

A Novel Domino Reaction of 1, 1'-bi-2-Naphthol Catalyzed by Copper(II)-amine Complexes

TAN, Duan-Ming(谭端明) LI, Hui-Hua(李惠华) WANG, Bo(汪波) LIU, Han-Biao(刘汉标)
XU, Zun-Le*(许遵乐)

Applied Chemistry Department, School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou, Guangdong 510275, China

1,1'-Bi-2-naphthol (**1**) was oxidized into 1-oxo-13c-alkyloxy-1, 13c-dihydro-dibenzo [a,kl]-xanthenes (**2—11**) with high isolated yields (58—94%) in alcohol solvents under the catalysis of copper(II)-amine complexes in the presence of oxygen. The conversion of **1** to **2—11** belongs to Domino-reaction.

Keywords 1,1'-Bi-2-naphthol, copper(II)-amine complexes, domino reaction, oxidative coupling

1,1'-Bi-2-naphthol (**1**, 1,1'-binaphthene-2,2'-diol, 2,2'-dihydroxyl-1,1'-binaphthyl) and its optical isomers have been widely used in organic synthesis, especially in asymmetric synthesis as chirality auxiliaries.¹ Optically active **1** can be prepared either from racemic **1**² or by asymmetric coupling of 2-naphthol^{2,3} by employing chiral copper(II)-amine complexes. In our investigation of asymmetric synthesis of **1**, 1-oxo-13c-methoxy-1,13c-dihydro-dibenzo[a,kl]-xanthene (**2**) was obtained as a by-product during the resolution of racemic **1** using copper(II)-amine complexes in methanol by heating the mother liquor in the presence of air (Scheme 1). The structure of **2** was confirmed by X-ray diffraction studies. It should be noted that three conversions occurred from **1** to **2**, *i. e.* 2'-O-C₈ coupling, 2-OH oxidation and C₁-OCH₃ coupling (Scheme 2). It implies a route to complicate multi-cyclic structure via a Domino-reaction⁴ under catalysis of copper(II)-amine complexes.

The synthesis of **2** using **1** was first described by Rieche *et al.*⁵ Compound **1** was treated with K₃Fe(CN)₆ followed by HClO₄ and NaOCH₃ in CH₃OH to yield **2**

(38.5%). Later, Schneider and coworkers reported that 3,3',6,6'-tetra-*tert*-butyl-binaphthol (a derivative of **1**) formed tetra-*tert*-butyl substituted **2** in the presence of K₃Fe(CN)₆ and KOH/CH₃OH (rt, 12 h, 38% yield).

The oxidation results of phenol⁷ or 2-naphthol^{8,9} vary with the copper-amine complexes, *e. g.* 2-naphthol can be oxidized into either 1,1'-bi-2-naphthol⁸ (**1**) or 4-(2-hydroxy-1-naphthyl)-1,2-naphthoquinone.⁹ Therefore, copper-amine complexes may be used as functional model compounds of phenol oxidases in biomimetic type synthesis of structurally complicate compounds. Further study on this biomimetic Domino reaction using copper-amine complexes as catalysts is now underway.

Here we report the conversion from **1** to **2—11** by using CuCl₂-amine complexes. In the presence of O₂ in MeOH, **1** could be converted into **2** almost quantitatively using 1:1 ratio of CuCl₂/amine as catalyst, and the yield was up to 94%. The oxidation in other alcoholic solvents (EtOH, PrOH, ⁱPrOH, ⁱBuOH, ⁿBuOH, glycol, 2-chloroethanol, glycol monomethyl ether and glycol monoethyl ether) yielded **3—11** in 58—94%. The effects of ligands, temperature, ratio of reactants and the concentration of O₂ will be discussed in detail.

Results and discussion

First of all, it has been found that the ratio of Cu(II)/amine is the most important factor in the reac-

* E-mail: cedc07@zsu.edu.cn

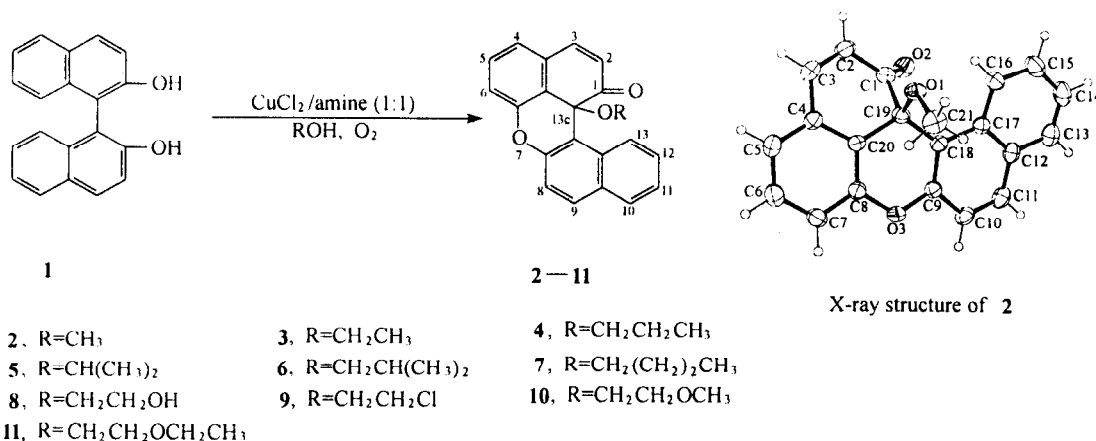
Received February 15, 2000; accepted August 17, 2000.

Project (No. 29772057) supported by the National Natural Science Foundation of China.

tion. The synthesis of **2** in the presence of air is used as an example. Without any amine added, **1** was inert towards CuCl_2 in methanol. When the ratio of Cu(II) /amine was 1:3 or 1:4, **1** was also inert at room temperature as shown by TLC. Even after 60 h reflux in

methanol, the conversion of **1** was still very low (at 1:3 $\text{Cu(II)}/2\text{-amino-1-butanol}$). The reaction went faster at the $\text{Cu(II)}/\text{amine}$ ratio of 1:2, and the rate was the highest when the ratio was 1:1, when the reaction could take place at rt without the presence of O_2 .

Scheme 1



The oxidation of one molecule of **1** into one molecule of **2** requires transfer of 4 electrons, and 4 eq. of CuCl_2 is necessary if CuCl_2 is the unique oxidant ($4\text{Cu}^{2+} + 4e \rightarrow 4\text{Cu}^+$). Our results indicated that oxygen could be the oxidant because 89% yield was obtained when 0.1 eq. of CuCl_2 -amine was used (Table 1

Entry 1). Therefore, CuCl_2 -amine was the catalyst in the reaction, which was further confirmed by the fact that the reaction was speeded up with increased concentration of O_2 . It was also found that reflux could accelerate the reaction significantly without loss of the selectivity.

Table 1 Oxidation of **1** by O_2 under CuCl_2 -ethanolamine in alcohol

Entry	Solvent	CuCl_2 : amine: 1 (eq.)	Oxidant	Temp. (°C)	Time (h)	Product	Isolated yield (%)
1	CH_3OH	0.1:0.1:1	O_2	65	48	2	89
2	CH_3OH	0.8:0.8:1	O_2	65	5	2	94
3	CH_3OH	2:2:1	air	rt	20	2	91
4	$\text{CH}_3\text{CH}_2\text{OH}$	1:1:1	O_2	rt	24	3	92
5	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	1:1:1	O_2	90	0.5	4	92
6	$(\text{CH}_3)_2\text{CHOH}$	1:1:1	O_2	65	1.5	5	92
7	$(\text{CH}_3)_2\text{CHCH}_2\text{OH}$	1:1:1	O_2	90	1	6	94
8	$\text{CH}_3(\text{CH}_2)_3\text{OH}$	1:1:1	air	60	5	7	87
9	$\text{HOCH}_2\text{CH}_2\text{OH}$	1:1:1	O_2	90	9	8	58
10	$\text{ClCH}_2\text{CH}_2\text{OH}$	1:2:1 ^a	air	rt	48	9	87
11	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$	1:1:1	air	rt	48	10	71
12	$\text{CH}_3\text{CH}_2\text{O}(\text{CH}_2)_2\text{OH}$	1:1:1	O_2	50	24	11	63

^a Powdered NaHCO_3 (2.0 eq.) was added in order to absorb HCl released from chloroethanol.

Under 1:1 ratio of $\text{Cu(II)}/\text{amine}$, many amines could be used in the conversion of **1** to **2** in good to ex-

cellent selectivity (ethanolamine, 94% isolated yield; 2-amino-1-butanol, 94%; *t*-butylamine, 77%; cyclohexamine, 77%; cyclopentamine, 66%; piperidine, 82%; mopholine 86%, (1*R*, 2*S*)-(–)-ephedrine, 64%; cinchonine, 82% and cinchonidine, 82%). Among these ligands used, ethanolamine is of the highest selectivity and reaction rate.

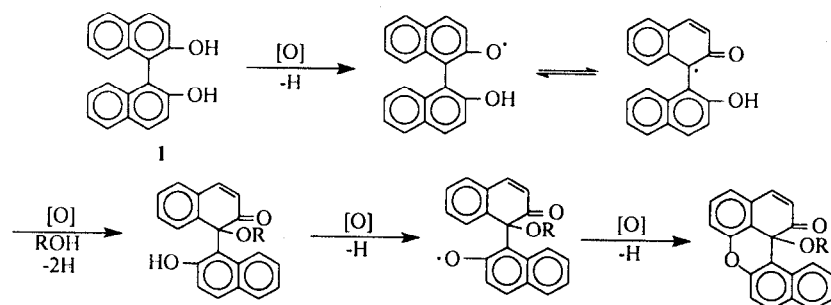
Table 1 shows the oxidation results of **1** under CuCl₂-ethanolamine in MeOH and other solvents. The reactions in methanol, ethanol, propanol, isopropanol and isobutanol proceed almost quantitatively (92–94% yields). The yields of **7** in glycol and **11** in glycol monoethyl ether are lower because of more by-products. As to the reaction in chloroethanol, the amount of ethanolamine is better doubled, and small amount of

NaHCO₃ could be added to absorb the HCl released by decomposition of the unstable chloroethanol.

When CuCl₂ complexes of chiral amines (such as 2-amino-1-butanol, ephedrine, cinchonine, cinchonidine) were used to catalyze the conversion of racemic **1** into **2** (yield 64–82%), no asymmetric coupling occurred. Similar result happened even when optically pure **1** was employed via non-chiral CuCl₂-amine. So we inferred that there was racemization in the process of the formation of **2**.

Considering that phenols can yield radicals under oxidative conditions, we rationalized the process in this oxidation to involving radicals as intermediates (Scheme 2), which were in agreement with the racemization result.

Scheme 2



The above results are in accord with what we observed in the resolution of racemic **1** via chiral Cu(II)-amine complexes in methanol. In order to obtain better resolution result and avoid the formation of **2**, it is better to (1) increase the ratio of amine/Cu(II) (> 4:1), (2) avoid long time heating and, (3) exclude the O₂.

Experimental

Melting points were determined on a Thiele tube and uncorrected. The IR spectra were recorded on a Nicolet FT-IR 5DX infrared spectrometer (in KBr). The ¹H NMR and ¹³C NMR spectra were obtained on a Varian Unity INOVA-500 spectrometer at 499.780 MHz and 125.681 MHz, respectively, in CDCl₃ with TMS as the internal standard. Mass spectra (FAB or EI) were taken on a VG ZAB-HS instrument. Elemental analyses were conducted on a Perkin-Elmer 204 elemental analyzer.

1 was prepared according to the reported procedure¹⁰ from oxidation of 2-naphthol by FeCl₃. Other reagents and solvents were of A.R. or C.P. grade without further purification.

General procedure

To 20 mL of stirred alcoholic solution of CuCl₂ · 2H₂O (0.17 g, 1 mmol) were added **1** (0.29 g, 1 mmol) and ethanolamine (0.06 g, 1 mmol). In the reaction of chloroethanol, more one mmol of ethanolamine was needed, and 0.1 g of powered NaHCO₃ was added every 24 h. The resulting mixture was stirred at certain temperature and under 1 atm O₂ or flowing air, till complete consumption of **1** (monitored by TLC).

For **2**: half the solvent CH₃OH was removed in vacuum from the reaction mixture to give a yellow crystal **2**. To the mother liquor 20 mL of EtOAc was added.

The mixture was washed with 50 mL of 1% dilute NH_3 aqueous solution and 3×10 mL of water respectively, then purified by a short Al_2O_3 column chromatography (eluted with petroleum ether-EtOAc 10:1) to obtain another crop of **2**.

For **3—7**: the solvents were removed in vacuum from the reaction mixture to give a dark brown solid. Then 40 mL of EtOAc and 50 mL of 1% dilute NH_3 aqueous solution were added. The EtOAc solutions were washed with 3×20 mL of water respectively. Then the EtOAc was removed in vacuum. Recrystallization in acetone and decolorization with activated carbon gave yellow crystals **3—7**. The mother liquor yielded another crop of **3—7** with a short Al_2O_3 column chromatography.

For **8—11**: to the reaction mixture were added 50 mL of EtOAc and 150 mL of 1% dilute NH_3 aqueous solution. The EtOAc solution was treated as above (**3—7**) to give yellow crystals **8—11**.

1-Oxo-13c-methoxy-1,13c-dihydro-dibenzo[*a, kl*]-xanthene (**2**)

mp: 165—167°C (Lit.⁵ 165—170°C). ν_{max} : 3064 (Ar—H), 2931, 1700 (s, C=O), 1454, 1053, 807, 751 cm^{-1} . δ_{H} : 2.83 (s, 3H, OCH_3), 6.26 (d, $J = 9.9$ Hz, 1H, 2-H), 7.06 (d, $J = 7.3$ Hz, 1H, 4-H), 7.09 (dd, $^3J = 8.2$ Hz, $^4J = 1.0$ Hz, 1H, 6-H), 7.19 (d, $J = 9.9$ Hz, 1H, 3-H), 7.31 (d, $J = 8.9$ Hz, 1H, 9-H), 7.37 (dd, $J_{4\text{H}-5\text{H}} = 7.3$ Hz, $J_{5\text{H}-6\text{H}} = 8.2$ Hz, 1H, 5-H), 7.40—7.44 (m, 2H, 10-H, 13-H), 7.79—7.82 (m, 1H, 11-H), 7.89 (d, $J = 8.9$ Hz, 1H, 8-H), 8.10—8.13 (m, 1H, 12-H). δ_{C} : 51.61 (OCH_3), 75.77 (13c-C), 107.36, 116.01, 116.46, 117.20, 124.03, 124.67, 125.84, 125.97, 127.71, 128.18, 130.70, 130.98, 131.95, 132.78, 133.32, 139.26, 151.61, 152.24, 197.68 (C=O). m/z (EI, $I = 5.9$ V, %): 314 (M^+ , 42), 299 ($\text{M}^+ - \text{CH}_3$, 12), 283 ($\text{M}^+ - \text{OCH}_3$, 100). Anal. $\text{C}_{21}\text{H}_{14}\text{O}_3$. Calcd: C, 80.24; H, 4.49. Found: C, 80.30; H, 4.43.

1-Oxo-13c-ethoxy-1,13c-dihydro-dibenzo[*a, kl*]-xanthene (**3**)

mp: 137—139°C. ν_{max} : 2970, 1709 (s, C=O), 1456, 1050, 806 cm^{-1} . δ_{H} : 0.92 (t, $J = 7.2$ Hz, 3H,

— CH_3), 2.86—3.00 (m, 2H, OCH_2), 6.26 (d, $J = 9.8$ Hz, 1H, 2-H), 7.05 (d, $J = 7.2$ Hz, 1H, 4-H), 7.07 (d, $J = 8.5$ Hz, 1H, 6-H), 7.17 (d, $J = 9.8$ Hz, 1H, 3-H), 7.30 (d, $J = 9.1$ Hz, 1H, 9-H), 7.36 (dd, $J_{4\text{H}-5\text{H}} = 7.2$ Hz, $J_{5\text{H}-6\text{H}} = 8.5$ Hz, 1H, 5-H), 7.39—7.42 (m, $2 \times 1\text{H}$, 10-H, 13-H), 7.78—7.80 (m, 1H, 11-H), 7.87 (d, $J = 9.1$ Hz, 1H, 8-H), 8.15—8.17 (m, 1H, 12-H). δ_{C} : 15.44 (CH_3), 60.03 (OCH_2), 75.29 (13c-C), 108.32, 116.39, 116.85, 117.17, 123.83, 124.58, 125.65, 126.10, 127.87, 128.11, 130.51, 130.96, 131.78, 132.88, 133.43, 139.10, 151.28, 151.95, 197.83 (C=O). FAB-MS, m/z (%): 329 ($\text{M}^+ + 1$, 27), 328 (M^+ , 13), 299 ($\text{M}^+ - \text{C}_2\text{H}_5$, 25), 284 (100), 283 ($\text{M}^+ - \text{OEt}$, 72). Anal. $\text{C}_{22}\text{H}_{16}\text{O}_3$. Calcd: C, 80.47; H, 4.91. Found: C, 80.63; H, 4.93.

1-Oxo-13c-propoxy-1,13c-dihydro-dibenzo[*a, kl*]-xanthene (**4**)

mp: 149—150°C. ν_{max} : 2959, 2931, 1700 (s, C=O), 1454, 1004, 814 cm^{-1} . δ_{H} : 0.62 (t, $J = 7.2$ Hz, 3H, — CH_3), 1.24—1.38 (m, 2H, CH_2), 2.81 (t, $J = 6.5$ Hz, 2H, OCH_2), 6.26 (d, $J = 9.8$ Hz, 1H, 2-H), 7.04 (d, $J = 7.2$ Hz, 1H, 4-H), 7.07 (d, $J = 8.5$ Hz, 1H, 6-H), 7.16 (d, $J = 10.4$ Hz, 1H, 3-H), 7.30 (d, $J = 9.1$ Hz, 1H, 9-H), 7.35 (dd, $J_{5\text{H}-4\text{H}} = 7.0$ Hz, $J_{6\text{H}-5\text{H}} = 8.5$ Hz, 1H, 5-H), 7.38—7.42 (m, 2H, 10-H, 13-H), 7.77—7.80 (m, 1H, 11-H), 7.87 (d, $J = 9.1$ Hz, 1H, 8-H), 8.14—8.17 (m, 1H, 12-H). δ_{C} : 10.65 (CH_3), 22.93 (CH_2), 66.06 (OCH_2), 75.15 (13c-C), 108.31, 116.34, 116.84, 117.20, 123.79, 124.59, 125.65, 126.27, 127.91, 128.10, 130.51, 130.95, 131.74, 132.88, 133.50, 139.00, 151.24, 152.02, 197.91 (C=O). FAB-MS, m/z (%): 343 ($\text{M}^+ + 1$, 12), 342 (M^+ , 20), 299 ($\text{M}^+ - \text{C}_3\text{H}_7$, 30), 284 (54), 283 ($\text{M}^+ - \text{OPr}$, 100). Anal. $\text{C}_{23}\text{H}_{18}\text{O}_3$. Calcd: C, 80.68; H, 5.30. Found: C, 80.97; H, 5.34.

1-Oxo-13c-iso-propoxy-1,13c-dihydro-dibenzo[*a, kl*]-xanthene (**5**)

mp: 173—175°C. ν_{max} : 2970, 1709 (s, C=O), 1453, 1008, 813 cm^{-1} . δ_{H} : 0.55 (d, $J = 7.0$ Hz, 3H, — CH_3), 0.68 (d, $J = 6.5$ Hz, 3H, — CH_3),

3.42—3.48(m, 1H, CH), 6.27(d, $J = 9.8$ Hz, 1H, 2-H), 7.04(d, $J = 7.2$ Hz, 1H, 4-H), 7.09(dd, $^3J = 9.1$ Hz, $^4J = 1.3$ Hz, 1H, 6-H), 7.15(d, $J = 9.8$ Hz, 1H, 3-H), 7.30(d, $J = 9.1$ Hz, 1H, 9-H), 7.36(dd, $J_{5H-4H} = 7.2$ Hz, $J_{6H-5H} = 8.5$ Hz, 1H, 5-H), 7.37—7.42(m, 2H, 13-H, 10-H), 7.76—7.80(m, 1H, 11-H), 7.87(d, $J = 9.1$ Hz, 1H, 8-H), 8.12—8.16(m, 1H, 12-H). δ_C : 23.52(CH₃), 23.69(CH₃), 67.82(CH), 75.18(13c-C), 109.32, 116.63, 117.19, 117.21, 123.58, 124.54, 125.31, 126.48, 128.03, 128.73, 130.57, 130.98, 131.77, 132.99, 133.85, 138.61, 150.99, 151.77, 197.92 (C = O). FAB-MS, m/z (%): 343(M⁺ + 1, 20), 342(M⁺, 18), 299(M⁺ - C₃H₇, 100), 284(88), 283(M⁺ - OPr, 33). Anal. C₂₃H₁₈O₃. Calcd: C, 80.68; H, 5.30. Found: C, 81.03; H, 5.45.

1-Oxo-13c-iso-butoxy-1, 13c-dihydro-dibenzo[*a*, *kl*]-xanthene (6)

mp: 146—148°C. ν_{\max} : 2959, 1700(s, C = O), 1454, 1046, 807 cm⁻¹. δ_H : 0.59(d, $J = 6.5$ Hz, 3H, -CH₃), 0.66(d, $J = 6.5$ Hz, 3H, -CH₃), 1.55—1.63(m, $J = 6.5$ Hz, 1H, CH), 2.57—2.63(m, 2H, -CH₂-), 6.26(d, $J = 9.8$ Hz, 1H, 2-H), 7.04(d, $J = 7.2$ Hz, 1H, 4-H), 7.07(d, $J = 8.5$ Hz, 1H, 6-H), 7.15(d, $J = 9.8$ Hz, 1H, 3-H), 7.30(d, $J = 8.5$ Hz, 1H, 9-H), 7.35(dd, $J_{5H-4H} = 7.2$ Hz, $J_{6H-5H} = 8.5$ Hz, 1H, 5-H), 7.38—7.42(m, 2 × 1H, 13-H, 10-H), 7.78—7.81(m, 1H, 11-H), 7.87(d, $J = 9.1$ Hz, 1H, 8-H), 8.14—8.17(m, 1H, 12-H). δ_C : 19.13(CH₃), 19.34(CH₃), 28.37(CH), 70.94(OCH), 75.03(13c-C), 108.35, 116.31, 116.82, 117.21, 123.71, 124.58, 125.61, 126.41, 127.96, 128.06, 130.49, 130.96, 131.70, 132.92, 133.61, 138.84, 151.21, 152.11, 197.80 (C = O). FAB-MS, m/z (%): 357(M⁺ + 1, 13), 356(M⁺, 20), 299(M⁺ - C₄H₉, 29), 283(M⁺ - OC₄H₉, 100). Anal. C₂₄H₂₀O₃. Calcd: C, 80.88; H, 5.66. Found: C, 81.00; H, 5.71.

1-Oxo-13c-butoxy-1, 13c-dihydro-dibenzo[*a*, *kl*]-xanthene (7)

mp: 117—119°C. ν_{\max} : 2954, 1705(s, C = O), 1456, 1029, 810 cm⁻¹. δ_H : 0.60(t, $J = 7.3$ Hz, 3H, CH₃), 1.03—1.14(m, 2H, O-C-C-CH₂), 1.20—1.32(m, 2H, O-C-CH₂), 2.80—2.88(m, 2H,

OCH₂), 6.25(d, $J = 10$ Hz, 1H, 2-H), 7.04(d, $J = 7.5$ Hz, 1H, 4-H), 7.07(d, $J = 8.5$ Hz, 1H, 6-H), 7.16(d, $J = 10$ Hz, 1H, 3-H), 7.30(d, $J = 9.0$ Hz, 1H, 9-H), 7.35(dd, $J_{5H-4H} = 7.5$ Hz, $J_{6H-5H} = 8.5$ Hz, 1H, 5-H), 7.38—7.43(m, 2 × 1H, 13-H, 10-H), 7.78—7.80(m, 1H, 11-H), 7.86(d, $J = 9.0$ Hz, 1H, 8-H), 8.14—8.16(m, 1H, 12-H). δ_C : 13.45(CH₃), 19.10(O-C-C-CH₂), 31.72(O-C-CH₂), 63.91(OCH₂), 75.15(13c-C), 108.32, 116.34, 116.86, 117.20, 123.79, 124.59, 125.65, 126.28, 127.88, 128.10, 130.52, 130.95, 131.74, 132.88, 133.52, 138.99, 151.24, 152.03, 197.92. FAB-MS, m/z (%): 357(M⁺ + 1, 19), 356(M⁺, 25), 299(M⁺ - C₄H₉, 28), 283(M⁺ - OC₄H₉, 100). Anal. C₂₄H₂₀O₃. Calcd: C, 80.88; H, 5.66. Found: C, 81.22; H, 5.85.

1-Oxo-13c-(2-hydroxy-ethoxy)-1, 13c-dihydro-dibenzo[*a*, *kl*]-xanthene (8)

mp: 190—192°C. ν_{\max} : 3389(br, OH), 1603(s, C = O), 1465, 1085, 826. δ_H : 3.68(dd, $^3J = 11.7$ Hz, $^4J = 3.3$ Hz, 1H, CH₂), 3.83(dd, $^3J = 11.7$ Hz, $^4J = 3.3$ Hz, 1H, CH₂), 3.91(dd, $^3J = 11.7$ Hz, $^4J = 3.3$ Hz, 1H, CH₂), 4.31(dd, $^3J = 11.7$ Hz, $^4J = 3.3$ Hz, 1H, CH₂), 6.14(d, $J = 9.8$ Hz, 1H, 2-H), 6.94(d, $J = 7.8$ Hz, 1H, 4-H), 6.96(d, $J = 9.8$ Hz, 1H, 3-H), 7.16(t, $J = 7.2$ Hz, 1H, 11-H), 7.21—7.25(m, 2 × 1H, 5-H, 10-H or 13-H), 7.27(d, distorted by 7.26 of CHCl₃, 1H, 10-H or 13-H), 7.30(d, $J = 9.1$ Hz, 1H, 9-H), 7.32(t, $J = 7.2$ Hz, 1H, 12-H), 7.47(d, $J = 8.5$ Hz, 1H, 6-H), 7.88(d, $J = 9.1$ Hz, 1H, 8-H), 8.29(s, 1H, -OH). δ_C : 60.06(CH₂), 63.66(CH₂), 76.64(13c), 94.54, 106.02, 112.34, 119.30, 121.05, 121.72, 124.11, 126.75, 128.66, 128.95, 129.20(2 × 1C), 129.97, 130.41, 131.42, 133.51, 133.68, 147.43, 154.06. FAB-MS, m/z (%): 345(M⁺ + 1, 48), 344(M⁺, 100), 284(64), 283(M⁺ - OCH₂CH₂OH, 40). Anal. C₂₂H₁₆O₄. Calcd: C, 76.73; H, 4.68. Found: C, 76.83; H, 4.49.

1-Oxo-13c-(2-chloro-ethoxy)-1, 13c-dihydro-dibenzo[*a*, *kl*]-xanthene (9)

mp: 159—161°C. ν_{\max} : 3064, 1700(s, C = O),

1454, 1032, 807 cm^{-1} . δ_{H} : 3.09—3.17 (m, 2H, CH_2Cl), 3.25—3.36 (m, 2H, OCH_2), 6.27 (d, $J = 10.0$ Hz, 1H, 2-H), 7.07 (d, $J = 7.4$ Hz, 1H, 4-H), 7.09 (dd, $^3J = 8.4$ Hz, $^4J = 1.0$ Hz, 1H, 6-H), 7.19 (d, $J = 10$ Hz, 1H, 3-H), 7.31 (d, $J = 9.1$ Hz, 1H, 9-H), 7.38 (dd, $J_{6\text{H}-5\text{H}} = 8.4$ Hz, $J_{5\text{H}-4\text{H}} = 7.4$ Hz, 1H, 5-H), 7.40—7.44 (m, 2H, 10-H, 13-H), 7.78—7.82 (m, 1H, 11-H), 7.89 (d, $J = 9.1$ Hz, 1H, 8-H), 8.11—8.15 (m, 1H, 12-H). δ_{C} : 42.68 (CH_2), 64.59 (CH_2), 75.63 (13-c), 107.59, 115.93, 116.58, 117.24, 124.07, 124.82, 125.96, 126.18, 127.76, 128.25, 130.99, 131.09, 132.21, 132.69, 133.61, 139.15, 151.38, 152.01, 196.94. FAB-MS, m/z (%): 365 ($\text{M}^+ + 3$, 4), 364 ($\text{M}^+ + 2$, 7), 363 ($\text{M}^+ + 1$, 12), 362 (M^+ , $\text{C}_{22}\text{H}_{15}\text{O}_3\text{Cl}$, 17), 299 ($\text{M}^+ - \text{CH}_2\text{CH}_2\text{Cl}$, 18), 283 ($\text{M}^+ - \text{OCH}_2\text{CH}_2\text{Cl}$, 100). Anal. $\text{C}_{22}\text{H}_{15}\text{O}_3\text{Cl}$. Calcd: C, 72.83; H, 4.17. Found: C, 72.71; H, 3.96.

1-Oxo-13c-(2-methoxy-ethoxy)-1, 13c-dihydro-dibenzo-[a, kl]-xanthene (10)

mp: 139—140°C. ν_{max} : 2912, 1709 (s, C = O), 1452, 1071, 810 cm^{-1} . δ_{H} : 2.95—3.08 (m, 2H, OCH_2), 3.08 (s, 3H, CH_3), 3.12—3.25 (m, 2H, OCH_2), 6.25 (d, $J = 10$ Hz, 1H, 2-H), 7.03 (d, $J = 7.5$ Hz, 1H, 4-H), 7.06 (dd, $^3J = 9.5$ Hz, $^4J = 1.0$ Hz, 1H, 6 = H), 7.15 (d, $J = 10$ Hz, 1H, 3-H), 7.28 (d, $J = 9.0$ Hz, 1H, 9-H), 7.34 (dd, $J_{4\text{H}-5\text{H}} = 7$ Hz, $J_{5\text{H}-6\text{H}} = 8$ Hz, 1H, 5-H), 7.38—7.41 (m, 2H, 10-H, 13-H), 7.76—7.79 (m, 1H, 11-H), 7.86 (d, $J = 9.0$ Hz, 1H, 8-H), 8.14—8.16 (m, 1H, 12-H). δ_{C} : 58.55 (OCH_3), 63.35 (CH_2), 71.38 (CH_2), 75.50 (13c-C), 107.91, 116.34, 116.47, 117.18, 123.94, 124.69, 125.77, 126.28, 127.91, 128.14, 130.74, 131.04, 131.99, 132.80, 133.54, 139.01, 151.40, 152.03, 197.46 (C = O). FAB-MS, m/z (%): 359 ($\text{M}^+ + 1$, 10), 358 (M^+ , 15), 299 ($\text{M}^+ - \text{CH}_2\text{CH}_2\text{OCH}_3$, 14), 283 ($\text{M}^+ - \text{OCH}_2\text{CH}_2\text{OCH}_3$, 100). Anal. $\text{C}_{23}\text{H}_{18}\text{O}_4$. Calcd: C, 77.08; H, 5.06. Found: C, 77.05; H, 5.19.

1-Oxo-13c-(2-ethoxy-ethoxy)-1, 13c-dihydro-dibenzo-[a, kl]-xanthene (11)

mp: 106—108°C. ν_{max} : 2867, 1703 (s, C = O), 1456, 1068, 808 cm^{-1} . δ_{H} : 0.97 (t, $J = 9.3$ Hz, 3H,

CH_3), 2.98—3.07 (m, 2H, CH_2), 3.20—3.24 (m, 2H, CH_2), 3.24—3.28 (m, 2H, CH_2), 6.25 (d, $J = 9.8$ Hz, 1H, 2-H), 7.03 (d, $J = 7.2$ Hz, 1H, 4-H), 7.07 (dd, $^3J = 8.3$ Hz, $^4J = 1.5$ Hz, 1H, 6 = H), 7.15 (d, $J = 9.8$ Hz, 1H, 3-H), 7.29 (d, $J = 9.0$ Hz, 1H, 9-H), 7.35 (dd, $J_{4\text{H}-5\text{H}} = 7.2$ Hz, $J_{5\text{H}-6\text{H}} = 8.3$ Hz, 1H, 5-H), 7.38—7.41 (m, 2H, 10-H, 13-H), 7.76—7.80 (m, 1H, 11-H), 7.86 (d, $J = 9.0$ Hz, 1H, 8-H), 8.14—8.17 (m, 1H, 12-H). δ_{C} : 15.03 (CH_3), 63.49 (CH_2), 66.07 (CH_2), 69.21 (CH_2), 75.45 (13c-C), 107.94, 116.38, 116.49, 117.20, 123.88, 124.65, 125.73, 126.26, 127.93, 128.13, 130.71, 131.04, 131.95, 132.83, 133.55, 138.98, 151.37, 152.04, 197.50 (C = O). FAB-MS, m/z (%): 372 (M^+ , 5), 299 ($\text{M}^+ - \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$, 16), 283 ($\text{M}^+ - \text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$, 100). Anal. $\text{C}_{24}\text{H}_{20}\text{O}_4$. Calcd: C, 77.40; H, 5.41. Found: C, 77.73; H, 5.18.

Acknowledgments

We thank Professor Chen, Xiao-Ming for the X-ray work and Professor Kang, Bei-Sheng for her helpful discussion.

CA Registry No. 1 [602-09-5], (\pm)-1 [41024-90-2], 2 [17915-83-2].

References

- (a) Rosini, C.; Franzini, L.; Raffaelli, A.; Salvadori, P. *Synthesis* **1992**, 503.
(b) Whitesell, J. *Chem. Rev.* **1989**, *89*, 1581.
(c) Narasaka, K. *Synthesis* **1991**, 1.
- Smrcina, M.; Lorenc, M.; Hanus, V.; Sedmera, P.; Kovcovsky, P. *J. Org. Chem.* **1992**, *57*, 1917.
- (a) Brussee, J.; Jansen, A. C. A., *Tetrahedron Lett.* **1983**, 3261.
(b) Brussee, J.; Groenendijk, J. L. G.; Koppele, J. M.; Jansen, A. C. A. *Tetrahedron* **1985**, *41*, 3313.
- Tietze, L. F. *Chem. Rev.*, **1996**, *96*, 115.
- Rieche, A.; Kirschke, K.; Schulz, M. *Liebigs Ann. Chem.* **1968**, 103.
- Schneider, H. P.; Streich, E.; Schurr, K.; Pauls, N.; Winter, W.; Rieker, A., *Chem. Ber.* **1984**, *117*, 2660.
- Feringa, B.; Wynberg, H. *Tetrahedron Lett.*, **1977**, 4447.
- Noji, M.; Nakajima, M.; Koga, K. *Tetrahedron Lett.* **1994**, 7983.
- Zhao, P.; Tan, D.; Xu, Z. *Zhongshan Daxue Xuebao (Nat. Sci. Edn.)*, **1998**, *37*, 131 (in Chinese).
- Toda, F.; Tanaka, K.; Iwata, S. *J. Org. Chem.* **1989**, *54*, 3007.

(E200002033 JIANG, X.H.; LING, J.)