to GLC analysis (5% Carbowax 20M, 6 ft × 0.125 in.), which showed the presence of 67% caproaldehyde, 12% 1-hexanol, and 21% unreacted amide.

Registry No. Lithium triethylborohydride, 22560-16-3; 1-hexanol, 111-27-3; benzyl alcohol, 100-51-6; 3-hexanol, 623-37-0; 3-ethyl-3-pentanol, 597-49-9; phenol, 108-95-2; 2,6-di-*tert*-butylphenol, 128-39-2; hexylamine, 111-26-2; benzenethiol, 108-98-5; 1-hexanethiol, 111-31-9; caproaldehyde, 66-25-1; benzaldehyde, 100-52-7; 2-heptanone, 110-43-0; norcamphor, 497-38-1; acetophenone, 98-86-2; benzophenone, 119-61-9; 2,2,4,4-tetramethyl-3-pentanone, 815-24-7; cinnamaldehyde, 104-55-2; *p*-benzoquinone, 106-51-4; anthraquinone, 84-65-1; caproic acid, 142-62-1; benzoic acid, 65-85-0; acetic anhydride, 108-24-7; succinic anhydride, 108-30-5; phthalic anhydride, 85-44-9; caproyl chloride, 142-61-0; benzoyl chloride, 98-88-4; ethyl caproate, 123-66-0; ethyl benzoate, 93-89-0; phenyl acetate, 122-79-2; γ-butyrolactone, 96-48-0; phthalide, 87-41-2; isopropenyl acetate, 591-87-7; 1,2-butylene oxide, 106-88-7; styrene oxide, 96-09-3; cyclohexene oxide, 286-20-4; 1-methyl-1,2-cyclohexene oxide, 1713-33-3; 2-phenyldioxolane, 936-51-6; 2-methyl-2-ethyldioxolane, 126-39-6; triethyl orthoformate, 122-51-0; caproamide, 628-02-4; benzamide, 55-21-0; *N,N*-dimethylcaproamide, 5830-30-8; *N,N*-dimethylbenzamide, 121-69-7; *N,N*-dimethylpivalamide, 24331-71-3; capronitrile, 628-73-9; benzonitrile, 100-47-0; nitropropane, 108-03-2; nitrobenzene, 98-95-3; azobenzene, 103-33-3; azoxybenzene, 495-48-7; cyclohexanone oxime, 100-64-1; phenyl isocyanate, 103-71-9; pyridine, 110-86-1; pyridine *N*-oxide, 694-59-7; dibutyl disulfide, 629-45-8; diphenyl disulfide, 882-33-7; methyl *p*-tolyl sulfide, 623-13-2; dimethyl sulfoxide, 67-68-5; dibutyl sulfone, 598-04-9; diphenyl sulfone, 127-63-9; methanesulfonic acid, 75-75-2; *p*-toluenesulfonic acid, 104-15-4; cyclohexyl tosylate, 953-91-3; cyclohexanol, 108-93-0; *tert*-butyl alcohol, 75-65-0; cyclohexanone, 108-94-1; water, 7732-18-5; 2,6-diisopropylphenol, 2078-54-8; butanethiol, 109-79-5; cinnamyl alcohol, 104-54-1; 9,10-dihydro-9,10-dihydroxyanthracene, 58343-58-1; 9,10-dihydro-9,10-dihydroxyanthracene diacetate, 6938-79-0; *endo*-2-norbornanol, 497-36-9; 1,4-butanediol, 110-63-4; 1-methylcyclohexanol, 590-67-0; neopentyl alcohol, 75-84-3; benzylamine, 100-46-9; ethylbenzene, 100-41-4.

Regiospecific Synthesis of Islandicin Methyl Ether

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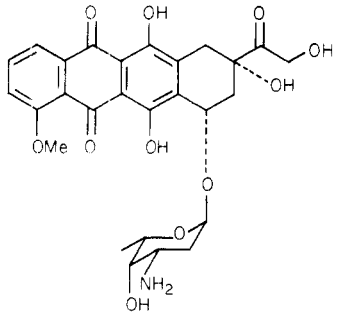
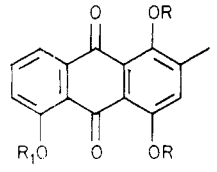
This paper presents a novel approach to the construction of highly functionalized anthraquinones. It involves an aryl cuprate–benzyl halide coupling followed by cycloacylation under mild conditions to an anthracenone. Several novel byproducts were encountered.

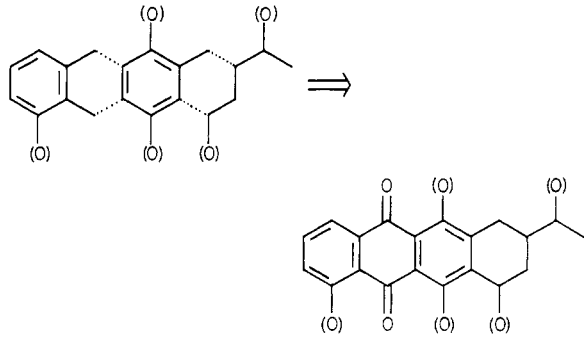
There is considerable interest in developing efficient synthetic routes to the aglycones of adriamycin and related anthracyclinone antibiotics.[1-15] Our general approach to this involves construction of suitably substituted anthracenes and subsequent elaboration of the D ring.[16]





1a, R = R_1 = CH_3
b, R = $CH_2C_6H_5$; R_1 = CH_3
c, R = R_1 = H
d, R = H; R_1 = CH_3
e, R = Ac; R_1 = CH_3

To this end we have devoted some attention to the development of a regiospecific synthesis of unsymmetrically substituted anthracenes as per eq 1. We selected islan-



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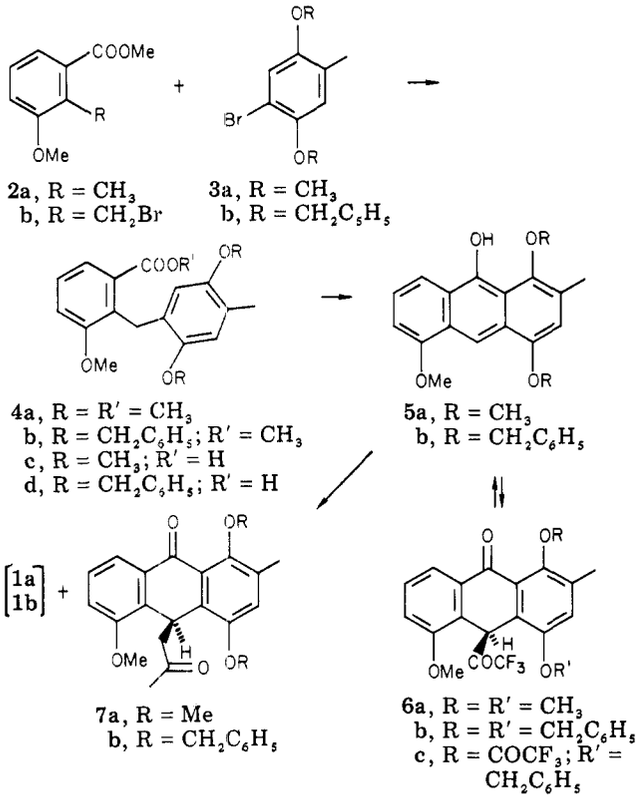
0022-3263/80/1945-0012$01.00/0

Scheme I



dicin and some of its derivatives as our initial goal with an eye toward using these as intermediates in the synthesis of daunomycin[18] and adriamycin. The construction methods presented here seem to be generally suitable for the preparation of various highly substituted anthraquinones. As an indication of the lability of functional groups that may be tolerated in this approach, the preparation, as an intermediate, of islandicin methyl dibenzyl ether (**1b**) is noteworthy.

Sih and co-workers[17] have recently reported an alternative approach to **1d**. Approaches to functionalized anthraquinones employing organometallic coupling reactions related to those reported here have appeared recently.[18-21] These reports and our work suggest that this is an efficient general method of constructing these molecules.

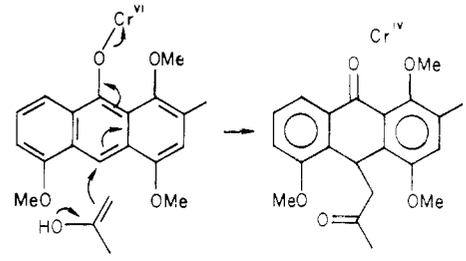
Results and Discussion

Islandicin Trimethyl Ether. As a model for construction of islandicin (**1c**) derivatives wherein the phenolic hydroxyls are chemically differentiated, we chose as an initial target its trimethyl ether (**1a**). The regiospecific approach employed is presented in Scheme I.

Trisubstituted **2a**, and hence **2b**, is available by Fieser's procedure.[23] Condensation of the relatively hindered benzyl bromide **2b** with the cuprate derived from **3a** [using bis(tributylphosphine)cuprous iodide][24] afforded diphenylmethane **4a** in excellent yield.

Cyclization of acid **4c** was effected most efficiently by treatment with trifluoroacetic anhydride (TFAA) in dichloromethane at 0 °C. Although the substitution pattern of the product **5a** is firmly established by its conversion to islandicin trimethyl ether of known structure, it should be noted that one does not expect a Hayashi-type rearrangement[25] to be observed in the **4c** and **5a** cyclization. If the reaction time for cyclization was increased or larger amounts of TFAA were employed, anthracenol **5a** was replaced as the major product by an unstable compound identified as (trifluoroacetyl)anthracenone **6a**. This substance, an air-sensitive oil, reverts quantitatively to **5a** in hydroxylic solvents or on treatment with alkaline dithionite. Formulation of **6a** as a C-acylated product rather than as the simple trifluoroacetate of **5a** rests on its carbon and proton NMR spectra. In particular, the bridging CH of **6a** appears at δ 40 (carbon) and 6.03 (proton) as compared to δ 8.6 (proton) in **5a**. Mechanistically, **6a** is a reasonable product to be expected from electrophilic attack on the quite electron rich tetraoxyanthracene **5a**. Its existence as an anthracenone rather than anthracenol is expected since tautomerization to the anthracenol would lead to severe buttressing effects between the trifluoroacetyl group and the peri-situated alkoxy groups.

Oxidation of anthracenol **5a** with Jones' reagent affords islandicin trimethyl ether (**1a**) identical with a naturally derived sample. There was also obtained, however, a product formulated as the acetonylanthracenone **7a**. The structure of **7a** rests on its elemental composition and spectra. Although the chirality of **7a** did not manifest itself in the appearance of diastereotopic methylene resonances in its NMR spectrum, the related structure (**7b**) in the benzyl series did show this feature in considerable detail (see below). The formation of **7a** is without direct precedence but can be rationalized in a straightforward manner as a process involving electrophilic attack of an anthracenol chromate on acetone (eq 2).



(2)

Islandicin Methyl Ether. With certain qualifications the synthesis of islandicin methyl dibenzyl ether (**1b**) and hence islandicin methyl ether (**1d**) follows closely the preparation of **1a**. Cyclization of diphenylmethane **4d** afforded the desired anthracenol **5b** which was smoothly oxidized to islandicin methyl dibenzyl ether **9b** and hence, by treatment with boron bromide, to the desired islandicin methyl ether (**1d**).

As was observed in the case of cyclization of **4a**, formation of the desired anthracenol **5b** was accompanied by (trifluoroacetyl)anthracenone **6b** when reaction conditions were prolonged. Again, anthracenone **6b** quantitatively underwent a retro-Claisen reaction when exposed to alkaline dithionite, so its appearance is of little synthetic significance. A minor unstable product identified as **6c** was isolated. It was subjected to the interconversion of eq 3. Although these products were identified only by

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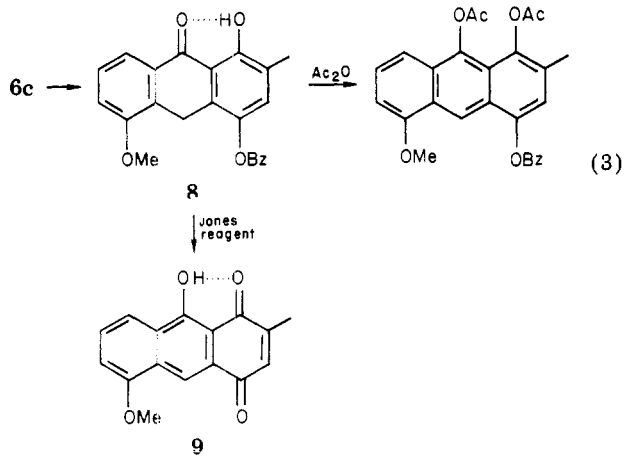

(3)

high-resolution mass spectra and NMR, quinone **9**, a minor byproduct arising in the Jones' oxidation of crude **5b**, is thought to arise as in eq 3. Considering the great usefulness of benzyl ethers as hydroxyl blocking groups, it is of some significance that only a minor (~10%) amount of debenzylation is observed in the trifluoroacetic anhydride mediated cycloacylation of **4d**.

As in the case of Jones' oxidation of **5a**, there was isolated the product **7b** arising from electrophilic attack on acetone. Complete proton-decoupling (270 MHz) NMR experiments confirmed the structural assignment and the presence of a chiral center, as shown by the diastereotopic methylene protons α to the ketone carbonyl and of the benzyl ethers.

Conclusions.

Construction of unsymmetrically substituted anthracenes by an organocuprate–benzyl halide coupling followed by cyclization of the resulting diphenylmethane appears to be a reasonably efficient and concise process for construction of substituted anthracenones.

Experimental Section[26]

Methyl 2-(Bromomethyl)-3-methoxybenzoate (2b). A mixture of 31.2 g (0.175 mol) of *N*-bromosuccinimide and 28.8 g (0.16 mol) of methyl 3-methoxy-2-methylbenzoate[23] (**2a**) in 190 mL of carbon tetrachloride was refluxed (200-W bulb) for 2 h. Workup afforded 37.6 g (92% yield) of **2b**: mp 103.5–105 °C (benzene); ^{1}H NMR δ 3.92 (6 H, s), 5.05 (2 H, s), 7.08–7.56 (3 H, m); ^{13}C NMR δ 24.5, 52.2, 56.1, 114.6, 122.8, 127,6, 129.2, 130.6, 157.9, 167.1; MS *m/e* 257.9899 (P^+; calcd for $C_{10}H_{11}{}^{79}BrO$, 257.9892), 227/229 (P – OCH_3), 179 (P – Br).

Diphenylmethane 4a. To a solution of 6.8 g (29.5 mM) of 2-bromo-5-methylhydroquinone dimethyl ether (**3a**)[27] in 30 mL of dry THF at 0 °C was added 20 mL of a 1.5 M solution of *n*-butyllithium in hexane (29.5 mM). After being stirred for 15 min, the solution was cooled to −78 °C, and 5.6 g (14.3 mM) of bis(tributylphosphine) cuprous iodide[24] in 25 mL of THF was added. After 10 min, 3.65 g (14.1 mM) of bromide **2b** in 55 mL of THF was added, and the resulting suspension was kept at −78 °C for 30 min and allowed to stand at room temperature overnight. Workup afforded 12.8 g of colorless solid, which upon crystallization (ethyl acetate–hexane) gave 3.8 g (82% yield) of ester (**4a**): mp 116–167 °C; ^{1}H NMR δ 2.17 (3 H, s), 3.61 (3 H, s), 3.79 (6 H, s), 3.81 (3 H, s), 4.29 (2 H, s), 6.41 (1 H, s), 6.61 (1 H, s), 7.01–7.25 (3 H, ABC); ^{13}C NMR δ 15.9, 26.4, 51.8, 55.8, 56.1, 113–158 (11 peaks), 168.6; MS *m/e* 330.1473 (P^+, calcd for $C_{19}H_{22}O_5$, 330.1467), 315 (P – CH_3), 299 (P – OCH_3), 283, 267; UV λ_{max} ($CHCl_3$) 295 nm (ϵ 7000); IR ν_{max} ($CHCl_3$) 1733 cm^{-1}.

Anal. Calcd for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71. Found: C, 69.06; H, 6.55.

Saponification of **4a** (10% ethanolic potassium hydroxide, 2-h reflux) afforded the corresponding acid **4c**: 75% yield from **2b**; mp 196–197 °C (ethyl acetate) (lit.[22] mp 191–192 °C); ^{1}H NMR δ (Me_2SO-d_6) 2.18, 3.64, 3.71, 3.78 (3 H, 3 s), 4.32 (2 H, s), 6.50 (1 H, s), 6.66 (1 H, s), 7.06–7.54 (3 H, ABC); ^{13}C NMR (Me_2SO-d_6) δ 15.7, 25.7, 55.5, 55.6, 112–157.8 (10 C), 169.1; MS *m/e* 316.1304 (calcd for $C_{18}H_{12}O_5$, 316.1311), 301, 283, 267.

1,4,5-Trimethoxy-2-methylanthraquinone (1a). (A) Cyclization of 4c to Anthracenol 5a. To a stirred solution of 0.5 g (1.58 mmol) of acid **4c** in 100 mL of chloroform at 0 °C was added 3.5 mL of trifluoroacetic anhydride (TFAA). After 20 min at 0 °C starting material had been consumed (TLC), so the bright yellow solution was evaporated to afford a yellow solid shown by NMR to be an 85:15 mixture of anthracenol **5a** and (see below) (trifluoroacetyl)anthracenone **6a**.

Anthracenol 5a. In some cases, when less TFAA was used (e.g., 3 mL rather than 3.5 mL), anthracenol **5a** was obtained as the sole product. It can be recrystallized (in low yield): mp 177–179 °C (EtOAc–C_6H_{14});[21] ^{1}H NMR δ 2.41, 3.89, 3.97, 4.00 (3 H, 3 s), 6.41 (1 H, s), 6.73 (1 H, d, J = 8 Hz), 7.32 (1 H, t, J = 8 Hz), 7.96 (1 H, d, J = 8 Hz), 8.60 (1 H, s), 10.4 (1 H, s); ^{13}C NMR δ 15.9, 55.4, 55.5, 62.1, 102–155.5 (13 C); MS *m/e* 298.1210 (calcd for $C_{18}H_{18}O_4$, 298.1205), 283, 268, 253; UV λ_{max} ($CHCl_3$) 411 nm (ϵ 4900), 388 (8200), 379 (9200), 360 (5500), 262 (60 000); IR ν_{max} ($CHCl_3$) 3300, 1625 cm^{-1}.

Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 73.26; H, 6.09.

Alternatively, the crude 85:15 **5a**/**6a** mixture from above was boiled for 45 min in a solution of 0.9 g of sodium dithionite and 0.9 g of sodium hydroxide in water. Acidification and workup afforded 0.5 g of a yellow solid identified (NMR, TLC) as **5a**.

Trifluoroacetylanthracenone 6a. Extending the reaction time to 20 h (rather than 20 min) permitted isolation of **6a** as an air-sensitive light yellow oil free of **5a**: ^{1}H NMR δ 2.39, 3.89, 3.90, 3.92 (3 H, 3 s), 6.03 (1 H, s), 7.00 (1 H, s), 7.10–7.94 (3 H, ABC); ^{13}C NMR δ 16.3, 40.1, 55.4 (2 peaks), 61.3, 113–155.1 (10 C); MS *m/e* 394.1035 (calcd for $C_{20}H_{17}F_3O_5$, 394.1028), 325, 298, 283.

Boiling of **6a** with aqueous sodium dithionite converted it in good yield to **5a**.

(B) Oxidation of 5a to Islandicin Trimethyl Ether (1a). Jones' reagent[28] (3.5 mL) was added to a solution of 0.5 g of crude **5a** in 35 mL of acetone. After 2 h ice was added, and the reaction mixture was worked up to afford 0.5 g of a yellow solid. Ether trituration followed by recrystallization (MeOH) afforded 0.36 g (73% yield from **4c**) of islandicin trimethyl ether (**1a**), mp 160.5–162.5 °C (lit.[29,30] mp 159–160 °C), identical with a sample prepared from authentic bioorganically grown islandicin:[31] ^{1}H NMR δ 2.40, 3.92, 4.00, 4.03 (3 H, 3 s), 7.18 (1 H, s), 7.25–7.76 (3 H, ABC); ^{13}C NMR δ 16.8, 56.5, 56.9, 61.4, 117–158.6 (12 C), 182.9, 183.9; UV λ_{max} ($CHCl_3$) 392 nm (ϵ 7100); IR ν_{max} ($CHCl_3$) 16 700 cm^{-1}; MS *m/e* 312.1001 (calcd for $C_{18}H_6O_5$, 312.0998).

From the ether-soluble fraction (0.2 g of a brown oil) acetonylanthracenone **7a** could be isolated in 20% yield: mp 141.5–143.5 °C (hexane); ^{1}H NMR δ 2.14 (3 H, s), 2.39 (3 H, s), 2.76 (2 H, d, J = 6 Hz), 3.96 (9 H, s), 5.08 (1 H, t, J = 6 Hz), 7.01 (1 H, s), 7.10–7.84 (3 H, ABC); NMR δ 16.1, 29.3, 50.9, 55.4, 61.3, 113–155.5 (12 C), 184.6, 206.3; MS *m/e* 354.1462 (calcd for $C_{21}H_{22}O_5$, 354.1467), 297; UV λ_{max} ($CHCl_3$) 330 nm (ϵ 4400), 281 (11 000); IR ν_{max} ($CHCl_3$) 1709, 1680, cm^{-1}.

Anal. Calcd for $C_{21}H_{22}O_5$: C, 71.18; H, 6.26. Found: C, 71.04; H, 6.34.

Diphenylmethanes 4b and 4d. A suspension of 11.5 g (30.5 mmol) of 2-bromo-5-methylhydroquinone dibenzyl ether[27] (**3b**) in 50 mL of ether at 0 °C was prepared. With stirring of the mixture, 19.5 mL of a 1.55 M solution of *n*-butyllithium in hexane

(26) Except as noted, NMR spectra were obtained in chloroform-*d* on a JEOL MH-100 (proton) or a JEOL FX-60 (carbon) spectrometer. Those spectra obtained at 270 MHz were obtained on a Bruker WH-270 spectrometer. Melting points are uncorrected.

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was added: the bromide dissolved.

After the mixture was cooled to −78 °C, 5.9 g (15 mmol) of cuprous iodide tributylphosphene[24] in 10 mL of ether was injected, and the resulting yellow solution was stirred at −78 °C for 15 min. After addition of 3.83 g (14.8 mmol) of bromide **2b** in 160 mL of ether, the mixture was stirred for 1 h at −78 °C and allowed to stand at room temperature overnight. The reaction mixture was poured onto ice and extracted with ether and chloroform. The organic extracts were washed successively with 6 N hydrochloric acid, saturated sodium bicarbonate solution, and water, dried, and evaporated to afford 24 g of an oil. Trituration (ether) of this afforded 5.6 g (76% yield) of **4b**: mp 115.5–117.5 °C (chloroform–hexane); ^{1}H NMR δ 2.16, 3.63, 3.70 (3 H, s), 4.32, 4.76 and 5.04 (2 H, s), 6.28 and 6.70 (1 H, s), 6.95 (1 H, d, J = 8 Hz), 7.1–7.3 (12 H, m); ^{13}C NMR δ 16.2, 26.4, 51.8, 55.7, 70.6, 70.8, 113–158.3 (18 C), 168.3; MS m/e 482.2099 (P^+; calcd for $C_{31}H_{30}O_5$, 482.2093), 391, 359, 269; UV λ_{max} ($CHCl_3$) 294 nm (ϵ 6500); IR ν_{max} ($CHCl_3$) 1733 cm^{-1}.

Anal. Calcd for $C_{31}H_{30}O_5$: C, 77.15; H, 6.27. Found: C, 77.28; H, 6.24.

Saponification of 4b was achieved by boiling a mixture of 5.6 g of it in 25 g of caustic potash in 125 mL of ethanol for 1.5 h. The cooled mixture was poured onto ice and acidified, and the resulting solid was removed by filtration to afford 4.3 g (62% yield from **2b**) of **4d**: mp 189–192 °C; ^{1}H NMR δ 2.17 and 3.62 (3 H, s), 4.36, 4.77 and 4.97 (2 H, s), 6.28 (1 H, s), 6.65 (1 H, s), 6.97 (1 H, d, J = 7 Hz), 7.1–7.4 (11 H, m), 7.52 (1 H, d, J = 7 Hz); ^{13}C NMR (Me_2SO-d_6) δ 15.8, 25.5, 55.6, 69.7, 69.9, 113–157.7 (16 C), 168.9; MS m/e 468.1937 (P^+; calcd for $C_{30}H_{28}O_5$, 468.1942), 377, 360, 359, 269.

Islandicin 1,4-Dibenzyl 5-Methyl Ether (1b). (A) Anthracenol 5b by Cyclization of 4d. A mixture of 220 mg (0.47 mmol) of acid **4d** and 2 mL of trifluoroacetic anhydride in 60 mL of chloroform was stirred at −5 °C for 10 min. The reaction mixture was poured onto ice and worked up to afford 210 mg of substantially pure anthracenol **5b**: mp 152.5–153.5 °C (chloroform–hexane); ^{1}H NMR δ 2.44 and 4.00 (3 H, s), 4.95 and 5.26 (2 H, s), 6.48 (1 H, s), 6.72 (1 H, d, J = 8 Hz), 7.3–7.7 (11 H, m), 7.97 (1 H, d, J = 8 Hz), 8.72 (1 H, s), 10.4 (1 H, s); ^{13}C NMR δ 16.3, 55.5, 70.3, 102–155.5 (19 C); MS m/e 450.1828 (P^+; calcd for $C_{30}H_{26}O_4$, 450.1831), 359, 268, 253; UV λ_{max} ($CHCl_3$) 412 nm (ϵ 3400), 388 (5000), 378 (5600), 359 (4200), 260 (27 000); IR ν_{max} ($CHCl_3$) 3300, 1628 cm^{-1}.

Anal. Calcd for $C_{30}H_{26}O_4$: C, 79.28; H, 5.82. Found: C, 79.07; H, 5.70.

Reaction of **4d** with TFAA at 0 °C for 28 h rather than 10 min afforded a bis(trifluoroacetyl) compound formulated as **6c**: mp 176–181 °C; ^{1}H NMR δ 2.18 and 3.84 (3 H, s), 5.18 (2 H, s), 6.03 and 6.90 (1 H, s), 7.00 (1 H, d, J = 8 Hz), 7.2–7.5 (6 H, m), 7.76 (1 H, d, J = 8 Hz); MS m/e 552, 455, 364.

Although quite unstable it could be saponified in good yield (alkaline dithionite, boil 30 min) to an anthracenone formulated as **8** in eq 3: mp 159–162 °C; ^{1}H NMR δ 2.29 and 3.95 (3 H, s), 4.10 and 5.16 (2 H, s), 7.11–7.14 (2 H, m), 7.3–7.6 (6 H, m), 8.00 (1 H, d, J = 8 Hz), 12.96 (1 H, s); ^{13}C NMR δ 15.6, 22.9, 55.7, 71.1; MS m/e 360.1352 (P^+; calcd for $C_{23}H_{20}O_4$, 360.1362); UV λ_{max} ($CHCl_3$) 390 nm (ϵ 2500), 326 (2600), 268 (14 000); IR ν_{max} 1630 cm^{-1}.

Acetylation of anthracenone **8** (acetic anhydride–pyridine) afforded diacetate (see eq 3): mp 210–212 °C; ^{1}H NMR δ 2.27, 2.42, 2.48 and 4.00 (3 H, s), 5.28 (2 H, s), 6.58 (1 H, s), 6.69 (1 H, d, J = 7 Hz), 7.2–7.6 (8 H, m), 9.22 (1 H, s); ^{13}C NMR δ 17.1, 20.8, 20.9, 55.7, 70.4, 102–169.3 (16 C), 192.3, 205.5; UV λ_{max} ($CHCl_3$) 410 nm (ϵ 3400), 390 (5200), 370 (5800); IR ν_{max} 1775 cm^{-1}; MS m/e 444.1569 (P^+; calcd for $C_{27}H_{24}O_6$, 444.1573), 402, 360, 311, 269.

(B) Oxidation of Anthracenol 5b. To anthracenol **5b** from above (0.21 g) in 50 mL of acetone was added 2.5 mL of Jones' reagent.[28] After 30 min the reaction mixture was poured onto ice and worked up to afford 240 mg of a red gum. Crystallization of this (chloroform–hexane) afforded 136 mg (63% yield from **5b**) of **1b** as bright yellow needles: mp 146–147.5 °C; ^{1}H NMR δ 2.36 and 3.99 (3 H, s), 4.99 and 5.27 (2 H, s), 7.13 (1 H, s), 7.23 (1 H, d, J = 8 Hz), 7.2–7.6 (11 H, m), 7.74 (1 H, d, J = 7 Hz); ^{13}C NMR δ 17.2, 56.5, 71.9, 76.0, 116–158.5 (14 C), 183.7; MS m/e 464.1618 (P^+; calcd for $C_{30}H_{24}O_5$, 464.1624), 447, 373, 284, 283; UV λ_{max} ($CHCl_3$) 390 nm (ϵ 8400); IR ν_{max} ($CHCl_3$) 1675 cm^{-1}.

Anal. Calcd for $C_{30}H_{24}O_5$: C, 77.57; H, 5.21. Found: C, 77.59; H, 5.17.

Chromatography of the mother liquors remaining from the recrystallization of **1b** afforded two compounds.

(a) Acetonylanthracenone **7b**: 26 mg, 11% yield from **5b**; mp 157.5–158.5 °C (ethyl acetate–hexane); ^{1}H NMR (270 MHz) δ 1.88 and 2.28 (3 H, s), 2.58 (1 H, dd, J = 7, 13 Hz), 2.87 (1 H, dd, J = 5, 13 Hz), 3.82 (3 H, s), 4.81 (1 H, d, J = 10 Hz), 5.05 (1 H, dd, J = 5, 7 Hz), 5.13 (2 H, s), 5.23 (1 H, d, J = 10 Hz), 7.00 (1 H, d, J = 7 Hz), 7.02 (1 H, s), 7.3–7.6 (11 H, m), 7.78 (1 H, dd, J = 1, 8 Hz); ^{13}C NMR δ 16.6, 29.2, 29.6, 50.9, 55.2, 70.9, 75.8, 113–155.6 (17 C), 184.6, 206.4; MS m/e 506.2100 (P^+; calcd for $C_{33}H_{30}O_5$, 506.2093), 448, 415, 357; UV λ_{max} ($CHCl_3$) 332 nm (ϵ 3400); IR ν_{max} ($CHCl_3$) 1710, 1670 cm^{-1}.

(b) 1,4-Anthraquinone **9** (~3 mg) was isolated as orange crystals. This material was not obtained in a completely pure form and could not be successfully recrystallized. It was obtained in somewhat larger amounts when chromic acid–acetic acid mixtures were used rather than Jones' reagent: ^{1}H NMR δ 2.22 and 4.00 (3 H, s), 6.86 (1 H, s), 7.04 (1 H, d, J = 7 Hz), 8.02 (1 H, d, J = 8 Hz), 8.50 (1 H, s), 13.9 (1 H, s); MS m/e 268.0725 (P^+; calcd for $C_{16}H_{12}O_4$, 268.0736), 253, 225; UV λ_{max} ($CHCl_3$) 493 nm (ϵ 4200); IR ν_{max} 1660 cm^{-1}.

Islandicin 5-Methyl Ether (1d). Into a solution of 102 mg (0.22 mmol) of **1b** in 5 mL of chloroform cooled in dry ice was injected 40 μL of boron bromide. The mixture was stirred for 10 min and then allowed to warm to 25 °C. Workup afforded 61 mg (95% yield) of **1d** as beautiful red-brown needles: mp 194–196.5 °C (ethyl acetate–hexane) (lit.[30] mp 197–199 °C); ^{1}H NMR δ 2.35 and 4.06 (3 H, s), 7.11 (1 H, s), 7.33 (1 H, d, J = 8 Hz), 7.72 (1 H, t, J = 8 Hz), 7.97 (1 H, d, J = 8 Hz), 12.3 (2 H, s); ^{13}C NMR δ 16.2, 56.5; UV λ_{max} ($CHCl_3$) 498 nm (ϵ 7600); MS m/e 284.0664 (P^+; calcd for $C_{16}H_{12}O_5$, 284.0685), 266, 238.

Acetylation of **1d** (acetic anhydride–pyridine) afforded the diacetate **1e**: mp 248–250 °C; ^{1}H NMR δ 2.31, 2.47, 2.48, 4.06 (3 H, s), 7.2–7.4 (2 H, m), 7.66 (1 H, t, J = 8 Hz), 7.80 (1 H, d, J = 8 Hz); ^{13}C NMR δ 16.5, 20.9, 21.2, 56.7, 117–169.5 (11 C), 182.2, 189.2; MS m/e 368.0916 (P^+; calcd for $C_{20}H_{16}O_7$, 368.0891).

Methylation of **1d** (methyl sulfate, alkali) afforded **1a**.[32]

Registry No. **1a**, 50457-06-2; **1b**, 71887-26-8; **1d**, 71786-00-0; **1e**, 71887-27-9; **2a**, 42981-93-1; **2b**, 71887-28-0; **3a**, 13321-74-9; **3b**, 13321-72-7; **4a**, 71887-29-1; **4b**, 71887-30-4; **4c**, 51837-74-2; **4d**, 71887-31-5; **5a**, 70946-22-4; **5b**, 71887-32-6; **6a**, 71887-33-7; **6c**, 71887-34-8; **7a**, 71887-35-9; **7b**, 71887-36-0; **8**, 71887-37-1; **9**, 71887-38-2; 1,9-diacetoxy-2-methyl-4-(benzyloxy)-5-methoxyanthracene, 71887-39-3.

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