Supplementary Information

N–N Atropisomer Synthesis via Electrolyte- and Base-Free Electrochemical Cobalt-Catalysed C–H Annulation

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1. General Remarks

Benzamides **1**[1,2] and Salox ligands[3,4] were prepared according to reported procedures. $Co(OAc)_2 \cdot 4H_2O$, TFE and other chemicals were purchased from J&K (China) and used without further purification.

Platinum electrodes (10 mm × 20 mm × 0.3 mm, 99.99%) and graphite felt electrodes (10 mm × 20 mm × 2 mm) were obtained from Jianhuxian Lianhua Labware (China) and connected using stainless steel adapters. Electrolysis was conducted using an MYWAVE MPD-3003S potentiostat in constant current mode.

Nuclear magnetic resonance (NMR) spectra recorded on JEOL 400 MHz spectrometers at ambient temperature (25 °C) in either $CDCl_3$. Abbreviations for data quoted are s, singlet; brs, broad singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; dt, doublet of triplets; td, triplet of doublets; m, multiplet. All NMR-data are reported in parts per million (ppm) relative to the solvent signal ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm).

High-resolution mass spectrometry (HRMS) analyses were obtained on an agilent TOF-G6230B mass spectrometer and Thermo-DFS mass spectrometer with positive ion mode. Headspace analysis of the reaction mixture was performed on GC-7920A gas chromatograph (GC) system by Beijing Zhongjiao Jinyuan Technology Co., Ltd (China).

Thin-layer chromatographies were done on pre-coated silica gel 60 F254 plates (Merck). Silica gel 60H (200-300 mesh) and preparative TLC (200x200 mm, 0.2-0.25 mm in thickness) manufactured by Qingdao Haiyang Chemical Group Co. (China) were used for general chromatography. The enantiomeric excess (ee) of the products was determined by high-performance liquid chromatography (HPLC) with a chiral stationary phase in comparison with the authentic racemate sample. All the chiral stationary phases including Chiralcel IB, IB-3, IC-3, ID-3, IE-3, OD-RH and AS-RH used in this study were purchased from Daicel Chirsal Technologies. Optical rotations were reported as follows: $[\alpha]_D^{20}$ = (c: g/100 mL, in CH_2Cl_2).

Melting points were measured on a Mettler Hanon-MP450 and not corrected.

2. Substrate List

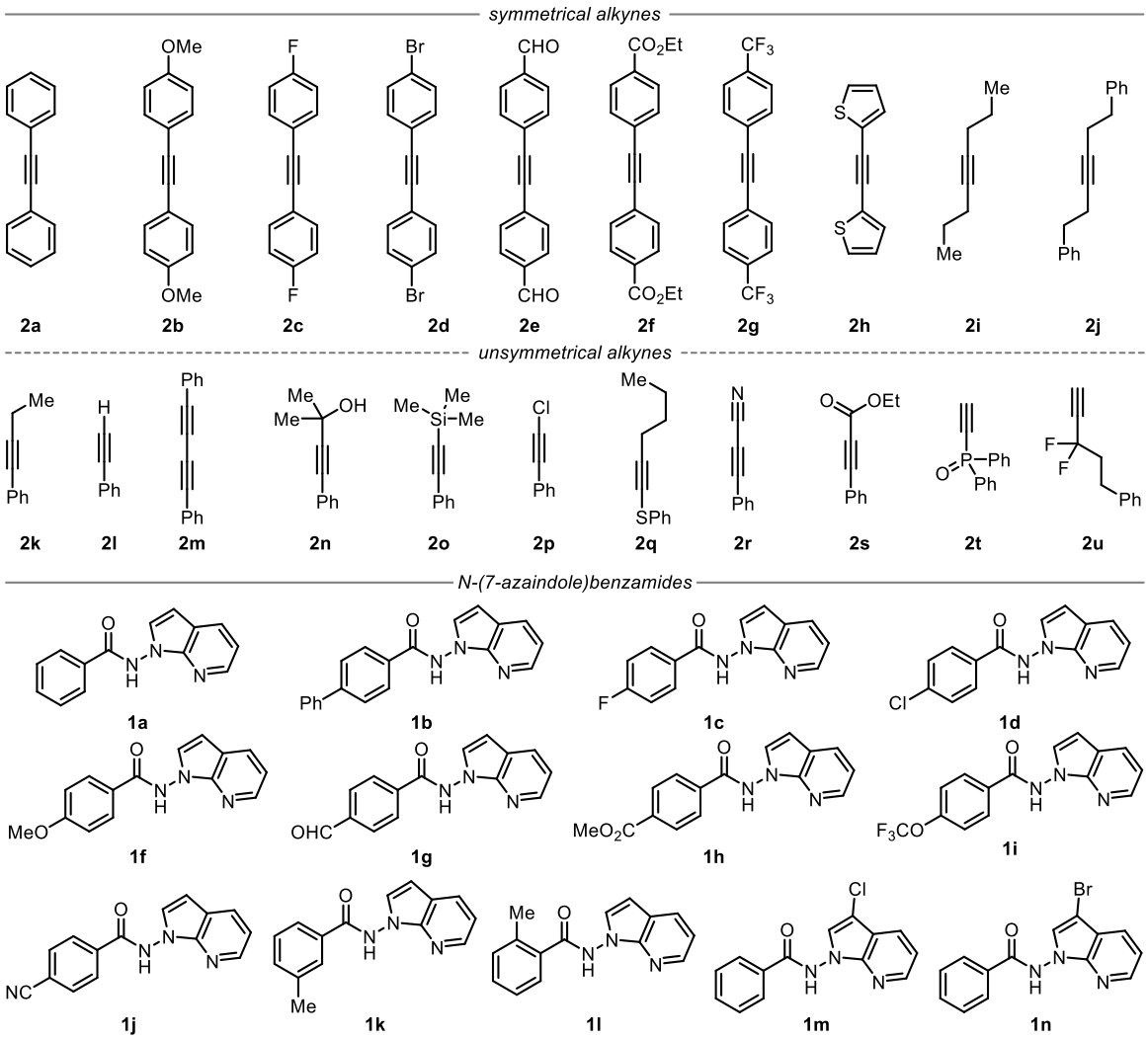
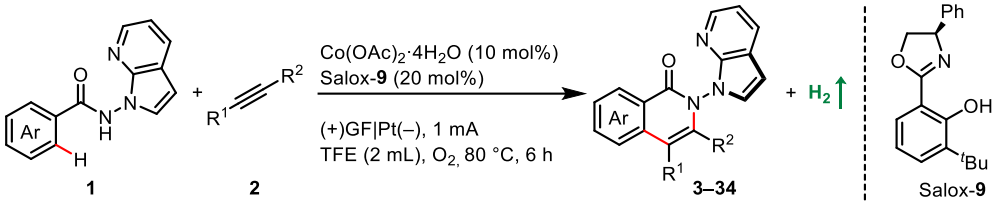


Figure S1. Tested alkyne and benzamides substrates.

3. General Procedure

General procedure (GP) for electrochemical cobalt-catalyzed atroposelective C–H annulation



A dry 10 mL undivided cell with a Teflon™-coated stirring bar was charged with benzamides **1** (0.08 mmol, 1 equiv.), alkynes **2** (0.16 mmol, 2 equiv.), $Co(OAc)_2·4H_2O$ (2.0 mg, 0.008 mmol, 10 mol%), Salox-**9** (4.7 mg, 0.016 mmol, 20 mol%), TFE (2 mL). The cell was sealed using a screw cap carrying a graphite felt anode (10 mm × 20 mm × 2 mm) and a platinum cathode (10 mm × 20 mm × 0.3 mm). The mixture was subjected to three cycles of vacuum/O_2 and then electrolyzed at a constant current of 1.0 mA for 6 h (cumulated charge: 2.8 $F·mol^{-1}$) at 80 °C with an aluminum block (Figure S4) under O_2 atmosphere. Once completed, the mixture was filtered through a pad of silica gel and washed with EtOAc (1 mL x 3). The volatiles were removed with a rotary evaporator under reduced pressure and the residue was subjected to flash column chromatography or preparative thin layer chromatography over silica gel to give the corresponding products.

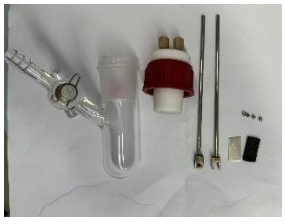


Figure S2. Detailed electrochemical parts.

Figure S3. Undivided cell.

Figure S4. Running electrolytic reactions.

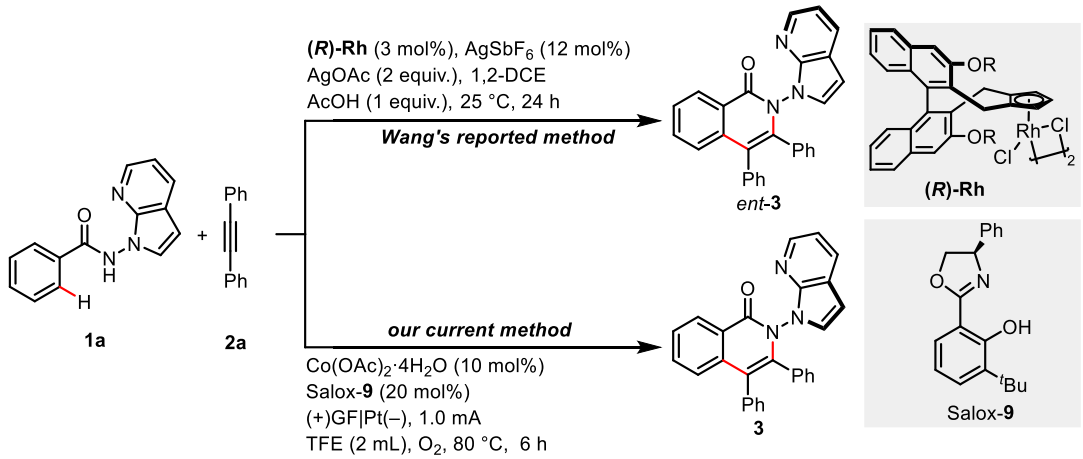
Figure S5. Power supply.

General procedure for the synthesis of racemic product.

A similar synthetic procedure was followed for synthesis of chiral products except that (*rac*-)-Salox-**9** was used.

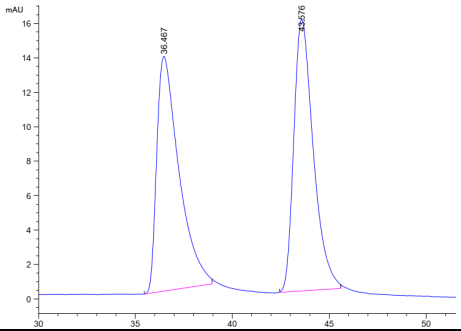
4. Determining the Absolute Configuration of Enantiopure Product

Product comparison with literature

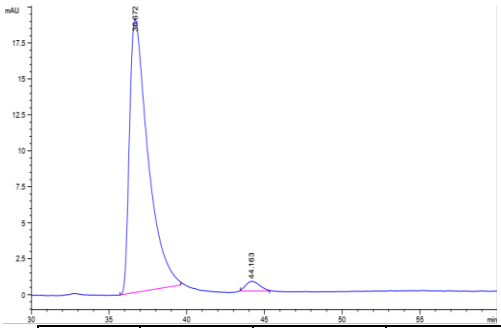


The procedure of Wang's report[5]: A dry 10 mL Schlenk tube with a Teflon™-coated stirring bar was charged with benzamide **1a** (24.0 mg, 0.1 mmol, 1 equiv.), alkyne **2a** (17.8 mg, 0.1 mmol, 1 equiv.), **(*R*)-Rh** (5.4 mg, 0.003 mmol, 3 mol%), $AgSbF_6$ (3.0 mg, 0.0012 mmol, 12 mol%), AgOAc (33.4 mg, 0.2 mmol, 2 equiv.), HOAc (6.0 mg, 0.1 mmol, 1.0 equiv.), and 1,2-DCE (1 mL). The reaction mixture was stirred at room temperature (25 °C) for 24 h. Then the mixture was filtered through a pad of silica gel and washed with EtOAc (1 mL x 3). The volatiles were removed with a rotary evaporator under reduced pressure and the residue was subjected to preparative thin layer chromatography over silica gel to give the corresponding product *ent*-**3**.

HPLC conditions: Daicel Chiralpak ID-3 column (85:15 *n*-hexane:2-propanol, 1.0 mL/min, 27 °C, 254 nm); t_r (minor) = 36.7 min, t_r (major) = 44.2 min, 95% ee.



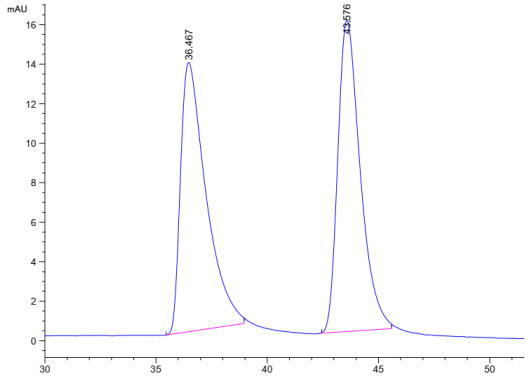
No.	Time	Area	Area (%)
1	36.5	1088.2	49.6
2	43.6	1105.5	50.4



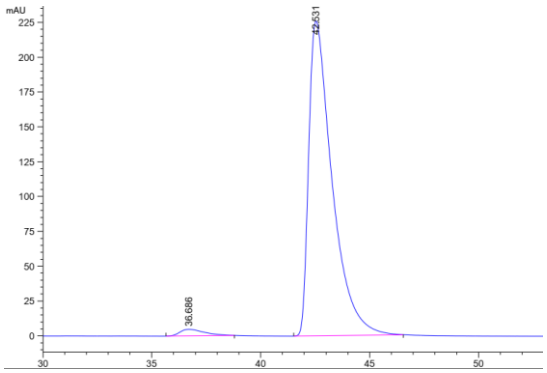
No.	Time	Area	Area (%)
1	36.7	1681.2	97.4
2	44.2	42.7	2.6

Our newly developed procedure: A dry 10 mL undivided cell with a Teflon™-coated stirring bar was charged with benzamide **1a** (19.2 mg, 0.08 mmol, 1 equiv.), alkyne **2a** (28.5 mg, 0.16 mmol, 2 equiv.), $Co(OAc)_2{\cdot}4H_2O$ (2.0 mg, 0.008 mmol, 10 mol%), Salox-**9** (4.7 mg, 0.016 mmol, 20 mol%), TFE (2 mL). The cell was sealed using a screw cap carrying a graphite felt anode (10 mm × 20 mm × 2 mm) and a platinum cathode (10 mm × 20 mm × 0.3 mm). The mixture was subjected to three cycles of vacuum/O_2 and then electrolyzed at a constant current of 1.0 mA for 6 h (cumulated charge: 2.8 $F{\cdot}mol^{-1}$) at 80 °C with an aluminum block under O_2 atmosphere. Once completed, the mixture was filtered through a pad of silica gel and washed with EtOAc (1 mL x 3). The volatiles were removed with a rotary evaporator under reduced pressure and the residue was subjected to preparative thin layer chromatography over silica gel to give the corresponding product **3**.

HPLC conditions: Daicel Chiralpak ID-3 column (85:15 *n*-hexane:2-propanol, 1.0 mL/min, 27 °C, 254 nm); t_r (minor) = 36.7 min, t_r (major) = 42.5 min, 96% ee.



No.	Time	Area	Area (%)
1	36.5	1088.2	49.6
2	43.6	1105.5	50.4

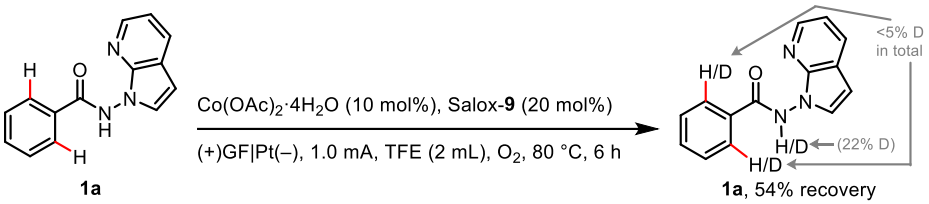


No.	Time	Area	Area (%)
1	36.7	377.4	2.2
2	42.5	16882.9	97.8

Analysis and conclusion: The product obtained by our newly developed method shows an opposite chiral HPLC traces with that of the one following the Wang's procedure, which was reported as (*S*)-chirality. Accordingly, the absolute configuration of our product **3** should be (*R*). In addition, this result can be supported by comparing the optical rotations from our new protocol ($[\alpha]_D^{25}$ = + 110.7, CH_2Cl_2) with Wang's initial report ($[\alpha]_D^{20}$ = −12 in $CHCl_3$). Overall, our product **3** was assigned to be (*R*)-chirality, which extrapolated to the other products.

5. Mechanistic Investigation

Reversibility of C−H activation



A dry 10 mL undivided cell with a Teflon™-coated stirring bar was charged with benzamide **1a** 19.2 mg, 0.08 mmol, 1 equiv.), $Co(OAc)_2·4H_2O$ (2.0 mg, 0.008 mmol, 10 mol%), Salox-**9** (4.7 mg, 0.016 mmol, 20 mol%), TFE (2 mL). The cell was sealed using a screw cap carrying a graphite felt anode (10 mm × 20 mm × 2 mm) and a platinum cathode (10 mm × 20 mm × 0.3 mm). The mixture was subjected to three cycles of vacuum/O_2 and then electrolyzed at a constant current of 1.0 mA for 6 h (cumulated charge: 2.8 $F·mol^{-1}$) at 80 °C with an aluminum block under O_2 atmosphere. Once completed, the mixture was filtered through a pad of silica gel through a pad of silica gel and washed with EtOAc (1 mL x 3). The volatiles were removed with a rotary evaporator under reduced pressure and the residue was subjected to preparative thin layer chromatography over silica gel to give the substrate **1a** in 54% recovery. ^{1}H NMR analysis indicated that there is no obvious deuterium (<5% D) at the *ortho*-positions, which implies that C−H bond cleavage in this case is irreversible (Figure S6).

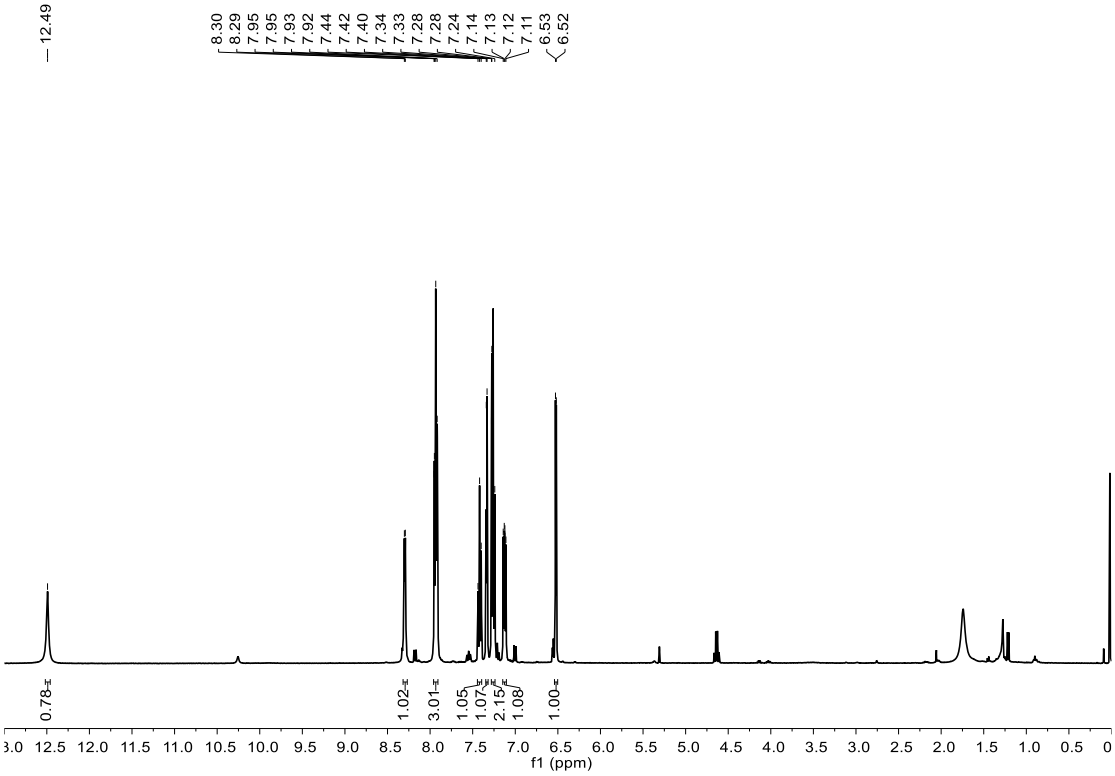
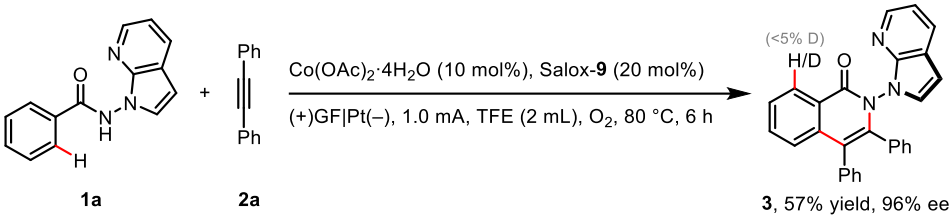


Figure S6. ^{1}H NMR spectrum of recovered **1a** (400 MHz, $CDCl_3$).

Reversibility of C−H activation



A dry 10 mL undivided cell with a Teflon™-coated stirring bar was charged with benzamide **1a** (19.2 mg, 0.08 mmol, 1 equiv.), alkyne **2a** (28.5 mg, 0.16 mmol, 2 equiv.), $Co(OAc)_2·4H_2O$ (2.0 mg, 0.008 mmol, 10 mol%), Salox-**9** (4.7 mg, 0.016 mmol, 20 mol%), TFE (2 mL). The cell was sealed using a screw cap carrying a graphite felt anode (10 mm × 20 mm × 2 mm) and a platinum cathode (10 mm × 20 mm × 0.3 mm). The mixture was subjected to three cycles of vacuum/O_2 and then electrolyzed at a constant current of 1.0 mA for 6 h (cumulated charge: 2.8 F·mol^{-1}) at 80 °C with an aluminum block under O_2 atmosphere. Once completed, the mixture was filtered through a pad of silica gel and washed with EtOAc (1 mL x 3). The volatiles were removed with a rotary evaporator under reduced pressure and the residue was subjected to preparative thin layer chromatography over silica gel to give the corresponding product **3**. ^{1}H NMR analysis indicated that there is no obvious deuterium (<5% D) at the unreacted *ortho*-position (Figure S7).

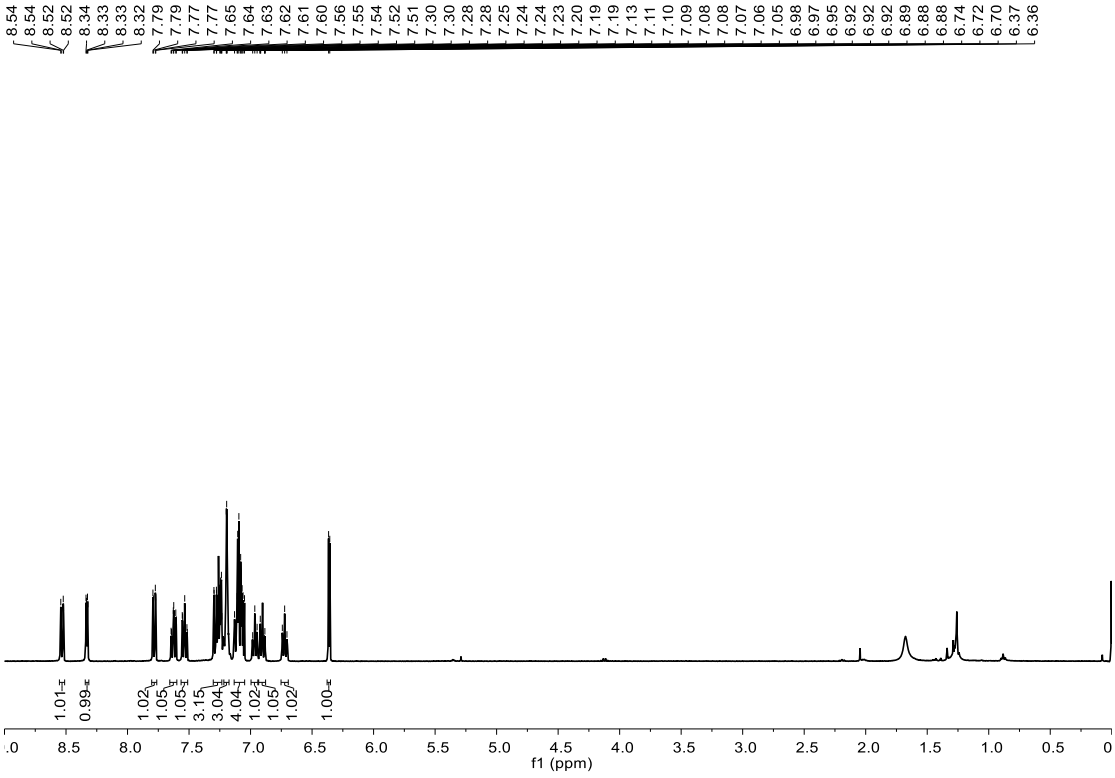
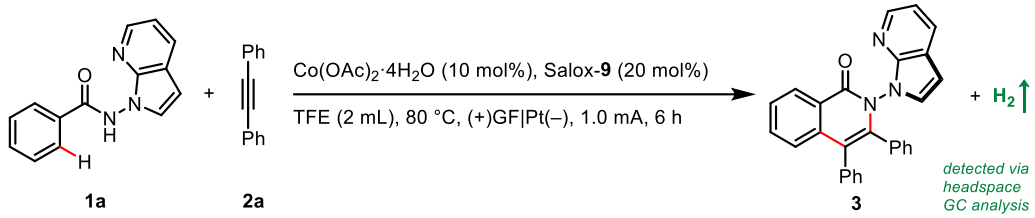


Figure S7. ^{1}H NMR spectrum of **3** (400 MHz, $CDCl_3$).

Detection of dihydrogen gas



A dry 10 mL undivided cell with a Teflon™-coated stirring bar was charged with benzamide **1a** (19.2 mg, 0.08 mmol, 1 equiv.), alkyne **2a** (28.5 mg, 0.16 mmol, 2 equiv.), $Co(OAc)_2{\cdot}4H_2O$ (2.0 mg, 0.008 mmol, 10 mol%), Salox-**9** (4.7 mg, 0.016 mmol, 20 mol%), TFE (2 mL). The cell was sealed using a screw cap carrying a graphite felt anode (10 mm × 20 mm × 2 mm) and a platinum cathode (10 mm × 20 mm × 0.3 mm). The mixture was subjected to three cycles of vacuum/O_2 and then electrolyzed at a constant current of 1.0 mA for 6 h (cumulated charge: 2.8 $F{\cdot}mol^{-1}$) at 80 °C with an aluminum block under O_2 atmosphere (balloon). Once completed, 1 mL gas volume was taken from the headspace of the reaction flask with a gas syringe and analyzed by headspace-GC (Figure S8).

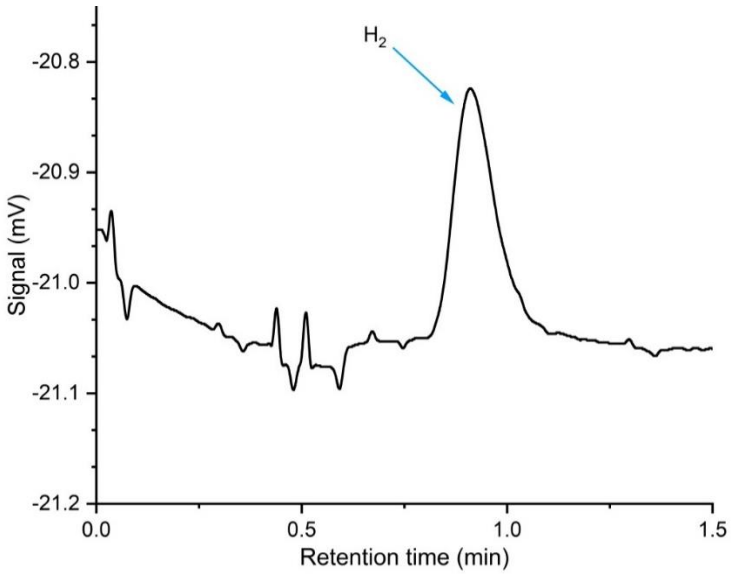


Figure S8. Chromatogram of the GC-headspace analysis.

Cyclic voltammetric studies

The cyclic voltammetry (CV) was carried out with a CHI600E-potentiostat and Electrochemical Software 22.1.0.0 by CH Instruments, Inc. A glassy-carbon electrode (3 mm diameter) was used as the working electrode, a Pt-wire as counter electrode and a silver chloride electrode was used as the reference. The measurements were carried out at a scan rate of 100 mV/s. Anhydrous 2,2,2-trifluoroethanol (TFE) was degassed by bubbling nitrogen into the liquid for at least 5 minutes. The samples were dissolved in TFE, including supporting electrolyte $^{n}Bu_4NBF_4$ (100 mM), benzamide **1a** (10 mM), alkyne **2a** (10 mM), $Co(OAc)_2{\cdot}4H_2O$ (10 mM), Salox-**3** (10 mM), Salox-**8** (10 mM), Salox-**9** (10 mM). For each sample, three to five potential sweeps between 0 and +2.0 V vs. Ag/AgCl were performed. No significant changes between the first and last ones were observed over these cyclic voltammetry cycles, which demonstrates that the electrode surface is stable at these potentials.

CV Analysis: In the CV experiment (Figure S9 andFigure **S10**), benzamide **1a** showed an oxidation peak at +1.14 V (vs Ag/AgCl, same below, curve b), being supportive of its tendency to anodic oxidation. Instead, alkyne **2a** has a much higher oxidation peak (+1.86 V). Although Salox-**9** exhibited two pairs of reversible redox peaks and $Co(OAc)_2{\cdot}4H_2O$ seemed redox inert (curve c/d), their combination led to a shift forward of the oxidation wave with a potential of 0.60 V (curve e) and the reversibility of **1a** is significantly less pronounced. This implies that the *in-situ* coordination of Co^{II} salt with Salox-**9** could not only prevent the ligand decomposition, but also facilitate the oxidation of Co^{II} to Co^{III}. Such facilitation effect can be further observed in the presence of **1a** (curve f), which showed a lower oxidation potential of +0.52 V.

Moreover, we measured the cyclic voltammograms of three representative Salox ligands, including Salox-**3**, Salox-**8**, and Salox-**9**. As illustrated in Figure S11, the first oxidation peak of Salox-**9** (E_{pa1} = +0.86 V, curve c) move slightly backward compared to those of Salox-**3** (E_{pa1} = +0.83 V, curve a) and Salox-**8** (E_{pa1} = +0.77 V, curve b). More importantly, although these three Salox ligands all exhibited two pairs of redox peaks, redox peaks of Salox-**9** appears much more reversible than those of Salox-**3** and Salox-**8**, which indicates the latter two ligands are more likely to degrade under electrolysis.

Finally, we conducted cyclic voltammograms of the combination of $Co(OAc)_2{\cdot}4H_2O$ with these three Salox ligands (Figure S12). The Co^{II}/Salox-**9** system shows an obvious oxidation peak at +0.59 V (curve c), which is significantly lower than those of both Co^{II}/Salox-**3** (E_{pa} = +1.05 V, curve a) and Co^{II}/Salox-**8** (E_{pa} = +0.91 V, curve b) combinations. Taking together, compared to Salox-**3** and Salox-**8**, Salox-**9** is less likely to electrochemically decompose and facilitate the oxidation of Co^{II} to Co^{III}.

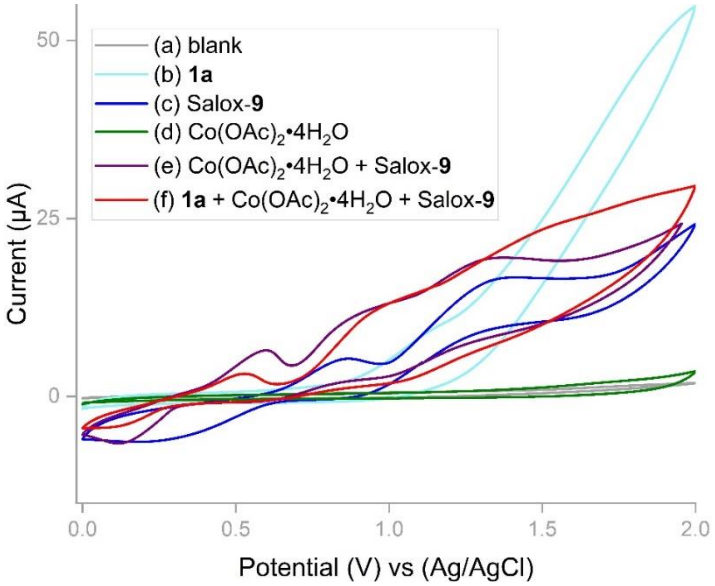


Figure S9. Cyclic voltammograms recorded on at the scan rate of 100 mV/s. (a) 3.0 mL $^{n}Bu_4NBF_4$ (100 mM) solution; (b) **1a** (10 mM) dissolved in 3.0 mL of $^{n}Bu_4NBF_4$ solution; (c) Salox-**9** (10 mM) dissolved in 3.0 mL of $^{n}Bu_4NBF_4$ solution; (d) $Co(OAc)_2{\cdot}4H_2O$ (10 mM) dissolved in 3.0 mL of $^{n}Bu_4NBF_4$ solution; (e) $Co(OAc)_2{\cdot}4H_2O$ (10 mM) and Salox-**9** (10 mM) dissolved in 3.0 mL of $^{n}Bu_4NBF_4$ solution; (f) **1a** (10 mM), $Co(OAc)_2{\cdot}4H_2O$ (10 mM) and Salox-**9** (10 mM) dissolved in 3.0 mL of $^{n}Bu_4NBF_4$ solution.

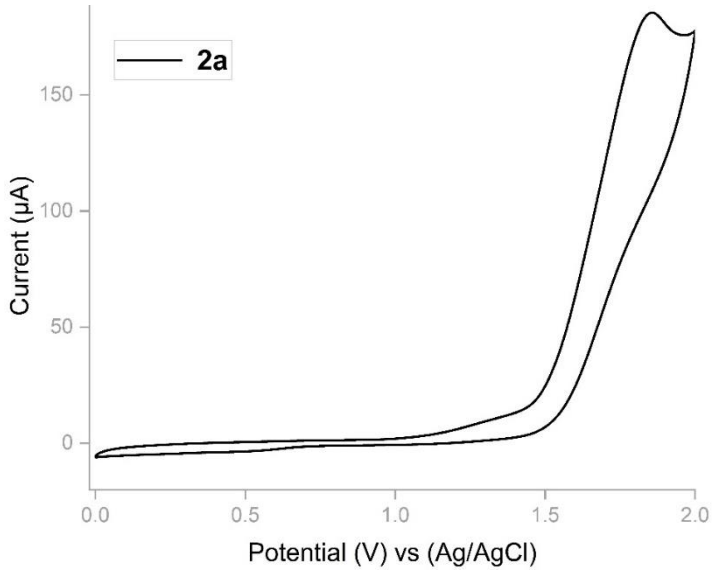


Figure S10. Cyclic voltammograms recorded on at the scan rate of 100 mV/s. **2a** (10 mM) dissolved in 3.0 mL of $^{n}Bu_4NBF_4$ solution.

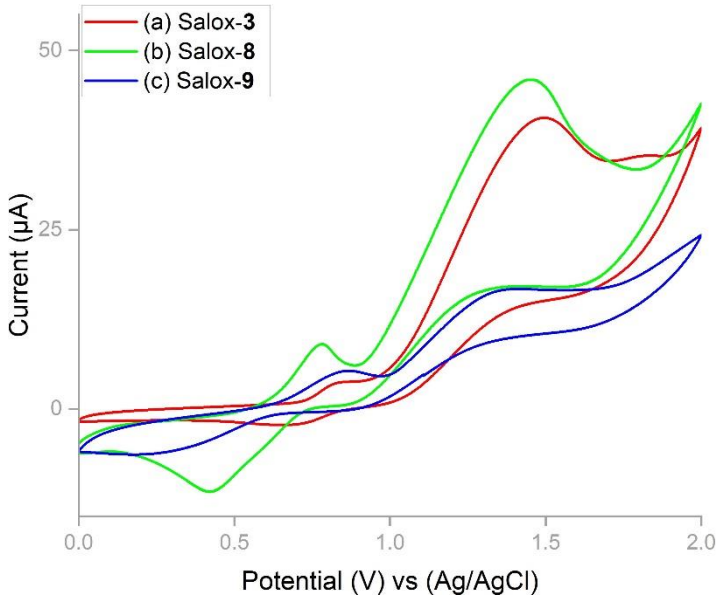


Figure S11. Cyclic voltammograms recorded on at the scan rate of 100 mV/s. (a) Salox-**3** (10 mM) dissolved in 3.0 mL of $^{n}Bu_4NBF_4$ solution; (b) Salox-**8** (10 mM) dissolved in 3.0 mL of $^{n}Bu_4NBF_4$ solution; (c) Salox-**9** (10 mM) dissolved in 3.0 mL of $^{n}Bu_4NBF_4$ solution.

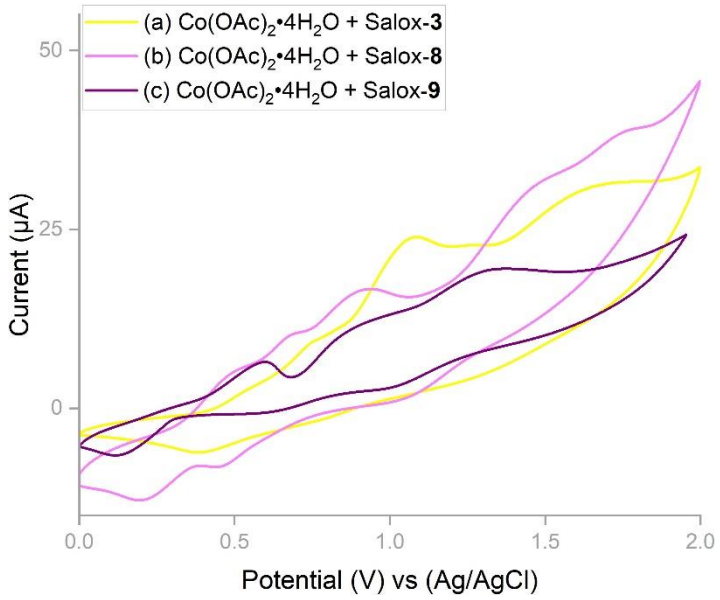
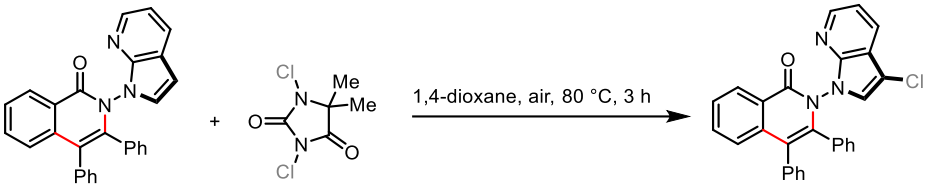


Figure S12. Cyclic voltammograms recorded on at the scan rate of 100 mV/s. (a) $Co(OAc)_2{\cdot}4H_2O$ (10 mM) and Salox-**3** (10 mM) dissolved in 3.0 mL of $^{n}Bu_4NBF_4$ solution; (b) $Co(OAc)_2{\cdot}4H_2O$ (10 mM) and Salox-**8** (10 mM) dissolved in 3.0 mL of $^{n}Bu_4NBF_4$ solution; (c) $Co(OAc)_2{\cdot}4H_2O$ (10 mM) and Salox-**9** (10 mM) dissolved in 3.0 mL of $^{n}Bu_4NBF_4$ solution.

6. Synthetic Application

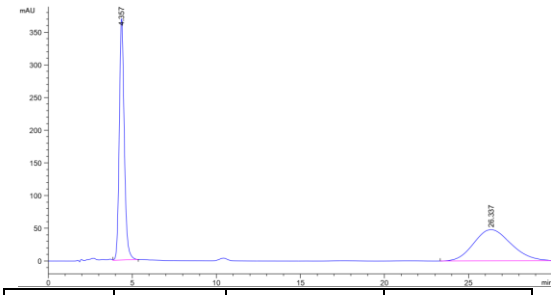
Electrophilic C−H chlorination



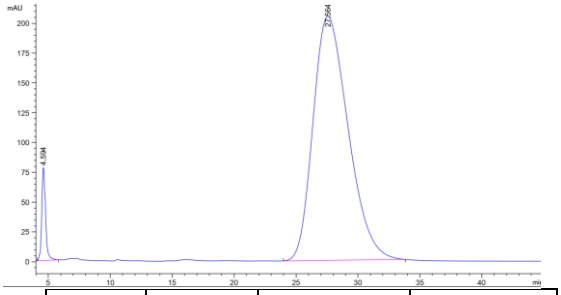
3, 98% ee DCDMH **34**, 44%, 92% ee

A dry 10 mL glass vessel with a Teflon™-coated stirring bar was charged with isoquinolinone **3** (41.3 mg, 0.1 mmol, 1 equiv.), 1,3-dichloro-5,5-dimethylhydantoin (DCDMH, 10.8 mg, 0.055 mmol, 0.55 equiv.) and 1,4-dioxane (1 mL) under air atmosphere. The reaction mixture was allowed to stir at 80 °C for 3 h. Upon completion, the reaction mixture was extracted with EtOAc (5 mL x 3). The combined organic phase was dried over Na_2SO_4 and filtered. The volatiles were removed with a rotary evaporator under reduced pressure and the residue was subjected to preparative thin layer chromatography over silica gel to give the chlorinated product **34** as white solid (19.7 mg, 0.044 mmol, 44%) with 92% ee. R_f = 0.7 (PE/EtOAc =3/1). m.p.: 162–164 °C.

HPLC conditions: Daicel Chiralpak AS-RH column (85:15 *n*-hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_r (minor) = 4.4 min, t_r (major) = 26.6 min, 92% ee.

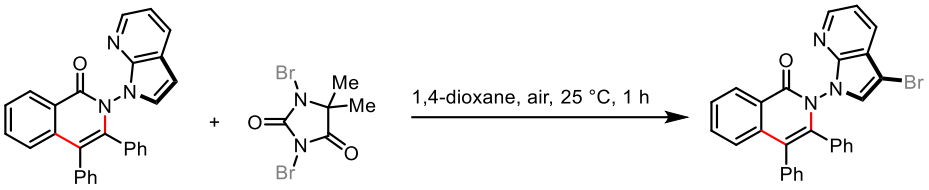


No.	Time	Area	Area (%)
1	4.4	7656.8	50.8510
2	26.3	7400.5	49.1490



No.	Time	Area	Area (%)
1	4.6	1675.1	3.9787
2	27.6	40426.2	96.0213

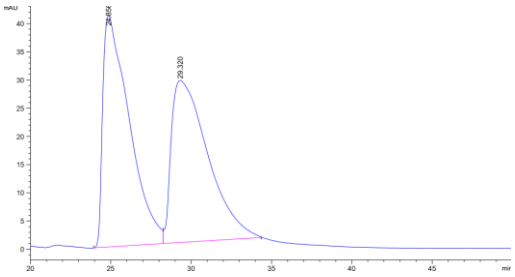
Electrophilic C−H bromination



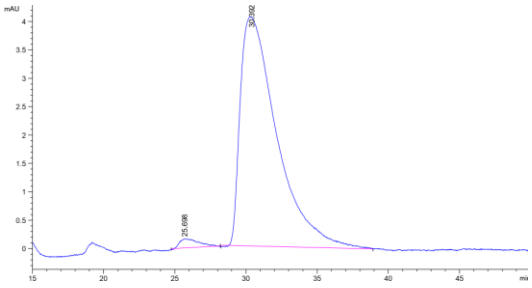
3, 98% ee DBDMH **35**, 41%, 98% ee

A dry 10 mL glass vessel with a Teflon™-coated stirring bar was charged with isoquinolinone **3** (41.3 mg, 0.1 mmol, 1 equiv.), 1,3-dibromo-5,5-dimethylhydantoin (DBDMH, 15.7 mg, 0.055 mmol, 0.55 equiv.) and 1,4-dioxane (1 mL) under air atmosphere. The reaction mixture was allowed to stir at room temperature (25 °C) for 1 h. Upon completion, the reaction mixture was extracted with EtOAc (5 mL x 3). The combined organic phase was dried over Na_2SO_4 and filtered. The volatiles were removed with a rotary evaporator under reduced pressure and the residue was subjected to preparative thin layer chromatography over silica gel to give the brominated product **35** as white solid (20.2 mg, 0.041 mmol, 41%) with 96% ee. R_f = 0.6 (PE/EtOAc =3/1). m.p.: 180–182 °C

HPLC conditions: Daicel Chiralpak IB-3 column (96:4 *n*-hexane: 2-propanol, 1.0 mL/min, 27 °C, 254 nm); t_r (minor) = 25.7 min, t_r (major) = 30.4 min, 96% ee.

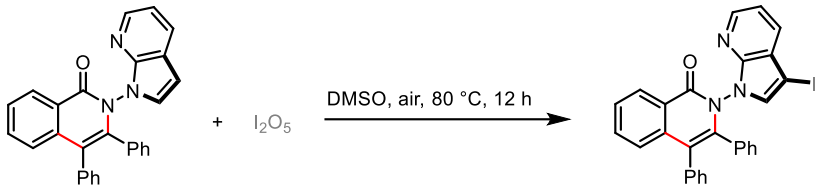


No.	Time	Area	Area (%)
1	24.9	4693.8	50.7784
2	29.3	4549.9	49.2216



No.	Time	Area	Area (%)
1	25.7	14.8	2.0167
2	30.4	721.1	97.9833

Electrophilic C−H iodination

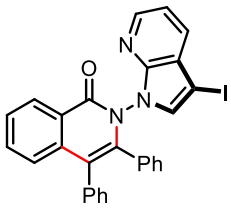


3, 98% ee

36, 74%, 82% ee

A dry 10 mL glass vessel with a Teflon™-coated stirring bar was charged with isoquinolinone **3** (41.3 mg, 0.1 mmol, 1 equiv.), I_2O_5 (40.1 mg, 0.12 mmol, 1.2 equiv.) and DMSO (1 mL) under air atmosphere. The reaction mixture was allowed to stir at 80 °C for 12 h. Upon completion, the reaction mixture was extracted with EtOAc (5 mL x 3). The combined organic phase was dried over Na_2SO_4 and filtered. The volatiles were removed with a rotary evaporator under reduced pressure and the residue was subjected to preparative thin layer chromatography over silica gel to give the brominated product **36** as pale yellow solid (39.9 mg, 0.074 mmol, 74%) with 82% ee. R_f = 0.5 (PE/EtOAc =3/1). m.p.: 218–220 °C.

(*R*)-2-(3-iodo-1H-pyrrolo[2,3-b]pyridin-1-yl)-3,4-diphenylisoquinolin-1(2H)-one **(36)**



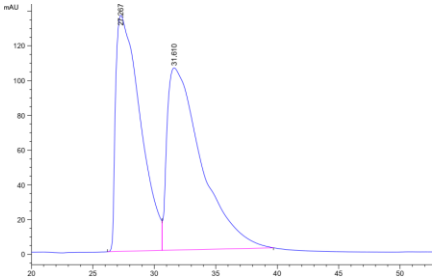
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 3.8 Hz, 1H), 8.33 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.63 (td, *J* = 8.3, 7.8, 1.4 Hz, 1H), 7.59 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.56 – 7.53 (m, 2H), 7.29 – 7.27 (m, 1H), 7.25 – 7.18 (m, 5H), 7.14 (dd, *J* = 7.9, 4.8 Hz, 1H), 7.08 (t, *J* = 8.5 Hz, 2H), 7.00 (t, *J* = 7.9 Hz, 1H), 6.94 – 6.91 (m, 1H), 6.72 (t, *J* = 7.6 Hz, 1H) ppm.

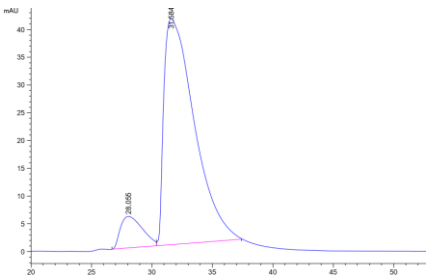
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.90, 146.67, 145.20, 141.72, 137.62, 135.46, 133.38, 132.76, 131.91, 131.50, 131.30, 129.93, 129.762, 129.756, 128.66, 128.36, 128.26, 128.01, 127.40, 127.27, 127.17, 127.04, 126.14, 125.23, 121.50, 119.56, 117.95 ppm.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{19}IN_3O$: 540.0567; Found: 540.0569.

$[\alpha]_D^{25}$ = +105.7 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak IB-3 column (96:4 *n*-hexane: 2-propanol, 1.0 mL/min, 27 °C, 254 nm); t_r (minor) = 28.1 min, t_r (major) = 31.6 min, 82% ee.

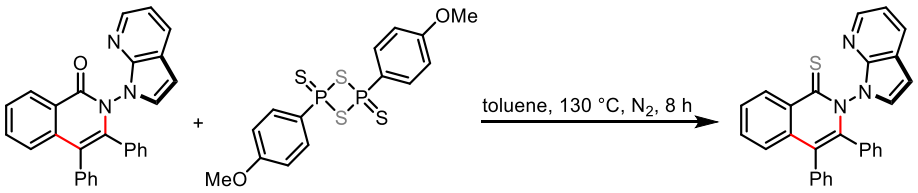




No.	Time	Area	Area (%)
1	27.3	18894.6	47.9349
2	31.6	20522.7	52.0651

No.	Time	Area	Area (%)
1	28.1	717.6	9.1236
2	31.6	7147.9	90.8764

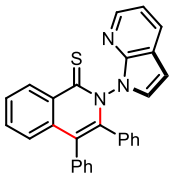
***O*-to-*S* exchange**



3 Lawesson's reagent **37**, 85%, 67% ee

A dry 10 mL Schlenk tube with a Teflon™-coated stirring bar was charged with isoquinolinone **3** (41.3 mg, 0.1 mmol, 1 equiv.), Lawesson's reagent (161.8 mg, 0.4 mmol, 4.0 equiv.), and toluene (1 mL). The mixture was subjected to three cycles of vacuum/nitrogen and was allowed to stir at 130 °C for 8 h. Upon completion, the reaction mixture was extracted with EtOAc (5 mL x 3). The combined organic phase was dried over Na_2SO_4 and filtered. The volatiles were removed with a rotary evaporator under reduced pressure and the residue was subjected to preparative thin layer chromatography over silica gel to give the product **37** as pale yellow solid (36.5 mg, 0.085 mmol, 85%) with 67% ee. R_f = 0.7 (PE/EtOAc =3/1). m.p.: 108–110 °C.

(*R*)-3,4-diphenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinoline-1(2H)-thione **(37)**



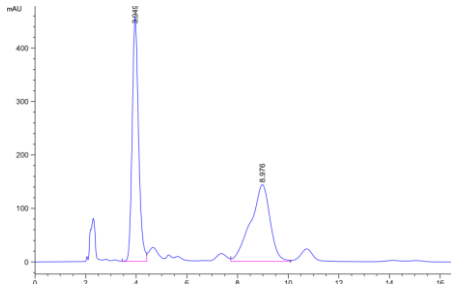
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.15 (d, *J* = 8.0 Hz, 1H), 8.34 (d, *J* = 3.1 Hz, 2H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.1 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.20 – 7.19 (m, 4H), 7.14 – 7.15 (m, 4H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.70 (t, *J* = 7.8 Hz, 1H), 6.38 (t, *J* = 1.6 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 186.70, 145.57, 144.39, 144.22, 135.34, 133.61, 133.59, 133.39, 133.23, 132.51, 131.30, 131.08, 129.80, 129.78, 129.56, 128.61, 128.37, 128.12, 128.10, 127.57, 127.02, 126.93, 126.54, 124.80, 118.44, 117.28, 100.58 ppm.

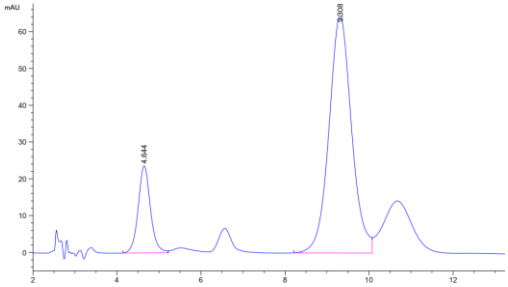
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{20}N_3S$: 430.1372; Found: 430.1375.

$[\alpha]_D^{25}$ = +109.0 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak AS-RH column (95:5 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 4.6 min, t_r (major) = 9.3 min, 67% ee.



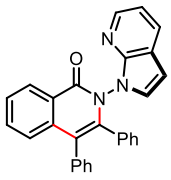
No.	Time	Area	Area (%)
1	4.0	8031.7	51.2245
2	9.0	7647.8	48.7755



No.	Time	Area	Area (%)
1	4.6	481.2	16.6203
2	9.3	2413.9	83.3797

7. Synthesis and Characterization of Products

(*R*)-3,4-diphenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(3)**



Following the general procedure, the title compound was obtained as white solid in 71% yield (23.2 mg, 0.06 mmol) with 96% ee. R_f = 0.6 (PE/EtOAc = 3/1). m.p.: 153–155 °C.

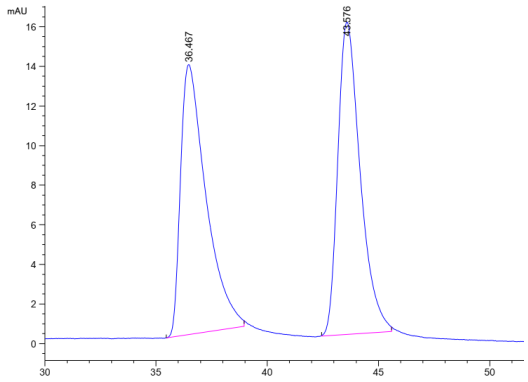
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.33 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.79 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.63 (td, *J* = 8.4, 7.8, 1.4 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.18 (m, 4H), 7.11 – 7.05 (m, 4H), 6.97 (t, *J* = 7.1 Hz, 1H), 6.93 – 6.88 (m, 1H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.36 (d, *J* = 3.8 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.20, 146.91, 144.21, 142.09, 137.75, 135.72, 133.34, 132.34, 131.68, 131.44, 129.96, 129.85, 129.54, 128.84, 128.75, 128.38, 128.25, 128.05, 127.38, 127.30, 127.09, 127.08, 126.15, 125.45, 119.46, 118.71, 117.25, 100.70 ppm.

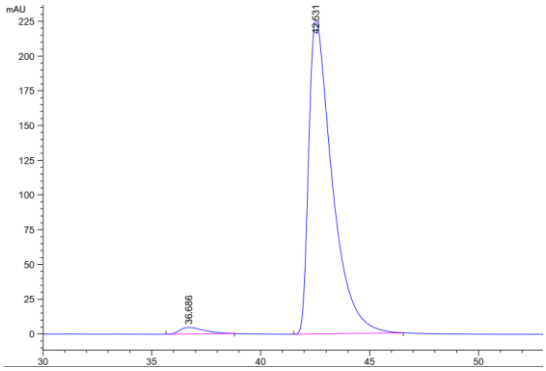
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{20}N_3O$: 414.1606; Found: 414.1596.

$[\alpha]_D^{25}$ = + 110.7 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (85:15 *n*-hexane: 2-propanol, 1.0 mL/min, 27 °C, 254 nm); t_r (minor) = 36.7 min, t_r (major) = 42.5 min, 96% ee.

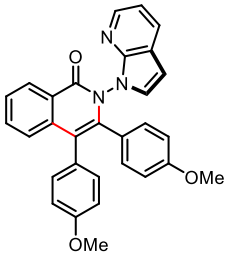


No.	Time	Area	Area (%)
1	36.5	1088.2	49.6
2	43.6	1105.5	50.4



No.	Time	Area	Area (%)
1	36.7	377.4	2.2
2	42.5	16882.9	97.8

(*R*)-3,4-bis(4-methoxyphenyl)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(4)**



Following the general procedure, the title compound was obtained as white solid in 54% yield (20.4 mg, 0.04 mmol) with 96% ee. R_f = 0.7 (PE/EtOAc = 1/1). m.p.: 109–113 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (ddd, *J* = 8.0, 1.5, 0.5 Hz, 1H), 8.32 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.80 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.61 (ddd, *J* = 8.2, 7.2, 1.5 Hz, 1H), 7.51 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.30 (ddd, *J* = 8.2, 1.2, 0.6 Hz, 1H), 7.14 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.08-7.05 (m, *J* = 7.6, 3.1, 1.6 Hz, 3H), 7.00 (ddd, *J* = 14.4, 8.5, 2.1 Hz, 2H), 6.81 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.74 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.49 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.38 (d, *J* = 3.8 Hz, 1H), 6.25 (dd, *J* = 8.5, 2.7 Hz, 1H), 3.76 (s, 3H), 3.56 (s, 3H) ppm.

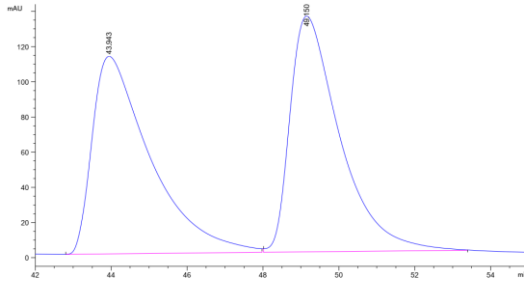
^{13}C NMR (100 MHz, $CDCl_3$): δ 161.29, 158.97, 158.48, 146.98, 144.19, 142.11, 138.15, 133.24, 132.72, 132.46, 131.25, 131.05, 129.54, 128.86, 128.69, 128.13, 127.20, 126.13, 125.37, 124.91, 119.30, 118.77, 117.19, 113.69, 113.63, 112.62, 112.49, 100.72, 55.24, 54.98

ppm.

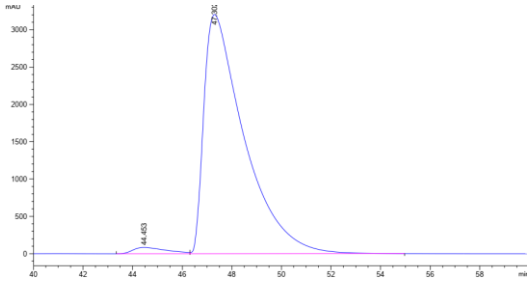
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{24}N_3O_3$: 474.1818; Found: 474.1814.

$[\alpha]_D^{25}$ = +315.3 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (80:20 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 44.5 min, t_r (major) = 47.3 min, 96% ee.

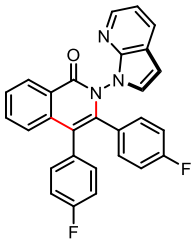


No.	Time	Area	Area (%)
1	43.9	11970.6	49.5
2	49.2	12235.8	50.5



No.	Time	Area	Area (%)
1	44.5	7863.8	2.1
2	47.3	362643	97.9

(*R*)-3,4-bis(4-fluorophenyl)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(5)**



Following the general procedure, the title compound was obtained as white solid in 48% yield (19.4 mg, 0.04 mmol) with 97% ee. R_f = 0.7 (PE/EtOAc = 1/1). m.p.: 97–99 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 8.3 Hz, 1H), 8.31 (d, *J* = 4.7 Hz, 1H), 7.82 – 7.80 (m, 1H), 7.67 – 7.63 (m, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.24 (s, 1H), 7.19 – 7.15 (m, 2H), 7.13 – 7.04 (m, 4H), 7.00 – 6.90 (m, 2H), 6.68 (td, *J* = 8.5, 2.5 Hz, 1H), 6.44 (td, *J* = 8.6, 2.5 Hz, 1H), 6.41 – 6.40 (m, 1H) ppm.

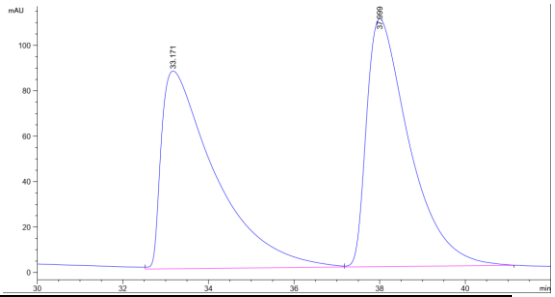
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.22 (d, J_{C-F} = 248.9 Hz), 161.97 (d, J_{C-F} = 247.3 Hz), 161.10, 146.82, 144.27, 141.45, 137.51, 133.52, 133.24 (d, J_{C-F} = 8.2 Hz), 132.96 (d, J_{C-F} = 8.3 Hz), 131.81 (d, J_{C-F} = 8.1 Hz), 131.62 (d, J_{C-F} = 8.5 Hz), 131.49 (d, *J* = 3.8 Hz), 129.70, 128.86, 128.65, 128.28 (d, J_{C-F} = 3.8 Hz), 127.66, 125.94, 125.51, 118.79, 118.75, 117.43, 115.61 (d, J_{C-F} = 21.3 Hz), 115.35 (d, *J* = 21.5 Hz), 114.58, 114.36, 101.01 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ -111.68 – -111.73 (m, 1F), -114.00 – -114.05 (m, 1F) ppm.

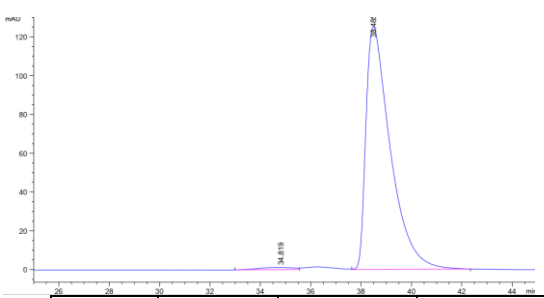
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{18}F_2N_3O$: 450.1418; Found: 450.1413.

$[\alpha]_D^{25}$ = +110.3 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (92:8 *n*-hexane: 2-propanol, 1.0 mL/min, 27 °C, 254 nm); t_r (minor) = 34.8 min, t_r (major) = 38.5 min, 97% ee.

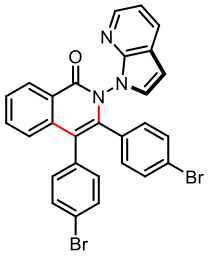


No.	Time	Area	Area (%)
1	33.2	7636.7	50.1620
2	38.0	7587.3	49.8380



No.	Time	Area	Area (%)
1	34.8	119.9	1.4000
2	38.5	8444.1	98.6000

(*R*)-3,4-bis(4-bromophenyl)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(6)**



Following the general procedure, the title compound was obtained as white solid in 40% yield (18.2 mg, 0.03 mmol) with 99.5% ee. R_f = 0.7 (PE/EtOAc = 1/1). m.p.: 121–123 °C.

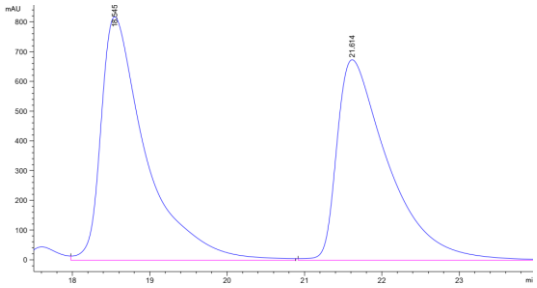
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 7.9 Hz, 1H), 8.30 (d, *J* = 4.7 Hz, 1H), 7.82 (dt, *J* = 7.9, 1.5 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.39 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 1H), 7.11 – 7.07 (m, 2H), 7.07 – 7.01(m, 3H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.41 (dd, *J* = 3.8, 1.3 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.99, 146.95, 144.30, 141.13, 137.19, 134.44, 133.57, 133.24, 132.99, 131.90, 131.59, 131.45, 131.30, 131.09, 130.64, 130.62, 129.77, 128.91, 128.65, 127.79, 125.89, 125.55, 122.96, 121.87, 118.83, 118.44, 117.52, 101.25 ppm.

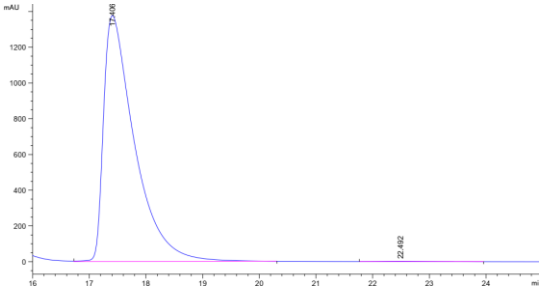
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{18}Br_2N_3O$: 569.9811; Found: 571.9787.

$[\alpha]_D^{25}$ = +264.9 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak IB column (70:30 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 17.4 min, t_r (major) = 22.5 min, 99.5% ee.

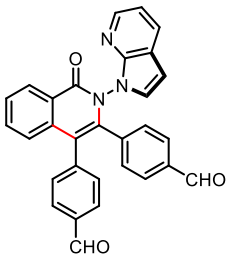


No.	Time	Area	Area (%)
1	18.5	33073.5	51.4519
2	21.6	31207.0	48.5481



No.	Time	Area	Area (%)
1	17.4	52170.5	99.7697
2	22.5	120.4	0.2303

(*R*)-4,4'-(1-oxo-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)-1,2-dihydroisoquinoline-3,4-diyl)dibenzaldehyde **(7)**



Following the general procedure, the title compound was obtained as black solid in 43% yield (16.2 mg, 0.03 mmol) with 98% ee. R_f = 0.4 (PE/EtOAc = 1/1). m.p.: 108–110 °C.

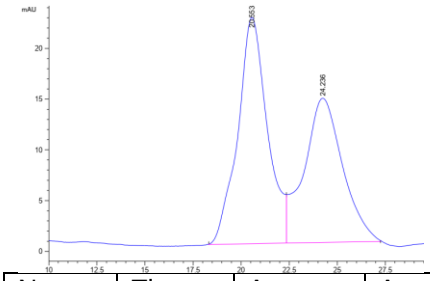
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.95 (s, 1H), 9.71 (s, 1H), 8.54 (dd, *J* = 8.1, 1.3 Hz, 1H), 8.32 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.80 (d, *J* = 1.6 Hz, 1H), 7.78 (d, *J* = 1.5 Hz, 1H), 7.76 – 7.73 (m, 1H), 7.67 (ddd, *J* = 8.3, 7.3, 1.5 Hz, 1H), 7.59 (td, *J* = 7.8, 7.3, 1.2 Hz, 1H), 7.50 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.41 (d, *J* = 1.9 Hz, 1H), 7.39 (d, *J* = 1.9 Hz, 1H), 7.36 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.27 (dt, *J* = 5.6, 3.6 Hz, 2H), 7.23 – 7.21 (m, 1H), 7.12 (d, *J* = 3.8 Hz, 1H), 7.09 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.39 (d, *J* = 3.8 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ. 191.74, 191.47, 160.86, 146.83, 144.40, 141.79, 140.99, 137.83, 136.65, 135.77, 135.45, 133.80, 132.39, 132.16, 130.75, 130.46, 130.08, 129.84, 129.49, 129.07, 128.71, 128.54, 128.43, 128.15, 125.77, 125.61, 118.74, 118.49, 117.67, 101.40 ppm.

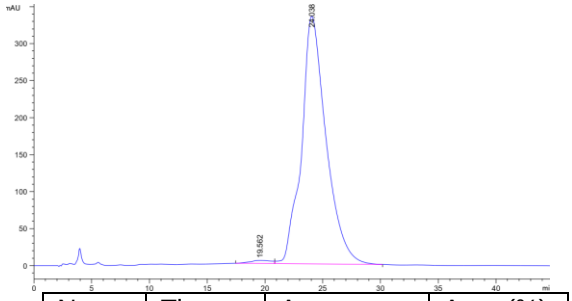
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{20}N_3O_3$: 470.1505; Found: 470.1496.

$[\alpha]_D^{25}$ = +195.7 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak OD-RH column (70:30 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 19.6 min, t_r (major) = 24.0 min, 98% ee.

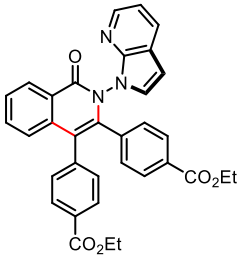


No.	Time	Area	Area (%)
1	20.6	2446.8	53.1648
2	24.2	2155.5	46.8352



No.	Time	Area	Area (%)
1	19.6	558.5	1.1087
2	24.0	49815.4	98.8913

(*R*)-diethyl 4,4'-(1-oxo-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)-1,2-dihydroisoquinoline-3,4-diyl) dibenzoate **(8)**



Following the general procedure, the title compound was obtained as white solid in 57% yield (25.4 mg, 0.05 mmol) with 97% ee. R_f = 0.4 (PE/EtOAc =2/1). m.p.: 136–138 °C.

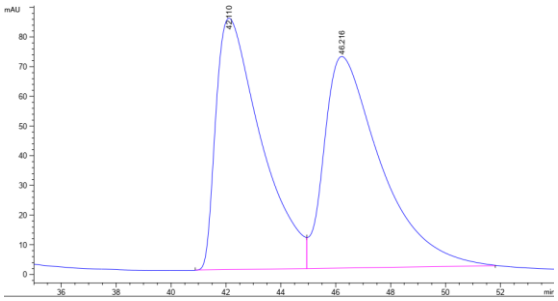
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, *J* = 8.0 Hz, 1H), 8.32 (d, *J* = 4.8 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.90 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.81 – 7.78 (m, 1H), 7.68 – 7.62 (m, 2H), 7.59 – 7.55 (m, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.29 (ddd, *J* = 13.4, 9.2, 2.7 Hz, 3H), 7.24 – 7.17(m, 3H), 7.09 (ddd, *J* = 7.7, 5.4, 3.3 Hz, 2H), 6.39 (dd, *J* = 3.8, 2.2 Hz, 1H), 4.35 (qd, *J* = 7.1, 1.9 Hz, 2H), 4.25 – 4.19 (m, 2H), 1.37 (td, *J* = 7.1, 1.9 Hz, 3H), 1.28 (td, *J* = 7.1, 2.0 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.31, 165.88, 160.96, 146.89, 144.36, 141.21, 140.17, 136.97, 136.46, 133.64, 131.69, 131.46, 130.30, 129.97, 129.87, 129.78, 129.67, 129.51, 128.94, 128.61, 128.56, 128.48, 127.89, 125.87, 125.53, 118.75, 118.69, 117.55, 101.25, 61.24, 14.42, 14.28 ppm.

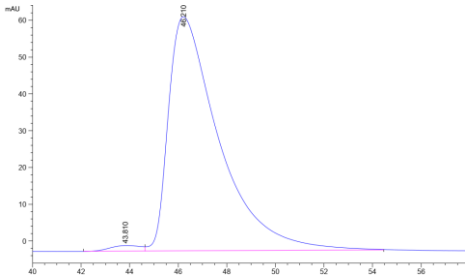
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{28}N_3O_5$: 558.2029; Found: 558.2021.

$[\alpha]_D^{25}$ = +184.0 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (80:20 *n*-hexane: 2-propanol, 1.0 mL/min, 27 °C, 254 nm); t_r (minor) = 43.8 min, t_r (major) = 46.2 min, 97% ee.

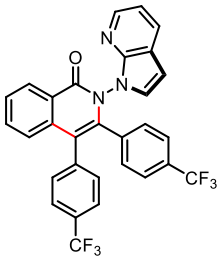


No.	Time	Area	Area (%)
1	42.1	9690.6	48.5931
2	46.2	10251.7	51.4069



No.	Time	Area	Area (%)
1	43.8	133.3	1.4210
2	46.2	9244.1	98.5790

(*R*)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)-3,4-bis(4-(trifluoromethyl)phenyl)isoquinolin-1(2H)-one **(9)**



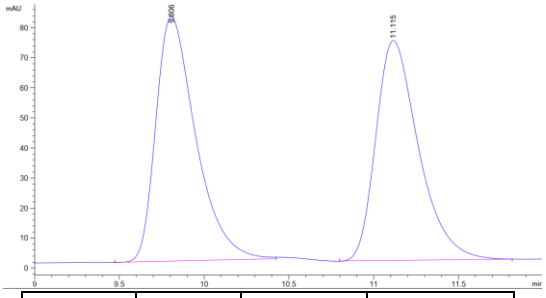
Following the general procedure, the title compound was obtained as white solid in 64% yield (28.2 mg, 0.05 mmol) with 97% ee. R_f = 0.4 (PE/EtOAc =3/1). m.p.: 95–97 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 7.9 Hz, 1H), 8.32 (dt, *J* = 4.8, 1.3 Hz, 1H), 7.82 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.69 – 7.65(m, 1H), 7.60 – 7.55 (m, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.6 Hz, 3H), 7.30 – 7.27 (m, 1H), 7.24 – 7.18 (m, 2H), 7.11 – 7.08 (m, 2H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.41 (dd, *J* = 3.8, 0.9 Hz, 1H) ppm.

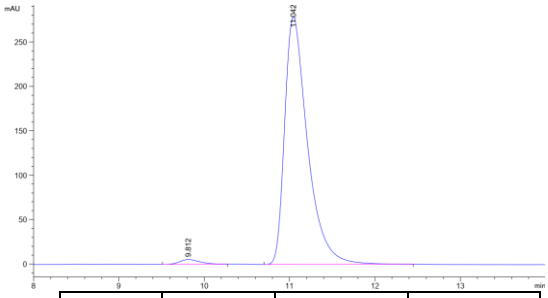
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.90, 146.90, 144.36, 140.95, 139.14, 136.85, 135.51, 133.77, 132.01, 131.78, 131.42, 131.06, 130.74, 130.37, 130.16, 130.07, 129.86, 129.75, 129.42, 129.28, 128.99, 128.58, 128.10, 127.59, 125.83, 125.66, 125.60, 125.38, 125.34, 124.88, 124.42, 124.38, 124.32, 124.28, 122.63, 122.17, 119.92, 119.46, 118.82, 118.43, 117.66, 101.45 ppm (coupling constants were difficult to provide owing to overlap posed by two very similar CF_3 groups).**HRMS (ESI)** m/z: $[M+H]^+$ Calcd $C_{30}H_{18}F_6N_3O$: 550.1351; Found: 550.1348.

$[\alpha]_D^{25}$ = +126.0 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (85:15 *n*-hexane: 2-propanol,1.0 mL/min, 27 °C, 254 nm); t_r (minor) = 9.8 min, t_r (major) = 11.0 min, 97% ee.

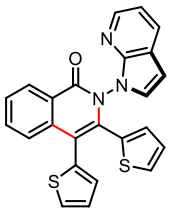


No.	Time	Area	Area (%)
1	9.8	1334.6	50.9174
2	11.1	1286.5	49.0826



No.	Time	Area	Area (%)
1	9.8	88.5	1.6748
2	11.0	5195.6	98.3252

(*R*)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)-3,4-di(thiophen-2-yl)isoquinolin-1(2H)-one **(10)**



Following the general procedure, the title compound was obtained as gray-black oily liquid in 69% yield (23.5 mg, 0.06 mmol) with 97% ee. R_f = 0.5 (PE/EtOAc =3/1).

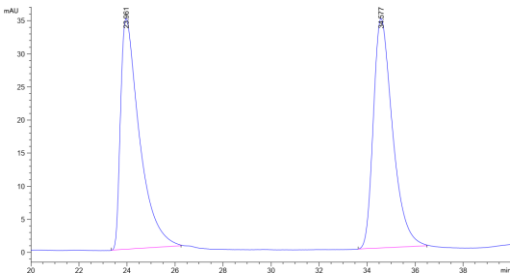
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (dd, *J* = 8.3, 1.1 Hz, 1H), 8.35 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.86 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.59 – 7.55 (m, 1H), 7.53 – 7.50 (m, 1H), 7.30 (ddd, *J* = 4.8, 1.5, 0.5 Hz, 1H), 7.15 (d, *J* = 3.8 Hz, 1H), 7.11 (ddd, *J* = 7.8, 4.8, 0.5 Hz, 1H), 7.03 (ddd, *J* = 5.1, 1.1, 0.5 Hz, 1H), 7.00 – 6.97 (m, 2H), 6.78 (ddd, *J* = 3.6, 1.2, 0.6 Hz, 1H), 6.54 (ddd, *J* = 5.1, 3.6, 0.5 Hz, 1H), 6.46 (dd, *J* = 3.8, 0.5 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.05, 147.02, 144.31, 137.60, 137.25, 136.21, 133.65, 131.75, 130.69, 130.20, 129.70, 128.94, 128.70, 128.10, 127.91, 127.03, 126.79, 126.33, 125.88, 125.46, 118.83, 117.44, 115.00, 100.88 ppm.

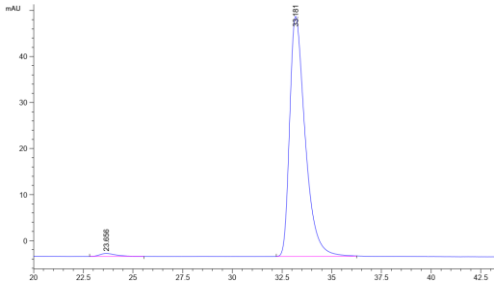
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{16}N_3OS_2$: 426.0735; Found: 426.0728.

$[\alpha]_D^{25}$ = +378.7 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (80:20 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 23.7 min, t_r (major) = 33.2 min, 97% ee.

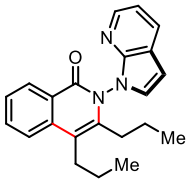


No.	Time	Area	Area (%)
1	24.0	1907.3	49.6753
2	34.6	1932.2	50.3247



No.	Time	Area	Area (%)
1	24.0	37.5	1.3089
2	33.2	1468.1	98.6911

(*R*)-3,4-dipropyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(11)**



Following the general procedure, the title compound was obtained as white solid in 63% yield (17.5 mg, 0.05 mmol) with 97% ee. R_f = 0.5 (PE/EtOAc =2/1). m.p.: 126–128 °C.

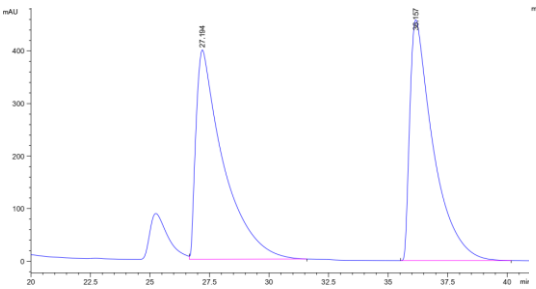
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (dt, *J* = 8.0, 1.1 Hz, 1H), 8.30 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.99 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.72 (dd, *J* = 2.1, 1.1 Hz, 1H), 7.71 (d, *J* = 1.1 Hz, 1H), 7.44 (ddd, *J* = 8.1, 5.2, 3.0 Hz, 1H), 7.28 (d, *J* = 3.8 Hz, 1H), 7.15 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.70 (d, *J* = 3.8 Hz, 1H), 2.77 (t, *J* = 8.3 Hz, 2H), 2.63 – 2.56 (m, 1H), 2.43 – 2.34 (m, 1H), 1.76 – 1.68 (m, 2H), 1.54 – 1.48 (m, 2H), 1.12 (t, *J* = 7.3 Hz, 3H), 0.74 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.61, 147.41, 144.61, 141.48, 137.20, 133.22, 129.83, 129.81, 128.95, 126.37, 125.30, 123.37, 119.23, 117.63, 114.53, 101.21, 31.28, 30.27, 23.64, 23.47, 14.72, 14.44 ppm.

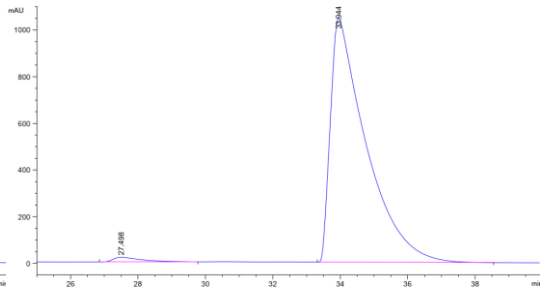
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{24}N_3O$: 346.1919; Found: 346.1910.

$[\alpha]_D^{25}$ = −216.0 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (80:20 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 27.5 min, t_r (major) = 33.9 min, 97% ee.

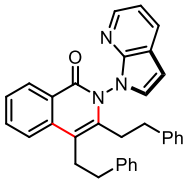


No.	Time	Area	Area (%)
1	27.2	31760.5	50.3894
2	36.2	31269.6	49.6106



No.	Time	Area	Area (%)
1	27.5	1171.3	1.5060
2	33.9	76603.1	98.4940

(*R*)-3,4-diphenethyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(12)**



Following the general procedure, the title compound was obtained as white solid in 35% yield (13.1 mg, 0.03 mmol) with 98% ee. R_f = 0.4 (PE/EtOAc =2/1). m.p.: 136–138 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (dd, *J* = 8.0, 1.1 Hz, 1H), 8.35 (dd, *J* =

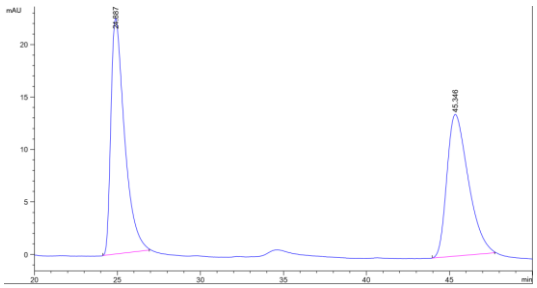
4.7, 1.4 Hz, 1H), 8.05 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.81 (ddd, *J* = 8.3, 7.1, 1.4 Hz, 1H), 7.54 – 7.52 (m, 1H), 7.39 – 7.36 (m, 2H), 7.30 – 7.27 (m, 4H), 7.20 (dd, *J* = 7.9, 4.7 Hz, 1H), 7.17 – 7.12 (m, 3H), 6.77 – 6.72 (m, 3H), 3.18 – 3.09 (m, 2H), 3.07 – 2.96 (m, 2H), 2.80 – 2.75 (m, 2H), 2.74 – 2.69 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.51, 147.34, 144.69, 141.30, 140.88, 140.50, 136.70, 133.47, 129.89, 129.56, 129.15, 128.71, 128.55, 128.37, 128.03, 126.70, 126.44, 126.32, 125.49, 123.13, 119.20, 117.73, 113.82, 101.44, 36.19, 35.69, 31.70, 30.09 ppm.

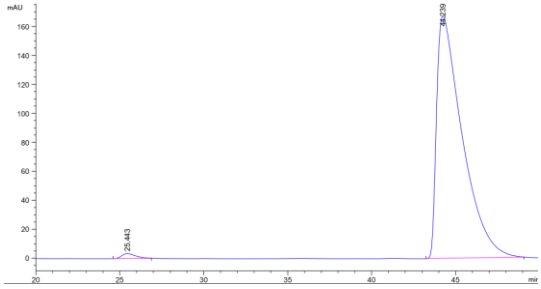
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{28}N_3O$: 470.2232; Found: 470.2233.

$[\alpha]_D^{25}$ = +58.0 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (80:20 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 25.4 min, t_r (major) = 44.2 min, 98% ee.

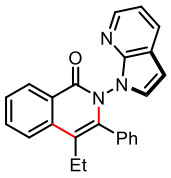


No.	Time	Area	Area (%)
1	24.9	1285.0	51.4390
2	45.3	1213.1	48.5610



No.	Time	Area	Area (%)
1	25.4	195.4	1.0916
2	44.2	17705.8	98.9084

(*R*)-4-ethyl-3-phenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(13)**



Following the general procedure, the title compound was obtained as white solid in 65% yield (19.0 mg, 0.05 mmol) with 99% ee. R_f = 0.4 (PE/EtOAc =3/1). m.p.: 158–160 °C.

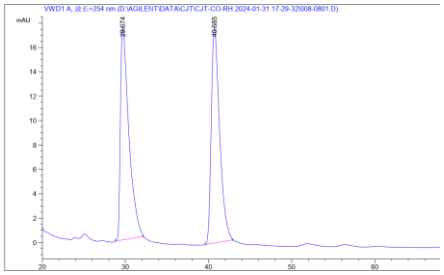
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 – 8.51 (m, 1H), 8.30 – 8.28 (m, 1H), 7.83 – 7.79 (m, 2H), 7.77 – 7.74 (m, 1H), 7.57 – 7.53 (m, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.23 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.06 – 7.02 (m, 2H), 6.97 – 6.93 (m, 1H), 6.32 (d, *J* = 3.8 Hz, 1H), 2.59 – 2.48 (m, 2H), 1.15 (t, *J* = 7.5 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.13, 146.74, 144.10, 141.04, 136.62, 133.40, 132.63, 129.42, 129.28, 129.24, 128.89, 128.78, 127.69, 127.12, 126.17, 123.93, 118.64, 117.49, 117.15, 100.43, 21.86, 14.80 ppm.

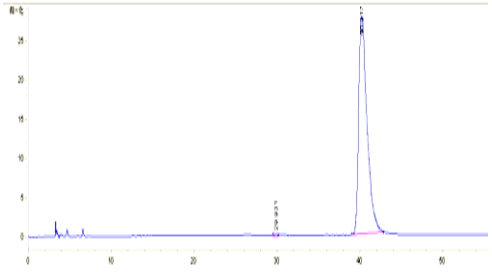
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}N_3O$: 366.1606; Found: 366.1622.

$[\alpha]_D^{25}$ = +34.3 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (80:20 *n*-hexane: 2-propanol, 1.0 mL/min, 27 °C, 254 nm); t_r (minor) = 29.9 min, t_r (major) = 40.2 min, 99% ee.



No.	Time	Area	Area (%)
1	29.67	1277.0	50.3500

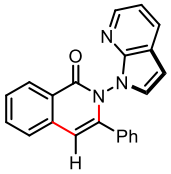


No.	Time	Area	Area (%)
1	29.93	9.4	0.4782

2	40.68	1259.2	49.6500

2	40.21	1966.2	99.5218

(*R*)-3-phenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(14)**



Following the general procedure, the title compound was obtained as white solid in 49% yield (13.5 mg, 0.04 mmol) with 99% ee. R_f = 0.7 (PE/EtOAc =2/1). m.p.: 142–144 °C.

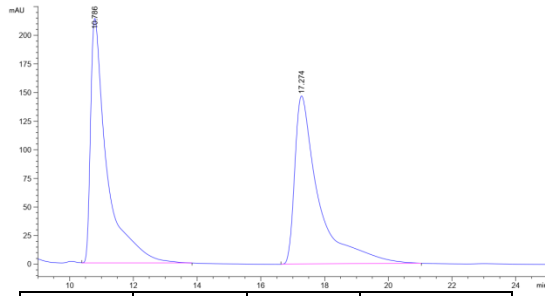
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, *J* = 8.0 Hz, 1H), 8.31 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.83 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.369 – 7.366 (m, 1H), 7.35 (t, *J* = 1.5 Hz, 1H), 7.23 – 7.17 (m, 1H), 7.14 – 7.06 (m, 4H), 6.64 (s, 1H), 6.44 (dd, *J* = 3.8, 0.8 Hz, 1H) ppm.

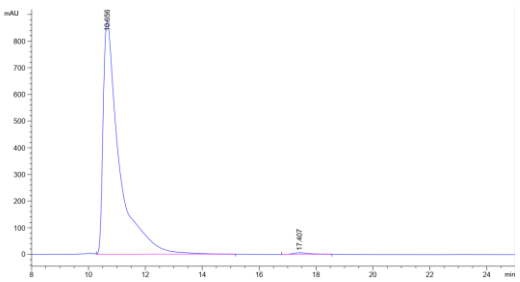
^{13}C NMR (100 MHz, $CDCl_3$): δ 161.73, 147.24, 144.59, 144.45, 136.76, 133.63, 133.55, 129.61, 129.09, 128.91, 128.74, 128.57, 127.88, 127.32, 126.56, 125.36, 118.83, 117.34, 107.89, 100.95 ppm.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{16}N_3O$: 338.1293; Found: 338.1283.

$[\alpha]_D^{25}$ = +191.0 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak IB-3 column (70:30 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 10.7 min, t_r (major) = 17.4 min, 99% ee.

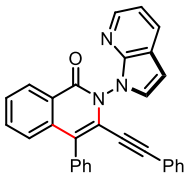




	Time	Area	Area (%)
1	10.8	7612.9	49.8038
2	17.3	7672.9	50.1962

No.	Time	Area	Area (%)
1	10.7	34422.2e	99.2758
2	17.4	251.1	0.7242

(*R*)-4-phenyl-3-(phenylethynyl)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(15)**



Following the general procedure, the title compound was obtained as white solid in 64% yield (22.4 mg, 0.05 mmol) with 97% ee. R_f = 0.4 (PE/EtOAc =3/1). m.p.: 180–182 °C.

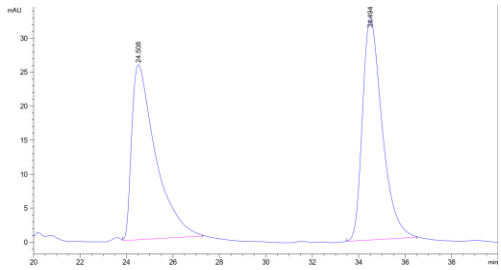
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.37 (dt, *J* = 5.1, 1.8 Hz, 1H), 8.04 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.59 – 7.47 (m, 6H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.19 – 7.14 (m, 2H), 7.09 – 7.05 (m, 2H), 6.74 (dd, *J* = 3.8, 2.3 Hz, 1H), 6.56 – 6.52 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.73, 146.70, 144.61, 136.80, 135.36, 133.40, 131.50, 131.27, 131.04, 129.63, 129.07, 129.04, 128.81, 128.54, 128.39, 128.37, 128.17, 128.16, 126.27, 126.21, 126.19, 125.22, 121.36, 119.03, 117.49, 100.69, 98.51, 80.94 ppm.

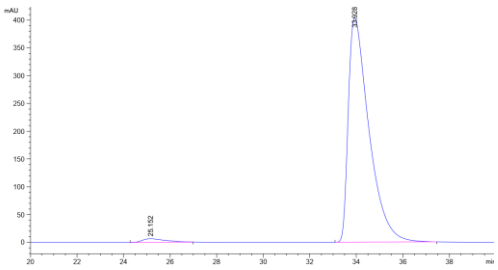
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{20}N_3O$: 438.1606; Found: 438.1625.

$[\alpha]_D^{25}$ = +163.3 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (80:20 *n*-hexane: 2-propanol, 1.0 mL/min, 27 °C, 254 nm); t_r (minor) = 25.2 min, t_r (major) = 33.9 min, 97% ee.

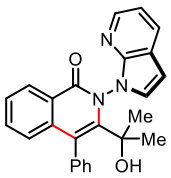


No.	Time	Area	Area (%)
1	24.5	1840.7	48.8393
2	34.5	1928.2	51.1607



No.	Time	Area	Area (%)
1	25.2	452.0	1.7846
2	33.9	24878.0	98.2154

(*R*)-4-(2-hydroxypropan-2-yl)-3-phenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(16)**



Following the general procedure, the title compound was obtained as black solid in 57% yield (18.0 mg, 0.05 mmol) with 99% ee. R_f = 0.4 (PE/EtOAc =1/1). m.p.: 85–87 °C.

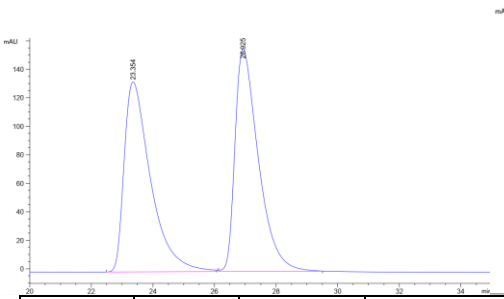
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 8.7 Hz, 1H), 8.51 (d, *J* = 9.6 Hz, 1H), 8.28 (d, *J* = 6.2 Hz, 1H), 7.77 – 7.72 (m, 2H), 7.53 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.20 – 7.16 (m, 2H), 7.12 – 7.08 (m, 1H), 7.04 (ddd, *J* = 7.8, 4.8, 0.5 Hz, 1H), 6.91 (d, *J* = 3.8 Hz, 1H), 6.86 – 6.81 (m, 1H), 6.28 (d, *J* = 3.8 Hz, 1H), 1.83 (s, 1H), 1.54 (s, 3H), 1.37 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): 160.78, 146.79, 144.01, 140.32, 136.30, 134.41, 132.28, 129.80, 129.72, 129.41, 129.11, 128.92, 127.31, 127.09, 126.99, 126.51, 122.42, 122.41, 118.55, 117.19, 100.46, 74.25, 33.76, 32.70 ppm.

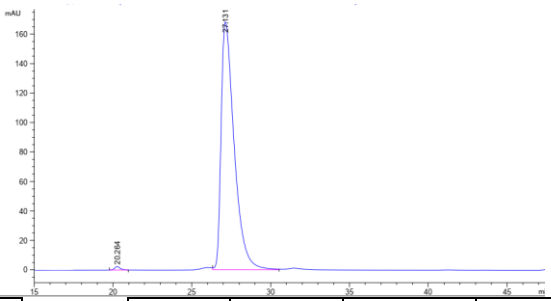
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}N_3O_2$: 396.1712; Found: 396.1737.

$[\alpha]_D^{25}$ = +130.5 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (80:20 *n*-hexane: 2-propanol, 1.0 mL/min, 27 °C, 254 nm); t_r (minor) = 20.3 min, t_r (major) = 27.1 min, 99% ee.

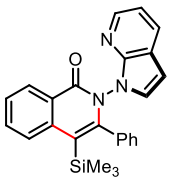


No.	Time	Area	Area (%)
1	23.4	7953.9	49.1025
2	26.9	8244.7	50.8975



No.	Time	Area	Area (%)
1	20.3	58.8	0.6004
2	27.1	9598.9	99.3996

(*R*)-3-phenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one **(17)**



Following the general procedure, the title compound was obtained as white solid in 41% yield (13.4 mg, 0.03 mmol) with 87% ee. R_f = 0.4 (PE/EtOAc =2/1). m.p.: 72–74 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (dt, *J* = 8.0, 1.5 Hz, 1H), 8.30 (dt, *J* = 4.6,

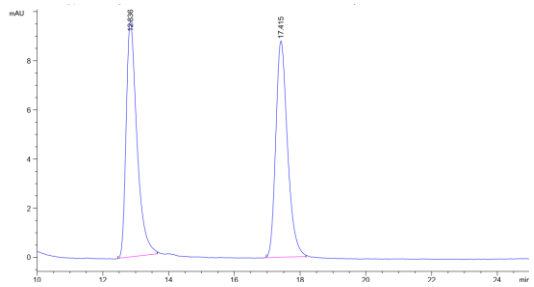
1.6 Hz, 1H), 7.96 (d, *J* = 9.0 Hz, 1H), 7.78 – 7.71 (m, 2H), 7.54 – 7.49 (m, 1H), 7.29 – 7.27 (m, 1H), 7.24 – 7.21 (m, 2H), 7.15 – 7.10 (m, 1H), 7.07 – 7.03(m, 1H), 6.95 (dd, *J* = 3.7, 1.8 Hz, 1H), 6.89 – 6.83 (m, 1H), 6.31 (dd, *J* = 3.8, 2.0 Hz, 1H), 0.02 – 0.00 (m, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.27, 149.30, 146.90, 144.09, 139.82, 134.77, 132.53, 130.29, 130.05, 129.42, 129.13, 129.11, 128.91, 127.92, 127.27, 127.17, 126.71, 126.20, 118.63, 117.14, 113.30, 100.50, 1.97 ppm.

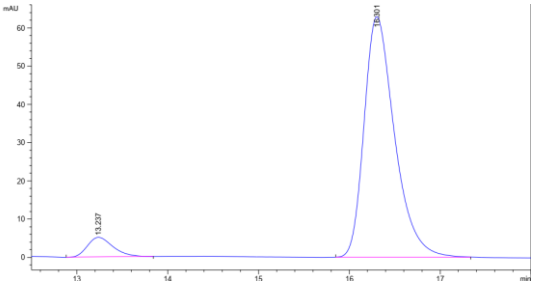
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{24}N_3OSi$: 410.1689; Found: 410.1670.

$[\alpha]_D^{25}$ = +61.0 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (94:6 *n*-hexane: 2-propanol, 1.0 mL/min, 27 °C, 254 nm); t_r (minor) = 13.2 min, t_r (major) = 16.3 min, 87% ee.

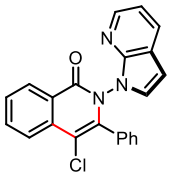


No.	Time	Area	Area (%)
1	12.8	219.1	50.0683
2	17.4	218.5	49.9317



No.	Time	Area	Area (%)
1	13.2	100.7	6.4164
2	16.3	1468.1	93.5836

(*R*)-4-chloro-3-phenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(18)**



Following the general procedure, the title compound was obtained as white solid in 45% yield (13.4 mg, 0.04 mmol) with 95% ee. R_f = 0.7 (PE/EtOAc =3/1). m.p.: 110–112 °C.

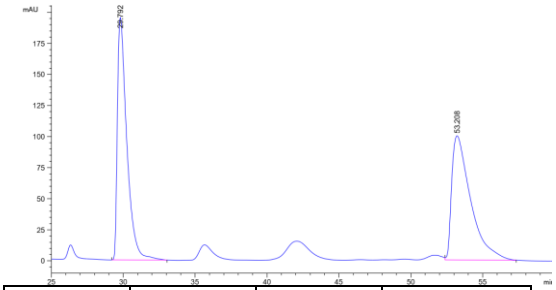
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, *J* = 8.0 Hz, 1H), 8.30 (d, *J* = 4.7 Hz, 1H), 8.09 (d, *J* = 8.1 Hz, 1H), 7.88 – 7.84 (m, 1H), 7.79 – 7.77 (m, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 6.2 Hz, 2H), 7.21 – 7.17 (m, 1H), 7.08 – 7.05 (m, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.36 (d, *J* = 3.8 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.65, 146.79, 144.36, 141.56, 135.08, 134.15, 131.56, 129.57, 129.41, 129.25, 129.05, 128.65, 128.43, 127.85, 127.84, 125.36, 124.59, 118.68, 117.47, 111.82, 100.92 ppm.

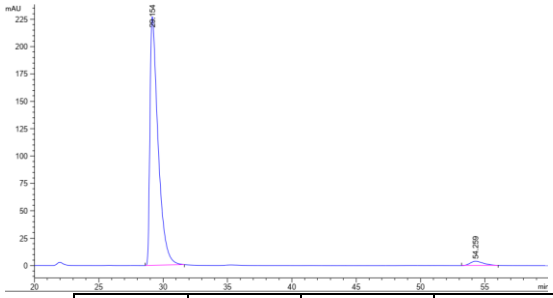
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{15}ClN_3O$: 372.0904; Found: 372.0888.

$[\alpha]_D^{25}$ = +14.3 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak IE-3 column (80:20 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 29.1 min, t_r (major) = 54.3 min, 95% ee.

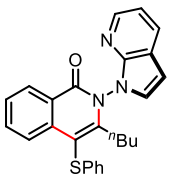


No.	Time	Area	Area (%)
1	29.8	8905.4	49.3347
2	53.2	9145.6	50.6653



No.	Time	Area	Area(%)
1	29.1	10006.2	97.3764
2	54.3	269.6	2.6236

(*R*)-3-butyl-4-(phenylthio)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(19)**



Following the general procedure, the title compound was obtained as black solid in 32% yield (10.9 mg, 0.03 mmol) with 98% ee. R_f = 0.7 (PE/EtOAc =3/1). m.p.: 50–52 °C.

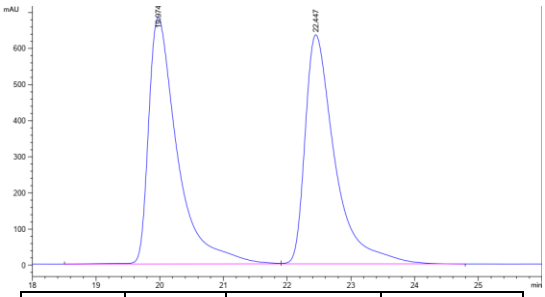
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, *J* = 8.0 Hz, 1H), 8.32 (d, *J* = 4.7 Hz, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 8.00 (dt, *J* = 7.9, 1.2 Hz, 1H), 7.67– 7.64 (m, 1H), 7.48 – 7.44 (m, 1H), 7.32 (d, *J* = 3.4 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 2H), 7.17 (dd, *J* = 7.8, 1.8 Hz, 3H), 7.14 – 7.10 (m, 1H), 6.72 (dd, *J* = 3.8, 0.8 Hz, 1H), 3.12 – 3.04 (m, 1H), 2.72 – 2.65 (m, 1H), 1.52 – 1.44 (m, 2H), 1.12 – 1.02 (m, 2H), 0.56 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.68, 153.40, 147.19, 144.73, 137.88, 137.51, 134.04, 129.91, 129.36, 129.23, 128.74, 127.27, 126.04, 125.83, 125.41, 125.08, 119.21, 117.88, 105.83, 101.53, 31.80, 31.68, 22.61, 13.24 ppm.

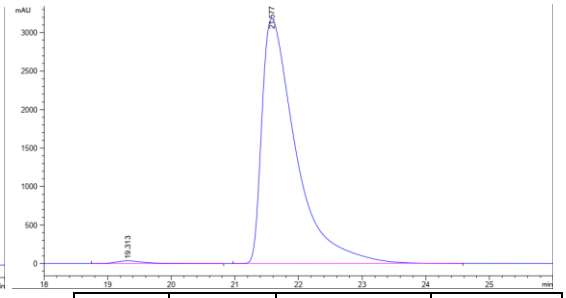
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{24}N_3OS$: 426.1640; Found: 426.1619.

$[\alpha]_D^{25}$ = +34.7 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (70:30 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 19.3 min, t_r (major) = 21.6 min, 98% ee.

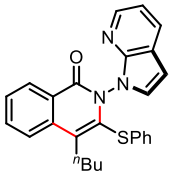


No.	Time	Area	Area (%)
1	19.9	21489.3	51.0085
2	22.4	20639.6	48.9915



No.	Time	Area	Area (%)
1	19.3	1123.8	0.9429
2	21.6	118055	99.0571

(*S*)-4-butyl-3-(phenylthio)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(19')**



Following the general procedure, the title compound was obtained as white solid in 50% yield (17.0 mg, 0.04 mmol) with >99% ee. R_f = 0.5 (PE/EtOAc =3/1). m.p.: 54–56 °C.

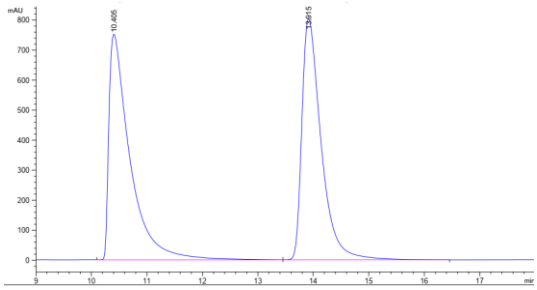
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 – 8.46 (m, 1H), 8.14 (dt, *J* = 4.7, 1.3 Hz, 1H), 7.88 – 7.79 (m, 3H), 7.60 – 7.56 (m, 1H), 7.11 – 7.05 (m, 3H), 7.03 (ddd, *J* = 7.7, 4.8, 1.2 Hz, 1H), 6.99 – 6.96 (m, 2H), 6.77 (d, *J* = 3.8 Hz, 1H), 6.41 – 6.40 (m, 1H), 3.31 – 3.15 (m, 2H), 1.65 (d, *J* = 5.9 Hz, 2H), 1.50 (dt, *J* = 14.8, 7.3 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.64, 146.67, 144.10, 136.01, 134.70, 133.95, 133.63, 129.40, 129.33, 129.27, 129.06, 128.38, 127.89, 127.61, 127.07, 126.78, 124.76, 118.80, 117.20, 100.12, 32.59, 30.97, 23.19, 14.03 ppm.

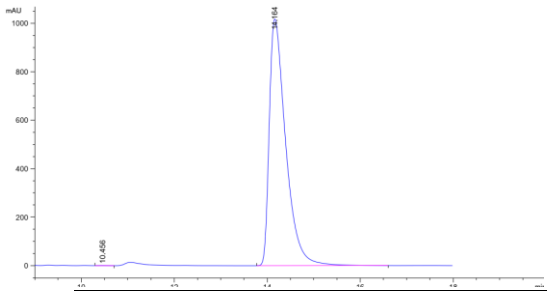
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{24}N_3OS$: 426.1640; Found: 426.1623.

$[\alpha]_D^{25}$ = −44.2 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (70:30 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 10.5 min, t_r (major) = 14.2 min, >99% ee.

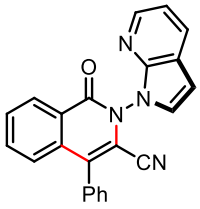


No.	Time	Area	Area (%)
1	10.4	19953.3	50.6828
2	13.9	19415.7	49.3172



No.	Time	Area	Area (%)
1	10.5	10.4	0.0418
2	14.2	24977.7	99.9582

(*R*)-1-oxo-3-phenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)-1,2-dihydroisoquinoline-4-carbonitrile **(20)**



Following the general procedure, the title compound was obtained as white solid in 43% yield (12.5 mg, 0.03 mmol) with 93% ee. R_f = 0.4 (PE/EtOAc =3/1). m.p.: 189–191 °C.

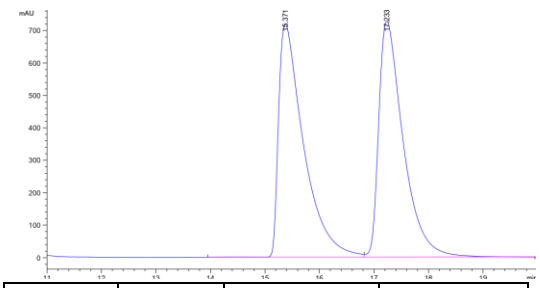
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 – 8.52 (m, 1H), 8.35 (dd, *J* = 4.8, 1.5 Hz, 1H), 8.02 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.77 – 7.68 (m, 2H), 7.62 – 7.54 (m, 4H), 7.53 – 7.49 (m, 1H), 7.47 – 7.45(m, 1H), 7.41 (d, *J* = 3.9 Hz, 1H), 7.21 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.76 (d, *J* = 3.9 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.36, 153.86, 146.84, 144.60, 134.99, 133.43, 130.74, 130.23, 129.88, 129.18, 129.06, 128.61, 128.31, 128.27, 125.00, 124.51, 118.72, 117.87, 115.26, 101.72, 93.41 ppm.

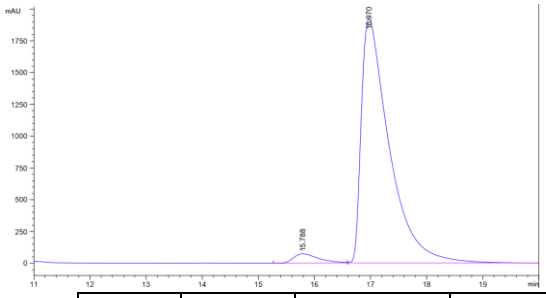
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{15}N_4O$: 363.1246; Found: 363.1235.

$[\alpha]_D^{25}$ = +76.3 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (70:30 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 15.8 min, t_r (major) = 17.0 min, 93% ee.

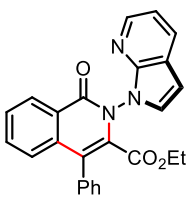


No.	Time	Area	Area (%)
1	15.4	22929.9	50.2721
2	17.2	22681.7	49.7279



No.	Time	Area	Area (%)
1	15.8	2349.7	3.3984
2	17.0	66792.8	96.6016

(*R*)-ethyl 1-oxo-4-phenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)-1,2-dihydroisoquinoline-3-carboxylate **(21)**



Following the general procedure, the title compound was obtained as white solid in 34% yield (11.1 mg, 0.03 mmol) with 97% ee. R_f = 0.5 (DCM/EtOAc =50/1). m.p.: 78–79 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, *J* = 8.0 Hz, 1H), 8.30 (d, *J* = 4.7 Hz, 1H), 7.87 – 7.83 (m, 1H), 7.81 – 7.76 (m, 2H), 7.60 – 7.55 (m, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.24 – 7.14 (m, 2H), 7.07 (ddd, *J* =

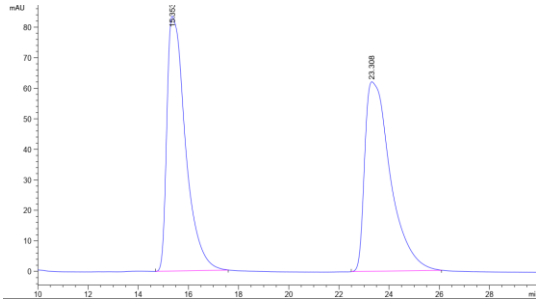
7.8, 4.8, 0.8 Hz, 1H), 7.03 (d, *J* = 3.8 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.38 (dd, *J* = 3.8, 0.8 Hz, 1H), 3.97 (q, *J* = 7.1 Hz, 2H), 0.83 – 0.78 (m, 3H) ppm.

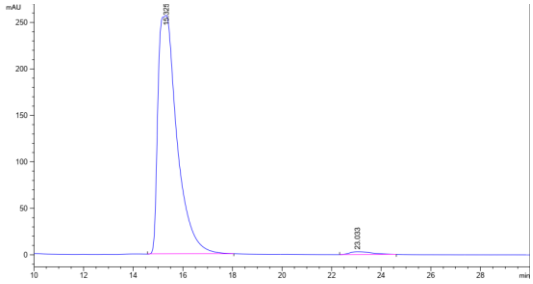
^{13}C NMR (100 MHz, $CDCl_3$): δ 166.26, 160.87, 147.02, 144.84, 144.40, 134.02, 133.82, 131.90, 129.57, 129.37, 129.07, 128.99, 128.81, 128.64, 127.98, 127.53, 125.17, 124.89, 118.67, 117.47, 113.26, 101.08, 61.42, 13.53 ppm.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{20}N_3O_3$: 410.1505; Found: 410.1502.

$[\alpha]_D^{25}$ = +117.7 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (80:20 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 15.3 min, t_r (major) = 23.0 min, 97% ee.

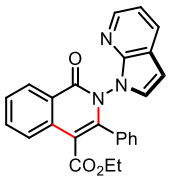




No.	Time	Area	Area(%)
1	15.4	4291.1	49.2324
2	23.3	4424.9	50.7676

No.	Time	Area	Area (%)
1	15.3	13692.7	98.6233
2	23.0	191.1	1.3767

(*R*)-ethyl 1-oxo-3-phenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)-1,2-dihydroisoquinoline-4-carboxylate **(21')**



Following the general procedure, the title compound was obtained as white solid in 31% yield (8.2 mg, 0.02 mmol) with 47% ee. R_f = 0.7 (DCM/EtOAc =50/1). m.p.: 76–78 °C.

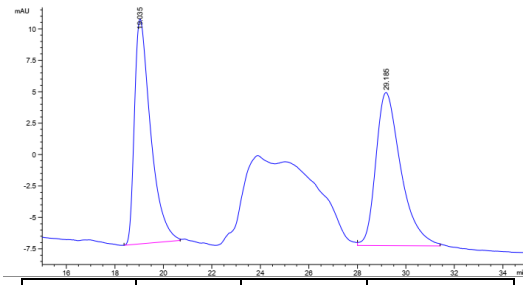
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 8.1 Hz, 1H), 8.36 (d, *J* = 4.8 Hz, 1H), 7.96 – 7.93 (m, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.55 – 7.53 (m, 1H), 7.48 – 7.43 (m, 3H), 7.39 (dd, *J* = 9.5, 2.4 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.15 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.65 (d, *J* = 3.9 Hz, 1H), 3.64 (q, *J* = 7.1 Hz, 2H), 0.54 (t, *J* = 7.1 Hz, 3H) ppm.

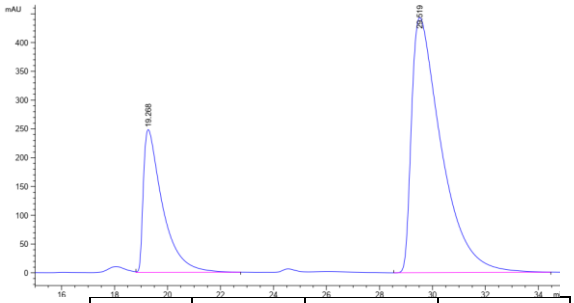
^{13}C NMR (100 MHz, $CDCl_3$): δ 161.48, 160.28, 147.36, 144.62, 136.82, 134.66, 133.73, 133.54, 131.12, 130.52, 129.72, 129.63, 128.87, 128.63, 128.61, 128.58, 128.48, 126.56, 126.07, 119.17, 118.67, 117.78, 101.59, 61.95, 13.10 ppm.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{20}N_3O_3$: 2410.1505; Found: 410.1502.

$[\alpha]_D^{25}$ = +79.7 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (60:40 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 19.3 min, t_r (major) = 29.5 min, 47% ee.





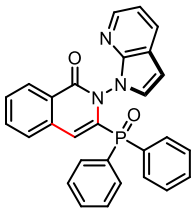
No.	Time	Area	Area (%)

No.	Time	Area	Area(%)

1	19.0	831.1	48.6299
2	29.2	878.0	51.3701

1	19.3	12552.5	26.5218
2	29.5	34776.5	73.4782

(*S*)-3-(diphenylphosphoryl)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(22)**



Following the general procedure, the title compound was obtained as white solid in 79% yield (27.7 mg, 0.06 mmol) with 99% ee. R_f = 0.3 (PE/EtOAc =1/2). m.p.: 178–180 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 4.7 Hz, 1H), 7.81 (dd, *J* = 12.1, 7.3 Hz, 2H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.63 – 7.54 (m, 5H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.45 (td, *J* = 7.7, 3.2 Hz, 2H), 7.36 (d, *J* = 3.9 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.12 (td, *J* = 7.3, 3.2 Hz, 2H), 6.87 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.78 (d, *J* = 11.6 Hz, 1H), 6.44 (d, *J* = 3.9 Hz, 1H) ppm.

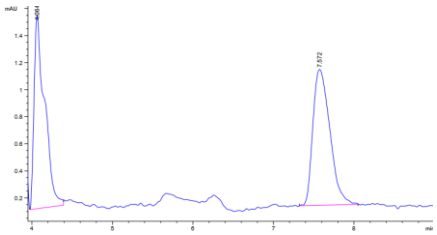
^{13}C NMR (100 MHz, $CDCl_3$): δ 161.13 (d, J_{C-P} = 2.6 Hz), 147.35, 143.26, 138.91 (d, J_{C-P} = 107.0 Hz), 134.68 (d, J_{C-P} = 13.1 Hz), 133.52, 132.61 (d, J_{C-P} = 2.7 Hz), 132.35 (d, J_{C-P} = 9.6 Hz), 131.68 (d, J_{C-P} = 2.7 Hz), 131.36, 130.79 (d, J_{C-P} = 10.3 Hz), 130.11, 129.54, 129.38, 128.79, 128.73, 128.64, 128.63, 128.28, 127.95, 127.87, 127.86, 127.54, 127.07, 118.87, 117.73 (d, J_{C-P} = 12.0 Hz), 117.15, 101.20 ppm.

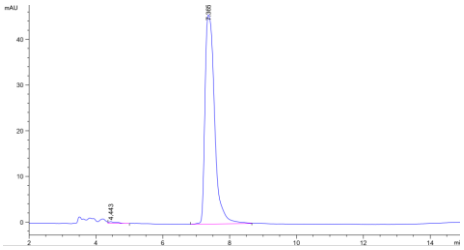
^{31}P NMR (162 MHz, $CDCl_3$): δ 22.76 ppm.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{21}N_3O_2P$: 462.1366; Found: 462.1365.

$[\alpha]_D^{25}$ = −31.0 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak IE-3 column (85:15 *n*-hexane: 2-propanol, 1.0 mL/min, 27 °C, 254 nm); t_r (minor) = 4.4 min, t_r (major) = 7.4 min, 99% ee.

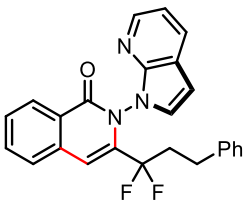




No.	Time	Area	Area (%)
1	4.1	13.0	46.9012
2	7.6	14.8	53.0988

No.	Time	Area	Area (%)
1	4.4	7.0	0.7527
2	7.4	918.4	99.2473

(*R*)-3-(1,1-difluoro-3-phenylpropyl)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(23)**



Following the general procedure, the title compound was obtained as off-white liquid in 50% yield (16.6 mg, 0.04 mmol) with >99% ee. R_f = 0.5 (PE/EtOAc =3/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 8.0 Hz, 1H), 8.28 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.98 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.80 – 7.76 (m, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 3.5 Hz, 1H), 7.19 – 7.12 (m, 4H), 7.06 (s, 1H), 6.91 – 6.89 (m, 2H), 6.70 (d, *J* = 3.9 Hz, 1H), 2.86 (td, *J* = 12.9, 5.3 Hz, 1H), 2.67 (dt, *J* = 13.3, 6.6 Hz, 1H), 2.34 – 2.20 (m, 1H), 2.18 – 1.99 (m, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.55, 148.64, 144.52, 139.82, 136.83 (dd, J_{C-F} = 32.7, 24.2 Hz), 135.02, 133.89, 131.14 (d, J_{C-F} = 2.5 Hz), 130.03, 128.91, 128.78, 128.47, 128.28, 127.65, 126.27, 126.11, 119.62, 119.46 (t, J_{C-F} = 245.0 Hz), 118.04, 107.35 (dd, J_{C-F} = 12.3, 5.8 Hz), 102.32, 38.42 (t, J_{C-F} = 25.5 Hz), 28.78 (d, J_{C-F} = 4.5 Hz) ppm.

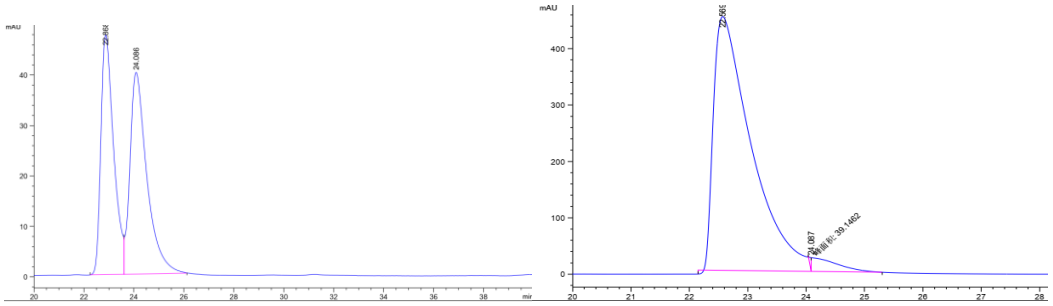
^{19}F NMR (376 MHz, $CDCl_3$): δ –88.85 (dt, *J* = 258.9, 9.8 Hz), –96.41 (dt, *J* = 257.8, 22.4 Hz)

ppm.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{20}F_2N_3O$: 416.1574; Found: 416.1566.

$[\alpha]_D^{25}$ = −265.3 (c = 0.1, CH_2Cl_2).

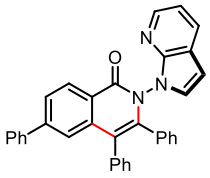
HPLC conditions: Daicel Chiralpak ID-3 column (85:15 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 22.6 min, t_r (major) = 24.1 min, >99% ee.



No.	Time	Area	Area (%)
1	22.9	1689.6	47.2289
2	24.1	1887.9	52.7711

No.	Time	Area	Area (%)
1	22.6	20946.8	99.8135
2	24.1	39.14625	0.1865

(*R*)-3,4,6-triphenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(24)**



Following the general procedure, the title compound was obtained as white solid in 75% yield (29.3 mg, 0.06 mmol) with 94% ee. R_f = 0.7 (PE/EtOAc =2/1). m.p.: 244–246 °C.

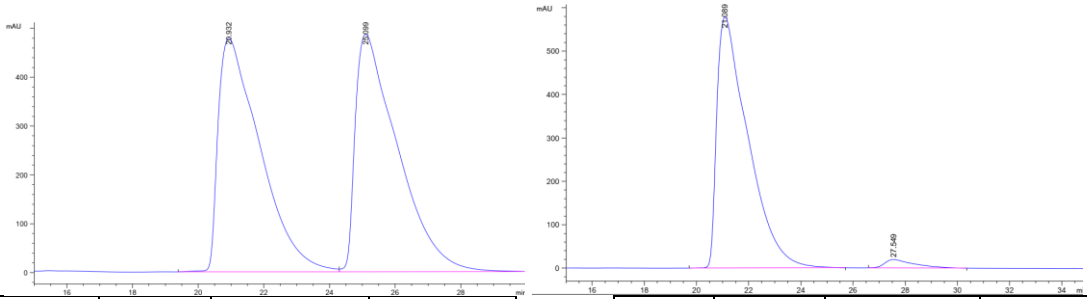
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (d, *J* = 8.3 Hz, 1H), 8.36 – 8.32 (m, 1H), 7.78 (td, *J* = 7.9, 1.6 Hz, 2H), 7.54 – 7.47 (m, 3H), 7.45 – 7.35 (m, 3H), 7.27 (d, *J* = 3.0 Hz, 2H), 7.23 – 7.16 (m, 3H), 7.15 – 7.09 (m, 3H), 7.09 – 7.05 (m, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.93 – 6.89(m, 1H), 6.73 (t, *J* = 7.5 Hz, 1H), 6.37 (d, *J* = 3.8 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.10, 146.97, 146.08, 144.22, 142.57, 140.23, 138.19, 135.65, 132.41, 131.72, 131.45, 129.95, 129.88, 129.49, 129.40, 129.03, 128.88, 128.43, 128.35, 128.25, 128.11, 127.62, 127.61, 127.59, 127.37, 127.09, 127.07, 126.54, 124.38, 124.34, 119.58, 118.72, 117.25, 100.68 ppm.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{24}N_3O$: 490.1914; Found: 490.1919.

$[\alpha]_D^{25}$ = +145.3 (c = 0.1, CH_2Cl_2).

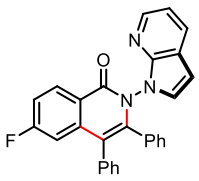
HPLC conditions: Daicel Chiralpak IB-3 column (80:20 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 21.1 min, t_r (major) = 27.5 min, 94% ee.



No.	Time	Area	Area (%)
1	20.9	42343.7	49.2317
2	25.1	43665.4	50.7683

No.	Time	Area	Area (%)
1	21.1	4.8095.9	96.9679
2	27.5	1503.9	3.0321

(*R*)-6-fluoro-3,4-diphenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(25)**



Following the general procedure, the title compound was obtained as white solid in 43% yield (14.8 mg, 0.03 mmol) with 93% ee. R_f = 0.7 (PE/EtOAc =2/1). m.p.: 185–187 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (dd, *J* = 8.8, 5.9 Hz, 1H), 8.33 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.80 – 7.78 (m, 1H), 7.29 – 7.27 (m, 1H), 7.23 – 7.22 (m, 2H), 7.20 (d, *J* = 3.6 Hz, 2H), 7.18 – 7.15 (m, 1H), 7.12 – 7.08 (m, 3H), 7.07 (dd, *J* = 4.9, 2.9 Hz, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.93 – 6.89 (m, 2H), 6.75 – 6.71 (m, 1H), 6.37 – 6.36 (m, 1H) ppm.

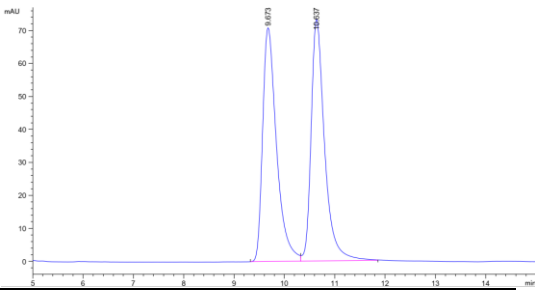
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.91 (d, J_{C-F} = 253.5 Hz), 160.35, 146.76, 144.13, 143.35, 140.30 (d, J_{C-F} = 10.1 Hz), 135.05, 131.95, 131.91 (d, J_{C-F} = 10.0 Hz), 131.40, 131.13, 129.63, 129.54, 129.47, 128.61, 128.45, 128.30, 128.14, 127.46, 127.03, 127.02, 121.91 (d, J_{C-F} = 1.9 Hz), 118.77 (d, J_{C-F} = 3.3 Hz), 118.58, 117.21, δ 115.81 (d, J_{C-F} = 23.5 Hz), 111.48 (d, J_{C-F} = 23.5 Hz), 100.70 ppm.

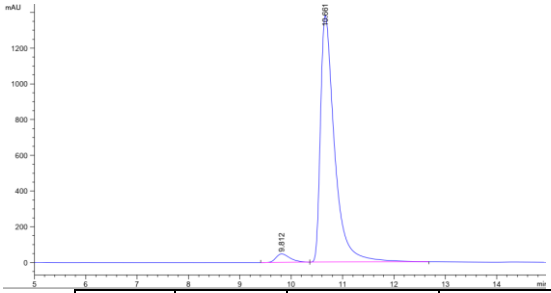
^{19}F NMR (376 MHz, $CDCl_3$) δ -103.65 – -103.71 (m, 1F) ppm.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{19}FN_3O$: 432.1507; Found: 432.1500.

$[\alpha]_D^{25}$ = +118.7 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (70:30 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 9.8 min, t_r (major) = 10.7 min, 93% ee.

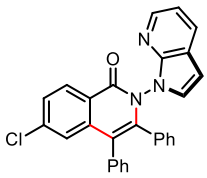




No.	Time	Area	Area (%)
1	9.7	1361.2	49.9391
2	10.6	1364.6	50.0609

No.	Time	Area	Area (%)
1	9.8	918.4	3.3769
2	10.7	26277.0	96.6231

(*R*)-6-chloro-3,4-diphenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(26)**



Following the general procedure, the title compound was obtained as white solid in 37% yield (13.3 mg, 0.03 mmol) with 92% ee. R_f = 0.7 (PE/EtOAc =2/1). m.p.: 172–174 °C.

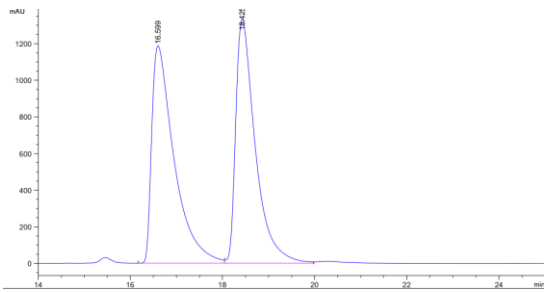
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, *J* = 8.6 Hz, 1H), 8.33 (d, *J* = 4.8 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 8.6 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.22 – 7.20 (m, 3H), 7.17 -7.15 (m, 1H), 7.10 – 7.06 (m, 4H), 6.96 (t, *J* = 7.5 Hz, 2H), 6.92 (d, *J* = 7.4 Hz, 1H), 6.36 (d, *J* = 3.8 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.59, 146.85, 144.25, 143.60, 140.15, 139.14, 135.00, 132.03, 131.57, 131.30, 130.53, 129.75, 129.68, 129.58, 128.66, 128.58, 128.42, 128.28, 127.90, 127.61, 127.13, 125.56, 123.82, 118.70, 118.60, 117.35, 100.86 ppm.

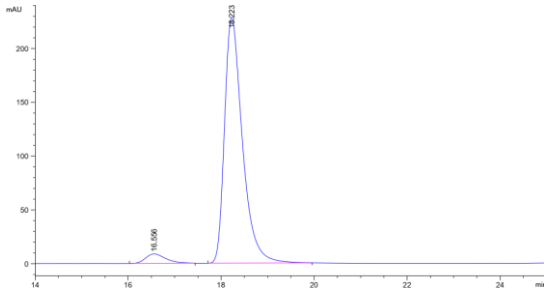
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{19}ClN_3O$: 448.1211; Found: 448.1214.

$[\alpha]_D^{25}$ = +101.0 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (80:20 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 16.6 min, t_r (major) = 18.2 min, 92% ee.

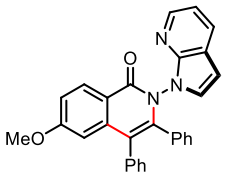


No.	Time	Area	Area (%)
1	16.6	40048.5	50.4644
2	18.4	39311.3	49.5356



No.	Time	Area	Area (%)
1	16.6	264.1	4.1469
2	18.2	6105.6	95.8531

(*R*)-6-methoxy-3,4-diphenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(27)**



Following the general procedure, the title compound was obtained as white solid in 64% yield (22.7 mg, 0.05 mmol) with 95% ee. R_f = 0.7 (PE/EtOAc =2/1). m.p.: 203–205 °C.

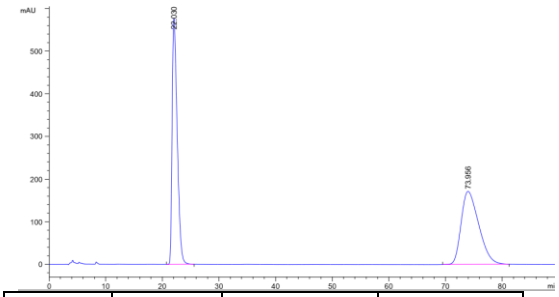
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, *J* = 8.9 Hz, 1H), 8.33 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.77 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.19 – 7.17 (m, 3H), 7.12 – 7.08 (m, 3H), 7.08 – 7.04 (m, 2H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.71 (t, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 2.4 Hz, 1H), 6.35 (d, *J* = 3.8 Hz, 1H), 3.74 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.62, 160.82, 147.01, 144.16, 142.70, 139.95, 135.80, 132.49, 131.65, 131.38, 130.99, 129.88, 129.80, 129.46, 128.99, 128.39, 128.19, 128.06, 127.30, 127.04, 119.18, 119.10, 118.70, 117.17, 115.72, 108.40, 100.56, 55.49 ppm.

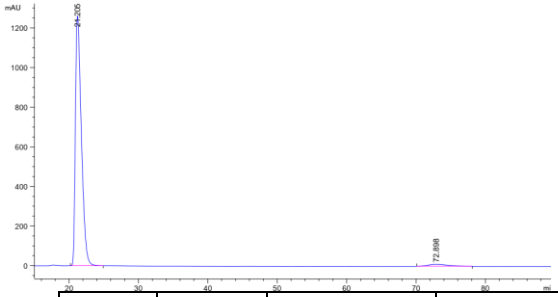
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{22}N_3O_2$: 444.1707; Found: 444.1707.

$[\alpha]_D^{25}$ = +148.3 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak IC-3 column (60:40 *n*-hexane: 2-propanol, 1.0 mL/min, 40°C, 254 nm); t_r (minor) = 21.2 min, t_r (major) = 72.9 min, 95% ee.

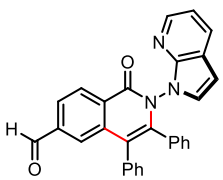


No.	Time	Area	Area (%)
1	22.0	35995.7	49.2656
2	73.9	37068.8	50.7344



No.	Time	Area	Area (%)
1	21.2	75401.3	97.3222
2	72.9	2074.64795	2.6778

(*R*)-1-oxo-3,4-diphenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)-1,2-dihydroisoquinoline-6-carbaldehyde **(28)**



Following the general procedure, the title compound was obtained as pale yellow solid in 69% yield (24.4 mg, 0.06 mmol) with 88% ee. R_f = 0.6 (DCM/EtOAc =20/1). m.p.: 250–252 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (s, 1H), 8.66 (d, *J* = 8.2 Hz, 1H), 8.33 (dd, *J* = 4.8, 1.5 Hz, 1H), 8.01 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.81– 7.77 (m, 2H), 7.31 (ddd, *J* = 8.3, 4.9, 3.2 Hz, 1H), 7.25 – 7.23 (m, 3H), 7.20 – 7.17 (m, 1H), 7.13 –

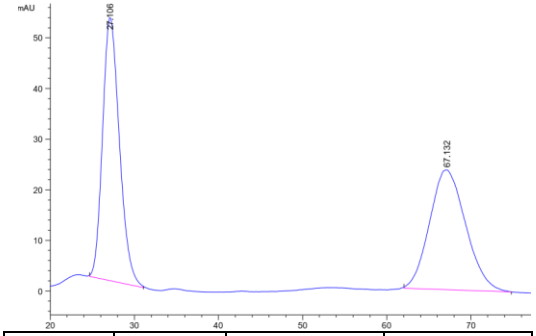
7.07 (m, 4H), 7.00 – 6.91 (m, 2H), 6.74 (dd, *J* = 8.1, 6.6 Hz, 1H), 6.38 (d, *J* = 3.8 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 192.01, 160.57, 146.78, 144.31, 143.59, 139.38, 138.26, 134.87, 131.86, 131.58, 131.31, 129.89, 129.77, 129.69, 129.49, 129.14, 128.70, 128.54, 128.53, 128.52, 128.39, 128.39, 127.79, 127.21, 125.79, 119.33, 118.74, 117.45, 101.05 ppm.

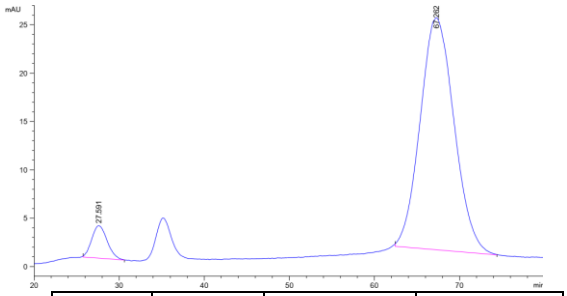
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{20}N_3O_2$: 442.1556; Found: 442.1542.

$[\alpha]_D^{25}$ = +93.7 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak AS-RH column (8:92 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 27.6 min, t_r (major) = 67.3 min, 88% ee.

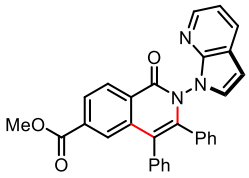


No.	Time	Area	Area (%)
1	27.1	7252.4	50.5791
2	67.1	7086.4	49.4209



No.	Time	Area	Area (%)
1	27.6	427.9	6.0260
2	67.3	6673.3	93.9740

(*R*)-methyl-1-oxo-3,4-diphenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)-1,2-dihydroisoquinoline-6-carboxylate **(29)**



Following the general procedure, the title compound was obtained as white solid in 36% yield (13.2 mg, 0.03 mmol) with 89% ee. R_f = 0.5 (PE/EtOAc =3/1). m.p.: 245–247 °C.

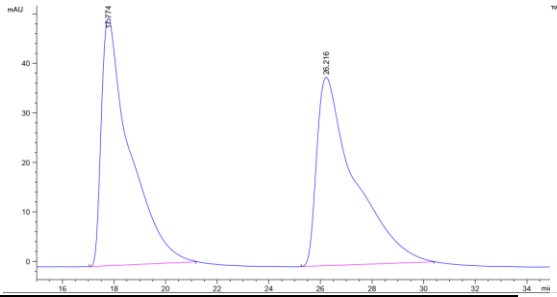
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.33 (dt, *J* = 4.8, 1.7 Hz, 1H), 8.13 (dt, *J* = 8.3, 1.7 Hz, 1H), 7.99 (t, *J* = 1.6 Hz, 1H), 7.79 (dt, *J* = 7.9, 1.6 Hz, 1H), 7.31 - 7.26 (m, 1H), 7.23 – 7.20 (m, 3H), 7.19 – 7.15 (m, 1H), 7.11 – 7.06 (m, 4H), 6.99 – 6.89 (m, 2H), 6.73 (td, *J* = 7.5, 1.7 Hz, 1H), 6.37 (dt, *J* = 3.8, 1.6 Hz, 1H), 3.89 (d, *J* = 1.6 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.44, 160.66, 146.82, 144.27, 143.11, 137.70, 135.02, 134.36, 132.06, 131.62, 131.36, 129.86, 129.78, 129.62, 129.18, 128.62, 128.57, 128.42, 128.27, 127.89, 127.62, 127.39, 127.16, 127.15, 127.14, 119.53, 118.73, 117.38, 100.92, 52.66 ppm.

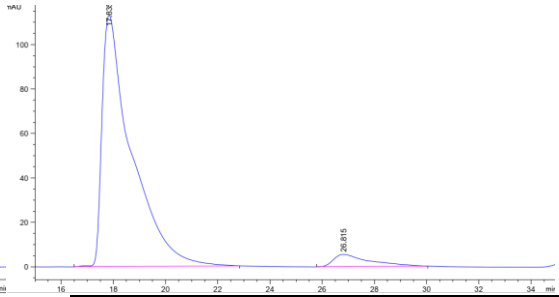
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{22}N_3O_3$: 472.1661; Found: 472.1644.

$[\alpha]_D^{25}$ = +90.7 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak IB-3 column (80:20 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 17.8 min, t_r (major) = 26.8 min, 89% ee.

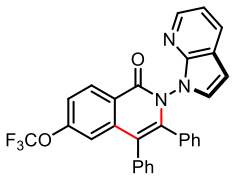


No.	Time	Area	Area (%)
1	17.8	3824.2	49.6726
2	26.2	3874.6	50.3274



No.	Time	Area	Area (%)
1	17.8	8892.1	94.2811
2	26.8	539.4	5.7189

(*R*)-3,4-diphenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)-6-(trifluoromethoxy)isoquinolin-1(2H)-one **(30)**



Following the general procedure, the title compound was obtained as white solid in 55% yield (21.9 mg, 0.04 mmol) with 93% ee. Rf = 0.7 (PE/EtOAc =3/1). m.p.: 77–79 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, *J* = 8.8 Hz, 1H), 8.33 (d, *J* = 4.7 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.35 (m, 1H), 7.30 – 7.27 (m, 1H), 7.22 (d, *J* = 3.0 Hz, 2H), 7.20 (d, *J* = 3.7 Hz, 1H), 7.18 – 7.16 (m, 1H), 7.11 – 7.08 (m, 4H), 7.07 (d, *J* = 4.5 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.37 (d, *J* = 3.8 Hz, 1H) ppm.

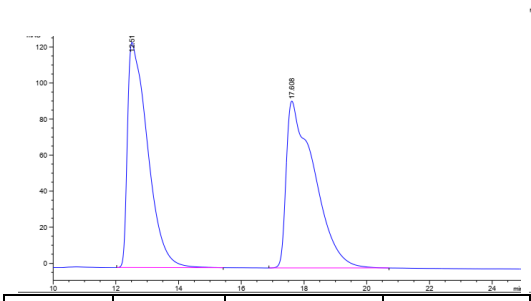
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.36, 153.03 (q, *J* = 1.8 Hz), 146.84, 144.29, 143.78, 139.80, 134.88, 131.96, 131.50, 131.47, 131.20, 129.72, 129.66, 129.61, 128.63, 128.62, 128.49, 128.32, 127.70, 127.18 (d, *J* = 1.3 Hz), 123.68, 120.35 (q, *J* = 257.7 Hz), 119.60 (q, *J* = 1.0 Hz), 118.86, 118.70, 117.39, 117.15 (q, *J* = 0.9 Hz), 100.91 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.31 (s, 3F) ppm.

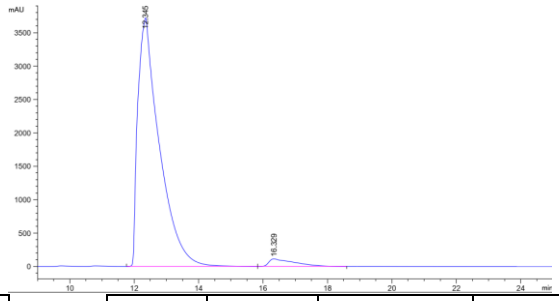
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{19}F_3N_3O$: 498.1424; Found: 498.1421.

$[\alpha]_D^{25}$ = +102.7 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak IB-3 column (80:20 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 12.3 min, t_r (major) = 16.3 min, 93% ee.

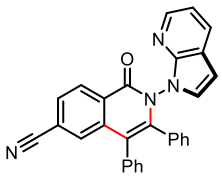


No.	Time	Area	Area (%)
1	12.5	5561.8	49.2018
2	17.6	5742.3	50.7982



No.	Time	Area	Area (%)
1	12.3	172353	96.5868
2	16.3	6090.7	3.4132

(*R*)-1-oxo-3,4-diphenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)-1,2-dihydroisoquinoline-6-carbonitrile **(31)**



Following the general procedure, the title compound was obtained as pale yellow solid in 40% yield (14.0 mg, 0.03 mmol) with 84% ee. Rf = 0.6 (PE/EtOAc =2/1). m.p.: 253–255 °C.

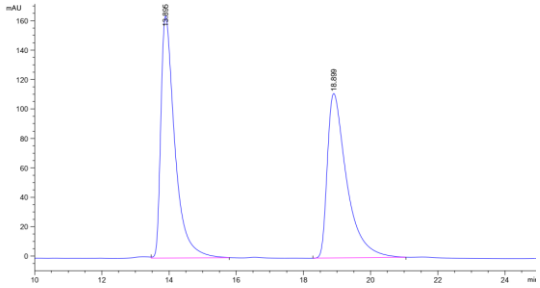
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, *J* = 8.2 Hz, 1H), 8.33 (d, *J* = 4.5 Hz, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.61 (s, 1H), 7.32 – 7.28 (m, 1H), 7.25 – 7.22 (m, 2H), 7.20 – 7.14 (m, 2H), 7.10 – 7.06 (m, 4H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.74 (t, *J* = 7.5 Hz, 1H), 6.38 (d, *J* = 3.8 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.13, 146.73, 144.42, 144.34, 138.09, 134.30, 131.58, 131.45, 131.17, 130.89, 129.86, 129.73, 129.63, 129.56, 129.08, 128.85, 128.69, 128.55, 128.37, 128.00, 127.91, 127.27, 127.26, 118.73, 118.51, 118.20, 117.53, 116.86, 101.18 ppm.

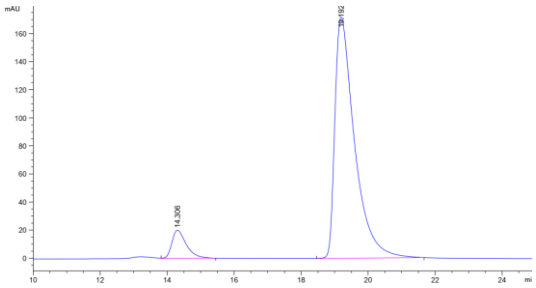
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{19}N_4O$: 439.1553; Found: 439.1542

$[\alpha]_D^{25}$ = +104.0 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (70:30 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 14.3 min, t_r (major) = 19.2 min, 84% ee.

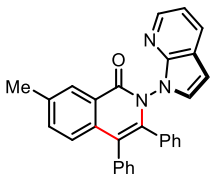


No.	Time	Area	Area (%)
1	13.9	4751.7	51.4586
2	18.9	4482.4	48.5414



No.	Time	Area	Area (%)
1	14.3	604.8	7.9578
2	19.2	6995.4	92.0422

(*R*)-7-methyl-3,4-diphenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(32)**



Following the general procedure, the title compound was obtained as white solid in 41% yield (14.0 mg, 0.03 mmol) with 92% ee. Rf = 0.5 (DCM/EtOAc =50/1). m.p.: 177–179 °C.

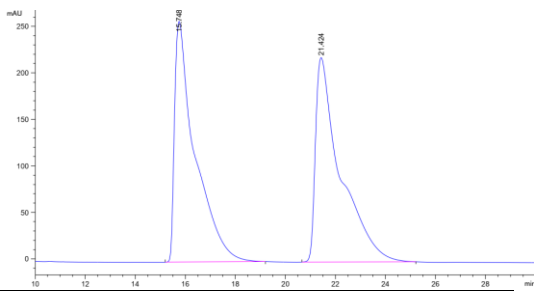
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 – 8.32 (m, 2H), 7.78 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.44 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.28 – 7.22 (m, 2H), 7.21 – 7.16 (m, 4H), 7.11 – 7.04 (m, 4H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.92 – 6.87(m, 1H), 6.73 – 6.69 (m, 1H), 6.35 (d, *J* = 3.8 Hz, 1H), 2.49 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.18, 146.92, 144.16, 141.12, 137.57, 135.91, 135.43, 134.72, 132.44, 131.67, 131.42, 130.05, 129.95, 129.47, 128.88, 128.35, 128.31, 128.15, 127.98, 127.20, 127.03, 126.12, 125.36, 119.39, 118.69, 117.18, 100.58, 21.47 ppm.

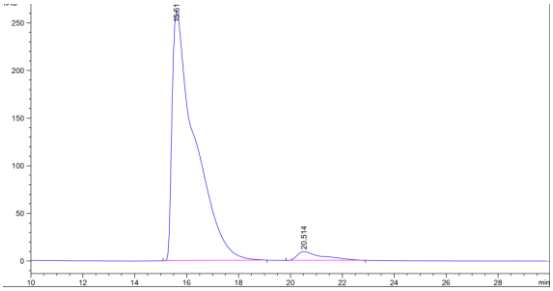
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{22}N_3O$: 428.1757; Found: 428.1755.

$[\alpha]_D^{25}$ = +51.7 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak IB-3 column (80:20 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 15.6 min, t_r (major) = 20.5 min, 92% ee.



No.	Time	Area	Area (%)
1	15.7	14714.0	49.2441

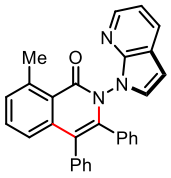


No.	Time	Area	Area (%)
1	15.6	15966.9	96.1342

2	21.4	15165.7	50.7559

2	20.5	642.07	3.8658

(*R*)-8-methyl-3,4-diphenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)isoquinolin-1(2H)-one **(33)**



Following the general procedure, the title compound was obtained as white solid in 39% yield (13.4 mg, 0.03 mmol) with 91% ee. Rf = 0.7 (PE/EtOAc =3/1). m.p.: 96–98 °C.

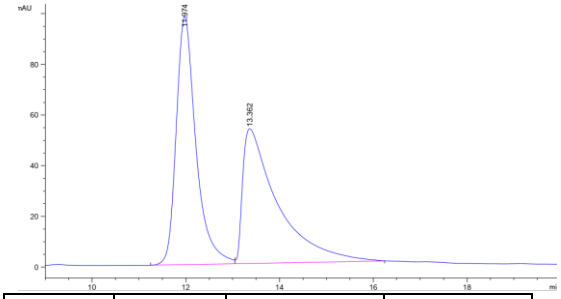
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.77 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.19 – 7.14 (m, 3H), 7.13 – 7.10 (m, 3H), 7.06 (dd, *J* = 7.8, 4.8 Hz, 2H), 6.95 (t, *J* = 7.9 Hz, 1H), 6.88 (tt, *J* = 7.4, 1.3 Hz, 1H), 6.71 (td, *J* = 7.7, 1.3 Hz, 1H), 6.37 (d, *J* = 3.8 Hz, 1H), 2.91 (s, 3H) ppm.

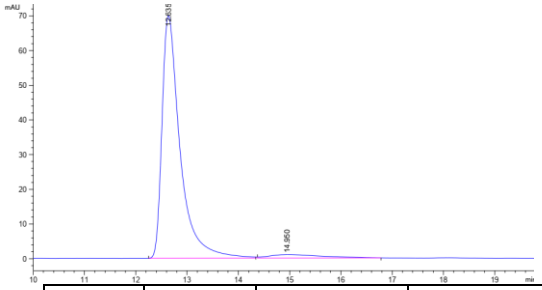
^{13}C NMR (100 MHz, $CDCl_3$): δ 161.69, 146.84, 144.17, 143.02, 142.02, 139.50, 136.44, 132.56, 132.46, 131.76, 131.54, 130.59, 129.79, 129.49, 129.03, 128.34, 128.10, 128.04, 127.17, 127.00, 124.56, 123.86, 119.32, 118.70, 117.19, 100.55, 24.22 ppm.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{22}N_3O$: 428.1757; Found: 428.1754.

$[\alpha]_D^{25}$ = +55.3 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak ID-3 column (90:10 *n*-hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); t_r (minor) = 12.6 min, t_r (major) = 15.0 min, 92% ee.

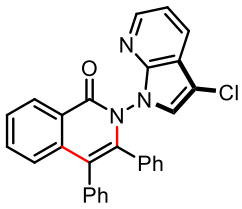




No.	Time	Area	Area (%)
1	11.9	2870.2	50.9180
2	13.4	2766.7	49.0820

No.	Time	Area	Area (%)
1	12.6	1721.2	95.7319
2	15.0	76.7	4.2681

(*R*)-2-(3-chloro-1H-pyrrolo[2,3-b]pyridin-1-yl)-3,4-diphenylisoquinolin-1(2H)-one **(34)**



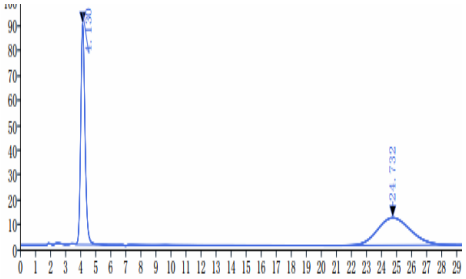
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (dd, *J* = 7.6, 0.7 Hz, 1H), 8.37 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.82 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.56 – 7.53 (m, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.26 (d, *J* = 4.7 Hz, 1H), 7.22 – 7.17 (m, 4H), 7.15 (dd, *J* = 7.9, 4.8 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.10 – 7.08 (m, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.96, 145.97, 145.27, 141.75, 137.62, 135.46, 133.38, 132.01, 131.50, 131.30, 129.78, 129.75, 128.64, 128.36, 128.27, 128.00, 127.40, 127.29, 127.27, 127.22, 127.09, 126.13, 125.47, 125.21, 119.56, 117.65, 117.17, 105.18 ppm.

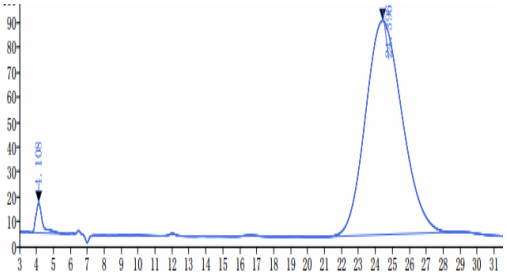
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{19}ClN_3O$: 448.1211; Found: 448.1215.

$[\alpha]_D^{25}$ = +82.0 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak AS-RH column (85:15 *n*-hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_r (minor) = 4.1 min, t_r (major) = 24.4 min, 95% ee.

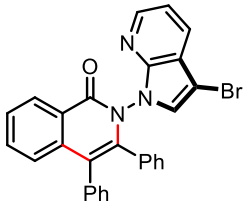


No.	Time	Area	Area (%)
1	4.1	9634.9	51.0009
2	24.7	9256.8	49.9991



No.	Time	Area	Area (%)
1	4.1	217.2	2.4461
2	24.4	8660.4	97.5539

(*R*)-2-(3-bromo-1H-pyrrolo[2,3-b]pyridin-1-yl)-3,4-diphenylisoquinolin-1(2H)-one **(35)**



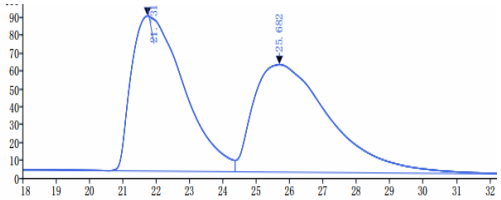
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (dd, *J* = 8.0, 1.1 Hz, 1H), 8.36 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.75 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.63 (ddd, *J* = 8.4, 7.3, 1.4 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.25 (d, *J* = 2.0 Hz, 1H), 7.22 – 7.17 (m, 4H), 7.16 – 7.14 (m, 2H), 7.11 (d, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 7.00 (t, *J* = 7.3 Hz, 1H), 6.95 – 6.92 (m, 1H), 6.74 (t, *J* = 7.4 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.92, 146.28, 145.23, 141.72, 137.62, 135.46, 133.39, 131.97, 131.50, 131.30, 129.78, 129.75, 128.65, 128.36, 128.27, 128.17, 128.01, 127.84, 127.40, 127.27, 127.21, 127.08, 126.14, 125.21, 119.56, 118.63, 117.79, 90.06 ppm.

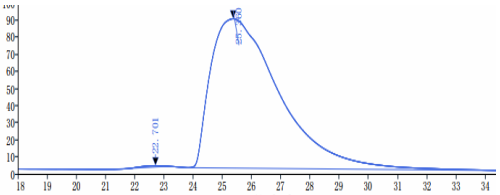
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{19}BrN_3O$: 492.0706; Found: 492.0715.

$[\alpha]_D^{25}$ = +86.0 (c = 0.1, CH_2Cl_2).

HPLC conditions: Daicel Chiralpak IB-3 column (96:4 *n*-hexane: 2-propanol, 1.0 mL/min, 27 °C, 254 nm); t_r (minor) = 22.7 min, t_r (major) = 25.4 min, >99% ee.



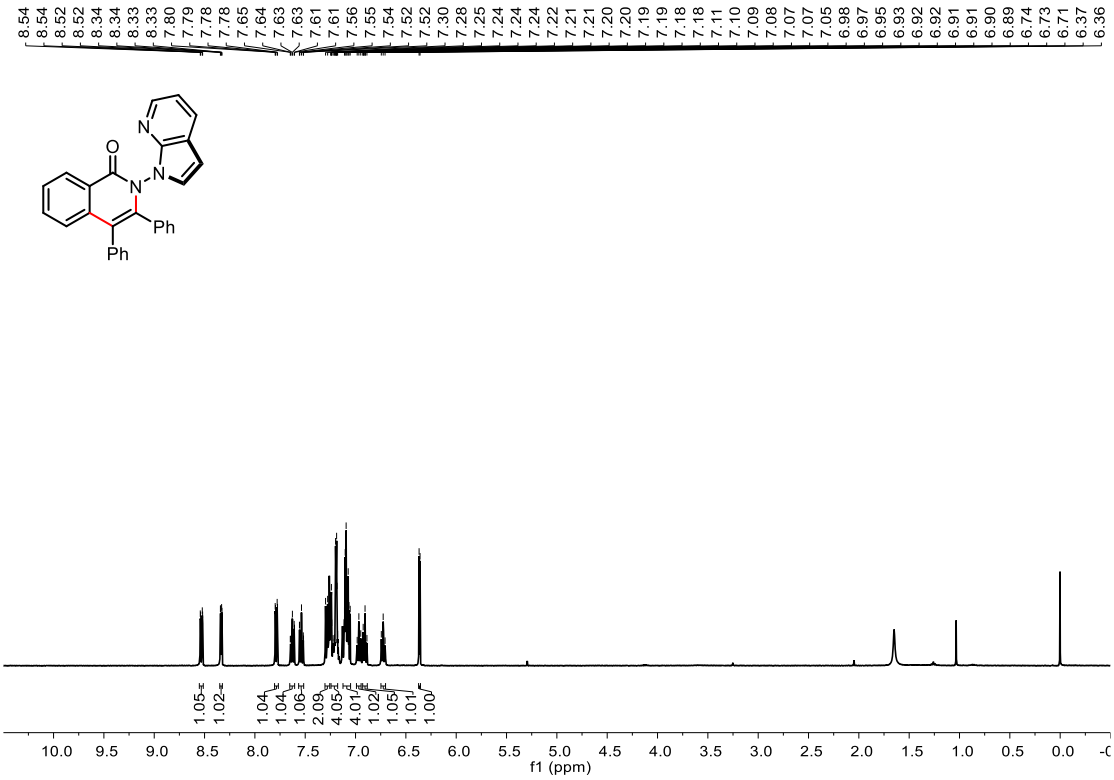
No.	Time	Area	Area (%)
1	21.7	7363.2	49.5453
2	25.7	7498.4	50.4547



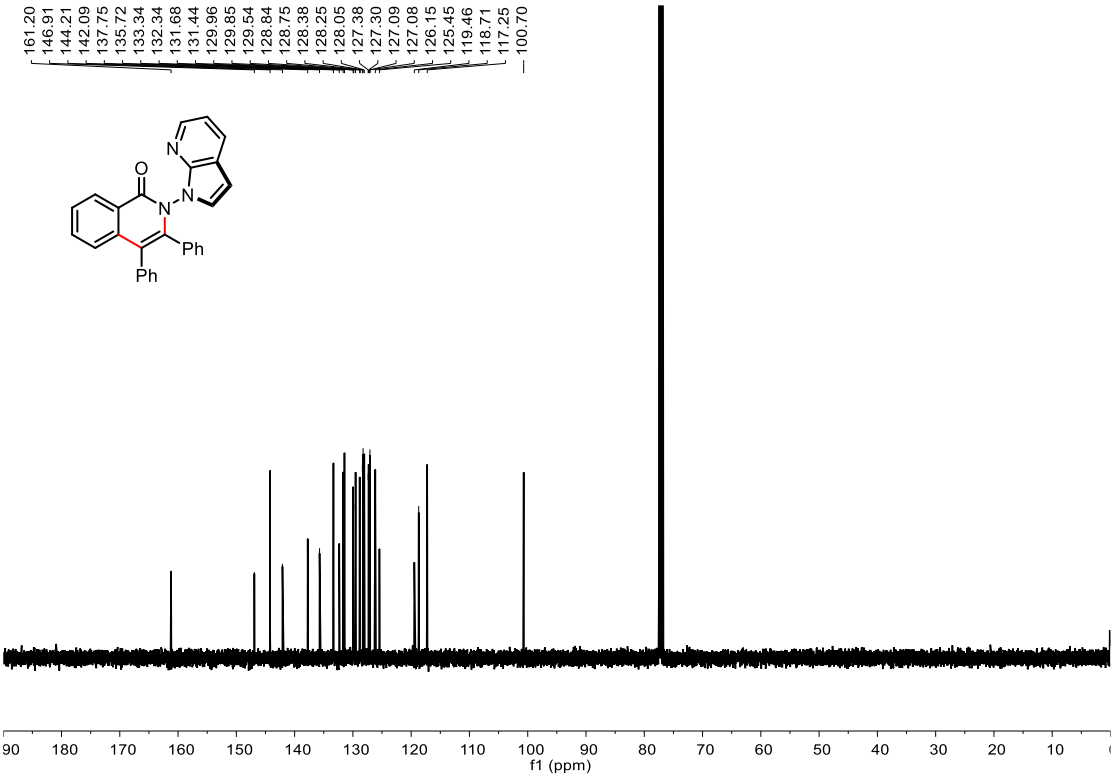
No.	Time	Area	Area (%)
1	22.7	36.2	0.2652
2	25.4	13611.9	99.7348

8. Copies of NMR spectra

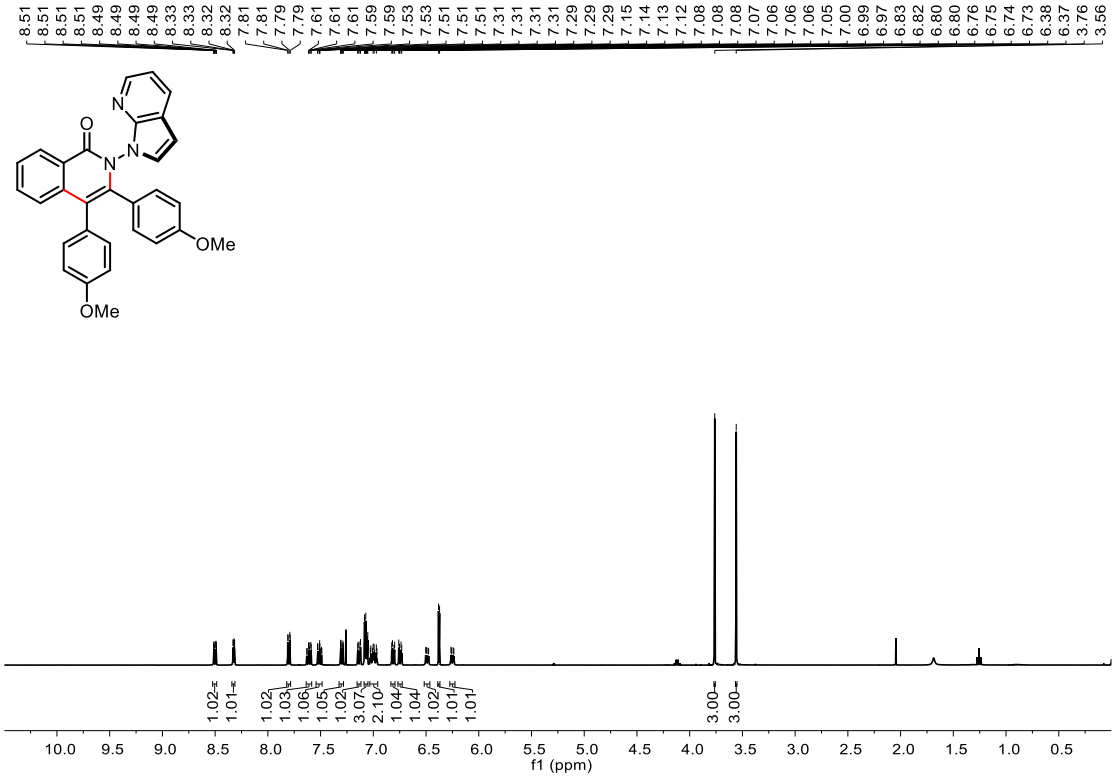
^{1}H NMR of **3** (400 MHz, $CDCl_3$)



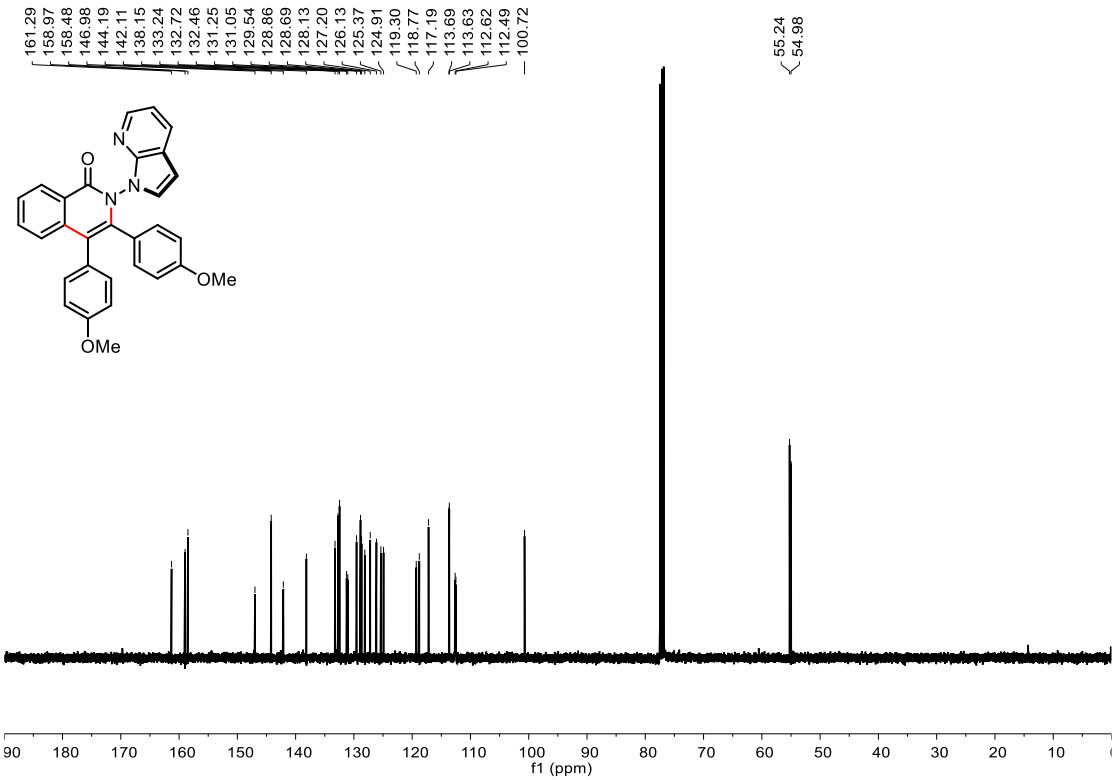
^{13}C NMR of **3** (100 MHz, $CDCl_3$)



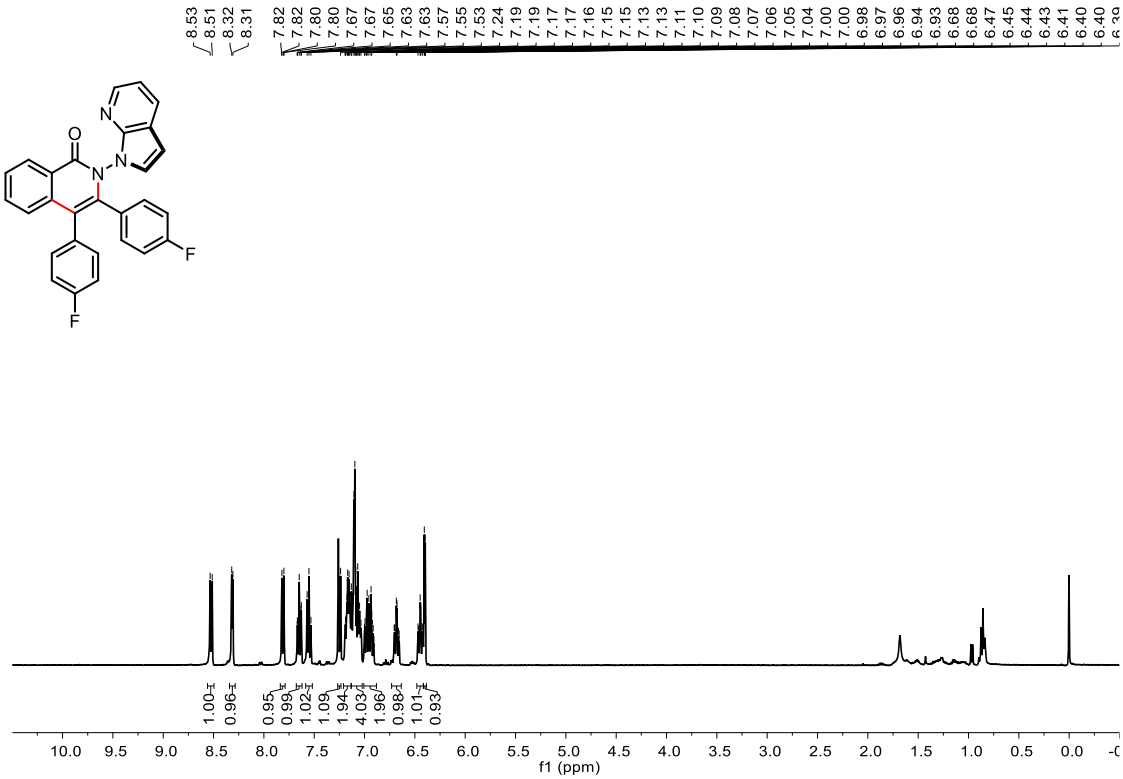
^{1}H NMR of **4** (400 MHz, $CDCl_3$)



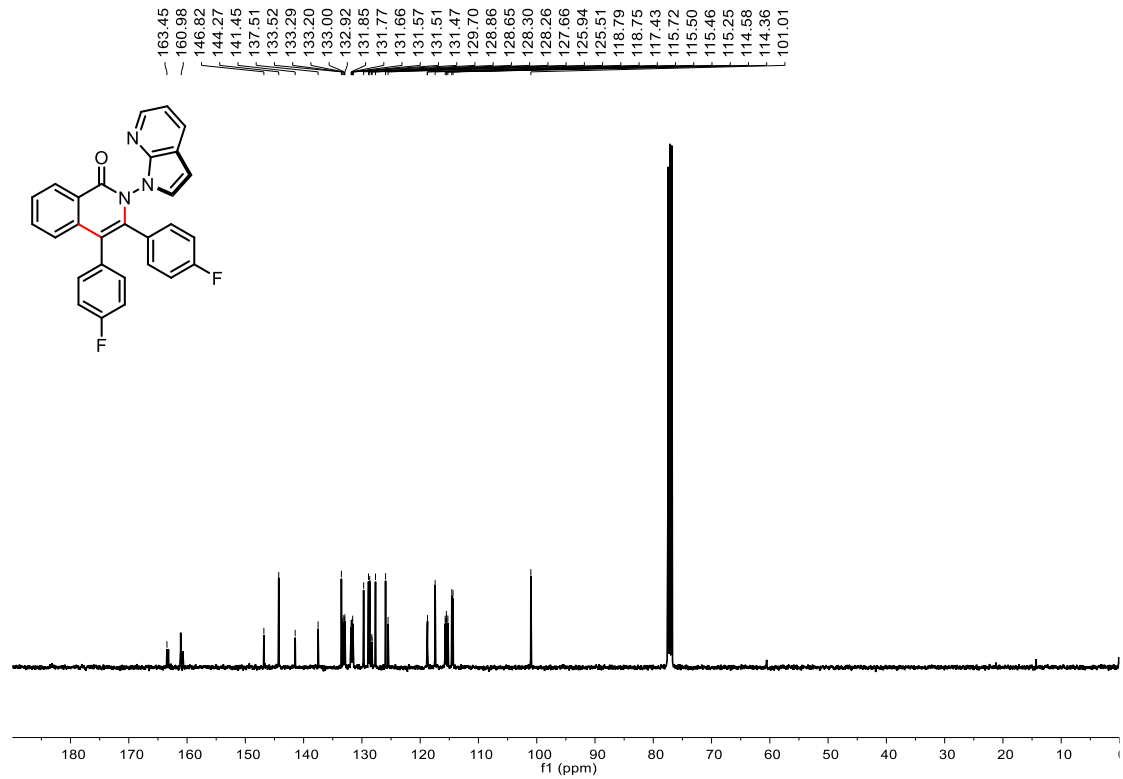
^{13}C NMR of **4** (100 MHz, $CDCl_3$)



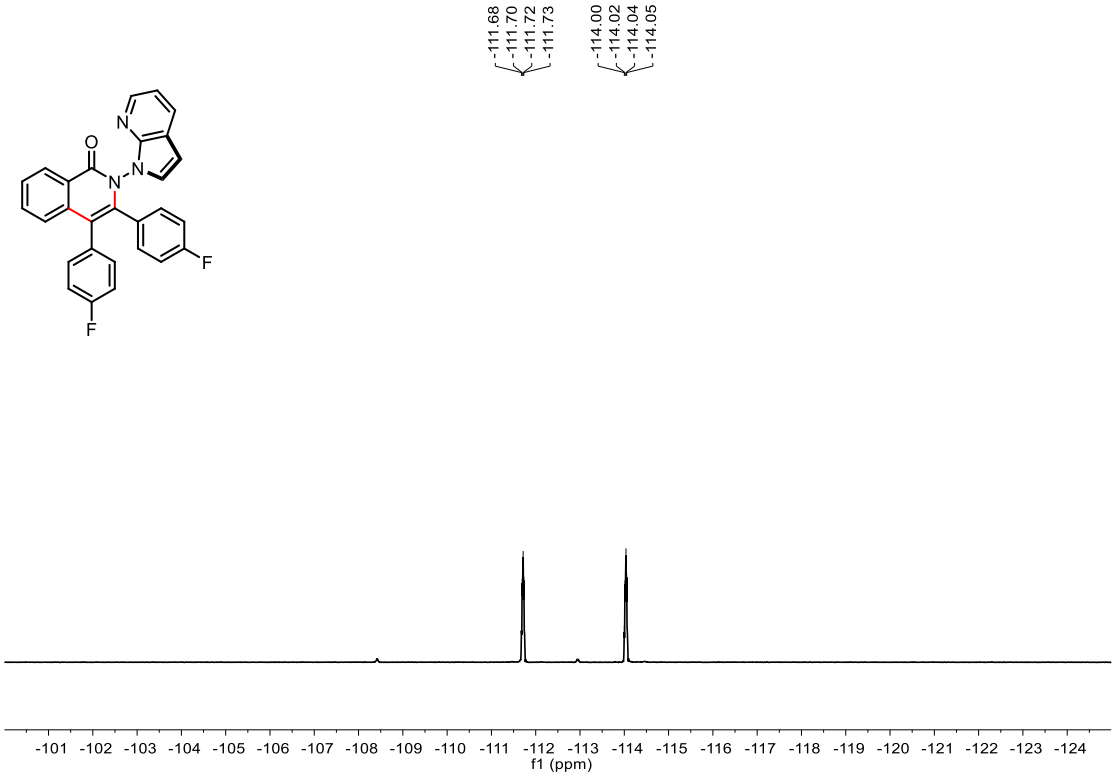
^{1}H NMR of **5** (400 MHz, $CDCl_3$)



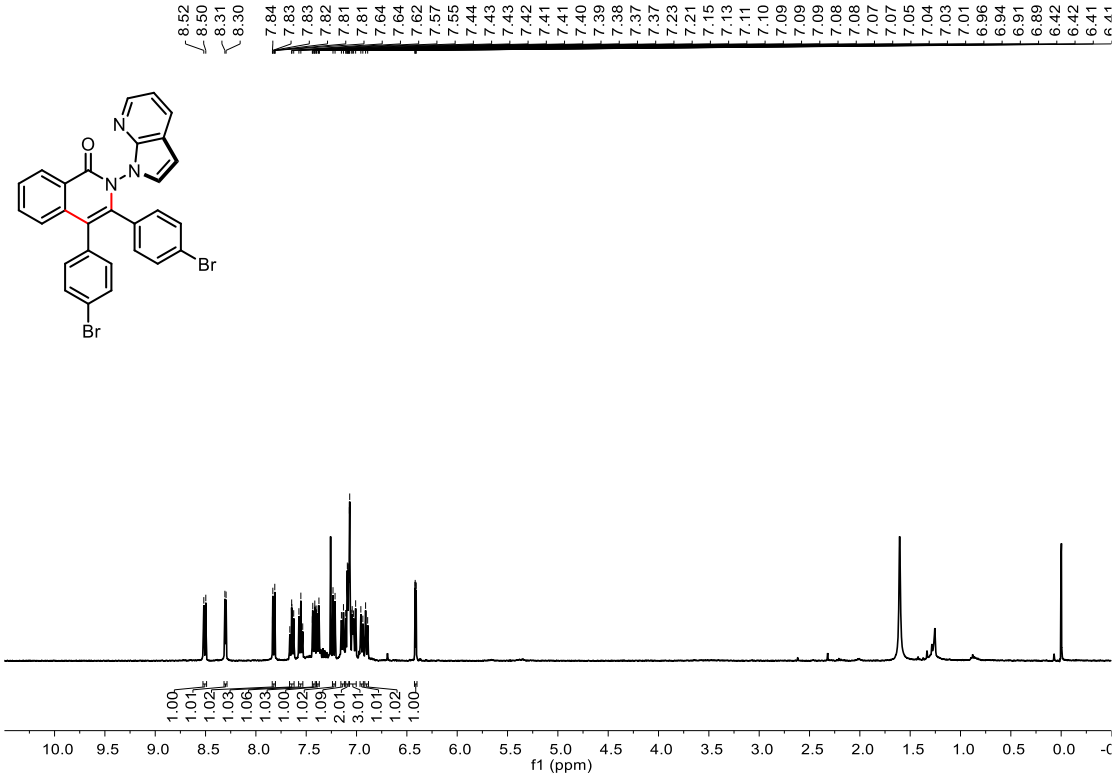
^{13}C NMR of **5** (100 MHz, $CDCl_3$)



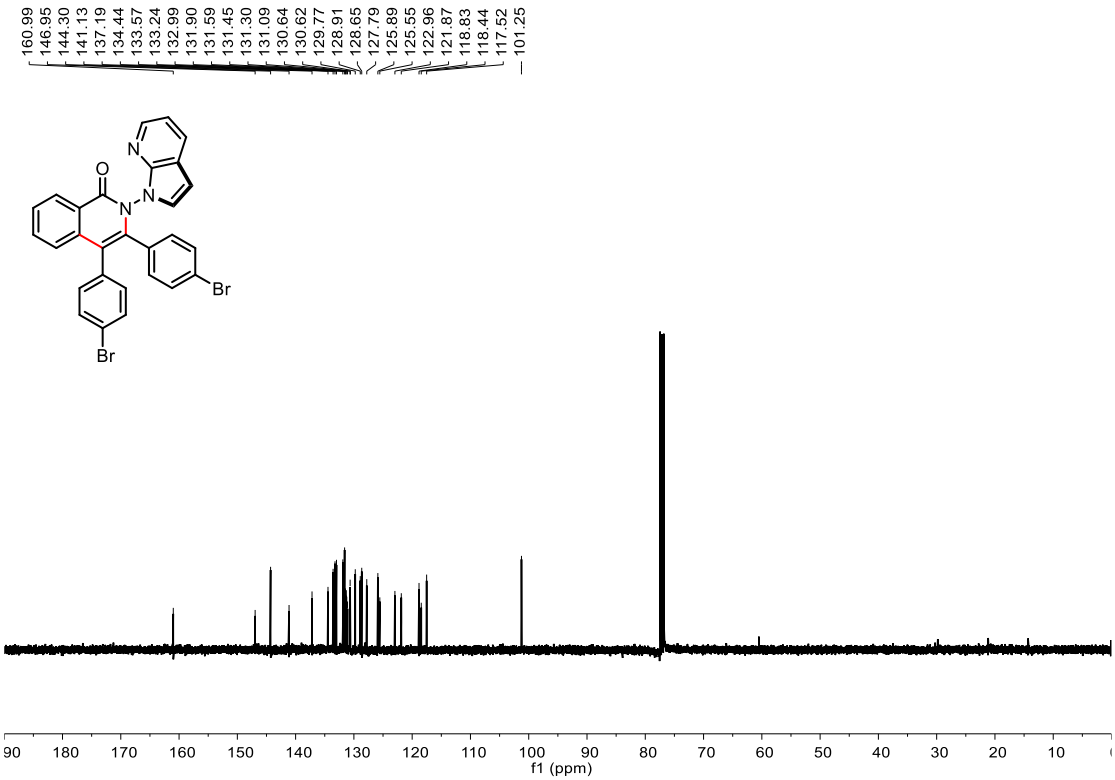
^{19}F NMR of **5** (376 MHz, $CDCl_3$)



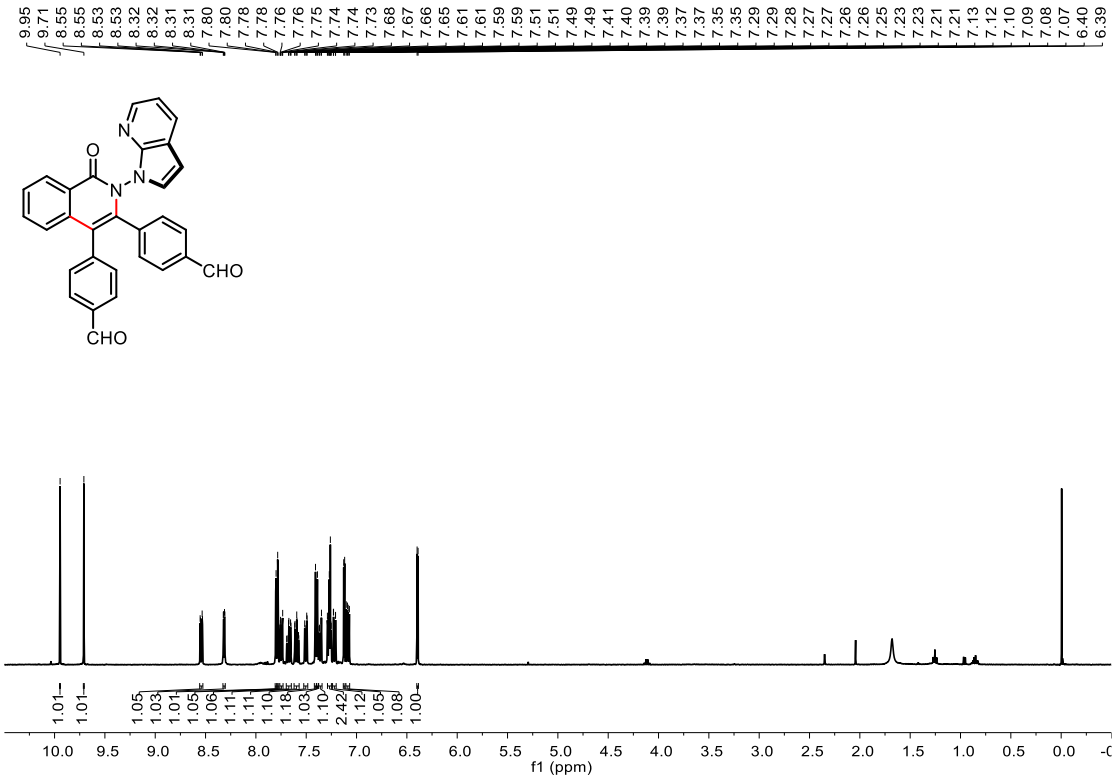
^{1}H NMR of **6** (400 MHz, $CDCl_3$)



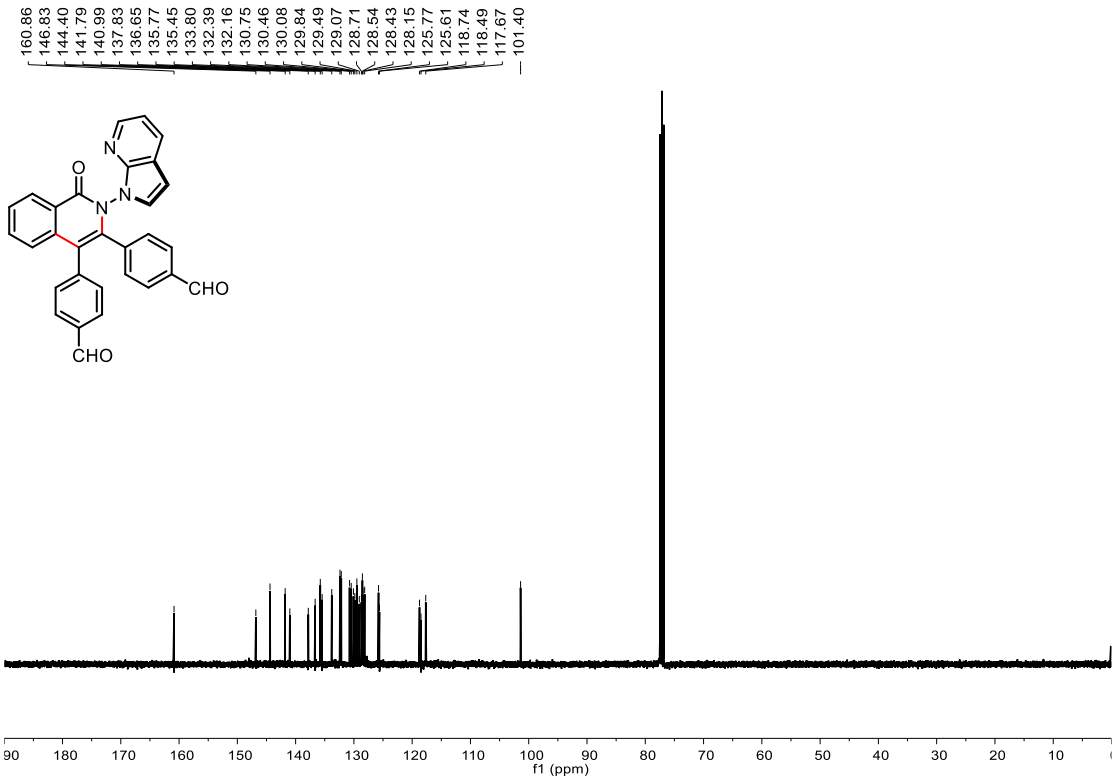
^{13}C NMR of **6** (100 MHz, $CDCl_3$)



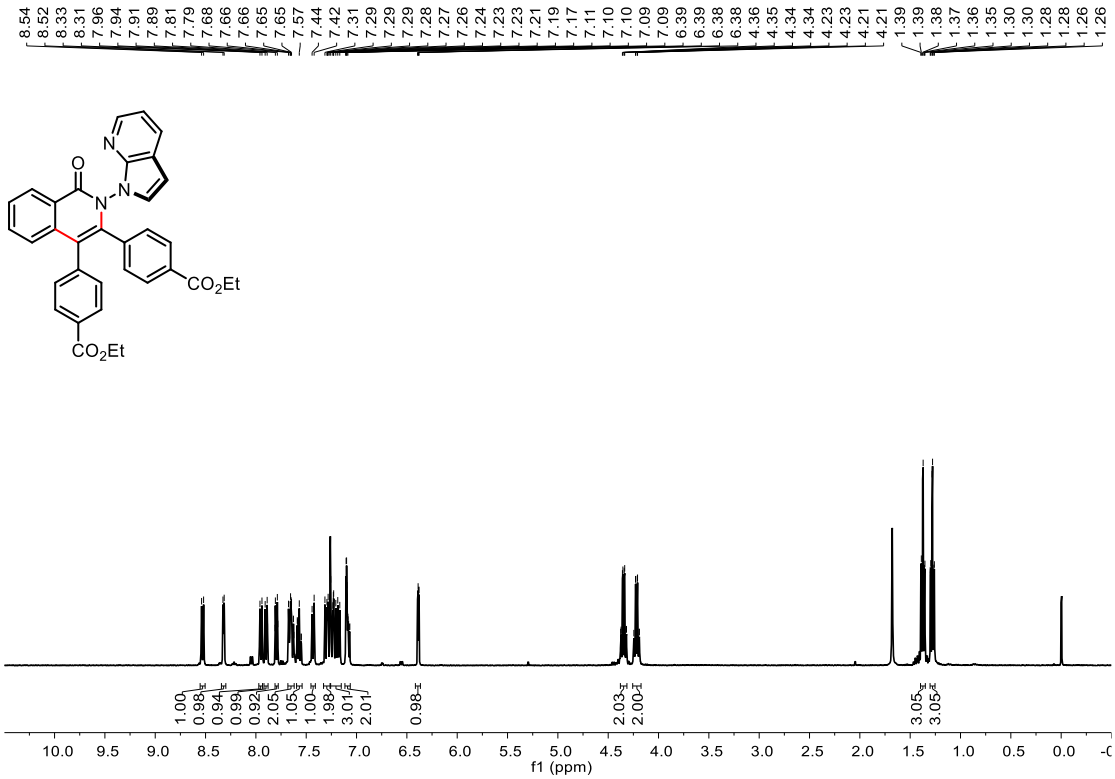
^{1}H NMR of **7** (400 MHz, $CDCl_3$)



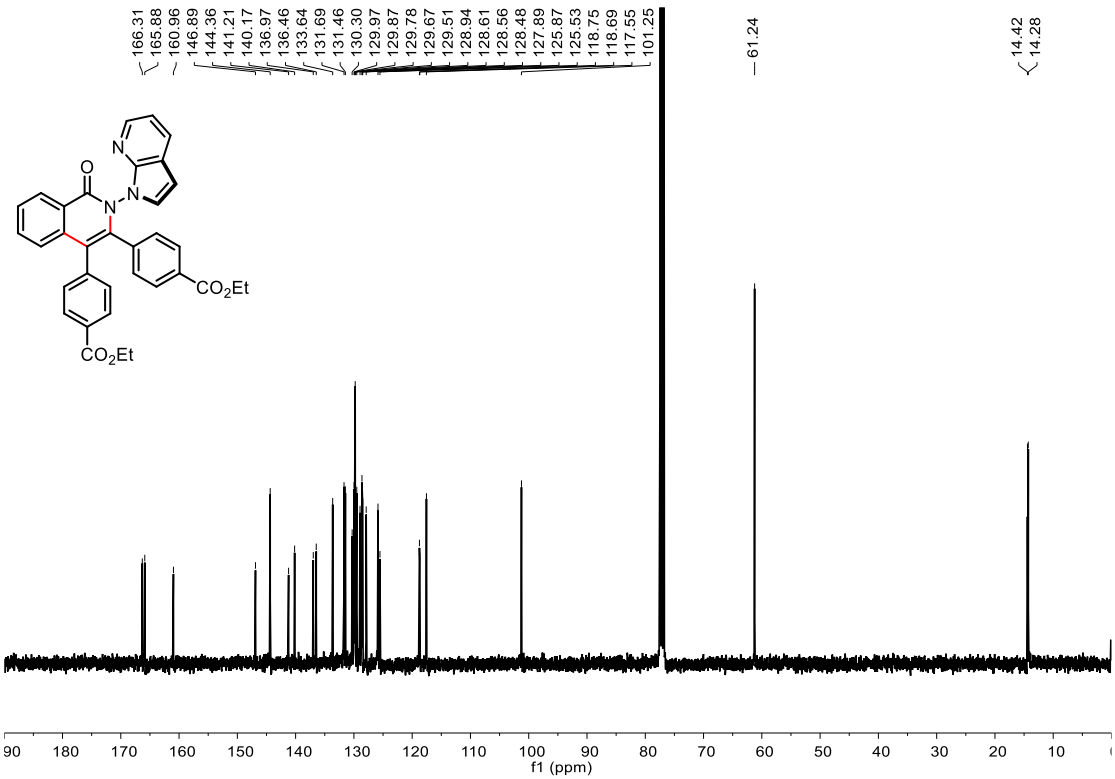
^{13}C NMR of **7** (100 MHz, $CDCl_3$)



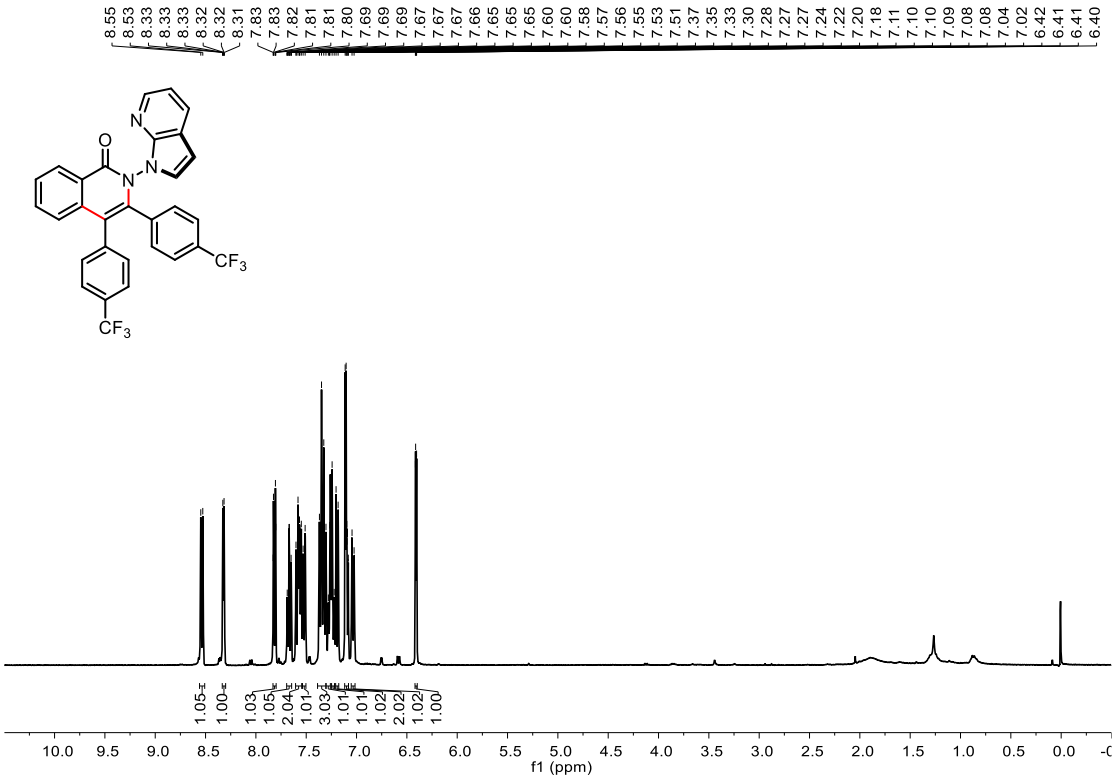
^{1}H NMR of **8** (400 MHz, $CDCl_3$)



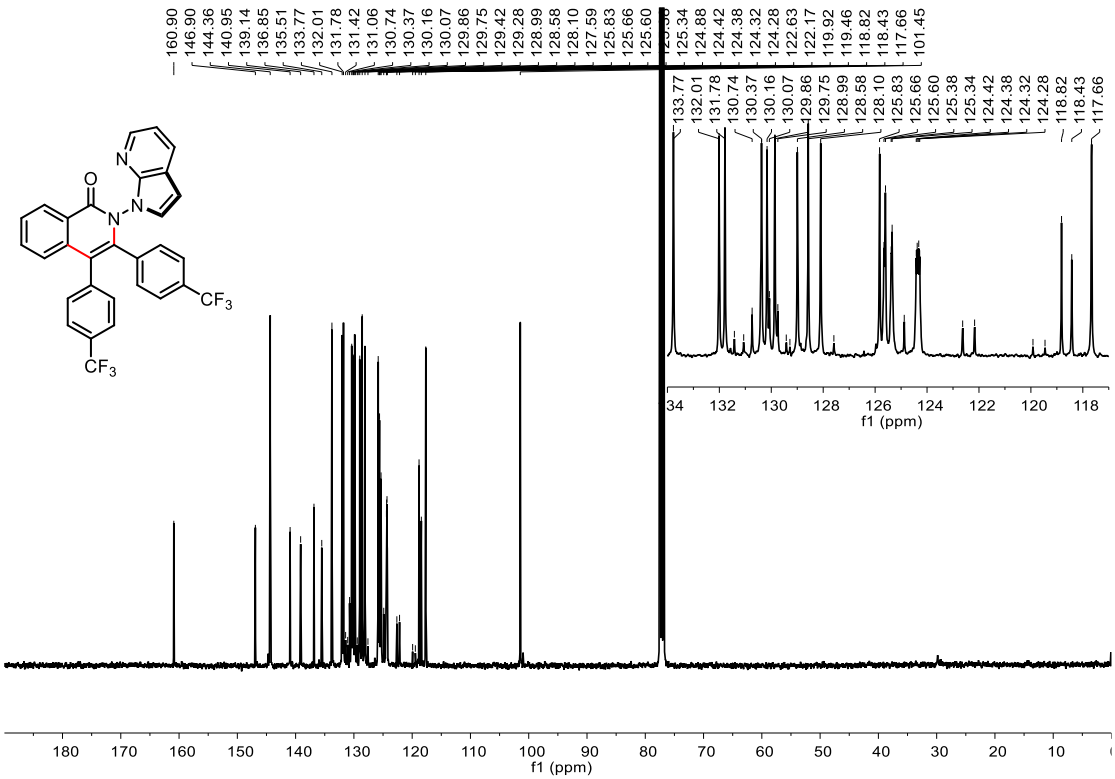
^{13}C NMR of **8** (100 MHz, $CDCl_3$)



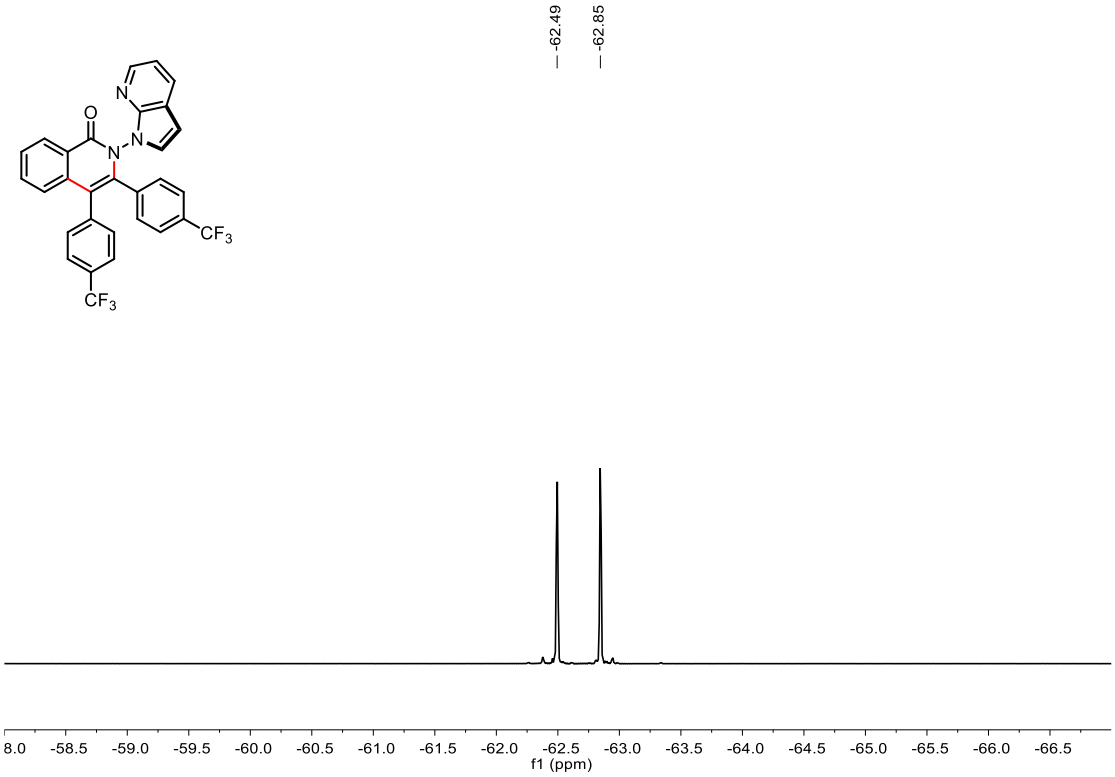
^{1}H NMR of **9** (400 MHz, $CDCl_3$)



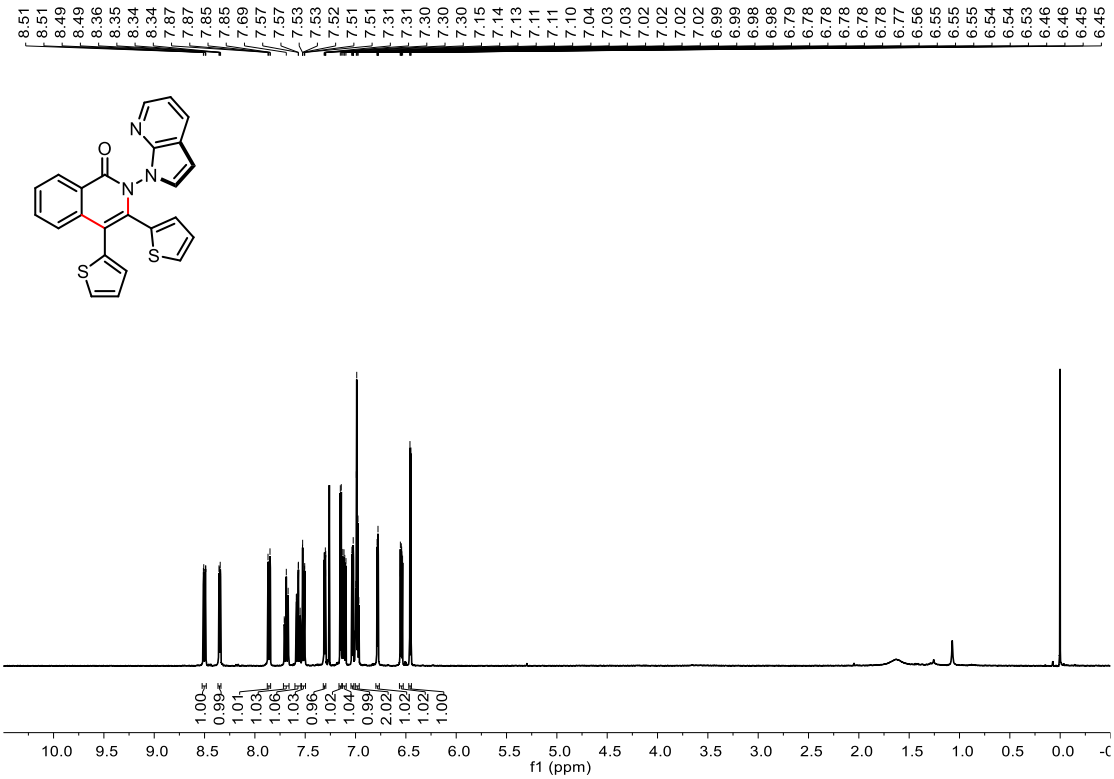
^{13}C NMR of **9** (100 MHz, $CDCl_3$)



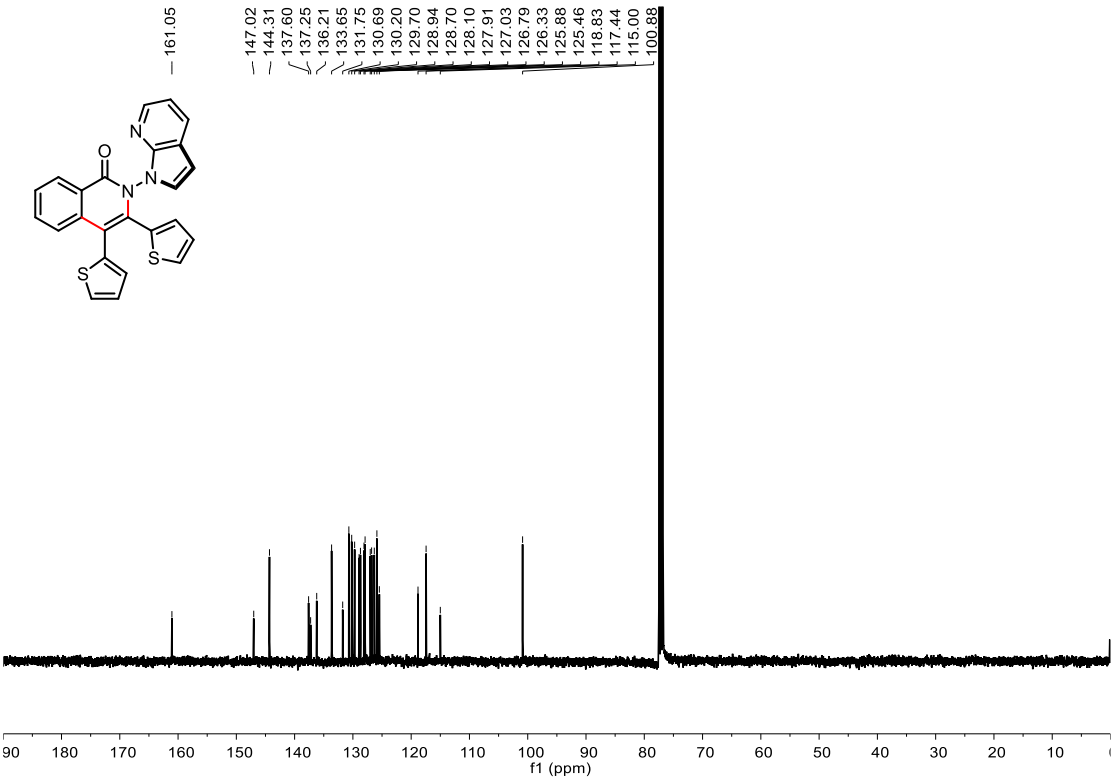
^{19}F NMR of **9** (376 MHz, $CDCl_3$)



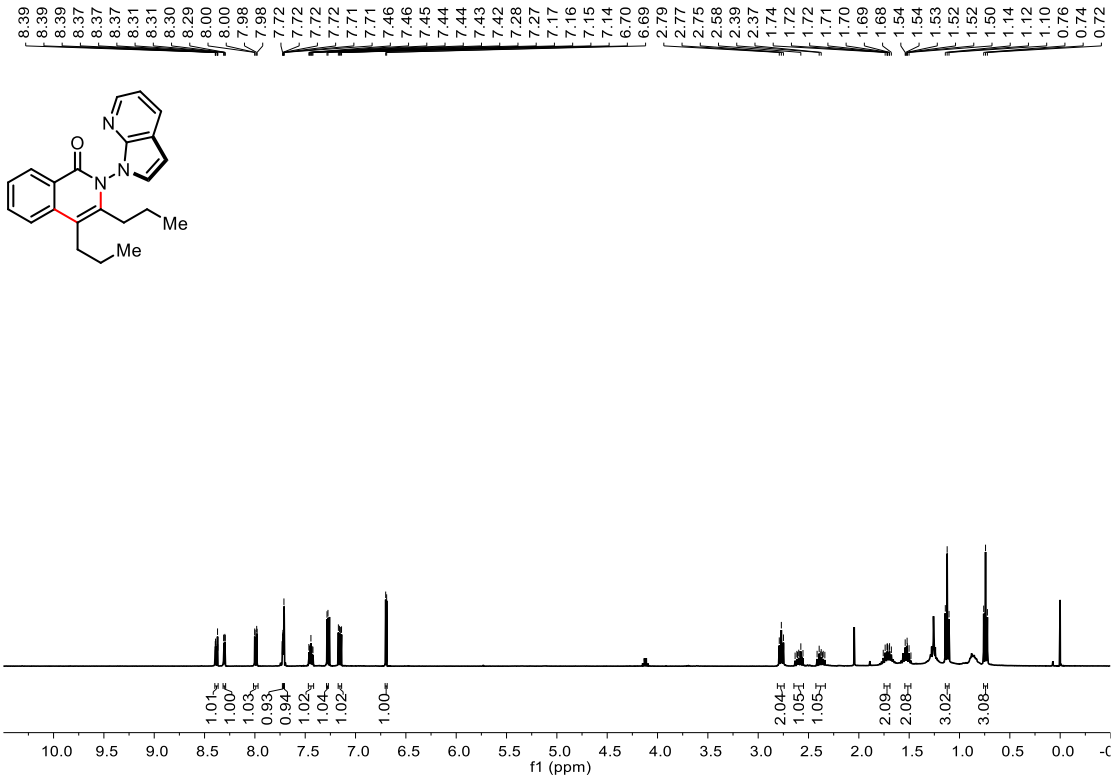
^{1}H NMR of **10** (400 MHz, $CDCl_3$)



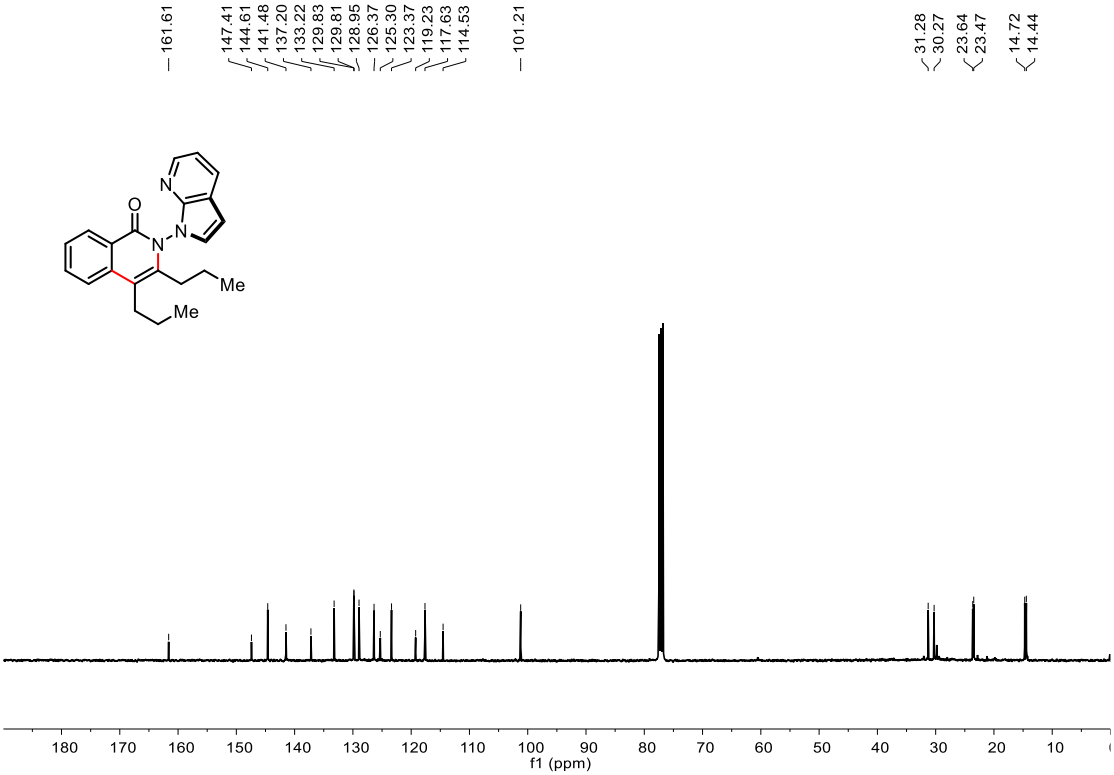
^{13}C NMR of **10** (100 MHz, $CDCl_3$)



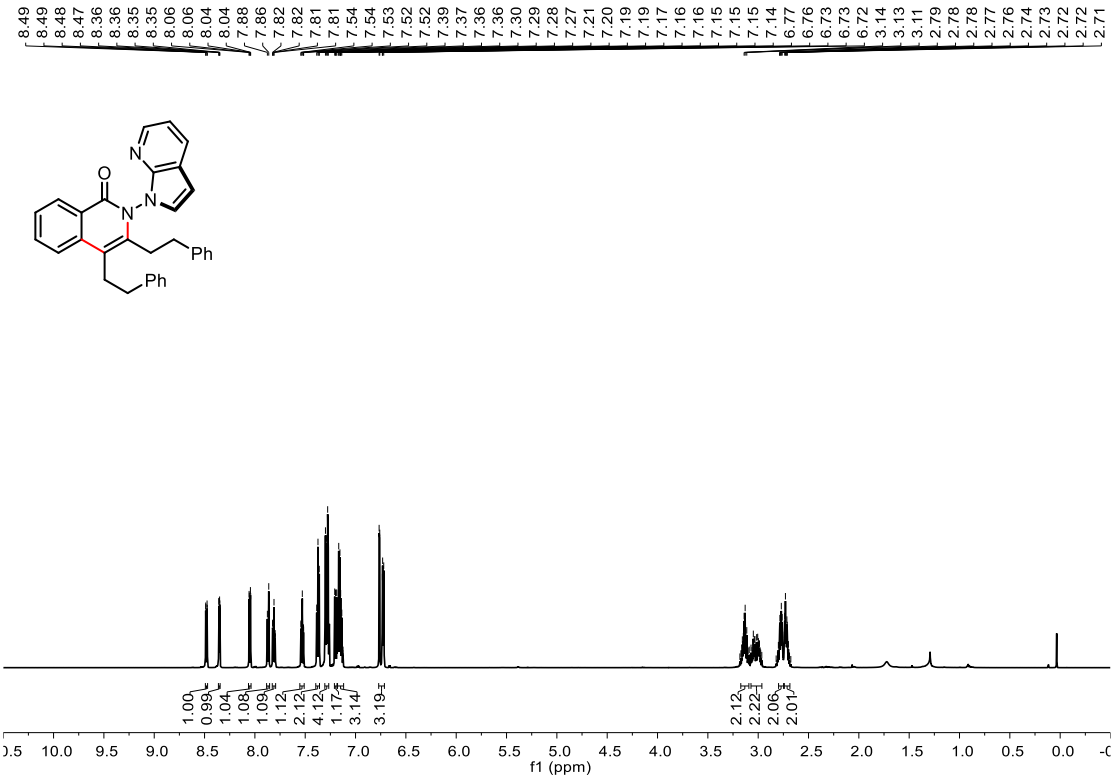
^{1}H NMR of **11** (400 MHz, $CDCl_3$)



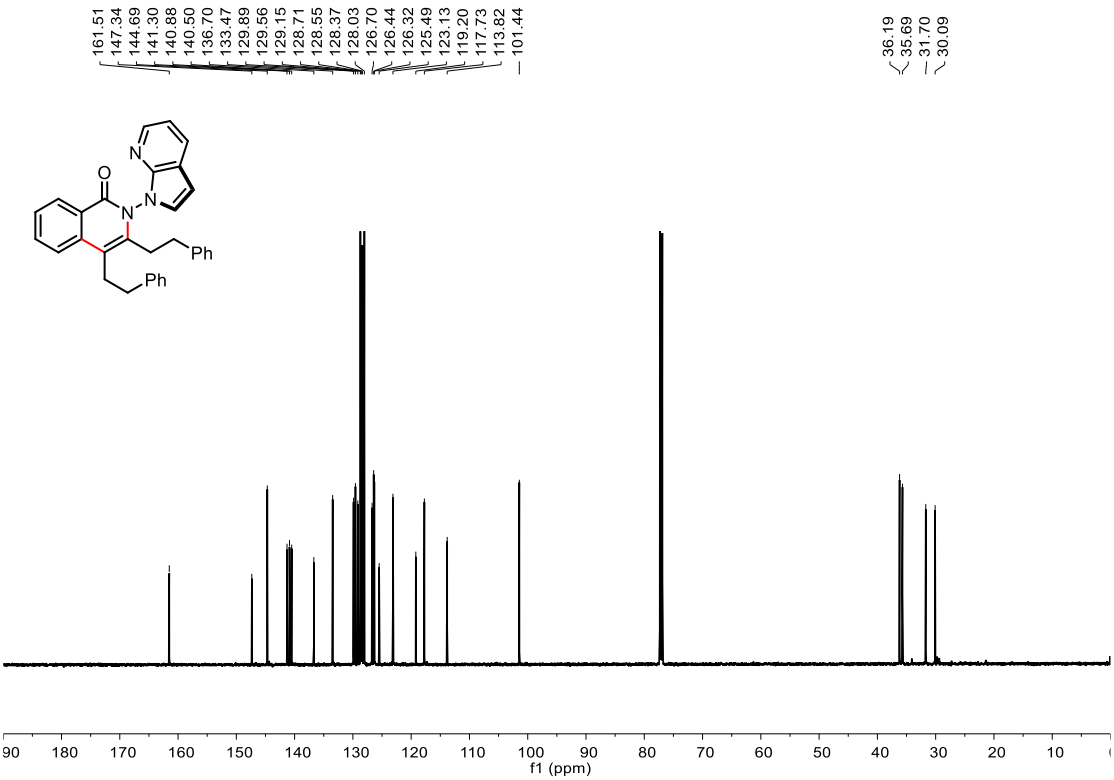
^{13}C NMR of **11** (100 MHz, $CDCl_3$)



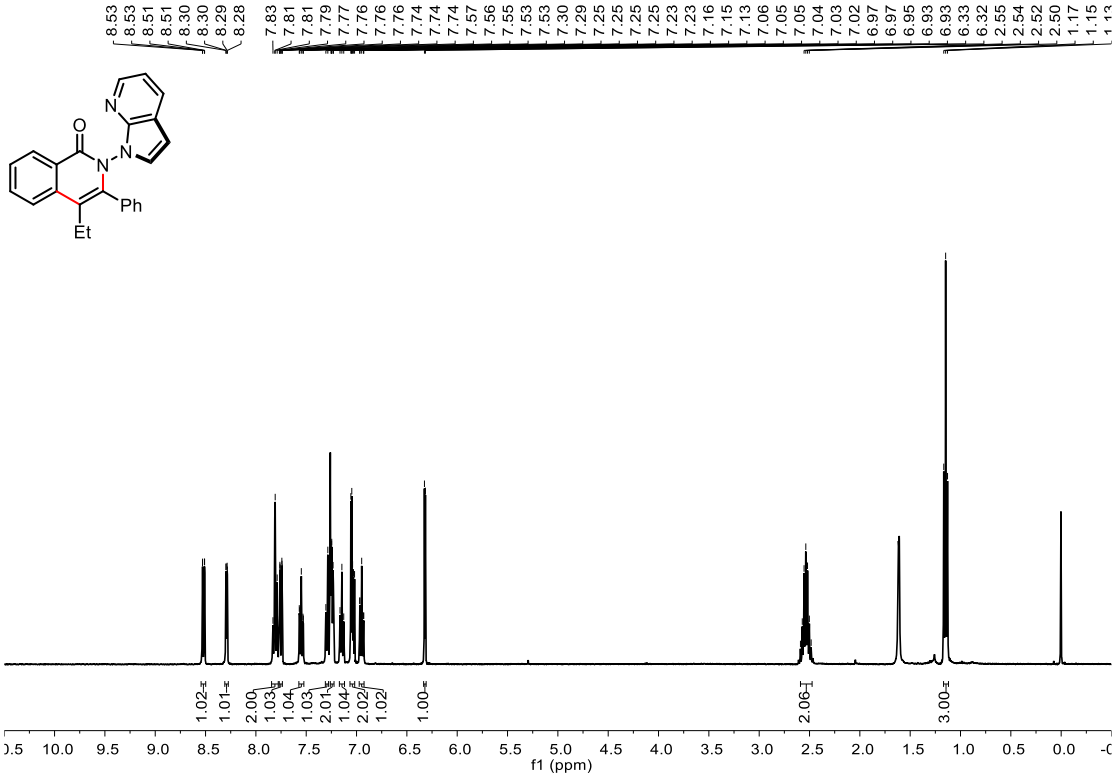
^{1}H NMR of **12** (400 MHz, $CDCl_3$)



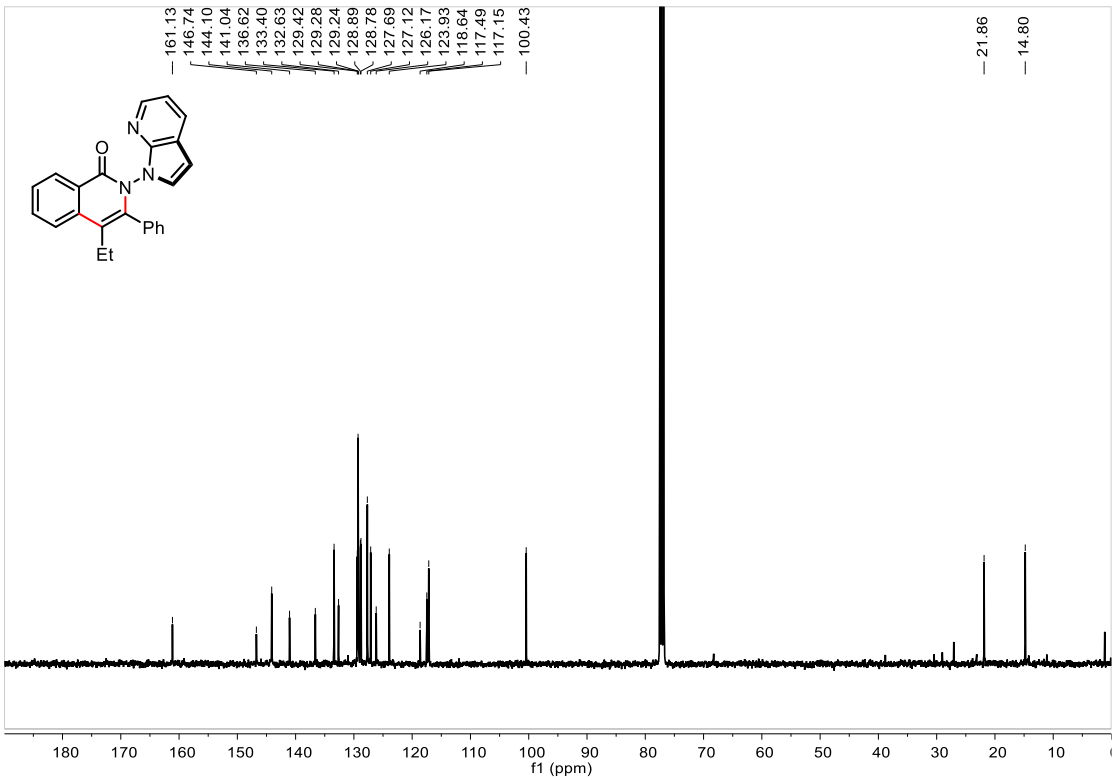
^{13}C NMR of **12** (100 MHz, $CDCl_3$)



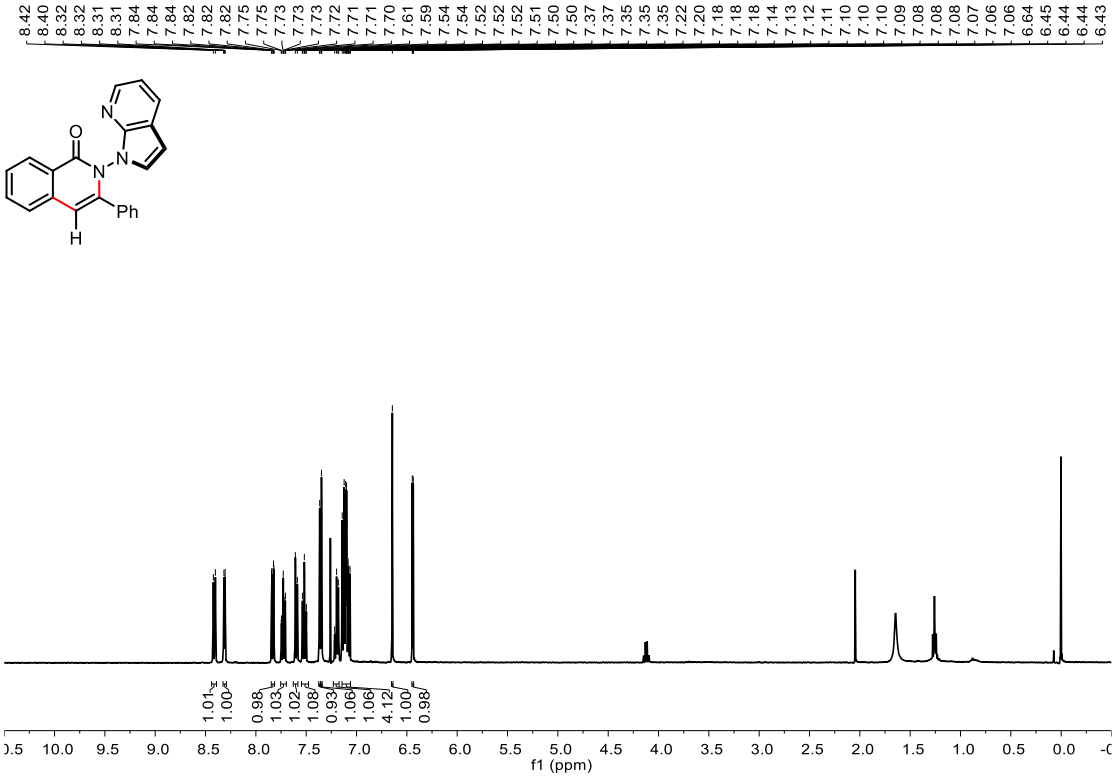
^{1}H NMR of **13** (400 MHz, $CDCl_3$)



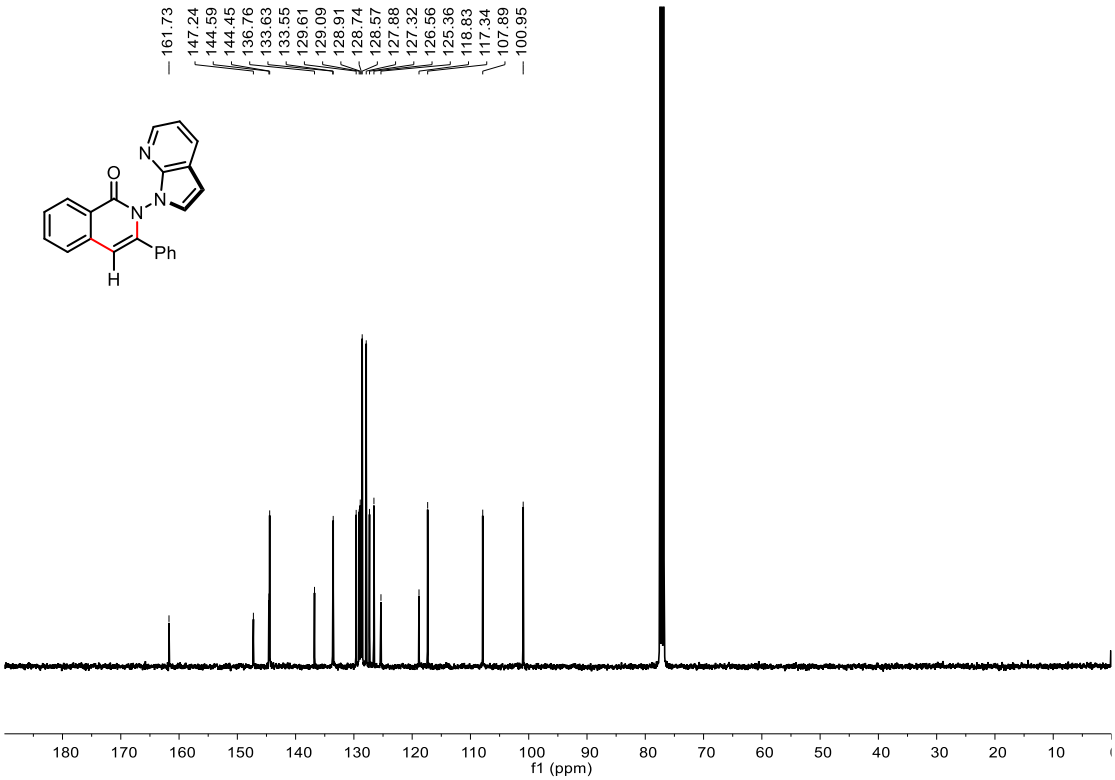
^{13}C NMR of **13** (100 MHz, $CDCl_3$)



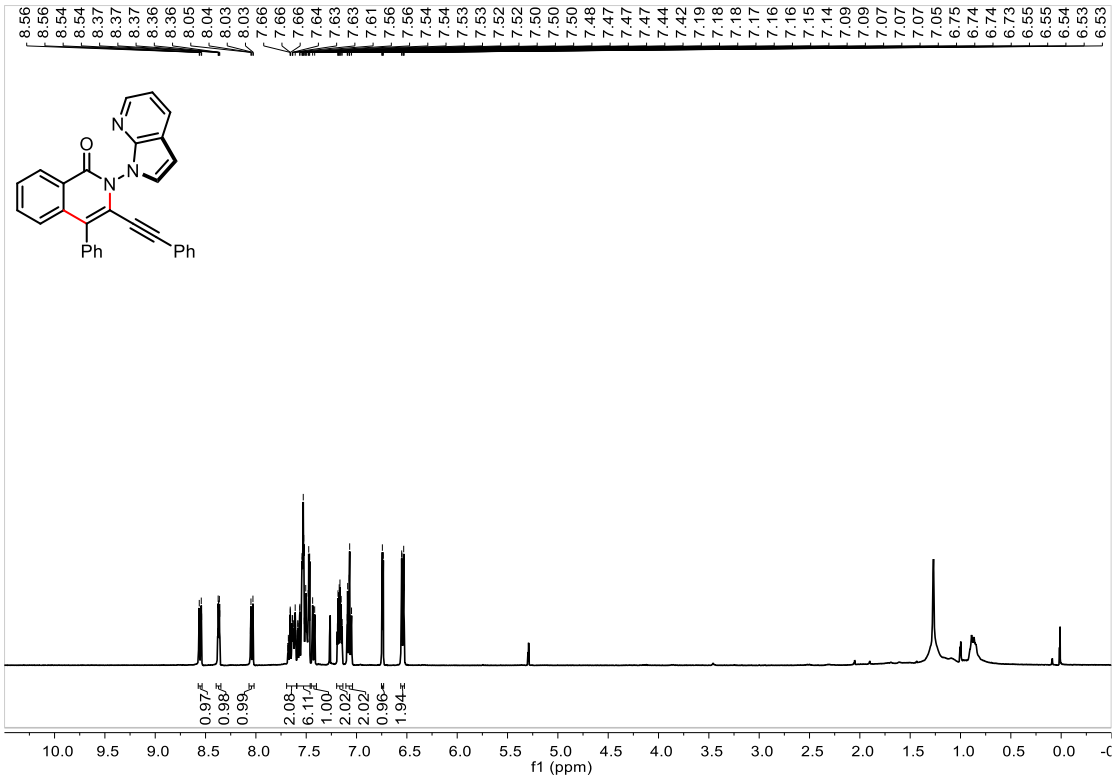
^{1}H NMR of **14** (400 MHz, $CDCl_3$)



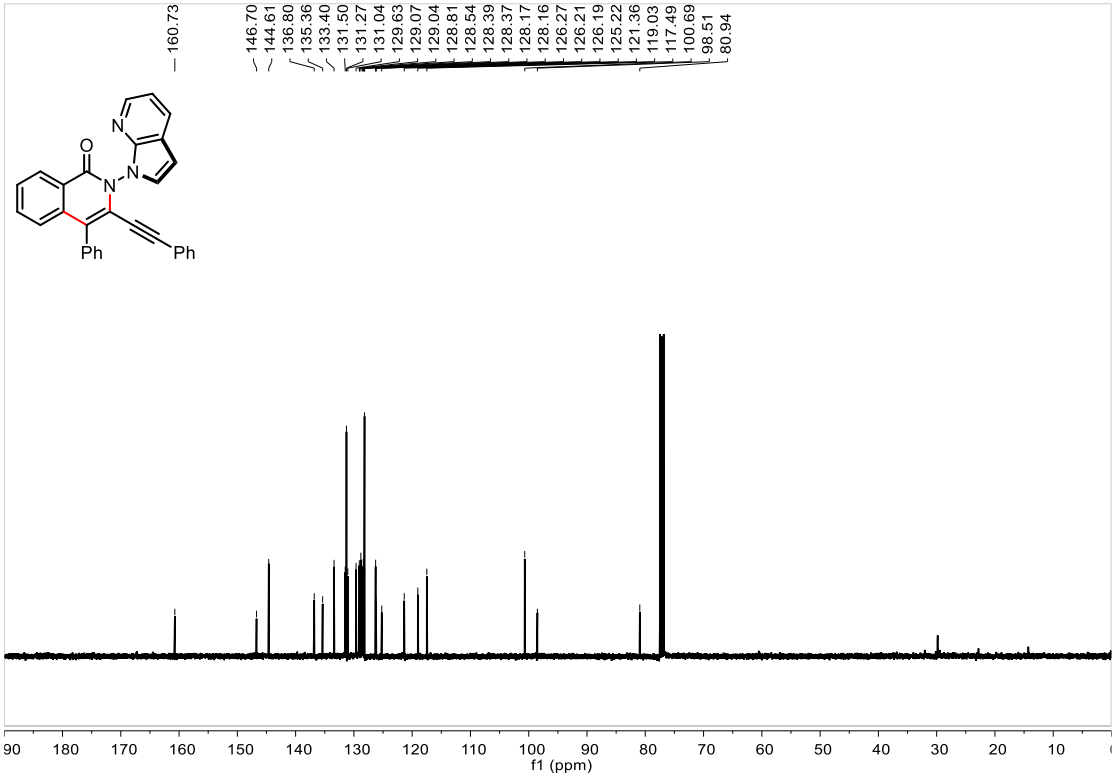
^{13}C NMR of **14** (100 MHz, $CDCl_3$)



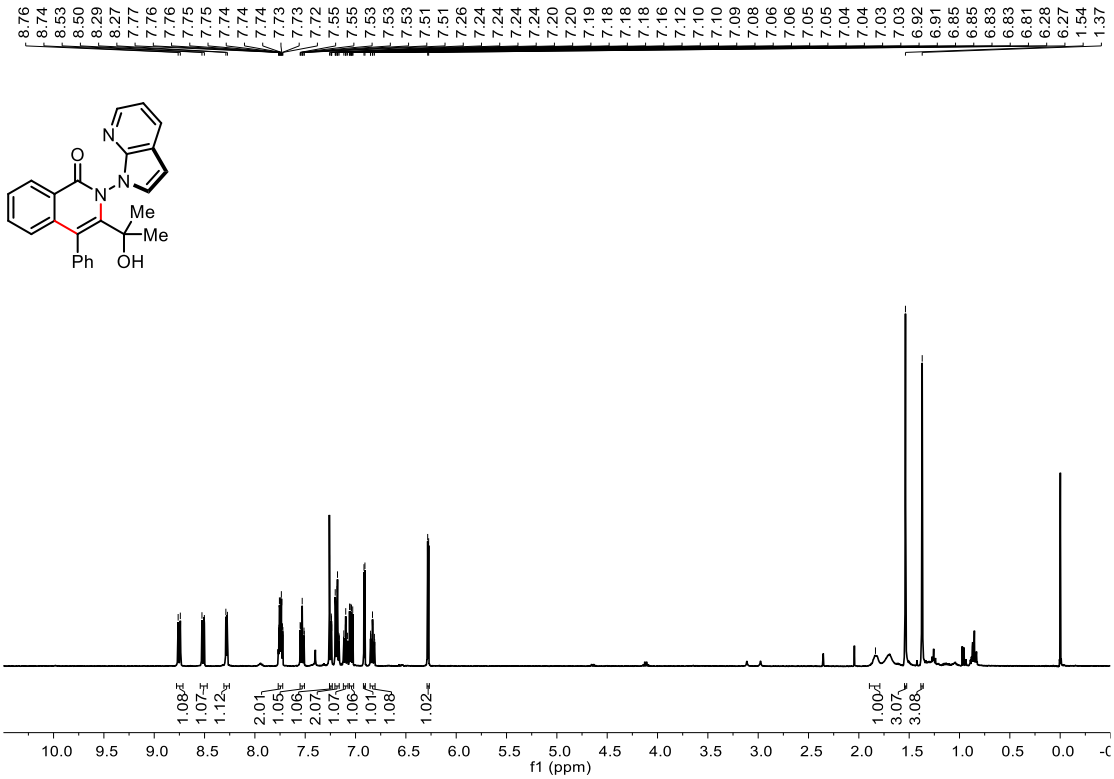
^{1}H NMR of **15** (400 MHz, $CDCl_3$)



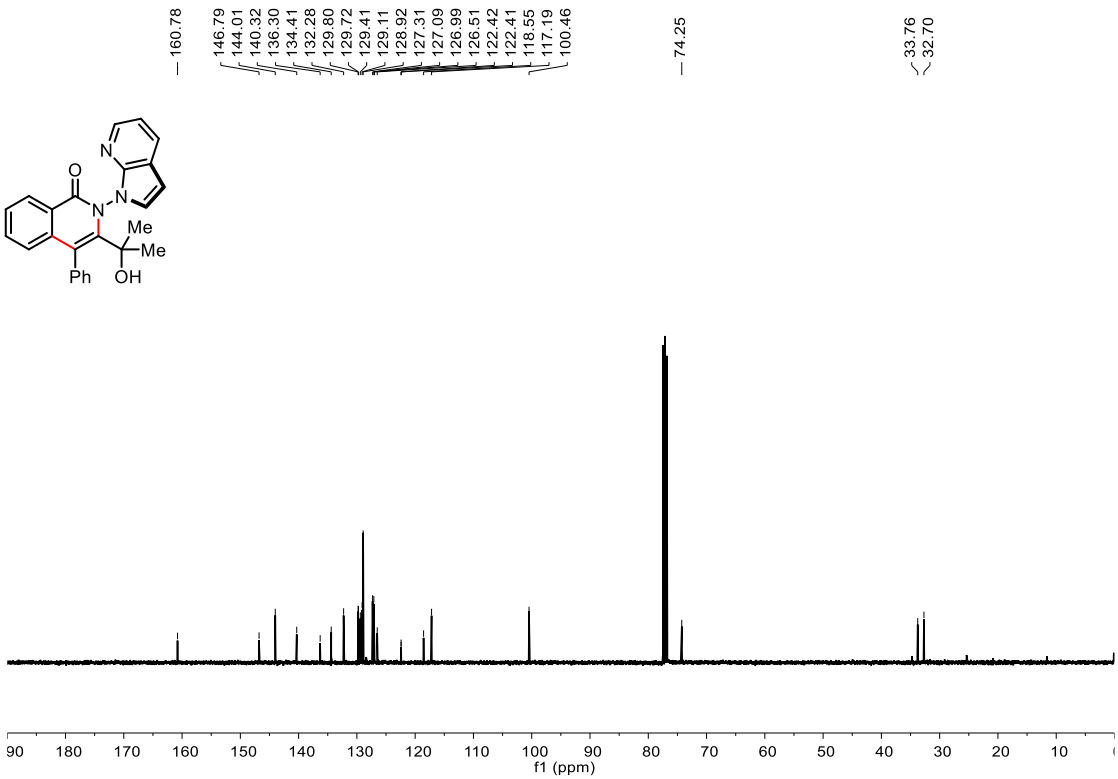
^{13}C NMR of **15** (100 MHz, $CDCl_3$)



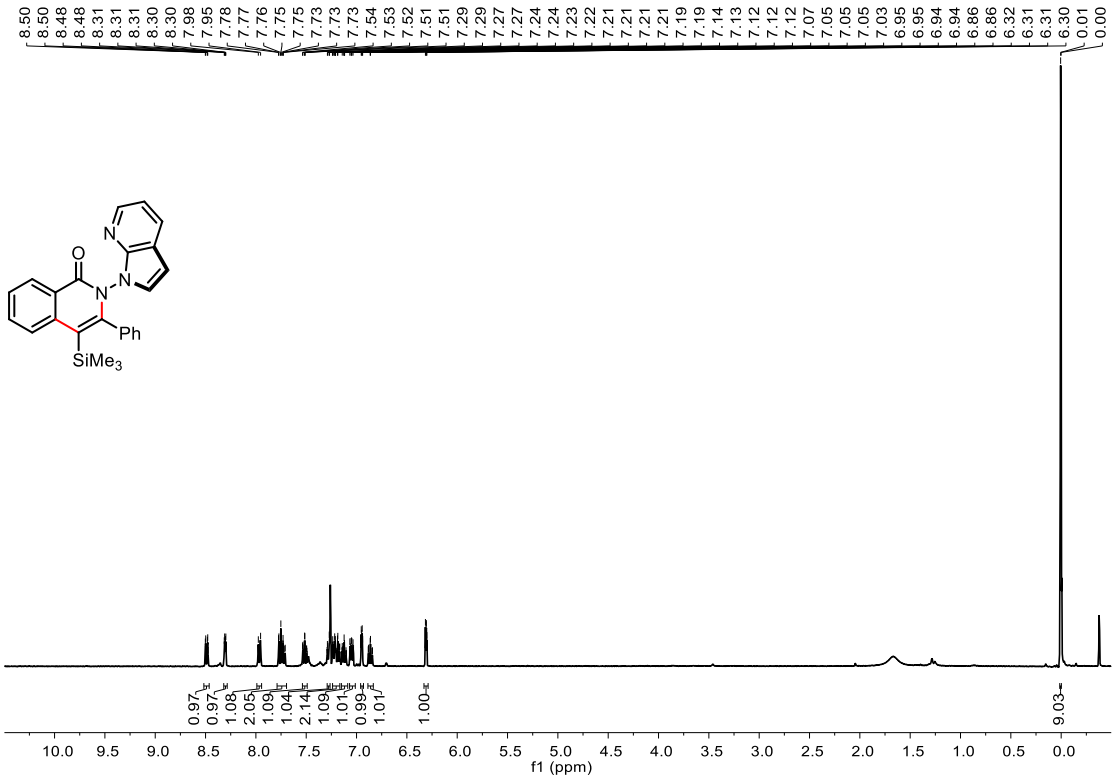
^{1}H NMR of **16** (400 MHz, $CDCl_3$)



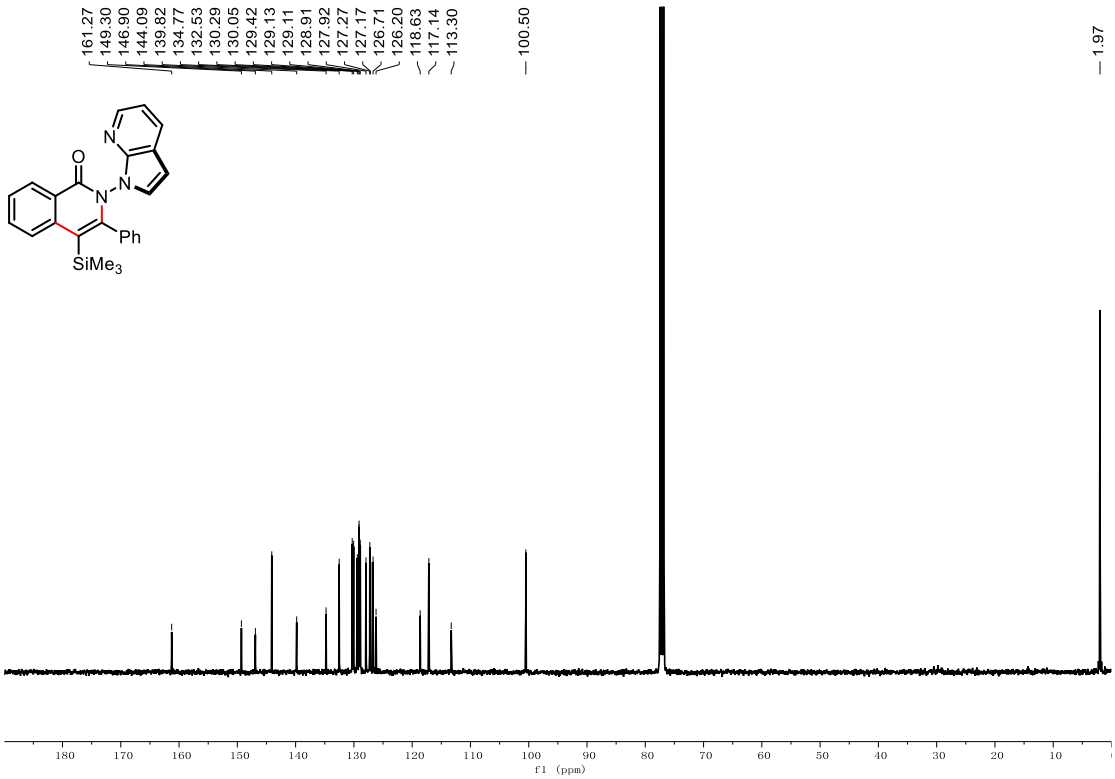
^{13}C NMR of **16** (100 MHz, $CDCl_3$)



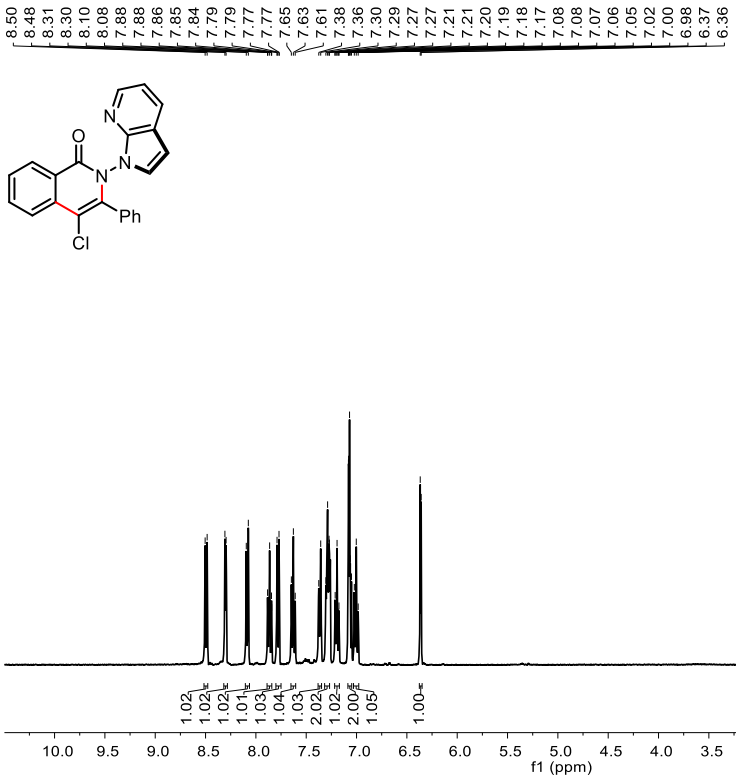
^{1}H NMR of **17** (400 MHz, $CDCl_3$)



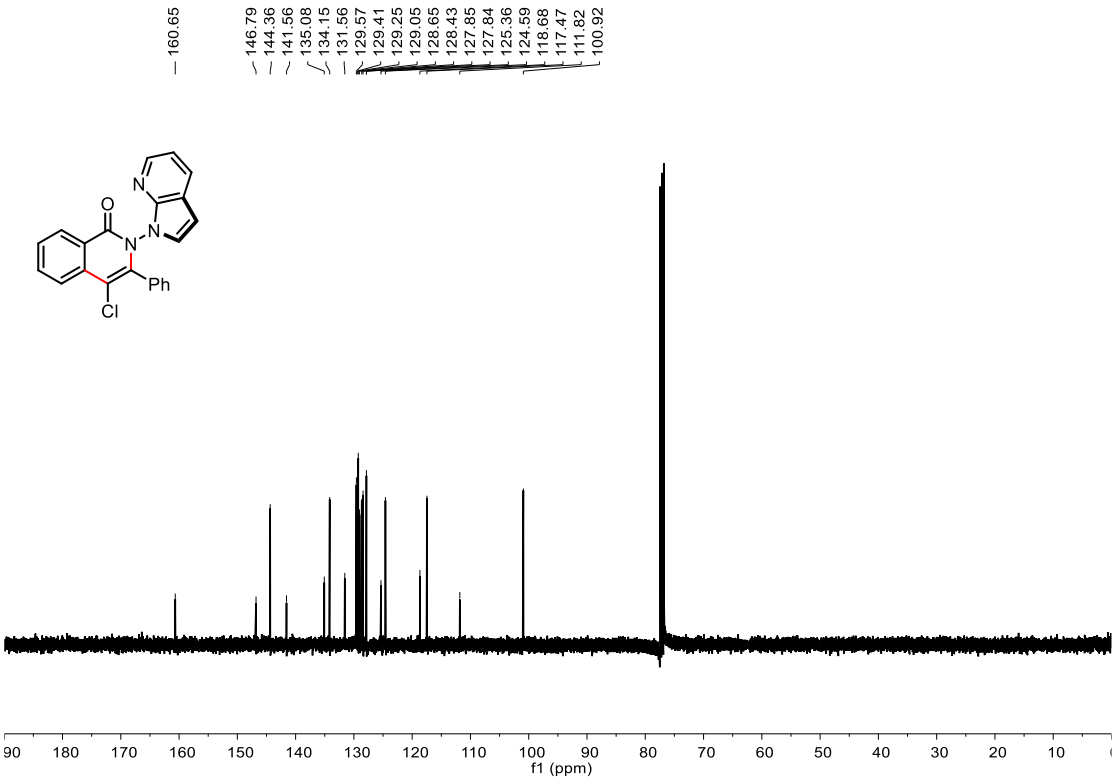
^{13}C NMR of **17** (100 MHz, $CDCl_3$)



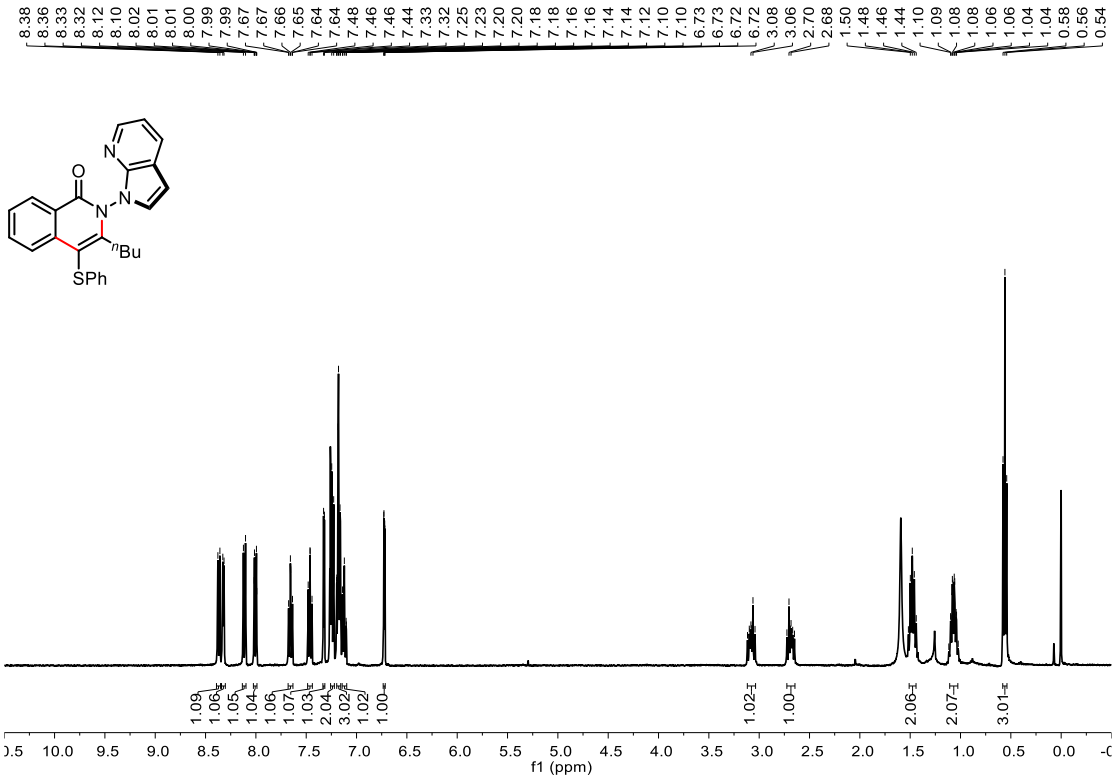
^{1}H NMR of **18** (400 MHz, $CDCl_3$)



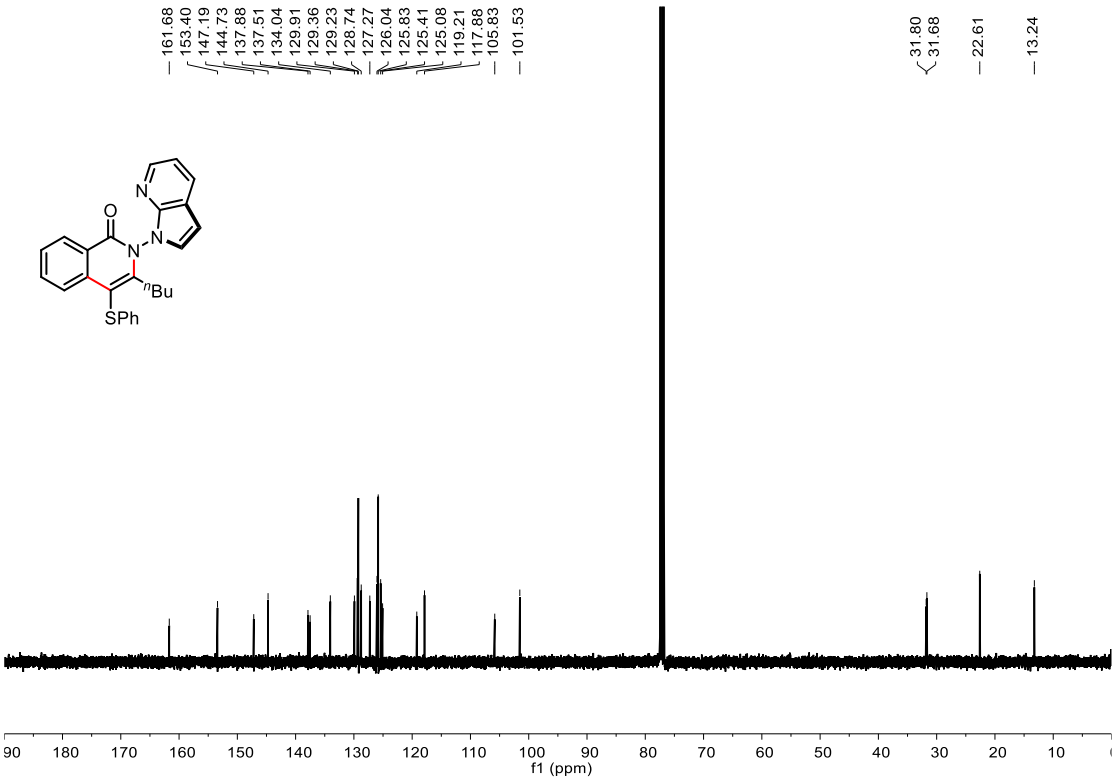
^{13}C NMR of **18** (100 MHz, $CDCl_3$)



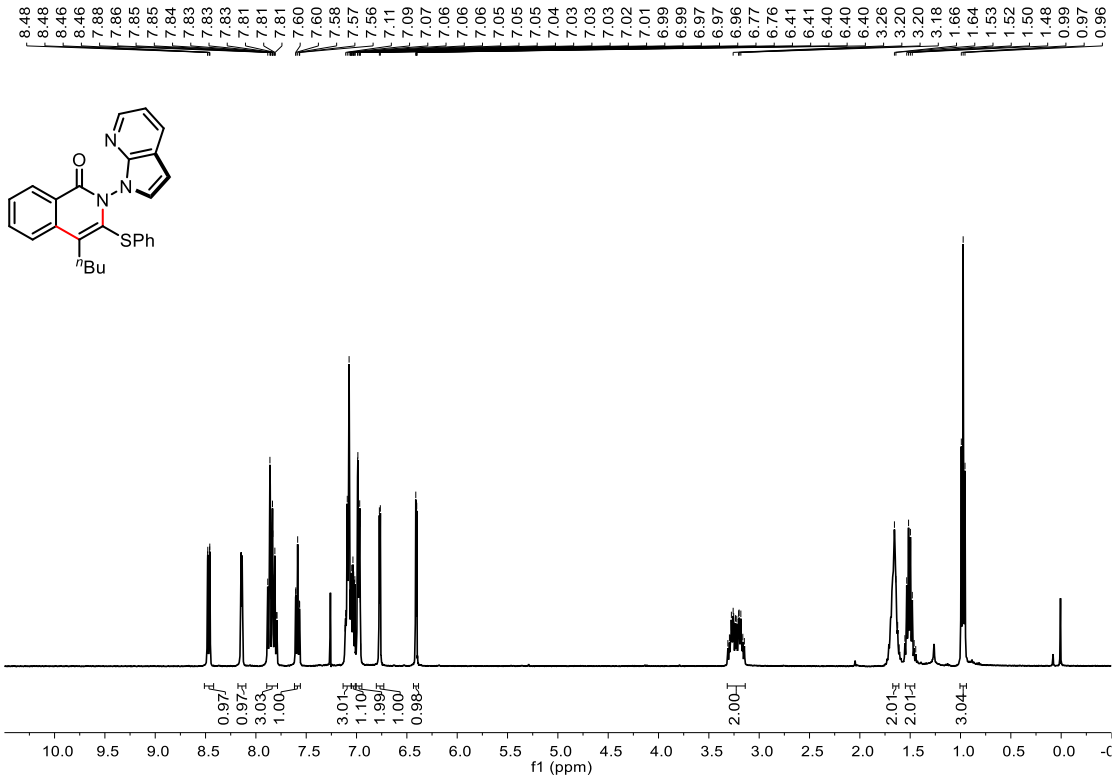
^{1}H NMR of **19** (400 MHz, $CDCl_3$)



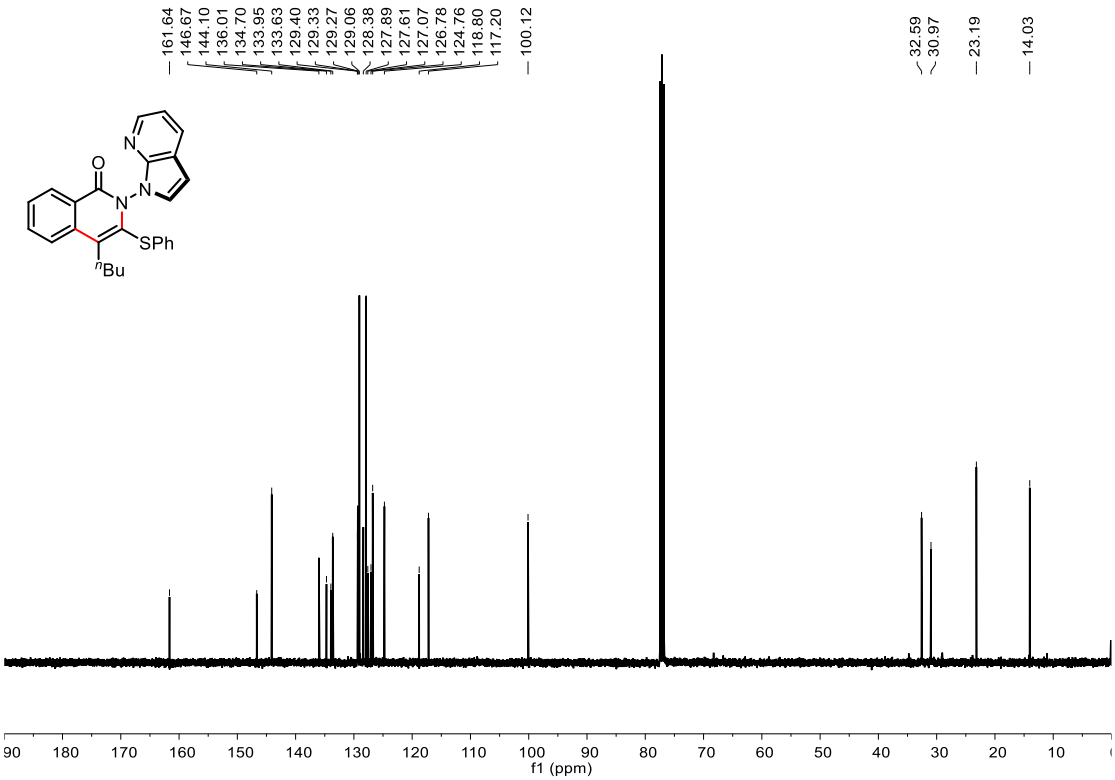
^{13}C NMR of **19** (100 MHz, $CDCl_3$)



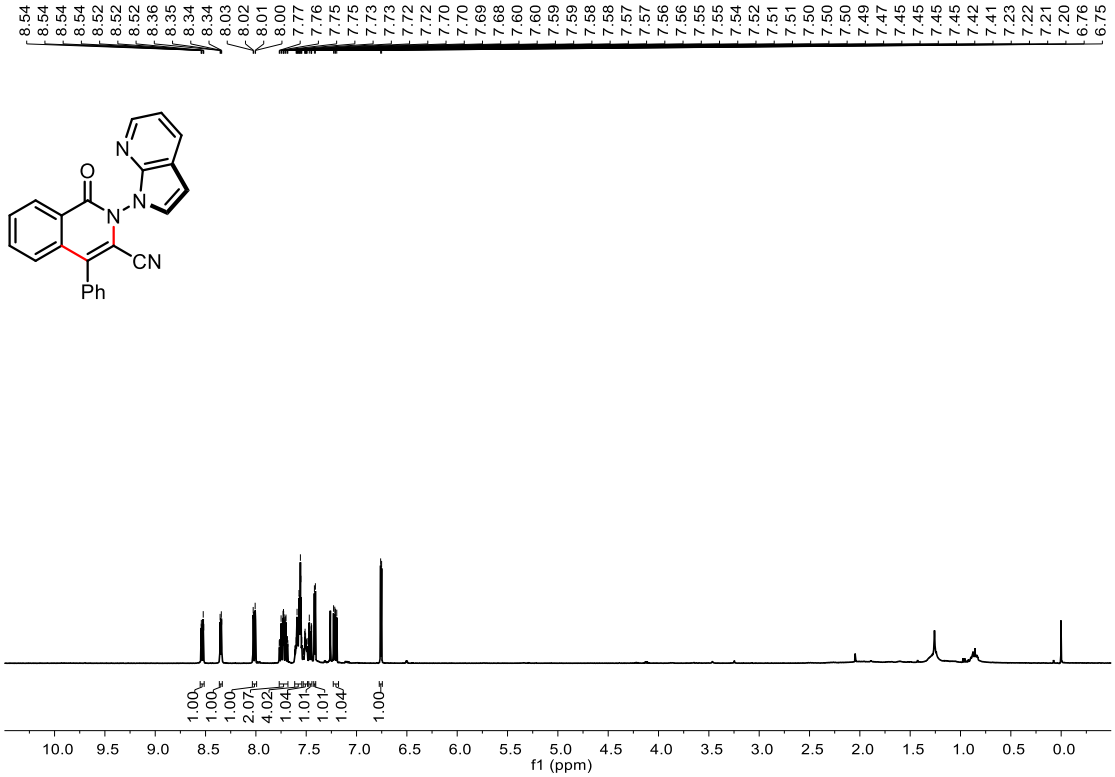
^{1}H NMR of **19'** (400 MHz, $CDCl_3$)



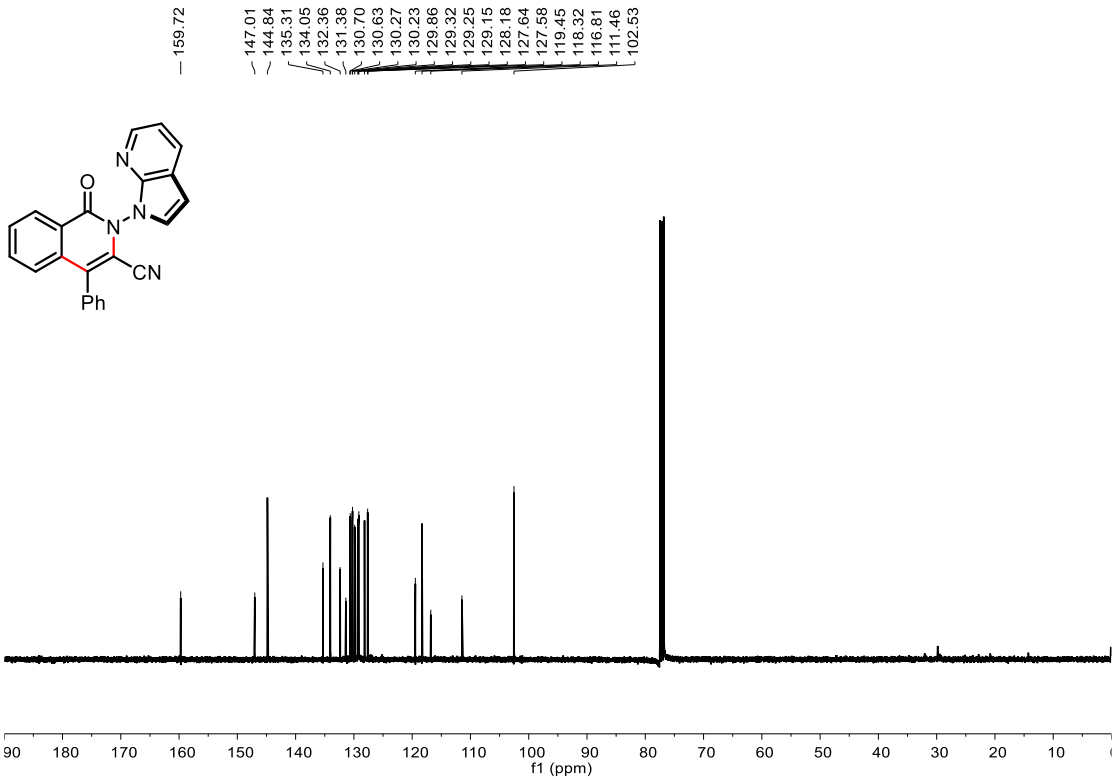
^{13}C NMR of **19'** (100 MHz, $CDCl_3$)



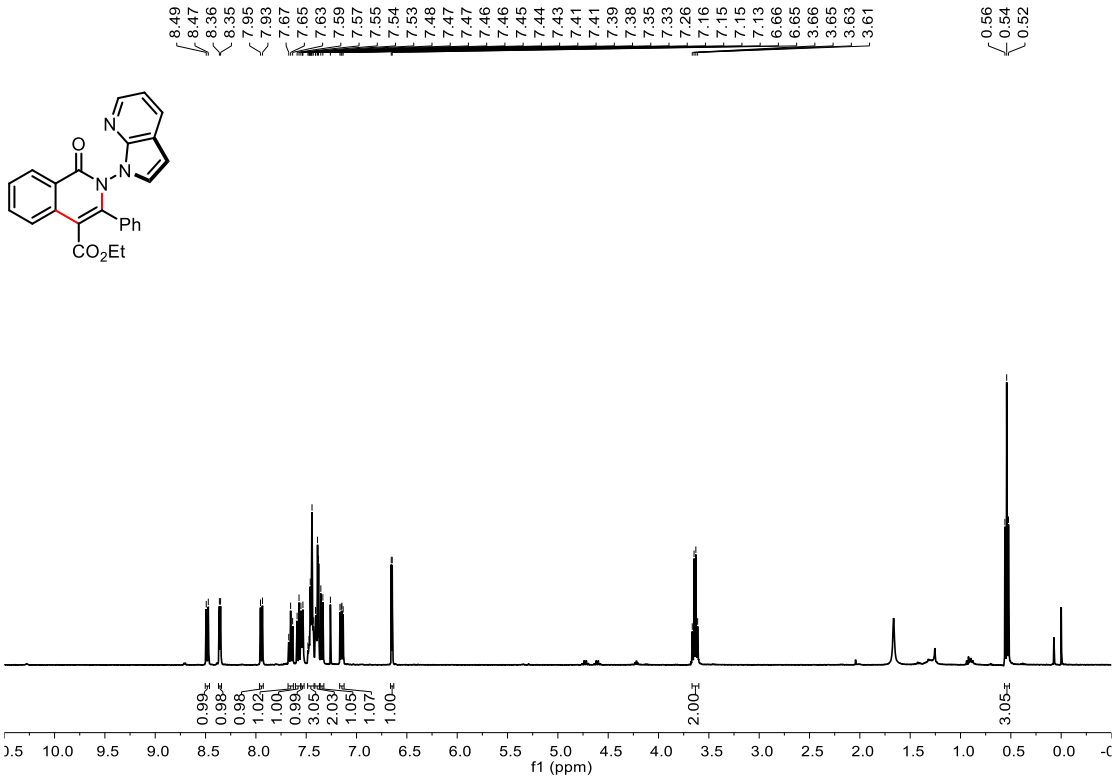
^{1}H NMR of **20** (400 MHz, $CDCl_3$)



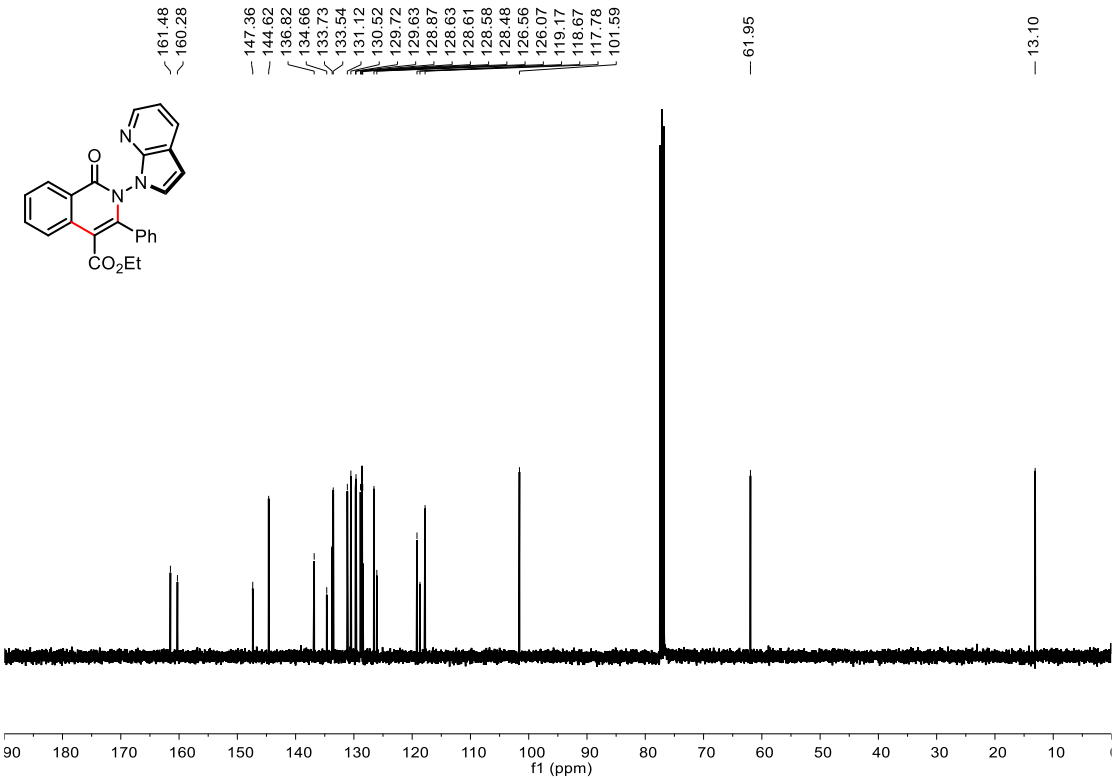
^{13}C NMR of **20** (100 MHz, $CDCl_3$)



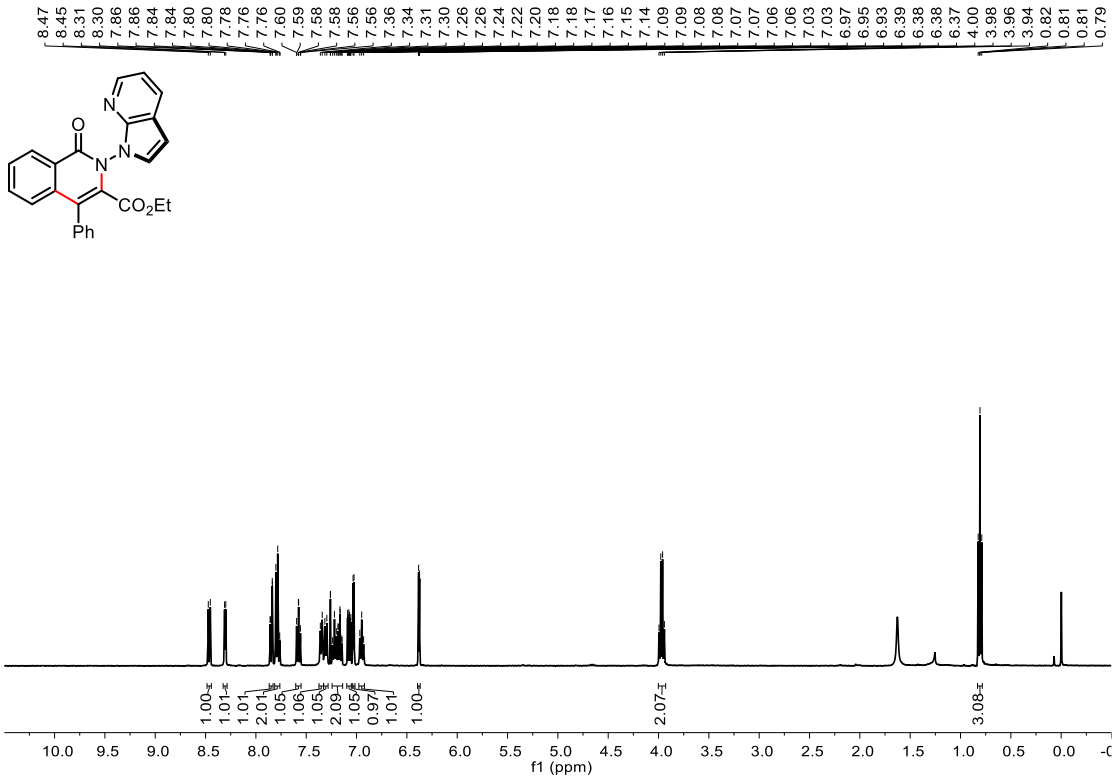
^{1}H NMR of **21** (400 MHz, $CDCl_3$)



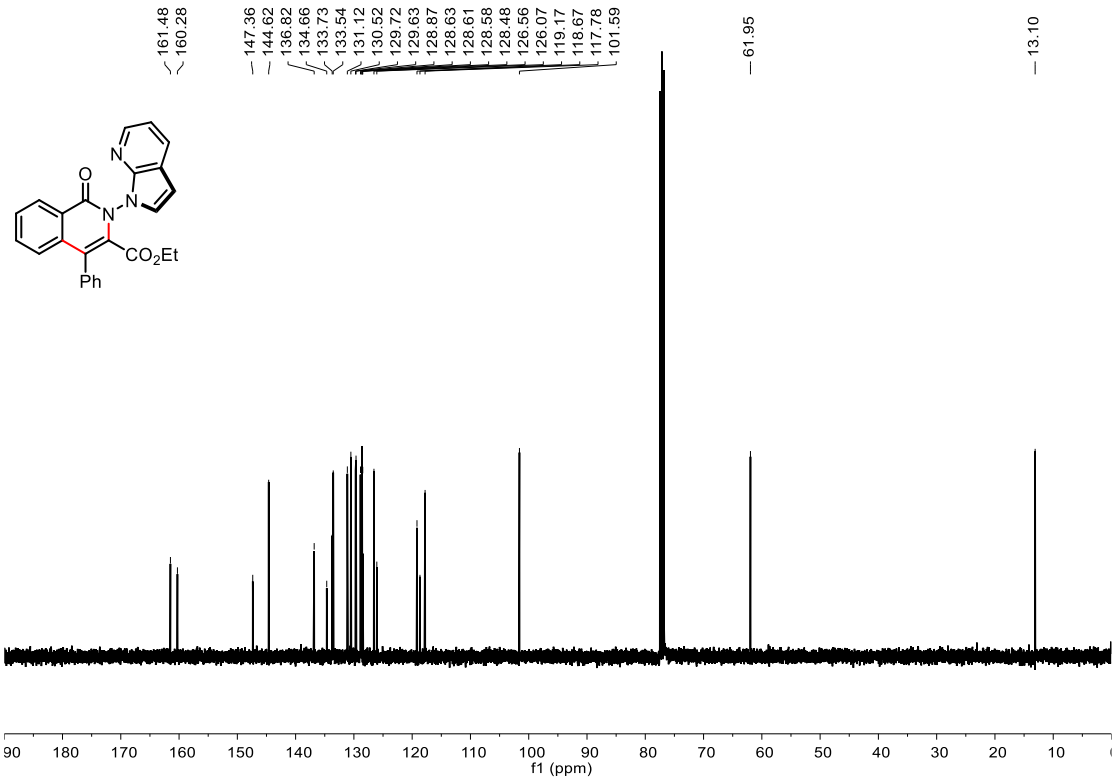
^{13}C NMR of **21** (400 MHz, $CDCl_3$)



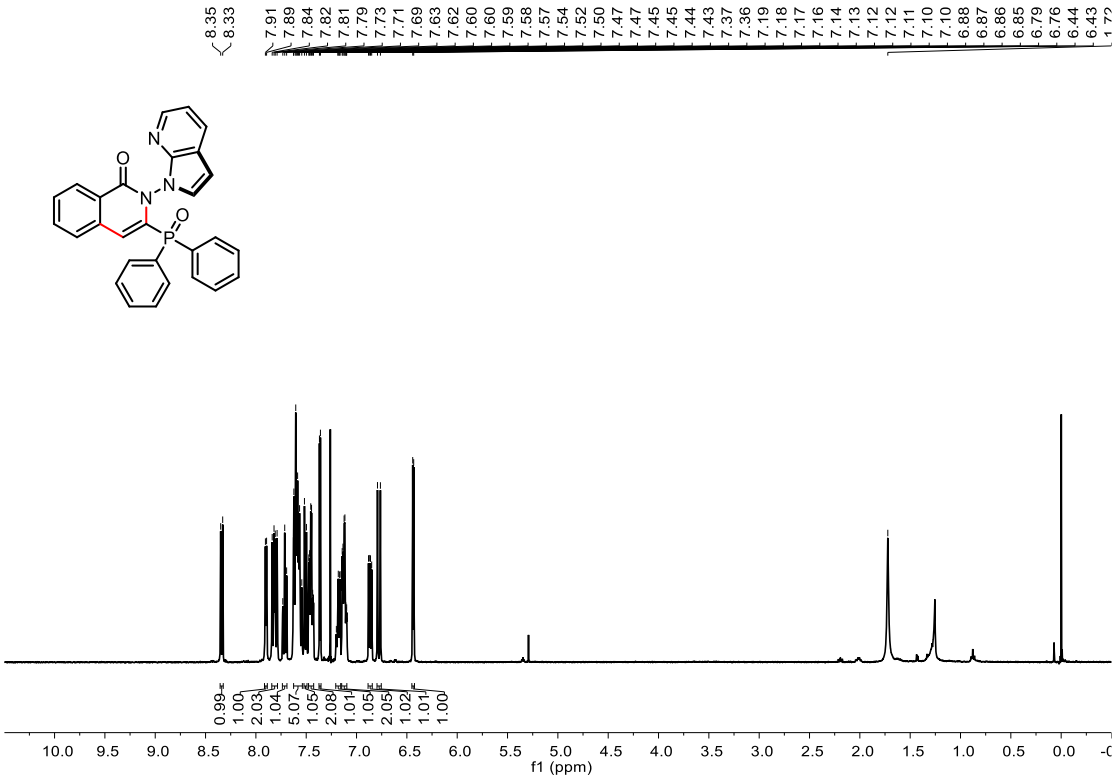
^{1}H NMR of **21'** (400 MHz, $CDCl_3$)



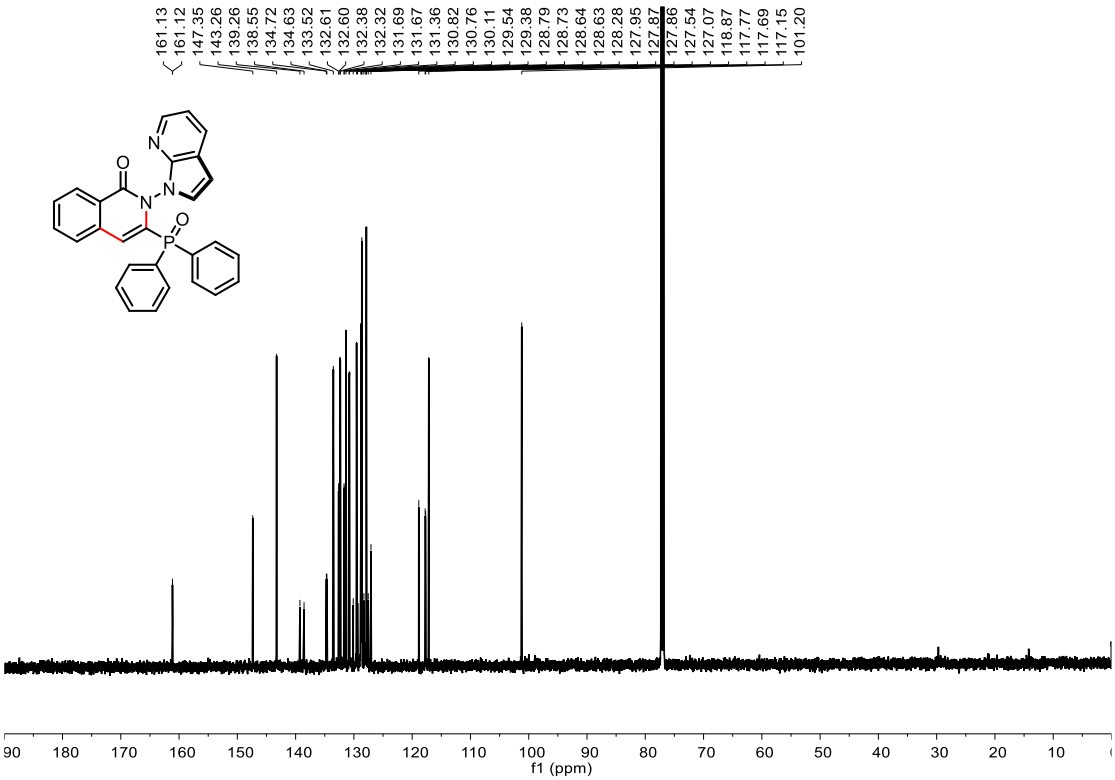
^{13}C NMR of **21'** (100 MHz, $CDCl_3$)



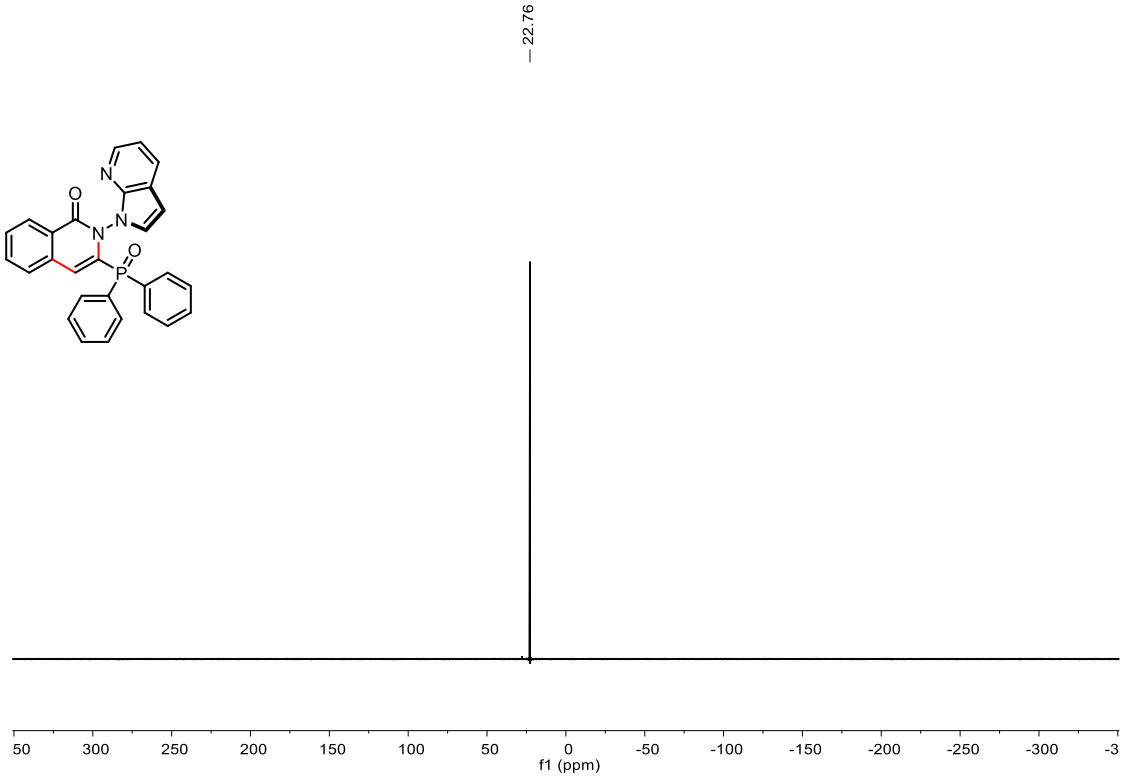
^{1}H NMR of **22** (400 MHz, $CDCl_3$)



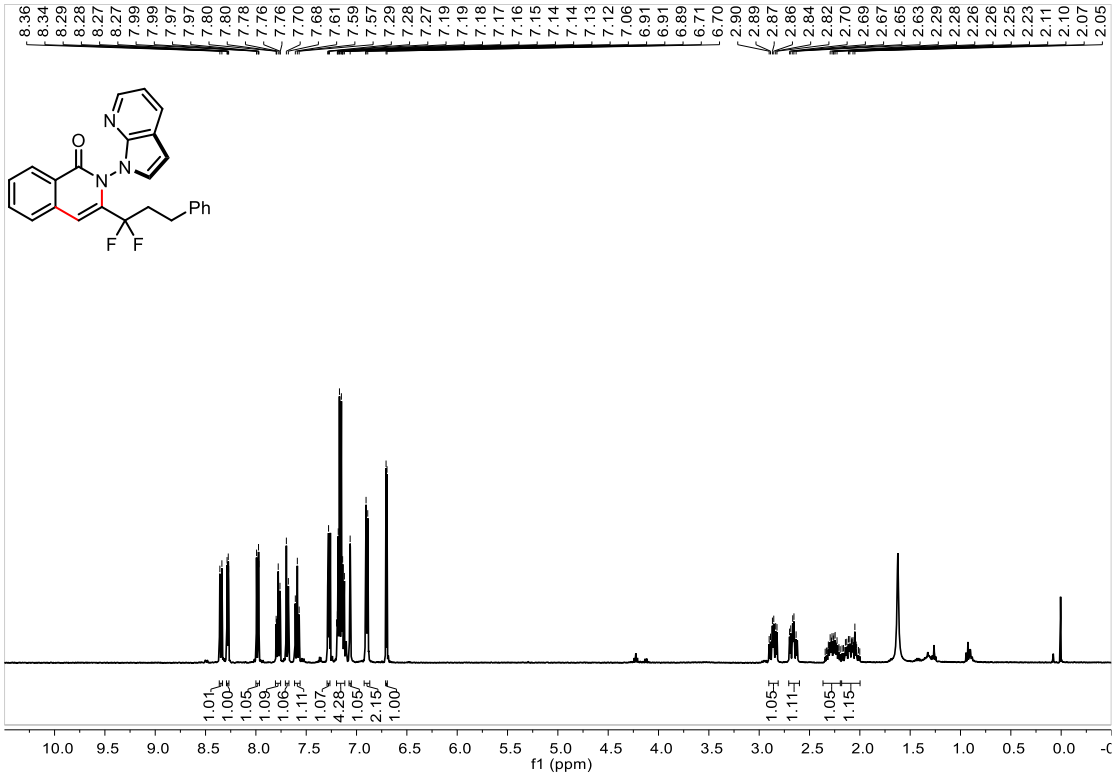
^{13}C NMR of **22** (100 MHz, $CDCl_3$)



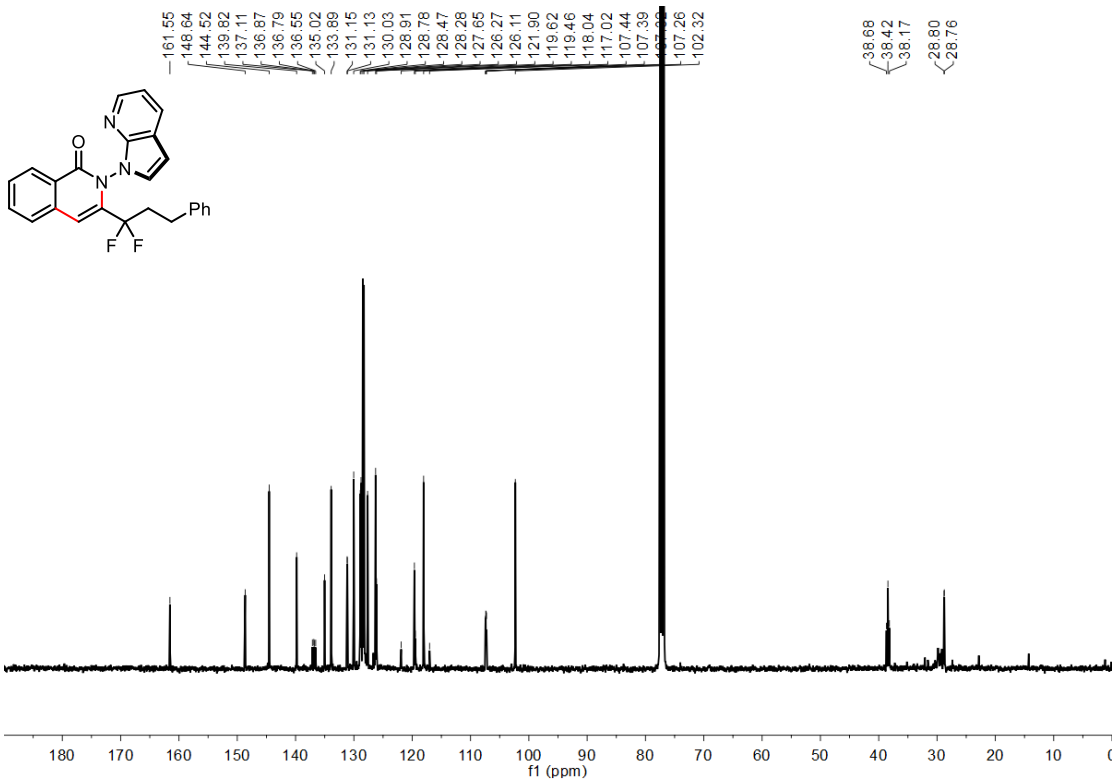
^{31}P NMR of **22** (162 MHz, $CDCl_3$)



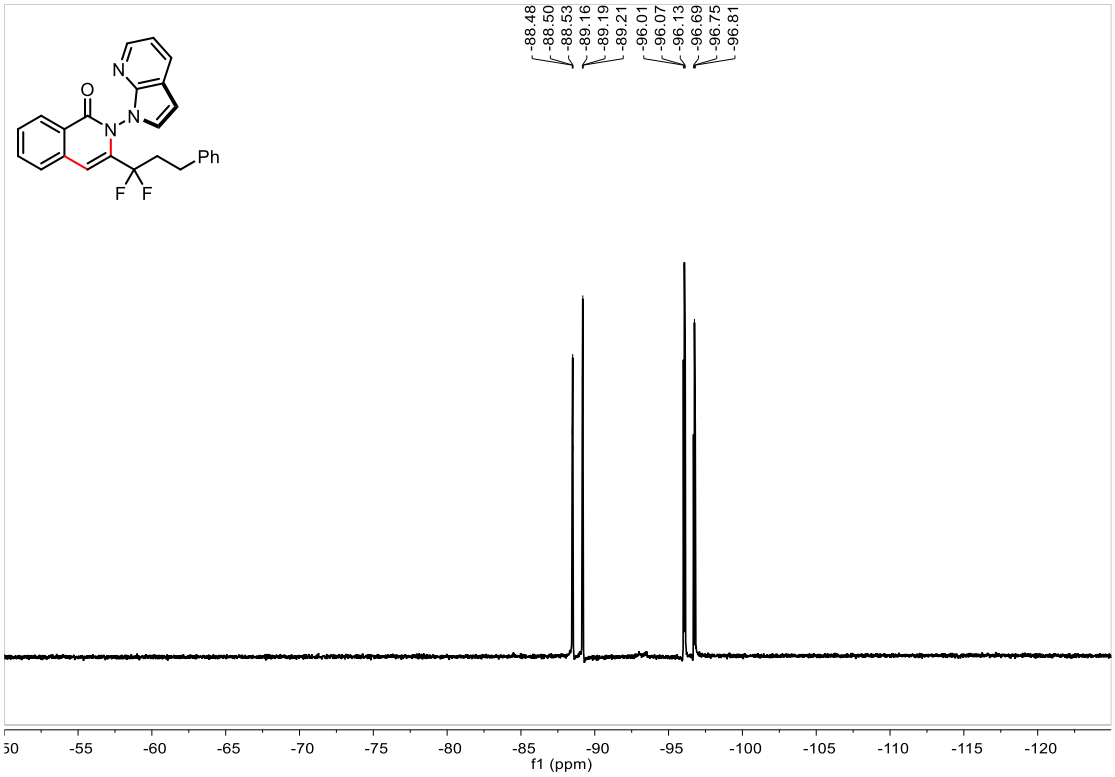
^{1}H NMR of **23** (400 MHz, $CDCl_3$)



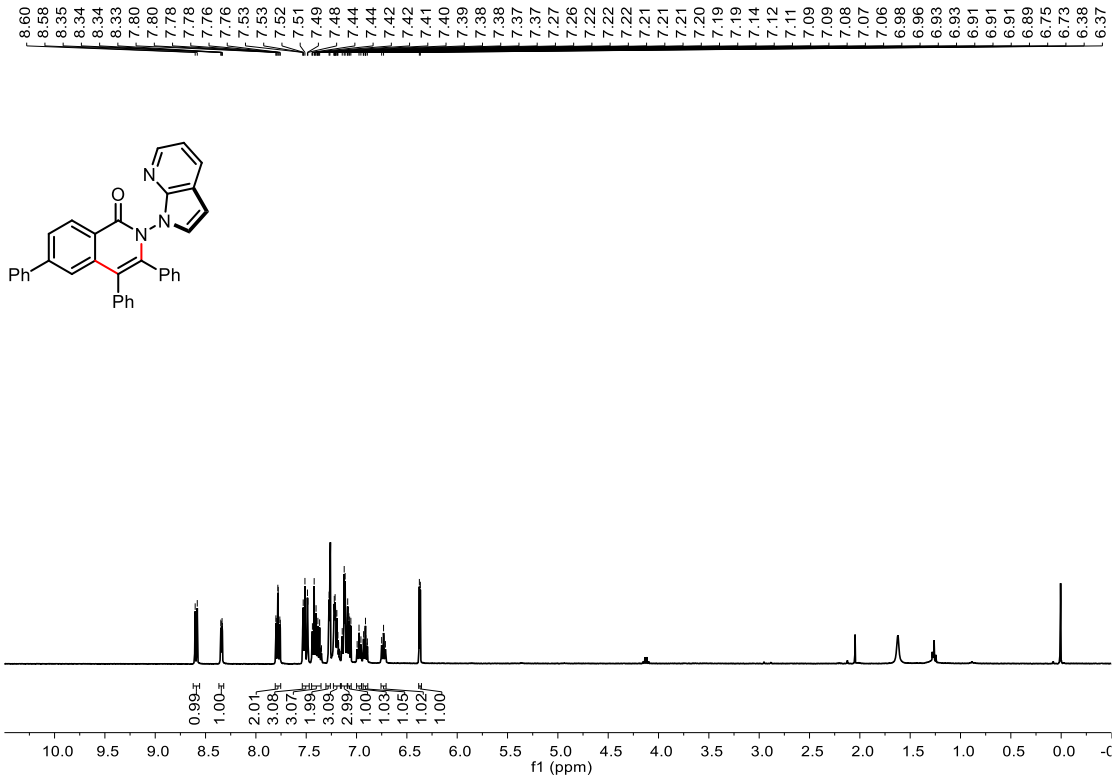
^{13}C NMR of **23** (100 MHz, $CDCl_3$)



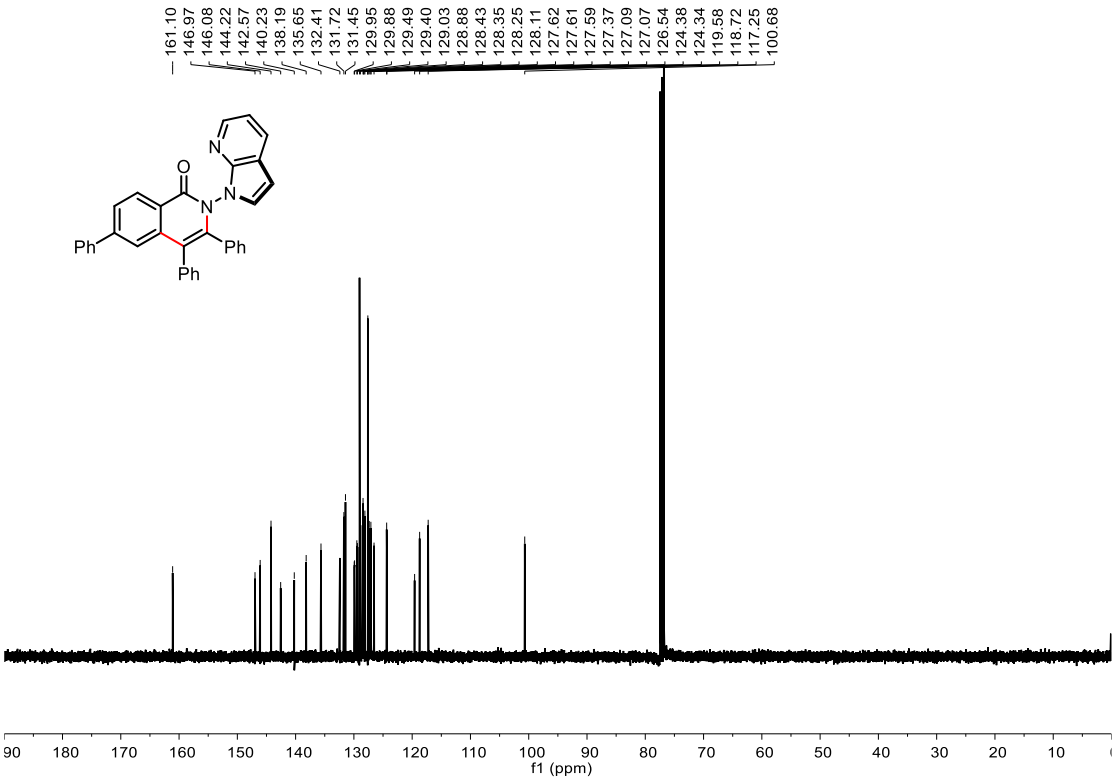
^{19}F NMR of **23** (376 MHz, $CDCl_3$)



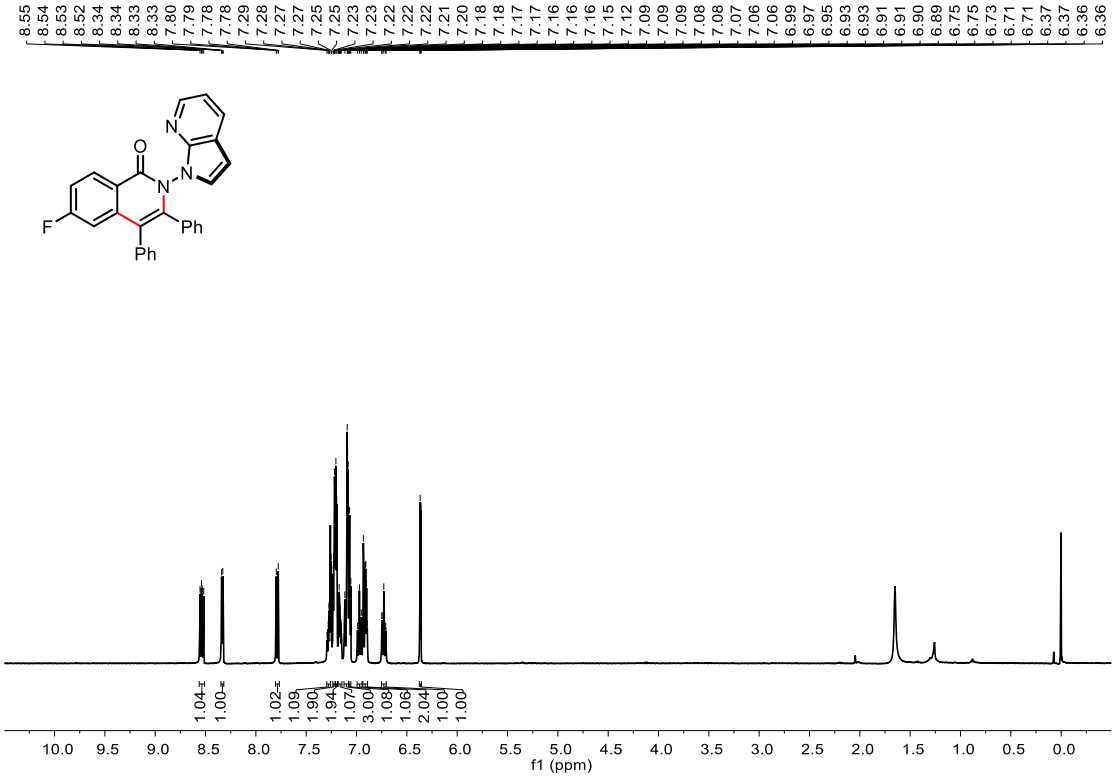
^{1}H NMR of **24** (400 MHz, $CDCl_3$)



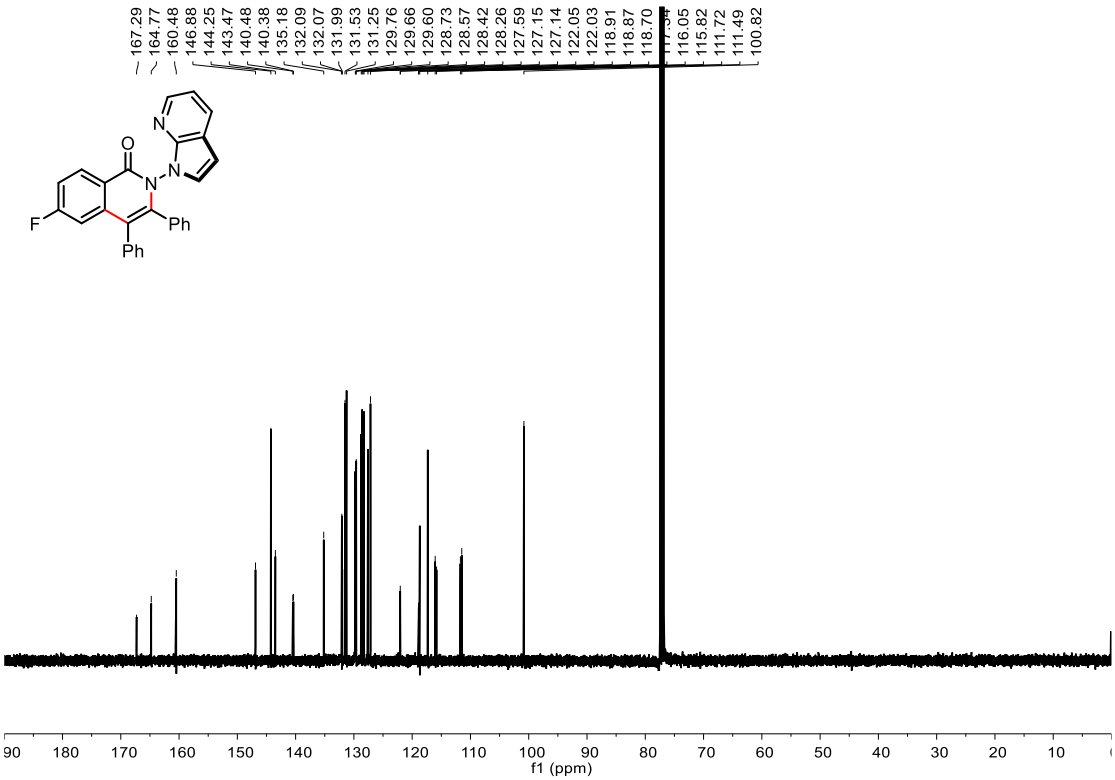
^{13}C NMR of **24** (100 MHz, $CDCl_3$)



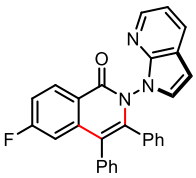
^{1}H NMR of **25** (400 MHz, $CDCl_3$)



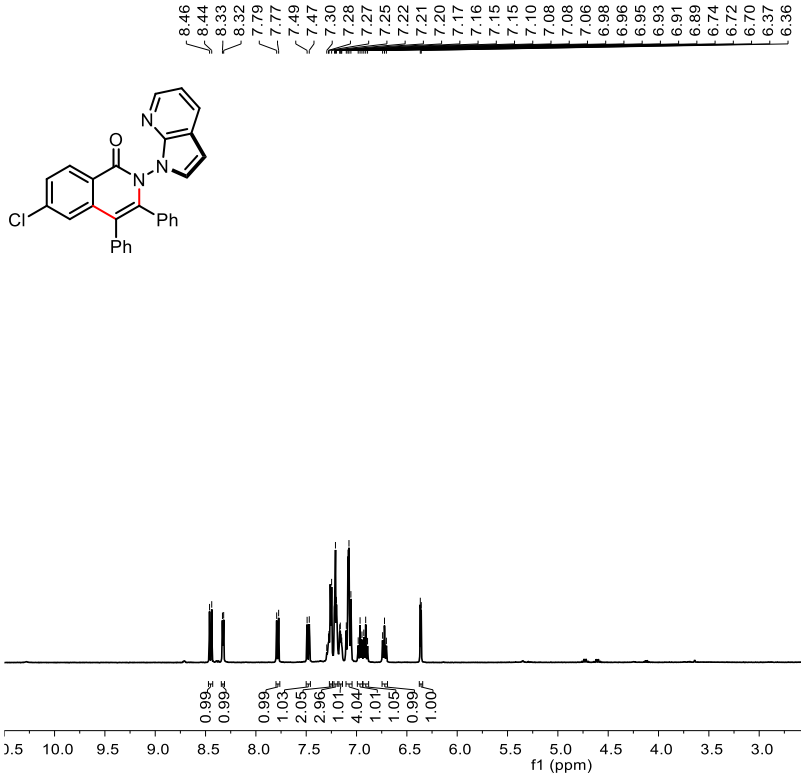
^{13}C NMR of **25** (100 MHz, $CDCl_3$)



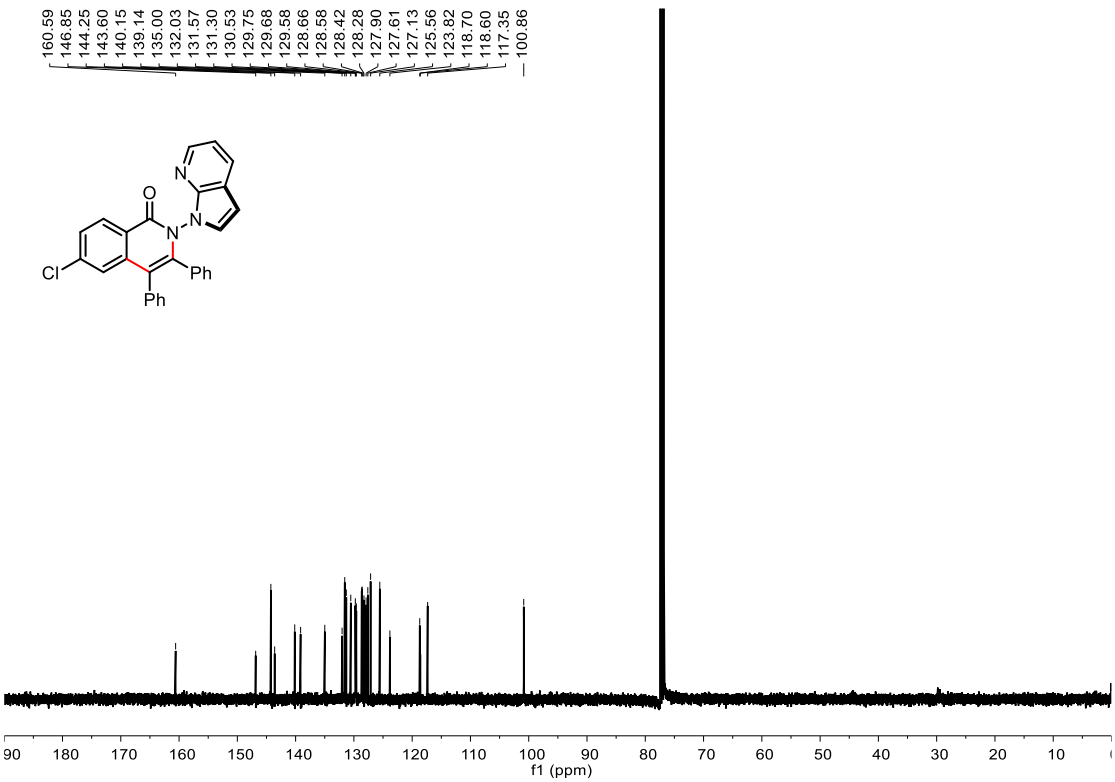
^{19}F NMR of **25** (376 MHz, $CDCl_3$)



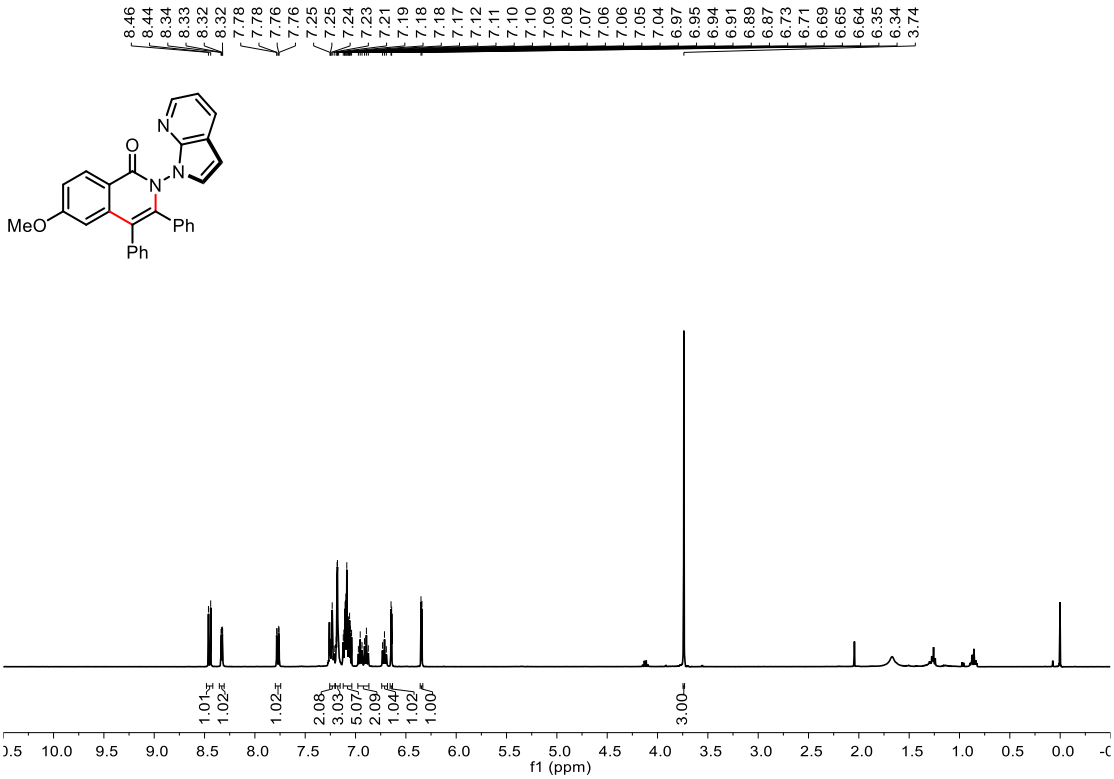
^{1}H NMR of **26** (400 MHz, $CDCl_3$)



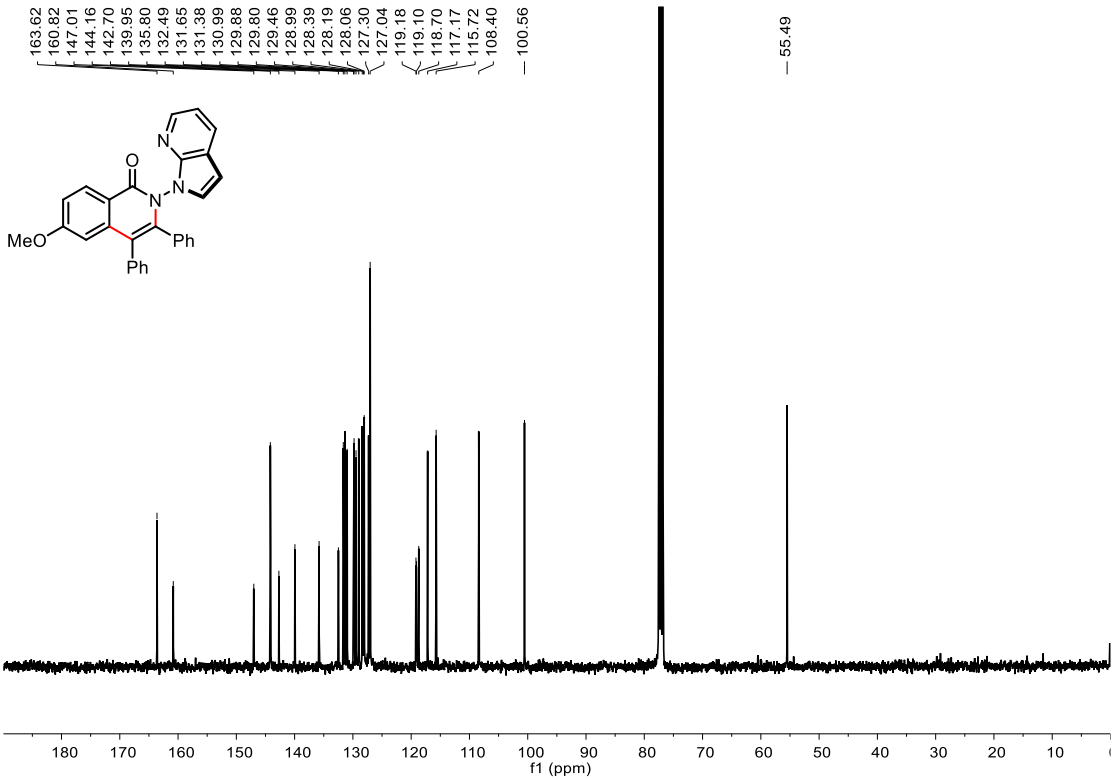
^{13}C NMR of **26** (100 MHz, $CDCl_3$)



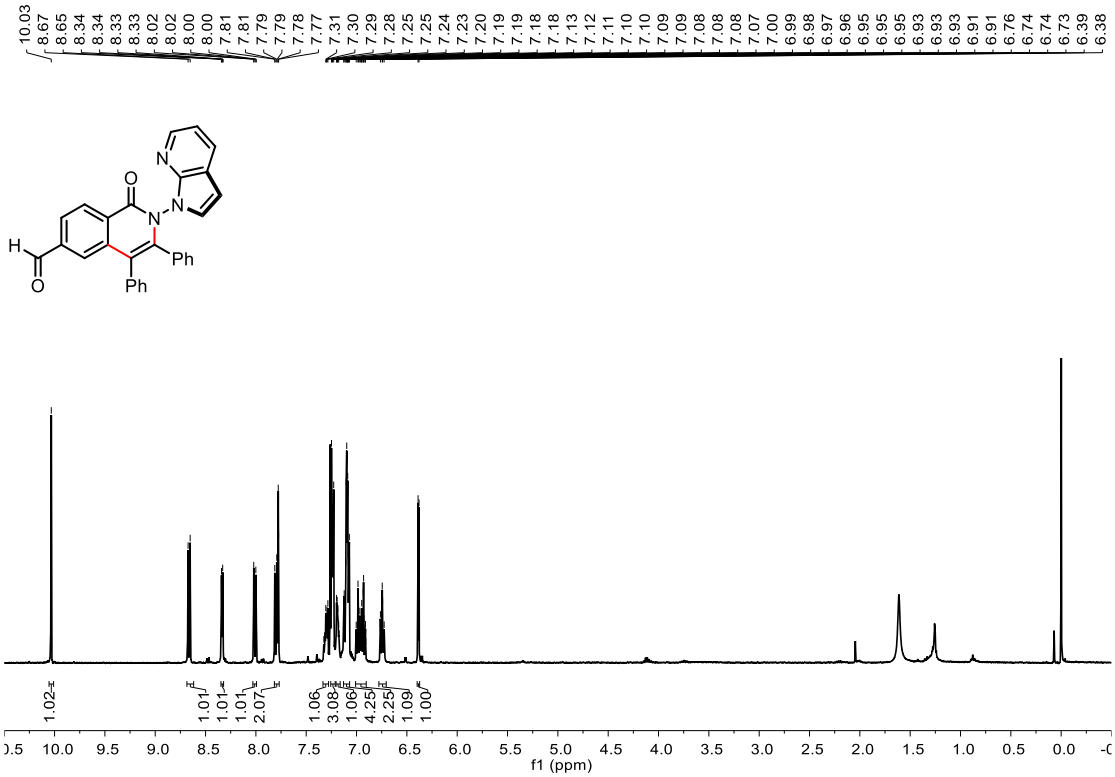
^{1}H NMR of **27** (400 MHz, $CDCl_3$)



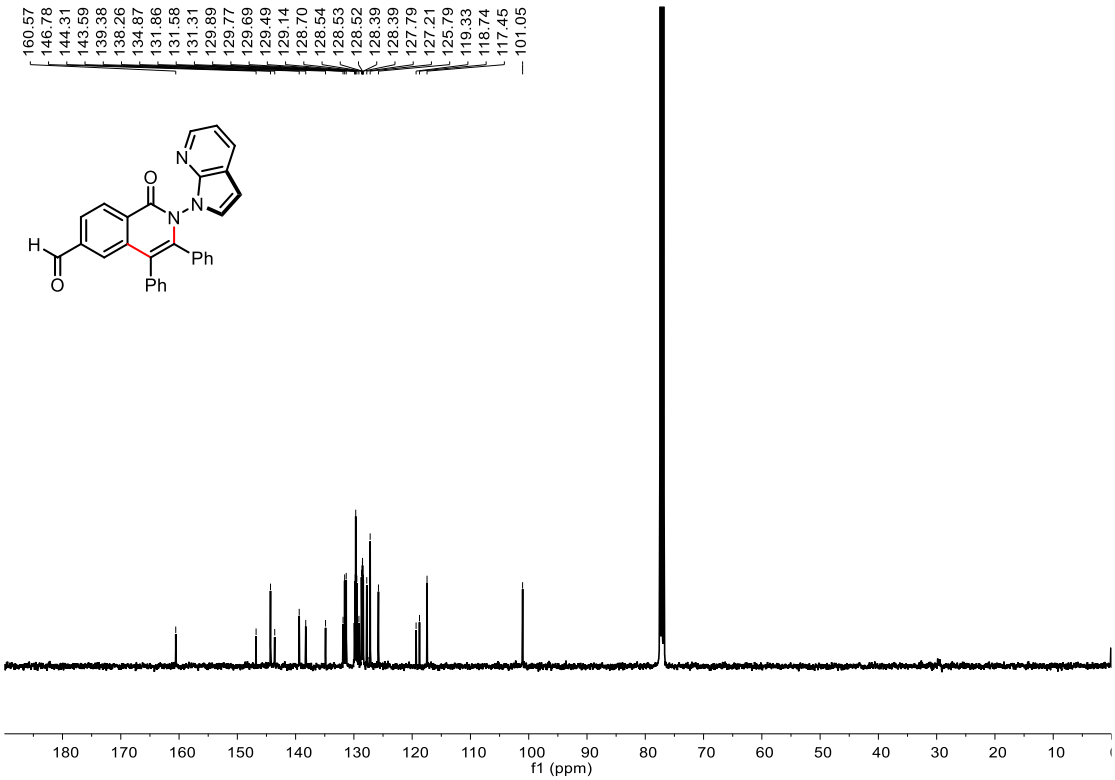
^{13}C NMR of **27** (100 MHz, $CDCl_3$)



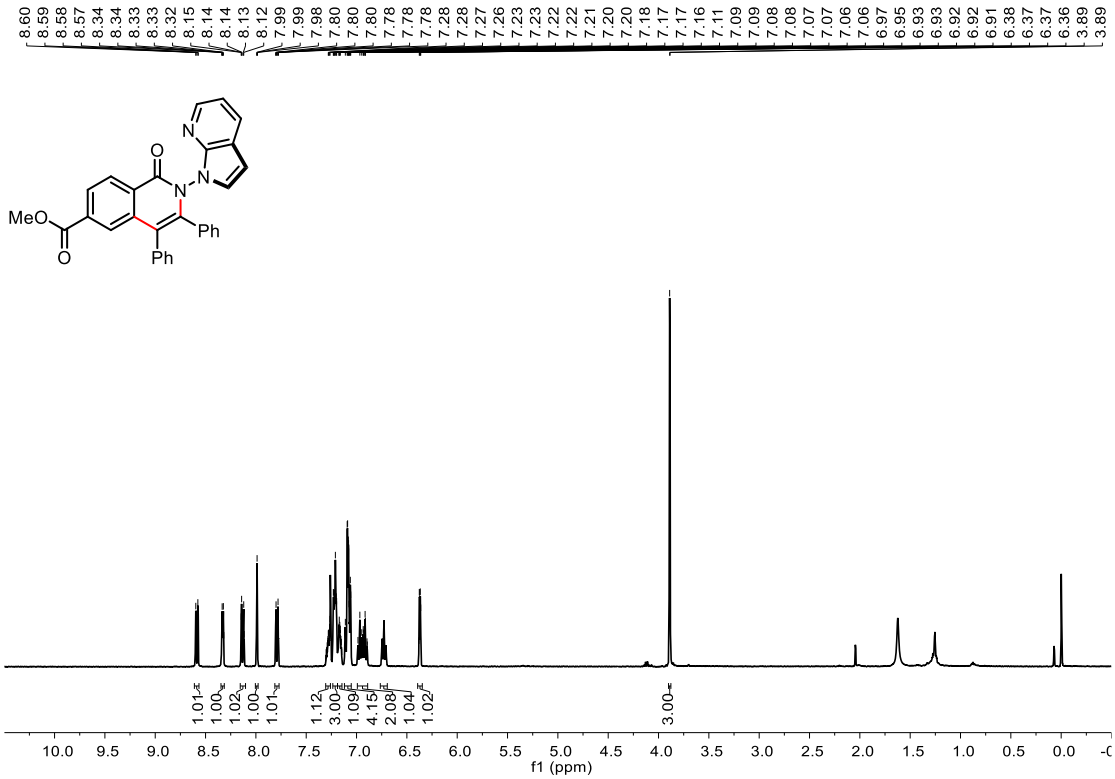
^{1}H NMR of **28** (400 MHz, $CDCl_3$)



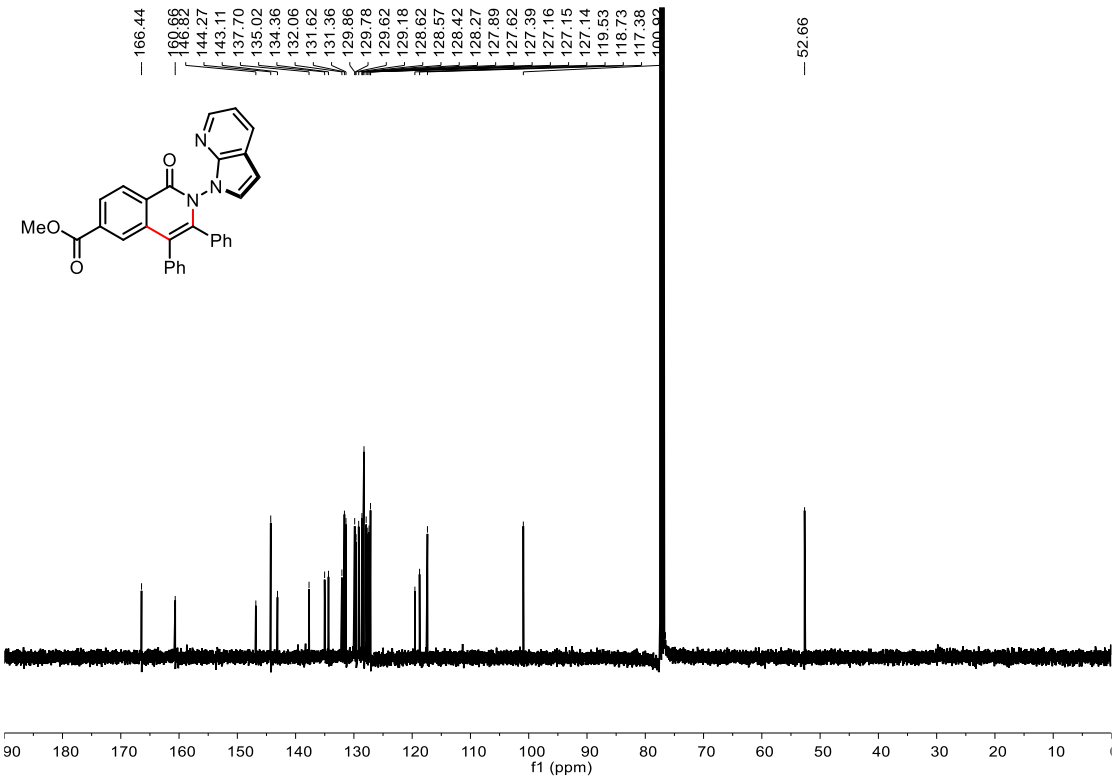
^{13}C NMR of **28** (100 MHz, $CDCl_3$)



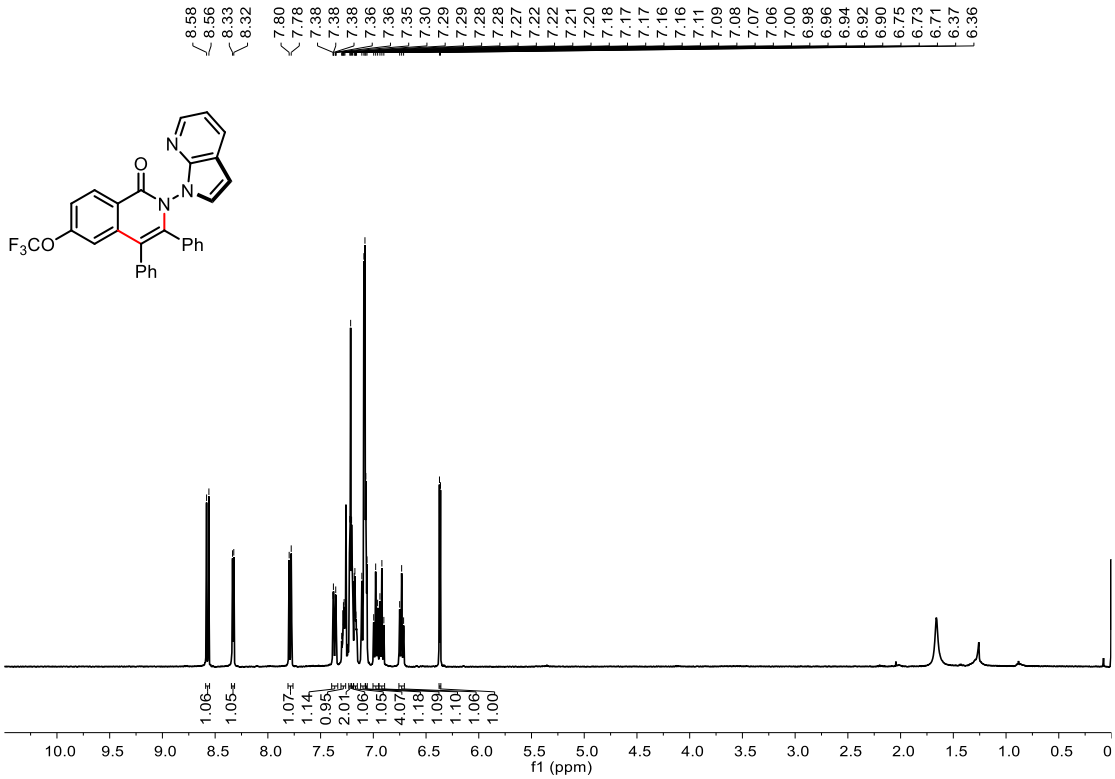
^{1}H NMR of **29** (400 MHz, $CDCl_3$)



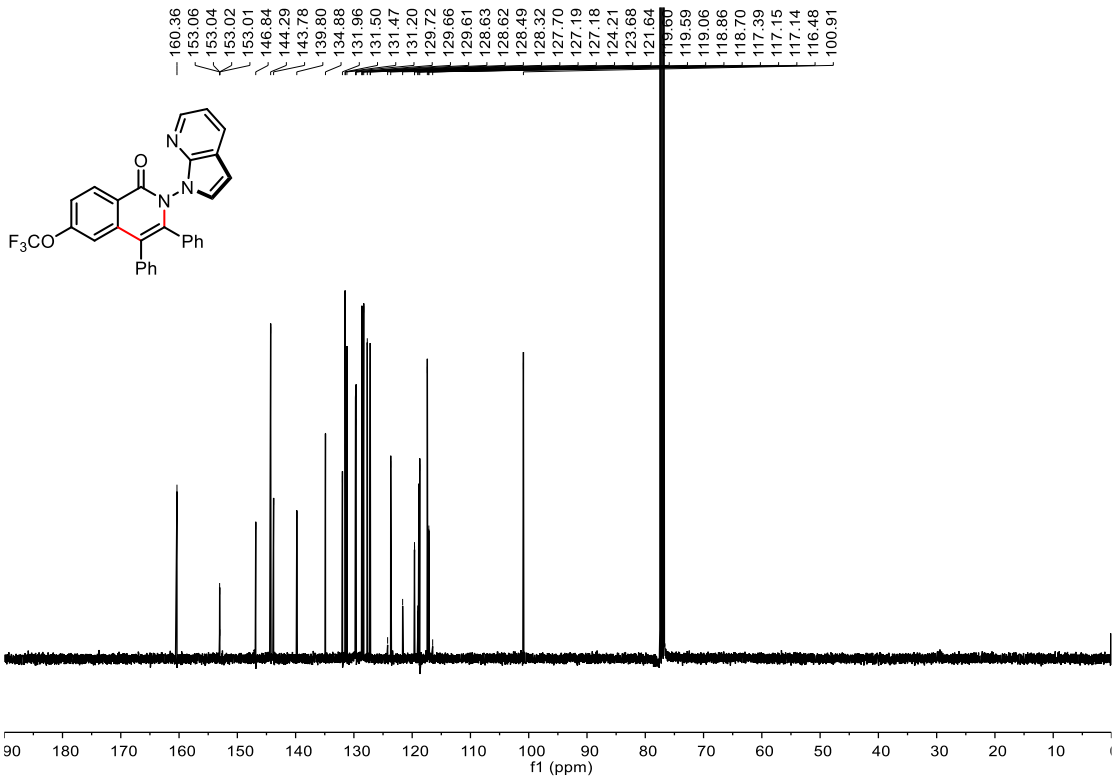
^{13}C NMR of **29** (100 MHz, $CDCl_3$)



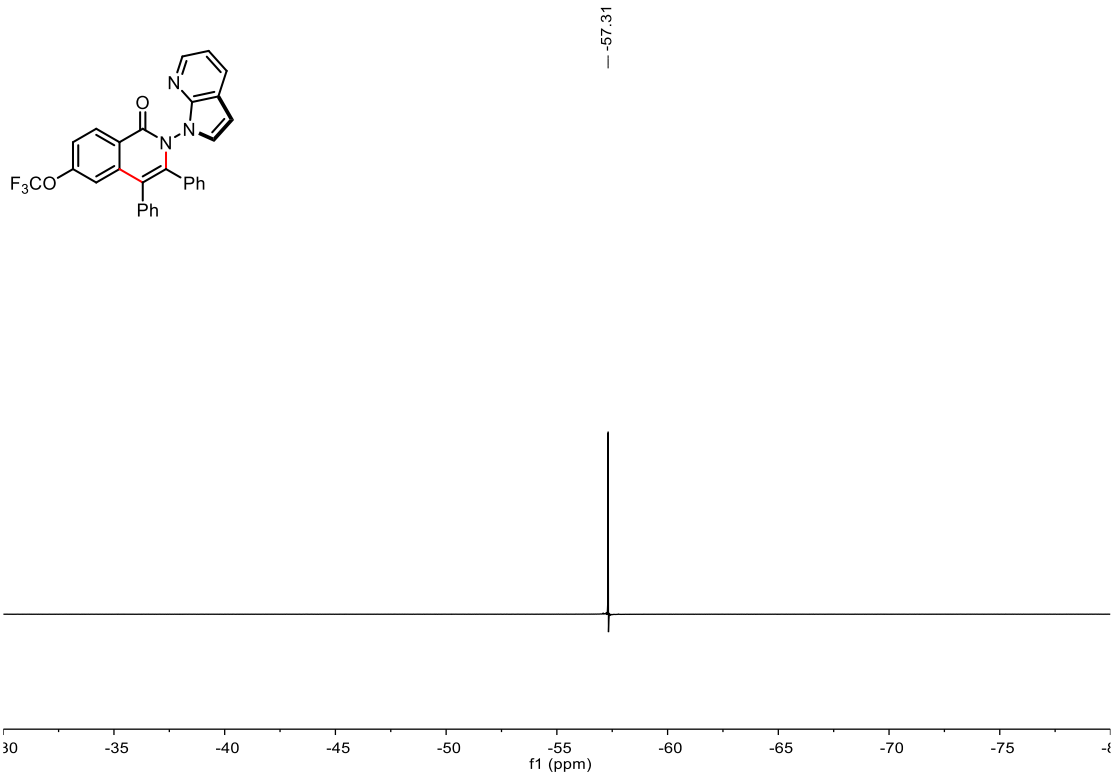
^{1}H NMR of **30** (400 MHz, $CDCl_3$)



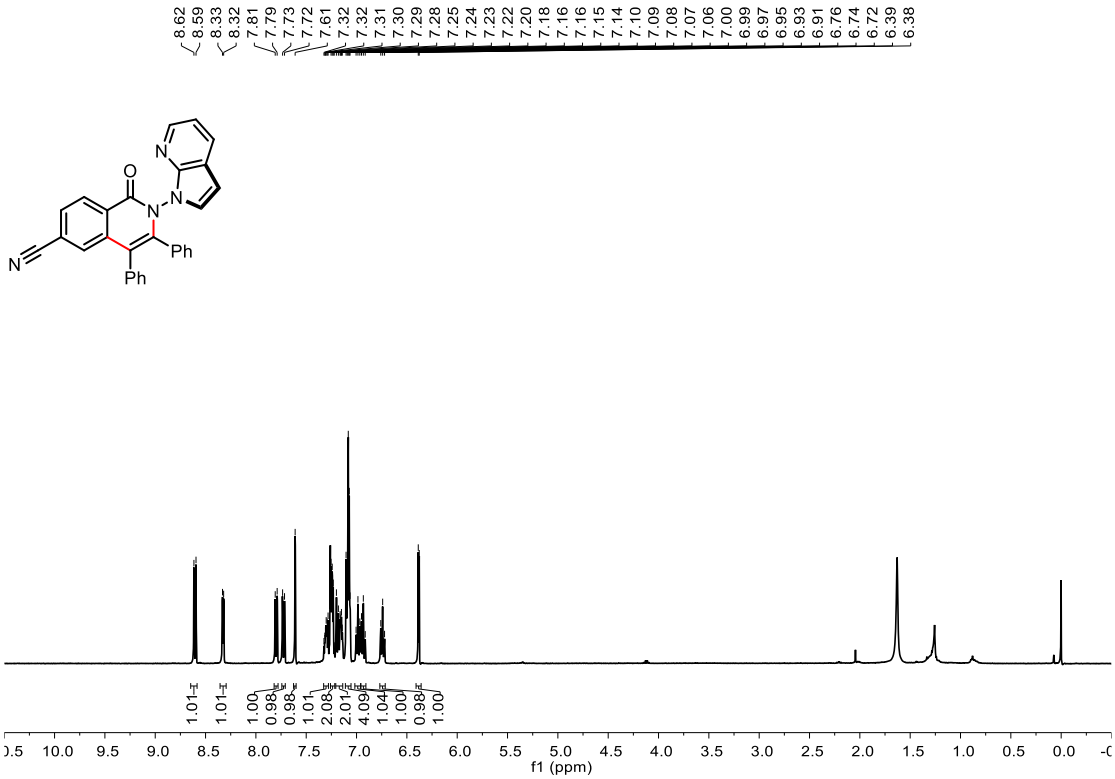
^{13}C NMR of **30** (100 MHz, $CDCl_3$)



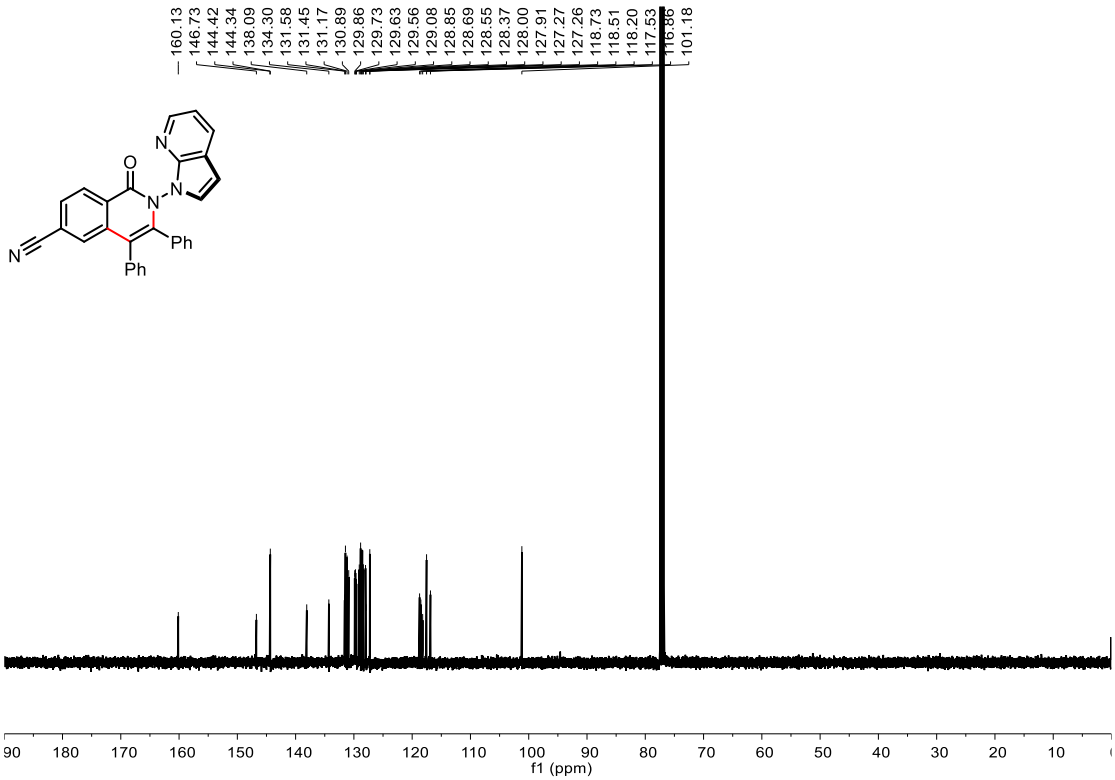
^{19}F NMR of **30** (376 MHz, $CDCl_3$)



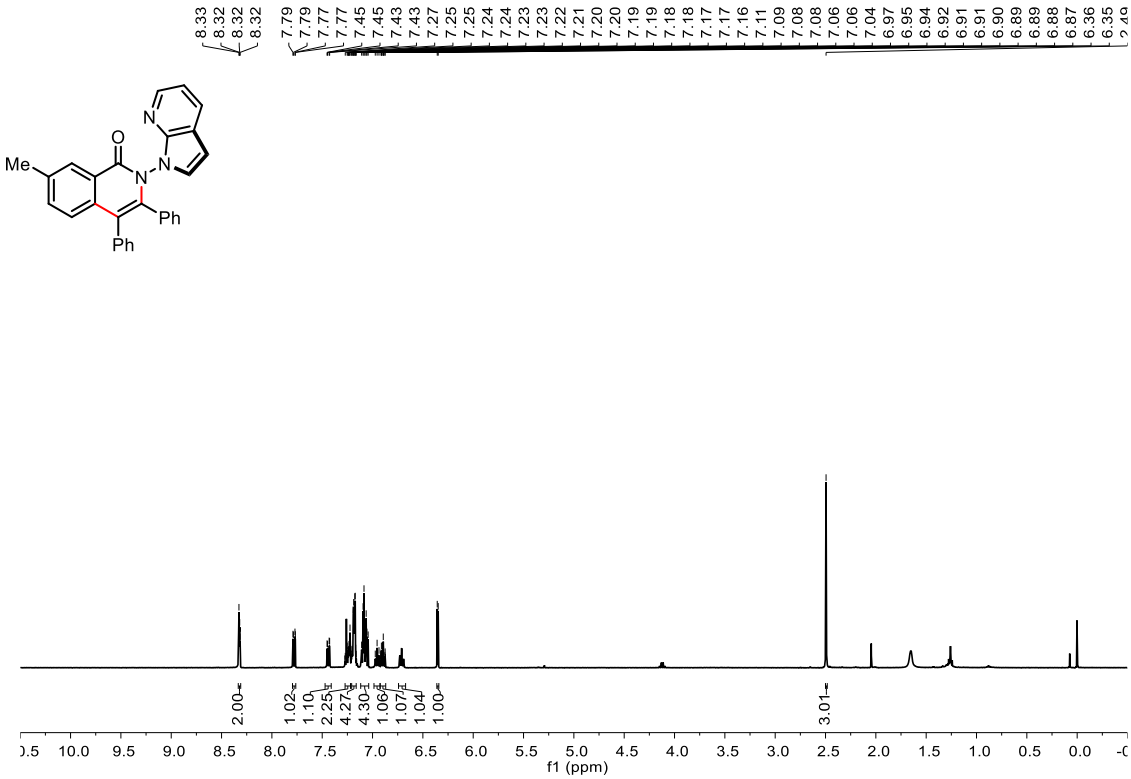
^{1}H NMR of **31**(400 MHz, $CDCl_3$)



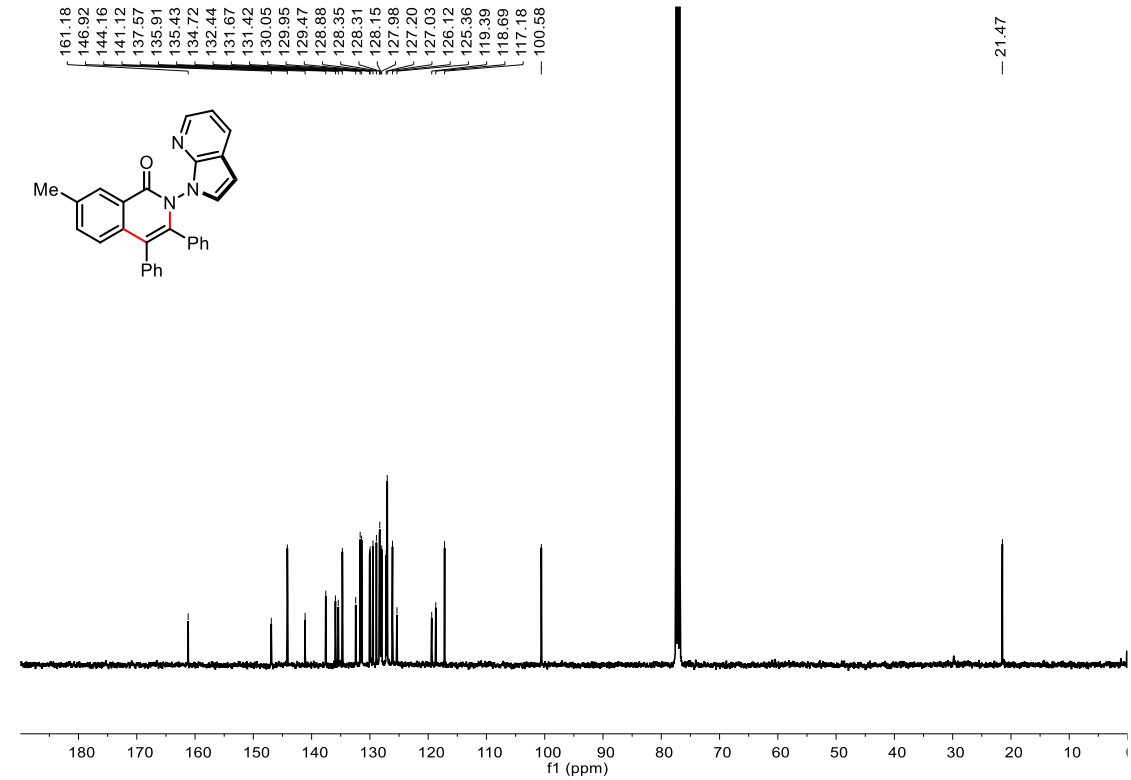
^{13}C NMR of **31** (100 MHz, $CDCl_3$)



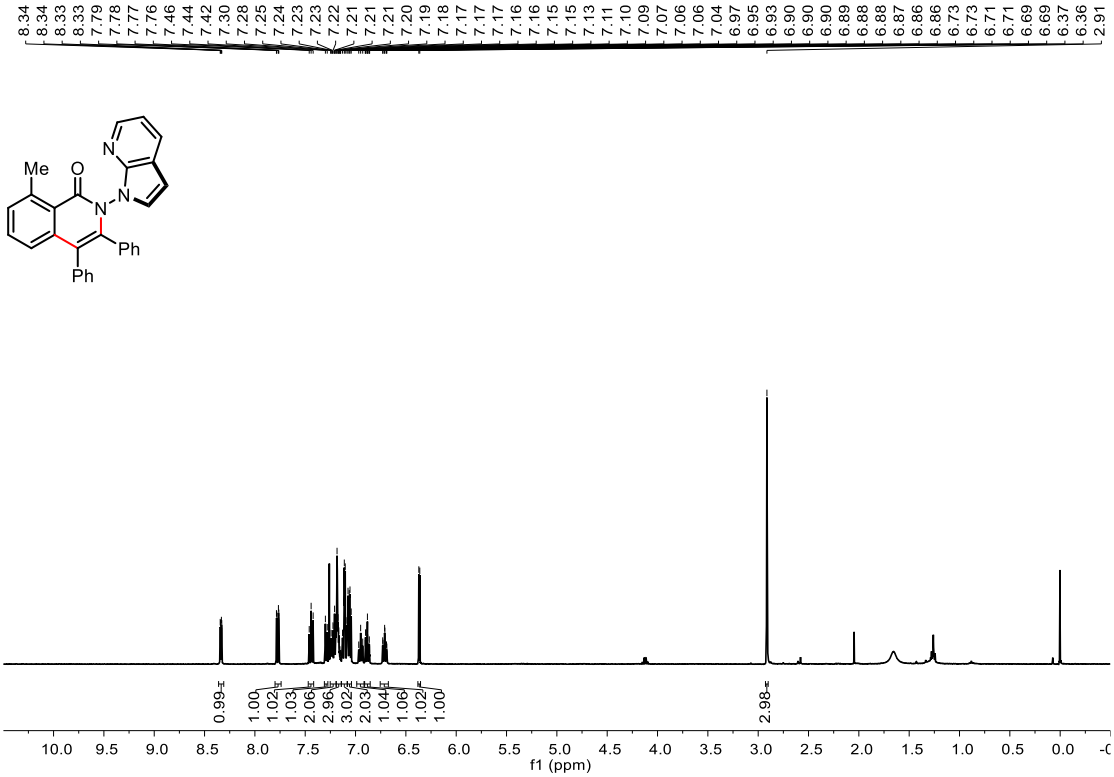
^{1}H NMR of **32**(400 MHz, $CDCl_3$)



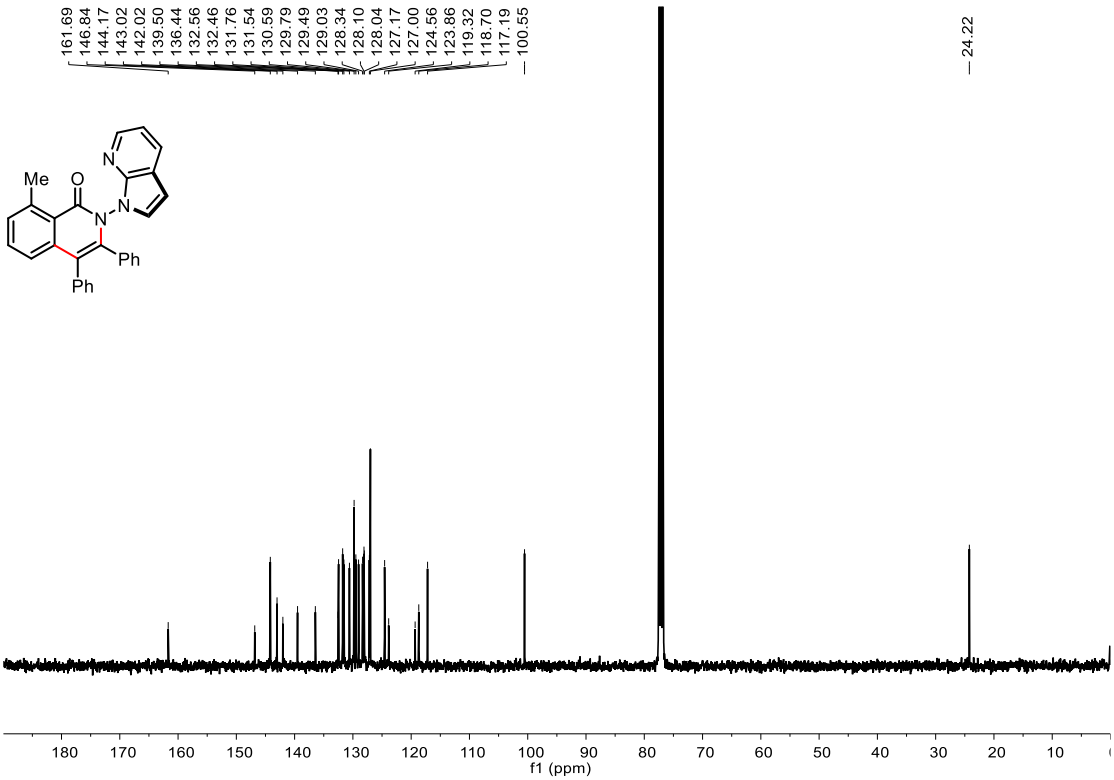
^{13}C NMR of **32** (100 MHz, $CDCl_3$)



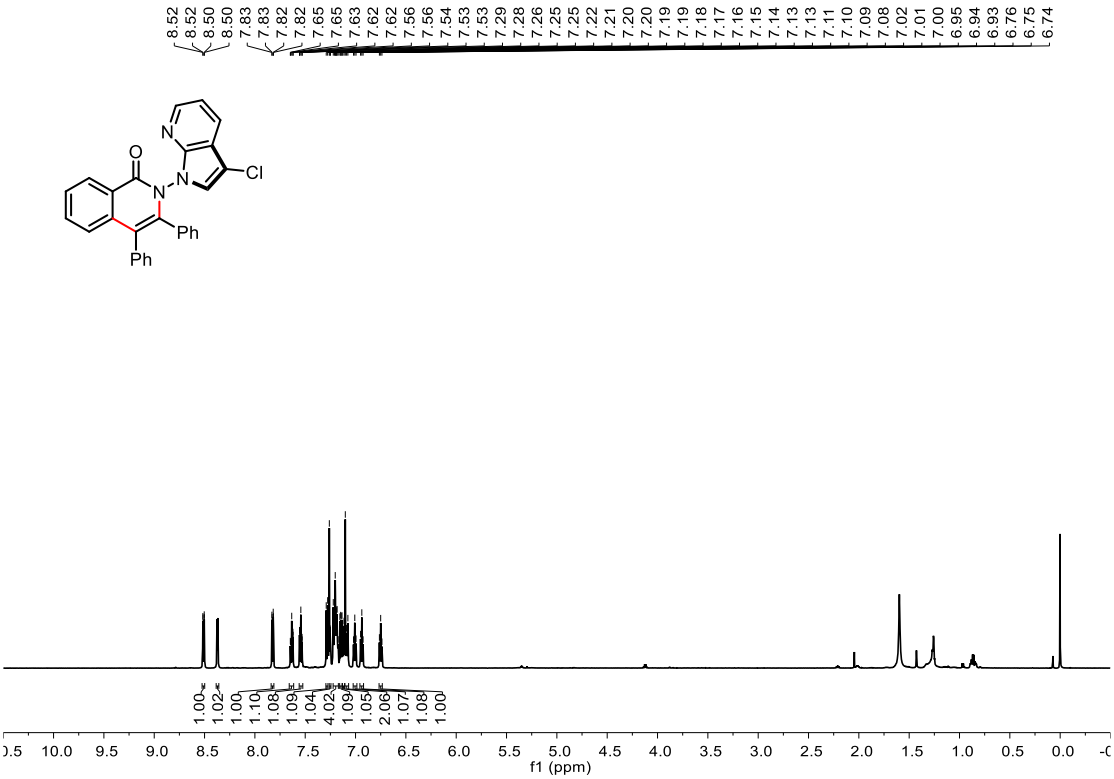
^{1}H NMR of **33** (400 MHz, $CDCl_3$)



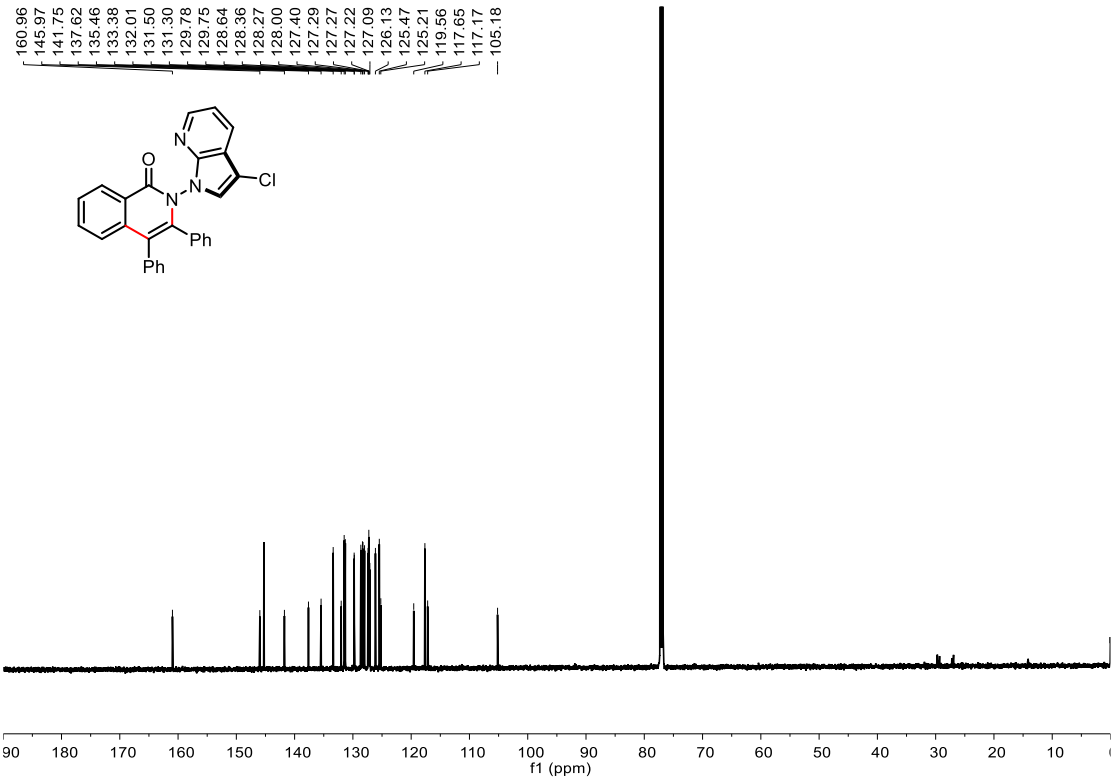
^{13}C NMR of **33** (100 MHz, $CDCl_3$)



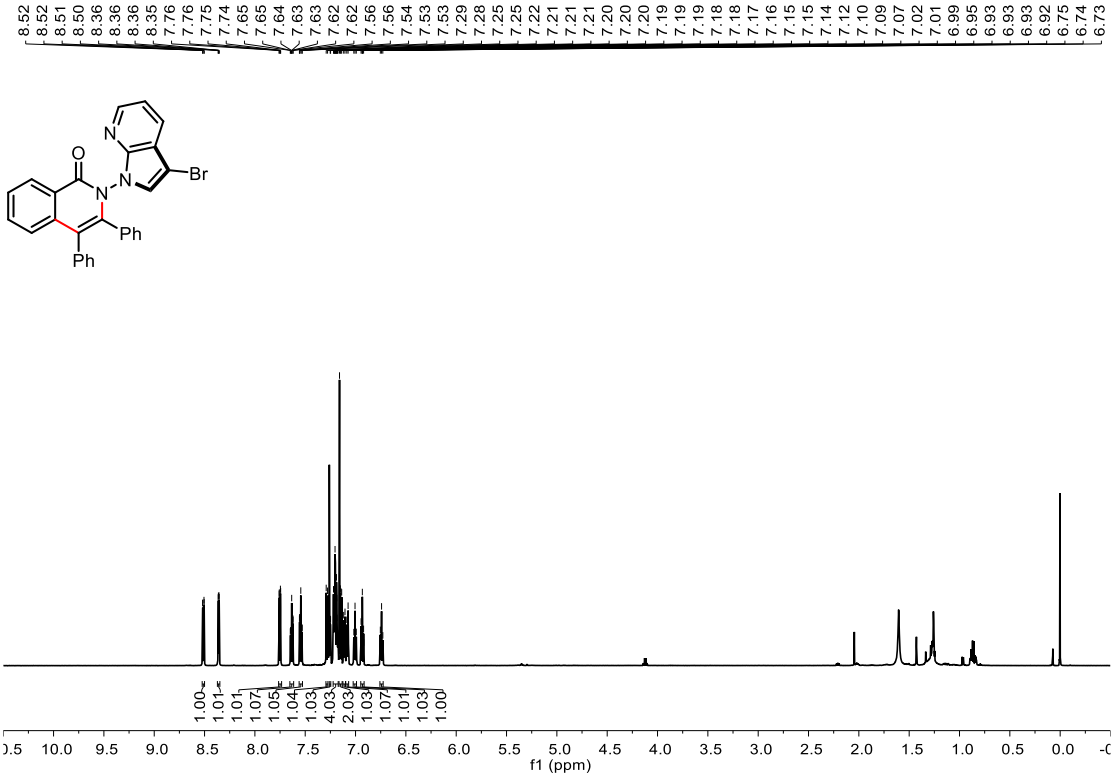
^{1}H NMR of **34** (400 MHz, $CDCl_3$)



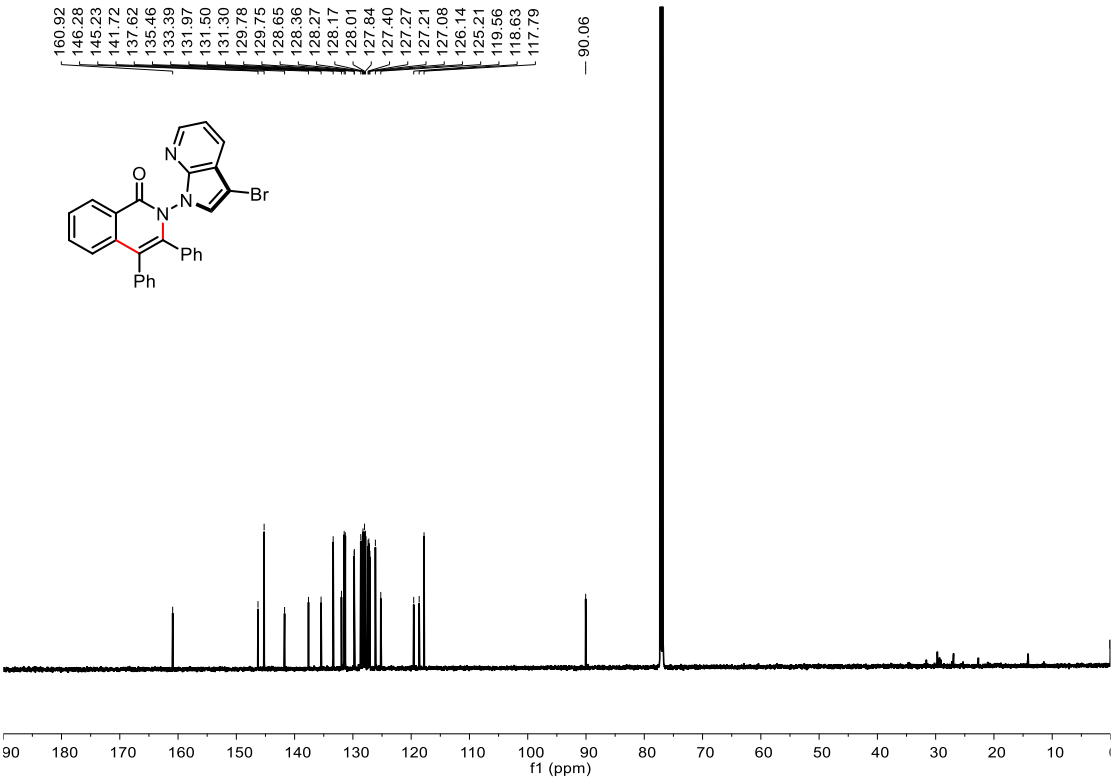
^{13}C NMR of **34**(100 MHz, $CDCl_3$)



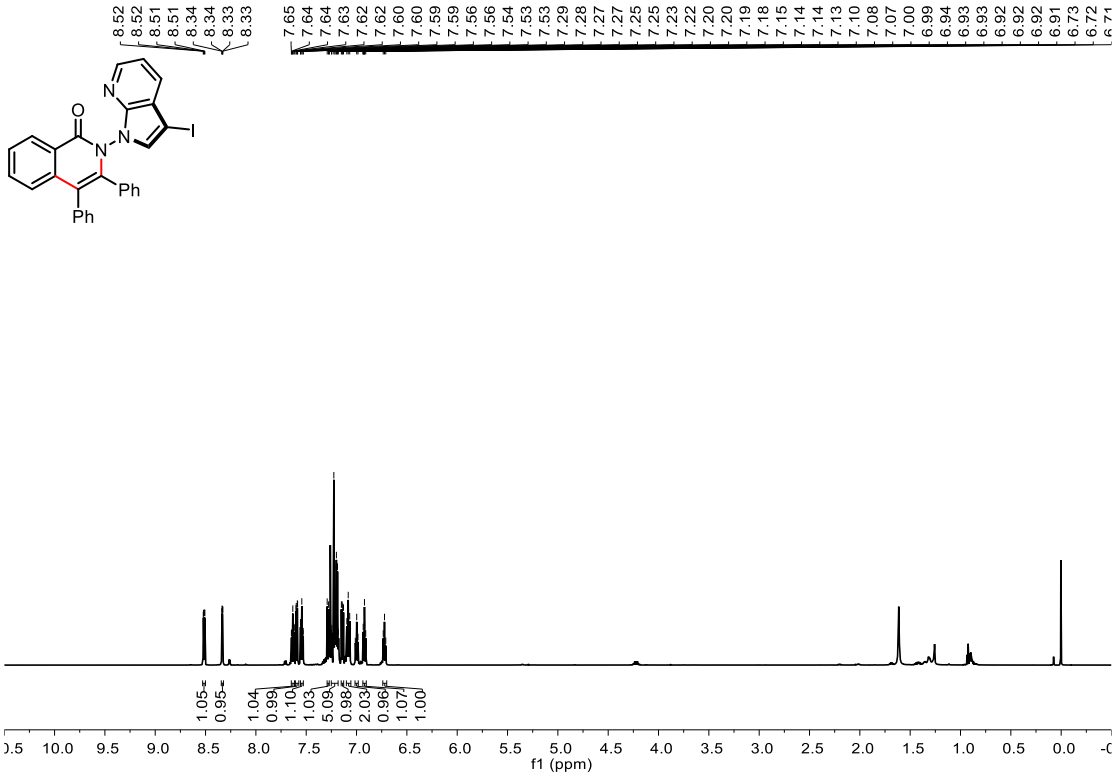
^{1}H NMR of **35** (400 MHz, $CDCl_3$)



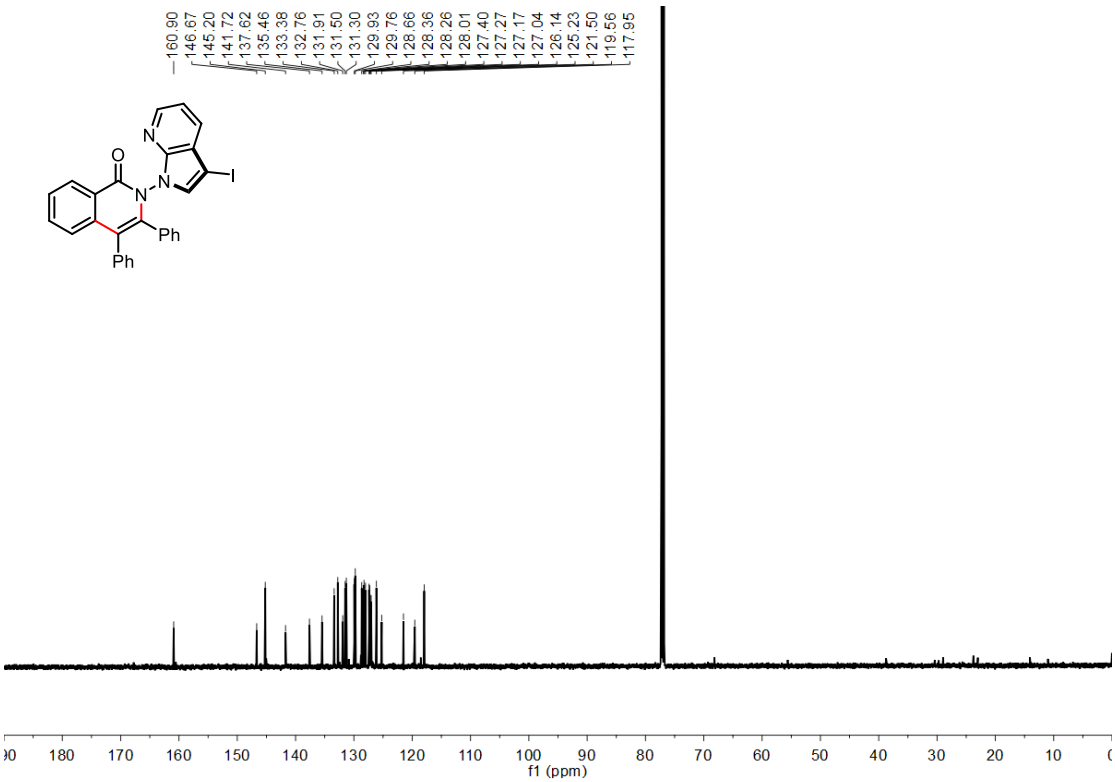
^{13}C NMR of **35** (100 MHz, $CDCl_3$)



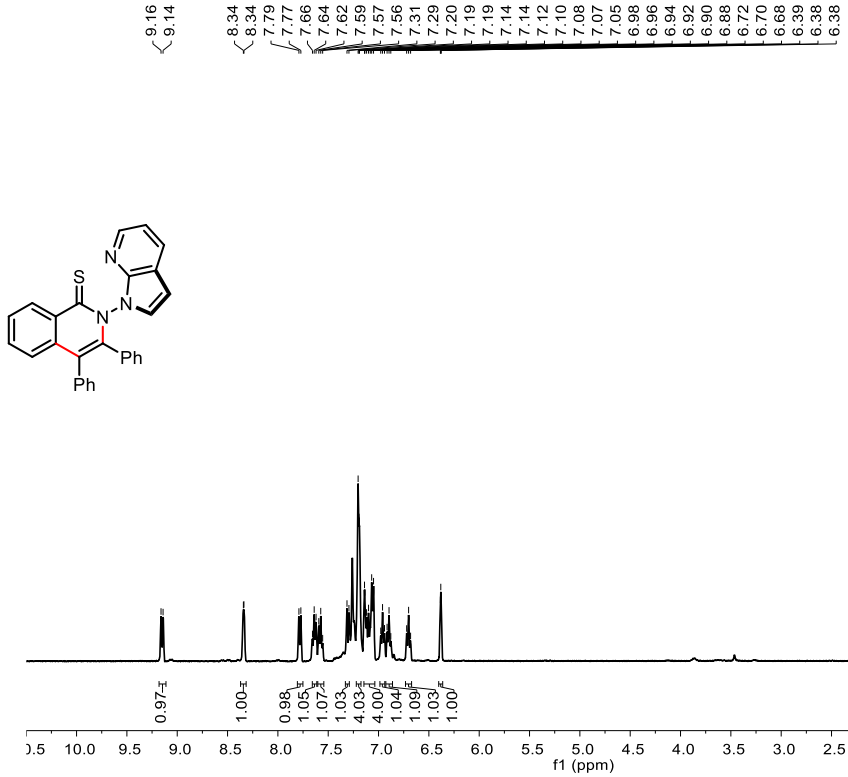
^{1}H NMR of **36** (400 MHz, $CDCl_3$)



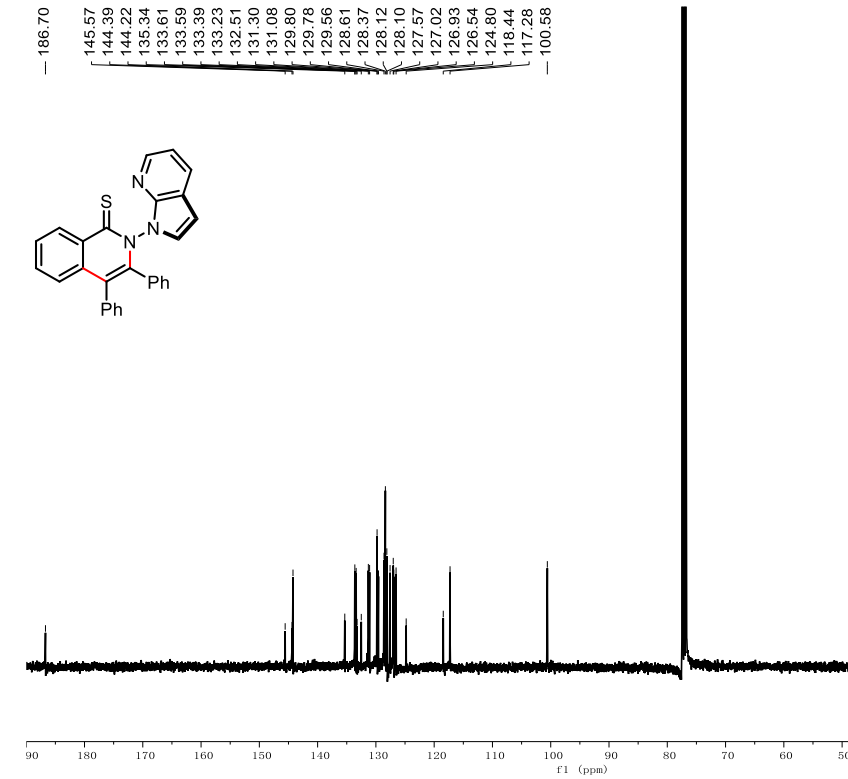
^{13}C NMR of **36** (100 MHz, $CDCl_3$)



^{1}H NMR of **37**(400 MHz, $CDCl_3$)



^{13}C NMR of **37** (100 MHz, $CDCl_3$)



9. References

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3 Q.-J. Yao, F.-R. Huang, J.-H. Chen, M.-Y. Zhong and B. Shi, *Angew. Chem. Int. Ed.*, 2023, **62**, e202218533.

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5 X. Zhu, H. Wu, Y. Wang, G. Huang, F. Wang and X. Li, *Chem. Sci.*, 2023, **14**, 8564–8569.