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A Convenient Synthetic Entry Into Aldehydes With Extended Conjugation

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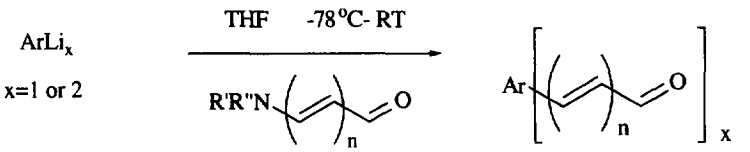
Abstract: Variable-length donor-acceptor polyenes **1-18** were synthesized. In the key step, a polyenal was appended to an aromatic donor through nucleophilic attack of an organolithium reagent on a vinylogous amide. Yields of aldehydes and dialdehydes in the one-pot process ranged from 12-64% and depended upon number of repeat units (n=1-3) in the polyene chain.

There is substantial interest in π-conjugated molecules and polymers for a wide variety of applications including electron transfer, magnetism, vision, nonlinear optics, conductivity, color chemistry, and light-emitting diodes.[1] Often, Wittig and Knoevenagel condensations are the key carbon-carbon bond forming steps in the syntheses of these materials that therefore necessitate a variety of polyene aldehyde and dialdehyde precursors. Current approaches to polyenal compounds include extensions of shorter aldehydes by either one[2] or two[3,4] or three[5] double bonds, or use of organometallic[6,7] or Vilsmeier[8] chemistry to exchange an amine end group for another functional group in an existing polyenal. We have found it expedient to convert aromatic halides and heteroaromatic compounds to aromatic polyenals with up to three ethylene repeat units in a reasonably general one-pot process. The procedure has been used to synthesize a variety of precursor aldehydes in order to explore the nonlinear optical properties of variable-length donor-acceptor polyenes without isoprene units.[9] However, many other applications of such compounds can be envisioned.

The key sequence in the general reaction scheme below follows from the synthetic method of Jutz,[6] in which Grignard or organolithium[7] reagents were treated with N-methyl, N-phenyl-3-aminopropen-1-al (**1a**) or its higher vinylog, **2a**, in yields of 5-95%. In our procedure, a wide variety of organolithium reagents, available from lithium-halogen exchange of alkyllithium

reagents with aryl bromides or by direct lithiation of heteroaromatic compounds, were employed. The bromides were commercially available, or in the case of julolidine, obtained by a high yield bromination procedure.[10] Here we demonstrate that organolithium reagents add to known ω-N,N-bis(dialkylamino)polyenals **1b**,[11] **2b**,[11,12] and **3**[11,13] to make substituted polyenals or polyenedialdehydes. The method provides a one-pot synthesis of short polyenals and polyenedials **4-15** (where n=2 or 3) in as much as 64% yield for pure aldehydes and 26% yield for dialdehydes.



1 (n=1)
a R' = Me, R" = Ph
b R' = R" = Me
2 (n=2)
a R' = Me, R" = Ph
b R' = R" = Et
3 (n=3) R' = R" = Me

4-15 where n=1-3

Several families of donor-substituted aldehydes were synthesized and characterized. The structures of the reagents and products, as well as yields, are given in Table 1. It is especially useful to make comparisons of reactivity and yield based on amide lengths and donor identities in the series **4** and **5**. Polyenals containing the commonly-utilized donor group N,N-bis(dimethylamino)phenyl were obtained in the highest overall yields. Interestingly, **4** and **5** (n=1) were formed in substantially lower yields than **4** and **5** (n=2 and 3). This is in contrast to the behavior reported[6] for reactions using amides **1a** and **2a**, where yields up to 95% were obtained with **1a** and up to 60% with **2a**. In our experience, those compounds derived from **3** were formed in lower yields than those derived from **2b**, possibly due to the combination of the poor solubility of **3** at low temperatures (resulting in incomplete reaction) and the relative instability of longer polyenes.

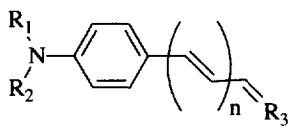
The Spangler strategy[2] using Wittig chemistry to extend polyenals iteratively by one double bond proceeded in high yield for aldehydes **4** (n=1 and 2).[14] However, in our hands, the analogous reaction using the strongly electron-donating julolidinyl group to make **5** led to mixtures of aldehydes containing the desired product and small amounts of higher vinylogs, despite efforts to exclude air water and acid.[14] In contrast, the procedure described above gave **5**

in satisfactory yields for n=2 and 3. The N-alkylated aniline derivative **6** was easily synthesized as a more soluble analog of **4** (n=2).

Hydroxyethyl-functionalized dye derivatives are commonly used to append chromophores to various polymer backbones for poled polymer applications.[1] Our methodology was successful for **7** (n=2 and 3) and **8** where tetrahydropyranyl (THP) or *t*-butyldimethylsilyl (TBDMS) ether protecting groups were used during the lithiation step. *t*-Butyllithium was added to **3** to produce the alkyl-capped polyenal **9** in an unoptimized 40% yield. While polyenals of this type are interesting as precursors to polyacetylene oligomer models,[15] the ease of formation of **9** shows that excess organolithium reagent in the lithium-halogen exchange step can compete with aryllithium reagent for the amide electrophile, lessening the yield of desired polyene. Dialdehydes **10** and **11** are examples of compounds with extended π systems, and result from the addition of two equivalents of aldehyde to the appropriate bis-organolithium reagent. When 1,4-dibromobenzene was used to generate the organolithium reagent, a monoaldehyde derivative, **12**, which contains differentiated functionalities at the polyene termini, was isolated in addition to the expected product. Heteroaromatic organolithium reagents also add readily to amides **3** and **2b**. Thus, a thiophene derivative, **13**, and two ferrocene derivatives **14** and **15** were obtained from the reaction of dibromothiophene and ferrocene, respectively, with two equivalents of *t*-butyllithium followed by the appropriate vinylogous amide.

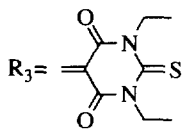
The results presented here demonstrate that an array of aryl-capped polyenals and polyenedials of various conjugation lengths may be produced using a one-pot general synthetic route in satisfactory yields for materials applications. Starting materials are either commercial or synthesized using literature procedures. The method is compatible with protected alcohols. Despite the low yields of the dialdehydes, the method is nonetheless a convenient approach to the compounds discussed here and other desirable compounds of this general class.

Once rapidly produced with the general procedure described here, aldehydes may be condensed or polycondensed using conventional chemistry. For example, highly polarizable and multiply functionalized molecules **7** and **8** were treated under Knoevenagel conditions with N,N-diethylthiobarbituric acid or 5-phenyl-3-isoxazolone to give **16-18**. The parent donor-acceptor polyenes are known to result in high first polarizabilities β[9,16] and some of the derivatized donor-acceptor polyenes have shown promise in poled polymers.[9,17]

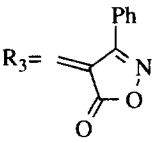


16 $R_1=R_2=CH_2CH_2OH$; n=2

17 **(n=2 and 3)** $R_1=CH_2CH_2OH$; $R_2=Et$



18 $R_1=CH_2CH_2OH$; $R_2=Et$; n=2



Experimental Part. Melting and boiling points are uncorrected. ^1H NMR spectra were run on a Bruker AM 500 instrument at 500 MHz and ^{13}C NMR spectra on a GE QE Plus instrument at 75 MHz in deuteriochloroform and referenced to chloroform unless noted otherwise. IR spectra were measured on a Perkin-Elmer 1760 Instument in KBr pellets unless noted otherwise. UV/VIS spectra were measured on a HP 8542A Diode Array Spectrophotometer. Quantification of log ε was often done only for the visible band with largest molar absorptivity, and was based on single measurement in each case. Mass spectra were measured at the Mass Spectroscopy Facility at University of California, Riverside using a Finnegan 7070 GC/MS Spectrometer at 50 or 20 eV. Elemental analyses were performed at Atlantic Microlabs, Norcross, Georgia. N-Ethyl-N-2-hydroxyethylaniline and N,N-bis(2-hydroxyethyl)aniline were obtained from Henkel Inc. *t*-Butyllithium, *n*-butyllithium, HPLC grade dimethyl formamide (DMF), N, N-dimethylaminoacrolein (**1b**) , 1-bromo-4-(N, N-dimethylamino)benzene, 2,4-hexadienal, N, N-dibutylaminobenzene, 1,3-dibromobenzene, 1,4-dibromobenzene, ferrocene, thiophene, and N, N-diethylthiobarbituric acid were purchased from Aldrich and used as received. THF was distilled from benzophenone ketyl before use.

General Procedure for Formation of Aromatic Polyenals and Polyenedials. Aromatic bromide (1.2 eq) was dissolved in THF (10 mL/mmol) and cooled to -78 °C under argon. *t*-Butyllithium (1.7 M, 2.4 eq) was added dropwise and the resulting solution stirred for 1h, then allowed to warm to 0 °C. *n*-Butyllithium may also be used (1.2 eq). The solution was recooled to -78 °C and vinylogous amide **1b**, **2b**, or **3** (1 eq) added in THF (10 mL/ mmol). The solution was allowed to warm to room temperature, then shaken in a separatory funnel with 2M HCl. 10% NaOH solution was added to pH 10, then the organic phase was separated, the aqueous washed with ether. The combined organic layers were dried over Na_2SO_4, evaporated, purified by flash chromatography on silica gel using 20% ethyl acetate in hexanes, then crystallized from a mixture of ethyl acetate and hexanes. Modifications of the above procedure are indicated for each compound.

7-(N,N-Dimethylamino)hepta-2,4,6-trien-1-al.(3)[12,13] According to a literature procedure[13] $POCl_3$ (122.4 g, 0.8 mol) was added dropwise to an ice-cooled solution of DMF (160 mL) and methanol (25.6 g), keeping the temperature of the solution around 15 °C. After addition was complete, the solution was gradually warmed in an oil bath to 75 °C. Hexa-2,4-dienal (38.4 g, 0.4 mol) was added and the mixture stirred 3 h at 75 °C. After cooling, the viscous solution was poured into 1 kg of ice, then N,N-dimethylamine hydrochloride (100 g) added. The dark solution was made basic (pH 10, pH meter) with 20% NaOH, then treated with saturated aqueous $NaClO_4$ to give shiny green crystals. After allowing at least 1 h for crystallization, the green mass was filtered, and washed with water, then ethanol, until the washings were nearly colorless. Second crops were generally negligible. Yield: 27.4-44.7 g (24.6-40.1%) after drying. Cyanine (27.4 g) was dissolved in methylene chloride (100 mL) and stirred vigorously with 20% aqueous NaOH (50 mL) for 2 h or until TLC (75% ethyl acetate in hexanes) indicated almost total conversion to yellow product aldehyde (R_f = 0.4). Layers were separated and aqueous extracted with methylene chloride until lightly colored. Emulsions were lessened by dilution with both solvents. The organic layer was concentrated, washed through a silica plug (4 cm) with ethyl acetate until the washings were light yellow. The solvent was evaporated, then the brown crystalline residue dissolved in hot toluene, treated with charcoal, and hot-filtered. Cooling produced burnt-sienna colored crystals, which lightened upon repeated recrystallization. Yield: 6.7 g (61.3%). mp 129-130 °C (lit[12] 144 °C); ^{1}H NMR (400 MHz) δ 9.38 (d, J=8.3 Hz, 1H), 7.09 (dd, J=14.6 Hz, J=11.5 Hz, 1H), 6.67 (dd, J=14.1 Hz, J=11.4 Hz, 1H), 6.59 (d, J=12.7 Hz, 1H), 6.06 (dd, J=14.1 Hz, J=11.5 Hz, 1H), 5.90 (dd, J=14.6 Hz, J=8.3 Hz, 1H), 5.14 (apparent t, J=12.0 Hz, 1H), 2.87 (s, 6H); ^{13}C NMR δ 192.96, 155.65, 149.81, 147.05, 123.84, 117.90, 98.61, 40.55, 40.52; UV/VIS λ_{max} (log ε) 440 (4.60), 304 (4.21); EIMS, m/z 151(M^+, 100), 122(35), 82(40), 79(31), 42(49). Attempts to modify the procedure to make the tetraethyl or tetrabutyl cyanines were unsuccessful.

3-(4-N,N-Dimethylaminophenyl)propen-1-al. (4, n=1)[2] 1-Bromo-4-(N,N-dimethylamino)-benzene (2.4 g, 12 mmol) was treated with *n*-butyllithium (7.5 mL, 12 mmol) then N,N-dimethylamino)acrolein (**1b**, 990 mg, 10 mmol) according to the general procedure. Yield: 455 mg (26%) yellow crystals. The ^{1}H NMR spectrum matched that of commercial material.

5-(4-N,N-Dimethylaminophenyl)penta-2,4-dien-1-al. (4, n=2)[2] 1-Bromo-4-(N,N-dimethyl-amino)benzene (2.4 g, 12 mmol) was treated with *n*-butyllithium (7.5 mL, 12 mmol) then 5-(N,N-diethylamino)penta-2,4-dien-1-al (**2b**, 1.53 g, 10 mmol) according to the general procedure. Yield: 1.28 g (64%) orange crystals. The ^{1}H NMR spectrum matched that of an authentic sample prepared according to literature.[2]

7-[4-(N,N-Dimethylamino)phenyl]hepta-2,4,6-trien-1-al. (4, n=3)[2] 1-Bromo-4-(N,N-di-methylamino)benzene (2.4 g, 12 mmol) was treated with *n*-butyllithium (7.5 mL, 12 mmol) then

5-(N,N-dimethylamino)hepta-2,4,6-trien-1-al (**3**, 1.51 g, 10 mmol) according to the general procedure. Yield: 1.12 g (54%) dark red crystals. The ^{1}H NMR spectrum matched that of an authentic sample prepared according to literature.[2]

3-(9-Julolidinyl)prop-2-en-1-al. (5, n=1) 9-Bromojulolidine[10] (5.54 g, 22 mmol) was treated with *n*-butyllithium (14.0 mL, 23 mmol) then N,N-dimethylaminoacrolein (**1b**, 0.99 g, 10 mmol) according to the general procedure. Column chromatography using 40% ethyl acetate in hexanes (R_f= 0.63) gave pure **5**, (**n=1**). Yield: 1.42 g (31%). Crystallization from ethyl acetate in hexanes gave 1.00 g (22%) orange plates: mp 124-125 °C. ^{1}H NMR δ 9.54 (d, J=7.7 Hz, 1H), 7.27 (d, J=15.5 Hz, 1H), 7.01 (s, 2H), 6.47 (dd, J=15.6, 7.9 Hz, 1H), 3.26 (t, J=5.7 Hz, 4H), 2.75 (t, J=6.3 Hz, 4H), 2.02-1.90 (m, center at 1.96, 4H); ^{13}C NMR δ 193.6, 154.4, 145.6, 128.1, 122.6, 120.8, 120.5, 49.8, 27.6, 21.3; IR 1653(C=O), 1586(C=C), 1523 cm^{-1}; UV/VIS λ_{max} (log ε) 412(4.47), 262(3.93); EIMS, m/z 227(M^+, 100), 226(M^+-1, 44), 198(29), 173(54); Anal. Calcd. for $C_{15}H_{17}NO$: C, 78.84; H, 7.50; N, 6.13. Found: C, 79.07; H, 7.59; N, 6.12.

5-(9-Julolidinyl)penta-2,4-dien-1-al (5, n=2) 9-Bromojulolidine[10] (2.77 g, 11 mmol) was treated with *n*-butyllithium (7.5 mL, 12 mmol) then 5-(N,N-diethylamino)penta-2,4-dien-1-al (**2b**, 1.53 g, 10 mmol) according to the general procedure. Column chromatography using 40% ethyl acetate in hexanes (R_f= 0.75) gave pure **5**, (**n=2**). Yield: 1.46 g (57.7%) red crystals: mp 107 °C; ^{1}H NMR δ 9.46 (d, 7.9 Hz, 1H), 7.16 (dd, J=14.9, 10.8 Hz, 1H), 6.89 (s, 2H), 6.77 (d, J=15.3 Hz, 1H), 6.68 (dd, J=15.2, 10.8 Hz, 1H), 6.06 (dd, J=14.9, 8.1 Hz, 1H), 3.15 (t, J=5.7 Hz, 4H), 2.67 (t, J=6.3 Hz, 4H), 1.91-1.87 (m, center at 2.26, 4H); ^{13}C NMR δ 193.4, 154.2, 144.7, 144.1, 128.0, 126.9, 122.3, 120.9, 120.4, 49.8, 27.6, 21.45; IR 1660(C=O), 1579(C=C), 1515(C=C) cm^{-1}; UV/VIS λ_{max} (log ε) 446(4.51), 282(4.24); EIMS, m/z 253(M^+, 100), 224 (33), 196(36); Anal. Calcd. for $C_{17}H_{19}NO$: C, 80.60; H, 7.56 ; N, 5.53. Found: C, 80.38; H, 7.35; N, 5.49; HRMS calcd. for $C_{17}H_{19}NO$: 253.1467. Found: 253.1468.

7-(9-Julolidinyl)hepta-2,4,6-trien-1-al (5, n=3). 9-Bromojulolidine[10] (3.02 g, 12 mmol) was treated with *t*-butyllithium (1.7 M in hexanes, 24.6 mmol, 14.5 mL) then 7-(N,N-dimethyl-amino)hepta-2,4,6-trien-1-al (**3**, 1.31 g, 10 mmol) according to the general procedure. During workup, the basic solution was extracted with methylene chloride instead of ether. 30% ethyl acetate in hexanes was used as eluent for chromatography. Yield (R_f=0.6 spot): 1.24 g (51%) shiny dark purple plates: mp 158-159.5 °C; ^{1}H NMR (300 MHz) δ 9.51 (d, J=8.1 Hz, 1H), 7.14 (dd, J=15.0, 11.3 Hz, 1H), 6.89 (s, 2H), 6.83-6.74 (m, max at 6.74, 2H), 6.64-6.63 (m, max at 6.63, 1H), 6.40 (dd, J=14.5, 11.3 Hz, 1H), 6.09 (dd, J=15.0, 8.1 Hz, 1H), 3.19 (t, J=5.7 Hz, 4H), 2.72 (t, J=6.4 Hz, 4H), 1.96-1.93 (m, max at 1.94, 4H); ^{13}C NMR δ 193.4, 153.0, 144.7, 143.8, 139.9, 129.1, 126.78, 126.3, 123.4, 122.4, 121.1, 49.9, 27.7, 21.7; IR 1653(C=O), 1577, 1574(C=C) cm^{-1}; UV/VIS λ_{max} (log ε) 310(4.33), 470(4.51); EIMS, m/z 279(M^+, 100),

250(35), 222(38), 186(41); Anal. Calcd. for $C_{19}H_{21}NO$: C, 81.68; H, 7.58 ; N, 5.01. Found: C, 81.48; H, 7.63; N, 4.93; HRMS calcd. for $C_{19}H_{21}NO$: 279.1623. Found: 279.1621.

5-(4-N,N-Dibutylaminophenyl)penta-2,4-dien-1-al (6). N,N-Dibutylaniline (10.25 g, 50 mmol) was brominated[10] in DMF to give 1-bromo-4-(N,N-dibutyl)aniline (13.9 g, 97.6%). Crude bromide (5.1 g, 18 mmol) was treated with *n*-butyllithium (11.3 mL, 18 mmol), then 5-(N,N-diethylamino)penta-2,4-dien-1-al (**2b**, 2.30 g, 15 mmol) according to the general procedure. Yield: 2.19 g (51%) The product was crystallized from cold hexanes: mp 42-42.5 °C; ^{1}H NMR δ 9.53 (d, J= 8.1 Hz, 1H), 7.34 (d, J=8.9 Hz, 2H), 7.22 (dd, J=11.0, 15.0 Hz, 1H), 6.90 (d, J=15.3 Hz, 1H), 6.76 (dd, J=15.2,11.0 Hz, 1H), 6.58 (d, J=8.9 Hz, 2H), 6.14 (dd, J=15.0, 8.1 Hz, 1H), 3.29 (t, J=7.7 Hz, 4H), 1.59-1.53 (m, center at 1.56, 4H), 1.38-1.31 (m, center at 1.35, 4H), 0.94 (t, J=7.4 Hz, 6H); ^{13}C NMR δ 193.0, 153.7, 149.0, 143.5, 129.2, 128.1, 122.2, 120.4, 111.1, 50.4, 29.1, 20.0, 13.7; IR 1683(C=O), 1588(C=C), 1520, 1150 cm^{-1}; UV/VIS λ_{max} (log ε) 432(4.56), 276(4.16); EIMS, m/z 285(M^+, 58), 242(M-43, 100), 200(32), 118(17); Anal. Calcd. for $C_{19}H_{27}NO$: C, 79.95; H, 9.53; N, 4.91. Found: C, 79.89; H, 9.59; N, 4.85.

1-Bromo-4-[N-ethyl, N-(2-tetrahydropyranyloxyethyl)amino]benzene. Bromination with N-bromosuccimide[10] converted N-ethyl, N-(2-hydroxyethyl)aminobenzene (8.25 g, 50 mmol) to 1-bromo-4-[N-ethyl, N-(2-hydroxyethyl)-amino]benzene (5.2 g, 42.6 %); ^{1}H NMR δ 7.28 (d, J= 8.5 Hz, 2H), 6.63 (d, J=9.0 Hz, 2H), 3.76 (t, J= 5.6 Hz, 2H), 3.42 (t, J=5.8 Hz, 2H), 3.38 (q, 7.1 Hz, 2H), 1.82 (bs, 1H, changes with water content), 1.14 (t, J= 7.1 Hz, 3H). Protection of the alcohol as the tetrahydropyranyl ether was done using 3,4-dihydro-2H-pyran (5.3 g, 3 eq) in dry methylene chloride with toluenesulfonic acid catalyst. When TLC indicated that the reaction was complete, the reaction mixture was washed with aqueous $NaHCO_3$, dried over Na_2SO_4, and solvent evaporated. Yield 6.88 g (99%); ^{1}H NMR δ 7.26 (d, J=8.8 Hz, 2H), 6.58 (d, J=8.9 Hz, 2H), 4.62 (t, J=4.1 Hz, 1H), 3.92-3.81 (m, center at 3.88, 2H), 3.61-3.47 (m, max at 3.52, 4H), 3.39 (q, J=6.9 Hz, 2H), 1.88-1.47 (m, max at 1.54, 6H), 1.16 (t, J=7.3 Hz, 3H); ^{13}C NMR δ 146.7, 131.6, 113.3, 107.1, 98.9, 64.8, 62.1, 50.1, 45.3, 30.5, 25.3, 19.3, 11.9; IR 3433 (OH), 1495, 1036 cm^{-1}; EIMS, m/z 329(M+2, 1), 327(M^+, 1), 214(96), 212(100), 201(16), 199(17); Anal. Calcd. for $C_{15}H_{22}NBrO_2$: C, 54.89; H, 6.76; N, 4.27. Found: C, 54.97; H, 6.79; N, 4.23.

5-[4-(N-Ethyl, N-(2-hydroxyethyl)amino]phenyl]penta-2,4-dien-1-al. (7, n=2) 1-Bromo-4-[N-ethyl, N-(2-tetrahydropyranyloxyethyl)amino]benzene (6.88 g, 21 mmol) was treated with *t* -butyllithium (26.3 mL, 44 mmol), then 5-(N,N-diethylamino)penta-2,4-dien-1-al (**2b**, 2.48 g, 16.2 mmol) according to the general procedure. After warming to room temperature, the solution was treated with 2 M HCl and heated to 40 °C for 1 h. Normal workup, then "flash" chromatography on silica using 50% ethyl acetate in hexanes, then crystallization from cold ethyl acetate and hexanes gave 1.45 g (57.6%) orange crystals: mp 101-102 °C; ^{1}H NMR δ 9.44 (d, J=8.1 Hz, 1H), 7.33 (d, J=8.9 Hz, 2H), 7.17 (dd, J=14.9, 11.3 Hz, 1H), 6.88 (d, J=15.3 Hz, 1H),

6.73 (partially hidden dd, 1H), 6.66 (d, J=8.8 Hz, 2H), 6.10 (dd, J=15.1, 8.1 Hz, 1H), 3.78 (t, J=5.9 Hz, 2H), 3.48 (t, J=6.1 Hz, 2H), 3.44 (q, J=7.1 Hz, 2H), 1.15 (t, J=7.1 Hz, 3H); ^{13}C NMR δ 193.8, 154.4, 149.3, 143.8, 129.4, 128.2, 123.0, 121.0, 111.6, 59.7, 52.0, 45.3, 11.1; IR 3493(OH), 1642(C=O), 1579(C=C) cm^{-1}; UV/VIS λ_{max} (log ε) 418(4.48), 272(4.27); EIMS, m/z 245(M^+, 30), 214(100); Anal. Calcd. for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.34; H, 7.89; N, 5.68.

7-[4-(N-Ethyl, N-(2-hydroxyethyl) amino]phenyl]hepta-2,4,6-trien-1-al. (7, n=3) 1-Bromo-4-[N-ethyl, N-(2-tetrahydropyranyloxyethyl)amino]benzene (5.81 g, 17.7 mmol) was treated with *t* -butyllithium (21 mL, 35.5 mmol), then 7-(N,N-dimethylamino)hepta-2,4,6-trien-1-al (**3**, 2.26 g, 14.8 mmol) according to the general procedure. After warming to room temperature, the solution was treated with 2 M HCl and heated to 40 °C for 1 h. Normal workup was carried out, then "flash" chromatography on silica using 50% ethyl acetate in hexanes. Crystallization from cold ethyl acetate and hexanes gave 1.23 g (34 %) purple crystals: mp 116.5-117.5 °C; ^{1}H NMR δ 9.48 (d, J=8.1 Hz, 1H), 7.29 (d, J= 8.7 Hz, 2H), 7.12 (dd, J=15.0, 11.4 Hz, 1H), 6.79 (dd, J=14.4, 9.1 Hz, 1H), 6.73-6.65 (m, 2H), 6.68 (d, J=8.9 Hz, 2H), 6.42 (dd, J=14.3, 11.5 Hz, 1H), 6.07 (dd, J=15.0, 8.1 Hz, 1H), 3.79 (t, J=5.7 Hz, 2H), 3.49 (t, H=5.7 Hz, 2H), 3.44 (q, J=6.9 Hz, 2H), 2.01 (bs, 1H), 1.16 (t, J=7.2 Hz, 3H); ^{13}C NMR δ 193.7, 153.0, 148.7, 144.5, 139.3, 129.4, 128.7, 127.5, 124.3, 123.2, 112.0, 60.1, 52.2, 45.5, 11.9; IR 3510(OH), 1645(C=O), 1570 cm^{-1}; UV/VIS λ_{max} (log ε) 438(4.57), 304; EIMS, m/z 271(M^+, 38), 241(18), 240(M^+-OCH_3, 100); Anal. Calcd. for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N, 5.16. Found: C, 75.25; H, 7.86; N, 5.14.

1-Bromo-4-[N,N-bis(2-*t*-butyldimethylsiloxyethyl)amino]benzene. N, N-Bis(2-hydroxyethyl)-aminobenzene (18.1 g, 0.1 mol) was converted with NBS (19.6 g, 0.11 mol) using a literature procedure[10] to 1-bromo-4-[N,N-bis(2-hydroxyethyl)amino]benzene (16.1 g, 62%). The crude material was treated with *t*-butyldimethylsilylchloride (TBDMSCl) using the method of Corey[18] in 60.5% yield. An analytical sample was obtained by crystallization from pentane at -78 °C; mp 40-41 °C; ^{1}H NMR (300 MHz) δ 7.22 (d, J=8.8 Hz, 2H), 6.55 (d, J=8.9 Hz, 2H), 3.71 (t, J=6.3 Hz, 4H), 3.45 (t, J=6.3 Hz, 4H), 0.86 (s, 18H), 0.01 (s, 12H); ^{13}C NMR δ 146.9, 131.7, 107.4, 113.7, 60.1, 53.6, 25.9, 25.7, 18.2; EIMS, m/z 490(M+2, 100), 488(M^+, 93), 344(32), 342(30); Anal. Calcd. for $C_{22}H_{42}BrNO_2Si_2$: C, 54.08; H, 8.66; N, 2.87. Found: C, 54.20; H, 8.65; N, 2.89.

5-[4-[N,N-Bis(2-hydroxyethyl)amino]phenyl]penta-2,4-dien-1-al. (8) 1-Bromo-4-[N,N-bis(2-*t*-butyl-dimethylsiloxyethyl)amino]benzene (5.86 g, 12 mmol) was treated with *n*-butyllithium 8.3 mL, 13.2 mmol), then 5-(N,N-diethylamino)penta-2,4-dien-1-al (**2b**, 1.53 g, 10 mmol) according to the general procedure. The protected diol was eluted from a silica column using 4% ethyl acetate in hexanes to give crude 5-[4-[bis(N,N-(2-*t*-butyldimethylsiloxyethyl)amino]-phenyl]penta-2,4-dien-1-al (5.25 g) as an orange oil. The oil was diluted with dry THF (50 mL)

and tetrabutyl ammonium fluoride (1 M, 30 mL) added. After 1 h, the dark red solution was evaporated, and the layers partioned between methylene chloride and water. The organic layer was extracted with water, dried over Na_2SO_4, and evaporated to a red solid. The solid was passed through a silica plug with hot ethyl acetate, the solution concentrated and cooled to give 1.25 g (47.7%) red-brown powder: mp 134-134.5 °C; ^{1}H NMR (300 MHz) δ 9.53 (d, J=8.1 Hz, 1H), 7.37 (d, J=8.8 Hz, 2H), 7.21 (dd, J=15.0, 10.6 Hz, 1H), 6.94-6.74 (m, max at 6.89, 2H), 6.68 (d, J=8.3 Hz, 2H), 6.14 (dd, J=15.0, 8.1 Hz, 1H), 3.08 (s, 2H), 3.89 (t, J=4.8 Hz, 4H), 3.64 (t, J=4.8 Hz, 4H); ^{13}C NMR (DMSO d_6) δ 193.6, 154.5, 149.4, 143.7, 129.5, 128.4, 122.7, 121.2, 111.5, 58.1, 53.1; IR 3356(OH), 1646(C=O), 1578(C=C), 1518, 1152 cm^{-1}; UV/VIS λ_{max} 412; EIMS, m/z 261(M^+, 31), 230(100), 128(19), 118(29); Anal. Calcd. for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33 ; N, 5.36. Found: C, 69.00; H, 7.37; N, 5.28.

7-*t*-Butylhept-2,4,6-trien-1-al. (9) 7-(N,N-Dimethylamino)hepta-2,4,6-trien-1-al (**3**, 302 mg, 2 mmol) was treated with *t*-butyllithium (1.3 mL, 2.2 mmol) under the reaction and workup conditions in the general procedure. Yield (R_f=0.9 spot): 132 mg (40%) pale yellow oil which solidified immediately in the freezer. Bp ~40 °C (0.03 Torr, onto cold finger); ^{1}H NMR δ 9.50 (d, J=8.0 Hz, 1H), 7.07 (dd, J=15.2, 11.1 Hz, 1H), 6.60 (dd, J=14.9, 10.2 Hz, 1H), 6.33 (dd, J=14.8, 11.1 Hz, 1H), 6.07 (two overlapping dd, J=15.4, 10.1 Hz, 1H and dd, J=15.2, 8.2 Hz, 1H), 5.99 (d, J=15.4 Hz, 1H), 1.02 (s, 9H); ^{13}C NMR δ 193.5, 152.9, 152.4, 143.7, 130.4, 127.93, 124.7, 33.8, 29.1; IR 1677(C=O), 1615(C=C) cm^{-1}; EIMS, m/z 164(M^+, 16), 149(M^+-CH_3, 8), 93(13), 58(31), 43(100); Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.20; H, 9.86.

(1,3-Phenylene)-5,5'-bis(penta-2,4-dien-1-al). (10) 1,3-Dibromobenzene (1.63 g, 6.93 mmol) was treated with *t*-butyllithium (17.0 mL, 29 mmol), then 5-(N,N-diethylamino)penta-2,4-dien-1-al (**2b**, 1.94 g, 12.6 mmol) according to the general procedure. During workup, the product was extracted with ether, then eluted from a silica gel column with 30% ethyl acetate in hexanes, concentrated, then diluted with hexanes to give 0.4 g (26.2%) pale yellow feathery needles: mp 111-113 °C (the sample shrinks, turns orange before melting); ^{1}H NMR δ 9.62 (d, J=7.7 Hz, 2H), 7.58 (bs, 1H), 7.47 (two overlapping d, J=7.8 Hz, 2H), 7.39 (dd, J=8.2, 7.1 Hz, 2H), 7.25 (ddd, J=15.2, 8.2, 2.1 Hz, 2H), 7.06-6.98 (m, max at 7.00, 3H), 6.31 (dd, J=15.3, 7.9 Hz, 2H); ^{13}C NMR δ 193.3, 151.4, 141.3, 136.1, 131.9, 129.4, 128.2, 126.9, 126.4; IR 1667(C=O), 1610 cm^{-1}; UV/VIS λ_{max} (log ε) 326(4.81), 330; EIMS, m/z 238(M^+, 100), 209(M^+-CHO, 30), 191(33), 179(45), 178(38), 170(36), 166(40), 165(81), 153(37), 152(46), 141(78), 129(43), 128(59), 115(46), 81(46); Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.39; H, 5.98.

(1,4-Phenylene)-5,5'-bis(penta-2,4-dien-1-al). (11) 1,4-Dibromobenzene (2.36 g, 10 mmol) was treated with *t*-butyllithium (26 mL, 44 mmol), then 5-(N,N-diethylamino)penta-2,4-dien-1-al

(**2b**, 3.37 g, 22 mmol) according to the general procedure. During workup, the product was extracted with methylene chloride, then eluted down a silica gel column with 30% ethyl acetate in hexanes, and concentrated to give a yellow solid. Recrystallization from ethyl acetate gave 0.29 g (12%) yellow feathery needles: mp >260 °C (at 150 °C the sample shrinks, turns orange); ^{1}H NMR δ 9.62 (d, J=7.8 Hz, 2H), 7.50 (s, 4H), 7.25 (dd, J=15.2, 9.7 Hz, 2H), 7.06-6.97 (m, max at 7.00, 4H), 6.28 (dd, J=15.2, 7.8 Hz, 2H); ^{13}C NMR δ 193.4, 151.5, 141.2, 136.7, 132.1, 128.0, 127.1; IR 1668(C=O), 1615 cm^{-1}; UV/VIS λ_{max} (log ε) 380(4.82); EIMS, m/z 238(M^+, 100), 209(M-CHO, 41), 207(72), 191(56), 179(63), 178(59), 166(53), 165(78), 152(47), 141(84), 129(63), 128(81), 115(88); Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.40; H, 6.00.

5-[4-Bromophenyl]penta-2,4-dien-1-al. (12) 1,4-Dibromobenzene (5.19 g, 22 mmol) was treated with *n*-butyllithium (29 mL, 48.5 mmol) then 5-(N,N-diethylamino)penta-2,4-dien-1-al (**2b**, 3.06 g, 20 mmol) according to the general procedure to give 0.99 g (20.8%) pale yellow needles: mp 83.5-84.5 °C; ^{1}H NMR δ 9.61 (d, J=7.9 Hz, 1H), 7.49 (d, J=8.4 Hz, 2H), 7.35 (d, J=8.4 Hz, 2H), 7.23 (dd, J=15.3, 9.6 Hz, 1H), 7.00-6.91 (m, max at 6.93, 2H), 6.27 (dd, J=15.2, 7.9 Hz, 1H); ^{13}C NMR δ 193.4, 151.4, 140.8, 134.4, 132.1, 132.0, 128.8, 126.7, 123.7; IR 1674(C=O), 1619 cm^{-1}; UV/VIS λ_{max} (log ε) 330(4.63), 244(3.88); EIMS, m/z 238(M+2, 37), 236(M^+, 33), 157(35), 129(97), 128(100), 127(35); Anal. Calcd. for $C_{11}H_9BrO$: C, 55.73; H, 3.83; Br, 33.70. Found: C, 55.62; H, 3.80; Br, 33.66.

2,5-Thiophenyl-7,7'-bis(hepta-2,4-6-trien-1-al) (13). 2,5-Dibromothiophene (798 mg, 3.3 mmol) was treated with *t*-butyllithium (7.8 mL, 13.4 mmol), then 7-(N,N-dimethylamino)hepta-2,4,6-trien-1-al (**3**, 906 mg, 6 mmol) according to the general procedure. During workup, the product was extracted with methylene chloride, and the organic layer dried and evaporated. A yellow fraction eluted from a two inch silica plug with methylene chloride, and an orange fraction with 5% ethanol in methylene chloride. The orange fraction was concentrated, hot filtered from ethyl acetate, and crystallized from ethyl acetate and hexanes to give 110 mg (12%) red-orange powder: mp 159-160 °C; ^{1}H NMR δ 9.57 (d, J=7.9 Hz, 2H), 7.15 (dd, J=15.1, 10.9 Hz, 2H), 6.97 (s, 2H), 6.86 (d, 14.8 Hz, 2H), 6.77 (dd, J=14.3, 11.0 Hz, 2H), 6.69 (dd, J=14.8, 11.0 Hz, 2H), 6.56 (dd, J=14.3, 11.3 Hz, 2H), 6.20 (dd, J=14.9, 7.9 Hz, 2H); ^{13}C NMR δ 193.4, 151.3, 142.8, 141.8, 131.3, 130.6, 130.3, 129.3, 128.3; IR 1659(C=O), 1583(C=C) cm^{-1}; EIMS, m/z 296(M^+, 100), 267(M-CHO, 16), 173(34), 115(42), 77(53). In spite of clean NMR spectra, a satisfactory analysis was not obtained. Use of thiophene as starting material resulted in a comparable yield.

Ferrocene (penta-2,4-dien-1-al) Compounds. Ferrocene (3.72 g, 20 mmol) was treated with *t*-butyllithium (25 mL, 40 mmol) according to the general procedure except that the organolithium reagent was stirred at room temperature for 2 h before cooling to -78 °C and adding 5-(N,N-

diethylamino)penta-2,4-dien-1-al (**2b**, 3.02 g, 10 mmol). The crude material was loaded as a solid on a silica gel column. Hexanes eluted ferrocene, 50% ethyl acetate in hexanes eluted a red fraction and ethyl acetate eluted a second major dark red product. Evaporation of the first fraction and crystallization from ethyl acetate in hexanes gave red needles assigned as:

5-(1-Ferrocenyl)penta-2,4-dien-1-al (14). Yield: 1.94 g, 36%; mp 134-134.5 °C; ^{1}H NMR (300 MHz) δ 9.54 (d, J=8.0 Hz, 1H), 7.14 (dd, J=15.1, 11.1 Hz, 1H), 6.87 (d, J=15.2 Hz, 1H), 6.58 (dd, J=15.3, 11.1 Hz, 1H), 6.13 (dd, J=15.1, 8.0 Hz, 1H), 4.48 (t, J=1.7 Hz, 2H), 4.42 (t, J=1.7 Hz, 2H), 4.14 (s, 5H); ^{13}C NMR δ 193.8, 152.8, 143.6, 128.9, 123.8, 80.3, 70.9, 69.7, 68.2; IR 1666(C=O), 1658(C=O), 1605(C=C) cm^{-1}; UV/VIS λ_{max} (log ε) 504(3.56), 338(4.43); EIMS, m/z 267(M+1, 19), 266(M$^+$, 100), 237(M-CHO, 20), 172(30), 121(26), 115(25), 56(27); Anal. Calcd. for $C_{15}H_{14}FeO$: C, 67.70; H, 5.30. Found: C, 67.58; H, 5.35.

Evaporation of the second fraction and crystallization from ethyl acetate resulted in brown powder assigned as:

(1,1'-Ferrocenediyl)-5,5'-bis(penta-2,4-dien-1-al) (15): Yield: 0.36 g, 10.2%; mp>260 °C; ^{1}H NMR (300 MHz) δ 9.51 (d, J=7.9 Hz, 2H), 7.04 (dd, J=15.1, 10.9 Hz, 2H), 6.61 (d, J=15.3 Hz, 2H), 6.45 (dd, J=15.3, 10.9 Hz, 2H), 6.09 (dd, J=15.1, 7.9 Hz, 2H), 4.43 (t, J=1.7 Hz, 4H), 4.37 (t, J=1.6 Hz, 4H); ^{13}C NMR δ 193.4, 152.2, 141.8, 129.3, 124.5, 81.7, 72.1, 69.3; IR 1670(C=O), 1607(C=C) cm^{-1}; UV/VIS λ_{max} (log ε) 506(3.6), 356(4.43), 316(4.54); EIMS, m/z 347(M+1, 25), 346(M$^+$, 100), 201(13), 171(38), 115(45), 91(10), 56(26); Anal. Calcd. for $C_{20}H_{18}FeO_2$: C, 69.39; H, 5.24. Found: C, 69.14; H, 5.57.

General Procedure for Knoevenagel Condensation of Aldehydes with Acceptors. Donor-substituted aldehyde (1 eq) was dissolved in warm anhydrous ethanol (20 mL/mmol). Acceptor (1.1 equivalent) was added in ethanol (minimum) and the mixture heated at reflux for 1 h under argon. If a color change did not occur swiftly, catalytic piperidine (1 drop or less) was added and the reaction continued until TLC indicated that the reaction was complete. Unless the product preferentially crystallized, the ethanol was evaporated and residue eluted from a silica column. Crystallization from methylene chloride in hexanes, or ethyl acetate in hexanes gave analytically pure materials. Modifications of the above procedure are indicated for each compound.

N,N'-Diethyl 5-[5-[4-(N,N-bis(2-hydroxyethylamino)phenyl]penta-2,4-dien-1-ylidene]thiobarbituric Acid. (16) 5-[4-[N,N-Bis(2-hydroxyethyl)amino]phenyl]penta-2,4-dien-1-al (**8**, 783 mg, 3 mmol) was treated with N,N-diethyl thiobarbituric acid (660 mg, 9.9 mmol) as in the general procedure for Knoevenagel condensation above. The major product precipitated as a green solid from the reaction mixture, was filtered and washed with ethanol to give 1.28 g (94 %) of a cottony green solid: mp 188-189 °C; ^{1}H NMR δ (200 MHz) 8.14-7.95 (m, max at 8.07, 2H), 7.37 (d, J= 9.0 Hz, 2H), 7.31 (dd, J=11.0, 13.3 Hz, 1H), 7.05-6.94 (m, 2H), 6.72 (bd, J= 9.0 Hz, 2H), 4.55, 4.53 (q, 4.0 Hz, 2H), 3.90 (t, J= 4.5 Hz, 4H), 3.67 (t, J= 4.7 Hz, 4H), 3.11 (bs, 2H),

1.30, 1.29 (t, J=7.3 Hz, 3H); ^{13}C NMR δ (DMSO d_6) 178.2, 160.3, 160.1, 159.3, 157.3, 150.8, 148.6, 131.1 (2C), 126.3, 123.7, 123.1, 112.0 (2C), 110.0, 58.2 (2C), 53.2 (2C), 42.9, 42.4, 12.3(2C); IR 3422(OH), 1654(C=O), 1508, 1388 cm^{-1}; UV/VIS λ_{max} (log ε) 580(4.75), 380, 348, 300; EIMS, m/z 443(M^+, 69), 412(100), 200(25); Anal. Calcd. for $C_{23}H_{29}N_3O_4S$: C, 62.28; H, 6.59; N, 9.47; S, 7.23. Found: C, 62.04; H, 6.66; N, 9.42.; S, 7.15.

N-N-Diethyl 5-[5-[4-[N-Ethyl,N-(2-hydroxyethyl)amino]phenyl]penta-2,4-dien-1-ylidene]-thiobarbituric Acid. (17, n=2) 5-[4-(N-Ethyl, N-(2-hydroxyethyl)amino]phenyl]penta-2,4-dien-1-al (**7, n=2,** 0.49 g, 2 mmol) was treated with N,N-diethylthiobarbituric acid (0.44 g, 2.2 mmol) as in the general procedure for Knoevenagel condensation above. The major product precipitated as a green solid from the reaction mixture, was filtered and washed with ethanol to give 446 mg (52.2%). The filtrate was concentrated and residue separated by column chromatography on silica gel using methylene chloride as eluent to give ~20 mg more: mp 173-173.5 °C ; ^{1}H NMR δ 8.09-7.98 (m, max at 8.09, 2H), 7.37 (d, J=8.9 Hz, 2H), 7.28 (dd, J=11.0, 8.7 Hz, 1H), 7.00 (d, J=15.1 Hz, 1H), 6.95 (dd, J=15.0, 11.0 Hz, 1H), 6.70 (d, J=8.8 Hz, 2H), 4.79 (q, J=6.8 Hz, 2H), 4.52 (q, J=6.8 Hz, 2H), 3.82 (q, J=4.4 Hz, 2H), 3.54 (t, J=5.9 Hz, 2H), 3.48 (q, J=7.0, 2H), 1.79 (bs, 1H), 1.28 (t, J=6.9 Hz, 3H), 1.26 (t, J=6.9 Hz, 3H), 1.19 (t, J=7.0 Hz, 3H); ^{13}C NMR δ 178.7, 161.0, 159.9, 158.6, 158.3, 150.2, 147.0, 130.6, 127.4, 123.9, 123.8, 112.0, 111.4, 60.2, 52.2, 45.8, 43.6, 43.0, 12.4 (2 C), 12.0; IR 3448(OH), 1655(C=O), 1498(C=C), 1388 cm^{-1}; UV/VIS λ_{max} (log ε) 604(4.76); EIMS, m/z 427(M^+, 44), 396(100); Anal. Calcd. for $C_{23}H_{29}N_3O_3S$: C, 64.61; H, 6.84; N, 9.83; S, 7.50. Found: C, 64.51; H, 6.87; N, 9.77; S, 7.51.

N,N'-Diethyl 5-[7-[4-[N-ethyl-N-(2-hydroxyethyl)amino]phenyl]hepta-2,4,6-trien-1-ylidene]thiobarbituric Acid. (17, n=3) 7-[4-(N-Ethyl, N-(2-hydroxyethyl)amino]phenyl]hepta-2,4,6-trien-1-al (**7, n=3**, 0.41 g, 1.5 mmol) was treated with N,N-diethylthiobarbituric acid (0.33 g, 1.65 mmol) according to the general procedure for Knoevenagel condensation above. The major product precipitated as a green solid from the reaction mixture, was filtered and washed with ethanol to give 646 mg (71%). The filtrate was concentrated and products separated by column chromatography on silica gel using methylene chloride as eluent to give 20 mg more: mp 185.3 °C, 189.4 °C dec., DSC); ^{1}H NMR δ 8.07 (d, J=12.7 Hz, 1H), 7.98 (apparent t, J=13.3 Hz, 1H), 7.34 (d, J=8.8 Hz, 2H), 7.22 (dd, J= 13.7, 12.0 Hz, 1H), 6.93 (dd, J=14.2, 9.7 Hz, 1H), 6.83-6.77 (m, max at 6.80, 2H), 6.69 (d, J= 8.8 Hz, 2H), 6.57 (dd, J=14.0, 11.8 Hz, 1H), 4.53, 4.51 (q, J=6.9 Hz, 2H), 3.82 (q, J=5.3 Hz, 2H), 3.52 (t, J=5.8 Hz, 2H), 3.47 (q, J=7.0 Hz, 2H), 1.61 (unresolved t, 1H), 1.28 (t, J=7.1 Hz, 3H), 1.27 (t, J=7.1 Hz, 3H), 1.18 (t, J=7.1 Hz, 3H); ^{13}C NMR δ 178.8, 160.9, 159.9, 158.0, 157.3, 149.3, 147.7, 141.8, 130.2, 129.5, 128.4, 124.4, 123.9, 112.2, 112.1, 60.3, 52.2, 45.6, 43.6, 43.1, 12.4 (2 C), 12.0; IR 3394(OH), 1656(C=O), 1516(C=C) cm^{-1}; UV/VIS/NIR λ_{max} (log ε) 618(4.78), 424, 398, 380, 314, 292;

EIMS, m/z 453(M^+, 33), 451(M-2, 47), 422(100), 420(92), 221(34); Anal. Calcd. for $C_{25}H_{31}N_3O_3S$: C, 66.20; H, 6.89 ; N, 9.26; S, 7.07. Found: C, 66.11; H, 6.93; N, 9.19; S, 7.13.

4-[5-[4-N-Ethyl,N-(2-hydroxyethyl)amino]phenyl]penta-2,4-dien-1-ylidene]-5-phenyl-3-isoxazolone. (18) 5-[4-(N-Ethyl, N-(2-hydroxyethyl)amino]phenyl]penta-2,4-dien-1-al (**7, n=2,** 0.49 g, 2.0 mmol) was treated with 5-phenyl-3-isoxazolone (0.35 g, 2.2 mmol) as in the general procedure for Knoevenagel condensation above. Two major products were separated by column chromatography on silica gel using 20 % ethyl acetate in methylene chloride eluent. The second fraction consisted of a 80 mg mixture of isomers; mp 130.4, 136.5 °C (201.5 °C dec, DSC); ^1H NMR δ 7.81 (dd, J=14.1, 12.3 Hz, 1H), 7.58-7.49 (m, max at 7.51, 5H), 7.36 (d, J=9.0 Hz, 2H), 7.33 (d, 12.4 Hz, 1H), 7.09 (ddd, J=14.2, 8.3, 2.2 Hz, 1H), 6.69 (d, J=9.0 Hz, 2H), 3.81 (t, J= 5.9 Hz, 2H), 3.53 (q, J=5.9 Hz, 2H), 3.48 (q, J=7.1 Hz, 2H), 1.76 (bs, 1H), 1.18 (t, J= 7.0 Hz, 3H); ^{13}C NMR δ (DMSO, d_6) 169.4, 161.9, 155.5, 150.4, 149.0, 147.7, 141.7, 130.6, 130.4, 129.3, 128.9, 127.9, 127.6, 124.3, 123.3, 123.2, 111.5, 58.3, 51.9, 44.6, 11.8; IR ~3400 (OH), 1734, 1716 , 1709 (C=O), 1614, 1506 (C=C) cm^{-1}; UV/VIS λ_{max} (log ε) 562(4.71), 334; EIMS, m/z 388(M^+, 40), 357(100), 315(43), 153(32), 103(48), 77(57), 44(58); Anal. Calcd. for $C_{24}H_{24}N_2O_3$: C, 74.21; H, 6.23 ; N, 7.21. Found: C, 73.93; H, 6.24; N, 7.15.

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