Effects of reducing structural symmetry on mesophase behaviour: the synthesis and characterization of the 2-alkoxy-6-[4-(4-alkoxyphenyl)buta-1,3-diynyl]naphthalenes

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Unsymmetrical 2-alkoxy-6-[4-(4-alkoxyphenyl)buta-1,3-diynyl]naphthalenes were synthesized and their mesomorphic properties studied. In addition to an increase the mesophase temperature range of $10°C$, the melting temperatures are significantly lower while there is a less pronounced decrease in the clearing temperatures when compared with those of the symmetrical 1,4-bis(6-alkoxy-2-naphthyl)butadiynes. Further reducing the symmetry by introducing the two terminal chains of unequal length shows little effect on the mesogenic properties. Shortening the linker from a butadiynyne unit to an ethyne unit significantly reduces the overall mesophase and nematic temperature ranges but the smectic range markedly increases.

1. Introduction

Controlling mesophase transition temperatures has always been an important issue in liquid crystal materials research. Varying the length of alkyl chains has often been used as an easy and systematic way by which to understand trends in phase transition temperatures [1]. However, many other structural factors can also be manipulated in order to adjust the melting and clearing temperatures as well as the mesophase temperature ranges. Examples include, the introduction of terminal [2] or lateral [3] fluorine-containing units, the introduction of double bonds into the terminal chains [4], and the introduction of a cyano group [5]; each of these approaches has been shown to exert a great impact on transition temperatures as well as on mesogenic properties.

Symmetry lowering has also played an important role in controlling the transition temperatures and temperature ranges of liquid crystals [6, 7]. For example, introducing side chains of different lengths, and the attachment of more than six side chains to a triphenylene core, have been shown to be effective ways of manipulating liquid crystal properties [8].

Previously, we reported the liquid crystalline materials, the 1,4-bis(6-alkoxyl-2-naphthyl)-1,3-butadiynes, to probe the effects of the terminal chains on the mesophase transition temperatures when compa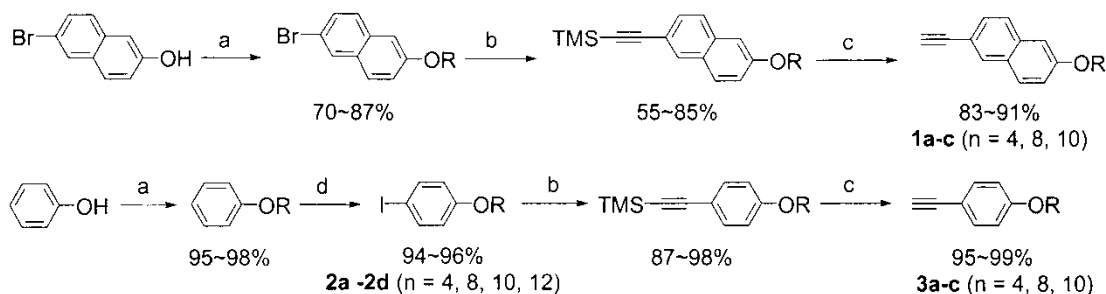red with those of the analogous compound without chains [9]. The naphthyl and ethynyl groups have been reported to show high optical anisotropy [10–15], which is an important characteristic for additives in mixtures of liquid crystal materials for displays. Here, the synthesis of the unsymmetric series, the 2-alkoxy-6-[4-(4-alkoxyphenyl)buta-1,3-diynyl]naphthalenes, is reported and the mesomorphic properties of these compounds compared with those of the symmetric systems, i.e. the bis-naphthyl and the bis-phenyl compounds. A further symmetry lowering by incorporating differing terminal chains is also achieved and its effect on liquid crystal behaviour is discussed. In addition, the butadiyne linker is shortened to an ethyne unit to investigate its effect on the ratio of the nematic/smectic temperature ranges.

2. Results and discussion

Scheme 1 outlines the syntheses of the two ethyne-containing fragments that are used to assemble the final unsymmetric mesogens. The naphthyl-containing-compounds, **1a–c**, were obtained from 2-bromo-6-alkoxynaphthalene. The ethyne group was introduced by the coupling of trimethylsilylacetylene using Sonogashira conditions followed by desilylation using K_2CO_3 in methanol. The analogous phenyl-containing compounds **3a–c**, were prepared from phenol by sequential alkylation, iodination, acetylene coupling, and desilylation.

As shown in scheme 2, the coupling of the naphthyl fragments, **1a–c**, with the phenyl fragments, **3a–c**, was carried out in the presence of copper acetate to afford

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Br—[naphthalene]—OH →(a) Br—[naphthalene]—OR →(b) TMS≡≡—[naphthalene]—OR →(c) ≡—[naphthalene]—OR

70~87%   55~85%   83~91%
                                                     1a-c (n = 4, 8, 10)

[benzene]—OH →(a) [benzene]—OR →(d) I—[benzene]—OR →(b) TMS≡≡—[benzene]—OR →(c) ≡—[benzene]—OR

95~98%   94~96%   87~98%   95~99%
                2a -2d (n = 4, 8, 10, 12)   **3a-c** (n = 4, 8, 10)

Scheme 1. Synthesis of the two ends **1a–1c** and **3a–3c**: (a) RBr, K$_2$CO$_3$, KI, butanone; (b) Pd(PPh$_3$)$_4$, PPh$_3$, CuI, TMSA, piperidine; (c) K$_2$CO$_3$, MeOH; (d) I$_2$, Pb(OAc)$_4$, glacial acetic acid.

1 + 3 →(a) RO—[benzene]≡≡—[naphthalene]—OR

4a n = 4, 8%
4b n = 8, 14%
4c n = 10, 21%

1c + 3d →(a) C$_{12}$H$_{25}$O—[benzene]≡≡—[naphthalene]—OC$_{10}$H$_{21}$

5, 46%

1c + 2c →(b) C$_{10}$H$_{21}$O—[benzene]≡—[naphthalene]—OC$_{10}$H$_{21}$

6, 63%
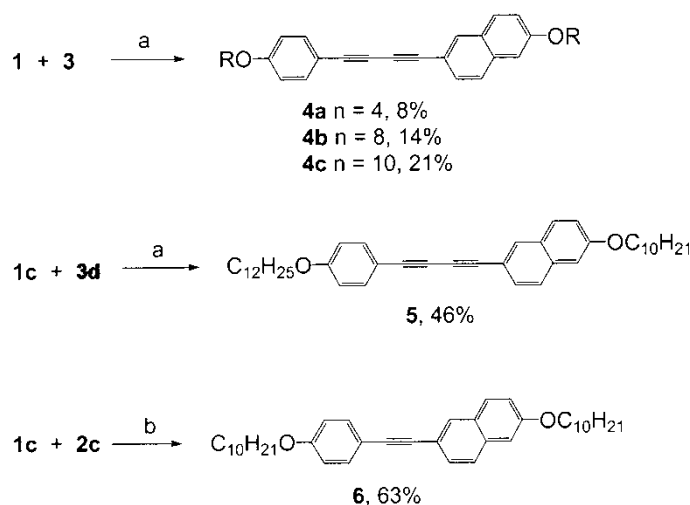
Scheme 2. Synthesis of compounds of **4a–4c**, **5**, and **6**: (a) Cu(OAc)$_2$, pyridine/MeOH(1/1); (b) Pd(PPh$_3$)$_4$, CuI, piperidine.

the butadiynyl compounds, **4a–c** and **5**. Under the same conditions, each fragment can also self-couple to form the respective dimers. The low yields of 8, 14, and 21% for **4a**, **4b**, and **4c**, respectively, are attributed to these accompanying self-coupling reactions. It is noted that the yields increased with increasing chain lengths. On increasing chain length, the solubilities of the naphthyl-containing moieties increase—both of the target compound and the self-coupling product, —and this gives the increased-yields. Compound **6**, the ethynyl analogue of **4c**, was prepared by the direct coupling of **1c** with 4-decyloxyl-2-bromobenzene, **2c**.

The mesogenic behaviour of **4a–c**, **5**, and **6** was investigated by polarizing optical microscopy (POM). On cooling from the isotropic melt, the compounds with shorter terminal chains, **4a** and **4b**, exhibited typical nematic schlieren or marbled textures before crystallizing. For compounds with longer terminal chains, of **4c** and **5**, cooling the nematic phase resulted in an additional smectic C phase. For compound **6** with one less ethyne unit than **4c**, both the nematic and lamellar mesophases are retained.

The thermal data for **4a–c**, **5**, and **6** measured by differential scanning calorimetry (DSC) are summarized in the table. All compounds exhibited enantiotropic mesophases based on POM and DSC investigations.

The dependence of the transition temperatures on the total chain length can be seen by comparing compounds **4a–c** in which the two terminal chains are of the same length. While both the melting and clearing temperatures fall with increasing chain length, the reduction of the clearing temperatures is more significant. For the shortest chain, compound **4a**, the widest mesophase range, 114°C, was seen. Increasing the chain length decreases the temperature range and compound **4c**, with decyloxyl chains, shows the smallest mesophase range, 77°C.

Further symmetry lowering, by introducing two chains of different lengths as in **5**, appears to stabilize the mesophase range when compared with **4c**. Compound **5** has a longer total chain length by an extra ethyl unit than **4c**, therefore its transition temperatures are expected to be lower and its mesophase range should be smaller. Interestingly, **4c** and **5** not only

Table. Phase behaviour of compounds **4a–4c**, **5**, and **6**. Transition temperatures (°C) and enthalpies (in parentheses/kJ mol^{-1}) were determined by DSC at 10°C min^{-1}. Cr, Cr1, Cr2, crystalline phases; SmC, smectic C; N, nematic; I, isotropic.

Compound	Phase transitions
4a	Cr1 ⇌ [106.0 (29.7) / 94.0 (21.8)] Cr2 → 110.9 (0.8) N ⇌ [225.4 (5.4) / 206.8 (0.4)] I (partial decomposition)
4b	Cr1 ⇌ [84.9 (35.4) / 63.4 (11.5)] Cr2 ⇌ 66.4 (17.5) N ⇌ [172.5 (3.2) / 171.7 (2.8)] I
4c	Cr ⇌ [76.0 (23.8) / 64.5 (15.6)] SmC ⇌ [85.9 (0.7) / 85.1 (0.7)] N ⇌ [153.1 (2.4) / 152.7 (2.3)] I
5	Cr ⇌ [73.9 (16.6) / 68.9 (16.1)] SmC ⇌ [105.08 (1.3) / 103.72 (1.1)] N ⇌ [151.6 (2.6) / 150.5 (2.3)] I
6	Cr1 ⇌ [87.1[a] / 64.6 (24.4)] Cr2 ⇌ [91.8[a] / 81.1 (9.2)] SmC ⇌ [110.9 (0.9) / 110.3 (0.8)] N ⇌ [140.1 (2.3) / 139.3 (2.1)] I

[a]The peaks at 87.1 and 91.8°C are overlapped.

showed a similar mesophase range but also similar melting and clearing points. The most pronounced difference between these two compounds is the smectic phase range. The unequal chain lengths do not appear to disrupt the lamellar structure; indeed, a much wider smectic range is found for compound **5**. This may be attributed to the introduction of similar total lengths of the phenyl and naphthyl fragments due to the extra ethyl unit on the phenyl end.

The influence on the thermal behaviour of replacing one of the naphthyl units in **7**, 1,4-bis(4-alkoxyl-2-naphthyl)-1,3-butadiyne, with a phenyl unit is shown in the figure. Compared with series **7** compounds, series **4** compounds show only a moderate increase in the overall mesophase ranges, 12–16°C. However, for compounds **4c** and **7c**, both of which show the nematic and smectic phases, the ranges of the two phases are very different. A 37°C increase in the nematic range accompanied by a 25°C suppression of the smectic range are found for **4c** when compared with **7c**. The resulting nematic/smectic range ratio for the unsymmetric system was increased by more than seven times. The suppression of the lamellar structure for the unsymmetric system may be attributed to the packing frustration associated with the different sizes of the two ends of the molecule. Most importantly, both the melting and clearing points for the unsymmetric series **4** compounds were significantly lower than those of the symmetric series **7** compounds. Compared with the symmetric series **7** compounds, the unsymmetric series **4** compounds show on average a 50°C lower melting

point. Less pronounced but still significant, is the almost uniform decrease in the clearing points by 39°C for the unsymmetric system. It should be noted that the replacement of a naphthalene ring with a phenyl ring not only lowers the symmetry but also reduces the size of the core. By lowering the symmetry, the interactions between the cores may be reduced by disrupting the packing arrangement, which results in lower transition temperatures. In addition, the weaker core–core interactions arising from the smaller cores will also lower the transition temperatures.

The thermal data of compounds **4c** and **6** reveal the effect of the length of the linker on liquid crystal behaviour. One less ethyne unit has resulted in a 29°C reduction of the overall mesophase range. In addition to the reduction in the total mesophase range, the shortening of the linker has also caused a 38°C reduction in the nematic range but a 10°C increase in the smectic range.

Replacing the naphthyl unit with a phenyl unit in **4a–c** gives the 1,4-bis(4-alkoxyl-2-phenyl)-1,3-butadiynes (**8**) reported by Grant [16]. Comparing these two series of compounds, compounds **4a–c** show much wider mesophase temperature ranges resulting from significantly lower melting points and much higher clearing points. The most pronounced difference was found for the C4 homologues. Thus, compared with 1,4-bis(4-butyloxy-2-phenyl)-1,3-butadiyne, compound **4a** showed a 43°C lower melting point, a 49°C higher clearing point, and a 93°C under mesophase range. For the C10 homologues, compound **4c** exhibited a 24°C
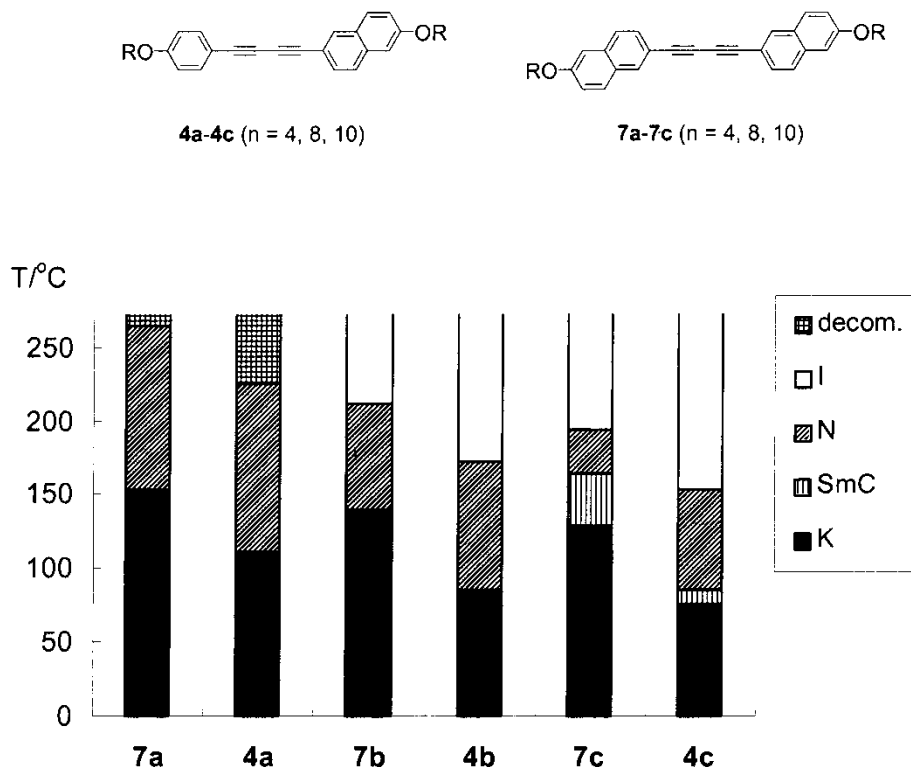
4a-4c (n = 4, 8, 10)   **7a-7c** (n = 4, 8, 10)

Figure.   Comparison of thermal data for the unsymmetrical compounds of **4a–4c** and the symmetrical compounds of **7a–7c**.

lower melting point, a 26°C higher clearing point, and a 50°C wider mesophase range. An additional lamellar phase was found for **4c**. The differences in transition temperatures and mesophase ranges are more pronounced between **4** and **8** than between **4** and **7**. Besides the symmetry effect, the differences in the relative core sizes are also responsible for the differences in mesophase properties. The larger difference in relative core sizes between compounds **4** and **8** is expected to cause more significant changes in transition temperatures and mesophase ranges, and these are observed.

3.   Summary and conclusion

The replacement of one naphthalene ring in 1,4-bis(6-alkoxyl-2-naphthyl)-1,3-butadiyne with a phenyl ring was accompanied by a moderate increase in the mesophase temperature ranges but pronounced decreases in the transition temperatures. The decrease of the core size as well as the unsymmetric structure of the core were considered to be responsible for these results. A further lowering of the symmetry by introducing unequal chain lengths to the two ends of the molecules appears to widen the mesophase range, giving a larger lamellar range. Finally, relative to the ethynyl linker, the longer butadiynyl linker gave wider

mesophase ranges although the smectic phase range was greatly suppressed.

4.   Experimental
4.1.   *General*

All chemicals and solvents were reagent grades (Aldrich Chemical Co.) and were used without further purification. Compounds **1**, **2**, **3**, and **6** were synthesized following literature procedures [17, 18]. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer. Chemical shifts are reported in ppm relative to residual $CHCl_3$ ($\delta = 7.24$, ^{1}H; 77.0, ^{13}C). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Differential scanning calorimetry was performed on a Perkin-Elmer Pyris1 instrument with heating and cooling rates of 5–10°C min^{-1}. Optical microscopy was carried out on a Nikon Eclipse E600 POL with a Mettler FP90/FP82HT hot stage system. Mass spectra were obtained on a Finnigan MAT-95XL. Elemental analyses were carried out on a Heraeus CHN-O-Rapid Analyzer.

4.2.   *Synthesis of 2-alkoxy-6-[4-(4-alkoxyphenyl)buta-1,3-diynyl]naphthalenes (4a–c, 5)*

To a 100 ml Schlenk flask fitted with a condenser and a nitrogen inlet, and containing pyridine/methanol (1/1,

40 ml), was added **1** (1.60 mmol), **3** (1.92 mmol), and copper acetate (1.51 mmol); the mixture was heated at reflux for 18 h. The reaction mixture was filtered and the filtrate dried under reduced pressure. The product was purified by column chromatography (SiO$_2$, hexanes/chloroform 9/1) and was recrystallized from methanol/hexanes to afford white crystals of the respective butadiynyl product.

4a: yield 8%, white crystals. ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.97 (s, 1H), 7.69 (d, $J = 9.0$ Hz, 1H), 7.65 (d, $J = 8.6$ Hz, 1H), 7.47 (m, 3H), 7.16 (dd, $J = 9.0$ Hz, 2.4 Hz, 1H), 7.09 (d, $J = 2.4$ Hz, 1H), 6.84 (d, $J = 8.7$ Hz, 2H), 4.09 (t, $J = 6.5$ Hz, 2H), 3.98 (t, $J = 6.5$ Hz, 2H), 1.8 (m, 4H), 1.52 (m, 4H), 0.99 (m, 6H). ^{13}C NMR (CDCl$_3$, 75 MHz) δ 159.9, 158.2, 134.6, 134.1, 132.6, 129.3, 129.1, 128.2, 126.9, 119.9, 116.6, 114.7, 113.6, 106.6, 81.8, 73.9, 72.9, 67.8, 31.24, 31.18, 19.3, 19.2, 13.84, 13.79. HRMS (EI) calcd for C$_{28}$H$_{28}$O$_2$ 396.2089, found 396.2089. Anal: calcd for C$_{28}$H$_{28}$O$_2$ C 84.81, H 7.12; found C 84.93, H 7.18%.

4b: yield 14%, white crystals. ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.97 (s, 1H), 7.68 (d, $J = 9.0$ Hz, 1H), 7.64 (d, $J = 8.6$ Hz, 1H), 7.47 (m, 3H), 7.16 (dd, $J = 9.0$ Hz, 2.4 Hz, 1H), 7.09 (d, $J = 2.4$ Hz, 1H), 6.85 (d, $J = 8.8$ Hz, 2H), 4.07 (t, $J = 6.6$ Hz, 2H), 3.96 (t, $J = 6.5$ Hz, 2H), 1.82 (m, 4H), 1.46 (m, 4H), 1.30 (m, 16H), 0.90 (t, $J = 6.6$ Hz, 6H). ^{13}C NMR (CDCl$_3$, 75 MHz) δ 159.9, 158.2, 134.6, 134.1, 132.6, 129.3, 129.1, 128.2, 126.9, 119.9, 116.6, 114.7, 113.6, 106.6, 81.8, 73.9, 73.0, 68.2, 31.8, 29.4, 29.3, 29.21, 29.15, 26.1, 26.0, 22.7, 14.1. HRMS (EI) calcd for C$_{36}$H$_{44}$O$_2$ 508.3341, found 508.3347. Anal: calcd for C$_{36}$H$_{44}$O$_2$ C 84.99, H 8.72; found C 84.86, H 8.79%.

4c: yield 21%, white crystals. ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.96 (s, 1H), 7.68 (d, $J = 9.0$ Hz, 1H), 7.64 (d, $J = 8.6$ Hz, 1H), 7.48 (m, 3H), 7.16 (dd, $J = 9.0$ Hz, 2.3 Hz, 1H), 7.09 (d, $J = 2.3$ Hz, 1H), 6.85 (d, $J = 8.8$ Hz, 2H), 4.07 (t, $J = 6.6$ Hz, 2H), 3.96 (t, $J = 6.6$ Hz, 2H), 1.81 (m, 4H), 1.48 (m, 4H), 1.29 (m, 24H), 0.90 (t, $J = 6.6$ Hz, 6H). ^{13}C NMR (CDCl$_3$, 75 MHz) δ 159.9, 158.2, 134.6, 134.1, 132.6, 129.3, 129.1, 128.3, 126.9, 119.9, 116.6, 114.7, 113.6, 106.6, 81.8, 73.9, 73.0, 68.2, 31.9, 29.6, 29.40, 29.36, 29.31, 29.19, 29.15, 26.1, 26.0, 22.7, 14.1. HRMS (EI) calcd for C$_{40}$H$_{52}$O$_2$ 564.3967, found 564.3967. Anal: calcd for C$_{40}$H$_{52}$O$_2$ C 85.06, H 9.28; found C 85.08, H 9.56%.

5: yield 46%, white crystals. ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.97 (s, 1H), 7.68 (d, $J = 9.0$ Hz, 1H), 7.64 (d, $J = 8.6$ Hz, 1H), 7.48 (m, 3H), 7.16 (dd, $J = 9.0$ Hz, 2.3 Hz, 1H), 7.09 (d, $J = 2.3$ Hz, 1H), 6.85 (d, $J = 8.8$ Hz, 2H), 4.07 (t, $J = 6.6$ Hz, 2H), 3.96 (t, $J = 6.6$ Hz, 2H), 1.82 (m, 4H), 1.48 (m, 4H), 1.28 (m, 28H), 0.89 (m, $J = 6.7$ Hz, 6H). ^{13}C NMR (CDCl$_3$, 75 MHz) δ 159.9, 158.2, 134.6, 134.1, 132.6, 129.3, 129.1, 128.3, 126.9,

119.9, 116.7, 114.7, 113.6, 106.7, 81.8, 73.9, 73.0, 68.2, 31.9, 29.63, 29.57, 29.4, 29.3, 29.19, 29.15, 26.1, 26.0, 22.7, 14.1. HRMS (EI) calcd for C$_{42}$H$_{56}$O$_2$ 592.4280, found 592.4276. Anal: calcd for C$_{42}$H$_{56}$O$_2$ C 85.08, H 9.52; found C 84.85, H 9.46%.

4.3. *Synthesis of 2-decyloxy-6-(4-decyloxyphenylethynyl)naphthalene (6)*

To a 100 ml Schlenk flask fitted with a condenser and nitrogen inlet, and containing piperidine (30 ml), was added **1c** (139 mg, 0.45 mmol), **2c** (110 mg, 0.45 mmol), copper(I) iodide (13 mg, 0.045 mmol), and tetrakis(triphenylphosphine)palladium(0) (20 mg, 0.017 mmol). The reaction mixture was heated at 80°C for 14 h. After cooling to room temperature, dichloromethane (30 ml) was added and the mixture was washed with aqueous NH$_4$Cl (50 ml × 2) and H$_2$O (50 ml × 2). The collected organic layer was dried with MgSO$_4$ and purified by column chromatography (SiO$_2$, hexanes/chloroform 8/1); it was recrystallized from methanol/hexanes to afford white crystals of **6** (152 mg, 0.28 mmol, 63%). ^{1}H NMR(CDCl$_3$, 300 MHz) δ 7.93 (s, H), 7.48 (d, $J = 2.4$ Hz, 2H), 7.09 (d, $J = 2.4$ Hz, H), 6.87 (d, $J = 8.7$ Hz, 2H). ^{13}C NMR (CDCl$_3$, 75 MHz) δ 159.1, 157.7, 134.0, 132.9, 130.8, 129.0, 126.7, 119.9, 118.4, 115.3, 114.5, 106.6, 88.7.

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