Synthesis of Dual State Emissive β-Carboline Boron Complexes

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1. General methods and materials

All chemical reactions were carried out under argon atmosphere in sealed pressure tubes. The chemicals used were obtained from commercial suppliers. The solvents like TEA, DCM, DCE were dried by distillation process over calcium hydride and THF was purified over sodium-benzophenone under argon atmosphere. All other solvents like ethanol, methanol, petroleum ether, chloroform, ethyl acetate, dimethyl sulphoxide used were from reputed companies of Analytical grade and used without purification. Reactions were monitored by thin-layer chromatography which was performed in commercially available 0.25 mm fluorescent silica gel plate (F-254) and visualized using a UV lamp (254 nm wavelength) or developed in iodine chamber or in alkaline $KMnO_4$ solution after heating. SC-XRD data was obtained using CrysAlisPro 1.171.40.57a (Rigaku Oxford Diffraction, 2019). High Resolution Mass Spectrometric (HRMS) analysis was performed using either 6540 UHD Accurate-Mass Agilent Q-TOF LC/MS instrument or Bruker Maxis Impact Q-TOF LC/MS instrument. Spectroscopic data was taken from JASCO V-670 spectrophotometer & JASCO FP-6500 spectrofluorometer. The excited state (S_1) lifetime measurements were done using an LED based time-correlated single-photon-counting (TCSPC) spectrometer, Edinburgh F980 instrument. ^{1}H & ^{13}C NMR spectra were recorded on 300 MHz Bruker FT-NMR & 500 MHz Varian FT-NMR instruments.

2. Synthetic procedure

Tryptophan methyl ester (2). Thionyl chloride (29.37 mmol, 2.13 mL) was added dropwise to the stirred solution of tryptophan (**1)** (24.48 mmol, 5 g) in dry methanol (100 mL) at 0 °C and the mixture was stirred at room temperature for 6 h. Next, excess solvent was removed in vacuum and crude product was triturated by dry ether (100 mL) to obtain solid tryptophan methyl ester hydrochloride salt. The resulting solid was dissolved in DCM (100 mL), basified by saturated aq. $NaHCO_3$ (100 mL) and after 30 min of stirring, the organic part was extracted with DCM (2 X 100 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum to obtain sticky liquid. After keeping it in refrigerator for overnight, off white solid product tryptophan methyl ester (**2)** was obtained (4.4 g, 83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.68 (s, 2H), 3.03-3.08 (dd, *J* = 14.5 Hz, 7.8 Hz, 1H), 3.27-3.31 (dd, *J* = 14.5 Hz, 4.6 Hz, 1H), 3.72 (s, 3H), 3.83-3.85 (dd, *J* = 7.9 Hz, 4.8 Hz, 1H), 7.00 (s, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.19 (t, *J* = 7.1 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 8.46 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 31.0, 52.3, 55.2, 111.2, 111.6, 118.9, 119.7, 122.4, 123.3, 127.7, 136.6, 176.1 ppm; HRMS (ESI-TOF): m/z $[M+H]^+$ calculated for $C_{12}H_{14}N_2O_2$: 219.1128, found 219.0835.

1-(2-pyridinyl)-3-carbomethoxy-β-carboline (4).[1] To a mixture of tryptophan methyl ester (**2**) (4.5 mmol, 981 mg) and 2-pyridine aldehyde (4.95 mmol, 473 μL) in toluene (15 mL), a catalytic amount of PTS (10 mol%) was added and the mixture was refluxed for 4 h. After completion of condensation (monitored by TLC), the solvent was removed under vacuum. The resulting reaction mixture was dissolved in DCM (100 mL) and washed with water (3 × 50 mL). The organic layer was then dried with anhydrous Na_2SO_4 and concentrated under vacuum to get the diastereomeric mixture of 1,2,3,4-tetrahydro-1-(2-pyridinyl)-3-carbomethoxy-β-carboline (**3**) (885 mg, 64%) which was used in the next step without further purification.

A suspension of crude product **3** (8 mmol, 2.5 g) and sulphur (24 mmol, 768 mg) in xylene (30 mL) were stirred at 135 °C for 8 h. The mixture was left open at room temperature for 24 h to obtain a solid precipitate which was purified by column chromatography (silica gel, EtOAc: petroleum ether, 30:70) to furnish 1-(2-pyridinyl)-3-carbomethoxy-β-carboline (**4**) (1.8 g, 74%) as an off-white solid. R_f = 0.77 (EtOAc /hexane, 30: 70, v/v); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.09 (s, 3H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 6.1 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.96 (t, *J* = 7.8, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 8.79-8.80 (m, 1H), 8.91-8.93 (m, 2H), 11.73 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.9, 112.5, 118.5, 121.0, 121.7, 122.1, 122.2, 123.7, 129.2, 130.8, 136.4, 136.9, 137.3, 137.9, 141.2, 148.5, 157.4, 167.0 ppm; HRMS (ESI-TOF): m/z $[M+H]^+$calculated for $C_{18}H_{13}N_3O_2$: 304.1081, found 304.0759.

1-(2-pyridinyl)-3-carbomethoxy-β-carboline diphenylboron complex (6). A mixture of **4** (0.33 mmol, 100 mg) and BPh_3 (0.66 mmol, 160 mg) in dry toluene (5 mL) was stirred at 90 °C under argon for 12 h. The resulting dark mixture was washed with saturated aq. $NaHCO_3$, water and brine. Resulting organic layer was dried over anhydrous Na_2SO_4. Removal of solvent in vacuo followed by column chromatography of the residue (silica gel, EtOAc: petroleum ether, 30:70) furnished dye **6** (117 mg, 76%) as the orange yellow solid. R_f = 0.35 (EtOAc /hexane, 40: 60, v/v); mp: > 260 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.09 (s, 3H), 6.95 (d, *J* = 8.3 Hz, 1H), 7.02-7.22 (m, 10H), 7.26-7.27 (m, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.49-7.54 (m, 1H), 8.17-8.22 (m, 2H), 8.52 (d, *J* = 6.0 Hz, 1H), 8.97 (s, 1H), 9.18 (d, *J* = 7.3 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 53.0, 115.9, 120.6, 120.8, 122.4, 122.7, 123.3, 124.7, 127.4, 128.1, 128.2, 129.0, 130.9, 131.7, 133.8, 133.9, 136.7, 138.9, 141.6, 146.5, 146.7, 151.2, 166.9, 171.5 ppm; HRMS (ESI-TOF): m/z $[M+H]^+$calculated for $C_{30}H_{22}BN_3O_2$: 468.1878, found 468.1497.

(1-Pyridin-2-yl-9-β-carbolin-3-yl)-methanol (7). The compound **4** (3.3 mmol, 1g) was subjected to react with $LiAlH_4$ (13.2 mmol, 528 mg) in dry THF (50 mL) at 0°C for 4 h. The reaction mixture passed through a small celite pad and eluted with 100 mL MeOH:$CHCl_3$ (20:80), evaporated under vacuum and the residue was purified by column chromatography **(**silica gel, EtOAc: petroleum ether, 30:70) to furnish **7** (741 mg, 74%) as yellow solid. R_f = 0.42 ($CH_3OH/CHCl_3$, 10: 90, v/v); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.99 (s, 2H), 7.28 (t, J = 7.0 Hz, 1H), 7.34 (t, *J* = 6.2 Hz, 1H), 7.56-7.62 (m, 2H), 7.88-7.92 (m, 2H), 8.13 (d, *J* = 7.8 Hz, 1H), 8.72 (d, *J* = 7.8 Hz, 1H), 8.80 (d, *J* = 4.8 Hz, 1H), 11.23 (s, 1H) ppm; ^{13}C NMR (125 MHz, CDCl3): δ 65.1, 112.2, 112.3, 120.2, 121.3, 121.5, 122.1, 123.3, 129.0, 132.1, 134.6, 136.7, 137.1, 141.6, 147.5, 148.7, 157.8 ppm.

3-Formyl-1-(2-pyridinyl)-β-carboline (8).[2] The compound **7** (3.3 mmol, 909 mg) was stirred with MnO_2 (26.4 mmol, 2.3 g) in dry DCM (15 mL) under oxygen atmosphere at room temperature for 24 h. The mixture was passed through a small celite pad and eluted by 50 ml MeOH:$CHCl_3$ (10:90), evaporated under vacuum and the residue was then purified by column chromatography (silica gel, EtOAc: petroleum ether, 30:70) to furnish **8** (400 mg, 44%) as white solid. R_f = 0.79 (EtOAc/hexane, 30:70, v/v); HRMS (ESI-TOF): m/z $[M+H]^+$ calculated for $C_{17}H_{11}N_3O$: 274.0975, found 274.0697.

3-(2'-phenyl-1',3',4'-oxadiazole)-1-(2-pyridinyl)-β-carboline (10).[3] A mixture of dye **8** (0.36 mmol, 100 mg) and benzhydrazide (0.36 mmol, 50 mg) in absolute EtOH (5 mL) was refluxed for 2 h. Then the solvent was evaporated under vacuum and the residue (**8'**) was dried which was used directly for the next step.

The mixture of the residue (**8'**), Cs_2CO_3 (0.73 mmol, 238 mg) and I_2 (0.73 mmol, 186 mg) in DMSO (5 mL) was stirred at 90 °C for 1 h. The reaction was quenched with aq. $Na_2S_2O_3$ (10%) and extracted with EtOAc. The organic layer was washed with H_2O (50 mL × 3) and dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by column chromatography (silica gel, EtOAc: petroleum ether, 30:70) to afford the desired product dye **10** (108 mg, 76%) as brown orange solid. R_f = 0.55 (EtOAc/hexane, 30:70, v/v); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28-7.33 (m, 2H), 7.54-7.59 (m, 5H), 7.90 (t, *J* = 7.8 Hz, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 8.22-8.23 (m, 2H), 8.71 (d, *J* = 4.6 Hz, 1H), 8.82-8.83 (m, 2H), 11.4 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 112.2, 115.5, 120.7, 121.1, 121.8, 121.9, 123.5, 124.2, 127.0, 129.0, 129.1, 130.7, 131.6, 131.9, 135.3, 136.9, 137.7, 140.9, 148.2, 156.9, 164.7, 165.1 ppm; HRMS (ESI-TOF): m/z $[M+H]^+$ calculated for $C_{24}H_{15}N_5O$: 390.1349, found 390.1046.

General procedure for the synthesis of BF_2 complexes. A mixture of the ligand (**4**/**8**/**10**) and Et_3N in dry DCE was stirred at 25 °C for 15 min. Then $BF_3 \cdot OEt_2$ was added drop wise into it, and the reaction mixture was stirred at 70 °C for 12 h. The reaction was quenched with saturated aq. $NaHCO_3$ and extracted with DCM. The organic layer was washed with H_2O (50 mL × 3) and dried over anhydrous Na_2SO_4. After removal of the solvent under a vacuum, the residue was purified by column chromatography on silica gel to afford the desired product.

1-(2-Pyridinyl)-3-carbomethoxy-β-carboline difluoroboron complex (5). Dye **5** was prepared by reaction of **4** (0.33 mmol, 100 mg), Et_3N (2 mmol, 278 μL) and $BF_3 \cdot OEt_2$ (2 mmol, 242 μL) in 10 mL of DCE according to the general procedure. The crude product was purified by column chromatography (silica gel, EtOAc/petroleum ether, 40:60) to furnish pure **5** (90 mg, 78%) as the yellow cadmium solid. R_f = 0.33 (EtOAc/hexane, 40:60, v/v); mp: 228.2–229.2 °C; HRMS (ESI-TOF): m/z $[M+H]^+$ calculated for $C_{18}H_{12}BF_2N_3O_2$: 352.1063, found 352.0782.

3-Formyl-1-(2-pyridinyl)-β-carboline difluoroboron complex (9). Dye **9** was prepared by reaction of **8** (0.18 mmol, 50 mg), Et_3N (1.08 mmol, 109 μL) and $BF_3 \cdot OEt_2$ (1.08 mmol, 153 μL) in 5 mL of DCE according to the general procedure. The crude product was purified by column chromatography (silica gel, EtOAc/petroleum ether, 30:70) to furnish pure **9** (27 mg, 55%) as greenish yellow solid. R_f = 0.57 (EtOAc/hexane, 30:70, v/v); mp: 223.1–224.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 (t, *J* = 7.6 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.83 (t, *J* = 6.7 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 8.39 (d, *J* = 7.8 Hz, 1H), 8.80 (s, 1H), 9.01 (d, *J* = 5.6 Hz, 1H), 9.18 (d, *J* = 8.1 Hz, 1H), 10.26 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 115.2, 117.5, 122.3, 122.4, 122.9, 123.4, 125.3, 129.9, 130.4, 131.5, 138.4, 143.0, 143.5, 144.6, 145.0, 150.1, 193.0 ppm; HRMS (ESI-TOF): m/z $[M+H]^+$ calculated for $C_{17}H_{10}BF_2N_3O$: 322.0958, found 322.0631.

3-(2’-Phenyl-1’,3’,4’-oxadiazole)-1-(2-pyridinyl)-β-carboline difluoroboron complex (11). Dye **11** was prepared by reaction of **10** (0.26 mmol, 105 mg), Et_3N (1.61 mmol, 225 μL) and $BF_3 \cdot OEt_2$ (1,88 mmol, 233 μL) in 7 mL of DCE according to the general procedure. The crude product was purified by column chromatography (silica gel, EtOAc/petroleum ether, 30:70) to furnish pure **9** (85 mg, 75%) as bright yellow solid; R_f = 0.26 (EtOAc/hexane, 40:60, v/v); mp: 236.1–237.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (t, *J* = 7.4 Hz, 1H), 7.60 (s, 3H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.79 (t, *J* = 6.1 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 8.24-8.28 (m, 3H), 8.38 (t, *J* = 7.2 Hz, 1H), 9.02 (d, *J* = 6.0 Hz, 1H), 9.06 (s, 1H), 9.23 (d, *J* = 7.2 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 109.0, 115.1, 118.6, 121.3, 122.1, 122.6, 122.9, 124.3, 125.2, 125.4, 127.5, 129.4, 129.9, 130.4, 131.8, 132.2, 133.6, 137.0, 142.9, 143.5, 145.1, 150.1, 165.1, 165.4 ppm; HRMS (ESI-TOF): m/z $[M+H]^+$ calculated for $C_{24}H_{14}BF_2N_5O$: 438.1332, found 438.1300.

3. Cyclic Voltammetric studies

Oxidation and reduction potentials were determined by cyclic voltammetry with a conventional 3-electrode system using a voltammetric analyzer equipped with a Glassy carbon working electrode and a platinum wire counter electrode. The reference electrode is constituted of a non-aqueous Pt electrode including the electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in DCM. Potentials were calibrated versus the Pt wire using the ferrocene/ferrocinium (Fc/Fc^+) couple as an internal reference and a conventional scan rate of 100 mV/s. Recrystallized tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte (0.1 M) in distilled and anhydrous DCM. All potentials are referred to the Pt wire electrode that was calibrated at 0.38 V vs Fc/Fc^+ system.

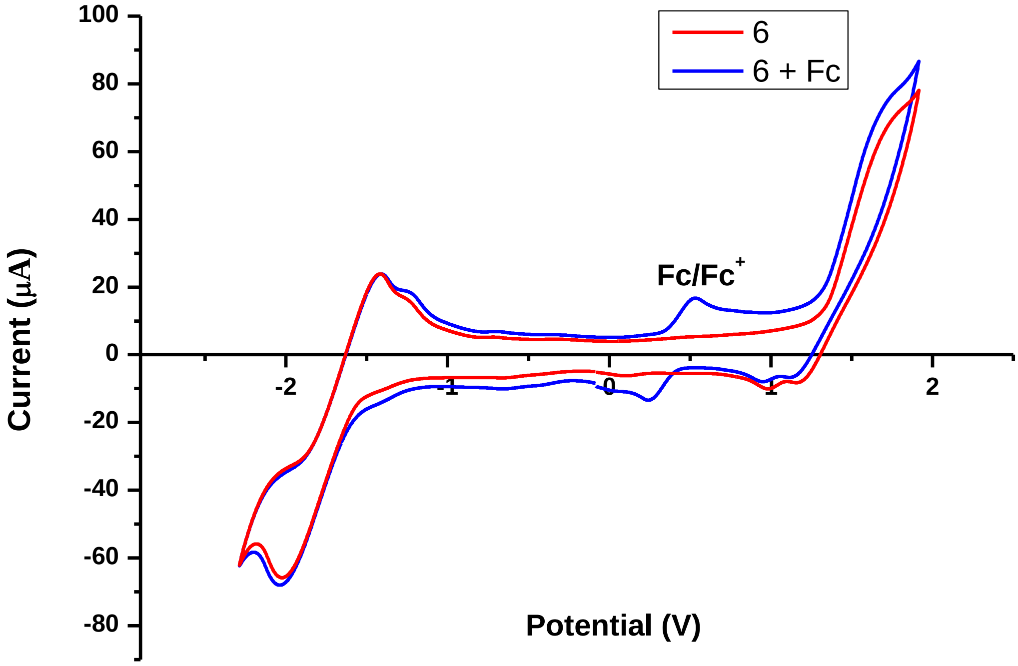
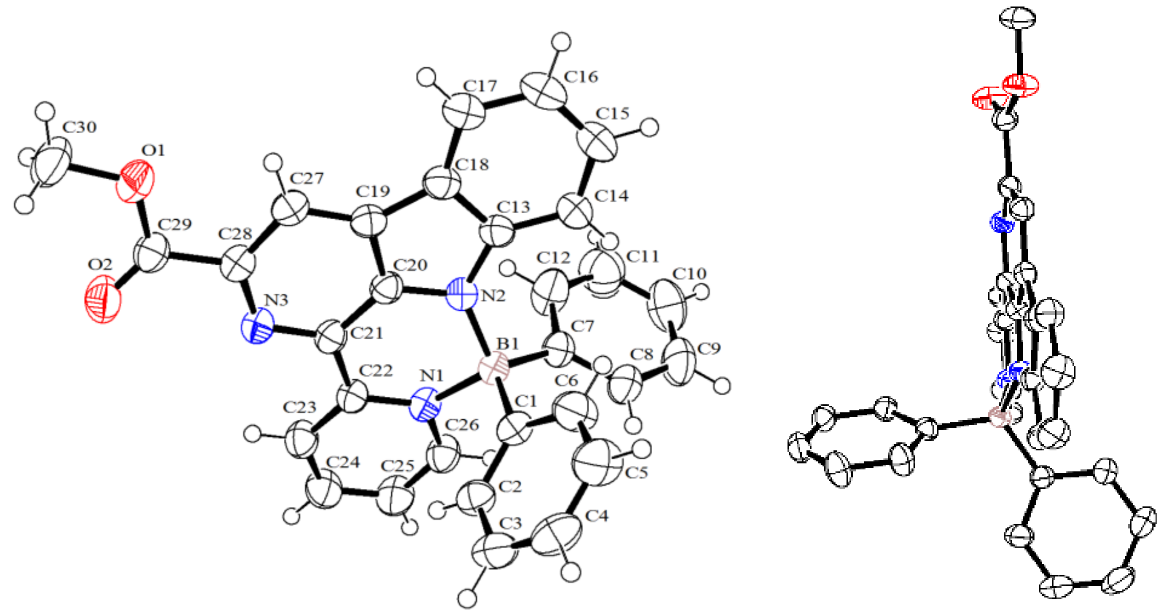


Figure S1. Cyclic voltammograms, in the anodic and cathodic region of dye **6** and dye **6** with ferrocene in DCM containing 0.1 M tetrabutylammonium hexafluorophosphate at 25 °C; scan rate 100 mVs^{-1}. All peaks were calibrated against ferrocene (Fc/Fc^+) at $E_{½}$ = 0.38 V vs Pt wire.

4. Crystallographic studies

The crystallographic data for dye **6** were collected using Cu K_α radiation (λ = 1.54184 Å) from a single crystal at 298(2) K on a XtaLAB Synergy, Dualflex, HyPix four-circle diffractometer with a micro-focus sealed X-ray tube using mirror as monochromator and a HyPix detector. All data were integrated with CrysAlis PRO and a multi-scan absorption correction using SCALE3 ABSPACK was applied.[4] The structure were solved by itertive methods using ShelXT and refined by full-matrix least-squares methods against F^2 by SHELXL-2017/1.[5, 6] Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was refined (weighted least squares refinement on F^2) to convergence. Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.[7] CCDC 2245158 contain the supplementary crystallographic data for this paper.

(a)



(b)

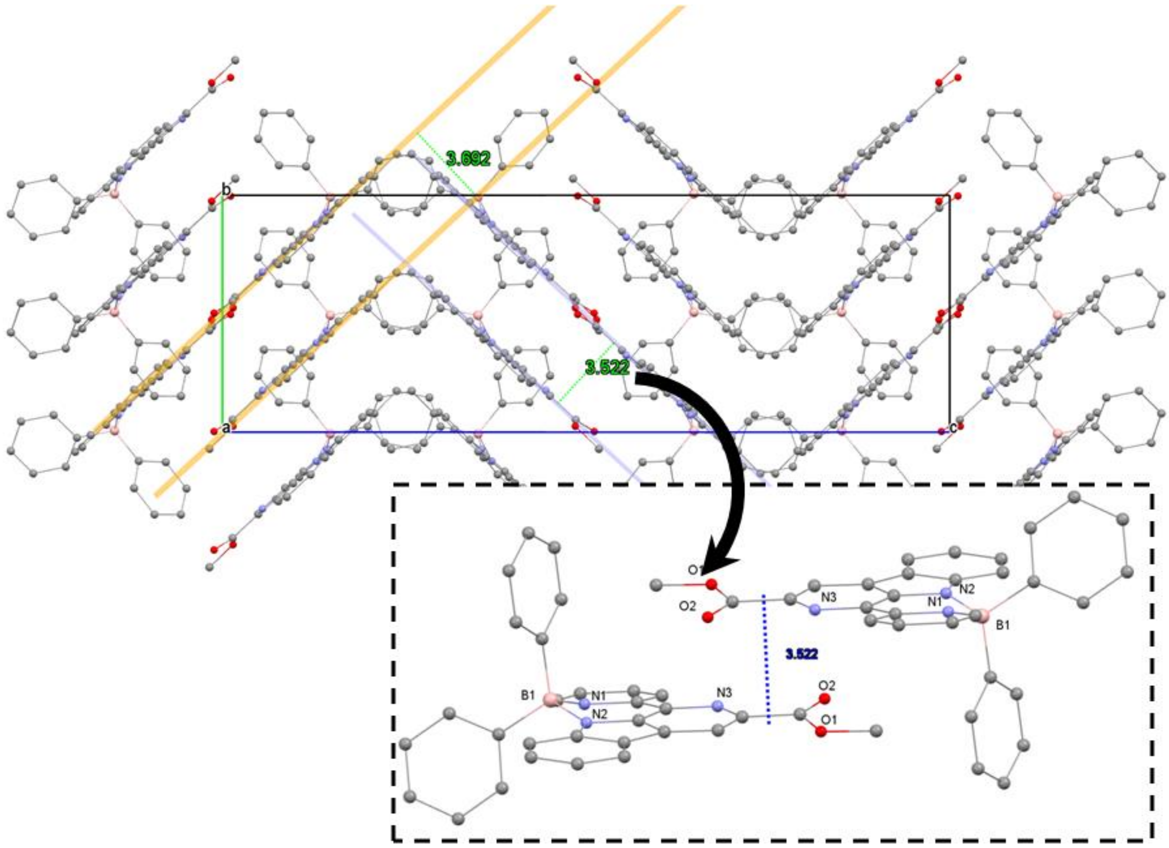


Figure S2. (a) Two orthogonal Ortep views of the crystal structure of dye **6**. (b) Packing diagram of dye **6** along *a*-axis. Inset: The arrangement of molecules along *b*-axis.

Table S1. Crystal data and structure refinement for shelx of dye **6**.

CCDC number	2245158
Empirical formula	$C_{30}H_{22}BN_3O_2$
Formula weight	467.31
Temperature [K]	298(2)
Crystal system	monoclinic
Space group (number)	$C2/c$ (15)
a [Å]	16.0809(2)
b [Å]	9.84330(10)
c [Å]	31.2561(3)
α [Å]	90
β [Å]	104.9550(10)
γ [Å]	90
Volume [$Å^3$]	4779.92(9)
Z	8
ρ_{calc} [g/cm^3]	1.299
μ [mm^{-1}]	0.649
F(000)	1952
Crystal size [mm^3]	0.090×0.080×0.010
Crystal colour	yellow
Crystal shape	plate
Radiation	Cu K_α (λ=1.54184 Å)
2Θ range [°]	5.85 to 154.36 (0.79 Å)
Index ranges	$-19 \le h \le 17$ $-12 \le k \le 12$ $-39 \le l \le 39$
Reflections collected	60396
Independent reflections	5027 R_{int} = 0.0831 R_{sigma} = 0.0346

Completeness to θ = 67.684°	99.9 %
Data / Restraints / Parameters	5027/0/326
Goodness-of-fit on F^2	1.060
Final R indexes [I≥2σ(I)]	R_1 = 0.0645 wR_2 = 0.2004
Final R indexes [all data]	R_1 = 0.0824 wR_2 = 0.2299
Largest peak/hole [eÅ^3]	1.25/-0.39

Table S2. Bond lengths and angles for shelx of dye **6.**

Atom–Atom	**Length [Å]**
C1–C2	1.397(3)
C1–C6	1.399(3)
C1–B1	1.622(3)
C2–C3	1.395(3)
C3–C4	1.364(3)
C4–C5	1.380(4)
C5–C6	1.383(3)
C7–C8	1.388(3)
C7–C12	1.401(3)
C7–B1	1.615(3)
C8–C9	1.390(3)
C9–C10	1.370(4)
C10–C11	1.377(4)
C11–C12	1.385(3)
C13–N2	1.394(2)
C13–C14	1.401(3)
C13–C18	1.418(3)
C14–C15	1.377(3)
C15–C16	1.396(4)
C16–C17	1.385(3)
C17–C18	1.392(3)
C18–C19	1.442(3)
C19–C27	1.388(3)
C19–C20	1.408(2)
C20–N2	1.360(2)
C20–C21	1.394(2)
C21–N3	1.337(2)
C21–C22	1.468(2)

C22–N1	1.370(2)
C22–C23	1.390(3)
C23–C24	1.368(3)
C24–C25	1.390(3)
C25–C26	1.369(3)
C26–N1	1.346(2)
C27–C28	1.397(3)
C28–N3	1.345(2)
C28–C29	1.502(3)
C29–O2	1.199(2)
C29–O1	1.336(2)
B1–N2	1.556(2)
B1–N1	1.645(2)
O1–C30	1.435(3)
Atom–Atom–Atom	**Angle [°]**
C2–C1–C6	115.20(17)
C2–C1–B1	125.25(16)
C6–C1–B1	119.47(17)
C3–C2–C1	122.09(19)
C4–C3–C2	120.7(2)
C4–C3–H3	119.6
C3–C4–C5	119.01(19)
C4–C5–C6	120.1(2)
C5–C6–C1	122.9(2)
C8–C7–C12	116.48(19)
C8–C7–B1	123.52(17)
C12–C7–B1	119.76(17)
C7–C8–C9	122.1(2)
C10–C9–C8	120.0(2)
C9–C10–C11	119.6(2)
C10–C11–C12	120.2(3)
C11–C12–C7	121.6(2)
N2–C13–C14	129.17(18)
N2–C13–C18	110.32(16)
C14–C13–C18	120.50(18)
C15–C14–C13	117.3(2)
C14–C15–C16	122.6(2)
C17–C16–C15	120.6(2)
C16–C17–C18	118.1(2)
C17–C18–C13	120.88(18)
C17–C18–C19	133.24(18)
C13–C18–C19	105.88(16)
C27–C19–C20	117.29(16)
C27–C19–C18	137.36(17)
C20–C19–C18	105.35(15)
N2–C20–C21	126.41(16)

N2–C20–C19	112.22(16)
C21–C20–C19	121.37(16)
N3–C21–C20	120.91(16)
N3–C21–C22	120.19(16)
C20–C21–C22	118.79(15)
N1–C22–C23	120.29(16)
N1–C22–C21	117.59(15)
C23–C22–C21	122.08(16)
C24–C23–C22	120.33(18)
C23–C24–C25	119.10(19)
C26–C25–C24	118.75(19)
N1–C26–C25	122.98(18)
C19–C27–C28	117.58(17)
N3–C28–C27	125.00(16)
N3–C28–C29	115.42(16)
C27–C28–C29	119.57(17)
O2–C29–O1	123.98(18)
O2–C29–C28	125.30(18)
O1–C29–C28	110.71(17)
N2–B1–C7	109.75(15)
N2–B1–C1	110.14(14)
C7–B1–C1	116.00(14)
N2–B1–N1	104.60(13)
C7–B1–N1	110.21(14)
C1–B1–N1	105.47(14)
C26–N1–C22	118.55(16)
C26–N1–B1	115.88(15)
C22–N1–B1	124.51(14)
C20–N2–C13	106.22(15)
C20–N2–B1	120.61(14)
C13–N2–B1	131.37(15)
C21–N3–C28	117.82(16)
C29–O1–C30	116.50(19)
O1–C30–H30C	109.5

5. Photophysical properties studies in solution

Table S3. Photophysical properties of the dyes **5**, **6**, **9** and **11** in dichloromethane (3.8-5.9 X 10^{-6} M) and solid state.

Dye	λ_{abs} (nm) (DCM/Solid)	λ_{ex} (nm) (DCM/Solid)	λ_{em} (nm) (DCM/Solid)	ν (cm^{-1})[a] (DCM/Solid)	ε_{max} ($M^{-1}cm^{-1}$)[b] (DCM)	Φ_{fl}[c] (DCM/Solid)	τ (ns)[d] (DCM)
5	414/432	405/425	481/502	3364/3228	10288	0.75/0.18	8.55
6	445/458	435/445	525/535	3424/ 3142	8009	0.36/0.13	14.88
9	415/430	405/420	481/520	3306/ 4025	9345	0.82 /0.07	8.10
11	428/432	420/425	489/516	2914/ 3715	11216	0.79/0.21	9.17

[a]Stokes shift; [b]Extinction co-efficient at λ_{abs}; [c]Quantum yield of fluorescence measured using Coumarin 153 in ethanol (Φ_{fl} = 0.54) as the reference; [d]Fluorescence life time.

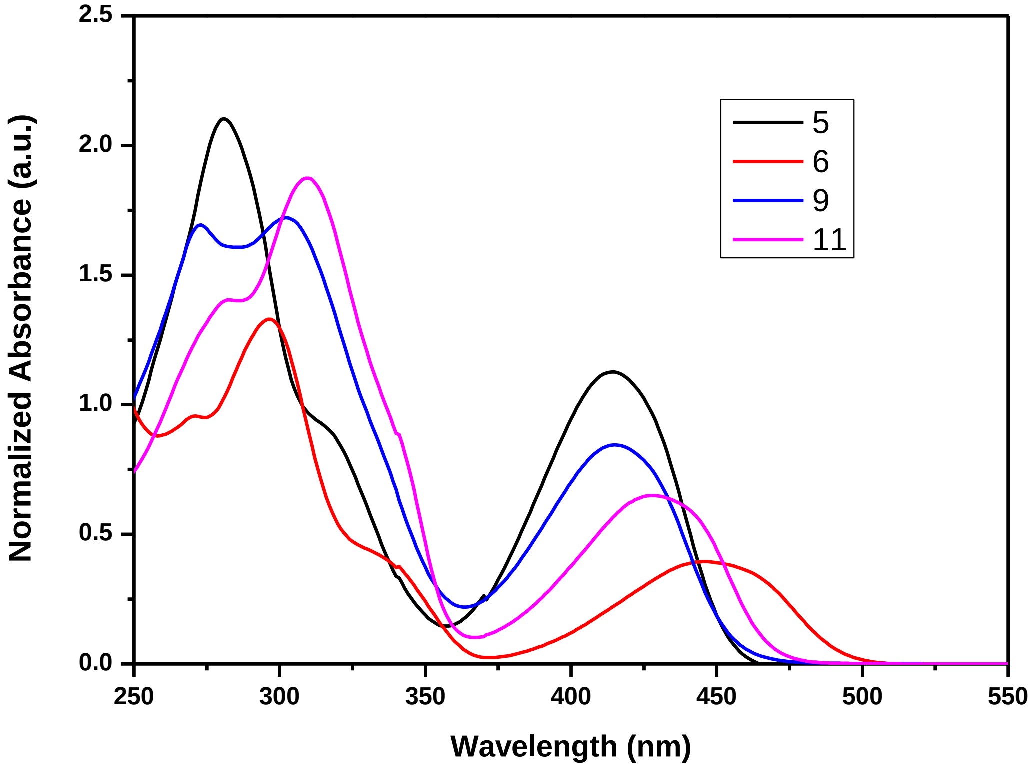


Figure S3. Absorption spectra of dyes **5**, **6**, **9** and **11** in DCM (3.8-5.9 X 10^{-6} M) at 25 ^{o}C.

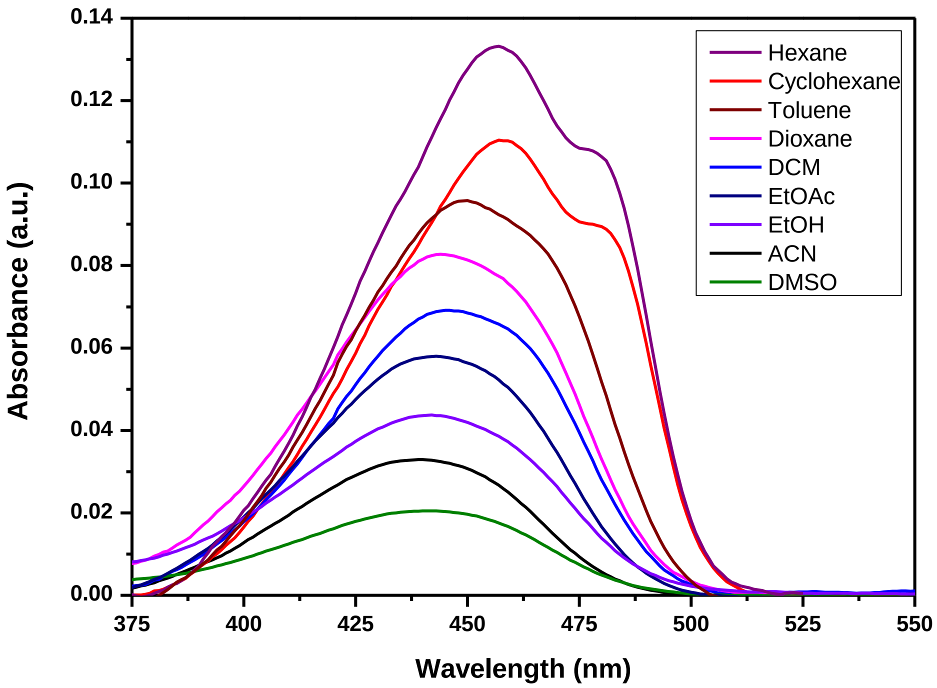


Figure S4. Absorption spectra of dye **6** in different polar solvents (3.5 X 10^{-6} M) at 25 ^{o}C.

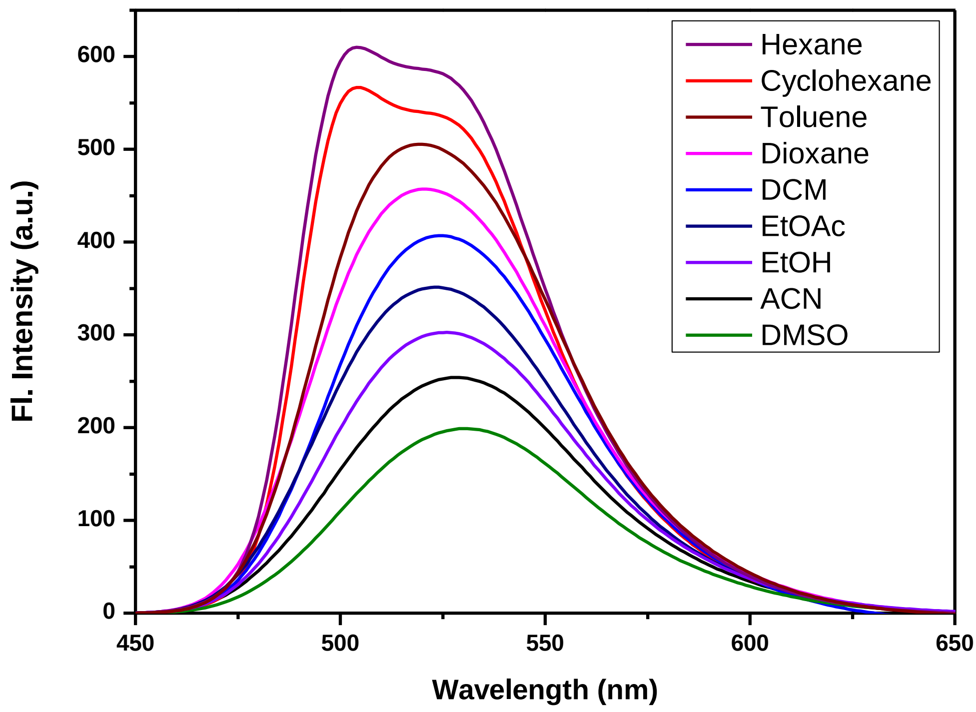


Figure S5. Emission spectra of dye **6** in different polar solvents (3.5 X 10^{-6} M) at 25 ^{o}C.

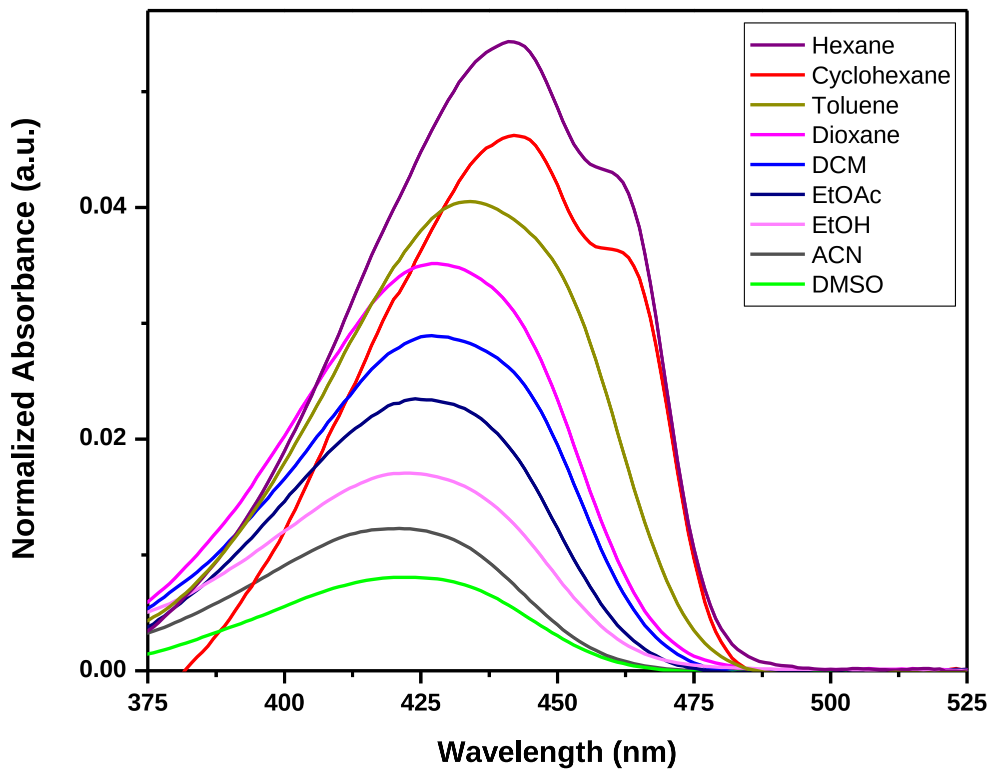


Figure S6. Absorption spectra of dye **11** in different polar solvents (3.4×10^{-6} M) at 25 °C.

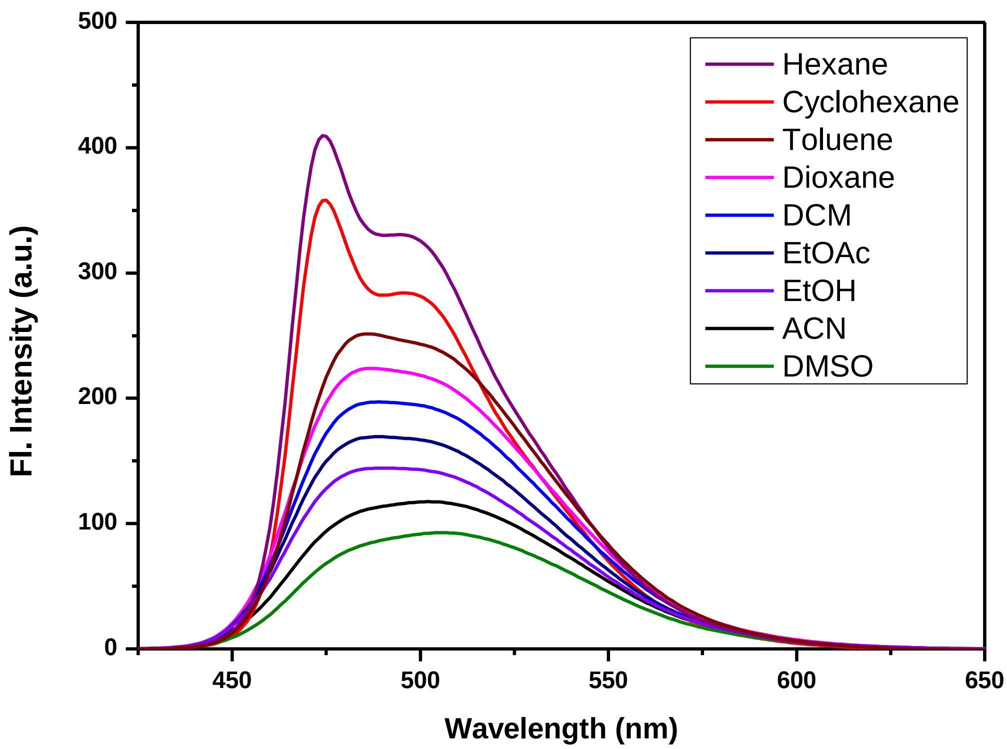


Figure S7. Emission spectra of dye **11** in different polar solvents (3.4×10^{-6} M) at 25 °C.

6. Photophysical properties studies in solid state

The dye solutions in DCM (5×10^{-3} M) were used to make thin films of a fixed area on 1.10 mm thin quartz slides. The films were dried properly to make moisture free. These thin films were used to take the absorbance using UV spectrophotometer.

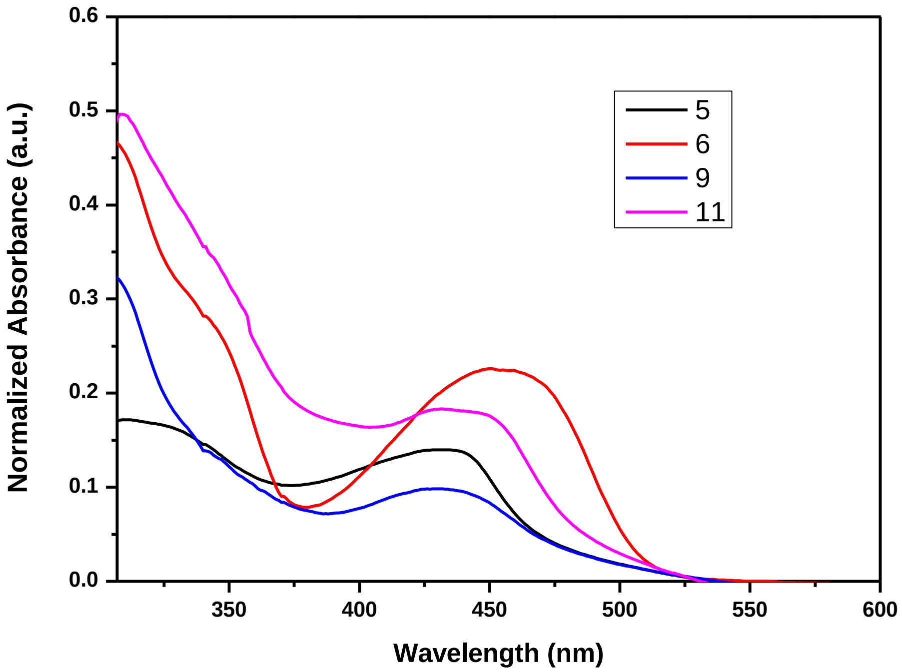


Figure S8. Absorption spectra of dye **5**, **6**, **9** and **11** in thin films at 25 °C.

Dry KBr (150 mg) and 0.5 mg of each dyes (**5**, **6**, **9** and **11**) separately were mixed and grinded properly using mortar and pestle. Then these mixtures were used to make pellets using a manual pelletor machine. The pellets were dried under Na lamp to make them moisture free. Fluorescence spectra of the dyes **5**, **6**, **9** and **11** were recorded using these pellets.

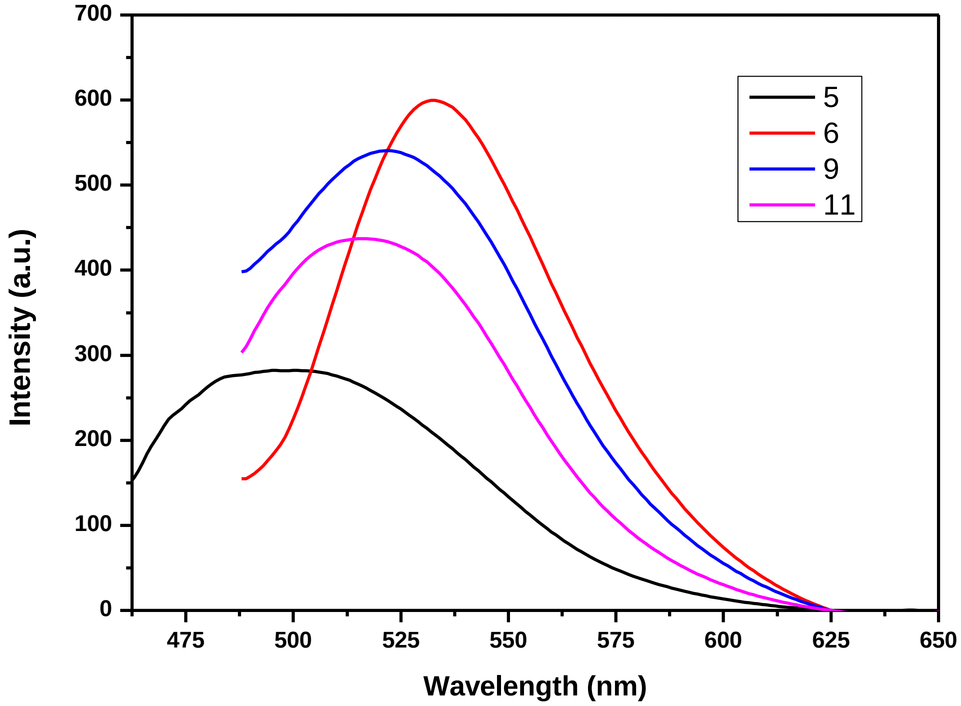


Figure S9. Emission spectra of the dyes **5** (λ_{ex} = 425 nm), **6** (λ_{ex} = 445 nm), **9** (λ_{ex} = 420 nm) and **11** (λ_{ex} = 425 nm) in KBr pellets at 25 °C.

7. Lifetime decay plot

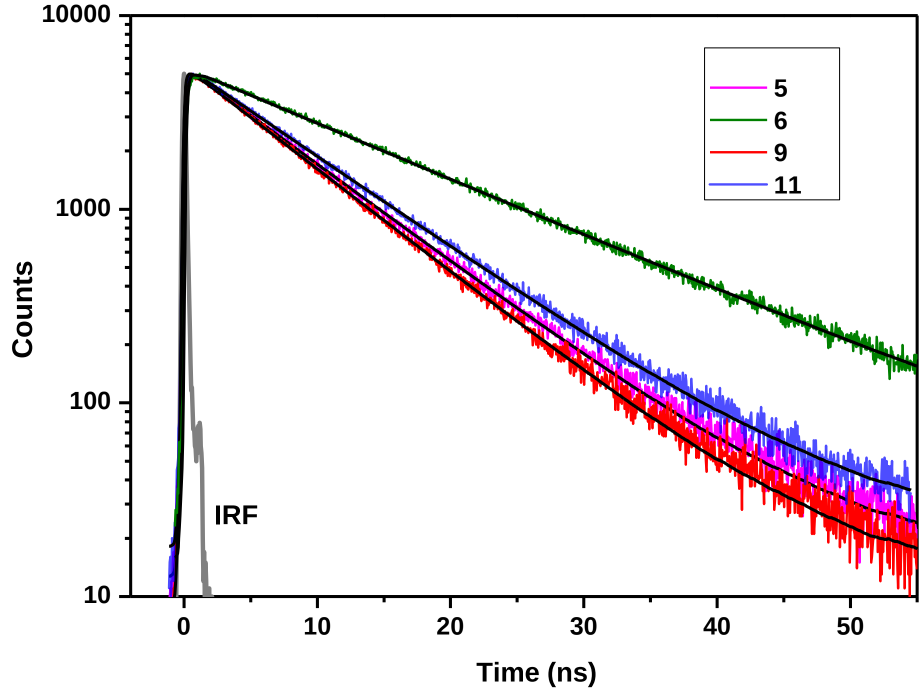
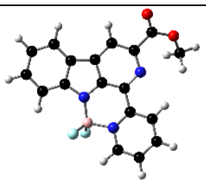
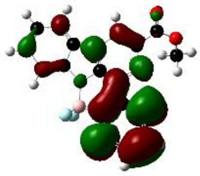
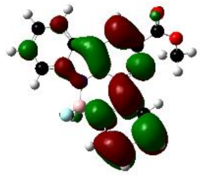
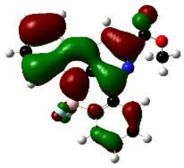
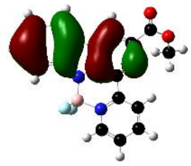
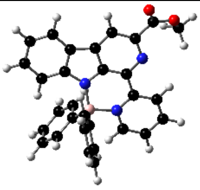
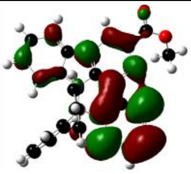
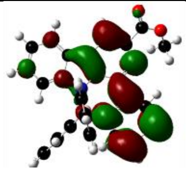
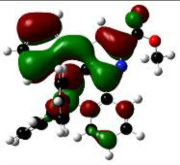
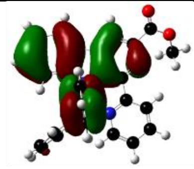
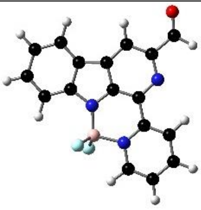
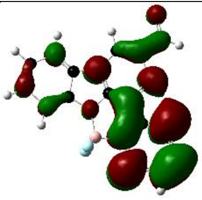
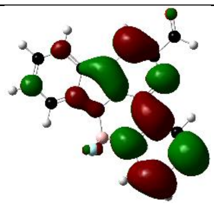
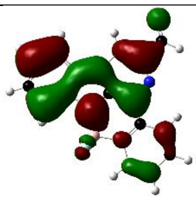
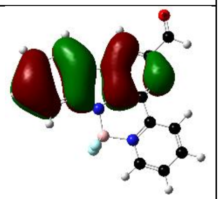
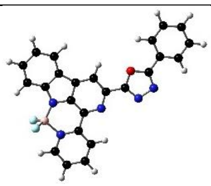
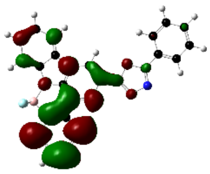
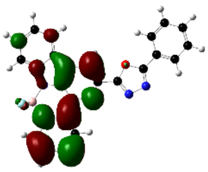
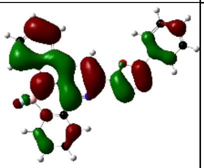
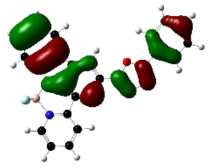


Figure S10. Fluorescence decays of the dyes **5**, **6**, **9** and **11** in DCM [λ_{ex} = 445 nm diode laser source]. The grey line represents the instrument response function (IRF).

8. DFT Calculations

Table S4. Ground state optimized structures and calculated HOMO and LUMO surfaces of dyes **5**, **6**, **9** and **11**.

Dye	Optimised Structure	LUMO+1	LUMO	HOMO	HOMO-1
5		 -2.304 eV	 -2.989 eV	 -6.265 eV	 -6.862 eV
6		 -2.127 eV	 -2.788 eV	 -5.938 eV	 -6.652 eV
9		 -2.289 eV	 -2.9674	 -6.299 eV	 -6.877 eV
11		 -2.1633	 -2.8662	 -6.0485	 -6.7424

9. ^{1}H NMR & ^{13}C NMR Spectra

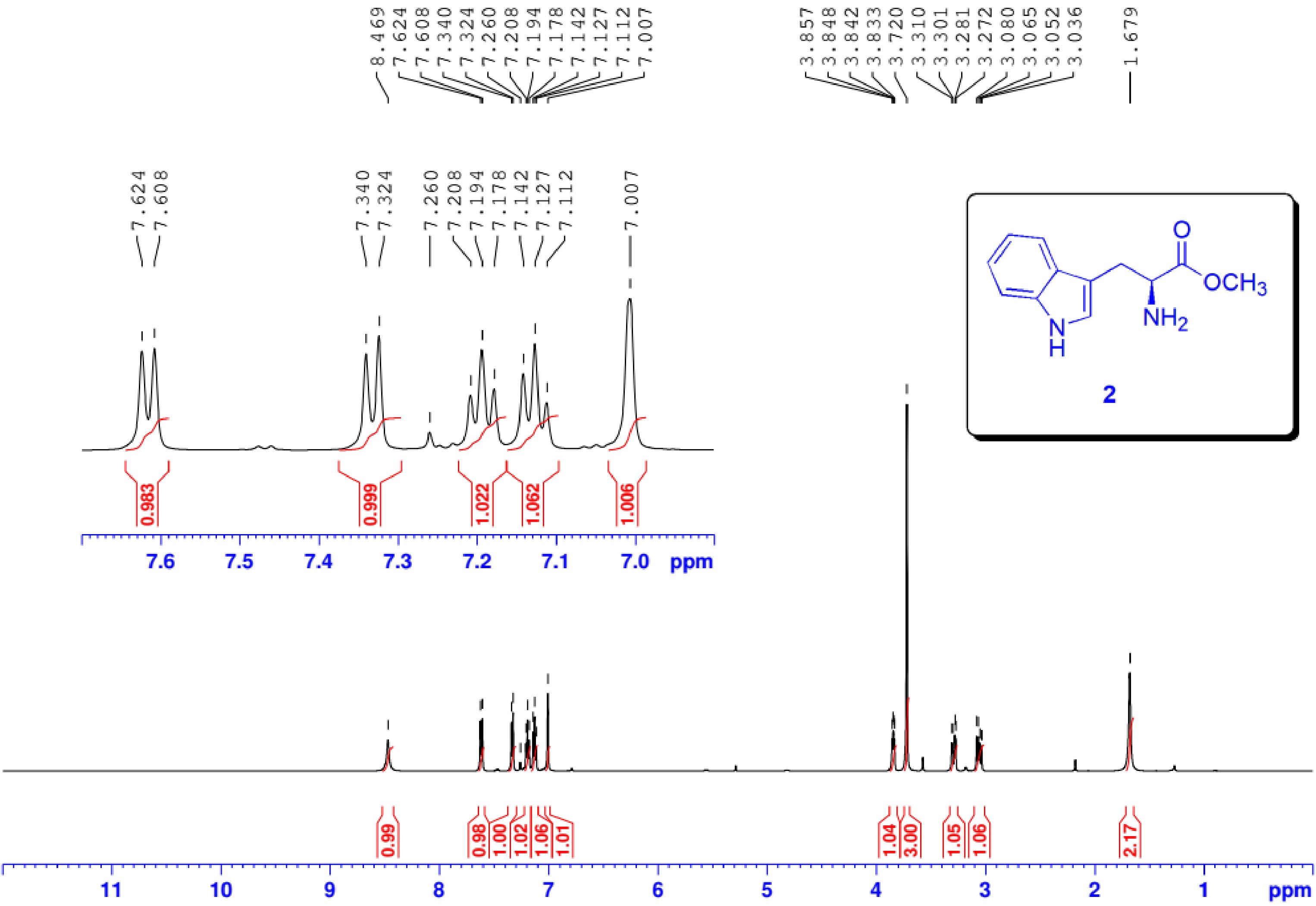


Figure S11. ^{1}H NMR (500 MHz) spectrum of **2** in $CDCl_3$.

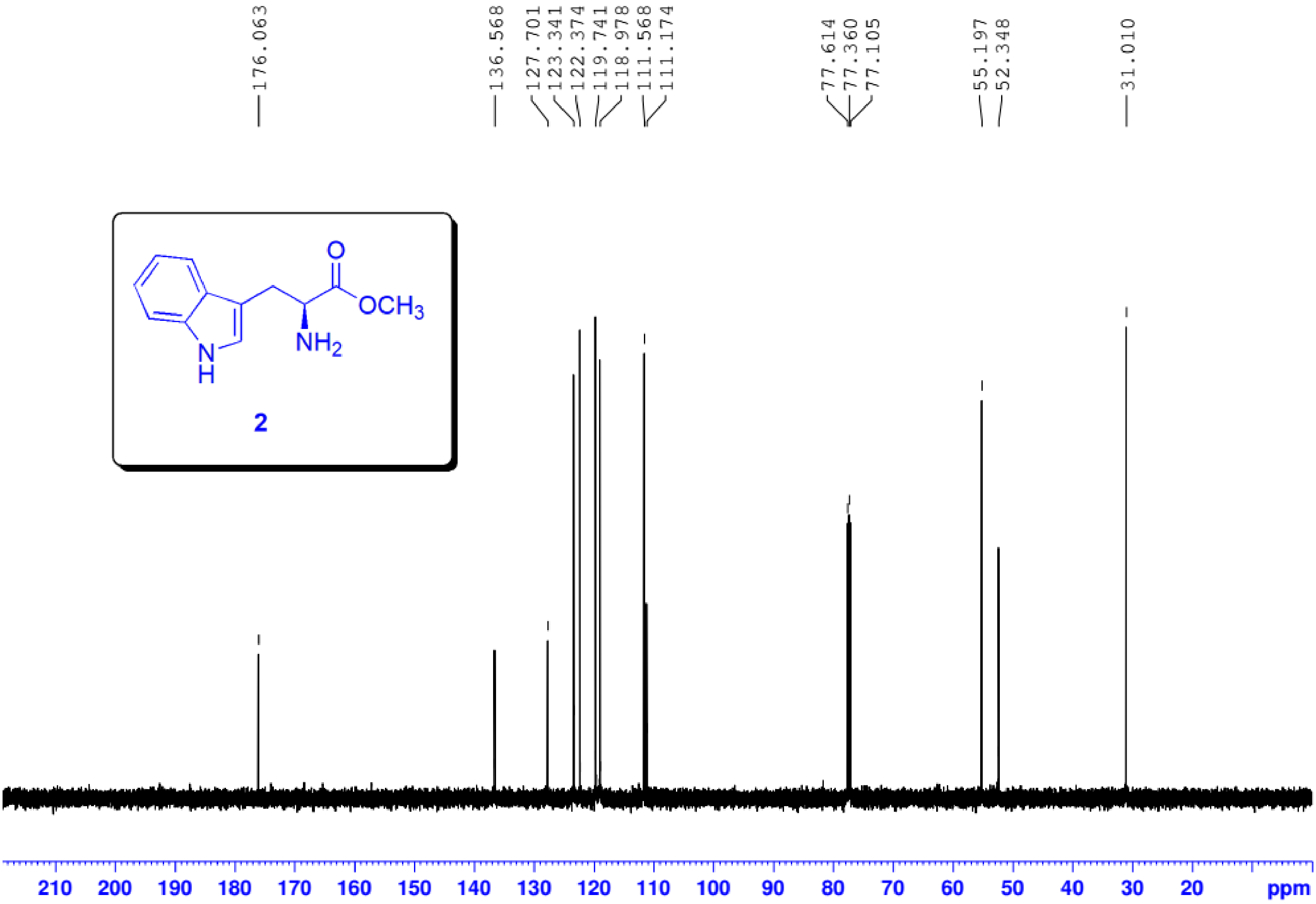


Figure S12. ^{13}C NMR (125 MHz) spectrum of **2** in $CDCl_3$.

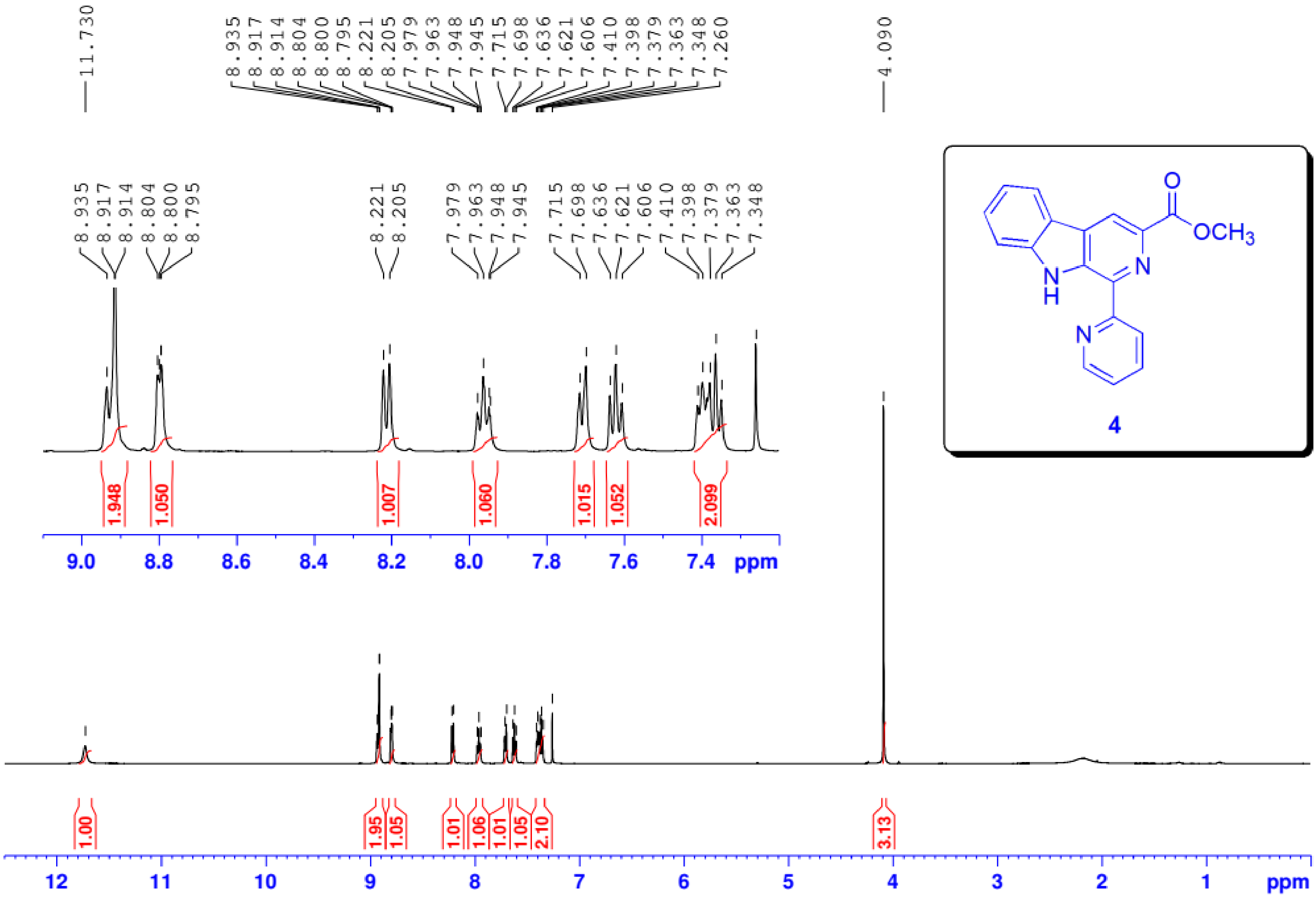


Figure S13. [1]H NMR (500 MHz) spectrum of **4** in $CDCl_3$.

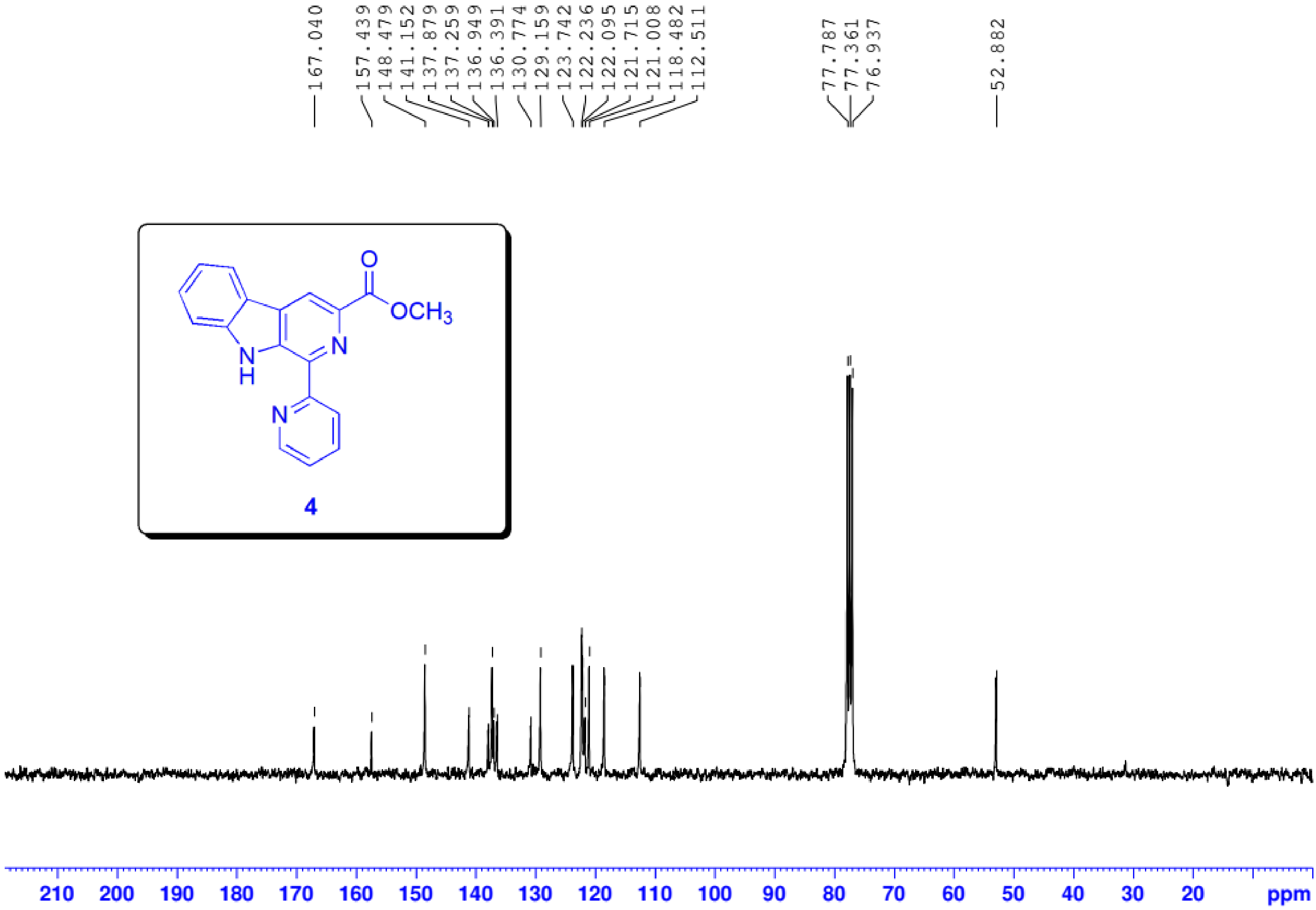


Figure S14. ^{13}C NMR (75 MHz) spectrum of **4** in $CDCl_3$.

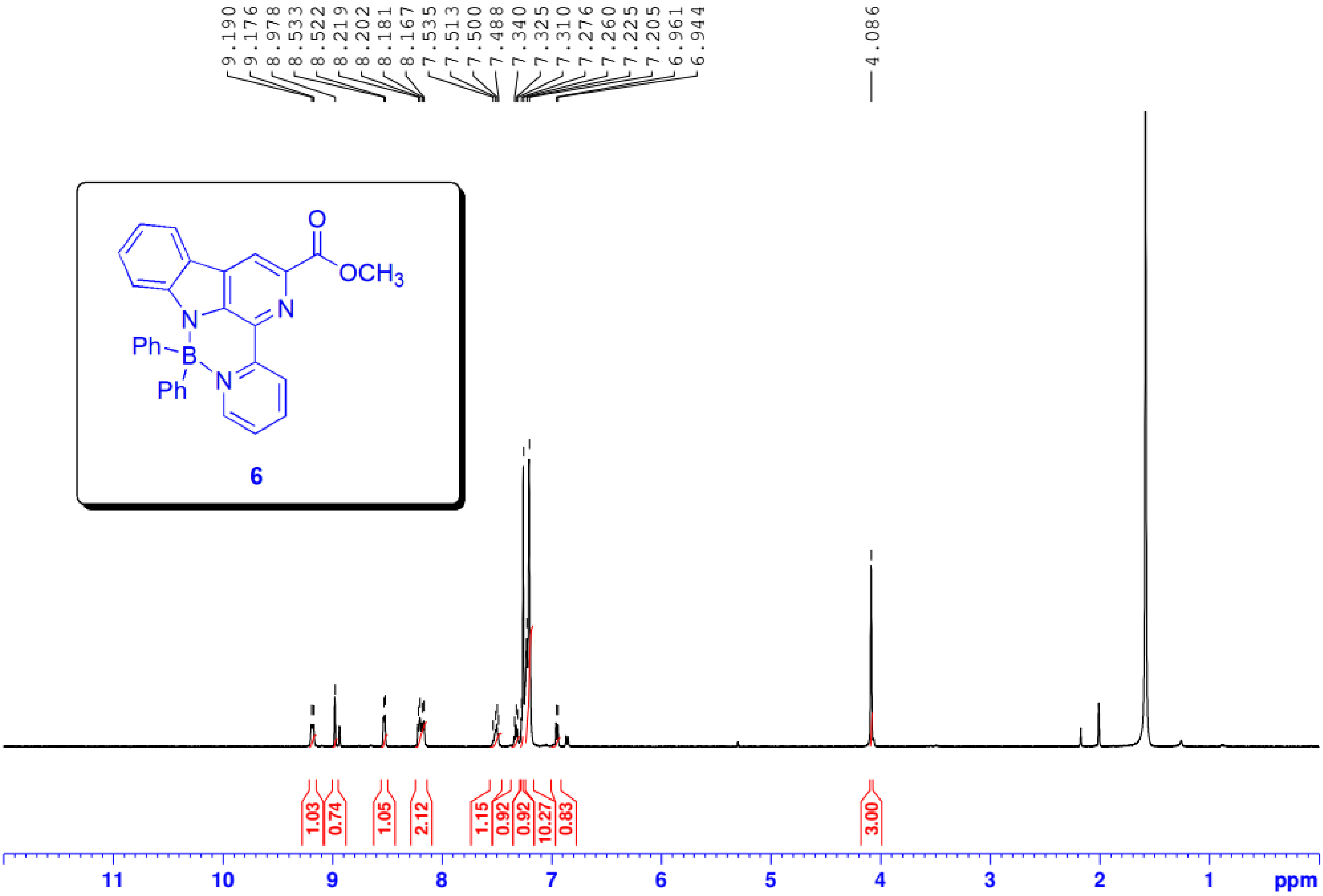


Figure S15. ^{1}H NMR (500 MHz) spectrum of **6** in $CDCl_3$.

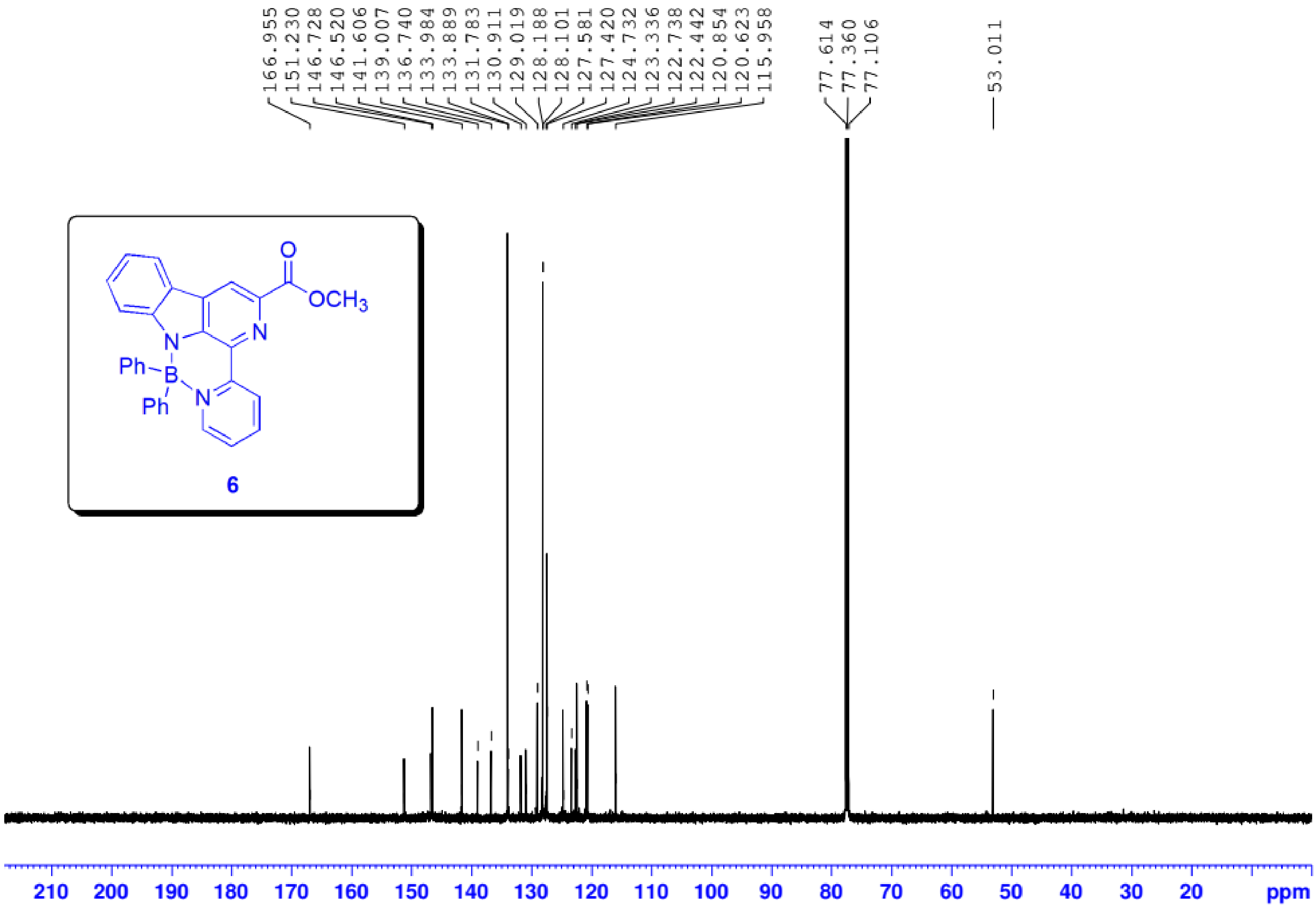


Figure S16. ^{13}C NMR (125 MHz) spectrum of **6** in $CDCl_3$

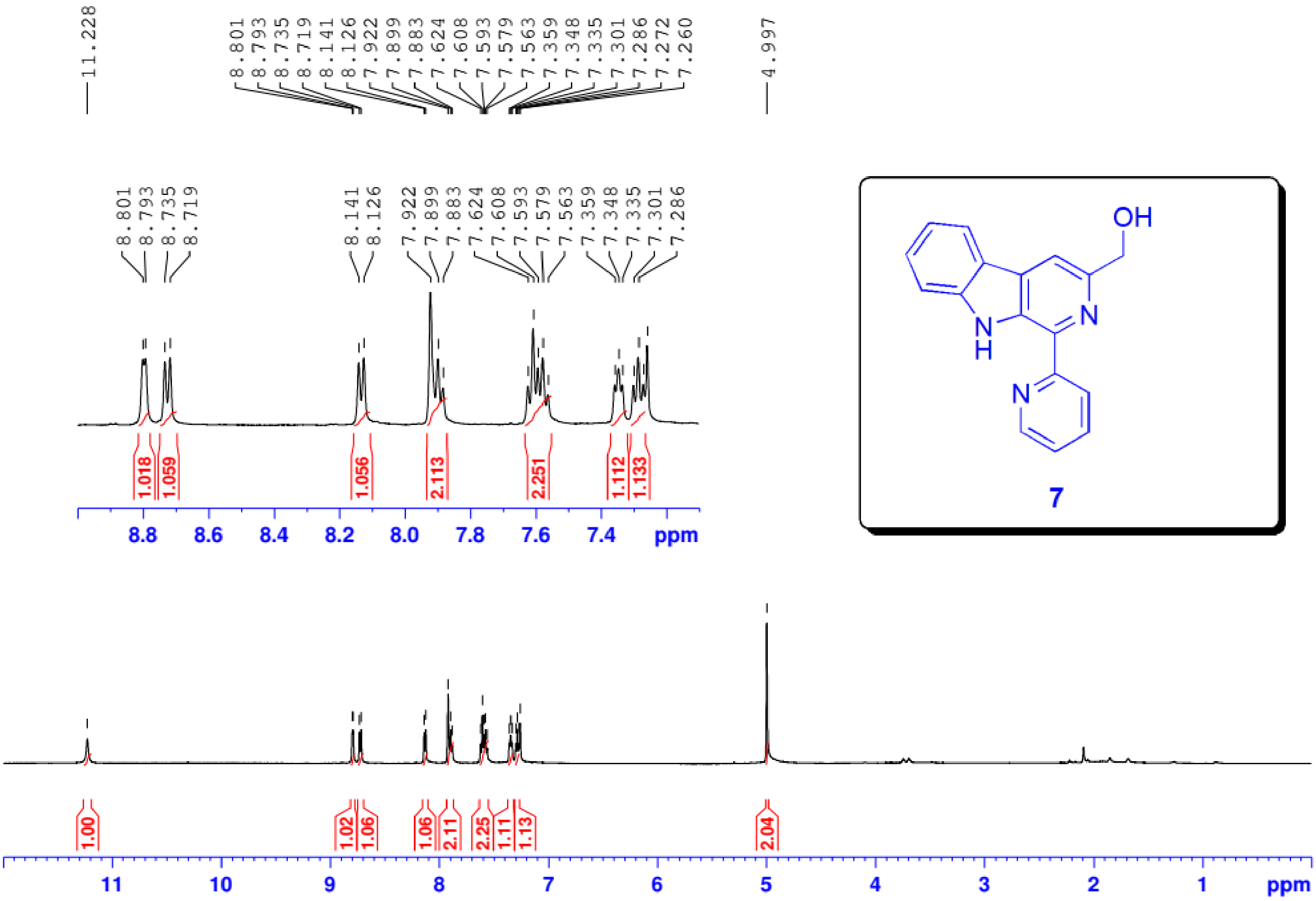


Figure S17. ^{1}H NMR (500 MHz) spectrum of **7** in $CDCl_3$.

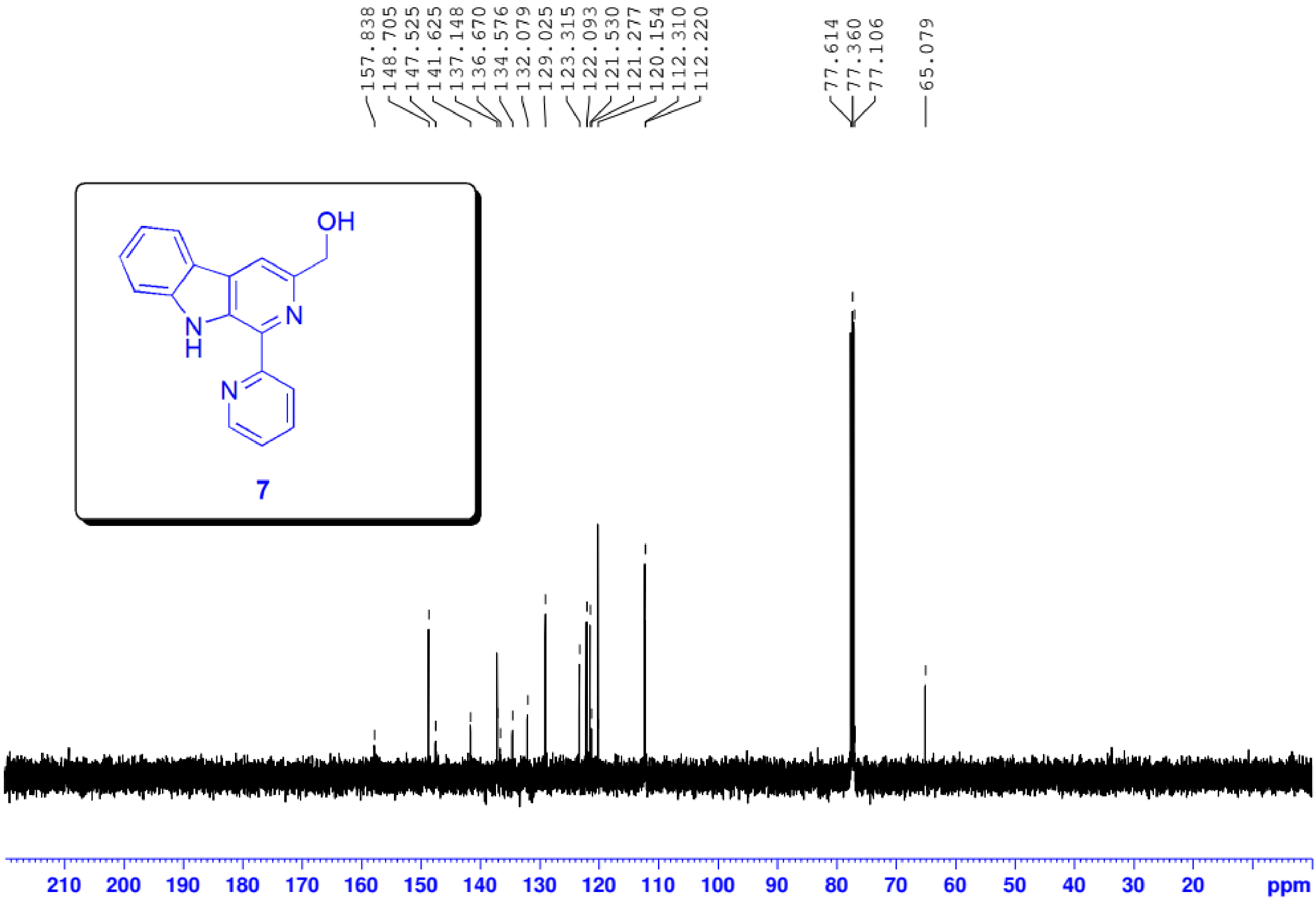


Figure S18. ^{13}C NMR (125 MHz) spectrum of **7** in $CDCl_3$.

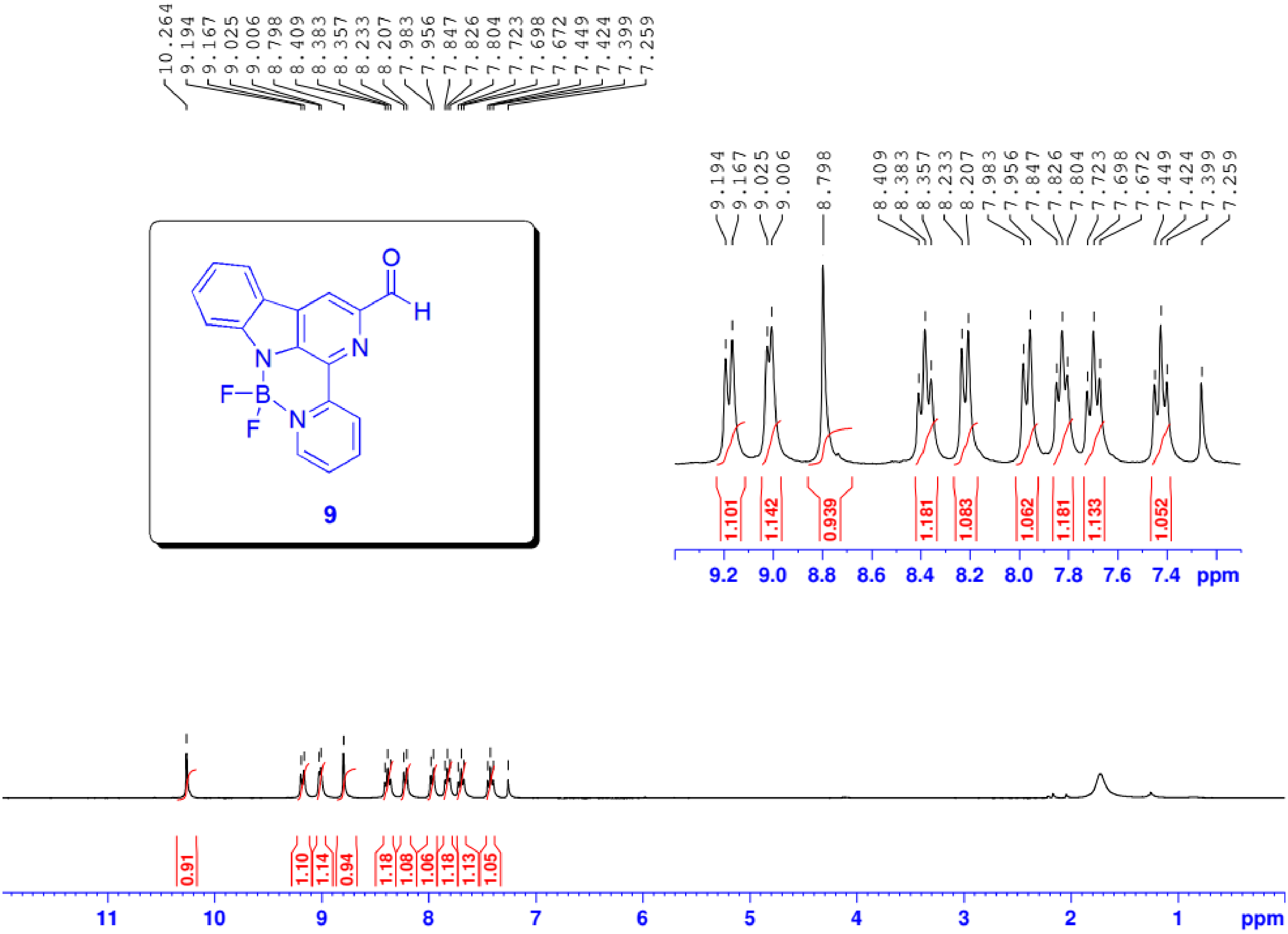


Figure S19. ^{1}H NMR (300 MHz) spectrum of **9** in $CDCl_3$.

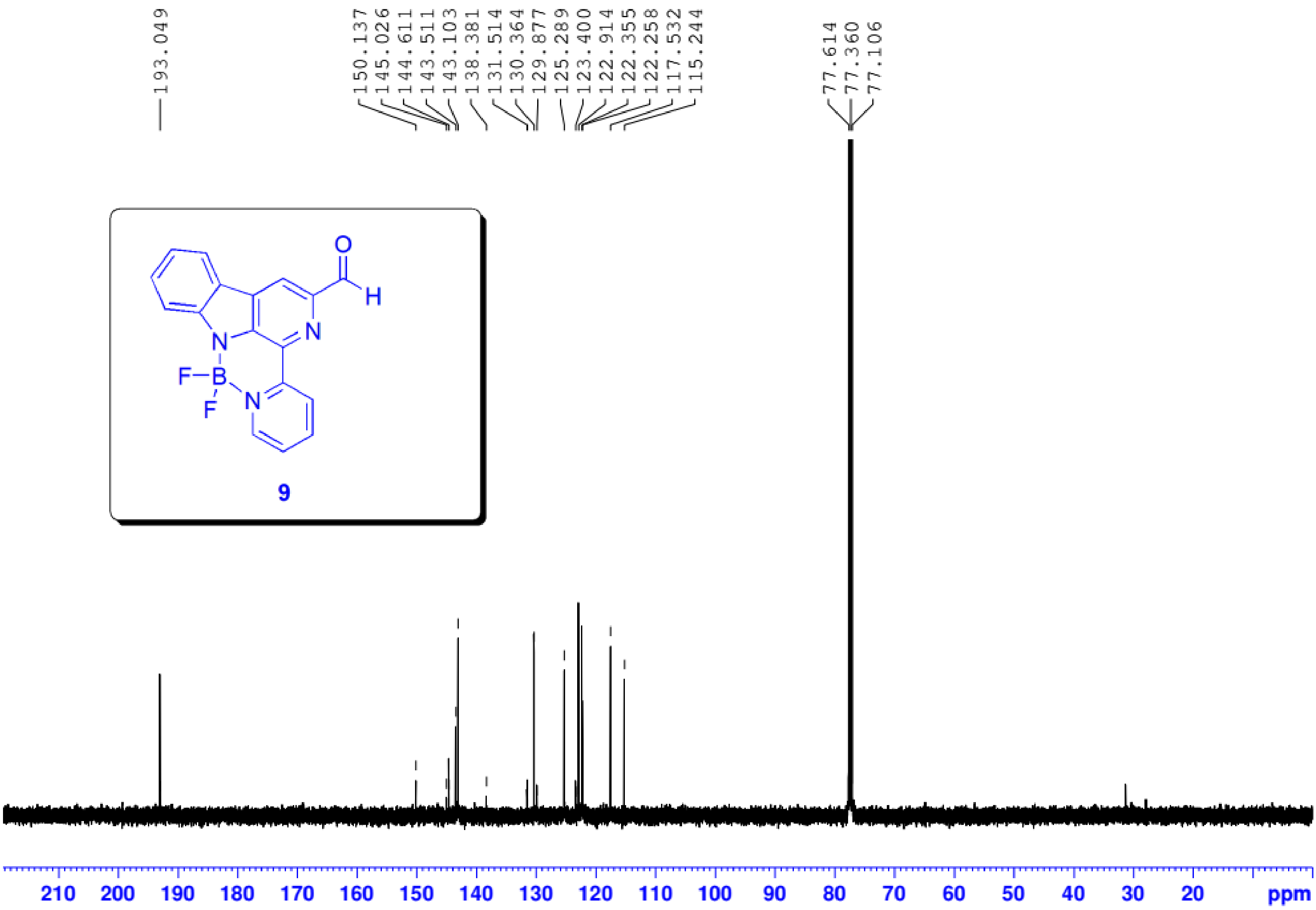


Figure S20. ^{13}C NMR (125 MHz) spectrum of **9** in $CDCl_3$.

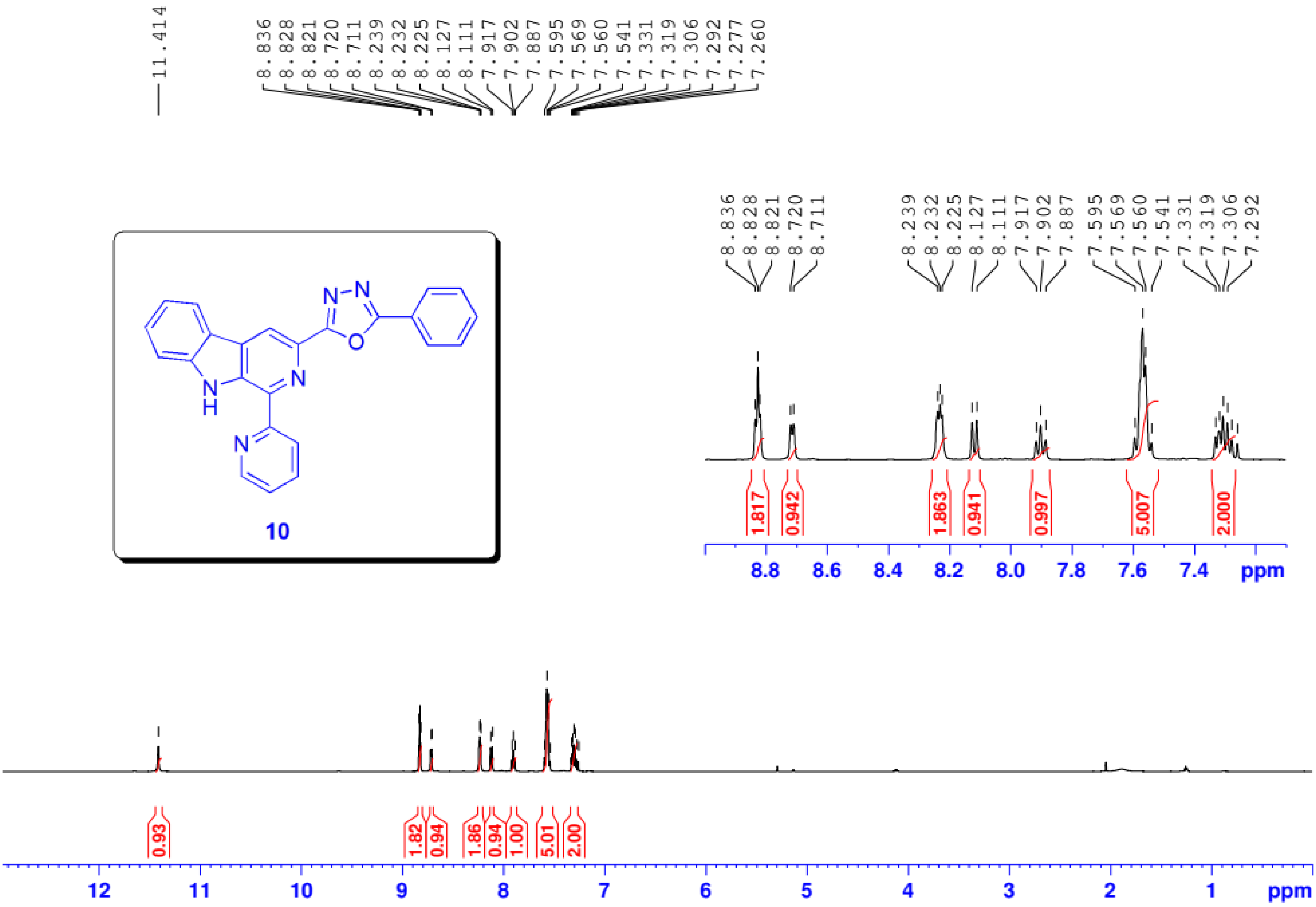


Figure S21. ^{1}H NMR (500 MHz) spectrum of **10** in $CDCl_3$.

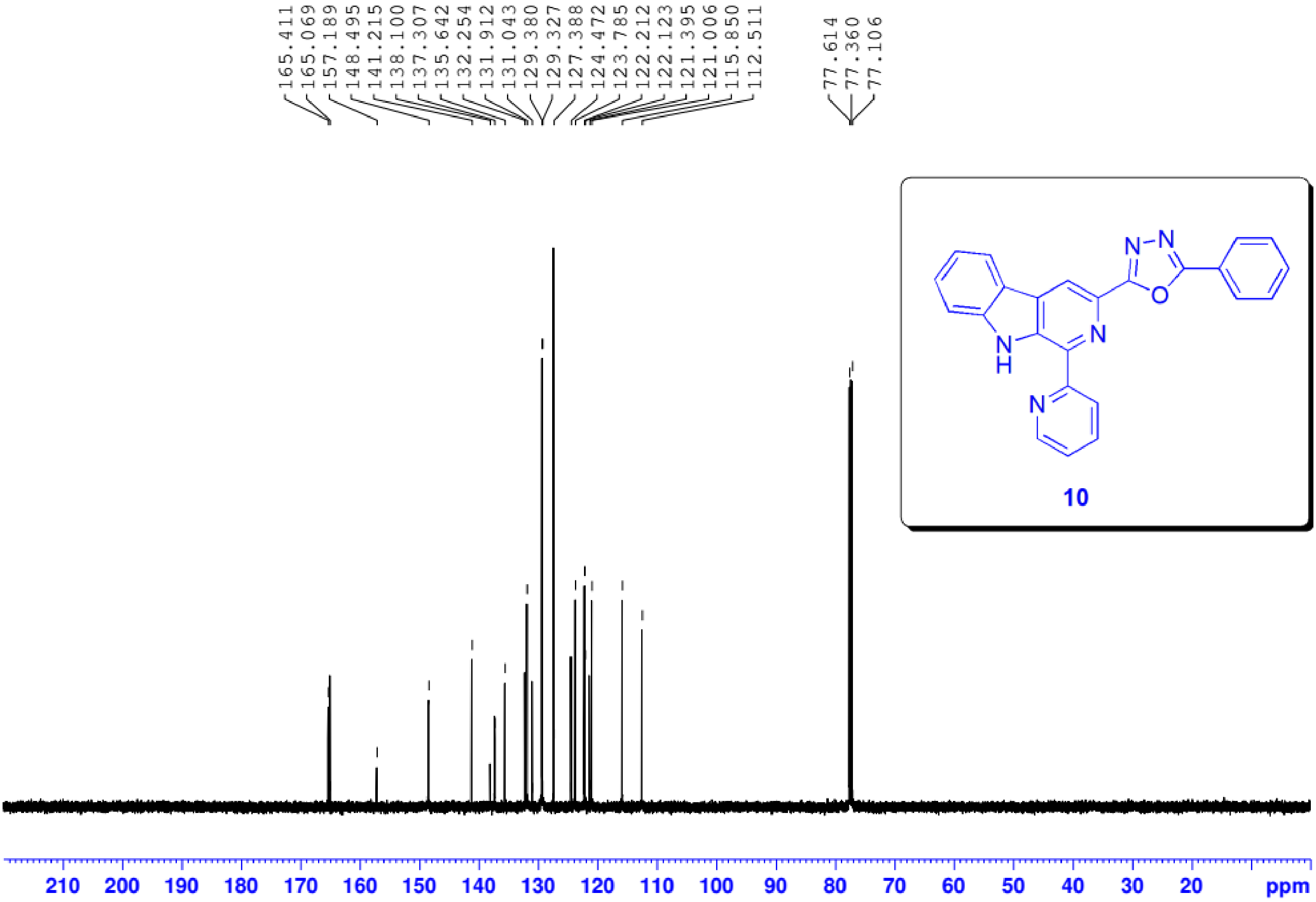


Figure S22. ^{13}C NMR (125 MHz) spectrum of **10** in $CDCl_3$.

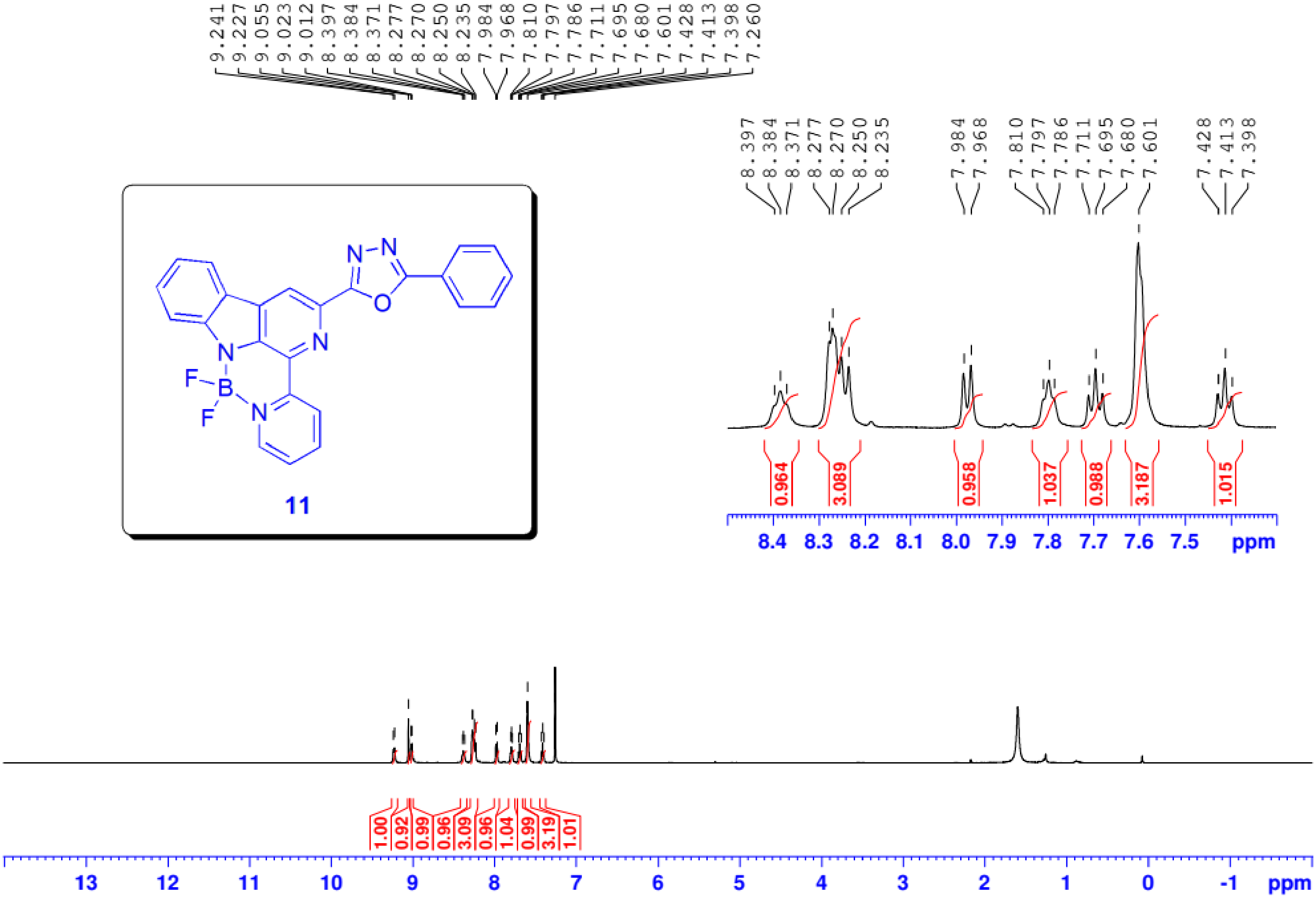


Figure S23. ^{1}H NMR (500 MHz) spectrum of **11** in $CDCl_3$.

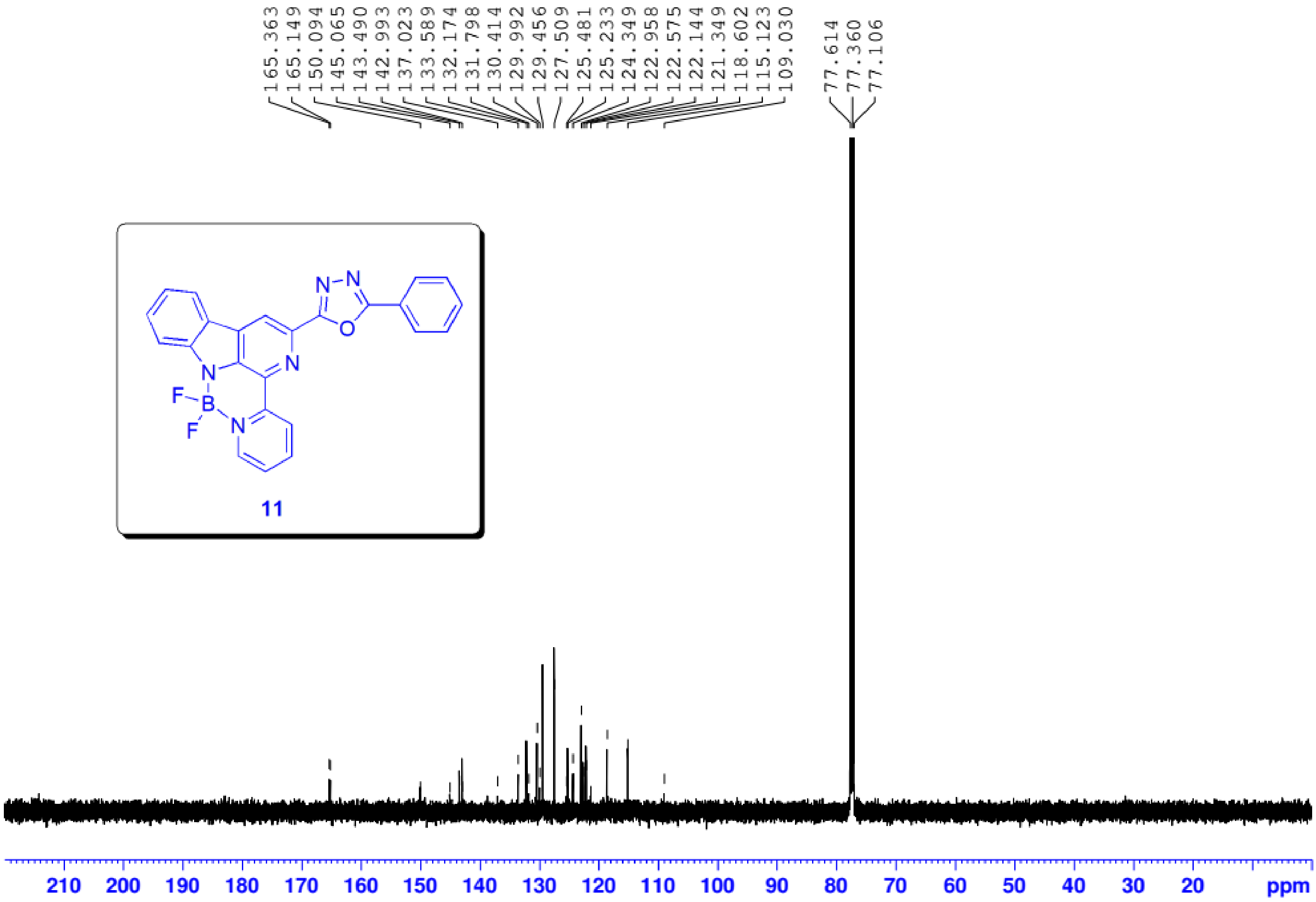


Figure S24. ^{13}C NMR (125 MHz) spectrum of **11** in $CDCl_3$.

10. References

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