

Autoxidation of Cycloalkenes by the System “Molecular Oxygen-bis(acetylacetonato) Cobalt (II) Complex-butyaldehyde”

Zhao Fang, Rui-ren Tang,* Rui-rong Zhang, and Ke-long Huang

School of Chemistry and Chemical Engineering, Central South University, Chang Sha, 410083, China

*E-mail: trr@mail.csu.edu.cn

Received March 6, 2009, Accepted August 6, 2009

Oxidation of cycloalkenes with O₂ promoted by heterogeneous bis(acetylacetonato) cobalt (II) complex catalyst which can be recycled has been performed under mild conditions. It was found that β-ionone, cyclohexene, 1-methylcyclohexene, and α-ionone were efficiently oxidized with O₂ in the presence of Co (II) complex and butyaldehyde at 55 °C. A simple treatment of the resulting products led to epoxides as predominant products and a small amounts of allylic oxides, the chemoselectivity for the former being 82.1 - 90.8% with a 70.6 - 98.6% substrate conversion. On the other hand, oxidation of 1-phenylcyclohexene, 1-cyclohex-1-enylethan-1-one, α-pinene, and β-pinene gave allylic oxides as major products.

Key Words: Epoxidation, Cycloalkenes, Acetylacetone cobalt (II), Molecular oxygen

Introduction

Epoxide compounds, due to their versatility as intermediates, are of great value in both synthetic organic chemistry and chemical technology. However, the homogeneous or heterogeneous catalytic epoxidation of alkenes other than ethene or cycloalkenes is very difficult due to the presence of labile allylic H atoms, which are easily oxidized to ketones or alcohols.¹

Recently, a series of new catalytic systems for the epoxidation of alkenes with molecular oxygen using metal complexes as manganese complex,²⁻⁶ copper complex,^{1,7-8} chromium complex,⁹ rare earth salts,¹⁰⁻¹² or cytochrome P450¹³⁻¹⁴ have been reported. Besides, some monooxygen transfer reagents, such as hydrogen peroxide¹⁵⁻¹⁸ or iodosylbenzene,¹⁹⁻²¹ were used as oxygen donors to accomplish the reaction. However, most of the reactions suffer from drawbacks, such as low conversions and selectivities, complicated work-up process, and the loss of catalyst.

It is notable that the conversion and epoxidation selectivity increase in similar catalytic systems when aldehyde was used as reductant.^{8,22-23} For example, in the presence of isobutyraldehyde the epoxidation of cyclohexene catalyzed by bis-2-acetoacetoxy-ethylmethacrylate copper for 24 h affords epoxycyclohexane with 99% selectivity and 84% conversion.⁸

On the other hand, epoxidation of alkenes in the presence of cobalt complexes has attracted much less attention,²⁴⁻²⁹ and the reported studies mainly focus on the oxidation of monoterpenes catalyzed by cobalt halides^{24,28} or a silica-supported cobalt complex.²⁵ In those catalytic systems, the defects of low conversion and selectivity still exists. For instance, CoCl₂ catalyzes the oxidation of α-pinene producing a wide variety of oxidation products with 50% conversion and 25% selectivity, and the molar ratio of allylic oxidation products and epoxides is *ca.* 1/1.²⁴

Chloromethylated polystyrene resin (CMPS) has a wide application. Benzyl chloride easily allows wide range of reactions such as ammonolysis, esterification, etherification, coup-

ling, *etc.* We report in the present paper the application of chloromethylated polystyrene resin grafted with bis(acetylacetonato) cobalt(II) complex combined with butyaldehyde as active and recyclable heterogeneous catalysts for the epoxidation of cycloalkenes by molecular oxygen and the effect of the structure of cycloalkenes on the ratio of allylic oxidation and epoxidation products.

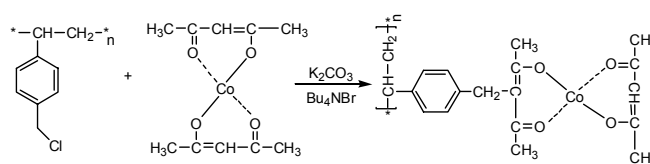
Result and Discussion

The bis(acetylacetonato) cobalt(II) complex catalyst (Co(acac)₂-CMPS) was synthesized by grafting of bis(acetylacetonato) cobalt(II) to CMPS (Scheme 1).

The IR spectrum of Co(acac)₂-CMPS shows C=C stretching vibration of acetylacetone structure at 1587 cm⁻¹ (conjugated to C=O). Strong peak at the 1464 cm⁻¹ is assigned to bending vibration of methyl, and the moderately strong peak at about 2922 cm⁻¹ is ascribed to stretching vibration of methylene bonded to benzene ring and acetylacetone structure. The intensity of C-Cl stretching vibration at 671 cm⁻¹ is obviously weakened (Fig. 1). The results indicate that bis(acetylacetonato) cobalt(II) has been grafted to CMPS.

The mass fractions of chlorine and cobalt elements were respectively determined by Volhard method³⁰ and ICP-AES (Table 1).

For complete grafting of bis(acetylacetonato) cobalt(II) to CMPS (where grafting ratio is 100%), the theoretical mass fraction of cobalt in the complex catalyst is 15.8%. Therefore, the actual grafting ratio is 55.7%. Likewise, a change in chlorine



Scheme 1

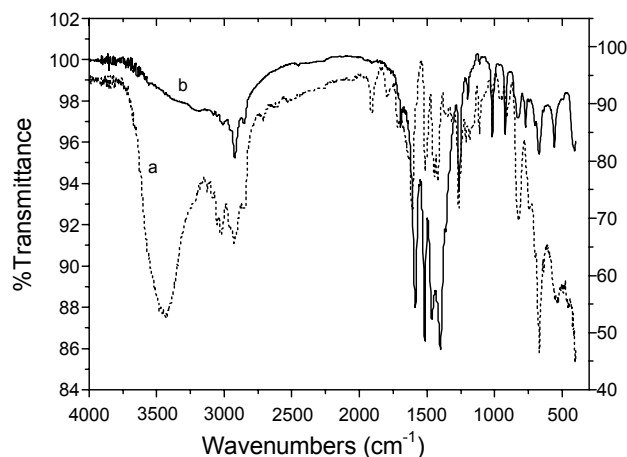
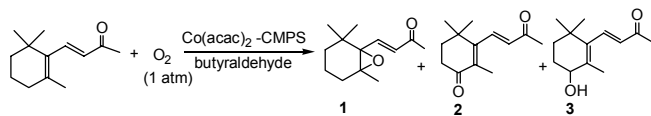


Figure 1. FT-IR patterns of CMPS (a) and Co(acac)₂-CMPS (b).

Table 1. Chlorine and cobalt analytical data for the CMPS and complex catalyst.

Compounds	Mass fractions (wt%)	
	Cl	Co
CMPS	21.4	0
Catalyst	9.3	8.8



Scheme 2

content provides evidence for the success of grafting reaction.

Aerobic oxidation of β -ionone, performed under reflux was chosen as model reaction. β -Ionone was oxidized in the presence of the above cobalt (II) catalyst and butyraldehyde to 5,6-epoxy-ionone (**1**) as a predominant product together with a small amount of oxoionone **2** and alcohol **3** (Scheme 2).

At first, the oxidation of β -ionone in acetone using homogeneous acetylacetone cobalt(II)-butyraldehyde catalytic system is studied, the results showed that the best conversion and selectivity of β -ionone were 80.4% and 78.9% respectively when 2 mol% of acetylacetone cobalt(II) and 180 mol% of butyraldehyde were employed at 55 °C under 1.01×10^5 Pa O₂.

Then, the Co(acac)₂-CMPS/butyraldehyde catalytic system was used in this oxidation process, and the results are presented in Table 2.

The results showed that β -ionone was oxidized to epoxide **1** with high selectivity (84%) with molecular oxygen without the catalyst Co(acac)₂-CMPS and butyraldehyde in acetone at 55 °C (Run 1), but the conversion remarkably increased from 24% to 69.7% and the selectivity maintained at high level by adding butyraldehyde (Run 3). Compared with Run 3 and Run 4-8, when the Co(acac)₂-CMPS was employed, the conversion markedly increased normally to more than 90%, and reached the highest level 96.5% with 2 mol% of the catalyst and 200 mol% of butyraldehyde. It is evident that without butyraldehyde the Co(acac)₂-CMPS increases conversion but

Table 2. Oxidation of β -ionone catalyzed by Co(acac)₂-CMPS combined with butyraldehyde.

Run	n(β -ionone): n(butyraldehyde): n (Catalyst)	Conv. (%)	Selectivity (%)		
			1	2	3
1	100:0:0	24.0	84.0	12.5	3.5
2	100:0:2	51.5	58.0	36.4	4.8
3	100:150:0	69.7	85.5	3.9	2.3
4	100:150:1	86.7	85.6	10.0	3.0
5	100:150:2	96.2	88.1	9.4	1.8
6	100:150:5	95.4	84.7	11.2	3.8
7	100:120:2	94.3	79.9	17.1	2.5
8	100:200:2	96.5	87.8	10.1	1.3

Conditions: β -ionone (0.02 mol), acetone (20 mL), 55 °C, O₂ (1.01×10^5 Pa), 6 h.

Table 3. The influence of the reaction time in the oxidation of β -ionone.

Time (h)	Conv. (%)	Yield (%)		
		1	2	3
2	48.7	43.3	4.1	1.0
4	79.5	70.4	7.2	1.6
6	96.2	84.8	9.1	1.7
8	96.8	84.4	8.8	2.0
10	97.0	82.9	8.0	1.6

Conditions: β -ionone (0.02 mol), acetone (20 mL), 55 °C, O₂ (1.01×10^5 Pa), butyraldehyde (150 mol%), catalyst (2 mol%).

decreases selectivity (Run 2). Runs 6 and 8 were uneconomical because of a large doses of the Co(acac)₂-CMPS or butyraldehyde, although both of them lead to high conversions and selectivities.

In summary, the Co(acac)₂-CMPS/butyraldehyde catalytic system could effectively catalyze the autoxidation of β -ionone. When 2 mol% of the catalyst and 150 mol% of butyraldehyde were employed at 55 °C under 1.01×10^5 Pa O₂ (Run 5), the optimal conversion (96.2%) and selectivity (88.1%) of epoxide **1** were obtained.

The influence of the reaction time for the oxidation of β -ionone, catalyzed by the Co(acac)₂-CMPS (2 mol%) and butyraldehyde (150 mol%), at 55 °C under 1.01×10^5 Pa O₂ in acetone is shown in Table 3.

The conversion gradually increased with time, but after 6 h it slowed down (96.2% at 6 h and 97.0% at 10 h). Both the yields of products **1** and **2** first increased and then decreased, and reached simultaneously maxima 84.8% and 9.1% at 6 h. The yields of alcohol **3** decreased analogously from 2.0% (at 8 h) to 1.6% (at 10 h).

We assume that the yields of products decreased due to the further oxidation of the primarily formed compounds. The predominance of product **1** indicates that the *endo* double bond of β -ionone is much more prone to epoxidation.

According to the commonly accepted mechanism of oxidation with molecular oxygen reported in literatures,^{22,31} we put forward a possible reaction mechanism in the Co(acac)₂-CMPS/

butyraldehyde system, taking β -ionone as an example (Fig. 2).

Butyraldehyde, by the action of $\text{Co}(\text{acac})_2$ -CMPS and O_2

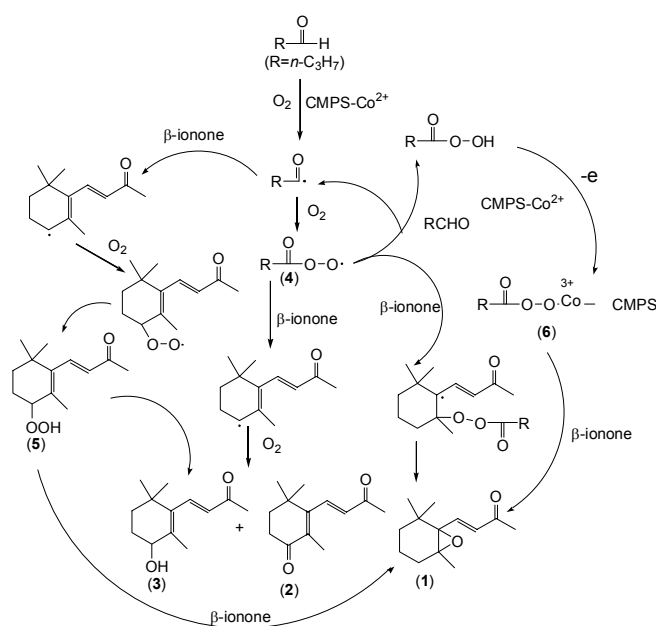


Figure 2. Reaction mechanism for autoxidation of β -ionone.

formed acylperoxy radical **4**, which could react with β -ionone by two different pathways. Radical addition to the *endo* double bond of β -ionone could give epoxide **1**; at the same time, β -ionone could also give products **2** and **3** by radical substitution of allylic H atom and oxidation with O_2 . The results discussed above suggested that the radical addition pathway is preferred to the radical substitution pathway under the conditions of our experiments. Hydroperoxide **5** could also give epoxide **1** by oxidation of the *endo* double bond of β -ionone and give products **2** and **3** by decomposition. By another pathway, butyric acid reacted with the $\text{Co}(\text{acac})_2$ -CMPS to form the cobalt-peroxy complex **6**, then oxidized directly β -ionone to give the main product **1**.

The Recycling test showed that the catalyst $\text{Co}(\text{acac})_2$ -CMPS can be used repeatedly with the neglected loss of active site, the conversion of β -ionone was 92.4%, the selectivity of epoxide kept stabilization in the third experiment.

On the basis of the results above, several other substrates were oxidized under the general conditions to give corresponding epoxides and allylic oxides resulting from oxidations of the double bond and allylic C-H bonds of cycloalkenes respectively (Table 4).

In the epoxidation reaction of cyclohexene (**7**), 1-methylcyclohexene (**8**), and α -ionone (**9**), excellent conversions ranging from 70.6% to 98.6% and selectivities for epoxides (**7a**,

Table 4. Oxidation of different cycloalkenes by $\text{Co}(\text{II})$ complex/butyraldehyde.

Run	Substrate	Product		Time (h)	Conversion (%)	Selectivity (%)	
		Epoxide	Allylic oxide			a	b
1				4	98.6	90.8	1.2
2				6	90.3	82.5	7.81
3				8	70.6	82.1	4.8
4				8	31.1	11.1	61.8
5				8	18.4	9.1	53.2
6				8	64.7	34.0	46.7
7				8	55	9	33

Conditions: substrates 0.02 mol, butyraldehyde 0.03 mol, catalyst 2 mol%, O_2 (1.01×10^5 Pa), acetone 20 mL, 55 °C.

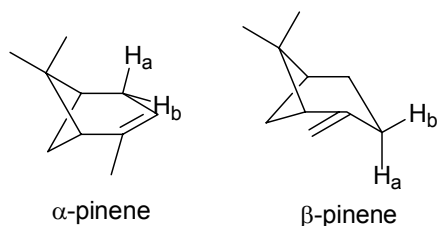


Figure 3. Conformational structures of α -pinene and β -pinene.

8a, 9a) from 82.1% to 90.8% were obtained. However, it is noteworthy that the oxidation of 1-cyclohex-1-enylethan-1-one (**10**) and 1-phenylcyclohex-1-ene (**11**) obtained relatively good allylic oxidation selectivities, 61.8% and 53.2%, respectively.

It can be seen from Fig. 2, the epoxidation of alkenes using the Co(acac)₂-CMPS/butyraldehyde system involves a radical addition. Therefore, steric hindrance in position of double bond played important roles in the reaction conversion and selectivity. The larger steric hindrance, the lower conversions and selectivities of epoxides were obtained (Runs 1~5 in Table 4). Especially, the oxidation of 1-cyclohex-1-enylethan-1-one (**10**) and 1-phenylcyclohexene (**11**) gave a low epoxidation selectivities with 11.1% and 9.1% but relatively good allylic oxidation selectivities due to the exist of acetyl and phenyl in position of double bond.

For the oxidation of monoterpenes, the results showed that oxidation of α -pinene (**12**) obtained similar epoxidation and allylic oxidation selectivities, but the oxidation of β -pinene (**13**) gave allylic oxidation product as the main product with 33% selectivities.

Reference to literature 24, we could explain it based on the structure of α -pinene and β -pinene (Fig. 3). The molecule of α -pinene is a rigid structure in which the four-membered ring is puckered and five carbons of the six-membered ring (including olefinic carbons) are approximately in the same plane, with two secondary allylic hydrogens (H_a and H_b) being at *ca.* 45° angle to this plane. Thus, orbital overlapping decreased the additional stabilization and hindered the form of allylic radical. On the other hand, β -pinene preferably adopts a pseudo-chair conformation, in which allylic hydrogen H_a is approximately orthogonal to the double bond and would be the best candidate for abstraction. So, The favorable for π -p interaction structure of the allylic radical formed from β -pinene makes the allylic oxidation become a major reaction.

In summary, a novel heterogeneous catalyst, chloromethylated polystyrene resin grafted with bis(acetylacetonato) cobalt(II) complex was synthesized and structurally characterized by ICP-AES and FT-IR. The catalyst Co(acac)₂-CMPS showed a reasonable catalytic activity and selectivity under mild conditions and proved to be recyclable for the oxidation with molecular oxygen. The selective heterogeneous oxidation of cycloalkenes leading to epoxide derivatives has been developed.

Experiments

Unless otherwise specified, all reagents were purchased from commercial suppliers and were used without purification. Gas chromatography (GC) analysis was performed in a 0.2

mm \times 30 m capillary column (HP-Ultra2). Infrared (IR) spectra were measured on Avatar-360-FT machine with KBr pellets. Gas chromatography-mass spectra (GC-MS) were obtained on an Agilent 6890 - 5973. LC-MS experiments were carried out on a shimadzu instrument 2010 EV. ¹H NMR was performed on an Inova - 400 MHz NMR instrument with CD₃Cl as solvent and tetramethylsilane (TMS) as the internal standard. The selectivity of products was estimated from the peak areas by the internal standard technique using GC and the structure of products was characterized from the mass spectrogram in GC-MS, LC-MS and ¹H NMR.

Content of cobalt(II) was determined by a Baird Plasma Spectrovac PS-6(N+1) type ICP-AES spectrometer, with a grating of 3600 grooves/mm and a 40.68 MHz RF generator. Chlorine content was determined by a improved Volhard method,³⁰ samples (CMPS and complex catalyst) were weighed accurately, then uniformly enwrapped with anhydrous sodium carbonate, were heated in a muffle furnace in air at 600 °C to constant weight and then dissolved in distilled water and filtrated.

Catalyst preparation. CMPS (1.2 g) was placed in a three-necked flask and swollen for 2 h in 1,2-dichloroethane at 60 °C, then Co(acac)₂·2H₂O (2.3 g), K₂CO₃ (1.0 g), Bu₄NBr (0.2 g) were added to the solution, and the mixture was stirred at reflux temperature for 8 h. After the reaction mixture was filtered, the crude solid product was thoroughly washed with distilled water and anhydrous ethanol respectively, and dried in a vacuum (< 133 pa) at 50 °C to yield 2.5 g of powdery product.

General procedure of autoxidation of cycloolefins. To a solution of cycloalkenes (0.02 mol) in acetone (20 mL) in a three-necked flask equipped with reflux condenser was added complex catalyst (2 mol%) and butyraldehyde (0.03 mol). The mixture was heated to 55 °C and stirred for 4 - 8 h under O₂ (1.01 \times 10⁵ Pa). The progress of the reaction was monitored by thin-layer chromatography (TLC). After the reaction completed, the reaction mixture was filtrated and removed the solvent under reduced pressure, and the enriched material purified by column chromatography on silica gel (n-hexane/AcOEt = 4 : 1) to give the corresponding products.

Characterization of oxidated products. Oxidated products **1**, **2**, **7a**, **7b**, **8a**, **8b**, **9a**, **9b**, **11a**, **11b**, **12a**, **12b**, **13a** and **13b** were identified by ¹H NMR and MS, and **3**, **10a**, **10b** were identified by MS in GC-MS.

1: ¹H NMR δ 0.94 (s, 6H), 1.15 (s, 3H), 2.28 (s, 1H), 7.05 (m, 1H, *J* = 16.0 Hz), 6.30 (d, 1H, *J* = 16.0 Hz), 1.30-1.60 (m, 4H), 1.70-1.93 (m, 2H); MS *m/z* (%) 208 (M⁺, 1), 135 (11.2), 124 (9.4), 123 (100), 107 (6.3), 79 (6.4), 55 (6.9), 43 (57.5).

2: ¹H NMR δ 1.14 (s, 6H), 1.80-1.83 (t, 2H, *J* = 7.0 Hz), 2.49 (t, 2H, *J* = 7.0 Hz), 1.68 (d, 3H, *J* = 1.0 Hz), 7.26-7.30 (q, 1H, *J*1 = 16.8 Hz, *J*2 = 1.0 Hz), 6.11-6.15 (d, 1H, *J* = 16.8 Hz), 2.32 (s, 3H); MS *m/z* (%) 206 (M⁺, 72), 163 (100), 149 (20), 135 (25), 121 (47).

3: MS *m/z* (%) 208 (M⁺, 1), 164 (53), 43 (93), 149 (66), 123 (100).

7a: ¹H NMR δ 0.89-1.05 (m, 4H), 1.45-1.58 (m, 4H), 3.1 (s, 2H); MS *m/z* (%) 98 (M⁺, 16.1), 83 (100), 57 (41), 54 (58.4), 42 (79), 41 (88), 39 (49), 27 (33).

7b: ¹H NMR δ 7.03 (d, 1H, *J* = 10.3 Hz), 6 (d, 1H, *J* = 10.3

Hz), 2.4 (m, 4H), 2 (m, 2H); MS m/z (%) 96 (M^+ , 29), 68 (100), 55 (6), 42 (8.3), 41 (6.9), 40 (19.6), 39 (19), 27 (7.6).

8a: ^1H NMR δ 2.87(br s, 1H), 1.82-1.78 (m, 2H), 1.59 (m, 2H), 1.36-1.31(m, 4H), 1.22 (s, 3H); MS m/z (%) 112 (M^+ , 2), 111 (5), 97 (100), 83 (10), 69 (25), 55 (41), 43 (84).

8b: ^1H NMR δ 1.95 (d, 3H), 1.5-2.5 (m, 4H), 2.98(t, 2H), 5.80 (b s, 1H); MS m/z (%): 110 (M^+ , 37.6), 82 (100), 54 (31), 39(29), 27(9), 41(8.8), 83(6), 55(4).

9a: ^1H NMR δ 0.96 (s, 6H), 1.30 (s, 3H), 2.30 (s, 3H), 7.13 (m, 1H, $J = 16.0$ Hz), 6.33 (d, 1H, $J = 16.0$ Hz), 1.24-1.49 (m, 4H), 2.76 (s, 1H), 2.25 (s, 1H); MS m/z (%) 208 (M^+ , 1), 179 (33.1), 165 (24.0), 151 (26.0), 123 (24.5), 111 (44.2), 109 (100), 107 (21.6), 95 (65.5), 69 (22.5), 55 (25.2).

9b: ^1H NMR δ 1.09-1.11 (s, 6H), 1.91 (s, 3H), 2.15 (d, 1H, $J = 16.8$ Hz), 2.37 (d, 1H, $J = 16.8$ Hz), 2.29 (s, 3H), 2.73 (d, 1H, $J = 9.6$ Hz), 5.99 (s, 1H), 6.20 (m, 1H, $J = 15.6$ Hz), 6.69 (q, 1H, $J_1 = 9.6$ Hz, $J_2 = 16.8$ Hz); MS m/z (%) 206 (M^+ , 1), 191 (1), 163 (1), 150 (23), 135 (6), 121 (3), 108 (100), 91 (5), 77 (10), 65 (2).

10a: MS m/z (%) 140 (M^+ , 4), 97 (18), 69 (25.6), 55 (24), 43 (100), 41 (61), 39 (32.6).

10b: MS m/z (%) 138 (M^+ , 28), 110 (100), 82 (79), 68 (64), 67 (51), 41 (35), 43 (19), 95 (11), 27 (7).

11a: ^1H NMR δ 1.26-1.59 (m, 4H), 1.95-2.00 (m, 2H), 2.12-2.13 (m, 1H), 2.23-2.27 (m, 1H), 3.06 (s, 1H), 7.08-7.38 (m, 5H); MS m/z (%) 174 (M^+ , 10), 145 (16.3), 98 (21), 89 (56), 85 (12), 71 (100), 69 (17.5), 56 (26), 55 (21), 43 (36), 41 (20).

11b: ^1H NMR δ 2.1-2.2 (m, 2H), 2.48-2.52 (t, 2H, $J = 6.6$ Hz), 2.76-2.81 (td, 2H, $J_1 = J_2 = 6.0$ Hz, $J_3 = J_4 = J_5 = 1.5$ Hz), 6.43-6.44 (t, 1H, $J = 1.5$ Hz), 7.41-7.43 (m, 2H), 7.44-7.48 (dd, 1H, $J_1 = 7.5$ Hz, $J_2 = 6.6$ Hz, $J_3 = 4.5$ Hz, $J_4 = 3.3$ Hz), 7.53-7.56 (m, 2H); MS m/z (%) 172 (M^+ , 63), 144 (100), 128 (11), 116 (51), 115 (77), 102 (8), 77 (7).

12a: ^1H NMR δ 0.91 (s, 6H), 1.19-1.58 (m, 9H), 1.34-1.94 (m, 6H), 2.61 (m, 1H); MS m/z (%) 152 (7.9), 119 (39.6), 108 (100), 93 (68.4), 83 (39), 67 (48.1), 55 (45.1), 41 (51.7), 27 (15.7).

12b: ^1H NMR δ 1.014 (s, 3H), 1.499 (s, 3H), 2.017-2.023 (d, 3 H, $J = 1.8$ Hz), 2.399-2.442 (td, 1H, $J_1 = J_2 = 6.6$ Hz, $J_3 = J_4 = J_5 = 1.2$ Hz), 2.632-2.677 (td, 1H, $J_1 = J_2 = 6.3$ Hz, $J_3 = J_4 = J_5 = 1.8$ Hz), 2.775-2.815 (t, 1H, $J = 5.4$ Hz), 2.805-2.842 (t, 1H, $J = 5.4$ Hz), 5.730-5.745 (dd, 1H, $J_1 = 3$ Hz, $J_2 = J_3 = 1.5$ Hz); MS m/z (%) 150 (M^+ , 48), 135 (79), 122 (17), 107 (100), 95 (13), 91 (59), 79 (36), 67 (15).

13a: ^1H NMR δ 0.91 (s, 6H, 2CH₃), 1.21-1.71 (m, 8H), 2.24-2.49 (m, 2H, OCH₂); MS m/z (%) 152 (M^+ , 1), 137 (41.4), 123(51.6), 109(60.3), 79(100), 71(92), 67(58), 43(44), 41(94), 39(42.9), 27(39).

13b: ^1H NMR δ 0.91 (s, 6H, 2CH₃), 1.61-2.29 (m, 4H), 2.51-3.05(m, 2H, O=CCH₂), 4.99 (d, 2H, $J = 4.2$ Hz, =CH₂); MS m/z (%) 152 (M^+ , 1), 150(30), 108(76), 107(39.8), 81 (100), 79(33.5), 69(42.4), 53(97), 41(67.3), 39(32), 27(30.7).

Acknowledgments. We gratefully acknowledge financial support of this work by the China Postdoctoral Science Foundation (NO. 20080431027) and the Postdoctoral Science Foundation of Central South University.

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