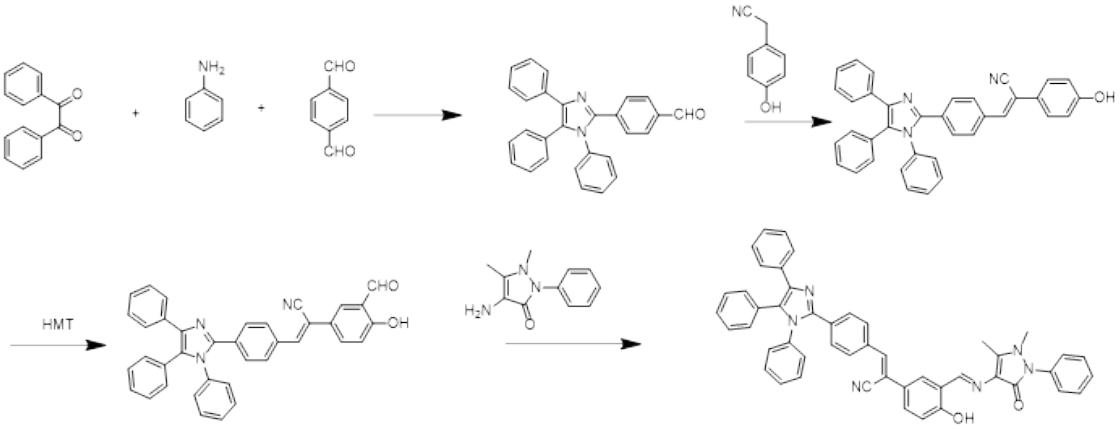
Electronic Supplementary Material (ESI) for Analytical Methods.

Supplementary Information

Highly Selective and Sensitive Detection of Arsenite Ions (III) Using a Novel Tetraphenylimidazole-based Probe

Rong Song[ab], Yeshuo Ma[a], Anyao Bi[ab], Bin Feng[ab], Liu Huang[ab], Shuai Huang[ab], Xueyan Huang[ab], Deling Yin[a], Fei Chen*[ab], and Wenbin Zeng*[ab]

[a]Xiangya School of Pharmaceutical Sciences, Central South University, Changsha, 410013, P. R. China.
[b]Hunan Key Laboratory of Diagnostic and Therapeutic Drug Research for Chronic Diseases, Changsha 410078, China



Scheme S1. Synthesis routes of the probe **TBAB**.

*Synthesis of compound **TB**（4-(1,4,5-triphenyl-1H-imidazol-2-yl)benzaldehyde）*

Benzil (2.10 g, 10 mmol), tetraphthalaldehyde (1.30 g, 10 mmol), and 20 mL of glacial acetic acid were added into a 100 mL round bottom flask and stirred at room temperature for one hour. The reaction system was added with ammonium acetate (2.00 g, excess), 10 mL of aniline, 5 mL of acetic acid. The reaction was refluxed at 120 °C. After 8 hours, the reaction was quenched with 200 mL of ice water, and was adjusting the pH to neutral with 0.2 M sodium hydroxide solution, then was extracted with ethyl acetate. After dried over $MgSO_4$, the organic layers were purified by silica gel column chromatography (petroleum ether: ethyl acetate=10:1) to offer a yellow solid (1.2 g, compound **TB**, white solid). ^{1}H NMR (500 MHz, DMSO-*d*6) δ 9.96 (s, 1H), 7.82 (d, J = 8.3 Hz, 2H), 7.59 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 7.5 Hz, 2H), 7.39 – 7.34 (m, 3H), 7.34 – 7.30 (m, 5H), 7.27 (t, J = 7.1 Hz, 4H), 7.20 (t, J = 7.3 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 192.99, 145.19, 138.02, 136.85, 136.06, 135.74, 134.53, 132.82, 131.58, 130.50, 129.82, 129.78, 129.54, 129.15, 129.09, 128.98, 128.96, 128.71, 127.17, 126.86

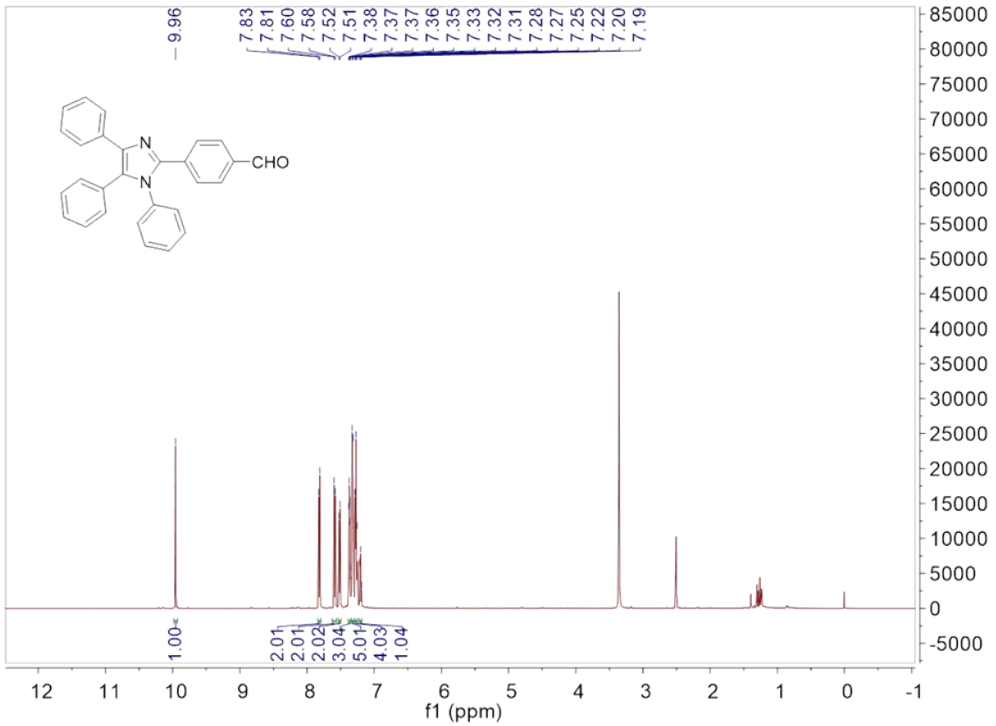


Figure S1. [1]H NMR spectrum of compound **TB** in DMSO-d6.

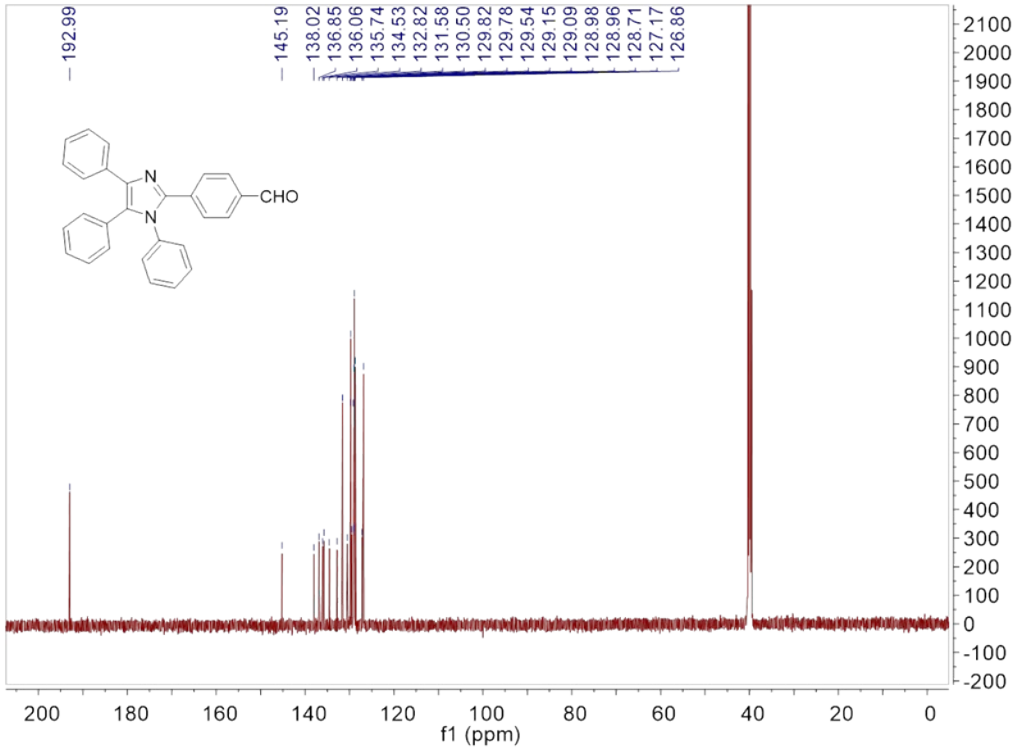


Figure S2. [13]C NMR spectrum of compound **TB** in DMSO-d6.

*Synthesis of compound **TBS**（(Z)-2-(4-hydroxyphenyl)-3-(4-(1,4,5-triphenyl-1H-imi dazol-2-yl)phenyl)acrylonitrile）*

Compound **TB** (0.80 g, 2 mmol) in 10 mL of methanol was added with potassium methoxide (1 g, excess) and p-hydroxyphenylacetonitrile (0.26 g, 2 mmol). The reaction mixture was stirred and refluxed at 90°C for 8 hours. The product was detected by TLC. The reaction was quenched by 100 mL of ice water and adjusted the pH to neutral by dilute hydrochloric acid, then extracted with ethyl acetate. The final purification was by silica gel column chromatography (chloroform: methanol = 50:1) to yield compound **TBS** (0.62 g, yield 58.4%, a white solid).

*Synthesis of compound **TBS-CHO** ((Z)-2-(3-formyl-4-hydroxyphenyl)-3-(4-(1,4,5-triphenyl-1H-imidazol-2-yl)phenyl)acrylonitrile*

Compound **TBS** (0.5 g, 1 mmol) in a 50 mL round bottom flask was added with 10 mL trifluoroacetic acid, then added with hexamethylenetetramine (1 g, excess). The reaction mixture was stirred and reflux at 90°C for 4 hours.The product was detected by TLC. Pour 100 mL of ice water to quench the reaction, adjust the pH to neutral with 0.2 M sodium hydroxide solution, extracted with dichloromethane, The final purification was by silica gel column chromatography (petroleum ether: ethyl acetate = 10:1) to yield a yellow solid **TBS-CHO** (0.4 g, yield 80.7%). ^{1}H NMR (500 MHz, DMSO-d6) δ 11.24 (s, 1H), 10.33 (s, 1H), 7.97 (s, 1H), 7.90 (s, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.51 (t, J = 8.2 Hz, 4H), 7.38 (d, J = 3.9 Hz, 3H), 7.32 (m, 5H), 7.27 (m, 5H), 7.14 (d, J = 8.2 Hz, 2H).

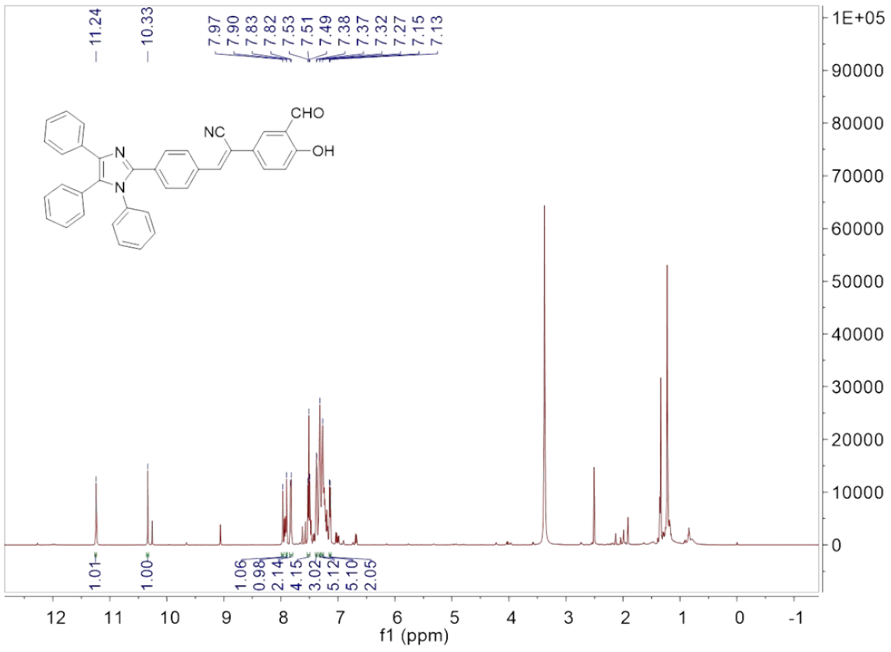


Figure S3. ^{1}H NMR spectrum of compound **TB** in DMSO-d6.

Synthesis of the probe ***TBAB*** *（(Z)-2-(3-((E)-((1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)imino)methyl)-4-hydroxyphenyl)-3-(4-(1,4,5-triphenyl-1H-imidazol-2-yl)phenyl)acrylonitrile）*

TBS-CHO (300 mg, 0.5 mmol) in 2 mL anhydrous methanol was mixed with 4-Aminoantipyrineone (200 mg, 1 mmol) ,then 10.5 mL of anhydrous methanol was added. The reaction mixture was stirred and refluxed at room temperature for 4 hours. When the formation of precipitation was observed, the reaction was quenched. The obtained yellow solid was washed with ice methanol. After dried over $MgSO_4$, the final product was purified to yield a yellow solid (0.4 g, yield 78.9%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.65 (s, 1H), 9.90 (s, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.69 – 7.59 (m, 4H), 7.59 – 7.49 (m, 4H), 7.42 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 8.9 Hz, 3H), 7.35 – 7.22 (m, 10H), 7.13 (dd, J = 23.6, 7.4 Hz, 4H), 7.04 (d, J = 8.7 Hz, 1H).

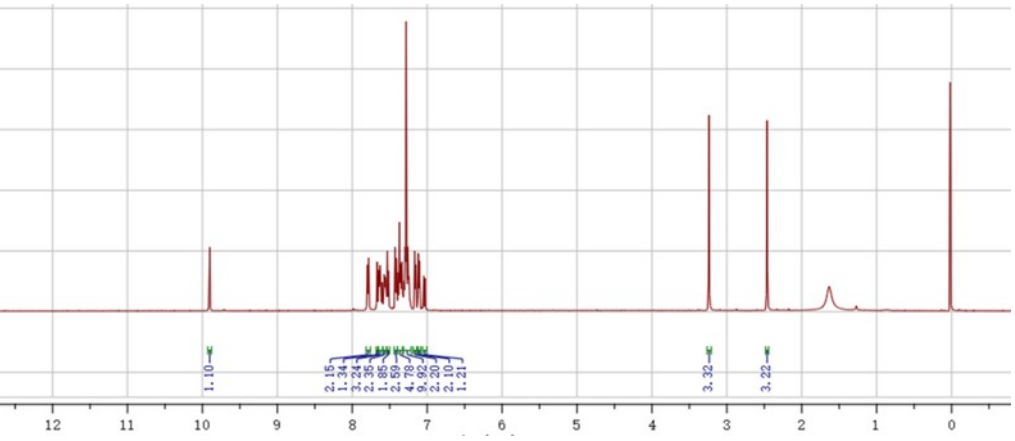


Figure S4. ^{1}H NMR spectrum of compound **TBAB** in $CDCl_3$.

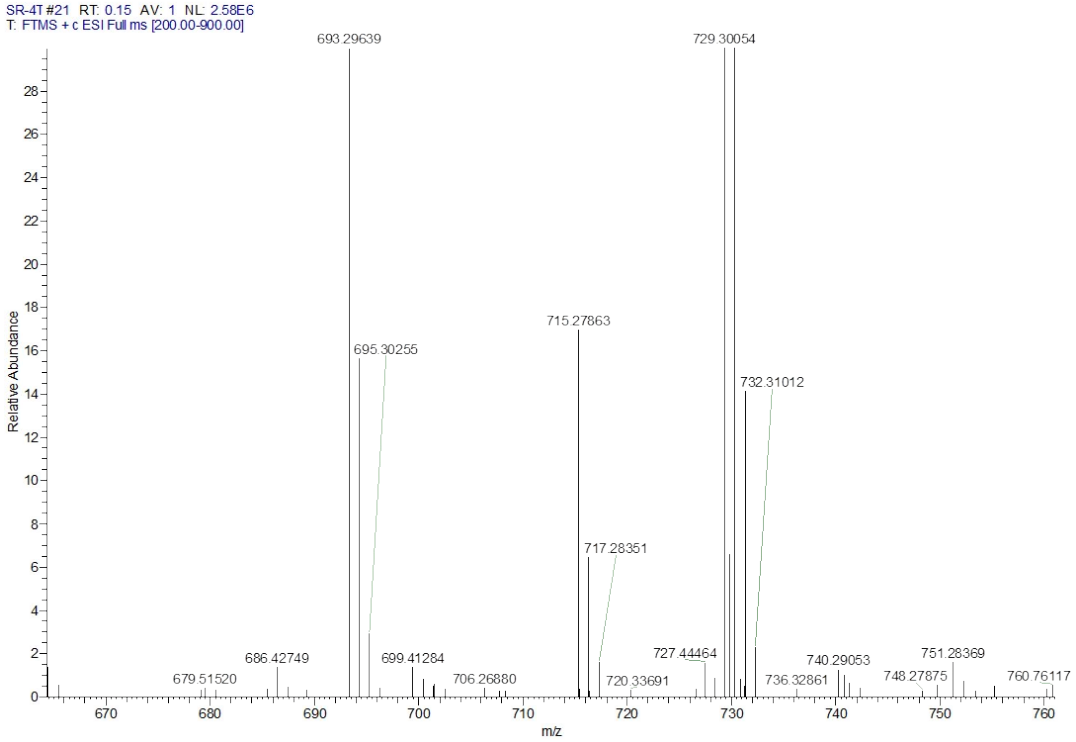


Figure S5. Mass spectrum of probe **TBAB**. HRMS (ESI): m/z calculated for $C_{48}H_{36}N_6O_2$+ $[M]^+$ 729.3005; found:729.30054.

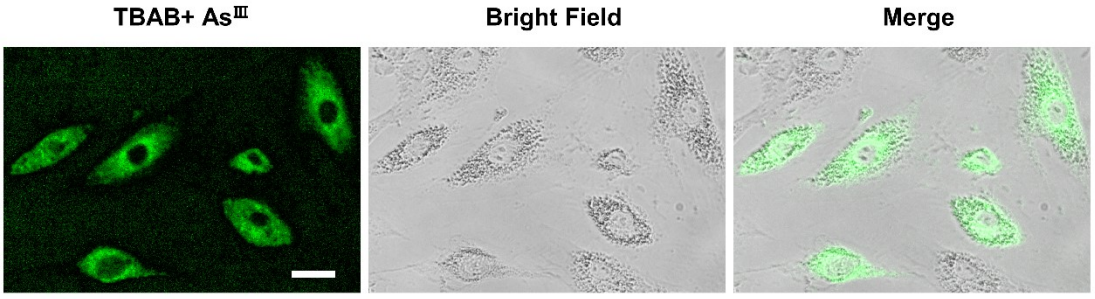


Figure S6. The H9c2 cell imaging of probe TBAB (10 μM) with As^{III} for 30 min. (scale bar, 25 μm).

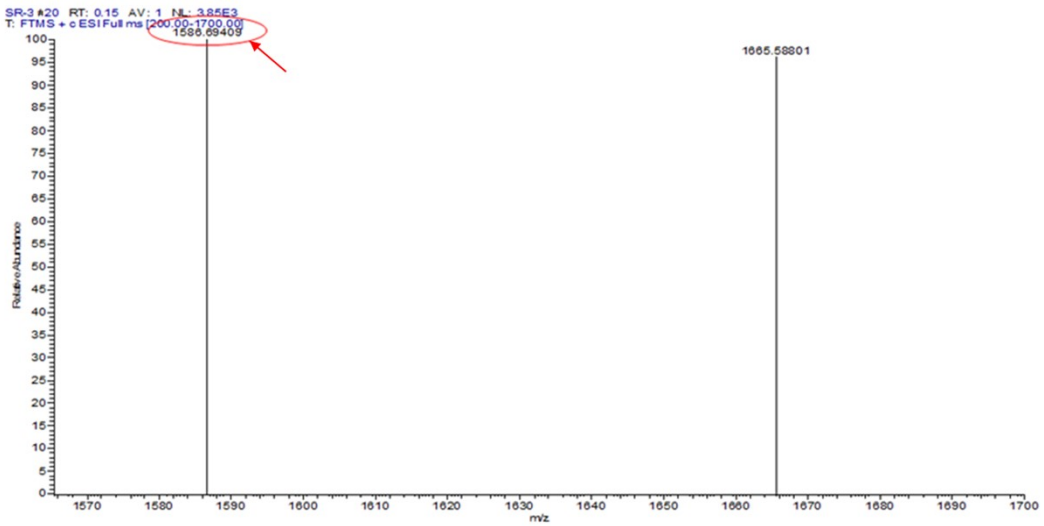


Figure S7. Mass spectrum of probe **TBAB** and As^{III}. HRMS (ESI): m/z calculated for $2C_{48}H_{36}N_6O_2+AsO_3^{3-}+[M]^+$ 1586.6940; found:1586.6940.

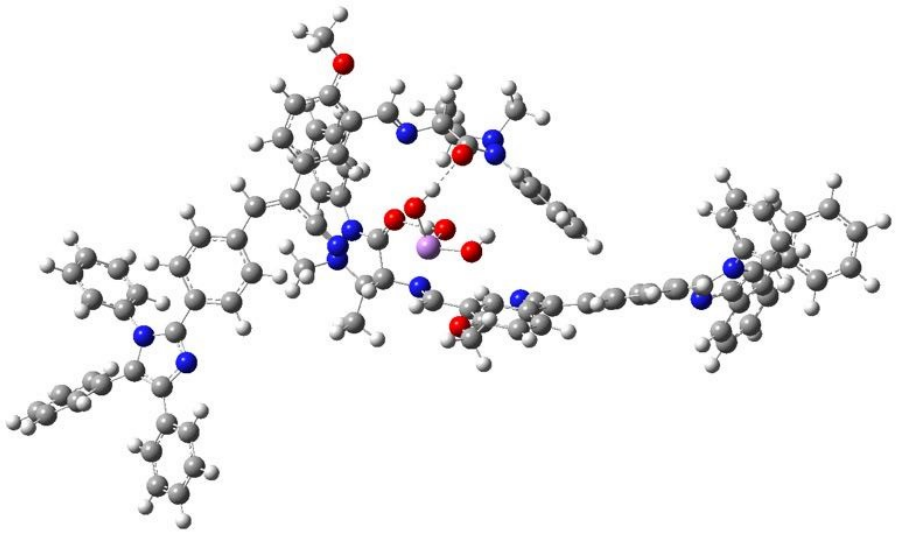


Figure S8. DFT calculation of TBAB with AsO_3^{3-}.