Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Mediation of water-soluble oligoaniline by phenol in the aniline-persulfate system under alkaline conditions

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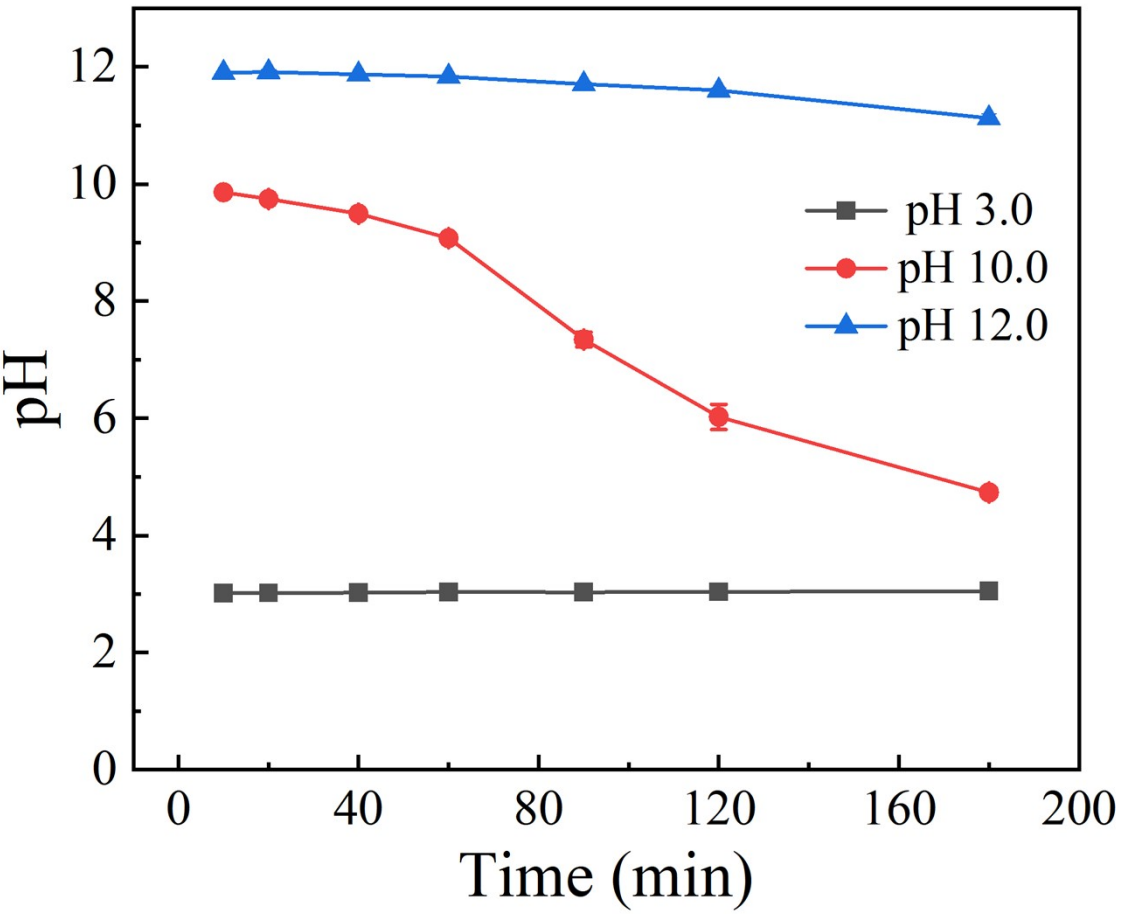

Fig. S1. pH variations in different reaction systems. Conditions: 2.0 mM aniline, 2.0 mM phenol and 5.0 mM SPS at pH_{ini} 3.0, 10.0 or 12.0.

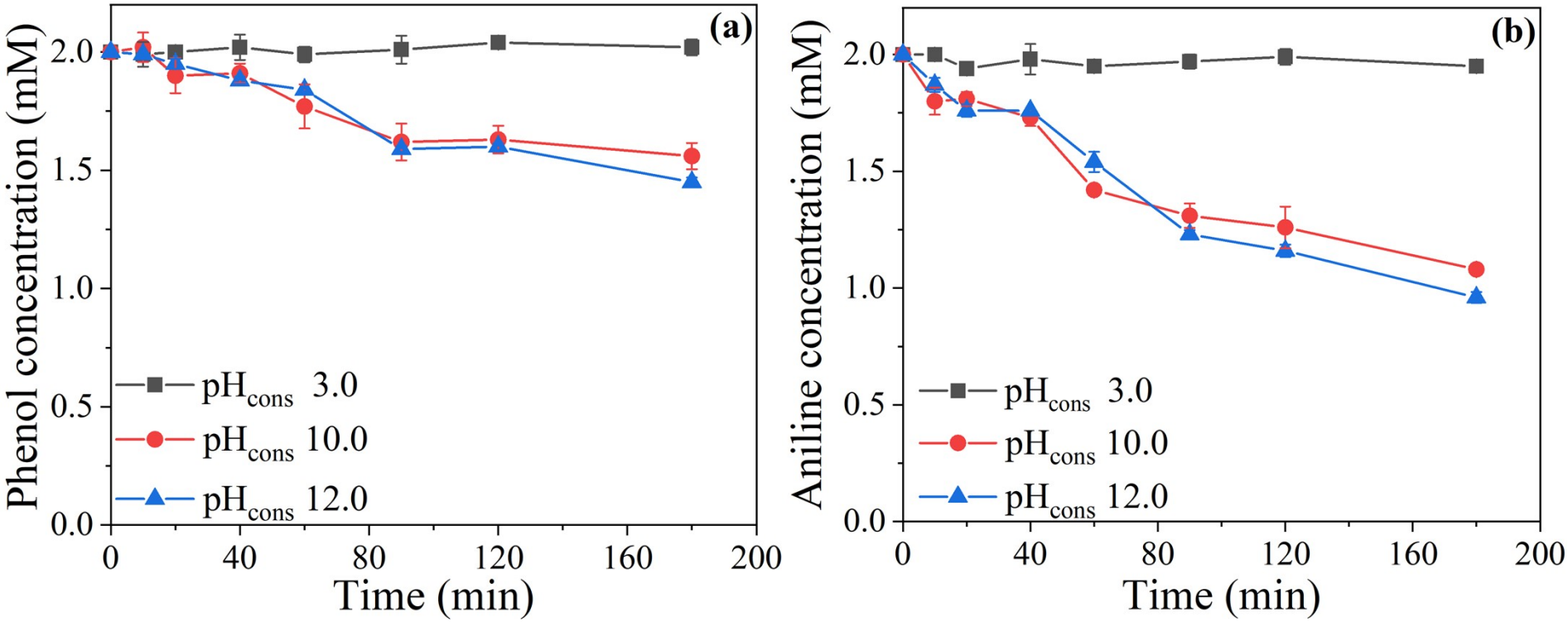

Fig. S2. Variations of phenol/aniline in the phenol-aniline-PS system at different pH_{cons} values. (a) Variations of phenol, (b) Variations of aniline. Conditions: 2.0 mM aniline, 2.0 mM phenol and 5.0 mM SPS.

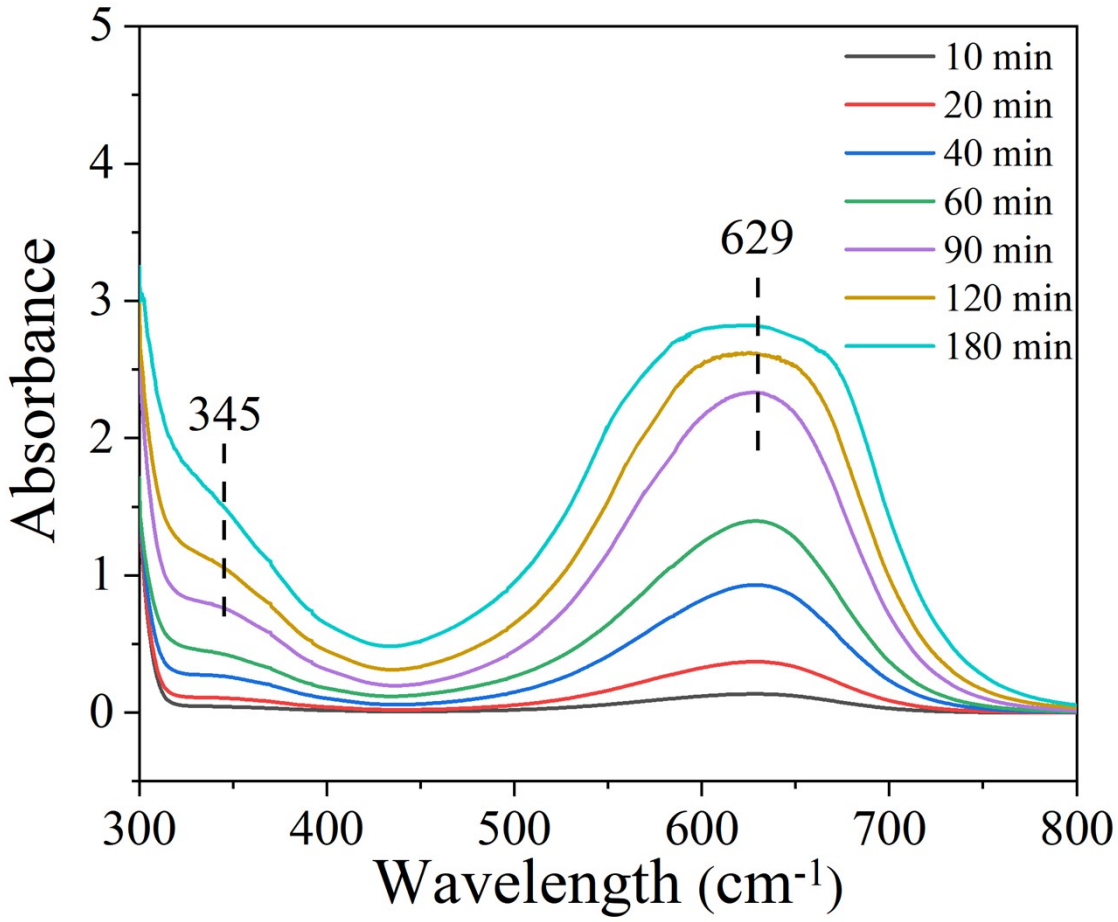

Fig. S3. UV-vis spectra of the oxidation products in the phenol-aniline-SPS system at pH_{cons} 10.0. Conditions: 2.0 mM aniline, 2.0 mM phenol and 5.0 mM SPS.

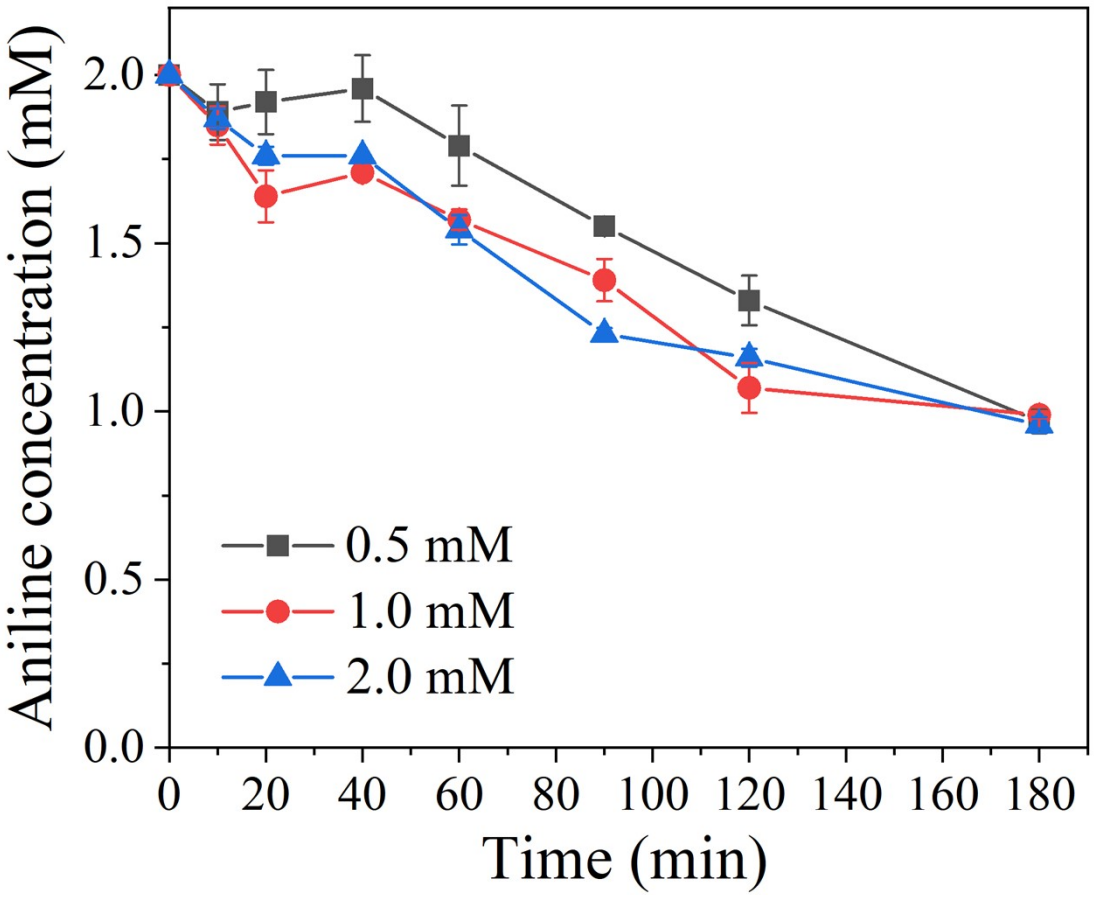

Fig. S4. Variations of aniline in the presence of different concentrations of phenol in the phenol-aniline-SPS system. Conditions: 2.0 mM aniline and 5.0 mM SPS at pH_{cons} 12.0.

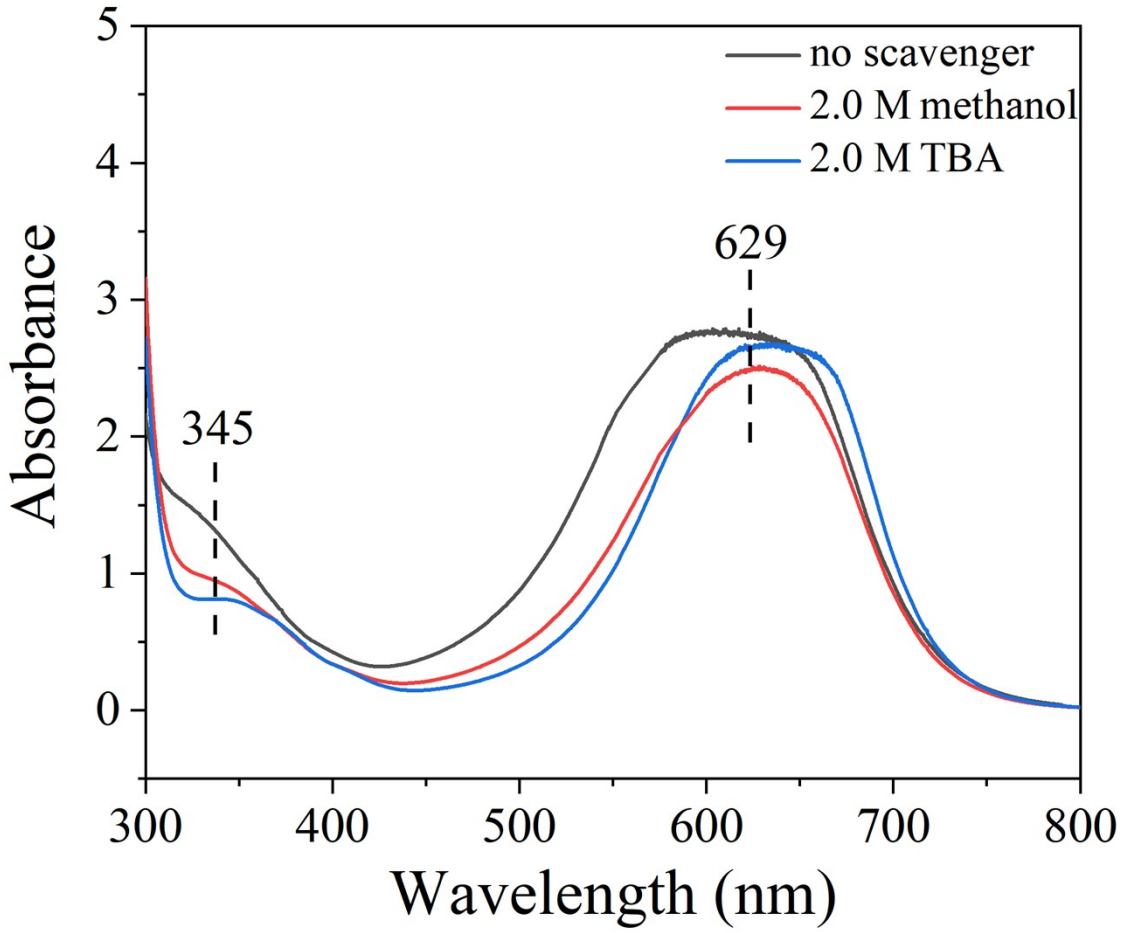

Fig. S5. Quenching experiments in the formation of OANI in the phenol-aniline-SPS system. Conditions: 2.0 mM aniline, 2.0 mM phenol and 5.0 mM SPS at pH_{cons} 12.0 at 180 min.

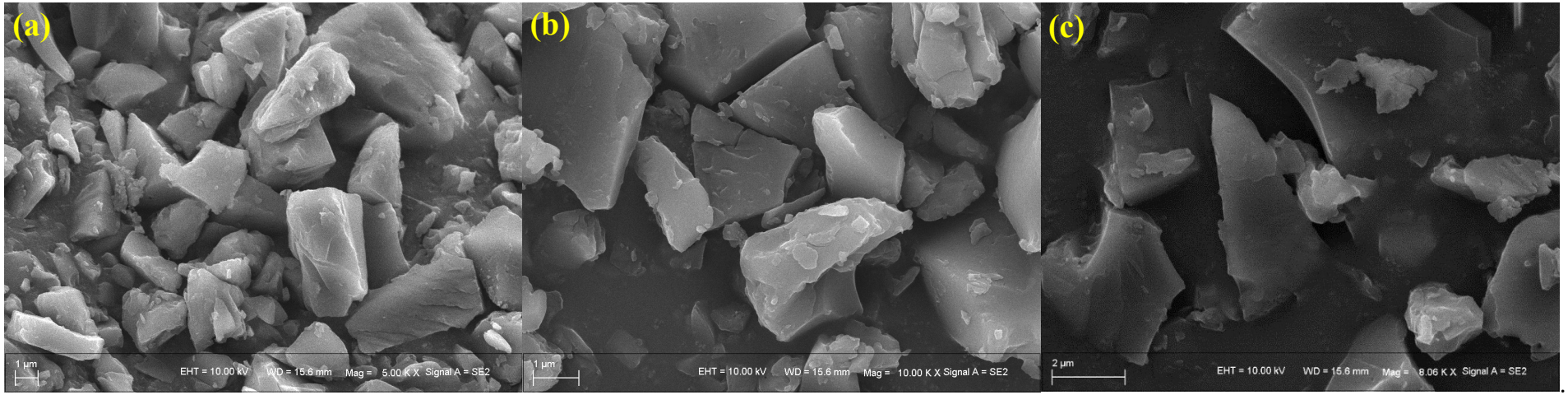

Fig. S6. SEM images of the oxidation products in the phenol-aniline-SPS system in the presence of different concentrations of phenol. (a) 0.5 mM phenol ($OANIs_{0.5}$), (b) 1.0 mM phenol ($OANIs_{1.0}$) and (c) 2.0 mM phenol ($OANIs_{2.0}$). Conditions: 2.0 mM aniline and 5.0 mM SPS at pH_{cons} 12.0 at 180 min.

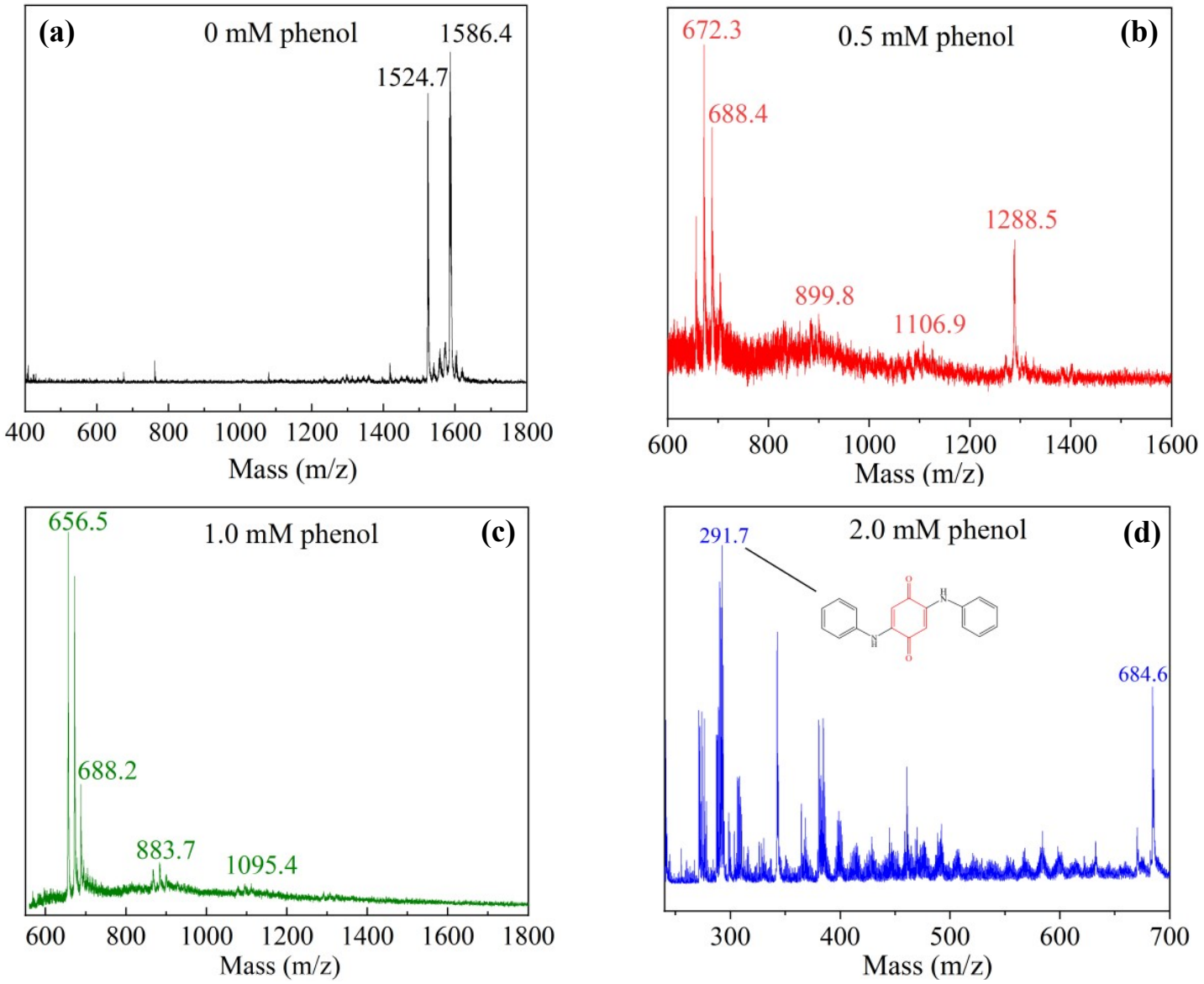

Fig. S7. MALDI-TOF analysis of the oxidation products of (a) $OANIs_0$, (b) $OANIs_{0.5}$, (c) $OANIs_{1.0}$ and (d) $OANIs_{2.0}$.

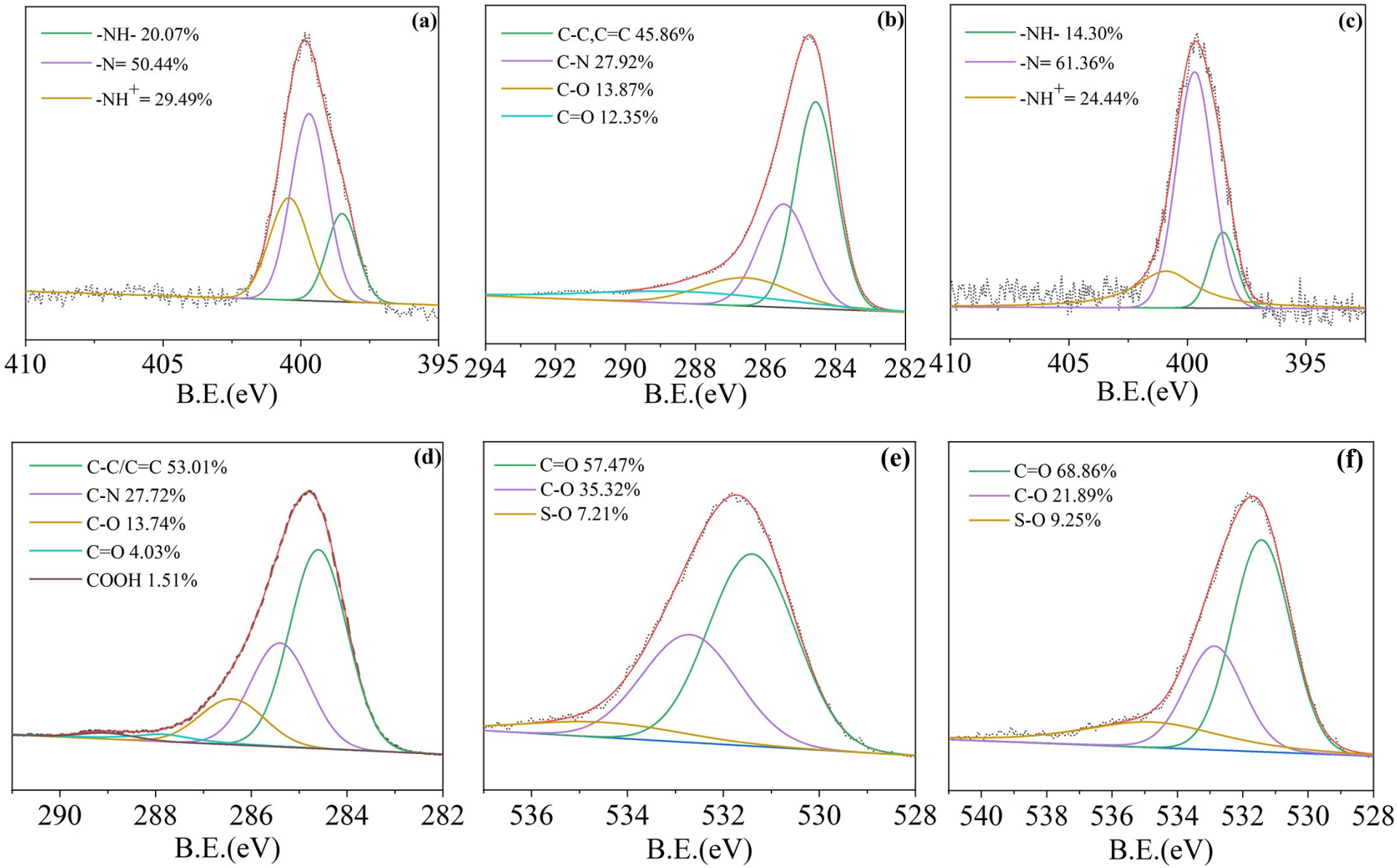

Fig. S8. XPS spectra of (a) N 1s of $OANIs_0$, (b) C 1s of $OANIs_0$, (c) N 1s of $OANIs_{2.0}$, (d) C 1s of $OANIs_{2.0}$, (e) O 1s of $OANIs_0$ and (f) O 1s of $OANIs_{2.0}$.

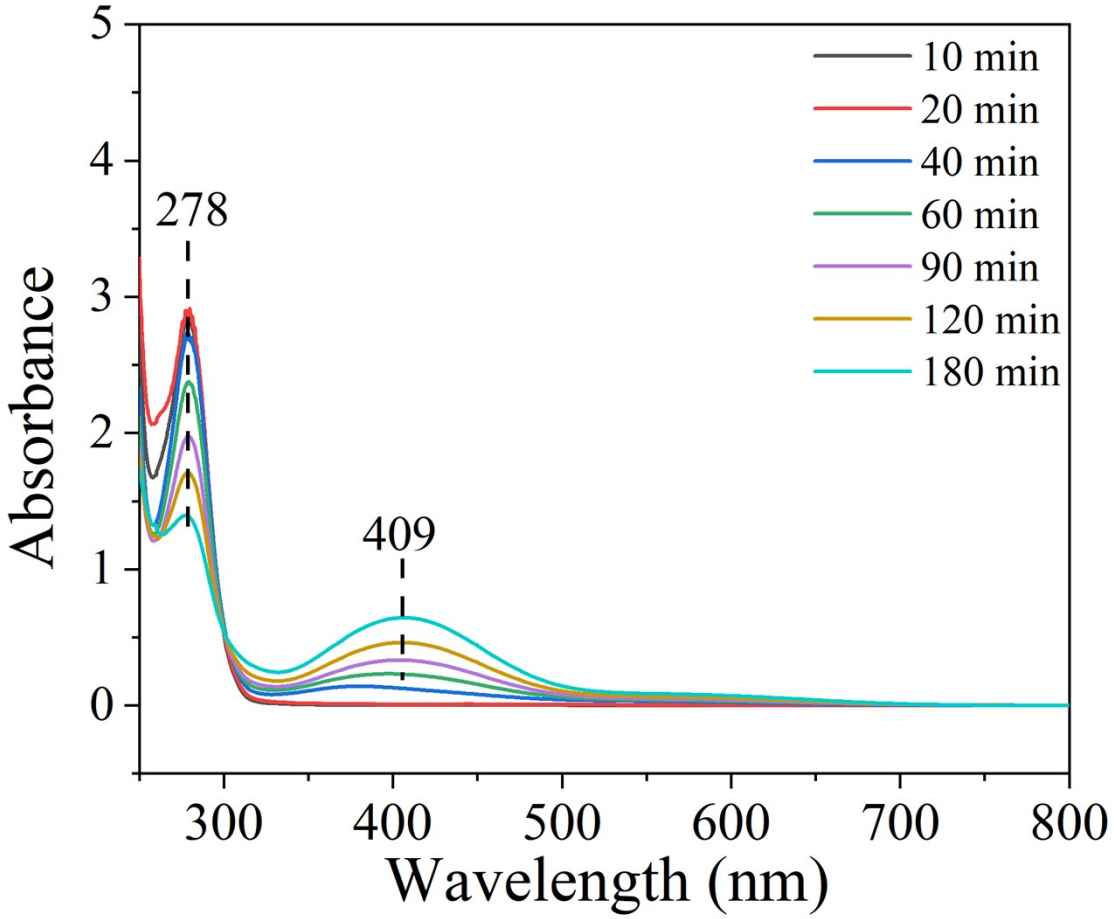

Fig. S9. UV-vis spectra of the oxidation products of aniline by SPS in the absence of phenol. Conditions: 2.0 mM aniline and 5.0 mM SPS at pH_{cons} 10.0.

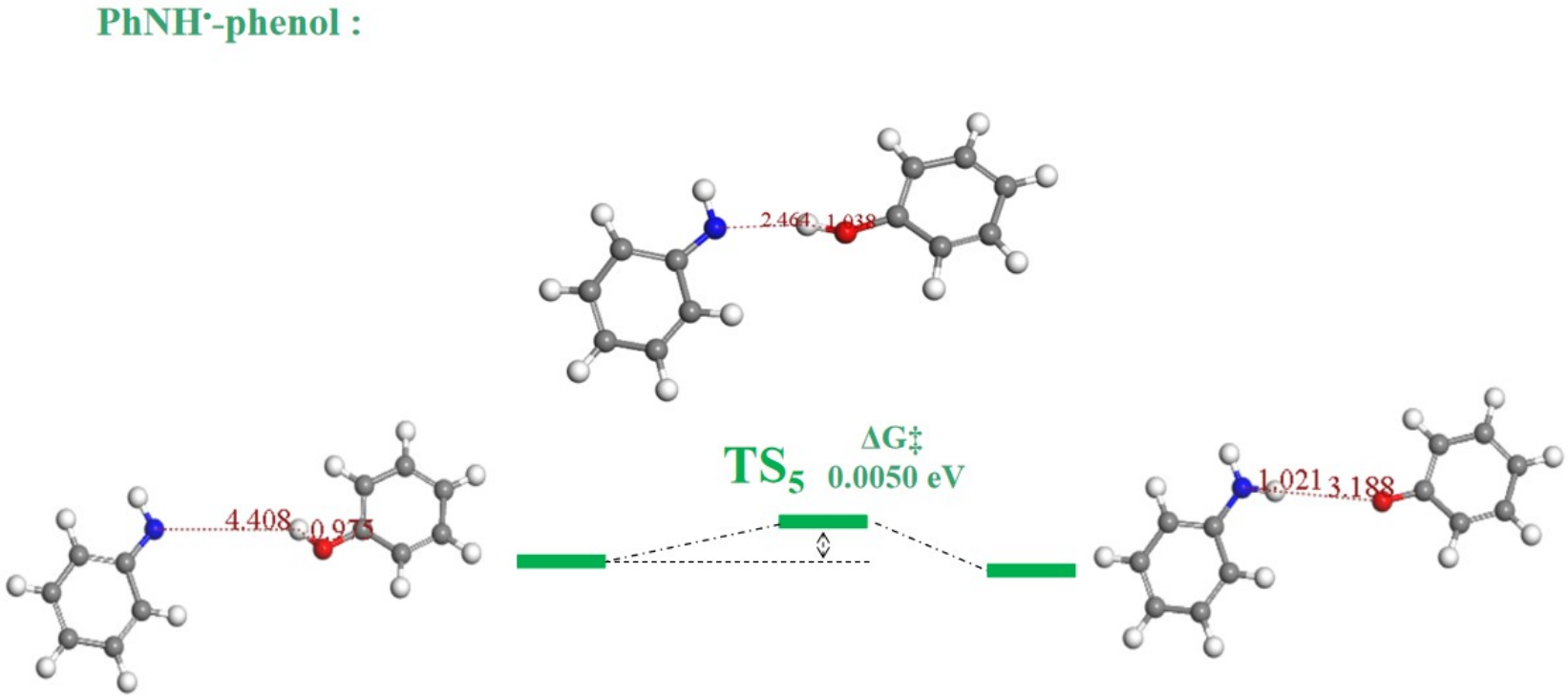

Fig. S10. DFT calculations of the bond length and the energy barriers in the reaction between PhNH• and phenol.

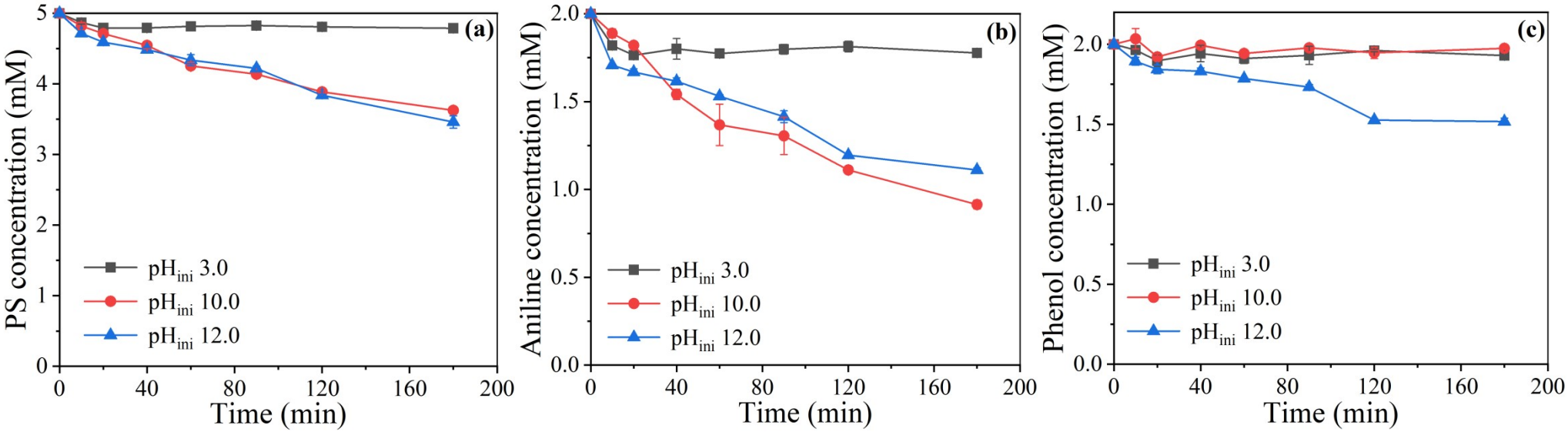

Fig. S11. Variations of (a) SPS, (b) aniline and (c) phenol in the phenol-aniline-SPS system at different pH_{ini} values. Conditions: 2.0 mM aniline, 2.0 mM phenol and 5.0 mM SPS.

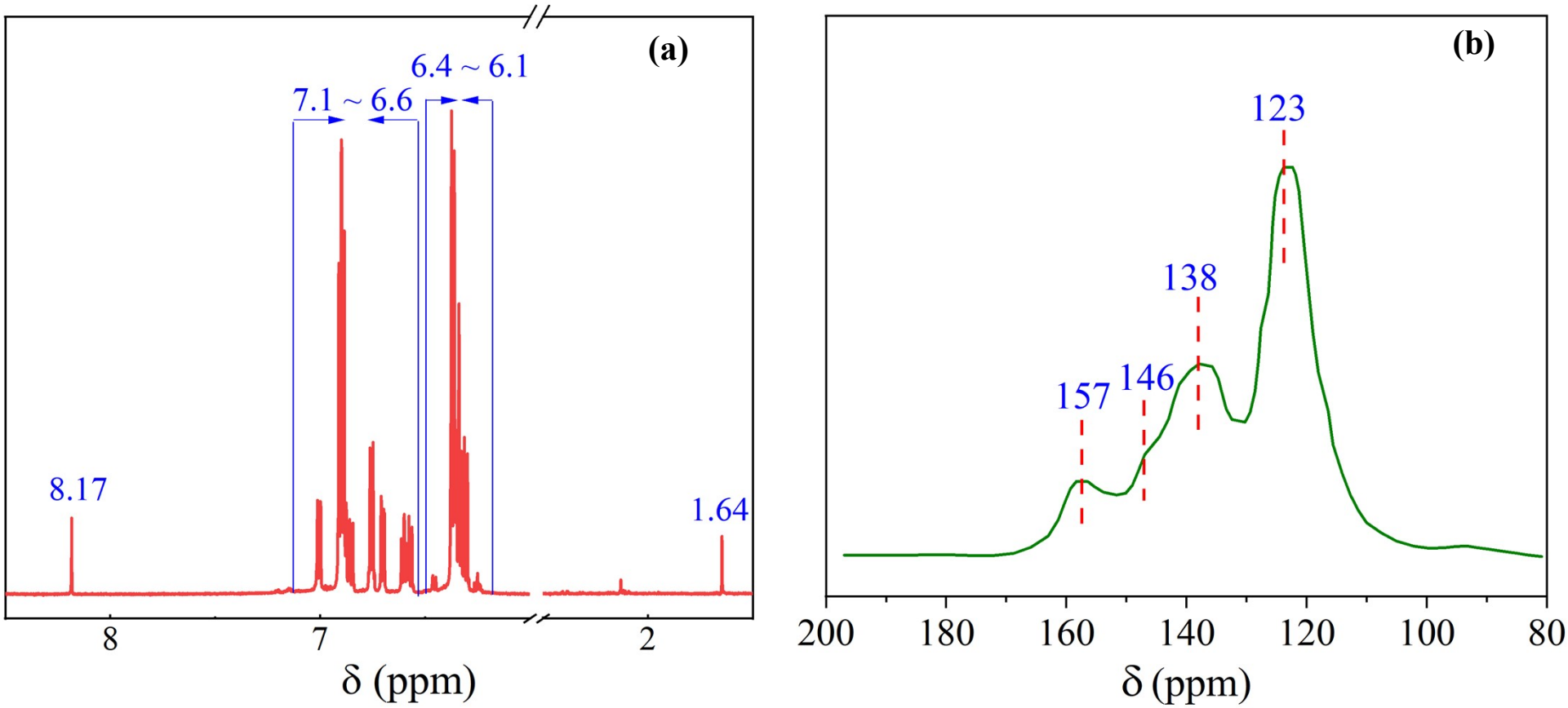

Fig. S12. The (a) ^{1}H-NMR and (b) C-13 NMR spectrum spectroscopy of $OANIs_{2.0}$.

Fig. S12(a) also provides ^{1}H-NMR spectroscopy of the $OANIs_{2.0}$ and the signal at 1.64 ppm indicates the presence of methylene or alkane groups in the oxidation products.[1] The signals in the range of 6.1-6.4 ppm are assigned to alkenes in the benzoquinone or benzoquinone monoimine moieties.[2] The signals in the range of 6.6-7.1 ppm represent aromatics.[2] The 8.17 ppm weak signal indicates the presence of the nitrogen-bonded hydrogens,[2] and the hydrogen signal of N-H is weakened upon D2O exchange.[3] Fig. S12(b) shows the C-13 NMR spectrum of the $OANIs_{2.0}$. The signal at 123 ppm is assigned not only to the carbon skeleton of the benzenoid-quinoid structure, but also to the amine structure.[4] Two signals at 138 and 146 ppm (shoulder) correspond to the two non-proton-

bonded carbons in the phenylene ring of the amine repeating unit and the four proton-bonded carbons in the quinoid ring, respectively.[4] The signal at 157 ppm represents the two non-proton bonded carbons in the quinoid ring.[4] The signals at 123, 138, 146 and 157 ppm in C-13 NMR spectrum of the produced $OANIs_{2.0}$ are similar to the signals at 124.5, 137.5, 148 and 158 ppm of PANI, reported previously (Hjertberg et al.),[5] indicating that $OANIs_{2.0}$ is composed of benzene rings and quinoid rings.

References

1. C. Wang, S. Jia, Y. Zhang, Y. Nian, Y. Wang, Y. Han, X. Han, Catalytic reactivity of Co_3O_4 with different facets in the hydrogen abstraction of phenol by persulfate. *Applied Catalysis B: Environmental.* 2020, **270**, 118819.

2. D.C. Ferreira, J.R. Pires, M.L. Temperini, Spectroscopic characterization of oligoaniline microspheres obtained by an aniline−persulfate approach. *The Journal of Physical Chemistry B*. 2011, **115(6)**, 1368-1375.

3. E. Rebourt, J.A. Joule, A.P. Monkman, Polyaniline oligomers; synthesis and characterisation. *Synthetic Metals*, 1997, **84(1-3)**, 65-66.

4. T. Hagiwara, M. Yamaura, K. Iwata. Structural analysis of deprotonated polyaniline by solid-state ^{13}C NMR, *Synthetic metals*, 1988, **26(2)**, 195-201.

5. T. Hjertberg, W.R. Salaneck, I. Lundstrom, N.L.D. Somasiri, A.G. MacDiarmid, A ^{13}C CP-MAS NMR investigation of polyaniline. *Journal of Polymer Science: Polymer Letters Edition*, 1985, **23(10)**: 503-508.