Electronic Supplementary Informations

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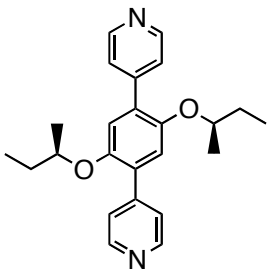
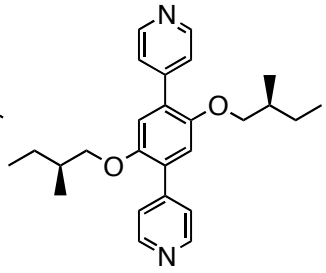
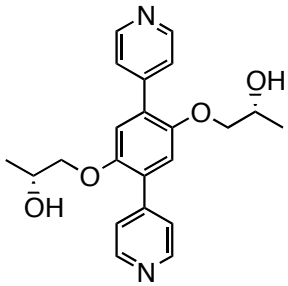
Experimental section



1 (*R*,*R*)

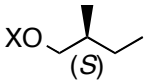


2 (*S*,*S*)

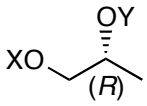


3 (*R*,*R*)

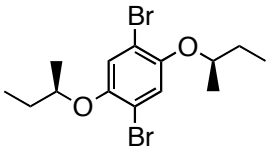
4 X = H
5 X = Ts



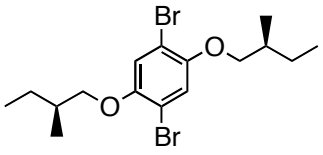
6 X = H
7 X = Ts



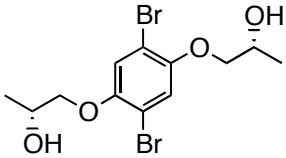
8 X = H, Y = H
9 X = Ts,Y = H
10 X = Ts, Y = THP



11 (*R*,*R*)



12 (*S*,*S*)



13 (*R*,*R*)

General:
CH_2Cl_2 and triethylamine were distilled over CaH_2 and KOH respectively. ^{1}H- and ^{13}C-NMR spectra were acquired at 25 °C on either Bruker AV 300, Brucker AV 400 spectrometers in deuterated solvents and residual solvent peak was used as the internal reference. Elemental analyses were performed on a Thermo Scientific Flash 2000 by the "Service Commun de Microanalyse of the University of Strasbourg. For X-Ray diffraction on single crystals, data were collected at 173(2) K on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. For all structures, diffraction data were corrected for absorption. Structures were solved using SHELXS-97 and refined by full matrix least-squares on F2 using SHELXL-97. The hydrogen atoms were introduced at calculated positions and not refined (riding model). Polarimetric measurements were performed on a Perkin Elmer (model 341).

All synthetic steps reported have been carried out under argon atmosphere.

Synthesis of **5** and **7**:

To a stirred solution of alcohol **4** (2 mL, 22 mmol) or **6** (2 mL, 19 mmol) in CH_2Cl_2 (50 mL), DMAP (0.1 eq) and Et_3N (2 eq) were added. To the mixture, a solution of Tosyl Chloride (1eq) in CH_2Cl_2 (50 mL) was added dropwise over 30 min. The reaction mixture was stirred overnight. The resulting yellowish solution was washed with water (100 ml) and aq.$NaHCO_3$ (10%, 2 x 100mL). The organic layer was dried over $MgSO_4$. The removal of the solvent under reduced pressure afforded a brownish oil. This latter was purified by column chromatography (SiO_2, eluent: Cyclohexane/CH_2Cl_2 4/1 then 1/1) to yield the desired compounds **5** (3.9 g, 79 % yield) and **7** (4.4 g, 98 yield %) as colorless oils.

(S)-sec-butyl 4-methylbenzenesulfonate **5**: DMAP: 266 mg, Et_3N: 6 mL TsCl: 4.35 g.

^{1}H-NMR ($CDCl_3$, 300 MHz, 25 °C) δ (ppm): 7.71 (d, 2H, ^{3}J = 8.3 Hz) 7.23 (d, 2H, ^{3}J = 8.1 Hz) 4.49 (m, 1H) 2.35 (s, 3H) 1.55 (m, 2H) 1.16 (d, 3H, ^{3}J = 6.3 Hz) 0.75 (t, 3H, ^{3}J = 7,6 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz, 25 °C): 144.7, 134.8, 130.0, 127.9, 82.1, 29.7, 21.9, 20.6, 9.6; $[\alpha]^{20}_D$ +10.2° (c = 1.17 in $CHCl_3$) (lit.[1] $[\alpha]^{20}_D$ +9.6°, c = 4.01 in $CHCl_3$). Elemental analysis (%) for $C_{11}H_{16}O_3S$ calc: C, 57.87; H, 7.06 found: C, 57.94; H, 7.08

(*S*)-2-methylbutyl 4-methylbenzenesulfonate **7**: DMAP: 226 mg, Et_3N: 5 mL TsCl: 3.70 g.

^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C) δ (ppm): 7.69 (d, 2H, ^{3}J = 8.4 Hz) 7.23 (d, 2H, ^{3}J = 8.3 Hz) 3.80 (dd, 1H, ^{2}J = 5.8 Hz, ^{3}J = 9.4 Hz) 3.73 (dd, 1H, ^{2}J = 6.4 Hz, ^{3}J = 9.4 Hz) 2.33 (s, 3H) 1.62 (m, 1H) 1.31 (m, 1H) 1.07 (m, 1H) 0.78 (d, 3H, ^{3}J = 6.8 Hz) 0.74 (t, 3H, ^{3}J = 7.5 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz, 25 °C) δ (ppm): 146.9, 135.3, 132.0, 130.0, 77.0, 36.5, 27.6, 23.8, 18.1, 13.1; $[\alpha]^{20}_D$ +5.0° (c = 1.14 in $CHCl_3$) (lit.[2] $[\alpha]^{21}_D$ +4.9°, c = 2.02 in $CHCl_3$). Elemental analysis (%) for $C_{12}H_{18}O_3S$ calc: C, 59.47; H, 7.49 found: C, 59.29; H, 7.40.

Synthesis of (*R*)-2-hydroxypropyl 4-methylbenzenesulfonate 9:

At -20 °C, to a stirred solution of alcohol **8** (3 g, 39 mmol) in CH_2Cl_2 (20 mL), Et_3N (6.6 mL, 49 mmol, 1.2 eq) was added. To the mixture, a solution of Tosyl Chloride (7.52 g, 39 mmol, 1eq) in CH_2Cl_2 (30 mL) was added dropwise over 2h. The reaction mixture was stirred at -20 °C for 4h before it was allowed to reach RT and further stirred for 40h. To the reaction media, a mixture of ice/water (100 mL) was added and the organic phase was collected and further washed with HCl (1M, 50 mL), water (100 mL) and aq.$NaHCO_3$ (sat., 100 mL). The organic layer was dried over $MgSO_4$ before the solvent was removed under reduced pressure affording a yellowish oil. The desired compound **9** was obtained in 50 % yield (4.8 g) by column chomatography (SiO_2, CH_2Cl_2) as a colorless solid. ^{1}H-NMR (CD_2Cl_2, 400 MHz, 25 °C) δ (ppm): 7.78 (d, 2H, ^{3}J = 8.2 Hz) 7.37 (d, 2H, ^{3}J = 8.1 Hz) 3.99 (m, 1H) 3.94 (dd, 1H, ^{2}J = 3.2 Hz, ^{3}J = 10.0 Hz) 3.83 (dd, 1H, ^{2}J = 7.1 Hz, ^{3}J = 9.9 Hz) 2.43 (s, 3H) 1.10 (d, 3H, ^{3}J = 6.4 Hz); ^{13}C-NMR (CD_2Cl_2, 100 MHz, 25°C) δ (ppm): 145.7, 133.0, 130.4, 128.3, 75.4, 65.9, 21.8, 18,8; m.p. 34 °C; $[\alpha]^{20}_D$: -11.7° (c = 1.08 in $CHCl_3$) (lit.[3] for the (s) enantiomer $[\alpha]^{20}_D$ +11.6°, c = 1.14 in $CHCl_3$).

Synthesis of (2*R*)-2-((tetrahydro-2*H*-pyran-2-yl)oxy)propyl 4-methylbenzenesulfonate **10:**

At 0 °C, to a stirred solution of compound **9** (2.90 g, 12.5 mmol) and DiHydroPyran (DHP) (2.22 g, 26.4 mmol, 2.1 eq) in dry CH_2Cl_2 (50 mL), Pyridinium *Para*-Toluene sulfonate (PPTS) (362 mg, 1.43 mmol, 0.1 eq) was added. The mixture was stirred at 0°C for 3 hours before it was allowed to reach RT and then further stirred for 20h. To the mixture, CH_2Cl_2 (50 mL) and H_2O/ice (100 mL) were added and the organic phase was collected and washed with water (2 x 100 mL). After drying over $MgSO_4$ and evaporation of the solvent under reduced pressure, a yellowish oil was collected which was purified by column chromatography (SiO_2, CH_2Cl_2) to yield the desired compound **10** (3.89 g, 98%) as a colorless oil and as a mixture of two diastereoisomers. ^{1}H-NMR (CD_2Cl_2, 400 MHz, 25 °C) δ (ppm): 7.76 (d, 1H, ^{3}J = 8.1 Hz) 7.74 (d, 1H, ^{3}J = 8.1 Hz) 7.35 (d, 2H, ^{3}J = 8.1 Hz) 4.57-4.63 (m, 1H) 3.71-4.01 (m, 4H) 3.34 (m, 1H) 2.43 (s, 3H) 1.41-1.70 (m, 6H) 1.08 and 1.14 (d, 3H, ^{3}J = 6.2 Hz); ^{13}C-NMR (CD_2Cl_2, 100 MHz, 25 °C) δ (ppm): 145.5, 145.4, 133.3, 130.3, 130.2, 128.3, 128.2, 99.0, 96.8, 73.7, 73.3, 70.7, 69.5, 62.8, 62.5, 31.2, 25.8, 21.8, 19.9, 19.7, 18.2, 16.2; $[\alpha]^{20}_D$: +16.7° (c = 1.11 in $CHCl_3$).

Synthesis of **11** and **12:**

To a degassed solution of 2,5-Dibromohydroquinone (1 g, 3.7 mmol) in DMF (50 mL), compound **5** (2.1 g, 2.5 eq,) or **7** (2.3 g, 2.5 eq) was added. After 10 min, Cs_2CO_3 (3.6 g, 3 eq) was added and the reaction mixture was allowed to stir overnight at 100 °C. After cooling to RT, the mixture was filtered over sintered glass buchner funnel. The filtrate was collected and evaporated to dryness under reduced pressure. The residue was purified by column chromatography (SiO_2, Eluent: CH_2Cl_2/cyclohexane, 1/1) to yield the desired compound as either a colorless oil for **11** (1.2 g, 86 % yield) or as a white solid for **12** (1.3 g, 85 % yield).

1,4-dibromo-2,5-di((R)-sec-butoxy)benzene **11**.

^{1}H-NMR (CD_2Cl_2, 400 MHz, 25 °C) δ (ppm): 7.12 (s, 2H) 4.11 (m, 2H) 1.77-1.60 (m, 4H) 1.28 (d, 6H, ^3J = 6.2 Hz) 1.00 (t, 6H, ^3J = 7.5 Hz); ^{13}C-NMR (CD_2Cl_2, 100 MHz, 25 °C) δ (ppm): 149.8, 121.2, 113.0, 78.8, 29.5, 19.4, 9.9; $[\alpha]^{20}_D$: -41.5° (c = 1.00 in $CHCl_3$). Elemental analysis (%) for $C_{14}H_{20}Br_2O_2$ calc: C, 44.24; H, 5.30 found: C, 44.05; H, 5.28.

1,4-dibromo-2,5-bis((S)-2-methylbutoxy)benzene **12**.

^{1}H-NMR (CD_2Cl_2, 400 MHz, 25 °C) δ (ppm): 7.11 (s, 2H) 3.84 (dd, 2H, ^2J = 5.9 Hz, ^3J = 8.8 Hz) 3.75 (dd, 2H, ^2J = 6.4 Hz, ^3J = 8.8 Hz) 1.89 (m, 2H) 1.63 (m, 2H) 1.35 (m, 2H) 1.05 (d, 6H, ^3J = 6.8 Hz) 0.98 (t, 6H, ^3J = 7.5 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz, 25 °C) δ (ppm): 150.5, 118.6, 111.3, 75.3, 35.2, 26.4, 16.7, 11.5; m.p = 36 °C; $[\alpha]^{20}_D$: +10.5° (c = 1.00 in $CHCl_3$). Elemental analysis (%) for $C_{16}H_{24}Br_2O_2$ calc: C, 47.08; H, 5.93 found: C, 47.10; H, 5.93

Synthesis of (2*R*,2'*R*)-1,1'-((2,5-dibromo-1,4-phenylene)bis(oxy))bis(propan-2-ol) **13:**

To a degassed solution of 2,5-Dibromohydroquinone (1.2 g, 4.5 mmol) in DMF (30 mL) compound **10** (2.95 g, 9.4 mmol, 2.5 eq) was added. After 10 min, Cs_2CO_3 (6 g, 18 mmol, 3 eq) was added and the reaction mixture was allowed to stir overnight at 100 °C. After cooling to RT, the mixture was filtered over sintered glass buchner funnel. The filtrate was collected and evaporated to dryness under reduced pressure. The resulting residue was dissolved in MeOH (50 mL) and 37 % HCl (2 mL) was added. The mixture was further stirred at RT for 3h. After evaporation to dryness under reduced pressure, the residue was dissolved in CH_2Cl_2 (100 mL) and washed with aq.$NaHCO_3$ sat.(3 x 100 mL) and H_2O (100 mL). After drying over $MgSO_4$ and evaporation of the solvent under reduced pressure, a white solid was collected and purified by column chomatography (SiO_2, CH_2Cl_2, then CH_2Cl_2/MeOH, 99/1 then CH_2Cl_2/MeOH, 98/2) to yield the desired compound **13** as a white solid (965 mg, 60 % yield). ^{1}H-NMR (CD_2Cl_2, 400 MHz, 25 °C) δ (ppm): 7.15 (s, 2H) 4.17-4.12 (m, 2H) 3.93-3.90 (dd, 2H, ^2J = 3.6 Hz, ^3J = 9.2 Hz) 3.81-3.77 (dd, 2H, ^2J = 7.3 Hz, ^3J = 9.2 Hz) 2.42 (d, 6H, ^3J = 6.4 Hz); ^{13}C-NMR (CD_2Cl_2, 100 MHz, 25 °C) δ (ppm): 150.5, 119.2, 111.6, 76.1, 66.2, 19.0; m.p = 126 °C; $[\alpha]^{20}_D$: -30.1° (c = 1.00 in $CHCl_3$). Elemental analysis (%) for $C_{12}H_{16}Br_2O_4$ calc: C, 37.53; H, 4.20 found: C, 37.71; H, 4.31

Synthesis of **1**, **2** and **3:**

To a degassed solution of compounds **11** (500 mg, 1.3 mmol)**, 12** (500 mg, 1.2 mmol) or **13** (500 mg, 1.3 mmol) and Pyridine-4-boronic acid (2.5 eq) in DMF (30 mL), Cs_2CO_3 (3 eq) and

$Pd(PPh_3)_4$ (0,1 eq) were added. The mixture was allowed to stir at 100 °C for 48h. After cooling to RT, the mixture was filtered over sintered glass buchner funnel. The filtrate was collected and evaporated to dryness under reduced pressure. The residue was purified by column chromatography (SiO_2) to yield desired tectons **1** (370 mg, 75 %), **2** (366 mg, 74 %) and **3** (371mg, 75 %) as white solids.

4,4'-(2,5-di((*R*)-*sec*-butoxy)-1,4-phenylene)dipyridine **1**: Pyridine-4-boronic acid: 404 mg, Cs_2CO_3: 1.3 g, $Pd(PPh_3)_4$: 150 mg, *Eluent (*CH_2Cl_2 then CH_2Cl_2/MeOH, 99/1 then CH_2Cl_2/MeOH, 98/2).

^{1}H-NMR (CD_2Cl_2, 400 MHz, 25 °C) δ (ppm): 8.62 (d, 4H, ^{3}J = 6.1 Hz) 7.53 (d, 4H, ^{3}J = 6.1 Hz) 7.01 (s, 2H) 4.27 (m, 2H) 1.70-1.52 (m, 4H) 1.20 (d, 6H, ^{3}J = 6.1 Hz) 0.90 (t, 6H, ^{3}J = 7.5 Hz); ^{13}C-NMR (CD_2Cl_2, 100 MHz, 25 °C) 149.9, 149.7, 146.4, 130.6, 124.7, 118.0, 77.3, 29.4, 19.2, 9.8; m.p. = 148 °C; $[\alpha]^{20}_D$: -35.2° (c = 1.00 in $CHCl_3$). Elemental analysis (%) for $C_{24}H_{28}N_2O_2$ calc: C, 76.56; H, 7.50; N, 7.44 found: C, 76.76; H, 7.62; N, 7.38.

4,4'-(2,5-bis((S)-2-methylbutoxy)-1,4-phenylene)dipyridine **2**: Pyridine-4-boronic acid: 376 mg, Cs_2CO_3: 1.2 g, $Pd(PPh_3)_4$: 140 mg; *Eluent (*CH_2Cl_2 then CH_2Cl_2/MeOH, 99/1 then CH_2Cl_2/MeOH, 98/2)**.**

^{1}H-NMR (CD_2Cl_2, 400 MHz, 25 °C) δ (ppm): 8.63 (d, 4H, ^{3}J = 6.2 Hz) 7.54 (d, 4H, ^{3}J = 6. Hz) 7.02 (s, 2H) 3.86-3.74 (m, 4H) 1.82 (m, 2H) 1.48 (m, 2H) 1.26 (m, 2H) 0.94 (d, 6H, ^{3}J = 6.7 Hz) 0.89 (t, 6H, ^{3}J = 7.4 Hz); ^{13}C-NMR (CD_2Cl_2, 100 MHz, 25 °C) δ (ppm): 150.8, 149.9, 146.1, 129.3, 124.6, 115.5, 74.6, 35.3, 26.5, 16.8, 11.5; m.p. = 169 °C; $[\alpha]^{20}_D$: +11.6° (c = 1.00 in $CHCl_3$). Elemental analysis (%) for $C_{26}H_{32}N_2O_2$ calc: C, 77.19; H, 7.97; N, 6.92 found: C, 77.07; H, 8.06; N, 6.73.

(2*R*,2'*R*)-1,1'-((2,5-di(pyridin-4-yl)-1,4-phenylene)bis(oxy))bis(propan-2-ol) **3:** Pyridine-4-boronic acid: 400 mg, Cs_2CO_3: 1.3 g, $Pd(PPh_3)_4$: 150 mg; *Eluent (*CH_2Cl_2/MeOH, 99/1 then CH_2Cl_2/MeOH, 97/3 then CH_2Cl_2/MeOH, 95/5).

^{1}H-NMR (CD_2Cl_2/MeOD, 400 MHz, 25 °C) δ (ppm): 8.57 (d, 4H, ^{3}J = 6.2 Hz) 7.62 (d, 4H, ^{3}J = 6.2 Hz) 7.06 (s, 2H) 4.06 (m, 2H) 3.88 (d, 4H, ^{3}J = 5.3 Hz) 1.18 (d, 6H, ^{3}J = 6.4 Hz); ^{13}C-NMR (CD_2Cl_2, 100 MHz, 25 °C) δ (ppm): 150.8, 149.3, 146.9, 129.5, 125.1, 116.2, 75.3, 66.3, 19.6; m.p. = 202 °C; $[\alpha]^{40}_D$: -24.4° (c = 0.5 in $CHCl_3$). Elemental analysis (%) for $C_{22}H_{24}N_2O_4$ calc: C, 69.46; H, 6.36; N, 7.36 found: C, 69.61; H, 6.45; N, 7.41.

Crystallization procedures for **1**.$ZnSiF_6$, **2**.$ZnSiF_6$ and **3**.$ZnSiF_6$

In a crystallization glass tube (height = 15 cm, diameter = 0.4 cm), slow diffusion through a layer of DMSO (0.1 mL) of an EtOH (1 mL) solution of $ZnSiF_6$ (5 mg) into a solution of **1** (3 mg) or **2** (3 mg) in $CHCl_3$ (1 mL) or **3** (3 mg) in a $CHCl_3$/MeOH 9/1 mixture (1 mL) afforded colorless prismatic crystals after few days.

[1] K. Umemura, H. Matsuyama, N. Kamigata, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2593-2600.
[2] T. Kitahara, S. Aono, K. Mori, *Biosci. Biotech. Biochem.* **1995**, *59*, 78-82.
[3] P. Huszthy, M. Oue, J. S. Bradshaw, C. Y. Zhu, T. Wang, N. K. Dalley, J. C. Curtis, R. M. Izatt, *J. Org. Chem.* **1992**, *57*, 5383-5394.

Table 1: Crystallographic parameters recorded at 173 K for **1**, **2** and **3**.

	1	**2**	**3**
Empirical formula	$C_{24}H_{28}N_2O_2$	$C_{26}H_{32}N_2O_2$	$C_{22}H_{24}N_2O_4$
Molecular weight	376.48	404.54	380.43
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	P2(1)2(1)2(1)	P1	P2(1)
a(Å)	5.9331(5)	6.4044(5)	10.9710(7)
b(Å)	7.4929(7)	9.3965(6)	7.7678(4)
c(Å)	46.754(3)	10.5878(7)	11.9253(8)
α(deg)	90	65.760(3)	90
β(deg)	90	86.256(3)	104.9420(10)
γ(deg)	90	84.669(3)	90
V(Å^3)	2078.5(3)	578.21(7)	981.92(10)
Z	4	1	2
Colour	Yellow	Colourless	Colourless
Crystal dim (mm^3)	0.08 x 0.06 x 0.06	0.08 x 0.05 x 0.05	0.07 x 0.05 x 0.04
D_{calc} (gcm^{-3})	1.203	1.162	1.287
F(000)	808	218	404
μ(mm^{-1})	0.077	0.073	0.089
Wavelength (Å)	0.71073	0.71073	0.71073
Number of data meas.	8887	8369	8330
Number of data with I> $2_{σ(I)}$	5547	5084	4560
R	0.0727	0.0735	0.0406
R_W	0.1538	0.0979	0.0475
GOF	1.028	1.029	1.000

Table 1: Crystallographic parameters recorded at 173 K for **1**-ZnSiF6, **2**-ZnSiF6 and **3**-ZnSiF6.

	1-$ZnSiF_6$	**2**-$ZnSiF_6$	**3**-$ZnSiF_6$
Empirical formula	$C_{48}H_{56}F_6N_4O_4SiZn.\ 3(CHCl_3)$	$C_{52}H_{66}F_6N_4O_4SiZn.\ 2(CHCl_3)$	$C_{44}H_{48}F_6N_4O_8SiZn.\ CHCl_3$
Molecular weight	1318.53	1255.27	1087.69
Crystal system	Tetragonal	Tetragonal	Tetragonal
Space group	P4	I4	P4
a(Å)	22.0656(6)	22.0927(4)	22.0440(15)
b(Å)	22.0656(6)	22.0927(4)	22.0440(15)
c(Å)	15.2730(7)	15.2503(5)	15.1513(18)
α(deg)	90	90	90
β(deg)	90	90	90
γ(deg)	90	90	90
V(Å^3)	7436.3(4)	7443.5(3)	7362.6(11)
Z	4	4	4
Colour	Colourless	Colourless	Colourless
Crystal dim (mm^3)	0.08 x 0.06 x 0.04	0.10 x 0.10 x 0.09	0.06 x 0.05 x 0.04
D_{calc} (gcm^{-3})	1.178	1.120	0.981
F(000)	2704	2600	2240
μ(mm^{-1})	0.721	0.614	0.511
Wavelength (Å)	0.71073	0.71073	0.71073
Number of data meas.	78262	61327	49262
Number of data with I> $2_{σ(I)}$	21762	9864	19262
R	0.1136	0.0685	0.0931
R_W	0.1980	0.1059	0.2082
GOF	1.270	1.030	1.041