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# Solvatochromic and Aggregation-Induced Emission Active Nitrophenyl-Substituted Pyrrolidinone-Fused-1,2-Azaborine with a Pre-Twisted Molecular Geometry

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**General Information**. Organic solutions were concentrated by rotary evaporation at ca. 12 Torr. 5-bromo-2-methylbenzoic acid was purchased from AmBeed. N-bromosuccinimide (NBS) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from TCI America, Inc. Anhydrous THF solvent was purchased from Thermo Fisher Scientific, Inc. and used without distillation. Solvents for workup and column chromatography, such as hexanes (Hex), petroleum ether (PET), ethyl acetate (EA), dichloromethane (DCM), and other chemicals such as benzene were obtained from commercial vendors and used without further purification. Regarding Pd-catalyzed cross coupling reaction reagents: $(PPh_3)_2PdCl_2$, 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile, and 4,4,5,5-tetramethyl-2-(4-nitrophenyl)-1,3,2-dioxaborolane were purchased from Fisher Scientific Warehouse. The NMR solvents, $CDCl_3$ was purchased from Cambridge Isotope Laboratories; and DMSO-$d_4$ was purchased from Thermo Fisher Scientific.

Starting materials were produced in the laboratory and solvents were purchased from commercial suppliers as reagent grade unless noted otherwise. **Benzo-azaborine** and **nitrobenzo-azaborine** were prepared by following the experimental procedure used by Huggins.[1]

All NMR spectra were recorded on a Bruker AM-400 spectrometer. $^1$H NMR spectra were recorded at 400 MHz, $^{13}C\{^1H\}$ spectra at 100 MHz, and $^{11}B\{^1H\}$ spectra (sodium tetraphenylborate as standard) at 128 MHz; chemical shifts are expressed in parts per million (δ scale) downfield from TMS (δ = 0.00) and are referenced to residual protium in the NMR solvent (DMSO: δ = 2.50 and $CDCl_3$: δ = 7.26) for $^1$H NMR, relative to the central $CDCl_3$ (δ = 77.16) and DMSO-$d_4$ (δ = 39.52) for $^{13}C\{^1H\}$ NMR and sodium tetraphenylborate as standard (δ = -6.61) for $^{11}B\{^1H\}$ NMR. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet and/or multiple resonances), coupling constant in Hertz (Hz), integration. FT-IR spectra were recorded on a PerkinElmer Spectrum 100 FTIR spectrometer. All samples were placed over the detector and crushed using the anvil attached on the Perkin Elmer Spectrum 100 FTIR spectrometer featuring an attenuated total reflection (ATR) sampler equipped with a diamond crystal. Spectra were obtained in the range of 600-4000 $cm^{-1}$. Melting points were recorded using Mpa161 Digimelt Melting Point apparatus from Stanford Research Systems. Reactions were performed at room temperature (25 °C) or with heat using a silicone oil bath, and reaction condition temperatures were those of the oil bath unless noted otherwise. Pd-cross coupling reactions were performed under a nitrogen ($N_2$) atmosphere in Schlenk flask glassware that had been oven-dried for 24 h. $N_2$ gas was purchased from Airgas. All reactions and manipulations involving air-sensitive compounds were performed using standard Schlenk techniques. Thin-layer chromatography was performed using TLC silica gel 60 $F_{254}$ aluminum sheets from Sorbtech. Flash column chromatography was performed using CombiFlash® $R_f$ from Teledyne ISCO. Celite 545 was purchased from Sigma Aldrich and was used in filtrations to remove fine Pd particles from Pd-catalyzed cross coupling reaction crude mixtures.

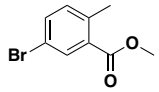
UV-vis data were collected on a Cary 60 UV-vis spectrometer (Agilent Technologies, Inc.) and fluorescence data were collected on a HORIBA Fluorolog QM-75-11-C Spectrofluorometer. Absolute fluorescence quantum yields were determined using a Hamamatsu C11347-11 Quantaurus-QY Absolute PL Quantum Yield Spectrometer. Samples were prepared inside the glovebox in quartz Petri dishes (solid sample) or 1 cm square quartz cuvettes (solutions). Solutions were collected with absorbance values below 0.1. To prepare the solid samples, the

PFAs were dissolved in $CHCl_3$, then a drop of the concentrated solution was pipetted onto a glass followed by solvent evaporation until only the solid remained.

**Computational Methods.** The geometries of PFAs **1**, **2**, and **3** were each optimized using density functional theory (DFT) with the B3LYP and 6-311+G* basis.[2,3] The calculations were also repeated using the CAM-B3LYP functional and 6-31+G* basis set.[4] Solvent effects were included using the conductor-like polarizable continuum model (C-PCM).[5–7] The dielectric constant and optical dielectric for THF were obtained from the Minnesota solvent descriptor database.[8] Vibrational frequency calculations were run to determine that the optimized geometries yield all positive frequencies. Vertical electronic excitation energies (VEEs) were computed with time-dependent DFT (TD-DFT) using the B3LYP/6-31+G* functional and basis set in THF. The Tamm-Dancoff Approximation was used for TD-DFT.[9] The C-PCM solvation model was also used for TD-DFT, although the non-equilibrium linear response formalism was used to account for the effect of solvation on the excitations.[10] Fluorescence wavelengths were computed as VEEs after optimizing the fluorescent (excited-state) geometry. Natural transition orbitals (NTOs) were computed to provide a more compact description of the excitation orbital character.[11] All calculations in this work were performed with the Q-Chem 5.3.1 electronic structure software package.[12]

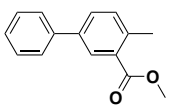
## Synthesis protocols

Preparation of methyl 5-bromo-2-methylbenzoate (**4**).




5-bromo-2-methylbenzoic acid (3.79 g, 17.62 mmol) was placed in a 500 mL round bottom flask and dissolved in methanol (300 mL). Sulfuric acid (2 mL) was then added to the flask, and the mixture was allowed to reflux for 24 h. After 24 h, the mixture was cooled to room temperature and the excess methanol was removed under reduced pressure resulting in a yellow oil. The yellow oil was then dissolved in EA (40 mL), followed by the addition of 5% $NaHCO_3$ (150 mL) and stirred vigorously. The mixture was transferred to a separatory funnel and the organic layer was extracted using EA (3x40 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, gravity filtered, and concentrated under reduced pressure to yield product (**4**) as a tan solid (3.73 g, 16.30 mmol, 93%). $R_f$: 0.88 (Hex:EA 4:1). M.p.: 45.70 – 46.40 °C. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 8.04 (d, J = 2.2 Hz, 1H), 7.50 (dd, J = 2.2 Hz, J = 8.2 Hz, 1H), 7.12 (d, J = 8.2 Hz, 1H), 3.89 (s, 3H), 2.54 (s, 3H). $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) 166.68, 139.17, 134.79, 133.33, 133.28, 131.19, 119.10, 52.09, 21.20.

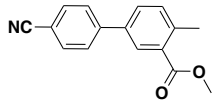
Preparation of methyl 4-methyl-[1,1'-biphenyl]-3-carboxylate (**5**)




Compound **4** (2.00 g, 8.73 mmol), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (1.87 g, 9.18 mmol, 1.05 eq.), $(PPh_3)_2PdCl_2$ (0.31 g, 0.44 mmol, 0.05 eq.), and a magnetic stir bar were added

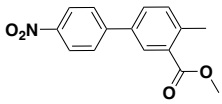
to a 200 mL Schlenk flask dried overnight in an oven. The Schlenk flask was evacuated and flushed with $N_2$ three times over 3-minute intervals. The Schlenk flask was then filled with $N_2$, sealed, followed by the addition of anhydrous THF (40 mL). The reaction mixture was heated to 65 °C while stirring to dissolve the starting materials, followed by the addition of $K_2CO_3$ (164 mL, 2 M). The mixture rapidly turned black, and it was left to stir at 65 °C under $N_2$ atmosphere for 24 h. The completion of the reaction was indicated via silica TLC in (H:EA 10:1). After 24 h, the reaction mixture was cooled to room temperature and the excess THF was removed under reduced pressure. The aqueous layer was transported into a 500 mL separatory funnel, followed by the addition of EA (40 mL) and the organic layers were extracted with EA (3x40 mL). The combined organic layers were filtered through celite and dried over anhydrous $Na_2SO_4$. The residual EA was removed under reduced pressure to yield the crude product as a yellow oil. The crude yellow oil was purified via silica flash column chromatography on a combiflash using hexanes and EA as eluents. The impurities were first separated with hexanes as the mobile phase, followed by the increase of the mobile phase polarity to 5% EA to elute the desired product. The excess solvent was removed under reduced pressure to produce pure product (**5**) as colorless oil (1.79 g, 7.91 mmol, 91%). $R_f$: 0.62 (Hex:EA 10:1). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 8.15 (d, J = 2.0 Hz, 1H), 7.64 – 7.59 (m, 3H), 7.44 (t, J = 7.4 Hz, 2H), 7.36 (d, J = 7.3 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 3.92 (s, 3H), 2.63 (s, 3H). $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) 168.03, 140.07, 139.11, 138.77, 132.22, 130.41, 129.95, 129.20, 128.83, 127.45, 126.95, 51.90, 21.39.

Preparation of methyl 4'-cyano-4-methyl-[1,1'-biphenyl]-3-carboxylate (**6**)




Following the experimental procedure of compound (**5**) presented above, Compound **4** (4.00 g, 17.46 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (3.81 g, 16.63 mmol, 0.95 eq.), and $(PPh_3)_2PdCl_2$ (0.61 g, 0.87 mmol, 0.05 eq.) were reacted together. After the reaction work up, the crude light-yellow solid was purified *via* flash column chromatography using a combi flash (5% EA, 80 g silica column). The pure product (**6**) was obtained as a colorless solid (2.98 g, 11.85 mmol, 71%). M.p.: 94.50 – 96.80 °C. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 8.14 (d, J = 2.1 Hz, 1H), 7.71 (d, J = 8.7 Hz, 2H), 7.67 (d, J = 8.7 Hz, 2H), 7.61 (dd, J = 2.1 Hz, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 3.93 (s, 3H), 2.64 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) 167.54, 144.37, 140.71, 136.60, 132.63, 132.60, 130.34, 130.28, 129.25, 127.45, 118.80, 111.07, 52.03, 21.47.

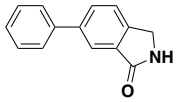
Preparation of methyl 4- methyl-4'-nitro-[1,1'-biphenyl]-3-carboxylate (**7**)




Following the experimental procedure of compound (**5**) presented above, Compound **4** (2.00 g, 8.73 mmol), 4,4,5,5-tetrmethyl-2-(4-nitrophenyl)-1,3,2-dioxaborolane (2.28 g, 9.16 mmol, 1.05 eq.) and $(PPh_3)_2PdCl_2$ (0.31 g, 0.44 mmol, 0.05 eq.) were reacted for 24 h at 65 °C. After the reaction completion and work up, the colorless crude solid was recrystallized in hot ethanol to afford the pure product (**7**) as a colorless crystal (2.08 g, 7.70 mmol, 88%). M.p.: 124.60–126.40

°C. $R_f$ = 0.45 (Hex:EA 7:1). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 8.31 (d, J = 8.8 Hz, 2H), 8.19 (d, J = 2.1 Hz, 1H), 7.76 (d, J = 8.8 Hz, 2H), 7.67 (dd, J = 2.1 Hz, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 3.95 (s, 3H), 2.67 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) 167.57, 147.20, 146.43, 141.05, 136.31, 132.66, 130.46, 129.46, 127.61, 124.20, 52.10, 21.52.

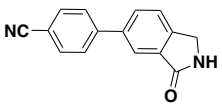
Preparation of 6-phenylisoindolin-1-one (**11**)




A 50 mL round bottom flask was charged with compound **5** (1.03 g, 4.55 mmol), NBS (0.81 g, 4.55 mmol, 1.0 eq.), benzoyl peroxide (0.03 g, 0.14 mmol, 0.03 eq.), benzene (15 mL), and a magnetic stir bar. The reaction mixture was allowed to stir vigorously at 75 °C under $N_2$ atmosphere for 24 h. The completion of the reaction was indicated via silica TLC in (Hex:EA 10:1). The reaction mixture was allowed to cool to room temperature, followed by cooling to 0 °C for 30 minutes in an ice bath. The colorless precipitate was removed by gravity filtration to remove the succinimide, and the excess benzene was removed under reduced pressure to yield the crude product containing both mono- and di-brominated isomers as a brown oil. The crude oil was purified via silica column chromatography on a combiflash in (Hex:DCM 1:1) to separate the two isomers, and the pure mono- brominated isomer (**8**) was obtained as a colorless solid (0.70 g, 2.30 mmol, 51%). $R_f$: 0.51 (1:1 Hex/DCM). M.p.: 56.30 – 62.10 °C. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 8.20 (d, J = 2.1 Hz, 1H), 7.72 (dd, J = 2.1 Hz, J = 8.0 Hz, 1H), 7.60 (d, J = 7.2 Hz, 2H), 7.54 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.2 Hz, 2H), 7.39 (t, J = 7.3 Hz, 1H), 5.00 (s, 2H), 3.97 (s, 3H). $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) 166.97, 141.57, 139.38, 137.99, 132.25, 130.90, 129.97, 129.47, 128.95, 128.03, 127.08, 52.38, 31.41.

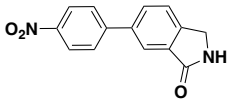
A 50 mL round bottom flask was charged with the brominated product **(8)** (0.891 g, 2.92 mmol), 7 N $NH_3$ in methanol (30 mL) and a magnetic stir bar. The reaction mixture was cooled to -5 °C in an ice-brine bath. The mixture was allowed to stir vigorously under $N_2$ atmosphere overnight while slowly warming to room temperature. The progression of the reaction was monitored by silica TLC (100 %, EA). After 24 h, the colorless precipitate formed was isolated by vacuum filtration, yielding the crude product as colorless solids. The desired product was purified via recrystallization in hot ethanol to produce the pure product (**11**) as colorless crystals (0.49 g, 2.34 mmol, 80%). $R_f$: 0.56 (100%, EA). M.p.: Decomposes at 246.0 °C. $^1$H NMR: (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 8.11 (d, J = 1.3 Hz, 1H), 7.82 (dd, J = 1.6 Hz, J = 8.0 Hz, 1H), 7.64 (d, J = 7.5 Hz, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.3 Hz, 2H), 7.39 (t, J = 7.3 Hz, 1H), 6.36 (s, N-H, 1H), 4.51 (s, 2H). $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) 171.45, 142.39, 141.55, 140.17, 132.66, 130.88, 128.96, 127.76, 127.25, 123.52, 122.26, 45.36.

Preparation of 4-(3-oxoisoindolin-5-yl)benzonitrile (**12**)



Following the experimental procedure of compound (**8**) presented above, compound **(6)** (2.88 g, 11.46 mmol), NBS (2.04 g, 11.46 mmol, 1.0 eq.), and benzoyl peroxide (0.083 g, 0.34 mmol, 0.03 eq.) were dissolved in benzene (60 mL) and reacted together at 75 °C under $N_2$ atmosphere. After the reaction work up, the crude yellow oil containing both mono- and di-brominated isomers was purified via flash column chromatography using a combi flash (15% EA, 80 g silica column) to separate the two isomers. The pure mono-brominated isomer (**9**) was obtained as a colorless solid (2.07 g, 6.27 mmol, 55%). M.p. 105.60 – 107.90° C. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 8.20 (d, J = 2.0 Hz, 1H), 7.76 (d, J = 8.5 Hz, 2H), 7.73 – 7.70 (m, 3H), 7.59 (d, J = 8.0 Hz, 1H), 5.00 (s, 2H), 3.99 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) 166.58, 143.77, 139.55, 139.41, 132.78, 132.57, 130.91, 130.08, 129.89, 127.73, 118.61, 111.80, 52.56, 30.87.
Compound **(9)** (1.88 g, 5.69 mmol) was dissolved in 7 N $NH_3$ in methanol (57 mL) and stirred for 24 hr. The colorless solid was washed with cold methanol and filtered to yield the pure product (**12**) as a colorless solid (1.26 g, 5.37 mmol, 94%). M.p. 266.00 – 269.00° C. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 8.11 (d, J = 1.2 Hz, 1H), 7.81 (dd, J = 1.7 Hz, J = 7.9 Hz, 1H), 7.77 (d, J = 8.6 Hz, 2H), 7.74 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 7.9 Hz, 1H), 6.60 (s, N-H, 1H), 4.54 (s, 2H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) 170.74, 144.59, 143.63, 139.55, 132.99, 132.80, 130.85, 127.89, 123.99, 122.58, 118.70, 111.57, 45.35. ATR-FTIR ($cm^{-1}$): 3409 (w), 3190 (m), 3062 (w), 2934 (w), 2857 (w), 2230 (m), 1705 (s), 1628 (m), 1608 (m), 1584 (w), 1482 (m), 1461 (s), 1404 (w), 1360 (m), 1327 (w), 1293 (w), 1146 (w), 853 (m), 818 (s), 771 (s), 717 (m). HRMS (DART) *m/z*: Calcd for $C_{15}H_{10}N_2O$, 235.0871 $(M + H)^+$; Found: 235.1667 $(M + H)^+$.

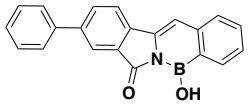
Preparation of 6-(4-nitrophenyl) isoindolin-1-one (**13**)




Following the experimental procedure of compound (**8**) presented above, compound **(7)** (2.00 g, 7.37 mmol), NBS (1.31 g, 7.37 mmol, 1.0 eq.), benzoyl peroxide (0.053 g, 0.221 mmol, 0.03 eq.) and benzene (24 mL) were reacted for 24 h at 75 °C under $N_2$ atmosphere. After the reaction completion and work up, the crude colorless solid containing both mono- and di-brominated isomers was purified via flash column chromatography using a combiflash to separate the two isomers. The sample was run with a constant (Hex:EA 15:1) gradient with a 24-gram silica column. The pure mono-brominated product (**10)** was obtained as a colorless solid (1.33 g, 3.80 mmol, 52%) M.p.: 130.00 – 133.00 °C. $R_f$ = 0.16 (Hex:EA 15:1). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm) 8.33 (d, J = 8.9 Hz, 2H), 8.23 (d, J = 2.0 Hz, 1H), 7.78 – 7.74 (m, 3H), 7.61 (d, J = 8.0 Hz, 1H), 5.01 (s, 2H), 4.00 (s, 3H). $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm) 166.53, 147.57, 145.67, 139.81, 139.02, 132.61, 131.06, 130.22, 129.94, 127.88, 124.28, 52.60, 30.81.
The brominated product **(10)** (1.00 g, 2.86 mmol) was dissolved in 7 N $NH_3$ in MeOH (30 mL) and reacted. After the reaction completion and work up, the white precipitate was vacuum filtered, washed with cold methanol and dried to afford the pure product **(13)** as a colorless solid (0.603 g, 2.37 mmol, 83%). M.p.: 237.60 – 241.80 °C. $R_f$ = 0.12 (Hex:EA 1:1). $^1$H NMR (400 MHz, DMSO, 25 °C): δ (ppm) 8.68 (s, N-H, 1H), 8.32 (d, J = 8.9 Hz, 2H), 8.06 – 8.01 (m, 4H), 7.74 (d, J = 8.5 Hz, 1H), 4.46 (s, 2H). $^{13}$C{$^1$H} NMR (100 MHz, DMSO, 25 °C): δ (ppm) 169.47, 146.87, 146.05, 144.84, 137.68, 133.74, 130.49, 128.21, 124.70, 124.18, 121.36, 44.93. ATR-FTIR ($cm^{-1}$): 3417 (w), 3195

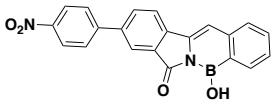
(w), 3075 (w), 2932 (w), 1710 (s), 1628 (w), 1597 (m), 1582 (w), 1512 (s), 1482 (w), 1465 (m), 1447 (w), 1346 (s), 1204 (w), 1112 (w), 859 (w), 851 (m), 825 (m), 772 (m), 750 (s), 625 (w). HRMS (DART) *m/z*: Calcd for $C_{14}H_{10}N_2O_3$, 255.0769 $(M + H)^+$; Found: 255.1667 $(M + H)^+$.

Preparation of 5-hydroxy-9-phenylbenzo[3,4][1,2]azaborinino[6,1-*a*]isoindol-7(5*H*)-one (**1**)




Compound **11** (0.44 g, 2.10 mmol) and (2-formylphenyl)boronic acid (0.25 g, 1.68 mmol, 0.8 eq.) were placed in a 100 mL round bottom flask and dissolved in ethanol (17 mL, 200 proof). DBU (1.90 g, 12.48 mmol, 1.88 mL, 6.0 eq.) was added to the mixture resulting in a yellow solution. The yellow reaction mixture was allowed to stir at reflux under $N_2$ atmosphere for 48 h. After 48 h, the color of the solution changed from yellow to dark red. The reaction mixture was allowed to cool to room temperature and was placed in an ice-water bath for 10 minutes, followed by the addition of HCl (35 mL, 1 M) resulting in an off-white precipitate. The mixture was then cooled below 0 °C for 24 h. After 24 h, the precipitate was filtered and washed with cold DI water to yield the pure product (**1**) (0.413 g, 1.28 mmol, 77%) M.p.: 177 – 183 °C. $^1$H NMR: (400 MHz, $CDCl_3$): δ (ppm) 8.18 (d, J = 7.4 Hz, 1H), 8.13 (d, J = 1.0 Hz, 1H), 7.99 (s, 1H), 7.91 (dd, J = 1.5 Hz, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 7.5 Hz, 2H), 7.59 (td, J = 1.3 Hz, J = 7.5 Hz, 1H), 7.53 – 7.48 (m, 3H), 7.42 (td, J = 1.4 Hz, J = 7.4 Hz, 2H), 6.88 (s, 1H). $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$): δ(ppm) 174.79, 142.84, 141.44, 139.56, 137.66, 134.57, 133.46, 133.10, 132.32, 130.00, 129.08, 128.20, 128.15, 127.12, 127.07, 123.12, 120.96, 107.55. $^{11}$B {$^1$H} NMR (sodium tetraphenyl borate as standard, 128 MHz, acetone-$d_6$, 25 °C): δ (ppm) 30.82. ATR-FTIR ($cm^{-1}$): 3452 (w), 3051 (w), 1695 (s), 1644 (w), 1474 (w), 1355 (m), 1283 (w), 1194 (w), 1120 (m), 1082 (w), 957 (w), 841 (w), 794 (w), 729 (m), 689 (s), 617 (w). HRMS (ESI) *m/z*: Calcd for $C_{21}H_{14}BNO_2$ , 324.1196 $(M + H)^+$; Found: 324.1667 $(M + H)^+$. UV-vis (acetonitrile, $\lambda_{max}$, ε, concentration, path length): 380 nm, 1.7 x $10^4$ $M^{-1}cm^{-1}$, 2.68 x $10^{-6}$ M, 1 cm. Emission (acetonitrile, $\lambda_{max}$): 443 nm.

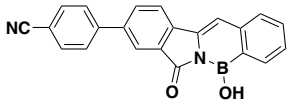
Preparation of 5-hydroxy-9-(4-nitrophenyl) benzo [3,4] [1,2] azaborinino[6,1-a] isoindol-7(5H)-one (**2**)**.**




Following the experimental procedure of compound (**1**) presented above, compound **(10)** (0.38 g, 1.50 mmol), (2-formylphenyl) boronic acid (0.18 g, 1.20 mmol, 0.8 eq.) and EtOH (40 mL, 200 proof) were added to a clean 250 mL round bottom flask. The starting materials were stirred under $N_2$ atmosphere followed by the addition of DBU (1.37 g, 1.34 mL, 9.00 mmol). The reaction mixture turned clear yellow reaction mixture and was allowed to reflux for 48 h. After 48 h, the red reaction mixture was left to cool to room temperature. Once cooled, the reaction mixture was placed in an ice bath for 15 min while stirring followed by the slow addition of HCl (40 mL, 1 M) resulting in an orange precipitate. The orange mixture was then cooled below 0 °C in freezer for 24 h. After 24 h, the orange precipitate was vacuumed filtered then the crude product was

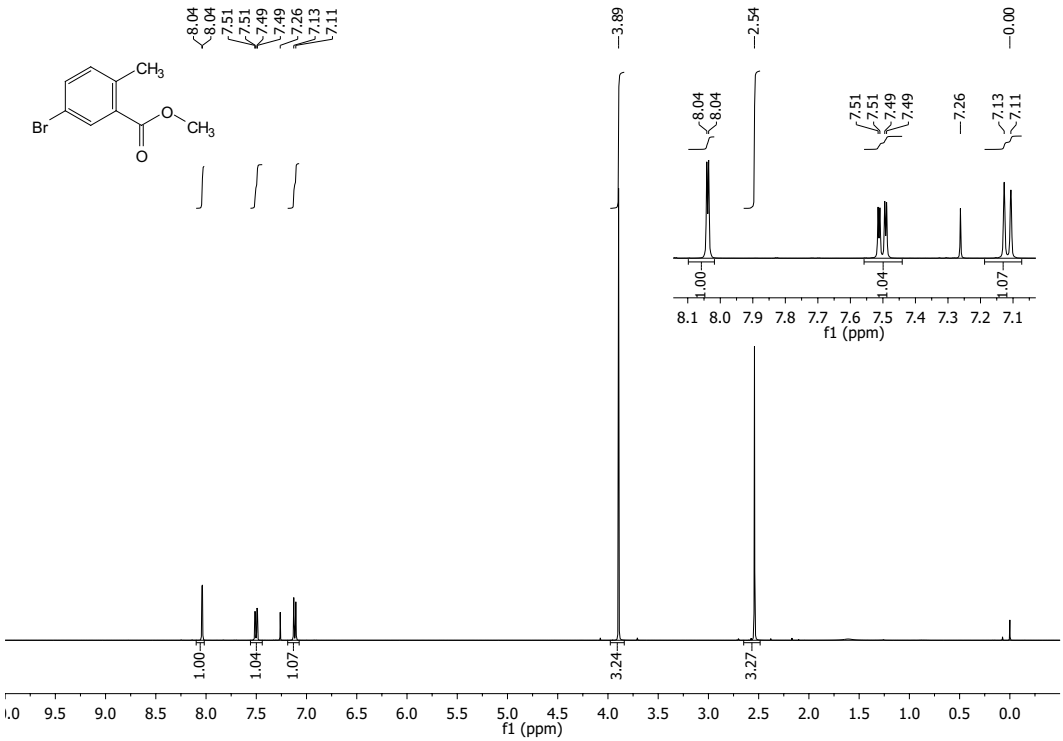
purified by triturated in hot EtOH yielding a yellow-orange solid (0.392 g, 1.06 mmol, 88%). M.p.: 333 – 338°C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.36 (d, J = 8.9 Hz, 2H), 8.20 (d, J = 7.2 Hz, 1H), 8.17 (s, 1H), 7.96 – 7.91 (m, 3H), 7.82 (d, J = 8.9 Hz, 2H), 7.62 (t, J = 7.7 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H) 7.44 (t, J = 7.3 Hz, 1H), 6.95 (s, 1H). $^{13}$C{$^{1}$H} NMR (100 MHz, DMSO): δ(ppm) 172.26, 147.53, 145.64, 141.63, 139.66, 139.08, 135.20, 133.84, 133.64, 132.73, 130.23, 128.74, 128.66, 127.41, 124.62, 123.29, 122.48, 108.27. $^{11}$B {$^{1}$H} NMR (sodium tetraphenyl borate as standard, 128 MHz, acetone-$d_6$, 25 °C): δ (ppm) 30.39. ATR-FTIR ($cm^{-1}$): 3474 (w), 3076 (w), 1716 (s), 1642 (w), 1596 (m), 1511 (s), 1473 (m), 1451 (w), 1397 (m), 1375 (m), 1340 (s), 1287 (m), 1187 (w), 1111 (m), 1078 (m), 954 (m), 860 (m), 828 (s), 792 (s), 752 (m), 726 (s), 683 (s), 617 (m). HRMS (DART) *m/*z: Calcd for $C_{21}H_{13}BN_2O_4$, 369.1048 $(M + H)^+$; Found: 369.1667 $(M + H)^+$. UV-vis (acetonitrile, $\lambda_{max}$, ε, concentration, path length): 380 nm, 3.7 x $10^3 M^{-1}cm^{-1}$, 2.97 x $10^{-6}$ M, 1 cm. Emission (acetonitrile, $\lambda_{max}$): 445, weak emission 655 nm.

Preparation of 4-(5-hydroxy-7-oxo-5,7-dihydrobenzo[3,4][1,2]azaborinino[6,1-*a*]isoindol-9-yl)benzonitrile (**3**)

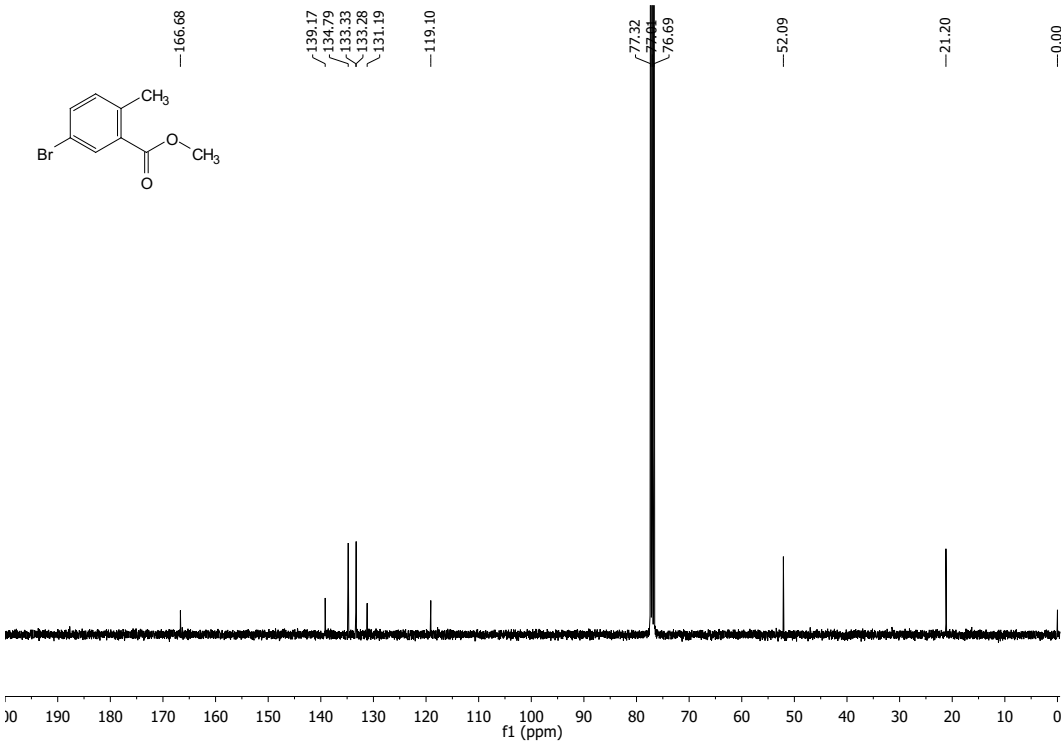



Following the experimental procedure of compound (**1**) presented above, compound **(12)** (0.41 g, 1.75 mmol) and (2-formylphenyl)boronic acid (0.21 g, 1.40 mmol, 0.8 eq.) were placed in a 100 mL round bottom flask and dissolved in ethanol (15 mL, 200 proof). DBU (1.60 g, 10.51 mmol, 1.56 mL, 6.0 eq.) was added to the mixture resulting in a yellow solution. The yellow reaction mixture was allowed to stir at reflux under $N_2$ atmosphere for 48 h. After 48 h, the color of the solution changed to dark red. The reaction mixture was allowed to cool to room temperature and was placed in an ice-water bath for 10 minutes, followed by the addition of HCl (35 mL, 1 M) resulting in an off-white precipitate. The mixture was then cooled below 0 °C for 24 h. After 24 h, the precipitate was filtered and washed with cold DI water to yield the pure product (0.316 g, 0.910 mmol, 65%). $^{1}$H NMR: (400 MHz, $CDCl_3$): δ (ppm) 8.19 (d, J = 7.5 Hz, 1H), 8.13 (d, J = 1.1 Hz, 1H), 7.95 (s, 1H), 7.90 (d, J = 1.1 Hz, 2H), 7.79 (d, J = 8.6 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H), 7.61 (td, J = 1.3 Hz, J = 7.7 Hz, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.43 (td, J = 1.0 Hz, J = 7.4 Hz, 1H), 6.93 (s, 1H). $^{13}$C {$^{1}$H} NMR (100 MHz, $CDCl_3$): δ(ppm) 174.30, 143.96, 141.20, 140.56, 138.80, 134.14, 133.56, 133.01, 132.88, 132.46, 130.26, 128.35, 127.76, 127.42, 123.41, 121.34, 118.57, 111.93, 108.43. $^{11}$B {$^{1}$H} NMR (sodium tetraphenyl borate as standard, 128 MHz, acetone-$d_6$, 25 °C): δ (ppm) 29.70. ATR-FTIR ($cm^{-1}$): 3445 (w), 3053 (w), 2227 (m), 1710 (s), 1644 (m), 1605 (m), 1472 (m), 1450 (w), 1400 (m), 1375 (m), 1346 (s), 1282 (s), 1182 (w), 1137 (m), 1117 (s), 1084 (s), 957 (m), 852 (m), 822 (s), 792 (s), 769 (m), 738 (m), 722 (s), 686 (s). HRMS (ESI) *m/*z: Calcd for $C_{22}H_{13}BN_2O_2$ , 349.1148 $(M + H)^+$; Found: 349.1667 $(M + H)^+$. UV-vis (chloroform, $\lambda_{max}$, ε, concentration, path length): 385 nm, 1.8 x $10^4$ $M^{-1}$ $cm^{-1}$, 3.11 x $10^{-6}$ M, 1 cm. Emission (acetonitrile, $\lambda_{max}$): 445 nm.

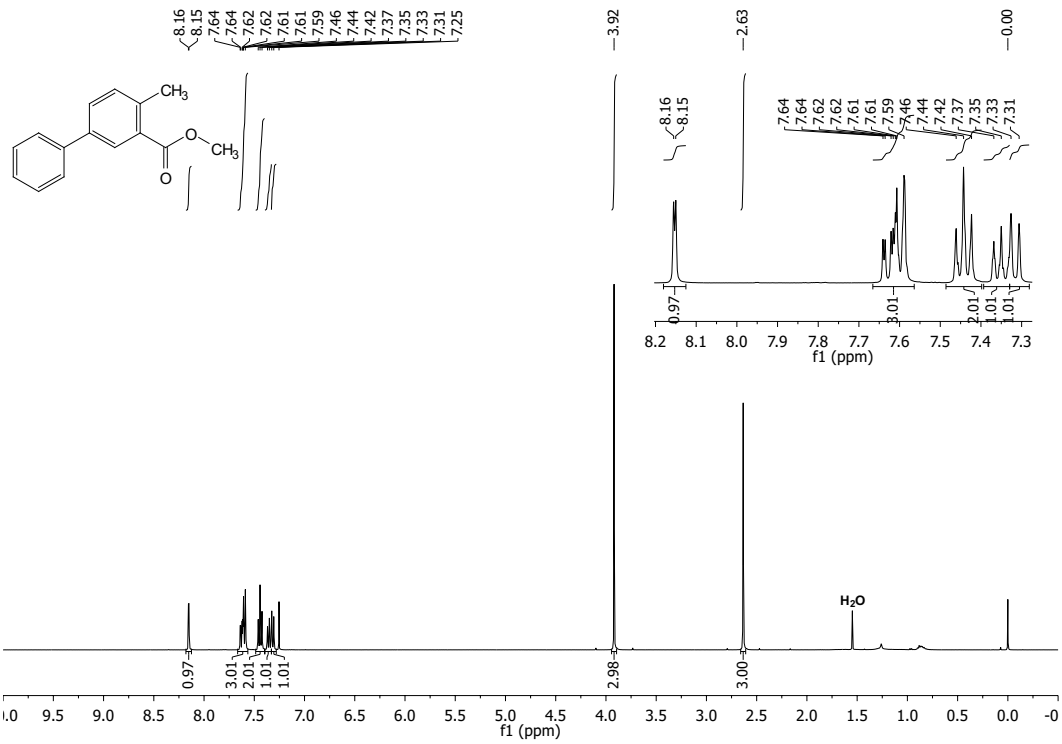
## NMR spectral characterization



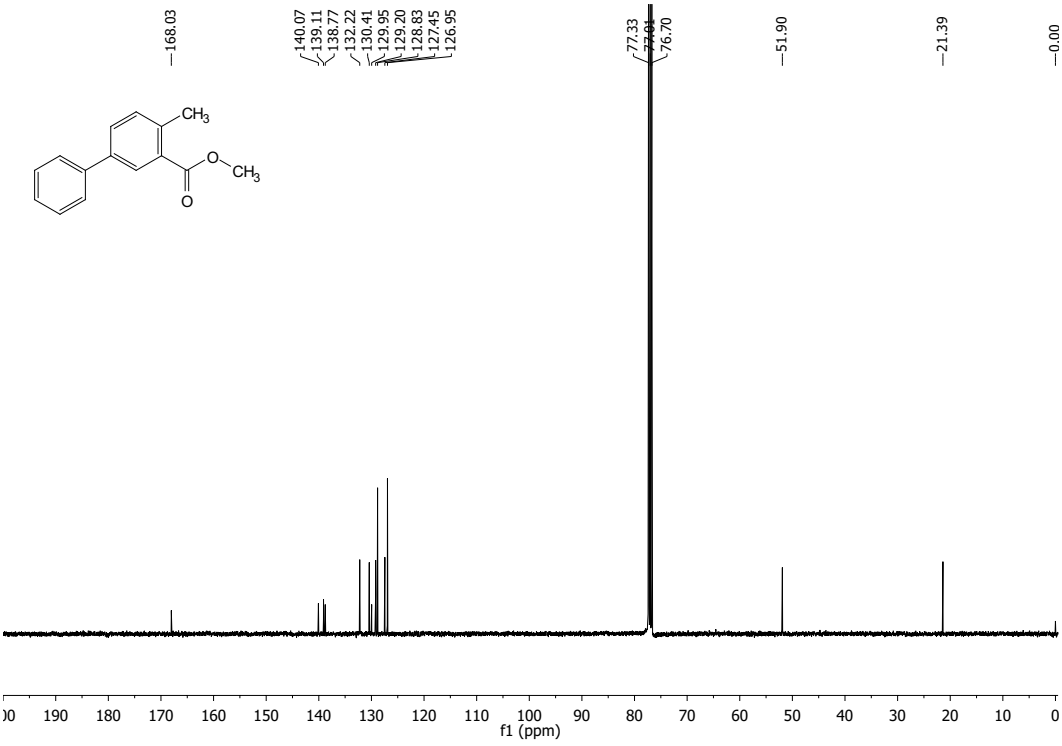

$^{1}$H NMR spectrum (400 MHz) of **4** in $CDCl_3$



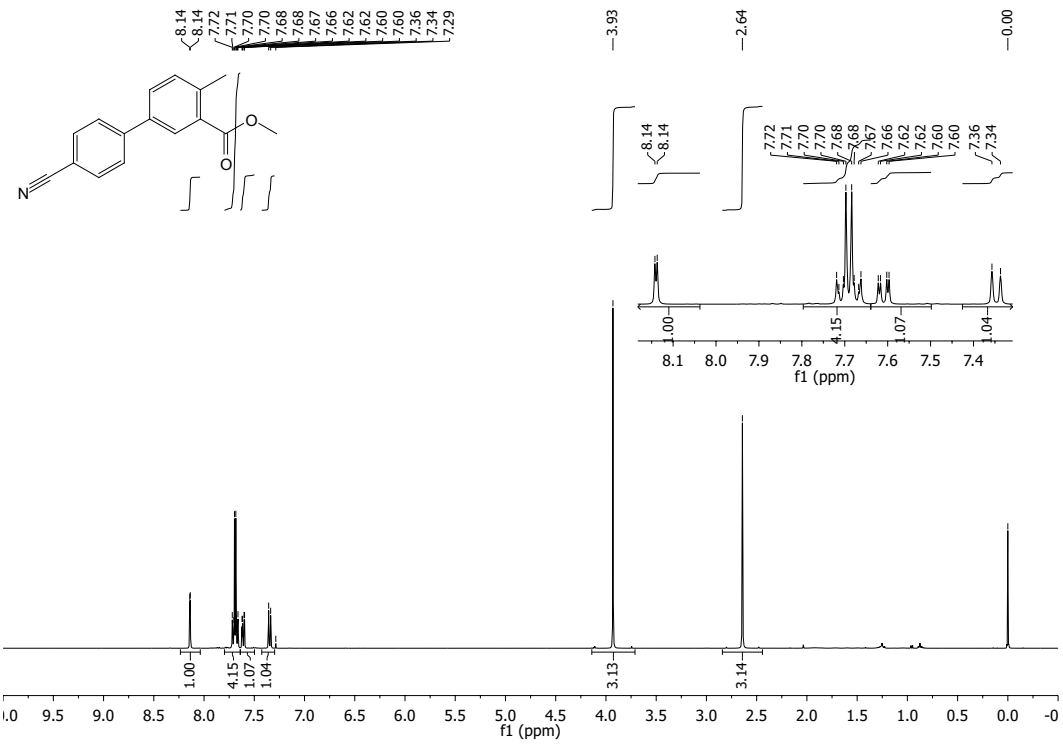

$^{13}$C {$^{1}$H} NMR spectrum (100 MHz) of **4** in $CDCl_3$



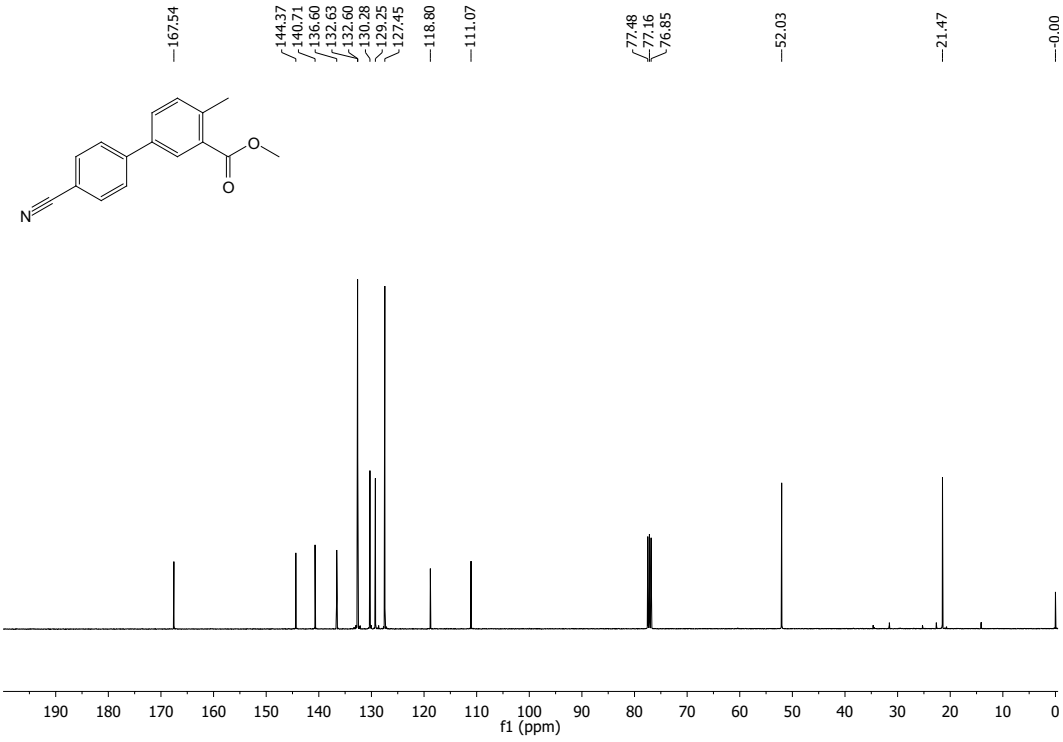

$^{1}$H NMR spectrum (400 MHz) of **5** in $CDCl_3$



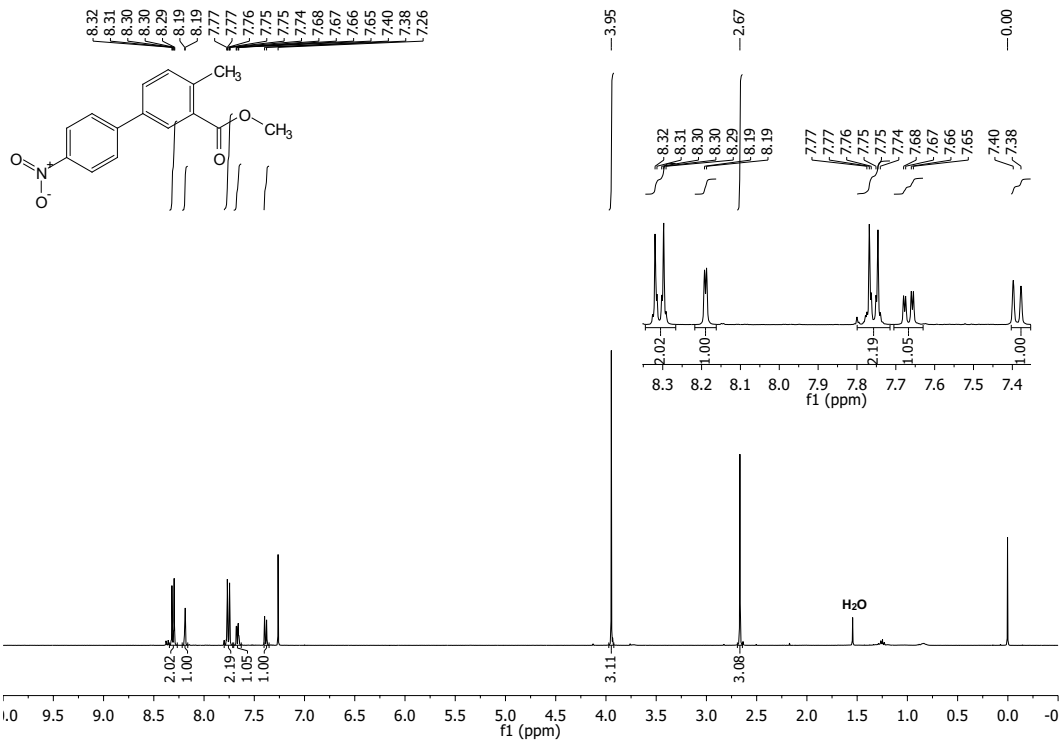

$^{13}$C {$^{1}$H} NMR spectrum (100 MHz) of **5** in $CDCl_3$



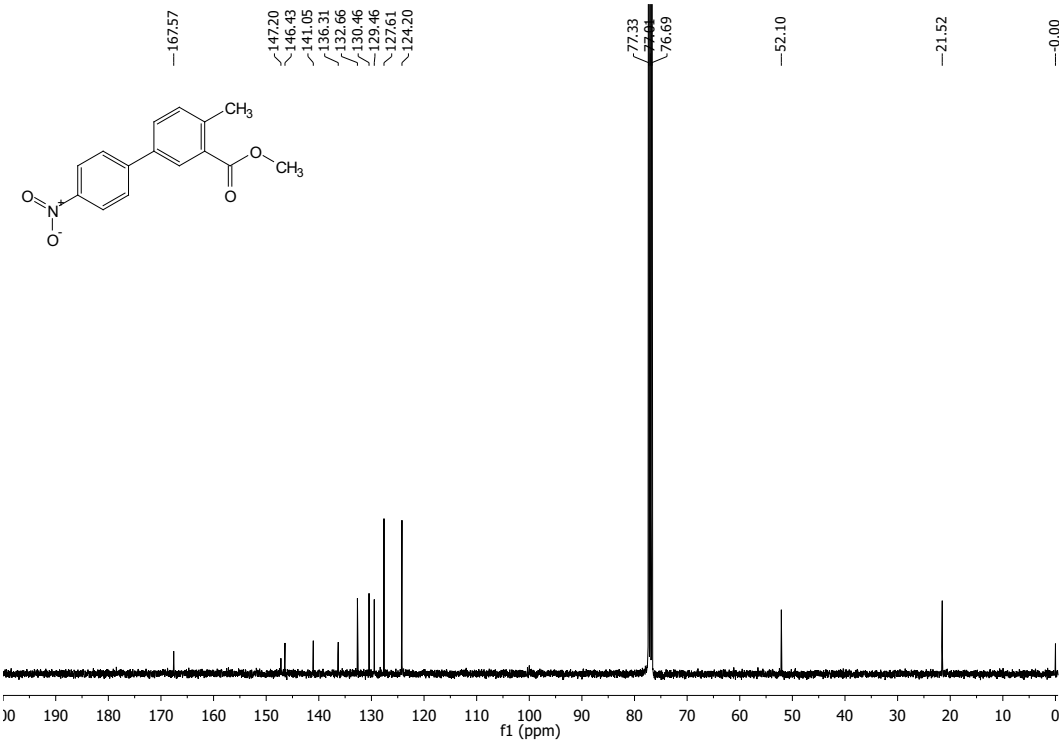

$^{1}$H NMR spectrum (400 MHz) of **6** in $CDCl_3$



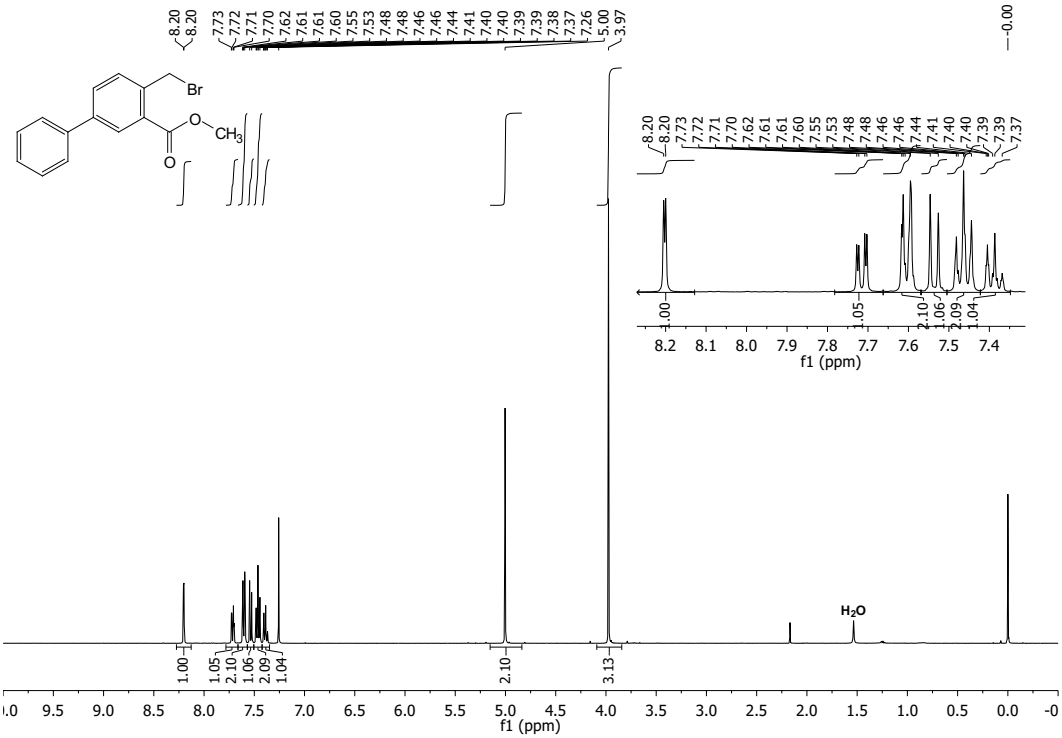

$^{13}$C {$^{1}$H} NMR spectrum (100 MHz) of **6** in $CDCl_3$



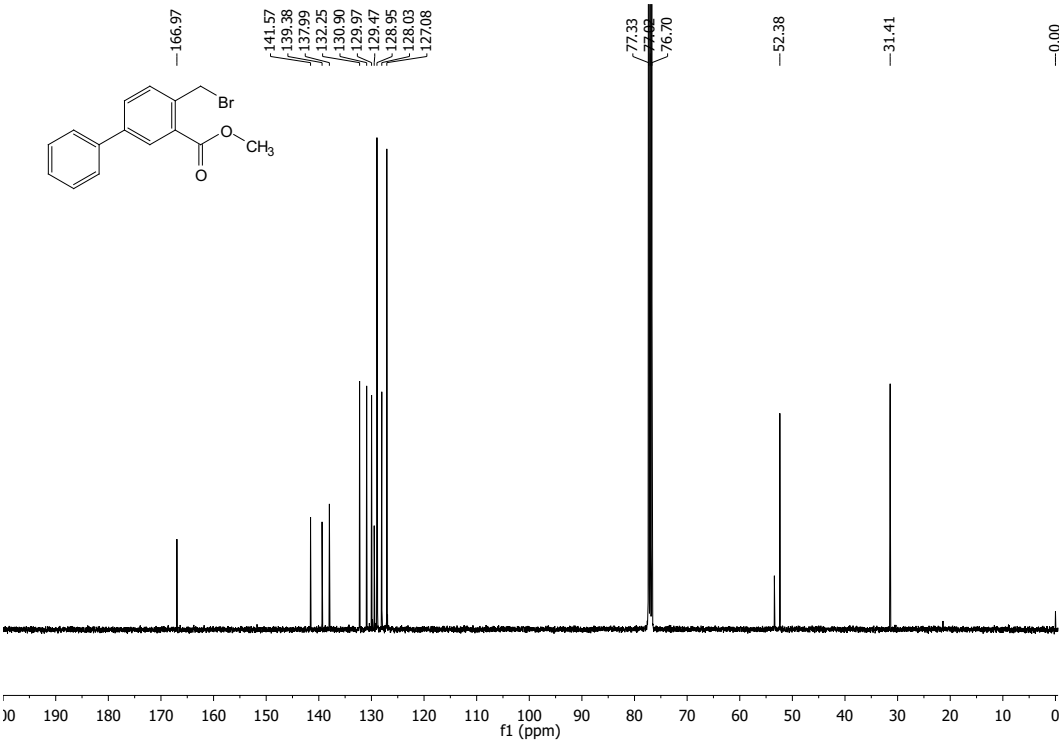

$^{1}$H NMR spectrum (400 MHz) of **7** in $CDCl_3$



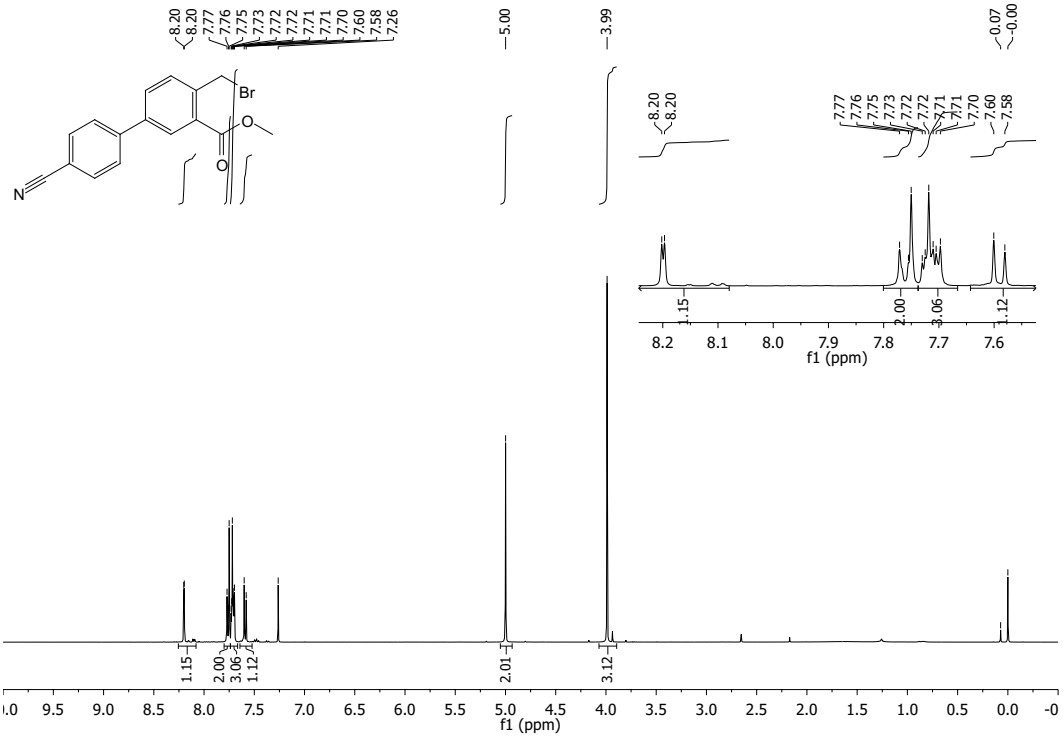

$^{13}$C {$^{1}$H} NMR spectrum (100 MHz) of **7** in $CDCl_3$



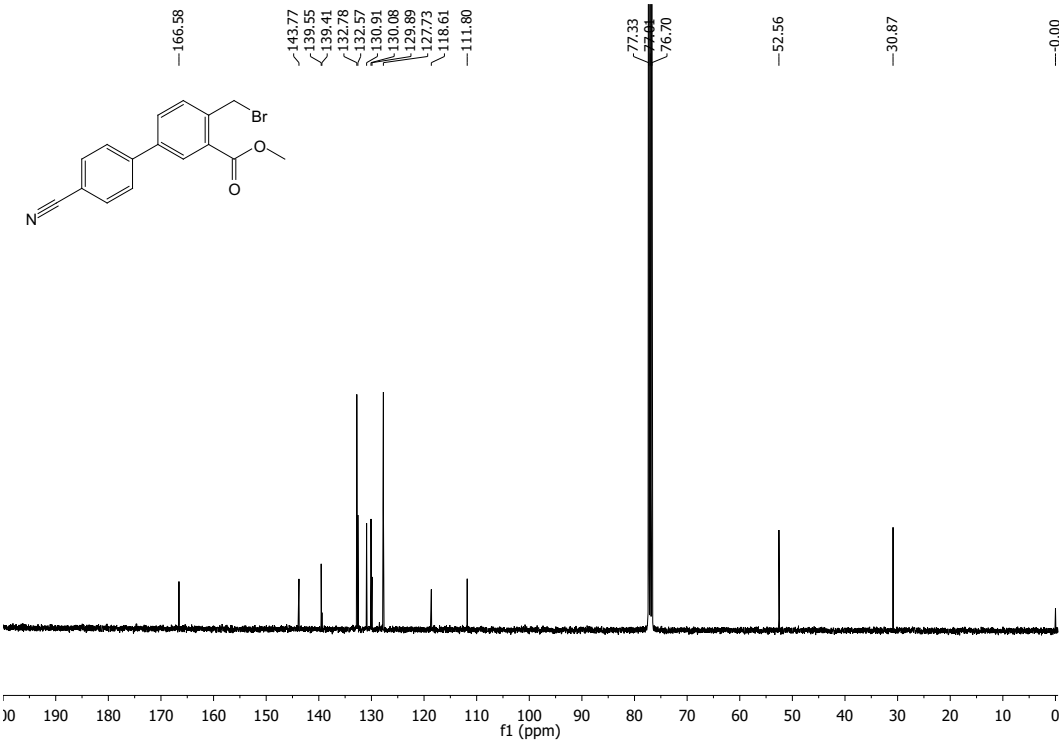

$^{1}$H NMR spectrum (400 MHz) of **8** in $CDCl_3$



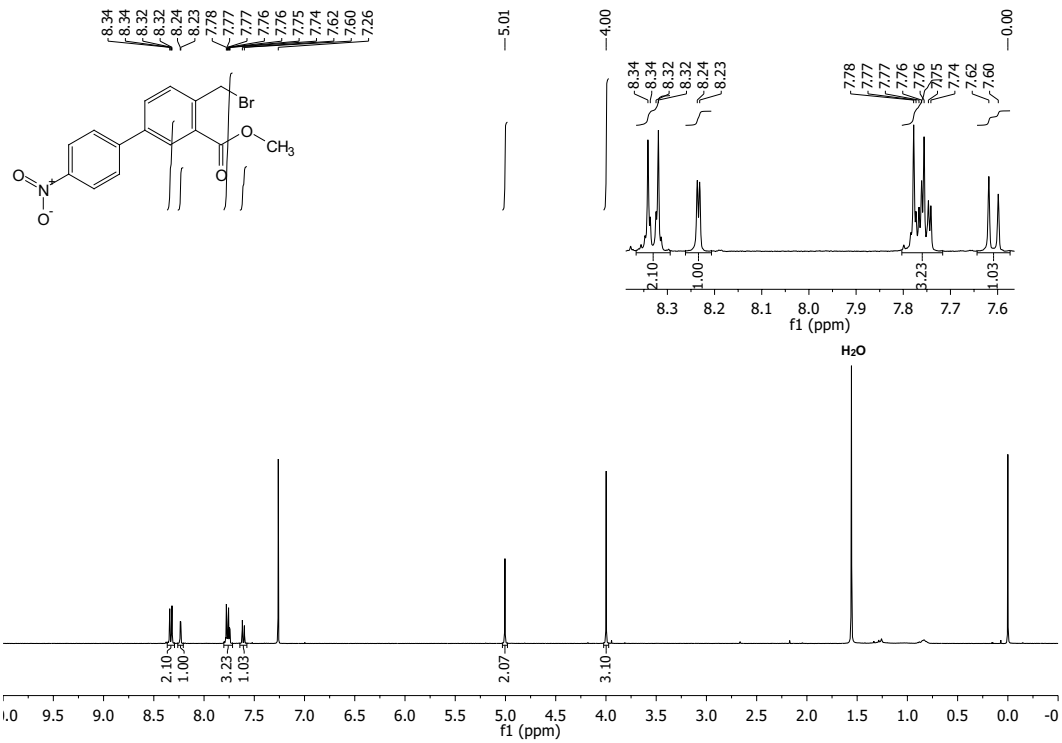

$^{13}$C {$^{1}$H} NMR spectrum (100 MHz) of **8** in $CDCl_3$



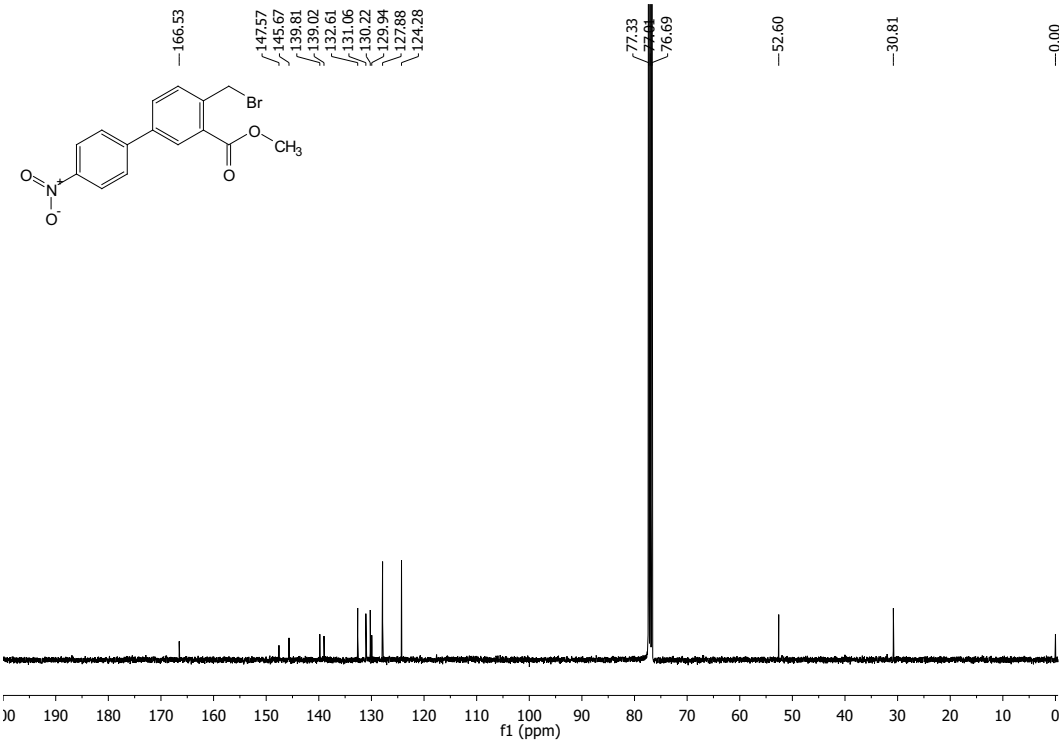

$^{1}$H NMR spectrum (400 MHz) of **9** in $CDCl_3$



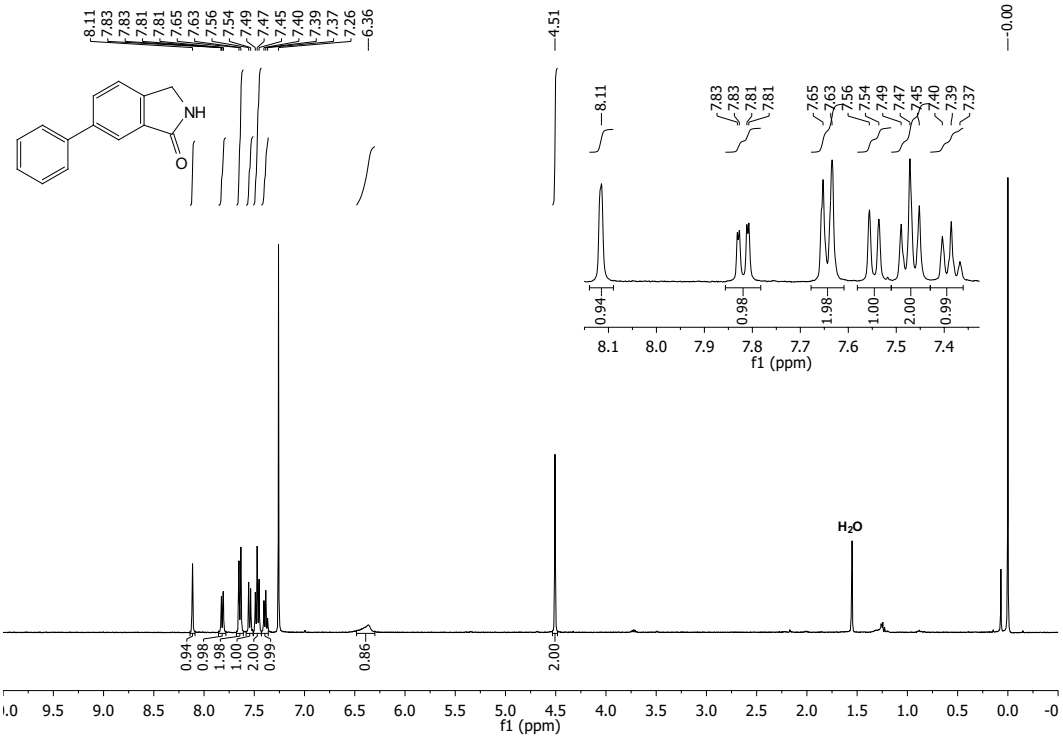

$^{13}$C {$^{1}$H} NMR spectrum (100 MHz) of **9** in $CDCl_3$



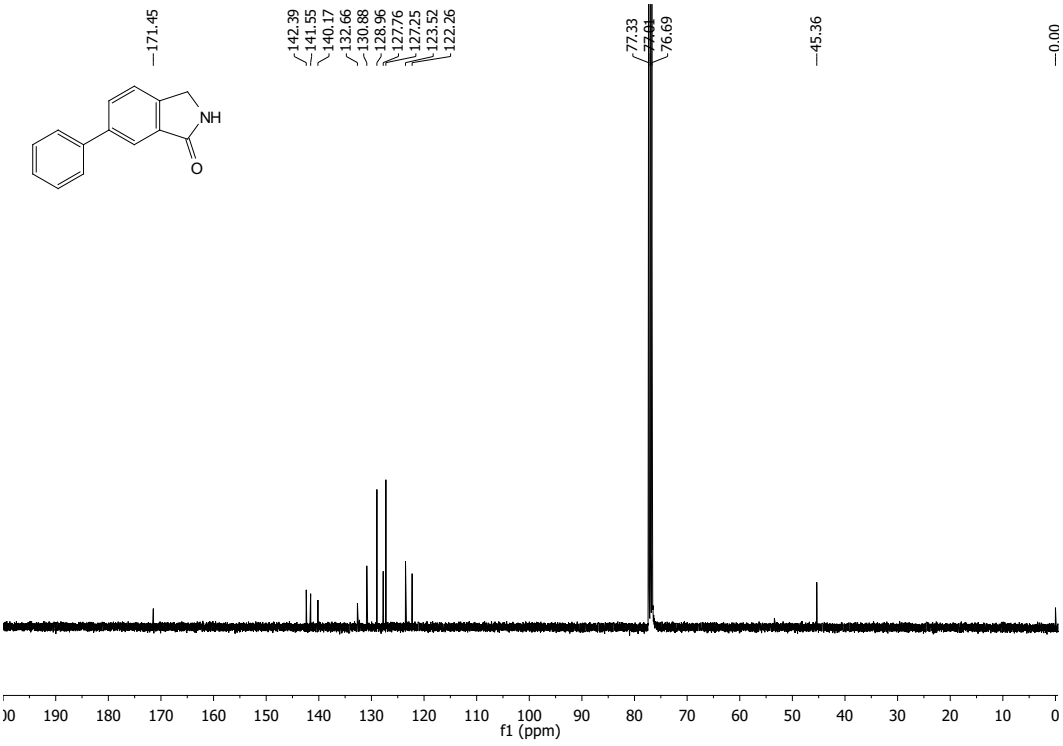

$^{1}$H NMR spectrum (400 MHz) of **10** in CDCl3



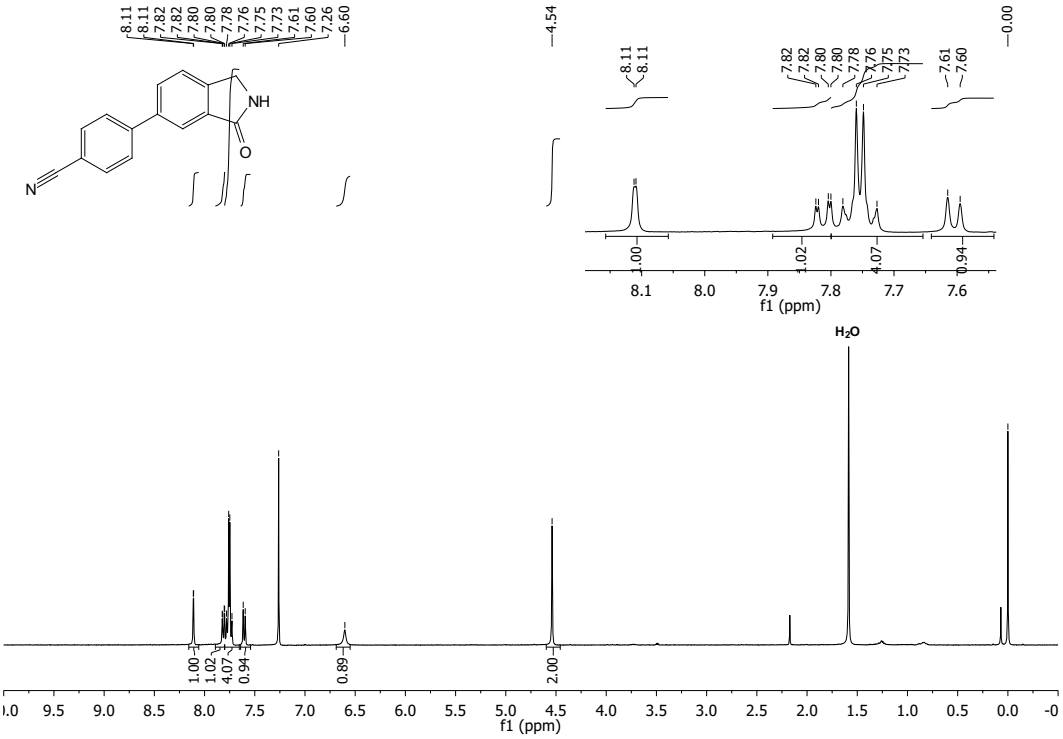

$^{13}$C {$^{1}$H} NMR spectrum (100 MHz) of **10** in $CDCl_3$



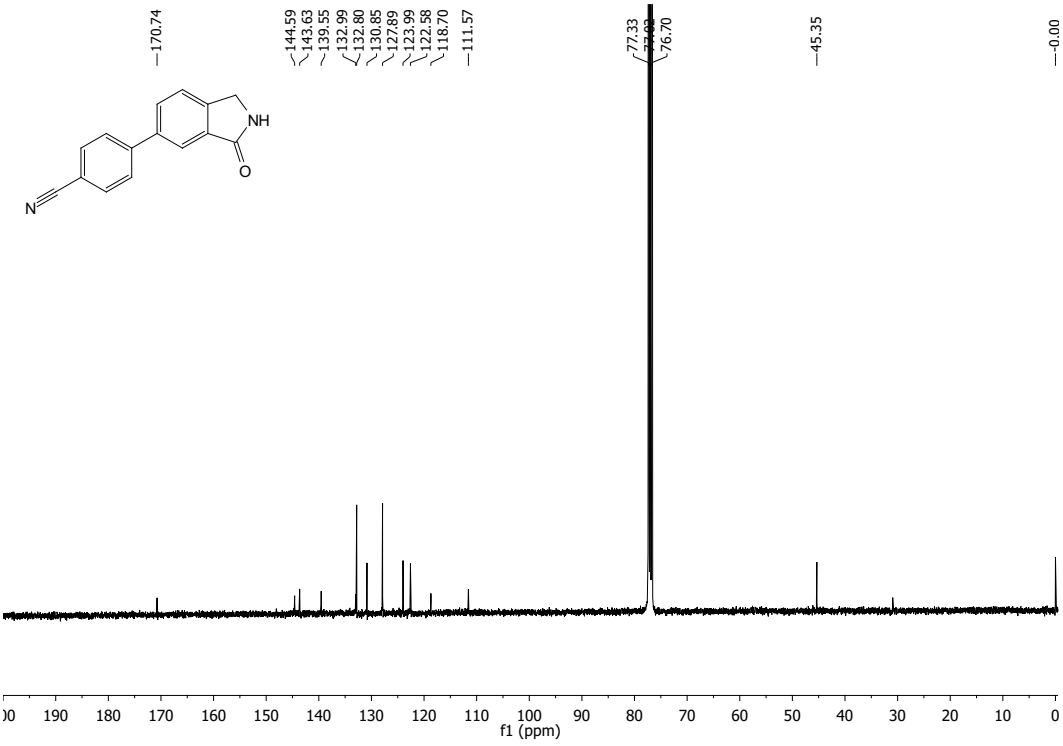

$^{1}$H NMR spectrum (400 MHz) of **11** in $CDCl_3$



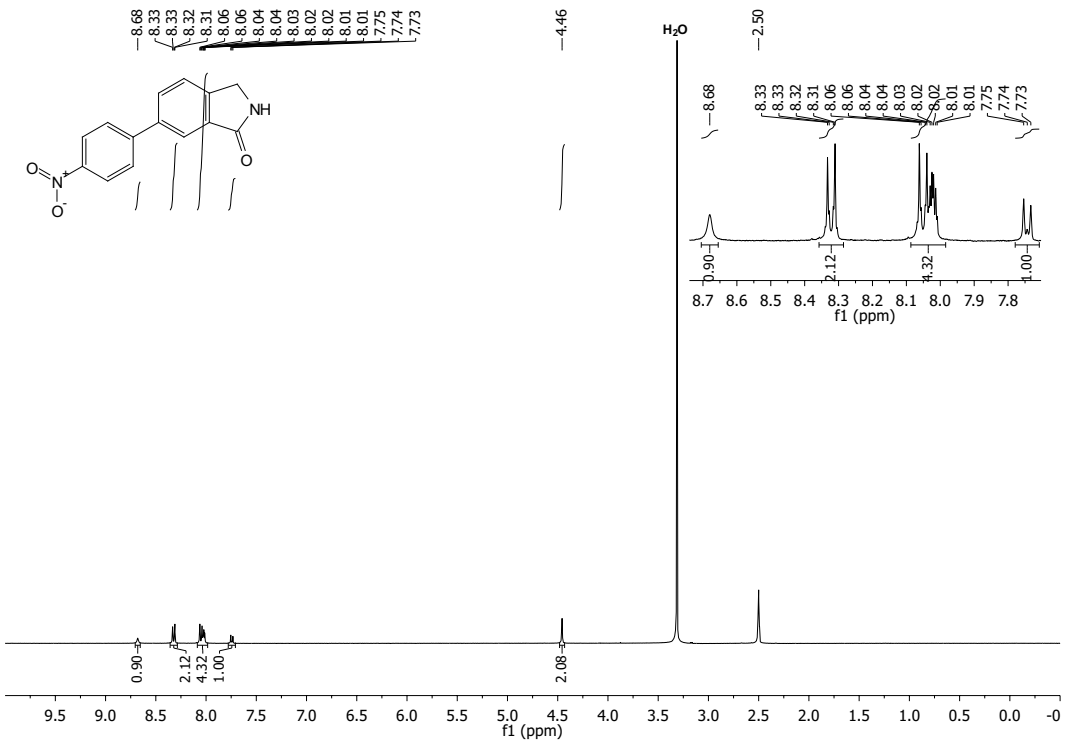

$^{13}$C {$^{1}$H} NMR spectrum (100 MHz) of **11** in $CDCl_3$



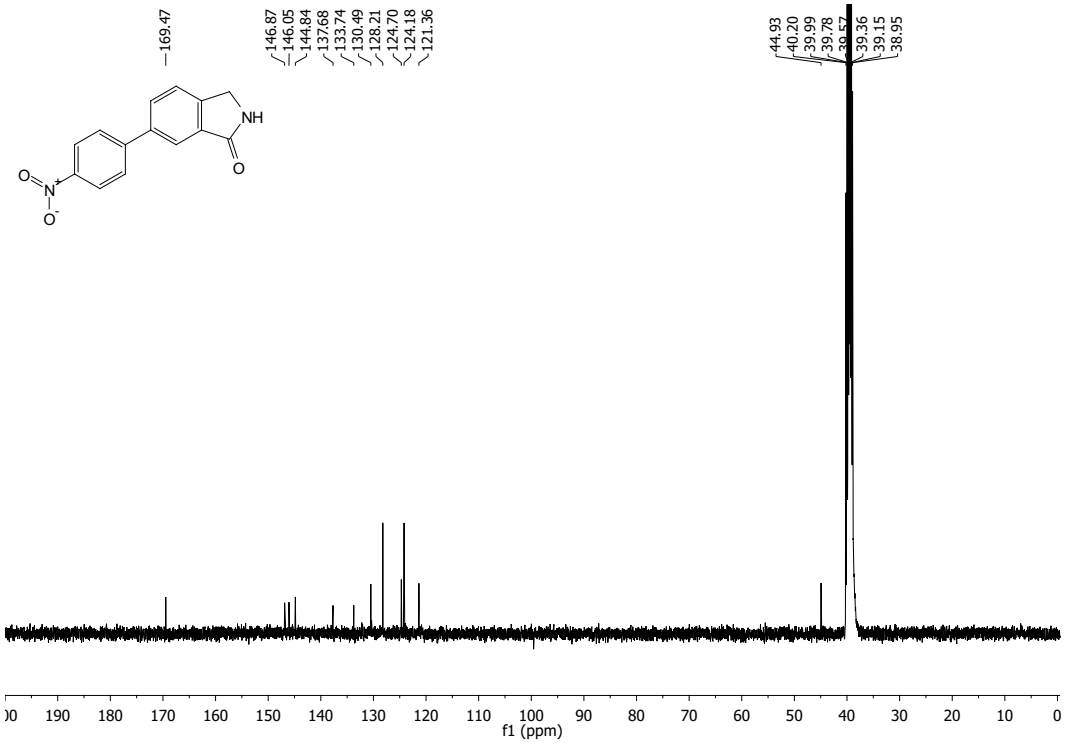

$^{1}$H NMR spectrum (400 MHz) of **12** in $CDCl_3$



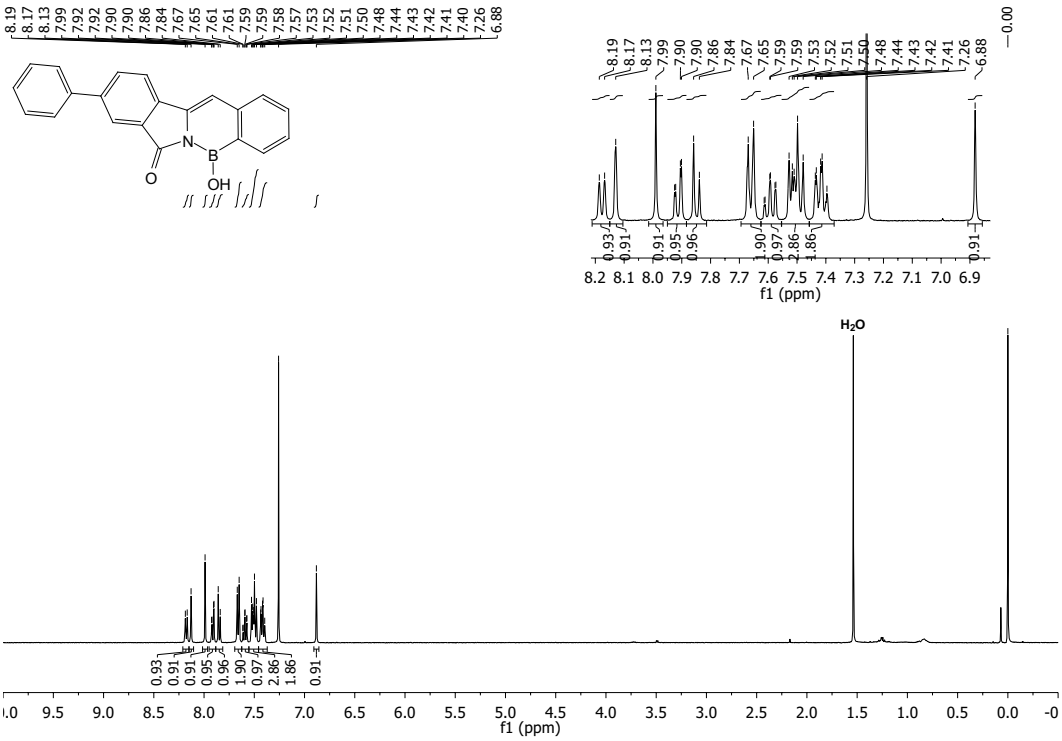

$^{13}$C {$^{1}$H} NMR spectrum (100 MHz) of **12** in $CDCl_3$



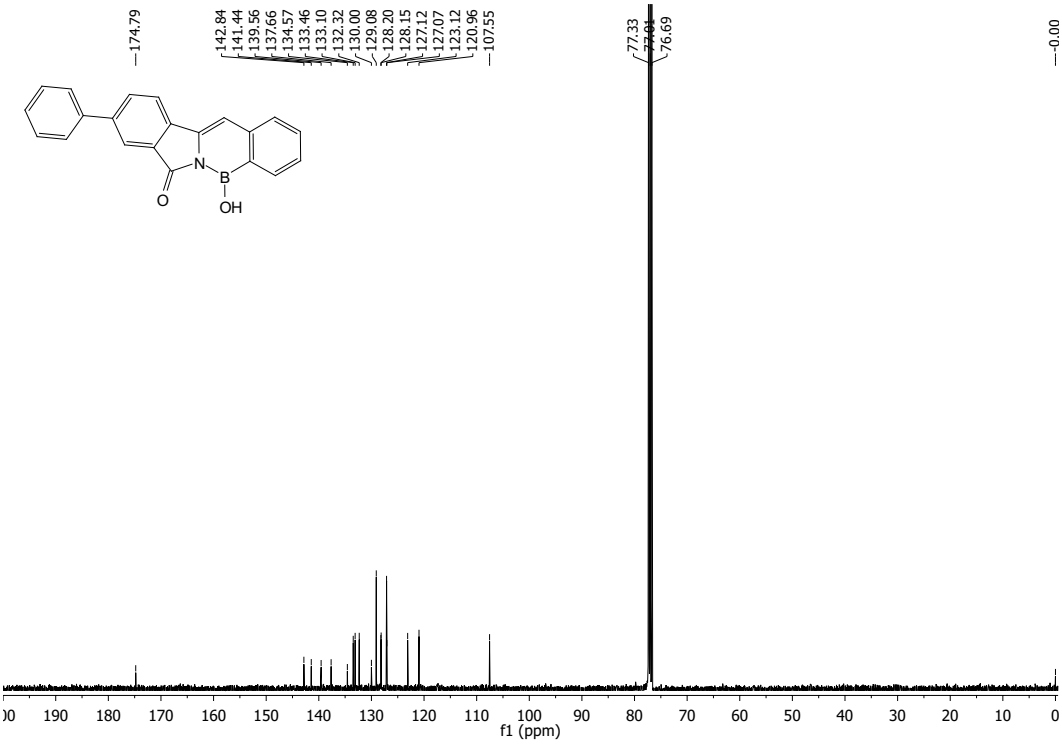

$^{1}$H NMR spectrum (400 MHz) of **13** in DMSO



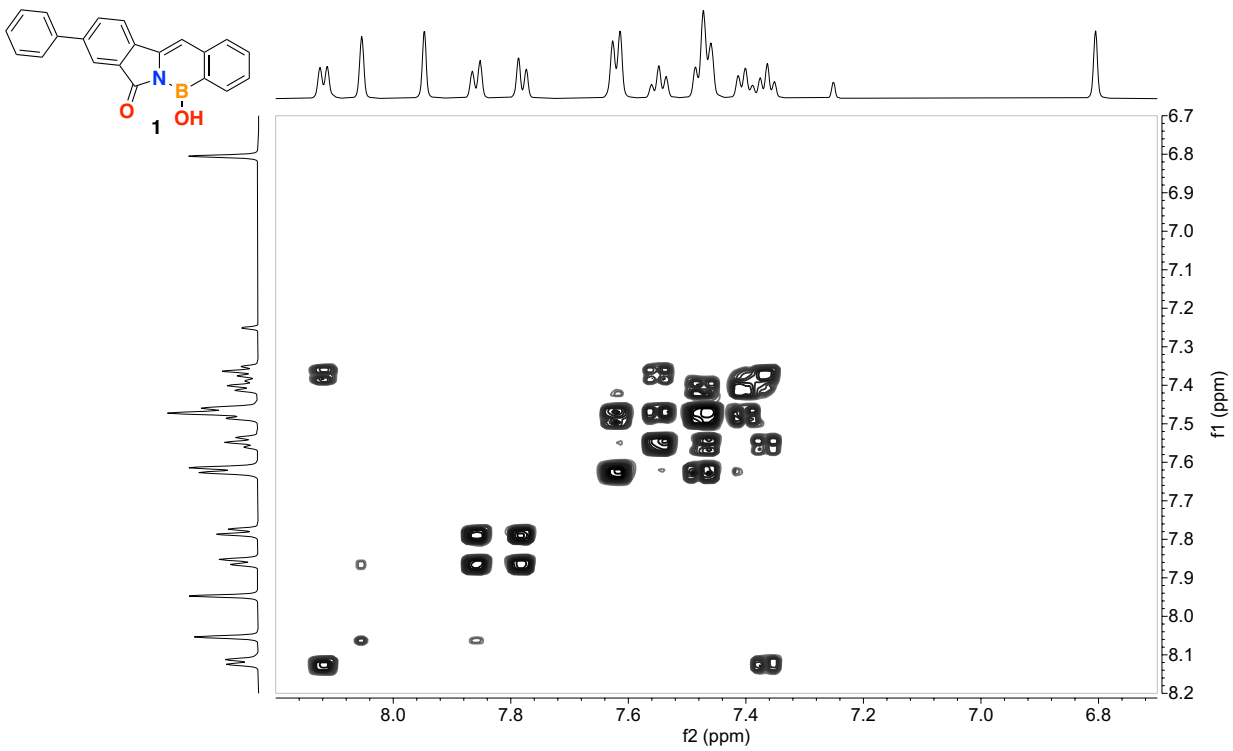

$^{13}$C {$^{1}$H} NMR spectrum (100 MHz) of **13** in DMSO



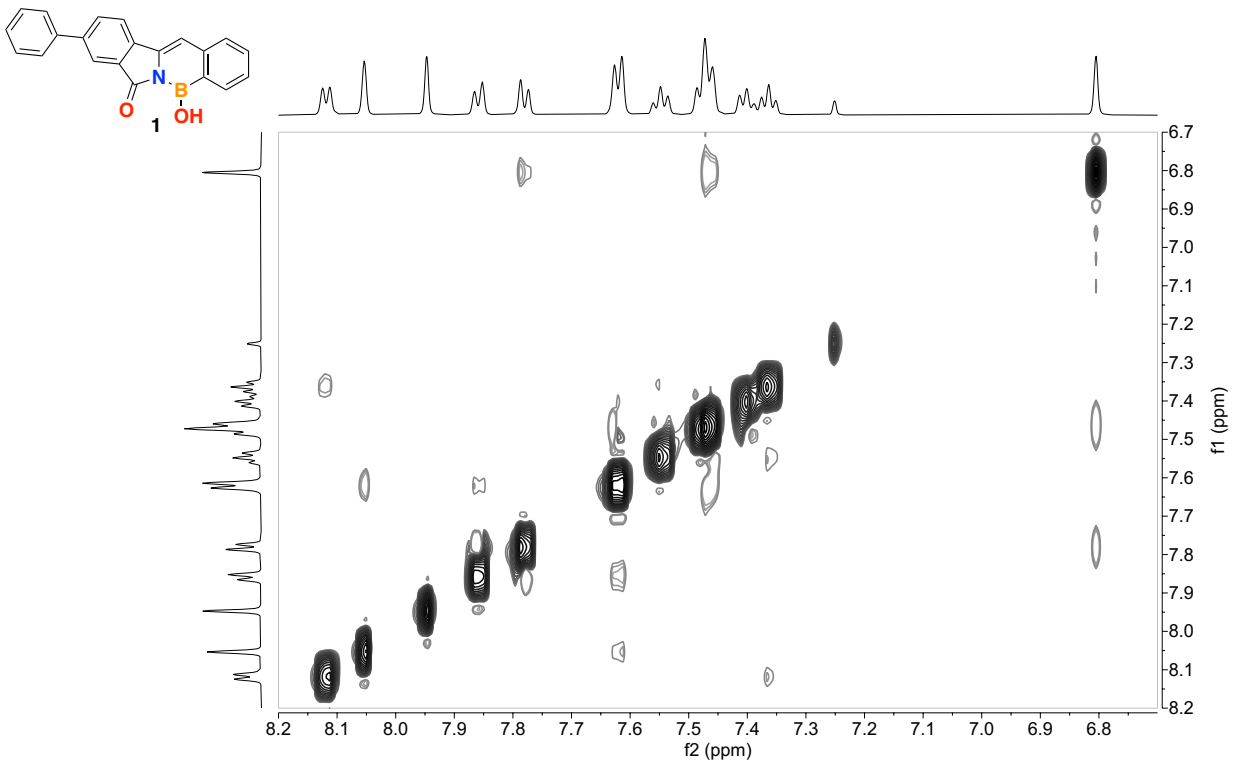

$^{1}$H NMR spectrum (400 MHz) of **1** in $CDCl_3$



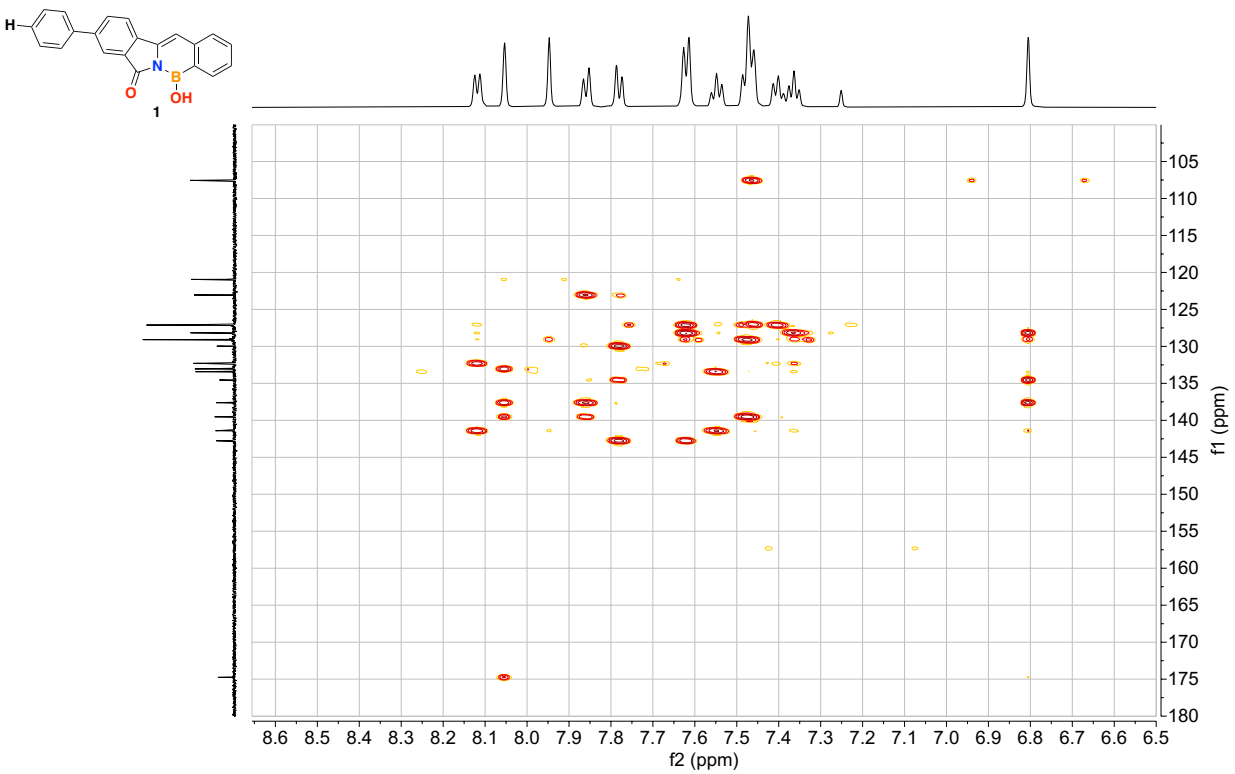

$^{13}$C {$^{1}$H} NMR spectrum (100 MHz) of **1** in $CDCl_3$



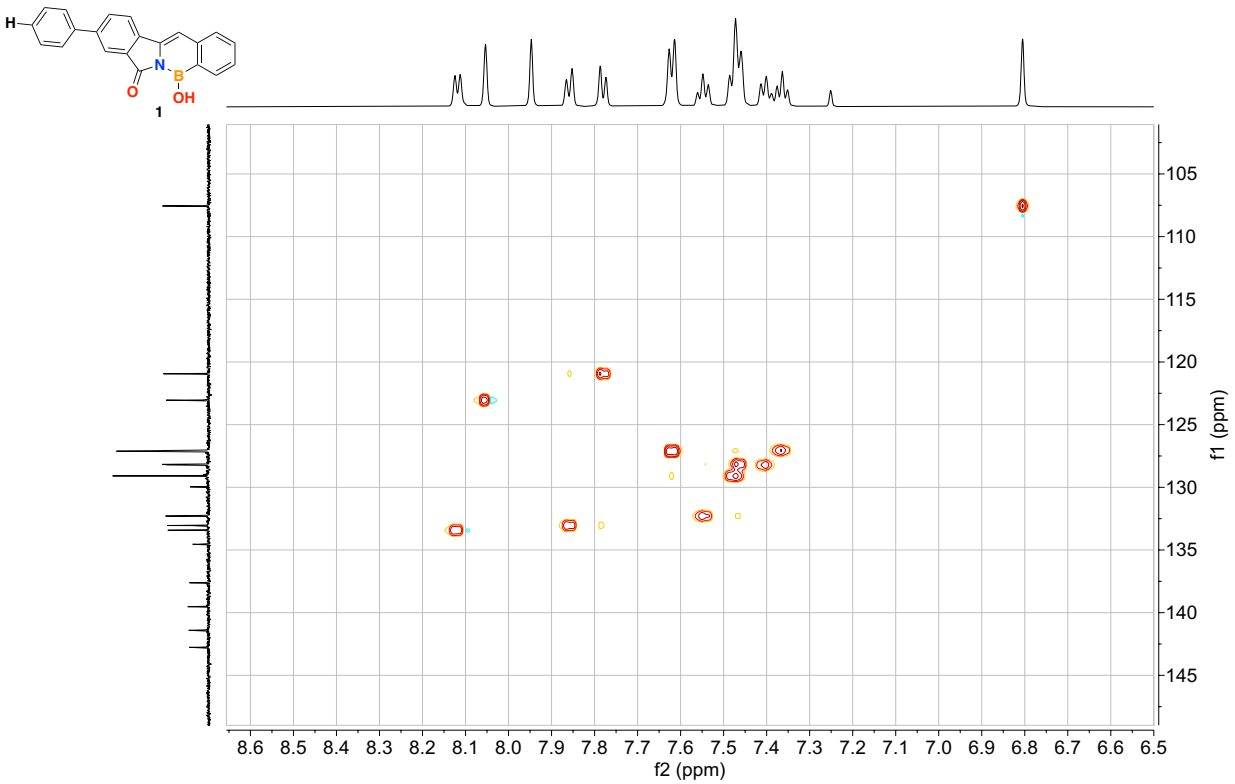

$^{1}$H-$^{1}$H COSY spectra of **1** ($CDCl_3$)



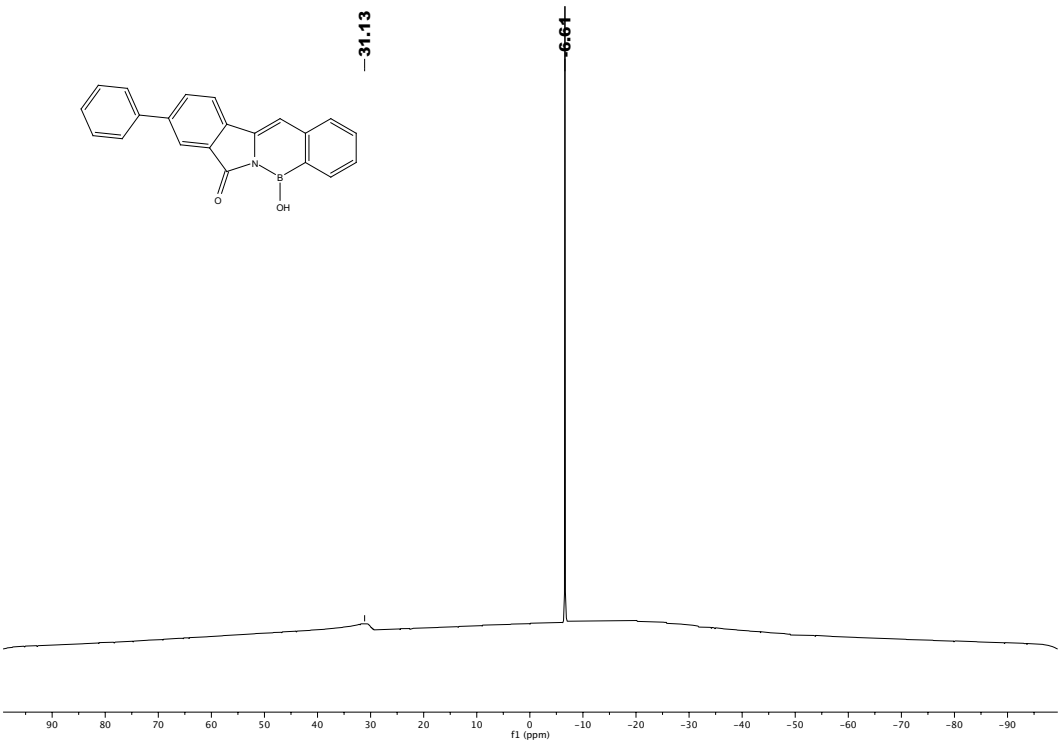

NOESY spectra of **1** ($CDCl_3$)



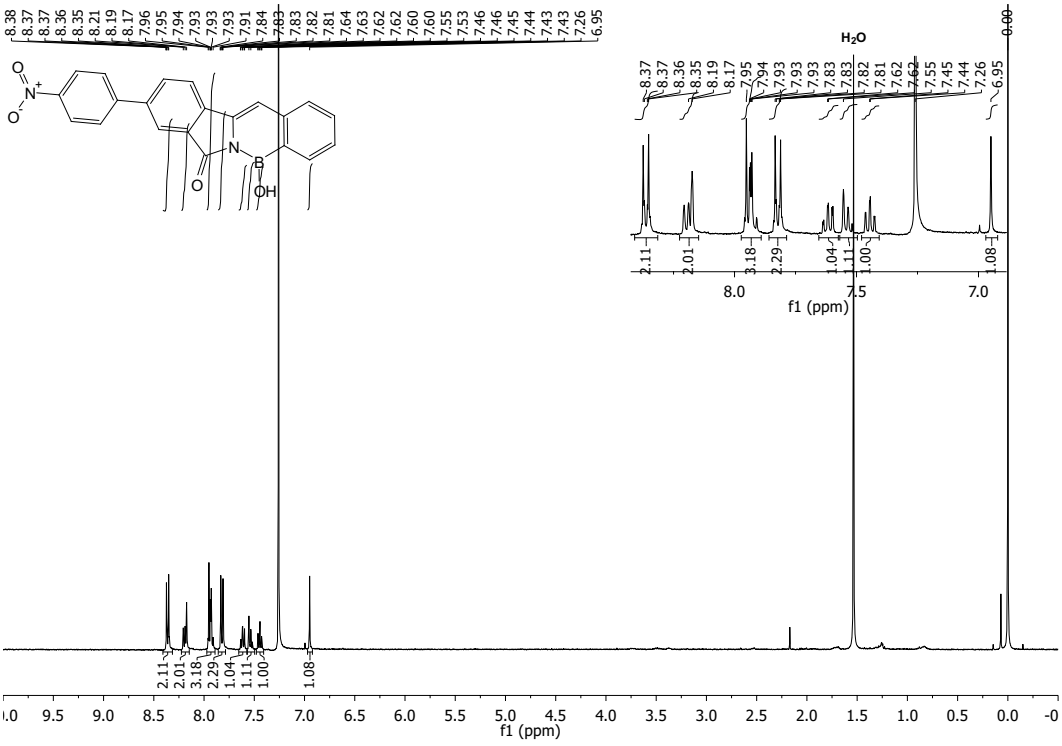

HMBC NMR spectra of **1** ($CDCl_3$)



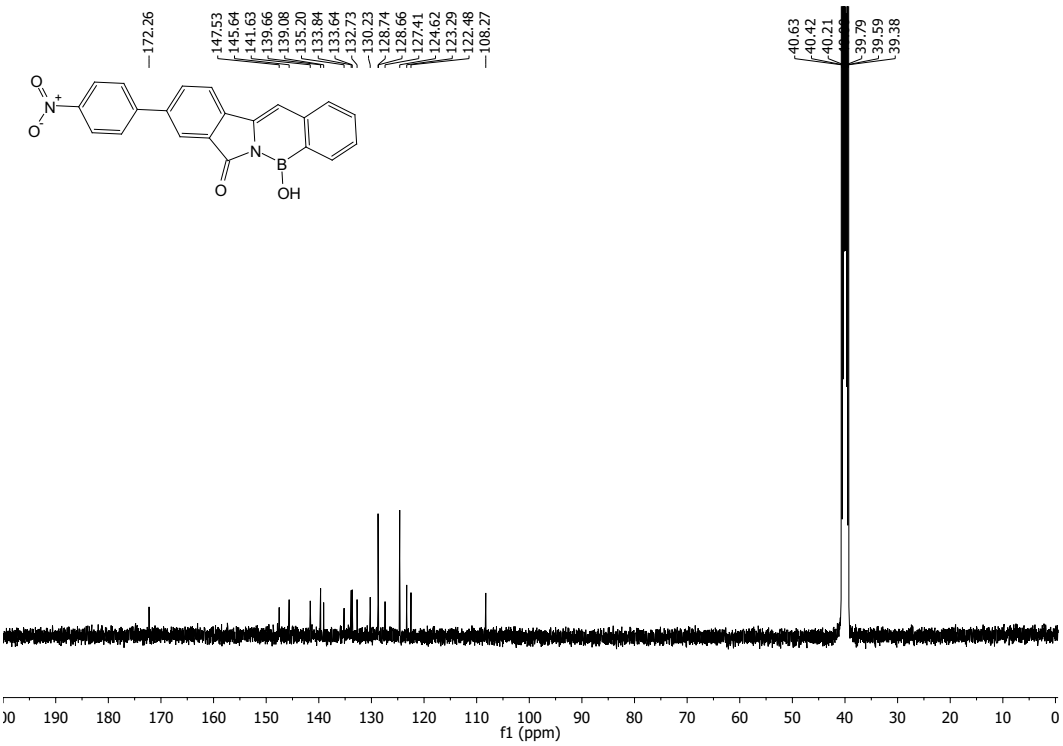

HSQC NMR spectra of **1** ($CDCl_3$)



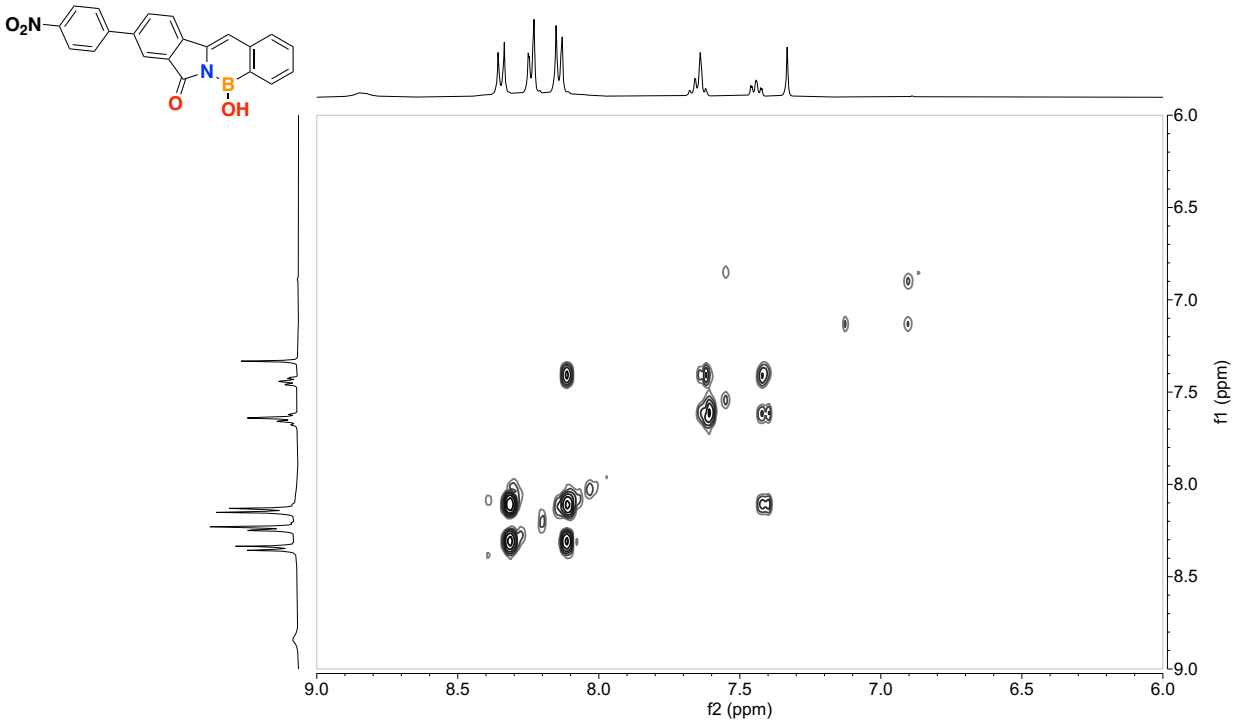

$^{11}B$ {$^{1}H$} NMR spectrum (128 MHz) of **1** in acetone $d_6$



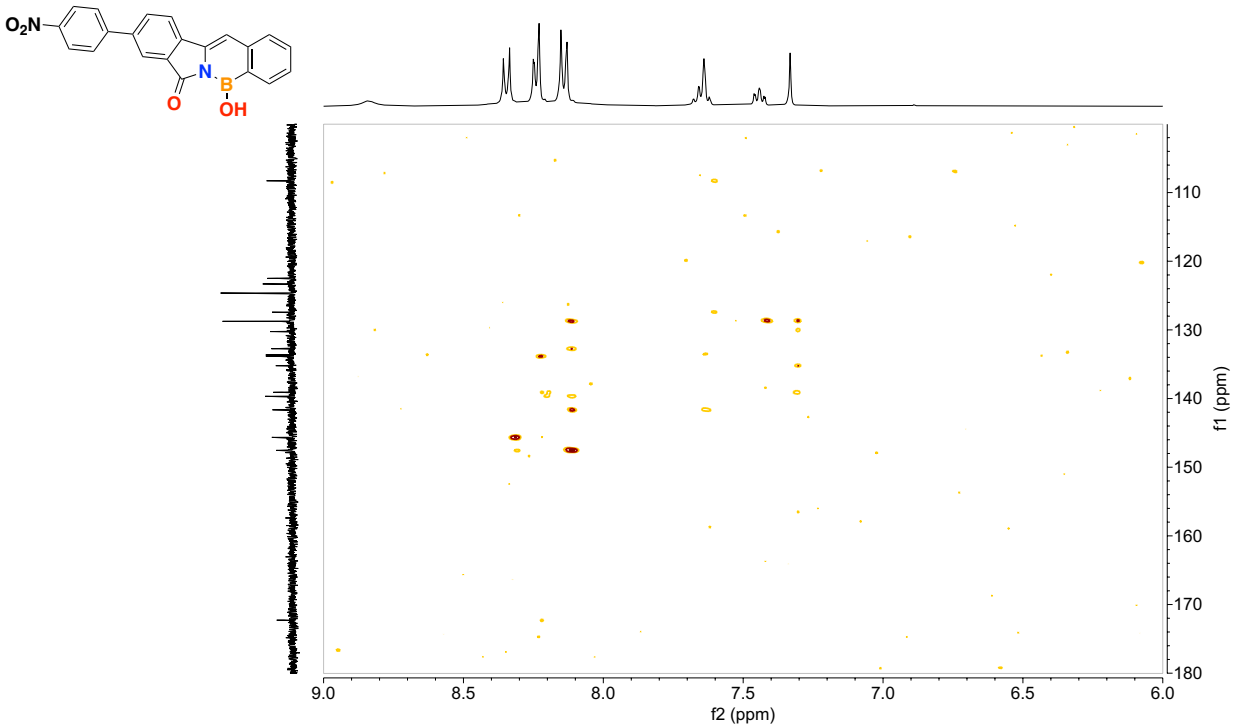

$^{1}H$ NMR spectrum (400 MHz) of **2** in $CDCl_3$



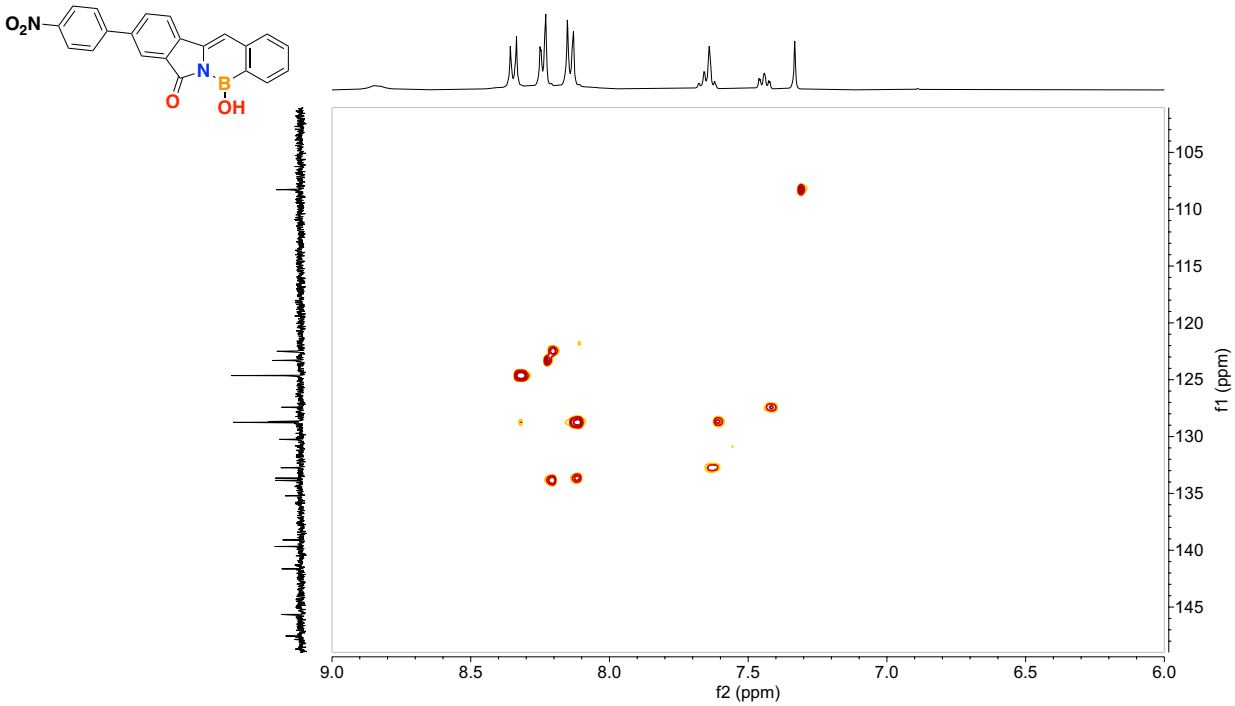

$^{13}C$ {$^{1}H$} NMR spectrum (100 MHz) of **2** in DMSO



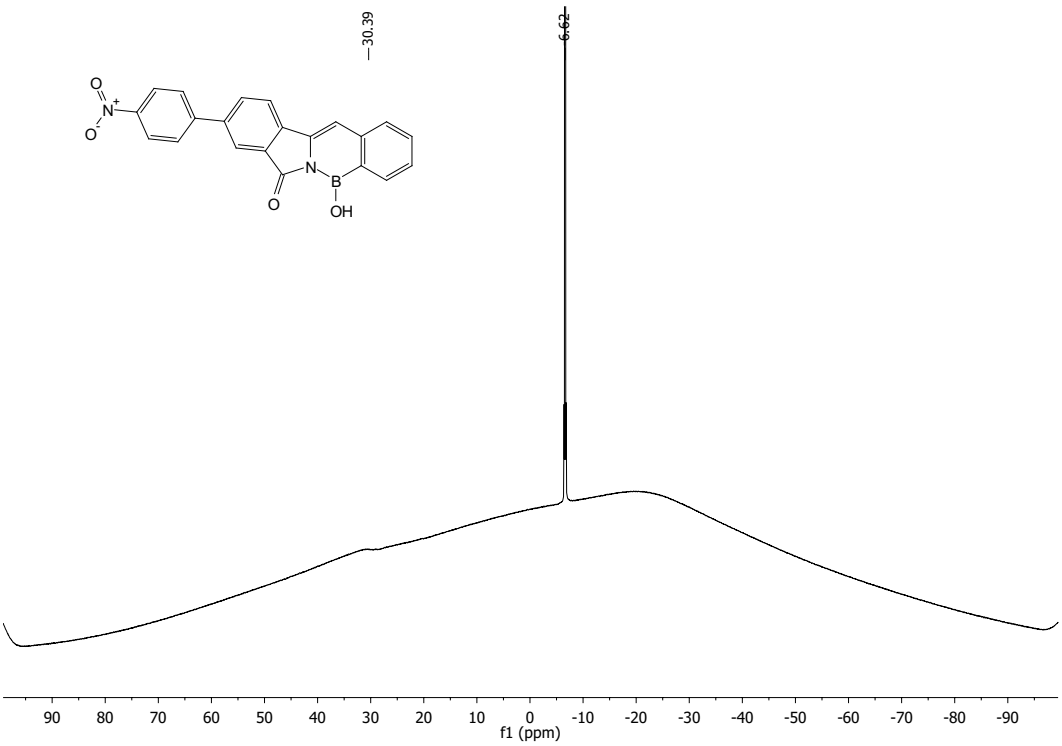

$^{1}H$-$^{1}H$ COSY spectra of **2** (DMSO)



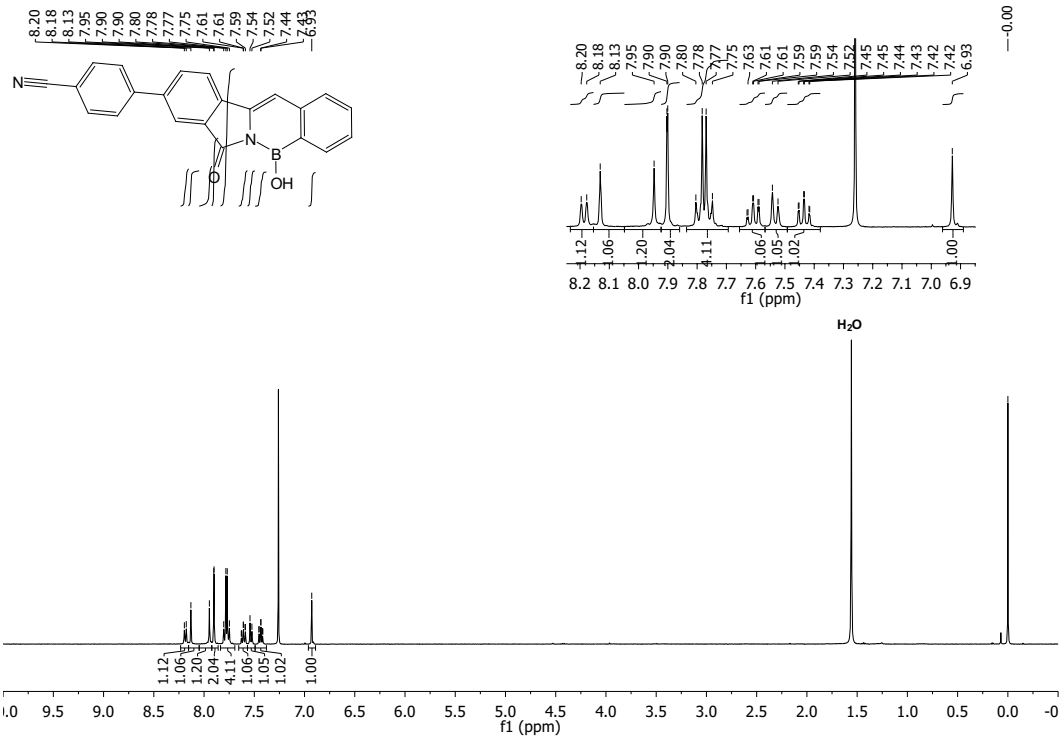

HMBC spectra of **2** (DMSO)



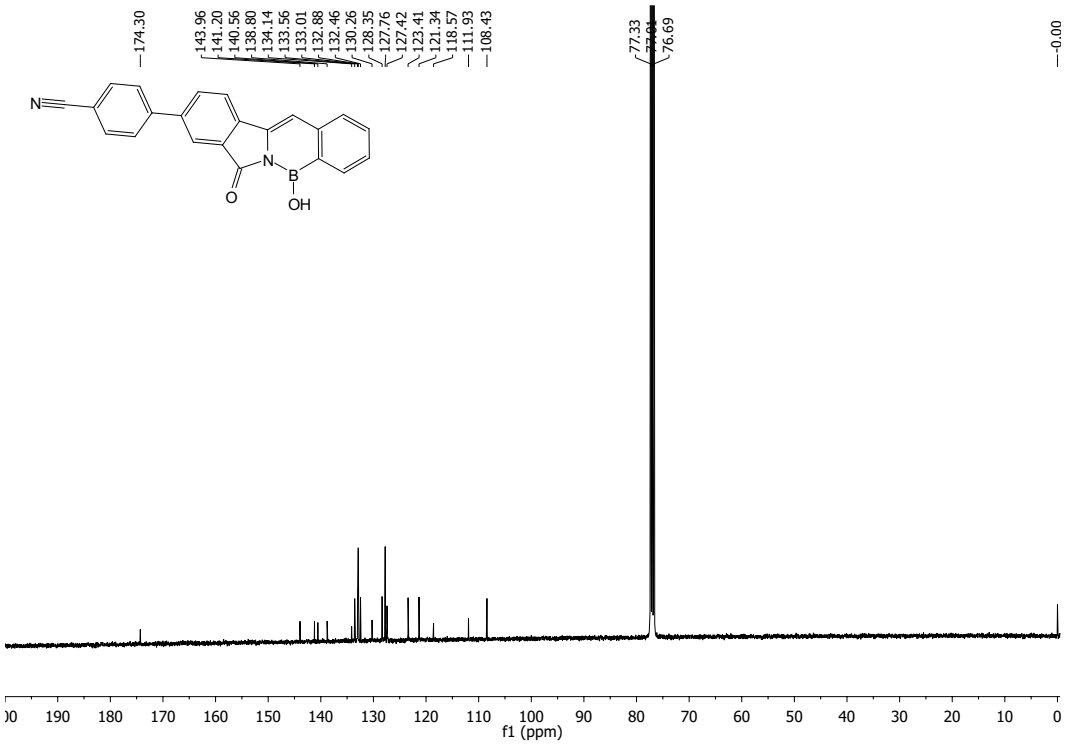

HSQC spectra of **2** (DMSO)



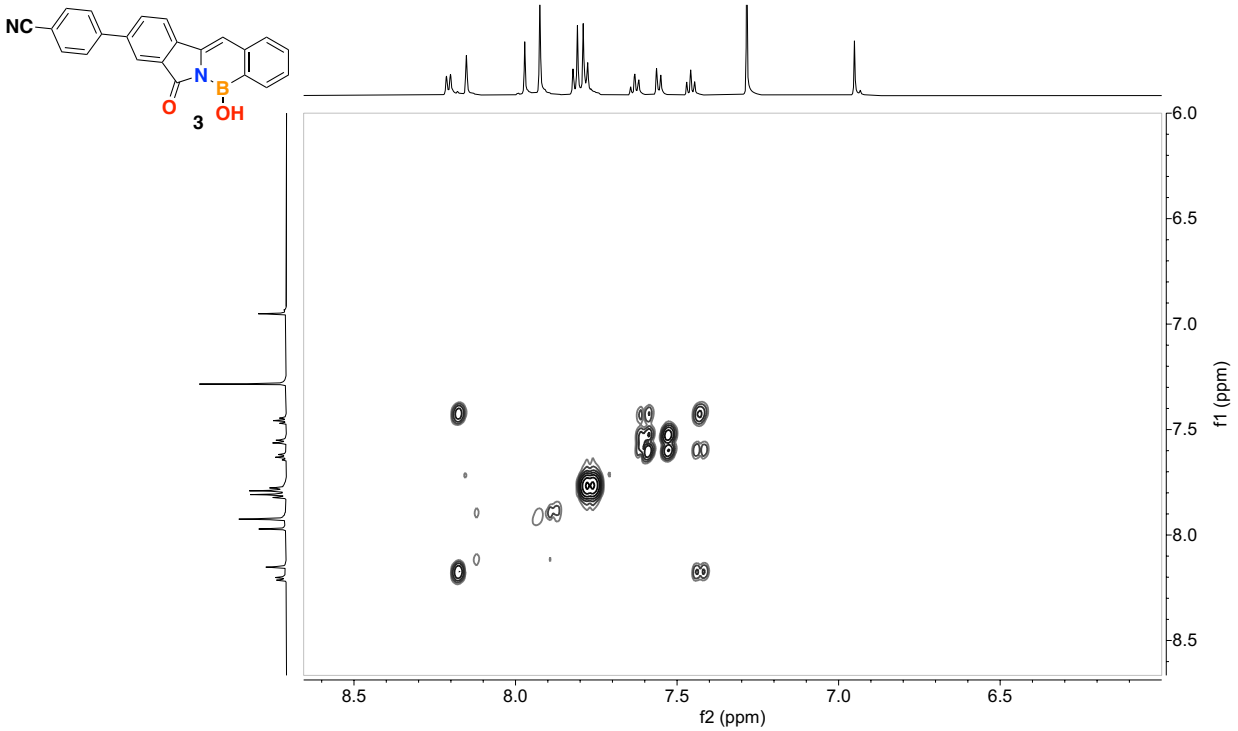

$^{11}B$ {$^{1}H$} NMR spectrum (128 MHz) of **2** in acetone $d_6$



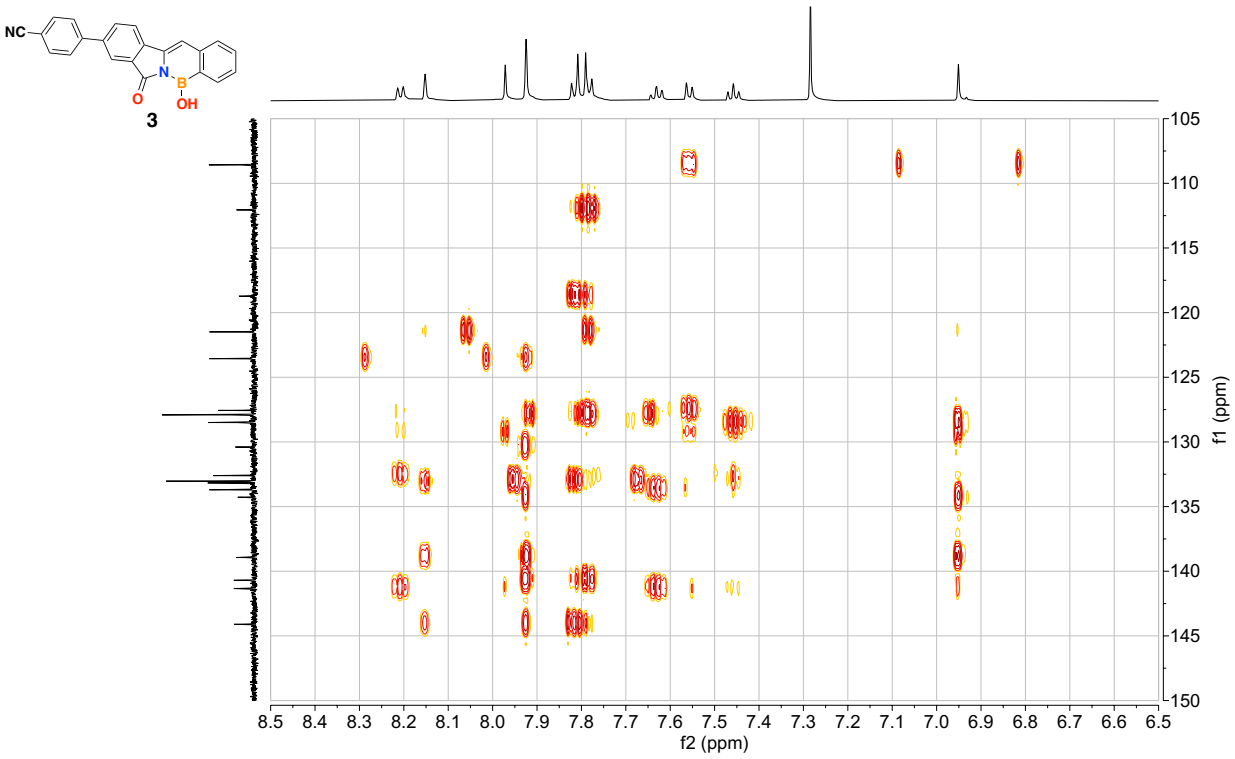

$^{1}H$ NMR spectrum (400 MHz) of **3** in $CDCl_3$



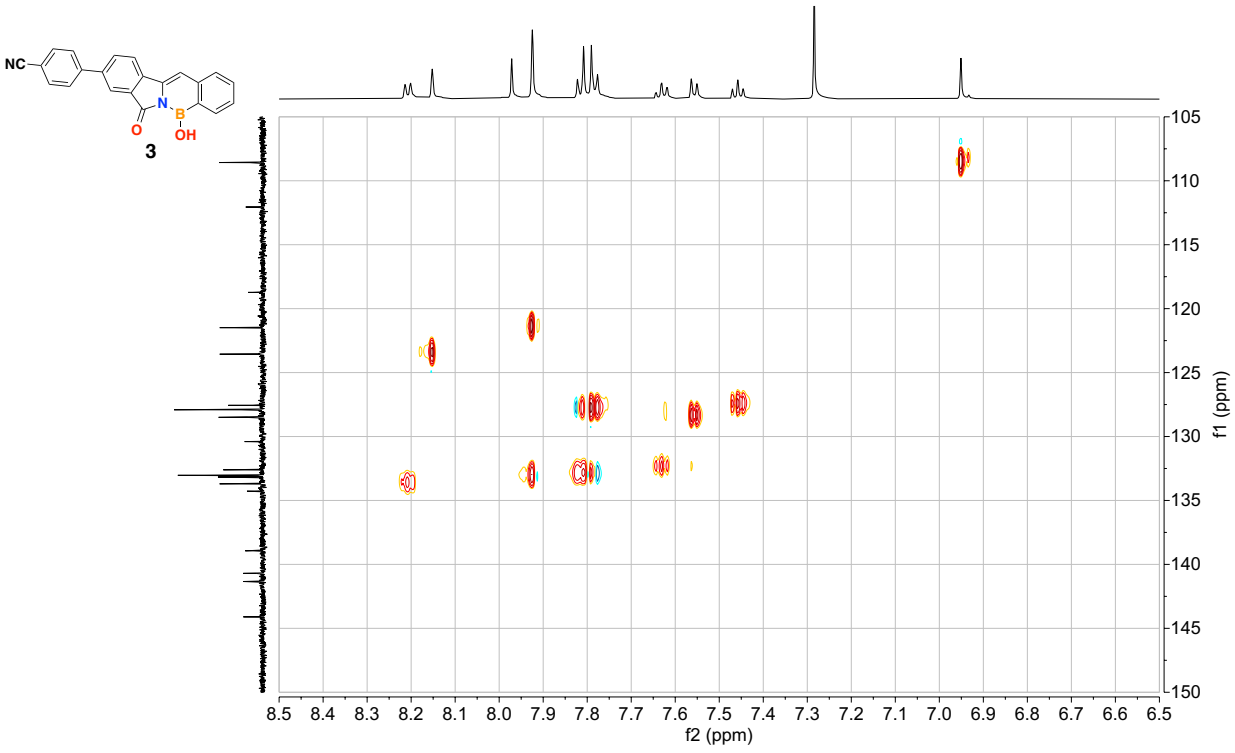

$^{13}C$ {$^{1}H$} NMR spectrum (100 MHz) of **3** in $CDCl_3$



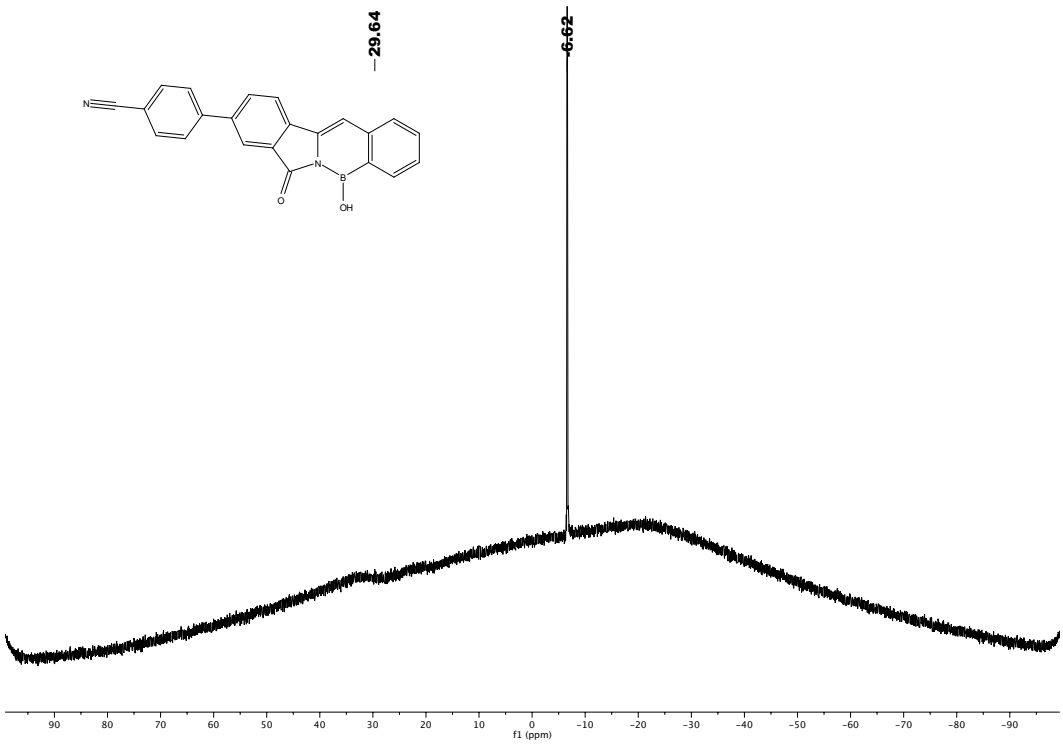

$^{1}H$-$^{1}H$ COSY spectra of **3** ($CDCl_3$)




HMBC NMR spectra of **3** ($CDCl_3$)

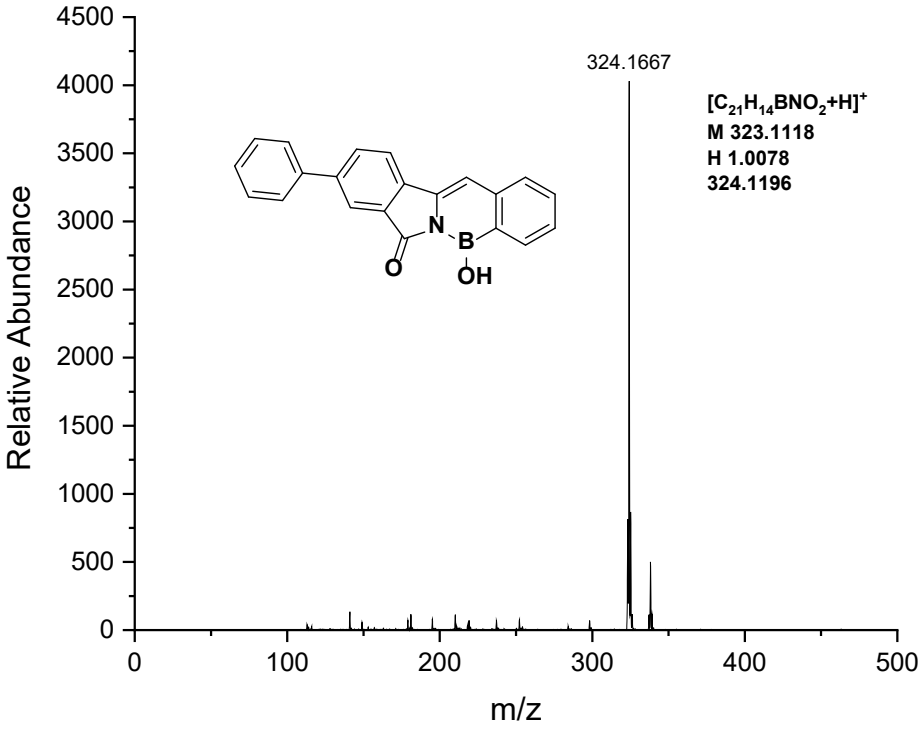



HSQC NMR spectra of **3** ($CDCl_3$)

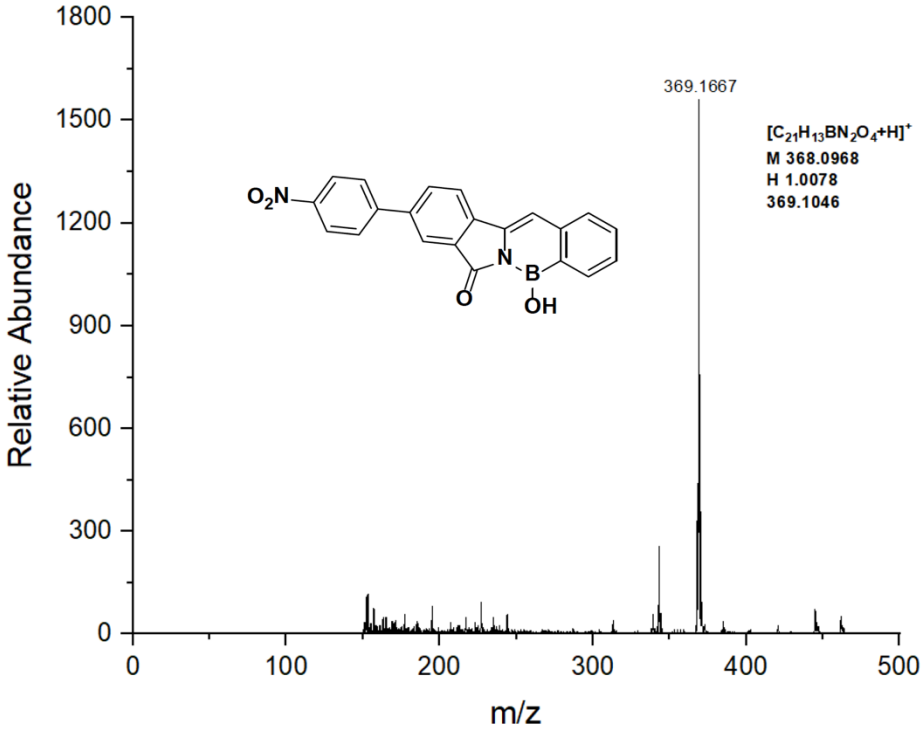



$^{11}B\{^{1}H\}$ NMR spectrum (128 MHz) of **3** in acetone $d_6$

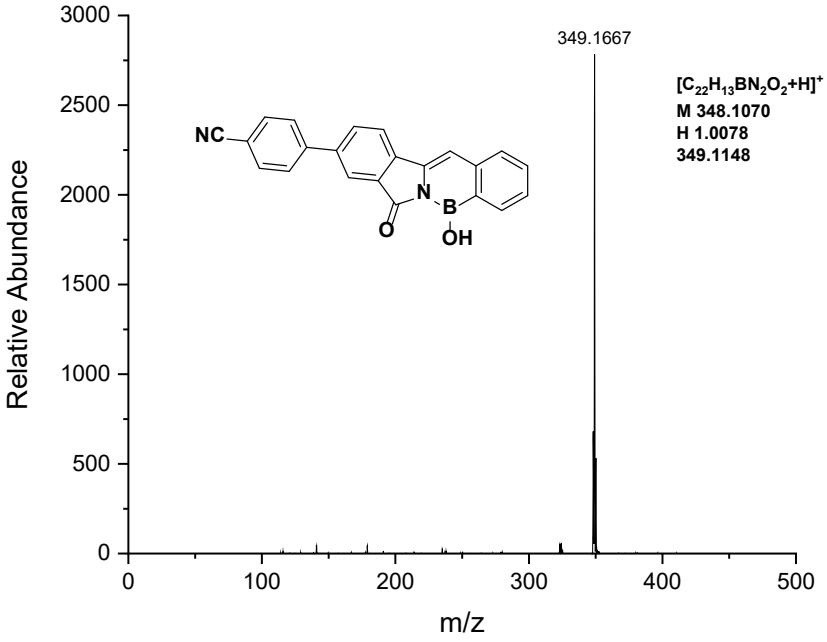
**HRMS**



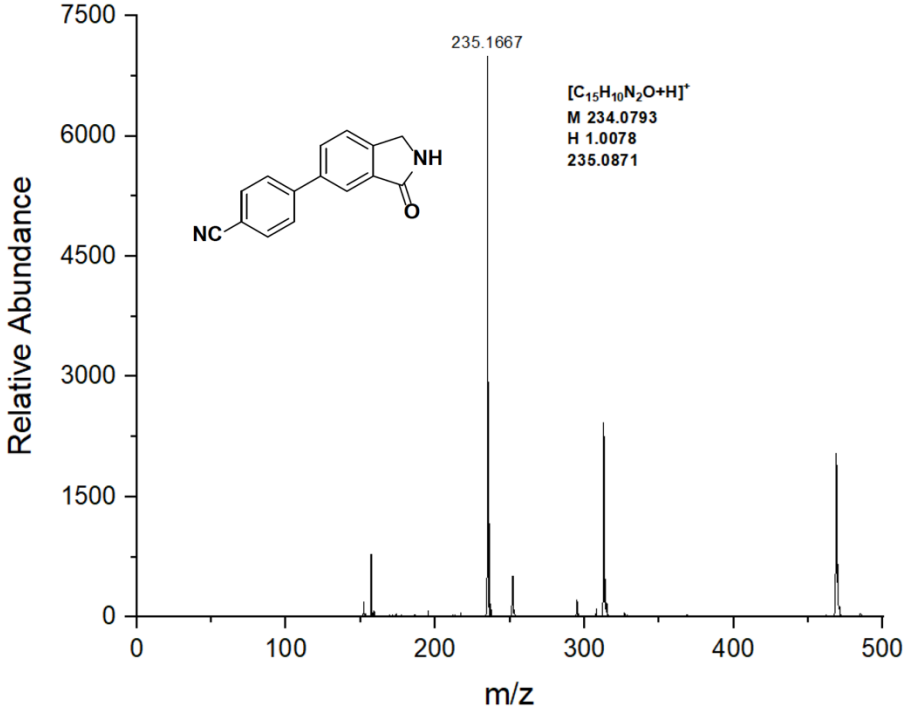

HRMS (ESI) of compound **1**



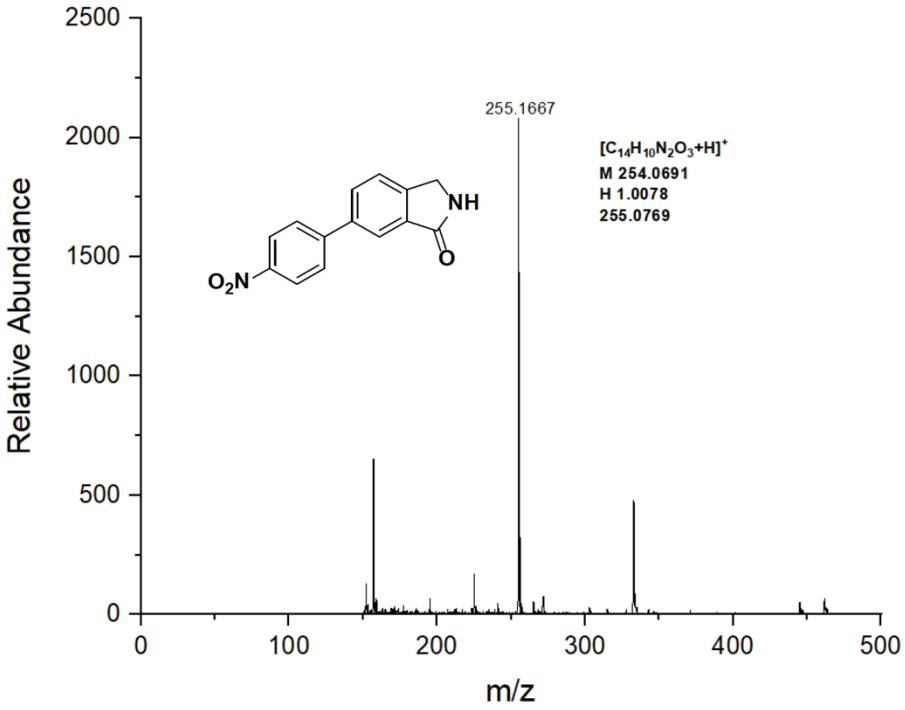

HRMS (DART) of compound **2**




HRMS (ESI) of compound **3**

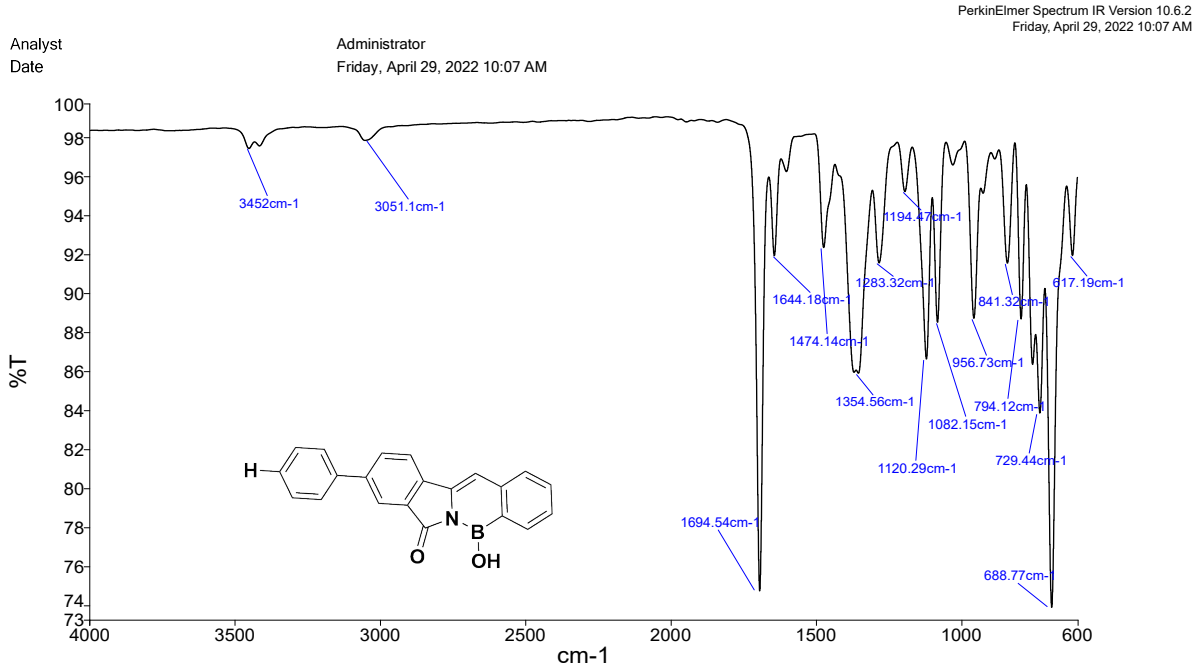



HRMS (DART) of compound **12**

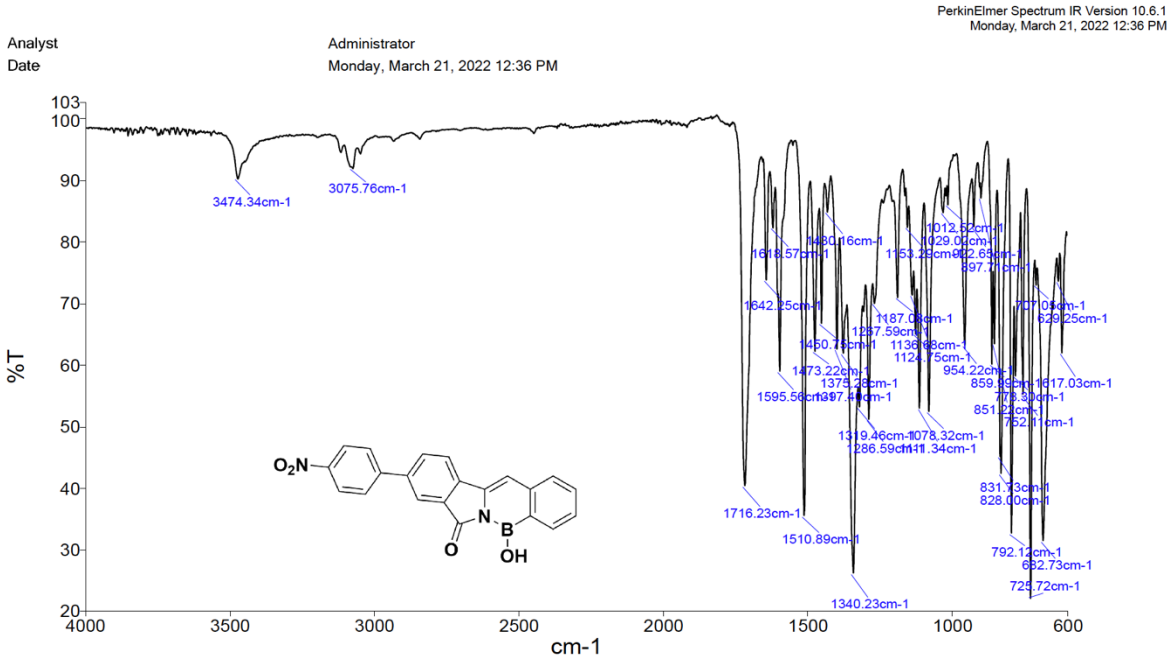



HRMS (DART) of compound **13**

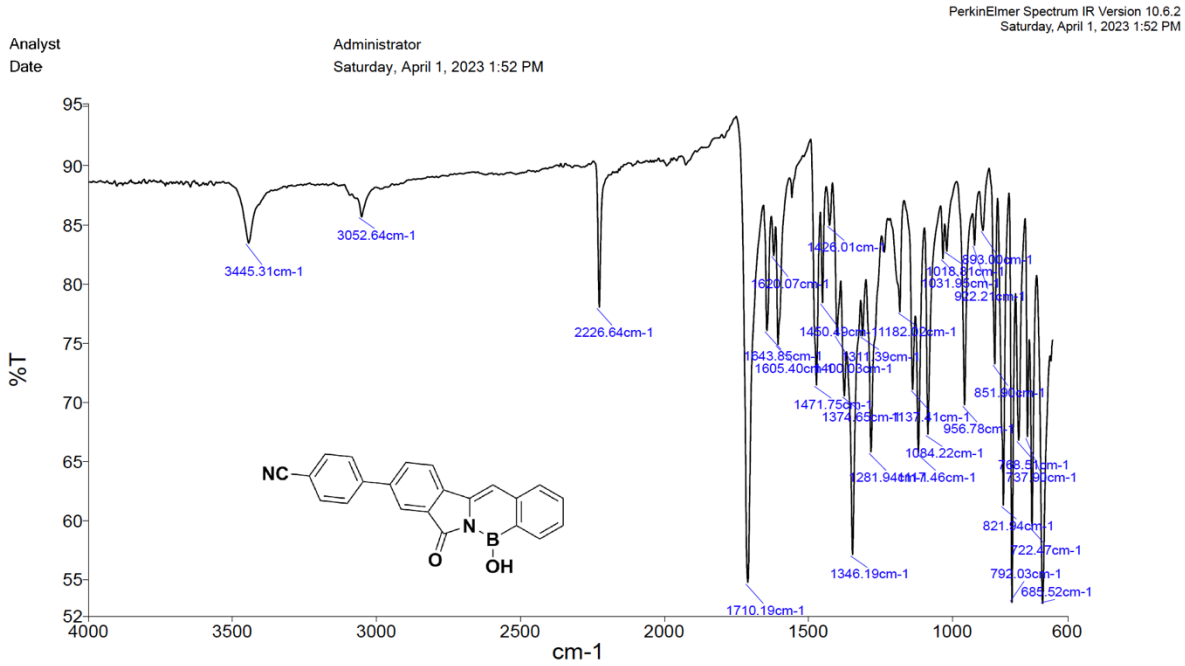
## FT-IR



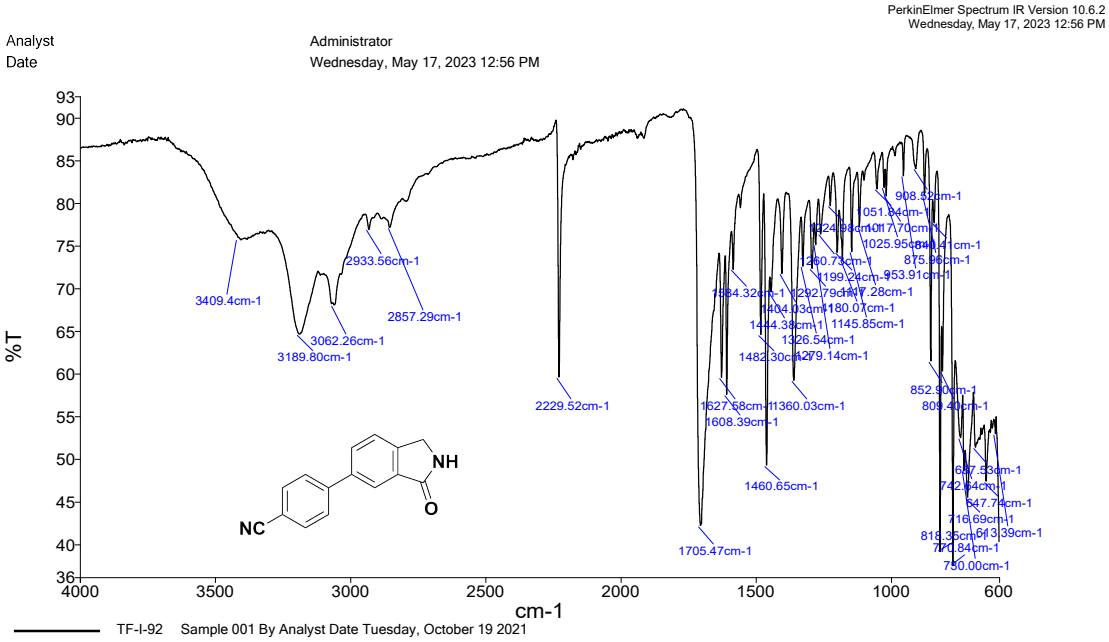

FTIR of compound **1**



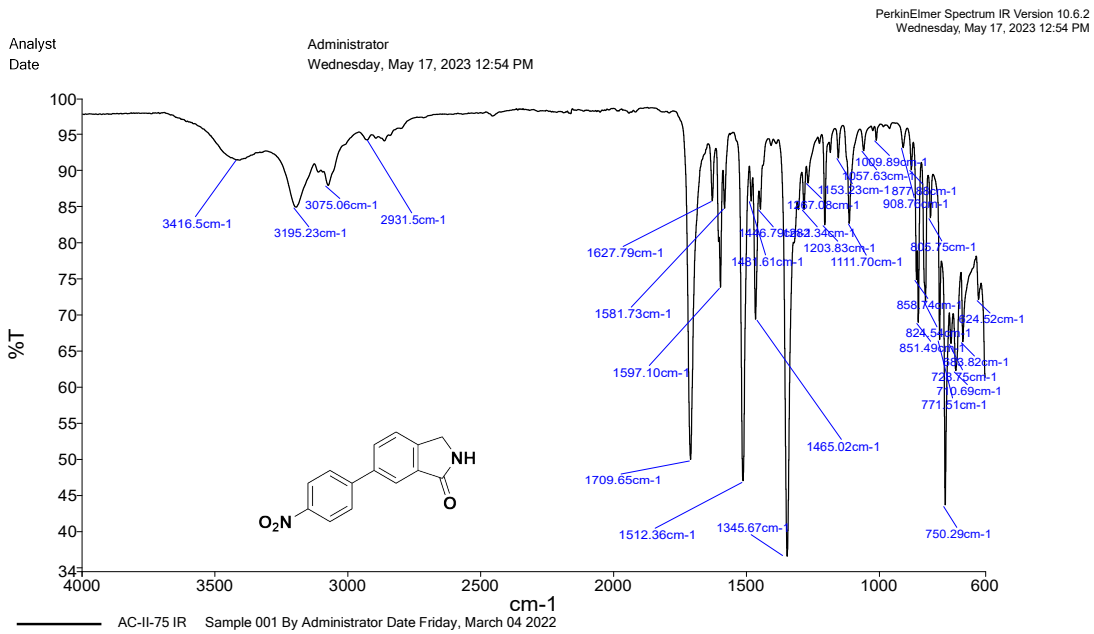

FTIR of compound **2**




FTIR of compound **3**

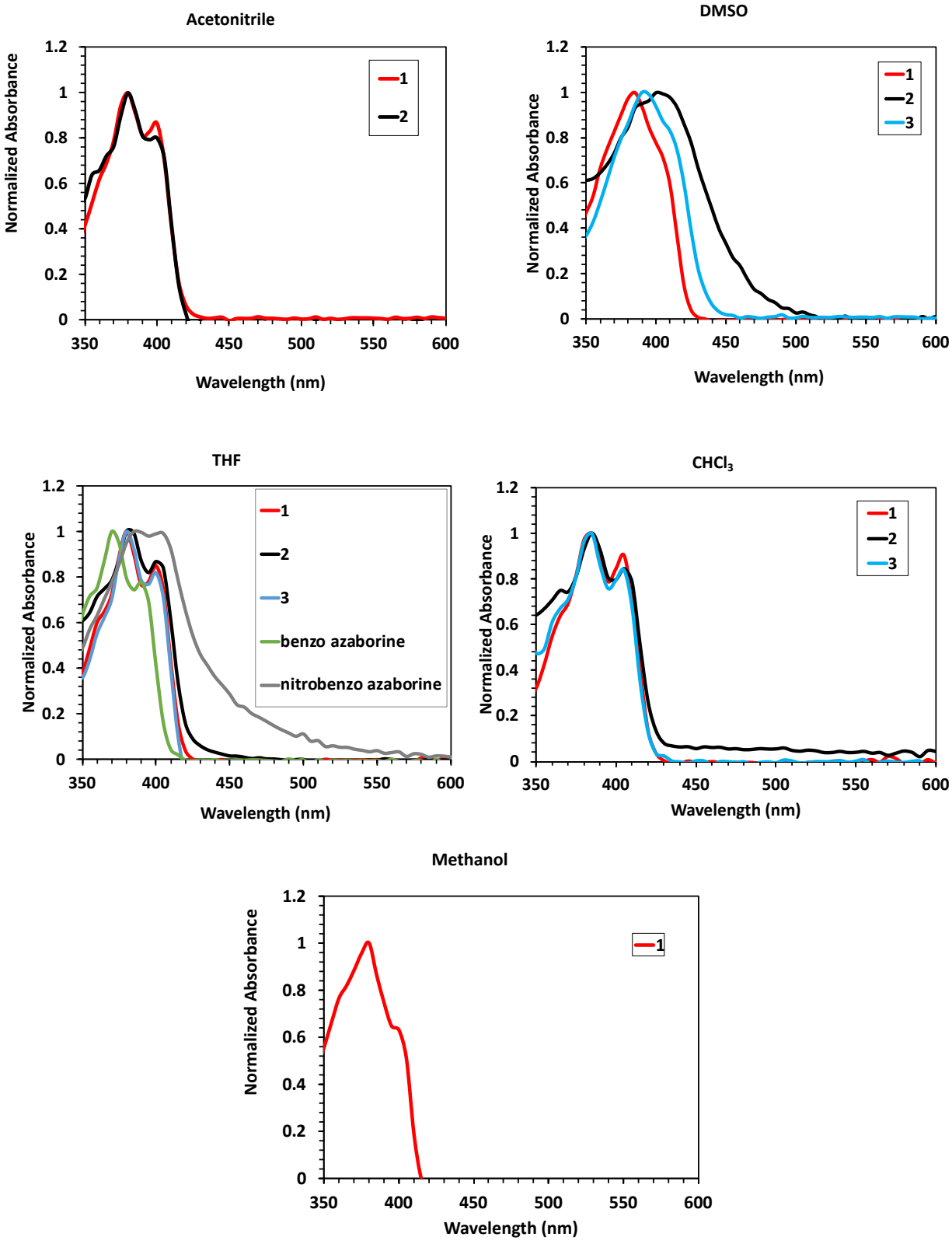



FTIR of compound **12**

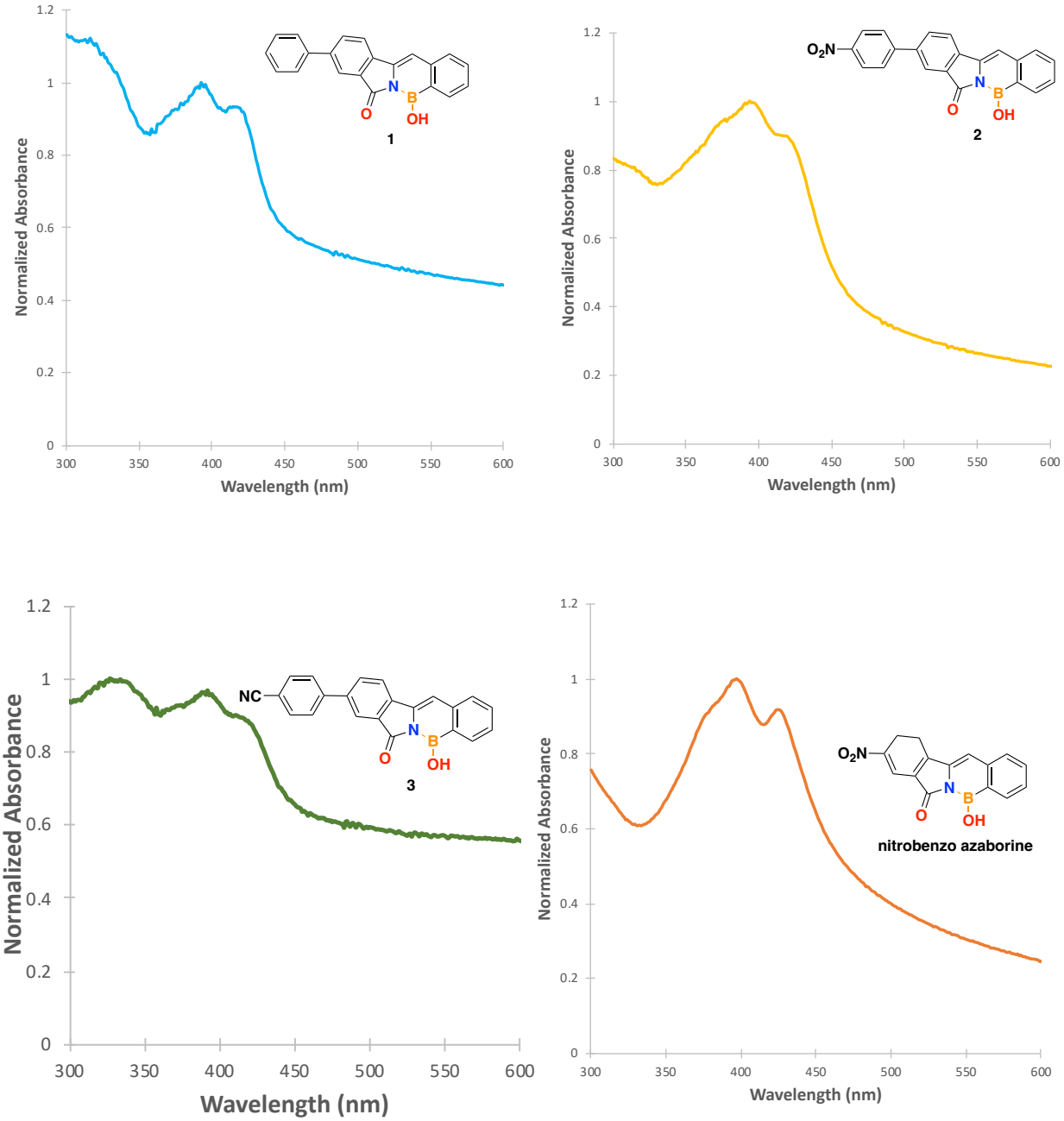



FTIR of compound **13**

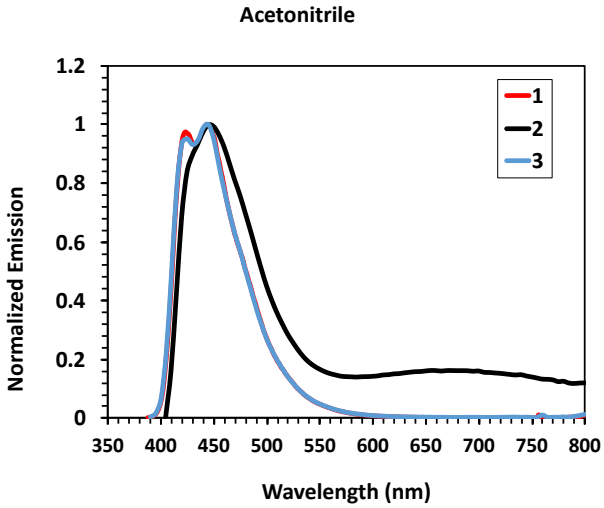
**Normalized UV-visible spectra of compounds 1-3 in acetonitrile, DMSO, THF, $CHCl_3$, and methanol**

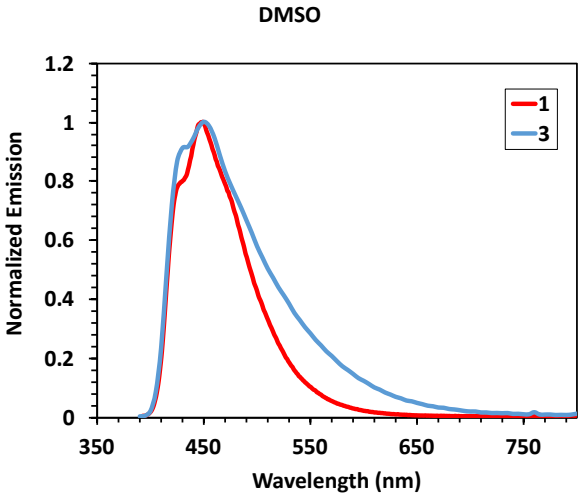


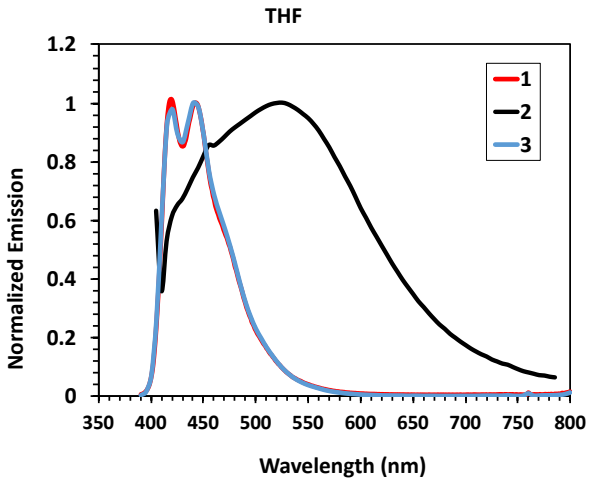
**Normalized solid-state excitation spectra of compounds 1-3, benzo- and nitrobenzo-azaborines**

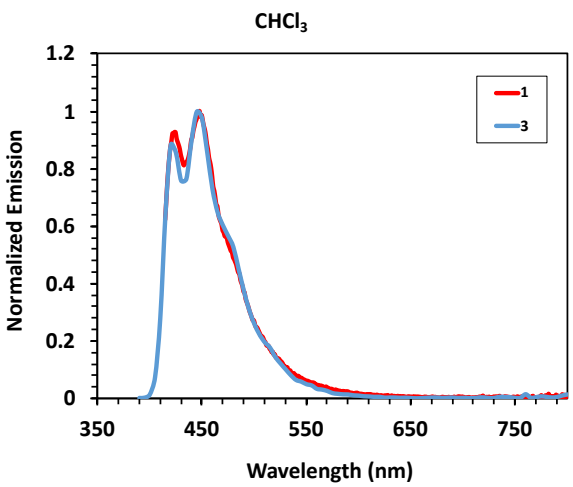


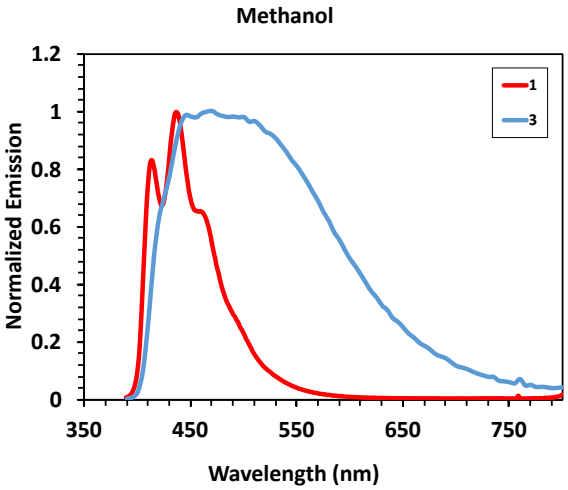
**Normalized emission spectra of compounds 1-3 in acetonitrile, DMSO, THF, $CHCl_3$, and methanol**



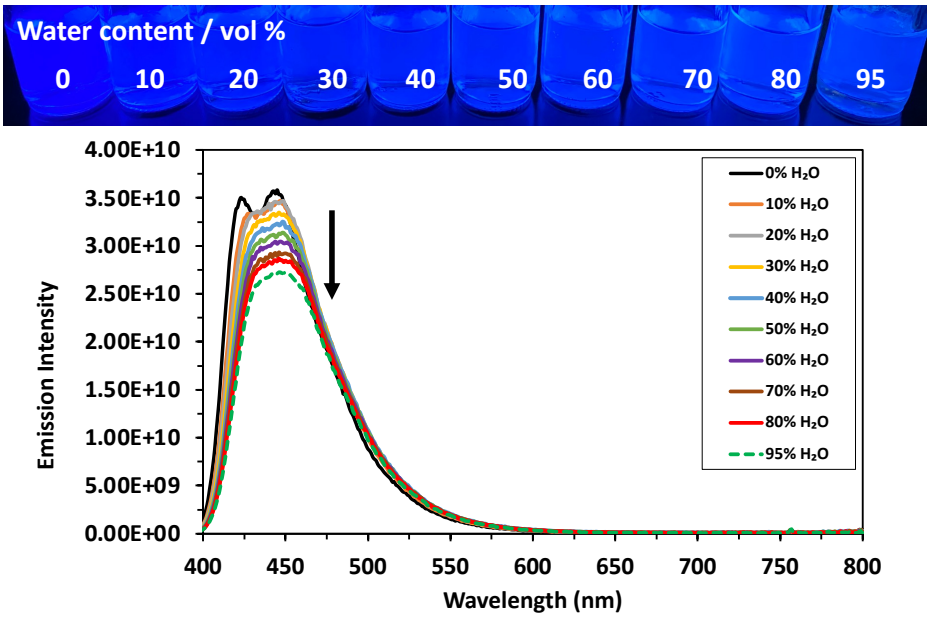



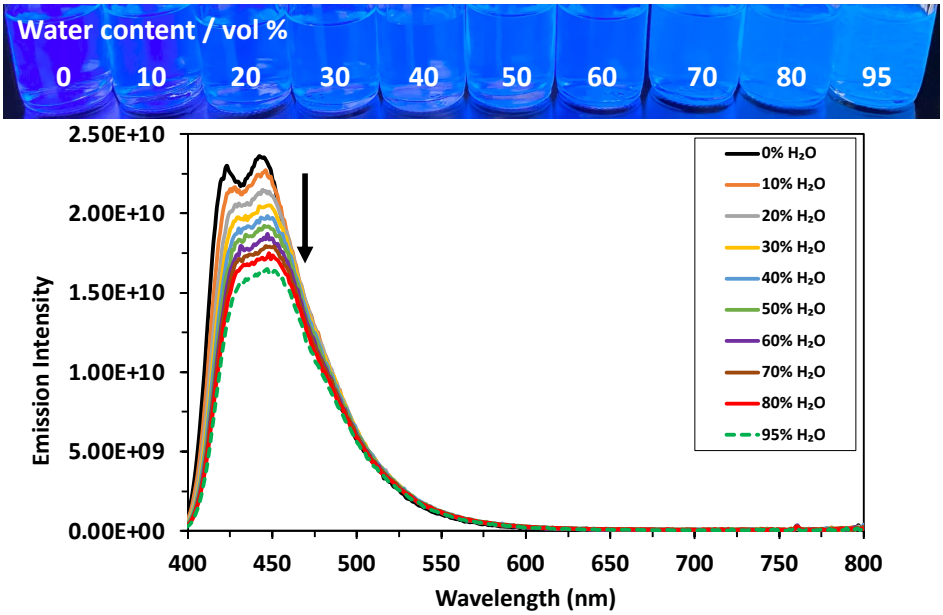



**AIE Experiment for PFAs 1 and 3**

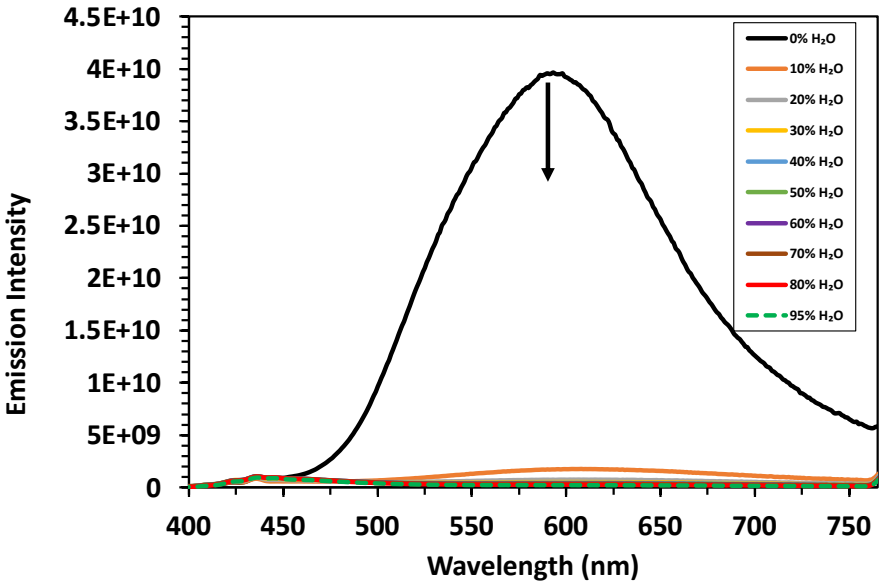



AIE experiment of **PFA 1** in acetonitrile/water, no evidence of AIE via J-aggregation for **PFA 1** was observed. As the $f_w$ of water is increased, the $\lambda_{max}$ at 443 nm stayed consistent. The decrease in emission intensity is due to the dilution of the sample as the volume fractions of water from $f_w$ = 0 to 0.95 at 0.10 increments is increased.

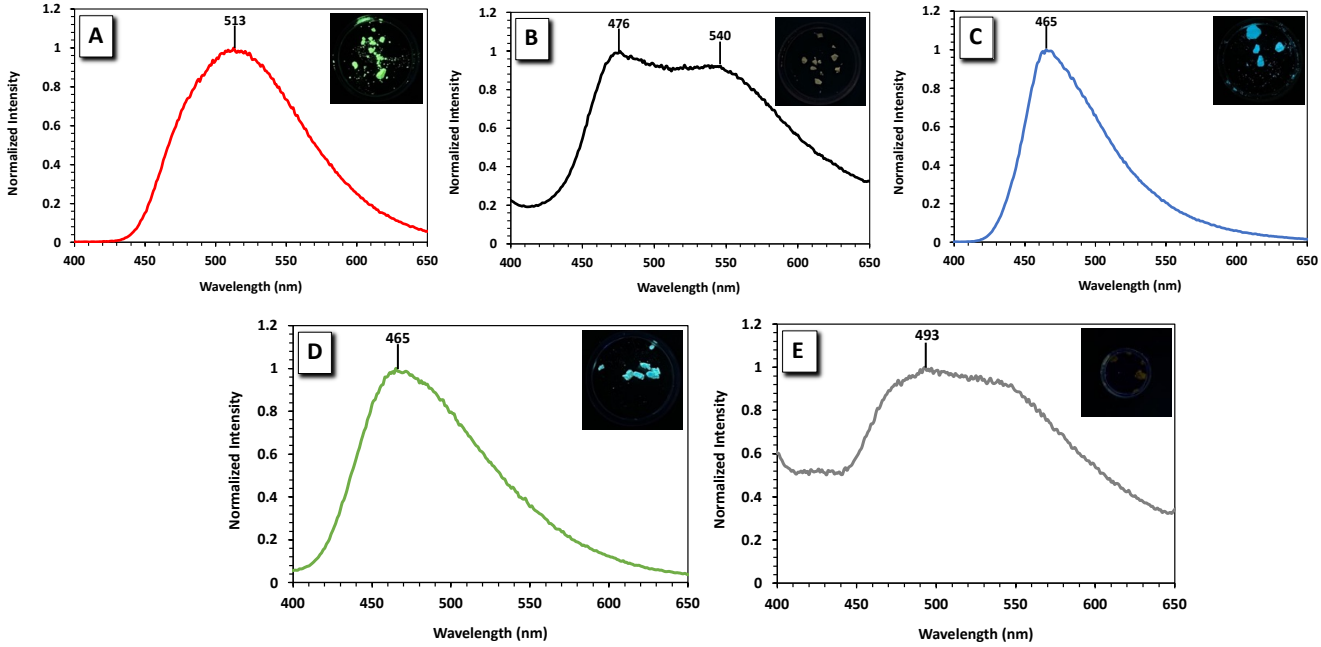



J-aggregation experiment of **PFA 3** in acetonitrile/water, no evidence of AIE via J-aggregation for **PFA 3** was observed. As the $f_w$ of water is increased, the $\lambda_{max}$ at 443 nm stayed consistent. The decrease in emission intensity is due to the dilution of the sample as the volume fractions of water from $f_w$ = 0 to 0.95 at 0.10 increments is increased.

**AIE Experiment for nitrobenzo-azaborine**



**Normalized solid-state emission spectra of 1(A), 2(B), 3(C), benzo-azaborine(D) and nitrobenzo-azaborine(E)**



## X-RAY CRYSTAL DATA FOR PFA 3

**Table S1**. Crystal data and structure refinement for **PFA 3**. CCDC:

| | |
|---|---|
| Empirical formula | $C_{22}H_{13}BN_2O_2$ |
| Formula weight | 348.15 |
| Temperature/K | 100.00(10) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 11.6124(5) |
| b/Å | 16.0428(7) |
| c/Å | 8.9292(3) |
| α/° | 90 |
| β/° | 99.327(4) |
| γ/° | 90 |
| Volume/Å$^3$ | 1641.48(12) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.409 |
| μ/mm$^{-1}$ | 0.727 |
| F(000) | 720.0 |
| Crystal size/mm$^3$ | 0.08 × 0.07 × 0.02 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 7.716 to 154.554 |
| Index ranges | -14 ≤ h ≤ 14, -19 ≤ k ≤ 17, -10 ≤ l ≤ 9 |
| Reflections collected | 9711 |
| Independent reflections | 3267 [$R_{int}$ = 0.0698, $R_{sigma}$ = 0.0730] |
| Data/restraints/parameters | 3267/0/245 |
| Goodness-of-fit on $F^2$ | 1.066 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0569, $wR_2$ = 0.1103 |
| Final R indexes [all data] | $R_1$ = 0.0976, $wR_2$ = 0.1297 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.24/-0.24 |

**Table S2**. Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for **PFA 3**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{IJ}$ tensor.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| O1 | 3695.0(16) | 4834.8(13) | 12570.3(19) | 31.7(5) |
| O2 | 2183.7(16) | 4748.9(12) | 9761(2) | 30.3(4) |
| N1 | 4037.7(18) | 4173.6(13) | 10212(2) | 24.9(5) |
| N004 | -1233(3) | 3656.4(17) | -1653(3) | 45.7(7) |
| C8 | 4759(2) | 3728.9(16) | 9363(3) | 24.0(5) |
| C9 | 4110(2) | 3645.4(16) | 7822(3) | 23.9(5) |
| C21 | 2975(2) | 4371.5(17) | 9298(3) | 24.8(6) |
| C20 | 3027(2) | 4035.9(16) | 7776(3) | 24.8(6) |
| C19 | 2217(2) | 4066.5(16) | 6461(3) | 25.5(6) |
| C18 | 903(2) | 4357.1(17) | 3292(3) | 26.8(6) |

| | | | | |
|---|---|---|---|---|
| C12 | 2482(2) | 3681.5(17) | 5154(3) | 26.8(6) |
| C1 | 5610(2) | 4050.8(17) | 12517(3) | 26.1(6) |
| C6 | 6273(2) | 3589.7(16) | 11593(3) | 24.7(5) |
| C13 | 1641(2) | 3678.6(17) | 3714(3) | 25.6(6) |
| C11 | 3575(2) | 3292.5(17) | 5224(3) | 28.0(6) |
| C7 | 5819(2) | 3452.6(17) | 10003(3) | 27.3(6) |
| C16 | 97(2) | 3670.1(17) | 968(3) | 26.6(6) |
| C17 | 146(2) | 4356.7(17) | 1931(3) | 28.4(6) |
| C10 | 4392(2) | 3268.1(17) | 6529(3) | 27.7(6) |
| C3 | 7154(2) | 3844.8(17) | 14664(3) | 30.4(6) |
| C5 | 7354(2) | 3262.0(18) | 12240(3) | 30.3(6) |
| C00M | -658(3) | 3670.5(19) | -485(3) | 33.4(6) |
| C14 | 1567(3) | 2995.5(18) | 2745(3) | 33.2(7) |
| C4 | 7791(2) | 3393.4(18) | 13752(3) | 32.1(6) |
| C2 | 6076(2) | 4168.9(18) | 14045(3) | 30.7(6) |
| C15 | 803(3) | 2986.7(18) | 1382(3) | 33.2(7) |
| B1 | 4398(3) | 4383(2) | 11794(3) | 26.3(6) |

**Table S3**. Anisotropic Displacement Parameters ($Å^2×10^3$) for **PFA 3.** The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{23}$** | **$U_{13}$** | **$U_{12}$** |
|---|---|---|---|---|---|---|
| O1 | 29.9(10) | 40.9(12) | 23.0(9) | -4.1(8) | 0.1(7) | 5.5(9) |
| O2 | 27.5(10) | 35.4(11) | 27.2(9) | -2.5(8) | 1.7(8) | 6.9(9) |
| N1 | 22.7(11) | 27.3(12) | 23.9(11) | -0.5(9) | 1.4(8) | 1.0(9) |
| N004 | 58.0(17) | 37.8(15) | 34.1(13) | 0.8(12) | -14.3(12). | -2.5(13) |
| C8 | 25.2(13) | 24.8(14) | 21.2(12) | 1.1(10) | 1.4(10) | 0.5(11) |
| C9 | 23.9(13) | 23.2(13) | 22.9(12) | 3.4(10) | -1.4(10) | -0.5(11) |
| C21 | 27.1(14) | 24.3(13) | 21.5(13) | 4.0(10) | -1.0(10) | 0.9(11) |
| C20 | 27.7(14) | 22.5(13) | 22.9(13) | 0.6(10) | 0.6(10) | -2.1(11) |
| C19 | 25.7(13) | 23.1(13) | 25.7(13) | 1.7(11) | -1.5(10) | 0.3(11) |
| C18 | 29.2(14) | 28.1(14) | 22.1(13) | -2.5(11) | 1.6(10) | 1.0(11) |
| C12 | 32.6(14) | 24.8(14) | 21.7(12) | 1.8(11) | 0.6(11) | 0.4(11) |
| C1 | 28.4(14) | 25.9(14) | 22.7(12) | 0.6(11) | 0.5(10) | -4.8(11) |
| C6 | 23.7(13) | 24.3(14) | 25.0(12) | 2.0(10) | 0.1(10) | -3.4(11) |
| C13 | 27.5(14) | 27.8(14) | 20.4(12) | 1.2(11) | 0.9(10) | 0.2(11) |
| C11 | 30.9(14) | 28.6(15) | 23.4(13) | -1.4(11) | 1.2(11) | 4.8(12) |
| C7 | 27.3(14) | 29.2(15) | 25.0(13) | 1.2(11) | 3.2(11) | -0.8(11) |
| C16 | 28.1(14) | 30.3(15) | 19.4(12) | 2.8(11) | -2.1(10) | -1.7(12) |
| C17 | 28.5(14) | 29.3(14) | 26.2(13) | 1.7(11) | 0.8(11) | 2.7(12) |
| C10 | 29.7(14) | 29.7(15) | 22.7(13) | 2.1(11) | 0.8(10) | 4.0(12) |
| C3 | 35.4(15) | 29.6(15) | 22.6(13) | 0.7(11) | -6.1(11) | -2.8(12) |
| C5 | 28.8(14) | 32.7(15) | 27.4(13) | 4.2(12) | -1.1(11) | 3.5(12) |
| C00M | 36.9(16) | 32.1(16) | 29.5(14) | -0.3(12) | -0.1(12) | -0.2(13) |
| C14 | 39.2(16) | 31.0(16) | 26.3(14) | -1.7(12) | -4.3(12) | 6.0(13) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C4 | 24.3(14) | 34.9(16) | 33.9(15) | 3.4(12) | -4.7(11) | -0.1(12) |
| C2 | 31.9(15) | 35.2(17) | 23.5(13) | 1.6(11) | -0.1(11) | -3.0(12) |
| C15 | 39.4(17) | 30.7(15) | 27.6(14) | -7.8(12) | -0.4(12) | 2.5(12) |
| B1 | 30.2(16) | 27.1(16) | 20.8(14) | -0.6(12) | 1.4(12) | -3.5(13) |

**Table S4**. Bond Lengths for **PFA 3.**

| Atom | Atom | Length/ Å | Atom | Atom | Length/ Å |
|---|---|---|---|---|---|
| O1 | B1 | 1.362(4) | C12 | C11 | 1.406(4) |
| O2 | C21 | 1.226(3) | C1 | C6 | 1.423(4) |
| N1 | C8 | 1.411(3) | C1 | C2 | 1.397(4) |
| N1 | C21 | 1.402(3) | C1 | B1 | 1.546(4) |
| N1 | B1 | 1.446(4) | C6 | C7 | 1.449(3) |
| N004 | C00M | 1.144(4) | C6 | C5 | 1.396(4) |
| C8 | C9 | 1.464(3) | C13 | C14 | 1.391(4) |
| C8 | C7 | 1.346(4) | C11 | C10 | 1.379(3) |
| C9 | C20 | 1.400(4) | C16 | C17 | 1.393(4) |
| C9 | C10 | 1.389(4) | C16 | C00M | 1.443(4) |
| C21 | C20 | 1.472(3) | C16 | C15 | 1.383(4) |
| C20 | C19 | 1.381(3) | C3 | C4 | 1.389(4) |
| C19 | C12 | 1.398(4) | C3 | C2 | 1.385(4) |
| C18 | C13 | 1.398(4) | C5 | C4 | 1.379(4) |
| C18 | C17 | 1.380(4) | C14 | C15 | 1.385(4) |
| C12 | C13 | 1.484(3) | | | |

**Table S5**. Bond Angles for **PFA 3**

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| C8 | N1 | B1 | 122.7(2) | C1 | C6 | C7 | 120.1(2) |
| C21 | N1 | C8 | 110.17(19) | C5 | C6 | C1 | 119.4(2) |
| C21 | N1 | B1 | 127.2(2) | C5 | C6 | C7 | 120.5(2) |
| N1 | C8 | C9 | 107.0(2) | C18 | C13 | C12 | 121.3(2) |
| C7 | C8 | N1 | 121.4(2) | C14 | C13 | C18 | 118.2(2) |
| C7 | C8 | C9 | 131.7(2) | C14 | C13 | C12 | 120.5(2) |
| C20 | C9 | C8 | 108.0(2) | C10 | C11 | C12 | 122.9(2) |
| C10 | C9 | C8 | 131.8(2) | C8 | C7 | C6 | 121.9(2) |
| C10 | C9 | C20 | 120.1(2) | C17 | C16 | C00M | 120.8(3) |
| O2 | C21 | N1 | 123.5(2) | C15 | C16 | C17 | 119.9(2) |
| O2 | C21 | C20 | 129.6(2) | C15 | C16 | C00M | 119.2(3) |
| N1 | C21 | C20 | 106.9(2) | C18 | C17 | C16 | 120.0(3) |
| C9 | C20 | C21 | 107.9(2) | C11 | C10 | C9 | 117.9(2) |
| C19 | C20 | C9 | 121.7(2) | C2 | C3 | C4 | 119.6(2) |
| C19 | C20 | C21 | 130.3(2) | C4 | C5 | C6 | 120.7(3) |
| C20 | C19 | C12 | 118.8(2) | N004 | C00M | C16 | 177.9(3) |
| C17 | C18 | C13 | 120.8(2) | C15 | C14 | C13 | 121.4(3) |
| C19 | C12 | C13 | 121.4(2) | C5 | C4 | C3 | 120.5(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C19 | C12 | C11 | 118.6(2) | C3 | C2 | C1 | 121.4(3) |
| C11 | C12 | C13 | 120.0(2) | C16 | C15 | C14 | 119.6(3) |
| C6 | C1 | B1 | 118.6(2) | O1 | B1 | N1 | 121.2(2) |
| C2 | C1 | C6 | 118.4(3) | O1 | B1 | C1 | 123.5(2) |
| C2 | C1 | B1 | 122.9(3) | N1 | B1 | C1 | 115.3(2) |

**Table S6**. Torsion Angles for **PFA 3.**

| **A** | **B** | **C** | **D** | **Angle/˚** | **A** | **B** | **C** | **D** | **Angle/˚** |
|---|---|---|---|---|---|---|---|---|---|
| O2 | C21 | C20 | C9 | -179.1(3) | C6 | C1 | B1 | O1 | -179.6(3) |
| O2 | C21 | C20 | C19 | 1.2(5) | C6 | C1 | B1 | N1 | 1.1(4) |
| N1 | C8 | C9 | C20 | 0.0(3) | C6 | C5 | C4 | C3 | 1.0(4) |
| N1 | C8 | C9 | C10 | -179.8(3) | C13 | C18 | C17 | C16 | 0.9(4) |
| N1 | C8 | C7 | C6 | 0.5(4) | C13 | C12 | C11 | C10 | -179.5(3) |
| N1 | C21 | C20 | C9 | 0.3(3) | C13 | C14 | C15 | C16 | 0.1(5) |
| N1 | C21 | C20 | C19 | -179.4(3) | C11 | C12 | C13 | C18 | -145.0(3) |
| C8 | N1 | C21 | O2 | 179.1(3) | C11 | C12 | C13 | C14 | 34.9(4) |
| C8 | N1 | C21 | C20 | -0.3(3) | C7 | C8 | C9 | C20 | 178.5(3) |
| C8 | N1 | B1 | O1 | 178.0(2) | C7 | C8 | C9 | C10 | -1.3(5) |
| C8 | N1 | B1 | C1 | -2.7(4) | C7 | C6 | C5 | C4 | 179.8(3) |
| C8 | C9 | C20 | C21 | -0.2(3) | C17 | C18 | C13 | C12 | 178.2(3) |
| C8 | C9 | C20 | C19 | 179.5(2) | C17 | C18 | C13 | C14 | -1.7(4) |
| C8 | C9 | C10 | C11 | 179.7(3) | C17 | C16 | C15 | C14 | -0.9(4) |
| C9 | C8 | C7 | C6 | -177.9(3) | C10 | C9 | C20 | C21 | 179.7(2) |
| C9 | C20 | C19 | C12 | 1.3(4) | C10 | C9 | C20 | C19 | -0.6(4) |
| C21 | N1 | C8 | C9 | 0.2(3) | C5 | C6 | C7 | C8 | 177.0(3) |
| C21 | N1 | C8 | C7 | -178.5(2) | C00M | C16 | C17 | C18 | -177.7(3) |
| C21 | N1 | B1 | O1 | -1.4(4) | C00M | C16 | C15 | C14 | 177.3(3) |
| C21 | N1 | B1 | C1 | 177.9(2) | C4 | C3 | C2 | C1 | 0.1(4) |
| C21 | C20 | C19 | C12 | -179.1(3) | C2 | C1 | C6 | C7 | 179.9(3) |
| C20 | C9 | C10 | C11 | -0.1(4) | C2 | C1 | C6 | C5 | 0.8(4) |
| C20 | C19 | C12 | C13 | 178.8(2) | C2 | C1 | B1 | O1 | 1.7(4) |
| C20 | C19 | C12 | C11 | -1.2(4) | C2 | C1 | B1 | N1 | -177.6(3) |
| C19 | C12 | C13 | C18 | 34.9(4) | C2 | C3 | C4 | C5 | -0.4(4) |
| C19 | C12 | C13 | C14 | -145.2(3) | C15 | C16 | C17 | C18 | 0.4(4) |
| C19 | C12 | C11 | C10 | 0.6(4) | B1 | N1 | C8 | C9 | -179.3(2) |
| C18 | C13 | C14 | C15 | 1.2(4) | B1 | N1 | C8 | C7 | 2.0(4) |
| C12 | C13 | C14 | C15 | -178.7(3) | B1 | N1 | C21 | O2 | -1.4(4) |
| C12 | C11 | C10 | C9 | 0.1(4) | B1 | N1 | C21 | C20 | 179.2(2) |
| C1 | C6 | C7 | C8 | -2.0(4) | B1 | C1 | C6 | C7 | 1.1(4) |
| C1 | C6 | C5 | C4 | -1.2(4) | B1 | C1 | C6 | C5 | -177.9(3) |
| C6 | C1 | C2 | C3 | -0.3(4) | B1 | C1 | C2 | C3 | 178.4(3) |

**Table S7**. Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å$^2$×$10^3$) for **PFA 3.**

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H1 | 3057.6 | 4930.39 | 12004.29 | 48 |
| H19 | 1492.57 | 4344.01 | 6445.67 | 31 |
| H18 | 924.09 | 4823.97 | 3950.38 | 32 |
| H11 | 3758.1 | 3035.28 | 4333.42 | 34 |
| H7 | 6283.52 | 3159.2 | 9394.23 | 33 |
| H17 | -341.77 | 4824.96 | 1650.52 | 34 |
| H10 | 5124.68 | 3001.75 | 6542.77 | 33 |
| H3 | 7455.91 | 3930.52 | 15706.11 | 36 |
| H5 | 7792.47 | 2944.99 | 11631.92 | 36 |
| H14 | 2051.12 | 2524.82 | 3023.37 | 40 |
| H4 | 8532.64 | 3173.77 | 14172.2 | 39 |
| H2 | 5645.07 | 4478.2 | 14672.93 | 37 |
| H15 | 764.39 | 2513.84 | 735.73 | 40 |

**References:**


1 C. J. Saint-Louis, R. N. Shavnore, C. D. C. McClinton, J. A. Wilson, L. L. Magill, B. M. Brown, R. W. Lamb, C. E. Webster, A. K. Schrock and M. T. Huggins, *Org. Biomol. Chem.*, 2017, **15**, 10172–10183.

2 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100.

3 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.

4 T. Yanai, D. P. Tew and N. C. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51-57.

5 T. N. Truong and E. V Stefanovich, *Chem. Phys. Lett.*, 1995, **240**, 253–260.

6 V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995–2001.

7 M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.*, 2003, **24**, 669–681.

8 P. Winget, D. M. Dolney, D. J. Giesen, C. J. Cramer and D. G. Truhlar, *Minnesota Solvent Descriptor Database version 1999*, 1999.

9 S. Hirata and M. Head-Gordon, *Chem. Phys. Lett.*, 1999, **314**, 291–299.

10 M. Cossi and V. Barone, *J. Chem. Phys.*, 2001, **115**, 4708–4717.

11 R. L. Martin, *J. Chem. Phys.*, 2003, **118**, 4775–4777.

12 E. Epifanovsky, A. T. B. Gilbert, X. Feng, J. Lee, Y. Mao, N. Mardirossian, P. Pokhilko, A. F. White, M. P. Coons, A. L. Dempwolff, Z. Gan, D. Hait, and P. R. Horn, *J. Chem. Phys.*, 2021, **155**, 84801.