Supramolecular liquid crystals containing isoquinoline hydrogen-bonded acceptors

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Preliminary communication

Supramolecular liquid crystals containing isoquinoline hydrogen-bonded acceptors

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6-Dodecyloxyisoquinoline IS (**1**) has been synthesized and utilized as a proton acceptor to generate a series of novel mesogenic supramolecules. Two mesogenic supramolecular dimers IS-OBA and IS-COOBA have been constructed from a 1:1 molar ratio of IS complexed either with 4-decyloxybenzoic acid OBA (**2**) or with 4-decyloxycarbonylbenzoic acid COOBA (**3**). A kinked mesogenic supramolecular trimer, i.e. a double H-bonded complex $(IS)_2$-THDA, has been constructed from a 2:1 molar ratio of IS complexed with 2,5-thiophenedicarboxylic acid THDA (**4**). The mesogenic properties of the H-bonded complex $(IS)_2$-THDA are compared with those of previously reported H-bonded complexes $(C12PS)_2$-THDA and $(C12PP)_2$-THDA consisting of a 2:1 molar ratio of *trans*-4-dodecyloxy-4′-stilbazole C12PS (**5**) or 4-dodecyloxypyridine C12PP (**6**) with THDA. Significantly, the first isoquinoline-based supramolecular liquid crystals have been built, and their mesogenic properties have been introduced or modified by fused-*N*-heterocyclic rings.

In recent years considerable interest in supramolecules has developed, due to the possibility of incorporating diversified molecular designs [1–3]. Significantly, novel mesogenic properties can be obtained from supramolecular architecture (including supramolecular liquid crystals (LCs) and liquid crystalline polymers) through hydrogen bonds between various proton donors and acceptors [4–10]. Among these supramolecular structures, heterocyclic molecules containing nitrogen hetero-atoms, e.g. pyridyl structures, are the most frequently used heterocyclic fragments (hydrogen-bonded acceptors) for the assembly of liquid crystalline complexes through hydrogen bonding. In previous studies, we found that quinoline systems bearing fused-heterocyclic rings may be successfully incorporated into the mesogenic cores to improve the tilted SmC arrangement in their fully-covalent molecular structures [11, 12]. However, very few fused-heterocyclic systems have been used in supramolecular LCs. Recently, we have developed fused-heterocyclic rings containing sulphur hetero-atoms, e.g. the thienothiophene unit, as proton donors in H-bonded cores [13]. Thus, fused-heterocyclic rings similar to the pyridyl unit, containing nitrogen hetero-atoms with lone-pair electrons,

should be feasible as proton acceptors. Equivalent to the covalent application of the quinoline structure to mesogenic cores, the isoquinoline structure is a useful H-bonded acceptor candidate to be used in the H-bonded core. Here, we present a series of novel isoquinoline-based supramolecular liquid crystals making use of *N*-heterocyclic fused ring structures as the H-bonded acceptors.

Until now, the most common rigid cores in supramolecular LCs have been linear structures with aromatic rings hydrogen-bonded through the pyridyl and carboxylic acid moieties. To begin this study, we would like to replace the pyridine group with the isoquinoline unit (*N*-heterocyclic fused ring) so as to investigate the fused-heterocyclic effect on the formation of linear H-bonded structures. In addition, some supramolecular LCs with nonlinear structures were reported to reveal interesting mesomorphic properties and our previous work showed that angular supramolecules containing different bending sites permit the manipulation of the mesomorphic properties of the complexes using angular H-bonded interactions [14, 15]. Nevertheless, the former H-bonded complexes contain only a single hydrogen bond in each system. Consequently, instead of adjusting the relative positions of the proton donor and acceptor moieties, the

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five-membered heterocyclic ring (e.g. thiophene) providing the kinked molecular structure may be complexed into double H-bonded LCs [16].

We have demonstrated the effects of nonlinear structures on the mesomorphism of double H-bonded supramolecules in supplying the benefits of lowered melting temperatures and reduced packing efficiency. Moreover, the other main function is to supply an extra dipole from the lone-pair electrons of the sulphur hetero-atom; the lateral dipole moment originating from the thiophene structure may enhance the negative dielectric anisotropy and reduce the phase transition temperatures of the mesophases. Hence, thiophene heterocyclic rings have been shown to promote the stability of H-bonded mesogenic phases; therefore the double H-bonded trimer containing both thiophene and isoquinoline groups is also investigated. In order to interpret the mesogenic behaviour of H-bonded fused-heterocyclic structures and to visualize the role of the fused-heterocyclic acceptor in the supramolecules, analogous double H-bonded trimer complexes bearing stilbazole, pyridine, and isoquinoline units are compared in this study.

The H-bonded dimer complexes IS-OBA and IS-COOBA were prepared from a mixture (1:1 molar ratio) of 6-dodecyloxyisoquinoline IS (**1**) either with 4-decyloxybenzoic acid OBA (**2**) or with 4-decyloxy-carbonylbenzoic acid COOBA (**3**). The double H-bonded trimer complex (IS)$_2$-THDA was prepared from a mixture (1:2 molar ratio) of 2,5-thiophenedicarboxylic acid THDA (**4**) with IS. All H-bonded acceptor and donor moieties are listed in figure 1, including the previously reported constituents C12PS (**5**) and C12PP (**6**) [16, 17]. The schematic structures of isoquinoline-based complexes IS-OBA, IS-COOBA, and (IS)$_2$-THDA, along with
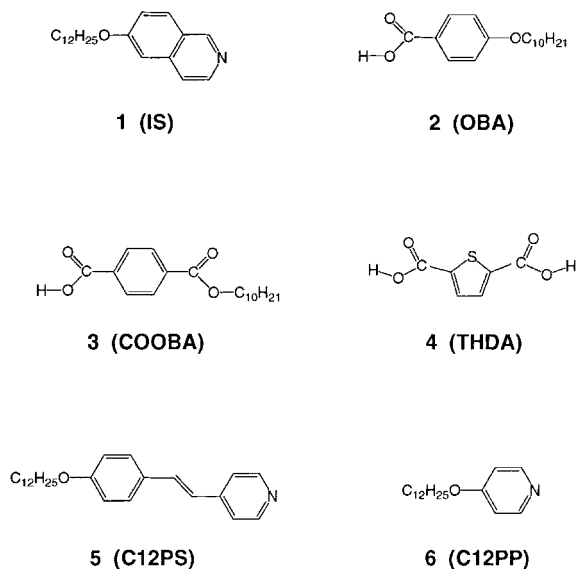

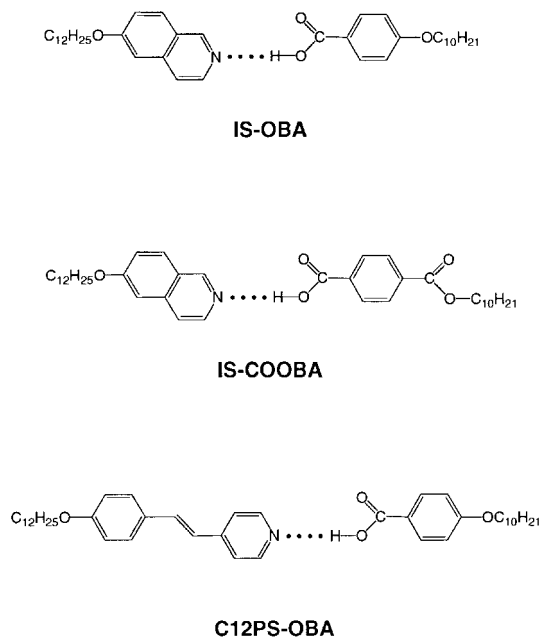Figure 1. Hydrogen-bonded acceptor and donor moieties.

Figure 2. Hydrogen-bonded dimers containing isoquinoline and stilbazole acceptors.

comparable systems, are shown in figures 2 and 3. The thermal behaviour of the H-bonded donors OBA and THDA were reported in our previous publications [14, 16]. However, IS, COOBA and THDA do not show desirable liquid crystallinity (see Appendix). They have isotropization temperatures at 48.1, 113.3, and higher than 300°C, respectively.

Table 1 shows the thermal properties of the H-bonded complexes IS-OBA, IS-COOBA, and (IS)$_2$-THDA. Phase transition temperatures and corresponding enthalpies were determined by the 2nd heating and cooling DSC scans (at heating and cooling rates of 10°C min^{-1}) using a Perkin Elmer DSC-7. The nematic phase was characterized by the schlieren texture coexisting with homeotropic alignment, and the smectic A phase was characterized by the focal-conic fan texture coexisting with homeotropic alignment. All mesophases were characterized by optical microscopy and confirmed by

Table 1. Phase transition temperatures (°C) and corresponding enthalpies (J g^{-1}), in parentheses, of H-bonded dimers IS-OBA and IS-COOBA and the double H-bonded complex (IS)$_2$-THDA.

(a)

(IS)₂ -THDA
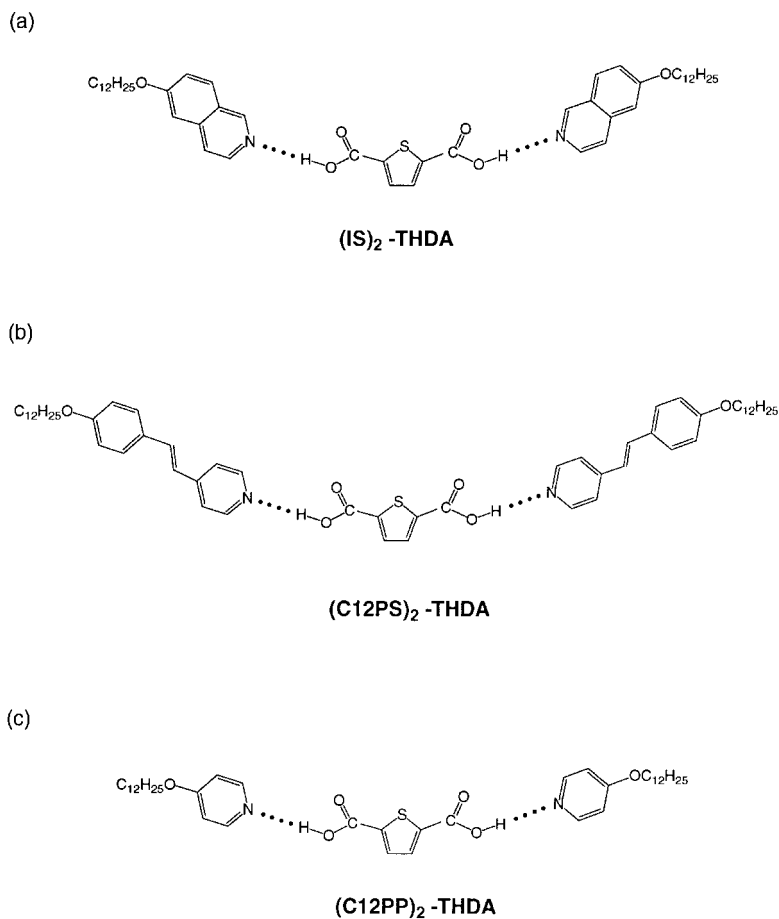
(b)

(C12PS)₂ -THDA

(c)

(C12PP)₂ -THDA

Figure 3.   Schematic drawing of double hydrogen-bonded complexes (*a*) (IS)₂-THDA, (*b*) (C12PS)₂-THDA, and (*c*) (C12PP)₂-THDA prepared from a mixture (2:1 molar ratio) of 6-dodecyloxyisoquinoline, 4-dodecyloxy-4′-stilbazole, or 4-dodecyloxypyridine with 2,5-thiophenedicarboxylic acid (see ref. [16]).

X-ray diffraction (XRD), powder patterns being obtained from a Siemens X-ray diffractometer D-5000 equipped with temperature controller TTK450. These H-bonded complexes all behave differently from their original moieties. For instance, the SmA phase of IS-OBA and IS-COOBA, and the nematic phase of (IS)₂-THDA are generated from non-mesogenic components, except that OBA reveals mesophases containing SmC and nematic phases. The phase behaviour of these complexes implies that the supramolecular structures have been established through H-bonding.

In comparison with the previously reported H-bonded complex C12PS-OBA containing stilbazole unit (see figure 2) [14], both of the H-bonded dimers IS-OBA and IS-COOBA exhibit small ranges of the SmA phase at lower temperatures; however, C12PS-OBA possesses broader ranges of the SmC phase at higher temperatures. This may be because C12PS-OBA has a longer H-bonded rigid core (stilbazole unit) in the complex, in comparison with the shorter isoquinoline unit in complexes IS-OBA and IS-COOBA. However, replacing the

stilbazole unit with the isoquinoline unit IS-OBA gave the SmA phase, instead of the SmC phase shown by C12PS-OBA. The differences in structure between supra-molecular LCs IS-OBA and IS-COOBA are only the ether and ester linking groups of the proton donors, which apparently do not affect the ranges and types of the mesophase. The only influence of the linking groups is to give IS-OBA higher transition temperatures than IS-COOBA.

For the kinked double H-bonded trimers, since the thiophene unit offers good solubility in solvents and good compatibility with proton acceptors, we would like to continue the comparison whilst keeping the central thiophene part in the nonlinear H-bonded complex (IS)₂-THDA. As described, comparing the published results for complexes (C12PS)₂-THDA and (C12PP)₂-THDA (figure 3) [16], the latter possesses only a highly ordered SmX phase due to the shorter rigid core resulting from removal of styryl groups. In addition, (C12PS)₂-THDA possesses SmA and nematic phases, though it exhibits a higher isotropization temperature than (C12PP)₂-THDA.

This indicates that (C12PS)$_2$-THDA, containing a supramolecular rigid core assembled from five single rings through angular H-bonds, has more desirable liquid crystalline properties (SmA and nematic phases) than (C12PP)$_2$-THDA which contains a shorter supramolecular rigid core.

With regard to the double H-bonded complex (IS)$_2$-THDA, possessing two isoquinoline units (N-heterocyclic fused rings) rather than the stilbazole in (C12PS)$_2$-THDA or pyridine groups in (C12PP)$_2$-THDA, this was prepared so as to investigate the influence of the fused-heterocyclic ring structure on the mesogenic properties. The mesogenic properties of these double H-bonded trimers may be affected by the non-linearity and dipole of the molecular architecture, assuming that they all contain 148° kinked H-bonded cores and that the kinks all originate from the thiophene unit in the centre of the double H-bonded structures. Their mesogenic properties suggest that the supramolecular trimer in (C12PS)$_2$-THDA, containing two stilbazole units, has the highest transition temperatures and the widest ranges of the mesophases; however, (C12PP)$_2$-THDA, containing two pyridine units, has the lowest mesophase stability and the lowest isotropization temperature. Importantly, on replacing the two pyridine units of (C12PP)$_2$-THDA with two isoquinoline units to give (IS)$_2$-THDA, (IS)$_2$-THDA still has a similar isotropization temperature to that of (C12PP)$_2$-THDA, i.e. 93.8°C vs. 90.0°C; but the isoquinoline units in (IS)$_2$-THDA have introduced the nematic phase to the isoquinoline-based supramolecular trimer. Therefore, in comparison with (C12PP)$_2$-THDA, the fused-heterocyclic ring (i.e. isoquinoline) structure helps to generate useful liquid crystallinity (nematic phase) and keeps a similar isotropization temperature in (IS)$_2$-THDA.

Table 2 shows the d-spacing values in the SmA phases of complexes IS-OBA and IS-COOBA, obtained from powder XRD patterns. Since the largest values are correlated with the length of the supramolecules, the molecules are orthogonal to the layer in the SmA phase. The lengths of each component calculated by molecular modelling are listed as follows: IS = 20.0 ∼ 23.2 Å, OBA = 19.1 ∼ 20.6 Å, COOBA = 20.2 ∼ 21.8 Å, and THDA = ∼ 8.7 Å; where the former value is the molecular projection length along the rigid core and the latter value is the fully extended molecular length. According to XRD patterns, complexes IS-OBA and IS-COOBA have largest d-spacing values 40.19 Å at 70°C (cooling) and 40.45 Å at 68°C (cooling), respectively. Both IS-OBA and IS-COOBA have similar largest d-spacing values, which are close to the sum (∼ 40 Å) of each component. Hence, they are approximately the same length in their supramolecular configurations, and the d-spacing value of IS-COOBA is a little larger than that of IS-OBA,

Table 2. The d-spacing values of H-bonded complexes IS-OBA and IS-COOBA in the SmA phase obtained from XRD measurements at different temperatures.

Complex		Temperature/°C[a]	d-spacing/Å
IS-OBA	(heating)	82	39.62
		84	39.42
		86	39.33
		88	39.22
	(cooling)	85	39.46
		80	39.68
		75	39.81
		70	40.19
IS-COOBA	(heating)	76	39.77
		78	39.43
	(cooling)	73	40.11
		70	40.15
		68	40.45

[a] All temperatures reported were first measured on a heating scan to the isotropization temperature and then on a cooling scan to room temperature. Small temperature deviations from DSC data may occur due to the annealing effect in XRD measurements.

because the ester linking group in IS-COOBA is longer than the ether linking group in IS-OBA. As with most mesogenic materials, the d-spacing values of the SmA phase in table 2 decrease as the temperature increases. Generally, the d-spacing data match the calculated molecular lengths from molecular modelling, and the XRD results have confirmed their supramolecular structures.

In conclusion, new supramolecular structures are evident from the distinct liquid crystalline properties introduced by H-bonded isoquinoline acceptors. Powder XRD measurements have confirmed their novel molecular architectures. The isoquinoline-based structures supply lone-pair electrons from fused-heterocyclic rings, thereby reducing the phase transition temperatures and improving the solubility of the moieties simultaneously, to form unique supramolecules. More importantly, this study demonstrates the first isoquinoline-based molecular architecture in supramolecular LCs. We have thus demonstrated interesting mesomorphism by the introduction of fused-heterocyclization in proton acceptors. This isoquinoline-based structure containing lone-pair electrons inside the fused-heterocyclic structures may be useful in the further design of supramolecular liquid crystals.

Appendix

Melting temperature of 6-dodecyloxyisoquinoline IS (**1**): m.p. = 48.1°C (enthalpy 124.2 J g^{-1}). Thermal properties of 4-decyloxybenzoic acid OBA (**2**): Heating, Cr 85.1°C (58.9 J g^{-1}) SmX 96.0°C (30.3 J g^{-1}) SmC 123.7°C (4.5 J g^{-1}) N 142.4°C (7.7 J g^{-1}) I; Cooling, I 139.6°C (7.2 J g^{-1}) N 120.5°C (4.3 J g^{-1}) SmC 90.2°C (31.1 J g^{-1}) SmX 69.4°C (21.5 J g^{-1}) Cr. Thermal properties of 4-decyloxycarbonylbenzoic acid COOBA (**3**): Heating, Cr 69.0°C (31.7 J g^{-1}) SmX 113.3°C (97.0 J g^{-1}) I; Cooling, I 104.7°C (90.4 J g^{-1}) SmX 41.3°C (25.5 J g^{-1}) Cr. Melting temperature of 2,5-thiophenedicarboxylic acid THDA (**4**): m.p. > 300°C. Abbreviations: Cr = the crystalline phase, SmC = the smectic C phase, SmX = the smectic X phase, N = the nematic phase, I = the isotropic liquid.

H-bonded complexes were prepared by slow evaporation from THF solution containing mixtures of a 1:2 molar ratio of the H-bonded donor and acceptor moieties, followed by drying *in vacuo* at 60°C. The synthesis of proton donor OBA was described before [14]; it was identified as the required material and judged to be pure by ^{1}H and ^{13}C NMR spectroscopy and elementary analysis. The proton donor THDA was used as received from Aldrich. The syntheses of proton acceptor and donor moieties are described below.

The synthetic route for *6-dodecyloxyisoquinoline* IS (**1**) was followed as described in the literature [18]. A solution of 4-hydroxybenzaldehyde (6.1 g, 50 mmol), potassium hydroxide (7.0 g, 125 mmol), and 1-bromo-dodecane (32.2 g, 125 mmol) in 50 ml of EtOH/H$_2$O (9/1) was heated under reflux for 24 h. After reaction, the precipitate was filtered and the solution concentrated at reduced pressure. The residue was mixed with water and extracted with CH$_2$Cl$_2$. The organic layer was dried with MgSO$_4$ and concentrated at reduced pressure. The crude product was purified by column chromatography on silica gel, using EtOAc/hexane (1/10) as eluent to give a pale yellow solid in 70% yield (10.2 g). A benzene (50 ml) solution of equimolar amounts of 4-dodecyloxy-benzaldehyde (7.1 g, 37.5 mmol) and aminoacetaldehyde dimethyl acetal (3.9 g, 37.5 mmol) was heated under reflux overnight using a Dean–Stark trap to remove water. The solution was evaporated *in vacuo* and then evaporated twice further with added benzene; the viscous residue was dissolved in dry THF. This solution was cooled to − 10°C and 1 equiv of ethyl chloroformate (4.1 g, 37.5 mmol) was added with rapid stirring; the mixture was further stirred for more than 5 min. The cooling bath was removed and 1.2 equiv of trimethyl phosphite (5.6 g, 45 mmol) was added with stirring. The solution was allowed to stir at room temperature for 15 h and then evaporated to an oily state. The residue was then re-evaporated twice with added toluene to

remove traces of trimethyl phosphite. The oily residue was dissolved in dry CH$_2$Cl$_2$, 6 equiv of titanium tetra-chloride (24 ml, 225 mmol) was added, and the solution heated under reflux for 36 h using a drying tube. The cooled solution was shaken with 1 equiv of aqueous NaOH to neutralize, whereupon TiO$_2$ precipitated as a white solid. The filtrate was extracted with 3N HCl, and the extract washed with CH$_2$Cl$_2$. This extract was further basified with aqueous alkali, and extracted again with CH$_2$Cl$_2$. Further treatment of the extract was followed by drying with MgSO$_4$ and then by evaporation of the organic phase. The crude product was purified by column chromatography on silica gel, using EtOAc/hexane (1/5) as eluent to give a yellow solid in 2.7% yield (0.32 g). 6-Dodecyloxyisoquinoline was identified as the resulting product and judged to be pure by ^{1}H and ^{13}C NMR spectroscopy. Elemental analytical results for C, H, and N were also satisfactory. ^{1}H NMR δ(CDCl$_3$): 0.88 (t, 3H, $J = 6.8$ Hz, CH$_3$), 1.27–1.51 (m, 18H, $9 \times$ CH$_2$), 1.81–1.90 (m, 2H, CH$_2$), 4.08 (t, 2H, $J = 6.4$ Hz, OCH$_2$), 7.03 (s, 1H, Ar-H), 7.22 (d, 1H, $J = 9.0$ Hz, Ar-H), 7.52 (d, 1H, $J = 5.6$ Hz, Ar-H), 7.84 (d, 1H, $J = 9.0$ Hz, Ar-H), 8.42 (d, 1H, $J = 5.6$ Hz, Ar-H), 9.09 (s, 1H, Ar-H). ^{13}C NMR δ(CDCl$_3$): 14.1, 22.7, 26.0, 29.0, 29.3, 29.5, 29.6, 31.9, 68.2, 104.5, 119.7, 120.6, 124.4, 129.2, 137.7, 143.4, 151.5, 160.4. Elemental analysis for C$_{21}$H$_{31}$NO: calculated, C 80.5, H 10.0, N 4.5; found, C 79.93, H 9.94, N 4.20%.

For the synthesis of *4-decyloxycarbonylbenzoic acid* COOBA (**3**), a solution of terephthalic acid (2.00 g, 12.0 mmol), 4-dimethylaminopyridine (0.15 g, 1.2 mmol), *N*,*N*-dicyclohexylcarbodiimide (2.48 g, 12.0 mmol), and decanol (1.90 g, 12.0 mmol) in pyridine (100 ml) was stirred at room temperature for 24 h. The precipitated solid was filtered and washed with ethyl acetate, and the combined solution concentrated at reduced pressure. The crude product was purified by column chromato-graphy on silica gel, using EtOAc/hexane (1/20) as eluent to give a white solid in 9% yield. 4-Decyloxy-carbonylbenzoic acid was identified as the required product and judged to be pure by ^{1}H and ^{13}C NMR spectroscopy. Elemental analytical results for C, H, and N were all satisfactory. ^{1}H NMR δ (CDCl$_3$): 0.88 (t, 3H, $J = 6.6$ Hz, CH$_3$), 1.27–1.47 (m, 14H, $7 \times$ CH$_2$), 1.74–1.84 (m, 2H, CH$_2$), 4.36 (t, 2H, $J = 6.6$ Hz, OCH$_2$), 8.12–8.20 (m, 4H, Ar-H). ^{13}C NMR δ (CDCl$_3$): 14.0, 22.6, 25.9, 28.6, 29.2, 29.5, 30.9, 31.8, 33.5, 65.7, 129.5, 130.0, 133.2, 134.8, 165.8, 170.5. Elemental analysis for C$_{18}$H$_{26}$O$_4$: calculated, C 70.56, H 8.55; found C 70.46, H 8.72%.

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