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Tuning mechanism in helical columnar thiophene host system with 2-thienylacetic acid by using (1*R*,2*S*)-2-amino-1,2-diphenylethanol

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ABSTRACT

A tunable supramolecular thiophene host system with a chiral channel-like cavity is developed using (1*R*,2*S*)-2-amino-1,2-diphenylethanol. This thiophene host system possesses a chiral helical columnar structure. The chiral cavities are formed by the self-assembly of the helical column, and guest molecules are included by varying the helical structure and packing arrangement of this column.

1. Introduction

In the field of host–guest chemistry, the use of solid-state fluorescence host systems and, in particular, supramolecular organic fluorescence host systems comprising two or more organic molecules, as molecular host systems has attracted considerable attention;[1] this is because the physical and chemical properties of these supramolecular host systems can be easily controlled by simply changing their component molecules.[2] However, it is difficult to predict the structure of solid-state supramolecular organic complexes with new component molecules. Moreover, there have been few reports of solid-state supramolecular fluorescence host systems with chiral cavities.[3] Therefore, basic fluorescence supramolecular building blocks have been increasingly used to determine the structural information of chiral supramolecular organic complexes as a bottom-up approach to the study of solid-state supramolecular fluorescence host–guest chemistry. We have recently developed a solid-state fluorescence host system using a chiral supramolecular organic fluorophore composed of (1*R*,2*S*)-2-amino-1,2-diphenylethanol [(1*R*,2*S*)-**1**] as the chiral unit and thiophene acid derivatives as the fluorescence unit.[4] Characteristically, this host system is formed by the self-assembly of a 1D columnar hydrogen- and ionic-bonded network structure that lacks strong interactions between individual columns. Guest molecules are included into a channel-like cavity, that is, formed by the self-assembly of this 1D columnar structure. Hence, guest molecules can be expected to be included in the host system by altering the packing arrangement of the 1D columns. However, the tuning mechanism in a 1D columnar thiophene host system has not been studied.

In this paper, we report the formation and structural information of a chiral helical columnar thiophene host system by employing a combination of supramolecular building blocks—(1*R*,2*S*)-**1** and 2-thienylacetic acid (**2**). Recently, numerous organic functional materials having various electrochemical and photochemical properties have been prepared using a polythiophene backbone.[5] Therefore, **2**, which is one of the most basic units of the polythiophene backbone, is used as a supramolecular building block although it hardly exhibits fluorescence. Four types of *n*-alkyl alcohols—methanol (MeOH), ethanol (EtOH), *n*-propanol (*n*-PrOH), and *n*-butanol (*n*-BuOH)—possessing different alkyl chain lengths are used as guest molecules in order to study the influence of the size of the constituent guest molecule on the host system. This study is expected to provide useful information on the construction

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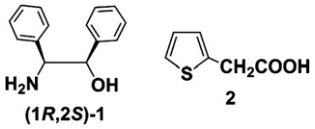
of novel solid-state supramolecular fluorescence host systems with thiophene units.



2. Results and discussion

We attempted to prepare the supramolecular thiophene host system by crystallization using guest solutions. First, a MeOH molecule was used as a guest. A mixture of (1*R*,2*S*)-**1** and **2** was dissolved in MeOH, and left to stand at room temperature. After 3–5 days, a colorless complex **I** was obtained. On the basis of X-ray crystal structure analysis, this complex was observed to comprise (1*R*,2*S*)-**1** and **2** and include MeOH as guest molecules, as shown in Figure 1.

The stoichiometry of complex **I** is (1*R*,2*S*)-**1**/**2**/MeOH=1:1:1, and its space group is *C*2. This complex has a characteristic pseudo-2_1-helical columnar network structure along the *b*-axis (Fig. 1a and b). This structure is mainly formed because of two types of bonds: (1) the hydrogen and ionic bonds between the ammonium hydrogen atom of the protonated amine (shown in Fig. 1 in green) and the carboxylate oxygen atom of the carboxylic acid anion (shown in Fig. 1 in blue) and (2) a thiophene–benzene edge-to-face interaction (2.81 Å; indicated in Fig. 1a by the red arrow *A*) between the hydrogen atom of the thiophene ring of **2** and the benzene ring of (1*R*,2*S*)-**1**.[6] As is expected, complex **I** is formed by the self-assembly of the helical column, resulting in the formation of two types of chiral channel-like cavities (indicated in Fig. 1c by red and blue circles). Characteristically, these channel-like cavities are maintained by two thiophene–benzene edge-to-face interactions (2.77 and 2.71 Å; indicated in Fig. 1c by the red arrow *B* and the blue arrow *C*, respectively) between the hydrogen atom of the thiophene ring in **2** and the benzene ring of (1*R*,2*S*)-**1**.[6] The guest MeOH molecules (shown in Fig. 1 in red) are trapped one-dimensionally along the direction of the cavity. Each MeOH molecule is connected to the column by two types of interactions. The first type of interaction is because of the hydrogen bonds between the hydroxyl group of the MeOH molecule and the carboxyl group of **2**, and between the hydroxyl group of the MeOH molecule and the hydroxyl group of (1*R*,2*S*)-**1**. The other type of interaction is the CH–π interaction (2.77 Å; indicated in Fig. 1c by the purple arrow *D*) between the α-proton of MeOH and the thiophene ring of **2**.[6]

In complex **I**, the channel-like cavities are formed by the packing arrangement of the helical columns without strong interactions. Therefore, the size and shape of these cavities may vary depending on the guest molecules, and a variety of guest molecules may be included into the thiophene host complex. In order to study this process, three other types of *n*-alkyl alcohol with longer alkyl chains (EtOH, *n*-PrOH, and *n*-BuOH) were used as guest molecules and their inclusion mechanism was investigated. Good-quality colorless complexes, **II**, **III**, and **IV**, were obtained from the EtOH, *n*-PrOH, and *n*-BuOH solutions, respectively, and their crystal structures were analyzed. The crystal structure of complex **II** containing guest EtOH molecules is shown in Figure 2.[4]

The X-ray analysis of complex **II** revealed that its stoichiometry is the same as that of complex **I**, i.e., (1*R*,2*S*)-**1**/**2**/EtOH=1:1:1. However, its space group is $P2_12_12_1$. Although the component molecule of **2** is disordered, this complex has a 2_1-helical columnar network structure (Fig. 2a). Further, the helical columnar structure in complex **II** is formed by the hydrogen and ionic bonds between the ammonium hydrogen atoms of the protonated amine (shown in Fig. 2 in green) and the carboxylate oxygen atom of the carboxylic

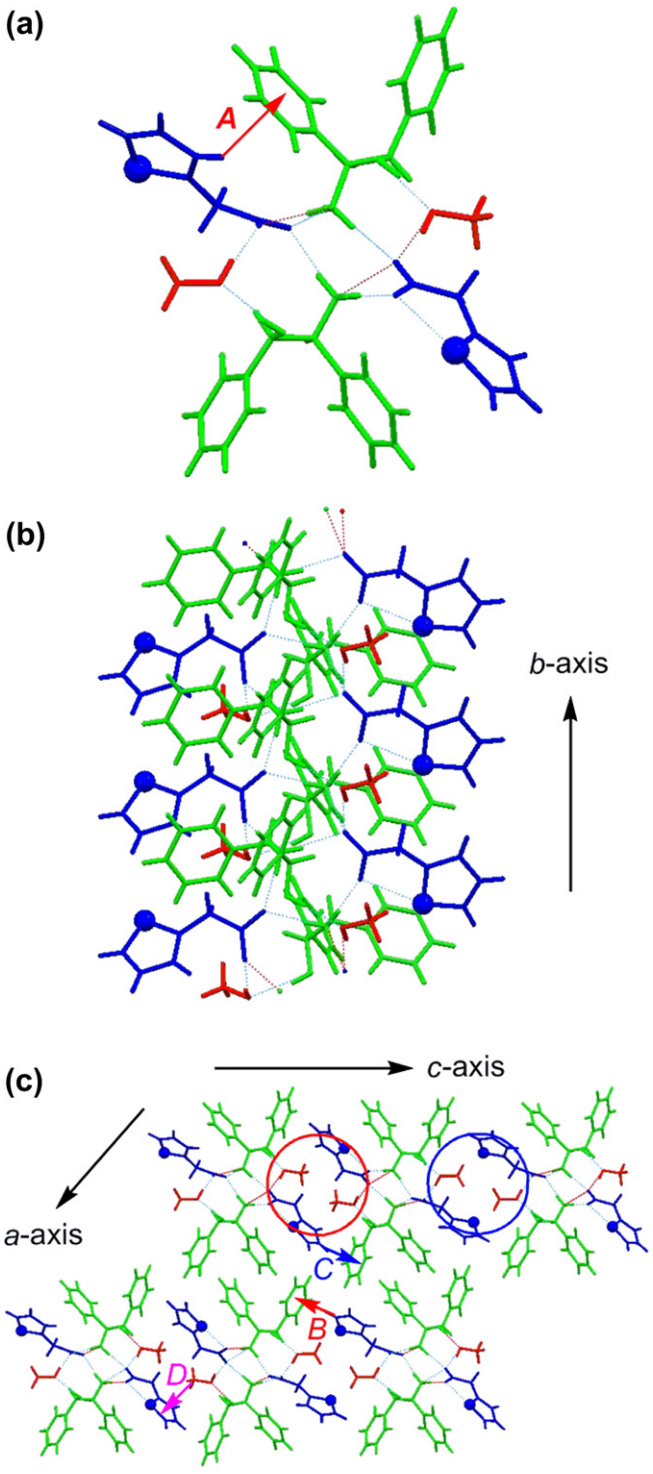


Figure 1. Crystal structure of complex **I**. (1*R*,2*S*)-**1**, **2**, and MeOH molecules are indicated in green, blue, and red, respectively. (a) Pseudo-2_1-helical columnar hydrogen- and ionic-bonded network observed along the *b*-axis. The red arrow (*A*) indicates a thiophene–benzene edge-to-face interaction. (b) View along the *a*-axis. (c) Packing structure observed along the *b*-axis. The red arrow (*B*) and blue arrow (*C*) indicate thiophene–benzene edge-to-face interactions. The purple arrow (*D*) indicates a CH–π interaction. The red and blue circles indicate the two types of channel-like cavities.

acid anion (shown in Fig. 2 in blue) and by the thiophene–benzene edge-to-face interactions (2.94 Å; indicated in Fig. 2b by the red arrows *A*) between the hydrogen atom of the thiophene ring of **2** and the benzene ring of (1*R*,2*S*)-**1**.[6] Complex **II** also has channel-like cavities formed by the assembly of the helical columns. These cavities are maintained by the thiophene–benzene edge-to-face

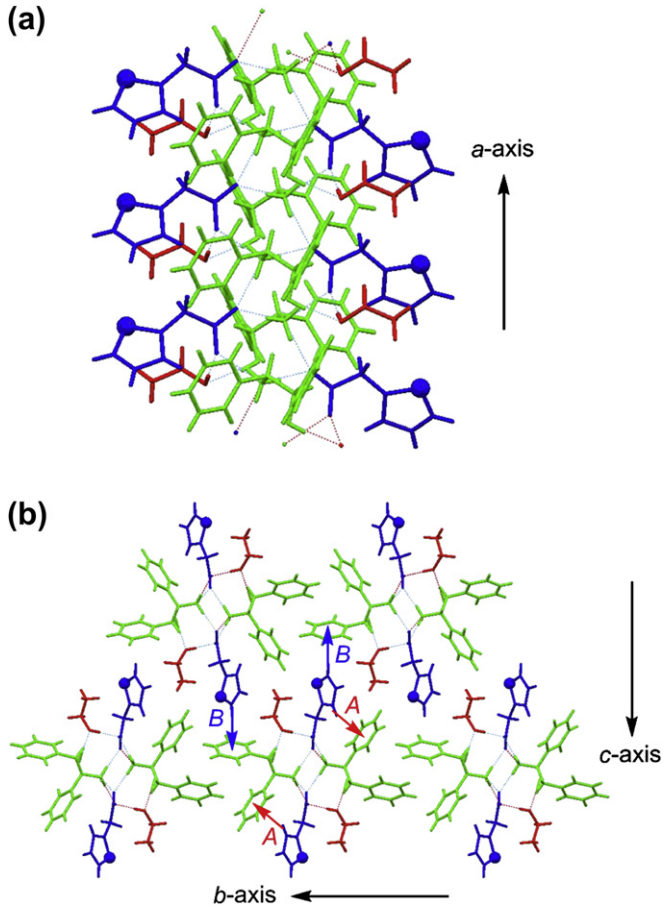


Figure 2. Crystal structure of complex **II**. (1*R*,2*S*)-**1**, **2**, and EtOH molecules are indicated in green, blue, and red, respectively. (a) 2_1-Helical columnar hydrogen- and ionic-bonded network observed along the *b*-axis. (b) Packing structure observed along the *a*-axis. The red arrow (*A*) and blue arrow (*B*) indicate thiophene–benzene edge-to-face interactions.

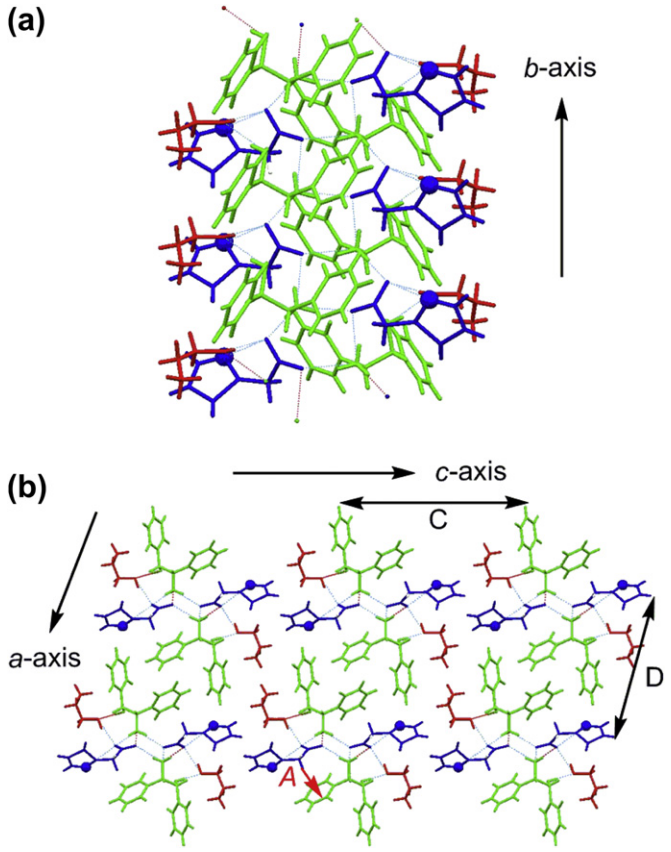


Figure 3. Crystal structure of complex **III**. (1*R*,2*S*)-**1**, **2**, and *n*-PrOH molecules are indicated in green, blue, and red, respectively. (a) 2_1-Helical columnar hydrogen- and ionic-bonded network observed along the *a*-axis. (b) Packing structure observed along the *b*-axis. The red arrow (*A*) indicates CH–π interaction.

intercolumnar interactions (2.75 Å; indicated in Fig. 2b by the blue arrows *B*) between the **2** and (1*R*,2*S*)-**1** molecules.[6] The guest EtOH molecules are included into the channel-like cavities by hydrogen bonds in the same manner as that observed in complex **I** (Fig. 2b). In complex **II**, the CH–π interaction between the EtOH molecules and the thiophene ring of **2** is not observed.[6] Interestingly, in this complex, the packing arrangement of the helical column is quite different from that observed in complex **I**. In complex **I**, two guest MeOH molecules are included into one channel-like cavity along the column. Moreover, the MeOH molecules are arranged in two manners in two types of cavities (indicated in Fig. 1c by red and blue circles, respectively). In contrast, in complex **II**, one guest EtOH molecule is included into one channel-like cavity along the column. In addition, the arrangement of the helical column in complex **II** is different from that in complex **I**. In complex **I**, the two thiophene rings of **2** along one helical column are in opposite directions (Fig. 1b). In contrast, in complex **II**, the two thiophene rings of **2** are in the same direction (Fig. 2a). These results suggest that guest molecules are included in this thiophene host system by varying the style and packing arrangement of the helical columns accordingly.

Furthermore, the crystal structures of complexes **III** and **IV**, which contain *n*-PrOH and *n*-BuOH, respectively, are studied; these structures are shown in Figures 3 and 4, respectively.

X-ray analyses revealed that these host complexes have the same stoichiometry as that of complexes **I** and **II**, i.e., (1*R*,2*S*)-**1**/**2**/*n*-PrOH (or *n*-BuOH)=1:1:1, and their space group is $P2_1$. Although the component molecule of **2** is disordered in complex **III**, complexes **III** and **IV** have the same 2_1-helical columnar hydrogen- and ionic-bonded network structure (shown in Figs. 3a and 4a, respectively). In contrast to the helical columns in complexes **I** and **II**, the helical column in these complexes is maintained by the CH–π intracolumnar interactions (2.80 and 2.69 Å; indicated in Figs. 3b and 4b, respectively, by red arrows *A*) between the hydrogen atom of the acetic acid group of **2** and the benzene ring of (1*R*,2*S*)-**1**.[6] The chiral channel-like cavities of these complexes are formed by the assembly of this helical column (shown in Figs. 3b and 4b, respectively). Guest *n*-PrOH and *n*-BuOH molecules (indicated in Figs. 3 and 4, respectively, in red) are inserted into the cavities because of the same hydrogen bonds as those in the cases of complexes **I** and **II**. The CH–π interaction (2.76 Å; indicated in Fig. 4b by blue arrows *B*) between the α-proton of *n*-BuOH and the thiophene ring of **2** is observed only in complex **IV**.[6]

As is expected, the packing arrangement of the helical columns in complexes **III** and **IV** is quite different from that in complexes **I** and **II** (as observed in Figs. 1c, 2b, 3b, and 4b). Moreover, in complex **II**, although sulfur atoms in the thiophene ring of **2** are in the direction of the guest molecule along the helical column (Fig. 2b), in complexes **III** and **IV**, these sulfur atoms are in the direction of the benzene ring of (1*R*,2*S*)-**1** (Figs. 3b and 4b, respectively). A comparison between the sizes of the channel-like cavities of **III** and **IV** reveals that the sizes depend on the type of the guest molecule. When the guest molecule is changed from *n*-PrOH to *n*-BuOH, the distance between the shared helical columns along the *c*-axis (indicated in Figs. 3b and 4b by *C*) increases from 16.21 to 16.41 Å. In contrast, the distance between the shared helical columns along the *a*-axis (indicated in Figs. 3b and 4b by *D*) reduces from 12.66 to

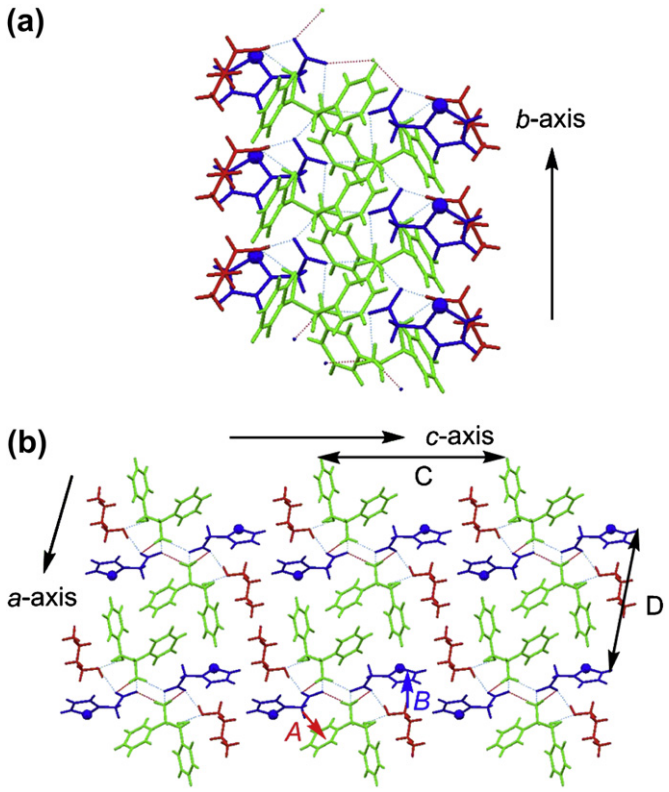


Figure 4. Crystal structure of complex **IV**. (1*R*,2*S*)-**1**, **2**, and *n*-BuOH molecules are indicated in green, blue, and red, respectively. (a) 2_1-Helical columnar hydrogen- and ionic-bonded network observed along the *a*-axis. (b) Packing structure observed along the *b*-axis. The red arrow (*A*) and blue arrow (*B*) indicate CH–π interactions.

12.51 Å. From these results, it is inferred that guest molecules can be included in the thiophene host system by changing the style and helical structure and packing arrangement of the helical columns accordingly.

3. Conclusion

On the basis of the X-ray crystallographic analyses, this two-component supramolecular thiophene host system was observed to comprise (1*R*,2*S*)-2-amino-1,2-diphenylethanol [(1*R*,2*S*)-**1**] and 2-thienylacetic acid (**2**). Suitable channel-like cavities are formed via recognition of the guest molecule in two tuning processes. In one process, a helical columnar network structure suitable for the guest molecule is formed by tuning the direction of the thiophene ring of **2**. In the other process, channel-like cavities suitable for the guest molecule are formed by varying the packing arrangement of the helical column. The effect of the solvent on the hydrogen-bonded network structure has not been widely studied thus far.[7] Our study is expected to be useful in analyzing the inclusion mechanisms of multicomponent host systems and in designing new types of molecular host systems, especially novel chiral supramolecular fluorescence host systems possessing a thiophene unit.

4. Experimental

4.1. General methods

All reagents were used directly as obtained commercially. Component molecule (1*R*,2*S*)-**1** was purchased from TOKYO CHEMICAL INDUSTRY Co., Ltd. Component molecule **2** and four guest solvents were purchased from Wako Pure Chemical Industry.

4.2. Formation of complex by crystallization from guest solution

(1*R*,2*S*)-**1** (10 mg, 0.047 mmol) and **2** (8 mg, 0.056 mmol) were dissolved in each guest solution (3 mL) under heat and left to stand at room temperature. After 3–5 days, a large number of crystals [crystals of complex **I** including MeOH (9 mg), crystals of complex **II** including EtOH (8 mg), crystals of complex **III** including *n*-PrOH (8 mg), and crystals of complex **IV** including *n*-BuOH (7 mg)] were obtained. The weight of crystal is the total weight of obtained crystals in one batch.

4.3. X-ray crystallographic study of crystal I

The X-ray diffraction data for single crystals were collected using *Bruker Apex*. The crystal structures were solved by the direct method[8] and refined by full-matrix least-squares using SHELXL97.[8] The diagrams were drawn using PLATON.[9] The absorption corrections were performed using SADABS.[10] The nonhydrogen atoms were refined with anisotropic displacement parameters, and the hydrogen atoms were included in the models at their calculated positions in the riding-model approximation. Crystallographic data of **I**: $2C_{14}H_{15}NO\cdot 2C_6H_6O_2S\cdot 2CH_4O$, M=774.96, Monoclinic, space group $C2$, a=35.488(3), b=5.7117(4), c=24.8421(19) Å, β=128.7950(10)°, V=3924.6(5) Å^3, Z=4, D_c=1.312 g cm^{-3}, μ(Mo Kα)=0.191 mm^{-1}, 12,296 reflections measured, 7373 unique, final $R(F^2)$=0.0567 using 6163 reflections with $I>2.0\sigma(I)$, R(all data)=0.0703, T=115(2) K. CCDC 764089. Crystallographic data of **II**[4]: $C_{14}H_{15}NO\cdot C_6H_6O_2S\cdot C_2H_6O$, M=401.51, Orthorhombic, space group $P2_12_12_1$, a=5.6782(5), b=14.9054(12), c=24.921(2) Å, V=2109.3(3) Å^3, Z=4, D_c=1.264 g cm^{-3}, μ(Mo Kα)=0.180 mm^{-1}, 129,612 reflections measured, 4822 unique, final $R(F^2)$=0.0708 using 4158 reflections with $I>2.0\sigma(I)$, R(all data)=0.0845, T=115(2) K. CCDC 746697. Crystallographic data of **III**: $C_{14}H_{15}NO\cdot C_6H_6O_2S\cdot C_3H_8O$, M=415.53, Monoclinic, space group $P2_1$, a=12.6628(13), b=5.5068(6), c=16.2066(16) Å, β=104.606(2)°, V=1093.6(2) Å^3, Z=2, D_c=1.262 g cm^{-3}, μ(Mo Kα)=0.176 mm^{-1}, 6653 reflections measured, 4466 unique, final $R(F^2)$=0.0750 using 3580 reflections with $I>2.0\sigma(I)$, R(all data)=0.0948, T=115(2) K. CCDC 764090. Crystallographic data of **IV**: $C_{14}H_{15}NO\cdot C_6H_6O_2S\cdot C_4H_{10}O$, M=429.56, Monoclinic, space group $P2_1$, a=12.5130(13), b=5.5796(6), c=16.4093(18) Å, β=100.127(2)°, V=1127.8(2) Å^3, Z=2, D_c=1.265 g cm^{-3}, μ(Mo Kα)=0.173 mm^{-1}, 7049 reflections measured, 4804 unique, final $R(F^2)$=0.0651 using 3894 reflections with $I>2.0\sigma(I)$, R(all data)=0.0841, T=115(2) K. CCDC 764091. Crystallographic data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336 033; deposit@ccdc.cam.ac.uk).

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Supplementary data

Supplementary data for this article can be found in the online version, at doi:10.1016/j.tet.2010.05.098.

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