Electronic Supplementary Material (ESI) for RSC Advances.

Sensing and discrimination of cyanide and hydrogen sulfide using an 8-alkenyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene derivative

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General Methods

^{1}H and ^{13}C NMR spectra were recorded on a 200 or 300 MHz spectrometers in deuterochloroform ($CDCl_3$) with either tetramethylsilane (TMS) (0.00 ppm ^{1}H, 0.00 ppm ^{13}C) or chloroform (7.26 ppm ^{1}H, 77.00 ppm ^{13}C) as internal reference unless otherwise stated. Data are reported in the following order: chemical shift in ppm, multiplicities (br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), sex (sextet), hex (hextet), m (multiplet), exch (exchangeable), app (apparent)), coupling constants, *J* (Hz), and integration. IR peaks are reported (cm^{-1}) with the following relative intensities: s (strong, 67-100%), m (medium 40-67%), and w (weak 20-40%). UV-vis absorption spectra were recorded using a 1 cm path length quartz cuvette on a Shimadzu UV-2101PC spectrophotometer. All measurements were carried out at 293 K (thermostated).

Starting materials

8-MethylthioBODIPY was donated by Cuantico de México (www.cuantico.mx), and CuTC,[1] was prepared according to the literature procedure. All of the other reactants, ligands, and catalysts were commercially available.

Synthesis of compound 1. An oven-dry Schlenk tube, equipped with a stir bar, was charged with the boronic acid (0.2520 mmol, 3 equiv), 8-methylthioBODIPY (0.0840 mmol, 20.0 mg, 1equiv) and dry THF (3.0 mL) under N_2. The stirred solution was sparged with N_2 for 10 min, whereupon CuTC (0.2520 mmol, 3 equiv), $Pd_2(dba)_3$ (2.5 mol %), and TFP (7.5 mol %) were added under N_2. The reaction mixture was immersed into a pre-heated oil bath at 55 ^{0}C. After 1 hour, the reaction mixture was allowed to reach room temperature and was adsorbed on SiO_2-gel. After flash-chromatography (SiO_2-gel, 20% EtOAc/hexanes) purification, compound **1** was as obtained as a cherry solid. For purposes of characterization, the solid product was crystallized from CH_2Cl_2/petroleum ether. According to procedure. Reaction time 1h. TLC (20% EtOAc/hexanes) R_f =0.5; mp 175-

176 °C; yield = 80%; IR (KBr, cm^{-1}) 1621 (w), 1547 (m), 1529 (w), 1489 (w), 1470 (w), 1411 (m), 1392 (m), 1268 (w), 1195 (w), 1121 (m), 1078 (s), 962 (m), 951 (m), 785 (w), 755(w); ^1H NMR (300 MHz, $CDCl_3$): δ 7.85 (s, 2H), 7.61-7.58 (m, 2H), 7.44-7.41 (m, 5H), 7.32 (d, *J* = 3Hz, 2H), 6.52 (d, *J* = 3Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.0, 144.0, 143.2, 135.8, 134.1, 130.8,129.4, 128.5, 128.2, 121.4, 118.1. HRMS (M^+) ($C_{17}H_{13}BF_2N_2$): calcd. 295.1213, found 295.1207.

Synthesis of compound 2. Compound **1** (20.0 mg, 0.068 mmol, 1 equiv) was dissolved in 2.7 mL of CH_3CN. Next, KCN (6.7 mg, 0.1020 mmol, 1.5 equiv) dissolved in 0.3 mL of H_20 was added to the solution and the mixture was stirring to room temperature. After TLC showed that the reaction went to completion, 5 mL of H_2O were added, the organic layer was extracted with EtOAc (2 x 10 mL), the organic phases were combined and washed with brine (2 x 10 mL). After, the organic phase was dried over $MgSO_4$ anhydrous to be filtered and concentrated in vacuo. The residue was re-dissolved in EtOAc and was adsorbed on SiO_2-gel. After flash-chromatography (SiO_2-gel, EtOAc/hexanes gradient) purification, compound **2** was obtained as orange solid. For purposes of characterization, the solid product was crystallized from CH_2Cl_2/petroleum ether. According to procedure. Reaction time 1h. TLC (30% EtOAc/Hexanes) R_f=0.3; orange solid; mp 179-180 ºC; yield = 84%; IR (KBr, cm^{-1}): 3144 (w), 2246 (w), 1578 (s), 1413 (s), 1397 (s), 1264 (s), 1198 (m), 1119 (s), 1088 (s), 1078 (s), 1031 (m), 951 (m) 766 (m), 755 (m), 701 (m); ^1H-NMR (200 MHz, $CDCl_3$): δ 7.88 (s, 2H), 7.34-7.26 (m, 5H), 7.09 (d, *J* = 4Hz, 2H), 6.51 (d, *J* = 4Hz, 2H), 4.18-4.11 (m, 1H), 3.60-3.50 (m, 1H), 3.37-3.27 (m, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$): δ 145.39, 142.17, 135.51, 134.38, 129.80, 129.38, 128.60, 127.58, 119.57, 119.15, 40.30, 37.28. HRMS (M^+) ($C_{18}H_{14}BF_2N_3$): calcd. 339.1587, found 339.1585.

Chromogenic detection of anions

10 equivalents of Cl^-, I^-, Br^-, F^-, HS^-, SCN^- and CN^-, anions were added to 3 mL aliquots of a $1x10^{-5}$ *M* acetonitrile solution of **1** and the mixtures were allowed to react at room temperature for 30 min. Then, the absorption intensity of the samples was measured. While hydrogen sulfide and cyanide anions are able to complete bleach of the solution, other anions (Cl^-, I^-, Br^-, F^-, SCN^-) induced negligible changes in the visible band.

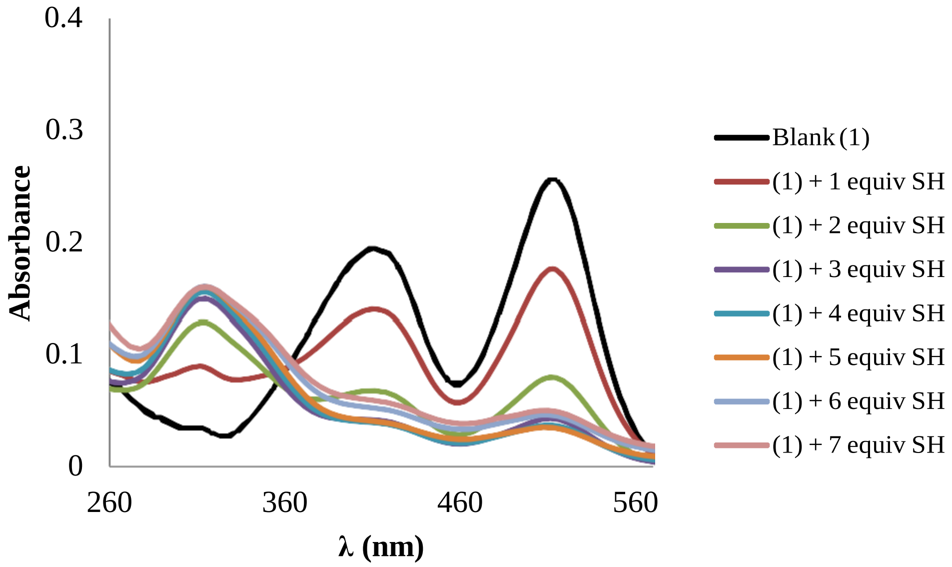


Figure SI-1. Titration of **1** ($1x10^{-5}$ M in CH_3CN) with increasing amounts of NaHS ($0\text{-}1x10^{-4}$ M in H_2O)

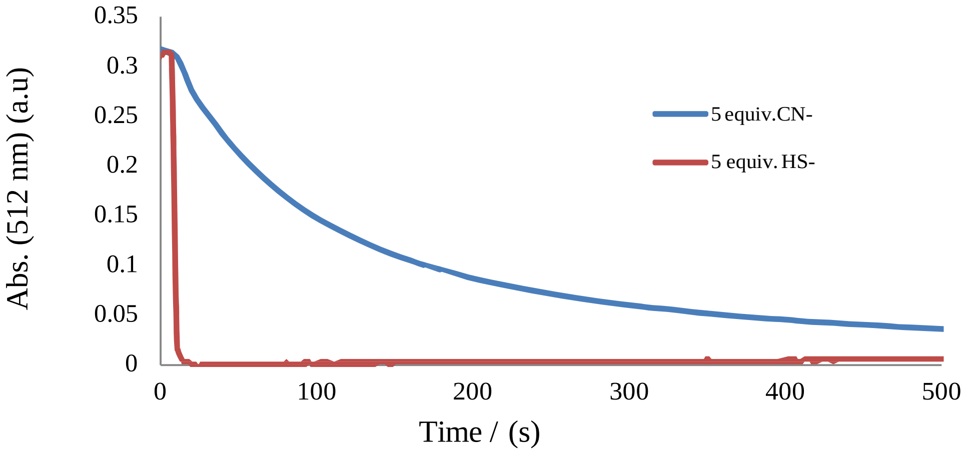


Figure SI-2. Kinetic plot of the absorption band at 512 nm of compound **1** ($1x10^{-5}$ *M*, CH_3CN) in the presence of 5 equivalents of CN^- (blue line) and 5 equivalents of HS^- (red line).

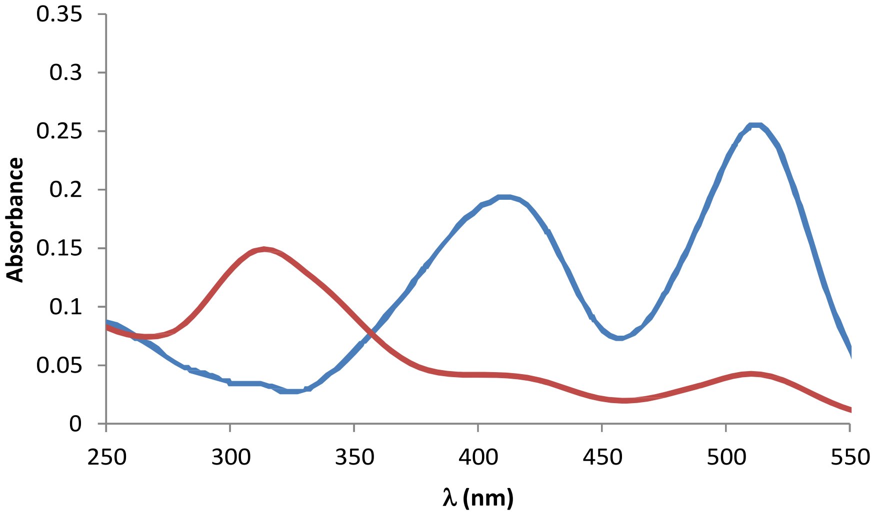


Figure SI-3. UV spectra of (red) **1** ($1x10^{-5}$ M in CH_3CN) + 5 equiv NaHS (in H_2O) (blue) the same solution after addition of 10 μL of H_2O_2 (6v)

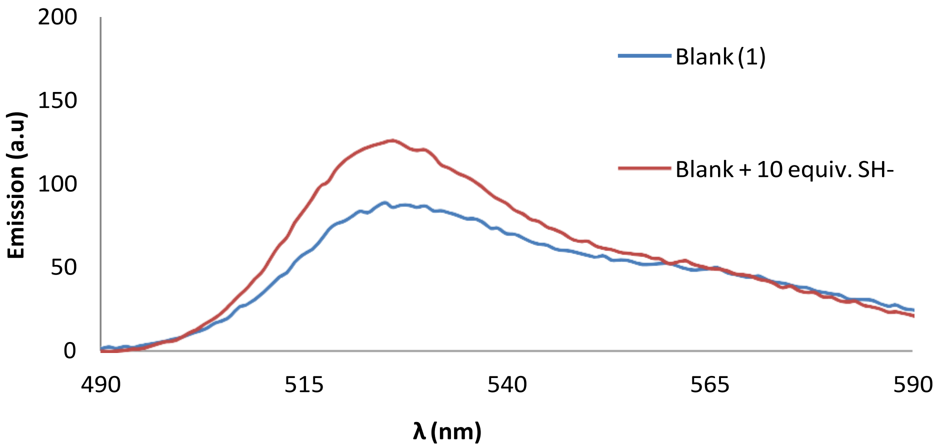


Figure SI-4. Fluorescence spectra of (blue) **1** ($1x10^{-5}$ M in CH_3CN) and (red) **1** ($1x10^{-5}$ M in CH_3CN) + 10 equiv NaHS (in H_2O).

Limit of detection (LOD) determination: Increasing quantities of a solution of the corresponding anion ($1x10^{-4}$ mol dm^{-3} in water) were added to a solution of **1** (1.0×10^{-5} mol dm^{-3} in acetonitrile). The UV spectra were recorded in 1-cm path length cells at 25°C.

Representation of absorbance at a specific wavelength vs. concentration of anion allowed calculation of LOD.

$$\mathrm{LOD} = \frac{3S_b}{m}$$

In which S_b is the standard deviation of blank measurements and *m* is the slope of the linear regression plot.[1]

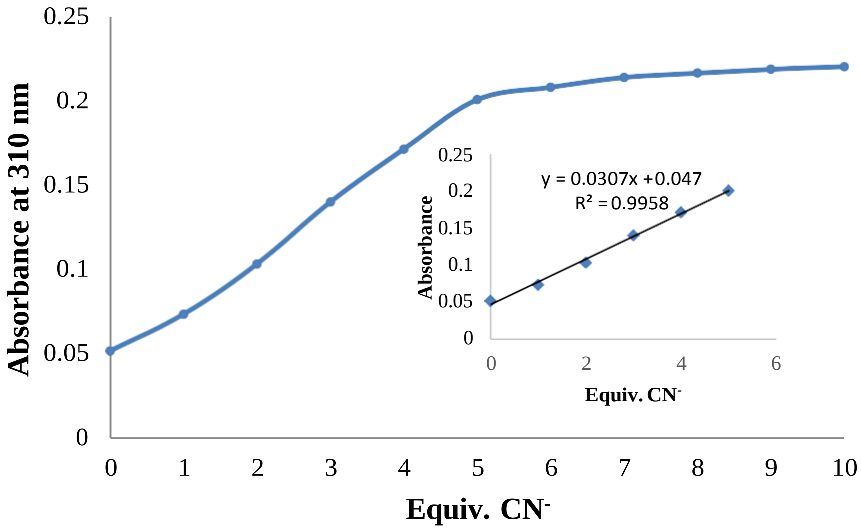


Figure SI-5. Absorption at 310 nm of **1**-CN^- (acetonitrile solution, 10^{-5}M) *versus* increasing amounts of CN^- ($1x10^{-4}$ M in water)at room temperature. (Inset: linear part of the graph)

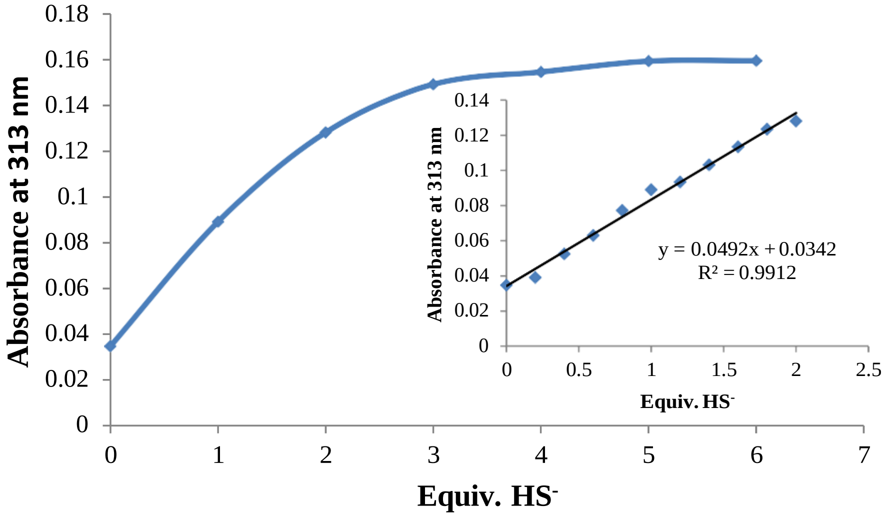


Figure SI-6. Absorption at 313 nm of **1**-HS^- (acetonitrile solution, 10^{-5}M) *versus* increasing amounts of HS^- ($1x10^{-4}$ M in water) at room temperature. (Inset: linear part of the graph)

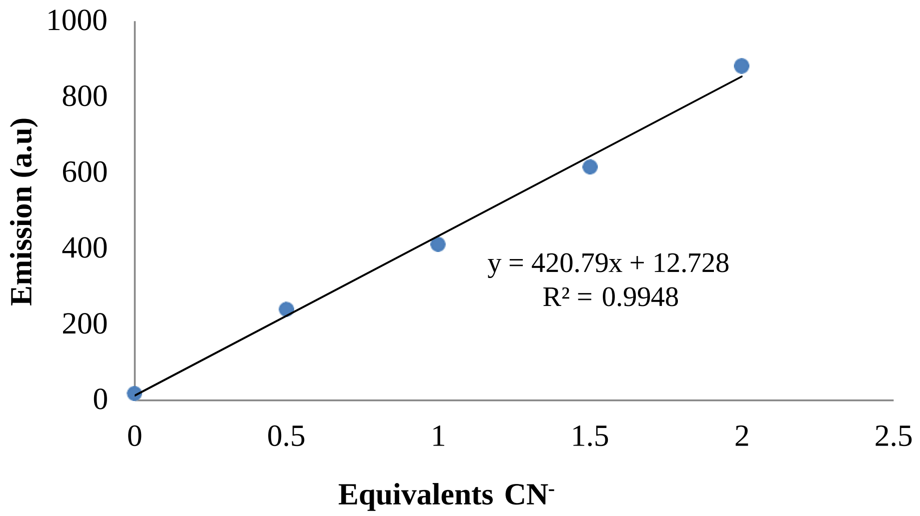


Figure SI-7. Linear part of the titration graph in fluorescente of **1**·(acetonitrile solution, 10^{-5}M) *versus* increasing amounts of CN^- ($1x10^{-4}$ M in water) at room temperature.

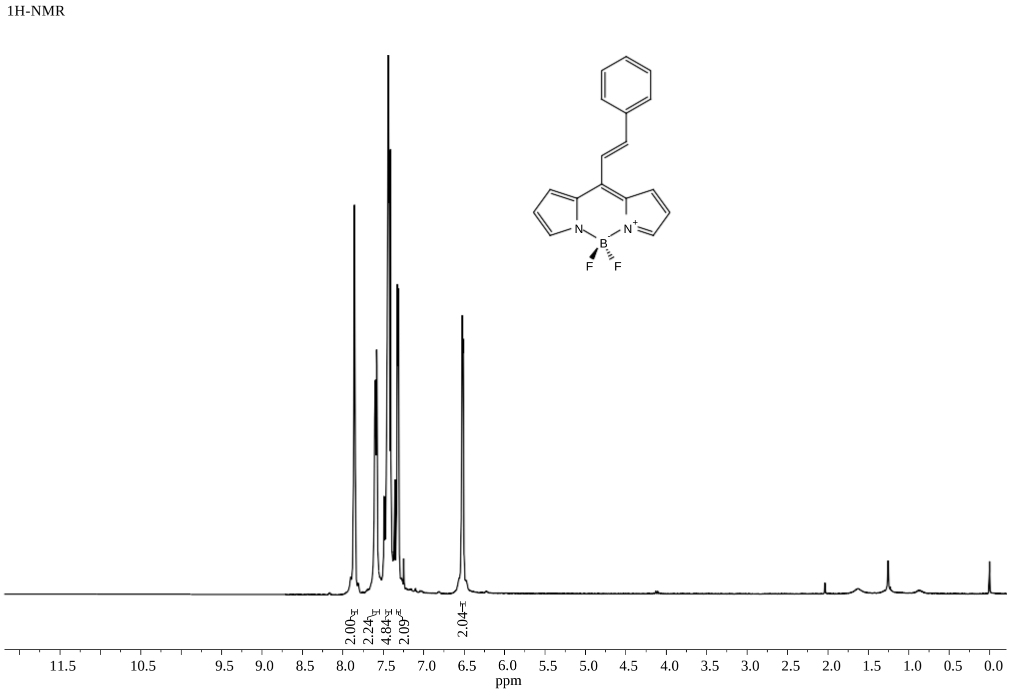


Figure SI-8. ^{1}H NMR spectrum of compound **1** in $CDCl_3$

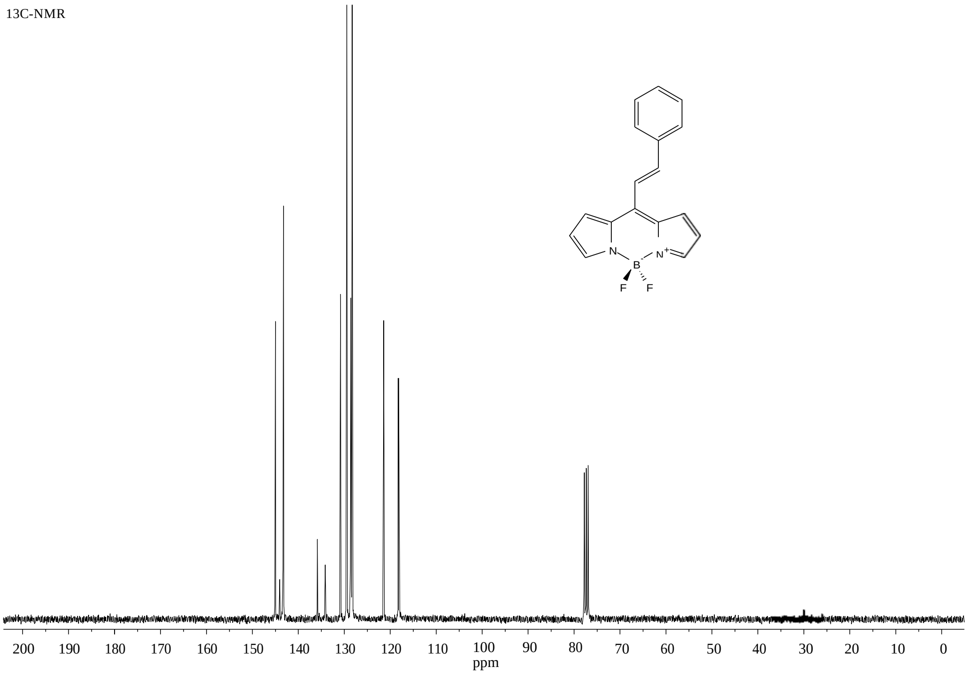
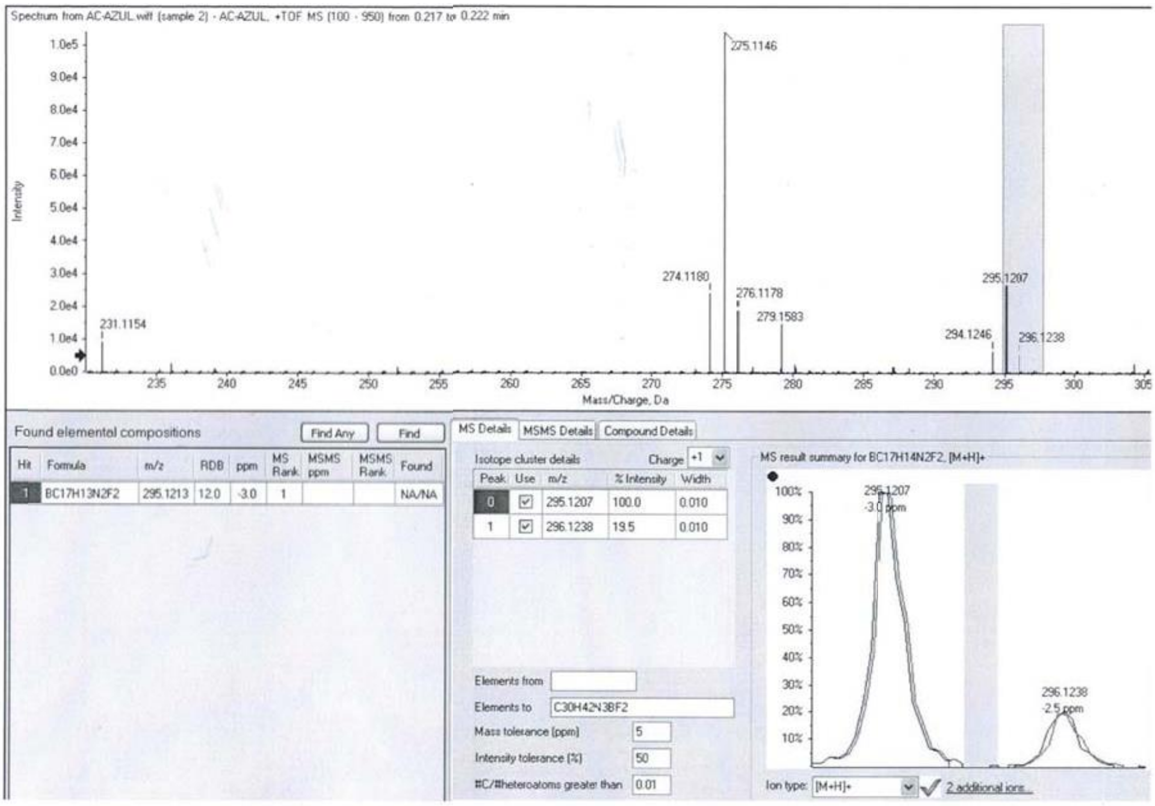


Figure SI-9. ^{13}C NMR spectrum of compound **1** in $CDCl_3$



Spectrum from AC-AZUL.wiff (sample 2) - AC-AZUL, +TOF MS (100 - 950) from 0.217 to 0.222 min

Found elemental compositions

Hit	Formula	m/z	RDB	ppm	MS Rank	MSMS ppm	MSMS Rank	Found
1	BC17H13N2F2	295.1213	12.0	-3.0	1			NA/NA

Isotope cluster details

Charge +1

Peak	Use	m/z	% Intensity	Width
0	☑	295.1207	100.0	0.010
1	☑	296.1238	19.5	0.010

Elements from

Elements to C30H42N3BF2

Mass tolerance (ppm) 5

Intensity tolerance (%) 50

#C/#heteroatoms greater than 0.01

MS result summary for BC17H14N2F2, [M+H]+

Ion type: [M+H]+

Figure SI-10. MS of compound **1**

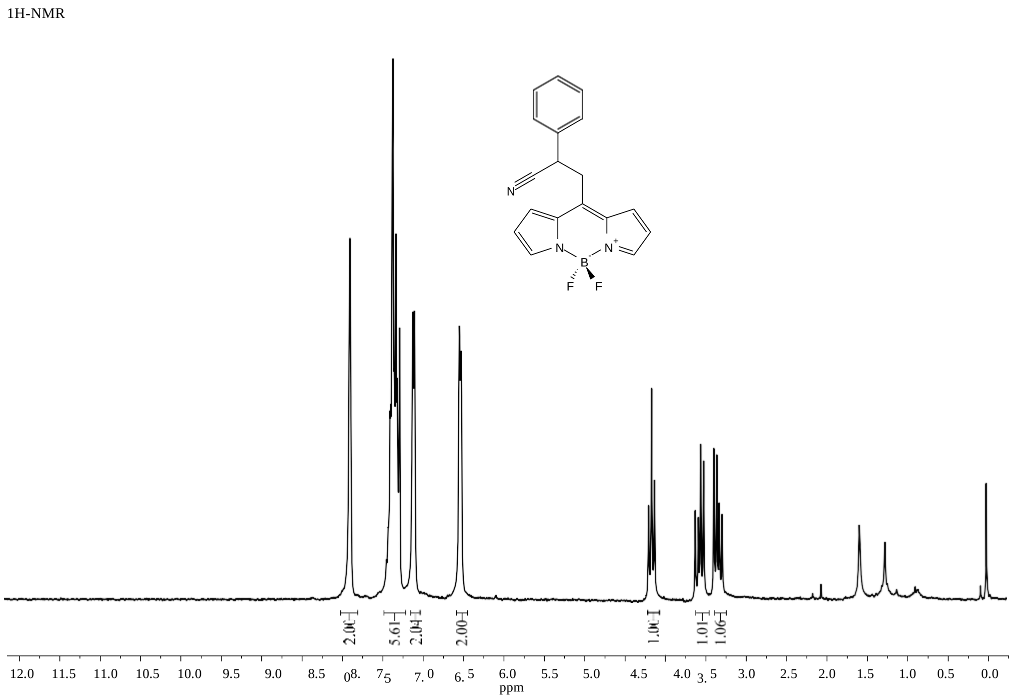


Figure SI-11. H1NMR spectrum of compound **2** in $CDCl_3$

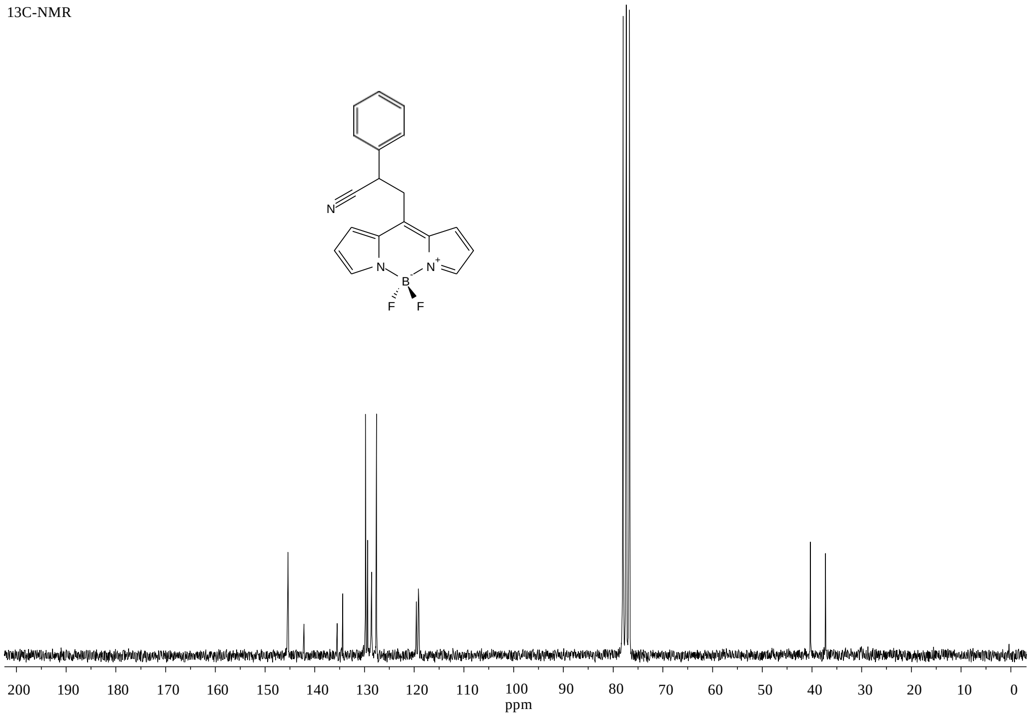
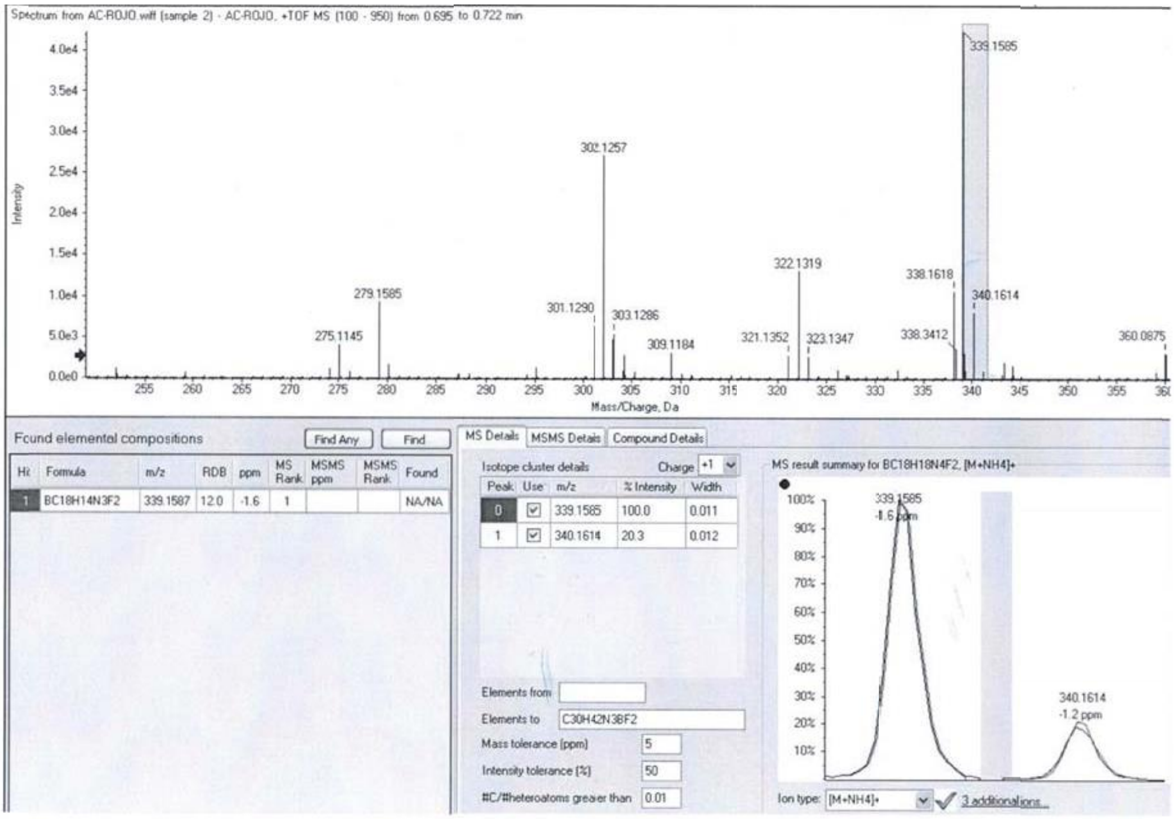


Figure SI-12. 13C NMR spectrum of compound **2** in $CDCl_3$



Found elemental compositions

Hit	Formula	m/z	RDB	ppm	MS Rank	MSMS ppm	MSMS Rank	Found
1	BC18H14N3F2	339.1587	12.0	-1.6	1			NA/NA

Isotope cluster details Charge +1

Peak	Use	m/z	% Intensity	Width
0	☑	339.1585	100.0	0.011
1	☑	340.1614	20.3	0.012

Elements from
Elements to C30H42N3BF2
Mass tolerance (ppm) 5
Intensity tolerance (%) 50
#C/#heteroatoms greater than 0.01

Ion type: [M+NH4]+

Figure SI-13. MS of compound **2**

1. M. Zhu, M. Yuan, X. Liu, J. Xu, J. Lv, C. Huang, H. Liu, Y. Li, S. Wang, D. Zhu, *Org. Lett.*, 2008, **10,** 1481.