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ORIGINAL ARTICLE

Synthesis of a novel tripodand having 3-hydroxy-2-naphthoeic amide groups and its anion recognition ability

Jie Hao · Kazuhisa Hiratani · Naohiro Kameta · Toru Oba

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Abstract A novel tripodand having 3-hydroxy-2-naphthoeic amide groups was prepared by the reaction of 1,3,5-tris(aminomethyl)-2,4,6-trimethylbenzene with 3-allyloxy-2-naphthoeic acid chloride followed by thermal Claisen rearrangement. This tripodand can exhibit the anion binding ability in chloroform solution. In particular, it can bind with acetate, dihydrogen phosphate, and fluoride ions to form 1:1 complexes.

Keywords Tripodand · Claisen rearrangement · Anion recognition · Naphthoeic acid derivatives

Introduction

Many kinds of tripodand-type noncyclic compounds have been reported [1–14]. Many functions and properties such as molecular recognition and complexation with metal ions have been investigated. More recently much attention has been paid to behaviors of self-assemblies on the surface [15, 16]. On the other hand, metallo-supramolecular systems and caged-type molecules including cryptand-type molecules forming three-dimensional structures have attracted much attention of supramolecular chemists due to their interesting optical properties and novel functional architectures [17–19].

J. Hao · K. Hiratani (✉) · T. Oba
Department of Applied Chemistry, Utsunomiya University, 7-1-2 Youtou, Utsunomiya 321-8585, Japan
e-mail: hiratani@cc.utsunomiya-u.ac.jp

N. Kameta
National Institute of Advanced Industrial Science and Technology, Tsukuba Central 5, 1-1-1 Higashi, Tsukuba 305-8565, Japan

Tripodands having functional groups as terminal groups could have many possibilities to exhibit molecular recognition and to design three-dimensional and functional molecules. The combination of tripodands with various metal ions will lead to the construction of finite and infinite structures [20–23]. Recently, we reported on the synthesis of tripodands containing catechol [24, 25] and quinolyl [26] end groups, respectively, which were prepared via Claisen rearrangement [27].

Experimental

General information

All reagents were obtained from commercial suppliers and used without further purification unless stated otherwise. ^{1}H-NMR spectra were recorded on a Varian NMR 500 MHz spectrometer. ^{1}H chemical shifts are reported as δ in ppm relative to residual protonated solvent resonances. All coupling constants are reported in Hertz (Hz). Mass spectra were recorded using a Bruker Daltonics Autoflex Maldi-Tof Mass Spectrometer with Scout-MTP Ion Source. IR spectra were recorded with a Jasco FTIR-430 spectrophotometer with samples as KBr pellets in the 4,000–400 cm^{-1} range. Elemental analyses were performed by Fisons. EA-1108 instrument.

Synthetic procedures for **2**

Synthesis of 2-allyloxy-3-naphthoeic acid methyl ester

To 150 mL of DMF solution of 3-hydroxy-3-naphthoic acid methyl ester (5.50 g, 0.025 mol) was added NaH (1.20 g, 0.030 mol, 60%). After the mixture was stirred for 1 h at

room temperature. 3-Bromopropene (3.0 g, 0.025 mol) was added to it and heated to 60 °C for 12 h. After removal of DMF under vacuum, the residue was extracted with $CHCl_3$, and the $CHCl_3$ layer was washed with water three times. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure by an rotary evaporator. The product was purified by silica gel column chromatography (hexane/AcOEt (5:1) to (3:1)) to give yellow solid (yield: 3.961 g, 83%). ^{1}H-NMR ($CDCl_3$, 500 MHz) 8.32 (s, H, naphthyl), 7.82 (d, H, $J = 8.0$ Hz, naphthyl), 7.72 (d, H, $J = 8.0$ Hz, naphthyl), 7.52 (t, H, naphthyl), 7.39 (t, H, naphthyl), 7.26 (s, H, naphthyl), 6.17 (m, 1H, –CH=), 5.59 (m, 1H, CH_2=), 5.35 (m, 1H, CH_2=), 4.73 (d, 2H, O–CH_2–), 3.96 (s, 3H, CH_3) ppm.

Synthesis of 1,3,5-tris(aminomethyl)-2,4,6-trimethylbenzene

To a solution of 1,3,5-tris(bromomethyl)-2,4,6-trimethybenzene (2.0 g, 5.01 mmol) in 150 mL of dry DMF was added phthalimide potassium salt (4.0 g, 22 mmol), and the solution was stirred at 70 °C for 12 h. The white solid formed was separated by filtration and washed with water to remove excess phthalimide potassium salt. The product was dried under vacuum (2.8 g, 93%). ^{1}H-NMR ($CDCl_3$, MHz) 7.79 (m, 6H, aromatic-H), 7.64 (m, 6H, aromatic-H), 4.95 (s, 6H, N–CH_2–), 2.50 (s, 9H, CH_3) ppm.

To the suspension of the tris(phthalimide) compound in dry 200 mL THF was added hydrazine monohydrate (2.5 g, 50 mmol) and the suspension was stirred at 70 °C for 12 h. The suspension was filtered. The solvent was evaporated and the reside was washed with THF to remove excess hydrazine to give yellow product (1,3,5-tris(aminomethyl)-2,4,6-trimethylbenzene) (0.72 g, 70%). ^{1}H-NMR (DMSO-d_6, 500 MHz) 3.75 (s, 6H, CH_2), 2.35 (s, 9H, CH_3) ppm.

*Synthesis of compound **1***

To a solution of 2-allyoxy-3-naphthoeic acid methyl ester (1.67 g, 6.9 mmol) in 200 mL of EtOH/THF (150 mL: 50 mL) was added 2 eq NaOH (0.6 g, 15.0 mmol), and the solution was heated at 60 °C for 12 h. After removal of EtOH/THF, water was added to the residue. The aqueous solution was acidified with conc. HCl. The white precipitate formed was filtered, and dried in vacuo. To a solid of acid (417 mg, 1.82 mmol) was added an excess of $SOCl_2$ and stirred at 60 °C for 1 h. The excess of $SOCl_2$ was removed under reduced pressure, and the residue was dried in vacuo for 3 h. The acid chloride obtained was used without further purification. A solution of acid chloride (0.450 g, 1.82 mmol) in 25 mL of dry THF was added to 50 mL of dry THF solution of 1,3,5-tris(aminomethyl)-2,4,6-trimethylbenzene (0.1 g, 0.48 mmol) at 0 °C. After the solution was stirred for 12 h at room temperature, the solvent were removed by rotary evaporator. The solid residue was dissolved in $CHCl_3$ and the solution was washed with water, dried over $MgSO_4$, and concentrated. The product was purified by silica gel column chromatography($CHCl_3$) to give white solid (0.21 g, 50%) ^{1}H-NMR ($CDCl_3$, 500 MHz) 8.80 (s, 3H, naphthyl), 8.03 (t, 3H, NH), 7.92 (d, 3H, $J = 8.5$ Hz, naphthyl), 7.71 (d, 3H, $J = 7.5$ Hz, naphthyl), 7.53 (t, 3H, naphthyl), 7.42 (t, 3H, naphthyl), 7.15 (s, 3H, naphthyl), 5.83 (m, 3H, =CH–), 5.18 (d, 3H, $J = 1.0$ Hz, CH_2=), 5.09 (d, 3H, $J = 10.0$ Hz, CH_2=), 4.82 (d, 6H, $J = 4.5$ Hz, N–CH_2–), 4.59 (d, 6H, $J = 5.5$ Hz, O–CH_2–). TOF-MS: *m/z* 860.50 (M + Na), 876.48 (M + K). Elemental analysis: calcd (%) for $C_{54}H_{51}N_3O_6$ + 1/4 H_2O: C: 76.98; H: 6.16; N: 4.99. Found: C: 76.96; H: 6.15; N: 5.07. FTIR (cm^{-1}, KBr): 3404, 2924, 2365, 2345, 1655, 1626, 1525, 1458, 1220.

*Synthesis of tripodand **2***

Compound **1** (0.1 g) was heated to 160 °C under vacuum for 20 min. The product was purified by silica gel column chromatography($CHCl_3$) to give yellow solid (0.08 g, 80%) ^{1}H-NMR ($CDCl_3$, 500 MHz) 11.93 (s, 3H, OH), 7.88 (d, 3H, $J = 8.5$ Hz, naphthyl), 7.77 (s, 3H, naphthyl), 7.65 (d, 3H, $J = 8.5$ Hz, naphthyl), 7.52 (t, 3H, naphthyl), 7.26 (t, 3H, naphthyl), 6.40 (t, 3H, NH), 6.05 (w, 3H, =CH–), 5.02 (w, 6H, CH_2=), 4.83 (d, 6H, $J = 4.5$ Hz, N–CH_2–), 3.86 (d, 6H, $J = 6.0$ Hz, O–CH_2–), 2.57(s, 9H, CH_3). TOF-MS: *m/z* 860.50 (M + Na), 876.48 (M + K). Elemental analysis: calcd (%) for $C_{54}H_{51}N_3O_6$ + 1/4 H_2O: C: 76.98; H: 6.16; N: 4.99. Found: C: 76.89; H: 6.14; N: 5.00. FTIR (cm^{-1}, KBr): 3423, 3074, 2925, 2372, 2346, 1648, 1523, 1236.

*Titration of **2** with anions*

^{1}H-NMR titration **2** with anions experiments were carried out at room temperature using a Varian NMR 500 MHz spectrometer. All chemical shifts are reported in ppm relative to TMS as an internal reference. A solution of the host species of known concentration, typically 0.02 M, was made up in an NMR tube using the appropriate deuterated solvent (0.5 mL) with TMS added. Solutions of the anions, as tetrabutylammonium salts, were made up in volumetric flasks (2 mL) with a concentration five times greater than that of the host. The guest solution was typically added in 10 μL aliquots, representing 0.1 equivalents of the guest with respect to the host. Larger aliquots were used in some cases where no inflection of the trace was evident. Spectra were recorded after each addition and the trace was followed simultaneously.

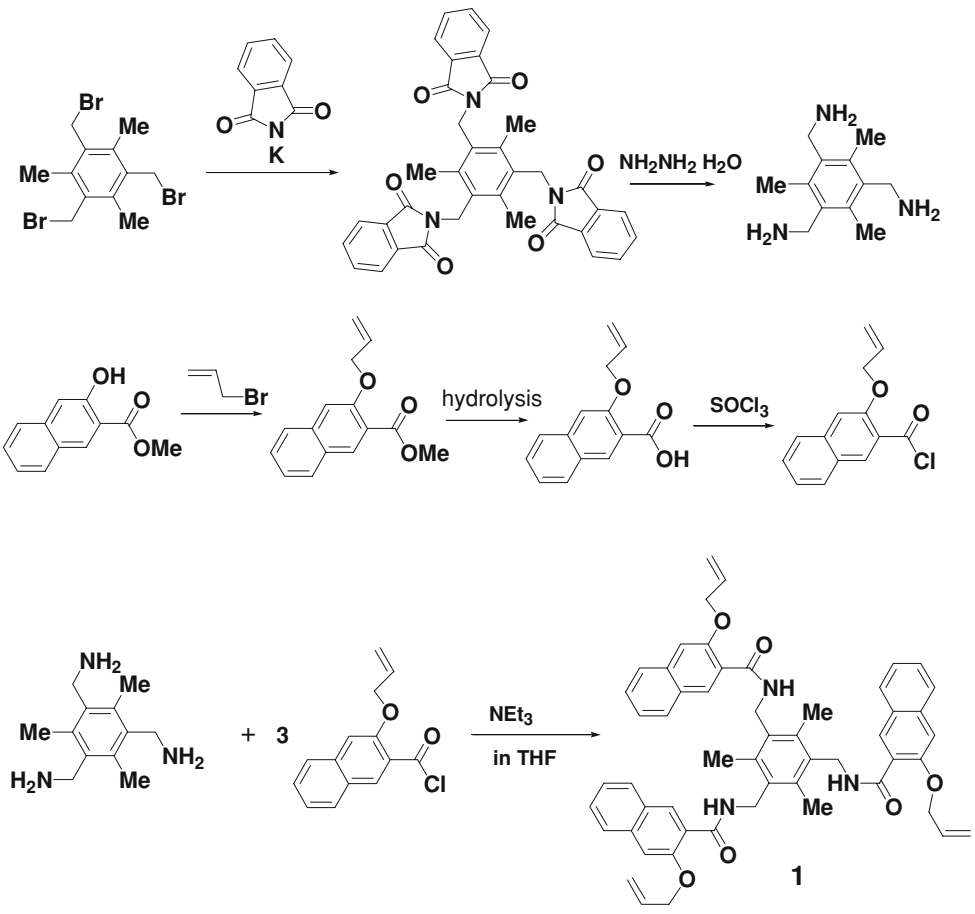
Results and discussion

In this paper, we report the synthesis of a novel tripodand having three amide groups and three hydroxyl groups in three arms. As shown in Scheme 1, we started from three commercially-available compounds to prepare a tripodand, that is, 1,3,5-tris(aminomethyl)-2,4,6-trimethylbenzene, 3-hydroxy-2-naphthoeic acid, and allyl bromide. 1,3,5-Tris (aminomethyl)-2,4,6-trimethylbenzene was prepared using 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene and potassium phthalimide followed by the treatment of hydrazine. The reaction of methyl 3-hydroxyl-2-naphthoate with allyl bromide gave methyl 3-allyloxy-2-naphthoate. After the hydrolysis of ester, 3-allyloxy-2-naphthoeic acid was obtained. Treatment of thionyl chloride gave acid chloride of the carboxylic acid. The reaction of the corresponding acid chloride with the triamine compound gave a tripodand-type compound (**1**). The thermal reaction of **1** at 160 °C for 1 h without solvent gave the target product (**2**) quantitatively (Scheme 2). Compound **2** was prepared via three times Claisen rearrangement. Compounds **1** and **2** were confirmed by elemental analysis and spectroscopic methods of NMR, IR, Mass spectroscopies.

Figure 1 shows the NMR spectrum of **1** and **2**. The OH proton of **2** appears at 11.93 ppm, though it should normally appear at much more upfield around 6–7 ppm. This means that carbonyl oxygen at the 3-position of naphthyl group interacts with OH group by intramolecular hydrogen bond formation as shown in Fig. 2 [20–23]. On the contrary, the chemical shifts of both proton at 4-position of naphthyl group and amide proton of **2** move to upfield compared to the same positions of protons of **1**, respectively. In the molecule **1**, two hydrogen bonds might be possible, that is, one is between carbonyl oxygen and C–H proton at 4-position of naphthyl group, and another one is between NH proton and allyl ether oxygen atom. It may be suggested that the hydrogen bond cleavage occurs accompanied with the formation of hydrogen bond between carbonyl oxygen atom and OH proton of **2** which was generated by Claisen rearrangement (Fig. 2).

While compound **1** has three amide and three allyl ether moieties, compound **2** has three amide and three hydroxyl groups in a molecule. They could be expected to exhibit the ability of the capture of guest molecules such as anionic species and organic molecules which can be bound through hydrogen bondings with these functional groups. In

Scheme 1 Synthesis of tripodand **1**



Scheme 2 Synthesis of tripodand **2** by thermal reaction of **1**

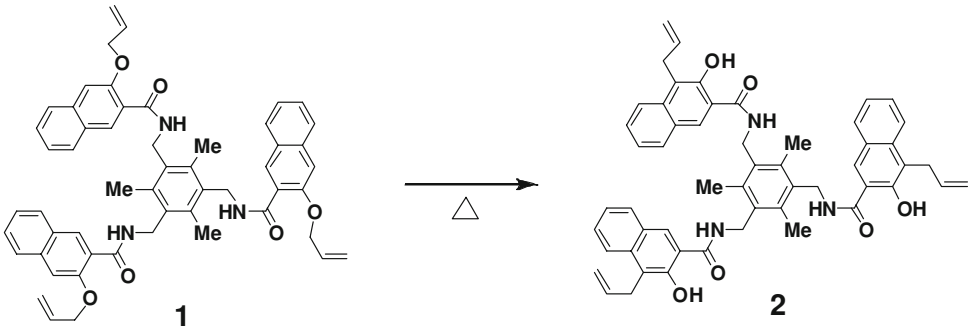
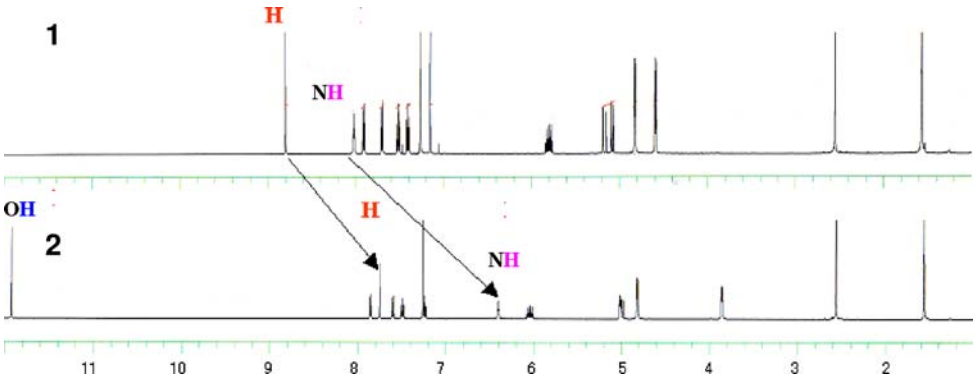


Fig. 1 NMR spectrum of **1** and **2**



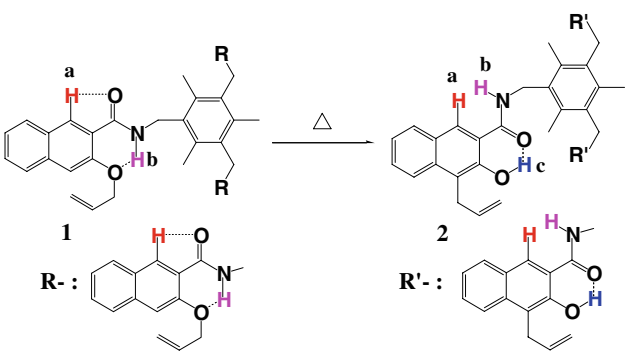


Fig. 2 Plausible formation of intramolecular hydrogen bondings between OH and NH groups of **1** and **2**

addition, they could also be expected to exhibit the complexation with metal ions accompanied with elimination of protons from phenolic hydroxyl groups because phenolic hydroxyl proton is weakly acidic.

The ability of interaction of compounds (**1** and **2**) toward cationic or anionic species was investigated. The complexation of **1** and **2** having three arms with lanthanoide ions has been attempted because lanthanoide ions have usually three valency. Each arm contains three phenyl allyl ether oxygens in **1** or phenolic parts in **2** and three amide groups. As a result, **1** and **2** did not work as cation binding host molecules. It is presumed that three binding sites cannot approach each other fittably and cooperatively to form 1:1 complex with lanthanoide ions probably because the benzene ring in the center of the molecules could interfere the intramolecular complexation. On the other hand, compound **2** exhibits interaction with anionic species, dihydrogen phosphate, acetate, and fluoride ions, whereas compound **1** cannot interact with any anionic and cationic species at all.

The complexation of **2** with anions was investigated because it has plural hydroxyl groups and amide NH moieties, totally six protons which might work as proton donating part toward anionic species. As anionic guest molecules, tetrabutyl ammonium salts of fluoride, chloride, bromide, iodide, acetate, sulfate, and dihydrogenphosphate ions were used for this experiment. Among these anion species, remarkable change in the NMR spectrum in $CDCl_3$ was observed when acetate, dihydrogenphosphate, and fluoride ions were added into the $CDCl_3$ solution of **2**. The proton NMR spectrum is shown in Fig. 3 when excess of each anion (acetate, dihydrogenphosphate, or fluoride ion) was added into the $CDCl_3$ solution of **2**. When added anion species, two phenolic OH protons disappear completely, while amide protons shift to downfield largely. Singlet peak of proton **a** of **2** is assigned to the proton of position 3 of naphthyl group as shown in Fig. 2. The chemical shift of **a** of **2** without any anion is 7.77 ppm. This proton shifts also downfield depending upon anions added as shown in Fig. 3. For example, in the case of addition of $H_2PO_4^-$, the chemical shift of **a** shifts from 7.77 to 9.13 ppm. The

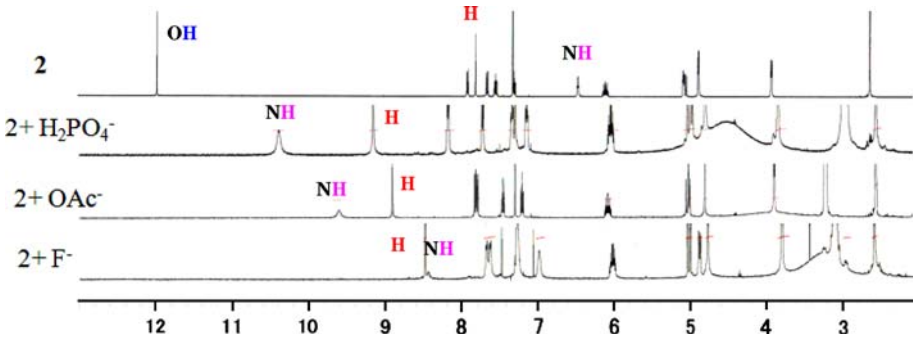


Fig. 3 ^{1}H-NMR spectrum of **2** with tetrabutylammonium salt of $H_2PO_4^-$, AcO^-, and F^- in $CDCl_3$

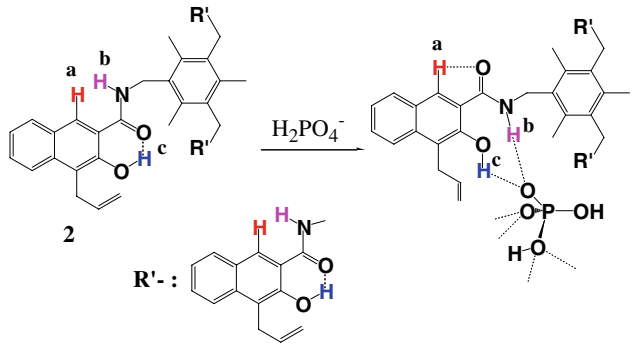


Fig. 4 Postulated conformational change of **2** depending upon the addition of anion

difference ($\Delta\delta = \delta_{\text{free ligand}} - \delta_{\text{complex}}$) of chemical shift from the original one is −1.36 ppm. The chemical shift 9.13 ppm is comparable to that (8.80 ppm) of **1** (see in Fig. 1). It may mean that when the host molecule **2** includes the guest anion into the cavity, the conformation seems to be the same as that of **1** of which the carbonyl is directed to the outside of the cavity as shown in Fig. 4 to result in the more advantageous formation of hydrogen bonding between OH (c) and NH (b) protons of **2** and the guest anion. Based on this hypothesis, it could be understood that not only NH protons but also protons **a** shift drastically downfield compared to other protons of host molecule **2**.

The titration plots were shown in Fig. 5 in the case of the addition of dihydrogenphosphate ion. From this result, the 1:1 complexation occurs between **2** and dihydrogenphosphate. In the case of the addition of acetate and fluoride ions, the similar results were obtained as in the case of dihydrogenphosphate ion. In the case of other ions except the above three anions used, little change of the proton chemical shifts in the NMR spectrum were observed. From these results, the binding constants toward three anions were calculated by using a least-squares fitting for the plots in Fig. 5 on the basis of the general equation [28]. For fluoride ion, acetate ion, and dihydrogenphosphate ion, the binding constants are 4.81 ± 0.23, 5.52 ± 0.64, and 4.74 ± 0.18, respectively. The order of the selectivity toward anions results in the following: acetate ion > fluoride ion > dihydrogenphosphate ion $\gg$ the other anions. Although this order reflects the order of nucleophilicity of anions, the binding constants of three anions seem to have almost the same value.

Conclusion

We synthesized novel tripodands containing plural amide and either ether or hydroxyl groups. Tripodand **1** having one amide and allyloxy groups for each arm has no ability of molecular recognition toward cations and anions. On the other hand, tripodand **2**, which was prepared by the thermal

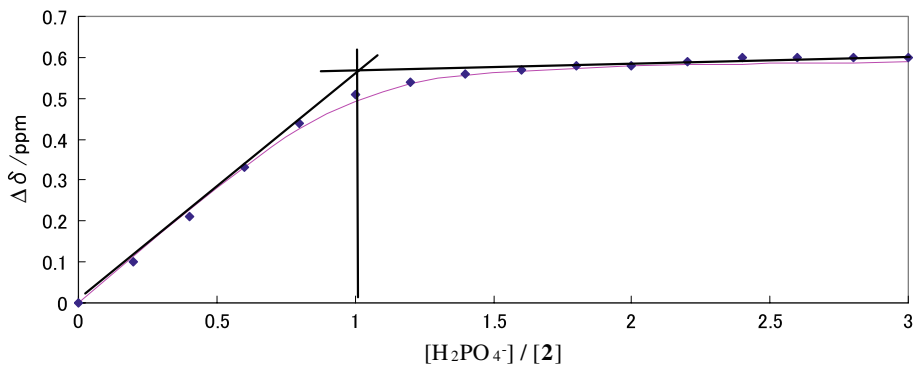


Fig. 5 ^{1}H-NMR titration of **2** with tetrabutylammonium dihydrogenphosphate in $CDCl_3$. $[\mathbf{2}] = 4.7 \times 10^{-3}$ mol dm^{-3}. The chemical shift change ($\Delta\delta$/ppm) and the best fitting curves by a 1:1 complexation model of naphthyl proton at the 8 position

reaction of **1**, having 2-hydroxy-3-carbamoylnaphthyl end groups can exhibit the interaction with three anions, i.e., fluoride, acetate, and dihydrogenphosphate ions. The binding constants toward these anions were evaluated from the titration experiments of **2** toward the corresponding anions. It was found that tripodand **2** having C3 symmetry can interact with limited anionic species. However, there is no ability to make complex with trivalent metal ions such as lanthanoide ions.

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