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Supplementary Information

Ligand Protonation Leads to Highly Fluorescent Boronium Cations

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Experimental Details

General Considerations. Solvents were purchased from Caledon Laboratories, dried using an Innovative Technologies Inc. solvent purification system, collected under vacuum, and stored under an N_2 atmosphere over 3 or 4 Å molecular sieves. Solvents used for UV-vis spectroscopy were distilled over CaH_2 and subjected to three freeze-pump-thaw cycles. Reagents were purchased from commercial sources and used as received unless otherwise stated. 2-(methylamino)benzohydrazide was prepared according to a published procedure.[1] NMR spectra were recorded at 25 °C on a Bruker Avance III HD 400 MHz spectrometer (^{1}H: 400 MHz, ^{11}B: 128 MHz, ^{13}C: 101 MHz, ^{19}F: 376 MHz) or a Bruker Neo 600 MHz spectrometer (^{1}H: 600 MHz, ^{11}B: 193 MHz, ^{13}C: 151 MHz, ^{19}F: 565 MHz) at 25 °C. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to tetramethylsilane at 0 ppm. ^{11}B NMR spectra were referenced to BF_3•OEt_2 at 0 ppm. ^{19}F NMR spectra were referenced to $CFCl_3$ at 0 ppm. Mass spectrometry data were recorded using a Bruker microTOF II electrospray ionization spectrometer. FT-IR spectra were recorded on a PerkinElmer Spectrum Two instrument using an attenuated total reflectance accessory.

Electronic Spectroscopy Methods. UV-vis absorption spectra were recorded on a Cary 5000 UV-Vis-NIR spectrophotometer or Cary 60 UV-vis spectrophotometer. Molar extinction coefficients were determined from the slope of a plot of absorbance against concentration using four solutions of known concentrations ranging from 10 to 40 μM. Emission spectra were obtained using a Photon Technology International (PTI) QM-4 SE spectrofluorometer. Absolute quantum yields were measured using a Hamamatsu C11347–11 Quantaurus Absolute PL Quantum Yield Spectrometer. Dilute solutions of analyte were irradiated using a UVGL-25 Compact UV Lamp (254 nm, 4 W).

Electrochemical Methods. Cyclic voltammetry experiments were performed with a Bioanalytical Systems Inc. (BASi) Epsilon potentiostat and analyzed using BASi Epsilon software. Electrochemical cells consisted of a three-electrode setup including a glassy carbon working electrode, a platinum wire counter electrode, and a silver wire *pseudo* reference electrode. Experiments were run at scan rates of 250 mV s^{-1} in dry, degassed solutions of CH_2Cl_2, the analyte (~1 mM), and supporting electrolyte (0.1 M [nBu$_4$N][PF$_6$]). Cyclic voltammograms were internally referenced against the ferrocene/ferrocenium redox couple (~1 mM internal standard) and corrected for internal cell resistance using the BASi Epsilon software.

Computational Methods. Electronic structure calculations were performed using the Gaussian 16 software package[2] on a local machine or through the Graham cluster of Compute Canada. Calculations were performed using the ωB97XD functional (ω=0.14), def2-SVP basis set.[3,4] Ground-state geometries were modelled using structure coordinates determined using X-ray crystallography as starting points, were modified as necessary, and optimized. All optimized structures were confirmed to be at an energetic minima through vibrational analysis. All TDDFT calculations were performed using non-equilibrium solvation models (CH_2Cl_2). Natural bond order and natural population analysis calculations were performed using NBO6.[5]

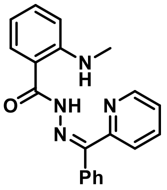
X-ray Crystallography Methods. Single crystals suitable for X-ray diffraction were grown through the slow evaporation of an acetonitrile solution (**3**) or the slow diffusion of pentane into a CH_2Cl_2 solution (**3·HCl**). Samples were mounted on a MiTeGen polyimide micromount with a small amount of Paratone-N oil. All X-ray measurements were made on a Bruker Kappa Axis Apex2 diffractometer at a temperature of 110 K. The data collection strategy was a number of ω and φ scans which collected data up to 64.186° for **3** and 74.146° for **3·HCl**. The frame integration was performed using SAINT.[6] The resulting raw data were scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.[7] The structures were solved by using a dual space methodology using the SHELXT program.[8] All non-hydrogen atoms were obtained from the initial solution. All hydrogen atoms were introduced at idealized positions and were allowed to refine isotropically. The structural models were fit to the data using full matrix least-squares based on F^2. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. Compound **3·HCl** exhibited twinning by inversion. A Flack parameter of 0.486(7) for **3·HCl** was calculated using Parsons' quotients.[9] All structures were refined using the SHELXL program from the SHELX suite of crystallographic software.[10] Graphic plots were produced using the Mercury program.[11] See Table S1 and CCDC 2376336 (compound **3**) and 2376337 (compound **3·HCl**) for additional information.

Table S1 X-ray diffraction data collection and refinement details for compounds **3** and **3·HCl**.

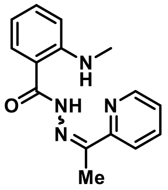
	3	**3·HCl**
Formula	$C_{28}H_{27}BN_4O_2$	$C_{34}H_{32}BCl_3N_4O$
Formula Weight (g/mol)	462.34	629.79
Crystal Dimensions (mm)	0.366 × 0.191 × 0.117	0.474 × 0.251 × 0.234
Crystal Color and Habit	red prism	green prism
Crystal System	monoclinic	orthorhombic
Space Group	$P\ 2_1/n$	$P\ 2_1\ 2_1\ 2_1$
Temperature (K)	110	110
a (Å)	10.156(3)	9.673(4)
b (Å)	21.597(7)	16.008(8)
c (Å)	10.710(3)	20.119(9)
α (°)	90	90
β (°)	94.847(15)	90
γ (°)	90	90
V ($Å^3$)	2340.7(13)	3115(2)
Z	4	4
F(000)	976	1312
ρ (g/cm)	1.312	1.343
λ, MoKα (Å)	0.71073	0.71073
μ, (cm^{-1})	0.084	0.329
Max 2θ for data collection (°)	64.186	74.146
Measured fraction of data	1.000	0.999
Number of reflections measured	85878	309951
Number of unique reflections measured	8169	15928
R_{merge}	0.0738	0.0600
Number of reflections included in refinement	8169	15928
Number of parameters in least-squares	424	516
R_1, wR_2	0.0500, 0.1210	0.0331, 0.0819
R_1, wR_2 (all data)	0.0824, 0.1403	0.0407, 0.0862
GOF	1.023	1.024
Min & Max peak heights on final DF Map (e^-/Å)	−0.299, 0.578	−0.309, 0.409

Where: $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma F_o wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(wF_o^4)]^{½}$. GOF = $[\Sigma(wF_o^2 - F_c^2)^2) / (\text{no. of reflns.} - \text{no. of params})]^{½}$

Synthesis and Characterization



Synthesis of hydrazone 1. In air, 2-benzoylpyridine (3.00 g, 16.4 mmol), 2-(methylamino)benzohydrazide (2.71 g, 16.4 mmol), and 1 mL of glacial acetic acid were dissolved in absolute ethanol (150 mL) and heated at reflux for 4 h. The yellow-orange reaction mixture was concentrated to approximately half its volume and was cooled to −20 °C, resulting in the formation of yellow crystals. These yellow crystals were collected in multiple crops via vacuum filtration and were washed with cold EtOH. This hydrazone was isolated as the *Z*-isomer. Yield: 4.48 g (83%). Mp (°C): 186−187. ^{1}H NMR (400 MHz, CDCl$_3$): δ 14.91 (br s, 1H, N*H*), 8.81 (ddd, $^{3}J_{HH}$ = 4.7 Hz, $^{4}J_{HH}$ = 1.8, 1.1 Hz, 1H, aryl C*H*), 7.81 (td, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 1.9 Hz, 1H, aryl C*H*), 7.91 (br s, 1H, N*H*) 7.64–7.58 (m, 3H, aryl C*H*), 7.42–7.35 (m, 6H, aryl C*H*), 6.71 (dd, $^{3}J_{HH}$ = 8.6 Hz, $^{4}J_{HH}$ = 1.1 Hz, 1H, aryl C*H*), 6.66 (ddd, $^{3}J_{HH}$ = 8.1, 7.1 Hz, $^{4}J_{HH}$ = 1.1 Hz, 1H, aryl C*H*), 2.89 (d, $^{3}J_{HH}$ = 5.1 Hz, 3H, NC*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 167.1, 153.3, 151.9, 148.0, 147.1, 138.1, 137.6, 133.5, 129.5, 129.1, 128.5, 127.8, 126.7, 124.1, 114.4, 113.5, 111.4, 29.8. FT-IR ATR (cm^{-1}): 3362 (m), 2899 (w), 1652 (m), 1571 (s), 1520 (s), 1404 (s), 1226 (s), 1110 (s), 891 (m), 775 (m), 660 (s), 692 (s), 649 (s). Mass Spec. (ESI, positive mode): exact mass calculated for $[C_{20}H_{18}N_4NaO]^+$, $[M+Na]^+$: 353.1373; exact mass found: 353.1388.



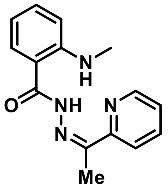
Synthesis of hydrazone 2. In air, 2-acetylpyridine (2.20 g, 18.2 mmol), 2-(methylamino)benzohydrazide (3.00 g, 18.2 mmol), and 0.7 mL of acetic acid were dissolved in absolute ethanol (50 mL) and heated at reflux for 4 h. The yellow-orange reaction mixture was concentrated to approximately half its volume and was cooled to −20 °C, resulting in the formation of pale-yellow crystals. These pale-yellow crystals were collected in multiple crops via vacuum filtration and were washed with cold EtOH. Yield: 4.18 g (86%).

This product was isolated as an approximately 1:1 mixture of *E* and *Z* isomers and was used as such in subsequent reactions. Unlike other examples of 2-pyridylhydrazones,[12] the isomers of hydrazone **2** co-eluted and could not be separated using column chromatography. Slow evaporation of a methanol solution of hydrazone **2** afforded yellow crystals as prisms or needles. When analyzed by NMR spectroscopy, the ^{1}H NMR spectrum of the prisms was consistent with the isolated *Z* isomer (evident by the extreme downfield signal of the intramolecularly bonded NH;

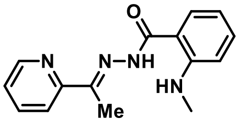
Fig. S5) and the ^{1}H NMR spectrum of the needles was consistent with the isolated *E* isomer (Fig. S7). The combination of the ^{1}H or ^{13}C{^{1}H} NMR spectra of both individual isomers **2-*Z*** and **2-*E*** were consistent with the respective ^{1}H NMR or ^{13}C{^{1}H} spectrum of the isolated bulk material of hydrazone **2**.

Hydrazone 2 (bulk material – mixture of **2-*Z*** and **2-*E***). Mp (°C): 168−170. ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.62 (br s, 1H, N*H*), 9.01 (br s, 1H, N*H*), 8.72 (ddd, $^{3}J_{HH}$ = 4.9 Hz, $^{4}J_{HH}$ = 1.9, 0.9 Hz, 1H, aryl C*H*), 8.59 (ddd, $^{3}J_{HH}$ = 4.9 Hz, $^{4}J_{HH}$ = 1.8, 1.0 Hz, 1H, aryl C*H*), 8.28 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H, aryl C*H*), 7.91 (td, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 1.9 Hz, 1H, aryl C*H*), 7.72 (td, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.8 Hz, 1H, aryl C*H*), 7.61 (ddd, $^{3}J_{HH}$ = 8.0, 7.0 Hz, $^{4}J_{HH}$ = 1.3 Hz, 2H, aryl C*H*), 7.50 (d, $^{3}J_{HH}$ = 7.9 Hz, 1H, aryl C*H*), 7.41–7.34 (m, 3H, aryl C*H*), 7.29–7.27 (m, 2H, aryl C*H*), 6.72 (ddd, $^{3}J_{HH}$ = 7.9, 6.5 Hz, $^{4}J_{HH}$ = 1.1 Hz, 2H, aryl C*H*), 6.65 (ddt, $^{3}J_{HH}$ = 8.8, 7.3 Hz, $^{4}J_{HH}$ = 1.3 Hz, 2H, aryl C*H*), 2.90 (s, 3H, NCH_3), 2.89 (s, 3H, NCH_3), 2.54 (s, 3H, -CH_3), 2.48 (s, 3H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 153.6, 151.8, 151.3, 148.5, 147.5, 142.4, 138.0, 136.5, 133.8, 133.3, 127.8, 124.13, 124.09, 124.0, 121.3, 114.7, 114.4, 113.7, 113.4, 111.5, 111.3, 29.9, 29.8, 22.8, 11.1. FT-IR ATR (cm^{-1}): 3399 (w), 3245 (w), 3002 (w), 2815 (w), 1635 (s), 1520 (s), 1437 (m), 1244 (s), 1151 (m), 900 (m), 788 (s), 741 (s), 605 (m), 565 (m). Mass Spec. (ESI, positive mode): exact mass calculated for $[C_{15}H_{16}N_4NaO]^+$, $[M+Na]^+$: 291.1216; exact mass found: 291.1248.

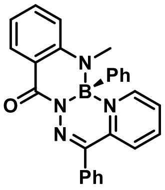
Hydrazone 2-*Z* (*Z*-isomer): ^{1}H NMR (400 MHz, $CDCl_3$) 15.62 (s, 1H, N*H*), 8.72 (dd, $^{3}J_{HH}$ = 4.9 Hz, $^{4}J_{HH}$ = 1.0 Hz, 1H, aryl C*H*), 7.91 (td, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 1.9 Hz, 2H, aryl C*H*), 7.61 (td, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 1.3 Hz, 2H, aryl C*H*), 7.45–7.31 (m, 2H, aryl C*H* and N*H*), 6.70 (d, $^{3}J_{HH}$ = 8.5 Hz, 1H, aryl C*H*), 6.65 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H, aryl C*H*), 2.90 (s, 3H, NCH_3), 2.54 (s, 3H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 153.6, 151.8, 147.5, 142.4, 138.0, 133.3, 127.8, 124.2, 124.0, 114.4, 113.7, 111.3, 29.8, 22.8.



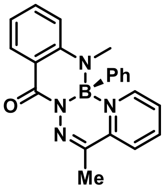
Hydrazone 2-*E* (*E*-isomer): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (br s, 1H, N*H*), 8.59 (d, $^{3}J_{HH}$ = 4.7 Hz, 1H, aryl C*H*), 8.28 (d, $^{3}J_{HH}$ = 7.9 Hz, 1H, aryl C*H*), 7.71 (td, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.8 Hz, 1H, aryl C*H*), 7.50 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, aryl C*H*), 7.39 (ddd, $^{3}J_{HH}$ = 8.6, 7.2 Hz, $^{4}J_{HH}$ = 1.6 Hz, 1H, aryl C*H*), 7.36 (br s, 1H, N*H*), 7.29–7.27 (m, 1H, aryl C*H*), 6.73 (dd, $^{3}J_{HH}$ = 8.5, 1.1 Hz, 1H, aryl C*H*), 6.65 (ddd, $^{3}J_{HH}$ = 8.0, 7.3 Hz, $^{4}J_{HH}$ = 1.1 Hz, 1H, aryl C*H*), 2.89 (s, 3H, NCH_3), 2.47 (s, 3H, -CH_3). ^{13}C NMR (101 MHz,



$CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 151.3, 148.6, 147.6, 138.0, 136.5, 133.9, 133.3, 124.1, 121.4, 114.7, 113.4, 111.6, 29.9, 11.1.

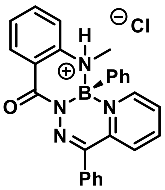


Synthesis of 3. In air, hydrazone **1** (2.00 g, 6.05 mmol) and phenylboronic acid (0.81 g, 6.7 mmol) were dissolved in 100 mL of toluene and heated at 110 °C for 18 h, resulting in the formation of a red solution and red-orange precipitate. The reaction mixture was cooled to −20 °C and filtered via vacuum filtration to isolate a red-orange powder, which was washed with cold toluene. Yield: 2.12 g (85%). Mp (°C): > 250. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.60 (dt, $^3J_{HH}$ = 5.7 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, aryl C*H*), 8.29 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, aryl C*H*), 8.14 (td, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, aryl C*H*), 7.85 (ddd, $^3J_{HH}$ = 7.3, 5.8 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, aryl C*H*), 7.61 (dt, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, aryl C*H*), 7.52 (dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.7 Hz, 2H, aryl C*H*), 7.44 (ddd, $^3J_{HH}$ = 8.7, 7.1 Hz, $^4J_{HH}$ = 1.9 Hz, 1H, aryl C*H*), 7.39–7.34 (m, 3H, aryl C*H*), 7.09–7.08 (m, 3H, aryl C*H*), 6.91 (br s, 2H, aryl C*H*), 6.87 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, aryl C*H*), 6.82–6.80 (m, 1H, aryl C*H*), 2.96 (s, 3H, NC*H*$_3$). ^{11}B NMR (193 MHz, $CDCl_3$): δ 3.5 (br s). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 162.7, 151.6, 151.0, 141.9, 141.4, 140.4, 134.13, 134.05, 131.8, 130.4, 129.9, 128.84, 128.76, 127.31, 127.27, 126.0, 124.2, 116.4, 116.3, 112.1, 36.3. UV-vis (CH_2Cl_2): λ_{max}: 467 nm (ε = 6,500 M^{-1} cm^{-1}), 385 nm (ε = 12,000 M^{-1} cm^{-1}). FT-IR ATR (cm^{-1}): 3059 (w), 2999 (w), 1652 (s), 1601 (m), 1489 (m), 1362 (m), 1284 (m), 1146 (s), 1041 (m), 754 (m), 701 (s), 642 (s). Mass Spec. (ESI, positive mode): exact mass calculated for $[C_{26}H_{21}BN_4NaO]^+$, $[M+Na]^+$: 439.1701; exact mass found: 439.1711.

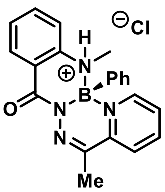


Synthesis of 4. In air, hydrazone **2** (0.50 g, 1.9 mmol) and phenylboronic acid (0.25 g, 2.1 mmol) were dissolved in 50 mL of toluene and heated at 110 °C for 18 h, resulting in the formation of a red solution and red-orange precipitate. The reaction mixture was cooled to −20 °C and filtered via vacuum filtration to isolate a red-orange powder, which was washed with cold toluene. Yield: 0.53 g (81%). Mp (°C): >250. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.57–8.56 (m, 1H, aryl C*H*), 8.29–8.26 (m, 2H, aryl C*H*), 7.85 (ddd, $^3J_{HH}$ = 7.4, 5.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, aryl C*H*), 7.79 (dt, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, aryl C*H*), 7.41 (ddd, $^3J_{HH}$ = 8.7, 7.1, $^4J_{HH}$ = 1.8 Hz, 1H, aryl C*H*), 7.13–7.07 (m, 3H, aryl C*H*), 6.83 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, aryl C*H*), 6.79 (ddd, $^3J_{HH}$ = 8.0, 7.1 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, aryl C*H*), 6.74 (br s, 2H, aryl C*H*), 2.89 (s, 3H, NC*H*$_3$), 2.40 (s, 3H, alkyl C*H*$_3$). ^{11}B NMR (128.4

MHz, $CDCl_3$): δ 3.4 (br s). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 162.5, 150.8, 148.1, 141.90, 141.86, 140.8, 133.9, 131.6, 130.4, 127.3, 127.1, 126.1, 121.8, 116.3, 115.0, 112.0, 36.3, 19.4. UV-vis (CH_2Cl_2): λ_{max}: 451 nm (ε = 2,200 M^{-1} cm^{-1}), 368 nm (ε = 7,800 M^{-1} cm^{-1}). FT-IR ATR (cm^{-1}): 3085 (w), 2978 (w), 2873 (w), 2818 (w), 1646 (s), 1602 (m), 1489 (m), 1429 (m), 1357 (s), 1286 (s), 1162 (s), 1041 (m), 782 (s), 749 (s), 702 (s), 603 (m). Mass Spec. (ESI, positive mode): exact mass calculated for $[M+H]^+$, $[C_{21}H_{20}BN_4O]^+$: 355.1725; exact mass found: 355.1709.



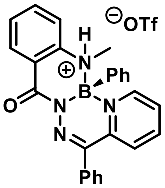
Synthesis of 3·HCl. Compound **3** (0.25 g, 0.60 mmol) was suspended in 5 mL CH_2Cl_2. Anhydrous HCl in dioxane (4.0 M solution, 0.17 mL, 0.66 mmol) was added and the opaque orange-red solution turned clear and yellow. This solution was stirred for 0.5 h, then triturated with pentane until a powdery beige solid was formed. The solid was isolated by vacuum filtration and washed with pentane. Yield: 0.26 g (95%). Mp (°C): 168−169 (decomp). ^1H NMR (600 MHz, $CDCl_3$): δ 13.18 (br s, 1H, N*H*), 10.88 (d, $^3J_{HH}$ = 5.4 Hz, 1H, aryl C*H*), 8.42 (d, $^3J_{HH}$ = 7.9 Hz, 1H, aryl C*H*), 8.27 (t, $^3J_{HH}$ = 7.5 Hz, 1H, aryl C*H*), 8.18 (d, $^3J_{HH}$ = 7.5 Hz, 1H, aryl C*H*), 8.08 (t, $^3J_{HH}$ = 6.2 Hz, 1H, aryl C*H*), 7.81 (d, $^3J_{HH}$ = 6.9 Hz, 3H, aryl C*H*), 7.60 (d, $^3J_{HH}$ = 6.6 Hz, 2H, aryl C*H*), 7.56−7.51 (m, 4H, aryl C*H*), 7.41 (t, $^3J_{HH}$ = 7.5 Hz, 1H, aryl C*H*), 7.18 (t, $^3J_{HH}$ = 7.4 Hz, 2H, aryl C*H*), 7.13 (t, $^3J_{HH}$ = 7.2 Hz, 1H, aryl C*H*), 3.06 (d, $^3J_{HH}$ = 4.6 Hz, 3H, NCH_3). ^{11}B NMR (193 MHz, $CDCl_3$): δ 3.2 (br s). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 162.7, 146.9, 144.6, 144.2, 140.9, 140.2, 135.1, 133.8, 131.4, 131.2, 130.4, 129.6, 129.5, 129.3, 129.1, 128.8, 128.6, 126.7, 125.1, 123.4, 42.0. UV-vis (CH_2Cl_2): λ_{max}: 386 nm (ε = 8,200 M^{-1} cm^{-1}). FT-IR ATR (cm^{-1}): 3038 (w), 2843 (w), 2766 (w), 2540 (w), 1687 (s), 1616 (m), 1261 (s), 1297 (m), 1154 (s), 982 (m), 722 (m), 702 (s), 650 (m). Mass Spec. (ESI, positive mode): exact mass calculated for $[M]^+$, $[C_{26}H_{22}BN_4O]^+$: 417.1881; exact mass found: 417.1862.

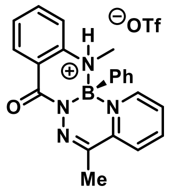


Synthesis of 4·HCl. Compound **4** (0.10 g, 0.28 mmol) was suspended in 5 mL CH_2Cl_2. Anhydrous HCl in dioxane (4.0 M solution, 0.09 mL, 0.34 mmol) was added and the opaque orange-red solution turned opaque and pale yellow. This solution was stirred for 1 h, then 10 mL of pentane was added to precipitate a pale-yellow solid. The solid was isolated by vacuum filtration and washed with pentane. Yield: 0.11 g (96%). Mp (°C): 162–163 (decomp). ^1H NMR (600 MHz, $CDCl_3$): δ 13.11 (s, 1H, N*H*), 10.81 (d, $^3J_{HH}$ = 5.7 Hz, 1H, aryl C*H*), 8.41–8.36 (m, 2H, aryl C*H*), 8.17 (dd, $^3J_{HH}$ = 7.8, 1.6 Hz, 1H, aryl C*H*), 8.07 (ddd, $^3J_{HH}$ = 7.5, 5.9 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, aryl C*H*), 7.94 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ =

1.3 Hz, 1H, aryl C*H*), 7.75–7.73 (m, 2H, aryl C*H*), 7.53 (td, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, aryl C*H*), 7.39 (td, *J* = 7.6, 1.1 Hz, 1H, aryl C*H*), 7.18–7.08 (m, 3H, aryl C*H*), 2.99 (d, $^3J_{HH}$ = 5.0 Hz, 3H, NC*H*$_3$), 2.68 (s, 3H, alkyl C*H*$_3$). ^{11}B NMR (193 MHz, CDCl$_3$): δ 2.9 (br s). ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): δ 162.7, 147.0, 145.1, 140.7, 140.1, 139.7, 135.0, 131.4, 131.1, 129.6, 129.1, 128.7, 128.6, 125.2, 124.4, 123.4, 41.8, 20.5. UV-vis (CH$_2$Cl$_2$): λ$_{max}$: 369 nm (ε = 5,200 M^{-1} cm^{-1}). FT-IR ATR (cm^{-1}): 3454 (w), 3034 (w), 2584 (w), 1685 (s), 1613 (m), 1463 (m), 1316 (s), 1264 (m), 1153 (s), 984 (m), 870 (m), 795 (m), 730 (s), 700 (s), 596 (m), 511 (m). Mass Spec. (ESI, positive mode): exact mass calculated for [M]$^+$, [C$_{21}$H$_{20}$BN$_4$O]$^+$: 355.1725; exact mass found: 355.1738.

Synthesis of 3·HOTf. Compound **3** (0.50 g, 1.20 mmol) was dissolved in 20 mL CH$_2$Cl$_2$. Anhydrous HCl in dioxane (4.0 M solution, 0.33 mL, 1.3 mmol) was added and the solution was stirred for 1 h. NaOTf (0.25 g, 1.3 mmol) was added to the solution, causing a colour change to dark red, and the solution was stirred for 18 h. The opaque solution was filtered through celite and the CH$_2$Cl$_2$ filtrate was triturated with pentane until a powdery magenta solid was formed. The solid was isolated by vacuum filtration and washed with pentane. Yield: 0.24 g (70%). Mp (°C): 171−172 (decomp). ^{1}H NMR (600 MHz, CDCl$_3$): δ 10.30 (d, *J* = 5.3 Hz, 1H, -N*H*), 9.74 (d, *J* = 6.0 Hz, 1H, aryl C*H*), 8.34 (t, *J* = 7.8 Hz, 1H, aryl C*H*), 8.21 (d, *J* = 7.8 Hz, 1H, aryl C*H*), 8.15 (t, *J* = 6.8 Hz, 1H, aryl C*H*), 7.86 (dd, *J* = 10.2, 8.0 Hz, 2H, aryl C*H*), 7.61 (d, *J* = 4.1 Hz, 3H, aryl C*H*), 7.56–7.50 (m, 5H, aryl C*H*), 7.46 (t, *J* = 7.6 Hz, 1H, aryl C*H*), 7.19 (dt, *J* = 12.6, 6.8 Hz, 3H, aryl C*H*), 3.07 (d, *J* = 5.0 Hz, 3H, NC*H*$_3$). ^{11}B NMR (193 MHz, CDCl$_3$): δ 2.9 (br s). ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): δ 162.3, 145.3, 145.2, 144.4, 140.1, 139.7, 135.6, 133.5, 131.6, 130.64, 130.60, 130.2, 129.6, 129.5, 129.4, 129.2, 129.1, 127.0, 124.9, 123.0, 121.7 (d, $^1J_{CF}$ = 319 Hz), 41.7. ^{19}F NMR (565 MHz, CDCl$_3$): δ −77.9 (s). UV-vis (CH$_2$Cl$_2$): λ$_{max}$: 510 nm (ε = 1,100 M^{-1} cm^{-1}), 375 nm (ε = 5,900 M^{-1} cm^{-1}). FT-IR ATR (cm^{-1}): 3074 (w), 2904 (w), 2832 (w), 1621 (m), 1553 (m), 1291 (s), 1167 (s), 1021 (s), 749 (m), 694 (m), 639 (s), 518 (m). Mass Spec. (ESI, positive mode): exact mass calculated for [M+H]$^+$, [C$_{26}$H$_{23}$BN$_4$O]$^+$: 418.1959; exact mass found: 418.1954.





Synthesis of 4·HOTf. Compound **4** (0.20 g, 0.56 mmol) was dissolved in 5 mL CH_2Cl_2. Anhydrous HCl in dioxane (4.0 M solution, 0.16 mL, 0.62 mmol) was added and the solution was stirred for 1 h. NaOTf (0.11 g, 0.62 mmol) was added to the solution, causing a colour change to dark red, and the solution was stirred for 18 h. The opaque solution was filtered through celite and the CH_2Cl_2 filtrate was triturated with pentane, turning the solution pale yellow and precipitating a pale-yellow solid from solution. The solid was isolated by vacuum filtration and washed with pentane. Yield: 0.196 g (69%). Mp (°C): 152–154 (decomp). ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.31 (br s, 1H, N*H*), 9.69 (s, 1H, aryl C*H*), 8.48 (t, $^3J_{HH}$ = 7.7 Hz, 1H, aryl C*H*), 8.19 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, aryl C*H*), 8.13 (t, $^3J_{HH}$ = 6.6 Hz, 1H, aryl C*H*), 8.01 (d, $^3J_{HH}$ = 8.0 Hz, 1H, aryl C*H*), 7.83 (d, $^3J_{HH}$ = 8.0 Hz, 1H, aryl C*H*), 7.59 (td, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, aryl C*H*), 7.45–7.42 (m, 3H, aryl C*H*), 7.18–7.11 (m, 3H, aryl C*H*), 3.00 (d, $^3J_{HH}$ = 5.1 Hz, 3H, NCH_3), 2.70 (s, 3H, alkyl CH_3). ^{11}B NMR (193 MHz, $CDCl_3$): δ 2.9 (br s). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 162.3, 145.8, 145.3, 140.1, 140.0, 139.6, 135.4 131.5, 130.6, 130.1, 129.4, 129.2, 129.0, 125.0, 124.9, 122.9, 120.6 ($^2J_{CF}$ = 319 Hz), 41.6, 20.5. ^{19}F NMR (565 MHz, $CDCl_3$): δ −78.0 (s). UV-vis (CH_2Cl_2): λ_{max}: 503 nm (ε = 608 M^{-1} cm^{-1}), 382 nm (ε = 8,500 M^{-1} cm^{-1}). FT-IR ATR (cm^{-1}): 3487 (br w), 3057 (w), 2962 (w), 1688 (m), 1619 (w), 1460 (w), 1294 (m), 1241 (m), 1157 (s), 1030 (s), 951 (w), 867 (m), 782 (m), 710 (m), 639 (s), 511 (m). Mass Spec. (ESI, positive mode): exact mass calculated for $[2M–H]^+$, $[C_{42}H_{39}B_2N_8O_2]^+$: 709.3377; exact mass found: 709.3414.

NMR Spectra

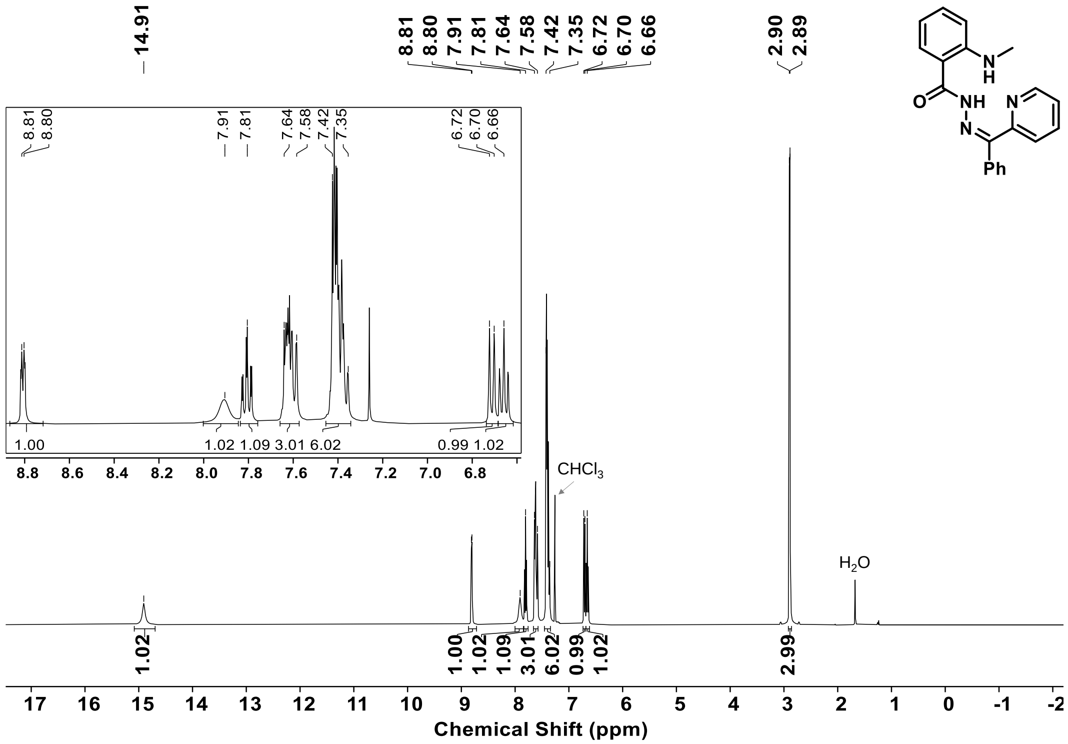


Fig. S1 ^{1}H NMR spectrum of compound **1** in CDCl$_3$. Inset: expanded view of aromatic region.

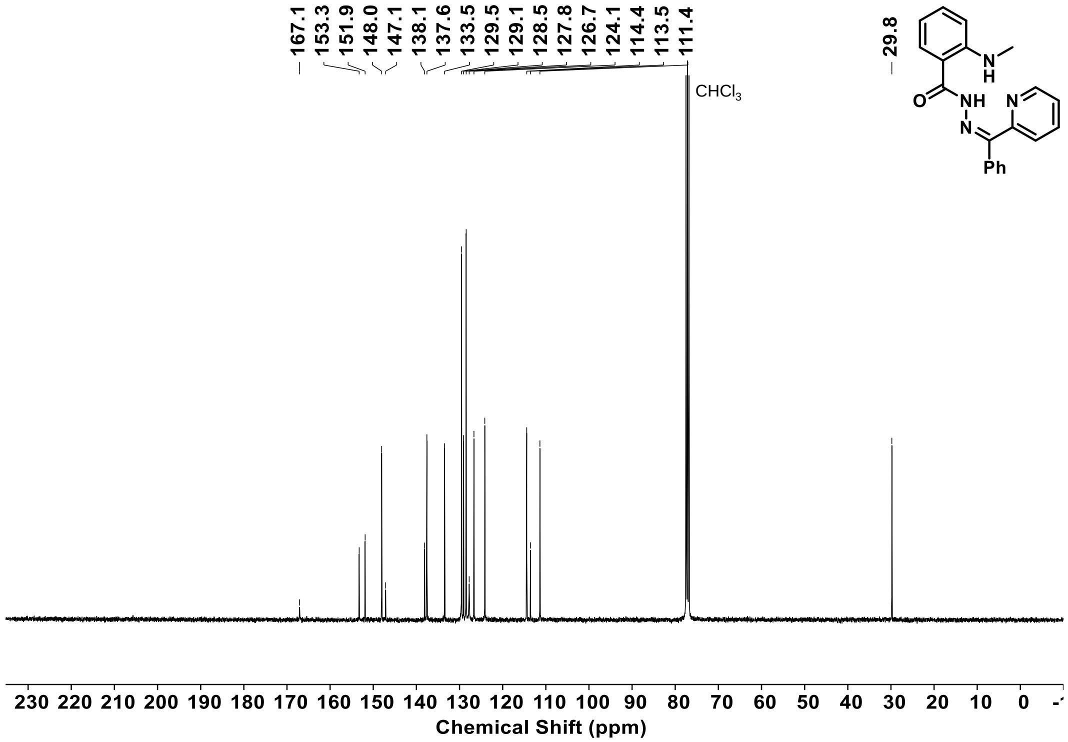


Fig. S2 ^{13}C{^{1}H} NMR spectrum of compound **1** in CDCl$_3$.

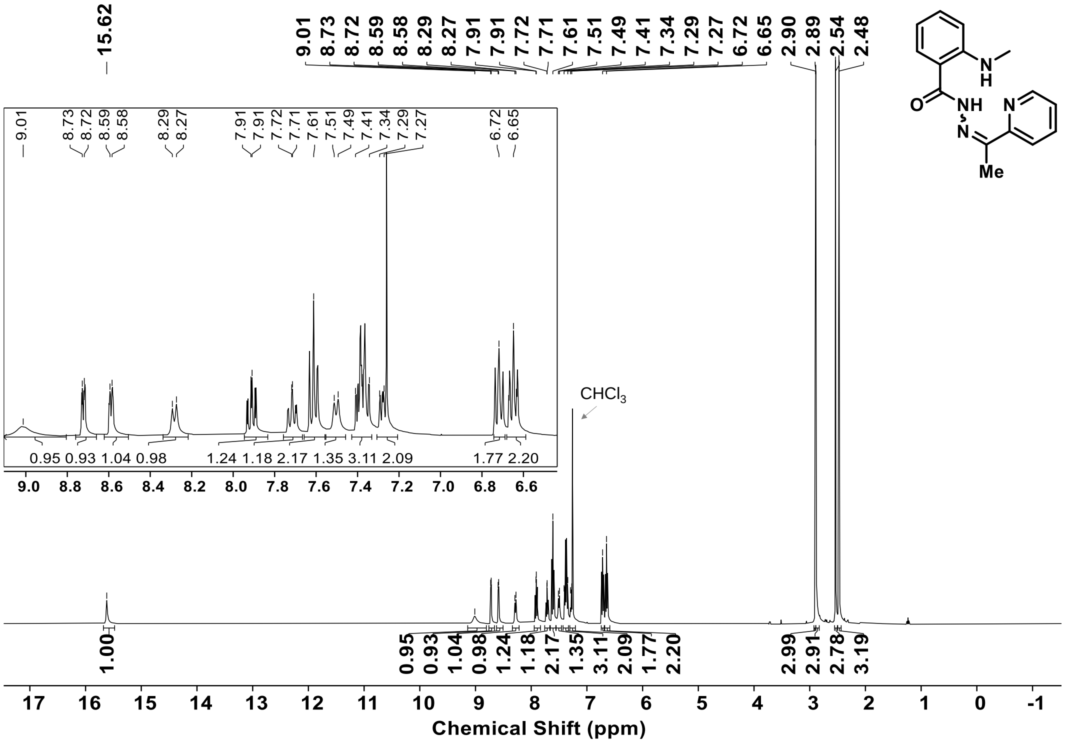


Fig. S3 ^{1}H NMR spectrum of compound **2** in CDCl$_3$ as a mixture of *E* and *Z* isomers. Inset: expanded view of aromatic region.

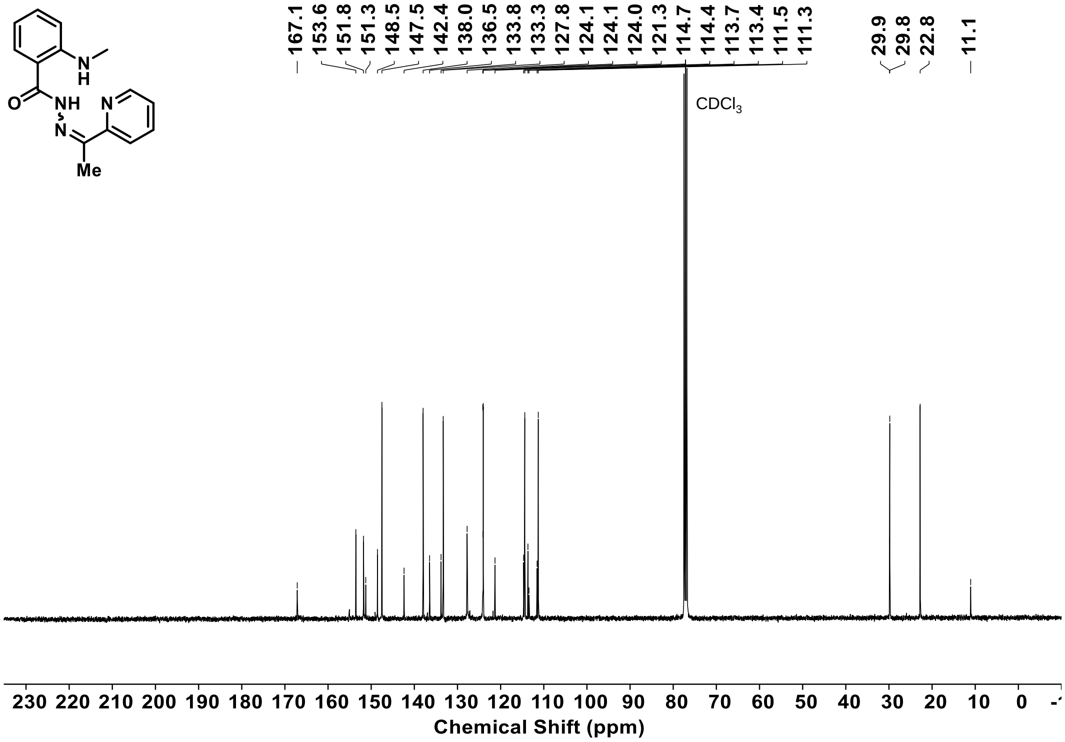


Fig. S4 ^{13}C{^{1}H} NMR spectrum of compound **2** in CDCl$_3$ as a mixture of *E* and *Z* isomers.

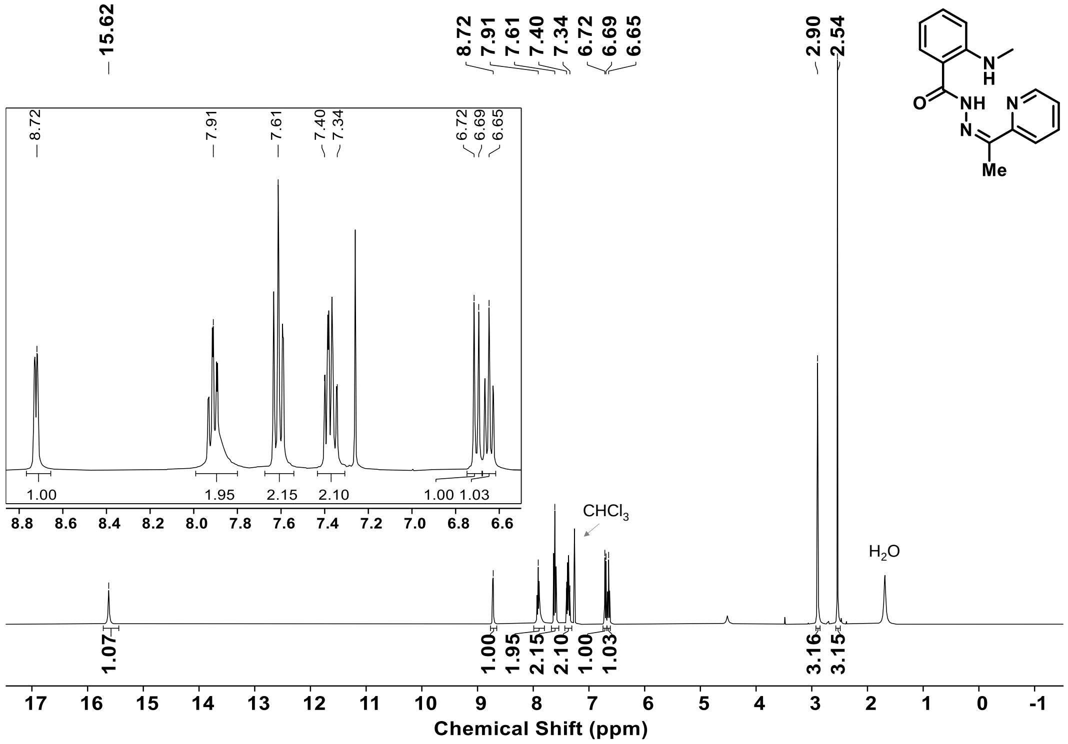


Fig. S5 ^{1}H NMR spectrum of compound **2-*Z*** in CDCl$_3$. Inset: expanded view of aromatic region.

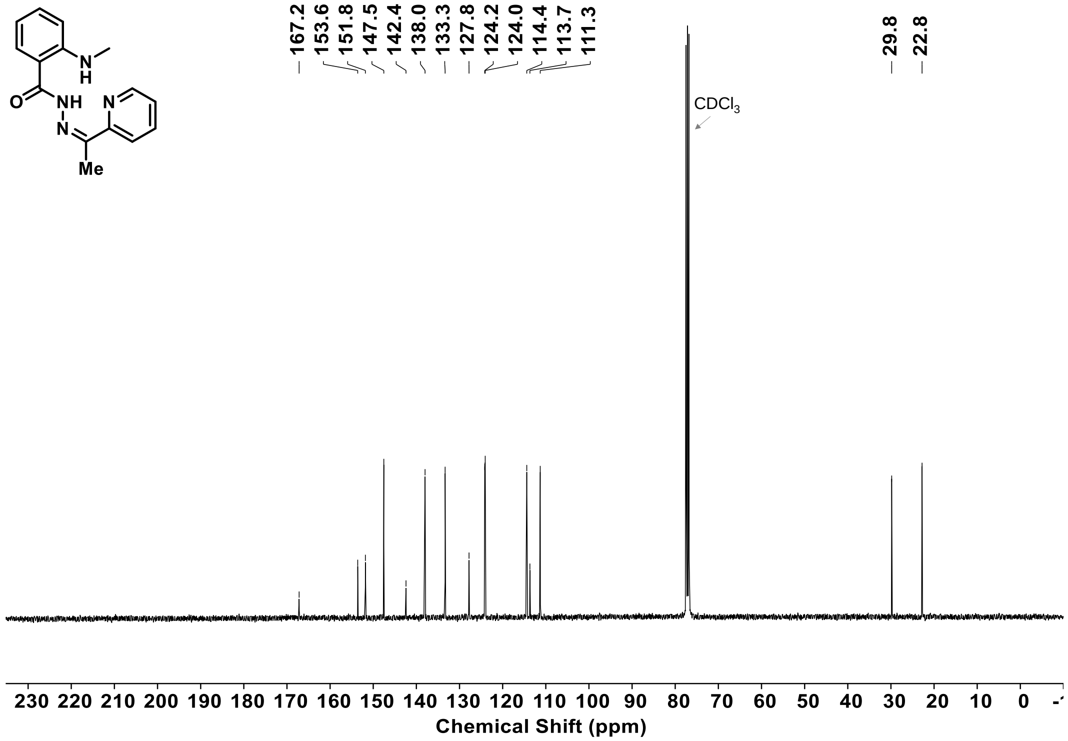


Fig. S6 ^{13}C{^{1}H} NMR spectrum of compound **2-*Z*** in CDCl$_3$.

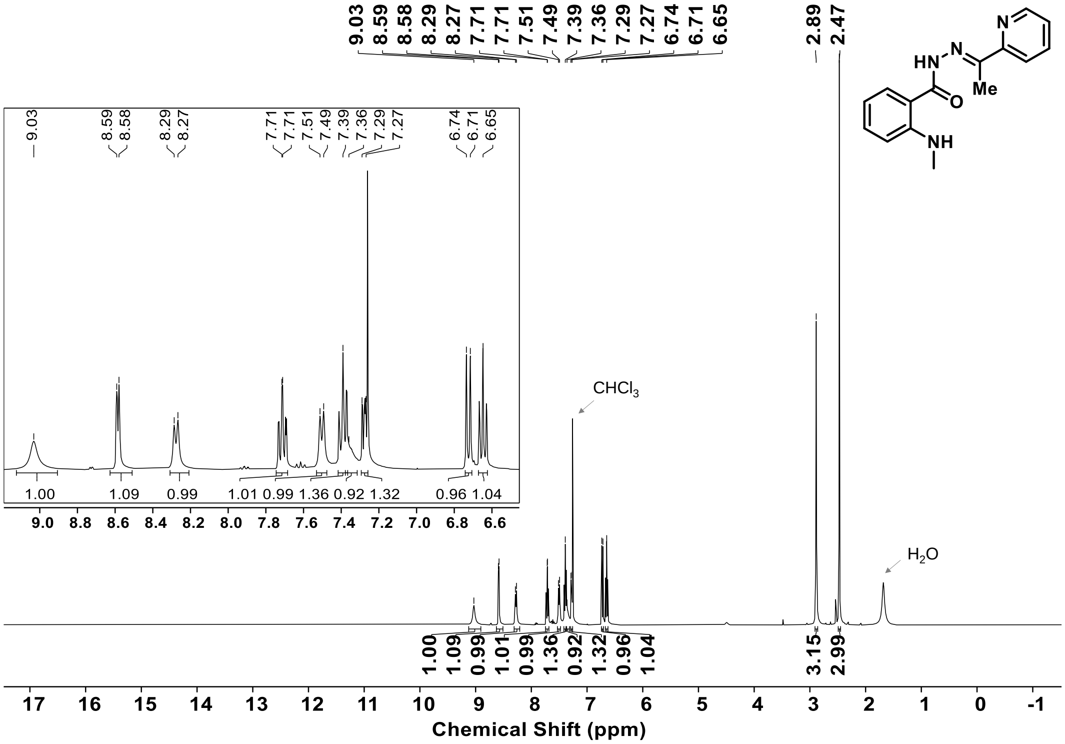


Fig. S7 ^{1}H NMR spectrum of compound **2-*E*** in CDCl$_3$. Inset: expanded view of aromatic region.

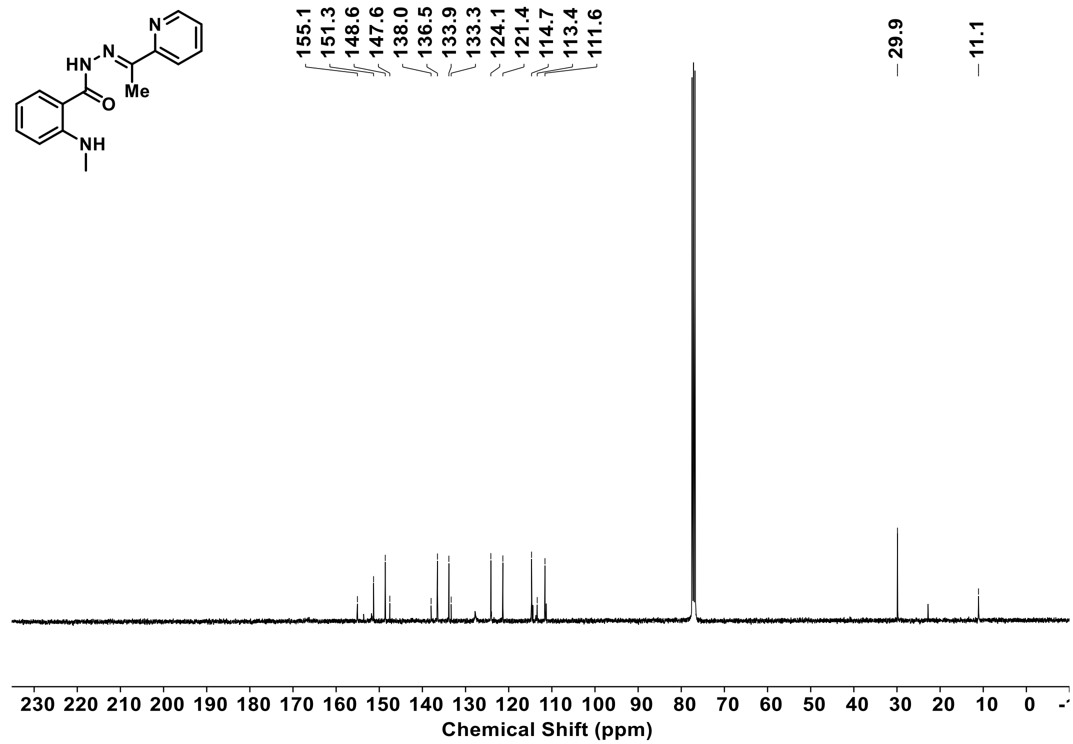


Fig. S8 ^{13}C{^{1}H} NMR spectrum of compound **2-*E*** in CDCl$_3$.

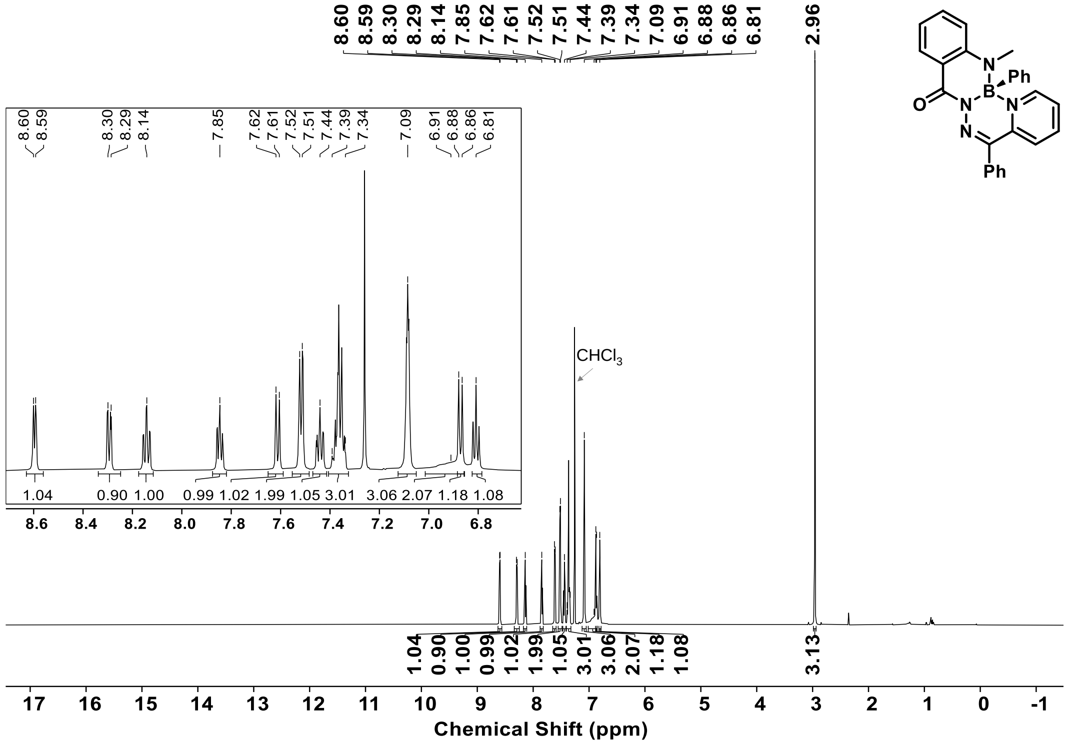


Fig. S9 ^{1}H NMR spectrum of compound **3** in $CDCl_3$. Inset: expanded view of aromatic region.

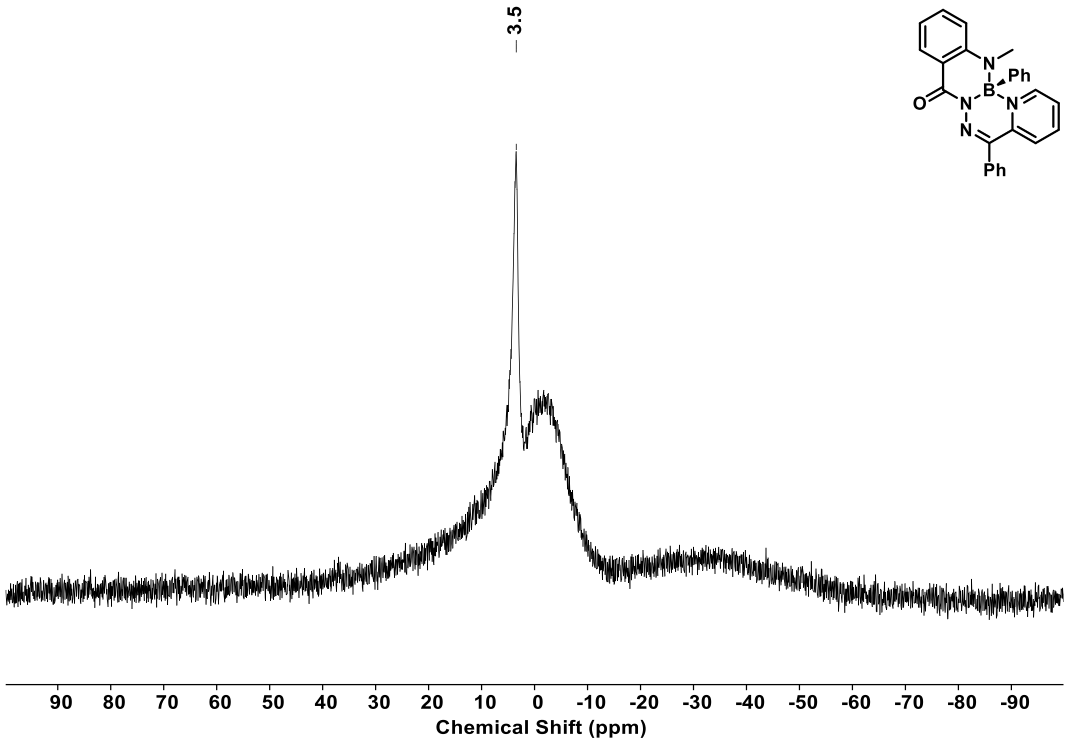


Fig. S10 ^{11}B NMR spectrum of compound **3** in $CDCl_3$.

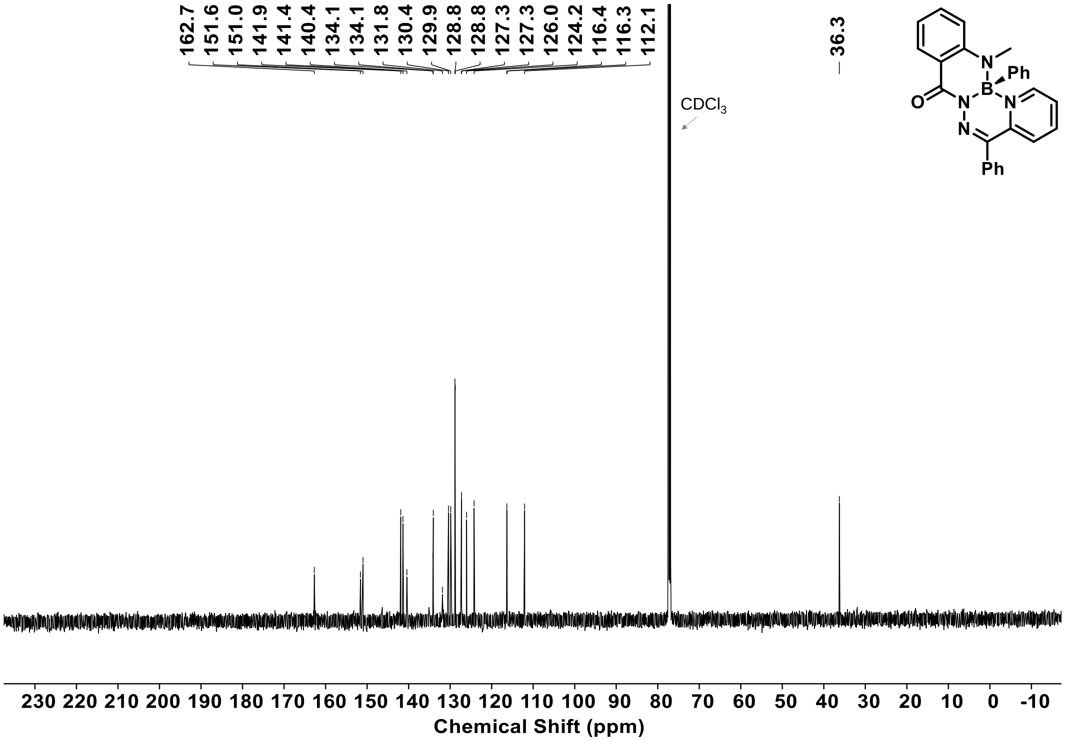


Fig. S11 $^{13}C\{^1H\}$ NMR spectrum of compound **3** in $CDCl_3$.

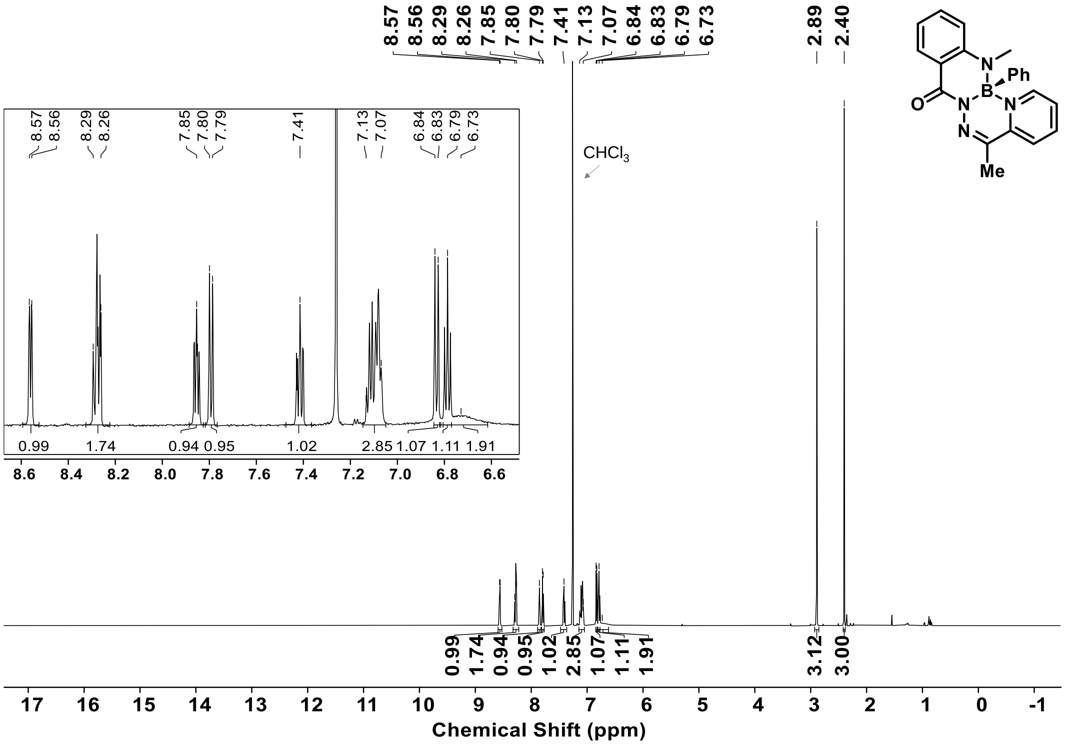


Fig. S12 ^1H NMR spectrum of compound **4** in $\mathbf{CDCl_3}$. Inset: expanded view of aromatic region.

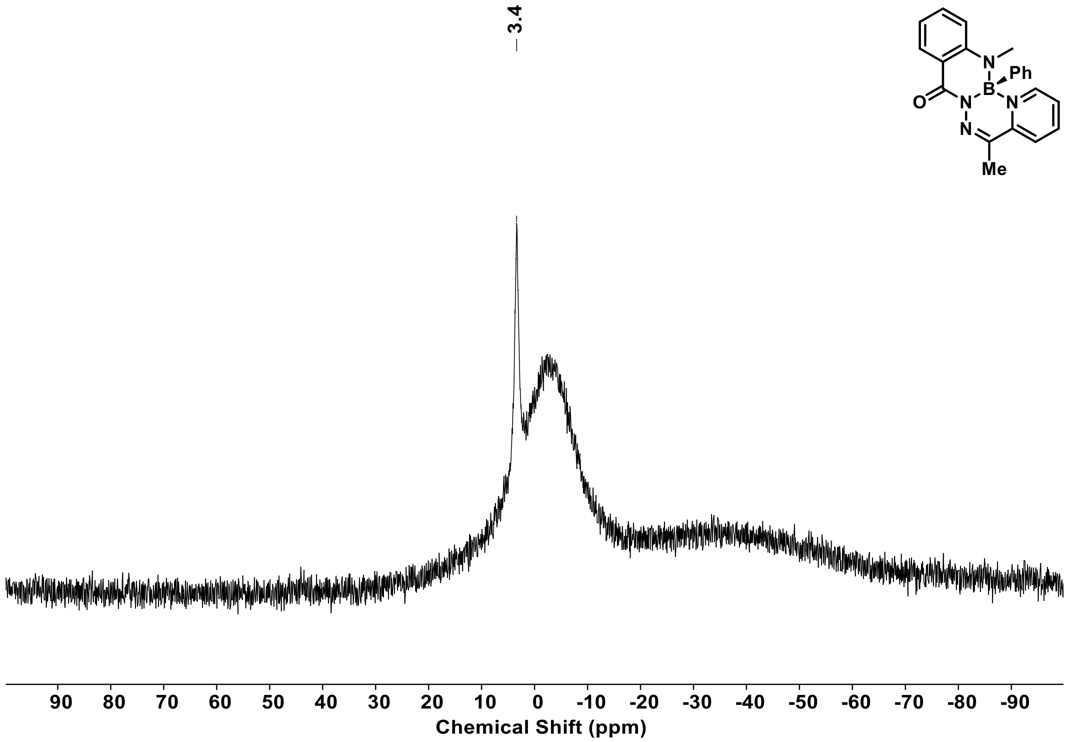


Fig. S13 ^{11}B NMR spectrum of compound **4** in $CDCl_3$.

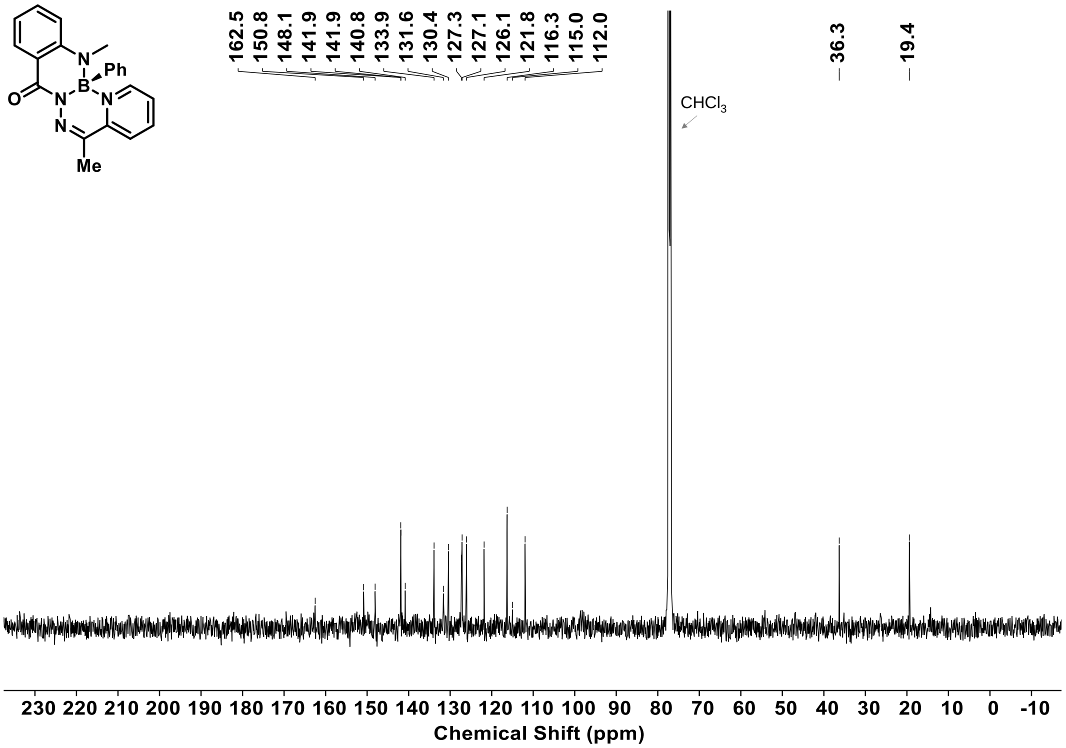


Fig. S14 ^{13}C{^{1}H} NMR spectrum of compound **4** in **$CDCl_3$**.

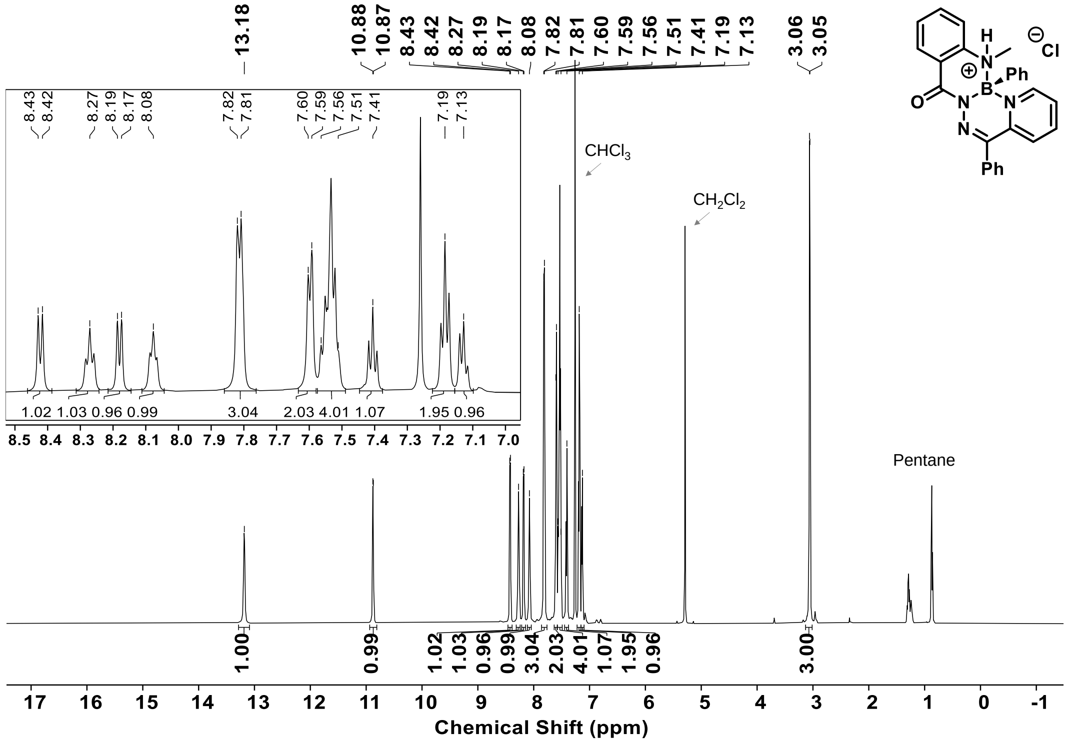


Fig. S15 ^{1}H NMR spectrum of compound **3·HCl** in CDCl$_3$. Inset: expanded view of aromatic region.

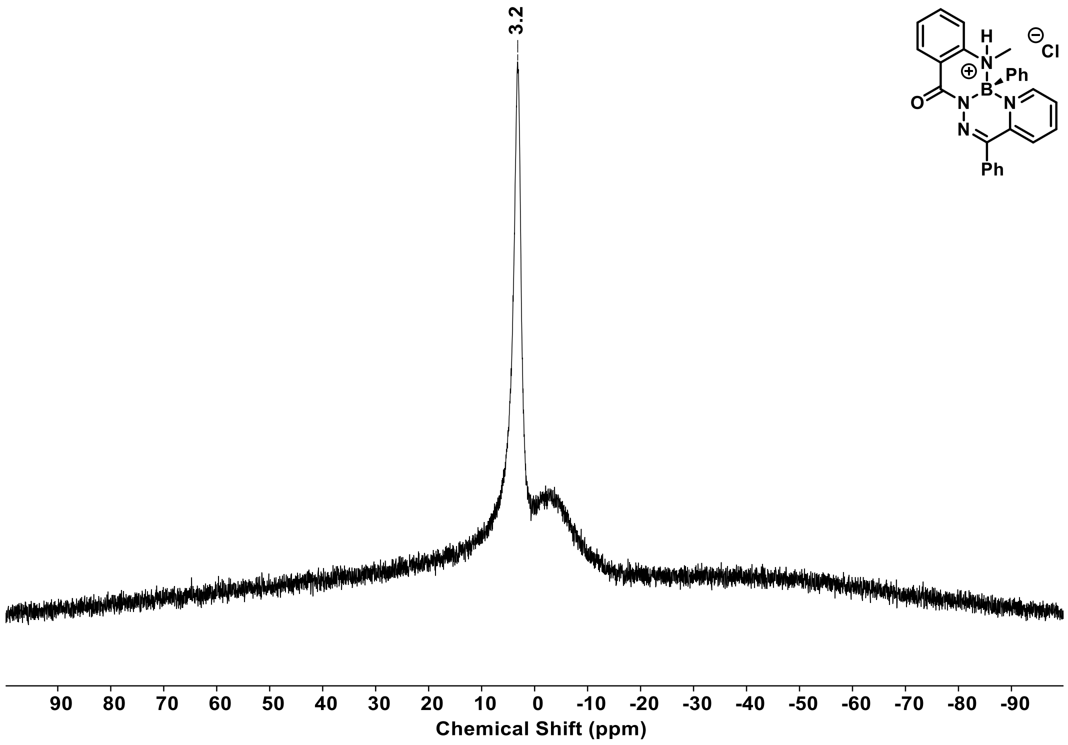


Fig. S16 ^{11}B NMR spectrum of compound **3·HCl** in CDCl$_3$.

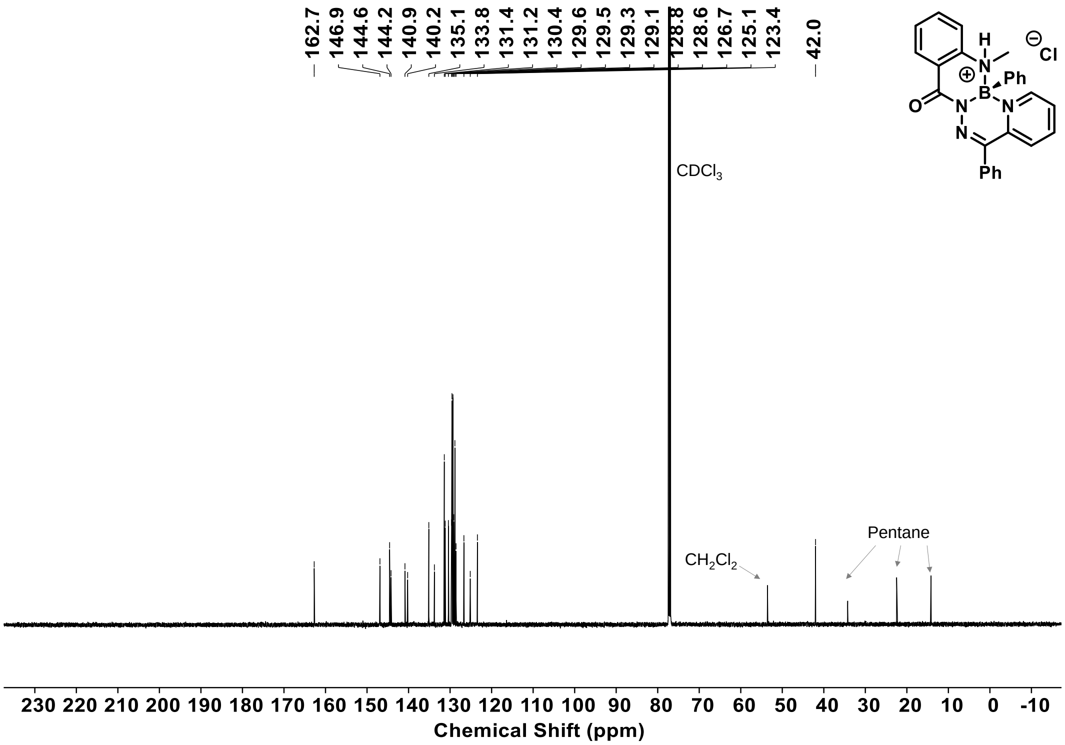


Fig. S17 $^{13}C\{^{1}H\}$ NMR spectrum of compound **3·HCl** in $CDCl_3$.

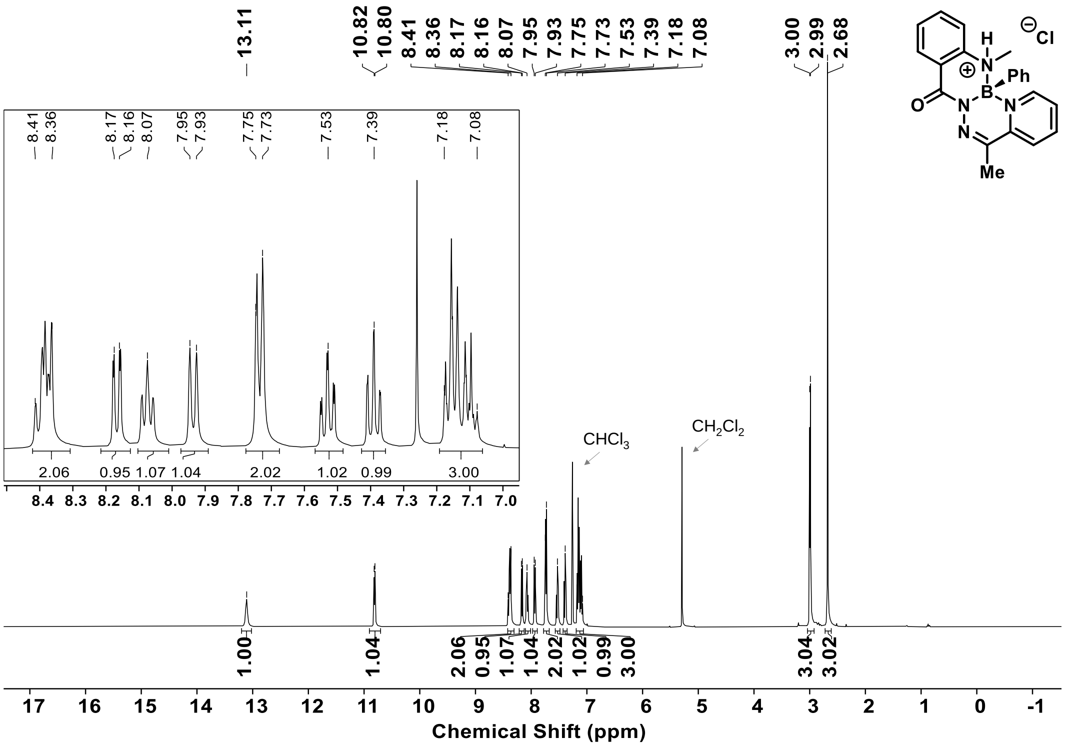


Fig. S18 ^{1}H NMR spectrum of compound **4·HCl** in $CDCl_3$. Inset: expanded view of aromatic region.

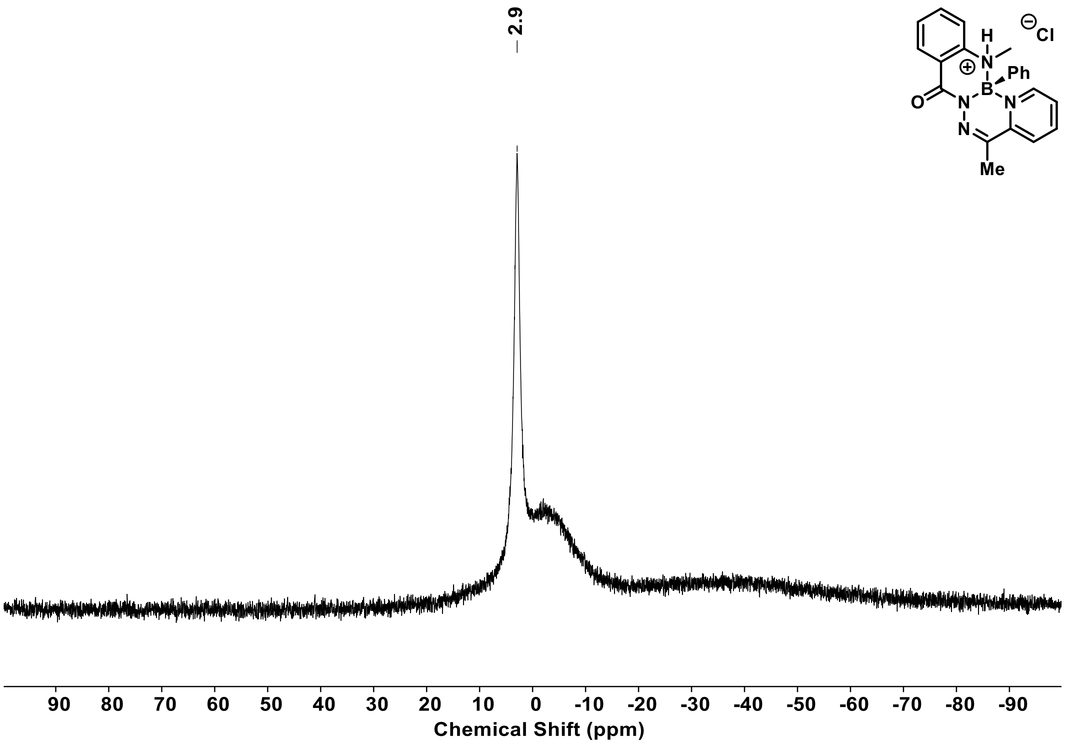


Fig. S19 ^{11}B NMR spectrum of compound **4·HCl** in $CDCl_3$.

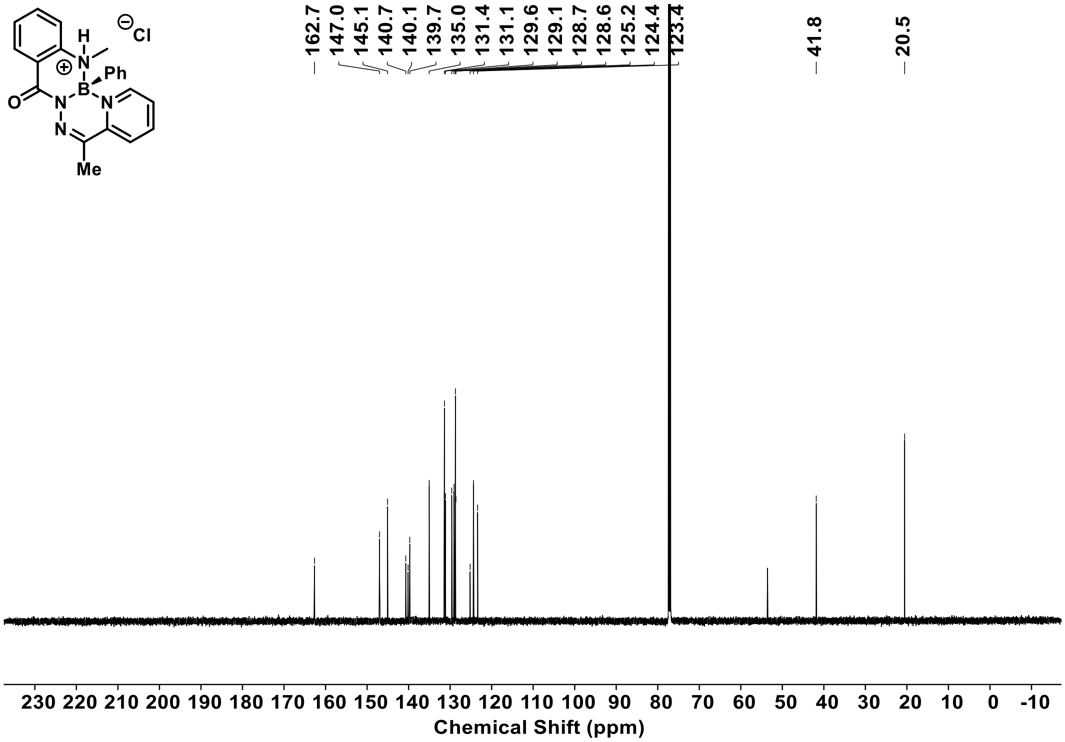


Fig. S20 $^{13}C\{^{1}H\}$ NMR spectrum of compound **4·HCl** in $CDCl_3$.

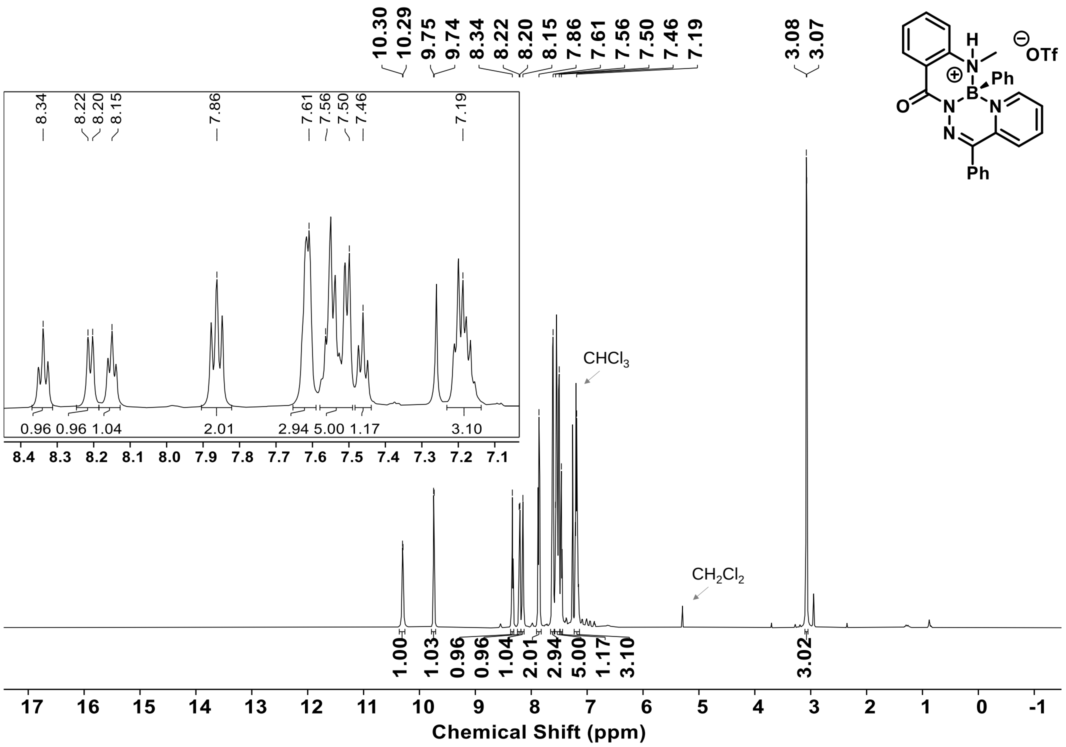


Fig. S21 ^{1}H NMR spectrum of compound **3·HOTf** in CDCl$_3$. Inset: expanded view of aromatic region.

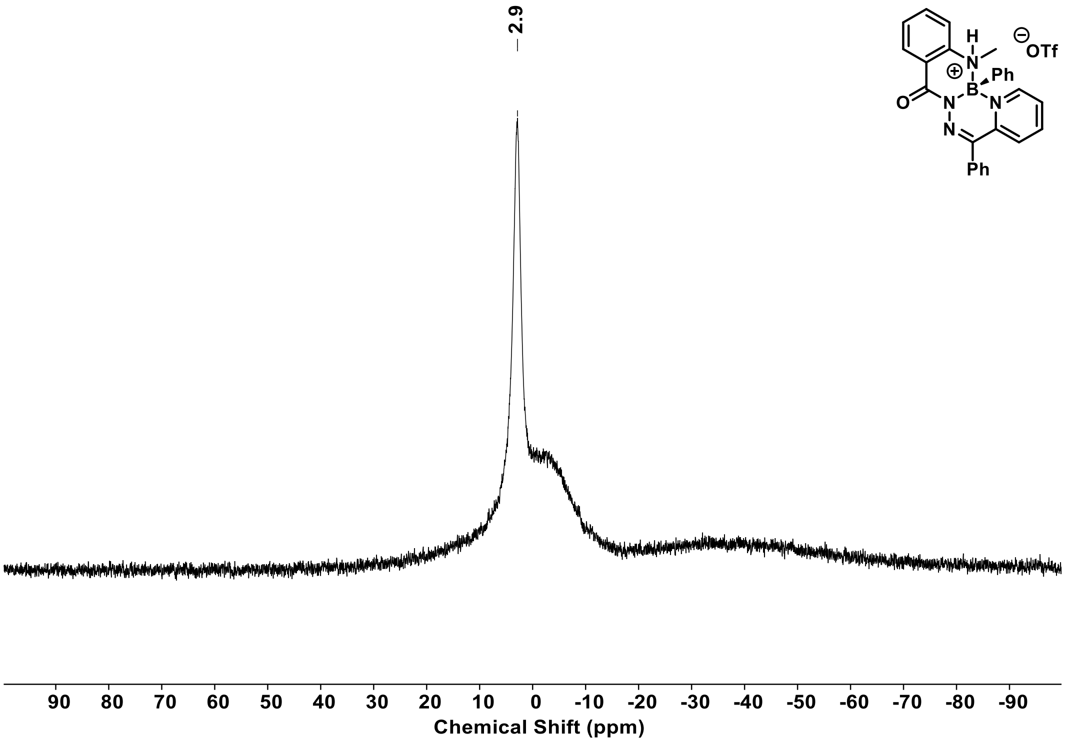


Fig. S22 ^{11}B NMR spectrum of compound **3·HOTf** in CDCl$_3$.

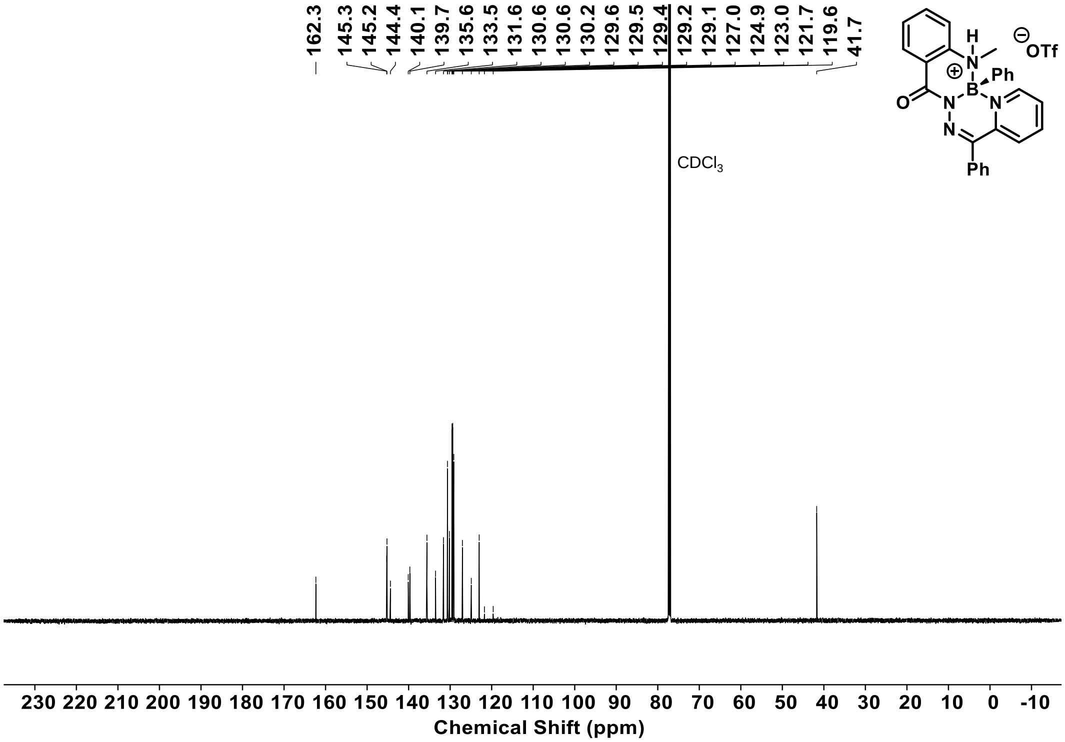


Fig. S23 $^{13}C\{^{1}H\}$ NMR spectrum of compound **3·HOTf** in $CDCl_3$.

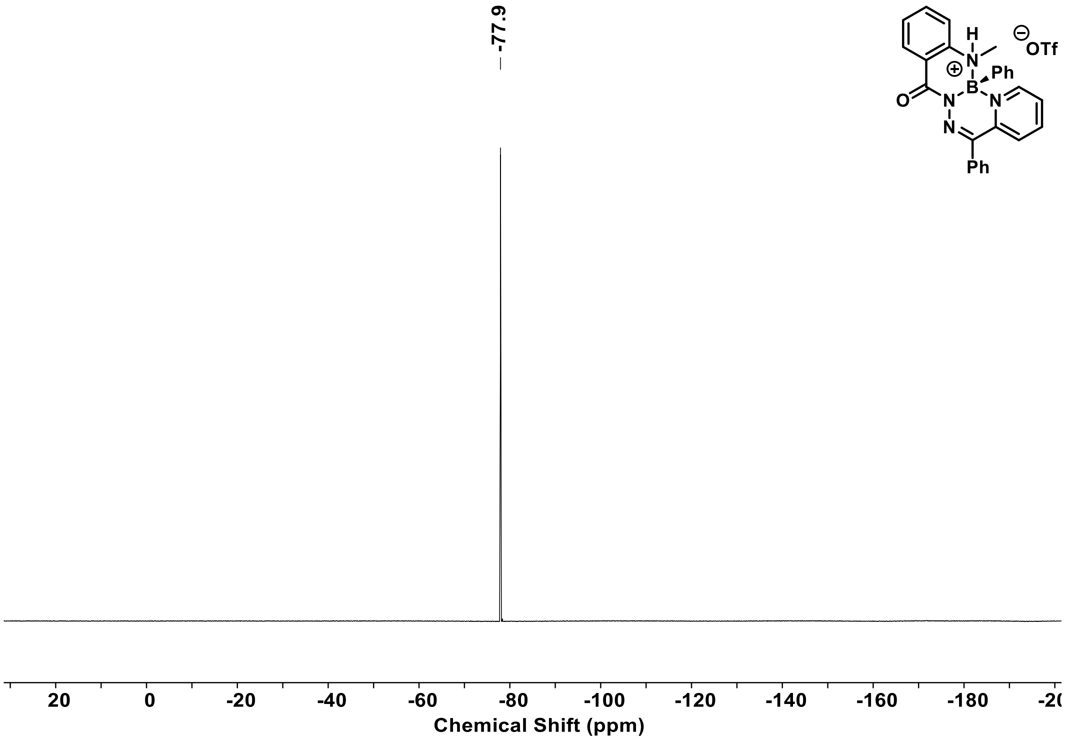


Fig. S24 ^{19}F NMR spectrum of compound **3·HOTf** in $CDCl_3$.

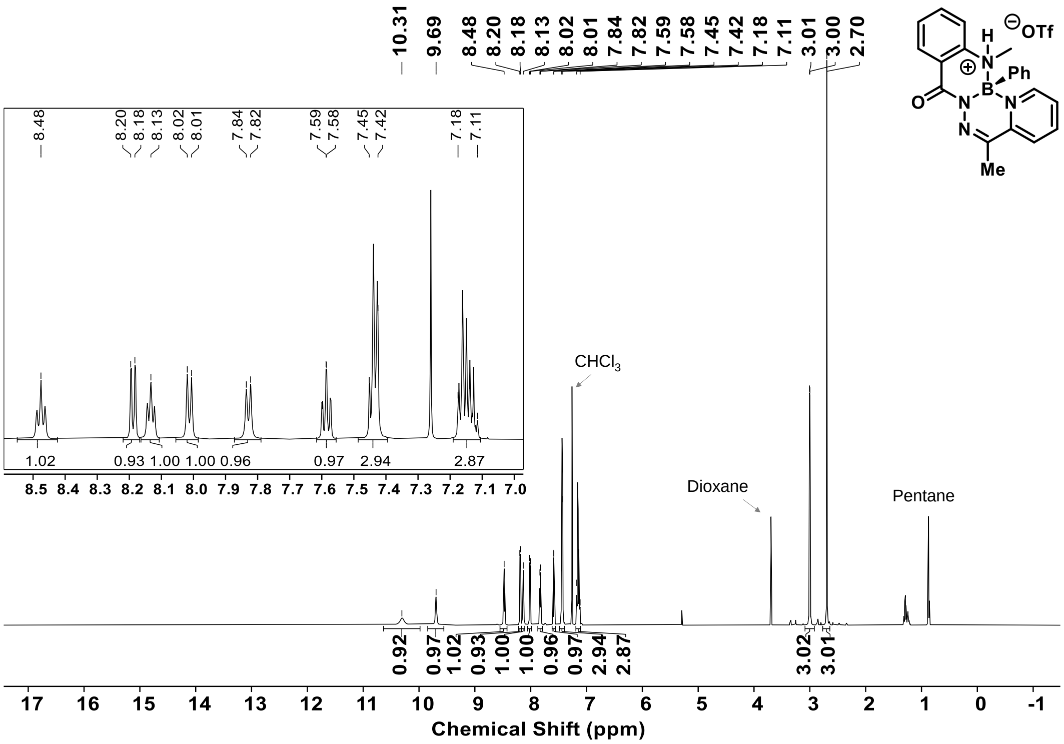


Fig. S25 ^{1}H NMR spectrum of compound **4·HOTf** in CDCl$_3$. Inset: expanded view of aromatic region.

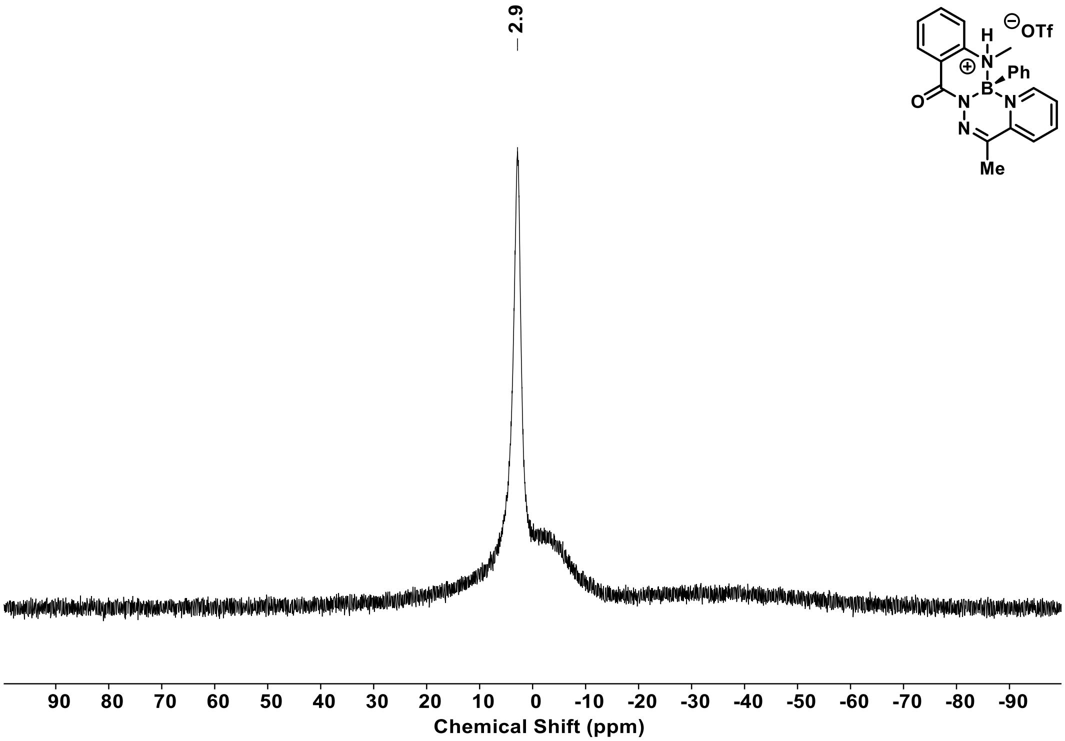


Fig. S26 ^{11}B NMR spectrum of compound **4·HOTf** in CDCl$_3$.

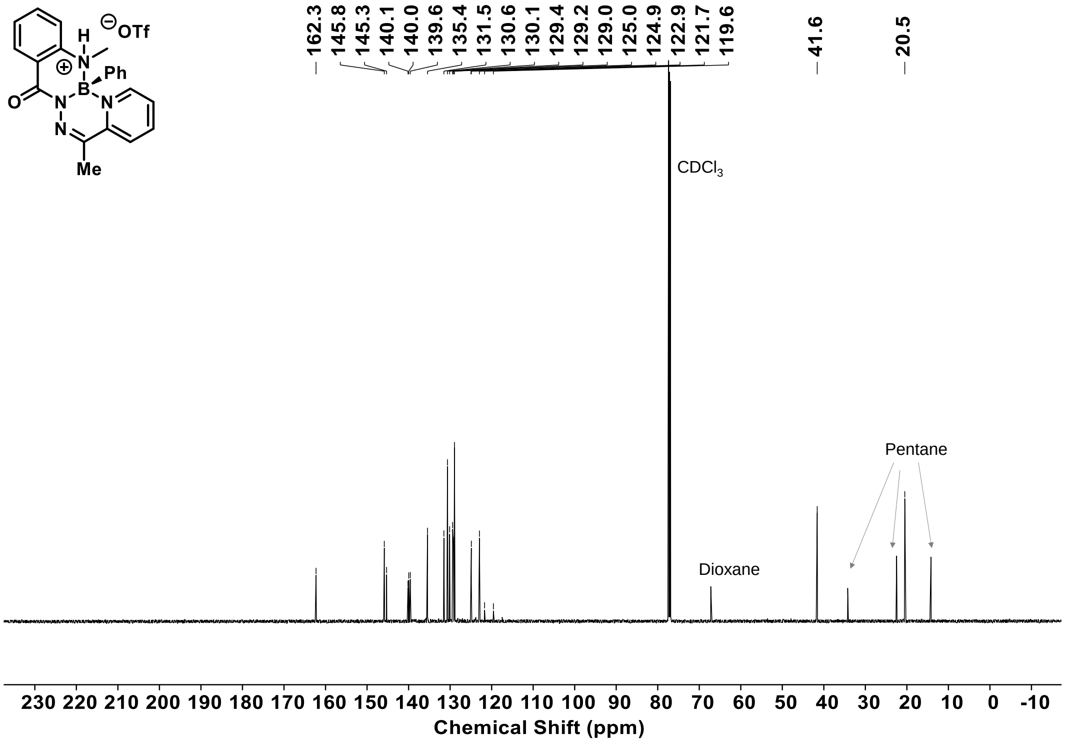


Fig. S27 $^{13}C\{^{1}H\}$ NMR spectrum of compound **4·HOTf** in CDCl$_3$.

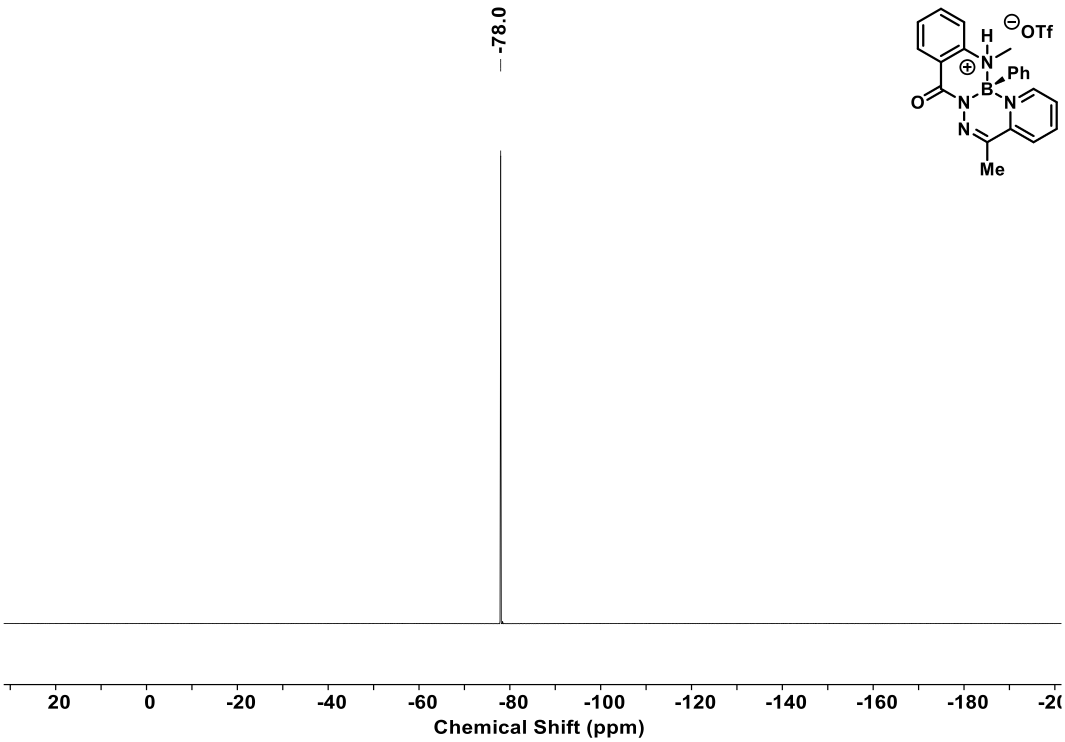


Fig. S28 ^{19}F NMR spectrum of compound **4·HOTf** in CDCl$_3$.

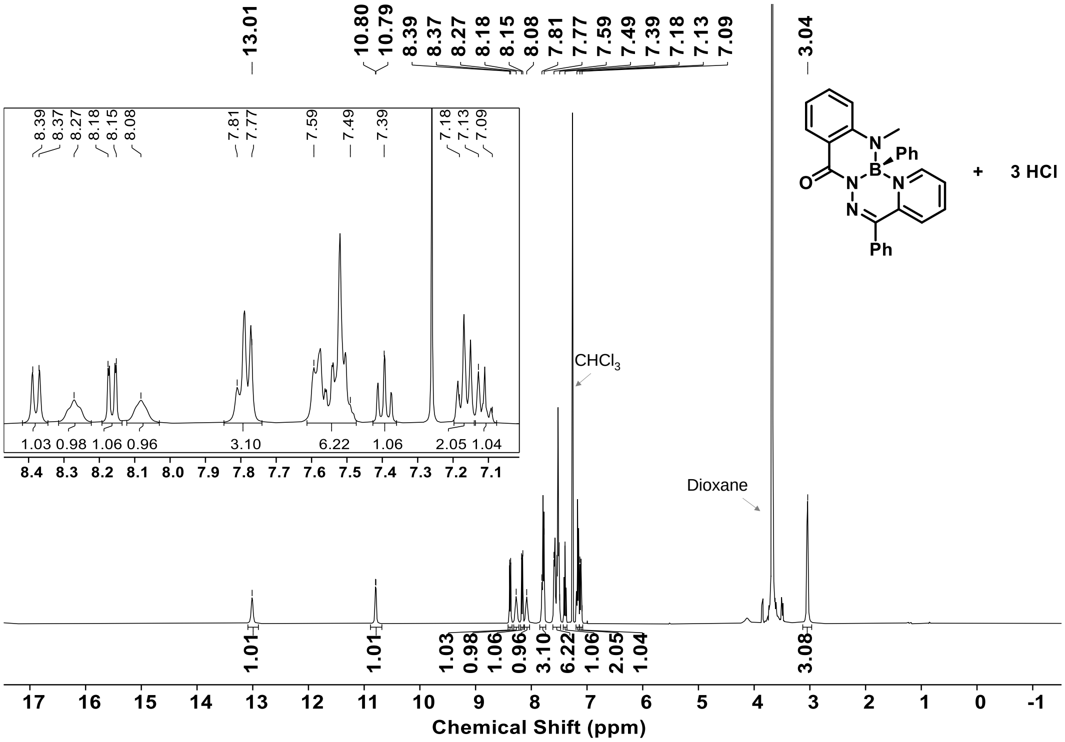


Fig. S29 ^{1}H NMR spectrum of compound **3** with 3 equiv. HCl in dioxane in $CDCl_3$. Inset: expanded view of aromatic region.

UV-Vis Absorbance and Photoluminescence Spectra

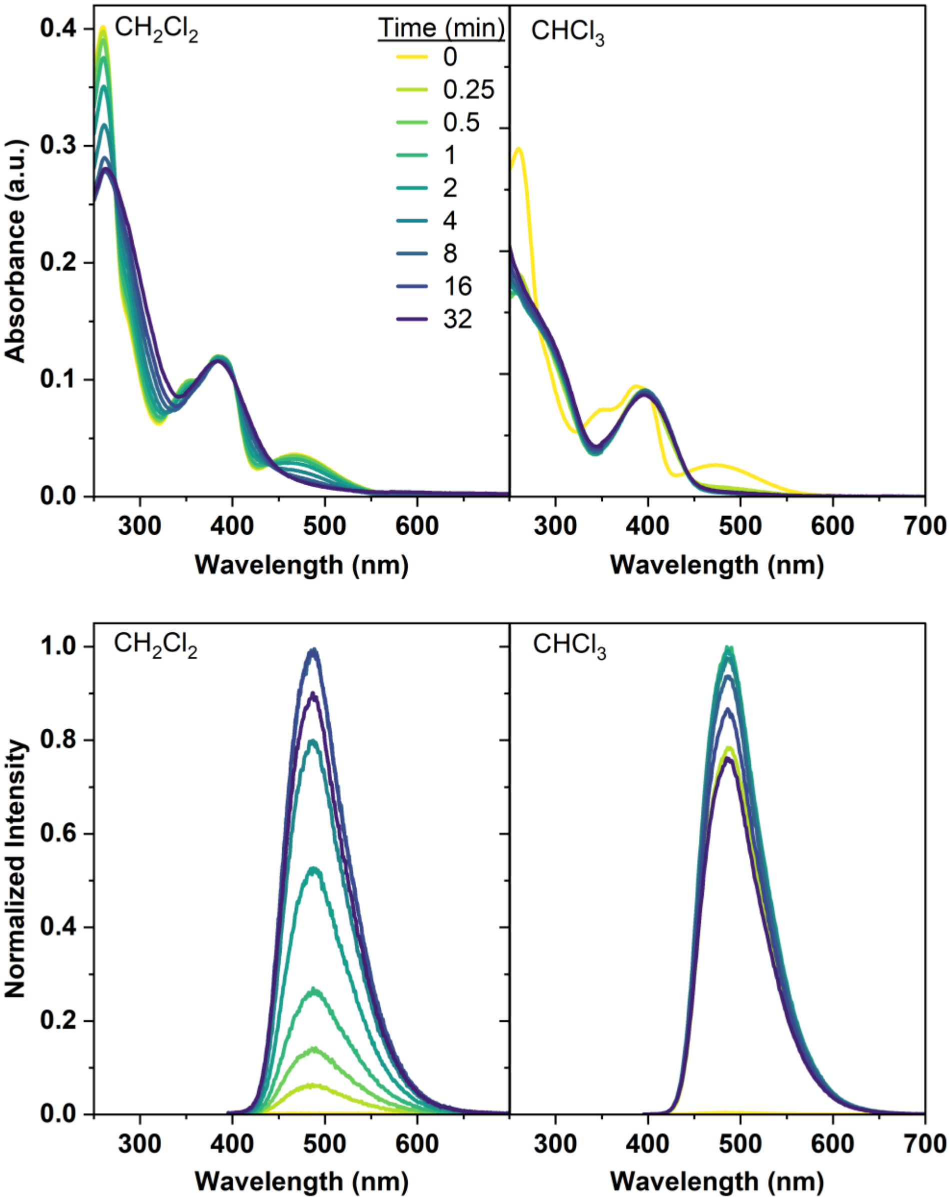


Fig. S30 UV-vis absorbance and photoluminescence spectra of compound **3** in 10 μM solutions of CH_2Cl_2 or $CHCl_3$ irradiated with UV light (254 nm) for 0–32 min.

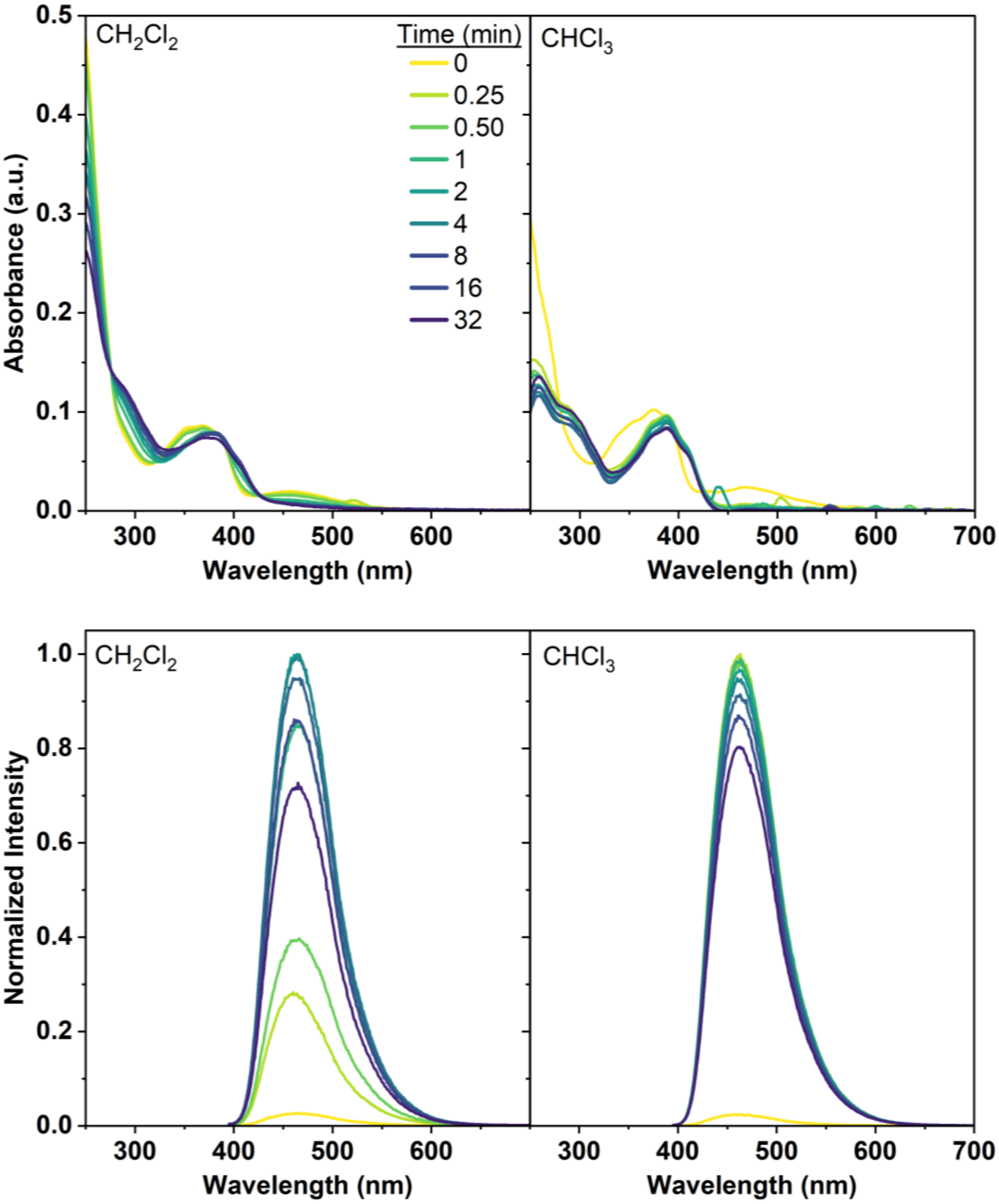


Fig. S31 UV-vis absorbance and photoluminescence spectra of compound **4** in 10 μM solutions of CH_2Cl_2 or $CHCl_3$ irradiated with UV light (254 nm) for 0–32 min.

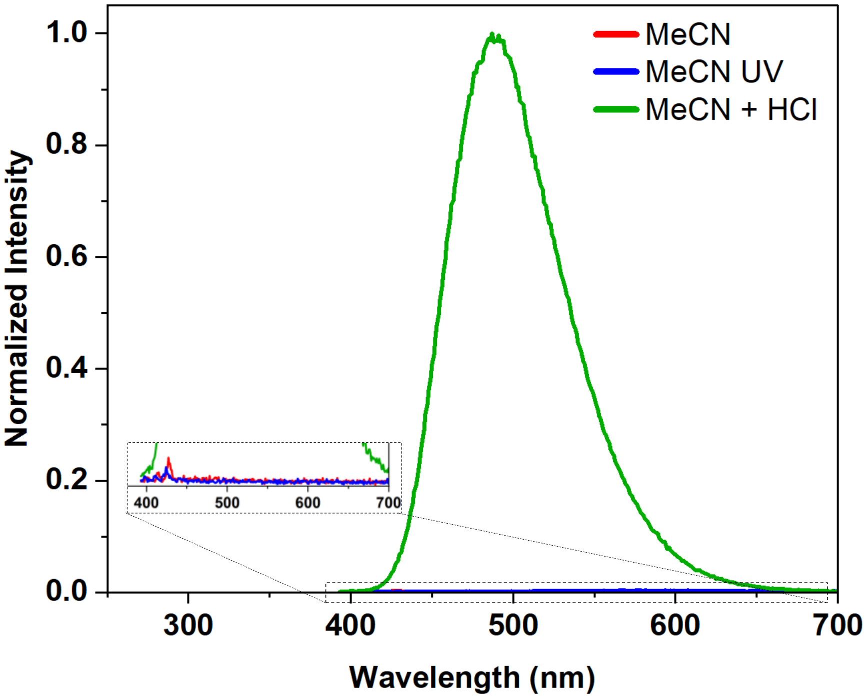


Fig. S32 Photoluminescence spectrum of compound **3** in a MeCN solution (red), irradiated with UV light for 1 min (blue), excess HCl added (green).

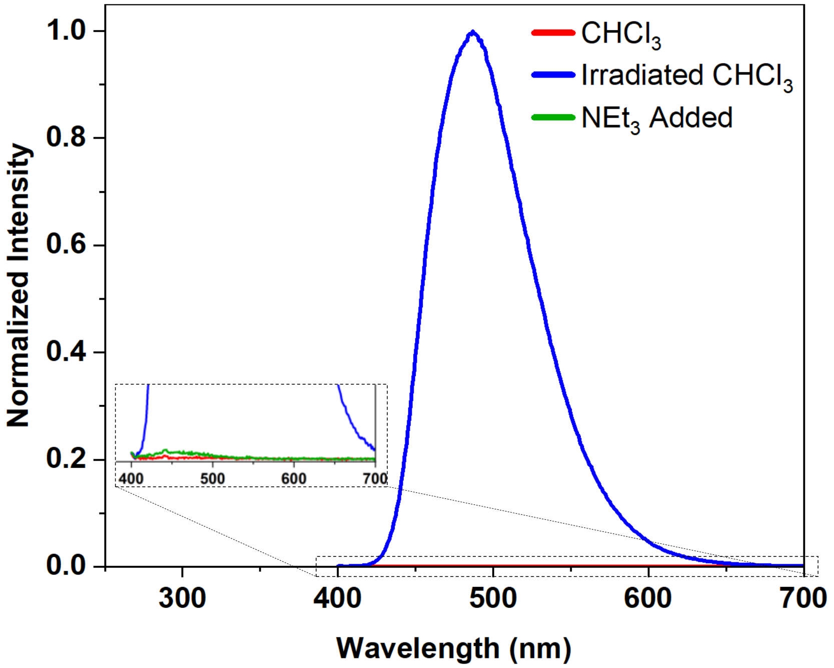


Fig. S33 Photoluminescence spectrum of compound **3** in a $CHCl_3$ solution (red), added to $CHCl_3$ that has been irradiated with UV light for 1 minute (blue), excess NEt_3 added (green).

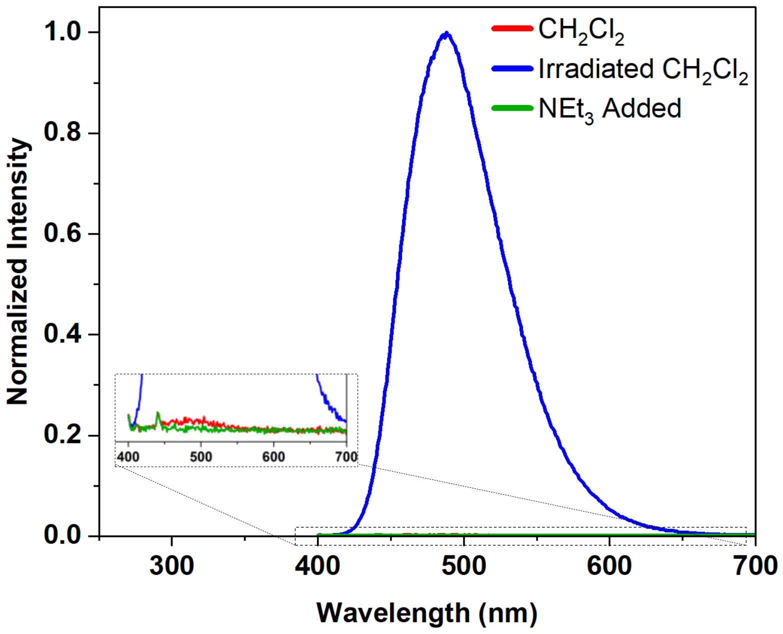


Fig. S34 Photoluminescence spectrum of compound **3** in a CH_2Cl_2 solution (red), added to CH_2Cl_2 that has been irradiated with UV light for 1 minute (blue), excess NEt_3 added (green).

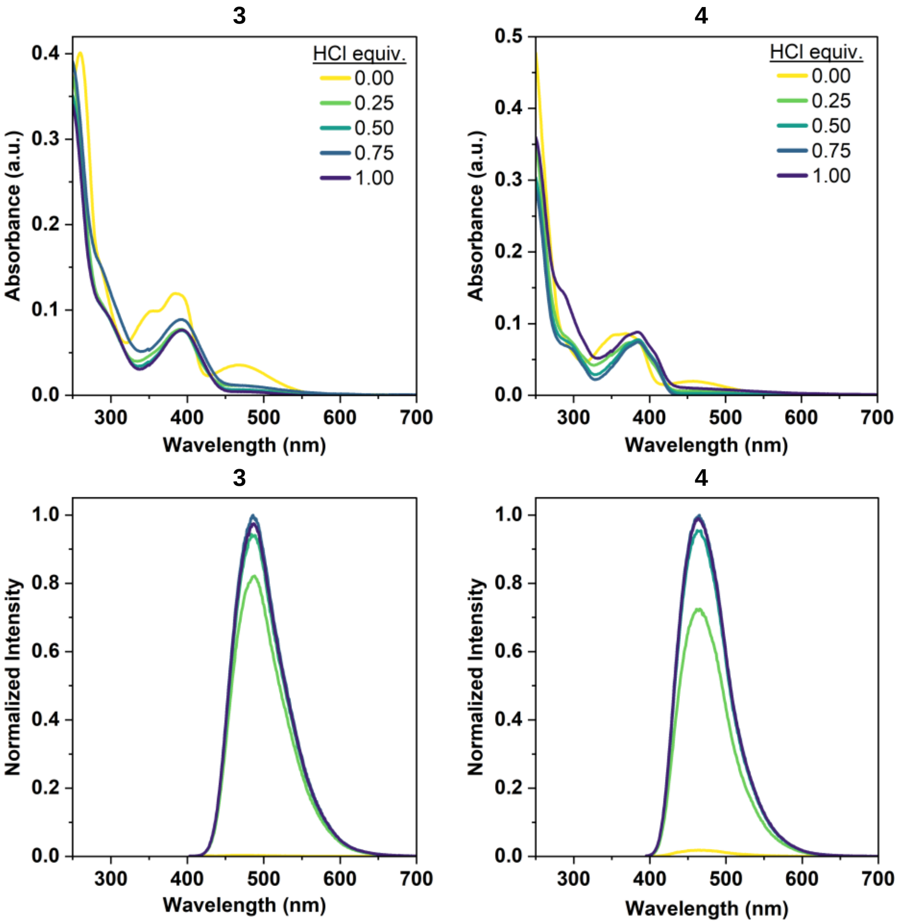


Fig. S35 UV-vis absorbance and photoluminescence spectra of compounds **3** and **4** in 10 μM solutions of CH_2Cl_2 with 0–1 molar equivalents of anhydrous HCl.

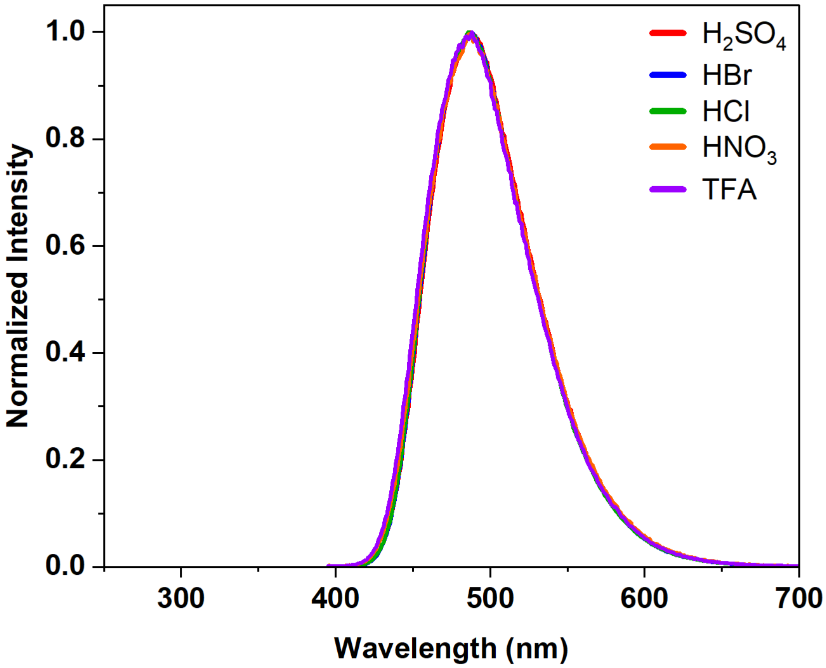


Fig. S36 Photoluminescence spectra of compound **3** in a CH_2Cl_2 solution with various acids added in excess: H_2SO_4, HBr, HCl, HNO_3 and trifluoroacetic acid (TFA).

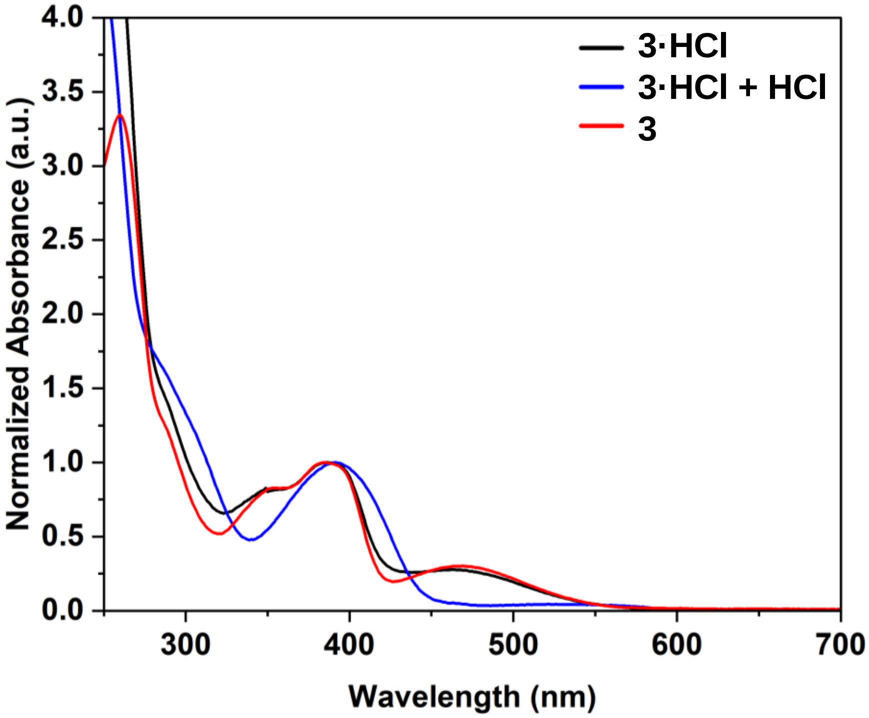


Fig. S37 Absorption spectra of compounds **3** and **3·HCl** in CH_2Cl_2, and compound **3·HCl** with 1 equiv. HCl in CH_2Cl_2.

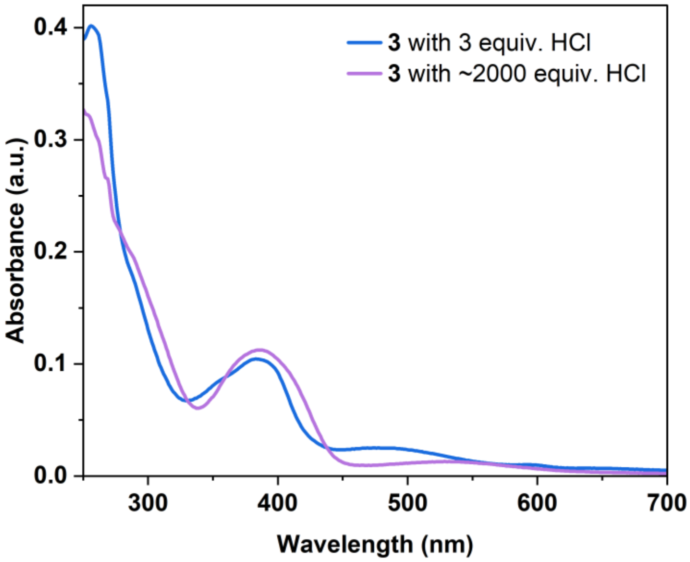


Fig. S38 UV-vis absorption spectrum of compound **3** in CH_2Cl_2 solution with excess HCl added.

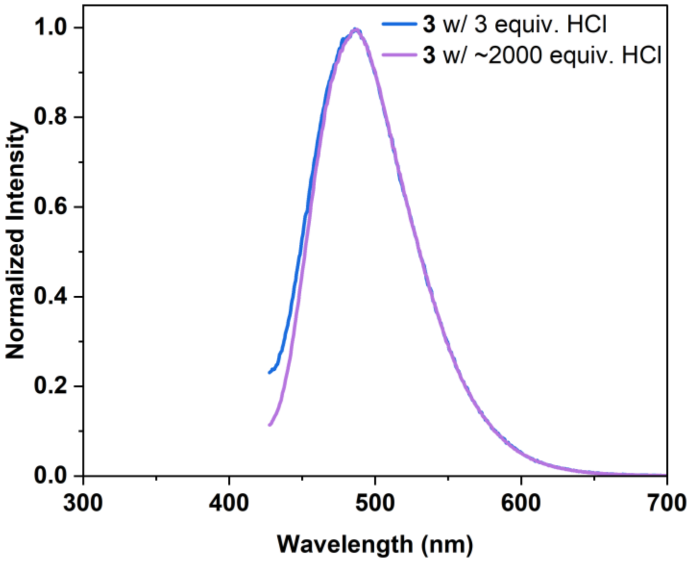


Fig. S39 UV-vis photoluminescence spectrum of compound **3** in CH_2Cl_2 solution with excess HCl added.

Cyclic Voltammetry

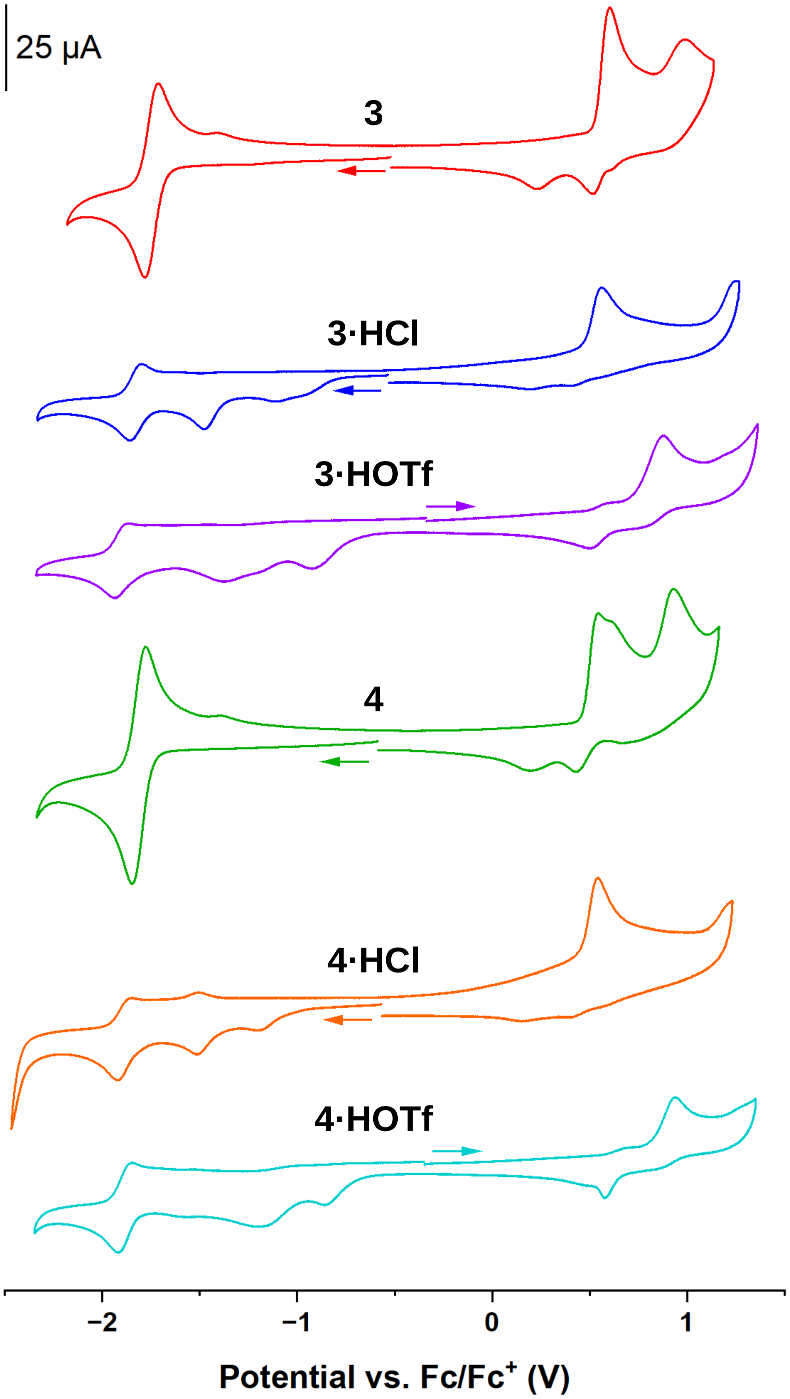


Fig. S40 Cyclic voltammograms of 0.1 mM solutions of compounds **3**, **3·HCl**, **3·HOTf**, **4**, **4·HCl**, and **4·HOTf** in dry, degassed CH_2Cl_2 solutions with 0.1 M [*n*Bu_4N][PF_6] as the supporting electrolyte. The scan rate was 250 mV s^{-1} and the arrows denote initial scan directions.

Density Functional Theory Calculations

All computed UV-Vis absorption spectra were modelled in solution (CH_2Cl_2) using a time dependent ωB97XD/def2-SVP (ω=0.14) method.

Table S2 Details of select experimental (CH_2Cl_2) and computed UV-vis absorption maxima.

	Experimental		**Theoretical**		
Compound	**λ_{max} (nm)**	**ε (M^{-1} cm^{-1})**	**λ_{max} (nm)**	**Oscillator Strength**	**Orbital Pair**
3	467	6,500	446	0.0732	HOMO→LUMO (88%) HOMO−1→LUMO (8%)
	385	12,000	367	0.1773	HOMO−1→LUMO (84%) HOMO→LUMO (9%) HOMO−7→LUMO (2%)
[3+H]$^{+a}$	386	8,200	386	0.2999	HOMO→LUMO (94%) HOMO−4→LUMO (3%)
4	451	2200	482	0.0113	HOMO→LUMO (93%) HOMO−1→LUMO (4%)
	368	7800	380	0.0844	HOMO−1→LUMO (85%) HOMO→LUMO (4%) HOMO→LUMO+1 (3%) HOMO−1→LUMO+1 (2%)
[4+H]$^{+a}$	369	5,200	371	0.1314	HOMO→LUMO (84%) HOMO−1→LUMO (7%) HOMO−2→LUMO (5%)

[a] Experimental values for compounds **3·HCl** and **4·HCl** were used as comparators.

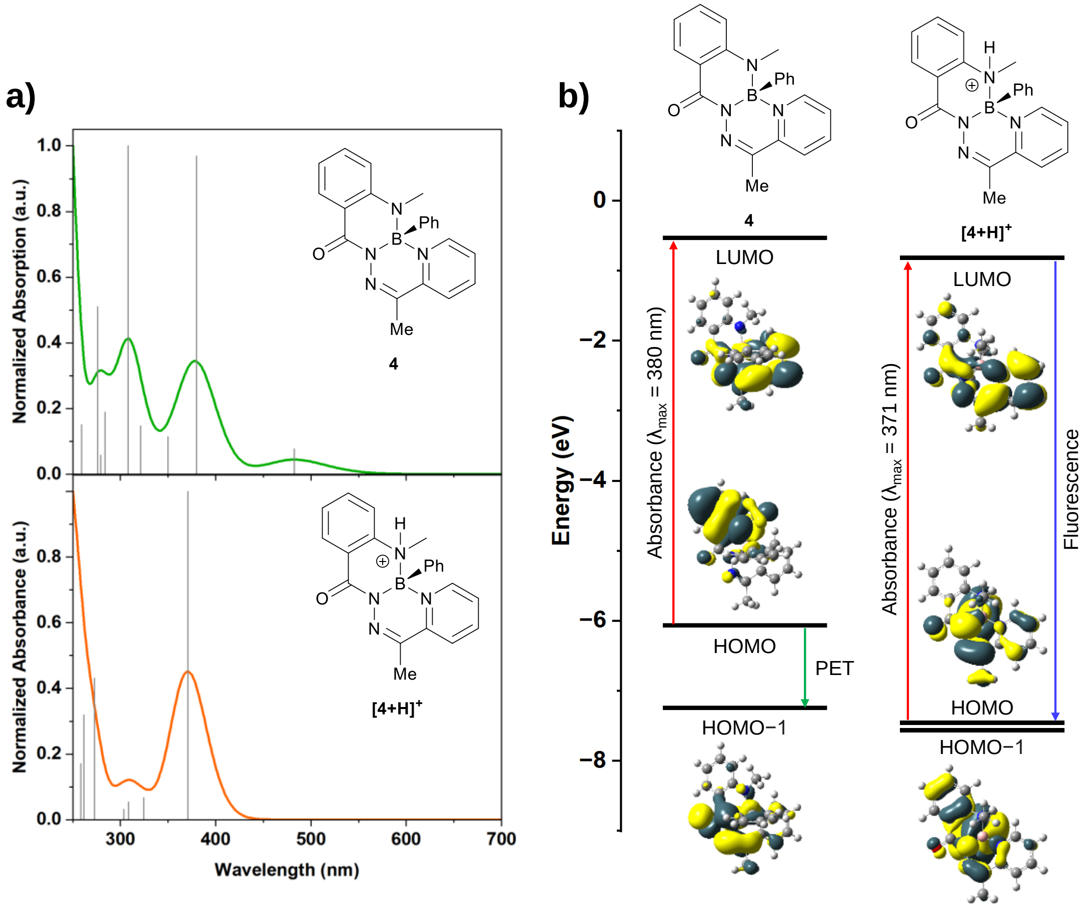


Fig. S41 a) Calculated UV-vis absorption spectra of compounds **4** and **[4+H]$^+$** by TD-DFT. b) Modelled frontier molecular orbitals of compounds **4** and **[4+H]$^+$**, molecular orbital energies, and associated photophysical processes.

Table S3 Calculated natural charge values for heteroatoms in cations **[3+H]$^+$** and **[4+H]$^+$**. Atoms are labelled according to their X-ray structure coordinates (see Fig. 3).

Compound	Atom	Natural Charge
[3+H]$^+$	B(1)	1.12
	N(1)	−0.56
	N(2)	−0.21
	N(3)	−0.57
	N(4)	−0.72
	O(1)	−0.60
[4+H]$^+$	B(1)	1.14
	N(1)	−0.60
	N(2)	−0.27
	N(3)	−0.57
	N(4)	−0.72
	O(1)	−0.60

Optimized Geometries

Compound **3** (C_1)

0 1

B	0.83729623	0.50377960	0.18128042
N	0.60542137	-0.94860077	-0.27550868
N	-0.67190313	-1.32489923	-0.48741360
N	-0.01972208	0.52456787	1.56191471
N	2.30136468	0.79207571	0.40156298
C	-1.59298002	-0.75414877	0.22677605
C	-1.26362917	-0.00885172	1.46388231
C	0.42879335	1.03236768	2.72200955
H	1.45434846	1.40898367	2.71973304
C	-0.37106418	1.07529386	3.85518487
H	0.02014689	1.51057421	4.77867684
C	-1.66779535	0.55605392	3.77800549
H	-2.32583824	0.57091495	4.65300847
C	-2.11137438	-0.00119466	2.58149908
H	-3.10427645	-0.45188755	2.50644076
C	-3.00923309	-1.04924412	-0.11672166
C	-3.99225156	-0.04912999	-0.01816553
H	-3.71926061	0.95316695	0.33452856
C	-5.31333112	-0.31754732	-0.38973403
H	-6.06977904	0.47181368	-0.31401084
C	-5.66491908	-1.58549855	-0.86432088
H	-6.70105162	-1.79652308	-1.15279311
C	-4.68797519	-2.58358057	-0.97309052
H	-4.95860491	-3.57835927	-1.34529727
C	-3.36767080	-2.31781687	-0.60564386
H	-2.59503100	-3.08927088	-0.69432531
C	1.57899879	-1.86569962	-0.65399332
O	1.30167999	-2.96029692	-1.11953760
C	2.97140139	-1.42148342	-0.39072135
C	3.99420299	-2.33998823	-0.67736965
H	3.69149666	-3.31739630	-1.06912515
C	5.33560546	-2.02670372	-0.48166138
H	6.12123544	-2.75432164	-0.71107605
C	5.65478904	-0.75395816	0.01245153
H	6.70354791	-0.47597861	0.17419775
C	4.66149465	0.17647718	0.30709671
H	4.95935597	1.15440042	0.69305206
C	3.28567281	-0.12823094	0.12426173
C	0.12947186	1.55917537	-0.85061046
C	-0.80751355	2.54423738	-0.49225349
H	-1.14212902	2.63217116	0.55105004
C	-1.33557047	3.43611604	-1.43643742

H	-2.06688061	4.19228035	-1.12582605
C	-0.93124463	3.35948727	-2.77234894
H	-1.34331720	4.05240041	-3.51567489
C	0.00684375	2.39085412	-3.15358061
H	0.33219548	2.32442520	-4.19901887
C	0.52623819	1.50900558	-2.20136472
H	1.26034171	0.75450376	-2.51778047
C	2.70347941	2.17006756	0.63770065
H	1.80933698	2.80713617	0.72197899
H	3.31443814	2.56956050	-0.19682309
H	3.29104335	2.28652237	1.56999463

Compound **[3+H]**$^+$ (C_1)

1 1

B	0.72078292	0.45039371	-0.32371824
N	0.16108574	-0.97065668	-0.16736295
N	-1.13295078	-1.23821842	0.07626606
N	-0.45321580	1.35985111	-0.87770745
N	1.85854263	0.31166426	-1.47232371
H	2.33825687	1.21346558	-1.57535946
C	-2.03917129	-0.35090239	-0.16264956
C	-1.74875933	0.95643419	-0.78659214
C	-0.14993729	2.57051622	-1.39751044
H	0.90246920	2.86710653	-1.38839178
C	-1.11405934	3.41749828	-1.91198653
H	-0.81795276	4.38523933	-2.32463501
C	-2.44823012	2.99710787	-1.88882251
H	-3.23987797	3.62821387	-2.30478520
C	-2.76139426	1.76789986	-1.31903049
H	-3.79549318	1.41853266	-1.28154531
C	-3.44328081	-0.73213482	0.16605471
C	-4.26811746	0.11510519	0.92690967
H	-3.89190054	1.08629730	1.27103906
C	-5.56338451	-0.28380850	1.26851102
H	-6.19569095	0.38101462	1.86752129
C	-6.04607968	-1.53055314	0.85555580
H	-7.06284048	-1.84087815	1.12177764
C	-5.22643928	-2.38161778	0.10527743
H	-5.59947488	-3.35980122	-0.21848990
C	-3.93067860	-1.98679431	-0.23615810
H	-3.28251492	-2.65078848	-0.81870790
C	1.02208301	-2.05472016	0.04260506
O	0.65234981	-3.14525828	0.41644487
C	2.46164824	-1.75766805	-0.25889733

C	3.43615216	-2.66362121	0.18014974
H	3.10579413	-3.54945111	0.73215825
C	4.78809118	-2.43239900	-0.07662104
H	5.54098142	-3.14288978	0.27986883
C	5.18013188	-1.29288779	-0.78664115
H	6.23966859	-1.10369174	-0.98804387
C	4.21957775	-0.38629439	-1.24546832
H	4.52048270	0.50597995	-1.80670739
C	2.87507847	-0.62598473	-0.97475720
C	1.34646092	1.07814620	1.02319544
C	2.30977471	2.10572438	1.02999721
H	2.72050785	2.50857982	0.09244733
C	2.79199150	2.64954040	2.22481988
H	3.54715774	3.44340161	2.19802325
C	2.31268568	2.17536667	3.45070182
H	2.68909678	2.59768826	4.38948960
C	1.35450484	1.15674580	3.47050714
H	0.97544210	0.77689912	4.42627760
C	0.88196796	0.61635949	2.26981653
H	0.13681512	-0.18875139	2.31041666
C	1.35887549	-0.08645080	-2.82768747
H	0.69801902	0.70088033	-3.21784461
H	0.79961748	-1.02840623	-2.73625769
H	2.21754008	-0.22067003	-3.50099794

Compound **4** (*C_1*)

0 1

B	4.50192484	12.37411383	8.61701316
N	5.32562627	13.53343298	9.25277782
N	5.02119690	13.86421689	10.55810224
N	3.04457168	12.90454048	8.57632898
N	5.08315279	11.96736335	7.19723415
C	3.72932537	13.93754530	10.79770109
C	2.68025750	13.60675116	9.66676030
C	2.19813778	12.65391168	7.56881031
H	2.53705784	12.11660555	6.70780199
C	0.90694706	13.07670379	7.64043032
H	0.23581519	12.87862295	6.83095765
C	0.46524559	13.74646429	8.73702625
H	-0.55529435	14.06181176	8.79990865
C	1.35291968	14.02316898	9.78305027
H	1.02113584	14.54806221	10.65443226
C	3.23718186	14.38426932	12.18688518
C	6.23656254	14.22153479	8.56442866

O	6.86158819	15.16380321	9.11673630
C	6.51361106	13.87547215	7.09486414
C	7.38417244	14.67344183	6.34264234
H	7.84667963	15.52825160	6.79017709
C	7.64216518	14.36419217	5.04796636
H	8.30617281	14.97844071	4.47639607
C	7.04366088	13.24267768	4.45361475
H	7.25540460	13.00604322	3.43181794
C	6.19859468	12.45654384	5.16623411
H	5.74951393	11.60145131	4.70575258
C	5.91181155	12.76107677	6.50307637
C	4.50748817	11.02867607	9.57213948
C	3.39172340	10.18396487	9.60582142
H	2.53151459	10.40988842	9.01092702
C	3.40135742	9.04114048	10.41959103
H	2.54660959	8.39788794	10.44266270
C	4.48862714	8.74591384	11.17836170
H	4.48473174	7.87163063	11.79521963
C	5.61671755	9.57980928	11.15856798
H	6.46942243	9.34062205	11.75905433
C	5.62673664	10.72476509	10.35322437
H	6.48523777	11.36316984	10.33547141
C	4.70588764	10.66695402	6.62495225
H	4.52092774	9.96966530	7.41519163
H	5.50156799	10.30432284	6.00827454
H	3.82055921	10.78031748	6.03483166
H	3.95571686	15.04563744	12.62414902
H	2.30012092	14.89112422	12.08731158
H	3.11376395	13.52643246	12.81440724

Compound **[4+H]**$^+$ (C_1)

1 1

B	6.26275066	11.25220195	14.15190033
N	7.58968615	11.48874444	14.96158803
N	7.73386989	10.51541101	15.96521122
N	6.25004910	9.77795512	13.61607988
N	6.19544358	12.29101484	12.96791844
H	5.36690721	12.13327253	12.43066167
C	7.49170989	9.25968166	15.70606464
C	6.80757673	8.84197834	14.38448832
C	5.68072556	9.47010013	12.44154183
H	5.25875281	10.24346549	11.83429804
C	5.63520139	8.17989229	12.02238165
H	5.18261842	7.93602629	11.08397980

C	6.18048657	7.16888612	12.82304119
H	6.13847821	6.14730756	12.50758511
C	6.76175039	7.49778776	13.99835507
H	7.18400363	6.73979314	14.62449113
C	7.90408007	8.17993760	16.72375988
C	7.52802729	12.83619995	15.53098480
O	8.07915317	13.08829123	16.63383601
C	6.78534195	13.94356219	14.75782702
C	6.73175411	15.24009738	15.28307601
H	7.19751476	15.46020196	16.22090381
C	6.06724367	16.24588004	14.57526353
H	6.02112383	17.24004482	14.96821307
C	5.46306933	15.94470779	13.34941432
H	4.95560185	16.71071683	12.80113802
C	5.52170983	14.63926650	12.83894940
H	5.05689348	14.41487720	11.90166865
C	6.16288153	13.65727167	13.52495102
C	4.95204619	11.46698000	15.13089175
C	3.74262602	11.92605299	14.59193276
H	3.66917842	12.13728363	13.54556425
C	2.62940091	12.10847075	15.42342273
H	1.70598224	12.45898474	15.01191587
C	2.72559536	11.83181347	16.79387132
H	1.87562280	11.97109186	17.42873208
C	3.93501612	11.37274242	17.33283066
H	4.00846295	11.16150923	18.37919871
C	5.04824138	11.19032516	16.50134078
H	5.97166023	10.83981177	16.91284775
C	7.37501281	12.13162177	12.10530016
H	7.39303929	11.13927851	11.70551283
H	8.26206275	12.30112255	12.67915719
H	7.32853439	12.83844343	11.30333826
H	8.76568998	8.51063360	17.26521026
H	7.09850666	8.00702619	17.40644073
H	8.13456049	7.27194122	16.20672859

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