Supporting information for

A reactive matrix for in-situ chemical derivatization and specific detection of cis-diol compounds by matrix-assisted laser desorption/ionization mass spectrometry

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1. Materials and Reagents

6-Quinolineboronic acid pinacol ester was purchased from Suzhou Sukailu Chemical Technology Co., Ltd. (Jiangsu, China). Methyl iodide was purchased from Zesheng Technology Co., Ltd. (Anhui, China). Methanol (MeOH), acetonitrile (ACN), diethyl ether, hydrochloric acid, and glycerol were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Trifluoroacetic acid (TFA), 2,5-dihydroxybenzoic acid (DHB), ethylene glycol, caffeic acid, dopamine hydrochloride, epinephrine hydrochloride, DL-norepinephrine hydrochloride, DL-xylose, baicalein, and luteolin were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). 1,3-Propanediol was purchased from Bide Medical Technology Co., Ltd. (Shanghai, China). Catechol, and glucose were bought from Fuchen Chemical Reagent Co., Ltd. (Tianjin, China). Benzocatechol, and adenosine were purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). Xylitol, and sorbitol were purchased from Xianding Biotechnology Co., Ltd. (Shanghai, China). DL-Dithiothreitol was purchased from Sigma-Aldrich (St. Louis, MO, USA). Catechin was purchased from Chengdu Push Bio-technology Co., Ltd. (Sichuan, China). Sugar-free foods were sourced from local supermarkets.

2. Sample Preparation

Ethylene glycol, 1,3-propanediol, glycerol, catechol, 1,2-dihydroxynaphthalene, caffeic acid, baicalein, luteolin, and catechin (10 mM) were dissolved in methanol, while dopamine hydrochloride, epinephrine hydrochloride, noradrenaline hydrochloride, xylose, glucose, adenosine, xylitol, dithiothreitol, and sorbitol (10 mM)

were prepared in water as stock solutions. All analyte solutions were stored at 4 °C prior to use. For MALDI-MS analysis, 1 μL of sample solution was mixed with 1 μL of matrix solution and incubated at room temperature for 10 min. Then, 1 μL of the mixed solution was deposited on the MALDI plate and followed by air drying before analysis.

3. Matrix Characterization

The NMR spectra of BMQI were acquired on JNM- ECZ500R/S1 spectrometer. Chemical shifts (δ) were expressed in ppm. DMSO-*d6* (2.5 ppm for 1 H, 40 for 13 C) with 1 drop of D_2O were used to calibrate the chemical shifts. The specific chemical shifts were as follows:

BMQI, ^{1}H NMR (DMSO-d_6 with 1 drop of D_2O, 500 MHz): δ 9.50 (d, 1H, J = 5.6 Hz), 9.26 (d, 1H, J = 8.3 Hz), 8.78 (s, 1H), 8.54 (d, 1H, J = 10.0 Hz), 8.44 (d, 1H, J = 8.9 Hz), 8.11 (dd, 1H, J = 8.3, 5.8 Hz), 4.62 (s, 3H) ppm. ^{13}C NMR (DMSO-d_6 with 1 drop of D_2O, 126 MHz): δ 150.59, 147.78, 140.16, 139.45, 137.01, 128.80, 122.06, 118.04, 45.44 ppm.

The FT-IR spectroscopy investigation was performed using a Nicolet 6700 FT-IR spectrometer (Thermo, USA). The UV-Vis absorption spectra were measured using a UV-9000S spectrophotometer (Metash, Shanghai).

4. Optimization of Experimental Conditions

Taking 2 μmol/mL catechol as a template, three parallel experiments were carried out, and six mass spectra for each sample point were obtained. To explore the influence of the main solvent on derivatization reaction, BMQI (2 mg/mL) was prepared in H_2O,

MeOH/H_2O (1/1, v/v), EtOH/H_2O (1/1, v/v), ACN/H_2O (1/1, v/v), and THF/H_2O (1/1, v/v) solutions, respectively. Catechol (2 μmol/mL) was dissolved in H_2O, MeOH, EtOH, ACN, and THF, respectively. And then, 1 μL of matrix solutions was mixed with the 1 μL of analyte solutions of the same solvent followed by deposition on a target plate for MALDI-MS detection. The solvents ratio after mixing the samples were 100% H_2O, 75% MeOH-H_2O, 75% EtOH-H_2O, 75% THF-H_2O, and 75% ACN-H_2O.

Figures

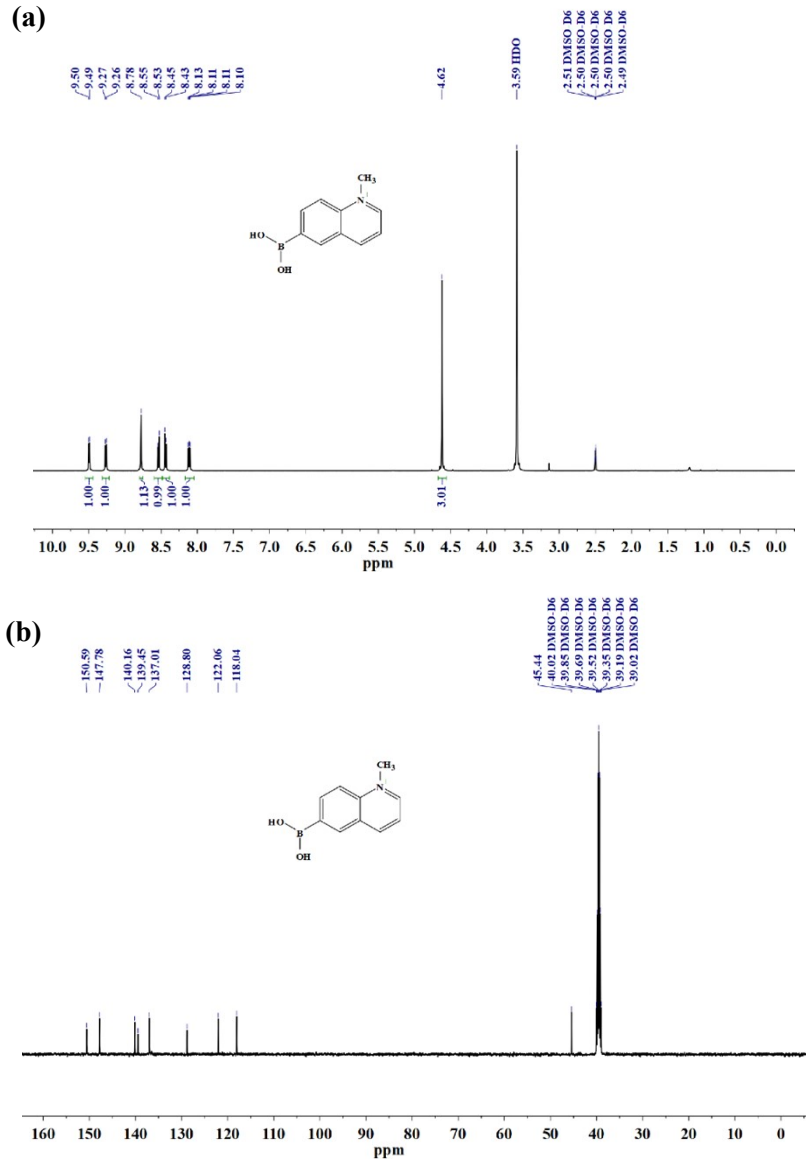


Fig. S1. (a) ^{1}H and (b) ^{13}C NMR spectra of BMQI.

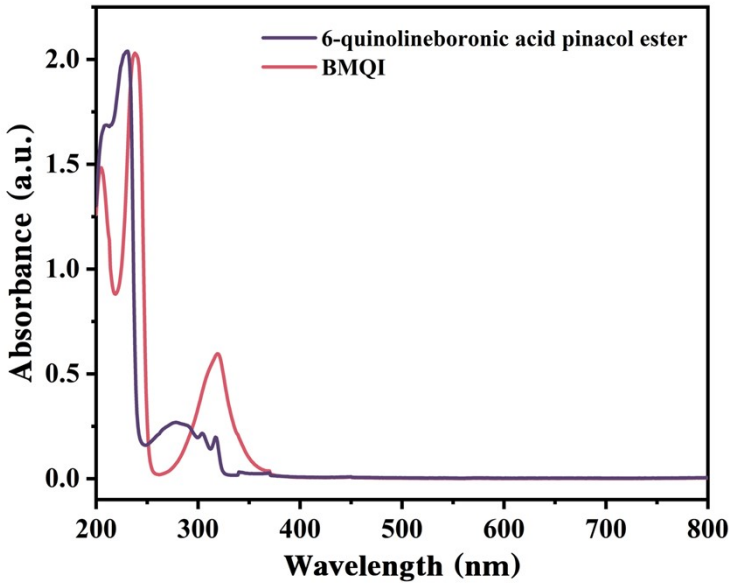


Fig. S2. UV-vis absorption spectra of 6-quinolineboronic acid pinacol ester and BMQI in solution.

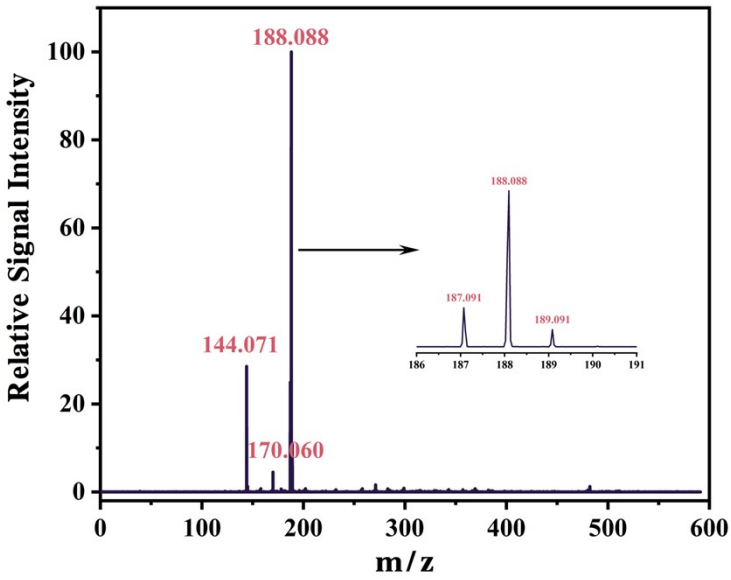


Fig. S3. MALDI-MS spectrum of BMQI (inset: isotope pattern of the boron atom).

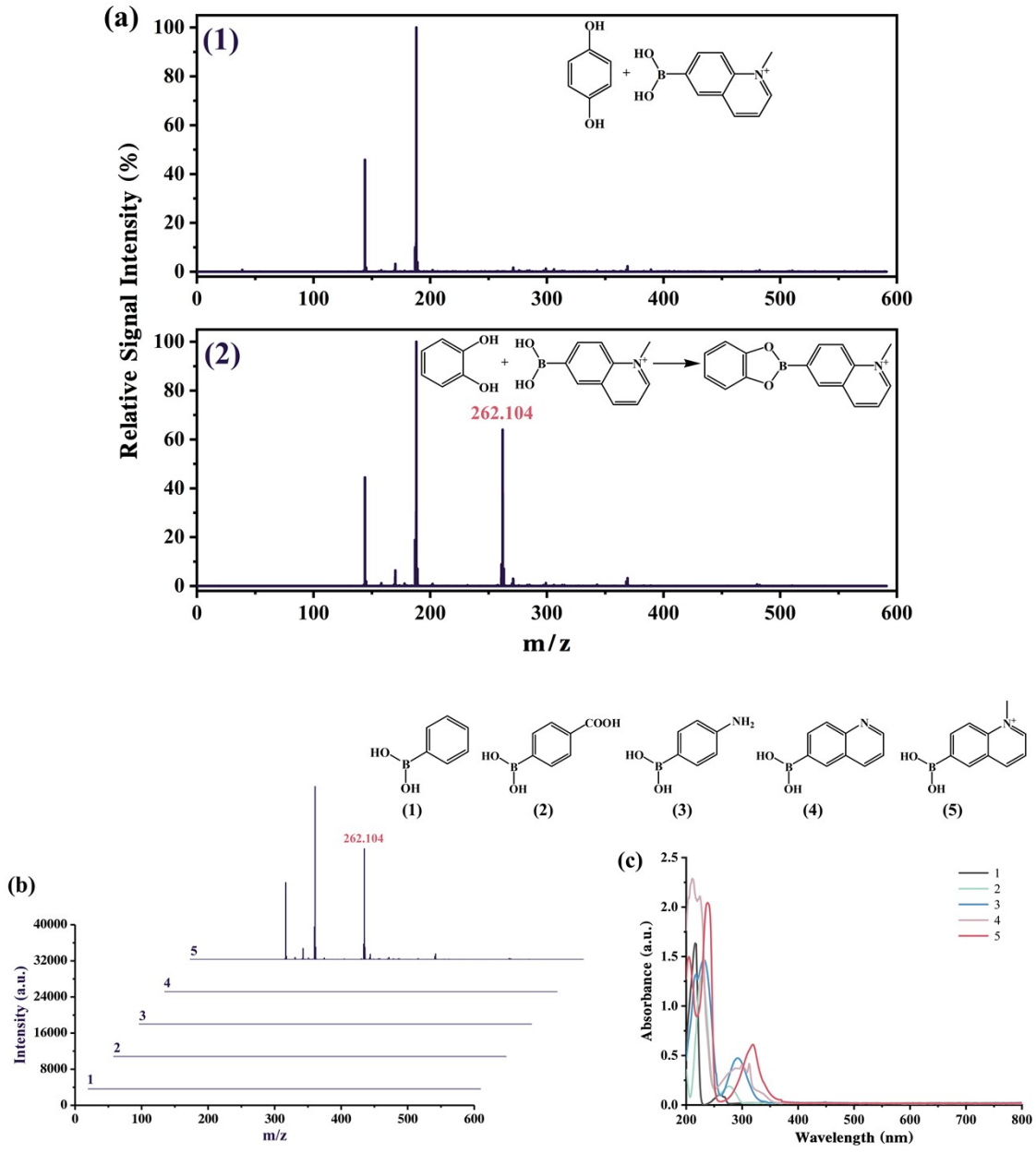
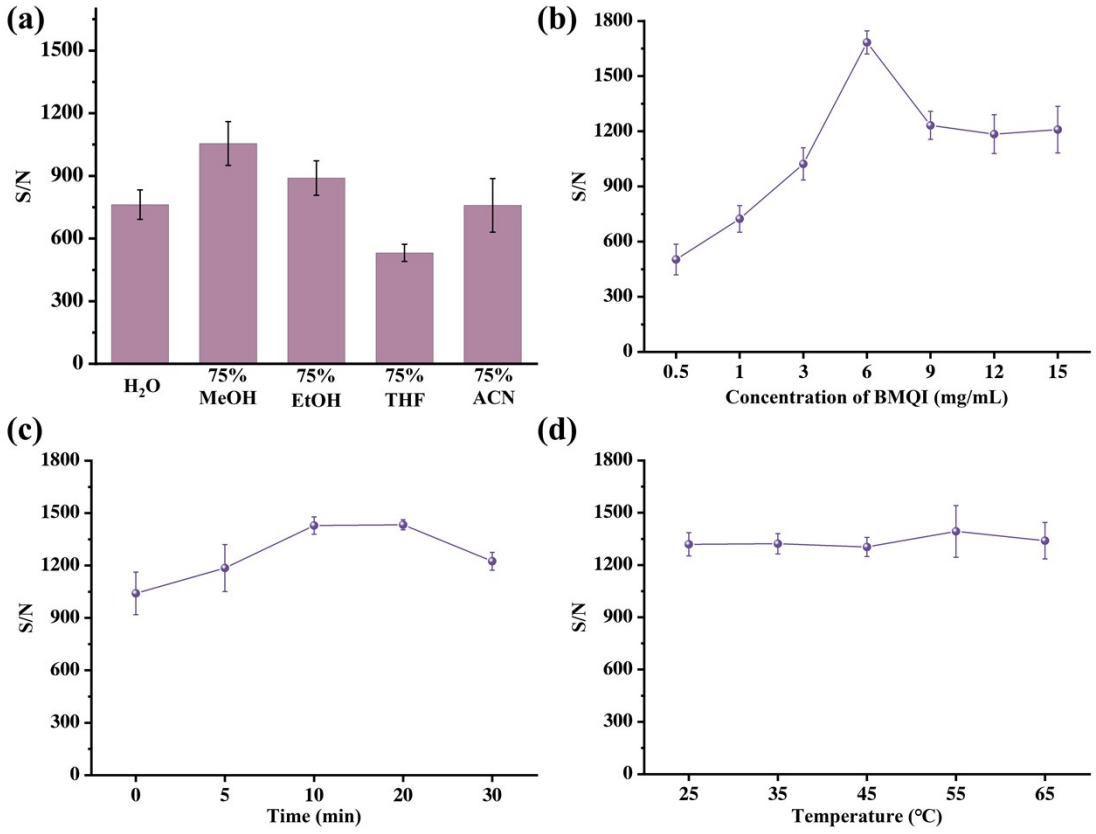


Fig. S4. (a) MALDI-MS spectra of (1) hydroquinone and (2) catechol using BMQI as reactive matrix, the amounts of hydroquinone and catechol were 1 nmol. (b) MALDI-MS spectra of catechol using boronic acid organic compounds as the matrices, (c) UV-Vis absorption spectra of boronic acid organic compounds, including (1) phenylboronic acid, (2) p-carboxyphenylboronic acid, (3) p-aminophenylboronic acid, (4) quinoline-6-boronic acid, and (5) BMQI, the concentrations of all boronic acid

112 compounds were 6 mg/mL.



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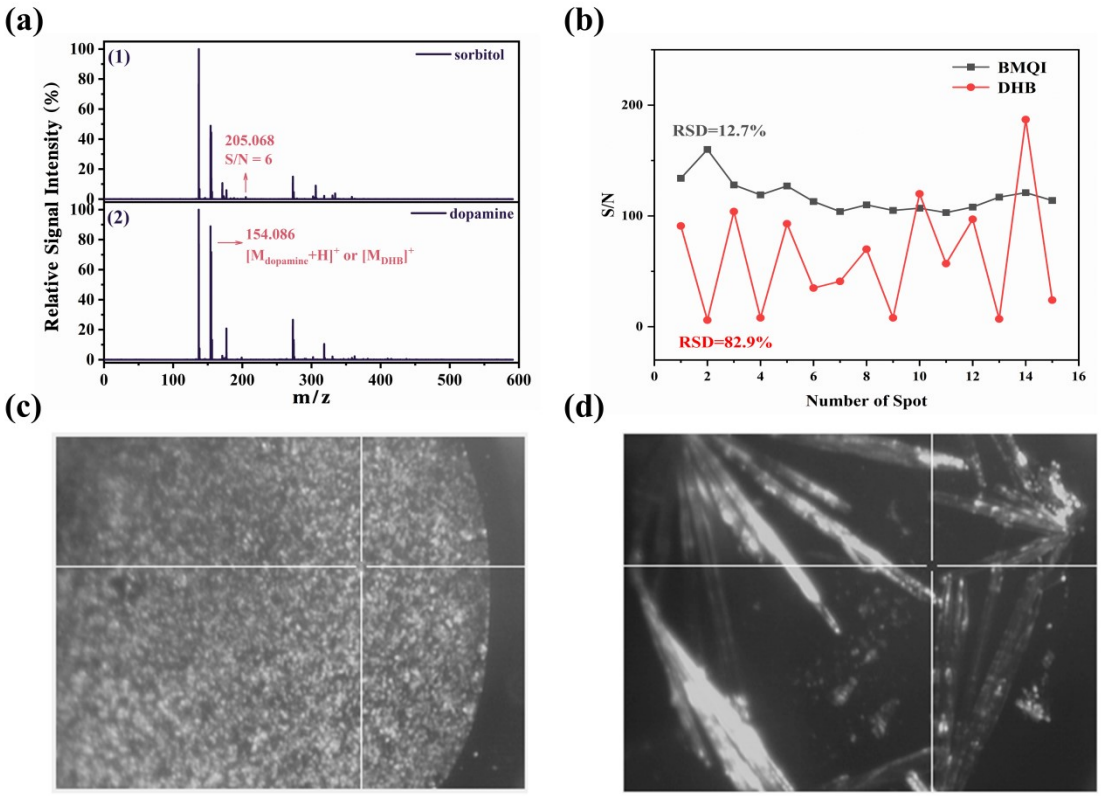
114 **Fig. S5.** The S/N ratio of 2 μmol/mL catechol by varying the reaction conditions,

115 including (a) solvent type (the solvents ratio after mixing the samples were: 100%

116 H_2O, 75% MeOH-H_2O, 75% EtOH-H_2O, 75% THF-H_2O, and 75% ACN-H_2O), (b)

117 concentration of BMQI, (c) reaction time, and (d) drying temperature.



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119 **Fig. S6.** (a) MALDI-MS spectra of (1) sorbitol and (2) dopamine using DHB as

120 matrix. (b) The S/N ratio of sorbitol repeatedly acquired from 15 different sample

121 spots using DHB (red line) as matrix and BMQI (gray line) as reactive matrix in

122 positive ion mode, the amounts of sorbitol and dopamine were 1 nmol. Photographs

123 of the sample spots using (c) BMQI as a reactive matrix and (d) DHB as the matrix.

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