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# Epoxidation of alkenes bearing a carboxylic acid group by iron complexes of the tetradentate ligand *N*,*N*'-dimethyl-*N*,*N*'-bis (2-pyridylmethyl)-1,2-diaminoethane and its derivatives



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# ABSTRACT

The addition of carboxylic acids enhances the rate and selectivity of alkene oxidations catalyzed by  $[(bpmen)Fe(OTf)_2]$  (bpmen = *N*,*N'*-dimethyl-*N*,*N'*-bis(2-pyridylmethyl)-1,2-diaminoethane). The syntheses and characterizations of four derivatives of this iron complex with varying substitutions on the pyridine ring and with a substituted piperazine backbone are reported. These  $[(L)Fe(OTf)_2]$  complexes and  $[(bpmen)Fe(OTf)_2]$  are employed as catalysts for the oxidation of alkenes bearing a carboxylic acid functional group, namely oleic acid, undecylenic acid, 5-hexenoic acid and 4-pentenoic acid, with hydrogen peroxide as the oxidant. Comparisons with the analogous ester substrates demonstrate the beneficial impact of the acid functional group on conversion and selectivity when using  $[(bpmen)Fe(OTf)_2]$  as catalyst. For the oleic and undecylenic acids, epoxide product is formed with moderate to high conversions and high selectivities. Under the conditions employed, 4-pentenoic acid is oxidized to a  $\gamma$ -lactone, most likely via the epoxide intermediate, and 5-hexenoic acid to a mixture of epoxide and  $\delta$ -lactone. Of the iron complexes with bpmen derivatives as ligands, only the *N*,*N'*-dimethyl-*N*,*N'*-bis(5-chloropyridin-2-ylmethyl)-1,2-diaminoethane variant shows appreciable activity. The effect of solvent choice is also investigated.

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# 1. Introduction

Significant research efforts have gone into the discovery of selective oxidations of alkenes [1,2]. One approach has involved the design of functional analogs to the active sites of iron-containing enzymes [3]. Of particular interest are iron catalysts that mimic non-heme enzymes such as the dinuclear methane monooxygenases and mononuclear Rieske dioxygenases, and other enzymes with the commonly encountered 2-his-1-carboxylate facial ligation of iron [4–7]. Many of these catalysts are employed in a diverse range of processes, ranging from C–H activations, to epoxidations and *cis*-dihydroxylations [3,5,8,9]. Iron complexes of the ligand *N*,*N*-dimethyl-*N*,*N*-bis(2-pyridylmethyl)-1,2-diaminoe-thane (bpmen) and its derivatives have been shown to be effective

\* Corresponding author. Tel.: +1 413 597 2387; fax: +1 413 597 4150. *E-mail address*: cgoh@williams.edu (C. Goh). catalysts for the epoxidation of alkenes using H<sub>2</sub>O<sub>2</sub> as an oxidant [10,11]. This oxidant offers good atom economy and is environmentally attractive generating water as an innocuous byproduct. Crucial to this work are the demonstrations that catalytic activities of these complexes and product selectivities for epoxide over cisdiol and other products are influenced by additives such as carboxylic acids [10,12–16]. The addition of acetic acid to the reaction, for example, has improved both catalytic activity and selectivity for epoxide over diol in the oxidation of terminal alkenes, such as 1octene [10,17]. Work by Lyakin et al. has also shown the beneficial impact from an increased steric bulk of added carboxylic acids on enantioselectivity of the asymmetric epoxidation catalyzed by chiral iron and manganese complexes [14]. Herein, we report on the epoxidation of substrates containing both alkene and carboxylic acid functionalities using iron catalysts like [(bpmen)Fe(OTf)<sub>2</sub>] without the need for additional carboxylic acid to enhance conversions or selectivities.

The substrates oleic acid, undecylenic acid, 5-hexenoic acid and 4-pentenoic acid represent a range of different types of olefins: oleic acid is a 1,2-*cis*-olefin, whereas the sequence of undecylenic, 5-hexenoic and 4-pentenoic acid represents examples of terminal

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olefins with varying lengths of the  $(CH_2)_n$ -spacer between the alkene and carboxylic acid functionalities. To ascertain the effect of the acid functional group, epoxidations of the substrates were carried out in parallel with the analogous ester substrates.

Oleic, undecylenic and other fatty acids are substrates of interest to efforts of incorporating plant-based epoxides into various polymers as replacements for traditional petroleum-based starting materials [18–23]. The development of efficient catalysts for the epoxidation of renewable olefins is an important component to this effort [21]. Previous reports of homogeneous catalysts for the epoxidations of fatty acids and their esters include the use of iron porphyrin, methyltrioxorhenium (MTO) and various molybdenum complexes [21,24–28].

We also examined the effect of varying the bpmen ligand framework on the oxidation efficiency. 6-Me-, 6-OMe- and 5-Cl-substituents were introduced on the pyridine rings. The pyridines were replaced with quinolines, and ethylenediamine was replaced by (2R,5S)-2,5-dimethylpiperazine as the amine backbone (Fig. 1). The iron(II) complexes of these ligands showed lower activities than the parent bpmen complex. Further optimization studies were carried out for the [(bpmen)Fe(OTf)<sub>2</sub>] system by examining the effect of solvent choice.

# 2. Experimental

# 2.1. General information

Ligand syntheses were conducted in air unless otherwise indicated. Metal complex syntheses and epoxidations were performed under an inert atmosphere using standard Schlenk techniques or in a MBraun Labmaster SP-150 glove box. Materials were purchased from commercial sources and used without further purification unless otherwise indicated. Commercially available ethyl 4-pentenoate was synthesized from 4-pentenoic acid and ethanol using standard acid-catalyzed protocols for the synthesis of esters [29]. Solvents for complexation and epoxidation reactions were obtained from a solvent purification system (dichloromethane, tetrahydrofuran and diethyl ether) [30] or dried using standard techniques (acetonitrile) [31]. Ligand purifications, when necessary, were performed on a Biotage Isolera<sup>™</sup> Flash Purification System using silica cartridges.

#### 2.2. Characterizations

NMR spectra were recorded using a Bruker Avance 500 MHz spectrometer. Chemical shifts are given in ppm relative to residual solvent peaks (CDCl<sub>3</sub>: <sup>1</sup>H NMR  $\delta$  7.26 ppm; <sup>13</sup>C NMR  $\delta$  77.21). Assignments are based on collecting combinations of <sup>1</sup>H, <sup>13</sup>C, COSY- and HMQC-NMR spectra. GC-MS data were collected on an Agilent Technologies 7890A GC system fitted with a HP-5MS column (30 m × 0.25 mm × 0.25 µm), an Agilent 7693 autosampler and an Agilent 5795C XL El/Cl MSD. Melting points were determined on a Mel-Temp apparatus equipped with a digital thermometer. Electrospray mass spectra were recorded in positive-ion mode using a Bruker Esquire 3000 Plus instrument, and theoretical isotope patterns were generated by the Bruker Daltonics IsotopePattern software. Absorption data were recorded with a Hewlett



Fig. 1. Ligands LX and their corresponding iron complexes CX utilized for the oxidation of alkenes bearing a carboxylic acid functional group by hydrogen peroxide (OTf = trifluoromethanesulfonate).

Packard 8425A Diode Array spectrophotometer using 1 cm quartz cells. Elemental analyses for C, H and N were obtained from the Microanalysis Lab at the University of Illinois at Urbana-Champaign.

Cyclic voltammetry measurements were carried out using a BASi Epsilon Electrochemical Workstation and the associated Epsilon-EC software. These electrochemical experiments were performed at room temperature in a glovebox under a dinitrogen atmosphere, using a BASi VC-2 voltammetry cell with a platinum working electrode (1.6 mm dia.), a platinum wire auxiliary electrode, and a non-aqueous silver/silver ion reference electrode. The reference electrode contained a silver wire immersed in a solution of 0.01 M silver nitrate dissolved in a 0.1 M solution of (Bu<sub>4-</sub> N)(PF<sub>6</sub>) in acetonitrile. Scan rates were varied from 200 to 20 mV s<sup>-1</sup>, with values reported at 50 mV s<sup>-1</sup> unless stated otherwise. The complexes were dissolved in 3 mL of acetonitrile or dichloromethane containing 0.1 M (Bu<sub>4</sub>N)(PF<sub>6</sub>) as supporting electrolyte. To facilitate comparisons to electrochemical measurements made by other research groups, electrochemical measurements were also run in presence of ferrocene as an internal standard, and potentials are reported relative to the position of the ferrocenium/ferrocene couple [32]. In our experimental set-up, values for  $E_{Fc}^{+}$  ranged from 0.104 to 0.109 V ( $\Delta E_{1/2}$  ranges 94– 120 mV;  $i_{\rm pf}/i_{\rm pr}$  ranges 0.93–0.99) in acetonitrile and from 0.230 to 0.246 V ( $\Delta E_{1/2}$  ranges 160–270 mV;  $i_{pf}/i_{pr}$  ranges 0.88–0.99) in dichloromethane versus the Ag<sup>+</sup>/Ag reference electrode employed.

# 2.3. Ligand syntheses

The ligands *N*,*N*'-dimethyl-*N*,*N*'-bis(2-pyridylmethyl-1,2-diaminoethane (bpmen, **L1**) and *N*,*N*'-dimethyl-*N*,*N*'-bis((6-methylpyridin-2-yl)methyl)-1,2-diaminoethane (**L2**) were prepared following published procedures [10,33,35]. **L3**, **L4** and **L5** were synthesized by modifications of a previously published protocol for the synthesis of **L1** [33]. The synthesis of (*2R*,*SS*)-2,5-dimethyl-1,4-bis(pyridin-2-ylmethyl)piperazine (**L6**) was reported elsewhere [34].

# 2.3.1. N,N'-dimethyl-N,N'-bis(6-methoxypyridin-2-ylmethyl)-1,2diaminoethane (**L3**)

6-Methoxy-pyridinecarboxaldehyde (1.382 g, 10.1 mmol) and N,N'-dimethylethane-1,2-diamine (0.296 g, 3.4 mmol) were added to a suspension of sodium triacetoxyborohydride (2.772 g, 13.1 mmol) in anhydrous 1,2-dichloroethane (80 mL). After 18 hours of stirring under a dinitrogen atmosphere, the reaction was quenched with saturated NaHCO<sub>3</sub> (50 mL). The organic layer was isolated, and the aqueous fraction extracted with ethyl acetate  $(3 \times 50 \text{ mL})$ . The organic extracts were dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield a yellow-brown oil. The oil was dissolved in anhydrous THF (50 mL), and the solution transferred to a flask containing NaH (0.161 g, 6.72 mmol). The mixture was stirred for 24 h. Solvent was removed under reduced pressure, and the product extracted with pentane (4  $\times$  50 mL). Removal of solvent from the extract under reduced pressure yielded an orange oil. Further purification by column chromatography using eluent gradients of ethyl acetate, ethyl acetate/methanol (95/5) and ethyl acetate/ methanol/triethylamine (90/5/5;  $R_f = 0.60$ ) followed by solvent removal vielded pure product **L3** as a vellow oil (0.505 g. 46% vield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  7.50 (t, I = 8.0 Hz, 2H, py), 6.96 (d, *J* = 7.0 Hz, 2H, py), 6.58 (d, *J* = 8.0 Hz, 2H, py), 3.90 (s, 6H, O–CH<sub>3</sub>), 3.62 (s, 4H, N-CH<sub>2</sub>-pyr), 2.66 (s, 4H, N-CH<sub>2</sub>), 2.32 (s, 6H, N-CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K): δ 163.7 (O-py), 157.2 (py), 138.8 (py), 115.7 (py), 108.5 (py), 63.8 (py-CH<sub>2</sub>-N), 55.5 (N-CH<sub>2</sub>), 53.4 (O-CH<sub>3</sub>), 41.2 (N-CH<sub>3</sub>) ppm. MS: *m*/*z* 330.1 (M<sup>+</sup>), *m*/*z* 165.0 (Me- $O-pyr-CH_2-N-CH_3-CH_2^+$ ).

#### 2.3.2. N,N'-dimethyl-N,N'-bis(quinolin-2-ylmethyl)-1,2diaminoethane (L4)

Quinoline-2-carboxaldehyde (1.100 g, 7.0 mmol) and N,N'dimethylethane-1,2-diamine (0.295 g, 3.3 mmol) were added to a suspension of sodium triacetoxyborohydride (2.700 g, 12.8 mmol) in anhydrous 1,2-dichloroethane (80 mL). After 24 h of stirring under a dinitrogen atmosphere, the deep red solution was quenched with saturated NaHCO<sub>3</sub> (50 mL). The organic layer was isolated, and the aqueous fraction extracted with ethyl acetate  $(3 \times 50 \text{ mL})$ . The organic extracts were dried over anhydrous magnesium sulfate, filtered and solvent was removed under reduced pressure to yield an orange oil. The oil was dissolved in anhydrous THF (50 mL), and the solution transferred to a flask containing NaH (0.250 g, 10.4 mmol). The mixture was stirred for 24 h. Solvent was removed under reduced pressure, and the product extracted with pentane  $(4 \times 50 \text{ mL})$  and dichloromethane  $(4 \times 50 \text{ mL})$ . Removal of solvent from the extract under reduced pressure vielded pure product as a yellow-brown oil (0.89 g, 71% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  8.07 (t, J = 8.5 Hz, 4H, Ar), 8.06 (d, J = 8.1 Hz, 2H, Ar), 7.67 (t, J = 8.0 Hz, 2H, Ar), 7.59 (d, J = 7.7 Hz, 2H, Ar) 7.50 (t, J = 7.6 Hz, 2H, Ar) 3.87 (s, 4H, N-CH2-Ar), 2.70 (s, 4H, N-CH2), 2.31 (s, 6H, N–CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  160.6 (Ar), 144.8 (Ar), 136.5 (Ar), 129.5 (Ar), 129.3 (Ar), 127.7 (Ar), 127.5 (Ar), 126.2 (Ar), 121.3 (Ar), 65.2 (N-CH<sub>2</sub>-Ar), 55.8 (N-CH<sub>2</sub>), 43.3 (N-CH<sub>3</sub>) ppm. MS: *m*/*z* 370.1 (M<sup>+</sup>), *m*/*z* 185.0 (Ar–CH<sub>2</sub>–NCH<sub>3</sub>–CH<sub>2</sub><sup>+</sup>).

# 2.3.3. N,N'-dimethyl-N,N'-bis(5-chloropyridin-2-ylmethyl)-1,2diaminoethane (L5)

5-Chloro-2-formylpyridine (0.428 g, 3.0 mmol) and N,N'dimethylethane-1,2-diamine (0.121 g, 1.4 mmol) were added to a suspension of sodium triacetoxyborohydride (1.019 g, 4.8 mmol) in anhydrous 1,2-dichloroethane (20 mL). After 13 hours of stirring under an inert atmosphere, the reaction was quenched with 5% aqueous NaHCO<sub>3</sub> (20 mL). The organic layer was isolated, and the aqueous fraction extracted with dichloromethane  $(3 \times 20 \text{ mL})$ . The organic extracts were dried over anhydrous magnesium sulfate, filtered and solvent was removed to vield a pale vellowwhite solid. The solid was dissolved in anhydrous THF (20 mL). and the solution transferred to a flask containing NaH (103 mg, 4.29 mmol). The mixture was stirred for 24 h. Solvent was removed under reduced pressure, and the product extracted with diethyl ether (3  $\times$  10 mL). Solvent removal under reduced pressure yielded product as a light-yellow crystalline solid (0.402 g, 86% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  8.45 (d, I = 2.5 Hz, 2H, py), 7.61 (d of d, J = 2.5 Hz, J = 8.0 Hz, 2H, py), 7.38 (d, J = 8.0 Hz, 2H, py), 3.65 (s, 4H, N-CH<sub>2</sub>-pyr), 2.61 (s, 4H, N-CH<sub>2</sub>), 2.26 (s, 6H, N-CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K): δ 158.1 (Cl–C), 148.1 (py), 136.4 (py), 130.5 (py), 124.0 (py), 63.7 (N-CH<sub>2</sub>-pry), 55.7 (N-CH<sub>2</sub>), 43.1 (N-CH<sub>3</sub>) ppm. MS: *m*/*z* 338.1 (M<sup>+</sup>), *m*/*z* 169.0 (Cl-pyr-CH<sub>2</sub>-N-CH<sub>3</sub>-CH<sub>2</sub><sup>+</sup>). m.p. = 54–58 °C.

#### 2.4. Complex syntheses

The complexes [(bpmen)Fe(OTf)<sub>2</sub>] (**C1**) and [(**L2**)Fe(OTf)<sub>2</sub>] (**C2**) were prepared following published procedures [11], and product identities confirmed by ESI-MS: m/z 470 ([(bpmen)Fe(OTf)]<sup>+</sup>) and m/z 503 ([(**L2**)Fe(OTf)]<sup>+</sup>).

# 2.4.1. N,N'-dimethyl-N,N'-bis(6-methoxypyridin-2-ylmethyl)-1,2diaminoethane iron(II) bis(triflate) [(L3)Fe(OTf)(CH<sub>3</sub>CN)]OTf (C3)

**L3** (0.355 g, 1.08 mmol) was added to a stirred suspension of  $Fe(OTf)_2$  (0.360 g, 1.02 mmol) in THF (30 mL). The tan-yellow suspension was stirred for 14 hours, after which the tan precipitate was allowed to settle and the translucent yellow supernatant was removed by pipet. The remaining solid was washed with diethyl ether and dried to yield [(L3)Fe(OTf)\_2] (0.511 g, 69% yield)

as a fine pale tan solid. The complex was further purified by recrystallization from acetonitrile/diethyl ether to yield complex **C3** as a crystalline solid. *Anal*. Calc. for acetonitrile solvate C<sub>22</sub>H<sub>29</sub>F<sub>6</sub>FeN<sub>5</sub>O<sub>8</sub> S<sub>2</sub>: C, 36.42; H, 4.03; N, 9.65. Found: C, 36.44; H, 3.95; N, 9.52%. ESI: *m/z* 535 [(**L3**)Fe(OTf)]<sup>+</sup>, *m/z* 193 [Fe(**L3**)]<sup>2+</sup>. UV–Vis (CH<sub>3</sub>CN)  $\lambda_{max}$  nm ( $\varepsilon$ ): 280 (16300), 330 (sh, 1220).

# 2.4.2. N,N'-dimethyl-N,N'-bis(quinolin-2-ylmethyl)-1,2diaminoethane iron(II) bis(triflate) [(**L4**)Fe(OTf)<sub>2</sub>] (**C4**)

**L4** (0.890 g, 2.40 mmol) was added to a stirred suspension of Fe(OTf)<sub>2</sub> (0.808 g, 2.28 mmol) in THF (30 mL). The orange suspension was stirred for 24 h, after which the precipitate was allowed to settle and the translucent yellow supernatant was removed by pipet. The remaining solid was washed with diethyl ether and dried to yield product (0.820 g, 50% yield) as a goldenrod solid. *Anal.* Calc. for C<sub>26</sub>H<sub>26</sub>F<sub>6</sub>FeN<sub>4</sub>O<sub>6</sub>S<sub>2</sub>: C, 43.10; H, 3.62; N, 7.73. Found: C, 42.55; H, 3.61; N, 7.60. ESI: *m/z* 574 [**(L4)**Fe(OTf)]<sup>+</sup>. UV–Vis (CH<sub>3</sub> CN)  $\lambda_{max}$  nm ( $\varepsilon$ ): 286 (13500), 364 (sh, 1050).

# 2.4.3. N,N'-dimethyl-N,N'-bis(5-chloropyridin-2-ylmethyl)-1,2diaminoethane [(L5)Fe(OTf)2] (C5)

**L5** (0.121 g, 0.36 mmol) was added to a stirred suspension of Fe(OTf)<sub>2</sub> (0.120 g, 0.34 mmol) in THF (30 mL). The solution turned yellow and a bright yellow precipitate formed immediately. The yellow suspension was stirred for 18 hours, after which the precipitate was allowed to settle and the translucent yellow supernatant was removed by pipet. The remaining solid was washed with diethyl ether and dried to yield product (0.165 g, 70% yield) as a fine bright yellow solid. *Anal.* Calc. for C<sub>18</sub>H<sub>20</sub>Cl<sub>2</sub>F<sub>6</sub>FeN<sub>4</sub>O<sub>6</sub>S<sub>2</sub>: C, 31.19; H, 2.91; N, 8.08. Found: C, 31.03; H, 2.77; N, 8.05. ESI: *m/z* 542 [(**L5**)Fe(OTf)]<sup>+</sup>. UV–Vis (CH<sub>3</sub>CN)  $\lambda_{max}$  nm ( $\varepsilon$ ): 272 (14300), 390 (3000), UV–Vis (CH<sub>3</sub>CN:DMF 15:1)  $\lambda_{max}$  nm ( $\varepsilon$ ): 422 (1900).

# 2.4.4. (2R,5S)-2,5-dimethyl-1,4-bis(pyridine-2-ylmethyl)piperazine iron(II) bis(triflate) [(**L6**)Fe(OTf)<sub>2</sub>] (**C6**)

**L6** (0.175 g, 0.59 mmol) was added to a stirred solution of  $Fe(OTf)_2$  (0.199 g, 0.56 mmol) in acetonitrile (15 mL). After stirring the yellow solution for 18 hours solvent was removed. The remaining solid was washed with diethyl ether (3 × 5 mL) and dried in vacuo to yield the product as a peach crystalline solid (0.278 g, 76% yield). *Anal.* Calc. for C<sub>20</sub>H<sub>24</sub>F<sub>6</sub>FeN<sub>4</sub>O<sub>6</sub>S<sub>2</sub>: C, 36.93; H, 3.72; N, 8.61. Found: C, 36.97; H, 3.66; N, 8.56. ESI-MS: m/z 501 [(**L6**)Fe(OTf)]<sup>+</sup>.

#### 2.5. General procedure for epoxidations

Epoxidations were performed in 25-mL Schlenk tubes under an inert atmosphere. In a typical run, the tube was charged with 1 equiv of catalyst (typically about 15 mg), degassed acetonitrile (20 mL) and 200 equiv of substrate. 600 equiv of the oxidant  $H_2O_2$  (30% w/v in water) were added via syringe over a two-minute period, often resulting in an immediate color change to brown. This color faded to a pale orange for most substrates over a period of 30 s. The reaction was allowed to stir for a total of 10 min, and then was quenched by pouring the solution into an Erlenmeyer flask containing silica gel and anhydrous magnesium sulfate. The solution was passed through a short column of silica gel, and solvent evaporated under moderate vacuum. As a control, samples of substrates were taken through this workflow without use of catalyst. and analyzed gravimetrically and by <sup>1</sup>H NMR. Pure substrate was recovered with no significant mass loss (typical recovery 98%). For other catalyst:substrate:oxidant ratios, the concentration of catalyst was kept constant, and amounts of substrate and oxidant varied. The products were analyzed by <sup>1</sup>H NMR in CDCl<sub>3</sub> with a relaxation delay of 10 s. <sup>1</sup>H NMR shifts of the epoxide products matched those reported in the literature [22,36–39]. For oleic acid and ethyl oleate, the shift of the CH<sub>3</sub> group of C18 does not change between the starting materials and products. This signal was therefore used as an internal standard to measure conversions by comparing the integrations of the alkene signals relative to the methyl signals [36]. Similarly, epoxide selectivities were calculated from the integrations of the epoxide signals and the methyl signals. For undecylenic acid and methyl undecenoate, a similar approach utilized the methylene group next to the carboxylic acid group as an internal standard. For the epoxidation of 4-pentenoic acid and 5-hexenoic acid, conversions were determined by comparing the integrations of the alkene signals with those of the epoxide and lactone signals. GC-MS data was used to confirm the presence of two major products only, the epoxide and the lactone [38]. Owing to the limit of sensitivity of NMR, in experiments where epoxide or lactone was the only product clearly detected, selectivities of >95% are reported, as low concentrations of other products can not be ruled out. Selected spectra and GC-MS chromatograms are available in the Supplemental information.

# 2.6. X-ray crystallography

Diffraction quality crystals of C3 and C4 were obtained by crystallization by vapor diffusion of diethyl ether onto acetonitrile solutions of the complexes. For C5, crystals suitable for crystallographic analysis were obtained by following a method used by the Jacobsen group [10]. A solution of approximately 10 mg of C5 in 45 µL of 1-decene and a minimal amount of a 1:1 mixture of acetonitrile: acetone was transferred into a 4 mL shell vial. The vial was capped with a lid with a small hole, and the assembly placed in a scintillation vial (22 mL) filled with diethyl ether (10 mL). Vapor diffusion resulted in the formation of bright yellow crystals of C5 after 24 h. Attempts at obtaining crystals of C6 suitable for crystallographic analysis were unsuccessful. Crystals were mounted on glass fibers. All measurements were made using graphite monochromated Cu Ka radiation on a Bruker-AXS three-circle diffractometer, equipped with a SMART APEX II CCD detector. Initial space group determination was based on a matrix of 120 frames (SMART Apex II, Data Collection Software, version 2.1; Bruker AXS Inc.: Madison, WI, 2005). The data were reduced using SAINT+(-SAINT Plus, Data Reduction Software, version 7.34a; Bruker AXS Inc.: Madison, WI, 2005) and empirical absorption correction applied using SADABS (Sheldrick, G.M. SADABS; University of Göttingen: Göttingen, Germany, 2005). Structures were solved using direct methods. Least-squares refinement for all structures was carried out on F<sup>2</sup>. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms in each structure were located by standard difference Fourier techniques and were refined with isotropic thermal parameters. Structure solution, refinement and the calculation of derived results were performed using the SHELXTL package of computer programs [40]. Diagrams were produced using Mercury or SHELXP. Details of X-ray experiments and crystal data are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2. Complete structure tables are provided in the Supplemental information.

#### 3. Results and discussion

# 3.1. Syntheses of ligands and complexes

The syntheses of ligands **L3–L5** were achieved using modifications of previously published protocols for related ligand frameworks and proceeded in moderate to good yields [40,41]. Reactions of ligands with suspensions of  $Fe(OTf)_2$  in acetonitrile or tetrahydrofuran led to immediate color changes and the formation of the respective metal complexes after stirring the reaction

#### Table 1

Crystallographic data and structure refinement for complexes [(L3)Fe(OTf)(CH<sub>3</sub>CN)](OTf) (C3), [(L4)Fe(OTf)<sub>2</sub>] (C4) and [(L5)Fe(OTf)<sub>2</sub>] (C5).

Compound	[(L3)Fe(OTf)(CH <sub>3</sub> CN)] (OTf)	[(L4)Fe(OTf) <sub>2</sub> ]	[(L5)Fe(OTf) <sub>2</sub> ]
Compound         Formula         Formula weight (g/mol)         Crystal system         Space group $a$ (Å) $b$ (Å) $c$ (Å) $\alpha$ (°) $\beta$ (°) $\gamma$ (°)	$[(L3)Fe(OTf)(CH_3CN)] (OTf)$ $C_{26}H_{29}F_6FeN_5O_8S_2$ 725.47 monoclinic P2_1/c 18.6636(5) 10.7401(3) 16.2118(4) 90.00 115.5630(10) 90.00	$[(L4)Fe(OTf)_2]$ $C_{26}H_{26}F_{6}FeN_4O_6S_2$ 724.48 monoclinic $P_{2_1/n}$ 9.66750(10) 16.4913(2) 18.7270(2) 90.00 100.3190(10) 90.00	$[(L5)Fe(OTf)_2] \\ \hline C_{18}H_{20}Cl_2F_6FeN_4O_6S_2 \\ 693.25 \\ monoclinic \\ P2_1/c \\ 8.7693(2) \\ 10.8924(6) \\ 16.4194(3) \\ 90.00 \\ 105.3010(10) \\ 90.00 \\ \end{tabular}$
V ( $\hat{A}^3$ ) T (K) Z $\rho_{calcd}$ (g cm <sup>-3</sup> ) $\mu$ (Cu K $\alpha$ , mm <sup>-1</sup> ) $\theta$ (°) Reflections measured Independent reflections ( $R_{int}$ ) Data/restraints /parameters Goodness-of-fit (GOF) on ( $F^2$ ) $R_1/wR_2$ [ $I > 2\sigma(I)$ ] <sup>a</sup> R indices (all data)	2931.53(14) 100(2) 4 1.644 6.307 3.88 to 64.22 29120 4779 (0.1071) 4779/0/402 1.036 0.0627/0.1442 0.0932/0.1676	2937.35(6) 100(2) 4 1.638 6.237 3.60 to 58.81 29352 4167 (0.0444) 4167/0/408 1.018 0.0252/0.0677 0.0274/0.0688	2584.29(9) 100(2) 4 1.782 8.908 3.66 to 67.00 28184 4460 (0.0327) 4460/0/354 1.006 0.0235/0.0621 0.0251/0.0629

<sup>a</sup>  $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|; wR_2 = [\sum \{w(F_0^2 - F_c^2)\} / \sum \{w(F_0^2)^2\}]^{1/2}.$ 

#### Table 2

Selected bond distances (Å) and angles (deg) for complexes [(L3)Fe(OTf)(CH<sub>3</sub>CN)](OTf) (C3), [(L4)Fe(OTf)<sub>2</sub>] (C4) and [(L5)Fe(OTf)<sub>2</sub>] (C5).

Compound	[(L3)Fe(OTf)(CH <sub>3</sub> CN)] (OTf)	[(L4)Fe(OTf) <sub>2</sub> ]	[(L5)Fe(OTf) <sub>2</sub> ]
Fe-N(1) <sup>a</sup>	2.237(5)	2.2534(16)	2.1989(15)
$Fe-N(4)^{a}$	2.245(4)	2.2493(16)	2.1848(15)
Fe–N(2) <sup>b</sup>	2.209(5)	2.2075(17)	2.2201(15)
Fe-N(3) <sup>b</sup>	2.188(5)	2.2203(17)	2.2064(15)
$Fe-N(5)/O(1)^{c}$	2.140(5)	2.1000(14)	2.1323(13)
$Fe-O(3)/O(4)^{c}$	2.079(4)	2.1548(14)	2.1237(13)
N(1)-Fe-N(2)	75.37(16)	75.31(6)	76.64(6)
N(2)-Fe-N(3)	82.32(16)	82.57(6)	82.88(5)
N(3)-Fe-N(4)	76.53(17)	75.71(6)	76.08(5)
N(1)-Fe- $N(4)$	168.07(17)	169.56(6)	170.22(6)
$N(2)-Fe-N(5)/O(1)^{c}$	174.25(12)	175.90(6)	161.57(5)
$N(3)-Fe-O(3)/O(4)^{c}$	174.58(16)	170.49(6)	168.70(5)
$N(5)/O(1)-Fe-O(3)/O(4)^{c}$	92.31(17)	95.18(6)	98.75(5)

<sup>a</sup> N(1), N(4) pyridine/quinoline N.

<sup>b</sup> N(2), N(3) amine N.

<sup>c</sup> Fe–N(5)/O(3) for **C3**, Fe–O(1)/O(4) for **C4** and **C5**.

mixtures overnight. Isolation was facile, with yields for the complexes ranging from 50% to 76%. Further purification by crystallization from acetonitrile/diethyl ether or dichloromethane/diethyl ether yielded crystalline products.

#### 3.2. Solid state structures of iron complexes

The ORTEP representations of the solid state structures of complexes **C3**, **C4** and **C5** are shown in Figs. 2 and 3 and in the Supplemental information. Crystallographic data are provided in Table 1 and selected bond lengths and bond angles in Table 2.

The iron centers in complexes **C3–C5** possess distorted octahedral geometries, owing to the steric requirements of the three 5-membered chelate rings of the tetradentate ligands. The two pyridine/quinoline donor moieties of the tetradentate ligands are *trans* to each other, and the ligands adopt the *cis*- $\alpha$  conformation typical of iron complexes with bpmen-type ligands [42]. In complexes **C4** and **C5**, the triflate anions occupy positions that are *cis* to each other. In contrast, for **C3**, one of the triflate anions is replaced by a coordinating acetonitrile solvent molecule. This preferential binding of the smaller acetonitrile is consistent with a larger steric demand of **L3**, as compared to **L4** or **L5**, and with



**Fig. 2.** Structure of complex **C3**:  $[(L3)Fe(OTf)(CH_3CN)](OTf)$  (L3 = N.N'-dimethyl-N.N'-bis(6-methoxypyridin-2-ylmethyl)-1,2-diaminoethane; OTf = triflate). Thermal ellipsoids are represented at 50% probability. Hydrogen atoms and the triflate anion are omitted for clarity.



**Fig. 3.** Structure of complex **C5**:  $[(L5)Fe(OTf)_2]$  (L5 = N,N'-dimethyl-N,N'-bis (5-chloropyridin-2-yl)methyl-1,2-diaminoethane; OTf = triflate). Thermal ellipsoids are represented at 50% probability. Hydrogen atoms are omitted for clarity.

the commonly observed exchange of the triflate anions with coordinated acetonitrile in solution (see for example [33,43]). A search of the Cambridge Structural Database [CSD, Version 5.34 (May 2013)] for tetradentate ligands with the pyridine-amine-aminepyridine framework show mean bond distances of 2.156, 2.212 and 2.140 Å for the Fe–N(pyridine), Fe–N(amine), and Fe–O(triflate) bond distances, respectively [44]. The Fe–N(amine), Fe– N(pyridine) and Fe–O(triflate) bond distances in **C3–C5** therefore generally fall within their expected ranges, though the Fe–O(triflate) bond in **C3** is on the lower end of reported values. The Fe– N distances range from 2.18 to 2.25 Å and are characteristic of high-spin Fe(II) complexes [33,43,45].

In complex C3 the two planes formed by the MeO-pyridine-CH<sub>2</sub>-segments of the ligand are positioned at an angle of 69° relative to each other. The bound acetonitrile molecule has a Fe-N-C angle of 163.5° which is at the lower end of reported angles for iron-bound acetonitrile, but no significant reduction in the C-N bond length (1.133(7) Å) is observed. For complex **C4**, the planes of the two quinoline rings are positioned at an angle of 61° relative to each other. Each quinoline ring is directed along one of the Fe-O(triflate) bonds, with torsion angles of 1.2° and 8.5° between the planes of the quinoline rings and the Fe-O bonds, leading to an increase in the N(quinoline)-Fe-O angle from the idealized 90° to 102.48(6)° and 105.15(6)°, respectively. The closely-related structures [(L4)FeCl<sub>2</sub>] and [(L2)Fe(OTf)<sub>2</sub>] (C2) have been reported previously [11,46]. Similar structural features are observed. The effect of moving from triflate to chloride anions is a reduction to about 43.3° for the torsion angle between the two quinoline rings. The quinoline rings are also directed along the Fe-Cl bonds, with slightly larger torsion angles of 3.2° and 15.2° between the planes of the two quinoline rings and the Fe-Cl bonds, and a N(quinoline)-Fe-Cl angle of 104.4°. For C2, the planes of the pyridine rings are positioned at an angle of 75°, and the Me-groups are also in a direction parallel to the Fe-O bonds, with torsion angles of 8.4° between the plane of the pyridine rings and the Fe-O bonds. The effect of the chloride for triflate substitution in [(L4)FeCl<sub>2</sub>] leads to a lengthening of all the Fe-N bond distances. The average Fe-N(pyridine) bond increases from 2.251 Å in the triflate complex C4 to 2.399 Å in the chloride complex, and the average Fe-N(amine) bond increases from 2.214 to 2.259 Å, presumably owing to the better donor ability of the chloride anion compared to triflate. Although one might expect **L2** to be a better  $\sigma$ -donor than **L4**, the average Fe–N(pyridine) bond lengths in **C2** is 2.290 Å, about 0.04 Å longer than in **C4** despite the slightly lower basicity and similar steric demand of quinoline.

The presence of a chloro group in the 5-position of the pyridine ring in complex C5 is expected to reduce the  $\sigma$ -donor ability of the pyridines relative to the unsubstituted pyridine ring. Since the iron complex of the latter was crystallized as the acetonitrile adduct [(bpmen)Fe(CH<sub>3</sub>CN)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> [47], a more suitable comparison for C5 to previously published structures is with the iron complex of the bpmen-derivative with a Me-group in the 5-position [11]. The differences in the Fe–N(pyridine) bond lengths in these 5-substituted complexes is negligible (average of 2.192 Å for C5, and 2.179 Å for the methyl-derivative), indicating that the Cl-substitution only has a minor effect on the Fe–N(pyridine) bond length in the solid state, despite the differences in electronic properties of the substituents (Hammett parameters  $\sigma_{\rm m}$ (Cl) 0.37 and  $\sigma_{\rm m}({\rm Me})$  – 0.06 [48]). The planes of the pyridine rings are positioned at an angle of 66° in **C5**, providing no clear correlation between bulk at the 6-position and the angle between the two planes formed by the pyridine rings in C2-C5. Interestingly, the 98.76(5)° angle between the two triflate anions in C5 is on the higher end of the range typically found (mean 92.55°), and the amine-Fe-triflate angle N(2)-Fe-O(1) of 161.57(5)° is at the lower end of its range, leading to a more severe distortion of the octahedral geometry than usual.

#### 3.3. ESI-MS studies of iron complexes

The ESI mass spectra of  $[(bpmen)Fe(OTf)_2]$ ,  $[(L2)Fe(OTf)_2]$ ,  $[(L3)Fe(OTf)(CH_3CN)](OTf)$ ,  $[(L4)Fe(OTf)_2]$ ,  $[(L5)Fe(OTf)_2]$ , and  $[(L6)Fe(OTf)_2]$  in acetonitrile solutions generally show the presence of one predominant species in positive-ion mode, that of the parent cation of the complex  $[(LX)Fe(OTf)]^+$  (Fig. 4 and Supplemental information). Experimental isotope patterns matched the expected theoretical isotopic patterns, confirming the formulation of the complex in acetonitrile solutions. One notable exception was the ESI-spectrum of  $[(L4)Fe(OTf)_2]$  where in addition to the base peak of  $[(L4)Fe(OTf)]^+$ , a prominent peak with a m/z = 1293 was detected. The  $[(L4)_2Fe_2(OTf)_3]^+$  dimer has an expected m/z = 1299, and is close to the mass detected, hinting at a dimerization or oligomerization of the species under the conditions of the ESI-MS experiment. No such oligomerization was observed in the solid state.



**Fig. 4.** ESI-MS spectrum of [(**L5**)Fe(OTf)<sub>2</sub>] (**L5** = *N*,*N*′-dimethyl-*N*,*N*′-bis(5-chloro-pyridin-2-ylmethyl)-1,2-diaminoethane) in acetonitrile taken in positive-ion mode.



**Fig. 5.** Cyclic voltammograms of complex  $[(L5)Fe(OTf)_2]$  (**C5**) in acetonitrile, dimethylformamide/acetonitrile (1:30 v/v) and dichloromethane with 0.1 M (Bu<sub>4-</sub> N)(PF<sub>6</sub>) supporting electrolyte at scan rates of 50 mV s<sup>-1</sup>. Potentials are reported relative to ferrocene. Key: acetonitrile – blue, dimethylformamide/acetonitrile – purple, dichloromethane – black dashed line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

 Table 3

 Electrochemical data for the Fe<sup>III</sup>/Fe<sup>II</sup> redox couple for complexes C1–C6.<sup>a-c</sup>

Complex	C1	C2	C3	C4	C5	C6
$E_{1/2}$ (V, MeCN) <sup>a,c</sup>	0.72	1.06 (IR) <sup>d</sup>	0.67	1.11 (IR) <sup>d</sup>	0.77	0.96 (IR) <sup>d</sup>
$\Delta E_{1/2}$ (mV, MeCN) <sup>a</sup>	109	х	260	х	260	х
$i_{\rm pf}/i_{\rm pr}~({\rm MeCN})^{\rm a}$	0.80	х	0.52	x	0.61	х
$E_{1/2}$ (V, CH <sub>2</sub> Cl <sub>2</sub> ) <sup>b,c</sup>	0.52	0.70	0.50	0.75	0.59	0.49
$\Delta E_{1/2}$ (mV, CH <sub>2</sub> Cl <sub>2</sub> ) <sup>b</sup>	206	140	190	128	280	135
$i_{ m pf}/i_{ m pr}$ , (CH <sub>2</sub> Cl <sub>2</sub> ) <sup>b</sup>	0.98	0.67	0.82	0.89	0.82	0.50

<sup>a</sup> Measurements carried out in CH<sub>3</sub>CN with 0.1 M (<sup>n</sup>Bu<sub>4</sub>N)(PF<sub>6</sub>) electrolyte and a 0.01 M AgNO<sub>3</sub>/Ag reference electrode.

<sup>b</sup> Measurements carried out in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M ("Bu<sub>4</sub>N)(PF<sub>6</sub>) electrolyte and a 0.01 M AgNO<sub>3</sub>/Ag reference electrode.

<sup>c</sup> Potentials are given relative to the ferrocenium/ferrocene couple run under the same conditions.

<sup>d</sup> Electrochemically irreversible feature; *E*<sub>p</sub> provided.

# 3.4. Redox potentials of iron complexes

Cyclic voltammetry was used to determine the reduction potentials of the complexes in acetonitrile and dichloromethane solutions. Potentials are reported vs the ferrocenium/ferrocene redox potential under the experimental conditions employed. Representative cyclic voltammograms are shown in Fig. 5, and relevant measurements are provided in Table 3 (see Supplemental information for remaining data). In acetonitrile, the complexes generally showed irreversible behavior. For C2, C4, and C6 only an anodic peak around +1.0 V was observed. Complexes C3 and C5 also displayed significant cathodic peaks, with peak-to-peak separations around 260 mV and ratios of the forward and reverse currents  $i_{\rm pf}/i_{\rm pr}$  of about 0.5–0.6. In contrast, the parent complex C1 presented quasi-reversible behavior, with the ratios of the forward and reverse currents  $i_{\rm pf}/i_{\rm pr}$  around 0.8 and  $\Delta E_{1/2}$  values around 110 mV. Under identical conditions, the  $Fc/Fc^+$  couple showed a  $\Delta E_{1/2}$  of about 90–100 mV and a current ratio  $i_{pf}/i_{pr}$  of 0.95–0.99. The electrochemical data for the chloro-analog of C1 and C2, [(LX)FeCl<sub>2</sub>] (LX = L1 and L2) have been reported recently and showed quasi-reversible features, with  $E_{1/2} = 0.385 \text{ V}$  (vs SHE;  $\Delta E_{1/2}$  = 90 mV, CH<sub>3</sub>CN) for [(bpmen)FeCl<sub>2</sub>] and  $E_{1/2}$  = 0.600 V (vs SHE;  $\Delta E_{1/2}$  = 110 mV, CH<sub>3</sub>CN) for [(L2)FeCl<sub>2</sub>] [49]. The impact of the chloro for triflate anion substitution thus led to more reversible electrochemical features. In acetonitrile solutions, triflate anions are often exchanged by acetonitrile in complexes of the kind studied in this report [33,43]. To probe the ability of solvent to replace bound triflate in solution, electrochemical measurements were also run in presence of small amounts of dimethylformamide (DMF) in acetonitrile (about 0.1 mL of DMF in 3 mL of solvent). The addition of DMF did not impact the half-way potential of the ferrocenium/ferrocene couple, but generated mostly quasi-reversible behavior at potentials lower by about 300 mV for **C1**, **C2**, **C3** and **C5** (**C1**  $E_{1/2} = 0.36$  V,  $i_{pf}/i_{pr} = 0.81$ ; **C2**  $E_{1/2} = 0.56$  V,  $i_{pf}/i_{pr} = 0.56$ ; **C3**  $E_{1/2} = 0.40$  V,  $i_{pf}/i_{pr} = 0.91$ ; **C5**  $E_{1/2} = 0.45$  V,  $i_{pf}/i_{pr} = 0.83$ ;  $E_{1/2}$  reported vs Fc<sup>+</sup>/Fc). The lowering of half-way potentials observed on addition of DMF is consistent with a change in the polarity of the solvent mixture or with the displacement of bound triflate anions or acetonitrile by DMF. UV–Vis measurements showed similar shifts (vide infra). For the [(**LX**)FeCl<sub>2</sub>] analogs, the methyl group of the 6-position of the pyridine ring increased the redox potential by about 200 mV, making it more difficult to oxidize the complex [49]. We observed similar trends when examining the complexes **C1** and **C2** in acetonitrile with DMF added.

To probe the effect of solvent coordination, we undertook electrochemical measurements in the non-coordinating solvent dichloromethane. In general, all complexes showed anodic and cathodic peaks, with values for  $E_{1/2}$  lowered by about 170–200 mV. As expected for this less polar solvent, larger peak-to-peak separations were observed (range 130-280 mV) with ratios of the forward and reverse currents often typical of quasi-reversible processes. Moving to dichloromethane yielded significant cathodic currents for complexes C2, C4 and C6 not observed in acetonitrile (C2  $E_{1/2} = 0.70$  V,  $i_{pf}/i_{pr} = 0.67$ ; **C4**  $E_{1/2} = 0.99$  V,  $i_{pf}/i_{pr} = 0.89$ ; **C6**  $E_{1/2} = 0.49$  V,  $i_{pf}/i_{pr} = 0.50$ ). Examining the effect of substitution on the pyridine ring, introducing the methyl group at the 6-position increased the redox potential by about + 200 mV (vide supra). A similar shift was observed for the quinoline derivative C4. However, moving to the 6-OMe substituted ligand framework in C3  $(E_{1/2} = 0.50 \text{ V}, i_{\text{pf}}/i_{\text{pr}} = 0.82)$ , the electrochemical behavior was similar to that of [(bpmen)Fe(OTf)<sub>2</sub>] (**C1**  $E_{1/2}$  = 0.52 V,  $i_{pf}/i_{pr}$  = 0.98) in dichloromethane. Changing the ethylene-diamine central unit in bpmen to a 3,5-dimethyl-substituted piperazine unit in L6 led to similar half-way potentials (**C6**  $E_{1/2}$  = 0.49 V,  $i_{pf}/i_{pr}$  = 0.50), and a significant reduction in the reversibility of the process, with much lower current ratios for **C6** than for **C1**. Introducing a chloro-substituent at the 5-position of the pyridine rings shifted the potential to about 70 mV more positive than that of the bpmen complex, i.e. making oxidation less facile for the Cl-substituted derivative. This trend is consistent with the reduced basicity of the chlorinated pyridine. No such agreement between basicity and half-way potential is observed for the 6-Me- and 6-OMe-substituted pyridines in C2 and C3, consistent with the steric importance of that position. There is no clear correlation between the values of the half-way potentials of the catalysts and their catalytic activities (vide infra).

#### 3.5. UV–Vis spectroscopy

The UV–Vis spectra of complexes **C1**, **C3**, **C4** and **C5** in acetonitrile at room temperature showed two major features (Table 4), a band around 330–400 nm (Fig. 6) and a stronger band around 260–290 nm (Supplemental information). These two bands were previously observed for other iron(II) complexes containing pyridine-based ligands and were attributed to metal-to-ligand charge transfer (MLCT) and ligand-centered  $\pi$  to  $\pi^*$  transitions, respectively [33,43,45,50,51]. The ligand-centered transitions were more intense than the MLCT bands. For **C1** and **C5**, the MLCT-bands were well defined. The former was reported previously with a similar  $\lambda_{max}$  and higher  $\varepsilon$  ( $\lambda_{max}$  375 nm;  $\varepsilon$  3800) – these differences may be due to differences in the temperature of measurement [33]. For complexes **C3** and **C4**, the MLCT processes appeared as shoulders.

The addition of small amounts of DMF to acetonitrile solutions of these complexes shifted the electrochemical potentials of complexes **C1** and **C5** to lower potentials. This observation prompted

#### Table 4

UV-Vis data for complexes C1, C3, C4 and C5.

Complex	C1	C3	C4	C5
$\pi$ to $\pi^*$ transition (CH <sub>3</sub> CN) $\lambda_{max}$ nm (ε) <sup>a</sup> MLCT (CH <sub>3</sub> CN) $\lambda_{max}$ nm (ε) <sup>a</sup>	262 (13100) 374 (2700)	280 (16300) 330 (sh, 1200)	286 (13500) 364 (sh, 1050)	272 (14300) 390 (3000)
MLCT (DMF:CH <sub>3</sub> CN 1:15 v/v) $\lambda_{max}$ nm ( $\varepsilon$ ) <sup>b</sup>	394 (1500)	x	x	422 (1900)

<sup>a</sup> Measurements carried out in indicated solvent with about 0.02 mM concentrations of complexes.

<sup>b</sup> Measurements carried out in indicated solvent with about 0.2 mM concentrations of complexes.



**Fig. 6.** (a) UV–Vis spectra of complexes  $[(L1)Fe(OTf)_2]$  (**C1**),  $[(L3)Fe(OTf)(CH_3-CN)](OTf)$  (**C3**),  $[(L4)Fe(OTf)_2]$  (**C4**), and  $[(L5)Fe(OTf)_2]$  (**C5**) in acetonitrile solutions of about 0.2 mM concentrations (key: **C1** – blue line, **C3** – red dotted line, **C4** – green dashed line, **C5** – black line); (b) UV–Vis spectra of complexes **C1** and **C5** in acetonitrile and in dimethylformamide/acetonitrile (1:15 v/v) solutions of about 0.20–0.25 mM concentrations (key: acetonitrile: **C1** – blue line, **C5** – black line; dimethylformamide/acetonitrile: **C1** – blue line, **C5** – black line; for interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the measurements of the UV–Vis spectra in mixtures of DMF and acetonitrile (1:15 v/v) for the two complexes **C1** and **C5** for which the MLCT-bands were well defined (Fig. 6). On the addition of DMF, the MLCT-bands for the two complexes shifted to higher wavelengths and became less intense. The bathochromic shift and hypochromic effect could be due to the change in solvent polarity and are also consistent with a change in the magnetism of these complexes to a more purely high-spin state due to the interaction of DMF with the iron centers.

#### 3.6. Epoxidation studies

# 3.6.1. Catalyst studies

The metal complexes **C1** to **C6** were examined for their efficiency in catalyzing the oxidation of oleic acid with hydrogen peroxide as the oxidant (Fig. 7). Initial runs were carried out using catalyst:substrate:oxidant ratios of 1:200:600. The oxidant was added over a 2-minute period, and reactions carried out for a total of 10 minutes. Increased reaction times did not lead to higher conversions. Where little or no substrate conversion was observed the run was repeated using a catalyst:substrate:oxidant ratio of 1:50:150. Table 5 summarizes the results of these oxidations. Conversions and selectivity were determined by <sup>1</sup>H NMR [36,38,52,53]. For oxidations where epoxide was the only product clearly identified, a selectivity of >95% is indicated to account for the limit of detecting low amounts of other products by NMR. Representative <sup>1</sup>H NMR spectra for 3 of the substrates are shown in Fig. 8.

For the oleic acid substrate, **C1** was the most efficient catalyst, generating the epoxide product with about 90% conversion and >80% selectivity, leading to turnover numbers (TON) of >140. These TON are similar to those reported for *meso*-tetrakis(2,6-dichloro-



**Fig. 7.** The alkene substrates bearing a carboxylic acid functional group investigated in these epoxidation studies using hydrogen peroxide as an oxidant.

phenyl)porphyrin iron chloride and iodosylbenzene as oxidant (TON 145) over 16 hours [24]. **C5** was also active in the epoxidation of oleic acid, leading to 50% conversion to epoxide and >70% selectivity (TON > 70) under the standard conditions. By switching to the catalyst:substrate:oxidant ratio of 1:50:150, near complete conversion was obtained (Fig. 8a). Examining the product distribution for **C2**, epoxide was generated as the major product with oleic acid rather than the 4:1 mixture of diol and epoxide seen previously for cyclooctene [11]. This observation is consistent with the previously observed influence of carboxylic acids on the selectivity of these catalysts. The remaining catalysts showed conversions of <15%. Almost no catalytic activity was observed for **C3**, **C4** and **C6** under the conditions employed. The introduction of an orthosubstituent on the pyridine ring thus led to a significant reduction in catalyst activity.

**C1** and **C5** gave good conversions and were selective for epoxide formation. These two catalysts were therefore also investigated for the oxidation of undecylenic acid with hydrogen peroxide. Conversions were generally lower than with oleic acid. Oxidations using **C1** resulted in the formation of largely epoxide whereas the use of **C5** led to less selective product distributions. **C1** afforded 60% conversion and >70% selectivity for undecylenic acid as a substrate (TON > 84; Fig. 8b). Alternative routes to the synthesis of this epoxide include the use of peracetic acid as an oxidant for undecylenic acid (80% yield [22]).

The oxidation of substrates 4-pentenoic acid and 5-hexenoic acid were then investigated using **C1**. These substrates provided a noteworthy deviation from the previously observed product distribution. Under standard conditions, little epoxide was detected for 4-pentenoic acid. Instead, the lactone dihydro-5-(hydroxymethyl)-2(*3H*)-furanone was the main product, forming with 18% conversion (TON 36). When running the reaction with a catalyst:substrate:oxidant ratio of 1:50:150 conversion increased to 95% (TON 47; Fig. 8c, Scheme 1), with about 95%  $\gamma$ -lactone and

Table 5	
Oxidation of acid substrates by H <sub>2</sub> O <sub>2</sub> catalyzed by six different iron catalysts.	a

Substrate	Catalyst	Cat:Subst:H <sub>2</sub> O <sub>2</sub> ratio	Substrate conversion (%) <sup>b</sup>	Epoxide selectivity (%) <sup>c</sup>
Oleic acid	$[(L1)Fe(OTf)_2]$	1:200:600	90	>80 <sup>d</sup>
Oleic acid	[( <b>L2</b> )Fe(OTf) <sub>2</sub> ]	1:200:600	15	65
Oleic acid	[(L3)Fe(OTf)(CH <sub>3</sub> CN)](OTf)	1:200:600	<5	x <sup>e</sup>
Oleic acid	$[(\mathbf{L4})Fe(OTf)_2]$	1:200:600	0	х
Oleic acid	[( <b>L5</b> )Fe(OTf) <sub>2</sub> ]	1:200:600	50	>70 <sup>d</sup>
Oleic acid	[( <b>L5</b> )Fe(OTf) <sub>2</sub> ]	1:50:150	>96	>70 <sup>d</sup>
Oleic acid	[( <b>L6</b> )Fe(OTf) <sub>2</sub> ]	1:50:150	0	х
Undecylenic acid	$[(L1)Fe(OTf)_2]$	1:200:600	60	>70 <sup>d</sup>
Undecylenic acid	$[(\mathbf{L5})Fe(OTf)_2]$	1:200:600	40	10
4-Pentenoic acid	$[(L1)Fe(OTf)_2]$	1:200:600	18	>95 <sup>f</sup>
5-Hexenoic acid	$[(L1)Fe(OTf)_2]$	1:200:600	90	>95 <sup>f</sup>

<sup>a</sup> Refer to experimental section for complete description of reaction conditions.

<sup>b</sup> Conversion of substrate into all products.

<sup>c</sup> Epoxide yield as a percentage of products.

<sup>d</sup> Sole product detected by <sup>1</sup>H NMR, selectivity reported based on relative integrations (see experimental for full details).

<sup>e</sup> Conversion too low to accurately determine selectivity by <sup>1</sup>H NMR.

<sup>f</sup> Epoxide and lactone are formed. Percentage given = sum of epoxide and lactone. Over time, all epoxide converted to lactone.



**Fig. 8.** <sup>1</sup>H NMR spectra of the products of oxidizing (a) oleic acid using  $[(L5)Fe(OTf)_2]$ ; (b) undecylenic acid and (c) 4-pentenoic acid using  $[(bpmen)Fe(OTf)_2]$  as catalyst ((b) and (c)) and  $H_2O_2$  as oxidant (CDCl<sub>3</sub>, assignments: A = alkene, E = epoxide, L = lactone, x = water, y =  $-CH_2CO_2H$ , z =  $-CH_3$ ).

5% epoxide detected. With time, the remaining epoxide converted to the lactone, consistent with the hypothesis that lactone formation is subsequent to epoxide formation.

For 5-hexenoic acid, conversion under standard conditions was higher than with 4-pentenoic acid at about 90% (TON 180) affording a product distribution of 63% epoxide and 37%  $\delta$ -lactone (Scheme 1), when the analysis was carried out immediately after quenching. On standing for prolonged times, these mixtures also converted to mainly lactone product, further supporting the sequential formation of lactone from epoxide. The oxidative cyclizations of 4-pentenoic and 5-hexenoic acids described here have been observed in other systems. With MTO, 4-pentenoic acid was converted to the  $\gamma$ -lactone in 98% yield (TON 20) over 14 h, and

5-hexenoic acid to the corresponding lactone in 80% yield (TON 16) over 10 h, with 5,6-dihydroxyhexanoic acid as a byproduct. Tan et al. also suggested that the lactonized products formed via the intermediacy of the epoxide [38]. A solid-phase supported phophotungstate anion [PW<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> catalyst converted 4-pentenoic acid in 70% yield (TON 205) and 5-hexenoic acid in 46% yield (TON 115) to the corresponding lactone over a 6–12 h period using H<sub>2</sub>O<sub>2</sub> as oxidant [39]. Using meso-tetrakis(2,6-dichlorophenyl)porphyrin iron chloride as catalyst and iodosylbenzene as oxidant the related substrate 2-propylpent-4-enoic acid was converted to the lactone with 56% conversion (TON 112) over 16 h [24]. The system presented in this work compares favorably with these previous reports, particularly with respect to the short reaction times. There is no discernible trend between the proximity of the carboxylic acid functional group to the reactive alkene and the conversions observed. Oleic and 5-hexenoic acid were oxidized to higher conversions under the conditions employed.

#### 3.6.2. Effect of carboxylic acid functional group

To probe the effect of the carboxylic acid functional group, the oxidations of oleic, undecylenic and 4-pentenoic acid by  $H_2O_2$  catalyzed by  $[(bpmen)Fe(OTf)_2]$  were compared to the oxidations of the corresponding esters. Results are summarized in Table 6. In all cases the substrates bearing the acid-functionality were oxidized to higher conversion and with greater selectivity than the esters, consistent with the previous observation that added acid increased conversion and selectivity [10,12,14-16]. The most pronounced example was the comparison of 4-pentenoic acid and ethyl 4-pentenoate, where the ester was not oxidized under the conditions tested. For oleic acid, a 3-fold increase in consumption



Scheme 1. The oxidation of 4-pentenoic acid and 5-hexenoic acid using C1 by hydrogen peroxide leading to epoxide and lactone.

#### Table 6

Oxidation of acid and ester substrates by H2O2 catalyzed with [(bpmen)Fe(OTf)2].<sup>a</sup>

Substrate	Cat:Subst: H <sub>2</sub> O <sub>2</sub> ratio	Substrate conversion (%) <sup>b</sup>	Epoxide selectivity (%) <sup>c</sup>
Oleic acid	1:200:600	90	>80 <sup>d</sup>
Ethyl oleate	1:200:600	35	25
Undecylenic acid	1:200:600	60	>70 <sup>d</sup>
Methyl undecenoate	1:200:600	40	35
4-Pentenoic acid	1:50:150	95	>95 <sup>e</sup>
Ethyl pentenoate	1:50:150	<5	x <sup>f</sup>

<sup>a</sup> Refer to experimental section for complete description of reaction conditions.

<sup>b</sup> Conversion of substrate into all products.

<sup>c</sup> Epoxide yield as a percentage of products.

<sup>d</sup> Sole product detected by <sup>1</sup>H NMR, selectivity reported based on relative integrations (see experimental for full details).

<sup>e</sup> Epoxide converted to lactone. Lactone major product.

<sup>f</sup> Conversion too low to accurately determine selectivity by <sup>1</sup>H NMR.

for the carboxylic acid substrate vs the ester was observed and a significant increase in epoxide selectivity. For undecylenic acid and its methyl ester, a corresponding increase from 40% conversion and 35% selectivity (TON 28) for the ester to 60% conversion and >70% selectivity (TON 84) for the acid was observed. These observations underline the importance of the carboxylic acid functional group in promoting epoxidation of the alkenes. This beneficial effect was observed independent of the length of the  $(CH_2)_n$ -spacer between the alkene and the carboxylic functional groups, consistent with an intermolecular effect. However, the effect was most pronounced with 4-pentenoic acid, where the possibility of the formation of a stable chelate ring could enhance the conversion in an intramolecular fashion.

#### 3.6.3. Effect of solvent choice

The effect of solvent choice on conversion was examined for the oxidation of oleic acid with  $H_2O_2$  and  $[(bpmen)Fe(OTf)_2]$  by running the reaction in nitromethane, propionitrile, butyronitrile and dimethoxyethane, in addition to the standard acetonitrile. A range of dielectric constants is represented (35.9, 27.2, 20.3, 7.20 and 37.5, respectively) [54]. These solvents also present small variations in the  $t_1$  (polarity) and  $t_2$  (polarizability) values from the commonly used acetonitrile. The order of decreasing  $t_1$  values is nitromethane (1.49), acetonitrile (1.27), propionitrile (0.68) and dimethoxyethane (-1.11) [54]. For  $t_2$ , the solvents can be grouped into two pairs of approximately similar values, with  $t_2 = -1.65$  for both acetonitrile and propionitrile and  $t_2 = 0.99$  and 0.98 for nitromethane and dimethoxyethane, respectively [54]. The values for butyronitrile were not listed but presumably  $t_1$  is lower than the value for propionitrile and  $t_2$  is similar to that propionitrile. Fig. 9



**Fig. 9.** Comparison of conversions for the oxidation of oleic acid by  $H_2O_2$  catalyzed with [(bpmen)Fe(OTf)<sub>2</sub>] in different solvents (298 K, inert atmosphere; Key: NM – nitromethane, BN – butyronitrile, DME – dimethoxyethane, PN – propionitrile, ACN – acetonitrile).

illustrates the conversions of these oxidations under the standard conditions. Overall, there is no clear trend between the solvent parameters and conversions. Acetonitrile leads to the highest conversions, and a decrease in conversion was observed with a decrease in the polarity and dielectric constant of the nitrile solvents tested. Unlike substrate consumption, the selectivity for the epoxide remained relatively consistent over the range of solvents examined at >80%.

#### 4. Conclusions

The iron catalyst [(bpmen)Fe(OTf)<sub>2</sub>] and its derivative [(**L5**)Fe(OTf)<sub>2</sub>] catalyzed the epoxidation of alkenes bearing a carboxylic acid functional group with hydrogen peroxide as the oxidant in good yields and with good to high selectivity. The presence of the carboxylic acid functional group enhanced the rate and selectivity of these oxidations, and led to the formation of epoxide product for oleic and undecylenic and the  $\gamma$ - and  $\delta$ -lactones for 4-pentenoic and 5-hexenoic acid, respectively. Substitutions at the 6-position of the pyridine rings (Me, OMe, and as quinoline) and changing the diamine backbone to a substituted piperazine backbone in the ligand framework led to significant decreases in alkene conversions. In acetonitrile, the solvent used for epoxidations, the most active catalyst [(bpmen)Fe(OTf)<sub>2</sub>] displayed the most reversible electrochemical behavior. Further experiments are planned to explore the scope of this catalyst.

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## Appendix A. Supplementary material

Supplementary (Crystallographic data for complexes **C3**, **C4** and **C5**; ESI-MS data for **C1–C6**; electrochemical data; UV–Vis data for **C1**, **C3**, **C4** and **C5**; NMR and GC-MS data for representative epoxidations.) data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.12.029.

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