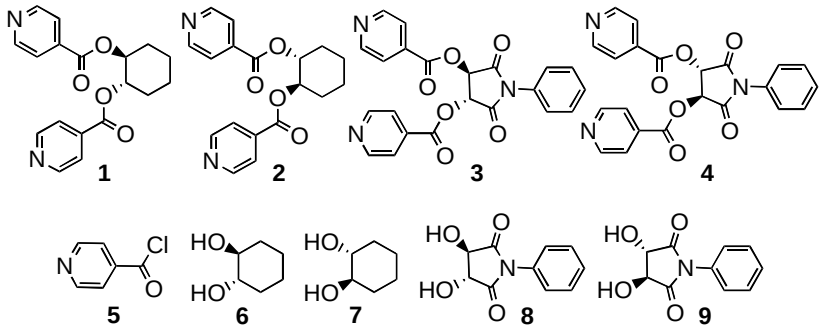
Electronic Supplementary Material (ESI) for Chemical Communications

Molecular tectonics: design of enantiomerically pure helical tubular crystals with controlled channel size and orientation

Mei-Jin Lin, Abdelaziz Jouaiti*, Philippe Grosshans, Nathalie Kyritsakas and Mir Wais Hosseini*

Synthesis of compounds 1-4:



General method for the syntheses of compounds 1 and 2:

Under nitrogen and at room temperature, to a degassed solution of alcohol **6** or **7** (5 mmol) in dry THF (20 ml), the hydrochloride salt of *iso*nicotinoyl chloride **5** (15 mmol) was added and the mixture was stirred at room temperature for 15 min. Et_3N (5 ml) was added to the mixture and stirring was further continued for two days. After evaporation to dryness, saturated aqueous solution of Na_2CO_3 (40 ml) was added to the residue and the mixture extracted with $CHCl_3$ (3 x 30 ml). The organic solvent was removed and the residue purified by column chromatography [SiO_2, $CHCl_3$] affording the pure products as a colorless powder.

Compound 1 (51% yield) Mp = 110 °C. ^{1}H-RMN (25 °C, 300 MHz, $CDCl_3$): δ (ppm) 1.45 (m, 2H,); 1.63 (m, 2H); 1.86 (m, 2H); 2.23 (m, 2H); 5.24 (m, 2H); 7.73 (dd, 4H, J = 1.6 Hz and 4.4 Hz); 8.71 (dd, 4H, J = 1.6 Hz and 4.4 Hz); ^{13}C-RMN (25 °C, 75 MHz, $CDCl_3$): δ (ppm) 23.4; 30.1; 75.2; 122.7; 137.1; 150.6; 164.5. Mw = 326.35. % Calc. for $C_{18}H_{18}N_2O_4$ C = 66.25; H = 5.56; N = 8.58, % Found C = 66.31; H = 5.72; N = 8.84.

Compound 2: (60% yield) Mp = 125 °C. ^{1}H-RMN (25 °C, 300 MHz, $CDCl_3$): δ (ppm) 1.45 (m, 2H); 1.62 (m, 2H); 1.82 (m, 2H); 2.21 (m, 2H); 5.23 (m, 2H); 7.71 (dd, 4H, J = 1.6 Hz and 4.4 Hz); 8.66 (dd, 4H, J = 1.6 Hz and 4.4 Hz); ^{13}C-RMN (25 °C, 75 MHz, $CDCl_3$): δ (ppm) 23.4, 30.1 ; 75.1; 122.7, 137.0, 150.6, 164.4. Mw = 326.35. % Calc. for $C_{18}H_{18}N_2O_4$ C = 66.25; H = 5.56; N = 8.58, % Found C = 66.70; H = 5.73; N = 8.46.

General method for the syntheses of compounds 3 and 4:

In the dark and under nitrogen, to a degassed solution of alcohol **8**[1] or **9**[1] (5 mmol) in dry THF (20 ml), the hydrochloride salt of *iso*nicotinoyl chloride **5** (12.5 mmol) was added and the mixture was stirred at room temperature for 15 min. Pyridine (3 ml) was added to the mixture and stirring was further continued for 24h. After evaporation to dryness, saturated aqueous solution of Na_2CO_3 (40 ml) was added to the residue and the mixture extracted with

CH_2Cl_2 (2 x 30 ml). The organic solvent was removed and the residue purified by column chromatography [SiO_2, CH_2Cl_2/MeOH 2%] affording the pure products as a colorless powder.

Compound 3 (42% yield) Mp > 200 °C. ^{1}H-RMN (25 °C, 300 MHz, $CDCl_3$): δ (ppm) 8.85-8.87 (d, 4H, J = 6.0), 7.91-7.93 (dd, 4H, J = 2.7 Hz and 1.8 Hz); 7.26-7.55 (m, 5H), 6.08 (s, 2H); ^{13}C-RMN (25 °C, 75 MHz, $CDCl_3$): δ (ppm) 73.7; 123.1; 126.1; 129.5; 135.1; 150.9; 164.4; 167.5. Mw = 417.38. % Calc. for $C_{22}H_{15}N_3O_6$ C 63.31, H 3.62 , N 10.07; % Found C 63.16, H 3.77, N 10.33.

Compound 4 (40% yield) Mp > 200 °C. ^{1}H-RMN (25 °C, 300 MHz, $CDCl_3$): δ (ppm) 8.85-8.87 (d, 4H, J = 6.0 Hz); 7.78-7.91 (dd, 4H, J = 3.0 Hz and 1.2 Hz); 7.41-7.54 (m, 5H), 6.08 (s, 2H); ^{13}C-RMN (25 °C, 75 MHz, $CDCl_3$): δ (ppm) 73.7; 123.1; 126.1; 129.5; 129.5; 135.2; 150.9; 164.4; 167.5. Mw = 417.38. % Calc. for $C_{22}H_{15}N_3O_6$ C 63.31, H 3.62, N 10.07; % Found C 63.28, H 3.74, N 10.32.

---

1 A. M. d', A. Rocha Gonsalves, M. E. S. Serra, D. Murtinho, V. F. Silva, A. Matos Beja, J. A. Paixão, M. Ramos Silva, L. Alte da Veiga, *J. Mol. Catal. A: Chem.*, 2003, **195**, 1.

Crystallography

Data (Tables TS1 and TS2) were collected on a Bruker SMART CCD diffractometer with Mo–Kα radiation. The structures were solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-97 with anisotropic thermal parameters for all non hydrogen atoms.[2] The hydrogen atoms were introduced at calculated positions and not refined (riding model). In the case **1**·$ZnSiF_6$ and **2**·$ZnSiF_6$, the SQUEEZE command was employed owing to the presence of highly disordered solvent molecules.[3]

CCDC 820939 - 820946 contain the supplementary crystallographic data for compounds **1**·$ZnSiF_6$ and **2**·$ZnSiF_6$, **3**·$ZnSiF_6$ and **4**·$ZnSiF_6$. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

Crystallisation: In a tube (0.5 cm diameter and 15 cm hight), upon slow diffusion of an EtOH solution of $ZnSiF_6$ (5 mg) into a $CHCl_3$ solution (1 mL) of tectons **1**-**3** (3 mg), colourless crystalline material was obtained after *ca* 24-48 hours. In the case of tectons **4**, in a tube (0.5 cm diameter and 15 cm hight), upon slow diffusion of an EtOH solution of $ZnSiF_6$ (5 mg) into a CH_2ClCH_2Cl solution (1 mL) of tecton **4** (3 mg) through a DMSO layer (0.1 ml), colourless crystalline material was obtained after *ca* 24-48 hours.

Both in the case of EtOH-$CHCl_3$ and EtOH-CH_2ClCH_2Cl mixtures, the crystallisation procedure in addition to the desired crystals produced an amorphous powder. In order to obtain the crystalline material, the mixture was manually sorted.

In the case of **1**·$ZnSiF_6$ and **2**·$ZnSiF_6$, the solvent molecules (EtOH and $CHCl_3$) were found to be disordered and the Squeeze command was used.

Table TS1. Crystallographic data (0.71073 Å, 173 K) for **X**·$ZnSiF_6$ (X = 1-3) obtained from a EtOH and $CHCl_3$ mixture.

Formula	**1**·$ZnSiF_6$	**2**·$ZnSiF_6$	**3**·$ZnSiF_6$	**4**·$ZnSiF_6$
Chemical formula	$C_{36}H_{36}F_6N_4O_8SiZn$ SQUEEZE	$C_{36}H_{36}F_6N_4O_8SiZn$ SQUEEZE	$2(C_{44}H_{30}F_6N_6O_{12}SiZn)$, $5(C_2H_6O)$, H_2O	$(C_{44}H_{30}F_6N_6O_{12}SiZn)$, $2(C_2H_6O)$, $(C_2H_4Cl_2)$
Molecular weight	860.17	860.15	2332.76	1233.29
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	C222(1)	C2221	C2	C2
a(Å)	7.6698(4)	7.6731(5)	24.0625(16)	23.2446(5)
b(Å)	21.0303(11)	21.0006(13)	7.6315(4)	7.5892(2)
c(Å)	28.3731(11)	28.3703(19)	16.3387(10)	16.6055(4)
α(deg)	90	90	90	90
β(deg)	90	90	99.928(3)	100.1650(10)
γ(deg)	90	90	90	90
V(Å3)	4576.5(4)	4571.6(5)	2955.4(3)	2883.36(12)
Z	4	4	2	2
Color	Colorless	Colorless	Colorless	Colorless
Crystal dim (mm)	0.08 x0.06x0.05	0.08x0.06x0.05	0.09x0.07x0.05	0.12x0.09x0.06
Dcalc (gcm^{-3})	1.248	1.250	1.310	1.421
F(000)	1768	1768	1200	1264
μ (mm^{-1})	0.634	0.635	0.519	0.625
Number of data meas.	23640	14563	24061	54470
Number of data with I> 2σ(I)	5232	5241	6428	6611
R(int)	0.048	0.0345	0.0304	0.0269
R	0.1025	0.1145	0.0542	0.03348
Rw	0.2626	0.2374	0.1541	0.0986
R(all)	0.1319	0.1441	0.0625	0.0351
Flack parameter	0.002(3)	0.03(1)	0.023(2)	0.017(7)
GOF	1.212	1.265	1.028	1.002

Crystallisation: In a tube (0.5 cm diameter and 15 cm hight), upon slow diffusion of an EtOH solution of $ZnSiF_6$ (7 mg) into a CH_2ClCH_2Cl solution (1 mL) of tectons **1-4** (4 mg), colourless crystalline material was obtained after ca 24-48 hours. For all combinations of tectons **1-4** with $ZnSiF_6$, the procedure leads both to the desired crystals of **X**·$ZnSiF_6$ (X = 1-4) and the parent $ZnSiF_6$ salt. Owing to similar morphologies and colours between **X**·$ZnSiF_6$ (X = 1-4) and $ZnSiF_6$, the identification could only be made by determining the unit cell for both crystals by X-ray diffraction. The procedure was repeated 4 times and statically, a 50/50 ratio was observed.

In the case of **1**·$ZnSiF_6$ and **2**·$ZnSiF_6$, the solvent molecules (EtOH and $C_2H_4Cl_2$) were found to be disordered and the Squeeze command was used.

Table TS2. Crystallographic Parameters (0.71073 Å, 173 K) for **X**·$ZnSiF_6$ (X = 1-4) obtained from EtOH and CH_2ClCH_2Cl mixture.

Formula	**1**·$ZnSiF_6$	**2**·$ZnSiF_6$	**3**·$ZnSiF_6$	**4**·$ZnSiF_6$
Chemical formula	$C_{36}H_{36}F_6N_4O_8SiZn$ SQUEEZE	$C_{36}H_{36}F_6N_4O_8SiZn$ SQUEEZE	($C_{44}H_{30}F_6N_6O_{12}SiZn$), 2($C_2H_6O$), ($C_2H_4Cl_2$)	($C_{44}H_{30}F_6N_6O_{12}SiZn$), 2($C_2H_6O$), ($C_2H_4Cl_2$)
Molecular weight	860.15	860.15	1233.29	1233.29
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2	C2	C2	C2
a(Å)	20.7481(11)	20.8352 (5)	23.2747(19)	23.2828(4)
b(Å)	7.6446(4)	7.6558(3)	7.5775(5)	7.59880(10)
c(Å)	14.9105(7)	14.9174(5)	16.5826(12)	16.6091(3)
α(deg)	90	90	90	90
β(deg)	107.187(3)	107.298(2)	100.139(2)	100.1650(10)
γ(deg)	90	90	90	90
V(Å3)	2259.4(2)	2271.85(15)	2878.9(4)	2892.38(8)
Z	2	2	2	2
Color	Colorless	Colorless	Colorless	Colorless
Crystal dim (mm)	0.08 x0.07x0.05	0.08x0.06x0.05	0.09x0.07x0.04	0.10 x 0.08 x 0.08
Dcalc (gcm^{-3})	1.264	1.257	1.423	1.416
F(000)	884	884	1264	1264
μ (mm^{-1})	0.642	0.639	0.626	0.623
Number of data meas.	8259	8033	14482	15335
Number of data with I> 2σ(I)	4559	4057	5951	6734
R(int)	0.0458	0.023	0.035	0.0205
R	0.1045	0.0792	0.0771	0.0411
Rw	0.2564	0.2235	0.1466	0.1140
R(all)	0.1317	0.0838	0.0917	0.0473
Flack parameter	0.08(4)	0.05(2)	0.004(17)	0.032(9)
GOF	1.122	1.062	1.254	1.023

2 G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.

3 A. L. Spek, *PLATON*, The University of Utrecht, Utrecht, The Netherlands, 1999.