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Rational design of a rapid fluorescent approach for detection of inorganic fluoride in MeCN/H_2O: a new fluorescence switch based on *N*-aryl-1,8-naphthalimide

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General

Absorbance spectra are collected by 8453 UV-Visible Spectrophotometer (Agilent Technologies). Fluorescence measurements are carried out in a FluoroMax-4 Spectrofluorometer (Horiba Jobin Yvon, USA). The fluorescence spectra are recorded in a 1 cm quartz cuvette at room temperature. The excitation and emission slits are set at 5 nm. ^{1}H and ^{13}C NMR spectra were recorded on (^{1}H 300MHz, ^{13}C 75MHz) Bruker 300 UltraShield at room temperature. All reagents used for synthesis and measurements were purchased from Sigma-Aldrich (MO, USA), Fisher Scientific (USA) and Acros Organics (USA) in analytical grade and used as received, unless otherwise stated. All of the measurements of the cations and anions were obtained by using their perchlorate salts and tetrabutylammonium salts. The TLC plate (Silica gel 60 F_{254}) was purchased from EMD (Germany). The silica gel used for column chromatography was purchased from Silicycle ((SiliaFlash® F60, 40-63μm, 60Å) Canada).

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Synthesis

6-bromo-2-(2-hydroxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (a1) A mixture of 4-bromo-1,8-naphthalic anhydride (1.00g, 3.60 mmol) and 2-aminophenol (0.79g, 7.20 mmol) in 20.0 mL 2-methoxyethanol was refluxed for 12 hr under argon atmosphere. Then, the reaction solution was poured into 6% HCl (50 mL) in ice bath to collect precipitate. The crude product was purified by column chromatography (silica, 220-400 mesh, dichloromethane: ethyl acetate = 4:1 v/v) to yield **a1** as a light yellow solid (1.18g, 89%). ^{1}H NMR (300 MHz, DMSO) δ: 6.88-7.02 (m, 2H), 7.19-7.34 (m, 2H), 8.05 (t, *J*=8.1 Hz, 1H), 8.27 (d, *J*=7.5Hz, 1H), 8.37 (d, *J*=7.8Hz, 1H), 8.57-8.66 (m, 2H), 9.65 (s, 1H); ^{13}C (75MHz, DMSO) δ: 117.0, 119.6, 123.0, 123.1, 123.9, 129.4, 129.6, 130.2, 130.5, 130.7, 131.4, 131,9, 132.1, 133.2, 153.8, 163.2, 163.3.

2-(2-hydroxyphenyl)-6-methoxy-1H-benzo[de]isoquinoline-1,3(2H)-dione (b1) a1 (1.00 g, 2.72 mmol), 25% wt sodium methoxide in methanol (1.29 mL, 5.44 mmol) and CuBr (100 mg) were refluxed in 10 mL anhydrous methanol for 8 hr under argon atmosphere. After the reaction, mixture was poured into 6% HCl (20 mL) in ice bath to collect precipitate as crude product that was purified in further by using column chromatography (silica, 220-400 mesh, CH_2Cl_2 : EtOAc = 4: 1 *v/v*). The product is isolated as an white solid **b1** (0.74g, 85%). ^{1}H NMR (300 MHz, DMSO) δ: 4.15 (s, 3H), 6.86-7.01 (m, 2H), 7.19 (d, *J*=7.8 Hz 1H), 7.27 (t, *J*=7.5 Hz, 1H), 7.37 (d, *J*=8.7Hz, 1H), 7.87 (t, *J*=7.8Hz, 1H), 8.44-8.53 (m, 2H), 8.60 (d, *J*=8.4 Hz 1H), 9.62 (s, 1H); ^{13}C (75MHz, DMSO) δ: 57.5, 106.8, 115.3, 116.8, 119.6, 123.0, 123.4, 123.6, 126.9, 128.8, 129.6, 129.9, 130.8, 131.5, 133.7, 153.9, 160.8, 163.4, 164.0.

6-methoxy-2-(2-(trimethylsilyloxy)phenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (FCS-1) b1 (0.60g, 1.88 mmol) and Chlorotrimethylsilane (0.64mL, 5.00 mmol) in 5.0 mL pyridine was heated for 12 hr at 50 °C under argon atmosphere. After cooling down to room temperature, reaction mixture was poured into 6% HCl (20 mL) in ice bath to remove pyridine and extracted with dichloromethane (50 mL) to collect crude product. Crude product was purified by column chromatography (silica, 220-400 mesh, Hexane : EtOAc = 1: 1 *v/v*). The product is isolated as a yellow solid **FCS-1** (0.47g, 67%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.13 (s, 9H), 4.21 (s, 3H), 7.03 (d, *J*=8.4 Hz, 1H), 7.08-7.19 (m, 2H), 7.31-7.42 (m, 2H), 7.78 (t, *J*=7.8 Hz, 1H), 8.62-8.72

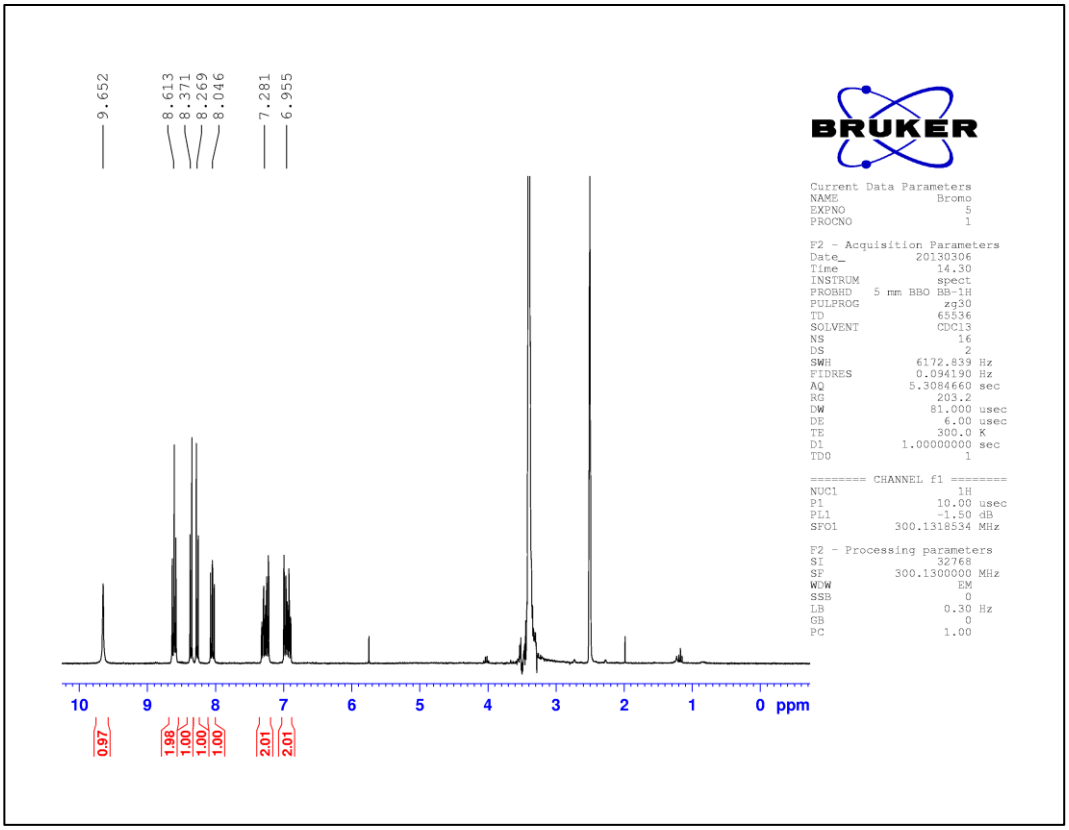
(m, 3H); ^{13}C (75MHz, $CDCl_3$) δ: 0.4, 56.3, 105.3, 115.3, 120.1, 121.8, 122.8, 123.7, 126.0, 127.2, 128.8, 129.7, 129.9, 130.2, 131.8, 133.7, 151.5, 161.0, 163.7, 164.2. TOF MS EI$^+$: M^+ *m/z* 392.1273 (calcd.), 392.1251 (found).

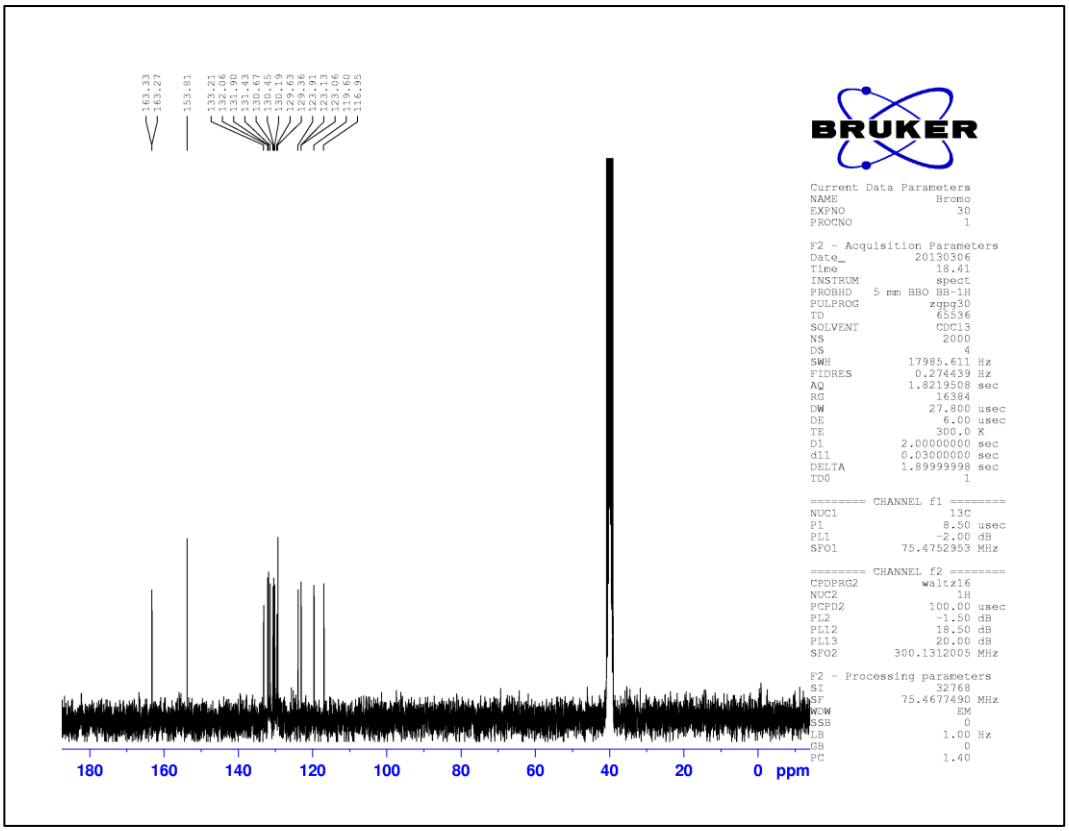
6-bromo-2-(4-hydroxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (a2) A mixture of 4-bromo-1,8-naphthalic anhydride (1.00g, 3.60 mmol) and 4-aminophenol (0.79g, 7.20 mmol) in 20.0 mL 2-methoxyethanol was refluxed for 15 min under argon atmosphere. Then, the reaction solution was poured into 6% HCl (50 mL) in ice bath to collect precipitate. The crude product was purified by column chromatography (silica, 220-400 mesh, dichloromethane: ethyl acetate = 4:1 v/v) to yield **a2** as a milky white solid (1.21g, 91%). ^{1}H NMR (300 MHz, DMSO) δ: 6.83-6.92 (m, 2H), 7.11-7.19 (m, 2H), 8.01 (t, *J*=8.1 Hz, 1H), 8.24 (d, *J*=7.8 Hz, 1H), 8.33 (d, *J*=8.1 Hz, 1H), 8.53-8.61(m, 2H), 9.69 (s, 1H); ^{13}C (75MHz, DMSO) δ: 115.9, 123.0, 123.8, 127.0, 129.1, 129.2, 129.5, 130.2, 130.3, 131.4, 131.8, 132.0, 133.1, 157.7, 163.7, 163.8.

2-(4-hydroxyphenyl)-6-methoxy-1H-benzo[de]isoquinoline-1,3(2H)-dione (b2) a2 (1.00 g, 2.72 mmol), 25% wt sodium methoxide in methanol (1.29 mL, 5.44 mmol) and CuBr (100 mg) were refluxed in 10 mL anhydrous methanol for 8 hr under argon atmosphere. After the reaction, mixture was poured into 6% HCl (20 mL) in ice bath to collect precipitate as crude product that was purified in further by using column chromatography (silica, 220-400 mesh, CH_2Cl_2 : EtOAc = 4: 1 *v/v*). The product is isolated as a white solid **b2** (0.72g, 83%). ^{1}H NMR (300 MHz, DMSO) δ: 4.18 (s, 3H), 6.86 (d, *J*=8.6 Hz 2H), 7.12 (d, *J*=8.6 Hz 1H), 7.37 (d, *J*=8.4 Hz, 1H), 7.86 (t, *J*=7.8Hz, 1H), 8.42-8.55 (m, 2H), 8.60 (d, *J*=8.4 Hz 1H), 9.63 (s, 1H); ^{13}C (75MHz, DMSO) δ: 57.2, 115.3, 115.9, 122.9, 123.3, 126.8, 127.5, 128.7, 129.4, 130.4, 131.6, 133.7, 157.5, 160.8, 163.9, 164.5.

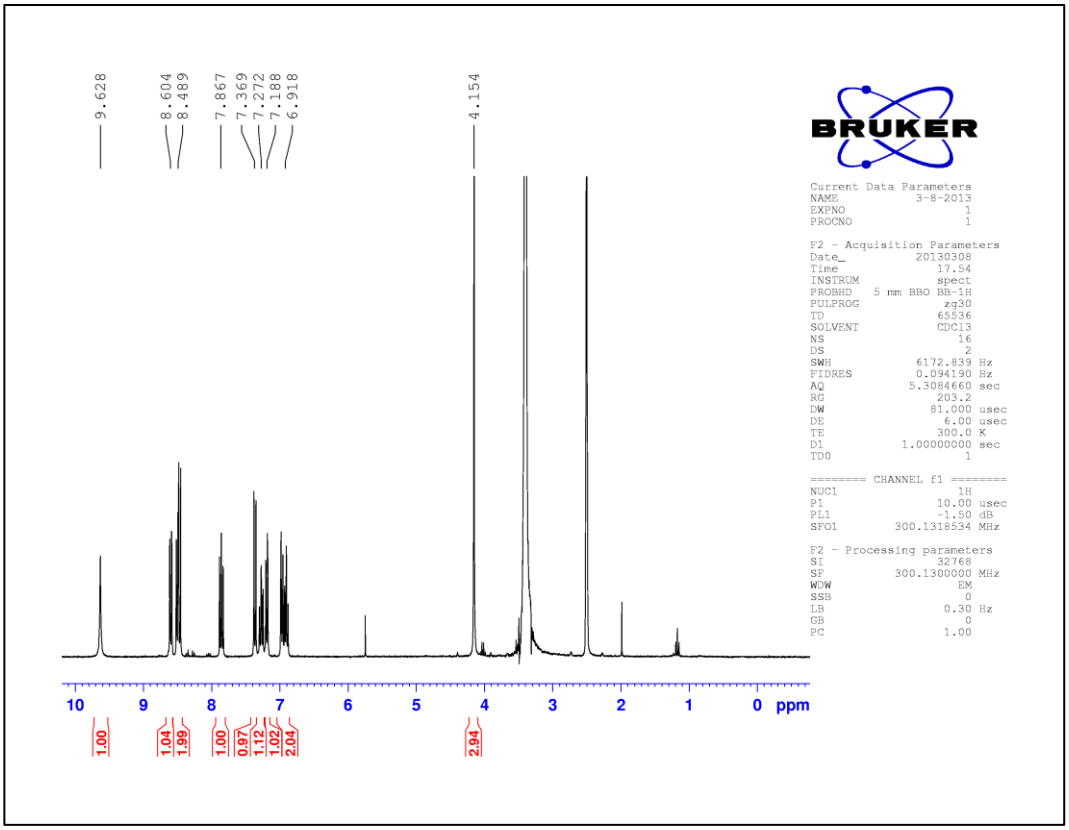
6-methoxy-2-(4-(trimethylsilyloxy)phenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (FCS-2) b2 (0.60g, 1.88 mmol) and Chlorotrimethylsilane (0.64mL, 5.00 mmol) in 5.0 mL pyridine was heated for 12 hr at 50 °C under argon atmosphere. After cooling down to room temperature, reaction mixture was poured into 6% HCl (20 mL) in ice bath to remove pyridine and extracted with dichloromethane (50 mL) to collect crude product. Crude product was purified by column chromatography (silica, 220-400 mesh, Hexane : EtOAc = 1: 1 *v/v*). The product is isolated as a yellow solid **FCS-2** (0.37g, 53%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.36 (s, 9H), 4.21 (s, 3H), 6.95-7.06 (m, 2H), 7.13 (d, *J*=8.3 Hz, 1H), 7.17-7.23 (m, 2H), 7.78 (t, *J*=7.8 Hz, 1H), 8.60-8.72 (m, 3H); ^{13}C (75MHz, $CDCl_3$) δ: 0.8, 57.4, 106.7, 115.2, 115.9, 123.0, 123.4, 127.0, 127.6, 128.9, 129.6, 130.5, 131.6, 133.9, 157.5, 160.8, 163.9, 164.5. TOF MS EI$^+$: M+ m/z 392.1273 (calcd.), 392.1292 (found).

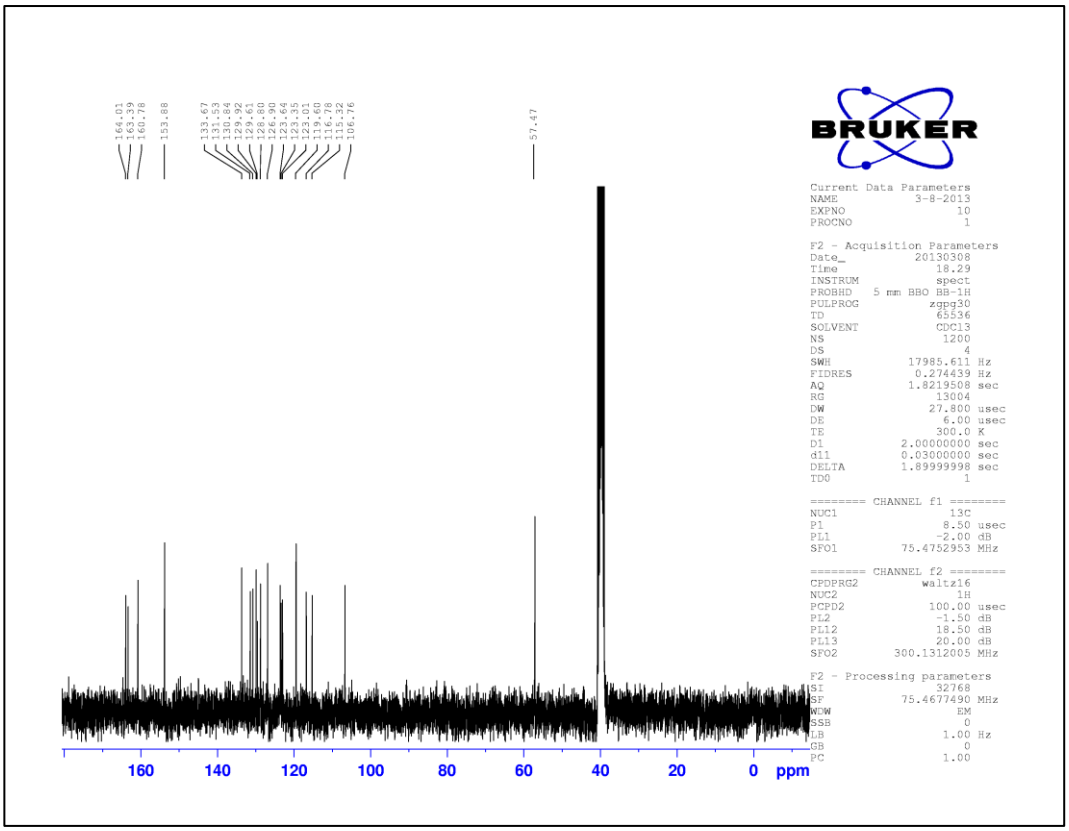
a1



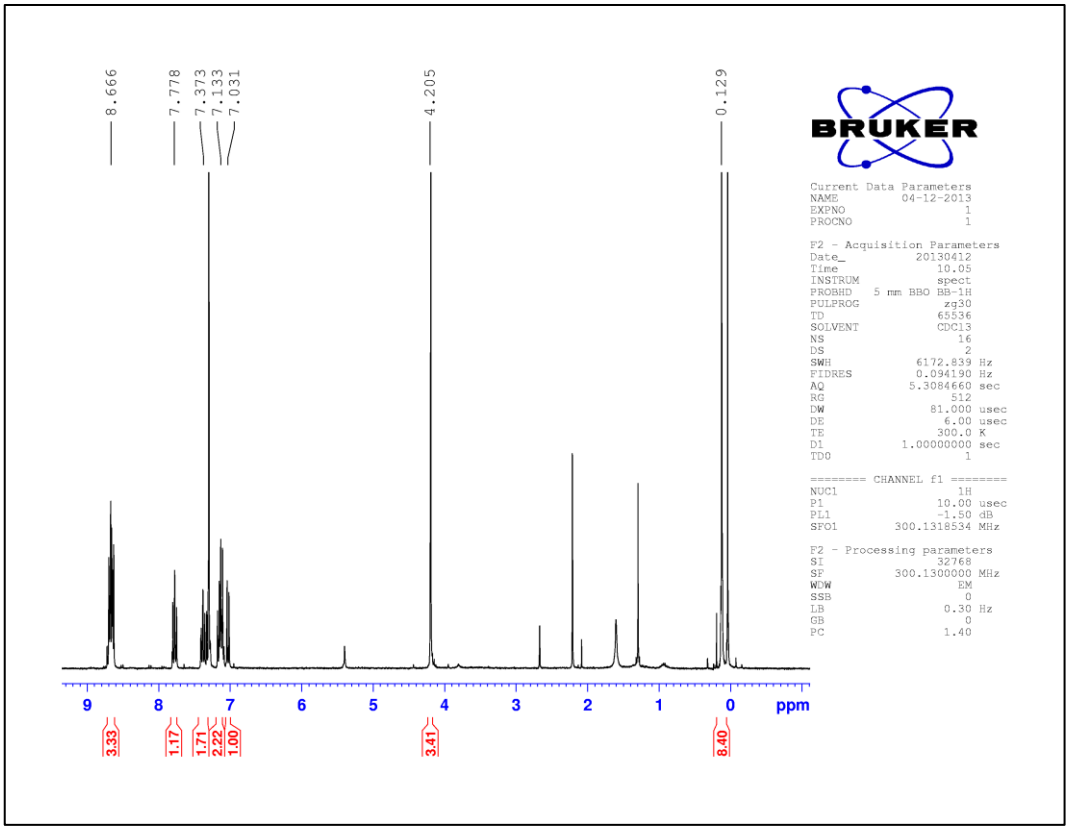


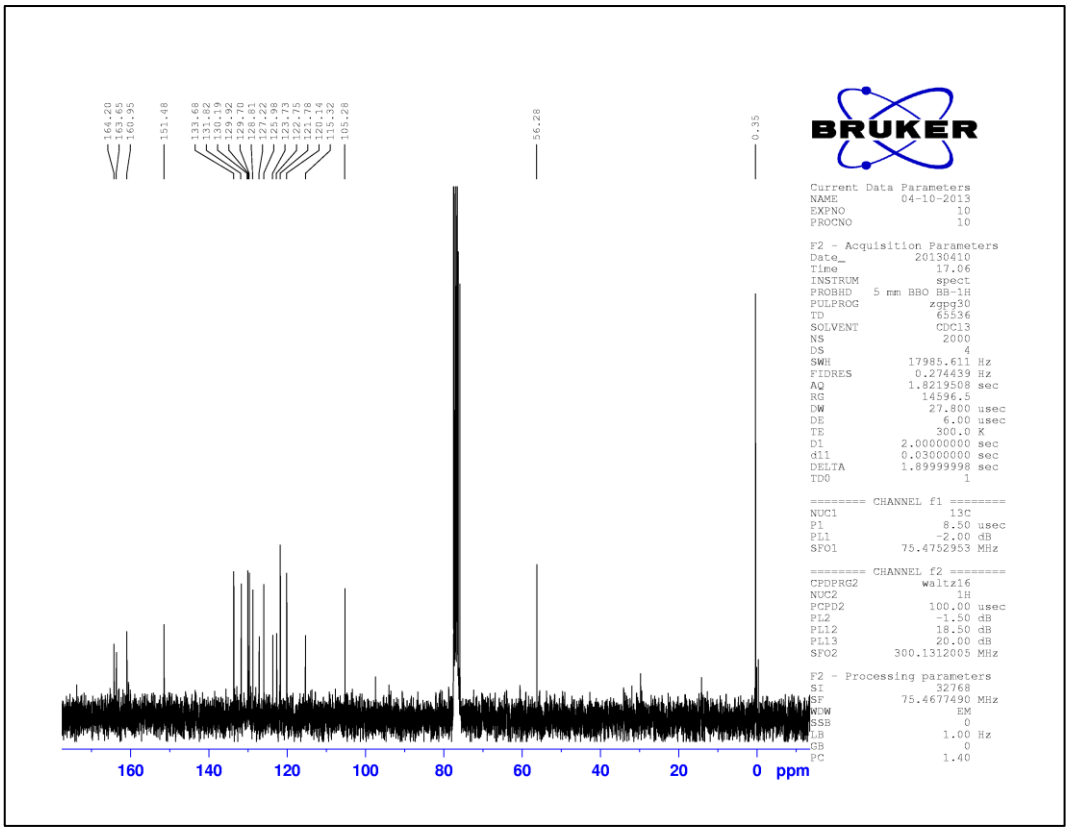
b1





FCS-1





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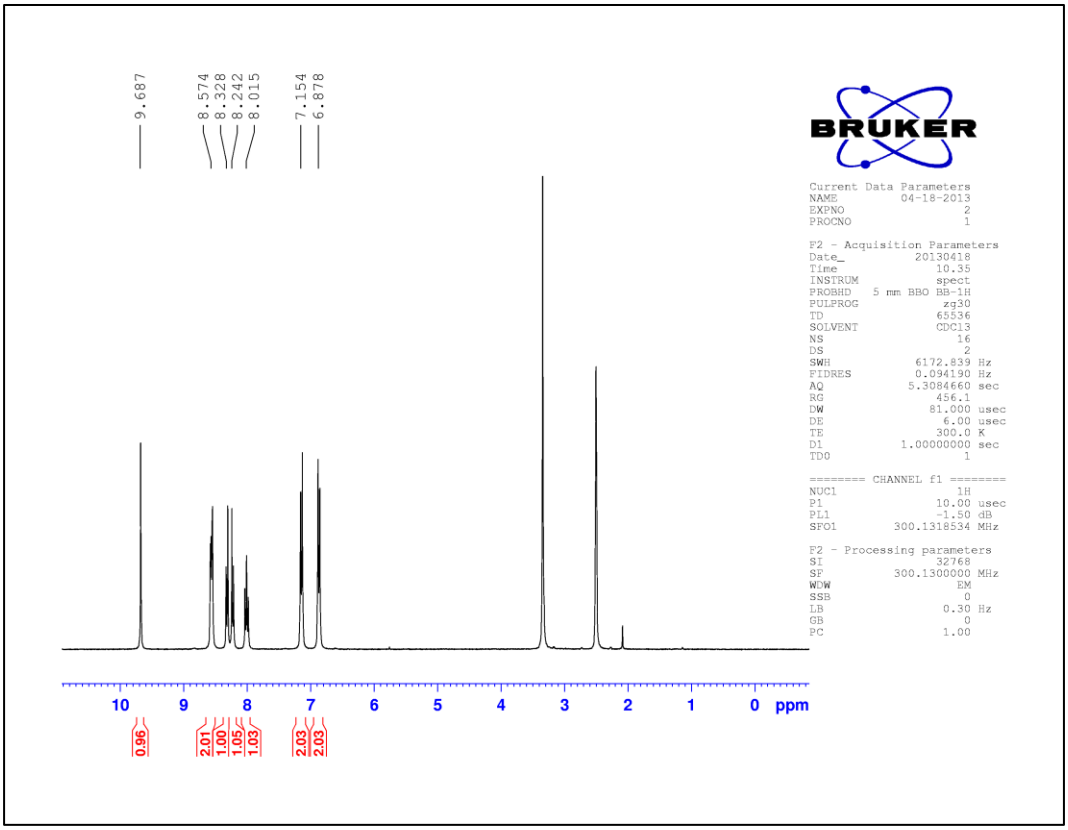
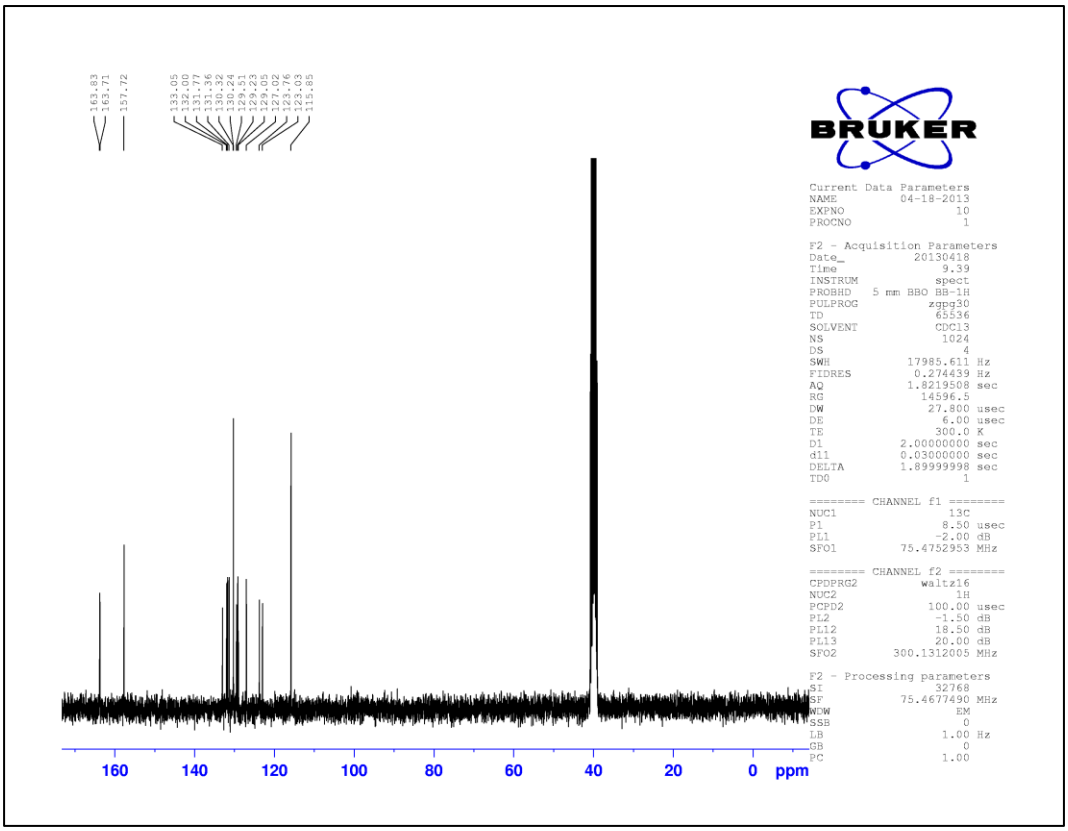
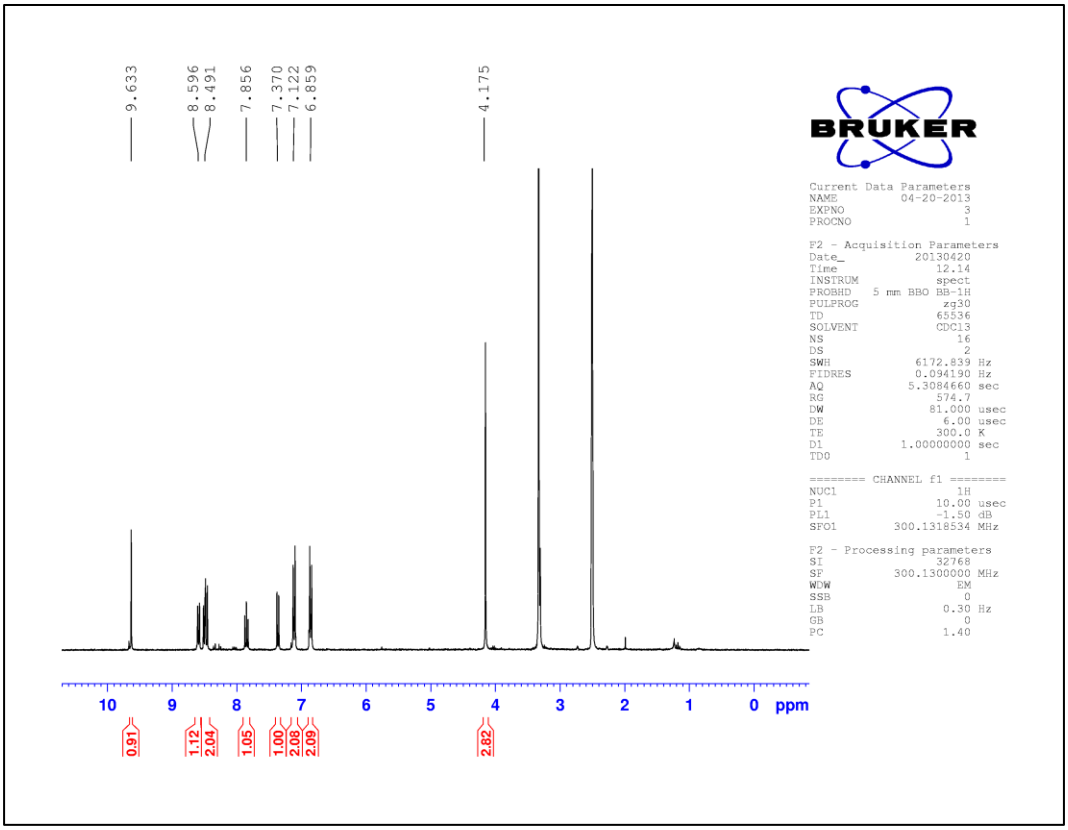
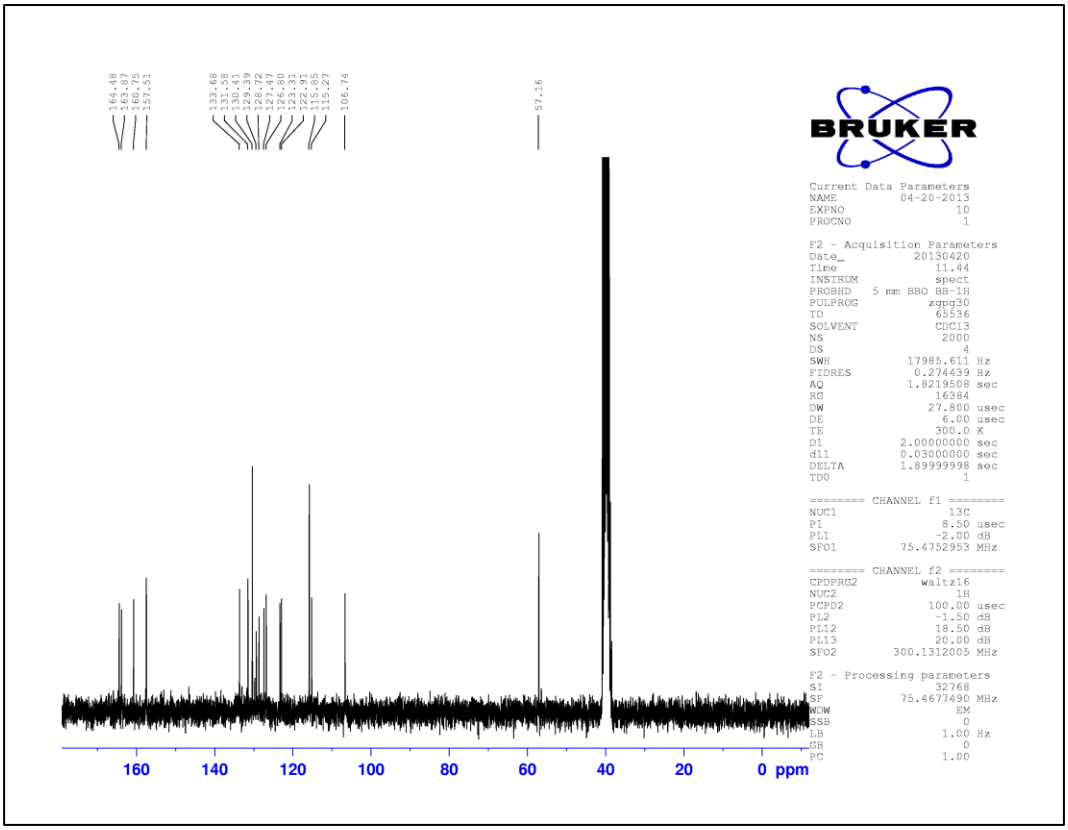




b2





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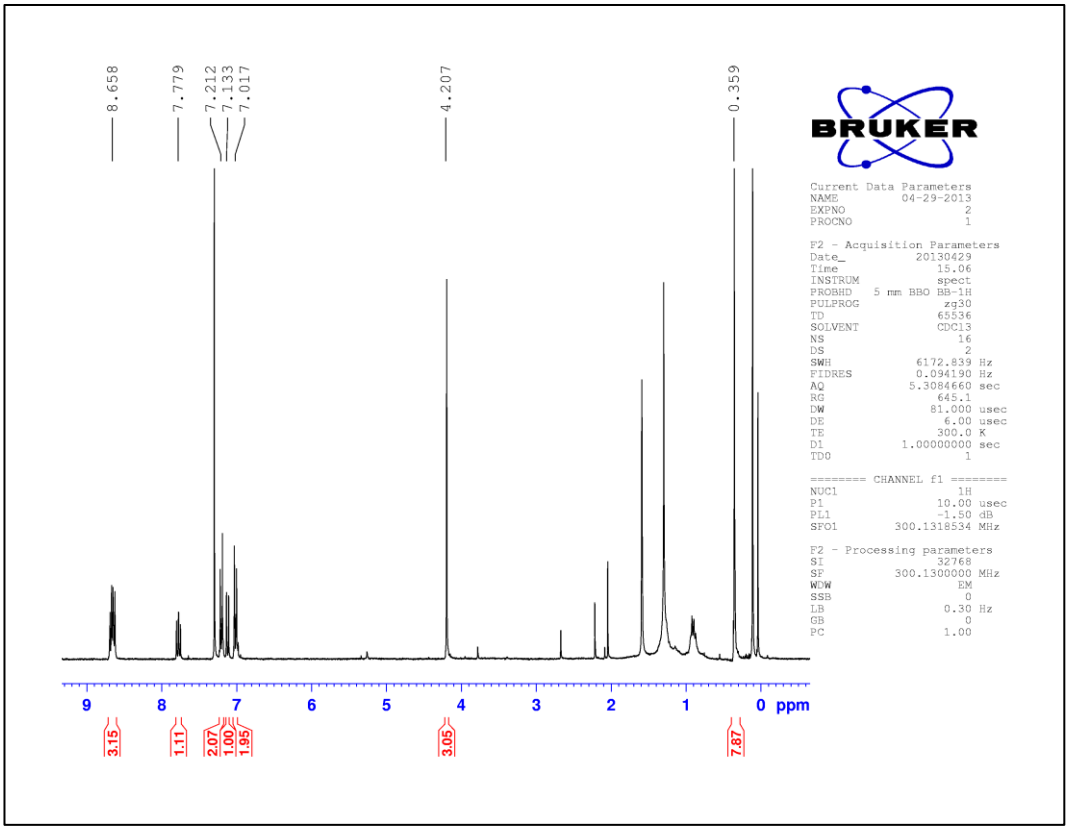
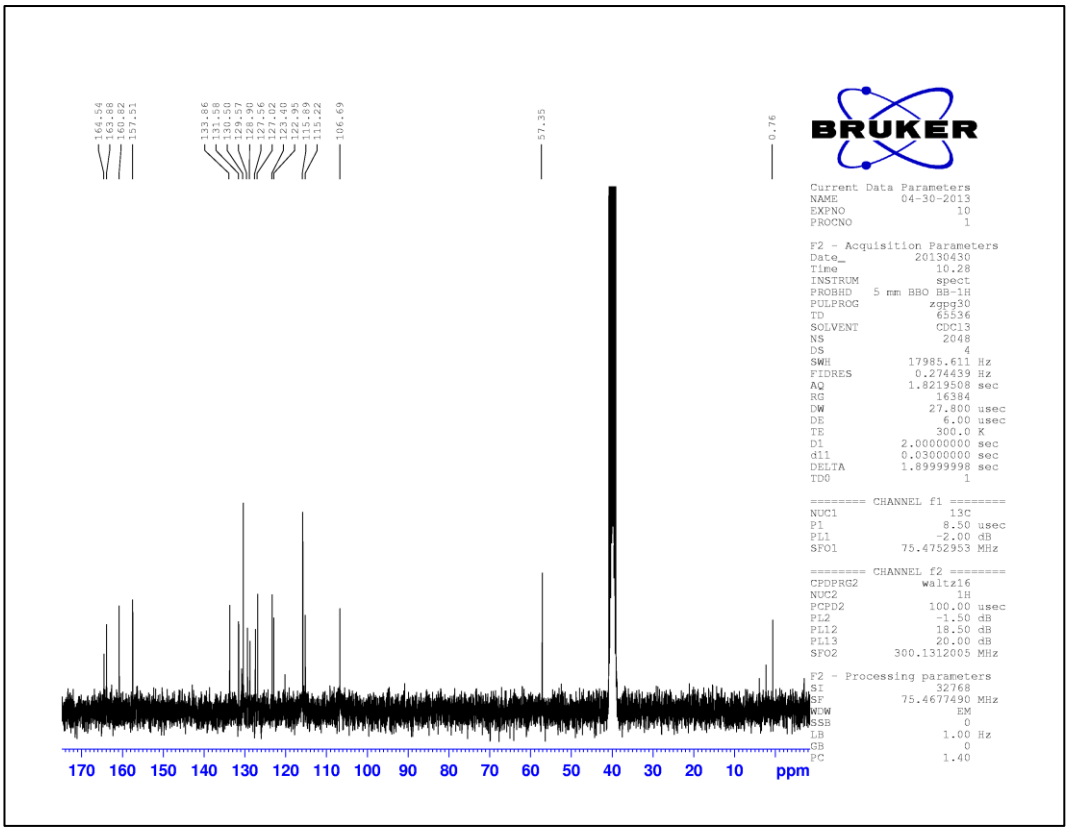
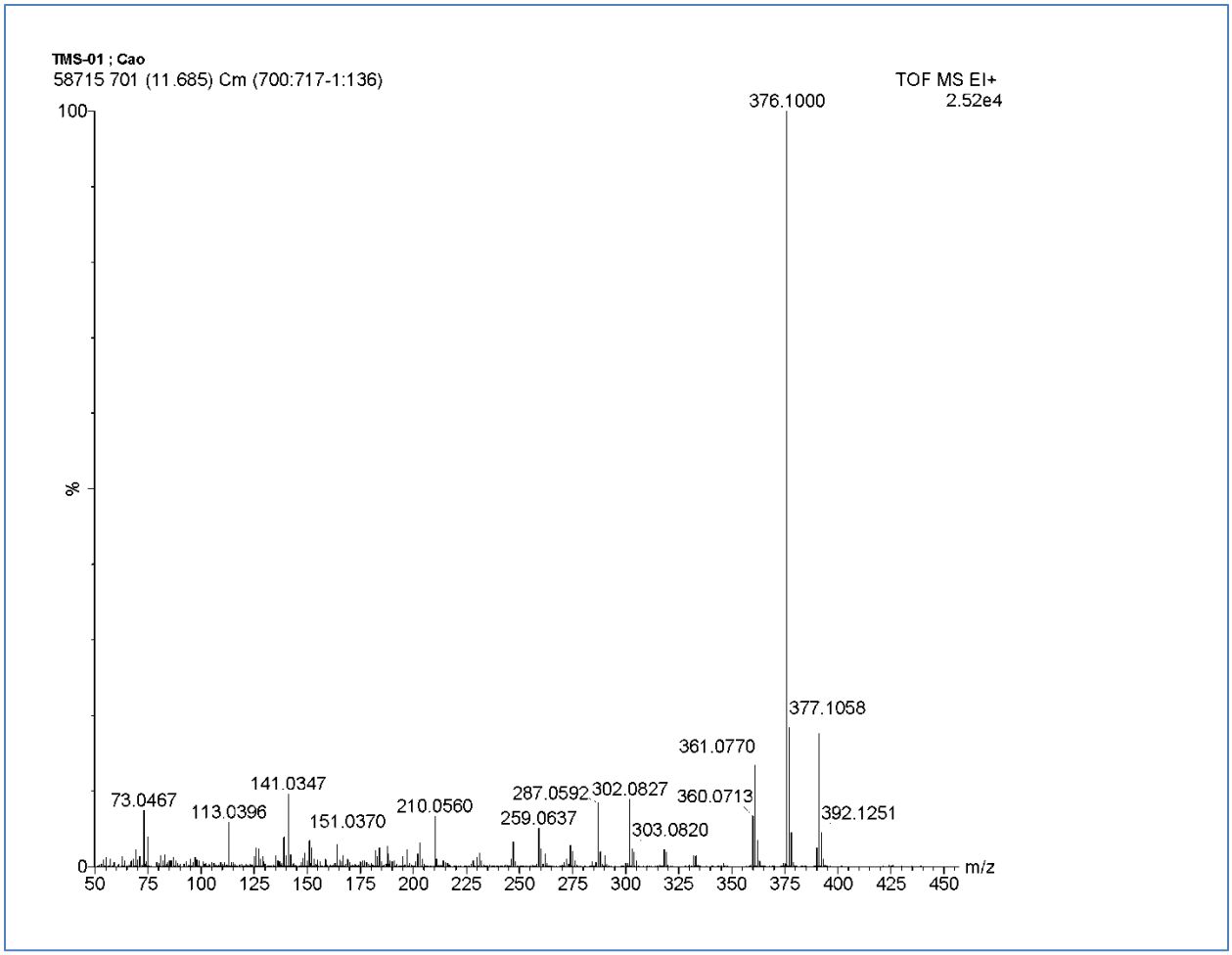


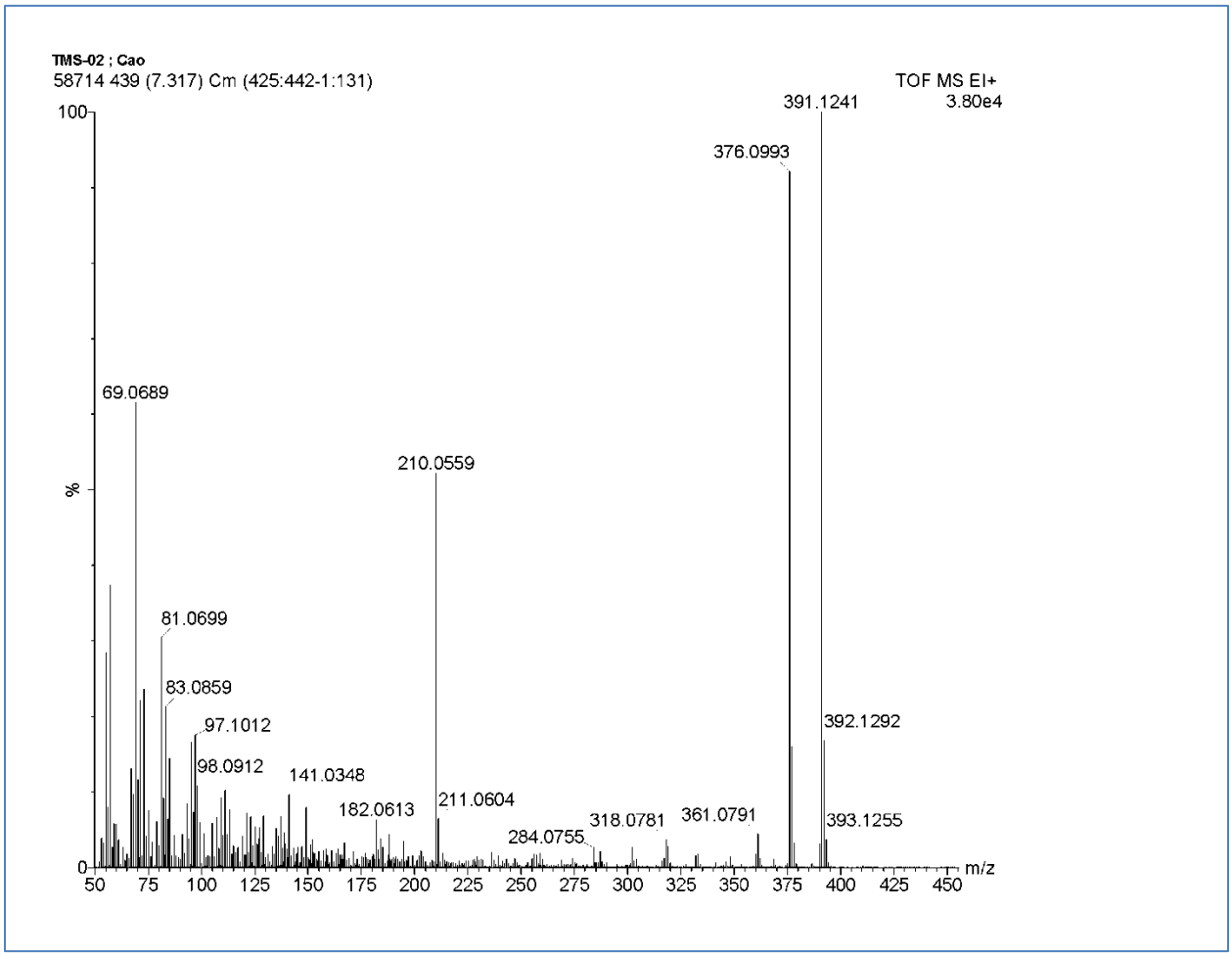


HRMS

FCS-1



FCS-2



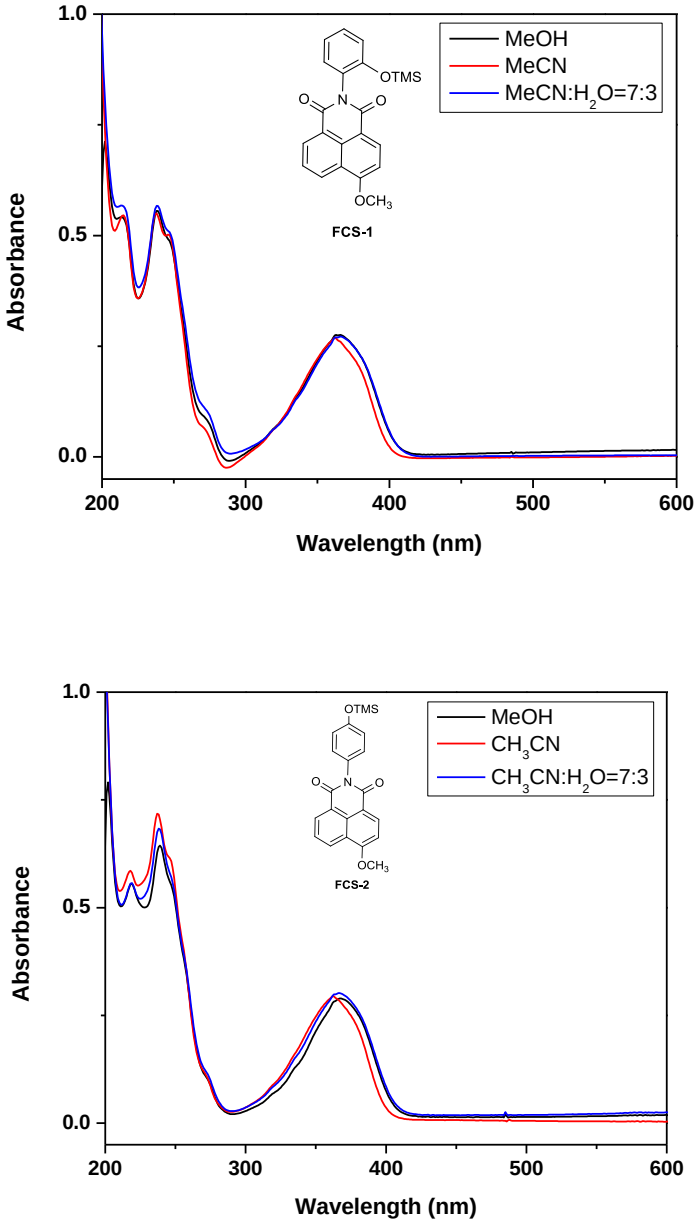


Figure S1: The absorption spectra of FCS-1 and FCS-2 (2.0×10^{-5}M) in MeOH, MeCN, and MeCN/H_2O (v:v=7:3) at room temperature.

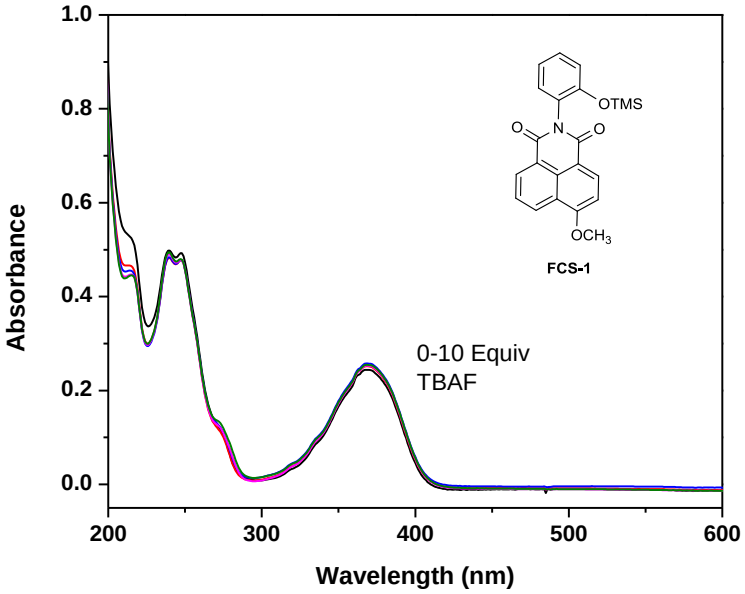


Fig. S2: The absorption spectra of FCS-1 (2.0×10^{-5}M) with addition of 1-10 equivalent TBAF in MeCN/H_2O (v:v=7:3) at room temperature.