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[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 a terminal oxidant†

Q1 Q2

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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 a terminal oxidant under mild conditions have been achieved with 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 is a useful tool for organic synthesis and fine chemical industry but remains to be accomplished with high selectivity and product yields using environmentally benign oxidants such as O$_2$/air or H$_2$O$_2$.[1] Therefore, we are attracted to the use of high valent iron–oxo complexes in organic synthesis as iron–oxo complexes with oxidation states IV and V as they are well documented for use as strong oxidants and are capable of performing oxidative functionalization of alkenes and alkanes.[2] We are particularly interested in developing synthetic applications of 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 the literature, examples of iron catalyzed selective organic oxidation reactions using O$_2$/air or H$_2$O$_2$ as a terminal oxidant that can be used in organic synthesis are spa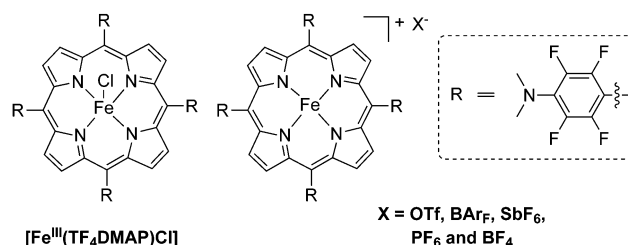rse but have been increasing over the past several years.[3,4] An organic oxidation reaction that has a profound impact in both industry and academia is the Wacker oxidation, which is the anti-Markovnikov oxidation of terminal alkenes to aldehydes without cleavage of C=C bonds by palladium compounds.[5] 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 repo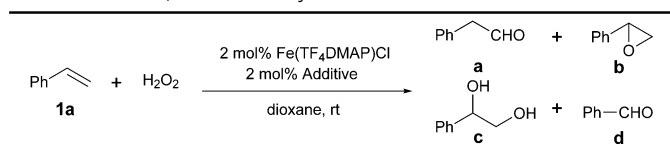rted that selective oxidation of terminal alkenes to aldehydes without C=C bond cleavage can be readily accomplished with high product yields *via* a tandem epoxidation–isomerization (E–I) pathway, which involves a reactive metal-oxo species such as Ru as reaction intermediate.[7] As iron is abundant and biocompatible,[3,8] we studied an iron porphyrin catalyzed anti-Markovnikov oxidation of both terminal aryl and aliphatic alkenes to aldehydes with 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 afforded phenylacetaldehyde with 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*-(dimethylamino)phenyl)porphyrin) is an analogue of [Fe^{III}(F$_{20}$TPP)]$^+$ obtained by replacing the *para*-F substituent of *meso*-C$_6$F$_5$ groups with the electron-donating dimethylamino (NMe$_2$) moiety. It is envisioned that the [(TF$_4$DMAP$^{•+}$)(Fe^{IV}=O)]$^+$ intermediate generated by the oxidation of [Fe^{III}(TF$_4$DMAP)]$^+$ with oxygen atom donors should be less oxidizing and more stable; thus, the accompanying side over oxidation reactions in the course of E–I oxidation may be minimized. Herein, we report [Fe^{III}(TF$_4$DMAP)OTf] as 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 a terminal oxidant.

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

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

R = (dimethylamino tetrafluorophenyl group)

Table 1   [Fe^III(TF4DMAP)X] catalysed E–I reaction^a
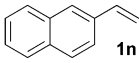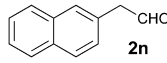
Entry	Additive	Time^b (h)	Conversion^c (%)	Yield^c (%) a	b	c	d
1	AgOTf	5 + 5	~100	77	0	15	7
2	NaBArF	5 + 5	~100	29	65	5	1
3	NaBArF	5 + 21	~100	57	21	20	2
4	AgSbF6	5.5 + 5	94	10	79	0	5
5	AgPF6	5 + 5	87	11	71	3	2
6	AgPF6	5 + 22	91	24	51	13	2
7	AgBF4	5 + 5	75	41	25	8	1
8	AgBF4	5 + 22	75	46	5	20	2

^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.

Initially, the oxidation of styrene by H_2O_2 was used for the optimization of the reaction conditions. As the ligand/counter-anion X may affect the reactivity of [Fe^III(Por)X] (for formulated as [Fe^III(Por)X]),[9,12] the catalytic activities of a panel of [Fe(TF4DMAP)X] (X = OTf^−, BArF^−, SbF6^−, PF6^− and BF4^−, generated in situ by reacting [Fe^III(TF4DMAP)Cl] with AgX, see ESI†) catalysts were evaluated (Table 1). [Fe^III(TF4DMAP)OTf] catalysed the oxidation of styrene with H_2O_2 to give phenylacetaldehyde with 77% yield along with 1-phenylethane-1,2-diol and benzaldehyde (15% and 7% yields, respectively) and no epoxide was observed (Table 1, entry 1). The use of other AgX additives (X = SbF6^−, PF6^− and BF4^−) and NaBArF resulted in lower substrate conversion and/or lower aldehyde selectivity (Table 1). The recrystallization of the product (obtained by the reaction of [Fe^III(TF4DMAP)Cl] and NaBArF in THF) in CH_2Cl_2/hexane (1 : 9) gave [Fe(TF4DMAP)2]O (see ESI†). **was**

Examination of solvent effect revealed dioxane to be the solvent of choice (Table S1, ESI† 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) were used (Table S1, ESI† entries 2–7). Phenylacetaldehyde was obtained with 47% yield when 1,2-dimethoxyethane (DME) was employed as solvent (Table S1, ESI† entry 8). 2-tert-Butoxy-2-phenylethanol via the ring opening reaction of styrene oxide was obtained with 70% yield when tert-butanol was used as a solvent (Table S1, ESI† entry 9). Products were obtained in acetal forms when methanol or acetone was used as a solvent (Table S1, ESI† entries 10 and 11). Even with dioxane as a 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 with 28% yield when the amount of H_2O_2 was increased to 5.0 equivalents (Table S2, ESI†). Pre-treatment of commercially available styrene (from Aldrich®) by filtration 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(TF4DMAP)OTf] (0.5 mol%), phenylacetaldehyde

Table 2   [Fe(TF4DMAP)OTf] catalysed E–I reaction^a
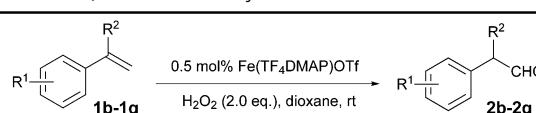
Entry	Substrate	Product	Conversion^b (%)	Yield^b (%)
1	1b: R1 = p-Me; R2 = H	2b	100	73
2	1c: R1 = p-OMe; R2 = H	2c	100	55
3	1d: R1 = p-ClCH2; R2 = H	2d	100	64
4	1e: R1 = p-F; R2 = H	2e	100	76
5	1f: R1 = p-Br; R2 = H	2f	100	72
6	1g: R1 = p-CF3; R2 = H	2g	90	58^c
7	1h: R1 = m-Me; R2 = H	2h	94	87^d,e
8	1i: R1 = m-NO2; R2 = H	2i	80	67^e,d
9	1j: R1 = m-F; R2 = H	2j	90	75^d
10	1k: R1 = m-Cl; R2 = H	2k	100	70^d
11	1l: R1 = m-Br; R2 = H	2l	100	80^e,d
12	1m: R1 = o-F; R2 = H	2m	92	60^d,e
13	1n	2n	86	60
14	1o: R1 = H; R2 = Me	2o	100	64
15	1p: R1 = H; R2 = Ph	2p	100	70
16	1q: R1 = H; R2 = BrCH2	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. ^d After addition of H_2O_2, it was heated to 80 °C. ^e 2 mol% catalyst was used.

^c Epoxide was obtained.

was obtained with the highest yield of 86% with minimal amounts of by-products, i.e. benzaldehyde (6%) and 1-phenylethane-1,2-diol. A trace amount of phenylacetaldehyde was obtained with <2% substrate conversion when the oxidant was changed to $^tBuOOBu^t$ or ^tBuOOH (Table S3, ESI†). Hence, the protocol with 0.5 mol% iron catalyst and 2.0 equivalents H_2O_2 was used in the subsequent experiments.

Using this protocol, we examined the substrate scope of the [Fe^III(TF4DMAP)OTf] catalysed E–I reaction. As listed in Table 2, a panel of aryl alkenes gave the corresponding aldehydes with good to high yields. Styrenes 1b–1f bearing para-substituents afforded the corresponding phenylacetaldehydes 2b–2f with 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 with 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 with 64%–73% yields (entries 14–16).

Oxidative cross coupling of tertiary amines with nucleophiles is a useful strategy for the synthesis of amino compounds.[13] In this study, oxidative cross coupling reaction of tertiary amines and TMSCF3 with [Fe^III(TF4DMAP)OTf] as catalyst and H_2O_2 as a 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, ESI†). 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

Table 3   [Fe(TF₄DMAP)OTf] catalysed formamide formation reaction[a]

Entry	Substrate	Product	Conversion[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}(TF₄DMAP)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. H₂O₂ (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 are shown in brackets.

N-methyl formamides with moderate to good yields (entries 1–8). Changing N,N-dimethyl aniline to N,N-diethyl aniline decreased both the substrate conversion and product yield dramatically. The corresponding N-ethyl acetamide was obtained with 21% yield and 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 (Et₃N⁺CH₂Ph)MnO₄⁻, pyridinium chlorochromate (PCC) and pyridinium dichromate (PDC) were reported as stoichiometric oxidants for this type of reaction.[14] To the best our knowledge, these are the first examples of Fe-catalysed formation of formamides from N-methyl amines using H₂O₂ as an oxidant.[15]

The time course for the [Fe^{III}(TF₄DMAP)OTf] catalysed E–I reaction is depicted in Fig. 1. Styrene was completely consumed within
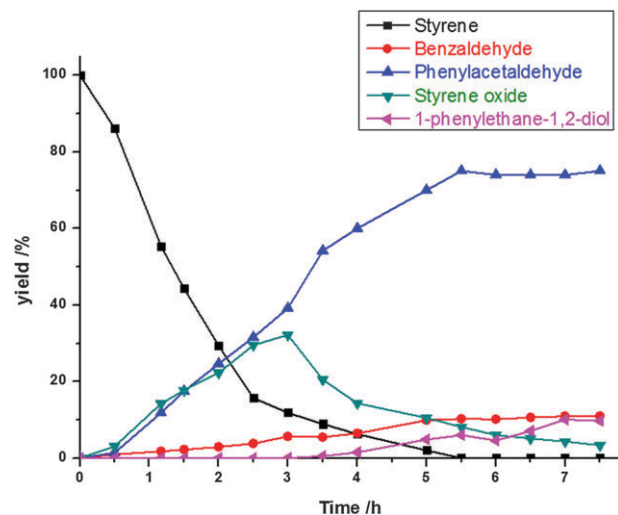

Fig. 1   Time-course plot for [Fe(TF₄DMAP)OTf] catalysed E–I reaction.

5.5 hours, whereas the amount of styrene oxide reached the maximum after 3 h, and then started to decrease afterwards and completely vanished after 7.5 h. The desired product, phenylacetaldehyde, together with two other side products, 1-phenyl-1,2-diol and benzaldehyde present in minor amounts, increased gradually as the reaction proceeded. Controlled experiments with styrene oxide as substrate revealed that phenylacetaldehyde was obtained with 78% yield with 1-phenylethane-1,2-diol and benzaldehyde with 13% and 9% yields, respectively. Upon replacing H₂O₂ by H₂^{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†).

High resolution ESI-MS experiments were performed to gain insight into the reaction mechanism. Analysis of a mixture of [Fe^{III}(TF₄DMAP)OTf] and H₂O₂ (5 equiv.) in acetonitrile revealed two new species at m/z 1144.1793 and 1160.1798 (Fig. S1, ESI†) attributable to [Fe(TF₄DMAP)O]⁺ (Fig. S2, ESI†) and [Fe(TF₄DMAP)O₂]⁺ (Fig. S3, ESI†), respectively. Collision-induced dissociation of both species could produce a daughter ion peak at m/z 1128.1 corresponding to [Fe(TF₄DMAP)]⁺ (Fig. S4 and S5, ESI†). 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(TF₄DMAP)]⁺ at m/z 1128.1, Fig. S6, ESI†). In the presence of H₂^{18}O (500 equiv.), the signal at m/z 1144.2 showed 85% ^{18}O incorporation (Fig. 2), whereas the signal at m/z 1160.2 showed 35% ^{18}O incorporation (Fig. S7, ESI†). [(Por$^{•+}$)Fe^{IV}=O]⁺ is known to exchange its oxo–ligand with H₂^{18}O and is reactive towards alkenes.[16] Based on the aforementioned findings, we assigned the m/z 1144.2 signal to be predominantly [(TF₄DMAP$^{•+}$)Fe^{IV}=O]⁺. The doubly-oxygenated signal at m/z 1160.2 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 TF₄DMAP to F₂₀TPP. Under similar conditions, reaction of [Fe(F₂₀TPP)OTf] with H₂O₂ produced a new signal at m/z 1043.9742,
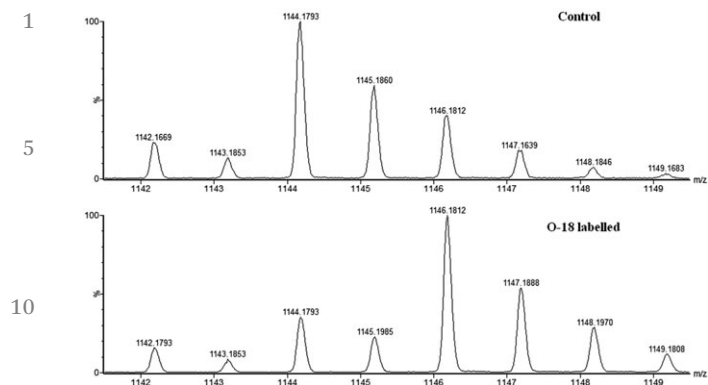
Fig. 2 ESI-MS spectrum of $[Fe(TF_4DMAP)O]^+$ in the absence (top) and presence of $^{18}O-H_2O$ (500 equiv., bottom).
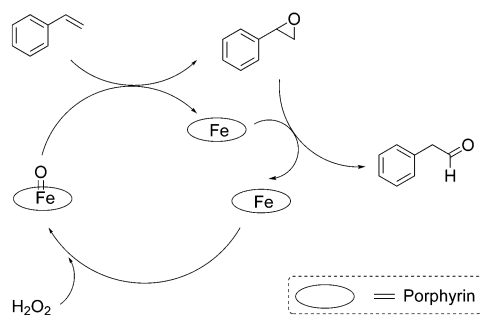

Fig. 3 Plausible mechanism for the E–I reaction.

which can be formulated as $[(F_{20}TPP^{\bullet+})Fe^{IV}=O]^+$ (Fig. S8, ESI†). Its signal intensity was largely diminished in the presence of 50 equiv. styrene (Fig. S9, ESI†) and it showed 80% ^{18}O incorporation with 500 equiv. $H_2^{18}O$ (Fig. S10, ESI†). These results are similar to those observed with the TF_4DMAP system, revealing the likely involvement of $[(Por^{\bullet+})Fe^{IV}=O]^+$ as reaction intermediate. Treatment of $[Fe^{III}(TF_4DMAP)OTf]$ with excess H_2O_2 in CH_2Cl_2 for 15 min led to broadening and red-shift of the lowest energy absorption peak maximum to 665 nm, which is similar to the absorption of porphyrin π-cation radical (Fig. S11, ESI†).[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, and the regenerated $[Fe(Por)]^+$ complex induces isomerization of styrene oxides to phenylacetaldehydes.

In summary, using $[Fe^{III}(TF_4DMAP)OTf]$ 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_2O_2 as a terminal oxidant under mild conditions has been achieved with moderate to good product yields.

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