1-position of the central ring. The size effect also confirms the discussions about the difference in mesogenic properties of **1c** and **T** in previous paragraph.

The rigid y-shaped geometry of **4** can be viewed as attaching a rigid lateral arm onto a linear or a V-shaped bisphenylethynylbenzene. Therefore, the influence on the mesogenic properties upon incorporating a rigid arm onto these two systems can be realized by comparisons between the rigid y-shaped **4** and 1,3-/1,4-biethynylbenzenes. The linear

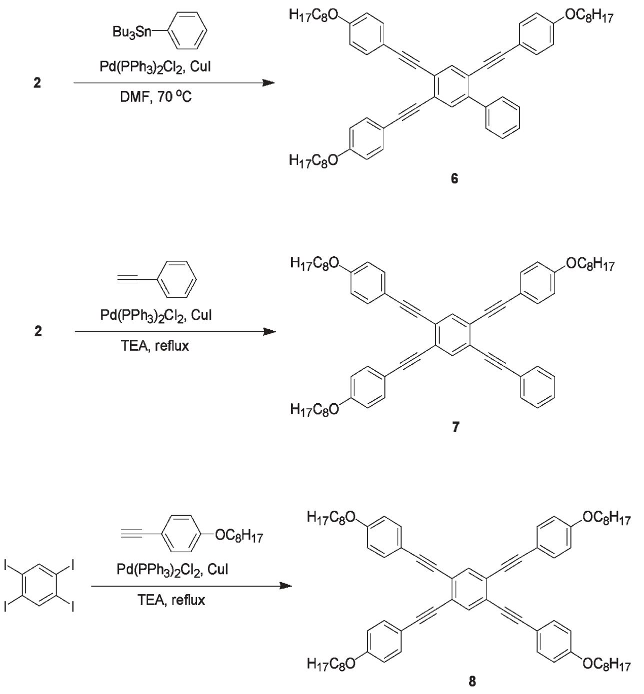


Scheme 2 Synthesis of **2**, **3**, and **4**.

Table 2 Phase behaviours of compounds **2**–**8**[a]

Compound	Phase behaviors
2	K $\underset{-7.8\ (-7.06)}{\overset{60.3\ (55.24)}{\rightleftharpoons}}$ N $\underset{66.6\ (-0.73)}{\overset{67.4\ (0.89)}{\rightleftharpoons}}$ I
3	K $\underset{-1.9\ (-17.21)}{\overset{24.7\ (30.66)}{\rightleftharpoons}}$ N $\underset{70.8\ (-0.80)}{\overset{71.6\ (0.89)}{\rightleftharpoons}}$ I
4	K $\underset{39.9\ (-3.80)}{\overset{68.7\ (34.22)}{\rightleftharpoons}}$ N $\underset{87.4\ (-0.82)}{\overset{88.4\ (0.90)}{\rightleftharpoons}}$ I
5	K $\underset{86.5\ (-60.24)}{\overset{95.5\ (60.65)}{\rightleftharpoons}}$ I
6	K $\xrightarrow{35.0\ (0.88)}$ I K $\xleftarrow{-11.9\ (-2.48)}$ N $\xleftarrow{34.5\ (-0.84)}$ I
7	K $\xrightarrow{84.4\ (39.59)}$ I K $\xleftarrow{58.8\ (-32.89)}$ N $\xleftarrow{68.9\ (-0.80)}$ I
8	K $\underset{107.5\ (-65.81)}{\overset{118.1\ (66.06)}{\rightleftharpoons}}$ I

[a] The transition temperatures (°C) and enthalpies (in parentheses/kJ mol^{-1}) were determined by DSC at 10 °C min^{-1}. K, crystalline phase; N, nematic mesophase; I, isotropic liquid.



Scheme 3 Synthesis of **6**, **7**, and **8**.

biethynyl compound, 1,4-bis(4-octyloxyphenylethynyl)benzene, was reported by Weder *et al.* to show two smectic phases between 128 and 182 °C and a nematic phase between 182 and 218 °C.[14] The bent analogue, 1,3-bis(4-octyloxyphenylethynyl)benzene (**5**), has not been reported and thus was prepared by reacting 1,3-diiodobenzene with 4-ethynyl-1-octyloxybenzene. No mesogenic behavior was observed for **5** and a melting point of 96 °C was obtained. Comparing the liquid crystal behaviors of **4** with its linear analog, it reveals that by incorporation of a rigid lateral of 4-octyloxy-1-phenylethyne to the linear 1,4-bis(4-octyloxyphenylethynyl)benzene, the transition temperatures are significantly lowered, lowerings of 60 and 129 °C for melting and clearing points respectively, while the nematic range was 16 °C smaller for **4**. Moreover, the lamellar phases in 1,4-bis(4-octyloxyphenylethynyl)benzene were suppressed to disappear in the y-shaped **4**. Apparently, incorporation of an additional rigid lateral group has not only disturbed the motif of the nematic phase but also prevented the smectic phase formation. On the contrary, the incorporation of a rigid 1-alkoxy-4-ethynylbenzene lateral onto the bent-shaped **5** induces liquid crystallinity.

Goodby *et al.* have reported 1,2,4,5-tetrakis(4-tridecyloxyphenylethynyl)benzene that can potentially show the biaxial nematic phase; however, the observed monotropic nematic phase within a narrow temperature range deterred further investigation of its biaxiallity.[9] Taking advantage of the available bromo group, compound **2** can be readily modified to compounds showing geometries stepwise towards a rectangle for realization of the unstable nematic phase formed by 1,2,4,5-tetraynylbenzene. Herein, systematic geometrical deviations from the y-shaped geometry by attaching a rigid lateral group with various lengths to the rectangle while keeping the molecular dipole constant are performed to comprehend the influence on mesogenic properties upon varying the molecular shape towards a rectangular shape of the board-like tetraynylbenzene. The bromide in **2** is readily converted to a phenyl or a phenylethynyl group to afford **6** and **7** in 70 and 76% yields respectively as depicted in Scheme 3. Also shown in Scheme 3 is the preparation of **8** (79% yield) by reacting 6 equivalents of hexyloxyphenylethyne with 1,2,4,5-tetraiodobenzene. The mesogenic properties of these derivatives, summarized in Table 2, together with those of **4** provide the information of the molecular geometry–mesomorphism relationship. Comparing compound **6** with **4**, the incorporation of an additional phenyl ring adjacent to the central benzene ring increases intermolecular steric repulsions to give rise to the monotropic behaviour of **6**. Insertion of an ethynyl unit into the biphenyl moiety in **6** affords **7** with a rectangular core and the newly introduced rotational freedom results in a monotropic nematic phase within a smaller range. Further attaching an alkoxy chain to the unique side-arm of **7** gives the more symmetrical **8** and no liquid crystallinity can be detected. In sum, with a similar molecular dipole, the more rod-like y-shaped **4** showed a enantiotropic nematic phase and with further extension of the molecular geometry towards being board-like, compound **6** and **7** exhibited monotropic behaviors while the board-like **8** is not liquid crystalline. The decreasing length-to-breadth ratios are attributed to the mesogenic trend of these four compounds.

Conclusions

For achieving low aspect ratios, calamitic nematogens, compounds **1**–**4**, with a rigid y-shaped molecular geometry were designed, synthesized and their mesogenic properties investigated. These triynylbenzene compounds showed better liquid crystallinity than their analogs with a central thiophene unit. By replacing the iodo group in **1c** with a smaller atom (Br, Cl, or H), superior mesogenic properties can be obtained for rigid y-shaped nematogens. It was found that the size of the substituent at the central benzene ring and not the resulting molecular dipole plays an important role for their corresponding mesogenic behaviors. These results showed that enantiotropic mesophase behaviors can be accomplished for molecules with a rigid extruding arm. Also, these studies provide information for future designing of rigid y-shaped liquid crystals with better liquid crystallinity. The identified calamitic nature of the nematic phase of the rigid y-shaped liquid crystals together with their low aspect-ratio make them suitable candidates as materials of the LC layer in LCD devices for improving viewing angles. Modifications of the rigid y-shaped geometry towards the rigid rectangular 1,2,4,5-tetraynylbenzene resulted in mesogens with even lower aspect-ratios. However, these modifications caused reduction of the liquid crystallinity. These results imply that for obtaining better liquid crystallinity from board-like molecules, the aspect ratio may have to be modified towards the calamitic end rather than the discotic end.

Experimental

General

All reactions were conducted under an atmosphere of nitrogen in oven-dried glassware using standard Schlenk techniques. THF was distilled over sodium–benzophenone. 1-Bromo-2,4,5-triiodobenzene,[14] 1-chloro-2,4,5-triiodobenzene,[14] and tetraiodobenzene[11] were prepared according to the published procedures. All other solvents and chemicals were reagent grades (Aldrich Chemical Co.) and used without further purification unless otherwise described.

Instrumental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer. Chemical shifts are reported in ppm relative to residual $CHCl_3$ (δ = 7.26, ^{1}H; 77.0, ^{13}C). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Differential scanning calorimetry (DSC) was measured on a Perkin-Elmer Pyris1 with heating and cooling rates of 5 and 10 °C min^{-1}. Polarized optical microscopy (POM) was carried out on a Nikon Eclipse E600 POL with a Mettler FP90/FP82HT hot stage system. X-Ray powder diffraction data were collected on the wiggler beamline BL17A of the National Synchrotron Radiation Research Center (NSRRC), Taiwan, using a triangular bent Si(111) monochromator and a wavelength of 1.33295 Å. The sample in a 1 mm capillary was mounted on the Huber 5020 diffractometer. An air stream heater is equipped at BL17A beamline and the temperature controller is programmable by a PC with a PID feed back system. Mass spectra were obtained on Jeol MStation MS-700 at the NSC Regional Instrumental Center at National Central University, Chungli, Taiwan and elemental analyses were carried out on a Heraeus CHN-O-Rapid Analyzer at the NSC Regional Instrumental Center at National Cheng Kung University, Tainan, Taiwan.

Synthesis

1-Iodo-2,4,5-tris(4-alkoxyphenylethynyl)benzene (1). To a mixture of *trans*-dichlorobis(triphenylphosphine)palladium(II) (83 mg, 0.12 mmol), copper iodide (297 mg, 1.56 mmol), tetraiodobenzene (1.15 g, 1.98 mmol) and triethylamine/dimethyl sulfoxide (10/5 mL) was added 1-alkoxy-4-ethynylbenzene (5.93 mmol) in triethylamine (15 mL) dropwise at room temperature. The solution was allowed to stir at room temperature for 21 h. The reaction mixture was diluted with dichloromethane (100 mL), washed with $NH_4Cl_{(aq)}$ (200 mL × 3), H_2O (200 mL × 3), and dried over $MgSO_4$. After removal of the solvents, the residue was purified by column chromatography (SiO_2, *n*-hexane–dichloromethane 8 : 1). Recrystallization from acetone yielded **1** as a white solid.

1a: (n = 4) yield 32%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.02 (s, 1H), 7.62 (s, 1H), 7.52 (d, J = 9.0 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 9.0 Hz, 2H), 6.90–6.84 (m, 6H), 3.98 (m, 6H), 1.83–1.74 (m, 6H), 1.57–1.44 (m, 6H), 0.99 (m, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.8, 159.7, 159.6, 141.1, 134.1, 133.20, 133.16 (2C), 129.4, 126.2, 125.8, 114.8, 114.7, 114.6 (3C), 114.5, 99.0, 96.2, 95.2, 95.1, 90.0, 86.0, 85.8, 67.8 (3C), 31.2 (3C), 19.2 (3C), 13.8 (3C). HRMS (FAB+) m/z for $C_{42}H_{41}IO_3$ 720.2100, found 720.2109. Anal. Calcd for $C_{42}H_{41}IO_3$ (720.7): C 70.00, H 5.73; found: C 69.76, H 5.74.

1b: (n = 6) yield 13%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.01 (s, 1H), 7.62 (s, 1H), 7.52 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 9.3 Hz, 2H), 7.47 (d, J = 9.0 Hz, 2H), 6.90–6.82 (m, 6H), 3.98 (m, 6H), 1.84–1.75 (m, 6H), 1.52–1.32 (m, 18H), 0.92 (m, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.8, 159.7, 159.6, 141.1, 134.1, 133.21, 133.16 (2C), 129.4, 126.2, 125.8, 114.8, 114.7, 114.6 (3C), 114.5, 99.0, 96.2, 95.2, 95.1, 90.0, 86.0, 85.8, 68.1 (3C), 31.6 (3C), 29.1 (3C), 25.7 (3C), 22.6 (3C), 14.0 (3C). HRMS (FAB+) m/z for $C_{48}H_{53}IO_3$ 804.3039, found 804.3065. Anal. Calcd for $C_{48}H_{53}IO_3$ (804.8): C 71.63, H 6.64; found: C 71.69, H 6.67.

1c: (n = 8) yield 24%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.01 (s, 1H), 7.62 (s, 1H), 7.52 (d, J = 9.0 Hz, 2H), 7.483 (d, J = 8.4 Hz, 2H), 7.478 (d, J = 9.3 Hz, 2H), 6.90–6.85 (m, 6H), 3.97 (m, 6H), 1.84–1.75 (m, 6H), 1.47–1.30 (m, 30H), 0.90 (m, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.8, 159.7, 159.6, 141.1, 134.1, 133.20, 133.16 (2C), 129.4, 126.2, 125.8, 114.8, 114.7, 114.6 (3C), 114.5, 99.0, 96.2, 95.2, 95.1, 90.0, 86.0, 85.8, 68.1 (3C), 31.8 (3C), 29.3 (3C), 29.2 (6C), 26.0 (3C), 22.6 (3C), 14.1 (3C). HRMS (FAB+) m/z for $C_{54}H_{65}IO_3$ 888.3978, found 888.3998. Anal. Calcd for $C_{54}H_{65}IO_3$ (889.0): C 72.96, H 7.37; found: C 72.91, H 7.36. The XRD pattern in the nematic temperature range showed a broad halo at ~4.3 Å.

1d: (n = 10) yield 21%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.01 (s, 1H), 7.62 (s, 1H), 7.52 (d, J = 9.0 Hz, 2H), 7.483 (d, J = 8.7 Hz, 2H), 7.476 (d, J = 9.0 Hz, 2H), 6.90–6.85 (m, 6H), 3.97 (m, 6H), 1.82–1.75 (m, 6H), 1.46–1.29 (m, 42H), 0.89 (m, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.8, 159.7, 159.6, 141.1, 134.1, 133.19, 133.15 (2C), 129.4, 126.2, 125.8, 114.8, 114.7, 114.6 (3C), 114.5, 99.0, 96.2, 95.2, 95.1, 90.0, 86.0, 85.8, 68.1 (3C), 31.9 (3C), 29.7 (3C), 29.6 (3C), 29.4 (3C), 29.3 (3C), 29.2

(3C), 26.0 (3C), 22.7 (3C), 14.1 (3C). HRMS (FAB+) *m/z* for $C_{60}H_{77}IO_3$ 972.4917, found 972.4905. Anal. Calcd for $C_{60}H_{77}IO_3$ (973.2): C 74.05, H 7.98; found: C 73.98, H 7.98.

1e: (n = 12) yield 25%. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.01 (s, 1H), 7.62 (s, 1H), 7.52 (d, J = 9.0 Hz, 2H), 7.490 (d, J = 9.0 Hz, 2H), 7.485 (d, J = 8.4 Hz, 2H), 6.90–6.85 (m, 6H), 3.97 (m, 6H), 1.84–1.75 (m, 6H), 1.49–1.29 (m, 54H), 0.90 (m, 9H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 159.7, 159.64, 159.58, 141.1, 134.1, 133.19, 133.15 (2C), 129.4, 126.2, 125.8, 114.8, 114.7, 114.6 (3C), 114.5, 99.0, 96.2, 95.2, 95.1, 90.0, 86.0, 85.8, 68.1 (3C), 31.9 (3C), 29.7 (6C), 29.6 (6C), 29.4 (3C), 29.3 (3C), 29.2 (3C), 26.0 (3C), 22.7 (3C), 14.1 (3C). HRMS (FAB+) *m/z* for $C_{66}H_{89}IO_3$ 1056.5856, found 1056.5867. Anal. Calcd for $C_{66}H_{89}IO_3$ (1057.3): C 74.97, H 8.48; found: C 74.85, H 8.48.

1f: (n = 14) yield 26%. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.01 (s, 1H), 7.62 (s, 1H), 7.52 (d, J = 9.0 Hz, 2H), 7.481 (d, J = 9.0 Hz, 2H), 7.476 (d, J = 9.0 Hz, 2H), 6.90–6.85 (m, 6H), 3.97 (m, 6H), 1.82–1.76 (m, 6H), 1.46–1.28 (m, 66H), 0.89 (m, 9H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 159.8, 159.7, 159.6, 141.1, 134.1, 133.22, 133.17 (2C), 129.4, 126.2, 125.8, 114.8, 114.7, 114.6 (3C), 114.5, 99.0, 96.2, 95.2, 95.1, 90.0, 86.0, 85.8, 68.1 (3C), 31.9 (3C), 29.7 (9C), 29.62 (6C), 29.59 (3C), 29.40 (3C), 29.37 (3C), 29.2 (3C), 26.0 (3C), 22.7 (3C), 14.1 (3C). HRMS (FAB+) *m/z* for $C_{72}H_{101}IO_3$ 1140.6795, found 1140.6754. Anal. Calcd for $C_{72}H_{101}IO_3$ (1441.5): C 75.76, H 8.92; found: C 75.89, H 8.97.

1g: (n = 16) yield 14%. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.01 (s, 1H), 7.62 (s, 1H), 7.52 (d, J = 9.0 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 9.3 Hz, 2H), 6.90–6.85 (m, 6H), 3.97 (m, 6H), 1.82–1.77 (m, 6H), 1.46–1.27 (m, 78H), 0.88 (m, 9H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 159.8, 159.7, 159.6, 141.1, 134.1, 133.21, 133.17 (2C), 129.4, 126.2, 125.8, 114.8, 114.7, 114.6 (3C), 114.5, 99.0, 96.2, 95.2, 95.1, 90.0, 86.0, 85.8, 68.2 (3C), 31.9 (3C), 29.7 (18C), 29.6 (9C), 29.4 (3C), 29.2 (3C), 26.0 (3C), 22.7 (3C), 14.1 (3C). HRMS (FAB+) *m/z* for $C_{78}H_{113}IO_3$ 1224.7734, found 1224.7751. Anal. Calcd for $C_{78}H_{113}IO_3$ (1225.6): C 76.44, H 9.29; found: C 76.52, H 9.29.

1-Bromo-2,4,5-tris(4-octyloxyphenylethynyl)benzene (2). To a mixture of *trans*-dichlorobis(triphenylphosphine)palladium(II) (260 mg, 0.37 mmol), copper iodide (142 mg, 0.75 mmol), and 1-bromo-2,4,5-triiodothiophene (2.00 g, 3.74 mmol) in triethylamine (50 mL) was added 1-ethynyl-4-octyloxybenzene (3.02 g, 13.09 mmol) dropwise at room temperature. The solution was allowed to stir at room temperature for 24 h and then dichloromethane (100 mL) was added. The reaction mixture was washed with $NH_4Cl_{(aq)}$ (100 mL × 3), H_2O (100 mL × 3), and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (SiO_2, *n*-hexane–dichloromethane 5 : 1) to yield **2** as a pale yellow solid (2.02 mg, 2.39 mmol, 64%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.75 (s, 1H), 7.67 (s, 1H), 7.51–7.46 (m, 6H), 6.90–6.85 (m, 6H), 3.98 (t, J = 6.5 Hz, 6H), 1.84–1.75 (m, 6H), 1.49–1.26 (m, 30H), 0.89 (t, J = 6.9 Hz, 9H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 159.8, 159.7, 159.6, 135.2, 134.9, 133.24 (4C), 133.15 (2C), 126.3, 125.1, 125.0, 123.9, 114.8, 114.6 (7C), 114.5, 96.3, 96.0, 94.9, 86.4, 86.0, 85.8, 68.1 (3C), 31.8 (3C), 29.3 (6C), 29.2 (3C), 26.0 (3C), 22.6 (3C), 14.1 (3C). HRMS (FAB+) *m/z* for $C_{54}H_{65}{}^{79}BrO_3$ 840.4117, found 840.4110; for $C_{54}H_{65}{}^{81}BrO_3$ 842.4097, found 842.4080. Anal. Calcd for $C_{54}H_{65}BrO_3$ (842.0): C 77.03, H 7.78; found: C 76.82, H 7.83.

1-Chloro-2,4,5-tris(4-octyloxyphenylethynyl)benzene (3). To a mixture of *trans*-dichlorobis(triphenylphosphine)palladium(II) (73 mg, 0.10 mmol), copper iodide (25 mg, 0.13 mmol), and 1-chloro-2,4,5-triiodothiophene (502 mg, 1.02 mmol) in triethylamine (30 mL) was added 1-ethynyl-4-octyloxybenzene (820 mg, 3.56 mmol) dropwise at room temperature. The solution was allowed to stir at room temperature for 24 h and then dichloromethane (100 mL) was added. The reaction mixture was washed with $NH_4Cl_{(aq)}$ (100 mL × 3), H_2O (100 mL × 3), and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (SiO_2, *n*-hexane–dichloromethane 5 : 1) to yield **3** as a white solid (760 mg, 0.95 mmol, 93%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.68 (s, 1H), 7.56 (s, 1H), 7.51–7.47 (m, 6H), 6.90–6.85 (m, 6H), 3.97 (t, J = 6.7 Hz, 6H), 1.84–1.75 (m, 6H), 1.49–1.30 (m, 30H), 0.90 (m, 9H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 159.8, 159.75, 159.70, 135.4, 134.4, 133.25 (2C), 133.23 (2C), 133.1 (2C), 131.7, 126.2, 124.5, 123.0, 114.8, 114.6 (7C), 114.5, 96.6, 96.2, 94.7, 86.2, 85.7, 84.5, 68.1 (3C), 31.8 (3C), 29.3 (3C), 29.2 (6C), 26.0 (3C), 22.6 (3C), 14.1 (3C). HRMS (EI+) *m/z* for $C_{54}H_{65}{}^{35}ClO_3$ 796.4622, found 796.4605; for $C_{54}H_{65}{}^{37}ClO_3$ 798.4593, found 798.4581. Anal. Calcd for $C_{54}H_{65}ClO_3$ (797.5): C 81.32, H 8.21; found: C 81.23, H 8.26.

1,2,4-Tris(4-octyloxyphenylethynyl)benzene (4). To a solution of **1c** (308 mg, 0.35 mmol) in THF (30 mL) at −70 °C was added 1.6 M *n*-BuLi (0.68 mmol) dropwise under a nitrogen atmosphere. When the addition was completed, the reaction mixture was stirred at −70 °C for further 30 min. The reaction mixture was allowed to stir at room temperature for 24 h and then to the reaction mixture was added dichloromethane (50 mL). The reaction mixture was washed with H_2O (100 mL × 3) and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (SiO_2, *n*-hexane–dichloromethane 5 : 1) to yield **4** as a white solid (216 mg, 0.28 mmol, 84%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.68 (d, J = 1.5 Hz, 1H), 7.51–7.39 (m, 8H), 6.88–6.86 (m, 6H), 3.97 (m, 6H), 1.82–1.77 (m, 6H), 1.46–1.30 (m, 30H), 0.90 (m, 9H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 159.5 (3C), 134.3, 133.1 (6C), 131.4, 130.3, 126.2, 125.3, 123.1, 115.1, 114.8, 114.6 (7C), 95.3, 94.1, 91.6, 87.3, 87.2, 86.6, 68.1 (3C), 31.8 (3C), 29.3 (3C), 29.2 (6C), 26.0 (3C), 22.6 (3C), 14.1 (3C). HRMS (EI+) *m/z* for $C_{54}H_{66}O_3$ 762.5012, found 762.5009. Anal. Calcd for $C_{54}H_{66}O_3$ (763.1): C 84.99, H 8.72; found: C 84.86, H 8.74.

1,3-Bis-(4-octyloxyphenylethynyl)benzene (5). To a mixture of *trans*-dichlorobis(triphenylphosphine)palladium(II) (31 mg, 0.05 mmol), copper iodide (10 mg, 0.05 mmol), and 1,3-diiodobenzene (300 mg, 0.91 mmol) in triethylamine (40 mL) was added 1-ethynyl-4-octyloxybenzene (520 mg, 2.26 mmol) dropwise at room temperature. The reaction mixture was allowed to stir stirred at room temperature for 3 h and then to the reaction mixture was added dichloromethane (100 mL). The reaction mixture was washed with $NH_4Cl_{(aq)}$ (100 mL × 3), H_2O (100 mL × 3), and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (SiO_2, *n*-hexane–dichloromethane 5 : 1) to yield **5** as a white solid (429 mg, 0.80 mmol, 88%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.66 (t, J = 1.5 Hz, 1H), 7.65–7.44 (m, 6H), 7.32 (dd, J = 8.5, 7.0 Hz, 1H), 6.88 (dt, J = 8.8, 2.5 Hz, 4H), 3.99 (t, J = 6.4 Hz, 4H), 1.84–1.75 (m, 4H), 1.47–1.31 (m, 20H), 0.90 (t, J = 6.7 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 160.0 (2C), 134.5, 133.5 (4C), 131.2 (2C), 128.9, 124.4 (2C), 115.2 (2C), 115.0 (4C), 90.4 (2C), 87.6 (2C), 68.6 (2C), 32.3 (2C), 29.8 (2C), 29.7 (2C), 29.6 (2C), 26.4 (2C), 23.1 (2C), 14.3 (2C). HRMS (FAB+) *m*/*z* for $C_{38}H_{46}O_2$ 534.3498, found 534.3502. Anal. Calcd for $C_{38}H_{46}O_2$ (534.8): C 85.35, H 8.67; found: C 85.10, H 8.64.

2,4,5-Tris(4-octyloxyphenylethynyl)biphenyl (6). To a mixture of trans-dichlorobis(triphenylphosphine)palladium(II) (24 mg, 0.10 mmol) and **2** (305 mg, 0.36 mmol) in dry *N*,*N*-dimethylformamide (50 mL) was added 2-(tributylstannyl)benzene (405 mg, 1.10 mmol) dropwise at 70 °C. The mixture was stirred at 70 °C for 6 h. After cooling, to the reaction mixture was added dichloromethane (100 mL) and washed with H_2O (200 mL × 2). The organic layer was dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (SiO_2, *n*-hexane–dichloromethane 5 : 1) to yield **6** as a yellow solid (210 mg, 0.25 mmol, 70%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.78 (s, 1H), 7.71 (d, J = 7.0 Hz, 2H), 7.60 (s, 1H), 7.55 ∼ 7.43 (m, 7H), 7.28 (d, 8.7 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 4.02–3.94 (m, 6H), 1.84–1.75 (m, 6H), 1.47–1.30 (m, 30H), 0.90 (m, 9H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 159.12, 159.1, 159.0, 142.0, 138.8, 134.8, 132.5 (4C), 131.8 (2C), 131.8, 128.6 (2C), 127.35 (2C), 127.27, 124.7, 124.0, 120.9, 114.19, 114.16, 114.09, 114.04 (4C), 113.9 (2C), 94.5, 93.62, 93.55, 86.5, 86.3, 85.6, 68.6 (3C), 32.2 (3C), 29.8 (3C), 29.6 (6C), 26.4 (3C), 23.1 (3C), 14.3 (3C). HRMS (EI+) *m*/*z* for $C_{60}H_{70}O_3$ 838.5325, found 838.5327. Anal. Calcd for $C_{60}H_{70}O_3$ (839.2): C 85.87, H 8.41; found: C 85.69, H 8.38.

1,2,4-Tris(4-octyloxyphenylethynyl)-5-phenylethynylbenzene (7). To a mixture of *trans*-dichlorobis(triphenylphosphine)palladium(II) (24 mg, 0.04 mmol), copper iodide (5 mg, 0.04 mmol), and **2** (305 mg, 0.362 mmol) in triethylamine (30 mL) was added 1-ethynylbenzene (70 mg, 0.71 mmol) dropwise under reflux under a nitrogen atmosphere. The mixture was stirred under reflux for 6 h. After cooling, to the reaction mixture was added dichloromethane (100 mL). The reaction mixture was washed with $NH_4Cl_{(aq)}$ (50 mL × 3), H_2O (70 mL × 3), and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (SiO_2, *n*-hexane–dichloromethane 7 : 1) to yield **7** as a yellow solid (233 mg, 0.27 mmol, 76%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.71 (s, 1H), 7.69 (s, 1H), 7.57 (dd, J = 6.1, 2.9 Hz, 2H), 7.51–7.48 (m, 6H), 7.37–7.35 (m, 3H), 6.89–6.86 (m, 6H), 3.97 (m, 6H), 1.84–1.75 (m, 6H), 1.47–1.30 (m, 30H), 0.90 (m, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.6 (3C), 134.6, 134.4, 133.2 (6C), 131.7 (2C), 128.6, 128.4 (2C), 125.5, 125.3, 125.1, 124.6, 123.2, 115.0, 114.9, 114.7 (7C), 95.6, 95.5, 94.9, 87.9, 86.53, 86.48, 68.2 (3C), 31.8 (3C), 29.3 (3C), 29.2 (6C), 26.0 (3C), 22.6 (3C), 14.1 (3C). HRMS (EI+) *m*/*z* for $C_{62}H_{70}O_3$ 862.5325, found 862.5341. Anal. Calcd for $C_{62}H_{70}O_3$ (863.2): C 86.27, H 8.17; found: C 86.09, H 8.18.

1,2,4,5-Tetrakis(4-octyloxyphenylethynyl)benzene (8). To a mixture of trans-dichlorobis(triphenylphosphine)palladium(II) (110 mg, 0.16 mmol), copper iodide (31 mg, 0.16 mmol), and 1,2,4,5-tetraiodobenzene (1.00 g, 1.71 mmol) in triethylamine (50 mL) was added 1-ethynyl-4-octyloxybenzene (1.96 g, 8.51 mmol) dropwise under reflux. The reaction mixture was stirred under reflux for 24 h. To the reaction mixture, dichloromethane (100 mL) was then added. The solution was washed with $NH_4Cl_{(aq)}$ (100 mL × 3), H_2O (100 mL × 3), and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (SiO_2, *n*-hexane–dichloromethane 7 : 1) to yield **8** as a yellow solid (1.33 g, 1.34 mmol, 79%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.68 (s, 2H), 7.49 (dt, J = 8.7, 2.4 Hz, 8H), 6.87 (dt, J = 8.9, 2.5 Hz, 8H), 3.98 (t, J = 6.6 Hz, 8H), 1.82–1.75 (m, 8H), 1.47–1.30 (m, 40H), 0.90 (t, J = 6.7 Hz, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.6 (4C), 134.4 (2C), 133.2 (4C), 125.1 (4C), 115.0 (4C), 114.7 (4C), 95.4 (4C), 86.7 (4C), 68.2 (4C), 31.8 (4C), 29.3 (4C), 29.2 (8C), 26.0 (4C), 22.6 (4C), 14.1 (4C). HRMS (FAB+) *m*/*z* for $C_{70}H_{86}O_4$ 990.6526, found 990.6551. Anal. Calcd for $C_{70}H_{86}O_4$ (991.4): C 84.80, H 8.74; found: C 84.70, H 8.74.

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