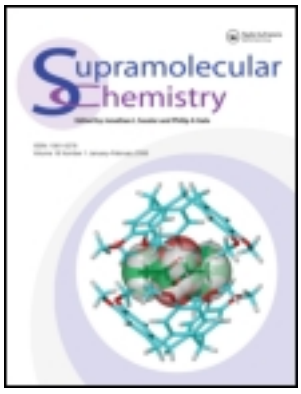


Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gsch20

Synthesis of novel dihydroxydiphosphines and dihydroxydicarboxylic acids having a tetra(thio-1,3-phenylene-2-yl) backbone

Yuki Akahira [a], Kazutoshi Nagata [a], Naoya Morohashi [a] & Tetsutaro Hattori [a]
[a] Department of Biomolecular Engineering, Graduate School of Engineering, Tohoku University, 6-6-11 Aramaki-Aoba, Aoba-ku, Sendai, 980-8579, Japan

Available online: 22 Feb 2011

To cite this article: Yuki Akahira, Kazutoshi Nagata, Naoya Morohashi & Tetsutaro Hattori (2011): Synthesis of novel dihydroxydiphosphines and dihydroxydicarboxylic acids having a tetra(thio-1,3-phenylene-2-yl) backbone, Supramolecular Chemistry, 23:01-02, 144-155

To link to this article: http://dx.doi.org/10.1080/10610278.2010.514913

Supramolecular Chemistry
Vol. 23, Nos. 1–2, January–February 2011, 144–155

Synthesis of novel dihydroxydiphosphines and dihydroxydicarboxylic acids having a tetra(thio-1,3-phenylene-2-yl) backbone

Yuki Akahira, Kazutoshi Nagata, Naoya Morohashi* and Tetsutaro Hattori*

Department of Biomolecular Engineering, Graduate School of Engineering, Tohoku University, 6-6-11 Aramaki-Aoba, Aoba-ku, Sendai 980-8579, Japan

(*Received 5 July 2010; final version received 6 August 2010*)

Novel tetradentate PPh_2–OH hybrid ligands **5** and CO_2H–OH hybrid ligands **6** have been successfully synthesised from tetra(thio-5-*tert*-butyl-2-hydroxy-1,3-phenylene) ($\mathbf{2_4}$) by replacing the hydroxy groups at both the 2-position and either the 2′-, 2″- or 2‴-position with diphenylphosphino or carboxy groups, after converting into bistriflates **8**; the substitution positions of newly introduced substituents are denoted hereafter by superscript 1,*n* as $\mathbf{5}^{1,n}$. Bistriflates $\mathbf{8}^{1,3}$ and $\mathbf{8}^{1,4}$ can be readily prepared by the regioselective detriflation of tetrakistriflate **7** with tetrabutylammonium fluoride (TBAF), conducted under different conditions. On the other hand, the preparation of bistriflate $\mathbf{8}^{1,2}$ requires a four-step process through protection/deprotection. Thus, the silylation of tetraol $\mathbf{2_4}$ with an excess of 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane gives *O*,*O*′- and *O*″,*O*‴-disiloxane-1,3-diyl-capped derivative **9**. One of the two disiloxane bridges is removed by the treatment with 0.5 mol equiv. of TBAF to give diol **10**. Triflation of diol **10**, followed by the removal of the remaining disiloxane bridge, affords bistriflate $\mathbf{8}^{1,2}$. Bistriflates **8** are subjected to palladium-catalysed phosphorylation, followed by the reduction of the resulting phosphine oxide $\mathbf{12}^{1,n}$ to give PPh_2–OH hybrid ligands $\mathbf{5}^{1,n}$ ($n = 2$–4), while CO_2H–OH hybrid ligands $\mathbf{6}^{1,n}$ ($n = 3,4$) are obtained from **8** via acetylation of the remaining hydroxy groups, followed by palladium-catalysed methoxycarbonylation of the TfO moieties, and subsequent hydrolysis of the resulting tetraesters **14**. X-ray structural analyses of dicarboxylic acids $\mathbf{6}^{1,3}$ and $\mathbf{6}^{1,4}$ reveal that they form quite different 3D network structures to each other. Interestingly, $\mathbf{6}^{1,4}$ constructs a porous channel with a potential for serving as a supramolecular host, by the stacking of its cyclic dimer that is formed by intermolecular hydrogen bondings between the carboxy groups.

Keywords: tetra(thio-*m*-phenylene); regioselective synthesis; hydroxyphosphine; hydroxyacid

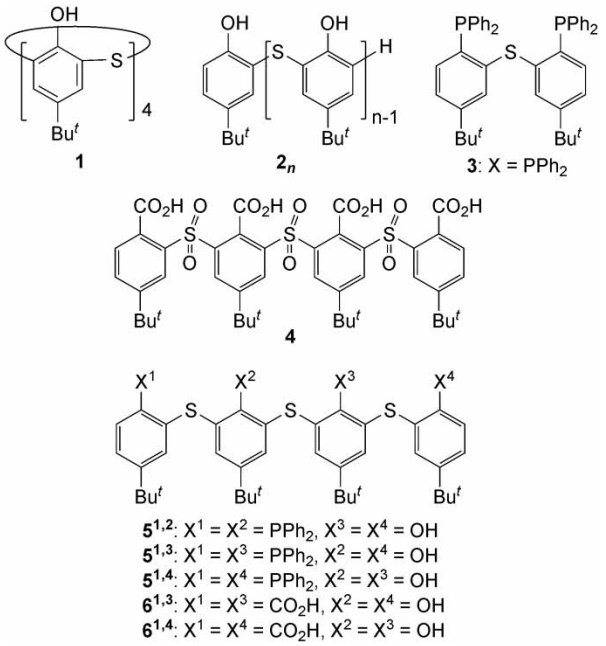
Introduction

The design of multidentate ligands has been a subject of intense research activity in the fields of developing sensors, metal extractants, catalysts and so on (*1–5*). Thiacalix[4]arene **1** (*6–8*), and its sulphur-oxidised derivatives, sulphinyl and sulphonylcalix[4]arenes are known to serve as multidentate ligands with high metal-binding ability, due to the cooperative coordination of the phenolic hydroxy groups with the bridging sulphur atomic groups (*9*), and have successfully been utilised for extractants (*10–13*), sensing reagents (*8*, *14*, *15*), ligands for cluster complexes (*9*) and catalysts (*16–18*), and so on. In some applications of thiacalix[4]arene **1** and its sulphur-oxidised derivatives as multidentate ligands, however, there are still problems to be addressed. For example, (1) they can extract metal ions only in relatively high pH regions due to the low acidity of the phenolic hydroxy groups. (2) They are not suitable as ligands for late transition metal catalysts, such as palladium and rhodium complexes, because the formation of strong O—metal bonds prevents necessary changes in the oxidation number of the metal centre during catalytic cycles. One solution for these difficulties may be to replace the hydroxy groups with other functions, such as carboxy or sulpho groups in the former case and phosphino or secondary amino groups in the latter case. However, the cleavage of the aryl-oxygen bonds of calix[4]arenes is quite difficult even by employing conventional C—O bond cleavage reactions of aryl triflates or other esters by using palladium or nickel catalysts because of steric hindrance caused by the sterically crowded cyclic structure (*19–21*).

*Corresponding authors. Email: morohashi@orgsynth.che.tohoku.ac.jp; hattori@orgsynth.che.tohoku.ac.jp

ISSN 1061-0278 print/ISSN 1029-0478 online

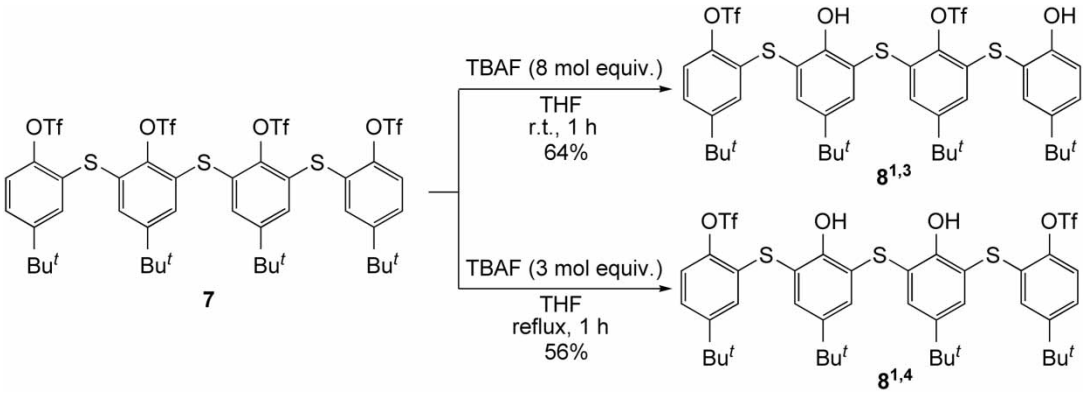
DOI: 10.1080/10610278.2010.514913
http://www.informaworld.com



We have recently reported that an acyclic analogue of thiacalix[4]arene **2**$_4$ exhibits comparable complexation ability to thiacalix[4]arene **1** towards soft to intermediate metal ions in solvent extraction experiments (*22*, *23*). We have also reported that diphosphine **3** (*24*) and tetracarboxylic acid **4** (*25*) are readily prepared from acyclic dimer **2**$_2$ and tetramer **2**$_4$ by using palladium-catalysed phosphorylation (*26*, *27*) and methoxycarbonylation (*28–30*) as a key step, respectively. Diphosphine **3** was found to bind to a palladium(II) ion with different coordination modes, i.e. bidentate P–P and tridentate P–S–P, depending on the electron density of the palladium centre (*24*). In addition, the epithio linkage could coordinate to two palladium ions by using its two lone pairs, which enabled diphosphine **3** to serve as a P–S ligand to form a dinuclear palladium complex. These properties are of special interest for catalytic applications. On the other hand, tetracarboxylic acid **4** extracted lanthanide ions even at pH 3.0 in solvent extraction experiments (*25*), indicating that **4** has higher extractability towards lanthanide ions than sulphonylcalix[4]arene. These observations indicate that acyclic oligo(thio-1,3-phenylene)s provide useful scaffolds for developing diverse multidentate ligands with a coordination mode, binding ability and metal selectivity that are suitable for serving their respective purposes. Herein, we report the synthesis of novel tetradentate PPh_2–OH hybrid ligands **5**^{1,n} ($n = 2$–4) and CO_2H–OH hybrid ligands **6**^{1,n} ($n = 3,4$), having a tetra(thio-1,3-phenylene) skeleton by converting two hydroxy groups of tetraol **2**$_4$ into diphenylphosphino and carboxy groups, respectively. X-ray structural analyses of CO_2H–OH hybrid ligands **6**^{1,n} ($n = 3,4$) are also reported.

Results and discussion

First, regioselective synthesis of bistriflates **8**^{1,n} ($n = 2$–4) was investigated with the intention of applying palladium-catalysed phosphorylation and methoxycarbonylation to the cleavage of the aryl-oxygen bonds of tetraol **2**$_4$. It is well known in calixarene chemistry that the dialkylation of calix[4]arenes with alkyl halides in the presence of a base preferentially proceeds at the distal hydroxy groups by virtue of a circular intramolecular hydrogen bonding in the monoalkylated intermediate (*31*, *32*), which provides an easy access to *O*,*O*″-dialkylated calix[4]arenes. The preferential *O*,*O*″-disubstitution is also the case with the bistriflation of thiacalix[4]arene **1** with triflic anhydride in the presence of pyridine (*33*). However, attempts to selectively esterify two hydroxy groups of tetraol **2**$_4$ with triflic anhydride under various reaction conditions were not fruitful. We then tried detriflation of readily preparable tetrakistriflate **7** (*25*). To our pleasure, the reaction of tetrakistriflate **7** with 8.0 mol equiv. of tetrabutylammonium fluoride (TBAF) in THF at room temperature gave bistriflate **8**^{1,3} as a major product (64%), while the same reaction carried out under refluxing conditions using a reduced amount of TBAF gave bistriflate **8**^{1,4} in 56% yield (Scheme 1). The reaction mechanisms for the selective formation of **8**^{1,3} and **8**^{1,4} are not clear at present. The fast atom bombardment (FAB) mass spectra of **8**^{1,3} and **8**^{1,4} exhibited the molecular ion peak at 954 (M^+), indicating that both of them are bistriflates. The ^{1}H NMR spectrum of **8**^{1,3} exhibited four singlets (9H each) for the *tert*-butyl protons, two pairs of doublets (1H each) for the aryl protons on the internal benzene rings and two sets of two doublets (1H each) and one double-doublet (1H) for the aryl protons on the terminal benzene rings. The unsymmetrical spectral pattern indicates that it is 1,2- or 1,3-bistriflate. However, the comparison of the physical properties of bistriflate **8**^{1,3} with those of authentic 1,2-bistriflate **8**^{1,2} prepared by a four-step process through protection/deprotection (vide infra) revealed that they are not the same compound. Therefore, **8**^{1,3} was assigned to be 1,3-bistriflate, which coincides with the assignment based on an X-ray crystallographic analysis after conversion into dicarboxylic acid **6**^{1,3} (vide infra). On the other hand, the ^{1}H NMR spectrum of **8**^{1,4} exhibited two singlets (18H each) for the *tert*-butyl protons, a pair of doublets (2H each) for the aryl protons on the internal benzene rings and a set of two doublets (2H each) and one double-doublet (2H) for the aryl protons on the terminal benzene rings; the magnetic equivalences suggest a C_2-*symmetric* structure, i.e. 1,4- or 2,3-bistriflate. Compound **8**^{1,4} was finally assigned to be 1,4-bistriflate by chemical correlation with

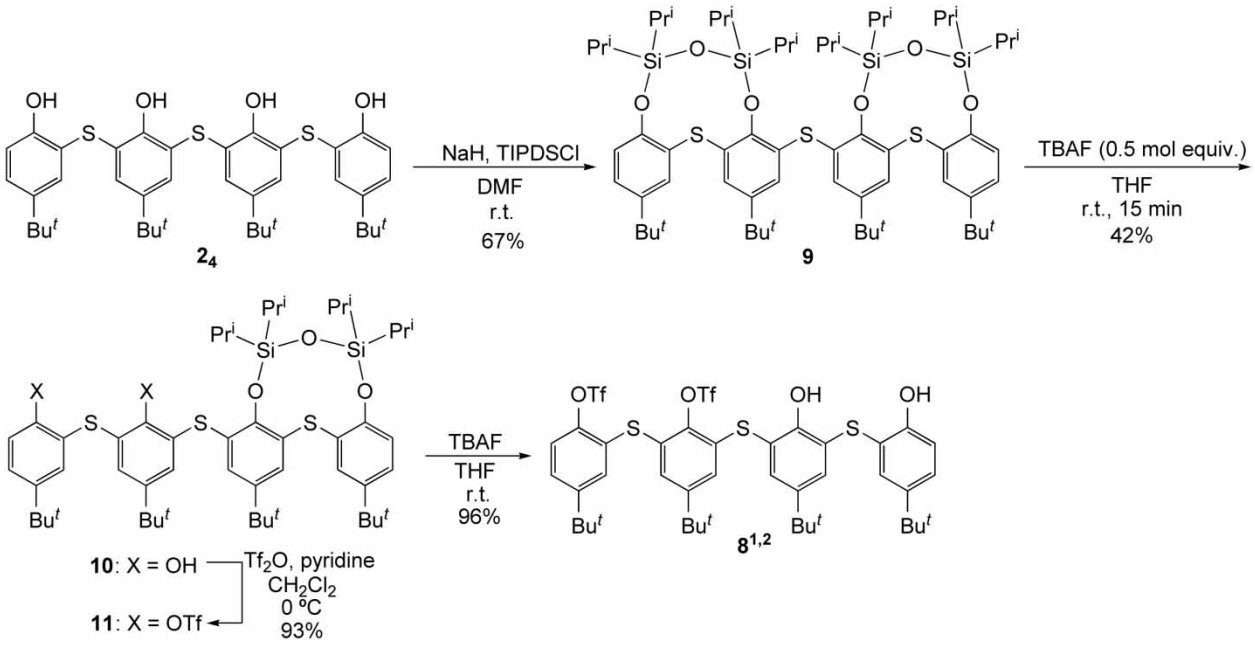


Scheme 1. Synthesis of 1,3- and 1,4-bistriflates $\mathbf{8}^{1,3}$ and $\mathbf{8}^{1,4}$.

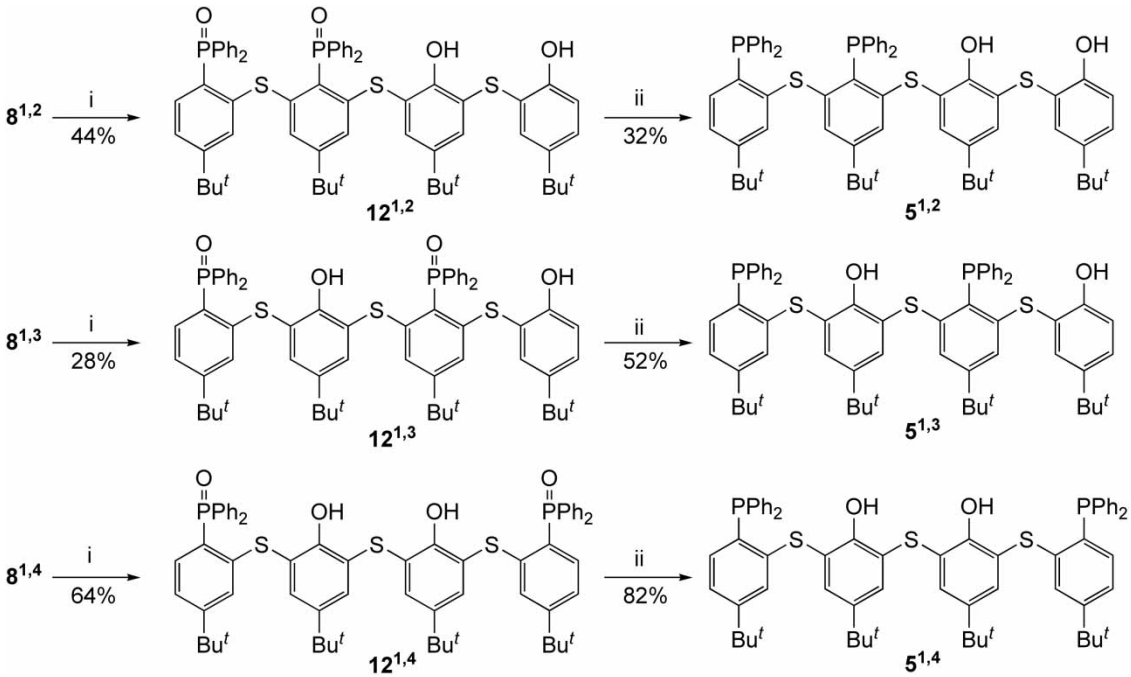
bis(phosphine oxide) $\mathbf{12}^{1,4}$, as well as an X-ray crystallographic analysis after conversion into dicarboxylic acid $\mathbf{6}^{1,4}$ (vide infra).

It has been reported from our laboratory that two adjacent hydroxy groups of calix[4]arenes can be protected with 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (TIPDSCl), which enables otherwise difficult regio- and stereoselective synthesis of *syn*- and *anti*-*O*,*O*′-dialkylated calix[4]arenes via dialkylation of the remaining hydroxy groups, followed by the deprotection of the TIPDS moiety (*34*). We supposed that a similar process through protection/deprotection would provide an easy access to 1,2-bistriflate $\mathbf{8}^{1,2}$ (Scheme 2). The treatment of tetraol $\mathbf{2_4}$ with 2.4 mol equiv. of TIPDSCl in the presence of NaH afforded *O*,*O*′- and *O*″,*O*‴-disiloxane-1,3-diyl-capped derivative **9** in a good yield. One of the two disiloxane bridges could be removed from **9** by a short treatment with 0.5 mol equiv. of TBAF, giving diol **10** in 42% yield with the recovery of **9** (39%). Increasing the amount of TBAF and/or prolonging the reaction time caused further desilylation of diol **10**. Triflation of diol **10** followed by the deprotection of the remaining disiloxane gave 1,2-bistriflate $\mathbf{8}^{1,2}$ in a total of 25% yield based on the starting tetraol $\mathbf{2_4}$.

As the desired bistriflates **8** were in hand, their transformation into diphosphines **5** was investigated. Bistriflates **8** were submitted to palladium-catalysed phosphorylation (*26*, *27*) with $Ph_2P(O)H$ to give bis(pho-



Scheme 2. Synthesis of 1,2-bistriflate $\mathbf{8}^{1,2}$.

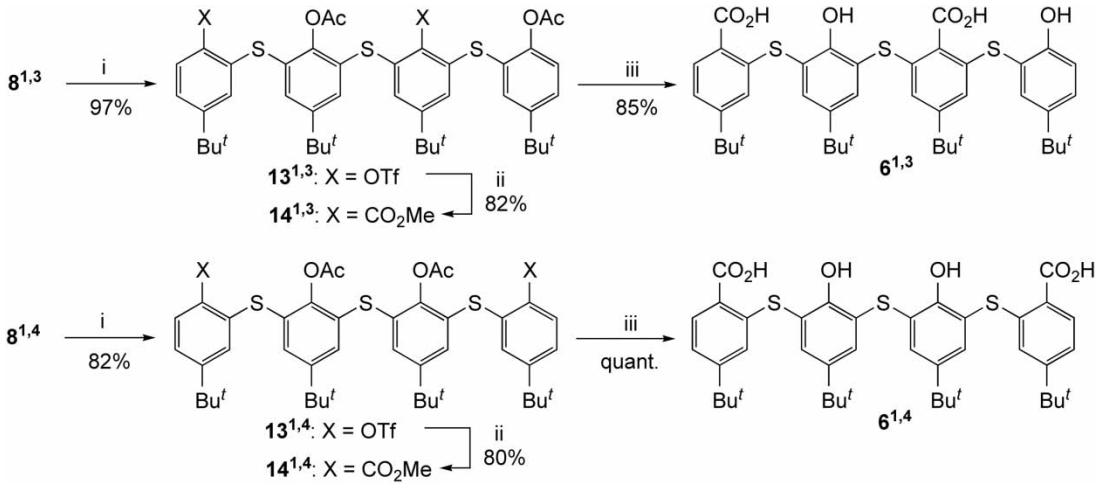


Scheme 3. Synthesis of diphosphines $\mathbf{5}^{1,2}$, $\mathbf{5}^{1,3}$ and $\mathbf{5}^{1,4}$. Reagents and conditions: (i) $Ph_2P(O)H$, $Pd(OAc)_2$, dppb, $^iPr_2EtN$, DMSO, 120°C and (ii) $HSiCl_3$, Et_3N, toluene, reflux.

sphine oxide)s **12**, which were then reduced with $HSiCl_3$ to give diphosphines **5** in varying yields, depending on the substitution positions of the two diphenylphosphino moieties (Scheme 3). Bis(phosphine oxide) $\mathbf{12}^{1,4}$ exhibited a resonance pattern agreeable to the *C_2-symmetric* structure in the ^{1}H NMR spectrum. The signals for the two adjacent protons on the terminal benzene ring (2H each) were found to be coupled to the phosphorus atom ($^3J_{H-P} = 12.7$ and $^4J_{H-P} = 1.9$ Hz, respectively), although another signal for the terminal benzene ring was unclear because of overlapping with the signals for the diphenylphosphinoyl moieties. The H–P couplings allowed us to assign the compound to be 1,4-bis(phosphine oxide), which coincides with the assignment based on the X-ray crystallographic analysis of dicarboxylic acid $\mathbf{6}^{1,4}$ (vide infra). Diphosphines **5**, bearing three different types of coordination sites, are expected to serve as multidentate ligands for the construction of heteronuclear multimetallic complexes (*16*, *24*).

The methoxycarbonylation (*28–30*) of bistriflate $\mathbf{8}^{1,4}$ was first attempted in the presence of 0.4 mol equiv. of $Pd(OAc)_2$, 0.8 mol equiv. of dppb and a large excess of Hunig's base in a 2:1 mixture of DMSO and methanol under 1 atm of CO atmosphere at 70°C. However, the reaction was sluggish and did not afford the desired dimethyl ester but a trace amount of monomethyl ester with the recovery of most of the starting bistriflate. We assumed that the phenolic hydroxy groups of $\mathbf{8}^{1,4}$ might prevent the reaction. The hydroxy groups of $\mathbf{8}^{1,4}$ were then acetylated with acetic anhydride and the resulting diacetate $\mathbf{13}^{1,4}$ was submitted to the methoxycarbonylation, which proceeded smoothly to give dimethyl ester $\mathbf{14}^{1,4}$ in 80% yield (Scheme 4). Alkaline hydrolysis of $\mathbf{14}^{1,4}$ gave the desired 1,4-dicarboxylic acid $\mathbf{6}^{1,4}$ in quantitative yield. In the same manner, 1,3-dicarboxylic acid $\mathbf{6}^{1,3}$ could be prepared from bistriflate $\mathbf{8}^{1,3}$ in a total of 68% yield. On the contrary, the diacetate of 1,2-bistriflare $\mathbf{8}^{1,2}$ resisted the methoxycarbonylation, presumably due to steric reasons, and we could not find any good synthetic route to 1,2-dicarboxylic acid $\mathbf{6}^{1,2}$.

X-ray crystallographic analyses of dicarboxylic acids $\mathbf{6}^{1,3}$ and $\mathbf{6}^{1,4}$ were carried out to determine the regiochemistries of $\mathbf{6}^{1,3}$ and $\mathbf{6}^{1,4}$, as well as those of bistriflates $\mathbf{8}^{1,3}$ and $\mathbf{8}^{1,4}$, and to understand how the arrangement of the carboxy and hydroxy groups effects on the stereostructures of **6**. Single crystals of $\mathbf{6}^{1,3}$ and $\mathbf{6}^{1,4}$ were grown by diffusion of hexane vapour into an acetone solution of $\mathbf{6}^{1,3}$ or diffusion of cyclohexane vapour into a benzene solution of $\mathbf{6}^{1,4}$. The X-ray structure of $\mathbf{6}^{1,3}$ revealed that the two carboxy groups reside at the 2, 2″-positions (Figure 1), which established the regiochemistry of dicarboxylic acid $\mathbf{6}^{1,3}$, as well as that of bistriflate $\mathbf{8}^{1,3}$, to be 1,3. The molecule of $\mathbf{6}^{1,3}$ adopts a bent structure, in which an intramolecular hydrogen bonding is observed between the hydroxy group at the 2′-postion and the carboxy group at the 2″-postion; the interatomic distance



Scheme 4. Synthesis of dicarboxylic acids $\mathbf{6}^{1,3}$ and $\mathbf{6}^{1,4}$. Reagents and conditions: (i) Ac_2O, pyridine, CH_2Cl_2, rt; (ii) CO (1 atm), MeOH, $Pd(OAc)_2$, dppb, $^{i}Pr_2EtN$, DMSO, 70°C and (iii) KOH, EtOH–H_2O (10:1), reflux.

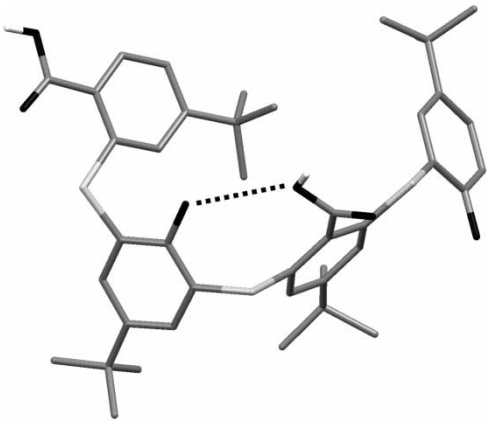


Figure 1. X-ray structure of $\mathbf{6}^{1,3}$. Hydrogen atoms except those of carboxy groups, disordered carbon atoms and included solvent molecules are omitted for clarity. Dotted line represents intramolecular hydrogen bonding.

between the two oxygen atoms is 3.129 (3) Å. In addition, one molecule is connected with two neighbouring molecules by intermolecular hydrogen bondings between each other's carboxy groups at the same position, by which a zigzag structure is created along the *a*-axis (Figure 2); the average bond length of the C(═O)O—H—O═C hydrogen bondings is 1.721 Å. On the other hand, the X-ray structure of $\mathbf{6}^{1,4}$ revealed that the two carboxy groups reside at the 2, 2‴-positions (Figure 3), which established the regiochemistry of dicarboxylic acid $\mathbf{6}^{1,4}$, as well as that of triflate $\mathbf{8}^{1,4}$, to be 1,4. In the crystal of $\mathbf{6}^{1,4}$, an intramolecular hydrogen bonding is observed between the hydroxy groups at the 2′- and 2″-positions; the interatomic distance between the two oxygen atoms is 2.853 (5) Å. The two molecules of $\mathbf{6}^{1,4}$ are associated by intermolecular hydrogen bondings between the carboxy groups to form a cyclic dimer; the average

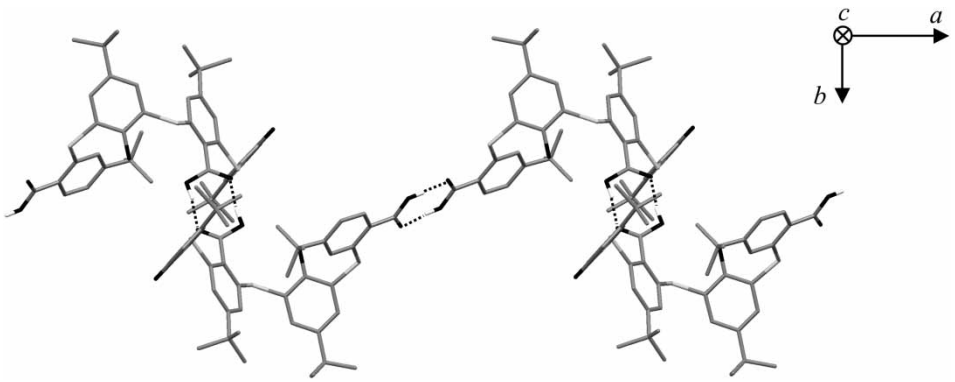


Figure 2. Crystal packing of $\mathbf{6}^{1,3}$ along the [001] plane. Included solvent molecules, disordered carbon atoms and hydrogen atoms except those of carboxy groups are omitted for clarity. Dotted lines represent intermolecular hydrogen bondings.

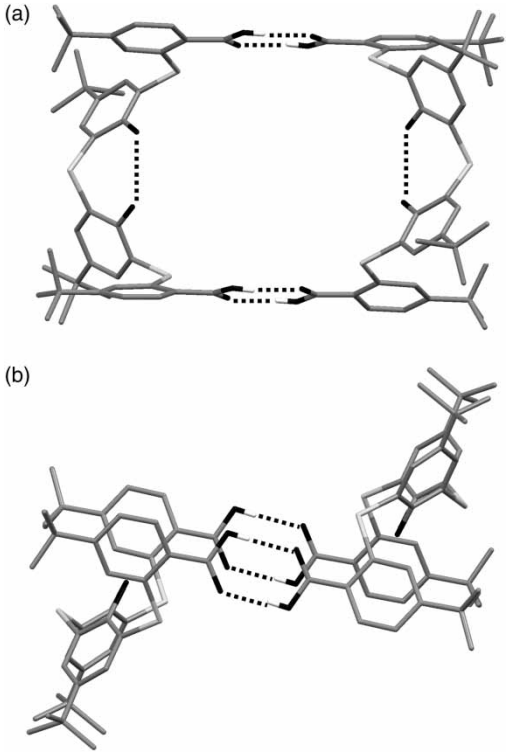


Figure 3. X-ray structure of dimeric $\mathbf{6}^{1,4}$. Top view (a) and side view. (b) Included solvent molecules, disordered carbon atoms and hydrogen atoms except those of carboxy groups are omitted for clarity. Dotted lines represent intermolecular hydrogen bondings.

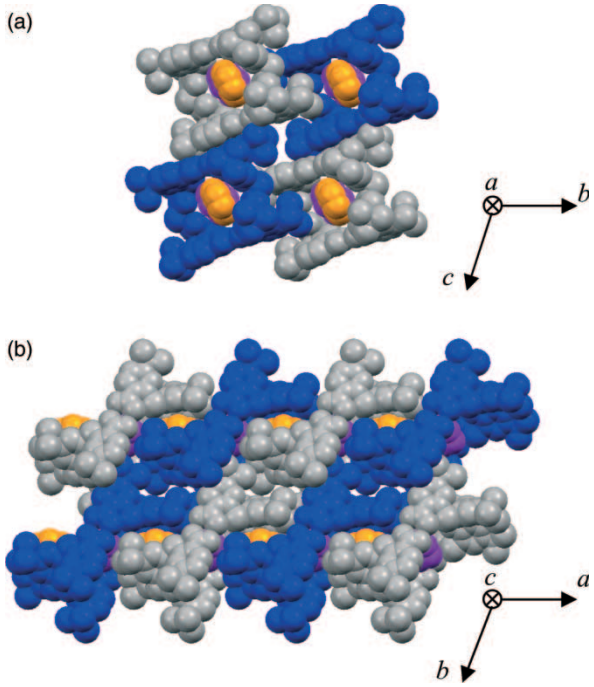


Figure 4. Crystal packing of $\mathbf{6}^{1,4}$ viewed along the [100] plane (a) and the [001] plane. (b) Included solvent molecules being out of the channel, disordered carbon atoms and hydrogen atoms except those of carboxy groups are omitted for clarity. Molecules are colour coded to make the packing structure easily understandable.

bond length of the C(=O)O—H—O=C hydrogen bondings is 1.898 Å. Furthermore, the dimers construct a porous channel along the *a*-axis and each one molecule of benzene and cyclohexane are included in each unit (Figure 4). This indicates that dicarboxylic acid $\mathbf{8}^{1,4}$ has a potential for serving as a supramolecular host, which can selectivity adsorb particular molecules in the solid state.

In summary, sulphur-bridged tetrakisphenol $\mathbf{2}_4$ could be regioselectively converted into bistriflates $\mathbf{8}^{1,3}$ and $\mathbf{8}^{1,4}$ via triflation to tetrakistriflate **7**, followed by regioselective detriflation with TBAF and into bistriflate $\mathbf{8}^{1,2}$ via a four-step process using a disiloxane protecting group (TIPDS). The bistriflates served as precursors for preparing novel tetradentate PPh_2–OH hybrid ligands $\mathbf{5}^{1,2}$, $\mathbf{5}^{1,3}$ and $\mathbf{5}^{1,4}$ and CO_2H–OH hybrid ligands $\mathbf{6}^{1,3}$ and $\mathbf{6}^{1,4}$. The X-ray analyses of $\mathbf{6}^{1,3}$ and $\mathbf{6}^{1,4}$ revealed that the arrangement of the carboxy and hydroxy groups greatly affected the association of the molecules and, as a result, the 3D packing structure in crystals. Studies to bring out inherent functions of these ligands and to synthesise other hybrid ligands bearing an oligo(thio-1,3-phenylene) skeleton are in progress.

Experimental

General

Melting points were taken using the Stuart SMP3 melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were measured using tetramethylsilane as an internal standard and $CDCl_3$ as a solvent, unless otherwise noted. IR spectra were recorded on a Shimazu FTIR-8300 spectrometer. Microanalyses were carried out in the Microanalytical Laboratory of the Institute of Multi-disciplinary Research for Advanced Materials, Tohoku University. HRMS spectra were measured using a Bruker Daltonics APEX III in Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University. Silica gel 60 (63–200 μm) was used for column chromatography. Water- and air-sensitive reactions were routinely carried out under nitrogen. DMF ($CaSO_4$), DMSO ($CaSO_4$), CH_2Cl_2 (CaH_2) and MeOH (Mg) were distilled from dehydrating agents and stored under nitrogen. Dry THF (water $<$ 20 ppm) was used as purchased. Compound $\mathbf{2}_4$ was prepared as described in the literature (*35*).

Synthesis

*Compound **7***

A solution of **2**$_4$ (0.500 g, 0.723 mmol) and pyridine (510 μl, 6.34 mmol) in CH_2Cl_2 (20 ml) was stirred at room temperature for 1 h. Triflic anhydride (1.88 ml, 11.5 mmol) was added to the mixture at 0°C and the resulting mixture was stirred at room temperature for 2 h. After being quenched with 2 M HCl (10 ml), the mixture was poured into water and extracted with $CHCl_3$ (100 ml×3). The organic layer was dried over $MgSO_4$ and evaporated to leave a residue, which was chromatographed on silica gel with $CHCl_3$–hexane (1:1) as the eluent to give **7** (0.786 g, 89%) as a colourless powder, mp 128.2–130.9°C; FAB-MS 1218 (M^+); ^{1}H NMR (400 MHz) δ 1.08 (s, 18H, C(CH_3)$_3$), 1.25 (s, 18H, C(CH_3)$_3$), 7.23 (d, 2H, J = 2.4 Hz, Ar*H*), 7.24 (d, 2H, J = 2.4 Hz, Ar*H*), 7.26 (d, 2H, J = 8.7 Hz, Ar*H*), 7.41 (dd, 2H, J = 8.7, 2.4 Hz, Ar*H*), 7.46 (d, 2H, J = 2.4 Hz, Ar*H*); ^{13}C NMR (100 MHz) δ 30.6, 31.0, 34.9, 117.0, 120.2, 121.7, 123.4, 127.2, 127.3, 130.0, 130.1, 131.1, 131.3, 132.2, 145.3, 146.9, 152.7, 152.7; IR (KBr) 2970, 1427, 1211, 1138 cm^{-1}. Anal. Calcd for $C_{44}H_{46}F_{12}O_{12}S_7$: C, 43.34; H, 3.80. Found: C, 43.15; H, 3.80.

*Compound **8**^{1,3}*

To a solution of **7** (50.0 mg, 41.0 μmol) in THF (3.0 ml), a 1.0 M solution of TBAF in THF (328 μl, 0.328 mmol) was added and the mixture was stirred at room temperature for 1 h. After being quenched with 2 M HCl (2.0 ml), the mixture was poured into water and extracted with CH_2Cl_2 (5.0 ml ×3). The organic layer was dried over $MgSO_4$ and evaporated to leave a residue, which was chromatographed on silica gel with $CHCl_3$–hexane (1:1) as the eluent to give **8**^{1,3} (25.5 mg, 64%) as an oil, FAB-MS 954 (M^+); ^{1}H NMR (400 MHz) δ 0.94 (s, 9H, C(CH_3)$_3$), 1.18 (s, 9H, C(CH_3)$_3$), 1.23 (s, 9H, C(CH_3)$_3$), 1.30 (s, 9H, C(CH_3)$_3$), 6.31 (s, 1H, O*H*), 6.62 (d, 1H, J = 2.3 Hz, Ar*H*), 6.76 (s, 1H, O*H*), 6.85 (d, 1H, J = 2.3 Hz, Ar*H*), 7.02 (d, 1H, J = 8.6 Hz, Ar*H*), 7.17 (d, 1H, J = 8.6 Hz, Ar*H*), 7.19 (d, 1H, J = 8.6 Hz, Ar*H*), 7.29 (dd, 1H, J = 8.6, 2.3 Hz, Ar*H*), 7.40 (d, 1H, J = 2.3 Hz, Ar*H*), 7.43 (dd, 1H, J = 8.6, 2.3 Hz, Ar*H*), 7.45 (d, 1H, J = 2.3 Hz, Ar*H*), 7.51 (d, 1H, J = 2.3 Hz, Ar*H*); ^{13}C (100 MHz) δ 30.6, 31.0, 31.2, 31.4, 34.2, 34.4, 34.7, 34.8, 113.3, 115.7, 117.3, 117.3, 117.4, 117.5, 119.9, 121.4, 124.9, 126.0, 126.7, 128.5, 129.2, 130.2, 130.2, 131.8, 133.6, 133.8, 134.0, 141.7, 144.6, 144.9, 145.8, 152.1, 152.3, 154.0, 155.2; IR (KBr) 3457, 2962 cm^{-1}. Anal. Calcd for $C_{42}H_{48}F_6O_8S_5$: C, 52.81; H, 5.07. Found: C, 52.98; H, 5.18.

*Compound **8**^{1,4}*

To a solution of **7** (50.0 mg, 41.0 μmol) in THF (3.0 ml), a 1.0 M solution of TBAF in THF (123 μl, 0.123 mmol) was added and the mixture was refluxed for 1 h. After being quenched with 2 M HCl (2.0 ml), the mixture was poured into water and extracted with CH_2Cl_2 (5.0 ml ×3). The organic layer was dried over $MgSO_4$ and evaporated to leave a residue, which was chromatographed on silica gel with $CHCl_3$–hexane (1:1) as the eluent to give **8**^{1,4} (22.0 mg, 56%) as a colourless powder, mp 107°C (decomp.); FAB-MS 954 (M^+); ^{1}H NMR (400 MHz) δ 1.14 (s, 18H, C(CH_3)$_3$), 1.20 (s, 18H, C(CH_3)$_3$), 6.96 (s, 2H, O*H*), 7.04 (d, 2H, J = 2.3 Hz, Ar*H*), 7.18 (d, 2H, J = 8.6 Hz, Ar*H*), 7.26 (dd, 2H, J = 8.6, 2.3 Hz, Ar*H*), 7.37 (d, 2H, J = 2.3 Hz, Ar*H*), 7.42 (d, 2H, J = 2.3 Hz, Ar*H*); ^{13}C (100 MHz) δ 31.0, 31.2, 34.3, 34.8, 116.2, 117.0, 119.8, 120.2, 121.3, 125.6, 128.4, 129.0, 132.6, 133.5, 144.7, 145.4, 155.2, 153.7; IR (KBr) 3458, 2964, 1213 cm^{-1}. HRMS Calcd for $C_{42}H_{48}F_6O_8S_5Na$: 977.1749. Found: 977.1747.

*Compound **9***

To a solution of **2**$_4$ (1.00 g, 1.45 mmol) in DMF (25 ml) NaH (208 mg, 6.88 mmol) was added and the mixture was stirred at room temperature for 2 h. To the mixture a solution of TIPDSCl (1.36 ml, 3.44 mmol) in DMF (15 ml) was added dropwise and the resulting mixture was stirred at room temperature for 12 h. After being quenched with 2 M HCl (10 ml), the mixture was poured into water and extracted with Et_2O (20 ml×3). The organic layer was dried over $MgSO_4$ and evaporated to leave a residue, which was chromatographed on silica gel with $CHCl_3$–hexane (1:3) as the eluent to give **9** (1.14 g, 67%) as a colourless powder, mp 103–105°C; FAB-MS 1131 ([M − ^{i}Pr]$^+$); ^{1}H NMR (500 MHz) δ 0.68–0.96 (m, 28H, CH(CH_3)$_2$), 1.10–1.20 (m, 28H, CH(CH_3)$_2$), 1.15 (s, 18H, C(CH_3)$_3$), 1.18 (s, 18H, C(CH_3)$_3$), 6.82 (d, 2H, J = 8.4 Hz, Ar*H*), 7.04–7.09 (m, 4H, Ar*H*), 7.16 (d, 2H, J = 2.5 Hz, Ar*H*), 7.49 (d, 2H, J = 2.5 Hz, Ar*H*); ^{13}C NMR (125 MHz) δ 13.8, 13.8, 17.3, 17.3, 17.5, 17.7, 31.3, 31.3, 34.2, 34.2, 120.6, 124.6, 124.8, 127.0, 127.1, 128.4, 128.9, 133.1, 144.8, 145.2, 150.8, 152.2; IR (KBr) 2951, 1486, 933 cm^{-1}. Anal. Calcd for $C_{64}H_{102}O_6S_3Si_4$: C, 65.36; H, 8.74. Found: C, 65.34; H, 8.53.

*Compound **10***

To a solution of **9** (50.0 mg, 42.5 μmol) in THF (3 ml) a 1.0 M solution of TBAF in THF (21.3 μl, 21.3 μmol) was added and the mixture was stirred at room temperature for 45 min. After being quenched with 2 M HCl (5 ml), the mixture was poured into water and extracted with CH_2Cl_2 (2 ml ×3). The organic layer was dried over $MgSO_4$ and evaporated to leave an oil, which was chromatographed on silica gel with $CHCl_3$–hexane (1:1) as the eluent to recover **9** (19.3 mg, 39%) and give **10** (16.7 mg, 42%) as a colourless powder, mp 83–85°C; FAB-MS 933 (M^+); ^{1}H

NMR (500 MHz) δ 0.95–1.08 (m, 14H, C*H*(CH_3)$_2$), 1.04 (s, 9H, C(CH_3)$_3$), 1.08–1.14 (m, 14H, C*H*(CH_3)$_2$), 1.15 (s, 9H, C(CH_3)$_3$), 1.20 (s, 9H, C(CH_3)$_3$), 1.29 (s, 9H, C(CH_3)$_3$), 6.47 (d, 1H, J = 2.4 Hz, Ar*H*), 6.71 (s, 1H, O*H*), 6.81 (s, 1H, O*H*), 6.82 (d, 1H, J = 8.5 Hz, Ar*H*), 6.95 (d, 1H, J = 8.5 Hz, Ar*H*), 7.10 (d, 1H, J = 2.3 Hz, Ar*H*), 7.11 (dd, 1H, J = 8.4, 2.4 Hz, Ar*H*), 7.20 (d, 1H, J = 2.4 Hz, Ar*H*), 7.29 (d, 1H, J = 2.4 Hz, Ar*H*), 7.32 (d, 1H, J = 2.3 Hz, Ar*H*), 7.35 (dd, 1H, J = 8.5, 2.4 Hz, Ar*H*), 7.57 (d, 1H, J = 2.4 Hz, Ar*H*); ^{13}C NMR (125 MHz) δ 13.6, 14.2, 17.4, 17.4, 17.5, 31.0, 31.2, 31.3, 31.4, 34.2, 34.2, 34.3, 115.0, 116.2, 116.3, 120.7, 121.6, 124.4, 125.0, 125.3, 126.2, 127.1, 129.0, 129.2, 130.1, 131.2, 132.4, 133.4, 144.0, 144.8, 145.3, 145.3, 149.8, 151.2, 152.8, 155.0; IR (KBr) 3432, 2962, 1487, 1266, 931 cm^{-1}. Anal. Calcd for $C_{52}H_{76}O_5S_3Si_2$: C, 66.90; H, 8.21. Found: C, 66.55; H, 8.24.

Compound ***11***

A solution of **10** (235 mg, 0.252 mmol) and pyridine (122 μl, 1.01 mmol) in CH_2Cl_2 (10 ml) was stirred at room temperature for 30 min. To the mixture, triflic anhydride (165 μl, 1.01 mmol) was added at 0°C and the resulting mixture was stirred at this temperature for 2 h. After being quenched with 2 M HCl (10 ml), the mixture was poured into water and extracted with CH_2Cl_2 (5.0 ml ×3). The organic layer was dried over $MgSO_4$ and evaporated to leave a residue, which was chromatographed on silica gel with $CHCl_3$–hexane (1:1) as the eluent to give **11** (280 mg, 93%) as a colourless powder, mp 84–85°C; FAB-MS 1197 ($[M + 1]^+$); ^{1}H NMR (400 MHz) δ 0.78–1.00 (m, 14H, CH(C*H*$_3$)$_2$), 1.06 (s, 9H, C(C*H*$_3$)$_3$), 1.06–1.16 (m, 14H, C*H*(C*H*$_3$)$_2$), 1.18 (s, 9H, C(C*H*$_3$)$_3$), 1.19 (s, 9H, C(C*H*$_3$)$_3$), 1.24 (s, 9H, C(C*H*$_3$)$_3$), 6.83 (d, 1H, J = 8.5 Hz, Ar*H*), 7.06 (d, 1H, J = 2.4 Hz, Ar*H*), 7.09 (d, 1H, J = 2.4 Hz, Ar*H*), 7.10 (dd, 1H, J = 8.5, 2.4 Hz, Ar*H*), 7.17 (d, 1H, J = 2.4 Hz, Ar*H*), 7.20 (d, 1H, J = 2.4 Hz, Ar*H*), 7.25 (d, 1H, J = 8.0 Hz, Ar*H*), 7.38 (dd, 1H, J = 2.4, 8.7 Hz, Ar*H*), 7.45 (d, 1H, J = 2.4 Hz, Ar*H*), 7.53 (d, 1H, J = 2.4 Hz, Ar*H*); ^{13}C (100 MHz) δ 13.7, 13.9, 17.2, 17.3, 17.4, 17.6, 30.7, 31.1, 31.2, 31.3, 34.2, 34.3, 37.8, 34.9, 117.0, 120.2, 120.8, 121.6, 123.4, 124.8, 125.3, 125.6, 126.3, 126.9, 127.8, 128.9, 129.2, 129.4, 130.0, 130.3, 131.8, 131.9, 133.9, 144.6, 145.3, 145.4, 146.8, 151.1, 152.1, 152.5, 152.7; IR (KBr) 2964, 1426, 1211, 859 cm^{-1}. HRMS Calcd for $C_{54}H_{74}F_6O_9S_5Si_2Na$: 1219.3271. Found: 1219.3263.

Compound ***8*^{1,2}**

To a solution of **11** (250 mg, 0.209 mmol) in THF (10 ml), TBAF (209 μl, 0.209 mmol) was added and the mixture was stirred at room temperature for 15 min. After being quenched with 2 M HCl (5.0 ml), the mixture was poured into water and extracted with CH_2Cl_2 (10 ml ×3). The organic layer was dried over $MgSO_4$ and evaporated to give a residue, which was chromatographed on silica gel with $CHCl_3$–hexane (1:1) as the eluent to give **8**^{1,2} (191 mg, 96%) as a colourless powder, mp 104–105°C; FAB-MS 954 (M^+); ^{1}H NMR (500 MHz) δ 0.98 (s, 9H, C(C*H*$_3$)$_3$), 1.15 (s, 9H, C(C*H*$_3$)$_3$), 1.25 (s, 9H, C(C*H*$_3$)$_3$), 1.29 (s, 9H, C(C*H*$_3$)$_3$), 6.57 (s, 1H, O*H*), 6.74 (d, 1H, J = 2.3 Hz, Ar*H*), 6.89 (s, 1H, O*H*), 6.95 (d, 1H, J = 8.6 Hz, Ar*H*), 7.05 (d, 1H, J = 2.3 Hz, Ar*H*), 7.08 (d, 1H, J = 2.3 Hz, Ar*H*), 7.26 (d, 1H, J = 9.3 Hz, Ar*H*), 7.36 (dd, 1H, J = 8.6, 2.3 Hz, Ar*H*), 7.38–7.43 (m, 3H, Ar*H*), 7.54 (d, 1H, J = 2.4 Hz, Ar*H*); ^{13}C NMR (125 MHz) δ 30.6, 31.1, 31.1, 31.4, 34.2, 34.3, 34.8, 34.9, 114,6, 115.1, 115.9, 117.3, 119.9, 121.7, 122.7, 123.4, 127.1, 127.3, 129.2, 129.5, 129.6, 130.5, 131.4, 132.1, 132.6, 133.4, 143.0, 144.2, 145.0, 146.9, 152.4, 152.5, 155.7, 155.0; IR (KBr) 3433, 2965, 1210 cm^{-1}. Anal. Calcd for $C_{42}H_{48}F_6O_8S_5$: C, 52.81; H, 5.07. Found: C, 52.91; H, 5.15.

Compound ***12*^{1,2}**

The mixture of $Ph_2P(O)H$ (143 mg, 0.706 mmol), $Pd(OAc)_2$ (16.7 mg, 74.4 μmol), dppb (31.7 mg, 74.4 μmol) and ^{i}Pr$_2$EtN (237 μl, 1.41 mmol) in DMSO (5 ml) was stirred at 120°C for 30 min. To the mixture, a solution of **8**^{1,2} (177 mg, 0.186 mmol) in DMSO (3 ml) was added and the resulting mixture was stirred at 120°C for 2 h. After being quenched with 2 M HCl (5 ml), the mixture was poured into water and extracted with $CHCl_3$ (7 ml ×3) and washed with water (10 ml ×3). The organic layer was dried over $MgSO_4$ and evaporated to give a residue, which was chromatographed on silica gel with AcOEt as the eluent to give **12**^{1,2} (86.3 mg, 44%) as a colourless powder, mp 141°C (decomp.); FAB-MS 1060 ($[M + 1]^+$); ^{1}H NMR (400 MHz) δ 0.88 (s, 9H, C(C*H*$_3$)$_3$), 1.12 (s, 9H, C(C*H*$_3$)$_3$), 1.21 (s, 9H, C(C*H*$_3$)$_3$), 1.27 (s, 9H, C(C*H*$_3$)$_3$), 6.39 (dd, 1H, J = 2.4, 1.2 Hz, Ar*H*), 6.89 (d, 1H, J = 1.8 Hz, Ar*H*), 6.91 (d, 1H, J = 6.9 Hz, Ar*H*), 7.06 (dd, 1H, J = 2.4, 1.1 Hz, Ar*H*), 7.28–7.37 (m, 12H, Ar*H*), 7.40–7.48 (m, 5H, Ar*H*), 7.52–7.59 (m, 5H, Ar*H*), 7.59–7.67 (m, 4H, Ar*H*); ^{13}C (100 MHz) δ 16.4, 17.1, 17.3, 17.5, 20.1, 20.2, 20.8, 21.1, 101.1, 103.2, 106.0, 109.5, 114.4 (d, J = 12.1 Hz), 111.0 (d, J = 11.9 Hz), 114.5 (d, J = 12.0 Hz), 114.6 (d, J = 12.6 Hz), 114.7, 115.0, 116.6 (d, J = 12.8 Hz), 117.5 (d, J = 2.8 Hz), 117.9 (d, J = 2.8 Hz), 117.7, 118.0, 118.1 (d, J = 13.1 Hz), 118.2, 118.2, 118.3, 118.5, 119.8, 121.1 (d, J = 10.5 Hz), 128.8, 129.5 (d, J = 10.0 Hz), 129.8, 130.1 (d, J = 6.1 Hz), 140.7, 140.7, 141.7, 142.8 (d, J = 2.6 Hz); IR (KBr) 3056, 2963, 1184 cm^{-1}. HRMS Calcd for $C_{64}H_{68}O_4P_2S_3Na$: 1081.3647. Found: 1081.3641.

Compound ***5*** ^{1,2}

To a solution of **12** ^{1,2} (90.0 mg, 85.0 μmol) and Et_3N (237 μl, 0.170 mmol) in toluene (10 ml), $HSiCl_3$ (172 μl, 0.170 mmol) was added at 0°C and the mixture was refluxed for 2 h. After the reaction was quenched with saturated aqueous $NaHCO_3$ (5 ml), the resulting precipitate was filtered off and the filtrate was poured into water and extracted with $CHCl_3$ (7 ml ×3). The organic layer was dried over $MgSO_4$ and evaporated to give a residue, which was chromatographed on silica gel with $CHCl_3$–hexane (1:1) as the eluent to give **5** ^{1,2} (29.0 mg, 32%) as a colourless powder, mp 99–101°C; FAB-MS 1028 ($[M + 1]^+$); ^{1}H NMR (400 MHz) δ 0.90 (s, 9H, C(CH_3)$_3$), 1.13 (s, 9H, C(CH_3)$_3$), 1.20 (s, 9H, C(CH_3)$_3$), 1.27 (s, 9H, C(CH_3)$_3$), 6.58 (t, 1H, J = 1.2 Hz, Ar*H*), 6.70–6.75 (m, 3H, Ar*H*), 6.93 (d, 1H, J = 6.8 Hz, Ar*H*), 7.02 (d, 1H, J = 1.7 Hz, Ar*H*), 7.12–7.20 (m, 6H, Ar*H*), 7.24 (d, 1H, J = 1.2 Hz, Ar*H*), 7.26–7.32 (m, 11H, Ar*H*), 7.33 (dd, 1H, J = 6.8, 1.8 Hz, Ar*H*), 7.43–7.49 (m, 4H, Ar*H*), 7.53 (d, 1H, J = 1.8 Hz, Ar*H*); ^{13}C (100 MHz) δ 30.5, 31.1, 31.2, 31.5, 34.2, 34.3, 34.7, 34.7, 115.0, 116.4, 121.8, 123.1 (d, J = 3.5 Hz), 125.4, 125.8 (d, J = 3.5 Hz), 128.1, 128.3 (d, J = 12.7 Hz), 128.3, 128.5, 129.0, 129.9, 131.4 (d, J = 2.3 Hz), 132.2 (d, J = 18.4 Hz), 132.7, 133.4, 133.5, 133.9 (d, J = 20.0 Hz), 134.5 (d, J = 10.9 Hz), 137.2 (d, J = 11.7 Hz), 138.4 (d, J = 8.8 Hz), 143.9, 144.5, 145.0, 145.1, 148.4, 152.6, 152.9, 153.7, 155.2; IR (KBr) 3406, 2962 cm^{-1}. HRMS Calcd for $C_{64}H_{68}O_2P_2S_3Na$: 1049.3749. Found: 1049.3754.

Compound ***12*** ^{1,3}

This compound was prepared by a similar procedure to that used for the preparation of **12** ^{1,2}. Starting from **8** ^{1,3} (434 mg), **12** ^{1,3} (134 mg, 28%) was obtained as a colourless powder, after column chromatography with AcOEt–hexane (2:1) as the eluent, mp 153°C (decomp.); FAB-MS 1060 ($[M + 1]^+$); ^{1}H NMR (400 MHz) δ 0.93 (s, 9H, C(CH_3)$_3$), 1.15 (s, 9H, C(CH_3)$_3$), 1.19 (s, 9H, C(CH_3)$_3$), 1.28 (s, 9H, C(CH_3)$_3$), 6.66 (d, 1H, J = 2.3 Hz, Ar*H*), 6.86 (d, 1H, J = 8.6 Hz, Ar*H*), 6.86 (dd, 1H, J = 12.8, 7.9 Hz, Ar*H*), 7.03 (dd, 1H, J = 3.6, 1.8 Hz, Ar*H*), 7.19 (dt, 1H, J = 8.1, 2.0 Hz, Ar*H*), 7.26–7.36 (m, 8H, Ar*H*), 7.42 (d, 1H, J = 2.3 Hz, Ar*H*), 7.48–7.60 (m, 7H, Ar*H*), 7.62 (dd, 1H, J = 3.4, 1.8 Hz, Ar*H*), 7.66–7.81 (m, 8H, Ar*H*), 9.54 (s, 1H, O*H*), 10.57 (s, 1H, O*H*); ^{13}C (100 MHz) δ 30.4, 30.4, 30.8, 31.4, 34.0, 34.0, 34.7, 35.0, 116.3, 118.9 (d, J = 12.5 Hz), 124.0, 124.7 (d, J = 11.9 Hz), 128.3 (d, J = 12.6 Hz), 128.7 (d, J = 11.4 Hz), 128.7, 129.7 (d, J = 8.2 Hz), 130.2 (d, J = 45.7 Hz), 130.2, 131.1 (d, J = 8.0 Hz), 131.2 (d, J = 46.3 Hz), 131.5 (d, J = 2.7 Hz), 131.6, 131.9 (d, J = 10.6 Hz), 132.0, 132.2 (d, J = 10.5 Hz), 132.6, 132.8 (d, J = 7.7 Hz), 133.3, 133.5 (d, J = 8.8 Hz), 133.9, 134.4, 140.1 (d, J = 9.0 Hz), 140.4 (d, J = 6.7 Hz), 142.1, 142.4, 145.2 (d, J = 7.0 Hz), 154.6, 156.4 (d, J = 2.1 Hz), 156.1; IR (KBr) 3057, 2963, 1185 cm^{-1}. HRMS Calcd for $C_{64}H_{68}O_4P_2S_3Na$: 1081.3647. Found: 1081.3642.

Compound ***5*** ^{1,3}

This compound was prepared by the same procedure as used for the preparation of **5** ^{1,2}. Starting from **12** ^{1,3} (92.2 mg), **5** ^{1,3} (46.9 mg, 52%) was obtained as a colourless powder, mp 118°C (decomp.); FAB-MS 1028 ($[M + 1]^+$); ^{1}H NMR (400 MHz) δ 0.85 (s, 9H, C(CH_3)$_3$), 1.16 (s, 9H, C(CH_3)$_3$), 1.18 (s, 9H, C(CH_3)$_3$), 1.27 (s, 9H, C(CH_3)$_3$), 5.95 (s, 1H, O*H*), 6.58 (t, 1H, J = 1.8 Hz, Ar*H*), 6.68–6.76 (m, 2H, Ar*H*), 6.90 (d, 1H, J = 8.6 Hz, Ar*H*), 7.00 (s, 1H, O*H*), 7.15 (dd, 1H, J = 1.8, 8.1 Hz, Ar*H*), 7.18 (d, 1H, J = 2.3 Hz, Ar*H*), 7.27–7.40 (m, 20H, Ar*H*), 7.54–7.63 (m, 4H, Ar*H*); ^{13}C (100 MHz) δ 30.5, 31.0, 31.5, 31.6, 34.2, 34.2, 34.7, 34.7, 115.1, 116.9 (d, J = 8.7 Hz), 119.5 (d, J = 9.5 Hz), 121.0 (d, J = 5.1 Hz), 122.7 (d, J = 3.0 Hz), 124.3 (d, J = 3.6 Hz), 126.1, 127.4, 127.5, 128.2, 128.5 (d, J = 6.3 Hz), 128.6 (d, J = 7.2 Hz), 128.8, 129.2, 132.2 (d, J = 18.4 Hz), 133.3, 132.9, 133.9 (d, J = 19.6 Hz), 134.0, 134.3, 134.4, 135.9 (d, J = 6.5 Hz), 136.5 (d, J = 8.8 Hz), 139.6, 139.9, 143.8, 144.0, 146.2 (d, J = 5.1 Hz), 146.3 (d, J = 9.5 Hz), 152.8, 153.8 (d, J = 8.0 Hz), 154.9; IR (KBr) 3420, 2962 cm^{-1}. HRMS Calcd for $C_{64}H_{68}O_2P_2S_3Na$: 1049.3749. Found: 1049.3747.

Compound ***12*** ^{1,4}

This compound was prepared by the same procedure as used for the preparation of **12** ^{1,3}. Starting from **8** ^{1,4} (250 mg), **12** ^{1,4} (178 mg, 64%) was obtained as a colourless powder, mp 183–185°C; FAB-MS 1059 (M^+); ^{1}H NMR (400 MHz) δ 1.12 (s, 18H, C(CH_3)$_3$), 1.18 (s, 18H, C(CH_3)$_3$), 6.97 (dd, 2H, J = 12.7, 8.1 Hz, Ar*H*), 7.11 (d, 2H, J = 2.4 Hz, Ar*H*), 7.18 (dt, 2H, J = 8.1, 1.9 Hz, Ar*H*), 7.36 (d, 2H, J = 2.4 Hz, Ar*H*), 7.43–7.59 (m, 14H, Ar*H*), 7.68–7.78 (m, 8H, Ar*H*), 10.0 (br, 2H, O*H*); ^{13}C (100 MHz) δ 30.8, 31.3, 34.0, 35.0, 119.1, 121.7, 124.4 (d, J = 11.9 Hz), 128.6 (d, J = 12.3 Hz), 123.0, 131.2 (d, J = 36.5 Hz), 131.8, 131.8, 131.8, 132.0 (d, J = 9.9 Hz), 132.7 (d, J = 30.2 Hz), 133.7 (d, J = 13.3 Hz), 140.4 (d, J = 6.9 Hz), 142.3, 155.0, 156.2 (d, J = 2.2 Hz); IR (KBr) 3407, 2962, 1186 cm^{-1}. HRMS Calcd for $C_{64}H_{68}O_4P_2S_3Na$: 1081.3647. Found: 1081.3646.

Compound ***5*** ^{1,4}

This compound was prepared by the same procedure as used for the preparation of **5** ^{1,2}. Starting from **12** ^{1,4}

(400 mg, 0.377 mmol), **5**[1,4] (315 mg, 82%) was obtained as a colourless powder, mp 117–119°C; FAB-MS 1027 (M^+); ^{1}H NMR (400 MHz) δ 1.15 (s, 18H, C(CH_3)$_3$), 1.16 (s, 18H, C(CH_3)$_3$), 6.72 (dd, 2H, J = 8.1, 3.5 Hz, Ar*H*), 7.15 (dd, 2H, J = 8.1, 1.8 Hz, Ar*H*), 7.20 (d, 2H, J = 2.3 Hz, Ar*H*), 7.26–7.41 (m, 22H, Ar*H*), 7.47 (d, 2H, J = 2.1 Hz, Ar*H*); ^{13}C (100 MHz) δ 31.0, 31.3, 34.2, 34.7, 119.6, 120.2 (d, J = 5.1 Hz), 120.1, 128.6 (d, J = 7.2 Hz), 128.9, 131.3, 132.0, 133.2, 133.8 (d, J = 19.6 Hz), 135.5 (d, J = 5.8 Hz), 136.3 (d, J = 8.1 Hz), 139.7, 134.0, 143.8, 152.9, 153.4; IR (KBr) 3406, 2962 cm^{-1}. HRMS Calcd for $C_{64}H_{68}O_2P_2S_3Na$: 1049.3749. Found: 1049.3752.

Compound ***13***[1,3]

To a solution of **8**[1,3] (413 mg, 0.433 mmol) in CH_2Cl_2 (10 ml), pyridine (599 mg, 7.62 mmol) and acetic anhydride (292 mg, 2.86 mmol) were added and the mixture was stirred for 2 h at room temperature. After being quenched with 2 M HCl (10 ml), the mixture was extracted with $CHCl_3$ (20 ml ×3). The organic layer was washed with water (20 ml ×3) and evaporated to give **13**[1,3] (437 mg, 97%) as an oil, FAB-MS 1038 (M^+); ^{1}H NMR (400 MHz) δ 1.04 (s, 9H, C(CH_3)$_3$), 1.14 (s, 9H, C(CH_3)$_3$), 1.20 (s, 9H, C(CH_3)$_3$), 1.26 (s, 9H, C(CH_3)$_3$), 2.22 (s, 3H, OCOCH_3), 2.58 (s, 3H, OCOCH_3), 6.97 (d, 1H, J = 2.4 Hz, Ar*H*), 7.08–7.11 (m, 1H, Ar*H*), 7.20–7.23 (m, 2H, Ar*H*), 7.29–7.34 (m, 4H, Ar*H*), 7.39–742 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, acetone-d_7) δ 20.5, 20.7, 31.0, 31.3, 31.4, 31.6, 35.4, 35.5, 35.6, 35.6, 118.4, 120.9, 122.7, 124.4, 125.8, 128.1, 128.6, 129.1, 129.3, 130.6, 130.9, 131.9, 132.0, 132.1, 132.5, 132.7, 144.8, 147.3, 149.2, 150.2, 151.3, 151.9, 153.4, 153.7, 169.0, 169.5; IR (KBr) 1772, 1425, 1209, 1193 cm^{-1}. Anal. Calcd for $C_{46}H_{52}F_6O_{10}S_5$: C, 53.16; H, 5.04. Found: C, 53.44; H, 4.86.

Compound ***14***[1,3]

To a solution of **13**[1,3] (400 mg, 0.385 mmol) in DMSO–MeOH (2:1; 24 ml), $Pd(OAc)_2$ (17.2 mg, 77.0 μmol), dppb (65.6 mg, 0.154 mmol) and ^{i}Pr$_2$NEt (438 mg, 3.38 mmol) were added and the resulting mixture was stirred under 1 atm of CO atmosphere at 70°C for 18 h. After cooling, the mixture was quenched with 2 M HCl (20 ml), poured into water (50 ml) and extracted with $CHCl_3$ (30 ml×3). The organic layer was dried over $MgSO_4$ and evaporated to give a residue, which was chromatographed on silica gel with hexane–AcOEt (2:1) as the eluent to give **14**[1,3] (273 mg, 82%) as an oil, FAB-MS 859 ($[M + 1]^+$); ^{1}H NMR (400 MHz) δ 1.08 (s, 9H, C(CH_3)$_3$), 1.13 (s, 9H, C(CH_3)$_3$), 1.17 (s, 9H, C(CH_3)$_3$), 1.26 (s, 9H, C(CH_3)$_3$), 2.20 (s, 3H, OCOCH_3), 2.23 (s, 3H, OCOCH_3), 3.88 (s, 3H, CO_2CH_3), 3.93 (s, 3H, CO_2CH_3), 6.97 (d, 1H, J = 2.3 Hz, Ar*H*), 7.04–7.07 (m, 2H, Ar*H*), 7.14–7.17 (m, 2H, Ar*H*), 7.31 (d, 1H, J = 2.3 Hz, Ar*H*), 7.35 (dd, 1H, J = 2.3, 8.4 Hz, Ar*H*), 7.40 (d, 1H, J = 2.3 Hz, Ar*H*), 7.44 (d, 1H, J = 2.3 Hz, Ar*H*), 7.89 (d, 1H, J = 8.4 Hz, Ar*H*); ^{13}C NMR (100 MHz, acetone-d_7) δ 20.5, 20.8, 31.1, 31.2, 31.5, 31.7, 35.4, 35.6, 35.8, 35.8, 52.5, 52.8, 123.2, 124.1, 126.2, 126.7, 127.8, 129.1, 129.1, 129.7, 131.5, 131.5, 132.2, 132.3, 133.8, 134.3, 135.7, 136.4, 141.2, 141.7, 144.5, 149.7, 150.9, 151.7, 155.0, 156.7, 167.1, 167.7, 169.1, 169.5; IR (KBr) 1769, 1716 cm^{-1}. Anal. Calcd for $C_{48}H_{58}O_8S_3$: C, 67.10; H, 6.80. Found: C, 67.32; H, 6.84.

Compound ***6***[1,3]

Compound **14**[1,3] (331 mg, 0.385 mmol) was boiled with KOH (2.16 g, 38.5 mmol) in EtOH–H_2O (10:1; 22.0 ml) for 3 days. The mixture was cooled in an ice water bath and quenched with 2 M HCl (50 ml). The resulting precipitate was collected by filtration, washed with water and recrystallised from acetone–hexane to give **6**[1,3] (226 mg, 85%) as a colourless powder, mp 147.2–148.6°C; FAB-MS 769 ($[M + Na]^+$); ^{1}H NMR (400 MHz) δ 1.06 (s, 9H, C(CH_3)$_3$), 1.19 (s, 9H, C(CH_3)$_3$), 1.20 (s, 9H, C(CH_3)$_3$), 1.30 (s, 9H, C(CH_3)$_3$), 6.85 (d, 1H, J = 1.7 Hz, Ar*H*), 6.97 (d, 1H, J = 8.6 Hz, Ar*H*), 7.25–7.27 (m, 3H, Ar*H*), 7.36–7.41 (m, 3H, Ar*H*), 7.56 (d, 1H, J = 2.5 Hz, Ar*H*), 7.87 (d, 1H, J = 8.2 Hz, Ar*H*); ^{13}C NMR (100 MHz) δ 30.4, 30.6, 31.2, 31.4, 34.1, 34.3, 34.8, 35.0, 115.3, 115.7, 117.2, 119.6, 122.4, 123.1, 124.3, 124.5, 126.4, 128.9, 129.6, 132.2, 133.8, 134.7, 135.3, 135.8, 137.2, 140.9, 144.2, 144.9, 154.3, 155.3, 155.3, 157.0, 171.7, 171.9; IR (KBr) 3421, 1690 cm^{-1}. Anal. Calcd for $C_{42}H_{50}O_6S_3$: C, 67.53; H, 6.75. Found: C, 67.28; H, 6.71.

Compound ***13***[1,4]

This compound was prepared by the same procedure as used for the preparation of **13**[1,3]. Starting from **8**[1,4] (875 mg, 0.917 mmol), **13**[1,4] (784 mg, 82%) was obtained as a colourless powder, mp 155.8–157.5°C; FAB-MS 1039 (M^+); ^{1}H NMR (400 MHz) δ 1.13 (s, 18H, C(CH_3)$_3$), 1.22 (s, 18H, C(CH_3)$_3$), 2.25 (s, 6H, OCOCH_3), 7.19–7.24 (m, 4H, Ar*H*), 7.22 (dd, 2H, J = 6.7, 1.4 Hz, Ar*H*), 7.29–7.33 (m, 4H, Ar*H*); ^{13}C NMR (100 MHz) δ 20.5, 31.1, 31.2, 34.9, 35.0, 121.4, 126.2, 127.5, 129.0, 130.4, 130.6, 130.8, 146.2, 147.7, 150.6, 152.3, 168.5; IR (KBr) 1773, 1425, 1214, 1191 cm^{-1}. Anal. Calcd for $C_{46}H_{52}F_6O_{10}S_5$: C, 53.16; H, 5.04. Found: C, 53.25; H, 5.12.

Compound ***14***[1,4]

This compound was prepared by a similar procedure to that used for the preparation of **14**[1,3]. Starting from **13**[1,4]

(400 mg), **14**^{1,4} (267 mg, 80%) was obtained as an oil, after column chromatography with hexane–AcOEt (2:1) as the eluent, FAB-MS 858 (M^+); ^{1}H NMR (400 MHz) δ 1.13 (s, 18H, C(CH_3)$_3$), 1.18 (s, 18H, C(CH_3)$_3$), 2.20 (s, 6H, OCOCH_3), 3.92 (s, 6H, CO_2CH_3), 6.99 (d, 2H, $J = 1.5$ Hz, Ar*H*), 7.16 (dd, 2H, $J = 6.6$, 1.5 Hz, Ar*H*), 7.34 (d, 2H, $J = 1.9$ Hz, Ar*H*), 7.45 (d, 2H, $J = 1.9$ Hz, Ar*H*), 7.89 (d, 2H, $J = 6.6$ Hz, Ar*H*); ^{13}C NMR (100 MHz) δ (ppm); 20.6, 30.9, 31.3, 34.9, 35.2, 52.3, 122.1, 124.8, 126.0, 127.9, 129.6, 130.8, 130.1, 133.5, 141.4, 149.6, 150.7, 156.0, 167.0, 168.7; IR (KBr) 1715, 1768 cm^{-1}. Anal. Calcd for $C_{48}H_{58}O_8S_3$: C, 67.10; H, 6.80. Found: C, 67.22; H, 6.83.

Compound **6**^{1,4}

This compound was prepared by a similar procedure to that used for the preparation of **6**^{1,3}. Starting from **14**^{1,4} (267 mg), **6**^{1,4} (232 mg, quant.) was obtained as a colourless powder, after recrystallisation from benzene–cyclohexane, mp 142.8–145.0°C; FAB-MS 769 ($[M + Na]^+$); ^{1}H NMR (400 MHz) δ 1.07 (s, 18H, C(CH_3)$_3$), 1.26 (s, 18H, C(CH_3)$_3$), 6.76 (d, 2H, $J = 1.4$ Hz, Ar*H*), 7.20 (dd, 2H, $J = 1.4$, 6.7 Hz, Ar*H*), 7.51 (d, 2H, $J = 1.9$ Hz, Ar*H*), 7.64 (d, 2H, $J = 1.9$ Hz, Ar*H*), 8.06 (d, 2H, $J = 6.7$ Hz, Ar*H*); ^{13}C NMR (100 MHz) δ 30.7, 31.4, 34.5, 35.2, 116.7, 120.2, 122.4, 123.1, 123.9, 132.5, 133.9, 135.3, 141.5, 145.0, 155.2, 157.3, 172.0; IR (KBr) 3401, 1681 cm^{-1}. Anal. Calcd for $C_{42}H_{50}O_6S_3$: C, 67.53; H, 6.75. Found: C, 67.86; H, 6.91.

X-ray crystallographic analyses of 6^{1,3} and 6^{1,4}

Single crystals of **6**^{1,3} and **6**^{1,4} were obtained by vapour diffusion of hexane to an acetone solution of **6**^{1,3} and that of cyclohexane to a benzene solution of **6**^{1,4}, respectively. X-ray crystallographic analyses were performed with a Bruker SMART APEX II diffractometer (graphite monochromator, MoKα radiation, $\lambda = 0.71073$ Å). The data integration and reduction were undertaken with SAINT and XPREP (*36*). The structure was solved by the direct methods using SHELXS-97 (*37*) and refined using least-squares methods on F2 with SHELXL-97 (*38*). Detailed crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-782706 and 782707.

Crystallographic data for **6**^{1,3}·$(CH_3OH)_{0.5}$·$(H_2O)_{0.5}$: $C_{43.5}H_{54}O_7S_3$, $f_w = 785.05$, monoclinic, $P2_1/n$, $a = 20.881$ (3) Å, $b = 9.5748$ (12) Å, $c = 22.624$ (3) Å, $\beta = 91.327$ (2)°, $V = 4521.9$ (10) Å^3, $Z = 4$, $T = 173$ (2) K, 24,367 reflections measured, 10,108 independent reflections, 8081 reflections were observed ($I > 2\sigma(I)$), $R_1 = 0.0753$, $wR_2 = 0.2154$ (observed), $R_1 = 0.903$, $wR_2 = 0.2339$ (all data).

Crystallographic data for **6**^{1,4}·$(C_6H_6)_{1.5}$·$(C_6H_{12})_{1.5}$: $C_{54}H_{65}O_6S_3$, $f_w = 906.24$, triclinic, $P\bar{1}$, $a = 13.0529$ (18) Å, $b = 14.404$ (2) Å, $c = 14.761$ (2) Å, $\alpha = 93.880$ (2)°, $\beta = 96.636$ (2)°, $\gamma = 100.681$ (2)°, $V = 2697.6$ (7) Å^3, $Z = 2$, $T = 223$ (2) K, 30,252 reflections measured, 12,024 independent reflections, 6960 reflections were observed ($I > 2\sigma(I)$), $R_1 = 0.0881$, $wR_2 = 0.2518$ (observed), $R_1 = 0.1398$, $wR_2 = 0.3036$ (all data).

References

(1) Galbraith, S.G.; Tasker, P.A. *Supramol. Chem.* **2005**, *17*, 191–207.
(2) Dam, H.H.; Reinhoudt, D.N.; Verboom, W. *Chem. Soc. Rev.* **2007**, *36*, 367–377.
(3) Arora, V.; Chawla, H.M.; Singh, S.P. *ARKIVOC* **2007**, *ii*, 172–200.
(4) Hierso, J.-C.; Smaliy, R.; Amardeil, R.; Meunier, P. *Chem. Soc. Rev.* **2007**, *36*, 1754–1769.
(5) Ambrosi, G.; Formica, M.; Fusi, V.; Giorgi, L.; Micheloni, M. *Coord. Chem. Rev.* **2008**, *252*, 1121–1152.
(6) Lhoták, P. *Eur. J. Org. Chem.* **2004**, 1675–1692.
(7) Morohashi, N.; Narumi, F.; Iki, N.; Hattori, T.; Miyano, S. *Chem. Rev.* **2006**, *106*, 5291–5316.
(8) Iki, N. *J. Incl. Phenom. Macrocycl. Chem.* **2009**, *64*, 1–13.
(9) Kajiwara, T.; Iki, N.; Yamashita, M. *Coord. Chem. Rev.* **2007**, *251*, 1734–1746.
(10) Iki, N.; Morohashi, N.; Narumi, F.; Miyano, S. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1597–1603.
(11) Morohashi, N.; Iki, N.; Sugawara, A.; Miyano, S. *Tetrahedron* **2001**, *57*, 5557–5563.
(12) Kikuchi, T.; Nogami, M.; Suzuki, K. *J. Alloys Compd.* **2004**, *374*, 272–276.
(13) Matusmiya, H.; Yasuno, S.; Iki, N.; Miyano, S. *J. Chromatogr. A* **2005**, *1090*, 197–200.
(14) Ali, M.B.; Bureau, C.; Martelet, C.; J-Renault, N.; Lamartine, R.; Ouada, H.B. *Mater. Sci. Eng. C* **2000**, *7*, 83–89.
(15) Kim, T.H.; Lee, J.K.; Bok, J.H.; Kim, J.S.; Kim, H. *Electrochim. Acta* **2004**, *49*, 3759–3763.
(16) Morohashi, N.; Hattori, T.; Yokomakura, K.; Kabuto, C.; Miyano, S. *Tetrahedron Lett.* **2002**, *43*, 7769–7772.
(17) Morohashi, N.; Yokomakura, K.; Hattori, T.; Miyano, S. *Tetrahedron Lett.* **2006**, *47*, 1157–1161.
(18) Proto, A.; Giugliano, F.; Capacchione, C. *Eur. Poly. J.* **2009**, *45*, 2138–2141.
(19) Chowdhury, S.; Bridson, J.N.; Georghiou, P.E. *J. Org. Chem.* **2000**, *65*, 3299–3302.
(20) Al-Saraierh, H.; Miller, D.O.; Georghiou, P.E. *J. Org. Chem.* **2005**, *70*, 8273–8280.
(21) Tanaka, S.; Serizawa, R.; Morohashi, N.; Hattori, T. *Tetrahedron Lett.* **2007**, *48*, 7660–7664.
(22) Iki, N.; Morohashi, N.; Yamane, Y.; Miyano, S. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1763–1768.
(23) Morohashi, N.; Teraura, H.; Ohba, Y. In *New Trend in Structural Organic Chemistry*; Takemura, H., Ed.; Chapter 2, Research Signpost: Kerala, 2005; pp 39–60.
(24) Morohasi, N.; Akahira, Y.; Tanaka, S.; Kajiwara, T.; Hattori, T. *Chem. Lett.* **2008**, *37*, 418–419.

(25) Morohasi, N.; Nagata, K.; Ohba, Y.; Hattori, T. *Chem. Lett.* **2008**, *37*, 1228–1229.
(26) Kurz, L.; Lee, G.; Morgans, D.; Waldyke, M.J.; Ward, T. *Tetrahedron Lett.* **1990**, *31*, 6321–6324.
(27) Uozumi, Y.; Tanahashi, A.; Lee, S.-Y.; Hayashi, T. *J. Org. Chem.* **1993**, *58*, 1945–1948.
(28) Cacchi, S.; Ciattini, P.G.; Morera, E.; Orter, G. *Tetrahedron Lett.* **1986**, *27*, 3931–3934.
(29) Hotta, H.; Suzuki, T.; Miyano, S.; Inoue, Y. *J. Mol. Catal.* **1989**, *54*, L5–L7.
(30) Ohta, T.; Ito, M.; Inagaki, K.; Takaya, H. *Tetrahedron Lett.* **1993**, *34*, 1615–1616.
(31) Araki, K.; Iwamoto, K.; Shigematu, S.; Shinkai, S. *Chem. Lett.* **1992**, 1095–1098.
(32) Yamamoto, H.; Sasaki, T.; Shinkai, S. *Chem. Lett.* **1994**, 469–472.
(33) Serizawa, R.; Tanaka, S.; Morohashi, N.; Narumi, F.; Hattori, T. *Tetrahedron Lett.* **2007**, *48*, 6281–6285.
(34) Narumi, F.; Hattori, T.; Morohashi, N.; Matsumura, N.; Yamabuki, W.; Kameyama, H.; Miyano, S. *Org. Biomol. Chem.* **2004**, *2*, 890–898.
(35) Ohba, Y.; Moriya, K.; Sone, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 576–582.
(36) SMART, SAINT and XPREP, *Area Detector Control and Data Integration and Reduction Software*; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1995.
(37) Sheldrick, G.M. *SHELXS97, Program for Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.
(38) Sheldrick, G.M. *SHELXS97, Program for the Refinement of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1997.