An Investigation of the Reaction Mechanism of the Bis-acylation of Aromatics with *o*-Phthaloyl Dichlorides: Regioselective Synthesis of Anthraquinones†

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Introduction

In our previous studies on the template effect in the *ortho*-regioselective electrophilic acylation of metal phenolates[1] we have reported simple and mild reaction conditions for preparing anthraquinones **5** *via* a one-pot bisacylation of aromatic substrates with *o*-phthaloyl dichlorides **1** (Scheme 1).[2]

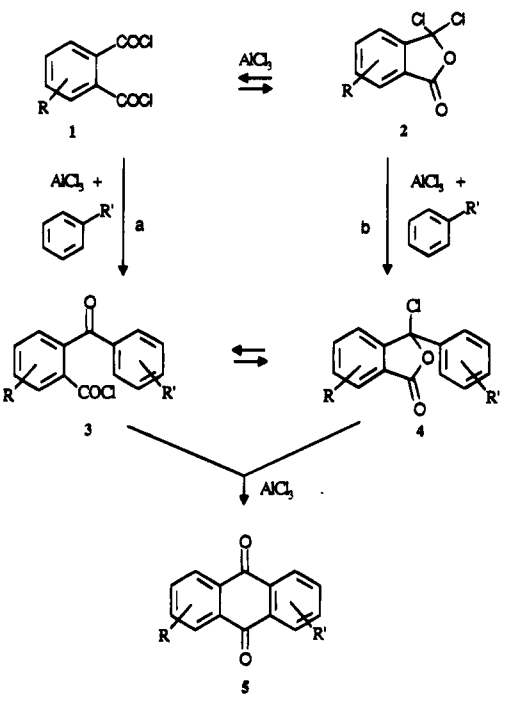
On the basis of our synthetic and mechanistic studies we thought that the entire process could be easily accomplished due to the temporary loss of the electron-withdrawing effect of the carbonyl group of the keto acid chlorides **3** which were converted into the corresponding pseudochlorides **4** *via* a "ring-chain tautomerism" (**3** ⇄ **4**).[3]

In this work, our aim was to further investigate the mechanism of the reaction with particular respect to the reactive complex between the phthaloyl dichloride and $AlCl_3$. Moreover, it was our interest to confirm the crucial role of benzoylbenzoic acid pseudochlorides **4** in the *ortho*-bisacylation process. Finally, we explored the possibility of utilizing compounds **4** and similar cyclic intermediates to perform a selective synthesis of variously substituted anthraquinones **5**, thus avoiding the "Hayashy rearrangement" which is responsible for the lack of selectivity in the cycloacylation of benzoylbenzoic acids to anthraquinones.[4]

Results and Discussion

Multinuclear NMR Studies and X-ray Analysis. Our preliminary spectroscopic ^{13}C-NMR studies gave some evidence in favor of the $AlCl_3$-promoted equilibration **1** ⇄ **2** (Scheme 1).[2] More recently ^{17}O- and ^{27}Al-NMR investigations were conducted in order to obtain detailed

Scheme 1



information on the real acylating complex between $AlCl_3$ and *o*-phthaloyl dichloride **1a** (R = H).

The ^{17}O-NMR spectrum of the asym-dichloride **2a**[5] in dichloromethane shows two well-distinguishible resonances at 351 and 234 ppm (line width $\Delta\nu_{1/2}$ = 180 Hz) due to the carbonyl and the bridging oxygen atoms respectively (Figure 1A). The small peaks at 376.8 and 264.1 ppm are due to traces of phthalic anhydride.[6]

The complex obtained by mixing in the same solvent equimolecular amounts of $AlCl_3$ and **2a** exhibits two ^{17}O-NMR lines at 259 and 218 ppm (Figure 1B). The upfield shift of the carbonyl oxygen of the complex **6a** relative to the free asym-dichloride **2a** ($\Delta\delta$ = 92 ppm) is rather large and strongly suggests a direct metal–oxygen interaction as was found for the 1:1 systems $AlCl_3$/pinacolone and $AlCl_3$/RCOCl.[7] In regard to the trace amount of phthalic anhydride, the interaction with $AlCl_3$ gives rise to a large signal at δ = 270 ppm, masked by the lower-field signal of complex **6a**.

Moreover, ^{27}Al chemical shift and line width values (δ = 96.2 ppm and $\Delta\nu_{1/2}$ = 750 Hz, respectively) indicate the presence of an unsymmetrical tetracoordinated aluminum complex **6a** with the carbonyl oxygen involved in the metal coordination (Figure 1C).[8]

This was confirmed by X-ray analysis of the 1:1 adduct between $AlCl_3$ and a suitable phthaloyl dichloride. Thus, addition of $AlCl_3$ to a solution of 4,5-dichlorophthaloyl dichloride **1b**[9] (molar ratio 1:1) in 1,2-dichloroethane resulted in a pale yellow solution from which X-ray quality white crystals of the complex **6b** were obtained (Scheme 2).

† Dedicated to the memory of Professor Giuseppe Casnati.
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(1) (a) Casnati, G.; Casiraghi, G.; Pochini, A.; Sartori, G.; Ungaro, R. *Pure Appl. Chem.* **1983**, *55*, 1677. (b) Sartori, G.; Casnati, G.; Bigi, F.; Predieri, G. *J. Org. Chem.* **1990**, 55, 4371.
(2) Sartori, G.; Casnati, G.; Bigi, F.; Foglio, F. *Gazz. Chim. Ital.* **1990**, *120*, 13.
(3) Valters, R. E.; Flitsch, W. *Ring-Chain Tautomerism*; Katritzky, A. R., Ed.; Plenum Press: New York, London, 1985.
(4) (a) Hayashi, M. *J. Chem. Soc.* **1927**, 2516; **1930**, 1513, 1520, 1524. (b) Newman, M. S. *Acc. Chem. Res.* **1972**, *5*, 354.
(5) Ott, E. *Organic Syntheses*; Wiley: New York, 1959; Collect. Vol. II, p 528.
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(7) Bigi, F.; Casnati, G.; Sartori, G.; Predieri, G. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1319.
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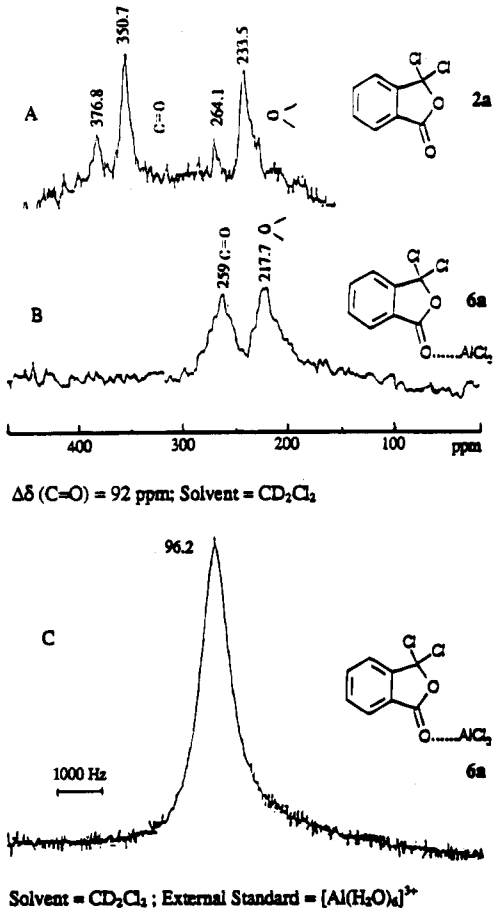
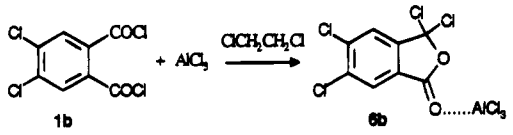


Figure 1. (A) ^{17}O-NMR spectrum of free **2a**; signals at 376.8 and 264.1 ppm are due to traces of phthalic anhydride.[6] (B) ^{17}O-NMR spectrum of the 1:1 complex between **2a** and $AlCl_3$: **6a**. (C) ^{27}Al-NMR spectrum of **6a**.

Scheme 2



The structure of **6b** and the atom numbering are shown in Figure 2.[10] The aluminum atom is tetrahedrally coordinated, in a flattened fashion, by three chlorine atoms and the carbonyl oxygen atom of the organic ligand. Apart from the chlorine atoms at position 3, the phthalide moiety is planar and the plane roughly bisects the Cl(2)–Al–Cl(3) angle. The bond distance Al–O of 1.847(5) Å is close to those observed for the *o*-, *m*-, and *p*-toluoyl chloride adducts of $AlCl_3$,[11] and for trichloro(propionyl chloride)aluminum,[12] but is significantly longer than that found in trichloro(ethyl benzoate-O)aluminum.[13] The value of the bond angle Al–O(1)–C(1) is 133.9(5)°, and it is far from the theoretical value of 120° for a sp^2 hybridized oxygen atom.

(10) The authors have deposited atomic coordinates, thermal parameters, and full details of molecular dimensions with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. Copies of the structure factor listing are available from the authors.

(11) Chevrier, B.; Le Carpentier, J.-M.; Weiss, R. *Acta Crystallogr.* **1972**, *B28*, 2659.

(12) Le Carpentier, J.-M.; Weiss, R. *Acta Crystallogr.* **1972**, *B28*, 1437.

(13) Sobota, P.; Mustafa, M. O.; Utko, J.; Lis, T. *J. Organomet. Chem.* **1989**, *368*, 257.

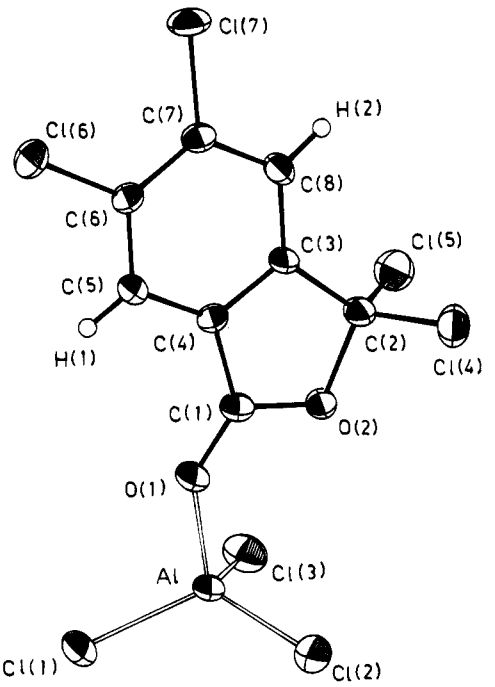
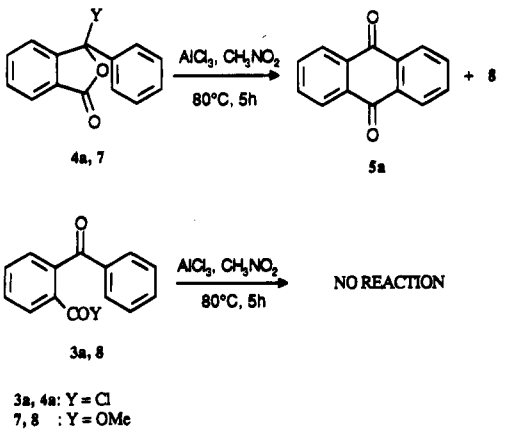


Figure 2. Perspective view of complex **6b**. The thermal ellipsoids are drawn at the 30% probability level.

Scheme 3



Thus, it appears from these analytical data that phthaloyl dichlorides **1** are "in situ"" converted into the corresponding asym-dichlorides **2** *via* a "ring-chain" tautomerism promoted by $AlCl_3$, and consequently, adducts **6** represent the actual acylating complexes.

Key Role of Pseudochlorides 4. Next, our attention was turned to the role played by the pseudochlorides **4** in favoring the entire process.

In order to confirm this hypothesis it was necessary to compare the reactivity of the two isomeric *o*-benzoylbenzoic acid chlorides **4a** and **3a** toward the conversion into anthraquinone **5a** (Scheme 3).

Because attempts to synthesize **4a** gave in all cases tautomeric mixtures difficult to manipulate and characterize,[3] we thus decided to examine the reactivity of the isomeric methyl esters **7** and **8** as the more stable derivatives. These compounds were easily prepared by methods reported in the literature.[14]

By heating a solution of the pseudoester **7** and $AlCl_3$ (molar ratio 1:1) in CH_3NO_2 at 80 °C for 5 h, the expected

(14) Bonner, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 439.

Scheme 4

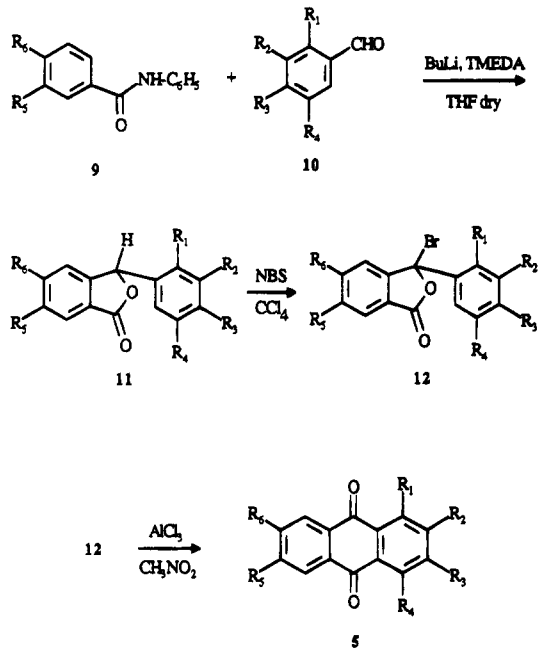


Table 1. Synthesis of Anthraquinones 5 by $AlCl_3$-Promoted Cycloacylation of Bromophthalides 12

product	R_1	R_2	R_3	R_4	R_5	R_6	yield (%)
5d	OH	H	OCH_3	H	CH_3	H	75
5e	H	OCH_3	H	H	H	OCH_3	70
5f	OH	H	H	H	H	OCH_3	65
5g	H	CH_3	OCH_3	H	H	H	67
5h	OH	Br	H	OH	H	H	70
5i	H	OCH_3	H	OCH_3	H	OCH_3	73

anthraquinone **5a** was obtained in 65% yield accompanied by traces of **8** (~8%). On the contrary, the keto ester **8** was completely inert under similar conditions; indeed, compound **8** is not convertible into **7**.[3]

Regioselective Synthesis of Anthraquinones. The above results confirm the crucial role of cyclic intermediates **4** in the one-pot bisacylation of aromatics with *o*-phthaloyl dichlorides and prompted us to explore the possibility of utilizing bromo derivatives **12** as valuable synthons for the anthraquinones **5** (Scheme 4).

Phthalides **11**,[15] were brominated with NBS in carbon tetrachloride affording bromophthalides **12** in good yields.[16] Compounds **12** were successively converted, without purification, into anthraquinones **5** by treatment with $AlCl_3$ in nitromethane solution in agreement with the above-described reaction mechanism.

Table 1 lists the anthraquinones which have been prepared in this study. The entire process is highly regioselective as only one regioisomer is obtained from reagents **9** and **10**.

Finally, our reaction finds some analogy with the route to anthraquinones previously reported by Snieckus, but it should be stressed that the present methodology may be alternatively used when the one-pot Snieckus protocol fails to produce anthraquinones in satisfactory yields, in particular when methoxylated aromatic substrates are involved.[15a]

(15) (a) Watanabe, M.; Snieckus, V. *J. Am. Chem. Soc.* **1980**, *102*, 1457. (b) Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306.

(16) Koten, I. A.; Sauer, R. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 145.

Conclusions

In conclusion, the present paper shows full results of our investigation on the mechanism of the bisacylation of aromatics with *o*-phthaloyl dichlorides **1**.

^{17}O- and ^{27}Al-NMR studies as well as X-ray analysis confirm that *o*-phthaloyl dichlorides **1** are converted by $AlCl_3$ into asym-dichlorides **2** which react with aromatic substrates giving *o*-benzoylbenzoic acid pseudochlorides **4**. Furthermore, our results confirm the importance of compounds **4** in favoring the electrophilic cycloacylation process.

Finally, variously substituted anthraquinones **5** were regioselectively synthesized by $AlCl_3$-promoted cycloacylation of bromophthalides **12**, in agreement with the present reaction mechanism.

Experimental Section

General. Melting points are uncorrected. ^1H NMR spectra were recorded at 100, 300, and 400 MHz. ^{27}Al and ^{17}O NMR spectra were recorded at 52.12 and 27.11 MHz, respectively. ^{27}Al chemical shifts are referred to external $[Al(H_2O)_6]^{3+}$; ^{17}O shifts are referred to external H_2O. Mass spectra were obtained in EI and CI mode at 70 eV. Microanalyses were carried out by the Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica dell'Università di Parma, Italy. TLC analyses and flash chromatography were performed on Merck 60 PF_{254} silica gel using mixtures of hexane–ethyl acetate (10–50%). All the reagents were of commercial quality from freshly opened containers, and $AlCl_3$ was sublimed. The solvents were dried on 4 Å molecular sieves before use.

Synthesis of Phthalides (11d-i). General Procedure.[15] To a solution of the selected anilide[17] (0.01 mol) and TMEDA (3.5 mL, 0.025 mol) in dry THF (80 mL) was added BuLi (16 mL of a solution 1.6 M in hexane, 0.025 mol) in dry THF (20 mL) dropwise under nitrogen at −78 °C. The solution was allowed to warm to −20 °C during 2 h. Then it was cooled to −78 °C, and the selected aldehyde (0.01 mol) in dry THF (20 mL) was added dropwise under nitrogen. The solution was stirred at room temperature overnight. A saturated solution of NH_4Cl (200 mL) was added with stirring, and the resulting mixture was extracted with Et_2O (3 × 100 mL). The combined extracts were successively washed with a solution of 2 N HCl and a saturated solution of $NaHCO_3$. The combined extracts were dried (Na_2SO_4), the Et_2O was distilled off, and the residue was flash-chromatographed. The products were recrystallized from toluene.

Synthesis of Anthraquinones (5d-i). General Procedure. The selected phthalide (0.005 mol) was dissolved in dry CCl_4 (100 mL) with stirring. NBS (0.85 g, 0.005 mol) and a small amount of benzoylperoxyde were added to the solution under nitrogen. The mixture was heated at reflux overnight under UV irradiation. The cooled solution was filtered under nitrogen, and the solvent was removed in vacuo. The residue was dissolved in dry nitromethane (50 mL), and a solution of $AlCl_3$ (0.67 g, 0.005 mol) in dry nitromethane (10 mL) was added dropwise under nitrogen. The mixture was stirred at room temperature for 1 h. A solution of 2 N oxalic acid (50 mL) was added with stirring. The resulting mixture was extracted with Et_2O (3 × 50 mL). The combined extracts were dried (Na_2SO_4), the Et_2O was distilled off, and the residue was chromatographed by silica gel plates to give the products.

3-(3′,5′-Dimethoxyphenyl)-5-methyl-1-isobenzofuranone (11d): yield 2.13 g (75%), pale yellow solid; mp 107–110 °C (toluene); ^1H NMR (100 MHz, $CDCl_3$) δ 7.82 (1 H, d, J = 7.9 Hz), 7.34 (1 H, br d, J = 7.9 Hz), 7.14 (1 H, br s), 6.43 (3 H, s), 6.26 (1 H, s), 3.77 (6 H, s), 2.44 (3 H, s); IR (KBr) 1750 cm^{-1} (C=O); MS m/z (M^+ + 29) 313 (20), (M^+ + 1) 285 (100). Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.80; H, 5.68. Found: C, 71.92; H, 5.81.

3-(3′-Methoxyphenyl)-5-methoxy-1-isobenzofuranone (11e): yield 2.16 g (80%), white solid; mp 70 °C (toluene); ^1H

(17) *Vogel's, Textbook of Practical Organic Chemistry*, 5th ed.; Longman Scientific and Technical,: England, 1989; p 1261.

NMR (400 MHz, $CDCl_3$) δ 7.84 (1 H, d, J = 8.5 Hz), 7.30 (1 H, t, J = 7.9 Hz), 7.04 (1 H, dd, J = 8.5, 2.0 Hz), 6.90 (1 H, d, J = 7.9 Hz), 6.88 (1 H, d, J = 7.9 Hz), 6.79 (1 H, t, J = 1.9 Hz), 6.74 (1 H, d, J = 2.0 Hz), 6.27 (1 H, s), 3.83 (3 H, s), 3.78 (3H, s); IR (KBr) 1750 cm^{-1} (C=O); MS m/z (M^+ + 1) 271 (100), 228 (24), 163 (18). Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.09; H, 5.22. Found: C, 71.28; H, 5.29.

3-(2′-Methoxyphenyl)-5-methoxy-1-isobenzofuranone (11f): yield 2.21 g (82%), yellow solid; mp 88–90 °C (toluene); ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (1 H, d, J = 8.5 Hz), 7.33 (1 H, ddd, J = 8.2, 7.6, 1.2 Hz), 7.09 (1 H, dd, J = 7.6, 1.2 Hz), 7.00 (1 H, dd, J = 8.5, 2.0 Hz), 6.96 (1 H, d, J = 8.2 Hz), 6.91 (1 H, t, J = 7.6 Hz), 6.86 (1 H, d, J = 2.0 Hz), 6.77 (1 H, s), 3.92 (3 H, s), 3.82 (3 H, s); IR (KBr) 1760 cm^{-1} (C=O); MS m/z (M^+) 270 (100), 255 (60), 135 (63). Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.09; H, 5.22. Found: C, 70.95; H, 5.32.

3-(3′-Methyl-4′-methoxyphenyl)-1-isobenzofuranone (11g): yield 1.98 g (78%), white solid; mp 122–124 °C (toluene); ^1H NMR (100 MHz, $CDCl_3$) δ 8.1–7.2 (4 H, m), 7.08 (1 H, dd, J = 8.3, 2.3 Hz), 6.98 (1 H, d, J = 2.3 Hz), 6.79 (1 H, d, J = 8.3 Hz), 6.34 (1 H, s), 3.82 (3 H, s), 2.17 (3 H, s); IR (KBr) 1748 cm^{-1} (C=O); MS m/z (M^+) 254 (100), 238 (36), 195 (57). Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.56; H, 5.55. Found: C, 75.70; H, 5.80.

3-(2′,5′-Dimethoxy-4′-bromophenyl)-1-isobenzofuranone (11h): yield 2.75 g (79%), white solid; mp 159–162 °C (toluene); ^1H NMR (300 MHz, $CDCl_3$) δ 7.94 (1 H, m), 7.63 (1 H, m), 7.53 (1 H, m), 7.46 (1 H, m), 7.19 (1 H, s), 6.80 (1 H, s), 6.66 (1 H, s), 3.91 (3 H, s), 3.74 (3 H, s); IR (KBr) 1754 cm^{-1} (C=O); MS m/z (M^+ + 2) 349 (80), (M^+) 347 (80). Anal. Calcd for $C_{16}H_{12}BrO_4$: C, 55.33; H, 3.49. Found: C, 55.36; H, 3.54.

3-(3′,5′-Dimethoxyphenyl)-5-methoxy-1-isobenzofuranone (11i): yield 1.16 g (77%), white solid; mp 156–158 °C (toluene); ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (1 H, d, J = 8.5 Hz), 7.02 (1 H, dd, J = 8.5, 1.7 Hz), 6.76 (1 H, d, J = 1.7 Hz), 6.42 (3 H, s), 6.20 (1 H, s), 3.82 (3 H, s), 3.74 (6 H, s); IR (KBr) 1760 cm^{-1} (C=O); MS m/z (M^+ + 1) 301 (100). Anal. Calcd for $C_{17}H_{16}O_5$: C, 67.98; H, 5.37. Found: C, 68.14; H, 5.51.

1-Hydroxy-3-methoxy-6-methyl-9,10-anthraquinone (5d): yield 1.01 g (75%), yellow solid; mp 180–183 °C (toluene) (lit.[18] mp 184–185 °C); ^1H NMR (100 MHz, $CDCl_3$) δ 12.88 (1 H, s), 8.11 (1 H, d, J = 7.9 Hz), 7.99 (1 H, d, J = 1.9 Hz), 7.54 (1 H, dd, J = 7.9, 1.9 Hz), 7.28 (1 H, d, J = 2.5 Hz), 6.64 (1 H, d, J = 2.5 Hz), 3.92 (3 H, s), 2.51 (3 H, s); IR (KBr) 3095 (OH), 1670 (C=O) cm^{-1}; MS m/z (M^+ + 29) 297 (15), (M^+ + 1) 269 (100). Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.62; H, 4.51. Found: C, 71.58; H, 4.76.

2,7-Dimethoxy-9,10-anthraquinone (5e): yield 0.94 g (70%), yellow solid; mp 214–215 °C (toluene) (lit.[19] mp 213 °C); ^1H NMR (100 MHz, $CDCl_3$) δ 8.25 (2 H, d, J = 8.7 Hz), 7.72 (2 H, d, J = 2.7 Hz), 7.26 (2 H, dd, J = 8.7, 2.7 Hz), 3.99 (6 H, s); IR (KBr) 1670 (C=O) cm^{-1}; MS m/z (M^+ + 29) 297 (20), (M^+ + 1) 269 (100). Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.62; H, 4.51. Found: C, 71.39; H, 4.63.

1-Hydroxy-7-methoxy-9,10-anthraquinone (5f): yield 0.83 g (65%), yellow solid; mp 192 °C (toluene); ^1H NMR (100 MHz, $CDCl_3$) δ 12.56 (1 H, s), 8.25 (1 H, d, J = 8.6 Hz), 8.0–7.1 (5 H, m), 4.00 (3 H, s); IR (KBr) 3480 (OH), 1660 (C=O) cm^{-1}; MS m/z (M^+) 254 (100). Anal. Calcd for $C_{15}H_{10}O_4$: C, 70.85; H, 3.97. Found: C, 71.02; H, 3.90.

2-Methyl-3-methoxy-9,10-anthraquinone (5g): yield 0.85 g (67%), pale yellow solid; mp 196–198 °C (toluene) (lit.[20] mp 196–197 °C); ^1H NMR (100 MHz, $CDCl_3$) δ 8.5–7.5 (6 H, m), 4.03 (3 H, s), 2.36 (3 H, s); IR (KBr) 1680 (C=O) cm^{-1}; MS m/z (M^+) 252 (83), 152 (100). Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 75.99; H, 4.82.

1,4-Dihydroxy-2-bromo-9,10-anthraquinone (5h): yield 1.19 g (70%), red solid; mp 227–228 °C (toluene) (lit.[21] mp 228–230 °C); ^1H NMR (100 MHz, $CDCl_3$) δ 13.56 (1 H, s), 12.80 (1 H, s), 8.3–8.5 (2 H, m), 8.0–7.8 (2 H, m), 7.66 (1 H, s); IR (KBr) 3450 (OH), 1670 (C=O) cm^{-1}; MS m/z (M^+ + 2) 321 (43), (M^+) 319 (43). Anal. Calcd for $C_{14}H_7BrO_4$: C, 52.69; H, 2.21. Found: C, 52.74; H, 2.10.

1,3,6-Trimethoxy-9,10-anthraquinone (5i): yield 1.09 g (73%), yellow solid; mp 230–232 °C (toluene); ^1H NMR (300 MHz, $CDCl_3$) δ 8.21 (1 H, d, J = 8.7 Hz), 7.62 (1 H, d, J = 2.5 Hz), 7.45 (1 H, d, J = 2.3 Hz), 7.24 (1 H, dd, J = 8.7, 2.5 Hz), 6.79 (1 H, d, J = 2.3 Hz), 4.00 (3 H, s), 3.98 (3 H, s), 3.96 (3 H, s); IR (KBr) 1657 (C=O), 1646 (C=O) cm^{-1}; MS m/z (M^+ + 29) 327 (17), (M^+ + 1) 299 (100). Anal. Calcd for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73. Found: C, 68.72; H, 4.56.

Structural Analysis for 6b·1/2$C_2H_4Cl_2$. Crystals of the complex **6b** suitable for X-ray structural analysis were obtained by recrystallization from 1,2-dichloroethane. Data collection was done at ambient temperature on a Siemens AED diffractometer with Nickel-filterd Cu–Kα radiation ($\bar{\lambda}$ = 1.541 838 Å). Thirty reflections were used for the unit cell determination, corresponding to a triclinic cell in the space group $P\bar{1}$ (No. 2) with the following lattice parameters: a = 12.357(5) Å, b = 10.158(4) Å, c = 7.293(3) Å, α = 86.56(2)°, β = 79.44(2)°, γ = 71.10(2)°, V = 851.4(6) Å^3. For Z = 2 and formula weight 454.74, the calculated density was 1.774 g cm^{-3}. θ range 3–70°. Of the 3220 unique total data, 2058 [$I > 2\sigma(I)$] were considered observed. A correction for absorption was applied (maximum and minimum values for the transmission factors were 1.000 and 0.601).[22] The structure was solved by Patterson methods.[23] R = 0.0680 (R_w = 0.0693). Atomic scattering factors, corrected for anomalous dispersion, were taken from *International Tables for X-Ray Crystallography*.[24] Figure 2 was prepared with the aid of ORTEP.[25]

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