Nano $CaCO_3$: playing a special role in the monofunctionalization of calixarenes by epoxides

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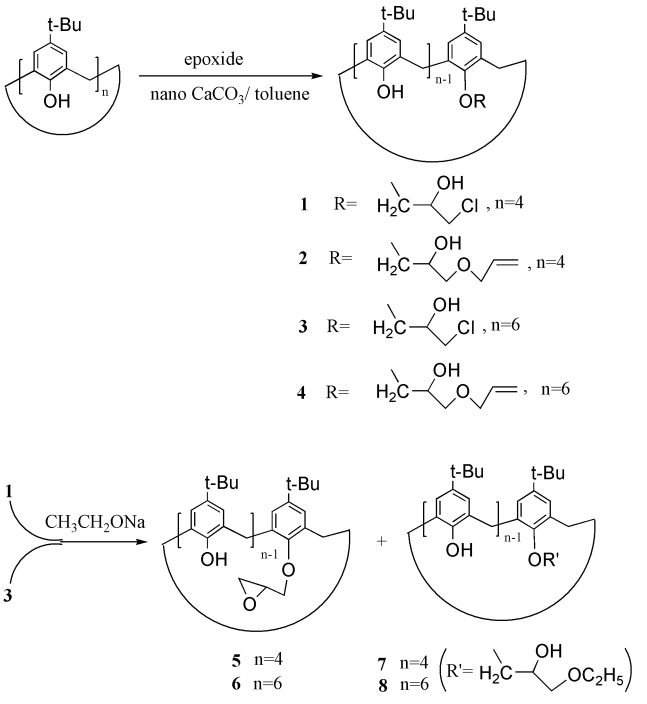
It was found that nano $CaCO_3$ played an interesting role in the reaction of *p-tert*-butylcalixarene with epoxides. In the presence of nano $CaCO_3$, a monosubstituted calixarene, a β ring-opening product of epoxide, was obtained regioselectively in good yield. When normal $CaCO_3$ was used under the same conditions, the yield was less than 2%. The β ring-opening product of epichlorohydrin could convert to monoglycidyl calixarene by reacting with C_2H_5ONa in tetrahydrofuran at room temperature in moderate yield.

Introduction

It is well known that as a high grade filler and a white pigment, nano $CaCO_3$ is widely used in the rubber, plastic, papermaking, coating, ink and pharmaceutical industries.[1] As nano $CaCO_3$ can not dissolve in water or organic solvents, it has never been used as a base or a condensation agent in any chemical reaction.

Calixarenes have been used as building blocks for the syntheses of a large number of host molecules because they are readily accessible for chemical modification on both lower and upper rims by attachment of a wide range of potential ligating groups.[2] The selective monofunctionalization of calixarenes is of important significance for many purposes, in particular for the construction of macromolecules with pendant calixarene moieties.[3] In principle, monofunctionalization of unsubstituted calixarene could be achieved by using mild conditions and less reactant, either strong base or weak base. For example, by using an excess of the alkylating agent and 0.6 equiv. K_2CO_3 or 1.2 equiv. CsF as a weak base,[4] or 1.2 equiv. alkylating agent with controlled NaH in toluene,[5,6] monosubstituted calix[4]arene could be obtained in fair to good yield. Recently, Santoyo-González described the selective monoalkylation of calixarenes using bis(butyltin) oxide in good yield.[7] The preparation of monosubstituted calix[6]arenes has been discussed by Magrans.[8] Monofunctionalized calixarenes could also be prepared from the equivalent disubstituted or tetrasubstituted calixarene indirectly.[9]

Epoxides are one of the most versatile intermediates in organic synthesis, and a large variety of reagents can open the oxirane ring,[10] but little is known about the reaction of epoxides with calixarenes.[11] In 1996 Neri first obtained 1,3-diglycidylcalix[4]arene and tetraglycidylcalix[4]arene by treating *p-tert*-butylcalix[4]arene with glycidyl tosylate in acetonitrile in the presence of K_2CO_3 as a base.[12] Meng *et al.* also synthesized 1,3-diglycidylcalix[4]arene by using epichlorohydrin instead of glycidyl tosylate in toluene.[13] No paper concerning the preparation of monoglycidyl calixarene from calixarene directly or separation of the ring-opening product of epoxide has appeared until now, although the first example of tri-*tert*-butylcalix[4]arenes bearing an epoxy group at the upper rim synthesized by a multi-step synthetic procedure has been reported.[14]



Scheme 1

Recently, when we investigated the reaction of calixarene and epoxides, we found that nano $CaCO_3$ can be used as a condensation agent in this case; surprisingly, the reaction proceeded smoothly and selectively, the monosubstituted calix[4]arene could be obtained in a yield of 52.6% or more (Scheme 1), and the product was the β cleavage product of epoxide solely, as proved by its ^{13}C DEPT NMR.

Results and discussion

In the syntheses of lower-rim substituted calixarene, the first step is ionization of hydroxyl of the phenolic group in general. Strong bases such as NaH, RONa, KOH *etc.* or weak bases including K_2CO_3, CsF *etc.* are frequently used. Due to its

low solubility and basicity, $CaCO_3$ is never considered to act as a base or condensation agent in any chemical reaction. Indeed, when normal $CaCO_3$ was used in the reaction of calixarene and epoxide, the conversion of calixarene was less than 2%. However, when nano $CaCO_3$ was used instead, the result was surprising. Monosubstituted calixarene could be obtained selectively in yields over 50%. No reaction could be observed in the absence of $CaCO_3$. The extraordinary influence of nano $CaCO_3$ on this reaction is undoubted.

Upon treating *p-tert*-butylcalix[4]arene with epichlorohydrin in the presence of nano $CaCO_3$ in toluene at 100 °C for 5 days, 5,11,17,23-tetra-*tert*-butyl-26,27,28-trihydroxy-25-(3′-chloro-2′-hydroxypropoxy)calix[4]arene (**1**), a β cleavage product of epichlorohydrin, was obtained. The yield reached 52.6%. The β cleavage mode was proved by the appearance of a CHOH resonance at 70.5 ppm, an $ArOCH_2$ signal at 78.1 ppm and a CH_2Cl signal at 43.9 ppm in its ^{13}C DEPT NMR. This indicated that *p-tert*-butylcalix[4]arene was attacked at the 3 position of the 2,3-epoxide ring. Encouraged by this observation, another epoxide, allyl glycidyl ether, was also tested. After treatment with *p-tert*-butylcalix[4]arene in the presence of nano $CaCO_3$ (2 equiv.) in toluene, the corresponding monosubstituted β cleavage product **2** was obtained, the yield reached 70.2% after 10 days reaction. The study was then extended to calix[6]arene using the same epoxides, the corresponding monofunctionalized derivatives **3**–**4** were obtained but the yields (14.1–15.6%) were lower than those obtained when *p-tert*-butylcalix[4]arene was used (see Table 1).

Can this reaction be expanded to other reactants than epoxides? We have tested a series of alkylating reagents including ethyl bromoacetate, benzyl chloride, 2-chloroethyltosylate. No remarkable reaction was observed, the conversion of *p-tert*-butylcalix[4]arene was less than 2%.

The reaction conditions were also investigated. *p-tert*-Butylcalix[4]arene reacted with epichlorohydrin in the presence of nano $CaCO_3$ (2 equiv.) in toluene at 100 °C for 2 days, the yield of **1** was 24.7%, and it was the sole product. Prolonging the reaction period to 5 days, the monosubstitued calix[4]arene was isolated in 52.6% yield, accompanied a minor by-product. Further increasing the reaction time to 10 days, the conversion of *p-tert*-butylcalix[4]arene was complete, but a more complex mixture of products was obtained, and the isolated yield of **1** decreased remarkably to 35%. The reaction was very sensitive to the solvent used. No reaction occurred when polar solvents such as acetonitrile, acetone and ethylene glycol dimethyl ether were used.

It is known that the first ionization constant of calix[4]arene is decreased by *ca.* 2 pH units as compared with corresponding acyclic analogue, and the Ka_1 is much higher than Ka_2 due to the occurrence of annular intramolecular hydrogen bonds.[2a,15] On the other hand, when the size of particles is reduced to the nano level, some special kind of particle may exhibit very high activity, *i.e.* the reactivity or other properties may change suddenly in terms of nano effects. It seems this is the case for nano $CaCO_3$. Thus, the high selectivity of monofunctionalization and the special behavior of nano $CaCO_3$ can be attributed to the nano effect combined with the occurrence of annular intramolecular hydrogen bonds in calixarenes. However, it is difficult to explain only the ring-opening product of epoxide being isolated, and the yield of ring-opening product **1** is not very sensitive to the amount of nano $CaCO_3$ used. Furthermore, the real nature of nano $CaCO_3$ is still unclear. Further work should be done to explore it.

Treatment of compound **1** or **3** in tetrahydrofuran with sodium ethylate (1 equiv.) at room temperature for 2 hours afforded the corresponding glycidyl derivatives **5** or **6**, and the nucleophilic substituted by-products **7** or **8**. The yield of **7** or **8** was increased with increased reaction time or increased amount of sodium ethylate used. When the reaction time was prolonged to 24 hours with an excess of sodium ethylate, **7** or **8** was obtained almost quantitatively. Upon using 40% sodium hydroxide aqueous solution instead of sodium ethylate, the yield of **5** or **6** reduced.

In conclusion, to the best of our knowledge, no paper concerning the application of nanoparticles in calixarene chemistry has been published. Though the real role of nano $CaCO_3$ is not fully understood, it is certain that nano $CaCO_3$ can be used as a unique condensation agent, or promoting agent, or catalyst in a few reactions, especially monofunctionalization of calixarene with epoxides. Besides, this is a convenient method for the preparation of monoglycidyl calixarene.

Table 1 Reaction conditions and yields of monosubstituted calixarene derivatives

Entry	Nano $CaCO_3$ (equiv.)	Epoxide	*n*	Time/ days	Yield (%)	Recovered calixarene (%)
1	1	epichlorohydrin	4	2	23.8	62.8
2	2	epichlorohydrin	4	2	24.5	64.0
3	2	epichlorohydrin	4	5	52.6	34.3
4	2	epichlorohydrin	4	10	35.2	0
5	10	epichlorohydrin	4	2	24.3	46.8
6	2	allyl glycidyl ether	4	2	26.5	66.2
7	2	allyl glycidyl ether	4	10	70.2	0
8	2	epichlorohydrin	6	5	14.1	55.6
9	2	allyl glycidyl ether	6	5	15.6	73.0

Experimental

Melting points were recorded on a Gallenkap melting point apparatus in open capillaries and are uncorrected. ^1H NMR and ^{13}C NMR were recorded on a Varian Mercury VX300 instrument at ambient temperature. ^1H NMR chemical shifts are given in ppm and referenced to internal $CHCl_3$ ($\delta = 7.27$) for $CDCl_3$ solutions. ^{13}C NMR chemical shifts are given in ppm and referenced to $CDCl_3$ ($\delta = 77.0$). FAB-MS spectra were obtained from a Kratos MS80RF mass spectrometry service, with *m*-nitrobenzyl alcohol as a matrix. Modified nano calcium carbonate (average particle size was 20 nm) was supplied by Inter Mongolia Mengxi High-tech materials Co. Ltd., China. Anhydrous solvents were purified by standard procedures and were freshly distilled prior to use. All other chemicals were analytically pure and used without further purification.

General procedure for the synthesis of compounds 1–4

To a suspension of nano $CaCO_3$ (2 mmol) in dry toluene (50 ml), *p-tert*-butylcalixarene (1 mmol) and epoxide (7–8 mmol) were added. The reaction was stirred for 5 days at 100 °C. Nano $CaCO_3$ was removed by centrifugation. After evaporation of the solvent and the excess of epoxide, the residue was taken up in CH_2Cl_2 and the unreacted calixarene was filtered off, then the solution was concentrated. The remaining crude product was purified by column chromatography.

5,11,17,23-Tetra-*tert*-butyl-26,27,28-trihydroxy-25-(3′-chloro-2′-hydroxypropoxy)calix[4]arene (**1**). Yield: 52.6%; mp: 116–118 °C; ^{1}HNMR (300 MHz, $CDCl_3$) δ 1.19 and 1.23 (s each, 9H each, *t*-Bu), 1.21 (s, 18H, *t*-Bu), 3.47 (d, 2H, $^2J = 13.8$ Hz, $ArCH_2Ar$), 3.48 (d, 2H, $^2J = 13.8$ Hz, $ArCH_2Ar$), 3.83 (dd, 1H, $^2J = 11.4$ Hz, $^3J = 7.5$ Hz, $ClCH_2$–), 3.89 (dd, 1H, $^2J = 11.4$ Hz, $^3J = 5.1$ Hz, $ClCH_2$–), 4.25 and 4.26 (dd each, 1H each, $^2J = 13.8$ Hz, $^3J = 1.5$ Hz, Ar–O–CH_2–), 4.33 (d, 2H, $^2J = 13.8$ Hz, $ArCH_2Ar$), 4.35 (overlapped, 1H, –CH(–O*H*)–), 4.37 (d, 2H, $^2J = 13.8$ Hz, $ArCH_2Ar$), 4.39 (m, 1H, –C*H*(–OH)–), 7.01, 7.07, 7.08 (d each, 2H each, $^4J = 2.1$ Hz

each, *H*–Ar), 7.11 (s, 2H, *H*–Ar), 9.61 (s, 1H, –O*H*), 9.71 (s, 1H, –O*H*), 10.28 (s, 1H, –O*H*); MS (FAB) m/z 741 for $[M+H]^+$.

5,11,17,23-Tetra-*tert*-butyl-26,27,28-trihydroxy-25-(4′-oxo-2′-hydroxyhepten-6′-yloxy)calix[4]arene (**2**). Reaction time: 10 days. Yield: 70.2%; mp: 208–210 °C; ^{1}HNMR (300 MHz, $CDCl_3$) δ 1.19, 1.21, 1.22 and 1.23 (s each, 9H each, *t*-Bu), 3.44 (d, 2H, $^2J = 13.2$ Hz, ArCH_2Ar), 3.47 (d, 2H, $^2J = 13.8$ Hz, ArCH_2Ar), 3.73 (dd, 1H, $^2J = 9.9$ Hz, $^3J = 7.2$ Hz, Allyl–O–CH_2–), 3.83 (dd, 1H, $^2J = 9.9$ Hz, $^3J = 5.4$ Hz, Allyl–O–CH_2–), 4.11–4.17 (m, 2H, –CH_2–O–Ar), 4.26 (d, 2H, $^2J = 13.2$ Hz, ArCH_2Ar), 4.31 (overlapped, 1H, –C*H*–(–OH)–), 4.33 (overlapped, 2H, Vinyl–CH_2–), 4.42 (d, 2H, $^2J = 13.2$ Hz, ArCH_2Ar), 5.21 (dd, 1H, $^2J = 1.5$ Hz, $^3J_{cis} = 10.5$ Hz, CH_2=), 5.31 (dd, 1H, $^2J = 1.5$ Hz, $^3J_{trans} = 15.9$ Hz, CH_2=), 5.43 (d, $^3J = 5.7$ Hz, 1H, –CH–(–O*H*)–), 5.95 (m, 1H, CH_2=C*H*–), 6.98, 7.01, 7.08, 7.11 (d each, 2H each, $^4J = 2.1$ Hz, *H*–Ar), 9.68, 9.78 and 10.35 (s each, 1H each, Ar–O*H*); MS (FAB) m/z 762 for $[M]^+$.

5,11,17,23,29,35-Hexa-*tert*-butyl-38,39,40,41,42-pentahydroxy-37-(3′-chloro-2′-hydroxypropoxy)calix[6]arene (**3**) Yield: 14.1%; mp: 278–280 °C (yellow above 240 °C); ^{1}HNMR (300 MHz, $CDCl_3$) δ 1.17 and 1.20 (s each, 9H each, *t*-Bu), 1.27 and 1.28 (s each, 18H each, *t*-Bu), 3.43 (d, 2H, $^2J = 13.2$ Hz, Ar*C*H_2Ar), 3.53 (d, 2H, $^2J = 12.6$ Hz, Ar*C*H_2Ar), 3.57 (d, 2H, $^2J = 13.2$ Hz, Ar*C*H_2Ar), 3.96–4.10 (m, 4H, ClCH_2– and Ar–O–CH_2–), 4.28–4.53 (m, 8H, ArCH_2Ar, –C*H*(–OH)– and –CH(–O*H*)–), 7.07 (s, 4H, *H*–Ar), 7.12 (s, 4H, *H*–Ar), 7.15 (s, 4H, *H*–Ar), 9.00, 9.35, 9.80 (s each, 1H each, –O*H*), 10.00 (s, 2H, –O*H*); MS (FAB) m/z 1065 for $[M+H]^+$.

5,11,17,23,29,35-Hexa-*tert*-butyl-38,39,40,41,42-pentahydroxy-37-(4′-oxo-2′-hydroxyhepten-6′-yloxy)calix[6]arene (**4**). Yield: 15.6%; mp: 170–172 °C; ^{1}HNMR (300 MHz, $CDCl_3$) δ 1.19 and 1.23 (s each, 9H each, *t*-Bu), 1.30 (s, 36H, *t*-Bu), 3.47 (d, 2H, $^2J = 13.8$ Hz, ArCH_2Ar), 3.53 (d, 2H, $^2J = 13.5$ Hz, ArCH_2Ar), 3.55 (d, 2H, $^2J = 15$ Hz, ArCH_2Ar), 3.61 (overlapped, 1H, –CH(–O*H*)–), 3.95–4.06 (m, 4H, Allyl–O–CH_2– and –CH_2–O–Ar), 4.19 (d, 2H, $^3J = 6$ Hz, Vinyl–CH_2–), 4.31 (d, 2H, $^2J = 14.1$ Hz, ArCH_2Ar), 4.38 (overlapped, 1H, –C*H*(–OH)–), 4.40 (d, 2H, $^2J = 13.2$ Hz, ArCH_2Ar), 4.49 (d, 2H, $^2J = 13.5$ Hz, ArCH_2Ar), 5.16 (dd, 1H, $^2J = 1.5$ Hz, $^3J_{cis} = 10.2$ Hz, CH_2=), 5.28 (dd, 1H, $^2J = 1.5$ Hz, $^3J_{trans} = 15.9$ Hz, CH_2=), 5.94 (m, 1H, CH_2=C*H*–), 7.05, 7.10, 7.14, 7.16, 7.18, 7.20 (s each, 2H each, *H*–Ar), 9.20 (br, 2H, Ar–O*H*), 9.90–10.00 (br, 3H, Ar–O*H*); MS (FAB) m/z 1087 for $[M+H]^+$.

General procedure for the synthesis of compounds 5 and 6

To a solution of compound **1** or **3** in 10 ml tetrahydrofuran, sodium ethylate (1 equiv.) in 1 mL absolute ethanol was added. The mixture was stirred for 2 hours at room temperature, and then neutralized with diluted HCl. After evaporating off the solvent, the residue was dissolved in dichloromethane (15 ml) and washed with water. The organic layer was dried over $MgSO_4$, filtered, concentrated, and then purifed by column chromatography on silica gel.

5,11,17,23-Tetra-*tert*-butyl-26,27,28-trihydroxy-25-glycidyloxycalix[4]arene (**5**). Yield: 45.6%. mp: 206–208 °C; ^{1}HNMR (300 MHz, $CDCl_3$) δ 1.12, 1.13, 1.14 and 1.15 (s each, 9H each, *t*-Bu), 2.90 (dd, 1H, $^2J = 4.8$ Hz, $^3J = 2.4$ Hz, –CH–(–O–)–CH_2), 2.99 (dd, 1H, $^2J = 4.8$ Hz, $^3J = 4.8$ Hz, –CH–(–O–)–CH_2), 3.36 (d, 4H, $^2J = 13.2$ Hz, ArCH_2Ar), 3.65 (m, 1H, –O–CH_2–C*H*(–O–)–CH_2), 3.95 (dd, 1H, $^2J = 10.8$ Hz, $^3J = 6.6$ Hz, –CH_2–O–Ar), 4.21 and 4.30 (d each, 2H each, $^2J = 13.8$ Hz each, ArCH_2Ar), 4.41 (dd, 1H, $^2J = 10.8$ Hz, $^3J = 3$ Hz, –CH_2–O–Ar), 6.92, 6.98, 7.00 (d each, 2H each, $^4J = 2.1$ Hz each, *H*–Ar), 7.03 (s, 2H, *H*–Ar), 9.14 (s, 1H, –O*H*), 9.47 (s, 1H, –O*H*), 10.11 (s, 1H, –O*H*); MS (FAB) m/z 705 for $[M+H]^+$. **7** was also obtained as a by-product in the yield of 3.5%.

5,11,17,23,29,35-Hexa-*tert*-butyl-38,39,40,41,42-pentahydroxy-37-glycidyloxycalix[6]arene (**6**). Yield: 42.3%. mp: 282–284 °C; ^{1}HNMR (300 MHz, $CDCl_3$) δ 0.94, 1.18, 1.22 and 1.24 (s each, 9H, 9H, 18H, 18H, *t*-Bu), 2.98 (m, 2H, –CH–(–O–)–CH_2), 3.03 (m, 1H, –C*H*(–O–)–CH_2), 3.69–4.32 (m, 14H, –CH_2–O–Ar and ArCH_2Ar), 6.95–7.14 (m, 12H, *H*–Ar), 8.65 (s, 2H, –O*H*), 9.42 (s, 1H, –O*H*), 9.65 (bs, 2H each, –O*H*); MS (FAB) m/z 1028 for $[M]^+$. **8** was also obtained as a by-product in 2.7% yield.

General procedure for the synthesis of compounds 7 and 8

To a solution of compound **1** or **3** in 10 ml tetrahydrofuran, an excess of sodium ethylate was added. The mixture was stirred for 24 hours at room temperature, and then neutralized with diluted HCl. After evaporating off the solvent, the residue was dissloved in dichloromethane (15 ml) and washed with water. The organic layer was dried over $MgSO_4$, filtered, concentrated, and then purifed by column chromatography on silica gel.

5,11,17,23-Tetra-*tert*-butyl-26,27,28-trihydroxy-25-(3′-ethoxy-2′-hydroxypropoxy)calix[4]arene (**7**). Yield: 95.2%; mp: 213–216 °C; ^{1}HNMR (300 MHz, $CDCl_3$) δ 1.21, 1.22, 1.23 and 1.24 (s each, 9H each, *t*-Bu), 1.26 (t, 3H, $^3J = 6.6$ Hz, –OCH_2CH_3), 3.44 (d, 2H each, $^2J = 13.2$ Hz, ArCH_2Ar), 3.46 (d, 2H, $^2J = 14.4$ Hz, ArCH_2Ar), 3.64 (q, 2H, $^3J = 6.6$ Hz, –OCH_2CH_3), 3.74 (dd, 1H, $^2J = 10.5$ Hz, $^3J = 3.3$ Hz, EtOCH_2–), 3.89 (dd, 1H, $^2J = 10.5$ Hz, $^3J = 5.4$ Hz, EtOCH_2–), 4.20–4.44 (m, 4H, Ar–O–CH_2–, –CH(–O*H*)– and –C*H*(–OH)–), 4.25 and 4.34 (d each, 2H each, $^2J = 13.8$ Hz each, ArCH_2Ar), 6.97–7.07 (m, 8H, *H*–Ar), 9.63, 9.72 and 10.29 (s each, 1H each, –O*H*); MS (FAB) m/z 750 for $[M]^+$.

5,11,17,23,29,35-Hexa-*tert*-butyl-38,39,40,41,42-pentahydroxy-37-(3′-ethoxy-2′-hydroxypropoxy)calix[6]arene (**8**). Yield: 86.9%; mp: 166–168 °C; ^{1}HNMR (300 MHz, $CDCl_3$) δ 1.11 and 1.16 (s each, 9H each, *t*-Bu), 1.18 (t, 3H, $^3J = 6.9$ Hz, OCH_2CH_3), 1.22 (s, 36H, *t*-Bu), 3.40 (d, 2H, $^2J = 15.3$ Hz, ArCH_2Ar), 3.48 (d, 2H, $^2J = 14.7$ Hz, ArCH_2Ar), 3.51 (d, 2H, $^2J = 14.7$ Hz, ArCH_2Ar), 3.65 (q, 2H, $^3J = 6.9$ Hz, –OCH_2CH_3), 3.82–3.97 (m, 5H, –CH_2–CH(–O*H*)–CH_2–OEt), 4.16 (d, 2H, $^2J = 13.2$ Hz, ArCH_2Ar), 4.23 (d, 2H, $^2J = 13.2$ Hz, ArCH_2Ar), 4.32 (d, 2H, $^2J = 14.2$ Hz, ArCH_2Ar), 4.34 (m, –C*H*(–OH)–), 6.97 and 7.02 (s each, 2H each, *H*–Ar), 7.06 and 7.08 (s each, 4H each, *H*–Ar), 9.03, 9.23, 9.72, 9.90 and 9.96 (s each, 1H each, –O*H*); MS (FAB) m/z 1074 for $[M]^+$.

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