#### Tetrahedron 72 (2016) 4854-4858

Contents lists available at ScienceDirect

# Tetrahedron

journal homepage: www.elsevier.com/locate/tet

# Synthesis and evaluation of a novel fluorescent sensor based on hexahomotrioxacalix[3]arene for $Zn^{2+}$ and $Cd^{2+}$

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# ARTICLE INFO

Article history: Received 20 May 2016 Received in revised form 20 June 2016 Accepted 21 June 2016 Available online 23 June 2016

Keywords: Hexahomotrioxacalix[3]arene Metal ion recognition Pyrenyl-appended triazole Fluorescent sensor Zinc cation

# ABSTRACT

A novel type of selective and sensitive fluorescent sensor having triazole rings as the binding sites on the lower rim of a hexahomotrioxacalix[3]arene scaffold in a *cone* conformation is reported. This sensor has desirable properties for practical applications, including selectivity for detecting  $Zn^{2+}$  and  $Cd^{2+}$  in the presence of excess competing metal ions at low ion concentration or as a fluorescence enhancement type chemosensor due to the cavity of calixarene changing from a 'flattened-cone' to a more-upright form and inhibition of PET. In contrast, the results suggested that receptor **1** is highly sensitive and selective for  $Cu^{2+}$  and  $Fe^{3+}$  as a fluorescence quenching type chemosensor due to the photoinduced electron transfer (PET) or heavy atom effect.

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# 1. Introduction

Owing to their simplicity, high sensitivity, and low detection limits for trace chemicals in chemistry, biology, and the environment,<sup>1,2</sup> fluorescent chemosensors have received much attention in the field of supramolecular chemistry. Generally, an effective fluorescent chemosensor consists of an ion recognition unit and a fluorogenic unit, which converts the actuating signal from the ionophore unit into a light signal. Amongst the different fluorogenic units, anthracene derivatives are key species in the design of fluorescent chemosensors materials, which have found wide utilization in lasers, phosphors, and light-emitting devices.<sup>3</sup> Although a tremendous number of anthracene-based organic materials have been investigated with the aim of potential applications as photoluminescence (PL) and/or electroluminescence (EL) devices in films and the solid state, the practical development of PL and EL devices is in fact restricted, usually owing to their poor stability. In contrast, strongly luminescent anthracene-based inorganic-organic hybrid materials with higher stability could be a class of promising candidates for light-emitting as well as EL applications.4

Calixarenes and their derivatives are attractive compounds for use in host–guest and supramolecular chemistry. In particular hexahomotrioxacalix[3]arene derivatives with  $C_3$ -symmetry can selectively bind ammonium ions which play important roles in both chemistry and biology.<sup>5,6</sup> Furthermore, the incorporation of two types of recognition sites via the introduction of different ionophores on the hexahomotrioxacalix[3]arene will create potential hetero-ditopic receptors with the capability of binding cations and anions, e.g., ammonium ions and halides. Therefore, many fluorescent chemosensors based on calixarenes, which show highly selective recognition of metal cations,<sup>7</sup> ammonium cations,<sup>8</sup> and fullerene derivatives, have been reported.<sup>9</sup> Additionally, the use of Click chemistry<sup>10</sup> has seen a significant

growth in the derivatization of calixarenes owing to its reliability, specificity, biocompatibility, and efficiency. It has been proven to be a promising strategy for the chemical modification of calixarenes. In 2005, Zhao and co-workers<sup>11</sup> applied Click chemistry to the synthesis of water soluble calixarenes, which laid a solid foundation for this methodology. Click chemistry has also been used to synthesize calixarene conjugates of chromophores and bioactive molecules such as glycosides,<sup>12</sup> sialoclusters,<sup>13</sup> and amino acids.<sup>14</sup> Because of the highly selective nature of the alkyne-azide cyclo-addition, the Click reaction is a general method to introduce various functional groups/moieties at the upper or lower rim of calixarenes. Therefore, we hypothesized that suitably arranged functionalized







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groups containing nitrogen atoms attached to a hexahomotrioxacalix[3]arene should be a good receptor candidate for cations. Therefore, with this in mind, we have synthesized chemosensor **1** and studied its cation-binding affinity.

### 2. Results and discussion

The synthesis of **1** was carried out as shown in Scheme 1. We first synthesized 3 in 55% yield by the reaction of hexahomotrioxacalix[3]arene and propargyl bromide in the presence of Cs<sub>2</sub>CO<sub>3</sub> in dry acetone solution. The <sup>1</sup>H NMR spectroscopic results suggested that **3** adopts a *partial-cone* structure.<sup>15</sup> Accordingly, fluorescent compound 1 can be obtained from the reaction of 3 with 9-azidomethylanthracene under standard conditions for Click chemistry. The coupling of **3** with 9-azidomethyl-anthracene afforded *cone* conformation compound **1** in 75% yield. The <sup>1</sup>H NMR spectrum of **1** shows a singlet for the *tert*-butyl protons at  $\delta$  0.94 ppm, and a doublet at  $\delta$  4.03 ppm for the bridge protons, and the <sup>13</sup>C NMR spectrum of **1** exhibits two peaks for the methyl and the quaternary carbon atoms of the *t*-Bu groups at  $\delta$  31.32, 34.04 ppm, three peaks for methylene carbon at 45.51, 66.94, 68.87 ppm and 14 peaks for aromatic carbon, respectively, indicating a  $C_3$ -symmetric structure for sensor **1**. The same procedure was also employed in the synthesis of 2 from 4-tert-butyl-2,6dimethylphenol (Scheme 1). Compound 1 contains both the calixarene and the triazole groups as metal ion binding sites, whereas 2 contains only a triazole for metal ion binding. Compare to compound **1**, the <sup>1</sup>H NMR spectrum of the reference compound **2** shows that the protons on the anthracene ring appeared at the lower magnetic fields at around  $\delta$  7.52–8.60 ppm ( $\Delta\delta$  0.05–0.2 ppm), and the proton on the triazole ring also appeared at the lower magnetic field at  $\delta$  7.08 ppm ( $\Delta \delta$  0.11 ppm) (Fig. S23). These findings strongly indicate the anthracene moieties appended on 1 were stericallyfixed to be in close proximity to allow the formation of  $\pi - \pi$ stacking between the anthracene moieties.



**Scheme 1.** Synthetic pathway for compounds **1** and **2**. (a) Cul in THF and water, reflux, 20 h.

Solutions giving concentrations of **1** (10  $\mu$ M) in CH<sub>3</sub>CN were prepared as follows. Test solutions were prepared by taking 70 mL of the calixarene stock solution in a 10 mL volumetric flask, adding 0, 0.2, 0.4, 0.6, 0.8 and 1.0 mL of stock solution, and making up to the volume with CH<sub>3</sub>CN. The fluorescence spectrum of **1** (10  $\mu$ M) in CH<sub>3</sub>CN exhibits a characteristic monomer emission of anthracene. The fluorescence emission of the solutions was measured at an excitation wavelength of 365 nm, and the emission intensities were measured at 418 nm. Measurements were repeated a minimum of three times for each addition. At high concentrations, emission quenching was observed, suggesting the formation of inter-molecular associates of **1**.

However, under dilute conditions, emission quenching was not observed. The critical association concentration value determined from the concentration-variable emission spectra was determined to be 10 µM. To remove effects of the inter-molecular associates, absorption and fluorescence measurements were carried out under critical association concentration. A similar procedure for the fluorescence measurements of 2 was conducted. The fluorescence emission of the solutions was measured at an excitation wavelength of 365 nm, and the emission intensities were measured at 418 nm. More interestingly, compared to 2, the fluorescence intensity of **1** is obviously different from reference compound **2** at the concentration (30  $\mu$ M). The fluorescence spectra of 1 and 2 under the same solutions are shown in Fig. 1. When 2 was excited at 365 nm, strong emission peaks near 400-500 nm were observed, which were assigned as emission from a single anthracene moiety, respectively. In contrast, when 1 was excited at 365 nm, the emission peaks were weak. These observations indicated that the formation of  $\pi - \pi$  stacking between the anthracene moieties appended on **1** can guench the fluorescence.



Fig. 1. Fluorescence spectra of 1 (10  $\mu$ M) and 2 (30  $\mu$ M) in CH<sub>3</sub>CN.

To get an insight into the binding properties of chemosensor **1** toward metal cations, we first investigated the fluorescence changes upon addition of a wide range of metal cations including  $K^+$ , Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Mn<sup>2+</sup>, Cr<sup>3+</sup>, Fe<sup>2+</sup>, Ni<sup>2+</sup>, Sr<sup>2+</sup>, Ag<sup>+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup>. The fluorescence changes are depicted in Figs. 2 and 3. Addition of Zn<sup>2+</sup> and Cd<sup>2+</sup> to the solution of **1** induced obvious ratiometric changes, where the emission increases. By contrast, no significant spectral changes were observed upon addition of most of the other metal cations apart from Cu<sup>2+</sup> and Fe<sup>3+</sup> where quenching was observed. These results suggest that complexations between **1** and Cu<sup>2+</sup>, Fe<sup>3+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> ions through inter-molecular interactions might be proposed.

In contrast to chemosensor **1**, chemosensor **2** exhibited a strong emission at 418 nm, and a similar experiment was carried out. The fluorescence intensity changes of **2** upon addition of different metal ions are shown in Fig. S3. Addition of  $Cu^{2+}$  and  $Fe^{3+}$  caused a strong and medium fluorescence quenching, respectively.

Upon addition of  $Zn^{2+}$ , the fluorescence intensity of solution **1** increased gradually (Fig. 4). The saturation behavior of the fluorescence intensity after adding 2 equiv of  $Zn^{2+}$  reveals that a 1:1 stoichiometry best describes the binding mode of  $Zn^{2+}$  and **1**, which is also supported by the Job's plot data (Fig. S6). According to



**Fig. 2.** Fluorescence spectra of **1** (10  $\mu$ M) in CH<sub>3</sub>CN in the presence of different metal ions (10 equiv). Metal ions include K<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup>, Ca<sup>2+</sup>, Cr<sup>3+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ag<sup>+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Fe<sup>3+</sup>, Fe<sup>2+</sup> and Pb<sup>2+</sup>. Excitation was performed at 365 nm.



**Fig. 3.** Fluorescence responses of receptor **1** (10  $\mu$ M) to 100  $\mu$ M various tested ions in CH<sub>3</sub>CN. I<sub>0</sub> is the fluorescence emission intensity at 418 nm for free receptor **1**, and I is the fluorescent intensity after adding ions at 298 K.  $\lambda_{ex}$ =365 nm.



Fig. 4. Changes in fluorescence emission spectra of 1 (10  $\mu M$ ) upon titration by  $Zn^{2+}$  (from 0–30  $\mu M$ ) in CH\_3CN (excitation at 365 nm). Inset is molar ratio plot.

the 1:1 model, the association constant of Zn<sup>2+</sup>, calculated from the Benesi-Hildebrand equation,<sup>16</sup> was found to be  $1.44 \times 10^4$  M<sup>-1</sup>. As a result, **1** can be regarded as being highly sensitive to the Zn<sup>2+</sup> ion, especially given the large fluorescence dynamic range and the low detection limit of  $3.79 \times 10^{-7}$  M. The quantum yield of **1** is  $\Phi$ =0.11.

To further study the sensitivity of 1 toward Cd<sup>2+</sup>, fluorescence titration experiments were carried out (Fig. 5). Upon addition of



Fig. 5. Changes in fluorescence emission spectra of 1 (10  $\mu$ M) upon titration by Cd<sup>2+</sup> (from 0–30  $\mu$ M) in CH<sub>3</sub>CN (excitation at 365 nm). Inset is molar ratio plot.

Cd<sup>2+</sup>, the fluorescence intensity of solution **1** increased gradually. A Job's plot binding between **1** and Cd<sup>2+</sup> ion reveals a 1:1 stoichiometry (Fig. S10), while the association constant ( $K_a$  value) for the complexation with Cd<sup>2+</sup> ion by **1** was determined to be  $4.06 \times 10^4$  M<sup>-1</sup> as observed by the fluorescence titration experiments in CH<sub>3</sub>CN. On the other hand, the fluorescence of **1** was efficiently quenched by Cu<sup>2+</sup> and Fe<sup>3+</sup>; over 99% fluorescence quenching was observed with 10 equiv. A Job's plot binding between **1** and Cu<sup>2+</sup> ion reveals a 1:1 stoichiometry (Fig. S15), while the association constant of Cu<sup>2+</sup>, calculated from the Benesi–Hildebrand equation,<sup>16</sup> was found to be  $5.79 \times 10^5$  M<sup>-1</sup>. The compound **1**, **1** ·Cu<sup>2+</sup> and **1** ·Zn<sup>2+</sup> mixtures were also analyzed by HPLC (Fig. 6). A chromatographic peak of derivative **1** 

The compound **1**,  $1 \cdot Cu^{2+}$  and  $1 \cdot Zn^{2+}$  mixtures were also analyzed by HPLC (Fig. 6). A chromatographic peak of derivative **1** appeared at 8.40 min. After the addition of  $Cu^{2+}$  and  $Zn^{2+}$ , the intensity of the peak at 8.40 min decreased, accompanied by the emergence of a new peaks at 6.30 min and 14.50 min, respectively; these results demonstrate clearly the formation of new products  $(1 \cdot Cu^{2+} \text{ and } 1 \cdot Zn^{2+} \text{ complexes})$ .



Fig. 6. HPLC chromatograms of derivative 1 and complex (a) 0.3 mM of 1; (b) 0.3 mM of 1 with 6 mM of  $Cu^{2+}$  is added; (c) 0.3 mM of 1 with 6 mM of  $Zn^{2+}$  is added.

To confirm the binding mechanism, <sup>1</sup>H NMR spectra of **1** and the  $1 \cdot 2n^{2+}$  complex were measured in a mixture of CDCl<sub>3</sub>/CD<sub>3</sub>CN (10:1, v/v). As shown in Fig. 7B, upon gradual addition of  $Zn^{2+}$  salt (0.5 equiv) to a solution of **1**, the resonances corresponding to the protons of receptor **1** were split into two sets of signals. After addition of 1 equiv.  $Zn^{2+}$  in receptor **1** the original proton signals disappeared. This result suggests the presence of the complexed form between  $1 \subset Zn^{2+}$  and the uncomplexed form of free **1**. The signal for proton H<sub>a</sub> on the triazole ring undergoes a downfield shift



**Fig. 7.** (A) Binding mode of **1** upon complexation with  $Zn^{2+}$  ion as perchlorate salt. (B) Partial <sup>1</sup>H NMR spectra of **1** (4.0 mM) in CDCl<sub>3</sub>: CD<sub>3</sub>CN (10:1, v/v) upon addition of  $Zn^{2+}$  ion at 298 K. (a) Free **1**, (b)  $1 \subset Zn^{2+}$  (0.5 equiv), and (c)  $1 \subset Zn^{2+}$  (1.0 equiv).

from  $\delta$  7.16 ppm–7.70 ppm ( $\Delta \delta_{\rm H}$ =0.64 ppm), and the OCH<sub>2</sub>-triazole linked proton of H<sub>d</sub> is shifted from  $\delta$  4.06 ppm–5.13 ppm (Fig. S22). These spectral changes suggested that the  $Zn^{2+}$  ion is selectively bound by the nitrogen atoms on the triazole rings. Moreover, the signal for the proton on the anthracene moiety revealed a downfield shift, which indicated that the anthracene moieties appended on **1** were alienated by  $Zn^{2+}$  to prohibit the formation of  $\pi - \pi$ stacking between the anthracene moiety. On the other hand, it is noted that the proton H<sub>b</sub> on the phenyl of hexahomotrioxacalix[3] arene also experienced a downfield shift from  $\delta$  6.60–6.81 ppm, and the  $\Delta \delta_{\rm H}$  value for H<sub>ax</sub> and H<sub>eq</sub> of the ArCH<sub>2</sub>O methylene protons changed to 0.58 ppm (Fig. S22), respectively. The large  $\Delta \delta_{\rm H}$  value for H<sub>ax</sub> and H<sub>eq</sub> indicated that the phenol groups in the complex are positioned in a more-upright form, the calix cavity changed from a 'flattened-cone' to a more-upright form that is similar to the previously reported examples.<sup>17,18</sup> The concept of Zn<sup>2+</sup> complexation by the host chemosensor **1** is shown in Fig. 7A. From the above discussion, the binding mode of  $1 \cdot Zn^{2+}$  indicated that the phenol groups in the complex are situated in an upright form and also the anthracene moieties are far apart from each other to reduce the  $\pi - \pi$  stacking in presence of Zn<sup>2+</sup> which results the fluorescence enhancement.

On the other hand, the peaks of  $H_a$ ,  $H_b$ ,  $H_c$  and  $H_d$  completely disappeared and the signals of the anthracene ring protons and benzyl protons were blurred, which is attributed to both the conformation changes and the paramagnetic effect of the Cu<sup>2+</sup>. Once the Cu<sup>2+</sup> was captured by the nitrogen, the protons adjacent to Cu<sup>2+</sup> were strongly affected by the Cu<sup>2+</sup> due to inherent paramagnetism of Cu<sup>2+</sup>. Thus, the complexation between the heavy metal ions and sensor **1** led to the quenching of the fluorescence emission through the heavy metal ion effect, and/or reversed PET that is similar to the previously reported examples.<sup>19</sup>

#### 3. Conclusions

In summary, we have synthesized a new type of selective and sensitive fluorescent sensor having triazole rings as the binding sites at the lower rim of a hexahomotrioxacalix[3]arene scaffold in a *cone* conformation. The selective binding behavior of chemosensor **1** has been evaluated by fluorescence spectra and <sup>1</sup>H NMR spectroscopic analysis. This sensor has desirable properties for practical applications, including selectivity for detecting  $Zn^{2+}$  and  $Cd^{2+}$  in the presence of excess competing metal ions at low ion concentration or as a fluorescence enhancement type chemosensor due to the cavity of calixarene changed from a 'flattened-cone' to a more-upright form and inhibition of photoinduced electron transfer (PET). In contrast, the results suggested that receptor **1** is highly sensitive and selective for  $Cu^{2+}$  and  $Fe^{3+}$  as a fluorescence quenching type chemosensor due to photoinduced electron transfer (PET) or heavy atom effect.

Further studies on the synthesis of tritopic receptors based on the hexahomotrioxacalix[3]arene are also underway in our laboratory.

#### 4. Experimental section

# 4.1. General

All melting points (Yanagimoto MP-S1) are uncorrected. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Nippon Denshi JEOL FT-300 NMR spectrometer and Varian-400MR-vnmrs400 with SiMe<sub>4</sub> as AQ2OM spectrophotometer. Mass spectra were obtained with a Nippon Denshi JMS-HX110A Ultrahigh Performance mass spectrometer at 75 eV by using a direct-inlet system. UV–vis spectra were recorded using a Shimadzu UV-3150 UV–vis-NIR spectrophotometer. Elemental analyses were performed by a Yanaco MT-5. Fluorescence quantum yields were recorded in solution (Hamamatsu Photonics K. K. Quantaurus-QY A10094) using the integrated sphere absolute PL quantum yield measurement method.

#### 4.2. Materials

Compounds **3** and **4** were synthesized according to our previous report.  $^{15}$ 

4.2.1. Synthesis of receptor 1. Copper iodide (20 mg) was added to a solution of compound 3 (200 mg, 0.28 mmol) and 9azidomethylanthracene (210 mg, 0.90 mmol) in 20 mL THF/H<sub>2</sub>O (4:1) and the mixture was heated at 65  $\degree$ C for 24 h. The resulting solution was cooled and diluted with water and extracted thrice with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated and dried (MgSO<sub>4</sub>) and evaporated to give the solid crude product. The residue was eluted from a column chromatography of silica gel with hexane/ ethyl acetate (v/v=4:1) to give the desired product *cone*-1 (290 mg. 75%) as colorless prisms. Mp 154–156 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.94 (27H, s, C(CH<sub>3</sub>)<sub>3</sub>), 4.03 (12H, d, OCH<sub>2</sub>O, *J*=4.0 Hz), 4.10 (6H, s, -OCH<sub>2</sub>), 6.29 (6H, s, An-CH<sub>2</sub>), 6.68 (6H, s, Ar-H), 7.08 (3H, s, triazole-H), 7.39-7.43 (6H, m, An-H), 7.47-7.51 (6H, m, An-H), 7.94 (6H, d, J=8.4 Hz, An-H), 8.28 (6H, d, J=8.4 Hz, An-H) and 8.42 (3H, s, An–H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 31.32, 34.12, 45.51, 66.94, 68.87, 122.71, 123.29, 124.42, 125.45, 125.77, 127.64, 129.42, 129.74, 130.77, 130.86, 131.43, 144.27, 146.23 and 151.78 ppm. IR:  $\nu_{\rm max}$  (KBr)/cm<sup>-1</sup>: 3310, 2960, 1575, 1436, 1367, 1268, 1090 and 1002. FABMS: *m/z*: 1389.58 (M<sup>+</sup>). Anal. Calcd for C<sub>90</sub>H<sub>87</sub>O<sub>6</sub>N<sub>9</sub> (1389.12): C, 77.73; H, 6.31. Found: C, 77.90; H, 6.37.

4.2.2. Synthesis of receptor **2**. Copper iodide (20 mg) was added to a solution of compound **4** (100 mg, 0.47 mmol) and 9-azidome-thylanthracene (340 mg, 1.45 mmol) in 20 mL THF/H<sub>2</sub>O (4:1) and the mixture was heated at 65  $\degree$ C for 24 h. The resulting solution was

cooled and diluted with water and extracted thrice with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated and dried (MgSO<sub>4</sub>) and evaporated to give the solid crude product. The residue was eluted from a column chromatography of silica gel with hexane/ethyl acetate (v/ v=4:1) to give the desired product **2** (170 mg, 81%) as colorless prisms. Mp 194–196 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  1.22 (s, 9H, C(*CH*<sub>3</sub>)<sub>3</sub>), 2.10 (s, 6H, Ar–*CH*<sub>3</sub>), 4.78 (s, 2H, –O*CH*<sub>2</sub>), 6.57 (s, 2H, An–*CH*<sub>2</sub>), 6.89 (s, 2H, Ar–*H*), 7.19 (s, 1H, trizole–*H*), 7.52–7.64 (m, 4H, An–*H*), 8.09 (d, 2H, *J*=6.0 Hz, An–*H*), 8.33 (d, 2H, *J*=6.0 Hz, An–*H*), 8.60 (s, 1H, An–*H*). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, CDCl<sub>3</sub>):  $\delta$  31.6, 34.2, 37.4, 46.7, 49.85, 62.2, 114.3, 122.5, 123.1, 123.8, 125.6, 126.3, 127.9, 129.7, 130.1, 130.9, 131.6, 144.0, 144.5, 156.0 IR: *v*<sub>max</sub> (KBr)/cm<sup>-1</sup>: 3019, 1966. FABMS: *m/z*: 449.78 (M<sup>+</sup>). Anal. Calcd for C<sub>30</sub>H<sub>31</sub>ON<sub>3</sub> (449.25): C, 80.14; H, 6.95. Found: C, 80.38; H, 7.03.

#### Acknowledgements

This work was performed under the Cooperative Research Program of 'Network Joint Research Center for Materials and Devices (Institute for Materials Chemistry and Engineering, Kyushu University)'. We would like to thank the OTEC at Saga University and the International Collaborative Project Fund of Guizhou province at Guizhou University for financial support. We also would like to thank the EPSRC (for a travel grant to C.R.).

# Supplementary data

Supplementary data (Details of the NMR spectra and titration experimental data) associated with this article can be found, in the online version at http://dx.doi.org/10.1016/j.tet.2016.06.055.

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