

1 Supporting Information

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3 **Understanding of TEMPO-Electrocatalyzed Acceptorless**
4 **Dehydrogenation of Tetrahydroquinoline by In-situ Extractive**
5 **Electrospray Ionization Mass Spectrometry**

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26 **Electrochemical AD of 1-methyl-1,2,3,4-tetrahydroquinoline by EC-EESI**

27 **MS.....S5**

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1 **Materials and reagents**

2 HPLC grade acetonitrile was obtained from Fisher Chemical (USA). Lithium
3 perchlorate, TEMPO, tetrahydroquinoline, quinoline, 1,2-dihydroquinoline and 1-methyl-
4 1,2,3,4-tetrahydroquinoline were purchased from Acros Organics. The dimer authentic
5 compounds of THQ and the dehydrogenation products of 1-methyl-1,2,3,4-
6 tetrahydroquinoline were purchased from HEOWNS (Tianjin, China) for the MS/MS
7 detection. Reticulated vitreous carbon and Pt wire was achieved from Aidahengsheng
8 (Tianjin, China). Ultrapure water was used throughout the experiment (resistivity >18 MΩ
9 cm). All of the chemical reagents were of analytical grade and utilized without further
10 purification.

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12 **Apparatus**

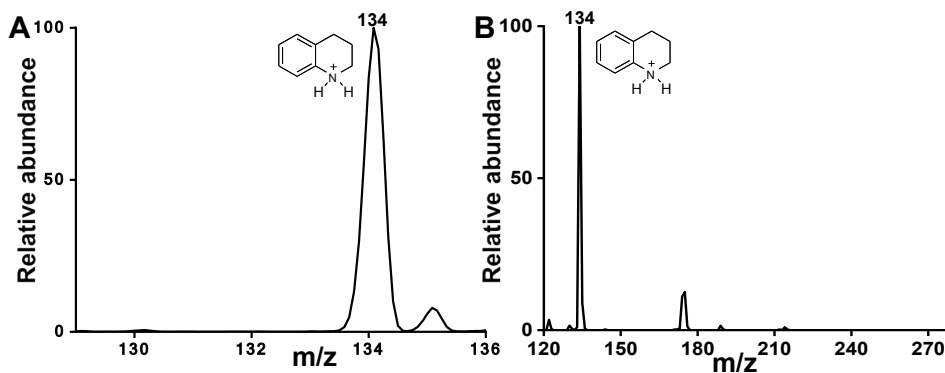
13 Experiments were performed by a LTQ XL linear ion trap instrument (Thermo Fisher
14 Scientific, San Jose, CA, USA) using a home-made ionization source. In addition, the
15 identification of ions was obtained by tandem mass spectrometry using collision induced
16 dissociation (CID). Voltametric measurements were performed with a CHI660E
17 electrochemical workstation from Chenhua Instruments Co. (Shanghai, China). A
18 saturated calomel electrode (SCE) (reference electrode), a Pt wire (auxiliary electrode)
19 and a glassy carbon electrode (GCE) with 4 mm diameter (working electrode) were used
20 for all electrochemical measurements. Uninterruptible power system (UPS) was obtained
21 from STKUPS (Shenzhen, China). The potentiostat was provided by RS Components Ltd
22 (Shanghai, China).

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24 **Electrochemical measurements**

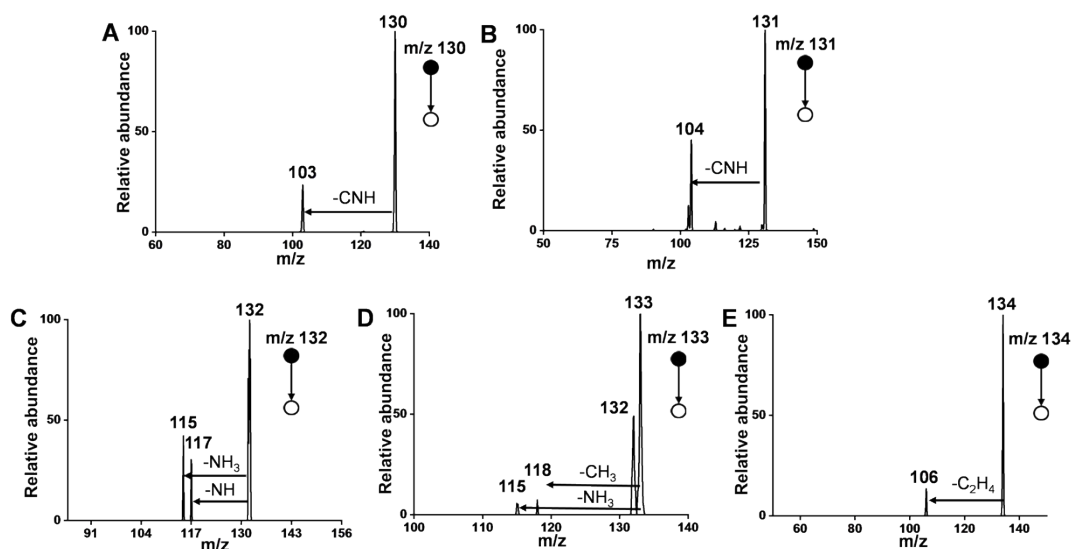
25 All voltametric measurements were employed in an electrochemical cell containing 9
26 mL of acetonitrile and 1 mL water with 0.1 M LiClO₄ added as a supporting electrolyte.
27 The scan rate was 50 mV/s. Before voltametric measurements, GCE was polished with
28 50 nm alumina slurry and then washed thoroughly with purified water and ethanol, which
29 provided a mirror-like surface. In addition, air in the reaction solution was removed by
30 bubbling nitrogen gas .

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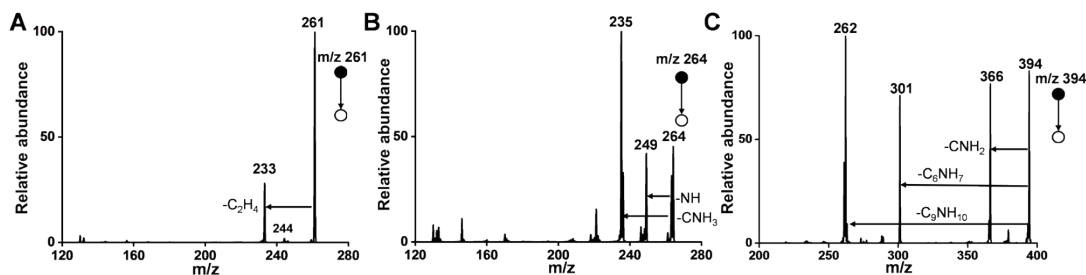
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2 **Figure S1.** Mass spectra of THQ at different concentrations without voltage applied to the
3 working electrode. (A) 2 μM THQ; (B) 2 mM THQ.

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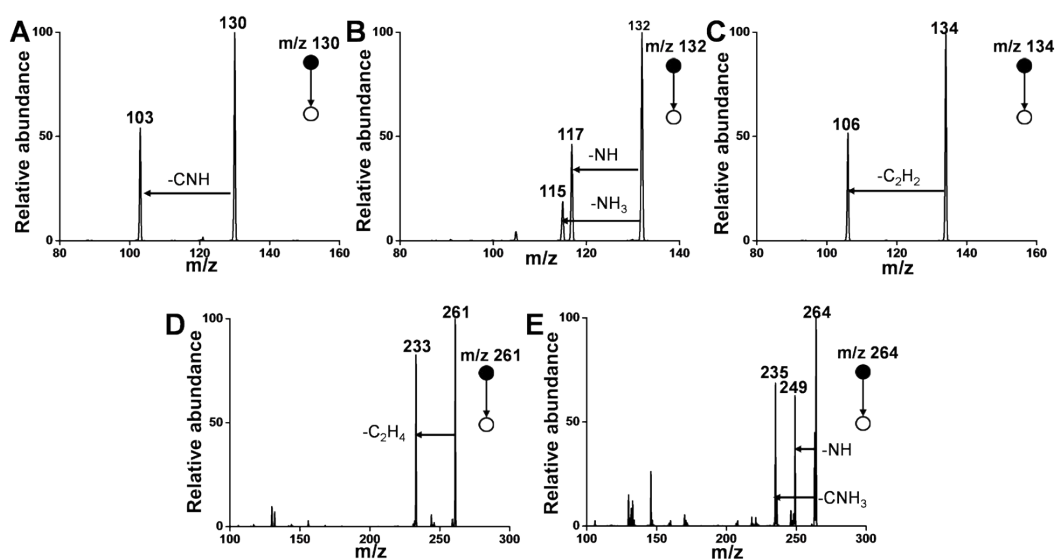
6
7 **Figure S2.** Structural confirmation of THQ-related ions by CID. (A) MS² CID of the ion at
8 m/z 130. (B) MS² CID of the ion at m/z 131. (C) MS² CID of the ion at m/z 132. (D) MS²
9 CID of the ion at m/z 133. (E) MS² CID of the ion at m/z 134.

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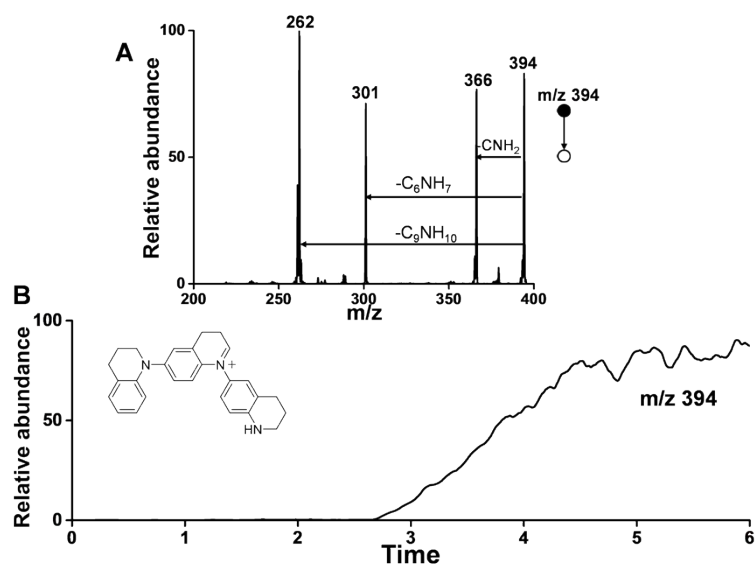
11
12 **Figure S3.** Structural confirmation on the oligomer species of THQ by CID. (A) MS² CID
13 of the ion at m/z 261. (B) MS² CID of the ion at m/z 264. (C) MS² CID of the ion at m/z
14 394.

1



2

3 **Figure S4.** MS/MS spectra of authentic species, including quinoline (m/z 130),
4 dihydroquinoline (m/z 132), THQ (m/z 134), and dimer species at m/z 261 and m/z 264.

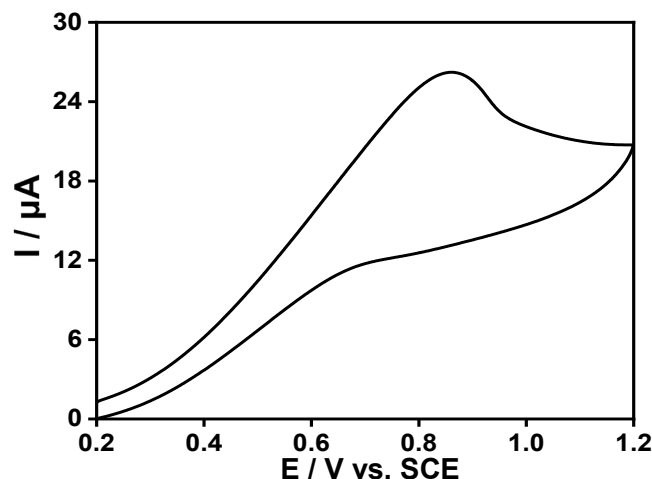


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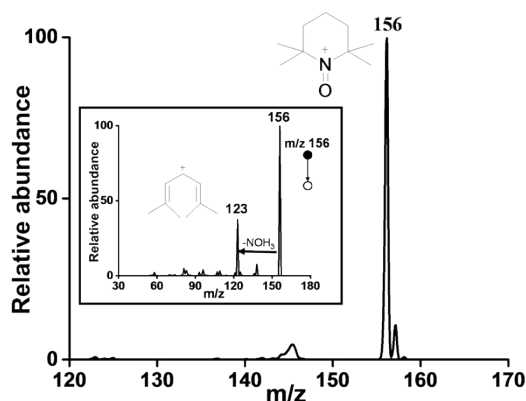
6 **Figure S5.** Characterizations of THQ electrochemical oxidation 2 mM THQ at 5 min.

7 (A) CID data for m/z 394. (B) EIC for THQ-THQ-THQ at m/z 394.

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 2 **Figure S6.** CV of 1,2-dihydroquinoline at 0.5 mM.
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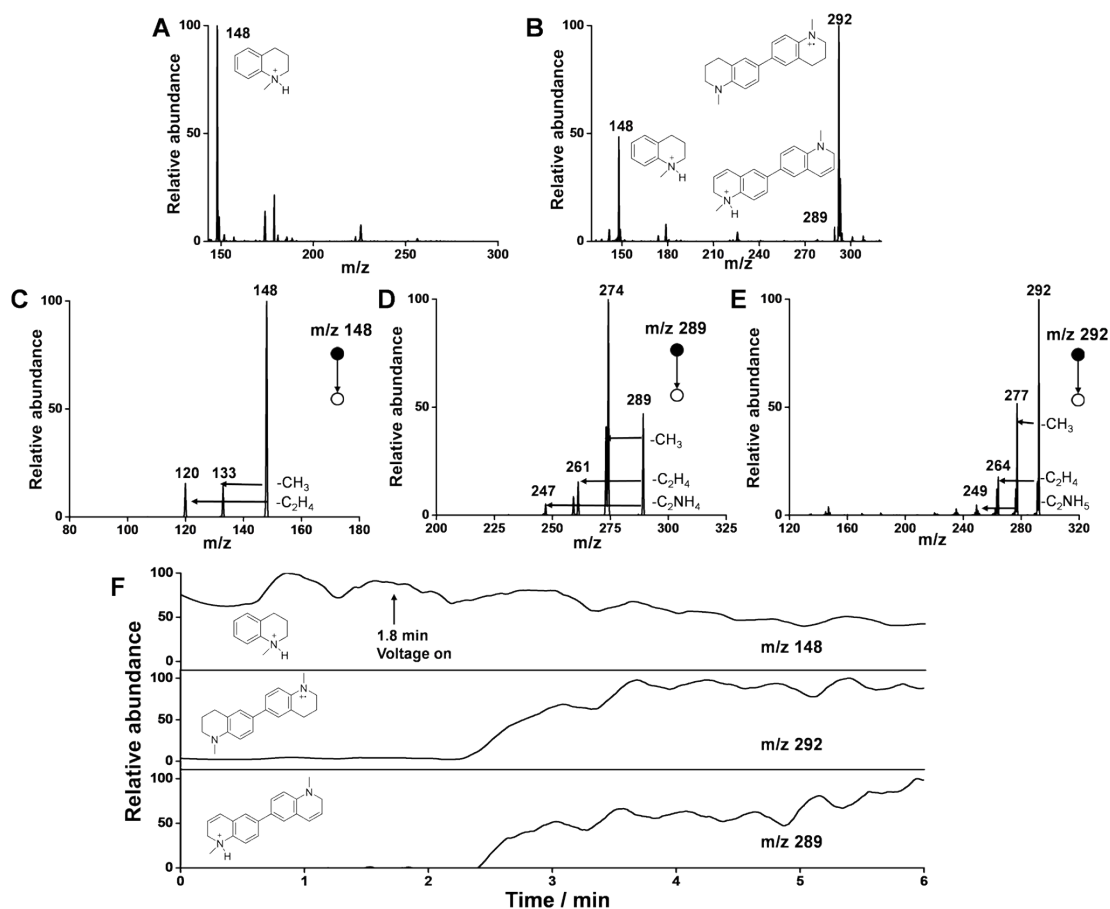


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 5 **Figure S7.** 2.0 V was applied to the working electrode in the 0.5 mM TEMPO solution.
 6 The inset is the CID of ions at m/z 156.

7
 8 **Electrochemical AD of 1-methyl-1,2,3,4-tetrahydroquinoline by EC-EESI**
 9 **MS**

10 The additional experiment on electrochemical AD of 1-methyl-1,2,3,4-
 11 tetrahydroquinoline (1MTHQ) has been carried out. As shown in Figure S8-A, for the
 12 detection of 1MTHQ before electrochemical AD reaction, we obtained significant
 13 peak of $[1MTHQ + H]^+$ at m/z 148. While 2.0 V was applied on the electrode, new
 14 ions at m/z 292 and m/z 298 were observed (Figure S8-B), which were demonstrated
 15 to be the dimer ions of the reactant by comparison with authentic compounds based
 16 on CID experiment (Figure S8-C to E). While we did not find the trimer of 1MTHQ,
 17 which should be due to the steric effect of methyl. Subsequently, the dynamic changes
 18 were also monitored by EC-EESI MS, which showed the increased signals of dimer

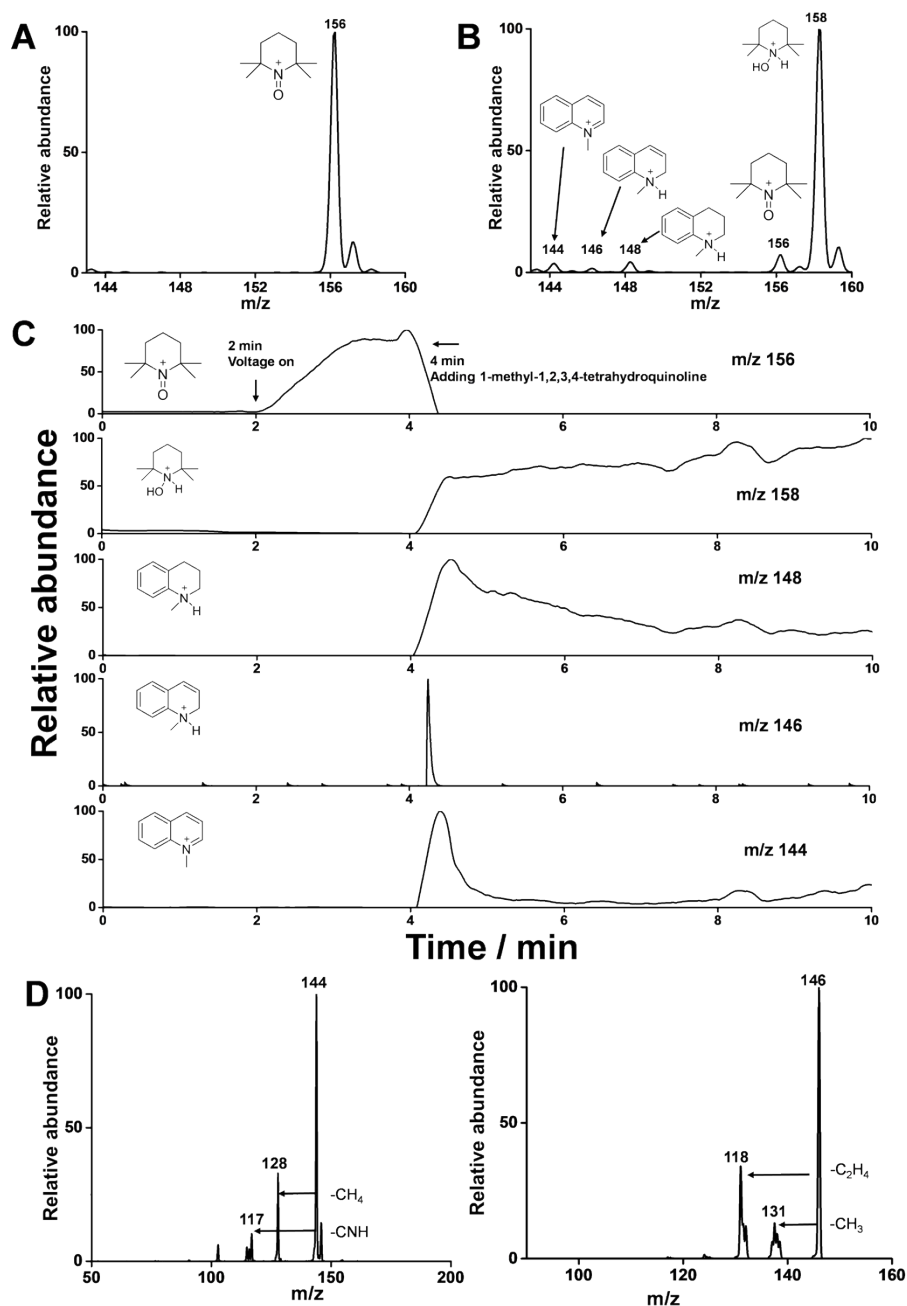
1 ions with the decrease of reactant ion at m/z 148 (Figure S8-F). Therefore, the
2 electrochemical AD was hardly employed without TEMPO, which was similar with
3 the THQ reaction demonstrated in Figure 3.



4
5 **Figure S8.** Electrochemical oxidation of 1MTHQ at 0.5 mM. (A) Mass spectrum of
6 the reactant before the reaction. (B) Electrocatalytic AD at 4 min. (C) CID data of m/z
7 148, 289 and 292. (D) Extracted ion chromatograms for m/z 148, 292 and 289.

8
9 Thereafter, with TEMPO added for electrochemical AD of 1MTHQ, we didn't
10 observe the significant intermediate ions, which was also similar with the results in
11 AD of THQ in Figure 4. Thus, the similar experiments with instantly amplified
12 concentration of $TEMPO^+$ have been employed further. As shown in Figure S9-A, the
13 instantly amplified concentration of $TEMPO^+$ (m/z 156) has been obtained before the
14 reactant of 1MTHQ added. Then, with the reactant added into $TEMPO^+$ system, new
15 ions including $[1MTHQ+H]^+$ (m/z 148) and $[TEMPOH+H]^+$ (m/z 158), intermediates
16 at m/z 146 as well as $[1\text{-Methylquinolinium}+H]^+$ m/z 144 were recorded. In addition,
17 the dynamic changes were also recorded by monitoring with EC-EESI MS (Figure
18 S9-C). The similar changes with that of THQ reaction (Figure 5C) was resulted, in

1 accordance with the proposed mechanism. Therefore, based on the reaction of another
 2 reactant with different structure to THQ, the proposed mechanism can be further
 3 confirmed.



4
 5 Figure S9. EC-EESI MS monitoring of electrochemical AD of 1MTHQ (0.5 mM)
 6 with TEMPO (0.5 mM) as catalyst. (A) Mass spectrum of the reaction system at 3
 7 min without 1MTHQ added. (B) Mass spectrum at 4.2 min with 1MTHQ added. (C)
 8 Extracted ion chromatograms for m/z 156, 158, 148, 146 and 144. (D) MS/MS spectra
 9 of species at m/z 144 and 146.

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