2.64 (dd, J = 18.0, 8.3 Hz, $CH_aH_bCOCH_3$), 2.59 (ddd, J = 11.7, 8.6, 5.9 Hz, $CH_\alpha CH_\beta CHCO_2$), 2.20 (s, 3 H, $COCH_3$), 1.77 (m, 1 H, $CH_2CH_aCH_bCHOCO$), 1.62 (m, 1 H, $CH_2CH_aCH_bCHOCO$), 1.50 (ddd, 1 H, J = 11.7, 11.7, 9.8 Hz, $CH_\alpha CH_\beta CHCO_2$), 1.45 (m, 1 H, $CH_3CH_2CH_aCH_b$), 1.36 (m, 3 H, $CH_3CH_2CH_aCH_b$), 0.91 (t, 3 H, J = 6.8 Hz, CH_3); ^{13}C NMR (125 MHz) δ 205.59, 178.27, 79.25, 43.52, 36.53, 35.27, 34.88, 29.84, 27.16, 22.26, 13.76; IR (neat) 2956, 2933, 2870, 1773, 1718, 1456, 1411, 1370, 1356, 1322, 1284, 1259, 1210, 1183, 1126, 1007, 971 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.77; H, 8.98.

(±)-*trans*-2-(2-Oxopropyl)-γ-octanoic Lactone (4t). By a procedure similar to that used for the preparation of **4c**, alkene **6t** (1.65 mmol) was oxidized to ketone **4t** in 80% yield: ^1H NMR (500 MHz, $CDCl_3$) δ 4.55 (dddd, 1 H, J = 8.8, 8.1, 5.8, 3.9 Hz, $CHOCO$), 3.03 (dd, 1 H, J = 19.0, 3.9 Hz, $CH_aH_bCOCH_3$), 3.02 (dddd, 1 H, J = 9.8, 9.3, 8.8, 3.4 Hz, $CHCO_2$), 2.69 (dd, J = 19.0, 9.3 Hz, $CH_aH_bCOCH_3$), 2.23 (ddd, 1 H, J = 13.7, 9.8, 3.9 Hz, $CH_\alpha CH_\beta CHCO_2$), 2.01 (ddd, J = 13.7, 8.8, 8.8 Hz, $CH_\alpha CH_\beta CHCO_2$), 2.20 (s, 3 H, $COCH_3$), 1.71 (m, 1 H, $CH_2CH_aCH_bCHOCO$), 1.58 (m, 1 H, $CH_2CH_aCH_bCHOCO$), 1.43 (m, 1 H, $CH_3CH_2CH_aCH_b$), 1.36 (m, 3 H, $CH_3CH_2CH_aCH_b$), 0.91 (t, 3 H, J = 6.8 Hz, CH_3); ^{13}C NMR (125 MHz) δ 205.55, 178.82, 78.86, 44.05, 35.02, 34.33, 33.07, 29.83, 27.29, 22.27, 13.82; IR (neat) 2957, 2934, 2862, 1766, 1718, 1458, 1356, 1161, 1007 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.86; H, 9.15.

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Synthesis of the First Branched Quaterthienyls

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The first synthesis of four of the 16 possible isomeric branched quaterthienyls (thienylterthiophenes) is reported. Thus, 5′-(2-thienyl)-2,2′:3′,2″-terthiophene, 5′-(2-thienyl)-2,2′:3′,3″-terthiophene, 5′-(3-thienyl)-2,2′:4′,2″-terthiophene, and 5′-(3-thienyl)-2,2′:4′,3″-terthiophene, **2a–5a**, were synthesized from the respective trithienyl-1,4-butanediones **10–13**, which were obtained in good yield via the Stetter reaction. The structures of **2a–5a** were supported by 2D COSY spectra.

In 1945, Zechmeister[1] et al. reported that α-terthienyl (2,2′:5′,2″-terthiophene, α-T, 1; Chart I), synthesized four years previously by Steinkopf,[2] was a natural component of marigolds (*Tagetes erecta*, L). In 1958, Uhlenbroek and Bijloo[3] discovered that 1 was a powerful nematocide, and in 1972, Gommers[4] observed that it was phototoxic. Numerous studies since then have shown that 1, which acts as a singlet-oxygen sensitizer, is one of the most phototoxic compounds known.[5] The isomers of α-T and its higher oligomers are also of growing interest as repeating units for the construction of electrically conductive polymers.[6] Recently, transition-metal-catalyzed aryl cross-coupling reactions have been used to synthesize all 14 possible isomeric terthiophenes.[7] These and numerous other structural modifications of 1 have been tested for phototoxicity,[8] but most (as well as Steinkopf's α,α,α-quaterthienyl, see below) are less phototoxic; additionally, there is—as with 1 itself—little or no species or target-cell specificity.

There are, on the other hand, 94 possible isomeric "quaterthienyls" (by which we mean any 4-thiophene-ring oligomer). The structure of 78 of these, by analogy to the alkanes, can be described as linear, having no ring attached to more than two others (these are quaterthiophenes by IUPAC nomenclature); the remaining 16 are branched and have a central ring attached to three others (IUPAC thienylterthiophenes).[9] Only two quaterthienyls have been synthesized to date, both linear: in 1937, Steinkopf[10a] reported a very poor yield, by Ullmann coupling, of 2,2′:5′,2″:5″,2‴-quaterthiophene, which he called "α,α,α-

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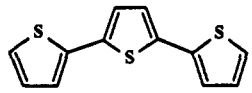
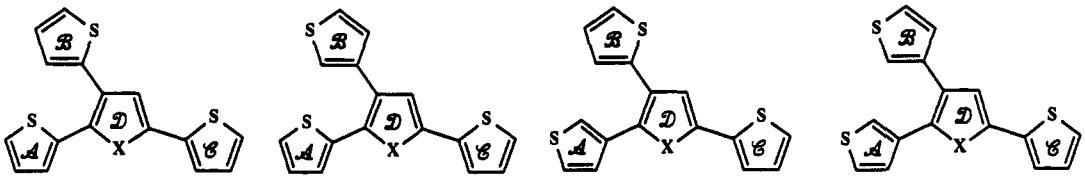
Chart I



1



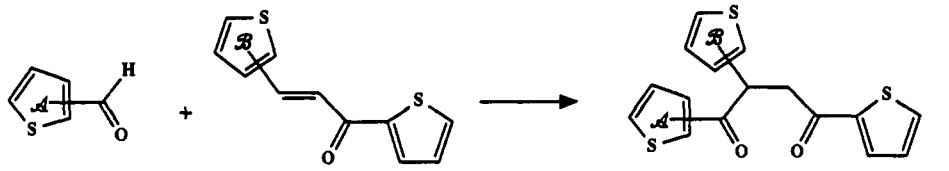
2a, X = S
2b, X = O

3a, X = S
3b, X = O

4a, X = S
4b, X = O

5a, X = S
5b, X = O

Scheme I



6: $\mathcal{A}$ = 2-Thienyl
7: $\mathcal{A}$ = 3-Thienyl

8: $\mathcal{B}$ = 2-Thienyl
9: $\mathcal{B}$ = 3-Thienyl

10: $\mathcal{A}$ = $\mathcal{B}$ = 2-Thienyl
11: $\mathcal{A}$ = 2-Thienyl; $\mathcal{B}$ = 3-Thienyl
12: $\mathcal{A}$ = 3-Thienyl; $\mathcal{B}$ = 2-Thienyl
13: $\mathcal{A}$ = $\mathcal{B}$ = 3-Thienyl

quaterthienyl"; Kagan's group has reported a greatly improved synthesis of this compound,[10b,c] and in 1988, Jayasuriya and Kagan synthesized 3,3′:2′,2″:3″,3‴-quaterthiophene in good yield by Kumada coupling.[11]

The 16 branched quaterthienyls consist of two groups, the 2,3,5- and the 2,3,4-trithienylthiophenes. The structure of the first group resembles 5-(4-chlorophenyl)-2,3-diphenylthiophene, one of the few phototoxic molecules to show some species selectivity.[12] Hence, we chose to attempt the synthesis of four quaterthienyls of this group: **2a–5a** (Chart I). These structures are of further interest as substrates for the Mallory oxidative photocyclization reaction, since they are derivatives of the four terthiophenes whose photocyclization has recently been studied.[13,14]

For our synthesis of **2a–5a** the Stetter reaction[15] provided trithienyl-1,4-butanediones **10–13** (Scheme I) in good yield. Formation of the central thiophene ring proved more problematic: all methods we attempted[16] resulted in concomitant formation of the corresponding furans **2b–5b**,[17] which could be detected as a small peak on reversed-phase HPLC immediately preceding **2b–5b**. Earlier workers have observed that, when the substituents on the 1,4-butanedione system are bulky, the furan/thiophene

(9) The topological problem of counting the oligothienyls is not entirely trivial: some authors have counted "ten possible isomeric terthienyls" ((a) Uhlenbroek, J. H.; Bijloo, J. D. *Recl. Trav. Chim. Pays-Bas* **1960**, *79*, 1181–1196); Steinkopf notes that "theoretisch sind 10 isomere Quaterthienyle möglich" ((b) Steinkopf, W.; Koehler, W. *Liebigs Ann. Chem.* **1936**, *522*, 17–27). For the nomenclature of the quaterthiophenes see: (c) *IUPAC Nomenclature of Organic Chemistry*; Rigaudy, J., Klesney, S. P., Eds.; Pergamon Press: Oxford, 1979; Rules A-52, p 42; A-54, p 44; C-71, p 128. For a combinatoric analysis of the poly(thiophene) isomers, see: (d) Perrine, D. M.; VandeVelde, J. R. Submitted for publication in *J. Chem. Educ.*

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(16) Lawesson's reagent: (a) Lawesson, S.-O.; Thomsen, I.; Clausen, K.; Scheibye, S. *Org. Synth.* **1984**, *62*, 158–163. (b) Shridhar, D. R.; Jogibhukta, M.; Rao, P. S.; Handa, V. K. *Synthesis* **1982**, 1061–1062. HCl and H_2S: (c) Duus, F. *Tetrahedron* **1976**, *32*, 2817–2825. (d) Campaigne, E.; Foye, W. O. *J. Org. Chem.* **1952**, *17*, 1405–1412. We have found that the very interesting thiating reagent developed by Steliou's group (*in situ* formation of B_2S_3 from bis(tricyclohexyltin) sulfide and BCl_3) for the conversion of ketones to thiones produces a good yield of thiophenes from 1,4-butanediones; however, the proportion of furan produced was the same as other methods and the workup was less convenient: (e) Steliou, K.; Mrani, M. *J. Am. Chem. Soc.* **1982**, *104*, 3104–3106. The most expeditious overall method was that of: (f) Scheeren, J. W.; Ooms, P. H. J.; Nivard, R. J. F. *Synthesis* **1973**, 149–151.

(17) This problem is as old as the original synthesis of 2,5-diphenylthiophene: (a) Kapf, S.; Paal, C. *Chem. Ber.* **1888**, *21*, 3053–3063. A recent study of the reaction of Lawesson's and Steliou's reagents with symmetric nonenolizable diketones leads us to believe that with our compounds the less hindered carbonyl is first converted to the thione, which then undergoes intramolecular substitution–elimination by the enolized form of the other keto group with irreversible formation of the furan: (b) Ishii, A.; Nakayama, J.; Ding, M.; Kotaka, N.; Hoshino, M. *J. Org. Chem.* **1990**, *55*, 2421–2427.

ratio increases[18] and often an intractably cocrystallizing mixture results.[19] While we could separate **2a** from **2b** by repeated flash chromatography,[20] isomers **3a–5a** could be separated from **3b–5b** neither by recrystallization from any of numerous solvent systems nor by column chromatography or by normal-phase HPLC. Since the separation by analytic reversed-phase HPLC was good, we finally used semipreparative reversed-phase HPLC. About 20 runs per compound were required because of the low solubility of the quaterthienyls in polar solvents; although this process was inconveniently labor-intensive, it finally resulted in small amounts of analytically pure **3a–5a**.

The structures proposed for **2a–5a** are well supported by high-field NMR spectra. The 400-MHz proton chemical shifts in each spectrum range from 6.96–7.32 ppm, typical for heteroaromatic rings; and there are distinct noncoupled proton peaks at 7.22, 7.18, 7.25, and 7.20 ppm for **2a–5a**, respectively, corresponding to the single proton in the $\mathcal{D}$ ring. Each 100-MHz ^{13}C spectrum shows six well-separated low-intensity signals from 130–136 ppm corresponding to quaternary carbons, and all compounds but **3a** have 10 distinct intense signals from 122 to 128 ppm (in **3a** there are only nine signals, due to coincidental chemical shifts).

The 45° 2D COSY[23] spectrum for each compound **2a–5a** (supplementary material, Figures 1–4) shows one noncoupled signal for the proton of ring $\mathcal{D}$ and correlations between a total of nine well-resolved sets of cross-peaks consisting of three distinct three-spin AMX systems for rings $\mathcal{A}$–$\mathcal{C}$. Any 2-thienyl substituents should display two vicinal (^3J_C) and one long-range (^4J_C) coupling, both via intervening carbons, while a 3-thienyl substituent should show one vicinal (^3J_C) and one long-range (^4J_C) coupling via intervening carbons and a further long-range (^4J_S) coupling via intervening sulfur, with $^3J_C > {}^4J_S > {}^4J_C$.[24] Examination of the relative strength of the coupling constants in all nine cross-peaks for each compound shows that there are three 2-thienyl substituents in **2a**, two 2- and one 3-thienyl substituent in both **3a** and **4a**, and one 2- and two 3-thienyl substituents in **5a**. The distinctive chemical shift pattern for the protons of ring $\mathcal{C}$ in **5a** can be seen in **2a–4a**, allowing the 2-thienyl $\mathcal{C}$ ring in these structures to be distinguished from 2-thienyl substituents at the $\mathcal{A}$ or $\mathcal{B}$ position. Consideration of the deshielding effect of an adjacent sulfur atom or aromatic substitution allows the assignment of all the remaining protons of **3a** and **4a**; however, no compelling assignments were possible for the $\mathcal{A}$ and $\mathcal{B}$ rings of **2a** and **5a**.

Ongoing studies of the photocyclization and phototoxicity of these compounds will be reported elsewhere.

Experimental Section

Melting points are uncorrected. Elemental analyses were by Micro-Tech, Skokie, IL, or Galbraith, Knoxville, TN.

1-(2-Thienyl)-3-(3-thienyl)-2-propen-1-one (9). This enone was made from 3-thiophenecarboxaldehyde and 2-acetylthiophene in 94% yield following the standard chalcone synthesis.[21] Recrystallization from *i*-PrOH gave off-white crystals, 100% pure by HPLC, mp 77–78 °C: IR (Nujol) ν 1635, 1575, 1280, 1210, 1060, 975, 800 cm^{-1}. Anal. Calcd for $C_{11}H_8OS_2$: C, 59.97; H, 3.66. Found: C, 60.03; H, 3.34.

General Procedure for Synthesis of Diones 10–13. Following previously reported procedures,[14,15] the indicated quantities of aldehyde, enone, a 20% molar quantity of 3,4-dimethyl-5-(2-hydroxyethyl)thiazolium iodide (Aldrich), and a 60% molar quantity of Et_3N were stirred under Ar for 12–16 h in the minimum volume of refluxing EtOH or 2-PrOH needed to effect solution. On cooling to 0 °C, a product crystallized determined to be 97–99% pure by HPLC and was used without further purification in the synthesis of **2a–5a**.

1,2,4-Tri-2-thienyl-1,4-butanedione (10). From 7.0 g (62.6 mmol) of 2-thiophenecarboxaldehyde (**6**) and 13.75 g (62.6 mmol) of 1,3-di-2-thienyl-2-propen-1-one (**8**)[22] was obtained 17.9 g (87%) of **10**. Recrystallization from 2:1 MeOH/acetone gave off-white crystals determined to be 100% pure by HPLC, mp 117 °C: IR (Nujol) ν 1655, 1230, 850, 735, 720 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) ABX (3 H) δ 3.28 (H_A, J_{AB} = 18 Hz), 4.03 (H_B, J_{BX} = 10 Hz), 5.38 (H_X, J_{AX} = 4 Hz), 6.80–7.27 (m, 5 H), 7.50–7.93 (m, 4 H); UV (MeOH) 261, 287 nm (log ϵ 4.26, 4.23). Anal. Calcd for $C_{16}H_{12}O_2S_3$: C, 57.80; H, 3.64. Found: C, 58.14; H, 3.57.

1,4-Di-2-thienyl-2-(3-thienyl)-1,4-butanedione (11). From 5.65 g (50.3 mmol) of **6** and 11.10 g (50.3 mmol) of **9** was obtained 14.61 g (87%) of **11**. Recrystallization from *i*-PrOH gave off-white crystals determined to be 100% pure by HPLC, mp 124.0–124.5 °C: IR (Nujol) ν 1650, 1220, 845, 780, 725 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) ABX (3 H) δ 3.35 (H_A, J_{AB} = 18 Hz), 4.13 (H_B, J_{BX} = 10 Hz), 5.35 (H_X, J_{AX} = 4 Hz), 6.97–7.40 (m, 5 H), 7.53–7.93 (m, 4 H); UV (MeOH) 260, 286 nm (log ϵ 4.26, 4.22). Anal. Calcd for $C_{16}H_{12}O_2S_3$: C, 57.80; H, 3.64; S 28.93. Found: C, 57.54; H, 3.61; S, 29.14.

2,4-Di-2-thienyl-1-(3-thienyl)-1,4-butanedione (12). From 11.3 g (101 mmol) of 3-thiophenecarboxaldehyde (**7**) and 22.2 g (101 mmol) of **8** was obtained 29.0 g (86%) of **12**. Recrystallization from *i*-PrOH gave off-white crystals determined to be 100% pure by HPLC, mp 120–121 °C: IR (Nujol) ν 1660, 1245, 1235, 800, 740 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) ABX (3 H) δ 3.43 (H_A, J_{AB} = 18 Hz), 4.20 (H_B, J_{BX} = 10 Hz), 5.45 (H_X, J_{AX} = 4 Hz), 7.00–7.47 (m, 5 H), 7.63–7.97 (m, 3 H), 8.35 (m); UV (MeOH) 213, 257 nm (log ϵ 4.16, 4.32). Anal. Calcd as for **11**. Found: C, 57.66; H, 3.51; S, 29.30.

4-(2-Thienyl)-1,2-di-3-thienyl-1,4-butanedione (13). From 5.67 g (50.6 mmol) of **7** and 11.10 g (50.4 mmol) of **9** was obtained 14.62 g (87%) of **13**. Recrystallization from *i*-PrOH gave off-white crystals determined to be 100% pure by HPLC, mp 129.0–130.0 °C: IR (Nujol) ν 1650, 1230, 790, 760, 745 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) ABX (3 H) δ 3.30 (H_A, J_{AB} = 18 Hz), 4.15 (H_B, J_{BX} = 10 Hz), 5.32 (H_X, J_{AX} = 4 Hz), 7.03–7.43 (m, 5 H) 7.57–7.90 (m, 3 H), 8.20 (m); UV (MeOH) 213, 256 nm (log ϵ 4.16, 4.28). Anal. Calcd as for **10**. Found: C, 57.56; H, 3.28.

General Procedure for Synthesis and Separation of Thienylterthiophenes 2a–5a: Synthesis. Following the procedure of Scheeren et al.,[16f] a stirred slurry of 5.0 g of the 1,4-butanedione, 10.0 g of P_4S_{10}, and 8.0 g of $NaHCO_3$ in 50 mL of MeCN and 15 mL of CH_2Cl_2 was refluxed under Ar until HPLC showed disappearance of starting dione (1–2 h). Solvents were removed by rotary evaporation; the residue was exhaustively extracted with boiling hexane; and the extracts forced under air pressure through a 2.5-cm plug of silica gel. Evaporation of solvent yielded crude crystalline material that was further purified by recrystallization from hexane.

Separation. Each isomer was found to be contaminated with 2–5% of the respective furan **2b–5b**. In a typical run using a 250 × 22.5 mm reversed-phase column, 1 mL of a saturated solution of **5a**/**5b** in MeOH (or in 1:1 THF/MeOH—with some loss in resolution, but a gain in efficiency) was run at 5.0 mL/min using MeOH as eluant. A 1% peak for furan **5b** occurred at 15.5 min and a 94% peak for **5a** at 16.8 min. The combined thiophene cuts from about 20 such runs afforded analytical material. The identity of the furan peak was determined by running a small sample of the furan obtained from the dione by standard methods (acetic anhydride, H_2SO_4).

5′-(2-Thienyl)-2,2′:3′,2″-terthiophene (2a). From 5.0 g of **10** was obtained 1.6 g (33%) of **2a**. Preparative HPLC and recrystallization from hexane gave pale yellow crystals, mp 59–60

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°C: IR (Nujol) ν 1245, 1040, 845, 825, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00–7.03 (m, 2 H), 7.04–7.05 (m, 1 H), 7.07–7.09 (m, 1 H), 7.13–7.14 (m, 1 H), 7.20–7.21 (m, 1 H), 7.22 (s, 1 H), 7.24–7.26 (m, 1 H), 7.28–7.31 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.99, 136.46, 135.81, 134.67, 132.41, 130.45, 127.91, 127.72, 127.22, 127.12, 126.80, 126.74, 126.28, 125.69, 124.89, 124.10; MS m/z (relative intensity) 330.2 (M$^+$, 100), 331.1 (25), 332.2 (25), 329.2 (23); UV (MeOH) 287, 344 nm (log ϵ 4.26, 4.16). Anal. Calcd for $C_{16}H_{10}S_4$: C, 58.15; H, 3.05; S, 38.81. Found: C, 58.04; H, 3.10; S, 39.25.

5′-(2-Thienyl)-2,2′:3′,3″-terthiophene (3a). From 5.0 g of **11** was obtained 2.8 g (56%) of **3a**. Preparative HPLC and recrystallization from hexane gave white crystals, mp 78–79 °C; IR (Nujol) ν 1080, 840, 830, 790, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97–6.99 (m, 1 H), 7.02–7.07 (m, 3 H), 7.18 (s, 1 H), 7.19–7.21 (m, 1 H), 7.23–7.26 (m, 2 H), 7.28–7.32 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.73, 136.05, 135.58, 135.44, 134.38, 130.21, 128.19, 127.91, 127.24, 126.84, 126.43, 126.13, 125.38, 124.72, 123.93, 123.46; MS m/z (relative intensity) 330.2 (M$^+$, 100), 329.2 (33), 331.1 (25), 332.2 (24); UV (MeOH) 207, 262, 345 nm (log ϵ 4.16, 4.17, 4.21). Anal. Calcd as for **2a**. Found: C, 58.18; H, 3.13; S, 38.77.

5′-(3-Thienyl)-2,2′:4′,2″-terthiophene (4a). From 5.0 g of **12** was obtained 3.7 g (76%) of **4a**. Preparative HPLC and recrystallization from hexane gave pale yellow crystals, mp 82–83 °C: IR (Nujol) ν 1230, 1080, 850, 825, 780, 700, 630 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99–7.08 (m, 4 H), 7.20–7.22 (m, 1 H), 7.24–7.27 (m, 3 H), 7.29–7.32 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.66, 136.64, 135.14, 133.57, 132.29, 131.41, 128.13, 127.83, 127.12 126.18, 126.08, 125.67, 125.11, 124.64, 123.87; MS m/z (relative intensity) 330.2 (M$^+$, 100), 285.2 (39), 329.2 (36), 331.1 (26), 332.2 (25); UV (MeOH) 203, 242, 254, 286, 333 nm (log ϵ 4.23, 4.06, 4.05, 4.26, 4.16). Anal. Calcd as for **2a**. Found: C, 58.03; H, 3.02; S, 39.13.

5′-(3-Thienyl)-2,2′:4′,3″-terthiophene (5a). From 5.0 g of **13** was obtained 3.2 g (64%) of **5a**. Preparative HPLC and recrystallization from hexane gave white crystals, mp 90–91 °C; IR (Nujol) ν 1230, 1170, 840, 820, 785, 705, 690, 650 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99–7.05 (m, 3 H), 7.19–7.20 (M, 1 H), 7.20 (m, 1 H), 7.22–7.24 (m, 3 H), 7.26–7.30 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.98, 136.60, 134.96, 134.21, 133.52, 132.05, 128.10, 127.98, 127.87, 126.38, 125.68, 125.37, 124.53, 123.75, 122.99, 122.72; MS m/z (relative intensity) 330.2 (M$^+$, 100), 329.2 (38), 285.2 (34), 331.1 (26), 332.2 (25); UV (MeOH) 207, 268, 334 nm (log ϵ 4.36, 4.15, 4.18). Anal. Calcd as for **2a**. Found: C, 57.94; H, 3.27; S, 39.19.

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Registry No. 2a, 134628-84-5; **3a**, 134628-85-6; **4a**, 134628-86-7; **5a**, 134628-87-8; **8**, 2309-48-0; **9**, 134628-88-9; **10**, 70314-42-0; **11**, 134628-89-0; **12**, 134628-90-3; **13**, 134704-87-3; 2-thiophenecarboxaldehyde, 98-03-3; 3-thiophenecarboxaldehyde, 498-62-4; 2-acetylthiophene, 88-15-3.

Supplementary Material Available: 2D COSY spectra for compounds **2a**, **3a**, **4a**, and **5a** (4 pages). Ordering information is given on any current masthead page.

Synthesis of 1,5- and 1,8-Dihydroxyanthraquinones from a Common Intermediate. A Direct Synthesis of Racemic 7-Deoxyaklavinone

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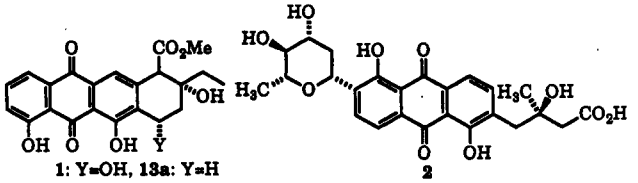
When quinone **6** was treated with diene **7** followed by oxidation, a 1,5-dihydroxyanthraquinone was obtained. When quinone **6** was subjected to a palladium-mediated aromatization, the resulting 5-hydroxy-1,4-naphthoquinone reacted with diene **7** followed by oxidation to produce a 1,8-dihydroxyanthraquinone, a key intermediate in a direct synthesis of 7-deoxyaklavinone, a known synthetic precursor of aklavinone.

In the past decade, a number of architecturally interesting and biologically active anthraquinones have been discovered. The anthracyclines, exemplified by aclacinomycinone (**1**), contain a 1,8-dihydroxyanthraquinone unit.[1] The vineomycins (**2**) have a 1,5-dihydroxyanthraquinone subunit.[2] Dynemicin, a recently discovered anticancer agent, contains a 1,4,5-trihydroxyanthraquinone subunit.[3] To date, synthetic routes to quinones **1** or **2** have been approached by quite different pathways.[4] We report herein that either the 1,5- or the 1,8-dihydroxyanthraquinone pattern can now be obtained from a common intermediate. In addition to these findings, we also describe a direct synthesis of aklavinone.



1: Y=OH, **13a**: Y=H **2**

Our approach to **1** was based on our previous studies of tandem photoenolization/intermolecular Diels–Alder reactions wherein the hydroxy diester **3** was obtained as a mixture of isomers.[5] This mixture could be converted into the keto diester **4** using the Jones oxidation. The reaction of **4** with ethyl vinyl ketone and Triton B in methanol produced diester **5** as a single stereoisomer (Scheme I). The selective transesterification of the less hindered ester was not planned; however, it was very welcome since it simplified the subsequent palladium chemistry. Oxidation of **5** by the method of Rapoport[6] afforded the unstable quinone **6**, which could not be purified by silica gel chro-

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