

Supplementary information

Taming Regioselective Oxidation toward Phenol via Atomically Dispersed Iron Sites on Carbon

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Supplementary figures

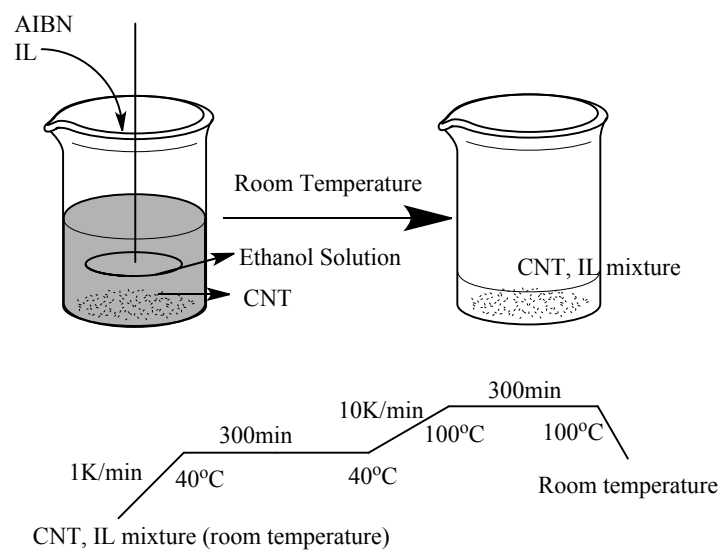


Fig. 1 Preparing procedures of the PIL/CNT.

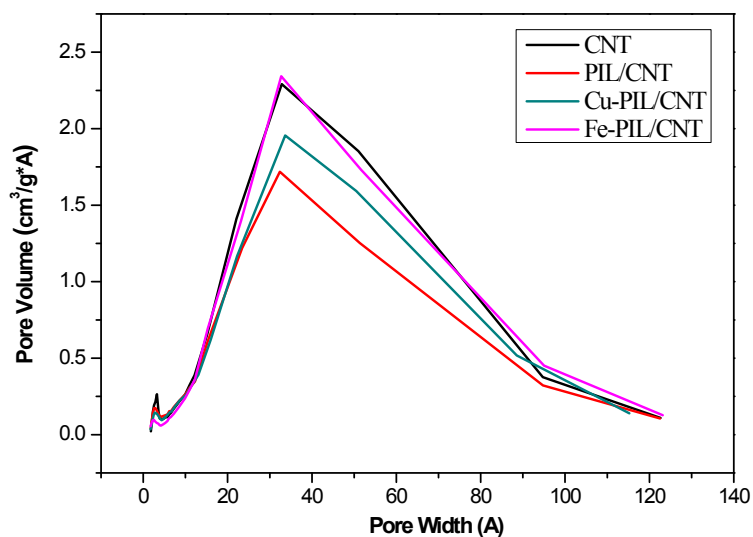


Fig. 2 The pore size distribution of different samples.

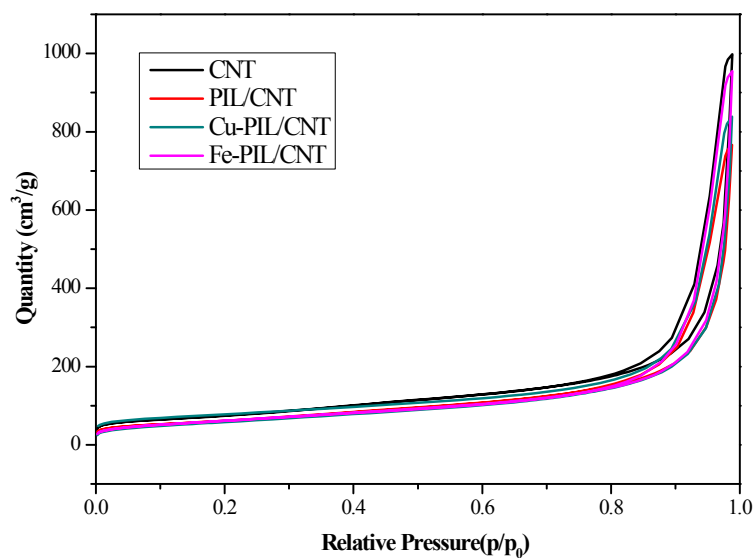


Fig. 3. Nitrogen adsorption/desorption isotherms of various samples.

Supplementary Fig. 2, 3 show the nitrogen adsorption isotherms and corresponding pore size distributions of different samples.

Copper acetate was also used during the synthesis process, applying the same methods and conditions as for the synthesis of Fe-PIL/CNT, to receive a Cu-PIL/CNT sample as reference. Similar results in comparison to the iron sample were obtained.

Table S1. Textural properties of various samples.

Samples	Surface area(m ² /g)	Pore width (nm)	Pore volume (cm ³ /g)
CNT	265.3	2.1	1.5
PIL/CNT	219.8	1.9	1.2
Cu- PIL/CNT	212.0	2.0	1.3
Fe- PILCNT	224.2	2.3	1.4

The surface area determined by nitrogen adsorption and BET analysis is 265 m²/g. The IL itself has no contribution to the surface area when covered on CNT surface. Therefore, the surface area of the PIL/CNT is as same as the surface area of the CNT, but with the weight of the CNT and the PIL together. In a typical synthesis, 500 mg of CNTs and 150 mg of IL are used, therefore the surface area of the PIL/CNT corresponds to the surface area of pure 500 mg CNTs (500 mg CNT \triangleq 132.5 m²). The total weight of the PIL/CNT is the sum of the individual weights of PIL and CNT.

The theoretical BET surface area of the PIL/CNT is

$$\frac{\text{the surface of the CNT}}{\text{the weight of the CNT} + \text{the weight of the added IL}} \\ = \frac{132.5}{150 + 500} \text{ m}^2/\text{mg} = 195 \text{ m}^2/\text{g}.$$

The practical (measured) BET surface area of the PIL/CNT is 219.8 m²/g, which means less IL is contributed to the final product than the used IL.

The practical BET surface area of the PIL/CNT is

$$\frac{\text{the surface of the CNT}}{\text{the weight of the CNT} + \text{the weight of the added IL}} \\ = \frac{132.5}{\text{the weight of the practical IL in the PIL/CNT} + 500} \text{ m}^2/\text{mg} = 219.8 \text{ m}^2/\text{g}.$$

The final IL content in the PIL/CNT can then be confirmed as 116.3 mg.

The IL content in the PIL/CNT sample is $116.3/(116.3+500) * 100\% = 18.8\%$.

The mole content of C(CO)₂ in 100 mg PIL/CNT is $18.8/228.5 = 0.082$ mmol.

The efficiency of the IL is $116.3 \text{ mg}/150 \text{ mg} = 77.6\%$.

Table S2. Distribution of element species of different samples obtained by XPS.

	C(At%)	O(At%)	Fe(At%)
CNT	98.5	1.5	--
PIL/CNT	87.5	11.2	--
Fe-PILCNT	88.2	10.4	0.7

X-ray photoelectron spectroscopy (XPS) provided detailed elemental information for the PIL/CNT surface. Table S2 shows the distribution of element species on the different samples, obtained by XPS. Note that the XPS detection depth reaches about only a few nanometers; the surface elemental analysis cannot represent the elemental data for the whole CNT (the CNT diameter is 6–8 nm). For the pristine CNT, there is only a little residual oxygen; whereas for the PIL/CNT and Fe-PIL/CNT, a large amount of oxygen content is obtained from the introduction of the acetylacetonate group on the CNT surface. Table S3 shows the bulk elemental information of the samples.

Table S3. Elemental analysis of different samples.

Samples	C	H	N	Cl	Fe	O
CNT	98	0.3	0.2	-	-	1.8
PIL/CNT	88.2	1.3	2.2	3.1	-	5.2
Fe-PILCNT	85.1	1.1	2.1	3.0	3.8	4.9

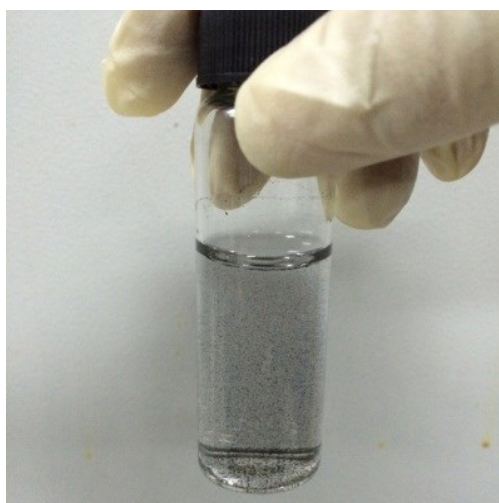


Fig. 4 Photograph images of pristine CNT dispersions in 10 mL water (the weight of both samples is 1 mg).

The CNT is treated at 1000 °C for 8 h, which is able to remove most of the hydrophilic species on the CNT surface. The π - π interaction between different CNT also causes the bad dispersion behaviour of the CNT sample as shown in supplementary Fig. 4. The Tyndall effect of the PIL/CNT in water not only proves that the PIL provide hydrophilic functional groups on the carbon surface, and also supports that the PIL is attached on the CNT surface.

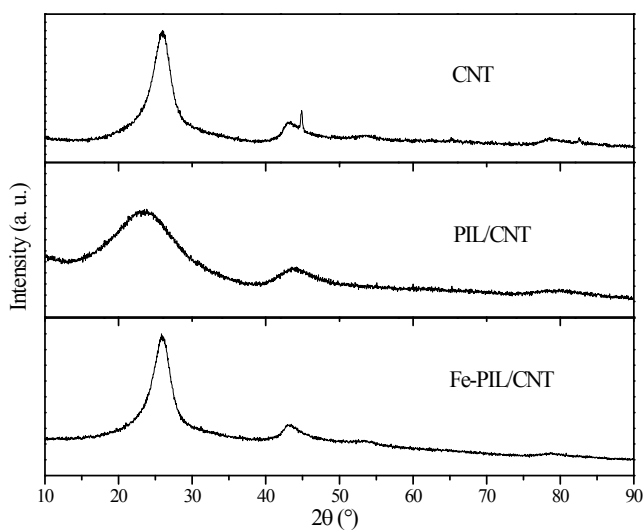


Fig. 5 XRD curves of different samples

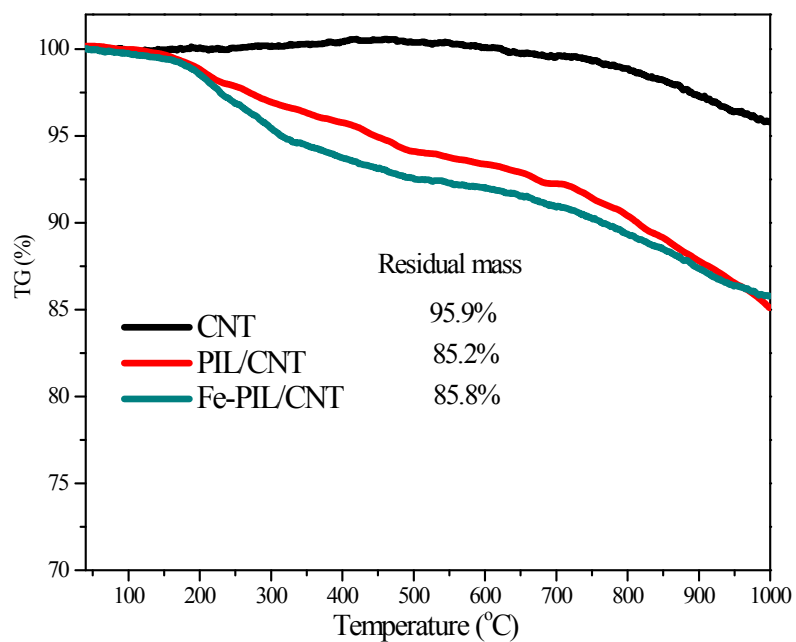


Fig. 6 TG curves (carrier gas: argon, 20 mL/min) of CNT, PIL/CNT and Fe-PIL/CNT.

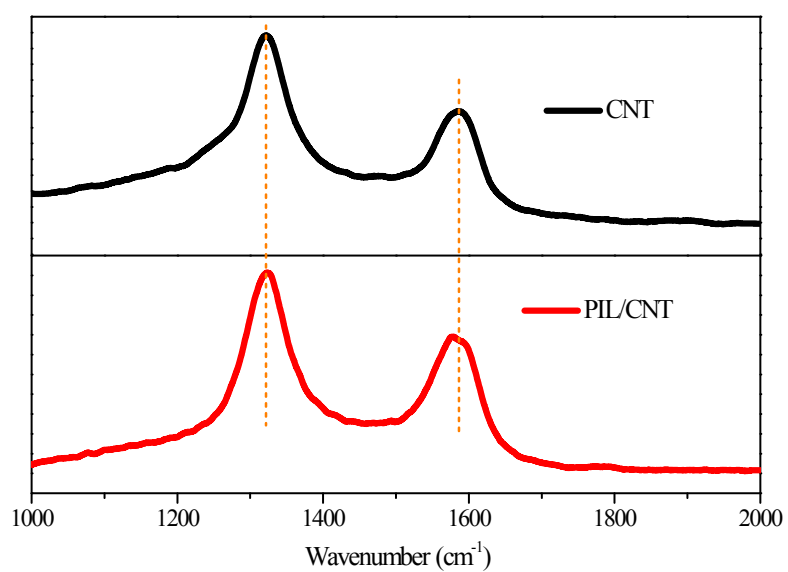


Fig. 7 Raman spectra of pristine CNT and PIL/CNT upon excitation at 633 nm.

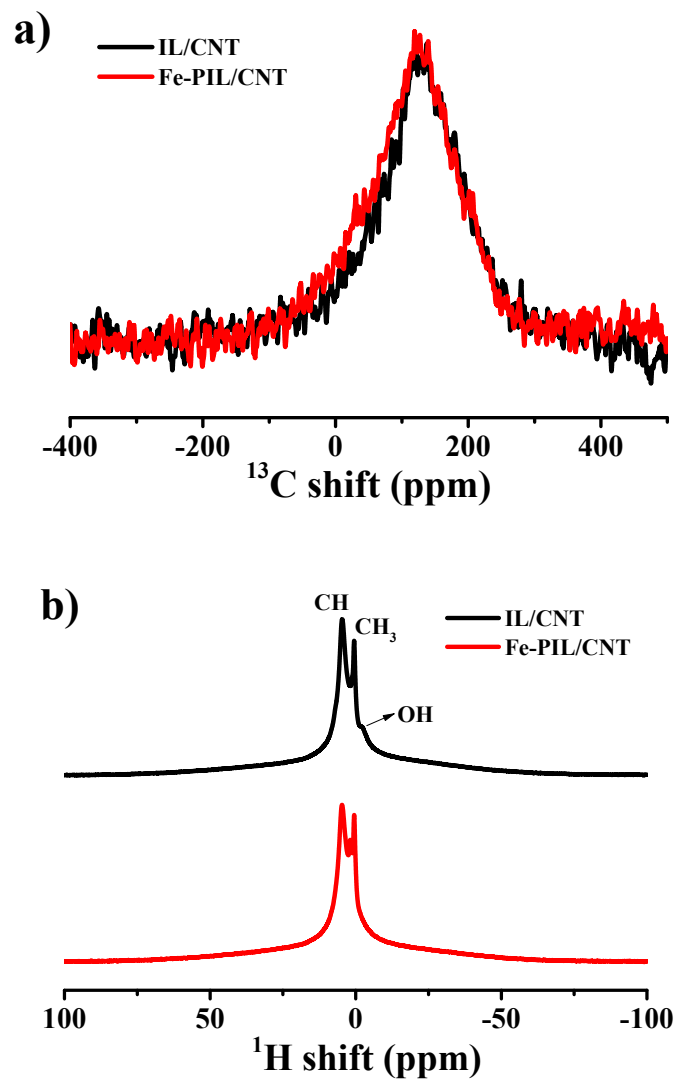


Fig. 8 NMR spectra of different samples. a) ^{13}C NMR spectrum, b) ^1H NMR spectra.

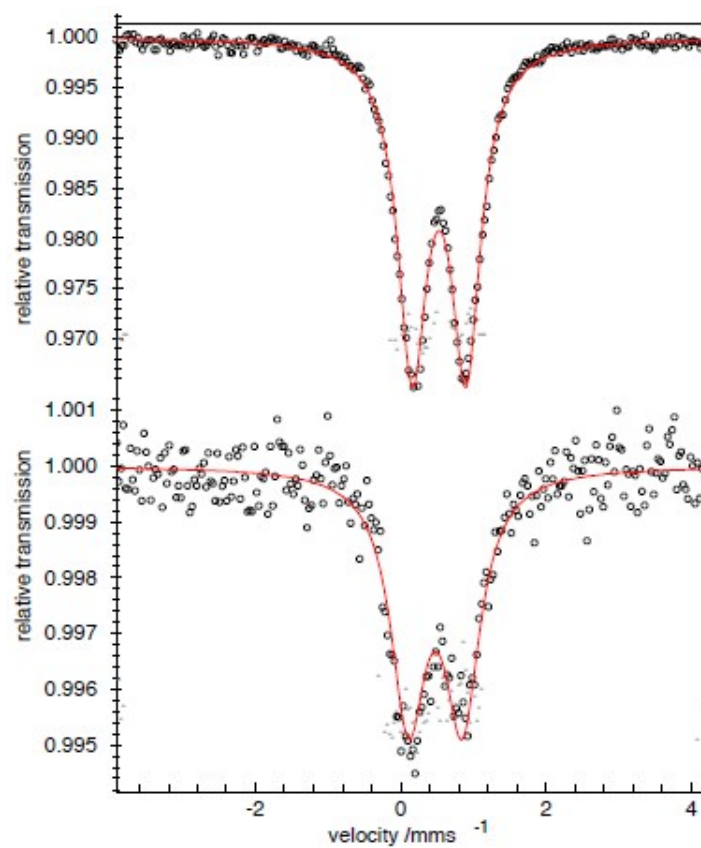


Fig. 9 Mössbauer spectra of the iron precursor $\text{Fe}(\text{CH}_3\text{COO})_2$ and the Fe-PIL/CNT.

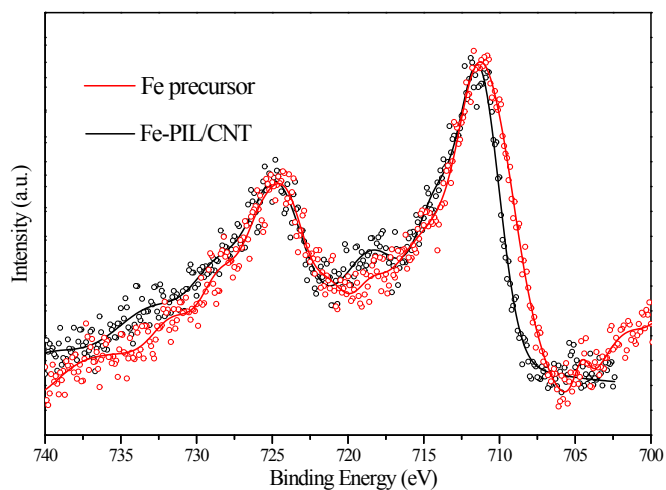
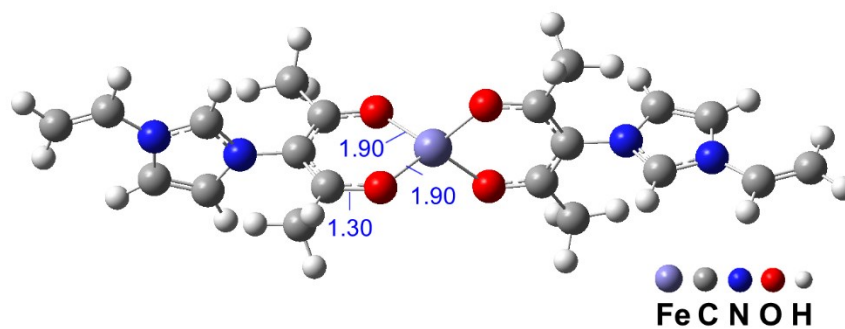


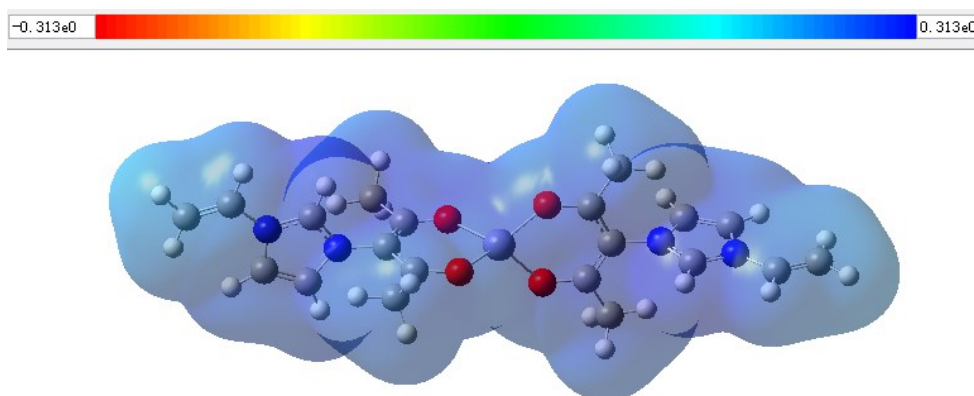
Fig. 10 XPS Fe 2p spectra of Fe-PIL/CNT and the Fe precursor ferrous acetate.

XPS Fe 2p spectra (Supplementary Fig. 10), as well as the Mössbauer Spectra in Supplementary Fig. 8 of Fe-PIL/CNT and the Fe acetate confirm that the iron oxidation state doesn't change during the synthesis process. Yet, a slight shift of the XPS Fe 2p spectrum of the Fe-PIL/CNT can be observed. This is because the coordinated sphere of the PIL is different with acetate, which also cause the configuration change of the iron species as being confirmed by the Fe L-edge. The lower binding energy of the Fe 2p electron in the Fe-PIL/CNT, indicates the electron density of the coordinator is higher. This makes the iron react with the oxidizing agent more easily. In addition, the octahedral configuration has more electrons exposed to the surface, which might be another reason why the Fe-PIL/CNT shows a higher activity to the phenol oxidation reaction.

a) the electronic structure :



b) the electron density :



c) NBO charges :

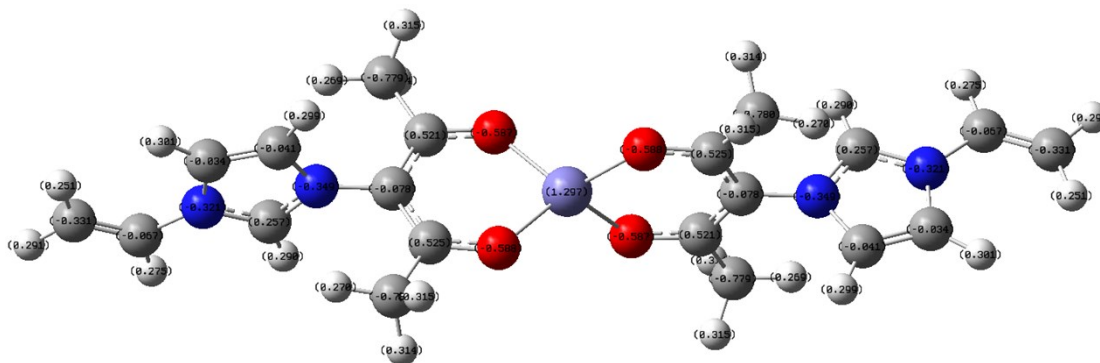


Fig. 11 a) The electronic structure of the ionic liquid coordinated iron species. The electron density in b) and NBO charges in c) show that the center Fe site is more electrophilic which can react with the deprotonated peroxide.

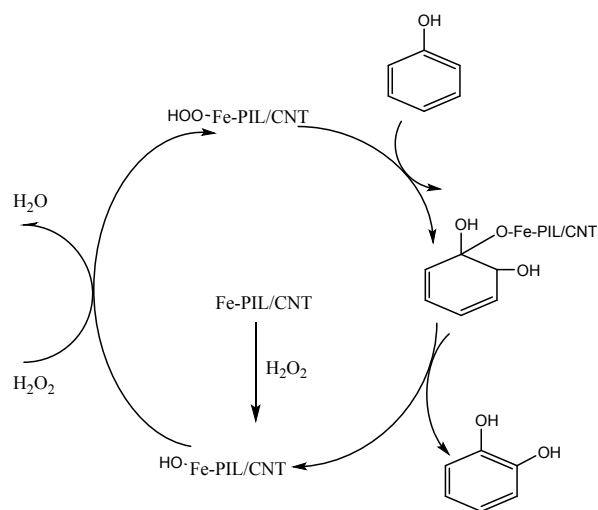


Fig. 12 Schematic process of the catalytic cycle.

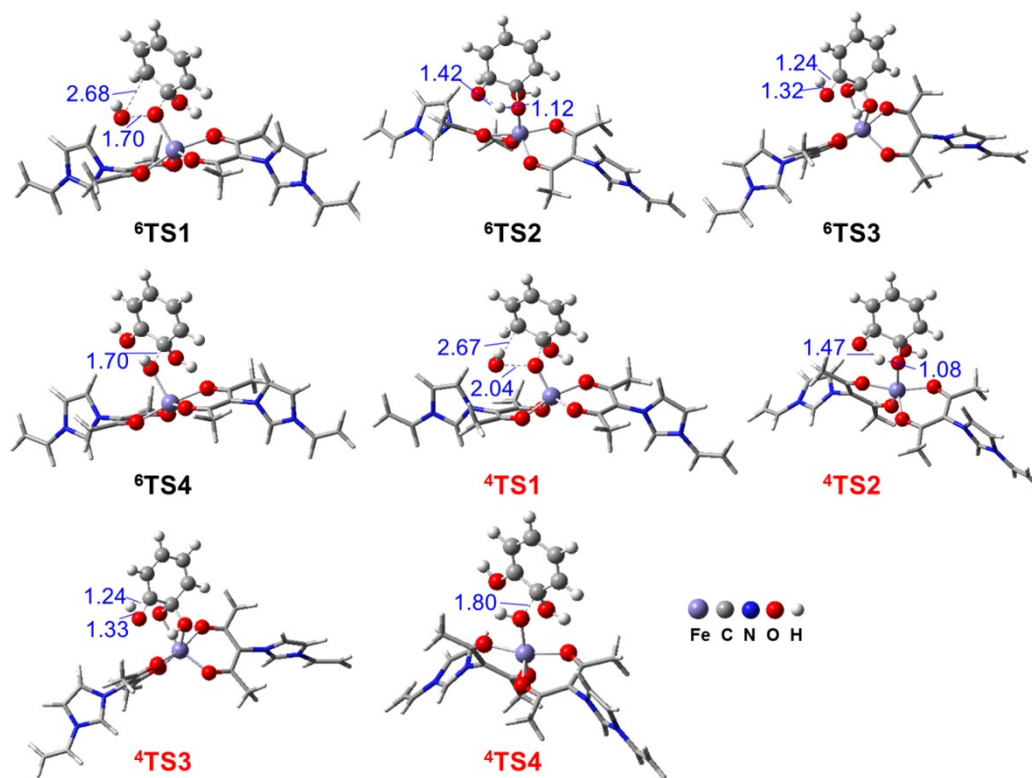


Fig. 13 Structural information for all transition states. Bond lengths are given in Å.