

Development of an efficient magnetically separable nanocatalyst: Theoretical approach on the role of ligand backbone on epoxidation capability

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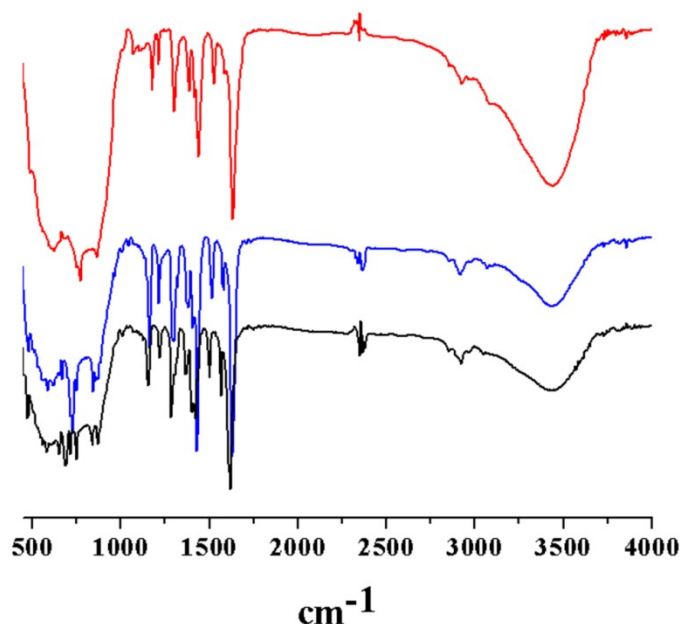


Fig.S1 FT-IR spectra of Complex 1 (Red), 2 (Blue) and 3 (Black).

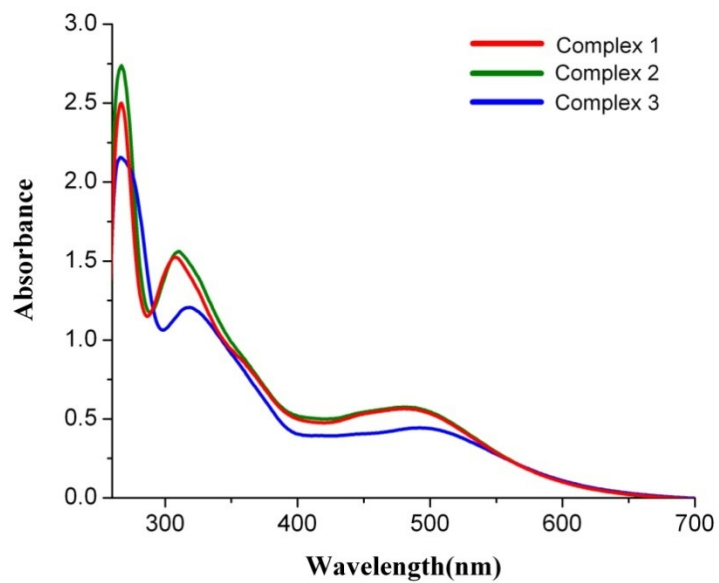


Fig. S2 UV-Vis spectra of Complex 1- 3.

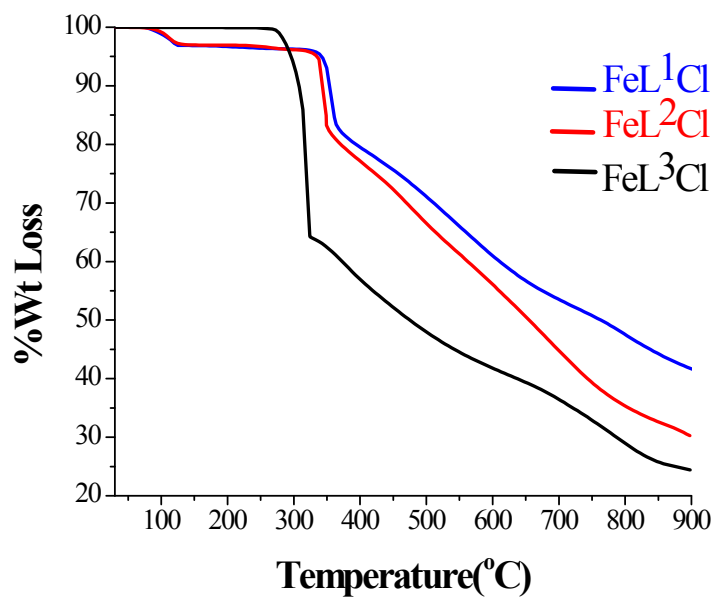


Fig.S3 TGA diagram of Complexes 1- 3.

Table S1 Selected bond lengths (Å) and angles (°) for complex **2** generated from X-ray structure.

Fe–Cl1	2.222(3)	Cl1–Fe–O1	103.8(2)
Fe–O1	1.888(6)	Cl1–Fe–O2	109.8(2)
Fe–O2	1.890(6)	Cl1–Fe–N1	103.4(2)
Fe–N1	2.093(8)	Cl1–Fe–N2	103.3(2)
Fe–N2	2.088(8)	O1–Fe–O2	94.9(3)
		O1–Fe–N1	85.6(3)
		O1–Fe–N2	150.8(3)
		O2–Fe–N1	145.6(3)
		O2–Fe–N2	85.9(3)
		N1–Fe–N2	77.8(3)

Table S2 Catalytic epoxidation of (*E*)-stilbene in CH₃CN and CH₂Cl₂ by PhIO using **3** as the catalyst under different conditions.

Entry	Catalyst (mmol)	Solvent	PhIO (mmol)	Time (h)	Conversion (%)	Yield ^a (%)
1	0.05	CH ₃ CN	30	4	62	57
		CH ₂ Cl ₂			51	45
2	0.1	CH ₃ CN	30	4	79	74
		CH ₂ Cl ₂			66	62
3	0.2	CH ₃ CN	30	4	81	75
		CH ₂ Cl ₂			70	63
4	0.1	CH ₃ CN	25	4	73	65
		CH ₂ Cl ₂			68	61
5	0.1	CH ₃ CN	30	4	78	74
		CH ₂ Cl ₂			66	62
6	0.1	CH ₃ CN	35	4	79	75
		CH ₂ Cl ₂			65	60
7	0.1	CH ₃ CN	30	2	73	67
		CH ₂ Cl ₂			70	65
8	0.1	CH ₃ CN	30	4	79	75
		CH ₂ Cl ₂			66	64
9	0.1	CH ₃ CN	30	6	83	76
		CH ₂ Cl ₂			80	64

^a Isolated epoxide yield

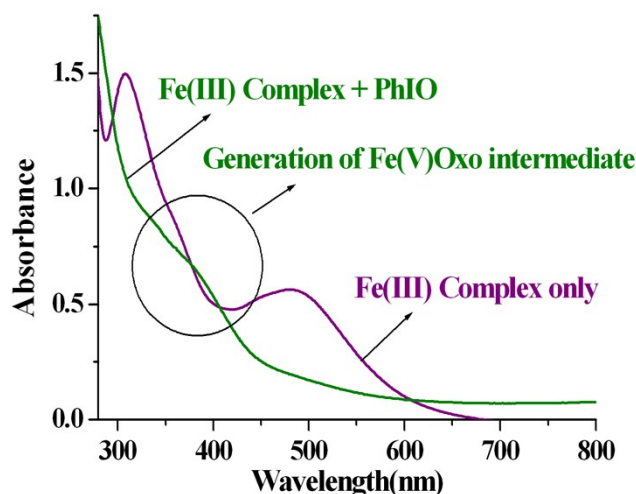


Fig. S4 Generation of Fe(V)oxo species during epoxidation.

UB3LYP/6-311+G(d,p) (LANL2DZ for Fe, Cl, Br, and I) Cartesian coordinates of the initial and oxidized iron complexes

Complex 1- high spin

```

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C,0,-0.6789724039,3.3016646642,0.2570460827
C,0,0.5546467019,3.227090759,-0.6537635925
C,0,1.4173532703,4.4803917696,-0.5268145299
O,0,-1.5515517827,-0.7237310176,0.152088123
Fe,0,-0.034916008,0.4005721404,0.4440820852
Cl,0,0.2784876795,0.6948033322,2.7710948021
O,0,1.375640755,-0.8155866584,0.0083224594
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Cl,0,2.8029390991,-3.4025219845,0.2097707211
Cl,0,-3.0026141887,-3.2873275312,-0.1108247652
Cl,0,-7.3605830395,-0.0433704103,-0.7254028573

Complex 2- high spin

Fe,0,-0.019021302,0.8093528591,0.5374548159
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C,0,2.4980035584,2.245975195,-0.4436189239
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C,0,-2.6340380991,2.3611413866,0.1078241756
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Complex 3- high spin

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Complex 1-OXO- high spin

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C,0,5.3872202191,-0.4391913088,-0.1569838597
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C,0,-5.4173475661,-0.3519441217,-0.1696798142
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Cl,0,-2.6506749406,-3.2319235836,-0.4386092434
Cl,0,-7.1963672646,-0.2493834325,-0.1672150156
Cl,0,-1.4329433457,-3.6843391531,2.4044369817

Complex 2-OXO- high spin

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N,0,1.3250670711,2.5948665365,-0.3051447202
N,0,-1.2427715188,2.6812282053,0.1048003945
C,0,4.7564556056,-1.2118378509,0.2035917657
C,0,2.5631006822,-0.0740131185,0.0052467392
C,0,3.2792090607,1.1665448351,-0.0916485907
C,0,4.6808802169,1.1908058707,-0.0476108298
C,0,2.598659694,2.4146437693,-0.3342248676
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C,0,-4.8322114154,-0.9723403576,0.1450110473
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Br,0,2.4779565886,-2.9352159878,0.2973184389
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C,0,-3.4565288516,-1.0612100397,0.1253546403
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Cl,0,1.7987376291,-3.3691289533,-2.5890788792

Complex 3-OXO- high spin

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H,0,2.3459834759,5.3342315904,-1.2386981225
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H,0,0.9117369871,6.2287881866,-0.7664055626
O,0,0.1865045101,1.6383019521,1.8544722459
C,0,3.310120702,-1.0170066045,0.1343977394
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I,0,-2.6340410479,-2.7829992645,0.1789630345
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Complex 1-low spin

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N,0,-1.2992487344,2.0603199933,-0.0838942497
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C,0,1.5328000672,4.5353021981,-0.5589182267
O,0,-1.3984220315,-0.679004316,-0.2438626249
Fe,0,-0.0345045619,0.610892964,-0.0622137458
Cl,0,0.2162304869,0.7386465389,2.260949006
O,0,1.2182029532,-0.7606919766,-0.3564433823
C,0,2.5091082892,-0.6692942433,-0.2476591545
C,0,3.2227110058,0.5679625067,-0.2479843488
C,0,4.6306447792,0.5926180744,-0.1574584783
C,0,5.3249775716,-0.5862034356,-0.0478027369
C,0,4.6725330999,-1.8224665546,-0.045923674
C,0,3.2994928,-1.8444498313,-0.1476151727
C,0,2.5463927737,1.8248991175,-0.4345023652
N,0,1.2680794111,1.9958458236,-0.4487667424
H,0,5.2313747029,-2.7445254161,0.0365127773
H,0,5.1511144206,1.5414927538,-0.1743102396
H,0,3.1902893606,2.6860054349,-0.5978839142
H,0,0.3935480948,3.2422788563,-1.8481346261
H,0,-0.4294439813,3.5617757006,1.0660910442
H,0,-1.3005487375,4.1624767864,-0.3649610168
H,0,-3.1650160674,2.889724211,-0.0365232472

H,0,-5.5172803328,-2.4700279637,-0.1560650961
H,0,-5.2132821163,1.8068459833,0.0463458537
H,0,2.3879484479,4.5588493751,-1.2358017525
H,0,1.8919971385,4.5837728111,0.4721685645
H,0,0.9427502983,5.4323289686,-0.7581552728
Cl,0,7.1147579222,-0.560435861,0.0835559426
Cl,0,2.4670409202,-3.4261300552,-0.1522594984
Cl,0,-2.786039031,-3.2795925755,-0.3176280954
Cl,0,-7.2890108651,-0.2033954822,0.0356272852

Complex 2-low spin

Fe,0,-0.0134798061,1.048727262,-0.0695470565
Cl,0,0.2396986603,1.2284075493,2.2513580158
O,0,1.2523114397,-0.3159886573,-0.3389002111
O,0,-1.3689407577,-0.2558537721,-0.2239353341
N,0,1.2743764264,2.4368759419,-0.4900519725
N,0,-1.2910086628,2.4860300878,-0.121024228
C,0,4.7189557,-1.3349383601,-0.000313461
C,0,2.5431494946,-0.2140106826,-0.2327386958
C,0,3.2430953052,1.0313741851,-0.2656359947
C,0,4.6505986553,1.0740696974,-0.1761403048
C,0,2.554265729,2.2768968019,-0.4777712474
C,0,0.648280568,3.7381900099,-0.8555205081
C,0,-0.6522580697,3.8063728259,-0.0574490967
C,0,-2.5768686926,2.380829129,-0.0973270304
C,0,-3.3167914618,1.1497285448,-0.0781713068
C,0,-2.6579200394,-0.1164248737,-0.1485859431
C,0,-4.8749561281,-1.176525874,-0.0713845768
C,0,-4.7238898102,1.2343321427,-0.0125969594
C,0,1.5167034127,4.9753758336,-0.6579382458
H,0,5.2881604684,-2.2479371061,0.1069503713
H,0,5.1543753505,2.0311883717,-0.2185117284
H,0,3.189574083,3.1400460041,-0.6629207467
H,0,0.3861788404,3.6440097148,-1.9153066473
H,0,-0.4334198117,4.0219121309,0.9926908258
H,0,-1.3132721157,4.5812008382,-0.449654316
H,0,-3.1639941763,3.299181566,-0.0859091002
H,0,-5.4763109406,-2.0750993412,-0.0633827726
H,0,-5.1932395235,2.2085163304,0.035893084
H,0,2.370781433,4.9908760732,-1.336409438
H,0,1.8769351076,5.0502628498,0.3712256639
H,0,0.9186632382,5.862577917,-0.8765441063
C,0,3.3443372748,-1.3795567562,-0.1016259739
Br,0,2.4596827053,-3.113056471,-0.0615615351
C,0,5.3630652163,-0.0924249199,-0.0352435327
Br,0,7.3101312992,-0.0361287172,0.1069223276
C,0,-3.5002449818,-1.2604327,-0.1417957
Br,0,-2.6744598025,-3.020335038,-0.2359184741
C,0,-5.4775842054,0.0855529223,-0.0044880436
Br,0,-7.4246794217,0.1953425397,0.0984619998

Complex 3- low spin

C,0,-5.4763798205,0.382770716,0.0075576157
C,0,-4.8621852882,-0.8778703105,-0.0479494844
C,0,-3.4853227402,-0.9703238647,-0.1227163633
C,0,-2.6484894394,0.1788234187,-0.1436279054
C,0,-3.3081141779,1.4456343802,-0.0858237178
C,0,-4.7149394863,1.529267838,-0.016484469
C,0,-2.5714568435,2.6776463819,-0.121268685
N,0,-1.2857537155,2.7869629268,-0.1475166761
C,0,-0.6522772142,4.1104372819,-0.1020125822
C,0,0.6453253744,4.0370755209,-0.9039282595
C,0,1.5098755271,5.2799073465,-0.725013298
O,0,-1.3575552495,0.0468462822,-0.221201344
Fe,0,-0.0023980361,1.3553486145,-0.07759639
Cl,0,0.2524569593,1.5684551651,2.2427388035
I,0,-2.5838362352,-2.8950376492,-0.2104236933
I,0,-7.6015347526,0.5036838769,0.1266776603
O,0,1.2714299165,-0.0060450651,-0.3330945495
C,0,2.5635395964,0.1000369212,-0.2328209227
C,0,3.2542120468,1.3501944789,-0.2858560181
C,0,4.6615774425,1.4034250116,-0.200046054
C,0,5.3913417919,0.2464914426,-0.0448891428
C,0,4.7456096691,-0.9983958034,0.0069878785
C,0,3.368659957,-1.0625618705,-0.0894581143
C,0,2.5580110943,2.5882355322,-0.5126467319
N,0,1.2770162512,2.7427019799,-0.523731397
I,0,2.4147859854,-2.9626460684,-0.0208393143
I,0,7.5167558458,0.3263720824,0.1064975793
H,0,5.3215879027,-1.9060737669,0.1240011993
H,0,5.1507232172,2.367606186,-0.2572570164
H,0,3.1882742071,3.4522530189,-0.7107803176
H,0,0.3797107991,3.929018027,-1.9615421783
H,0,-0.4302476826,4.3399397162,0.9445331914
H,0,-1.3177808209,4.8779082612,-0.5012090765
H,0,-3.160956693,3.5947202046,-0.1208405891
H,0,-5.4626991761,-1.7769729034,-0.0279768391
H,0,-5.1772574081,2.5074992631,0.0220051423
H,0,2.3621610211,5.2897090788,-1.4058600584
H,0,1.8727349522,5.3695358673,0.3020931534
H,0,0.9080452226,6.1621094805,-0.9534090358

Complex 1-OXO - low spin

Fe,0,0.0437144354,0.7065326141,0.0972009739
O,0,1.2796302819,-0.625370031,-0.442862142
O,0,-1.3199012412,-0.6455001381,-0.1870032537
N,0,1.2997681639,2.1212542825,-0.2640006854
N,0,-1.273928767,2.1198094737,0.1206391937
C,0,4.7442917534,-1.67768431,-0.2599606766
C,0,2.5678528316,-0.534203532,-0.3371239323
C,0,3.2720135022,0.7054028708,-0.2326456407
C,0,4.6803695681,0.7373990239,-0.1486735391

C,0,2.5791601129,1.9624249615,-0.3079747931
C,0,0.6591011464,3.4501460128,-0.4801932591
C,0,-0.6395356931,3.42529153,0.326764003
C,0,-2.5526875579,1.9997819079,0.0671279882
C,0,-3.2728233302,0.7553634529,-0.0538121552
C,0,-2.5903703727,-0.5065077797,-0.1765097651
C,0,-4.8104885498,-1.6002568032,-0.2826563938
C,0,-4.6693985221,0.8106913213,-0.0501083962
C,0,1.5238349463,4.6609277201,-0.1469088671
H,0,5.3132237692,-2.5972715276,-0.2674922099
H,0,5.1917744295,1.6891096384,-0.0820544932
H,0,3.2056375242,2.8418549313,-0.435735201
H,0,0.3918682316,3.4742853353,-1.542345841
H,0,-0.4171888321,3.5201233784,1.3941232721
H,0,-1.3033144507,4.2380631582,0.0274950769
H,0,-3.1580656194,2.9046958981,0.1237696884
H,0,-5.4018184165,-2.5014068007,-0.3675218651
H,0,-5.168321154,1.7670758341,0.0398888801
H,0,2.3765042894,4.7540978947,-0.8206465117
H,0,1.8855193255,4.6217847353,0.8836853839
H,0,0.9229179235,5.5649421999,-0.2656638756
O,0,0.2383261245,0.6588682002,1.6968877758
C,0,3.3714920964,-1.7064167653,-0.354145497
C,0,5.3856695023,-0.4396474514,-0.1490768178
C,0,-3.4306106684,-1.6628393849,-0.3085915109
C,0,-5.4149608391,-0.3542963455,-0.1567165402
Cl,0,2.5570736187,-3.2883846181,-0.5092615651
Cl,0,7.1749868912,-0.4102801505,-0.0217058327
Cl,0,-2.6451785674,-3.2263674623,-0.472807708
Cl,0,-7.1945474534,-0.2550038274,-0.1434648563
Cl,0,-1.4509415133,-3.6999033276,2.3572129284

Complex 2-OXO - low spin

Fe,0,0.0286587085,1.2589331956,0.2548478483
O,0,1.2839458901,-0.1736733424,-0.0633405348
O,0,-1.3202887784,-0.0675166856,0.086522025
N,0,1.3251349067,2.5952853627,-0.3057541378
N,0,-1.2430952942,2.6821722794,0.1013157925
C,0,4.753099701,-1.2143647064,0.201186727
C,0,2.560924964,-0.0738631086,0.0055919078
C,0,3.2781773481,1.166715501,-0.08449111
C,0,4.6798719275,1.1895247591,-0.0372214805
C,0,2.5988891895,2.4153473196,-0.3287158017
C,0,0.702836639,3.8968002312,-0.6804094933
C,0,-0.5857370599,3.9923456972,0.1368639535
C,0,-2.5283710089,2.5779885307,0.0816249443
C,0,-3.2691106653,1.3488896909,0.119571696
C,0,-2.6082110944,0.0805023033,0.1218327692
C,0,-4.8313065529,-0.9729579827,0.1511272488
C,0,-4.6779526773,1.4373435475,0.1340810886
C,0,1.5883924006,5.1264063094,-0.5114041109

H,0,5.3157868329,-2.1310973973,0.3100620973
 H,0,5.1953275034,2.1375229259,-0.1260232043
 H,0,3.2414460595,3.2587766439,-0.5714046229
 H,0,0.4223986513,3.7905910441,-1.7342913964
 H,0,-0.3487864948,4.2205727987,1.1807758393
 H,0,-1.2407949764,4.7710010312,-0.2576052265
 H,0,-3.1118847284,3.497551581,0.0325131567
 H,0,-5.4345429745,-1.8702772446,0.1640912499
 H,0,-5.1458154297,2.4134869878,0.1311122176
 H,0,2.4313377203,5.124821293,-1.2037213838
 H,0,1.9661088794,5.2079825389,0.5110473929
 H,0,0.9969481293,6.0179944609,-0.7299503481
 O,0,0.2544235914,1.4200334262,1.8450195035
 C,0,3.3695681854,-1.244505713,0.1523505685
 Br,0,2.4730086212,-2.9367155558,0.2784493699
 C,0,5.3982535589,0.0160765187,0.1156534642
 Br,0,7.3420642541,0.0790843695,0.2006271993
 C,0,-3.4555959009,-1.0612803262,0.1306099554
 Br,0,-2.6324460748,-2.8250860469,0.1216133223
 C,0,-5.4342716346,0.2911026125,0.1541874996
 Br,0,-7.3839085799,0.4052552899,0.1832371573
 Cl,0,1.8152817232,-3.3609783903,-2.6121056742

Complex 3-OXO - low spin

26	-0.0385	1.47396	0.26319
8	1.21705	0.05024	-0.06671
8	-1.39311	0.14606	0.10059
7	1.25029	2.81061	-0.31287
7	-1.31473	2.89504	0.10338
6	4.69388	-0.97393	0.20036
6	2.49836	0.15046	-0.00063
6	3.20956	1.39228	-0.08685
6	4.61368	1.42375	-0.02679
6	2.52568	2.63599	-0.33332
6	0.62354	4.10737	-0.69563
6	-0.6605	4.20659	0.12781
6	-2.59992	2.78915	0.08346
6	-3.34049	1.56092	0.12955
6	-2.68229	0.29087	0.14118
6	-4.90596	-0.75359	0.1863
6	-4.7492	1.65162	0.14506
6	1.50659	5.34093	-0.54307
1	5.2591	-1.88949	0.30763
1	5.11432	2.38057	-0.10849
1	3.16398	3.48211	-0.57827
1	0.33717	3.99199	-1.74699
1	-0.41794	4.44229	1.16886
1	-1.31911	4.98164	-0.26811
1	-3.18397	3.7082	0.02863
1	-5.51077	-1.64979	0.20956
1	-5.20738	2.63255	0.13368

1	2.34662	5.33424	-1.23895
1	1.88871	5.43407	0.47675
1	0.9119	6.22875	-0.76814
8	0.18964	1.64133	1.85327
6	3.3101	-1.01688	0.1316
6	5.34539	0.25984	0.12879
6	-3.52814	-0.85323	0.1656
6	-5.51687	0.51018	0.17634
53	-7.64512	0.64176	0.20774
53	-2.63304	-2.78346	0.1807
53	2.33522	-2.87391	0.25234
53	7.46979	0.33619	0.24404
17	1.81568	-2.9921	-2.74724

Table S3 UB3LYP/6-311+G(d,p) (LANL2DZ for Fe, Cl, Br, and I) absolute electronic and Gibbs energies (a.u.), eigenvalue of S^2 , and difference between high and low spin states for each iron complex.

Species	absolute electronic energy (a.u.)	G (a.u.)	S^2	ΔE (high spin-low spin. Kcal/mol)	ΔG (high spin-low spin. Kcal/mol)
phIO	-318,214139	-318,157968			
phI	-243,090759	-243,032953			
complex -1- low spin	-1.113,526092	- 1.113,322881	0,7633		
complex -2-low spin	-1.106,388726	- 1.106,192064	0,7633		
complex -3-low spin	-1.099,262551	- 1.099,070086	0,7633		
complex -1- high spin	-1.113,546229	- 1.113,347905	8,7501	-12,6	-15,7
complex -2-high spin	-1.106,409093	- 1.106,217159	8,7501	-12,8	-15,7
complex -3-high spin	-1.099,283304	- 1.099,095355	8,7501	-13,0	-15,9
complex -1-OXO low spin	-1.188,658927	- 1.188,457952	0,847		
complex -2-OXO low spin	-1.181,526568	- 1.181,331503	0,8415		

complex -3-OXO low spin	-1.174,407713	- 1.174,216248	0,8432		
complex -1-OXO high spin	-1.188,659012	- 1.188,458370	3,7503	-0,1	-0,3
complex -2-OXO high spin	-1.181,526614	- 1.181,332262	3,7503	0,0	-0,5
complex -3-OXO high spin	-1.174,407705	- 1.174,217096	3,7503	0,0	-0,5

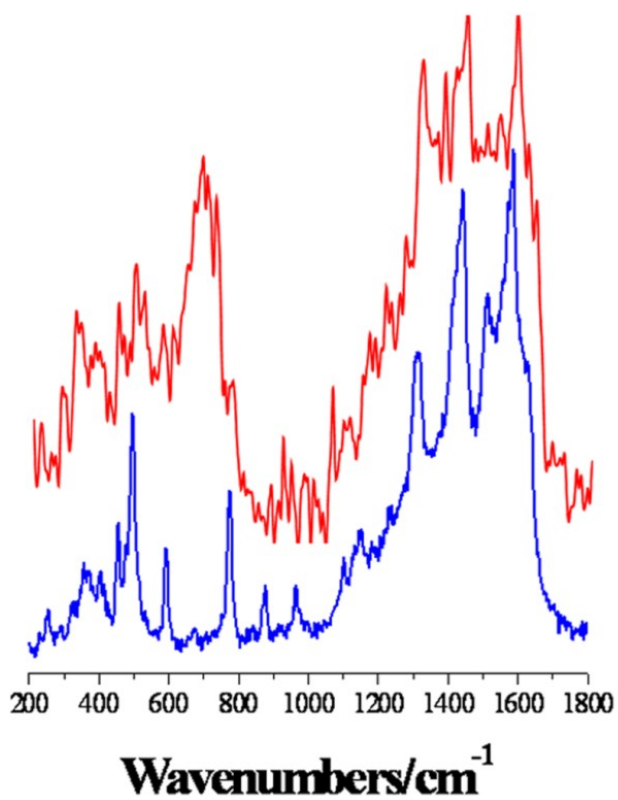


Fig. S5 Raman spectra of FeL³Cl(Blue) and Fe₃O₄@dopa@FeL³Cl(Red).

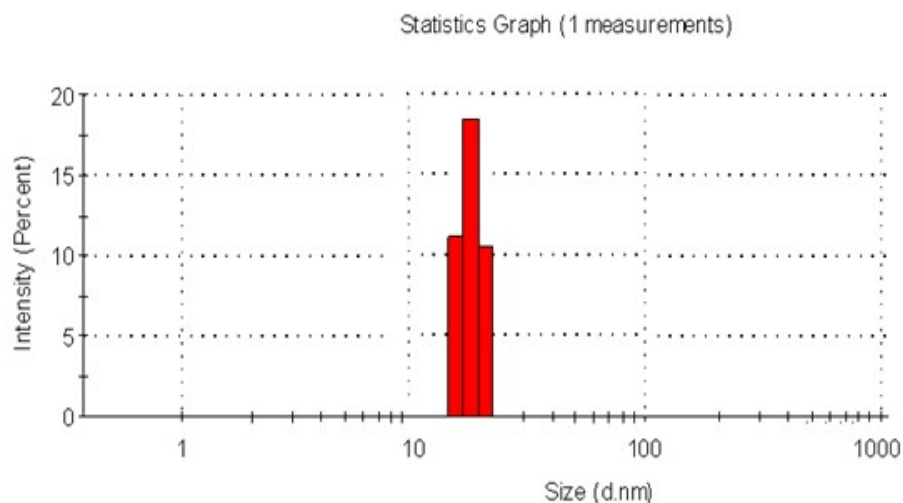


Fig. S6 Dynamic light scattering of Fe₃O₄-NPs.

TableS4Catalytic epoxidation of (*E*)-stilbene in CH₃CN and CH₂Cl₂ by PhIO using Fe₃O₄@dopa@FeL³Clas the catalysts under different conditions.

Entry	Catalyst (mg)	Solvent	PhIO (mmol)	Time (h)	Conversion (%)	Yield ^a (%)
1	50	CH ₃ CN	3	6	62	57
		CH ₂ Cl ₂			50	45
2	100	CH ₃ CN	3	6	69	62
		CH ₂ Cl ₂			62	57
3	200	CH ₃ CN	3	6	71	63
		CH ₂ Cl ₂			60	56
4	100	CH ₃ CN	2	6	60	55
		CH ₂ Cl ₂			54	47
5	100	CH ₃ CN	3	6	68	64
		CH ₂ Cl ₂			60	55
6	100	CH ₃ CN	4	6	70	65
		CH ₂ Cl ₂			64	57
7	100	CH ₃ CN	3	4	63	57
		CH ₂ Cl ₂			60	55
8	100	CH ₃ CN	3	6	69	63
		CH ₂ Cl ₂			57	54
9	100	CH ₃ CN	3	8	73	63
		CH ₂ Cl ₂			60	56

^a Isolated epoxide yield