Supporting Information

A Manganese-based Catalyst System for General Oxidations of Unactivated Olefins, Alkanes, and Alcohols

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Table of Contents

General Remarks

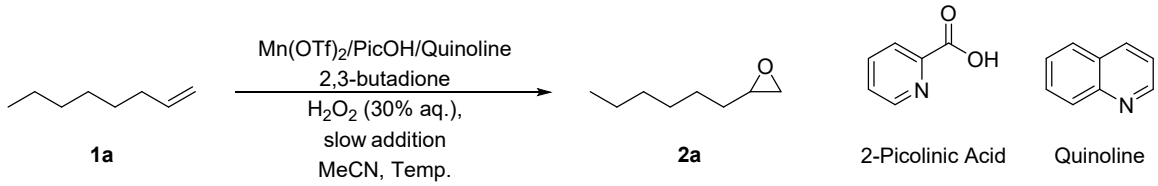
Chemicals used in this work were purchases from ABCR, BLD Pharm, Sigma Aldrich and TCI and used without further purification, unless otherwise stated. All reactions were carried out under ambient conditions, unless otherwise specified. Solvents used for reactions were HPLC grade. Solvents used for chromatography 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).

Optimization of the Reaction Conditions

Variation of numerical parameters as initial screening

Testing the reactivity of this quinoline-promoted epoxidation system we started with conditions close to our previously reported manganese-pincer protocol and consecutively reduced the amount of the employed catalyst, additives etc. to test where the lower limits are, and which respective ratios are necessary. In this initial screening effort the catalyst loading was reduced to 0.25 mol% and the required amount of quinoline to 5 mol%, giving 37% yield of 1,2-epoxyoctane **2a** (entry 12). Further variations of numerical parameters will be conducted at later stages of the optimization process.

Table S1: Initial screening of numerical parameters and ratios for manganese-catalysed epoxidation of 1-octene.

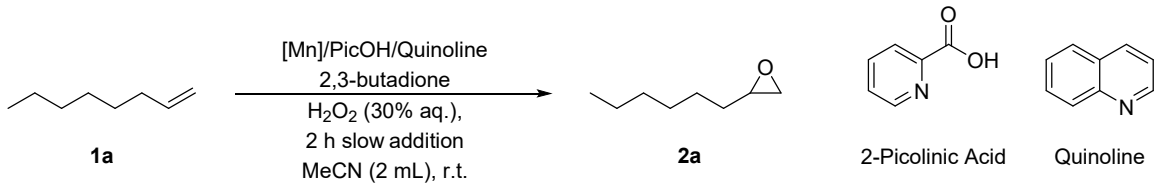


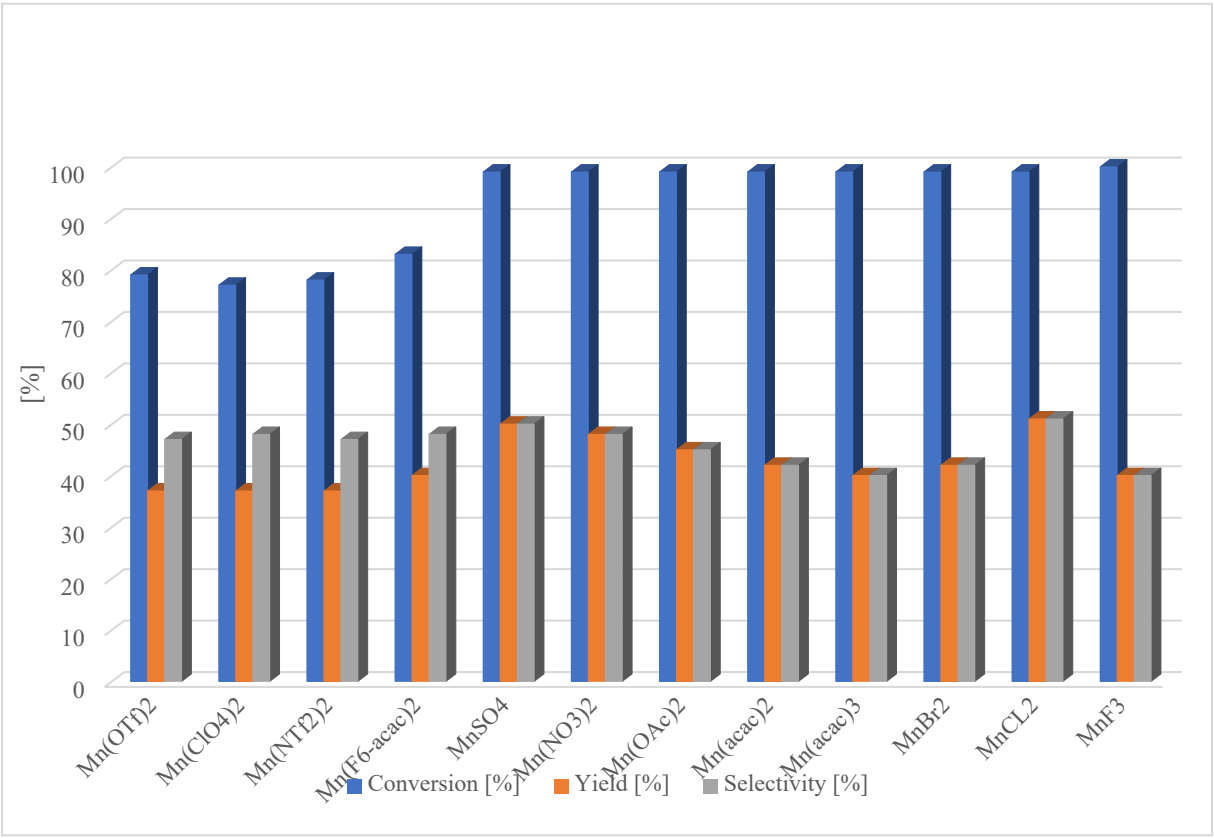
Entry	$Mn(OTf)_2$ [mol%]	PicOH [mol%]	Quinoline [mol%]	2,3-Butadione [eq.]	H_2O_2 [eq.]	Conc. [M]	Temp. [°C]	Conv. (1a) [%]	Yield (2a) [%]	Sel. (2a) [%]
1	5	10	30	0.5	5	0.125	rt	59	24	41
2	5	-	30	0.5	5	0.125	rt	3[a]	0	0
3	5	20	30	**0.25**	5	0.125	rt	13[a]	9	69
4	5	**20**	**10**	0.5	5	0.125	rt	27	0	0
5	5	**20**	30	0.5	5	0.125	rt	41	25	61
6	5	10	30	0.5	**2**	0.125	rt	44	13	30
7	**1**	**5**	30	0.5	5	0.125	rt	66	24	36
8	-	5	30	0.5	5	0.125	rt	36	6	17
9	1	5	30	0.5	5	**0.250**	rt	72	33	46
10	**0.5**	**5**	30	0.5	5	0.250	rt	78	34	44
11	0.5	5	**15**	0.5	5	0.250	**0 °C**	72	32	44
12	**0.25**	**5**	**5**	0.5	5	0.250	rt	79	37	47
13	**0.025**	**0.5**	**0.5**	0.5	5	0.250	rt	63	27	43

Conversion and yield determined by GC analysis with hexadecane as IST, **a**: 30 min reaction time,
Reaction conditions: The indicated amount of substrate, manganese precursor, picolinic acid, 2,3-butadione and quinoline were stirred in MeCN at the indicated temperature for 2 h with slow addition of H_2O_2 (30% aq., diluted in MeCN) *via* syringe pump.

Precursor Screening

Of note, for the precursor screening stock solutions needed to be prepared as weighing the amount for one catalytic reaction is too inaccurate at these low catalyst loadings. Solubility issues occurred with MnF_3 and $Mn(SO_4)_2$, which is why the latter was not used for the comparison of the best working precursors $MnNO_3$ and $MnCl_2$.





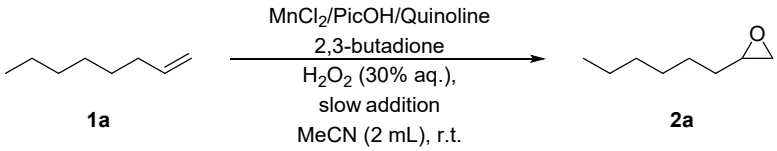
Conversion and yield determined by GC analysis with hexadecane as IST. Reaction conditions: 0.5 mmol substrate (0.250 M), 0.25 mol% manganese precursor, 5 mol% picolinic acid, 5 mol% quinoline, 0.5 eq. 2,3-butadione, MeCN (2 mL), 25 °C, 2 h slow addition of H_2O_2 (30% aq., 5 eq., diluted in MeCN) *via* syringe pump.

Figure S1: Screening of different manganese precursors for epoxidation of 1-octene.

Second variation of numerical parameters after precursor screening

A second, minor screening of numerical parameters was conducted after identifying the best precursor. Here, we reduced the reaction time and the amount of oxidant to find conditions where only partial conversion of **1a** is achieved (Table S2, entry 3). Thus, we will be able to better observe changes in the reactivity of this system during the upcoming screening efforts.

Table S2: Further variation of numerical parameters for manganese-catalysed epoxidation of 1-octene.



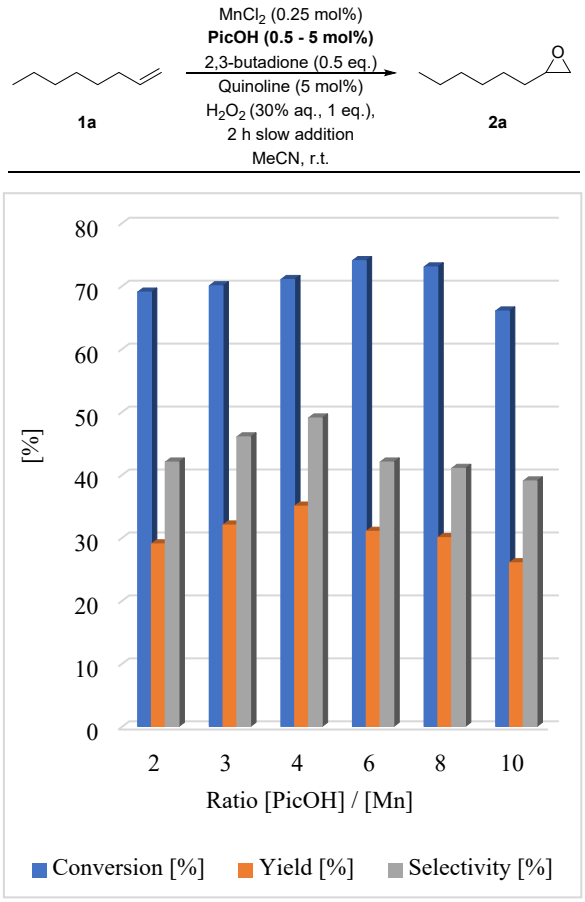
1a **2a**

Entry	Variation from standard conditions	Conv. (1a) [%]	Yield (2a) [%]	Sel. (2a) [%]
1	None	99	51	51
2	2.5 eq. H_2O_2	97	49	51
3	1.0 eq. H_2O_2	66	26	39
4	0.5 h slow addition 1.0 eq. H_2O_2	51	16	31
5	0.5 h slow addition 1.5 eq. H_2O_2	62	25	40

Conversion and yield determined by GC analysis with hexadecane as IST. Reaction conditions: 0.5 mmol substrate (0.250 M), 0.25 mol% manganese(II)chloride, 5 mol% picolinic acid, 5 mol% quinoline, 0.5 eq. 2,3-butadione, MeCN (2 mL), 25 °C, 2 h slow addition of H_2O_2 (30% aq., 5 eq., diluted in MeCN) *via* syringe pump.

Experiments regarding the required amount of picolinic acid

The best results were obtained employing a 4-fold excess of picolinic acid to $MnCl_2$.



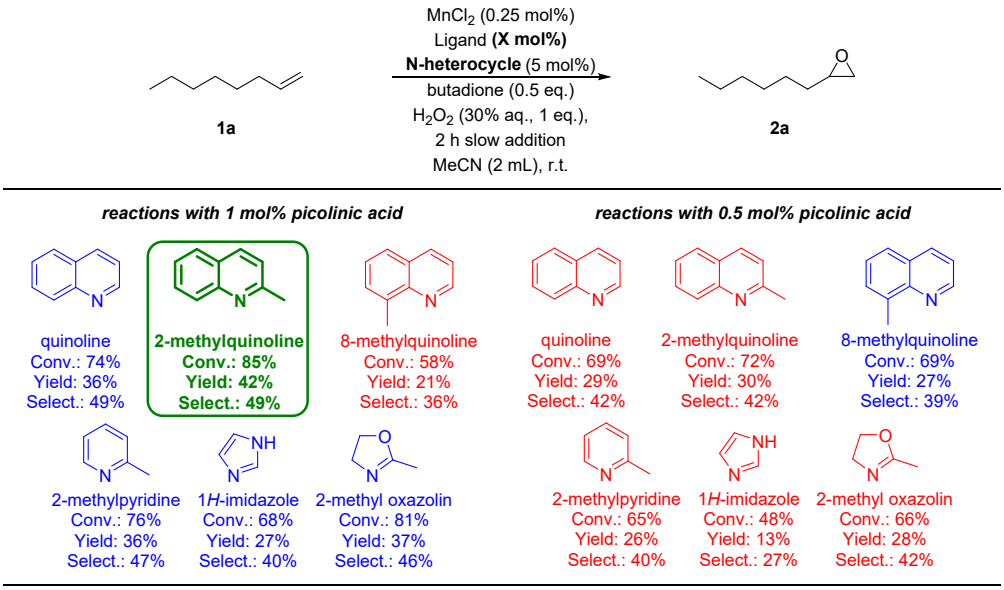
Conversion and yield determined by GC analysis with hexadecane as IST. Reaction conditions: 0.5 mmol substrate (0.250 M), 0.25 mol% manganese(II)chloride, X mol% picolinic acid, 5 mol% quinoline, 0.5 eq. 2,3-butadione, MeCN (2 mL), 25 °C, 2 h slow addition of H_2O_2 (30% aq., 1 eq., diluted in MeCN) *via* syringe pump.

Figure S2: Variation of the [PicOH] : [Mn] ratio.

Comparison of selected heterocycles at different ligand concentrations.

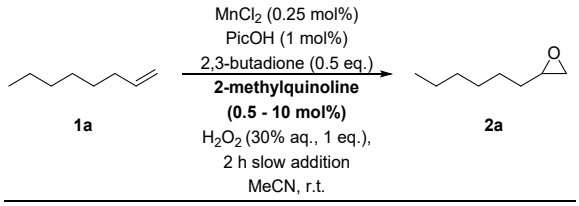
Having observed the pronounced difference between a 2-methyl and an 8-methyl substituted quinoline, prompted us to investigate the interplay of ligand concentration and additive concentration. Employment of a few selected heterocycles at lower ligand concentration led to the expected results (see Figure S2), giving lower conversions and yields of the products. However, in contrast to all other tested compounds, the sterically hindered 8-methylquinoline gave a better yield of **2a** at lower ligand concentration than at higher ligand concentration (see Table S3). This could indicate that a coordination of the quinoline moiety to the metal center is relevant for the reaction efficiency. The negative steric effect of 8-methylquinoline is less pronounced, when there is less ligand inside the reaction which possibly leads to species with only one picolinic acid ligand and one coordinated 8-methylquinoline, rather than two picolinic acid ligands (see literature)[1-3] with one heterocyclic moiety. In the latter case, the steric effect of the 8-methyl group could negatively influence the reaction by preventing the formation of the active (oxidation) complex while in the former case this effect would be less relevant.

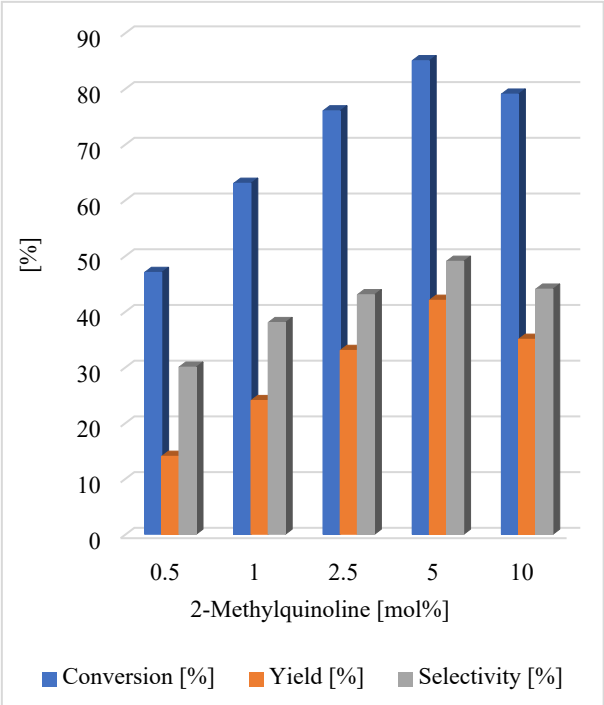
Table S3: Comparison of selected heterocycles at different ligand concentrations.



Conversion and yield determined by GC analysis with hexadecane as IST. Reaction conditions: 0.5 mmol substrate (0.250 M), 0.25 mol% manganese(II)chloride, 1 mol% or 0.5 mol% picolinic acid, 5 mol% N-heterocycle, 0.5 eq. 2,3-butadione, MeCN (2 mL), 25 °C, 2 h slow addition of H_2O_2 (30% aq., 1 eq., diluted in MeCN) *via* syringe pump.

Investigation of the required amount of 2-methylquinoline as additive



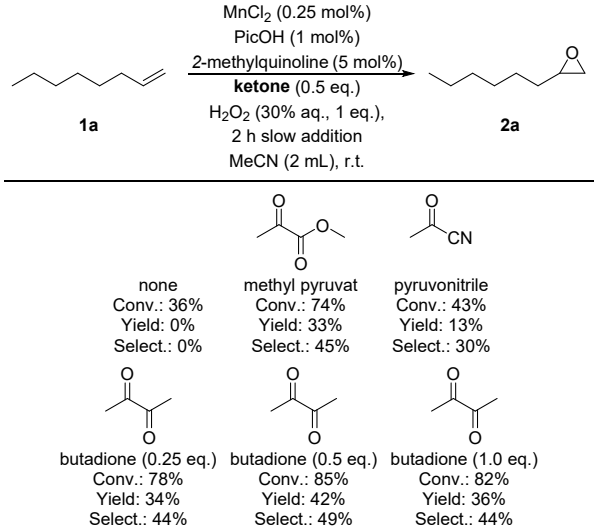


Conversion and yield determined by GC analysis with hexadecane as IST. Reaction conditions: 0.5 mmol substrate (0.250 M), 0.25 mol% manganese(II)chloride, 1 mol% picolinic acid, 0.5 - 10 mol% 2-methylquinoline, 0.5 eq. 2,3-butadione, MeCN (2 mL), 25 °C, 2 h slow addition of H_2O_2 (30% aq., 1 eq., diluted in MeCN) *via* syringe pump.

Figure S3: Variation of the 2-methylquinoline amount.

Screening of ketones and verification of their necessity

Table S4: Screening of different ketones additives.

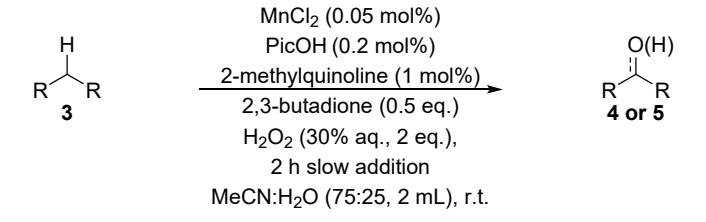


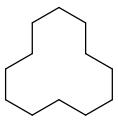
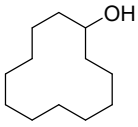
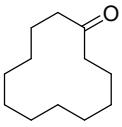
Conversion and yield determined by GC analysis with hexadecane as IST. Reaction conditions: 0.5 mmol substrate (0.250 M), 0.25 mol% manganese(II)chloride, 0.5 mol% picolinic acid, 5 mol% 2-methylquinoline, 0.5 eq. ketone, MeCN (2 mL), 25 °C, 2 h slow addition of H_2O_2 (30% aq., 1 eq., diluted in MeCN) *via* syringe pump.

Short optimization for C-H oxidation model substrates

Under standard epoxidation reaction conditions, cyclohexane **3a** was converted with 49% conversion and 22% yield to cyclohexanone **5a**, with only traces of cyclohexanol **4a** being detected, demonstrating the selectivity of this protocol towards the ketone. Decreasing the amount of substrate to 0.25 mmol, we observed higher conversion (63%) and yield (30%) of cyclohexanone **5a** with no cyclohexanol **4a** being detected. Since the solubility of cyclic alkanes is rather poor in an MeCN:H_2O (75:25) solvent mixture, we switched to the less polar ratio (MeCN:H_2O = 95:5), obtaining almost identical conversion of cyclohexane **3a**. However, the yield of cyclohexanone **5a** was raised to 43% (only traces of cyclohexanol **4a** were observed). We also performed the same reactions with cyclododecane **3b**. Probably due to poor solubility, we observed 17% conversion and 5% yield of cyclododecanone **5b**. Halving the substrate concentration also improved on this result, affording 25% conversion and 10% of the corresponding ketone product **5b**. Substituting for the less polar solvent mixture (MeCN:H_2O = 95:5) led to a significant increase in reactivity, giving 65% conversion and 31% yield of the desired ketone **5b** (with traces of cyclododecanol **4b**). Increasing the reaction temperature to 40 °C or increasing the reaction/slow addition time did not change the reaction outcome (see Table S5).

Table S5: Cyclohexane and cyclododecane as model substrates for manganese-catalysed C-H oxidation.

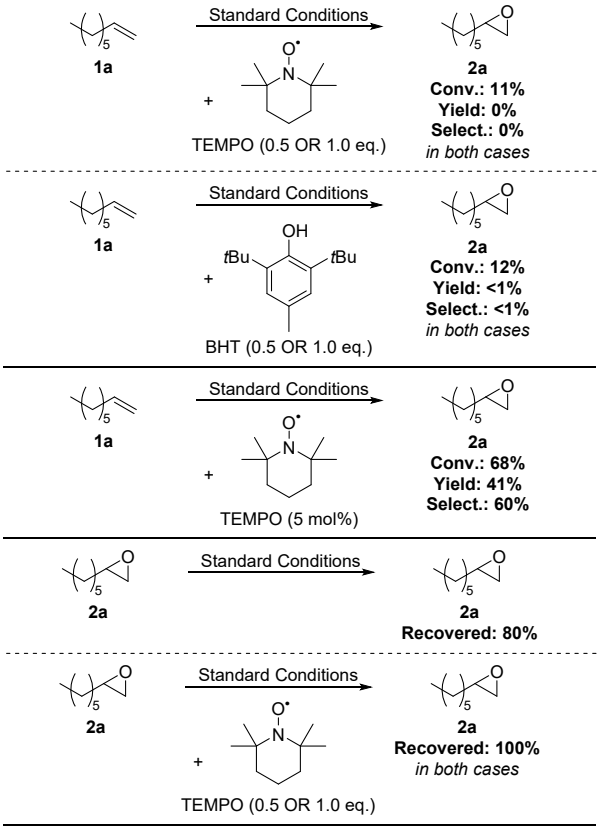


Substrate	Product(s)	
		
3a	**4a**	**5a**
Conv.: 49%	traces	22%
Conv.: 63%[a]	0%[a]	30%[a]
Conv.: 60%[b]	traces[b,c]	43%[b,c]
		
3b	**4b**	**5b**
Conv.: 17%	traces	5%
Conv.: 25%[a]	traces[a]	10%[a]
Conv.: 65%[b]	traces[b,c]	31%[b,c]

Conversion and yield determined by GC analysis with hexadecane as IST. Reaction conditions: 0.5 mmol substrate (0.250 M), 0.05 mol% $MnCl_2$, 0.2 mol% picolinic acid, 1 mol% 2-methylquinoline, 0.5 eq. 2,3-butadione, MeCN:H_2O (75:25, 2 mL), 25 °C, 2 h slow addition of H_2O_2 (30% aq., 2 eq., diluted in MeCN) *via* syringe pump. a: 0.25 mmol of substrate employed, b: MeCN:H_2O (95:5) as solvent, c: same yields were obtained at 40 °C reaction temperature and/or reaction/slow addition times of up to 16 h.

Experiments with radical scavengers

Adding (stoichiometric) TEMPO to standard reaction conditions resulted in 11% conversion with no product formation. Interestingly, there is no difference in the reaction outcome between employing 0.5 equivalent or 1.0 equivalent of the radical scavenger. Almost identical results were obtained when performing the same reactions with BHT. Employing 5 mol% TEMPO, partial inhibition of this system was observed, obtaining 68% conversion and 41% yield, respectively. Of note, the selectivity is barely influenced here. This suggests that these compounds might not act as radical scavengers but rather that they interfere with the catalyst, *e.g.*, blocking the complex or competing with the (co-)ligand.



Conversion and yield determined by GC analysis with hexadecane as IST. Reactions conditions: 0.5 mmol substrate (0.250 M), 0.05 mol% $MnCl_2$, 0.2 mol% picolinic acid, 1 mol% 2-methylquinoline, 0.5 eq. 2,3-butadione, X mol% TEMPO or BHT, MeCN:H_2O (75:25, 2 mL), 25 °C, 2 h slow addition of H_2O_2 (30% aq., 2 eq., diluted in MeCN) *via* syringe pump.

Scheme S1: Influence of TEMPO and BHT on the reaction outcome and product stability.

General Procedures

General procedure for the epoxidation of olefins

An 8 mL glass vial equipped with a Teflon coated stirring bar was charged with stock solutions of $MnCl_2$ (0.25 µmol, 31.5 µg, 0.05 mol% in 250 µL H_2O), picolinic acid (1 µmol, 0.123 mg, 0.2 mol% in 250 µL H_2O) and freshly distilled 2-methylquinoline (5.0 µmol, 0.716 mg, 1.0 mol% in 250 µL MeCN). The resulting mixture was stirred for 5 minutes. Next, a solution of 2,3-butadione (0.25 mmol, 43 mg, 0.5 eq. in 250 µL MeCN) was added. The resulting mixture was further diluted with MeCN to a total volume of 2 mL (MeCN:H_2O = 75:25) and stirred for additional 5 minutes. Then, 1-octene (0.5 mmol, 56.1 mg, 0.250 M) was added. Next, a solution of hydrogen peroxide (H_2O_2) (1.0 mmol, 2.0 eq., 104 µL, 30% aq.) in MeCN (896 µL) was added *via* a syringe pump to the reaction mixture over the course of 2 hours.

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 by 5-point calibration of the respective compounds.

For NMR analysis the mixture was extracted with *n*-pentane or Et_2O, washed with water and saturated aqueous NaCl solution, dried with Na_2SO_4, filtered and concentrate *in vacuo*. Then, dibromomethane was added as an internal standard for quantification of the product yield.

For isolation the mixture was extracted with *n*-pentane or Et_2O, washed with water and saturated aqueous NaCl solution, dried with Na_2SO_4, filtered and concentrate *in vacuo*. Then, the dried compound was adsorbed to celite and subjected to flash column chromatography for purification.

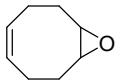
For alcohol oxidation, the same procedure was applied.

General procedure for the oxidation of alkanes

An 8 mL glass vial equipped with a Teflon coated stirring bar was charged with stock solutions of $MnCl_2$ (0.25 µmol, 31.5 µg, 0.1 mol% in 50 µL H_2O), picolinic acid (1.0 µmol, 0.123 mg, 0.4 mol% in 50 µL H_2O) and freshly distilled 2-methylquinoline (5.0 µmol, 0.716 mg, 2.0 mol% in 250 µL MeCN). The resulting mixture was stirred for 5 minutes. Next, a solution of 2,3-butadione (0.25 mmol, 43 mg, 1 eq. in 250 µL MeCN) was added. The resulting mixture was further diluted with MeCN to a total volume of 2 mL (MeCN:H_2O = 95:5) and stirred for additional 5 minutes. Then, cyclohexane (0.25 mmol, 21.0 mg, 0.125 M) was added. Next, a solution of hydrogen peroxide (H_2O_2) (1.0 mmol, 4.0 eq., 104 µL, 30% aq.) in MeCN (896 µL) was added *via* a syringe pump to the reaction mixture over the course of 2 hours. 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 by 5-point calibration of the respective compounds.

Isolated Compounds

(Z)-9-oxabicyclo[6.1.0]non-4-ene (2k-1)



(*Z*)-9-oxabicyclo[6.1.0]non-4-ene

The title compound was prepared according to the general procedure for epoxidation (1.5 eq. H_2O_2 (30% aq.), extraction with *n*-pentane) and obtained as colorless oil after flash column chromatography (eluent: *n*-pentane : Et_2O); (38.5 mg, 62%).

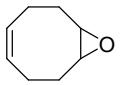
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.57 (ddd, *J* = 5.1, 2.5, 1.0 Hz, 2H), 3.12 – 2.98 (m, 2H), 2.57 – 2.34 (m, 2H), 2.26 – 2.09 (m, 2H), 2.08 – 1.96 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 129.0, 56.9, 28.2, 23.8.

NMR data matches those previously reported in the literature.[4]

Note: Due to the compound volatility, solvent impurities are still visible in the ^{1}H NMR spectrum.

(Z)-9-oxabicyclo[6.1.0]non-4-ene (2k-1) 5 g scale



(*Z*)-9-oxabicyclo[6.1.0]non-4-ene

Large scale epoxidation procedure of cyclooctadiene

A 500 mL round bottom flask equipped with a large Teflon coated stirring bar was charged with $MnCl_2$ (23.1 µmol, 2.9 mg, 0.05 mol%) and picolinic acid (92.4 µmol, 11.4 mg, 0.2 mol%). Then 46 mL H_2O were added, and the solution was stirred for 30 minutes to ensure a homogeneous solution. Next, freshly distilled 2-methylquinoline (4.62 mmol, 66.2 mg, 1.0 mol%) and 100 mL MeCN were added, and the resulting mixture was stirred for another 30 minutes. Followingly, 2,3-butadione (23.1 mmol, 4.0 g, 0.5 eq.) was added and the resulting mixture was further diluted with MeCN to a total volume of 185 mL (MeCN:H_2O = 75:25) and stirred for an additional 10 minutes. Then, cyclooctadiene (46.2 mmol, 5.0 g, 0.250 M) was added. Next, a solution of hydrogen peroxide (H_2O_2) (69.3 mmol, 1.5 eq., 7.2 mL, 30% aq.) in MeCN (85.2 mL) was added *via* four syringes (volume evenly distributed) suspended in a syringe pump to the reaction mixture over the course of 2 hours. After 2 hours (plus another 15 minutes of additional stirring), a few drops of $Na_2S_2O_3$ solution were added to ensure all the H_2O_2 has reacted. Afterwards, the mixture was extracted with pentane three times, washed with water and saturated aqueous NaCl solution, dried with Na_2SO_4, filtered and concentrated *in vacuo*. The residue was adsorbed on celite and purified. The title compound was obtained as a colorless oil after flash column chromatography (eluent: *n*-pentane : Et_2O); (3.1 g, 55%).

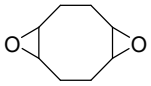
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.64 – 5.48 (m, 2H), 3.11 – 2.94 (m, 2H), 2.53 – 2.33 (m, 2H), 2.20 – 2.09 (m, 2H), 2.08 – 1.98 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 123.0, 56.9, 28.2, 23.8.

NMR data matches those previously reported in the literature.[4]

Note: Due to the compound volatility, solvent impurities are still visible in the ^{1}H NMR spectrum.

5,10-dioxatricyclo[7.1.0.0^{4,6}]decane (2k-2)



5,10-dioxatricyclo[7.1.0.0^{4,6}]decane

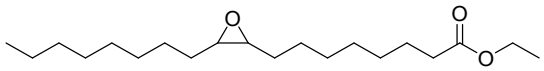
The title compound was prepared according to the general procedure for epoxidation (0.25 mmol substrate, 5 eq. H_2O_2 (30% aq.), extraction with Et_2O) and obtained a pale-yellow, viscous oil after flash column chromatography (eluent: *n*-pentane : Et_2O); (19.3 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.04 – 2.95 (m, 4H), 2.09 – 1.96 (m, 4H), 1.95 – 1.83 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 56.2, 22.2.

NMR data matches those previously reported in the literature.[5]

ethyl 8-(3-octyloxiran-2-yl)octanoate (2v)



ethyl 8-(3-octyloxiran-2-yl)octanoate

The title compound was prepared according to the general procedure for epoxidation (solvent: MeCN:H_2O = 95:5, extraction with *n*-pentane) and obtained as a pale-yellow oil after flash column chromatography (eluent: *n*-pentane : EtOAc); (107 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.12 (q, *J* = 7.1 Hz, 2H), 2.95 – 2.84 (m, 2H), 2.28 (t, *J* = 7.5 Hz, 2H), 1.68 – 1.17 (m, 29H), 0.87 (t, *J* = 6.1 Hz, 2H).

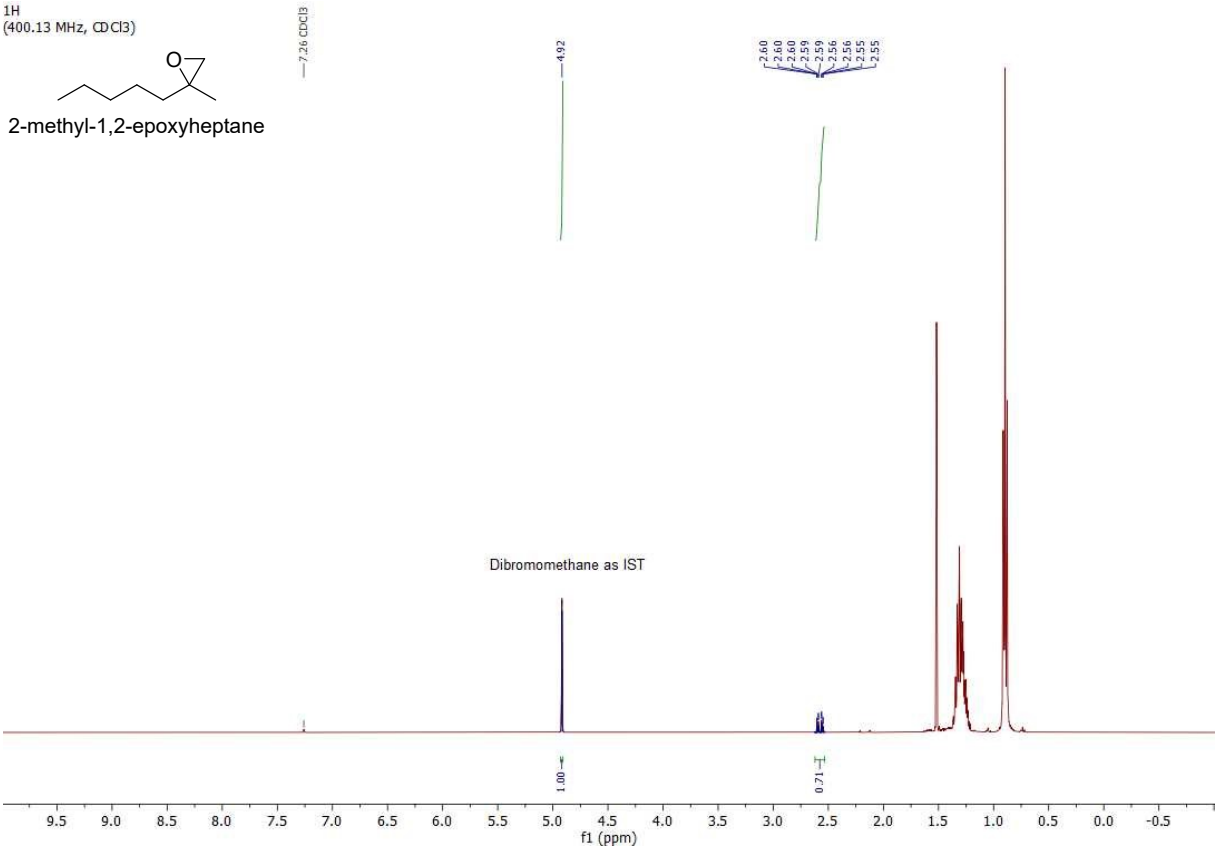
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.8, 60.1, 57.2, 57.2, 34.3, 31.8, 29.5, 29.5, 29.3, 29.2, 29.2, 29.0, 27.8, 27.8, 26.6, 26.5, 24.9, 22.6, 14.2, 14.1.

NMR data matches those previously reported in the literature.[6]

Copies of NMR Spectra

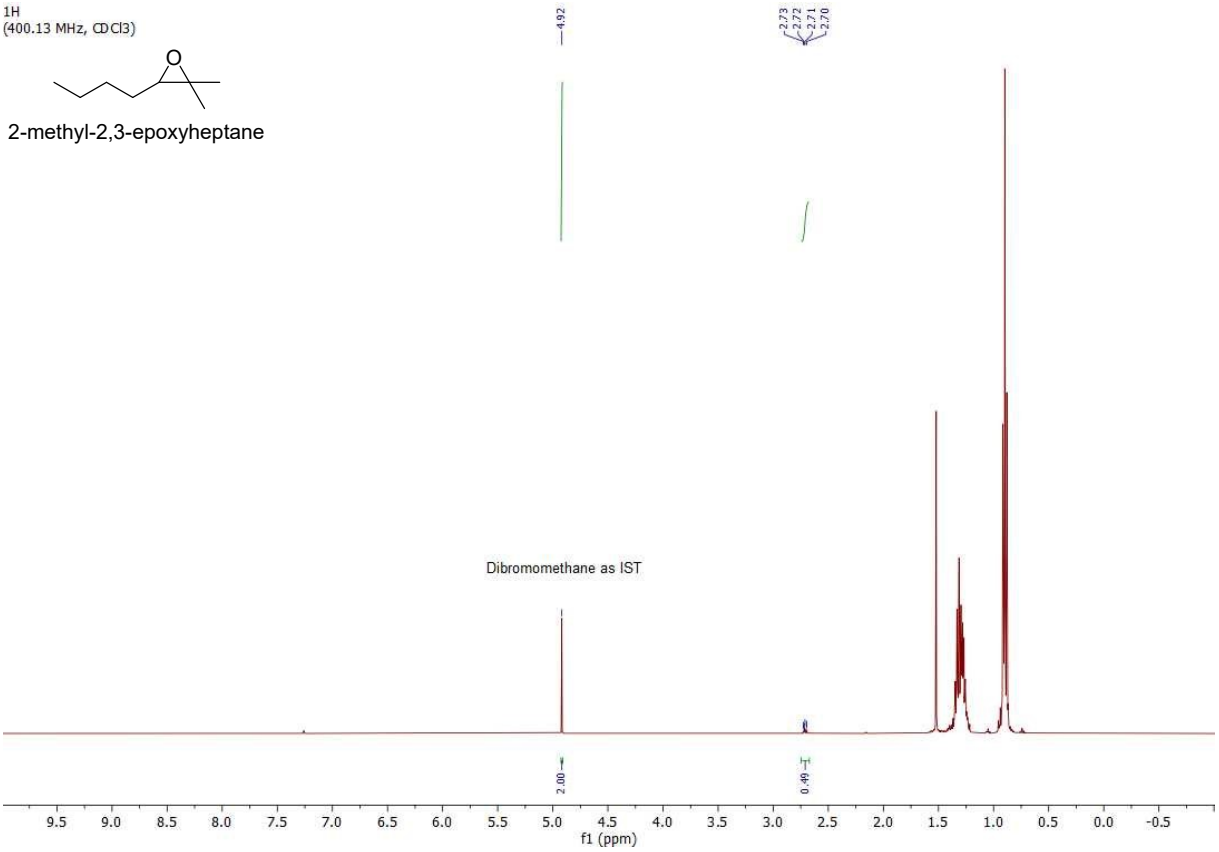
2-methyl-1,2-epoxyheptane (2f)

Crude spectrum for ^{1}H NMR quantification with dibromomethane as internal standard. Data matches those previously reported in the literature.[7]

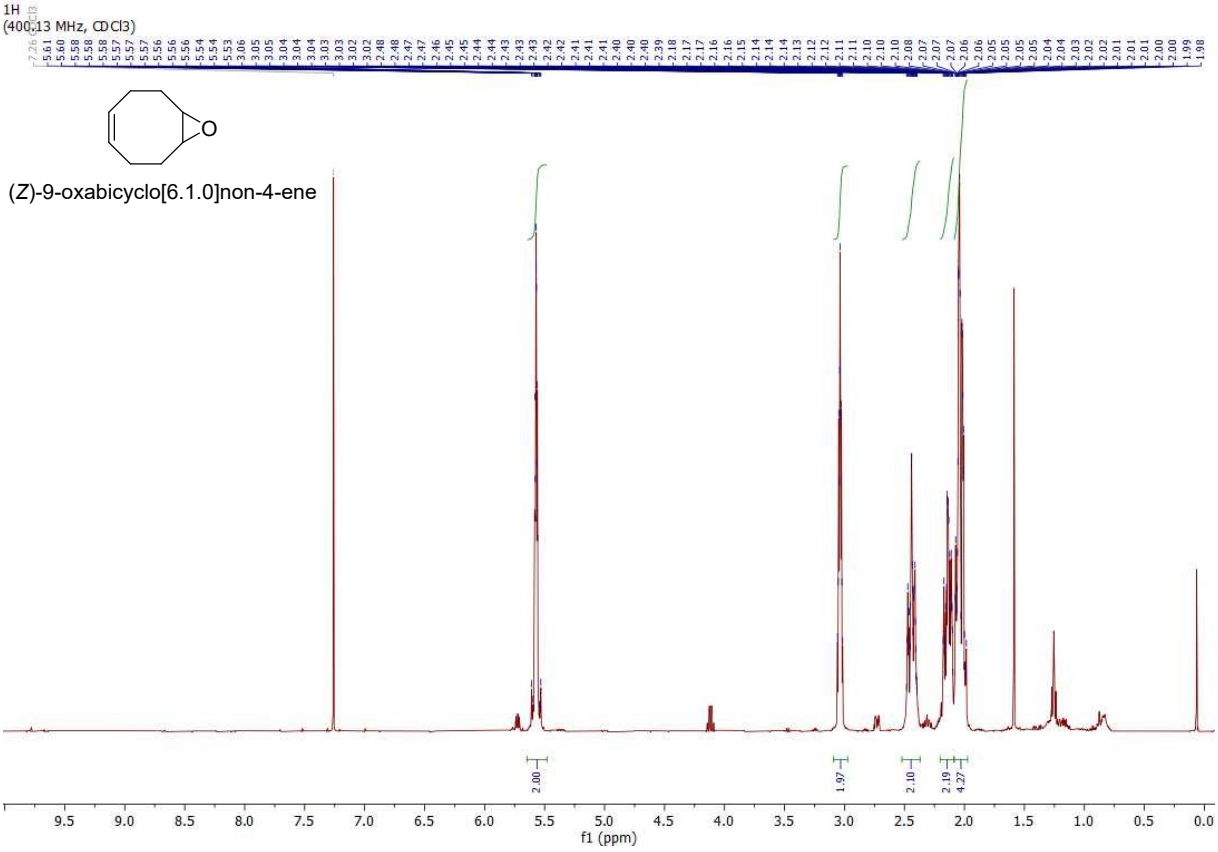


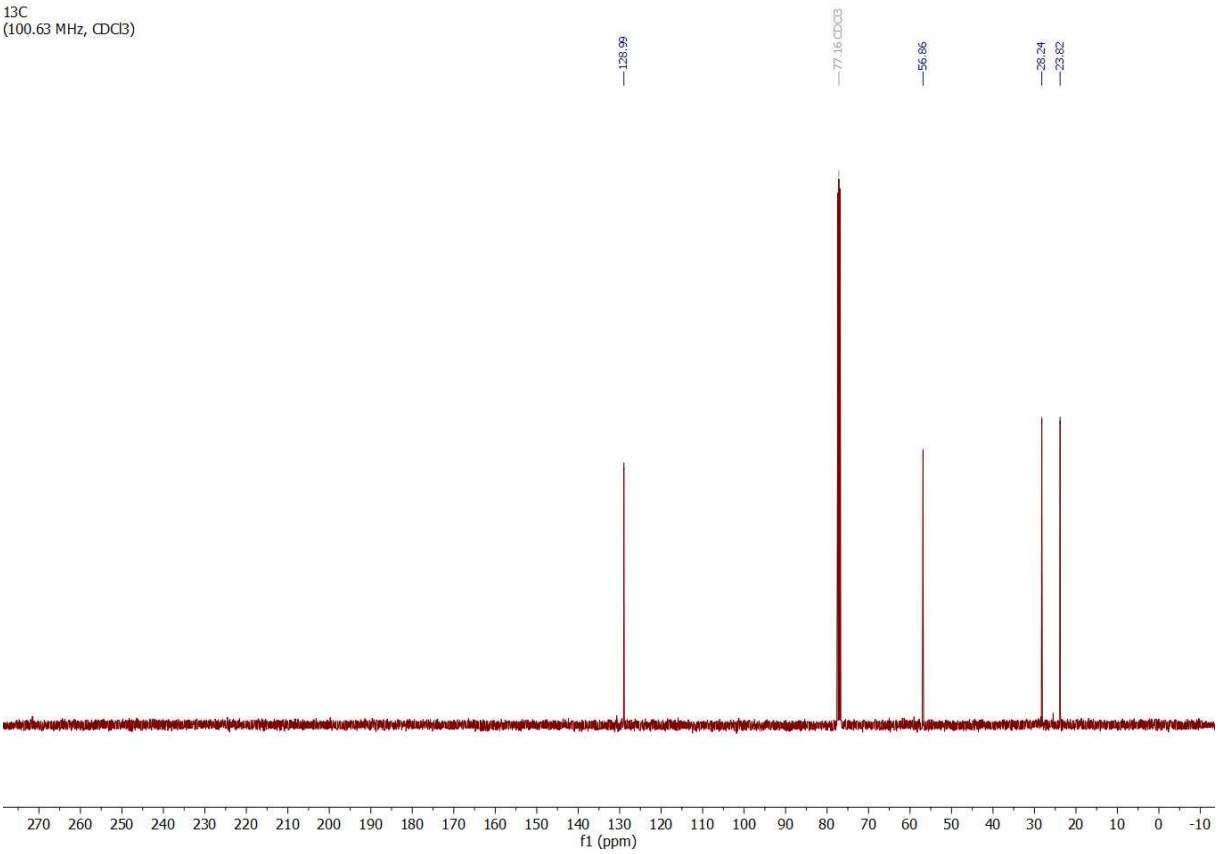
2-methyl-2,3-epoxyheptane (2g)

Crude spectrum for ^{1}H NMR quantification with dibromomethane as internal standard. Data matches those previously reported in the literature.[8]

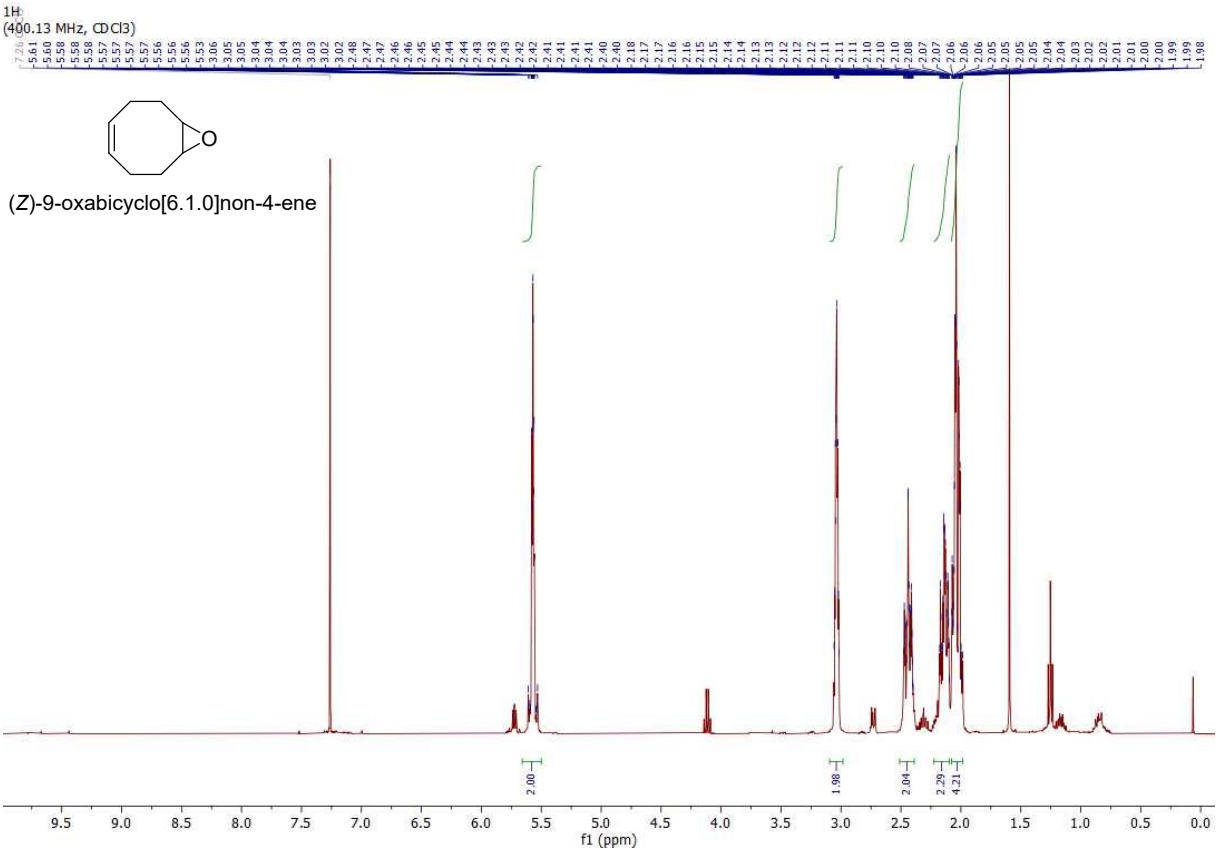


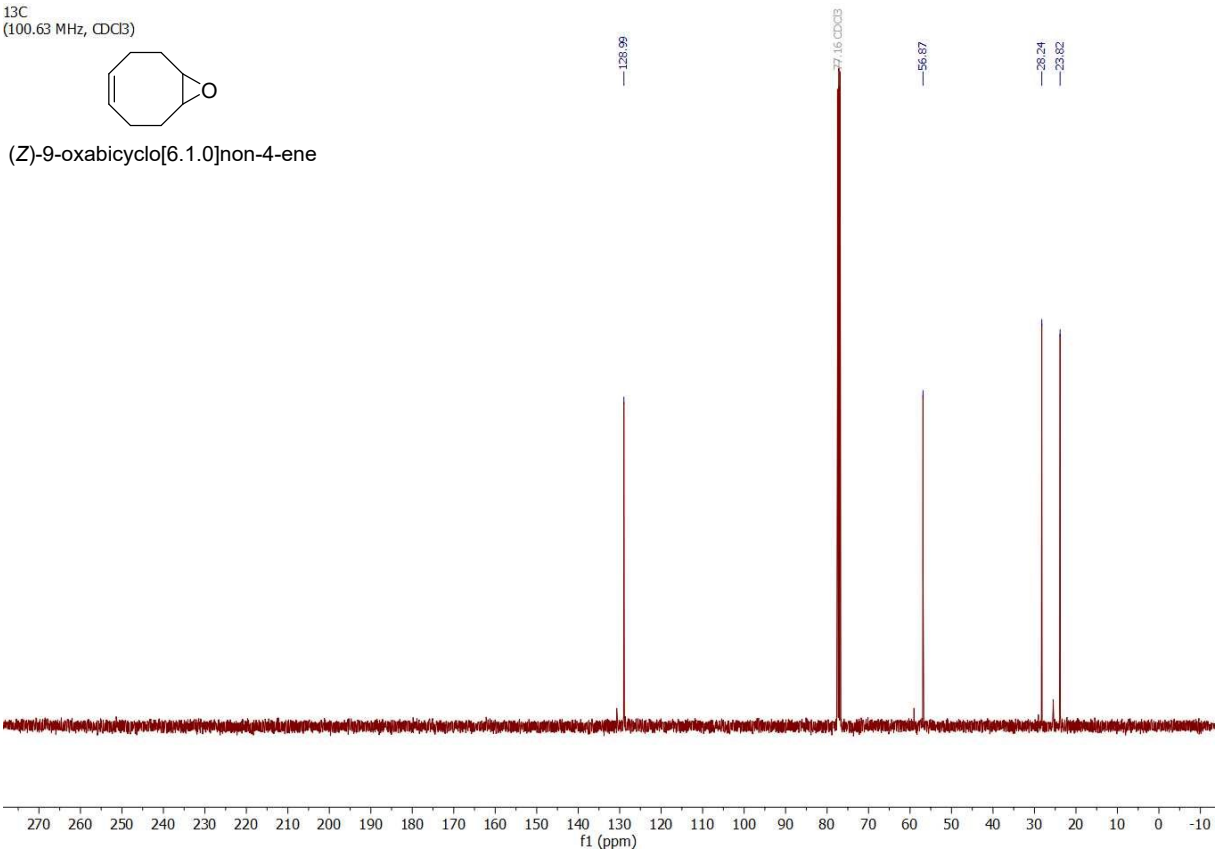
(Z)-9-oxabicyclo[6.1.0]non-4-ene (2k-1)



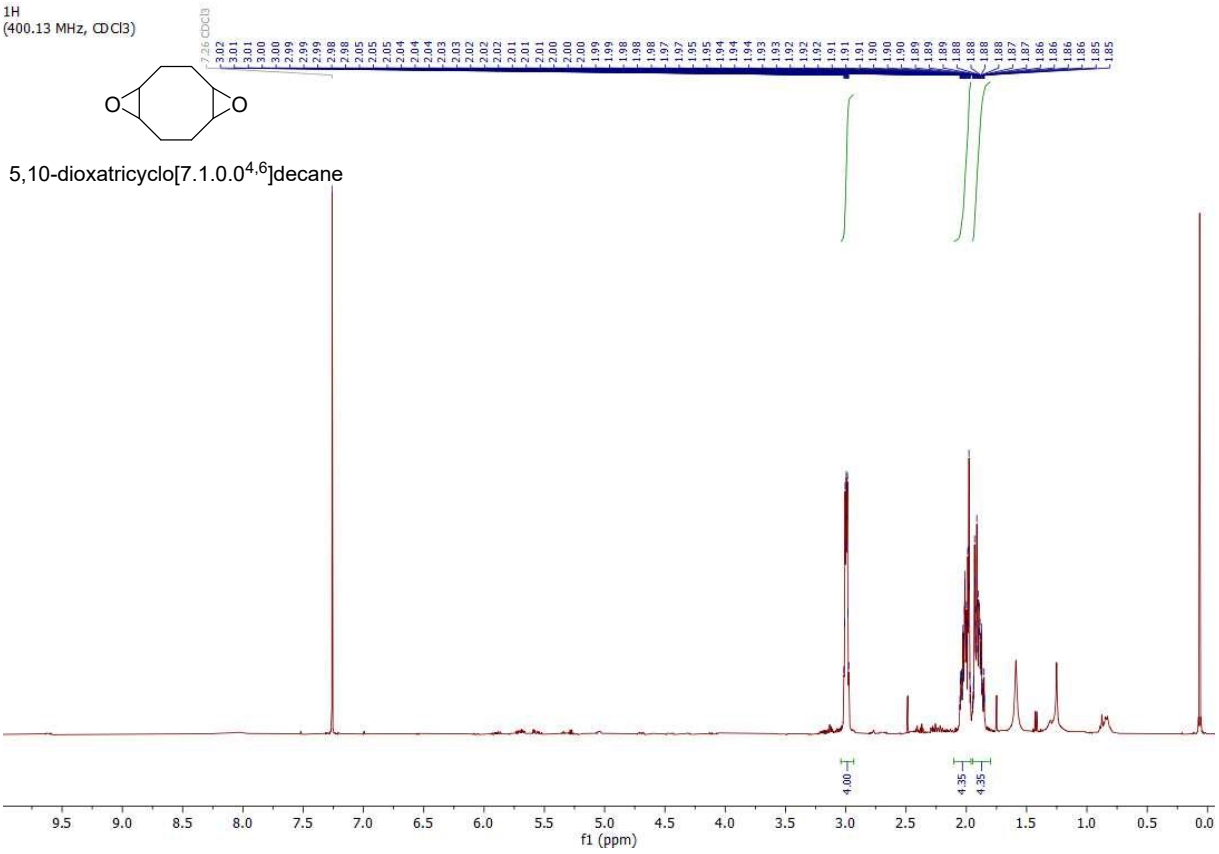


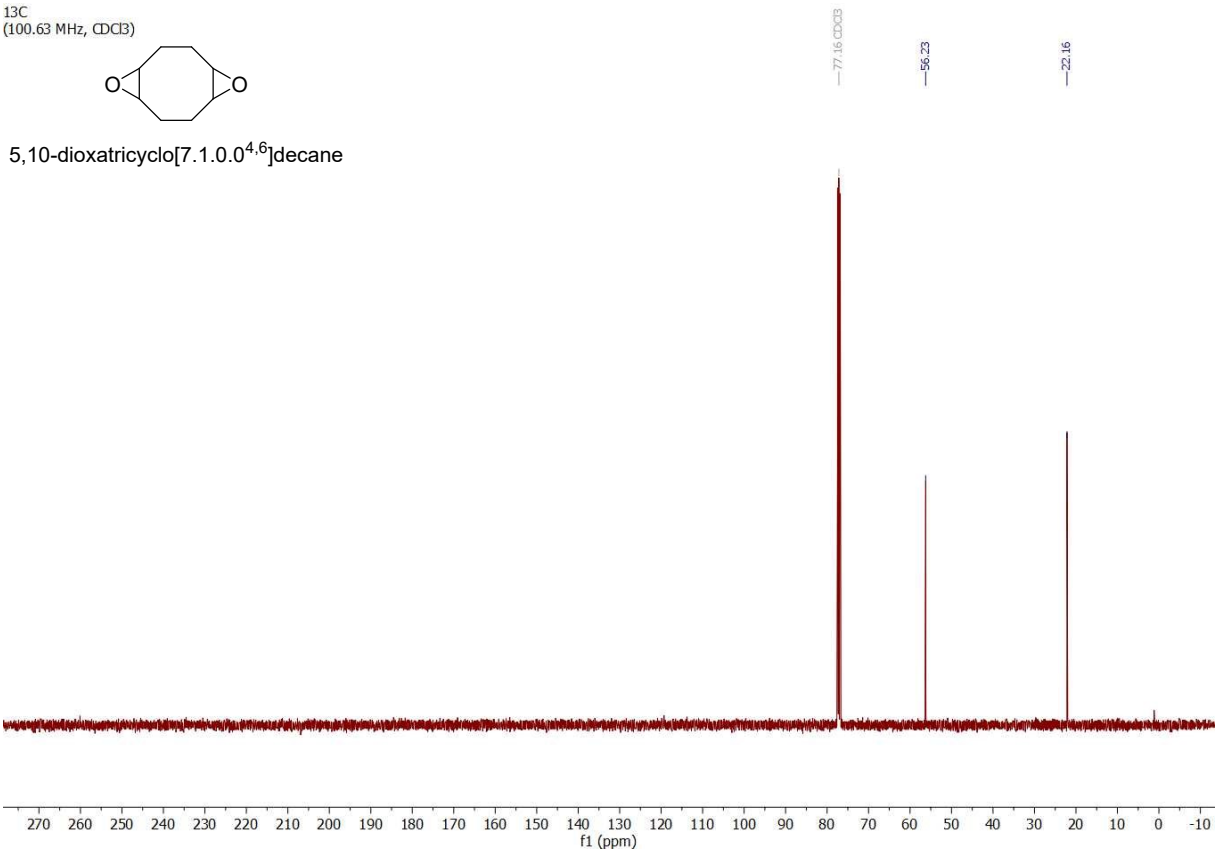
(Z)-9-oxabicyclo[6.1.0]non-4-ene (2k-1) 5 g scale



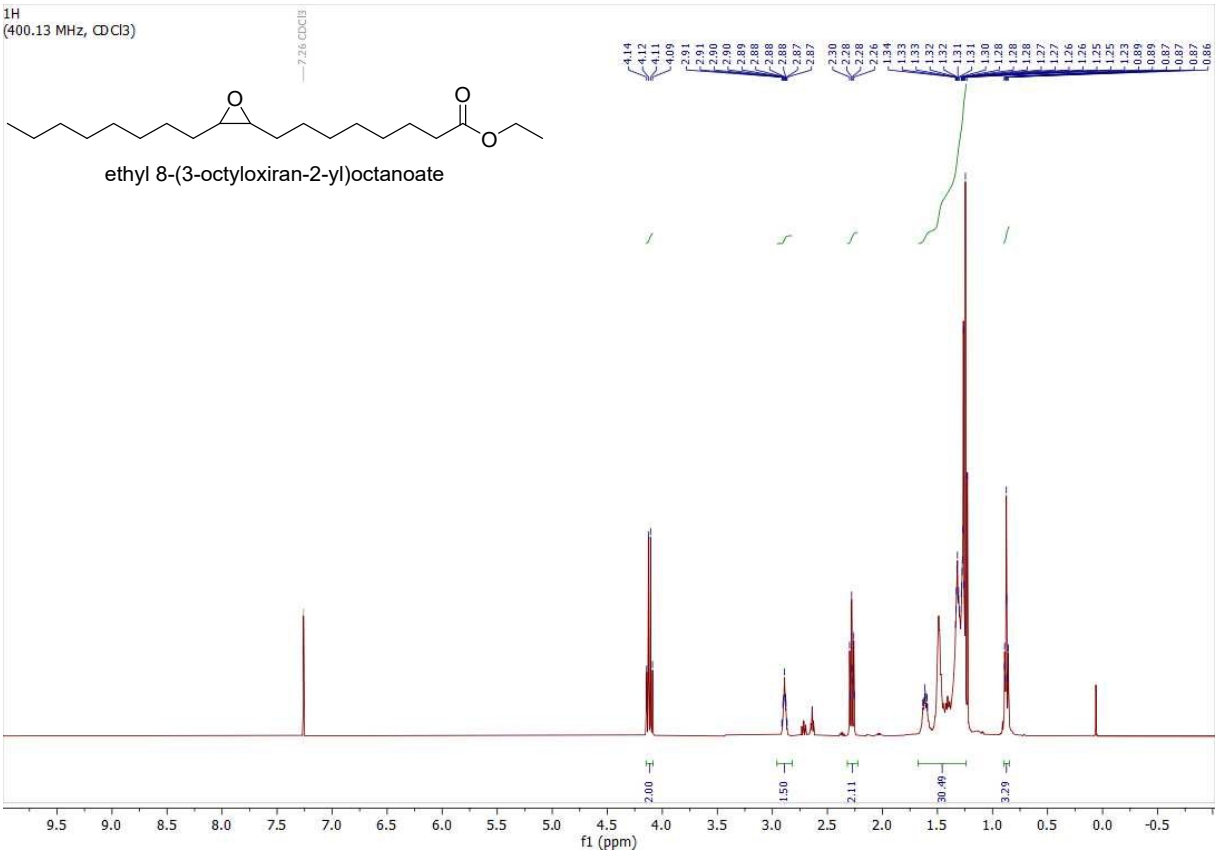


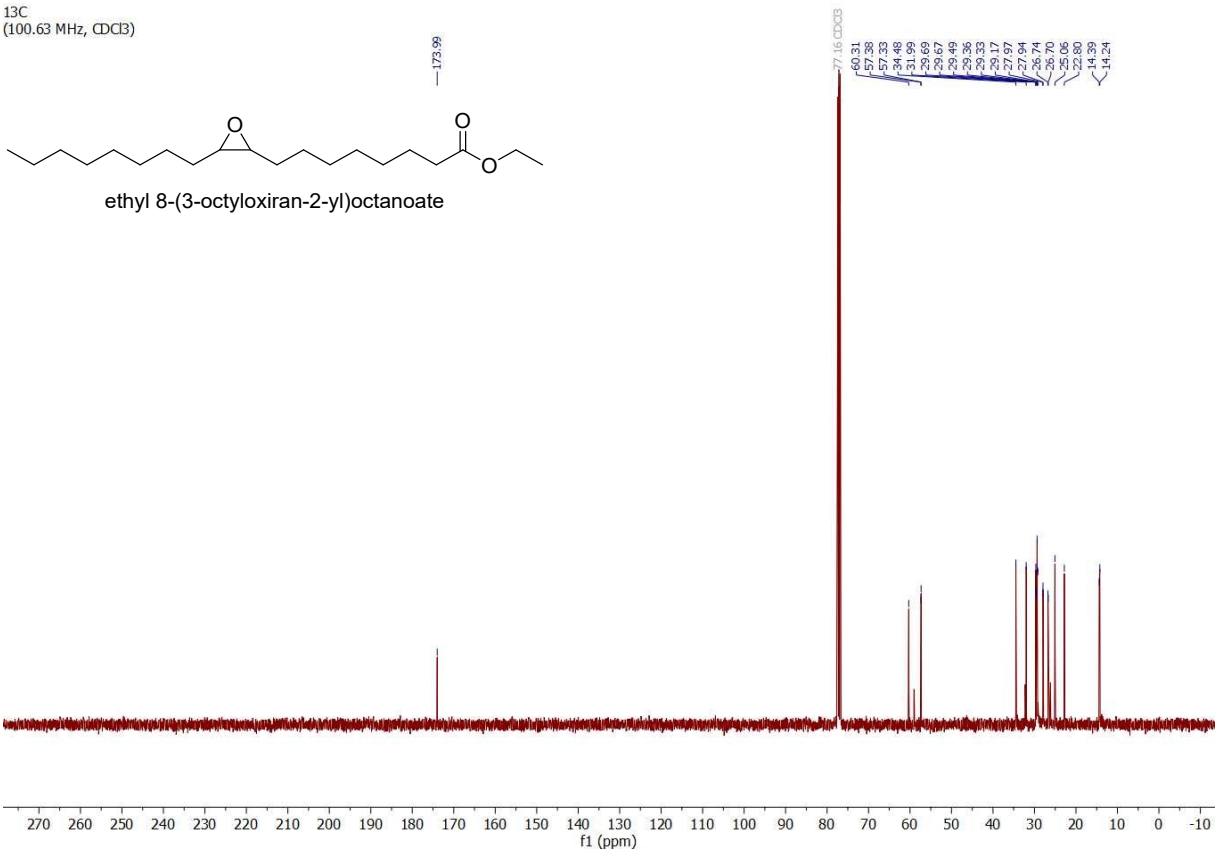
5,10-dioxatricyclo[7.1.0.0^{4,6}]decane (2k-2)





ethyl 8-(3-octyloxiran-2-yl)octanoate (2v)





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