Electronic Supplementary Information (ESI)

Photocatalytic asymmetric epoxidation of *trans*-stilbene with manganese-porphyrin/graphene oxide nanocomposite and molecular oxygen: axial ligand effect

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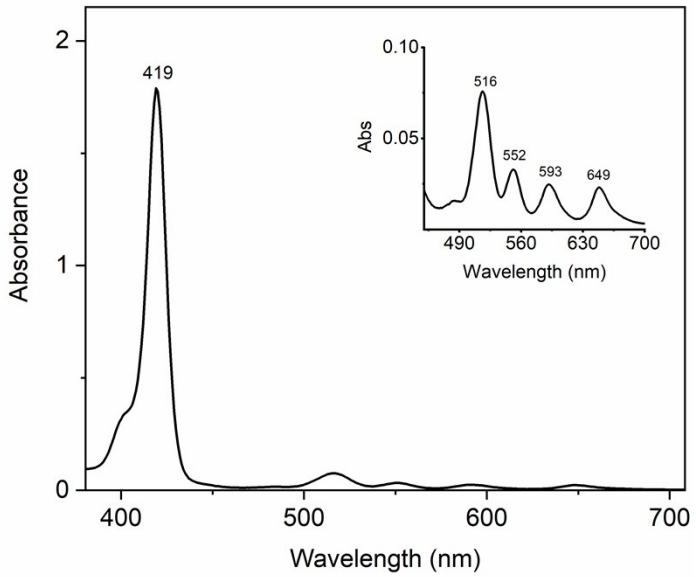


Fig. S1 Electronic absorption of the synthesized H_2T2PyP in CH_2Cl_2 (c = 0.05 M); inset shows the Q bands

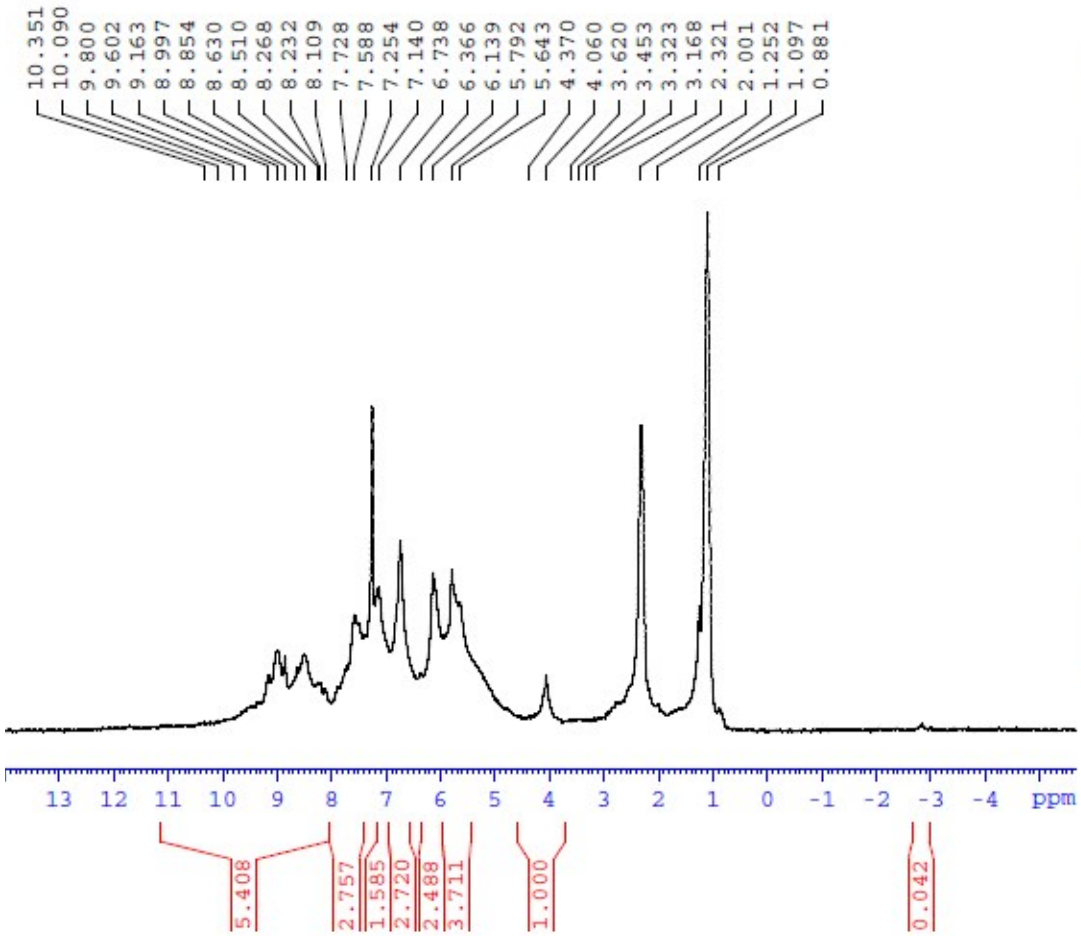


Fig. S2 ^{1}H-NMR spectrum of the synthesized H_2T2PyP in $CDCl_3$ (250 MHz): δ ppm = -2.80 (2H, br, s, NH), 7.50-8.47 (4 *m*-H, adjacent to heteroatom), 5.78-6.74 (4 m-H), 8.86-8.98 (4 o-H), 5.73-5.78 (4 p-H), 8.53 ($8H_\beta$).

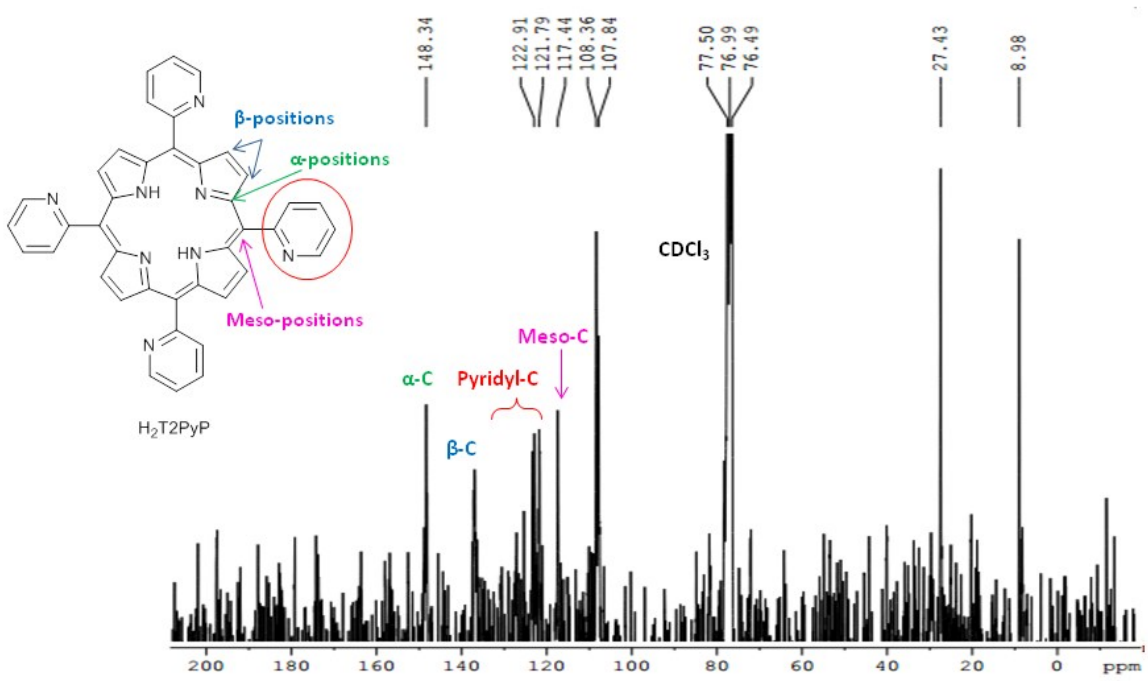


Fig. S3 ^{13}C-NMR spectrum of the synthesized s H_2T2PyP in $CDCl_3$ (250 MHz).

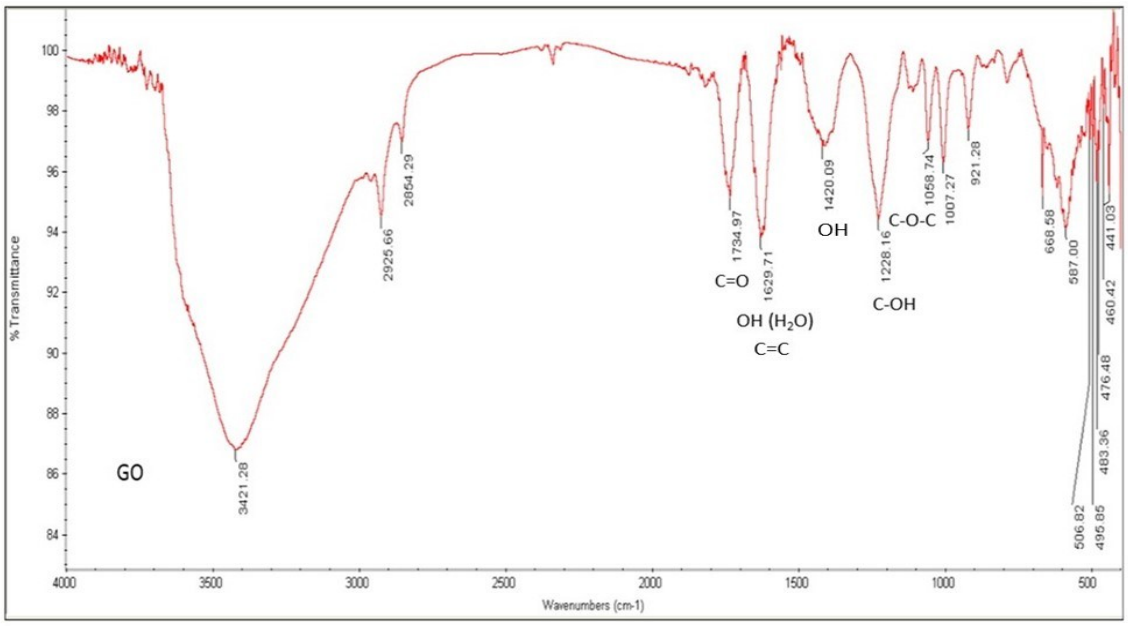


Fig. S4 FT-IR spectrum of the synthesized GO

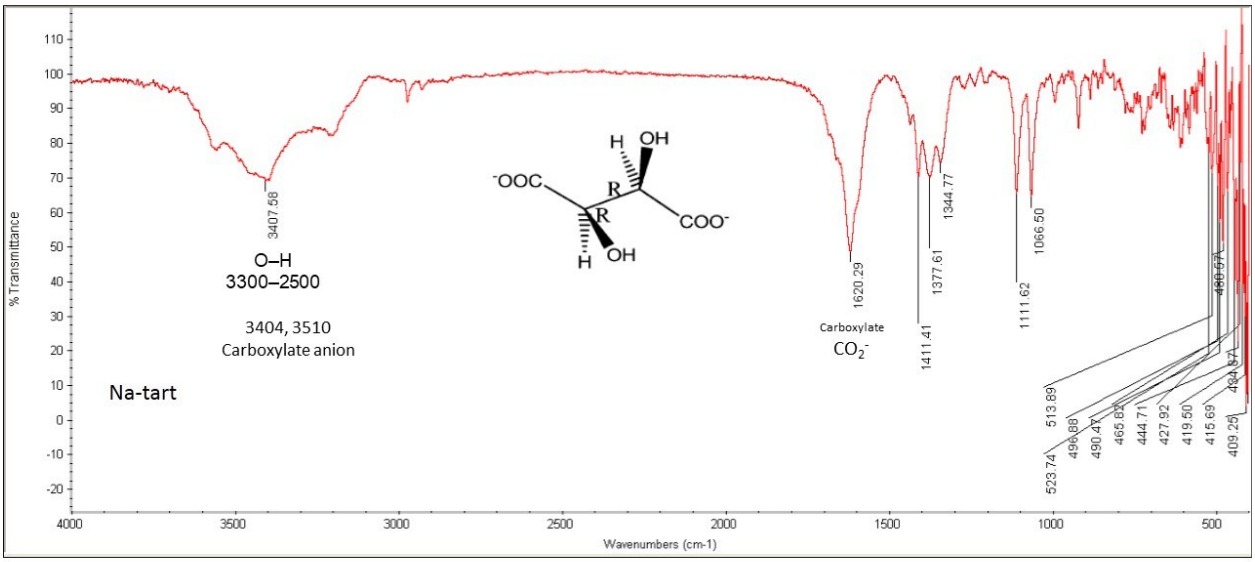


Fig. S5 FT-IR spectrum of sodium tartrate.

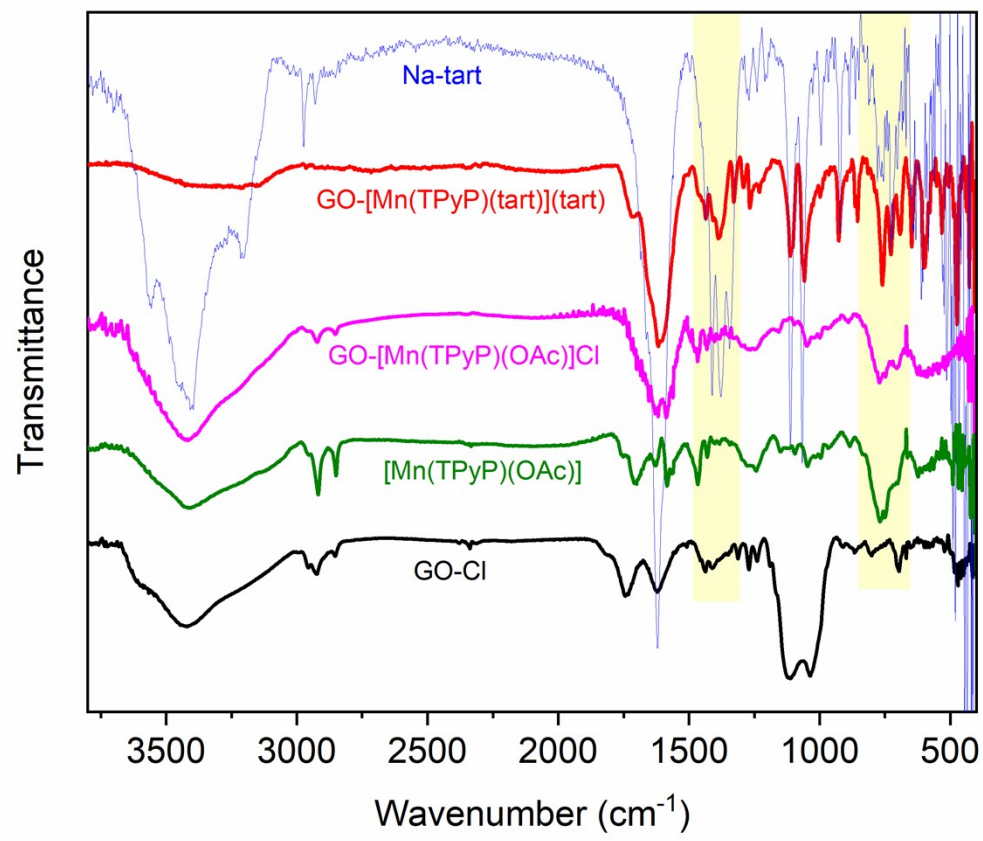
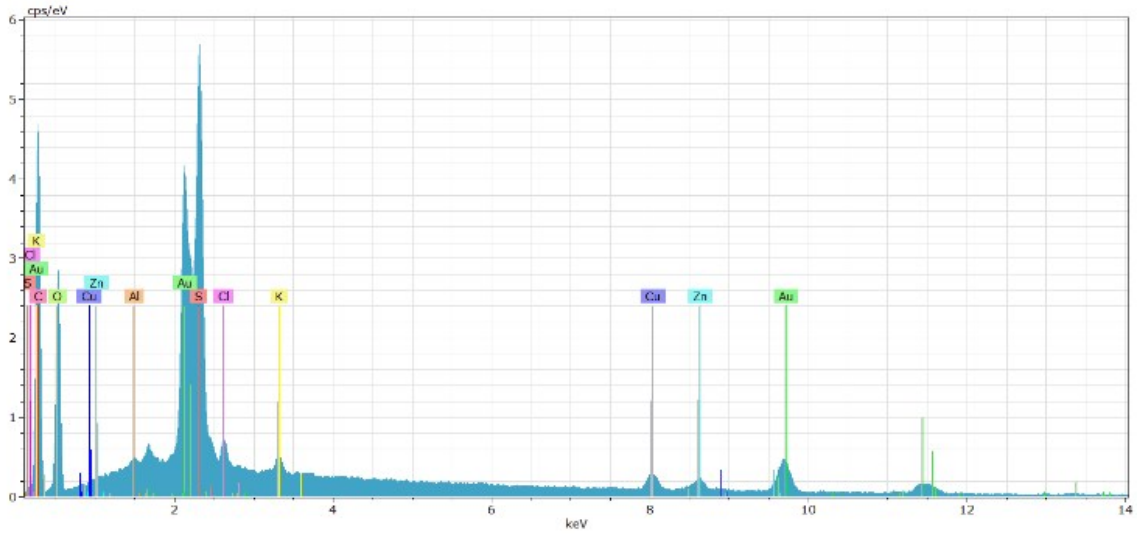
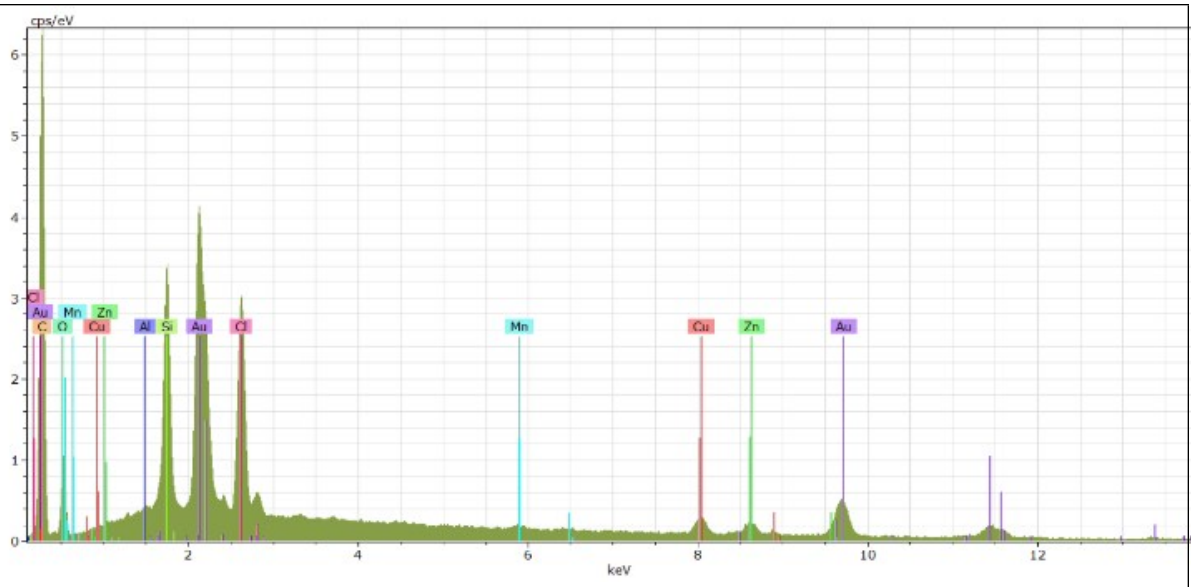


Fig. S6 FTIR spectra of the photocatalyst and the intermediates.



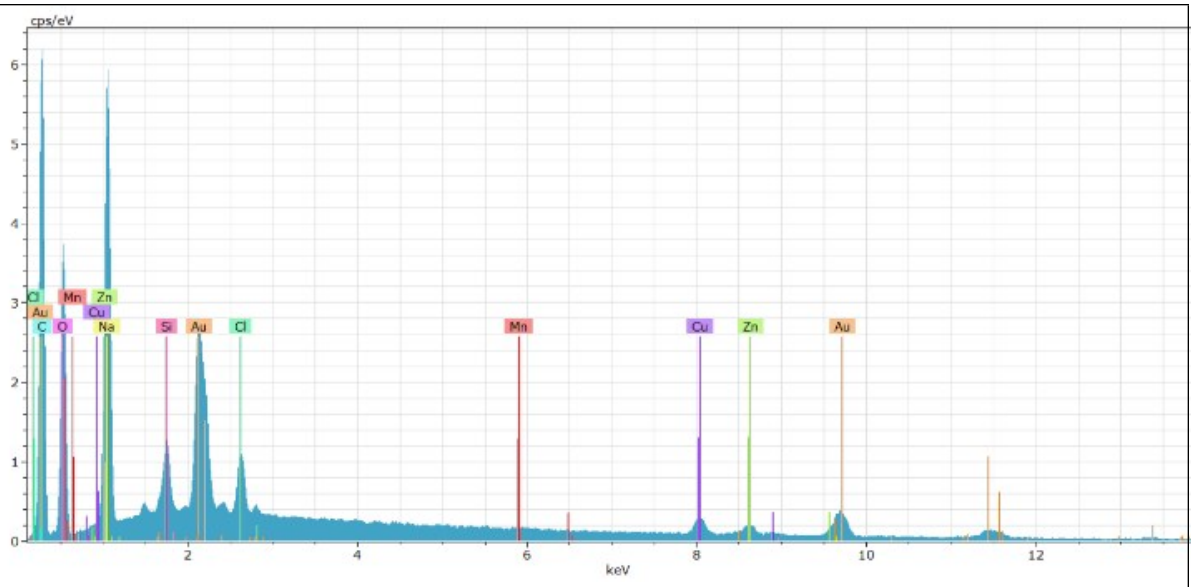
El	OZ	Serie	unn. C [Gew.%]	norm. C [Gew.%]	Atom. C [At.%]	Fehler (1 Sigma) [Gew.%]
C	6	K-Serie	33.92	40.68	66.55	4.48
O	8	K-Serie	15.34	18.39	22.59	2.17
S	16	K-Serie	8.15	9.78	5.99	0.32
Au	79	L-Serie	20.71	24.83	2.48	0.68
Cu	29	K-Serie	2.05	2.45	0.76	0.10
Zn	30	K-Serie	1.68	2.01	0.60	0.09
Cl	17	K-Serie	0.83	1.00	0.55	0.06
K	19	K-Serie	0.53	0.64	0.32	0.05
Al	13	K-Serie	0.18	0.22	0.16	0.04
		Summe:	83.39	100.00	100.00	

EDX of GO



El	OZ	Serie	unn. C [Gew.%]	norm. C [Gew.%]	Atom. C [At.%]	Fehler (1 Sigma) [Gew.%]
C	6	K-Serie	46.63	50.15	81.73	5.93
O	8	K-Serie	6.41	6.89	8.43	1.09
Au	79	L-Serie	27.30	29.36	2.92	0.88
Cl	17	K-Serie	4.90	5.27	2.91	0.20
Si	14	K-Serie	3.38	3.64	2.53	0.17
Cu	29	K-Serie	2.24	2.40	0.74	0.10
Zn	30	K-Serie	1.88	2.02	0.61	0.10
Al	13	K-Serie	0.08	0.09	0.06	0.03
Mn	25	K-Serie	0.16	0.17	0.06	0.04
		Summe:	92.98	100.00	100.00	

EDX of GO-[Mn(T2PyP)(OAc)]Cl



El	OZ	Serie	unn. C [Gew.%]	norm. C [Gew.%]	Atom. C [At.%]	Fehler (1 Sigma) [Gew.%]
C	6	K-Serie	29.86	41.93	63.17	3.81
O	8	K-Serie	15.18	21.32	24.12	2.06
Na	11	K-Serie	7.68	10.79	8.49	0.53
Au	79	L-Serie	13.92	19.55	1.80	0.47
Cl	17	K-Serie	1.03	1.44	0.74	0.06
Cu	29	K-Serie	1.73	2.42	0.69	0.09
Si	14	K-Serie	0.56	0.78	0.50	0.05
Zn	30	K-Serie	1.21	1.70	0.47	0.07
Mn	25	K-Serie	0.05	0.07	0.02	0.03
		Summe:	71.21	100.00	100.00	

EDX of GO-[Mn(T2PyP)(tart)](tart)

Fig. S7 EDX analysis of GO, GO-[Mn(T2PyP)(OAc)]Cl and GO-[Mn(T2PyP)(tart)](tart).

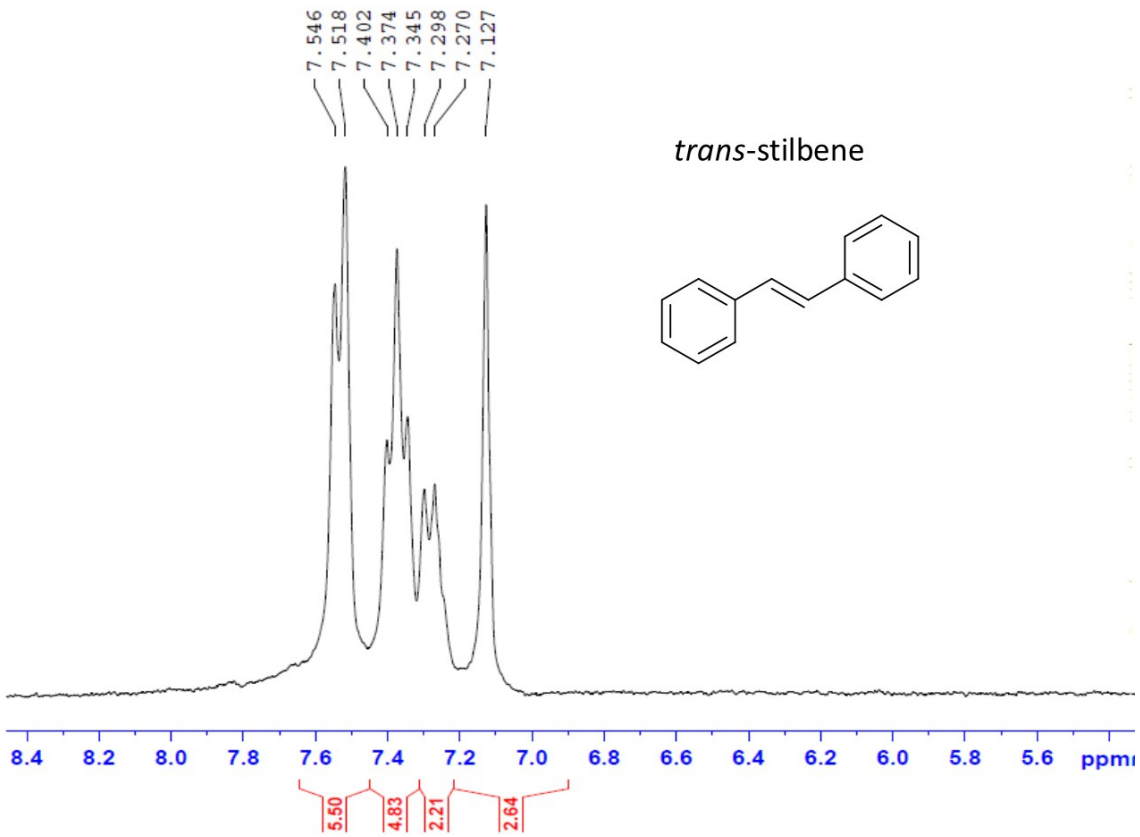
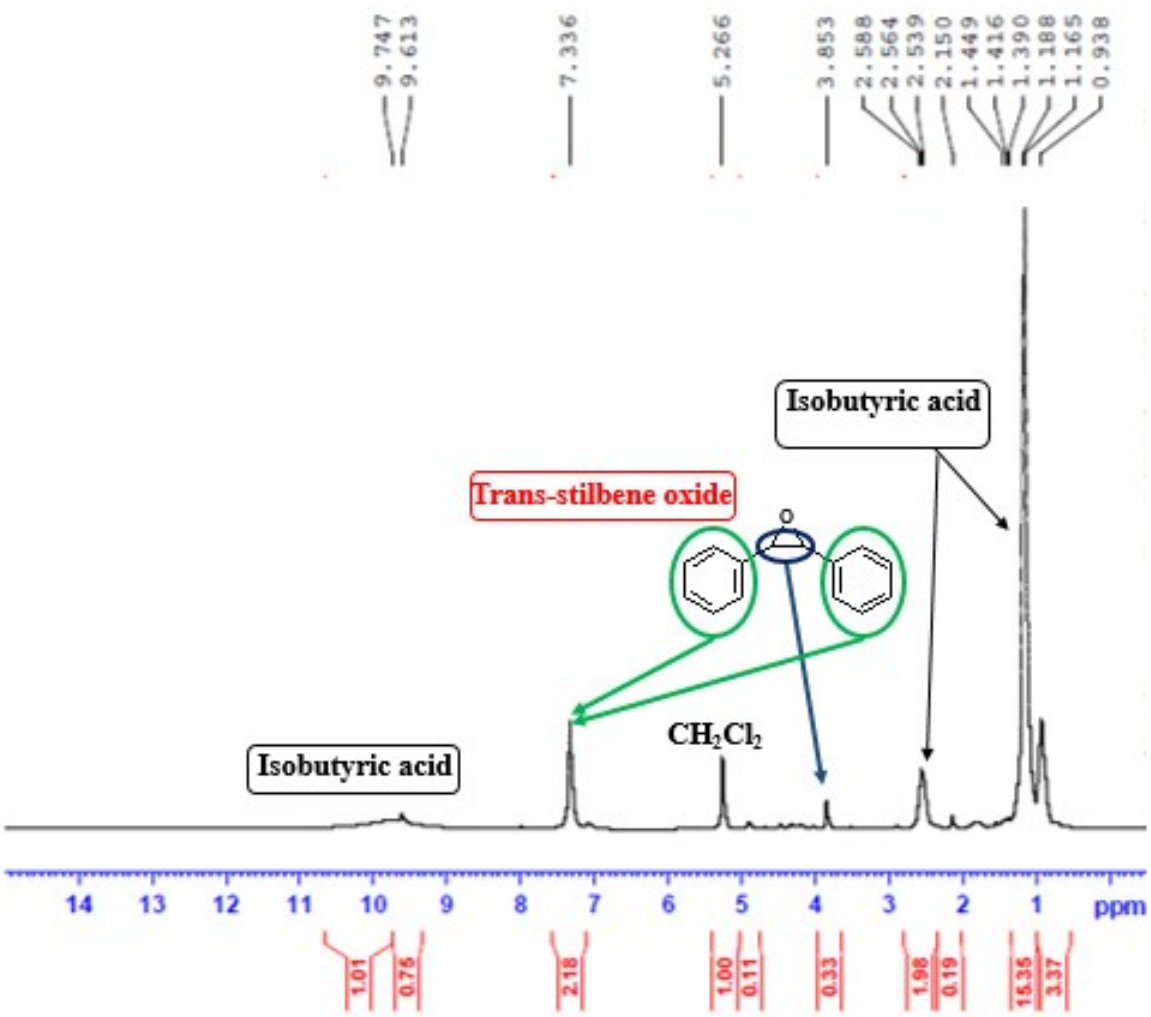


Fig. S8 ^{1}H-NMR spectrum of the starting substrate in $CDCl_3$ (250 MHz).


9.747
9.613
7.336
5.266
3.853
2.588
2.564
2.539
2.150
1.449
1.416
1.390
1.188
1.165
0.938
Isobutyric acid
Trans-stilbene oxide
O
CH_2Cl_2
Isobutyric acid
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.01
0.76
2.18
1.00
0.11
0.33
1.98
0.19
16.35
3.37

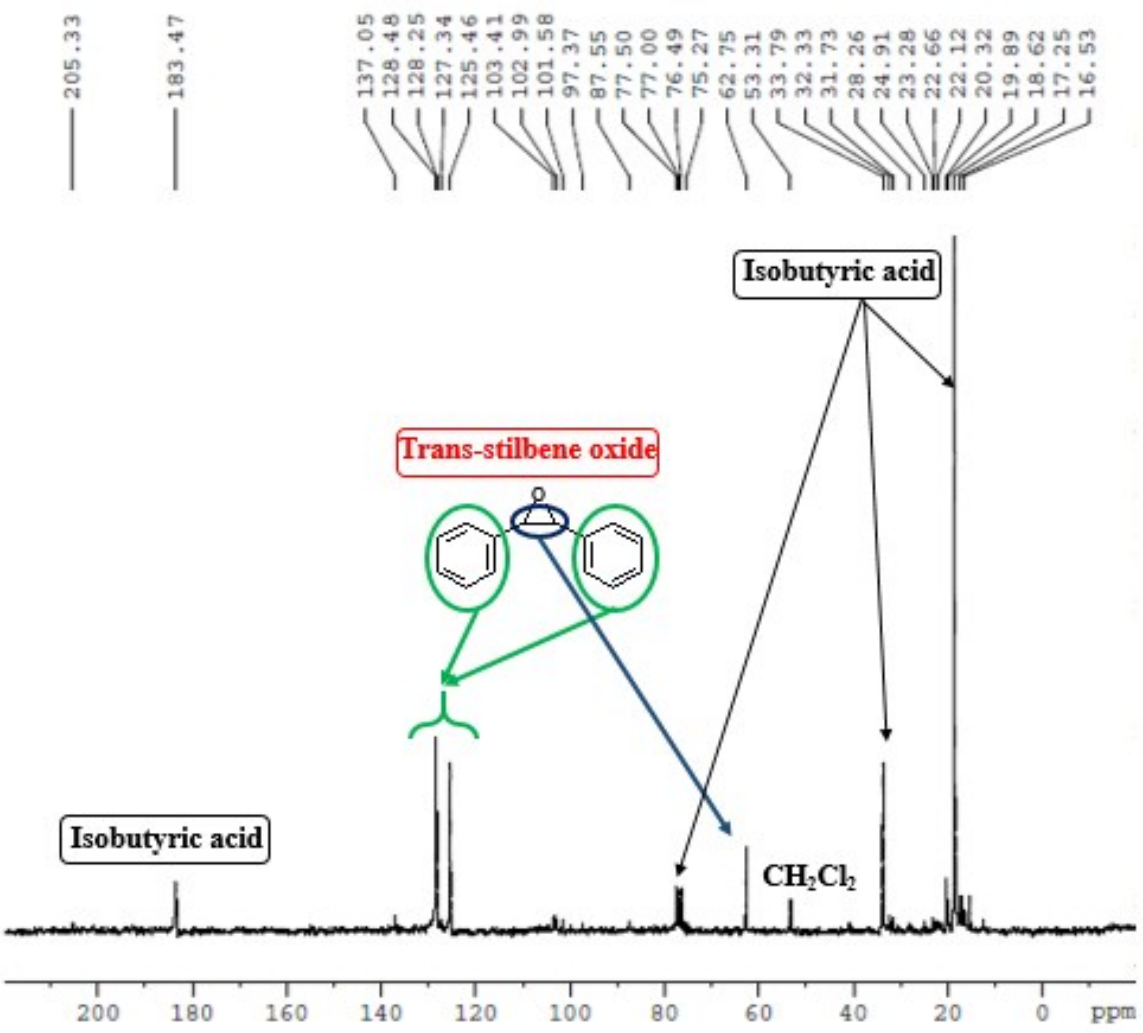


Fig. S9 ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of the crude reaction mixture in $CDCl_3$. Reaction conditions: [Mn(T2PyP)(OAc)] (0.50 mg, 0.00071 mmol) or chiral GO-[Mn(T2PyP)(tart)](tart) (0.0397 g, containing 0.71 μmol Mn), imidazole (0.096 mg, 0.00142 mmol), *trans*-stilbene (0.127 g, 0.71 mmol), isobutyraldehyde (250 mg, 3.55 mmol), and reaction time 80 min.

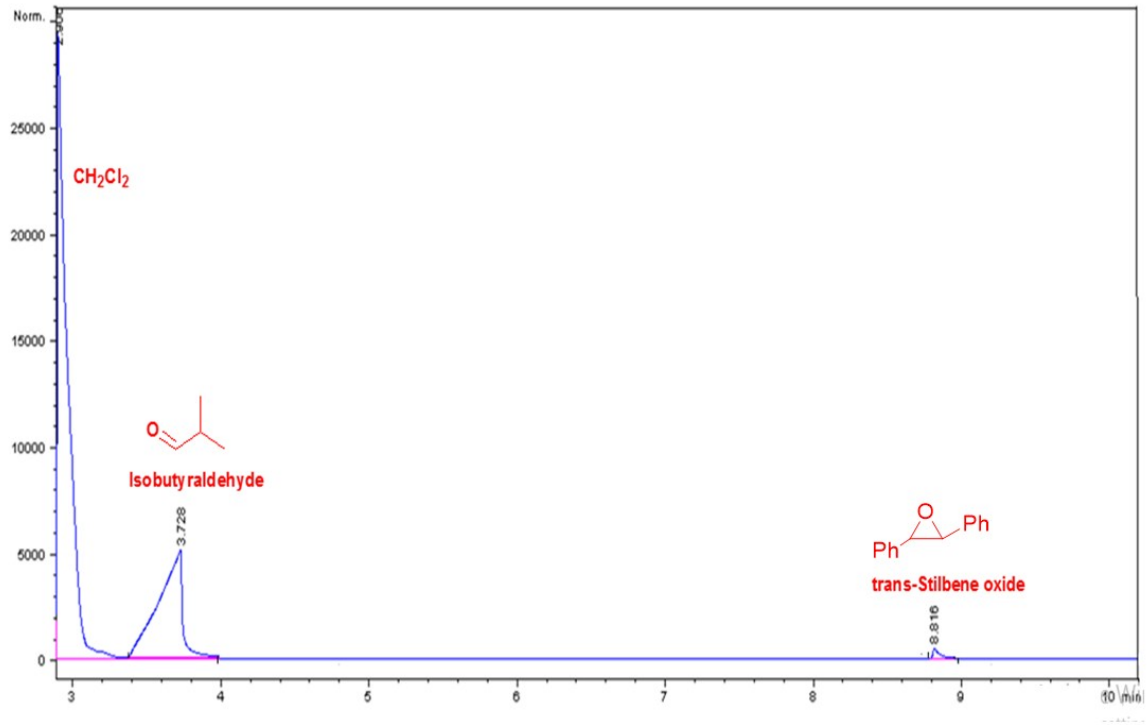


Fig. S10 Chromatogram of the reaction products.

Reaction conditions: [Mn(T2PyP)(OAc)] (0.50 mg, 0.00071 mmol), imidazole (0.096 mg, 0.00142 mmol), *trans*-stilbene (0.127 g, 0.71 mmol), isobutyraldehyde (250 mg, 3.55 mmol), and reaction time 80 min. GC column HP-5, flow rate 10 mL/min, initial temperature 25 °C, final temperature 190 °C, temperature gradient 10 °C/min, injected volume 2 microliter.

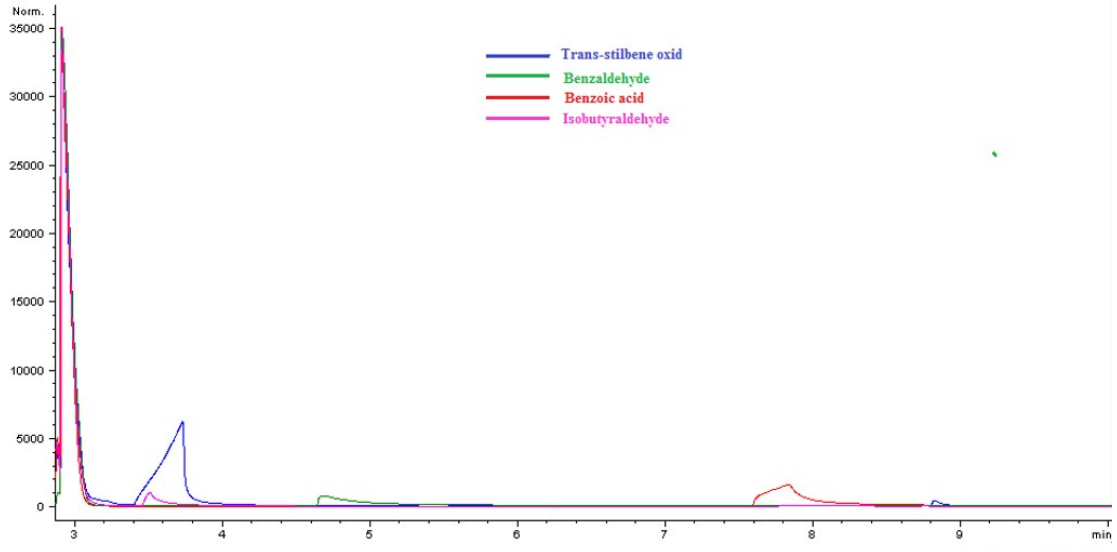
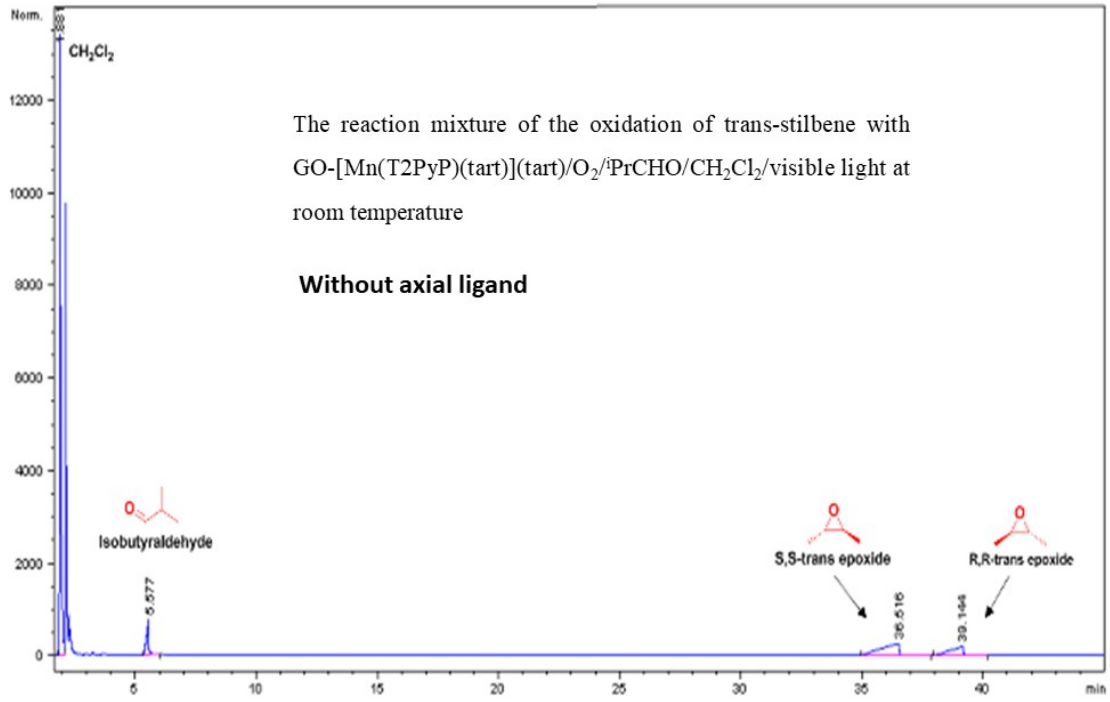


Fig. S11 GC chromatograms of the authentic samples: the reaction mixture (blue line); benzaldehyde (green); benzoic acid (red); ispbutyraldehyde (pink) in CH_2Cl_2.

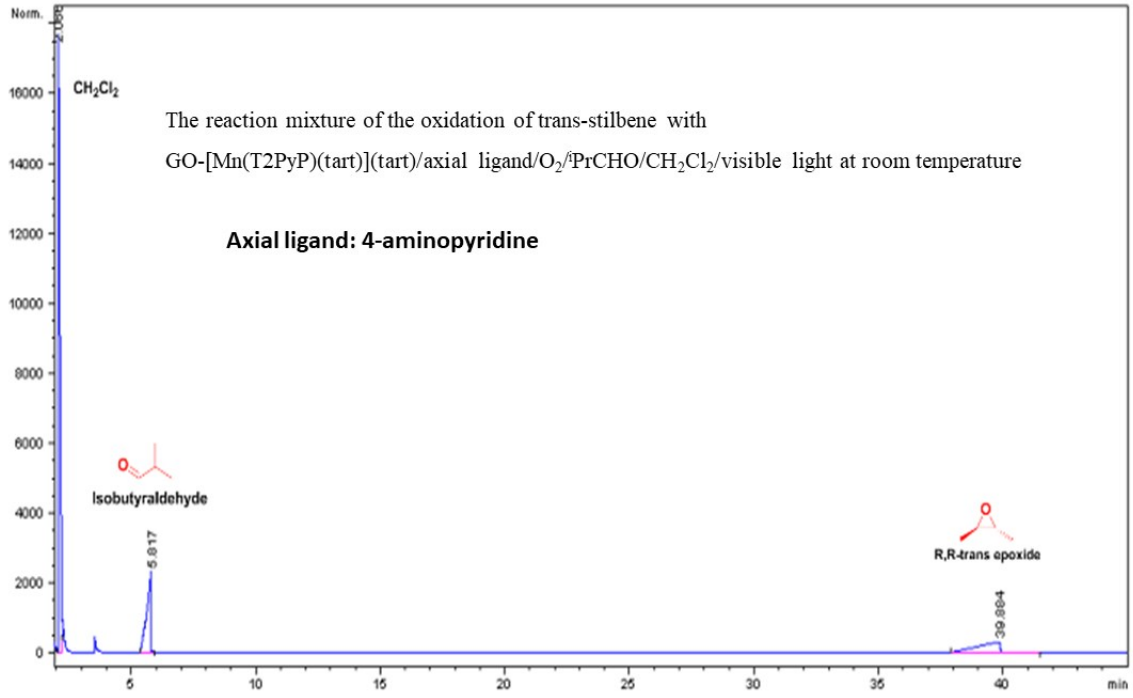
Reaction conditions: GO-[Mn(T2PyP)(tart)](tart) (0.0397 mg, 0.00071 mmol), imidazole (0.096 mg, 0.00142 mmol), *trans*-stilbene (0.127 g, 0.71 mmol), isobutyraldehyde (250 mg, 3.55 mmol), white LED light (80 W), O_2 1.0 atm, temperature 25 °C and reaction time 80 min.

GC column HP-5, flow rate 10 mL/min, initial temperature 25 °C, final temperature 190 °C, temperature gradient 10 °C/min, injected volume 2 microliter.



The reaction mixture of the oxidation of trans-stilbene with GO-[Mn(T2PyP)(tart)](tart)/O_2/^{i}PrCHO/CH_2Cl_2/visible light at room temperature

Without axial ligand



The reaction mixture of the oxidation of trans-stilbene with GO-[Mn(T2PyP)(tart)](tart)/axial ligand/O_2/^{i}PrCHO/CH_2Cl_2/visible light at room temperature

Axial ligand: 4-aminopyridine

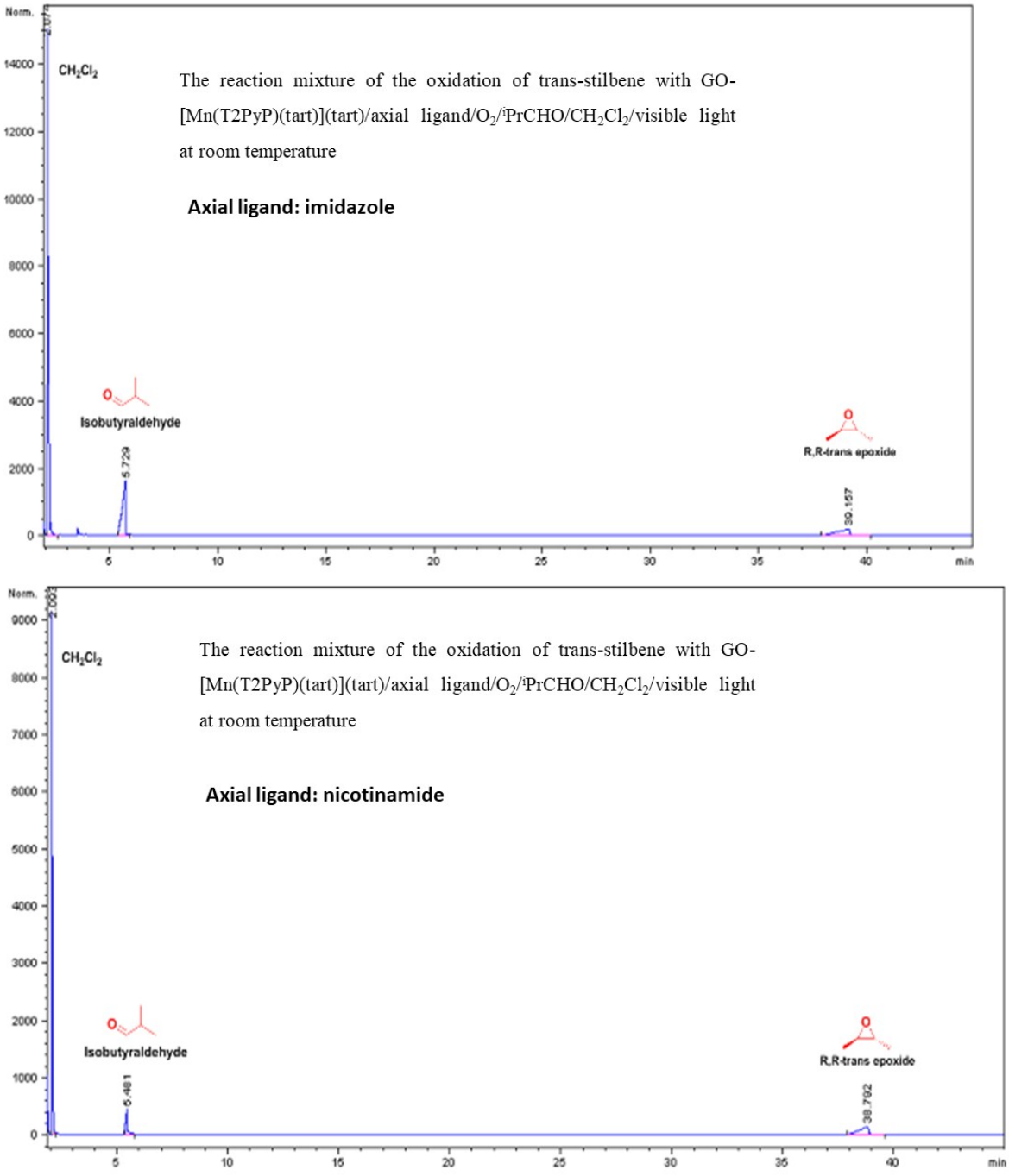


Fig. S12 GC chromatograms the reaction products with chiral column. GC column SGE-CYDEX-B capillary column (25 m × 0.22 mm ID × 0.25 μm), flow rate 10 mL/min, initial temperature 25 °C, final temperature 190 °C, temperature gradient 10 °C/min. Reaction conditions: Catalyst GO-[Mn(T2PyP)(tart)](tart) (0.71 μmol), axial ligand (1.42 μmol), ^{i}PrCHO (3.55 mmol), oxygen 1 bar, CH_2Cl_2 1 mL at room temperature under white LED (40 W) light.

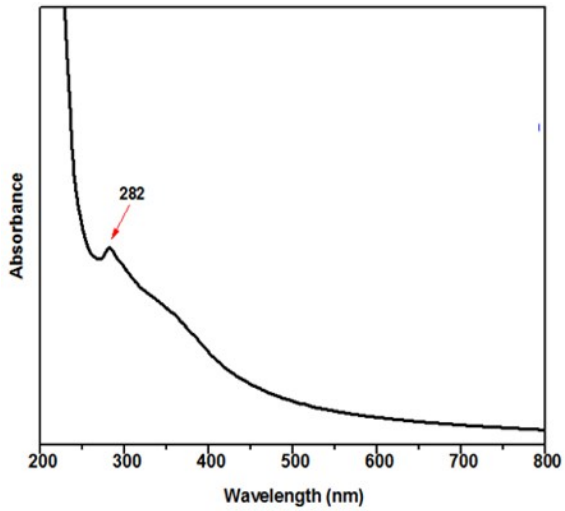


Fig. S13 UV–vis spectrum of GO-Cl in water

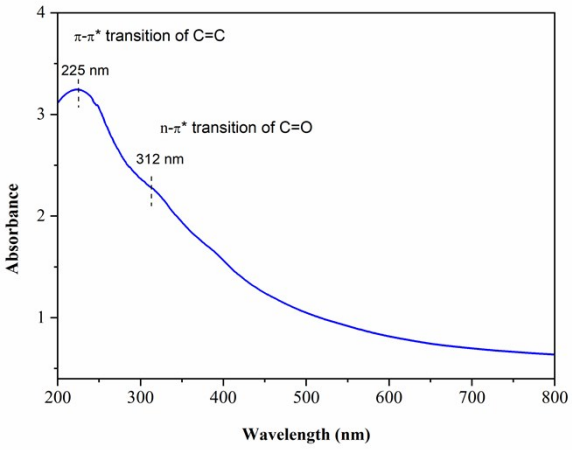


Fig. S14 UV-vis spectrum of GO recorded in aqueous solution.

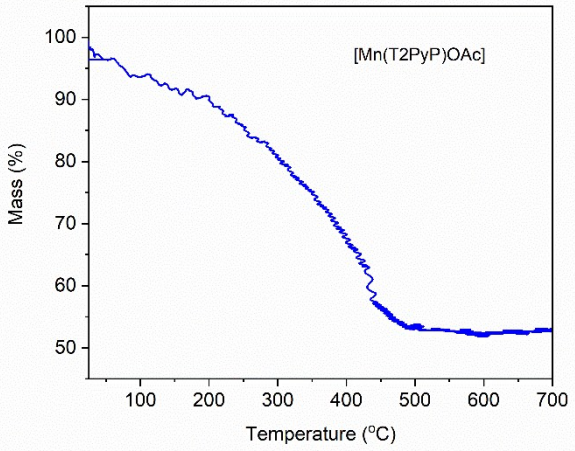


Fig. S15 Thermogravimetric analysis of [Mn(T2PyP)Oac]