

## Unexpected mesophase behaviour in novel triphenylene multi-alkenes

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**Abstract**—The first series of hexaalkenyloxytriphenylenes, where the unsaturation resides at the termini of the side chains, has been synthesised and characterised. Most interestingly, the synthesis of these alkenyloxytriphenylenes, by alkylation of hexahydroxytriphenylene, is found to yield additional products resulting from a single C-alkylation alongside exhaustive O-alkylation; surprisingly several homologues of these materials retain columnar mesophase behaviour.

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Triphenylene derivatives are the most widely studied class of discotic liquid crystals.<sup>1</sup> Such disc-like molecules form liquid crystal phases in which, most usually, the molecules assemble as columns to give so-called columnar mesophases (which can be likened to the smectic mesophases formed by rod-like/calamitic molecules) (Fig. 1). In some cases a less ordered nematic phase is exhibited in which the molecules retain only orientational order. Triphenylene discotics have received particular interest because of their ability to act as one-dimensional charge transport materials, acting as photoconductors or semiconductors on doping.<sup>2</sup>

Triphenylene has proved to be a versatile scaffold for more fundamental interrogation of structural factors controlling mesophase behaviour (stability, type etc.). Unraveling the interesting and diverse properties of triphenylene based discotic mesogens has proceeded in parallel with synthetic advances. New and improved synthetic protocols have now led to characterisation of a wide range of symmetrical (most common) and unsymmetrically substituted derivatives.<sup>3</sup>

Our work, and that of others in this area, has established a set of qualitative parameters governing mesophase formation. In particular we have argued that the central core of such discotic molecules extends beyond the

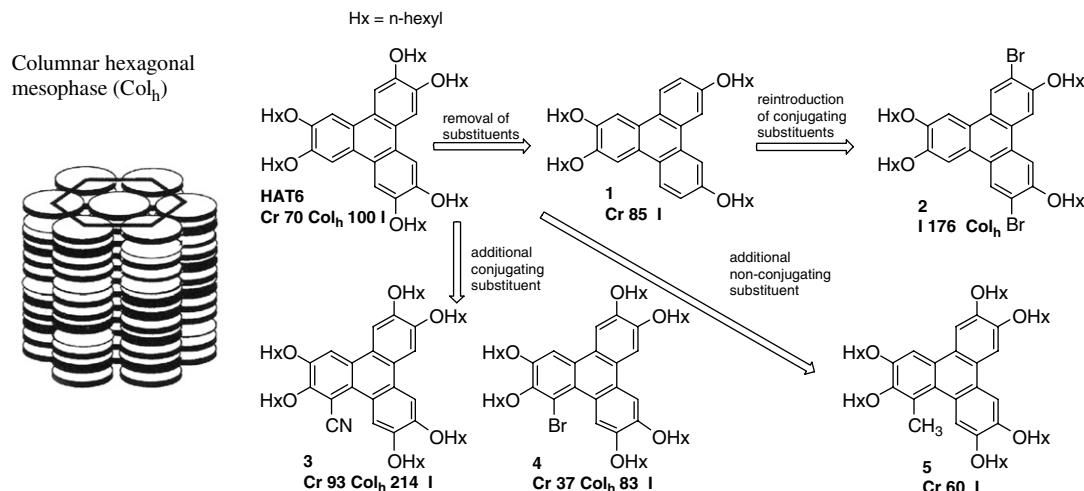
central aromatic triphenylene unit to include the attached conjugated substituents.<sup>4</sup> Perturbation of this extended core has a dramatic effect on the mesophase behaviour and this is most easily seen by example. Hexaalkoxytriphenylenes (HATs) such as HAT6 are the most studied triphenylene based discotic liquid crystals and are typically characterised as giving columnar hexagonal mesophases (Fig. 1).<sup>5</sup> Removal of one (or more) alkoxy chains,<sup>3d,6</sup> or even moving a side chain,<sup>6</sup> generally results in destabilisation or destruction of the mesophase. Replacement of a chain or chains with groups that extend the  $\pi$ -system such as bromide,<sup>3d,7,8</sup> methoxy<sup>9</sup> or nitrile,<sup>7</sup> however, reinstates columnar mesophase formation, despite the fact that a flexible chain is not included (Fig. 1).<sup>10</sup> Introduction of a flexible (alkyl) chain alone (without linking via a conjugating group or atom) does not reinstate columnar mesophase formation.<sup>3g</sup>

Molecules such as HAT6 itself can be modified by addition of further substituents. Once again, evidence points to a qualitative inference that introduction of additional conjugating substituents (at the  $\alpha$ -position) supports mesophase formation<sup>6,11</sup> whereas introduction of small, non-polarisable groups (e.g., methyl) does not (Fig. 1).<sup>12</sup>

As part of a wider study on the structural parameters affecting mesophase behaviour in triphenylene discotics we initiated a programme to investigate the consequence of replacing the typical alkoxy substituents of HAT derivatives with terminal alkenyloxy groups. The effect of such substitution within calamitic systems is well

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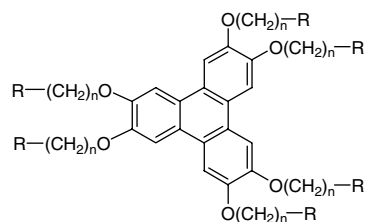


**Figure 1.** Examples illustrating the importance of a central  $\pi$ -extended core in triphenylene based liquid crystals. Simple conjugating substituents, like cyanide or bromide, can lead to formation of columnar mesophases but non-conjugating ones (H, Me) suppress mesophase formation.

known to lower transition temperatures.<sup>13</sup> Most modern syntheses of symmetrical triphenylene hexaalkoxides are based on the oxidative trimerisation of dialkoxybenzenes.<sup>3a</sup> Unfortunately, this method proved unsuccessful for alkenyloxy derivatives and alkylation of hexahydroxytriphenylene **6**, with the appropriate alkenyl bromide, proved most successful (Scheme 1).<sup>5,14</sup>

Replacement of alkoxy chains with terminal alkene chains does indeed affect mesophase behaviour and the results are summarised in Table 1. In the case of hexyl/hexenyl chains, this effect is modest with both the transitions into the mesophase (64 °C) and clearing point (92 °C) lowered by less than 10 °C for hexaalkene **8** compared with the parent HAT6. This mesophase, like all reported here, gives a texture characteristic of a columnar hexagonal phase when examined by polarised optical microscopy. Hexapentenyl homologue **7**, although displaying comparable transition temperatures to **8**, shows a significantly reduced mesophase stability to its saturated counterpart HAT5. Such destabilisation is even more apparent in the higher homologues **9** and

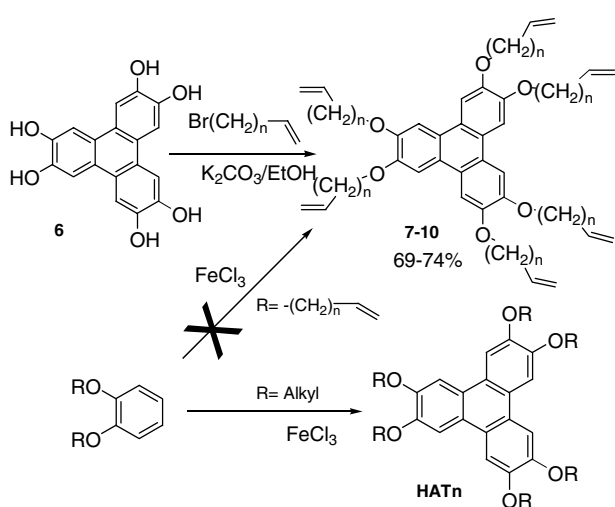
**Table 1.** Comparison of the transition temperatures of alkyl- and alkenyloxytriphenylenes



Chain length	Alkoxy (HATn) R = CH <sub>2</sub> CH <sub>3</sub>	Alkenyloxy R = CH=CH <sub>2</sub>
C <sub>5</sub> (n = 3)	<b>HAT5</b> Cr69Col <sub>h</sub> 122I	<b>7</b> Cr62Col <sub>h</sub> 95I
C <sub>6</sub> (n = 4)	<b>HAT6</b> Cr70Col <sub>h</sub> 100I	<b>8</b> Cr64Col <sub>h</sub> 92I
C <sub>7</sub> (n = 5)	<b>HAT7</b> Cr69Col <sub>h</sub> 93I	<b>9</b> Cr57I
C <sub>8</sub> (n = 6)	<b>HAT8</b> Cr67Col <sub>h</sub> 86I	<b>10</b> Cr49I

**10**, where columnar mesophase formation is completely suppressed. The trend therefore broadly follows that expected; replacing alkyl substituents with terminal alkenes tends to lower the clearing points resulting in complete suppression of the mesophase in longer chain derivatives. Introduction of terminal unsaturation has only modest effect on the flexibility and conformational freedom of the side chains. It is reasonable to speculate, therefore, that the observed behaviour stems from differences in the ability to easily pack alkenyl chains while maintaining a columnar structure of the cores, combined with the inherent subtle change in core-chain ratio. However, attempts to examine the details of packing and molecular structure by X-ray crystallography have been unsuccessful because, as is most often the case for such discotic triphenylenes, suitable crystals cannot be grown.

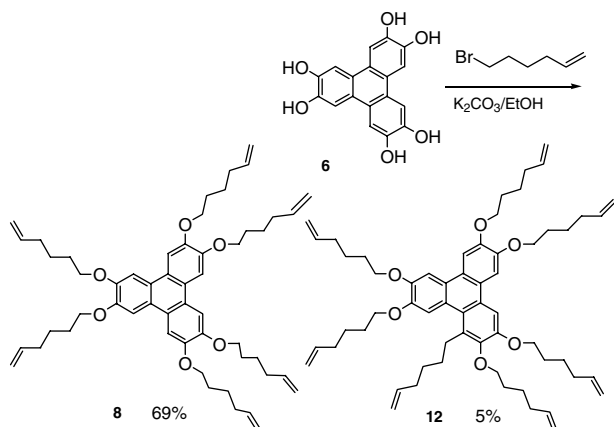
The most interesting result from this study, however, stemmed from a somewhat serendipitous discovery. During synthesis of symmetrical hexahexenyl derivative **8** an additional product was observed to form. Careful chromatographic separation permitted isolation of this material, which was characterised as **12** (Scheme 2),



**Scheme 1.** Synthesis of hexaalkenyloxytriphenylenes.

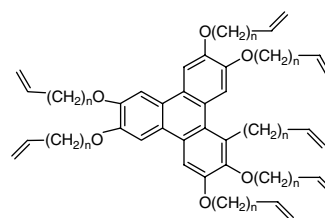
the product from (single) C-alkylation and exhaustive O-alkylation.<sup>14</sup> The existence of such C-alkylated products has been assumed from other syntheses but, to the best of our knowledge, their isolation has never been achieved. It is likely that further products of additional C-alkylation are also formed, in trace quantities, in these reactions.

According to our assumptions, introduction of such a substituent at the triphenylene  $\alpha$ -site should destabilise the columnar mesophase (see compound **5** in Fig. 1, for example). We were very surprised, therefore, to observe that **12** in fact exhibits a columnar mesophase over a comparable range (62–83 °C) to the symmetrical hexasubstituted parent compounds HAT6 and **8**. The reactions leading to **7–10** were therefore carefully re-examined and isolation of the related C-alkylated products from the full series was successfully performed. As expected, the reaction was indeed general and yields of 5–11% of the C-alkylated products were obtained. The intriguing mesophase behaviour of the series is summarised in Table 2. Pentenyl derivative **11** shows a columnar mesophase below 69 °C, much lower than both symmetrical alkyl (HAT5) and alkenyl (**7**) materials. Heptenyl derivative (**13**), unlike **9**, exhibits a mesophase below 62 °C. The materials give an exquisite example of the subtle structural balance required for mesophase formation in triphenylene based liquid crystals. In addition to the surprising observation that the additional alkenyl group supports mesophase formation at all, attention should be focused on the derivatives of intermediate chain length. Indeed, there are known examples within series of triphenylene derivatives where hexyl homologues are unique.<sup>3d</sup> The C6 chain derivative **12** in this series also stands out. Its stability (highest clearing point) does not follow a simple trend, implying that, once again, a favourable balance between core and chain is present. Heptenyl material **13** also deserves special mention. Whereas the corresponding symmetrical 6-chain analogue **9** is non-mesogenic, in this material we found that introduction of the extra (directly linked) alkenyl chain actually induces mesophase behaviour. This effect could not be predicted based on previous investigations of triphenylene discotics.



**Scheme 2.** Alkylation of hexahydroxytriphenylene to give the C-alkylated product.

**Table 2.** Mesophase behaviour of hexa(alkenyloxy)-alkenyltriphenylenes



Chain length	
$\text{C}_5$ ( $n = 3$ )	<b>11</b> Cr41Col <sub>h</sub> 69I
$\text{C}_6$ ( $n = 4$ )	<b>12</b> Cr62Col <sub>h</sub> 83I
$\text{C}_7$ ( $n = 5$ )	<b>13</b> Cr33Col <sub>h</sub> 62I
$\text{C}_8$ ( $n = 6$ )	<b>14</b> Cr47I

We have demonstrated that replacing alkyl chains with terminal alkenyl substituents in hexaalkoxytriphenylenes has the overall effect of lowering transition temperatures and mesophase stability. Transition temperatures for the  $\text{C}_6$  derivatives are least sensitive to this subtle structural change. The syntheses also produce the corresponding 7-chain derivatives resulting from an additional single C-alkylation. Some of these intriguing products also show mesophases with the hexenyl derivative again showing least perturbation due to the structural change. Introduction of the extra chain actually induces mesophase behaviour in the heptenyl derivative **13**. These are the only known examples of mesophase-forming triphenylenes bearing a substituent linked to the core by a saturated methylene group. They might prove to be something of a special case but the result nevertheless impacts on the way we view the structural parameters governing mesophase behaviour in these important systems, and further demonstrates the subtle structural balance influencing mesophase behaviour in triphenylene discotics. Further studies are in progress to investigate the generality of these observations and will be reported in due course, along with detailed mesophase characterisation for all compounds.

### Acknowledgement

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  - Triphenylenes **9** and **13**: A mixture of hexahydroxytriphenylene **6** (0.52 g, 1.60 mmol), 7-bromohept-1-ene (2.50 g, 14.12 mmol) and potassium carbonate (4 g) were stirred in refluxing ethanol (20 mL) under nitrogen for 26 h. Aqueous workup followed by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether) and recrystallisation (ethanol) gave pure **9** and **13** as colourless solids. **9**: Yield 1.04 g, 72%;  $\nu_{\max}$  (thin film)/cm<sup>-1</sup> 1640, 1615; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.53–1.60 (m, 24H), 1.95 (quin,  $J = 7.2$ , 12H), 2.10–2.15 (m, 12H), 4.23 (t,  $J = 6.8$ , 12H), 4.95–5.06 (m, 12H), 5.80–5.90 (m, 6H), 7.83 (s, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 25.57, 28.65, 29.24, 33.65, 69.62, 107.50, 114.52, 123.73, 138.92, 149.11. HR-MS (EI): [M<sup>+</sup>] calcd for C<sub>60</sub>H<sub>84</sub>O<sub>6</sub>, 900.6262; found, 900.6262. Compound **13**: Yield 0.096 g, 6%;  $\nu_{\max}$  (thin film)/cm<sup>-1</sup> 1640, 1614, 1596; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.51–1.66 (m, 28H), 1.83–1.96 (m, 14H), 2.08–2.15 (m, 14H), 3.19 (t,  $J = 8.3$ , 2H), 4.04 (t,  $J = 6.4$ , 2H), 4.13 (t,  $J = 6.4$ , 2H), 4.18–4.25 (m, 8H), 4.95–5.06 (m, 14H), 5.78–5.90 (m, 7H), 7.73 (s, 1H), 7.77 (s, 1H), 7.79 (s, 1H), 7.80 (s, 1H), 7.86 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 25.6, 25.7, 25.8, 28.7, 28.9, 29.1, 29.3, 29.4, 29.7, 30.3, 30.5, 31.1, 33.7, 33.8, 33.9, 40.0, 68.4, 69.1, 69.4, 69.5, 69.7, 72.8, 76.7, 77.0, 77.3, 104.1, 106.8, 107.5, 108.2, 112.1, 114.5, 114.6, 114.7, 123.9, 124.2, 124.5, 124.6, 126.8, 132.6, 138.7, 138.8, 138.9, 139.0, 139.1, 147.3, 147.4, 147.9, 148.7, 149.2, 150.5. HR-MS (EI): [M<sup>+</sup>] calcd for C<sub>67</sub>H<sub>96</sub>O<sub>6</sub>, 996.7201; found, 996.7195.
  - Triphenylenes **7** and **11**: Prepared as above using hexahydroxytriphenylene **6** (0.50 g, 1.54 mmol), 5-bromopent-1-ene (2.30 g, 15.4 mmol) to give **7** and **11** as colourless solids. **7**: Yield 0.83 g, 74%;  $\nu_{\max}$  (thin film)/cm<sup>-1</sup> 1640, 1615; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 2.03–2.08 (m, 12H), 2.34–2.39 (m, 12H), 4.25 (t,  $J = 6.6$ , 12H), 5.03–5.14 (m, 12H), 5.89–5.99 (m, 6H), 7.83 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 28.6, 30.3, 68.8, 107.4, 115.2, 123.6, 137.9, 148.8. HR-MS (EI): [M<sup>+</sup>] calcd for C<sub>48</sub>H<sub>60</sub>O<sub>6</sub>, 732.4384; found, 732.4392. **11**: Yield 0.079 g, 7%;  $\nu_{\max}$  (thin film)/cm<sup>-1</sup> 1640, 1614, 1596; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.96–2.06 (m, 12H), 2.08–2.26 (m, 2H), 2.28–2.35 (m, 14H), 3.23 (t,  $J = 8.3$ , 2H), 4.07 (t,  $J = 6.4$ , 2H), 4.16 (t,  $J = 6.4$ , 2H), 4.18–4.25 (m, 8H), 4.99–5.14 (m, 14H), 5.87–5.98 (m, 7H), 7.73 (s, 1H), 7.77 (s, 1H), 7.79 (s, 1H), 7.80 (s, 1H), 7.86 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 28.5, 28.6, 28.7, 28.8, 29.4, 29.7, 29.8, 30.2, 30.3, 30.4, 30.6, 34.7, 67.8, 68.4, 68.7, 68.8, 69.0, 72.4, 76.7, 77.0, 77.3, 104.2, 106.9, 107.5, 108.2, 112.1, 114.8, 114.9, 115.2, 115.3, 115.4, 123.9, 124.3, 124.4, 124.5, 124.6, 126.9, 132.3, 137.8, 137.9, 138.0, 138.1, 138.2, 138.3, 138.4, 147.3, 147.5, 147.9, 148.7, 149.2, 150.4. HR-MS (EI): [M<sup>+</sup>] calcd for C<sub>53</sub>H<sub>68</sub>O<sub>6</sub>, 800.5010; found, 800.5008. Triphenylenes **8** and **12**: Prepared as above using hexahydroxytriphenylene **6** (0.50 g, 1.54 mmol), 6-bromohex-1-ene (2.29 g, 14.0 mmol) to give **8** and **12** as colourless solids. **8**: Yield 0.87 g, 69%;  $\nu_{\max}$  (thin film)/cm<sup>-1</sup> 1639, 1615; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.65–1.73 (m, 12H), 1.92–1.97 (m, 12H), 2.17–2.25 (m, 12H), 4.24 (t,  $J = 6.6$ , 12H), 4.98–5.10 (m, 12H), 5.82–5.92 (m, 6H), 7.83 (s, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 25.72, 29.12, 33.75, 69.68, 107.46, 114.97, 123.82, 138.85, 149.14. HR-MS (ES+): [M+H]<sup>+</sup> calcd for C<sub>54</sub>H<sub>73</sub>O<sub>6</sub>, 817.5402; found, 817.5403. **12**: Yield 0.07 g, 5%;  $\nu_{\max}$  (thin film)/cm<sup>-1</sup> 1640, 1614, 1596; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.61–1.74 (m, 14H), 1.86–1.97 (m, 14H), 2.07–2.09 (m, 2H), 2.16–2.22 (m, 12H), 3.20 (t,  $J = 8.4$ , 2H), 4.05 (t,  $J = 6.4$ , 2H), 4.15 (t,  $J = 6.4$ , 2H), 4.19–4.26 (m, 8H), 4.95–5.09 (m, 14H), 5.81–5.92 (m, 7H), 7.73 (s, 1H), 7.77 (s, 1H), 7.79 (s, 1H), 7.80 (s, 1H), 7.86 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 25.67, 25.71, 15.73, 25.84, 29.09, 29.14, 29.17, 30.30, 30.39, 31.29, 33.75, 33.90, 34.25, 68.57, 69.28, 69.52, 69.67, 69.89, 72.95, 104.37, 107.02, 107.72, 108.40, 112.32, 114.79, 114.90, 114.97, 115.80, 124.15, 124.50, 124.82, 127.12, 132.75, 138.71, 138.78, 138.83, 138.88, 138.91, 138.96, 147.58, 147.70, 148.17, 148.99, 149.48, 150.71. HR-MS (ES+): [M+H]<sup>+</sup> calcd for C<sub>60</sub>H<sub>83</sub>O<sub>6</sub>, 899.6184; found, 899.6185. Triphenylenes **10** and **14**: Prepared as above using hexahydroxytriphenylene **6** (0.50 g, 1.54 mmol), 8-bromooct-1-ene (2.59 g, 13.5 mmol) to give **10** and **14** as colourless solids. **10**: Yield 1.06 g, 70%;  $\nu_{\max}$  (thin film)/cm<sup>-1</sup> 1640, 1615; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.45–1.61 (m, 36H), 1.92–1.99 (m, 12H), 2.08–2.11 (m, 12H), 4.24 (t,  $J = 6.6$ , 12H), 4.95–5.06 (m, 12H), 5.79–5.88 (m, 6H), 7.84 (s, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 26.1, 28.9, 29.0, 29.5, 33.7, 69.8, 107.7, 114.5, 123.9, 139.3, 149.3. HR-MS (EI): [M<sup>+</sup>] calcd for C<sub>66</sub>H<sub>96</sub>O<sub>6</sub>, 984.7201; found, 984.7201. Compound **14**: Yield 0.084 g, 5%;  $\nu_{\max}$  (thin film)/cm<sup>-1</sup> 1640, 1614, 1596; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.83–1.07 (m, 14H), 1.44–1.55 (m, 32H), 1.83–1.95 (m, 12H), 2.06–2.09 (m, 12H), 3.18 (t,  $J = 8.3$ , 2H), 4.03 (t,  $J = 6.4$ , 2H), 4.13 (t,  $J = 6.4$ , 2H), 4.18–4.24 (m, 8H), 4.92–5.03 (m, 14H), 5.76–5.88 (m, 7H), 7.72 (s, 1H), 7.77 (s, 1H), 7.79 (s, 1H), 7.80 (s, 1H), 7.87 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 26.1, 26.2, 27.1, 28.9, 29.0, 29.2, 29.4, 29.5, 29.6, 29.8, 30.1, 30.5, 30.7, 30.8, 31.2, 32.0, 33.7, 33.8, 33.9, 68.7, 69.4, 69.7, 69.8, 73.1, 104.5, 107.3, 107.9, 108.7, 112.5, 114.5, 114.6, 124.3, 124.6, 124.9, 127.1, 132.9, 139.2, 146.9, 147.7, 147.9, 148.3, 149.1, 149.6, 150.0. HR-MS (EI): [M<sup>+</sup>] calcd for C<sub>74</sub>H<sub>110</sub>O<sub>6</sub>, 1094.8297; found, 1094.8291.