Supporting Information for

A Chiral Metal-Organic Framework for Sequential Asymmetric Catalysis

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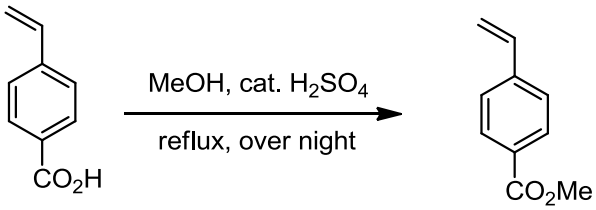
1. General Experimental

All of the solvents were purchased from Fisher and used without further purification. ^{1}H NMR spectra were recorded on a Bruker NMR 400 DRX spectrometer at 400 MHz and referenced to the proton resonance resulting from incomplete deuteration of chloroform-D (7.26) or DMSO-D_6 (2.49). Mass Spectrometric analyses were conducted using positive-ion electrospray ionization on a Bruker BioTOF mass spectrometer. Thermogravimetric analysis (TGA) was performed in air using a Shimadzu TGA-50 equipped with a platinum pan. Single crystal X-ray diffraction and Powder X-ray diffraction (PXRD) patterns were collected on a Bruker SMART APEX II diffractometer using Cu radiation. The PXRD patterns were processed with the APEX 2 package using PILOT plug-in. The conversions and *ee* values were determined by Shimadzu GC-2010 equipped with FID detector and Supelco β–DEX 120 column, or Shimadzu HPLC SCL-10A equipped with SPD-M10A diode Array detector and Chiralcel AD, OJ columns.

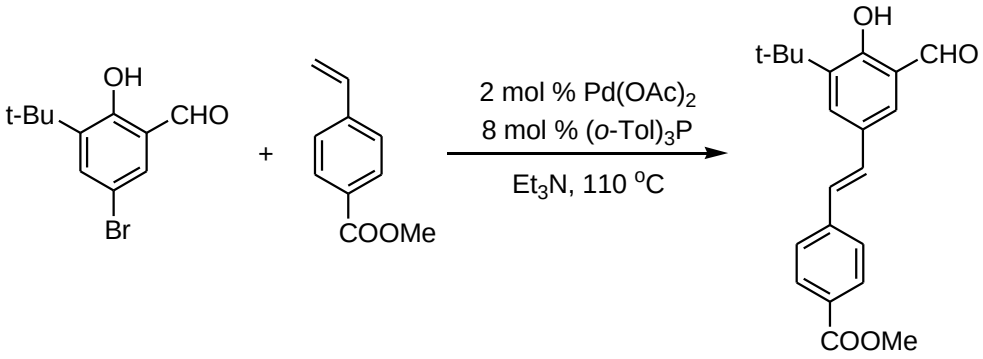
2. Ligand Synthesis.

Methyl 4-vinylbenzoate



4-Vinylbenzoic acid (30 mmol, 4.44 g) was dissolved in methanol (120 mL) and conc. H_2SO_4 (2 mL) was then added. After refluxing for 24 h, the volatile was evaporated and the residue was diluted with H_2O. The resulting solution was extracted with EtOAc. The combined organic phase was washed with brine and H_2O, dried with $MgSO_4$. The solvent was removed and 3.83 g product was obtained in 78% yield. ^{1}H NMR ($CDCl_3$) δ 3.91 (s, 3H), 5.38 (d, *J* = 10.8 Hz, 1H), 5.86 (d, *J* = 17.6 Hz, 1H), 6.75 (dd, *J* = 17.6 Hz, 10.8 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H).

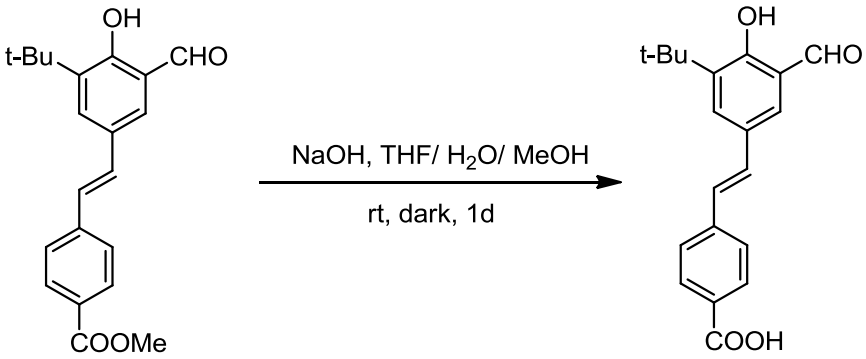
(*E*)-Methyl 4-(3-*tert*-butyl-5-formyl-4-hydroxystyryl)benzoate



5-Bromo-3-*tert*-butyl-2-hydroxybenzaldehyde (5.14 g, 20 mmol), methyl-4-vinylbenzoate (3.57 g, 22 mmol), $Pd(OAc)_2$ (0.090 g, 0.4 mmol), and P(*o*-Tol)$_3$ (0.49 g, 1.6 mmol) were dissolved in Et_3N (15 mL). The resulting solution was heated at 110 ^{o}C under Argon for 2 days. After cooling to r. t., water, ice and 2 N HCl were successively added, and the product was extracted with EtOAc. The combined organic phase was washed with brine and dried with $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography on silica gel (Hex: EtOAc = 10:1 to 5:1) to afford 4.16 g of the desired

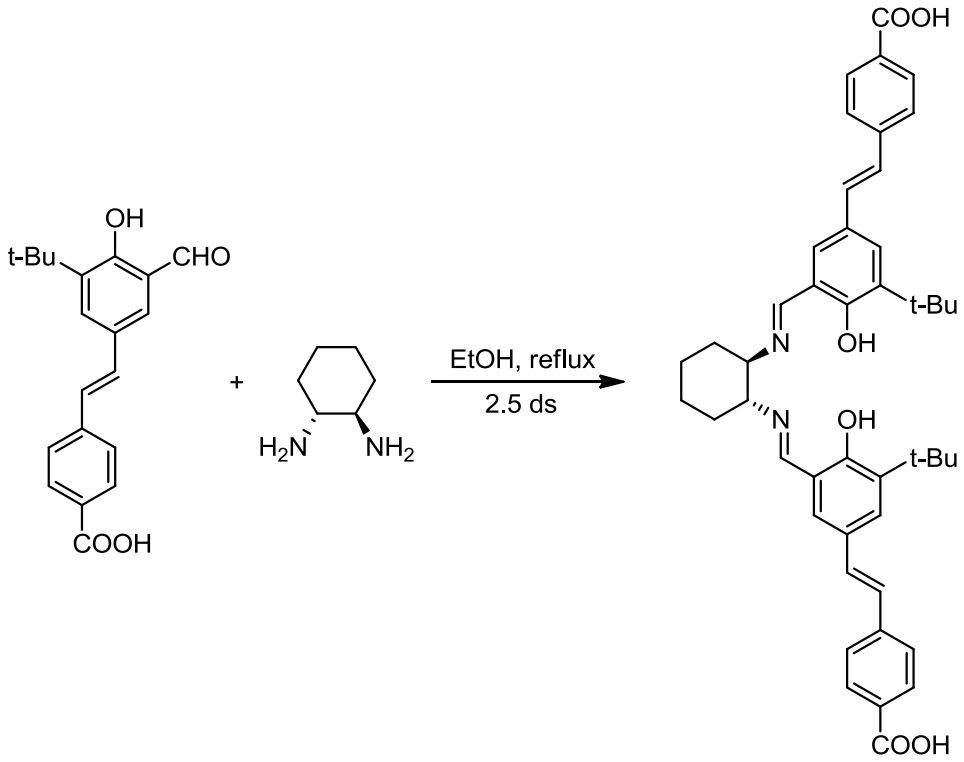
product (61% yield). ^{1}H NMR ($CDCl_3$) δ 1.46 (s, 9H), 3.92 (s, 3H), 7.03 (d, *J* = 16.4 Hz, 1H), 7.18 (d, *J* = 16.4 Hz, 1H), 7.55-7.57 (m, 3H), 7.71 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 9.93 (s, 1H), 11.86 (s, 1H).

(*E*)-4-(3-*tert*-Butyl-5-formyl-4-hydroxystyryl) benzoic acid



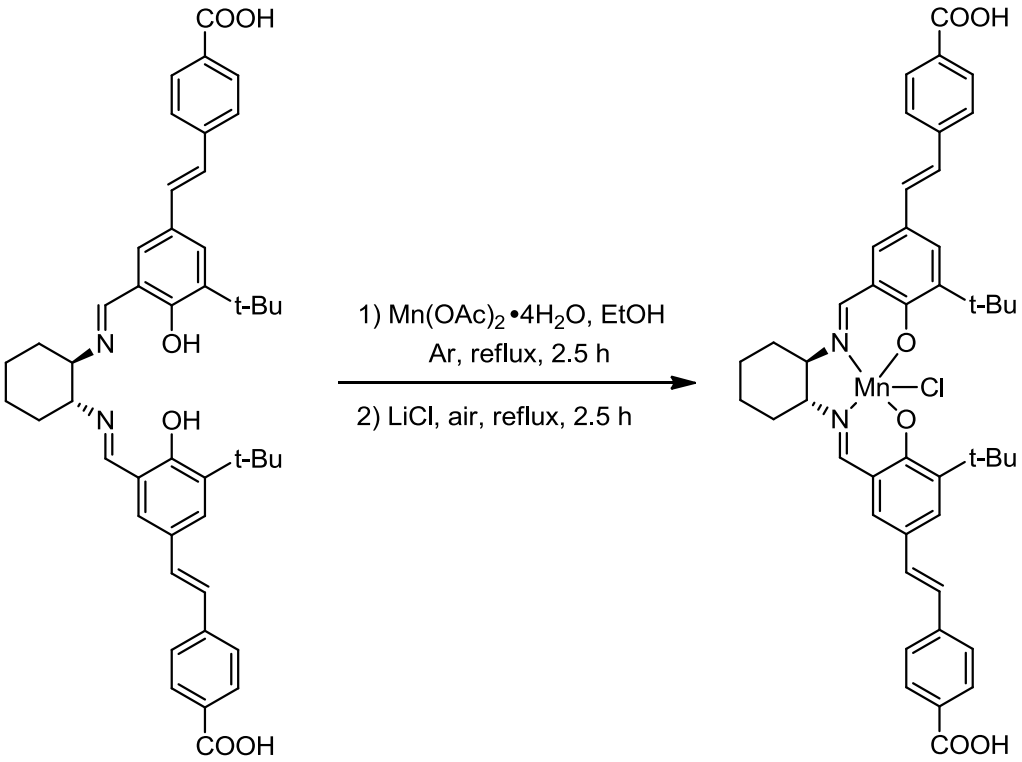
To a solution of (*E*)-methyl 4-(3-*tert*-butyl-5-formyl-4-hydroxystyryl)benzoate (4.16 g, 12.3 mmol) in mixed solvent of THF (65 mL) and MeOH (150 mL) was added aqueous NaOH solution (0.33 M, 120 mL). After stirring in the dark for 24 h, the volatile was evaporated. The residue was diluted with H_2O and washed with CH_2Cl_2 for 3 times. The aqueous phase was acidified with concentrated HCl to a pH of <1. The precipitate was collected by filtration, washed with H_2O and dried in air. 3.74 g of brown solid was obtained (94% yield). ^{1}H NMR (DMSO) δ 1.40 (s, 9H), 7.24 (d, *J* = 15.6 Hz, 1H), 7.42 (d, *J* = 15.2 Hz, 1H), 7.69-7.93 (m, 6H), 9.99 (s, 1H), 11.85 (s, 1H), 12.90 (bs, 1H).

4,4'-(1*E*,1'*E*)-2,2'-(5,5'-(1*E*,1'*E*)-(1*R*,2*R*)-cyclohexane-1,2-diylbis(azan-1-yl-1-yli-dene)bis(methan-1-yl-1-ylidene)bis(3-*tert*-butyl-4-hydroxy-5,1-phenylene))bis(e-thene-2,1-diyl)di benzoic acid



To a solution of (1*R*,2*R*)-cyclohexane-1,2-diamine (0.46 g, 4.0 mmol) in EtOH (80 mL) was added (*E*)-4-(3-*tert*-butyl-5-formyl-4-hydroxystyryl)benzoic acid (2.60 g, 8.0 mmol). The reaction mixture was refluxed for 2.5 days to lead to the formation of yellow precipitate. After cooling to r. t., the solid was filtered, washed with EtOH and dried in air. 1.78 g of product was obtained (61% yield). ^{1}H NMR (DMSO) δ 1.35 (s, 18H), 1.48-1.50 (m, 2H), 1.68-1.70 (m, 2H), 1.82 (m, 2H), 1.96-1.99 (m, 2H), 3.50 (t, *J* = 3.6 Hz, 2H), 7.02 (d, *J* = 16.4 Hz, 2H), 7.27 (d, *J* = 16.4 Hz, 2H), 7.45 (d, *J* = 6.8 Hz, 4H), 7.62 (d, *J* = 8.0 Hz, 4H), 7.89 (d, *J* = 8.4 Hz, 4H), 8.53 (s, 2H). MS (EI) for $[M+H]^{+}$: calcd 727.37, found 727.41.

4,4'-(1*E*,1'*E*)-2,2'-(5,5'-(1*E*,1'*E*)-(1*R*,2*R*)-Cyclohexane-1,2-diylbis(azan-1-yl-1-yli-dene)-bis(methan-1-yl-1-ylidene)bis(3-*tert*-butyl-4-hydroxy-5,1-phenylene))bis(ethene-2,1-diyl) dibenzoic acid manganese (III) chloride (L-H_2)



4,4'-(1*E*,1'*E*)-2,2'-(5,5'-(1*E*,1'*E*)-(1*R*,2*R*)-cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(3-*tert*-butyl-4-hydroxy-5,1-phenylene))bis(ethene-2,1-diyl)dibenzoic acid (0.73 g, 1.0 mmol), $Mn(OAc)_2$•$4H_2O$ (0.30 g, 1.2 mmol) and EtOH (90 mL) were added to a 2-necked flask and heated to reflux for 3 h under Ar atmosphere. LiCl (0.14 g, 3.2 mmol) was added and the resulting solution was refluxed for another 2.5 hours with O_2 bubbled through the reaction mixture. After removing the organic solvents, the residue was thoroughly washed with water (with sonication) to afford dark green solid (0.66 g, 85% yield). MS (EI) for $[M\text{-}Cl]^+$: calcd 779.29, found 779.31.

3. Synthesis and characterization of CMOF-1.

$Zn_4O(L)_3$•$(DBF)_{40}$•$(EtOH)_6$•(H_2O) (CMOF-**1**): **L**-H_2 (10 mg, 0.012 mmol) and $Zn(NO_3)_2$•$6H_2O$ (10 mg, 0.034 mmol) were dissolved in DBF (4 mL) in a 2-dram, screw-capped vial. Ethanol (1.0 mL) was then added and the vial was heated at 80 ^oC for four days. Dark crystals were obtained after filtration (21.33 mg, 57% yield). Solvent content calculated from proposed formula: DBF, 67.6%; EtOH, 3.0%; H_2O, 0.2%; determined by ^1H NMR/ TGA: DBF, 67.5%; EtOH, 2.9%; H_2O, 0.1%.

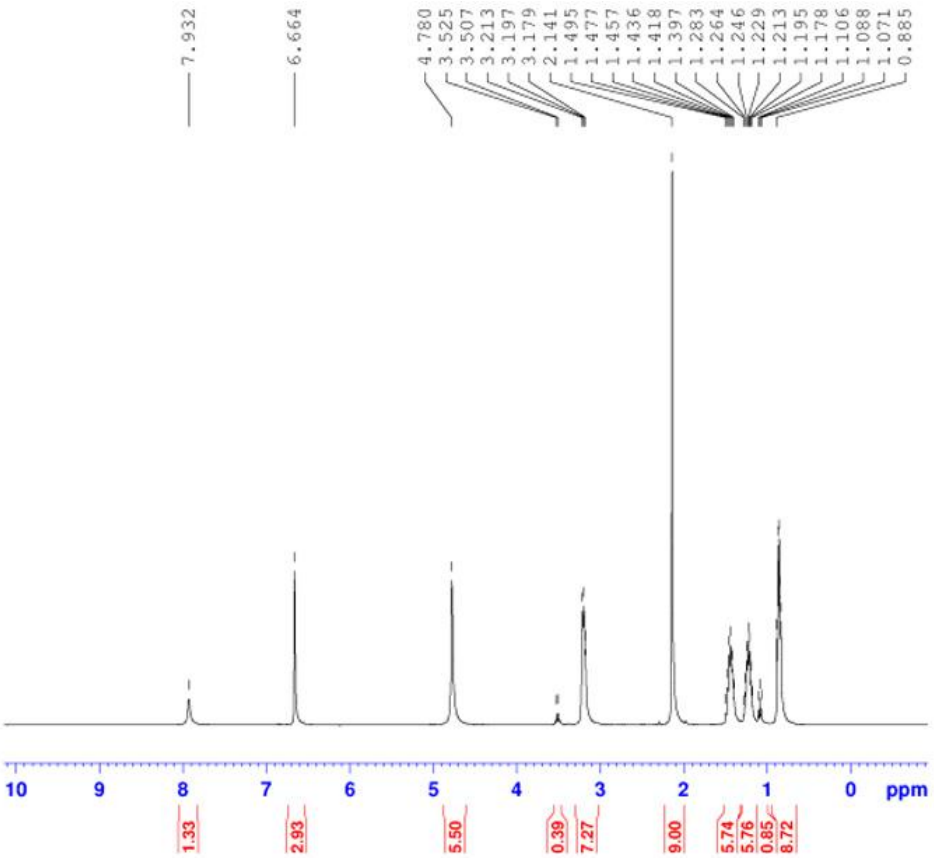


Figure S3.1. ^{1}H NMR spectroscopic determination of solvent content in $Zn_4O(L)_3$•$(DBF)_{40}$•$(EtOH)_6$•(H_2O) (CMOF-**1**)**.** 22.27 mg of CMOF-**1** was used and mesitylene was added as an internal standard.

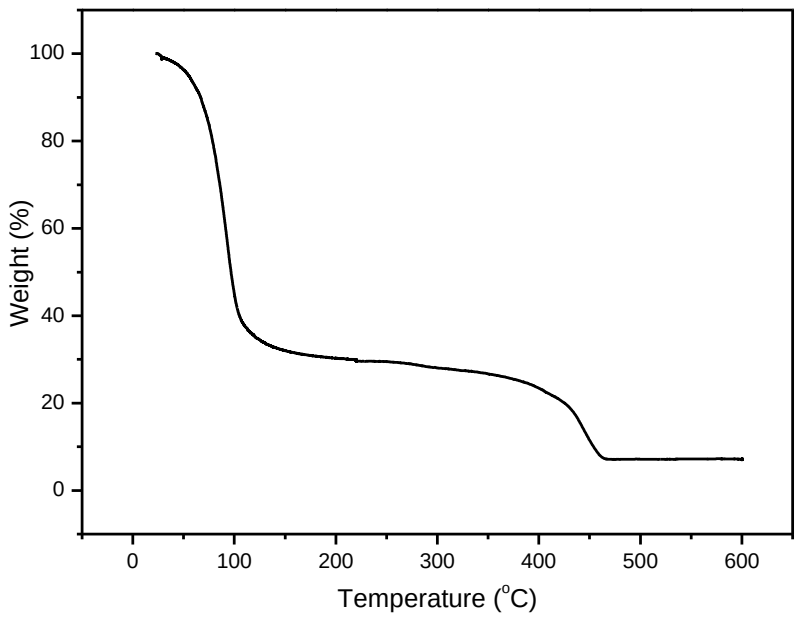


Figure S3.2. TGA curve for $Zn_4O(L)_3$•$(DBF)_{40}$•$(EtOH)_6$•(H_2O) (CMOF-**1**). The sample was heated to 600

ºC at a heating rate of 1 ºC/ min.

4. Procedure for dye uptake measurement

Fresh crystals of CMOF-**1** (2.51 mg, 0.0008mmol) were briefly dried on a filter paper and soaked in a methanol solution of Brilliant Blue R-250 (24.2 mM, 0.5 mL) for 16 h. The resulting crystals were washed carefully with water until the washings become colorless. The solids remained were digested by Na_2EDTA (0.05 M, 2 mL) and NaOH (6 M, 0.1 mL), the resulting clear solution was diluted to 25 mL with water and adjusted to pH = 1.2 with 3 M HCl. Absorption experiments were performed on Shimadzu UV-2401PC UV-VIS spectrophotometer. The concentration of BBR-250 was determined by comparing the UV-Vis absorption with a standard curve.

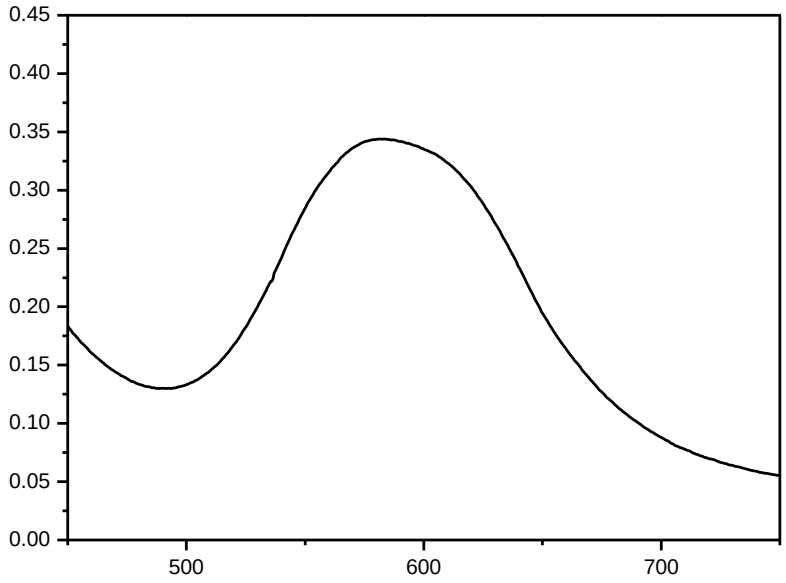


Figure S4.1. UV-Vis spectra of the BBR-250 samples that have been released from the CMOF-**1** after Na_2EDTA digestion.

5. X-ray Structure Determination

All crystallographic measurements were made on a Bruker SMART Apex II CCD-based X-ray diffractometer system operated at 1600 watts (Cu-target X-ray tube). The crystals were mounted inside a capillary tube (0.7 mm ID) with small amount of mother liquid to prevent solvent loss from the crystal frameworks. The frames were integrated with the Bruker SAINT© build in APEX II software package using a narrow-frame integration algorithm,

which also corrects for the Lorentz and polarization effects. Absorption corrections were applied using SADABS. Structures were solved by direct methods and refined to convergence by least squares method on F2 using the SHELXTL software suite.[1]

X-ray structure refinement for CMOF-1

SQUEEZE subroutine of the PLATON software suite[2] was applied to remove the scattering from the highly disordered guest molecules. The resulting new HKL4 files were used to further refine the structures. Due to the relatively weak diffraction and low resolution (>1.5 Å), which is not uncommon for this kind of framework with very large solvent accessible void space, restraints (SIMU and DELU) on displacement parameters, and DFIX for bond lengths are applied, and all the phenyl rings are constrained to ideal six-membered rings. Non-hydrogen atoms are refined isotropically, except Zn atoms which are refined anisotropically. The structure solution (direct method) leads to two interpenetrating networks of full occupancy.

Table S1. Crystal data and structure refinements for CMOF-**1** and **5a**

Compound	*CMOF-**1***	***5a***
Empirical formula	$Zn_4(\mu_4\text{-}O)(\mathbf{L})_3]\cdot 40dbf\cdot 8EtOH\cdot H_2O$	$C_{12}H_{15}N_3O_3$
Formula weight	10312.36	249.27
Temperature (K)	296	100
Wavelength (Å)	1.54178	1.54178
Crystal system	Trigonal	Orthorhombic
Space group	*R*3	$P2_12_12_1$
Unit cell dimensions	a = 77.9421(3)	a = 8.9026(2)
	b = 77.9421(3)	b = 9.2288(2)
	c = 47.734(2)	c = 14.7549(4)
	α = 90	α = 90
	β = 90	β = 90
	γ =120	γ = 90
Volume ($Å^3$)	251133(11)	1212.27(5)
Z	3	4
Density (calcd. g/cm^3)	0.205	1.366
Absorption coeff. (mm^{-1})	0.654	0.831
F(000)	15216	528
Crystal size (mm)	0.40×0.40×0.40	0.30×0.20×0.20
Crystal color & shape	Brown cuboctahedron	Colorless block

θ range data collection	1.13 – 33.41	5.65 – 71.89
Limiting indices	-41 < *h* < 51	-10 < *h* < 10
	-54 < *k* < 45	-10 < *k* < 11
	-34 < *l* < 33	-14 < *l* < 17
Reflections collected	70530	8212
Independent reflections	36814	2313
R(int)	0.0442	0.0218
Refinement method		
Data/restraints/parameters	36814/829/501	2313/0/223
Goodness-of-fit on F^2	0.837	1.175
Final R indices [I>2σ(I)]	R1 = 0.0982	R1 = 0.0320
	wR2 = 0.2656	wR2 = 0.0961
R indices (all data)	R1 = 0.1298	R1 = 0.0321
	wR2 = 0.2943	wR2 = 0.0962
Flack parameter	0.29 (12)	0.10 (13)

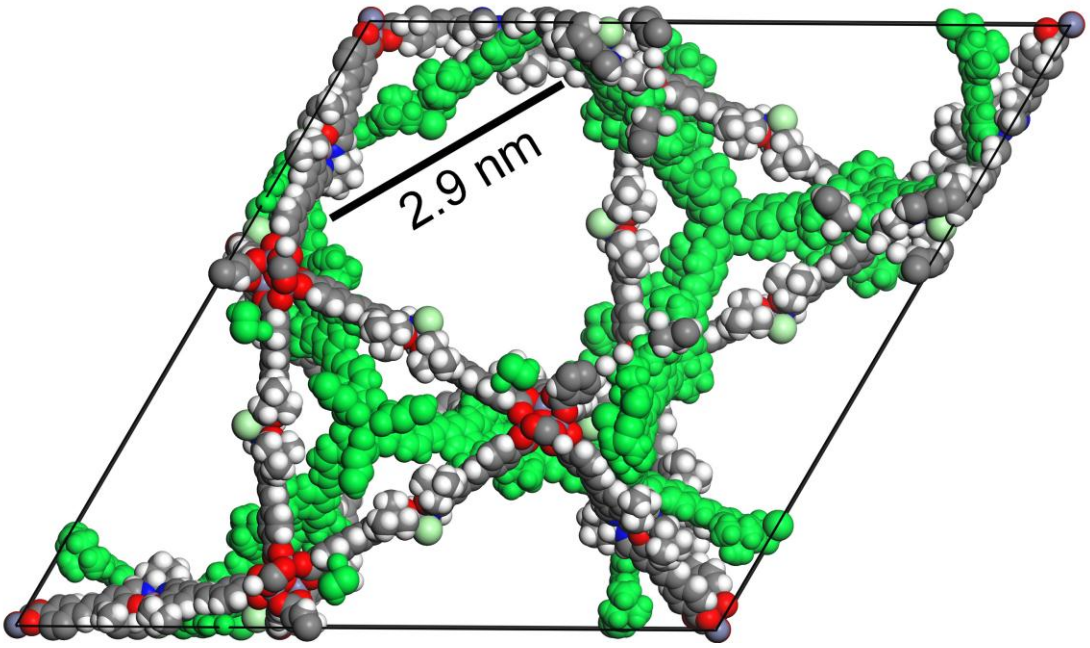


Figure S5.1. Space-filling model of CMOF-**1** along [001] direction.

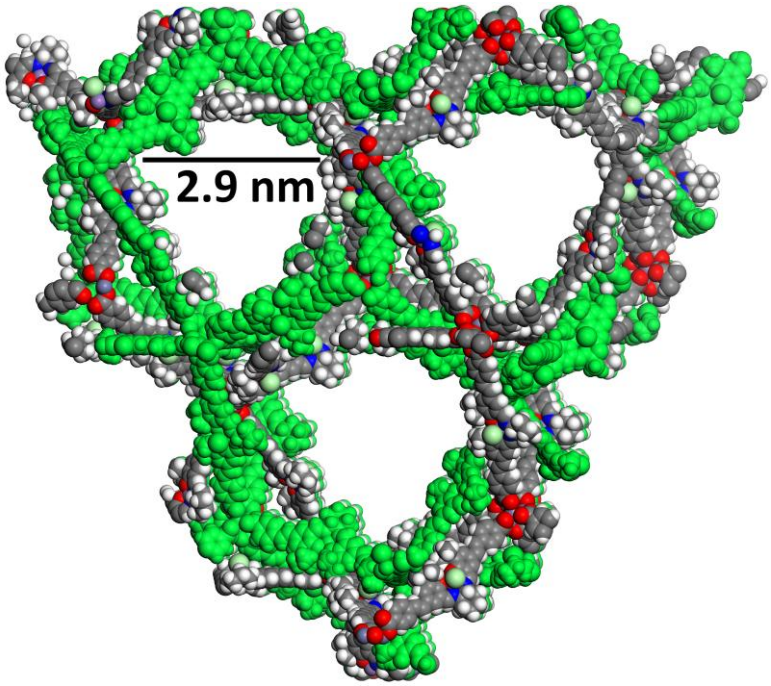


Figure S5.2. Space-filling model of CMOF-**1** along [1-1-1] direction.

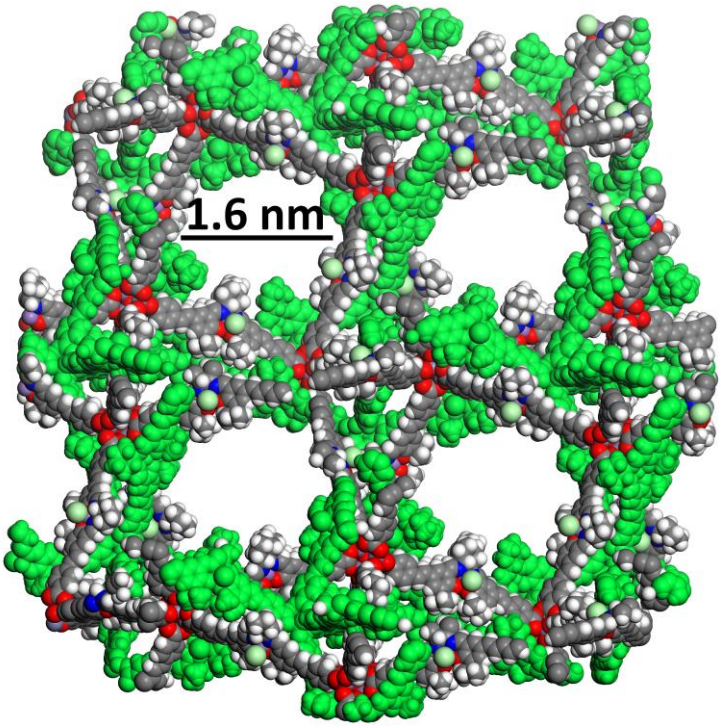


Figure S5.3. Space-filling model of CMOF-**1** along [1-12] direction.

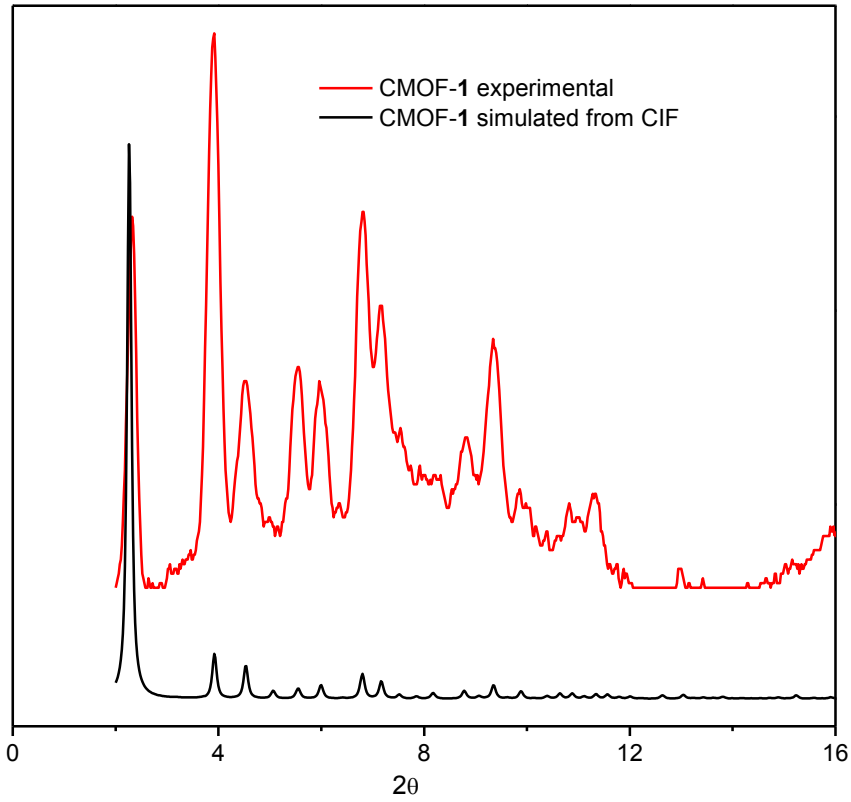


Figure S5.4. Powder X-ray diffraction patterns of CMOF-**1**, simulated from CIF of CMOF-**1** (black), experimental PXRD pattern (red).

6. CMOF-1 catalyzed enantioselective epoxidation reactions and sequential reactions of unactivated alkenes.

General procedure for the enantioselective epoxidation reaction of alkene.

CMOF-**1** (1.08 mg, 0.0006 mmol) was charged into a 2-dram, screw-capped vial and washed with CH_2Cl_2 for 3 times and sonicated for 10 min. To this vial was added alkene (0.6 mmol), undecane (0.063 mL, 0.3 mmol) and CH_2Cl_2 (0.5 mL). 2-(*tert*-Butylsulfonyl)iodosylbenzene (0.010 g, 0.03 mmol) was then added. The same amount of oxidant was added 9 more times at 15 min intervals. Aliquots of the reaction solution was taken (10 μL), diluted with EtOAc and filtered through a syringe filter. The filtrate was analyzed by GC to give the conversion and by GC or HPLC to give the enantioselectivity.

Indene oxide: (HPLC, Chiracel OJ, 4.6 mm x 100 mm, ^{i}PrOH:Hex = 1 : 99, 1mL/min): $t_{(1R, 2S)}$ = 18.1min; $t_{(1S, 2R)}$ = 20.2 min.

2,2-Dimethyl-2*H*-chromene oxide: (GC, Supelco β-Dex, 30 m × 0.25 mm x 0.25 μm; injector: 240 °C; Column: 140 °C; Detector: 250 °C; carrier gas: He (0.57 mL/min)): $t_{(S, S)}$ = 32.7 min; $t_{(R, R)}$ = 34.3 min.

2,2-dimethyl-6-methoxy-*2H*-chromene oxide: (HPLC, Chiracel AD, 4.6 mm x 100 mm, ^{i}PrOH : Hex = 1 : 99, 1mL/min): $t_{(R, R)}$ =15.4 min; $t_{(S, S)}$ =19.8 min.

2,2-dimethyl-6-methyl-*2H*-chromene oxide: (HPLC, Chiracel AD, 4.6 mm x 100 mm, ^{i}PrOH : Hex = 0.4 : 99.6, 1mL/min): $t_{(R, R)}$ =13.9 min; $t_{(S, S)}$ =16.7 min.

2,2-dimethyl-6-cyano-*2H*-chromene oxide: (GC, Supelco β-Dex, 30 m × 0.25 mm x 0.25 μm; injector: 240 °C; Column: kept at 100 °C for 5 min, then programmed at 15 °C/min to 175 °C, kept at 175 °C for 60 min; Detector: 250 °C; carrier gas: He (1.29 mL/min): $t_{(S, S)}$ = 41.3 min, $t_{(R, R)}$ = 41.6 min.

2,2-dimethyl-6-nitro-*2H*-chromene oxide: (GC, Supelco β-Dex, 30 m × 0.25 mm x 0.25 μm; injector: 240 °C; Column: kept at 100 °C for 5 min, then programmed at 15 °C/min to 175 °C, kept at 175 °C for 60 min; Detector: 250 °C; carrier gas: He (1.29 mL/min): $t_{(S, S)}$ = 59.6 min, $t_{(R, R)}$ = 61.5 min.

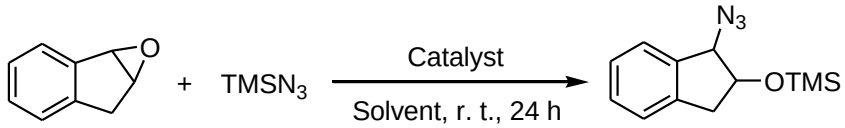
1,2-Dihydronaphthalene oxide: (GC, Supelco β-Dex, 30 m × 0.25 mm x 0.25 μm; injector: 240°C; Column: 140 °C; Detector: 250 °C; carrier gas: He (0.57 mL/min)): $t_{(1S, 2R)}$ = 29.6 min; $t_{(1R, 2S)}$ = 30.6 min.

Control experiments of MOF-5 or CMOF-1 catalyzed ring-opening reaction of indene oxide.

MOF-5 (1.8 mg, 0.005 mmol) was charged into a 2-dram, screw-capped vial, and washed with CH_2Cl_2 for 3 times. To this vial was added indene oxide (0.066 g, 0.5 mmol), $TMSN_3$

(0.099 mL, 0.75 mmol) and CH_2Cl_2 (0.5 mL). The resulting mixture was stirred at r.t. and monitored by GC.

Table S2. MOF-5 and CMOF-**1** catalyzed ring-openning reactions of indene oxide



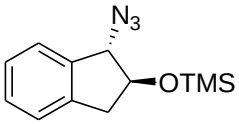
Catalyst	Solvent	Yield(%)[a]
0.1mol% MOF-5	CH_2Cl_2	6%
1mol% MOF-5	CH_2Cl_2	30%
5 mol% MOF-5	CH_2Cl_2	41%
1mol% CMOF-**1**	Cyclohexane	67%

[a]Yield is determined by GC.

Representative procedure for sequential reactions of indene catalyzed by CMOF-1.

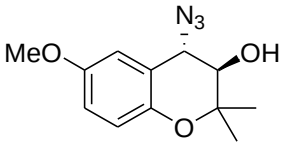
CMOF-**1** (9.37 mg, 0.003 mmol) was charged into a 2-dram, screw-capped vial and washed with CH_2Cl_2 for 3 times. To this vial was added indene (0.039 mL, 0.3 mmol) and CH_2Cl_2 (0.5 mL). 2-(*tert*-Butylsulfonyl)iodosylbenzene (0.010 g, 0.03 mmol) was then added and the same amount of oxidant was added 9 more times at 15 min intervals (totally 0.3 mmol). After the addition of all of the oxidants, the reaction mixture was stirred for 30 min. Cyclohexane (1.0 mL) was added and most of the solvent was removed under vacuum. Then more cyclohexane (1.0 mL) was added and evacuated to ~ 0.5 mL to make sure that all of the CH_2Cl_2 was removed. $TMSN_3$ (0.060 mL, 0.45 mmol) was added and the reaction mixture was stirred at r. t. for 2 days. The product was separated by column (silica gel, Hex: EtOAc = 50: 1) to give 44.5 mg of desired product (60% yield). *Ee* was 50% as determined by GC.

((1*S*,2*S*)-1-Azido-2,3-dihydro-1*H*-inden-2-yloxy)trimethylsilane (5b)



^{1}H NMR ($CDCl_3$) δ 0.22 (s, 9H), 2.84 (dd, *J* = 15.2 Hz, 7.2 Hz, 1H), 3.16 (dd, *J* = 15.2 Hz, 7.2 Hz, 1H), 4.40-4.45 (m, 1H), 4.70 (d, *J* = 6.0 Hz, 1H), 7.20-7.32 (m, 4H); ^{13}C NMR ($CDCl_3$) δ -0.04, 39.34, 72.07, 79.54, 124.28, 125.01, 127.24, 128.77, 138.22, 139.31. GC conditions: Supelco β-Dex (30 m × 0.25 mm x 0.25 μm); injector: 240 °C; Column: 130 °C; Detector: 250 °C; carrier gas: He (0.58 mL/min); retention time: $t_{(1R, 2R)}$ = 69.2 min, $t_{(1S, 2S)}$ = 70.2 min. MS (EI) for $[M-N_3]^+$: calcd 205.10, found 205.12.

(3*R*,4*S*)-4-Azido-6-methoxy-2,2-dimethylchroman-3-ol (5a)

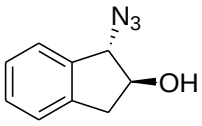


The reaction time of the ring-opening reaction is 3 days. ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 3H), 1.46 (s, 3H), 2.74 (bs, 1H), 3.77 (d, *J* = 7.6 Hz, 1H), 3.78 (s, 3H), 4.35 (d, *J* = 8.8 Hz, 1H), 6.74-6.81 (m, 2H), 6.87 (d, *J* = 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.70, 26.15, 55.80, 61.89, 74.82, 77.61, 112.20, 116.57, 118.20, 119.65, 146.46, 153.90. HPLC conditions: Chiracel AD (4.6 mm x 100 mm); ^{i}PrOH : Hex = 1 : 99, 1 mL/min; retention time: $t_{(3R, 4S)}$ = 42.4 min; $t_{(3S, 4R)}$ = 48.2 min. MS (EI) for $[M+H]^+$: calcd 250.12, found 250.03.

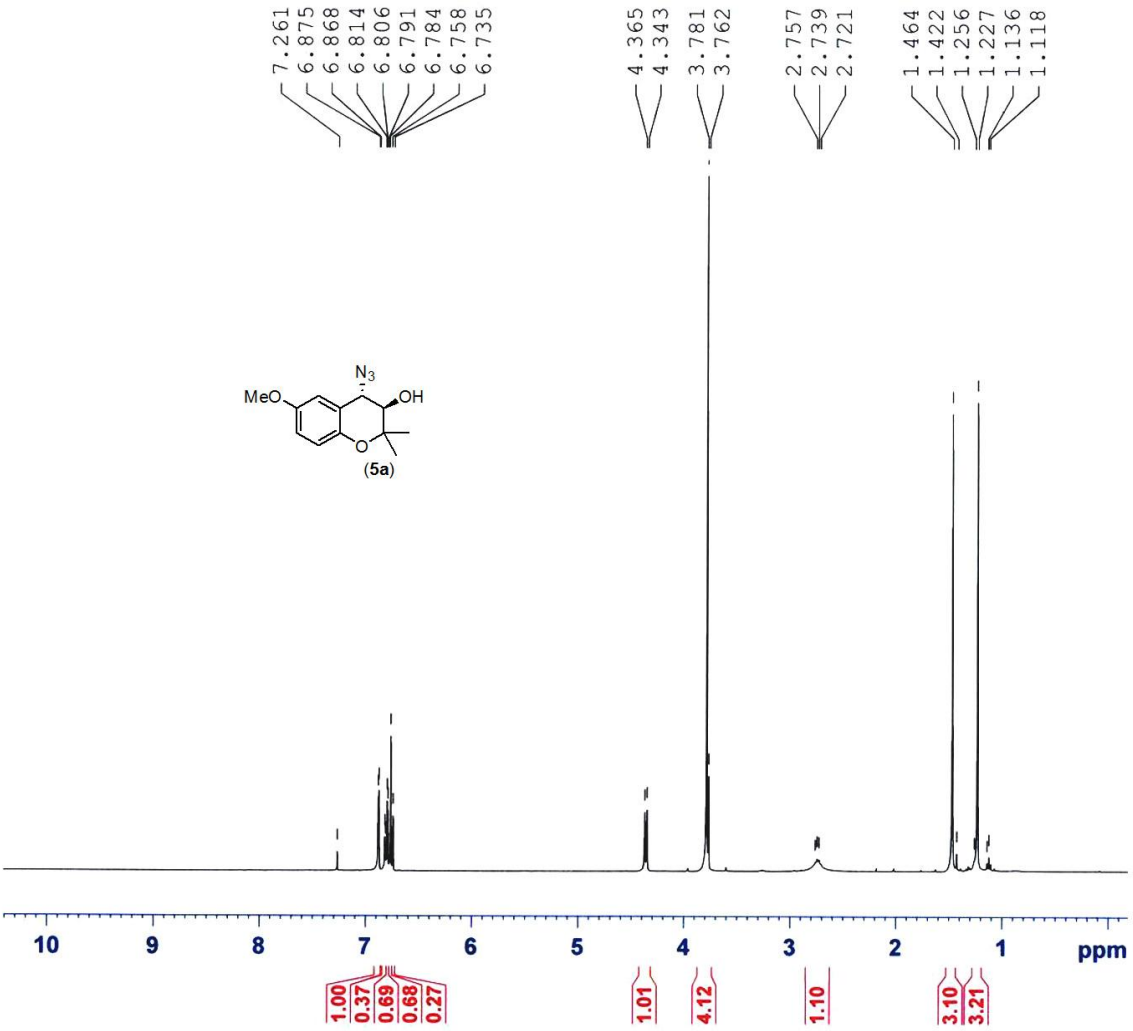
Reaction procedure for the deprotection of TMS group of ((1*S*,2*S*)-1-azido-2,3--dihydro-1*H*-inden-2-yloxy)trimethylsilane.

((1*S*,2*S*)-1-Azido-2,3-dihydro-1*H*-inden-2-yloxy)trimethylsilane (23 mg, 0.09 mmol) was dissolved in MeOH (5 mL). The reaction solution was cooled to 0 ^{o}C and K_2CO_3 (41 mg, 0.3 mmol) was added. After stirring at 0 ^{o}C for another 30 minutes, the volatile was evaporated. The residue was diluted with H_2O and extracted with EtOAc. The organic phase was washed with brine and dried with $MgSO_4$. The product was separated by column (silica gel, Hex: EtOAc = 5: 1) to give 15 mg of desired product (92% yield).

(1*S*,2*S*)-1-Azido-2,3-dihydro-1*H*-inden-2-ol[4]



^{1}H NMR ($CDCl_3$) δ 2.26 (s, 1H), 2.89 (dd, *J* = 16.0 Hz, *J* = 6.0 Hz, 1H), 3.32 (dd, *J* = 16.0 Hz, 6.8 Hz, 1H), 4.50-4.52 (m, 1H), 4.71 (d, *J* = 4.8 Hz, 1H), 7.26-7.39 (m, 4H).



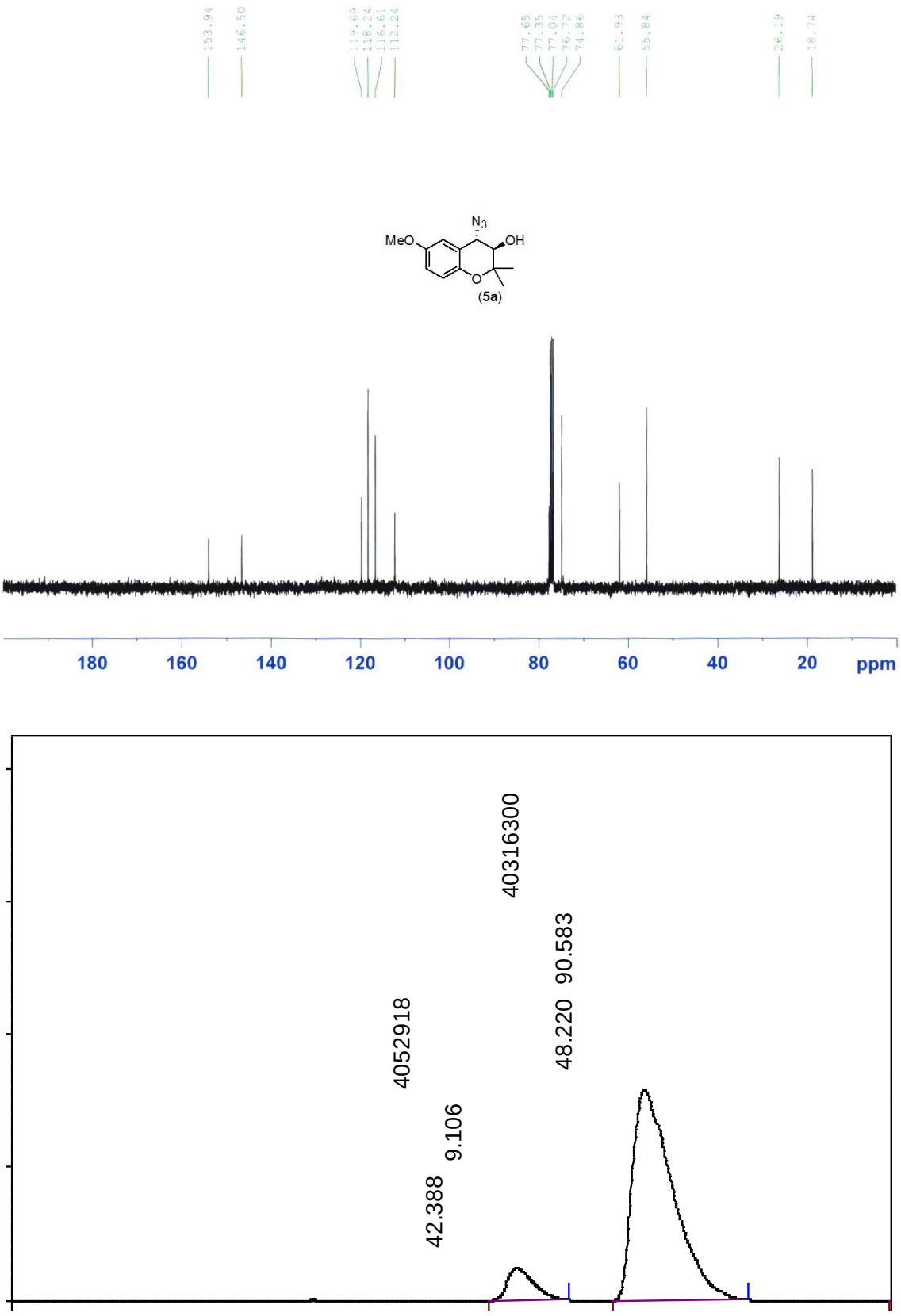
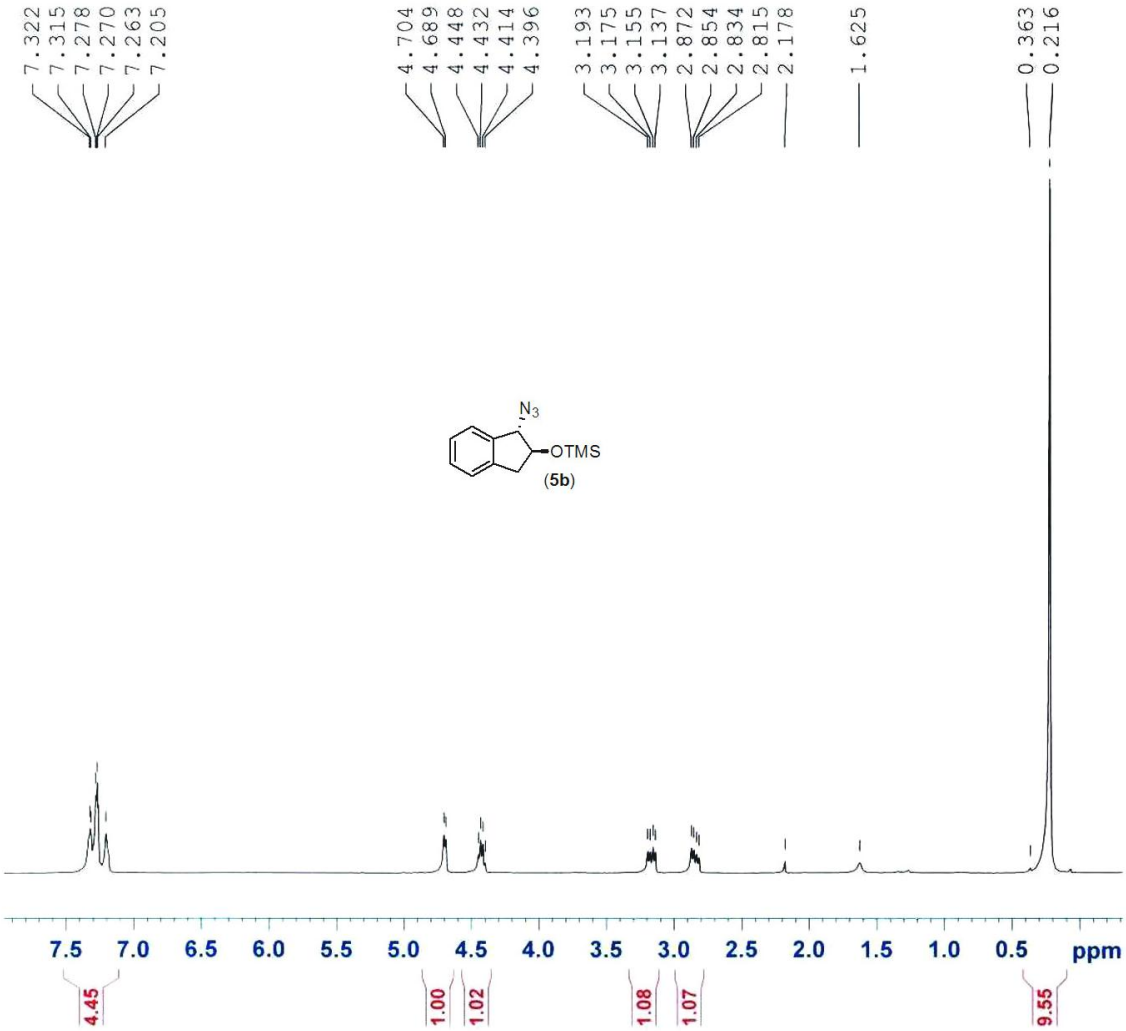
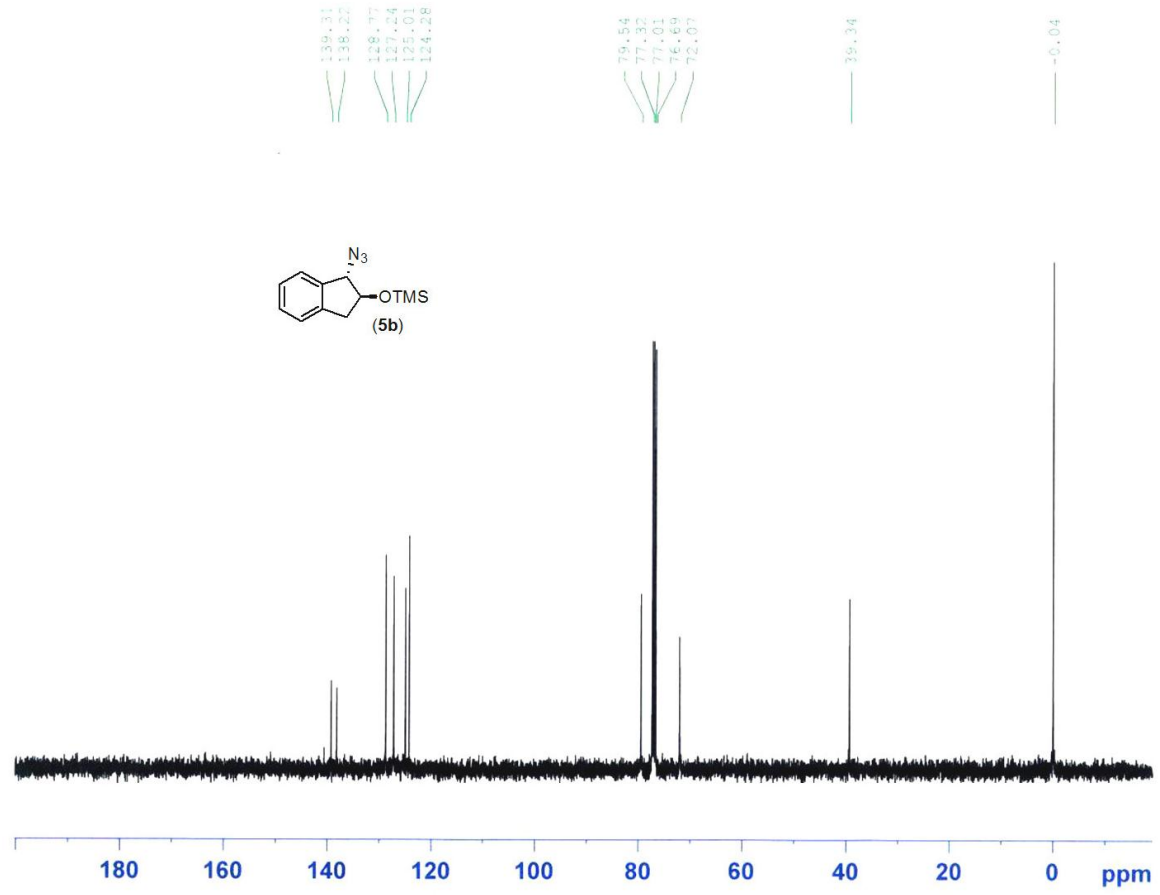
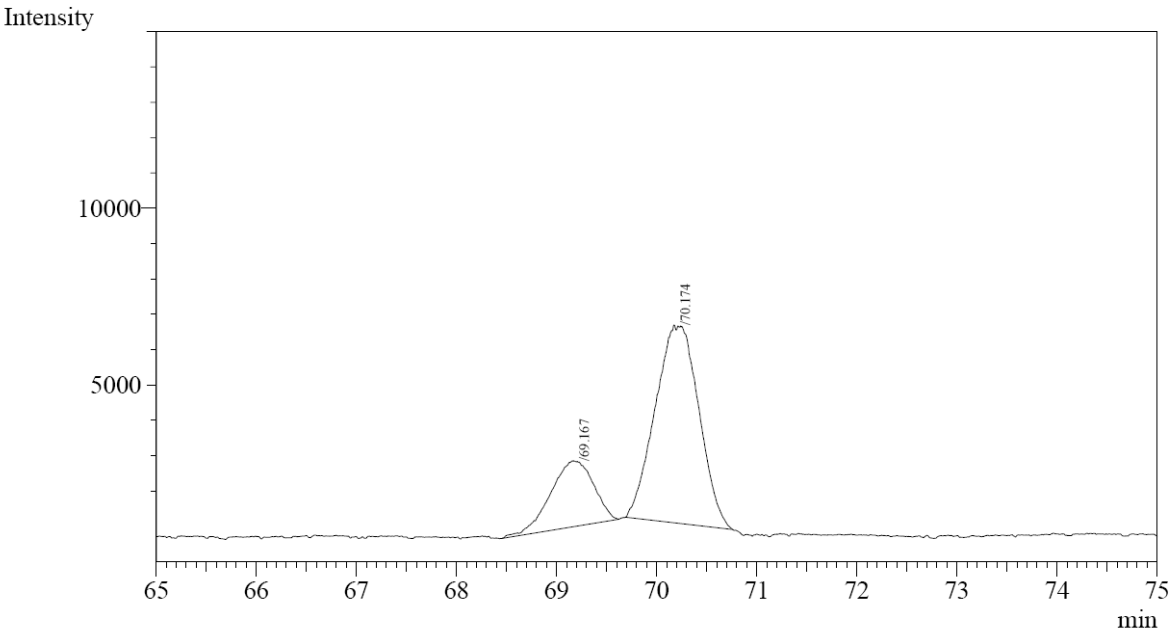


Figure S6.1. NMR and HPLC trace of product **5a**.


7.322
7.315
7.278
7.270
7.263
7.205
4.704
4.689
4.448
4.432
4.414
4.396
3.193
3.175
3.155
3.137
2.872
2.854
2.834
2.815
2.178
1.625
0.363
0.216
N3
OTMS
(5b)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.45
1.00
1.02
1.08
1.07
9.55





Peak Table - Channel 1

Peak#	Ret.Time	Area	Area%	Height
1	69.167	55932	24.7425	1864
2	70.174	170123	75.2575	5596
Total		226055	100.0000	7460

Figure S6.2. NMR and GC trace of product **5b**.

References.

[1] Bruker AXS SHELXTL version 6.10. Structure Determination Package. Bruker AXS 2000. Madison, WI, USA.

[2] A. L. Spek, (2008) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands

[3] Materials Studio v 5.0. Accelrys Software Inc., San Diego, CA 92121, USA

[4] C. Bit, A. A. Mitrochkine, G. Gil, M. Pierrot, M. Réglier, *Tetrahedron: Asymmetry* **1993**, *9*, 3263-3273.