Electronic Supplementary Material (ESI) for ChemComm.


*Supporting Information*

# Regioselective Synthesis of Phenanthridine-Fused Quinazolinones using 9-Mesityl-10-Methylacridinium Perchlorate Photocatalyst

CONTENTS

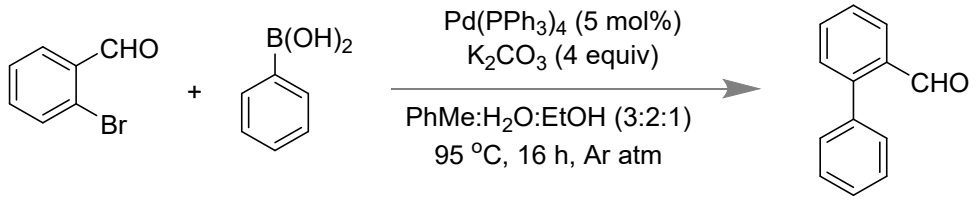
**EXPERIMENTAL SECTION**

**General Information**. Commercially available reagents and solvents were used as received. Column chromatographic purifications of the compounds were performed using silica gel (mesh 230–400, 100-200) and hexane – ethyl acetate solvent mixtures. NMR spectra were recorded on a 400 MHz or 700 MHz instrument at 25 °C. The chemical shift values are reported in parts per million (ppm) with respect to residual trichloromethane (7.26 ppm for $^{1}$H and 77.16 ppm for $^{13}$C) or dimethyl sulfoxide (2.50 ppm for $^{1}$H and 39.52 ppm for $^{13}$C). The peak patterns are designated as follows: s: singlet; d: doublet; t: triplet; q: quartet; m: multiplet; dd: doublet of doublets; td: triplet of doublets; brs: broad singlet. The coupling constants (*J*) are reported in hertz (Hz). High-resolution mass spectra (HR-MS) were recorded on an ESI-TOF (time of flight) mass spectrometer. Infrared spectral data are reported in wave number ($cm^{-1}$). All the reactions were performed in a 10 mL screw-capped quartz tube upon irradiation of Blue LEDs light for the 24 h. FT-IR spectra were recorded after making thin layer of the compounds on the surface of NaCl crystal using dichloromethane. Melting points of the compounds were determined using a digital melting point apparatus and are uncorrected.

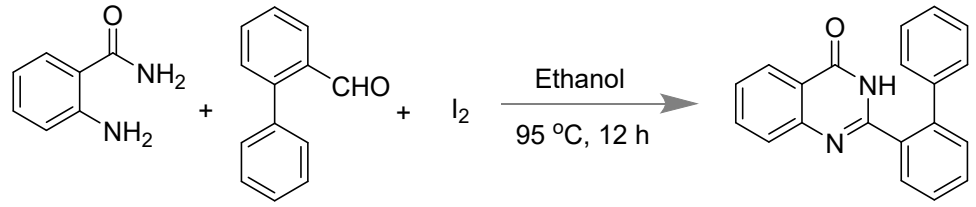
**Preparation of starting material (2-([1,1'-biphenyl]-2-yl)quinazolin-4(3*H*)-one):**

**Synthesis of [1,1'-biphenyl]-2-carbaldehyde.[1]** In an oven dried sealed tube, 2-bromobenzaldehyde (5.4 mmol, 1 equiv), aryl boronic acid (6.48 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (0.27 mmol, 0.05 equiv) and potassium carbonate (21.6 mmol, 4 equiv) were taken in Toluene:$H_2O$:EtOH (9 mL:6 mL:3 mL) solvent. Then the reaction mixture was stirred at 100 °C under an argon atmosphere until the starting material was completely consumed (typically 16 h). After cooling down to room temperature, the reaction mixture was concentrated and

diluted with brine (25 mL). Then organic layer was extracted with EtOAc (25 mL × 2) and dried over $Na_2SO_4$. The concentrated crude product was purified by column chromatography to obtained [1,1'-biphenyl]-2-carbaldehyde, which was used for the next step.



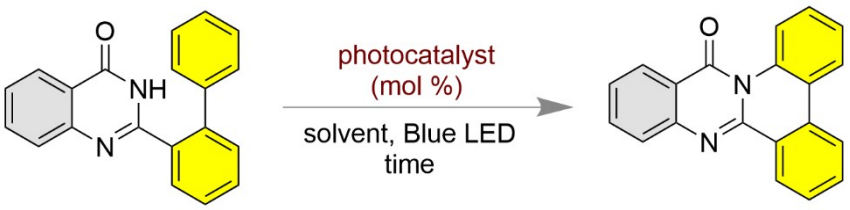

**Synthesis of 2-([1,1'-biphenyl]-2-yl)quinazolin-4(3*H*)-one.** To a solution of anthranilamide (4.19 mmol, 1.0 equiv, 570 mg), [1,1'-biphenyl]-2-carbaldehyde (4.19 mmol, 1.0 equiv, 763 mg) and iodine (4.61 mmol, 1.1 equiv, 1.16 mg) were taken in ethanol solvent (15 mL). Then the reaction mixture was heated at 95 ºC for 12 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum and appropriate amount aqueous of sodium thiosulpahte solution was added to it. The mixture was extracted with EtOAc and the organic layer was dried over $Na_2SO_4$, filtered and concentrated in a vacuum. The residue was purified by column chromatography to give the product (96 % as a white solid).




**Representative Procedure for preparation of 14*H*-quinazolino[3,2-f]phenanthridin-14-one (2aa).** In an oven dried quartz tube, 2-([1,1'-biphenyl]-2-yl)quinazolin-4(3*H*)-one **1aa** (60 mg, 0.201 mmol), and Mes-Acr-Me$ClO_4$ (10 mol %, 8 mg, 0.0201 mmol) were dissolved in 3.0 mL acetonitrile ($CH_3CN$). Then the reaction mixture was irradiated by Blue LEDs light for 24 h. The progress of the reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, the resulting solution was evaporated to dryness. The crude residue

was purified on silica gel column chromatography (20% EtOAc in hexane) to get the pure product 14*H*-quinazolino[3,2-f]phenanthridin-14-one **2aa** (56.5 mg, yield 95%)


**Table S1.** Optimization of the reaction condition.[a]




| entry | photocatalyst (mol %) | solvent | yield (%)[b] |
|---|---|---|---|
| 1 | Mes-Acr-$MeClO_4$ (5) | $CH_3CN$ | 66 |
| **2** | **Mes-Acr-$MeClO_4$ (10)** | **$CH_3CN$** | **95** |
| 3 | Mes-Acr-$MeBF_4$ (10) | $CH_3CN$ | 80 |
| 4 | Rose Bengal (10) | $CH_3CN$ | NR[c] |
| 5 | Rhodamine-B (10) | $CH_3CN$ | NR |
| 6 | Eosyin-Y (10) | $CH_3CN$ | NR |
| 7 | $Ru(bpy)_3(PF_6)_2$ (10) | $CH_3CN$ | NR |
| 8 | 1-Chloroanthraquinone (10) | $CH_3CN$ | NR |

| | | | |
|---|---|---|---|
| 9 | Mes-Acr-$MeClO_4$ (10) | DCE | 49 |
| 10 | Mes-Acr-$MeClO_4$ (10) | DCM | 47 |
| 11 | Mes-Acr-$MeClO_4$ (10) | THF | 32 |
| 12 | Mes-Acr-$MeClO_4$ (10) | Toluene | 64 |
| 13 | Mes-Acr-$MeClO_4$ (10) | DMSO | NR |
| 14 | --[d] | $CH_3CN$ | NR |
| 15 | Mes-Acr-$MeClO_4$ (10) | $CH_3CN$ | NR[e] |

[a]Reaction conditions: 0.201 mmol of **1aa** and 0.0201 mmol of photocatalyst (10 mol %) in 2.0 mL of solvent upon blue light irradiation for 24 h. [b]Yield of isolated product after silica-gel column chromatography. [c]No product. [d]Without any photocatalyst. [e]No product could be isolated in $N_2$ atmosphere.

Towards the optimization of the reaction conditions, 2- ([1,1'-biphenyl]-2-yl)quinazolin-4(3*H*)-one (**1aa**) was used as the model substrate (Table S1). Initially, the treatment of 1aa with 5 mol % of Mes-Acr-$MeClO_4$ photocatalyst led to the formation of 14*H*-quinazolino[3,2-f]phenanthridin-14-one (**2aa**) with 66% yield upon irradiation of blue LED over 24 h in acetonitrile at room temperature (Table S1, entry 1). Further, with the increase of the catalyst loading from 5 to 10 mol % the product yield was increased to 95% (Table S1, entry 2). However, the desired product 2aa was isolated in 80% yield (Table S1, entry 3) using 10 mol % of 9-mesityl-10- methylacridinium tetrafluroborate (Mes-Acr-$MeBF_4$) photocatalyst. No desired product was observed, when the commonly used photocatalysts such as rose bengal, rhodamine-B, eosin-Y, $Ru(bpy)_3(PF_6)_2$ and 1- chloroantraquinone were used (Table S1, entries 4-8). Additionally, various solvents were screened using 10 mol % of Mes-Acr-$MeClO_4$

photocatalyst, which did not lead to improvement on the reaction yield. The use of dichloroethane (DCE), dichloromethane (DCM), tetrahydrofuran (THF) and toluene provided inferior results (Table S1, entries 9-12). However, the reaction failed in dimethyl sulfoxide (DMSO) (Table S1, entry 13). The reaction failed in the absence of any photocatalyst (Table S1, entry 14). Under $N_2$ atmosphere no product could be isolated (Table S1, entry 15). The standard reaction condition was established when the reaction was carried out using of 10 mol % Mes-Acr-Me$ClO_4$ photocatalyst with respect to the quinazolinones substrate upon irradiation under blue LED for 24 h in acetonitrile at room temperature.

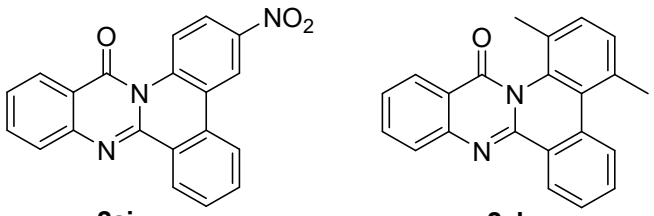



**Figure S1.** Unsuccessful substrates.

**Radical trapping experiment with TEMPO/BHT/Diphenylethelene.** The compound 2-([1,1'-biphenyl]-2-yl)quinazolin-4(3H)-one **1aa** (40 mg, 0.134 mmol), and Mes-Acr-Me$ClO_4$ (10 mol %, 5.5 mg, 0.0134 mmol) were dissolved in 3.0 mL acetonitrile ($CH_3CN$) and TEMPO (2 equiv, 42 mg, 0.268 mmol ) was added in a 10 mL screw-capped quartz tube. Then the reaction mixture was irradiated by Blue LEDs light for the 24 h. The progress of the reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, the resulting solution was evaporated to dryness and the crude residue was purified on silica gel column chromatography. However, the product yield (**2aa**) was dramatically decreased and giving 12% (4.7 mg) yield. The same experiment was carried out using BHT (2 equiv, 59 mg, 0.268 mmol) and 1,1-diphenylethylene (2 equiv, 48 mg, 0.268 mmol). In both the cases, the product yield (**2aa**) was reduced and only 18% and 20% yield was obtained. Whereas, other

radical scavenger (such as *Tributyltin hydride*, $Bu_3SnH$) did not produced any yield of the product (**2aa**).

Under the standard reaction condition, the reaction was unsuccessful using 2 equiv of DABCO and only 13% yield of the desire product (**2aa**) was obtained in the presence of 1 equiv sodium azide as a quencher.

Additionally, when the reaction was carried out in the presence of 1 equivalent of (electron scavenger) $CuCl_2$ (0.134 mmol, 18 mg) under the standard reaction condition, resulted no desired product.

When 1 equivalent of benzoquinone (14.5 mg, 0.134 mmol) was used as a superoxide radical anion scavenger under the standard reaction conditions, only 08% of product formation was observed.

**Light ON-OFF-ON Experiment.** 2-([1,1'-Biphenyl]-2-yl)quinazolin-4(3*H*)-one **1aa** (60 mg, 0.201 mmol), and Mes-Acr-$MeClO_4$ (10 mol %, 8 mg, 0.0201 mmol) were dissolved in 3.0 mL acetonitrile ($CH_3CN$). Then the reaction mixture was irradiated by Blue LEDs light for the 24 h. Further the successive progress of the reaction was monitored by $^1H$ NMR experiment. Initially, the reaction was irradiated for 6 h and then 3 h light off. Followed by 6 h light on and 3 h light off. Then repetition was carried out such as 3 h light on and 3 h light off followed by 6 h light on.

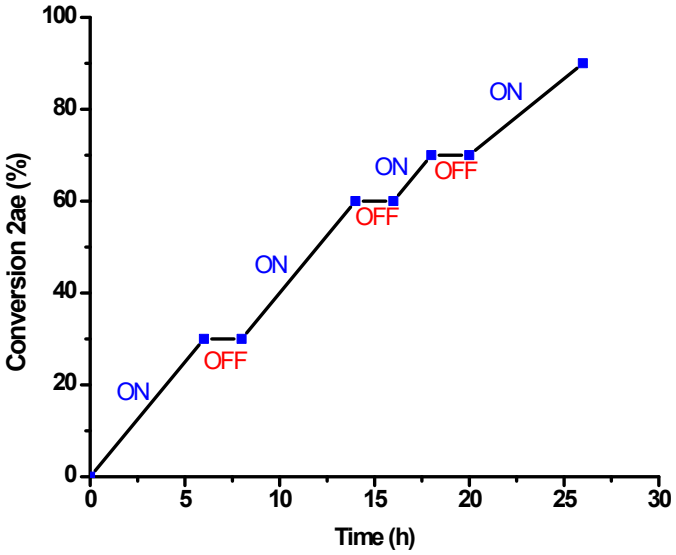



**Figure S2.** Conversion of **2ae** with respect to time in the presence and absence of light.

**EPR Experiments.** 2-([1,1'-Biphenyl]-2-yl)quinazolin-4(3*H*)-one **1aa** (60 mg, 0.201 mmol), and Mes-Acr-MeClO$_4$ (10 mol %, 8 mg, 0.0201 mmol) were dissolved in 3.0 mL acetonitrile ($CH_3CN$) and DMPO (20 µL) was added in a 10 mL quartz flask in the presence of air. Then the reaction mixture was irradiated by Blue LEDs light for the 6 h and the EPR experiment was performed.

**Fluorescence Quenching Experiment.** The emission maximum of the photocatalyst Mes-Acr-MeClO$_4$ ($3\times 10^{-3}$ M in DCE) was recorded upon excitation wavelength at 360 nm. Furthermore, the fluorescence intensity decreased with the gradual addition of **1aa** ($3\times 10^{-1}$ M in DCE), which is shown below.

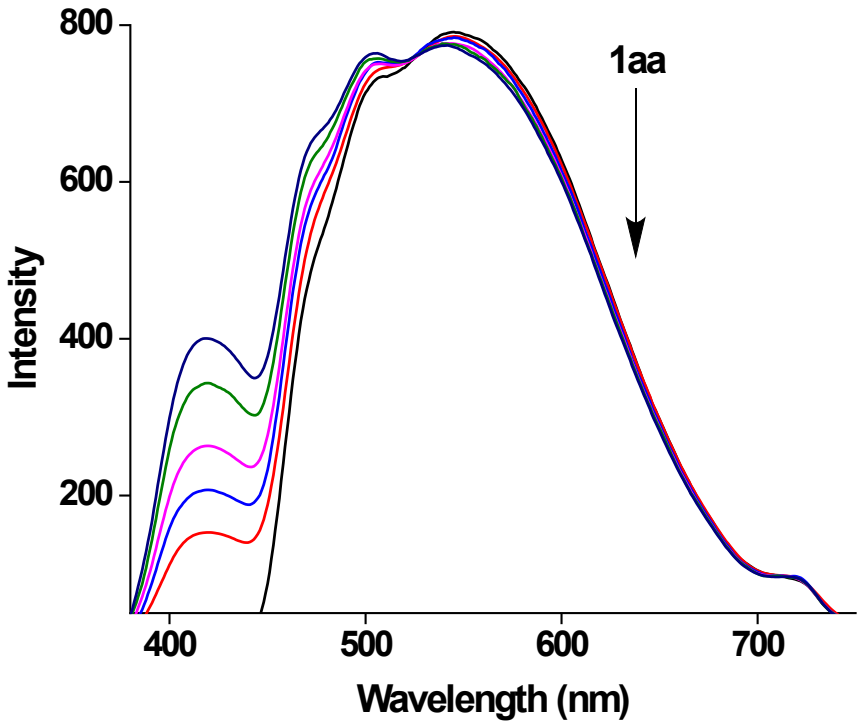



**Figure S3.** Fluorescence spectra of Mes-Acr-Me$ClO_4$ upon gradual addition of **1aa**.

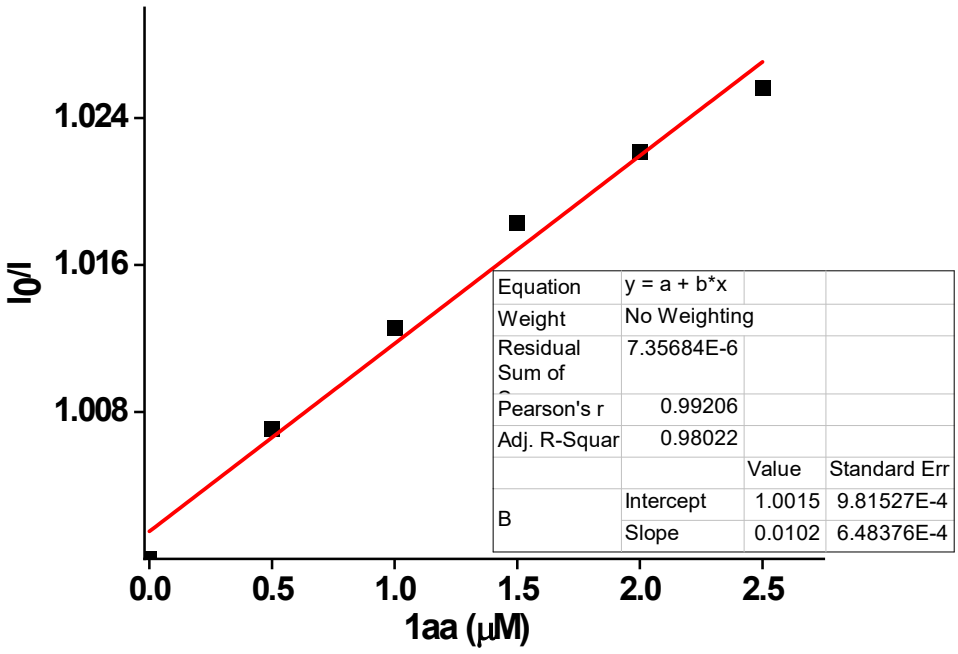



**Figure S4.** Stern−Volmer plot of **1aa**.

**Cyclic voltammetry experiment (CV).** Cyclic voltametric data was recorded on the CorrTest Electrochemical Station (Model: CS310, S/N: 1711458) in dry and oxygen-free DCE containing 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte and 0.1 mM 2-([1,1'-biphenyl]-2-yl)quinazolin-4(3*H*)-one (**1aa**) as the analyte with a decoration of a glassy carbon electrode, a Ag/AgCl electrode and a platinum wire as the working electrode (with a circular geometry of the surface), reference electrode, and counter electrode, respectively starting from +2.0 V initial potential to -2.0 V switching potential with an oxidative direction of initial scan using a scan rate 100 mV/s at 25 ℃. Redox potential was referenced against ferrocene/ferrocenium ($Fc/Fc^{+}$). Before and after using the glassy carbon (working electrode), it is polished using 0.5 micron of $Al_2O_3$ and a few drops of water over a flat glass surface. The deoxygenation of DCE was done by purging Ar gas into the electrolytic solution with the help of a long needle for 2 min.

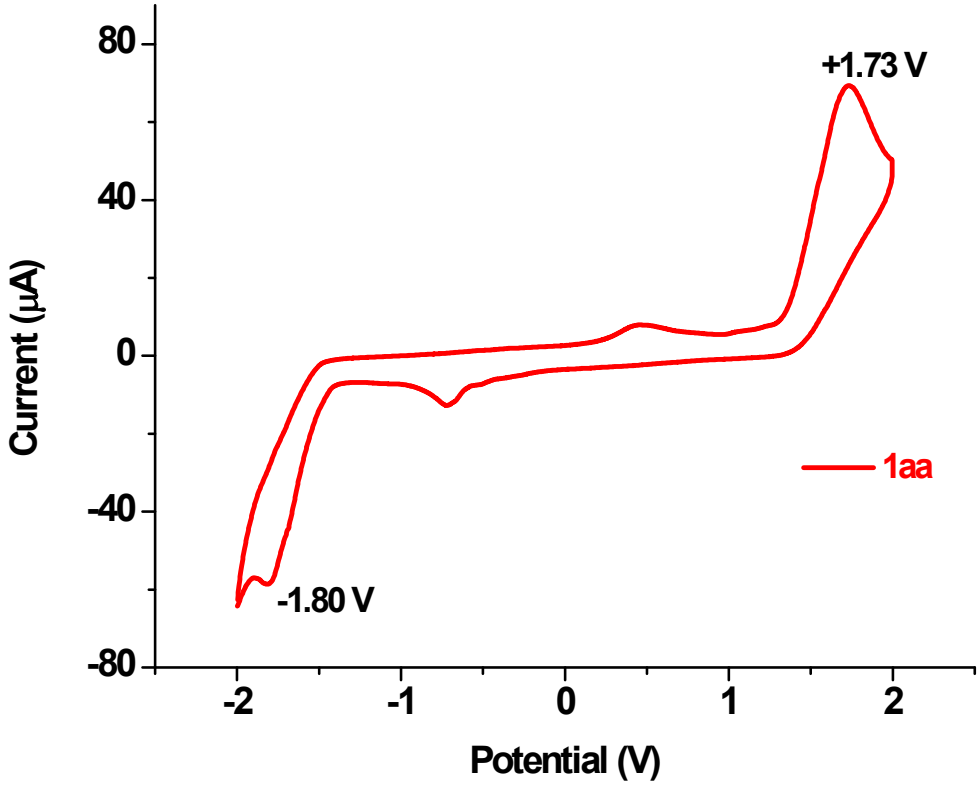



**Figure S5.** Cyclic voltammetry of **1aa**.

**Detection of hydrogen peroxide ($H_2O_2$).**[2] The KI-Starch test was performed to confirm the evolution of $H_2O_2$ as a by-product during the reaction. For the test, a solution of KI (0.05 M), starch (4 mg/mL), and glacial acetic acid (0.5 M) in 2 mL $H_2O$ was prepared in vial **A**. To vial **B** reaction mixture was transferred from quartz tube after the reaction, where the reaction was performed using 0.201 mmol of 2-([1,1'-biphenyl]-2-yl)quinazolin-4(3H)-one **1aa** and 0.0201 mmol of photocatalyst (10 mol %) in 2.0 mL of acetonitrile solvent upon blue light irradiation for 24 h. When 100 µL of solution **B** was added to solution **A**, the resulting solution turned to dark purple-black colour, which confirmed the evolution of $H_2O_2$ (vial **C**).

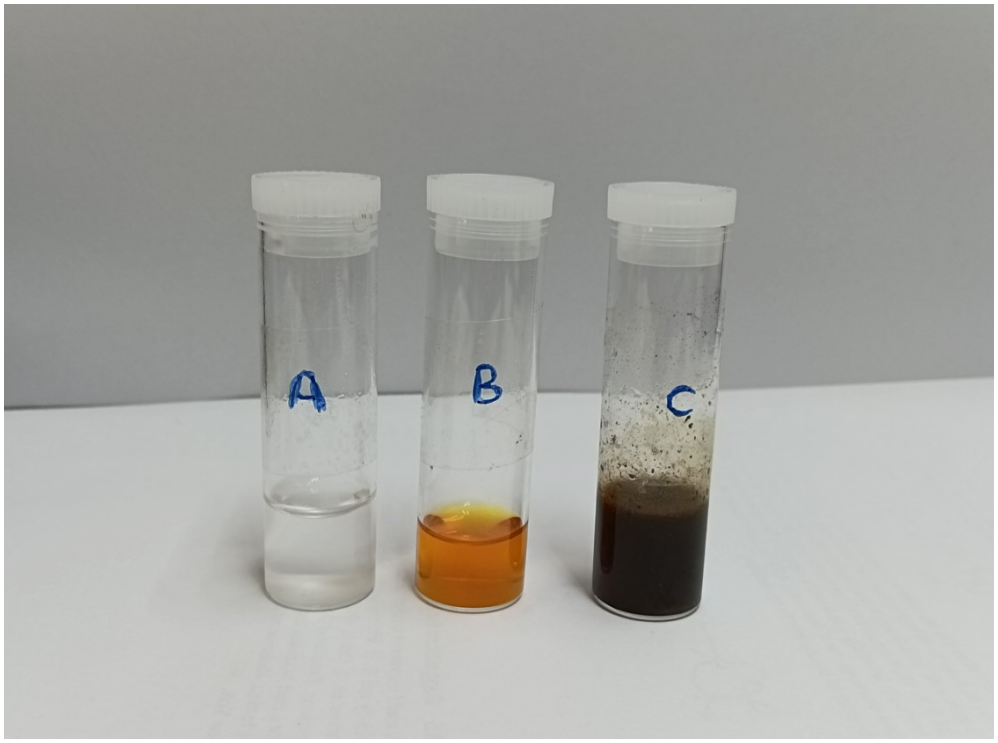
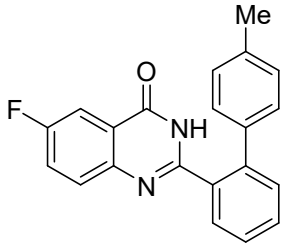



**Figure S6.** KI-Starch test for detection of $H_2O_2$

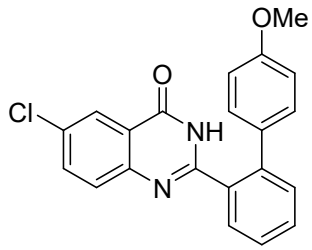
## CHARATERIZATION DATA

**6-Fluoro-2-(4'-methyl-[1,1'-biphenyl]-2-yl)quinazolin-4(3H)-one (3bd):** $R_f$ = 0.50 (hexane/ethyl acetate 4:1); white solid; yield 98% (210 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ



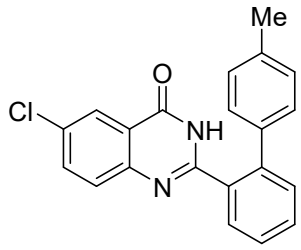

8.92 (s, 1H), 7.91 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.87 – 7.84 (m, 1H), 7.83 (dd, *J* = 4.0, 2.8 Hz, 1H), 7.62 (td, *J* = 7.6, 1.6 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.26 (s, 1H), 7.24 (s, 1H), 7.17 (s, 1H), 7.15 (s, 1H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 161.1 (d, *J* = 248.8 Hz), 160.9, 160.8, 153.0 (d, *J* = 2.2 Hz), 145.9, 140.5, 138.4, 136.1, 132.4, 131.2 (d, *J* = 15.4 Hz), 130.6, 130.4 (d, *J* = 8.1 Hz), 129.9, 128.9, 128.0, 123.4 (d, *J* = 24.1 Hz), 122.1 (d, *J* = 8.7 Hz), 111.5 (d, *J* = 23.5 Hz), 21.3; IR (KBr) $\tilde{\nu}$ = 3035, 1661, 1614, 1478, 1290, 926, 828 cm$^{-1}$; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{16}FN_2O$ $[M + H]^+$ 331.1247, found 331.1241. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -112.34.

**6-Chloro-2-(4'-methoxy-[1,1'-biphenyl]-2-yl)quinazolin-4(3H)-one (3bh):** $R_f$ = 0.40 (hexane/ethyl acetate 7:3); white solid; yield 88% (282 mg); $^1$H NMR (700 MHz, $CDCl_3$) δ



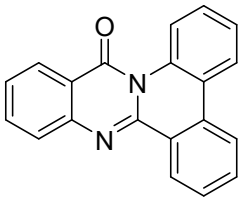

9.62 (s, 1H), 8.12 (dd, *J* = 4.2, 3.5 Hz, 1H), 7.84 -7.78 (m, 1H), 7.75 – 7.69 (m, 2H), 7.57 – 7.52 (m, 1H), 7.47 – 7.40 (m, 2H), 7.24 – 7.17 (m, 2H), 6.84 – 6.75 (m, 2H), 3.76 (s, 3H); $^{13}$C NMR (175 MHz, $CDCl_3$) δ 161.1, 159.7, 154.2, 147.8, 140.3, 135.2, 132.9, 132.3, 131.3, 131.0, 130.5, 130.3, 130.2, 129.6, 127.7, 125.9, 121.9, 114.4, 55.3; IR (KBr) $\tilde{\nu}$ = 3034, 2950, 1664, 1605, 1493, 1462, 1235, 939 cm$^{-1}$; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{16}ClN_2O_2$ $[M + H]^+$ 363.0900, found 363.0903.

**6-Chloro-2-(4'-methyl-[1,1'-biphenyl]-2-yl)quinazolin-4(3H)-one (3bj):** $R_f$ = 0.45 (hexane/ethyl acetate 4:1); white solid; yield 96% (196 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ



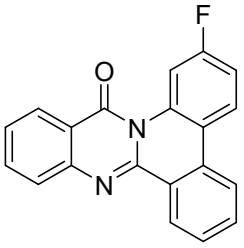

10.15 (s, 1H), 8.09 (t, *J* = 1.2 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.70 (s, 1H), 7.70 (s, 1H), 7.54 – 7.48 (m, 1H), 7.44 (d, *J* = 6.8 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.14 (s, 1H), 7.12 (s, 1H), 7.00 (s, 1H), 6.98 (s, 1H), 2.26 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 161.4, 154.2, 147.7, 140.7, 137.8, 136.2, 135.1, 132.7, 132.3, 131.1, 130.9, 130.2, 129.5, 129.4, 128.9, 127.6, 125.8, 121.8, 21.2; IR (KBr) $\tilde{\nu}$ = 3036, 2918, 1660, 1607, 1462, 1289, 828 cm$^{-1}$; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{16}ClN_2O$ $[M + H]^+$ 347.0951, found 347.0976.

**14H-Quinazolino[3,2-f]phenanthridin-14-one (2aa):[3]** $R_f$ = 0.60 (hexane/ethyl acetate 9:1); white solid; yield 95% (56.5 mg). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.09 (d,




*J* = 8.4 Hz, 1H), 9.00 (d, *J* = 8.0 Hz, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 8.28 – 8.20 (m, 2H), 7.82 (d, *J* = 3.6 Hz, 2H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.54 – 7.45 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.1, 146.6, 146.3, 134.7, 133.2, 132.4, 131.5, 128.7, 128.4, 128.3, 127.6, 127.4, 127.1, 126.6, 126.4, 123.2, 122.3, 121.9, 120.9.

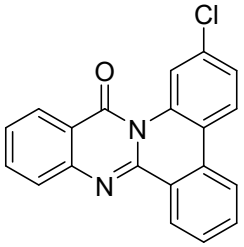
**2-Fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one (2ab):[3]** $R_f$ = 0.70 (hexane/ethyl acetate 9:1); white solid; yield 86% (68 mg); $^1$H NMR (700 MHz, $CDCl_3$)



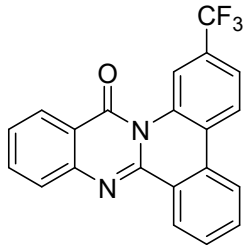

δ 9.04 (d, *J* = 12.6 Hz, 1H), 9.01 (d, *J* = 8.4 Hz, 1H), 8.43 (d, *J* = 7.7 Hz, 1H), 8.27 – 8.22 (m, 1H), 8.15 (d, *J* = 7.7 Hz, 1H), 7.83 (s, 2H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.0 Hz, 1H), 7.53 (d, *J* = 3.5 Hz, 1H), 7.27 (s, 1H); $^{13}$C NMR (175 MHz, $CDCl_3$) δ 163.1, 161.9 (d, *J* = 246.7 Hz), 146.4, 146.1, 134.9, 134.4 (d, *J* = 11.3 Hz), 132.5, 130.9, 128.6, 128.5, 127.7, 127.2, 126.9, 126.7,

124.8 (d, *J* = 9.1 Hz), 121.8, 120.7, 119.7, 114.4 (d, *J* = 22.7 Hz), 109.8 (d, *J* = 29.7 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$ + TFA-D) δ -109.69.

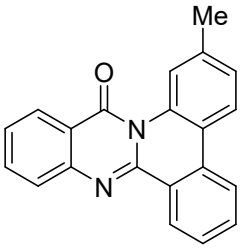
**2-Chloro-14H-quinazolino[3,2-f]phenanthridin-14-one (2ac):[3]** $R_f$ = 0.60 (hexane/ethyl acetate 9:1); white solid; yield 85% (51 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 9.24 (d, *J* = 2.0 Hz, 1H), 9.01 – 8.97 (m, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 3.6 Hz, 1H), 8.14 (d, *J* = 3.2 Hz, 1H), 7.83 (dd, *J* = 4.0, 2.0 Hz, 2H), 7.75 – 7.69 (m, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.45 (dd, *J* = 8.4, 2.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.0, 146.2, 146.1, 134.9, 134.3, 133.9, 132.5, 130.7, 128.9, 128.5, 127.6, 127.2, 127.2, 126.9, 126.7, 124.3, 122.4, 121.9, 121.8, 120.8.



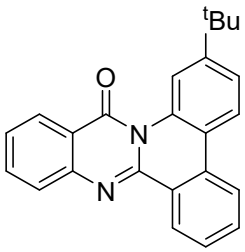

**2-(Trifluoromethyl)-14H-quinazolino[3,2-f]phenanthridin-14-one (2ad):[4]** $R_f$ = 0.60 (hexane/ethyl acetate 9:1); white solid; yield 84% (58 mg); $^1$H NMR (700 MHz, $CDCl_3$) δ 9.51 (s, 1H), 8.93 (d, *J* = 7.7 Hz, 1H), 8.40 (d, *J* = 7.7 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 7.7 Hz, 1H), 7.82 (t, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.69 (dd, *J* = 17.5, 8.4 Hz, 2H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.0 Hz, 1H); $^{13}$C NMR (175 MHz, $CDCl_3$) δ 162.9, 145.9, 145.9, 135.0, 133.2, 132.5, 130.0, 129.8, 129.7, 128.5, 127.9, 127.6, 127.3, 126.9, 125.9, 123.9 (q, *J* =271.3 Hz), 123.8, 122.9 (q, *J* = 3.2 Hz), 122.3, 120.8, 119.8 (q, *J* = 4.2 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.46.



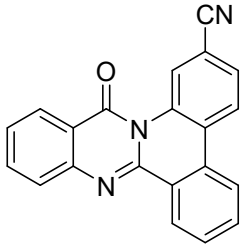
**2-Methyl-14H-quinazolino[3,2-f]phenanthridin-14-one (2ae):**[3] $R_f$ = 0.60 (hexane/ethyl acetate 9:1); white solid; yield 91% (54.2 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 9.00 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.93 (s, 1H), 8.43 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.84 – 7.81 (m, 2H), 7.74 – 7.69 (m, 1H), 7.60 – 7.55 (m, 1H), 7.53 – 7.48 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 2.51 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.3, 146.8, 146.3, 138.6, 134.7, 133.2, 132.4, 131.7, 128.4, 128.3, 127.8, 127.5, 127.1, 127.0, 126.3, 123.1, 122.6, 121.8, 120.9, 120.8, 22.1.



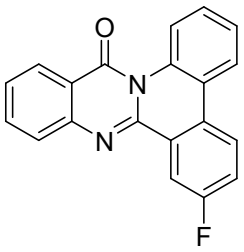

**2-(Tert-butyl)-14H-quinazolino[3,2-f]phenanthridin-14-one (2af):**[5] $R_f$ = 0.60 (hexane/ethyl acetate 9:1); white solid; yield 88% (87 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 9.21 (d, *J* = 2.0 Hz, 1H), 8.99 (d, *J* = 8.0 Hz, 1H), 8.45 (d, *J* = 8.0 Hz, 1H), 8.18 (t, *J* = 7.6 Hz, 2H), 7.85 – 7.79 (m, 2H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.54 – 7.48 (m, 2H), 1.44 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.3, 151.6, 146.9, 146.3, 134.6, 133.2, 132.3, 131.6, 128.4, 128.3, 127.6, 127.1, 127.1, 126.3, 124.0, 122.8, 121.8, 121.0, 120.7, 119.5, 35.5, 31.4.



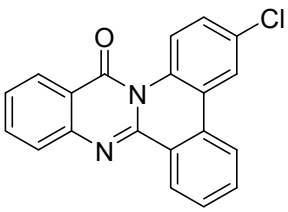

**14-Oxo-14H-quinazolino[3,2-f]phenanthridine-2-carbonitrile (2ag):**[3] $R_f$ = 0.65 (hexane/ethyl acetate 9:1); white solid; yield 83% (49.5 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 9.04 (d, *J* = 8.0 Hz, 1H), 8.43 (d, *J* = 8.0 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 6.0 Hz, 2H), 7.78 (t, *J* = 7.2 Hz, 1H), 7.71 (dd, *J* = 13.6, 7.2 Hz, 2H), 7.56 (t, *J* = 6.0 Hz, 1H); $^{13}$C NMR (175 MHz, $CDCl_3$) δ 162.9, 145.9, 145.6, 135.3, 133.4, 132.8, 130.4, 129.8, 129.3, 128.7, 128.3, 127.7, 127.3, 127.1, 127.1, 126.5, 124.1, 122.6, 120.7, 118.5, 111.8.



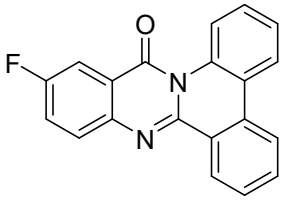
**7-Fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one (2ah):[3]** $R_f$ = 0.65 (hexane/ethyl acetate 9:1); white solid; yield 93% (92.4 mg); $^1$H NMR (700 MHz, $CDCl_3$) δ 9.11 (d, *J* = 8.4 Hz, 1H), 8.68 (dd, *J* = 9.8, 2.8 Hz, 1H), 8.43 (d, *J* = 7.7 Hz, 1H), 8.22 (dd, *J* = 8.4, 4.9 Hz, 1H), 8.19 (d, *J* = 7.7 Hz, 1H), 7.84 (d, *J* = 3.5 Hz, 2H), 7.56 – 7.48 (m, 3H), 7.46 – 7.42 (m, 1H); $^{13}$C NMR (175 MHz, $CDCl_3$) δ 163.0, 162.8 (d, *J* = 248.8 Hz), 146.1, 145.7 (d, *J* = 3.7 Hz), 134.9, 132.9, 129.5 (d, *J* = 8.8 Hz), 128.2, 128.0, 127.6, 127.2, 126.8, 124.5, 124.4, 123.1, 122.6, 122.4, 121.1, 120.6 (d, *J* = 23.1 Hz), 114.1 (d, *J* = 24.3 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -111.47.




**3-Chloro-14H-quinazolino[3,2-f]phenanthridin-14-one (2ai):[4]** $R_f$ = 0.65 (hexane/ethyl acetate 9:1); white solid; yield 87% (52 mg). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.14 (d, *J* = 9.2 Hz, 1H), 9.02 (d, *J* = 8.0 Hz, 1H), 8.43 (d, *J* = 7.6 Hz, 1H), 8.21 (s, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.84 (s, 2H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.54 (s, 1H), 7.47 (d, *J* = 8.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.9, 146.1, 134.9, 132.5, 132.3, 131.7, 130.3, 129.4, 128.5, 128.2, 127.7, 127.6, 127.2, 126.7, 125.9, 124.9, 123.9, 122.9, 122.1, 120.8.

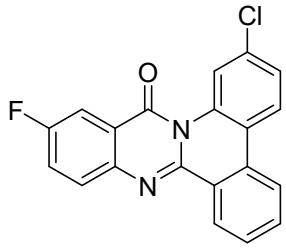



**12-Fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one (4ba):[3]** $R_f$ = 0.60 (hexane/ethyl acetate 9:1); white solid; yield 91% (54.2 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 9.13 – 9.07 (m, 1H), 9.01 – 8.91 (m, 1H), 8.25 (dd, *J* = 7.6, 2.0 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.04 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.82 (dd, *J* = 8.8, 4.8 Hz, 1H), 7.75 – 7.69 (m, 1H), 7.60 (dd, *J* = 11.2, 4.0 Hz, 1H), 7.56 – 7.47 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.4, 160.7 (d, *J* = 247.6 Hz), 146.0, 142.9, 133.0,

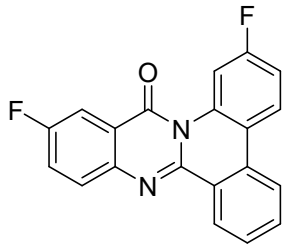


132.4, 131.4, 129.5, 129.4, 128.8, 128.3 (d, $J$ = 9.4 Hz), 127.2, 126.9, 123.6, 123.4 (d, $J$ = 5.3 Hz), 123.3, 122.3, 122.0, 121.9, 112.2 (d, $J$ = 23.9 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -113.18.

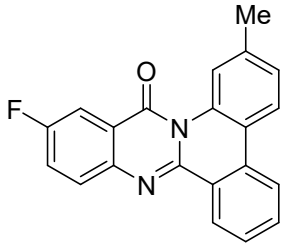
**2-Chloro-12-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one (4bb):[3]** $R_f$ = 0.60 (hexane/ethyl acetate 9:1); white solid; yield 89% (53 mg); $^1$H NMR (700 MHz, $CDCl_3$) δ 9.26 (d, $J$ = 1.4 Hz, 1H), 8.98 (d, $J$ = 8.4 Hz, 1H), 8.18 (t, $J$ = 8.4 Hz, 2H), 8.06 (dd, $J$ = 8.4, 2.8 Hz, 1H), 7.84 (dd, $J$ = 8.4, 4.9 Hz, 1H), 7.74 (t, $J$ = 7.0 Hz, 1H), 7.62 (t, $J$ = 7.7 Hz, 1H), 7.56 (td, $J$ = 8.4, 2.8 Hz, 1H), 7.48 (dd, $J$ = 8.4, 1.4 Hz, 1H). $^{13}$C NMR (175 MHz, $CDCl_3$) δ 162.4, 160.9 (d, $J$ = 248.3 Hz), 145.7, 142.8, 134.4, 133.7, 132.6, 130.6, 129.6 (d, $J$ = 8.3 Hz), 129.1, 128.4, 127.2, 127.1, 124.4, 123.8 (d, $J$ = 24.5 Hz), 122.4, 121.9, 121.9, 121.8 (d, $J$ = 8.7 Hz), 112.4 (d, $J$ = 23.9 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -112.53.



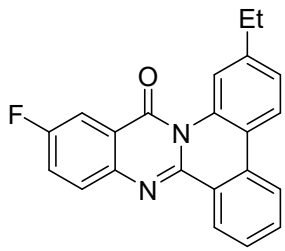

**2,12-Difluoro-14H-quinazolino[3,2-f]phenanthridin-14-one (4bc):[3]** $R_f$ = 0.60 (hexane/ethyl acetate 9:1); white solid; yield 86% (51.2 mg); $^1$H NMR (700 MHz, $CDCl_3$) δ 9.04 (d, $J$ = 12.6 Hz, 1H), 8.97 (d, $J$ = 7.7 Hz, 1H), 8.28 – 8.20 (m, 1H), 8.15 (d, $J$ = 7.7 Hz, 1H), 8.05 (d, $J$ = 8.4 Hz, 1H), 7.83 (dd, $J$ = 8.4, 4.2 Hz, 1H), 7.73 (t, $J$ = 7.7 Hz, 1H), 7.60 (t, $J$ = 7.7 Hz, 1H), 7.56 (t, $J$ = 7.0 Hz, 1H), 7.24 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR (175 MHz, $CDCl_3$) δ 162.4, 161.9 (d, $J$ = 247.0 Hz), 160.9 (d, $J$ = 248.1 Hz), 145.9, 142.8, 134.2 (d, $J$ = 11.4 Hz), 132.6, 130.8, 129.7, 129.6, 128.5 (d, $J$ = 39.5 Hz), 126.7, 124.8 (d, $J$ = 9.2 Hz), 123.8 (d, $J$ = 24.3 Hz), 121.8, 121.8 (d, $J$ = 8.3 Hz), 119.8 (d, $J$ = 2.2 Hz), 114.6 (d, $J$ = 22.6 Hz), 112.4 (d, $J$ = 23.8 Hz), 109.9 (d, $J$ = 29.7 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -109.48, -112.75.



**12-Fluoro-2-methyl-14H-quinazolino[3,2-f]phenanthridin-14-one (4bd):** $R_f$ = 0.60 (hexane/ethyl acetate 9:1); white solid; yield 93% (92.4 mg); $^1$H NMR (700 MHz, $CDCl_3$) δ 8.90 (d, *J* = 4.9 Hz, 2H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 8.02 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.78 (dd, *J* = 8.4, 4.9 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.28 (d, *J* = 8.4 Hz, 1H), 2.49 (s, 3H); $^{13}$C NMR (175 MHz, $CDCl_3$) δ 162.5, 160.7 (d, *J* = 247.6 Hz), 146.2 (d, *J* = 1.6 Hz), 142.9, 138.6, 132.9, 132.3, 131.5, 129.5, 129.4, 128.2 (d, *J* = 10.3 Hz), 127.9, 126.8, 123.4 (d, *J* = 24.3 Hz), 123.1, 122.5, 121.9 (d, *J* = 8.8 Hz), 121.7, 120.8, 112.1 (d, *J* = 23.9 Hz), 22.1; IR (KBr) $\tilde{\nu}$ = 2918, 1675, 1549, 1484, 1330, 1291, 1149 cm$^{-1}$; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{14}FN_2O$ $[M + H]^+$ 329.1090, found 329.1108. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -113.31.

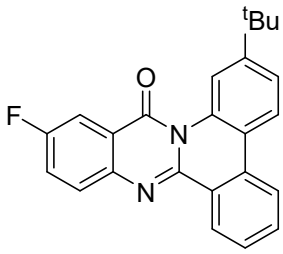



**2-Ethyl-12-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one (4be):[3]** $R_f$ = 0.65 (hexane/ethyl acetate 9:1); white solid; yield 92% (54.8 mg); $^1$H NMR (700 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.87 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 8.01 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.75 (dd, *J* = 8.4, 4.9 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 2.79 (q, *J* = 7.7 Hz, 2H), 1.33 (t, *J* = 7.7 Hz, 3H); $^{13}$C NMR (175 MHz, $CDCl_3$) δ 162.4, 160.6 (d, *J* = 247.7 Hz), 146.1, 144.9, 142.9, 133.1, 132.3, 131.5, 129.4 (d, *J* = 8.4 Hz), 128.2 (d, *J* = 7.6 Hz), 126.7, 126.7, 123.4,



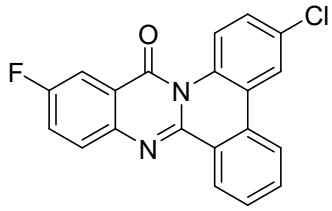
123.3, 123.1, 121.9 (d, $J$ = 8.7 Hz), 121.7, 121.5, 120.9, 112.1 (d, $J$ = 23.8 Hz), 29.3, 15.6. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -113.39.

**2-(Tert-butyl)-12-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one (4bf):[3]** $R_f$ = 0.65 (hexane/ethyl acetate 9:1); white solid; yield 86% (51.3 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ



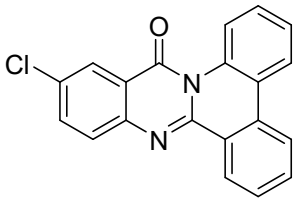

9.20 (d, $J$ = 2.0 Hz, 1H), 8.94 – 8.83 (m, 1H), 8.18 – 8.11 (m, 2H), 8.05 (dd, $J$ = 8.4, 2.8 Hz, 1H), 7.76 (dd, $J$ = 8.8, 4.8 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.54 – 7.46 (m, 3H), 1.44 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.5, 160.6 (d, $J$ = 247.5 Hz), 151.7, 146.2, 142.9, 132.9, 132.3, 131.4, 129.4 (d, $J$ = 8.2 Hz), 128.3, 128.2, 126.9, 124.2, 123.3 (d, $J$ = 24.3 Hz), 122.8, 121.9 (d, $J$ = 8.6 Hz), 121.7, 120.7, 119.5, 112.2 (d, $J$ = 23.8 Hz), 35.5, 31.4. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -113.45.

**3-Chloro-12-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one (4bg):[3]** $R_f$ = 0.60

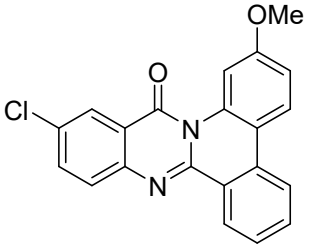



(hexane/ethyl acetate 9:1); white solid; yield 83% (49.5 mg); $^1$H NMR (700 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.99 (d, $J$ = 8.4 Hz, 1H), 8.19 (t, $J$ = 8.4 Hz, 2H), 8.06 (dd, $J$ = 8.4, 2.8 Hz, 1H), 7.85 (dd, $J$ = 8.4, 4.9 Hz, 1H), 7.75 (t, $J$ = 7.7 Hz, 1H), 7.63 (t, $J$ = 7.7 Hz, 1H), 7.57 (dd, $J$ = 11.2, 5.6 Hz, 1H), 7.49 (d, $J$ = 8.4 Hz, 1H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -112.50.

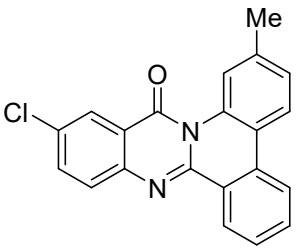
**12-Chloro-14H-quinazolino[3,2-f]phenanthridin-14-one (4bh):**[3] $R_f$ = 0.60 (hexane/ethyl acetate 9:1); white solid; yield 88% (52.4 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, *J* = 8.0 Hz, 1H), 8.91 (d, *J* = 7.6 Hz, 1H), 8.33 (s, 1H), 8.20 (dd, *J* = 14.0, 7.6 Hz, 2H), 7.70 (s, 3H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.49 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.1, 146.8, 144.7, 135.1, 133.0, 132.6, 131.9, 131.5, 128.8, 128.7, 128.5, 128.4, 127.1, 126.8, 126.8, 123.3, 122.9, 122.3, 121.9, 121.8.




**12-Chloro-2-methoxy-14H-quinazolino[3,2-f]phenanthridin-14-one (4bi):** $R_f$ = 0.45 (hexane/ethyl acetate 4:1); white solid; yield 79% (47 mg); $^1$H NMR (400 MHz, $CDCl_3$ + TFA-D) δ 8.87 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 2.4 Hz, 1H), 8.28 (d, *J* = 2.4 Hz, 1H), 8.20 (d, *J* = 3.2 Hz, 1H), 8.18 (d, *J* = 4.4 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.90 – 7.80 (m, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.16 (dd, *J* = 9.2, 2.4 Hz, 1H), 3.91 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$ + TFA-D) δ 160.3, 148.7, 138.4, 137.1, 135.8, 134.1, 133.3, 132.5, 128.9, 127.8, 127.4, 124.8, 124.2, 122.2, 119.8, 119.6, 116.5, 116.2, 113.8, 106.2, 55.9; IR (KBr) $\tilde{\nu}$ = 3076, 2925, 1678, 1598, 1545, 1456, 1289, 807 cm$^{-1}$; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{14}ClN_2O_2$ $[M + H]^+$ 361.0744, found 361.0775.

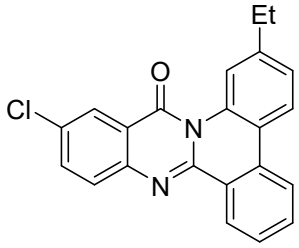



**12-Chloro-2-methyl-14H-quinazolino[3,2-f]phenanthridin-14-one (4bj):** $R_f$ = 0.60 (hexane/ethyl acetate 9:1); white solid; yield 92% (91.4 mg); $^1$H NMR (700 MHz, $CDCl_3$) δ 8.94 (d, *J* = 8.4 Hz, 1H), 8.89 (s, 1H), 8.37 (s, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.75 – 7.69 (m, 3H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 2.51 (s, 3H); $^{13}$C NMR (175 MHz, $CDCl_3$) δ 162.2, 146.9, 144.8, 138.7,

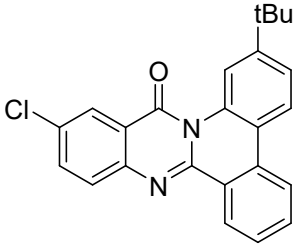


135.1, 132.9, 132.6, 131.9, 131.7, 128.7, 128.4, 128.3, 128.0, 126.8, 126.7, 123.2, 122.5, 121.8, 121.8, 120.8, 22.1; IR (KBr) $\tilde{\nu}$ = 3079, 2916, 1678, 1545, 1465, 1331, 1152 $cm^{-1}$; HR-MS (ESI-TOF) m/z calcd for $C_{21}H_{14}ClN_2O$ $[M + H]^+$ 345.0795, found 345.0818.

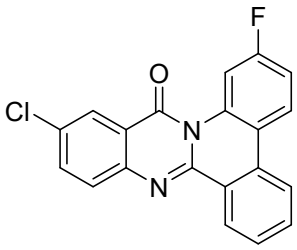
**12-Chloro-2-ethyl-14H-quinazolino[3,2-f]phenanthridin-14-one (4bk):**[3] $R_f$ = 0.65 (hexane/ethyl acetate 9:1); white solid; yield 91% (90.5 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.95 (t, *J* = 2.0 Hz, 1H), 8.93 (d, *J* = 1.2 Hz, 1H), 8.37 (d, *J* = 1.6 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.76 – 7.68 (m, 3H), 7.60 – 7.53 (m, 1H), 7.35 (dd, *J* = 8.0, 1.6 Hz, 1H), 2.81 (q, *J* = 7.6 Hz, 2H), 1.34 (t, *J* = 7.6 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 162.2, 147.0, 145.0, 144.8, 135.1, 133.1, 132.6, 131.9, 131.7, 128.7, 128.4 (×2), 128.3, 126.8, 126.8, 126.7, 123.3, 121.8, 121.5, 121.0, 29.4, 15.6.



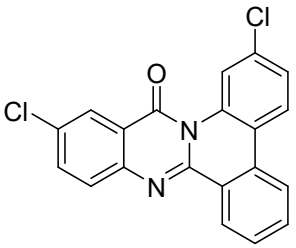

**2-(Tert-butyl)-12-chloro-14H-quinazolino[3,2-f]phenanthridin-14-one (4bl):**[3] $R_f$ = 0.65 (hexane/ethyl acetate 9:1); white solid; yield 81% (80 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.18 (d, *J* = 2.0 Hz, 1H), 8.91 – 8.85 (m, 1H), 8.40 – 8.35 (m, 1H), 8.15 (d, *J* = 2.8 Hz, 1H), 8.13 (d, *J* = 3.2 Hz, 1H), 7.72 – 7.62 (m, 3H), 7.52 (dt, *J* = 7.6, 4.0 Hz, 2H), 1.44 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 162.2, 151.7, 147.0, 144.7, 134.9, 132.9, 132.5, 131.8, 131.5, 128.7, 128.3, 128.3, 126.8, 126.7, 124.3, 122.8, 121.8, 121.7, 120.7, 119.4, 35.5, 31.4.



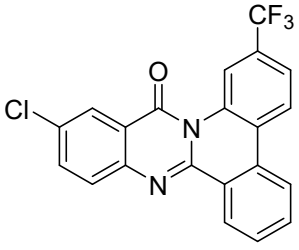
**12-Chloro-2-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one (4bm):**[3] $R_f$ = 0.60 (hexane/ethyl acetate 9:1); white solid; yield 85% (58 mg); $^1$H NMR (700 MHz, $CDCl_3$) δ 9.02 (d, *J* = 12.6 Hz, 1H), 8.98 (d, *J* = 8.4 Hz, 1H), 8.38 (s, 1H), 8.28 – 8.21 (m, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.80 – 7.72 (m, 3H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.26 (s, 1H); $^{13}$C NMR (175 MHz, $CDCl_3$) δ 161.9, 161.8 (d, *J* = 247.3 Hz), 146.5, 144.5, 135.3, 134.1 (d, *J* = 11.1 Hz), 132.6, 132.1, 130.9, 128.7, 128.5, 128.4, 126.8, 126.5, 124.7 (d, *J* = 9.6 Hz), 121.7, 121.5, 119.6, 114.6 (d, *J* = 22.6 Hz), 109.7 (d, *J* = 29.6 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -109.33.




**2,12-Dichloro-14H-quinazolino[3,2-f]phenanthridin-14-one (4bn):**[3] $R_f$ = 0.60 (hexane/ethyl acetate 9:1); white solid; yield 78% (46.5 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 9.24 (d, *J* = 2.0 Hz, 1H), 8.99 (d, *J* = 8.0 Hz, 1H), 8.39 (s, 1H), 8.20 (d, *J* = 4.0 Hz, 1H), 8.18 (d, *J* = 3.6 Hz, 1H), 7.77 (d, *J* = 3.2 Hz, 3H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.49 (dd, *J* = 8.4, 2.0 Hz, 1H).

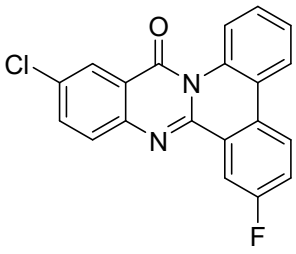



**12-Chloro-2-(trifluoromethyl)-14H-quinazolino[3,2-f]phenanthridin-14-one (4bo):** $R_f$ = 0.80 (hexane/ethyl acetate 4:1); white solid; yield 83% (49.5 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 8.98 (d, *J* = 8.0 Hz, 1H), 8.39 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.81 – 7.72 (m, 4H), 7.67 (t, *J* = 7.6 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.0, 146.2, 144.5, 135.5, 133.1, 132.9, 132.6, 130.3, 130.2, 129.9, 128.9, 128.6, 127.7, 126.9, 126.1, 123.9, 123.9 (q, *J* = 271.2 Hz), 123.3 (q, *J* = 3.4 Hz), 122.5, 121.7, 119.8 (q, *J* = 4.2 Hz); IR (KBr) $\tilde{\nu}$ = 3079, 2920, 1677, 1548, 1326, 1231, 1108, 828 cm$^{-1}$; HR-MS (ESI-TOF) m/z



calcd for $C_{21}H_{11}ClF_3N_2O$ $[M + H]^+$ 399.0512, found 399.0544. $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -62.52.

**12-Chloro-7-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one (4bp):**[3] $R_f$ = 0.60 (hexane/ethyl acetate 9:1); white solid; yield 87% (52.0 mg); $^1H$ NMR (400 MHz, $CDCl_3$ + TFA-D) δ 8.96 – 8.89 (m, 1H), 8.72 (d, *J* = 7.6 Hz, 1H), 8.57 (dd, *J* = 9.2, 4.8 Hz, 1H), 8.43 (d, *J* = 1.6 Hz, 2H), 8.06 (d, *J* = 8.8 Hz, 1H), 8.03 – 7.95 (m, 1H), 7.85 (t, *J* = 7.2 Hz, 1H), 7.81 – 7.70 (m, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$ + TFA-D) δ 163.1 (d, *J* = 255.1 Hz), 158.6, 148.4 (d, *J* = 3.4 Hz), 138.3, 135.9, 135.4, 130.7, 130.2, 130.2, 129.5, 128.0, 126.3, 126.2 (d, *J* = 4.5 Hz), 125.9, 123.8, 122.3 (d, *J* = 29.8 Hz), 122.2, 120.1 (d, *J* = 8.8 Hz), 119.2, 113.3 (d, *J* = 25.8 Hz). $^{19}F$ NMR (376 MHz, $CDCl_3$ + TFA-D) δ -111.19.

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2. S. Singh, N. Dagar and S. R. Roy, *Chem. Commun.*, 2022, **58**, 3831.
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4. P. K. Gupta, N. Yadav, S. Jaiswal, M. Asad, R. Kant and K. Hajela, *Chem. Eur. J.*, 2015, **21**, 13210.
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## NMR Spectra

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

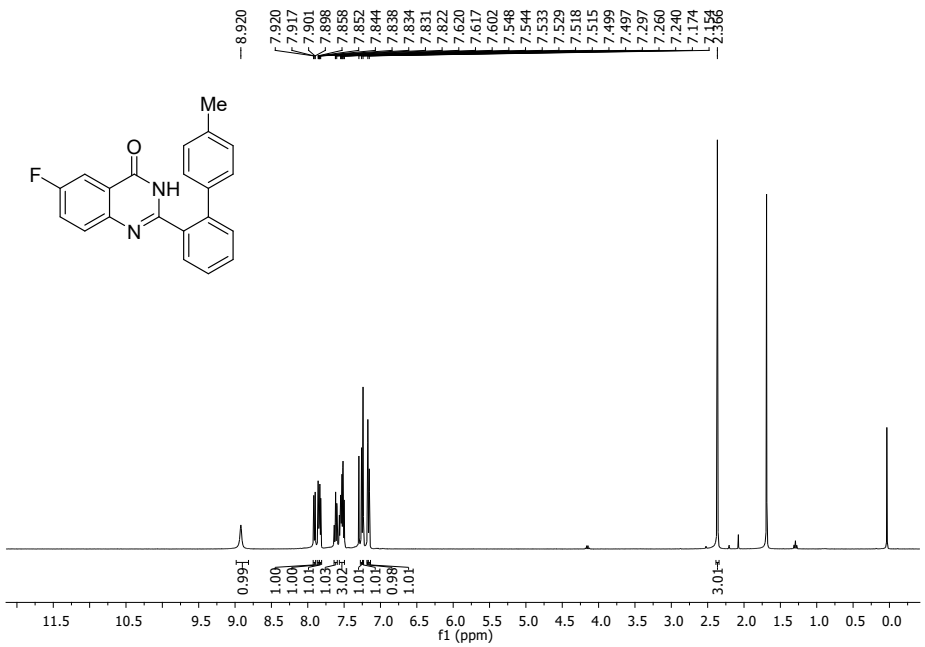



**Figure S7.** $^{1}$H NMR spectrum of 6-fluoro-2-(4'-methyl-[1,1'-biphenyl]-2-yl)quinazolin-4(3H)-one **(3bd)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

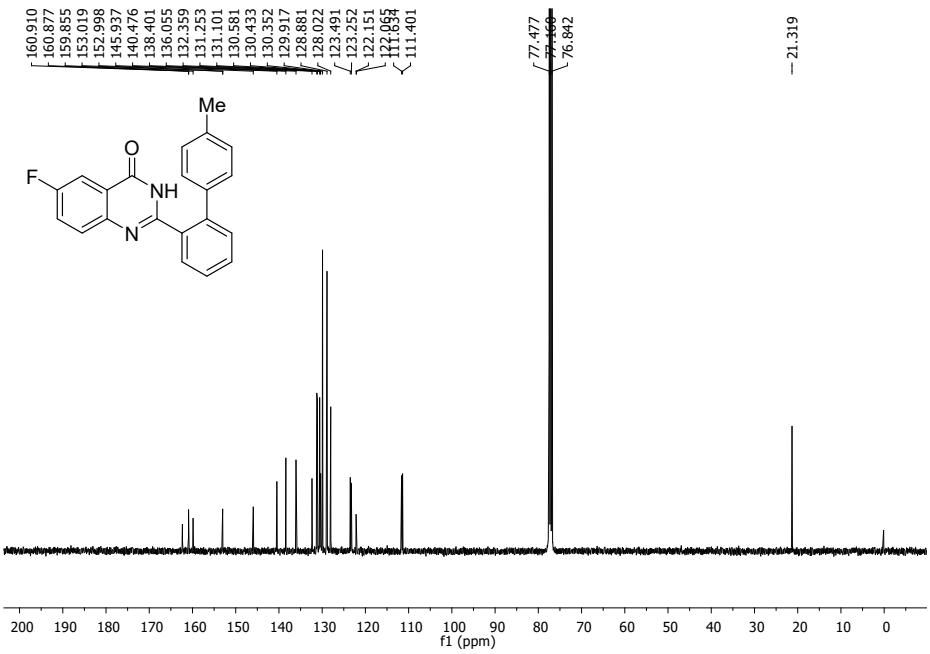



**Figure S8.** $^{13}$C NMR spectrum of 6-fluoro-2-(4'-methyl-[1,1'-biphenyl]-2-yl)quinazolin-4(3H)-one **(3bd)**

**$^{19}$F NMR (376 MHz, $CDCl_3$)**

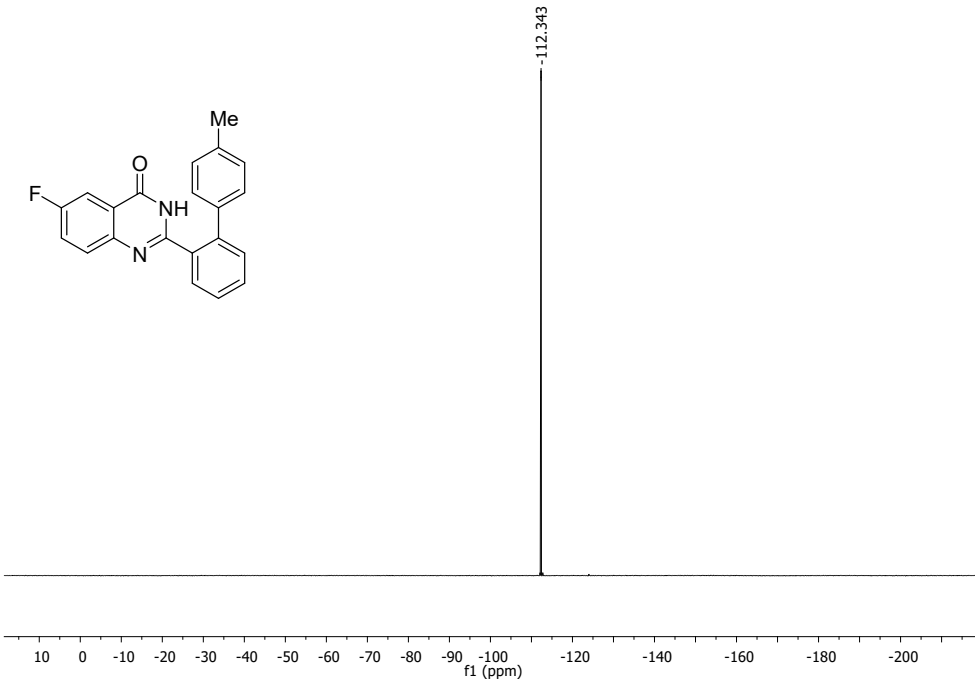



**Figure S9.** $^{19}$F NMR spectrum of 6-fluoro-2-(4'-methyl-[1,1'-biphenyl]-2-yl)quinazolin-4(3H)-one **(3bd)**

**$^{1}$H NMR (700 MHz, $CDCl_3$)**

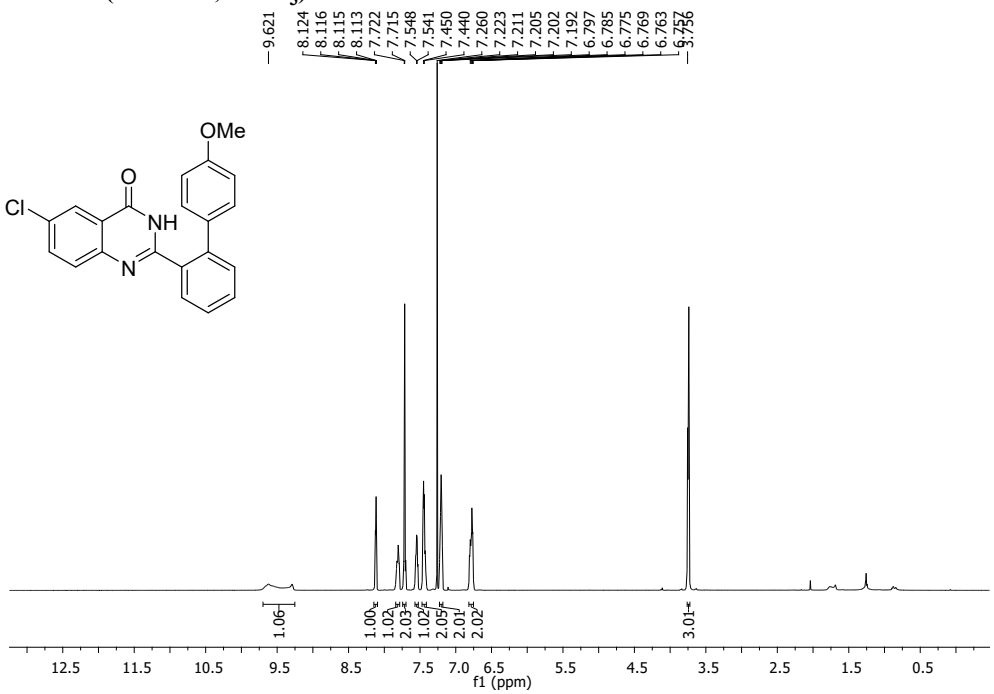



**Figure S10.** $^{1}$H NMR spectrum of 6-chloro-2-(4'-methoxy-[1,1'-biphenyl]-2-yl)quinazolin-4(3H)-one **(3bh)**

**$^{13}$C NMR (175 MHz, $CDCl_3$)**

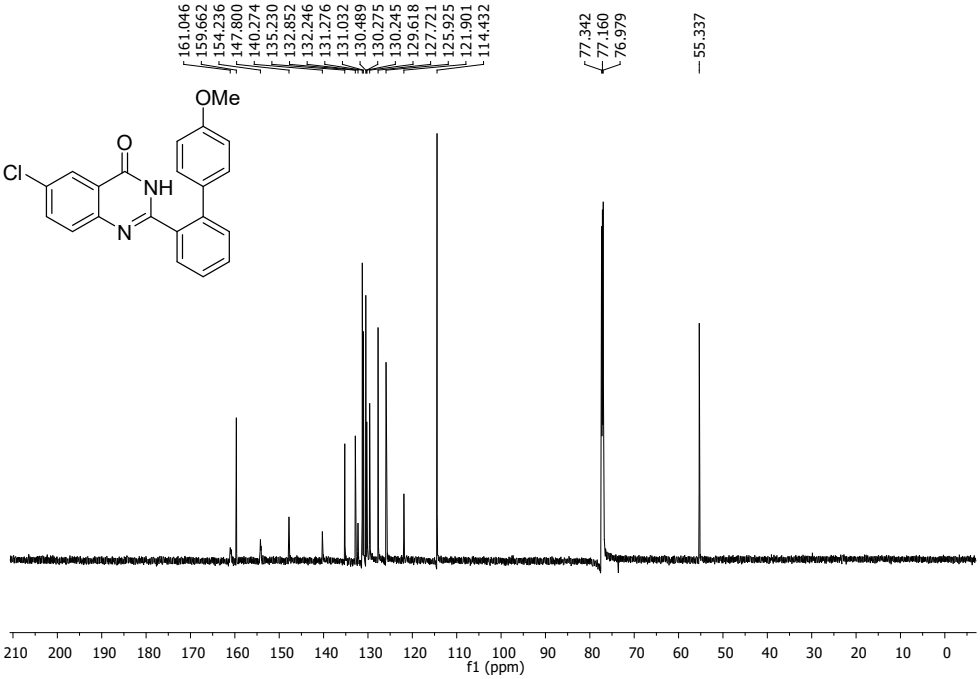



**Figure S11.** $^{13}$C NMR spectrum of 6-chloro-2-(4'-methoxy-[1,1'-biphenyl]-2-yl)quinazolin-4(3H)-one **(3bh)**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

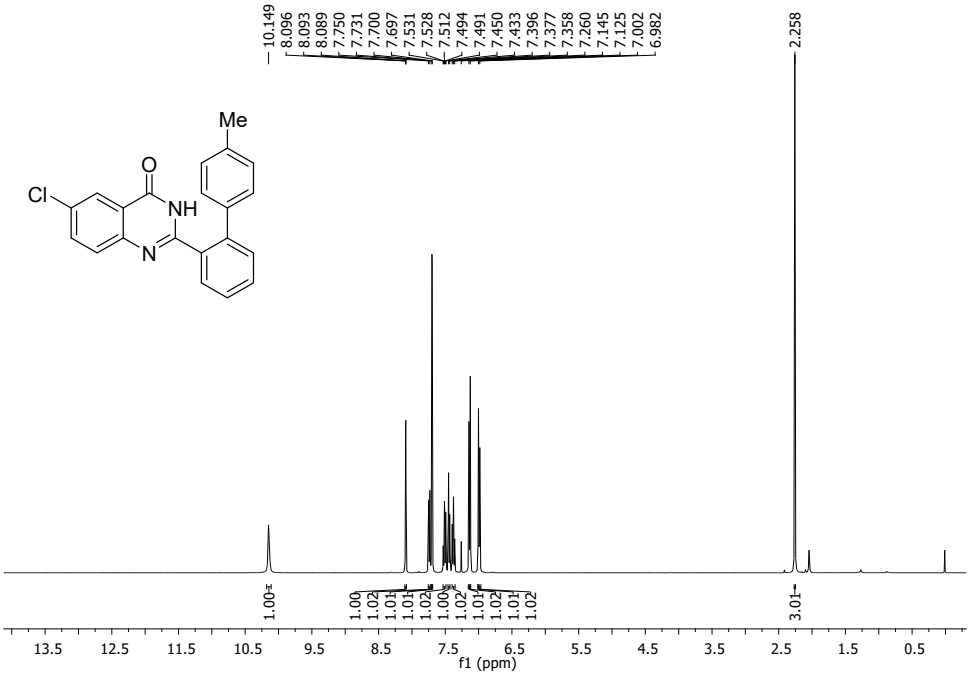



**Figure S12.** $^{1}$H NMR spectrum of 6-chloro-2-(4'-methyl-[1,1'-biphenyl]-2-yl)quinazolin-4(3H)-one **(3bj)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

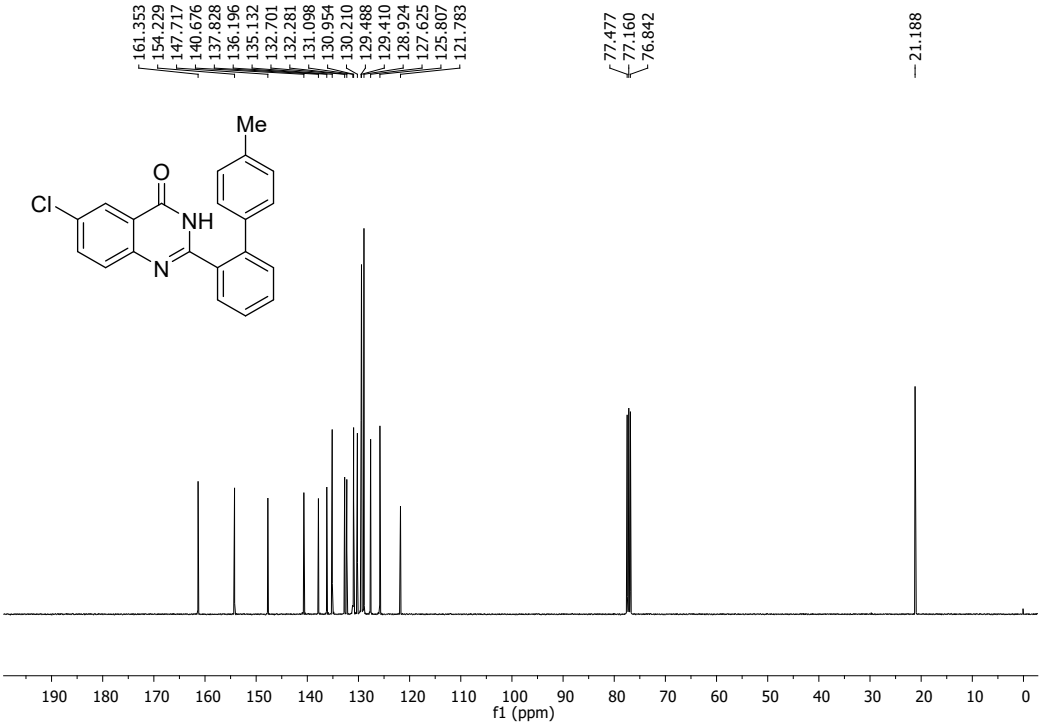



**Figure S13.** $^{13}$C NMR spectrum of 6-chloro-2-(4'-methyl-[1,1'-biphenyl]-2-yl)quinazolin-4(3H)-one **(3bj)**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

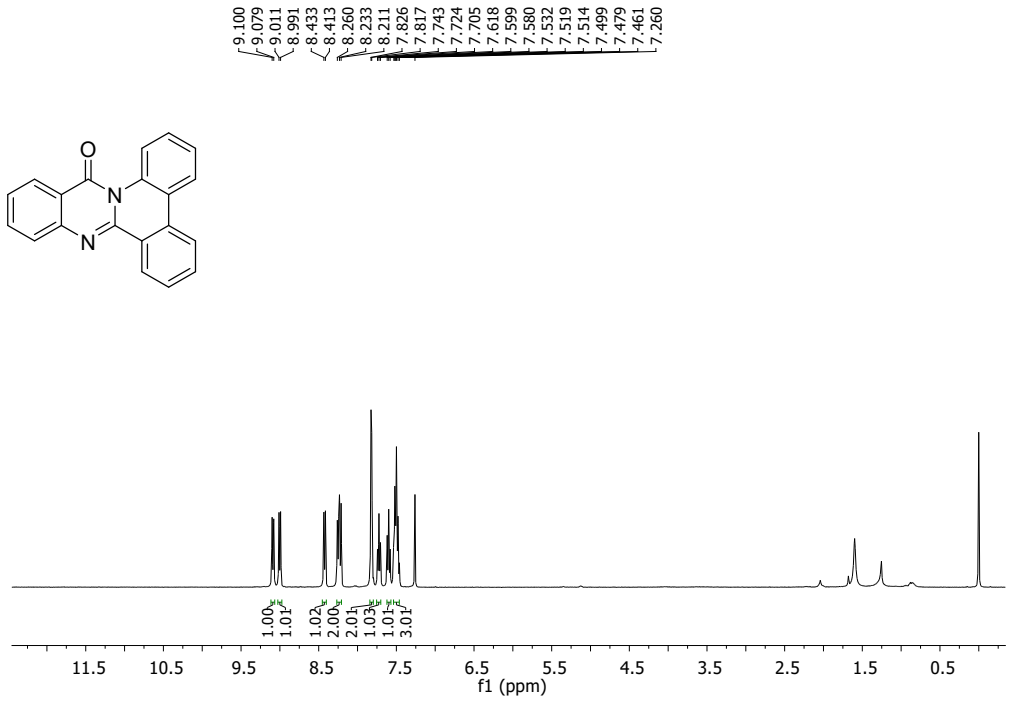



**Figure S14.** $^{1}$H NMR spectrum of 14H-quinazolino[3,2-f]phenanthridin-14-one **(2aa)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

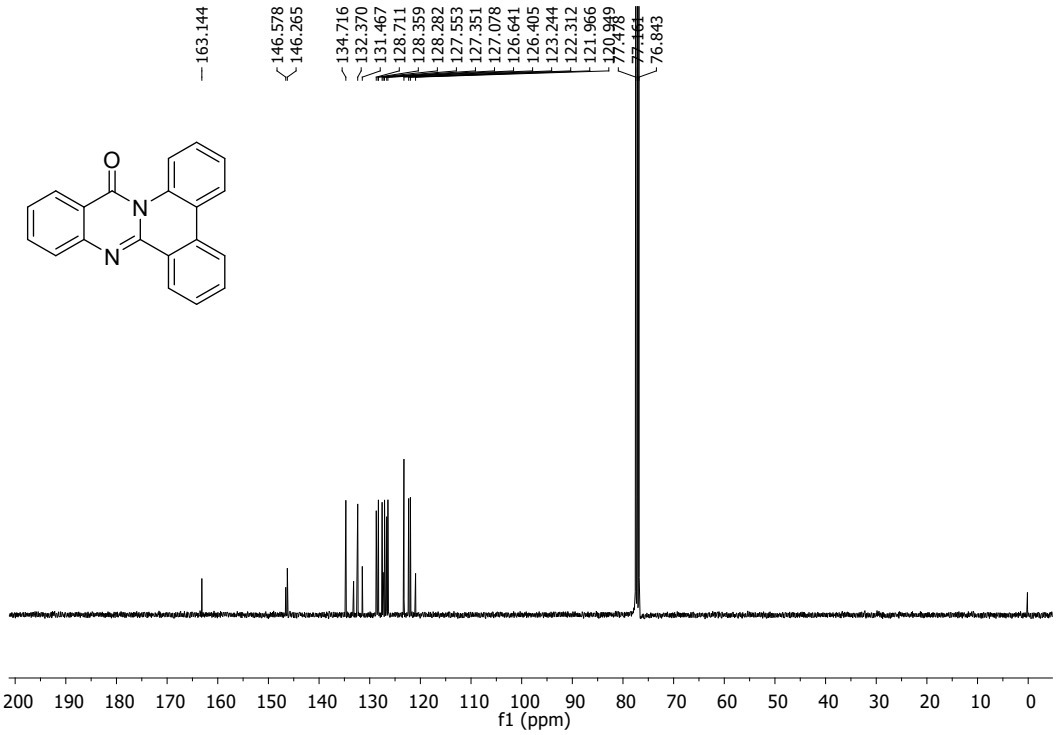



**Figure S15.** $^{13}$C NMR spectrum of 14H-quinazolino[3,2-f]phenanthridin-14-one **(2aa)**

**$^{1}$H NMR (700 MHz, $CDCl_3$)**

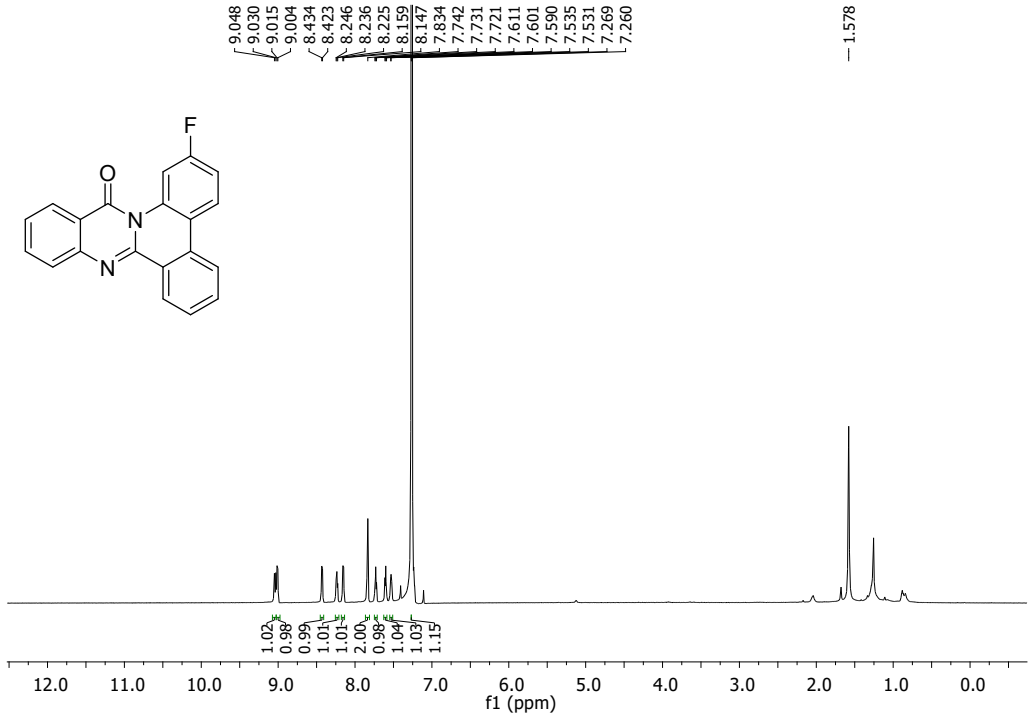



**Figure S16.** $^{1}$H NMR spectrum of 2-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one one **(2ab)**

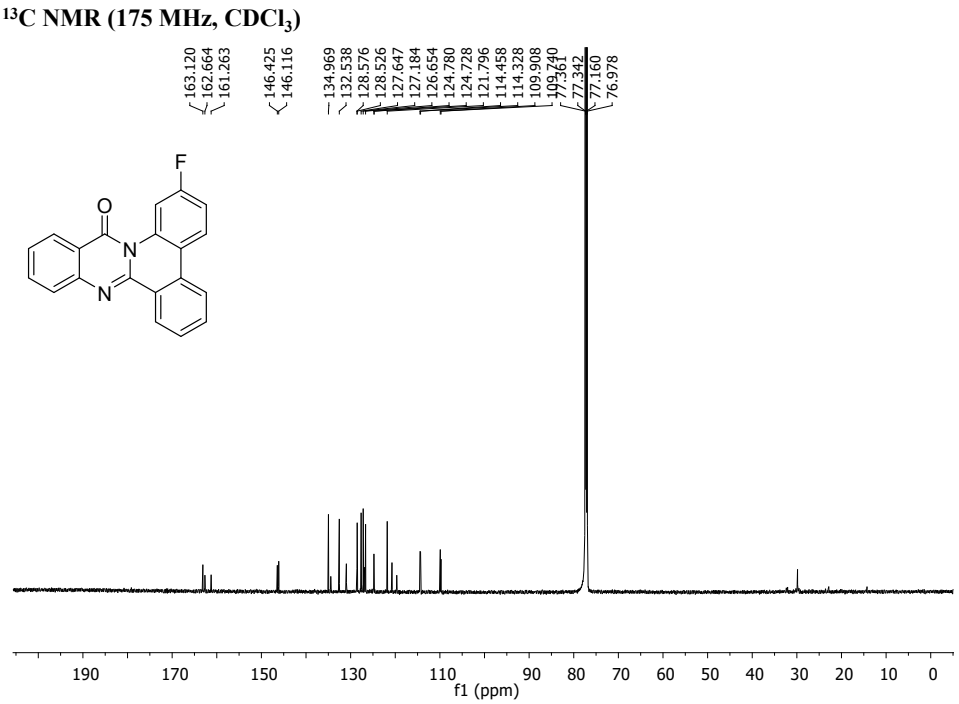



**Figure S17.** $^{13}$C NMR spectrum of 2-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one one **(2ab)**

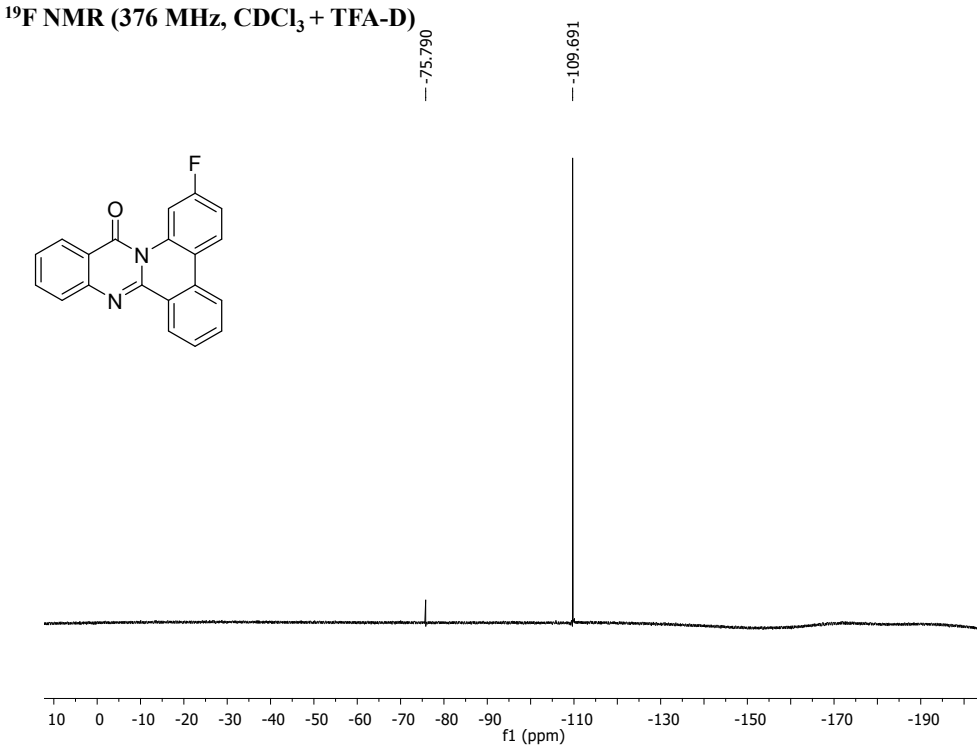



**Figure S18.** $^{19}$F NMR spectrum of 2-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one one **(2ab)**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

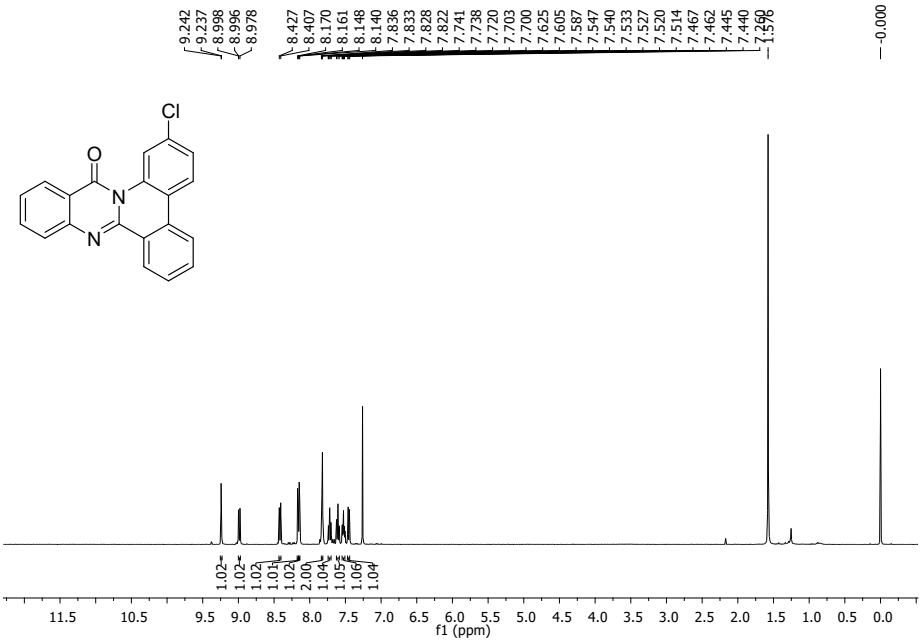



**Figure S19.** $^{1}$H NMR spectrum of 2-chloro-14H-quinazolino[3,2-f]phenanthridin-14-one **(2ac)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

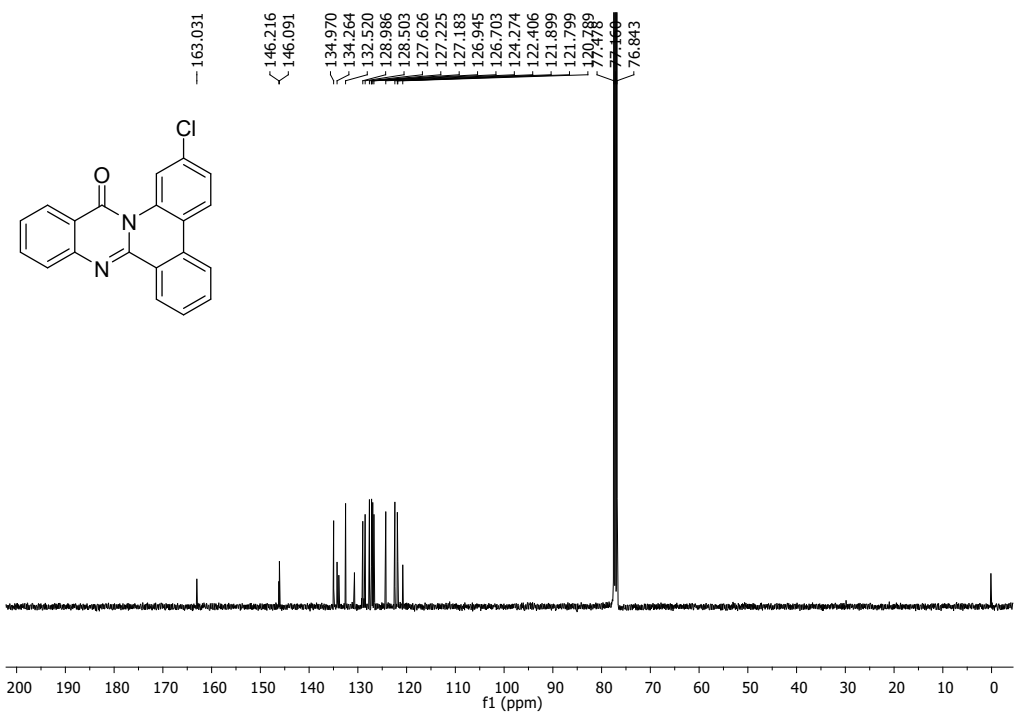



**Figure S20.** $^{13}$C NMR spectrum of 2-chloro-14H-quinazolino[3,2-f]phenanthridin-14-one **(2ac)**

**$^{1}$H NMR (700 MHz, $CDCl_3$)**

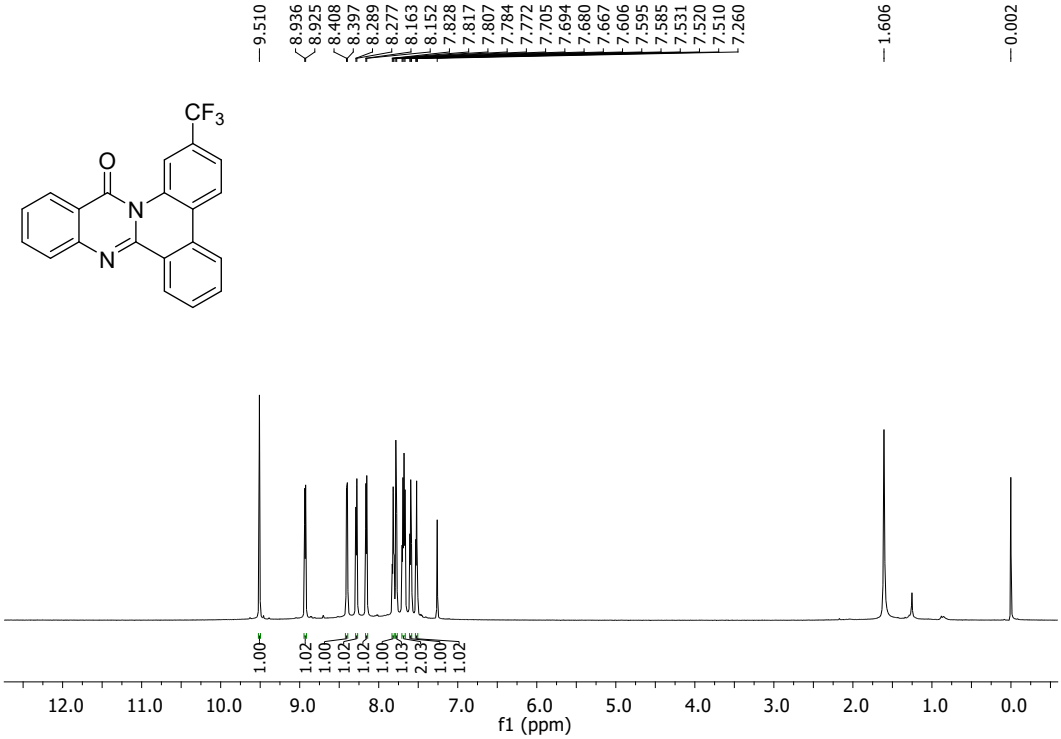



**Figure S21.** $^{1}$H NMR spectrum of 2-(trifluoromethyl)-14H-quinazolino[3,2-f]phenanthridin-14-one **(2ad)**

**$^{13}$C NMR (175 MHz, $CDCl_3$)**

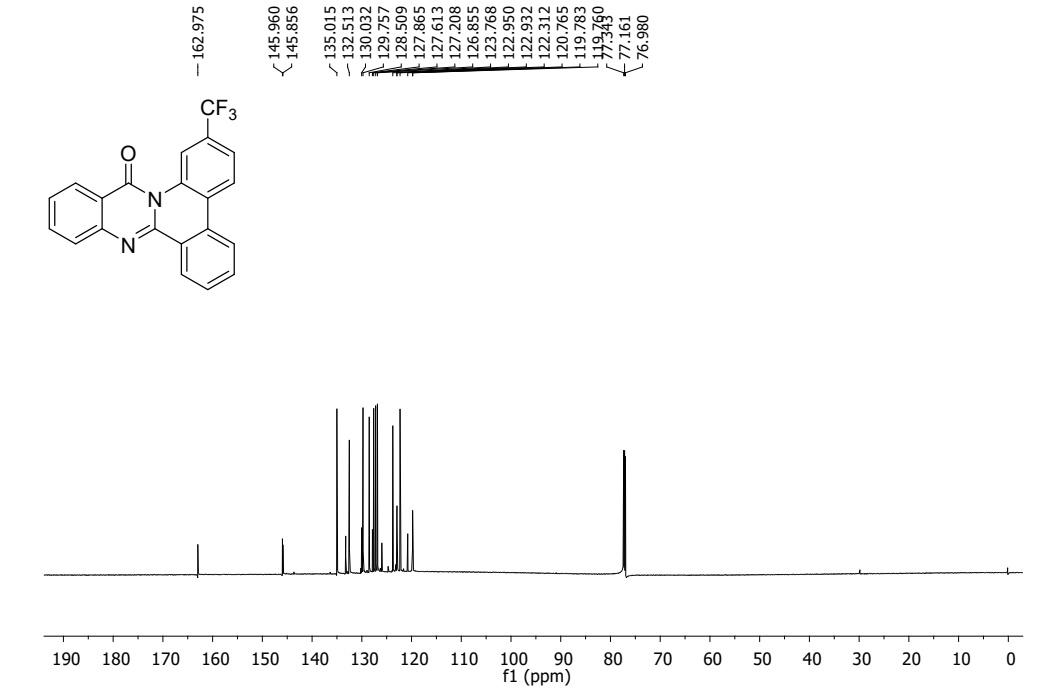



**Figure S22.** $^{13}$C NMR spectrum of 2-(trifluoromethyl)-14H-quinazolino[3,2-f]phenanthridin-14-one **(2ad)**

**$^{19}$F NMR (376 MHz, $CDCl_3$)**

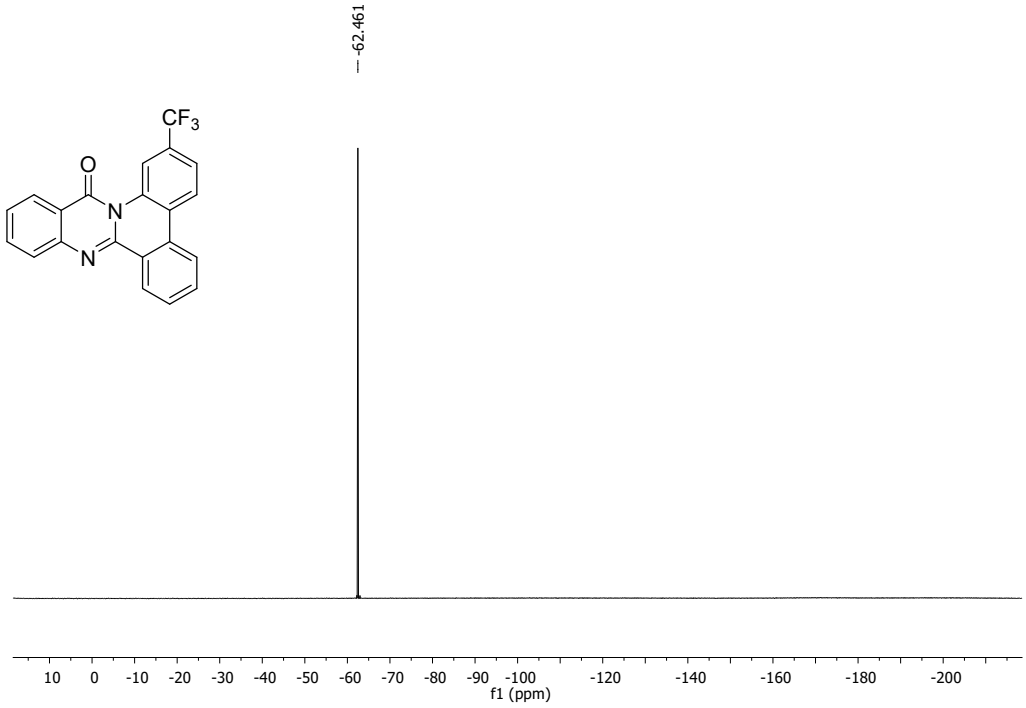



**Figure S23.** $^{19}$F NMR spectrum of 2-(trifluoromethyl)-14H-quinazolino[3,2-f]phenanthridin-14-one **(2ad)**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

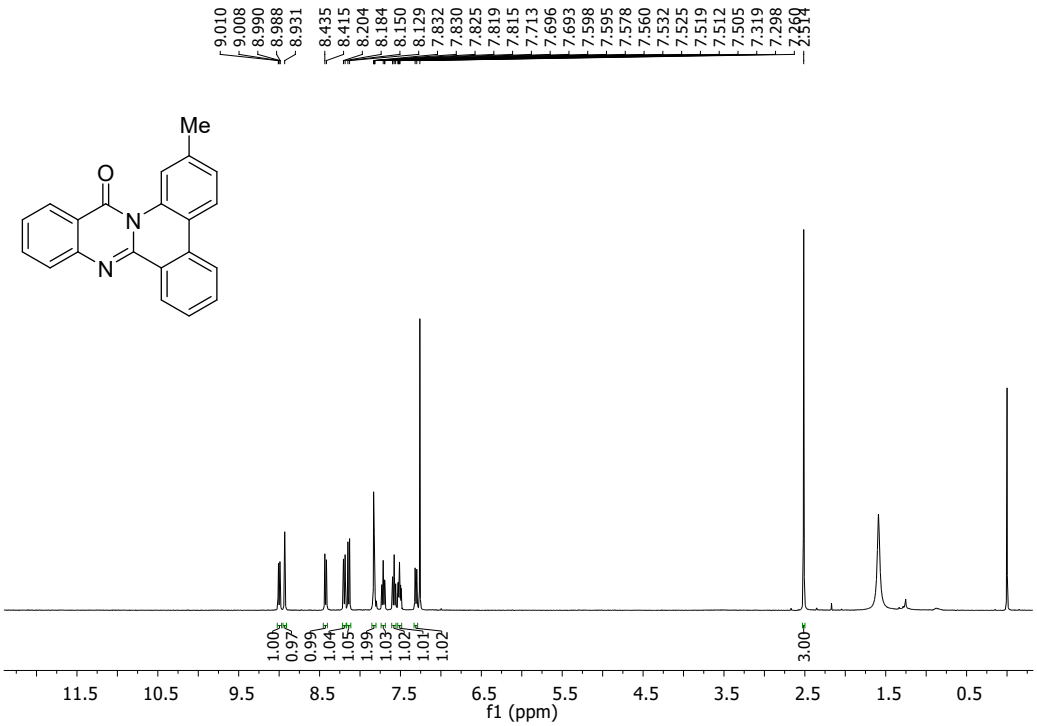



**Figure S24.** $^{1}$H NMR spectrum of 2-methyl-14H-quinazolino[3,2-f]phenanthridin-14-one **(2ae)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

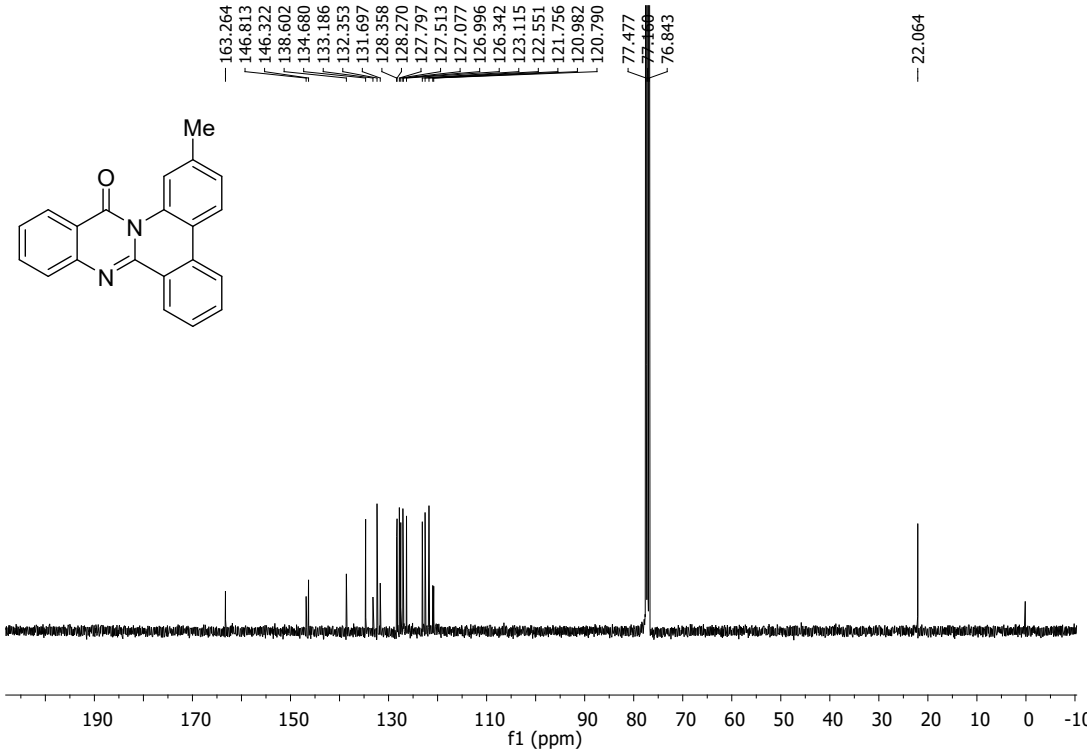



**Figure S25.** $^{13}$C NMR spectrum of 2-methyl-14H-quinazolino[3,2-f]phenanthridin-14-one **(2ae)**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

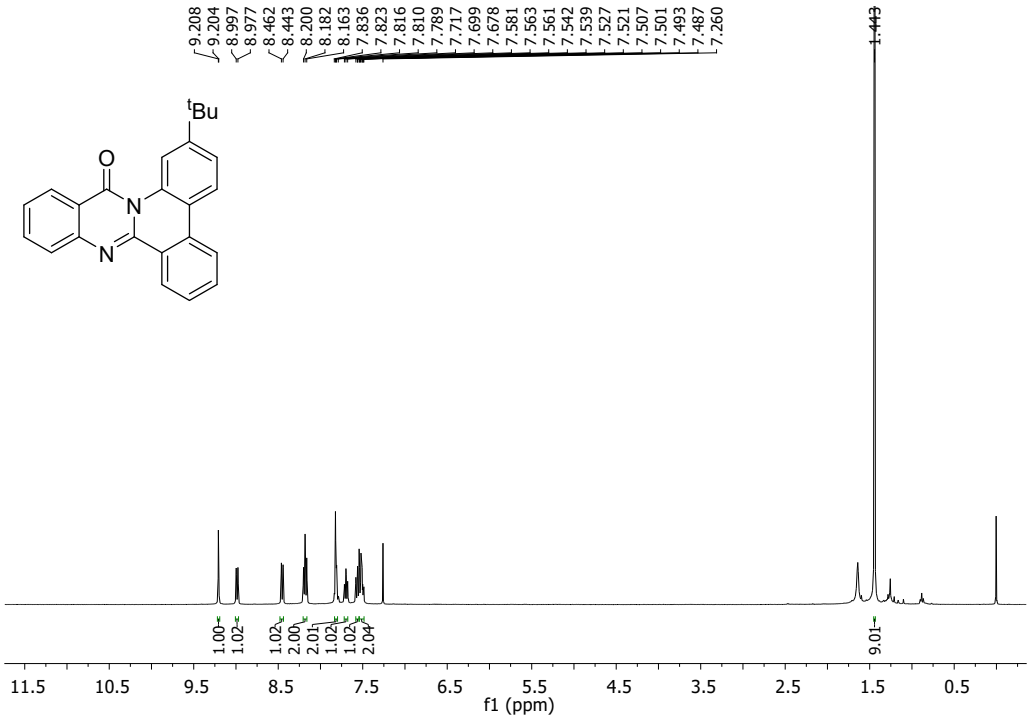



**Figure S26.** $^{1}$H NMR spectrum of 2-(tert-butyl)-14H-quinazolino[3,2-f]phenanthridin-14-one **(2af)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

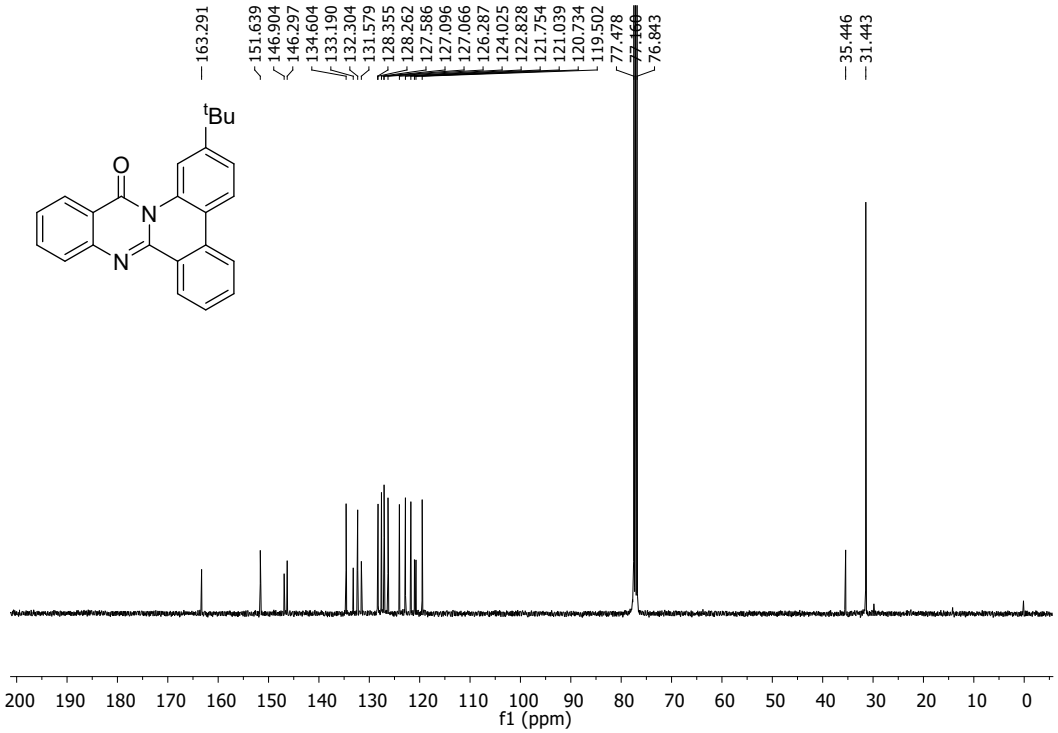



**Figure S27.** $^{13}$C NMR spectrum of 2-(tert-butyl)-14H-quinazolino[3,2-f]phenanthridin-14-one **(2af)**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

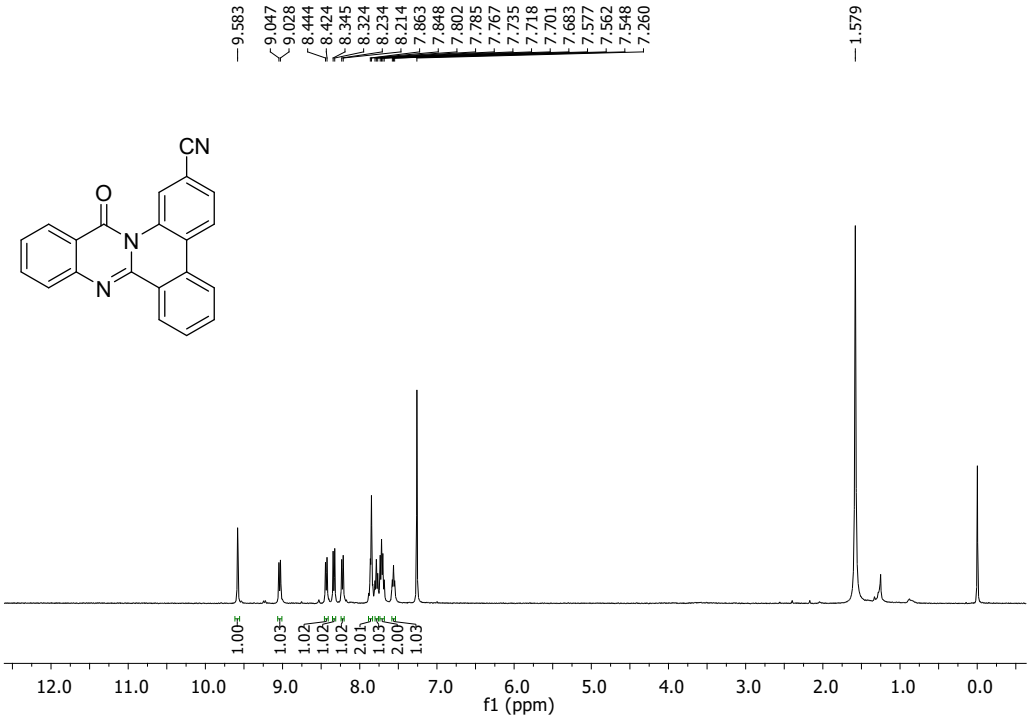



**Figure S28.** $^{1}$H NMR spectrum of 14-oxo-14H-quinazolino[3,2-f]phenanthridine-2-carbonitrile **(2ag)**

**$^{13}$C NMR (175 MHz, $CDCl_3$)**

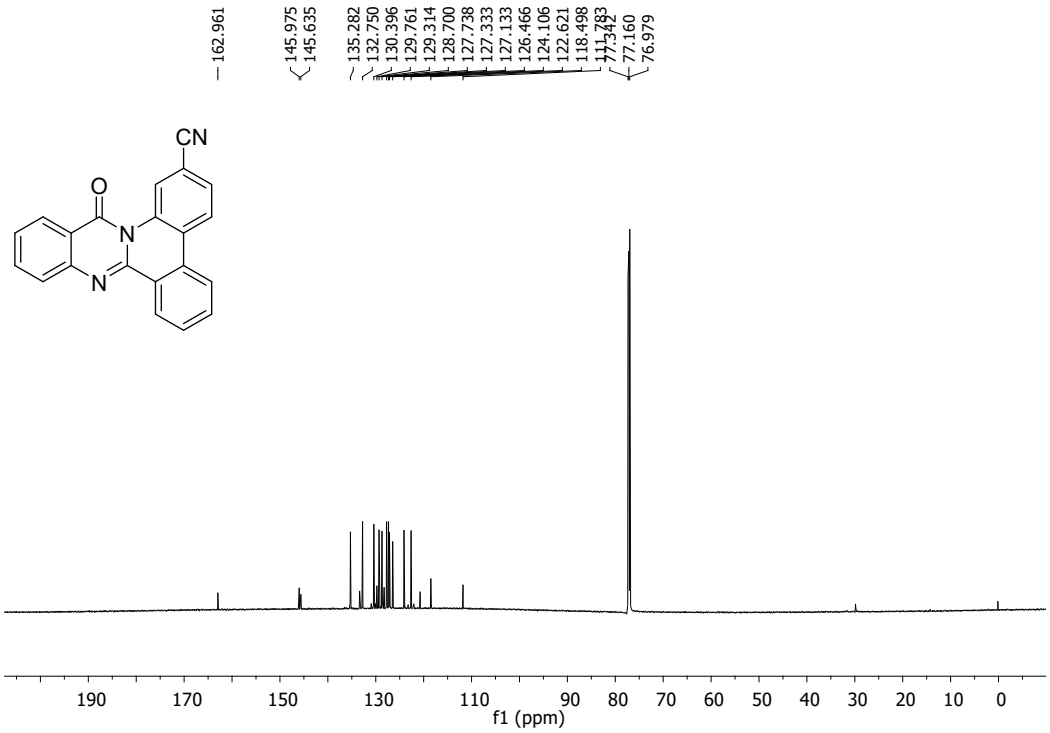



**Figure S29.** $^{13}$C NMR spectrum of 14-oxo-14H-quinazolino[3,2-f]phenanthridine-2-carbonitrile **(2ag)**

**$^{1}$H NMR (700 MHz, $CDCl_3$)**

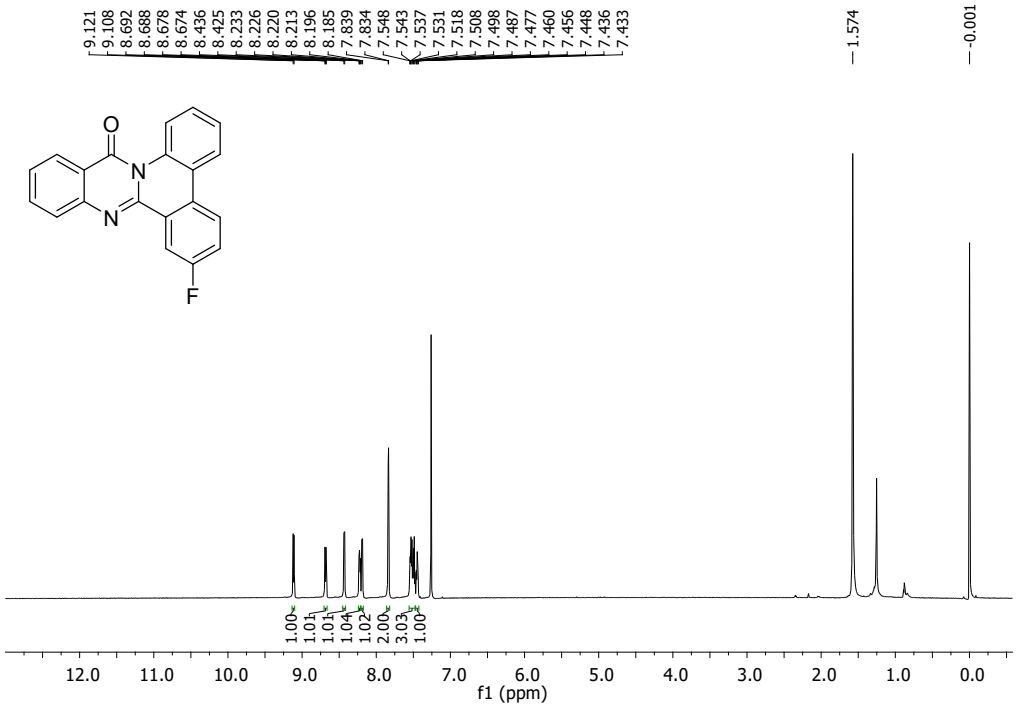



**Figure S30.** $^{1}$H NMR spectrum of 7-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(2ah)**

**$^{13}$C NMR (175 MHz, $CDCl_3$)**

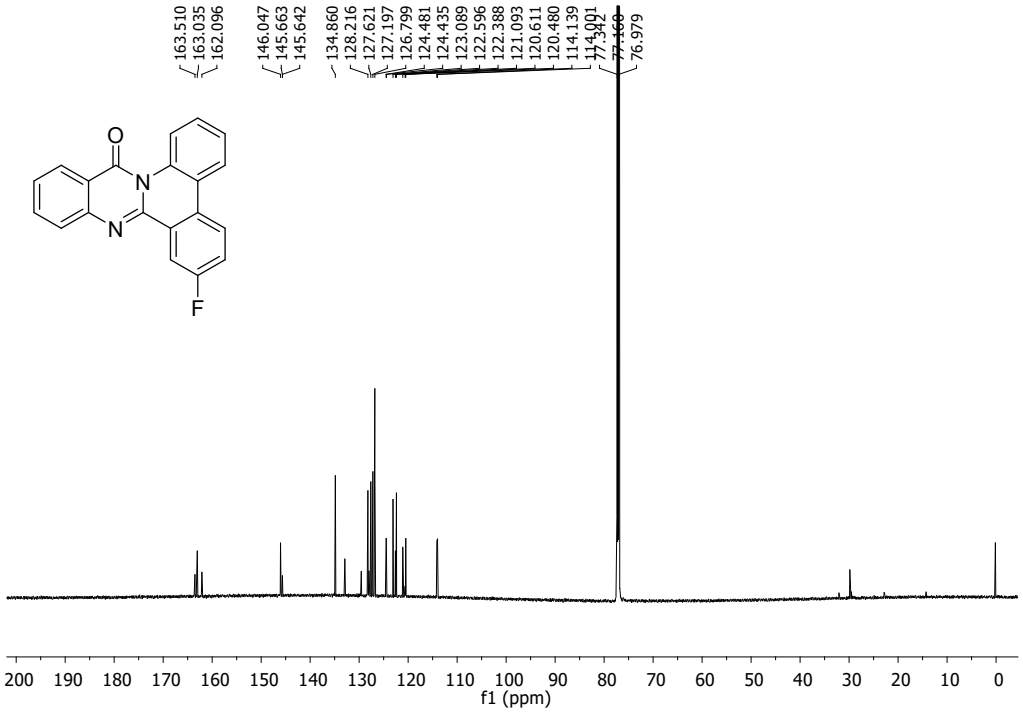



**Figure S31.** $^{13}$C NMR spectrum of 7-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(2ah)**

**$^{19}$F NMR (376 MHz, $CDCl_3$)**

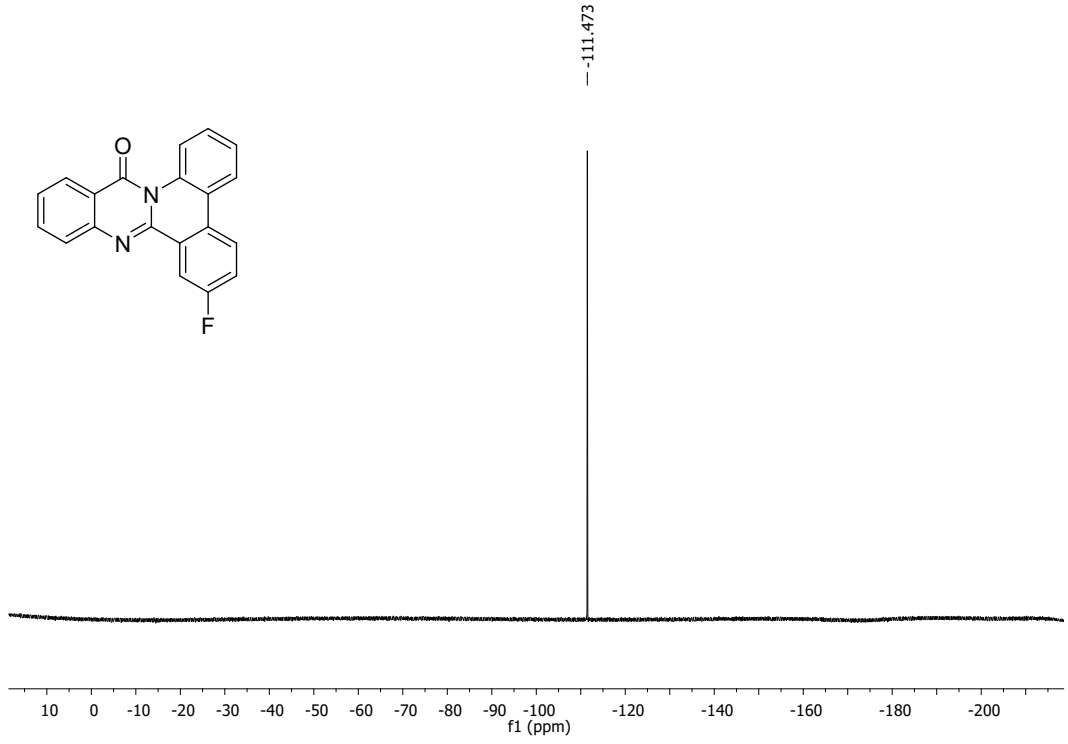



**Figure S32.** $^{19}$F NMR spectrum of 7-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(2ah)**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

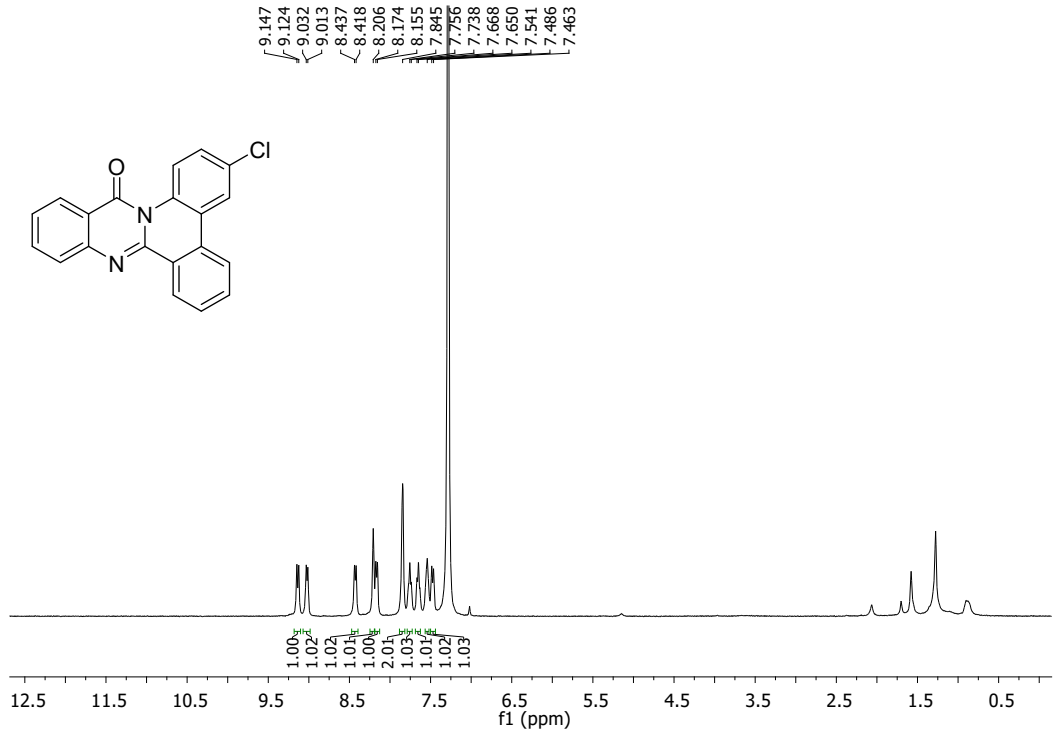



**Figure S33.** $^{1}$H NMR spectrum of 3-chloro-14H-quinazolino[3,2-f]phenanthridin-14-one **(2ai)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

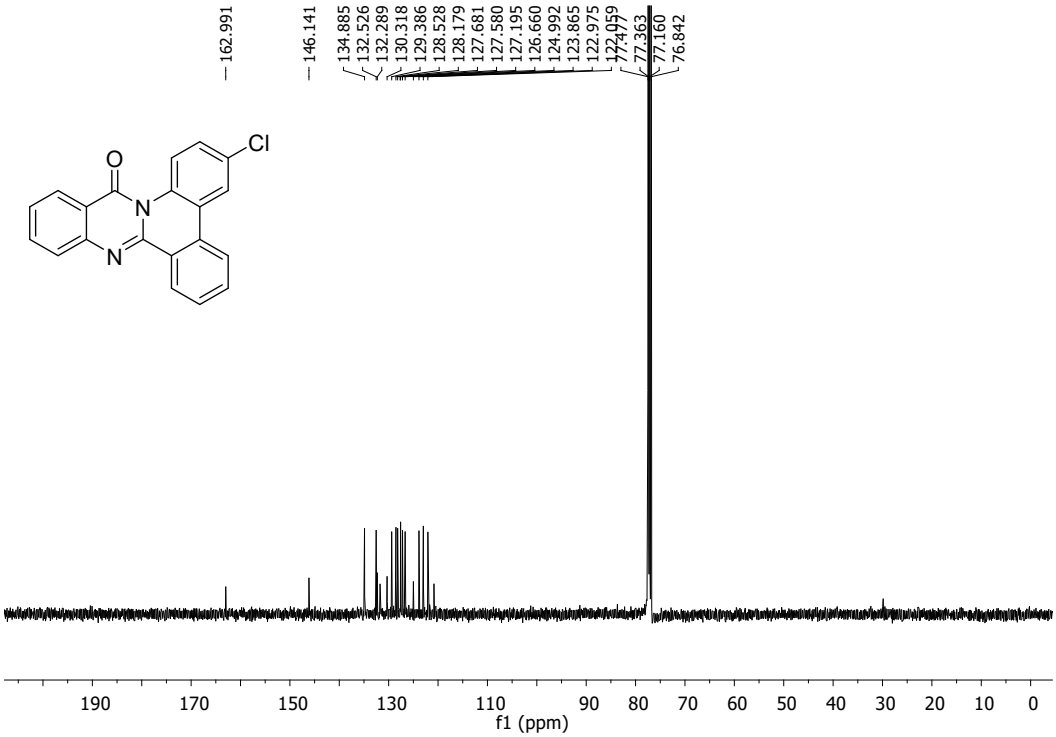



**Figure S34.** $^{13}$C NMR spectrum of 3-chloro-14H-quinazolino[3,2-f]phenanthridin-14-one **(2ai)**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

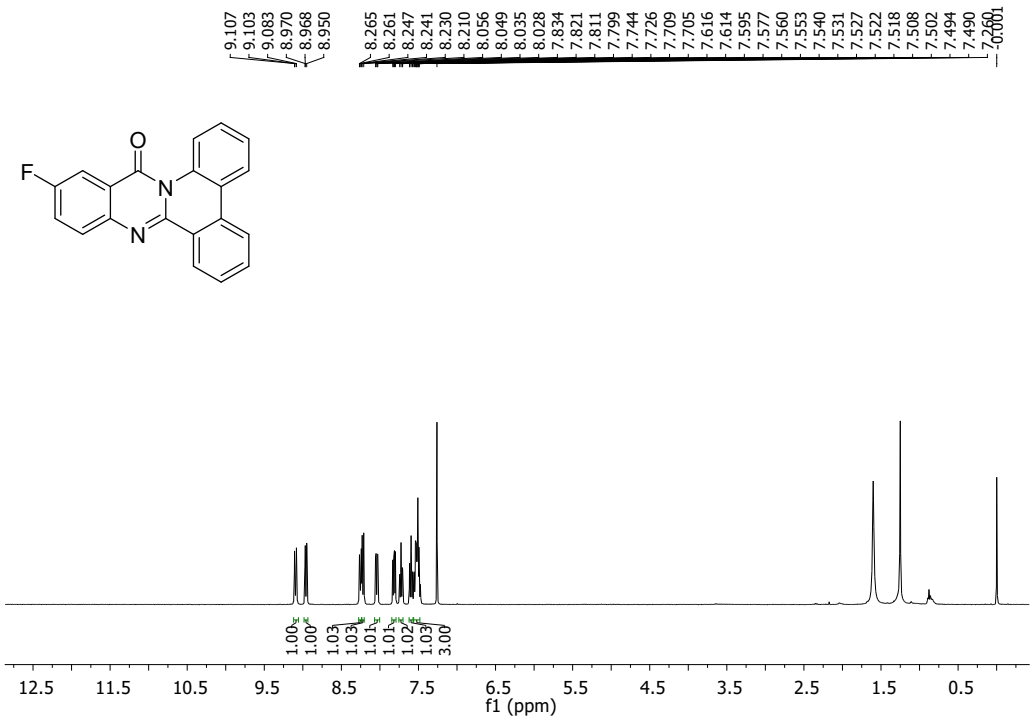



**Figure S35.** $^{1}$H NMR spectrum of 12-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4ba)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

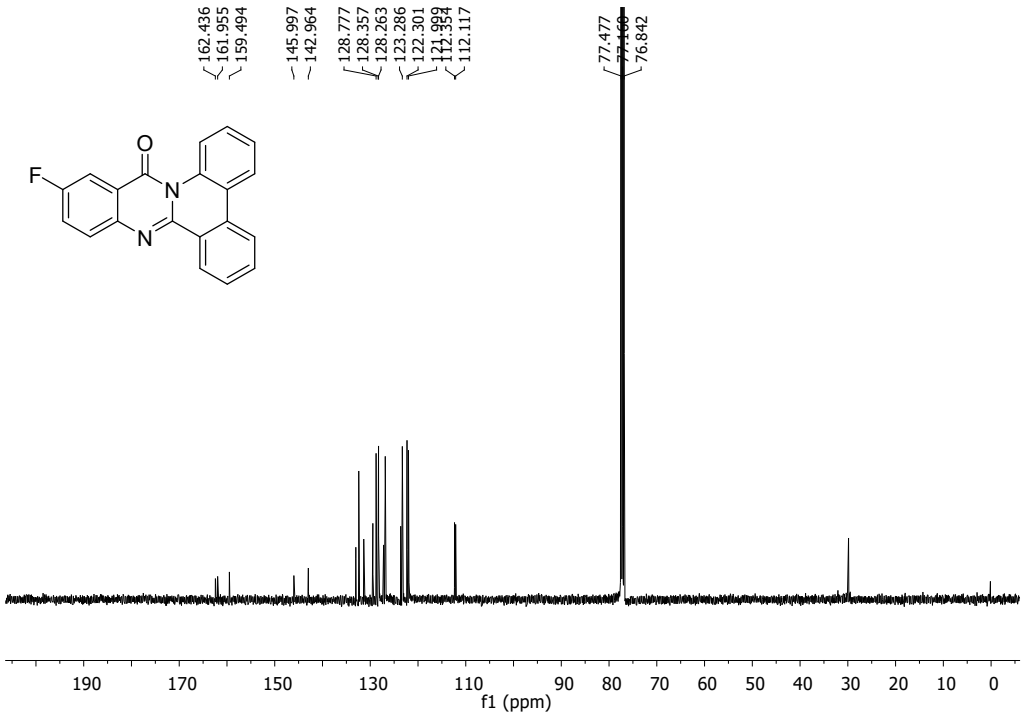



**Figure S36.** $^{13}$C NMR spectrum of 12-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4ba)**

**$^{19}$F NMR (376 MHz, $CDCl_3$)**

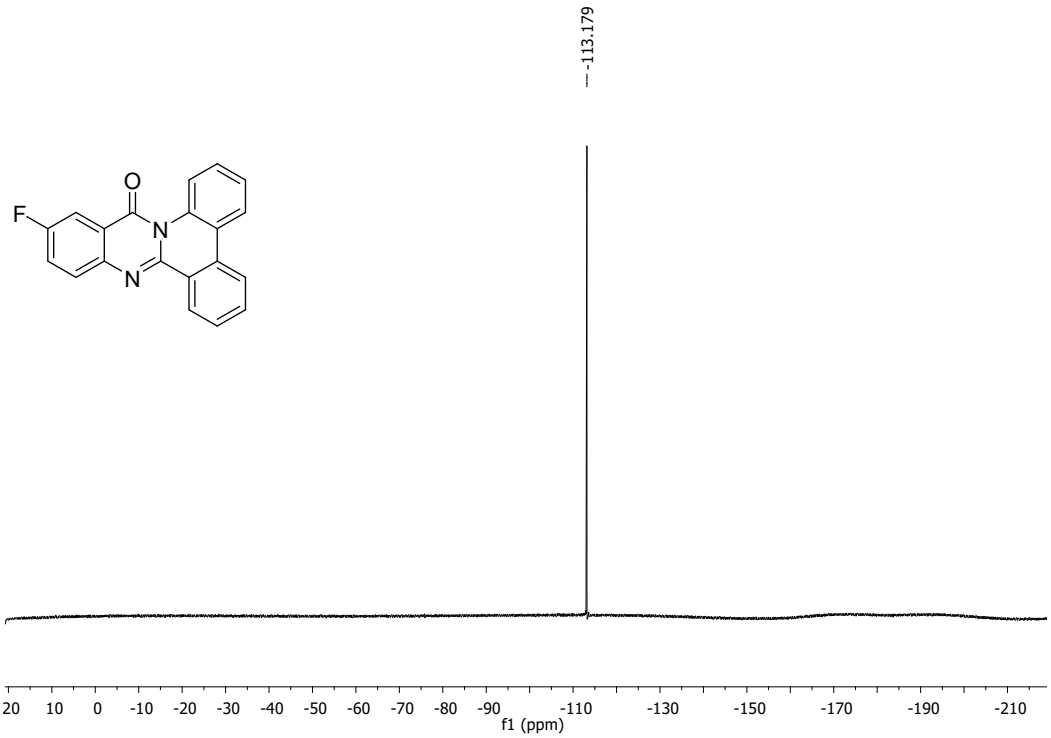



**Figure S37.** $^{19}$F NMR spectrum of 12-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4ba)**

**$^{1}$H NMR (700 MHz, $CDCl_3$)**

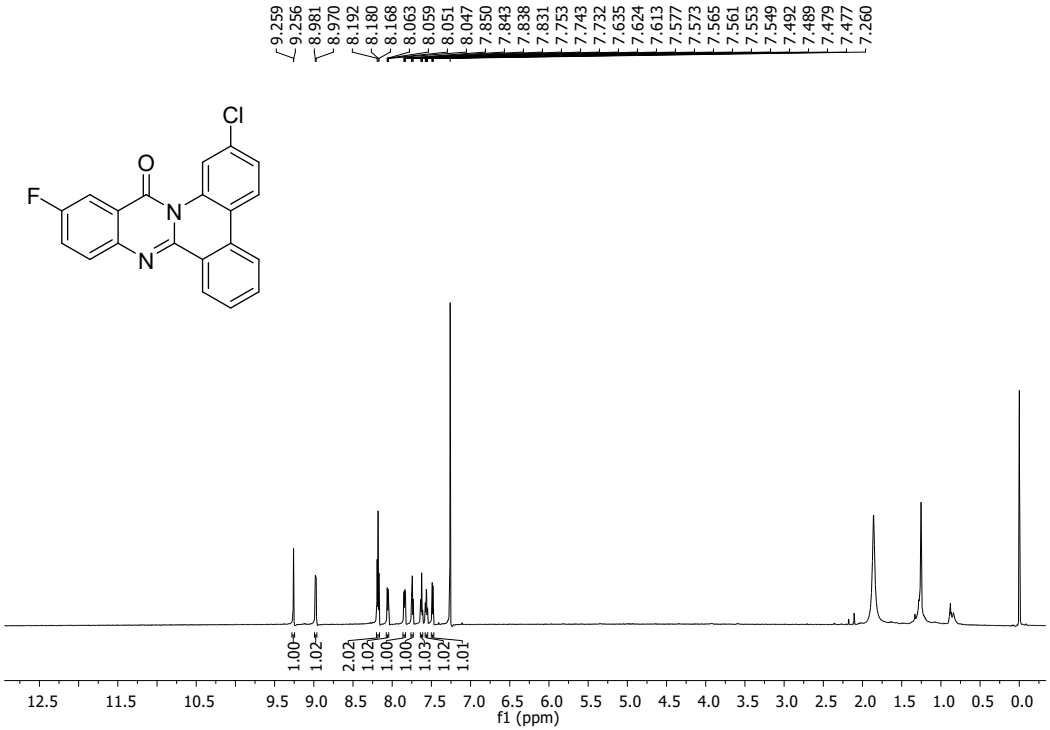



**Figure S38.** $^{1}$H NMR spectrum of 2-chloro-12-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bb)**

**$^{13}$C NMR (175 MHz, $CDCl_3$)**

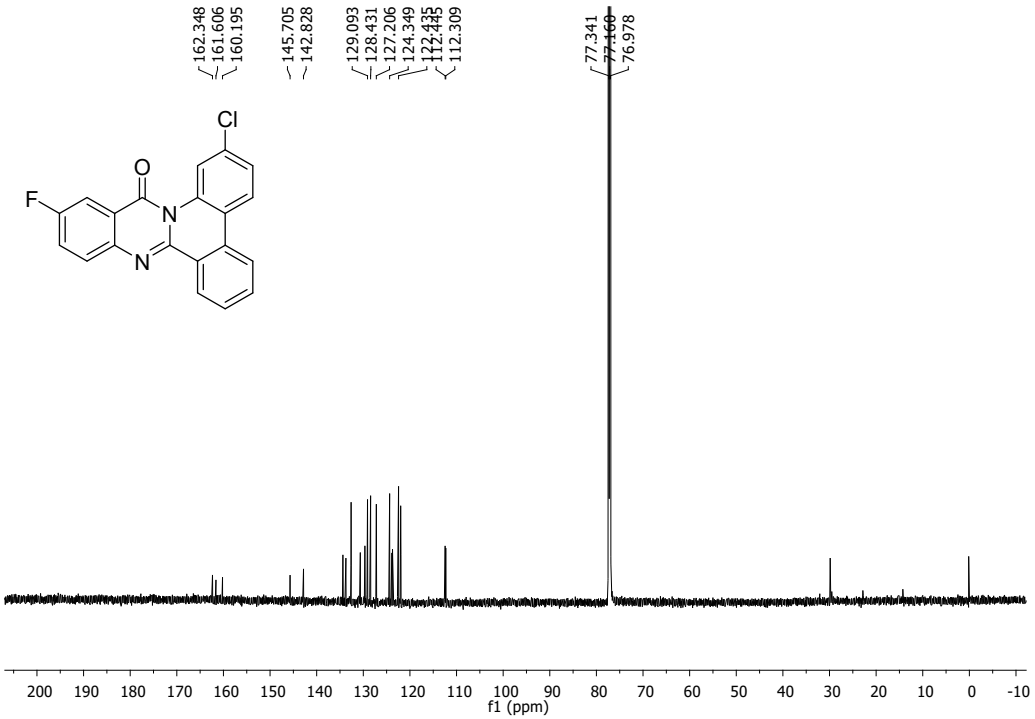



**Figure S39.** $^{13}$C NMR spectrum of 2-chloro-12-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bb)**

**$^{19}$F NMR (376 MHz, $CDCl_3$)**

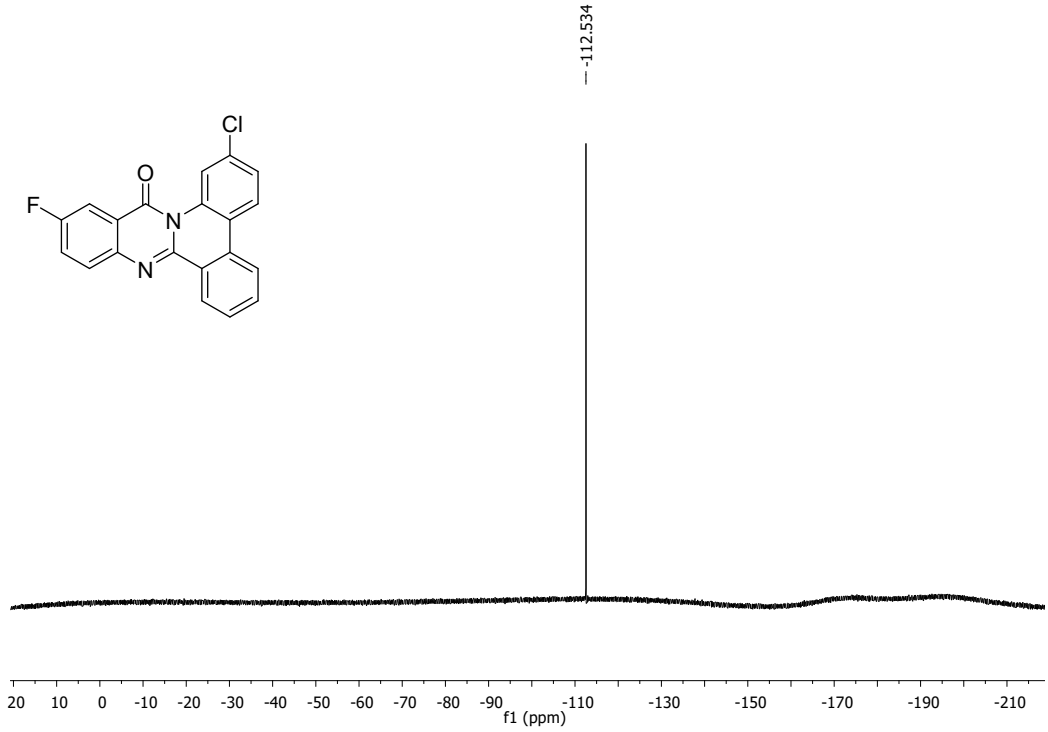



**Figure S40.** $^{19}$F NMR spectrum of 2-chloro-12-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bb)**

**$^{1}$H NMR (700 MHz, $CDCl_3$)**

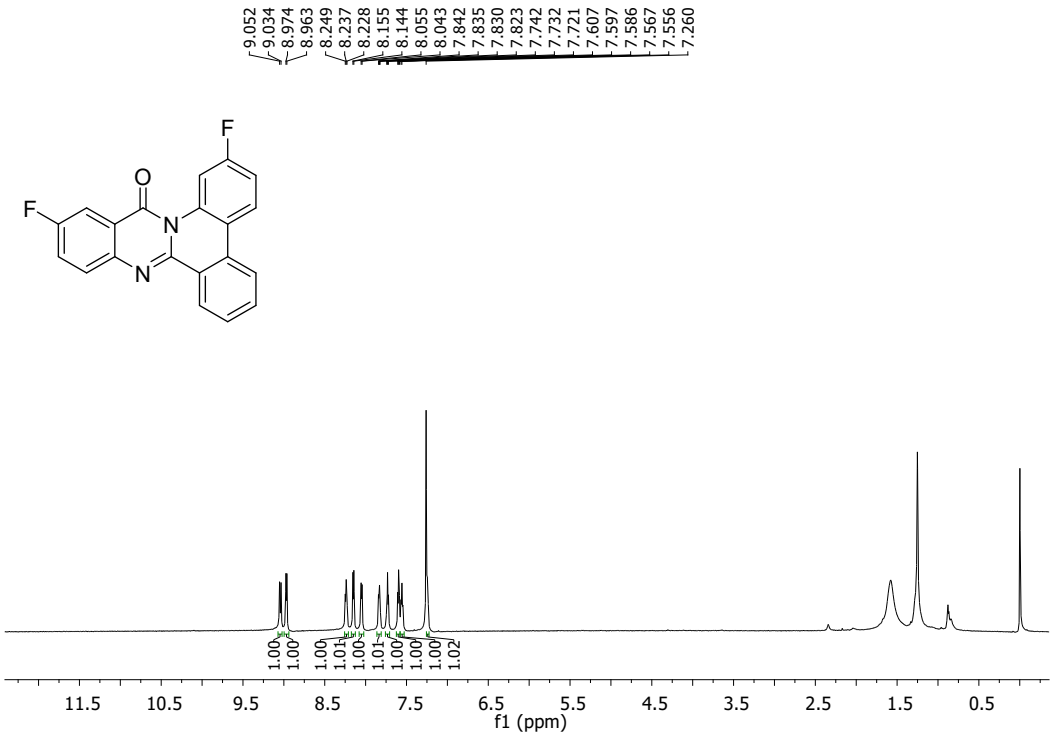



**Figure S41.** $^{1}$H NMR spectrum of 2,12-difluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bc)**

**$^{13}$C NMR (175 MHz, $CDCl_3$)**

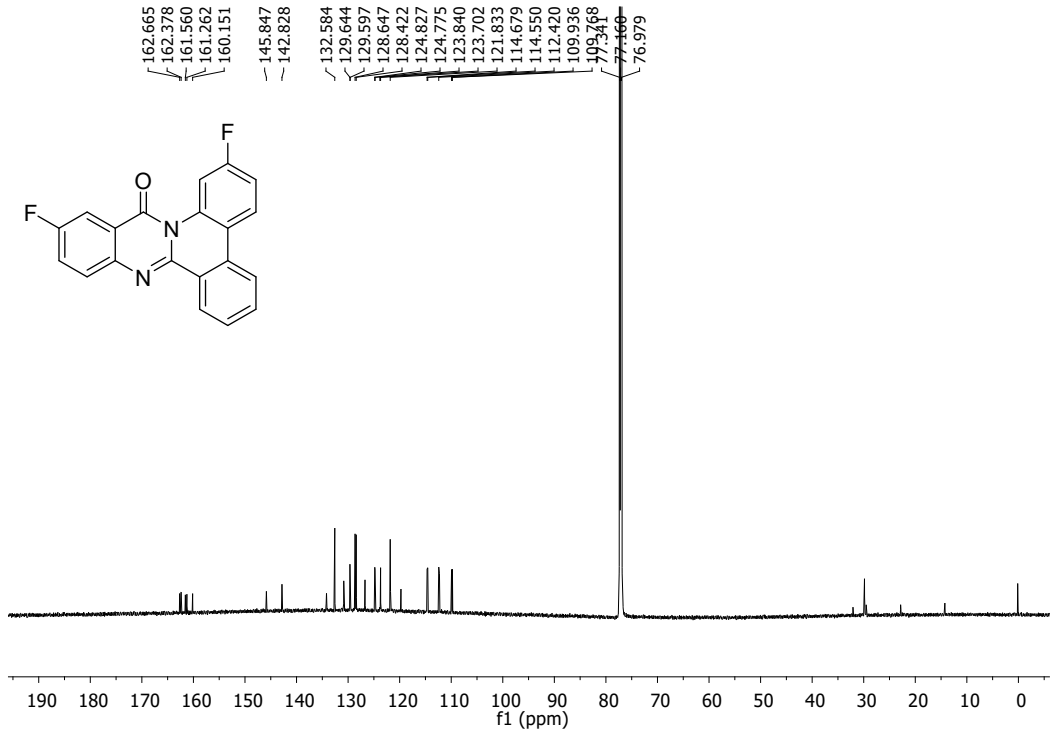



**Figure S42.** $^{13}$C NMR spectrum of of 2,12-difluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bc)**

**$^{19}$F NMR (376 MHz, $CDCl_3$)**

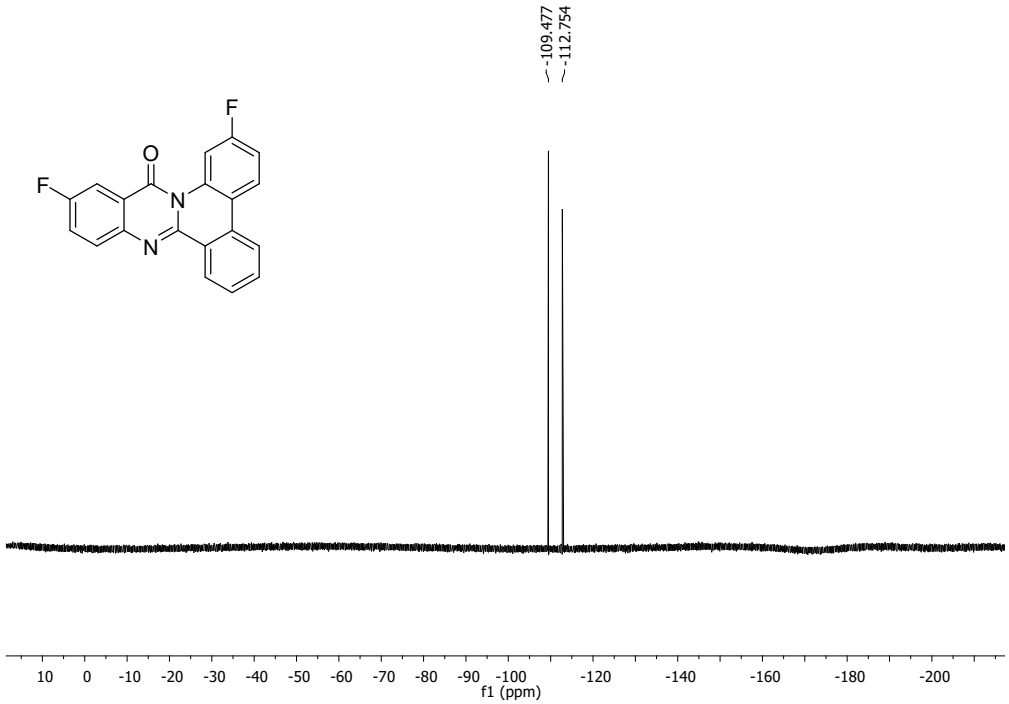



**Figure S43.** $^{19}$F NMR spectrum of of 2,12-difluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bc)**

**$^{1}$H NMR (700 MHz, $CDCl_3$)**

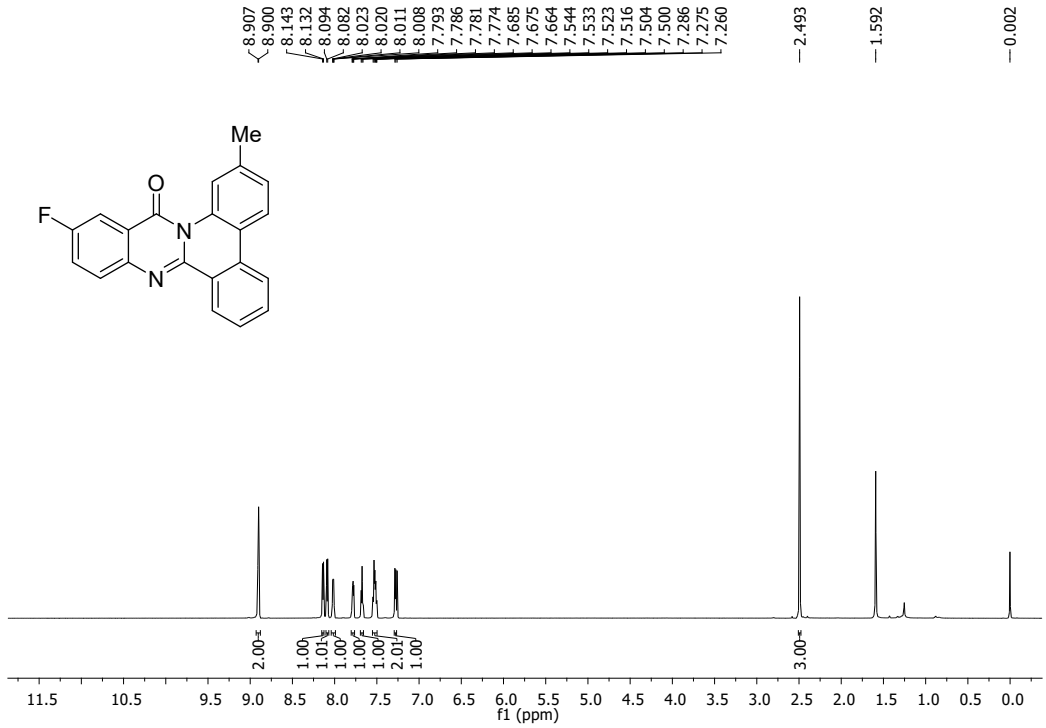



**Figure S44.** $^{1}$H NMR spectrum of 12-fluoro-2-methyl-14H-quinazolino[3,2-f]phenanthridin-14-one (**4bd**)

**$^{13}$C NMR (175 MHz, $CDCl_3$)**

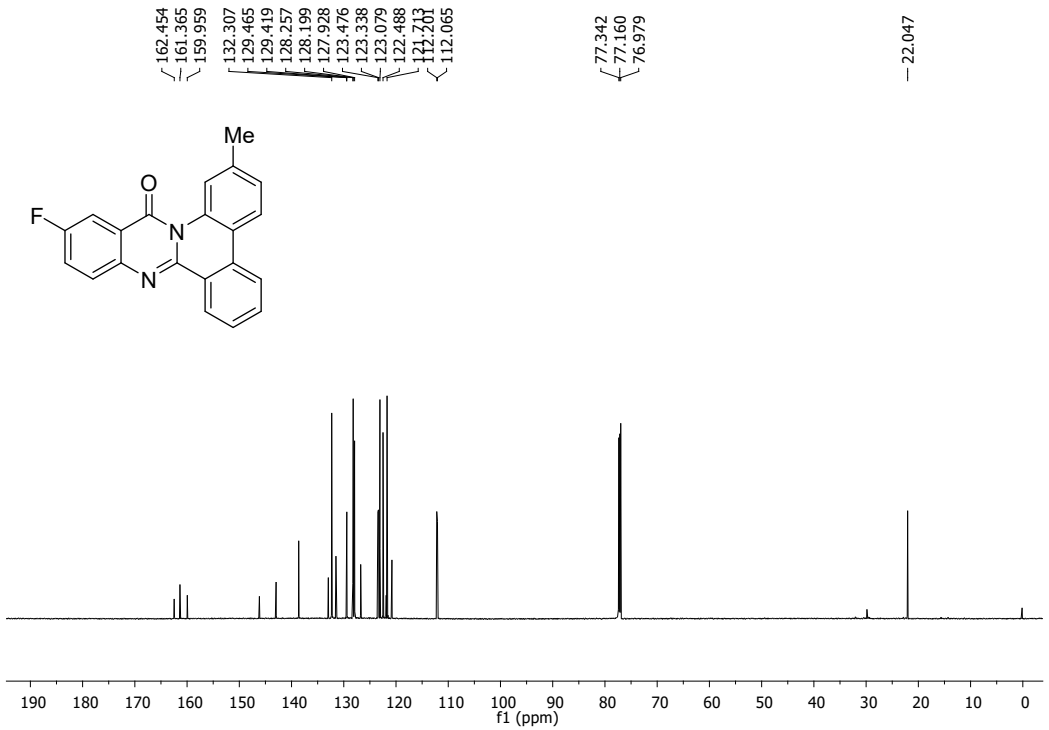



**Figure S45.** $^{13}$C NMR spectrum of 12-fluoro-2-methyl-14H-quinazolino[3,2-f]phenanthridin-14-one (**4bd**)

**$^{19}$F NMR (376 MHz, $CDCl_3$)**

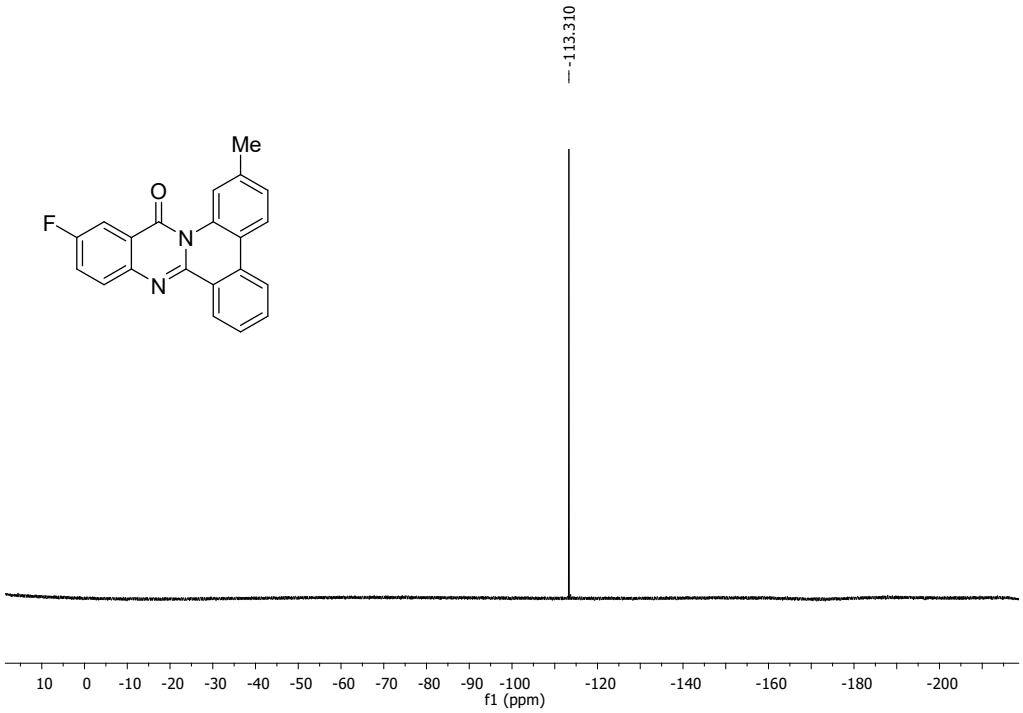



**Figure S46.** $^{19}$F NMR spectrum of 12-fluoro-2-methyl-14H-quinazolino[3,2-f]phenanthridin-14-one (**4bd**)

**$^1$H NMR (700 MHz, $CDCl_3$)**

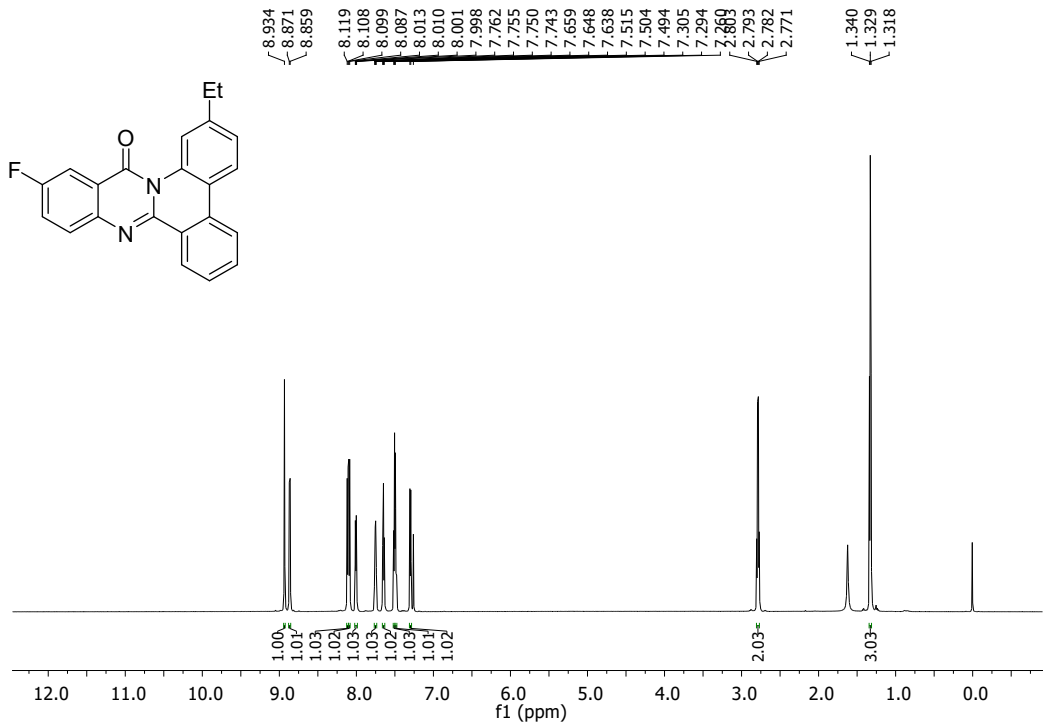



**Figure S47.** $^1$H NMR spectrum of 2-ethyl-12-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4be)**

**$^{13}$C NMR (175 MHz, $CDCl_3$)**

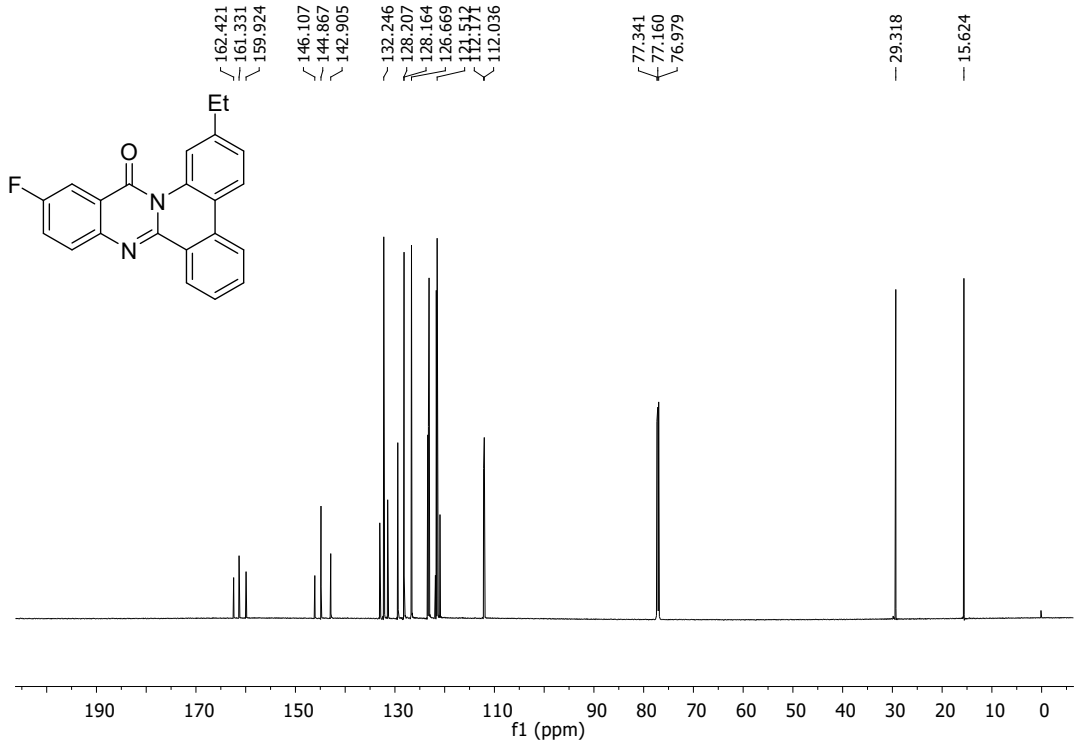



**Figure S48.** $^{13}$C NMR spectrum of 2-ethyl-12-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4be)**

**$^{19}$F NMR (376 MHz, $CDCl_3$)**

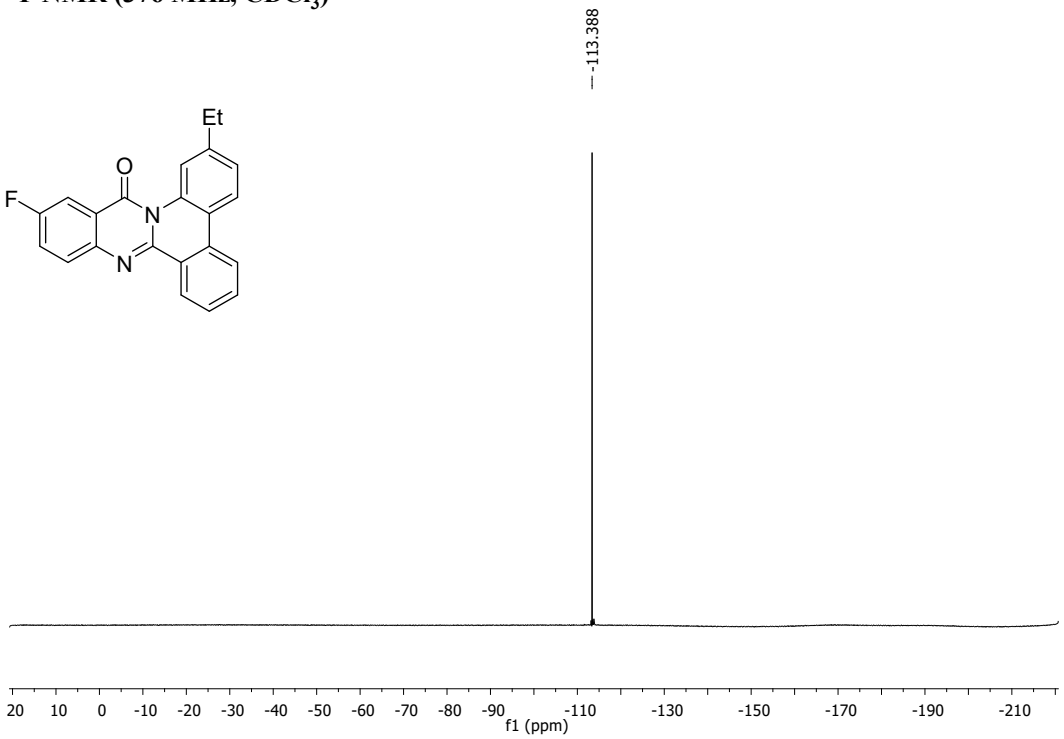



**Figure S49.** $^{19}$F NMR spectrum of 2-ethyl-12-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4be)**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

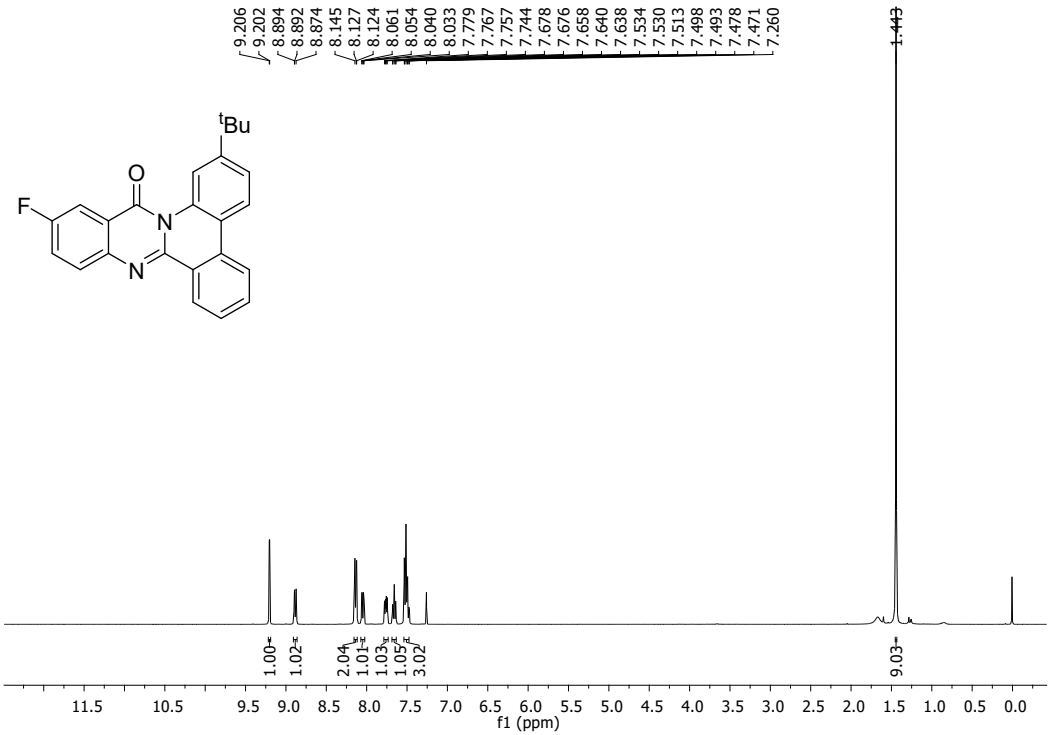



**Figure S50.** $^{1}$H NMR spectrum of 2-(tert-butyl)-12-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bf)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

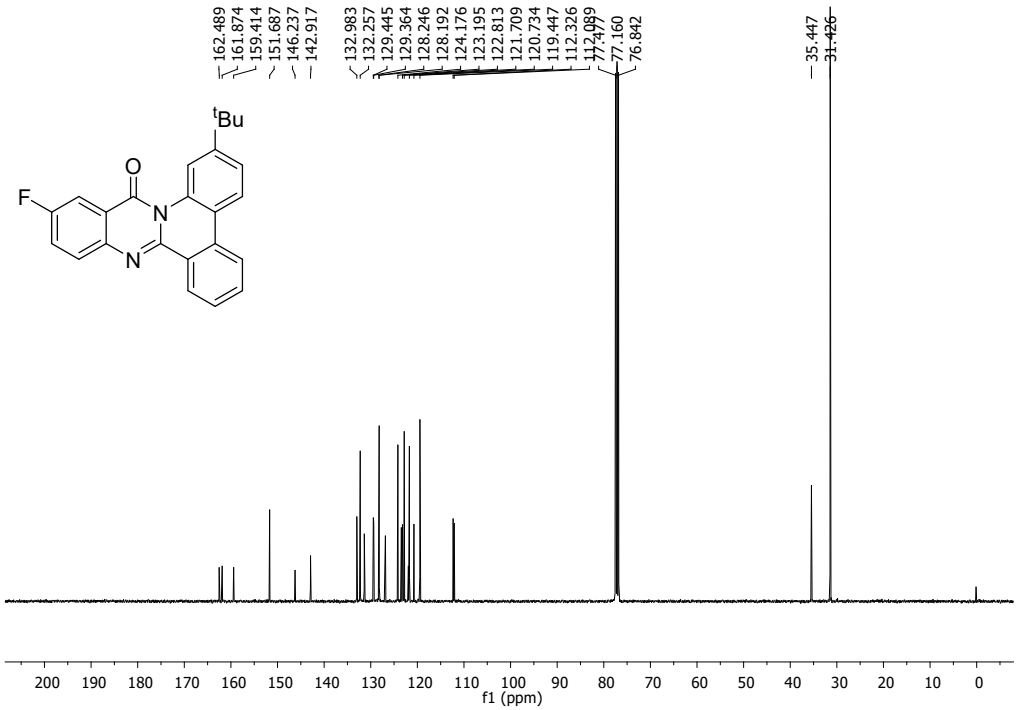



**Figure S51.** $^{13}$C NMR spectrum of 2-(tert-butyl)-12-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bf)**

**$^{19}$F NMR (376 MHz, $CDCl_3$)**

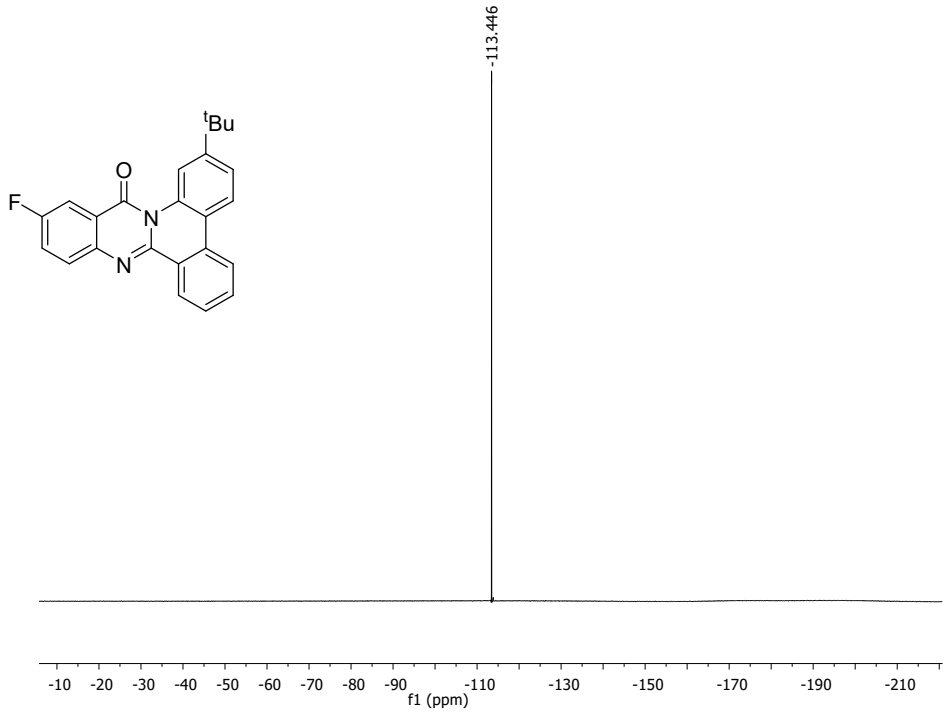



**Figure S52.** $^{19}$F NMR spectrum of 2-(tert-butyl)-12-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bf)**

**$^1$H NMR (700 MHz, $CDCl_3$)**

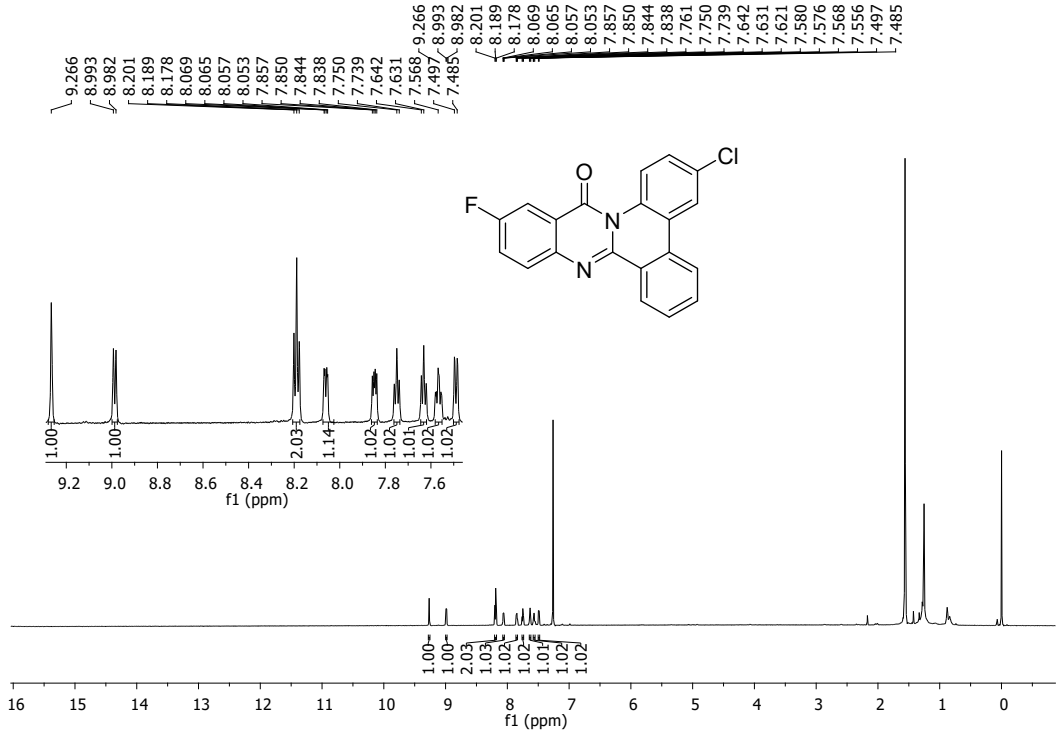



**Figure S53.** $^1$H NMR spectrum of 3-chloro-12-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bg)**

**$^{19}$F NMR (376 MHz, $CDCl_3$)**

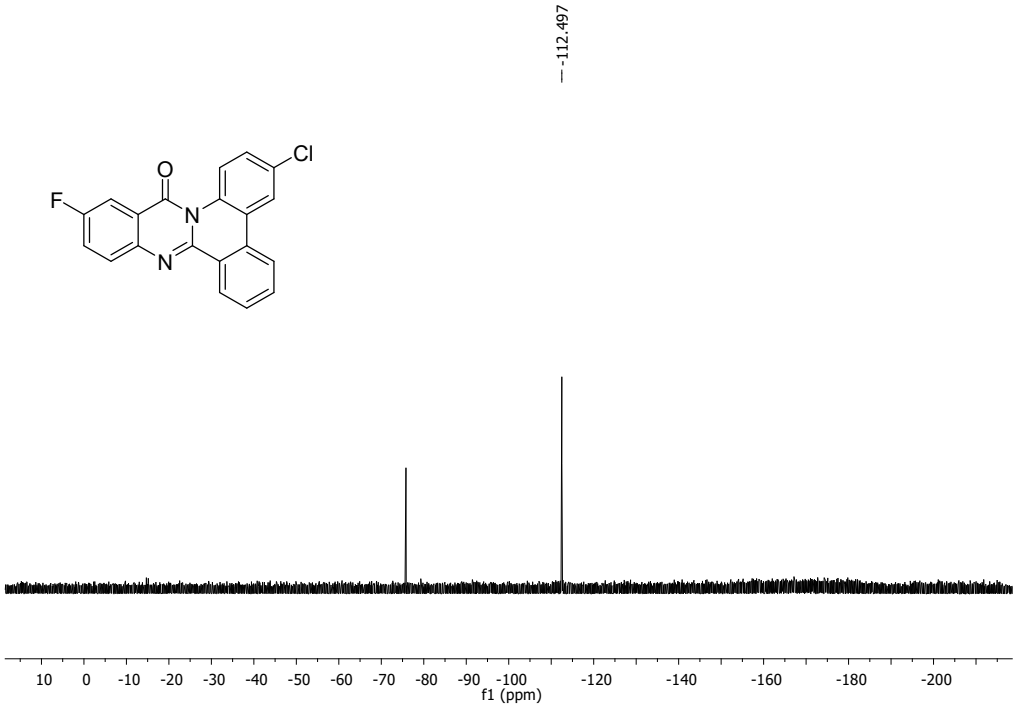



**Figure S54.** $^{19}$F NMR spectrum of 3-chloro-12-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bg)**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

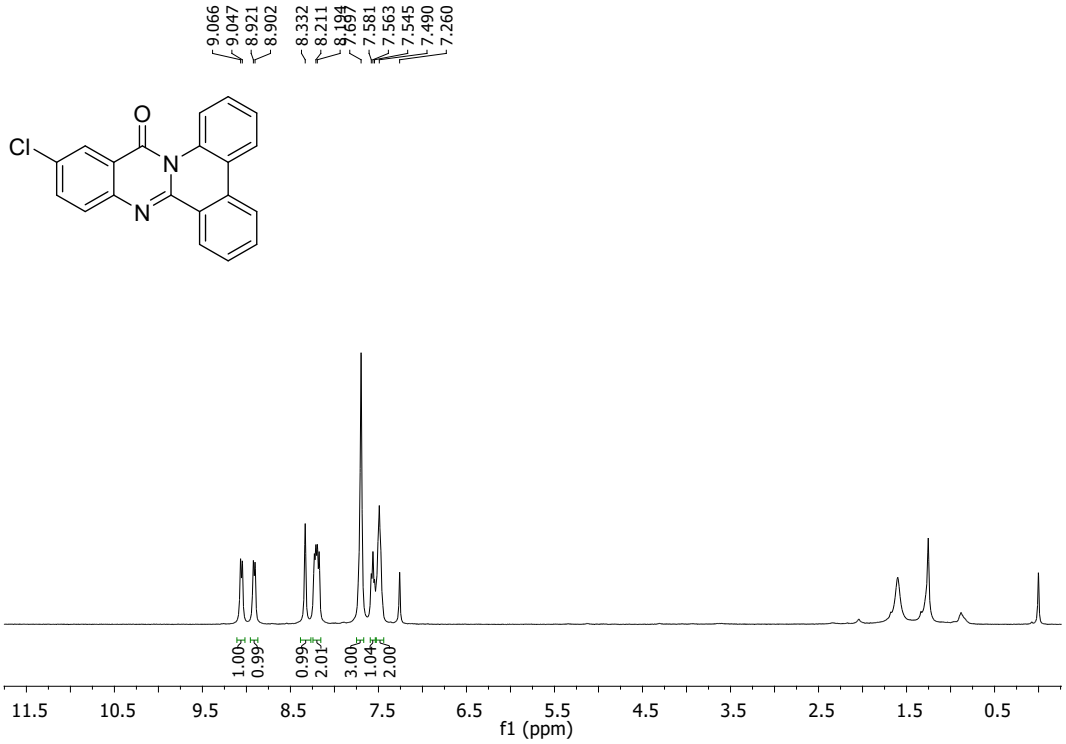



**Figure S55.** $^{1}$H NMR spectrum of 12-chloro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bh)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

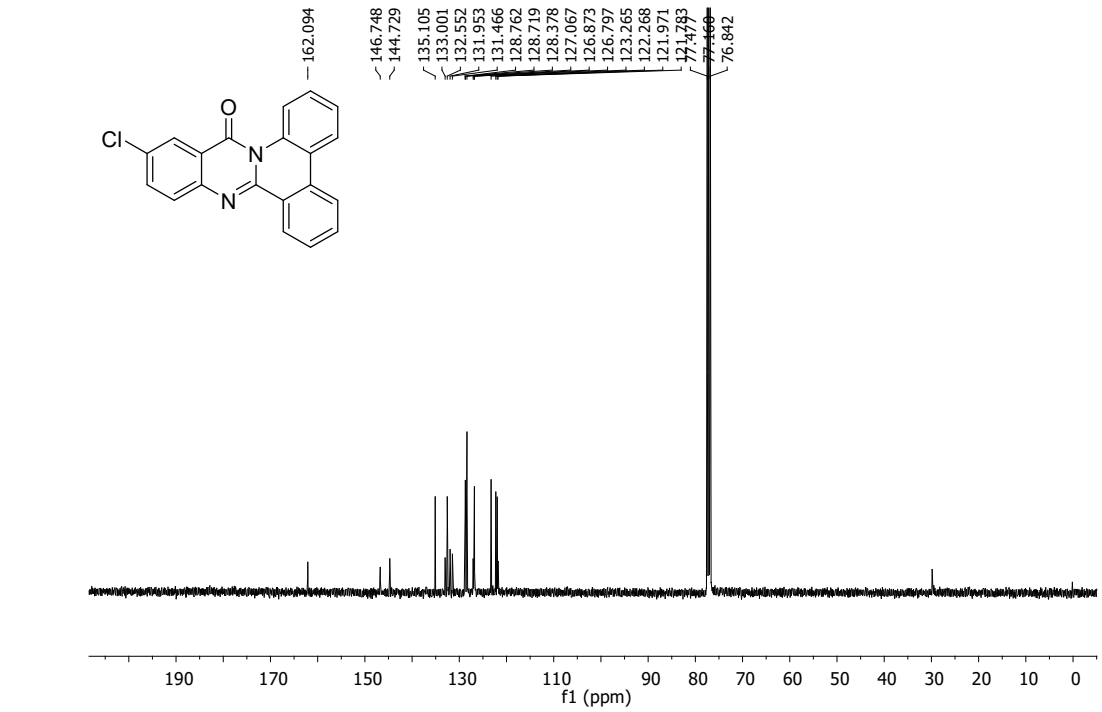



**Figure S56.** $^{13}$C NMR spectrum of 12-chloro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bh)**

**$^{1}$H NMR (400 MHz, $CDCl_3$ + TFA-D)**

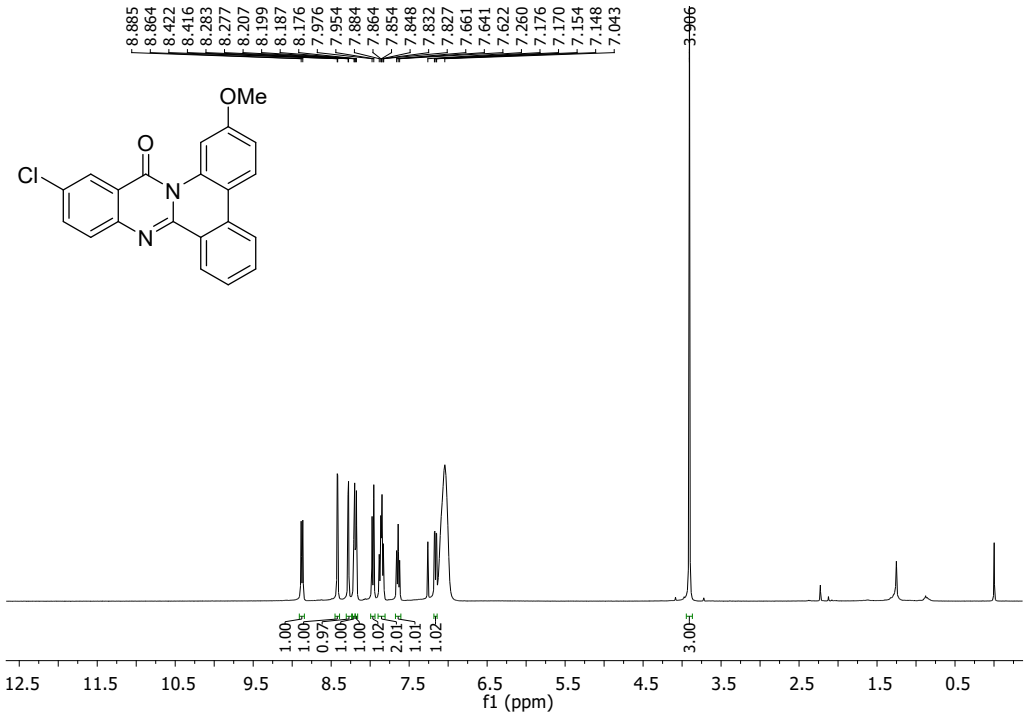



**Figure S57.** $^{1}$H NMR spectrum of 12-chloro-2-methoxy-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bi)**

**$^{13}$C NMR (100 MHz, $CDCl_3$ + TFA-D)**

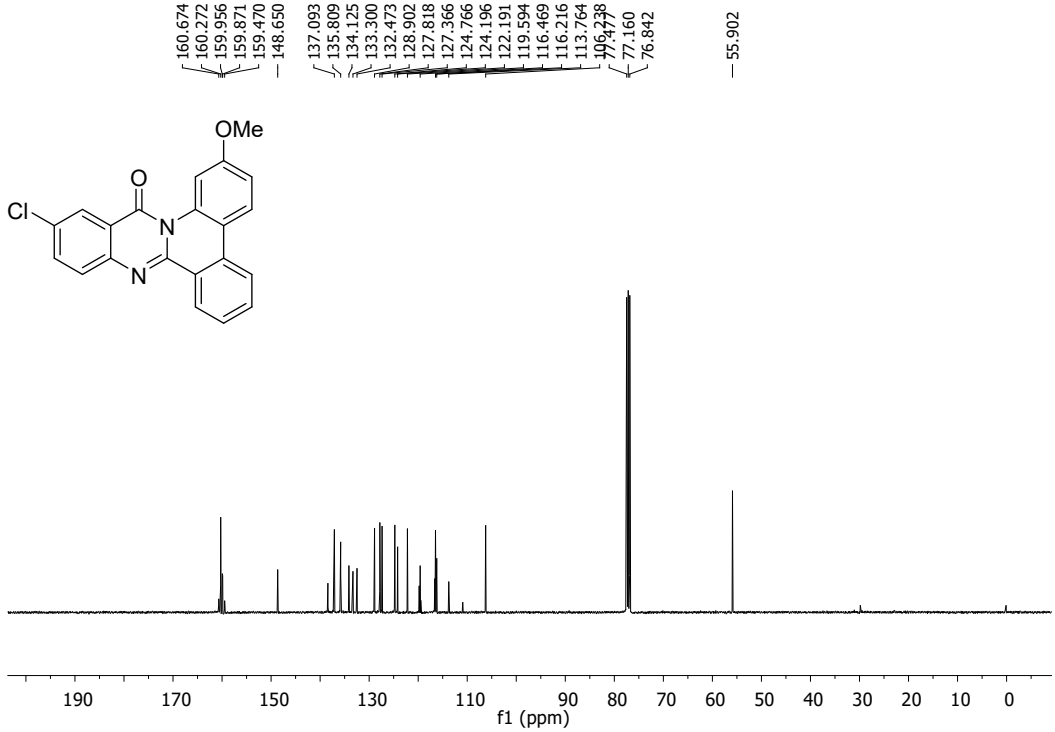



**Figure S58.** $^{13}$C NMR spectrum of 12-chloro-2-methoxy-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bi)**

**$^{1}$H NMR (700 MHz, $CDCl_3$)**

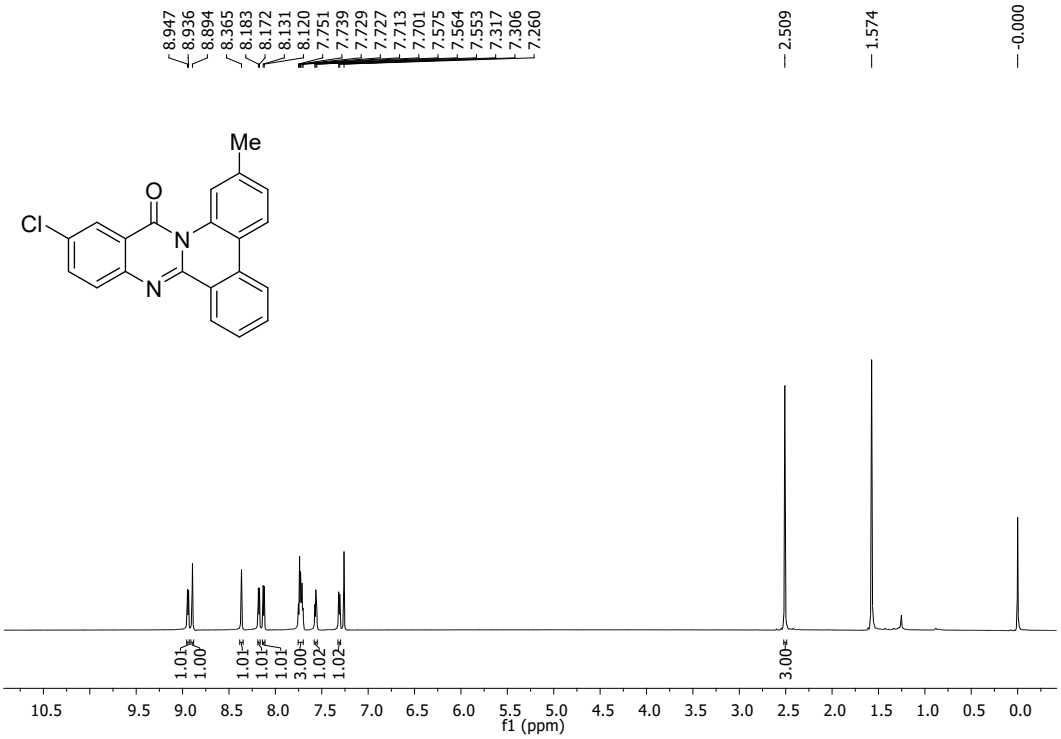



**Figure S59.** $^{1}$H NMR spectrum of 12-chloro-2-methyl-14H-quinazolino[3,2-f]phenanthridin-14-one (**4bj**)

**$^{13}$C NMR (175 MHz, $CDCl_3$)**

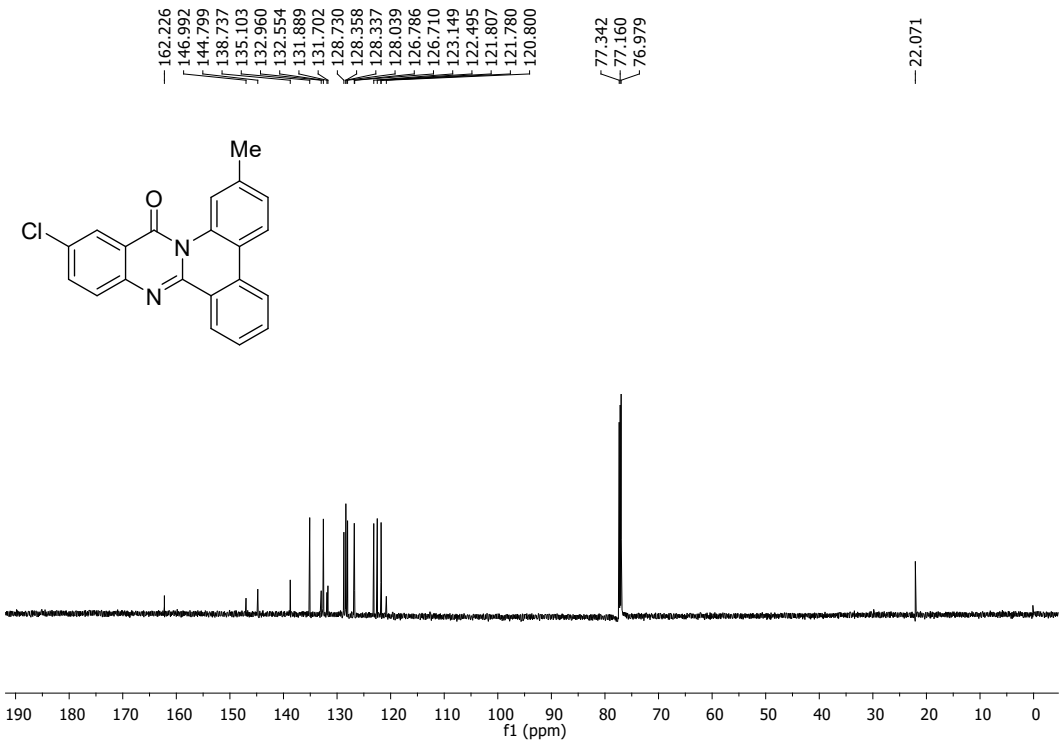



**Figure S60.** $^{13}$C NMR spectrum of 12-chloro-2-methyl-14H-quinazolino[3,2-f]phenanthridin-14-one (**4bj**)

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

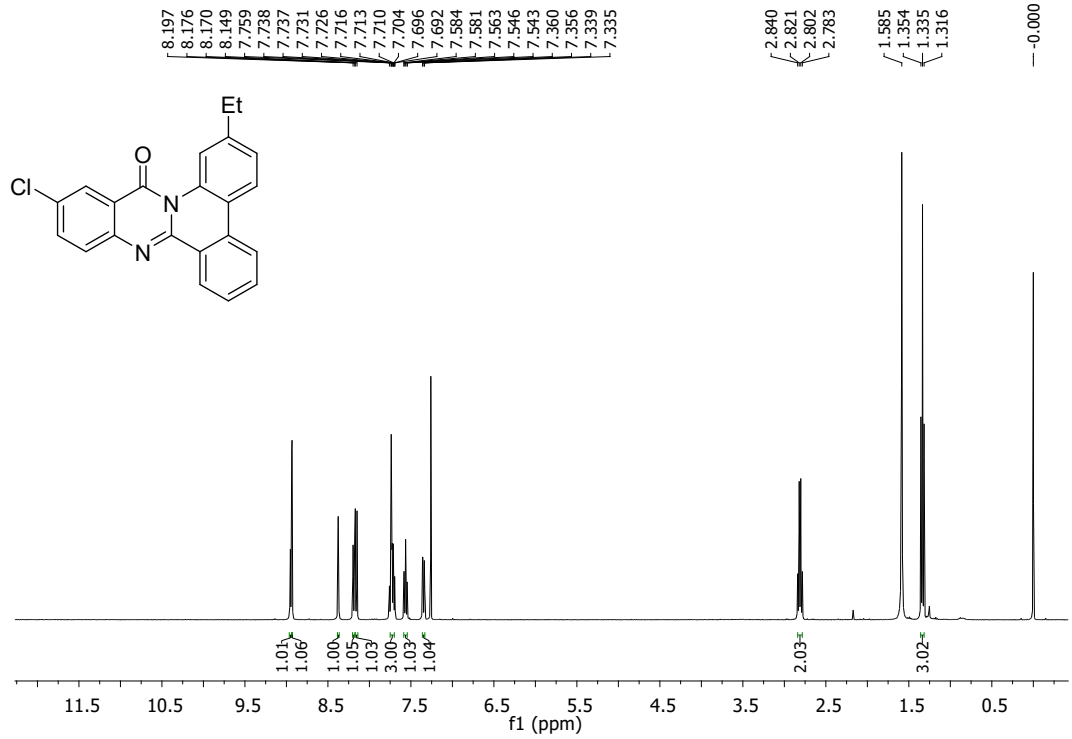



**Figure S61.** $^{1}$H NMR spectrum of 12-chloro-2-ethyl-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bk)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

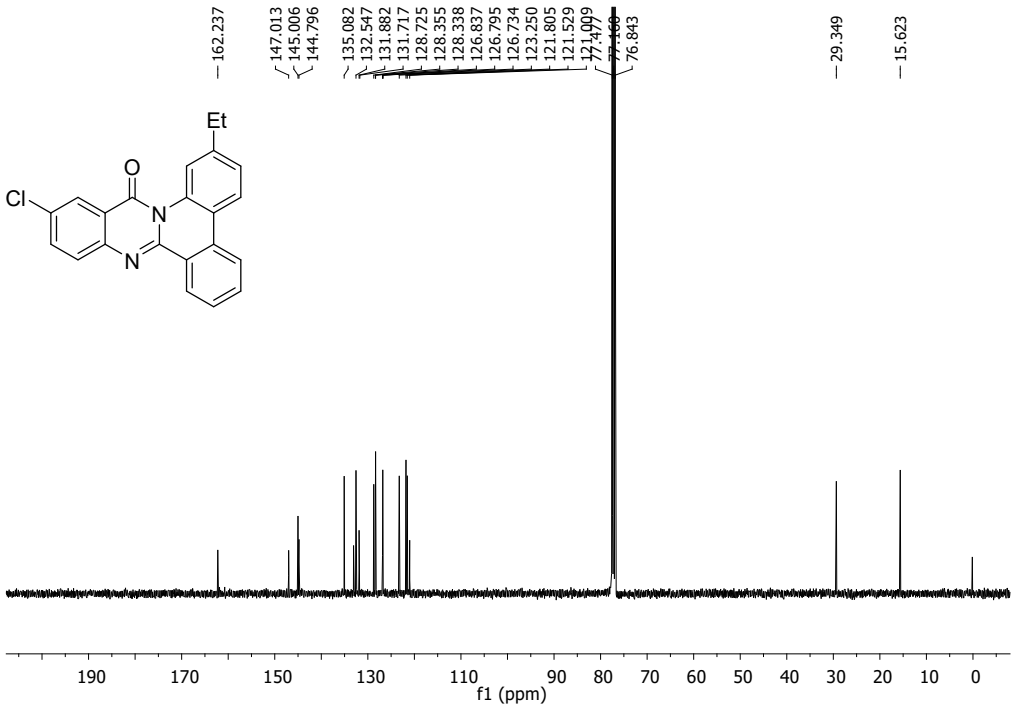



**Figure S62.** $^{13}$C NMR spectrum of 12-chloro-2-ethyl-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bk)**

**$^1$H NMR (400 MHz, $CDCl_3$)**

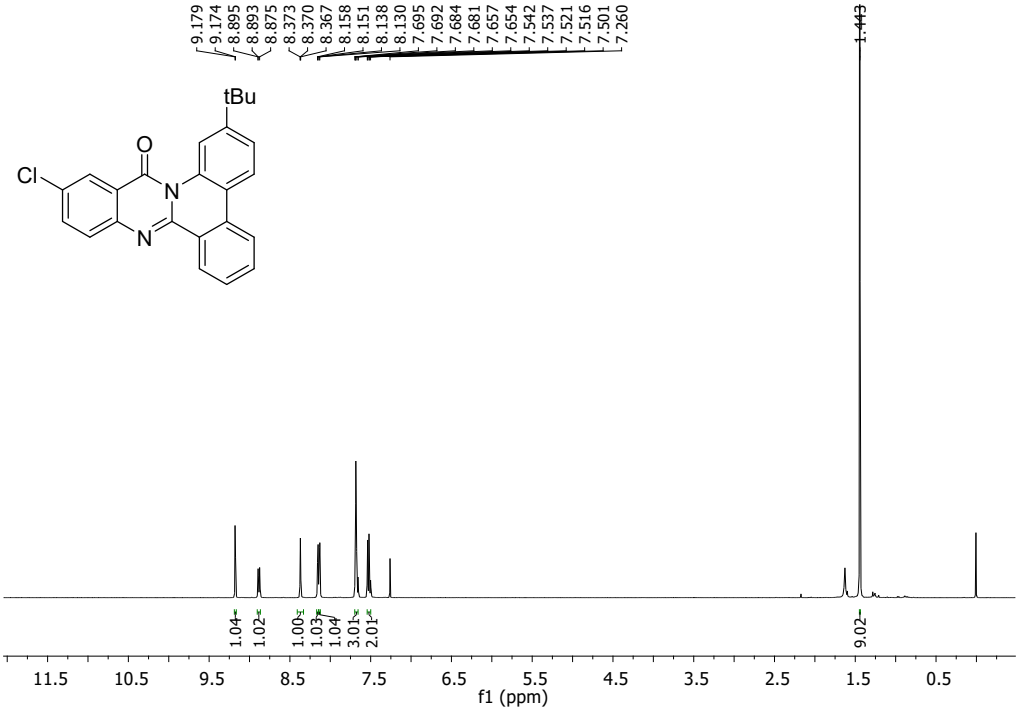



**Figure S63.** $^1$H NMR spectrum of 2-(tert-butyl)-12-chloro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bl)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

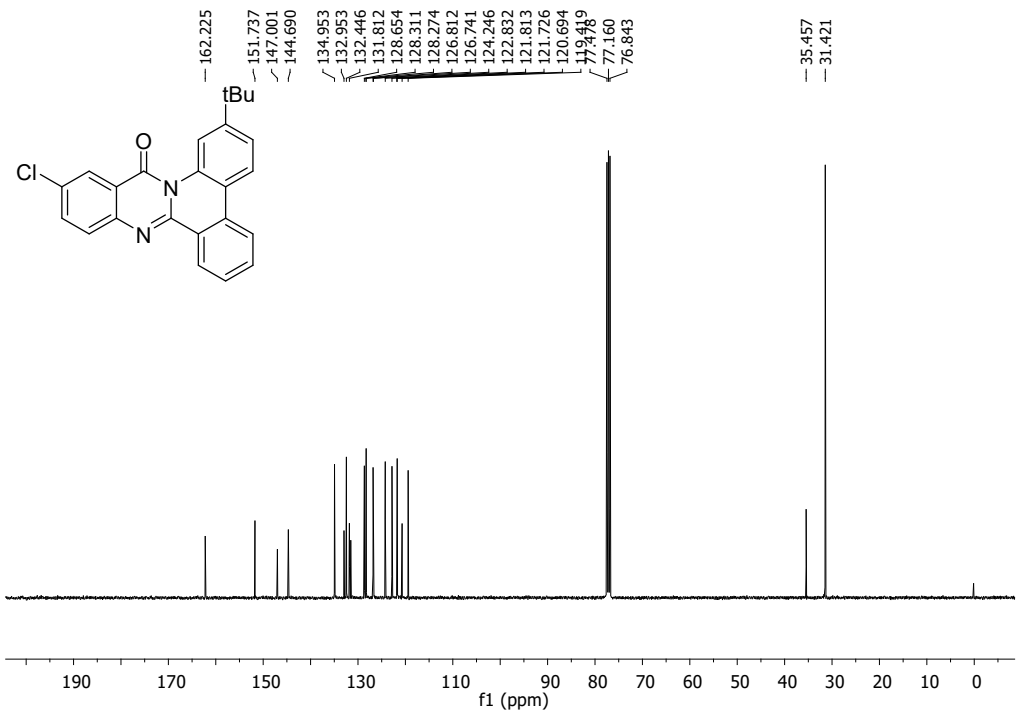



**Figure S64.** $^{13}$C NMR spectrum of 2-(tert-butyl)-12-chloro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bl)**

**$^{1}$H NMR (700 MHz, $CDCl_3$)**

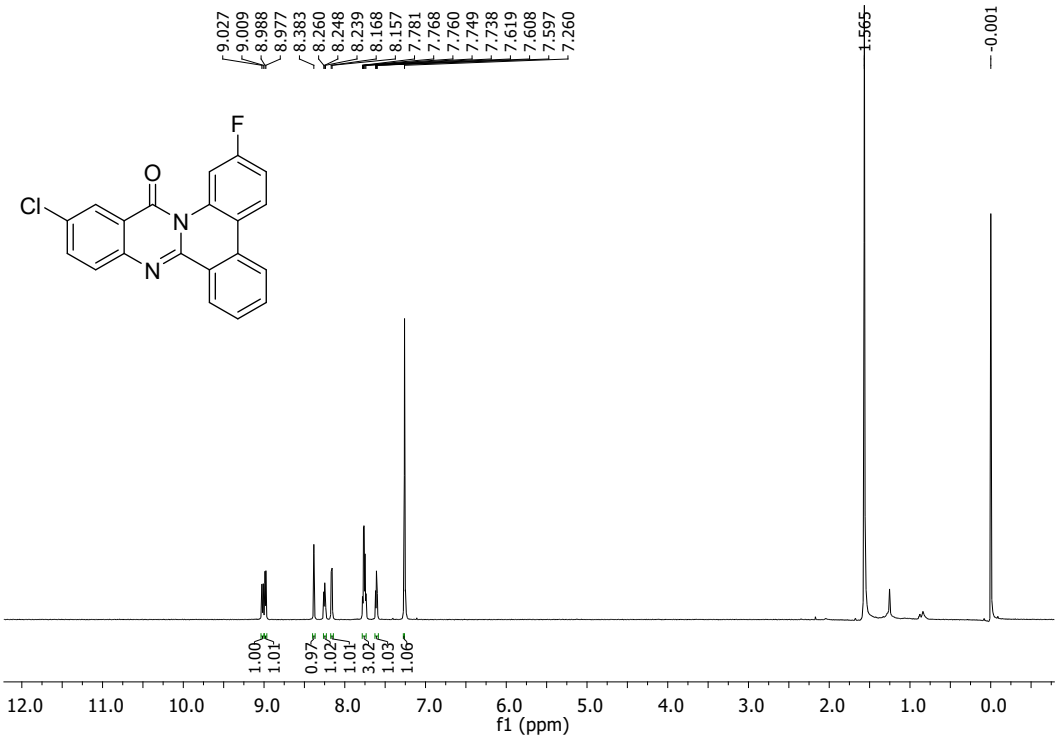



**Figure S65.** $^{1}$H NMR spectrum of 12-chloro-2-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bm)**

**$^{13}$C NMR (175 MHz, $CDCl_3$)**

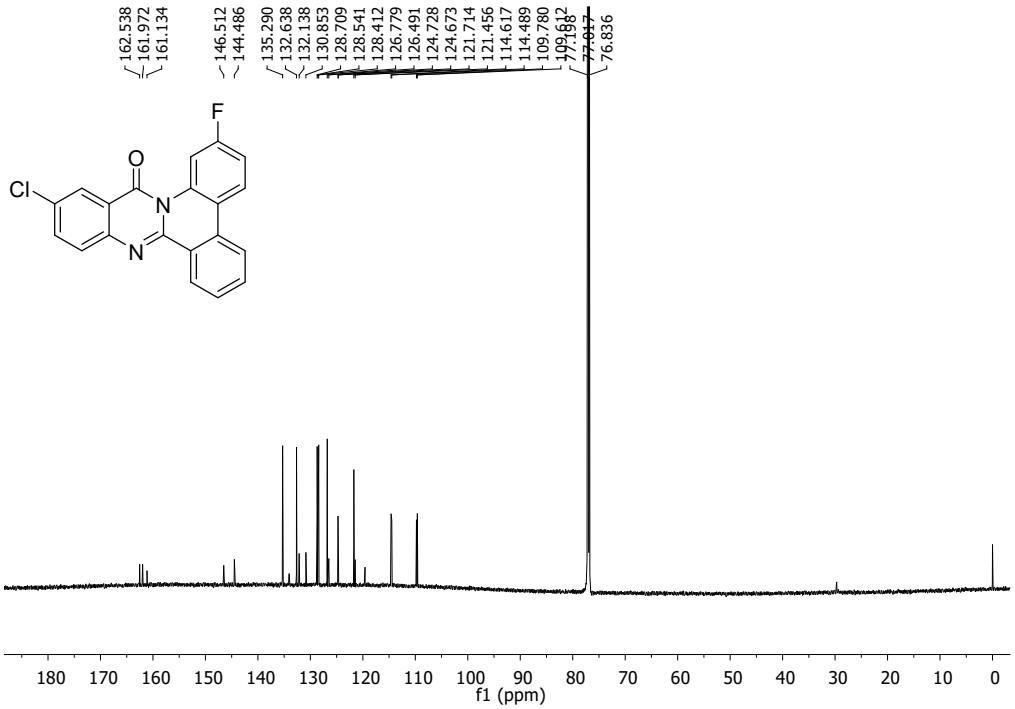



**Figure S66.** $^{13}$C NMR spectrum of 12-chloro-2-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bm)**

**$^{19}$F NMR (376 MHz, $CDCl_3$)**

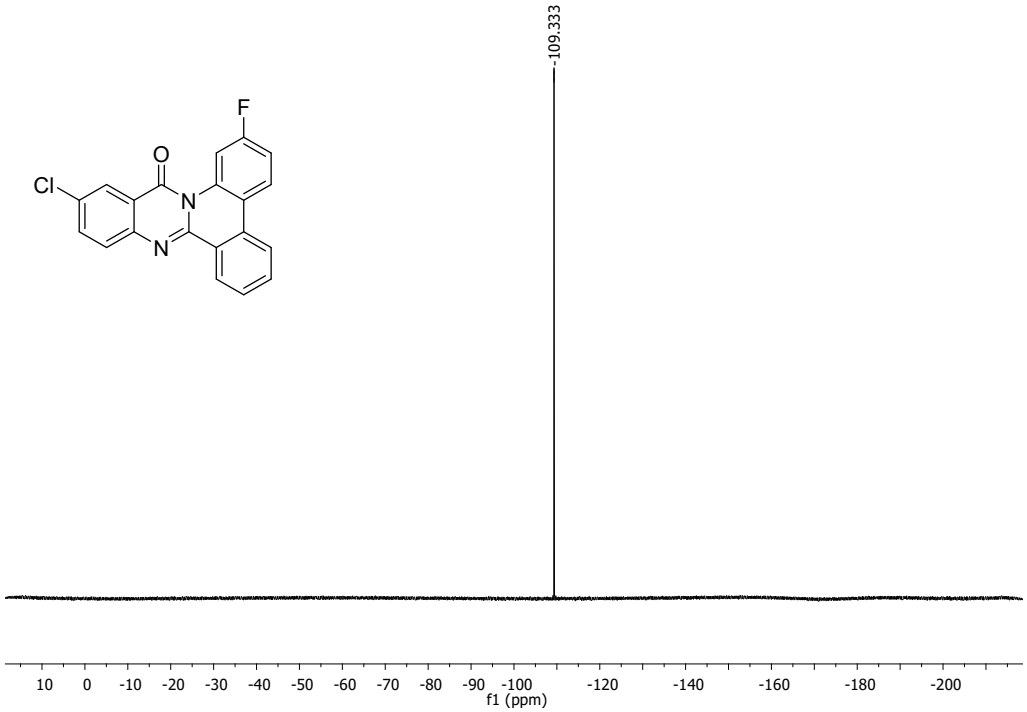



**Figure S67.** $^{19}$F NMR spectrum of 12-chloro-2-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bm)**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

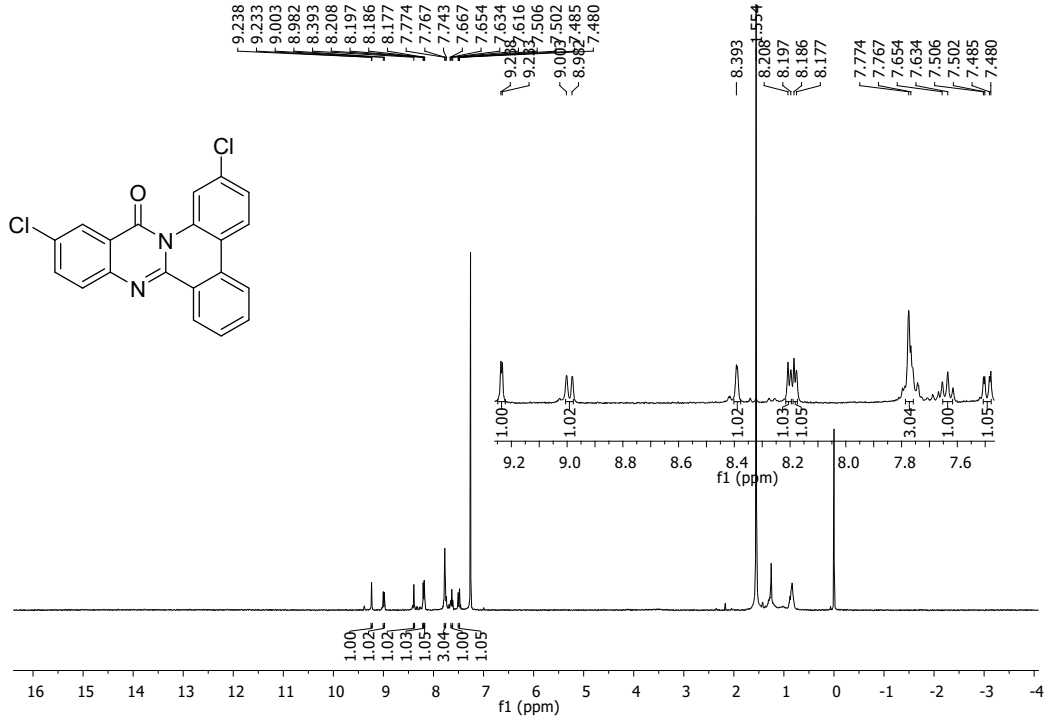



**Figure S68.** $^{1}$H NMR spectrum of 2,12-dichloro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bn)**

**$^{1}$H NMR (400 MHz, $CDCl_3$)**

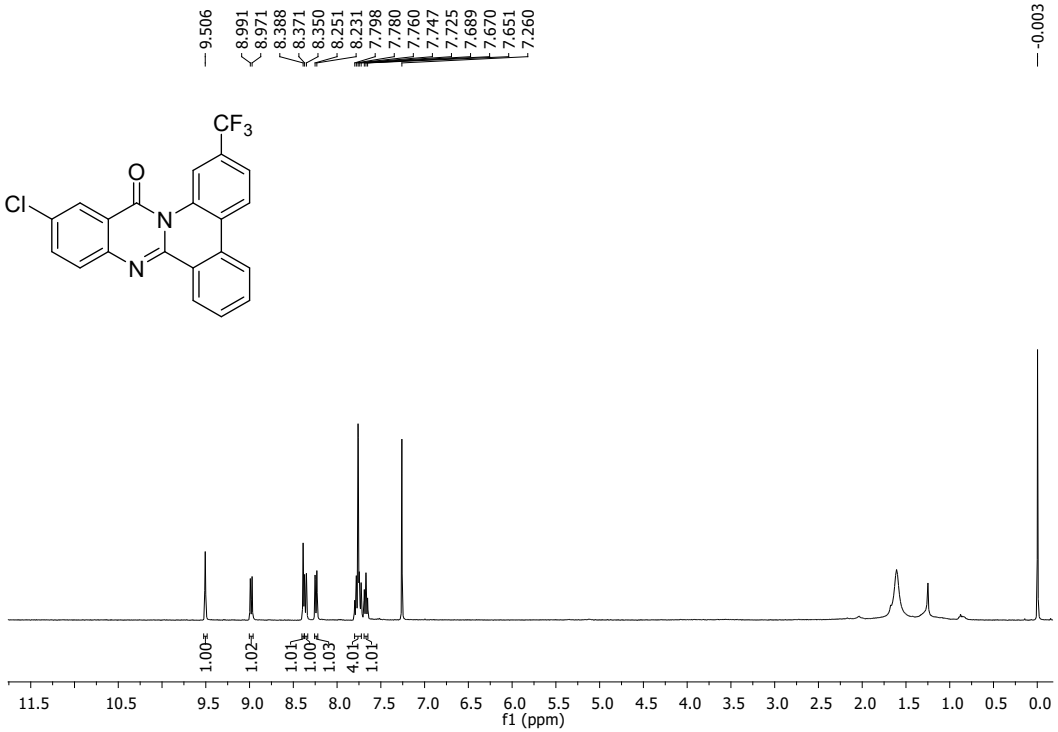



**Figure S69.** $^{1}$H NMR spectrum of 12-chloro-2-(trifluoromethyl)-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bo)**

**$^{13}$C NMR (100 MHz, $CDCl_3$)**

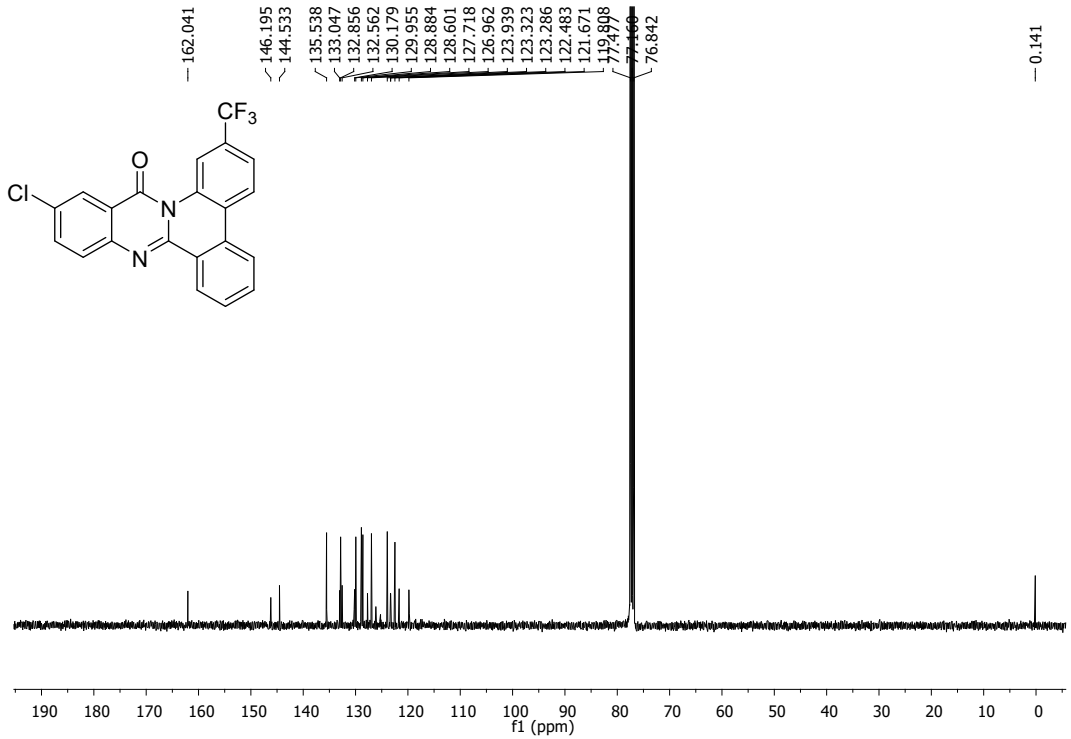



**Figure S70.** $^{13}$C NMR spectrum of 12-chloro-2-(trifluoromethyl)-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bo)**

**$^{19}$F NMR (376 MHz, $CDCl_3$)**

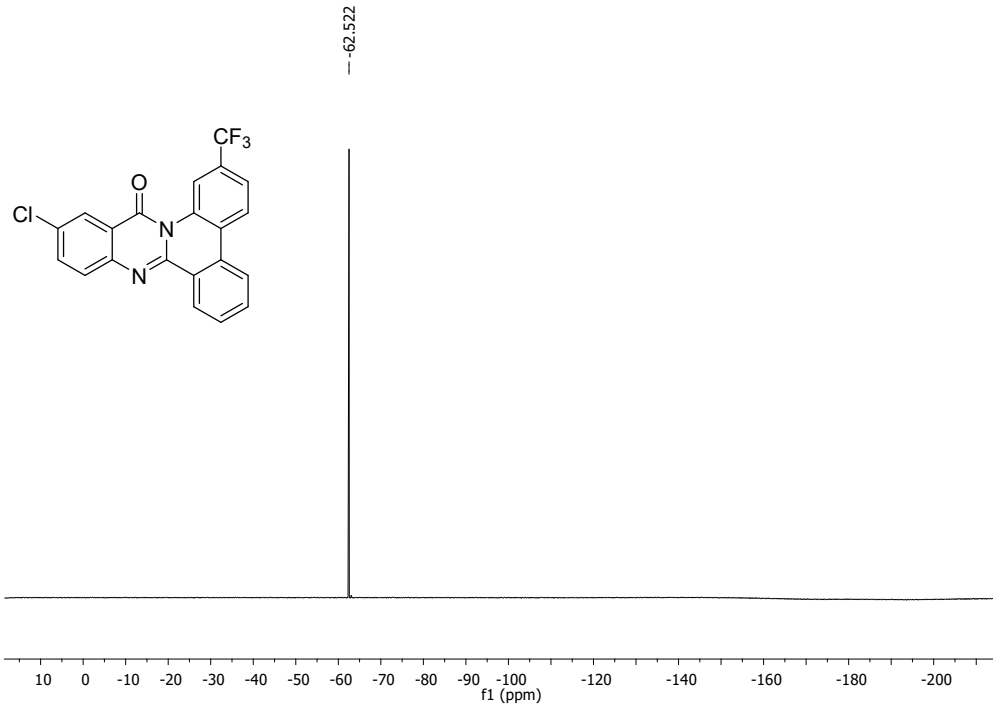



**Figure S71.** $^{19}$F NMR spectrum of 12-chloro-2-(trifluoromethyl)-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bo)**

**$^{1}$H NMR (400 MHz, $CDCl_3$ + TFA-D)**

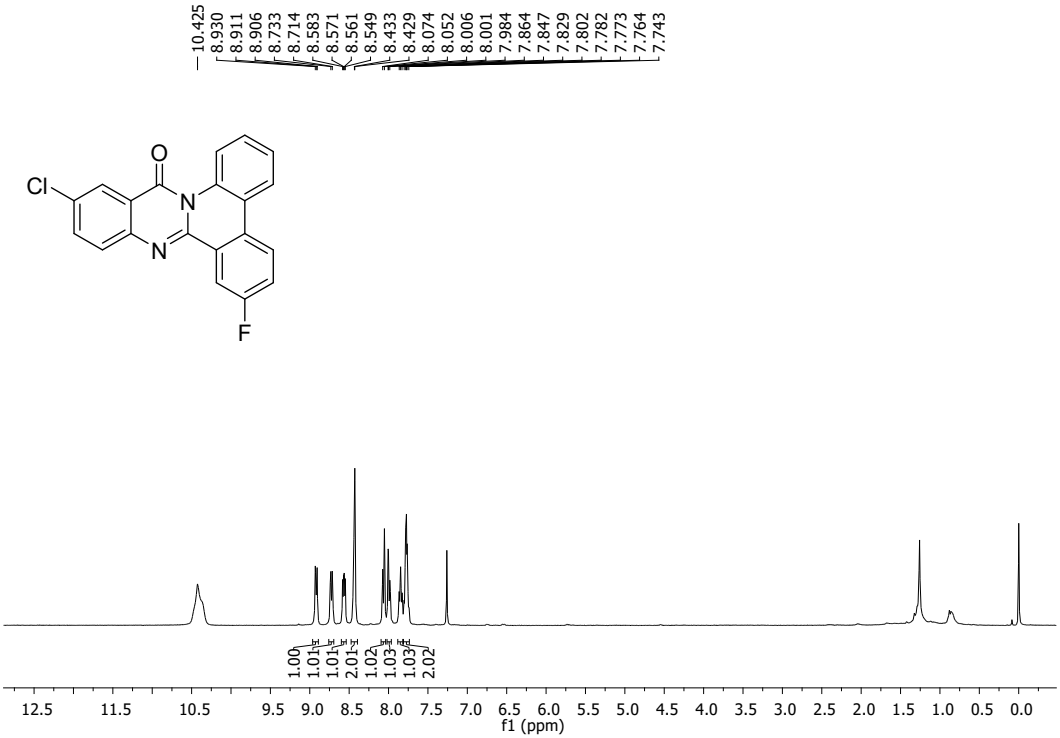



**Figure S72.** $^{1}$H NMR spectrum of 12-chloro-7-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bp)**

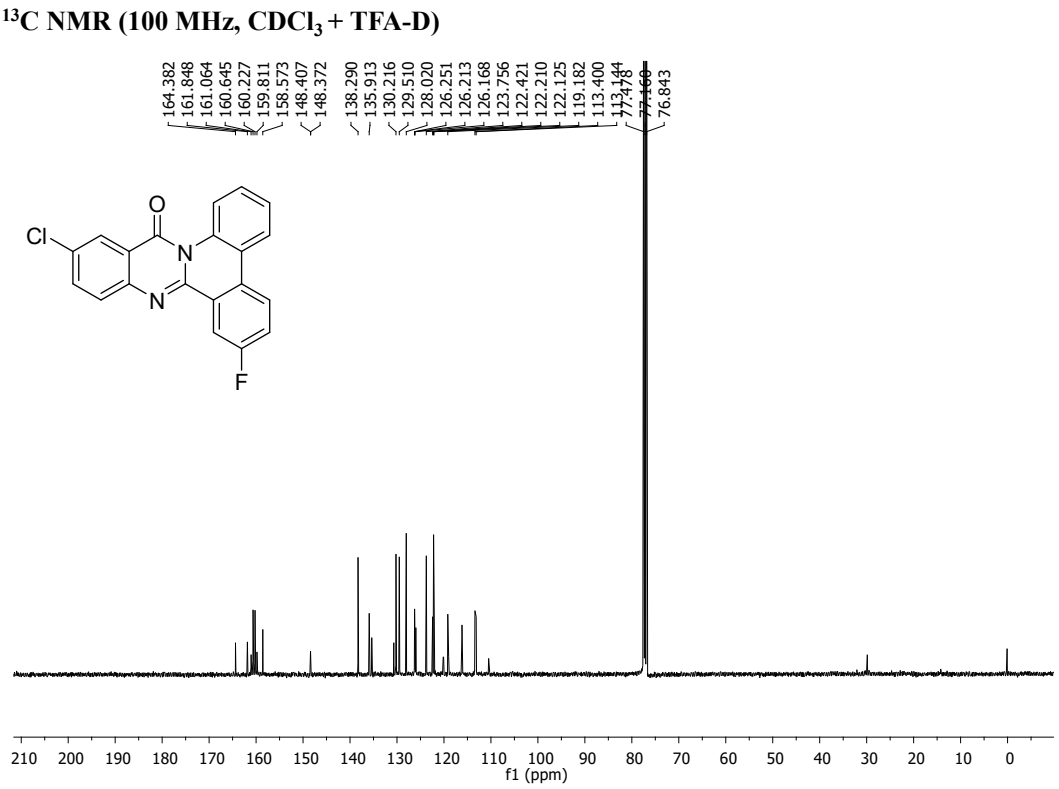



**Figure S73.** $^{13}$C NMR spectrum of 12-chloro-7-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bp)**

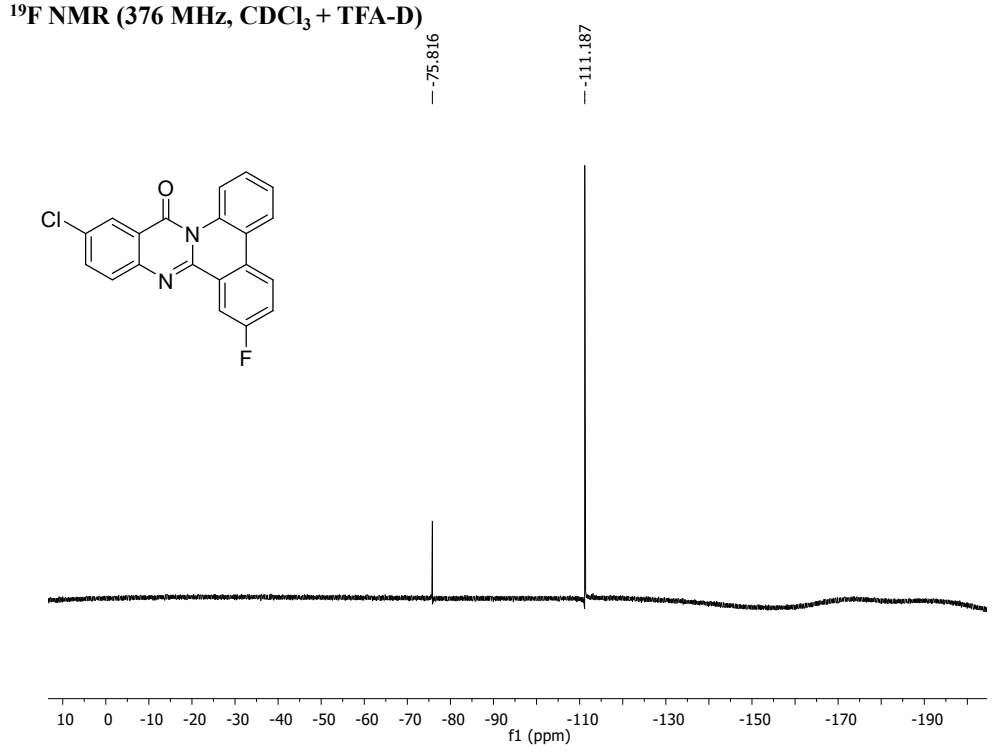



**Figure S74.** $^{19}$F NMR spectrum of 12-chloro-7-fluoro-14H-quinazolino[3,2-f]phenanthridin-14-one **(4bp)**

**Description of Light Source**. Blue LED set up (Led Photochemical Reactor) was purchased from commercial source CRYONANO VL-PHOTON. The intensity of the blue LED was (417 × 100) lx (measured by Sigma-Digital Lux Meter 101, Model: 20036176). Quartz glass (brand name: Luzchem) was used as reaction vessel. No filter was used for the reaction. Other features of the photoreactor are as follows:

**CRYONANO Labs LED Photochemical Reactor - CNPHOTON 101**

The CN-Photon LED Photochemical Reactor from CRYONANO Labs is a compact desktop instrument for conducting research in areas of Photo-biology, Inorganic, Organometallic and Organic Photochemistry (e.g., Drug-DNA Interaction) etc. It has a ventilated illumination chamber with tunable high intensity LEDs and fully automatic operation with countdown timer for setting the reaction time and switching it off automatically. The intensity of light can also be automatically controlled using inbuilt microprocessors.

The reactor includes a controller in a separate housing for light intensity control and automation with display. It also comes with a carousel for liquid samples.

**Main Features of the reactor are:**

- High flux per LED
- Blue led - 2100 lumens
- White led - 10000 lumens
- Good color uniformity
- Industry best moisture sensitivity level
- JEDEC Level 1
- Low Voltage DC operated
- Instant light (less than 100ns)
- No UV Component
- Dimensions: Internal : 5.5" Diameter, 7" height, Anodized aluminium enclosure
- Power Rating: 220 V AC, 50 Hz, 2Amp

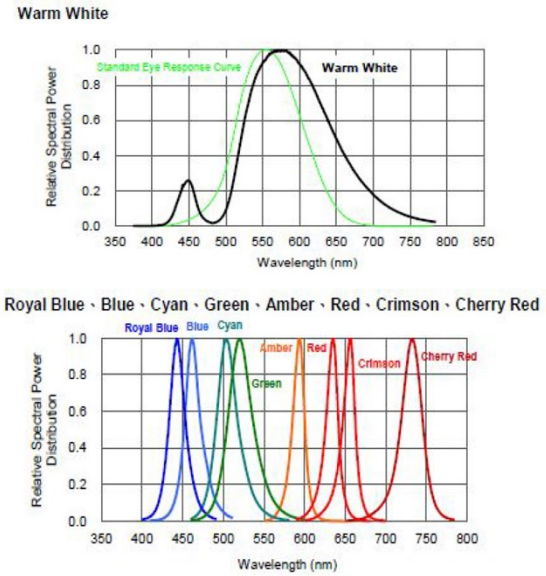
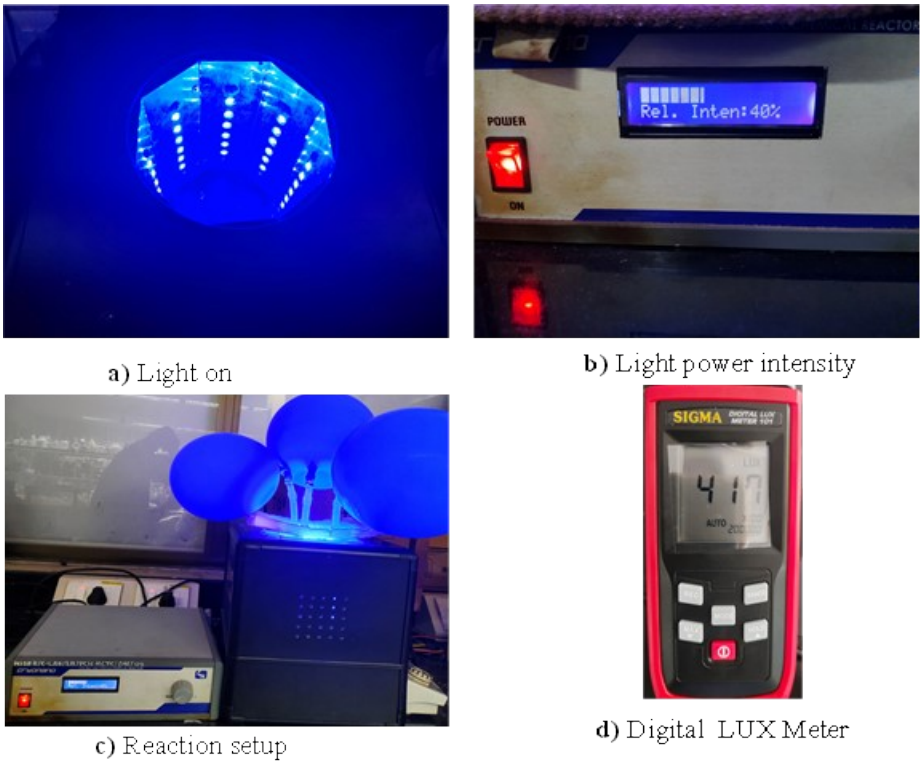



**Fig S74**. The instrument configuration details provided by the manufacturer (CRYONANO VL-PHOTON). The full-width-at-half-maximum (FWHM) of the Blue LED is 450-470 nm.




a) Light on

b) Light power intensity

c) Reaction setup

d) Digital LUX Meter

**Fig S75.** Blue LED photoreactor and digital LUX meter