Design, synthesis, and characterization of a series of novel $\beta$-cyclodextrin functional monomers

Zhimin Liu$^{1,2}$, Zhigang Xu$^2$ and Liping Ma$^1$

Abstract
In order to increase its solubility in water and improve $\beta$-cyclodextrin combination with guest molecules, chemical modification of $\beta$-cyclodextrin is a feasible and effective method. A variety of $\beta$-cyclodextrin derivatives are designed and introduced for pharmaceutical complexation and analytical chemistry application. In this study, a series of $\beta$-cyclodextrin derivatives containing unsaturated bonds is designed and synthesized. The products are characterized by MS, FTIR, $^1$H NMR, and $^{13}$C NMR. Some of the functional monomers may be used in the preparation of molecularly imprinted polymers, and preliminary studies have shown excellent molecular recognition ability. The prepared $\beta$-cyclodextrin functional monomers have potential application value in molecular recognition materials based on polymers.

Keywords
$\beta$-cyclodextrin, cyclodextrin derivatives, functional monomers, monosubstituted, polymers

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Design and synthesis 12 novel $\beta$-cyclodextrin functional monomers

Corresponding authors:
Zhigang Xu, Faculty of Science, Kunming University of Science and Technology, Kunming 650500, P.R. China.
Email: xuzgkmust@gmail.com

Liping Ma, Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, P.R. China.
Email: lpma2522@hotmail.com

1Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming, P.R. China
2Faculty of Science, Kunming University of Science and Technology, Kunming, P.R. China
Introduction

β-Cyclodextrin (β-CD) is a cyclic oligosaccharide composed of seven glucopyranose units attached by α-1,4 glucosidic bonds and has an interesting structure with a conical cavity.1–2 β-CD can achieve supramolecular assemblies with small lipophilic molecules because of its inherent properties, the outer region is hydrophilic while the inner is hydrophobic. Hence, β-CD can be applied in many areas, such as molecular recognition, catalysis, chromatographic separation, solubilization, drug release, and biotechnology.1–5 However, the solubility of β-CD in water is relatively low, it cannot be dissolved in most organic solvents, and its molecular recognition ability is also poor. Modified β-CDs have functional groups on their surfaces, and their molecular recognition ability can be increased by introducing various groups.5–8 For example, some hydrophobic drugs with appropriate size and shape can enter into the cavity to form noncovalent supramolecular complexes. The formation of these complexes not only enhances their aqueous solubility but also improves their general stability in some cases.

In the past few decades, the synthesis of modified β-CD derivatives has attracted wide attention due to their unique properties.2 On the one hand, β-CD derivatives have been used as functional monomers in the synthesis of molecularly imprinted polymers in order to improve the recognition ability of the imprinted derivatives and increase their solubility in water.7–11 On the other hand, β-CD derivatives have been used as chiral solid phases to separate chiral compounds,12–17 especially those containing unsaturated double bonds.19–21 In this paper, the 12 β-CD derivatives shown in Figure 1 were designed and synthesized. Mono-(6-O-p-tolylsulfonyl)-β-CD was used as an important intermediate in this study and was synthesized by the reaction of β-CD with toluene p-sulfonyl chloride in NaOH solution.22 In addition, this intermediate also could be obtained by using toluene p-sulfonyl anhydride reacting with β-CD in NaOH solution24,25 or by toluene p-sulfonyl chloride reacting with β-CD in dry pyridine.26 The products are characterized by MS, IR, 1H NMR, and 13C NMR. Partially synthetic novel β-CD derivatives have been used as monomers to prepare interesting molecularly imprinted polymers.27–29

Results and discussion

These interesting functional monomers may be utilized to construct unique molecularly imprinted polymers easily. Compounds 1 and 2 were prepared in one step by directly reacting an acid chloride with β-CD. Compounds 3, 4, 5, and 6 were prepared by reaction of mono-(6-O-tolyl p-sulfonyl)-β-CD, which has been synthesized first by our group (Scheme 1). Compounds 7, 8, 9, 10, 11, and 12 were prepared by reactions of mono-6-deoxy-6-ethylendiamine-β-CD, which had also been synthesized first by us (Scheme 2). The optimization of the preparation of product 2 is presented in Table 1. The results show the best molar ratio of β-CD to p-vinylbenzene sulfonyl chloride is 1:0.75, the optimum reaction temperature is 5 °C, and the reaction time is 4 h.

Conclusion

A series of novel β-CD derivatives has been designed and synthesized, members of which contain unsaturated double bonds, with some products having three unsaturated double bonds. The products have different functional groups and should be more active toward polymerization. The structures of all products were confirmed by MS, IR, 1H NMR, and 13C NMR analysis. These β-CD derivatives are useful and interesting monomers for the preparation of molecularly imprinted polymers and other functional materials.

Experimental section

Reagents and instruments

Allylamine (99%), diallylamine (98%), acryloyl chloride (98%), mono-propargylamine (98%), D- penicillamine (99%), allyl glycidyl ether (99%), 10-undecylenol chloride (99%), and methacryloyl chloride (99%) were purchased from Xiya Reagent Co. Ltd. (Shan Dong, China). 1,2-Epoxy-5-hexene (≥96.0) was purchased from Tokyo Chemical Industry Co., Ltd. and 1,2-hydroxy-7-octene (97%) was purchased from Thermo Fisher Scientific Co., Ltd. (China). β-Cyclodextrin (β-CD) was purchased from Shandong Binzhou Zhiyuan Bio-Technology Co., Ltd. (Binzhou, China). A FA2004 type electronic balance (Shanghai Hengping Scientific Instrument Ltd.) and XMTD-204 digital thermostat water bath equipment (Jiangsu Jintan Huacheng Kaiyuan Experimental Instrument Factory) were used in the experiments. An EQUINOX 55 Fourier transform infrared spectrometer (German Bruker Optics Company) and an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (Agilent Technologies Inc) were used for product characterization. NMR spectra were obtained on a Bruker AV-600 MHz nuclear magnetic resonance spectroscopy, using DMSO-d_6 or D_2O as solvents. The chemical shifts (δ) are given in ppm relative to the TMS signal at 0.00 ppm as an internal reference, coupling constants (J) are given in Hertz (Hz).

Synthesis of mono-(6-O-acryloyl-6-deoxy)-β-CD (1)

β-CD (7.9 g, 7.0 mmol) was added to a 500 mL round-bottomed flask. Next, NaOH (4.3 g, 0.11 mol) and distilled water 250 mL were added. After the solids had dissolved, the flask was placed in an ice-water bath (1.5 °C). Acryloyl chloride 10 mL was added to the flask by using a constant-voltage funnel. After stirring for 30 min, the solution was filtered and dried under reduced pressure at 40 °C. Then crude product was dissolved in N,N-dimethylformamide 20 mL, and the solution filtered to remove sodium chloride. Acetone 200 mL was added and the product precipitated
and was collected. It was dissolved in methanol 20 mL and acetone 200 mL was added and the precipitate collected. The resulting product was dried under reduced pressure at 40 °C for 5 h.

Off white powder (yield 63%); m.p. 280–283 °C. The molecular weight of compound 1 is 1189.3803, with the found mass-charge ratio of 1157.3579 corresponding to [M – acryloyl + Na]+. The FTIR spectrum of the compound revealed vibration bands at \( \nu_{\text{max}} \) cm\(^{-1}\) 3418, 2935, 1719, 1638, 1514, 1441, 1300, 1030, and 867; \(^1\)H NMR (600 MHz, D\(_2\)O): \( \delta \) 5.64 (s, 1H), 5.33 (s, 1H), 5.06 (s, 1H), 3.88 (m, 3H), 3.68 – 3.49 (m, 2H), 1.85 (s, 3H), 1.67 (s, 1H), 1.45 (s, 1H), 1.31 (s, 1H), 1.04 (d, \( J = 6.8 \) Hz, 1H); \(^{13}\)C NMR (151 MHz, D\(_2\)O): \( \delta \) 177.53, 142.21, 122.03, 120.57, 101.93, 81.06, 76.20, 75.07, 72.92, 72.03, 60.28, 45.99, 28.55, 25.21, 24.05, 19.02, 17.59.

**Figure 1.** The structures of the 12 target compounds.

**Synthesis of mono-(6-O-p-vinylbenzene sulfonyl-6-deoxy)-β-CD (2)**

β-CD (22.7 g, 20 mmol) was added to a 250 mL three-necked flask. Next, NaOH (4 g, 0.1 mol) and distilled water 200 mL were added. After the solids had dissolved, the flask was placed in an ice-water bath (1.5 °C). Then p-vinylbenzene sulfonyl chloride (2.9 g, 15 mmol) was dissolved in acetonitrile 8 mL and added to the flask by a constant-voltage funnel. After stirring for 4 h, the pH of solution was adjusted to 1.5 with 1 mol/L HCl and the flask
was placed in a refrigerator at 4 °C for overnight. Then the solution was filtered and recrystallized. The obtained product was dried under reduced pressure for 5 h at 55 °C.

White powder (yield 37%); m.p. 230–233 °C. The molecular weight of compound 2 is 1323.3677, with the found mass-charge ratio of 1324.3762 corresponding to [M + Na]+. The FTIR spectrum of the compound revealed vibration bands at ν max cm⁻¹ 3417, 2923, 1637, 1417, 1367, 1193, 1177, 1157, 1079, 1029, 937, 836, 757, 663, and 578; 1H NMR (600 MHz, DMSO-d₆): δ 7.84 (d, J = 8.1 Hz, 2H, Ph-H), 7.70 (d, J = 8.1 Hz, 2H, Ph-H), 6.83 (dd, J = 17.5, 11.0 Hz, 1H, -CH=CH₂), 6.05 (d, J = 18.0 Hz, 1H, -CH=CH₂), 5.51 (d, J = 10.9 Hz, 1H, -CH=CH₂), 4.82 (d, J = 8.9 Hz, 5H), 4.75 (d, J = 2.8 Hz, 2H), 4.35 (d, J = 10.1 Hz, 1H, -CH₂), 4.23 – 4.18 (m, 1H, -CH₂); 13C NMR (151 MHz, DMSO-d₆): δ 143.04, 135.52, 134.69, 128.55, 127.39, 119.27, 102.69, 102.41, 82.12, 81.97, 81.75, 81.29, 73.50, 73.33, 73.21, 72.85, 72.50, 72.32, 69.37, 60.33, 60.01, 59.76.

Synthesis of mono-(6-N-allylamino-6-deoxy)-β-CD (3)
The mono-(6-N-allylamino-6-deoxy)-β-CD (3) was obtained after optimization of the synthetic conditions based on the literature. The reaction solvent was allylamine, and the ratio of reactants was 1:225. The reaction time was 4.5 h, while the reaction temperature was 60...
The FTIR spectrum of the compound revealed vibration bands at $\nu_{\text{max}}$ cm$^{-1}$ 3385, 2926, 1645, 1419, 1370, 1298, 1215, 1157, 1079, and 1029; $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 5.74 (s, 1H), 5.69 (d, $J = 6.5$ Hz, 3H), 5.66 (s, 1H), 5.04 (d, $J = 17.1$ Hz, 1H, -CH=CH2), 4.99 (d, $J = 10.3$ Hz, 1H, -CH=CH2), 4.75 (s, 4H), 4.44 (d, $J = 2.5$ Hz, 2H), 3.54 (d, $J = 8.8$ Hz, 8H), 3.47 (d, $J = 9.3$ Hz, 5H), 3.22 (s, 5H), 2.42 (s, 2H, -CH$_2$N); $^{13}$C NMR (151 MHz, DMSO-$d_6$): $\delta$ 143.55, 138.53, 133.02, 130.36, 128.66, 128.04, 127.05, 125.93, 102.64, 102.36, 101.67, 82.61, 81.92, 81.52, 81.11, 73.49, 73.12, 72.80, 72.45, 70.20, 69.34, 60.33, 59.92, 59.64, 21.67, 21.28.

**Synthesis of mono-$(6\text{-N-propargyl-6-deoxy})\beta$-CD (5)**

Compound 5 was synthesized with a method similar to that used for compound 3. The reaction solvent was propargylamine. The ratio of reactants of synthesis compound 5 was 5:1. The reaction time was 5 h, and the reaction temperature was 85 °C. After the reaction, the solution was collected and cooled to room temperature. Then methanol 10 mL was added to dilute this solution, and acetonitrile 100 mL was also added. Then the solution was filtered and the white solid was collected. The purification process was repeated until the filtrate was colorless. The resulting product was obtained after optimization and dried under reduced pressure at 50 °C.

White powder (yield 84%); m.p. 290–291 °C. The molecular weight of compound 5 is 1172.4048. The mass-charge ratio of 1172.4087 corresponded to $[\text{M} + \text{H}]^+$. The FTIR spectra of the compound revealed vibration bands at $\nu_{\text{max}}$ cm$^{-1}$ 3383, 2927, 1643, 1417, 1371, 1245, 1156, 1080, and 1031; $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 5.81 – 5.61 (m, 2H), 4.75 (s, 1H, -CH$_2$N), 4.44 (dd, $J = 13.9, 5.6$ Hz, 1H), 3.59 – 3.52 (m, 2H), 3.55 (d, $J = 9.8$ Hz, 2H), 3.48 (d, $J = 9.6$ Hz, 1H), 3.48 (d, $J = 9.6$ Hz, 2H), 3.23 (s, 1H), 3.07 (d, $J = 4.8$ Hz, 1H), 2.43 (s, 1H, -CH$_2$N), 2.43 (s, 1H, -CH$_2$N); $^{13}$C NMR (151 MHz, DMSO-$d_6$): $\delta$ 137.63, 128.63, 125.94, 115.97, 102.65, 102.39, 102.24, 84.24, 81.94, 81.63, 73.47, 72.80, 72.44, 70.58, 60.32, 51.93, 49.33.
the product precipitated and was collected. The purification process was repeated twice. The product was dissolved in water 3 mL and methanol 10 mL was added. Finally, aceticone 100 mL was added and the precipitate was collected. The obtained product was dried at 45 °C for 5 h.

White powder (yield 84%); m.p. 242–245 °C. The molecular weight of compound 6 is 1265.4102, with the found mass-charge ratio of 1245.4575, with the found mass-charge ratio of 1265.4188 corresponding to [M+H]+. The FTIR spectrum of the compound revealed vibration bands at $\nu_{\text{max}}$ cm$^{-1}$ 3419, 2928, 1642, 1393, 1032, and 579; $^1$H NMR (600 MHz, D2O): $\delta$ 7.90 (s, 1H), 4.94 (s, 1H, -OH), 4.79 (s, 7H), 3.60 (s, 18H), 3.53 (s, 9H), 2.85 (s, 1H), 2.69 (s, 1H), 2.46 (s, 3H), 2.04 (s, 3H), 1.37 (s, 3H, -S-C-CH3), 1.27 (s, 1H), 1.14 (s, 3H); $^{13}$C NMR (151 MHz, DMSO-\(d_6\)): $\delta$ 145.32, 133.08, 130.37, 128.07, 102.68, 102.39, 101.72, 82.09, 81.94, 81.58, 81.17, 73.51, 73.16, 72.86, 72.49, 72.30, 70.19, 69.35, 60.34, 59.94, 59.68, 21.68.

**Synthesis of mono-(6-ethylenediamine-(N-acryloyl)-6-deoxy)-\(\beta\)-CD (7) and mono-(6-ethylenediamine-(N-methacryloyl)-6-deoxy)-\(\beta\)-CD (8)**

Compounds 7 and 8 were synthesized as follows. Mono-(6-ethylenediamine-6-deoxy)-\(\beta\)-CD (4 g, 3 mmol) was added to a 250 mL three-necked flask. Next, NaOH (4 g, 0.1 mol) and distilled water 200 mL were added. After the solids had dissolved, the flask was placed in an ice-water bath (–1.5 °C). Acryloyl chloride (2.8 g, 0.0306 mol; or 3.2 g methacryloyl chloride) was added to the flask by a constant-voltage funnel. After stirring for 2 h, the flask was placed in a refrigerator at 4 °C for overnight. The solution was filtered and precipitated by acetone 20 mL. The methanol solution was precipitated and was collected. The purification process was repeated twice again. The obtained product was dried under reduced pressure at 45 °C. Then the crude product was dissolved in N,N-dimethylformamide 20 mL. The solution was filtered to remove sodium chloride. After that, ether 100 mL was added. The DMF collected and acetone 100 mL was added. The product was precipitated and was collected. Then it was dissolved in 70 °C water 10 mL. Ether 100 mL was added and the water phase was collected. Next, acetone 100 mL was added and the precipitate collected. The purification process was repeated twice. The product was dissolved in methanol 10 mL and placed in a water bath at 70 °C. Finally, acetone 100 mL was added at room temperature and the precipitate collected. This purification process was repeated twice again. The obtained product was dried at 45 °C for 7 h.

Compounds 9 and 10 were synthesized as follows. Mono-(6-ethylenediamine-6-deoxy)-\(\beta\)-CD (3.5 g, 3 mmol) and 0.1 mol/L sodium bicarbonate 40 mL were added to a 250 mL single neck round-bottom flask. And 1,2-epoxy-5-hexene (1.8 g, 17.88 mmol; or 2.3 g 1,2-hydrorxido-7-octene) was added. Then the flask with a reflux condenser was placed in a water bath at 70 °C. After 10 h, the pH of the solution was adjusted to 7 with 1 mol/L HCl. The solution was dried under reduced pressure at 45 °C. Then the crude product was dissolved in N,N-dimethylformamide 20 mL. The solution was filtered to remove sodium chloride. After that, ether 100 mL was added. The DMF collected and acetone 100 mL was added. The product was precipitated and was collected. Then it was dissolved in 70 °C water 10 mL. Ether 100 mL was added and the water phase was collected. Next, acetone 100 mL was added and the precipitate collected. The purification process was repeated twice. The product was dissolved in methanol 10 mL and placed in a water bath at 70 °C. Finally, acetone 100 mL was added at room temperature and the precipitate collected. This purification process was repeated twice again. The obtained product was dried at 45 °C for 7 h.

**Synthesis of mono-(6-N-ethylenediamine\((N-(2-bis(2-hydroxy-5-hexene)) \cdot (N-(2-hydroxy-7-hexene)) \cdot (6-deoxy) \cdot \beta\)-CD (9) and mono-(6-N-ethylenediamine\((N-(2-bis(2-hydroxy-7-octene)) \cdot (N-(2-hydroxy-7-octene)) \cdot (6-deoxy) \cdot \beta\)-CD (10)**

Compounds 9 and 10 were synthesized as follows. Mono-(6-ethylenediamine-6-deoxy)-\(\beta\)-CD (3.5 g, 3 mmol) and 0.1 mol/L sodium bicarbonate 40 mL were added to a 250 mL single neck round-bottom flask. And 1,2-epoxy-5-hexene (1.8 g, 17.88 mmol; or 2.3 g 1,2-hydrorxido-7-octene) was added. Then the flask with a reflux condenser was placed in a water bath at 70 °C. After 10 h, the pH of the solution was adjusted to 7 with 1 mol/L HCl. The solution was dried under reduced pressure at 45 °C. Then the crude product was dissolved in N,N-dimethylformamide 20 mL. The solution was filtered to remove sodium chloride. After that, ether 100 mL was added. The DMF collected and acetone 100 mL was added. The product was precipitated and was collected. Then it was dissolved in 70 °C water 10 mL. Ether 100 mL was added and the water phase was collected. Next, acetone 100 mL was added and the precipitate collected. The purification process was repeated twice. The product was dissolved in methanol 10 mL and placed in a water bath at 70 °C. Finally, acetone 100 mL was added at room temperature and the precipitate collected. This purification process was repeated twice again. The obtained product was dried at 45 °C for 7 h.
vibration bands at $\nu_{max}$ cm$^{-1}$: 3384, 2925, 2854, 1645, 1421, 1365, 1340, 1249, 1155, 1082, and 1029; $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 6.02 (s, 1H), 5.71 (m, 2H), 5.00–4.85 (m, 1H, -OH), 4.76 (s, 1H, -CH=CH$_2$), 4.71 (s, 1H, -CH=CH$_2$), 4.54 (s, 1H), 4.50–4.41 (m, 1H), 4.30 (s, 1H), 3.98 (s, 1H), 3.98 (s, 1H), 3.71 (s, 1H), 3.55 (d, $J$ = 9.1 Hz, 2H), 3.49 (d, $J$ = 6.8 Hz, 2H), 3.31 (s, 1H), 3.23 (s, 1H), 3.02 (s, 1H), 2.78 (s, 1H), 2.45 (dd, $J$ = 15.1, 13.4 Hz, 2H), 2.33 (d, $J$ = 11.1 Hz, 1H), 2.18 (m, 1H), 1.99–1.89 (m, 1H), 1.38–1.21 (m, 2H), 1.18 (d, $J$ = 14.2 Hz, 1H), 1.02 (t, $J$ = 7.0 Hz, 1H); $^{13}$C NMR (151 MHz, DMSO-$d_6$): $\delta$ 139.11, 115.36, 102.45, 81.91, 73.51, 72.85, 72.46, 72.33, 60.18, 34.79, 33.63, 28.72, 24.90.

**Synthesis of mono-(6-ethylenediamicine-(N-(2-bis(3-allyloxy-2-hydroxy-propyl)-6-deoxy)-cyclodextrin) (11)**

Compound 11 was synthesized as follows. Mono-(6-ethylenediamine-6-deoxy)-β-CD (3.5 g, 3 mmol) and 0.1 mol/L sodium bicarbonate 40 mL were added to a 250 mL single neck round-bottom flask. Allyl glycidyl ether (1.9 g, 16.5 mmol) was added. Then the flask with a reflux condenser was placed in a water bath at 70 °C. After 10 h, the pH of the solution was adjusted to 7 with 1 mol/L HCl. The solution was filtered to remove sodium chloride. After that, acetone 100 mL was added. The product was precipitated and was collected. Then the product was dissolved in methanol 10 mL. Then acetone 100 mL was added and the precipitate collected. This purification process was repeated twice. And it was dissolved in methanol 10 mL. Then acetone 100 mL was added. The solution was precipitated by acetone 200 mL again. The precipitate was collected and then dissolved in methanol 20 mL. Then acetone 100 mL was added. The methanol solution was precipitated by acetone 200 mL again. The obtained product was dried under reduced pressure for 3 h at 40 °C.

White powder (yield 50%); m.p. 209–212 °C. The molecular weight of compound 11 is 1518.6355, with the found mass-charge ratio of 1519.6399 corresponding to [M + H]$^+$. The FTIR spectrum of the compound revealed vibration bands at $\nu_{max}$ cm$^{-1}$: 3404, 2924, 1645, 1634, 1418, 1369, 1337, 1300, 1247, 1207, 1155, 1080, 1032, 945, 864, 756, 708, 611, and 584; $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 5.89 (dt, $J$ = 11.5, 8.2 Hz, 1H, -CH=CH$_2$), 5.31 (s, 2H, -CH=CH$_2$), 5.28 (s, 1H, -CH=CH$_2$), 3.93 – 3.76 (m, 19H), 3.69 (s, 5H), 3.60 (d, $J$ = 8.9 Hz, 7H), 3.57 – 3.44 (m, 10H), 3.39 (s, 1H), 3.17 (s, 1H), 1.14 (t, $J$ = 7.1 Hz, 1H); $^{13}$C NMR (151 MHz, DMSO-$d_6$): $\delta$ 135.67, 116.93, 102.75, 102.38, 81.80, 73.50, 73.24, 72.87, 72.38, 71.70, 68.23, 67.88, 60.20, 58.74.

**Synthesis of mono-(6-ethylenediamicine-(N-undecylenyl)-6-deoxy)-β-CD (12)**

Compound 12 was synthesized with a method similar to that used for compounds 7 and 8. Mono-(6-ethylenediamine-6-deoxy)-β-CD (2 g, 3 mmol) was added in a 250 mL three-necked flask. Then NaOH (4 g, 0.1 mol) and distilled water 200 mL were added. After the solids had dissolved, the flask was placed in an ice-water bath (0 °C). Then 10-Undecenoyl chloride 0.02039 mol was added to the flask by a constant-voltage funnel. After stirring for 2 h, the flask was placed in a refrigerator at 4 °C for overnight. The solution was filtered and pH adjusted to 7 with 1 mol/L HCl. Then it was evaporated under reduced pressure at 50 °C. The crude product was dissolved in N,N-dimethylformamide 20 mL. The solution was filtered and precipitated by acetone 200 mL. The solid was collected and then dissolved in water 20 mL. The solution was precipitated by acetone 200 mL again. The purification process was repeated 4 times. The solid was collected and then dissolved in methanol 20 mL. The methanol solution was precipitated by acetone 200 mL again. The obtained product was dried under reduced pressure for 3 h at 40 °C.

Off white powder (yield 70%); m.p. 243–247 °C. The molecular weight of compound 12 is 1343.5671, with the found mass-charge ratio of 1343.5695 corresponding to [M + H]$^+$. The FTIR spectrum of the compound revealed vibration bands at $\nu_{max}$ cm$^{-1}$: 3406, 2923, 2854, 1638, 1561, 1418, 1157, 1080, 1031, 947, and 560; $^1$H NMR (600 MHz, D$_2$O): $\delta$ 5.77 (s, 2H), 4.77 (s, 1H, -CH=CH$_2$), 4.47 (s, 1H), 3.58 (s, 3H), 3.25 (s, 2H), 2.45 (s, 1H), 1.96 (s, 1H), 1.43 – 1.07 (m, 2H); $^{13}$C NMR (151 MHz, D$_2$O): $\delta$ 183.05, 166.12, 139.00, 138.26, 114.94, 103.70, 102.82, 101.90, 81.74, 81.44, 81.02, 73.88, 73.13, 72.86, 72.43, 71.87, 60.76, 60.03, 59.29, 39.13, 38.29, 37.83, 32.78, 29.23, 28.88, 28.46, 28.04, 26.90, 26.18, 25.69.

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**ORCID iD**

Zhigang Xu https://orcid.org/0000-0002-9308-3866

**Supplemental material**

Supplemental material for this article is available online.

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