Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Base-catalyzed aerobic oxidation of hydroquinones to benzoquinones under metal-free conditions

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1. Materials

All chemicals were commercially available and directly used without any further purification unless indicated. 2-Aminopyridine and 4-aminopyridine were purchased from J&K Scientific (China). Diamylamine, 2,3-dimethylhydroquinone, amylamine, methoxyhydroquinone, n-octylamine, triamylamine, 2,6-dimethylhydroquinone and hexylamine were purchased from Tokyo Chemical Industry Co., Ltd. Deuterated acetonitrile was purchased from Cambridge Isotope Laboratories, Inc. Other chemicals and also solvents were purchased from Energy Chemical (China).

2. HPLC method

The detection of H_2O_2 by high performance liquid chromatography (HPLC), the HPLC system used was a Thermo ULTIMATE 3000 equipped with a DAD-3000 diode array detector. The separation was conducted using Kromasil 100-5-C18 (4.6 x 250 mm) column. The mobile phase consisted of water (A) and acetonitrile (B) in a gradient elution programmed as follows: 0–3 min, maintain at 20% B; 3–18 min, linear gradient from 20% to 90% B; 18–21 min, linear gradient from 90% to 10% B. The solvent flow rate was 0.5 ml·min^{-1} and the temperature of the column oven was 30 ^{o}C. The analysis was carried out within the wavelength interval of 190-400 nm and the optimal wavelength value for the detection of H_2O_2 is 210 nm. Identification of various substances was carried out according to the retention time compared to the reference sample.

3. Solvent and base recovery

For the recycling studies, the following procedure was adopted. As the amount of catalyst needed was small, the amount of substrates was magnified to 4 times, and the reaction was carried out in a 100 ml round-bottom glass. After reaction, the solution was evaporated under reduced pressure to recycle *n*-butylamine and 1,4-dioxane at 40-60 ^{o}C. Next, the recovered *n*-butylamine and 1,4-dioxane were reused in the next reaction run.

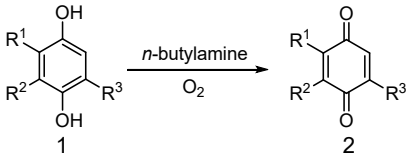
4. Reaction data

Table S1. Effect of *n*-butylamine dosage

Entry	*n*-butylamine (mol%)	Conv. (%)	Sel. (%)
1	2.5	37	99.8
2	4.5	53.4	99.8
3	9	60.2	98.1
4	13.5	68.9	97.2
5	18	77.6	95.9
6[b]	4.5	<1	N.D.

[a] Reaction conditions: THQ (3 mmol), 1,4-dioxane (4.0 g), O_2 balloon (1atm), **70** °C, **1** h. [b] The reaction was done in nitrogen atmosphere. N.D.: No product was detected.

Table S2. Base catalyzed aerobic oxidation of various hydroquinones.[a]



1 2

Entry	R_1	R_2	R_3	Benzoquinone	Yield [b] (%)
1	Me	Me	Me	2a	83.5
2	Me	Me	H	2b	23.9
3	Me	H	Me	2c	51.5
4	Me	H	H	2d	9.0
5	OMe	H	H	2e	6.2
6	Bu^t	H	H	2f	8.3
7	H	H	H	2g	5.3
8	Cl	H	H	2h	4.1

[a] Reaction conditions: substrates (3 mmol), n-butylamine (4.5 mol%), acetonitrile (4.0 g), O_2 balloon (1atm), 70 °C.

[b] Determined by GC analysis.

Table S3. Comparison of the fresh and recovered base.

Entry	THQ Conv. (%)	TBQ Sel. (%)
1[a]	99.6	97.2
2[b]	99.4	97.4
3[c]	99.9	96.8

[a] Reaction conditions: THQ (12 mmol), butylamine (4.5 mol%), dioxane (16.0 g), O_2 balloon (1atm), 70 °C, 6 h.

[b] Reaction conditions: THQ (12 mmol), recovered butylamine and dioxane, fresh dioxane (5.2 g), 70 °C, 6 h.

[c] Reaction conditions: THQ (3 mmol), butylamine (4.5 mol%), dioxane (4.0 g), O_2 balloon (1atm), 70 °C, 6 h.

5. HPLC results

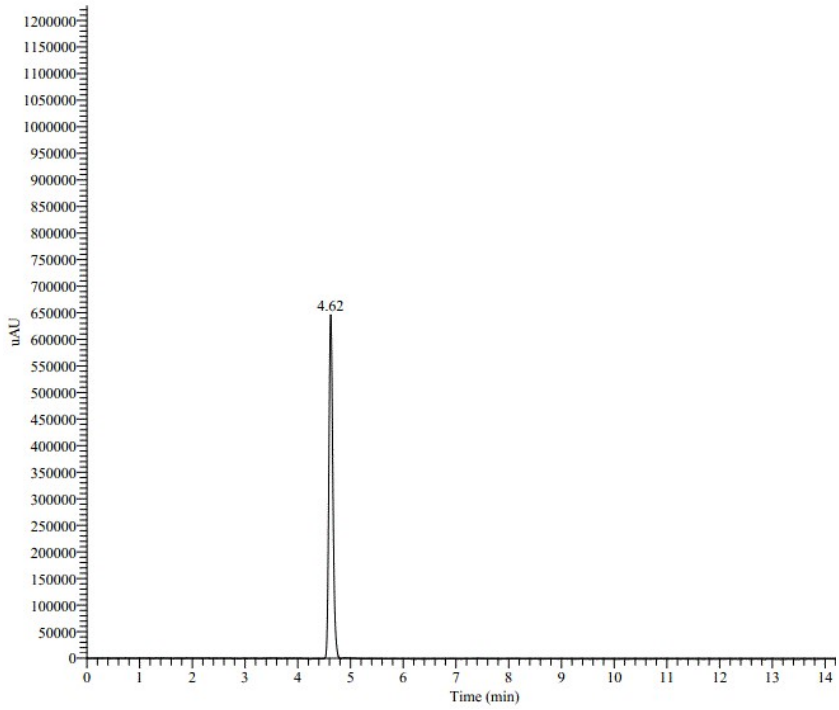


Figure S1. HPLC spectra of hydrogen peroxide.

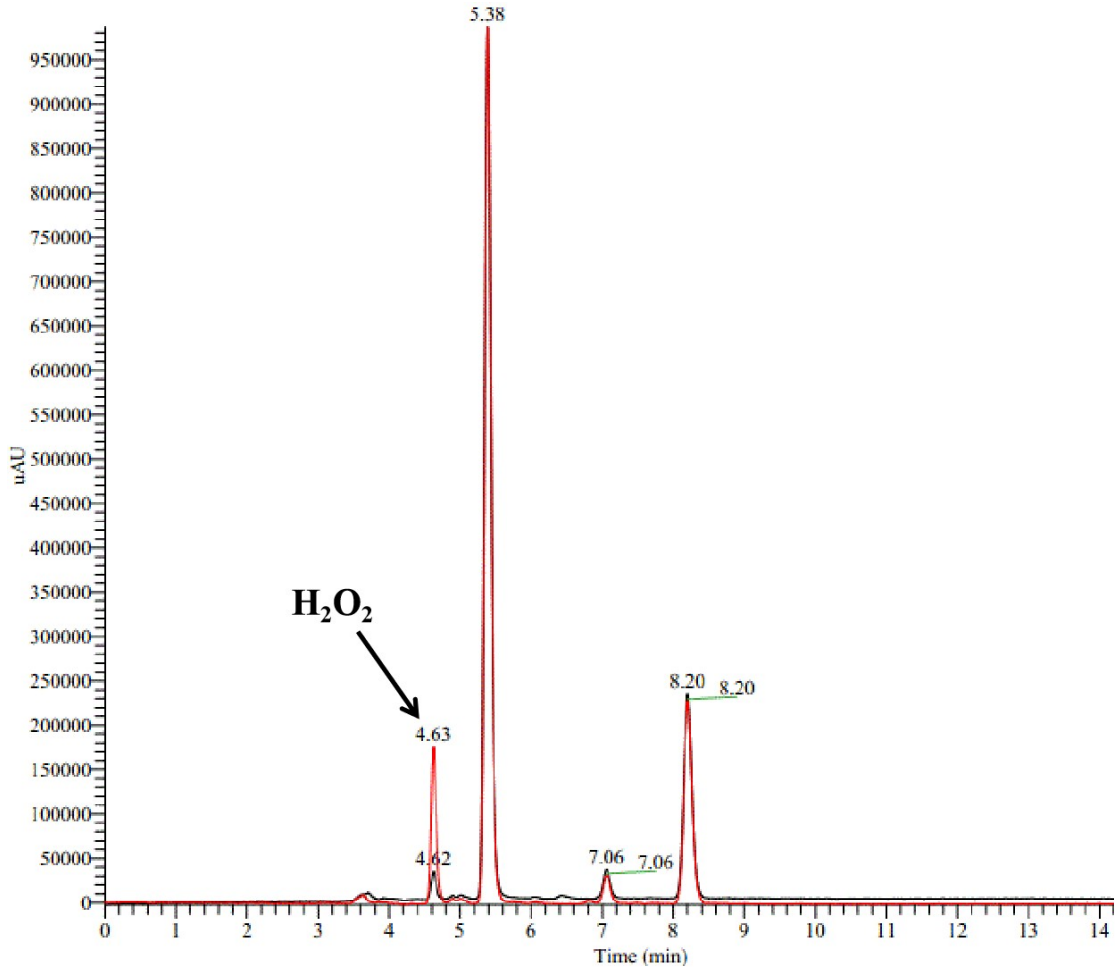


Figure S2. HPLC spectra of reaction solution (black) and add hydrogen peroxide to the mixture after the reaction (red). Reaction conditions: THQ (3 mmol), *n*-butylamine (4.5 mol%), acetonitrile (4.0 g), O_2 balloon (1atm), 60 °C, 1 h.

6. HPLC-MS results

An Ultimate 3000 UPLC system (Thermo Scientific, USA) equipped with an on-line degasser, a quaternary pump, anautosampler and a column temperature compartment, coupled with a Thermo Q-Exactive mass spectrometer with a heated electrosprayionization source, was used for the HPLC–MS analysis. The by-product structure was shown in Figure S3.

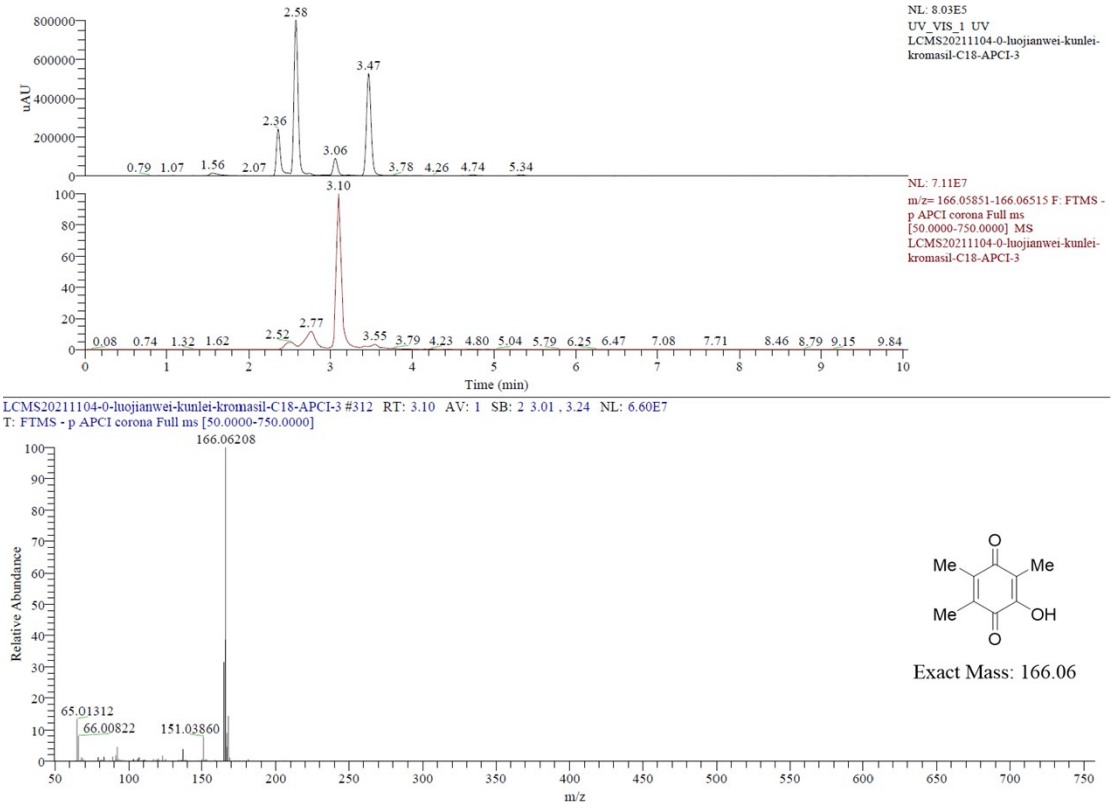


Figure S3. HPLC-MS spectra of by-product.

7. NMR Spectroscopic Data

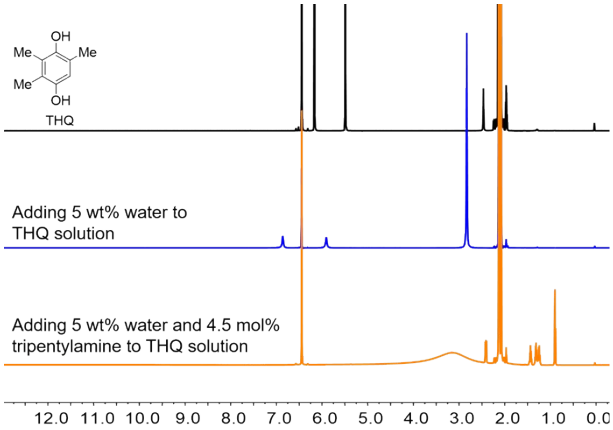


Figure S4. ^{1}H NMR spectra of THQ (black line), added 5 wt% water (blue line), and mixed with tripentylamine.

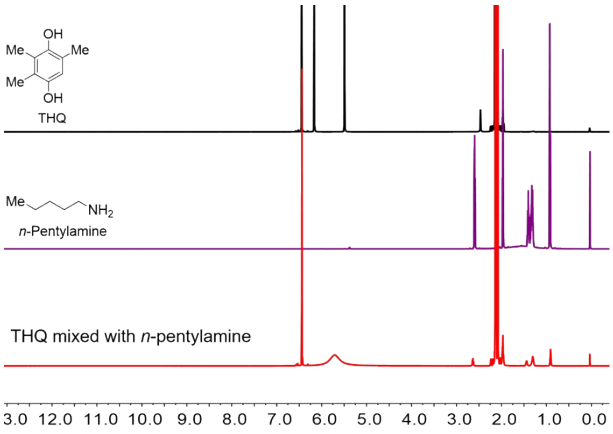


Figure S5. ^{1}H NMR spectra of THQ (black), mixed with *n*-pentylamine (purple) under N_2 atmosphere.

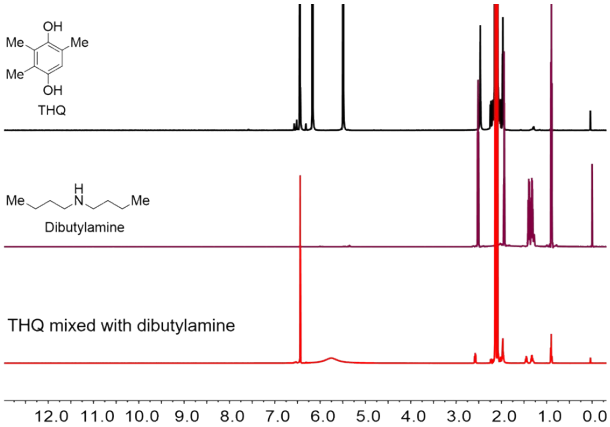


Figure S6. ^{1}H NMR spectra of THQ (black line), mixed with dibutylamine (dark purple line) under N_2 atmosphere.

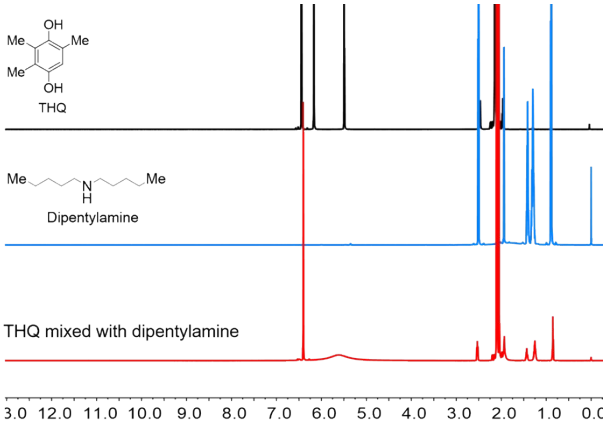


Figure S7. ^{1}H NMR spectra of THQ (black), mixed with dipentylamine (gray blue) under N_2 atmosphere.

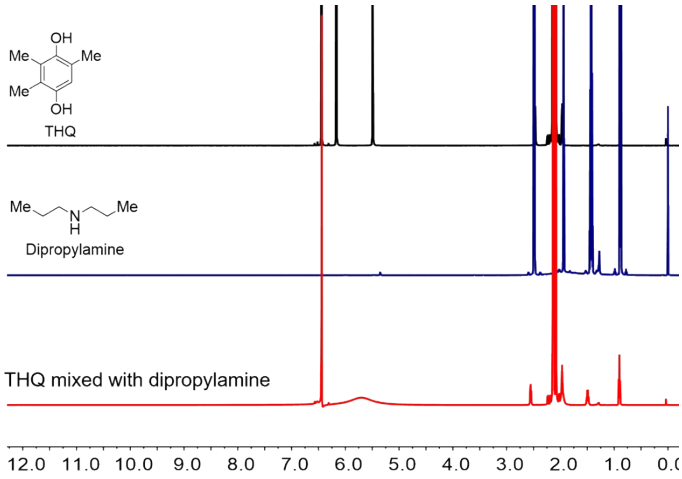


Figure S8. ^{1}H NMR spectra of THQ (black), mixed with dipropylamine (dark blue) under N_2 atmosphere.

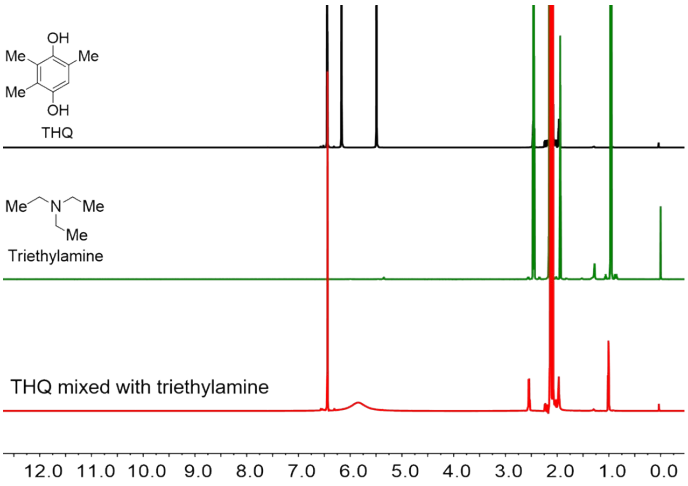


Figure S9. ^{1}H NMR spectra of THQ (black), mixed with triethylamine (green) under N_2 atmosphere.

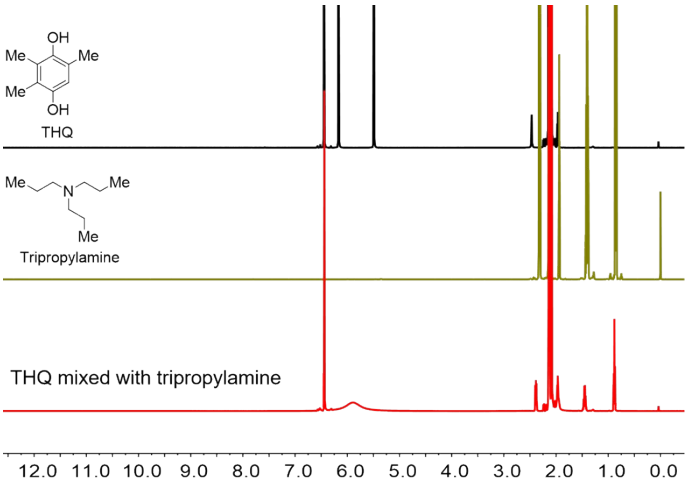


Figure S10. ^{1}H NMR spectra of THQ (black), mixed with tripropylamine (olive) under N_2 atmosphere.

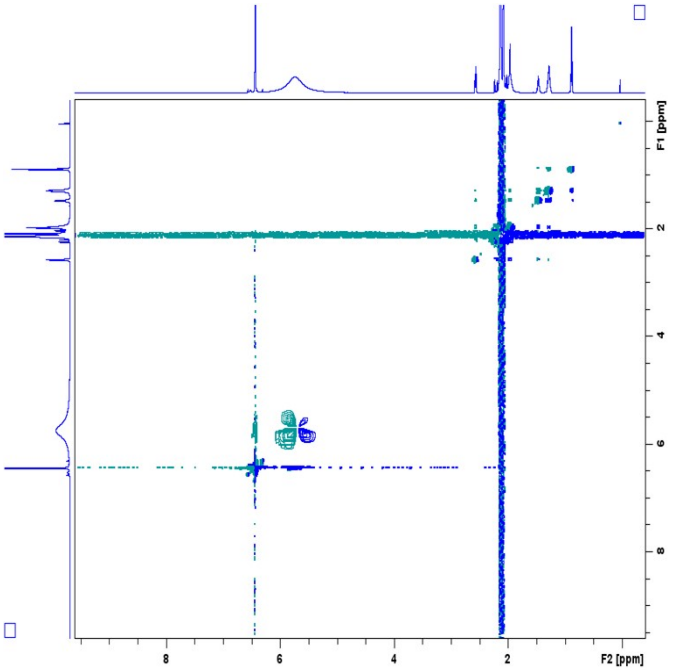


Figure S11. 2D-NOESY ^{1}H NMR (600 MHz) spectrum of dipentylamine and THQ mixture at 20 ^{o}C.

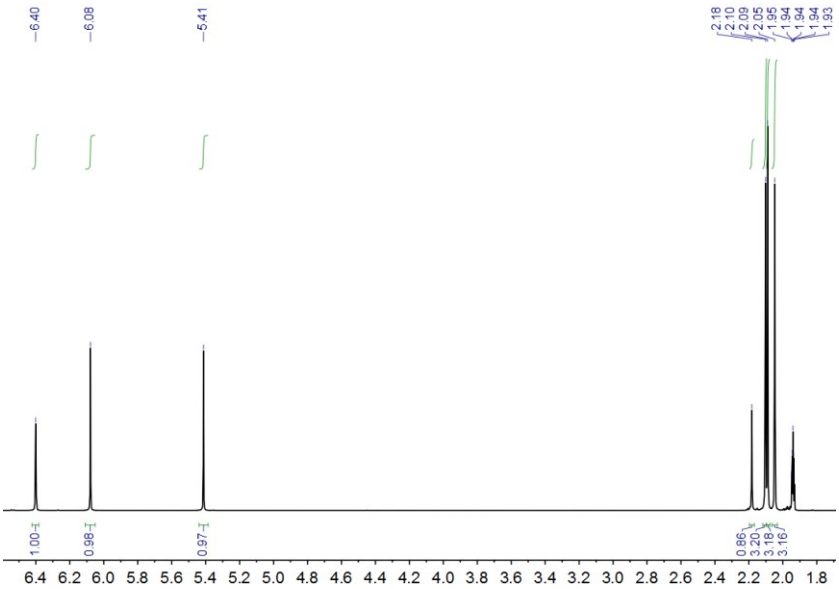


Figure S12. ^{1}H NMR spectra of 2,3,5-trimethylhydroquinone.

^{1}H NMR, CD_3CN, 600M, 6.40 (1H, s, H-6), 6.07 (1H, s, -OH), 5.41 (1H, s, -OH), 2.10 (3H, s, 5-CH_3), 2.09 (3H, s, 2-CH_3), 2.04 (3H, s, 3-CH_3)

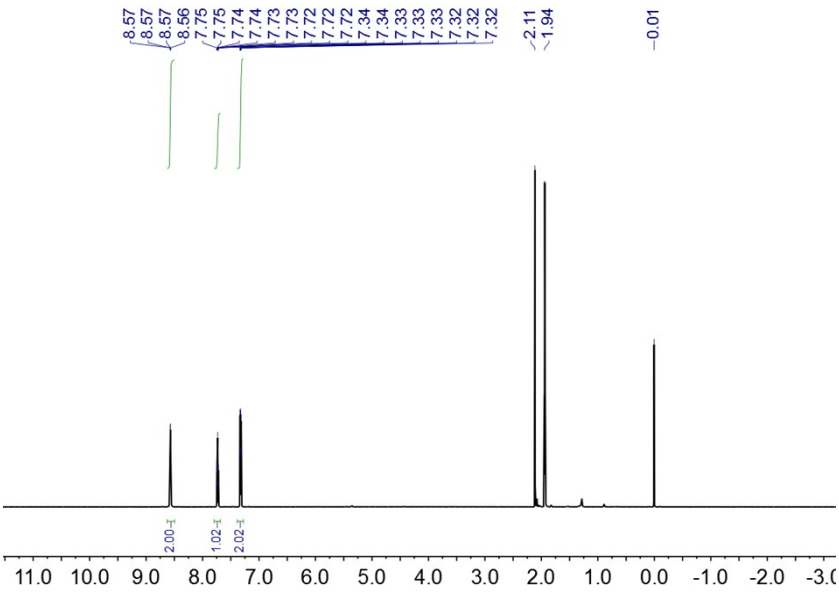


Figure S13. ^{1}H NMR spectra of pyridine.

^{1}H NMR, CD_3CN, 600M, ppm: 8.57 (2H, dd, *J*=4.1, 1.8 Hz, C<u>H</u>-N-C<u>H</u>), 7.75-7.72 (H, tt, *J* = 7.7, 1.8 Hz, CH-C<u>H</u>-CH), 7.75-7.32 (2H, ddd, *J* = 7.7, 4.2, 1.5 Hz, C<u>H</u>-CH-C<u>H</u>).

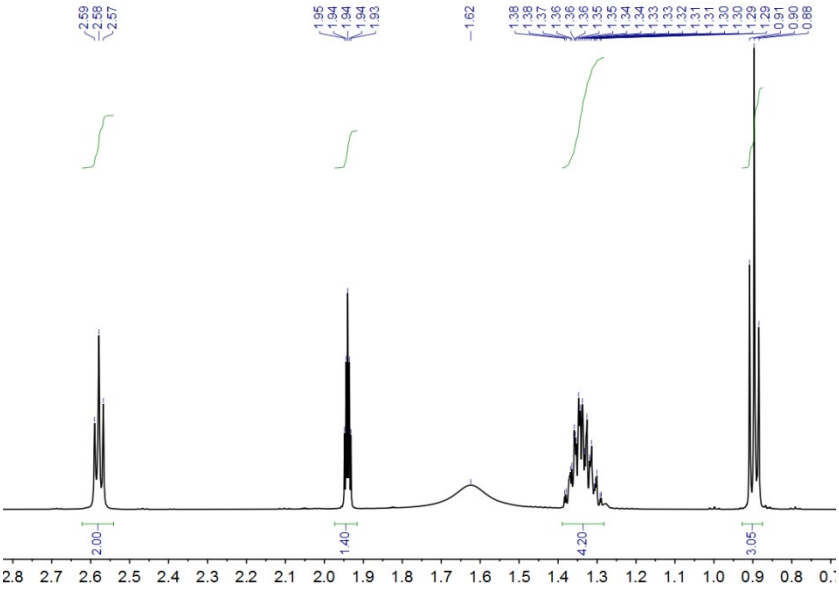


Figure S14. ^{1}H NMR spectra of *n*-butylamine.

^{1}H NMR, CD_3CN, 600M, ppm: 2.57 (2H, t, J= 6.6 Hz, $CH_3CH_2CH_2C\underline{H}_2NH_2$), 1.62 (2H, s, $-NH_2$), 1.38-1.28 (4H, m, $CH_3C\underline{H}_2C\underline{H}_2CH_2NH_2$), 0.89 (3H, t, J= 7.2 Hz, $C\underline{H}_3CH_2CH_2CH_2NH_2$).

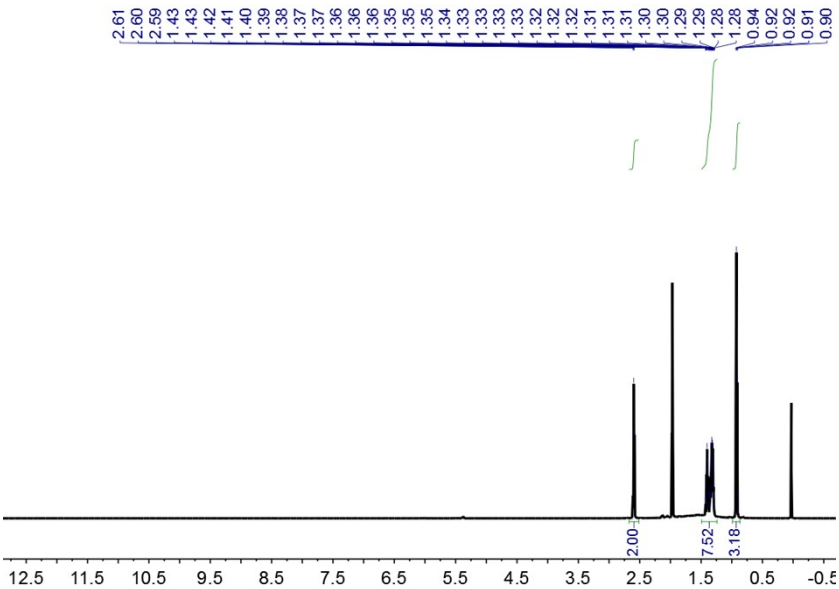


Figure S15. ^{1}H NMR spectra of *n*-pentylamine.

^{1}H-NMR, CD_3CN, 600M, ppm: 0.90 (3H, t, J=7.05 Hz, $C\underline{H}_3CH_2CH_2CH_2CH_2NH_2$), 1.28-1.43 (8H, m, $CH_3C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2NH_2$), 2.59 (1H, t, J=6.96 Hz, $CH_3CH_2CH_2CH_2C\underline{H}_2NH_2$).

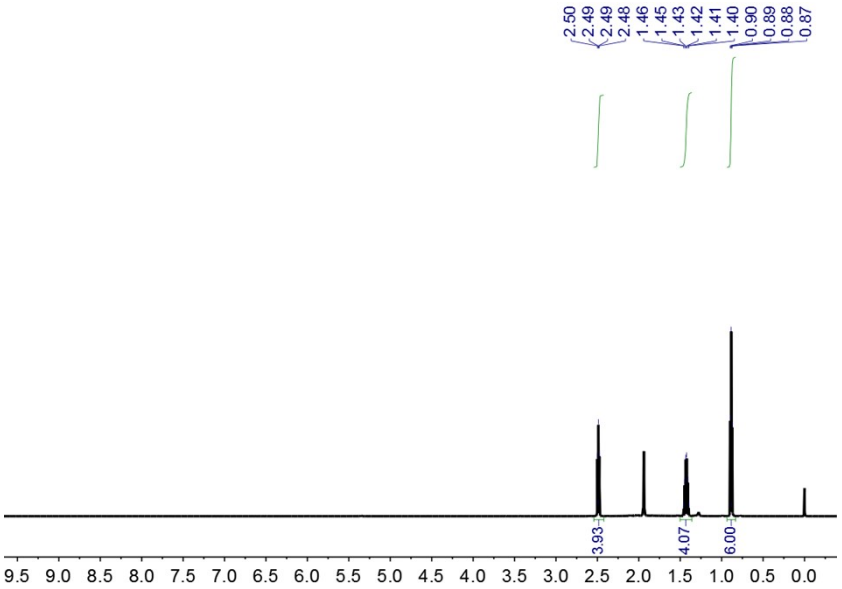


Figure S16. ^{1}H NMR spectra of dipropylamine.

^{1}H-NMR, CD_3CN, 600M, ppm: 0.87 (6H, t, J=7.41 Hz, ($C\underline{H}_3CH_2CH_2)_2NH$), 1.40-1.46 (4H, m, ($CH_3C\underline{H}_2CH_2)_2NH$), 2.49 (4H, t, J=7.2 Hz, ($CH_3CH_2C\underline{H}_2)_2NH$).

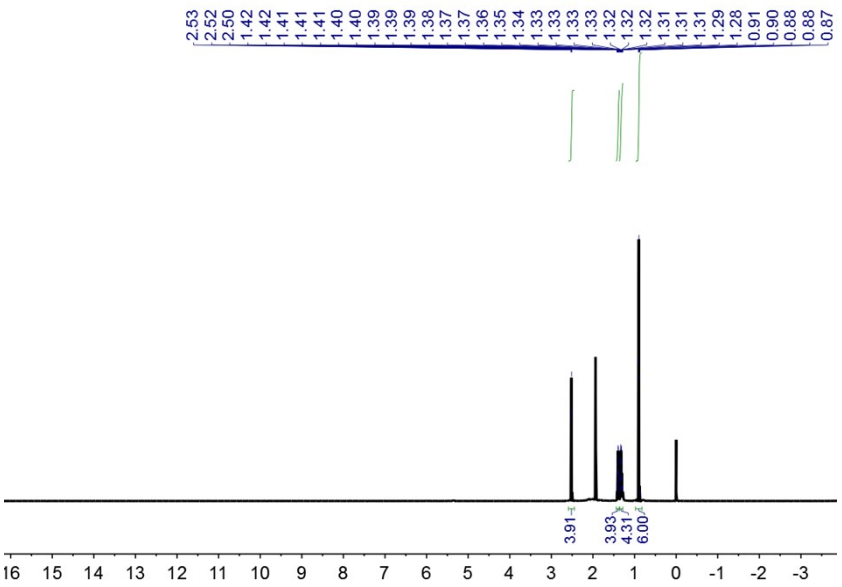


Figure S17. ^{1}H NMR spectra of dibutylamine.

^{1}H-NMR, CD_3CN, 600M, ppm: 0.87 (6H, t, J=7.29 Hz, ($C\underline{H}_3CH_2CH_2CH_2)_2NH$), 1.28-1.35 (4H, m, ($CH_3C\underline{H}_2CH_2CH_2$)2NH), 1.37-1.42 (4H, m, ($CH_3CH_2C\underline{H}_2CH_2)_2NH$), 2.52 (4H, t, J=7.2 Hz, ($CH_3CH_2CH_2C\underline{H}_2)_2NH$).

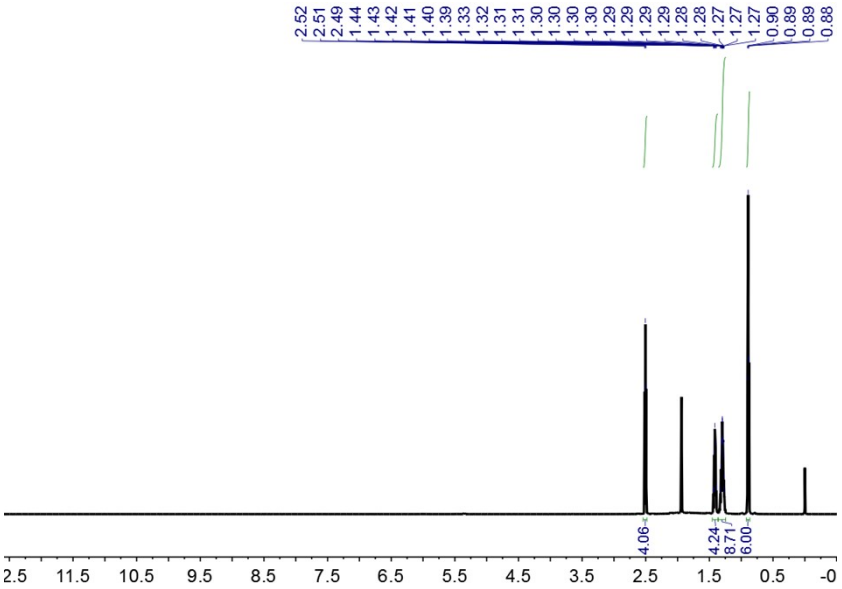


Figure S18. ^{1}H NMR spectra of dipentylamine.

^{1}H-NMR, CD_3CN, 600M, ppm: 0.88 (1H, t, J=7.05 Hz, $(C\underline{H}_3CH_2CH_2CH_2CH_2)_2NH$), 1.27-1.33 (8H, m, $(CH_3C\underline{H}_2C\underline{H}_2CH_2CH_2)_2NH$), 1.39-1.44 (4H, m, $(CH_3CH_2CH_2C\underline{H}_2CH_2)_2NH$), 2.49 (4H, t, J=7.2 Hz, $(CH_3CH_2CH_2CH_2C\underline{H}_2)_2NH$).

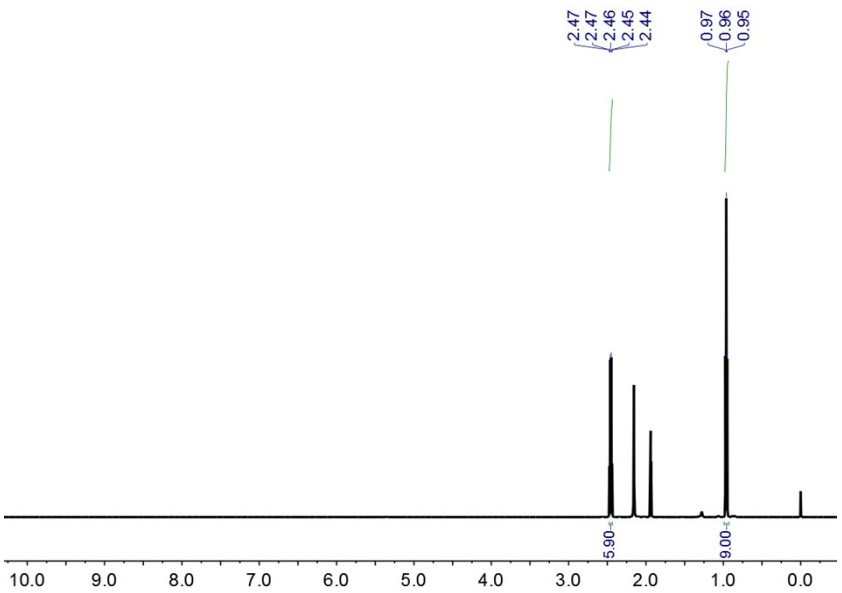


Figure S19. ^{1}H NMR spectra of triethylamine.

^{1}H-NMR, CD_3CN, 600M, ppm: 0.95 (9H, t, J=7.14 Hz, $(C\underline{H}_3CH_2)_3N$), 2.44 (6H, q, J=7.14 Hz, $(CH_3C\underline{H}_2)_3N$).

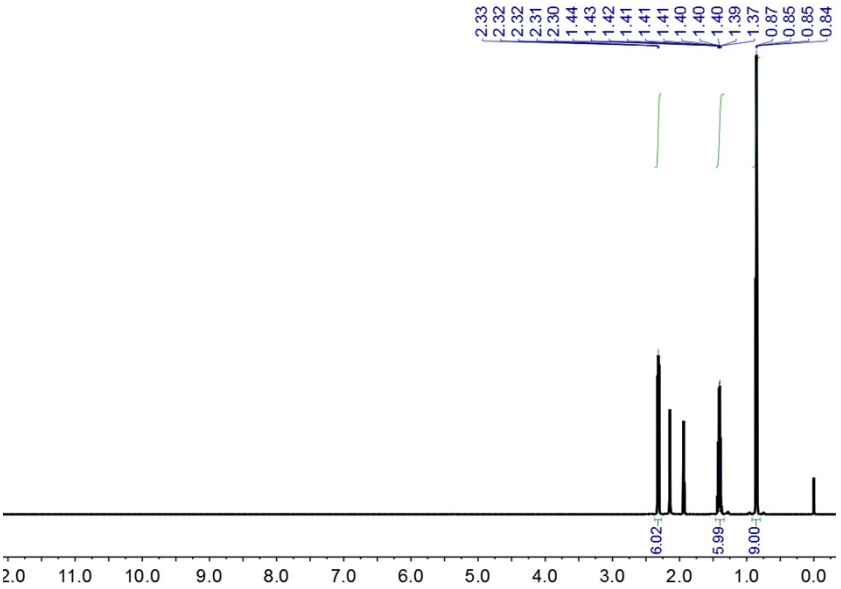


Figure S20. ^{1}H NMR spectra of tripropylamine.

^{1}H-NMR, CD_3CN, 600M, ppm: 0.84 (1H, t, J=7.38 Hz, $(C\underline{H}_3CH_2CH_2)_3N$), 1.37-1.44 (6H, m, $(CH_3C\underline{H}_2CH_2)_3N$), 2.31 (6H, t, J=7.38 Hz, $(CH_3CH_2C\underline{H}_2)_3N$).

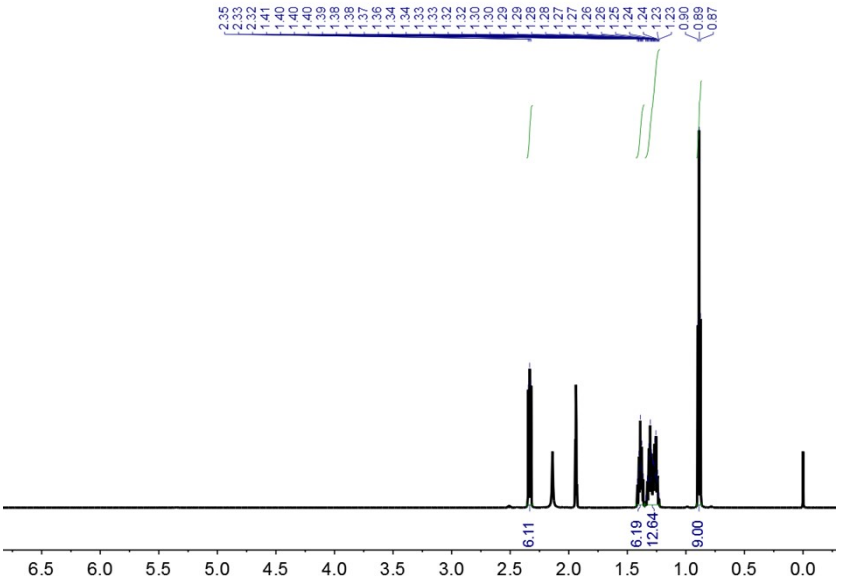


Figure S21. ^{1}H NMR spectra of tripentylamine.

^{1}H-NMR, CD_3CN, 600M, ppm: 0.89 (9H, t, J=7.20 Hz,$(C\underline{H}_3CH_2CH_2CH_2CH_2)_3N$), 1.23-1.34 (12H, m, $(CH_3C\underline{H}_2C\underline{H}_2CH_2CH_2)_3N$), 1.39 (6H, m, $(CH_3CH_2CH_2C\underline{H}_2CH_2)_3N$), 2.32 (6H, t, J=7.2 Hz, $(CH_3CH_2CH_2CH_2C\underline{H}_2)_3N$)

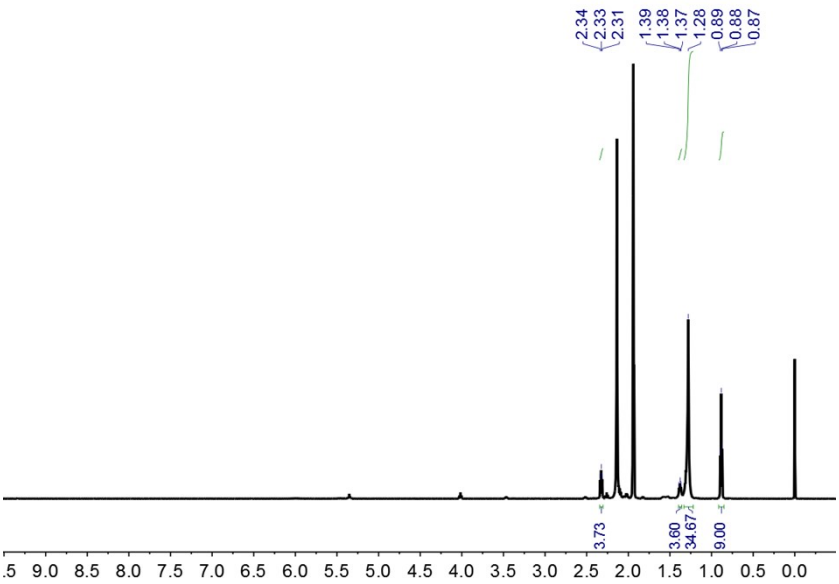


Figure S22. ^{1}H NMR spectra of trioctylamine.

^{1}H-NMR, CD_3CN, 600M, ppm: 0.87 (9H, t, J=6.99 Hz, ($C\underline{H}_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2)_3N$), 1.28 (34H, m, ($CH_3C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2CH_2)_3N$), 1.37 (4H, m, ($CH_3CH_2CH_2CH_2CH_2CH_2C\underline{H}_2CH_2)_3N$), 2.31 (4H, t, J=7.2 Hz, ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2C\underline{H}_2)_3N$).

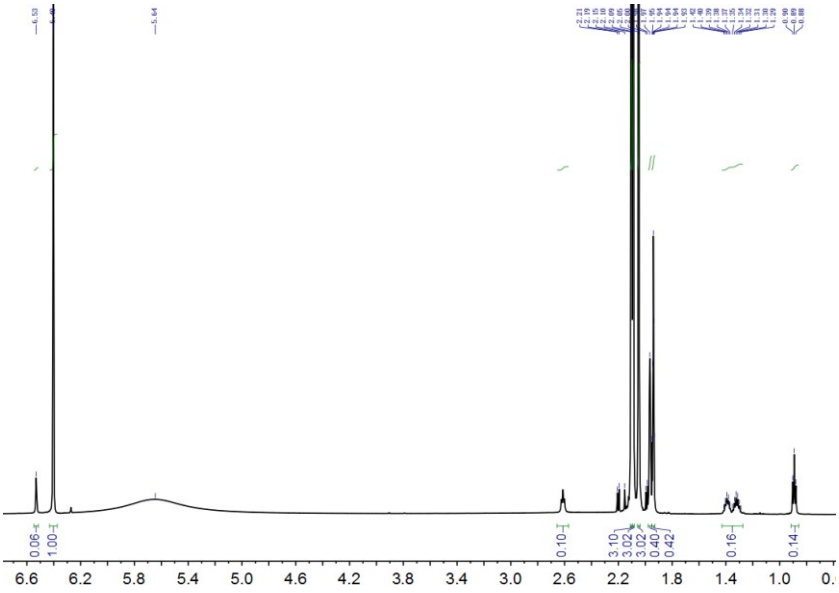


Figure S23. ^{1}H NMR spectra of 2,3,5-trimethylhydroquinone mixed with n-butylamine under nitrogen atmosphere (600 MHz, CD_3CN).

9. GC-MS results

1.

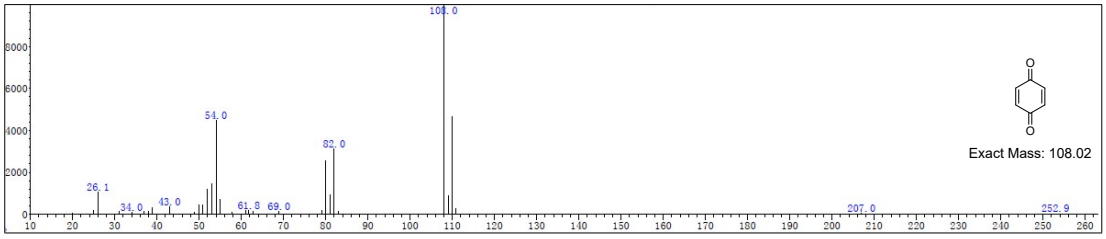


Figure S24. Mass spectrum of benzoquinone.

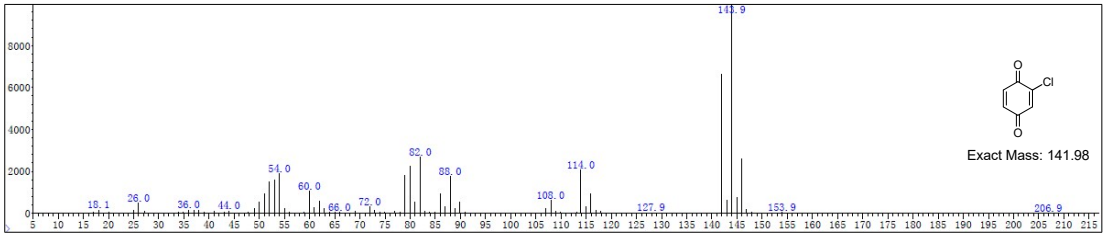


Figure S25. Mass spectrum of 2-chloro-1,4-benzoquinone.

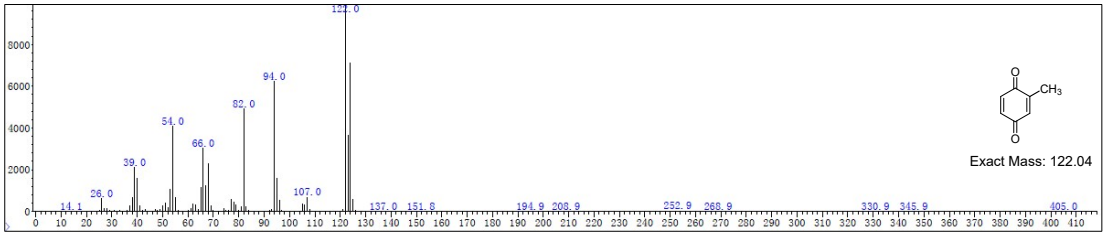


Figure S26. Mass spectrum of p-toluquinone.

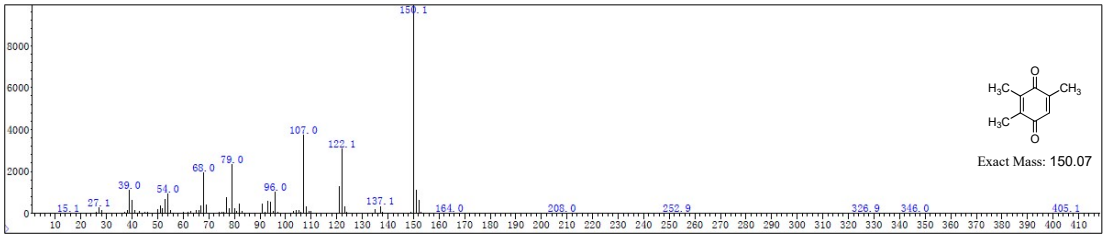


Figure S27. Mass spectrum of 2,3,5-trimethylbenzoquinone.

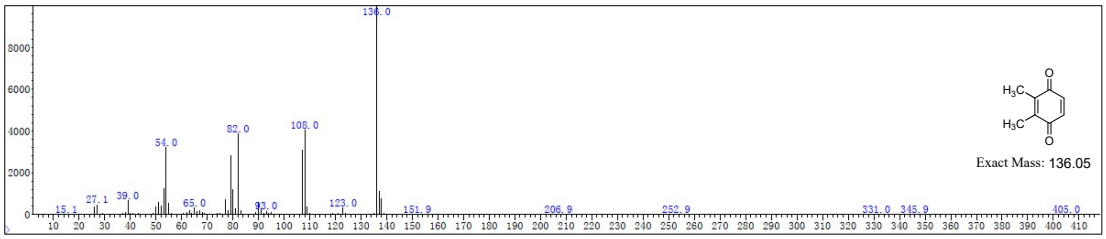


Figure S28. Mass spectrum of 2,3-dimethyl-p-benzoquinone.

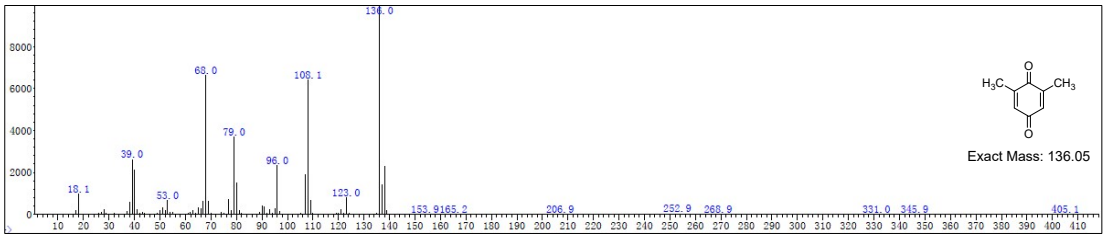


Figure S29. Mass spectrum of 2,6-dimethyl-p-benzoquinone.

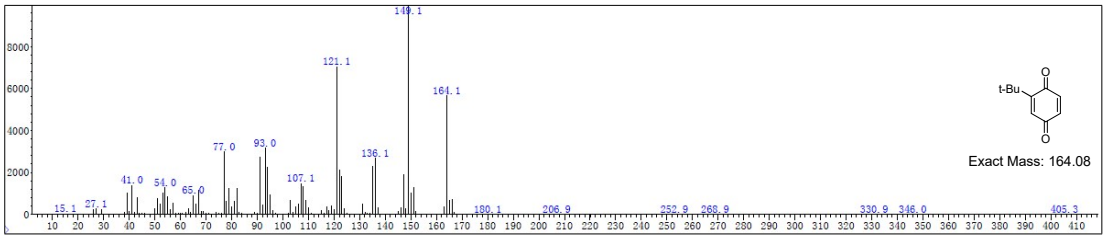


Figure S30. Mass spectrum of 2-tert-butyl-1,4-benzoquinone.