Supporting Information

Manganese *N,N,N*-Pincer Complex-catalyzed Epoxidation of Unactivated Aliphatic Olefins

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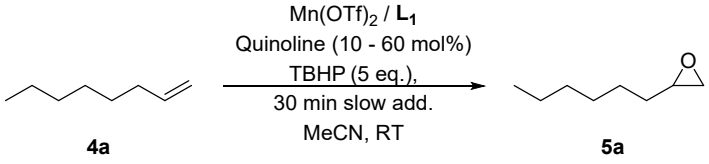
General Remarks

Chemicals used in this work were purchases from ABCR, BLD Pharm, Sigma Aldrich and TCI and used without further purification, unless otherwise stated. All reactions were carried out under ambient conditions, unless otherwise specified. Solvents used for reactions were HPLC grade. Solvents used for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography was performed on Machery-Nagel pre-coated ALUGRAM Xtra SIL G/UV_{254} TLC sheets and visualized with $Ce(SO_4)_2$ stain and by irradiation with UV light. Flash Column chromatography was performed with a Combi *Flash Rf* + from Teledyne ISCO using Pentane : Et_2O (: NEt_3) as eluent. Gas chromatography was performed on an Agilent HP 6890 with a HP5 column. Conversions and yields were determined by a 5-point calibration of the respective compounds with hexadecane as internal standard. NMR spectra were recorded using a Bruker AV300 or AV400 NMR spectrometer. Chemical shifts (δ) are reported in ppm, coupling constants (*J*) are reported in Hz, multiplicities are indicated: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). ATR-IR spectra were recorded on a Nicolet iS5 FT-IR (Thermo Fisher). Mass spectra were recorded using a Finnigan MAT 95-XP (Thermo Electron) chromatograph with EI or ESI as ionization method. All measurements were carried out at room temperature unless otherwise stated. X-Ray data were collected on a Bruker Kappa APEX II Duo diffractometer. The structures were solved by direct methods (SHELXS-97: Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.) and refined by full-matrix least-squares procedures on F^2 (SHELXL-2018: Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3.). XP (Bruker AXS) was used for graphical representations. CCDC 2187359 and 2187360 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

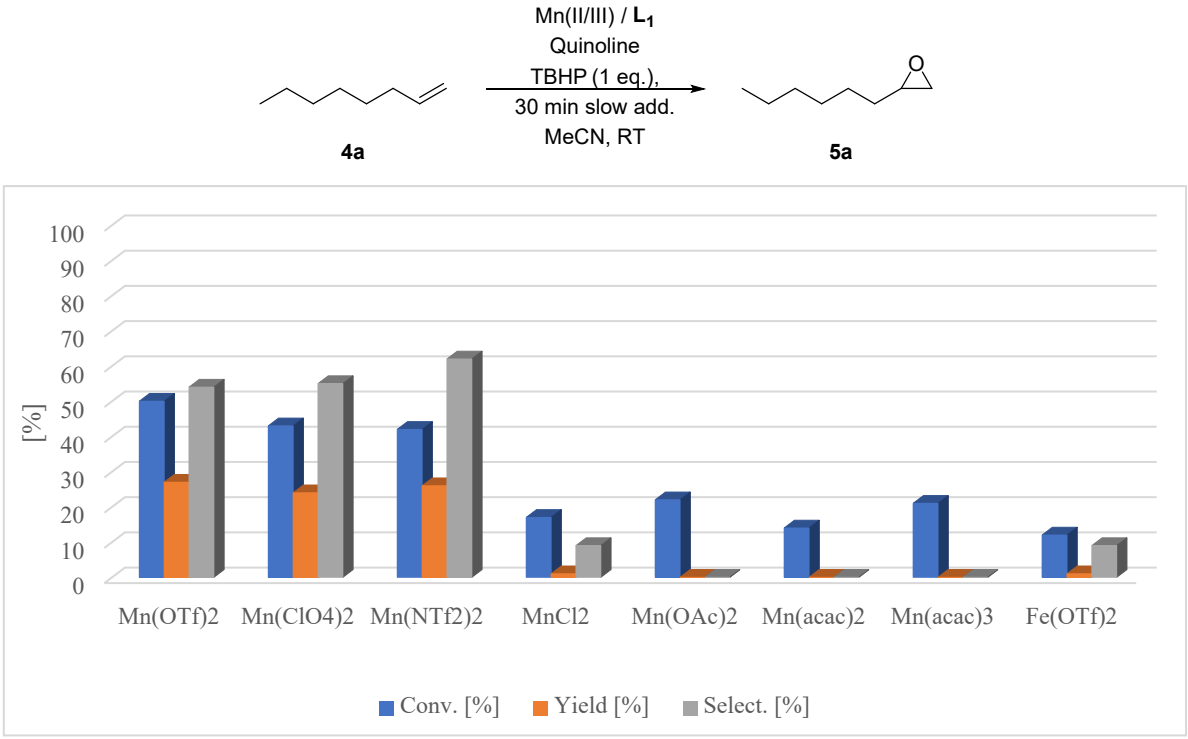
Optimization of the Reaction Conditions

Table S1: Quinoline loading screening for epoxidation reaction.



Entry	Quinoline [mol%]	Conv.[a] [%]	Yield[a] (5a) [%]	Sel. (5a) [%]
1	10	90	55	61
2	20	<99	62	62
3	30	<99	67	67
4	40	<99	60	60
5	50	99	62	62
6	60	99	61	61

*TBHP = tert-Butyl Hydroperoxide, **a**: Conversion and yield determined by GC analysis with hexadecane as IST. Reaction conditions: 0.5 mmol substrate (0.125 M), 5 mol% manganese precursor, 6 mol% **L1**, 30 mol% quinoline, MeCN (4 mL), 25 °C, 30 min slow addition of oxidant via syringe pump.*



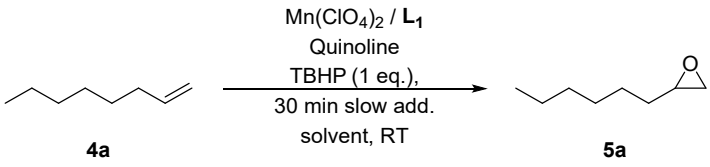
Reactions conditions: Conversion and yield determined by GC analysis with hexadecane as IST. 0.5 mmol substrate (0.125 M), 5 mol% manganese precursor, 6 mol% $\mathbf{L_1}$, 30 mol% quinoline, MeCN (4 mL), 25 °C, 30 min slow addition of TBHP (70% aq., 1 eq.) via syringe pump.

Figure S1: Initial precursor screening.

Screened solvents for epoxidation of 1-octene.

The solvent screening was conducted with $Mn(ClO_4)_2$. Product formation was only observed when using MeCN as reaction solvent.

Table S2: Solvent screening of epoxidation reaction.



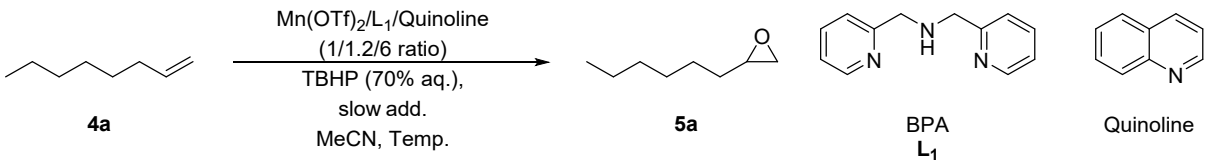
Entry	Solvent	Conv.[a] [%]	Yield[a] (5a) [%]	Sel. (5a) [%]
1	MeCN	43	24	55
2	MeOH	18	0	0
3	*tert*-Amyl Alcohol	<1	0	0
4	1,4-Dioxane	<1	0	0
5	THF	<1	0	0
6	DMSO	<1	0	0
7	DMF	<1	0	0

*TBHP = tert-Butyl Hydroperoxide, **a**: Conversion and yield determined by GC analysis with hexadecane as IST. Reaction conditions: 0.5 mmol substrate (0.125 M), 5 mol% $Mn(ClO_4)_2$, 6 mol% **L1**, 30 mol% quinoline, solvent (4 mL), 25 °C, 30 min slow addition of TBHP (70% aq., 1 eq.) via syringe pump.*

Variation of numerical parameters

Several numerical parameters were changed subsequently to either enhance the reaction efficiency by lowering the amount of the needed compounds or to achieve higher yields. Here, none of the applied changes improved the previous best result.

Table S3: Variation of numerical parameters after the initially finished optimization process.



Entry	$Mn(OTf)_2$ [mol%]	BPA [mol%]	Quinoline [mol%]	TBHP [eq.]	Conc. [M]	Time [min]	Temp. [°C]	Conv.[a] [%]	Yield[a] (5a) [%]	Sel. (5a) [%]
1[b]	5	6	30	5	0.125	30	RT	<99	67	67
2[c]	5	6	30	5	0.125	30	RT	<99	57	57
2	5	6	30	3	0.125	40	RT	94	59	63
3	5	6	30	5	0.125	40	RT	<99	61	61
4	5	6	30	5	0.125	10	RT	93	52	55
5	5	6	30	3	0.125	30	40	86	49	57
6	5	6	30	5	0.125	30	40	98	57	58
7	3	3.6	18	5	0.125	30	RT	<99	52	52
8	10	12	60	5	0.125	30	RT	<99	61	61
9[d]	5	6	30	5	0.125	30	RT	<99	64	64
10[e]	5	6	30	5	0.125	30	RT	<99	61	61
10	5	6	30	7.5	0.125	30	RT	<99	58	58
11	7.5	9	45	7.5	0.125	30	RT	<99	54	54
12[f]	5	6	30	5	0.250	30	RT	<99	57	57
13[g]	5	6	30	5	0.0625	30	RT	<99	54	54

***a**: Conversion and yield determined by GC analysis with hexadecane as IST, **b**: Best result after initial screening; performing the reaction under an atmosphere of argon gives almost identical results, **c:** TBHP solution in decane (5.5 M) was employed. **d**: 60 min of precursor/ligand stirring instead of 30 min, **e**: No extra pre-stirring time, **f**: 2.0 mL MeCN, **g**: Reaction scale halved to 0.25 mmol with 4 mL MeCN. Reaction conditions: The indicated amount of substrate, manganese precursor, ligand and quinoline were stirred in MeCN at the indicated temperature for the indicated time with slow addition of TBHP (70% aq.) via syringe pump.*

X-Ray Crystal Structure Analysis of **Mn-1** and **Mn-2**

Crystal data of **Mn-1**: $C_{16}H_{16}F_6MnN_4O_6S_2$, M = 593.39, triclinic, space group $P\bar{1}$, a = 8.8255(10), b = 11.6235(14), c = 12.5980(15) Å, α = 73.4523(18), β = 75.8056(18), γ = 72.4567(18)°, V = 1163.1(2) Å^3, T = 200(2) K, Z = 2, 52834 reflections measured, 6252 independent reflections (R_{int} = 0.0299), final R values ($I > 2\sigma(I)$): R_1 = 0.0404, wR_2 = 0.0966, final R values (all data): R_1 = 0.0576, wR_2 = 0.1089, 461 parameters.

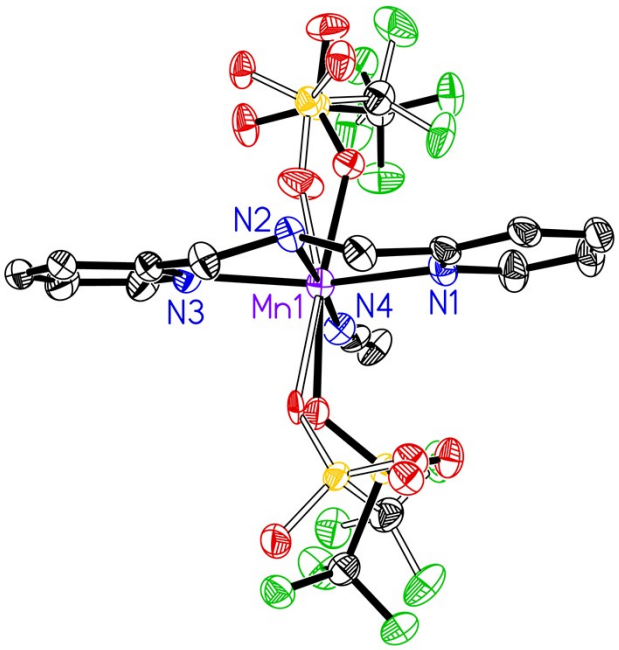


Figure S2: ORTEP representation of **Mn-1** (S yellow, O red, F green). Displacement ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity. The triflate units are disordered over two sites with occupancies of 0.748(2): 0.252(2) and 0.724(3): 0.276(3), respectively. The lower occupied parts of the disorder are shown with unfilled bonds.

Crystal data of **Mn-2**: $C_{14}H_{15}F_6MnN_3O_7S_2$, M = 570.35, monoclinic, space group $P2/n$, a = 8.9946(7), b = 9.9209(8), c = 12.2244(9) Å, β = 105.646(3)°, V = 1050.42(14) Å^3, T = 150(2) K, Z = 2, 21629 reflections measured, 2532 independent reflections (R_{int} = 0.0213), final R values ($I > 2\sigma(I)$): R_1 = 0.0466, wR_2 = 0.1046, final R values (all data): R_1 = 0.0473, wR_2 = 0.1049, 237 parameters.

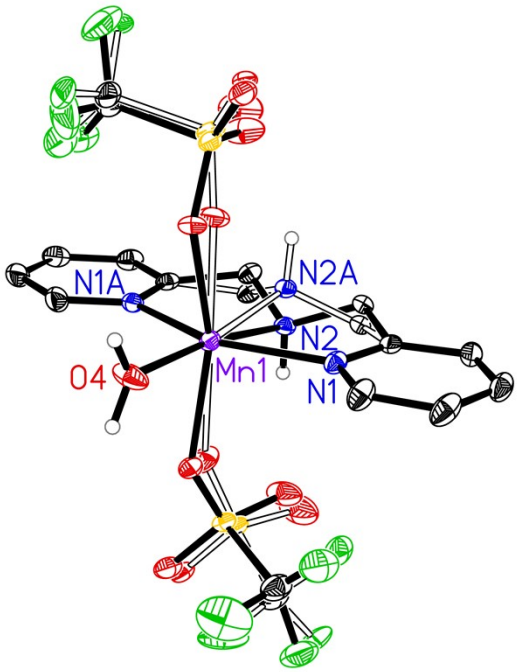
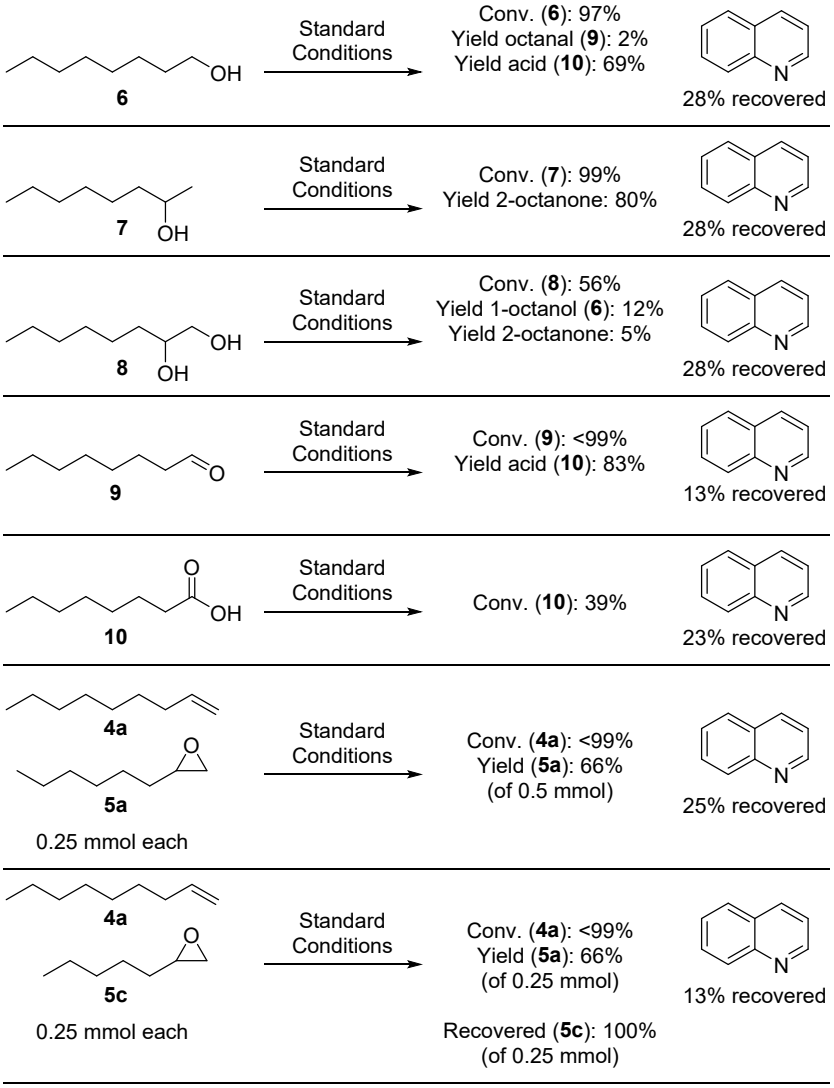


Figure S3: ORTEP representation of **Mn-2** (S yellow, F green). Displacement ellipsoids correspond to 30% probability. C-bound hydrogen atoms are omitted for clarity. The triflate units and the backbone of the *N,N,N* – ligand are disordered over two sites with occupancies of 0.6 : 0.4 and 0.5 : 0.5, respectively. The lower occupied part of the disordered triflate as well as one orientation of the backbone of the *N,N,N* – ligand are shown with unfilled bonds. Operator for generating equivalent atoms: -x+1/2, y, -z+3/2.

Stability of potential Side Products or Intermediates

Potential side products such as 1- and 2-octanol (**6**, **7**), 1,2-octanediol **8**, *n*-octanal **9** and octanoic acid **10** were subjected to our catalytic protocol. While 1-octanol **6** is converted to octanoic acid **10** in 69%, the secondary alcohol 2-octanol **7** is converted to the corresponding ketone 2-octanone in 80% yield. The 1,2-diol **8** displays 56% conversion with low amounts of decomposition or oxidation products being detected. In all three reactions 28% of the additive quinoline were recovered, while no other products could be detected in the GC spectra. The aldehyde *n*-octanal **9** is not stable under the reaction conditions, as is expected with a substance that is easily oxidized. On the other hand, octanoic acid **10** is much less affected under the applied reaction conditions, though no formation of the acid was observed in our catalytic reaction by chromatographic or spectroscopic methods. Submitting a 50:50 mixture of the starting material 1-octene **4a** and the product 1,2-epoxyoctane **5a** to our reaction protocol gives the same result as our model system, yielding 66% of the epoxide **5a** after 30 minutes. Finally, as a competition experiment, we subjected a 50:50 mixture of 1-octene **4a** and 1,2-epoxyheptane **5c** to our standard protocol. Here, the epoxide **5c** was fully recovered while the olefin was fully consumed, yielding 66% of 1,2-epoxyoctane **5a**. This indicates that, although epoxides are not entirely stable under these conditions, the olefin is the preferred reaction partner in this catalytic system.

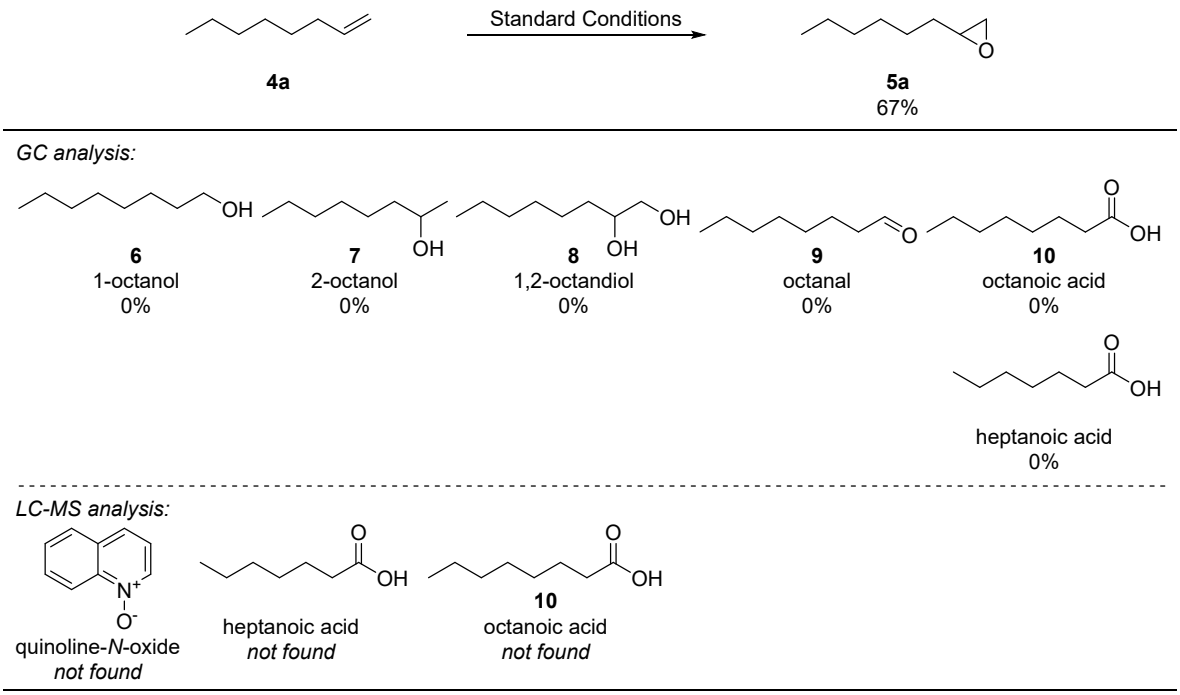
Scheme S1: Conversion of potential intermediates or side products of 1-octene epoxidation.



Conversion and yield determined by GC analysis with hexadecane as IST. *n*-Octanoic acid **10** and 1,2-octanediol **8** were quantified by NMR using dibromomethane as IST. Reaction conditions: 0.5 mmol substrate (0.125 M), 5 mol% $Mn(OTf)_2$, 6 mol% $\mathbf{L_1}$, 30 mol% quinoline, MeCN (4 mL), 25 °C, 30 min slow addition of TBHP (70% aq., 5 eq.) via syringe pump.

Side Product Analyses

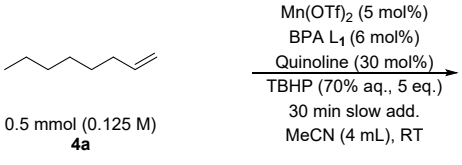
Table S4: Chromatographic analysis of potential side products.



Yields determined by GC analysis with hexadecane as IST and 5-point calibrations of the respective products. Reaction conditions: 0.5 mmol substrate (0.125 M), 5 mol% $Mn(OTf)_2$, 6 mol% $\mathbf{L_1}$, 30 mol% quinoline derivative, MeCN (4 mL), 25 °C, 30 min slow addition of TBHP (70% aq., 5 eq.) via syringe pump.

Mechanistic Considerations

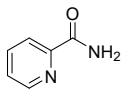
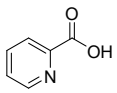
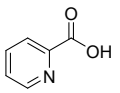
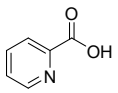
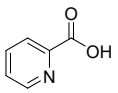
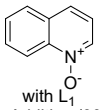
Table S5: Employment of Potential Oxidative Degradation Products of the Ligand and the Additive.



0.5 mmol (0.125 M)
4a

5a

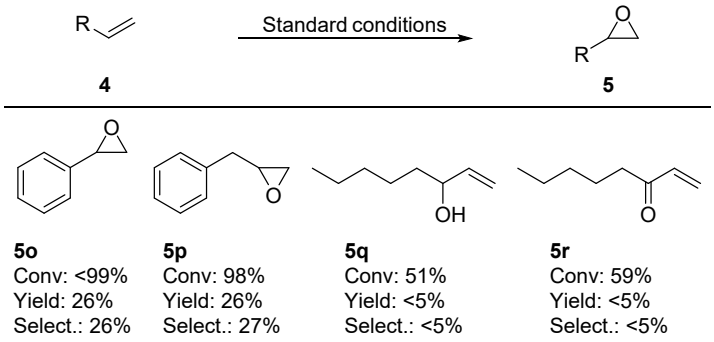
BPA
L_1

					
As Ligand Conv.: 0% Yield: 0% Select.: 0%	As Ligand Conv.: 3% Yield: 0% Select.: 0%	with L_1 Pic-OH (6 mol%) (No Quinoline) Conv.: 53% Yield: 6% Select.: 12%	with L_1 Pic-OH (6 mol%) (With Quinoline) Conv.: 93% Yield: 64% Select.: 69%	with L_1 Pic-OH (15 mol%) (With Quinoline) Conv.: 60% Yield: 38% Select.: 63%	with L_1 QNO as Additive (30 mol%) Conv.: 44% Yield: 18% Select.: 41% (1 eq. of TBHP)

Conversion and yield determined by GC analysis with hexadecane as IST. Reaction conditions: 0.5 mmol substrate (0.125 M), 5 mol% $Mn(OTf)_2$, 6 mol% **L_1**, 30 mol% quinoline, MeCN (4 mL), 25 °C, 30 min slow addition of TBHP (70% aq., 5 eq.) via syringe pump.

Limitations of Substrate Scope

Table S6: Substrates with low selectivity.



5o	**5p**	**5q**	**5r**
Conv: <99%	Conv: 98%	Conv: 51%	Conv: 59%
Yield: 26%	Yield: 26%	Yield: <5%	Yield: <5%
Select.: 26%	Select.: 27%	Select.: <5%	Select.: <5%

Conversion and yield determined by GC analysis with hexadecane as IST. Reaction conditions: 0.5 mmol substrate (0.125 M), 5 mol% $Mn(OTf)_2$, 6 mol% $\mathbf{L_1}$, 30 mol% quinoline, MeCN (4 mL), 25 °C, 30 min slow addition of TBHP (70% aq., 5 eq.) via syringe pump.

General Procedures

General procedure for epoxidation of aliphatic olefins

An 8 mL glass vial equipped with a Teflon coated stirring bar was charged with stock solutions of $Mn(OTf)_2$ (0.025 mmol, 8.8 mg, 5 mol% catalyst loading), bis(2-picolyl amine) (0.03 mmol, 6.0 mg, 6 mol%) and freshly distilled quinoline (0.15 mmol, 19.4 mg, 30 mol%). The resulting mixture was further diluted with MeCN to a total volume of 4 mL and stirred for 5 minutes. Then, 1-octene (0.5 mmol, 56.1 mg, 0.125 M) was added. Next, a solution of *tert*-butyl hydroperoxide (TBHP) (2.5 mmol, 5 eq., 340 µL, 70% aq.) in MeCN (760 µL) was added via a syringe pump to the reaction mixture over the course of 30 minutes. Afterwards, the reaction was terminated by the addition of a few drops of a saturated aqueous $Na_2S_2O_3$ solution. (*Note*: In most cased the addition of $Na_2S_2O_3$ is not necessary as all TBHP was already consumed at this point).

For GC analysis the reaction mixture was then diluted with EtOAc, filtered, and analyzed using hexadecane (30 µL) as an internal standard to determine conversion and yield.

For NMR analysis the solvent of the crude reaction mixture was removed, the residue was dried over night at high vacuum, and analyzed using dibromomethane (35 µL) as an internal standard to determine conversion and yield.

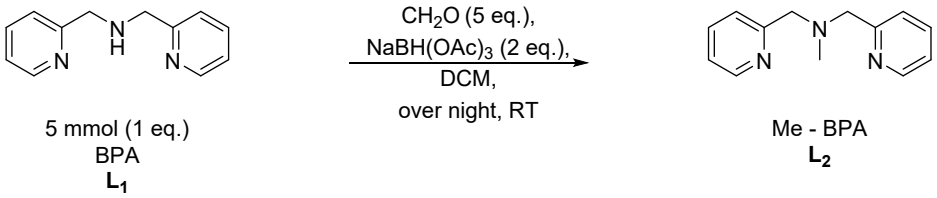
For LC-MS analysis the reaction mixture was diluted with EtOAc and filtered through a syringe filter.

For isolation the reaction mixture was diluted with water, extracted with Et_2O, washed with brine, dried over Na_2SO_4 and purified by silica column chromatography using pentane (containing 1% NEt_3) and Et_2O as the eluent.

General procedure for the kinetic profile of epoxidation reaction

A total of five 8 mL glass vials equipped with Teflon coated stirring bars were each charged with stock solutions of $Mn(OTf)_2$ (0.025 mmol, 8.8 mg, 5 mol% catalyst loading), bis(2-picolyl amine) (0.03 mmol, 6.0 mg, 6 mol%) and freshly distilled quinoline (0.15 mmol, 19.4 mg, 30 mol%). The resulting mixtures were further diluted with MeCN to a total volume of 4 mL and stirred for 5 minutes. Then, 1-octene (0.5 mmol, 56.1 mg, 0.125 M) was added to each vial. Next, five solutions of *tert*-butyl hydroperoxide (TBHP) (2.5 mmol, 5 eq., 340 µL, 70% aq.) in MeCN (660 µL) were added via a syringe pump to each of the reaction vials over the course of 30 minutes. After 5, 10, 15, 20 and 25 minutes the respective reaction was stopped by removing the syringe needle and consecutively adding a few drops of saturated $Na_2S_2O_3$ solution. For GC analysis the reaction mixture was then diluted with EtOAc, filtered and analyzed using hexadecane (30 µL) as an internal standard to determine conversion, yield and selectivity.

*Synthesis of N-methyl-1-(pyridin-2-yl)-N-(pyridin-2-ylmethyl)methanamine (Me – BPA **L₂**)*



The title compound was synthesized according to the literature procedure.[1]

Bis(2-picolyl amine) **L_1** (5 mmol, 1 g, 1 eq.) was dissolved in DCM (25 mL) in a 100 mL round bottom flask. Next, a formaldehyde solution (37% aq., 10 mmol, 810 mg) was added dropwise to the solution. After a few minutes, $NaBH(OAc)_3$ (10 mmol, 2.1 g) was added portionwise to the solution. The resulting mixture was allowed to stir over night at room temperature and was then quenched by the addition of aqueous NaOH solution (2.5 M, 25 mL). The biphasic mixture was extracted with DCM, washed with saturated aqueous NaCl solution and dried over Na_2SO_4. After the removal of DCM under reduced pressure, a yellow oil was obtained as the crude product, which was then dispersed in Et_2O (5 mL) and filtered through a syringe filter. After the removal of Et_2O under reduced pressure the title compound was obtained as a yellow oil (1.0 g, 98%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 8.55 – 8.52 (m, 2H, Ar-H), 7.65 – 7.62 (m, 2H, Ar-H), 7.52 – 7.49 (m, 2H, Ar-H), 7.16 – 7.12 (m, 2H, Ar-H), 3.76 (s, 4H, CH_2), 2.30 (s, 3H, CH_3).

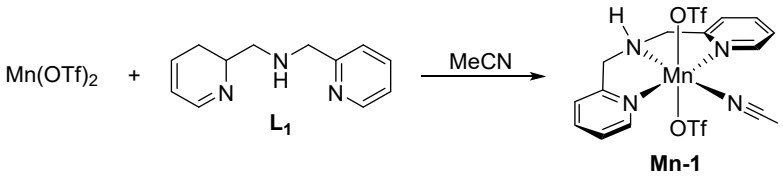
^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 159.4, 149.2, 136.6, 123.2, 122.1, 63.7, 42.9.

Preparation of manganese catalyst

A flame dried Schlenk flask was charged with manganese bis(trifluoromethanesulfonate) (1.35 mmol, 477.0 mg, 1 eq.) and the atmosphere was replaced with argon. The manganese salt was dissolved in degassed and dry MeCN (40 mL). In a separate Schlenk flask freshly distilled bis(2-picolyl amine) **L_1** (1.35 mmol, 269.2 mg, 1 eq.) was dissolved in MeCN (15 mL). Afterwards, the ligand solution was transferred to a Schlenk dropping funnel and was added dropwise to the manganese bis(trifluoromethanesulfonate) solution. The light-yellow solution was allowed to stir at room temperature overnight. Afterwards, the solvent was removed *in vacuo*, giving a white solid material (715.8 mg, 96%).

Crystallization for X-Ray analysis

*Synthesis of **Mn-1***



Mn-1

The white solid (0.73 mmol, 404.7 mg) was then dissolved in degassed *and dry* MeCN (5 mL). The resulting solution was filtered with a syringe filter. Finally, crystallization was achieved by diffusion of degassed and dry Et_2O into the MeCN solution, yielding colorless crystals (155 mg, 36%).

NMR: Paramagnetic

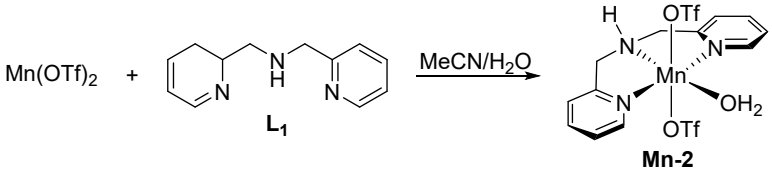
IR-ATR (solid) $\tilde{\upsilon}_{max}/cm^{-1}$: 3392, 3260, 1636, 1605, 1445, 1287, 1237, 1223, 1180, 1156, 1098, 1032, 1018, 769, 639, 517.

EI-HRMS calcd. for $[C_{13}H_{13}F_3MnN_3O_3S]^+$: 403.00047, found: 403.00062 $[M\text{-}OTf]^+$.

EA: Found: C 30.6, H 2.8, S 11.6, N 7.8. Calc. for $C_{14}H_{13}F_6MnN_3O_6S_2$, M = 552,32 g/mol: C 30.4, H 2.4, S 11.6, N 7.6.

Note: The coordinating MeCN is removed in vacuo.

*Synthesis of **Mn-2***



Mn-2

The white solid (0.27 mmol, 150 mg) was then dissolved in degassed *undried* MeCN (5 mL). The resulting solution was filtered with a syringe filter. Finally, crystallization was achieved by diffusion of degassed and dry benzene into the MeCN solution, yielding colorless prismatic crystals (28 mg, 18%).

NMR: Paramagnetic

IR-ATR (solid) $\tilde{\upsilon}_{max}/cm^{-1}$: 3392, 3261, 1637, 1605, 1446, 1288, 1237, 1223, 1180, 1032, 1018, 769, 763, 639, 516.

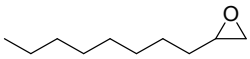
EI-HRMS calcd. for $[C_{13}H_{13}F_3MnN_3O_3S]^+$: 403.00047, found: 402.99944 $[M\text{-}OTf]^+$.

EA: Found: C 30.0, H 2.7, S 11.7, N 7.4. Calc. for $C_{14}H_{13}F_6MnN_3O_6S_2$, M = 552,32 g/mol: C 30.4, H 2.4, S 11.6, N 7.6.

Note: The coordinating H_2O is removed in vacuo.

Isolated Compounds

1,2-epoxydecane (5e)



The title compound was prepared according to the general procedure for epoxidation and obtained as a pale-yellow oil after flash column chromatography (eluent: *n*-pentane : Et_2O; 1% NEt_3); (35.9 mg, 46%).

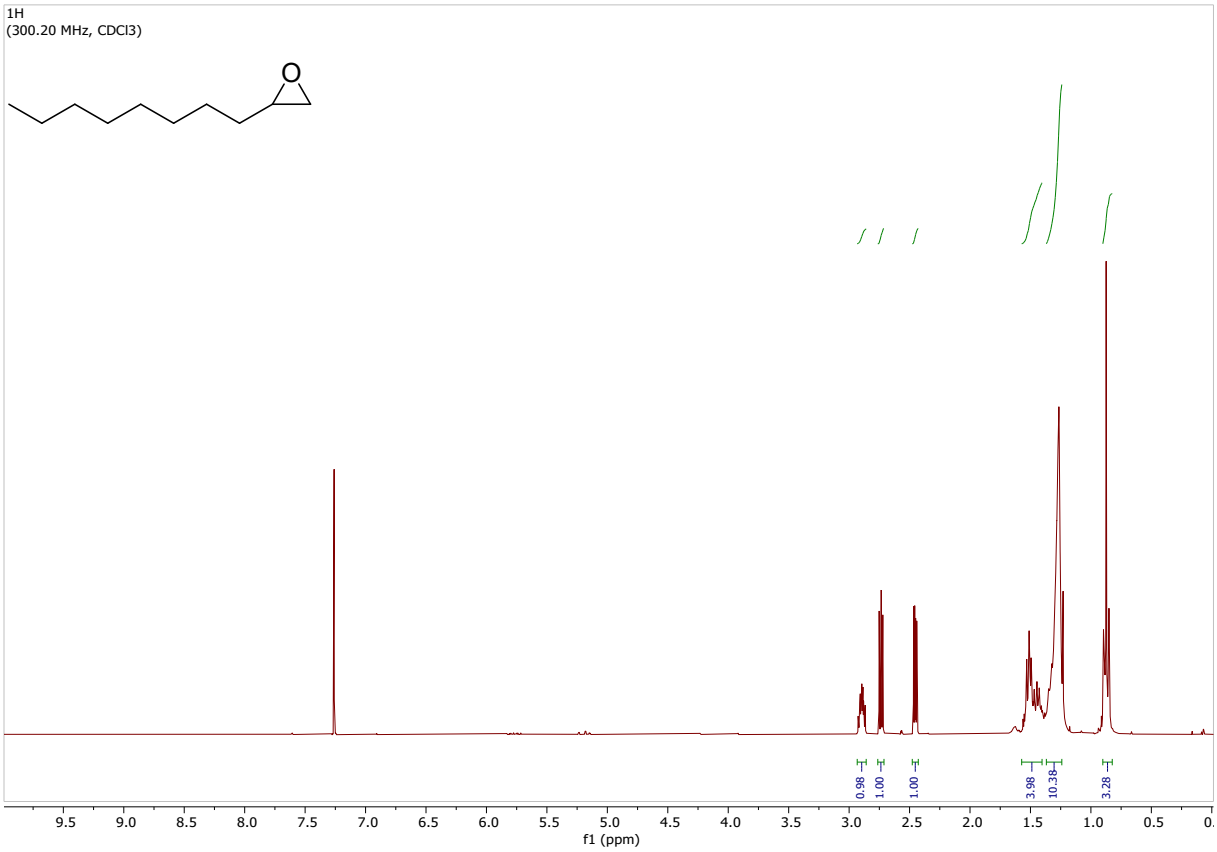
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.90 (tdd, *J* = 5.2, 4.0, 2.7 Hz, 1H, CH), 2.74 (dd, *J* = 5.2, 4.0 Hz, 1H, CH), 2.45 (dd, *J* = 5.2, 2.7 Hz, 1H, CH), 1.59 – 1.36 (m, 4H, CH_2), 1.30 – 1.26 (m, 11H, CH_2), 0.91 – 0.84 (m, 3H, CH_3).

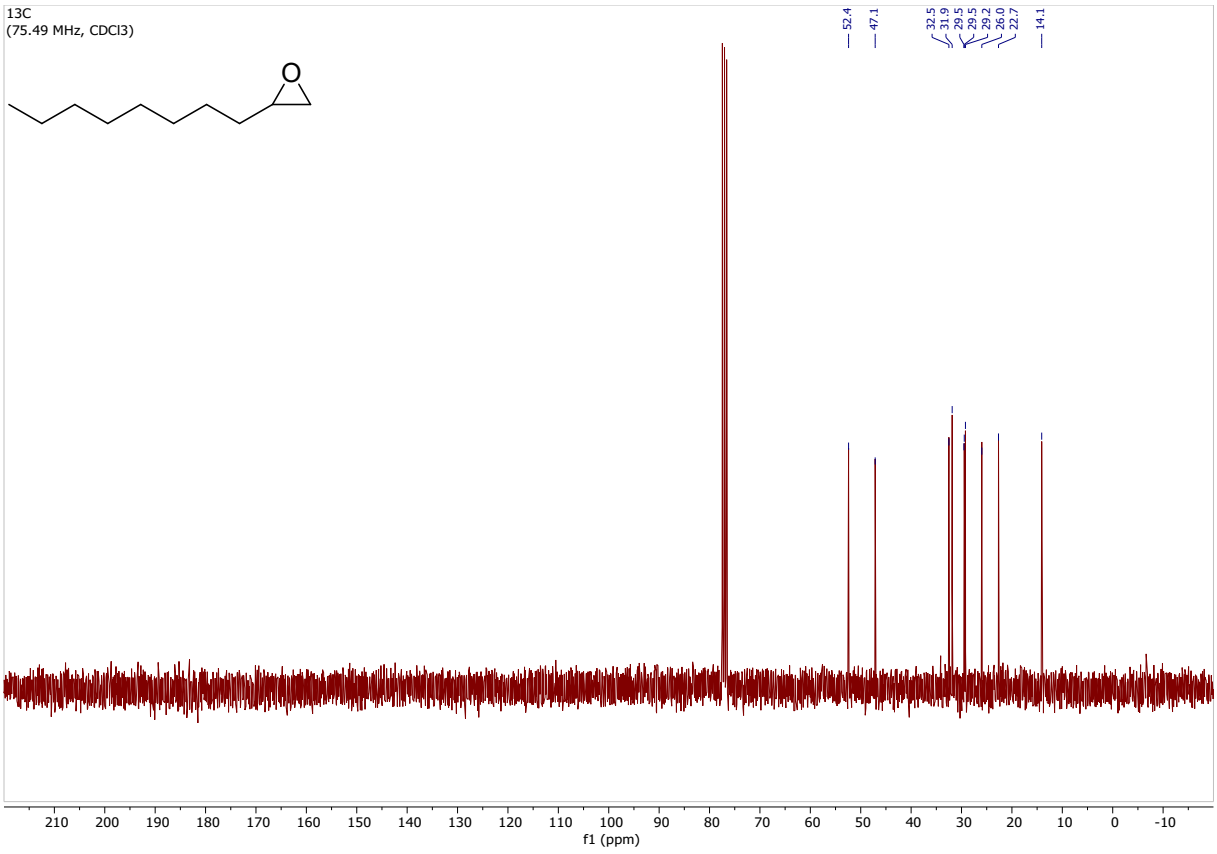
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 52.4, 47.1, 32.5, 31.9, 29.5, 29.5, 29.2, 26.0, 22.7, 14.1.

NMR data matches those previously reported in the literature.[2]

Copies of NMR Spectra

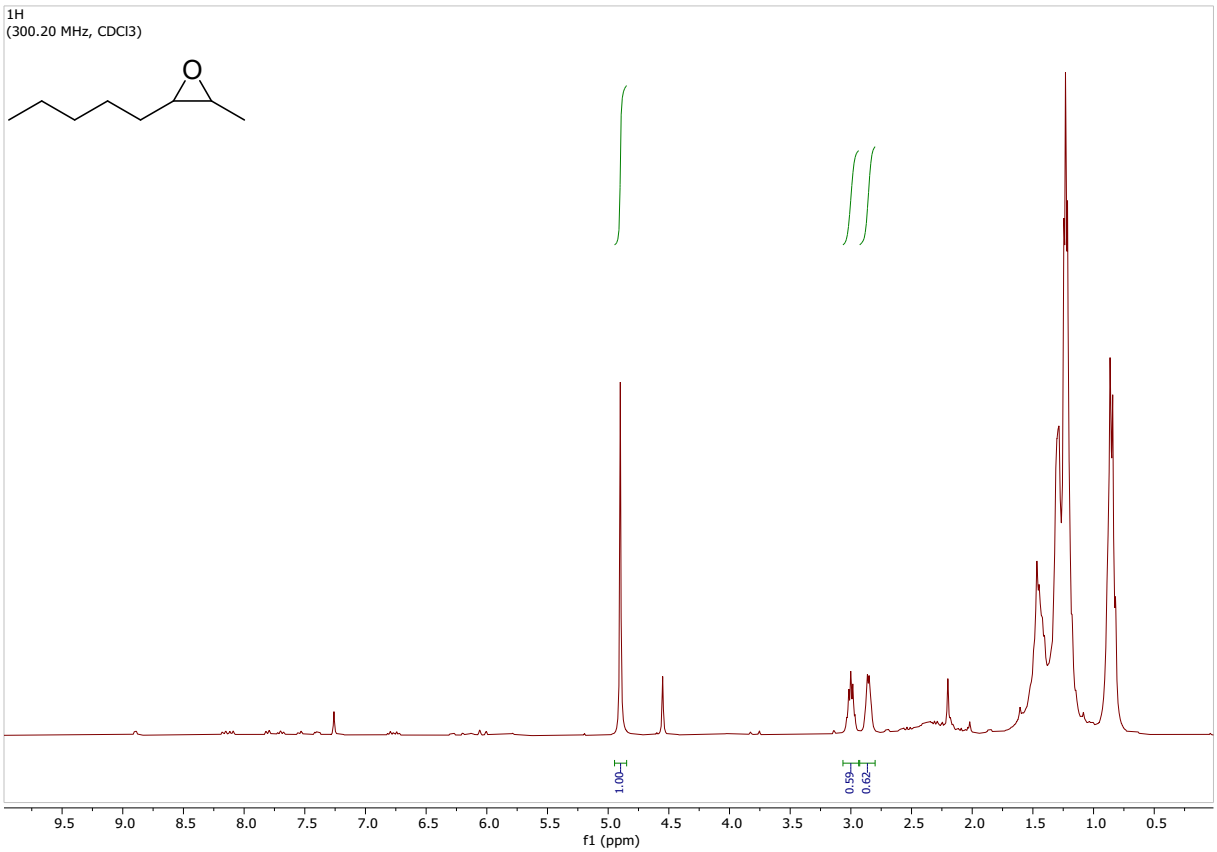
1,2-epoxydecane (5e)




13C
(75.49 MHz, CDCl3)
O
52.4
47.1
32.5
31.9
29.5
29.5
29.2
26.0
22.7
14.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

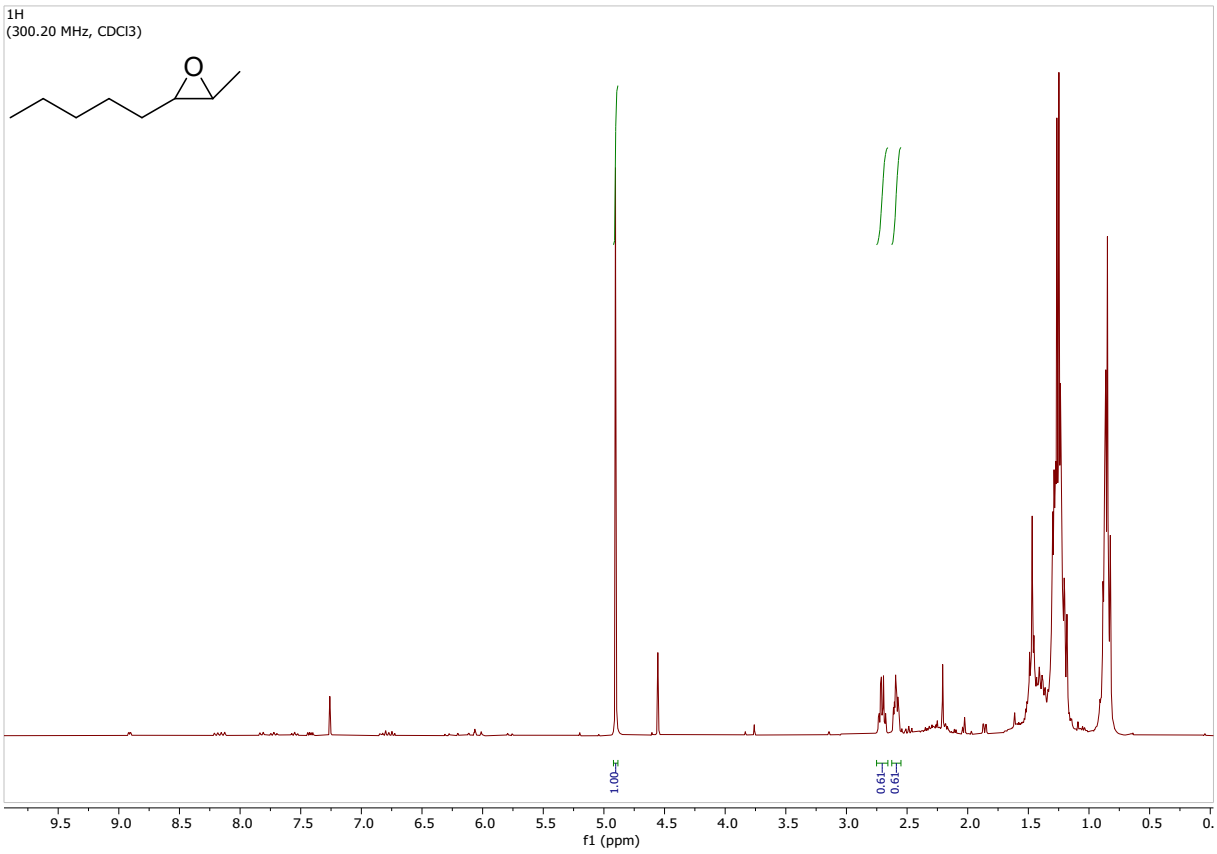
cis-2,3-Epoxyoctane (5g)

Crude Spectrum for Quantification. NMR data matches those previously reported in the literature.[3]



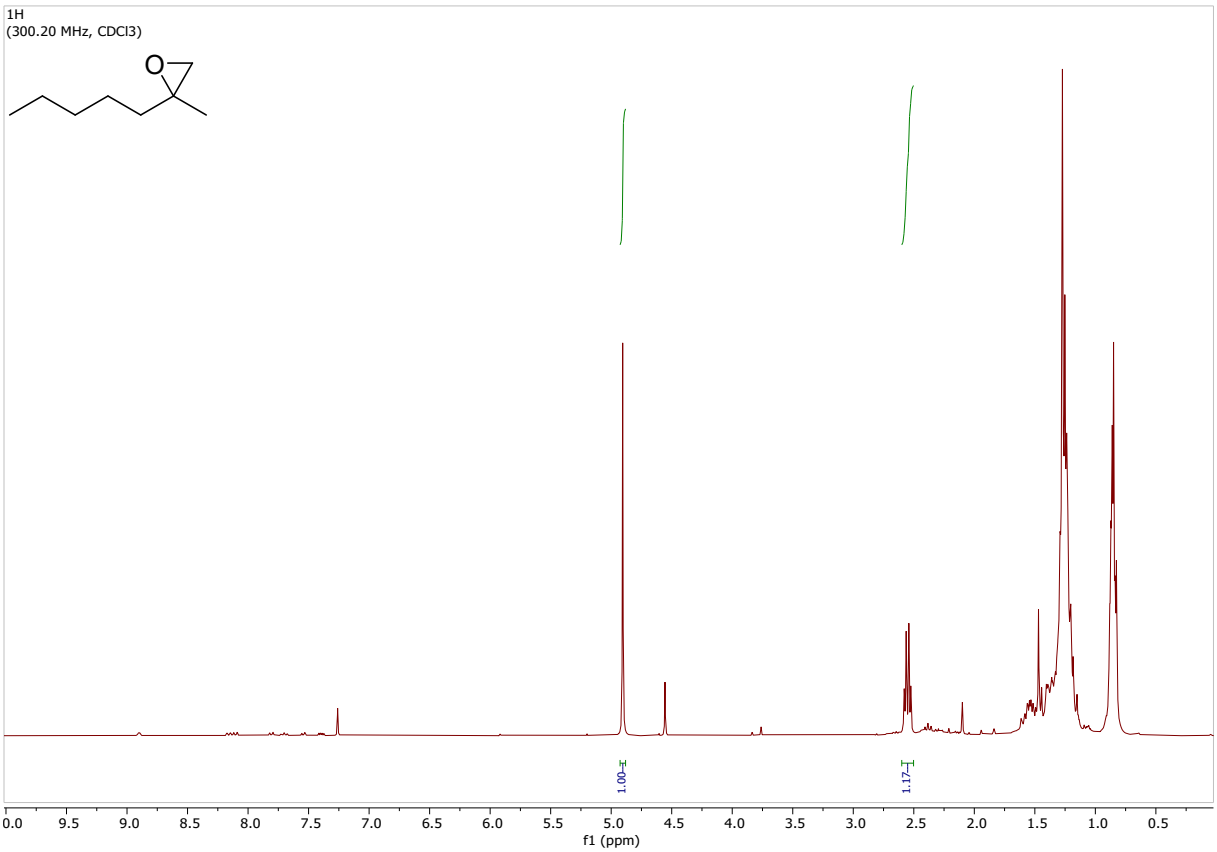
trans-2,3-Epoxyoctane (5h)

Crude Spectrum for Quantification. NMR data matches those previously reported in the literature.[3]



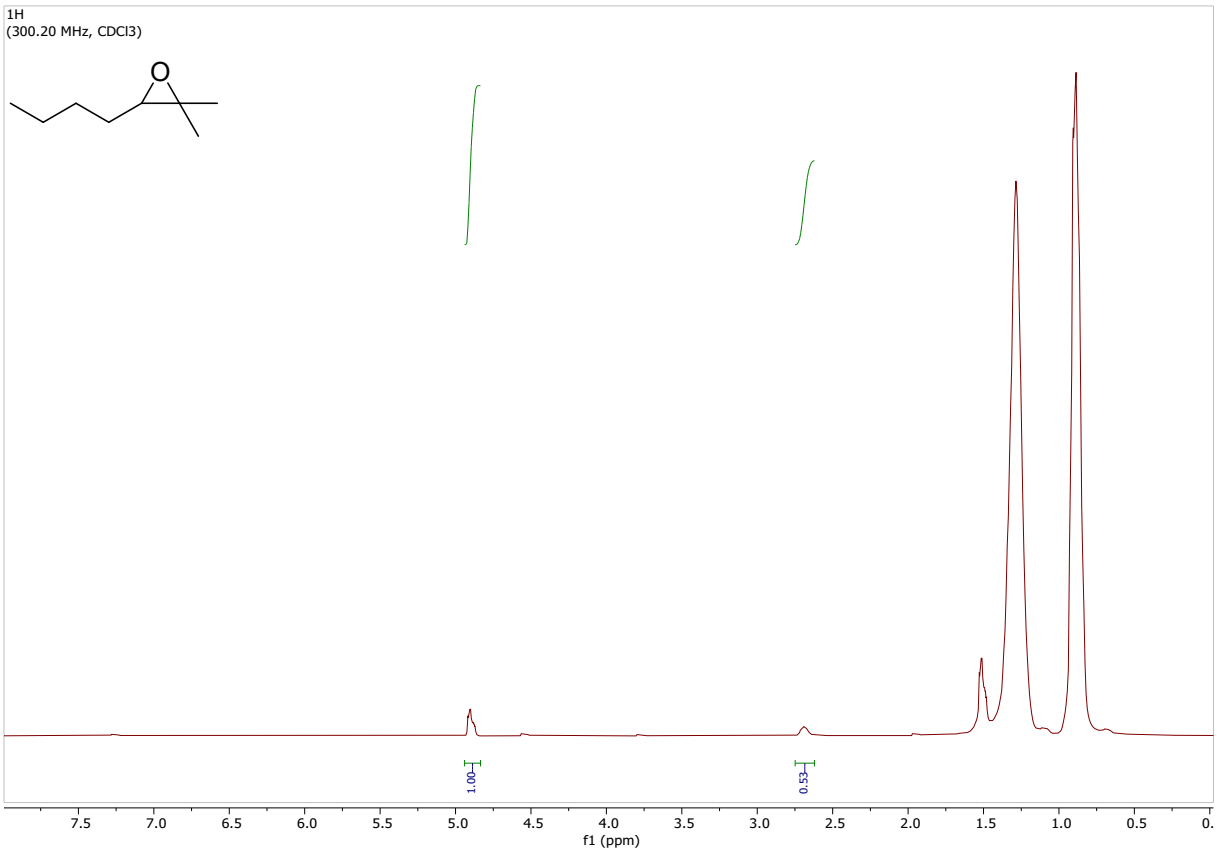
2-Methyl-1,2-epoxyheptane (5i)

Crude Spectrum for Quantification. NMR data matches those previously reported in the literature.[4]



2-Methyl-2,3-epoxyheptane (5j)

Crude Spectrum for Quantification. NMR data matches those previously reported in the literature.[5]



Literature

1. S. Budweg, K. Junge and M. Beller, *Chem. Comm.*, 2019, **55**, 14143.
2. S. Mao, S. Budweg, A. Spannenberg, X. Wen, Y. Yang, Y.-W. Li, K. Junge and M. Beller, *ChemCatChem*, 2021, DOI: https://doi.org/10.1002/cctc.202101668, e202101668.
3. P. Besse and H. Veschambre, *Tetrahedron Asymm.*, 1993, **4**, 1271-1285.
4. A. K. Hubbell, A. M. LaPointe, J. R. Lamb and G. W. Coates, *J. Am. Chem. Soc.*, 2019, **141**, 2474-2480.
5. M. A. Goodman and M. R. Detty, *Synlett*, 2006, **2006**, 1100-1104.