Supporting information

Highly sensitive and selective detection of triphosgene with a 2-(2'-hydroxyphenyl)benzimidazole derived fluorescent probe

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1. Optimization of triethylamine for the generation of phosgene

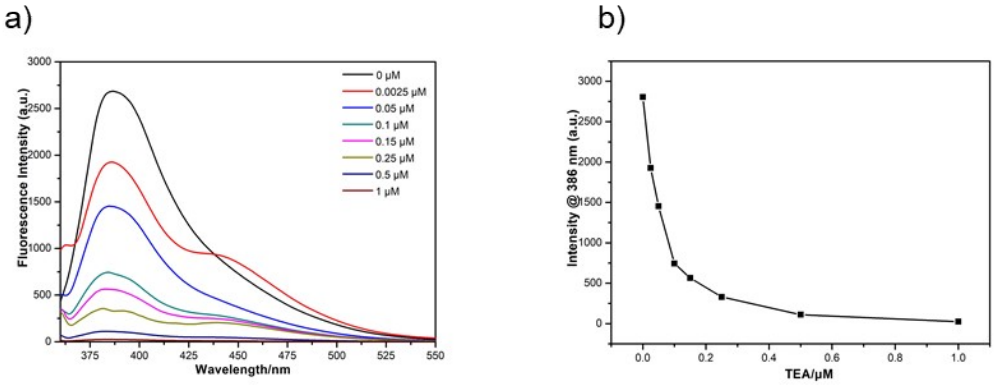

Figure S1 a) Fluorescence spectra of 10 μM **4-AHBI** solutions containing triethylamine (TEA) (0-1 μM) upon addition of triphosgene (3.5 μM), λex = 357 nm, slit width = 2.5/2.5 nm; b) Fluorescence intensities @386 nm vs concentration of TEA.

2. Investigation of the effect of solvents

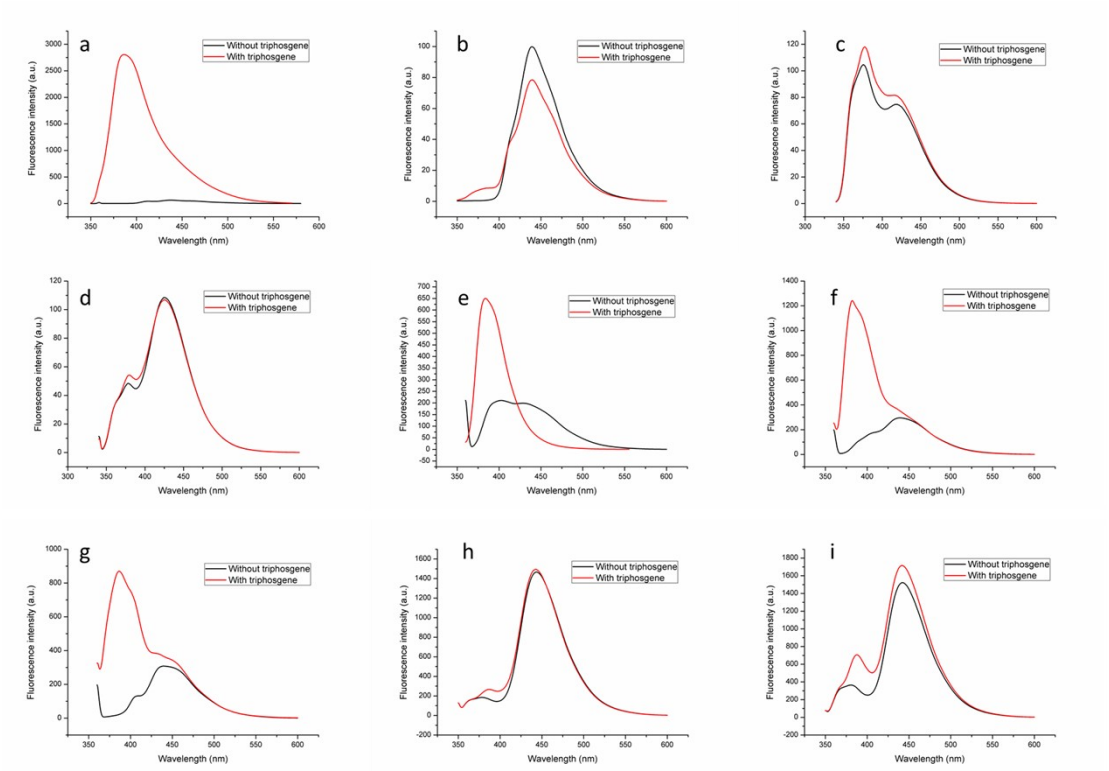

Figure S2 The fluorescence spectra of **4-AHBI** (10 μM) in different solvents without (black) and with (red) triphosgene (3.5 μM). a: CH_2Cl_2 (λex = 357 nm, λem = 386 nm), b: $CHCl_3$ (λex = 343 nm, λem = 440 nm), c: MeOH (λex = 330 nm, λem = 377 nm), d: EtOH (λex = 339 nm, λem = 425 nm), e: MeCN (λex = 357 nm, λem = 386 nm), f: acetone (λex = 357 nm, λem = 383 nm), g: EtOAc (λex = 357 nm, λem = 386 nm), h: DMF (λex = 346 nm, λem = 444 nm), i: DMSO (λex = 346 nm, λem = 441 nm). Slit width = 2.5/2.5 nm.

3. Measurement of the fluorescence quantum yield

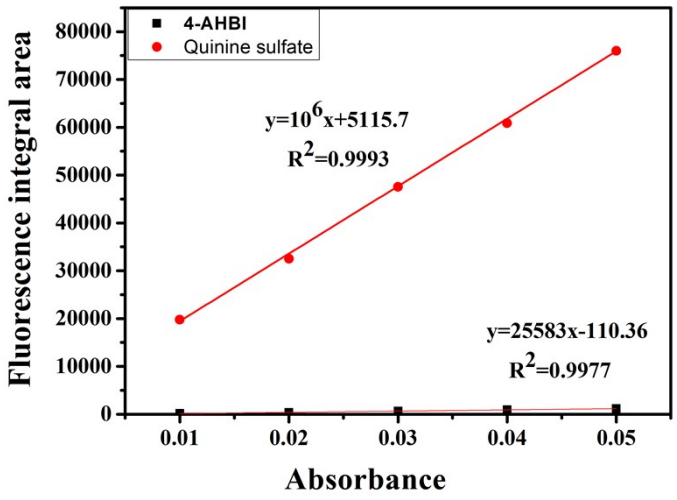

Figure S3 Measurement of the fluorescence quantum yields (Φf) of **4-AHBI**. **4-AHBI** were determined in CH_2Cl_2 with solvent refractive index correction. Quinine sulfate in 1.0 M H_2SO_4 was used as the reference (Φf = 54%) at an excitation wavelength of 340 nm. The fluorescence quantum yield was calculated by the following equation: $\Phi_x = \Phi_s (F_x/F_s)(A_s/A_x)(n_x/n_s)^2$. Where x and s indicate the **4-AHBI** and quinine sulfate, respectively, F is the area of the fluorescence peak, A is the optical density at the excitation wavelength and n is the refractive index of the solvent.

4. Measurement of the LoD for 4-AHBI

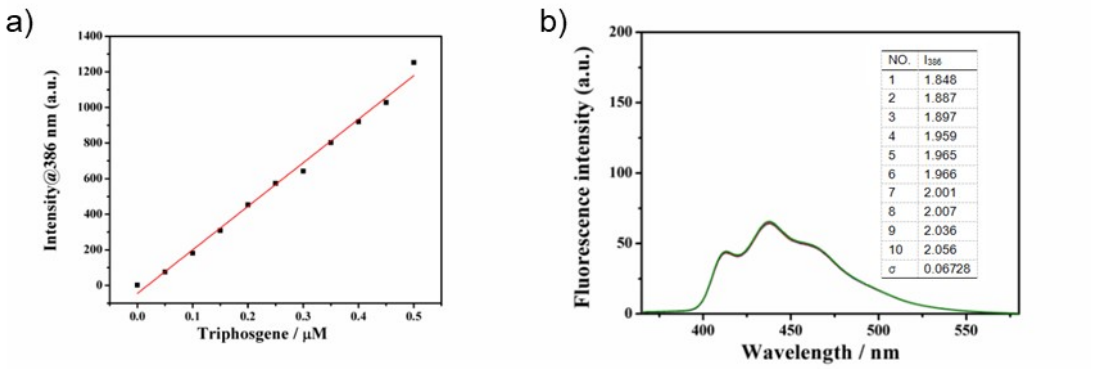

Figure S4 Measurement of the LoD for **4-AHBI** to triphosgene. a) The emission intensities at 386 nm *vs* triphosgene concentration. Equation: y = 2416.7x-40.195, R^2 = 0.9948; b) Ten times of the blank experiment to evaluate the standard deviation σ (0.06728). The triphosgene detection limit was determined to be 0.08 nM (LoD = 3σ/k, where σ is the standard deviation of the blank experiment, and k is the slope of the relationship between the emission intensities and triphosgene concentration.

5. Fluorescence spectra of 4-AHBI with triphosgene in the presence of interfering compounds

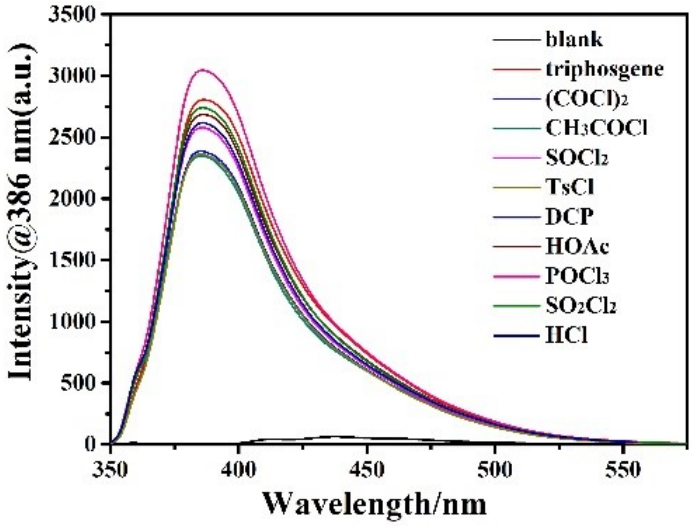

Figure S5 Fluorescence spectra of **4-AHBI** (10 μM) in CH_2Cl_2 with triphosgene (3.5 μM) in the presence of various analytes (5 μM). λex = 357 nm.

6. Table S1 Determination of triphosgene in the presence of interfering compounds

Interferents compounds (5 μM)	Triphosgene added (μM)	Triphosgene found (μM)	Recovery
$(COCl)_2$	3.5	2.8	80.1%
CH_3COCl	3.5	2.7	77.1%
$SOCl_2$	3.5	3.1	88.6%
TsCl	3.5	2.8	79.6%
DCP	3.5	3.1	88.6%
HOAc	3.5	3.2	91.4%
$POCl_3$	3.5	3.9	111.4%
SO_2Cl_2	3.5	3.0	84.3%
HCl	3.5	3.1	88.6%

7. Exploration of the sensing mechanism

The reaction mixture was analysed by HPLC with a High-resolution mass spectra (HRMS) on Agilent Technologies 6530 Accurate mass Q-TOF LC/MS using ESI as ion source. A minor peak at 1.959 min corresponded with the remnant **4-AHBI** (HRMS: $[M+H]^+$: calcd for $C_{13}H_{12}N_3O$: 226.0975, found: 226.0975.). A major peak at 3.812 min was obviously obtained and the HRMS spectrum showed the m/z 252.0776, which should be the single sensing product **4-AHBI-CO** (for $C_{14}H_{10}N_3O_2$: $M+H^+$: calculated 252.0768).

The sensing product **4-AHBI-CO** was synthesized as follows: **4-AHBI** (0.113 g, 0.5 mmol) was stirred and dissolved in dry CH_2Cl_2 (25 mL) at 0 °C, then triphosgene (0.15 g,

0.5 mmol) in dry CH_2Cl_2 (10 mL) was added over a period of 10 min. Then the mixture was continually stirred at 0 °C until the completion of the reaction. Saturated $NaHCO_3$ aqueous solution was added into the mixture and extracted with CH_2Cl_2 (20 mL × 2). The organic phase was collected, dried over anhydrous Na_2SO_4 and evaporated to give the crude product. The crude product was further purified by column chromatography (ethyl acetate : petroleum ether = 1 : 5) to give the sensing product (0.096 g, yield 78%) as a white solid.

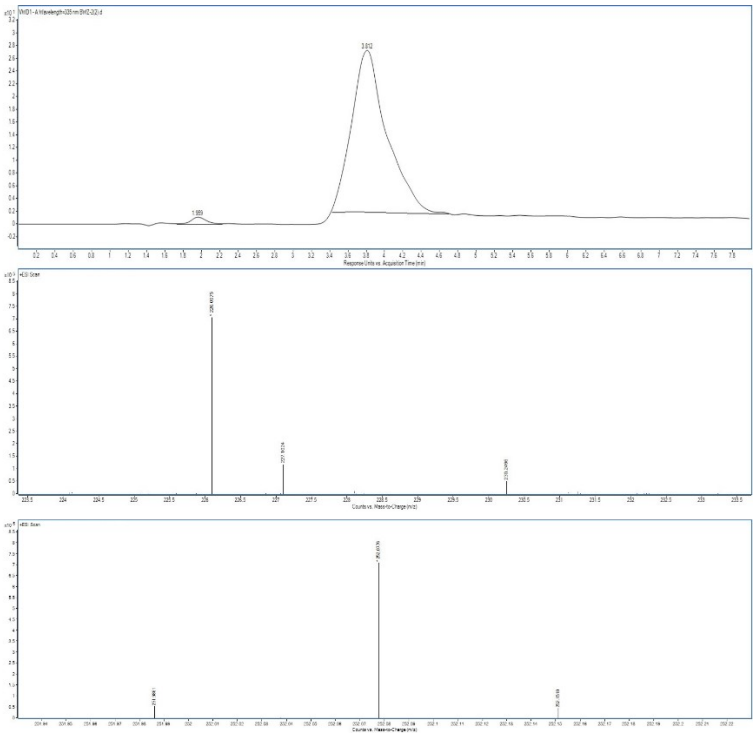

Figure S6 HPLC chromatogram of the reaction mixture (up) and HRMS spectrum of the peak at 1.959 min (middle) and 3.812 min (down).

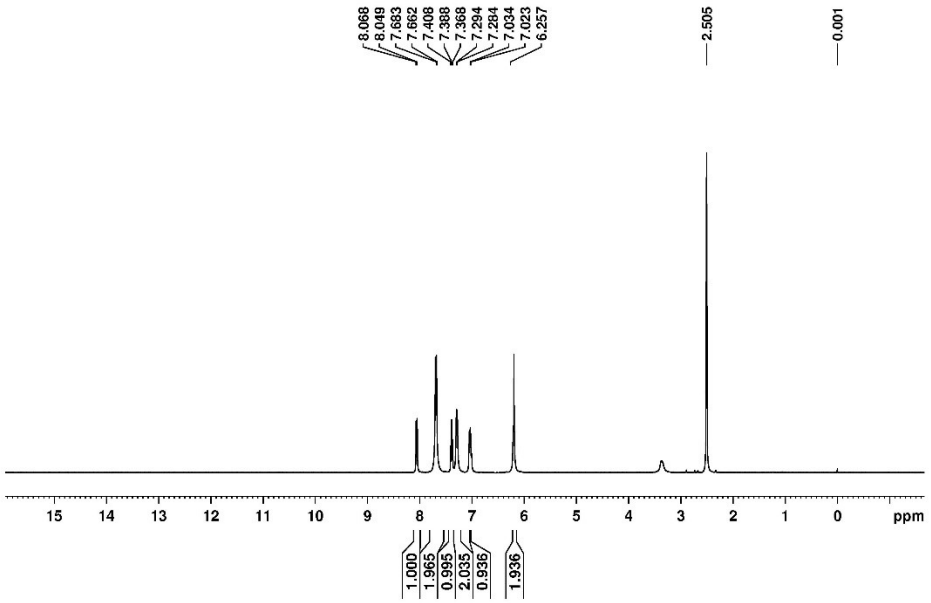

Figure S7 ^{1}H NMR of **4-AHBI-CO.**

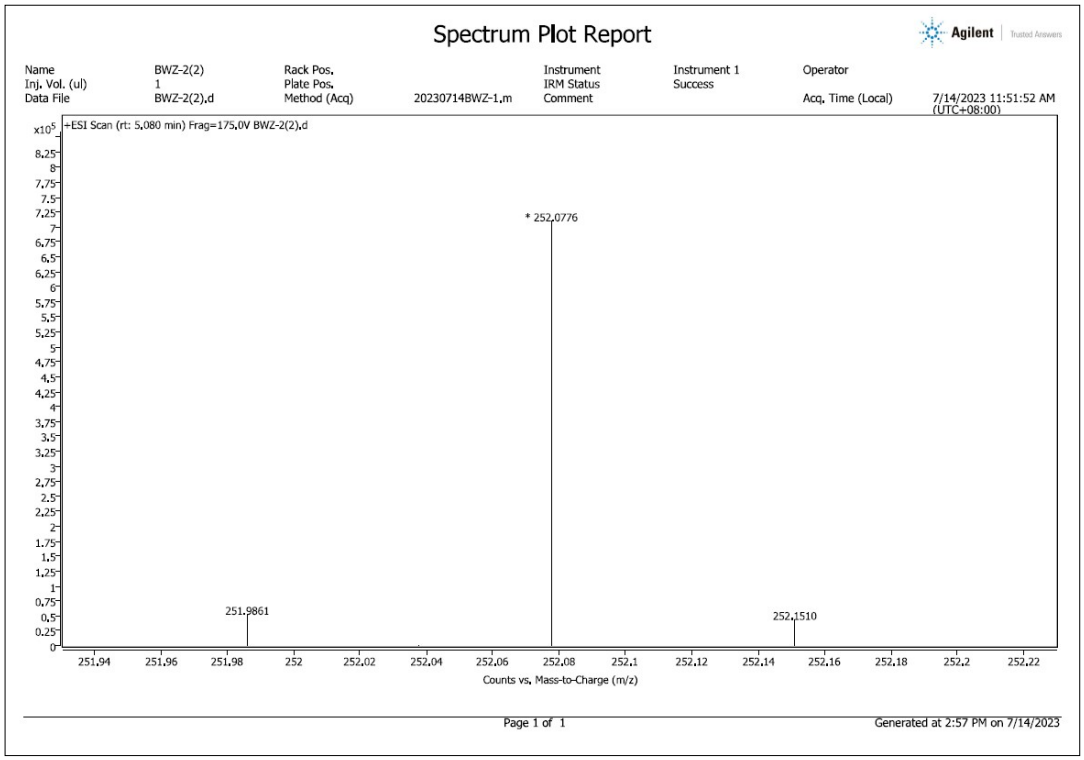

Figure S8 HRMS copy of **4-AHBI-CO.**

8. ^{1}H NMR, ^{13}C NMR and HRMS copies of 4-AHBI

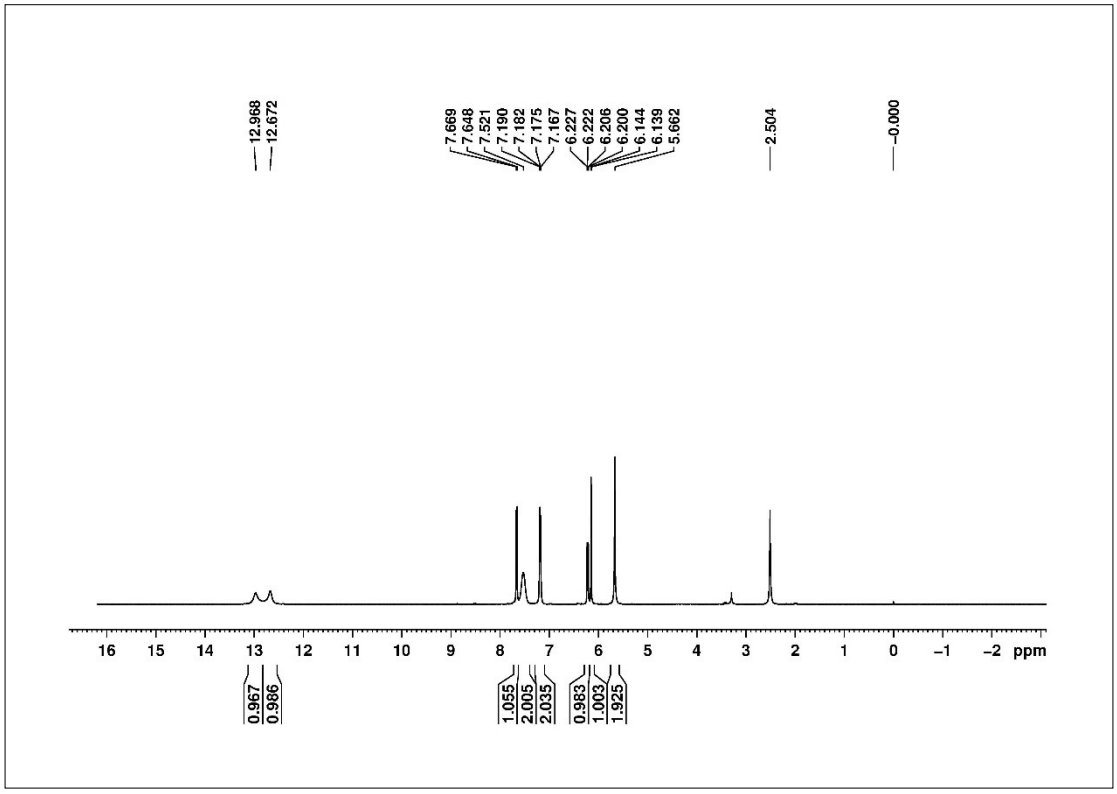

Figure S9 ^{1}H NMR copy of **4-AHBI**

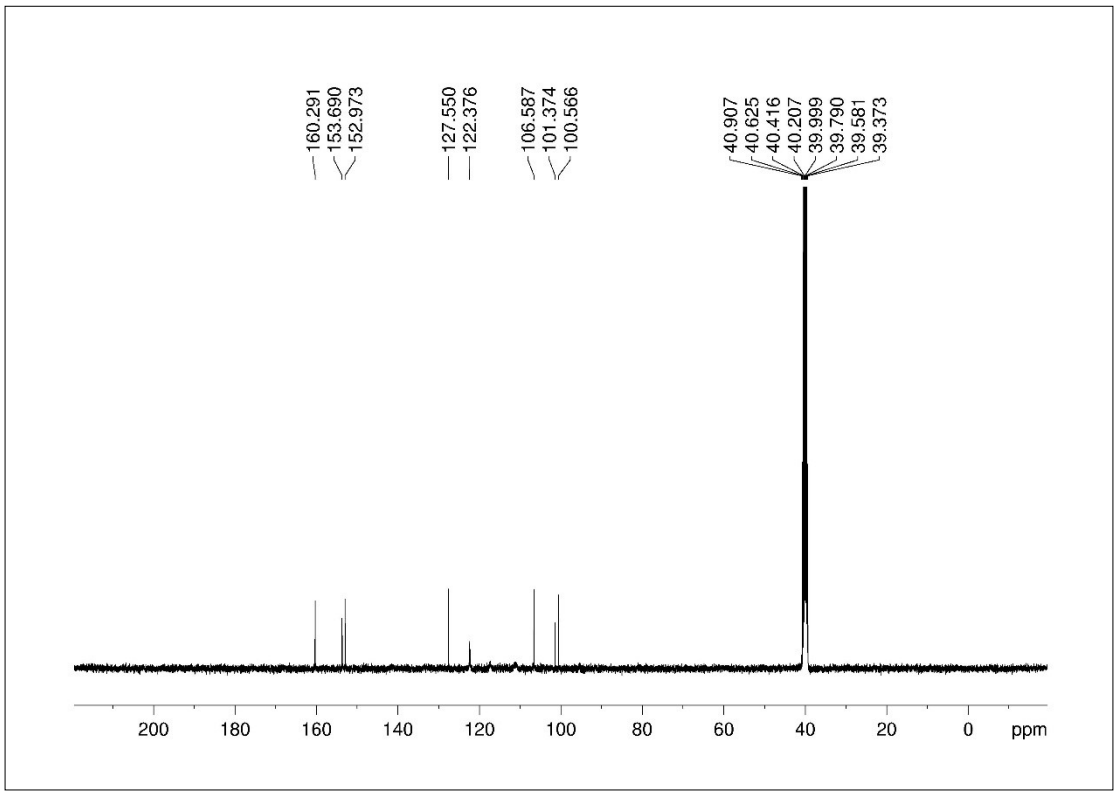

Figure S10 ^{13}C NMR copy of **4-AHBI**

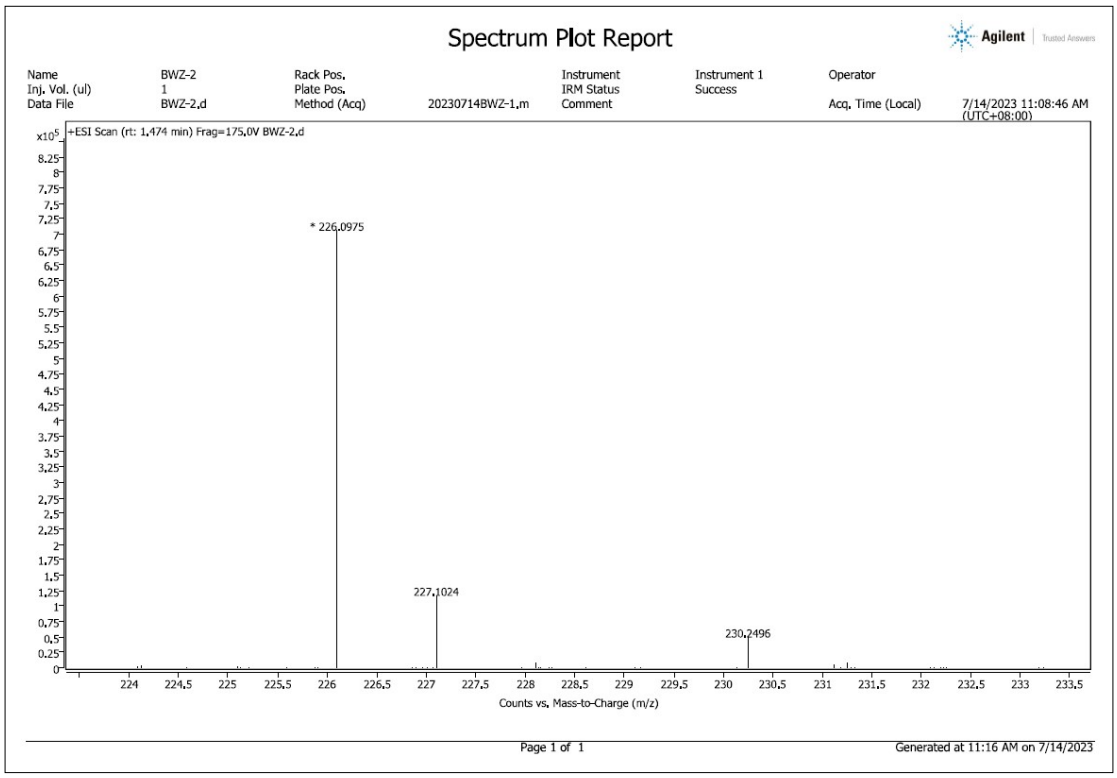

Figure S11 HRMS copy of **4-AHBI**