Application of a chiral metal-organic framework in enantioselective separation

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Supporting Information

1. General Information

Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. Toluene was purified by distillation over CaH_2 prior to use. Triethylamine was distilled over CaH_2 and was transferred under argon. 2-bromo terephthalic acid was purchased from Acros. K_2CO_3 was dried by heating at 110 °C for 12 h and left to cool under argon and stored in the glove box. *N*,*N*-Diethylformamide (DEF) was distilled from phosphorus pentoxide and stored under argon. (*S*)-4-Isopropyl-2- oxazolidinone and (*S*)-4-benzyl-2-oxazolidinone were prepared by the literature procedures.[1]

Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished with short UV light or $KMnO_4$ staining solutions followed by heating.

Flash chromatography was performed on Merck silica gel (40-63 mesh) by standard techniques eluting with solvents as indicated. All compounds were fully characterized.

^1H and ^{13}C liquid-state NMR spectra were recorded on Bruker AV 300, or AV 400 MHz INOVA instruments in solvents as indicated. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta H = 7.26$ ppm, $\delta C = 77.16$ ppm), (DMSO-d_6 : $\delta H = 2.50$ ppm, $\delta C = 39.52$ ppm).

$^{13}C\{^1H\}$ cross-polarization (CP) MAS solid-state NMR spectra were measured with a mixing time of 5 ms on a Bruker Avance 300 spectrometer using a commercial double-resonance MAS NMR probe (4 mm outer rotor diameter). The temperature inside the rotor was calibrated using the well known temperature dependence of the ^{207}Pb NMR signal of lead nitrate.

Infrared spectra were recorded on a Varian Associated FT-IR 3100 Excalibur with ATR unit. The wave numbers (n) of recorded IR-signals are quoted in cm^{-1}. ESI mass spectra were recorded on a Bruker Daltonics MicroTof. The SEM images were taken on a Cambridge CamScan 44 scanning electron microscope at an excitation voltage of U = 5 kV.

For the powder X-ray diffraction experiments a Bruker ASX D8 Advance or STOE STADI P diffractometer was used, Cu-Kα_1 (λ= 1.5406 Å). The N_2 and H_2 physisorption isotherms were measured up to 1 bar at 77 K using a Quantachrome Autosorb1C (or 3B) apparatus.

The chromatographic experiments were carried out on a Hewlett-Packard 1100 series HPLC with degasser, autosampler, temperable column compartment and a DAD. Additional a new Agilent 1200 series RID was used. The typical analysis conditions were: an isocratic flow of *n*-heptane at 0.5 ml min^{-1}, eluent / column temperature of 30 °C, detector temperature of 40 °C (RID) and detection at 254 nm wavelength (DAD). From the taken chromatograms the performance parameters selectivity α, the resolution R_S, the capacity factor k, the plate height H and the plate number N were calculated.

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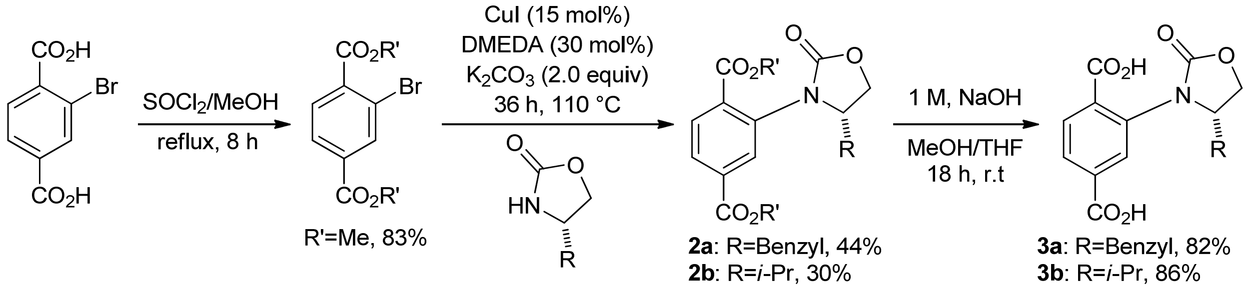
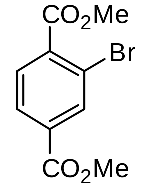
[1] M. J. McKennon, A. I. Meyers, K. Drauz, M. Schwarm, *J. Org. Chem*. 1993, **58**, 3568.

2. Synthesis of ChirBDC derivatives



Scheme 1. Synthesis of chiral auxiliary substituted BDC derivatives.

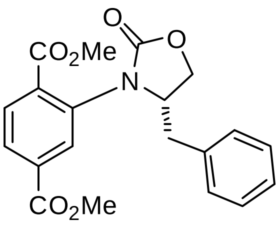
Dimethyl 2-bromoterephthalate



Following the known procedure[2] a three necked 250 mL flask was charged with 2-bromoterephthalic acid (4.90 g, 20 mmol) and MeOH (168 mL). The reaction mixture was heated 70°C, and $SOCl_2$ (30 mL, 400 mmol) was added dropwise and the reaction mixture was stirred for 30 minutes. After the addition of $SOCl_2$ the reaction mixture was refluxed for 6 h. Then the reaction mixture cooled to r.t. MeOH was removed under reduced pressure. The reaction mixture was extracted with Et_2O (3 x 25 mL), the combined organic phases washed with 10% KOH (3 x 25 mL), followed by brine (3 x 25 mL), the combined organic phases were dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography to give dimethyl 2-bromoterephthalate as a white solid (4.40 g, 83%).

R$_f$ (EtOAc/pentane = 10/90): 0.48; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.31 (d, *J* = 1.6 Hz, 1H), 8.00 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 3.96 (s, 3H), 3.94 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 166.28, 165.14, 136.25, 135.34, 133.84, 131.16, 128.24, 121.59, 52.92, 52.84. **ESI-MS**: calculated $[M+Na]^+$ for $C_{10}H_9BrO_4Na$: 296.9556, found: 296.9561. **ATR-FTIR (cm^{-1})**: 3073, 3023, 2964, 2851, 2362, 1742, 1724, 1557, 1480, 1434, 1374, 1284, 1242, 1191, 1112, 1041 953, 912, 853, 814, 744, 677, 661, 602.

(S)-Dimethyl 2-(4-benzyl-2-oxooxazolidin-3-yl)terephthalate



Dimethyl 2-bromoterephthalate (4.00 g, 14.6 mmol), (*S*)-4-benzyloxazolidi-2-one (2.85 g, 16.1 mmol), CuI (0.42 g, 2.20 mmol) and K_2CO_3 (4.05 g, 29.3 mmol) were weighted under argon in to flame dried reaction vessel with a Teflon screw cap. Toluene (24 mL) and DMEDA (0.48 mL, 4.40 mmol) were added and the reaction mixture stirred at 110 °C for 36 hrs. The reaction mixture allowed to cool to room temperature and was filtered through a short silica column (eluent: EtOAc 150 mL). The solvents were removed under reduced pressure. The

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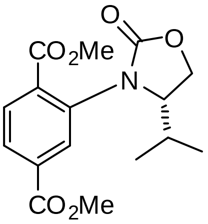
[2] E. D. Chenot, D. Bernardi, A. Comel, G. Kirsch, *Synth. Commun.* 2007, **37**, 483.

residue was purified by column chromatography to give (*S*)-dimethyl 2-(4-benzyl-2-oxooxazolidin-3-yl)terephthalate as a yellowish foam solid (2.40 g, 44%).

R_f (EtOAc/pentane = 50/50): 0.45; $[\alpha]^{20}$ = + 75.8 (c = 0.027 in DCM); **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.02 (d, *J* = 1.6 Hz, 2H), 7.94 (t, *J* = 1.0 Hz, 1H), 7.28 – 7.07 (m, 5H), 4.67 – 4.63 (m, 1H), 4.46 (t, *J* = 8.5 Hz, 1H), 4.25 (dd, *J* = 8.7, 6.6 Hz, 1H), 3.96 (s, 3H), 3.94 (s, 3H), 3.11 (dd, *J* = 13.5, 4.7 Hz, 1H), 2.91 (dd, *J* = 13.5, 9.8 Hz, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 165.77, 165.45, 156.81, 136.44, 135.49, 134.14, 132.59, 131.78, 129.30, 129.03, 128.99, 128.52, 127.25, 68.14, 59.48, 52.93, 52.82, 39.49. **ESI-MS**: calculated $[M+Na]^+$ for $C_{20}H_{19}NO_6Na$: 392.1105, found: 392.1106. **ATR-FTIR (cm^{-1})**: 3028, 2953, 2846, 2362, 1755, 1720, 1572, 1496, 1435, 1399, 1287, 1251, 1216, 1112, 1085, 1038, 1008, 962, 913, 817, 754, 702, 663, 610.

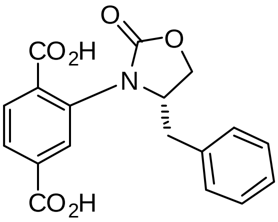
(S)-Dimethyl 2-(4-isopropyl-2-oxooxazolidin-3-yl)terephthalate



Dimethyl 2-bromoterephthalate (3.00 g, 11.0 mmol), (*S)*-4-isopropyloxazolidin-2-one (1.56 g, 12.0 mmol), CuI (0.32 g, 1.65 mmol) and K_2CO_3 (3.03 g, 22.0 mmol) were weighted under argon in to flame dried reaction vessel with a Teflon screw cap. Toluene (18 mL) and DMEDA (0.36 mL, 3.29 mmol) were added and the reaction mixture stirred at 110°C for 36 hrs. The reaction mixture allowed to cool to room temperature and was filtered through a short silica column (eluent: EtOAc 150 mL). The solvents were removed under reduced pressure. The residue was purified by column chromatography to give (*S*)-dimethyl 2-(4-isopropyl-2-oxooxazolidin-3-yl)terephthalate as a yellowish solid (1.05 g, 30%).

R_f (EtOAc/pentane = 50/50): 0.60; $[\alpha]^{20}$ = + 130.3 (c = 0.031 in DCM); **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.01 (s, 2H), 7.91 (s, 1H), 4.54 – 4.47 (m, 1H), 4.37 – 4.24 (m, 2H), 3.94 (s, 3H), 3.91 (s, 3H), 2.04 (m, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 7 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 165.81, 165.56, 157.30, 137.00, 134.01, 131.98, 131.94, 128.20, 128.11, 64.10, 62.46, 52.83, 52.79, 28.85, 18.34, 15.12. **ESI-MS**: calculated $[M+Na]^+$ for $C_{16}H_{19}NO_6Na$: 344.1105, found: 344.1108. **ATR-FTIR (cm^{-1})**: 2990, 2957, 2360, 1724, 1610, 1574, 1492, 1426, 1401, 1375, 1327, 1302, 1259, 1239, 1214, 1148, 1105, 1055, 1027, 957, 900, 860, 816, 772, 754, 710, 659, 608.

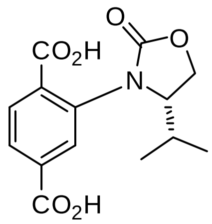
(S)-2-(4-Benzyl-2-oxooxazolidin-3-yl)terephthalic acid



Following a procedure by Guichou et al. (*S*)-dimethyl 2-(4-benzyl-2-oxooxazolidin-3-yl)terephthalate (1.89 g, 5.12 mmol) was dissolved in THF (200 mL) and MeOH (200 mL). Aqueous NaOH (*c* = 1 mol L^{-1}, 4.32 g, 108 mmol) was added dropwise over a period of 20 minutes at room temperature and the mixture stirred at room temperature for 16 h. The mixture was acidified with concentrated HCl to pH 5-6 and the organic solvents were removed under reduced pressure. The aqueous residue was diluted with H_2O (100 mL) and the mixture was extracted with CHCl3/*i*-PrOH (5:1, 3 x 50 mL). The combined organic phases were dried over $MgSO_4$ and the solvents were removed under reduced pressure. The crude product was dissolved in acetone and the product was precipitated by dropwise addition of Pentane. The solids were collected by filtration and dried in vacuo. The product (*S*)-2-(4-benzyl-2-oxooxazolidin-3-yl)terephthalic acid was obtained as colorless solid (1.45 g, 82%).

$[\alpha]^{20}$ = + 66.8 (c = 0.029 in DMSO); **^{1}H NMR (300 MHz, $CDCl_3$)** δ 13.39 (bs, 2H), 7.92 – 7.87 (m, 3H), 7.21 – 7.13 (m, 5H), 4.81 – 4.74 (m, 1H), 4.46 – 4.42 (m, 1H), 4.22 – 4.18 (m, 1H), 2.97 – 2.87 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 166.54, 166.02, 156.01, 136.25, 136.04, 134.24, 133.19, 131.16, 128.94, 128.41, 127.82, 126.51, 67.63, 58.49, 30.72. **ESI-MS**: calculated $[M+Na]^+$ for C18H15NO6Na: 364.0797, found: 364.0793. **ATR-FTIR (cm^{-1})**: 3098, 3061, 3021, 1737, 1702, 1603, 1571, 1497, 1479, 1417, 1291, 1262, 1220, 1196, 1179, 1121, 1082, 1037, 1004, 903, 868, 825, 755, 731, 703, 665, 607.

(S)-2-(4-Isopropyl-2-oxooxazolidin-3-yl)terephthalic acid



Following a procedure by Guichou et. al. (*S*)-dimethyl 2-(4-isopropyl-2-oxooxazolidin-3-yl)terephthalate (1.20 g, 3.73 mmol) was dissolved in THF (150 mL) and MeOH (150 mL). Aqueous NaOH (c = 1 mol L^{-1}, 3.04 g, 76 mmol) was added drop wise over a period of 20 minutes at room temperature and the mixture stirred at room temperature for 16 h. The mixture was acidified with concentrated HCl to pH 5-6 and the organic solvents were removed under reduced pressure. The aqueous residue was diluted with H_2O (100 mL) and the mixture was extracted with CHCl3/*i*-PrOH (5:1, 3 x 50 mL). The combined organic phases were dried over $MgSO_4$ and the solvents were removed under reduced pressure. The crude product was dissolved in acetone and the product was precipitated by drop wise addition of Pentane. The solids were collected by filtration and dried in vacuum. The product (*S*)-2-(4-isopropyl-2-oxooxazolidin-3-yl)terephthalic acid was obtained as colorless solid (0.94 g, 86%).

$[\alpha]^{20}$ = + 131.7 (c = 0.034 in DMSO); **^{1}H NMR (300 MHz, $CDCl_3$)** δ 13.43 (s, 2H), 7.99 – 7.52 (m, 3H), 4.53 – 4.34 (m, 2H), 4.27 (dd, J = 6.4, 4.5 Hz, 1H), 1.94 – 1.80 (m, 1H), 0.90 (d, J = 6.8 Hz, 3H), 0.81 (d, J = 6.9 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 169.76, 167.30, 151.19, 135.76, 132.15, 113.85, 112.78, 112.45, 61.02, 58.68, 28.54, 19.71, 17.48. **ESI-MS**: calculated $[M+Na]^+$ for $C_{14}H_{15}NO_6Na$: 316.0797, found: 316.0792. **ATR-FTIR (cm^{-1})**: 2966, 2888, 2819, 2655, 1760, 1685, 1612, 1571, 1500, 1483, 1442, 1409, 1291, 1260, 1208, 1148, 1123, 1085, 1052, 971, 935, 904, 860, 781, 756, 691, 611.

3. MOFs synthesis

For the synthesis of oxazolidinone substituted UMCMs-1, the reaction conditions reported by Matzger et al. should be optimized. The ratio between the two linkers and the metal salt used in the reaction was crucial for the phase purity of the product. For the Bn-ChirUMCM-1 a ratio 1:1.56:6.2 of H_3BTB, Chir-H_2BDC and $Zn(NO_3)_2(H_2O)_4$ was used, and for *i*Pr-ChirUMCM-1 the ratio 1:2.13:8.55, respectively. Also the reaction temperature was increased from 85 °C to 100 °C. The purity of synthesized compounds was proved *via* powder X-ray diffraction (PXRD) experiments (Figure S1).

Synthesis of $Zn_4O(BTB)_{4/3}$(iPr-ChirBDC)$(DEF)_{19}(H_2O)_6$ (1): H_3BTB (22.2 mg, 0.0506 mmol), *i*Pr-ChirH_2BDC (31.7 mg, 0.108 mmol) and $Zn(NO_3)_2(H_2O)_4$ (113.3 mg, 0.433 mmol) were dissolved in DEF (4 ml). The solution was heated in a Pyrex® tube at 100 °C for 48 h. The resulting crystals were collected by filtration under argon, washed twice with DEF, and dried in an argon flow at room temperature. Yield: 274 mg (75.4%). Elemental analysis: calc (%): C 54.8, H 8.1, N 8.8, O 20.1, Zn 8.2; found (%): C 55.3±0.5, H 7.6±0.2, N 8.7±0.2, O 20.5±0.2, Zn 8.6±0.07.

Synthesis of $Zn_4O(BTB)_{4/3}$(Bn-ChirBDC)$(DEF)_{20}(H_2O)_8$ (2): H_3BTB (30.7 mg, 0.069 mmol), Bn-Chir-H_2BDC (37.1 mg, 0.108 mmol) and $Zn(NO_3)_2(H_2O)_4$ (113.3 mg, 0.433 mmol) were dissolved in DEF (4 ml). The solution was heated in a Pyrex® tube at 100 °C for 48 h. The resulting crystals were collected by filtration under argon, washed twice with DEF, and dried in an argon flow at room temperature. Yield: 384 mg (73.2 %). Elemental analysis: calc (%): C 54.9, H 8.1, N 8.7, O 20.4, Zn 7.77; found (%): C 54.5±0.5, H 8.0±0.2, N 8.8±0.2, O 20.1±0.2, Zn 7.68±0.04.

4. Crystal structure determination

The single crystals of **1** and **2** were sealed in a glass capillary with a small amount of solvent. The reflection intensities were measured at 20°C using synchrotron radiation on beamline BL14.2 of the Joint Berlin-MX Laboratory at BESSY-II (Berlin, Germany) with a MX-225 CCD detector (Rayonics, Illinois). The data images were integrated and scaled with the XDS software.[3] The structures were solved using direct methods with the help of SHELXS-97 and refined by full-matrix least squares techniques using SHELXL-97.[4] All non-hydrogen atoms, except disordered chiral substituents in BDC residue, were refined in anisotropic approximation. Several geometrical constraints were used to fix the geometry of the phenyl rings and carboxylic groups. Both structures show positional statistic disorder of chiral substituent in BDC moiety. Only the positions of nitrogen atoms could be localized from difference Fourier map. In the case of compound **1**, the chiral substituent is disordered over two equally occupied positions, which are located at the same side of the phenyl ring. In the structure of compound **2** four positions for the nitrogen atom are found. All others atoms of the chiral subtituents are highly disordered and could not be located from difference Fourier map. The Forcite geometry optimization tool (Material Studio 5.0) was used for modeling of the chiral substituents in each disordered position. The calculated coordinates of the substituent atoms are omitted from refinement but included in the final *.cif files. The SQUEEZE/PLATON routine has been applied to modify the intensities, corresponding to the highly disordered chiral substituents and solvent molecules.[5] The hydrogen atoms were positioned geometrically and refined using a riding model. The main experimental data are summarized in Table S1.

Table S1. Crystallographic data for *i*Pr-ChirUMCM-1 and Bn-ChirUMCM-1.

	*i*Pr-ChirUMCM-1 (**1**)	Bn-ChirUMCM-1 (**2**)
Empirical formula	$C_{50} H_{32} N O_{15} Zn_4$	$C_{54} H_{30} N O_{15} Zn_4$
Formula weight	1148.25	1194.27
Crystal system, space group	Hexagonal, $P6_3$	Hexagonal, $P6_3$
Unit cell dimensions	$a = 41.459(6)$	$a = 41.414(6)$
	$c = 17.561(4)$	$c = 17.637(3)$
Volume	26140(7)	26197(7)
Z, Calculated density	6, 0.438	6, 0.454
Absorption coefficient	1.016	1.015
F(000)	3474	3606
θ Range	1.61 to 31.82	1.23 to 32.24
Limiting indices	$-49 \leq h \leq 33$	$-19 \leq h \leq 49$
	$-33 \leq k \leq 49$	$-49 \leq k \leq 49$
	$-18 \leq l \leq 17$	$-16 \leq l \leq 19$
Reflections collected / unique	80884 / 28147 [R(int) = 0.0501]	83244 / 28628 [R(int) = 0.0354]
Data/restraints/parameters	28147 / 313 / 502	28628 / 308 / 682
GooF	1.042	0.942
Final R indices [I>2sigma(I)]	$R_1 = 0.0427$, $wR_2 = 0.1142$	$R_1 = 0.0398$, $wR_2 = 0.1066$
R indices (all data)	$R_1 = 0.0532$, $wR_2 = 0.1181$	$R_1 = 0.0533$, $wR_2 = 0.1115$
Largest diff. peak and hole	0.398 and -0.352	0.342 and -0.482

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[3] W. Kabsch *J. Appl. Crystallogr.* 1988, **21**, 67.

[4] G. M. Sheldrick *Acta Cryst*. 2008, **A64**, 112.

[5] A. L. Spek PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2010.

5. PXRD

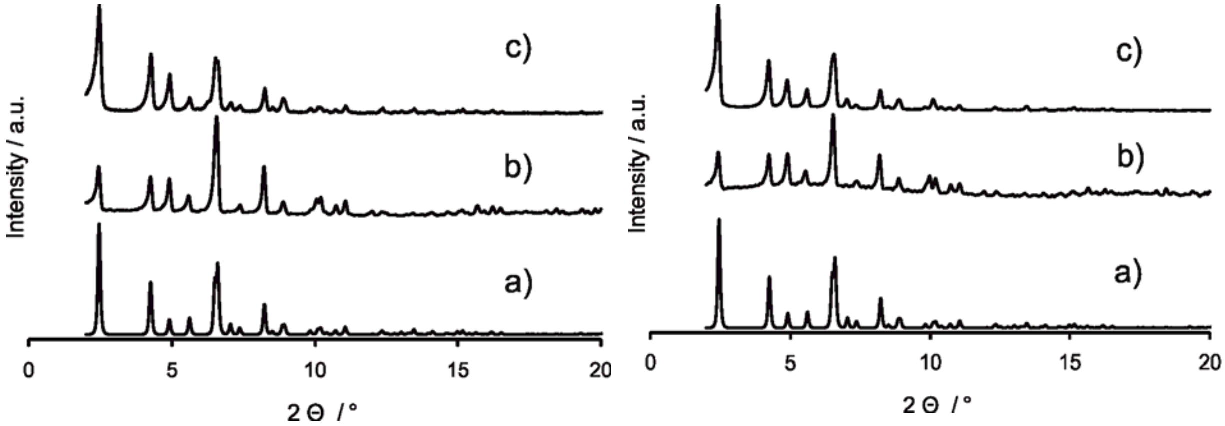


Figure S1. Powder X-ray diffraction patterns (PXRD) of *i*Pr-ChirUMCM-1 (**1**) (left) and Bn-ChirUMCM-1 (**2**) (right). a) Calculated for UMCM-1; b) as-synthesized; c) activated.

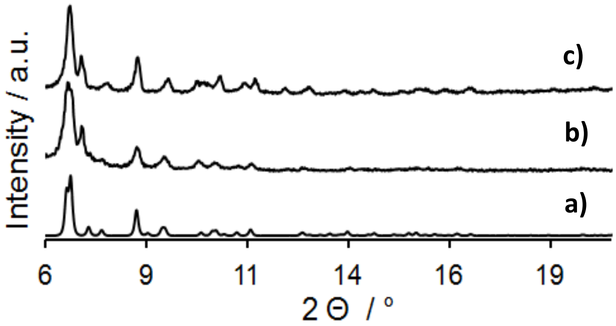


Figure S2. PXRD patterns of Bn-ChirUMCM-1: a) calculated; b) as-synthesized material; c) after treatment with isopropanol.

6. Adsorption experiments

For physisorption measurements, the synthesized materials were washed with fresh DEF and in the next step DEF included in the MOF pores was exchanged with DCM. Prior the measurements, the materials were dried in vacuum at ambient temperature for 24h.

The multipoint BET surface area was calculated using the p/p_0 range from 6×10^{-3} to 1×10^{-1} for **1** and from 6×10^{-3} to 5×10^{-2} for **2**. The pore volume was calculated at 0.9 p/p_o.

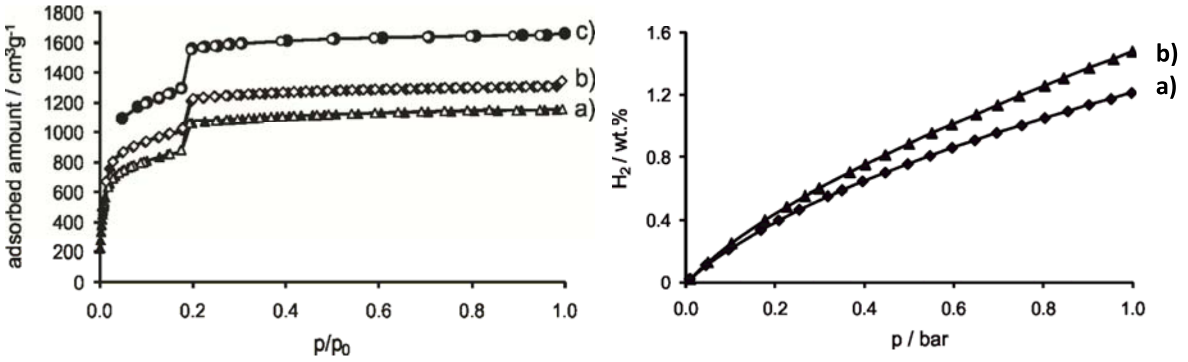


Figure S3. Nitrogen (left) and hydrogen (right) physisorption isotherms for **2** (a), **1** (b) and UMCM-1 (c) at 77 K.

7. Infrared spectroscopy (IR)

The IR spectra of **1** and **2** (Figure S4 and S5) show the specific vibrational bands in the typical region for symmetric vibrations of bridging mode coordinating carboxylate groups (1685 cm^{-1} (**1**); 1687 cm^{-1} (**2**)). The C-O vibration of the R-C=ONR$_2$ group of the chiral substituent was obtained at 1762 cm^{-1} in both cases. For compound **2** vibration bands at 709 cm^{-1} and 748 cm^{-1} are detected. They can be assigned to the hydrogen atoms of the phenyl ring of the chiral oxazolidinone.

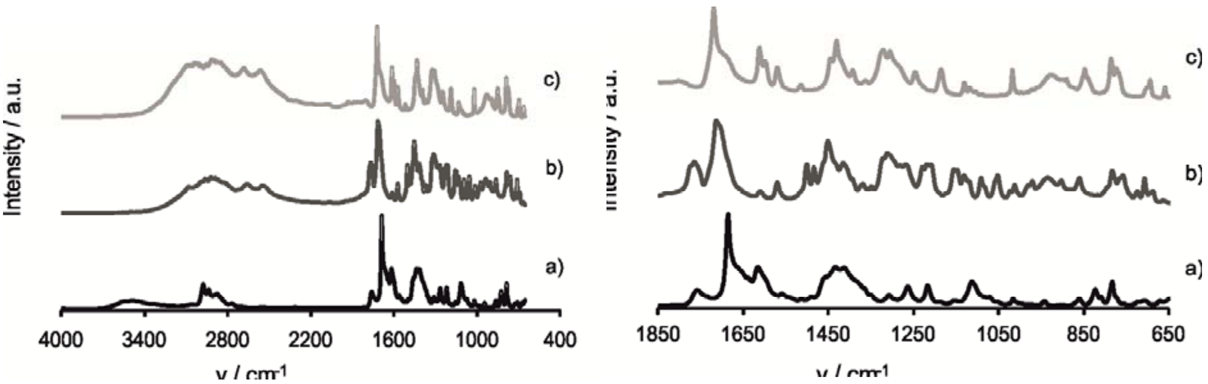


Figure S4. IR spectrum of: a) *i*Pr-Chir-UMCM-1 (**1**), b) *i*Pr-ChirH$_2$BDC, c) H$_3$BTB.

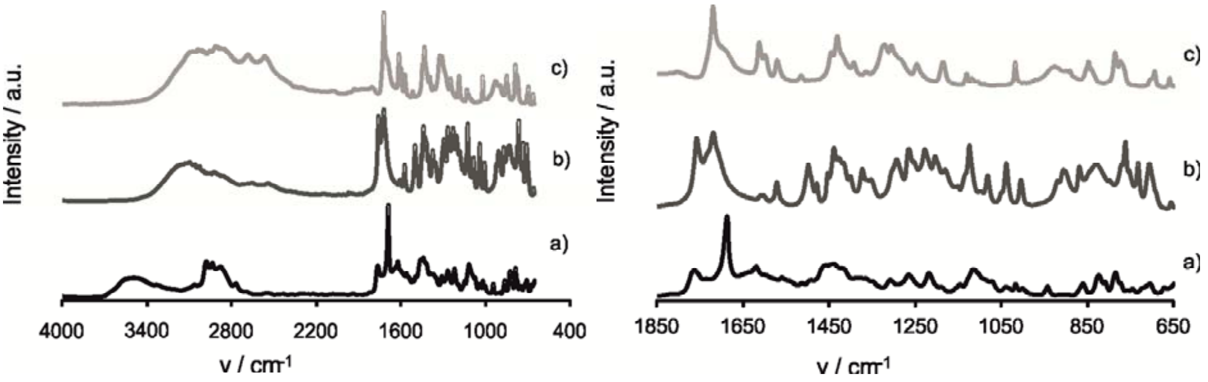


Figure S5. IR spectrum of: a) Bn-Chir-UMCM-1 (**2**), b) Bn-ChirH$_2$BDC c) H$_3$BTB.

8. Thermal analysis (TGA)

The thermo gravimetric analysis was performed on the argon flow dried samples of **1** and **2** in air atmosphere using a Netzsch STA 409 PC Luxx thermal analyzer. Both compounds are stable up to 300 °C. In the temperature range from 300 °C to 500 °C the network collapses with a weight loss of 71.6 % in the case of **1** and 66.6 % for **2**. For **2** a small amount (7 %) of residual solvent is observed up to 300 °C. (Figures S6 and S7).

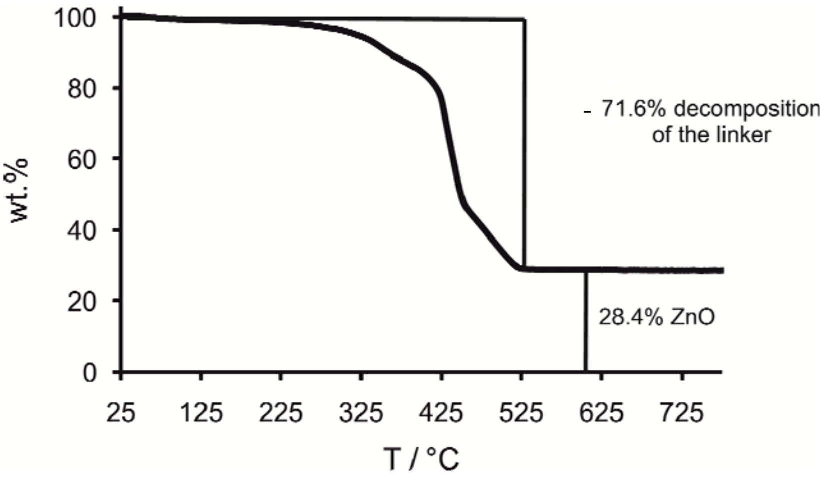


Figure S6. TGA of *i*Pr-Chir-UMCM-1 (**1**).

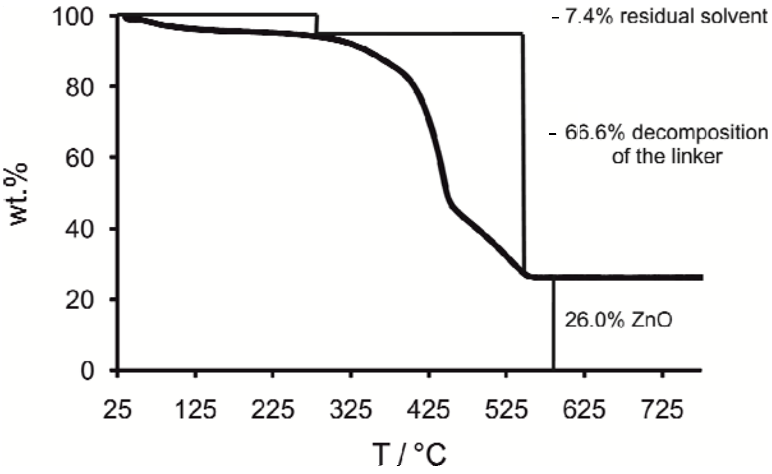


Figure S7. TGA of Bn-Chir-UMCM-1 (**2**).

9. Liquid state NMR of MOFs

Unless otherwise specified, the NMR experiments were performed in DMSO-*d*$_6$. The synthesized and completely dried MOF samples were dissolved in aqueous NaOH (1 M) and the linkers were precipitated using diluted hydrochloric acid. In the case of $Zn_4O(BTB)_{4/3}$(Bn-ChirBDC) (**2**) the NMR experiment verifies the presence of an intact Bn-ChirBDC linker (Fig. S9). The BTB:Bn-ChirBDC ratio, determined by the integrated aromatic protons, is 20.0 : 3.0 (Fig. S11) and is consistent with the theoretical value of 20.0 : 3.0 (4/3 : 1). The NMR spectra of $Zn_4O(BTB)_{4/3}$(*i*Pr-ChirBDC) (**1**) also show the typical peaks originated from the chiral oxazolidinone moiety (Figure S14). The aromatic protons of the BDC are observed only once proving that no chemical modification of *i*Pr-Chir-BDC occurs during the synthesis or drying process. Surprisingly, the BTB : BDC aryl proton ratio was determined as 121.3 : 3.2 (Fig. S15). This value would correspond to a linker ratio of 7.6 : 1 indicating a leaching of linker during sample preparation. For the next experiment the dry *i*Pr-ChirUMCM-1, DMSO-d$_6$, and DCl (37% in D_2O) were mixed directly in a NMR tube. After 3 hours the NMR measurements was performed. The spectra show an aromatic proton ratio of 20.1 : 3.0 corresponding to a BTB : *i*Pr-ChirBDC ratio of 4/3 : 1 (Fig. S16 - S18).

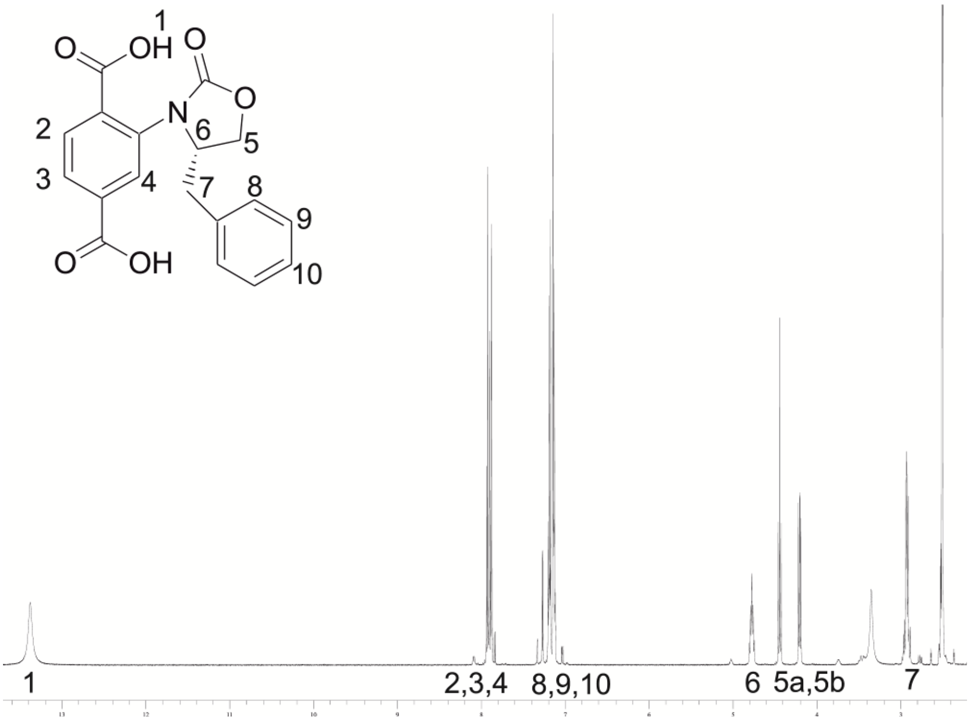


Figure S8. NMR spectrum of Bn-ChirH_2BDC.

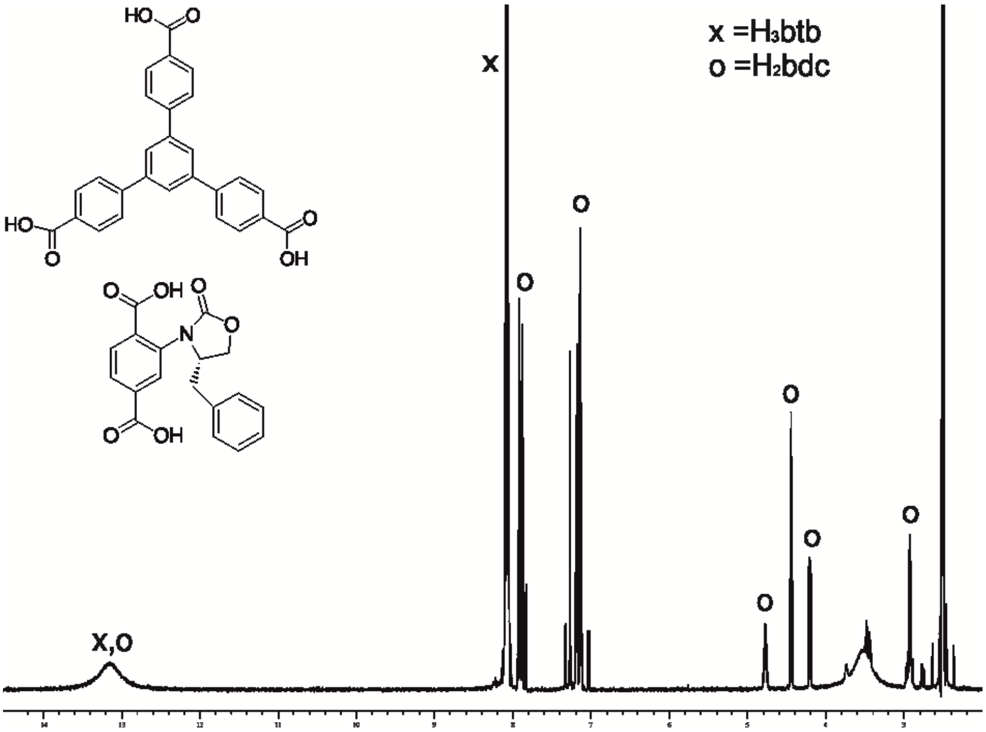


Figure S9. NMR spectrum of dissolved **2**; crosses and circles indicate the H_3BTB and Bn-Chir-H_2BDC signals, respectively.

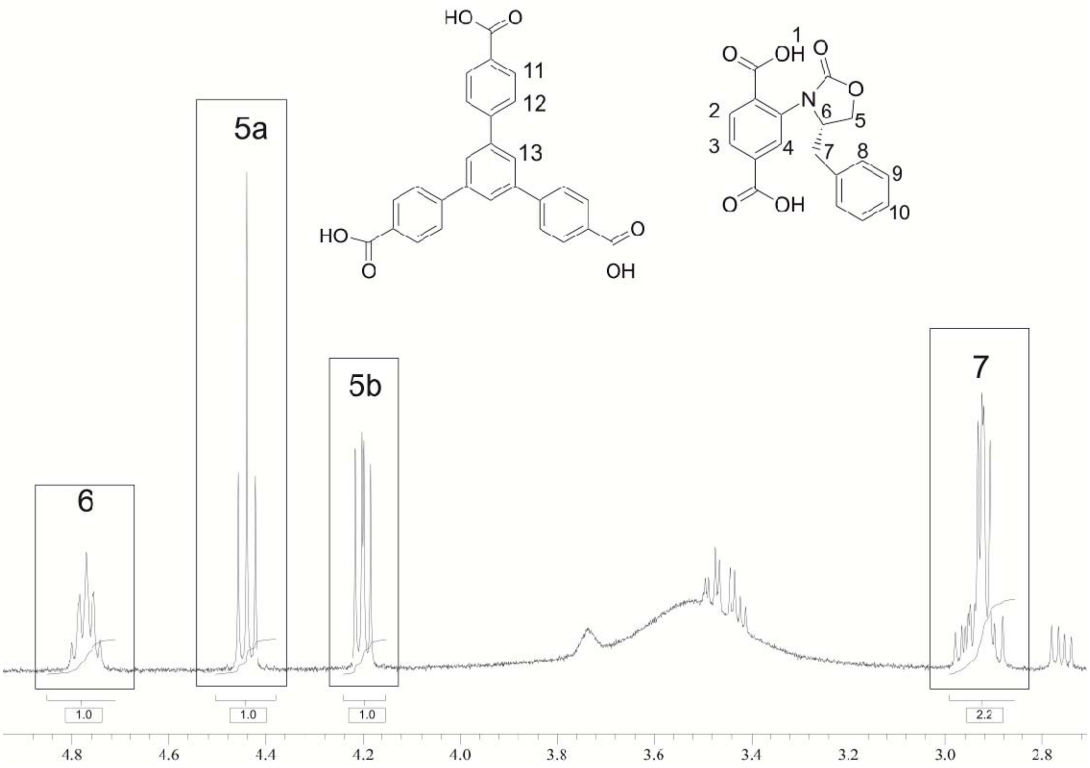


Figure S10. NMR spectrum of dissolved **2** in the range of 2.7-4.9 ppm showing the aliphatic protons of Bn-Chir-H_2BDC.

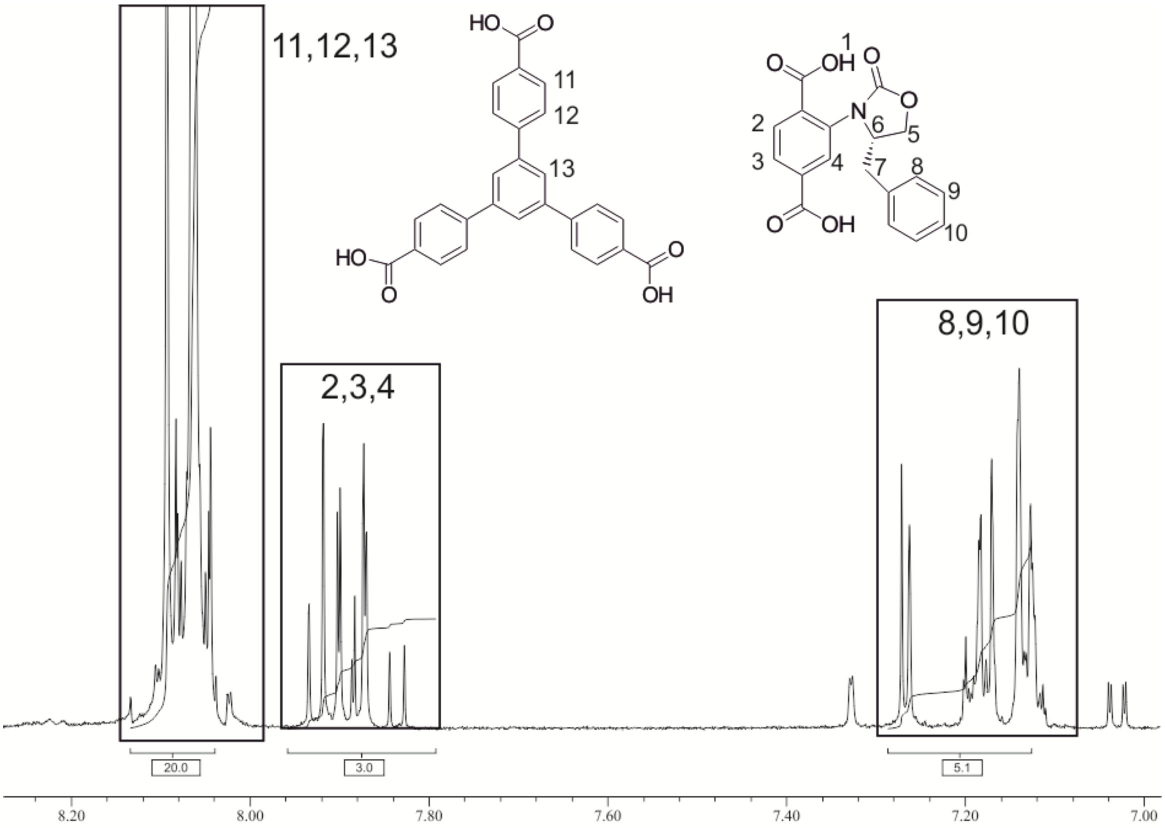


Figure S11. NMR spectrum of dissolved **2** in the range of 7.0-8.3 ppm showing the aromatic protons of Bn-Chir-H_2BDC and H_3BTB ligand.

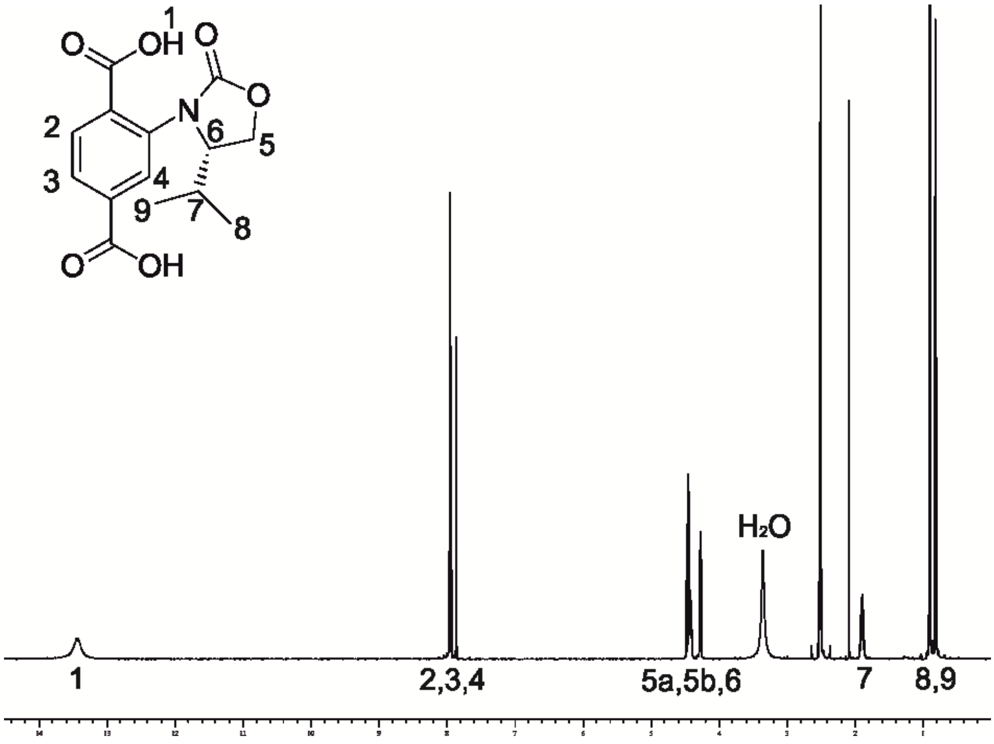


Figure S12. NMR spectrum of *i*Pr-Chir-H_2BDC.

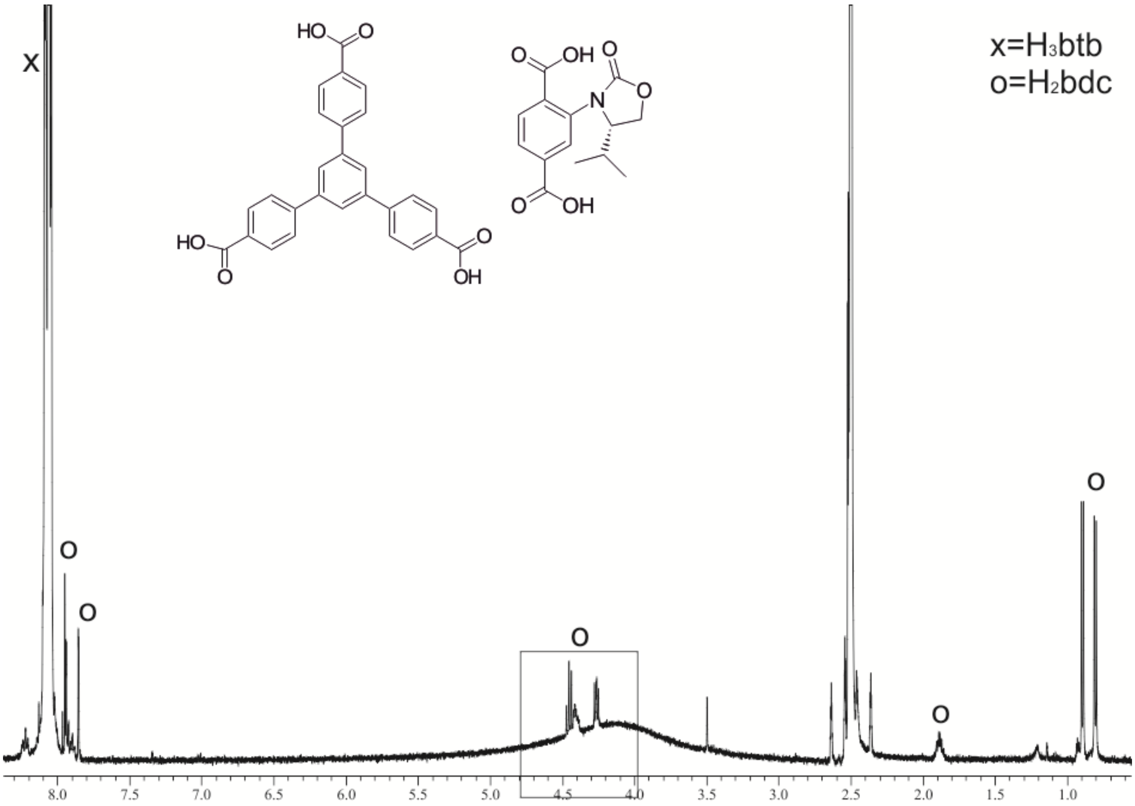


Figure S13. NMR spectrum of dissolved **1**; crosses and circles indicate the H_3BTB and *i*Pr-Chir-H_2BDC signals, respectively.

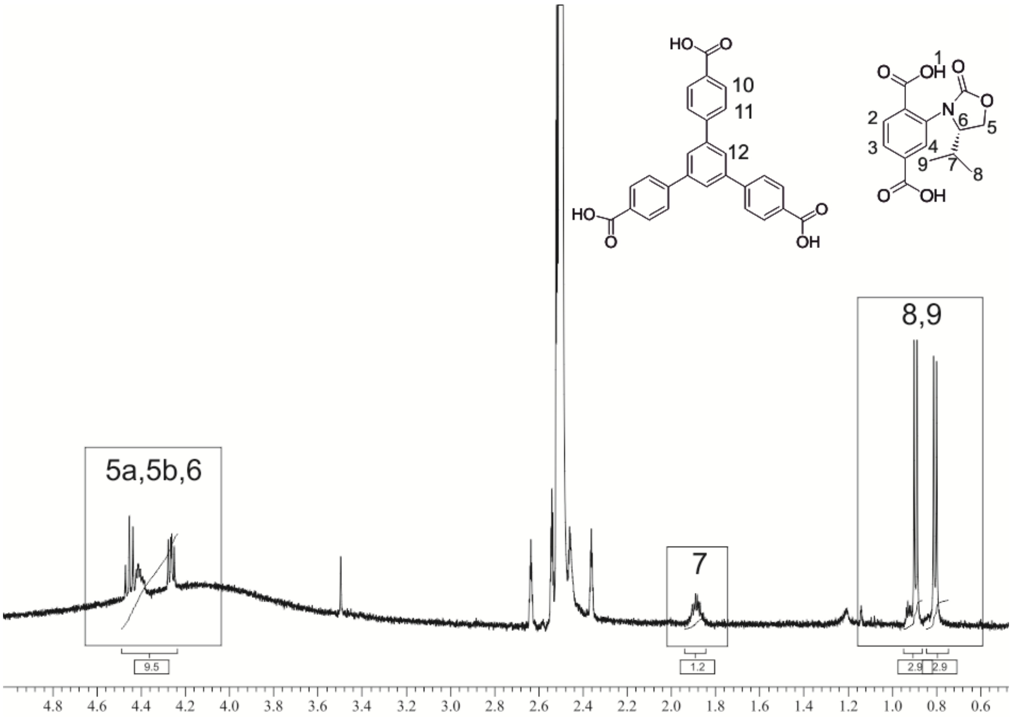


Figure S14. NMR spectrum of dissolved **1** in the range of 0.7-4.9 ppm showing the aliphatic protons of *i*Pr-Chir-H_2BDC.

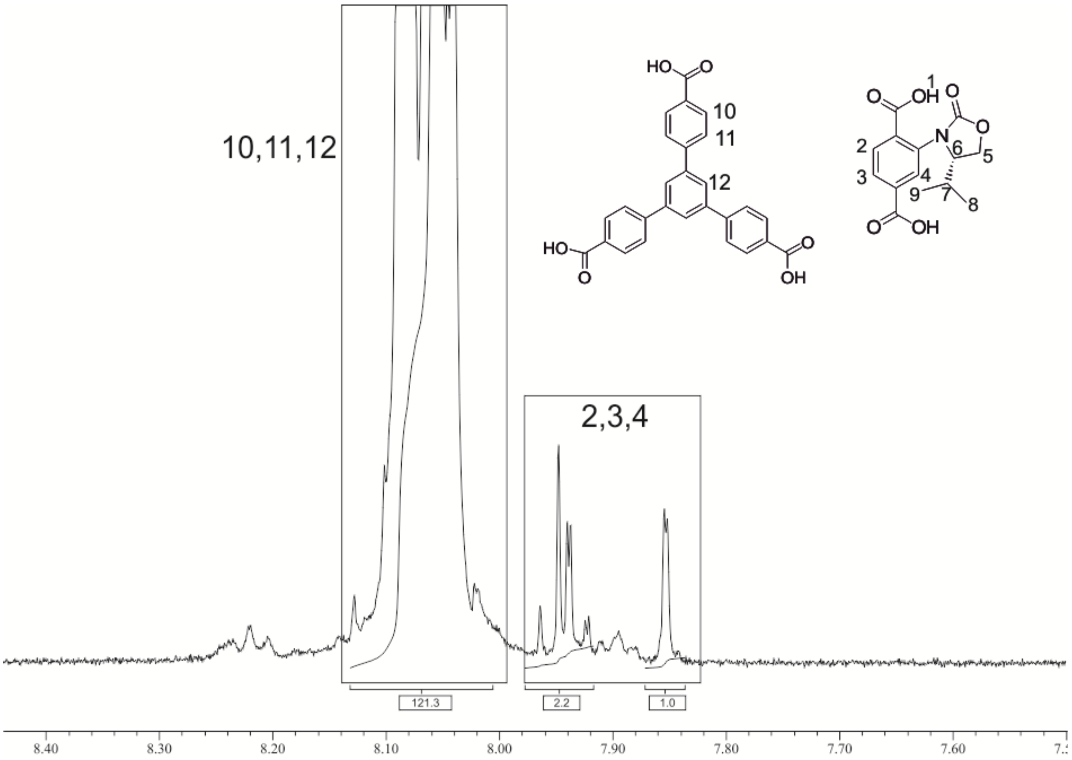


Figure S15. NMR spectrum of dissolved **1** in the range of 7.5-8.4 ppm showing the aromatic protons of *i*Pr-Chir-H_2BDC and H_3BTB ligand.

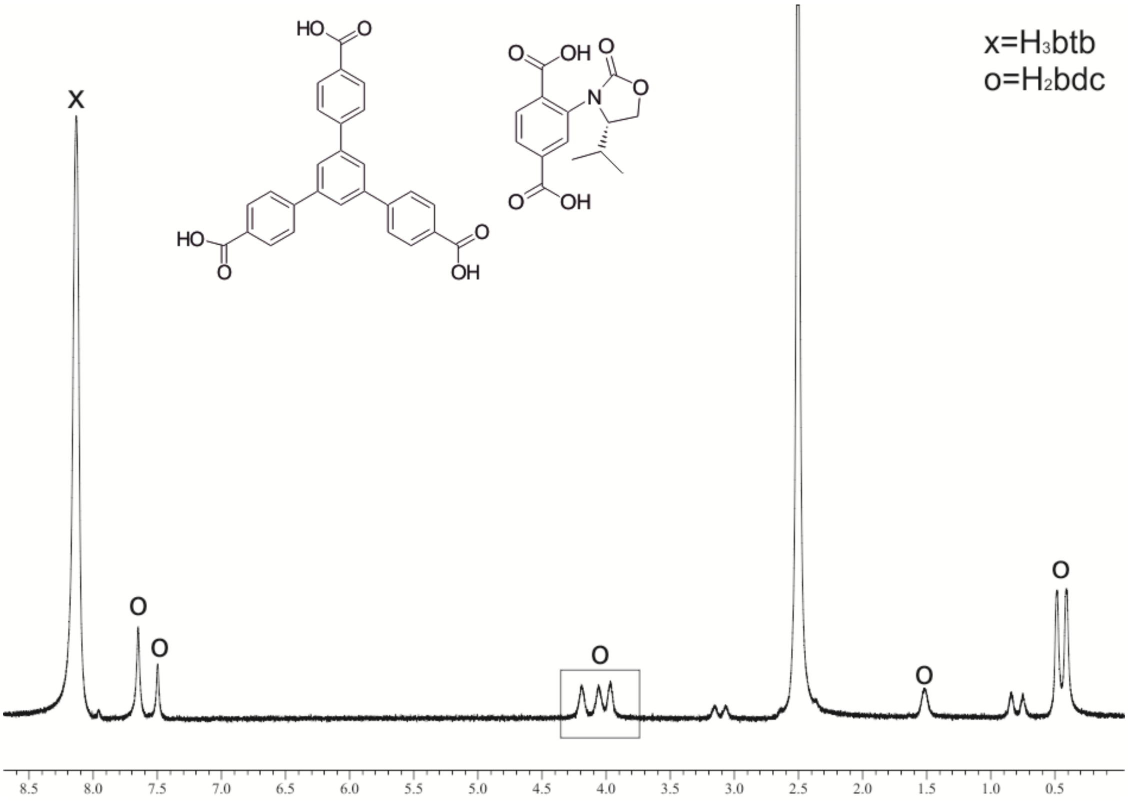


Figure S16. NMR spectrum of **1** in a DCl/D_2O/DMSO-*d6* mixture; crosses and circles indicate the H_3BTB and *i*Pr-Chir-H_2BDC signals, respectively.

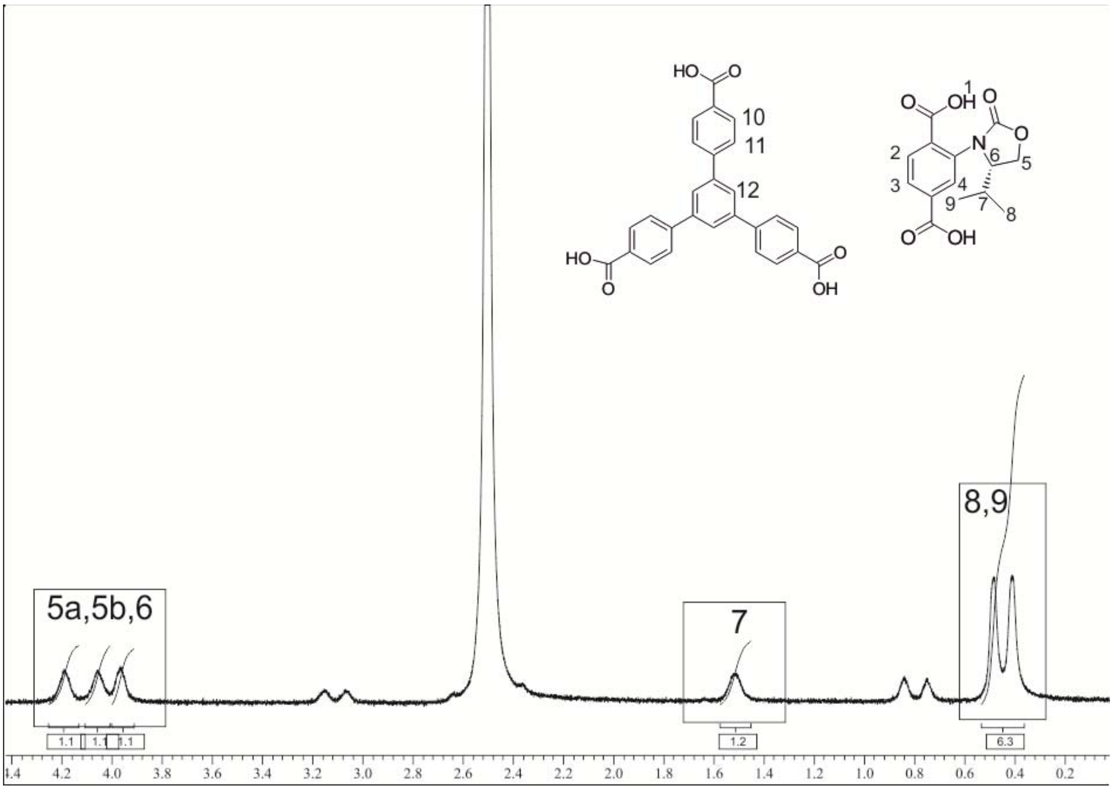


Figure S17. NMR spectrum of **1** in a DCl/D_2O/DMSO-*d6* mixture in the range of 0.1-4.4 ppm showing the aliphatic protons of *i*Pr-Chir-H_2BDC.

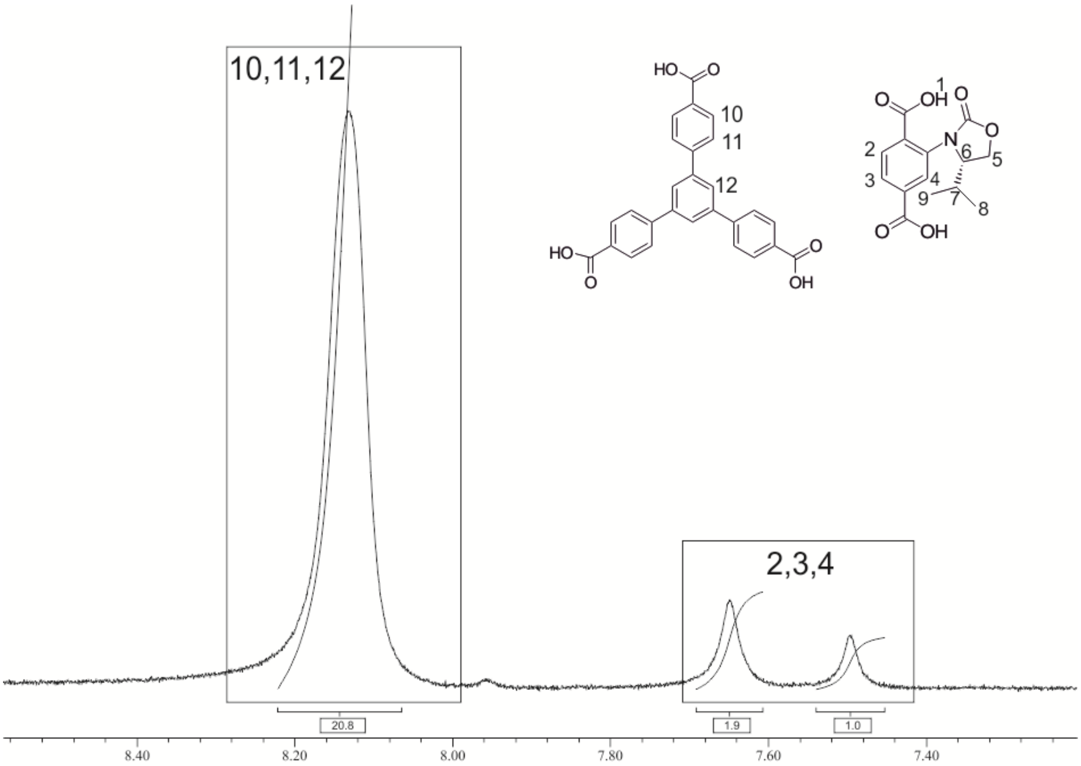


Figure S18. NMR spectrum of dissolved **1** in the range of 7.3-8.5 ppm showing the aromatic protons of *i*Pr-Chir-H_2BDC and H_3BTB ligand.

10. Solid state NMR

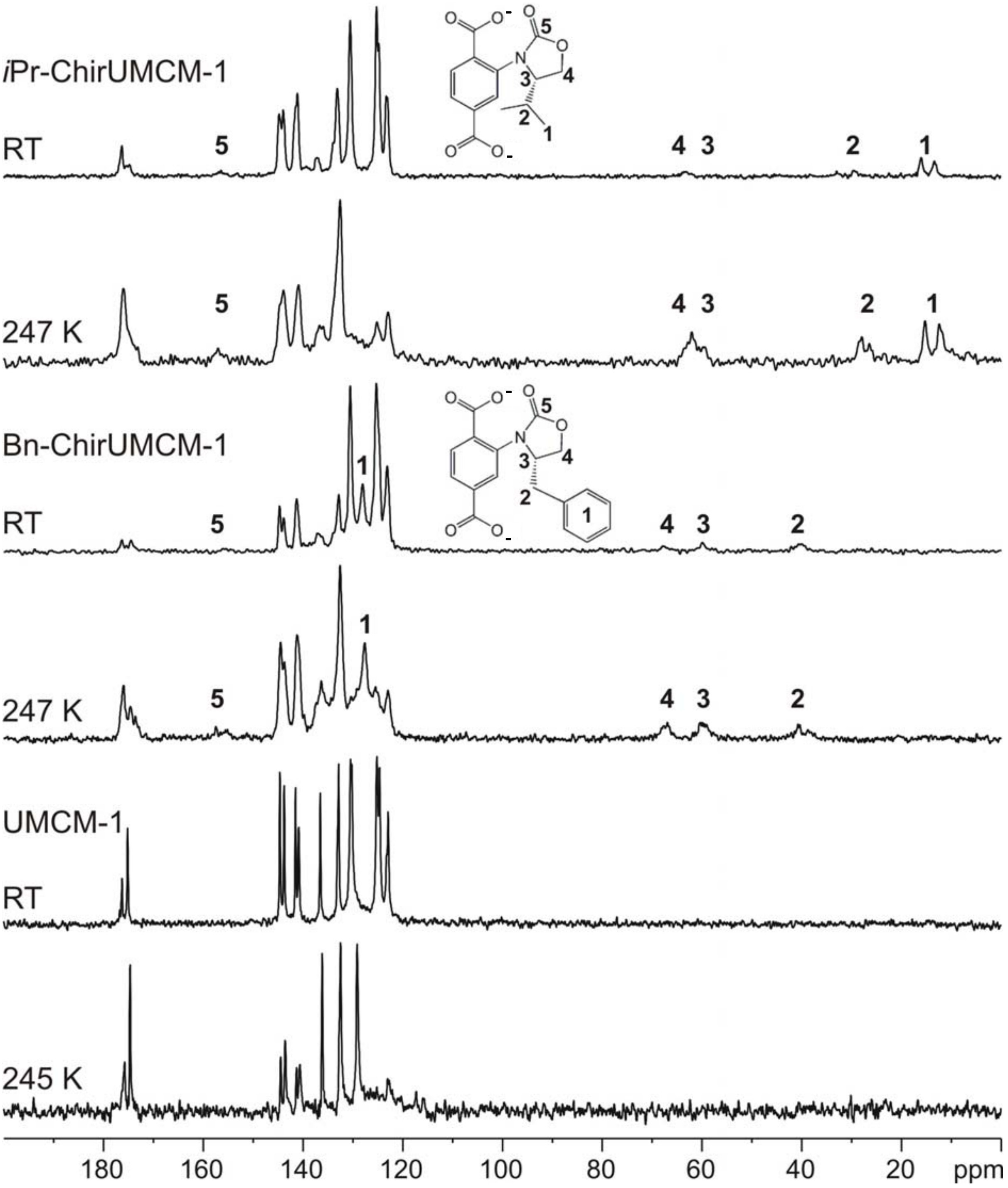


Figure S19. $^{13}C\{^1H\}$ cross-polarization (CP) MAS NMR spectra of compounds **1** (*i*Pr-ChirUMCM-1) and **2** (Bn-ChirUMCM-1) measured at room temperature (RT) and 247 K. For comparison the spectrum of unmodified UMCM-1 is also shown. Note the pronounced temperature-dependence of the spectra.

11. Column packing procedure for HPLC measurements

The columns (with 5 cm length and 2 mm inner diameter) for the experiments were obtained from Bischoff Chrom Leonberg, Germany. Before the packing the material was crushed under dry inert atmosphere in dichloromethane applying soft pressure. After crushing, the crystals are suspended in iso-propanol. The slurry is pressed with a maximum pressure of 200 bar and *n*-hexane as eluent into the empty column. By changing the solvent while pressing the slurry into the column, the crystals could dispose slowly to get a better packing.

After packing, the column was conditioned by flushing with *n*-heptane for 15 minutes at a flow of 0.5 ml min^{-1}. Afterwards, an injection of a certain amount of interacting analyte and flushing for another 30 minutes with pure eluent followed.

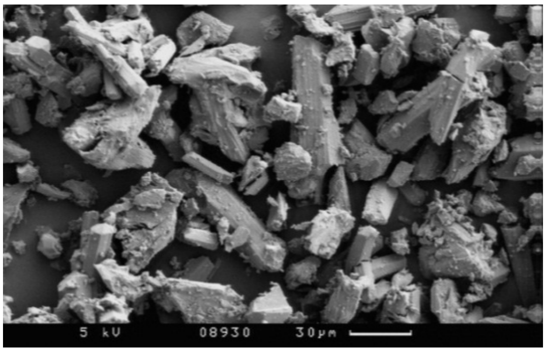


Figure S20. SEM image of the crushed Bn-ChirUMCM-1 crystals.

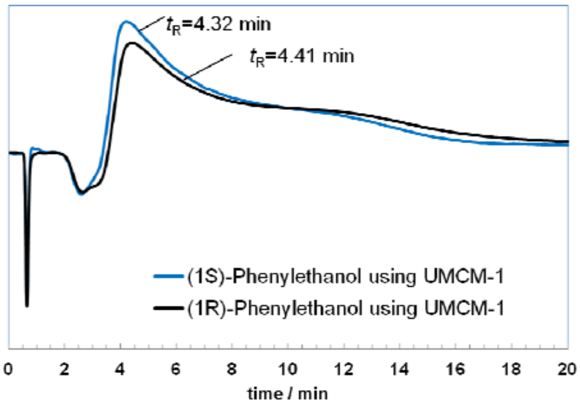


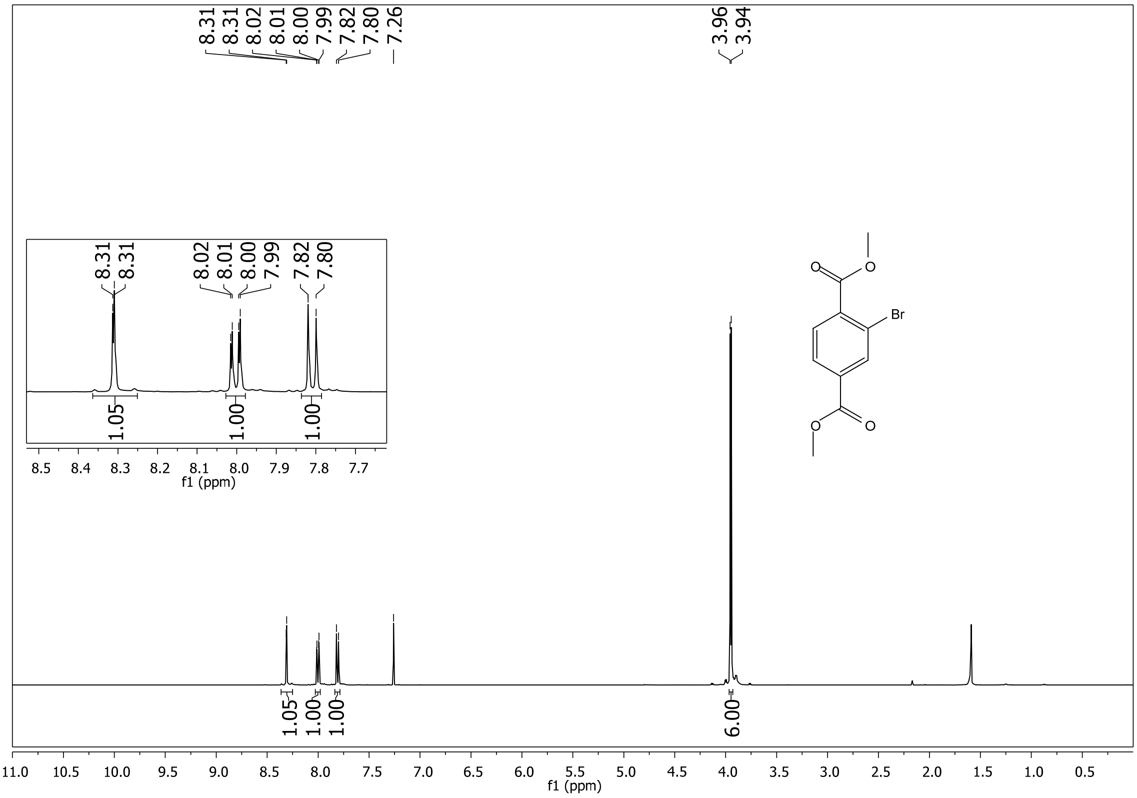
Figure S21. Chromatogram of 1-phenylethanol enantiomers using UMCM-1.

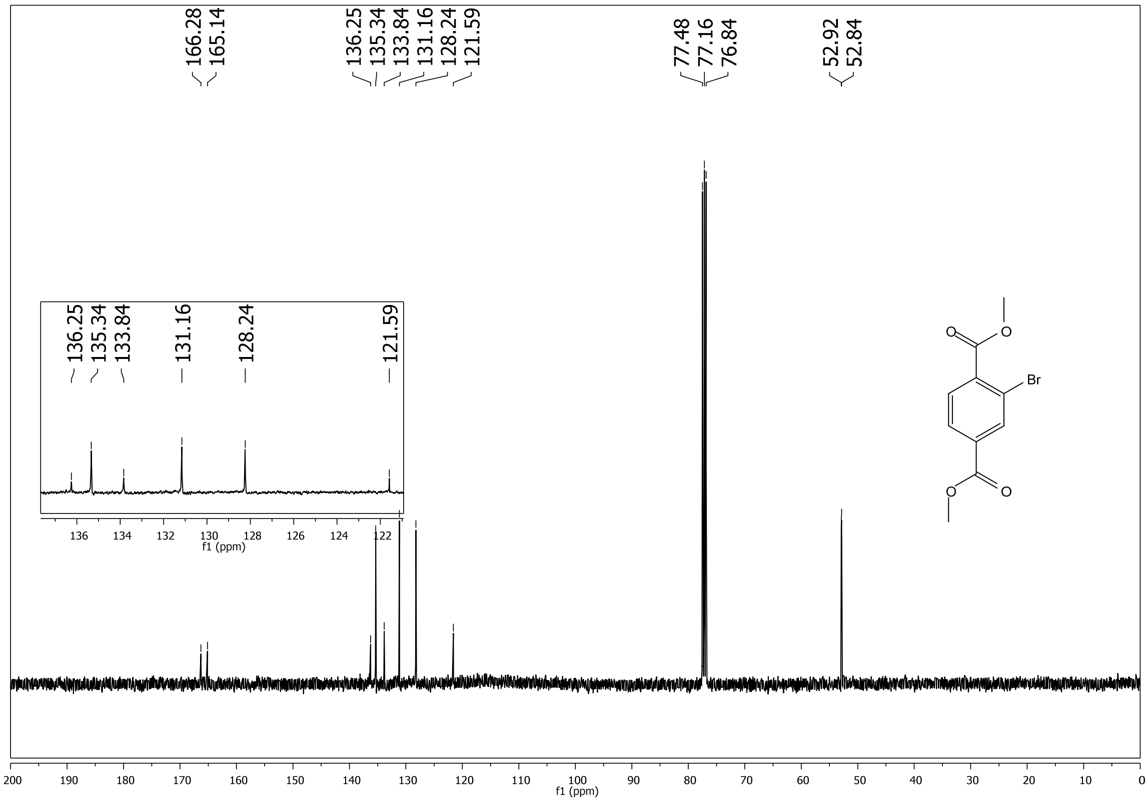
Table S2. Comparison of chosen analytes on non-chiral UMCM-1 and chiral modified Bn-ChirUMCM-1 columns.

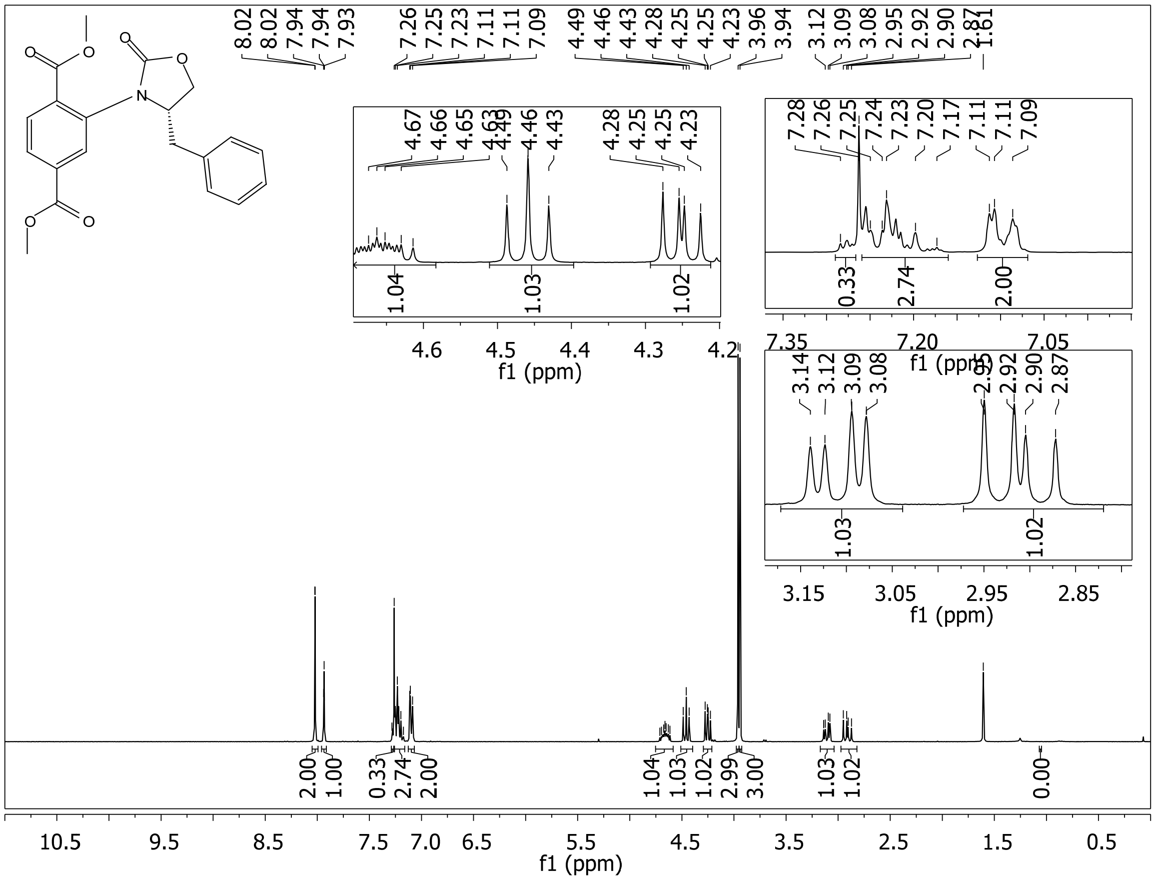
Analyte	UMCM-1 column t_R / min	Bn-ChirUMCM-1column t_R / min
(4*R*)-benzyl-2-oxazolidinone	0.60[1]	3.40
(4*S*)-benzyl-2-oxazolidinone	0.60[1]	3.40
(4*R*)-phenyl-2-oxazolidinone	0.60[1]	3.26
(4*S*)-phenyl-2-oxazolidinone	0.60[1]	3.26
cis-(4*R*,5*S*)-diphenyl-2-oxazolidinone	0.60[1]	3.33
cis-(4*S*,5*R*)-diphenyl-2-oxazolidinone	0.60[1]	3.33
(1*R*)-2-butanol	n.m	3.28
(1*S*)-2-butanol	n.m	3.28
(1*R*)-phenylethanol	4.41	11.21
(1*S*)-phenylethanol	4.32	7.84
1-phenylethanamine	---[2]	---[2]
D,L-alanine	---[2]	---[2]

[1] hold-up time; [2] broad peak, no t_R assignable, analyte remained on column; n. m. – not measured

12. Further ^{1}H and ^{13}C NMR Spectra



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7.11
7.11
7.09
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4.46
4.43
4.28
4.25
4.25
4.23
3.96
3.94
3.12
3.09
3.08
2.95
2.92
2.90
2.87
1.61
4.67
4.66
4.65
4.63
4.49
4.46
4.43
4.28
4.25
4.25
4.23
1.04
1.03
1.02
4.6
4.5
4.4
4.3
4.2
f1 (ppm)
7.28
7.26
7.25
7.24
7.23
7.20
7.17
7.11
7.11
7.09
0.33
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2.00
7.35
7.20
7.05
f1 (ppm)
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3.12
3.09
3.08
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2.92
2.90
2.87
1.03
1.02
3.15
3.05
2.95
2.85
f1 (ppm)
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1.00
0.33
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1.03
1.02
2.99
3.00
1.03
1.02
0.00
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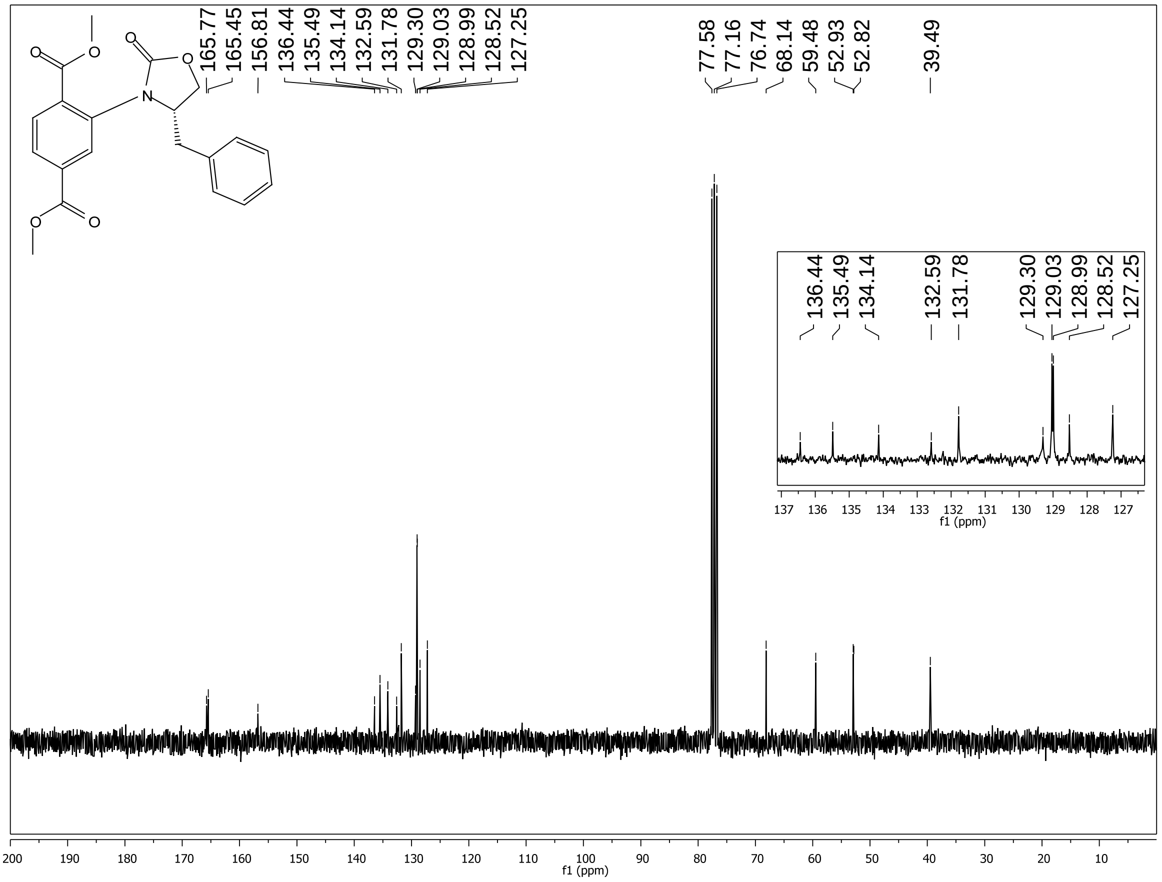
f1 (ppm)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128.99
128.52
127.25
77.58
77.16
76.74
68.14
59.48
52.93
52.82
39.49
136.44
135.49
134.14
132.59
131.78
129.30
129.03
128.99
128.52
127.25
137
136
135
134
133
132
131
130
129
128
127
f1 (ppm)
200
190
180
170
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140
130
120
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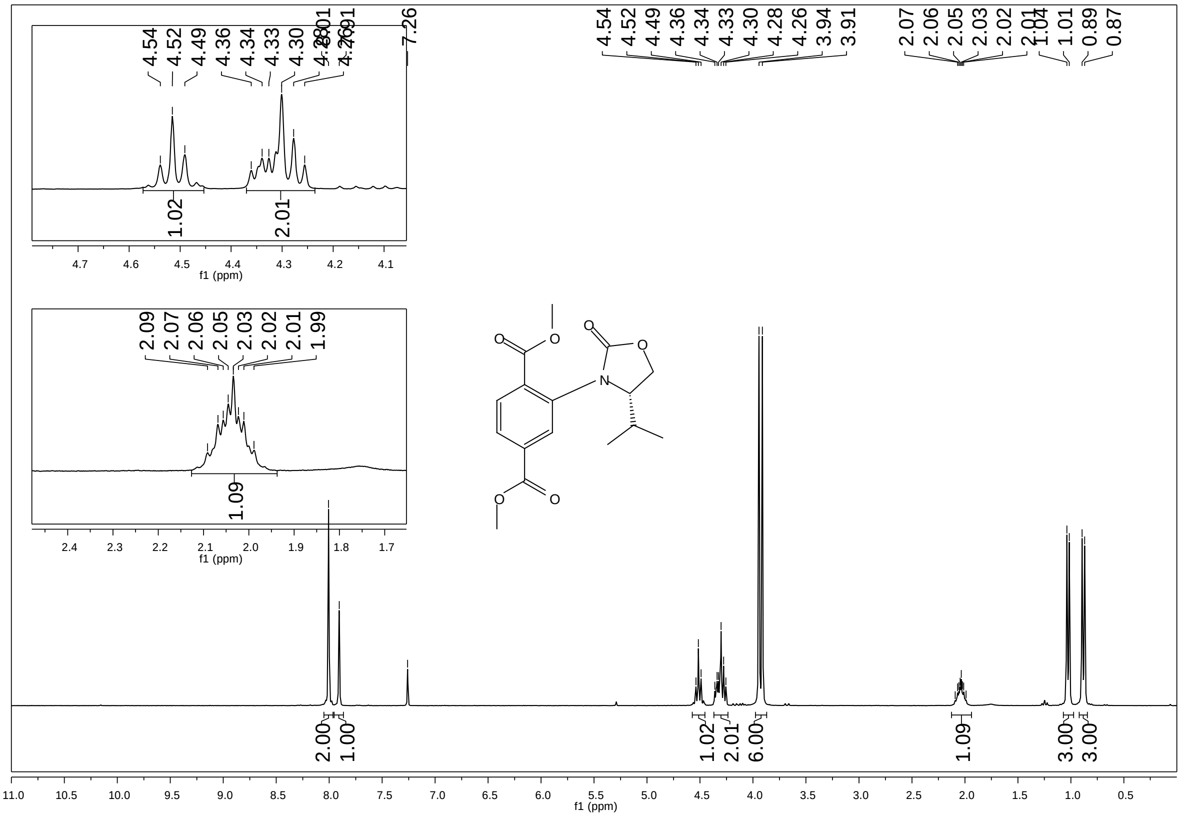
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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2.06
2.05
2.03
2.02
2.01
1.04
1.01
0.89
0.87
7.26
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2.00
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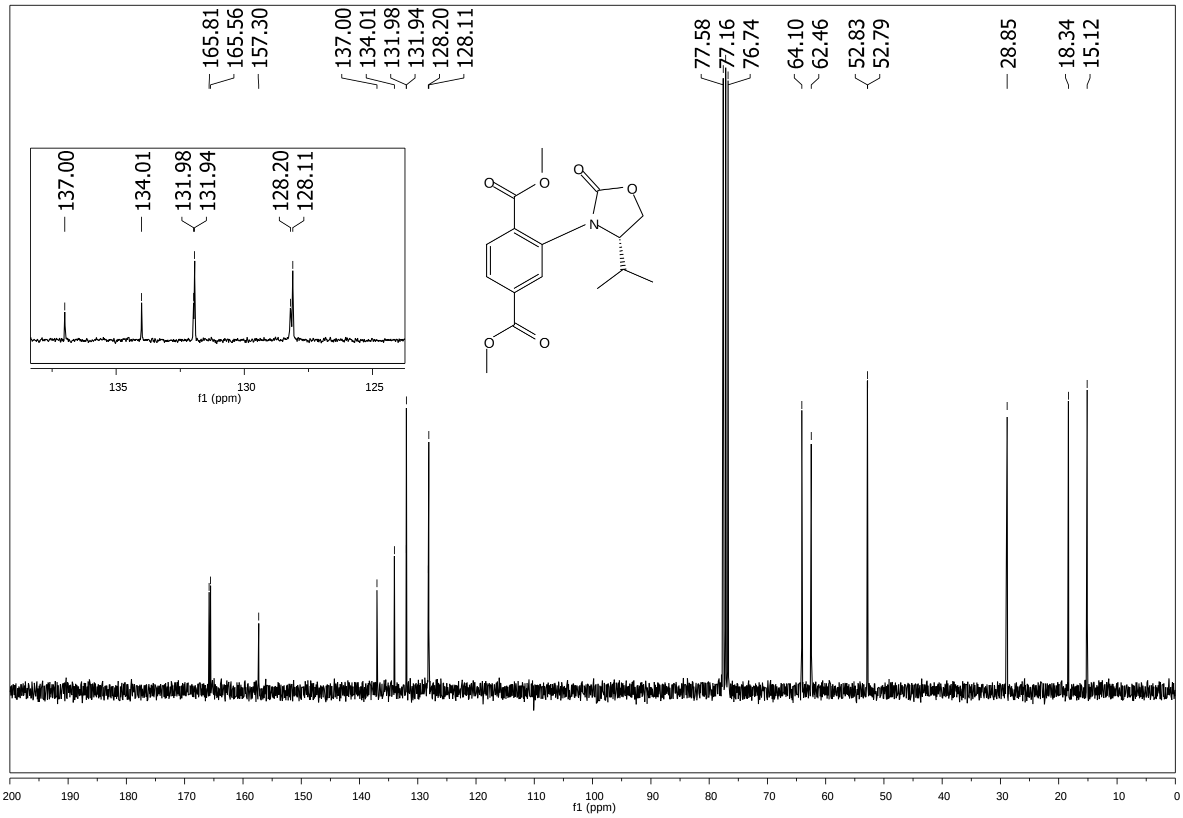
N
f1 (ppm)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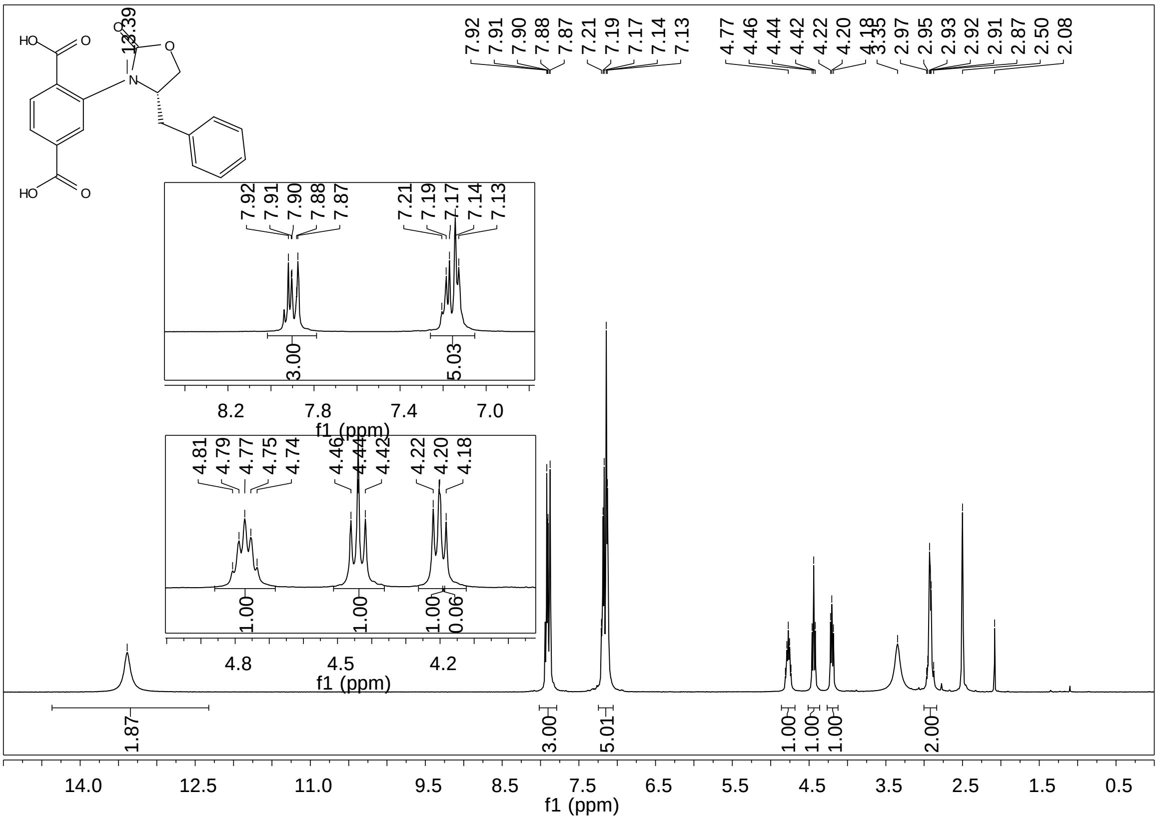
O
N
f1 (ppm)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2.50
2.08
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5.03
8.2
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7.4
7.0
f1 (ppm)
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4.79
4.77
4.75
4.74
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4.44
4.42
4.22
4.20
4.18
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1.00
1.00
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4.5
4.2
f1 (ppm)
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3.00
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1.00
1.00
2.00
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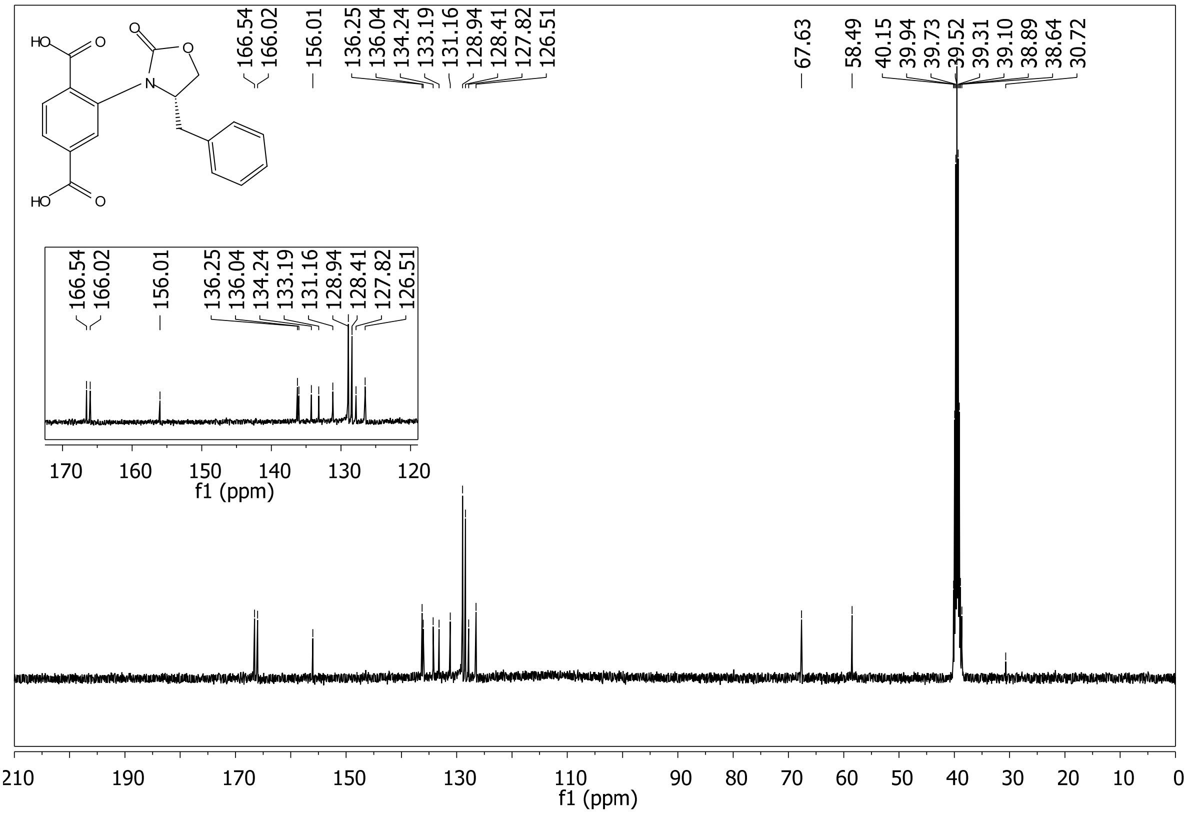
f1 (ppm)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130
120
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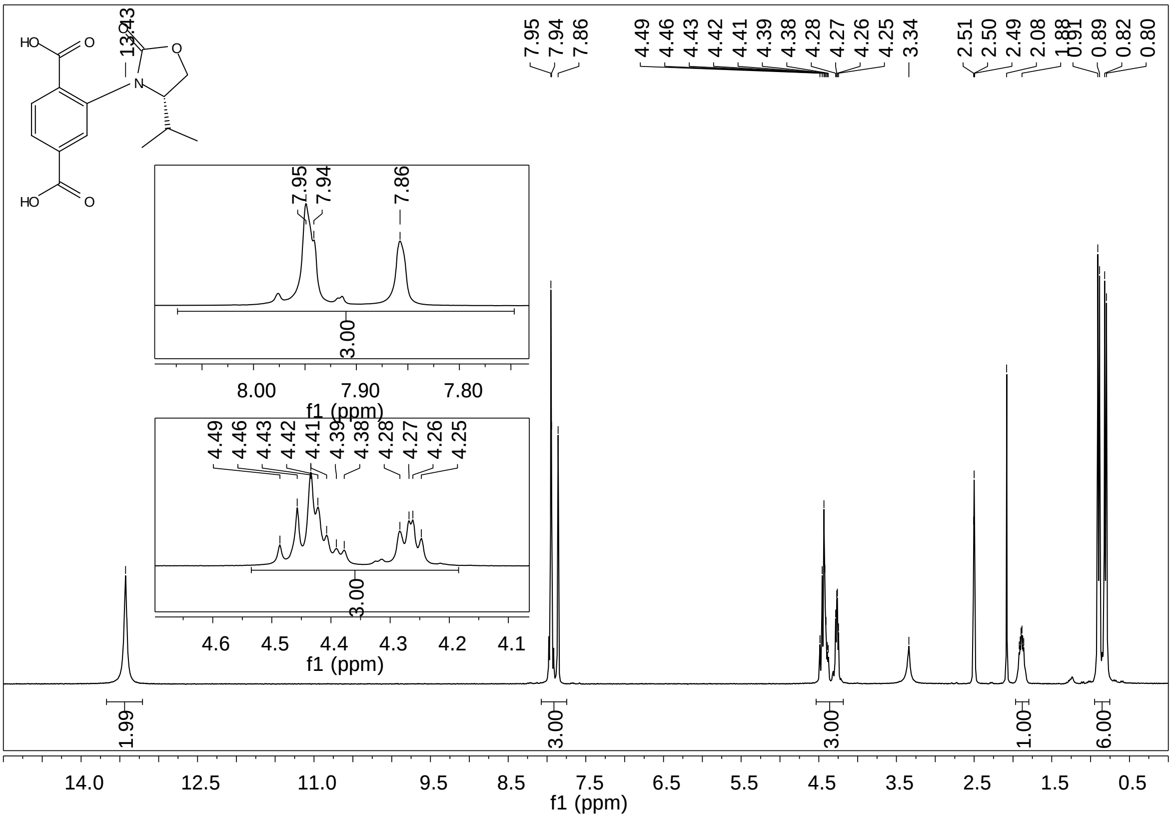
f1 (ppm)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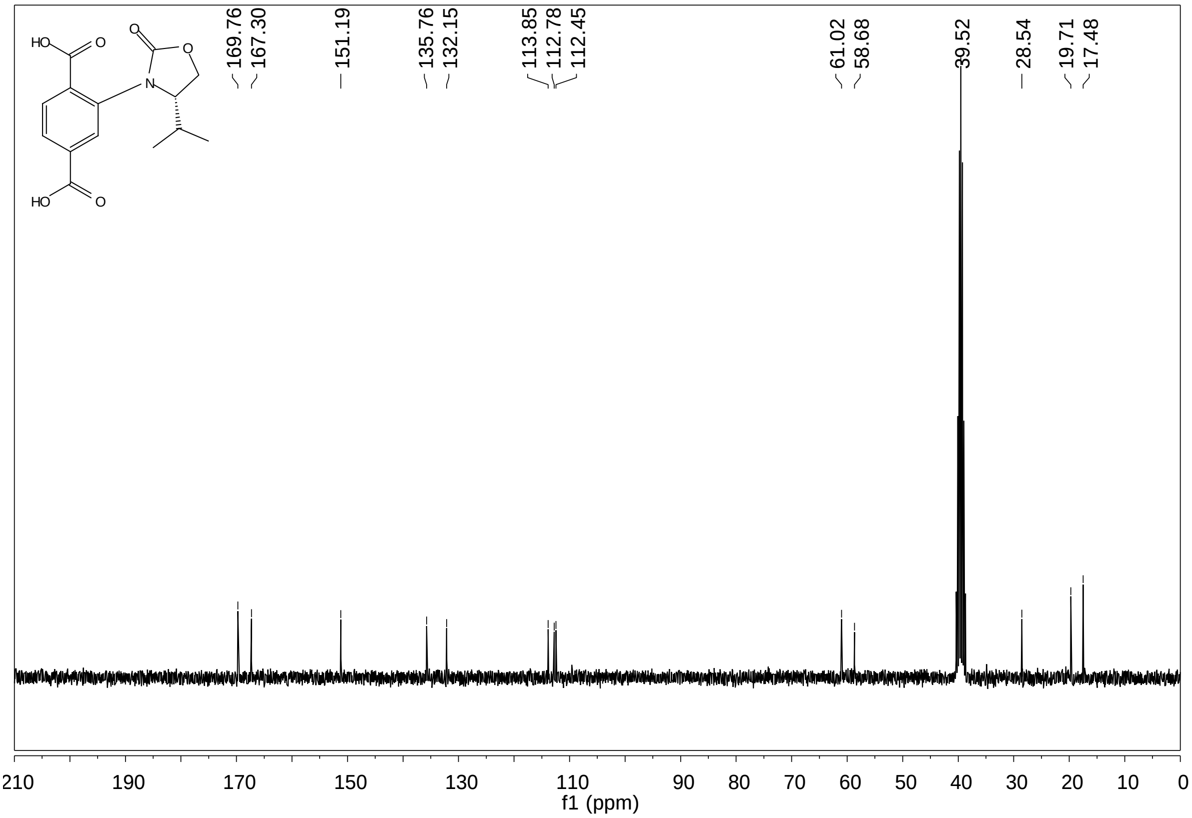
f1 (ppm)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f1 (ppm)