Tandem Michael Reaction. Synthesis of Bridged Diketones

T. R. Kasturi,* P. V. P. Pragnacharyulu, and P. Amrutha Reddy

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India

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Addition of NaOMe, NaOEt, or NaOPr^i to dispironaphthalenone 1 resulted in the formation of diketones 4a–c and 5a–c. The structure assigned to 4a was confirmed by conversion to the known hemiacetal 3. Similar addition of carbon nucleophiles like diethyl malonate, dimethyl malonate, methyl cyanoacetate, and ethyl cyanoacetate afforded diketones 4d–g. Formation of these compounds has been rationalized.

Formation of dispironaphthalenone 1 by oxidative coupling of bis(2-hydroxynaphthyl)methane by a variety of oxidizing agents (DDQ, NaOBr, $K_4Fe(CN)_6$) has been reported.[1] On the basis of the fact that the two naphthalenone rings in 1 are nearly parallel to each other,[1] compounds 2 and 3 have, respectively, been synthesized by photochemically allowed $\pi_2S + \pi_2S$ addition[2] or borohydride reduction followed by intramolecular Michael addition[3] (Scheme I). It may be mentioned that intramolecular Michael reaction is a key step in the synthesis of polycyclic structures.[4] It was visualized that addition of oxygen or carbon nucleophiles to 1 could lead to compounds of the type 4 and 5 having two keto groups (Scheme II). With suitable modifications it may be possible to transform 4 or 5 to tweezer type of host molecules.[5] Results obtained in the tandem Michael reaction of dispironaphthalenone 1 are discussed below.

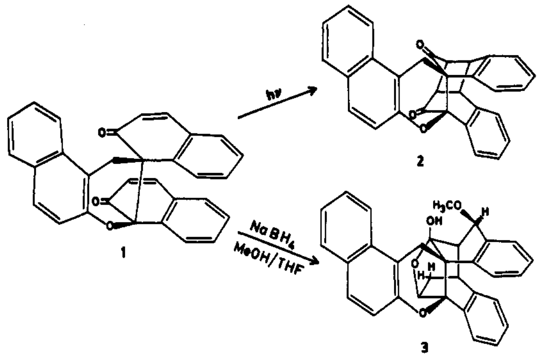
Results and Discussion

Addition of dispironaphthalenone 1 to a well-stirred solution of NaOMe at room temperature resulted, after purification, in two isomeric ($C_{32}H_{24}O_4$, *m/e* 472) keto compounds in the ratio (7:1) designated as A and B in the order of increasing polarity. Compound A showed in its ^1H NMR spectrum a multiplet at δ 2.68–2.77 (2 H), a singlet at δ 3.33 (3 H, OMe), an AB quartet of naphthopyran methylene protons centered at δ 3.93 (J = 18.5 Hz), and a broad singlet at δ 4.40 (1 H). The presence of two keto groups was evident from its ^{13}C NMR spectrum. Compound B showed in its ^1H NMR spectrum two doublet of doublets at δ 2.47 (J = 19.1, 5.1 Hz, 1 H) and 2.65 (J = 19.1, 1.0 Hz, 1 H) constituting an AB quartet centered at δ 2.56 further split by a vicinal one-proton multiplet at δ 3.61–3.65, a doublet at 4.59, and an AB quartet centered at δ 3.63 (J = 14.2 Hz).

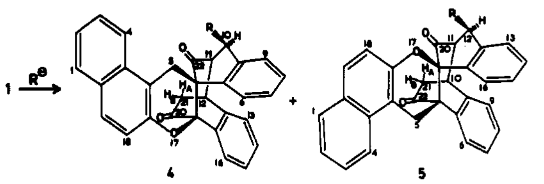
The above spectral characteristics of the two compounds indicate that the alkoxide addition followed by Michael reaction has taken place. The isomeric ketones A and B isolated may be the result of the initial alkoxide addition either in D or E ring followed by intramolecular Michael reaction. The individual assignment of structures to compounds A and B was made on the basis of chemical transformation to a known compound. $NaBH_4$ reduction of ketone A in MeOH/THF at 0 °C resulted in the formation of the known hemiacetal 3, while that of B gave a new hemiacetal 6 (Scheme III). As the methoxy group in compound 3 is present in the D ring, structure 4a was tentatively assigned to compound A. Accordingly, the isomeric structure 5a was assigned to compound B.

The observed major difference in the ^1H NMR signals of the two compounds can be explained in terms of structures 4a and 5a. In the case of compound 4a, the nonbenzylic methylene protons appear as a multiplet at δ 2.62–2.77, whereas they appear as two doublet of doublets at δ 2.47 (J = 19.1, 5.1 Hz, 21-H_A) and 2.65 (J = 19.1, 1.0 Hz, 21-H_B) in 5a (Figure 1). This could be the result of different dihedral angles subtended by 21-H_A and 21-H_B with 12-H. The characteristic splitting pattern of the two methylene protons (Figure 1) in the compounds 4a and 5a

Scheme I



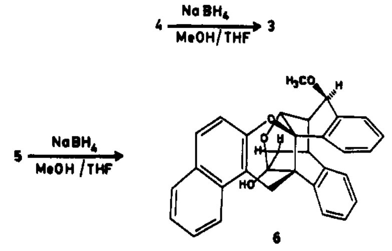
Scheme II



4
(a) R = OCH_3
(b) R = OC_2H_5
(c) R = OC_3H_7
(d) R = $CH(COOEt)_2$
(e) R = $CH(COOMe)_2$
(f) R = $CH(CN)COOMe$
(g) R = $CH(CN)COOEt$

5
(a) R = OCH_3
(b) R = OC_2H_5
(c) R = OC_3H_7

Scheme III



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[1] (a) Kasturi, T. R.; Rajasekhar, B.; Raju, G. J.; Madhusudhan Reddy, G.; Sivaramakrishnan, R.; Ramasubbu, N.; Venkatesan, K. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2375–82. (b) Kasturi, T. R.; Jayaram, S. K. *Ind. J. Chem.* **1991**, *30B*, 385–389.

[2] Kasturi, T. R.; Amrutha Reddy, P.; Raju, G. J.; Madhusudhan Reddy, G.; Ramamurthy, V. *Ind. J. Chem.* **1988**, *27B*, 5–11.

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[4] (a) Gurst, J. E.; Miller, R. W.; McPhail, A. J. *Tetrahedron Lett.* **1980**, *21*, 3223. (b) Corey, E. J.; Ohno, M.; Mitra, R. B.; Vatakencherry, P. A. *J. Am. Chem. Soc.* **1964**, *86*, 478. (c) Woodward, R. B.; Brutschy, F. J. *J. Am. Chem. Soc.* **1948**, *70*, 4216.

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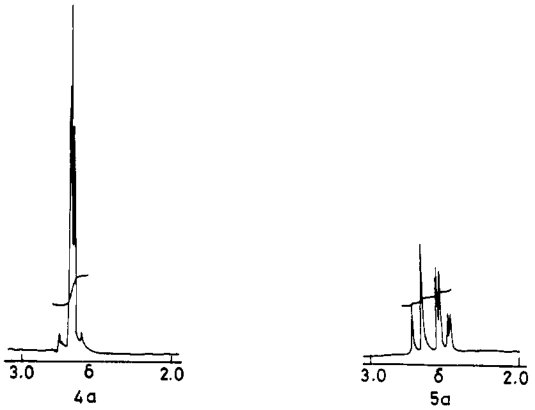


Figure 1. Splitting pattern of nonbenzylic methylene protons.

could be used as a diagnostic tool in assigning structures to these sets of compounds (vide infra).

When similar reaction of dispironaphthalenone 1 was carried out with NaOEt or NaOPr^i, sets of two isomeric ketones **4b**,**5b** and **4c**,**5c** were, respectively, obtained. The structures of these compounds were evident from the splitting pattern of the nonbenzylic methylene protons discussed above.

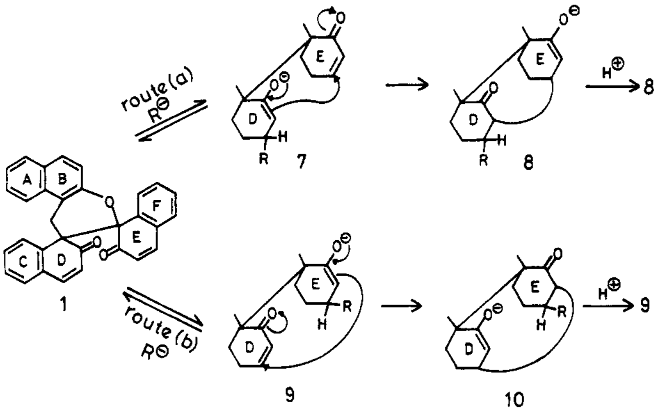
As already mentioned, it was envisaged to extend the above reaction to carbon nucleophiles like malonates, cyanoacetates, etc. The Michael reaction of malonates with a wide variety of enone systems in the presence of various basic reagents has been well-documented in the literature.[6] The reaction of dispironaphthalenone 1 (0.5 mmol) with the anion (0.5 mmol) generated from diethyl malonate and KOBu^t in *tert*-butyl alcohol–THF (1 h, 0 °C) afforded, after workup and purification, surprisingly a single white crystalline [$C_{38}H_{32}O_7$, *m*/*e* 600] keto compound. The presence of ester groups in this compound was evident from the signals at δ 1.16 (t, *J* = 7.0 Hz, 3 H), 1.18 (t, *J* = 8.0 Hz, 3 H), and 3.98–4.22 (m, 4 H) in its ^{1}H NMR spectrum. The other important signals are a two-proton multiplet at δ 2.57–2.75, an AB quartet centered at δ 3.94 (naphthopyran methylene protons), and one-proton signals at δ 3.53 (d, *J* = 8.3 Hz), 3.57 (d, *J* = 6.9 Hz), 3.69–3.74 (m), and 3.80 (d, *J* = 6.9 Hz). The spectral characteristics indicate that the expected tandem Michael reaction has occurred. On the basis of the nature of splitting of the nonbenzylic methylene protons (vide supra), this compound is tentatively assigned the structure **4d**. The one-proton signals at δ 3.53, 3.57, 3.69–3.74, and 3.80 were assigned to 11-H, ester methine, 12-H, and 10-H, respectively, based on double-irradiation experiments. The appearance of protons 10-H and 11-H as only doublets may be attributed to the dihedral angle of nearly 90° subtended by them.

When similar reactions of the dispironaphthalenone 1 were carried out with the anions of dimethyl malonate, methyl cyanoacetate, and ethyl cyanoacetate, corresponding diketones **4e–g** were obtained.

It is thus evident that the D-ring enone system is more susceptible to 1,4-addition compared to the E-ring enone system in oxygen as well as carbon nucleophilic additions.

Formation of the diketones **4** and **5** can be visualized to occur as shown in Scheme IV. Even though a protic solvent (*tert*-butyl alcohol) is present in the reaction mixture, we believe that the protonation of enolates **8** and **10** takes place by glacial acetic acid used for quenching.

Scheme IV



It is well-known that in Michael reactions conducted with 1 full equiv of base the proton is supplied by the neutralization step.[6a]

The diketones **4** and **5** can thus be conveniently prepared in two steps from bis(2-hydroxynaphthyl)methane.

Experimental Section

General. All melting points are uncorrected. NMR spectra were recorded in $CDCl_3$ on a Bruker WH-270 spectrometer. Mass spectra were recorded at 70 eV and with a built-in direct-inlet system. Analytical and preparative TLC were carried out using silica gel supplied by BDH (Bombay). For column chromatography, silica gel supplied by Acme Synthetic Chemicals (Bombay) was used. All anhydrous solvents used were prepared by standard procedures. Ether refers to diethyl ether. Petroleum ether refers to the fraction boiling between 60 and 80 °C. All organic extracts were dried over anhydrous Na_2SO_4. All compounds reported are racemic mixtures.

General Procedure for Reaction of Dispironaphthalenone 1 with Alkoxides. Sodium alkoxide was prepared by dissolving sodium (23 mg, 1 mmol) in absolute alcohol under N_2 and diluted with dry THF (5 mL). To a well-stirred solution of this, dispironaphthalenone 1 (440 mg, 1 mmol) in dry THF (20 mL) was added dropwise over 30 min at 25 °C. It was stirred at the same temperature for 3 h by which time the yellow color of the starting material disappeared. The reaction mixture was treated with a few drops of glacial HOAc, and the solvent was removed in vacuo. After the addition of water (50 mL), the compound was extracted with ether (3 × 30 mL) and the combined ethereal layer was washed thoroughly with water (3 × 30 mL) and dried.

11,12-Dihydro-5*H*,10*H*-12,16b-ethano-5a,11-methano-10-methoxydibenzo[3,4:8,9]cyclonona[1,2-*b*]naphtho[1,2-*e*]pyran-20,22-dione (4a) and 11,12-Dihydro-5*H*,10*H*-5a,10-ethano-11,16b-methano-12-methoxydibenzo[3,4:8,9]cyclonona[1,2-*b*]naphtho[1,2-*e*]pyran-20,22-dione (5a). The reaction of dispironaphthalenone 1 with NaOMe in methanol–THF, after purification by preparative TLC (benzene–EtOAc(7:1)) gave (i) **4a** (180 mg, 38%) as white silky needles [mp 178–180 °C (CH_2Cl_2–MeOH); UV ($CHCl_3$) 322 (2700), 317 (2200), 288 (4300), 278 (6500), 267 (6500), 244 (26000); IR (Nujol) 1725, 1705 (two C=Os); ^{1}H NMR 2.62–2.77 (m, 2 H, 21-H_2), 3.33 (s, 3 H, OCH_3), 3.42 (d, *J* = 18.5 Hz, 1 H, 5-H), 3.68–3.78 (m, 2 H, 11-H and 12-H), 4.43 (d, *J* = 18.5 Hz, 1 H, 5-H), 4.40 (br s, 1 H, 10-H), 6.73–6.78 (m, 2 H), 6.90–7.01 (m, 3 H), 7.10–7.21 (m, 3 H), 7.37 (d, *J* = 8.9 Hz, 1 H, 18-H), 7.43 (ddd, 1 H, 2-H/3-H), 7.56 (ddd, 1 H, 2-H/3-H), 7.80 (d, *J* = 8.9 Hz, 1 H, 19-H), 7.88 (d, *J* = 7.7 Hz, 1 H, 1-H), 7.96 (d, *J* = 8.3 Hz, 1 H, 4-H); ^{13}C NMR 23.81 (t, C-5), 36.76 (d, C-12), 39.18 (t, C-21), 55.30 (s, C-5a), 55.46 (d, C-11), 55.93 (q, OCH_3), 83.83 (d, C-10), 87.59 (s, C-16b), 111.32 (s, C-4b), 111.83 (d, C-18), 122.08 (d), 123.82 (d), 126.53 (d), 126.75 (d), 127.32 (d), 127.42 (d), 128.04 (d), 128.12 (d), 128.71 (d), 129.11 (d), 129.54 (d), 129.78 (s), 131.86 (s), 133.43 (s), 135.11 (s), 137.24 (s), 140.31 (s), 149.46 (s, C-17a), 202.96 (s, C=O), 207.37 (s, C=O); MS *m*/*e* (relative intensity) 472 (M$^+$, 76), 440 (30), 381 (70), 282 (43), 281 (100), 269 (58); HRMS calcd for $C_{32}H_{24}O_4$ 472.1675, found 472.1663] and (ii) **5a** (25 mg, 5.3%) as white silky needles: mp 303–305 °C dec ($CHCl_3$–petroleum ether); UV ($CHCl_3$) 330 (2100),

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[6] (a) Bergmann, E. D.; Ginsburg, D.; Pappo, R. *Org. React.* **1959**, *10*, 179. (b) House, H. O. *Modern Synthetic Reactions*; Benjamin: New York, 1972; p 595.

315 (2000), 288 (5000), 278 (6800), 270 (6400), 244 (15 100); IR (Nujol) 1725, 1710 (C=O); ^{1}H NMR 2.47 (dd, *J* = 19.1, 5.1 Hz, 1 H, 21-H_A), 2.65 (dd, *J* = 19.1, 0.9 Hz, 1 H, 21-H_B), 3.28 (s, 3 H, OCH_3), 3.49 (d, *J* = 14.3 Hz, 1 H, 5-H), 3.61–3.65 (m, 1 H, 10-H), 3.73 (dd, 1 H, 11-H), 3.76 (d, *J* = 14.3 Hz, 1 H, 5-H), 4.59 (d, 1 H, 12-H), 6.87–7.21 (m, 7 H, 7.41 (ddd, 2 H), 7.57 (ddd, 2 H), 7.76 (d, *J* = 8.8 Hz, 1 H), 7.86 (d, *J* = 8.1 Hz, 1 H), 8.12 (d, *J* = 8.5 Hz, 1 H); MS *m/e* (relative intensity) 472 (M^+, 86), 282 (37), 281 (100); HRMS calcd for $C_{32}H_{24}O_4$ 472, 1675, found 472.1653.

11,12-Dihydro-5*H*,10*H*-12,16b-ethano-10-ethoxy-5a,11-methanodibenzo[3,4:8,9]cyclonona[1,2-*b*]naphtho[1,2-*e*]pyran-20,22-dione (4b) and 11,12-Dihydro-5*H*,10*H*-5a,10-ethano-12-ethoxy-11,16b-methanodibenzo[3,4:8,9]cyclonona[1,2-*b*]naphtho[1,2-*e*]pyran-20,22-dione (5b). The reaction of dispironaphthalenone 1 with NaOEt in ethanol–THF followed by purification of reaction product by preparative TLC (benzene–EtOAc(9:1)) afforded two compounds viz. (i) **4b** (140 mg, 29%) as white silky needles [mp 176–177 °C ($CHCl_3$–petroleum ether); MS *m/e* (relative intensity) 486 (M^+, 85), 381 (72), 282 (54), 281 (100), 269 (67); HRMS calcd for $C_{33}H_{26}O_4$ 486.1831, found 486.1819] and (ii) **5b** (25 mg, 5.1%) as a white crystalline solid: mp 238–240 °C ($CHCl_3$–petroleum ether); MS *m/e* (relative intensity) 486 (M^+, 100), 282 (33), 281 (72); HRMS calcd for $C_{33}H_{26}O_4$, 486.1831, found 486.1804.

11,12-Dihydro-5*H*,10*H*-12,16b-ethano-10-isopropoxy-5a,11-methanodibenzo[3,4:8,9]cyclonona[1,2-*b*]naphtho[1,2-*e*]pyran-20,22-dione (4c) and 11,12-Dihydro-5*H*,10*H*-5a,10-ethano-12-isopropoxy-11,16b-methanodibenzo[3,4:8,9]cyclonona[1,2-*b*]naphtho[1,2-*e*]pyran-20,22-dione (5c). The crude product obtained in the reaction of dispironaphthalenone 1 with $NaOPr^i$ in isopropyl alcohol–THF on preparative TLC (benzene–EtOAc (23:2)) followed by crystallization afforded (i) **4c** (135 mg, 27%) as a white crystalline solid [mp 237–239 °C (benzene–petroleum ether); MS *m/e* (relative intensity) 500 (M^+, 64), 282 (48), 281 (100), 269 (56); HRMS calcd for $C_{34}H_{28}O_4$ 500.1988, found 500.1975] and (ii) **5c** (30 mg, 6%) as a white crystalline solid: mp 235–237 °C ($CHCl_3$–petroleum ether); MS *m/e* (relative intensity) 500 (M^+, 88), 282 (40), 281 (100), 269 (17), 43 (30); HRMS calcd for $C_{34}H_{28}O_4$ 500.1988, found 500.1909.

11,12-Dihydro-5*H*,10*H*-12,20-methano-10-methoxy-16b,5a,11-(methanoxymethano)dibenzo[3,4:8,9]cyclonona-[1,2-*b*]naphtho[1,2-*e*]pyran-22-ol (3). To a solution of diketone **4a** (200 mg) s in absolute methanol–dry THF (1:1 v/v, 20 mL) mixture was added $NaBH_4$ (20 mg) slowly with stirring at 0 °C. Stirring was continued for 1 h at 0 °C and then at room temperature for 1 h more. Solvent was completely removed in vacuo and the residue stirred with saturated NH_4Cl solution (25 mL). The compound was extracted into CH_2Cl_2 (3 × 30 mL) and the combined extract washed with water (3 × 25 mL) and brine (25 mL) and dried. Removal of solvent followed by recrystallization of the residue from $CHCl_3$–petroleum ether afforded the known hemiacetal 3 (190 mg, 95%) as a white crystalline solid, mp 273 °C dec (lit.[3] 272 °C dec).

11,12-Dihydro-5*H*,10*H*-10,22-methano-12-methoxy-5a,11,16b-(methanoxymethano)dibenzo[3,4:8,9]cyclonona-[1,2-*b*]naphtho[1,2-*e*]pyran-20-ol (6). A similar reaction of diketone **5a** (20 mg) with $NaBH_4$ (5 mg) in absolute methanol–dry THF (1:1, v/v 10 mL) for 2 h furnished the hemiacetal **6** (16 mg, 80%) as a white crystalline solid: mp 265–266 °C (acetone–petroleum ether); IR (Nujol) 3425 (OH); ^{1}H NMR 1.35 (d with further splitting, 1 H, 23-H_A), 2.19 (d with further splitting, 1 H, 23-H_B), 2.90 (dd, *J* = 6.0, 1.0 Hz, 11-H), 3.20–3.30 (m, 1 H, 10-H), 3.52 (s, 3 H, OCH_3), 3.71 (AB quartet center, $\Delta\nu_{AB}$ = 212 Hz, J_{AB} = 14.5 Hz, 2 H, 5-H_2), 3.81 (br s, 1 H, 22-H), 4.11 (d, *J* = 1.0 Hz, 1 H, 12-H), 4.58 (s, 1 H, D_2O exchangeable, OH), 6.90–7.17 (m, 7 H), 7.31 (d, *J* = 8.8 Hz, 1 H), 7.40 (ddd, 1 H), 7.47–7.56 (m, 2 H), 7.82 (d, *J* = 8.8 Hz, 1 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.99 (d, *J* = 8.5 Hz, 1 H); MS *m/e* (relative intensity) 474 (M^+, 30), 442 (52), 370 (38), 282 (43), 281 (100), 265 (36), 252 (23), 239 (32), 128 (79), 115 (30); HRMS calcd for $C_{32}H_{26}O_4$ 474.1831 found 474.1848.

Addition of Carbon Nucleophiles to Dispironaphthalenone 1. General Procedure. To a solution of potassium (20 mg, 0.5 mmol) in dry *tert*-butyl alcohol (5 mL) was added either malonates or cyanoacetates (2.5 mmol) with stirring at 0 °C in nitrogen atmosphere. After 15 min, a solution of dispironaphthalenone 1 (220 mg, 0.5 mmol) in THF (15 mL) was introduced dropwise over a 30-min period. The yellow color of the starting material disappeared instantaneously during the addition itself. Stirring was continued for another 30 min at the same temperature and the reaction quenched by the addition of a few drops of glacial HOAc. Solvent was removed in vacuo, and after the addition of water (30 mL), the compound was extracted with CH_2Cl_2 (3 × 25 mL). The combined CH_2Cl_2 extract was washed with water (3 × 25 mL) and brine (25 mL) and dried.

11,12-Dihydro-5*H*,10*H*-12,16b-ethano-5a,11-methano-10-(dicarbethoxymethyl)dibenzo[3,4:8,9]cyclonona[1,2-*b*]-naphtho[1,2-*e*]pyran-20,22-dione (4d). The reaction of dispironaphthalenone 1 with the anion generated from diethyl malonate and $KOBu^t$, after purification by column chromatography over silica gel using EtOAc–petroleum ether (3:17) as eluent, gave **4d** (160 mg, 53%) as white needles: mp 176–178 °C ($CHCl_3$–petroleum ether); UV ($CHCl_3$) 332 (2800), 318 (2300), 290 (4500), 278 (6800), 268 (6900), 244 (27 700); IR (Nujol) 1755–1715 (br), 1705 (C=O); ^{1}H NMR 1.16 (t, *J* = 7.0 Hz, 3 H, OCH_2CH_3), 1.18 (t, *J* = 7.0 Hz, 3 H, OCH_2CH_3), 2.57–2.75 (m, 2 H, 21-H_2), 3.36 (d, *J* = 18.7 Hz, 1 H, 5-H), 3.53 (d, *J* = 8.3 Hz, 11-H), 3.57 (d, *J* = 6.9 Hz, 1 H, $CH(COOEt)_2$), 3.69–3.74 (m, 1 H, 12-H), 3.80 (d, *J* = 6.9 Hz, 1 H, 10-H), 3.98–4.22 (m, 4 H, $CH(COOCH_2CH_3)_2$), 4.51 (d, *J* = 18.7 Hz, 1 H, 5-H), 6.54 (dd, *J* = 7.7, 2.5 Hz, 1 H), 6.70–6.74 (m, 1 H), 6.79–6.87 (m, 2 H), 6.96 (ddd, 1 H), 7.07 (d, *J* = 7.9 Hz, 1 H), 7.18 (ddd, 1 H), 7.28 (d, *J* = 8.4 Hz, 1 H), 7.36 (d, *J* = 8.9 Hz, 1 H, 18-H), 7.43 (ddd, 1 H, 2-H/3-H), 7.56 (ddd, 1 H, 2-H/3-H), 7.79 (d, *J* = 8.9 Hz, 1 H, 19-H), 7.88 (d, *J* = 7.9 Hz, 1 H, 1-H), 7.97 (d, *J* = 8.4 Hz, 1 H, 4-H); MS *m/e* (relative intensity) 600 (M^+, 6), 310 (62), 282 (89), 281 (100), 269 (39); HRMS calcd for $C_{38}H_{32}O_7$ 600.2148, found 600.2160.

11,12-Dihydro-5*H*,10*H*-12,16b-ethano-5a,11-methano-10-(dicarbomethoxymethyl)dibenzo[3,4:8,9]cyclonona[1,2-*b*]-naphtho[1,2-*e*]pyran-20,22-dione (4e). The reaction of dispironaphthalenone 1 with dimethyl malonate in the presence of $KOBu^t$ after purification by column chromatography (silica gel, EtOAc–petroleum ether (1:5)) afforded **4e** (150 mg, 52%) as a white crystalline solid: mp 234–236 °C ($CHCl_3$–petroleum ether); MS *m/e* (relative intensity) 572 (M^+, 5), 310 (30), 287 (78), 281 (100), 269 (48); HRMS calcd for $C_{36}H_{28}O_7$ 572.1835, found 572.1836.

11,12-Dihydro-5*H*,10*H*-12,16b-ethano-5a,11-methano-10-(carbomethoxycyanomethyl)dibenzo[3,4:8,9]cyclonona[1,2-*b*]naphtho[1,2-*e*]pyran-20,22-dione (4f). The reaction of dispironaphthalenone 1 with methyl cyanoacetate in presence of $KOBu^t$ after purification by column chromatography (silica gel, EtOAc–petroleum ether (1:4)) gave **4f** (130 mg, 48%) as a white crystalline solid: mp 297–298 °C ($CHCl_3$–petroleum ether); MS *m/e* (relative intensity) 539 (M^+, 100), 381 (57), 281 (70), 269 (64); HRMS calcd for $C_{35}N_{25}O_5N$ 539.1733, found 539.1732.

11,12-Dihydro-5*H*,10*H*-12,16b-ethano-5a,11-methano-10-(carbethoxycyanomethyl)dibenzo[3,4:8,9]cyclonona[1,2-*b*]-naphtho[1,2-*e*]pyran-20,22-dione (4g). Reaction of dispironaphthalenone 1 with ethyl cyanoacetate in the presence of $KOBu^t$, after purification by column chromatography (silica gel, EtOAc–petroleum ether (1:4)), afforded **4g** (145 mg, 52%) as white crystalline solid: mp 220–221 °C ($CHCl_3$–petroleum ether); MS *m/e* (relative intensity) 553 (M^+, 100), 381 (55), 282 (60), 269 (50); HRMS calcd for $C_{36}H_{27}O_5N$ 553.1989, found 553.1924.

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Registry No. 1, 79091-73-9; 3, 135214-50-5; **4a**, 135106-92-2; **4b**, 135106-93-3; **4c**, 135106-94-4; **4d**, 135106-95-5; **4e**, 135106-96-6; **4f**, 135106-97-7; **4g**, 135106-98-8; **5a**, 135106-90-0; **5b**, 135144-09-1; **5c**, 135106-91-1; 6, 135144-10-4; $EtO_2CCH_2CO_2Et$, 105-53-3; $MeO_2CCH_2CO_2Me$, 108-59-8; $NCCH_2CO_2Me$, 105-34-0; $NCCH_2CO_2Et$, 105-56-6.

Supplementary Material Available: ^{1}H NMR spectra of **4a–g**, **5a–c**, **6**, and **3**, ^{13}C NMR spectrum of **4a**, and a table comprising UV, IR, and ^{1}H NMR data of **4b,c**, **4e–g**, and **5b,c** (17 pages). Ordering information is given on any current masthead page.