## Supporting Information

# Two Homochiral Organocatalytic Metal-Organic-Materials with Nanoscopic Channels 

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## 1. General methods.

Commercially available reagents were purchased in high purity from Fisher Scientific or Frontier Scientific and used without further purification. $L_{1}$ was synthesized according to the literature ${ }^{1-2} . L_{2}$ was also synthesized based upon a literature method ${ }^{1,2}$ but using 3,5-Bis(methoxycarbonyl)phenylboronic acid as an intermediate rather than 4-(methoxycarbonyl)phenylboronic acid. Solvents were purified according to standard methods and stored in the presence of molecular sieves. Thermogravimetric analysis (TGA) was performed under nitrogen on a TA Instrument TGA 2950 Hi -Res from $30^{\circ} \mathrm{C}-700^{\circ} \mathrm{C}$ at a speed of $10^{\circ} \mathrm{C} / \mathrm{min}$. X-ray powder diffraction (XPRD) data were recorded on a Bruker D8 Advance X-ray diffractometer at 20 $\mathrm{kV}, 5 \mathrm{~mA}$ for $\mathrm{Cu}_{\mathrm{kR}}(\lambda=1.5418 \AA)$, with a scan speed of $0.5 \mathrm{~s} / \mathrm{step}\left(6^{\circ} / \mathrm{min}\right)$ and a step size of $0.05^{\circ}$ in $2 \theta$ at room temperature. Calculated XPRD patterns were produced using Powder Cell for Windows Version 2.4 (programmed by W. Kraus and G. Nolze, BAM Berlin, 2000). Thin-layer-chromatography (TLC) analysis of reaction mixtures was performed using Merck silica gel 60 F254 plates. Flash column chromatography was carried out on Merck 60 silica gel (230-400 mesh). Enantiomeric excess (ee) was determined using a Varia Prostar HPLC system with a Prostar 210 binary pump and a 335 diode array detector with Daicel Chiralcel OD-H chiral columns (eluent and flow rates shown below). NMR spectra were recorded on a Varian Inova 400 Spectrometer ( 400 MHz for ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$.). ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). Proton spectra are reported as follows: $\delta$ (position of proton, multiplicity, coupling constant J , number of protons). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet).

## 2. Synthesis of ocMOM-1

A mixture of $\mathrm{L}_{1}(10.0 \mathrm{mg}), \operatorname{In}\left(\mathrm{NO}_{3}\right)_{3} \cdot \mathrm{H}_{2} \mathrm{O}(10.0 \mathrm{mg})$ in 1.5 mL of solvent (DMF:EtOH $=2: 1$ ) was sealed in a Pyrex tube under vacuum and heated to $100^{\circ} \mathrm{C}$ for 24 hours, and then $130{ }^{\circ} \mathrm{C}$ for 72 h . The resulting pale yellow block crystals were washed with DMF to afford ocMOM-1 ( $7.4 \mathrm{mg}, 57 \%$ based on $L_{1}$ )

## 3. Synthesis of ocMOM-2

A mixture of $\mathrm{L}_{2}(10.0 \mathrm{mg}), \mathrm{CdCl}_{2} \cdot 2.5 \mathrm{H}_{2} \mathrm{O}(10.0 \mathrm{mg})$, and 1.5 mL DMF with 3 drop of 3 M HCl was sealed in a Pyrex tube under vacuum and heated to $120^{\circ} \mathrm{C}$ for 72 hours. The resulting pale yellow leaf-like crystals were washed with DMF to afford ocMOM-2 (7.1mg, $65 \%$ based on $L_{2}$ )

## 4. X-ray Structure Determination

The X-ray diffraction data for ocMOM-1 were collected using synchrotron radiation, $\lambda=0.41328 \AA$, at the Advanced Photon Source, Argonne National Lab, Chicago Il. Indexing was performed using APEX2 ${ }^{3}$ (Difference Vectors method). Data integration and reduction were performed using SaintPlus $6.01{ }^{4}$. Absorption correction was performed by a multi-scan method implemented in SADABS ${ }^{5}$. The space groups were determined using XPREP implemented in APEX2 ${ }^{3}$. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full-matrix least-squares on $\mathrm{F}^{2}$ ) contained in the APEX2 ${ }^{3}$ and WinGX v1.70.01 ${ }^{6,7,8,9}$ programs package. All non-H atoms were found in the difference Fourier map and due to the disorder were refined using the distance restraints. Restraints were also used to refine the anisotropic displacement parameters of some of disordered carbon atoms. Some of the disordered carbon atoms were refined isotropically. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using a riding model with isotropic thermal parameters: $\operatorname{Uiso}(\mathrm{H})=1.2 \mathrm{Ueq}(-\mathrm{CH})$. Restraints (AFIX 66, AFIX 116) were used to refine disordered benzene and naphthalene moieties. The contribution of heavily disordered solvent molecules was treated as diffuse using Squeeze procedure implemented in the program Platon ${ }^{10,11}$ According to TGA, all solvent molecules are lost before $100^{\circ} \mathrm{C}$. At this point, the solvent molecules removed by the SQUEEZE process could be regarded as EtOH molecules as well as nitrate anions. In every single unit cell, there are 6 nitrate anions containing 186 electrons, so the rest of $8510-186=8324$ electrons belong to EtOH molecules. As a result, there are 320 EtOH molecules per unit cell. The theoretical occupied volume of a single EtOH molecule and anitrate anion are $49.41 \AA^{3}$ and $38.61 \AA^{3}$ respectively, indicating total volume of free molecules is $49.41 * 320+38.61 * 6=16042 \AA^{3}$ per unit cell. This is much smaller than 28926 $\AA^{3}$ calculated by PLATON. When taking the contribution of disordered solvent into consideration, a reasonable estimate of the molecular formula is $\left[\left(\mathrm{In}_{3} \mathrm{O}\right)_{6}\left(\mathrm{NO}_{3}\right)_{6}\left(\mathrm{~L}_{1}\right)_{9}\right] \cdot[320 \mathrm{EtOH}]$. Based on this formula the weight percent of EtOH is around $60 \%$ which matches with TGA pattern. As required by the referee, the overall formula, formula weight, density, $\mathrm{F}(000)$, etc., calculations have been regenerated in the crystal-data text and in the cif files. Further, discussion on this matter in now been included in the ESI.

X-ray diffraction data for ocMOM-2 were collected using Bruker-AXS SMART-APEXII CCD diffractometer using $\operatorname{CuK} \alpha\left(\lambda=1.54178 \AA\right.$ ). Indexing was performed using APEX2 ${ }^{3}$ (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01 ${ }^{4}$. Absorption correction was performed by a multi-scan method implemented in SADABS ${ }^{5}$. The space group was determined using XPREP implemented in APEX2 ${ }^{3}$. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full-matrix least-squares on $\mathrm{F}^{2}$ ) contained in the APEX2 ${ }^{3}$ and WinGX v1.70.01 $6,7,8,9$ program packages. All non-H atoms were found in the difference Fourier map and refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using a riding model with isotropic thermal parameters: $\operatorname{Uiso}(\mathrm{H})=1.2 \mathrm{Ueq}(-\mathrm{CH})$. The contribution of disordered solvent molecules was treated as diffuse using Squeeze procedure implemented in the program Platon ${ }^{10,11}$. According to TGA, solvent molecules evaporated before $150^{\circ} \mathrm{C}$. At this point, the solvent molecules removed by the SQUEEZE
process could be regarded as DMF molecules with dimethylammonium cations ( $\mathrm{DMA}^{+}$) as counterions. In every unit cell, there are 16 dimethylammonium cations containing 416 electrons, so the remaining $2594-416=2178$ electrons belong to DMF molecules. As a result, there are $\sim 55 \mathrm{DMF}$ molecules per unit cell. The theoretical occupied volume of a single DMF molecule and a dimethylammonium cation are $75.26 \AA^{3}$ and $55.33 \AA^{3}$ respectively, indicating that the total volume of free molecules is $75.26 * 54+55.33 * 16=5024.58 \AA^{3}$ per unit cell. This is much smaller than the volume of $7921 \AA^{3}$ calculated by PLATON. When taking the contribution of disordered solvent into consideration, a reasonable estimate of the molecular formula is $\left[\mathrm{Cd}_{8}\left(\mathrm{DMA}^{+}\right)_{16}\left(\mathrm{~L}_{2}\right)_{4}\right] \cdot[55 \mathrm{DMF}]$. Based on this formula the weight percent of DMF is around $41 \%$ which matches well with the TGA pattern. Crystal data and refinement parameters with/without the contribution of any disordered solvents are given in Table S 2 as ocMOM-2 and ocMOM-2-1 respectively.


| Limiting indices | $-17<=\mathrm{h}<=34,-31<=\mathrm{k}<=32,-50<=\mathrm{l}<=50$ |
| :--- | :--- |
| Completeness to theta $=13.43$ | $99.8 \%$ |
| Max. and min. transmission | 0.9720 and 0.9720 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | $23627 / 370 / 871$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.066 |
| Final R indices [I>2sigma(I)] | $\mathrm{R}_{1}=0.0491, \mathrm{wR} 2=0.1155$ |
| R indices (all data) | $\mathrm{R}_{1}=0.0735, \mathrm{wR} 2=0.1208$ |
| Absolute structure parameter | $0.090(9)$ |
| Largest diff. peak and hole | 0.639 and $-0.449 \mathrm{e} . \mathrm{A}^{-3}$ |


| Table S1. Crystal data and structure refinement for ocMOM-1-1 |  |  |
| :---: | :---: | :---: |
| Identification code | ocMOM-1 |  |
| Empirical formula | $\mathrm{C}_{357.33} \mathrm{H}_{712} \mathrm{O}_{156.67} \mathrm{~N}_{2} \mathrm{P}_{3} \mathrm{In}_{6}$ |  |
| Formula weight | 8352.79 |  |
| Temperature | 298K |  |
| Wavelength | 0.41328 |  |
| Crystal system, space group | R 3 |  |
| Unit cell dimensions | $\begin{aligned} & \mathrm{a}=31.1023(19) \\ & \mathrm{b}=31.1023(19) \\ & \mathrm{c}=45.205(3) \end{aligned}$ | alpha $=90$ <br> beta=90 <br> gamma=120 |
| Volume | 37870(4) $\mathrm{A}^{3}$ |  |
| Z, Calculated density | $3,1.095 \mathrm{~g} \mathrm{~cm}^{-3}$ |  |


| Absorption coefficient | $0.366 \mathrm{~mm}-1$ |
| :---: | :---: |
| $F(000)$ | 13387 |
| Crystal size | $0.08 * 0.08 * 0.08 \mathrm{~mm}$ |
| Theta range for data collection | 0.68 to 13.43 deg. |
| Limiting indices | $-17<=\mathrm{h}<=34,-31<=\mathrm{k}<=32,-50<=\mathrm{l}<=50$ |
| Completeness to theta $=13.43$ | 99.8\% |
| Max. and min. transmission | 0.9713 and 0.9713 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 23627 / 380 / 1015 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.991 |
| Final R indices [I>2sigma(I)] | $\mathrm{R}_{1}=0.0458, \mathrm{wR} 2=0.1066$ |
| R indices (all data) | $\mathrm{R}_{1}=0.0702, \mathrm{wR} 2=0.1120$ |
| Absolute structure parameter | 0.088(8) |
| Largest diff. peak and hole | 0.599 and -0.434 e. $\mathrm{A}^{-3}$ |


| Table S2. Crystal data and structure refinement for ocMOM-2 |  |
| :--- | :--- |
| Identification code | ocMOM-2 |
| Empirical formula | $\mathrm{C}_{52} \mathrm{H}_{20} \mathrm{O}_{20} \mathrm{P}_{1} \mathrm{Cd}_{2}$ |
| Formula weight | 1220.47 |
| Temperature | 230 K |
| Wavelength | 1.54178 |
| Crystal system, space group | P 212121 |


| Unit cell dimensions | $\begin{array}{ll} a=17.4396(10) & \text { alpha=90 } \\ b=22.4040(15) & \text { beta=90 } \\ c=22.4040(15) & \text { gamma }=90 \end{array}$ |
| :---: | :---: |
| Volume | 11437.4(12) $\mathrm{A}^{3}$ |
| Z, Calculated density | $4,0.709 \mathrm{~g} \mathrm{~cm}^{-3}$ |
| Absorption coefficient | $3.415 \mathrm{~mm}^{-1}$ |
| $F(000)$ | 2408 |
| Crystal size | $0.1 * 0.1 * 0.1 \mathrm{~mm}$ |
| Theta range for data collection | 2.48 to 64.74 deg. |
| Limiting indices | $-18<=\mathrm{h}<=20,-26<=\mathrm{k}<=26,-33<=\mathrm{l}<=34$ |
| Reflections collected / unique | $96572 / 19193[\mathrm{R}(\mathrm{int})=0.0718]$ |
| Completeness to theta $=64.74$ | 99.5\% |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 19193 / 11/676 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.923 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R}_{1}=0.0314 \quad \mathrm{wR}_{2}=0.0691$ |
| R indices (all data) | $\mathrm{R}_{1}=0.0364 \quad \mathrm{wR}_{2}=0.0707$ |
| Absolute structure parameter | 0.007(3) |
| Largest diff. peak and hole | 0.589 and -0.248 e. $\mathrm{A}^{-3}$ |

Table S2. Crystal data and structure refinement for ocMOM-2-1

| Identification code | ocMOM-2-2 |
| :---: | :---: |
| Empirical formula | $\mathrm{C}_{104.25} \mathrm{H}_{148.25} \mathrm{O}_{33 .} 75 \mathrm{~N}_{17.75} \mathrm{P}_{1} \mathrm{Cd}_{2}$ |
| Formula weight | 2445.93 |
| Temperature | 230K |
| Wavelength | 1.54178 |
| Crystal system, space group | P 212121 |
| Unit cell dimensions | $\begin{array}{ll} \mathrm{a}=17.4396(10) & \text { alpha=90 } \\ \mathrm{b}=22.4040(15) & \text { beta }=90 \\ \mathrm{c}=22.4040(15) & \text { gamma }=90 \end{array}$ |
| Volume | 11437.4(12) $\mathrm{A}^{3}$ |
| Z, Calculated density | $4,1.420 \mathrm{~g} \mathrm{~cm}^{-3}$ |
| Absorption coefficient | $3.836 \mathrm{~mm}^{-1}$ |
| $F(000)$ | 5116 |
| Crystal size | $0.1 * 0.1 * 0.1 \mathrm{~mm}$ |
| Theta range for data collection | 2.48 to 64.74 deg. |
| Limiting indices | $-18<=\mathrm{h}<=20,-26<=\mathrm{k}<=26,-33<=\mathrm{l}<=34$ |
| Reflections collected / unique | $96572 / 19193[\mathrm{R}($ int $)=0.0718]$ |
| Completeness to theta $=64.74$ | 99.5\% |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 19193 / 11/676 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.923 |
| Final R indices [ $\mathrm{I}>2$ sigma(I)] | $\mathrm{R}_{1}=0.0314 \quad \mathrm{wR}_{2}=0.0691$ |


| R indices (all data) | $\mathrm{R}_{1}=0.0364$ | $\mathrm{wR}_{2}=0.0707$ |
| :--- | :--- | :--- |
| Absolute structure parameter | $0.007(3)$ |  |
| Largest diff. peak and hole | 0.589 and $-0.248 \mathrm{e} . \mathrm{A}^{-3}$ |  |

## 5. Gas Adsorption Experiments

Gas adsorption isotherms of ocMOM-1 and ocMOM-2 were collected using a surface area analyzer (ASAP-2020). Before the measurements, freshly prepared samples were soaked with ethanol. ocMOM-1 was degassed at $60^{\circ} \mathrm{C}$ for 24 h under vacuum whereas ocMOM-2 was activated using supercritical $\mathrm{CO}_{2}$ in a Tousmimis Samdri PVT-3D critical point dryer. $\mathrm{N}_{2}$ gas adsorption isotherms were measured at 77 K using a liquid $\mathrm{N}_{2}$ bath and $\mathrm{CO}_{2}$ gas adsorption isotherms were measured at 273 K using an ice-water bath.

## 6. General Procedure for transfer hydrogenation of benzoxazine reactions.

ocMOM-1 samples were exchanged with EtOH 3 times in 3 days and then soaked in the $\mathrm{CHCl}_{3}$ with a drop of concentrated acetic acid to protonate the phosphoric acid for 1 day. The substrate, catalyst ( $5 \mathrm{~mol} \%$ ) and Hantzsch dihydropyridine ( 1.25 equiv.) were suspended in $\mathrm{CHCl}_{3}$ in a screw-capped vial. The resulting mixture was allowed to stir at RT for 3d. The solvent was removed under reduced pressure and purification of the crude product by column chromatography on silica gel (ethyl acetate/hexane) afforded the pure product. Enantiomeric excess was determined by chiral HPLC analysis.


Figure S1. Comparison of experimental and calculated powder x-ray diffraction patterns of ocMOM-1


Figure S2. FT-IR of ocMOM-1 (Nicolet Avatar 320 FTIR, solid state)


Figure S3. Thermogravimetric analysis of ocMOM-1


Figure S4. Comparison of experimental and calculated powder x-ray diffraction patterns of ocMOM-2


Figure S5. FT-IR of ocMOM-2 (Nicolet Avatar 320 FTIR, solid state).


Figure S6. Thermogravimetric analysis of ocMOM-2


Figure S7. 4 connected square planar node to 4 connected pseudo-tetrahedron node ${ }^{12}$


Figure S8. 4 member rings in 1.2 nm channel


Figure S9. 4 member rings in 0.8 nm channel


Figure S10. Comparison of experimental XPRD pattern of ocMOM-1 before and after catalytic reaction.


Figure S11. The pore size distribution of ocMOM-1


Figure $12 . \mathrm{N}_{2}$ adsorption isotherm of ocMOM-1 at 77 K ;


Figure 13. $\mathrm{CO}_{2}$ adsorption at 273 K .


Figure 14. (a) Schematic of the tessellation in ocMOM-2; (b) A stick model of tessellation.

## 3-phenyl-3,4-dihydro-2H-1,4-benzoxazine



Colorless oil; HPLC analysis: Chiralcel OD-H (hexane $/ \mathrm{iPrOH}=80 / 20,0.6 \mathrm{~mL} / \mathrm{min}$ ), tR (major) $=$ $15.52 \mathrm{~min}, \mathrm{tR}($ minor $)=21.60 \mathrm{~min} .{ }^{1} \mathrm{H}$ NMR $\quad\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=7.36-7.42(\mathrm{~m}, 5 \mathrm{H}), 6.82-6.90$ $(\mathrm{m}, 2 \mathrm{H}), 6.67-6.75(\mathrm{~m}, 2 \mathrm{H}), 4.50(\mathrm{dd}, J=2.8,8.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.30(\mathrm{dd}, J=2.8,10.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.99-4.03$ $\operatorname{ppm}(\mathrm{m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=143.5,139.2,133.9,128.8,128.3,127.2,121.5$, $118.9,116.6,115.4,71.0,54.2$

## 3-(4-bromophenyl)-3,4-dihydro-2H-1,4-benzoxazine



Pale yellow oil; HPLC analysis: Chiralcel OD-H (hexane $/ \mathrm{iPrOH}=80 / 20,0.6 \mathrm{~mL} / \mathrm{min}$ ), tR (major) $=$ $18.89 \mathrm{~min}, \mathrm{tR}($ minor $)=35.29 \mathrm{~min} .{ }^{1} \mathrm{H} \operatorname{NMR} \quad\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=7.50(\mathrm{~d}, J=6.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.27$ (d, $J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.79-6.85(\mathrm{~m}, 2 \mathrm{H}), 6.66-6.72(\mathrm{~m}, 2 \mathrm{H}), 4.47(\mathrm{dd}, J=2.8,8.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.24$ (dd, $J=2.8,10.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.92-3.97 \mathrm{ppm}(\mathrm{m}, 2 \mathrm{H}){ }^{13} \mathrm{C} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=143.5,138.2,133.5$, $131.9,128.8,122.2,121.6,119.1,116.6,115.4,70.6,53.6$

## 3-(2-naphthalenyl)-3,4-dihydro-2H-1,4-benzoxazine



Pale yellow oil; HPLC analysis: Chiralcel OD-H (hexane $/ \mathrm{iPrOH}=80 / 20,0.6 \mathrm{~mL} / \mathrm{min}$ ), tR (major) $=$ $25.11 \mathrm{~min}, \mathrm{tR}$ (minor) $=48.04 \mathrm{~min} .{ }^{1} \mathrm{H} \operatorname{NMR} \quad\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \quad \delta=7.85-7.89(\mathrm{~m}, 4 \mathrm{H}), 7.49-7.53$ $(\mathrm{m}, 3 \mathrm{H}), 6.84-6.92(\mathrm{~m}, 2 \mathrm{H}), 6.71-6.77(\mathrm{~m}, 2 \mathrm{H}), 4.65(\mathrm{dd}, \mathrm{J}=2.8,8.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.36(\mathrm{dd}, J=2.8,10.6 \mathrm{~Hz}$, $1 \mathrm{H}), 4.07-4.11 \mathrm{ppm}(\mathrm{m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=143.6,136.5,133.9,133.4,133.3$, $128.6,127.9,127.7,126.4,126.2,126.2,125.0,121.6,119.0,116.7,115.5,71.0,54.3$

## 3-phenyl-6-bromo-3,4-dihydro-2H-1,4-benzoxazine



Pale yellow oil; HPLC analysis: Chiralcel OD-H (hexane $/ \mathrm{iPrOH}=80 / 20,0.6 \mathrm{~mL} / \mathrm{min}$ ), tR (major) $=$ 16.63 min , tR (minor) $=19.31 \mathrm{~min} .{ }^{1} \mathrm{H} \operatorname{NMR} \quad\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \quad \delta=7.41-7.32(\mathrm{~m}, 5 \mathrm{H}), 6.68-6.78$ $(\mathrm{m}, 3 \mathrm{H}), 6.67-6.57(\mathrm{~m}, 2 \mathrm{H}), 4.47(\mathrm{dd}, J=3.2,8.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.26(\mathrm{dd}, J=3.2,10.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.05(\mathrm{~s}, 1 \mathrm{H})$, $3.94 \mathrm{ppm}(\mathrm{t}, J=9.6 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=142.5,138.6,135.2,128.9,128.5$, 127.1, 121.3, 117.9, 117.5, 113.4, 70.7, 53.9

## 3-(4-bromophenyl)-6-bromo-3,4-dihydro-2H-1,4-benzoxazine



Colorless oil; HPLC analysis: Chiralcel OD-H (hexane $/ \mathrm{iPrOH}=80 / 20,0.6 \mathrm{~mL} / \mathrm{min}), \mathrm{tR}($ major $)=$ $17.65 \mathrm{~min}, \mathrm{tR}($ major $)=27.08 \mathrm{~min} .{ }^{1} \mathrm{H} \mathrm{NMR} \quad\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=7.50(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.23$ $(\mathrm{d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.78-6.68(\mathrm{~m}, 3 \mathrm{H}), 4.45(\mathrm{dd}, J=3.2,8.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.22(\mathrm{dd}, J=3.2,10.8 \mathrm{~Hz}, 1 \mathrm{H})$, 4.04(s, 1H), $3.90 \mathrm{ppm}(\mathrm{t}, J=9.6 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=142.5,137.7,134.9$, $132.0,128.7,122.4,121.6,118.0,117.7,113.5,70.4,53.4$

## 3-(2-naphthalenyl)-6-bromo-3,4-dihydro-2H-1,4-benzoxazine



Pale yellow oil; HPLC analysis: Chiralcel OD-H (hexane $/ \mathrm{iPrOH}=80 / 20,0.6 \mathrm{~mL} / \mathrm{min}$ ), tR (major) $=$ $34.45 \mathrm{~min}, \mathrm{tR}$ (minor) $=49.89 \mathrm{~min} .{ }^{1} \mathrm{H} \operatorname{NMR} \quad\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=7.87-7.82(\mathrm{~m}, 4 \mathrm{H}), 7.51-7.44$ $(\mathrm{m}, 3 \mathrm{H}), 6.83-6.71(\mathrm{~m}, 3 \mathrm{H}), 4.65(\mathrm{dd}, \mathrm{J}=3.2,8.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.33(\mathrm{dd}, J=3.2,10.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.16(\mathrm{~s}, 1 \mathrm{H})$, 4.03ppm $(\mathrm{t}, J=9.6 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=142.6,135.9,135.2,133.3,128.7$, $127.9,127.7,126.5,126.3,126.1,124.7,121.4,118.0,117.6,113.5,70.7,54.0$

## References:

(1) Zheng, M.; Liu, Y.; Wang, C.; Lin, W. Chem. Sci. 2012, 3, 2623-2627.
(2) Yamashita, Y.; Ishitani, H.; Shimizu, H.; Kobayashi, S.; J. Am. Chem. Soc. 2002, 124, 9. 3292-3302.
(3) Bruker (2010). APEX2). Bruker AXS Inc., Madison, Wisconsin, USA.
(4) Bruker (2009). SAINT. Data Reduction Software. Bruker AXS Inc., Madison, Wisconsin, USA.
(5) Sheldrick, G. M. (2008). SADABS. Program for Empirical Absorption

Correction. University of Gottingen, Germany.
(6) Farrugia L.J. Appl. Cryst. (1999). 32, 837 $\pm 838$
(7) Sheldrick, G.M. (1997) SHELXL-97. Program for the Refinement of Crystal
(8) Sheldrick, G.M. (1990) Acta Cryst. A46, 467-473
(9) Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.
(10) Spek, T.L., Acta Cryst. (1990). A46, 194-201.
(11) Spek, T.L., Acta Cryst. (1990). A46, c34.
(12) Schoedel, A.; Wojtas, L.; Kelley, S. P.; Rogers, R. D.; Eddaoudi, M.; Zaworotko, M. J. Angew. Chem. ,Int. Ed.2011, 50, 1-5.

Chiral HPLC analysis of different entries in table 2.
Entry1

Chromatogram : YJ-II-195ODH80-20-0.61_channel1


Peak results :

| Index | Name | Time [Min] | Quantity [\% Area] | Height <br> [mAU] | Area [mAU.Min] | Area \% <br> [\%] |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 15.23 | 49.74 | 168.4 | 119.3 | 49.735 |
| 2 | UNKNOWN | 21.17 | 50.26 | 124.0 | 120.6 | 50.265 |
| Total |  |  | 100.00 | 292.5 | 239.9 | 100.000 |
|  |  |  |  |  |  |  |
| Index | Name | Time [Min] | Quantity [\% Area] | $\begin{aligned} & \text { Height } \\ & \text { [ } \mathrm{mAU}] \\ & \hline \end{aligned}$ | $\begin{array}{r} \text { Area } \\ \text { [mAU.Min] } \\ \hline \hline \end{array}$ | $\begin{array}{r\|} \hline \text { Area \% } \\ {[\%]} \\ \hline \hline \end{array}$ |
| 1 | UNKNOWN | 15.52 | 73.02 | 251.0 | 141.7 | 73.022 |
| 2 | UNKNOWN | 21.60 | 26.98 | 67.8 | 52.3 | 26.978 |
| Total |  |  | 100.00 | 318.8 | 194.0 | 100.000 |

Entry2

## Chromatogram : YJ-II-169ODH 80-20-0.61_channel1



Peak results :
YJ-II-222ODH 80-20-0.61.DATA [Prostar 335 Absorbance Analog Channel $\left.1^{\wedge}{ }^{\wedge} \mathrm{A}^{\prime} \mathrm{C} \square f \mathrm{qB} \% @ \ldots \square \mathrm{~A} G I \mathrm{~A}:\right]$

| Index | Name | Time <br> [Min] | Quantity <br> [\% Area] | Height <br> [mAU] | Area <br> [mAU.Min] | Area \% <br> $[\%]$ |
| :---: | :---: | ---: | ---: | ---: | ---: | ---: |
| 2 | UNKNOWN | 18.88 | 49.75 | 171.5 | 110.1 | 49.750 |
| 1 | UNKNOWN | 35.35 | 50.25 | 94.0 | 111.2 | 50.250 |
|  |  |  |  |  |  |  |
| Total |  |  | 100.00 | 265.4 | 221.4 | 100.000 |


| Index | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | $\begin{array}{r} \text { Area } \\ \text { [mAU.Min] } \\ \hline \end{array}$ | Area \% [\%] |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 18.89 | 81.20 | 245.7 | 175.6 | 81.205 |
| 2 | UNKNOWN | 35.29 | 18.80 | 33.4 | 40.6 | 18.795 |
| Total |  |  | 100.00 | 279.2 | 216.3 | 100.000 |

Entry3

## Chromatogram : YJ-II-170ODH 80-20-0.61_channel1



Peak results:
YJ-II-181-2-ODH-80-20-0.61.DATA [Prostar 335 Absorbance Analog Channel $\left.1^{\wedge}{ }^{\wedge} \dot{\mathrm{A}} \square \mathrm{C} \square f \mathrm{qB} \% @ \ldots \square \mathrm{~A} G I \mathrm{~A}:\right]$

| Index |  |  |  |  |  |  |
| :---: | ---: | ---: | ---: | ---: | ---: | ---: |
| Name | Time <br> [Min] | Quantity <br> [\% Area] | Height <br> [mAU] | Area <br> [mAU.Min] | Area $\%$ <br> $[\%]$ |  |
| 1 | UNKNOWN | 25.15 | 49.59 | 277.7 | 242.0 | 49.586 |
| 2 | UNKNOWN | 47.87 | 50.41 | 145.4 | 246.1 | 50.414 |
|  |  |  |  |  |  |  |
| Total |  |  | 100.00 | 423.0 | 488.1 | 100.000 |


| Index | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | $\begin{array}{r} \text { Area } \\ \text { [mAU.Min] } \\ \hline \end{array}$ | $\begin{array}{r} \text { Area \% } \\ {[\%]} \\ \hline \end{array}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 25.11 | 92.20 | 479.3 | 428.4 | 92.195 |
| 2 | UNKNOWN | 48.04 | 7.80 | 23.1 | 36.3 | 7.805 |
| Total |  |  | 100.00 | 502.4 | 464.7 | 100.000 |

Entry4

## Chromatogram : YJ-II-186ODH 80-20-0.61_channel1



Peak results :

| Index | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | $\begin{array}{r} \text { Area } \\ \text { [mAU.Min] } \end{array}$ | Area \% [\%] |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 16.65 | 50.12 | 81.2 | 54.1 | 50.116 |
| 2 | UNKNOWN | 19.32 | 49.88 | 72.2 | 53.9 | 49.884 |
| Total |  |  | 100.00 | 153.4 | 108.0 | 100.000 |


| Index | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% <br> [\%] |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 16.63 | 64.80 | 23.5 | 13.9 | 64.796 |
| 2 | UNKNOWN | 19.31 | 35.20 | 11.5 | 7.5 | 35.204 |
| Total |  |  | 100.00 | 35.1 | 21.4 | 100.000 |

Entry5

## Chromatogram : YJ-II-188ODH 80-20-0.61_channel1

| System : HPLC | Acquired : 6/4/2012 10:04:01 PM |
| :--- | :--- |
| Method : Youngran | Processed :6/4/2012 10:41:18 PM |
| User : User1 | Printed : 6/24/2012 3:14:51 PM |



Peak results :

| Index | Name | Time [Min] | Quantity [\% Area] | Height <br> [mAU] | $\begin{array}{r} \text { Area } \\ \text { [mAU.Min] } \end{array}$ | Area \% [\%] |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 17.49 | 49.57 | 13.0 | 9.3 | 49.572 |
| 2 | UNKNOWN | 27.05 | 50.43 | 9.0 | 9.5 | 50.428 |
| Total |  |  | 100.00 | 21.9 | 18.7 | 100.000 |


| Index | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | $\begin{array}{r} \text { Area } \\ \text { [mAU.Min] } \\ \hline \end{array}$ | $\begin{array}{r} \text { Area \% } \\ {[\%]} \\ \hline \hline \end{array}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 17.65 | 78.25 | 89.7 | 65.4 | 78.251 |
| 2 | UNKNOWN | 27.08 | 21.75 | 17.3 | 18.2 | 21.749 |
| Total |  |  | 100.00 | 107.0 | 83.5 | 100.000 |

Entry6

## Chromatogram : YJ-II-189ODH 80-20-0.61_channel1



Peak results :

| Index | Name | Time [Min] | Quantity <br> [\% Area] | Height [mAU] | $\begin{array}{r} \text { Area } \\ \text { [mAU.Min] } \end{array}$ | Area \% <br> [\%] |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 | UNKNOWN | 33.73 | 49.61 | 131.5 | 159.3 | 49.609 |
| 1 | UNKNOWN | 49.23 | 50.39 | 95.2 | 161.8 | 50.391 |
| Total |  |  | 100.00 | 226.6 | 321.0 | 100.000 |


| Index | Name | Time [Min] | Quantity [\% Area] | Height <br> [mAU] | $\begin{array}{r} \text { Area } \\ {[\mathrm{mAU} . \mathrm{Min]}]} \\ \hline \end{array}$ | Area \% <br> [\%] |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 34.45 | 73.25 | 7.0 | 9.2 | 73.252 |
| 2 | UNKNOWN | 49.89 | 26.75 | 2.0 | 3.4 | 26.748 |
|  |  |  |  |  |  |  |
| Total |  |  | 100.00 | 8.9 | 12.6 | 100.000 |

