Supporting Information

Dual-State Emission of Pyrazolyl-Pyrrolo[3,4-*b*]pyridin-5-ones *via* Excited-State Intramolecular Proton Transfer (ESIPT): Multicomponent Synthesis and Optical Characterization

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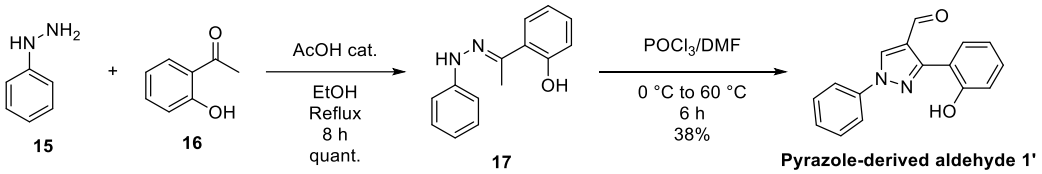
General remarks

All reagents and solvents were obtained from Sigma-Aldrich-Merck and used as received, without further purification, distillation, or drying. Solvents were dried following standard procedures. **^{1}H**, **^{11}B**, **^{13}C**, and **^{19}F** Nuclear Magnetic Resonance (NMR) spectra were acquired on a Bruker AMX Advance III spectrometer (500 MHz, Fällande, Uster, Switzerland) using chloroform ($CDCl_3$) as solvent. Chemical shifts (δ) are reported in parts per million (ppm) relative to $Si(CH_3)_4$. Coupling constants (*J*) are reported in hertz (Hz). Peak multiplicity is indicated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, bs = broad signal for proton spectra. The spectra were processed using MestReNova software, version 12.0.0-20080 (A Coruña, Spain). **FT-IR spectra** were recorded on an Agilent Cary 630 FT-IR instrument. **High-Resolution Mass Spectrometry** (HRMS) data were acquired by electrospray ionization (ESI) using a Micro-TOF II mass spectrometer (Bruker Daltonics GmbH, Bremen, Germany). The sample was injected directly through an Apollo source and analyzed using the time-of-flight (TOF) method. HRMS spectra were analyzed with Compass software (version 1.5, Bruker Daltonik GmbH, Bremen, Germany). **Microwave-assisted reactions** were carried out in a closed-vessel mode using a CEM Discover SP MW reactor (Matthews, North Carolina, USA). **The reaction progress** was monitored by thin-layer chromatography (TLC), with spots visualized under ultraviolet (UV) light at 254 or 365 nm. **The purification of the final products** was performed using preparative glass plates (20 x 20 cm) coated with silica gel 60 containing a UV indicator (F254). **Chemical structures** were generated using ChemDraw software, version 15.0.0.106 Professional (Perkin Elmer Informatics, Cambridge, MA, USA). **Absorption spectra** were recorded in high performance liquid chromatography (HPLC) grade chloroform, acetonitrile and dimethylsulfoxide at 293 K on a Perkin Elmer Lambda 950 spectrophotometer. For the determination of the molar extinction coefficients (ε), absorption measurements at five different concentrations were carried out. **Emission spectra in solution** were recorded in HPLC grade chloroform, acetonitrile and dimethylsulfoxide at 293 K on a Perkin Elmer LS 55 Luminescence Spectrometer. **PL and PLQY measurements** were obtained in an Edinburgh Instruments FS5 fluorometer with a 150 W CW Ozone-free xenon arc lamp, and Czerny–Turner monochromators, using an SC-05 (standard cuvette), SC-10 (solid-state holder) and SC-30 (Integrating Sphere) modules, respectively. **Single-crystal X-ray diffraction data** were collected at 100 K on a Rigaku XtaLAB Synergy-s diffractometer equipped with a HyPix-6000HE detector. The structures were solved using SHELXT and refined by full-matrix least squares on F^2 by SHELXL, interfaced through the program OLEX. All atoms were refined anisotropically and hydrogen atoms were included at geometrically estimated positions. Images were produced using the software Crystal Maker 2.3.

Organic synthesis

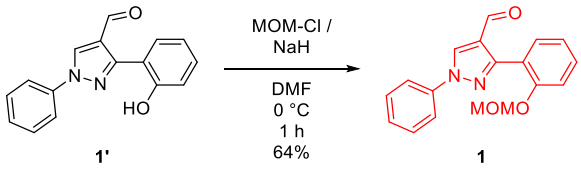
3-(2-(Methoxymethoxy)phenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (**1**).

The pyrazole-derived aldehyde **1'** was synthesized following a previously reported method in two steps.[i] The first step involved an acetic acid-catalyzed condensation between phenylhydrazine **15** and 2'-hydroxyacetophenone **16**, yielding the corresponding hydrazone **17** in quantitative yield. The second step consisted of a double Vilsmeier-Haack formylation. In this step, the first equivalent of the Vilsmeier reagent reacts with the hydrazone to form a pyrazole ring, which is subsequently formylated by a second equivalent of the Vilsmeier reagent, affording the target compound **1'** with an overall yield of 38% (Scheme S1).



Scheme S1. Synthesis of 3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde **1**'.

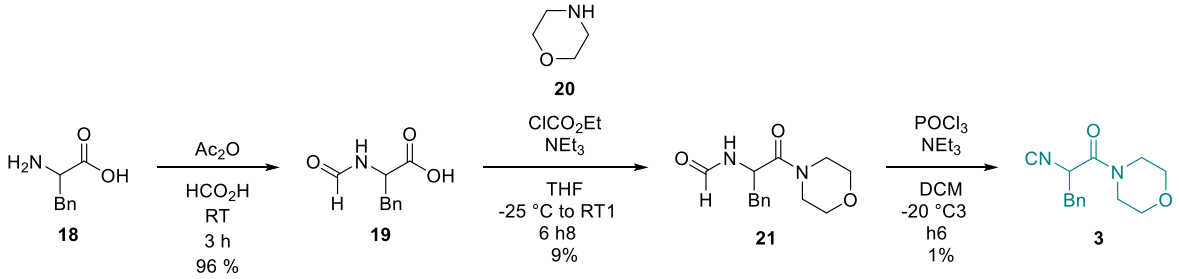
The protection of the pyrazole-derived aldehyde was carried out following the procedure reported by DeShong and Seganish,[ii] which involved an S_N2 reaction using methoxymethyl chloride (MOM-Cl) in the presence of NaH, as shown in Scheme S2. The *O*-protected aldehyde **1** was obtained with a yield of 64% (Scheme S2).



Scheme S2. Synthesis of 3-(2-(methoxymethoxy)phenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde **1**.

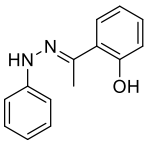
2-Isocyano-1-morpholino-3-phenylpropan-1-one (**3**)

The α-isocyanoacetamide **3** was synthesized following a previously reported method.[iii] Initially, racemic phenylalanine **18** underwent formylation using a mixed anhydride. This was followed by a peptide coupling reaction with morpholine **20**, and finally, an Ugi-type dehydration to yield the target compound **3**. The overall yield of α-isocyanoacetamide was 52% (Scheme S3).



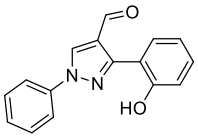
Scheme S3. Synthesis of the α-isocyanoacetamide **3**.

(*E*)-2-(1-(2-Phenylhydrazono)ethyl)phenol (**17**).



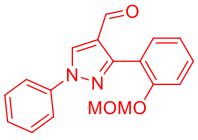
In a 50 mL round-bottom flask equipped with a magnetic stirring bar, 2.4 mL of 2'-hydroxyacetophenone (20.0 mmol, 1.0 equiv.) and 2.0 mL of phenylhydrazine (20.0 mmol, 1.0 equiv.) were dissolved in 25 mL of absolute ethanol, with 0.5 mL of glacial acetic acid used as a catalyst. The reaction mixture was stirred and refluxed for 8 hours. Subsequently, the mixture was allowed to cool to room temperature, and the volume was reduced to half through evaporation. The remaining solution was then placed in a freezer to induce crystallization of the desired product. The crystallized product was collected by filtration, washed with cold water, and dried. A total of 4.51 g of an orange crystalline solid was obtained, representing a quantitative yield. R_f = 0.51 (AcOEt:Hex 1:4 v/v). **^{1}H RMN (500 MHz, $CDCl_3$):** d 7.41 (ddd, *J* = 8.0, 1.6, 0.4 Hz, 1H, H-3), 7.30 (dd, *J* = 8.6, 7.4 Hz, 2H, H-13, H-15), 7.24–7.19 (m, 1H, H-5), 7.02 (d, *J* = 7.6 Hz, 1H, H-12, H-16), 6.99 (ddd, *J* = 8.2, 1.3, 0.4 Hz, 1H, H-6), 6.93 (tt, *J* = 7.4, 1.1 Hz, 1H, H-14), 6.88 (ddd, *J* = 8.0, 7.2, 1.3 Hz, 1H, H- 4), 2.31 (s, 3H, H-10). **^{13}C RMN (126 MHz, $CDCl_3$):** d 157.9 (C-8), 147.3 (C-1), 143.9 (C-11), 129.9 (C-5), 129.5 (C-13, C-15), 126.7 (C-3), 121.1 (C-14), 120.0 (C-2), 118.8 (C-4), 117.3 (C-6), 113.1 (C-12, C- 16), 11.6 (C-10).

3-(2-Hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (**1'**).



In a 50 mL round-bottom flask, 1.8 mL of DMF (23.4 mmol, 3.0 equiv.) was placed at 0 °C under an inert gas atmosphere, followed by the dropwise addition of 1.8 mL of $POCl_3$ (19.3 mmol, 2.5 equiv.). After that, the reaction mixture was stirred at room temperature for 1 hour. Subsequently, a solution of 1.76 g of (*E*)-2-(1-(2-phenylhydrazono)ethyl)phenol (7.8 mmol, 1.0 equiv.) in 3 mL of DMF was added dropwise to the mixture, which was then heated to 60 °C for 8 hours. Upon completion of the reaction, the mixture was allowed to cool to room temperature and poured into ice-cold water. Finally, a saturated $NaHCO_3$ solution was added until a pH of 6 was reached. The resulting precipitate was filtered, washed with water, and dried. A total of 0.78 g of a brown solid was obtained in an isolated yield of 38%. R_f = 0.33 (AcOEt:Hex 3:7 v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.19 (s, 1H, H-19), 8.58 (d, *J* = 0.4 Hz, 1H, H-5), 7.94 (dd, *J* = 7.8, 1.7 Hz, 1H, H-17), 7.72 (dd, *J* = 8.6, 1.2 Hz, 2H, H-7, H-11), 7.57–7.50 (m, 2H, H-8, H-10), 7.47–7.40 (m, 1H, H-9), 7.36 (ddd, *J* = 8.3, 7.3, 1.7 Hz, 1H, H-15), 7.11 (ddd, *J* = 8.2, 1.3, 0.4 Hz, 1H, H-14), 7.03 (ddd, *J* = 7.8, 7.3, 1.2 Hz, 1H, H-16). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 184.3 (C-18), 156.0 (C-13), 152.7 (C-3), 138.2 (C-6), 132.6 (C-5), 131.2 (C-15), 129.9 (C-8, C-10), 129.7 (C-17), 128.4 (C-9), 123.1 (C-4), 119.9 (C-16), 119.6 (C-7, C-11), 117.4 (C-14), 115.4 (C-12).

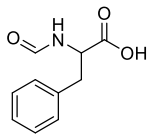
3-(2-(Methoxymethyl)phenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (**1**).



A suspension of 0.15 g of NaH (3.8 mmol, 1.7 equiv., 60% dispersion in mineral oil) was formed in a 50 mL round-bottom flask at 0 °C in 5 mL of DMF. To the resulting mixture, 0.60 g of 3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (2.3 mmol, 1.0 equiv.) was added in portions and stirred for 30 minutes. After this time, 0.3 mL of MOM-Cl (3.8 mmol, 1.7 equiv.) was added, and the reaction was stirred at room temperature. After 30 minutes, 30 mL of H_2O was added, and the mixture was extracted with 3 × 30 mL of ethyl acetate (AcOEt). The organic phase was dried over anhydrous Na_2SO_4 and concentrated to dryness. The product was purified by column chromatography using a mixture of AcOEt:Hex (1:4, v/v), yielding 0.45 g of a light yellow solid with a yield of 64%. R_f = 0.40 (AcOEt:Hex 3:7 v/v); melting point = 67 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.84 (d, *J* = 0.5 Hz, 1H, H-1), 8.51 (d, *J* = 0.4 Hz, 1H, H-3), 7.77 (dd, *J* = 8.7, 1.2 Hz, 2H, H-9, H-13), 7.61 (ddd, *J* =

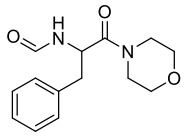
7.5, 1.8, 0.4 Hz, 2H, H-18), 7.50–7.44 (m, 2H, H-10, H-12), 7.42 (ddd, *J* = 8.4, 7.4, 1.8 Hz, 2H, H-16), 7.37–7.31 (m, 1H, H-11), 7.28 (dd, *J* = 8.4, 0.7 Hz, 1H, H-17), 7.14 (td, *J* = *7.5*, 1.1 Hz, 1H, H-15), 5.14 (s, 2H, H-21), 3.40 (s, 3H, H-23). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 186.2 (C-1), 154.9 (C-14), 152.0 (C-6), 139.1 (C-8), 131.2 (C-18), 130.8 (C-16), 129.5 (C-10, C-12), 128.8 (C-3), 127.6 (C-11), 123.3 (C-2), 122.2 (C-15), 121.3 (C-7), 119.5 (C-9, C-13), 115.0 (C-17), 95.1 (C-21), 56.2 (C-23). **HRMS:** (ESI+) m/z calculated for [M−H]+ $C_{18}H_{17}N_2O_3$ + 309.1234, found 309.1239 (error = 1.8 ppm).

N-Formyl phenylalanine (**19**).



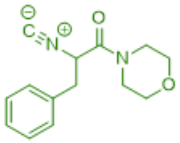
In a 250 mL round-bottom flask, 4.13 g of phenylalanine (25.0 mmol, 1 equiv.) were suspended in 50 mL of formic acid at 0 °C. Subsequently, 17 mL of Ac_2O (180.0 mmol, 7.2 equiv.) were added dropwise to the mixture under stirring. The reaction mixture was stirred for 2 hours at room temperature. After this time, 20 mL of a water/ice mixture was added, and the reaction mixture was concentrated to dryness. The crude reaction product was used for the next step without purification. A total of 4.65 g (96%) of a grayish-white powder was obtained.

N-(1-Morpholino-1-oxo-3-phenylpropan-2-yl)formamide (**21**).



In a 250 mL round-bottom flask, 4.5 g (23.3 mmol, 1.0 equiv.) of the product obtained in the previous step were diluted in 80 mL of THF. The mixture was cooled to –25 °C under an inert gas atmosphere, and 2.5 mL of ethyl chloroformate (25.6 mmol, 1.1 equiv.) and 4.3 mL of Et_3N (30.3 mmol, 1.3 equiv.) were added. After 30 minutes, 2.5 mL of morpholine (27.9 mmol, 1.2 equiv.) were added, and the reaction mixture was stirred at –25 °C for one hour, then at room temperature for 16 hours. After this time, a saturated $NaHCO_3$ solution was added, and the mixture was extracted with 3 × 50 mL of AcOEt. The organic phase was washed with a saturated NaCl solution, dried over anhydrous Na_2SO_4, concentrated to dryness, and the crude reaction product was used in the next step without purification. A total of 5.29 g (89%) of a yellow oil was obtained.

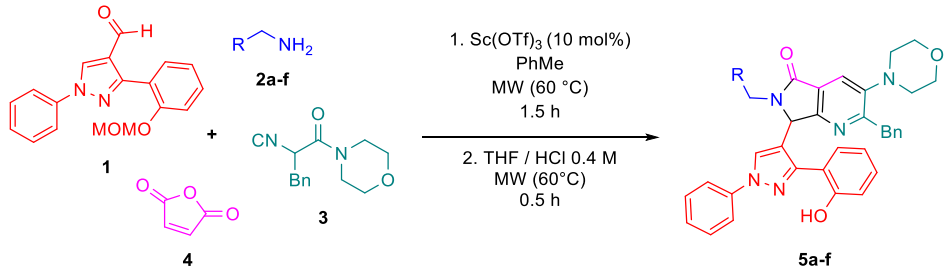
2-Isocyano-1-morpholino-3-phenylpropan-1-one (**3**).



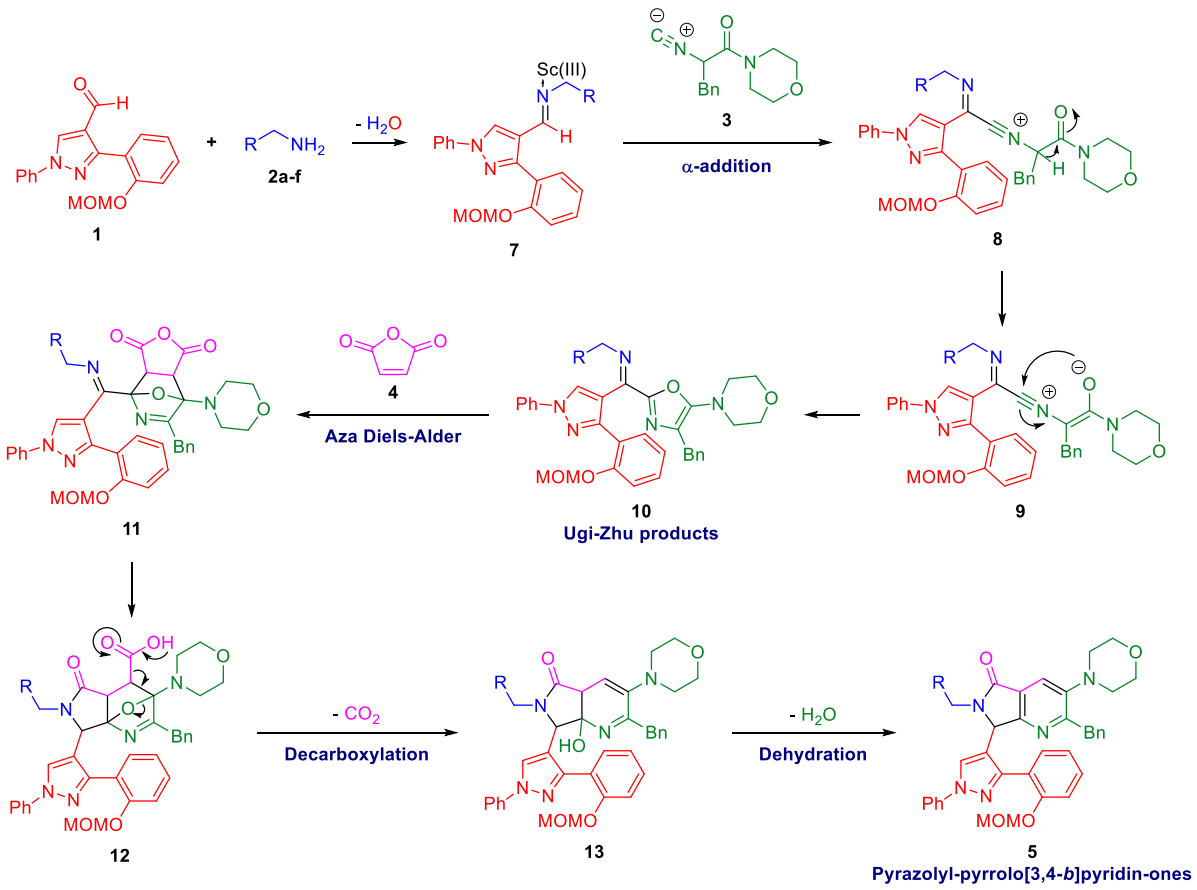
In a 250 mL round-bottom flask, 4.8 g of the product obtained in the previous step were diluted in 90 mL of DCM under an inert gas atmosphere with constant stirring. The temperature was lowered to –25 °C, 15.5 mL of Et_3N (111.2 mmol, 6.1 equiv.) were added, and the mixture was stirred for 10 minutes. Subsequently, 2.7 mL of $POCl_3$ (28.9 mmol, 1.6 equiv.) were added dropwise, and the reaction mixture was stirred for 3 hours at –25 °C. After this time, a saturated K_2CO_3 aqueous solution was added, and the mixture was extracted with 3 × 50 mL of DCM. The organic phase was washed with a saturated NaCl aqueous solution, dried over anhydrous Na_2SO_4, concentrated to dryness, and purified by column chromatography using an AcOEt:Hex 2:3 (v/v) mixture. A total of 3.0 g of a white crystalline solid was obtained with a isolated yield of 61%. R_f = 0.40 (AcOEt:Hex 2:3 v/v); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.37–7.24 (m, 5H, H-8, H-9, H-10, H-11, H-12), 4.54 (dd, *J* = 7.9, 6.7 Hz, 1H, H-1), 3.71–3.17 (m, 10H, H-6, H-13, H-14, H-16, H-17). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 163.4 (C-2), 160.1 (C-18), 135.0 (C-7), 129.4 (C-9, C-11), 128.8 (C-8, C-12), 127.7 (C-10), 66.4 (C-1), 46.3 (C-14, C-16), 42.9 (C-13, C-17), 39.0 (C-6).

Synthesis of the pyrazole-derived pyrrolo[3,4-*b*]pyridin-5-ones **6a-f**.

The MOM-protected aldehyde **1** (1.0 equiv.) and the corresponding amine **2a-f** (1.2 equiv.) were introduced into a sealed 10 mL CEM Discover microwave reaction tube and dissolved in 1.0 mL of dry toluene. The reaction mixture was stirred and heated under microwave irradiation (60 °C, 100 W) for 30 minutes. Subsequently, $Sc(OTf)_3$ (10 mol%) was added, and the mixture was stirred and further heated under microwave irradiation (60 °C, 100 W) for 5 minutes. The isocyanide **3** (1.2 equiv.) was then added, and the reaction was again stirred and irradiated (60 °C, 100 W) for 30 minutes. Maleic anhydride (1.4 equiv.) was added, and the mixture was subjected to additional stirring and microwave irradiation (60 °C, 100 W) for 30 minutes. The crude product was purified via column chromatography using a 2:3 (v/v) mixture of hexane and ethyl acetate (Hex). The isolated compound was subsequently dissolved in 3 mL of THF, to which 0.1 mL of concentrated HCl was added. The solution was heated under microwave irradiation (60 °C, 100 W) for 30 minutes. After evaporating the THF, the reaction mixture was neutralized with a saturated $NaHCO_3$ aqueous solution and extracted with 3 × 5 mL of ethyl acetate. The organic phase was dried over Na_2SO_4, evaporated, and the final compound was purified by preparative thin-layer chromatography (TLC) using a mixture of hexane and ethyl acetate as the mobile phase in either a 2:3 (v/v) or 1:4 (v/v) ratio.

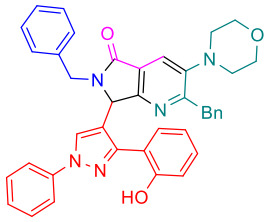


Scheme S4. Multicomponent assembly of pyrrolo[3,4-*b*]pyridin-5-ones derived from pyrazole via an Ugi-Zhu/Aza-Diels-Alder sequence.



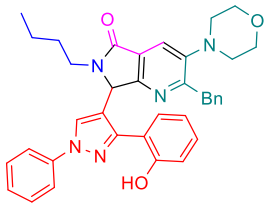
Scheme S5. Reaction mechanism of the UZ-3CR process and the transformation of 5-aminooxazoles into pyrazolyl-pyrrolo[3,4-*b*]pyridin-5-ones.

2,6-Dibenzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6a**).



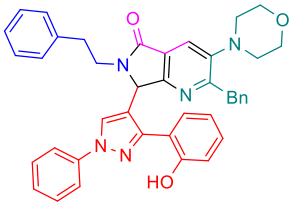
According to the general procedure, 3-(2-(methoxymethyl)phenyl)-1-phenyl-1*H*-pyrazol-4-carbaldehyde (92.9 mg), benzylamine (39.3 µL), $Sc(OTf)_3$ (14.8 mg), 2-isocyanomorpholino-3-phenylpropan-1-one (89.6 mg), and maleic anhydride (29.9 mg) were used. The compound (23.4 mg, 12%) was isolated as a pale yellow solid. R_f = 0.25 (AcOEt-Hex 2:3 v/v); M.P. = 190–192 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.77 (s, 1H, H-48), 7.91 (s, 1H, H-6), 7.81 (s, 1H, H-43), 7.63 (s, 1H, H-27), 7.59 (dt, *J* = 8.0, 1.1 Hz, 2H, H-37, H-41), 7.50–7.39 (m, 2H, H-38, H-40), 7.31 (ddt, *J* = 7.8, 7.0, 1.1 Hz, 1H, H-39), 7.29–7.01 (m, 13H, H-17, H-18, H-19, H-20, H-21, H-22, H-23, H-24, H-25, H-26, H-45, H-46), 6.73 (td, *J* = 7.5, 1.2 Hz, 1H, H-44), 5.62 (s, 1H, H-9), 5.20 (d, *J* = 14.7 Hz, 1H, H-11), 4.40 (d, *J* = 13.8 Hz, 1H, H-14), 4.09 (t, *J* = 14.4 Hz, 2H, H-11', H-14'), 3.85 (ddd, *J* = 5.2, 3.7, 1.2 Hz, 4H, H-32, H-34), 2.87 (ddt, *J* = 39.1, 11.9, 4.6 Hz, 4H, H-31, H-35). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 166.6 (C-7), 162.2 (C-4), 160.3 (C-2), 155.3 (C-47), 151.1 (C-13), 147.9 (C-5), 139.1 (C-15), 138.9 (C-36), 136.3 (C-12), 130.1 (C-45), 129.6 (C-38, C-40), 129.3 (C-43), 129.1 (C-22, C-26), 128.7 (C-17, C-21), 128.5 (C-18, C-20), 128.3 (C-23, C-25), 127.7 (C-19), 127.3 (C-30), 127.3 (C-27, C-39), 127.2 (C-24), 124.0 (C-6), 123.6 (C-1), 119.7 (C-44), 118.8 (C-37, C-41), 116.9 (C-46), 116.7 (C-42), 67.1 (C-31, C-35), 56.3 (C-9), 53.1 (C-32, C-34), 44.4 (C-11), 39.7 (C-14). **FT-IR** (ν cm^{-1}): 3365, 2825, 2364, 1688, 1596, 1508, 1388, 1221, 1112, 824, 755, 697, 478. **HRMS: (ESI$^+$)** m/z calcd. for $[M-H]^+$ $C_{40}H_{36}N_5O_3^+$ 634.2813; found 634.2825 (error = 1.9 ppm).

2-Benzyl-6-butyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6b**).



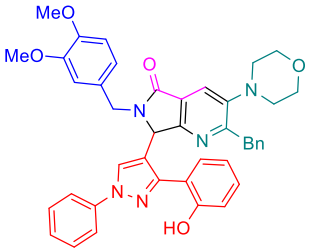
According to the general procedure, 3-(2-(methoxymethyl)phenyl)-1-phenyl-1*H*-pyrazol-4-carbaldehyde (92.8 mg), butylamine (35.6 µL), $Sc(OTf)_3$ (7.4 mg), 2-isocyanomorpholino-3-phenylpropan-1-one (89.4 mg), and maleic anhydride (29.3 mg) were used. The compound (46.2 mg, 26%) was isolated as a pale yellow solid. R_f = 0.20 (AcOEt-Hex 2:3 v/v); M.P. = 224 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.16 (s, 1H, H-33), 7.89 (s, 1H, H-6), 7.69 (s, 1H, H-18), 7.63 (dd, *J* = 8.7, 1.1 Hz, 2H, H-24, H-28), 7.46 (dd, *J* = 8.4, 7.6 Hz, 2H, H-25, H-27), 7.35–7.29 (m, 2H, H-26, H-31), 7.25–7.18 (m, 5H, H-41, H-42, H-43, H-44, H-45), 7.11 (dd, *J* = 8.2, 1.2 Hz, 1H, H-30), 6.89 (td, *J* = 7.5, 1.2 Hz, 1H, H-32), 5.85 (s, 1H, H-9), 4.44 (d, *J* = 13.7 Hz, 1H, H-17), 4.10 (d, *J* = 13.7 Hz, 1H, H-17'), 3.99 (dt, *J* = 13.8, 7.9 Hz, 1H, H-11), 3.86 (ddd, *J* = 5.2, 3.7, 1.2 Hz, 4H, H-36, H-38), 3.01–2.77 (m, 5H, H-11', H-35, H-39), 1.49–1.37 (m, 2H, H-12), 1.27–1.18 (m, 2H, H-13), 0.81 (t, *J* = 7.3 Hz, 3H, H-14). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 166.7 (C-7), 161.9 (C-4), 160.3 (C-2), 155.5 (C-29), 151.0 (C-21), 147.9 (C-5), 139.3 (C-40), 138.9 (C-22), 130.1 (C-31), 129.6 (C-25, C-27), 129.1 (C-42, C-44), 128.3 (C-41, C-45), 127.2 (C-26), 126.8 (C-18), 126.3 (C-43), 123.9 (C-1), 123.9 (C-6), 119.8 (C-32), 118.7 (C-24, C-28), 117.1 (C-30), 116.8 (C-23), 67.2 (C-36, C-38), 56.4 (C-9), 53.1 (C-35, C-39), 40.0 (C-17), 39.7 (C-17), 30.2 (C-12), 19.9 (C-13), 13.6 (C-14). **FT-IR** (ν cm^{-1}): 3356, 2975, 2828, 2102, 1688, 1606, 1502, 1445, 1376, 1218, 1114, 957, 816, 755, 696, 481. **HRMS: (ESI$^+$)** m/z calcd. for $[M-H]^+$ $C_{37}H_{38}N_5O_3^+$ 600.2969; found 600.2970 (error = 0.1 ppm)

2-Benzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6-phenethyl-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6c**).



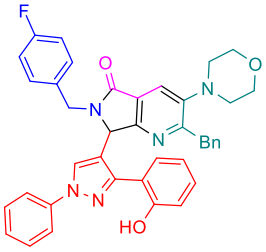
According to the general procedure, 3-(2-(methoxymethyl)phenyl)-1-phenyl-1*H*-pyrazol-4-carbaldehyde (154.3 mg), phenethylamine (75.4 µL), $Sc(OTf)_3$ (12.3 mg), 2-isocyan-1-morpholino-3-phenylpropan-1-one (146.9 mg), and maleic anhydride (49.0 mg). The compound (63.6 mg, 20%) was isolated as a light yellow solid. R_f = 0.45 (AcOEt-Hex 3:2 v/v); M.P. = 195−197 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.90 (s, 1H, H-43), 7.89 (s, 1H, H-6), 7.60 (dd, *J* = 8.7, 1.2 Hz, 2H, H-28, H-32), 7.56 (s, 1H, H-17), 7.45 (dd, *J* = 8.5, 7.6 Hz, 1H, H-29, H-31), 7.35–7.27 (m, 2H, H-27, H-30), 7.26–6.95 (m, 12H, H-24, H-25, H-33, H-34, H-35, H-36, H-37, H-45, H-46, H-47, H-48, H-49), 6.82 (t, *J* = 7.6 Hz, 1H, H-26), 5.55 (s, 1H, H-9), 4.38 (d, *J* = 13.8 Hz, 1H, H-16), 4.27 (ddd, *J* = 13.9, 7.4, 6.3 Hz, 1H, H-11), 4.09 (d, *J* = 13.8 Hz, 1H, 16'), 3.86 (t, *J* = 3.8 Hz, 4H, H-39, H-41), 3.23 (dt, *J* = 14.0, 7.5 Hz, 1H, H-11'), 3.00–2.74 (m, 6H, H-12, H-38, H-42). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 166.8 (C-7), 161.9 (C-4), 160.2 (C-2), 155.4 (C-20), 151.0 (C-14), 147.8 (C-5), 139.2 (C-44), 138.8 (C-21), 138.2 (C-13), 130.1 (C-27), 129.6 (C-23, C-31), 129.2 (C-47), 129.0 (C-48, C-46), 128.5 (C-34, C-36), 128.5 (C-33, C-37), 128.3 (C-45, C-49), 127.2 (C-30), 127.0 (C-17), 126.6 (C-25), 126.3 (C-24), 123.8 (C-6), 119.8 (C-26), 118.7 (C-28, C-32), 117.0 (C-35), 116.6 (C-1), 67.2 (C-39, C-41), 57.1 (C-9), 53.1 (C-38, C-42), 41.7 (C-11), 39.7 (C-16), 34.6 (C-12). **FT-IR** (ν cm^{-1}): 3339, 2973, 2879, 2831, 1688, 1601, 1507, 1439, 1391, 1212, 1156, 1111, 948, 815, 753, 694, 542, 480. **HRMS: (ESI$^+$)** m/z calcd. for $[M-H]^+$ $C_{41}H_{37}N_5O_3$ $^+$ 648.2969 found 648.2969 (error = 0 ppm).

2-Benzyl-6-(3,4-dimethoxybenzyl)-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6d**).



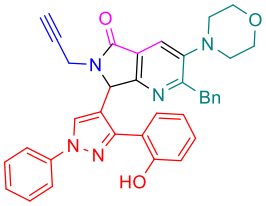
According to the general procedure, 3-(2-(methoxymethyl)phenyl)-1-phenyl-1*H*-pyrazol-4-carbaldehyde (154.0 mg), 3,4-dimethoxybenzylamine (90.5 µL), $Sc(OTf)_3$ (22.7 mg), 2-isocyan-1-morpholino-3-phenylpropan-1-one (146.3 mg), and maleic anhydride (49.0 mg). The compound (34.3 mg, 10%) was isolated as a light yellow solid. R_f = 0.38 (AcOEt-Hex 3:2 v/v); M.P. = 65 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.89 (s, 1H, H-31), 7.96 (s, 1H, H-25), 7.90 (s, 1H, H-6), 7.65 (s, 1H, H-15), 7.61 (dd, *J* = 8.7, 1.1 Hz, 2H, H-26, H-30), 7.50–7.42 (m, 2H, H-27, H-29), 7.36–7.30 (m, 1H, H-28), 7.29 (d, *J* = 1.7 Hz, 1H, H-23), 7.25–7.12 (m, 5H, H-46, H-47, H-48, H-49, H-50), 7.10 (dd, *J* = 8.2, 1.2 Hz, 1H, H-22), 6.76 (td, *J* = 7.4, 1.2 Hz, 1H, H-24), 6.58 (s, 1H, H-41), 6.55 (d, *J* = 1.1 Hz, 2H, H-37, H-38), 5.64 (s, 1H, H-9), 5.14 (d, *J* = 14.4 Hz, 1H, H-12), 4.43 (d, *J* = 13.8 Hz, 1H, H-44), 4.03 (dd, *J* = 17.0, 14.1 Hz, 2H, H-12', H-44'), 3.86 (ddd, *J* = 5.3, 3.6, 1.4 Hz, 4H, H-33, H-35), 3.72 (s, 3H, H-43), 3.57 (s, 3H, H-42), 2.97–2.77 (m, 4H, H-32, H-36). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 166.6 (C-7), 162.2 (C-4), 160.4 (C-2), 155.3 (C-21), 151.2 (C-14), 149.1 (C-40), 148.6 (C-39), 147.8 (C-5), 139.2 (C-45), 138.9 (C-19), 130.2 (C-23), 129.6 (C-27, C-29), 129.3 (C-25), 129.1 (C-47, C-49), 128.8 (C-13), 128.3 (C-46, C-50), 127.2 (C-28), 127.1 (C-15), 126.3 (C-48), 124.0 (C-6), 123.5 (C-1), 121.2 (C-37), 119.8 (C-24), 118.7 (C-26, C-30), 116.9 (C-22), 116.7 (C-18), 116.6 (C-20), 111.6 (C-41), 111.1 (C-38), 67.1 (C-33), 57.0 (C-9), 53.1 (C-36, C-42), 41.7 (C-12), 39.7 (C-44), 34.7 (C-12). **FT-IR** (ν cm^{-1}): 3332, 2970, 2879, 2080, 1685, 1601, 1592, 1512, 1441, 1391, 1259, 1106, 1031, 809, 759, 695, 551, 479. **HRMS: (ESI$^+$)** m/z calcd. for $[M-H]^+$ $C_{43}H_{43}N_5O_5$ $^+$ 670.3307 found 670.3310 (error = 0.4 ppm).

2-Benzyl-6-(4-fluorobenzyl)-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6e**).



According to the general procedure, 3-(2-(methoxymethyl)phenyl)-1-phenyl-1*H*-pyrazol-4-carbaldehyde (154.0 mg), 4-fluorobenzylamine (68.6 µL), $Sc(OTf)_3$ (24.6 mg), 2-isocyanomorpholino-3-phenylpropan-1-one (147.0 mg), and maleic anhydride (50.2 mg) were used. The compound (84.2 mg, 26%) was isolated as a light yellow solid. R_f = 0.38 (AcOEt-Hex 3:2 v/v); Melting Point = 185–187 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.91 (s, 1H, H-6), 7.82 (s, 1H, H-27), 7.62 (s, 1H, H-17), 7.60 (dd, *J* = 8.7, 1.1 Hz, 1H, H-33, H-37), 7.50–7.43 (m, 2H, H-34, H-36), 7.36–7.29 (m, 1H, H-35), 7.28 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H, H-25), 7.25–7.12 (m, 5H, H-28, H-29, H-30, H-31, H-32), 7.11 (dd, *J* = 8.3, 1.1 Hz, 1H, H-24), 6.98 (dd, *J* = 8.7, 5.3 Hz, 2H, H-44, H-48), 6.81–6.74 (m, 3H, H-26, H-45, H-47), 5.60 (s, 1H, H-9), 5.15 (d, *J* = 14.7 Hz, 1H, H-14), 4.41 (d, *J* = 13.7 Hz, 1H, H-12), 4.06 (dd, *J* = 18.7, 14.2 Hz, 2H, H-12', H-14'), 3.86 (ddd, *J* = 5.2, 3.7, 1.1 Hz, 4H, H-40, H-42), 2.96–2.80 (m, 4H, H-39, H-43). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 166.6 (C-7), 163.2 ($^1J_{C\text{-}F}$ = 246.5 Hz, C-46), 162.3 (C-4), 160.2 (C-2), 155.2 (C-23), 151.1 (C-16), 147.9 (C-5), 139.1 (C-13), 138.9 (C-21), 132.1 ($^4J_{C\text{-}F}$ = 3.4 Hz, C-15), 130.2 (C-25), 130.2 ($^3J_{C\text{-}F}$ = 7.6 Hz, C-44, C-48), 129.6 (C-34, C-36), 129.2 (C-27), 129.1 (C-29, C-31), 128.3 (C-28, C-32), 127.3 (C-35), 127.2 (C-17), 126.3 (C-30), 124.0 (C-6), 123.5 (C-1), 119.8 (C-26), 118.7 (C-33, C-37), 117.0 (C-24), 116.6 (C-20), 115.6 ($^2J_{C\text{-}F}$ = 21.9 Hz, C-45, C-47), 67.1 (C-40, C-42), 56.1 (C-9), 53.1 (C-39, C-43), 43.6 (C-14), 39.7 (C-12). **^{19}F NMR (471 MHz, $CDCl_3$):** δ -115.95 (tt, $J_{F\text{-}H}$ = 8.5, 5.2 Hz). **FT-IR** (ν cm^{-1}): 3337, 2964, 2830, 2102, 1686, 1595, 1507, 1442, 1384, 1217, 1107, 1029, 909, 817, 759, 691, 477. **HRMS:** (ESI^+) m/z calcd. for $[M-H]^+$ $C_{40}H_{35}FN_5O_3^+$ 652.2718 found 652.2707 (error = 1.7 ppm).

2-Benzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6-(prop-2-yn-1-yl)-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6f**).



According to the general procedure, 3-(2-(methoxymethyl)phenyl)-1-phenyl-1*H*-pyrazol-4-carbaldehyde (92.6 mg), propargylamine (23.1 µL), $ScOTf_3$ (14.8 mg), 2-isocyanomorpholino-3-phenylpropan-1-one (88.1 mg), and maleic anhydride (40.0 mg) were used. The compound (43.0 mg, 25%) was isolated as a light pink solid. R_f = 0.50 (AcOEt-Hex 3:2 v/v); Melting Point = 90–92 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.00 (s, 1H, H-28), 7.89 (s, 1H, H-6), 7.81 (s, 1H, H-18), 7.69–7.59 (m, 2H, H-34, H-38), 7.46 (dd, *J* = 8.7, 7.3 Hz, 2H, H-35, H-37), 7.38–7.29 (m, 1H, H-36), 7.29–7.14 (m, 6H, H-26, H-29, H-30, H-31, H-32, H-33), 7.08 (dd, *J* = 8.2, 0.9 Hz, 1H, H-25), 6.82 (td, *J* = 7.5, 1.3 Hz, 1H, H-27), 6.04 (s, 1H, H-9), 4.77 (dd, *J* = 17.6, 2.6 Hz, 1H, H-14), 4.41 (d, *J* = 13.8 Hz, 1H, H-12), 4.11 (d, *J* = 13.8 Hz, 1H, H-12'), 3.90–3.80 (m, 5H, H-14', H-41, H-43), 2.95–2.78 (m, 4H, H-40, H-44), 2.11 (t, *J* = 2.5 Hz, 1H, H-16). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 166.3 (C-7), 162.5 (C-4), 160.0 (C-2), 155.4 (C-24), 151.1 (C-21), 148.0 (C-5), 139.1 (C-13), 138.9 (C-22), 130.1 (C-31), 129.6 (C-35, C-37), 129.2 (C-28), 129.0 (C-30, C-32), 128.3 (C-29, C-33), 127.5 (C-18), 127.2 (C-36), 126.3 (C-26), 123.9 (C-6), 123.2 (C-1), 119.6 (C-27), 118.8 (C-34, C-38), 116.9 (C-25), 116.7 (C-23), 116.2 (C-17), 77.6 (C-15), 72.8 (C-16), 67.1 (C-41, C-43), 56.6 (C-9), 53.1 (C-40, C-44), 39.8 (C-12), 30.2 (C-14). **FT-IR** (ν cm^{-1}): 3337, 2966, 2885, 1684, 1601, 1503, 1448, 1383, 1259, 1118, 1030, 956, 814, 750, 691, 549, 482. **HRMS: (ESI^+)** m/z calcd. for $[M-H]^+$ $C_{36}H_{32}N_5O_3^+$ 582.2500 found 582.2493 (error = 1.1 ppm).

NMR spectra of all synthetized compounds.

(*E*)-2-(1-(2-Phenylhydrazono)ethyl)phenol.

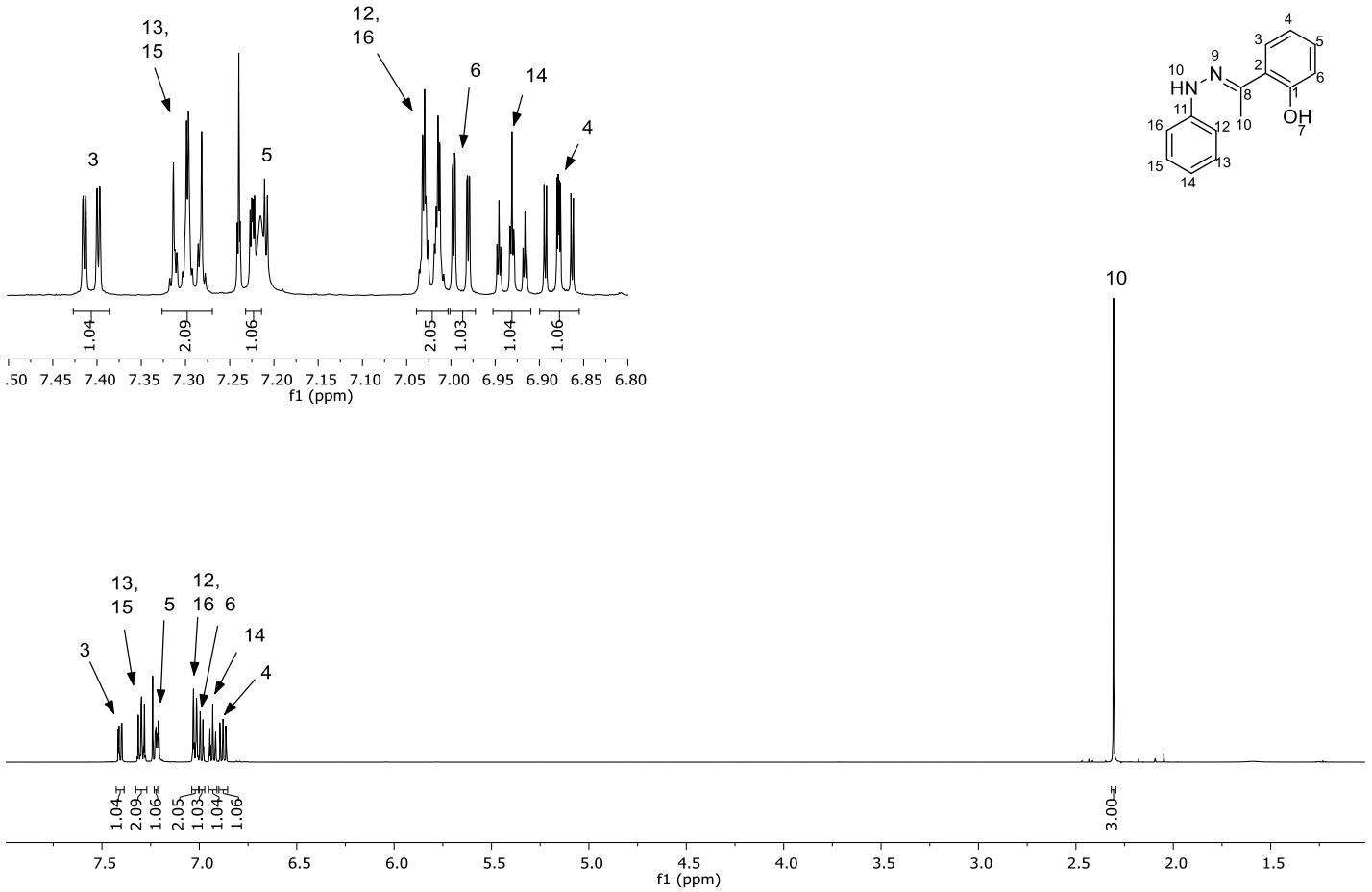


Figure S1. ^{1}H NMR spectrum of (*E*)-2-(1-(2-Phenylhydrazono)ethyl)phenol in $CDCl_3$ at 500 MHz.

3-(2-Hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde.

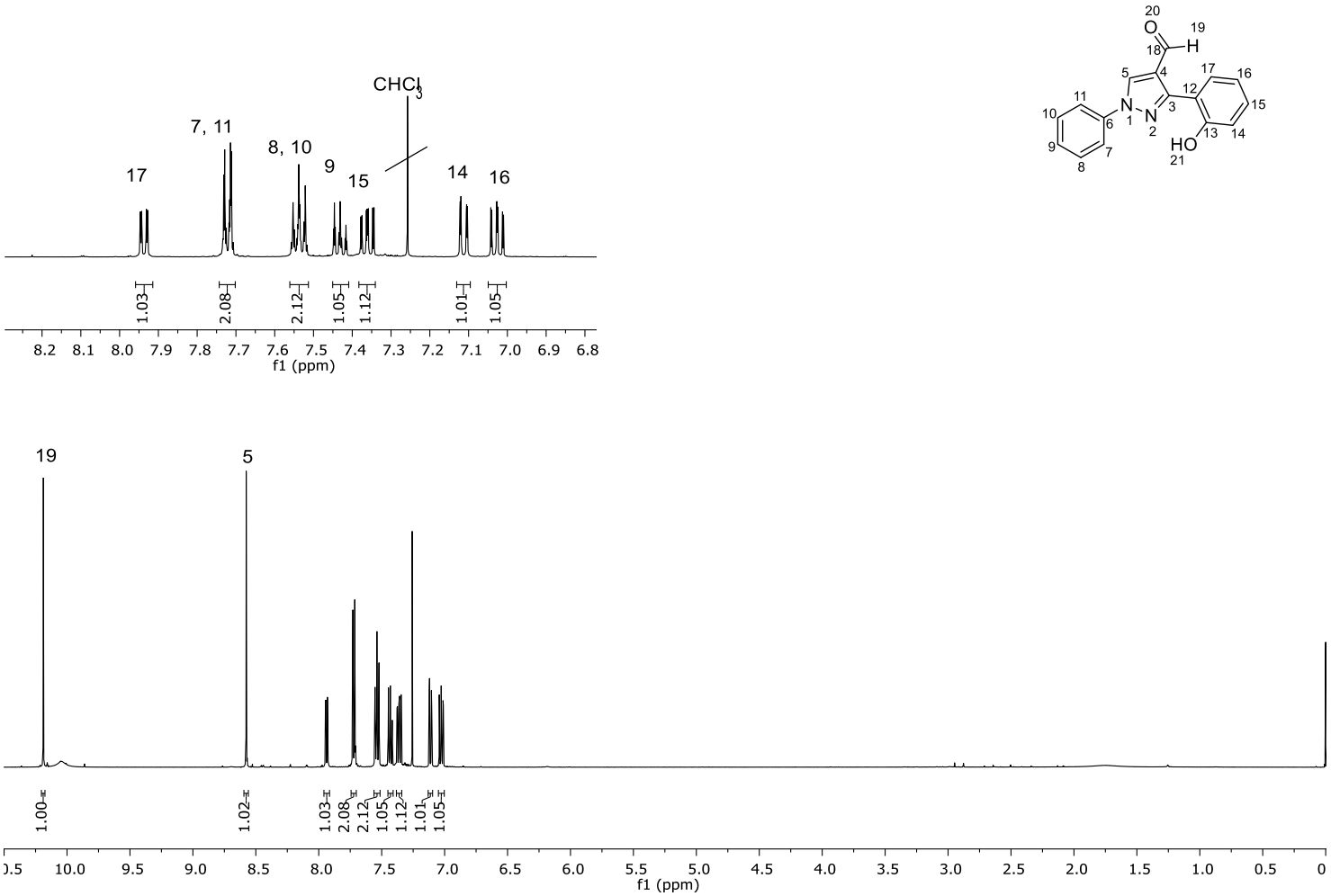


Figure S2. [1]H NMR spectrum of 3-(2-Hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde in $CDCl_3$ at 500 MHz.

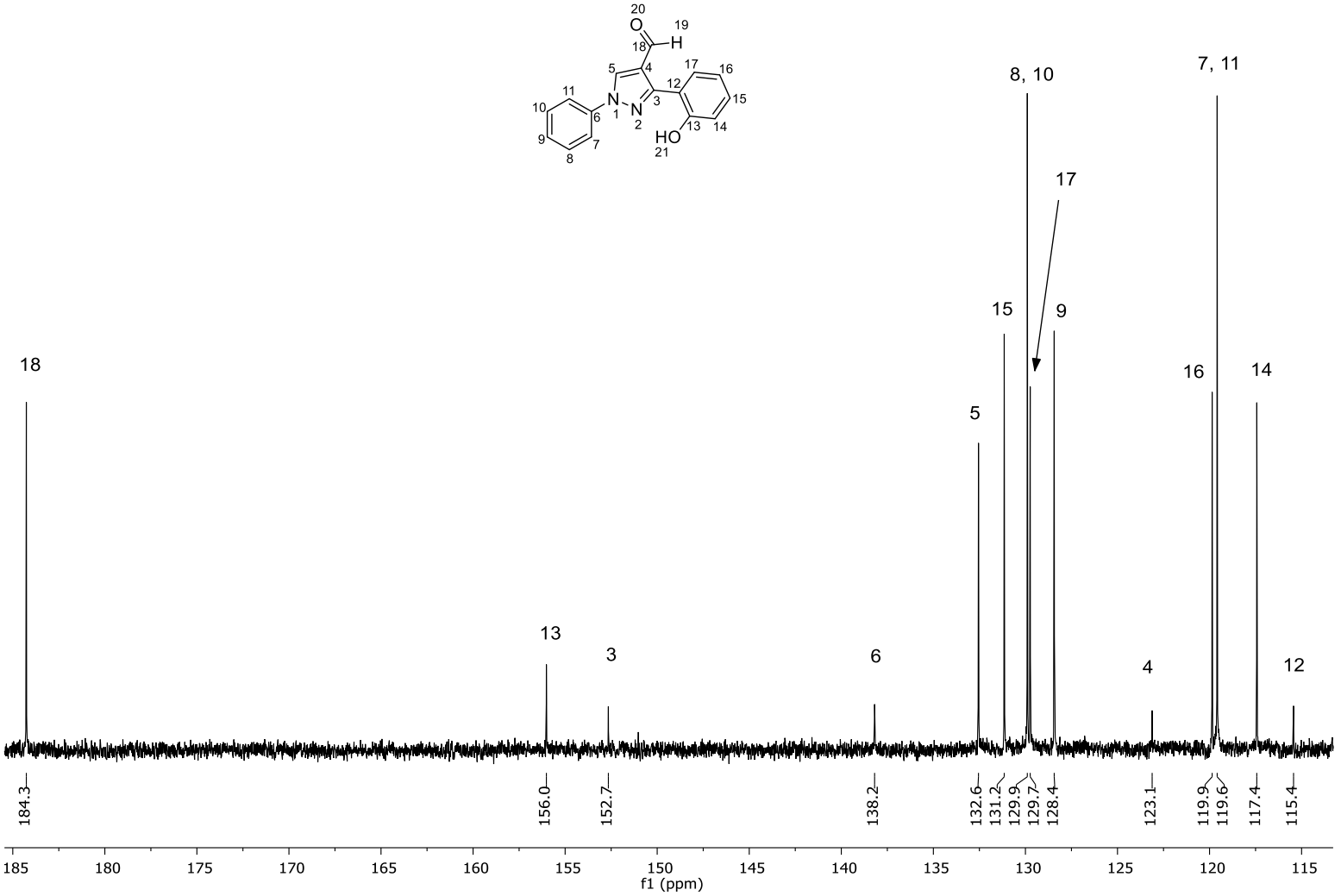


Figure S3. ^{13}C NMR spectrum of 3-(2-Hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde in $CDCl_3$ at 126 MHz.

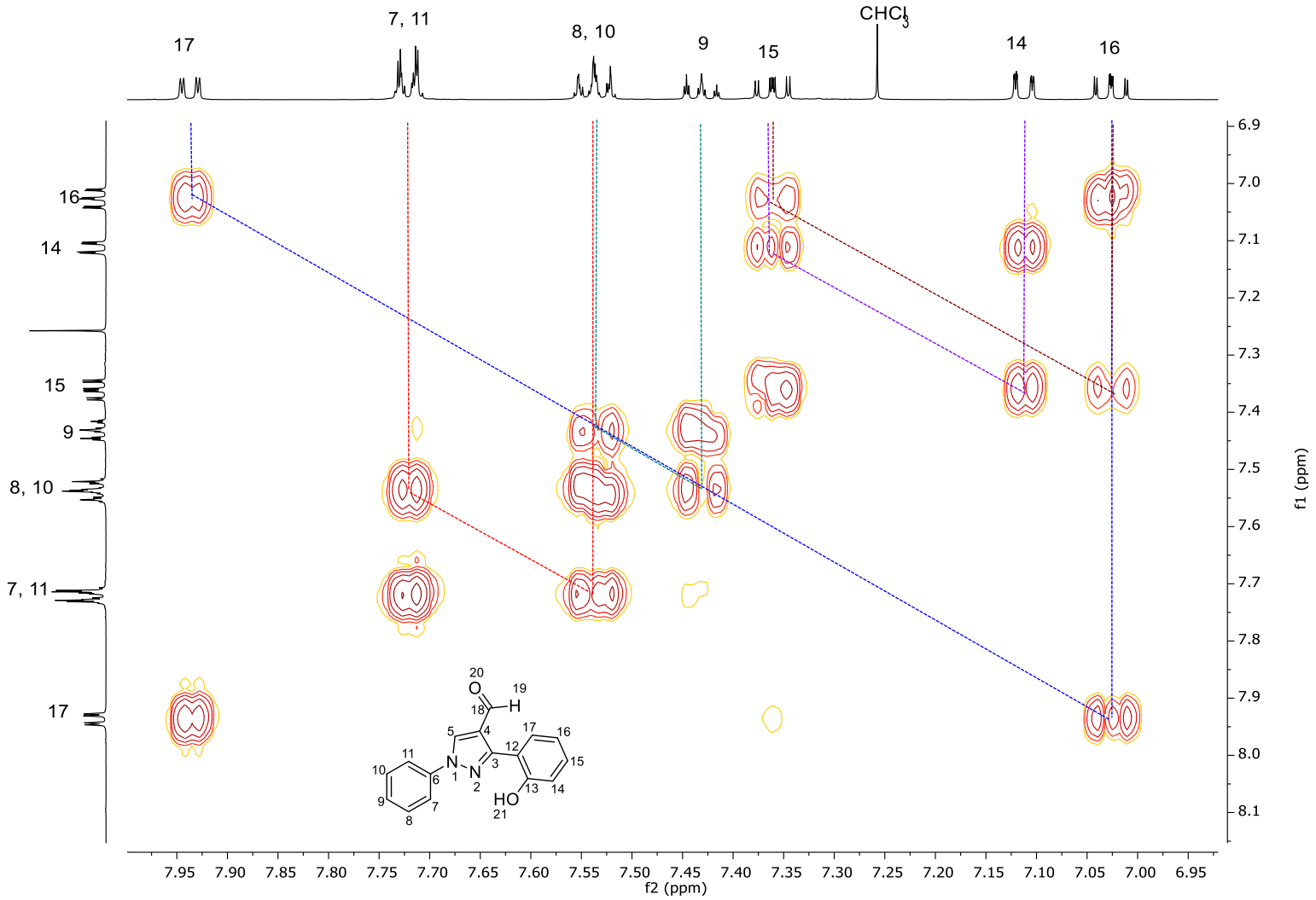


Figure S4. 2D NMR (COSY) spectrum of 3-(2-Hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde.

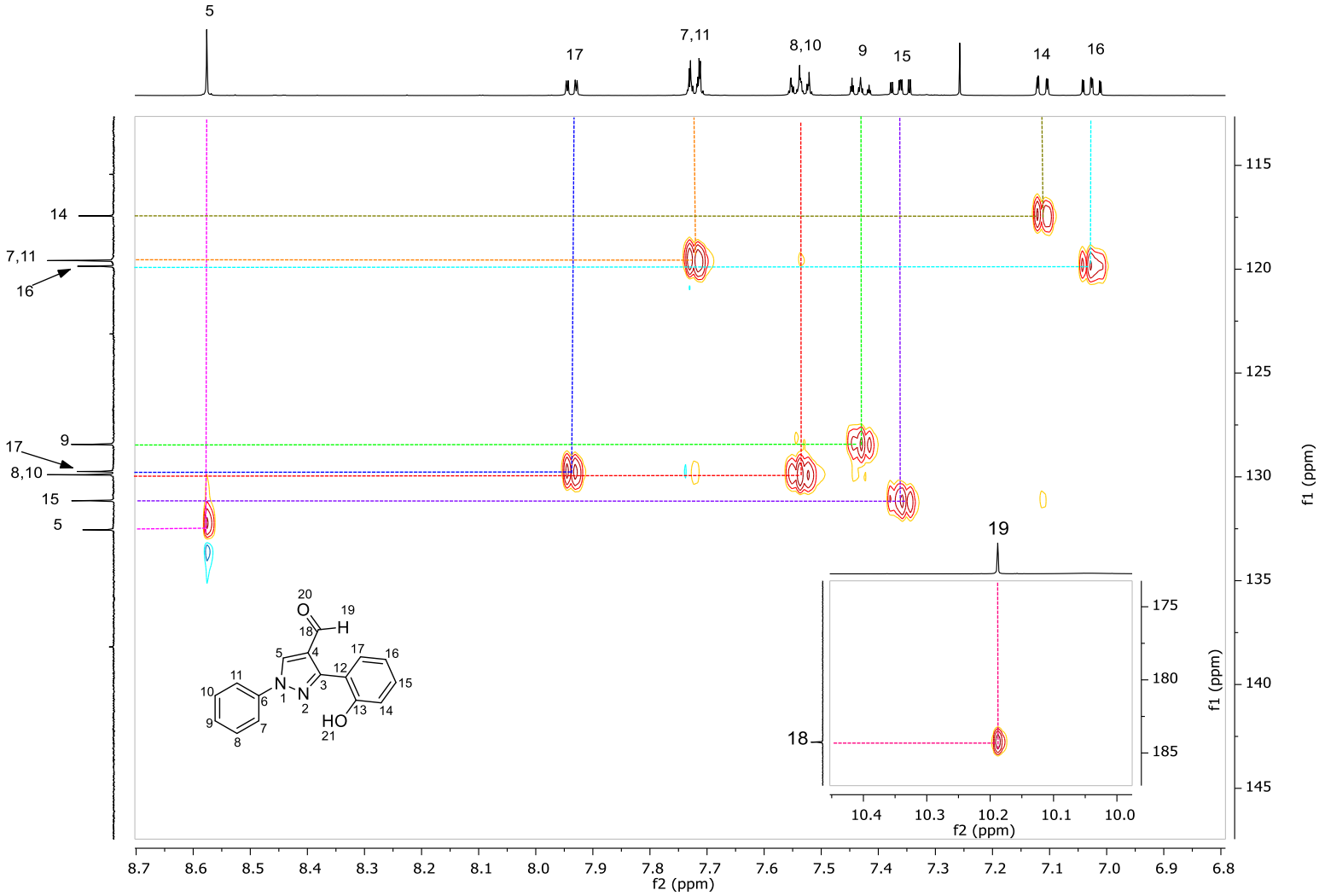


Figure S5. 2D NMR (HSQC) spectrum of 3-(2-Hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde.

3-(2-(Methoxymethyl)phenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (**1**).

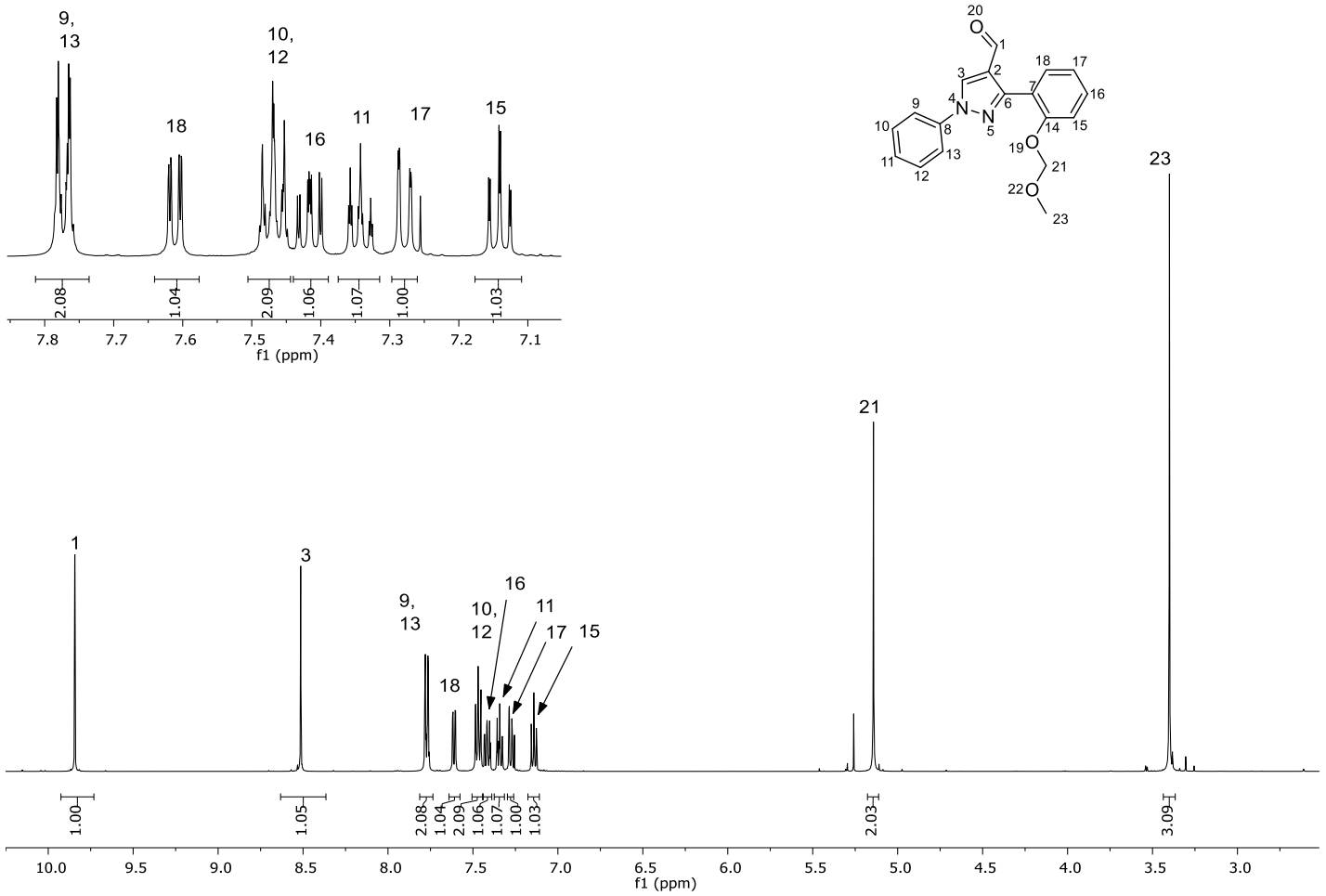


Figure S6. ^{1}H NMR spectrum of 3-(2-(Methoxymethyl)phenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (**1**) in $CDCl_3$ at 500 MHz.

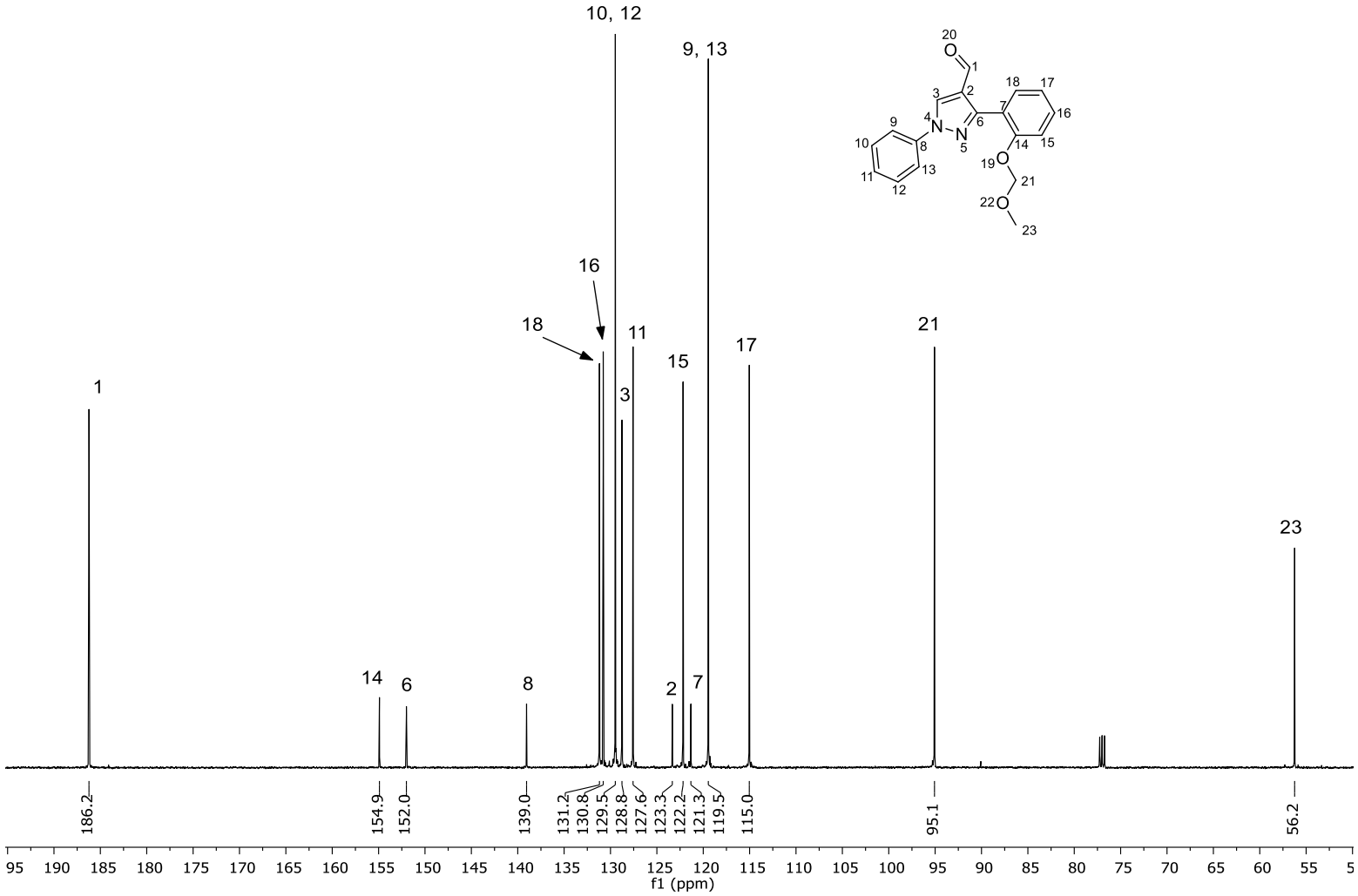


Figure S7. ^{13}C NMR spectrum of 3-(2-(Methoxymethyl)phenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (**1**) in $CDCl_3$ at 126 MHz.

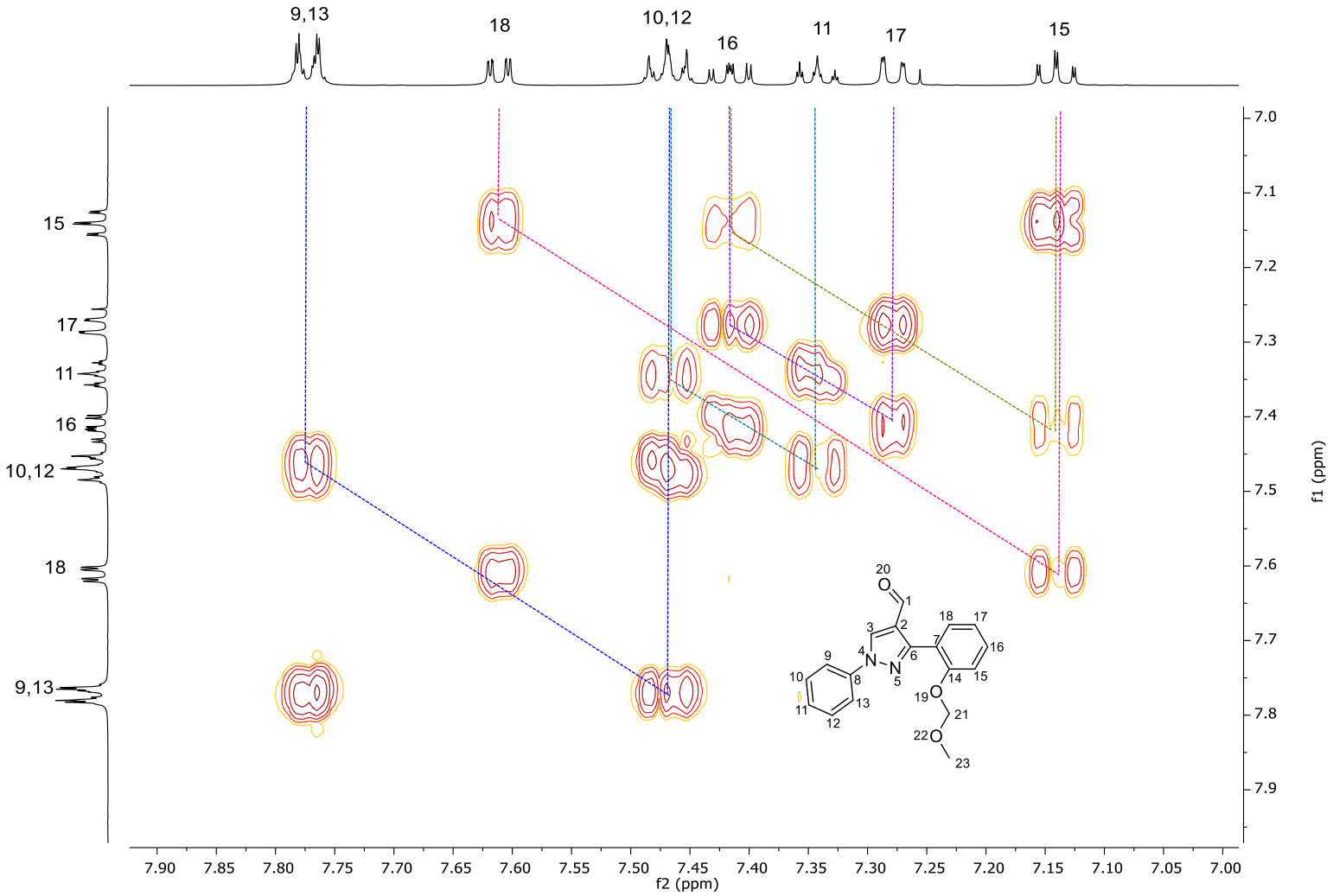


Figure S8. 2D NMR (COSY) spectrum of 3-(2-(Methoxymethyl)phenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (**1**).

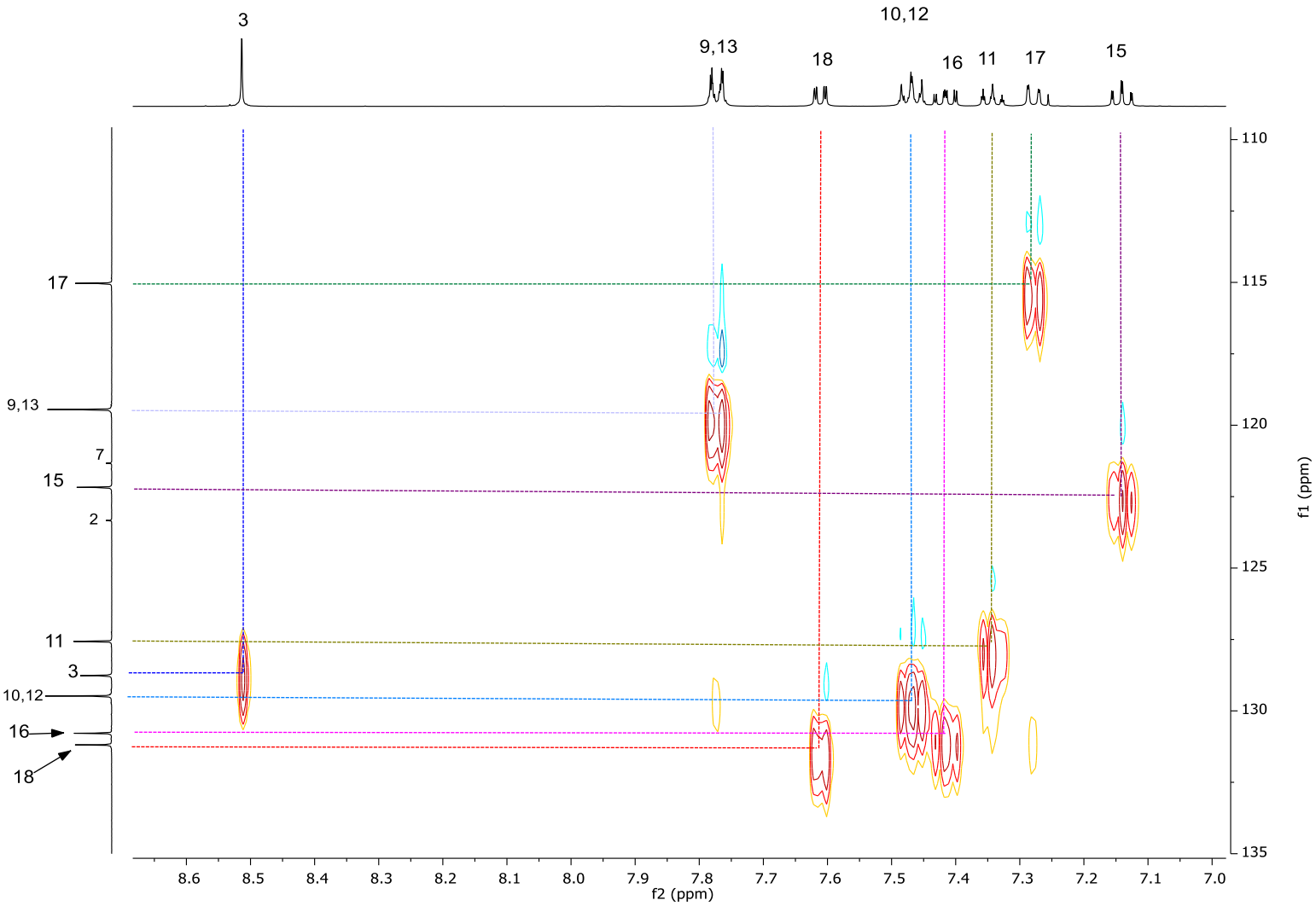


Figure S9. 2D NMR (HSQC) spectrum of 3-(2-(Methoxymethyl)phenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (**1**).

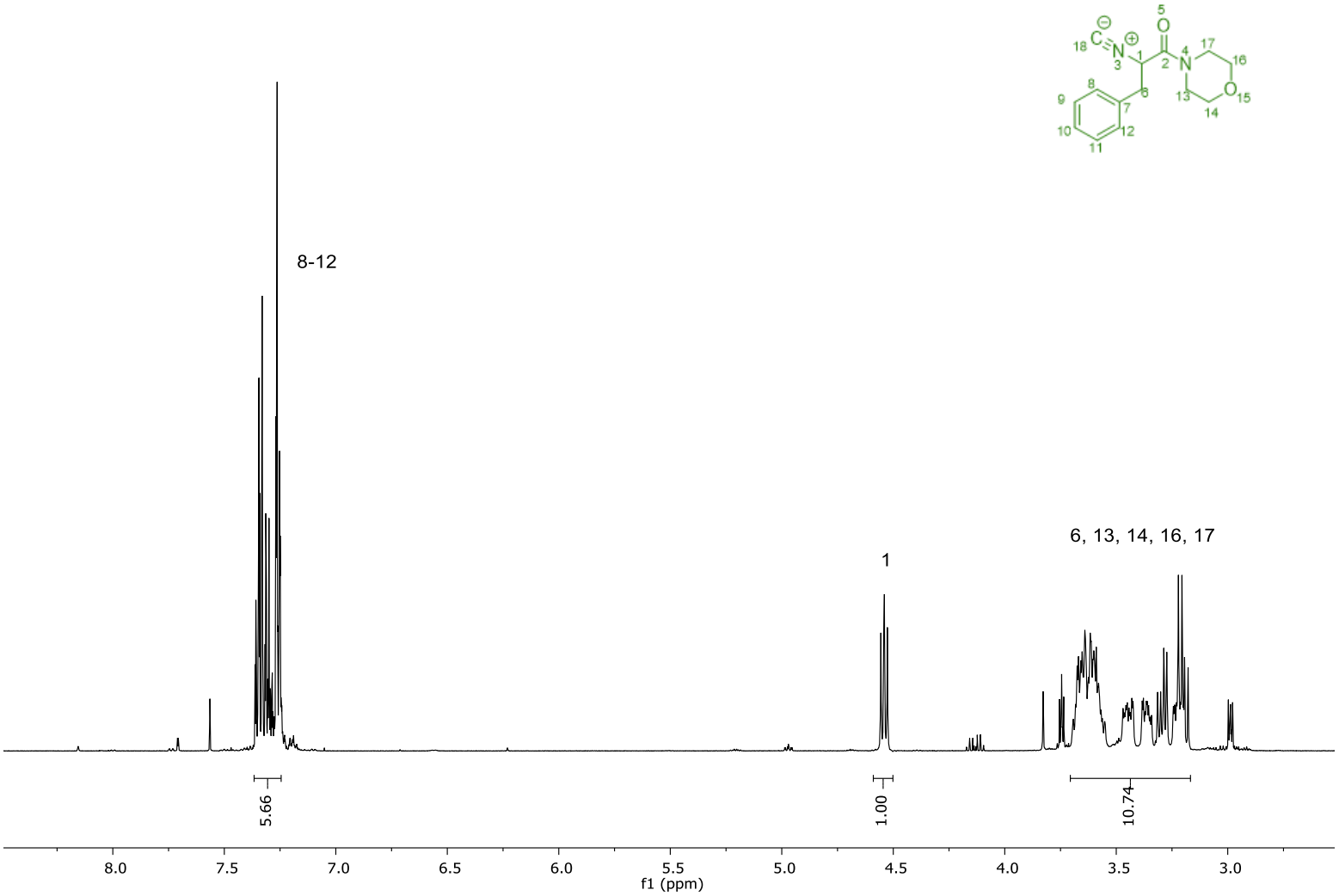


Figure S10. ^{1}H NMR spectrum of 2-Isocyano-1-morpholino-3-phenylpropan-1-one (**3**) in $CDCl_3$ at 500 MHz.

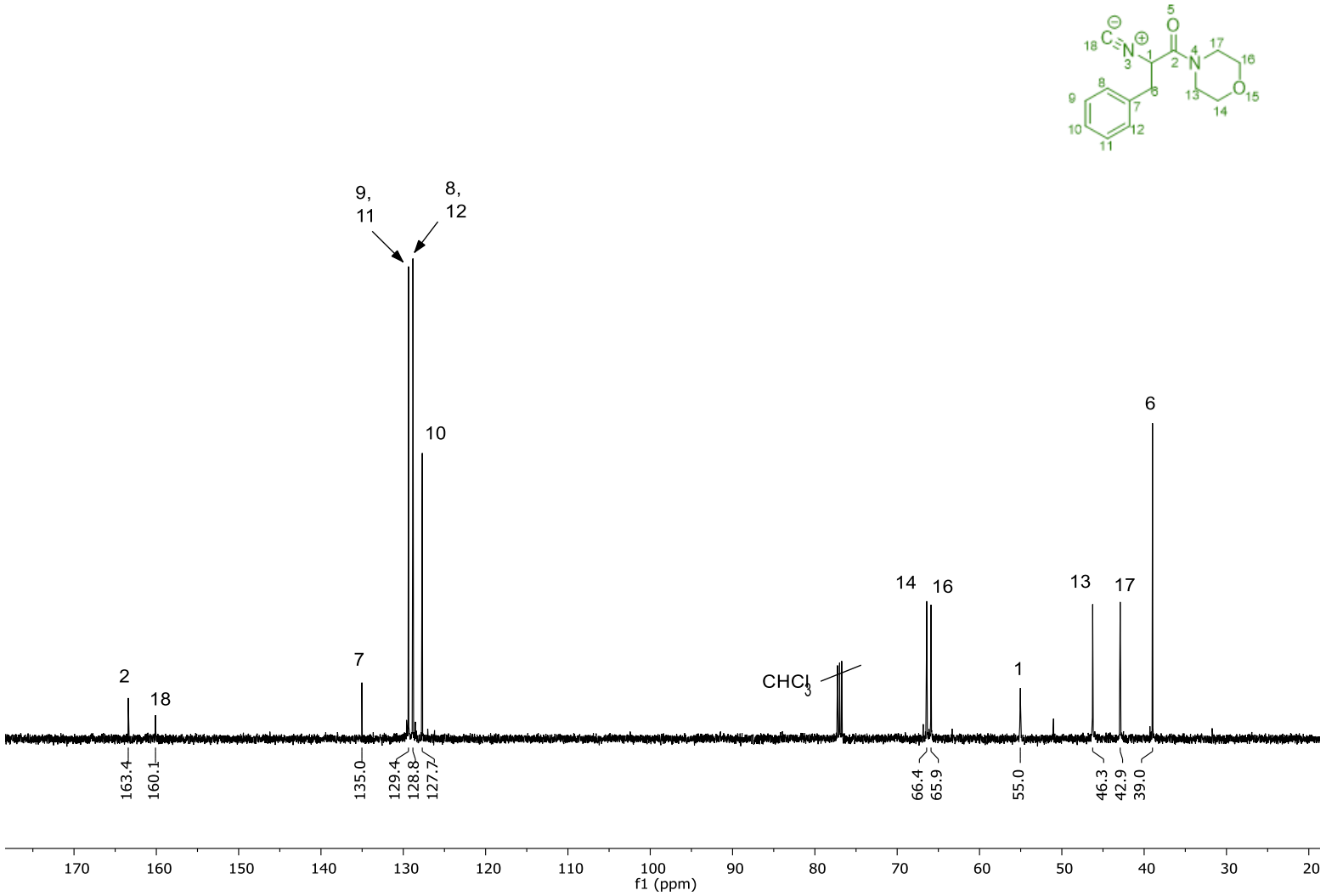


Figure S11. ^{13}C NMR spectrum of 2-Isocyano-1-morpholino-3-phenylpropan-1-one (**3**) in $CDCl_3$ at 126 MHz.

2,6-Dibenzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6a**).

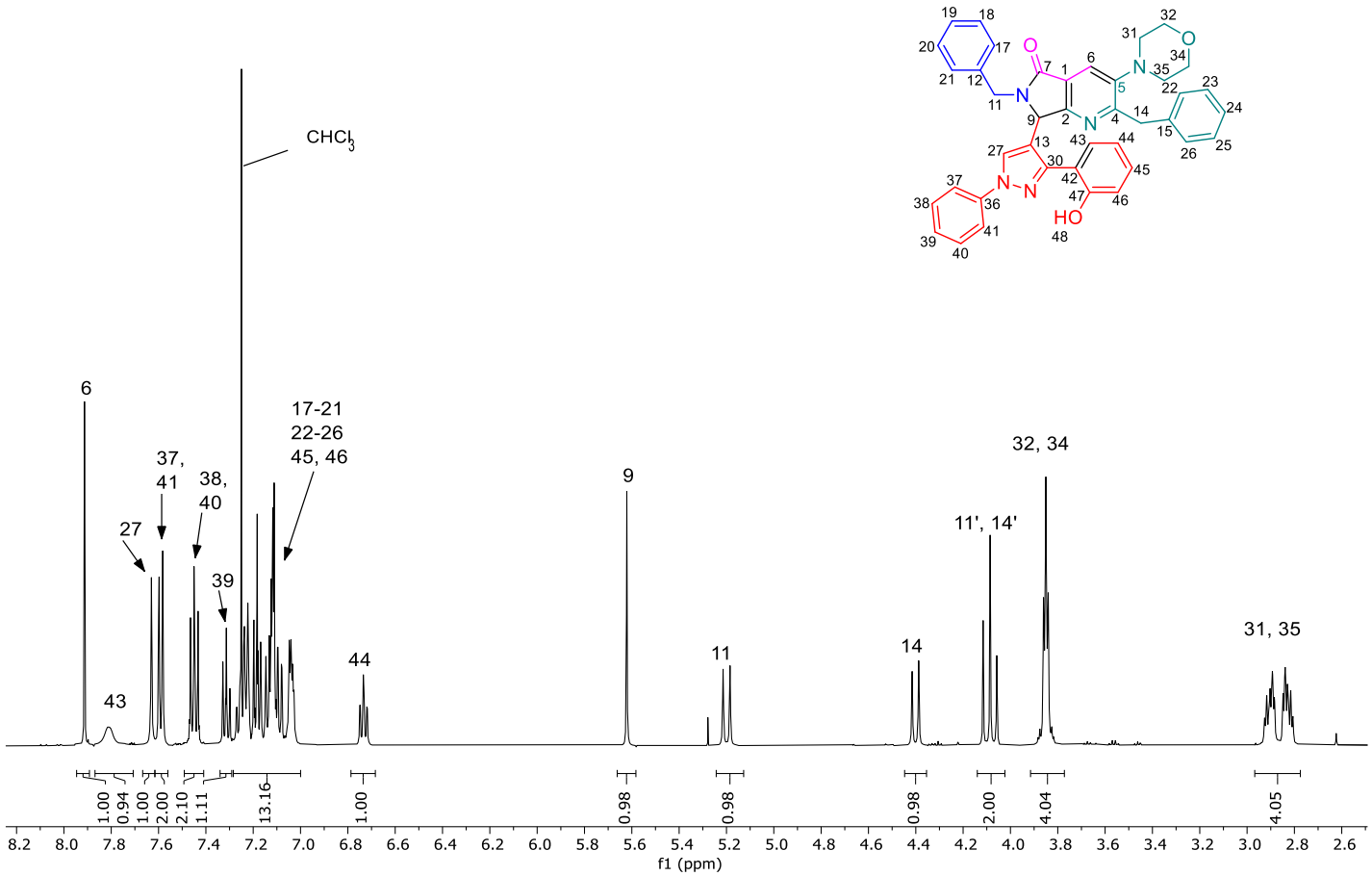


Figure S12. ^{1}H NMR of compound **6a** in $CDCl_3$ at 500 MHz.

2,6-Dibenzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6a**).

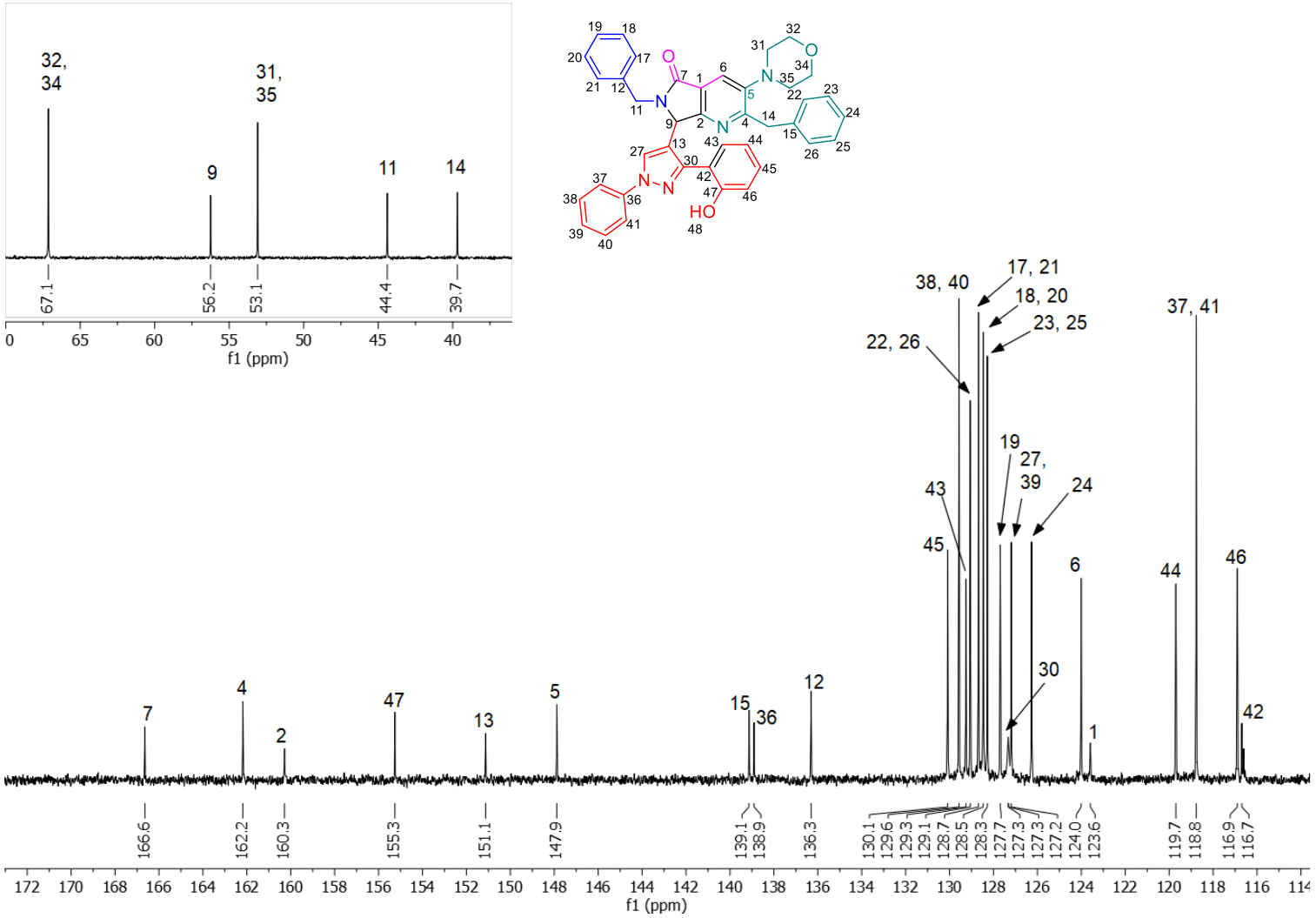


Figure S13. ^{13}C NMR of compound **6a** in $CDCl_3$ at 126 MHz.

2,6-Dibenzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6a**).

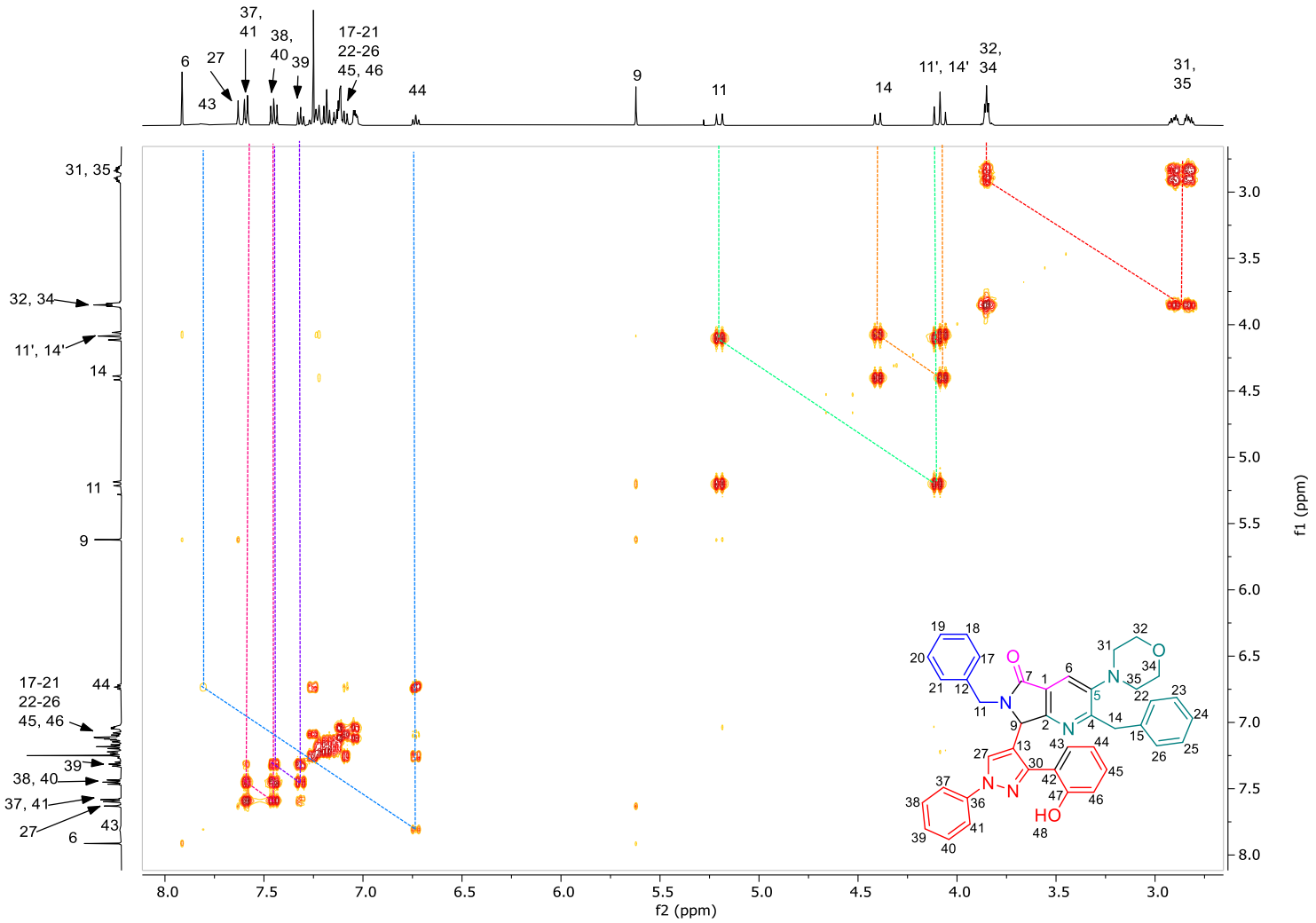


Figure S14. 2D NMR (COSY) Spectrum of compound **6a**.

2,6-Dibenzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6a**).

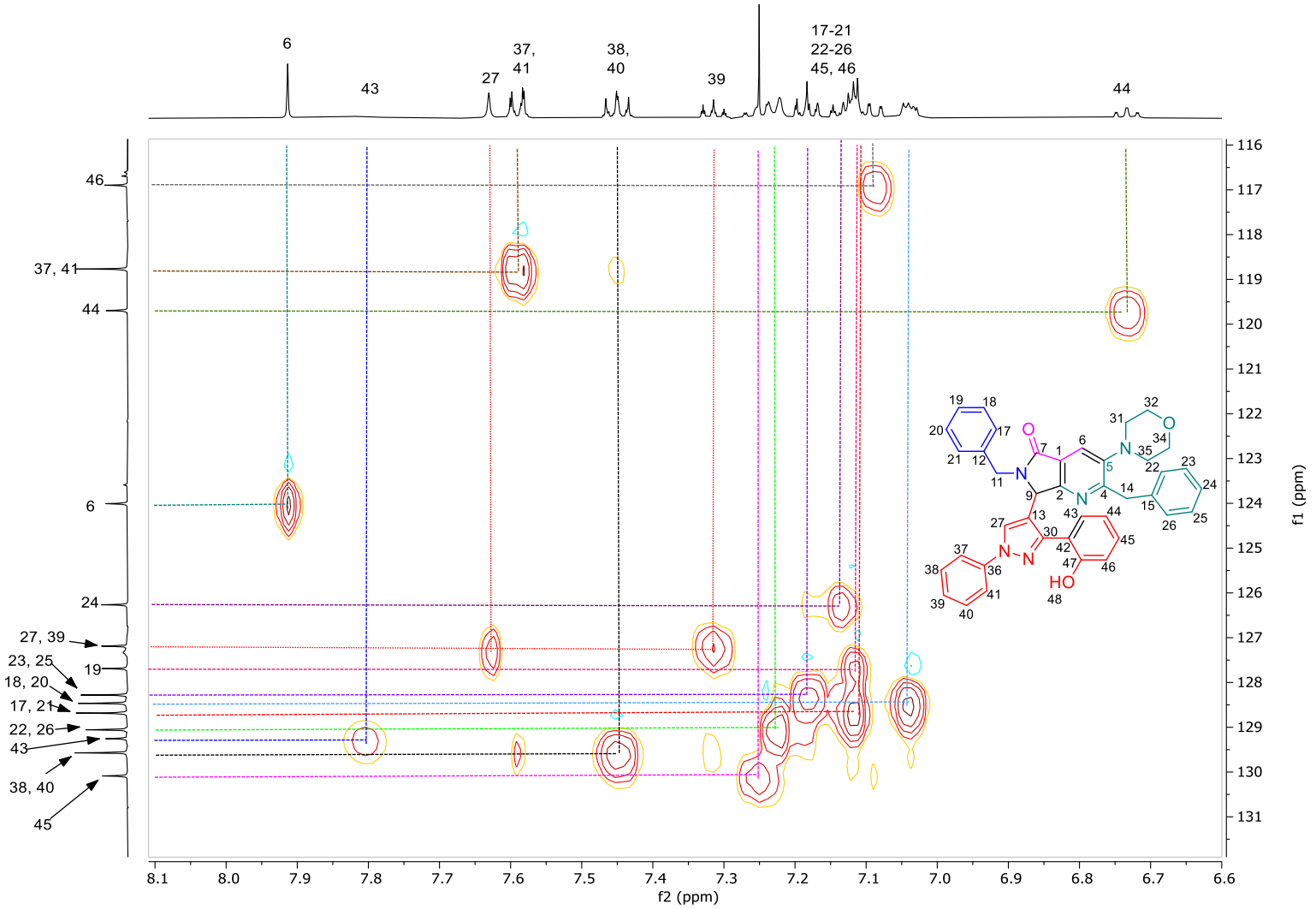


Figure S15. 2D NMR (HSQC) Spectrum of the aromatic region of compound **6a**.

2,6-Dibenzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6a**).

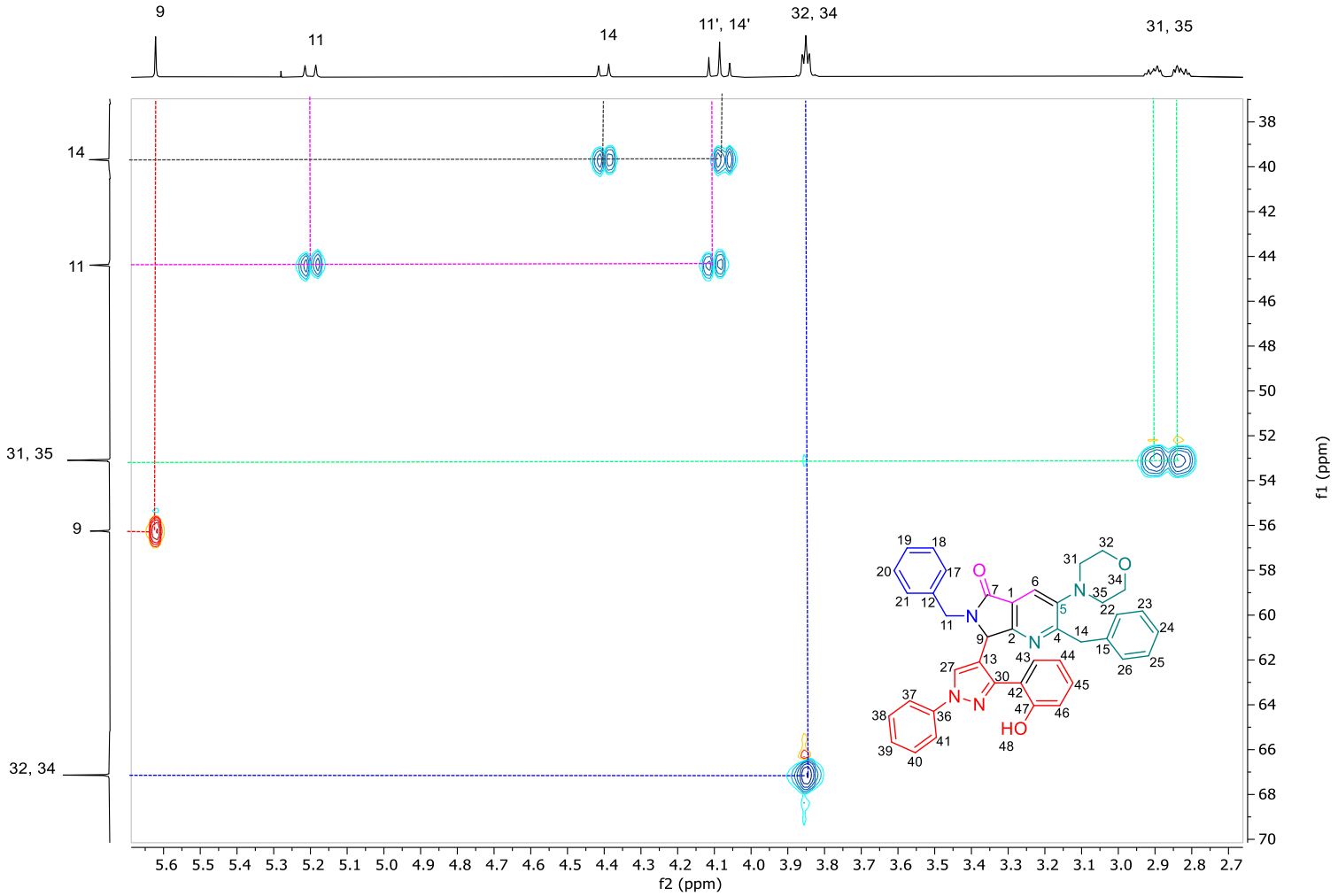


Figure S16. 2D NMR (HSQC) Spectrum of the aliphatic region of compound **6a**.

2,6-Dibenzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6a**).

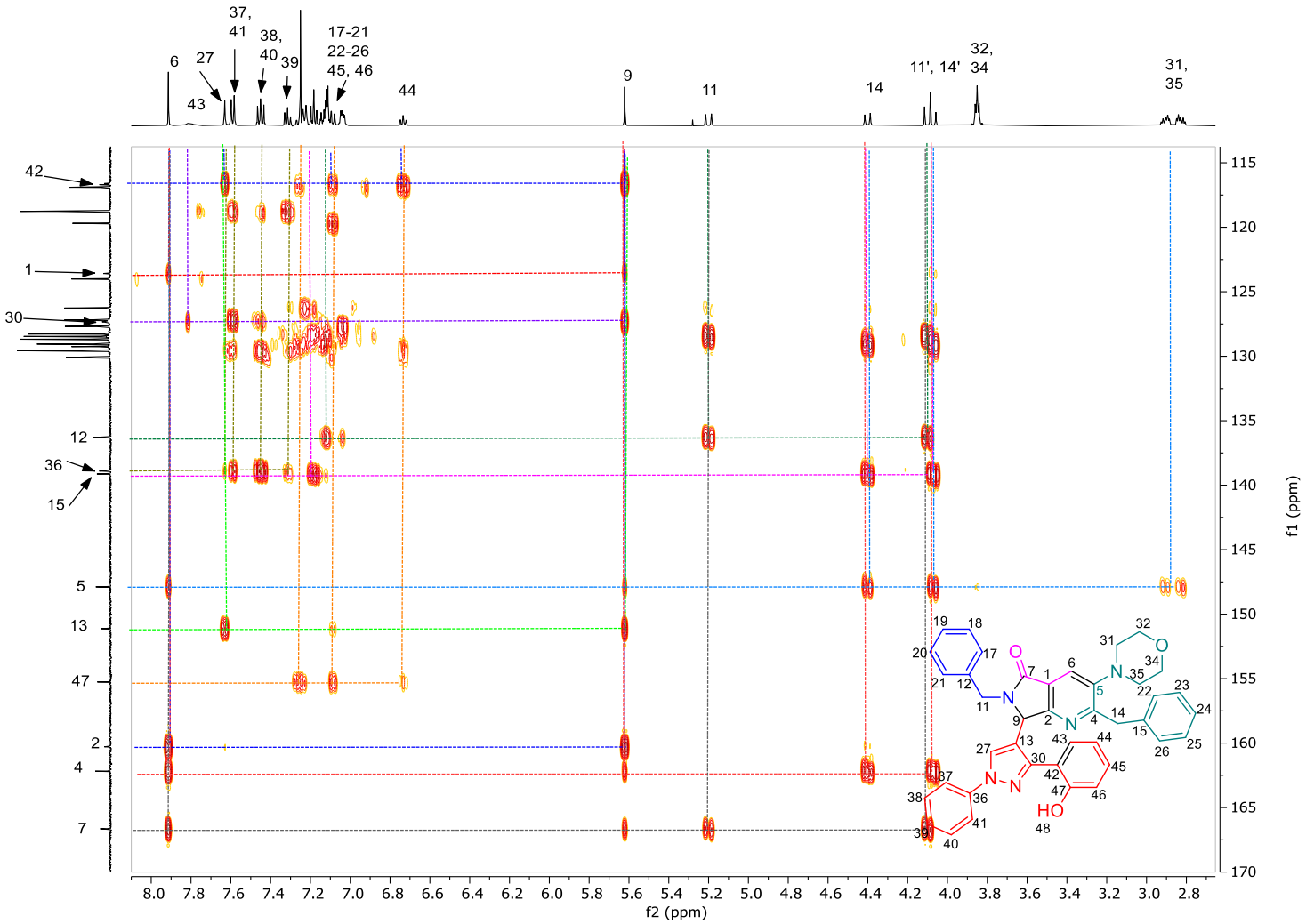


Figure S17. 2D NMR (HMBC) Spectrum of compound **6a**.

2-Benzyl-6-butyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6b**).

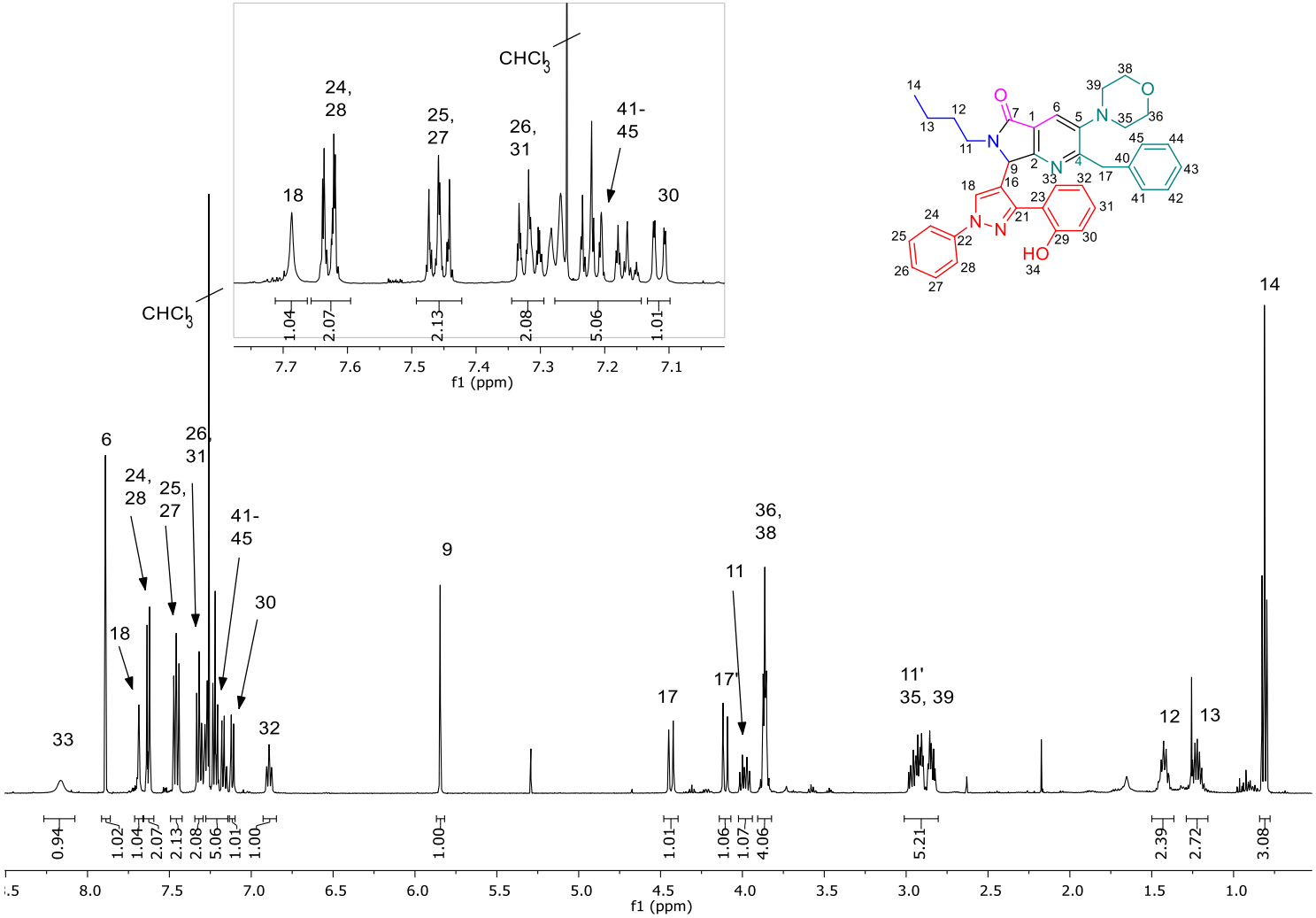


Figure S18. ^{1}H NMR of compound **6b** in $CDCl_3$ at 500 MHz

2-Benzyl-6-butyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6b**).

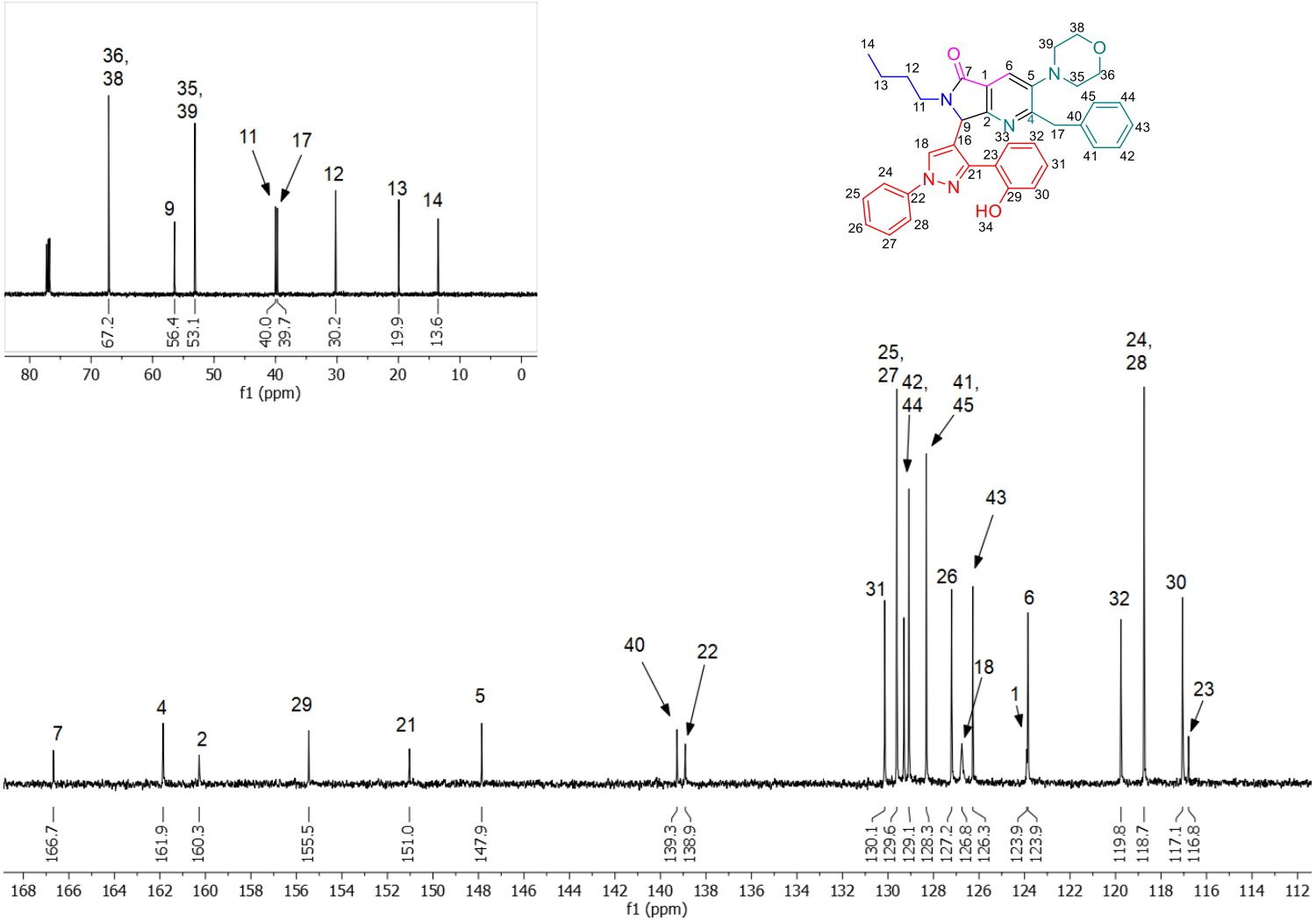


Figure S19. ^{13}C NMR of compound **6b** in $CDCl_3$ at 126 MHz.

2-Benzyl-6-butyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6b**).

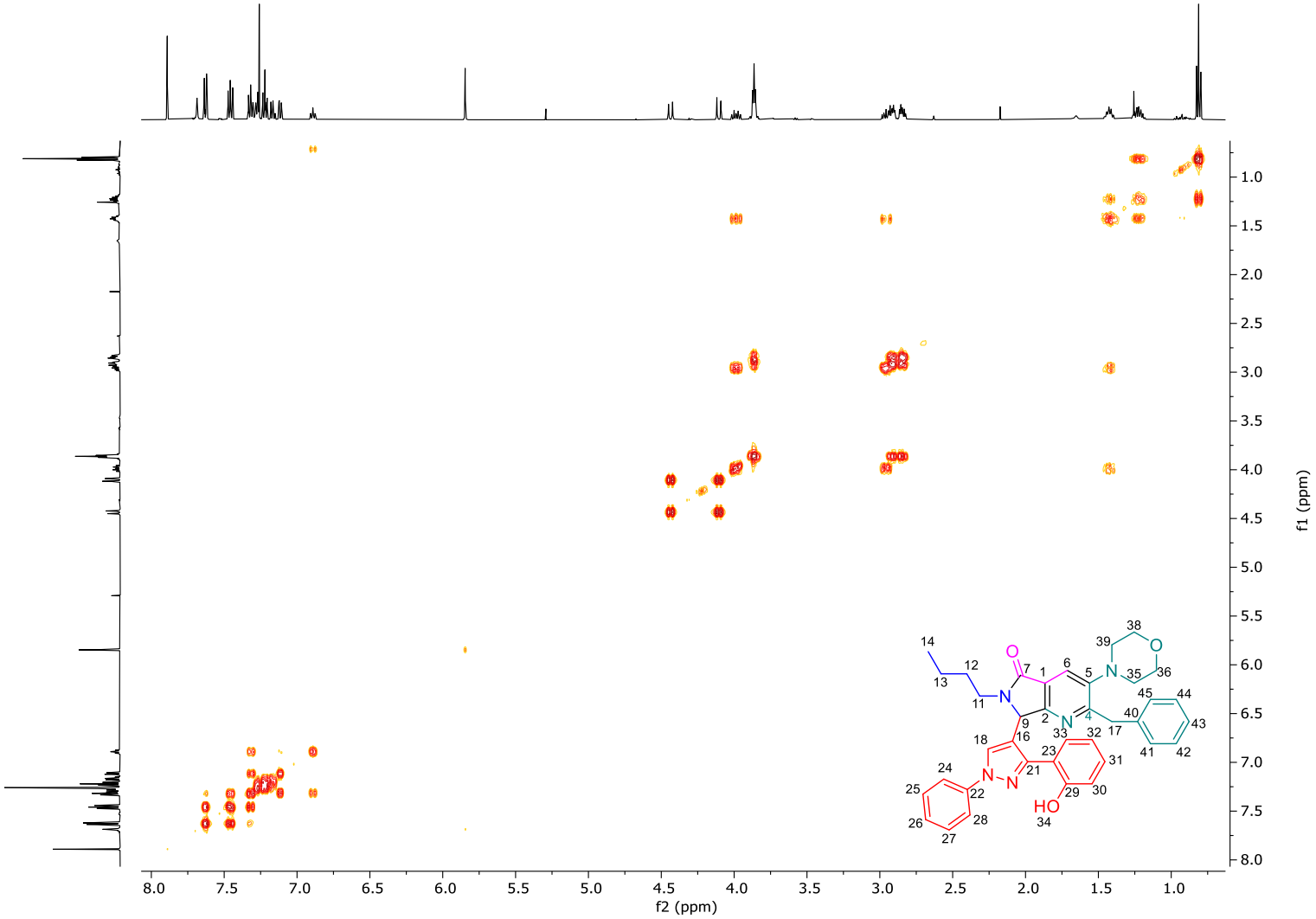


Figure S20. 2D COSY NMR Spectrum of compound **6b**.

2-Benzyl-6-butyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6b**).

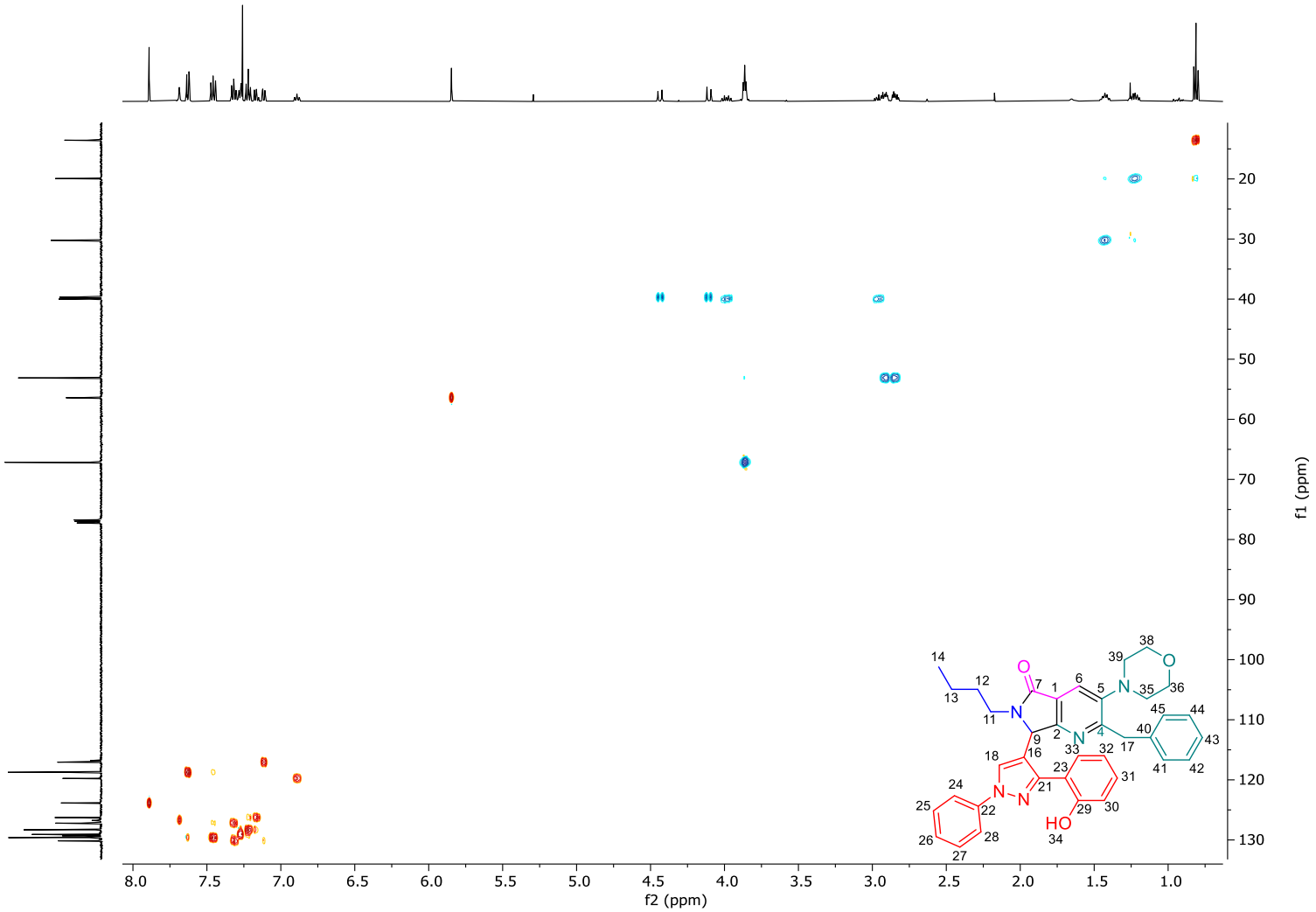


Figure S21. 2D HSQC NMR Spectrum of compound **6b**.

2-Benzyl-6-butyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6b**).

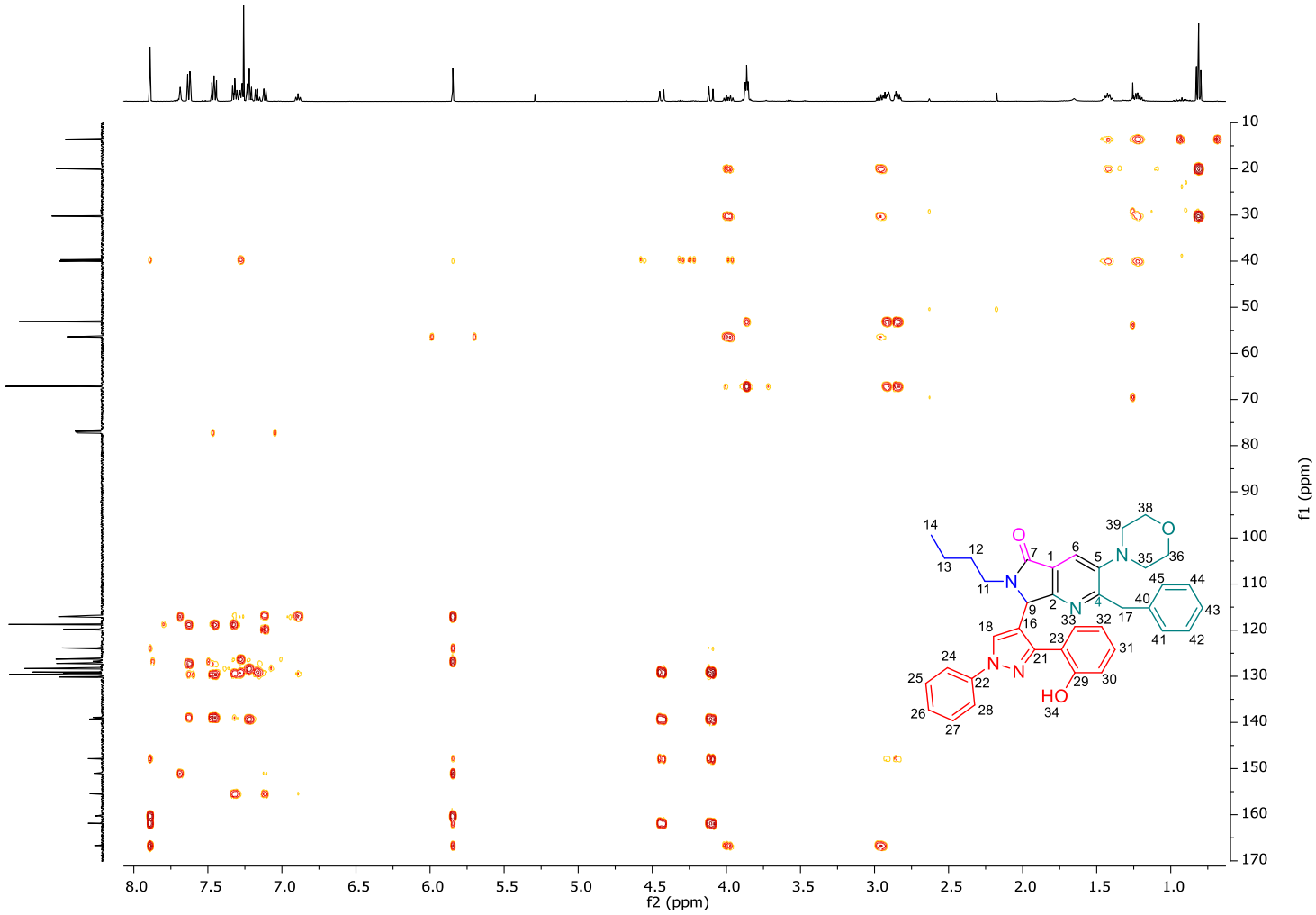


Figure S22. 2D HMBC NMR Spectrum of compound **6b**.

2-Benzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6-phenethyl-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6c**).

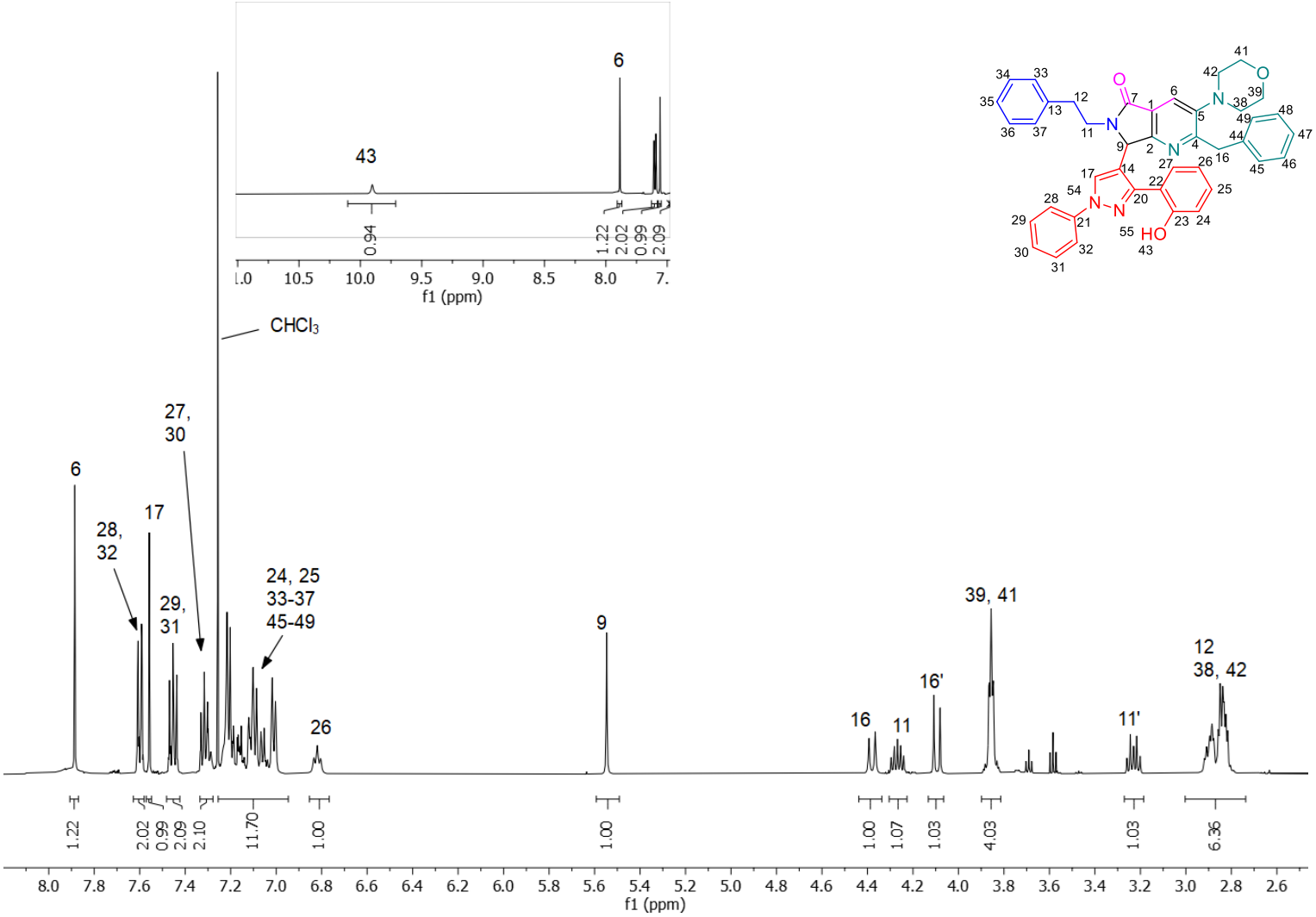


Figure S23. ^{1}H NMR of compound **6c** in $CDCl_3$ at 500 MHz.

2-Benzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6-phenethyl-6,7-dihydro-5*H*-pyrrolo[3,4-b]pyridin-5-one (**6c**).

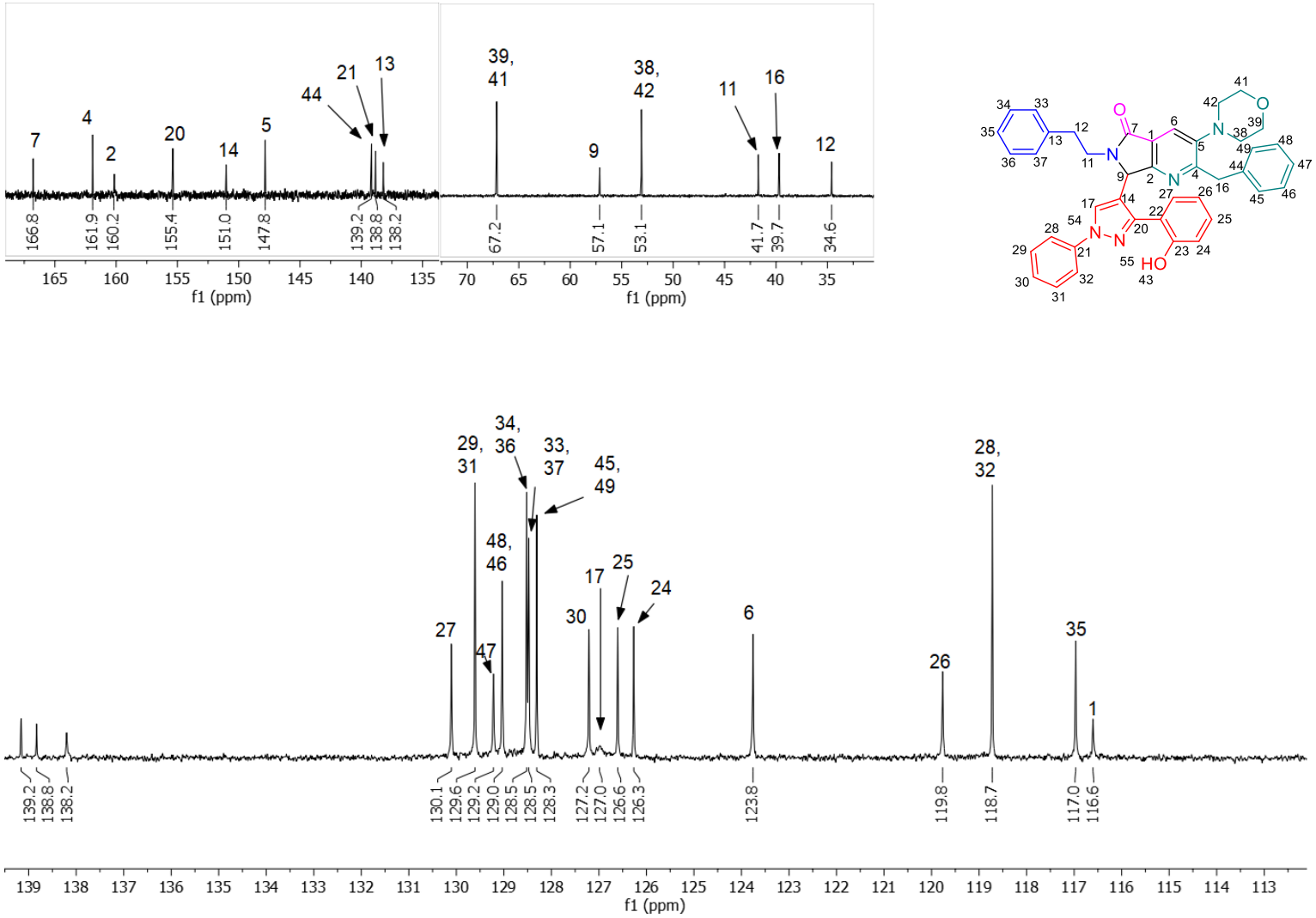


Figure S24. ^{13}C NMR of compound **6c** in $CDCl_3$ at 126 MHz.

2-Benzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6-phenethyl-6,7-dihydro-5*H*-pyrrolo[3,4-b]pyridin-5-one (**6c**).

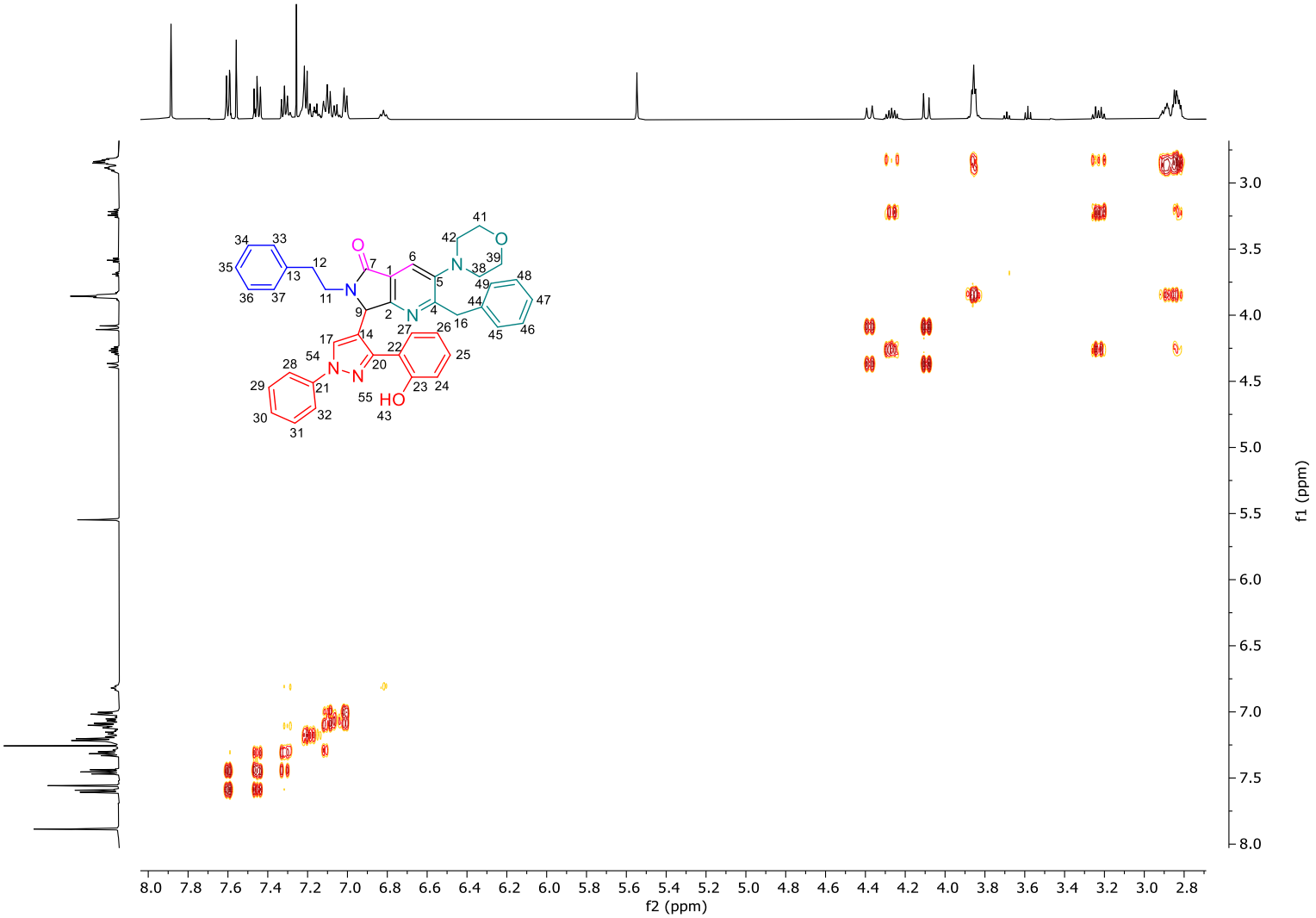


Figure S25. 2D COSY NMR Spectrum of compound **6c**.

2-Benzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6-phenethyl-6,7-dihydro-5*H*-pyrrolo[3,4-b]pyridin-5-one (**6c**).

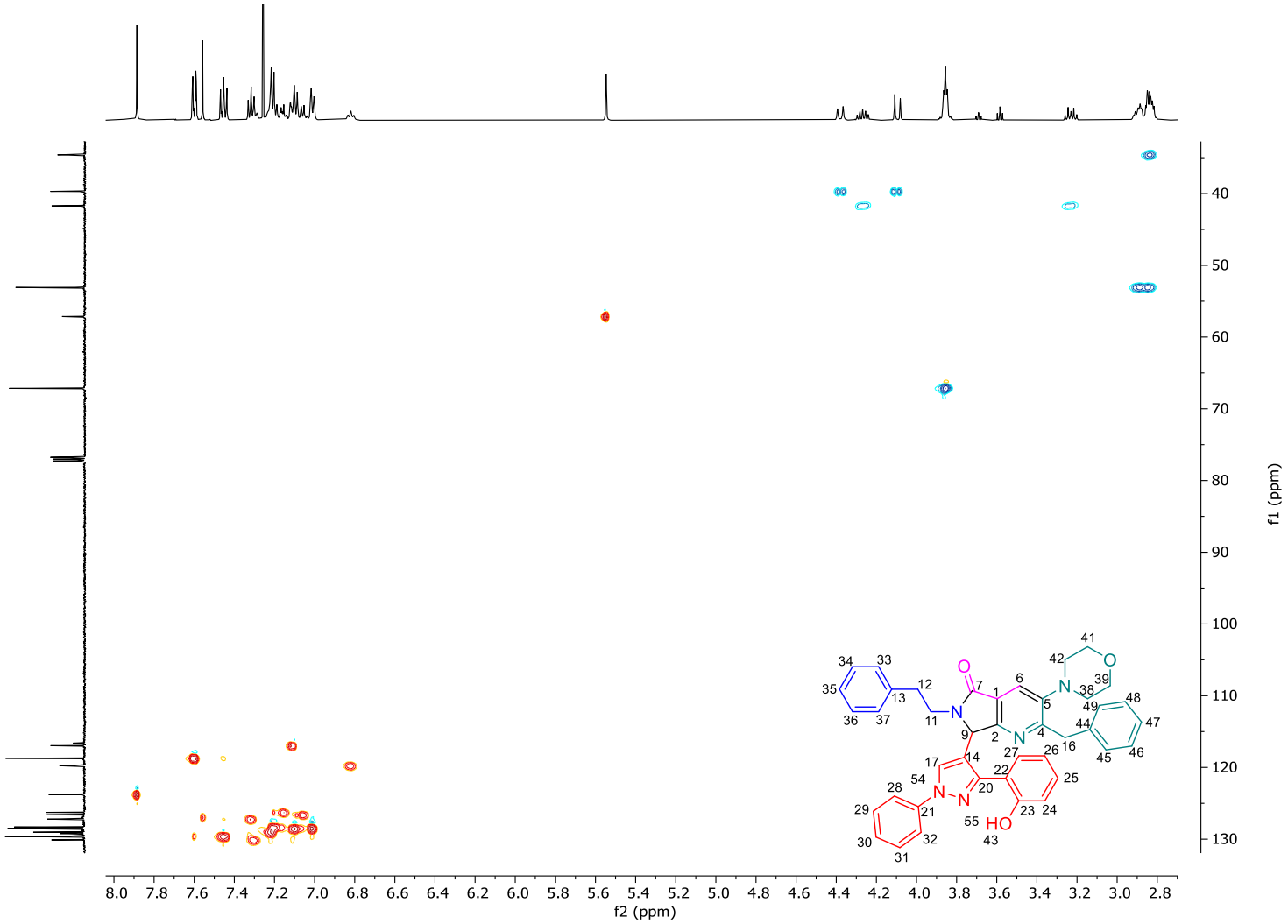


Figure S26. 2D HSQC NMR Spectrum of compound **6c**.

2-Benzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6-phenethyl-6,7-dihydro-5*H*-pyrrolo[3,4-b]pyridin-5-one (**6c**).

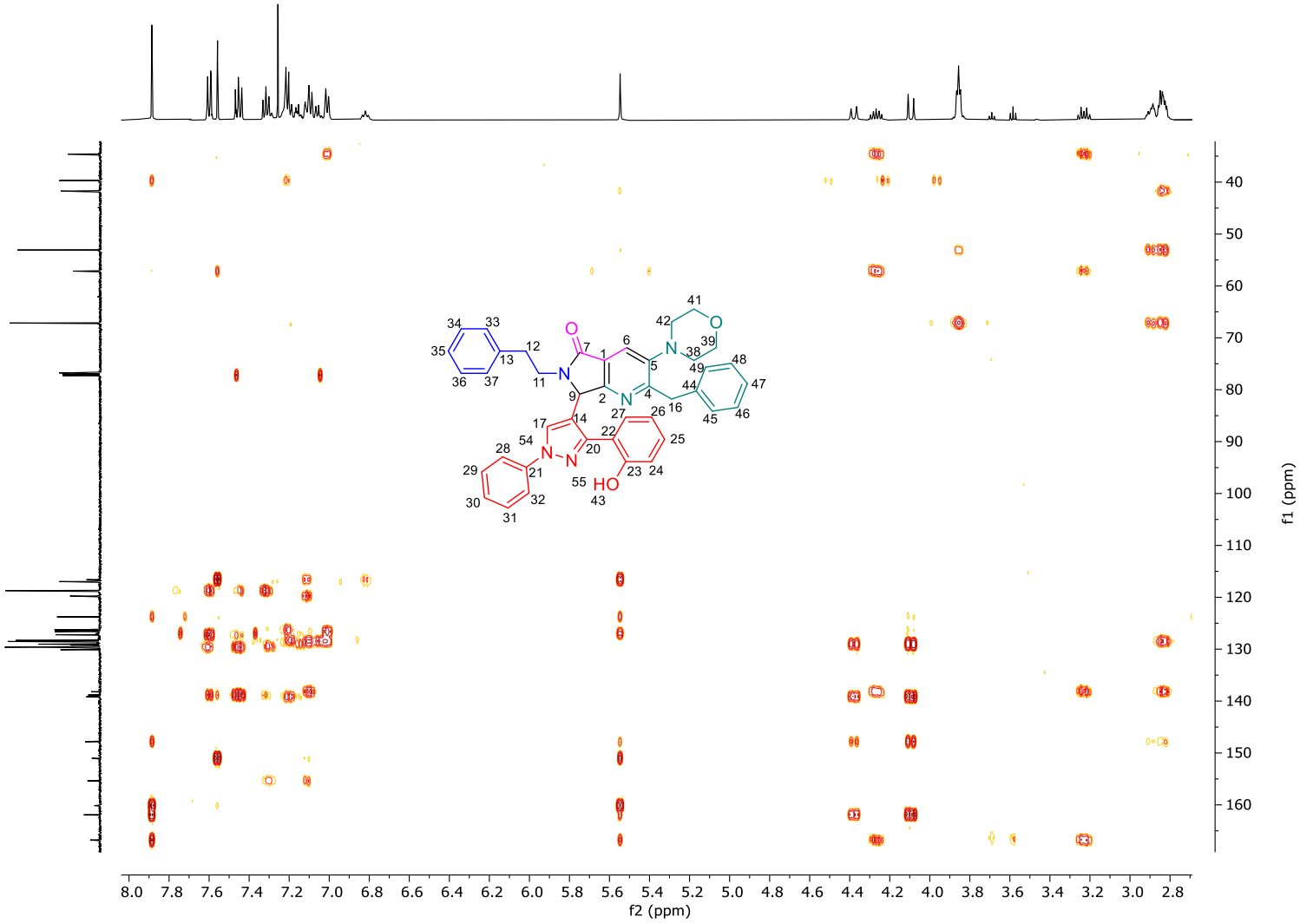


Figure S27. 2D HMBC NMR Spectrum of compound **6c.**

2-Benzyl-6-(3,4-dimethoxybenzyl)-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6d**).

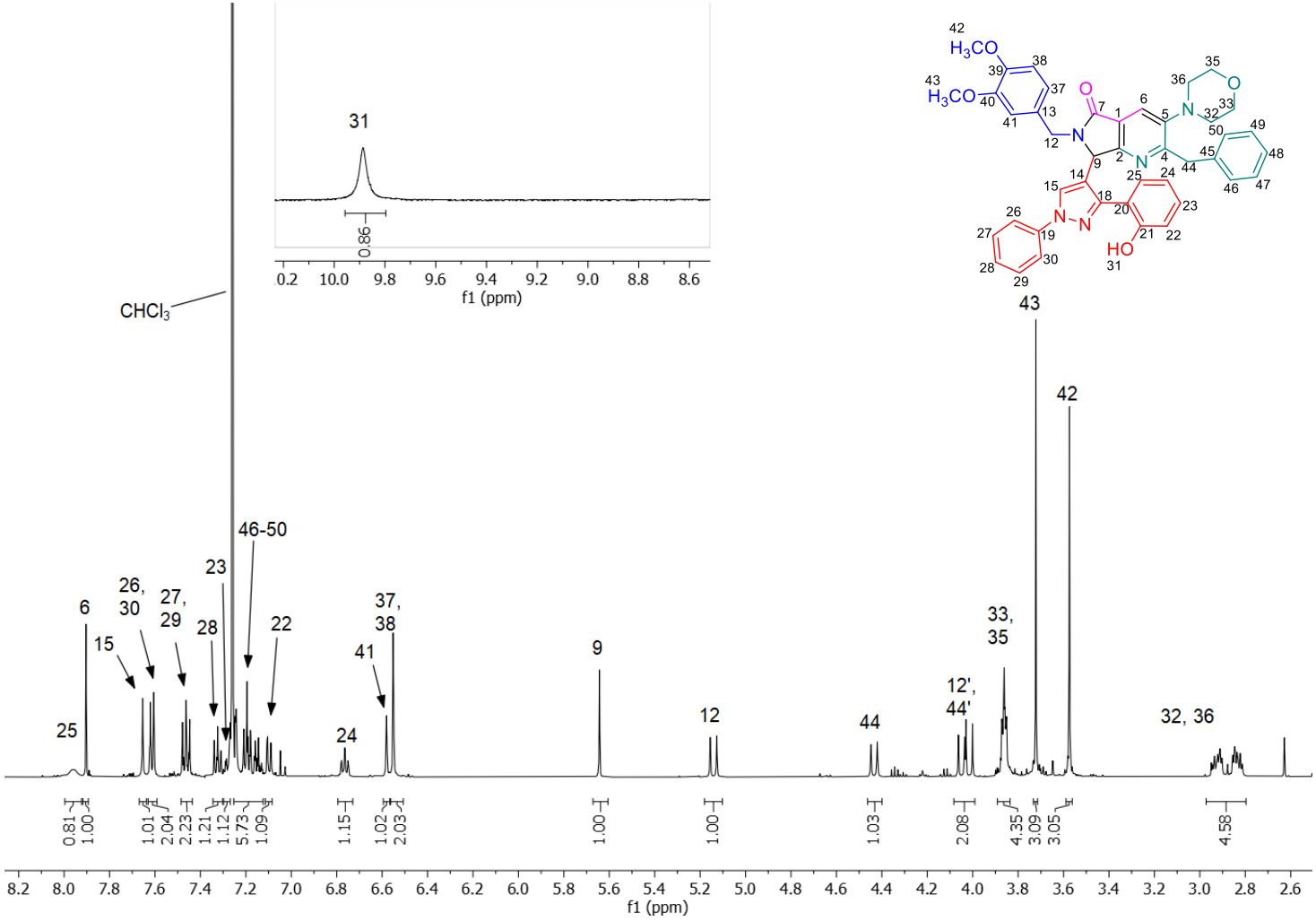


Figure S28. ^{1}H NMR of compound **6d** in $CDCl_3$ at 500 MHz.

2-Benzyl-6-(3,4-dimethoxybenzyl)-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6d**).

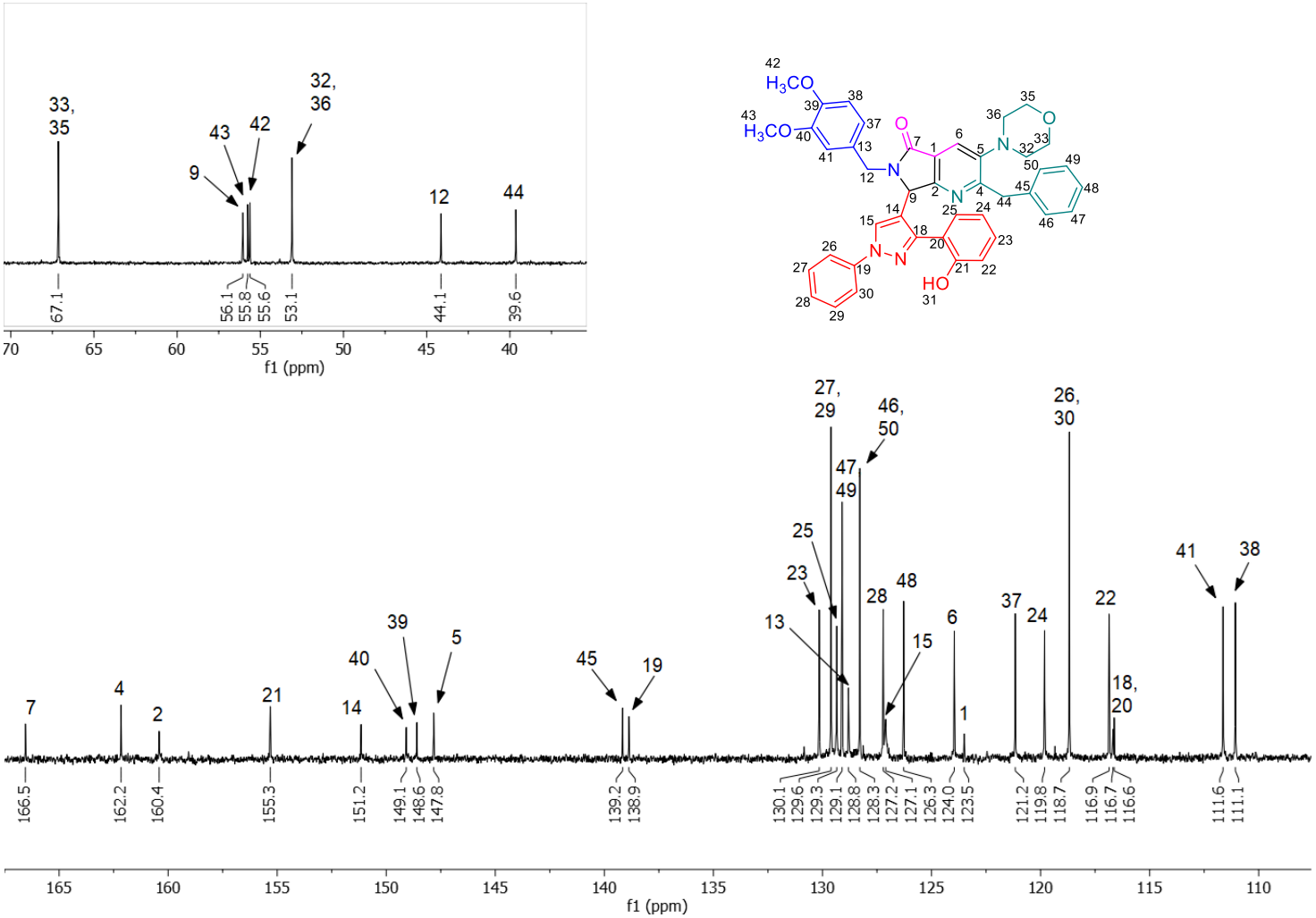


Figure S29. ^{13}C NMR of compound **6d** in $CDCl_3$ at 126 MHz.

2-Benzyl-6-(3,4-dimethoxybenzyl)-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-b]pyridin-5-one (**6d**).

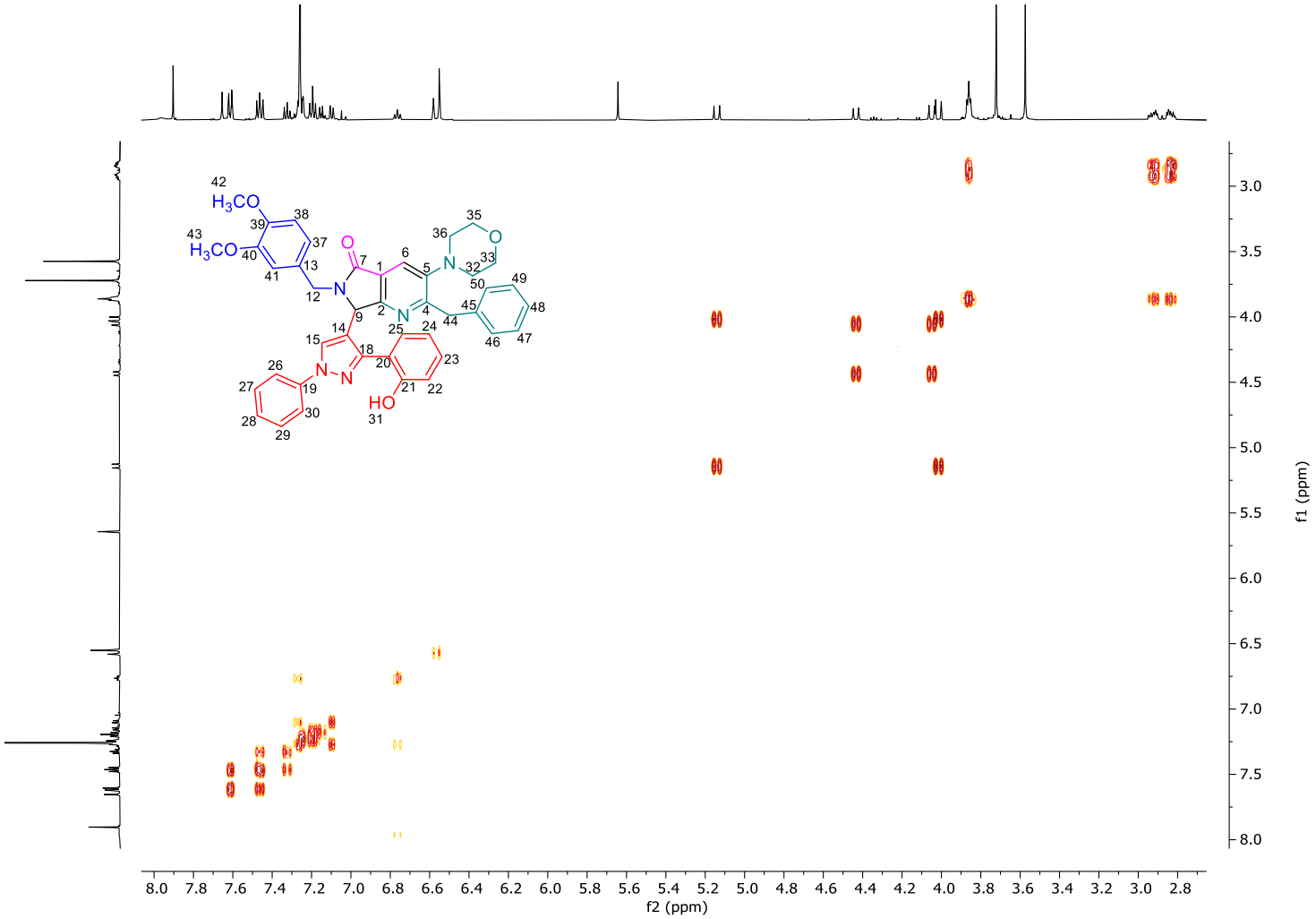


Figure S30. 2D COSY NMR Spectrum of compound **6d.**

2-Benzyl-6-(3,4-dimethoxybenzyl)-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-b]pyridin-5-one (**6d**).

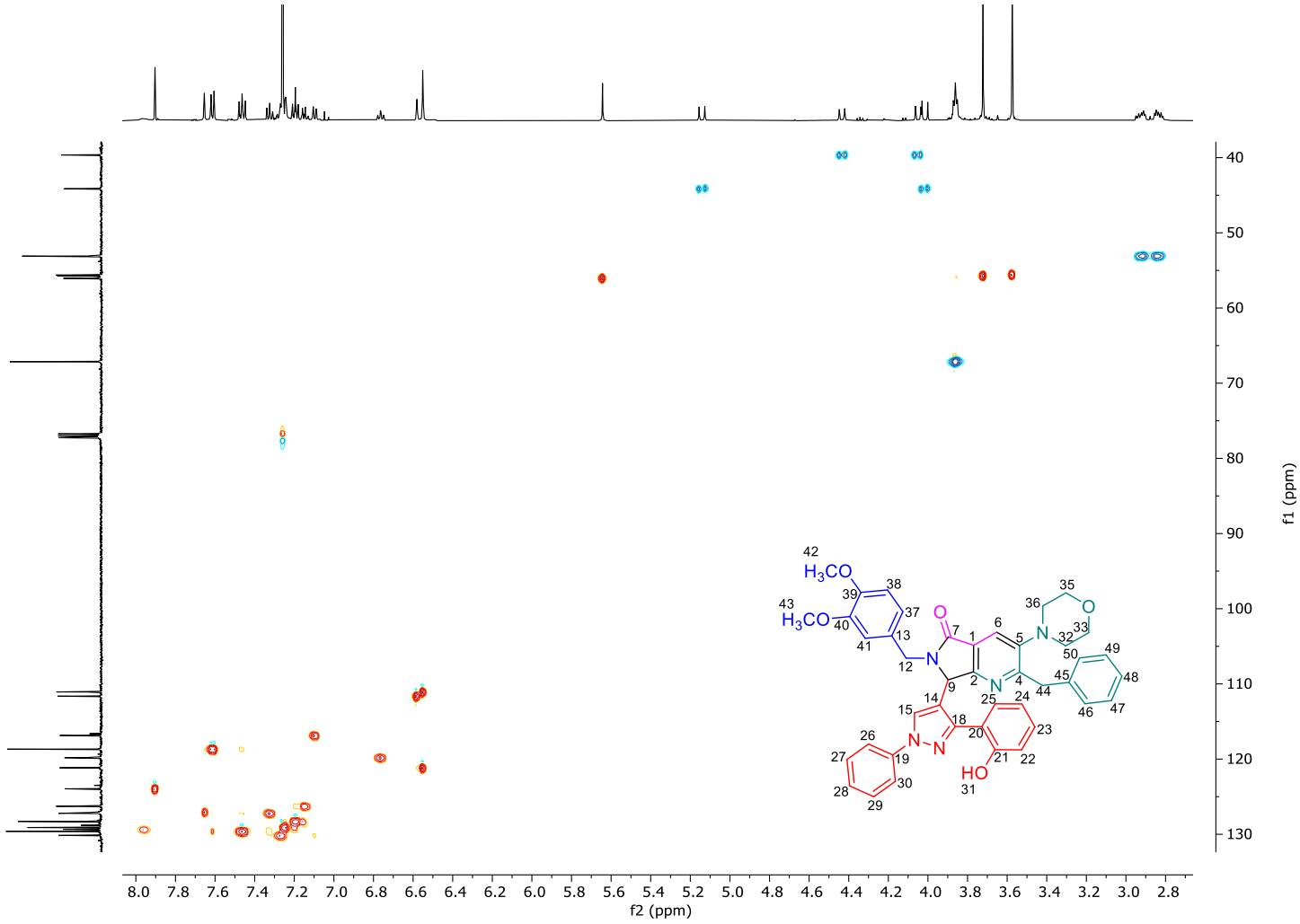


Figure S31. 2D HSQC NMR Spectrum of compound **6d.**

2-Benzyl-6-(3,4-dimethoxybenzyl)-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-b]pyridin-5-one (**6e**).

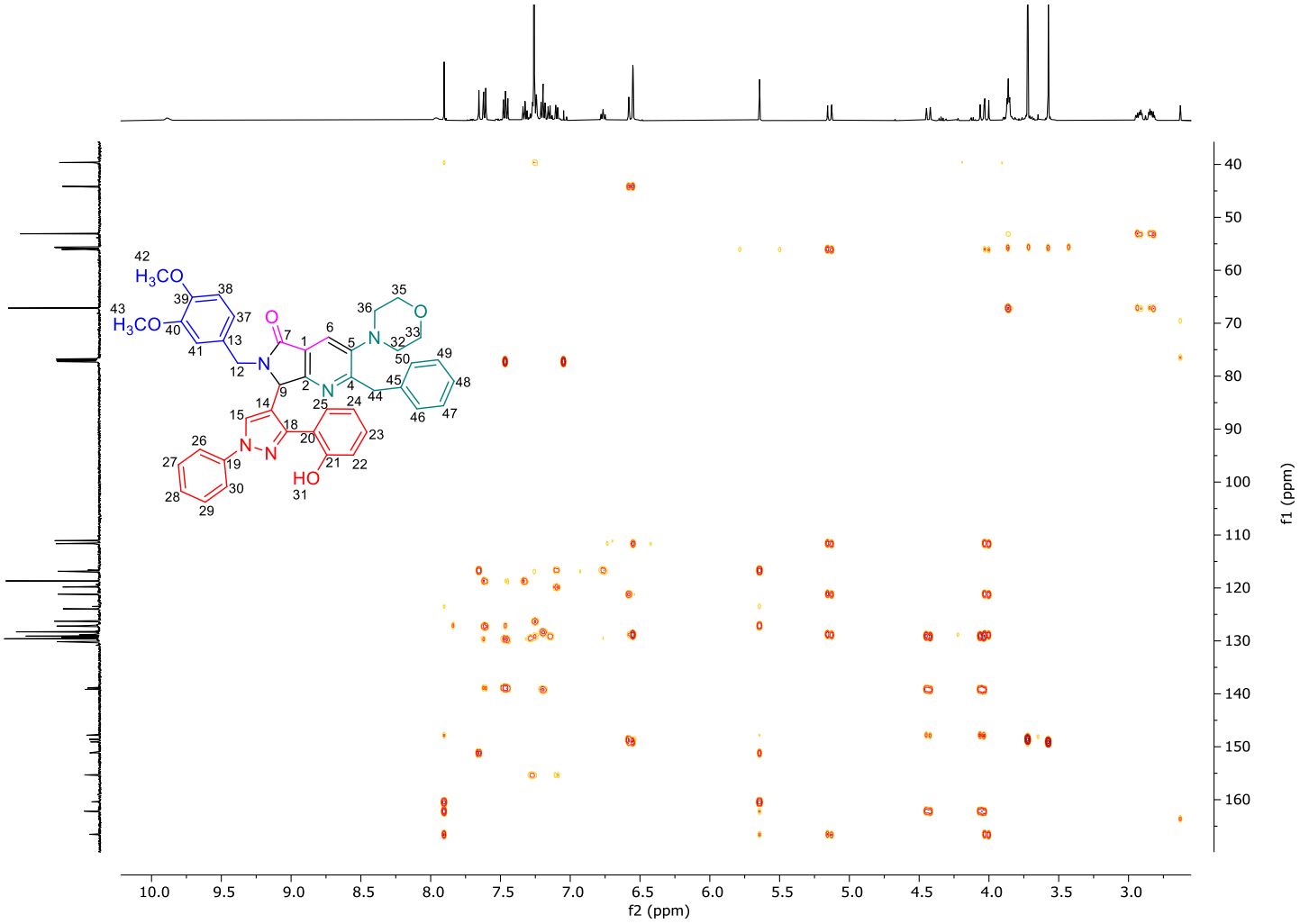


Figure S32. 2D HMBC NMR Spectrum of compound **6d.**

2-Benzyl-6-(4-fluorobenzyl)-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6e**).

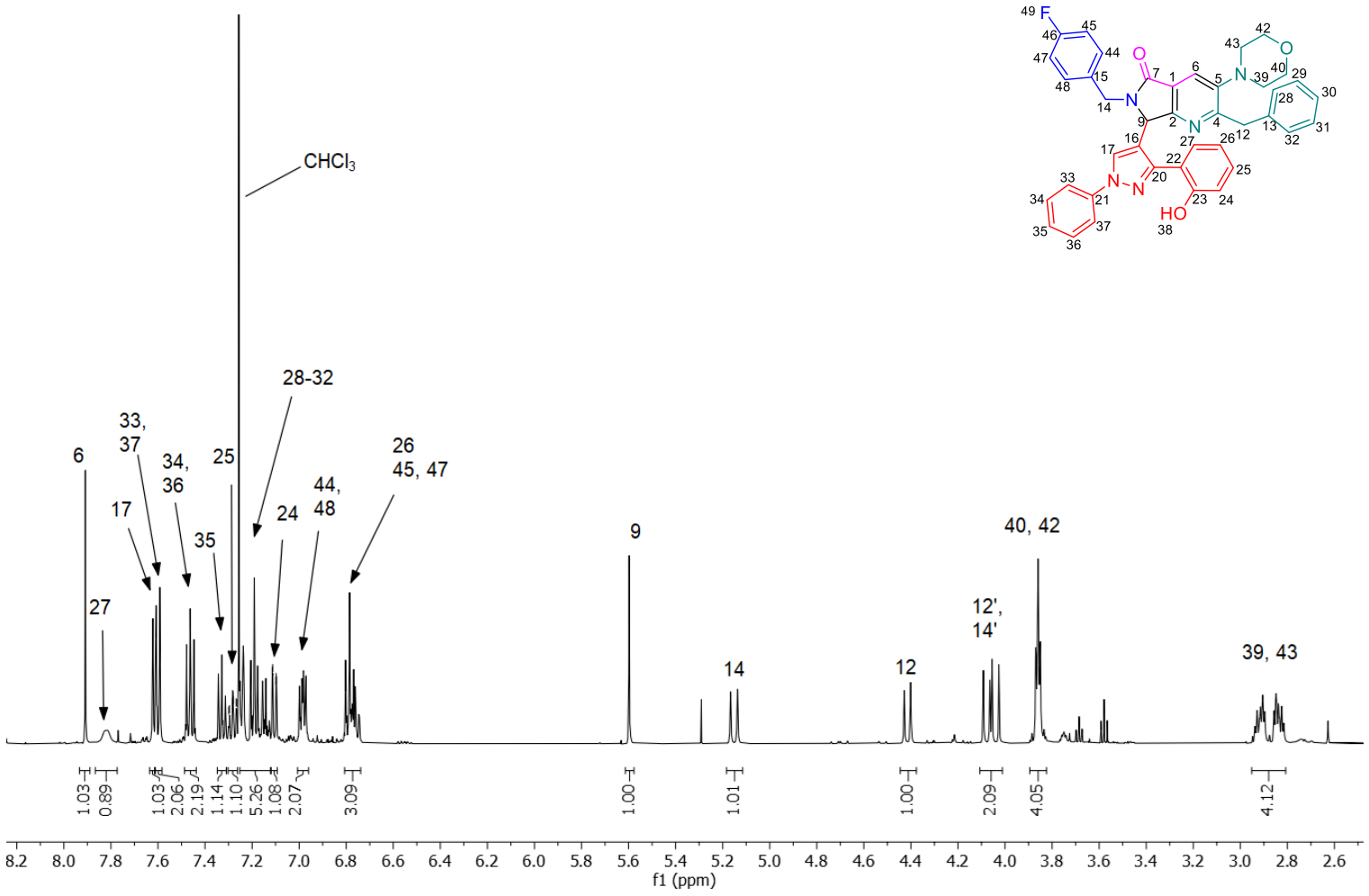


Figure S33. ^{1}H NMR of compound **6e** in $CDCl_3$ at 500 MHz.

2-Benzyl-6-(4-fluorobenzyl)-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6e**).

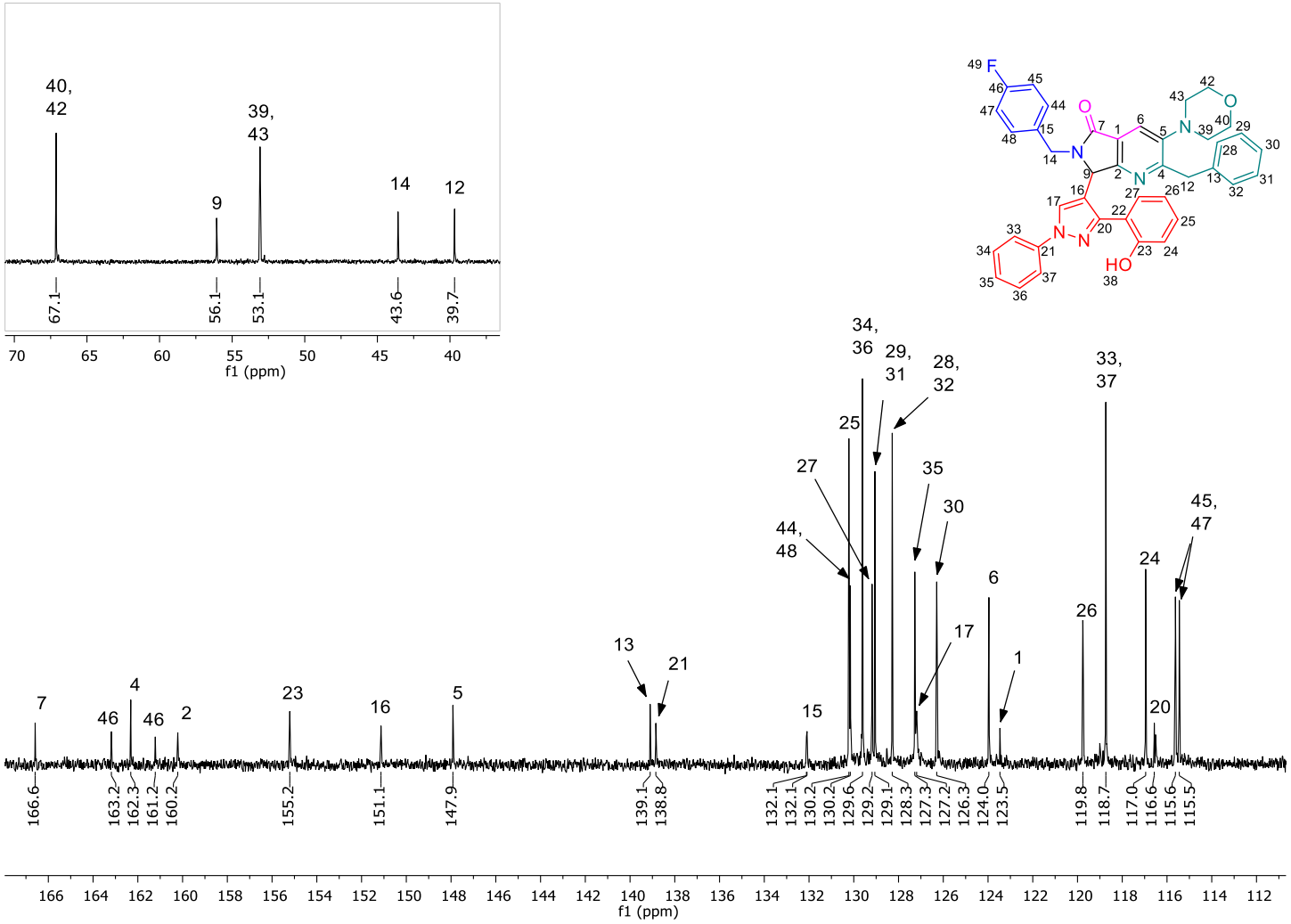


Figure S34. ^{13}C NMR of compound **6e** in $CDCl_3$ at 126 MHz

2-Benzyl-6-(4-fluorobenzyl)-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6e**).

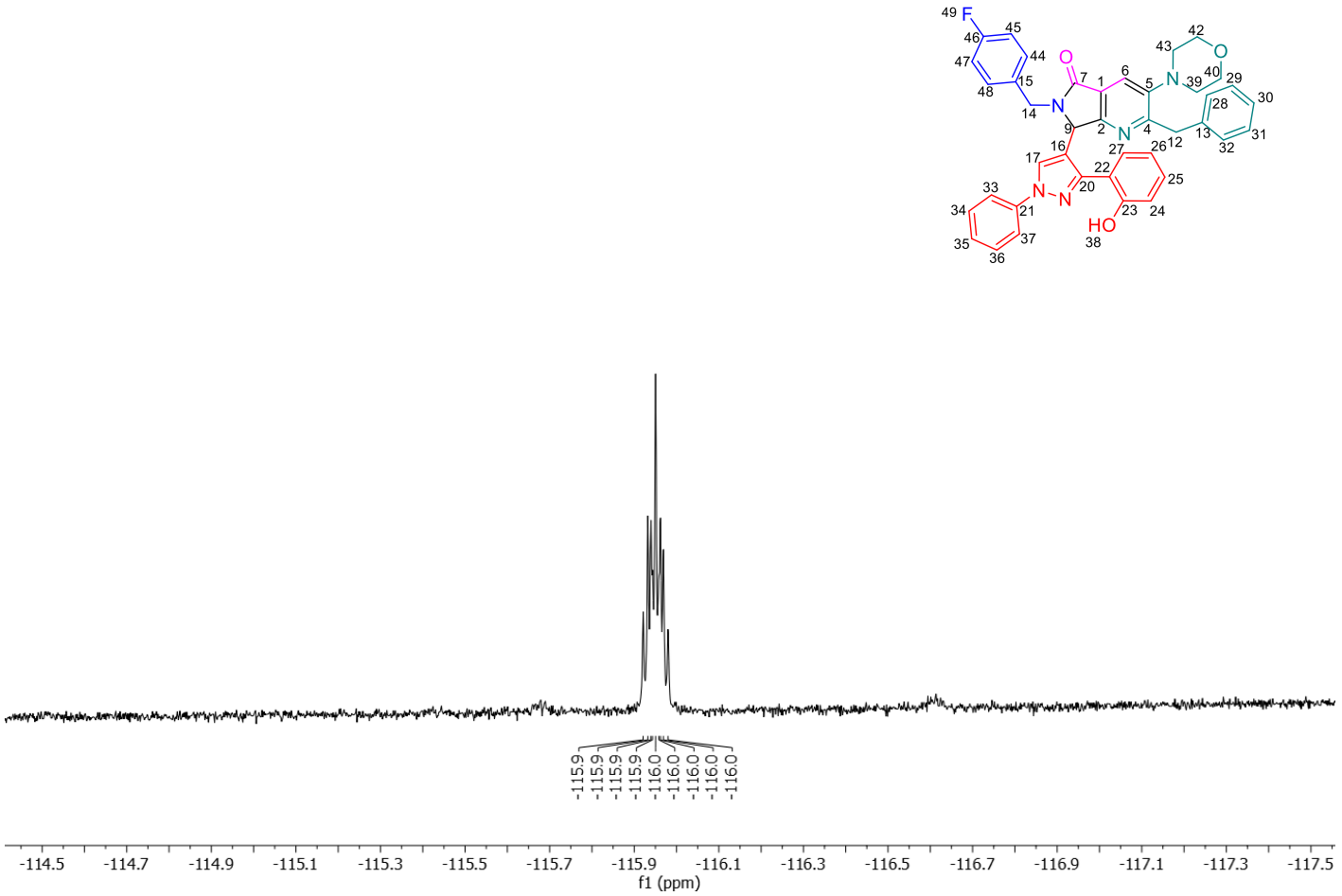


Figure S35.[19]F NMR of compound **6e** in $CDCl_3$ at 471 MHz.

2-Benzyl-6-(4-fluorobenzyl)-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6e**).

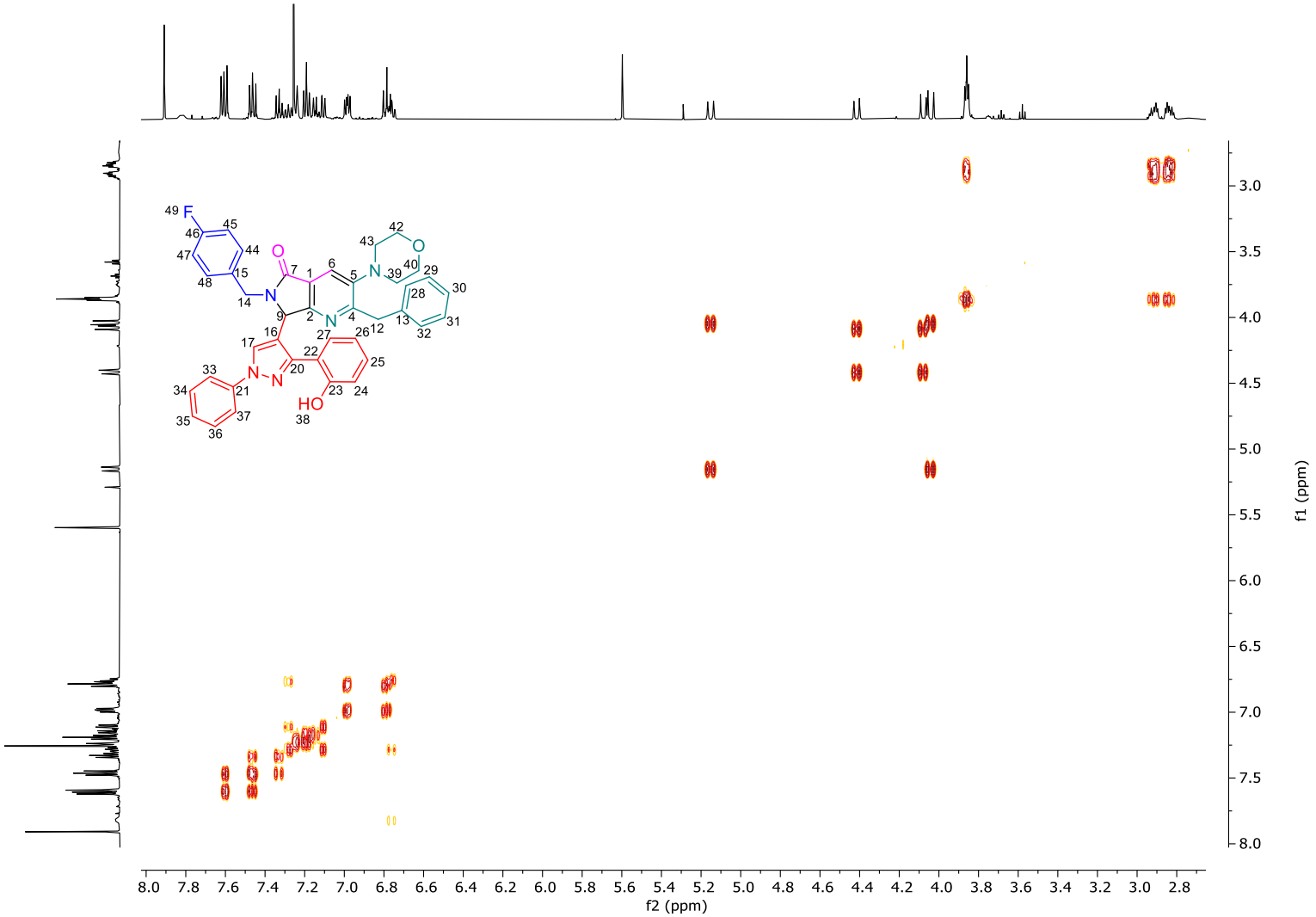


Figure S36. 2D COSY NMR Spectrum of compound **6e.**

2-Benzyl-6-(4-fluorobenzyl)-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6e**).

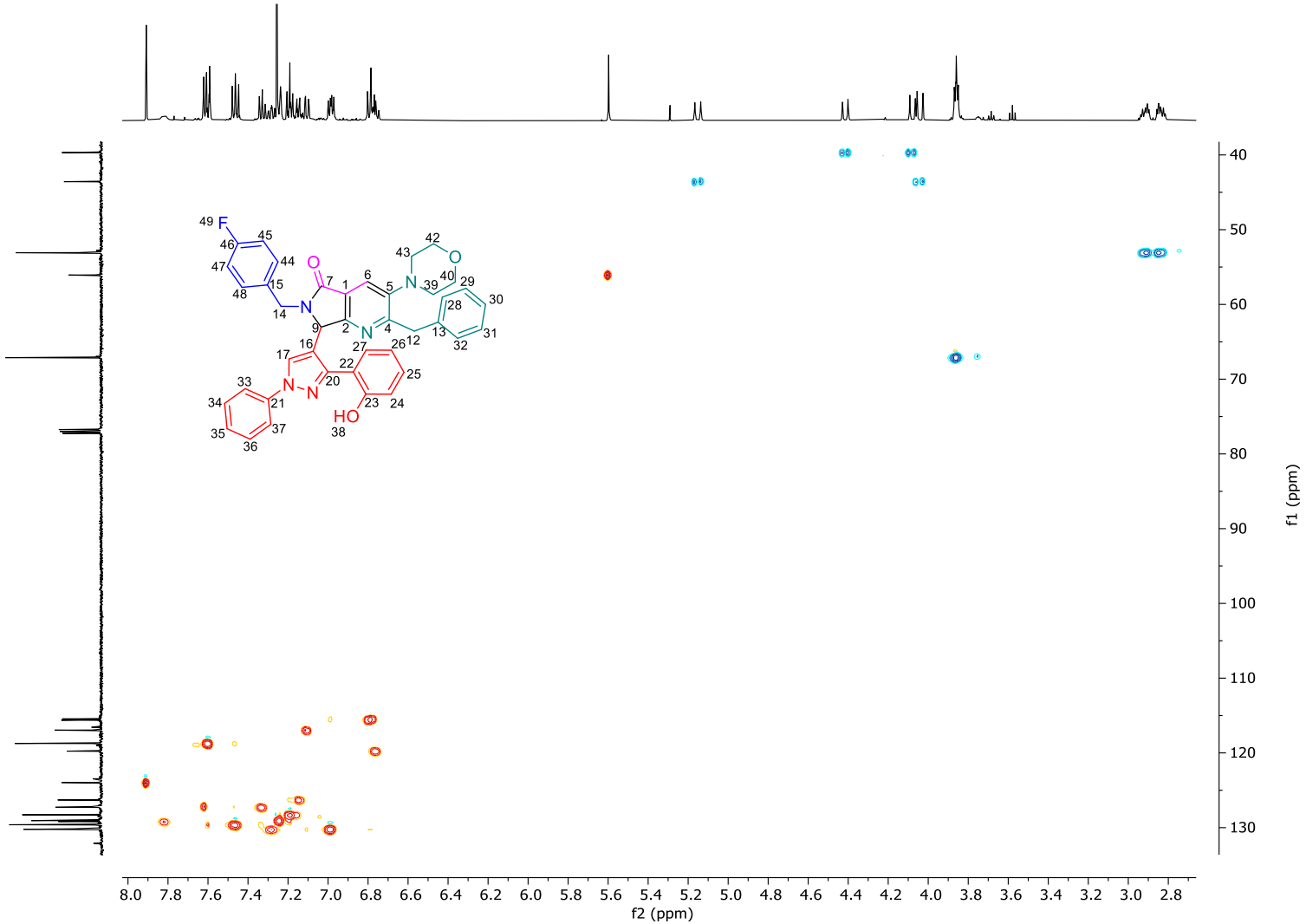


Figure S37. 2D HSQC NMR Spectrum of compound **6e.**

2-Benzyl-6-(4-fluorobenzyl)-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6e**).

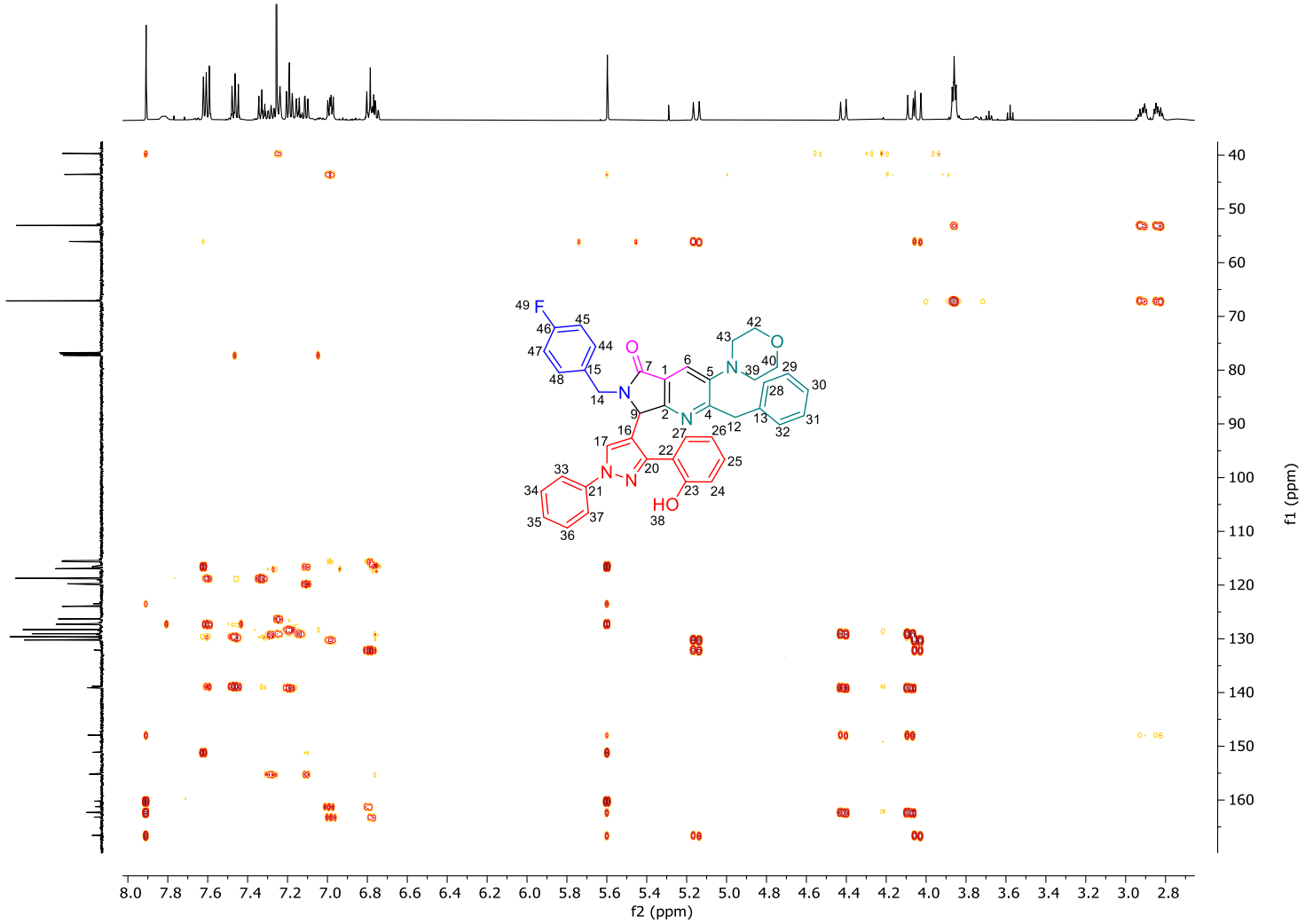


Figure S38. 2D HMBC NMR Spectrum of compound **6e.**

2-Benzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6-(prop-2-yn-1-yl)-6,7-dihydro-5*H*-pyrrolo[3,4-b]pyridin-5-one (**6f**).

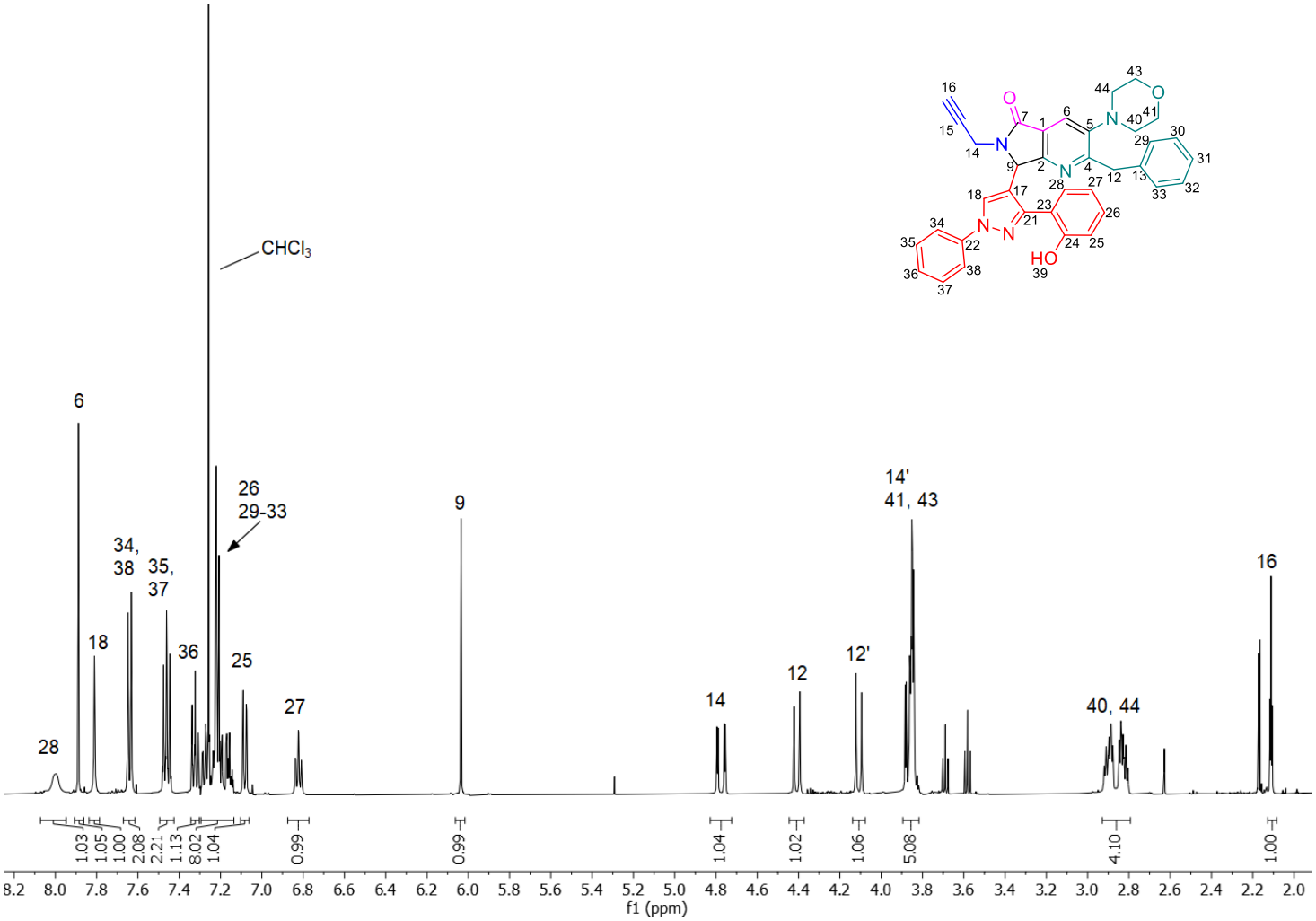


Figure S39. ^{1}H NMR of compound **6f** in $CDCl_3$ at 500 MHz.

2-Benzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6-(prop-2-yn-1-yl)-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6f**).

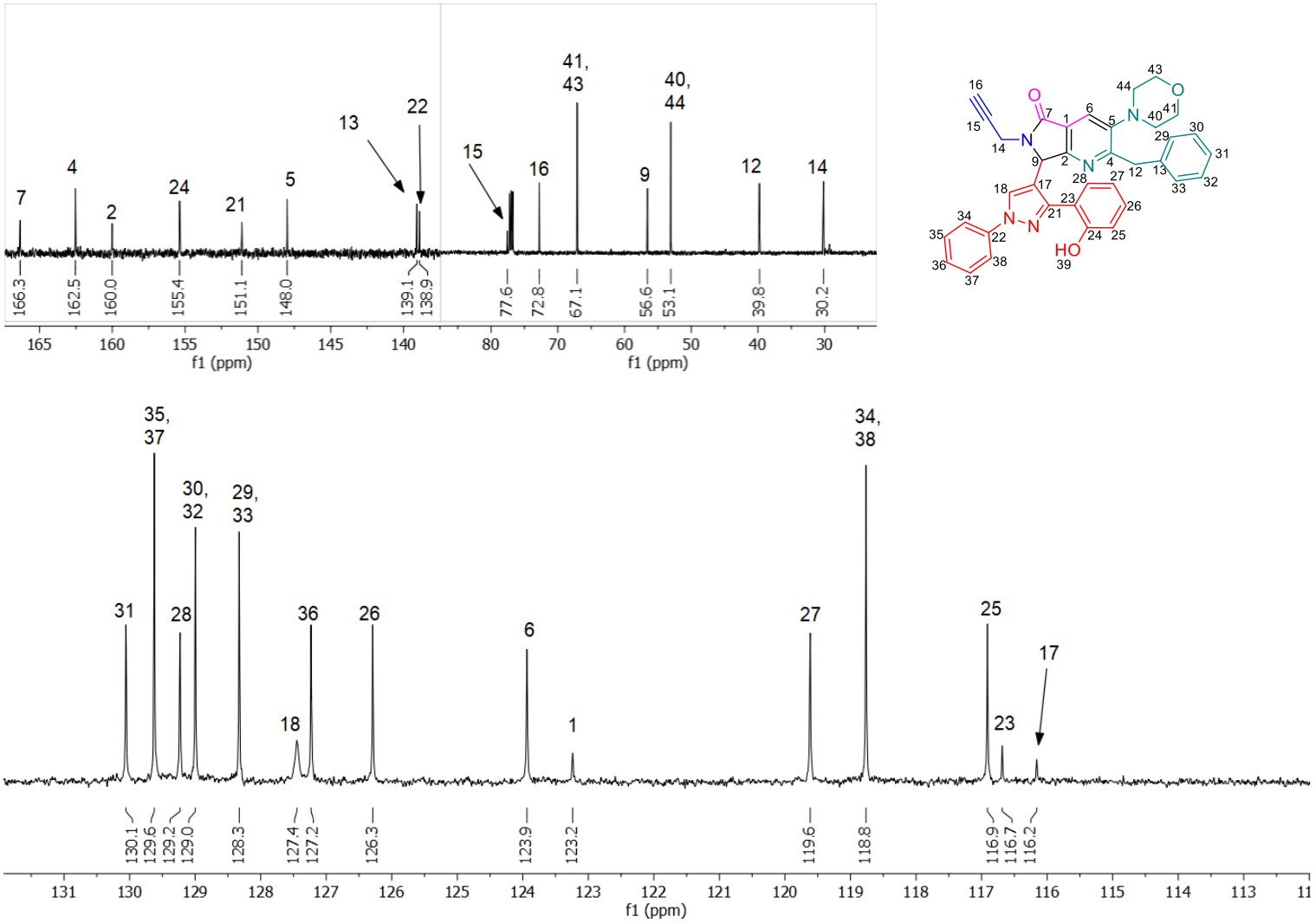


Figure S40. ^{13}C NMR of compound **6f** in $CDCl_3$ at 126 MHz.

2-Benzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6-(prop-2-yn-1-yl)-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6f**).

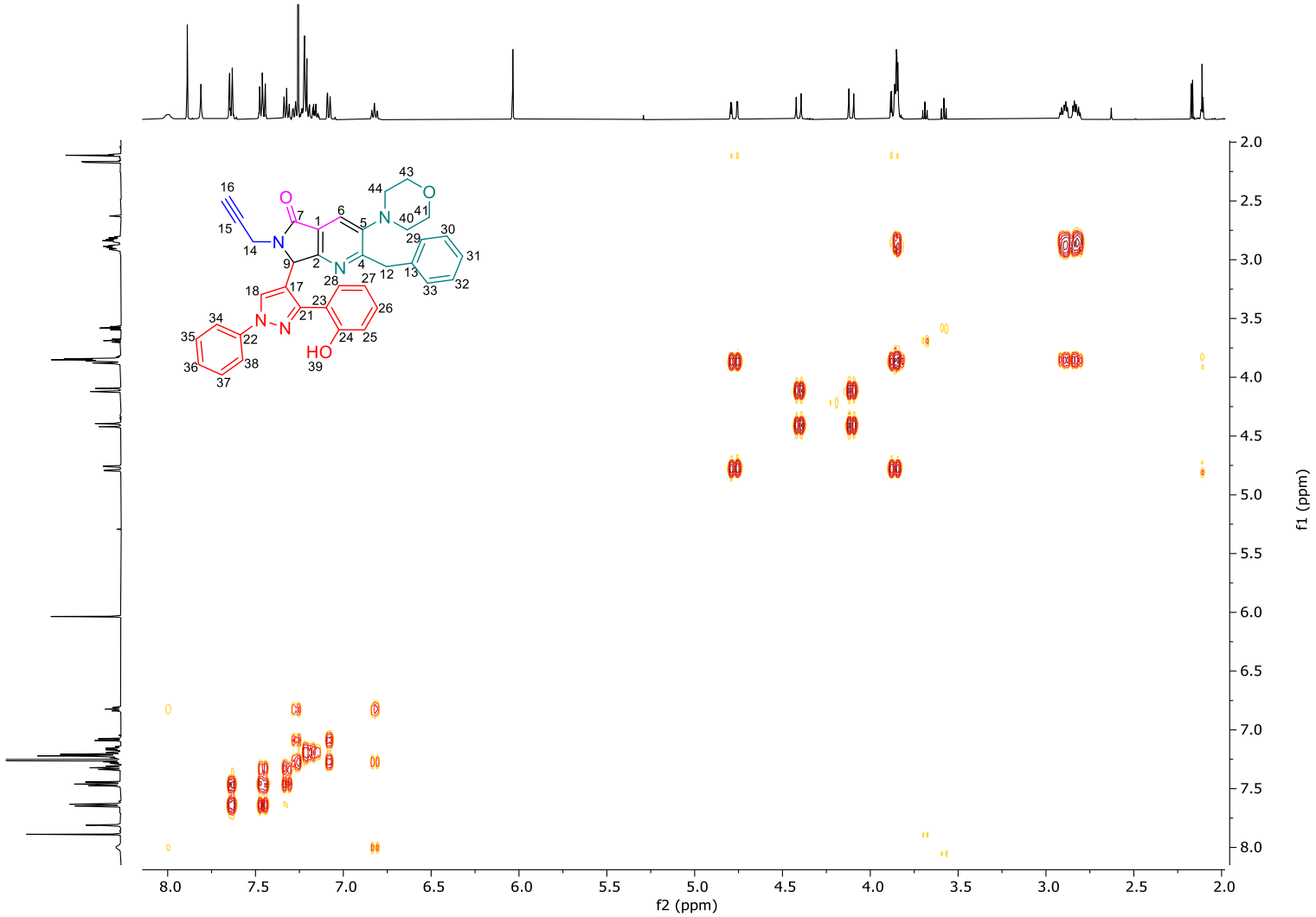


Figure S41. 2D COSY spectrum of compound **6f**.

2-Benzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6-(prop-2-yn-1-yl)-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6f**).

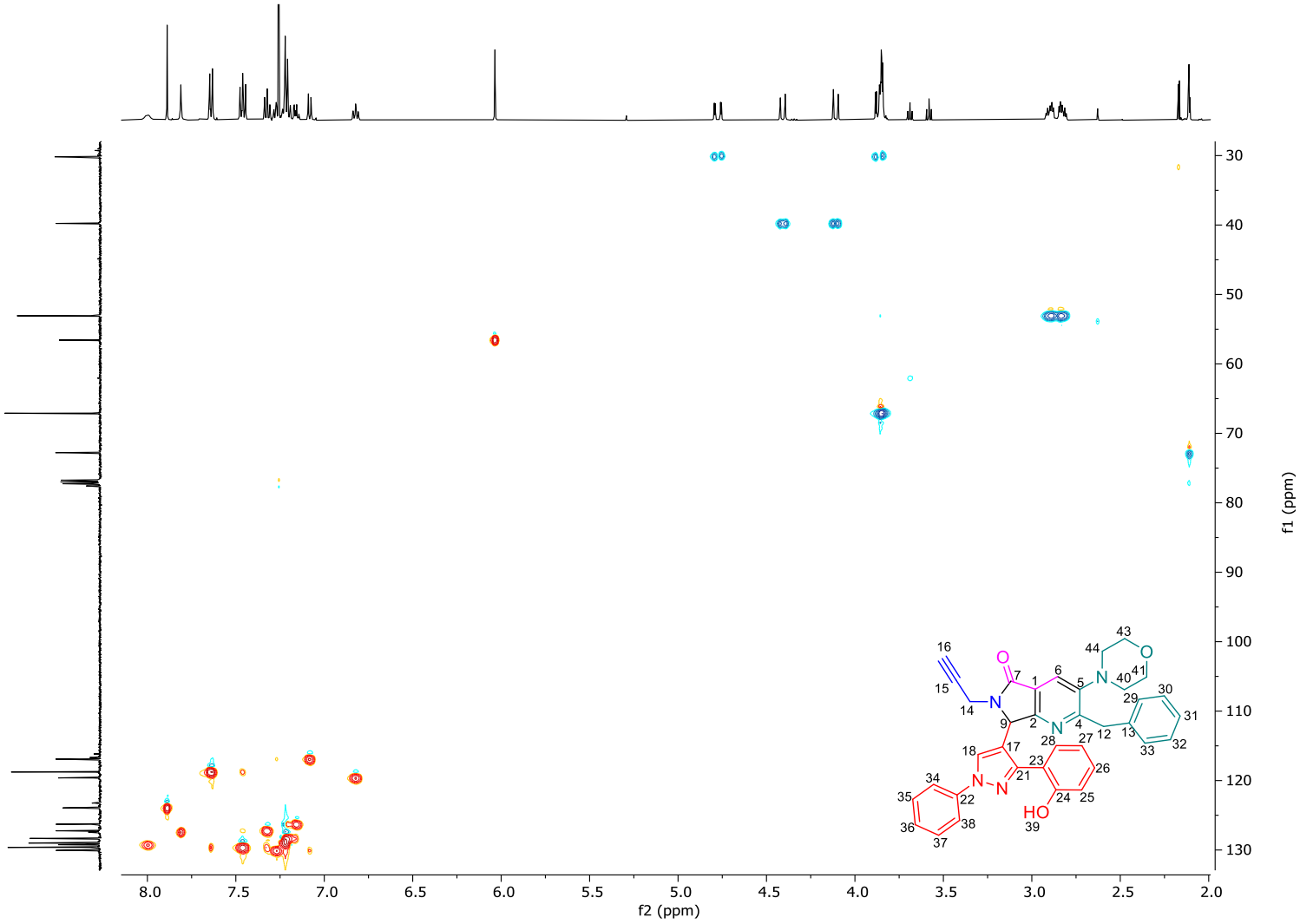


Figure S42. 2D HSQC spectrum of compound **6f**.

2-Benzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6-(prop-2-yn-1-yl)-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6f**).

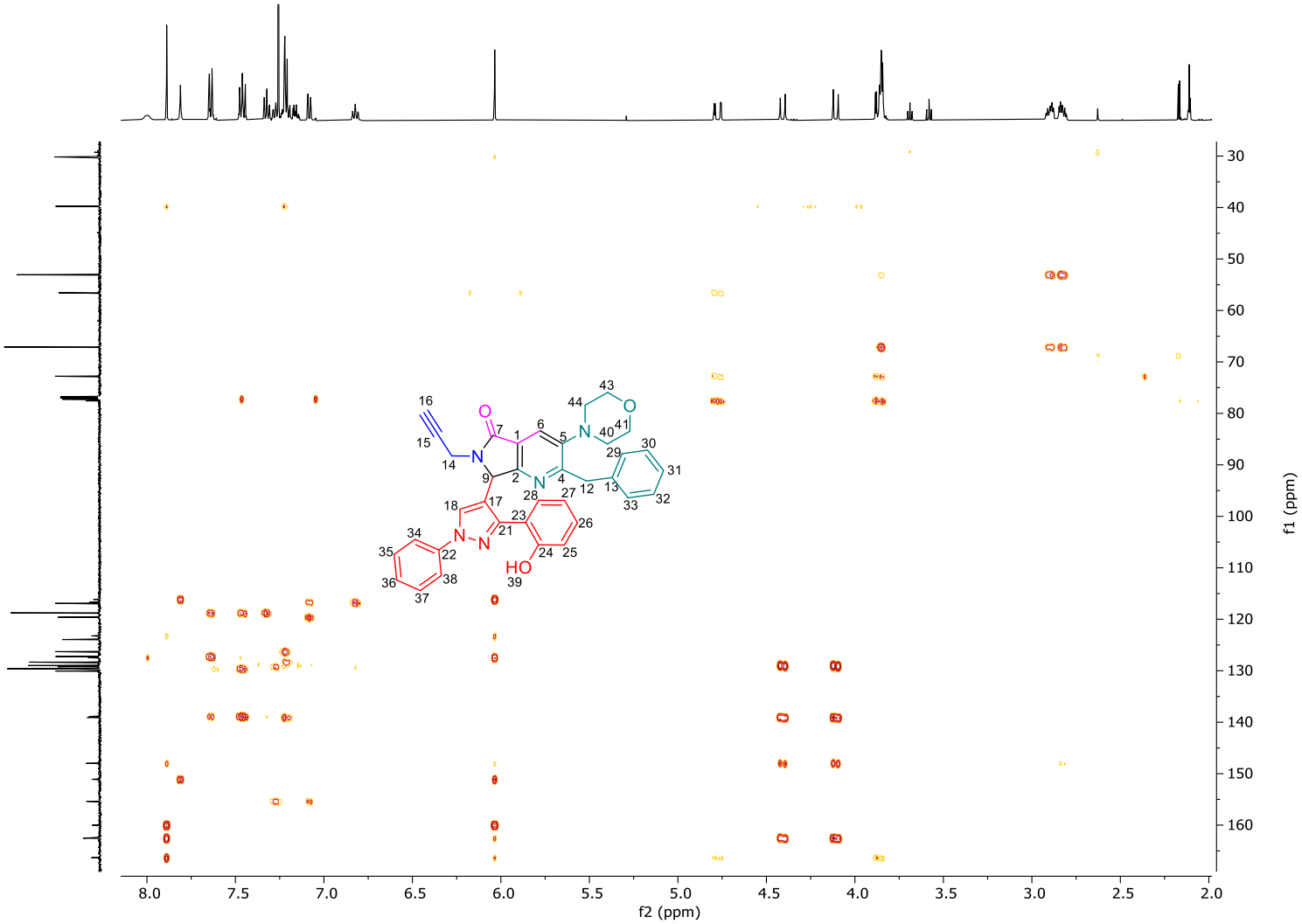


Figure S43. 2D HMBC spectrum of compound **6f**.

HRMS spectra of MOM-protected pyrazole aldehyde **1** and pyrazolyl-pyrrolo[3,4-*b*]pyridin-5-ones **6a-f**.

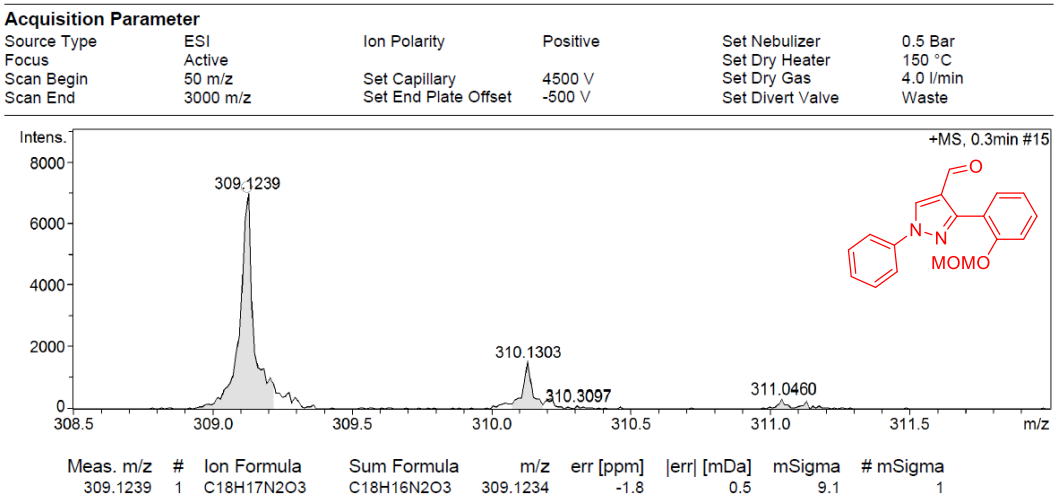


Figure S44. HRMS spectrum of 3-(2-Hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde.

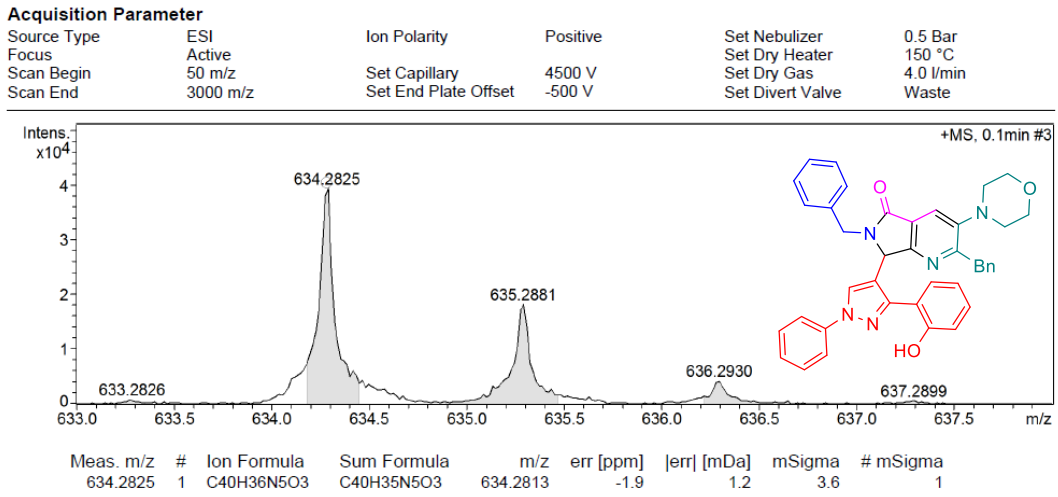


Figure S45. HRMS spectrum of 2,6-Dibenzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6a**).

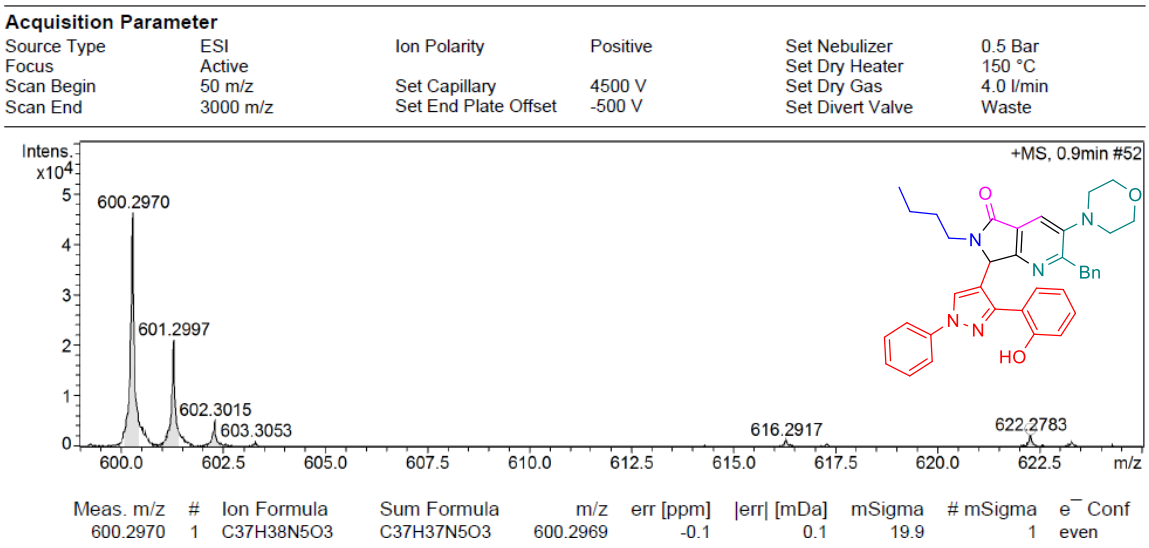


Figure S46. HRMS spectrum of 2-Benzyl-6-butyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6b**).

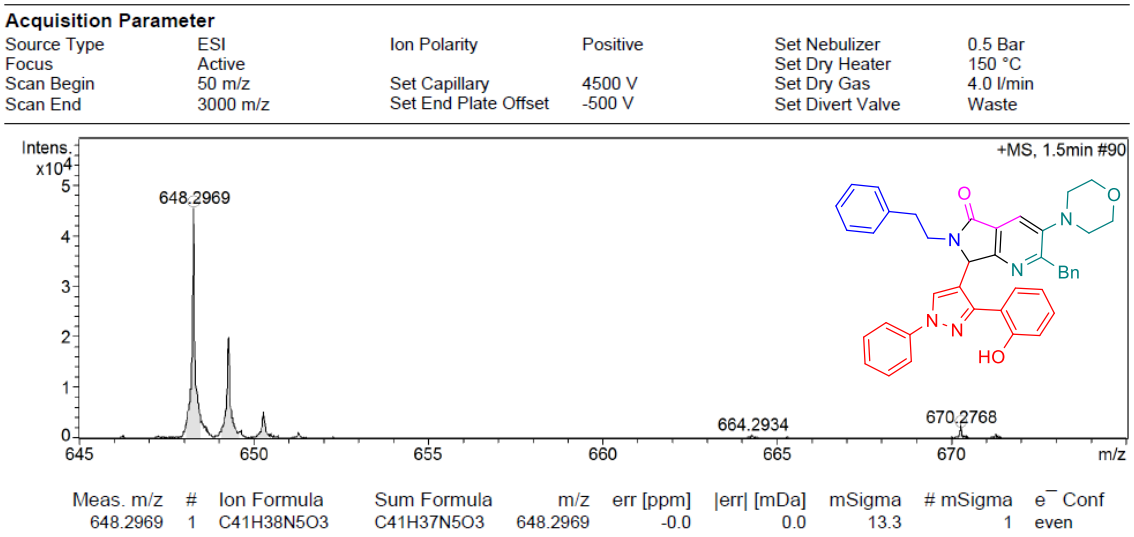


Figure S47. HRMS spectrum of 2-Benzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6-phenethyl-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6c**).

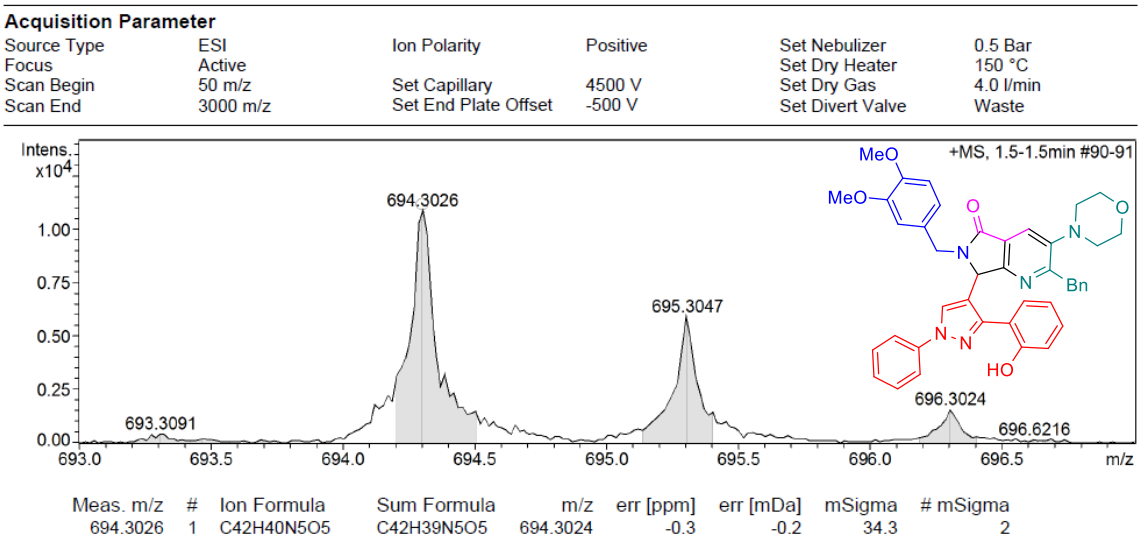


Figure S48. HRMS spectrum of 2-Benzyl-6-(3,4-dimethoxybenzyl)-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6d**).

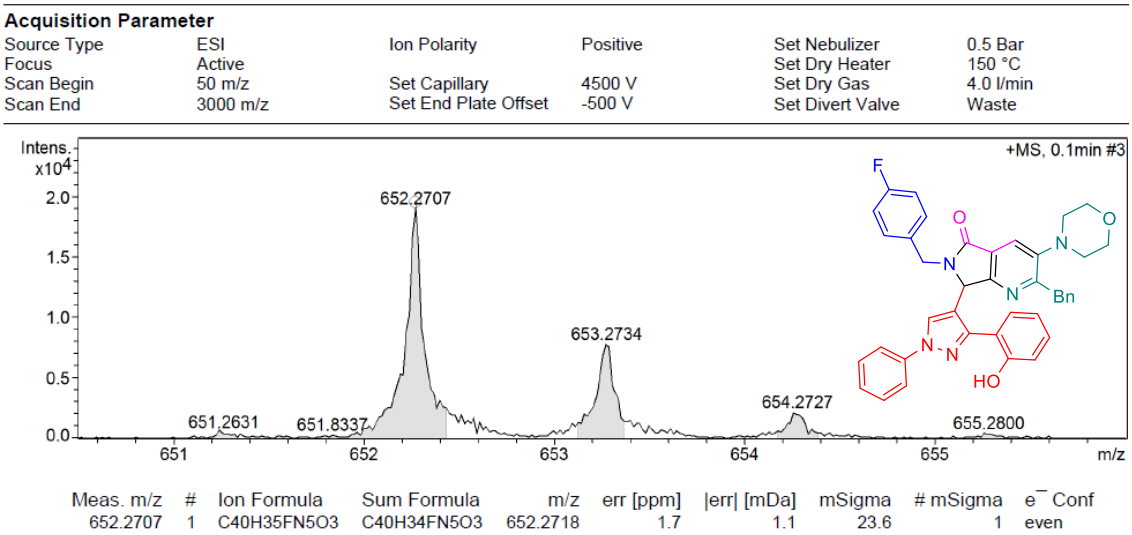


Figure S49. HRMS spectrum of 2-Benzyl-6-(4-fluorobenzyl)-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6e**).

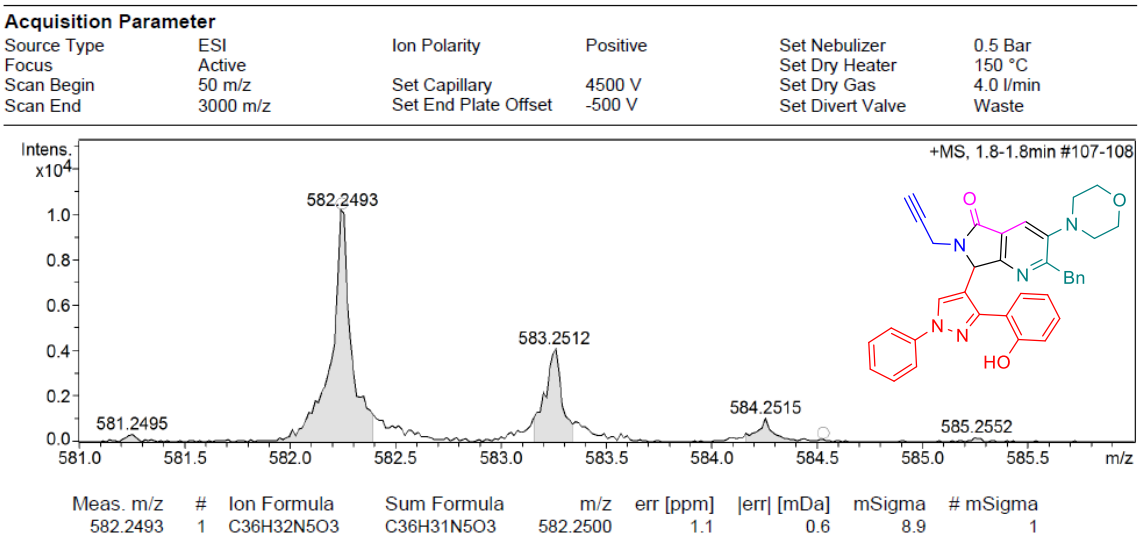


Figure S50. HRMS spectrum of 2-Benzyl-7-(3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-3-morpholino-6-(prop-2-yn-1-yl)-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyridin-5-one (**6f**).

Data of DFT and TD-DFT calculations

Optimized xyz coordinates (B3LYP/6-31G(d), SMD, chloroform) and excitation energies and oscillator strengths (B3LYP/6-311+G(d,p)) of compound **6a**.

1.	**C**	-3.292123	-0.820934	-1.878067	43.	**N**	-4.434312	-2.127890	0.493649
2.	**C**	-3.599913	0.586455	-2.361509	44.	**C**	-5.278373	-2.155491	1.695977
3.	**C**	-2.770299	1.234172	-3.281950	45.	**C**	-6.655879	-2.692787	1.326997
4.	**C**	-3.063476	2.524625	-3.722506	46.	**O**	-6.567542	-4.000747	0.766849
5.	**C**	-4.192495	3.188649	-3.246269	47.	**C**	-5.750230	-3.998069	-0.400992
6.	**C**	-5.027175	2.552087	-2.328008	48.	**C**	-4.350090	-3.477018	-0.101579
7.	**C**	-4.732485	1.262395	-1.891020	49.	**H**	-4.219949	-1.386260	-1.819036
8.	**C**	-2.594598	-0.848109	-0.528368	50.	**H**	-2.642319	-1.317505	-2.604499
9.	**C**	-3.183591	-1.460007	0.614588	51.	**H**	-1.889427	0.724766	-3.657303
10.	**C**	-2.511772	-1.363629	1.838917	52.	**H**	-2.409137	3.008446	-4.439679
11.	**C**	-1.291509	-0.707247	1.858486	53.	**H**	-4.422391	4.191321	-3.589648
12.	**C**	-0.777506	-0.189040	0.682699	54.	**H**	-5.911194	3.058358	-1.955046
13.	**N**	-1.396594	-0.242082	-0.486895	55.	**H**	-5.391118	0.772152	-1.181264
14.	**C**	0.581792	0.441038	0.943916	56.	**H**	-2.920518	-1.792761	2.745271
15.	**N**	0.725478	0.212604	2.393969	57.	**H**	0.538680	1.516448	0.747613
16.	**C**	-0.347668	-0.429566	2.968294	58.	**H**	1.762247	0.280698	0.157534
17.	**O**	-0.478731	-0.697740	4.154825	59.	**H**	2.774638	0.450368	2.720412
18.	**C**	1.830004	0.756172	3.177005	60.	**H**	-0.016912	2.287227	4.484417
19.	**C**	1.794272	2.268115	3.318676	61.	**H**	-0.077694	4.747481	4.713892
20.	**C**	0.760030	2.891991	4.028312	62.	**H**	1.704020	6.139882	0.687349
21.	**C**	0.727469	4.277485	4.159535	63.	**H**	3.545334	5.050090	2.428076
22.	**C**	1.730036	5.060563	0.584734	64.	**H**	3.598979	2.589553	0.193703
23.	**C**	2.763624	4.449250	2.879837	65.	**H**	2.045595	-2.139357	1.137161
24.	**C**	2.792810	3.060461	2.747164	66.	**H**	4.521789	-2.305949	-2.718761
25.	**C**	1.708206	-0.168373	0.144337	67.	**H**	6.027864	-4.255321	-2.992046
26.	**C**	2.437127	0.351417	-0.967241	68.	**H**	6.495687	-5.749630	-1.063347
27.	**N**	3.396752	-0.510940	-1.328044	69.	**H**	5.464851	-5.262532	1.143874
28.	**N**	3.300950	-1.567028	-0.490118	70.	**H**	4.006354	-3.299049	1.429644
29.	**C**	2.290027	-1.393325	0.399683	71.	**H**	4.295569	3.924869	-3.267707
30.	**C**	4.166521	-2.687627	-0.635406	72.	**H**	2.127807	5.138052	-3.377514
31.	**C**	4.741238	-2.953135	-1.880364	73.	**H**	0.069892	4.076474	2.449265
32.	**C**	5.582837	-4.051896	-2.024690	74.	**H**	0.212269	1.855785	-1.402118
33.	**C**	5.842999	-4.892707	-0.943599	75.	**H**	4.586296	0.706532	1.947210
34.	**C**	5.262246	-4.621058	0.293857	76.	**H**	-4.854426	-2.797035	2.485182
35.	**C**	4.429278	-3.517557	0.457055	77.	**H**	-5.373473	-1.141563	2.092276
36.	**C**	2.334146	1.640655	-1.669835	78.	**H**	-7.279466	-2.776869	2.218867
37.	**C**	3.484411	2.231187	2.252735	79.	**H**	-7.146031	-2.011440	0.616348
38.	**C**	3.394745	3.494222	-2.845714	80.	**H**	-5.701147	-5.031257	-0.749968
39.	**C**	2.178871	4.163211	2.904895	81.	**H**	-6.219042	-3.384138	-1.183935
40.	**C**	1.027412	3.574311	-2.380930	82.	**H**	-3.769722	-3.439483	-1.024991

41.	**C**	1.113368	2.326980	1.773459	83.	**H**	-3.840891	-4.170079	0.588088
42.	**O**	4.698414	1.629287	-2.258795					

Excited State 3: Singlet-A 4.0029 eV 309.73 nm f=0.3633 <S**2>=0.000

166 -> 169 -0.12827

167 -> 168 -0.10562

167 -> 169 0.67788

Excited State 8: Singlet-A 4.5215 eV 274.21 nm f=0.1919 <S**2>=0.000

158 -> 168 0.10780

159 -> 168 -0.14252

161 -> 168 -0.12465

162 -> 168 -0.12101

163 -> 168 -0.30719

164 -> 168 0.37373

165 -> 169 0.34838

167 -> 171 0.16776

Optimized xyz coordinates (B3LYP/6-31G(d), SMD, chloroform) and excitation energies and oscillator strengths (B3LYP/6-311+G(d,p)) of compound **6b**.

1.	**C**	-3.380417	-0.783791	-1.784071	42.	**C**	-4.496648	-3.233812	0.206835
2.	**C**	-3.609783	0.599097	-2.369841	43.	**H**	-4.344165	-1.265665	-1.632372
3.	**C**	-2.802569	1.095312	-3.397699	44.	**H**	-2.811271	-1.388168	-2.496570
4.	**C**	-3.027196	2.363947	-3.932515	45.	**H**	-1.993641	0.484432	-3.783347
5.	**C**	-4.063032	3.157777	-3.443547	46.	**H**	-2.391778	2.729614	-4.731963
6.	**C**	-4.874907	2.672722	-2.418348	47.	**H**	-4.239693	4.143295	-3.860346
7.	**C**	-4.649482	1.404352	-1.888094	48.	**H**	-5.687333	3.280558	-2.034473
8.	**C**	-2.618946	-0.756562	-0.469327	49.	**H**	-5.291070	1.031505	-1.096112
9.	**C**	-3.190586	-1.244267	0.740961	50.	**H**	-2.855841	-1.416267	2.881972
10.	**C**	-2.463217	-1.089497	1.927177	51.	**H**	0.699807	1.499916	0.492436
11.	**C**	-1.207934	-0.508558	1.845360	52.	**H**	2.044957	0.421672	3.918559
12.	**C**	-0.714412	-0.119704	0.612303	53.	**H**	2.944266	0.574683	2.406523
13.	**N**	-1.387350	-0.223698	-0.524301	54.	**H**	2.054170	-2.183597	1.120837
14.	**C**	0.690143	0.442334	0.772075	55.	**H**	4.337022	-2.816996	-2.791471
15.	**N**	0.883822	0.317516	2.228896	56.	**H**	5.790724	-4.821408	-2.915716
16.	**C**	-0.202928	-0.200283	2.892372	57.	**H**	6.333248	-6.097654	-0.854874
17.	**O**	-0.302784	-0.360486	4.101519	58.	**H**	5.431375	-5.339134	1.331971
18.	**C**	2.032532	0.880754	2.928131	59.	**H**	4.024601	-3.317183	1.463261

19.	**C**	1.748322	-0.286565	-0.020641	60.	**H**	4.346974	3.387235	-3.875394
20.	**C**	2.448578	0.106921	-1.200738	61.	**H**	2.238436	4.702058	-3.968033
21.	**N**	3.356090	-0.823663	-1.525955	62.	**H**	0.184991	3.822800	-2.856714
22.	**N**	3.254767	0.800218	-0.597547	63.	**H**	0.277165	1.681707	-1.648538
23.	**C**	2.291312	-1.510348	0.313868	64.	**H**	4.554587	0.269758	-2.316499
24.	**C**	4.084565	-2.954459	-0.662933	65.	**H**	-4.846369	-2.378816	2.760969
25.	**C**	4.587882	-3.371241	-1.896913	66.	**H**	-5.285268	-0.718469	2.294921
26.	**C**	5.400608	-4.499220	-1.956939	67.	**H**	-7.275830	-2.225861	2.595681
27.	**C**	5.703184	-5.217444	-0.800906	68.	**H**	-7.169478	-1.560304	0.946944
28.	**C**	5.193582	-4.794224	0.425500	69.	**H**	-5.962268	-4.736926	-0.294775
29.	**C**	4.390881	-3.659595	0.503166	70.	**H**	-6.399660	-3.088871	-0.806979
30.	**C**	2.368664	1.338665	-2.002348	71.	**H**	-3.953349	-3.289997	-0.737982
31.	**C**	3.512180	1.820928	-2.689683	72.	**H**	-4.002422	-3.913414	0.920333
32.	**C**	3.450976	3.038253	-3.374973	73.	**C**	1.982750	2.408783	3.058531
33.	**C**	2.267858	3.764366	-3.423783	74.	**H**	1.055442	2.688598	3.571135
34.	**C**	1.119770	3.278410	-2.796755	75.	**H**	1.945067	2.861002	2.060708
35.	**C**	1.178468	2.077829	-2.098634	76.	**C**	3.185570	2.968189	3.826331
36.	**O**	4.692566	1.156951	-2.711430	77.	**H**	4.111162	2.677176	3.314915
37.	**N**	-4.477885	-1.848541	0.719176	78.	**H**	3.224610	2.506904	4.820469
38.	**C**	-5.267238	-1.756730	1.954701	79.	**C**	3.144273	4.490824	3.974309
39.	**C**	-6.688891	-2.229434	1.675341	80.	**H**	4.006025	4.858530	4.539307
40.	**O**	-6.702563	-3.569723	1.189440	81.	**H**	3.152616	4.985951	2.997839
41.	**C**	-5.936114	-3.684241	-0.006650	82.	**H**	2.240666	4.813350	4.501706

Excited State 3: Singlet-A 4.0240 eV 308.11 nm f=0.3435 <S**2>=0.000

158 -> 161 0.16923

159 -> 160 -0.15351

159 -> 161 0.65550

Excited State 8: Singlet-A 4.5368 eV 273.28 nm f=0.2473 <S**2>=0.000

153 -> 160 -0.13950

154 -> 160 -0.10247

156 -> 160 0.45216

157 -> 161 0.38565

159 -> 163 0.20545

159 -> 164 -0.12423

Optimized xyz coordinates (B3LYP/6-31G(d), SMD, chloroform) and excitation energies and oscillator strengths (B3LYP/6-311+G(d,p)) of compound **6c**.

1.	**C**	-3.428725	-0.921770	-1.761763	44.	**H**	-2.867959	-1.569469	-2.442068
2.	**C**	-3.710100	0.402973	-2.450439	45.	**H**	-2.087310	0.244152	-3.852447
3.	**C**	-2.921577	0.849432	-3.515173	46.	**H**	-2.576591	2.387945	-4.975619
4.	**C**	-3.197403	2.061270	-4.148348	47.	**H**	-4.484125	3.788046	-4.216911
5.	**C**	-4.267052	2.847119	-3.723240	48.	**H**	-5.898654	3.013154	-2.327240
6.	**C**	-5.060228	2.411612	-2.661963	49.	**H**	-5.410406	0.864224	-1.212979
7.	**C**	-4.783402	1.199700	-2.032850	50.	**H**	-2.722876	-1.199017	2.915613
8.	**C**	-2.624864	-0.777272	-0.480409	51.	**H**	0.691321	1.582462	0.200600
9.	**C**	-3.146443	-1.173172	0.784336	52.	**H**	2.275338	0.633089	3.581029
10.	**C**	-2.371432	-0.935577	1.925648	53.	**H**	3.030284	0.831435	1.997419
11.	**C**	-1.124262	-0.356766	1.752915	54.	**H**	2.153693	-2.028968	0.972231
12.	**C**	-0.687202	-0.046947	0.476748	55.	**H**	4.300040	-2.804894	-3.008172
13.	**N**	-1.402245	-0.239287	-0.621505	56.	**H**	5.787697	-4.785003	-3.100366
14.	**C**	0.714189	0.541826	0.538002	57.	**H**	6.415897	-5.971172	-1.009688
15.	**N**	0.976052	0.501340	1.989586	58.	**H**	5.565125	-5.144437	1.173057
16.	**C**	-0.076998	0.021413	2.732941	59.	**H**	4.123145	-3.147638	1.269973
17.	**O**	-0.118265	-0.062195	3.952758	60.	**H**	4.103480	3.296494	-4.413727
18.	**C**	2.156770	1.093961	2.599124	61.	**H**	1.963607	4.560658	-4.495044
19.	**C**	1.748877	-0.211283	-0.262053	62.	**H**	-0.026186	3.700432	-3.260697
20.	**C**	2.384306	0.128600	-1.494438	63.	**H**	0.158450	1.630746	-1.945129
21.	**N**	3.296050	-0.800917	-1.809836	64.	**H**	4.439168	0.271358	-2.704765
22.	**N**	3.261171	-1.724688	-0.824351	65.	**H**	-4.740433	-2.098620	2.956795
23.	**C**	2.335713	-1.402185	0.115095	66.	**H**	-5.182400	-0.486634	2.347073
24.	**C**	4.112745	-2.864245	-0.869294	67.	**H**	-7.171888	-1.939964	2.855068
25.	**C**	4.587447	-3.319409	-2.101212	68.	**H**	-7.116188	-1.433627	1.148225
26.	**C**	5.419655	-4.433925	-2.143029	69.	**H**	-5.974213	-4.723532	0.171006
27.	**C**	5.770685	-5.101194	-0.970323	70.	**H**	-6.417375	-3.125952	-0.477903
28.	**C**	5.290444	-4.639567	0.253941	71.	**H**	-3.972059	-3.339685	-0.474923
29.	**C**	4.468396	-3.517715	0.312732	72.	**H**	-3.964863	-3.811303	1.233246
30.	**C**	2.244102	1.312726	-2.357674	73.	**C**	2.060890	2.627941	2.753023
31.	**C**	3.349377	1.779892	3.114832	74.	**H**	1.197460	2.861189	3.382163
32.	**C**	3.235264	2.957490	-3.860272	75.	**H**	1.883682	3.077483	1.771592
33.	**C**	2.034901	3.655076	-3.902499	76.	**C**	3.317481	3.206530	3.362438
34.	**C**	0.922400	3.179833	-3.206949	77.	**C**	3.443676	3.341422	4.750174
35.	**C**	1.034059	2.019929	-2.448936	78.	**C**	4.399262	3.580422	2.555695
36.	**O**	4.542583	1.140007	-3.148416	79.	**C**	4.617079	3.836500	5.316873
37.	**N**	-4.436038	-1.768850	0.861485	80.	**H**	2.612743	3.060620	5.389946
38.	**C**	-5.182554	-1.552932	2.107767	81.	**C**	5.574472	4.075024	3.118742
39.	**C**	-6.615909	-2.035876	1.920564	82.	**H**	4.317637	3.487921	1.477013
40.	**O**	-6.654159	-3.415804	1.563714	83.	**C**	5.687417	4.203830	4.502393
41.	**C**	-5.930168	-3.648959	0.358097	84.	**H**	4.694069	3.938858	6.394052
42.	**C**	-4.480984	-3.194320	0.479439	85.	**H**	6.399892	4.363197	2.476588
43.	**H**	-4.375404	-1.410208	-1.540742	86.	**H**	6.600099	4.590990	4.941867

Excited State 3: Singlet-A 4.0168 eV 308.66 nm f=0.3607 <S**2>=0.000

170 -> 173 0.15638

171 -> 172 0.12632

171 -> 173 0.66685

Excited State 8: Singlet-A 4.5110 eV 274.85 nm f=0.2600 <S**2>=0.000

162 -> 172 0.11571

163 -> 172 -0.26825

166 -> 172 -0.11133

167 -> 172 -0.21266

168 -> 172 0.46892

169 -> 173 0.23650

170 -> 174 -0.10923

171 -> 175 0.12545

Optimized xyz coordinates (B3LYP/6-31G(d), SMD, chloroform) and excitation energies and oscillator strengths (B3LYP/6-311+G(d,p)) of compound **6d**.

1.	**C**	-3.301499	-0.628823	-1.717893	47.	**C**	-5.977839	-3.627390	-0.327714
2.	**C**	-3.537628	0.811306	-2.140837	48.	**C**	-4.531139	-3.249170	-0.035426
3.	**C**	-2.759350	1.413239	-3.133647	49.	**H**	-4.261065	-1.138779	-1.661267
4.	**C**	-2.995923	2.731826	-3.523666	50.	**H**	-2.697313	-1.133764	-2.476991
5.	**C**	-4.014151	3.468994	-2.922439	51.	**H**	-1.963986	0.846790	-3.605972
6.	**C**	-4.795792	2.878630	-1.929179	52.	**H**	-2.383581	3.181077	-4.298132
7.	**C**	-4.558734	1.561391	-1.543675	53.	**H**	-4.199617	4.493438	-3.226062
8.	**C**	-2.582501	-0.749099	-0.385546	54.	**H**	-5.592981	3.443178	-1.457465
9.	**C**	-3.189051	-1.362206	0.747974	55.	**H**	-5.175020	1.106154	-0.775080
10.	**C**	-2.489492	-1.351235	1.960896	56.	**H**	-2.907924	-1.782427	2.861685
11.	**C**	-1.231251	-0.770918	1.978098	57.	**H**	0.705769	1.381728	0.911949
12.	**C**	-0.707922	-0.241889	0.811197	58.	**H**	1.928123	-0.030354	4.245331
13.	**N**	-1.349227	-0.218373	-0.347577	59.	**H**	2.905164	0.197501	2.791494
14.	**C**	0.689532	0.299072	1.068812	60.	**H**	0.295263	1.980739	4.879208
15.	**N**	0.845914	0.009455	2.506015	61.	**H**	3.597863	4.822527	2.539980
16.	**C**	-0.254218	-0.585956	3.078919	62.	**H**	3.639132	2.393394	2.207913
17.	**O**	-0.382495	-0.884544	4.258598	63.	**H**	2.055102	-2.340015	1.186567
18.	**C**	1.979462	0.495134	3.290162	64.	**H**	4.407596	-2.563510	-2.737989
19.	**C**	1.972855	1.996401	3.506413	65.	**H**	5.854807	-4.549081	-3.061944
20.	**C**	1.029202	2.587274	4.359548	66.	**H**	6.356307	-6.052100	-1.148382
21.	**C**	0.993143	3.959115	4.559121	67.	**H**	5.419183	-5.537833	1.094138

22.	**C**	1.925921	4.790991	3.897025	68.	**H**	4.019752	-3.537932	1.428657
23.	**C**	2.876035	4.207232	3.060257	69.	**H**	4.421090	3.690204	-3.207882
24.	**C**	2.894650	2.822373	2.870303	70.	**H**	2.300101	4.989441	-3.239294
25.	**C**	1.767347	-0.343351	0.229036	71.	**H**	0.230086	3.998303	-2.261834
26.	**C**	2.487272	0.164485	-0.894235	72.	**H**	0.314486	1.759637	-1.246919
27.	**N**	3.402377	-0.729148	-1.292558	73.	**H**	4.619626	0.446377	-1.929998
28.	**N**	3.287183	-1.793007	-0.467233	74.	**H**	-4.917373	-2.681552	2.594701
29.	**C**	2.306829	-1.594094	0.451174	75.	**H**	-5.297864	-0.966699	2.312190
30.	**C**	4.115648	-2.937026	-0.642994	76.	**H**	-7.336624	-2.437806	2.398272
31.	**C**	4.639960	-3.216118	-1.907187	77.	**H**	-7.173011	-1.590898	0.839589
32.	**C**	5.449352	-4.334759	-2.079672	78.	**H**	-6.028255	-4.638041	-0.737577
33.	**C**	5.728922	-5.179752	-1.006591	79.	**H**	-6.404973	-2.928112	-1.061445
34.	**C**	5.199994	-4.893226	0.250617	80.	**H**	-3.969875	-3.212227	-0.970476
35.	**C**	4.400313	-3.769681	0.441679	81.	**H**	-4.072195	-4.022337	0.602501
36.	**C**	2.417360	1.466524	-1.577231	82.	**O**	1.807093	6.126740	4.126646
37.	**C**	3.573160	2.017614	-2.187956	83.	**O**	0.004962	4.488614	5.352657
38.	**C**	3.516640	3.290575	-2.763542	84.	**C**	0.435258	5.060916	6.597056
39.	**C**	2.326672	4.007499	-2.779468	85.	**H**	1.077095	5.930063	6.437680
40.	**C**	1.168676	3.458398	-2.227524	86.	**H**	-0.471737	5.370021	7.117561
41.	**C**	1.222295	2.200682	-1.638188	87.	**H**	0.963548	4.316790	7.203425
42.	**O**	4.761231	1.367463	-2.235293	88.	**C**	2.689378	7.015220	3.440503
43.	**N**	-4.486151	-1.933900	0.633991	89.	**H**	2.570585	6.934126	2.355501
44.	**C**	-5.301083	-1.959552	1.855788	90.	**H**	2.405759	8.017150	3.759915
45.	**C**	-6.728684	-2.353524	1.495595	91.	**H**	3.734213	6.832674	3.712152
46.	**O**	-6.768317	-3.628256	0.858133					

Excited State 4: Singlet-A 4.0169 eV 308.66 nm f=0.3226 <S**2>=0.000

182 -> 184 -0.21617

182 -> 185 0.21539

183 -> 184 -0.10953

183 -> 185 0.60959

Excited State 10: Singlet-A 4.5266 eV 273.90 nm f=0.1929 <S**2>=0.000

174 -> 184 0.10920

175 -> 184 -0.18817

176 -> 184 -0.12277

178 -> 184 -0.17449

179 -> 184 0.48914

180 -> 185 0.29890

183 -> 187 0.14006

Optimized xyz coordinates (B3LYP/6-31G(d), SMD, chloroform) and excitation energies and oscillator strengths (B3LYP/6-311+G(d,p)) of compound **6e**.

1.	**C**	-3.442456	-0.803374	-1.714644	43.	**N**	-4.548755	-1.895876	0.767006
2.	**C**	-3.552429	0.557156	-2.378974	44.	**C**	-5.337197	-1.844012	2.005033
3.	**C**	-2.755913	0.895823	-3.476183	45.	**C**	-6.759530	-2.306756	1.712162
4.	**C**	-2.876298	2.143536	-4.088327	46.	**O**	-6.774781	-3.630351	1.182766
5.	**C**	-3.794023	3.074648	-3.605823	47.	**C**	-6.011539	-3.703990	-0.018550
6.	**C**	-4.593205	2.748069	-2.510055	48.	**C**	-4.571001	-3.262063	0.206244
7.	**C**	-4.472189	1.500314	-1.903132	49.	**H**	-4.443789	-1.195095	-1.541566
8.	**C**	-2.689130	-0.778146	-0.396021	50.	**H**	-2.929570	-1.494183	-2.391206
9.	**C**	-3.265766	-1.287402	0.804017	51.	**H**	-2.036945	0.177595	-3.855607
10.	**C**	-2.548107	-1.141119	1.997324	52.	**H**	-2.249875	2.387138	-4.939635
11.	**C**	-1.296690	-0.549419	1.931049	53.	**H**	-3.889608	4.044752	-4.081195
12.	**C**	-0.797152	-0.140689	0.706720	54.	**H**	-5.313487	3.464647	-2.129783
13.	**N**	-1.461599	-0.235598	-0.435273	55.	**H**	-5.102490	1.251805	-1.054970
14.	**C**	0.599419	0.436015	0.882521	56.	**H**	-2.944235	-1.483656	2.945066
15.	**N**	0.786711	0.282670	2.338371	57.	**H**	0.596220	1.500165	0.627144
16.	**C**	-0.300399	-0.254424	2.988299	58.	**H**	1.935258	0.346113	4.034679
17.	**O**	-0.403850	-0.433170	4.194548	59.	**H**	2.850682	0.510950	2.534299
18.	**C**	1.940374	0.821236	3.052235	60.	**H**	0.282884	2.339913	4.601767
19.	**C**	1.919390	2.332399	3.200093	61.	**H**	0.244658	4.820317	4.843983
20.	**C**	0.988091	2.948508	4.046600	62.	**H**	3.505930	5.152305	2.091980
21.	**C**	0.957353	4.332001	4.190302	63.	**H**	3.553219	2.674460	1.840714
22.	**C**	1.872982	5.091826	3.476960	64.	**H**	1.974692	-2.194016	1.156270
23.	**C**	2.809799	4.522360	2.632323	65.	**H**	4.481970	-2.546206	-2.695153
24.	**C**	2.824023	3.133962	2.499194	66.	**H**	5.979000	-4.510500	-2.874294
25.	**C**	1.674016	-0.258978	0.082165	67.	**H**	6.383986	-5.956022	-0.893959
26.	**C**	2.396681	0.188500	-1.064628	68.	**H**	5.295896	-5.402753	1.270037
27.	**N**	3.323835	-0.716354	-1.403419	69.	**H**	3.848158	-3.423014	1.464494
28.	**N**	3.213347	-1.731480	-0.517676	70.	**H**	4.291850	3.594276	-3.580230
29.	**C**	2.224097	-1.489258	0.380705	71.	**H**	2.147288	4.845101	-3.723064
30.	**C**	4.064748	-2.868454	-0.612369	72.	**H**	0.083619	3.878390	-2.708809
31.	**C**	4.671816	-3.171525	-1.833497	73.	**H**	0.198083	1.713787	-1.545403
32.	**C**	5.508649	-4.279522	-1.925287	74.	**H**	4.536830	0.445019	-2.096070
33.	**C**	5.734184	-5.092181	-0.815373	75.	**H**	-4.914909	-2.491496	2.790369
34.	**C**	5.121274	-4.783498	0.397644	76.	**H**	-5.355028	-0.817358	2.378572
35.	**C**	4.293285	-3.669872	0.508923	77.	**H**	-7.345240	-2.332352	2.632943
36.	**C**	2.311045	1.443553	-1.828489	78.	**H**	-7.240459	-1.614034	1.006402
37.	**C**	3.463329	1.976635	-2.460886	79.	**H**	-6.039682	-4.745882	-0.343293
38.	**C**	3.389837	3.207085	-3.120329	80.	**H**	-6.476761	-3.080225	-0.795786

39.	**C**	2.186500	3.896773	-3.198290	81.	**H**	-4.031836	-3.285477	-0.741907
40.	**C**	1.032128	3.361817	-2.625202	82.	**H**	-4.075220	-3.966503	0.893861
41.	**C**	1.102454	2.147339	-1.952805	83.	**F**	1.848873	6.443035	3.615349
42.	**O**	4.664636	1.349052	-2.452252					

Excited State 3: Singlet-A 3.9935 eV 310.47 nm f=0.3467 <S**2>=0.000

170 -> 173 0.15955

171 -> 172 -0.13238

171 -> 173 0.66472

Excited State 8: Singlet-A 4.5030 eV 275.34 nm f=0.1855 <S**2>=0.000

167 -> 172 -0.31985

168 -> 172 0.47294

169 -> 173 0.28140

170 -> 174 0.10234

171 -> 175 -0.13508

Optimized xyz coordinates (B3LYP/6-31G(d), SMD, chloroform) and excitation energies and oscillator strengths (B3LYP/6-311+G(d,p)) of compound **6f**.

1.	**C**	-3.402168	-0.819848	-1.746133	39.	**C**	-6.716377	-2.279171	1.705770
2.	**C**	-3.540179	0.528017	-2.430957	40.	**O**	-6.702801	-3.622165	1.227990
3.	**C**	-2.695578	0.899417	-3.480731	41.	**C**	-5.932365	-3.728131	0.033693
4.	**C**	-2.837179	2.137924	-4.106532	42.	**C**	-4.502271	-3.246770	0.245893
5.	**C**	-3.826831	3.025549	-3.688015	43.	**H**	-4.394295	-1.233525	-1.572266
6.	**C**	-4.674867	2.665527	-2.640775	44.	**H**	-2.866631	-1.508360	-2.407316
7.	**C**	-4.532145	1.426818	-2.019573	45.	**H**	-1.921497	0.215256	-3.811039
8.	**C**	-2.656673	-0.750842	-0.424423	46.	**H**	-2.173175	2.407298	-4.920747
9.	**C**	-3.233508	-1.235488	0.785276	47.	**H**	-3.939247	3.987831	-4.175439
10.	**C**	-2.521957	-1.054497	1.977080	48.	**H**	-5.451129	3.347705	-2.310764
11.	**C**	-1.278250	-0.447494	1.902617	49.	**H**	-5.200255	1.151426	-1.209587
12.	**C**	-0.780376	-0.057835	0.671079	50.	**H**	-2.916764	-1.381986	2.930610
13.	**N**	-1.437255	-0.191075	-0.471299	51.	**H**	0.607715	1.590597	0.558114
14.	**C**	0.612901	0.531847	0.833566	52.	**H**	1.877374	0.618370	4.026134
15.	**N**	0.798071	0.407409	2.291310	53.	**H**	2.862147	0.639425	2.560582
16.	**C**	-0.289399	-0.119971	2.956283	54.	**H**	1.981386	-2.078360	1.198704
17.	**O**	-0.385504	-0.274050	4.163786	55.	**H**	4.382238	-2.644685	-2.691071
18.	**C**	1.925020	0.993186	3.001115	56.	**H**	5.821713	-4.657662	-2.818769
19.	**C**	1.683554	-0.187009	0.049719	57.	**H**	6.234623	-6.027028	-0.787062
20.	**C**	2.388652	0.204126	-1.129100	58.	**H**	5.214017	-5.351457	1.374970

21.	**N**	3.292891	-0.731273	-1.449330	59.	**H**	3.820219	-3.325635	1.513370
22.	**N**	3.186021	-1.707169	-0.520965	60.	**H**	4.289811	3.434530	-3.863376
23.	**C**	2.221839	-1.411739	0.387735	61.	**H**	2.197285	4.775271	-3.939778
24.	**C**	4.007785	-2.866928	-0.587807	62.	**H**	0.148989	3.933076	-2.789719
25.	**C**	4.576393	-3.238442	-1.808126	63.	**H**	0.230544	1.806969	-1.563130
26.	**C**	5.380277	-4.372632	-1.870581	64.	**H**	4.486461	0.336683	-2.267248
27.	**C**	5.610461	-5.142765	-0.731531	65.	**H**	-4.875767	-2.386740	2.801617
28.	**C**	5.035252	-4.765537	0.480689	66.	**H**	-5.345235	-0.738307	2.322466
29.	**C**	4.239931	-3.626135	0.561656	67.	**H**	-7.308098	-2.280384	2.623023
30.	**C**	2.314104	1.431399	-1.938305	68.	**H**	-7.205049	-1.623463	0.970581
31.	**C**	3.452976	1.891618	-2.648821	69.	**H**	-5.935888	-4.783138	-0.246670
32.	**C**	3.397031	3.102717	-3.345717	70.	**H**	-6.407778	-3.148274	-0.770925
33.	**C**	2.222902	3.843295	-3.385570	71.	**H**	-3.959736	-3.290585	-0.699657
34.	**C**	1.078395	3.378927	-2.736224	72.	**H**	-3.992589	-3.915682	0.958270
35.	**C**	1.131978	2.184641	-2.027556	73.	**C**	1.909384	2.460418	3.007825
36.	**O**	4.625178	1.214092	-2.682989	74.	**C**	1.902980	3.662362	3.004941
37.	**N**	-4.508682	-1.861408	0.758048	75.	**H**	1.895471	4.727780	3.002904
38.	**C**	-5.305338	-1.778334	1.989348					

Excited State 3: Singlet-A 3.9740 eV 311.99 nm f=0.3804 <S**2>=0.000

153 -> 155 0.68765

Excited State 9: Singlet-A 4.5008 eV 275.47 nm f=0.1186 <S**2>=0.000

151 -> 155 0.48966

152 -> 156 -0.13650

153 -> 156 0.41363

153 -> 157 0.15238

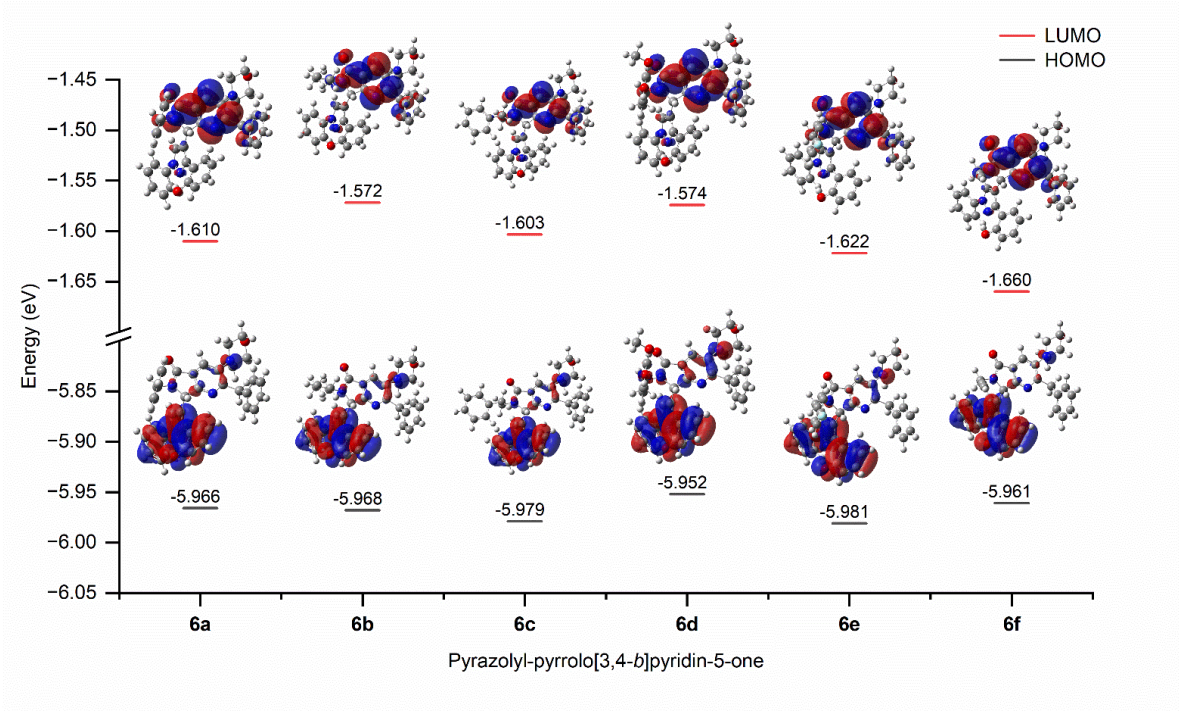


Figure S51. Representation of the frontier molecular orbitals (HOMO and LUMO) for compounds **6a-f**.

Single-crystal X-ray diffraction data

A single crystal X-ray structure of **6e** was collected at 100 K on a Rigaku XtaLAB Synergy-s diffractometer equipped with a HyPix-6000HE detector. The structures were solved using SHELXT,[iv] and refined by full-matrix least squares on F^2 by SHELXL,[v] interfaced through the program OLEX.[vi] All atoms were refined anisotropically and hydrogen atoms were included at geometrically estimated positions. Images were produced using the software Crystal Maker 2.3. X-ray experimental data is given in Table S1 (ESI). CIF data have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number CCDC 2402623.

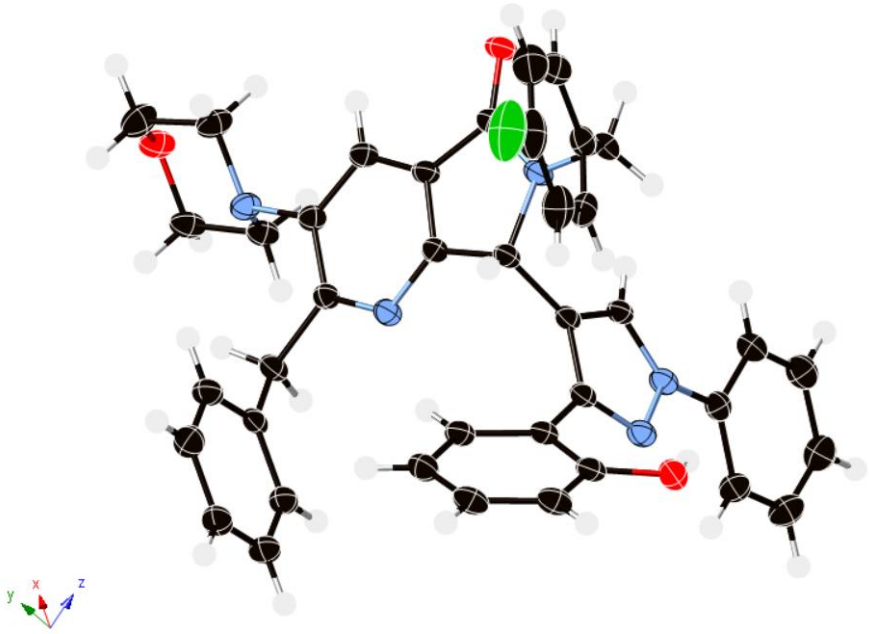


Figure S52: Perspective view of the asymmetric unit of **6e** with all non-hydrogen atoms represented with thermal ellipsoids at the 50% probability level (C, black; oxygen, red; nitrogen, blue; fluorine, green; hydrogen, grey). A second perspective view is provided below to clarify those moieties not clearly visible here.

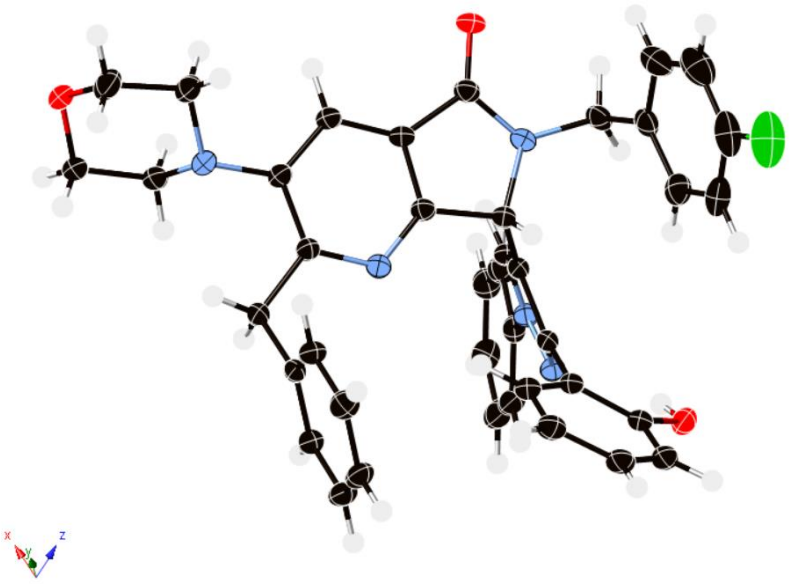


Figure S53. Alternative perspective view of the asymmetric unit of **6e** with all non-hydrogen atoms represented with thermal ellipsoids at the 50% probability level (C, black; oxygen, red; nitrogen, blue; fluorine, green; hydrogen, grey).

Table S1 Crystal data and structure refinement for **6e**.

Identification code	**6e**
Empirical formula	$C_{40}H_{34}FN_5O_3$
Formula weight	651.746
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	12.2204(4)
b/Å	12.5095(4)
c/Å	13.1640(5)
α/°	80.664(3)
β/°	66.465(4)
γ/°	63.540(4)
Volume/Å^3	1651.41(12)
Z	2
ρ_{calc}g/cm^3	1.311
μ/mm^{-1}	0.714
F(000)	686.3
Crystal size/mm^3	0.286 × 0.133 × 0.105

Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.32 to 157.38
Index ranges	$-14 \leq h \leq 15$, $-15 \leq k \leq 15$, $-12 \leq l \leq 16$
Reflections collected	28611
Independent reflections	6587 [R_{int} = 0.0414, R_{sigma} = 0.0285]
Data/restraints/parameters	6587/0/443
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0407, wR_2 = 0.1064
Final R indexes [all data]	R_1 = 0.0496, wR_2 = 0.1182
Largest diff. peak/hole / e $Å^{-3}$	0.24/-0.23
CCDC Reference Number	2402623

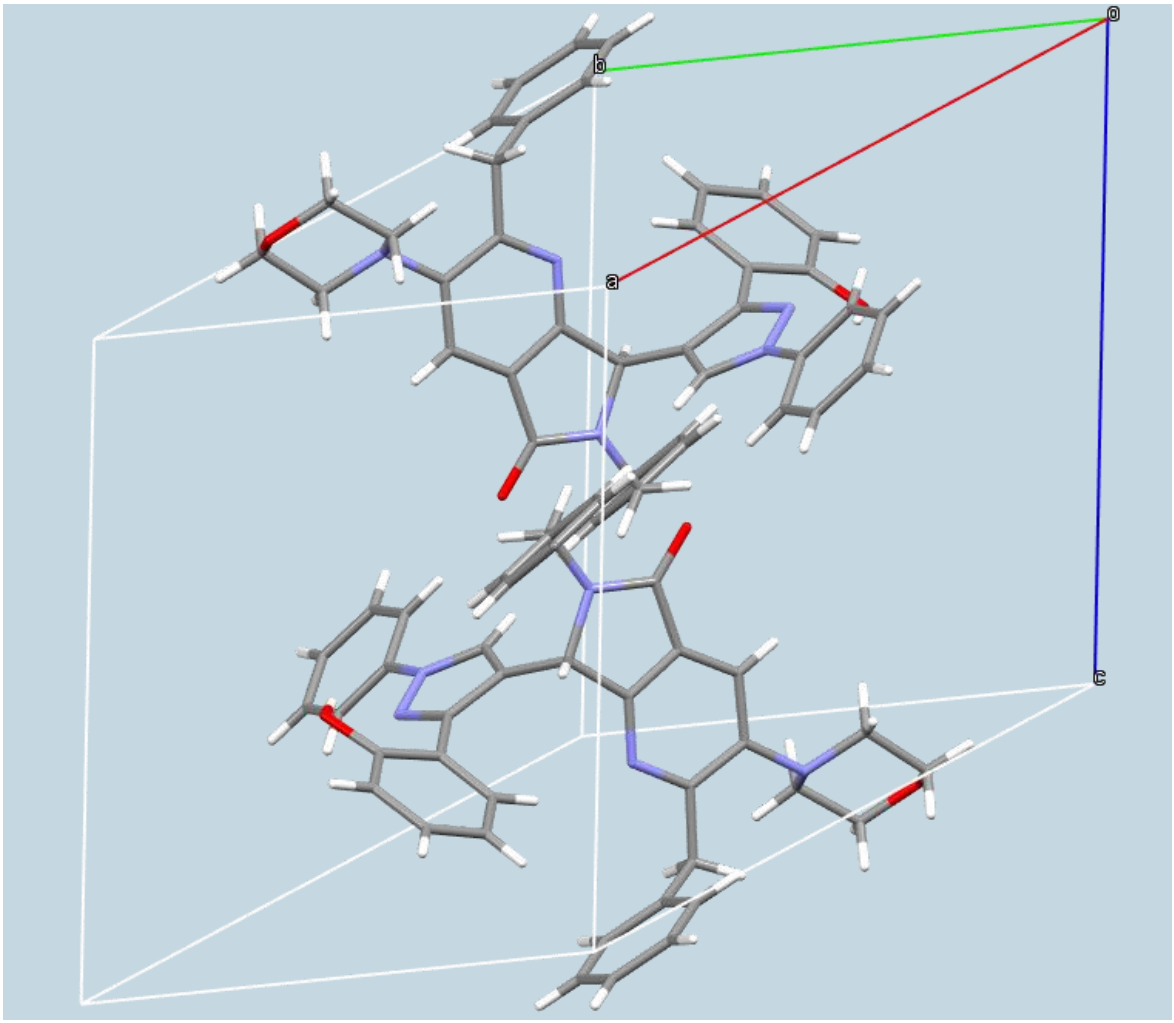


Figure S54. Crystal packing in the single crystal of **6e**

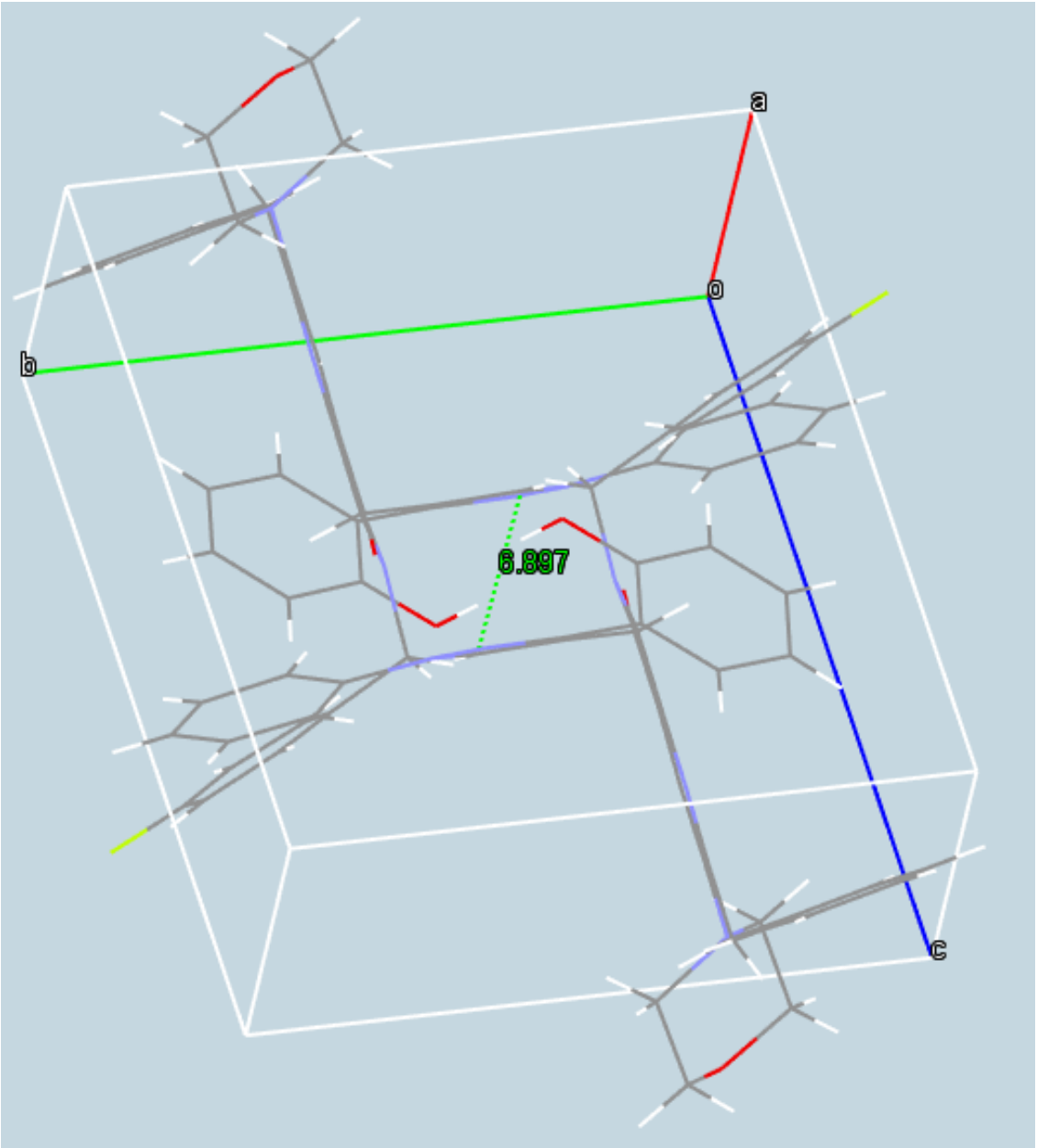


Figure S55. Molecular interactions (in Å) involving the pyrazole moiety of compound **6e**.

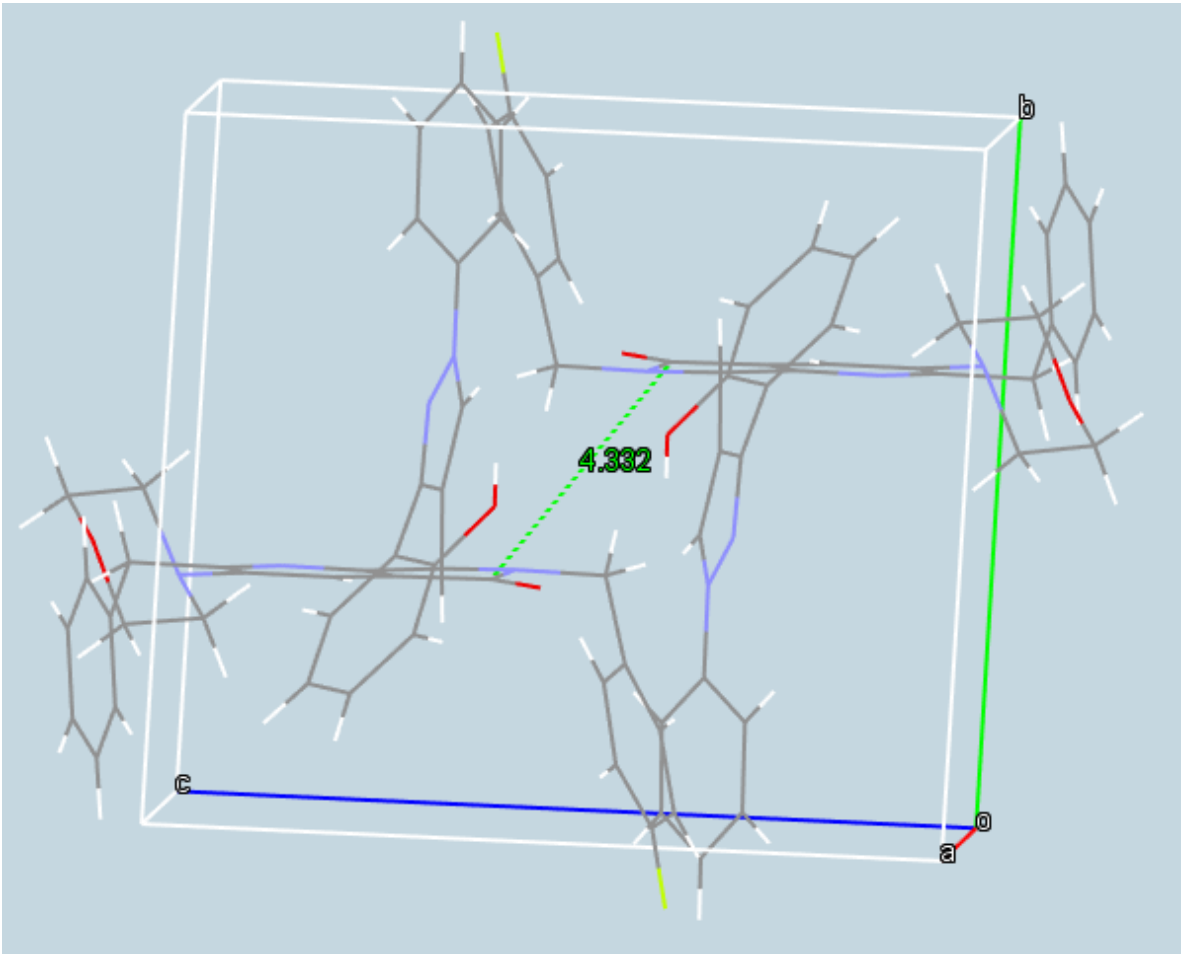


Figure S56. Molecular interactions (in Å) involving the pyrrolo[3,4-*b*]pyridin-5-one moiety of compound **6e**.

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