Volume 1 | Number 1 | Jan 2013 | Pages 1–100

ChemComm

Chemical Communications
www.rsc.org/chemcomm

ROYAL SOCIETY OF CHEMISTRY

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

www.rsc.org/chemcomm

ChemComm

COMMUNICATION

[Fe^{III}(TF$_4$DMAP)OTf] Catalysed Anti-Markovnikov Oxidation of Terminal Aryl Alkenes to Aldehydes and Transformation of Methyl Aryl Tertiary Amines to Formamides with H$_2$O$_2$ as Terminal Oxidant

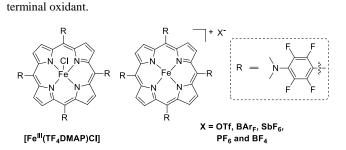Yi-Dan Du,[a] Chun-Wai Tse,[b] Zhen-Jiang Xu,*[a] Yungen Liu,[b] and Chi-Ming Che*[ab]

Anti-Markovnikov oxidation of terminal aryl alkenes to aldehydes and transformation of *N*-methyl aryl tertiary amines to formamides with H$_2$O$_2$ as terminal oxidant under mild conditions have been achieved in moderate to good product yields using [Fe^{III}(TF$_4$DMAP)OTf] as catalyst.

Metal catalysed selective oxidation of C=C and C–H bonds are useful tools for organic synthesis and fine chemical industry but remain to be accomplished with high selectivity and product yields using environmental benign oxidants such as O$_2$/air or H$_2$O$_2$.[1] In these endeavours, we are attracted to the uses of high valent iron-oxo complexes in organic synthesis as iron-oxo complexes with oxidation states IV and V are well documented to be strong oxidants capable of performing oxidative functionalization of alkenes and alkanes.[2] We are particularly interested to develop synthetic applications of the oxidation reactions that proceed via [Fe(Por)O]$^+$ (Por = porphyrinato dianion) reaction intermediates, as their methods of generation and reactivity have already been subjected to extensive studies over the past several decades.[2,3] In literature, examples of iron catalyzed selective organic oxidation reactions using O$_2$/air or H$_2$O$_2$ as terminal oxidant and which can be used in organic synthesis are sparse but such examples are increasing over the past several years.[3,4] An organic oxidation reaction which has a profound impact in both industry and academia is anti-Markovnikov oxidation of terminal alkenes to aldehydes without cleavage of C=C bonds by palladium compounds, the Wacker oxidation.[5] Very recently, Grubbs reported PdCl$_2$(MeCN)$_2$ catalyzed selective oxidation of styrenes to phenyl acetaldehydes with *p*-benzoquinone or O$_2$ as oxidant.[6] We have previously reported that selective oxidation of terminal alkenes to aldehydes without C=C bond cleavage can be readily accomplished in high product yields via a tandem epoxidation–isomerization (E–I) pathway which involves a reactive metal-oxo species such as that of Ru as reaction intermediate.[7] As iron is earth abundant and biocompatible,[3,8] we studied an iron porphyrin catalyzed anti-Markovnikov oxidation of both terminal aryl and aliphatic alkenes to aldehydes in high yields, but with a shortcoming of using PhIO as oxidant.[9] Our attempts to replace PhIO by H$_2$O$_2$ for [Fe(2,6-Cl$_2$TPP)OTf] or [Fe^{III}(F$_{20}$TPP)OTf][10] (2,6-Cl$_2$TPPH$_2$ = *meso*-

tetrakis(2,6-dichlorophenyl)porphyrin), H$_2$F$_{20}$TPP = *meso*-tetrakis(pentafluorophenyl)porphyrin) catalysed E–I reaction using styrene as substrate gave phenylacetaldehyde in 30% yield and with low selectivity. We envisioned that the highly oxidizing [(Por$^{•+}$)(Fe^{IV}=O)]$^+$ intermediate[11] once generated, underwent C=C bond epoxidation as well as over oxidation. [Fe^{III}(TF$_4$DMAP)]$^+$ (H$_2$TF$_4$DMAP = *meso*-tetrakis(*o,o,m,m*-tetrafluoro-*p*-(dimethy1amino)phenyl)porphyrin) is an analogue of [Fe^{III}(F$_{20}$TPP)]$^+$ by replacing the *para*-F substituent of *meso*-C$_6$F$_5$ groups with electron donating dimethylamino (NMe$_2$) moiety. It is envisioned that the [(TF$_4$DMAP$^{•+}$)(Fe^{IV}=O)]$^+$ intermediate generated by oxidation of [Fe^{III}(TF$_4$DMAP)]$^+$ with oxygen atom donors should be less oxidizing and more stable thereby the accompanying side over oxidation reactions in the course of E–I oxidation may be minimized. Herein is described that [Fe^{III}(TF$_4$DMAP)OTf] is an effective catalyst for anti-Markovnikov oxidation of terminal aryl alkenes to aldehydes with good product yields. The synthetic application of the putative [(TF$_4$DMAP$^{•+}$)(Fe^{IV}=O)]$^+$ intermediate has also been revealed by the examples of Fe^{III}(TF$_4$DMAP)]$^+$ catalysed selective oxidation of a panel of *N*-methyl aryl tertiary amines to formamides using H$_2$O$_2$ as terminal oxidant.

[Fe^{III}(TF$_4$DMAP)Cl]

X = OTf, BAr$_F$, SbF$_6$, PF$_6$ and BF$_4$

Initially, the oxidation of styrene by H$_2$O$_2$ was used for optimization of the reaction conditions. As the ligand/counter-anion X may affect the reactivity of [Fe^{III}(Por)X] (or formulated as [Fe^{III}(Por)]X),[9,12] the catalytic activities of a panel of [Fe(TF$_4$DMAP)X] (X = OTf$^-$, BAr$_F^-$, SbF$_6^-$, PF$_6^-$ and BF$_4^-$, generated in situ by reacting [Fe^{III}(TF$_4$DMAP)Cl] with AgX, see ESI†) catalysts were evaluated (Table 1). [Fe^{III}(TF$_4$DMAP)OTf] catalysed the

oxidation of styrene with H_2O_2 to give phenylacetaldehyde in 77% yield along with 1-phenylethane-1,2-diol and benzaldehyde in 15% and 7% yields, respectively, and no epoxide was observed (Table 1, entry 1). The use of other AgX additives (X = SbF_6^-, PF_6^- and BF_4^-) and $NaBAr_F$ resulted in lower substrate conversion and /or lower aldehyde selectivity (Table 1). Recrystallization of the product (obtained by the reaction of $[Fe^{III}(TF_4DMAP)Cl]$ and $NaBAr_F$ in THF) in CH_2Cl_2/hexane (1:9) gave $[Fe(TF_4DMAP)_2]O$ (see ESI†).

Table 1 $[Fe^{III}(TF_4DMAP)X]$ Catalysed E–I reaction[a]

entry	additive	time (h)[b]	conversion (/%)[c]	yield (%)[c]			
				a	b	c	d
1	AgOTf	5+5	~100	77	0	15	7
2	$NaBAr_F$	5+5	~100	29	65	5	1
3	$NaBAr_F$	5+21	~100	57	21	20	2
4	$AgSbF_6$	5.5+5	94	10	79	0	5
5	$AgPF_6$	5+5	87	11	71	3	2
6	$AgPF_6$	5+22	91	24	51	13	2
7	$AgBF_4$	5+5	75	41	25	8	1
8	$AgBF_4$	5+22	75	46	5	20	2

[a] styrene (0.2 mmol), catalyst (2 mol%) and additive were mixed in dioxane (1.5 mL) at room temperature, and then H_2O_2 (0.4 mmol, diluted in dioxane (0.5 mL)) was added via syringe pump; [b] the first number was the addition time of H_2O_2 and the second number was the further stirring time; [c] determined by GC.

Examination of solvent effect revealed dioxane to be the solvent of choice (Table S1, entry 1). Low product yields were obtained when THF, toluene, CH_3CN, diethyl ether, methyl *tert*-butyl ether (MTBE), or $MeOH/CH_2Cl_2$ (3/1) was used (Table S1, entries 2–7). Phenylacetaldehyde was obtained in 47% yield when 1,2-dimethoxyethane (DME) was employed as solvent (Table S1, entry 8). 2-*tert*-Butoxy-2-phenylethanol via ring opening reaction of styrene oxide was obtained in 70% yield when *tert*-butanol was used as solvent (Table S1, entry 9). Products were obtained in acetal forms when methanol or acetone was used as solvent (Table S1, entry 10 and 11). Even with dioxane as solvent, the substrate conversion decreased significantly from 100% to 40% when the amount of H_2O_2 was decreased from 2.0 equivalents to 1.2 equivalents. 2-Phenylacetic acid (the over-oxidized product from phenylacetaldehyde) was obtained in 28% yield when the amount of H_2O_2 was increased to 5.0 equivalents (Table S2). Pre-treatment of commercially available styrene (from Aldrich®) by filtrating through Al_2O_3 and adding 1% BHT (BHT = 2,6-di-*tert*-butyl-4-methylphenol) did not significantly improve the substrate conversion, product yield and selectivity. Using 2.0 equivalents of H_2O_2, dioxane as solvent and a lower loading of $[Fe^{III}(TF_4DMAP)OTf]$ (0.5 mol%), phenylacetaldehyde was obtained in the highest 86% yield with minimal amounts of by-products benzaldehyde (6%) and 1-phenylethane-1,2-diol. Trace amount of phenylacetaldehyde was obtained with < 2% substrate conversion when the oxidant was changed to $^tBuOOBu^t$ or ^tBuOOH (Table S3). Hence, the protocol "0.5 mol% iron catalyst + 2.0 equivalents H_2O_2" was used in the subsequent experiments.

Using this protocol, we examined the substrate scope of the $[Fe^{III}(TF_4DMAP)OTf]$ catalysed E–I reaction. As depicted in Table 2, a panel of aryl alkenes gave the corresponding aldehydes in good to high yields. Styrenes **1b–1f** bearing *para*-substituents afforded the corresponding phenylacetaldehydes **2b–2f** in 55–76% yields (entries 1–5), while 58% *p*-trifluoromethyl styrene oxide was obtained from **1g** (entry 6). Compounds **1i–1l** bearing electron-withdrawing *meta*-

substituents afforded **2i–2l** in 67–80% yields (entries 8–11); however, a higher reaction temperature or higher loading of catalyst was needed in these cases. α-Substituted styrenes **1o–1q** could also be converted to corresponding aldehydes in 64–73% yields (entries 14–16).

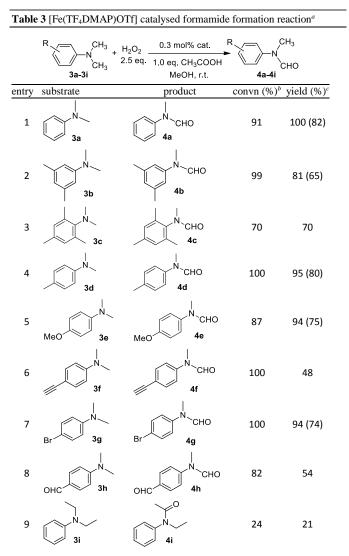**Table 2** $[Fe(TF_4DMAP)OTf]$ catalysed E–I reaction[a]

entry	substrate	product	convn (%)[b]	yield (%)[b]
1	**1b**: R_1 = *p*-Me; R_2 = H	**2b**	100	73
2	**1c**: R_1 = *p*-OMe; R_2 = H	**2c**	100	55
3	**1d**: R_1 = *p*-$ClCH_2$; R_2 =H	**2d**	100	64
4	**1e**: R_1 = *p*-F; R_2 = H	**2e**	100	76
5	**1f**: R_1 = *p*-Br; R_2 = H	**2f**	100	72
6	**1g**: R_1 = *p*-CF_3; R_2 = H	**2g**	90	58
7	**1h**: R_1 = *m*-Me; R_2 = H	**2h**	94	87
8	**1i**: R_1 = *m*-NO_2; R_2 = H	**2i**	80	67[c,d]
9	**1j**: R_1 = *m*-F; R_2 = H	**2j**	90	75[c]
10	**1k**: R_1 = *m*-Cl; R_2 = H	**2k**	100	70[c]
11	**1l**: R_1 = *m*-Br; R_2 = H	**2l**	100	80[c,d]
12	**1m**: R_1 = *o*-F; R_2 = H	**2m**	92	60
13	**1n**	**2n**	86	60
14	**1o**: R_1 = H; R_2 = Me	**2o**	100	64
15	**1p**: R_1 = H; R_2 = Ph	**2p**	100	70
16	**1q**: R_1 = H; R_2 = $BrCH_2$	**2q**	100	73

[a] 0.2 mmol substrate, catalyst (0.5 mol%) in dioxane (1.5 mL), H_2O_2 (0.4 mmol, diluted in dioxane(0.5 mL)) was added via syringe pump over 5 h, r.t., 8~9 h; [b] based on ^1H NMR with PhTMS as the internal standard; [c] after addition of H_2O_2, it was heated to 80 °C; [d] 2 mol% catalyst was used.

Oxidative cross coupling of tertiary amines with nucleophiles is a useful strategy for the synthesis of amino compounds.[13] In this work, oxidative cross coupling reaction of tertiary amines and $TMSCF_3$ with $[Fe^{III}(TF_4DMAP)OTf]$ as catalyst and H_2O_2 as terminal oxidant gave formamides as the major product. Adding 1 equivalent (based on amine) of acetic acid increased both the substrate conversion and product yield (Table S4). Further optimization of the reaction conditions led to the use of 0.3 mol% of Fe catalyst with acetic acid (1 equivalent) as the additive, MeOH as the solvent, and H_2O_2 (2.5 equivalent) as terminal oxidant at room temperature. As shown in Table 3, a panel of *N,N*-dimethyl anilines having electron-donating or electron-withdrawing substituents were oxidized to corresponding *N*-methyl formamides in moderate to good yields (entries 1–8). Changing *N,N*-dimethyl aniline to *N,N*-diethyl aniline, both of the substrate conversion and product yield decreased dramatically, and the corresponding *N*-ethyl acetamide was obtained in 21% yield with 24% substrate conversion (entry 9). Direct formation of formamides from *N*-methyl amines is an important synthetic strategy in organic
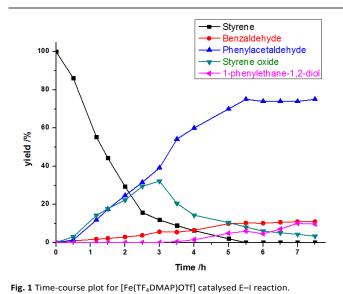
chemistry. In the literature, l-oxo-2,2,6,6-tetramethylpiperidinium ion, benzyltriethylammonium permanganate (Et$_3$N$^+$CH$_2$Ph)·MnO$_4^-$, pyridinium chlorochromate (PCC) and pyridinium dichromate (PDC) were reported as stoichiometric oxidants for this type of reactions.[14] *To the best our knowledge, these are the first examples of Fe-catalysed formation of formamides from N-methyl amines using H$_2$O$_2$ as oxidant.*[15]

Table 3 [Fe(TF$_4$DMAP)OTf] catalysed formamide formation reaction^a

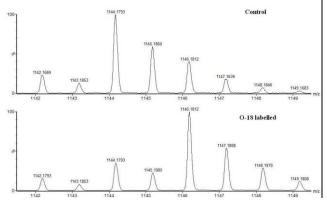| entry	substrate	product	convn (%)^b	yield (%)^c
1	3a	4a	91	100 (82)
2	3b	4b	99	81 (65)
3	3c	4c	70	70
4	3d	4d	100	95 (80)
5	3e	4e	87	94 (75)
6	3f	4f	100	48
7	3g	4g	100	94 (74)
8	3h	4h	82	54
9	3i	4i	24	21

^{a} [Fe^{III}(TF$_4$DMAP)OTf] (3 µmol), substrate (1.0 mmol), and the additive (acetic acid 1.0 mmol) were added successively to MeOH (1.2 mL), and it was stirred under argon at room temperature. H$_2$O$_2$ (2.5 mmol) were added via syringe pump over 1 h. ^{b} Analysed by GC and GC-MS. ^{c} Determined by GC and GC-MS based on conversions, and the isolated yields were shown in brackets.
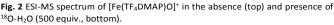
The time course for the [Fe^{III}(TF$_4$DMAP)OTf] catalysed E–I reaction is depicted in Fig 1. Styrene was completely consumed within 5.5 hours whereas the amount of styrene oxide reached maximum after 3 hr but started to decrease afterwards and completely vanished after 7.5 hr. The desired product, phenylacetaldehyde and together with two other side products, 1-phenyl-1,2-diol and benzaldehyde present in minor amount, increased gradually as the reaction proceeded. Controlled experiment with styrene oxide as substrate revealed that phenylacetaldehyde was obtained in 78% yield with 1-phenylethane-1,2-diol and benzaldehyde in 13% and 9% yields, respectively. Upon replacing H$_2$O$_2$ by H$_2^{18}$O in the aforementioned

controlled experiment of ring-opening reaction of styrene oxide, no ^{18}O labelled diol was observed (a mixture of partially ^{18}O labelled phenylacetaldehyde, benzaldehyde and styrene oxide was detected). Thus, phenylacetaldehyde was formed from isomerization of styrene oxide via a tandem epoxidation–isomerization (E–I) pathway (see ESI†).

Fig. 1 Time-course plot for [Fe(TF$_4$DMAP)OTf] catalysed E–I reaction.

High resolution ESI-MS experiments were performed to gain insight into the reaction mechanism. Analysis of a mixture of [Fe^{III}(TF$_4$DMAP)OTf] and H$_2$O$_2$ (5 equiv.) in acetonitrile revealed two new species at m/z 1144.1793 and 1160.1798 (Fig. S1) attributable to [Fe(TF$_4$DMAP)O]$^+$ (Fig. S2) and [Fe(TF$_4$DMAP)O$_2$]$^+$ (Fig. S3) respectively. Collision-induced dissociation of both species could produce a daughter ion peak at m/z 1128.1 corresponding to [Fe(TF$_4$DMAP)]$^+$ (Fig. S4, S5). In the presence of styrene (50 equiv.), the two oxygenated species could also be detected but their signal intensities were weakened by 40% and 50% respectively (relative to [Fe(TF$_4$DMAP)]$^+$ at m/z 1128.1, Fig. S6). In the presence of H$_2^{18}$O (500 equiv.), the signal at m/z 1144.2 showed 85% ^{18}O incorporation (Fig. 2) whereas signal at m/z 1160.2 showed 35% ^{18}O incorporation (Fig. S7). [(Por$^{•+}$)Fe^{IV}=O]$^+$ is known to exchange its oxo-ligand with H$_2^{18}$O and is reactive towards alkenes.[16] Based on the aforementioned findings, we assign the m/z 1144.2 signal to be predominantly [(TF$_4$DMAP$^{•+}$)Fe^{IV}=O]$^+$. The doubly-oxygenated signal at m/z 1160.2

Fig. 2 ESI-MS spectrum of [Fe(TF$_4$DMAP)O]$^+$ in the absence (top) and presence of ^{18}O-H$_2$O (500 equiv., bottom).

might be a mixture of species, the nature of which remains to be studied. We also made attempts to generate analogous species by changing the porphyrin ligand from TF$_4$DMAP to F$_{20}$TPP. Under similar conditions, reaction of [Fe(F$_{20}$TPP)OTf] with H$_2$O$_2$ produced a new signal at m/z 1043.9742 which can be formulated as [(F$_{20}$TPP$^{•+}$)Fe^{IV}=O]$^+$ (Fig. S8). Its signal intensity was largely diminished in the presence of 50 equiv. styrene (Fig. S9) and it showed 80% ^{18}O incorporation with 500 equiv. H$_2$^{18}O (Fig. S10). These results are similar to that observed with the TF$_4$DMAP system revealing the likely involvement of [(Por$^{•+}$)Fe^{IV}=O]$^+$ as reaction intermediate. Treatment of [Fe^{III}(TF$_4$DMAP)OTf] with excess H$_2$O$_2$ in CH$_2$Cl$_2$ for 15 min led to broadening and red-shift of the lowest energy absorption peak maximum to 665 nm that is reminiscent to the absorption of porphyrin π-cation radical (Fig. S11).[11]

A plausible mechanism for tandem epoxidation-isomerization (E–I) pathway is proposed (Fig. 3). Firstly, [Fe(Por)]$^+$ is converted to [Fe(O)(Por)]$^+$ which reacts with aryl alkenes to give the corresponding epoxides; the regenerated [Fe(Por)]$^+$ complex induces isomerization of styrene oxides to phenylacetaldehydes.
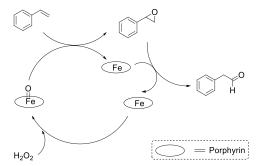

Fig. 3 Plausible Mechanism for the E-I Reaction

In summary, using [Fe^{III}(TF$_4$DMAP)OTf] as catalyst, anti-Markovnikov oxidation of terminal aryl alkenes to aldehydes via tandem epoxidation-isomerization reaction and transformation of *N*-methyl aryl tertiary amines to formamides with H$_2$O$_2$ as terminal oxidant under mild conditions have been achieved in moderate to good product yields.

Notes and references

^{a} Shanghai-Hong Kong Joint Laboratory in Chemical Synthesis, Shanghai Institute of Organic Chemistry,354 Feng Lin Road, Shanghai, China. E-mail: xuzhenjiang@mail.sioc.ac.cn; cmche@hku.hk.

^{b} Department of Chemistry and State Key Laboratory of Synthetic Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, China. Fax: (852)2857-1586; Tel: (852) 2859-2154.

1   For selected reviews, see: (*a*) B. S. Lane and K. Burgess, *Chem. Rev.* 2003, **103**, 2457; (*b*) T. Punniyamurthy, S. Velusamy and J. Iqbal, *Chem. Rev.* 2005, **105**, 2329; (*c*) S.-I. Murahash and D. Zhang, *Chem. Soc. Rev.* 2008, **37**, 1490; (*d*) Z. Shi, C. Zhang, C. Tang and N. Jiao, *Chem. Soc. Rev.* 2012, **41**, 3381.

2   (*a*) C. Krebs, D. G. Fujimori, C. T. Walsh and J. M. Bollinger Jr., *Acc. Chem. Res.* 2007, **40**, 484; (*b*) S. Shaik, H. Hirao and D. Kumar, *Acc. Chem. Res.* 2007, **40**, 532; (*c*) A. Gunay and K. H. Theopold, *Chem. Rev.* 2010, **110**, 1060; (*d*) W. Nam, Y.-M. Lee and S. Fukuzumi, *Acc. Chem. Res.* 2014, **47**, 1146.

3   C. Bolm, J. Legros, J. Le Paih and L. Zani, *Chem. Rev.,* 2004, **104**, 6217.

4   For selected examples, see: (*a*) M. S. Chen and M. C. White, *Science*, 2007, **318**, 783; (*b*) H. Egami and T. Katsuki, *J. Am. Chem. Soc.,* 2009, **131**, 6082; (*c*) M. S. Chen and M. C. White, *Science*, 2010, **327**, 566; (*d*) T. Kunisu, T. Oguma and T. Katsuki, *J. Am. Chem. Soc.,* 2011, **133**, 12937.

5   (*a*) J. Smidt, W. Hafner, J. Jira, R. Sieber, J. Sedlmeier and A. Sabel, *Angew. Chem., Int. Ed. Engl.,* 1962, **1**, 80; (*b*) H. Pellissier, P.-Y. Michellys and M. Santelli, *Tetrahedron,* 1997, **53**, 10733; (*c*) J. Tsuji, *Palladium Reagents and Catalysts: Innovation in Organic Synthesis,* Wiley, New York, 1998. (*d*) J. Muzart, *Tetrahedron* 2007, **63**, 7505; (*e*) J. Guo and P. Teo, *Dalton Trans.*, 2014, **43**, 6952.

6   (*a*) G. Dong, P. Teo, Z. K. Wickens and R. H. Grubbs, *Science* 2011, **333**, 1609; (*b*) P. Teo, Z. K. Wickens, G. Dong and R. H. Grubbs, *Org. Lett.* 2012, **14**, 3237; (c) Z. K. Wickens, B. Morandi, and R. H. Grubbs, *Angew. Chem. Int. Ed.* 2013, **52**, 11257; (*d*) Z. K. Wickens, K. Skakuj, B. Morandi, and R. H. Grubbs, *J. Am. Chem. Soc.* 2014, **136**, 890.

7   (*a*) J. Chen and C.-M. Che, *Angew. Chem., Int. Ed.,* 2004, **43**, 4950; (*b*) G. Jiang, J. Chen, H.-Y. Thu, J.-S. Huang, N. Zhu and C.-M. Che, *Angew. Chem., Int. Ed.,* 2008, **47**, 6638.

8   Reviews of iron-catalysed reactions: A. Correa, O. G. Mancheño and C. Bolm, *Chem. Soc. Rev.* 2008, **37**, 1108.

9   G.-Q. Chen, Z.-J. Xu, C.-Y. Zhou and C.-M. Che, *Chem. Commun.,* 2011, **47**, 10963. For a related iron(II) catalysed EI reaction with PhIO as terminal oxidant, see: A. D. Chowdhury, R. Ray and G. K. Lahiri, *Chem. Commun.*, 2012, **48**, 5497.

10   For selected Fe(F$_{20}$TPP)X catalysed epoxidation, see: (*a*) W. Nam, M. H. Lim, S. Y. Oh, J. H. Lee, H. J. Lee, S. K. Woo, C. Kim, and W. Shin, *Angew. Chem.,Int. Ed.,* 2000, **39**, 3646; (*b*) W. Nam, S. Y. Oh, Y. J. Sun, J. Kim, W. K. Kim, S. K. Woo, W. Shin, *J. Org. Chem.,* 2003, **68**, 7903.

11   (*a*) J. T. Groves and Y. Watanabe, *J. Am. Chem. Soc.*, 1986, **108**, 507; (*b*) H. Fujii, *J. Am. Chem. Soc.* 1993, **115**, 4641.

12   (*a*) K. Suda, K. Baba, S. Nakajima and T. Takanami, *Tetrahedron Lett.*, 1999, **40**, 7243; (*b*) K. Suda, K. Baba, S. Nakajima and T. Takanami, *Chem. Commun.*, 2002, 2570.

13   Reviews: (*a*) 1c (*b*) C.-J. Li, *Acc. Chem. Res.,* 2009, **42**, 335; (*c*) W.-J. Yoo, C.-J. Li, *Top. Curr. Chem.* 2010, **292**, 281; (*d*) C. Liu, H. Zhang, W. Shi, and A. Lei, *Chem. Rev.* 2011, **111**, 1780; (e) A. E. Wendlandt, A. M. Suess, S. S. Stahl, *Angew. Chem. Int. Ed.* 2011, **50**, 11062.

14   For the oxidation with other oxidants, see: (*a*) M. E. Kuehne and P. J. Seaton, *J. Org. Chem.,* 1985, **50**, 4790; (*b*) D. H. Hunter, J. S. Racok, A. W. Rey and Y. Zea-Ponce, *J. Org. Chem.,* 1988, **53**, 1278; (*c*) H. Wu, F. Xue, X. Xiao and Y. Qin, *J. Am. Chem. Soc.* 2010, **132**, 14052; (*d*) J. Danielsson and P. Somfai, *Org. Lett.* 2014, **16**, 784.

15   For a relative work, see: (*a*) S. Murata, M. Miura and M. Nomura, *J. Org. Chem.* 1989, **54**, 4700; (*b*) S. Murata, K. Suzuki, A. Tamatani, M. Miura and M. Nomura, *J. Chem. Soc.,Perkin Trans.1* 1992, 1387.

16   W. Nam and J. S. Valentine *J. Am. Chem. Soc.* 1993, **115**, 1772