

# Synthesis and Characterization of 5,10-Bis(2-thienyl)indeno[2,1-*a*]indene Derivatives: The First Examples of Conducting Polymers Containing a Rigid Bis(thienyl)butadiene Core

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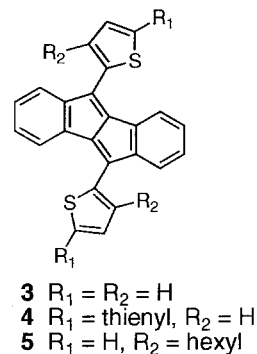
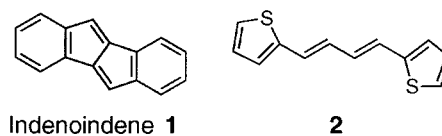
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During the past few decades, thiophene-based conducting polymers have become popular objects of research due to their inherent electronic and optical properties, as well as their environmental stability.<sup>1–3</sup> To reduce the polymer band gap ( $E_g$ ), which is a key criterion for favorable electronic properties, much work has been done in altering the structure of the precursors.<sup>4–7</sup> In this regard, maintaining the least deviation from planarity of these conjugated polymers is one of the fundamental factors in achieving a low band gap.<sup>3</sup> Recent studies in this direction have shown that the insertion of olefinic spacers between thiophene units not only improves effective conjugation across the extended structure, but also results in a reduction of band gap values as compared to those of polythiophene.<sup>8</sup> However, the insertion of more than a single vinyl unit was limited by the lack of thermal stability and deviations from planarity caused by the mutual twisting of the olefinic subunits in bis(thienyl)polyenes.<sup>9,10</sup>

In this paper we report the first examples of a rigid bis(thienyl)butadiene, namely 5,10-bis(2-thienyl)indeno[2,1-*a*]indene **3** and its derivatives **4** and **5**, which contain a ladder-type  $\pi$ -conjugated moiety. Indenoindene **1**, inserted between thiophene rings, was aimed at increasing thermal stability while eliminating the undesired twisting of the unsaturated subunits of the central bis(thienyl)butadiene.



The key starting material, dihydroindeno[2,1-*a*]indene-dione **10**,<sup>11</sup> containing the basic indenoindene skeleton, was prepared according to known procedures from benzaldehyde **6** and benzyl cyanide **7**, to give 2,3-diphenylsuccinonitrile **8**.<sup>12</sup> Hydrolysis gave 2,3-diphenylsuccinic acid **9**,<sup>11b,13</sup> which was cyclized with sulfuric acid to yield diketone **10** (Scheme 1). The first target molecule **3** was then prepared by the action of the 2-thienyl Grignard reagent on the diketone **10**, followed by acid dehydration of the alcohol intermediate to give **3** in high yield (86%). Additionally, an extended oligomer **4** was prepared through the reaction of diketone **10** with 2-lithiated  $\alpha, \alpha'$ -bithiophene.

To increase the solubility of **3**, the grafting of a solubilizing alkyl chain onto the  $\beta$ -position of the thiophene was studied. Ketone **6** was thus reacted with the known 3-*n*-hexyl-2-thienyl Grignard reagent.<sup>14</sup> The dehydration step with HCl/MeOH, however, resulted in the formation of a significant amount of the unexpected methoxy compound **11** along with **5**. The formation of **11** suggested that this product resulted from the reaction between MeOH and a monoketone under acidic conditions. Attempts to avoid the formation of the methoxy compound **11** were unsuccessful.

Alkylated compound **5** did show a significant enhancement in solubility over compound **3**.

Comparison of the electronic absorption spectra of the rigid **3** with that of the analogous compound 1,4-bis(2-thienyl)buta-1,3-diene **2**, which has a similar structure without the annulated benzene rings, showed a considerable extension of conjugation in the rigidified system. This was indicated by a bathochromic shift of 126 nm. Further increase in the length of the conjugated spacer as in **4** led to an enhanced bathochromic shift. Thus, for **4**,  $\lambda_{\text{max}}$  reached a value of 514 nm compared to 474 nm for **3**. The introduction of the alkyl chains at the  $\beta$ -positions of the thiophene units of **5** had a modest influence

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Scheme 1

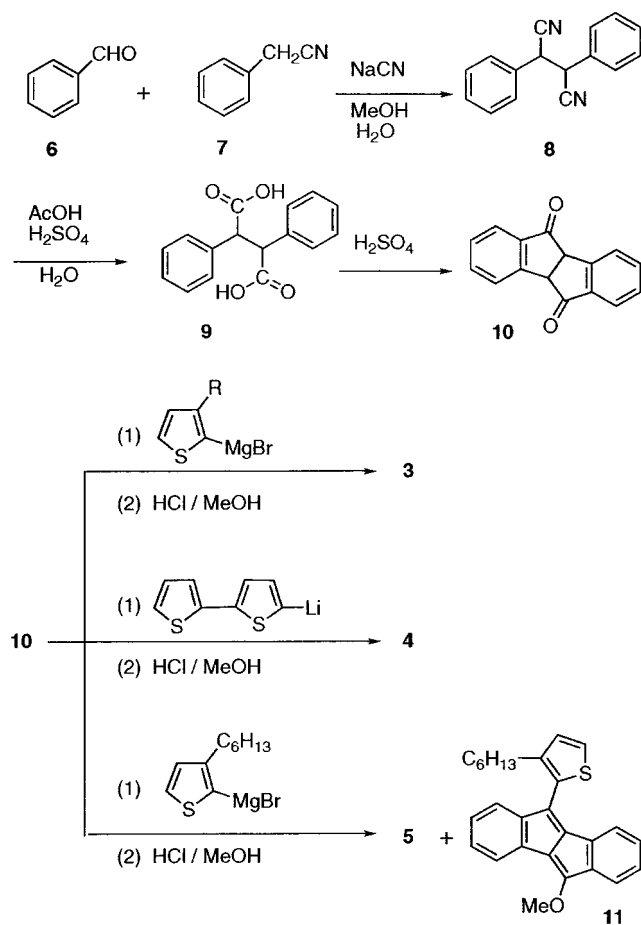
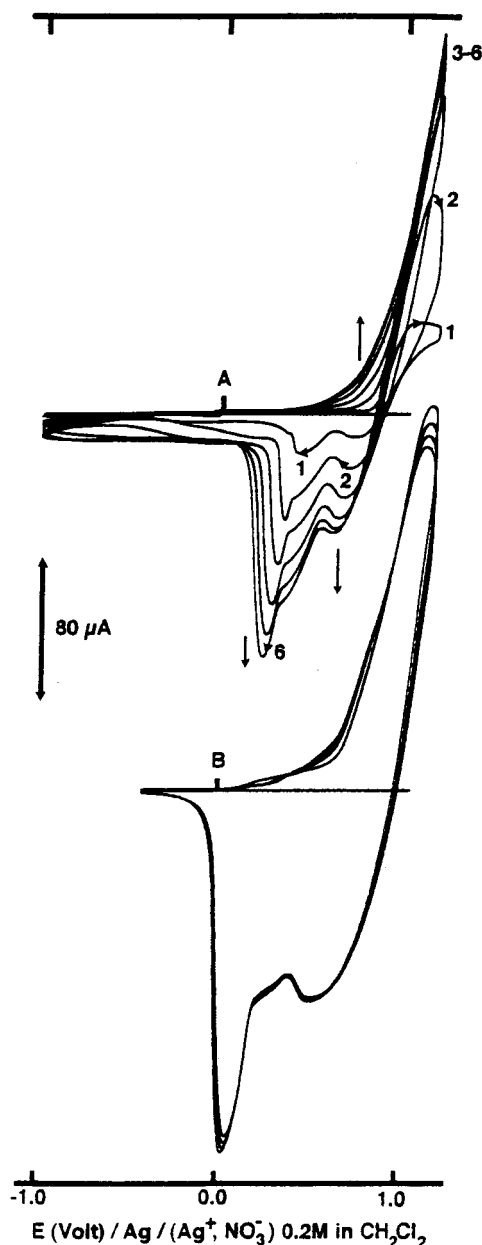


Table 1. CV and UV-Visible Data for Compounds 2–5

compound	$E_{pa1}$ (V)	$E_{pa2}$ (V)	$\lambda_{max}$ (nm)
3	1.29	1.62	474
4	1.05	1.27	514
5	1.45	1.72	454
2	1.01	—	348

on the electronic structure of the  $\pi$ -conjugated system, since some steric hindrance to planarity induced by the hexyl chains lowered the  $\lambda_{max}$  to 454 nm from 474 nm. (Table 1)

**Electrochemical Studies.** A preliminary cyclic voltammetric (CV) analysis of **3**, **4** and **5** as well as **2**<sup>15</sup> was carried out in dichloromethane solution containing 0.1 M tetrabutylammonium hexafluorophosphate, using standard calomel electrode as the reference electrode (Table 1). In the case of **3** and **4**, film formation on the working electrode (Pt disk) was discernible. However, the redox behavior of the polymeric films was erratic from experiment to experiment. Therefore, a more detailed study was carried out on the more abundant **3**. The CV of **3** was carried out in dichloromethane containing 0.2 M tetrabu-



**Figure 1.** (A) Cyclic voltammogram of a  $10^{-2}$  M solution of **3** in 0.2 M  $\text{Bu}_4\text{NBF}_4$  in  $\text{CH}_2\text{Cl}_2$ . Initial potential:  $-1.0$  V, switching potential: 1.2 V, six recurrent sweeps. (B) Study of the deposit formed in (A) in 0.2 M  $\text{Bu}_4\text{NBF}_4$  in  $\text{CH}_2\text{Cl}_2$ . Initial potential:  $-0.2$  V, switching potential: 1.2 V four recurrent sweeps. Scan rate:  $100 \text{ mV s}^{-2}$ . Working electrode: platinum disk diameter 1 mm.

tylammonium tetrafluoroborate, using  $\text{Ag}(\text{Ag}^+\text{NO}_3^- 0.2 \text{ M in } \text{CH}_2\text{Cl}_2)$  reference electrode, a platinum working electrode, and a vitreous carbon counter electrode in a separate compartment. Upon scanning between  $-1.0$  and  $2.0$  V (not shown), an oxidation peak at 1.08 V was observed, recurrent sweeps in this potential range showing a regular decrease of the current leading up to total passivation of the electrode surface at the fifth sweep. The electrode was covered by a nonelectro-active deposit. However, as we scanned between  $-1.0$  and  $1.2$  V, the growth of a new redox system was seen on the CVs especially during the cathodic sweep as depicted in Figure 1A. After such CVs, the electrode was taken out and washed free of monomer using  $\text{CH}_2\text{Cl}_2$ . This modified electrode was then studied between either  $-0.2$  and  $1.2$

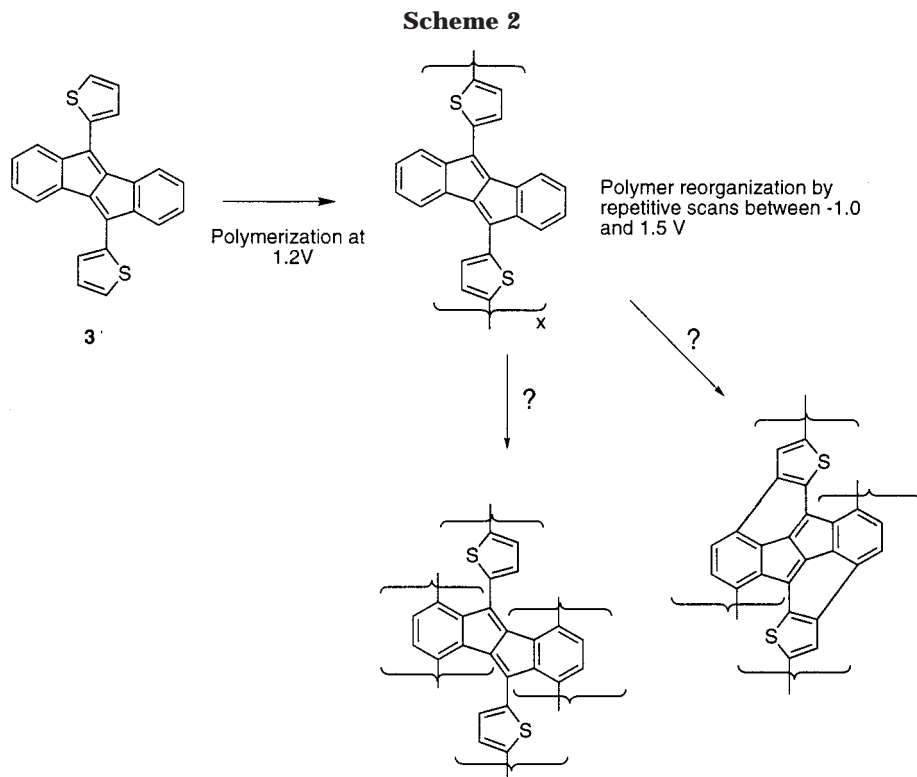
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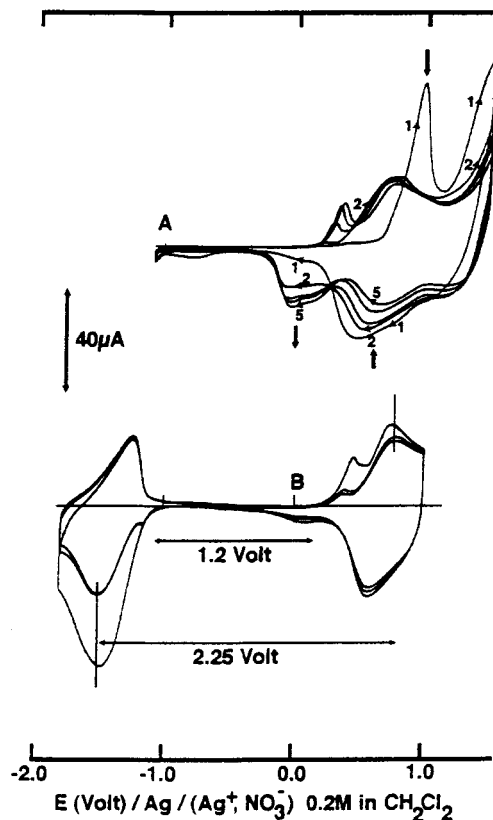
V (Figure 1B) or 1.0 and 1.5 V (Figure 2A) in a fresh 0.2 M  $\text{Bu}_4\text{NBF}_4$  solution in dichloromethane. Figure 1B showed a reversible oxidation peak at 1.15 V, the reduction process being divided into two peaks at 50 and 500 mV. Attempted reduction of the polymer between  $-1.0$  and  $-2.4$  V led to CVs neither stable nor reproducible, showing no well-defined n-doping process and leading to lost polymer electroactivity. Contrariwise, when the anodic study was carried out between  $-1.0$  and  $+1.5$  V (Figure 2A), the CV shape indicated that the original species was being modified, perhaps by intramolecular cyclization or polymerization through the benzene moiety as proposed in Scheme 2. The polymer p-doping process (presented in the anodic range of Figure 2B) is then different from the one presented in Figure 1B. This "restructured" polymer shows a classical n-doping process when the potential is swept between  $-1.0$  and  $-1.8$  V (Figure 2B).

The band gap based on the onset of redox potentials is about 1.2 V, indicating a rather low band gap material. However, when the band gap is measured as the difference between the doping peak potentials it is 2.25 V. A preliminary UV-visible spectroscopic analysis (Figure 3) indicates that the band gap is 2.2 V in close agreement with the difference between the doping peak potentials.

**Conclusion.** Several rigid bis(thienyl)butadienes have been prepared, and their oxidative electrochemical polymerization has been carried out. A qualitative comparison of the band-gap of the polymer derived from **3** with that reported in the literature for the polymer from the analogous flexible monomer **2** does not show any lowering of the band-gap by virtue of rigidity.

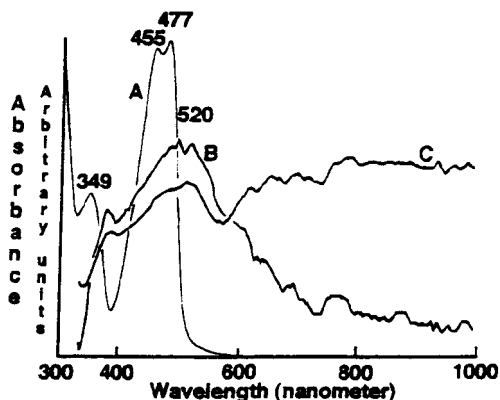
### Experimental Section

**5,10-Bis(2-thienyl)indeno[2,1-a]indene (3).** 2-Bromothiophene (4.7 g, 28.8 mmol) dissolved in THF (25 mL) was slowly added to a refluxing mixture of magnesium turnings (0.9 g, 36.0 mmol) and iodine (catalytic amount) in THF (25 mL).



**Figure 2.** Voltammetric response in 0.2 M  $\text{Bu}_4\text{NBF}_4$  in  $\text{CH}_2\text{Cl}_2$ . (A) Platinum disk electrode (diameter 1 mm) previously coated with a polymer obtained by oxidation of a  $10^{-2}$  M solution of **3** in 0.2 M  $\text{Bu}_4\text{NBF}_4$  in  $\text{CH}_2\text{Cl}_2$  during five recurrent sweeps between  $-1.0$  and 1.2 V. Initial potential:  $-1.0$  V switching potential: 1.5 V, five recurrent sweeps. (B) Subsequent study between  $-1.8$  and 1.0 V. Scan rate:  $100 \text{ mV s}^{-1}$ .

The reaction mixture was stirred at gentle reflux for 1 h. The Grignard reagent was then added dropwise to a solution of



**Figure 3.** Vis spectra of (A) **3**, (B) neutral poly (**3**), and (C) p-doped poly (**3**).

diketone **10**<sup>11</sup> (1.7 g, 7.26 mmol) in THF (60 mL) at 0 °C. The reaction mixture was stirred for 3 h at room temperature and was then poured onto ice containing HCl. The alcohol intermediate was isolated by extraction with ethyl acetate. A methanolic solution (250 mL) of the residue was refluxed gently for 3 h after addition of HCl (0.1 mL). Crude **3** was precipitated by dilution with water. Crystallization from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O gave pure **3** (1.81 g, 68%) as a brown solid: mp 215–218 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.61 (d, 2H, *J* = 6.7), 7.51 (m, 4H), 7.30 (d, 2H, *J* = 6.7), 7.23 (t, 2H, *J* = 8.8), 6.95 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 148.91, 142.99, 135.24, 134.66, 133.08, 128.76, 127.91, 127.74, 127.67, 127.01, 122.75, 122.14; MS *m/z* (relative intensity), 367 (*M* + 1, 41%), 366 (*M*<sup>+</sup>, 100%), 332 (23%), 319 (18%); UV-vis (CHCl<sub>3</sub>) λ<sub>max</sub> nm (ε), 475 (16500), 454 (16280), 348 (9034), 274 (52500), 231 (22573). Anal. Calcd for C<sub>24</sub>H<sub>14</sub>S<sub>2</sub>: C, 78.65; H, 3.85; S, 17.50. Found: C, 78.69; H, 3.86; S, 17.39.

**5,10-Bis(2-bithienyl)indeno[2,1-*a*]indene (4).** A solution of bithiophene (0.851 g, 5.12 mmol) in THF (20 mL) was cooled to 0 °C under N<sub>2</sub> and was then treated with a solution of *n*-BuLi (2.32 mL, 2.2 M in hexane). After 30 min stirring at 0 °C, the mixture was treated with diketone **6** (0.3 g, 1.28 mmol) dissolved in THF (30 mL). The mixture was stirred at room temperature for 8 h and poured onto ice containing HCl. Dehydration of the alcohol intermediate was carried out as described above for **3**. Column chromatography of the crude product on silica gel with hexane/CH<sub>2</sub>Cl<sub>2</sub> (20:1) gave **4** (0.19 g, 28%) as a black-red solid: mp 239 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.68 (d, 2H, *J* = 6.63), 7.46 (d, 2H, *J* = 3.58), 7.36 (d, 2H, *J* = 7.47), 7.29 (d, 4H, *J* = 4.35), 7.07 (t, 2H, *J* = 4.44), 6.98 (m, 4H); UV-vis (CHCl<sub>3</sub>) λ<sub>max</sub> nm(ε) 514

(30431), 347 (18007), 290 (45150), 233 (32691), 212 (20000); MS *m/z* (relative intensity) 530 (*M*<sup>+</sup>, 100%), 265 (16%), 127 (9%); HRMS calcd for C<sub>32</sub>H<sub>18</sub>S<sub>4</sub> 530.029, found 530.028.

**5,10-Bis(3-hexyl-2-thienyl)indeno[2,1-*a*]indene (5) and 5-(3-Hexyl-2-thienyl)-10-methoxyindeno[2,1-*a*]indene (11).** 2-Bromo-3-hexylthiophene (3.5 g, 14.2 mmol) was slowly added to a refluxing mixture of magnesium turnings (0.35 g, 14.4 mmol) and iodine (cat. amount) in THF. After the formation of the Grignard reagent (2 h reflux), a solution of diketone **6** (0.66 g, 2.83 mmol) in THF (70 mL) was slowly added via an addition funnel to the Grignard reagent. The reaction mixture was stirred for 6 h under reflux, cooled to room temperature, poured onto ice containing HCl, extracted with CH<sub>2</sub>Cl<sub>2</sub>, and dried over MgSO<sub>4</sub>, and the solvent was removed under reduced pressure. HCl (0.05 mL) was added to the alcohol intermediate dissolved in MeOH (150 mL), and the mixture was stirred at gentle reflux for 4 h, diluted with water, and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with a solution of NaHCO<sub>3</sub> and dried over MgSO<sub>4</sub>, and the solvent was evaporated in vacuo. The crude product was purified by column chromatography on silica gel with hexane/CH<sub>2</sub>Cl<sub>2</sub> (20:1) as an eluent, to give **5** as a thick liquid (0.22 g, 21%) and **11** (0.26 g, 33%). Crystallization of **11** from MeOH/hexane mixture afforded pure **11** in the form of red crystals.

**5:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.40 (d, 2H, *J* = 5.2), 7.08 (d, 2H, *J* = 5.1), 6.84–6.95 (m, 8H), 2.66 (m, 4H), 1.59 (m, 4H), 1.19 (m, 12H), 0.78 (m, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 150.41, 142.47, 134.39, 133.38, 130.12, 129.29, 127.88, 127.43, 125.69, 122.64, 122.61, 122.13, 31.56, 30.83, 29.35, 28.66, 22.54, 13.99; MS *m/z* (relative intensity) 534 (*M*<sup>+</sup>, 100%), 463 (24%), 377 (29%), 309 (44%), 295 (46%); UV-vis (CHCl<sub>3</sub>) λ<sub>max</sub> nm (ε) 454 (25370), 360 (11111), 276 (70741), 231 (50648), 216 (32870). Anal. Calcd for C<sub>36</sub>H<sub>28</sub>S<sub>2</sub>: C, 80.90; H, 7.12; S, 11.98. Found: C, 80.87; H, 7.15; S, 11.88.

**11:** mp 132 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.41 (m, 1H), 7.37 (d, 1H, *J* = 5.12), 6.85–7.07 (m, 8H), 4.40 (s, 3H), 2.59 (m, 2H), 1.55 (m, 2H), 1.15 (m, 6H), 0.67 (t, 3H, *J* = 6.95); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 158.70, 149.21, 145.59, 143.59, 141.56, 134.29, 132.93, 128.96, 128.91, 128.77, 127.59, 127.42, 126.07, 125.02, 122.13, 122.03, 121.53, 31.53, 30.66, 29.03, 28.66, 22.51, 13.96; MS *m/z* (relative intensity) 398 (*M*<sup>+</sup>, 100%), 327 (31%), 313 (42%), 295 (38%), 282 (33%); UV-vis (CHCl<sub>3</sub>) λ<sub>max</sub> nm (ε) 431 (13597), 411 (14101), 291 (36079), 269 (36619), 216 (18921). Anal. Calcd for C<sub>27</sub>H<sub>26</sub>SO: C, 81.41; H, 6.53; S, 8.04. Found: C, 81.43; H, 6.55; S, 8.00.

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