Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Neighbouring effects on catalytic epoxidation by Fe-cyclam in M_2-PDIxCy complexes

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ESI-MS data for [Fe(PDIeCy)](OTf)$_2$]

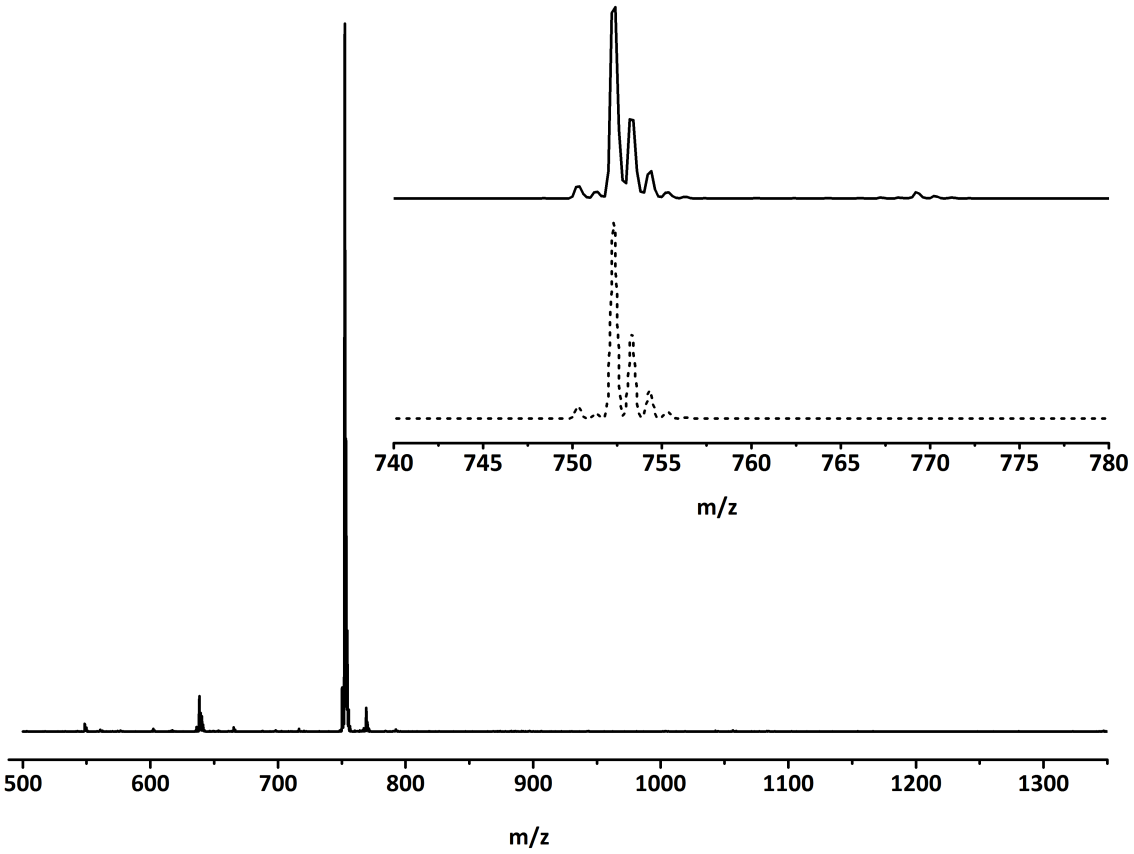


Fig. S1 ESI-MS data for the monometallic [Fe(PDIeCy)](OTf)$_2$]; (m/z: 752.3 [M−(OTf$^-$)]$^+$. The data shows no mass signal corresponding to a bimetallic complex.

Absorption spectrum of [Fe(PDIeCy)](OTf)$_2$]

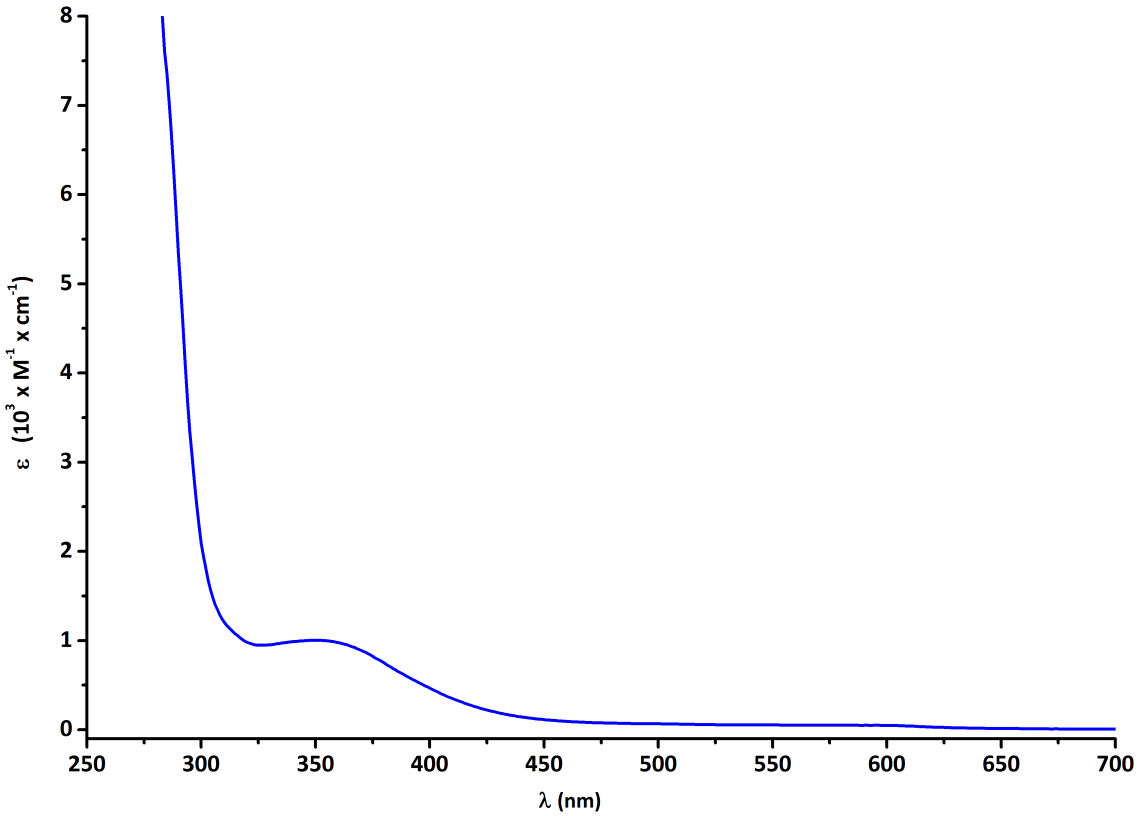


Fig. S2 Absorption spectrum of the monometallic [Fe(PDIeCy)](OTf)$_2$] in MeCN at room temperature; $\lambda_{max}(\varepsilon)$ = 351 nm (995 mol^{-1}dm^{3}cm^{-1}).

^{1}H NMR spectra of compounds 3, 4 and 5

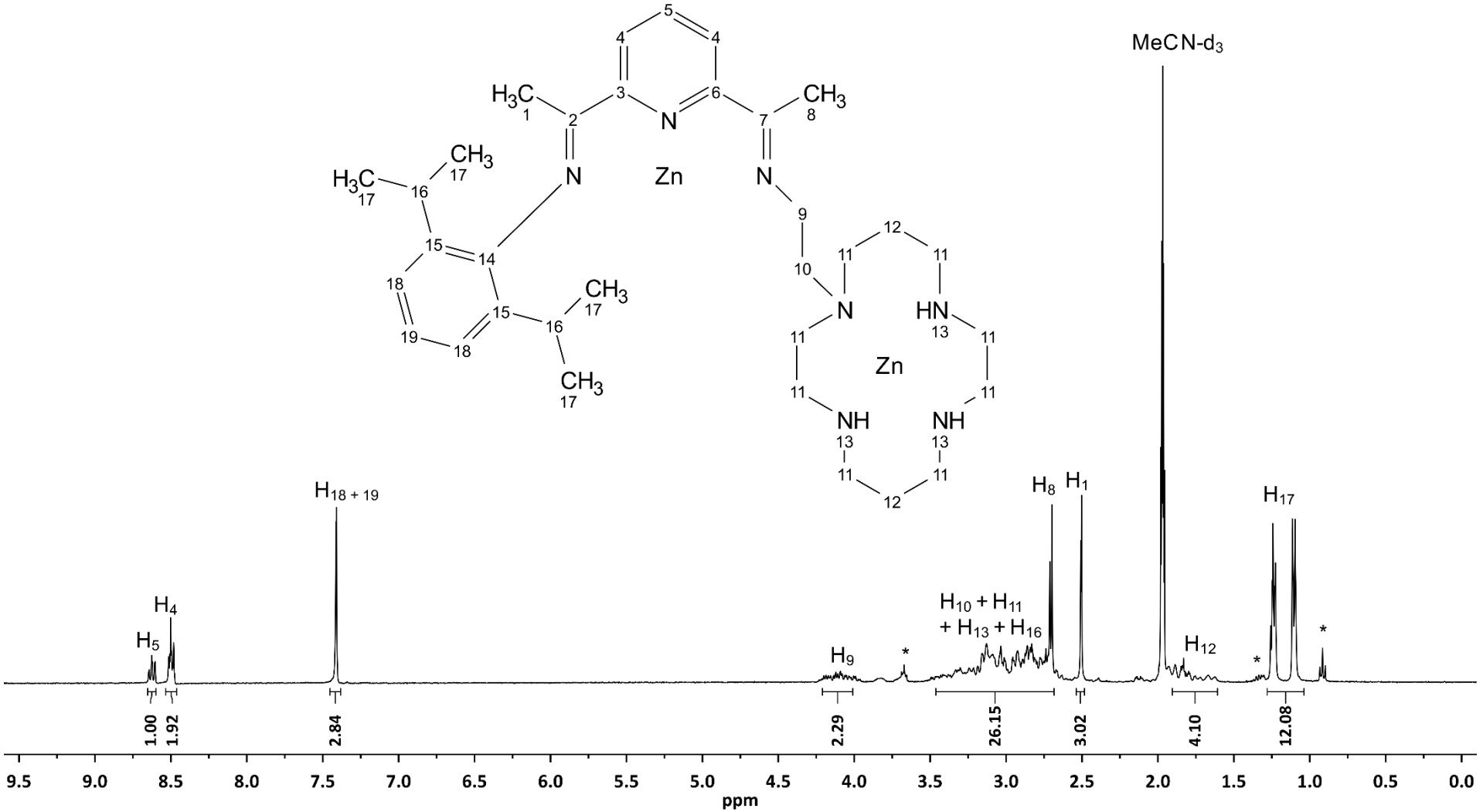


Fig. S3 ^{1}H NMR spectrum of **5** in MeCN-d_3; * = residual solvent.

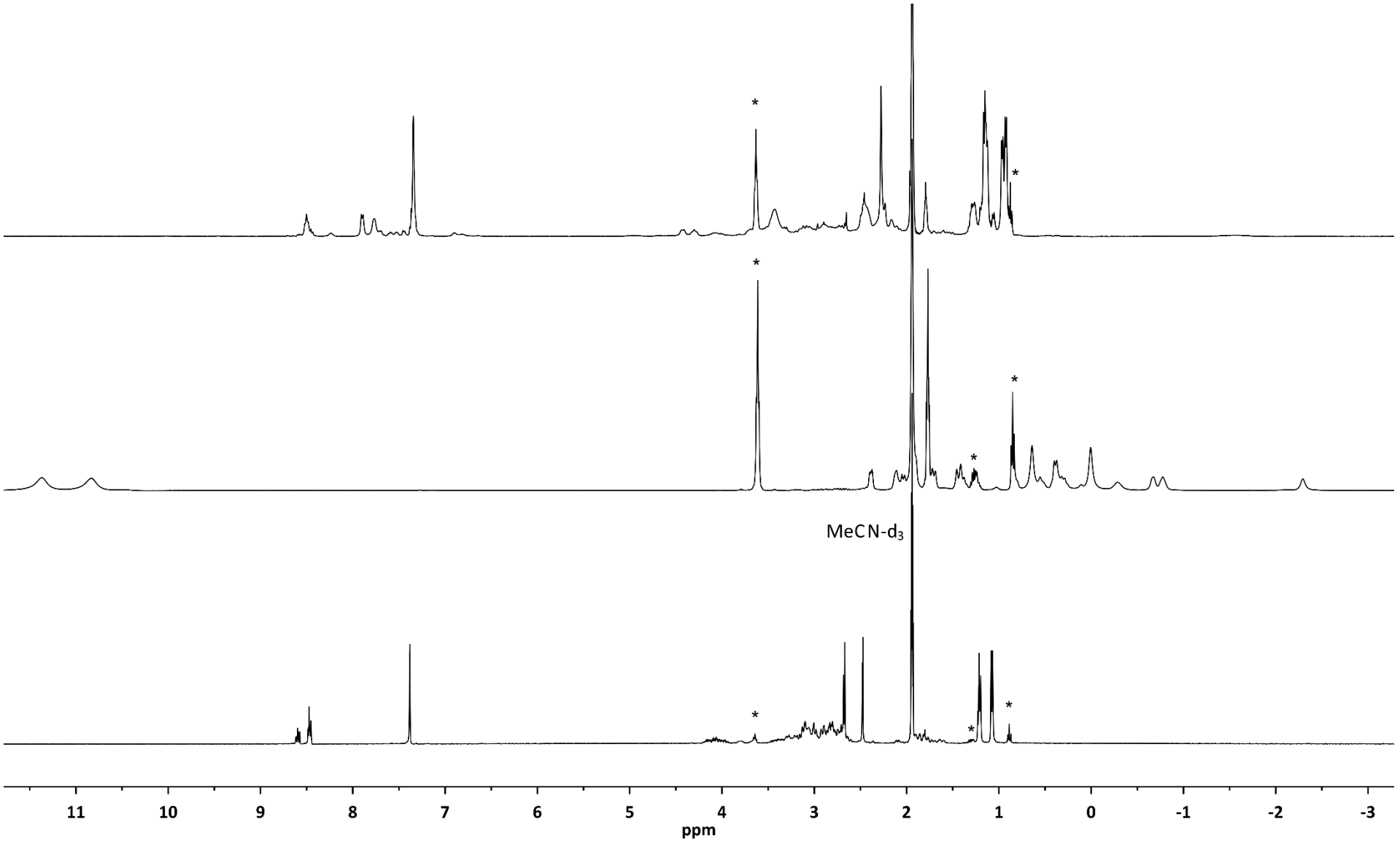


Fig. S4 ^{1}H NMR spectra of **3** (top), **4** (middle) and **5** (bottom) in MeCN-d_3; * = residual solvent.

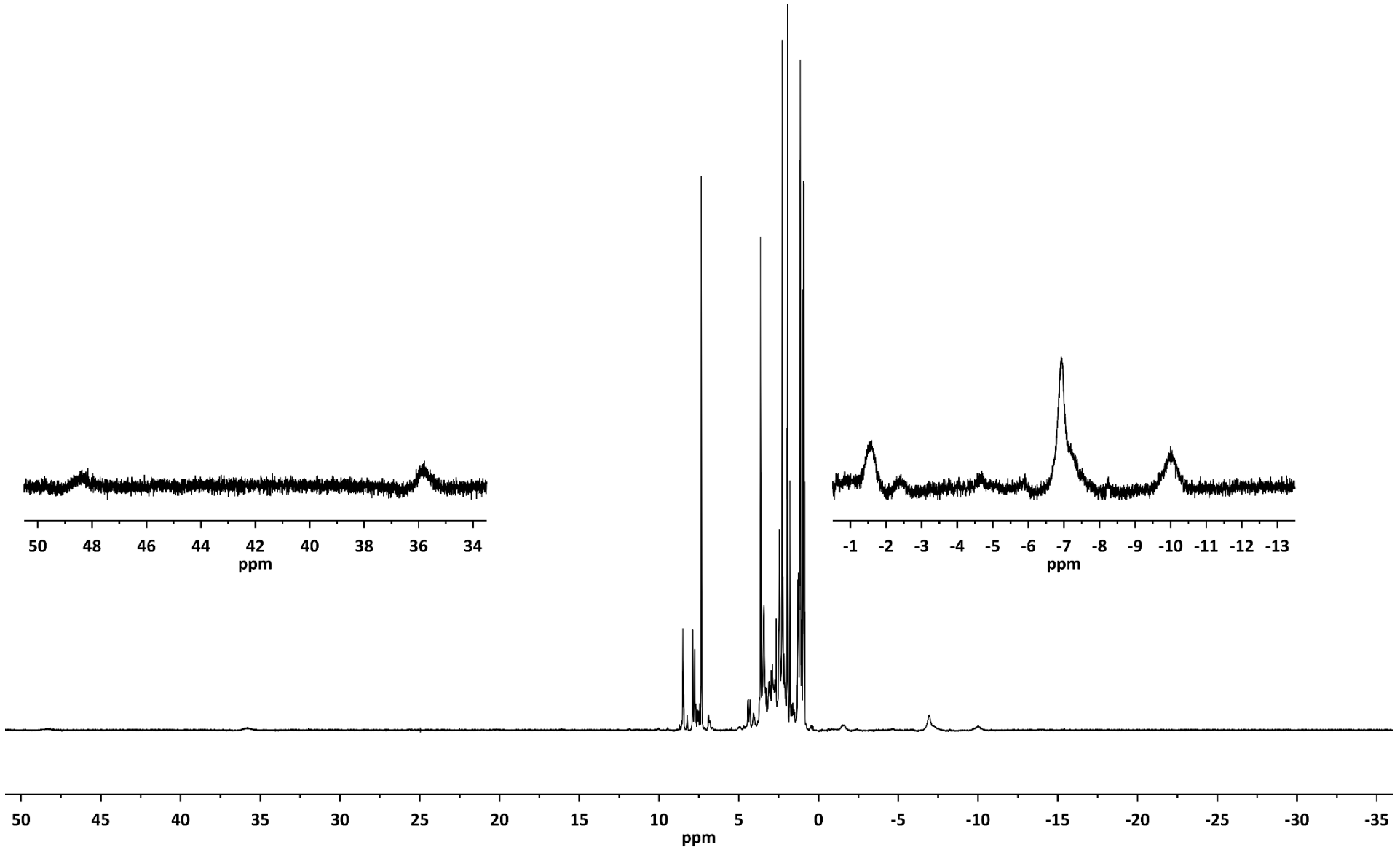


Fig. S5 ^{1}H NMR spectrum of **3** (full spectral region) in MeCN-d_3.

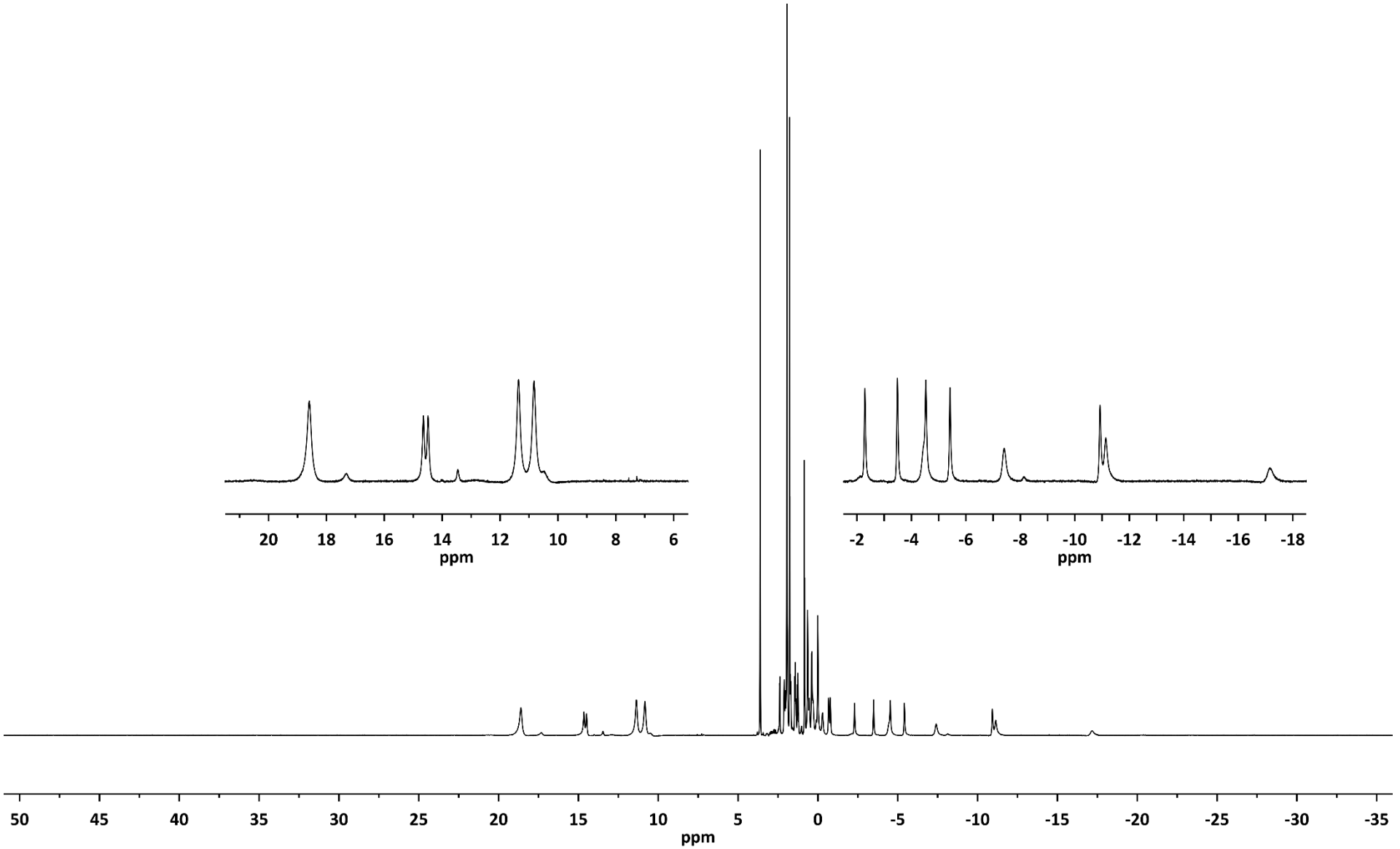


Fig. S6 ^{1}H NMR spectrum of **4** (full spectral region) in MeCN-d_3.

Molecular structures of 5

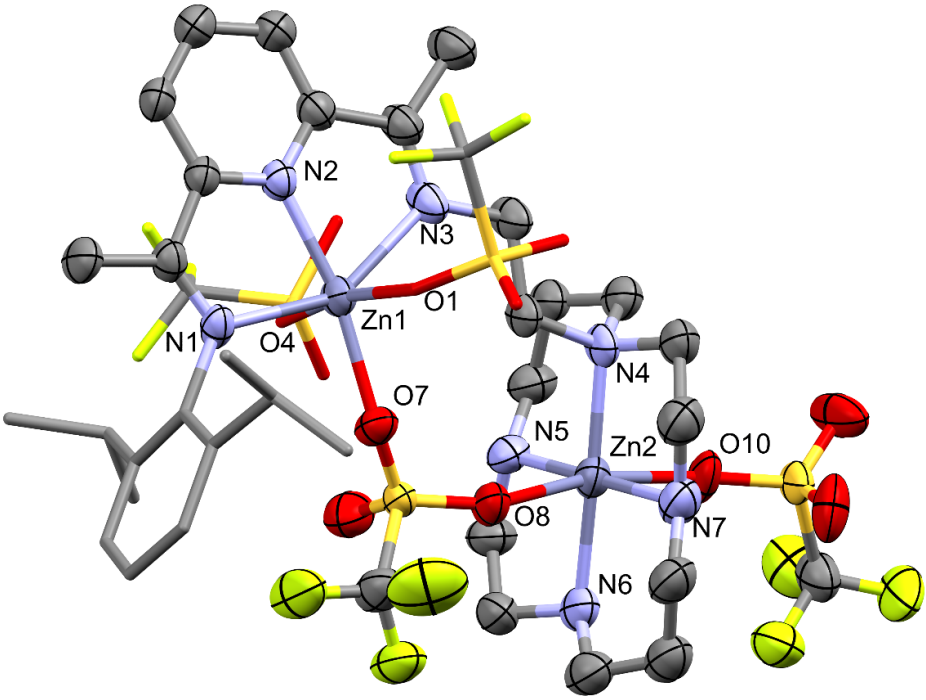


Fig. S7 Molecular structures of **5**; 50% probability ellipsoids. Hydrogen atoms, solvent molecules and partial disorder are omitted for clarity. Parts of the structure are shown as wireframe for clarity.

^{1}H NMR spectroscopy of 5 with hydrogen peroxide

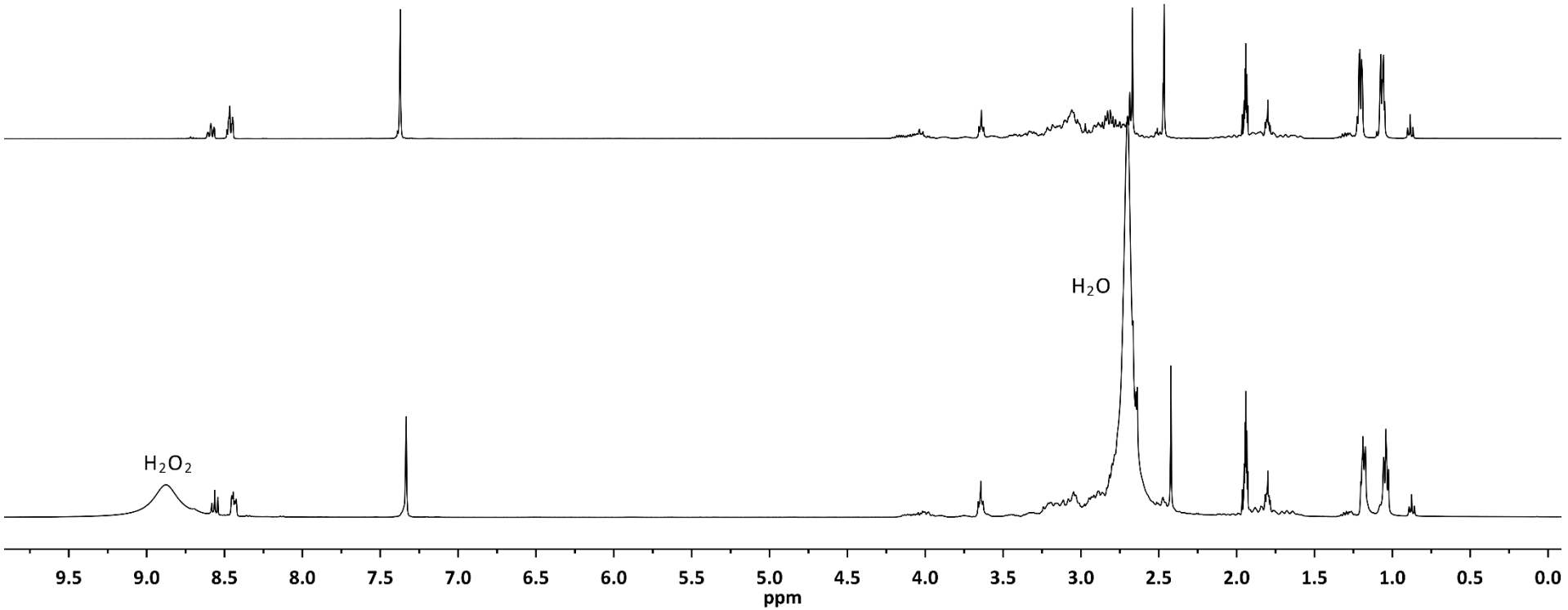


Fig. S8 **^{1}H** NMR spectra of a 4 mM solution of **5** in CD_3CN before (top) and after (bottom; 20 min reaction time) addition of 25 equiv. of a 35% aqueous H_2O_2 solution.

Absorption spectrum of 3 with hydrogen peroxide

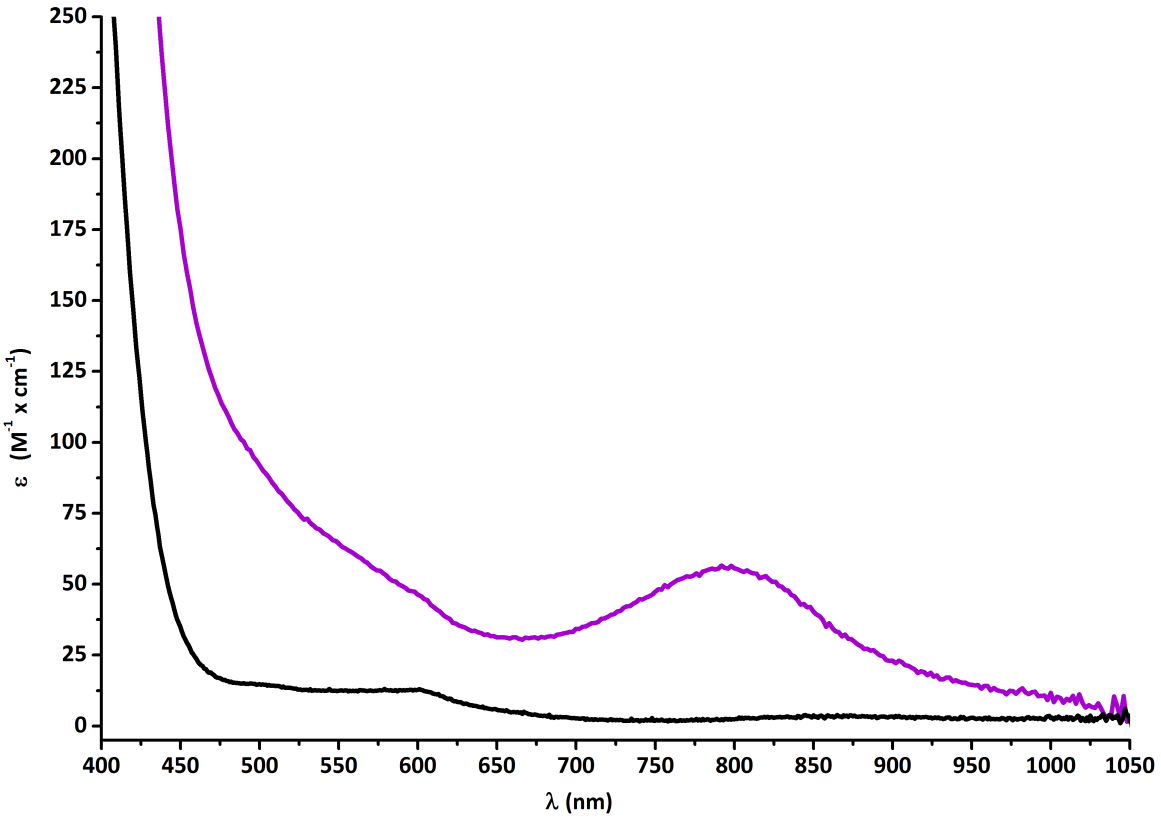


Fig. S9 Absorption spectrum of a 2 mM solution of **3** in acetone at −80 °C before (black) and after (purple) addition of two equivalents of hydrogen peroxide. The resulting peak at 794 nm is consistent with an iron(IV)-oxo band, as shown by Ray et al. for the $[Fe^{IV}(O)(cyclam)]^{2+}$ species generated under similar conditions.[1]

Catalytic epoxidation studies

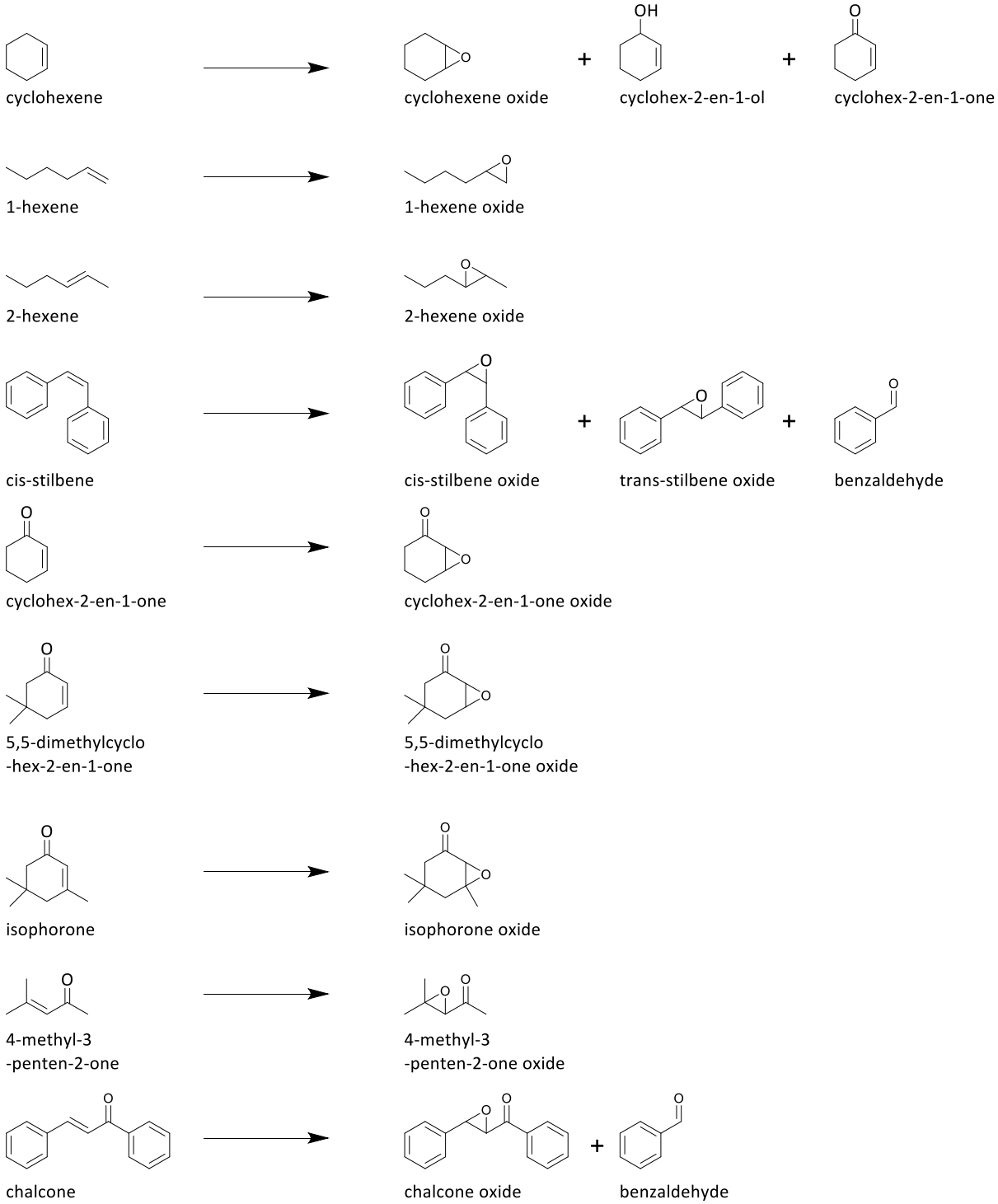
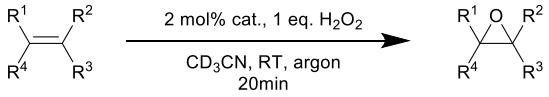


Chart S1. Structures of the substrates used in the epoxidation assays, and of the corresponding products.

Results of epoxidation assays

Table S1. Complete list of substrates screened in the epoxidation assays and yields of products, including side-products, generated.



Entry	Catalyst	Substrate	Products	Epoxide (%)/error
1	[Fe(cyclam)OTf$_2$]	cyclohexene	cyclohexene oxide	41 (3)
			cyclohex-2-en-1-ol	1.0 (0.3)
			cyclohex-2-en-1-one	0.5 (0.2)
2	**1**	cyclohexene	cyclohexene oxide	17 (1)
			cyclohex-2-en-1-ol	1.4 (0.2)
			cyclohex-2-en-1-one	0.8 (0.2)
3	**2**	cyclohexene	cyclohexene oxide	28 (2)
			cyclohex-2-en-1-ol	1.2 (0.2)
			cyclohex-2-en-1-one	0.9 (0.1)
4	**3**	cyclohexene	cyclohexene oxide	31 (1)
			cyclohex-2-en-1-ol	1.3 (0.3)
			cyclohex-2-en-1-one	0.8 (0.2)
5	**4**	cyclohexene	cyclohexene oxide	0
6	**5**	cyclohexene	cyclohexene oxide	0
7	[(^{iPr}PDI)Fe(OTf)$_2$]	cyclohexene	cyclohexene oxide	28(1)
8	[Fe(cyclam)OTf$_2$]	cyclohexene	cyclohexene oxide	28(1)
	+ [(PDI)Fe(OTf)$_2$]		cyclohex-2-en-1-ol	1.1 (0.3)
			cyclohex-2-en-1-one	0.6 (0.3)
9	[Fe(cyclam)OTf$_2$]	1-hexene	1-hexene oxide	25 (2)
10	**1**	1-hexene	1-hexene oxide	24 (0.5)
11	**2**	1-hexene	1-hexene oxide	31 (1)
12	**3**	1-hexene	1-hexene oxide	26 (1)
13	[Fe(cyclam)OTf$_2$]	2-hexene	2-hexene oxide	35 (1)
14	**1**	2-hexene	2-hexene oxide	29 (2)
15	**2**	2-hexene	2-hexene oxide	28(1)
16	**3**	2-hexene	2-hexene oxide	34 (1)
17	[Fe(cyclam)OTf$_2$]	cis-stilbene	cis-stilbene oxide	26 (2)
			trans-stilbene oxide	1.9 (0.2)
			benzaldehyde	3.5 (0.4)
18	**1**	cis-stilbene	cis-stilbene oxide	10 (0.5)
			trans-stilbene oxide	0.7 (0)
			benzaldehyde	4.0 (0.3)
19	**2**	cis-stilbene	cis-stilbene oxide	10 (0.5)
			trans-stilbene oxide	1.5 (0.1)
			benzaldehyde	3.8 (0.2)
20	**3**	cis-stilbene	cis-stilbene oxide	20 (1)
			trans-stilbene oxide	1.5 (0.2)
			benzaldehyde	2.9 (0.2)

Entry	Catalyst	Substrate	Products	Epoxide (%)/error
21	[Fe(cyclam)OTf$_2$]	cyclohex-2-en-1-one	cyclohex-2-en-1-one oxide	1 (1)
22	**1**	cyclohex-2-en-1-one	cyclohex-2-en-1-one oxide	19 (2)
23	**2**	cyclohex-2-en-1-one	cyclohex-2-en-1-one oxide	22 (0.5)
24	**3**	cyclohex-2-en-1-one	cyclohex-2-en-1-one oxide	11 (0.5)
25	**4**	cyclohex-2-en-1-one	cyclohex-2-en-1-one oxide	0
26	**5**	cyclohex-2-en-1-one	cyclohex-2-en-1-one oxide	0
27	[(PDI)Fe(OTf)$_2$]	cyclohex-2-en-1-one		0
28	[Fe(cyclam)OTf$_2$] + [(PDI)Fe(OTf)$_2$]	cyclohex-2-en-1-one	cyclohex-2-en-1-one oxide	3 (0.5)
29	[Fe(cyclam)OTf$_2$]	5,5-dimethylcyclohex-2-en-1-one	5,5-dimethylcyclohex-2-en-1-one oxide	1 (1)
30	**1**	5,5-dimethylcyclohex-2-en-1-one	5,5-dimethylcyclohex-2-en-1-one oxide	19 (1)
31	**2**	5,5-dimethylcyclohex-2-en-1-one	5,5-dimethylcyclohex-2-en-1-one oxide	17 (1)
32	**3**	5,5-dimethylcyclohex-2-en-1-one	5,5-dimethylcyclohex-2-en-1-one oxide	11 (2)
33	[Fe(cyclam)OTf$_2$]	isophorone	isophorone oxide	17 (0.5)
34	**1**	isophorone	isophorone oxide	35 (2)
35	**2**	isophorone	isophorone oxide	31 (1)
36	**3**	isophorone	isophorone oxide	34 (1)
37	[Fe(cyclam)OTf$_2$]	4-methyl-3-penten-2-one	4-methyl-3-penten-2-one oxide	6 (0.5)
38	**1**	4-methyl-3-penten-2-one	4-methyl-3-penten-2-one oxide	23 (2)
39	**2**	4-methyl-3-penten-2-one	4-methyl-3-penten-2-one oxide	25 (1)
40	**3**	4-methyl-3-penten-2-one	4-methyl-3-penten-2-one oxide	18 (0.5)
41	[Fe(cyclam)OTf$_2$]	chalcone	chalcone oxide	15 (2)
			benzaldehyde	2.9 (0.1)
42	**1**	chalcone	chalcone oxide	19 (1)
			benzaldehyde	4.2 (0.4)
43	**2**	chalcone	chalcone oxide	21 (0.5)
			benzaldehyde	4.7 (0.4)
44	**3**	chalcone	chalcone oxide	21 (3)
			benzaldehyde	4.1 (0.3)

Product analysis

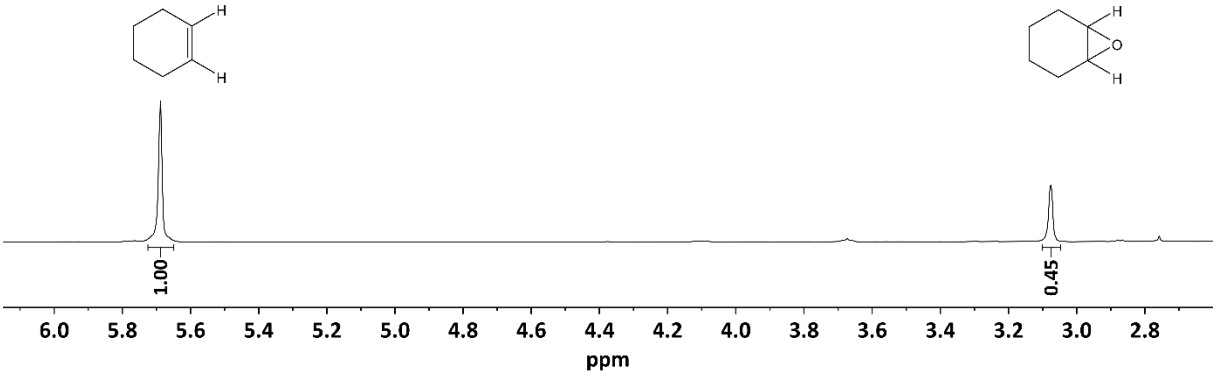


Fig. S10 Representative ^{1}H NMR spectrum of cyclohexene in CD_3CN after the reaction with **3** under the catalytic conditions.

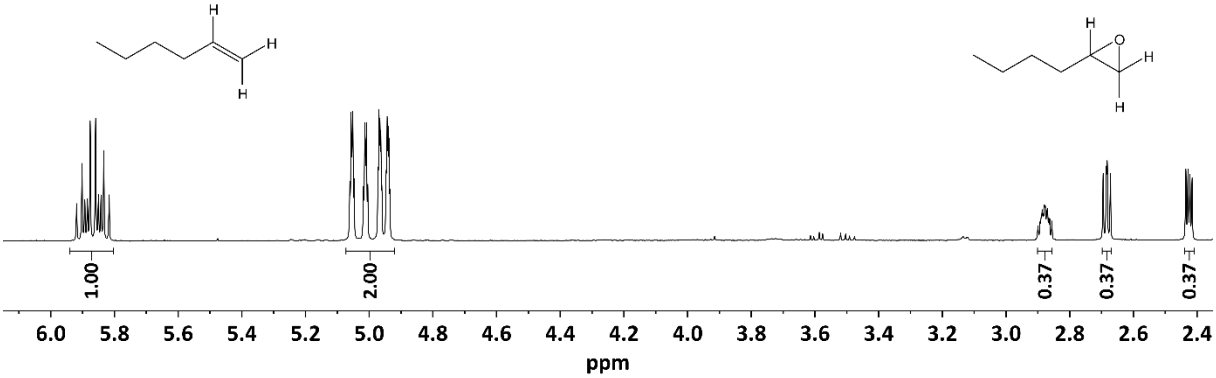


Fig. S11 Representative ^{1}H NMR spectrum of 1-hexene in CD_3CN after the reaction with **3** under the catalytic conditions.

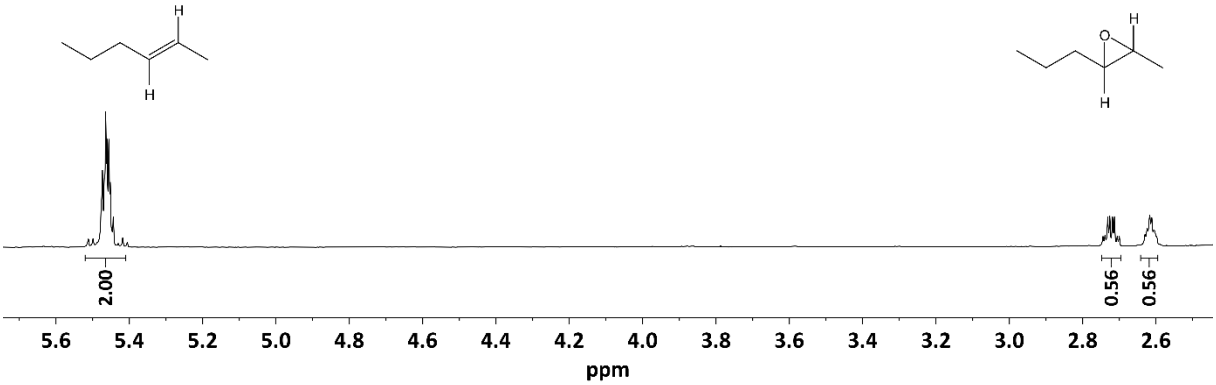


Fig. S12 Representative ^{1}H NMR spectrum of 2-hexene in CD_3CN after the reaction with **3** under the catalytic conditions.

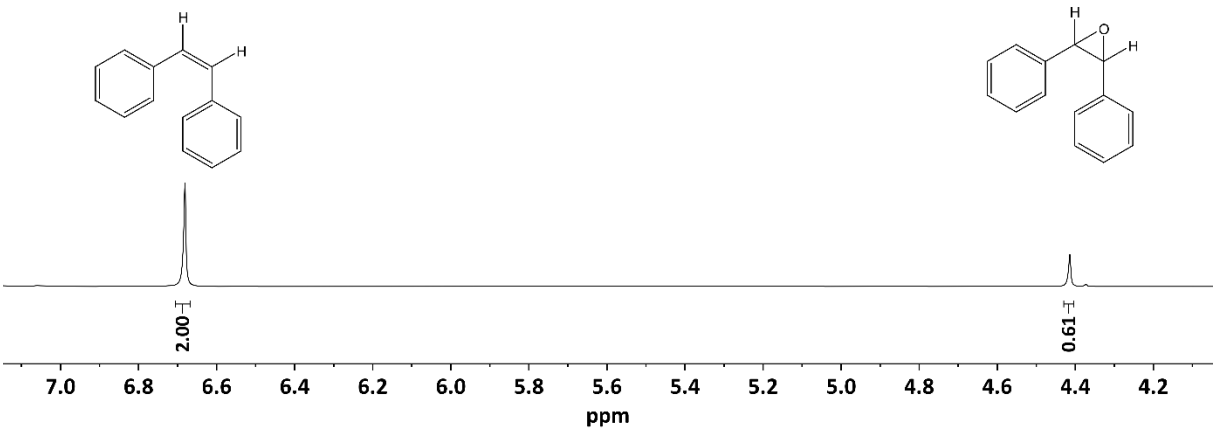


Fig. S13 Representative ^{1}H NMR spectrum of cis-stilbene in CD_3CN after the reaction with **3** under the catalytic conditions.

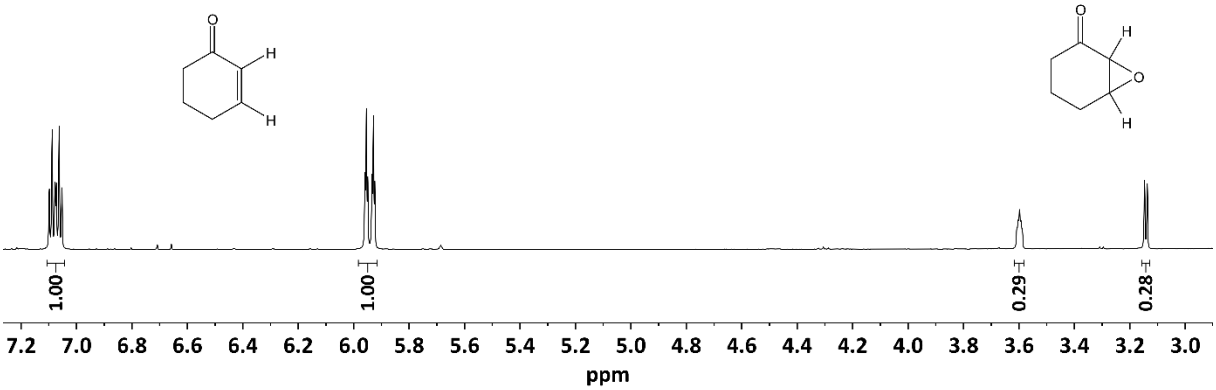


Fig. S14 Representative ^{1}H NMR spectrum of cyclohex-2-en-1-one in CD_3CN after the reaction with **1** under the catalytic conditions.

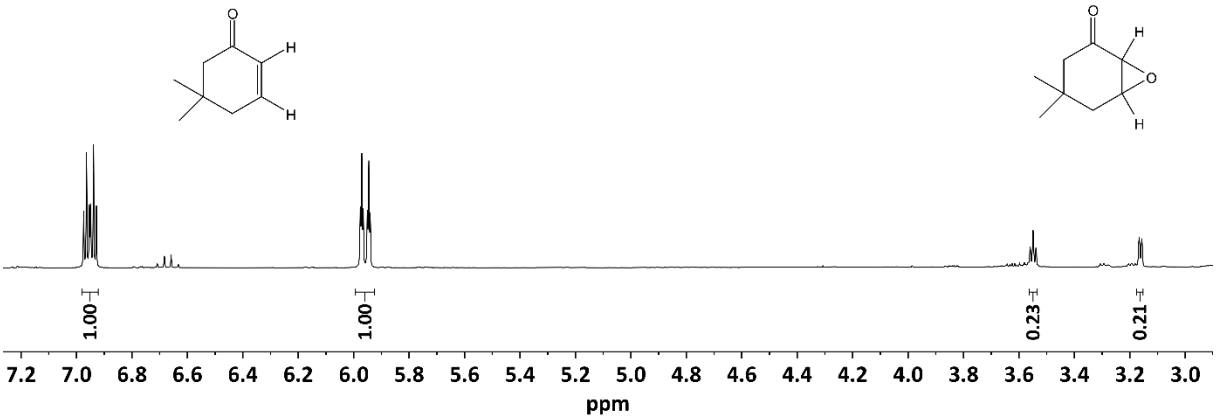


Fig. S15 Representative ^{1}H NMR spectrum of 5,5-dimethylcyclohex-2-en-1-one in CD_3CN after the reaction with **1** under the catalytic conditions.

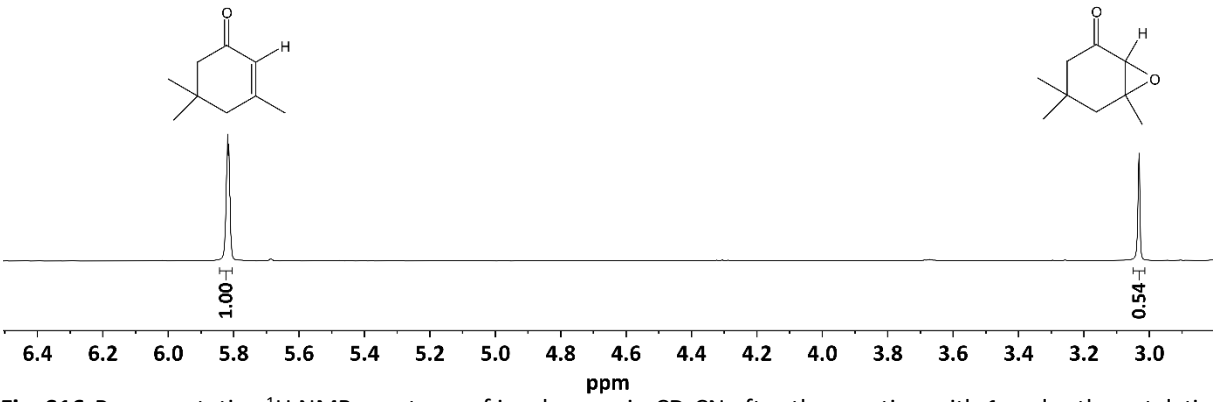


Fig. S16 Representative ^{1}H NMR spectrum of isophorone in CD_3CN after the reaction with **1** under the catalytic conditions.

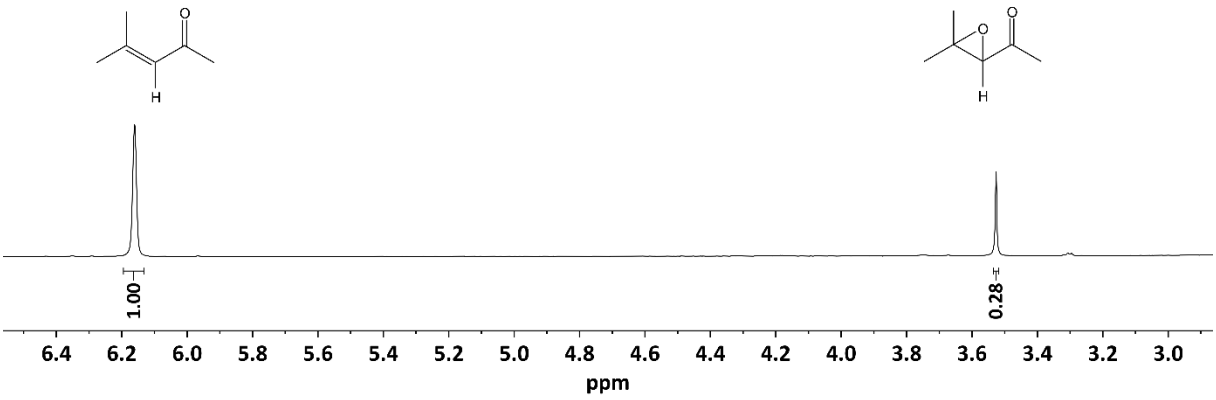


Fig. S17 Representative ^{1}H NMR spectrum of 4-methyl-3-penten-2-one in CD_3CN after the reaction with **1** under the catalytic conditions.

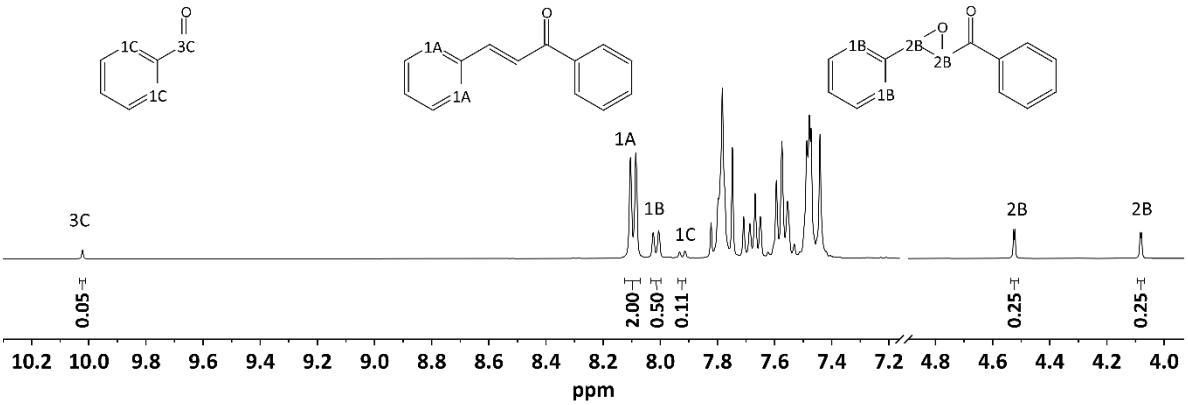


Fig. S18 Representative ^{1}H NMR spectrum of chalcone in CD_3CN after the reaction with **3** under the catalytic conditions.

Crystallographic tables

Table S2. Crystallographic data for **4** and **5**.

	4	**5**
Empirical formula	$C_{37}H_{53}F_{12}FeN_7O_{12}S_4Zn$	$C_{37}H_{53}F_{12}N_7O_{12}S_4Zn_2$
Formula weight	1265.29	1274.84
Crystal system	Triclinic	Triclinic
Space group	P -1	P -1
a (Å)	12.6710(9)	12.8764(16)
b (Å)	15.7641(12)	15.6215(19)
c (Å)	15.7646(12)	15.7745(19)
α (°)	71.790(2)	71.766(5)
β (°)	80.340(3)	77.414(5)
γ (°)	77.624(3)	80.424(5)
Volume (Å^3)	2904.4(4)	2924.7(6)
Z	2	2
ρcalc (mg mm^{-3})	1.447	1.448
μ (mm^{-1})	0.901	1.057
F (000)	1296	1304
Reflns. collected	87726	79287
Indep. reflns/R_{int}	10626	10709
Data/restraints/param	10626/766/893	10709/1623/1077
GOF on F^2	1.034	1.056
Final R_1 indexes [I ≥ 2σ(I)]	0.0803	0.0734
Final wR_2 indexes (all data)	0.2129	0.2260
Δρmin/max (e Å^3)	1.658 and -1.244	1.188 and -0.936
CCDC number	2030817	2030816

Table S3. Select bond distances (Å) and angles (°) for **4** and **5**. Multiple entries are due to disorder.

	4		**5**
Fe1···Zn1	5.598(1)	Zn1···Zn2	5.634(1)
Fe1-O1	2.236(7)(2.010(12), 2.100(10))	Zn1-O1	2.108(4)
Fe1-O4	2.2119(5)	Zn1-O4	2.15(3)
Fe1-O7	1.934(7)(2.171(6))	Zn1-O7	2.111(6)(1.922(14))
Fe1-N1	2.245(4)	Zn1-N1	2.264(4)
Fe1-N2	2.097(4)	Zn1-N2	2.052(4)
Fe1-N3	2.243(5)	Zn1-N3	2.225(4)
Zn1-O8	2.358(8)	Zn2-O8	2.356(11)
Zn1-O10	2.352(4)	Zn2-O10	2.361(4)
Zn1-N4	2.128(5)	Zn2-N4	2.108(6)(2.240(14))
Zn1-N5	2.077(5)	Zn2-N5	2.095(7)(2.016(16))
Zn1-N6	2.100(6)	Zn2-N6	2.141(7)(2.014(15))
Zn1-N7	2.058(7)	Zn2-N7	2.061(7)(2.143(16))
N1-Fe1-N2	73.92(16)	N1-Zn1-N2	75.05(16)
N2-Fe1-N3	73.80(17)	N2-Zn1-N3	75.50(17)
N4-Zn1-N5	90.5(2)	N4-Zn2-N5	92.5(2)(90.8(6))
N5-Zn1-N6	86.3(3)	N5-Zn2-N6	84.4(3)(89.4(6))
N6-Zn1-N7	93.7(3)	N6-Zn2-N7	94.6(3)(96.6(6))
N4-Zn1-N7	89.5(3)	N4-Zn2-N7	88.5(3)(83.2(6))

References

1 X. Engelmann, D. D. Malik, T. Corona, K. Warm, E. R. Farquhar, M. Swart, W. Nam and K. Ray, *Angew. Chem. Int. Ed.*, 2019, **58**, 4012-4016.