

[Fe^{III}(TF₄DMAP)OTf] catalysed anti-Markovnikov oxidation of terminal aryl alkenes to aldehydes and transformation of methyl aryl tertiary amines to formamides with H₂O₂ as a terminal oxidant†

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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 H₂O₂ as a terminal oxidant under mild conditions have been achieved with moderate to good product yields using [Fe^{III}(TF₄DMAP)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 O₂/air or H₂O₂.¹

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 catalysed selective organic oxidation reactions using O₂/air or H₂O₂ as a terminal oxidant that can be used in organic synthesis are sparse 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 PdCl₂(MeCN)₂ catalysed selective oxidation of styrenes to phenyl acetaldehydes with *p*-benzoquinone or O₂ as oxidant.⁶ We have previously reported that selective oxidation of terminal

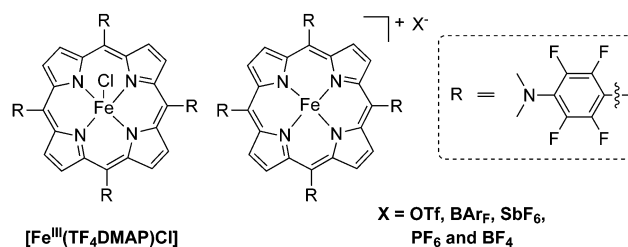
alkenes to aldehydes without C=C bond cleavage can be readily accomplished with high product yields via a tandem epoxidation-isomerization (E-I) pathway, which involves a reactive metal-oxo species such as Ru as reaction intermediate.⁷ As iron is abundant and biocompatible,^{3,8} we studied an iron porphyrin catalysed 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 H₂O₂ for [Fe(2,6-Cl₂TPP)OTf] or [Fe^{III}(F₂₀TPP)OTf]¹⁰ (2,6-Cl₂TPPH₂ = *meso*-tetrakis(2,6-dichlorophenyl)porphyrin), H₂F₂₀TPP = *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}(TF₄DMAP)]⁺ (H₂TF₄DMAP = *meso*-tetrakis(*o,o,m,m*-tetrafluoro-*p*-(dimethylamino)phenyl)porphyrin) is an analogue of [Fe^{III}(F₂₀TPP)]⁺ obtained by replacing the *para*-F substituent of *meso*-C₆F₅ groups with the electron-donating dimethylamino (NMe₂) moiety. It is envisioned that the [(TF₄DMAP^{•+})(Fe^{IV}=O)]⁺ intermediate generated by the oxidation of [Fe^{III}(TF₄DMAP)]⁺ 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}(TF₄DMAP)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 [(TF₄DMAP^{•+})(Fe^{IV}=O)]⁺ intermediate has also been revealed by the examples of [Fe^{III}(TF₄DMAP)]⁺ catalysed selective oxidation of a panel of *N*-methyl aryl tertiary amines to formamides using H₂O₂ as a terminal oxidant.

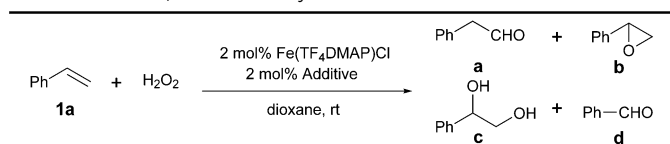
alkenes to aldehydes without C=C bond cleavage can be readily accomplished with high product yields via a tandem epoxidation-isomerization (E-I) pathway, which involves a reactive metal-oxo species such as Ru as reaction intermediate.⁷ As iron is abundant and biocompatible,^{3,8} we studied an iron porphyrin catalysed 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 H₂O₂ for [Fe(2,6-Cl₂TPP)OTf] or [Fe^{III}(F₂₀TPP)OTf]¹⁰ (2,6-Cl₂TPPH₂ = *meso*-tetrakis(2,6-dichlorophenyl)porphyrin), H₂F₂₀TPP = *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}(TF₄DMAP)]⁺ (H₂TF₄DMAP = *meso*-tetrakis(*o,o,m,m*-tetrafluoro-*p*-(dimethylamino)phenyl)porphyrin) is an analogue of [Fe^{III}(F₂₀TPP)]⁺ obtained by replacing the *para*-F substituent of *meso*-C₆F₅ groups with the electron-donating dimethylamino (NMe₂) moiety. It is envisioned that the [(TF₄DMAP^{•+})(Fe^{IV}=O)]⁺ intermediate generated by the oxidation of [Fe^{III}(TF₄DMAP)]⁺ 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}(TF₄DMAP)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 [(TF₄DMAP^{•+})(Fe^{IV}=O)]⁺ intermediate has also been revealed by the examples of [Fe^{III}(TF₄DMAP)]⁺ catalysed selective oxidation of a panel of *N*-methyl aryl tertiary amines to formamides using H₂O₂ as a terminal oxidant.

^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

^b Department of Chemistry and State Key Laboratory of Synthetic Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, China.
E-mail: cmche@hku.hk; Fax: +852-2857-1586; Tel: +852-2859-2154

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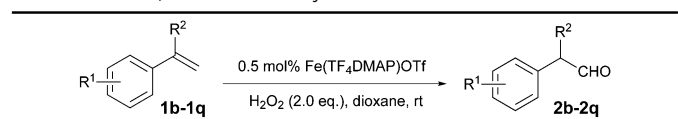
1 **Table 1** [Fe^{III}(TF₄DMAP)X] catalysed E-I reaction^a

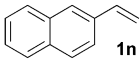
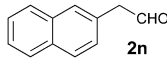
Entry	Additive	Time ^b (h)	Conversion ^c (%)	Yield ^c (%)			
				a	b	c	d
1	AgOTf	5 + 5	~100	77	0	15	7
2	NaBAR _F	5 + 5	~100	29	65	5	1
3	NaBAR _F	5 + 21	~100	57	21	20	2
4	AgSbF ₆	5.5 + 5	94	10	79	0	5
5	AgPF ₆	5 + 5	87	11	71	3	2
6	AgPF ₆	5 + 22	91	24	51	13	2
7	AgBF ₄	5 + 5	75	41	25	8	1
8	AgBF ₄	5 + 22	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 H₂O₂ (0.4 mmol, diluted in dioxane (0.5 mL)) was added *via* syringe pump. ^b The first number was the addition time of H₂O₂ and the second number was the further stirring time. ^c Determined by GC.

Initially, the oxidation of styrene by H₂O₂ was used for the 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(TF₄DMAP)X] (X = OTf⁻, BAR_F⁻, 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 H₂O₂ 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 NaBAR_F 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 NaBAR_F in THF) in CH₂Cl₂/hexane (1 : 9) gave [Fe(TF₄DMAP)₂O] (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, CH₃CN, diethyl ether, methyl *tert*-butyl ether (MTBE), or MeOH/CH₂Cl₂ (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 H₂O₂ 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 H₂O₂ was increased to 5.0 equivalents (Table S2, ESI[†]). Pre-treatment of commercially available styrene (from Aldrich[®]) by filtration through Al₂O₃ 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 H₂O₂, dioxane as solvent and a lower loading of [Fe^{III}(TF₄DMAP)OTf] (0.5 mol%), phenylacetaldehyde

2 **Table 2** [Fe(TF₄DMAP)OTf] catalysed E-I reaction^a

Entry	Substrate	Product	Conversion ^b (%)	Yield ^b (%)
1	1b : R ₁ = <i>p</i> -Me; R ₂ = H	2b	100	73
2	1c : R ₁ = <i>p</i> -OMe; R ₂ = H	2c	100	55
3	1d : R ₁ = <i>p</i> -ClCH ₂ ; R ₂ = H	2d	100	64
4	1e : R ₁ = <i>p</i> -F; R ₂ = H	2e	100	76
5	1f : R ₁ = <i>p</i> -Br; R ₂ = H	2f	100	72
6	1g : R ₁ = <i>p</i> -CF ₃ ; R ₂ = H	2g	90	58
7	1h : R ₁ = <i>m</i> -Me; R ₂ = H	2h	94	87
8	1i : R ₁ = <i>m</i> -NO ₂ ; R ₂ = H	2i	80	67 ^{d,e}
9	1j : R ₁ = <i>m</i> -F; R ₂ = H	2j	90	75 ^d
10	1k : R ₁ = <i>m</i> -Cl; R ₂ = H	2k	100	70 ^d
11	1l : R ₁ = <i>m</i> -Br; R ₂ = H	2l	100	80 ^{d,e}
12	1m : R ₁ = <i>o</i> -F; R ₂ = H	2m	92	60
13			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), H₂O₂ (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 H₂O₂, it was heated to 80 °C. ^d 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 H₂O₂ 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 H₂O₂ 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 H₂O₂ (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

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

Entry	Substrate	Product	Conversion ^b (%)	Yield ^c (%)
1			91	100 (82)
2			99	81 (65)
3			70	70
4			100	95 (80)
5			87	94 (75)
6			100	48
7			100	94 (74)
8			82	54
9			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, I-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 of 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

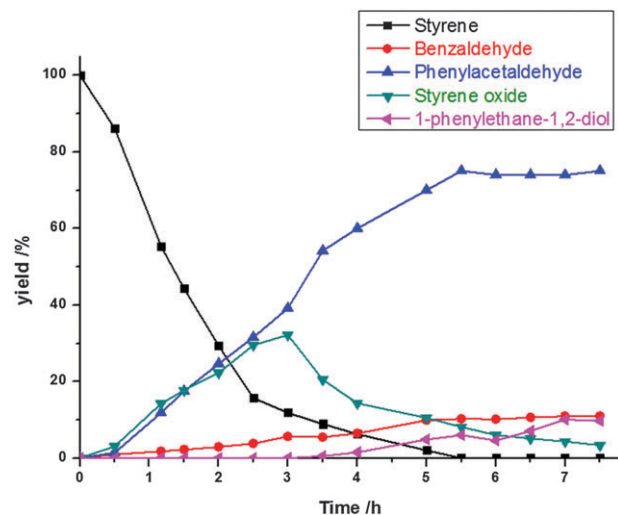


Fig. 1 Time-course plot for [Fe(TF₄DMAP)OTf] catalysed E–I reaction.

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 H₂¹⁸O in the aforementioned controlled experiment of ring-opening reaction of styrene oxide, no ¹⁸O labelled diol was observed (a mixture of partially ¹⁸O 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 H₂¹⁸O (500 equiv.), the signal at *m/z* 1144.2 showed 85% ¹⁸O incorporation (Fig. 2), whereas the signal at *m/z* 1160.2 showed 35% ¹⁸O incorporation (Fig. S7, ESI[†]). [(Por^{•+})Fe^{IV}=O]⁺ is known to exchange its oxo-ligand with H₂¹⁸O 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,

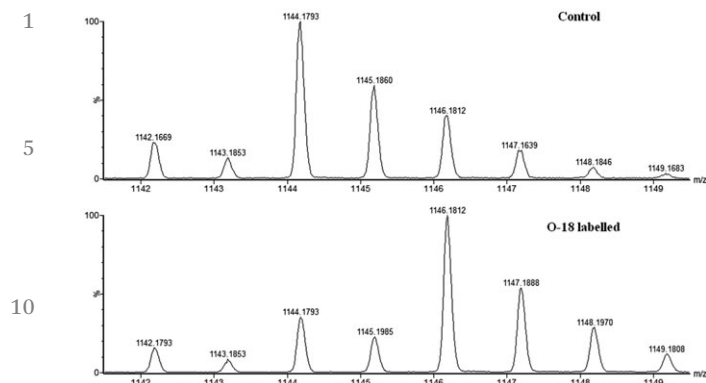


Fig. 2 ESI-MS spectrum of $[\text{Fe}(\text{TF}_4\text{DMAP})\text{O}]^+$ in the absence (top) and presence of $^{18}\text{O}\text{-H}_2\text{O}$ (500 equiv., bottom).

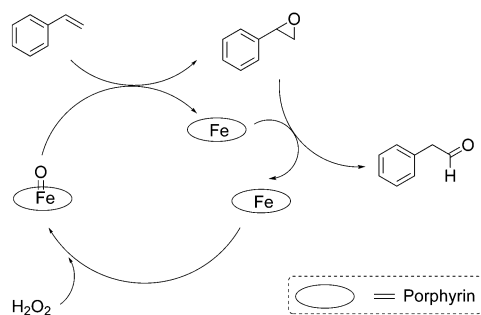


Fig. 3 Plausible mechanism for the E-I reaction.

which can be formulated as $[(\text{F}_{20}\text{TPP}^{\bullet+})\text{Fe}^{\text{IV}}=\text{O}]^+$ (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 $[(\text{Por}^{\bullet+})\text{Fe}^{\text{IV}}=\text{O}]^+$ as reaction intermediate. Treatment of $[\text{Fe}^{\text{III}}(\text{TF}_4\text{DMAP})\text{OTf}]$ 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, $[\text{Fe}(\text{Por})]^+$ is converted to $[\text{Fe}(\text{O})(\text{Por})]^+$ which reacts with aryl alkenes to give the corresponding epoxides, and the regenerated $[\text{Fe}(\text{Por})]^+$ complex induces isomerization of styrene oxides to phenylacetaldehydes.

In summary, using $[\text{Fe}^{\text{III}}(\text{TF}_4\text{DMAP})\text{OTf}]$ 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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