Supporting Information

Rapid and sensitive detection of acrylic acid using a novel fluorescence assay

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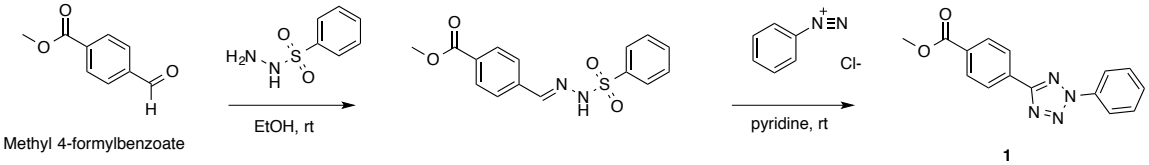
Contents:

1. Synthetic details of diaryltetrazoles and characterization of pyrazoline product

All chemicals and solvents were purchased from commerical sources and used directly without purification. Flash chromatography was performed using SiliCycle P60 silica gel (40-63 μm, 60Å). ^{1}H NMR spectra were recorded with Bruker Avance III 400, and chemical shifts were reported in ppm using either TMS or deuterated solvents as internal standards (TMS, 0.00; $CDCl_3$, 7.26; C_6D_6, 7.15; DMSO-d_6, 2.50). Multiplicity was reported as the follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. ^{13}C NMR spectra were recorded at 75.4 MHz, and chemical shifts were reported in ppm using the deuterated solvents as internal standards ($CDCl_3$, 77.0; DMSO-d_6, 39.5; C_6D_6, 128.0). LC-MS analysis was performed using Waters 3100 Single Quadrupole LCMS System. Kinetic studies were performed using Phenomenex Kinetex 2.6u XB-C18 column (50x4.6 mm). Flow rate was 1 mL/min and UV detection was set at 254 and 370 nm as indicated. Gas chromatography was carried out on a Shimadzu GCMS QP 2010 using a 30.0 m x 0.25 mm, inner diameter of 0.25 μm HP- INNOWAX column which was programmed from 40 to 250°C at 10°C /min. Fluorescence detection were performed with Tecan Infinite M1000.

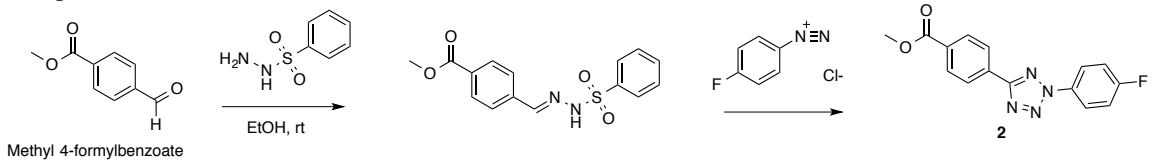
Compound 1



Methyl 4-formylbenzoate (0.824 g, 5 mmol) was dissolved in ethanol (50 mL), and benzenesulfonohydrazine (0.863 g, 5 mmol) was added. The mixture was stirred at room temperature for 1h, then quenched with water (100 mL) and stirred for 15 min at room temperature. The precipitate was filtered and washed with cold ethanol. The precipitate was then dissolved in pyridine (30 mL) for the next reaction. Aniline (0.465 g, 0.46 mL, 5 mmol) was separately dissolved in water: ethanol (1:1, 8 mL) and concentrated HCl (1.3 mL) was added. $NaNO_2$ (0.346 g, 5 mmol) was also separately dissolved in water (2 mL). The aniline solution was cooled in an ice bath for 5 min before addition of $NaNO_2$ solution to the aniline solution drop wise in an ice bath. The reaction mixture was added dropwise to the cooled product

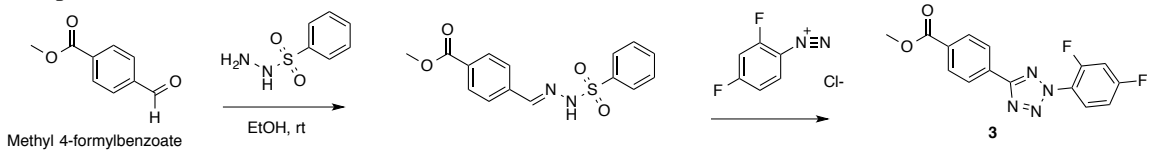
from the first reaction in an ice bath. The reaction mixture was stirred for 1 h at room temperature. Extraction was then carried out with ethyl acetate (100 mL X 3). 3 M HCl (250 mL) was added to the combined organic layers and stirred vigorously for 10 min. The organic layer was concentrated and the product was precipitated with hexanes. The product was further washed with cold hexanes to obtain a pale orange solid (0.538 g, 38%). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.35 (dd, *J* = 8.2, 0.6 Hz, 2H), 8.24 – 8.18 (m, 4H), 7.63 – 7.56 (m, 2H), 7.56 – 7.50 (m, 1H), 3.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.52, 164.41, 136.87, 131.92, 131.28, 130.24, 129.89, 129.75, 127.01, 119.97, 52.32. HRMS (ESI) calcd for $C_{15}H_{12}N_4O_2$ 280.096 [M + H+], found 280.096.

Compound 2



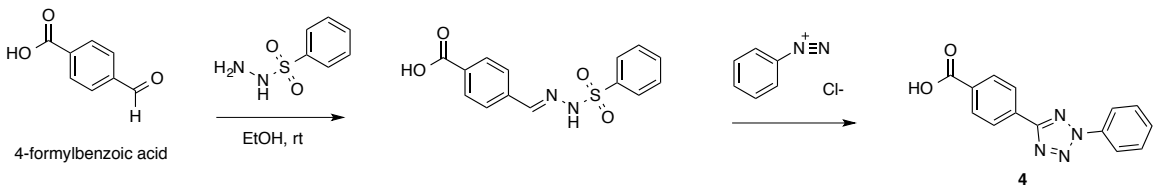
Methyl 4-formylbenzoate (0.820 g, 5 mmol) was dissolved in ethanol (50 mL), followed by addition of benzenesulfonohydrazine (0.862 g, 5 mmol). The mixture was stirred at room temperature for 1h, then quenched with water (100 mL) and stirred for 15 min at room temperature. Precipitate was filtered, washed with cold ethanol and dissolved in pyridine (30 mL) to form solution A. 4-fluoroaniline was then dissolve (0.555 g, 0.48 mL, 5 mmol) in water: ethanol (1:1, 8 mL) and concentrated HCl (1.3 mL). $NaNO_2$ was dissolved (0.345 g, 5 mmol) in water (2 mL). Both mixtures were cooled in ice bath for 5 min before addition of $NaNO_2$ solution to 4-fluoroaniline solution drop wise in ice bath to form solution B. Solution B was added to solution A drop wise in ice bath. Mixture was then stirred for 1h at room temperature. Mixture was extracted with Ethyl Acetate (100 mL X 3). 3M HCl (250 mL) was added to combine organic layer and stirred vigorously for 10 min. Organic layer was concentrated and product was precipitated with hexanes. Product was washed with cold hexanes to obtain pale pink solid (0.777 g, 52%) ^{1}H NMR (400 MHz, Chloroform-d) δ 8.36 – 8.29 (m, 2H), 8.24 – 8.16 (m, 4H), 7.29 (dd, *J* = 9.1, 7.9 Hz, 2H), 3.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.46, 164.49, 164.40, 161.91, 131.97, 131.07, 130.24, 126.97, 121.96, 121.87, 116.90, 116.67, 52.33. HRMS (ESI) calcd for $C_{15}H_{11}FN_4O_2$ 298.0865 [M + H+], found 298.0866.

Compound 3



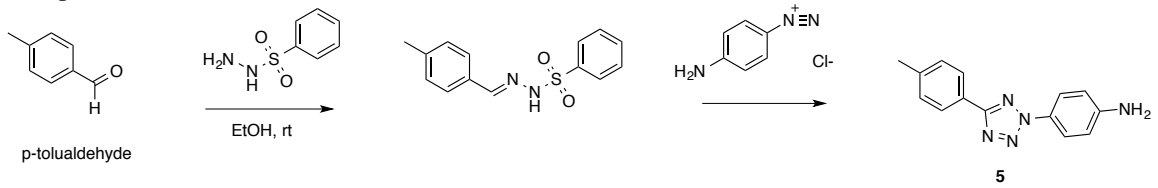
Methyl 4-formylbenzoate (0.820 g, 5 mmol) was dissolved in ethanol (50 mL), followed by addition of benzenesulfonohydrazine (0.859 g, 5 mmol). The mixture was stirred at room temperature for 1h, then quenched with water (100 mL) and stirred for 15 min at room temperature. Precipitate was filtered, washed with cold ethanol and dissolved in pyridine (30 mL) to form solution A. 2, 4-fluoroaniline was then dissolve (0.645 g, 0.50 mL, 5 mmol) in water: ethanol (1:1, 8 mL) and concentrated HCl (1.3 mL). $NaNO_2$ was dissolved (0.345 g, 5 mmol) in water (2 mL). Both mixtures were cooled in ice bath for 5 min before addition of $NaNO_2$ solution to 2, 4-fluoroaniline solution drop wise in ice bath to form solution B. Solution B was added to solution A drop wise in ice bath. Mixture was then stirred for 1h at room temperature. Mixture was extracted with Ethyl Acetate (100 mL X 3). 3M HCl (250 mL) was added to combine organic layer and stirred vigorously for 10 min. layer was concentrated and product was precipitated with hexanes. Product was washed with cold hexanes to obtain red solid (0.173 g, 11%). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.35 – 8.30 (m, 2H), 8.23 – 8.18 (m, 2H), 7.91 (td, *J* = 8.6, 5.6 Hz, 1H), 7.19 – 7.10 (m, 2H), 3.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.88, 129.90, 129.11, 127.89, 127.14, 77.32, 77.20, 77.00, 76.68, 30.89. HRMS (ESI) calcd for $C_{15}H_{10}F_2N_4O_2$ 316.0765 [M + H+], found 316.0772.

Compound 4



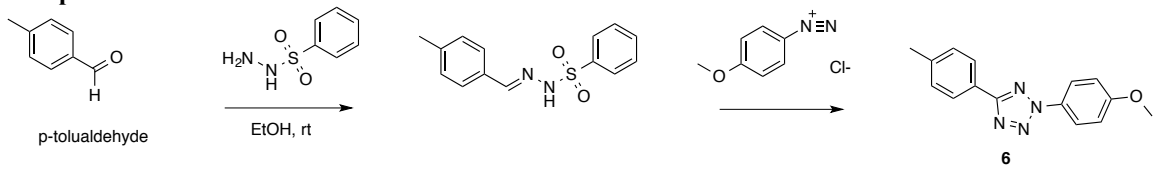
4-formylbenzoic acid (1.000 g, 6 mmol) was dissolved in ethanol (100 mL), followed by addition of benzenesulfonohydrazine (1.160 g, 6 mmol). The mixture was stirred at room temperature for 1h, then quenched with water (100 mL) and stirred for 15 min at room temperature. Precipitate was filtered, washed with cold ethanol and dissolved in pyridine (30 mL) to form solution A. Aniline was then dissolved (0.587 g, 0.60 mL, 5 mmol) in water: ethanol (1:1, 8 mL) and concentrated HCl (1.3 mL). $NaNO_2$ was dissolved (0.455 g) in water (2 mL). Both mixtures were cooled in ice bath for 5 min before addition of $NaNO_2$ solution to aniline solution drop wise in ice bath to form solution B. Solution B was added to solution A drop wise in ice bath. Mixture was then stirred for 1h at room temperature. Mixture was extracted with Ethyl Acetate (100 mL X 3). 3M HCl (250 mL) was added to combine organic layer and stirred vigorously for 10 min. Solvent were removed and then dissolved in dichloromethane. Product was precipitated with hexanes. Product was washed with cold hexanes to obtain red solid (0.820 g, 45%). ^{1}H NMR (400 MHz, Methanol-d4) δ 8.39 – 8.34 (m, 2H), 8.27 – 8.22 (m, 4H), 7.71 – 7.66 (m, 2H), 7.63 (d, J = 7.3 Hz, 1H). ^{13}C NMR (101 MHz, MeOD) δ 147.01, 141.50, 141.48, 129.93, 129.60, 127.95, 127.89, 127.44, 127.41, 125.52, 119.62. HRMS (ESI) calcd for $C_{14}H_{10}N_4O_2$ 266.0805 [M + H+], found 266.0804.

Compound 5



p-tolualdehyde (1.000 g, 8 mmol) was dissolved in ethanol (60 mL), followed by addition of benzenesulfonohydrazine (1.433 g, 8 mmol). The mixture was stirred at room temperature for 1h, then quenched with water (100 mL) and stirred for 15 min at room temperature. Precipitate was filtered, washed with cold ethanol and dissolved in pyridine (30 mL) to form solution A. 1, 4-phenylenediamine was then dissolved(0.905 g, 8 mmol) in water: ethanol (1:1, 10 mL) and concentrated HCl (1.3 mL). $NaNO_2$ was dissolved (0.583 g, 8 mmol) in water (2 mL). Both mixtures were cooled in ice bath for 5 min before addition of $NaNO_2$ solution to 1, 4-phenylenediamine solution drop wise in ice bath to form solution B. Solution B was added to solution A drop wise in ice bath. Mixture was then stirred for 1h at room temperature. Mixture was extracted with Ethyl Acetate (100 mL X 3). 3M HCl (250 mL) was added to combine organic layer and stirred vigorously for 10 min. Organic layer was concentrated to obtain a red solid. Crude product was purified with column chromatography (Hex:EA 1:1) to collect as yellow solid (1.149 g, 54.9%). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.47 – 8.39 (m, 1H), 8.02 – 7.97 (m, 2H), 7.76 (s, 1H), 7.54 (d, J = 7.2 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.46 – 7.42 (m, 2H), 7.12 (d, J = 7.9 Hz, 2H), 2.32 (s, 3H) . ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.27, 140.92, 138.32, 133.17, 130.26, 129.34, 128.93, 127.85, 127.31, 29.62, 21.39.HRMS (ESI) calcd for $C_{14}H_{13}N_5$ 251.1161 [M + H+], found 251.1171.

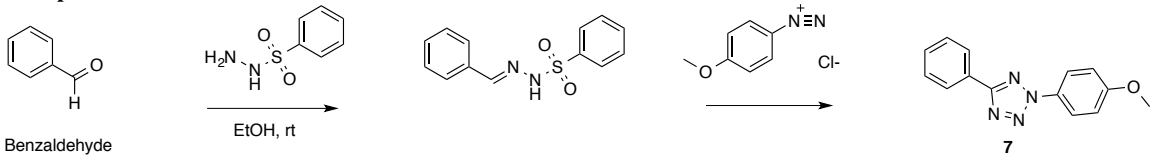
Compound 6



p-tolualdehyde (1.000 g, 8 mmol) was dissolved in ethanol (60 mL), followed by addition of benzenesulfonohydrazine (1.433 g, 8 mmol The mixture was stirred at room temperature for 1h, then quenched with water (100 mL) and stirred for 15 min at room temperature. Precipitate was filtered, washed

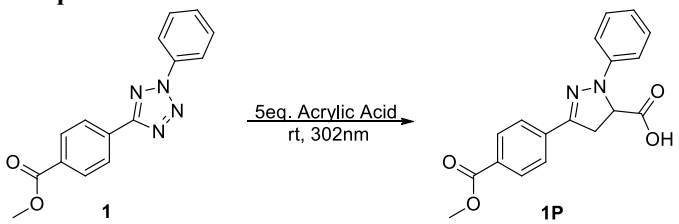
with cold ethanol and dissolved in pyridine (30 mL) to form solution A. 4-methoxyaniline was then dissolved (1.067 g, 8 mmol) in water: ethanol (1:1, 10 mL) and concentrated HCl (1.3 mL). $NaNO_2$ was dissolved (0.583 g, 8 mmol) in water (2 mL). Both mixtures were cooled in ice bath for 5 min before addition of $NaNO_2$ solution to 4-methoxyaniline solution drop wise in ice bath to form solution B. Solution B was added to solution A drop wise in ice bath. Mixture was then stirred for 1h at room temperature. Mixture was extracted with Ethyl Acetate (100 mL X 3). 3M HCl (250 mL) was added to combine organic layer and stirred vigorously for 10 min. Organic layer was concentrated to obtain a red solid. Crude product was purified with column chromatography (Hex:EA 5:1) to obtain a orange red solid (0.8921 g, 41.6%). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.11 (d, *J* = 8.2 Hz, 2H), 8.09 – 8.06 (m, 2H), 7.32 – 7.29 (m, 2H), 7.05 – 7.01 (m, 2H), 3.86 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.05, 160.46, 140.62, 129.62, 126.90, 121.37, 114.69, 55.73, 21.53. HRMS (ESI) calcd for $C_{15}H_{14}N_4O$ 266.1166 [M + H+], found 266.1168.

Compound 7



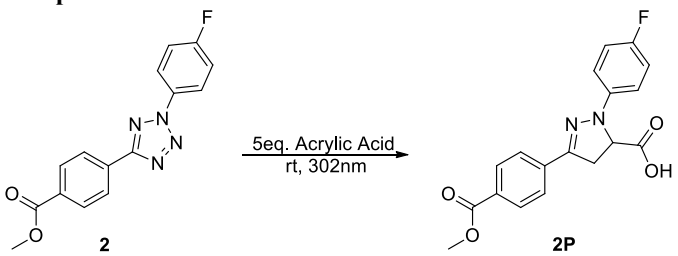
Benzaldehyde (1.000 g, 8 mmol) was dissolved in ethanol (60 mL), followed by addition of benzenesulfonohydrazine (1.623 g, 8 mmol). The mixture was stirred at room temperature for 1h, then quenched with water (100 mL) and stirred for 15 min at room temperature. Precipitate was filtered, washed with cold ethanol and dissolved in pyridine (30 mL) to form solution A. 4-methoxyaniline was then dissolved (1.067 g, 8 mmol) in water: ethanol (1:1, 10 mL) and concentrated HCl (1.3 mL). $NaNO_2$ was dissolved (0.583 g, 8 mmol) in water (2 mL). Both mixtures were cooled in ice bath for 5 min before addition of $NaNO_2$ solution to 4-methoxyaniline solution drop wise in ice bath to form solution B. Solution B was added to solution A drop wise in ice bath. Mixture was then stirred for 1h at room temperature. Mixture was extracted with Ethyl Acetate (100 mL X 3). 3M HCl (250 mL) was added to combine organic layer and stirred vigorously for 10 min. Organic layer was concentrated to obtain a red solid. Crude product was purified with column chromatography (DCM: MeOH 9:1) to obtain a red solid (1.420 g, 59.7%). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.23 (dd, *J* = 7.9, 1.7 Hz, 2H), 8.09 (d, *J* = 9.1 Hz, 2H), 7.53 – 7.47 (m, 3H), 7.04 (d, *J* = 9.1 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.68, 159.20, 129.10, 127.60, 125.68, 120.09, 113.37, 54.35. HRMS (ESI) calcd for $C_{14}H_{12}N_4O$ 252.1003 [M + H+], found 252.1011.

Compound 1P



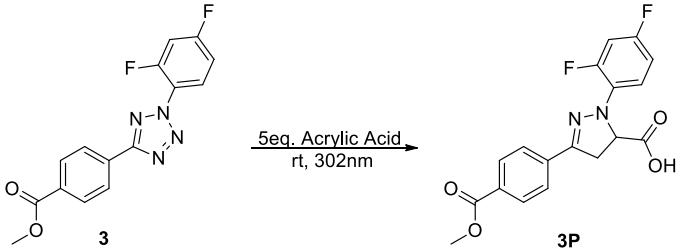
A 4 mL ethyl acetate solution of **1** (20 mg, 0.0713 mmol) and acrylic acid (24.5 μL, 5 equiv molar) were irradiated with 302nm UV lamp for 3h. The excess solvent and reagent were removed by reduced pressure to produce crude product which was subsequently purified by silica gel column chromatography. (Hex: EA, 1:1) Product **1P** was collected as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.05 (d, *J* = 8.5 Hz, 2H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 2H), 7.45 – 7.34 (m, 3H), 6.52 (dd, *J* = 16.8, 1.8 Hz, 1H), 6.30 (t, *J* = 13.9 Hz, 1H), 5.72 (dd, *J* = 10.3, 1.8 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.09, 165.61, 141.09, 140.99, 135.42, 133.35, 131.17, 129.97, 129.75, 129.41, 127.58, 120.30, 115.38, 60.19, 52.38, 29.68. HRMS (ESI) calcd for $C_{18}H_{16}N_2O_4$ 324.1115 [M + H+], found 324.111.

Compound 2P



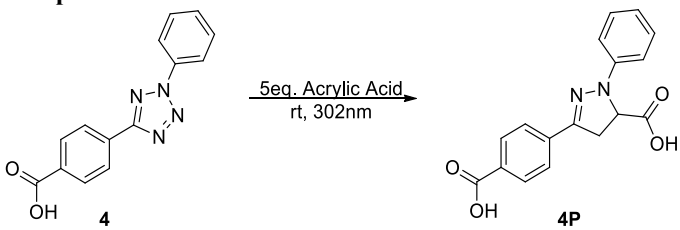
A 4 mL ethyl acetate solution of **2** (20 mg, 0.0671 mmol) and acrylic acid (23 µL, 5 equiv molar) were irradiated with 302nm UV lamp for 3h. The excess solvent and reagent were removed by reduced pressure to produce crude product which was subsequently purified by silica gel column chromatography. (Hex: EA, 1:1) Product **2P** was collected as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.12 (dd, *J* = 9.0, 8.1 Hz, 2H), 6.52 (dd, *J* = 16.8, 1.7 Hz, 1H), 6.26 (t, 1H), 5.74 (d, *J* = 10.8 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.99, 164.83, 160.02, 150.68, 145.03, 142.12, 135.95, 135.91, 134.31, 132.52, 130.29, 129.40, 128.81, 127.03, 126.82, 126.48, 125.76, 115.49, 115.27, 59.07, 51.39, 28.64.HRMS (ESI) calcd for $C_{18}H_{15}FN_2O_4$ 342.1022 [M + H+], found 342.1016

Compound 3P



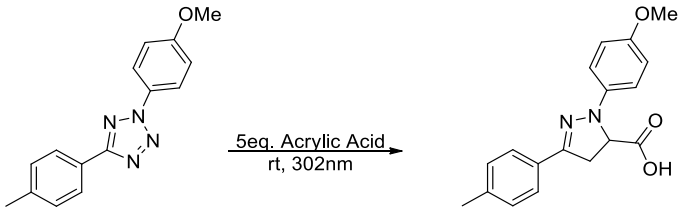
A 4 mL ethyl acetate solution of **3** (20 mg, 0.0633 mmol) and acrylic acid (21.7 µL, 5 equiv molar) were irradiated with 302nm UV lamp for 3h. The excess solvent and reagent were removed by reduced pressure to produce crude product which was subsequently purified by silica gel column chromatography. (Hex: EA, 1:1) Product **3P** was collected as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.8 Hz, 2H), 7.86 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.6 Hz, 1H), 6.95 (d, J = 8.1 Hz, 2H), 6.54 (dd, J = 16.8, 1.6 Hz, 1H), 6.12 (d, J = 16.9 Hz, 1H), 5.77 (d, J = 10.4 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.86, 160.41, 154.83, 133.10, 131.43, 130.11, 129.03, 127.70, 125.37, 123.60, 122.80, 110.13, 109.90, 103.05, 102.79, 102.55, 58.21, 50.26, 27.51. HRMS (ESI) calcd for $C_{18}H_{14}F_2N_2O_4$ 360.0929 [M + H+], found 360.0922.

Compound 4P



A 4 mL dichloromethane and methanol solution of **4** (20 mg, 0.0751 mmol) and acrylic acid (25.8 μL, 5 equiv molar) were irradiated with 302nm UV lamp for 3h. The excess solvent and reagent were removed by reduced pressure to produce crude product which was subsequently purified by silica gel column chromatography. (MeOH: DCM, 3:17) Product **4P** was collected as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.1 Hz, 2H), 7.58 – 7.54 (m, 2H), 7.45 (dt, J = 13.4, 7.2 Hz, 3H), 6.58 (d, J = 16.8 Hz, 1H), 6.27 (dd, J = 16.7, 10.4 Hz, 1H), 5.78 (d, J = 10.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.96, 167.23, 166.23, 146.56, 145.65, 140.65, 136.11, 132.18, 131.04, 129.61, 129.07, 128.09, 127.77, 127.54, 126.79, 112.96, 65.83, 53.38, 29.69. HRMS (ESI) calcd for $C_{17}H_{14}N_2O_4$ 310.0948 [M + H+], found 310. 0954

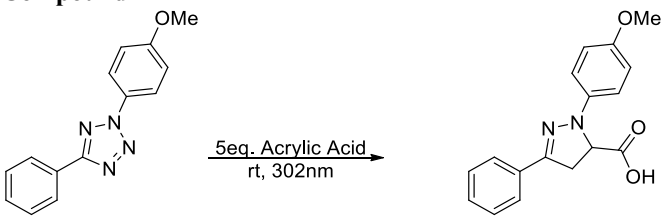
Compound 6P



6 **6P**

A 4 mL ethyl acetate solution of **6** (20 mg, 0.0751 mmol) and acrylic acid (25.7 µL, 5 equiv molar) were irradiated with 302nm UV lamp for 3h. The excess solvent and reagent were removed by reduced pressure to produce crude product which was subsequently purified by silica gel column chromatography. (MeOH: DCM, 1:20) Product **6P** was collected as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.9 Hz, 2H), 7.10 (d, J = 7.7 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 6.40 (dd, J = 16.8, 1.9 Hz, 1H), 6.18 (s, 1H), 5.63 – 5.57 (m, 1H), 3.74 (s, 3H), 2.29 (s, 3H ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.72, 158.84, 158.57, 141.81, 133.06, 133.06, 130.00, 128.26, 128.20, 126.45, 113.45, 59.25, 54.48, 28.65, 20.45. HRMS (ESI) calcd for $C_{18}H_{18}N_2O_3$ 310.1325 [M + H+], found 310.1317.

Compound 7P

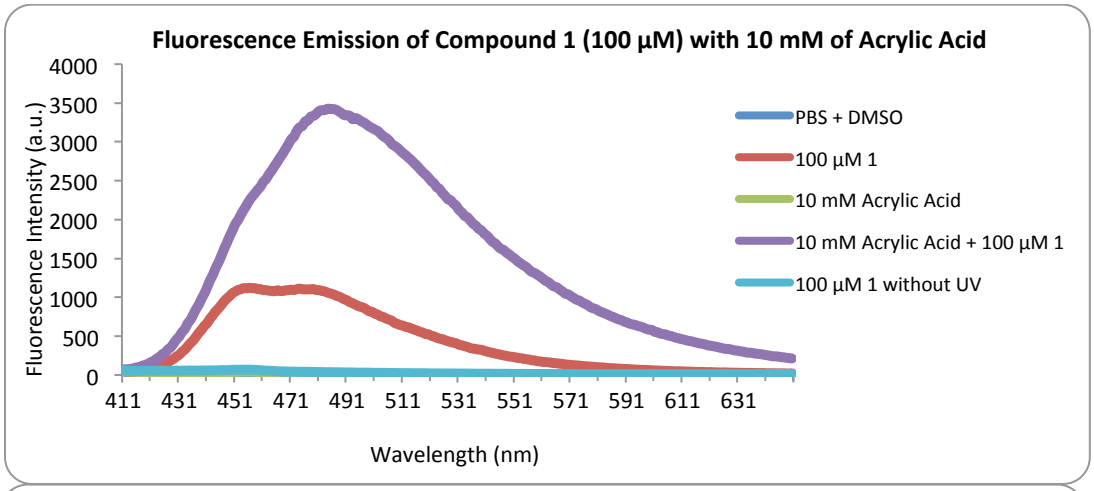


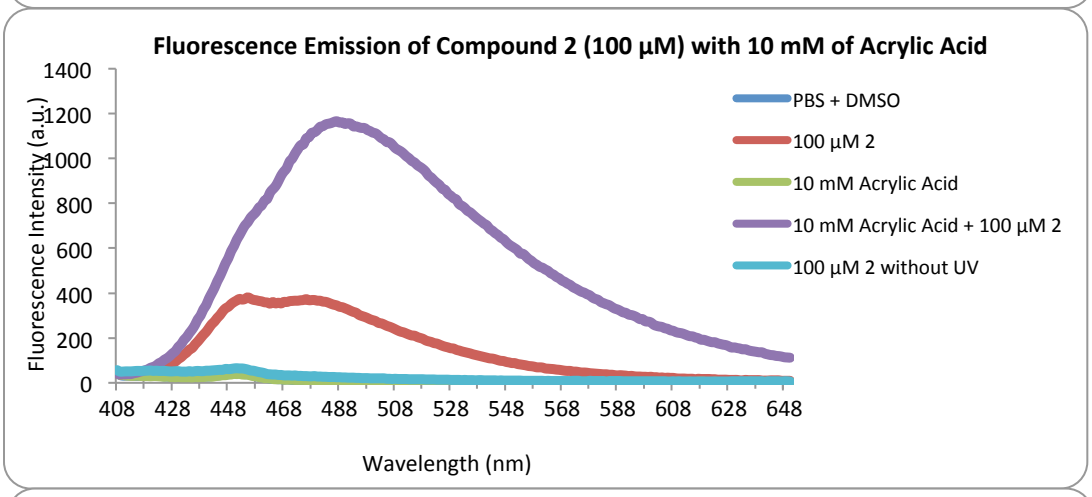
7 **7P**

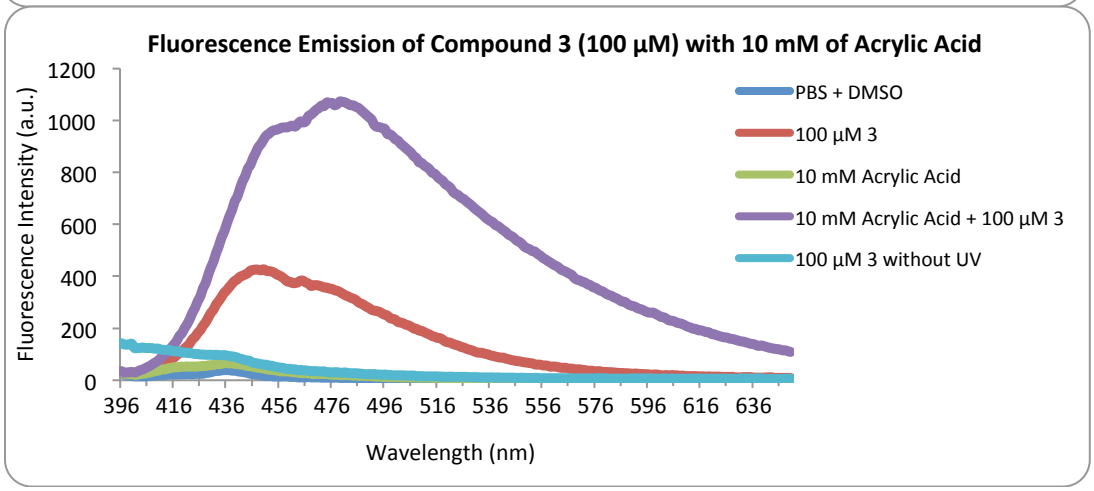
A 4 mL ethyl acetate solution of **7** (20 mg, 0.0793 mmol) and acrylic acid (27.2 μL, 5 equiv molar) were irradiated with 302nm UV lamp for 3h. The excess solvent and reagent were removed by reduced pressure to produce crude product which was subsequently purified by silica gel column chromatography. (MeOH: DCM, 1:20) Product **7P** was collected as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 2H), 7.42 – 7.33 (m, 4H), 7.30 (d, J = 6.9 Hz, 2H), 6.83 (d, J = 9.0 Hz, 2H), 6.42 (dd, J = 16.8, 1.9 Hz, 1H), 6.18 (s, 1H), 5.64 – 5.58 (m, 1H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.78, 158.60, 132.97, 131.27, 130.91, 128.50, 127.60, 126.44, 126.22, 113.79, 113.50, 59.22, 54.49, 28.65. HRMS (ESI) calcd for $C_{17}H_{16}N_2O_3$ 296.1169 [M + H+], found 296.1161.

2. Fluorescence characterization of reaction between diaryltetrazoles and acrylic acid

A solution containing each diaryltetrazole (0.022 mmol) and acrylic acid (0.022-0.050 mmol) was irradiated with a hand-held 302-nm UV lamp for 1 minute. Experiments were performed in a black 96-well plate with a total reaction volume of 100 µL The maximum excitation wavelengths indicated in Table 1 were used for each of the scans. Bandwidth was set at 5nm.







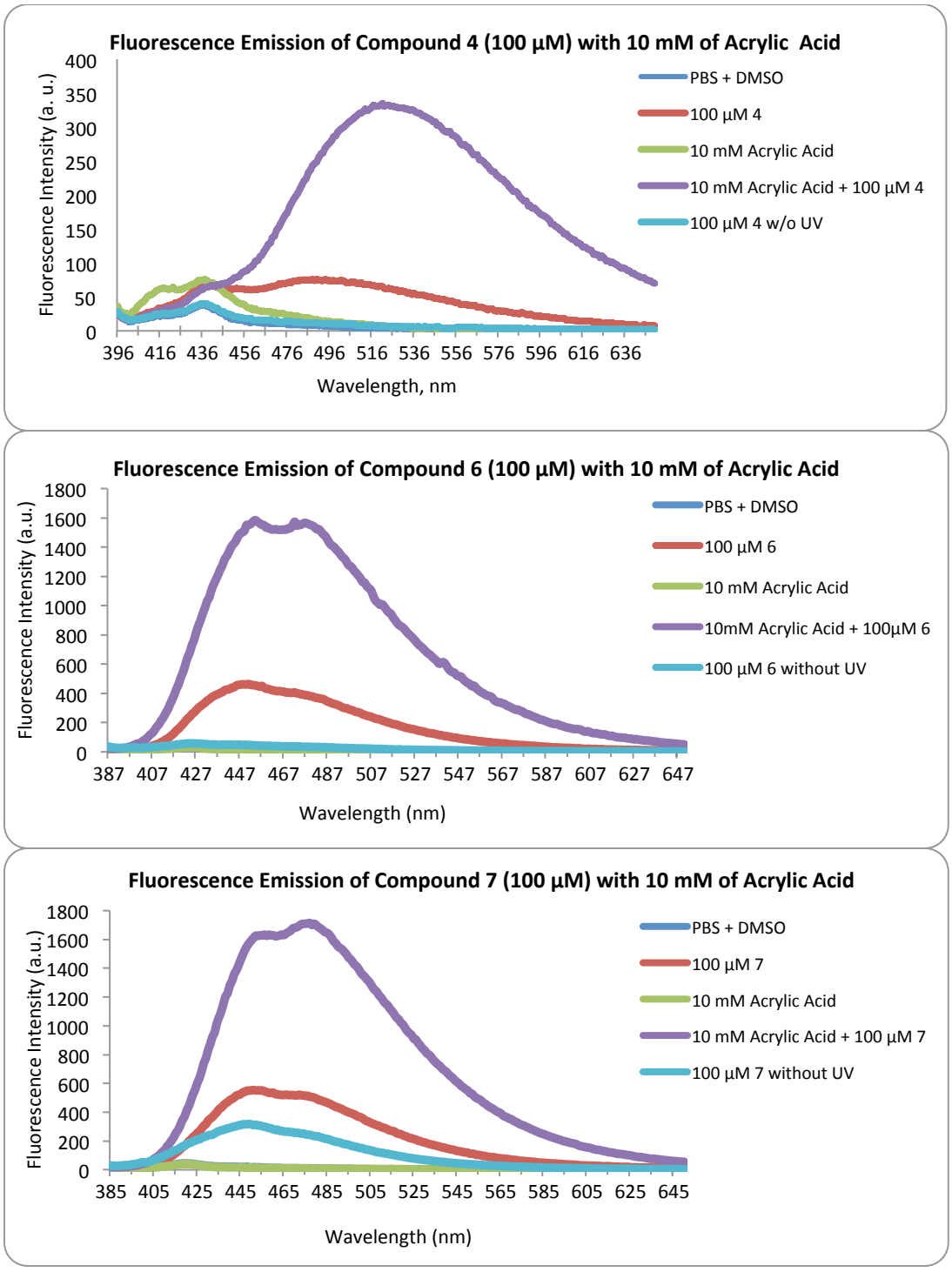


Figure S1. Fluorescence emission curves of each of the diaryltetrazoles with acrylic acid.

3. Limit of detection of Compound 4

Conc. of **4**	100 µM	100 µM	100 µM	100 µM
Conc. of acrylic acid	100 µM	10 µM	1 µM	500 nM
Fold increase in fluorescence	132	17	1.58	1.12

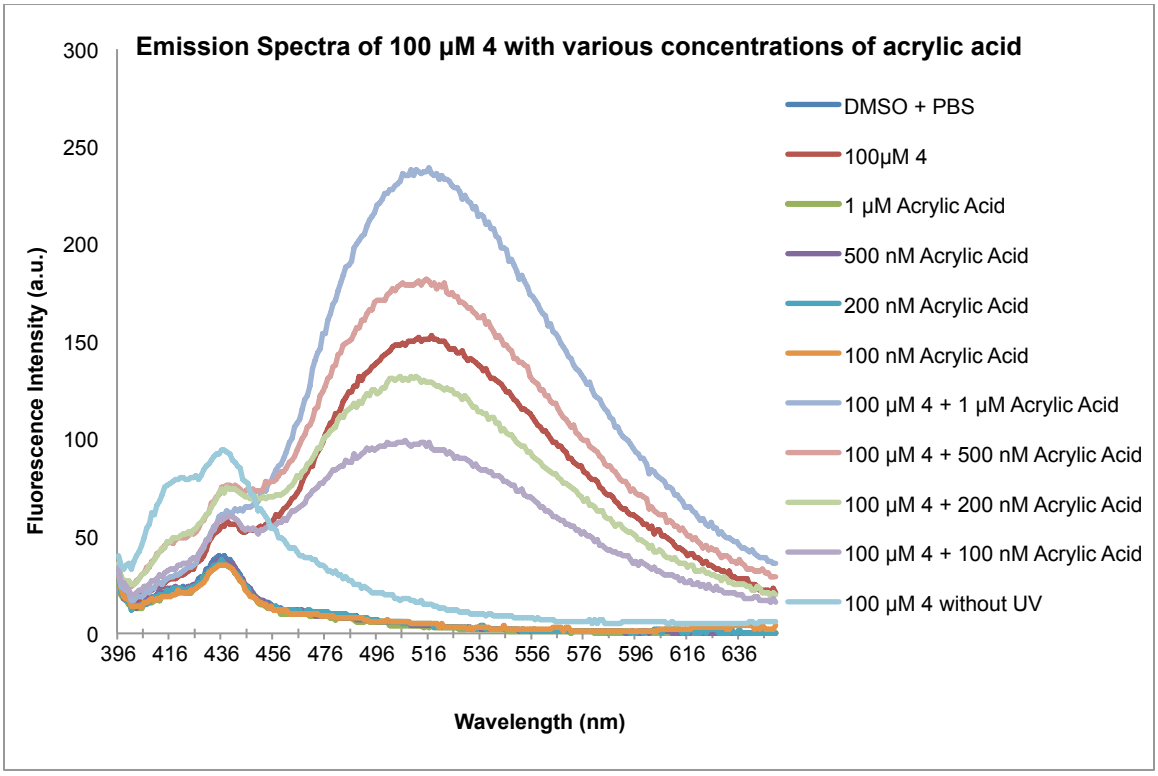


Figure S2. Detection limit of acrylic acid was 500 nM (36 ppb) as determined by measuring the emission spectrum of the reaction between **4** and various concentrations of acrylic acid.

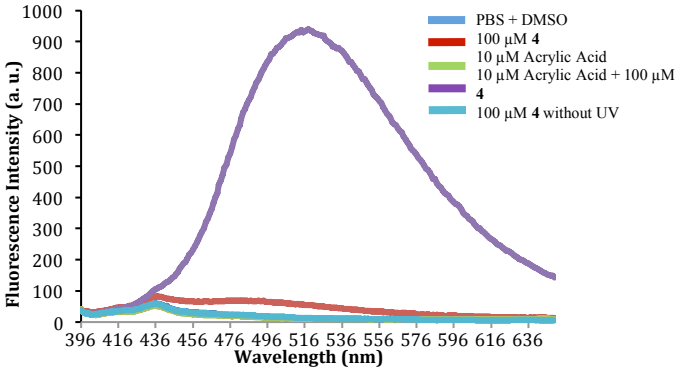


Fig. S3. Emission spectra of **4** (100 µM) with acrylic acid (10 µM) in PBS buffer.

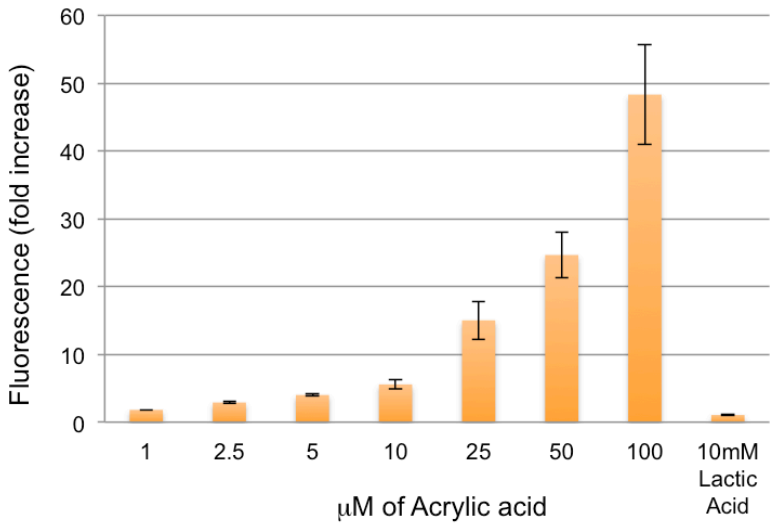


Figure S4. Fold increase in fluorescence upon the addition of acrylic acid at the indicated concentrations to 100 μM of the compound **4** in minimal media (n = 2 ± SD). A 100-fold excess of lactic acid (10 mM) shows negligible fluorescence signal compared to acrylic acid indicating the specificity of **4**.

4. Reaction monitoring of photoactivated cycloaddition using HPLC and fluorescence

Experimental details for reaction monitoring with HPLC

10 mM ZY1_69 was dissolved in dichloromethane and methanol (1:1). A separate solution of 10 mM of acrylic acid was dissolved in methanol. 10 µL of 10 mM ZY1_69 and 10 µL of 10 mM AA were then dissolved in 80 µL of methanol. After vigorous stirring, the mixtures were irradiated with 302nm UV lamp for 0 sec, 15 sec, 30 sec, 45 sec, 60 sec, 90 sec and 120 sec, respectively. An aliquot (10 µL) of reaction solution from each sample was withdrawn and immediately injected in the HPLC column. **4** (A) and **4P** (B) in each sample were monitored by UV absorbance at 254 nm and 370 nm. A linear gradient of 5-90% MeOH was applied after 3 min for 10 min, then kept constant for 10 min before a 7 min linear declining gradient of 90-5% MeOH. Compound **4** and compound **4P** were eluted at about 13.4 min and 12.4 min respectively.

Experimental details for reaction monitoring with fluorescence

All samples were prepared with the same method: 1 µL of 1 mM compound **4** and 1 µL of 1 mM acrylic acid were dissolved in 98 µL of methanol. Distances between all sample vials and UV lamp during photoactivation were equal. Fluorescence turn on of reaction mixture after 15 seconds. From left to right: No UV activation, 15s, 30s, 45s, 60s, 90 and 120s of UV activation.

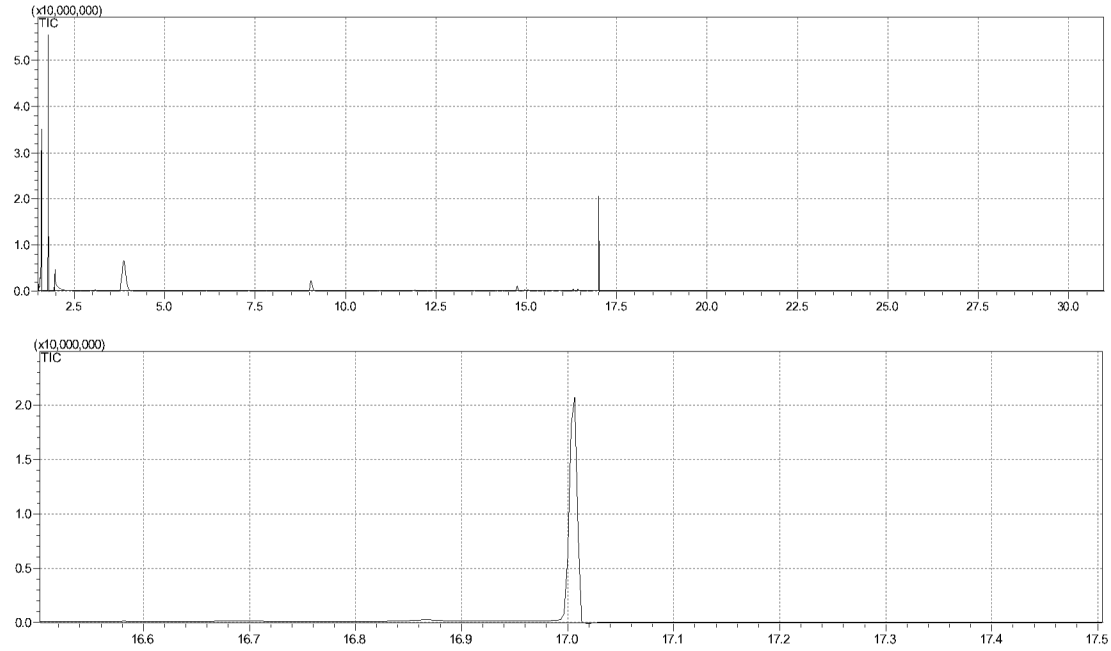
5. GC results of extracted LB samples containing with acrylic acid standards

Experimental details for GCMS detection of acrylic acid

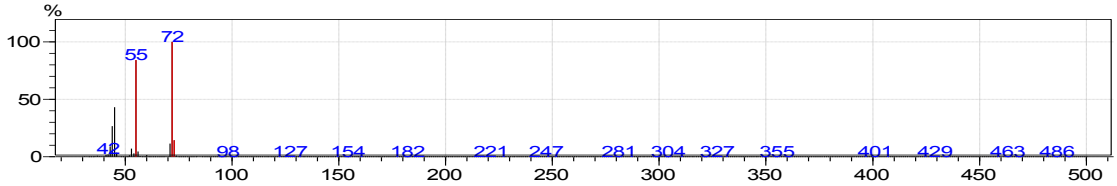
Acrylic acid (6.8 µL, 99 µmol) was dissolved in LB medium (993.2 µL) and stirred vigorously for 10 seconds before being diluted to their respective concentration with LB. 1000 µL of samples of each concentration were transfer to a 2 mL Eppendorf tube and acidified with 30-50 µL of 5M HCl. Each sample was stirred vigorously for about 10 sec and left to stand for 3-5 min. pH of each sample were tested to ensure the pH ≤2. Ether (1000 µL ×2) was then added to the acidified samples for extraction. Combined ether layers were concentrated to about 60 µL for GCMS. Extracted samples were not allowed to evaporate completely as it will affect the GCMS result. Acrylic acid was detected at a retention time of around 17.4 min.

Concentration of acrylic acid	Peak Intensity
100 mM	22,000,000
10 mM	22,000,000
1 mM	5,700,000
750 µM	2,600,000
500 µM	2,600,000
250 µM	1,350,000
100 µM	650,000
10 µM	350,000
0 µM	700,000

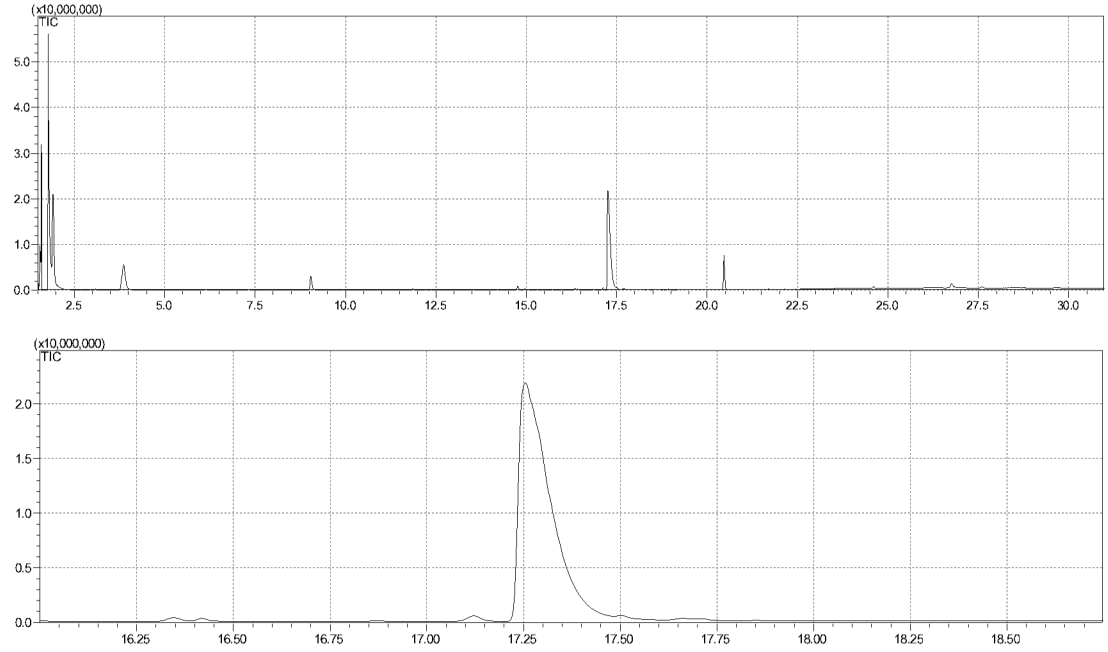
a. Extracted 100 mM acrylic acid in LB



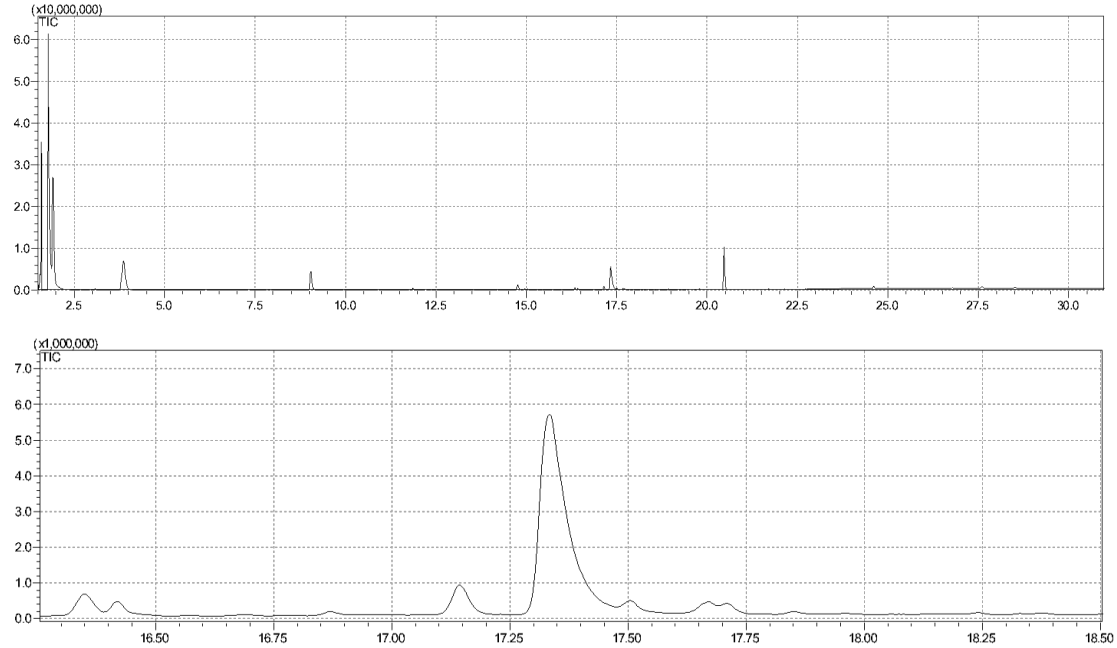
Event#1:Scan Ret.Time : [16.997 -> 17.017] Scan# : [4650 -> 4656]



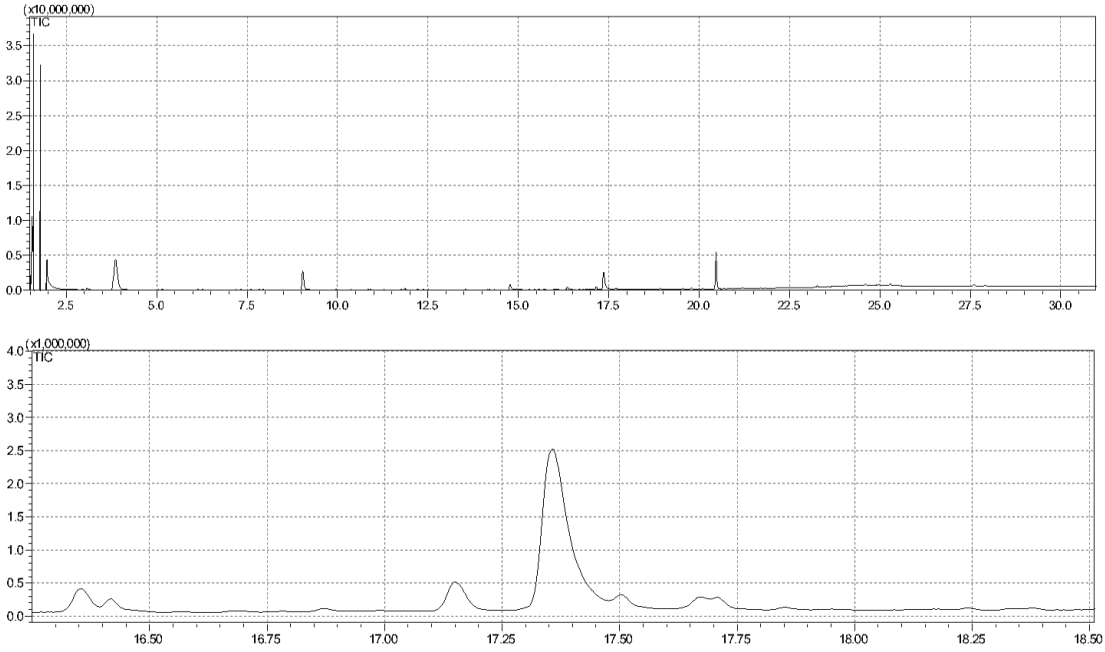
b. Extracted 10 mM acrylic acid in LB



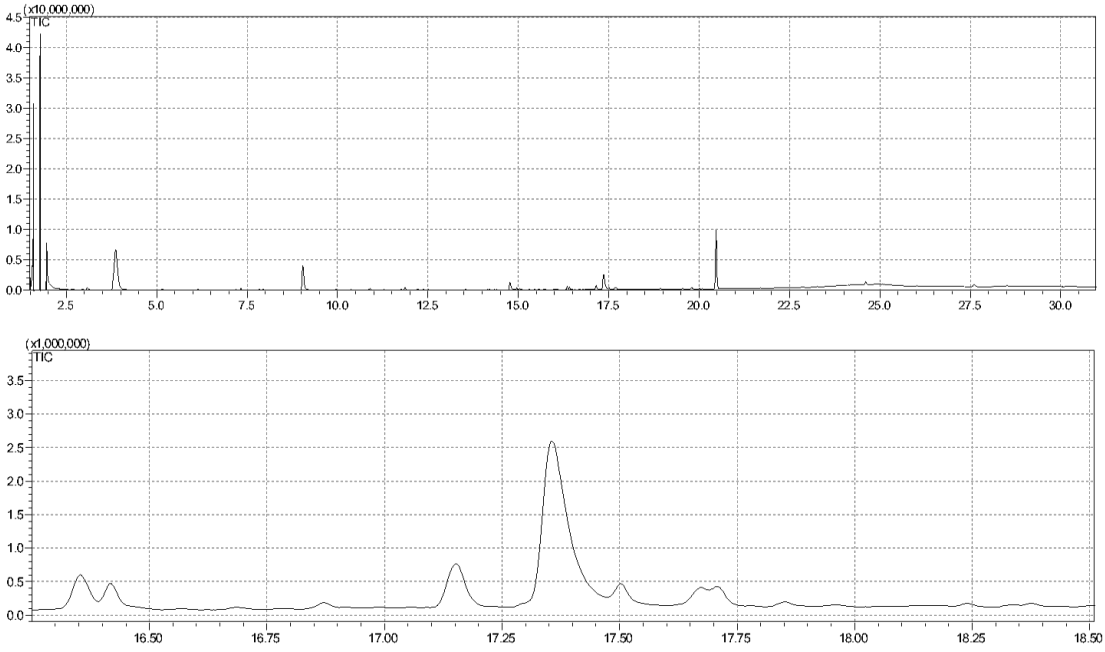
c. Extracted 1 mM acrylic acid in LB



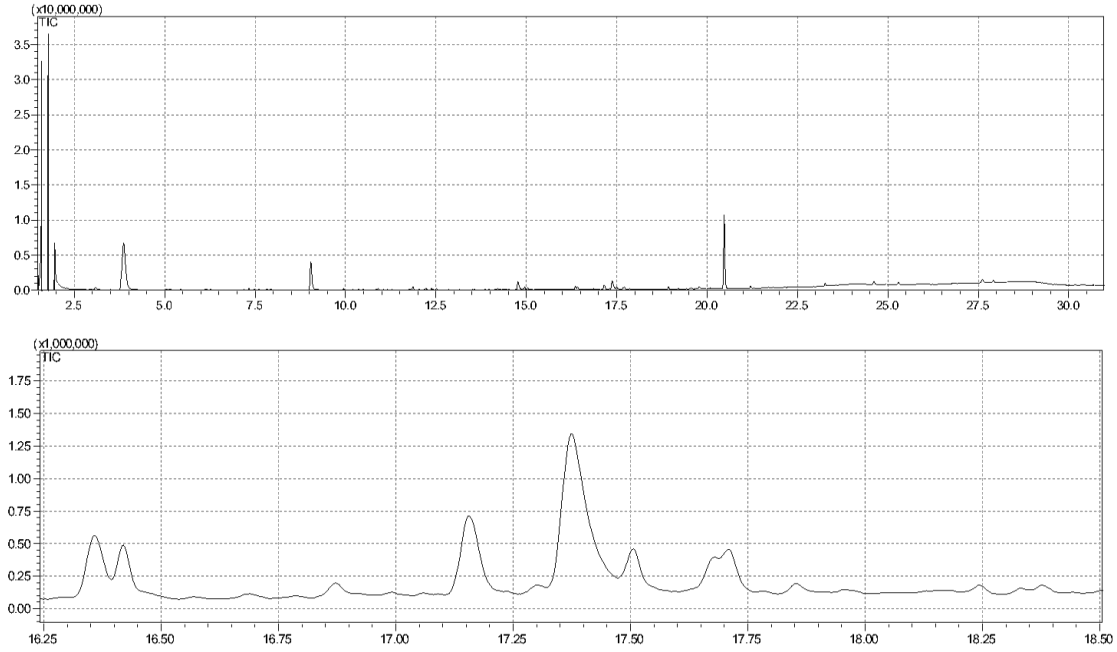
d. Extracted 750 µM acrylic acid in LB



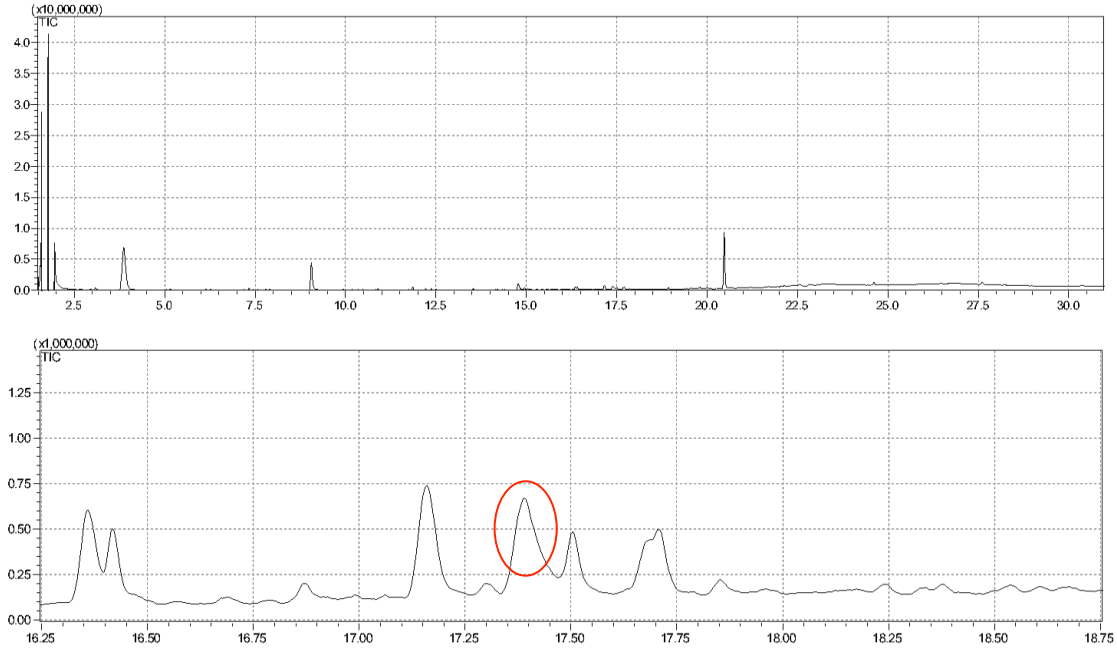
e. Extracted 500 µM acrylic acid in LB



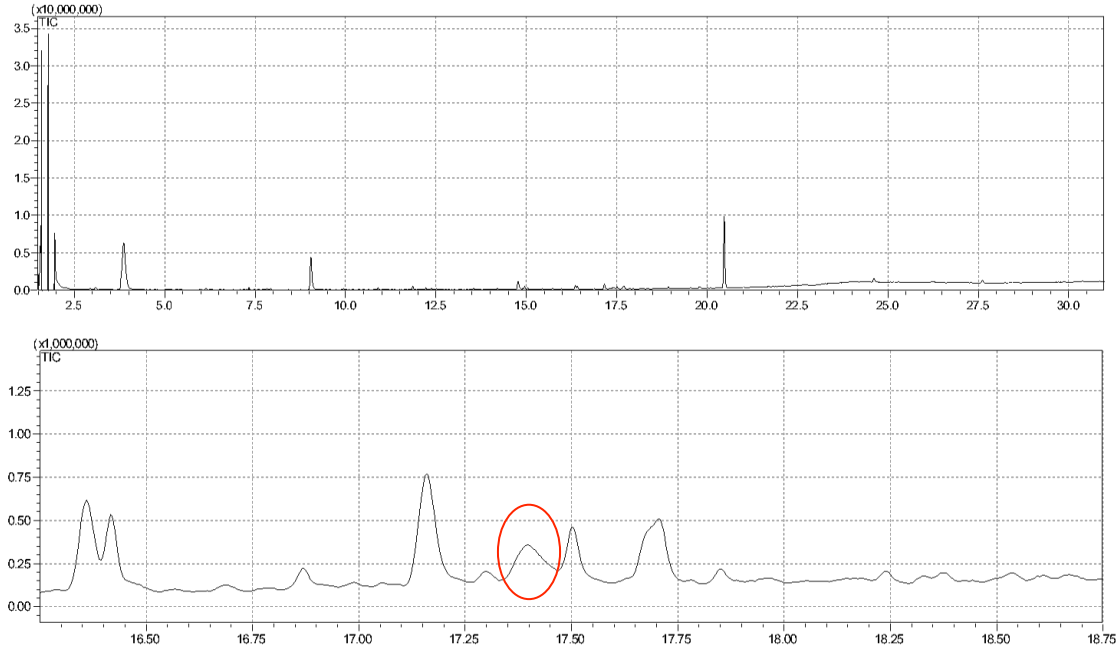
f. Extracted 250 µM acrylic acid in LB



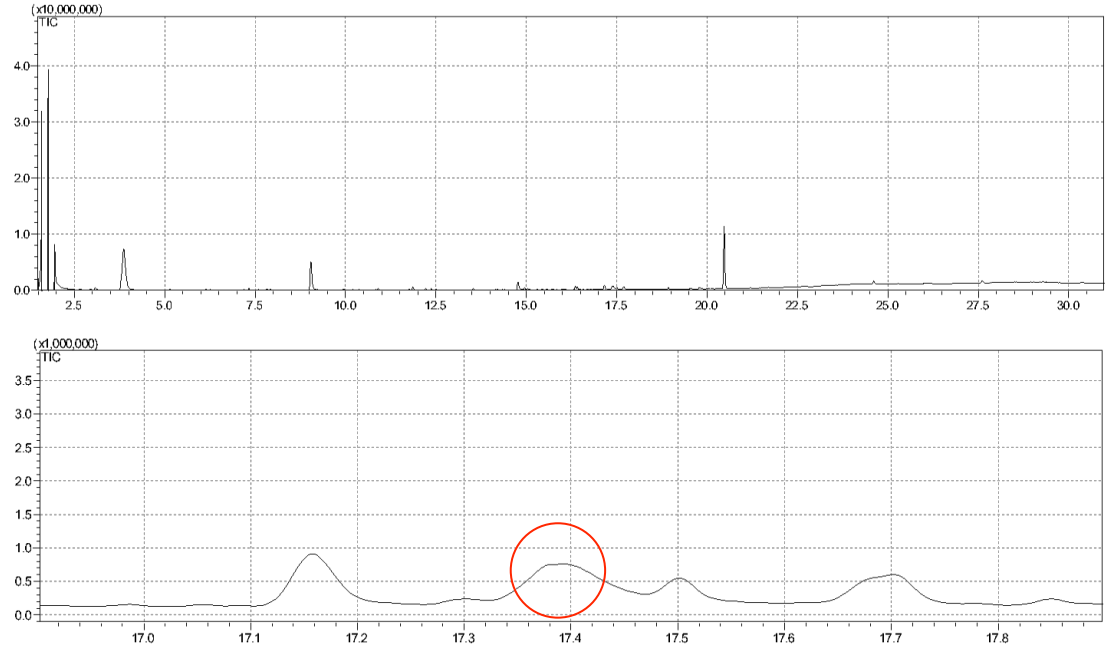
g. Extracted 100 µM acrylic acid in LB



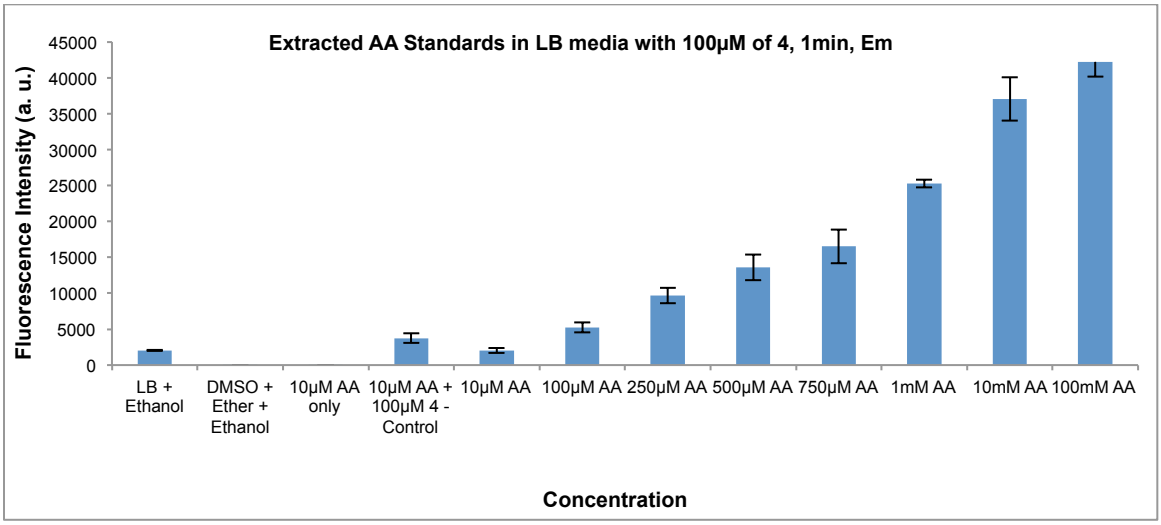
h. Extracted 10 µM acrylic acid in LB



i. Extracted LB Sample (no acrylic acid added)



6. Fluorescence assay of acrylic acid standards in LB media and minimal media



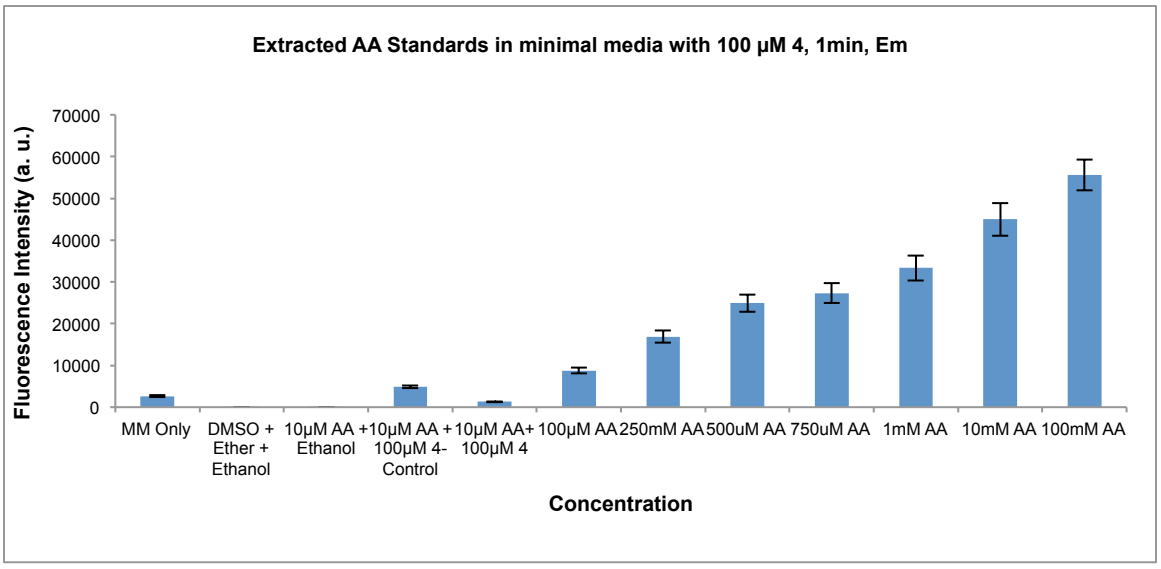


Figure S6. Fluorescence assay of acrylic acid standards in LB media and minimal media (MM), after extraction for GCMS analysis. Control samples are performed in ethanol solvent.

7. Fluorescence of 3-butynoic acid using compound 4

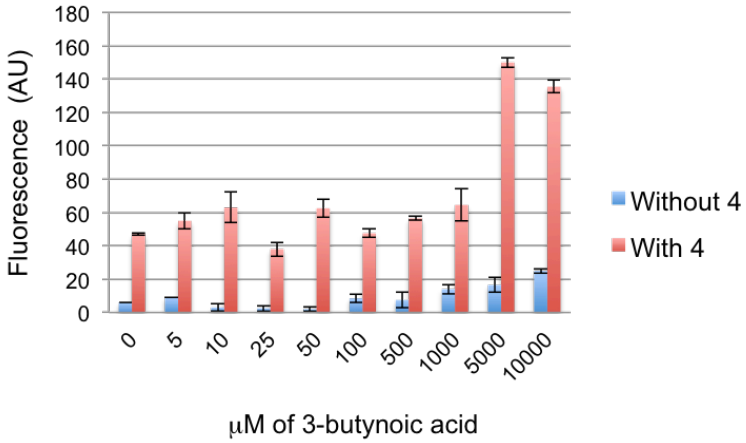


Figure S7. Fluorescence signals of indicated range of 3-butynoic acid concentrations treated with 500 μM compound **4** (n = 2 +/- SD).

8. Experimental details for fluorescence characterization of reaction between compound 4 and acrylic acid at various pH conditions

A solution containing compound **4** (100 μmol) and acrylic acid (100 μmol) was irradiated with a hand-held 302-nm UV lamp for 1 minute. Experiments were performed in Corning flat black 96-well plate with a total reaction volume of 100 μL with buffers of different pH. Excitation wavelength used was 380 nm and emission wavelength was 520 nm. Bandwidth was set at 5nm.