Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Efficient epoxidation of propene using molecular catalysts

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Supporting Information

1. Experimental

All preparations were performed using standard Schlenk techniques, if not mentioned otherwise. Methyltrioxorhenium was generously donated by Clariant. Hydrogen peroxide 50 % wt. in H_2O was purchased from Acros Organics. TBHP (5.5 M solution in n-decane) was purchased from Sigma-Aldrich. Chloroform HPLC grade was purchased from VWR. Acetonitrile was purchased from Fischer Chemicals. Deuterated solvents were purchased from Euriso-top®. The CpMo-catalysts **3**, **4** and **5** were synthetized as reported in literature.[S1] Catalyst **2** was purchased from Aldrich and used without further purification.

1.1. General procedure for the NMR experiments

In situ ^{1}H NMR kinetic measurements were performed in a pressure NMR tube, which was charged with the desired amount of solvent, catalyst, oxidation agent and 10 µL toluene (internal standard for integration). Afterwards the tube was charged with 5 bar propylene, closed and immediately measured. The conversions and selectivities were calculated from the integrals referenced to the standard added to the reaction mixture. The recycling experiments were carried out as follows: after the desired amount of time (3 h) the NMR tube was charged with the desired amount of oxidation agent and 5 bar propylene was added. The tube was closed and another spectrum was recorded.

The Fisher-Porter bottle was charged with 25 mg (0.1 mmol) MTO and 2 mL acetonitrile-d_3. The desired amount of co-catalysts (2, 5, 10 equiv.) was added afterwards followed by the addition of 1.420 mL hydrogen peroxide (50 wt.% in water). The vessel was closed and flushed once with argon and then charged with 10 mmol (3 bar) propene. The conversions and selectivities were determined by addition of an external standard (toluene 100 µL) to the reaction mixture. An aliquot of 0.5 mL of the solution was added in an NMR tube and subsequently measured.

1.2. Synthesis of the imidazolium salts

General. All chemicals were purchased from commercial suppliers and used without further purification. Heteroaromatic substituted imidazoles were synthesized as previously described.[S2] 1-Methyl-3-pyridin-2-yl imidazolium iodide was synthesized according to literature procedure[S3] and transferred into the hexafluorophosphate salt by salt metathesis with NH_4PF_6 analogue to **a**. The imidazolium salts **a-e** were synthesized after a modified literature procedure.[S4]

1,3-bis(pyridin-2-yl) imidazolium bromide. Pyridin-2-yl-imidazole (500 mg, 3.44 mmol, 1.00 equiv.) is dissolved in 2-bromopyridine (816 mg, 5.17 mmol, 1.50 equiv.) in a Schlenk tube equipped with a

stirring bar. The stirred mixture is carefully degassed (three times), put under an argon atmosphere and heated to 160 °C for 16 h. After cooling to r.t. the formed precipitate is washed with Et_2O and suspended in a small amount of methanol (2 mL). The suspension is filtrated to leave the product as an off-white solid which is filtrated and dried under vacuum. Yield: 937 mg (90 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.79 (t, ^{4}J = 1.5 Hz, 1H, NCHN), 8.74 (d, ^{4}J = 1.5 Hz, 2H, NCHCHN), 8.72 (d, ^{3}J = 4.9 Hz, 2H, H_{Py}), 8.27 (dd, ^{3}J = 9.6 Hz, ^{3}J = 7.6 Hz, 2H, H_{Py}), 8.26 (d, ^{3}J = 9.6 Hz, 2H, H_{Py}), 7.71 (dd, ^{3}J = 7.6 Hz, ^{3}J = 4.9 Hz, 2H, H_{Py}) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 149.3 (C_{Py}), 146.2 (C_{Py}), 140.6 (C_{Py}), 133.8 (NCHN), 125.6 (C_{Py}), 120.1 (NCHCHN), 114.9 (C_{Py}) ppm. Anal. Calcd for $C_{13}H_{11}N_4Br$ (303.16): C, 51.09; H, 3.66; N, 18.48; Found: C, 51.09; H, 3.65; N, 18.35.

1,3-Bis-(pyridin-2-yl) imidazolium hexafluorophosphate (a). A saturated solution of ammonium hexafluorophosphate (169 mg, 1.04 mmol, 1.05 equiv) in water is added to a saturated solution 1,3-bis(pyridin-2-yl) imidazolium bromide (300 mg, 990 µmol, 1.00 equiv.) in water an stirred for 30 min. A precipitate is formed which is filtrated, washed with water and dried under high vacuum. The product is isolated as an off-white powder. Yield: 328 mg (90 %). M.p. 210 °C ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.80 (t, ^{4}J = 1.5 Hz, 1H, NCHN), 8.74 (d, ^{4}J = 1.5 Hz, 2H, NCHCHN), 8.72 (d, ^{3}J = 4.9 Hz, 2H, H_{Py}), 8.27 (dd, ^{3}J = 9.6 Hz, ^{3}J = 7.6 Hz, 2H, H_{Py}), 8.25 (d, ^{3}J = 9.6 Hz, 2H, H_{Py}), 7.71 (dd, ^{3}J = 7.6 Hz, ^{3}J = 4.9 Hz, 2H, H_{Py}) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 149.3 (C_{Py}), 146.2 (C_{Py}), 140.6 (C_{Py}), 133.8 (NCHN), 125.7 (C_{Py}), 120.2 (NCHCHN), 114.9 (C_{Py}) ppm. Anal. Calcd for $C_{13}H_{11}N_4PF_6$ (368.22): C, 42.40; H, 3.01; N, 15.22; Found: C, 42.36; H, 3.12; N, 15.17.

1,3-Bis(pyridin-2-yl) imidazolium tetrafluoroborate (b). A saturated solution of sodium tetrafluorobroate (114 mg, 1.04 mmol, 1.05 equiv.) in water is added to a saturated solution 1,3-bis(pyridin-2-yl) imidazolium bromide (300 mg, 990 µmol, 1.00 equiv.) in water. The clear solution is extracted three times with dichloromethane (ca. 5 mL) and the combined organic phases are dried over $MgSO_4$. After evaporation of the solvent, the product is isolated as an off-white solid. Yield: 187 mg (61 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.80 (s, 1H, NCHN), 8.75 (d, ^{4}J = 1.5 Hz, 2H, NCHCHN), 8.72 (d, ^{3}J = 4.9 Hz, 2H, H_{Py}), 8.27 (dd, ^{3}J = 9.6 Hz, ^{3}J = 7.6 Hz, 2H, H_{Py}), 8.26 (d, ^{3}J = 9.6 Hz, 2H, H_{Py}), 7.71 (dd, ^{3}J = 7.6 Hz, ^{3}J = 4.9 Hz, 2H, H_{Py}) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 149.3 (C_{Py}), 146.2 (C_{Py}), 140.6 (C_{Py}), 133.8 (NCHN), 125.7 (C_{Py}), 120.2 (NCHCHN), 114.9 (C_{Py}). Anal. Calcd for $C_{13}H_{11}N_4BF_4$ (310.06): C, 50.36; H, 3.58; N, 18.07; Found: C, 50.32; H, 3.52; N, 17.87.

1,3-Bis-(pyrimidin-2-yl) imidazolium hexafluorophosphate (d).

1,3-bis(pyrimid-2-yl)imidazolium hexaflourophosphate: 1,3-bis(pyrimid-2-yl)imidazolium hexaflourophosphate was synthetized analogously to compound **a**. Yield: 530 mg (84 %).^{1}H-NMR (400 MHz, DMSO-d_6, r.t.) δ 10.45 (t, ^{3}J = 1.6 Hz, 1H, NCHN), 9.15 (d, 4H ^{3}J = 4.9 Hz, CHCHN), 8.72 (d, ^{3}J =

1.65 Hz, 2H, NCHCHN), 7.87 (t, ^3J = 4.9 Hz, 2H, 5 H_{pyri}). EA: calc.: C, 35.69; H, 2.45; N, 22.70, found: C, 35.58; H, 2.41; N, 22.42.

1,3-Bis-(6-methyl-pyridin-2-yl) imidazolium hexafluorophosphate (e). 6-Methyl-pyridin-2-yl-imidazole (500 mg, 3.14 mmol, 1.00 equiv.) is dissolved in 2-bromo-6-methyl-pyridine (810 mg, 4.71 mmol, 1.50 equiv.), degassed and set under Ar atmosphere. The mixture is stirred for 16 h at 160 °C. After cooling to r.t. Et_2O (10 mL) is added and the suspension is filtrated. The residue is dissolved in MeOH (2 mL), precipitated with Et_2O, filtrated and dried under high vacuum. After dissolving in water (5 mL) a saturated aqueous ammonium hexafluorophosphate (538 mg, 3.30 mmol, 1.05 equiv.) solution is added. A precipitate is formed which filtrated, washed with water and dried under high vacuum. The product is isolated as a slightly beige powder. Yield: 396 mg (68 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.62 (t, ^4J = 1.5 Hz, 1H, NCHN), 8.69 (d, ^4J = 1.5 Hz, 2H, NCHCHN), 8.14 (dd, ^3J = 8.1 Hz, ^3J = 7.6 Hz, 2H, H_{Py}), 8.01 (d, ^3J = 8.1 Hz, 2H, H_{Py}), 7.56 (d, ^3J = 7.6 Hz, 2H, H_{Py}), 2.62 (s, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6): δ 158.7 (C_{Py}), 145.5 (C_{Py}), 140.6 (NCHN), 133.2 (C_{Py}), 125.0 (C_{Py}), 120.1 (NCHCHN), 111.7 (C_{Py}), 23.7 (CH_3) ppm. $C_{13}H_{11}N_4PF_6$ (396.28): C, 45.46; H, 3.82; N, 14.14; Found: C, 45.42; H, 3.91; N, 14.24.

1.3. Recycling experiments

Table S1. Catalyst reusability.

Run	Conversion [%]	Selectivity [%]
1	96	89
2	68	80
3	40	77

Reaction conditions: 1 mol % MTO, 1.2 equiv. additive **a**, cat.:substrate:oxidant ratio 1:100:250, 40 °C, 3 h reaction time.

2. Crystallographic Details of Compound a (CCDC 1012169)

Data were collected on an X-ray single crystal diffractometer equipped with a CCD detector (Bruker APEX II, κ-CCD), a rotating anode (Bruker AXS, FR591) with MoK_α radiation ($\lambda = 0.71073$ Å), and a Montel mirror by using the APEX 2 software package.[S5] The measurements were performed on a single crystal coated with perfluorinated ether. The crystal was fixed on the top of a glass fiber and transferred to the diffractometer. The crystal was frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT.[S5] Absorption corrections, including odd and even ordered spherical harmonics, were performed using SADABS.[S5] Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps,[S6] and were refined against

all data using SHELXL-97[S6] in conjunction with SHELXLE.[S7] If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal positions using the SHELXL riding model. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$ with SHELXL-97[S6] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.[S8] Images of the crystal structures were generated by PLATON.[S9]

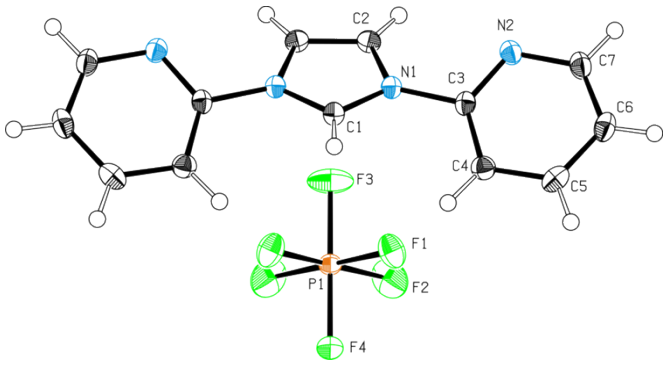

Figure S1. ORTEP drawing of the X-ray crystal structure of compound **a** with 50% ellipsoid probability.

Table S2. X-ray data for compound **a**.

Chemical formula	$C_{13}H_{11}N_4F_6P$
Formula weight	368.23
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal size	0.310 x 0.470 x 0.520 mm
Crystal habit	clear colourless fragment
Crystal system	monoclinic
Space group	*P* $2_1/m$
Unit cell dimensions	a = 6.2172(2) Å α = 90°
	b = 16.4455(5) Å β = 102.836(1)°
	c = 7.0797(2) Å γ = 90°
Volume	705.77(4) $Å^3$
Z	4
Density (calculated)	1.733 g/cm^3
Absorption coefficient	0.270 mm^{-1}
F(000)	372
Diffractometer	Bruker Kappa APEX II CCD
Radiation source	FR591 rotating anode, Mo
Theta range for data collection	2.95 to 25.37°
Index ranges	-7<=h<=7, -19<=k<=19, -8<=l<=-8
Reflections collected	21380

Independent reflections	1334 [R(int) = 0.0527]
Coverage of independent reflections	99.1%
Absorption correction	multi-scan
Max. and min. transmission	0.9211 and 0.8720
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 1990)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-97 (Sheldrick, 1997)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	1334 / 0 / 116
Goodness-of-fit on F^2	1.101
Δ/σ_{max}	0.001
Final R indices	1315 data; I>2σ(I) R1 = 0.0279, wR2 = 0.0681 all data R1 = 0.0282, wR2 = 0.0683
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0270P)^2+0.3497P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.218 and -0.230 eÅ^{-3}

3. ^{1}H-NMR Studies

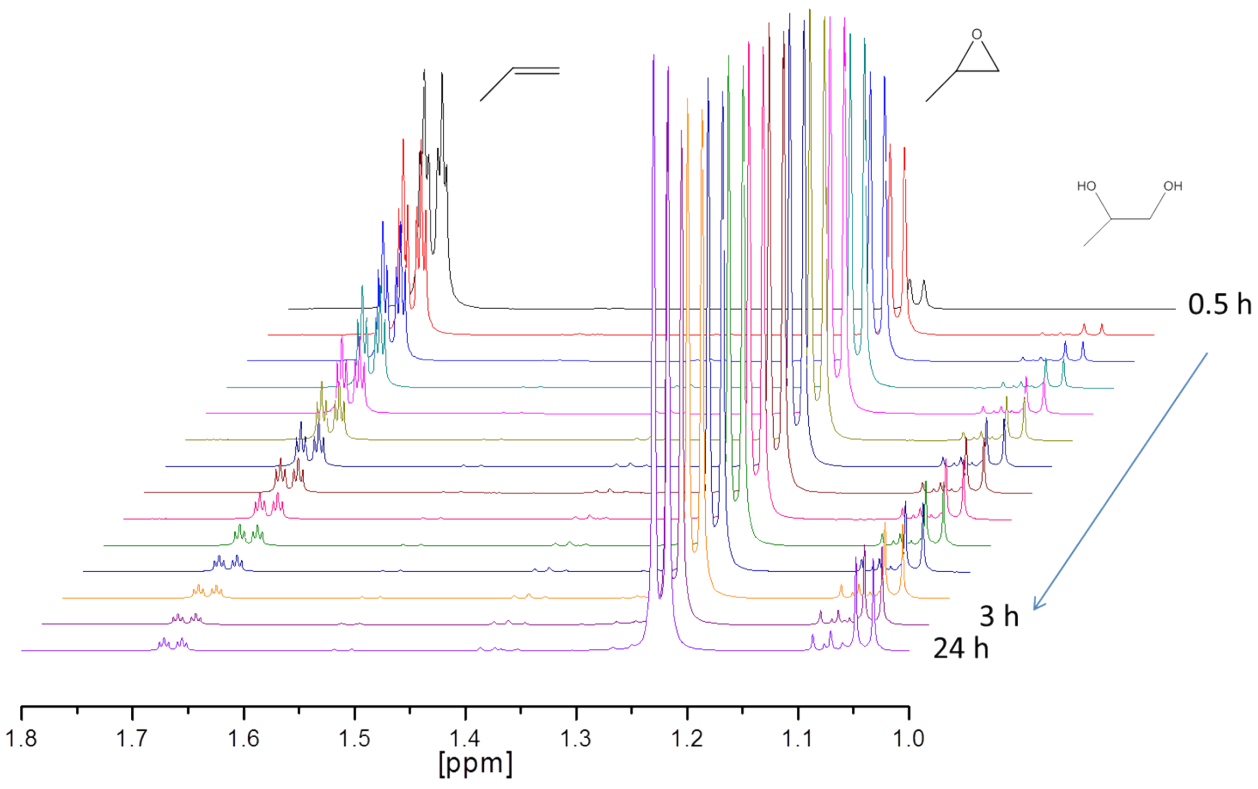

Figure S2. ^{1}H-NMR kinetic measurement series of the epoxidation of propylene using MTO (4.78 **µ**mol) as catalyst, additive **a** (9.56 **µ**mol) and H_2O_2 (67.83 **µ**L, 50% in water) as oxidant in acetonitrile (0.4 mL) at 40 °C, molar ratio catalyst:additive:substrate:oxidant 1:2:100:250.

4. References

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