Electronic Supplementary Information

Practical manganese-catalysed highly enantioselective *cis*-dihydroxylation of electron-deficient alkenes and detection of *cis*-dioxomanganese(V) intermediate by high-resolution ESI-MS analysis

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NMR spectroscopy and mass spectrometry

^{1}H NMR and ^{13} NMR spectra were recorded on a Bruker DPX-300 spectrometer, with chemaical shifts relative to tetramethylsilane. EI mass spectra were measured on a Finnigan MAT 95 mass spectrometer. ESI mass spectra were obstianed on a Waters Micromess Q-Tof Premier quadrupole time-of-flight tandem mass spectrometer.

Preparation of [Mn^{II}((*S,S*)-BQCN)Cl_2] (1)

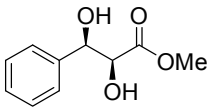
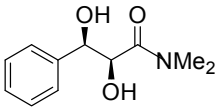
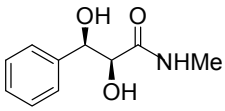
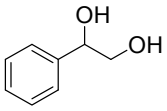
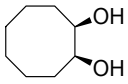
A mixture of (*S,S*)-BQCN (0.50 mmol) and $MnCl_2$•$4H_2O$ (2.50 mmol) in acetonitrile/ methanol (1:2 v/v, 15 mL) was refluxed for 18 h. The mixture was then filtered and concentrated by rotary evaporation, followed by addtion of diethyl ether for precipitation of **1**. The resulted yellow crude product was washed by small amount of methanol and recrystallized from acetonitle-diethyl ether to give **1** as a yellow crystalline solid. Yield: 94%. ESI-MS: *m/z* 486.1 ([Mn^{II}((*S,S*)-BQCN)Cl]$^{+}$).

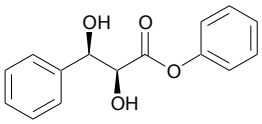
General procedure for asymmetric *cis*-dihydroxylation of alkenes with Oxone catalysed by 1

A solution of Oxone (1.0 mmol) and $NaHCO_3$ (3.0 mmol) in water (6 mL) was added in two portions to a solution of alkene (0.5 mmol) and **1** (2-5 mol%) in acetonitrile (6 mL) at room temperature within 5 min. The reaction mixture was stirred and monitored by TLC. Upon quenching by aqueous saturated Na_2SO_3 solution, the mixture was extracted with ethyl acetate (10 mL) conatining 1,4-dichlorobenzene (GC internal standard, 0.1 mmol) and the aliquot of the extract was analyzed by GC. Afterwards, the mixture was further extracted with ethyl acetate (3 x 50 mL) and the oragnic crude products were identified and quantified by ^{1}H NMR analysis. The *cis*-diol product was isolated after purification by column chromatography on silica gel. The enatiomeric excess of purified *cis*-diol product was determined by chiral HPLC (Chiralpak OD-3 and AD-3).

Characterization of *cis*-diol products

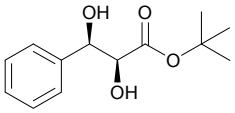
The previously known *cis*-diol products corresponding to substrates **2a**, **4a**, **5a**, **6b** and **7** were characterised on the basis of the spectral data described in literature.

Compound	Reference
 (product for **2a**)	(*a*) B. Plietker, M. Niggemann and A. Pollrich, *Org. Biomol. Chem.*, 2004, **2**, 1116; (*b*) B. Plietker and M. Niggemann, *J. Org. Chem.*, 2005, **70**, 2402.
 (product for **4a**)	T. W.-S. Chow, E. L.-M. Wong, Z. Guo, Y. Liu, J.-S. Huang and C.-M. Che, *J. Am. Chem. Soc.*, **2010**, *132*, 13229.
 (product for **5a**)	T. W.-S. Chow, E. L.-M., Wong, Z. Guo, Y. Liu, J.-S. Huang and C.-M. Che, , *J. Am. Chem. Soc.*, **2010**, *132*, 13229.
 (product for **6b**)	(*a*) B. Plietker, M. Niggemann and A. Pollrich, *Org. Biomol. Chem.*, 2004, **2**, 1116; (*b*) K. C. Nicolaou, S. A. Snyder, D. A. Longbottom, A. Z. Nalbandian and X. Huang, *Chem. Eur. J.*, 2004, **10**, 5581.
 (product for **7**)	J. W. De Boer, J. Brinksma, W. R. Browne, A. Meetsma, P. L. Alsters, R. Hage and B. L. Feringa, *J. Am. Chem. Soc.*, 2005, **127**, 7990.



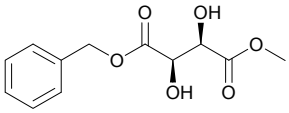
(product for **2b**)

^{1}H NMR (300 MHz, CD_3OD) δ 4.54 (d, J = 4.46 Hz, 1H), 5.10 (d, J = 4.44 Hz, 1H), 6.95 (d, J = 7.46 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.31-7.41 (m, 5H), 7.49 (d, J = 7.13 Hz, 2H). ^{13}C NMR (75 MHz, CD_3OD) δ 76.38, 77.19, 122.56, 127.01, 128.03, 128.82, 129.24, 130.38, 142.13, 151.97, 172.55. EI-MS: *m/z* 258 $[M]^+$; HRMS (EI): *m/z* for $C_{15}H_{14}O_4$, calcd 258.0887, found 258.0880.



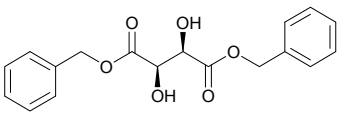
(product for **2c**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 9H), 4.26 (d, J = 3.61 Hz, 1H), 4.91 (d, 3.57 Hz, 1H), 7.28-7.46 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.97, 74.96, 74.99, 83.35, 126.64, 128.03, 128.42, 140.22, 172.00. EI-MS: *m/z* 238 $[M]^+$; HRMS (EI): *m/z* for $C_{13}H_{18}O_4$, calcd 238.1200, found 238.1195.



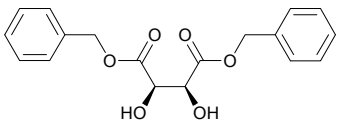
(product for **3a**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.56 (br, 2H), 3.81 (s, 3H), 4.60 (d, J = 6.25 Hz, 2H), 5.26 (d, J = 12.15 Hz, 1H), 5.27 (d, J = 12.16 Hz, 1H), 7.30-7.38 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.16, 68.05, 72.23, 72.31, 128.44, 128.71, 128.73, 134.93, 171.51, 172.04. EI-MS: *m/z* 254 $[M]^+$; HRMS (EI): *m/z* for $C_{12}H_{14}O_6$, calcd 254.0785, found 254.0784.



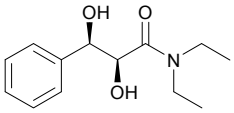
(product for **3b**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.24 (d, J = 7.07 Hz, 2H), 4.61 (d, J = 6.63 Hz, 2H), 5.26 (d, J = 12.18 Hz, 2H), 5.27 (d, J = 12.17, 2H), 7.33-7.42 (m, 10H). ^{13}C N MR (75 MHz, $CDCl_3$) δ 68.21, 72.22, 128.53, 128.82, 134.89, 171.50. EI-MS: *m/z* 239 $[M - PhCH_2]^+$; HRMS (EI): *m/z* for $C_{11}H_{11}O_6$, calcd 239.0550, found 239.0551.



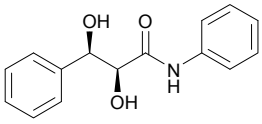
(product for **3c**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.19 (d, J = 5.55 Hz, 2H), 4.60 (d, J = 4.98 Hz, 2H), 5.04 (d, J = 11.94 Hz, 2H), 5.08 (d, J = 11.94 Hz, 2H), 7.23-7.27 (m, 5H), 7.32-7.35 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 68.19, 73.04, 128.74, 128.83, 128.86, 134.63, 170.97. EI-MS: *m/z* 239 $[M - PhCH_2]^+$; HRMS (EI): *m/z* for $C_{11}H_{11}O_6$, calcd 239.0550, found 239.0550.



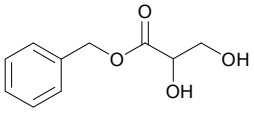
(product for **4b**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, J = 7.13 Hz, 3H), 1.05 (t, J = 7.11 Hz, 3H), 2.60-2.72 (m, 1H), 2.77-2.87 (m, 1H), 3.02-3.13 (m, 1H), 3.49-3.61 (m, 1H), 4.30 (d, J = 6.06 Hz, 1H), 4.74 (d, J = 6.05 Hz, 1H), 7.26-7.40 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.64, 13.88, 40.52, 40.91, 72.82, 76.11, 126.70, 128.23, 128.42, 139.26, 171.18. EI-MS: *m/z* 238 [M + H^+]$^+$; HRMS (EI): *m/z* for $C_{13}H_{20}O_3N$, calcd 238.1438, found 238.1440.



(product for **5b**)

^{1}H NMR (300 MHz, CD_3OD) δ 4.25 (d, J = 2.76 Hz, 1H), 5.13 (d, J = 2.62 Hz, 1H), 7.12 (t, J = 7.40 Hz, 1H), 7.25-7.37 (m, 5H), 7.48 (d, J = 7.28 Hz, 2H), 7.58 (d, J = 8.37 Hz, 2H). ^{13}C NMR (75 MHz, CD_3OD) δ 75.50, 77.69, 121.48, 125.57, 127.59, 128.39, 129.10, 129.80, 138.91, 143.11, 173.28. EI-MS: *m/z* 257 [M]$^+$; HRMS (EI): *m/z* for $C_{15}H_{15}O_3N$, calcd 257.1046, found 257.1040.



(product for **6a**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.81-3.92 (m, 2H), 4.30 (t, J = 3.39 Hz, 1H), 5.21 (d, J = 12.23 Hz, 1H), 5.22 (d, J = 12.23, 1H), 7.29-7.39 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 64.17, 67.69, 71.97, 128.38, 128.67, 128.76, 135.13, 173.02. EI-MS: *m/z* 196 [M]$^+$; HRMS (EI): *m/z* for $C_{10}H_{12}O_4$, calcd 196.0730, found 196.0730.

Detection of reaction intermediates by ESI-MS

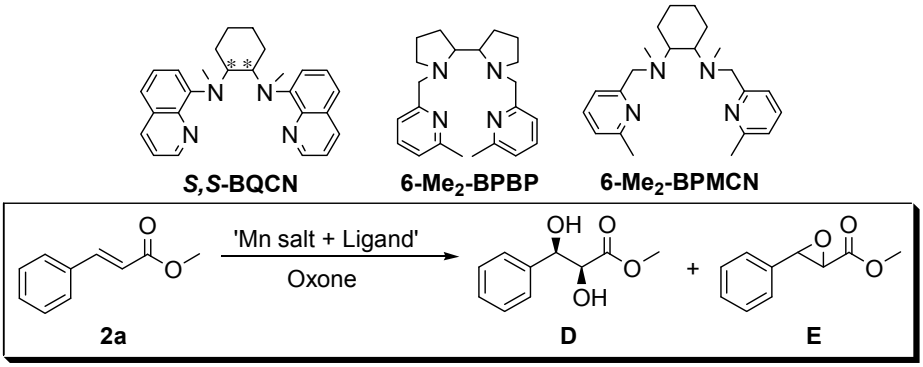
A solution of complex **1** in a mixture of acetonitrile and distilled water (10:1 v/v) was treated with Oxone (2 equiv.) and $NaHCO_3$ (6 equiv.). The reaction mixture at different reaction time was introduced into the ESI source by a syringe pump operating at a flow of 5 μL min^{-1}. For accurate mass measurement, sodium formate was used as an internal reference. The mass resolution was fixed at about 8000 (full width at half-height) with mass accuracy limited within 10 ppm. The TOF-MS mass spectra were acquired in the mass range 100-1200 Th with an accumulation time of 1 sec and interscan time of 0.1 sec. In the MS/MS experiments, the parent ions were separately mass-selected by the first quadrupole mass analyzer (operating at about unit mass resolution). The selected ion was transmitted into a T-wave collision cell (filled with argon gas at 7.01 x 10^{-3} Torr, measured in the quadrupole mass-analyzer

housing) where it underwent collision-induced dissociation at a collision energy of 10-25 eV (laboratory frame). The parent ion and fragment ions were analyzed by the TOF mass analyzer and detected by a multichannel plate (MCP) detector at 1.8 kV. The MS/MS spectrum was obtained by averaging 150-200 scans.

Table S1. Crystal data and structural refinement for complex **1**.

	1•MeCN
Formula	$C_{26}H_{28}Cl_2MnN_4$•C_2H_3N
*M*r	563.42
Crystal system	Monoclinic-P
Space group	$P2_1$ (#4)
a, Å	11.3578(13)
b, Å	8.7479(10)
c, Å	14.5673(17)
α,deg	90
β, deg	103.890(2)
γ, deg	90
F(000)	586
V, Å^3	1405.0(3)
Z	2
ρ_{calc}, g cm^{-3}	1.332
μ(MoK$_\alpha$), mm^{-1}	0.685
$2\theta_{max}$, deg	57.48
Reflections collected	9382
Independent reflections	5814
Parameters	329
Final *R* indices	*R*1= 0.0287
($F^2 > 2\sigma(F^2)$)	*R*w = 0.0671
Goodness-of-fit	1.015
Flack parameter	0.031(13)
Largest diff. peak/hole, e Å^{-3}	0.20/–0.19

Table S2 Oxidation of methyl cinnamte (**2a**) with Oxone at room temperature using various manganese complexes *in situ* generated from reaction of ligand with Mn(II) or Mn(III) salt[a]



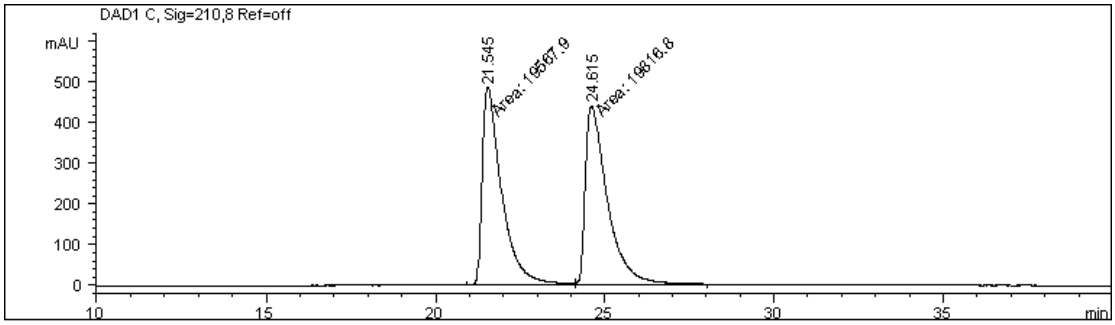
Entry	Ligand used	Mn salt used	Conv. (%)[b]	Yield based on conversion (%)		D/E
				cis-Diol[b]	Epoxide[b]	
1	---	$Mn(OAc)_3•6H_2O$	5	0	56	---
2	*S,S*-BQCN	$Mn(OAc)_3•6H_2O$	93	66 [c]	19	3.5
3		$Mn(OTf)_2$	97	28	52	0.54
4	6-Me_2-BPBP	$Mn(OAc)_3•6H_2O$	7	0	73	---
5		$Mn(OTf)_2$	27	23	43	0.53
6	6-Me_2-BPMCN	$Mn(OAc)_3•6H_2O$	7	0	91	---
7		$Mn(OTf)_2$	24	11	42	0.26

[a] Reaction conditions: Mn salt (5 mol%, 0.025 mmol) and ligand (5 mol% 0.025 mmol) was stirred in MeCN (6 mL) for 10 min. After addition of methyl cinnamate (**2a**) (0.5 mmol), Oxone (2 equiv.) and $NaHCO_3$ (6 equiv.) in H_2O (6 mL) were added in 2 portions within 5 min, R.T., 2 h. [b] Determined by ^1H NMR. [c] Isolated yield.

Chiral HPLC chromatographic analysis of *cis*-diol of **2a**

- Column: Analytical Chiralpak OD-3 (25 cm x 0.46 cm x 3 μm).
- Condition: isopronanol/*n*-hexane (7:93) at 1.0 mL/min, enantiomeric excess determined at 210 nm.

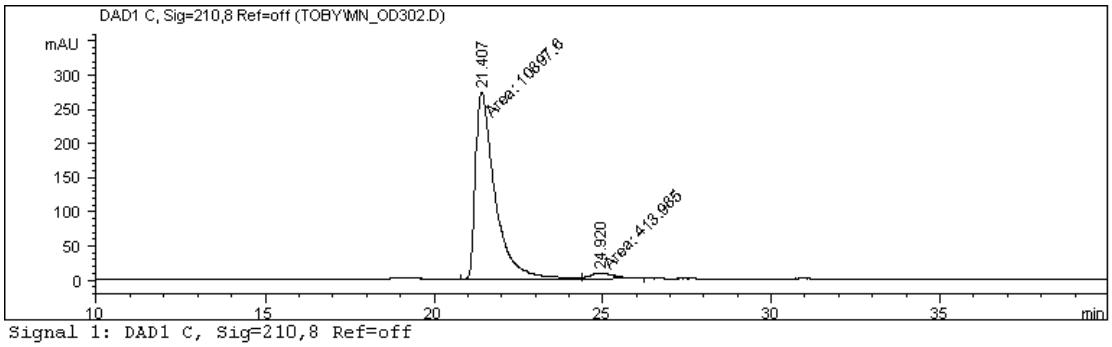
(I): Racemic standard of *cis*-diol of **2a**.



Signal 1: DAD1 C, Sig=210,8 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.545	MF	0.6692	1.95679e4	487.37738	49.6840
2	24.615	FM	0.7527	1.98168e4	438.79230	50.3160

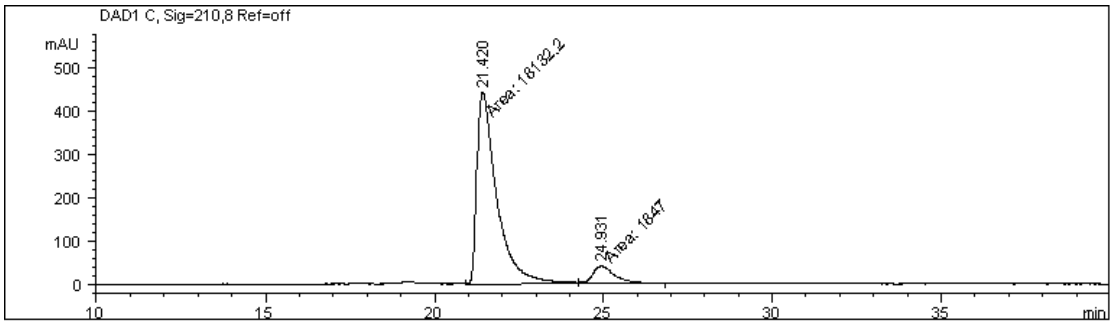
(II): *cis*-Diol from asymmetric *cis*-dihydroxylation of **2a** with Oxone catalysed by **1**.



Signal 1: DAD1 C, Sig=210,8 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.407	MF	0.6646	1.08976e4	273.27890	96.3402
2	24.920	FM	0.7951	413.98526	8.67786	3.6598

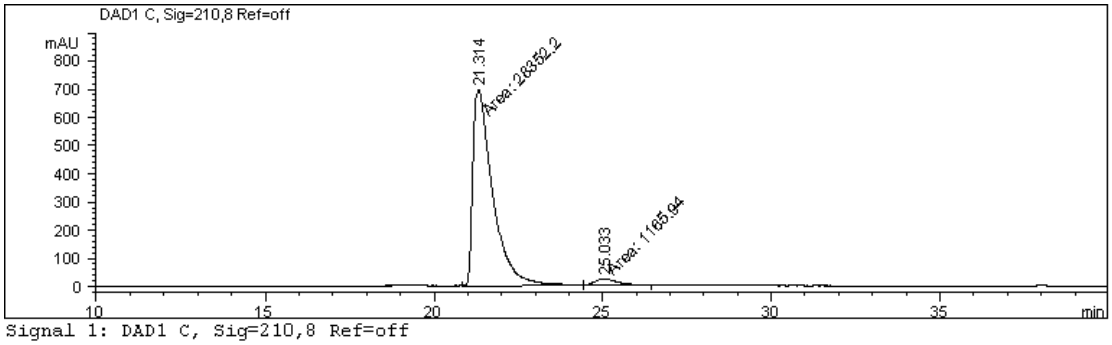
(III) *cis*-Diol from asymmetric *cis*-dihydroxylation of **2a** with Oxone catalysed by the manganese complex *in situ* generated from reaction of $Mn(OAc)_3 \cdot 6H_2O$ with *S,S*-BQCN.



Signal 1: DAD1 C, Sig=210,8 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.420	MF	0.6816	1.81322e4	443.35577	90.7554
2	24.931	FM	0.7750	1847.00012	39.71991	9.2446

(IV) *cis*-Diol from gram-scale asymmetric *cis*-dihydroxylation of **2a** with Oxone catalysed by **1**.



Signal 1: DAD1 C, Sig=210,8 Ref=off

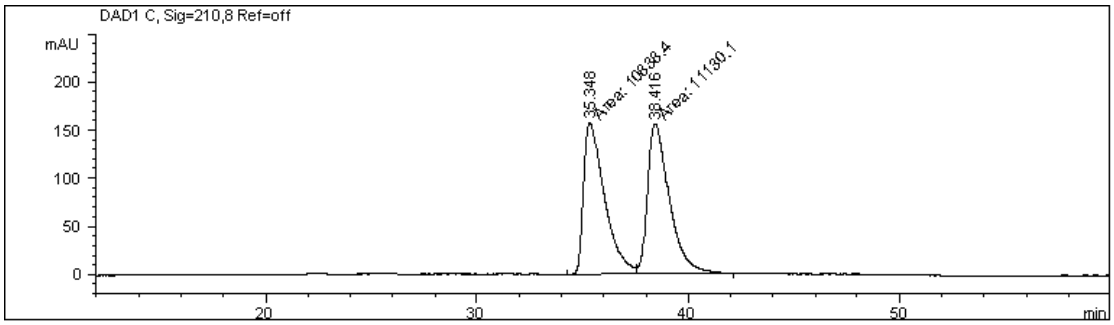
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.314	MF	0.6795	2.83522e4	695.46814	96.0501
2	25.033	FM	0.7777	1165.94238	24.98541	3.9499

Fig. S1 Chiral HPLC chromatographic analysis of *cis*-diol of **2a**. **(I)**: Racemic *cis*-diol standard. **(II)**: Asymmetric *cis*-dihydroxylation of **2a** catalysed by **1**. **(III)** Asymmetric *cis*-dihydroxylation of **2a** catalysed by *in situ* generated manganese complex. **(IV)** Gram-scale asymmetric *cis*-dihydroxylation of **2a** catalysed by **1**.

Chiral HPLC chromatographic analysis of *cis*-diol of **2b**

- Column: Analytical Chiralpak OD-3 (25 cm x 0.46 cm x 3 μm).
- Condition: isopronanol/*n*-hexane (7:93) at 1.0 mL/min, enantiomeric excess determined at 210 nm.

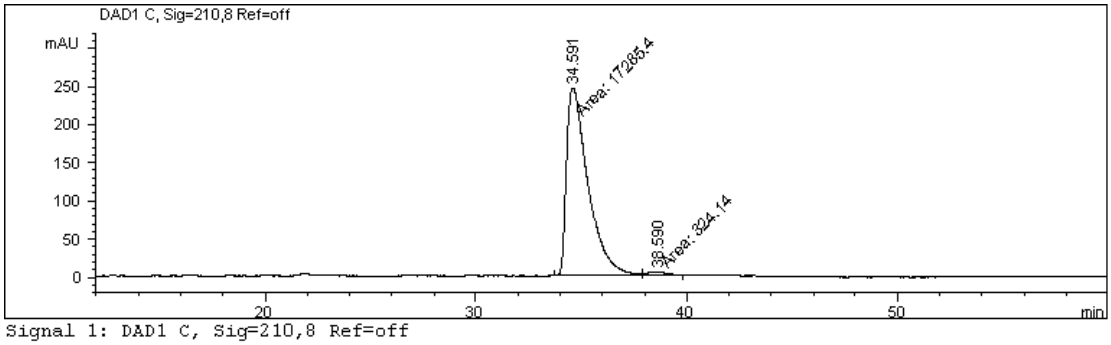
(I): Racemic standard of *cis*-diol of **2b**



Signal 1: DAD1 C, Sig=210,8 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.348	MF	1.1510	1.08384e4	156.94080	49.3360
2	38.416	FM	1.1959	1.11301e4	155.12111	50.6640

(II): *cis*-Diol from asymmetric *cis*-dihydroxylation of **2b** with Oxone catalysed by **1**.



Signal 1: DAD1 C, Sig=210,8 Ref=off

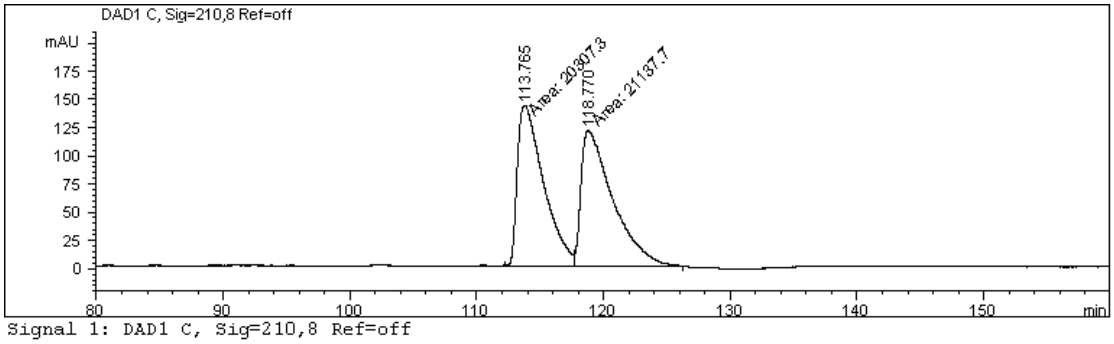
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.591	MF	1.1738	1.72854e4	245.42444	98.1593
2	38.590	FM	1.0922	324.13953	4.94606	1.8407

Fig. S2 Chiral HPLC chromatographic analysis of *cis*-diol of **2b**. **(I)**: Racemic *cis*-diol standard. **(II)**: Asymmetric *cis*-dihydroxylation of **2b** catalysed by **1**.

Chiral HPLC chromatographic analysis of *cis*-diol of **2c**

- Column: Analytical Chiralpak OD-3 (25 cm x 0.46 cm x 3 μm).
- Condition: isopronanol/*n*-hexane (1:99) at 0.5 mL/min, enantiomeric excess determined at 210 nm.

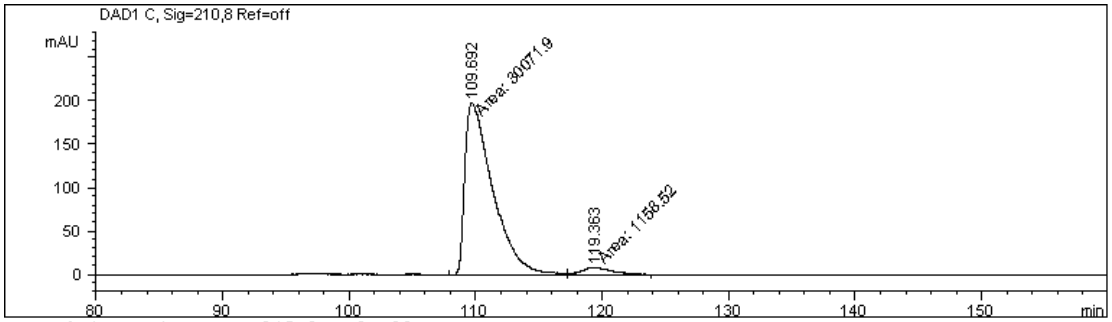
(I): Racemic standard of *cis*-diol of **2c**



Signal 1: DAD1 C, Sig=210,8 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	113.765	MF	2.3863	2.03073e4	141.83356	48.9983
2	118.770	FM	2.9193	2.11377e4	120.67837	51.0017

(II): *cis*-Diol from asymmetric *cis*-dihydroxylation of **2c** with Oxone catalysed by **1**.



Signal 1: DAD1 C, Sig=210,8 Ref=off

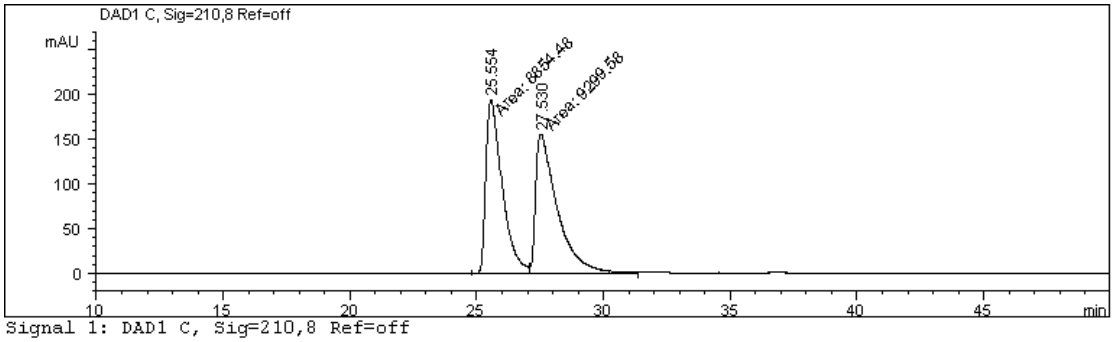
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	109.692	MF	2.5371	3.00719e4	197.54805	96.2904
2	119.363	FM	2.5385	1158.51526	7.60633	3.7096

Fig. S3 Chiral HPLC chromatographic analysis of *cis*-diol of **2c**. **(I)**: Racemic *cis*-diol standard. **(II)**: Asymmetric *cis*-dihydroxylation of **2c** catalysed by **1**.

Chiral HPLC chromatographic analysis of *cis*-diol of **3a**

- Column: Analytical Chiralpak OD-3 (25 cm x 0.46 cm x 3 μm).
- Condition: isopronanol/*n*-hexane (10:90) at 1.0 mL/min, enantiomeric excess determined at 210 nm.

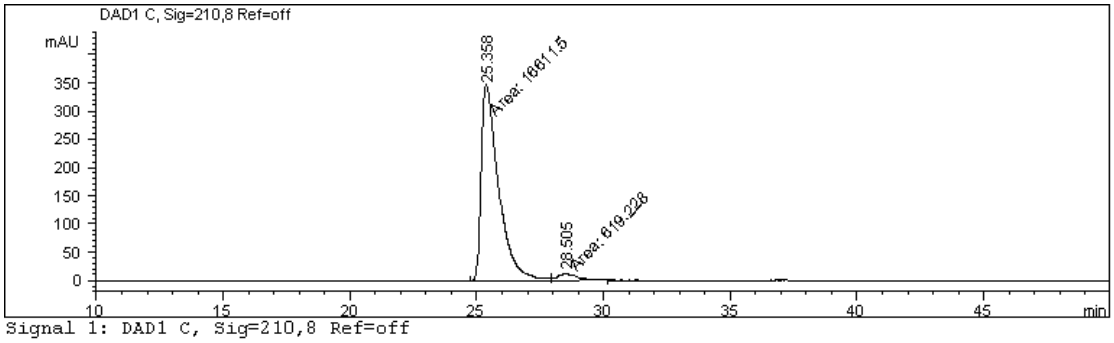
(I): Racemic standard of *cis*-diol of **3a**



Signal 1: DAD1 C, Sig=210,8 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.554	MF	0.7604	8854.47949	194.06836	48.7741
2	27.530	FM	0.9898	9299.57715	156.59552	51.2259

(II): *cis*-Diol from asymmetric *cis*-dihydroxylation of **3a** with Oxone catalysed by **1**.



Signal 1: DAD1 C, Sig=210,8 Ref=off

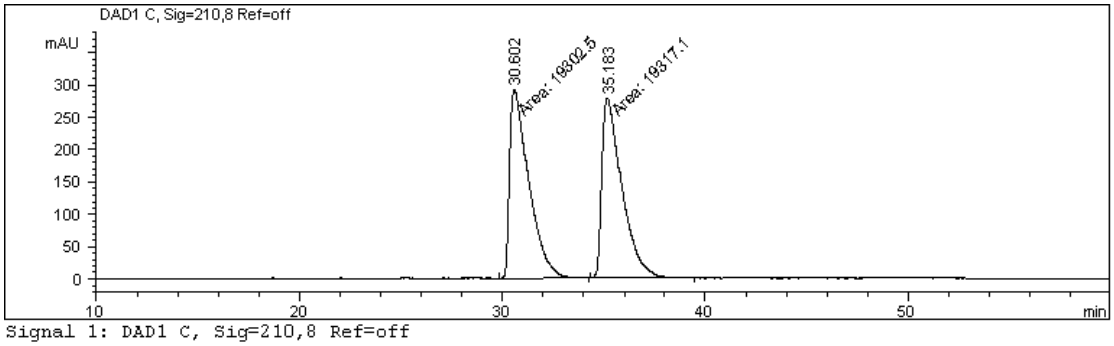
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.358	MF	0.7984	1.66115e4	346.75702	96.4062
2	28.505	FM	1.0157	619.22809	10.16066	3.5938

Fig. S4 Chiral HPLC chromatographic analysis of *cis*-diol of **3a**. **(I)**: Racemic *cis*-diol standard. **(II)**: Asymmetric *cis*-dihydroxylation of **3a** catalysed by **1**.

Chiral HPLC chromatographic analysis of *cis*-diol of **3b**

- Column: Analytical Chiralpak OD-3 (25 cm x 0.46 cm x 3 μm).
- Condition: isopronanol/*n*-hexane (10:90) at 1.0 mL/min, enantiomeric excess determined at 210 nm.

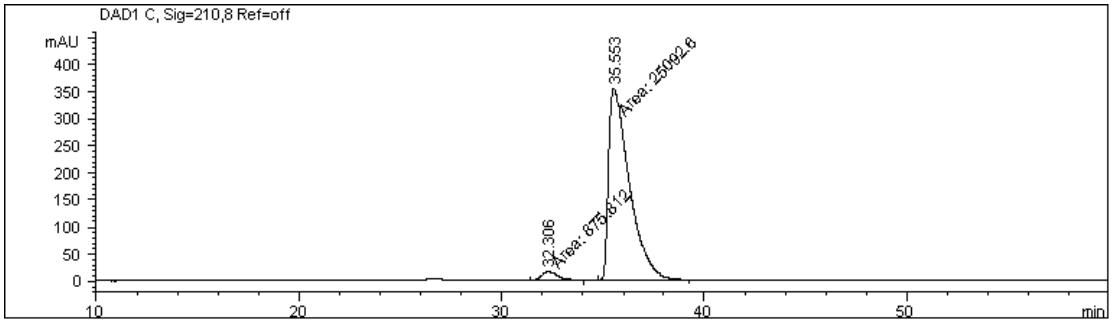
(I): Racemic standard of *cis*-diol of **3b**



Signal 1: DAD1 C, Sig=210,8 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.602	MM	1.1061	1.93025e4	290.83929	49.9811
2	35.183	MM	1.1614	1.93171e4	277.20825	50.0189

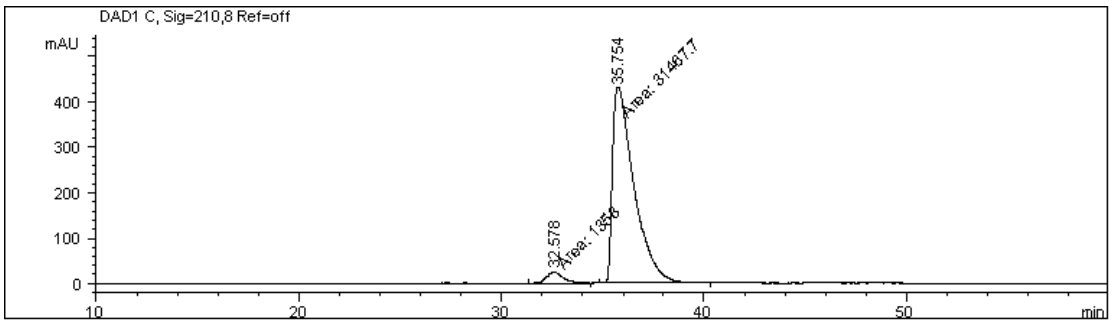
(II): *cis*-Diol from asymmetric *cis*-dihydroxylation of **3b** with Oxone catalysed by **1**.



Signal 1: DAD1 C, Sig=210,8 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.306	MM	0.9784	875.81189	14.91904	3.3726
2	35.553	MM	1.1849	2.50926e4	352.95462	96.6274

(II): *cis*-Diol from gram-scale asymmetric *cis*-dihydroxylation of **3b** with Oxone catalysed by **1**.



Signal 1: DAD1 C, Sig=210,8 Ref=off

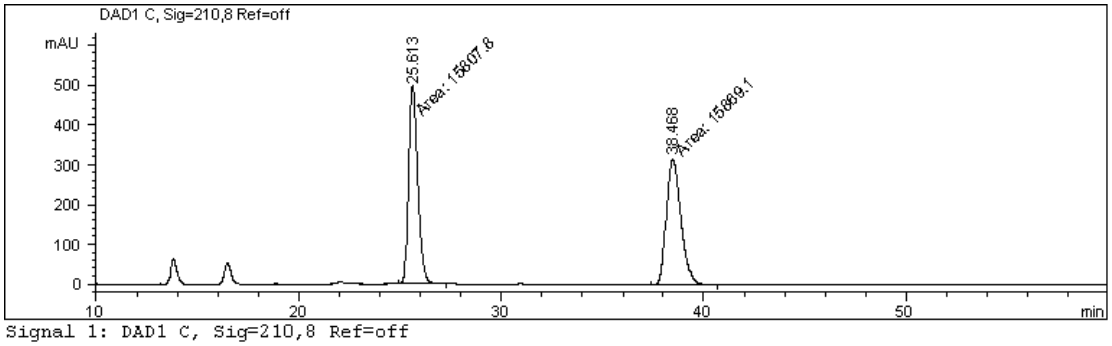
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.578	MM	0.9665	1358.00403	23.41710	4.1370
2	35.754	MM	1.2184	3.14677e4	430.44431	95.8630

Fig. S5 Chiral HPLC chromatographic analysis of *cis*-diol of **3b**. **(I)**: Racemic *cis*-diol standard. **(II)**: Asymmetric *cis*-dihydroxylation of **3b** catalysed by **1**. **(III)** Gram-scale asymmetric *cis*-dihydroxylation of **3b** catalysed by **1**.

Chiral HPLC chromatographic analysis of *cis*-diol of **4a**

- Column: Analytical Chiralpak AD-3 (25 cm x 0.46 cm x 3 µm).
- Condition: isopronanol/*n*-hexane (10:90) at 1.0 mL/min, enantiomeric excess determined at 210 nm.

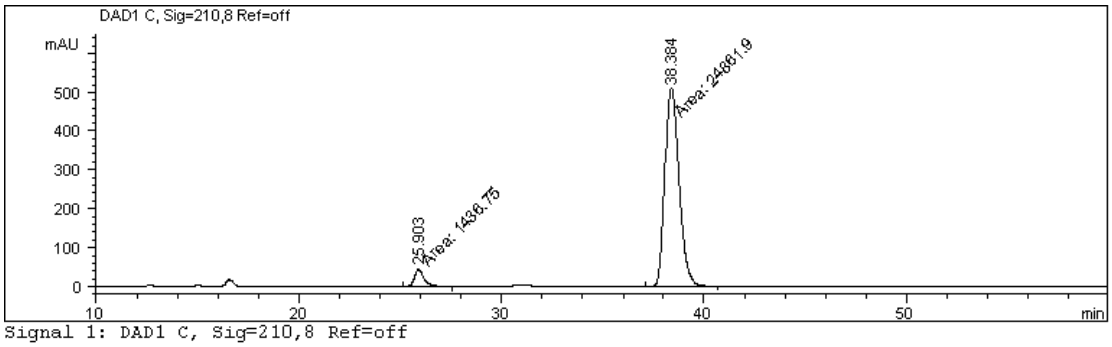
(I): Racemic standard of *cis*-diol of **4a**.



Signal 1: DAD1 C, Sig=210,8 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.613	MM	0.5288	1.58078e4	498.23163	49.9032
2	38.468	MM	0.8389	1.58691e4	315.27380	50.0968

(II): *cis*-Diol from asymmetric *cis*-dihydroxylation of **4a** with Oxone catalysed by **1**.



Signal 1: DAD1 C, Sig=210,8 Ref=off

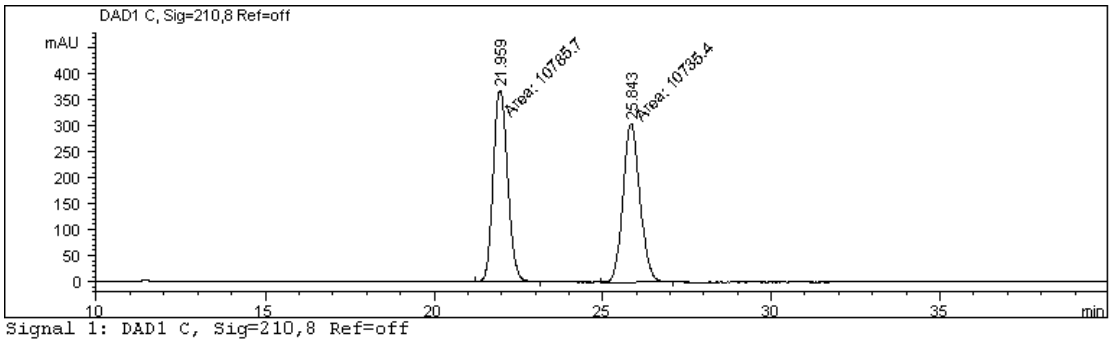
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.903	MM	0.5564	1436.75012	43.03362	5.4632
2	38.384	MM	0.8080	2.48619e4	512.85632	94.5368

Fig. S6 Chiral HPLC chromatographic analysis of *cis*-diol of **4a**. **(I)**: Racemic *cis*-diol standard. **(II)**: Asymmetric *cis*-dihydroxylation of **4a** catalysed by **1**.

Chiral HPLC chromatographic analysis of *cis*-diol of **4b**

- Column: Analytical Chiralpak AD-3 (25 cm x 0.46 cm x 3 μm).
- Condition: isopronanol/*n*-hexane (10:90) at 1.0 mL/min, enantiomeric excess determined at 210 nm.

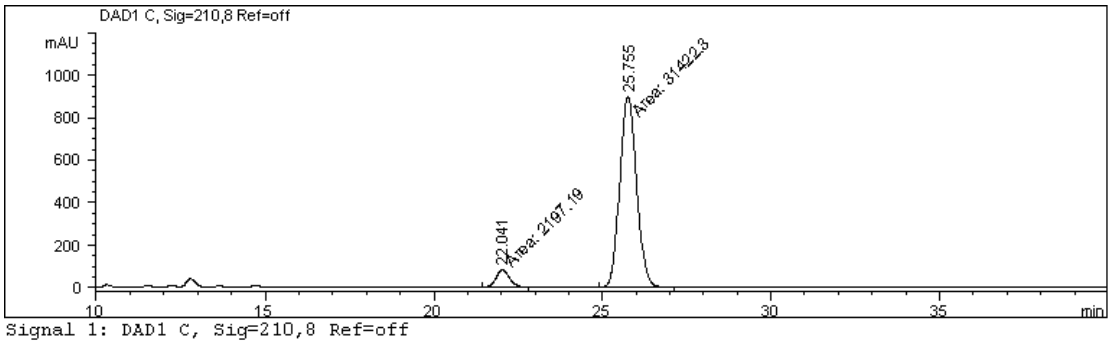
(I): Racemic standard of *cis*-diol of **4b**.



Signal 1: DAD1 C, Sig=210,8 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.959	MM	0.4884	1.07857e4	368.08688	50.1169
2	25.843	MM	0.5871	1.07354e4	304.73276	49.8831

(II): *cis*-Diol from asymmetric *cis*-dihydroxylation of **4b** with Oxone catalysed by **1**.



Signal 1: DAD1 C, Sig=210,8 Ref=off

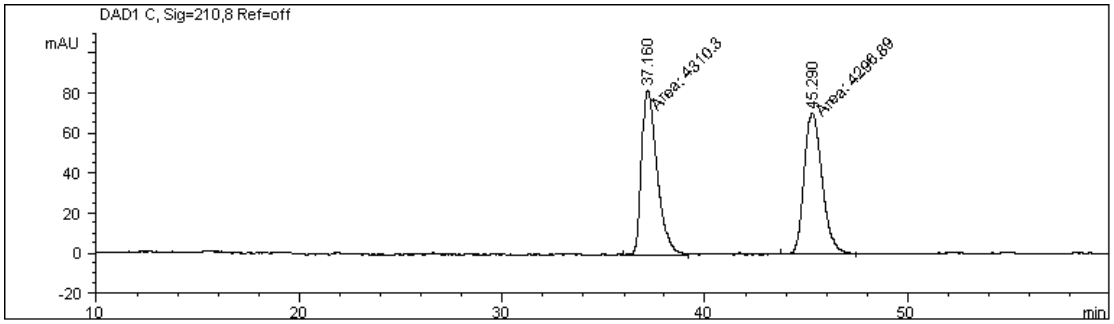
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.041	MM	0.4636	2197.19214	78.99866	6.5355
2	25.755	MM	0.5842	3.14223e4	896.40131	93.4645

Fig. S7 Chiral HPLC chromatographic analysis of *cis*-diol of **4b**. **(I)**: Racemic *cis*-diol standard. **(II)**: Asymmetric *cis*-dihydroxylation of **4b** catalysed by **1**.

Chiral HPLC chromatographic analysis of *cis*-diol of **5a**

- Column: Analytical Chiralpak AD-3 (25 cm x 0.46 cm x 3 µm).
- Condition: isopronanol/*n*-hexane (10:90) at 1.0 mL/min, enantiomeric excess determined at 210 nm.

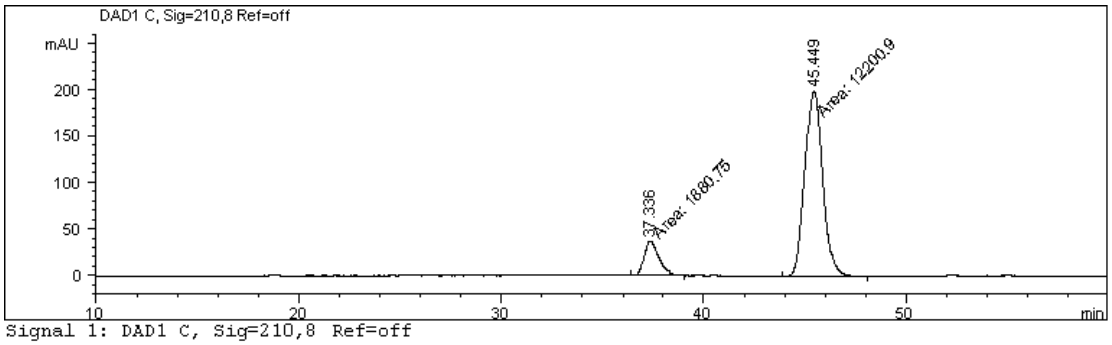
(I): Racemic standard of *cis*-diol of **5a**.



Signal 1: DAD1 C, Sig=210,8 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.160	MM	0.8752	4310.29834	82.08109	50.0779
2	45.290	MM	1.0180	4296.88867	70.34590	49.9221

(II): *cis*-Diol from asymmetric *cis*-dihydroxylation of **5a** with Oxone catalysed by **1**.



Signal 1: DAD1 C, Sig=210,8 Ref=off

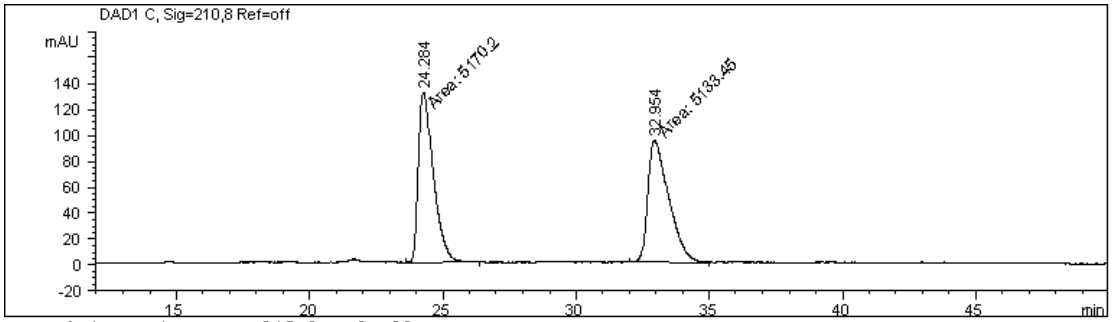
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.336	MM	0.8635	1880.74609	36.30133	13.3560
2	45.449	MM	1.0231	1.22009e4	198.76157	86.6440

Fig. S8 Chiral HPLC chromatographic analysis of *cis*-diol of **5a**. **(I)**: Racemic *cis*-diol standard. **(II)**: Asymmetric *cis*-dihydroxylation of **5a** catalysed by **1**.

Chiral HPLC chromatographic analysis of *cis*-diol of **5b**

- Column: Analytical Chiralpak AD-3 (25 cm x 0.46 cm x 3 μm).
- Condition: isopronanol/*n*-hexane (10:90) at 1.0 mL/min, enantiomeric excess determined at 210 nm.

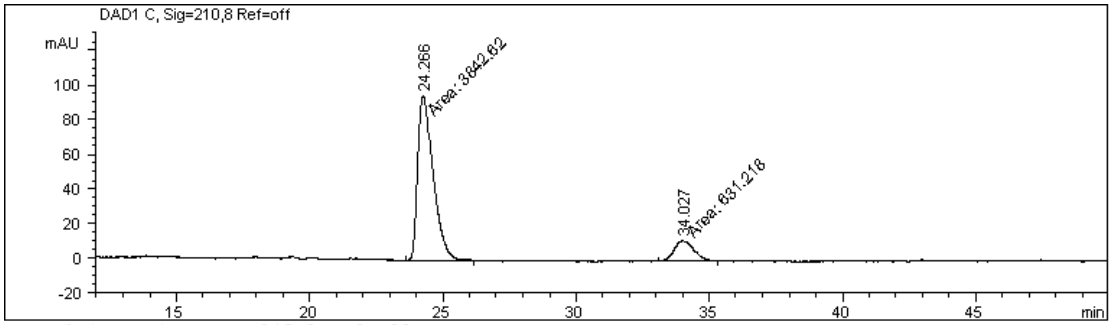
(I): Racemic standard of *cis*-diol of **5b**.



Signal 1: DAD1 C, Sig=210,8 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.284	MM	0.6563	5170.20313	131.28798	50.1783
2	32.954	MM	0.9131	5133.45166	93.70220	49.8217

(II): *cis*-Diol from asymmetric *cis*-dihydroxylation of **5b** with Oxone catalysed by **1**.



Signal 1: DAD1 C, Sig=210,8 Ref=off

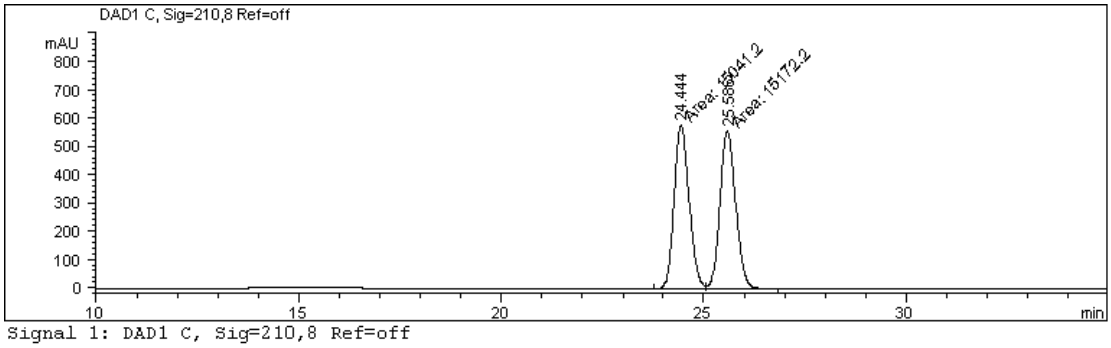
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.266	MM	0.6724	3842.61694	95.24311	85.8909
2	34.027	MM	0.8881	631.21796	11.84594	14.1091

Fig. S9 Chiral HPLC chromatographic analysis of *cis*-diol of **5b**. **(I)**: Racemic *cis*-diol standard. **(II)**: Asymmetric *cis*-dihydroxylation of **5b** catalysed by **1**.

Chiral HPLC chromatographic analysis of *cis*-diol of **6a**

- Column: Analytical Chiralpak AD-3 (25 cm x 0.46 cm x 3 μm).
- Condition: isopronanol/*n*-hexane (7:93) at 1.0 mL/min, enantiomeric excess determined at 210 nm.

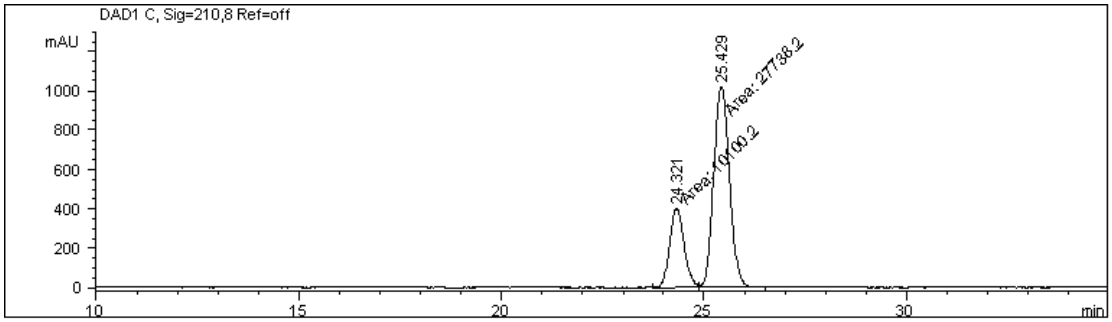
(I): Racemic standard of *cis*-diol of **6a**.



Signal 1: DAD1 C, Sig=210,8 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.444	MF	0.4336	1.50412e4	578.13281	49.7832
2	25.586	FM	0.4536	1.51722e4	557.42047	50.2168

(II): *cis*-Diol from asymmetric *cis*-dihydroxylation of **6a** with Oxone catalysed by **1**.



Signal 1: DAD1 C, Sig=210,8 Ref=off

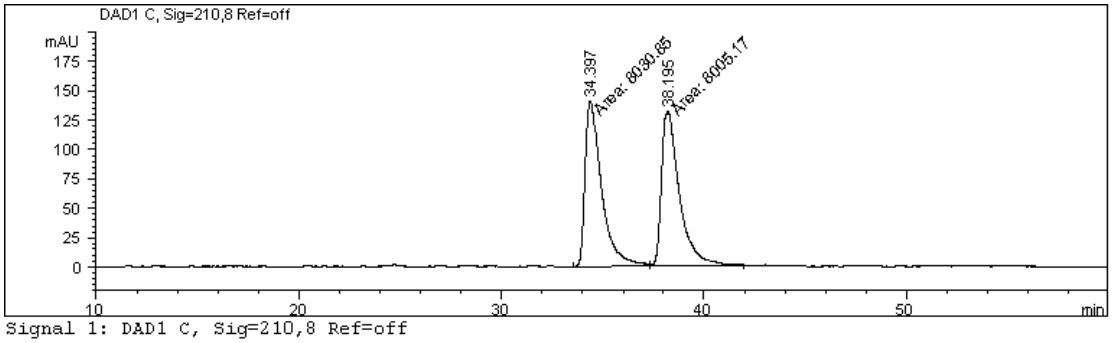
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.321	MF	0.4168	1.01002e4	403.89407	26.6930
2	25.429	FM	0.4521	2.77382e4	1022.67493	73.3070

Fig. S10 Chiral HPLC chromatographic analysis of *cis*-diol of **6a**. **(I)**: Racemic *cis*-diol standard. **(II)**: Asymmetric *cis*-dihydroxylation of **6a** catalysed by **1**.

Chiral HPLC chromatographic analysis of *cis*-diol of **6b**

- Column: Analytical Chiralpak OD-3 (25 cm x 0.46 cm x 3 μm).
- Condition: isopronanol/*n*-hexane (7:93) at 1.0 mL/min, enantiomeric excess determined at 210 nm.

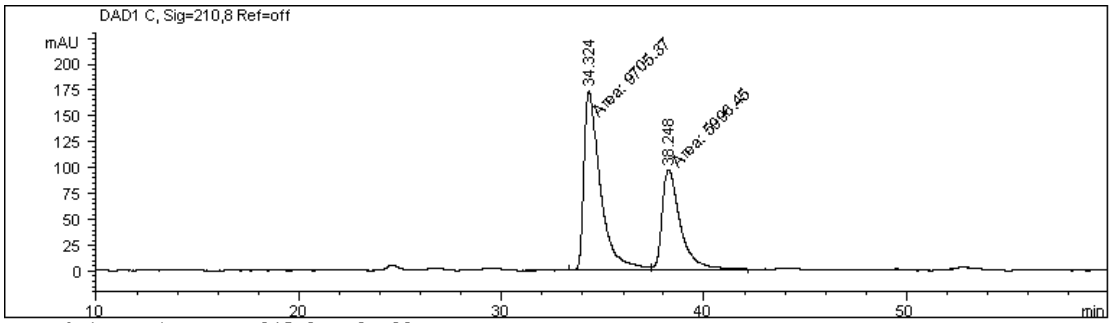
(I): Racemic standard of *cis*-diol of **6b**.



Signal 1: DAD1 C, Sig=210,8 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.397	MF	0.9495	8030.85400	140.96153	50.0801
2	38.195	FM	1.0083	8005.17383	132.32330	49.9199

(II): *cis*-Diol from asymmetric *cis*-dihydroxylation of **6b** with Oxone catalysed by **1**.



Signal 1: DAD1 C, Sig=210,8 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.324	MF	0.9382	9705.37305	172.41531	61.8105
2	38.248	FM	1.0392	5996.45410	96.17506	38.1895

Fig. S11 Chiral HPLC chromatographic analysis of *cis*-diol of **6b**. **(I)**: Racemic *cis*-diol standard. **(II)**: Asymmetric *cis*-dihydroxylation of **6b** catalysed by **1**.

A: $[BQCN - Me]^+$
B: $[BQCN + H^+]^+$
C: $[Mn(BQCN)]^{+\bullet}$
D: $\{[Mn_2(BQCN)_2(O)_3] - 2H^+\}^{2+}$
E: $[Mn(BQCN)(O)_2]^+$

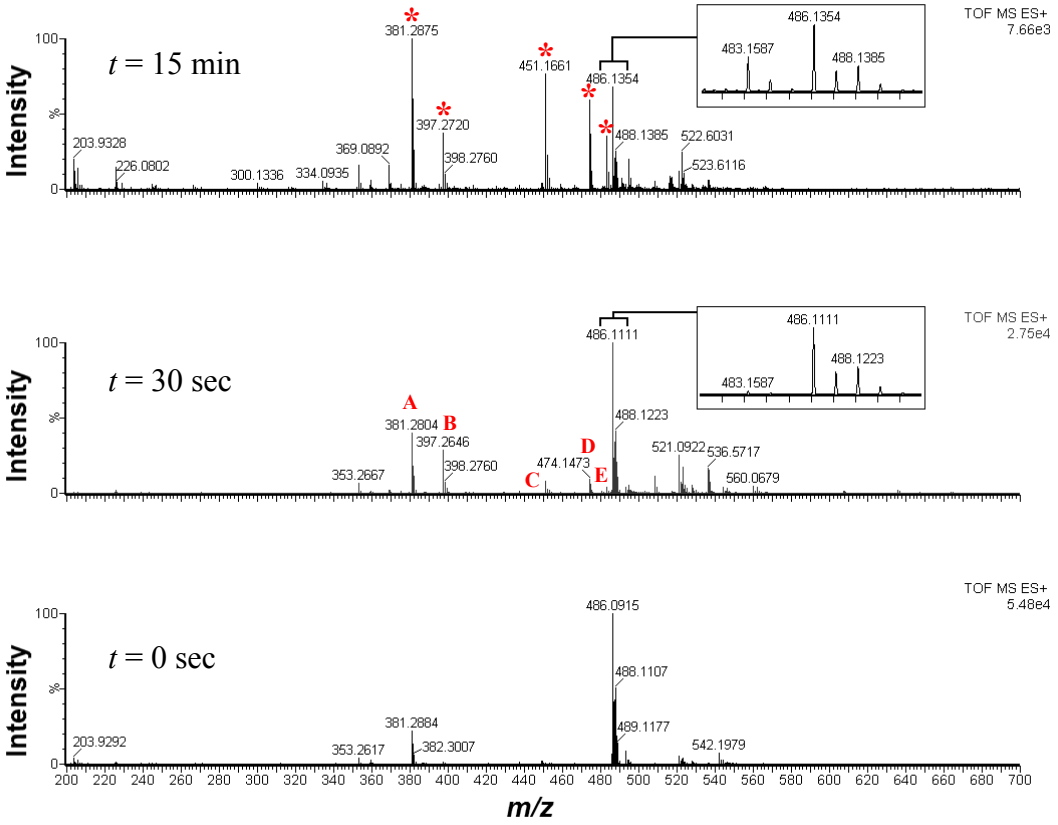


Fig. S12 Electrospray ionization mass spectrometric measurements of the reaction mixture of **1** with Oxone (2 equiv.) in MeCN/H_2O (10:1 v/v) at different reaction time (*t*): 0 sec (i.e. before addition of Oxone), 30 sec and 15 min.

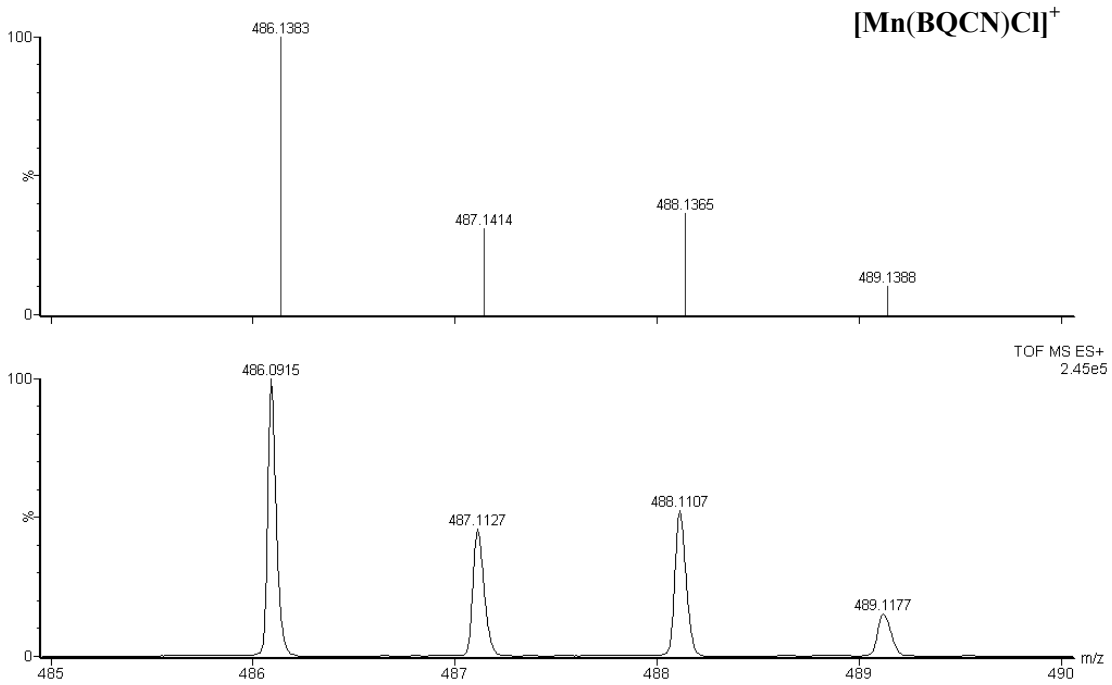


Fig. S13 Electrospray ionization mass spectrometric measurement of $[Mn(BQCN)Cl]^+$ for **1** in MeCN: (**Upper**) Simulated isotope pattern of $[MnC_{26}H_{28}N_4Cl]^+$ and (**Lower**) Experimental mass measurement.

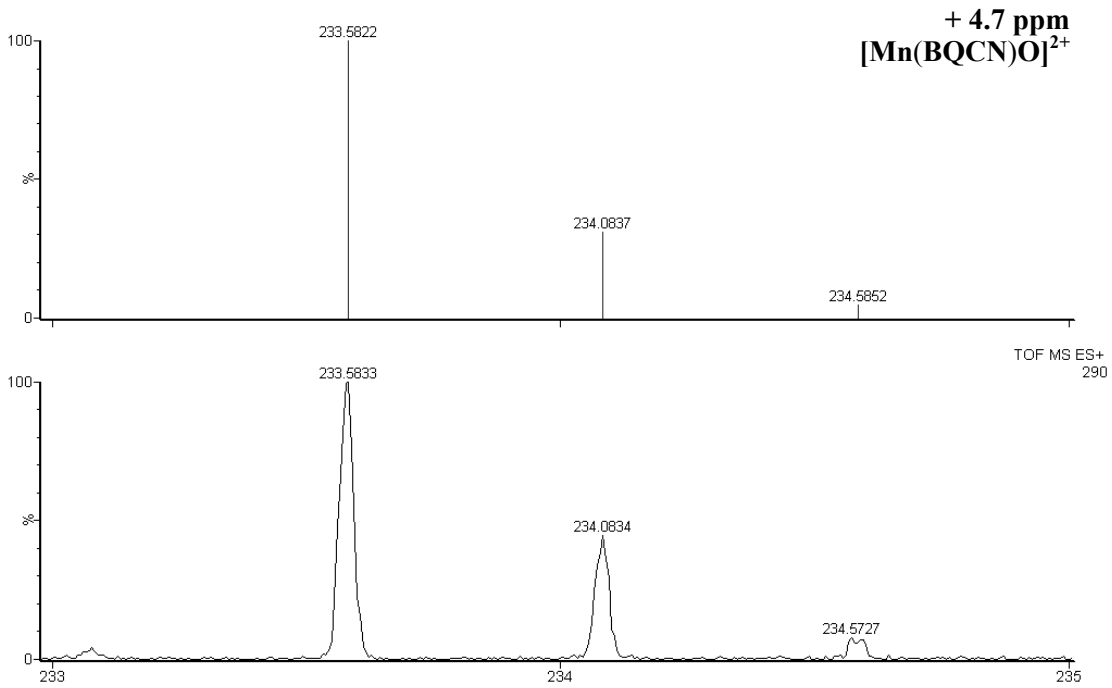


Fig. S14 Electrospray ionization mass spectrometric measurement of $[Mn(BQCN)O]^{2+}$ in the reaction of **1** with Oxone (2 equiv.): (**Upper**) Simulated isotope pattern of $[MnC_{26}H_{28}N_4O]^{2+}$ and (**Lower**) Experimental mass measurement.

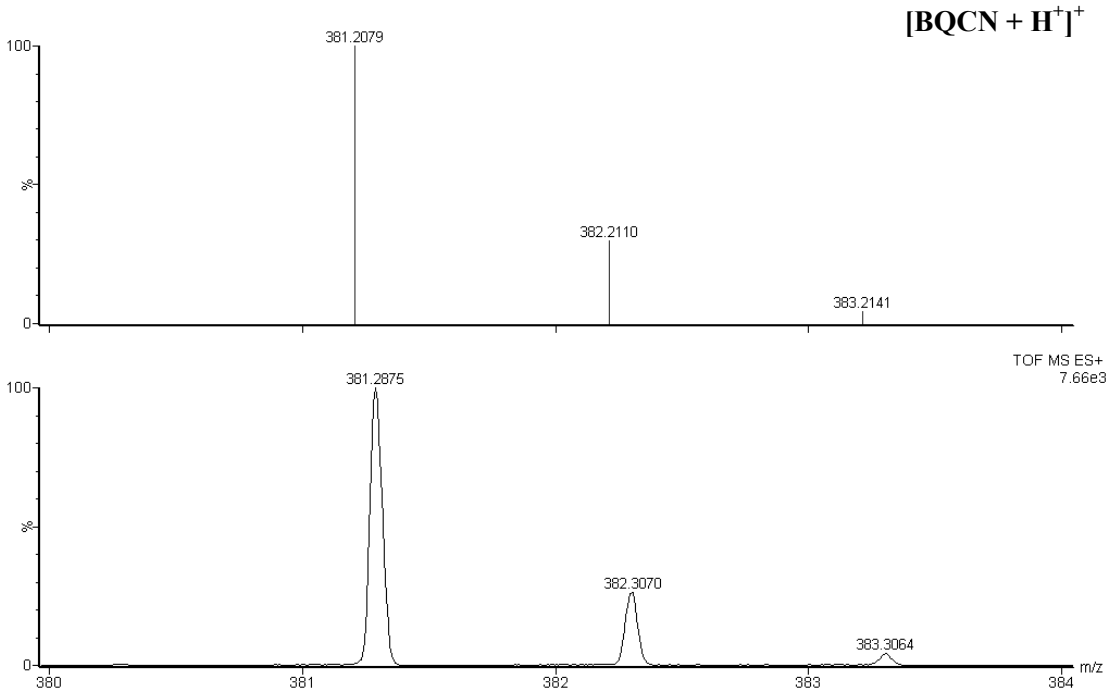


Fig. S15 Electrospray ionization mass spectrometric measurement of $[BQCN + H^+]^+$ in the reaction of **1** with Oxone (2 equiv.): (**Upper**) Simulated isotope pattern of $[C_{25}H_{25}N_4]^+$ and (**Lower**) Experimental mass measurement.

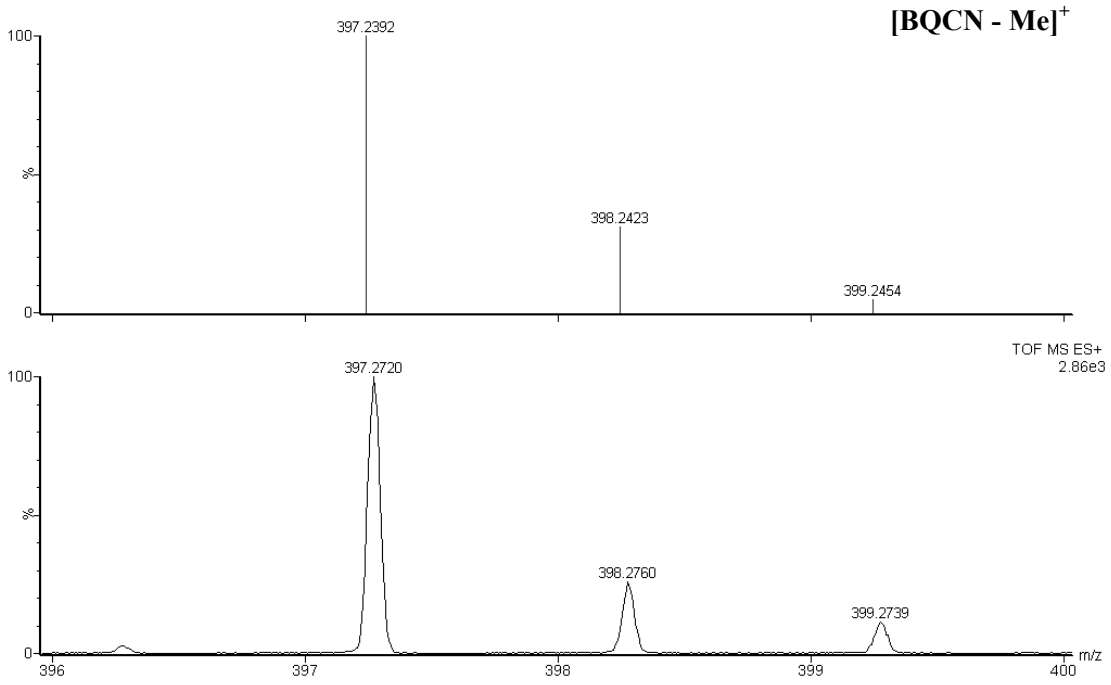


Fig. S16 Electrospray ionization mass spectrometric measurement of $[BQCN\text{-}Me]^+$ in the reaction of **1** with Oxone (2 equiv.): (**Upper**) Simulated isotopic pattern of $[C_{26}H_{29}N_4]^+$ and (**Lower**) Experimental mass measurement.

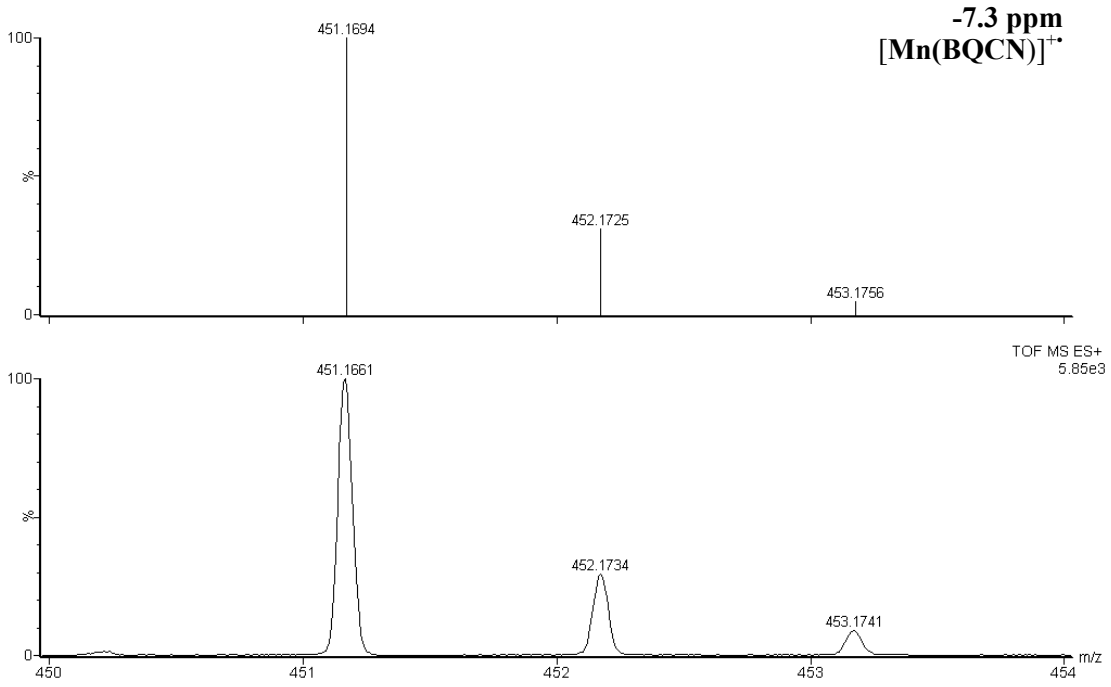


Fig. S17 Electrospray ionization mass spectrometric measurement of $[Mn(BQCN)]^{+\bullet}$ in the reaction of **1** with Oxone (2 equiv.): (**Upper**) Simulated isotope pattern of $[MnC_{26}H_{28}N_4]^+$ and **Lower**) Experimental mass measurement.

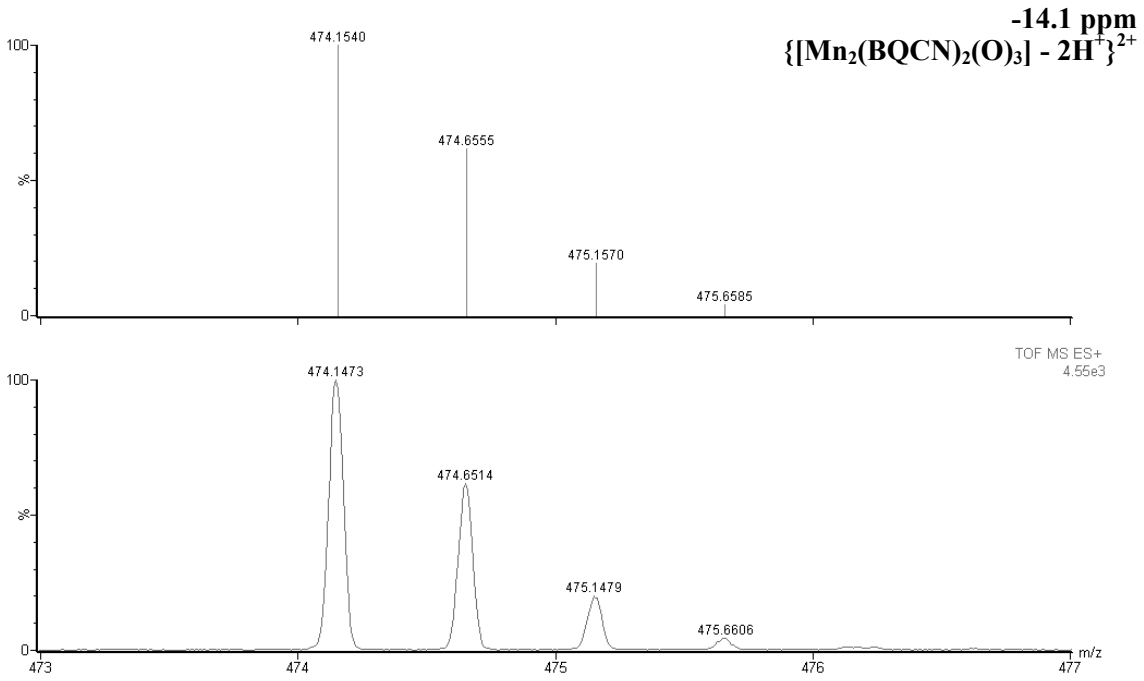


Fig. S18 Electrospray ionization mass spectrometric measurement of $\{[Mn_2(BQCN)_2(O)_3] - 2H^+\}^{2+}$ in the reaction of **1** with Oxone (2 equiv.): (**Upper**) Simulated isotope pattern of $[Mn_2C_{52}H_{54}N_8O_3]^{2+}$ and (**Lower**) Experimental mass measurement.

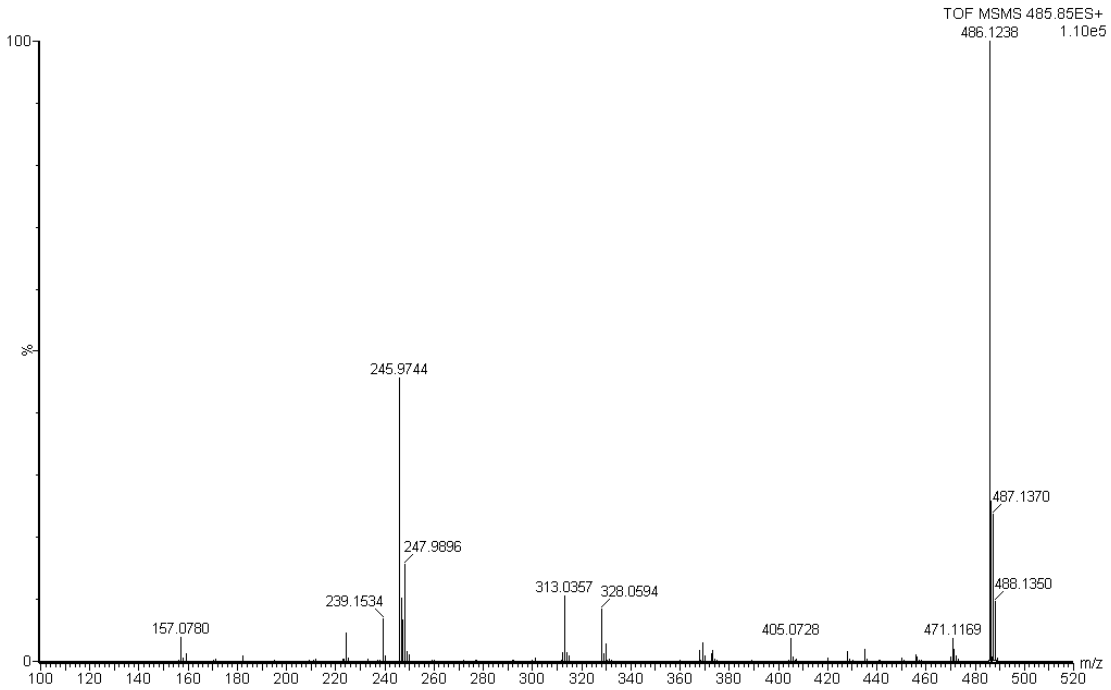


Fig. S19 Collision-induced dissociation of $[Mn(BQCN)Cl]^+$ for **1** in MeCN recorded at the collision energy of 25 eV.

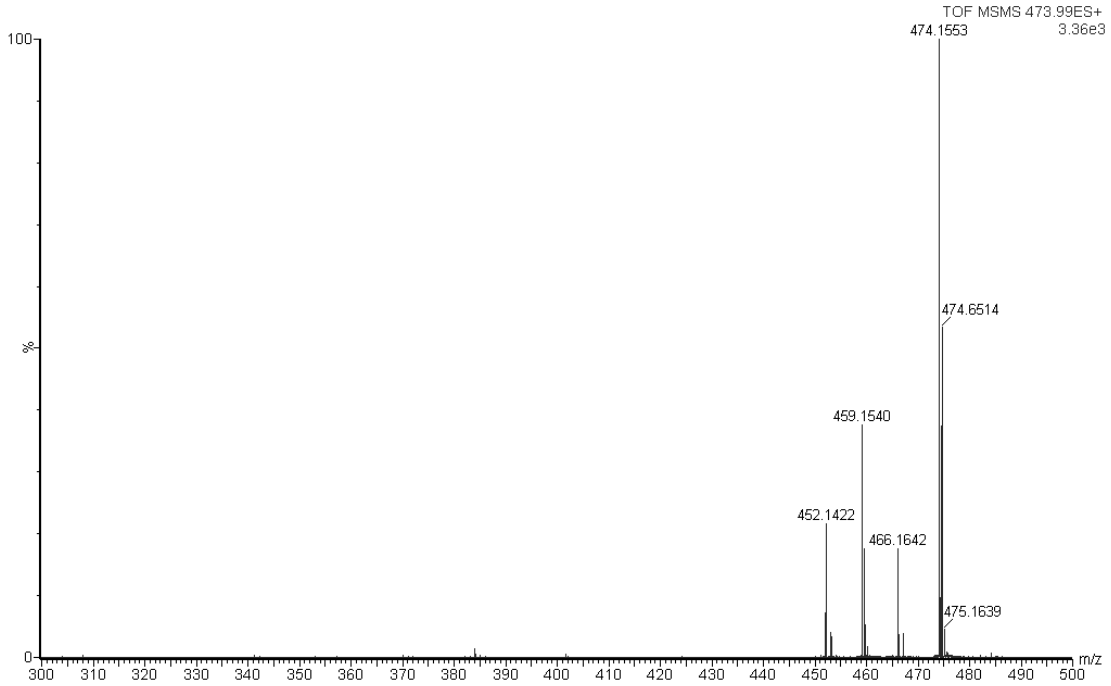


Fig. S20 Collision-induced dissociation of $\{[Mn_2(BQCN)_2(O)_3] - 2H^+\}^{2+}$ for the reaction of **1** with Oxone (2 equiv.) recorded at the collision energy of 12 eV.

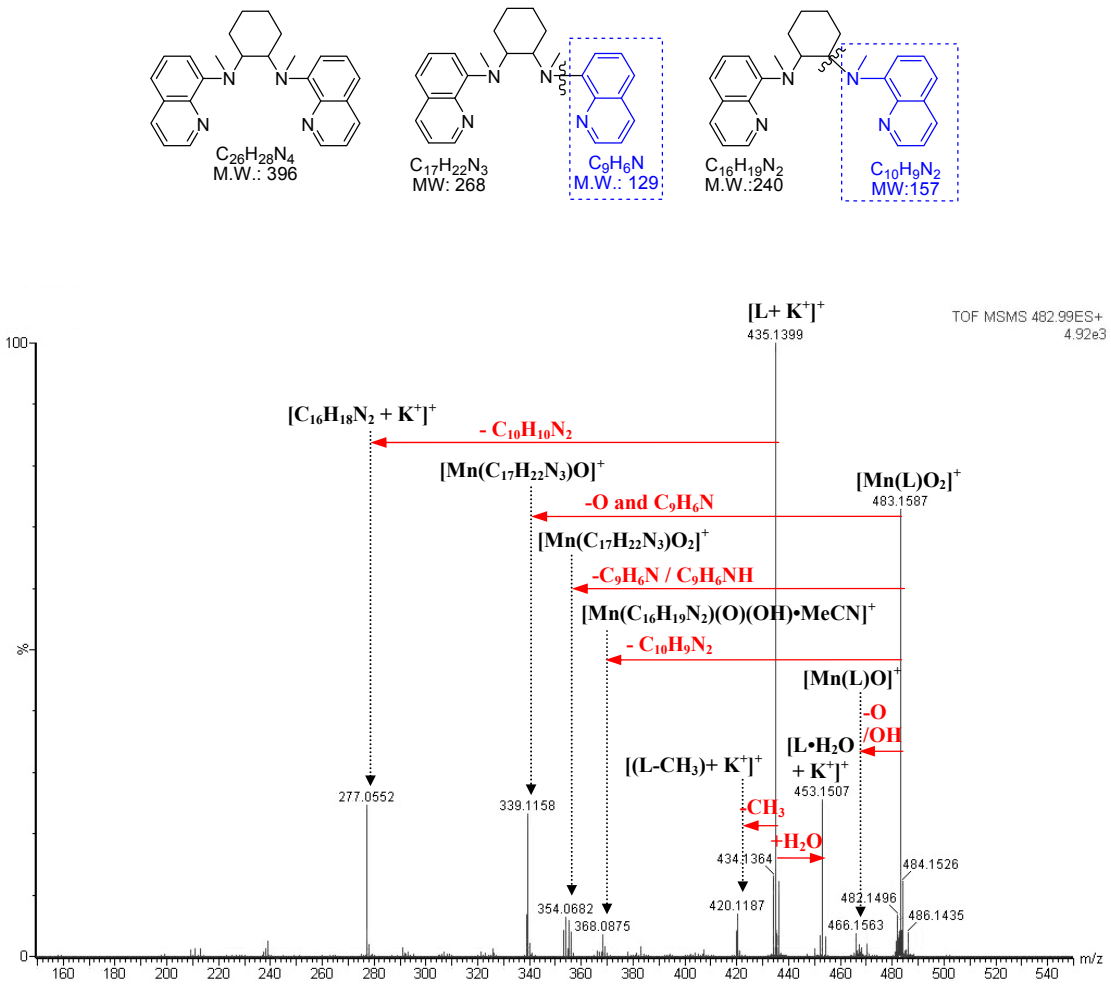


Fig. S21 Collision-induced dissociation of $[Mn(BQCN)(O)_2]^+$ for the reaction of **1** with Oxone (2 equiv.) recorded at the collision energy of 10 eV. L = BQCN = $C_{26}H_{28}N_4$.