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Electronic Supplementary Information (ESI†)

Synthesis of cyanoaminopyridyl enaminoates for their fluorescent "turn off" response towards Fe(III) ions

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1. Experimental section

Experimental section

Reagents and Instruments

All the commercially available reagents and substrates were purchased from Sigma Aldrich and were used as such without further purification. All the experiments were performed in an oven dried glass apparatus. The progress of reaction was monitored by thin layer chromatography (TLC) using silica gel pre-coated aluminum sheets (60 F254, Merck). Solvents were distilled before their use in extraction and purification and further, a rotary evaporator was used to remove them. For photophysical characterization (UV−Vis absorption and fluorescence emission), spectroscopic grade solvents (Merck or Aldrich) and deionized water were used. Melting point (°C) measurements were done using glass capillaries using Perfit melting point apparatus and were uncorrected. The reaction was monitored using the thin-layer chromatography (TLC) plates (60 F254, Merck). Spots were visualized using ultraviolet light (UV) light at 365 and 254 nm. The other visualizing materials include an iodine vapor chamber, Draggendorff reagent and anisaldehyde reagent. The crude product purification was done over column chromatography (silica gel, 60−120 mesh) using a gradient of ethyl acetate and petroleum ether as eluent.The IR spectra (ν, cm^{-1}) were performed using a PerkinElmer FTIR spectrophotometer aided by KBr discs. The ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AC-400 spectrometer where the working frequencies were set at 400 and 101 MHz, respectively. The internal standard used was tetramethylsilane (TMS). The chemical shifts δ are expressed in parts per million (ppm) downfield from TMS. *J* values are given in hertz (Hz). All the ^{13}C NMR spectra are proton decoupled. The abbreviations s, d, q and m in ^{1}H NMR spectra refer to singlet, doublet, quartet and multiplet respectively. Electrosprayionization mass spectra MS (ESI) were recorded on Micro Mass VG-7070 H mass spectrometer at 70 eV. HRMS was recorded using XEVO-G2 XS QTOF with an ESI source in positive mode. UV−Vis and fluorescence spectra were recorded with Perkin Elmer UV/VIS/NIR spectrophotometer Lambda 1050+ and a PTIQM40 spectrofluorometer, respectively, using quartz cuvettes with an optical path length of 10×10 mm. Deionized water was obtained from a Direct-Q3 UV deionizer from Millipore. All pH measurements of samples were carried out using a digital pH meter.

General procedure for the synthesis of 2

A mixture of ethyl cyclopentanone-2-carboxylate **4** (1 mmol) and substituted 2-amino-3-cyanopyridines **3** (1 mmol) was taken in an oven dried round bottom flask (25 mL) in glacial

acetic acid (1 mL) and refluxed in oil bath. The progress of the reaction was monitored by TLC. After completion, acetic acid was removed and residue was poured into ethylacetate (20 mL), washed with water (2×10mL) and brine (1×10mL). After drying over anhydrous sodium sulfate, ethylacetate was removed on rotavapor and the residue after column chromatography gave the desired product (**2a-2i**).

General procedure for metal sensing studies

For absorption and emission titration studies, a stock solution (1.0×10^{-4} M) of **2e** was prepared in an optimized THF/water solution (6:4, v/v) and 10 μM was set as the working concentration. Stock solutions with concentrations of 10×10^{-2} and 1.0×10^{-2} M of various metal salts (LiCl, NaCl, KCl, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, $Pb(NO_3)_2$, $FeCl_2$, $FeCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2$, $CdCl_2$ and $HgCl_2$) were prepared in deionized water. All the spectral measurements were carried out at room temperature. To study the binding behavior of **2e** towards different metal cations, 100 eq. of metal salts was added independently to 2 mL of 10 μM solution of **2e** in a quartz cuvette. Before taking the electronic absorption as well as fluorescence spectra, the solutions were mixed properly. For UV experiments, the slit width of the instrument was set at 2.00 nm, and for fluorescence studies, slit widths of both excitation and emission were set at 3.00 nm with excitation wavelength λex = 365 nm. Titration studies were performed by varying the concentration of metal ions (2−100 equiv) and keeping the concentration of **2e** constant at 10 μM to get the required molar ratios between the sensor **2e** and the metal ions. The total volume of the solution used for the measurements was maintained at ∼2 mL throughout the experiment. Dilution was not allowed to exceed by more than a factor of 10% to minimize the dilution effects.

Stern−Volmer plot

The fluorescence quenching nature of **2e**, when exposed to Fe^{3+} was explained by constructing the Stern−Volmer plot[58,59] according to eq.1

$$\frac{F_0}{F} = 1 + K_{SV}[Q] \qquad (1)$$

Here, F_0 and F refer to the fluorescence intensities at 440 nm in the absence and presence of a quencher, respectively. K_{SV} (M) refers to the Stern−Volmer constant, which indicates the quenching efficiency, and [Q] is the concentration of the quencher.

Binding stoichiometry and binding constant (K_a) calculation

The binding ratio and binding constant (K_a) for the complex (**2e**-Fe^{3+}) was determined from fluorescence titration studies by using Job's continuous variation method and the Benesi−Hildebrand equation, respectively.[48,49] For constructing Job's plot, various solutions of (**2e**-Fe^{3+}) with different mole ratios of **2e** and Fe^{3+}, were prepared by holding the overall concentration and volume of solution constant [10 μM and 2 mL (THF/water, 6:4 v/v)] and their fluorescence spectra were recorded. The graph was plotted between ΔI. χ_{2e} versus χ_{2e} (ΔI is the change of the fluorescence intensity of the sensor at 440 nm and χ_{2e} is the mole fraction of **2e** in each case). The value of the mole fraction of **2e** corresponding to the inflection point was then analyzed for the determination of binding stoichiometry of the complex. The binding constant value was determined from the Benesi−Hildebrand plot according to eq.2[60]

$$\frac{1}{F_0 - F} = \frac{1}{K_a(F_0 - F_{min})[Fe^{3+}]} + \frac{1}{F_0 - F_{min}} \quad (2)$$

Here, F_0 represents the fluorescence intensity of the free sensor **2e**, F represents the fluorescence intensity of **2e** in the presence of different concentrations of Fe^{3+} in the solution and F_{min} is the fluorescence intensity at 440 nm at the maximum concentration of Fe^{3+} in solution. K_a represents the binding constant, which was determined from the linear graph's slope and intercept plotted between $1/(F_0-F)$ and $1/[Fe^{3+}]$.

Measurement of limit of detection (LOD)

To determine the limit of detection, fluorescence titration of **2e** with Fe^{3+} was performed at 440 nm. The limit of detection was calculated by using eq.3

$$LOD = \frac{3\sigma}{S} \quad (3)$$

Here, σ represents the standard deviation of the blank sample and S is the slope refers to the calibration curve slope.[61] S was determined using the plot of (F/F_0) versus concentration of Fe^{3+}. Here, F_0 refers to the fluorescence intensity of **2e** without Fe^{3+} and F refers to the fluorescence intensity at different Fe^{3+} concentrations. The concentration of **2e** during the fluorescence titration experiments was kept at 10 μM [THF/water (6:4, v/v)]. Each fluorescence titration was repeated thrice.

2. Spectral data of the synthesized compounds:

2,3-dihydrocyclopenta[*d*]pyrido[1,2-*a*]pyrimidin-10(1*H*)-one (5)

Yellow crystalline solid, Yield: 80%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): *δ* 9.10 (d, 1H), 7.70-7.67 (m, 1H), 7.62-7.60 (m, 1H), 7.14-7.10 (m, 1H), 3.06-3.00 (q, *J*=8.0, 4H), 2.21-2.13 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm): *δ* 170.82, 155.76, 151.17, 135.23, 127.32, 125.92, 115.34, 114.92, 35.62, 28.03, 21.72.

Ethyl 2-((3-cyanopyrid-2-yl)amino)cyclopent-1-ene-1-carboxylate (2a)

Yellow crystalline solid, Yield: 92%, Mp 90-95 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): *δ* 10.89 (s, 1H), 8.35 (d, *J*=4.0Hz, 1H), 7.8 (d, *J*=8.0 Hz, 1H), 6.87-6.84 (m, 1H), 4.30 (q, *J*=8.0 Hz, 2H). 3.35 (t, *J*=8.0 Hz, 2H), 2.58 (t, *J*=8.0 Hz, 2H), 1.98-1.90 (m, 2H), 1.33 (t, *J*=8.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm): *δ* 167.96, 155.65, 154.61, 151.94, 141.67, 115.79, 115.41, 105.82, 95.08, 59.89, 35.40, 28.45, 21.40, 14.60; **ESI-MS**: m/z 258 $[M + H]^+$; **HRMS**: (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{15}N_3O_2$, 258.1164; found, 258.1240; **FTIR** (KBr, υ_{max} cm^{-1}): 3079 (NH), 2964 and 2871 (CH), 2219 (CN), 1641 (C=O), 1579, 1485, 1408, 1253 (C-O).

Ethyl 2-((3-cyano-4,6-diphenylpyrid-2-yl)amino)cyclopent-1-ene-1-carboxylate (2b)

Yellow solid. Yield: 95%. Mp 157-158 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): *δ* 11.05 (s, 1H), 8.05-8.03 (m, 2H), 7.67-7.65 (m, 2H), 7.56-7.51 (m, 6H), 7.38 (s, 1H), 4.34 (q, *J*=8.0 Hz, 2H), 3.57 (t, *J*=8.0 Hz, 2H), 2.64 (t, *J*=8.0 Hz, 2H), 2.06-1.99 (m, 2H), 1.35 (t, *J*=8.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm): *δ* 167.85, 158.82, 155.57, 155.55, 155.47, 137.77, 136.74, 130.40, 129.97, 129.05, 128.93, 128.30, 127.39, 116.16, 112.77, 105.87, 92.00, 59.90, 36.05, 28.59, 21.67, 14.66; **ESI-MS**: m/z 410 $[M + H]^+$. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{23}N_3O_2$, 410.1790; found, 410.1874; **FTIR** (KBr, υ_{max} cm^{-1}): 3047 (NH), 2852 and 2942 (CH), 2210 (CN), 1630 (C=O), 1552, 1358, 1266 (C-O).

Ethyl 2-((3-cyano-4-(4-methoxyphenyl)-6-phenylpyrid-2-yl)amino)cyclopent-1-ene-1-carboxylate (2c)

Yellow solid; Yield: 95%; Mp 158-160 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 11.02 (s, 1H), 8.05-8.02 (m, 2H), 7.64 (d, *J*=8.0 Hz, 2H), 7.54-7.50 (m, 3H), 7.36 (s, 1H), 7.07 (d, *J*=0.8 Hz, 2H), 4.34 (q, *J*=8.0 Hz, 2H), 3.91 (s, 3H), 3.56 (t, *J*=8.0 Hz, 2H), 2.64 (t, *J*=8.0 Hz, 2H), 2.06-1.98 (m, 2H), 1.35 (t, *J*=8.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm): δ 167.82, 161.08, 158.69, 155.63, 155.57, 155.16, 137.95, 130.28, 129.76, 129.00, 128.89, 127.37, 116.47, 114.49, 112.55, 105.76, 91.77, 59.84, 55.46, 36.02, 28.60, 21.68, 14.64; **ESI-MS**: m/z 440 $[M + H]^+$; **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{25}N_3O_3$, 440.1896; found, 440.1970; **FTIR** (KBr, υ_{max} cm^{-1}): 3201 (NH), 2953 and 2852 (CH), 2209 (CN), 1674 (C=O), 1622, 1540, 1365, 1253 (C-O).

Ethyl 2-((3-cyano-4-phenyl-6-(p-tolyl)pyrid-2-yl)amino)cyclopent-1-ene-1-carboxylate (2d)

Yellow solid; Yield: 95%; Mp 180-182 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 11.02 (s, 1H), 7.94 (d, *J*=8.0 Hz, 2H), 7.67 -7.65 (m, 2H), 7.58-7.54 (m, 3H), 7.35 (s, 1H), 7.33 (d, *J*=0.8 Hz, 2H), 4.34 (q, *J*=8.0 Hz, 2H), 3.57 (t, *J*=8.0 Hz, 2H), 2.64 (t, *J*=8.0 Hz, 2H), 2.45 (s, 3H), 2.06-1.98 (m, 2H), 1.35 (t, *J*=8.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm): δ 167.85, 165.38, 158.87, 155.64, 155.45, 140.79, 136.85, 135.05, 129.91, 129.67, 129.03, 128.29, 127.34, 116.26, 112.48, 105.74, 91.66, 59.88, 36.05, 28.59, 21.68, 21.46, 14.65; **ESI-MS**: m/z 424 $[M + H]^+$; **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{25}N_3O_2$, 424.1947 found,424.2025. **FTIR** (KBr, υ_{max} cm^{-1}): 3094 (NH), 2938 and 2863 (CH), 2210 (CN), 1637 (C=O), 1560, 1360, 1274 (C-O).

Ethyl 2-((3-cyano-4-(4-methoxyphenyl)-6-(p-tolyl)pyrid-2-yl)amino)cyclopent-1-ene-1-carboxylate (2e)

Yellow solid; Yield: 96%; Mp 188-190 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 10.99 (s, 1H), 7.93 (d, *J*=8.0 Hz, 2H), 7.63 (d, *J*=8.0 Hz, 2H), 7.33-7.31 (m, 3H), 7.07 (d, *J*=0.8 Hz, 2H), 4.33 (q, *J*=8.0 Hz, 2H), 3.91 (s, 3H), 3.56 (t, *J*=8.0 Hz, 2H), 2.63 (t, *J*=8.0 Hz, 2H), 2.45 (s, 3H), 2.05-1.98 (m, 2H), 1.35 (t, *J*=8.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm): δ 167.81, 161.03, 158.72, 155.70, 155.54, 155.03, 140.64, 135.19, 129.75, 129.62, 129.10, 127.30, 116.55, 114.46, 112.22, 105.61, 91.40, 59.82, 55.45, 36.03, 28.60, 21.67, 21.41, 14.64; **ESI-MS**: m/z 454 $[M + H]^+$; **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{28}H_{27}N_3O_3$,

454.2052; found, 454.2128. **FTIR** (KBr, υ_{max} cm^{-1}): 3199 (NH), 2945 and 2853 (CH), 2208 (CN), 1635 (C=O), 1531, 1357, 1255 (C-O).

Ethyl 2-((3-cyano-4-(4-methoxyphenyl)-6-(thiophen-2-yl)pyrid-2-yl)amino)cyclopent-1-ene-1-carboxylate (2f)

Yellow solid; Yield: 90%; Mp 192-193 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 10.99 (s, 1H), 7.67-7.66 (m, 1H), 7.62 (d, *J*=8.0 Hz, 2H), 7.52-7.51 (m, 1H), 7.23 (s, 1H), 7.16 (t, *J*=4 Hz, 1H), 7.07 (d, *J*=8.0 Hz, 2H), 4.33 (q, *J*=8.0 Hz, 2H), 3.91 (s, 3H), 3.54 (t, *J*=4.0 Hz, 2H), 2.63 (t, *J*=8.0 Hz, 2H), 2.06-1.99 (m, 2H), 1.35 (t, *J*=8.0 Hz, 3H); **^{13}C NMR** (101 MHz, CDCl3, ppm): δ 167.81, 161.10, 155.66, 155.36, 155.05, 153.34, 144.04, 129.72, 129.70, 128.81, 128.41, 126.64, 116.42, 114.48, 110.55, 105.98, 91.00, 59.85, 55.45, 35.98, 28.61, 21.66, 14.63; **ESI-MS**: m/z 446 $[M + H]^+$; **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{23}N_3O_3S$, 446.1460; found, 446.1536. **FTIR** (KBr, υ_{max} cm^{-1}): 3102 (NH), 2960 and 2851 (CH), 2210 (CN), 1622 (C=O), 1536, 1363, 1253 (C-O).

Ethyl 2-((3-cyano-6-(furan-2-yl)-4-(4-methoxyphenyl)pyrid-2-yl)amino)cyclopent-1-ene-1-carboxylate (2g)

Yellow solid;Yield: 89%; Mp 160-162 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 10.96 (s, 1H), 7.64 (d, *J*=8.0 Hz, 2H), 7.59 (s, 1H), 7.31 (s, 1H), 7.13 (d, *J*=4 Hz, 1H), 7.06 (d, *J*=0.8 Hz, 2H), 6.60-6.59 (m, 1H), 4.33 (q, *J*=8.0 Hz, 2H), 3.91 (s, 3H), 3.51 (t, *J*=8.0 Hz, 2H), 2.62 (t, *J*=8.0 Hz, 2H), 2.04-1.97 (m, 2H), 1.35 (t, *J*=8.0 Hz, 3H); **^{13}C NMR** (101 MHz, CDCl3, ppm): δ 167.83, 161.07, 155.72, 155.50, 155.14, 152.96, 149.72, 144.62, 129.77, 128.82, 116.56, 114.42, 112.53, 111.93, 110.32, 105.77, 91.06, 59.87, 55.46, 35.76, 28.58, 21.61, 14.65; **ESI-MS**: m/z 430 $[M + H]^+$. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{23}N_3O_4$, 430.1689; found, 430.1759; **FTIR** (KBr, υ_{max} cm^{-1}): 3155 (NH), 2955, and 2846 (CH), 2209 (CN), 1624 (C=O), 1549, 1356, 1255 (C-O).

Ethyl 2-((3-cyano-6-(3-methoxyphenyl)-4-(4-methoxyphenyl)pyrid-2-yl)amino)cyclopent-1-ene-1-carboxylate (2h)

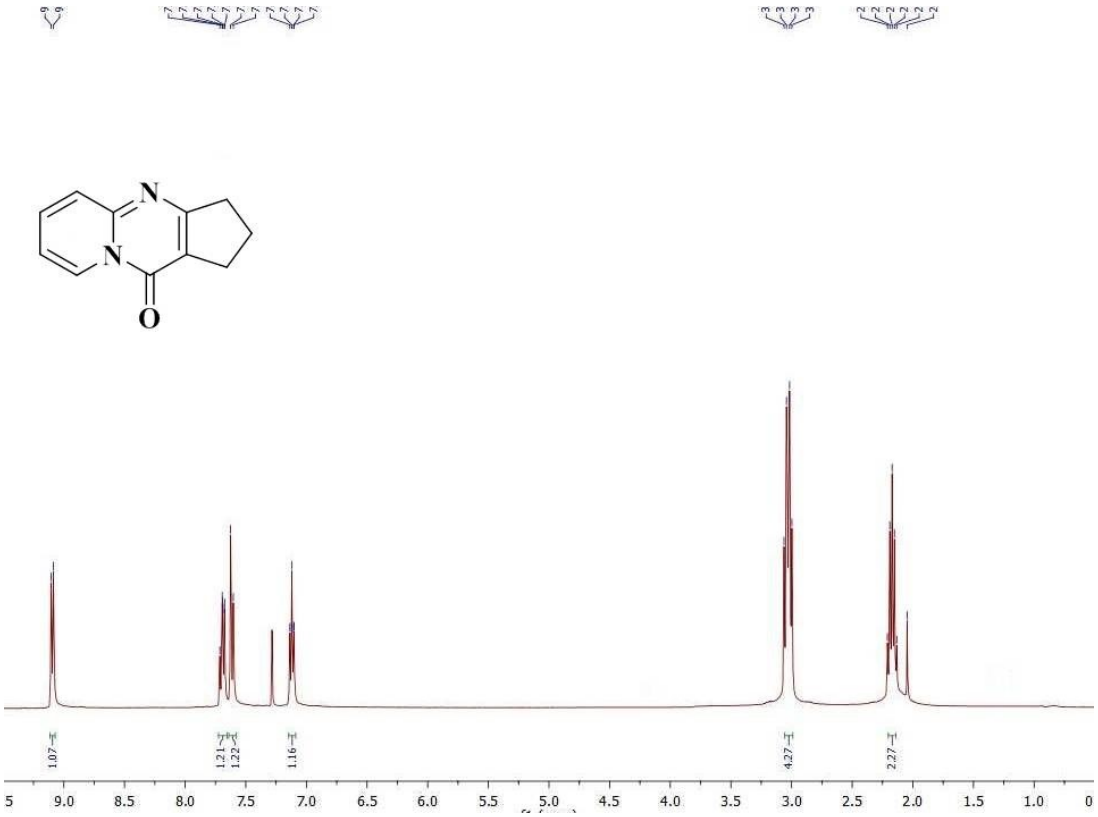
Yellow solid; Yield: 86%; Mp 152-154 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 11.02 (s, 1H), 7.65-7.59 (m, 4H), 7.42 (d, *J*=8.0 Hz, 1H), 7.34 (s, 1H), 7.08-7.03 (m, 3H), 4.34 (q, *J*=8.0 Hz, 2H), 3.91 (s, 6H), 3.57 (t, *J*=8.0 Hz, 2H), 2.63 (t, *J*=8.0 Hz, 2H), 2.04-1.97 (m, 2H), 1.35 (t, *J*=8.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm): δ 167.84, 161.07, 160.00, 158.35, 155.59, 155.46, 155.13, 139.33, 129.89, 129.78, 128.93, 119.68, 116.48, 116.00,

114.48, 112.77, 112.62, 105.75, 91.81, 59.87, 55.47, 55.36, 36.08, 28.60, 21.64, 14.66; **ESI-MS**: m/z 470 $[M + H]^+$. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{28}H_{27}N_3O_4$, 470.2002; found, 470.2078; **FTIR** (KBr, υ_{max} cm^{-1}): 3183 (NH), 2962 and 2845 (CH), 2208 (CN), 1643 (C=O), 1560, 1358, 1258 (C-O).

Ethyl 2-((3-cyano-6-(3-methoxyphenyl)-4-(p-tolyl)pyrid-2-yl)amino)cyclopent-1-ene-1-carboxylate (2i)

Greenish-Yellow solid; Yield: 95%; Mp 140-142 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 11.03 (s, 1H), 7.32 (d, *J*=4.0 Hz, 1H), 7.59 (d, *J*=4.0 Hz, 2H), 7.56 (s, 1H), 7.43 (t, *J*=8.0 Hz, 1H), 7.37 (d, *J*=4.0 Hz, 3H), 7.06-7.03 (m, 1H), 4.34 (q, *J*=8.0 Hz, 2H), 3.91 (s, 3H), 3.58 (t, *J*=8.0 Hz, 2H), 2.64 (t, *J*=8.0 Hz, 2H), 2.47 (s, 3H), 2.05-1.97 (m, 2H), 1.35 (t, *J*=8.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm): δ 167.84, 160.01, 158.44, 155.60, 155.55, 155.40, 140.27, 139.31, 133.84, 129.90, 129.76, 128.19, 119.71, 116.29, 116.05, 112.80, 112.77, 105.81, 92.08, 59.88, 55.36, 36.07, 28.60, 21.65, 21.41, 14.64; **ESI-MS**: m/z 454 $[M + H]^+$; **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{28}H_{27}N_3O_3$, 454.2052; found, 454.2129; **FTIR** (KBr, υ_{max} cm^{-1}): 3187 (NH), 2961 and 2869 (CH), 2215 (CN), 1625 (C=O), 1558, 1357, 1259 (C-O).

3. ^{1}H and ^{13}C NMR spectra of the synthesized compounds



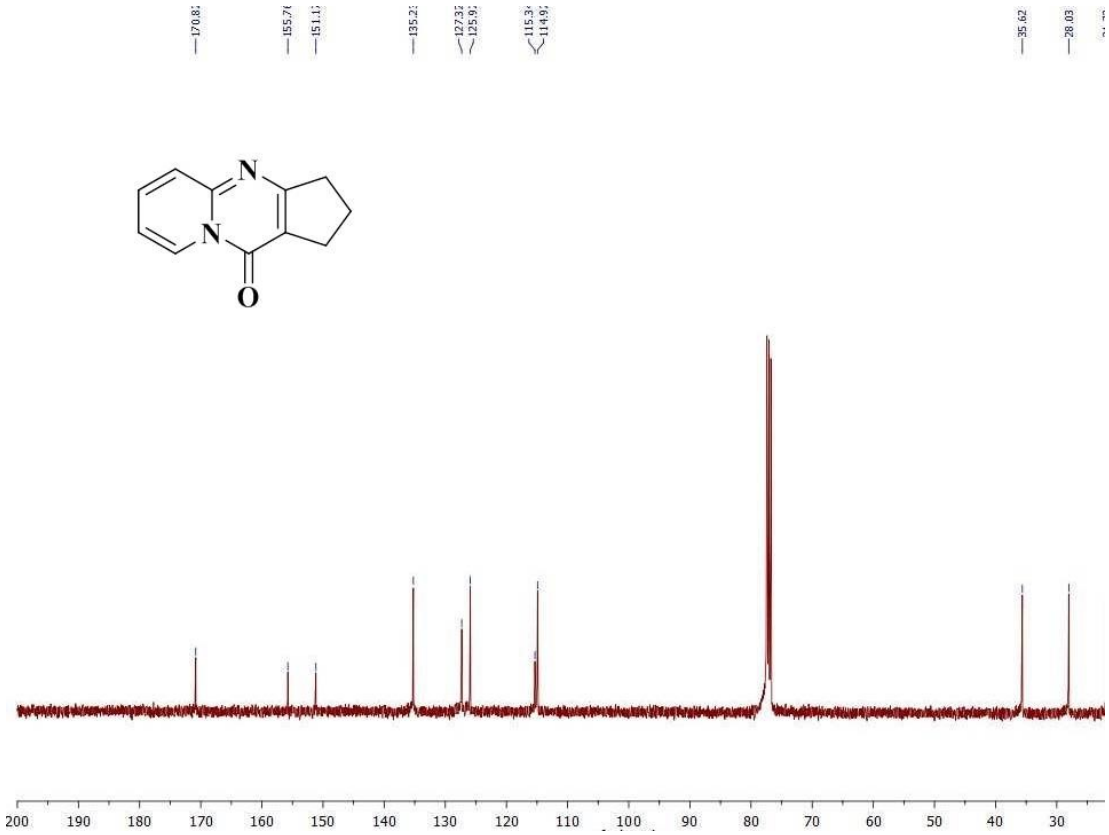


Fig. S1 ^{1}H and ^{13}C NMR spectra of 2,3-dihydrocyclopenta[*d*]pyrido[1,2-*a*]pyrimidin-10(1*H*)-one (**5**)

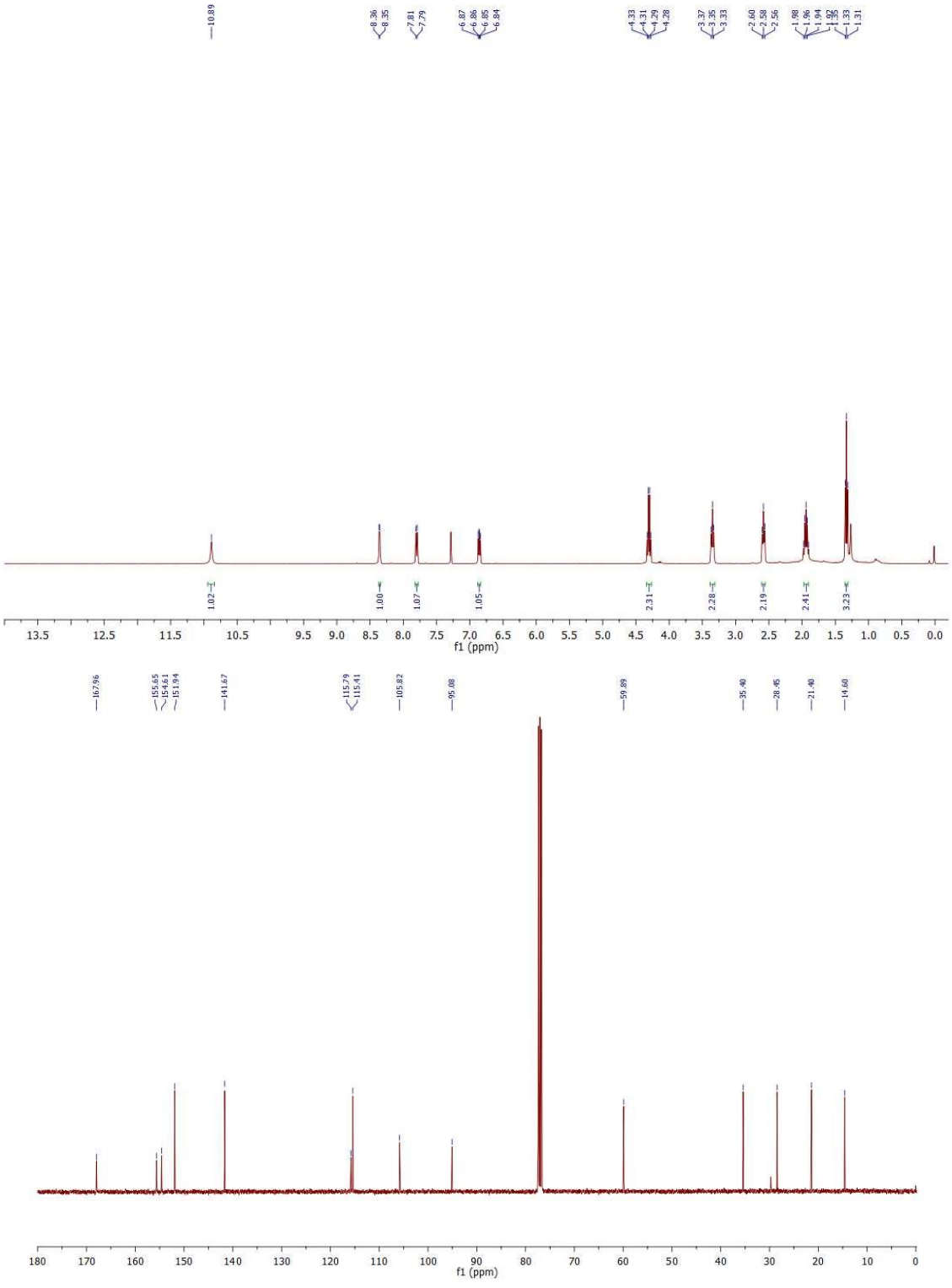


Fig. S2 ^{1}H and ^{13}C NMR spectra of Ethyl 2-((3-cyanopyridin-2-yl)amino)cyclopent-1-ene-1-carboxylate (**2a**)

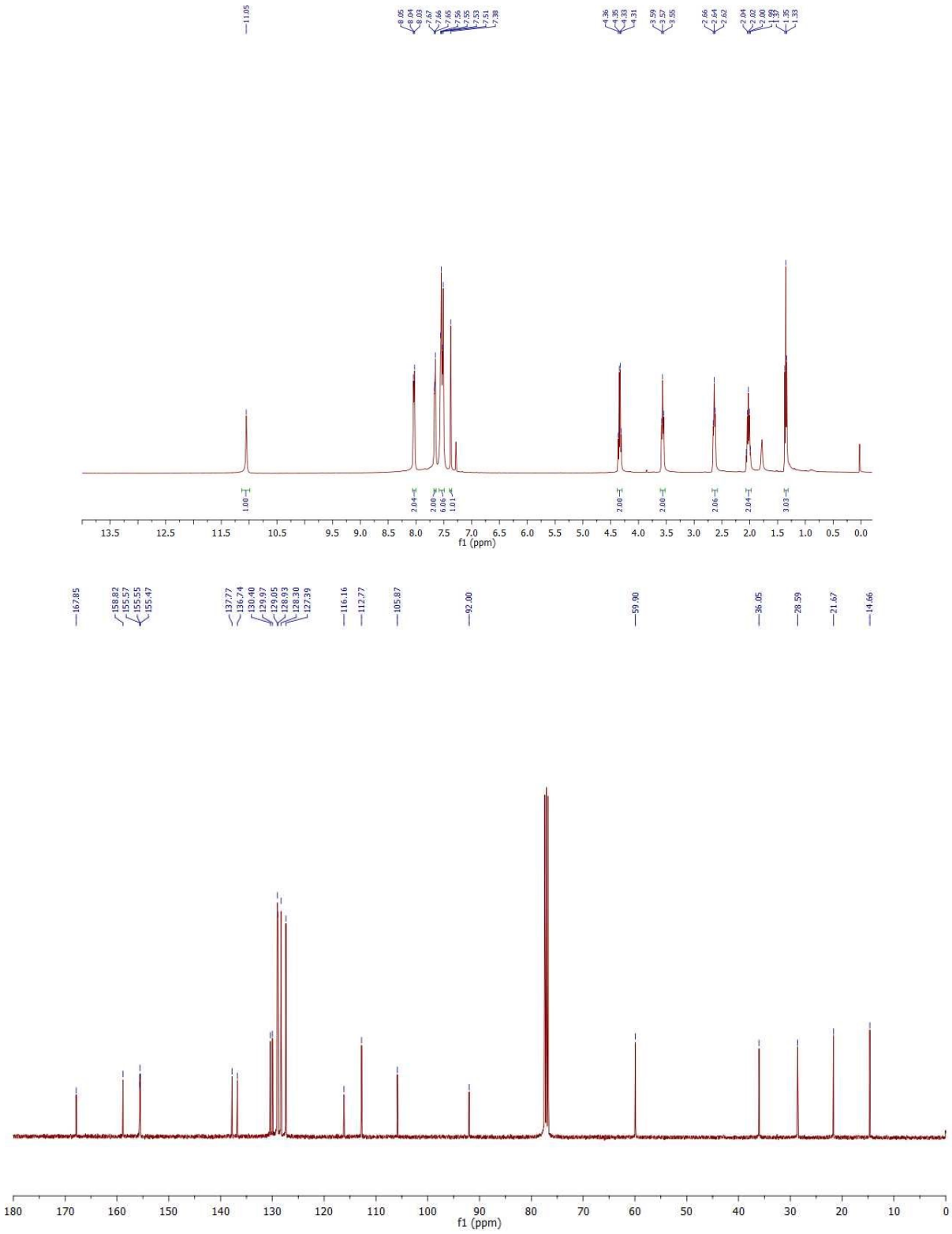


Fig. S3 ^{1}H and ^{13}C NMR spectra of Ethyl 2-((3-cyano-4,6-diphenylpyridin-2-yl)amino)cyclopent-1-ene-1-carboxylate (**2b**)

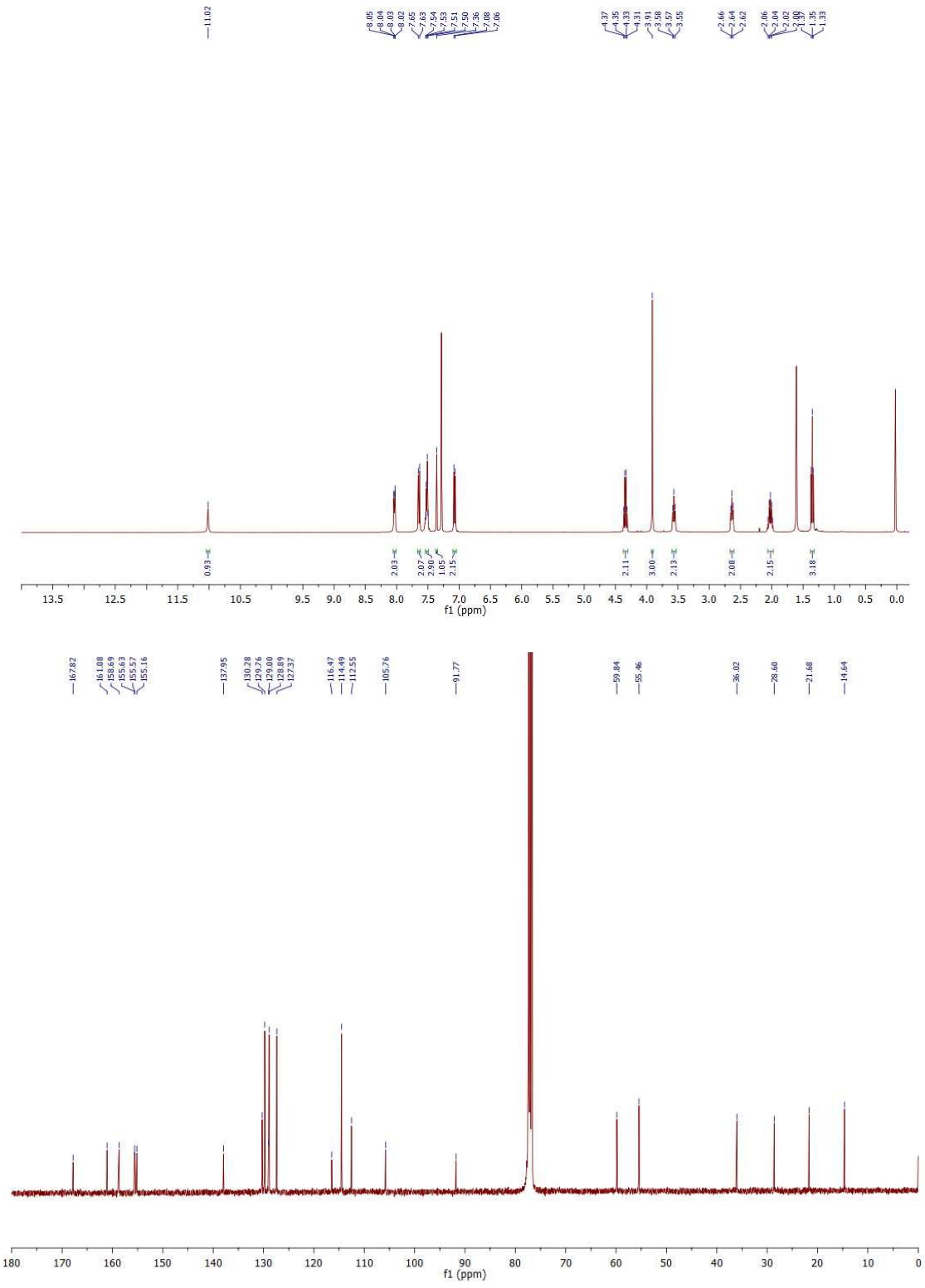


Fig. S4 ^{1}H and ^{13}C NMR spectra of Ethyl 2-((3-cyano-4-(4-methoxyphenyl)-6-phenylpyridin-2-yl)amino)cyclopent-1-ene-1-carboxylate (**2c**)

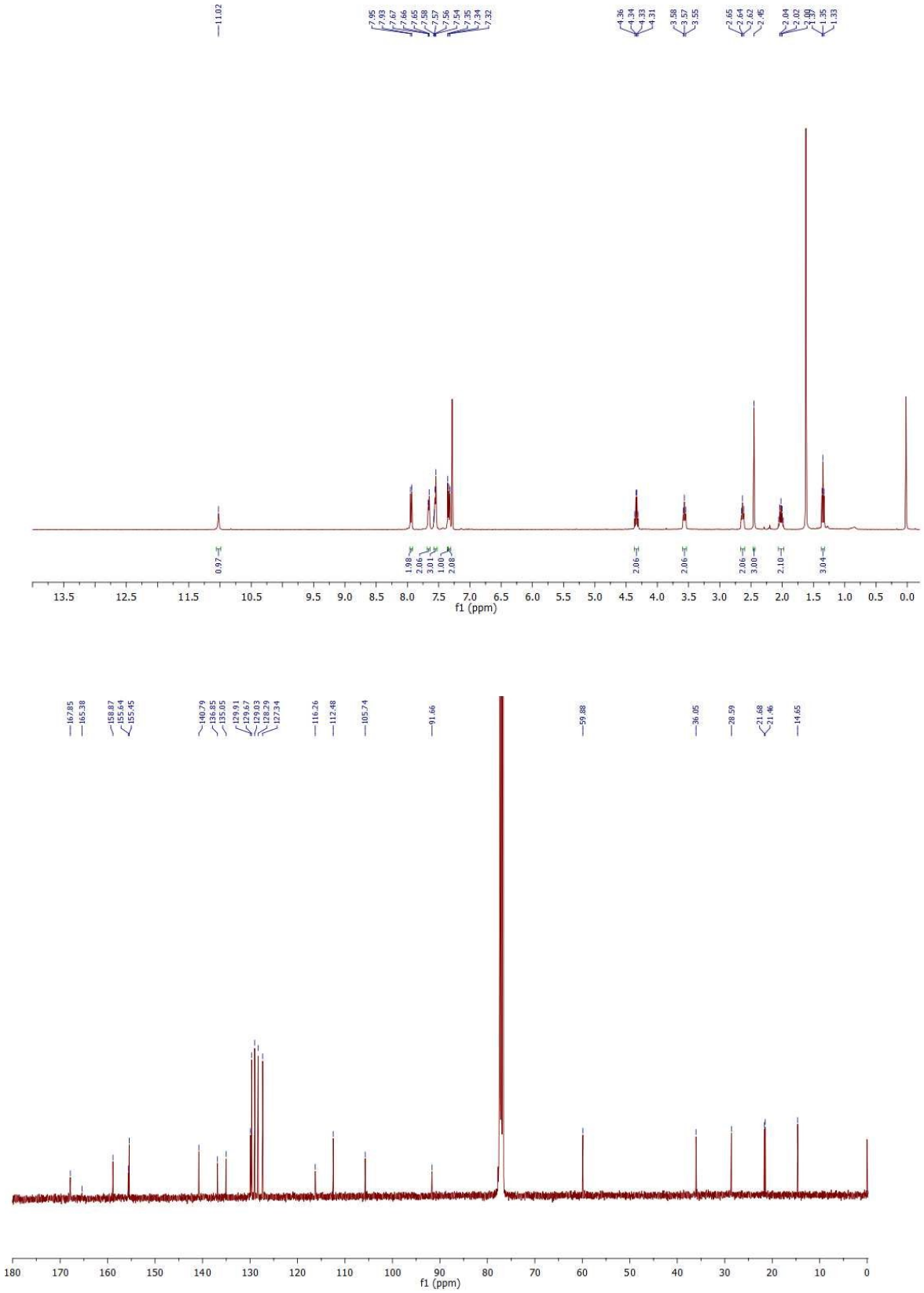


Fig. S5 ^{1}H and ^{13}C NMR spectra of Ethyl 2-((3-cyano-4-phenyl-6-(p-tolyl)pyridin-2-yl)amino)cyclopent-1-ene-1-carboxylate (**2d**)

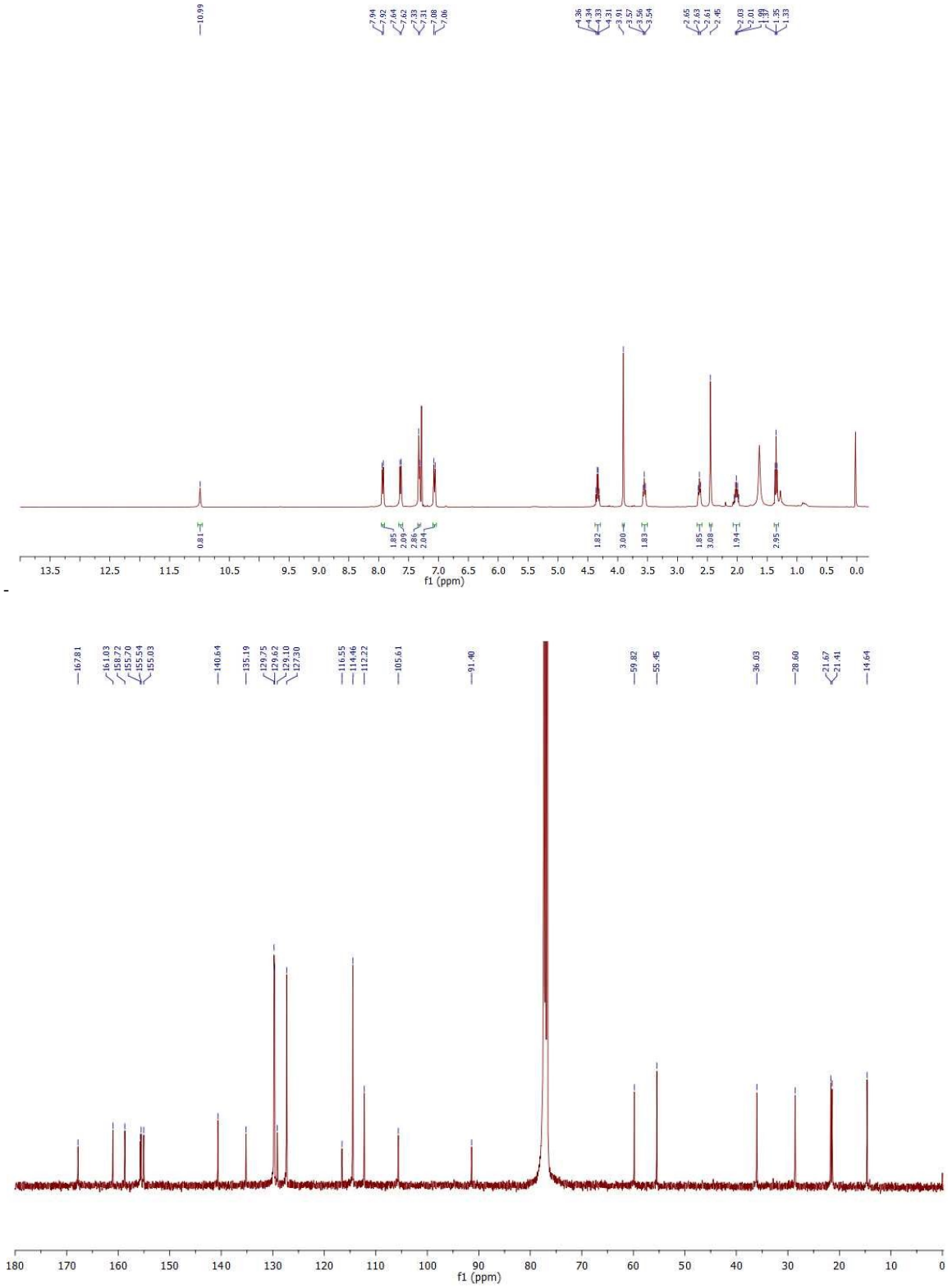


Fig. S6 ^{1}H and ^{13}C NMR spectra of Ethyl 2-((3-cyano-4-(4-methoxyphenyl)-6-(p-tolyl)pyridin-2-yl)amino)cyclopent-1-ene-1-carboxylate (**2e**)

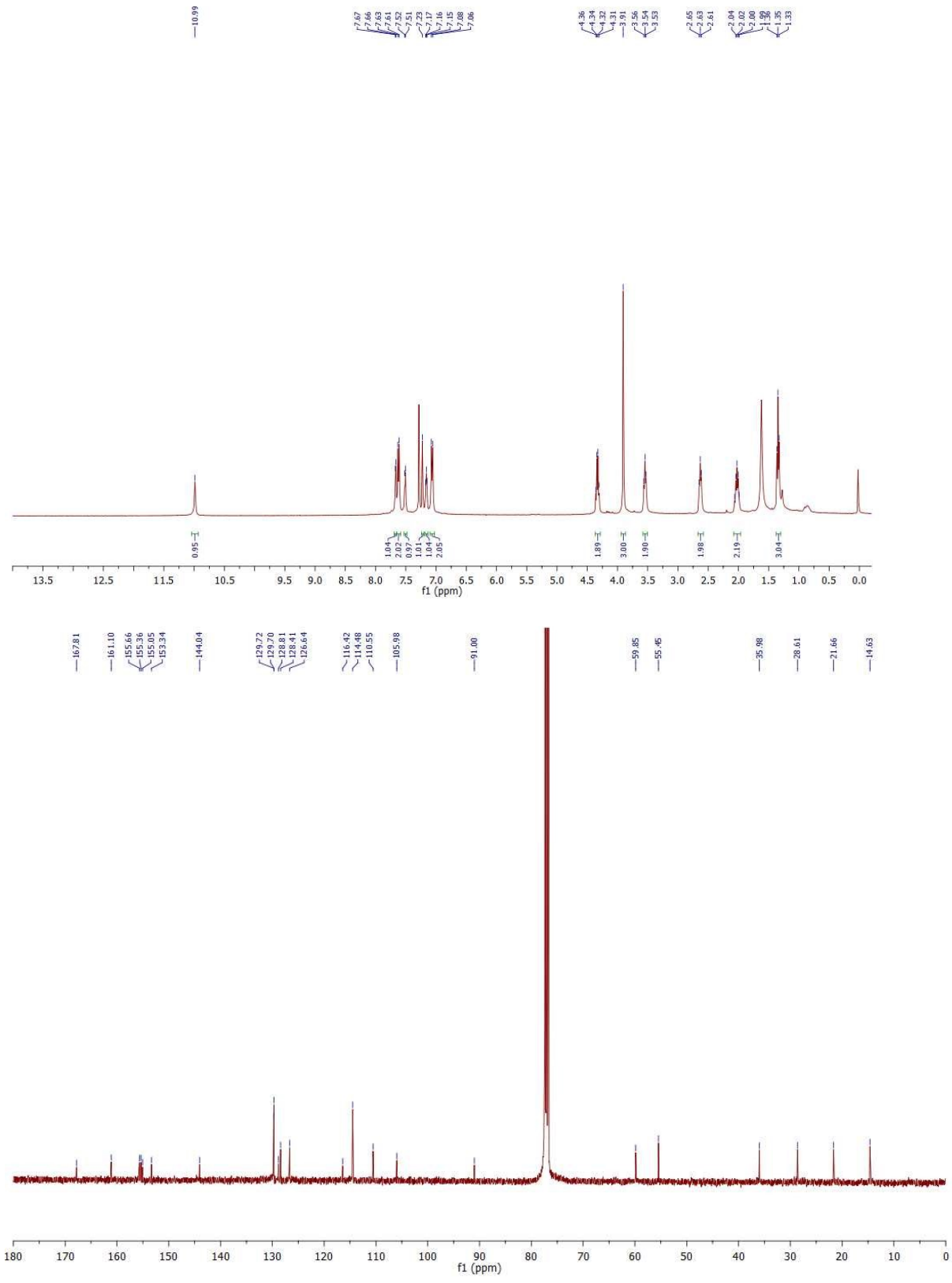


Fig. S7 ^{1}H and ^{13}C NMR spectra of Ethyl 2-((3-cyano-4-(4-methoxyphenyl)-6-(thiophen-2-yl)pyridin-2-yl)amino)cyclopent-1-ene-1-carboxylate (**2f**)

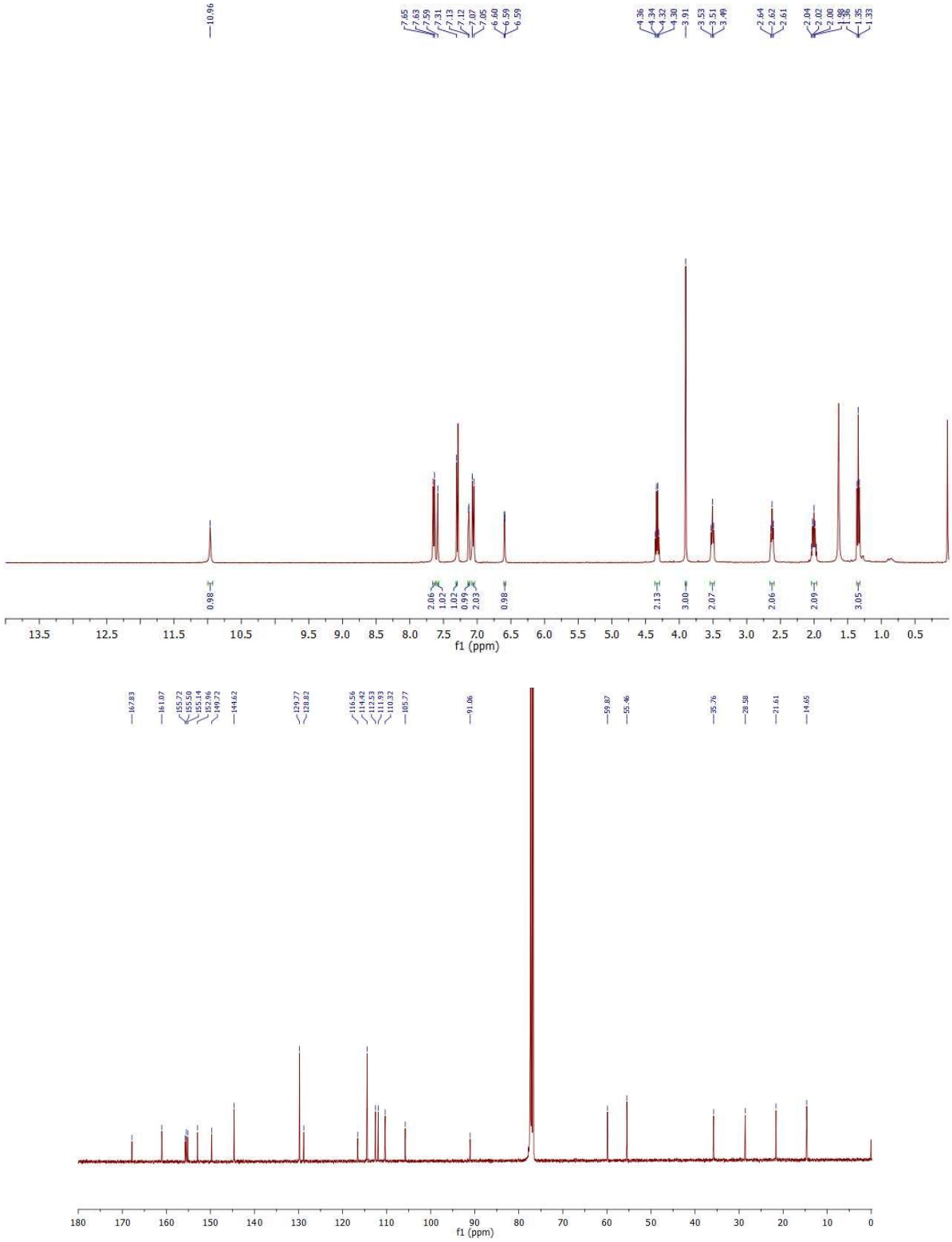


Fig. S8 ^{1}H and ^{13}C NMR spectra of Ethyl 2-((3-cyano-6-(furan-2-yl)-4-(4-methoxyphenyl)pyridin-2-yl)amino)cyclopent-1-ene-1-carboxylate (**2g**)

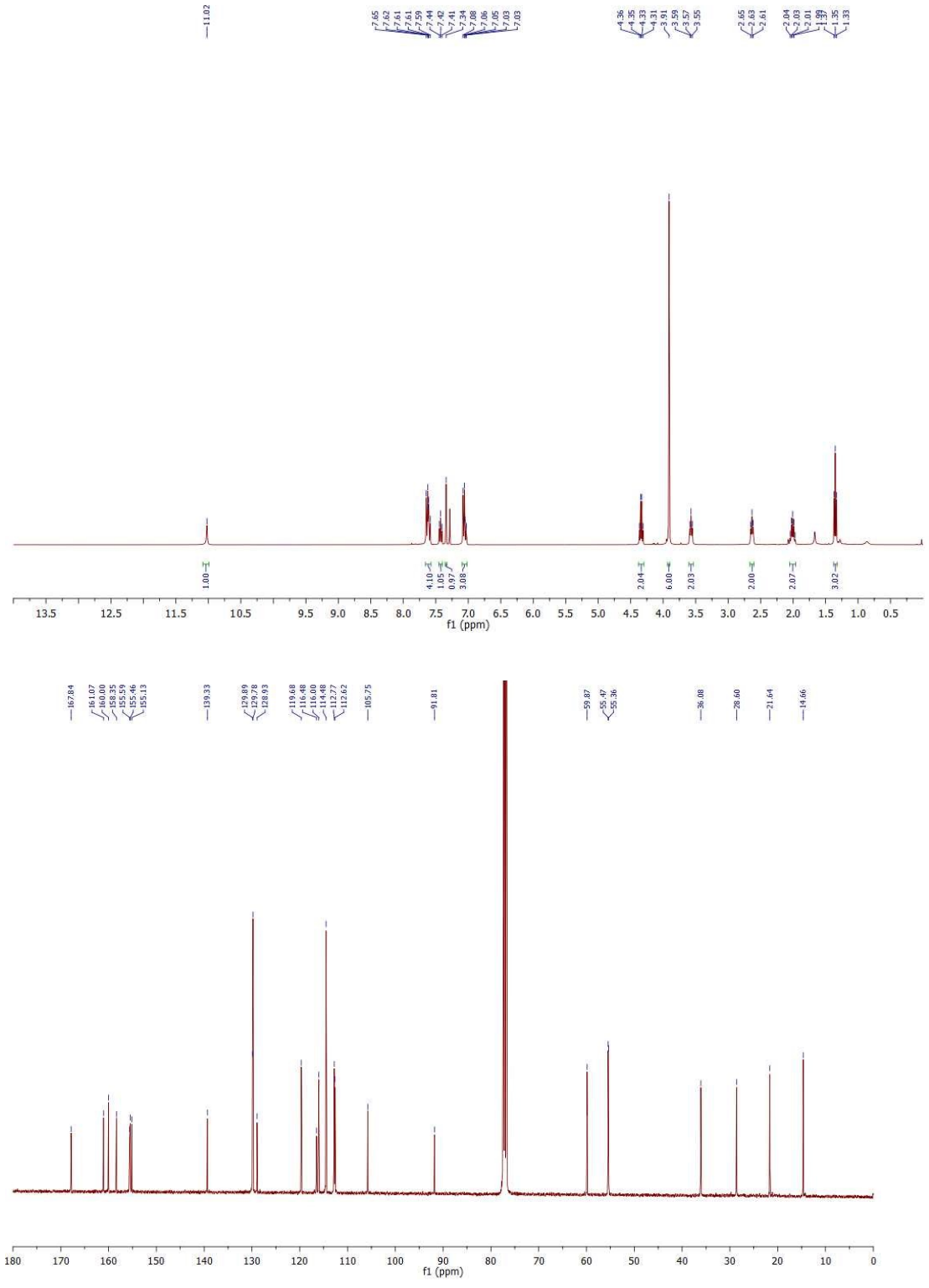


Fig. S9 ^{1}H and ^{13}C NMR spectra of Ethyl 2-((3-cyano-6-(3-methoxyphenyl)-4-(4-methoxyphenyl)pyridin-2-yl)amino)cyclopent-1-ene-1-carboxylate (**2h**)

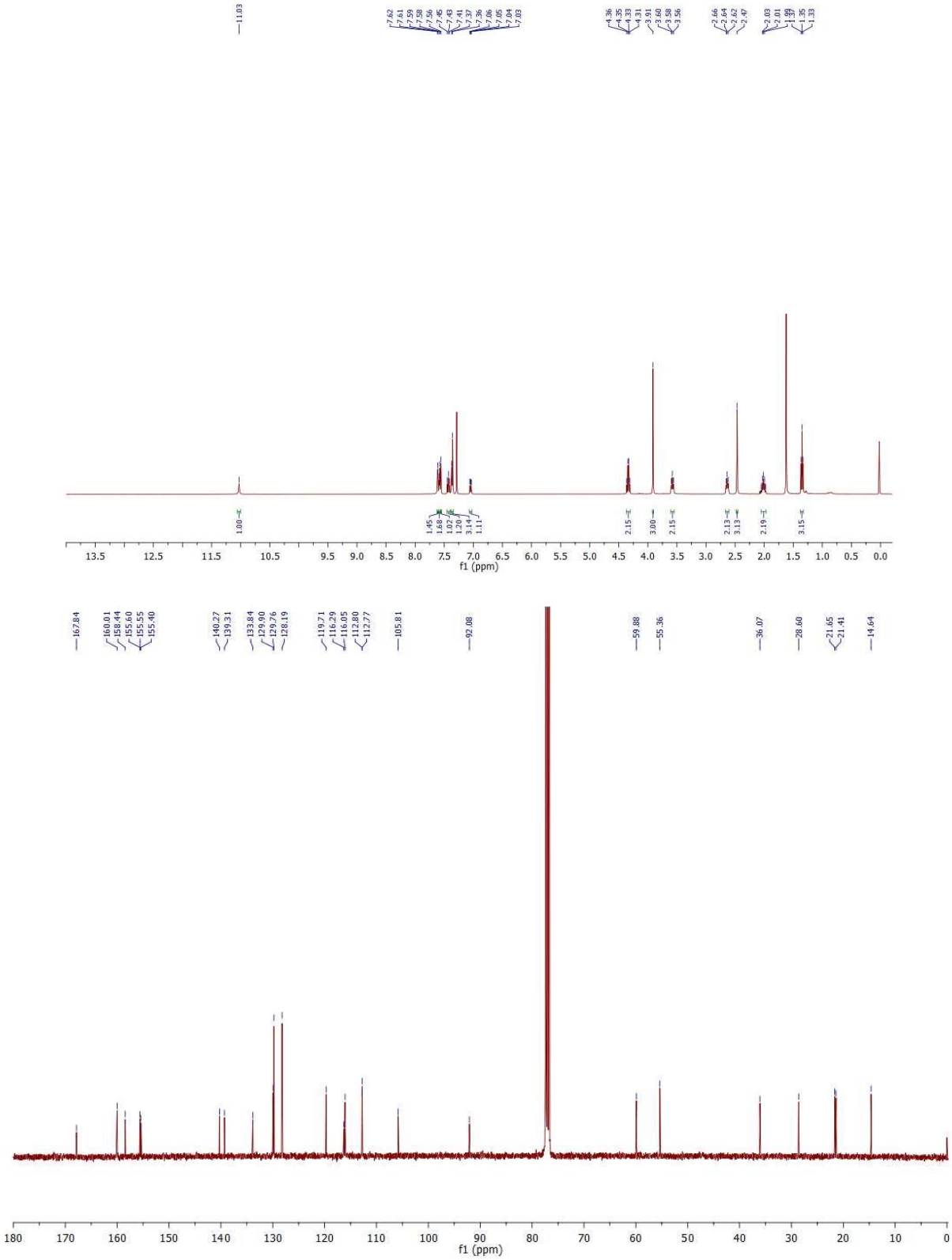


Fig. S10 ^{1}H and ^{13}C NMR spectra of Ethyl 2-((3-cyano-6-(3-methoxyphenyl)-4-(p-tolyl)pyridin-2-yl)amino)cyclopent-1-ene-1-carboxylate (**2i**)

4. FTIR Spectra of synthesized compounds 2a-2i

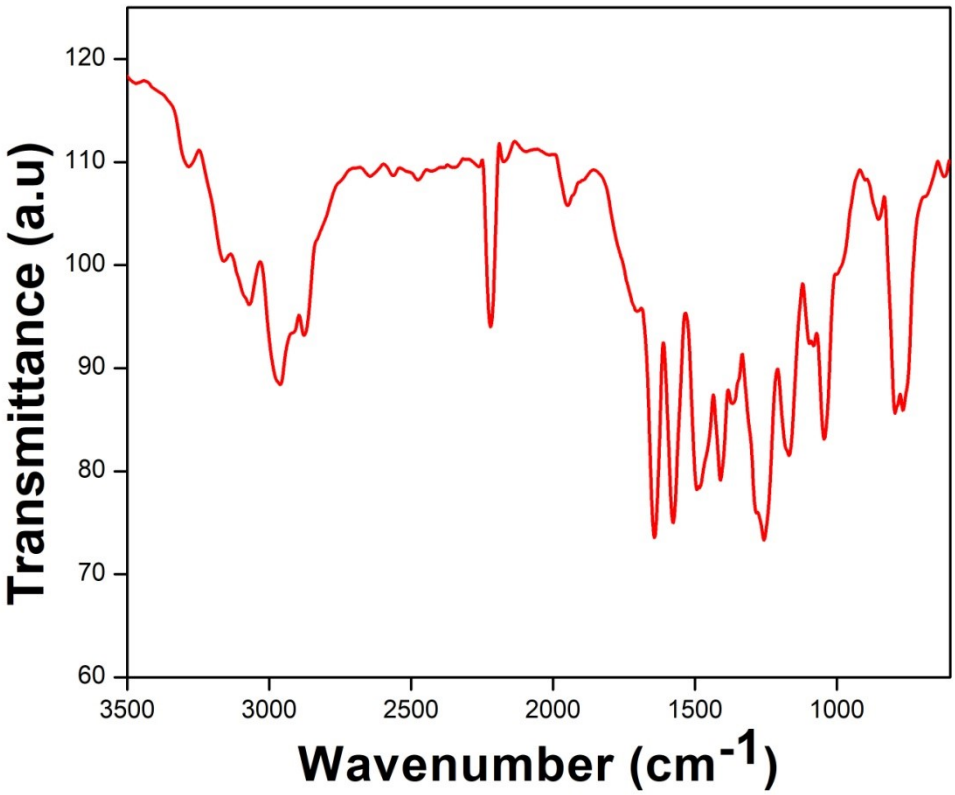


Fig. S11 FTIR spectrum of **2a**

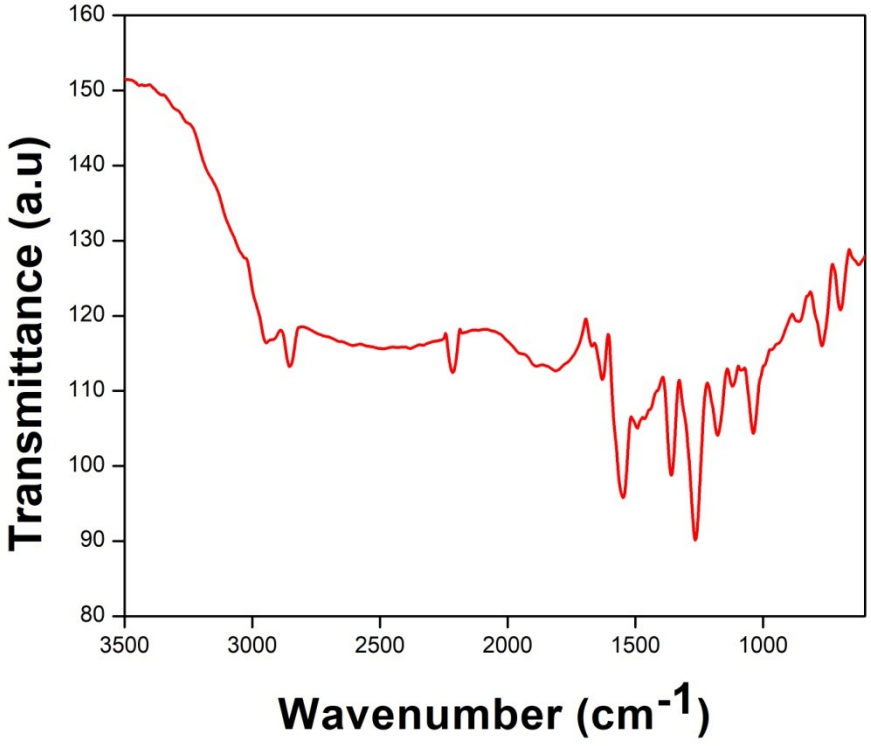


Fig. S12 FTIR spectrum of **2b**

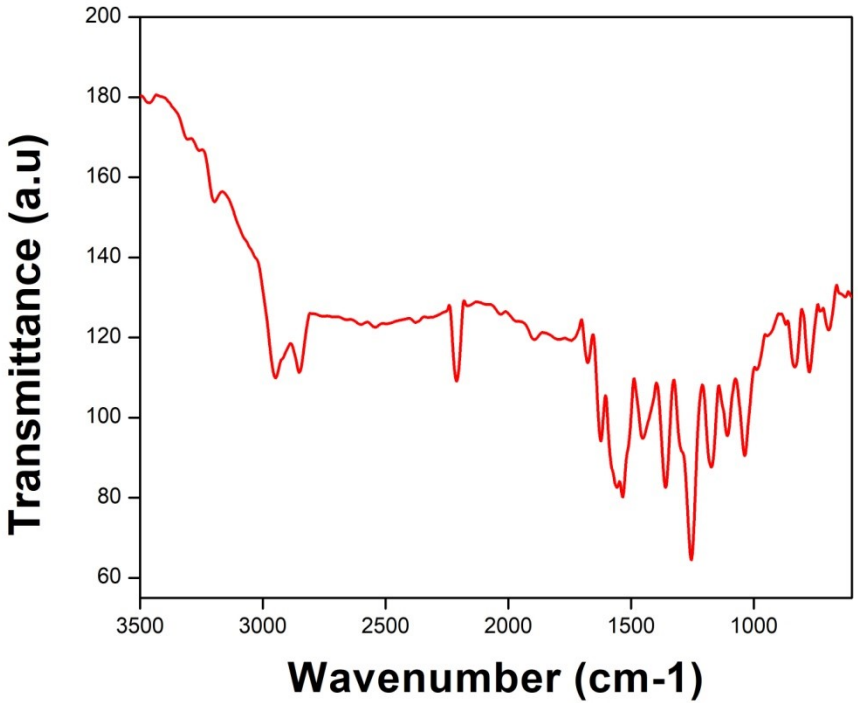


Fig. S13 FTIR spectrum of **2c**

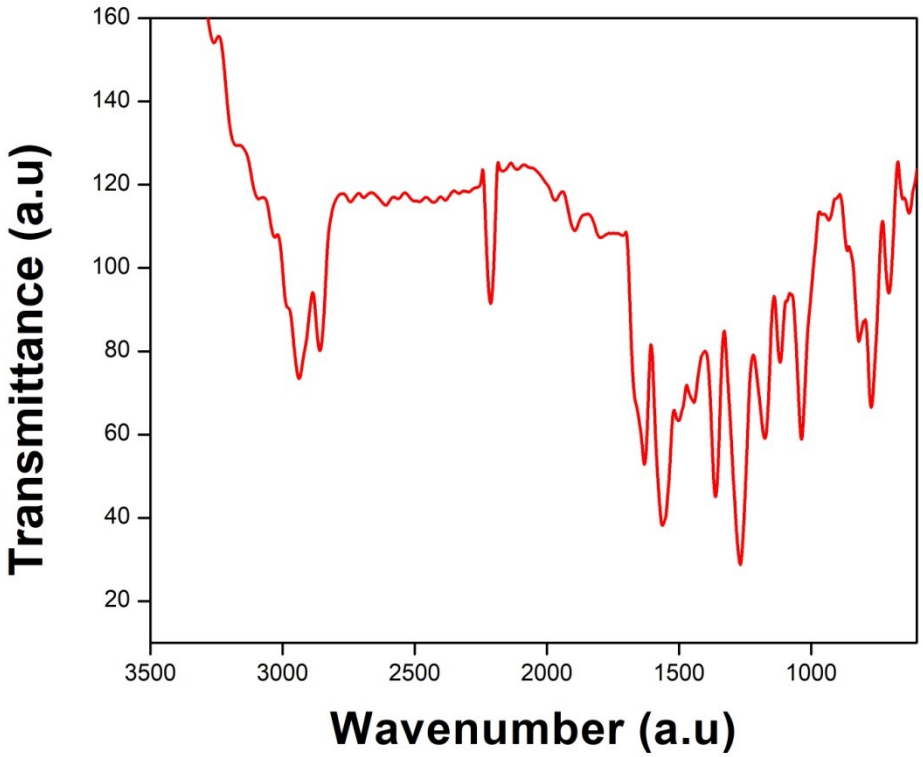


Fig. S14 FTIR spectrum of **2d**

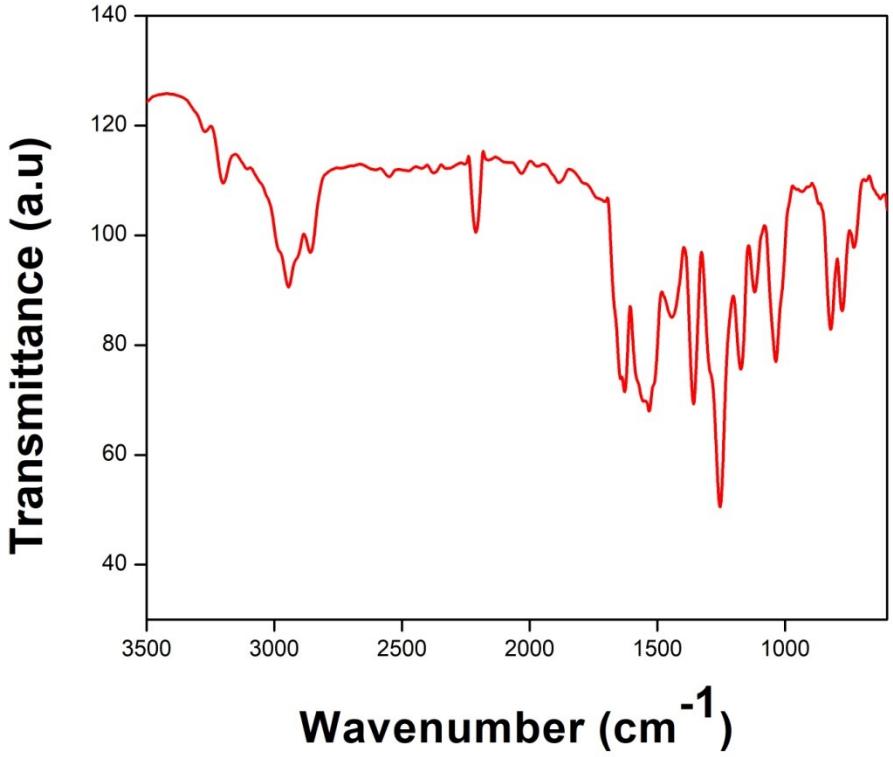


Fig. S15 FTIR spectrum of **2e**

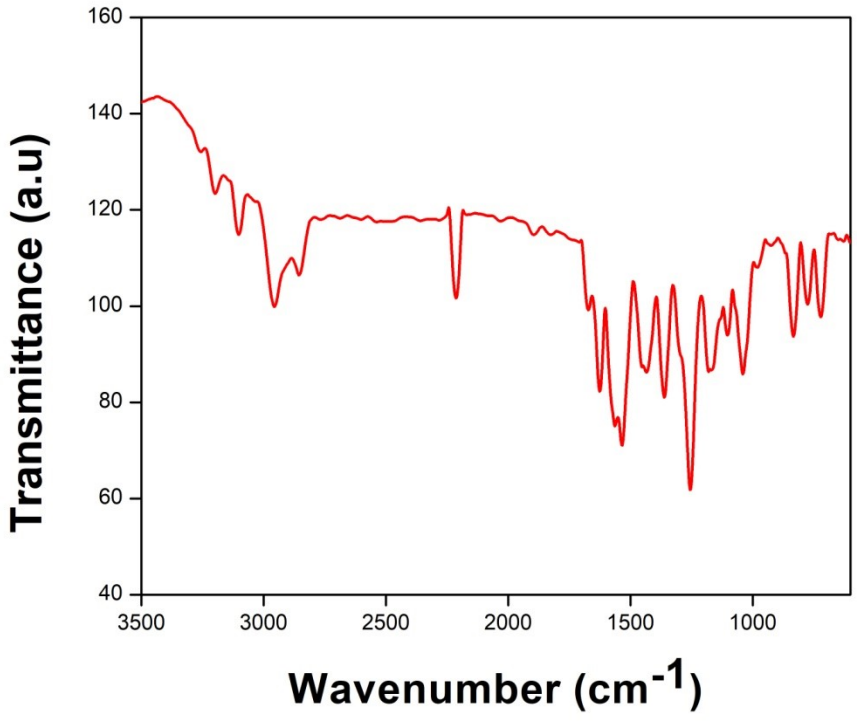


Fig. S16 FTIR spectrum of **2f**

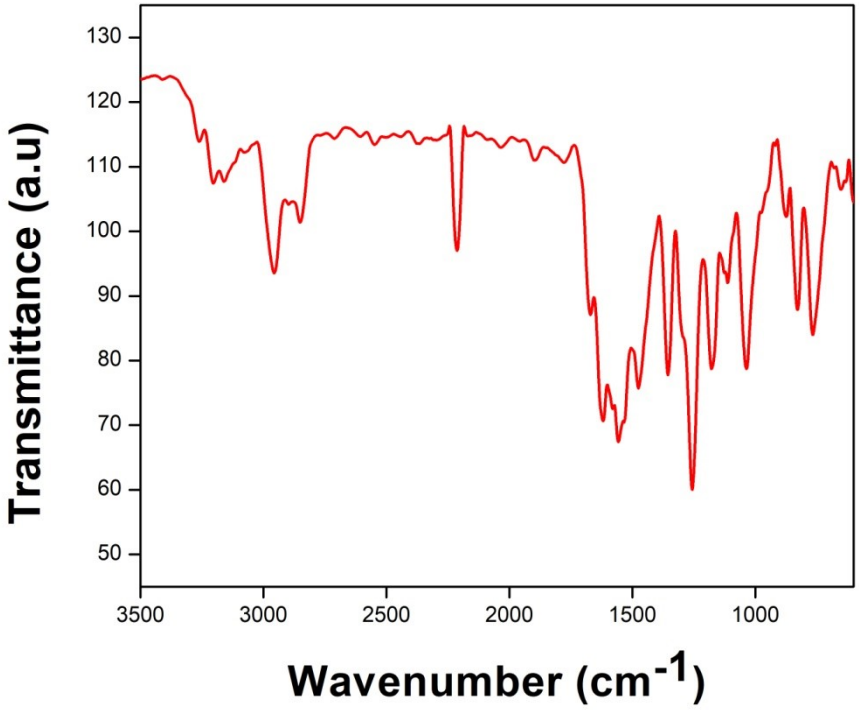


Fig. S17 FTIR spectrum of **2g**

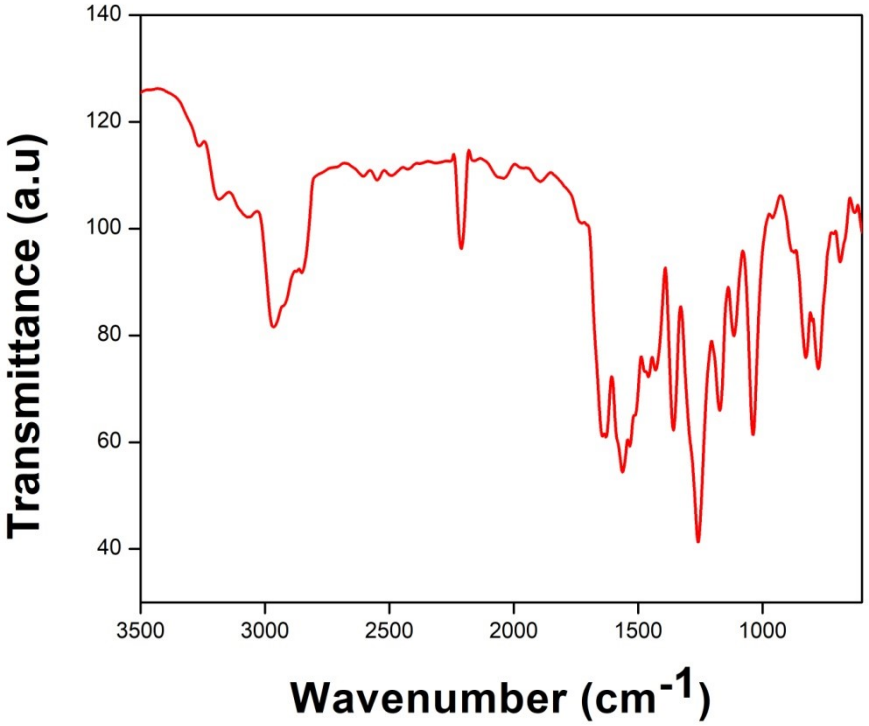


Fig. S18 FTIR spectrum of **2h**

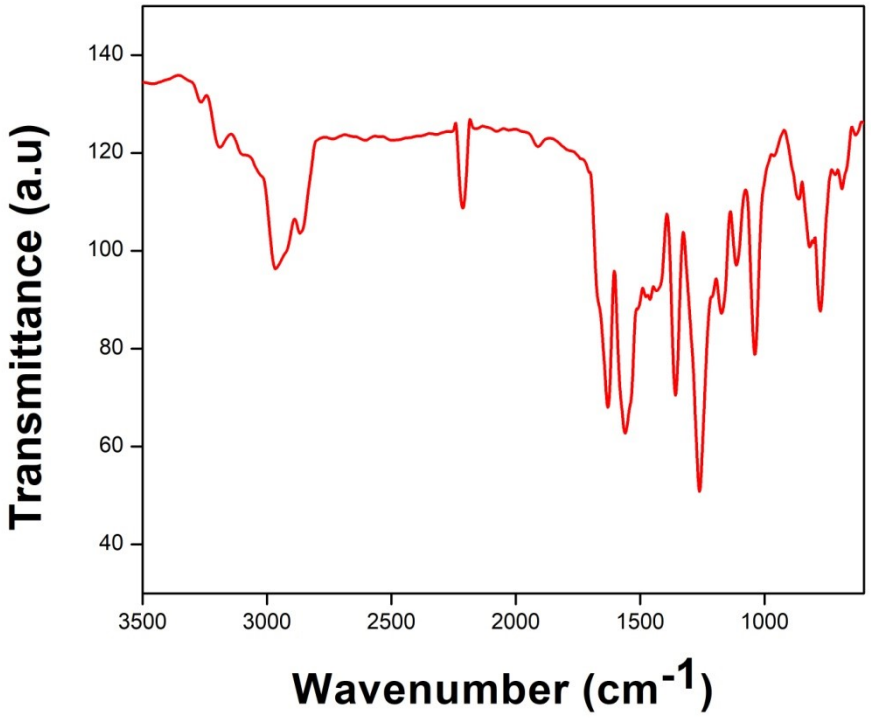


Fig. S19 FTIR spectrum of **2i**

5. Photophysical graphs of compound 2e

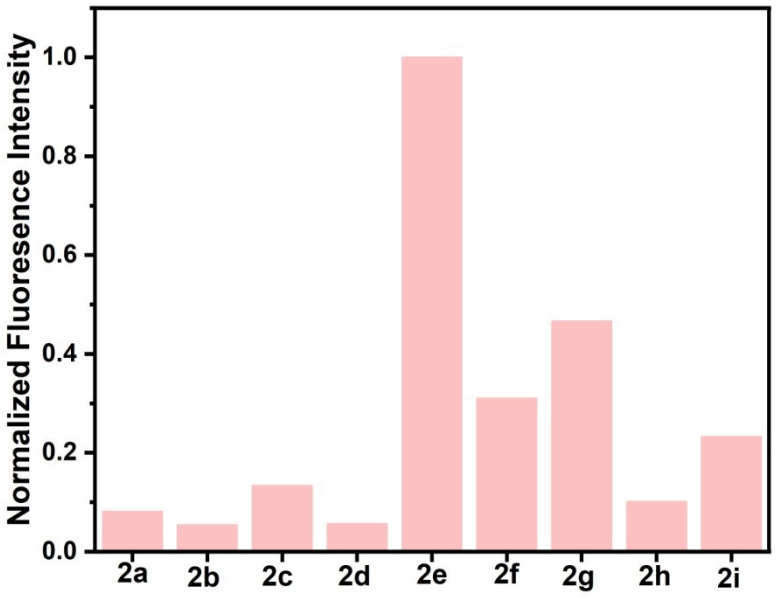


Fig. S20 Bar graph showing normalized emission intensities of **2a-2i** in THF/water (6:4, v/v).

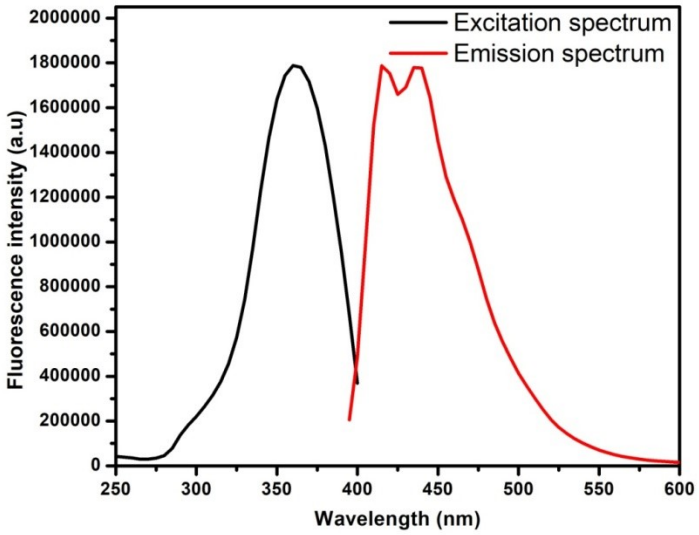


Fig. S21 Excitation emission spectrum of **2e** in THF/water (6:4, v/v).

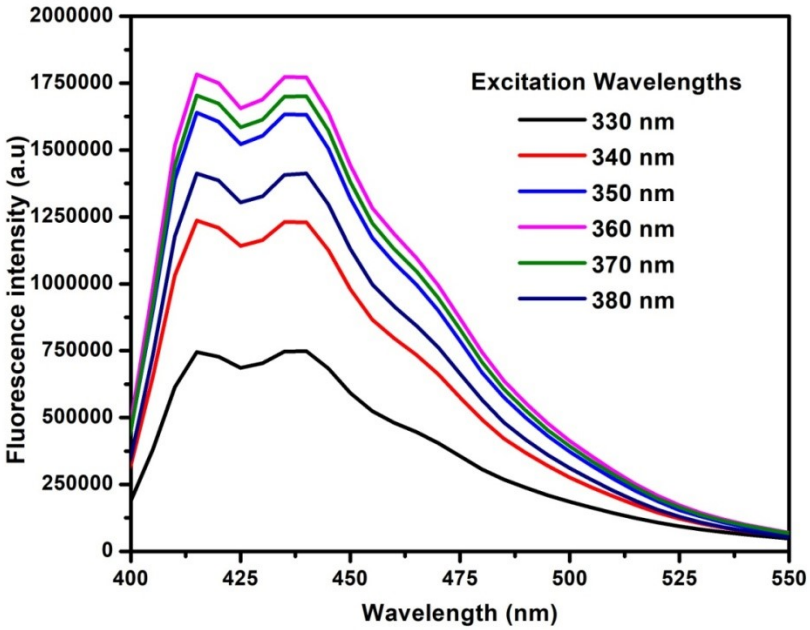


Fig. S22 Fluorescence spectrum of **2e** at different excitation wavelengths (330-380 nm).

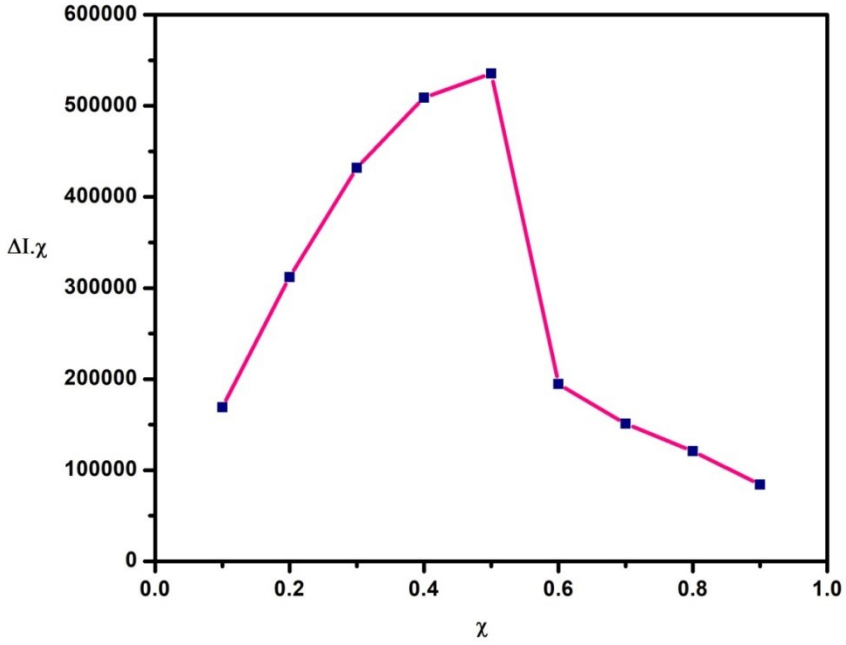


Fig. S23 Job's plot for determining the stoichiometry of **2e** and Fe^{3+} in THF/water (6:4, v/v).

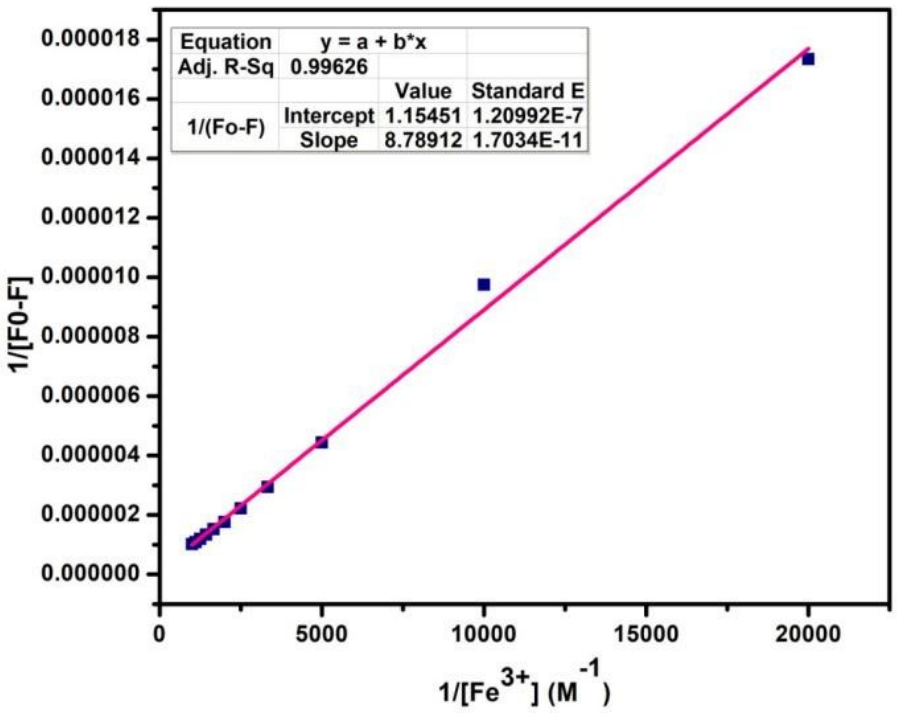


Fig. S24 Benesi-Hildebrand plot of **2e** (10 μM) with Fe^{3+} (0-100 eq.) using the emission at 440 nm.

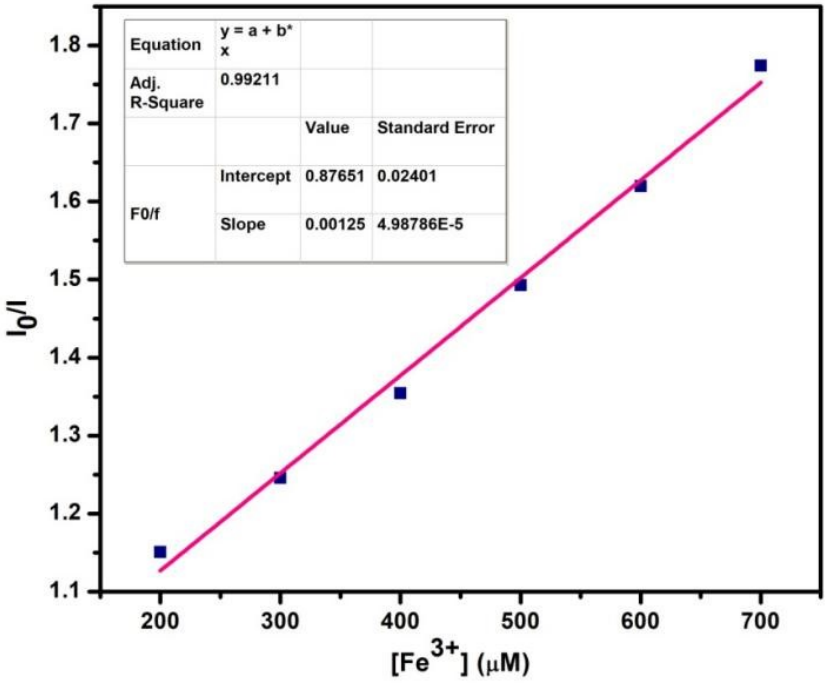


Fig. S25 Stern–Volmer plot for **2e.**

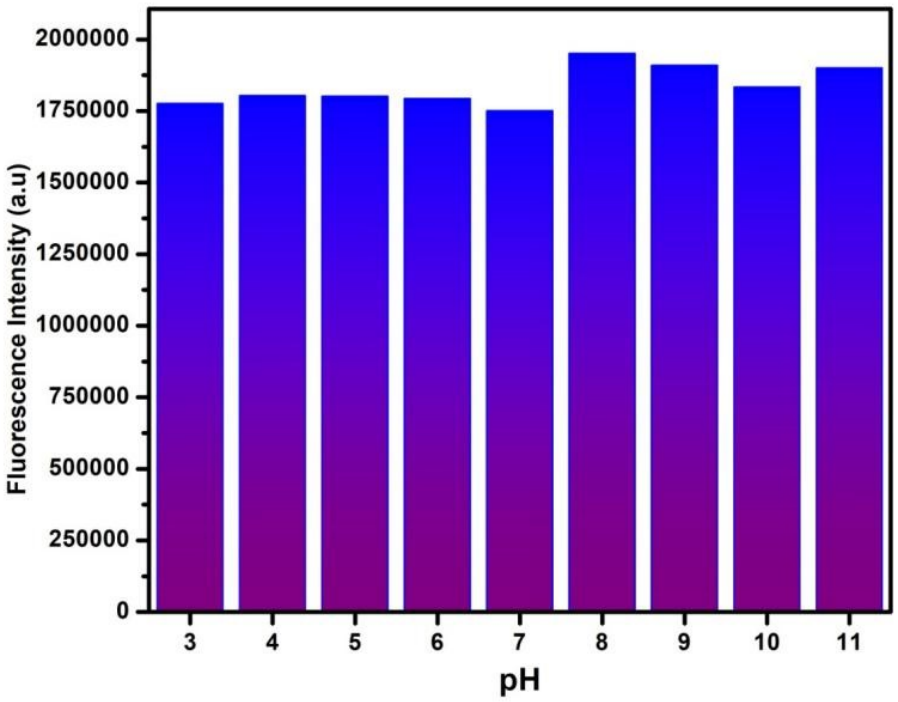


Fig. S26 Effect of pH on the fluorescence intensity of **2e** (10 μM).

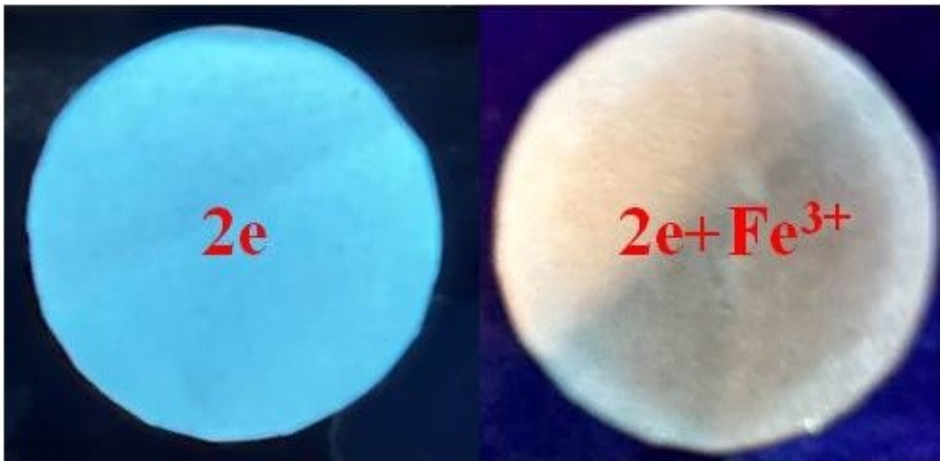


Fig. S27 Fluorescence changes of whatman filter paper before and after dipped in Fe^{3+} solution under UV light at 365 nm.

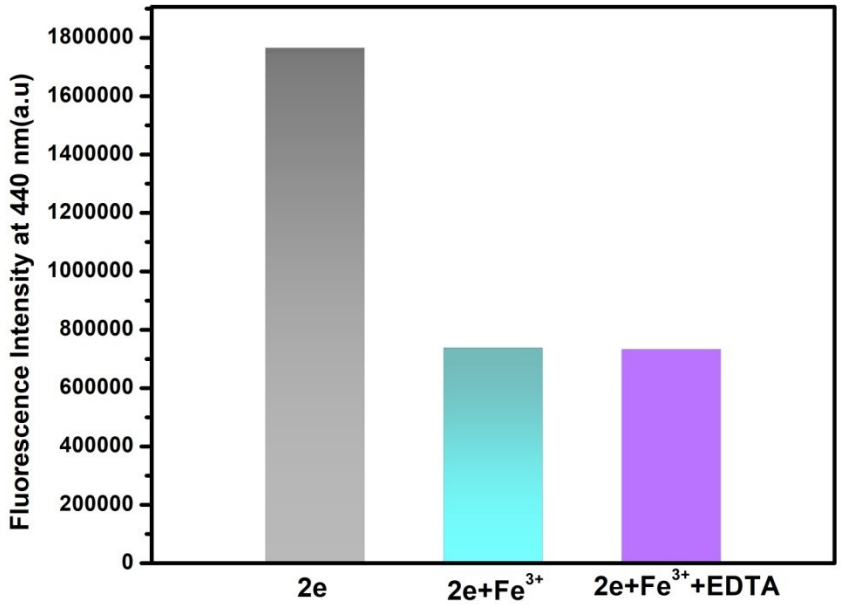


Fig. S28 Irreversible nature of **2e** (10 μM) for Fe^{3+} with addition of Na_2H_2EDTA.

6. Optimized Cartesian Coordinates of Different Stationary Points

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Ligand

Number of imaginary frequencies : 0
The smallest frequencies are : 19.1322 24.6938 30.5456 cm(-1)
Electronic energy : -1473.3118849
Zero-point correction= 0.495314 (Hartree/Particle)
Thermal correction to Energy= 0.526543
Thermal correction to Enthalpy= 0.527487
Thermal correction to Gibbs Free Energy= 0.430502
Sum of electronic and zero-point Energies= -1472.816571
Sum of electronic and thermal Energies= -1472.785342
Sum of electronic and thermal Enthalpies= -1472.784398
Sum of electronic and thermal Free Energies= -1472.881383

.....

Cartesian Coordinates

.....

6	-0.495159	0.040348	0.064729
6	0.575944	-0.902434	0.029184
6	1.902575	-0.416301	-0.020314
6	2.078787	0.969180	-0.054300
6	0.969695	1.824567	-0.046221
1	3.083926	1.368486	-0.045984
7	-1.790813	-0.439568	0.119779
7	-0.292065	1.352783	0.015490
6	0.271185	-2.290145	-0.005206
7	-0.052508	-3.411835	-0.046568
6	1.118453	3.298466	-0.087442

6	0.053570	4.129461	0.307310
6	2.305991	3.910481	-0.524103
6	0.181806	5.513831	0.281540
1	-0.874881	3.679942	0.639461
6	2.425026	5.298027	-0.551682
1	3.139472	3.308503	-0.869995
6	1.370462	6.126420	-0.144641
1	-0.653100	6.133831	0.597740
1	3.350674	5.745913	-0.902545
6	3.080874	-1.310502	-0.035755
6	4.161524	-1.031851	-0.895795
6	3.179936	-2.424863	0.810279
6	5.283944	-1.845044	-0.919477
1	4.108483	-0.181319	-1.567937
6	4.306733	-3.246257	0.802926
1	2.383475	-2.646053	1.512479
6	5.364530	-2.960042	-0.069832
1	6.109311	-1.638520	-1.592763
1	4.351164	-4.089511	1.480586
6	1.509055	7.626497	-0.142456
1	0.587453	8.112209	-0.478500
1	1.715623	7.996294	0.869613
1	2.329254	7.954966	-0.786767
8	6.511658	-3.695853	-0.165829
6	6.635161	-4.869043	0.647858
1	5.842452	-5.591507	0.424670
1	7.603577	-5.302246	0.395075
1	6.615275	-4.618773	1.714293
1	-1.926586	-1.443298	-0.011475
6	-2.975086	0.234937	0.272710
6	-3.122220	1.707699	0.565438
6	-4.199429	-0.375154	0.174602
6	-4.601276	1.833431	0.993891
1	-2.898338	2.282788	-0.340450
1	-2.419550	2.047327	1.328156
6	-5.322277	0.621926	0.360398
1	-4.663527	1.761287	2.084566
1	-5.037432	2.790755	0.699042
1	-6.127748	0.236781	0.992957
1	-5.775575	0.880388	-0.606527
6	-4.375833	-1.774952	-0.132878
8	-3.461018	-2.605385	-0.263401
8	-5.677179	-2.119741	-0.267230
6	-5.954853	-3.512439	-0.572793
1	-5.467730	-3.769721	-1.518380
1	-5.523197	-4.138341	0.214202
6	-7.459028	-3.660685	-0.651682
1	-7.927521	-3.386570	0.298215
1	-7.873618	-3.027360	-1.441638
1	-7.711867	-4.701436	-0.875051

Ligand-Fe^{3+} Complex

Number of imaginary frequencies : 0
The smallest frequencies are : 11.6783 23.1827 32.5559 cm(-1)
Electronic energy : -1596.7385476
Zero-point correction= 0.496449 (Hartree/Particle)
Thermal correction to Energy= 0.528348
Thermal correction to Enthalpy= 0.529292
Thermal correction to Gibbs Free Energy= 0.430763
Sum of electronic and zero-point Energies= -1596.242098
Sum of electronic and thermal Energies= -1596.210199
Sum of electronic and thermal Enthalpies= -1596.209255
Sum of electronic and thermal Free Energies= -1596.307785

Cartesian Coordinates

6	-0.039353	-0.701636	-0.085349
6	-0.458551	0.663992	-0.059803
6	-1.844482	0.939589	-0.061033
6	-2.693279	-0.173998	-0.084717
6	-2.189563	-1.491435	-0.089175
1	-3.761563	-0.007575	-0.044679
7	1.334052	-0.924301	-0.143643
7	-0.859100	-1.732346	-0.093136
6	0.574118	1.631995	-0.034663
7	1.589338	2.200920	-0.008301
6	-3.075459	-2.665161	-0.064847
6	-2.571433	-3.917259	0.341683
6	-4.429237	-2.578366	-0.439643
6	-3.399635	-5.030363	0.391614
1	-1.530216	-4.005116	0.631285
6	-5.248356	-3.702327	-0.395319
1	-4.845271	-1.640941	-0.793076
6	-4.754842	-4.944933	0.028653
1	-2.995287	-5.984114	0.719691
1	-6.287922	-3.616309	-0.698290
6	-2.382590	2.307624	-0.039392
6	-3.498289	2.632921	-0.839028
6	-1.815933	3.313543	0.760951
6	-4.005894	3.920612	-0.854208
1	-3.946615	1.876875	-1.475801
6	-2.328021	4.608932	0.764375
1	-0.995750	3.082013	1.433950
6	-3.424972	4.919950	-0.053152
1	-4.851426	4.180511	-1.482296
1	-1.880534	5.354007	1.409810
6	-5.648471	-6.152881	0.117247

1	-5.154743	-7.041476	-0.289436
1	-5.892079	-6.373968	1.163861
1	-6.588596	-5.998690	-0.418835
8	-4.000980	6.149073	-0.137349
6	-3.489632	7.202187	0.691096
1	-2.443646	7.422469	0.451580
1	-4.104701	8.075476	0.471619
1	-3.579685	6.948352	1.752854
1	1.919282	-0.105134	-0.349651
6	2.072761	-2.017111	0.015367
6	1.634009	-3.417317	0.283390
6	3.489790	-1.930042	-0.048156
6	2.936529	-4.127544	0.720956
1	1.227286	-3.824640	-0.652182
1	0.825741	-3.457028	1.016862
6	4.094613	-3.271245	0.153135
1	2.996100	-4.132875	1.812489
1	2.976159	-5.159350	0.371693
1	4.983731	-3.232666	0.789863
1	4.436641	-3.645971	-0.825906
6	4.222139	-0.672890	-0.241244
8	3.607793	0.388115	-0.527567
8	5.511944	-0.759406	-0.097621
6	6.314139	0.466534	-0.279083
1	6.055361	0.881693	-1.256031
1	6.013413	1.167752	0.505313
6	7.763276	0.062433	-0.172353
1	7.976966	-0.371622	0.808019
1	8.024407	-0.659012	-0.951074
1	8.384067	0.953805	-0.301315
26	3.569943	2.347176	0.055836