Serendipity and Rational Design of One-Dimensional Doubly Stranded Chains with Nanometric Cavities Based on Ag^I Coordination Chemistry

Lamia Mimassi,[a] Carine Guyard-Duhayon,[a] Laurence Raehm,[a] and Hani Amouri*[a]

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Spontaneous and cooperative self-assembly processes allowed the preparation of two complexes $\{[AgL^1_2][X]\}_n$ [X = CF_3SO_3, (**3a**); X = BF_4, (**3b**)] in quantitative yields, identified as 1-D doubly stranded chains. The X-ray molecular structures of **3a,b** are reported. Complexes **3a,b** are isostructural and crystallize in the triclinic unit cell. The structures of **3a** and **3b** show the formation of a one-dimensional coordination polymer exhibiting as an outstanding feature the presence of infinite chained metallomacrocycles with nanometric cavities. Interestingly, NMR spectroscopy and electrospray mass spectrometry suggest that the identified elemental sub-unit $[AgL^1_2]^+$ is the key building block which self-assembles to provide the inorganic polymers **3a,b**. The effect of weakly coordinating counteranions and the assembling ligand L^1 on the supermolecule design are presented and discussed.

Introduction

The design of mono- and double-stranded chains is a great challenge for supramolecular chemists.[1] These supramolecular architectures are aesthetically appealing and exhibit potential applications as molecular wires,[2] electrical conductors,[3] molecular magnets,[4] in host-guest chemistry[5] and in catalysis.[6] Particular interest has been devoted to the construction of helical chains. For instance, polymetallic double helices have been elegantly self-assembled from poly-2,2′-bipyridine ligand strands with ether linkages and tetrahedral Ag^I ions.[7] More recently, efforts have been directed to the preparation of infinite coordination helices. Such infinite chains have been reported by Jung and co-workers,[8] von Zelewsky and co-workers,[9] Ciani and co-workers[10] and Erxleben[10] using tectonic bridging ligands[11] and taking advantage of the tetrahedral nature of Ag^I ions. Although this process sounds relatively straightforward, the rational design of these materials is complicated by the uncertain coordination propensity of the metal ion, which is influenced by such factors as the counteranion,[12] the solvent and the ligand geometry. Thus, controlling these elements is at the heart of controlling supramolecular coordination chemistry.

Pursuing our research in the area of supramolecular chemistry, in particular the design of metallomacrocyles, metallocryptands, and metallocryptates as anion hosts,[13] we extended our investigations to the construction of 1-D chains with appropriate cavities that would host anionic guests. In this work we report novel and rare infinite doubly stranded chains with a propeller arrangement around each metal center, using the tectonic ligand L^1 (Scheme 1) and Ag^I ions. Initially this assembly was discovered by serendipity, as are most assemblies in the area of supramolecular chemistry, but later it was rationally reproduced with $AgCF_3SO_3$ (**1a**) and $AgBF_4$ (**1b**).

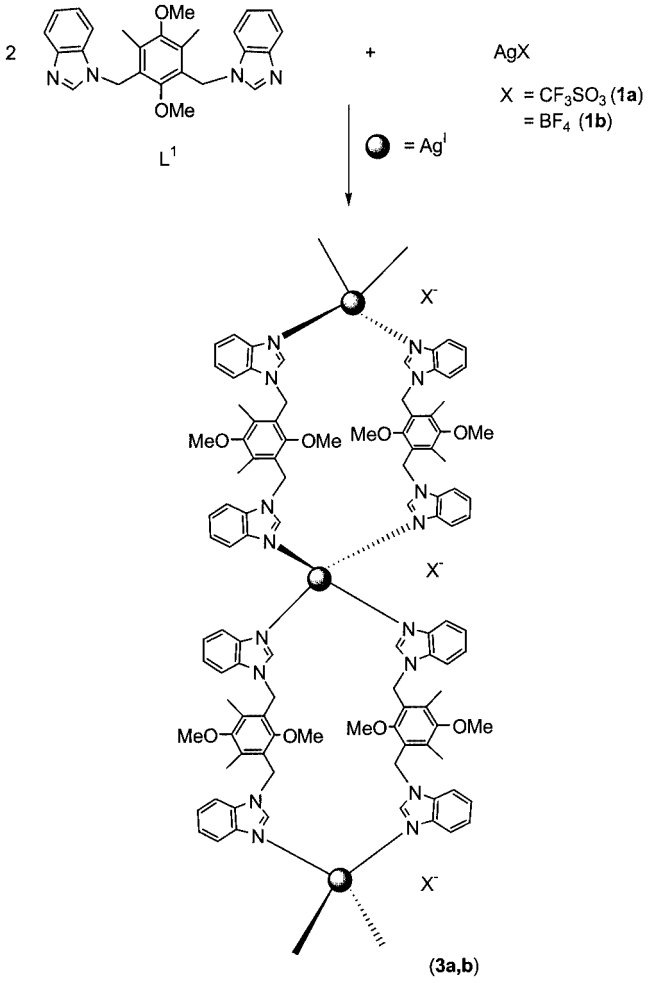
Results and Discussion

Self-Assembly of the Doubly Stranded Chain Complexes $\{[AgL^1_2][X]\}_n$ [X = CF_3SO_3, (3a); X = BF_4, (3b)]

To demonstrate the viability of our strategy we prepared the bidentate ligand 1,3-bis(benzimidazol-1-ylmethyl)-2,5-dimethoxy-4,6-dimethylbenzene (L^1, **2a**). It was synthesized by allowing the corresponding bis(chloromethyl) derivative to react with two equivalents of benzimidazole in the presence of K_2CO_3 in CH_3CN (overall yield: 90%). Its spectroscopic data are consistent with the proposed structure.

Significantly, treatment of $AgCF_3SO_3$ (**1a**) with two equivalents of L^1 in CH_3CN/CH_2Cl_2 solution gave a white precipitate after five minutes of stirring. The reaction was allowed to proceed for several hours without any further change being observed. The white precipitate was isolated in quantitative yield and identified as 1-D doubly stranded chains of $\{[AgL^1_2][CF_3SO_3]\}_n$ (**3a**). Complex **3a** was found to be soluble in polar solvents such as methanol, acetonitrile and dimethyl sulfoxide, hence the ^1H NMR spectrum was recorded in CD_3CN (Figure 1). The ^1H and ^{13}C NMR spectroscopic data are consistent with the proposed formulae and show that the coordinated ligand L^1 displays a sym-

[a] Laboratoire de Chimie Inorganique et Matériaux, Moléculaires UMR CNRS 7071, Université Pierre et Marie Curie
4, place Jussieu, case 42, 75252 Paris cedex 05, France
Fax (internat.) +33-1/4427-3841
E-mail: amouri@ccr.jussieu.fr



Scheme 1. General synthetic strategy for 1-D chains (**3a,b**)

metric pattern close to that of the free ligand L^1. Most remarkably, the resonances ascribed to the protons of the benzimidazole group appear at δ = 7.92 (s, 2 H), 7.71 (m, 4 Hz, 4 H), 7.55 (m, 4 H) and 7.29 ppm (m, 8 H) (see Figure 1). The NMR symmetry is probably due to the fragmentation of the polymer and formation of oligomeric species during the dissolution process. The electrospray (ES) mass spectrum shows a peak at m/z = 961.19 which corresponds to the formation of $[Ag(L^1)_2]^+$ species in solution. This suggests that the $[Ag(L^1)_2]^+$ sub-unit is the key building block which leads to the formation of the doubly stranded chains $\{[AgL^1_2][CF_3SO_3]\}_n$ (**3a**) through self-assembly. Variable temperature ^{1}H NMR spectra recorded for **3a** in CD_3CN show no signal broadening, suggesting that the exchange phenomenon may be fast on the NMR time scale. It is worth noting that von Zelewsky and co-workers have reported that a polymeric double-helix silver complex breaks down in solution to produce circular helicates or oligomers which are in rapid dynamic equilibrium.[9]

Suitable crystals of **3a** were obtained by slow evaporation of Et_2O into a CH_3CN solution. The complex crystallizes in the triclinic unit cell space group $P\bar{1}$. Crystallographic data for **3a** are shown in Table 1. Selected bond lengths and angles are shown in Table 2. The structure shows that complex **3a** consists of one-dimensional doubly stranded chains (Figure 2a). Four L^1 ligands wrap around the Ag^I ion to give a tetrahedral coordination geometry and are disposed in a propeller arrangement with a dihedral angle θ of 80.3°. Each ligand L^1 connects another Ag^I center through the other benzimidazole arm generating a 1D-doubly stranded chain. Further we note the presence of a center of symmetry lying half way between two parallel phenyl rings within the double stranded chain (Figure 2b). Interestingly, the phenyl rings of two close doubly stranded chains show an offset π-stacking phenomenon, with a plane-to-plane

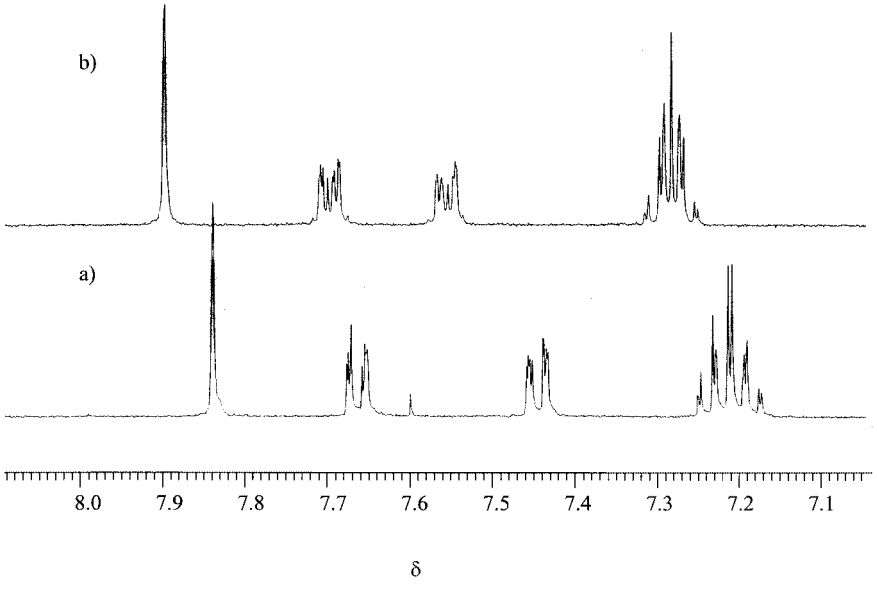


Figure 1. Section of the ^{1}H NMR spectra (400 MHz) showing the aromatic region for: a) the free ligand L^1 recorded in CD_3CN, and b) **3a** recorded in CD_3CN

Table 1. Crystal data and structures refinement for **3a**

	3a
Formula	$Ag(N_4C_{26}O_2H_{26})_2{\cdot}(CF_3SO_3){\cdot}H_2O$
M_r	1127.99
Crystal size	0.2 × 0.2 × 0.4
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	11.752 (1)
b (Å)	12.689 (2)
c (Å)	20.672 (3)
α (deg)	95.78 (1)
β (deg)	100.71 (1)
γ (deg)	116.87 (1)
V (Å^3)	2641.2 (7)
Z	2
$\rho_{calcd.}$ (g·cm^{-3})	1.42
Temp (°C)	27
λ (Mo-K_α) (Å)	0.71069
μ (cm^{-1})	4.93
$R(F_o)$[a]	0.056
$R_w(F_o)$[b]	0.061

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma F_o$. [b] $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$.

Table 2. Selected interatomic distances [Å] and angles for **3a**

Ag(1)−N(1)	2.246 (3)
Ag(1)−N(101)	2.266(3)
N(1)−Ag(1)−N(4)	99.02(13)
N(1)−Ag(1)−N(101)	132.97(15)
N(4)−Ag(1)−N(104)	112.50(14)
Ag(1)−N(4)	2.357(4)
Ag(1)−N(104)	2.455 (4)
N(1)−Ag(1)−N(104)	105.79(13)
N(4)−Ag(1)−N(101)	110.70 (14)
N(101)−Ag(1)−N(104)	95.69 (13)

distance of 3.8 Å. This weak π-interaction is observed throughout the infinite chain and only between alternate metallomacrocycles (Figure 2c).[14] In a well-documented paper, Janiak reported on π-π stacking in metal complexes with aromatic ligands. He showed that strong interactions exist when plane-to plane-distances are around 3.3 Å. These interactions are weaker when the distance is above 3.6 Å with 3.8 Å being approximately the maximum for which π-π interactions are accepted.[14d] It is clear that the two L^1 ligands and the two Ag^I centers describe a 25-membered ring with a nanometric cavity where both extremities are capped by the silver centers (Figure 2b). The average Ag−Ag distance in **3a** is 12.7 Å (1.27 nm), while the average distance between the two phenyl rings is 8.4 Å (0.84 nm). Perhaps due to the steric hindrance presented by the internal methoxy groups, all the $CF_3SO_3^-$ anions are located outside the metallomacrocyclic cavity and in between two doubly stranded chains (Figure 2c). The average Ag−Ag distance between two close doubly stranded chains is 11.3 Å. Taken together, this is a rare one-dimensional structure for Ag^I ions connected by benzimidazole ligands. Related complexes of this family are often obtained as classical mono-helix or doubly stranded helical chains.[8−10]

It is interesting to speculate as to the extent to which this π-π stacking interaction is responsible for the self-assembly and stability of these doubly stranded chains. In this context we note that Lehn and co-workers have elegantly shown that a pre-organized helical conformation of discrete encoded oligoheterocyclic strand can be envisaged through π-π interactions between parallel aromatic heterocycles of neighboring molecules.[15a] Furthermore, Stoddart and co-workers have beautifully shown that an infinite two-dimensional polymeric supramolecular network is generated as a result of extended π-π stacking interactions.[15b]

We then examined the role of the anion on the formation of this one-dimensional chain. Thus we repeated the above experiment but using $AgBF_4$ (**1b**) instead of $AgCF_3SO_3$ (**1a**). A white precipitate was similarly obtained in quantitative yield and was identified as 1D-doubly stranded chains of $\{[AgL^1_2][BF_4]\}_n$ (**3b**) analogous to **3a**. The spectroscopic data were identical to those obtained for **3a**. To confirm the solid-state structure of **3b** an X-ray structural determination was carried out on a single crystal of **3b**. Although complete refinement could not be achieved due to the small size of the crystals, we were able to obtain valuable information about complex **3b**.

The structure shows indeed that **3b** consists of doubly stranded chains, and that the BF_4 anions are located outside the metallomacrocyles and in between the two doubly stranded chains. The average Ag−Ag distance in **3b** is 12.3 Å (1.23 nm), while the average distance between the two phenyl rings is 8.5 Å (0.85 nm). The Ag−Ag distance between two close doubly stranded chains is 12.1 Å (1.21 nm). These results are similar to those obtained for **3a** and they show that the size of the weakly coordinating counterion does not affect the overall structure.

It is noteworthy, however, that it has been reported recently that treatment of $AgCF_3SO_3$ or $Cu(ClO_4)_2$ with the analogous bidentate ligands L^2 and L^3 possessing two benzimidazole arms in the 1,3- and 1,4-positions of a phenyl ring, respectively, afforded the binuclear boxes M_2L_3 and M'_2L_4 (M = Ag, M′ = Cu) in which an anion guest is encapsulated.[16] Our results contrast sharply with those reported and this is no doubt related to the steric factors displayed by our ligand L^1.

Conclusion

In conclusion, using the tetrahedral coordination chemistry of Ag^I ions and the tectonic ligand L^1, we have reported a rational synthetic strategy for the formation of rare doubly stranded chains (**3a,b**). The cavity size in these 1D-chains is of nanometric size and we expect that it can be modulated, depending on the bridging di-benzimidazole ligands used. These surprising results address once again the important role of assembling tectonic ligands, metal and ligand geometries, coordination sites, π-π interactions and steric effects which determine the final structure of the supramolecular species obtained. Thus, ligand tailoring is at the heart of the art and science of inorganic supramolecular construction.

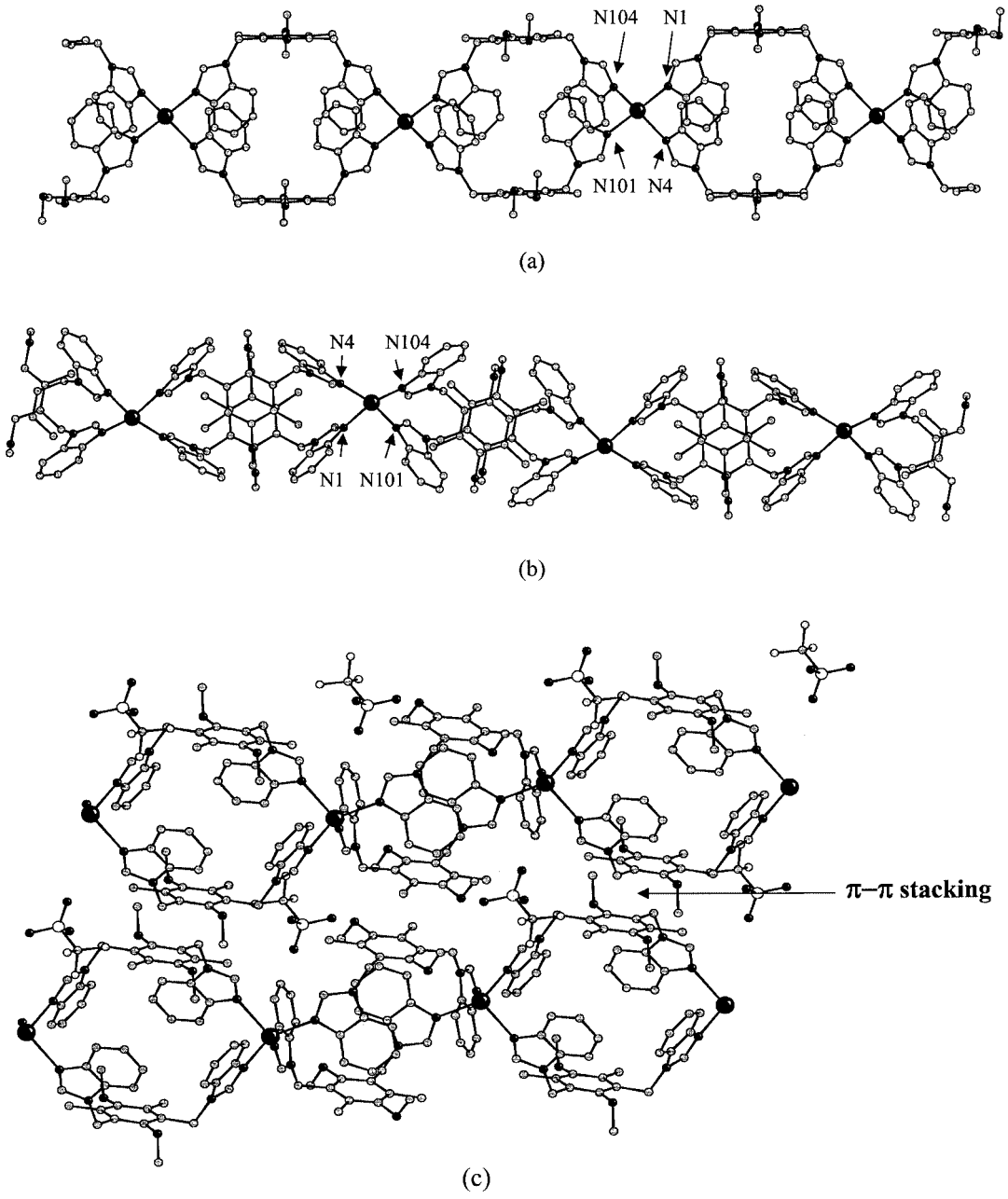


Figure 2. a) Crystallographic structure of the cationic part of the doubly stranded infinite chains **3a** perpendicular to the *b* axis with atom numbering system; hydrogens have been omitted for clarity; b) crystallographic structure of the cationic part of **3a** showing the two coplanar phenyl rings within each metallomacrocyle of the infinite chain; note the alternate arrangement of the metallomacrocycles; c) view of the infinite 1D-chain of $\{[AgL_2][CF_3SO_3]\}_n$ (**3a**) showing the triflate anions lying in between two doubly stranded chains as well as the offset π-π stacking phenomenon between the phenyl rings of two neighboring doubly stranded chains

Further investigations are ongoing on this and related 1-D and 2-D supramolecular assemblies with the aim of obtaining selective hosts for a variety of anionic guests.

Experimental Section

All experimental manipulations were carried out under argon using Schlenk tube techniques.

Synthesis of L[1]: This bidentate ligand was prepared by addition of 1,3-di(chloromethyl)-2,5-dimethoxy-4,6-dimethylbenzene (1.09 g, 4.41 mmol) in CH_3CN to benzimidazole (0.98 g, 8.3 mmol) in the presence of K_2CO_3 (1.14 g, 8.24 mmol). The reaction was stirred for 30 minutes before being refluxed for 12 hours. The resulting precipitate was filtered and extracted with $CHCl_3$. After being washed with distilled water the organic phase was isolated before being dried over $MgSO_4$. The solvent was removed on a rotary evaporator to yield an off-white microcrystalline solid. Yield: 1.58 g (90%). $C_{26}H_{26}N_4O_2{\cdot}H_2O$ (444): calcd. C 70.27, H 6.30, N 12.61; found C 70.64, H 6.10, N 12.57. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.10 (s, 2 H, =CH), 7.63 (d, 2 H, =CH), 7.47 (d, 2 H, =CH), 7.16 (m, 4 H, H-aromatic), 5.49 (s, 4 H, -CH_2-), 3.70 (s, 3 H, MeO), 3.50 (s, 3 H, MeO), 2.12 (s, 6 H, CH_3).

Synthesis of 3a: A solution of L^1 (**2a**) (438 mg, 1.02 mmol) in $CHCl_3$ (10 mL) was added to a solution of $AgCF_3SO_3$ (**1a**; 126 mg, 0.5 mmol) in CH_3CN (10 mL). After 5 minutes stirring, a white precipitate was formed. The reaction was allowed to proceed for several hours without any further changes. The precipitate was filtered and washed several times with CH_2Cl_2 then dried under vacuum. Yield: 550 mg (quantitative). ^1H NMR (400 MHz, [D$_6$]DMSO): δ = 8.25 (s, 2 H, =CH), 7.74 (dd, 4 H, H-aromatic), 7.58 (dd, 4 H, H-aromatic), 7.23 (m, 8 H, H-aromatic), 5.56 (s, 8 H, -CH$_2$-N), 3.70 (s, 6 H, -OCH$_3$), 3.53 (s, 6 H, -OCH$_3$), 2.16 (s, 12 H, -CH$_3$) ppm. ^{13}C NMR (100.62 MHz, [D$_6$]DMSO): δ = 154.4, 153.8, 144.5, 142.4, 133.5, 133.1, 125.9, 123.3, 122.6, 119.5, 111.2, 63.5, 60.2, 41.3, 12.5 ppm. ^{19}F NMR (376.49 MHz, [D$_6$]DMSO): δ = −78.18 (s, free CF_3SO_3) ppm. IR (KBr): $\tilde{\nu}$=1267 s (ν_{C-F}) cm^{-1}.

Synthesis of 3b: Compound **3b** was prepared in a similar way to **3a** but using $AgBF_4$ instead of $AgCF_3SO_3$. It was obtained quantitatively. $C_{52}H_{52}AgBF_4N_8O_4$ (1047.8): calcd. C 59.61, H 5.00, N 10.70; found C 59.38, H 5.01, N 11.60. ^1H NMR (400 MHz, [D$_6$]DMSO): δ = 8.26 (s, 2 H, =CH), 7.76 (dd, 4 H, H-arom.), 7.62 (dd, 4 H, H-arom.), 7.26 (m, 8 H, H-arom.), 5.57 (s, 8 H, -CH$_2$-N), 3.69 (s, 6 H, -OCH$_3$), 3.55 (s, 6 H, -OCH$_3$), 2.17 (s, 12 H, -CH$_3$) ppm. ^{13}C NMR (100.62 MHz, [D$_6$]DMSO): δ = 154.5, 153.8, 144.6, 142.1, 133.4, 133.2, 125.8, 123.5, 122.8, 119.5, 111.3, 63.5, 60.2, 41.3, 12.5 ppm. ^{19}F NMR (376.49 MHz, [D$_6$]DMSO): δ = −148.70 (s, free BF_4) ppm. IR (KBr): $\tilde{\nu}$ = 1068 s (ν_{B-F}) cm^{-1}.

X-ray Structure Determination: A colorless needle-shaped crystal of **3a** was mounted on a glass fiber. All measurements were made on a Enraf−Nonius Mach-3 diffractometer, Mo-K_α radiation (λ = 0.71069 Å), collection range 2θ = 2−50°. The Ψ-scan curve of **3a** was flat, hence no absorption correction was applied. The structure was determined by direct methods and subsequent difference-Fourier syntheses, and refined by full-matrix least-squares on *F* using the programs of the PC version of CRYSTALS. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on a difference-Fourier map and their coordinates were refined with an overall isotropic thermal parameter.

CCDC-166133 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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