Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information for

Lewis acid improved dioxygen activation by non-heme Iron(II) complex towards tryptophan 2,3-dioxygenase activity for olefin oxygenation

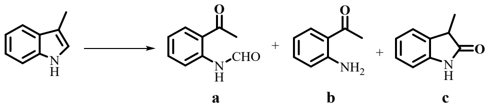
Guangjian Liao, Fuming Mei, Zhuqi Chen, Guochuan Yin*

School of Chemistry and Chemical Engineering, Key laboratory of Material Chemistry for Energy Conversion and Storage (Huazhong University of Science and Technology), Ministry of Education, Hubei Key Laboratory of Material Chemistry and Service Failure, Huazhong University of Science and Technology, Wuhan 430074, PR China.

E-mail: gyin@hust.edu.cn

Contents

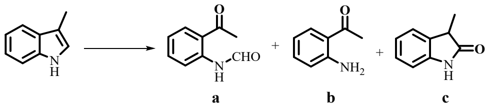
Table S1. The influence of solvent on 3-methylindole oxygenation catalyzed by Fe(bpmen)(OTf)$_2$/Sc(OTf)$_3$.



Entry	Solvent	Conv. (%)	Yield (%)		
			a	b	c
1[a]	DMF	88	19	18	0.3
2	DMA	91	18	14	4.3
3	Dioxane	61	/	/	/
4	DMSO	/	/	/	/
5	MeCN	/	/	/	/
6	MeOH	/	/	/	/
7	DCE	/	/	/	/

Conditions: Substrate 0.1 M, Fe(bpmen)(OTf)$_2$ 2 mol%, Sc(OTf)$_3$ 4 mol% in 1 mL solvent, dioxygen balloon, 353 K, 6 h ; [a]4 h. The conversion was determined by GC, and the yields of the products determined by HPLC.

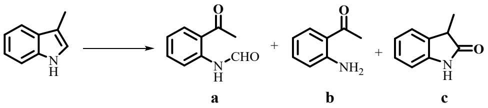
Table S2. The influence of temperature on 3-methylindole oxygenation catalyzed by Fe(bpmen)$(OTf)_2$/$Sc(OTf)_3$.



Entry	Temp.	Conv. (%)	Yield (%)		
			a	b	c
1	40 °C	64	12	12	4
2	60 °C	85	18	20	0.3
3	80 °C	88	19	18	0.3
4	100 °C	95	22	14	0.8

Conditions: Substrate 0.1 M, Fe(bpmen)$(OTf)_2$ 2 mol%, $Sc(OTf)_3$ 4 mol% in 1 mL DMF, dioxygen balloon, 4 h. The conversion was determined by GC, and the yields of the products determined by HPLC.

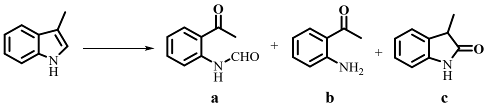
Table S3. The influence of the amounts of the Fe(bpmen)(OTf)$_2$ and Sc(OTf)$_3$ on 3-methylindole oxygenation.



Entry	Cat. + Sc^{3+} (mol%)	Conv. (%)	Yield (%)		
			a	b	c
1	0.1+0.2	47	7	9	0.6
2	0.5+1	73	14	15	0.7
3	1+2	88	19	18	0.3
4	2+4	89	20	18	0.9
5	4+8	96	22	19	0.9

Conditions: Substrate 0.1 M in 1 mL DMF, dioxygen balloon, 353 K, 4 h. The conversion was determined by GC, and the yields of the products determined by HPLC.

Table S4. The influence of the Fe(bpmen)$(OTf)_2$/$Sc(OTf)_3$ ratio on 3-methylindole oxygenation.



Entry	Cat./Sc^{3+} (mol%)	Conv. (%)	Yield (%)		
			a	b	c
1	1:0	67	14	14	0.3
2	1:0.25	71	14	15	0.6
3	1:0.5	76	17	18	0.5
4	1:1	82	18	17	0.5
5	1:2	88	19	18	0.3
6	1:4	98	21	18	0.6

Conditions: Substrate 0.1 M in 1mL DMF, dioxygen balloon, 353 K, 4 h. The conversion was determined by GC, and the yields of the products determined by HPLC.

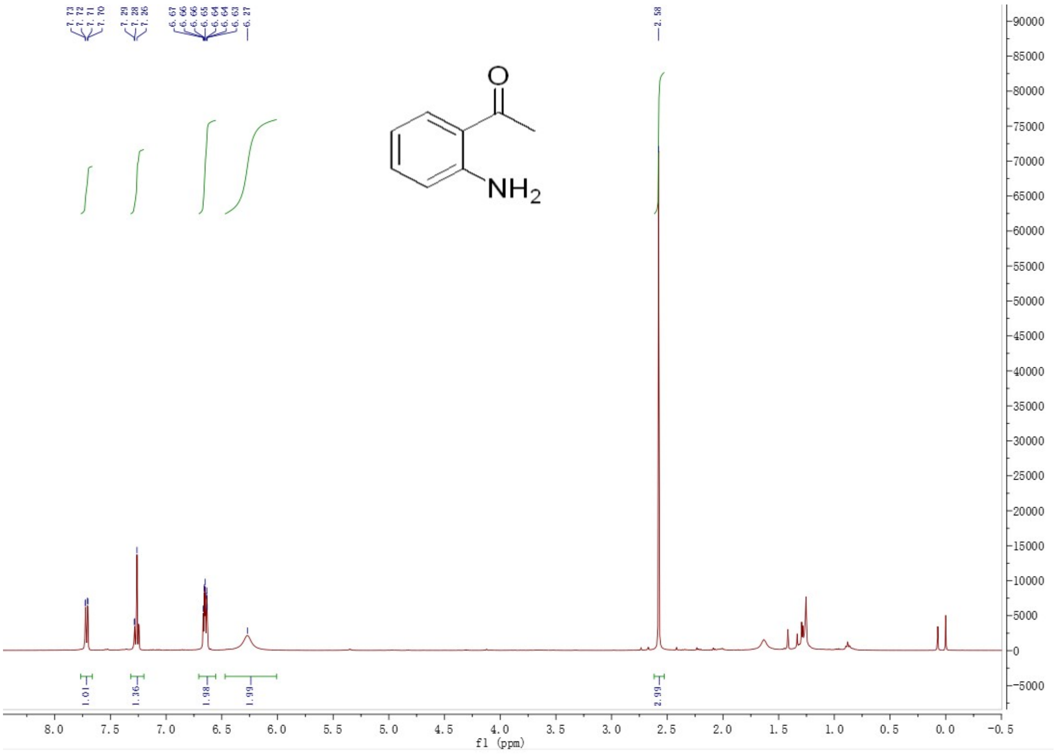


Figure S1. ^{1}H NMR spectrum of the product 2-aminoacetophenone in $CDCl_3$ (400 MHz, 298 K, $CDCl_3$): δ 7.73−7.70 (d, 1H), δ 7.28−7.70 (t, 1H), δ 6.67−6.63 (m, 2H), 6.27 (s, 1H), 2.58 (s, 3H).

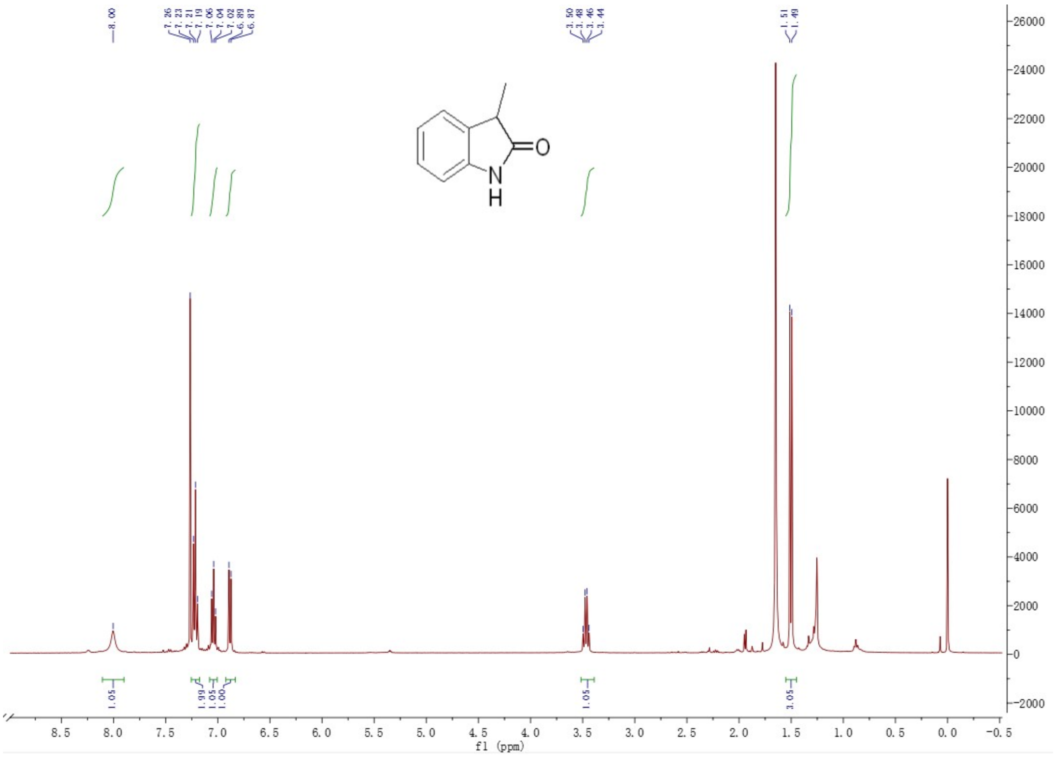


Figure S2. ^{1}H NMR spectrum of the product 3-methylindolin-2-one in $CDCl_3$ (400 MHz, 298 K, $CDCl_3$): δ 8.0 (s, 1H), δ 7.23−7.19 (t, 2H), δ 7.06−7.02 (t, 1H), 6.89-6.87 (d, 1H), 3.5-3.44 (m, 1H), δ 1.51-1.49 (d, 3H).

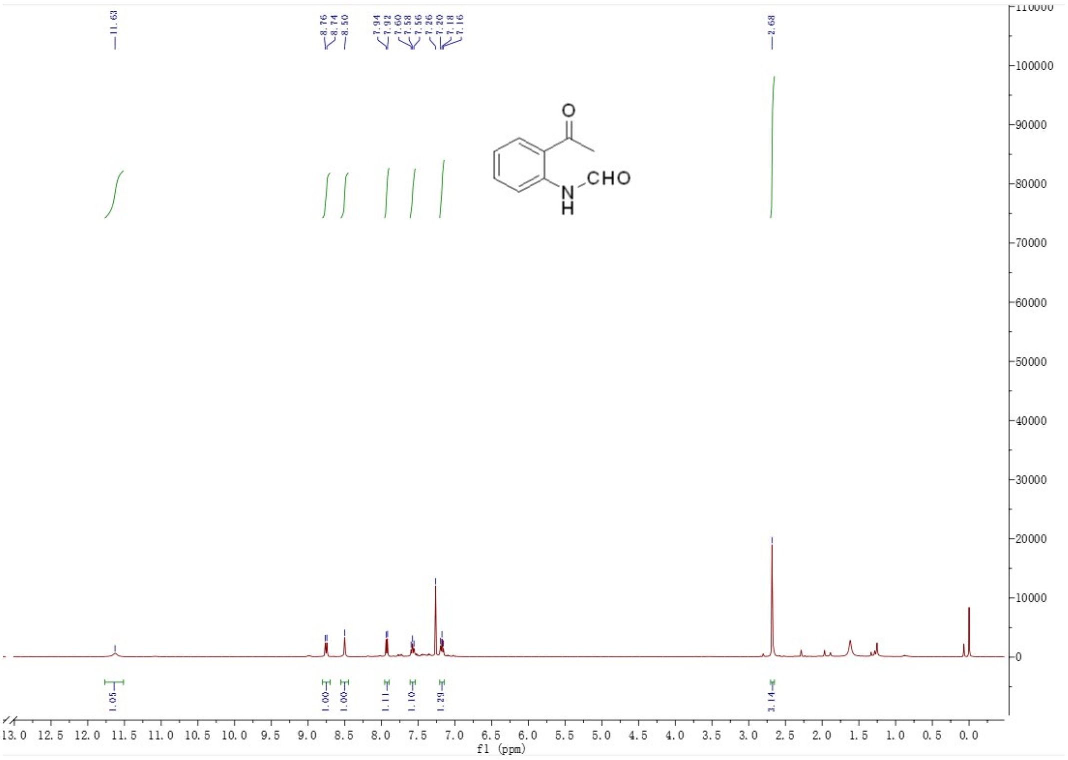
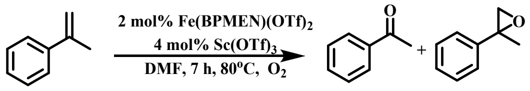


Figure S3. ^{1}H NMR spectrum of the product *N*-(2-acetylphenyl)formamide in $CDCl_3$ (400 MHz, 298 K, $CDCl_3$): δ 11.63 (s, 1H), δ 8.77−8.74 (d, 1H), δ 8.50 (s, 1H),δ 7.94−7.92 (d, 1H), δ 7.60-7.56 (t, 1H), δ 7.20-7.16 (t, 1H), δ 2.68 (s, 3H).



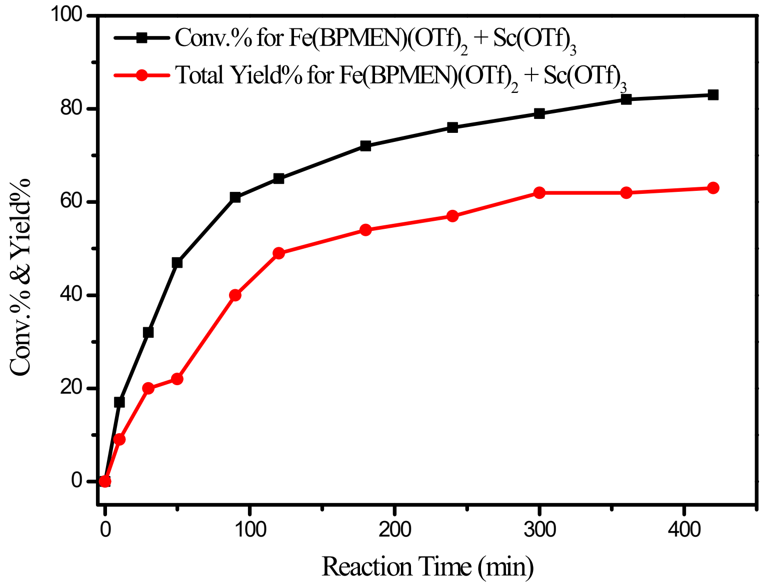


Figure S4. Time-course of α-methylstyrene oxygenation catalyzed by Fe(bpmen)(OTf)$_2$ in the presence of Sc(OTf)$_3$. Conditions: α-methylstyrene 0.1 M, Fe(bpmen)(OTf)$_2$ 2 mol%, Sc(OTf)$_3$ 4 mol% in 1 mL DMF, dioxygen balloon, 353 K.

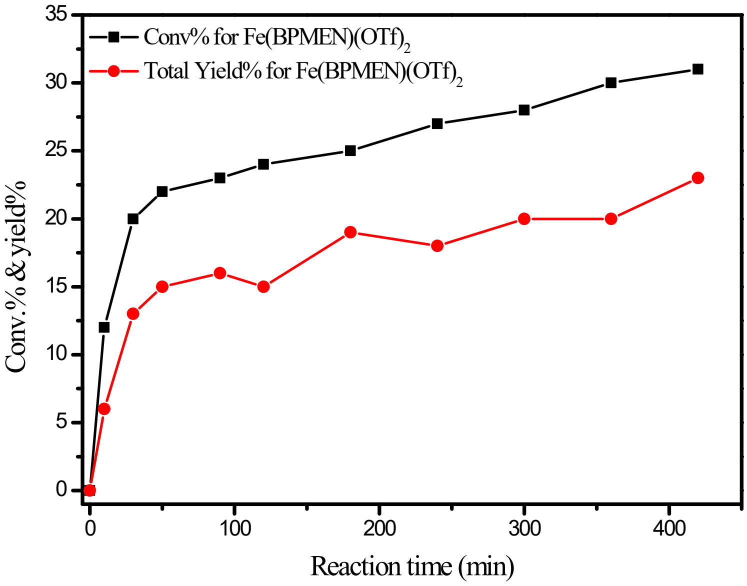


Figure S5. Time-course of α-methylstyrene oxygenation catalyzed by Fe(bpmen)(OTf)$_2$ in the absence of Sc(OTf)$_3$. Conditions: α-methylstyrene 0.1 M, Fe(bpmen)(OTf)$_2$ 2 mol% in 1 mL DMF, dioxygen balloon, 353 K.

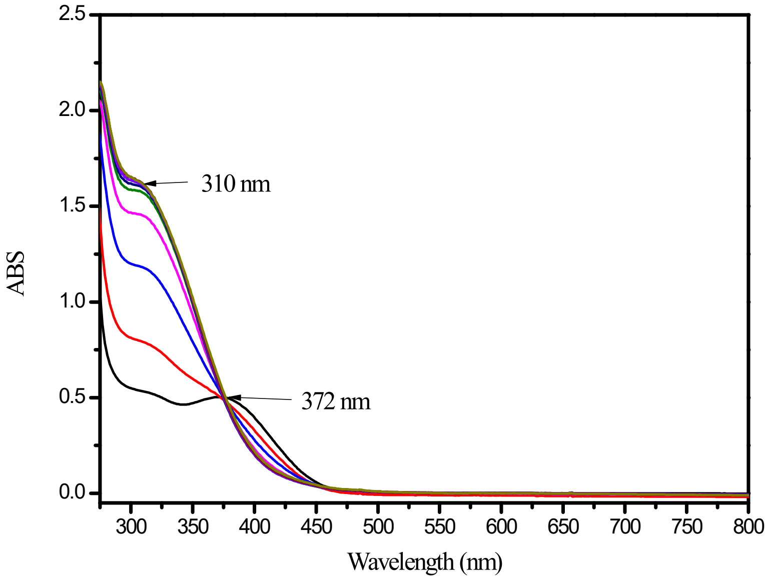
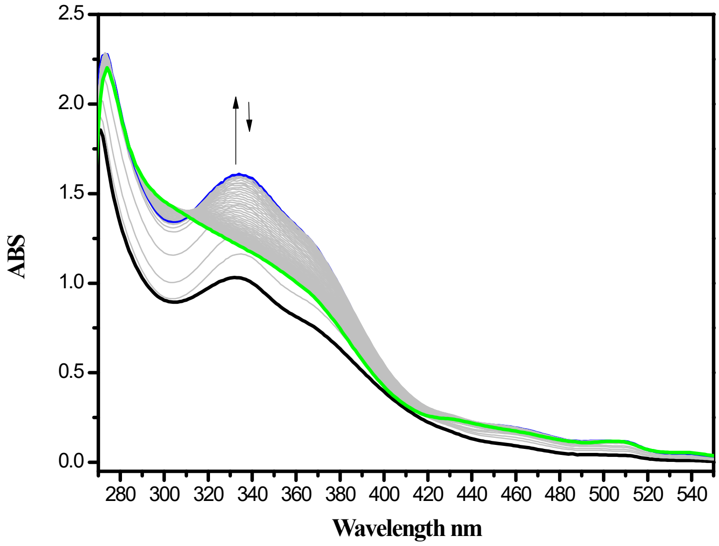


Figure S6. Time traces for the UV-vis spectral changes of Fe(BPMEN)(OTf)$_2$ and Al(OTf)$_3$ under O_2 atmosphere in DMF at 323 K.



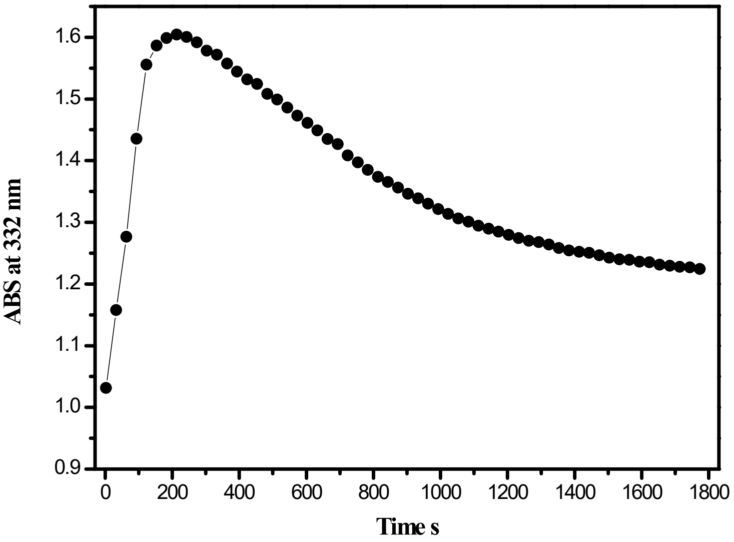
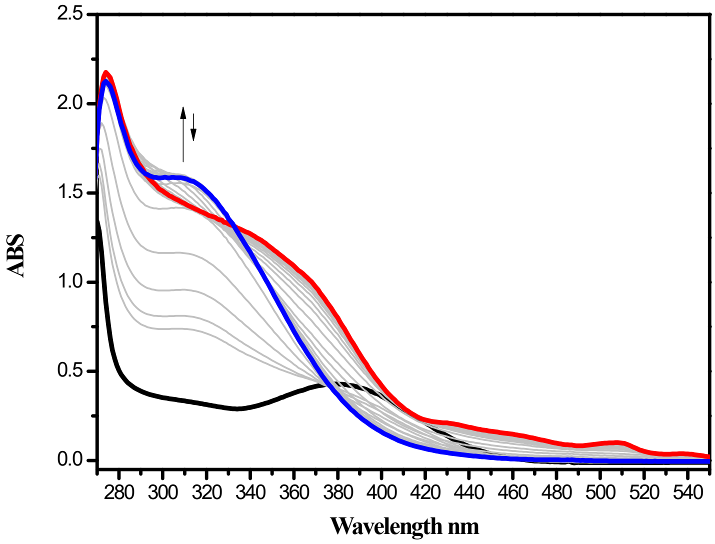


Figure S7. Time trace of UV-vis spectra of 0.4 mM Fe(BPMEN)(OTf)$_2$ under O_2 atmosphere in DMF at 323 K (top) and the ABS change at 332 nm with time (bottom).



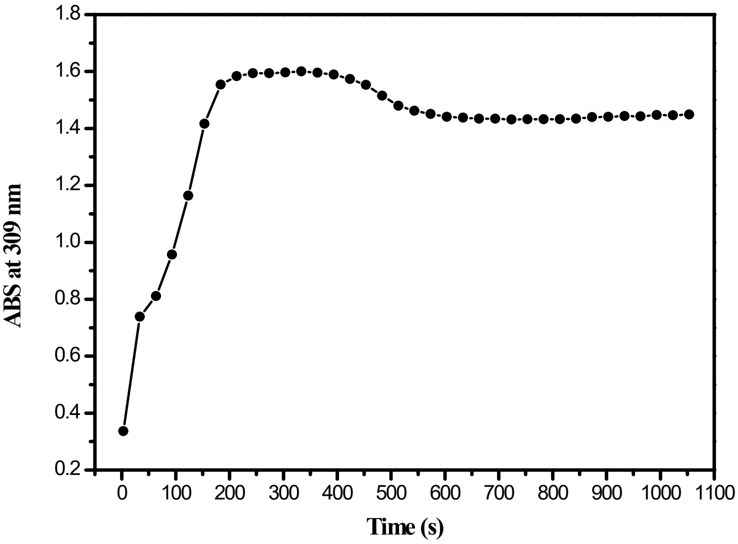


Figure S8. Time trace of UV-vis spectra of 0.4 mM Fe(BPMEN)(OTf)$_2$ with 0.8 mM Sc(OTf)$_3$ under O_2 atmosphere in DMF at 323 K (top) and the ABS change at 309 nm with time (bottom).