Synthesis and Structure of 2,2′-Dihydroxybenzophenones and 1,8-Dihydroxyfluorenones

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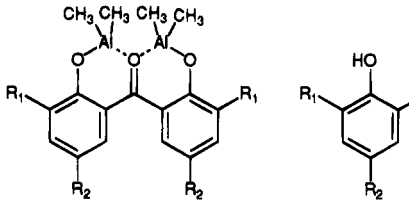
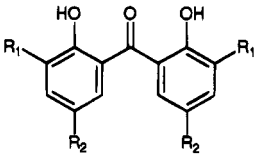
Derivatives of 2,2′-dihydroxybenzophenone and 1,8-dihydroxyfluorenone are interesting because their structures juxtapose a carbonyl group and two hydroxyl groups, thereby permitting them to be used to study the double electrophilic activation of carbonyl compounds by Lewis and Brønsted acids. Efficient syntheses of selected 2,2′-dihydroxybenzophenones **2a,b** and 1,8-dihydroxyfluorenones **3a–c** are described. Spectroscopic and X-ray crystallographic studies show that the carbonyl oxygen atom in each series of compounds accepts two approximately symmetric intramolecular hydrogen bonds. This observation illustrates the ability of carbonyl compounds to interact simultaneously with multiple electrophilic sites.

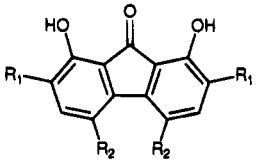
We have recently shown that derivatives of 2,2′-dihydroxybenzophenone provide a molecular framework suitable for studies of the double electrophilic activation of carbonyl groups by Lewis acids.[3] For example, the framework holds the two Lewis acidic atoms of aluminum in phenoxide **1** in an orientation that permits their simultaneous interaction with the oxygen atom of the carbonyl group. This work has established that the double coordination of ketones by main-group Lewis acids is enthalpically feasible and has marked effects on the geometry, spectroscopic properties, and reactivity of the bound carbonyl group.[3] The magnitude of these effects should depend on the precise orientation of the adjacent sites of Lewis acidity. In phenoxide **1**, the characteristic preference of benzophenones for approximate C_2 conformations[4] prevents the Lewis acidic sites from both lying in the carbonyl plane, where their bonding to the carbonyl oxygen should be strongest,[5] and forces them instead to lie distinctly above and below the plane. To evaluate the effect of this distortion, we decided to compare phenoxides derived from 2,2′-dihydroxybenzophenones, such as compound **1**, with essentially planar analogues derived from 1,8-dihydroxyfluorenones. In this paper, we describe syntheses of 2,2′-dihydroxybenzophenones **2a,b**[6] and 1,8-dihydroxyfluorenones **3a–c**,[7] and we report X-ray crystallographic studies of the intramolecular hydrogen bonding in compounds **2b** and **3c**.



1 (R_1 = *t*-Bu, R_2 = Br)

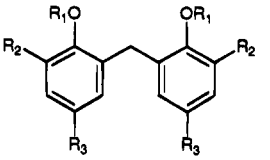


2a ($R_1 = R_2$ = *t*-Bu)
2b (R_1 = *t*-Bu, R_2 = Br)

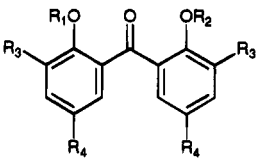


3a ($R_1 = R_2$ = H)
3b (R_1 = *t*-Bu, R_2 = H)
3c (R_1 = *t*-Bu, R_2 = Br)

Syntheses of 2,2′-Dihydroxybenzophenones 2a,b. Treatment of diphenylmethane **4a**[8] with pyridine in acetic anhydride provided the corresponding diacetate **4b** in 98% yield, which was converted into benzophenone **5a** in 33% yield by oxidation with CrO_3 in acetic anhydride.[9]



4a (R_1 = H, $R_2 = R_3$ = *t*-Bu)
4b (R_1 = $COCH_3$, $R_2 = R_3$ = *t*-Bu)
4c (R_1 = H, R_2 = *t*-Bu, R_3 = Br)
4d (R_1 = CH_3, R_2 = *t*-Bu, R_3 = Br)



5a ($R_1 = R_2$ = $COCH_3$, $R_3 = R_4$ = *t*-Bu)
5b ($R_1 = R_2$ = CH_3, $R_3 = R_4$ = *t*-Bu)
5c (R_1 = H, R_2 = CH_3, $R_3 = R_4$ = *t*-Bu)
5d ($R_1 = R_2$ = CH_3, R_3 = *t*-Bu, R_4 = Br)

Basic hydrolysis then produced dihydroxybenzophenone **2a** in 73% yield.[6] Deprotonation using excess KH, followed by methylation with CH_3I, gave dimethoxybenzophenone **5b** in 84% yield, and a similar sequence using 1 equiv of KH produced monomethoxybenzophenone **5c** in 93% yield.

Dihydroxybenzophenone **2b** was synthesized from 4-bromo-2-(1,1-dimethylethyl)phenol,[10] which was converted into diphenylmethane **4c** in 66% yield by conden-

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(2) Killam Research Fellow, 1992–1994.

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(7) For previous syntheses of 1,8-dihydroxyfluorenone (**3a**) and derivatives, see: Kajigaeshi, S.; Kobayashi, K.; Kurata, S.; Kitajima, A.; Nakahara, F.; Nago, H.; Nishiida, A.; Fujisaki, S. *Nippon Kagaku Kaishi* **1989**, 2052.

(8) Wegler, R.; Faber, K. *Chem. Ber.* **1949**, *82*, 327.

(9) For similar oxidations, see: Hakimelahi, G. H.; Moshfegh, A. A. *Helv. Chim. Acta* **1981**, *64*, 599.

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sation with formaldehyde.[11] Deprotonation with excess KH, followed by methylation with CH_3I, then provided diphenylmethane **4d** in 80% yield. Oxidation with CrO_3 in acetic anhydride gave the corresponding benzophenone **5d** in 63% yield,[9] and demethylation using BBr_3 then provided dihydroxybenzophenone **2b** in 81% yield.

Structure of 2,2′-Dihydroxybenzophenone 2b. In derivatives of 2,2′-dihydroxybenzophenone, two acidic hydroxyl groups are held in an orientation that should allow them to act simultaneously as donors of hydrogen bonds to the oxygen atom of the carbonyl group. In principle, 2,2′-dihydroxybenzophenones therefore provide the structural elements required for studies of the double electrophilic activation of carbonyl groups by Brønsted acids.[12] Studies using IR, ^1H NMR, ^{13}C NMR, and ^{17}O NMR spectroscopy have provided evidence suggesting that the carbonyl oxygen atom in 2,2′-dihydroxybenzophenone can accept two intramolecular hydrogen bonds in solution despite the preference of benzophenones for nonplanar C_2 conformations.[13] In addition, X-ray crystallographic studies have established that similar structures are favored in the solid state;[14] however, 2,2′-dihydroxybenzophenone and simple derivatives participate simultaneously in networks of intermolecular hydrogen bonds, which introduce unsymmetric perturbations of the intramolecular hydrogen bonds.

We expected that intermolecular hydrogen bonds would be absent in suitably hindered 3,3′-disubstituted derivatives of 2,2′-dihydroxybenzophenone, thereby allowing us to examine the double intramolecular hydrogen bonding of a carbonyl group in a symmetric system free of significant perturbations. The IR and ^1H NMR spectra of solutions of 2,2′-dihydroxybenzophenone **2b** in chloroform showed a broad OH stretch and deshielded OH hydrogens diagnostic of hydrogen bonding, and the insensitivity of the spectra to changes in concentration confirmed that the hydrogen bonds must be intramolecular. To permit a more detailed examination, the structure of derivative **2b** was determined by X-ray crystallography. Two independent but closely similar molecules are present in the asymmetric unit, and both are shown in Figure 1. As expected, the carbonyl oxygen atom accepts two intramolecular hydrogen bonds, and intermolecular hydrogen bonds are absent. In both molecules, the intramolecular hydrogen bonds are strong and nearly symmetric; in molecule 1, the distances O(12)–O(13) and O(12)–O(11) are 2.606(3) and 2.587(3) Å, respectively, and the corresponding distances in molecule 2 are 2.624(3) and 2.617(3) Å. The average O···O distance (2.608(3) Å) is shorter than that measured for 2,2′-dihydroxybenzophenone itself (2.629(2) Å),[14a] presumably because the intramolecular hydrogen bonds in the unsubstituted derivative are weakened by intermolecular hydrogen bonds. In addition, the *tert*-butyl groups may exert small buttressing effects. As expected, the average O···O distance in compound **2b** is longer than the corresponding distance in 2,4-dihydroxybenzophenone (2.550(4) Å),[15] in which only a single intramolecular hydrogen bond is possible. This indicates that the formation of two hydrogen bonds to a single carbonyl oxygen atom is accompanied by a decrease in their average strength. The average carbonyl C–O distance in compound **2b** (1.244(3) Å) is slightly longer than the corresponding distance in simple benzophenones (1.22–1.23 Å)[16] but similar to that in 2,4-dihydroxybenzophenone (1.253(4) Å)[15] and 2,2′-dihydroxybenzophenone (1.242(2) Å).[14a] The lengthening can therefore be attributed to electron-donating resonance effects of the hydroxyl groups rather than to a specific consequence of double hydrogen bonding.

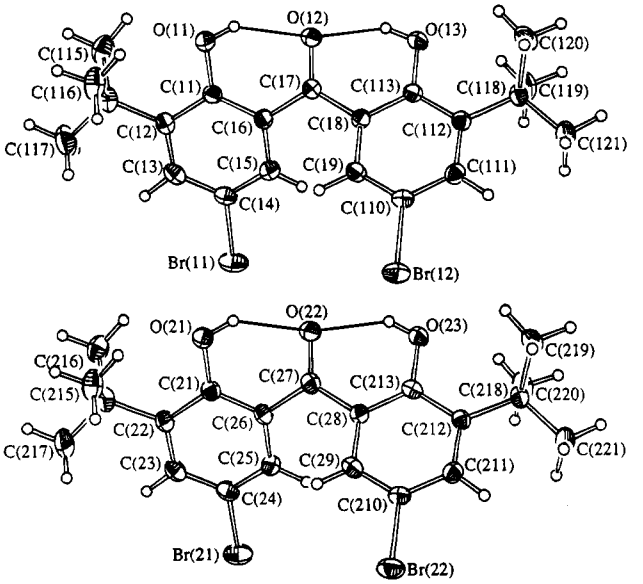

Figure 1. ORTEP drawings of the structures of the two independent molecules of 2,2′-dihydroxybenzophenone **2b**. The upper figure shows molecule 1, and the lower shows molecule 2. Hydrogen atoms appear as spheres of arbitrary size, and other atoms are represented by ellipsoids corresponding to 40% probability. Hydrogen bonds are represented by narrow lines.

The characteristic preference of benzophenones for approximate C_2 conformations[4] forces the intramolecular hydrogen bonds in 2,2′-dihydroxybenzophenone **2b** to lie distinctly above and below the carbonyl plane, rather than in the carbonyl plane where they should be strongest.[17] A measure of this distortion is provided by the dihedral angles C(19)–C(18)–C(17)–O(12) and C(15)–C(16)–C(17)–O(12) in molecule 1 and the corresponding angles in molecule 2, which have an average absolute value of 30.8(4)°. The average nonbonded H(15)–H(19) and H(25)–H(29) distances are 2.50(4) Å. Similar values are observed in other 2,2′-dihydroxybenzophenones,[14a] but the dihedral angles in aluminum phenoxide **1** are markedly smaller (8.3(1)°),[3b] presumably because the dative Lewis acid–Lewis base interactions are stronger

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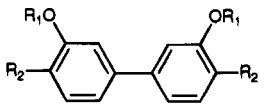
and more resistant to deformations,[5] or because the electron-donating resonance effects of the $(CH_3)_2AlO$ groups enforce a more nearly coplanar orientation of the carbonyl group and the aromatic rings.

Syntheses of 1,8-Dihydroxyfluorenones 3a–c. Despite the structural simplicity of 1,8-dihydroxyfluorenone, there is only one report of a previous synthesis, which requires eight steps and provides an overall yield of only 3%.[7] We were optimistic that more efficient syntheses of 1,8-dihydroxyfluorenone and its derivatives could be devised by using ortho-metalations of appropriately substituted biphenyls.[18] Specifically, double lithiation of 3,3′-dimethoxybiphenyl (**6a**)[19] or 4,4′-disubstituted derivative **6b**, followed by the addition of formate or chloroformate esters, might be expected to provide the corresponding fluorenols or fluorenones. Substituted

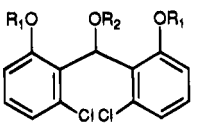


6a ($R_1 = CH_3$, $R_2 = H$)
6b ($R_1 = CH_3$, $R_2 = t$-Bu)
6c ($R_1 = CON(C_2H_5)_2$, $R_2 = t$-Bu)
6d ($R_1 = H$, $R_2 = t$-Bu)

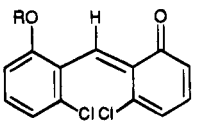
biphenyl **6b** was synthesized from 5-bromo-2-(1,1-dimethylethyl)-1-methoxybenzene[20] in 50% yield by Ni(0)-induced aryl–aryl coupling.[19] Unfortunately, lithiation of 3,3′-dimethoxybiphenyl (**6a**) occurred at both activated ortho positions without marked selectivity,[21] while lithiation of substituted derivative **6b** and subsequent trapping with formate and chloroformate esters under a variety of conditions failed to provide useful amounts of the corresponding fluorenol or fluorenone. In this case, the methoxy groups are presumably forced by the substituents at positions 4 and 4′ to adopt conformations unsuitable for ortho-metalation.[22,23]

We expected double ortho-lithiation of dicarbamate **6c** to be more efficient,[18a] and we hoped that a single anionic ortho-Fries rearrangement would then occur, allowing a fluorenone to be formed by subsequent intramolecular acylation.[18b] Dicarbamate **6c** was prepared in 64% overall yield by BBr_3-induced demethylation of compound **6b**, followed by carbamoylation of the resulting dihydroxybiphenyl **6d** with diethylcarbamoyl chloride. Unfortunately, standard metalation of dicarbamate **6c** using a slight excess of *sec*-butyllithium and TMEDA at −78 °C, followed by quenching with H_2O at low temperature, yielded primarily the product of a double anionic ortho-Fries rearrangement and only traces of the desired fluorenone. We propose that the presence of substituents at positions 4 and 4′ accelerates the Fries rearrangements and makes them faster than the formation of the fluorenone that results from intramolecular trapping of the initial intermediate.

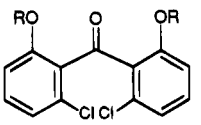
These instructive failures forced us to devise alternative syntheses of 1,8-dihydroxyfluorenones that are longer but nevertheless more efficient. Treatment of the diethylcarbamate of 3-chlorophenol[18a] with *sec*-butyllithium/TMEDA, followed by the addition of ethyl formate, provided a modest yield of ethyl benzhydryl ether **7a** instead of the expected benzhydrol **7b**. We propose that compound **7a** is derived from benzhydrol **7b** by base-induced transacylation and elimination, followed by



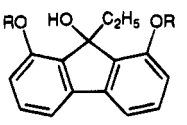
7a ($R_1 = H$, $R_2 = C_2H_5$)
7b ($R_1 = CON(C_2H_5)_2$, $R_2 = H$)
7c ($R_1 = CH_3$, $R_2 = C_2H_5$)
7d ($R_1 = CH_3$, $R_2 = H$)



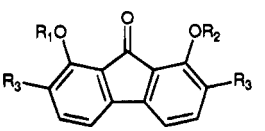
8 ($R = CON(C_2H_5)_2$)



9 ($R = CH_3$)



10 ($R = CH_3$)



11a ($R_1 = R_2 = CH_3$, $R_3 = H$)
11b ($R_1 = R_2 = CH_3$, $R_3 = t$-Bu)
11c ($R_1 = H$, $R_2 = CH_3$, $R_3 = t$-Bu)

conjugate addition of ethoxide to intermediate **8** or a related structure. Support for this hypothesis is provided by the observation that the yield of compound **7a** could be raised to 55% by treating the initial products with excess sodium ethoxide. Deprotonation of diphenol **7a** with excess KH, followed by methylation with CH_3I, then provided compound **7c** in 86% yield. Standard conditions for Ullmann coupling failed to convert compound **7c** into the corresponding fluorene, but we hoped that benzophenone **9** would be more reactive. An attempt to prepare compound **9** from benzhydryl ether **7c** by direct benzylic oxidation using trityl tetrafluoroborate[24] gave a 76% yield of benzhydrol **7d** instead, presumably because the activated hydrogen atoms of the ethoxy group are more accessible. Further oxidation of benzhydrol **7d** gave a 94% yield of the desired benzophenone **9**, but it did not undergo standard Ullmann coupling. Fortunately, we found that treatment of benzhydryl ether **7c** with Ni(0) under the conditions of Caubère[19] led to aryl–aryl coupling accompanied by a Wittig rearrangement, thereby providing fluorenol **10** in 52% yield. Compound **10** was dehydrated by the action of acetic acid and acetic anhydride, and the crude product was immediately subjected to oxidation with CrO_3 to give dimethoxyfluorenone **11a** in 69% overall yield.[25] BBr_3-induced demethylation finally provided 1,8-dihydroxyfluorenone

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(19) Lourak, M.; Vanderesse, R.; Fort, Y.; Caubère, P. *J. Org. Chem.* **1989**, *54*, 4840.
(20) Carpenter, M. S.; Easter, W. M.; Wood, T. F. *J. Org. Chem.* **1951**, *16*, 586.
(21) For a discussion of the regioselective 2,2′-dilithiation of biphenyl, see: Neugebauer, W.; Kos, A. J.; Schleyer, P.v.R. *J. Organomet. Chem.* **1982**, *228*, 107.
(22) Schuster, I. I.; Parvez, M.; Freyer, A. J. *J. Org. Chem.* **1988**, *53*, 5819. Hummel, W.; Huml, K.; Bürgi, H.-B. *Helv. Chim. Acta* **1988**, *71*, 1291.
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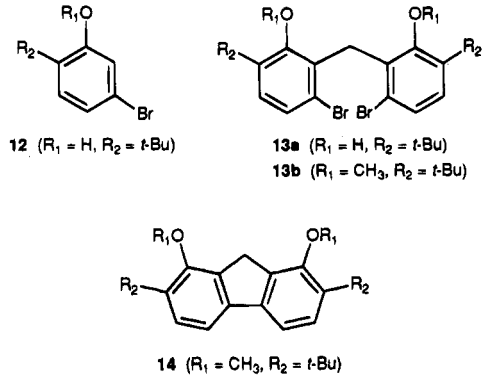
(24) Barton, D. H. R.; Magnus, P. D.; Smith, G.; Streckert, G.; Zurr, D. *J. Chem. Soc., Perkin Trans. 1* **1972**, 542.
(25) For a similar procedure, see: Riegel, B.; Moffett, R. B.; McIntosh, A. V. *Org. Synth.* **1944**, *24*,38, 41.

(**3a**) in 92% yield. Conversion of 3-chlorophenol into 1,8-dihydroxyfluorenone by this route required six steps and proceeded in an overall yield of 15%.

We devised a second route to 1,8-dihydroxyfluorenones starting with 5-bromo-2-(1,1-dimethylethyl)-1-methoxybenzene,[20] which could be converted into the corresponding phenol **12** in 90% yield by demethylation with BBr_3. Treatment with ethylmagnesium bromide, followed by condensation with formaldehyde,[11] then provided diphenylmethane **13a** regioselectively in 56% yield. Deprotonation with KH, followed by methylation with CH_3I, gave a 92% yield of compound **13b**, which was then converted into fluorene **14** in 62% yield by Ni(0)-induced aryl–aryl coupling.[26] Subsequent oxidation with CrO_3 in pyridine produced fluorenone **11b** in 87% yield. Monodemethylation using BBr_3 provided hydroxyfluorenone **11c** in 80% yield, and complete demethylation using LiI in hot collidine gave 1,8-dihydroxyfluorenone **3b** in 93% yield, while the action of HBr in hot acetic acid produced 1,8-dihydroxyfluorenone (**3a**)[7] in 86% yield. Conversion of 5-bromo-2-(1,1-dimethylethyl)-1-methoxybenzene into 1,8-dihydroxyfluorenone (**3a**) by this second route required six steps, proceeded in an overall yield of 22%, and also provided access to substituted dihydroxyfluorenone **3b**.



Structure of 1,8-Dihydroxyfluorenone 3c. In principle, derivatives of 1,8-dihydroxyfluorenone hold two acidic hydroxyl groups in an orientation permitting them to act simultaneously as donors of hydrogen bonds to the oxygen atom of the carbonyl group; moreover, the hydrogen bonds are constrained to lie close to the carbonyl plane, thereby maximizing their strength.[17] However, no previous studies of intramolecular hydrogen bonding in this intriguing system have been reported. An ideal candidate for studies of this type is substituted 1,8-dihydroxyfluorenone **3c**, since it is unlikely to participate in intermolecular hydrogen bonds; in addition, its structure can be compared directly with that of the closely analogous 2,2′-dihydroxybenzophenone **2b**. Compound **3c** was prepared in 60% yield by direct bromination of dihydroxyfluorenone **3b**, and its structure was determined by X-ray crystallography. Two independent but closely similar molecules are present in the asymmetric unit, and both are shown in Figure 2. As expected, the carbonyl oxygen atom accepts two intramolecular hydrogen bonds, and intermolecular hydrogen bonds are absent. In both molecules, the intramolecular hydrogen bonds are nearly symmetric but relatively long; in molecule 1, the distances O(12)–O(13) and O(12)–O(11) are 2.739(5) and 2.754(5) Å, respectively, and the corresponding distances in molecule 2 are 2.746(5) and 2.744(5) Å. The average O···O distance (2.746(5) Å) is significantly longer than the corresponding distance in 2,2′-dihydroxybenzophenone **2b** (2.608(3) Å), even though the hydrogen bonds in 1,8-dihydroxyfluorenone **3c** lie close to the carbonyl plane. This difference is presumably due to angular deformations characteristic of the strained fluorenone skeleton,[27] principally the opening of angles at C(16), C(17), C(18), C(26), C(27), and C(28) within the enol rings of molecules 1 and 2 to an average value of 125.4(4)°. Even larger angular deformations at these positions are observed in 9-fluorenone itself,[27] indicating that the intramolecular hydrogen bonds in 1,8-dihydroxyfluorenone **3c** are strong enough to exert a measurable structural effect by bringing the hydrogen-bonded oxygen atoms into closer proximity.

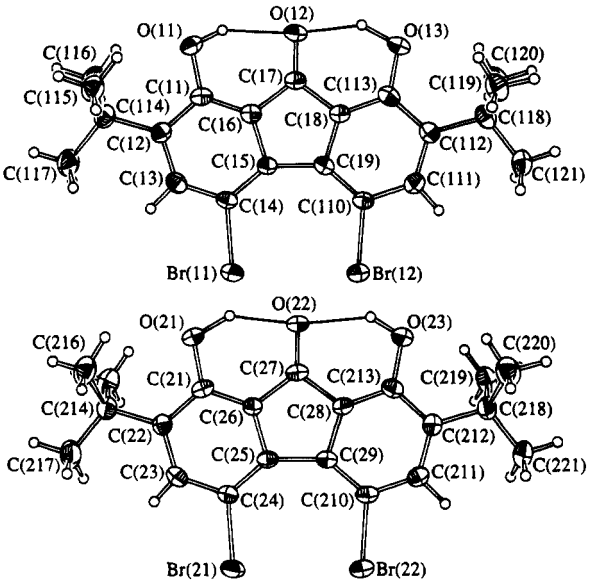


Figure 2. ORTEP drawings of the structures of the two independent molecules of 1,8-dihydroxyfluorenone **3c**. The upper figure shows molecule 1, and the lower shows molecule 2. Hydrogen atoms appear as spheres of arbitrary size, and other atoms are represented by ellipsoids corresponding to 40% probability. Hydrogen bonds are represented by narrow lines.

Careful comparison of the structures of 9-fluorenone and 1,8-dihydroxyfluorenone **3c** reveals other significant differences. Of special interest are distortions that arise from the close juxtaposition of atoms of bromine at positions 4 and 6. This causes angle C(15)–C(14)–Br(11), angle C(14)–C(15)–C(19), distance C(15)–C(19), and the related angles and distances in molecules 1 and 2 to increase to average values of 126.7(3)°, 139.1(4)°, and 1.520(6) Å, respectively, whereas the corresponding average values in 9-fluorenone are 119.7(2)°, 131.1(2)°, and 1.475(4) Å. Despite these deformations, the average Br···Br separation (3.331(1) Å) is still much shorter than the sum of the van der Waals radii (3.90 Å).[28] Nevertheless, the average C–Br distance (1.896(4) Å) is very similar to that in dihydroxybenzophenone **2b** (1.898(3) Å) and other aryl bromides.

The average carbonyl C–O distance in dihydroxyfluorenone **3c** is 1.248(5) Å, which is longer than that in 9-fluorenone itself (1.220(2) Å).[27] This elongation is presumably a consequence of the electron-donating reso-

(26) Colon, I.; Kelsey, D. R. *J. Org. Chem.* **1986**, *51*, 2627.

(27) Luss, H. R.; Smith, D. L. *Acta Crystallogr.* **1972**, *B28*, 884.

(28) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; p 514.

nance effects of the hydroxyl groups rather than a result of double hydrogen bonding. Support for this conclusion is provided by the observation that the distance corresponding to C(16)–C(17) in molecules 1 and 2 of dihydroxyfluorenone **3c** is shortened to an average value of 1.453(6) Å, whereas the corresponding distance in 9-fluorenone is 1.486(3) Å.[27]

Conclusion. Our work provides convenient access to selected derivatives of 2,2′-dihydroxybenzophenone and 1,8-dihydroxyfluorenone. These compounds are interesting because their structures juxtapose a carbonyl group and two hydroxyl groups, thereby permitting them to be used to study the double electrophilic activation of carbonyl compounds by Lewis and Brønsted acids. Spectroscopic and X-ray crystallographic studies show that the carbonyl oxygen atom in each series of compounds accepts two approximately symmetric intramolecular hydrogen bonds, illustrating the ability of carbonyl compounds to interact simultaneously with multiple electrophilic sites.

Experimental Section

Pyridine, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), 2,4,6-collidine, CH_2Cl_2, and dimethylformamide (DMF) were dried by distillation from CaH_2, and ether and tetrahydrofuran (THF) were dried by distillation from the sodium ketyl of benzophenone. Other commercial reagents were used without further purification. Flash chromatography was performed in the normal way.[29]

2,2′-Methylenebis[4,6-bis(1,1-dimethylethyl)phenol] Diacetate (4b). A solution of 2,2′-methylenebis[4,6-bis(1,1-dimethylethyl)phenol] (**4a**; 1.48 g, 3.48 mmol)[8] and pyridine (3 mL) in acetic anhydride (20 mL) was heated at reflux for 4 h. Volatiles were then removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (95%)/ethyl acetate (5%)). This yielded 2,2′-methylenebis[4,6-bis(1,1-dimethylethyl)phenol] diacetate (**4b**; 1.73 g, 3.40 mmol, 98%) as a white solid. Further purification was achieved by crystallization from hexane: mp 120–122 °C; IR (KBr) 1760 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.23 (s, 18H), 1.34 (s, 18H), 2.15 (bs, 6H), 3.65 (bs, 2H), 6.87 (bs, 2H), 7.28 (bs, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 21.0, 30.4, 31.2, 31.9(b), 34.4, 34.6, 122.0, 125.8, 131.8(b), 140.1, 145.3(b), 147.6, 169.0. Anal. Calcd for $C_{33}H_{46}O_5$: C, 75.83; H, 8.87. Found: C, 75.95; H, 9.16.

Bis[2-(acetyloxy)-3,5-bis(1,1-dimethylethyl)phenyl]methanone (5a). A stirred solution of 2,2′-methylenebis[4,6-bis(1,1-dimethylethyl)phenol] diacetate (**4b**; 2.65 g, 5.21 mmol) in acetic anhydride (30 mL) was treated with CrO_3 (1.83 g, 18.3 mmol), added during 30 min at a rate that kept the temperature from exceeding 35 °C. The mixture was warmed at 40 °C for 12 h, treated with H_2O and 10% aqueous HCl, and extracted with $CHCl_3$. The extracts were washed with water and saturated aqueous $NaHCO_3$, and volatiles were then removed by evaporation under reduced pressure. Flash chromatography (silica, $CHCl_3$ (80%)/hexane (20%)) of the residue provided analytically pure bis[2-(acetyloxy)-3,5-bis(1,1-dimethylethyl)phenyl]methanone (**5a**; 0.897 g, 1.72 mmol, 33%) as a colorless solid. Recrystallization from hexane gave an analytically pure sample: mp 136–138 °C; IR (KBr) 1765, 1660 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.32 (s, 18H), 1.38 (s, 18H), 1.79 (s, 6H), 7.50 (d, ^4J = 2.4 Hz, 2H), 7.59 (d, ^4J = 2.4 Hz, 2H); ^{13}C (75.4 MHz, $CDCl_3$) δ 20.7, 30.2, 31.2, 34.7, 34.9, 127.1, 127.6, 132.2, 140.6, 145.4, 147.6, 169.5, 193.5; HRMS (EI) calcd for $C_{33}H_{46}O_5$ 522.3345, found 522.3396.

Bis[3,5-bis(1,1-dimethylethyl)-2-hydroxyphenyl]methanone (2a).[6] A mixture of bis[2-(acetyloxy)-3,5-bis(1,1-dimethylethyl)phenyl]methanone (**5a**; 1.41 g, 2.70 mmol) in CH_3OH (20 mL) and 10% aqueous NaOH (25 mL) was heated at reflux for 10 h. After neutralization with 10% aqueous HCl, the mixture was extracted with ether, volatiles were removed from the combined extracts by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane). Recrystallization from hexane provided analytically pure bis[3,5-bis(1,1-dimethylethyl)-2-hydroxyphenyl]methanone (**2a**; 0.866 g, 1.97 mmol, 73%)[6] as a colorless solid: mp 202–203 °C (lit.[6] 202–204 °C); IR (CH_2Cl_2) 3200, 1605 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.28 (s, 18H), 1.47 (s, 18H), 7.38 (d, ^4J = 2.4 Hz, 2H), 7.57 (d, ^4J = 2.4 Hz, 2H), 11.21 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 29.4, 31.4, 34.2, 35.2, 119.5, 127.5, 130.4, 137.7, 139.7, 158.8, 204.6.

Bis[3,5-bis(1,1-dimethylethyl)-2-methoxyphenyl]methanone (5b). A suspension of KH (0.265 g, 6.61 mmol) in THF (3 mL) was stirred at 0 °C under dry N_2 and treated with a solution of bis[3,5-bis(1,1-dimethylethyl)-2-hydroxyphenyl]methanone (**2a**; 1.16 g, 2.64 mmol) in THF (5 mL). Neat CH_3I (0.93 g, 6.6 mmol) was then added, and the mixture was heated at reflux for 3 h. Volatiles were removed by evaporation under reduced pressure, and the residue was extracted with hexane. Crystallization of the hexane-soluble fraction from hexane yielded analytically pure bis[3,5-bis(1,1-dimethylethyl)-2-methoxyphenyl]methanone (**5a**; 1.04 g, 2.23 mmol, 84%) as a colorless solid: mp 195–197 °C; IR (Nujol) 1645 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 18H), 1.38 (s, 18H), 3.52 (s, 6H), 7.42 (d, ^4J = 2.5 Hz, 2H), 7.49 (d, ^4J = 2.5 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 30.6, 31.3, 34.4, 35.2, 62.6, 126.8, 127.4, 132.1, 141.8, 144.3, 157.9, 197.6; HRMS (FAB) calcd for $C_{31}H_{47}O_3$ 467.3525, found 467.3520. Anal. Calcd for $C_{31}H_{46}O_3$: C, 79.78; H, 9.94. Found: C, 80.54; H, 10.17.

[3,5-Bis(1,1-dimethylethyl)-2-hydroxyphenyl][3,5-bis(1,1-dimethylethyl)-2-methoxyphenyl]methanone (5c). A suspension of KH (49.0 mg, 1.22 mmol) in THF (2 mL) was stirred at 0 °C under dry N_2 and treated with a solution of bis[3,5-bis(1,1-dimethylethyl)-2-hydroxyphenyl]methanone (**2a**; 539 mg, 1.23 mmol) in THF (3 mL). Neat CH_3I (460 mg, 3.2 mmol) was then added, and the mixture was heated at reflux for 3 h. Volatiles were removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane). This provided [3,5-bis(1,1-dimethylethyl)-2-hydroxyphenyl][3,5-bis(1,1-dimethylethyl-2-methoxyphenyl]methanone (**5c**; 519 mg, 1.15 mmol, 93%) as an analytically pure pale yellow solid: IR (Nujol) 1620, 1590 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.20 (s, 9H), 1.32 (s, 9H), 1.44 (s, 9H), 1.49 (s, 9H), 3.61 (s, 3H), 7.18 (d, ^4J = 2.4 Hz, 1H), 7.29 (d, ^4J = 2.4 Hz, 1H), 7.48 (d, ^4J = 2.4 Hz, 1H), 7.58 (d, ^4J = 2.4 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 29.3, 30.4, 31.1, 31.3, 34.1, 34.5, 35.1, 35.3, 61.9, 118.6, 124.7, 126.1, 128.0, 131.2, 131.4, 137.3, 139.8, 141.6, 141.8, 155.0, 160.7, 204.0. Anal. Calcd for $C_{30}H_{44}O_3$: C, 79.60; H, 9.80. Found: C, 80.39; H, 10.04.

2,2′-Methylenebis[4-bromo-6-(1,1-dimethylethyl)phenol] (4c). A solution of 4-bromo-2-(1,1-dimethylethyl)phenol (12.2 g, 53.2 mmol)[10] in ether (115 mL) was stirred at 25 °C under dry N_2 and treated dropwise with a solution of ethylmagnesium bromide (18 mL, 3.0 M in ether, 54 mmol). Volatiles were then removed by evaporation under reduced pressure, and the residue of white solid was treated with benzene (200 mL) and paraformaldehyde (0.800 g, 26.6 mmol). The mixture was heated at reflux for 12 h, treated with saturated aqueous NH_4Cl, and extracted with ether. The organic extracts were then washed with water and brine, and volatiles were removed by evaporation under reduced pressure. Flash chromatography (silica, hexane (93%)/ethyl acetate (7%)) of the residue then provided 2,2′-methylenebis[4-bromo-6-(1,1-dimethylethyl)phenol] (**4c**; 8.28 g, 17.6 mmol, 66%) as an analytically pure tan solid: IR (KBr) 3426 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 18H), 3.83 (s, 2H), 6.16 (s, 2H), 7.22 (d, ^4J = 2.4 Hz, 2H), 7.25 (d, ^4J = 2.4 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 29.6, 30.7, 34.4, 113.2, 128.6, 128.7, 130.7, 138.6, 150.8.

1,1′-Methylenebis[5-bromo-3-(1,1-dimethylethyl)-2-methoxybenzene] (4d). 1,1′-Methylenebis[5-bromo-3-(1,1-dimethylethyl)-2-methoxybenzene] (**4d**) was prepared from 2,2′-methylenebis[4-bromo-6-(1,1-dimethylethyl)phenol] (**4c**) in 80% yield by the method used to synthesize bis[3,5-bis(1,1-dimethylethyl)-2-methoxyphenyl]methanone (**5b**). An analytically pure sample of colorless crystals was prepared by

(29) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

crystallization from hexane: mp 108–110 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 18H), 3.70 (s, 6H), 4.03 (s, 2H), 7.01 (d, ^4J = 2.4 Hz, 2H), 7.32 (d, ^4J = 2.4 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 30.2, 30.7, 35.2, 61.5, 116.5, 128.7, 131.5, 135.6, 145.1, 157.4; HRMS (EI) calcd for $C_{23}H_{30}Br_2O_2$ 498.0592, found 498.0569. Anal. Calcd for $C_{23}H_{30}Br_2O_2$: C, 55.44; H, 6.07. Found: C, 55.80; H, 6.36.

Bis[5-bromo-3-(1,1-dimethylethyl)-2-methoxyphenyl]-methanone (5d). A stirred solution of 1,1′-methylenebis[5-bromo-3-(1,1-dimethylethyl)-2-methoxybenzene] (**4d**; 3.48 g, 6.98 mmol) in acetic anhydride (70 mL) was treated with CrO_3 (1.74 g, 17.4 mmol), added during 30 min at a rate that kept the temperature from exceeding 35 °C. The mixture was kept at 25 °C for 12 h and was then heated at reflux for 1 h. After the addition of water and 10% aqueous HCl, the green mixture was extracted with ethyl acetate, and the combined organic phases were washed with water and saturated aqueous $NaHCO_3$. Volatiles were removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (94%)/ethyl acetate (6%)). This provided an analytically pure sample of bis[5-bromo-3-(1,1-dimethylethyl)-2-methoxyphenyl]methanone (**5d**; 2.25 g, 4.39 mmol, 63%) as white needles: mp 167–168 °C; IR (KBr) 1675 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 18H), 3.48 (s, 6H), 7.58 (s, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 30.3, 35.3, 63.2, 115.3, 131.8, 133.6, 133.8, 145.6, 159.6, 193.4; HRMS (EI) calcd for $C_{23}H_{28}Br_2O_3$ 512.0384, found 512.0363.

Bis[5-bromo-3-(1,1-dimethylethyl)-2-hydroxyphenyl]-methanone (2b). A solution of bis[5-bromo-3-(1,1-dimethylethyl)-2-methoxyphenyl]methanone (**5d**; 2.25 g, 4.39 mmol) in CH_2Cl_2 (25 mL) was stirred at −78 °C under dry N_2 and treated dropwise with a solution of BBr_3 (11 mL, 1.0 M in CH_2Cl_2, 11 mmol). After 1 h, the cooling bath was removed and the mixture was stirred at 25 °C for 12 h. Saturated aqueous $NaHCO_3$ was then added, and the mixture was extracted with CH_2Cl_2. Volatiles were removed from the combined extracts by evaporation under pressure, and the residue was purified by flash chromatography (silica, hexane). Recrystallization from hexane provided an analytically pure sample of bis[5-bromo-3-(1,1-dimethylethyl)-2-hydroxyphenyl]methanone (**2b**; 1.73 g, 3.57 mmol, 81%) as yellow needles: mp 196–197 °C; IR (KBr) 3185, 1590 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 18H), 7.50 (d, ^4J = 2.4 Hz, 2H), 7.60 (d, ^4J = 2.4 Hz, 2H), 11.00 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 29.0, 35.3, 110.4, 120.8, 132.5, 136.1, 141.4, 159.8, 201.6; HRMS (EI) calcd for $C_{21}H_{24}Br_2O_3$ 484.0071, found 484.0054. Anal. Calcd for $C_{21}H_{24}Br_2O_3$: C, 52.09; H, 5.00. Found: C, 52.09; H, 5.22.

4,4′-Bis(1,1-dimethylethyl)-3,3′-dimethoxy-1,1′-biphenyl (6b). A stirred mixture of NaH (2.88 g, 120 mmol), $Ni(OOCCH_3)_2$ (3.54 g, 20.0 mmol), 2,2′-bipyridyl (6.30 g, 40.3 mmol), and *tert*-amyl alcohol (3.50 g, 39.7 mmol) in THF (80 mL) was heated at reflux under dry N_2 for 2 h. A solution of 5-bromo-2-(1,1-dimethylethyl)-1-methoxybenzene (4.83 g, 19.9 mmol)[20] in THF (20 mL) was then added, and refluxing was continued for 19 h. After the addition of ethanol (10 mL) and 10% aqueous HCl (90 mL), the mixture was extracted with ether. Volatiles were removed from the combined extracts by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (95%)/ethyl acetate (5%)). Recrystallization from hexane provided analytically pure 4,4′-bis(1,1-dimethylethyl)-3,3′-dimethoxy-1,1′-biphenyl (**6b**; 1.63 g, 4.99 mmol, 50%) as a colorless solid: mp 102.0–104.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41 (s, 18H), 3.90 (s, 6H), 7.07 (d, ^4J = 1.8 Hz, 2H), 7.10 (dd, ^3J = 8.0 Hz, ^4J = 1.8 Hz, 2H), 7.33 (d, ^3J = 8.0 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 29.7, 34.6, 55.0, 110.4, 118.8, 126.7, 137.1, 140.2, 158.6; HRMS (EI) calcd for $C_{22}H_{30}O_2$ 326.2246, found 326.2237.

4,4′-Bis(1,1-dimethylethyl)[1,1′-biphenyl]-3,3′-diol (6d). A solution of 4,4′-bis(1,1-dimethylethyl)-3,3′-dimethoxy-1,1′-biphenyl (**6b**; 881 mg, 2.70 mmol) in CH_2Cl_2 (20 mL) was stirred at −78 °C under dry N_2 and treated dropwise with a solution of BBr_3 (5.4 mL, 1.0 M in CH_2Cl_2, 5.4 mmol). The mixture was kept at 25 °C for 17 h, cooled to 0 °C, treated successively with saturated aqueous $NaHCO_3$ (20 mL) and water (50 mL), and extracted with ether. Volatiles were removed from the combined extracts by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (85%)/ethyl acetate (15%)). Recrystallization from hexane provided analytically pure 4,4′-bis(1,1-dimethylethyl)[1,1′-biphenyl]-3,3′-diol (**6d**; 731 mg, 2.45 mmol, 91%) as white needles: mp 184–185 °C; IR (KBr) 3522 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 18H), 4.87 (bs, 2H), 6.84 (d, ^4J = 1.8 Hz, 2H), 7.06 (dd, ^3J = 8.2 Hz, ^4J = 1.8 Hz, 2H), 7.31 (d, ^3J = 8.2 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 29.5, 34.3, 114.9, 118.9, 127.3, 135.2, 139.3, 154.2; HRMS (EI) calcd for $C_{20}H_{26}O_2$ 298.1933, found 298.1908.

4,4′-Bis(1,1-dimethylethyl)[1,1′-biphenyl]-3,3′-diol Bis-(diethylcarbamate) (6c). A stirred mixture of 4,4′-bis(1,1-dimethylethyl)[1,1′-biphenyl]-3,3′-diol (**6d**; 181 mg, 0.607 mmol) and diethylcarbamoyl chloride (984 mg, 7.26 mmol) in pyridine (1 mL) was heated at reflux for 19 h. Water was then added, and the mixture was extracted with ether. Volatiles were removed from the combined extracts by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (83%)/ethyl acetate (17%)). This gave 4,4′-bis(1,1-dimethylethyl)[1,1′-biphenyl]-3,3′-diol bis(diethylcarbamate) (**6c**; 210 mg, 0.423 mmol, 70%) as a colorless solid. Recrystallization from hexane/ether acetate provided an analytically pure sample: mp 157–159 °C; IR (KBr) 1716 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21 (t, ^3J = 7.1 Hz, 6H), 1.29 (t, ^3J = 7.1 Hz, 6H), 1.38 (s, 18H), 3.43 (q, ^3J = 7.1 Hz, 4H), 3.54 (q, ^3J = 7.1 Hz, 4H), 7.19 (d, ^4J = 1.7 Hz, 2H), 7.32 (dd, ^3J = 8.2 Hz, ^4J = 1.7 Hz, 2H), 7.39 (d, ^3J = 8.2 Hz, 2H); HRMS (EI) calcd for $C_{30}H_{44}N_2O_4$ 496.3301, found 496.3298.

2,2′-(Ethoxymethylene)bis(3-chlorophenol) (7a). A solution of 3-chlorophenol diethylcarbamate (28.0 g, 123 mmol)[18a] and TMEDA (14 g, 120 mmol) in THF (200 mL) was stirred at −78 °C under dry N_2 and treated dropwise with a solution of *sec*-BuLi (87.5 mL, 1.36 M in hexane, 119 mmol), added at a rate that prevented the temperature from exceeding −65 °C. The resulting mixture was kept at −78 °C for 70 min, and then ethyl formate (2.9 g, 39 mmol) was added dropwise. After an additional 60 min at −78 °C, the mixture was kept at 25 °C for 20 h. Volatiles were removed by evaporation under reduced pressure, a 15% solution of $NaOC_2H_5$ in ethanol (250 mL) was added, and the mixture was heated at reflux for 12 h. Volatiles were removed by evaporation under reduced pressure, the residue was treated with water (150 mL) and 10% aqueous HCl (300 mL), and the mixture was extracted with $CHCl_3$. The combined extracts were washed with saturated aqueous $NaHCO_3$, solvent was removed from the organic phase by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (85%)/ethyl acetate (15%)). Recrystallization from $CHCl_3$ provided analytically pure 2,2′-(ethoxymethylene)bis(3-chlorophenol) (**7a**; 6.76 g, 21.6 mmol, 55%) as a colorless solid: 171–176 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30 (t, ^3J = 7.0 Hz, 3H), 3.77 (q, ^3J = 7.0 Hz, 2H), 6.54 (s, 1H), 6.80 (dd, ^3J = 8.1 Hz, ^4J = 1.2 Hz, 2H), 6.94 (dd, ^3J = 8.1 Hz, ^4J = 1.2 Hz, 2H), 7.11 (t, ^3J = 8.1 Hz, 2H), 8.27 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 15.0, 65.8, 78.4, 115.9, 121.6, 121.9, 129.6, 134.5, 156.7. Anal. Calcd for $C_{15}H_{14}Cl_2O_3$: C, 57.53; H, 4.51. Found: C, 57.37; H, 4.64.

1,1′-(Ethoxymethylene)bis(2-chloro-6-methoxybenzene) (7c). A suspension of KH (3.08 g, 76.8 mmol) in DMF (40 mL) was stirred at 0 °C under dry N_2 and treated dropwise with a solution of 2,2′-(ethoxymethylene)bis(3-chlorophenol) (**7a**; 8.88 g, 28.4 mmol) in DMF (44 mL). The mixture was then stirred at 25 °C for 1 h, recooled to 0 °C, treated dropwise with CH_3I (14.1 g, 99.3 mmol), and kept at 25 °C for 15 h. After the addition of water, the mixture was extracted with $CHCl_3$, and volatiles were removed from the combined extracts by evaporation under reduced pressure. Crystallization of the residue from $CHCl_3$/hexane provided analytically pure 1,1′-(ethoxymethylene)bis(2-chloro-6-methoxybenzene) (**7c**; 8.37 g, 24.5 mmol, 86%) as a white powder: mp 161.0–163.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30 (t, ^3J = 7.0 Hz, 3H), 3.62 (s, 6H), 3.63 (q, ^3J = 7.0 Hz, 2H), 6.35 (s, 1H), 6.71 (dd, ^3J = 8.2 Hz, ^4J = 1.0 Hz, 2H), 6.99 (dd, ^3J = 8.2 Hz, ^4J = 1.0 Hz, 2H), 7.11 (t, ^3J = 8.2 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 15.1,

55.6, 65.4, 75.2, 109.7, 122.4, 126.9, 128.1, 135.5, 158.9. Anal. Calcd for $C_{17}H_{18}Cl_2O_3$: C, 59.84; H, 5.32. Found: C, 57.90; H 5.37.

2-Chloro-6-methoxy-α-(2-chloro-6-methoxyphenyl)benzenemethanol (7d). A solution of $Ph_3C^+ BF_4^-$ (2.20 g, 6.66 mmol) in CH_2Cl_2 (10 mL) was stirred at 25 °C under dry N_2 and treated dropwise with a solution of 1,1'-(ethoxymethylene)-bis(2-chloro-6-methoxybenzene) (**7c**; 0.760 g, 2.23 mmol) in CH_2Cl_2 (15 mL). The mixture was kept at 25 °C for 12 h, silica was added, and volatiles were removed by evaporation under reduced pressure. Flash chromatography (silica, hexane (70%)/ethyl acetate (30%)) of the adsorbed residue provided 2-chloro-6-methoxy-α-(2-chloro-6-methoxyphenyl)benzenemethanol (**7d**; 0.532 g, 1.70 mmol, 76%) as white needles. An analytically pure sample was prepared by recrystallization from $CHCl_3$: mp 167.5–169.0 °C; IR (KBr) 3570 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.76 (s, 6H), 5.49 (d, ^3J = 10.2 Hz, 1H), 6.64 (d, ^3J = 10.2 Hz, 1H), 6.79 (dd, ^3J = 8.3 Hz, ^4J = 1.0 Hz, 2H), 6.98 (dd, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 2H), 7.15 (dd, ^3J = 8.3 Hz, ^3J = 8.0 Hz, 2H). Anal. Calcd for $C_{15}H_{14}Cl_2O_3$: C, 57.53; H, 4.51. Found: C, 57.24; H, 4.56.

Bis(2-chloro-6-methoxyphenyl)methanone (9). A mixture of 2-chloro-6-methoxy-α-(2-chloro-6-methoxyphenyl)benzenemethanol (**7d**; 176 mg, 0.562 mmol) and pyridinium chlorochromate (1.26 g, 5.85 mmol) in CH_2Cl_2 (10 mL) was heated at reflux for 12 h. The mixture was cooled to 25 °C and filtered through a short column of silica (Merck 60, 230–400 mesh). Removal of volatiles by evaporation under reduced pressure left a residue of bis(2-chloro-6-methoxyphenyl)methanone (**9**; 165 mg, 0.530 mmol, 94%). Recrystallization from $CHCl_3$ provided an analytically pure sample: mp 206–207 °C; IR (KBr) 1686 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.54 (s, 6H), 6.79 (dd, ^3J = 8.3 Hz, ^4J = 0.8 Hz, 2H), 7.01 (dd, ^3J = 8.1 Hz, ^4J = 0.8 Hz, 2H), 7.26 (dd, ^3J = 8.3 Hz, ^3J = 8.1 Hz, 2H); HRMS (EI) calcd for $C_{15}H_{12}Cl_2O_3$ 310.0163, found 310.0157.

9-Ethyl-1,8-dimethoxy-9*H*-fluoren-9-o1 (10). A stirred mixture of NaH (5.24 g, 218 mmol), $Ni(OOCCH_3)_2$ (4.64 g, 26.2 mmol), 2,2'-bipyridyl (8.27 g, 52.9 mmol), and *tert*-amyl alcohol (4.7 g, 53 mmol) in THF (25 mL) was heated at reflux under N_2 for 2 h. A solution of 1,1'-(ethoxymethylene)bis(2-chloro-6-methoxybenzene) (**7c**; 2.99 g, 8.76 mmol) in THF (75 mL) was then added, and refluxing was continued for 19 h. After the addition of water (10 mL) and 10% aqueous HCl (250 mL), the mixture was extracted with ether. The combined extracts were washed with saturated aqueous $NaHCO_3$ and brine, and volatiles were removed by evaporation under reduced pressure. Flash chromatography (silica, hexane (70%)/ethyl acetate (30%)) of the residue, followed by decolorization with activated carbon, gave 9-ethyl-1,8-dimethoxy-9*H*-fluoren-9-o1 (**10**; 1.23 g, 4.55 mmol, 52%) as a beige solid. Recrystallization from toluene provided an analytically pure sample: mp 123–125 °C; IR (KBr) 3537, 3465 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.35 (t, ^3J = 7.5 Hz, 3H), 2.62 (q, ^3J = 7.5 Hz, 2H), 2.96 (bs, 1H), 3.93 (s, 6H), 6.81 (d, ^3J = 8.0 Hz, 2H), 7.22 (d, ^3J = 7.4 Hz, 2H), 7.31 (dd, ^3J = 8.0 Hz, ^3J = 7.4 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 9.1, 28.9, 55.3, 85.6, 110.2, 112.8, 130.1, 133.1, 141.8, 156.3. Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.57; H, 6.63.

1,8-Dimethoxy-9*H*-fluoren-9-one (11a).[7] A solution of 9-ethyl-1,8-dimethoxy-9*H*-fluoren-9-o1 (**10**; 86.3 mg, 0.319 mmol) in acetic acid (3 mL) and acetic anhydride (3 mL) was heated at reflux for 1 h, treated with 10% aqueous H_2SO_4 (10 mL) and excess CrO_3 (189 mg, 1.89 mmol), and then warmed at 80 °C for 20 min. After the addition of water, the resulting mixture was extracted with CH_2Cl_2, the combined extracts were washed with saturated aqueous $NaHCO_3$, and volatiles were removed by evaporation under reduced pressure. Flash chromatography (silica, hexane (30%)/ethyl acetate (70%)) of the residue gave 1,8-dimethoxy-9*H*-fluoren-9-one (**11a**, 52.8 mg, 0.220 mmol, 69%).[7] Recrystallization from $CHCl_3$ provided analytically pure yellow needles: mp 234–237 °C (lit.[7] 240–242 °C); IR (KBr) 1706 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.98 (s, 6H), 6.85 (d, ^3J = 8.4 Hz, 2H), 7.14 (d, ^3J = 7.3 Hz, 2H), 7.43 (dd, ^3J = 8.4 Hz, ^3J = 7.3 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 55.8, 112.6, 113.2, 120.1, 135.7, 145.2, 157.9, 190.0; HRMS (EI) calcd for $C_{15}H_{12}O_3$ 240.0786, found 240.0789.

1,8-Dihydroxy-9*H*-fluoren-9-one (3a).[7] A solution of 1,8-dimethoxy-9*H*-fluoren-9-one (**11a**; 50.5 mg, 0.210 mmol) in CH_2Cl_2 (2 mL) was stirred at 0 °C under dry N_2 and treated dropwise with a solution of BBr_3 (1.0 mL, 1.0 M in CH_2Cl_2, 1.0 mmol). The mixture was stirred at 25 °C for 16 h, and then 10% aqueous HCl was added. The mixture was extracted with CH_2Cl_2, and volatiles were removed form the combined extracts by evaporation under reduced pressure. Purification of the residue by preparative thin-layer chromatography (silica, hexane (40%)/ethyl acetate (60%)) provided 1,8-dihydroxy-9*H*-fluoren-9-one (**11a**; 40.9 mg, 0.193 mmol, 92%).[7] Recrystallization from $CHCl_3$ gave analytically pure yellow needles: mp 188–190 °C (lit.[7] 238–240 °C); IR (KBr) 3416, 1667 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.77 (d, ^3J = 8.4 Hz, 2H), 7.05 (d, ^3J = 7.3 Hz, 2H), 7.37 (dd, ^3J = 8.4 Hz, ^3J = 7.3 Hz, 2H), 8.00 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 113.6, 117.4, 118.2, 137.3, 143.5, 156.8, 197.5; HRMS (EI) calcd for $C_{13}H_8O_3$ 212.0473, found 212.0459.

5-Bromo-2-(1,1-dimethylethyl)phenol (12). A solution of 5-bromo-2-(1,1-dimethylethyl)-1-methoxybenzene (17.4 g, 71.6 mmol)[20] in CH_2Cl_2 (50 mL) was stirred at −78 °C under dry N_2 and treated dropwise with neat BBr_3 (18 g, 72 mmol). After 30 min, the cooling bath was removed and the mixture was kept at 25 °C for 12 h. Saturated aqueous $NaHCO_3$ was then added, the mixture was extracted with ether, the combined ether extracts were washed with water and brine, and volatiles were removed from the organic phase by evaporation under reduced pressure. Flash chromatography (silica, hexane) of the residue provided a colorless sample of 5-bromo-2-(1,1-dimethylethyl)phenol (**12**; 14.7 g, 64.2 mmol, 90%), which was used in the next step without further purification: IR (liquid film) 3543 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.37 (s, 9H), 5.05 (bs, 1H), 6.81 (d, ^4J = 2.0 Hz, 1H), 6.98 (dd, ^3J = 8.4 Hz, ^4J = 2.0 Hz, 1H), 7.11 (d, ^3J = 8.4 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 29.3, 34.2, 119.2, 119.3, 123.3, 128.3, 135.4, 154.9; HRMS (EI) calcd for $C_{10}H_{13}BrO$ 228.0149, found 228.0144.

2,2'-Methylenebis[3-bromo-6-(1,1-dimethylethyl)phenol] (13a). A solution of 5-bromo-2-(1,1-dimethylethyl)phenol (**12**; 7.55 g, 33.0 mmol) in ether (50 mL) was treated with a solution of ethylmagnesium bromide (11 mL, 3.0 M in ether, 33 mmol), and the resulting salt was isolated and heated in benzene (30 mL) with paraformaldehyde (0.495 g, 16.5 mmol) according to the procedure used to synthesize compound **4c**. The product was isolated in the normal manner and purified by flash chromatography (silica, hexane). This gave an analytically pure sample of 2,2'-methylenebis[3-bromo-6-(1,1-dimethylethyl)phenol] (**13a**; 4.37 g, 9.29 mmol, 56%) as a white solid: mp 134–138 °C; IR (KBr) 3555 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.31 (s, 18H), 4.54 (s, 2H), 5.42 (s, 2H), 7.08 (d, ^3J = 8.6 Hz, 2H), 7.17 (d, ^3J = 8.6 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 29.4, 33.5, 34.5, 122.7, 123.1, 124.8, 127.1, 136.9, 154.9; HRMS (EI) calcd for $C_{21}H_{26}Br_2O_2$ 470.0278, found 470.0239.

1,1'-Methylenebis[6-bromo-3-(1,1-dimethylethyl)-2-methoxybenzene] (13b). A mixture of KH (1.45 g, 36.2 mmol) and 18-crown-6 (0.468 g, 1.77 mmol) in DMF (10 mL) was stirred at 0 °C under dry Ar and treated dropwise with a solution of 2,2'-methylenebis[3-bromo-6-(1,1-dimethylethyl)-phenol] (**13a**; 7.70 g, 16.4 mmol) in DMF (30 mL). The mixture was kept at 0 °C for 1 h and at 25 °C for 1 h, excess CH_3I (11.4 g, 80.3 mmol) was then added, and the mixture was heated at 70 °C for 12 h. Water was added and the resulting mixture was extracted with ether. The combined organic extracts were washed with water and brine, volatiles were removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane). This provided 1,1'-methylenebis[6-bromo-3-(1,1-dimethylethyl)-2-methoxybenzene] (**13b**; 7.54 g, 15.1 mmol, 92%) as an analytically pure white solid: mp 164–166 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.33 (s, 18H), 3.65 (s, 6H), 4.42 (s, 2H), 7.03 (d, ^3J = 8.6 Hz, 2H), 7.17 (d, ^3J = 8.6 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 30.6, 32.3, 34.8, 61.6, 122.9, 125.8, 127.8, 133.2, 141.7, 160.0; HRMS (EI) calcd for $C_{23}H_{30}Br_2O_2$ 498.0592, found 498.0620. Anal. Calcd for $C_{23}H_{30}Br_2O_2$: C, 55.44; H, 6.07. Found: C, 55.70; H, 6.28.

2,7-Bis(1,1-dimethylethyl)-1,8-dimethoxy-9*H*-fluorene (14). A mixture of Zn dust (1.64 g, 25.1 mmol) and $NiCl_2(PPh_3)_2$ (2.58 g, 3.94 mmol) in DMF (10 mL) was stirred at 25 °C under Ar, PPh_3 (6.27 g, 23.9 mmol) and NaBr (2.43 g, 23.6 mmol) were added, and the mixture was then heated at 80 °C for 30 min. The hot blood-red mixture was treated dropwise with a solution of 1,1′-methylenebis[6-bromo-3-(1,1-dimethylethyl)-2-methoxybenzene] (**13b**; 3.94 g, 7.91 mmol) in DMF (10 mL), and heating was continued at 80 °C for 12 h. The mixture was diluted with water and extracted with ether, and the combined extracts were washed with water and brine. Removal of volatiles by evaporation under reduced pressure left a residue that was then purified by flash chromatography (silica, hexane (99%)/ethyl acetate (1%)). This provided 2,7-bis(1,1-dimethylethyl)-1,8-dimethoxy-9*H*-fluorene (**14**; 1.67 g, 4.93 mmol, 62%) as an analytically pure white solid: mp 114–115 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.43 (s, 18H), 4.03 (s, 6H), 4.09 (s, 2H), 7.33 (d, ^3J = 8.2 Hz, 2H), 7.38 (d, ^3J = 8.2 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 30.7, 33.9, 35.0, 59.5, 114.4, 126.0, 133.7, 140.3, 141.9, 156.3; HRMS (EI) calcd for $C_{23}H_{30}O_2$ 338.2245, found 338.2227.

2,7-Bis(1,1-dimethylethyl)-1,8-dimethoxy-9*H*-fluoren-9-one (11b). A solution of 2,7-bis(1,1-dimethylethyl)-1,8-dimethoxy-9*H*-fluorene (**14**; 0.864 g, 2.55 mmol) in pyridine (16 mL) was treated with CrO_3 (1.47 g, 14.7 mmol), and the mixture was heated at reflux for 12 h. The resulting dark green product was diluted with water and extracted with ether, and the combined extracts were washed successively with 10% aqueous HCl, water, and brine. Volatiles were removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (98%)/ethyl acetate (2%)). This gave 2,7-bis(1,1-dimethylethyl)-1,8-dimethoxy-9*H*-fluoren-9-one (**11b**; 0.780 g, 2.21 mmol, 87%) as an analytically pure yellow solid: mp 109–111 °C; IR (KBr) 1701 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 18H), 4.10 (s, 6H), 7.11 (d, ^3J = 7.7 Hz, 2H), 7.39 (d, ^3J = 7.7 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 30.4, 35.3, 62.3, 114.3, 124.9, 132.9, 143.6, 144.5, 159.4, 189.8; HRMS (EI) calcd for $C_{23}H_{28}O_3$ 352.2038, found 352.2015. Anal. Calcd for $C_{23}H_{28}O_3$: C, 78.38; H, 8.01. Found: C, 78.87; H, 8.14.

2,7-Bis(1,1-dimethylethyl)-1-hydroxy-8-methoxy-9*H*-fluoren-9-one (11c). A solution of 2,7-bis(1,1-dimethylethyl)-1,8-dimethoxy-9*H*-fluoren-9-one (**11b**; 104 mg, 0.295 mmol) in CH_2Cl_2 (6 mL) was stirred at −78 °C under dry N_2 and treated dropwise with a solution of BBr_3 (0.30 mL, 1.0 M in CH_2Cl_2, 0.30 mmol). After 1 h, the cooling bath was removed and the mixture was stirred at 25 °C for 12 h. Saturated aqueous $NaHCO_3$ was then added, and the mixture was extracted with ether. Volatiles were removed from the extracts by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (98%)/ethyl acetate (2%)). This provided 2,7-bis(1,1-dimethylethyl)-1-hydroxy-8-methoxy-9*H*-fluoren-9-one (**11c**; 80.0 mg, 0.236 mmol, 80%) as a yellow solid: mp 92–94 °C; IR (KBr) 3412, 1671 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 9H), 1.41 (s, 9H), 4.11 (s, 3H), 6.88 (d, ^3J = 7.5 Hz, 1H), 7.08 (d, ^3J = 7.7 Hz, 1H), 7.28 (d, ^3J = 7.5 Hz, 1H), 7.38 (d, ^{3}J = 7.7 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 29.3, 30.3, 34.7, 35.3, 62.3, 111.6, 115.3, 118.0, 124.7, 133.4, 133.4, 139.2, 140.4, 143.9, 144.3, 157.2, 159.4, 195.5.

2,7-Bis(1,1-dimethylethyl)-1,8-dihydroxy-9*H*-fluoren-9-one (3b). A mixture of 2,7-bis(1,1-dimethylethyl)-1,8-dimethoxy-9*H*-fluoren-9-one (**11b**; 0.632 g, 1.79 mmol) and anhydrous LiI (1.77 g, 13.2 mmol) in 2,4,6-collidine (8 mL) was heated at reflux for 18 h under dry N_2. The mixture was then diluted with water and extracted with ether, and the combined extracts were washed with 10% aqueous HCl, water, and brine. Volatiles were removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane). This provided 2,7-bis(1,1-dimethylethyl)-1,8-dihydroxy-9*H*-fluoren-9-one (**3b**; 0.539 g, 1.66 mmol, 93%) as an analytically pure yellow solid: mp 153–155 °C; IR (KBr) 3351, 1662, 1623 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 18H), 6.87 (d, ^3J = 7.5 Hz, 2H), 7.27 (d, ^3J = 7.5 Hz, 2H), 8.76 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 29.4, 34.8, 113.0, 118.1, 133.8, 139.3, 140.9, 156.7, 199.5; HRMS (EI) calcd for $C_{21}H_{24}O_3$ 324.1725, found 324.1725. Anal. Calcd for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 77.51; H, 7.50.

1,8-Dihydroxy-9*H*-fluoren-9-one (3a).[7] A mixture of 2,7-bis(1,1-dimethylethyl)-1,8-dimethoxy-9*H*-fluoren-9-one (**11b**; 5.0 mg, 0.014 mmol) in CH_3COOH (2 mL) and 48% aqueous HBr (0.5 mL) was heated at reflux for 12 h, diluted with water, and extracted with CH_2Cl_2. Volatiles were removed from the combined extracts by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (96%)/ethyl acetate (4%)). This provided 1,8-dihydroxy-9*H*-fluoren-9-one (**3a**; 2.5 mg, 0.012 mmol, 86%),[7] which proved to be identical with a sample prepared by the procedure described above.

4,6-Dibromo-2,7-bis(1,1-dimethylethyl)-1,8-dihydroxy-9*H*-fluoren-9-one (3c). A solution of 2,7-bis(1,1-dimethylethyl)-1,8-dihydroxy-9*H*-fluoren-9-one (**3b**; 150 mg, 0.462 mmol) in DMF (10 mL) was treated with *N*-bromosuccinimide (387 mg, 2.17 mmol), and the mixture was stirred at 25 °C for 12 h. Water was added, the mixture was extracted with ether, and volatiles were removed from the combined extracts by evaporation under reduced pressure. The residue was purified by flash chromatography (silica, hexane), and recrystallization from hexane provided an analytically pure sample of 4,6-dibromo-2,7-bis(1,1-dimethylethyl)-1,8-dihydroxy-9*H*-fluoren-9-one (**3c**; 133 mg, 0.276 mmol, 60%) as a yellow solid: mp 196–199 °C; IR (KBr) 3466, 3218, 1652 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 18H), 7.44 (s, 2H), 9.69 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 29.1, 34.8, 107.5, 120.4, 138.8, 141.3, 142.5, 157.2, 196.6; HRMS (EI) calcd for $C_{21}H_{22}Br_2O_3$ 479.9934, found 479.9981.

X-ray Crystallographic Study of Bis[5-bromo-3-(1,1-dimethylethyl)-2-hydroxyphenyl]methanone (2b).[30] Crystals of dihydroxybenzophenone **2b** belong to the triclinic space group $P\bar{1}$ with a = 9.1701(9) Å, b = 11.696(3) Å, c = 20.448(3) Å, α = 73.564(14)°, β = 86.806(10)°, γ = 77.149(15)°, V = 2050.8(6) Å^3, D_{calcd} = 1.568 g cm^{-3}, and Z = 4. Data were collected at 295 K, and the structure was refined to R_f = 0.031, R_w = 0.034 for 6123 reflections with $I > 3.00\,\sigma(I)$.

X-ray Crystallographic Study of 4,6-Dibromo-2,7-bis-(1,1-dimethylethyl)-1,8-dihydroxy-9*H*-fluoren-9-one (3c).[30] Crystals of dihydroxyfluorenone **3c** belong to the triclinic space group $P\bar{1}$ with a = 10.8423(6) Å, b = 12.0504(9) Å, c = 15.2181(9) Å, α = 94.081(5)°, β = 101.012(5)°, γ = 90.028(5)°, V = 1946.55(21) Å^3, D_{calcd} = 1.645 g cm^{-3}, and Z = 4. Data were collected at 295 K, and the structure was refined to R_f = 0.036, R_w = 0.040 for 4996 reflections with $I > 3.00\,\sigma(I)$.

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(30) The authors have deposited X-ray crystallographic data, a description of the structure determination, and tables of atomic coordinates and isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, and refined and calculated hydrogen atom coordinates with the Cambridge Crystallographic Data Centre. The data can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ UK.