Convenient Syntheses of Condensed Phenalenones. The Synthesis of Indeno[1,2-*a*]phenalene-6,8-dione and Its Dication

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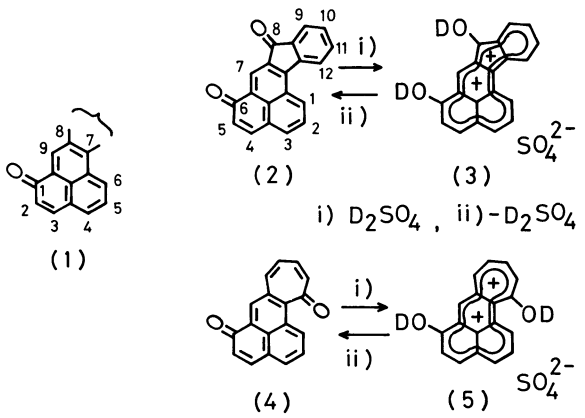
Synopsis. Convenient and general syntheses of condensed phenalenones with various ring systems fused at the 7 and 8-positions are described together with the synthesis of indeno[1,2-*a*]phenalene-6,8-dione (quinone) and the formation of its di-cationic species in strong acidic media.

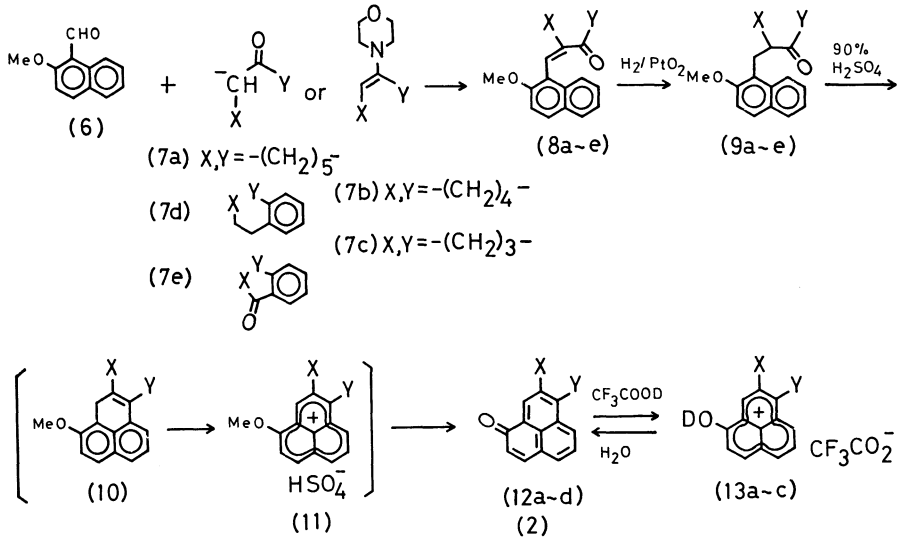
Although many types of condensed phenalenones have been actively studied,[1] there have been few general methods for their synthesis. Other condensed phenalenones such as those having fused rings at 7- and 8-positions have remained to be investigated.[2] In the course of our synthetic study of such new systems we devised a new convenient and general method for the synthesis of condensed phenalenones (**1**). Further the title cationic species (**3**) generated from quinone (**2**) is of interest regarding its tropicity, since the structurally related dication (**5**) generated from cyclohepta[*a*]phenalene-6,12-dione (**4**) was found to show diatropicity[3] in spite of the 16-π epectron system.



The reaction of cycloheptanone (**7a**) with one equivalent of 1-formyl-2-methoxynaphthalene (**6**) in the presence of sodium methoxide in dry tetrahydrofuran (THF) under reflux for 3.5 h gave an α,β-unsaturated ketone (**8a**) as pale yellow needles in 90% yield. The direct cyclodehydration of **8a** by 90% sulfuric acid (H_2SO_4) at 45 °C for 25 min provided an expected phenalenone derivative (**12a**) as yellow needles, but in very low yield. The alternative method was next employed. The catalytic hydrogenation of **8a** with H_2/PtO_2 at 2.7 atm for 3 h gave a saturated ketone (**9a**) as pale yellow oil almost quantitatively. This was subjected cyclodehydration under similar conditions without further pruification to give **12a** in 60% yield. This cyclization might have proceeded through the cationic species **11** generated by oxidation of cyclodehydrated product **10** with H_2SO_4.[4] For the synthesis of systems fused with five and six membered ring, the enamines **7b** and **7c** were used instead of ketones to avoid double condensation of **6** with cyclic ketones. The compounds **8b** and **8c** were obtained in 75% and 76% yield, respectively, by the reaction of **7**, and **7c** with **6** in toluene under reflux for 5 h follwed by hydrolysis. Then similar treatment as above furnished phenalenone derivatives **12b** and **12c** in 60% and 35% yield, respectively, via saturated ketones **9b** and **9c**, and cationic intermediates **11**.

The IR spectra showed that the absorption band of a carbonyl group shifted to larger wavenumber in the order of **12a**, **12b**, and **12c**. This suggests that the contribution of the dipolar structure decreases in this order. The same tendency was observed in the ^1H NMR spectra; the ^1H NMR singals of the phenalenone moiety slightly shifted up-field in the same order. In the UV spectra also, the bathochromic shifts (hexane to ethanol) of longest absorption maxima of these compounds decreases as the fused ring size decreases. These indicate that the increased strain in the fused ring diminishes the contribution of the dipolar structure. These compounds generated the cationic species **13a**, **13b**, and **13c** in a strong acid such as trifluoroacetic acid, as confirmed by the spectral evidences especially from the ^1H NMR and UV spectroscopy. The ^1H NMR signals of these cationic species showed the down field shifts by ca. 1 ppm. However, the electronic state of the cationic species does not seem to be greatly affected by the size of the fused ring, as is deduced from the similarity of their chemical shift values. In the UV spectra, the longest absorption maxima of these compounds shifted to longer wavelength by 30—50 nm as compared with those of phenalenones.

The syntheses of **12d** and the title new quinone **2** were similarly achieved as shown in the scheme. The structures of these compounds, including the synthetic intermediates, were determined spectroscopically and by elemental analysis. It is noted that the IR spectrum of **2** showed the characteristic absorption band of a carbonyl group in a five-membered ring at 1708 cm^{-1}. The dicationic species **3** generated by dissolving **2** in strong acid was confirmed by the UV and ^1H NMR spectra. In the UV spectrum, the larger shift of the longest wavelength absorption band of **3** (about 100 nm) compared to the above-mentioned condensed penalenones (about 50 nm) suggests the generation of a dicationic species. Unfortunately, because of its low solubility in various solvents such as DMSO, DMF, and $CDCl_3$, the ^{13}C NMR spectrum of **2** could not be obtained. However, the ^1H chemical shifts of **2** in D_2SO_4 showed that all protons of both the phenalenone moiety and the indenone moiety were shifted to low field by 0.70 ppm and 0.38 ppm, respectively, (av. 0.57 ppm) compared to those of **2** in $CDCl_3$. The down field shifts of the



indenone moiety could not be interpreted only by the deshielding effect of the monocation generated in the phenalenone moiety, but it should be considered as due to the generation of the dicationic species. Then, it is to be noted that the protons of the phenalenone moiety of **3** (av. 8.70 ppm) in D_2SO_4 resonated at higher field than those of the dicationic species **5** (av. 9.15 ppm) by 0.45 ppm. This might be interpreted by some contribution of a paratropic rather than the diatropic character expected for 18-π electrons, in accord with the case of the dicationic species of cyclohepta[*a*]-phenalene-6,12-dione **5**[2] in which the diatropic character was observed in spite of its 16-π electronic system.[3]

Experimental

All melting points are uncorrected. The ^1H NMR spectra were taken on a Hitachi R-24 (60 MHz) and on a JEOL-FX 90 (90 MHz) spectrometers, in chloroform-*d* (TMS as internal standard) trifluoroacetic acid-*d* (TMS), and deuteriosulfuric acid (dichloromethane as internal standard). The ^{13}C NMR spectra were taken on a JEOL-FX 90 (23 MHz) spectrometer, in chloroform-*d* (TMS as internal standard) and trifluoroacetic acid-*d* (TMS). The mass spectra were taken on a JEOL-OISG-2 mass spectrometer. The UV and IR spectra were taken on a Hitachi EPS-3T spectrometer and on a IR-810 spectrometer, respectively.

The Following Procedures a) and b) Are Representative for the Preparation of Condensed Compounds 8a, 8b, 8c, 8d, and 8e. a) Condensation of Cyclic Ketones with 1-Formyl-2-methoxynaphthalene 6. To a solution of 3.00 g (16 mmol) of **6** and 1.80 g (16 mmol) of **7a** in 30 mL of anhydrous THF 0.90 g (16 mmol) of sodium methoxide was added and refluxed for 3 h. After cooling the solution was poured onto dil. hydrochloric acid (HCl) and extracted three times with 20 mL of ether. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was chromatographed on silica gel to give 4.32 g (90%) of **8a**, from benzene elution.

8a; pale yellow oil; IR (film) 3027w, 1665vs, 1250s, 926m, 788m, 730m cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.70—7.50 (m, 4H), 7.40—7.10 (m, 4H), 3.78 (s, 3H, -OMe), 2.60 (m, 2H), 2.30 (m, 2H), 1.60 (m, 6H); MS *m/z* 280 (M^+, 100%), and HRMS Found: 280.1461, Calcd for $C_{19}H_{20}O_2$: 280.1461.

8d; pale yellow needles (recrystallized from hexane); mp 72—74 °C; IR (KBr) 3060w, 1670vs, 1610m, 1258vs, 740m, 706m cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.70 (m, 1H), 8.75—7.10 (m, 6H), 3.81 (s, 3H, -OMe), 2.70 (m, 2H), 2.58 (m, 2H); MS *m/z* 314 (M^+, 100%); Anal. ($C_{22}H_{18}O_2$) C, H.

8e; (56%); orange needles (recrystallized from hexane and dichloromethane); mp 218—219 °C; IR (KBr) 3055w, 2925w, 1680vs, 1615s, 1248vs, 725m cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.18 (s, 1H), 7.90—7.00 (m, 10H), 3.75 (s, 3H, -OMe), MS *m/z* 294 (M^+, 100%); Anal. ($C_{21}H_{14}O_3$) C, H.

b) Condensation Reaction of Enamines with 6. The mixture of 2.30 g (13.5 mmol) of **6** and 2.35 g (13.5 mmol) of *N*-cyclohexenylmorpholine **7b** in 15 mL of dry toluene was refluxed for 12 h. The cooled reaction mixture was added to 10 mL of 3 M-HCl solution and refluxed for 30 min. The resulting mixture was extracted with ether (15 mL×3). The combined organic layer was washed with water and brine three times each, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel to give 4.45 g (76%) of pale yellow solid of **8b** from benzene elution, and recrystallized from hexane.

8b; pale yellow needles; mp 107—109 °C; IR (KBr) 3045w, 2850w, 1680vs, 1615s, 1245vs, 800m, 740m cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.70 (m, 7H), 3.26 (s, 3H, -OMe), 2.50—2.00 (m, 4H), 1.95—1.40 (m, 4H), MS *m/z* 266 (M^+, 28%), 236 (100%); Anal. ($C_{18}H_{18}O_2$) C, H.

Similarly **8c** was obtained in 74% yield; pale yellow needles hexane); mp 97—98.5 °C; IR (KBr) 3050w, 1710vs, 1610m, 780m cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.80—7.60 (m, 4H), 7.50—7.15 (m, 3H), 3.84 (s, 3H, -OMe), 2.42 (t, *J*=7.2 Hz, 2H), 2.40 (t, *J*=7.2 Hz, 2H), MS *m/z* 252 (M^+, 20%), 221 (100%); Anal. ($C_{17}H_{16}O_2$) C, H.

General Procedure for the Catalytic Hydrogenation of α,β-Unsaturated Ketones and the Following Cyclodehydration Reaction. To a solution of ca. 15 mmol of the unsaturated ketone in excess of ten times its weight of ethyl acetate (ca. 50—60 mL) a catalytic amount of platinum dioxide (ca. 1 mg) was added and hydrogenated under medium pressure (2.7—3.0 atm) of hydrogen at room temperature for 3.5 h. The resulting mixture was filtered and concentrated under reduced pressure to give the hydrogenated product. The resulting residue was added to about ten times its weight of 90% sulfuric acid and stirred at 45 °C for 25 min in an oil bath. The mixture was poured onto a large excess (ca. ten times of weights) of ice-water, and extracted with dichloromethane (50 mL×3). The combined organic layer was washed three times with water and brine, and dried over anhydr. $MgSO_4$.

After removal of the solvent, the residure was chromatographed on silica gel to give phenalenone derivatives from dichloromethane eluent; These were recrystallized from hexane.

9a; pale yellow oil; IR (film) 3050w, 2930w, 1730vs, 1690s, 1250s, 938m, 800m, 745m cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.60—6.90 (m, 6H), 3.75 (s, 3H, -OMe), 3.40—3.15 (m, 3H), 2.80—2.35 (m, 4H), 1.80—1.40 (m, 6H); MS *m/z* 282 (M^+, 100%), 141 (98%), HRMS Found: 282.1635, Calcd for $C_{19}H_{22}O_2$: 282.1620.

9b; pale yellow oil; IR (film) 3050w, 3000w, 1700vs, 1620m, 1590s, 1150m, 802m, 749m cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.05—7.00 (m, 6H), 3.80 (s, 3H), 3.50 (m, 1H), 2.50—1.50 (m, 10H), MS *m/z* 270 (M^+, 100%); HRMS Found: 268.1421, Calcd for $C_{18}H_{20}O_2$: 268.1460.

9c; pale yellow oil; IR (film) 3060w, 2940w, 1736vs, 1625s, 1255vs, 1160s, 810m, 750m cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.95 (d, *J*=8.8 Hz, 1H), 7.70 (m, 2H), 7.55—7.18 (m, 3H), 3.88 (s, 3H, -OMe), 3.52 (dd, *J*=4.8 and 14.0 Hz, 1H), 3.10 (dd, *J*=12.0 and 14.0 Hz, 1H), 2.60—2.10 (m, 3H), 2.0—1.50 (m, 4H); MS *m/z* 252 (M^+, 35%), 171 (100%); HRMS Found: 252.1296, Calcd for $C_{17}H_{18}O_2$: 252.13404.

9d; pale yellow needles (hexane); mp 110—111 °C; IR (KBr) 3025w, 1662vs, 1608s, 1240vs, 796m, 732m cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.02 (m, 2H), 7.70 (m, 2H), 7.25 (m, 6H), 3.85 (m, 1H), 3.83 (s, 3H, -OMe), 3.22 (dd, *J*=12.0 and 16.0 Hz, 1H), 2.80 (m, 3H), 1.94 (m, 2H), MS *m/z* 316 (M^+, 100%); Anal. ($C_{22}H_{20}O_2$) C, H.

9e; pale yellow needles (hexane); mp 169—172 °C; IR (KBr) 3040w, 2920vs, 1721s, 1685vs, 1238vs, 1066s, 786m, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.02—7.63 (m, 6H), 7.55—7.10 (m, 4H), 3.77 (s, 3H, -OMe), 3.61 (d, *J*=6.2 Hz, 2H), 3.33 (dd, *J*=6.2 and 8.6 Hz, 1H), MS *m/z* 316 (M^+, 100%); Anal. ($C_{21}H_{16}O_3$) C, H.

12a; pale yellow needles (hexane); mp 122—123 °C; IR (KBr) 3055w, 3030w, 1625vs, 1575s, 1200vs, 828m, 733m cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.37 (s, H-9), 8.22 (dd, *J*=2.0 and 7.0 Hz, H-6), 7.63 (d, *J*=10 Hz, H-3), 7.50 (dd, *J*=2.0 and 7.0 Hz, H-4), 7.47 (t, *J*=7.0 Hz, H-5), 6.62 (d, *J*=10 Hz, H-2); ^{13}C NMR ($CDCl_3$) δ=185.6 (s), 148.3 (s), 142.6 (d), 141.6 (d), 132.1 (d), 130.5 (s), 130.4 (d), 128.8 (d), 128.5 (s), 128.1 (d), 127.8 (s), 127.3 (s), 126.1 (d), 36.4 (t), 32.0 (t), 29.0 (t), 27.3 (t), 26.8 (t); UV (hexane) λ_{max} 390 (log ε=4.14), 325 (3.57), 255 nm (4.42); UV (EtOH) λ_{max} 405 (log ε=4.04), 330 (3.70), 255 nm (4.35); MS *m/z* (M^+, 100%); 219 (20%); Anal. ($C_{18}H_{16}O_2$) C, H.

12b; (35%); pale yellow needles (hexane); mp 81.5—82.5 °C; IR (KBr) 3040w, 1637vs, 1585m, 1402m, 1185s, 833m, 750m, 707m cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.36 (s, H-9), 8.18 (dd, *J*=2.0 and 7.0 Hz, H-6), 7.60 (d, *J*=10.0 Hz, H-3), 7.58 (dd, *J*=2.0 and 7.0 Hz, H-4), 7.46 (t, *J*=7.0 Hz, H-5), 6.61 (d, *J*=10.0 Hz, H-2); ^{13}C NMR ($CDCl_3$) δ=185.8 (s), 142.0 (d), 141.2 (s), 136.2 (s), 132.6 (d), 131.3 (s), 130.3 (s), 128.8 (d), 128.0 (s), 127.9 (s), 127.1 (d), 126.2 (d), 126.1 (d), 30.3 (t), 26.4 (t), 22.7 (t), 22.5 (t); UV (hexane) λ_{max} 375 (log ε=4.08), 325 (3.53), 260 nm (4.40); UV (EtOH) λ_{max} 385 (log ε=4.10), 330 (3.40), 260 nm (4.35); MS *m/z* 234 (M^+, 100%); Anal. ($C_{17}H_{14}O$) C, H.

12c; (25%) pale yellow needles (hexane); mp 88—89 °C; IR (KBr) 3055w, 1645vs, 1580s, 1372s, 855m, 772m cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.35 (s, H-9), 7.83 (dd, *J*=2.0 and 7.0 Hz, H-6), 7.45 (t, *J*=7.0 Hz, H-5), 7.55 (d, *J*=10.0 Hz, H-3), 7.54 (dd, *J*=2.0 and 7.0 Hz, H-4), 6.60 (d, *J*=10.0 Hz, H-2); ^{13}C NMR ($CDCl_3$) δ=185.7 (s), 148.9 (s), 142.7 (s), 141.4 (d), 130.4 (d), 128.9 (s), 128.7 (d), 128.5 (d), 128.3 (s), 128.1 (s), 127.2 (d), 126.4 (s), 126.2 (d), 33.3 (t), 31.6 (t), 24.3 (t); UV (hexane) λ_{max} 385 (log ε=4.10), 330 (3.40), 255 nm (4.40); UV (EtOH) λ_{max} 390 (log ε=4.09), 330 sh (3.30), 260 nm (4.41); MS *m/z* 220 (M^+, 100%); 159 (20%); Anal. ($C_{16}H_{12}O$) C, H.

12d; (78%); yellow needles (hexane); mp 185—186.5 °C; IR (KBr) 3025w, 1625vs, 1342s, 1118s, 778m, cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.61 (dd, *J*=1.5 and 8.2 Hz, H-6), 8.56 (s, H-9), 7.77 (d, *J*=9.8 Hz, H-3), 7.56 (m, 6H), 6.75 (d, *J*=9.8 Hz, H-2); 3.08 (t, *J*=8.3 Hz, 2H), 2.84 (t, *J*=8.3 Hz, 2H); MS *m/z* 282 (M^+, 100%); Anal. ($C_{21}H_{14}O$) C, H.

2; (61% from **7e**); red needles (*N,N*-dimethylformamide); mp 330—332 °C; IR (KBr) 1708s, 1637vs, 1615s, 830m, 725m cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.87 (s, H-7), 8.73 (dd, *J*=0.8 and 8.06 Hz, H-1), 8.18 (d, *J*=8.06 Hz, H-3), 7.83 (d, *J*=6.80 Hz, H-12), 7.81 (d, *J*=6.85 Hz, H-9), 7.72 (d, *J*=9.67 Hz, H-4); 7.71 (dd, *J*=8.06 and 8.46 Hz, H-2), 7.64 (dd, *J*=1.4 and 6.80 Hz, H-11), 7.44 (ddd, *J*=0.8, 6.80, and 6.85 Hz, H-10), 6.75 (d, *J*=9.67 Hz, H-5), MS *m/z* 282 (M^+, 100%); UV (CH_2Cl_2) λ_{max} 480 sh (log ε=3.35), 455 (3.50), 425 (3.50), 407 (3.85), 380 (3.75), 345 (3.82), 335 (3.90), 265sh nm (4.30); Anal. ($C_{20}H_{10}O_2$) C, H.

3; ^1H NMR (D_2SO_4-CH_2Cl_2) δ=9.44 (s, H-7), 9.40 (d, *J*=5.89 Hz, H-1), 8.89 (d, *J*=7.23 Hz, H-3), 8.84 (d, *J*=9.20 Hz, H-4), 8.40 (bd, *J*=7.90 Hz, H-12), 8.30 (bd, *J*=8.10 Hz, H-9), 8.06 (dd, *J*=5.89 and 7.23 Hz, H-2), 7.85 (dd, *J*=7.76 and 7.90 Hz, H-11), 7.69 (dd, *J*=7.76 and 8.10 Hz, H-10), 7.64 (d, *J*=9.20 Hz, H-5); ^{13}C NMR (D_2SO_4) δ=199.20 178.05, 160.28, 155.81, 150.67, 142.81, 141.84, 141.59, 135.06, 134.79, 134.68, 132.92, 132.21, 130.40, 129.21, 128.05, 126.99, 122.63, 120.49; UV (H_2SO_4) λ_{max} 600 sh (log ε=2.90), 520sh (3.85), 495 (3.92), 465 (3.96), 390 (4.25), 330 (3.95), 270 nm (3.23).

13a; ^1H NMR (CF_3COOD-TMS) δ=9.19 (s, H-9), 9.18 (dd, *J*=8.0 and 1.0 Hz, H-6), 8.73 (d, *J*=9.0 Hz, H-3), 8.70 (dd, *J*=7.0 and 1.0 Hz, H-4), 8.15 (dd, *J*=8.0 and 7.0 Hz, 5-H), 7.66 (d, *J*=9.0 Hz, H-2); ^{13}C NMR (CF_3COOD) δ=179.7 (s), 167.7 (s), 153.5 (d), 148.5 (s), 145.6 (s), 142.4 (d), 140.7 (d), 131.6 (s), 130.2 (d), 128.7 (d), 125.4 (s), 122.3 (s), 121.5 (s), 37.3 (t), 32.5 (t), 32.1 (t), 28.0 (t), 27.9 (t); UV (H_2SO_4) λ_{max} 445 (log ε=4.10), 435 (4.12), 370 (4.25), 260sh nm (4.15).

13b; ^1H NMR (CF_3COOD) δ=9.11 (s, H-9), 9.06 (d, *J*=8.0 Hz, H-6), 8.67 (d, *J*=9.0 Hz, H-3), 8.59 (d, *J*=8.0 Hz, H-4), 8.08 (t, *J*=8.0 Hz, H-5), 7.59 (d, *J*=9.0 Hz, H-2); ^{13}C NMR (CF_3COOD) δ=179.7 (s), 159.4 (s), 153.6 (d), 143.6 (s), 143.2 (d), 141.6 (s), 138.6 (d), 131.7 (s), 129.4 (d), 127.7 (s), 124.2 (d), 121.5 (s), 120.7 (d), 30.3 (t), 28.1 (t), 21.9 (t), 21.8 (t); UV (H_2SO_4) λ_{max} 476sh (log ε=3.20), 435 (4.18), 390 (3.95), 297 (4.21), 250 nm (4.15).

13c; ^1H NMR (CF_3COOD) δ=9.24 (s, H-9), 8.89 (dd, *J*=8.1 and 1.0 Hz, H-6), 8.71 (d, *J*=9.2 Hz, H-3), 8.67 (dd, *J*=8.1 and 1.0 Hz, H-4), 8.14 (t, *J*=8.1 Hz, H-5), 7.65 (d, *J*=9.2 Hz, H-2); ^{13}C NMR (CF_3COOD) δ=179.5 (s), 168.0 (s), 152.7 (d), 148.4 (s), 144.9 (d), 140.7 (d), 137.2 (d), 129.6 (s), 129.2 (d), 128.1 (s), 124.9 (d), 122.7 (s), 121.0 (d), 33.5 (t), 33.0 (t), 24.6 (t); UV (H_2SO_4) λ_{max} 440 (log ε=4.20), 435sh (4.18), 390sh (3.95), 375 (4.15), 297 (4.21), 250 nm (4.15).

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