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Experimental Procedures

Materials and Instruments

All reagents were purchased from commercial sources without further treatment unless noted. GC-MS experiments were carried out on a Shimadzu GC/MS-QP2010 system (Shimadzu, Germany). Gas chromatography with flame ionization detector (GC-FID) was obtained on GC-2010 (Shimadzu, Japan). 1H NMR at 600 MHz and ^{13}C NMR at 150 MHz spectra were collected on Agilent DD2-600. The high-resolution mass spectrometry (HRMS) spectra were obtained on Agilent 6545 Q-TOF.

General Procedure for Oxidation

To a 25 mL Schlenk tube equipped the magnetic bar, 1,4-Benzoquinone (0.1622 mg, 1.5 mmol) was added and dissolved by 1.4 g CH_3CN and 0.6 g H_2O, followed by adding A (0.5 mmol) and TfOH (20 mmol%). The solution was charged with 1 atm N_2 after vacuation and was linked to an N_2, and then the solution was stirred at 70 °C. After reaction, the conversion and yield were determined via gas chromatography or column chromatography isolation.

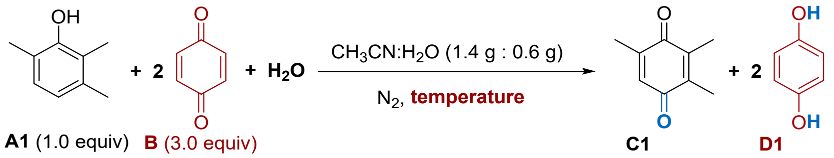
^{18}O-Labelling Experiments

1,4-Benzoquinone (4 mmol) was added in 5 g $H_2{}^{18}O$ and 0.1 g CH_3CN at 25 mL Schlenk tube equipped the magnetic bar. After vacuation, then the solution was stirred at room temperature (25 °C). The products were detected by GC-MS (Figure S3). After the exchange is completed, the solution was extracted with ethyl acetate. The organic phase was washed with ethyl acetate and dried with anhydrous Na_2SO_4. The solvent in the filtrate was removed under reduced pressure, and the resulted product was dried in vacuum.

Verification Experiments of Hydroxy Cation Transfer Mechanism

To a 25 mL Schlenk tube equipped the magnetic bar, 1,4-Benzoquinone (0.1622 mg, 1.5 mmol) was added and dissolved by 1.4 g acetonitrile and 0.6 g ROH (MeOH or ^{i}PrOH), followed by adding A (0.5 mmol) and TfOH (0.1 mmol). The solution was charged with 1 atm N_2 after vacuation and was linked to an N_2, and then the solution was stirred at 70 °C. The yield of **D-OR** was determined and analyzed using gas chromatography calibrated with standard commercial samples.

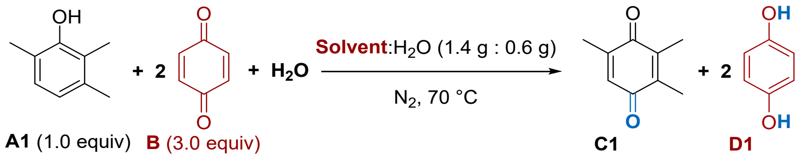
Table S1. Effect of Temperature on the Reaction.



Entry	Temperature (°C)	Conv. (%)		Yield (%)	
		A1	**B**	**C1**	**D1**
1	30	54	18	18	65
2	50	63	32	32	12
3	70	77	44	44	54
4	80	84	49	49	23

[a] Conditions: **A1** (0.5 mmol), **B** (1.5 mmol), CH_3CN/H_2O (1.4 g : 0.6 g); The conversion and yield were determined after 24 hours by GC using methyl benzoate as the internal standard. No acid catalyst was added. **C1** selectivity is calculated based on the loading amount of **A1**, while **D1** selectivity is calculated based on the loading amount of **B**.

Table S2. Effect of Solvent Conditions on the Reaction.

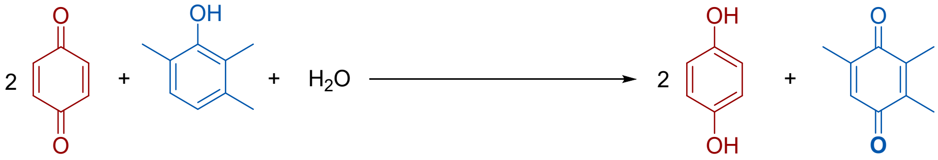


Entry	Solvent	Conv. (%)		Yield (%)	
		A1	**B**	**C1**	**D1**
1	Acetonitrile	77	44	46	54
2	Acetone	92	63	49	26
3	Toluene	46	65	16	6
4	1-Butanol	99	89	63	25
5	*tert*-Butanol	100	85	57	24
6	DMSO	100	98	26	37
7	MeOH	100	96	68	42

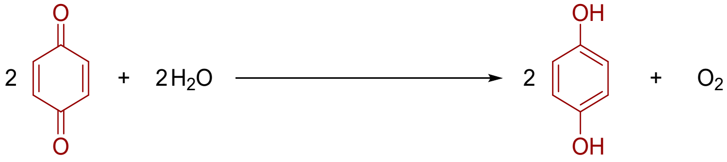
[a] Conditions: **A1** (0.5 mmol), **B** (1.5 mmol); The conversion and yield were determined after 24 hours by GC using methyl benzoate as the internal standard. No acid catalyst was added. **C1** selectivity is calculated based on the loading amount of **A1**, while **D1** selectivity is calculated based on the loading amount of **B**.

Table S3. Thermodynamic Data Sources and Calculation Procedures

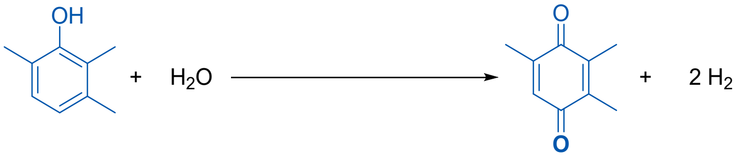
Entry	Substance	CAS	$\Delta_r G^0$ (kJ/mol)	Notes
1	2,3,6-Trimethylphenol	2416-94-6	-42.25	Database
2	2,3,5-Trimethylquinone	935-92-2	-157.09	Estimated based on Aspen Joback
3	Hydroquinone	123-31-9	-185.8	Database
4	1,4-Benzoquinone	106-51-4	-69.2	Database
5	H_2	1333-74-0	0	Database
6	H_2O	7732-18-5	-228.572	Database
7	O_2	7782-44-7	0	Database



$$\Delta_r G^0 = [2 \times (-185.8) + (-157.09)] - [2 \times (-69.2) + (-42.25) + (-228.572)] =- 119.5 kJ/mol$$

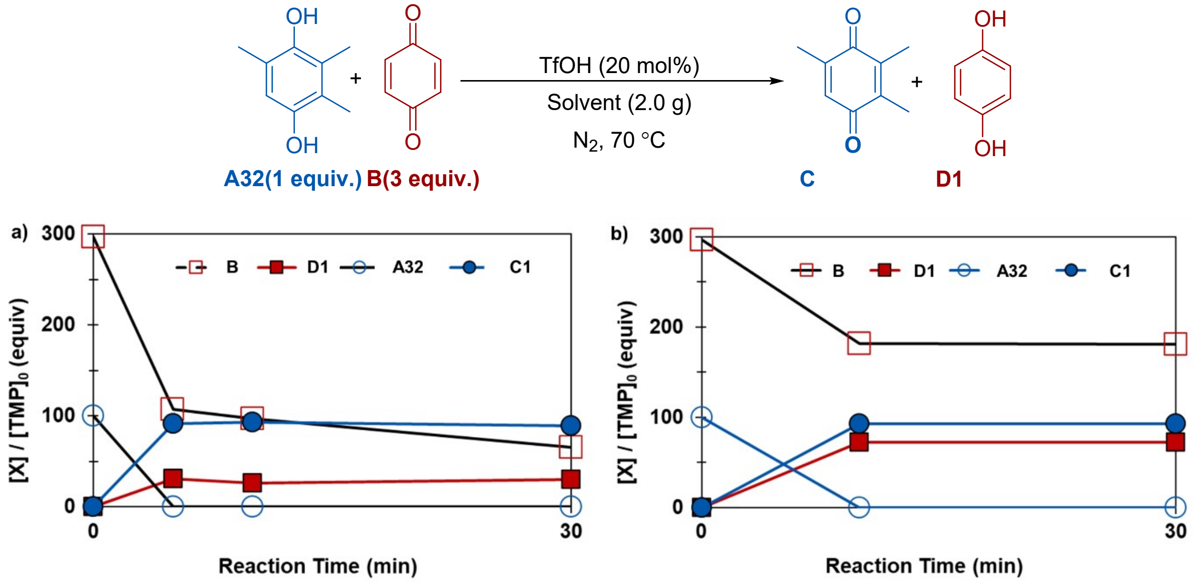


$$\Delta_r G^0 = [2 \times (-185.8) + 0] - [2 \times (-69.2) + 2 \times (-228.572)] = 223.9 kJ/mol$$



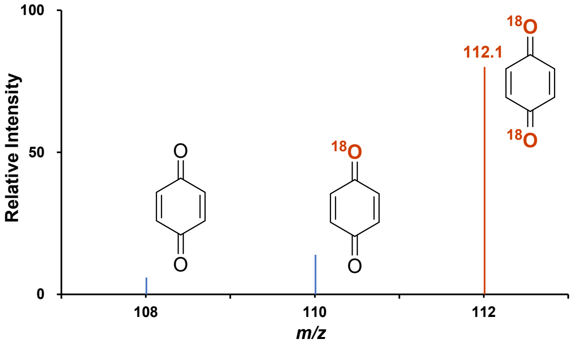
$$\Delta_r G^0 = [(-157.09) + 2 \times 0] - [(-42.25) + (-228.272)] = 113.7 kJ/mol$$

Figure S1. The process of verifying the conversion of trimethylhydroquinone to trimethylbenzoquinone



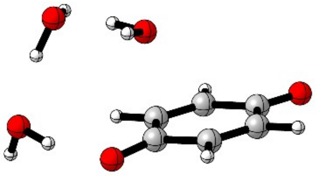
[a] Conditions: **A32** (0.5 mmol), **B** (1.5 mmol), solvent (2 g); The conversion and yield were determined by GC using methyl benzoate as the internal standard. **C1** selectivity is calculated based on the loading amount of **A1**, while **D1** selectivity is calculated based on the loading amount of **B**. Solvent a): CH_3CN/H_2O (1.4 g : 0.6 g); Solvent b): CH_3CN/H_2O (2.0 g : 0.0 g).

Figure S2. The GC-MS spectrum for the ^{18}O-labeled **B**



Computational Details

All the DFT calculations were performed in Gaussian 09 D.01.9[1] The geometries were fully optimized using the dispersion-corrected density functional method B3LYP[2, 3] with the 6-31G(d)[4-7] basis set. The frequency analyses were performed at the same level to confirm that the structure was either a minimum or a transition state and thermal corrections at 343.15 K. A correction of 1.9 kcal/mol is added to the free energies of all structures except dioxygen to correct the Gibbs free energies with standard state in gas (1 atm) to that in solution (1 mol/L). All energies are given in Hartree. Computed structures are illustrated using CYLView[8]. The intrinsic bond orbitals are illustrated using IboView (http://www.iboview.org/index.html) under PBE0 method and def2-TZVP basis set.



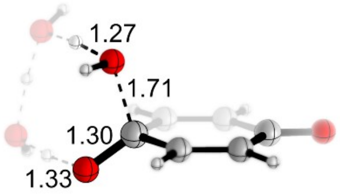
B-$(H_2O)_3$

G = -610.649806

0 imaginary frequencies

O	0.8171030	0.6711880	1.8414230
O	3.2607340	-0.3862260	-1.2432090
H	2.5510830	0.2905470	-1.3471970
O	2.8417270	-1.1408860	1.3542950
H	3.1042190	-0.9655910	0.4196920
C	-1.0822150	1.5773030	-0.3038560
C	-2.2251720	0.9988520	0.0927550
C	-2.3520540	-0.4763020	0.1835760
C	-1.1630830	-1.2851440	-0.1835300
C	-0.0192690	-0.7070800	-0.5766670
C	0.0919160	0.7662690	-0.6941120
H	-0.9624620	2.6534220	-0.3838460
H	-3.1069910	1.5690340	0.3686600

H	-1.2805350	-2.3619000	-0.1047300
H	0.8701000	-1.2719370	-0.8344330
O	-3.3963900	-1.0071640	0.5420860
H	1.5309110	-0.0061840	1.7525800
O	1.0809300	1.3027950	-1.2016240
H	2.5289750	-2.0568070	1.3621760
H	3.2903950	-0.8676110	-2.0819790
H	1.3059730	1.5020700	1.9400000



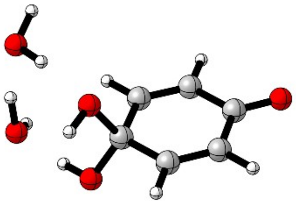
TS-2

G = -610.611825

1 imaginary frequencies: -1239.53

O	0.9046320	0.6177660	1.3817110
O	3.1233500	-0.3024670	-1.1413300
H	2.2069530	0.3464420	-1.1914900
O	2.8829890	-0.7857770	1.2114490
H	3.0894010	-0.6702600	0.0730620
C	-0.9494590	1.4841400	0.0107930
C	-2.1958220	1.0013570	0.0808210
C	-2.4718000	-0.4482000	-0.0275730
C	-1.3044600	-1.3345320	-0.2649680
C	-0.0577870	-0.8553030	-0.3270190
C	0.2554260	0.6133950	-0.1976500
H	-0.7393450	2.5499670	0.0553890
H	-3.0628800	1.6432060	0.2051430

H	-1.5316570	-2.3885560	-0.3977980
H	0.7899270	-1.5063270	-0.5230770
O	-3.6074770	-0.9018910	0.0576780
H	1.9298060	-0.1301840	1.3651520
O	1.1357650	1.1123620	-1.0130140
H	2.6659520	-1.7053370	1.4310990
H	3.0192060	-1.0303230	-1.7728580
H	1.2569490	1.5246270	1.4466160



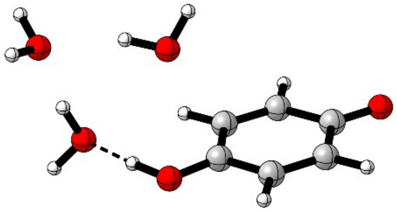
B-water-adduct-$(H_2O)_2$

G = -610.643274

0 imaginary frequencies

O	0.9352030	0.8023520	1.2684440
O	3.1432050	-0.4194110	-1.2870060
H	1.7839500	0.6354420	-1.1954760
O	3.0215740	-1.0130070	1.3518720
H	3.2635000	-0.7598060	-0.3653630
C	-1.0285280	1.5115950	0.0815020
C	-2.2554550	0.9827600	0.0458430
C	-2.4683320	-0.4731470	-0.1165200
C	-1.2510880	-1.3119010	-0.2472140
C	-0.0237960	-0.7881950	-0.1847390
C	0.2323820	0.6890740	-0.0045950
H	-0.8694350	2.5840820	0.1705830
H	-3.1521560	1.5905880	0.1187050

H	-1.4220480	-2.3743590	-0.3945180
H	0.8682890	-1.4011730	-0.2731460
O	-3.5899660	-0.9653930	-0.1491590
H	2.2814330	-0.3745640	1.4805530
O	1.0038470	1.2304650	-1.0233060
H	2.7004800	-1.8494530	1.7191070
H	3.0448360	-1.2019270	-1.8484120
H	1.3145270	1.6995580	1.2686780



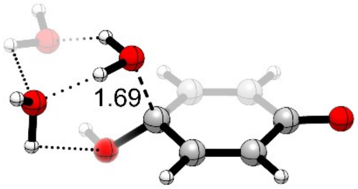
B-$(H_3O)^+$-$(H_2O)_2$

G = -611.003873

0 imaginary frequencies

O	-1.3011030	-0.8478470	1.3519780
O	-2.7455080	1.1085220	-0.7884100
H	-1.6674350	0.2205040	-1.2329210
O	-4.1313620	-0.3414150	1.0757830
H	-3.3395970	0.6457540	-0.1461760
C	1.3028560	-1.1254670	-1.1579360
C	2.5164840	-0.8961840	-0.6229910
C	2.7623100	0.3042650	0.2254150
C	1.6190420	1.2285810	0.4603990
C	0.4036670	0.9817660	-0.0619080
C	0.2184900	-0.1919510	-0.9044530
H	1.0802150	-1.9814570	-1.7860080
H	3.3620570	-1.5579060	-0.7810670

H	1.8230980	2.0966580	1.0789420
H	-0.4519730	1.6256330	0.1035770
O	3.8590670	0.5178310	0.7128030
H	-2.2698620	-0.8887870	1.4469420
O	-0.8839970	-0.4287680	-1.4989760
H	-4.5775070	0.1399270	1.7923060
H	-3.3051850	1.4736570	-1.4926400
H	-0.9535120	-1.0550290	2.2318070
H	-4.7528370	-1.0364500	0.8022590



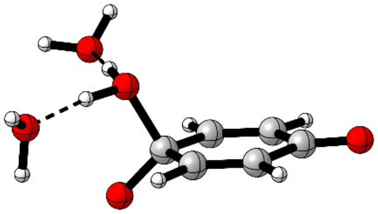
TS-1

G = -610.977829

1 imaginary frequencies: -66.15

O	1.0308050	-0.1089090	-1.0750360
O	2.7685690	1.6897930	-0.2227620
H	1.5783510	0.8331940	1.3729840
O	3.0689060	-1.5283850	-0.3107400
H	3.5964120	1.1777860	-0.2176040
C	-0.6105280	-1.2790580	0.3655640
C	-1.9213410	-1.2791750	0.1031750
C	-2.6639320	-0.0173260	-0.1629230
C	-1.8943330	1.2536010	-0.0539220
C	-0.5816750	1.2587110	0.1998200
C	0.1704840	-0.0146720	0.3752570
H	-0.0583290	-2.1864280	0.5924810
H	-2.5076350	-2.1922630	0.0913710

H	-2.4626490	2.1699340	-0.1774920
H	-0.0159330	2.1826400	0.2974770
O	-3.8491960	-0.0192330	-0.4415730
H	1.7135640	-0.8440290	-0.9207730
O	1.1241970	-0.0329750	1.3391910
H	3.5143670	-2.2826150	-0.7312790
H	3.0171650	2.5928180	-0.4833290
H	1.6078670	0.7104970	-1.0632220
H	2.9383730	-1.7710450	0.6212700



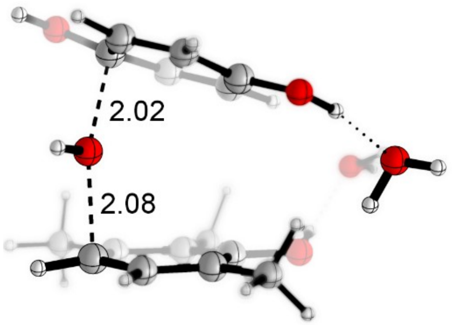
B-water-adduct-$(H_3O)^+$-H_2O

G = -610.981784

0 imaginary frequencies

O	-1.3089790	-0.0523860	0.7979630
O	-2.5599540	2.2154730	0.6113960
H	-1.3405560	0.5402510	-1.9599270
O	-2.9645830	-1.9145550	0.2271210
H	-3.5294390	2.2367000	0.5452180
C	0.4978640	-1.3238750	-0.1661090
C	1.8003100	-1.2438020	0.1178080
C	2.5057790	0.0621060	0.1867490
C	1.7010550	1.2772510	-0.1247240
C	0.3965500	1.2056700	-0.4042530
C	-0.3274220	-0.1034930	-0.4281930
H	-0.0245800	-2.2731300	-0.2427160
H	2.4059700	-2.1260150	0.2979160

H	2.2386080	2.2202490	-0.1188440
H	-0.1965740	2.0896180	-0.6330450
O	3.6862810	0.1430420	0.4749000
H	-1.9678820	-0.8365130	0.6734350
O	-1.1164950	-0.3086730	-1.5400640
H	-3.0994190	-2.7514880	0.7003270
H	-2.3282270	2.8787720	1.2832960
H	-1.8434160	0.8187720	0.7857490
H	-2.8922480	-2.1265160	-0.7182380



TS-3

G = -1036.265417

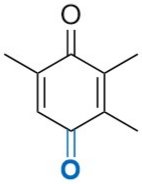
1 imaginary frequencies: -381.57

O	-2.1372450	0.0311420	0.6566460
O	-3.4787770	1.3377770	-1.3314630
H	-2.6791970	0.3306380	1.4171410
H	2.4078740	-1.1340740	-0.9917120
C	-1.4450200	-1.7516490	1.4684490
C	-0.4338260	-1.2162190	2.2973130
C	0.8242420	-0.9640290	1.7977650
C	1.0818780	-1.3508260	0.4515200
C	0.1352930	-2.0149230	-0.3624720
C	-1.1397550	-2.2239680	0.1517620
H	-2.3872320	-2.0575360	1.9110880

H	-0.6697990	-0.9486050	3.3227880
O	2.3323790	-1.0992240	-0.0018290
C	-2.3016070	1.5184590	-0.7061900
C	-1.1423250	1.1145140	-1.4469490
C	-2.1278540	2.4487490	0.3788190
C	0.1082410	1.4301940	-0.9994900
H	-1.2946240	0.5158670	-2.3378230
C	-0.8686160	2.7837170	0.8128760
H	-3.0083160	2.8709480	0.8580530
C	0.2640060	2.2533370	0.1582850
H	0.9845790	1.0965370	-1.5457160
H	-0.7165110	3.4553260	1.6498860
O	1.4508900	2.5982070	0.6419460
H	-4.2138150	1.6838870	-0.7990040
C	0.5207400	-2.4502600	-1.7548530
H	-0.2024610	-3.1549200	-2.1657740
H	0.5830650	-1.5987820	-2.4432410
H	1.4966770	-2.9493670	-1.7625730
C	-2.2375710	-2.8590760	-0.6541200
H	-3.1645090	-2.9111570	-0.0792510
H	-2.4432180	-2.2838780	-1.5639770
H	-1.9749000	-3.8775840	-0.9630510
C	1.9046310	-0.3089870	2.6124260
H	1.5884400	-0.1977740	3.6523700
H	2.8317720	-0.8918740	2.5962930
H	2.1318250	0.6938860	2.2279300
O	3.5916900	1.2853300	-0.3133730
H	3.3624920	0.4489800	-2.0719720
H	2.2113860	2.1851030	0.1512900
O	2.8046020	-0.2580040	-2.4532060
H	3.2669270	-0.5938780	-3.2363020

H	4.4143170	1.6177640	0.0814400
H	3.3806890	0.4326900	0.1276100

Compounds Characterizations

1)  **C1**

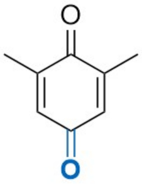
Reaction conditions: yellow solid; The oxidation of 2,3,6-TMP (68.1 mg, 0.5 mmol) by benzoquinone (162.3 mg, 1.5 mmol) was performed in 2.0 g CH_3CN/H_2O mixture (weight ratio: 7:3) under 1atm N_2 catalyzed by trifluoromethanesulfonic acid (15mg, 20 mol%), at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C1** is approximately at 8.3 minutes.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.51 (s, 1H), 2.00 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 187.79, 187.40, 145.26, 140.82, 140.66, 133.00, 15.81, 12.28, 11.98.

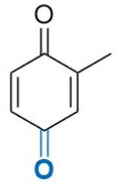
HRMS (+EI): m/z calculated for $[C_9H_{10}O_2]^+$: 150.0681. Found: 150.0675.

2)  **C2**

Reaction conditions: The oxidation of 2,6-dimethylphenol (64.9 mg, 0.5 mmol) by benzoquinone (164.4 mg, 1.5 mmol) was performed in 2.0 g CH_3CN/H_2O mixture (weight ratio: 7:3) under 1atm N_2 catalyzed by trifluoromethanesulfonic acid (15mg, 20 mol%), at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

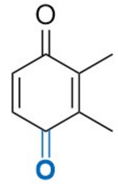
GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C2** is approximately at 4.9 minutes.

3)  **C3**

Reaction conditions: The oxidation of 2-methylphenol (54.7 mg, 0.5 mmol) by benzoquinone (163.6 mg, 1.5 mmol) was performed in 2.0 g CH_3OH/H_2O mixture (weight ratio: 7:3) under 1atm N_2 at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

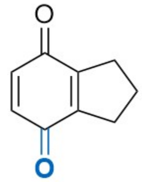
GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C3** is approximately at 3.3 minutes.

4)  **C4**

Reaction conditions: The oxidation of 2,3-dimethylphenol (60.5 mg, 0.5 mmol) by benzoquinone (163.1 mg, 1.5 mmol) was performed in 2.0 g CH_3CN/H_2O mixture (weight ratio: 7:3) under 1atm N_2 catalyzed by trifluoromethanesulfonic acid (15mg, 20 mol%), at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

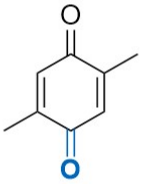
GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C4** is approximately at 5.1 minutes.

5)  **C5**

Reaction conditions: The oxidation of 2,3-dihydro-1H-inden-4-ol (67.2 mg, 0.5 mmol) by benzoquinone (164.7 mg, 1.5 mmol) was performed in 2.0 g CH_3OH/H_2O mixture (weight ratio: 7:3) under 1atm N_2 at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

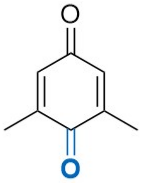
GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C5** is approximately at 11.3 minutes.

6)  **C6**

Reaction conditions: The oxidation of 2,5-dimethylphenol (60.6 mg, 0.5 mmol) by benzoquinone (162.2 mg, 1.5 mmol) was performed in 2.0 g CH_3CN/H_2O mixture (weight ratio: 7:3) under 1atm N_2 catalyzed by trifluoromethanesulfonic acid (15mg, 20 mol%), at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

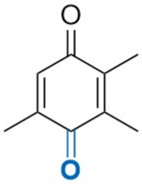
GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C6** is approximately at 4.8 minutes.

7)  **C7**

Reaction conditions: The oxidation of 3,5-dimethylphenol (62.1 mg, 0.5 mmol) by benzoquinone (163.0 mg, 1.5 mmol) was performed in 2.0 g CH_3OH/H_2O mixture (weight ratio: 7:3) under 1atm N_2 at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

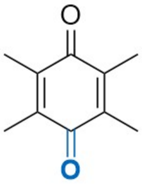
GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C7** is approximately at 4.9 minutes.

8)  **C8**

Reaction conditions: yellow solid; The oxidation of 2,3,5-TMP (68.1 mg, 0.5 mmol) by benzoquinone (162.3 mg, 1.5 mmol) was performed in 2.0 g CH_3CN/H_2O mixture (weight ratio: 7:3) under 1atm N_2 catalyzed by trifluoromethanesulfonic acid (15mg, 20 mol%), at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

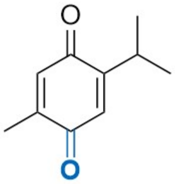
GC-MS conditions: The initial temperature is 150 °C and is maintained for 3 minutes. Subsequently, the temperature is increased to 250 °C at a heating rate of 30 °C per minute held for 8 minutes, then the temperature is increased to 300 °C at a heating rate of 30 °C per minute and finally held for 5 minutes. The peak emergence position of **C8** is approximately at 4.3 minutes.

9)  **C9**

Reaction conditions: The oxidation of 2,3,5,6-tetramethylphenol (74.3 mg, 0.5 mmol) by benzoquinone (163.0 mg, 1.5 mmol) was performed in 2.0 g CH_3CN/H_2O mixture (weight ratio: 7:3) under 1atm N_2 catalyzed by trifluoromethanesulfonic acid (15mg, 20 mol%), at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

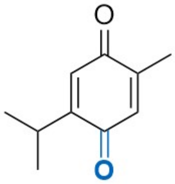
GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C9** is approximately at 11.8 minutes.

10)  **C10**

Reaction conditions: The oxidation of 5-methyl-2-(1-methylethyl)phenol (73.6 mg, 0.5 mmol) by benzoquinone (163.8 mg, 1.5 mmol) was performed in 2.0 g CH_3CN/H_2O mixture (weight ratio: 7:3) under 1atm N_2 catalyzed by trifluoromethanesulfonic acid (15mg, 20 mol%), at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

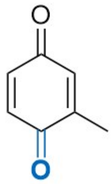
GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C10** is approximately at 5.0 minutes.

11)  **C11**

Reaction conditions: The oxidation of 2-methyl-5-(1-methylethyl)phenol (77.0 mg, 0.5 mmol) by benzoquinone (161.8 mg, 1.5 mmol) was performed in 2.0 g CH_3CN/H_2O mixture (weight ratio: 7:3) under 1atm N_2 catalyzed by trifluoromethanesulfonic acid (15mg, 20 mol%), at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

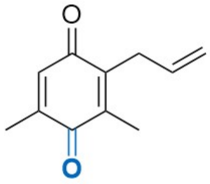
GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C11** is approximately at 9.8 minutes.

12)  **C12**

Reaction conditions: The oxidation of 3-methylphenol (54.9 mg, 0.5 mmol) by benzoquinone (162.5 mg, 1.5 mmol) was performed in 2.0 g CH_3OH/H_2O mixture (weight ratio: 7:3) under 1atm N_2 at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

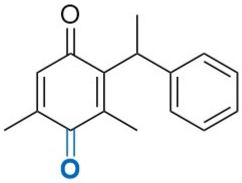
GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C12** is approximately at 3.3 minutes.

13)  **C13**

Reaction conditions: yellow solid; The oxidation of 2-allyl-3,5-dimethylphenol (82.7 mg, 0.5 mmol) by benzoquinone (163.0 mg, 1.5 mmol) was performed in 2.0 g CH_3OH/H_2O mixture (weight ratio: 7:3) under 1atm N_2 at 70 °C for 24 h;

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.54 (s, 1H), 5.81-5.59 (m, 1H), 5.07-4.87 (m, 2H), 3.21 (d, *J* = 6.3 Hz, 2H), 2.02 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 188.08, 186.70, 145.35, 141.64, 141.63, 133.17, 133.03, 116.39, 30.14, 15.80, 12.02.

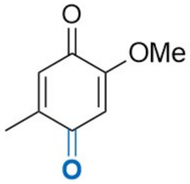
HRMS (+EI): m/z calculated for $[C_{11}H_{12}O_2]^+$: 176.0832. Found: 176.0829.

14)  **C14**

Reaction conditions: yellow solid; The oxidation of 3,5-dimethyl-2-(1-phenylethyl)phenol (125.8 mg, 0.5 mmol) by benzoquinone (163.5 mg, 1.5 mmol) was performed in 2.0 g CH_3OH/H_2O mixture (weight ratio: 7:3) under 1atm N_2 at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

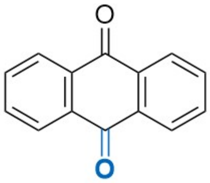
GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C14** is approximately at 14.5 minutes.

15)  **C15**

Reaction conditions: yellow solid; The oxidation of 5-methyl-2-methoxyphenol (69.8 mg, 0.5 mmol) by benzoquinone (162.9 mg, 1.5 mmol) was performed in 2.0 g CH_3CN/H_2O mixture (weight ratio: 7:3) under 1atm N_2 catalyzed by trifluoromethanesulfonic acid (15mg, 20 mol%), at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

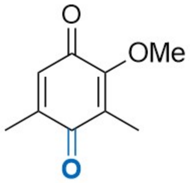
GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C15** is approximately at 11.9 minutes.

16)  **C16**

Reaction conditions: The oxidation of 9-anthrol (98.0 mg, 0.5 mmol) by benzoquinone (162.7 mg, 1.5 mmol) was performed in 2.0 g CH_3CN/H_2O mixture (weight ratio: 7:3) under 1atm N_2 catalyzed by trifluoromethanesulfonic acid (15mg, 20 mol%), at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

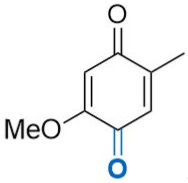
GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C16** is approximately at 10.5 minutes.

17)  **C17**

Reaction conditions: yellow solid; The oxidation of 3,5-dimethylguaiacol (79.1 mg, 0.5 mmol) by benzoquinone (162.2 mg, 1.5 mmol) was performed in 2.0 g CH_3OH/H_2O mixture (weight ratio: 7:3) under 1atm N_2 at 70 °C for 24 h;

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.42 (s, 1H), 4.00 (s, 3H), 2.02 (s, 3H), 1.94 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 188.46, 183.56, 155.50, 145.66, 131.40, 128.76, 60.81, 15.76, 8.81.

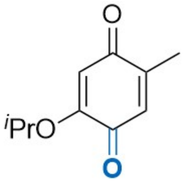
HRMS (+EI): m/z calculated for $[C_9H_{10}O_3]^+$: 166.0624. Found: 166.0621.

18)  **C18**

Reaction conditions: yellow solid; The oxidation of 5-methoxy-2-methyl-phenol (69.7 mg, 0.5 mmol) by benzoquinone (162.7 mg, 1.5 mmol) was performed in 2.0 g CH_3OH/H_2O mixture (weight ratio: 7:3) under 1atm N_2 at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

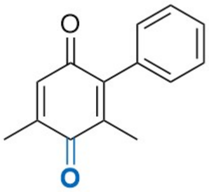
GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C18** is approximately at 11.9 minutes.

19)  **C19**

Reaction conditions: The oxidation of 5-isopropoxy-2-methylphenol (85.1 mg, 0.5 mmol) by benzoquinone (162.7 mg, 1.5 mmol) was performed in 2.0 g CH_3OH/H_2O mixture (weight ratio: 7:3) under 1atm N_2 at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

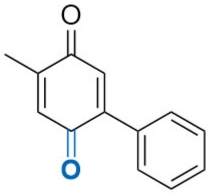
GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C19** is approximately at 13.0 minutes.

20)  **C20**

Reaction conditions: yellow solid; The oxidation of 2-Hydroxy-4,6-dimethylbiphenyl (98.5 mg, 0.5 mmol) by benzoquinone (163.0 mg, 1.5 mmol) was performed in 2.0 g CH_3CN/H_2O mixture (weight ratio: 7:3) under 1atm N_2 catalyzed by trifluoromethanesulfonic acid (15mg, 20 mol%), at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

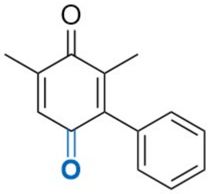
GC-MS conditions: The initial temperature is 100 °C and is maintained for 7 minutes. Subsequently, the temperature is increased to 180 °C at a heating rate of 30 °C per minute held for 6 minutes, then the temperature is increased to 300 °C at a heating rate of 30 °C per minute and finally held for 4 minutes. The peak emergence position of **C20** is approximately at 16.3 minutes.

21)  **C21**

Reaction conditions: gelb solid; The oxidation of 4-methylbiphenyl-3-ol (92.7 mg, 0.5 mmol) by benzoquinone (162.1 mg, 1.5 mmol) was performed in 2.0 g CH_3CN/H_2O mixture (weight ratio: 7:3) under 1atm N_2 catalyzed by trifluoromethanesulfonic acid (15mg, 20 mol%), at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

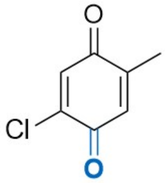
GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C21** is approximately at 15.1 minutes.

22)  **C22**

Reaction conditions: gelb solid; The oxidation of 2,4-dimethyl-[1,1'-biphenyl]-3-ol (99.6 mg, 0.5 mmol) by benzoquinone (163.3 mg, 1.5 mmol) was performed in 2.0 g CH_3CN/H_2O mixture (weight ratio: 7:3) under 1atm N_2 catalyzed by trifluoromethanesulfonic acid (15mg, 20 mol%), at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

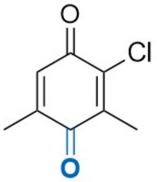
GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C22** is approximately at 15.1 minutes.

23)  **C23**

Reaction conditions: yellow solid; The oxidation of 5-chloro-2-methyl-phenol (70.8 mg, 0.5 mmol) by benzoquinone (163.9 mg, 1.5 mmol) was performed in 2.0 g CH_3CN/H_2O mixture (weight ratio: 7:3) under 1atm N_2 catalyzed by trifluoromethanesulfonic acid (15mg, 20 mol%), at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

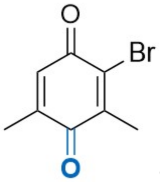
GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C23** is approximately at 8.8 minutes.

24)  **C24**

Reaction conditions: yellow solid; The oxidation of 2-chloro-3,5-dimethylphenol (77.3 mg, 0.5 mmol) by benzoquinone (162.5 mg, 1.5 mmol) was performed in 2.0 g CH_3CN/H_2O mixture (weight ratio: 7:3) under 1atm N_2 catalyzed by trifluoromethanesulfonic acid (15mg, 20 mol%), at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

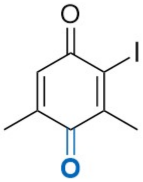
GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C24** is approximately at 11.1 minutes.

25)  **C25**

Reaction conditions: orange solid; The oxidation of 2-bromo-3,5-dimethylphenol (99.7 mg, 0.5 mmol) by benzoquinone (162.5 mg, 1.5 mmol) was performed in 2.0 g CH_3CN/H_2O mixture (weight ratio: 7:3) under 1atm N_2 catalyzed by trifluoromethanesulfonic acid (15mg, 20 mol%), at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

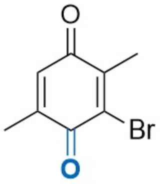
GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C25** is approximately at 12.6 minutes.

26)  **C26**

Reaction conditions: brown solid; The oxidation of 2-iodo-3,5-dimethylphenol (122.6 mg, 0.5 mmol) by benzoquinone (161.8 mg, 1.5 mmol) was performed in 2.0 g CH_3OH/H_2O mixture (weight ratio: 7:3) under 1atm N_2 at 70 °C for 24 h;

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.82 (s, 1H), 2.31 (s, 3H), 2.07 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 182.91, 180.17, 152.30, 145.66, 131.63, 121.92, 22.78, 15.90.

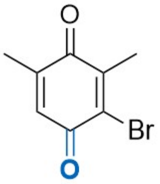
HRMS ((+)-ESI): m/z calculated for $([C_8H_7IO_2]+Na)^+$: 284.9383. Found: 284.9382.

27)  **C27**

Reaction conditions: yellow solid; The oxidation of 3-bromo-2,5-dimethylphenol (99.9 mg, 0.5 mmol) by benzoquinone (163.5 mg, 1.5 mmol) was performed in 2.0 g CH_3CN/H_2O mixture (weight ratio: 7:3) under 1atm N_2 catalyzed by trifluoromethanesulfonic acid (15mg, 20 mol%), at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C27** is approximately at 12.4 minutes.

28)  **C28**

Reaction conditions: orange solid; The oxidation of 3-bromo-2,6-dimethylphenol (99.6 mg, 0.5 mmol) by benzoquinone (162.4 mg, 1.5 mmol) was performed in 2.0 g CH_3CN/H_2O mixture (weight ratio: 7:3) under 1atm N_2 catalyzed by trifluoromethanesulfonic acid (15mg, 20 mol%), at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of **C28** is approximately at 12.6 minutes.

29)  **D1**

Reaction conditions: white solid; Oxidation of 2,3,6-TMP (68.1 mg, 0.5 mmol) by benzoquinone (162.3 mg, 1.5 mmol) was performed in 2.0 g CH_3CN/H_2O mixture (weight ratio: 7:3) under 1 atm N_2 catalyzed by trifluoromethanesulfonic acid (15 mg, 20 mol%), at 70 °C for 24 h;

GC-MS model: SHIMADAZU SH-5;

GC-MS conditions: The initial temperature is 70 °C and is maintained for 10 minutes. Subsequently, the temperature is increased to 300 °C at a heating rate of 25 °C per minute, and finally held for 2 minutes. The peak emergence position of C1 is approximately at 10.7 minutes.

^{1}H NMR (600 MHz, DMSO-d6) δ 8.58 (s, 2H), 6.53 (s, 4H). **^{13}C NMR** (151 MHz, DMSO-d6) δ 150.15, 116.08.

HRMS ((–)-ESI): m/z calculated for ($[C_6H_6O_2]{-}H^+$): 109.0295. Found: 109.0294.

References

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Journal*, 2016.
2. A. D. Becke, *The Journal of Chemical Physics*, 1993, **98**, 5648-5652.
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5. W. J. Hehre, R. Ditchfield and J. A. Pople, *Journal of Chemical Physics*, 1972, **56**, 2257-2261.
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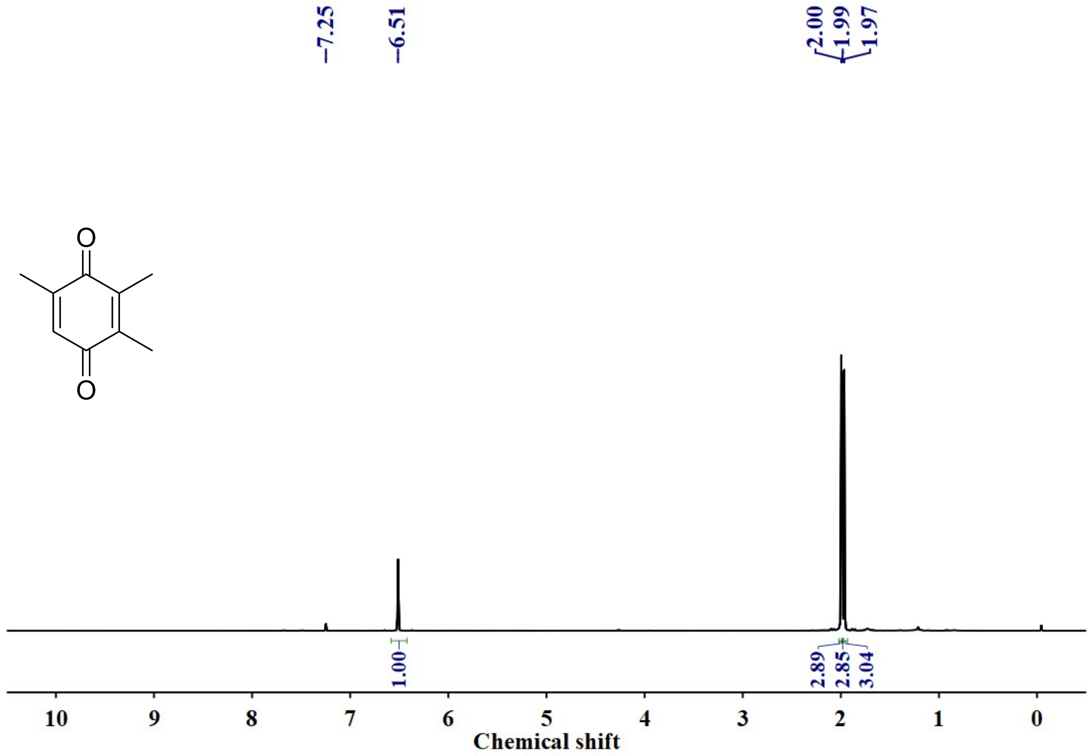
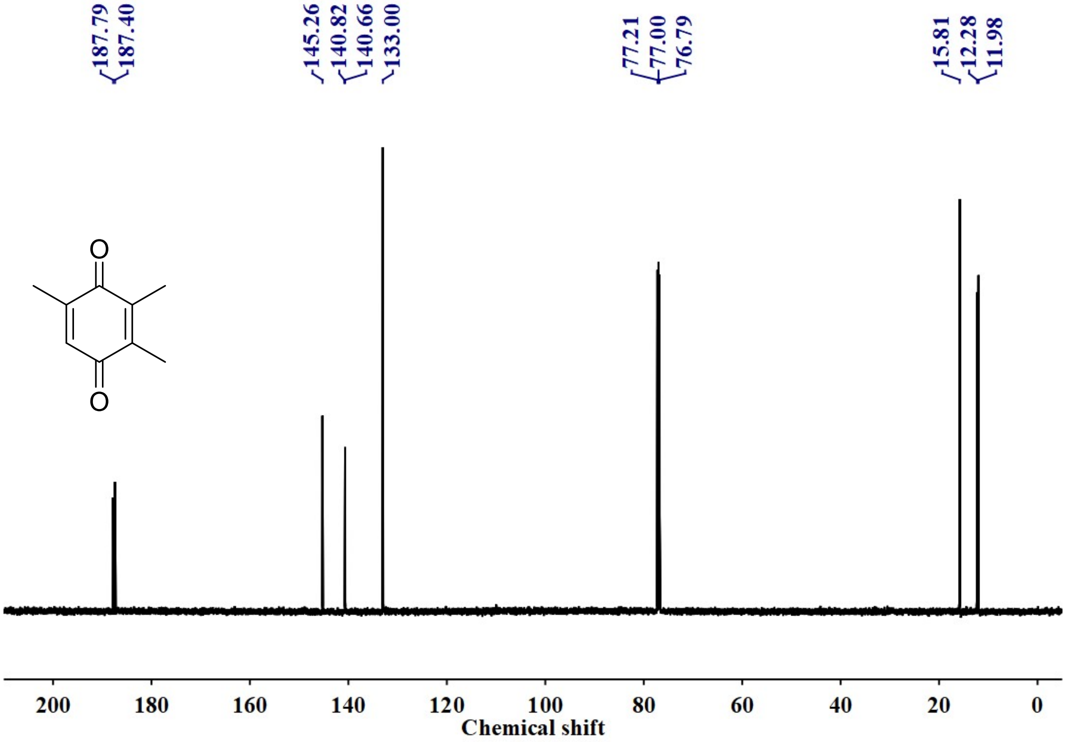
8. C. Legault, *CYLview User Manual*, 2012.

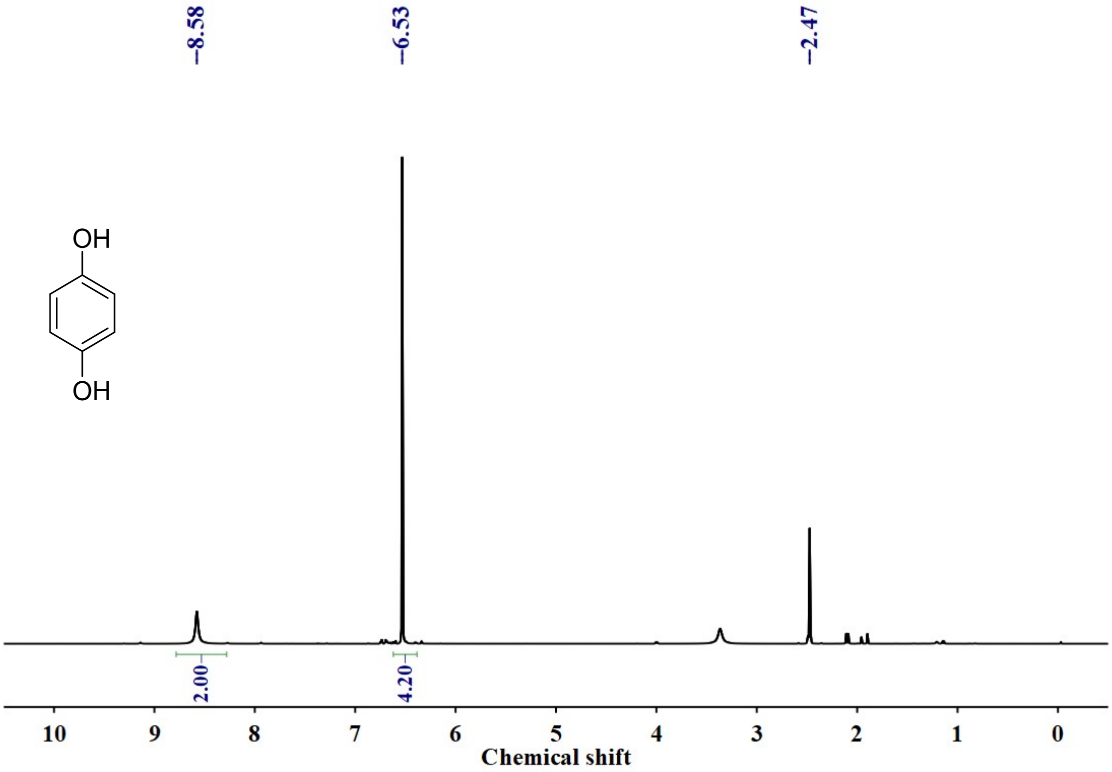
NMR Spectroscopic Data



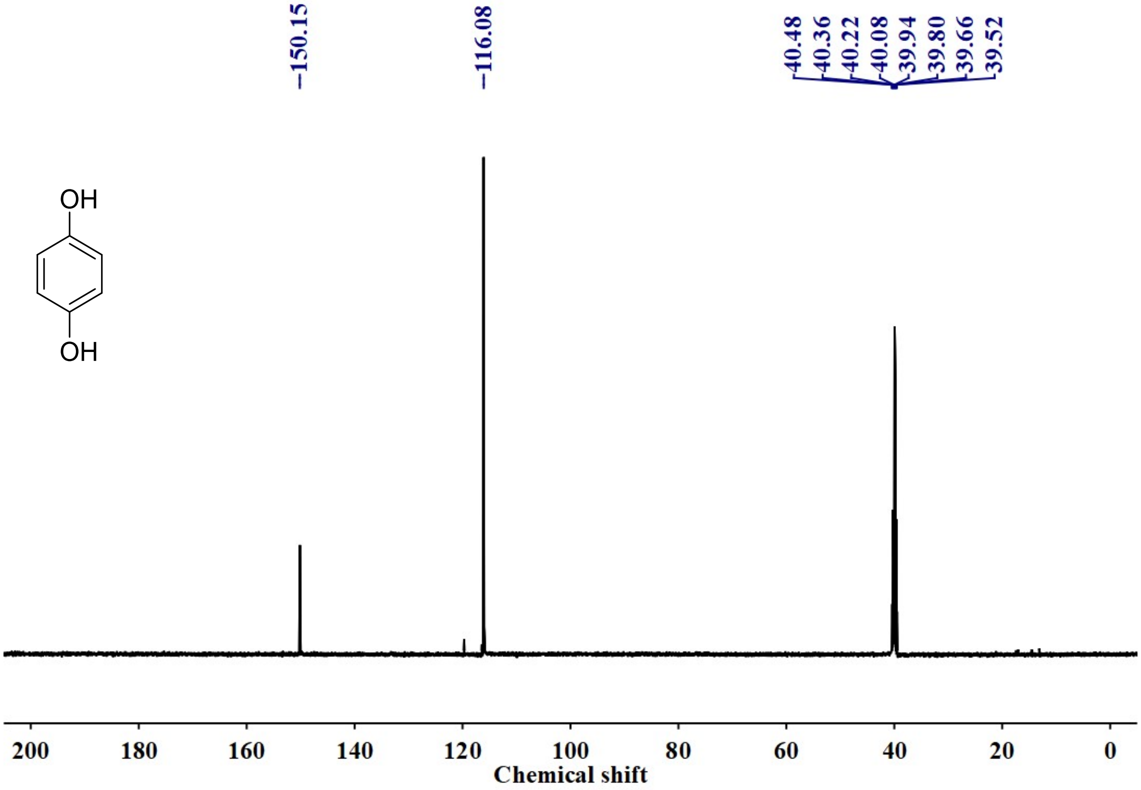
^{1}**H NMR** (600 MHz, CDCl$_3$) of 2,3,5-trimethyl-1,4-benzoquinone (**C1**).



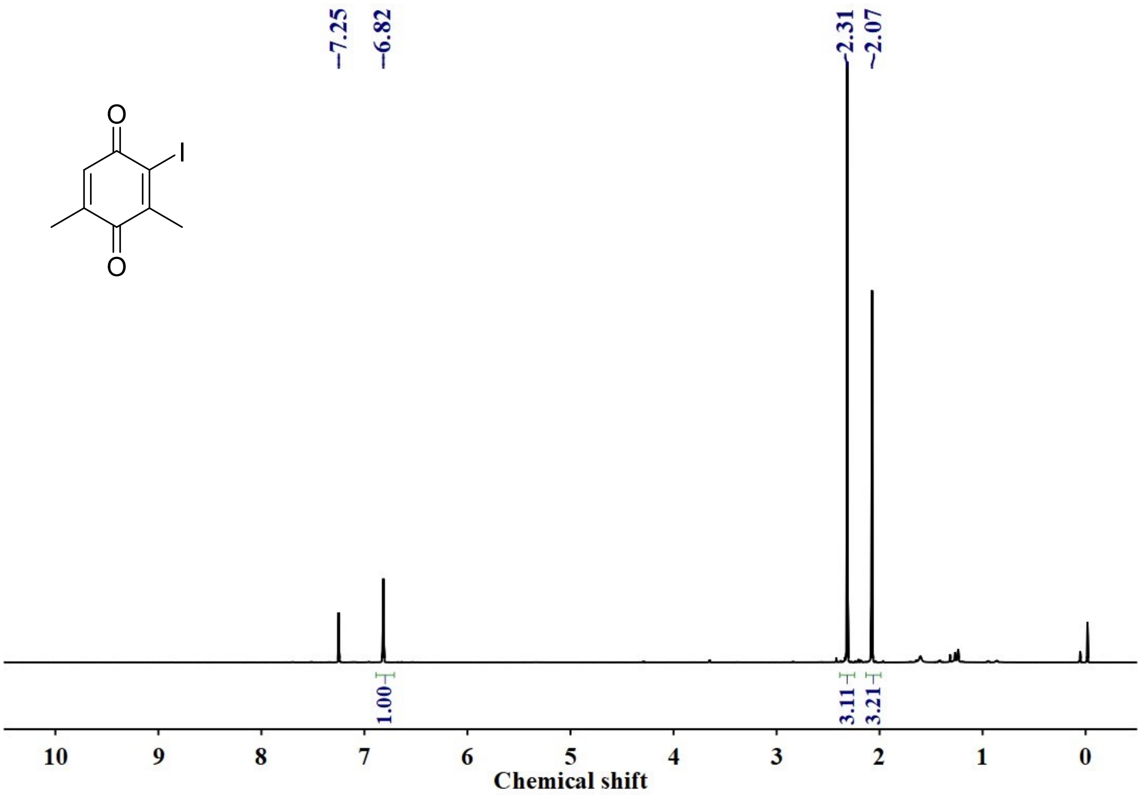
^{13}**C NMR** (126 MHz, CDCl$_3$) of 2,3,5-trimethyl-1,4-benzoquinone (**C1**).



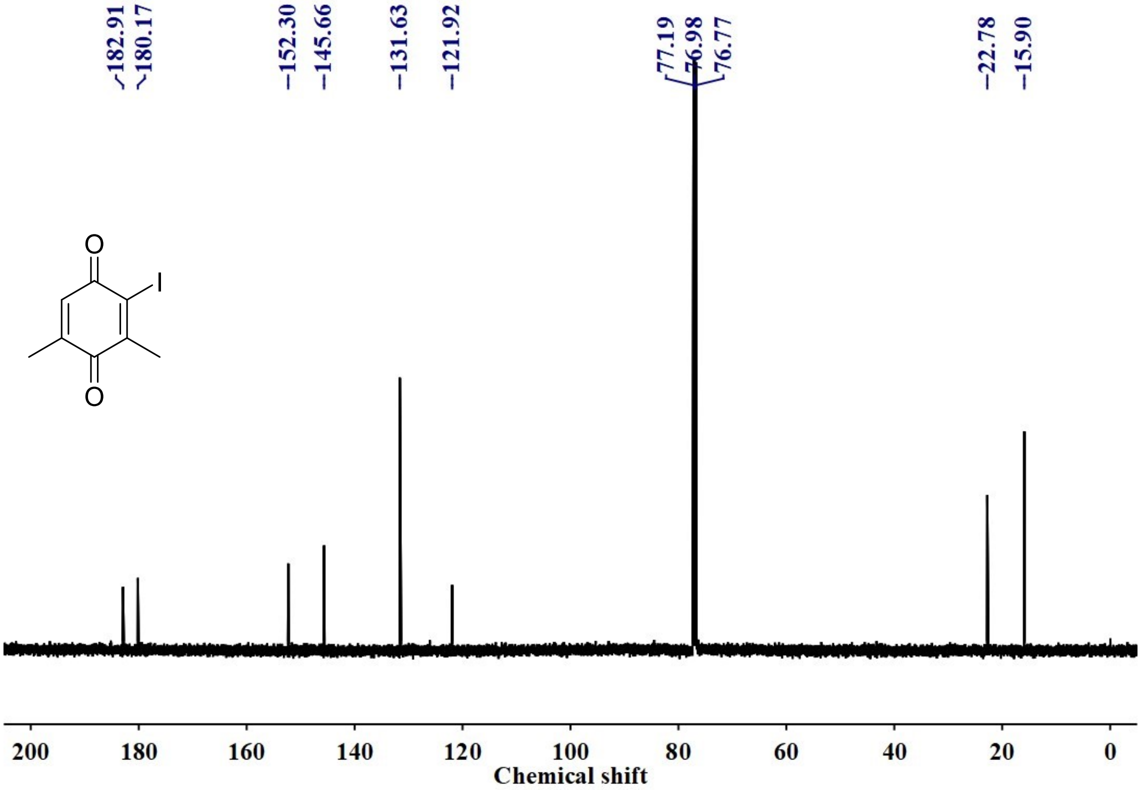
^{1}**H NMR** (600 MHz, DMSO-d6) of hydroquinone (**D1**).



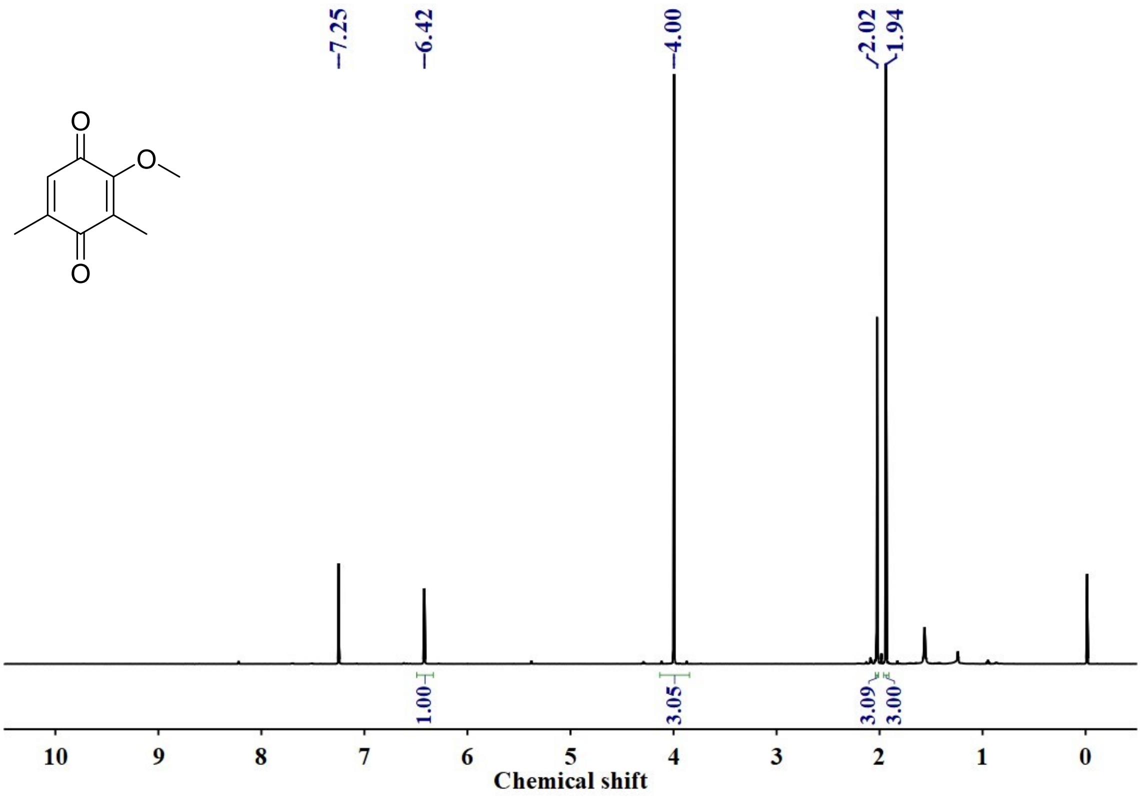
^{13}**C NMR** (126 MHz, DMSO-d6) of hydroquinone (**D1**).



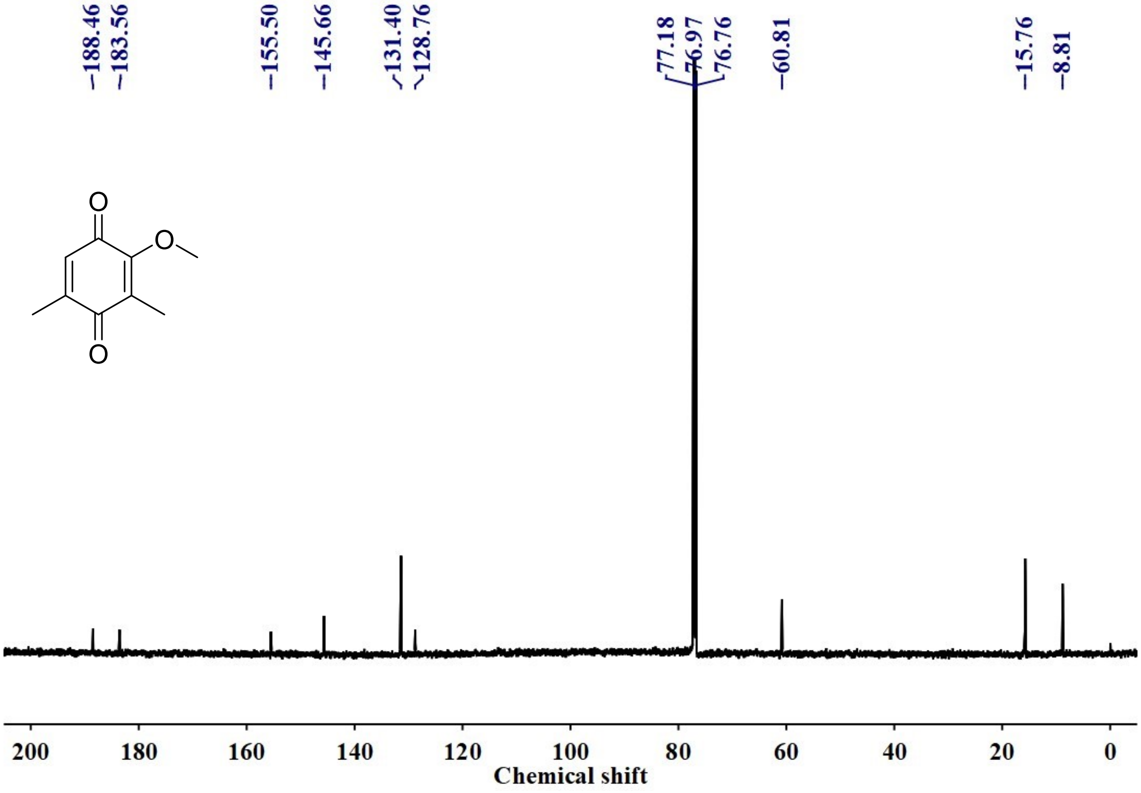
^{1}**H NMR** (600 MHz, CDCl$_3$) of 3-iodo-2,6-dimethyl-p-benzoquinone (**C26**).



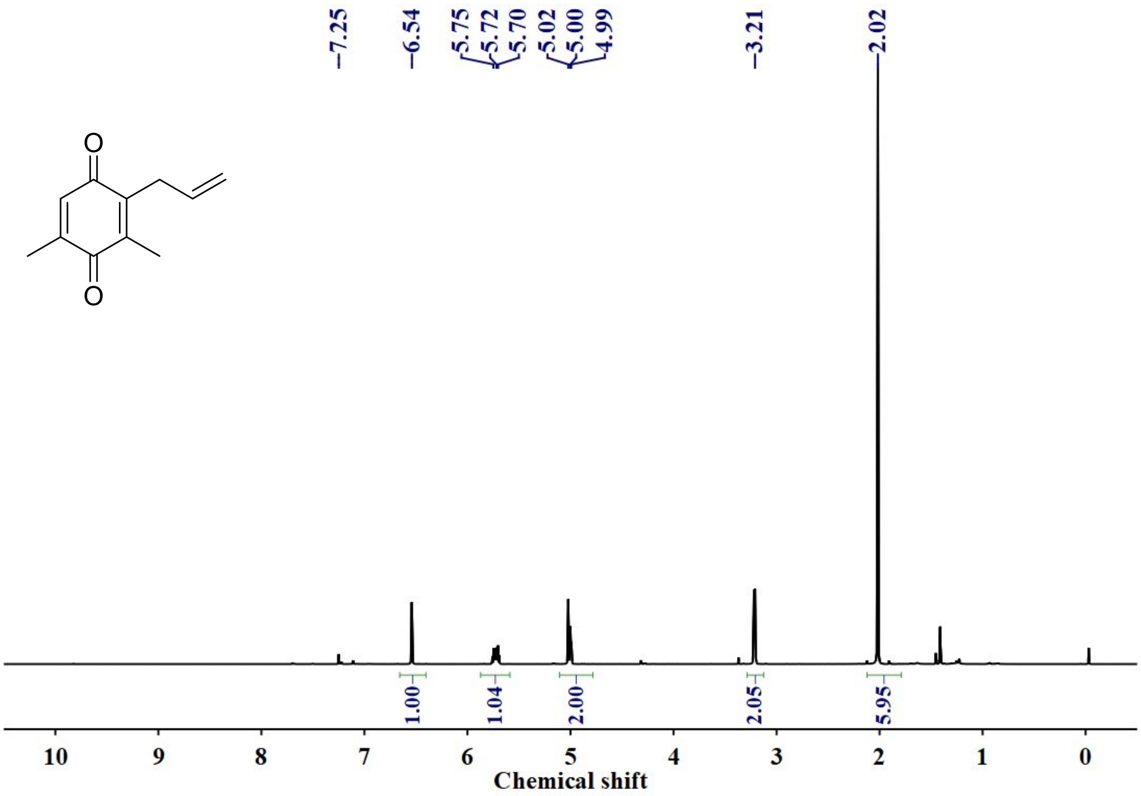
^{13}**C NMR** (126 MHz, CDCl$_3$) of 3-iodo-2,6-dimethyl-p-benzoquinone (**C26**).



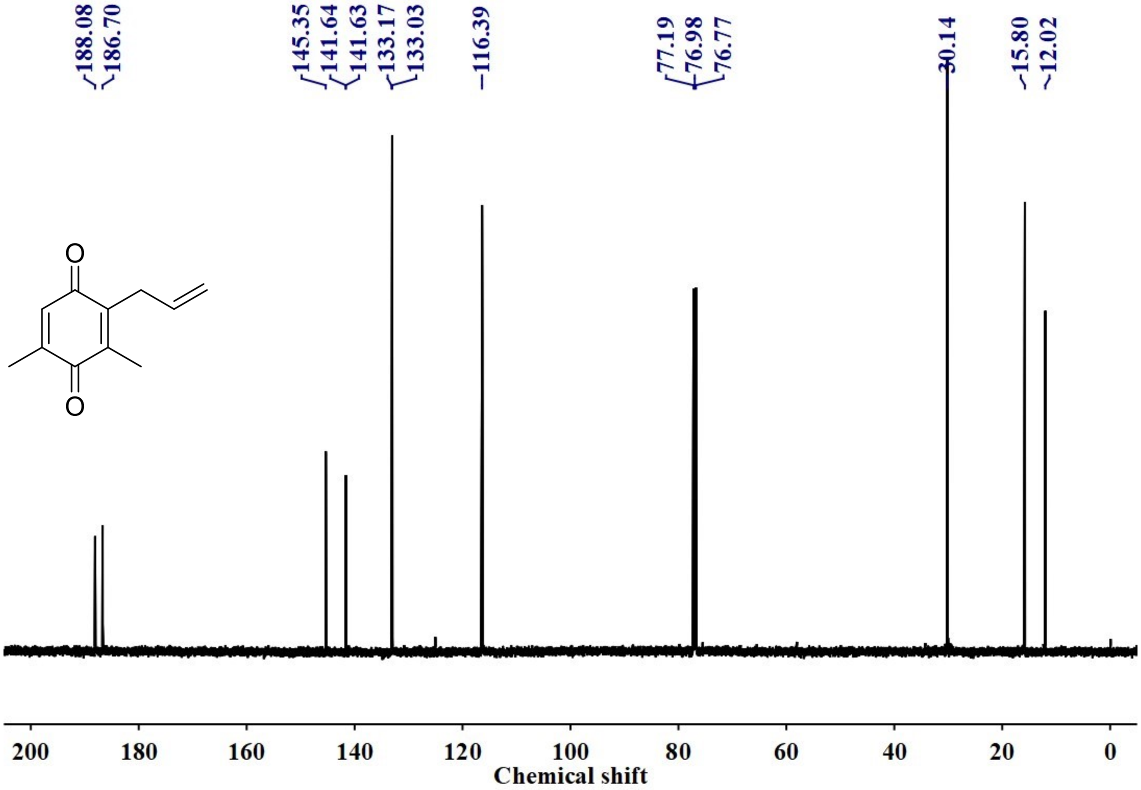
^{1}H NMR (600 MHz, $CDCl_3$) of 3,5-dimethyl-2-methoxybenzoquinone (**C17**).



^{13}C NMR (126 MHz, $CDCl_3$) of 3,5-dimethyl-2-methoxybenzoquinone (**C17**).

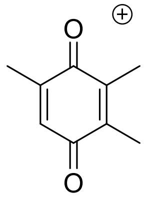


^{1}**H NMR** (126 MHz, $CDCl_3$) of 3,5-dimethyl-2-allyl-p-benzoquinone (**C13**).



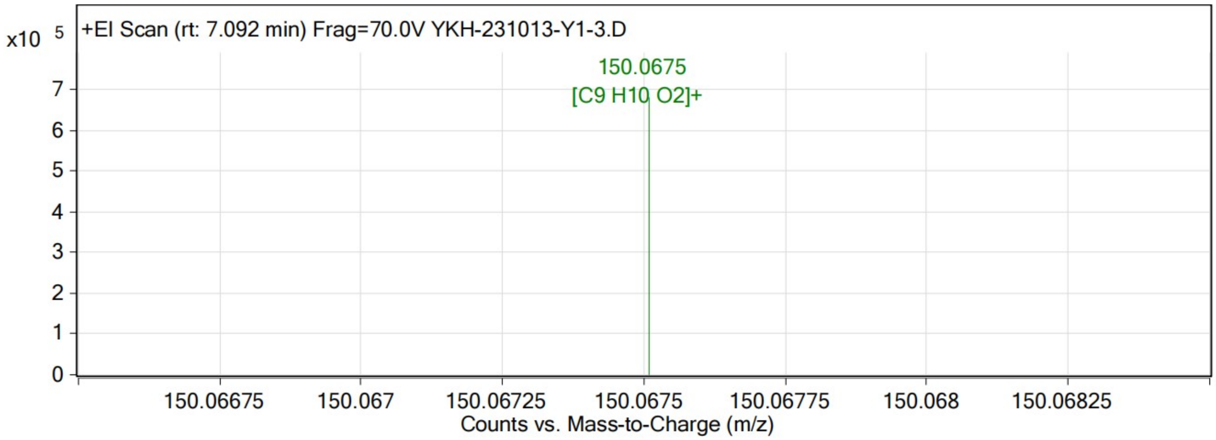
^{13}**C NMR** (126 MHz, $CDCl_3$) of 3,5-dimethyl-2-allyl-p-benzoquinone (**C13**).

High Resolution MS Data



1) Exact Mass: 150.0681 **C1**

Fragmentor Voltage	**Collision Energy**	**Ionization Mode**
	0	EI

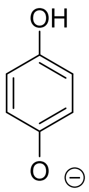


Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	5

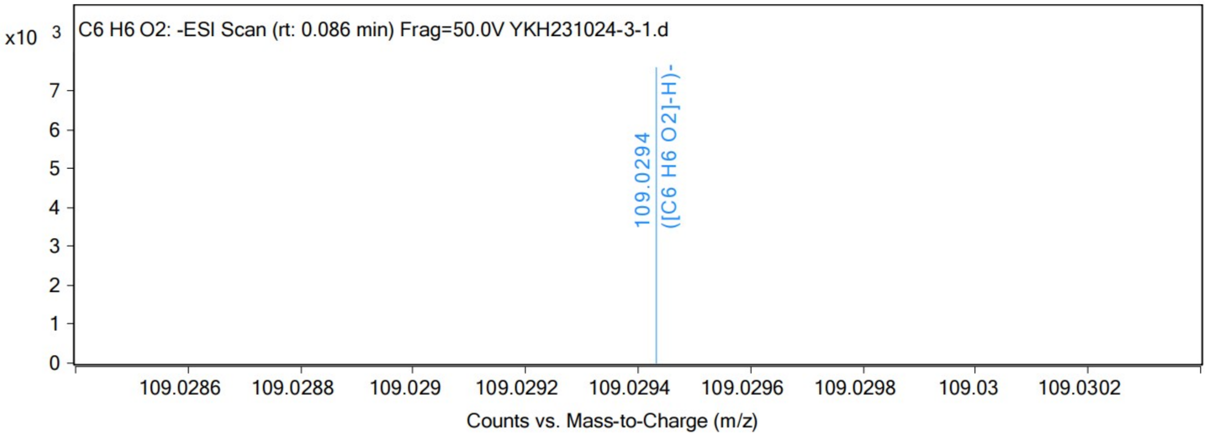
Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C9 H10 O2	True	150.0681	150.0681	-0.23	C9 H10 O2	86.86



2) Exact Mass: 109.0295 **D1**

Fragmentor Voltage	Collision Energy	Ionization Mode
50	0	ESI

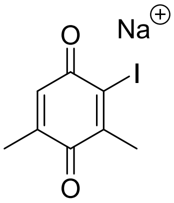


Formula Calculator Element Limits

Element	Min	Max
C	0	100
H	0	100
O	0	5

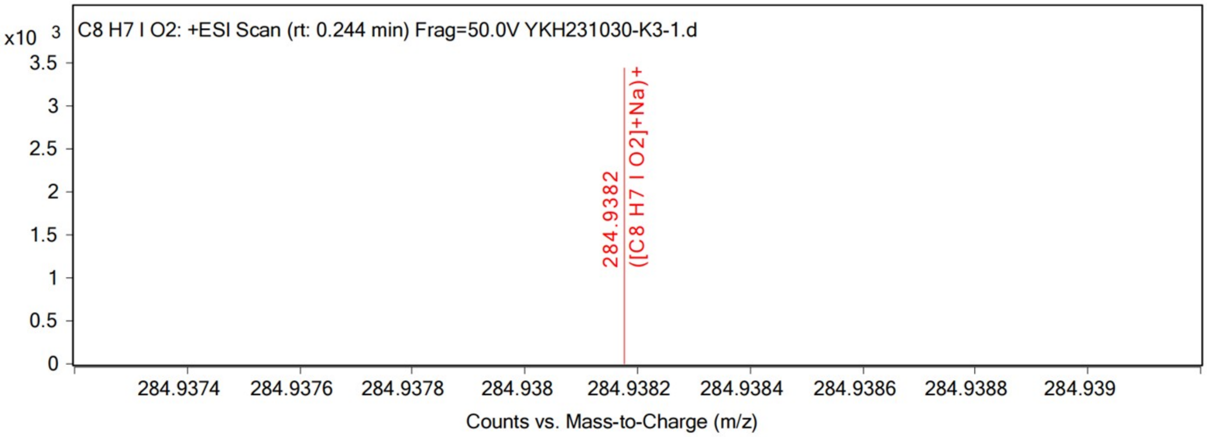
Formula Calculator Results

Formula	Best	Measured Mass	Tgt Mass	Diff (ppm)	Score
C6 H5 O2	True	109.0294	109.0295	0.94	99.84



3) Exact Mass: 294.9383 **C29**

Fragmentor Voltage	Collision Energy	Ionization Mode
50	0	ESI

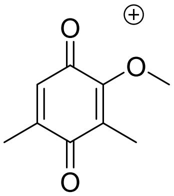


Formula Calculator Element Limits

Element	Min	Max
C	0	100
H	0	100
O	0	5
I	1	1

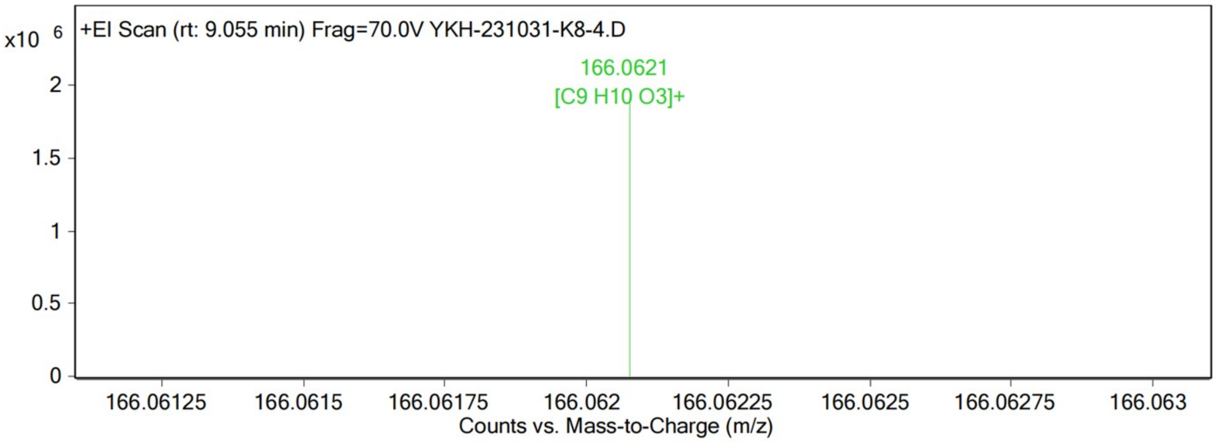
Formula Calculator Results

Formula	Best	Measured Mass	Tgt Mass	Diff (ppm)	Score
C8 H7 I Na O2	True	284.9382	284.9383	0.45	99.89



4) Exact Mass: 166.0624 **C18**

Fragmentor Voltage	Collision Energy	Ionization Mode
	0	EI

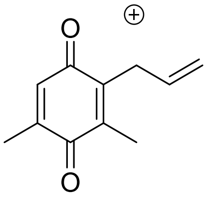


Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	5

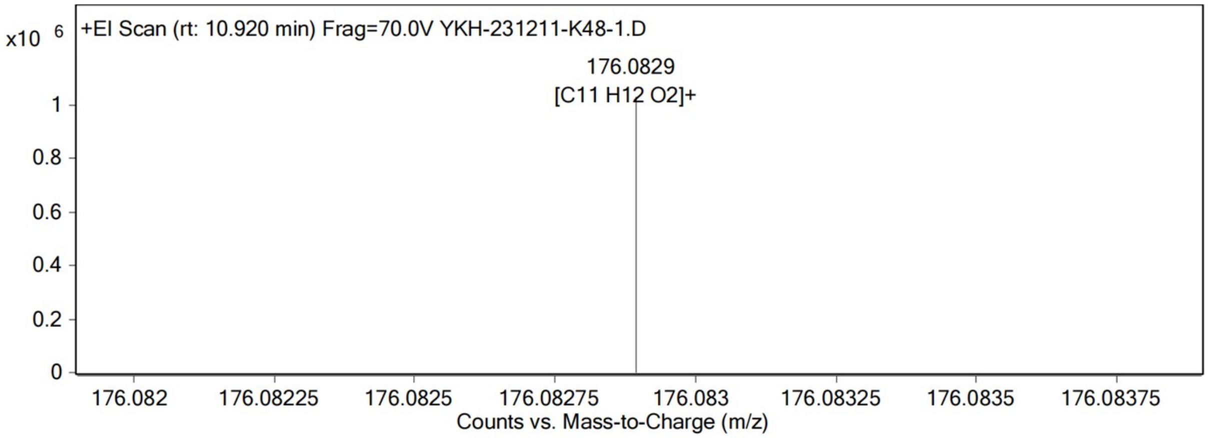
Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C9 H10 O3	True	166.0627	166.063	1.61	C9 H10 O3	98.52



5) Exact Mass: 176.0832 **C13**

Fragmentor Voltage	Collision Energy	Ionization Mode
	0	EI

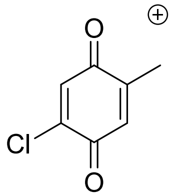


Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	5

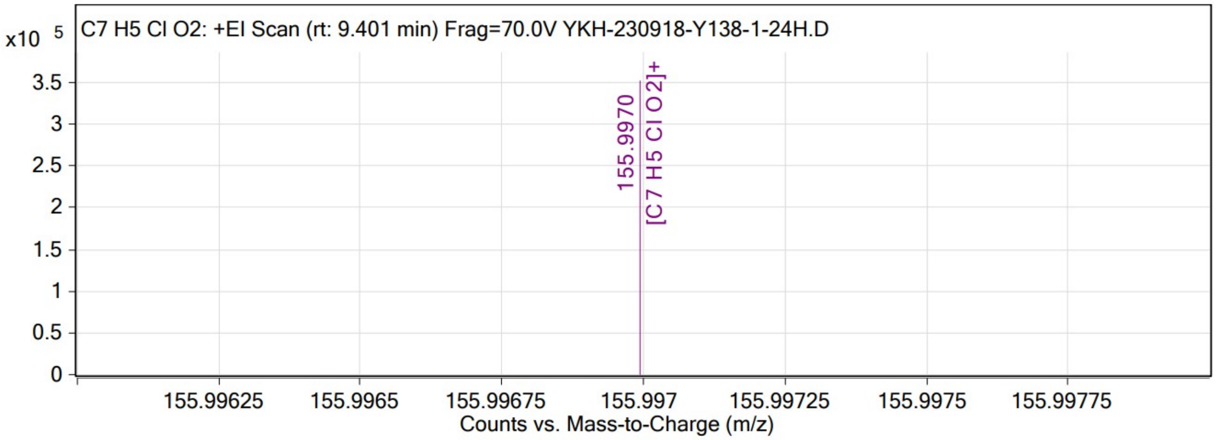
Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C11 H12 O2	True	176.0837	176.0837	0.17	C11 H12 O2	92.39



6) Exact Mass: 155.9973 **C23**

Fragmentor Voltage	Collision Energy	Ionization Mode
	0	EI



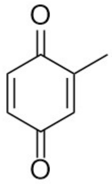
Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	3
Cl	0	1

Formula Calculator Results

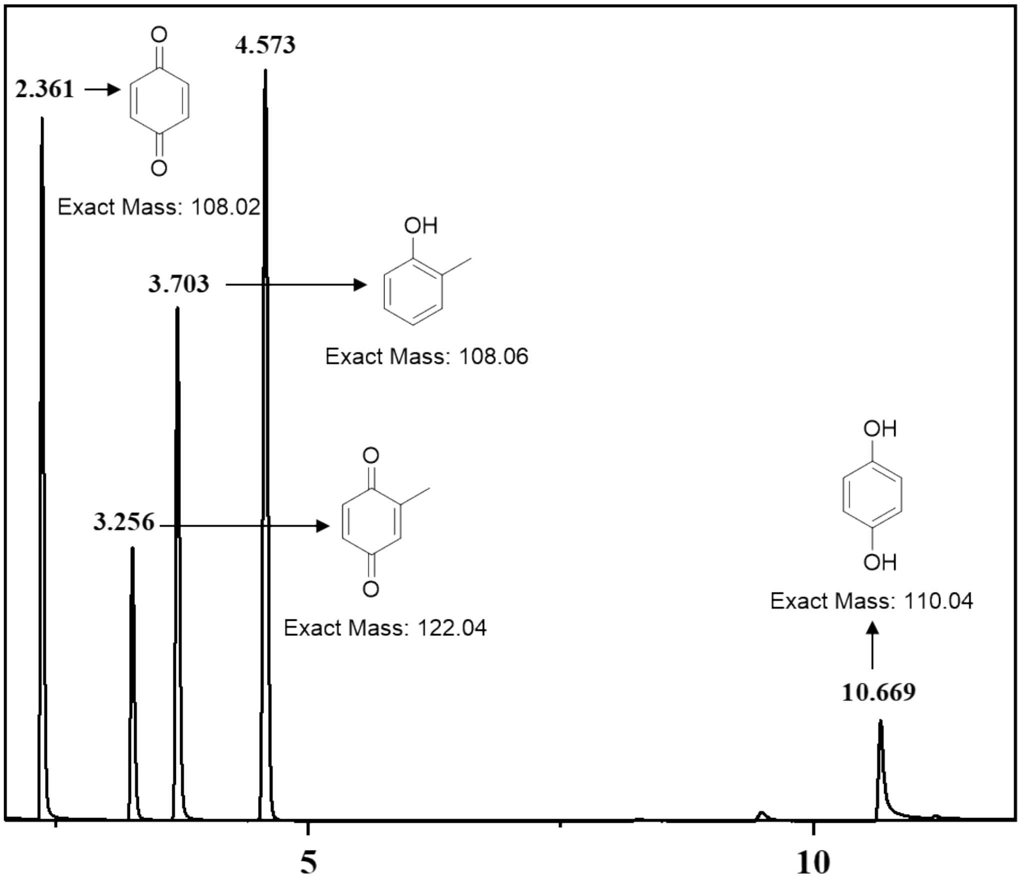
Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Score
C7 H5 Cl O2	True	155.9975	155.9978	1.69	C7 H5 Cl O2	99.16

GC-MS Spectroscopic Data

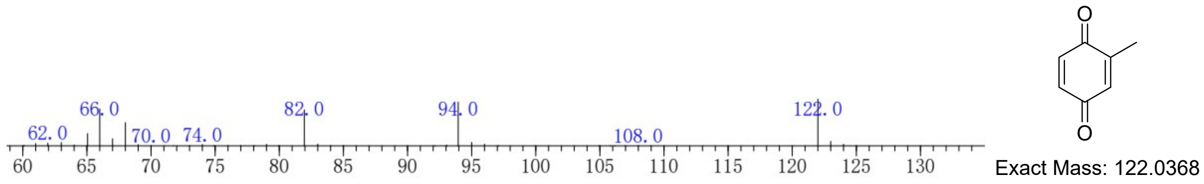


1) **C3**

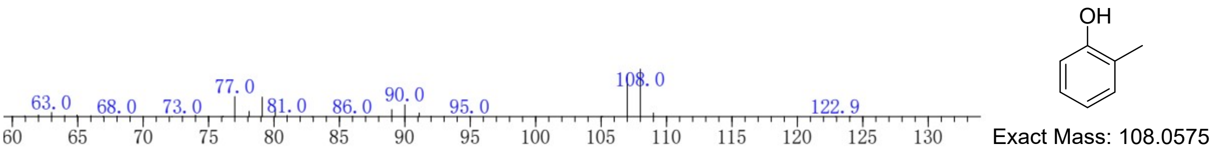
Exact Mass: 122.0368

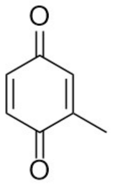


The corresponding mass spectrogram of the above GC-MS peak at 3.26 min:

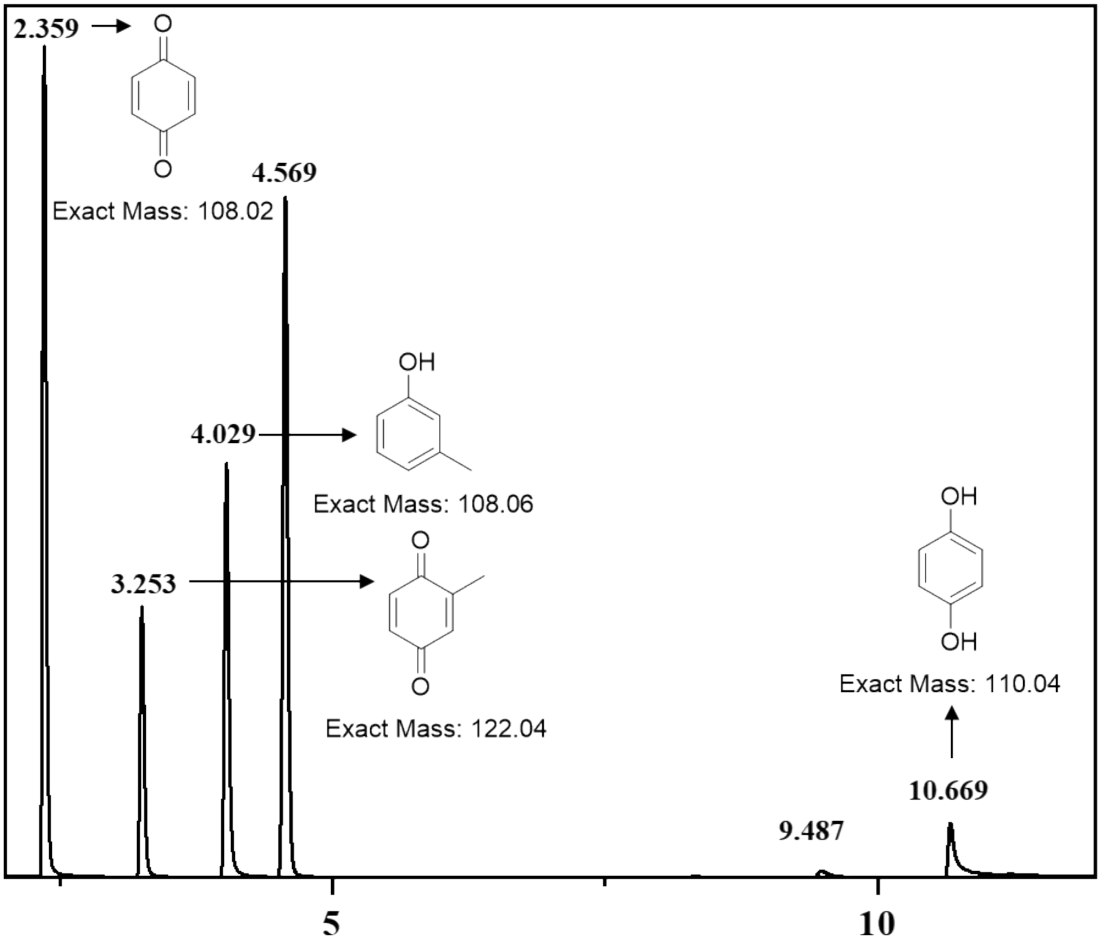


The corresponding mass spectrogram of the above GC-MS peak at 3.70 min:

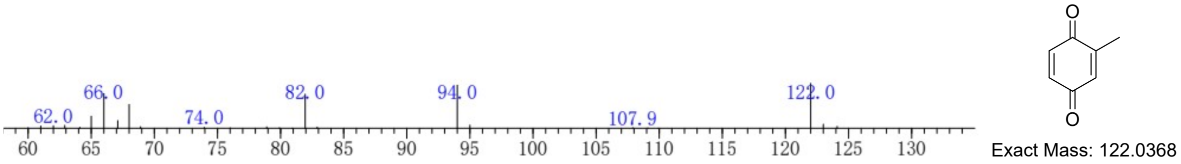


2)  **C12**

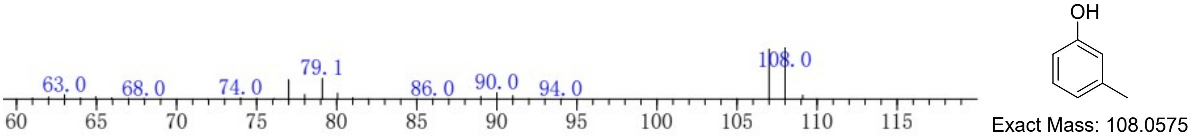
Exact Mass: 122.0368

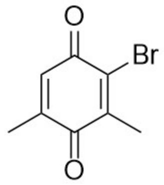


The corresponding mass spectrogram of the above GC-MS peak at 3.25 min:

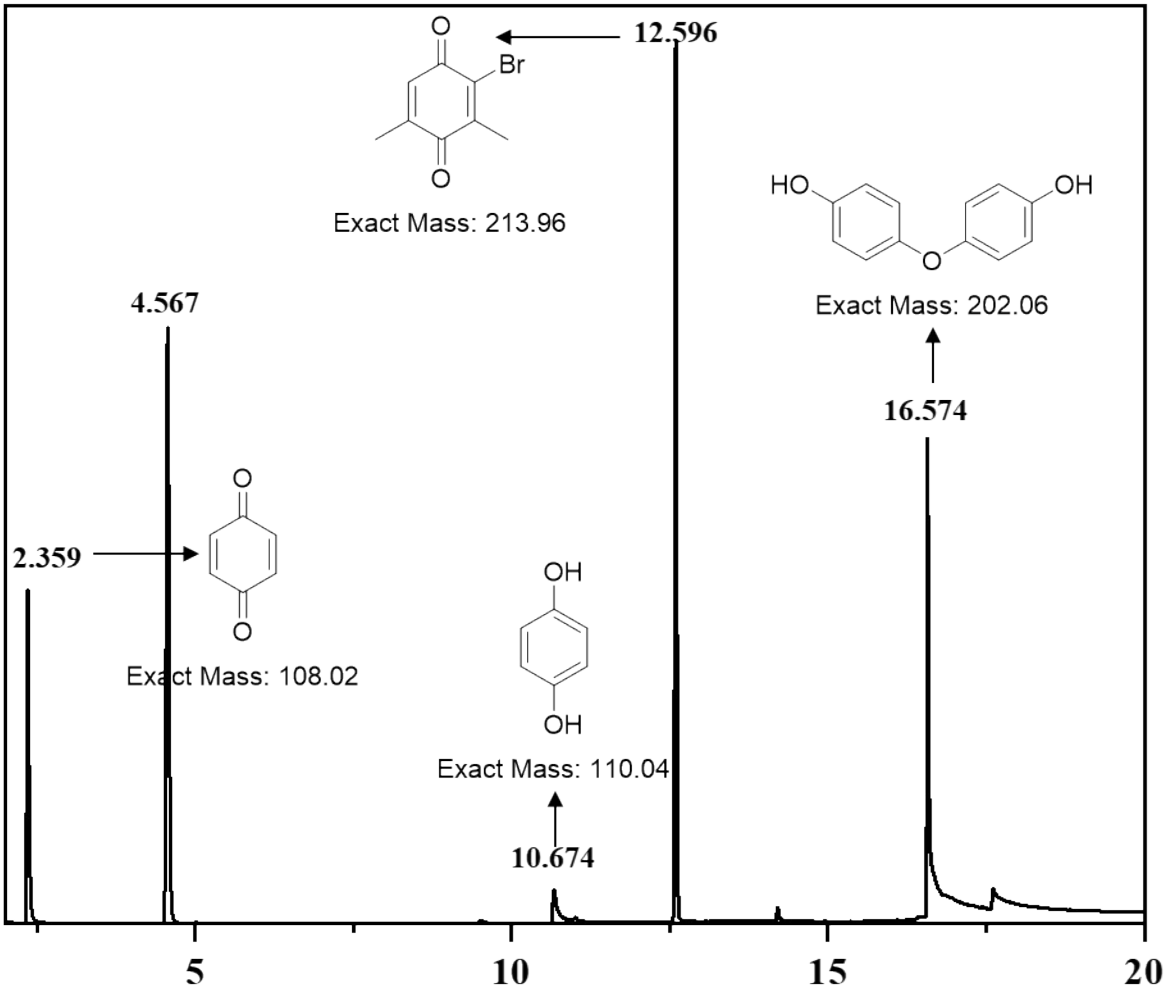


The corresponding mass spectrogram of the above GC-MS peak at 4.03 min:

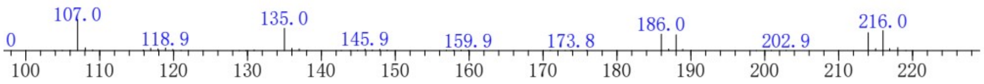


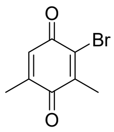
3)  **C25**

Exact Mass: 213.9629

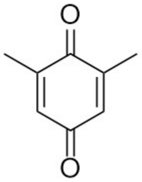


The corresponding mass spectrogram of the above GC-MS peak at 12.60 min:



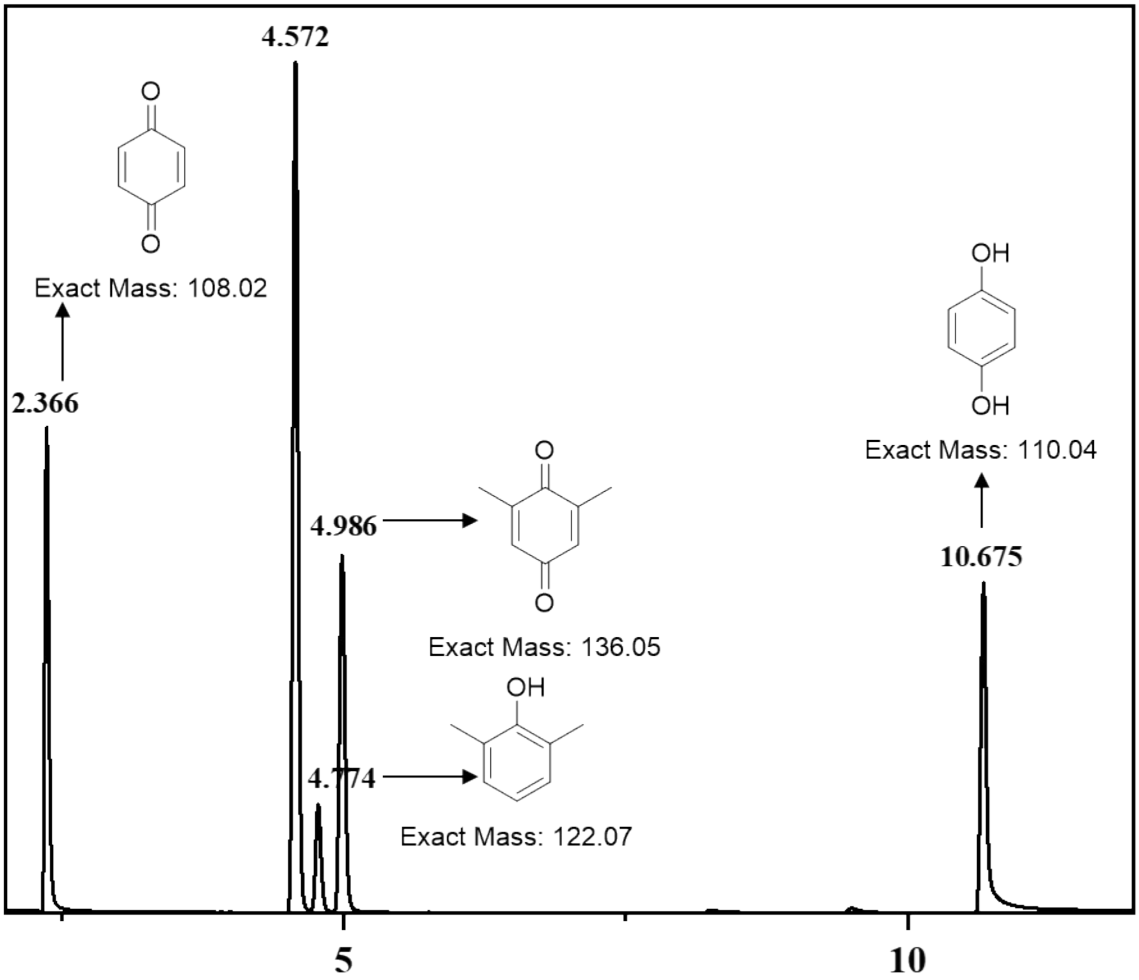


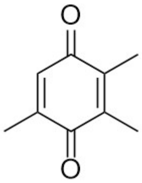
Exact Mass: 213.9629



4) **C2**

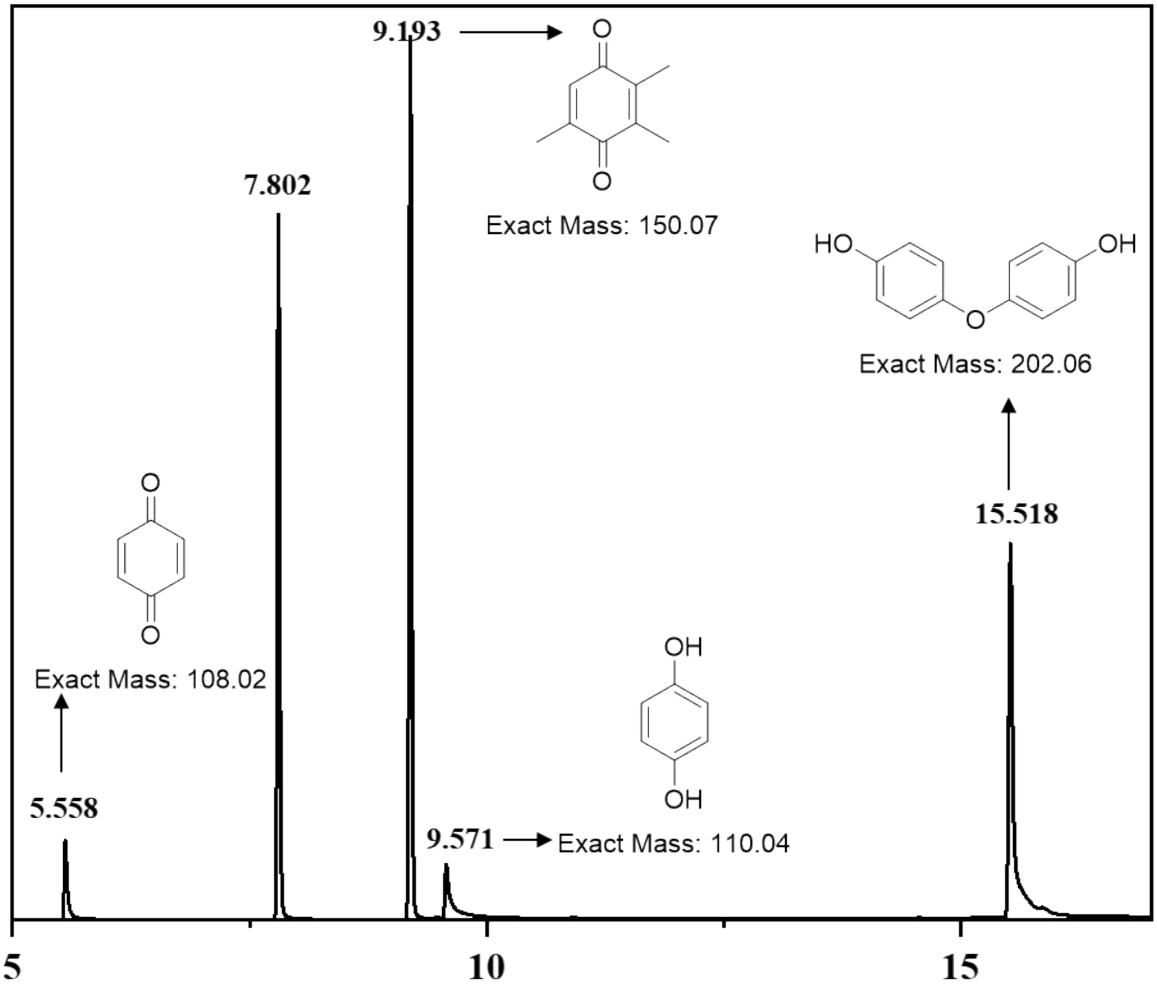
Exact Mass: 136.0524



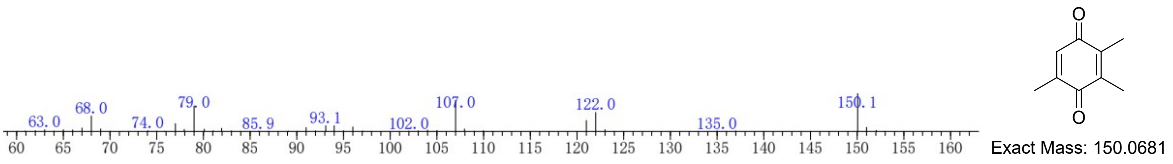


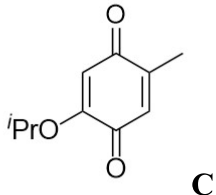
5) **C8**

Exact Mass: 150.0681



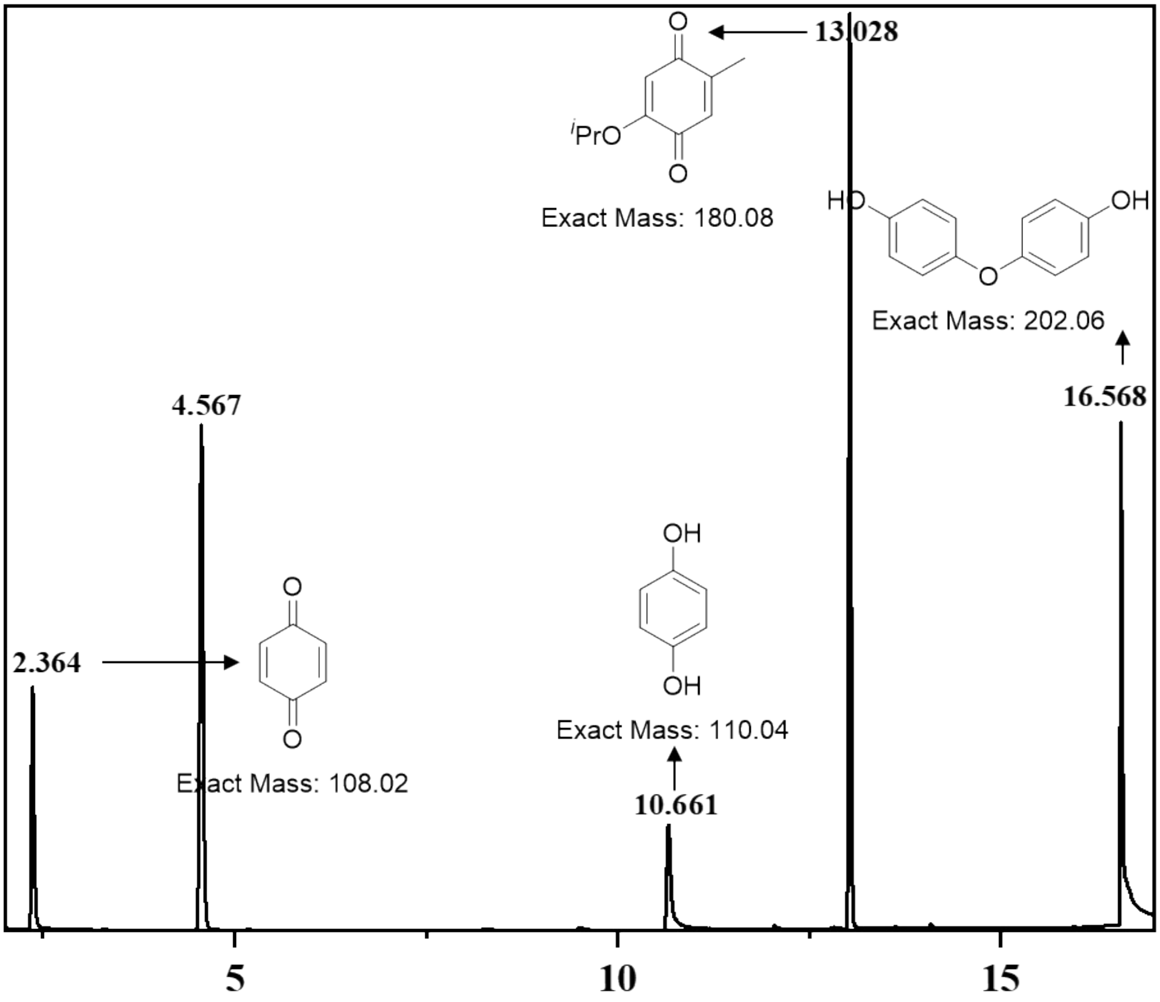
The corresponding mass spectrogram of the above GC-MS peak at 9.19 min:



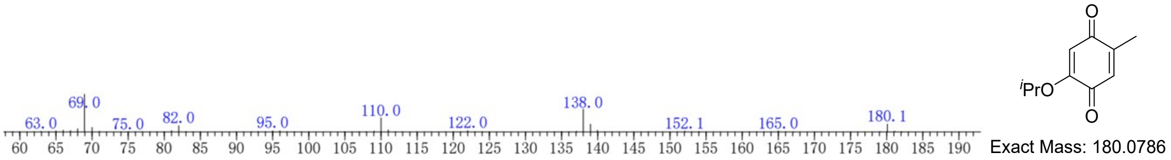


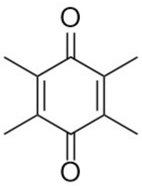
6) **C19**

Exact Mass: 180.0786

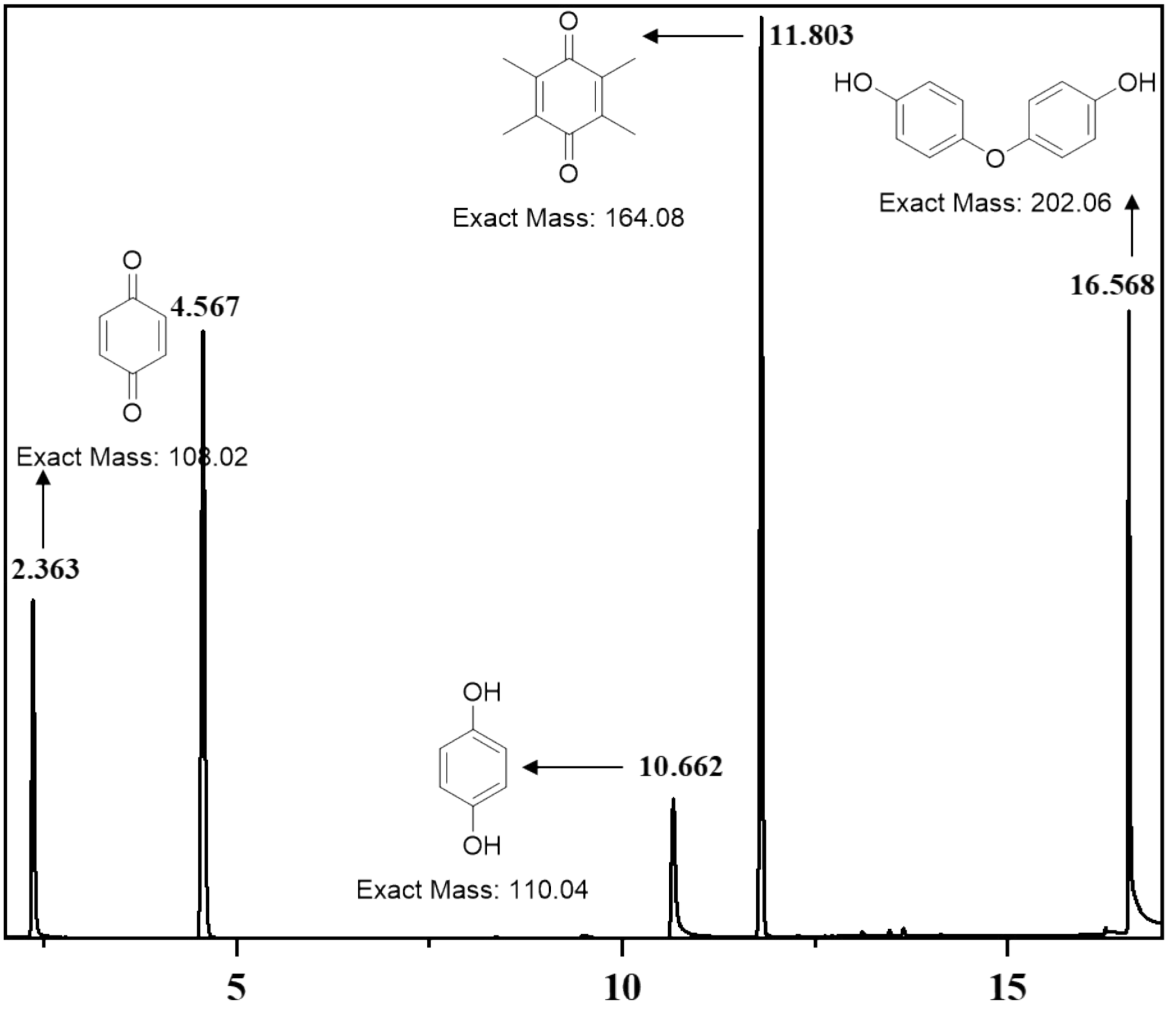


The corresponding mass spectrogram of the above GC-MS peak at 13.03 min:

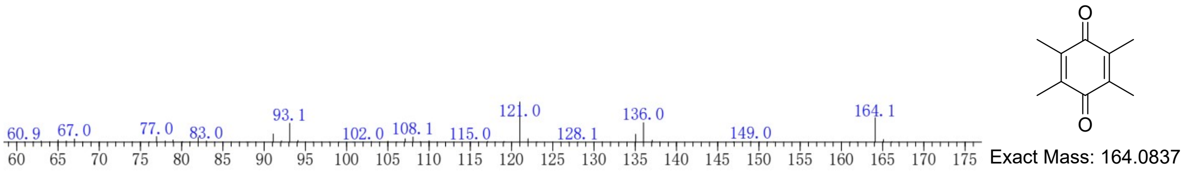


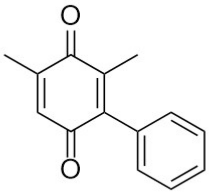
7)  **C9**

Exact Mass: 164.0837

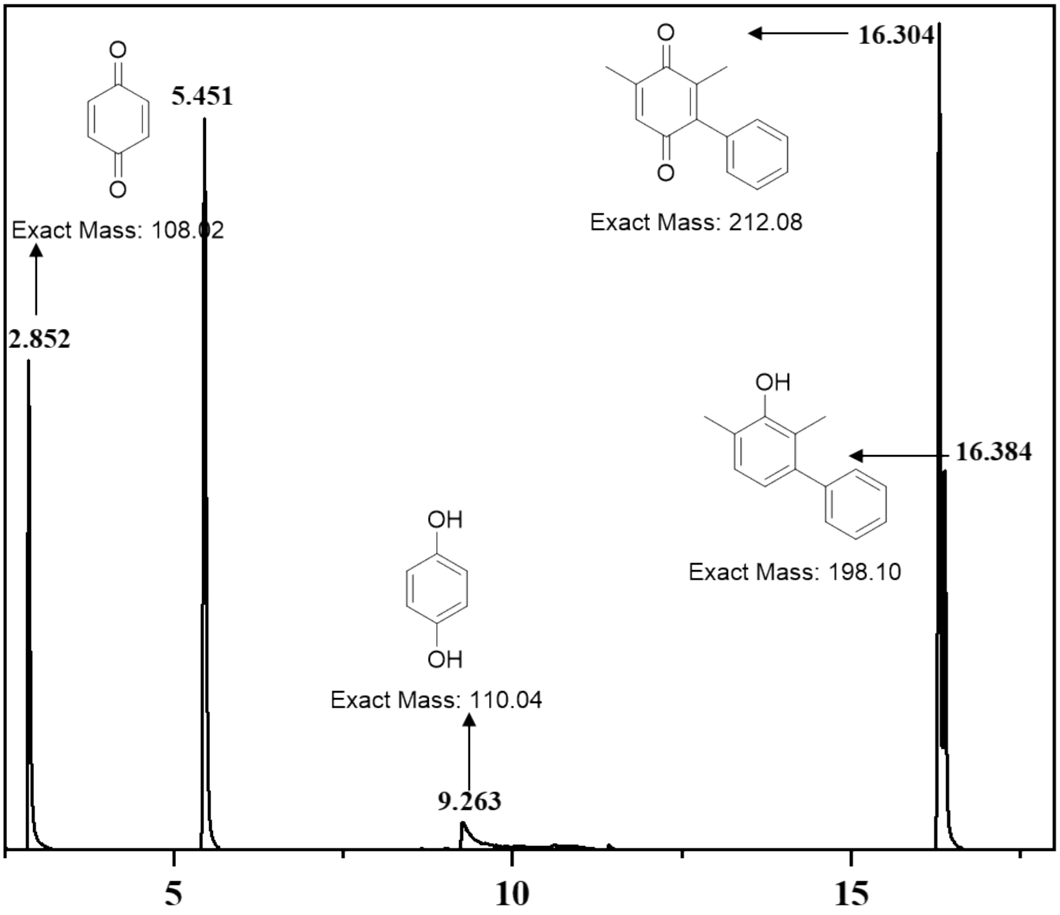


The corresponding mass spectrogram of the above GC-MS peak at 11.80 min:

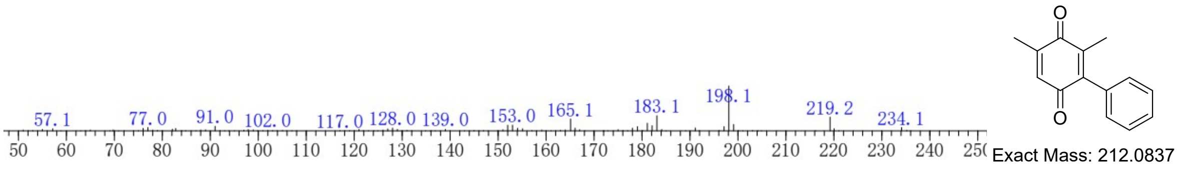


8)  **C22**

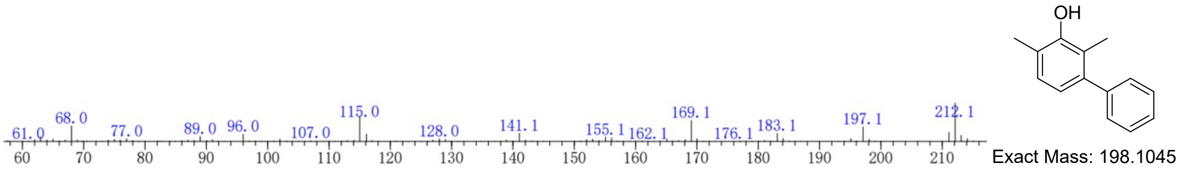
Exact Mass: 212.0837

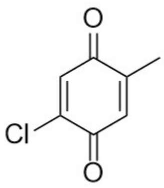


The corresponding mass spectrogram of the above GC-MS peak at 16.38 min:

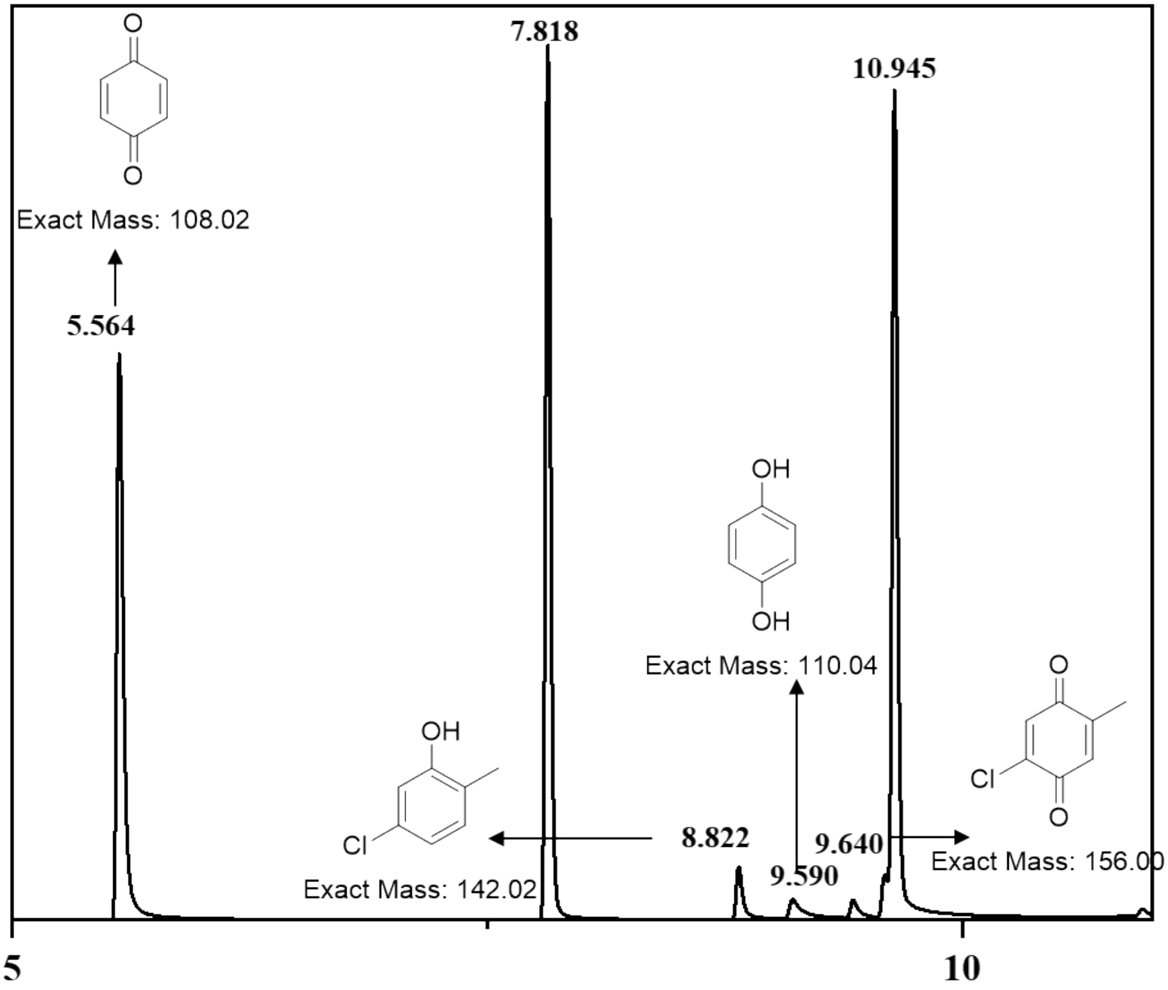


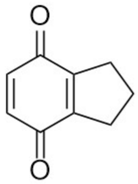
The corresponding mass spectrogram of the above GC-MS peak at 16.30 min:



9)  **C23**

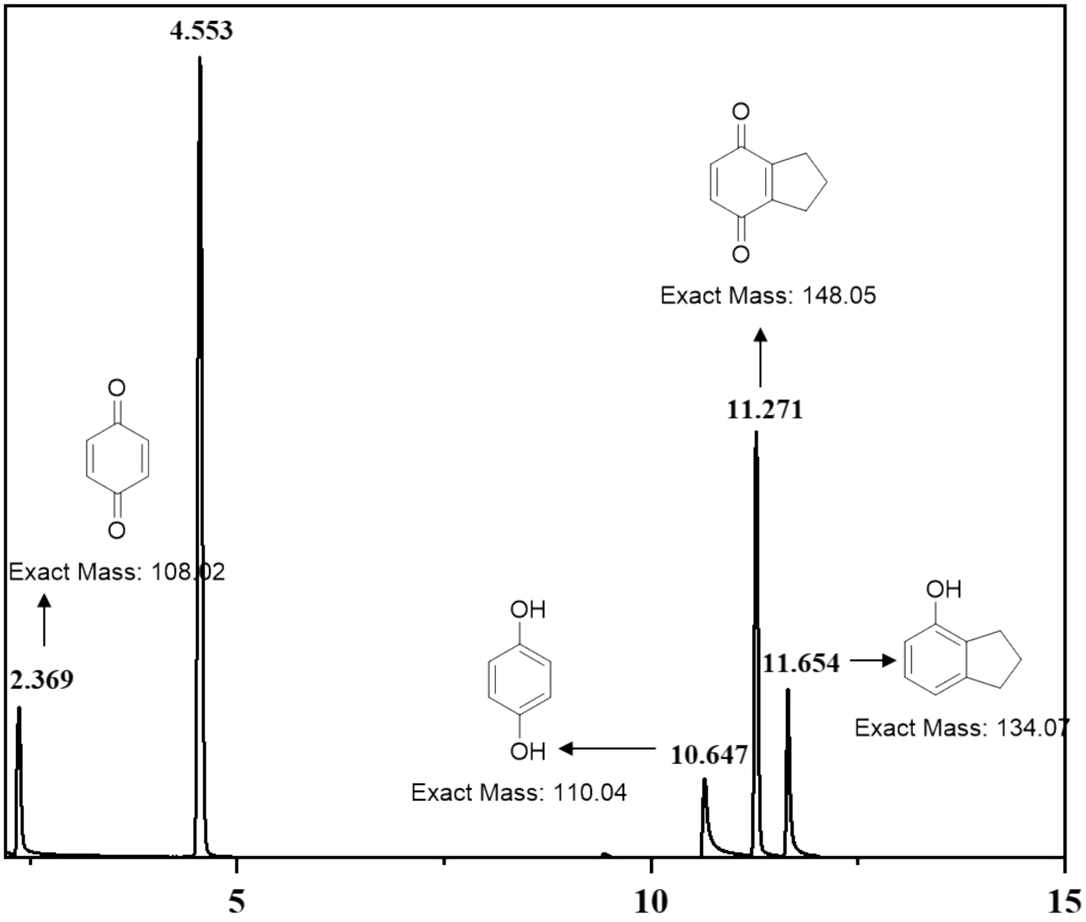
Exact Mass: 155.9978



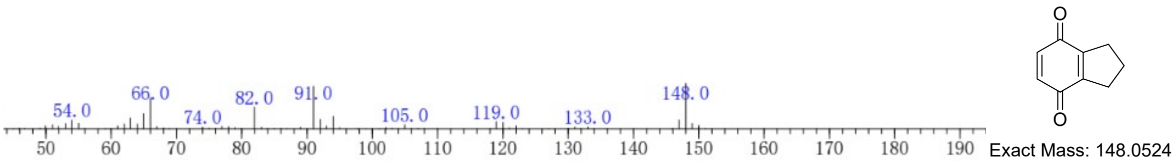


10) **C5**

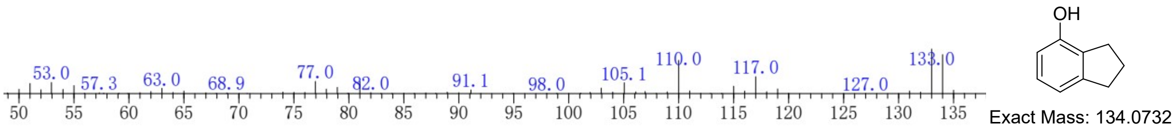
Exact Mass: 148.0524

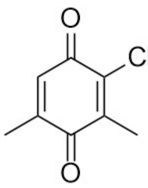


The corresponding mass spectrogram of the above GC-MS peak at 11.27 min:



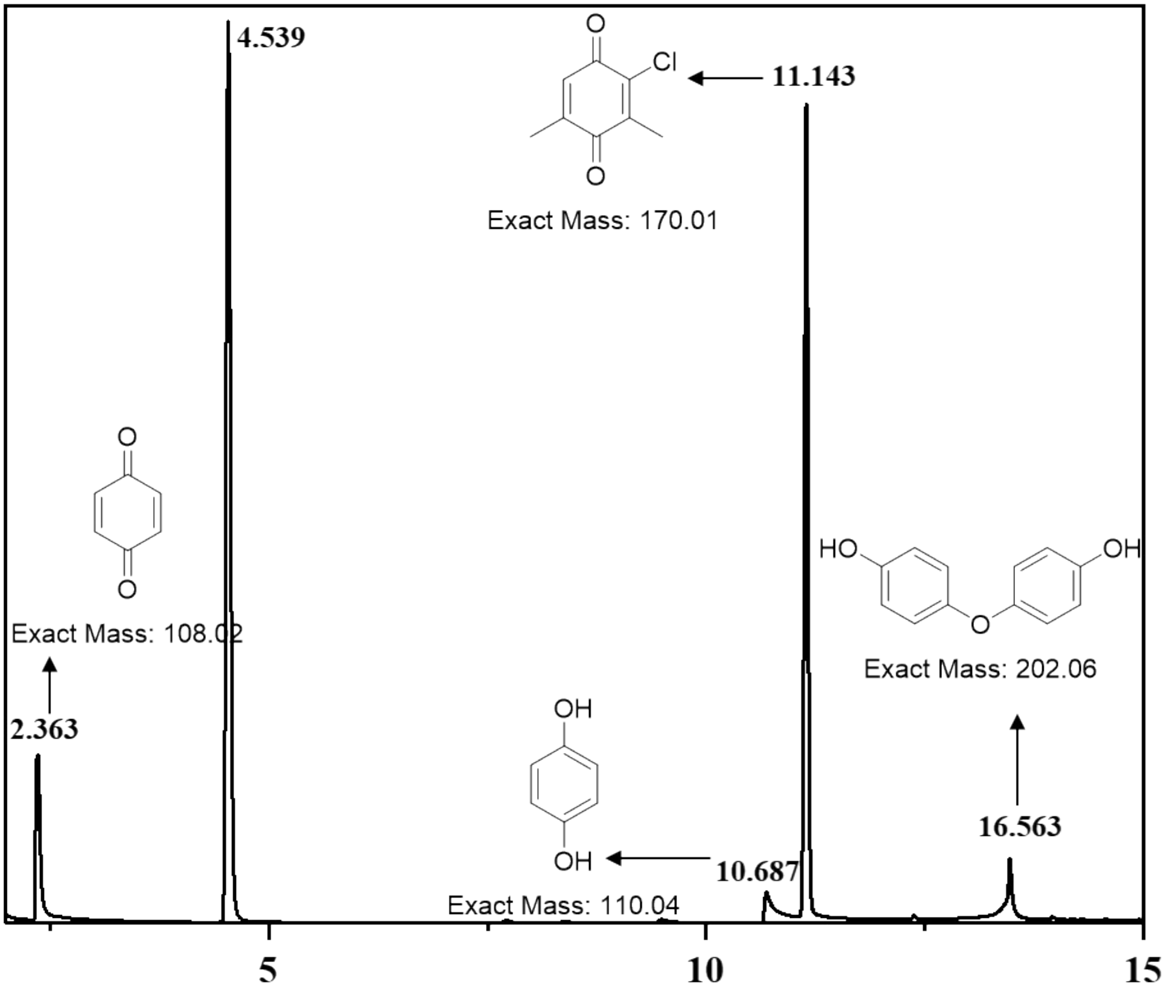
The corresponding mass spectrogram of the above GC-MS peak at 11.07 min:



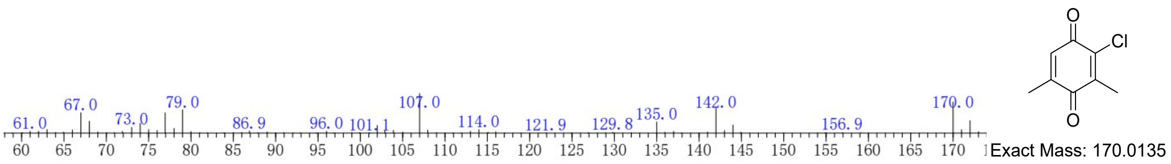


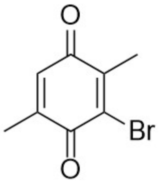
11) **C24**

Exact Mass: 170.0135

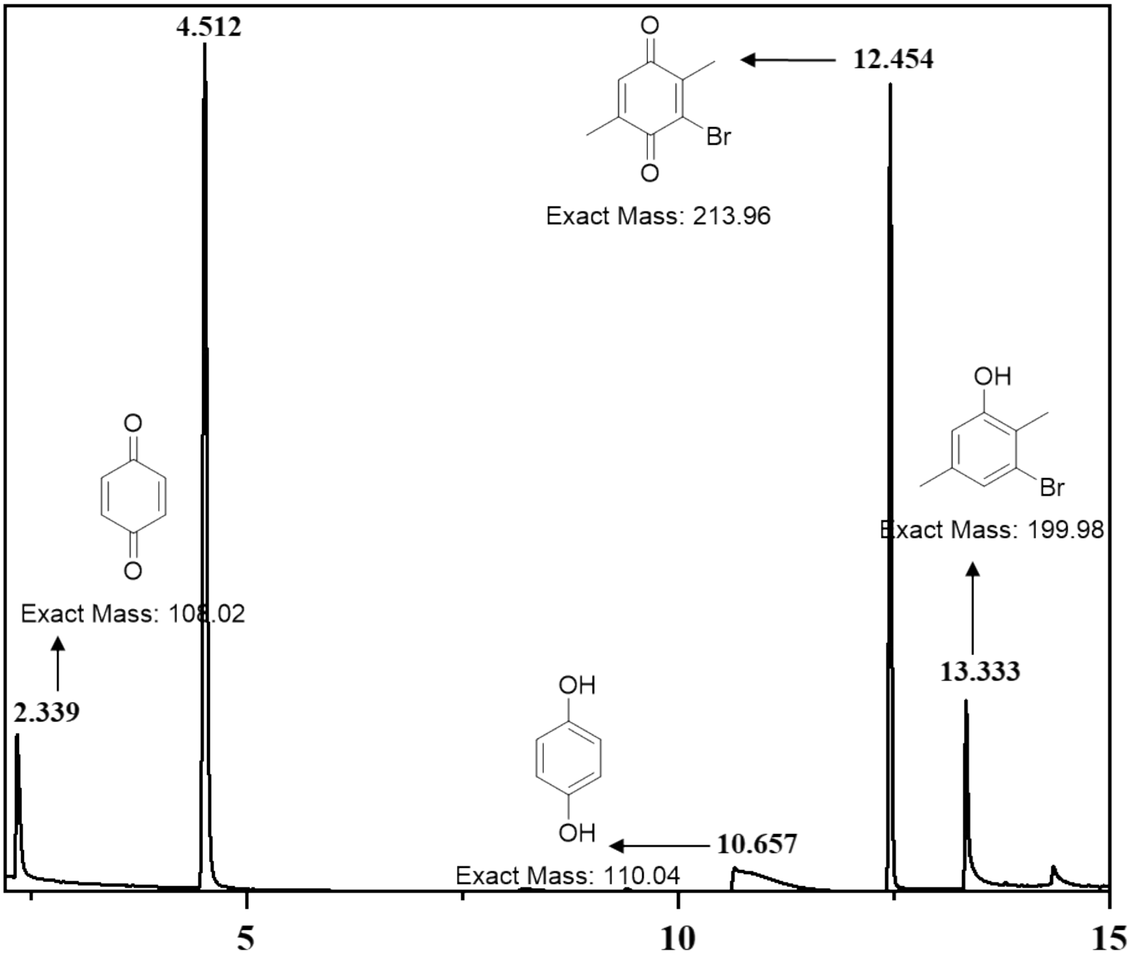


The corresponding mass spectrogram of the above GC-MS peak at 11.14 min:

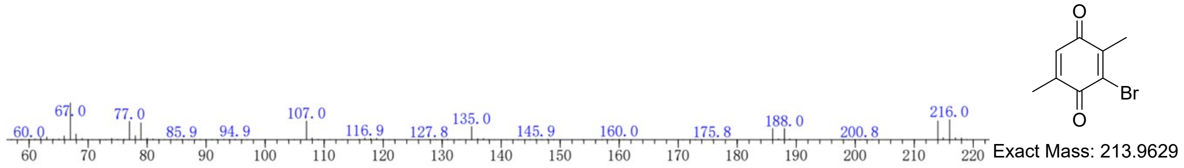


12)  **C27**

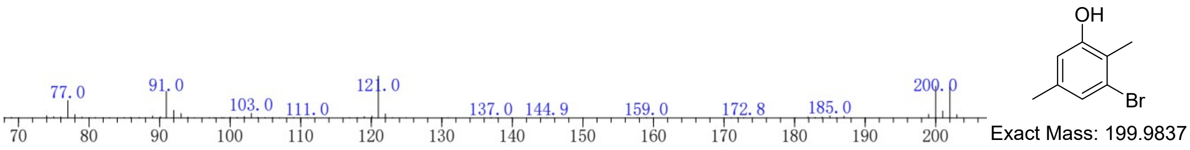
Exact Mass: 213.9629

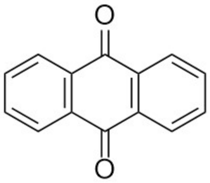


The corresponding mass spectrogram of the above GC-MS peak at 12.45 min:



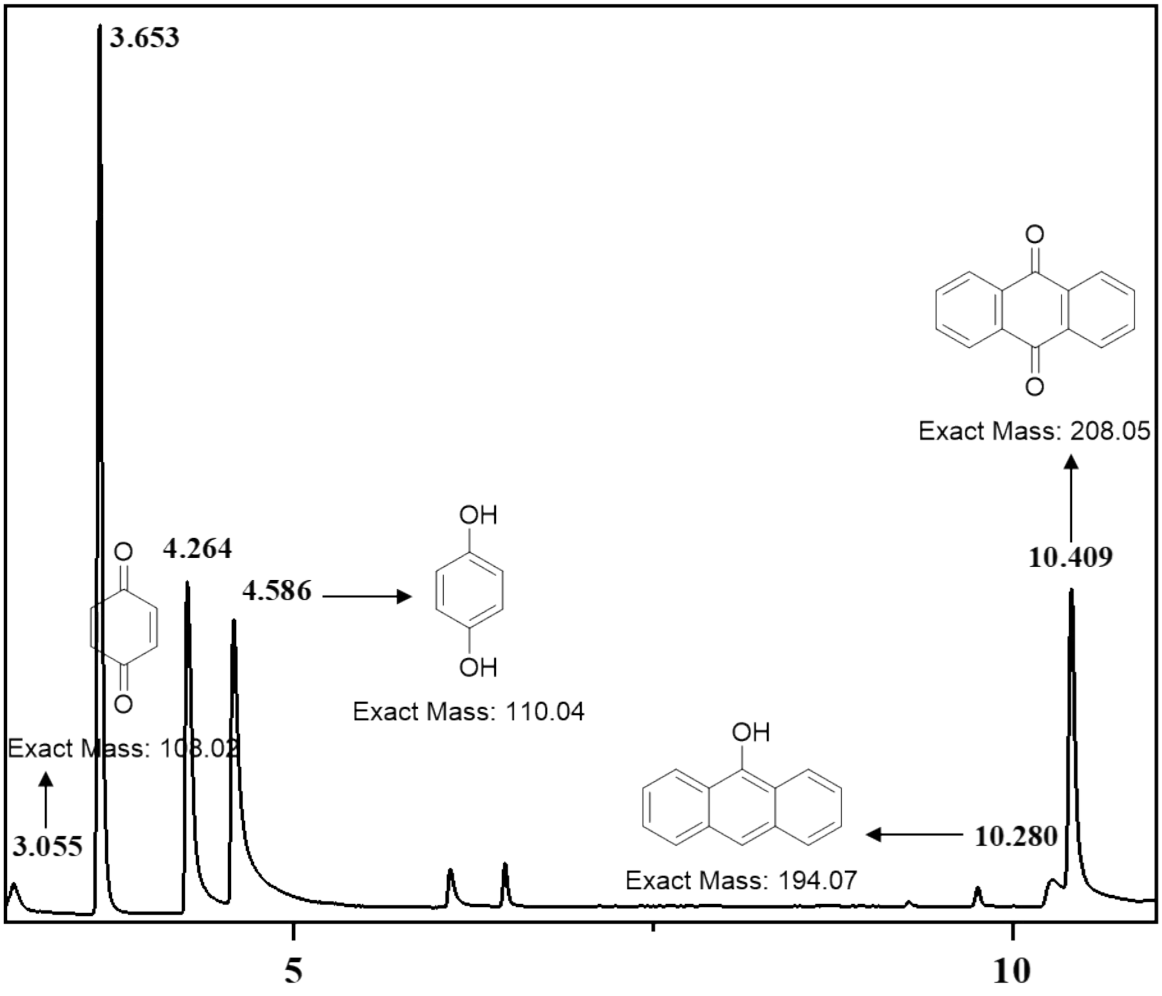
The corresponding mass spectrogram of the above GC-MS peak at 13.33 min:



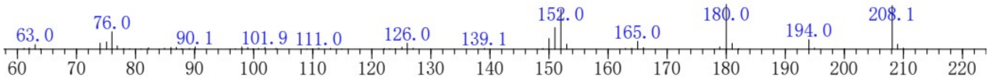


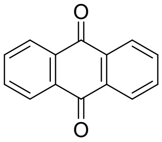
13) **C16**

Exact Mass: 208.0524

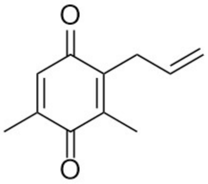


The corresponding mass spectrogram of the above GC-MS peak at 10.41 min:

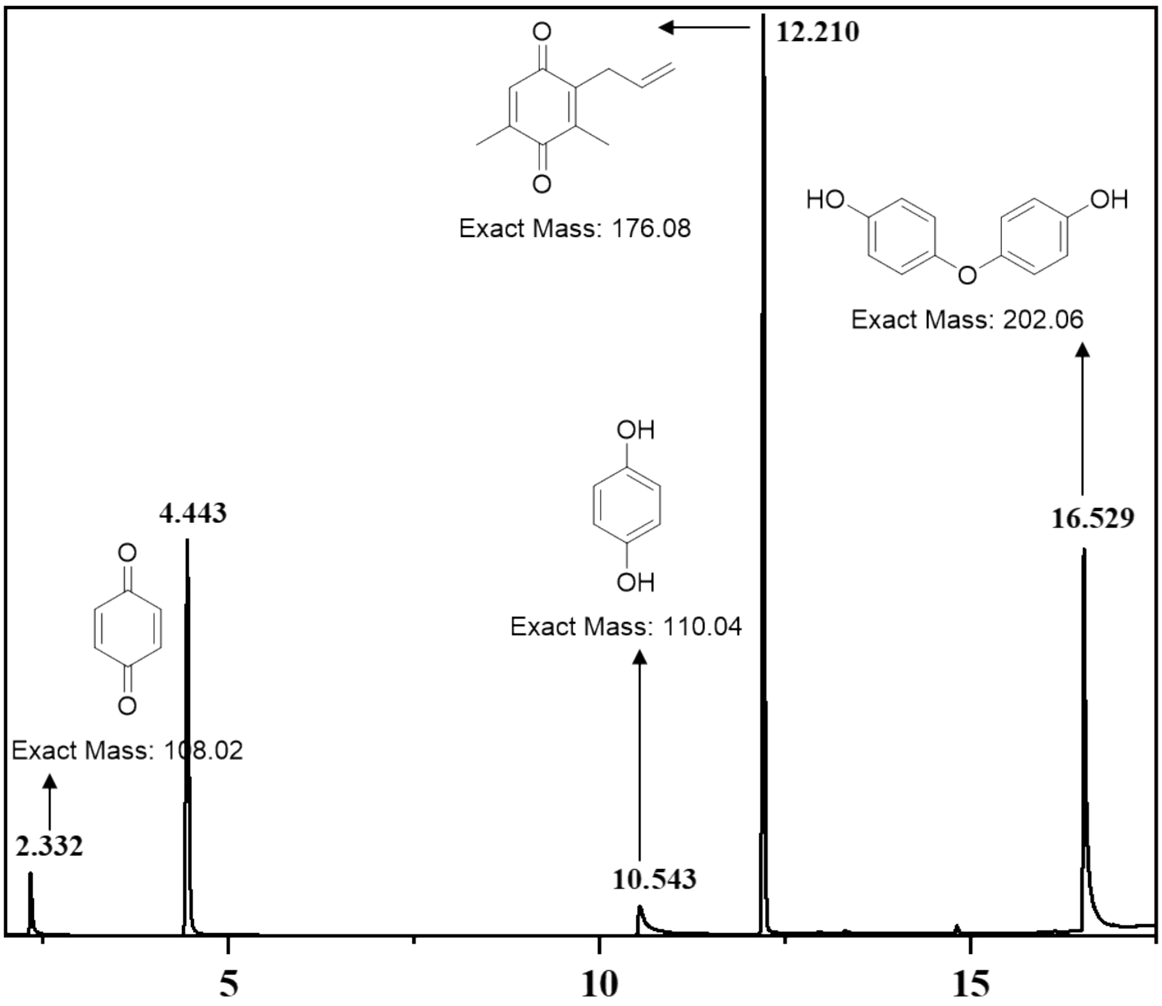




Exact Mass: 208.0524

14)  **C13**

Exact Mass: 176.0837



The corresponding mass spectrogram of the above GC-MS peak at 12.21 min: