Electronic Supplementary Material (ESI) for ChemComm.

Rhodium-Catalyzed C–H Activation of Hydrazines Leads to Isoquinolones with Tunable Aggregation-Induced Emission Property

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Supporting Information

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1. General Informations

All reactions were carried out under an atmosphere of nitrogen unless otherwise noted. Reaction temperatures were reported as those of the oil bath. The dry solvents used were purified by distillation and were transferred under nitrogen.

Commercially available reagents were purchased from Adamas-beta, Sigma-Aldrich, Alfa Aesar, TCI, Accela, J&K and Aladdin and used as received unless otherwise stated. Dichloro(pentamethylcyclopentadienyl)rhodium(III) dimer 99%, was purchased from Sinocompound Technology Co., Ltd.

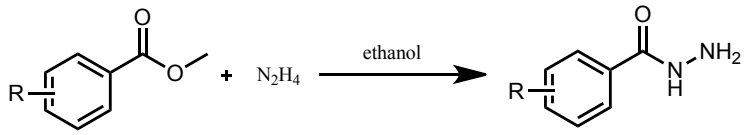
Reactions were monitored with analytical thin-layer chromatography (TLC) on silica. ^{1}H NMR and ^{13}C NMR data were recorded on Bruker nuclear resonance (500MHz) spectrometers, respectively. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H=7.26 ppm, δ_c=77.16 ppm; DMSO-d_6: δ_H = 2.50 ppm, δ_C = 39.52 ppm; MeOD-d_4: δ_H=3.31 ppm, δ_c=49.00 ppm; Acetone-d_6: δ_H = 2.05 ppm, δ_C = 29.84 ppm, 206.26 ppm). HRMS (ESI and APCI) analysis were performed by the Analytical Instrumentation Center at Peking University, Shenzhen Graduate School and (HRMS) data were reported with ion mass/charge (m/z) ratios as values in atomic mass units. All melting points were uncorrected.

Fluorescence spectra were measured on a Shimadzu RF-5301PC spectrometer with a slit width of 3 nm for excitation and 3 nm for emission. The water/THF mixtures with different water fractions were prepared by slowly adding distilled water into the THF solution of samples under ultrasound at room temperature. Fluorescence quantum yields of compounds in solution and in powders were measured on Absolutely Photoluminescence Quantum Yield Measurement System (HAMAMARSU, C11347-11Quantaurus-QY). Scanning Electron Microscopy (SEM) images were obtained on a JSM-7800F microscope operated at 2 kV.

2. General Procedure for the Preparation of Starting Materials

Benzoylhydrazine,[1] 1,2-di-p-tolylethyne, 1,2-bis(4-tert-butyl-phenyl)ethyne, 1,2-bis(4-fluorophenyl)ethyne, 1,2-bis(4-chlorophenyl)ethyne, 1,2-bis(4-trifluoromethyl-phenyl)ethyne, 1-cyclopropyl-1-phenylethyne[2], *t*BuCOOD[3] and $[Cp^*Rh(OAc)_2]$[4] were prepared according to literature reports.

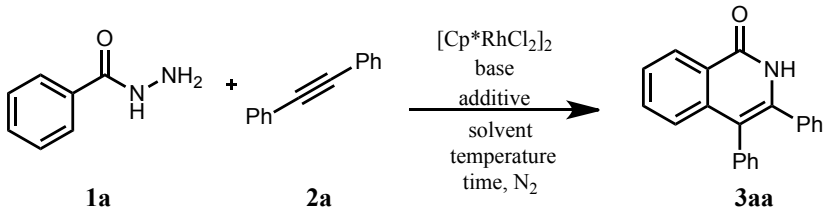
Procedure of the preparation of benzoylhydrazine.



To a solution of methyl benzoate (2.04 g, 15 mmol) in anhydrous ethanol (20 mL) was added 85% hydrazine hydrate (3.5 mL). The resulting mixture was refluxed for 4 h and then cooled to room temperature. The product precipitated out of solution, white crystals were collected by filtration, and these were washed with cold water and dried to give benzoylhydrazine (1.85 g, 90%).

3. Optimization of the Rh(III)-catalyzed isoquinolone synthesis.

Table S1 Optimization of the Rh(III)-catalyzed isoquinolone synthesis[a].



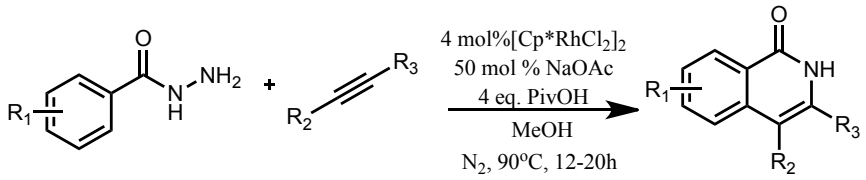
1a **2a** **3aa**

Entry	Solvent	$[Cp^*RhCl_2]_2$	Base	Additive	Temperature	Time	Yield
1	MeOH	2.5%	CsOAC 25%	-	70 °C	16 h	-
2	MeOH	2.5%	CsOAC 25%	HOAc 1.2 eq.	70 °C	16 h	38%
3	MeCN	2.5%	CsOAC 25%	HOAc 1.2 eq.	70 °C	16 h	11%
4	DCE	2.5%	CsOAC 25%	HOAc 1.2 eq.	70 °C	16 h	27%
5	MeOH	2.5%	CsOAC 25%	HOAc 1.2 eq.	90 °C	16 h	50%
6	MeOH	2.5%	CsOAC 25%	HOAc 2 eq.	90 °C	16 h	53%
7	MeOH	2.5%	CsOAC 25%	HOAc 4 eq.	90 °C	16 h	61%
8	MeOH	5%	CsOAC 25%	HOAc 4 eq.	90 °C	16 h	82%
9	MeOH	5%	CsOAC 50%	HOAc 4 eq.	90 °C	16 h	86%
10	MeOH	5%	CsOAC 50%	PivOH 4 eq.	90 °C	16 h	88%
11	MeOH	5%	NaOAC 50%	PivOH 4 eq.	90 °C	16 h	95%
12	MeOH	5%	KOAC 50%	PivOH 4 eq.	90 °C	16 h	86%
13	MeOH	4%	NaOAC 50%	PivOH 4 eq.	90 °C	16 h	95%
14	MeOH	4%	NaOAC 50%	PivOH 4 eq.	90 °C	12 h	95%
15[b]	MeOH	-	-	PivOH 4 eq.	90 °C	12h	90%

[a]Yield determined by NMR spectroscopy using 1,4-dimethoxybenzene as aninternal standard. [b]$[Cp^*Rh(OAc)_2]$ (8 mol%) was used as the catalyst.

4. Experimental Procedure and Characterization of Products

4.1 The synthesis and characterization of compounds 3

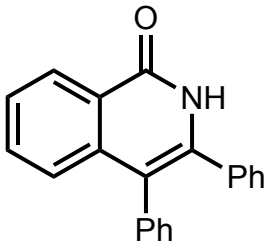


1 **2** **3**

A mixture of benzoylhydrazine (1) (0.20 mmol, 1.0 equiv.), the alkyne (2) (if solid) (1.2 equiv.), $[Cp^*RhCl_2]_2$ (4.0 mol %), pivalic acid (4 equiv.) and NaOAc (50.0 mmol %) were weighed into a 15ml pressure tube. Dry MeOH (1.0 mL) was added (followed immediately by the alkyne if it is a liquid) and the mixture was stirred at 90°C for 12-20 hours under N_2 atmosphere. Afterwards, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel.

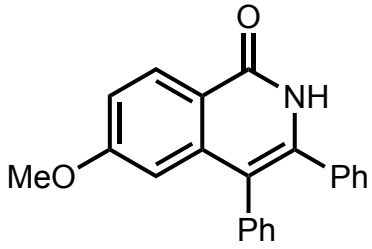
4.2 Characterization Data of compound 3.

3,4-Diphenylisoquinolin-1(2*H*)-one 3aa[5]



Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (42.7 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. **3aa** was an off-white solid obtained in 91% yield (54.1 mg). The product was isolated by column chromatography using 20~50% EtOAc in petroleum ether. **^{1}H NMR (500 MHz, DMSO-d_6):** δ 11.55 (s, 1H), 8.33 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.68 – 7.60 (m, 1H), 7.57 – 7.47 (m, 1H), 7.34 – 7.21 (m, 8H), 7.16 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, DMSO-d_6):** δ 163.17, 140.04, 139.58, 137.33, 136.06, 133.95, 133.18, 131.30, 129.69, 129.64, 129.14, 128.50, 128.29, 127.70, 126.51, 126.39, 116.93. **HRMS (ESI):** m/z calcd for $C_{21}H_{16}NO$ (+): 298.1232, found: 298.1226.

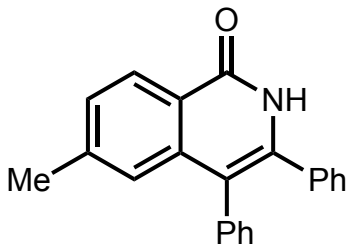
6-Methoxy-3,4-diphenylisoquinolin-1(2*H*)-one 3ba[5]



Following the general procedure, the reaction was carried out with 4-methoxy-benzoylhydrazine (33.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-

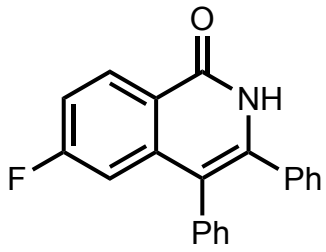
diphenylethyne (42.7 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. **3ba** was an off-white solid obtained in 95% yield (62.1 mg). The product was isolated by column chromatography using 20~50% EtOAc in petroleum ether. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 8.87 (s, 1H), 8.34 (d, *J* = 8.8 Hz, 1H), 7.41 – 7.15 (m, 10H), 7.07 (d, *J* = 8.7 Hz, 1H), 6.69 (s, 1H), 3.72 (s, 3H). **^{13}C NMR (126 MHz, CD_2Cl_2):** δ 164.19, 162.75, 141.93, 138.90, 136.93, 136.36, 132.78, 130.29, 130.23, 129.56, 129.32, 129.24, 128.25, 119.93, 117.78, 116.19, 108.66, 56.23. **HRMS (ESI):** m/z calcd for $C_{22}H_{18}NO_2$ (+): 328.1338, found: 328.1336.

6-Methyl-3,4-diphenylisoquinolin-1(2*H*)-one 3ca[6]



Following the general procedure, the reaction was carried out with 4-methyl-benzoylhydrazine (30.0 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (42.7 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. **3ca** was an off-white solid obtained in 95% yield (59.1 mg). The product was isolated by column chromatography using 20~50% EtOAc in petroleum ether. **^{1}H NMR (500 MHz, DMSO-d_6):** δ 11.43 (s, 1H), 8.21 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.12 (m, 11H), 6.93 (s, 1H), 2.31 (s, 3H). **^{13}C NMR (126 MHz, DMSO-d_6):** δ 163.07, 143.87, 140.14, 139.72, 137.41, 136.16, 133.21, 131.27, 129.67, 129.57, 129.16, 129.10, 128.48, 128.39, 125.97, 124.42, 116.74, 23.07. **HRMS (ESI):** m/z calcd for $C_{22}H_{18}NO$ (+): 312.1388, found: 312.1384.

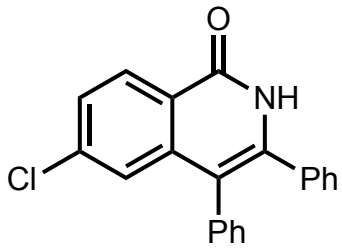
6-Fluoro-3,4-diphenylisoquinolin-1(2*H*)-one 3da[6]



Following the general procedure, the reaction was carried out with 4-fluoro-benzoylhydrazine (30.8 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (42.7 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. **3da** was an off-white solid obtained in 86% yield (54.2 mg). The product was isolated by column chromatography using 20~50% EtOAc in petroleum ether. **^{1}H NMR (500 MHz, DMSO-d_6):** δ 11.67 (s, 1H), 8.39 (dd, *J* = 8.9, 6.1 Hz, 1H), 7.38 (td, *J* = 8.6, 2.5 Hz, 1H), 7.34 – 7.22 (m, 8H), 7.16 (dd, *J* = 7.9, 1.4 Hz, 2H), 6.74 (dd, *J* = 10.9, 2.5 Hz, 1H). **^{13}C NMR (126 MHz, DMSO-d_6):** δ 166.08 (d, *J* = 250.7 Hz), 162.48, 142.18 (d, *J* = 10.1 Hz), 141.70, 136.83, 135.74, 133.05, 131.98 (d, *J* = 10.1 Hz), 131.22, 129.86, 129.17, 128.76, 123.42, 116.40 (d, *J* = 2.5 Hz), 116.12 (d, *J* = 23.9 Hz), 111.09 (d, *J* =

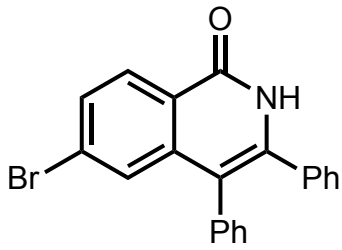
22.7 Hz) (one signal missing due to overlap). **HRMS (ESI):** m/z calcd for $C_{21}H_{15}FNO$ (+): 316.1138, found: 316.1134.

6-Chloro-3,4-diphenylisoquinolin-1(2*H*)-one 3ea[6]



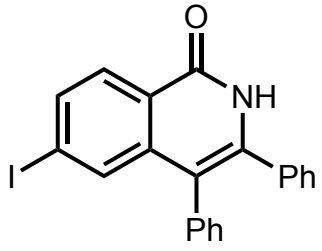
Following the general procedure, the reaction was carried out with 4-chloro-benzoylhydrazine (34.0 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (42.7 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. **3ea** was an off-white solid obtained in 92% yield (60.9 mg). The product was isolated by column chromatography using 20~50% EtOAc in petroleum ether. **^{1}H NMR (500 MHz, DMSO-d_6):** δ 11.71 (s, 1H), 8.32 (d, *J* = 8.6 Hz, 1H), 7.55 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.33 – 7.22 (m, 8H), 7.17 (d, *J* = 6.7 Hz, 2H), 7.05 (d, *J* = 1.8 Hz, 1H). **^{13}C NMR (126 MHz, DMSO-d_6):** δ 162.56, 141.83, 141.19, 139.10, 136.66, 135.69, 133.10, 131.22, 130.79, 129.89, 129.17, 128.83, 127.85, 125.27, 125.13, 116.01(one signal missing due to overlap). **HRMS (ESI):** m/z calcd for $C_{21}H_{15}ClNO$ (+): 332.0842, found: 332.0838.

6-Bromo-3,4-diphenylisoquinolin-1(2*H*)-one 3fa[5]



Following the general procedure, the reaction was carried out with 4-bromo-benzoylhydrazine (42.8 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (42.7 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. **3fa** was an off-white solid obtained in 94% yield (70.5 mg). The product was isolated by column chromatography using 20~70% Et_2O in petroleum ether. **^{1}H NMR (500 MHz, DMSO-d_6):** δ 11.68 (s, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 7.66 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.35 – 7.13 (m, 11H). **^{13}C NMR (126 MHz, DMSO-d_6):** δ 162.70, 141.82, 141.38, 136.66, 135.72, 133.12, 131.23, 130.79, 130.61, 129.89, 129.16, 128.84, 128.38, 128.23, 125.40, 115.90 (one signal missing due to overlap). **HRMS (ESI):** m/z calcd for $C_{21}H_{15}BrNO$ (+): 376.0337, found: 376.0337.

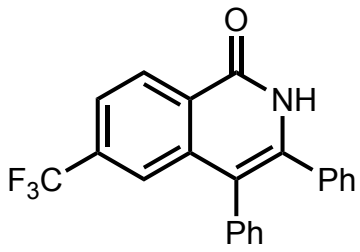
6-Iodo-3,4-diphenylisoquinolin-1(2*H*)-one 3ga[6]



Following the general procedure, the reaction was carried out with 4-iodo-benzoylhydrazine (52.4 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne

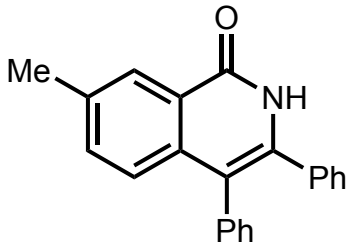
(42.7 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. The mixture was filtered, washing with cold methanol. **3ga** was collected from the filter paper as an off-white solid obtained in 96% yield (81.2 mg). **^{1}H NMR (500 MHz, DMSO-d_6):** δ 11.68 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.85 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.45 (d, *J* = 1.4 Hz, 1H), 7.35 – 7.19 (m, 8H), 7.18 – 7.13 (m, 2H). **^{13}C NMR (126 MHz, DMSO-d_6):** δ 162.90, 141.47, 141.24, 136.71, 136.28, 135.76, 134.72, 133.14, 131.23, 130.27, 129.86, 129.84, 129.15, 128.81, 125.68, 115.70, 102.62. **HRMS (ESI):** m/z calcd for $C_{21}H_{15}INO$ (+): 424.0198, found: 424.0194.

6-(Trifluoromethyl)-3,4-diphenylisoquinolin-1(2*H*)-one 3ha[6]



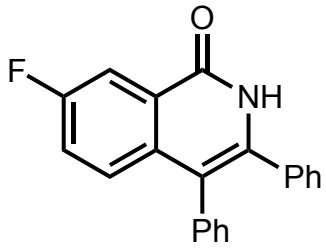
Following the general procedure, the reaction was carried out with 4-(trifluoromethyl)-benzoylhydrazine (40.8 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (42.7 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. **3ha** was a yellow solid obtained in 88% yield (70.5 mg). The product was isolated by column chromatography using EtOAc / petroleum ether = 1/5-2/1. **^{1}H NMR (500 MHz, DMSO-d_6):** δ 11.91 (s, 1H), 8.53 (d, *J* = 8.3 Hz, 1H), 7.82 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.40 (s, 1H), 7.36 – 7.25 (m, 8H), 7.20 (dd, *J* = 7.9, 1.4 Hz, 2H). **^{13}C NMR (126 MHz, DMSO-d_6):** δ 162.39, 142.04, 139.85, 136.43, 135.57, 133.74 (d, *J* = 31.5 Hz), 133.11, 131.25, 130.11, 129.96, 129.93, 129.20, 128.96, 126.31, 124.14, 123.40 (q, *J* = 2.5 Hz), 123.07(q, *J* = 2.5 Hz), 116.59. **HRMS (ESI):** m/z calcd for $C_{22}H_{15}F_3NO$ (+): 366.1106, found: 366.1106.

7-Methyl-3,4-diphenylisoquinolin-1(2*H*)-one 3ia[7]



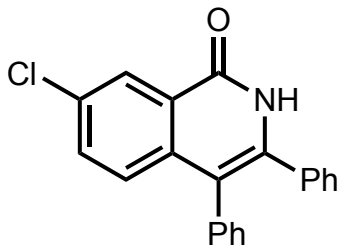
Following the general procedure, the reaction was carried out with 3-,methyl-benzoylhydrazine (30.0 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (42.7 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 20h. **3ia** was an off-white solid obtained in 77% yield (47.9 mg). The product was isolated by column chromatography using 20~50% EtOAc in petroleum ether. **^{1}H NMR (500 MHz, DMSO-d_6):** δ 11.45 (s, 1H), 8.13 (s, 1H), 7.47 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.31 – 7.20 (m, 8H), 7.15 – 7.12 (m, 2H), 7.06 (d, *J* = 8.3 Hz, 1H), 2.45 (s, 3H). **^{13}C NMR (126 MHz, DMSO-d_6):** δ 163.07, 139.03, 137.49, 137.34, 137.28, 136.14, 135.24, 133.14, 131.30, 129.66, 129.53, 129.12, 128.44, 127.84, 126.49, 126.44, 116.88, 22.33. **HRMS (ESI):** m/z calcd for $C_{22}H_{18}NO$ (+):312.1388, found: 312.1384.

7-Fluoro-3,4-diphenylisoquinolin-1(2*H*)-one 3ja



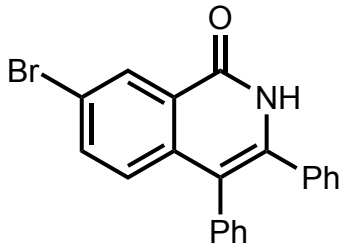
Following the general procedure, the reaction was carried out with 3-fluoro-benzoylhydrazine (30.8 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (42.7 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 20h. **3ja** was an off-white solid obtained in 67% yield (42.2 mg). The product was isolated by column chromatography using 20~50% EtOAc in petroleum ether. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 10.02 (s, 1H), 8.21 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.44 (td, *J* = 8.0, 4.5 Hz, 1H), 7.30 – 7.19 (m, 11H). **^{13}C NMR (126 MHz, CD_2Cl_2):** δ 162.49, 159.72 (d, *J* = 255.8 Hz), 139.96, 138.76 (d, *J* = 3.8 Hz), 135.95, 132.13 (d, *J* = 3.8 Hz), 130.56, 129.53, 129.03, 128.35, 128.28, 128.18 (d, *J* = 8.8 Hz), 127.75, 124.49 (d, *J* = 3.8 Hz), 120.54 (d, *J* = 22.7 Hz), 113.99 (one signal missing due to overlap). **HRMS (ESI):** m/z calcd for $C_{21}H_{15}FNO$ (+): 316.1138, found: 316.1133.

7-Chloro-3,4-diphenylisoquinolin-1(2*H*)-one 3ka[8]



Following the general procedure, the reaction was carried out with 3-chloro-benzoylhydrazine (34.0 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (42.7 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 20h. **3ka** was an off-white solid obtained in 71% yield (47.0 mg). The product was isolated by column chromatography using 20~50% EtOAc in petroleum ether. **^{1}H NMR (500 MHz, DMSO-d_6):** δ 11.76 (s, 1H), 8.25 (d, *J* = 2.3 Hz, 1H), 7.70 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.33 – 7.22 (m, 8H), 7.16 (dd, *J* = 7.6, 5.4 Hz, 3H). **^{13}C NMR (126 MHz, DMSO-d_6):** δ 162.11, 140.68, 138.32, 136.88, 135.75, 134.11, 133.11, 132.42, 131.27, 129.79, 129.16, 128.80, 128.69, 127.76, 127.26, 116.54 (one signal missing due to overlap). **HRMS (ESI):** m/z calcd for $C_{21}H_{15}ClNO$ (+): 332.0842, found: 332.0836.

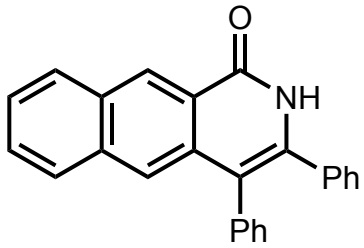
7-Bromo-3,4-diphenylisoquinolin-1(2*H*)-one 3la



Following the general procedure, the reaction was carried out with 3-bromo-benzoylhydrazine (42.8 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (42.7 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 20h. **3la** was an off-white solid obtained in 77% yield (57.8 mg). The product was

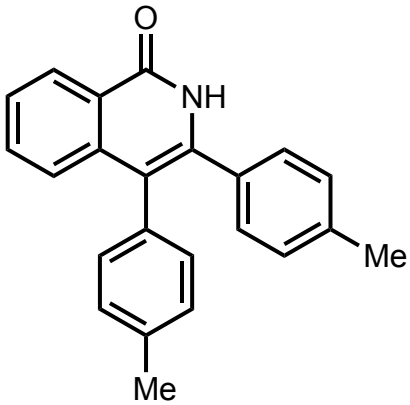
isolated by column chromatography using 20~70% Et_2O in petroleum ether. **^{1}H NMR (500 MHz, DMSO-d_6):** δ 11.76 (s, 1H), 8.39 (d, *J* = 2.2 Hz, 1H), 7.82 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.33 – 7.21 (m, 8H), 7.17 – 7.13 (m, 2H), 7.09 (d, *J* = 8.8 Hz, 1H). **^{13}C NMR (126 MHz, DMSO-d_6):** δ 162.01, 140.85, 138.57, 136.83, 136.80, 135.78, 133.11, 131.25, 130.39, 129.79, 129.16, 128.92, 128.69, 128.04, 120.67, 116.59 (one signal missing due to overlap). **HRMS (ESI):** m/z calcd for $C_{21}H_{15}BrNO$ (+): 376.0337, found: 376.0339.

3,4-Diphenylbenzo[g]isoquinolin-1(*2H*)-one 3ma[6]



Following the general procedure, the reaction was carried out with 2-naphthoichydrazide (37.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (42.7 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 20h. **3ma** was an orange solid obtained in 70% yield (48.6 mg). The product was isolated by column chromatography using 20~50% EtOAc in petroleum ether. **^{1}H NMR (500 MHz, DMSO-d_6):** δ 11.38 (s, 1H), 9.03 (s, 1H), 8.24 – 8.20 (m, 1H), 7.88 – 7.83 (m, 1H), 7.64 (s, 1H), 7.59 – 7.54 (m, 2H), 7.36 – 7.22 (m, 10H). **^{13}C NMR (126 MHz, DMSO-d_6):** δ 163.66, 138.93, 137.61, 136.34, 136.26, 136.15, 133.28, 132.25, 131.32, 130.57, 129.79, 129.72, 129.56, 129.26, 129.14, 128.59, 127.61, 125.42, 124.83, 116.72 (one signal missing due to overlap). **HRMS (ESI):** m/z calcd for $C_{25}H_{18}NO$ (+): 348.1388, found: 348.1384.

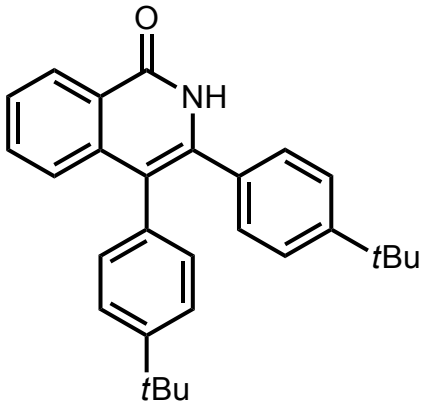
3,4-Di-*p*-tolylisoquinolin-1(*2H*)-one 3ab[6]



Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-di-*p*-tolylethyne (49.4 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 20h. **3ab** was an off-white solid obtained in 64% yield (41.6 mg). The product was isolated by column chromatography using EtOAc / petroleum ether = 1/5-2/1. **^{1}H NMR (500 MHz, DMSO-d_6):**δ 11.42 (s, 1H), 8.30 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.65 – 7.57 (m, 1H), 7.53 – 7.46 (m, 1H), 7.13 (dd, *J* = 7.2, 5.5 Hz, 5H), 7.03 (dd, *J* = 8.0, 2.7 Hz, 4H), 2.29 (s, 3H), 2.24 (s, 3H). **^{13}C NMR (126 MHz, DMSO-d_6):** δ 163.19, 139.92, 139.88, 138.95, 137.48, 134.45, 133.82, 133.34, 133.01, 131.15, 130.37, 129.76, 128.22, 127.51, 126.44, 126.42,

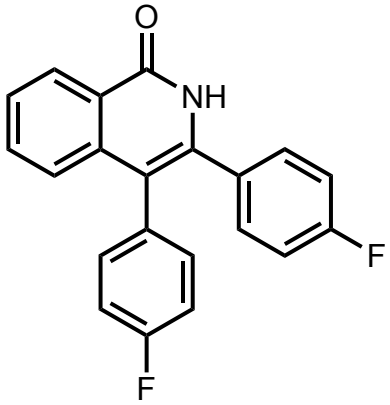
116.62, 22.23, 22.20. **HRMS (ESI):** m/z calcd for $C_{23}H_{20}NO$ (+): 326.1545, found: 326.1539.

3,4-Bis(4-tert-butyl-phenyl)isoquinolin-1(*2H*)-one 3ac



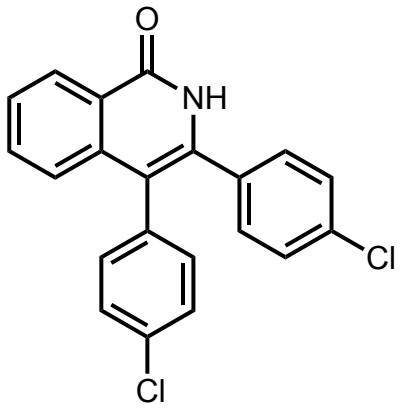
Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-bis(4-tert-butyl-phenyl)ethyne (69.6 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 20h. **3ac** was an off-white solid obtained in 60% yield (49.1 mg). The product was isolated by column chromatography using EtOAc / petroleum ether = 1/5-2/1. **^{1}H NMR (500 MHz, DMSO-d_6):** δ 11.41 (s, 1H), 8.30 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.01 (m, 9H), 1.23 (d, *J* = 25.6 Hz, 18H). **^{13}C NMR (126 MHz, DMSO-d_6):** δ 163.12, 151.95, 150.74, 140.02, 139.77, 134.42, 133.86, 133.35, 132.86, 130.98, 128.24, 127.52, 126.43, 126.28, 125.76, 116.74, 35.72, 35.67, 32.55, 32.40. **HRMS (ESI):** m/z calcd for $C_{29}H_{31}NONa$ (+): 432.2303, found: 432.2297.

3,4-Bis(4-fluorophenyl)isoquinolin-1(*2H*)-one 3ad[6]



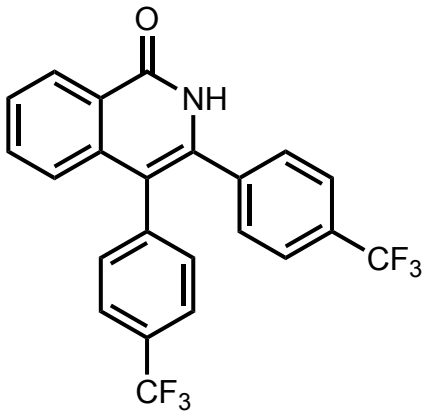
Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-bis(4-fluorophenyl)ethyne (51.4 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 20h. **3ad** was an off-white solid obtained in 62% yield (41.3 mg). The product was isolated by column chromatography using EtOAc / petroleum ether = 1/5-2/1. **^{1}H NMR (500 MHz, DMSO-d_6):** δ 11.61 (s, 1H), 8.32 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.56 – 7.51 (m, 1H), 7.30 – 7.26 (m, 2H), 7.21 – 7.08 (m, 7H). **^{13}C NMR (126 MHz, DMSO-d_6):** δ 163.92 (d, *J* = 70.6 Hz), 163.13, 161.98 (d, *J* = 69.3 Hz), 139.47, 135.17 (d, *J* = 8.8 Hz), 134.06, 133.60 (d, *J* = 8.8 Hz), 133.50 (d, *J* = 3.8 Hz) 132.40 (d, *J* = 2.5 Hz), 128.33, 127.82, 126.57, 126.27, 116.68 (d, *J* = 21.4 Hz), 116.16 (d, *J* =21.4 Hz) (two signals missing due to overlap). **HRMS (ESI):** m/z calcd for $C_{21}H_{13}F_2NONa$ (+): 356.0863, found: 356.0856.

3,4-Bis(4-chlorophenyl)isoquinolin-1(*2H*)-one 3ae



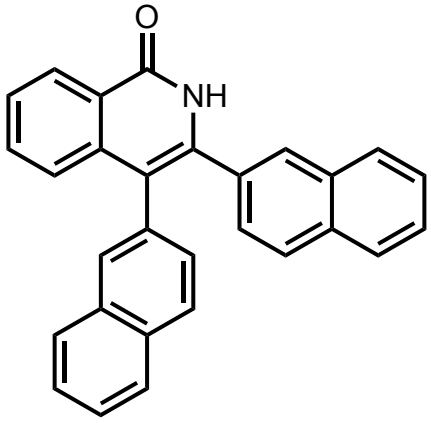
Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-bis(4-chlorophenyl)ethyne (59.0 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 20h. **3ae** was an off-white solid obtained in 65% yield (47.5 mg). The product was isolated by column chromatography using EtOAc / petroleum ether = 1/5-2/1. **^{1}H NMR (500 MHz, DMSO-d_6):** δ 11.51 (s, 1H), 8.32 (d, *J* = 7.8 Hz, 1H), 7.67 (t, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.36 (dd, *J* = 26.6, 8.4 Hz, 4H), 7.23 (dd, *J* = 32.1, 8.3 Hz, 4H), 7.14 (d, *J* = 8.1 Hz, 1H). **^{13}C NMR (126 MHz, DMSO-d_6):** δ 163.11, 139.17, 136.06, 135.03, 134.70, 134.63, 134.16, 133.48, 133.23, 129.88, 129.33, 128.36, 128.00, 126.62, 126.26, 115.97(one signal missing due to overlap). **HRMS (ESI):** m/z calcd for $C_{21}H_{14}Cl_2NO$ (+): 366.0452, found: 366.0451.

3,4-Bis(4-trifluoromethyl-phenyl)isoquinolin-1(*2H*)-one 3af



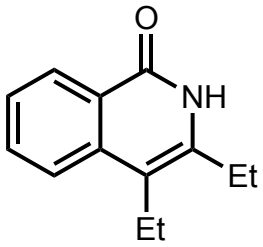
Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-bis(4-trifluoromethyl-phenyl)ethyne (75.4 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 20h. **3af** was an off-white solid obtained in 67% yield (47.5 mg). The product was isolated by column chromatography using EtOAc / petroleum ether = 1/5-2/1. **^{1}H NMR (500 MHz, DMSO-d_6):** δ 11.75 (s, 1H), 8.34 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.70 – 7.54 (m, 6H), 7.45 (dd, *J* = 26.2, 8.0 Hz, 4H), 7.10 (d, *J* = 8.1 Hz, 1H). **^{13}C NMR (126 MHz, DMSO-d_6):** δ 163.06, 141.49, 139.73, 139.07, 138.77, 134.34, 134.13, 132.36, 130.24 (d, *J* = 31.5 Hz), 129.36 (d, *J* = 31.5 Hz), 128.44, 128.32, 126.75, 126.66 (q, *J* = 3.8 Hz), 126.25, 126.15 (q, *J* = 2.5 Hz), 124.57, 124.33, 116.21. **HRMS (ESI):** m/z calcd for $C_{23}H_{14}F_6NO$ (+): 434.0980, found: 434.0973.

3,4-Di(naphthalen-2-yl)isoquinolin-1(*2H*)-one 3ag



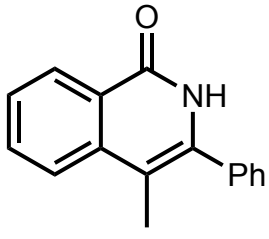
Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-di(naphthalen-2-yl)ethyne (66.7 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 20h. **3ag** was an off-white solid obtained in 70% yield (55.6 mg). The product was isolated by column chromatography using EtOAc / petroleum ether = 1/5-2/1. **^{1}H NMR (500 MHz, DMSO-d_6):** δ 11.71 (s, 1H), 8.38 (d, *J* = 7.6 Hz, 1H), 7.99 (s, 1H), 7.82 (dd, *J* = 26.3, 16.9 Hz, 6H), 7.64 – 7.19 (m, 10H). **^{13}C NMR (126 MHz, DMSO-d_6):** δ 163.25, 140.23, 139.74, 134.91, 134.30, 134.06, 133.72, 133.61, 133.30, 132.08, 131.30, 130.89, 129.56, 129.16, 128.97, 128.85, 128.76, 128.36, 128.16, 127.82, 127.63, 126.53, 117.10 (two signals missing due to overlap). **HRMS (ESI):** m/z calcd for $C_{29}H_{20}NO$ (+): 398.1545, found: 398.1541.

3,4-Diethylisoquinolin-1(*2H*)-one 3ah[6]



Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), hex-3-yne (19.7 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 20h. **3ah** was an off-white solid obtained in 67% yield (26.9 mg). The product was isolated by column chromatography using 20~50% EtOAc in petroleum ether. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 11.28 (s, 1H), 8.41 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.80 – 7.64 (m, 2H), 7.44 (ddd, *J* = 8.0, 6.8, 1.4 Hz, 1H), 2.80 – 2.70 (m, 4H), 1.33 (t, *J* = 7.6 Hz, 3H), 1.21 (t, *J* = 7.5 Hz, 3H).**^{13}C NMR (126 MHz, CD_2Cl_2):** δ 164.60, 140.32, 139.32, 133.28, 128.47, 126.19, 126.15, 123.92, 114.72, 25.18, 20.41, 15.65, 14.68. **HRMS (ESI):** m/z calcd for $C_{13}H_{16}NO$ (+):202.1232, found: 202.1225.

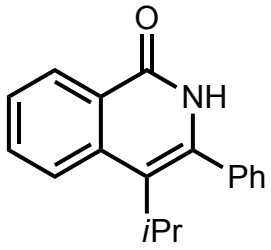
4-Methyl-3-phenylisoquinolin-1(*2H*)-one 3ai[5]



Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1-phenyl-1-propyne (27.8 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 20h. **3ai** was an off-white solid obtained in 71% yield (33.4 mg). The product was isolated by column chromatography using 20~50% EtOAc in petroleum ether. **^{1}H**

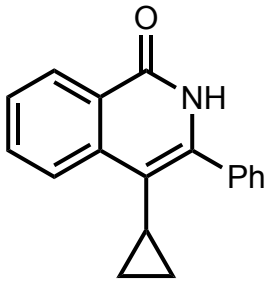
NMR (500 MHz, DMSO-d_6): δ 11.23 (s, 1H), 8.28 (d, *J* = 7.7 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.56 – 7.45 (m, 6H), 2.12 (s, 3H). **^{13}C NMR (126 MHz, DMSO-d_6):** δ 162.90, 139.73, 139.28, 136.33, 133.99, 131.12, 130.12, 129.70, 128.37, 127.54, 126.91, 125.20, 108.60, 14.95. **HRMS (ESI):** m/z calcd for $C_{16}H_{14}NO$ (+):236.1075, found: 236.1069. **NOESY (500 MHz, DMSO-d_6, 293K, TMS)**.

4-Propyl-3-phenylisoquinolin-1(*2H*)-one 3aj



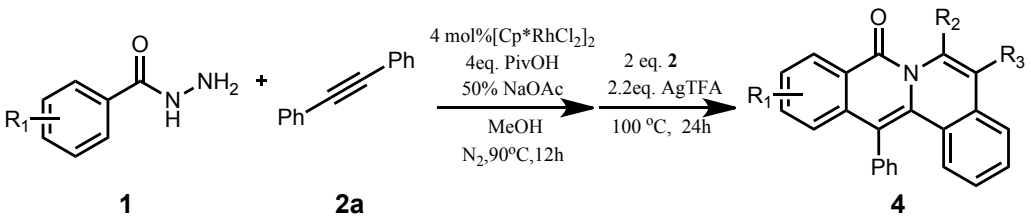
Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), [Cp*$RhCl_2$]$_2$ (4.9 mg, 0.008 mmol), 1-phenyl-1-pentyne (27.8 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 20h. **3aj** was an off-white solid obtained in 71% yield (33.4 mg). The product was isolated by column chromatography using 20~50% EtOAc in petroleum ether. **^{1}H NMR (500 MHz, DMSO-d_6):** δ 11.23 (s, 1H), 8.28 (d, *J* = 7.9 Hz, 1H), 7.85 – 7.73 (m, 2H), 7.58 – 7.36 (m, 6H), 2.50 – 2.44 (m, 2H), 1.55 – 1.44 (m, 2H), 0.79 (t, *J* = 7.3 Hz, 3H).**^{13}C NMR (126 MHz, DMSO-d_6):** δ 162.70, 139.77, 138.87, 136.54, 133.91, 130.75, 130.13, 129.73, 128.59, 127.39, 127.29, 125.18, 113.54, 30.20, 24.79, 15.42. **HRMS (ESI):** m/z calcd for $C_{18}H_{17}NONa$ (+): 286.1208, found: 286.1204. **NOESY (500 MHz, DMSO-d_6, 293K, TMS)**.

4-Cyclopropane-3-phenylisoquinolin-1(*2H*)-one 3ak



Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), [Cp*$RhCl_2$]$_2$ (4.9 mg, 0.008 mmol), 1-cyclopropyl-1-phenylethyne (34.1 mg, 0.24 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 20h. **3ak** was an off-white solid obtained in 65% yield (33.9 mg). The product was isolated by column chromatography using 20~50% EtOAc in petroleum ether. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 9.41 (s, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 7.79 – 7.74 (m, 1H), 7.62 – 7.57 (m, 2H), 7.53 – 7.46 (m, 4H), 1.91 (tt, *J* = 8.2, 5.5 Hz, 1H), 0.86 – 0.76 (m, 2H), 0.12 – 0.02 (m, 2H). **^{13}C NMR (126 MHz, CD_2Cl_2):** δ 163.34, 140.96, 140.01, 136.74, 133.29, 130.19, 129.85, 129.33, 128.19, 127.16, 126.40, 125.95, 115.19, 10.44, 10.22. **HRMS (ESI):** m/z calcd for $C_{18}H_{15}NONa$ (+): 284.1051, found: 284.1044.

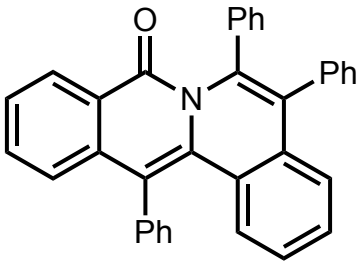
4.3 The synthesis and characterization of compounds 4



A mixture of benzoylhydrazine (1) (0.20 mmol, 1.0 equiv.), 1,2-diphenylethyne (42.7 mg, 0.21 mmol) (1.05 equiv.), $[Cp^*RhCl_2]_2$ (4.0 mol %), pivalic acid (4 equiv.) and NaOAc (50.0 mmol %) were weighed into a 15ml pressure tube. Dry MeOH (1.0 mL) was added and the mixture was stirred at 90°C for 12 hours under N_2 atmosphere. After cooling to room temperature, the alkyne (2) (2 equiv.) and AgTFA (2.2 equiv.) were added and the mixture was stirred at 100°C for 24 hours under N_2 atmosphere. Afterwards, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel.

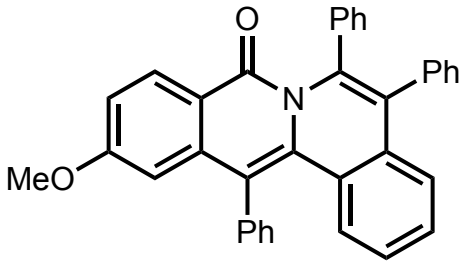
4.4 Characterization Data of compound 4.

5,6,13-Triphenyl-*8H*-dibenzo[*a,g*]quinolizin-8-one 4aa[9]



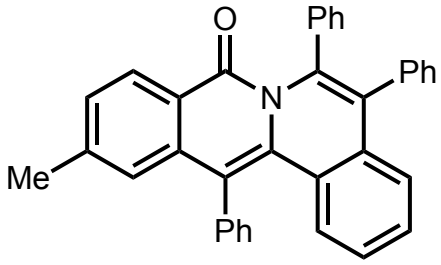
Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (37.4 mg, 0.21 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. Then, 1,2-diphenylethyne (71.2 mg, 0.40 mmol) and AgTFA (89.3 mg, 0.44 mmol) was added, the mixture was stirred at 100°C for 24 h. **4aa** was yellow crystal obtained in 69% yield (65.3 mg). The product was isolated by column chromatography using 50% CH_2Cl_2 in petroleum ether. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 8.15 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.64 – 7.50 (m, 6H), 7.45 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.22 (m, 3H), 7.20 – 7.13 (m, 4H), 7.10 – 7.04 (m, 6H), 6.88 (ddd, *J* = 8.5, 7.1, 1.4 Hz, 1H). **^{13}C NMR (126 MHz, CD_2Cl_2):** δ 162.94, 139.61, 138.44, 138.22, 137.37, 137.18, 134.83, 134.27, 133.26, 133.14, 132.49, 130.61, 130.13, 130.08, 129.39, 129.08, 128.85, 128.80, 128.05, 127.94, 127.72, 127.54, 127.39, 127.21, 126.87, 126.60, 126.58, 117.97. **HRMS (ESI):** m/z calcd for $C_{35}H_{24}NO$ (+): 474.1858, found: 474.1851.

11-Methoxy-5,6,13-triphenyl-*8H*-dibenzo[*a,g*]quinolizin-8-one 4ba[9]



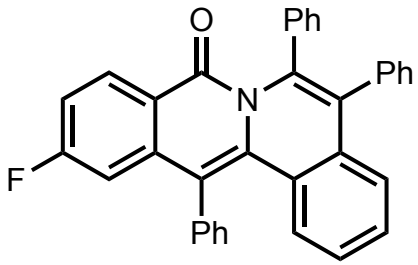
Following the general procedure, the reaction was carried out with 4-methoxy-benzoylhydrazine (33.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (37.4 mg, 0.21 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. Then, 1,2-diphenylethyne (71.2 mg, 0.40 mmol) and AgTFA (89.3 mg, 0.44 mmol) was added, the mixture was stirred at 100°C for 24 h. **4ba** was yellow crystal obtained in 72% yield (72.4 mg). The product was isolated by column chromatography using 50% CH_2Cl_2 in petroleum ether. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 8.09 (d, *J* = 8.8 Hz, 1H), 7.57 – 7.51 (m, 5H), 7.24 (ddd, *J* = 7.1, 6.4, 2.0 Hz, 3H), 7.18 – 7.11 (m, 4H), 7.08 – 7.04 (m, 6H), 7.01 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.89 – 6.85 (m, 1H), 6.71 (d, *J* = 2.4 Hz, 1H), 3.73 (s, 3H). **^{13}C NMR (126 MHz, CD_2Cl_2):** δ 164.06, 162.49, 140.33, 139.70, 138.65, 137.46, 137.29, 135.61, 134.43, 133.13, 132.54, 130.64, 130.35, 130.12, 130.09, 129.41, 129.12, 128.85, 128.70, 127.91, 127.89, 127.46, 127.33, 127.13, 126.54, 120.89, 117.66, 116.09, 108.59, 56.28. **HRMS (ESI):** m/z calcd for $C_{36}H_{26}NO_2$ (+): 504.1964, found: 504.1960.

11-Methyl-5,6,13-triphenyl-*8H*-dibenzo[*a,g*]quinolizin-8-one 4ca[9]



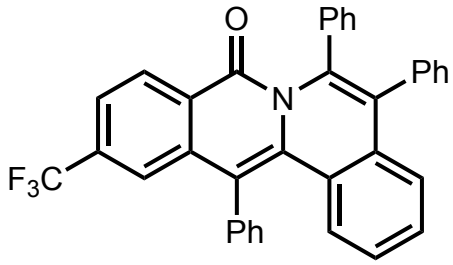
Following the general procedure, the reaction was carried out with 4-methyl-benzoylhydrazine (30.0 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (37.4 mg, 0.21 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. Then, 1,2-diphenylethyne (71.2 mg, 0.40 mmol) and AgTFA (89.3 mg, 0.44 mmol) was added, the mixture was stirred at 100°C for 24 h. **4ca** was yellow crystal obtained in 70% yield (68.2 mg). The product was isolated by column chromatography using 50% CH_2Cl_2 in petroleum ether. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 8.05 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.50 (m, 5H), 7.28 – 7.05 (m, 15H), 6.86 (t, *J* = 7.6 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR (126 MHz, CD_2Cl_2):** δ 162.86, 144.12, 139.68, 138.56, 138.29, 137.45, 137.25, 134.96, 134.32, 133.21, 132.52, 130.59, 130.12, 130.09, 129.30, 129.04, 129.02, 128.90, 128.85, 128.12, 127.92, 127.90, 127.54, 127.50, 127.15, 126.55, 126.32, 124.81, 117.91, 22.83. **HRMS (ESI):** m/z calcd for $C_{36}H_{26}NO$ (+): 488.2014, found: 488.2008.

11-Fluoro-5,6,13-triphenyl-*8H*-dibenzo[*a,g*]quinolizin-8-one 4da[9]



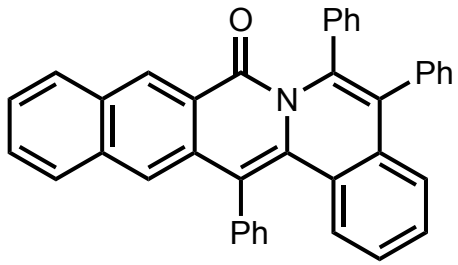
Following the general procedure, the reaction was carried out with 4-fluoro-benzoylhydrazine (30.8 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (37.4 mg, 0.21 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. Then, 1,2-diphenylethyne (71.2 mg, 0.40 mmol) and AgTFA (89.3 mg, 0.44 mmol) was added, the mixture was stirred at 100°C for 24 h. **4da** was yellow crystal obtained in 61% yield (59.9 mg). The product was isolated by column chromatography using 50% CH_2Cl_2 in petroleum ether. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 8.18 (dd, *J* = 8.7, 6.0 Hz, 1H), 7.54 (ddd, *J* = 17.1, 10.9, 6.6 Hz, 5H), 7.29 – 7.22 (m, 3H), 7.18 – 7.11 (m, 5H), 7.07 (d, *J* = 9.3 Hz, 6H), 6.96 (dd, *J* = 11.0, 2.3 Hz, 1H), 6.88 (t, *J* = 7.2 Hz, 1H). **^{13}C NMR (126 MHz, CD_2Cl_2):** δ166.48 (d, *J* = 250.7 Hz), 162.24, 140.77 (d, *J* = 10.1 Hz), 139.23, 138.35, 137.25, 137.13, 136.28, 134.42, 133.01, 132.47, 131.44 (d, *J* = 10.1 Hz), 130.84, 130.19, 130.12, 129.78, 129.35, 128.90, 128.36, 128.00, 127.87, 127.64, 127.33, 126.69, 123.44, 117.21 (d, *J* = 3.8 Hz), 115.80 (d, *J* = 23.9 Hz), 111.63 (d, *J* = 23.9 Hz). **HRMS (ESI):** m/z calcd for $C_{35}H_{23}FNO$ (+): 492.1764, found: 492.1760.

11-Trifluoromethyl-5,6,13-triphenyl-*8H*-dibenzo[*a,g*]quinolizin-8-one 4ea



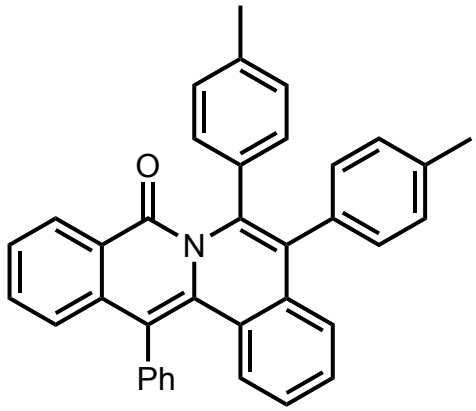
Following the general procedure, the reaction was carried out with 4-trifluoromethyl-benzoylhydrazine (40.8 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (37.4 mg, 0.21 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. Then, 1,2-diphenylethyne (67.1 mg, 0.40 mmol) and AgTFA (89.3 mg, 0.44 mmol) was added, the mixture was stirred at 100°C for 24 h. **4ea** was yellow crystal obtained in 62% yield (68.2 mg). The product was isolated by column chromatography using 50% CH_2Cl_2 in petroleum ether. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 8.28 (d, *J* = 8.1 Hz, 1H), 7.64 – 7.56 (m, 5H), 7.53 – 7.50 (m, 2H), 7.31 – 7.15 (m, 7H), 7.12 – 7.07 (m, 6H), 6.91 (dd, *J* = 10.4, 3.3 Hz, 1H). **^{13}C NMR (126 MHz, CD_2Cl_2):** δ 162.16, 138.75, 138.29, 138.00, 137.05, 136.95, 136.33, 134.66, 134.41, 134.31, 132.99, 132.39, 130.93, 130.20, 130.14, 129.94, 129.57, 129.28, 128.91, 128.60, 128.41, 128.22, 128.05, 127.78, 127.45, 127.33, 126.78, 123.84 (q, *J* = 3.8 Hz), 123.10 (q, *J* = 2.5 Hz), 117.44. **HRMS (ESI):** m/z calcd for $C_{36}H_{23}F_3NO$ (+): 542.1732, found: 542.1724.

5,6,15-Triphenyl-8*H*-benzo[g]isoquinolino[2,1-b]isoquinolin-8-one 4fa



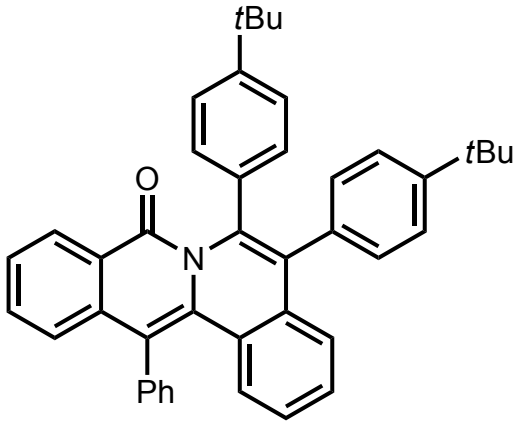
Following the general procedure, the reaction was carried out with 2-naphthoichydrazide (37.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (37.4 mg, 0.21 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. Then, 1,2-diphenylethyne (67.1 mg, 0.40 mmol) and AgTFA (89.3 mg, 0.44 mmol) was added, the mixture was stirred at 100°C for 24 h. **4fa** was yellow crystal obtained in 65% yield (68.0 mg). The product was isolated by column chromatography using 50% CH_2Cl_2 in petroleum ether. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 8.76 (s, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.65 – 7.48 (m, 7H), 7.15 (m, 13H), 6.87 (t, *J* = 7.7 Hz, 1H). **^{13}C NMR (126 MHz, CD_3Cl):** δ 163.54, 139.78, 138.06, 137.29, 136.41, 134.75, 134.46, 133.80, 133.32, 132.53, 132.48, 130.66, 130.28, 130.07, 129.67, 129.41, 129.17, 129.01, 128.89, 128.15, 127.92, 127.82, 127.27, 127.09, 126.56, 125.98, 125.60, 118.42. **HRMS (ESI):** m/z calcd for $C_{39}H_{26}NO$ (+): 524.2014, found: 524.2008.

5,6-Di-*p*-tolyl-13-phenyl-*8H*-dibenzo[*a,g*]quinolizin-8-one 4ab



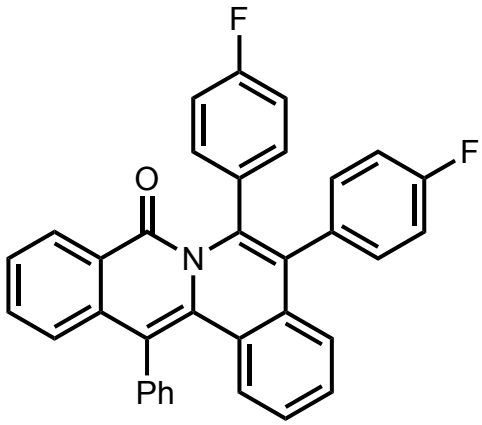
Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (37.4 mg, 0.21 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. Then, 1,2-di-p-tolylethyne (82.4 mg, 0.40 mmol) and AgTFA (89.3 mg, 0.44 mmol) was added, the mixture was stirred at 100°C for 24 h. **4ab** was yellow crystal obtained in 63% yield (63.1 mg). The product was isolated by column chromatography using 50% CH_2Cl_2 in petroleum ether. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 8.14 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.62 – 7.50 (m, 6H), 7.46 – 7.42 (m, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.15 – 7.02 (m, 7H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.91 – 6.84 (m, 3H), 2.33 (s, 3H), 2.24 (s, 3H). **^{13}C NMR (126 MHz, CD_2Cl_2):** δ 163.06, 139.65, 138.19, 137.66, 137.27, 137.17, 135.52, 134.94, 134.66, 134.42, 133.17, 132.28, 130.58, 129.99, 129.96, 129.58, 129.31, 129.05, 128.82, 128.72, 127.99, 127.54, 127.32, 127.05, 126.93, 126.66, 126.54, 117.83, 21.88. **HRMS (ESI):** m/z calcd for $C_{37}H_{28}NO$ (+): 502.2171, found: 502.2163.

5,6-Bis(4-tert-butyl-phenyl)-13-phenyl-*8H*-dibenzo[*a,g*]quinolizin-8-one 4ac



Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (37.4 mg, 0.21 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. Then, 1,2-bis(4-tert-butyl-phenyl)ethyne (116.0 mg, 0.40 mmol) and AgTFA (89.3 mg, 0.44 mmol) was added, the mixture was stirred at 100°C for 24 h. **4ac** was yellow crystal obtained in 66% yield (77.2 mg). The product was isolated by column chromatography using 50% CH_2Cl_2 in petroleum ether. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 8.18 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.63 – 7.51 (m, 6H), 7.47 – 7.43 (m, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.20 – 7.13 (m, 3H), 7.03 (ddd, *J* = 6.3, 3.5, 1.9 Hz, 4H), 6.94 – 6.90 (m, 2H), 6.87 (ddd, *J* = 8.5, 6.9, 1.7 Hz, 1H), 1.28 (s, 9H), 1.21 (s, 9H). **^{13}C NMR (126 MHz, CD_2Cl_2):** δ 162.93, 150.84, 150.24, 139.74, 138.22, 137.40, 135.55, 134.99, 134.42, 134.30, 133.17, 132.11, 130.59, 130.05, 129.65, 129.32, 129.03, 128.72, 128.04, 127.70, 127.26, 126.99, 126.81, 126.58, 126.53, 125.51, 124.62, 117.77, 35.31, 35.22, 32.02, 31.90. **HRMS (ESI):** m/z calcd for $C_{43}H_{40}NO$ (+): 586.3110, found: 586.3103.

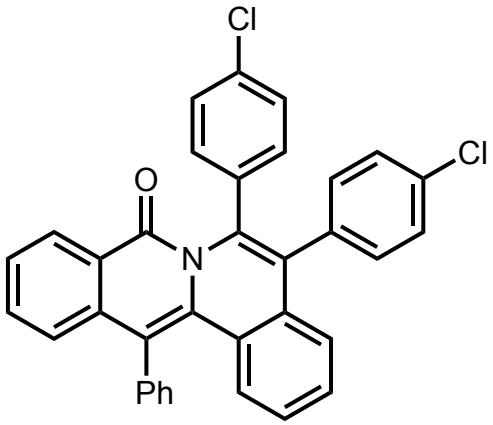
5,6-Bis(4-fluorophenyl)-13-phenyl-*8H*-dibenzo[*a,g*]quinolizin-8-one 4ad



Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (37.4 mg, 0.21 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. Then, 1,2-bis(4-fluorophenyl)ethyne (85.6 mg, 0.40 mmol) and AgTFA (89.3 mg, 0.44 mmol) was added, the mixture was stirred at 100°C for 24 h. **4ad** was yellow crystal obtained in 51% yield (51.9 mg). The product was isolated by column chromatography using 50% CH_2Cl_2 in petroleum ether. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 8.16 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.62 (ddd, *J* = 8.4, 7.1, 1.4 Hz, 1H), 7.59 – 7.49 (m, 5H), 7.48 – 7.44 (m, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.20 – 7.12 (m, 4H), 7.07 – 6.97 (m, 5H), 6.90 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 6.83 – 6.77 (m, 2H). **^{13}C NMR (126 MHz, CD_2Cl_2):** δ 163.58 (d, *J* = 71.8 Hz), 162.84, 161.63 (d, *J* = 69.3 Hz), 139.46, 138.20, 136.67, 134.62, 134.40 (d, *J* = 7.8 Hz), 134.11 (d, *J* = 8.8 Hz), 133.99, 133.39, 133.13 (d, *J* = 7.8 Hz), 133.08, 131.84 (d,

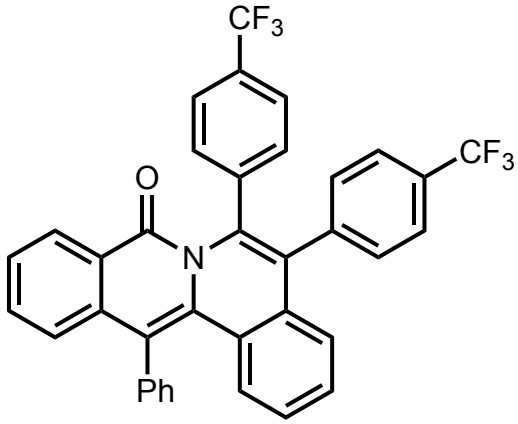
J = 7.6 Hz), 130.64, 130.17, 129.48, 129.15, 128.83, 128.04, 127.48 (d, *J* = 10.1 Hz), 127.03, 126.80, 126.64, 126.40, 118.20, 115.98 (d, *J* = 21.4 Hz), 115.04 (d, *J* = 21.4 Hz). **HRMS (ESI):** m/z calcd for $C_{35}H_{22}F_2NO$ (+): 510.1669, found: 510.1670.

5,6-Bis(4-chlorophenyl)-13-phenyl-*8H*-dibenzo[*a,g*]quinolizin-8-one 4ae



Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (37.4 mg, 0.21 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. Then, 1,2-bis(4-chlorophenyl)ethyne (98.4 mg, 0.40 mmol) and AgTFA (89.3 mg, 0.44 mmol) was added, the mixture was stirred at 100°C for 24 h. **4ae** was yellow crystal obtained in 66% yield (71.4 mg). The product was isolated by column chromatography using 50% CH_2Cl_2 in petroleum ether. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 8.17 (d, *J* = 7.7 Hz, 1H), 7.63 (t, *J* = 7.1 Hz, 1H), 7.58 – 7.46 (m, 6H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.19 – 7.12 (m, 4H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.03 (t, *J* = 7.8 Hz, 3H), 6.90 (t, *J* = 7.7 Hz, 1H). **^{13}C NMR (126 MHz, CD_2Cl_2):** δ 162.82, 139.39, 138.21, 136.85, 136.31, 135.62, 134.47, 134.18, 133.82, 133.67, 133.47, 133.40, 133.05, 131.44, 130.66, 130.18, 129.52, 129.33, 129.19, 128.86, 128.40, 128.08, 127.60, 126.93, 126.73, 126.69, 126.41, 118.34. **HRMS (ESI):** m/z calcd for $C_{35}H_{22}Cl_2NO$ (+): 542.1078, found: 542.1066.

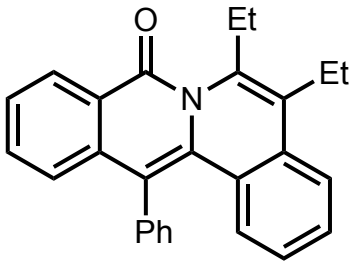
5,6-Bis(4-trifluoromethyl-phenyl)-13-phenyl-*8H*-dibenzo[*a,g*]quinolizin-8-one 4af



Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (37.4 mg, 0.21 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. Then, 1,2-bis(4-trifluoromethyl-phenyl)ethyne (125.6 mg, 0.40 mmol) and AgTFA (89.3 mg, 0.44 mmol) was added, the mixture was stirred at 100°C for 24 h. **4af** was yellow crystal obtained in 66% yield (80.4 mg). The product was isolated by column chromatography using 50% CH_2Cl_2 in

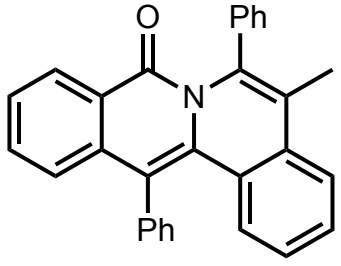
petroleum ether. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 8.17 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.64 (ddd, *J* = 8.4, 7.1, 1.4 Hz, 1H), 7.60 – 7.50 (m, 7H), 7.50 – 7.46 (m, 1H), 7.37 – 7.31 (m, 5H), 7.22 – 7.15 (m, 4H), 7.00 (dd, *J* = 7.9, 0.9 Hz, 1H), 6.93 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H). **^{13}C NMR (126 MHz, CD_2Cl_2):** δ 162.73, 141.95, 140.88, 139.29, 138.27, 136.06, 134.25, 133.64, 133.17, 133.01, 132.92, 130.71, 130.31, 130.28, 129.64, 129.37,129.27, 128.90, 128.16, 127.91, 127.76, 127.21, 126.78, 126.62, 126.41, 126.00 (d, *J* = 3.8 Hz), 126.02 (d, *J* = 3.8 Hz), 125.10 (q, *J* = 3.8 Hz), 124.03 (d, *J* = 5.0 Hz), 118.62. **HRMS (ESI):** m/z calcd for $C_{37}H_{22}F_6NO$ (+):610.1606, found: 610.1605.

5,6-Bis(4-ethylphenyl-phenyl)-13-phenyl-*8H*-dibenzo[*a,g*]quinolizin-8-one 4ag



Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (37.4 mg, 0.21 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. Then, hex-3-yne (32.8 mg, 0.40 mmol) and AgTFA (89.3 mg, 0.44 mmol) was added, the mixture was stirred at 100°C for 24 h. **4ag** was yellow crystal obtained in 45% yield (47.6 mg). The product was isolated by column chromatography using 50% CH_2Cl_2 in petroleum ether. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 8.42 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.60 (ddd, *J* = 8.3, 7.1, 1.5 Hz, 1H), 7.55 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.52 – 7.47 (m, 4H), 7.41 – 7.38 (m, 2H), 7.32 – 7.26 (m, 2H), 7.04 (dd, *J* = 8.3, 0.9 Hz, 1H), 6.83 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 3.06 (q, *J* = 7.3 Hz, 2H), 2.84 (q, *J* = 7.5 Hz, 2H), 1.25 (d, *J* = 7.5 Hz, 3H), 1.12 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (126 MHz, CD_2Cl_2):** δ 163.20, 139.64, 138.85, 137.87, 135.03, 133.26, 133.23, 132.98, 130.39, 130.36, 129.46, 129.40, 128.88, 127.92, 127.23, 126.67, 126.31, 126.24, 124.09, 123.60, 117.92, 22.83, 21.68, 14.94, 14.33. **HRMS (ESI):** m/z calcd for $C_{27}H_{24}NO$ (+):378.1858, found: 378.1852.

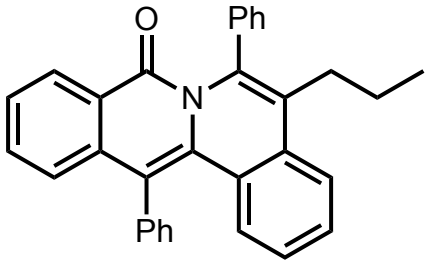
5-Methyl-6,13-diphenyl-*8H*-dibenzo[*a,g*]quinolizin-8-one 4ah



Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (37.4 mg, 0.21 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. Then, 1-phenyl-1-propyne (46.4 mg, 0.40 mmol) and AgTFA (89.3 mg, 0.44 mmol) was added, the mixture was stirred at 100°C for 24 h. **4ah** was yellow crystal obtained in 64% yield (52.6 mg). The product was isolated by column chromatography using 50% CH_2Cl_2 in

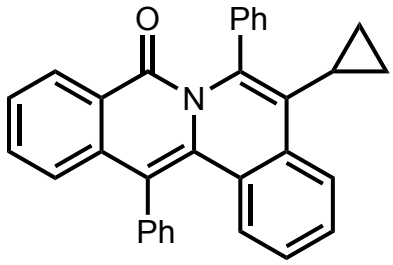
petroleum ether. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 8.14 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.61 – 7.57 (m, 2H), 7.56 – 7.51 (m, 3H), 7.48 – 7.41 (m, 3H), 7.39 – 7.32 (m, 5H), 7.29 – 7.26 (m, 2H), 7.09 (dd, *J* = 8.3, 0.7 Hz, 1H), 6.92 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 2.15 (s, 3H). **^{13}C NMR (126 MHz, CD_2Cl_2):** δ 162.57, 139.53, 138.74, 138.02, 135.95, 134.76, 134.71, 133.18, 133.07, 130.53, 130.03, 129.94, 129.62, 129.24, 129.02, 128.63, 128.16, 128.04, 127.27, 127.10, 127.04, 126.48, 124.46, 119.67, 117.75, 16.13. **HRMS (ESI):** m/z calcd for $C_{30}H_{22}NO$ (+):412.1701, found: 412.1697.

5-Propyl-6,13-diphenyl-*8H*-dibenzo[*a,g*]quinolizin-8-one 4ai



Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (37.4 mg, 0.21 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. Then, 1-phenyl-1-pentyne (57.6 mg, 0.40 mmol) and AgTFA (89.3 mg, 0.44 mmol) was added, the mixture was stirred at 100°C for 24 h. **4ai** was yellow crystal obtained in 60% yield (52.7 mg). The product was isolated by column chromatography using 50% CH_2Cl_2 in petroleum ether. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 8.11 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.62 – 7.50 (m, 5H), 7.47 – 7.45 (m, 2H), 7.43 – 7.40 (m, 1H), 7.38 – 7.31 (m, 5H), 7.30 – 7.27 (m, 2H), 7.11 (dd, *J* = 8.3, 0.8 Hz, 1H), 6.90 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 2.55 (dd, *J* = 8.7, 6.8 Hz, 2H), 1.53 – 1.48 (m, 2H), 0.73 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, CD_2Cl_2):** δ 162.45, 139.53, 138.66, 138.02, 136.41, 134.86, 133.35, 133.24, 133.12, 133.05, 130.58, 130.49, 130.40, 130.20, 129.73, 129.51, 128.98, 128.56, 128.14, 128.02, 127.21, 127.06, 126.95, 126.42, 124.57, 124.32, 117.59, 30.66, 23.80, 14.55. **HRMS (ESI):** m/z calcd for $C_{32}H_{26}NO$ (+):440.2014, found: 440.2011.

5-Cyclopropyl-6,13-diphenyl-*8H*-dibenzo[*a,g*]quinolizin-8-one 4aj



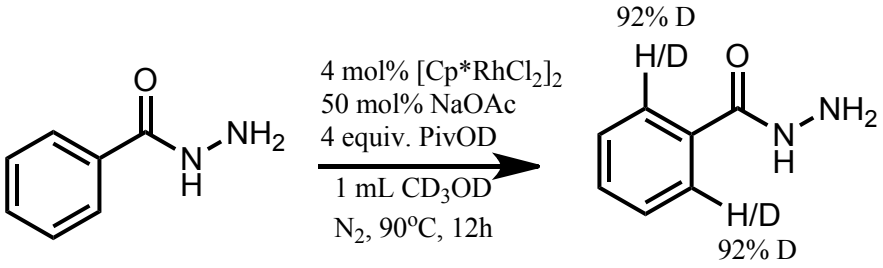
Following the general procedure, the reaction was carried out with benzoylhydrazine (27.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (4.9 mg, 0.008 mmol), 1,2-diphenylethyne (37.4 mg, 0.21 mmol), pivalic acid (81.6 mg, 0.80 mmol), NaOAc (8.2 mg, 0.10 mmol) and MeOH (1.0 mL) at 90°C for 12h. Then, 1-cyclopropyl-1-phenylethyne (56.8 mg, 0.40 mmol) and AgTFA (89.3 mg, 0.44 mmol) was added, the mixture was stirred at 100°C for 24 h. **4aj** was yellow crystal obtained in 55% yield (48.1 mg). The product was isolated by column chromatography using 50% CH_2Cl_2 in petroleum ether. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 8.14 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.99 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.62 –

7.58 (m, 1H), 7.54 – 7.48 (m, 4H), 7.47 – 7.42 (m, 3H), 7.34 (dt, *J* = 8.9, 3.2 Hz, 6H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.92 – 6.87 (m, 1H), 1.96 (tt, *J* = 8.4, 5.6 Hz, 1H), 0.70 – 0.62 (m, 2H), -0.04 (dt, *J* = 10.5, 5.5 Hz, 2H). **^{13}C NMR (126 MHz, CD_2Cl_2):** δ 162.85, 155.30, 139.42, 138.99, 138.42, 138.03, 135.40, 134.75, 133.19, 133.11, 132.11, 130.44, 129.84, 129.70, 129.32, 129.25, 128.98, 128.38, 128.02, 128.00, 127.28, 127.24, 126.73, 126.44, 125.78, 123.86, 117.70, 11.85, 10.21. **HRMS (ESI):** m/z calcd for $C_{32}H_{24}NO$ (+):438.1858, found: 438.1854.

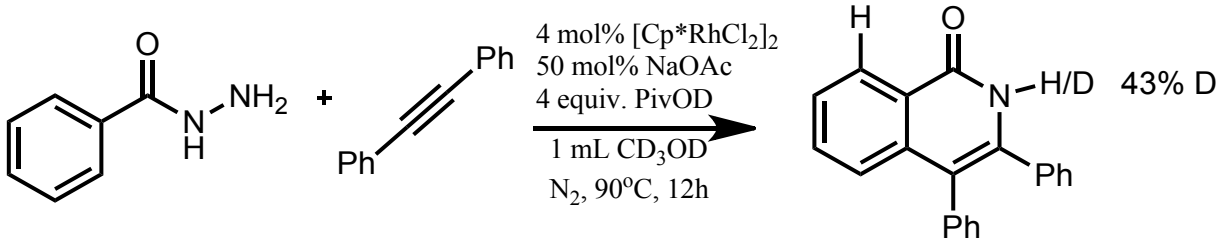
5. Mechanism Studies

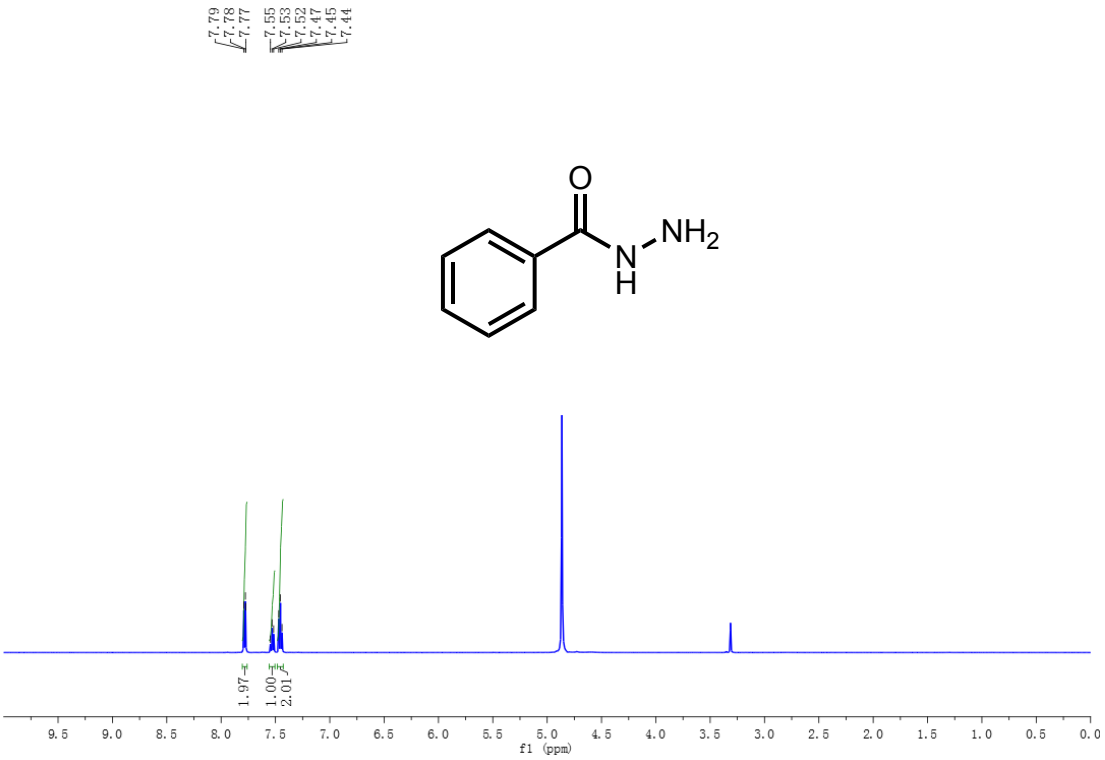
5.1 General procedure for the catalytic deuterium labeling experiments.

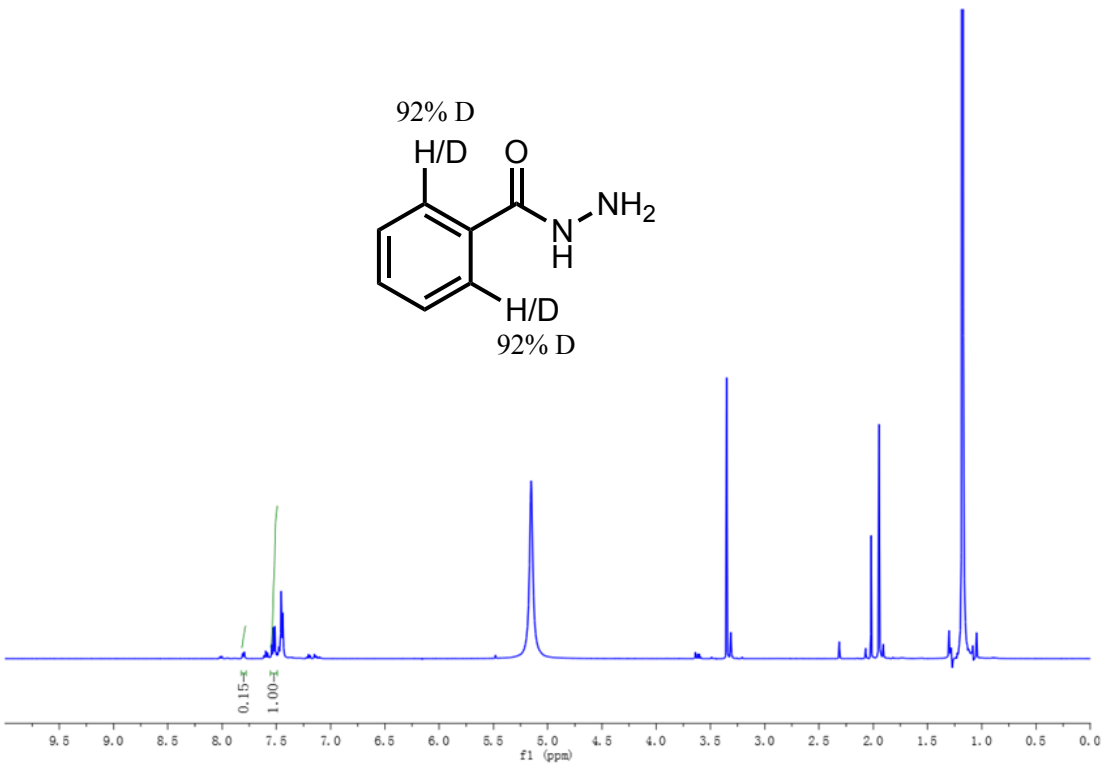
A mixture of benzoylhydrazine (1) (0.20 mmol, 1.0 equiv.), $[Cp^*RhCl_2]_2$ (4.0 mol %), PivOD (4 equiv.) and NaOAc (50.0 mmol %) were weighed into a 15ml pressure tube. CD_3OD (1.0 mL) was added and the mixture was stirred at 90°C for 12hours under N_2 atmosphere. After reaction, the mixture was subjected to ^{1}HNMR.

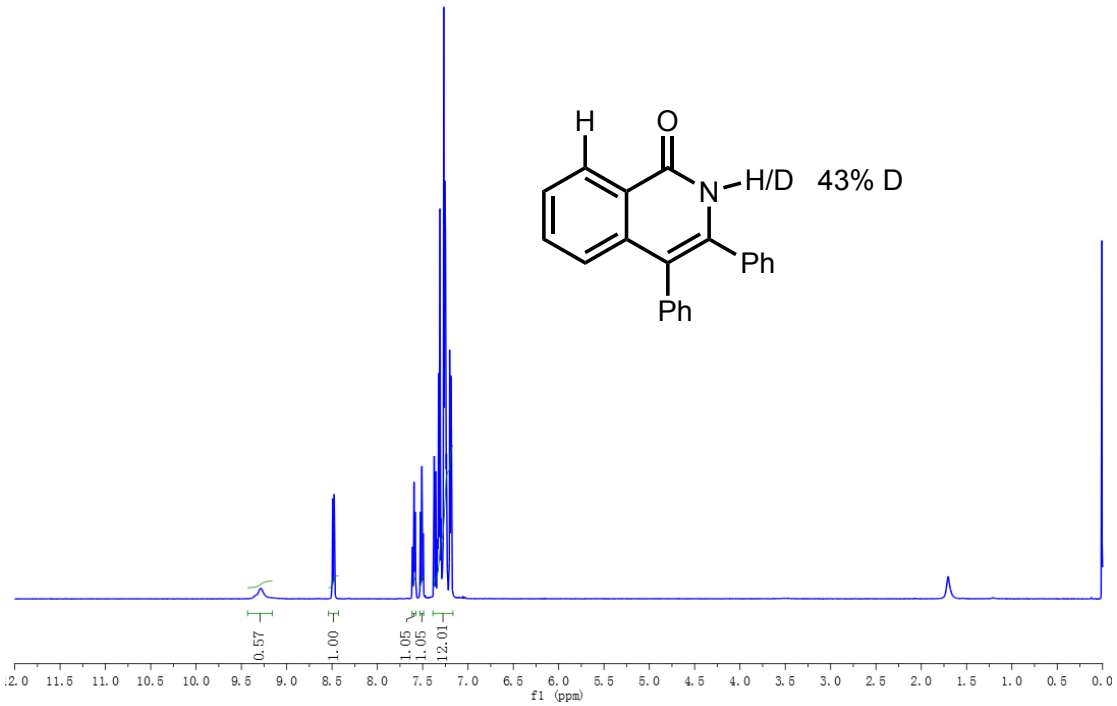


A mixture of benzoylhydrazine (1) (0.20 mmol, 1.0 equiv.), 1,2-diphenylethyne (1.2 equiv.), $[Cp^*RhCl_2]_2$ (4.0 mol %), PivOD (4 equiv.) and NaOAc (50.0 mmol %) were weighed into a 15ml pressure tube. CD_3OD (1.0 mL) was added and the mixture was stirred at 90°C for 12hours under N_2 atmosphere. The product was isolated by column chromatography using 20~50% EtOAc in petroleum ether and obtained in 90% yield (53.5 mg).




7.79
7.78
7.77
7.55
7.53
7.52
7.47
7.45
7.44
O
NH2
N
H
1.97
1.00
2.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

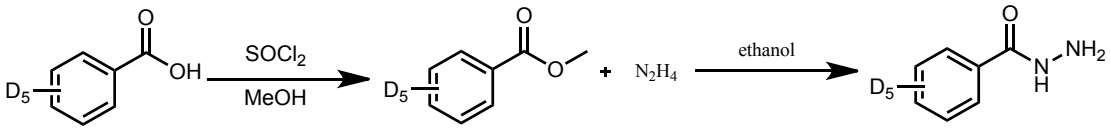

92% D
H/D
O
NH2
N
H
H/D
92% D
0.15
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

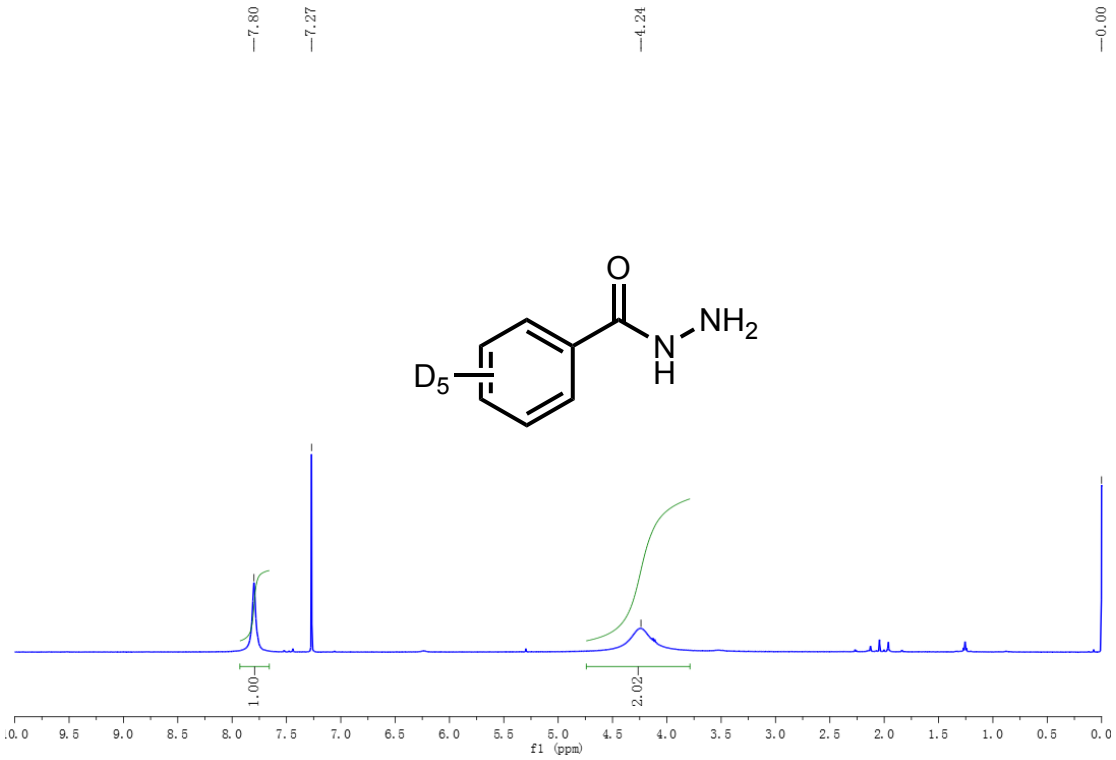


5.2 KIE Experiment

Synthesis of deuterated substrate **1a-d$_5$**

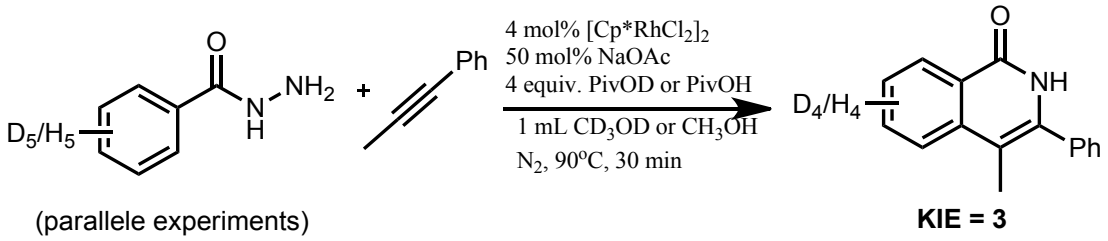
Following the general procedure for the synthesis of substrate 1, deuterated substrate **1a-d$_5$** was obtained from benzoic-D_5 acid.

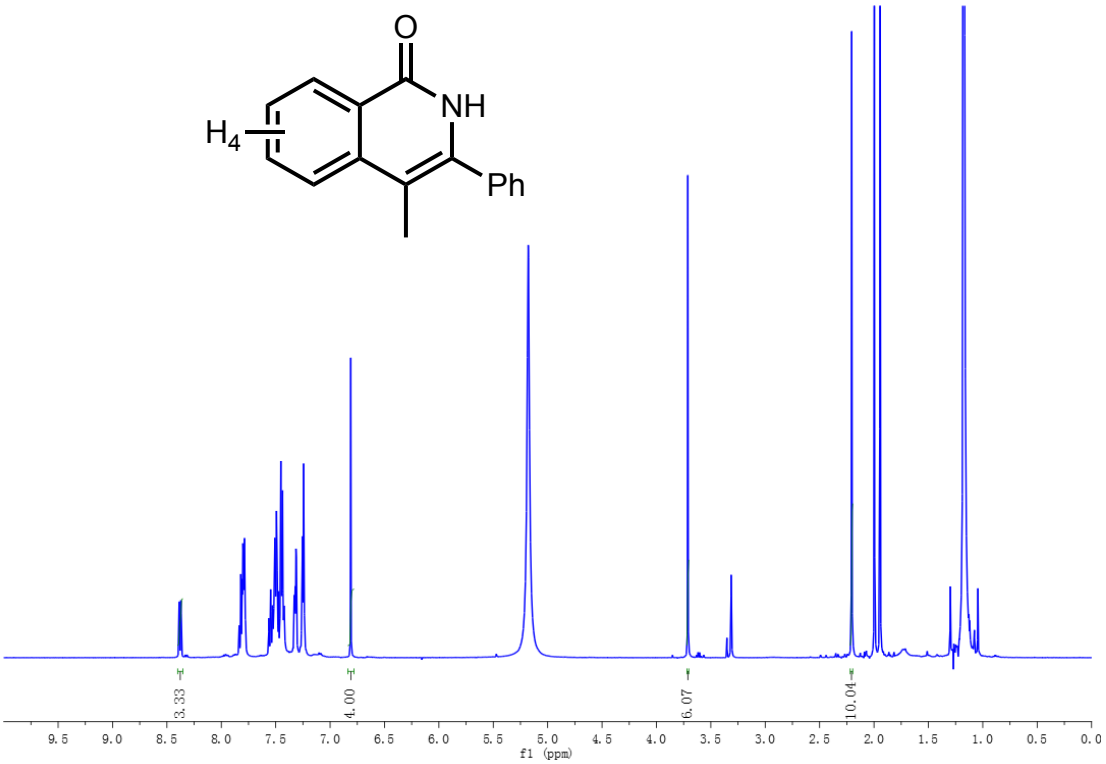


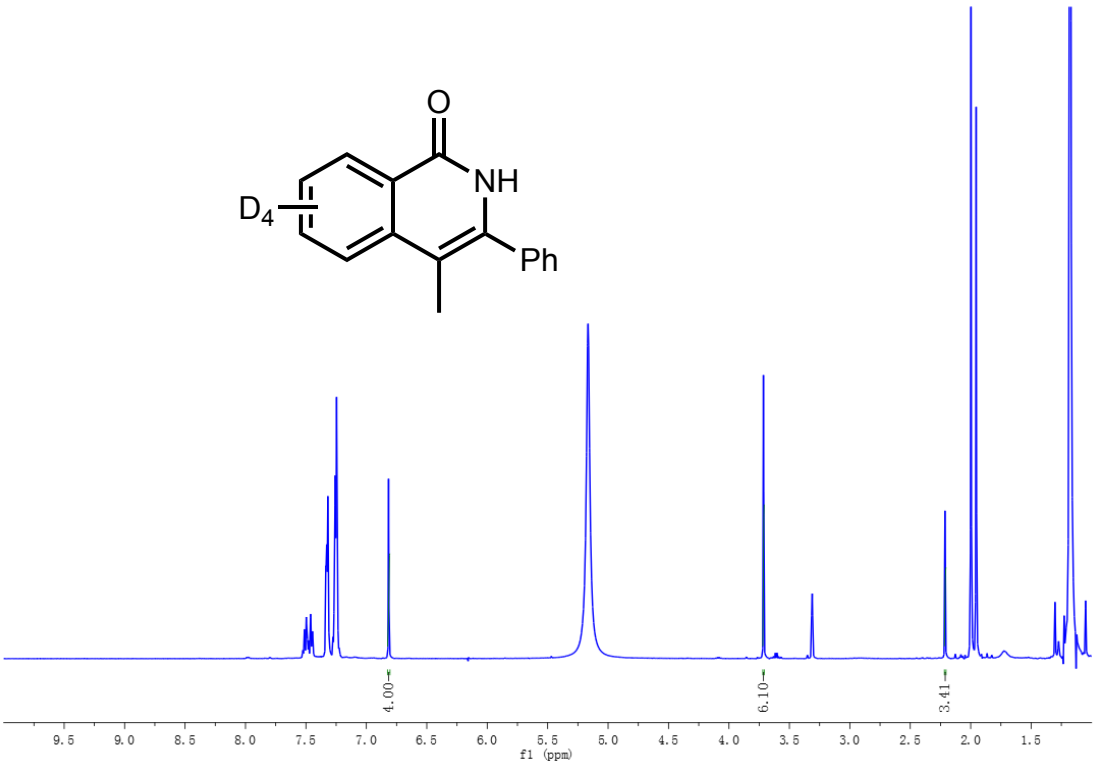


5.3 Determination of kinetic isotope effect from two parallel reactions.

A mixture of benzoylhydrazine (1) (0.20 mmol, 1.0 equiv.), 1-phenyl-1-propyne (1.2 equiv.), $[Cp^*RhCl_2]_2$ (4.0 mol %), PivOH or PivOD (4 equiv.) and NaOAc (50.0 mmol %) were weighed into a 15ml pressure tube. MeOH or CD_3OD (1.0 mL) was added and the mixture was stirred at 90°C for 10 min under N_2 atmosphere. After reaction, 1,4-dimethoxybenzene (0.025 mmol) was added as an internal standard. Then the mixture was subjected to ^{1}HNMR.




O
NH
H4
Ph
3.33
4.00
6.07
10.04
f1 (ppm)


O
NH
D4
Ph
4.00
6.10
3.41
f1 (ppm)

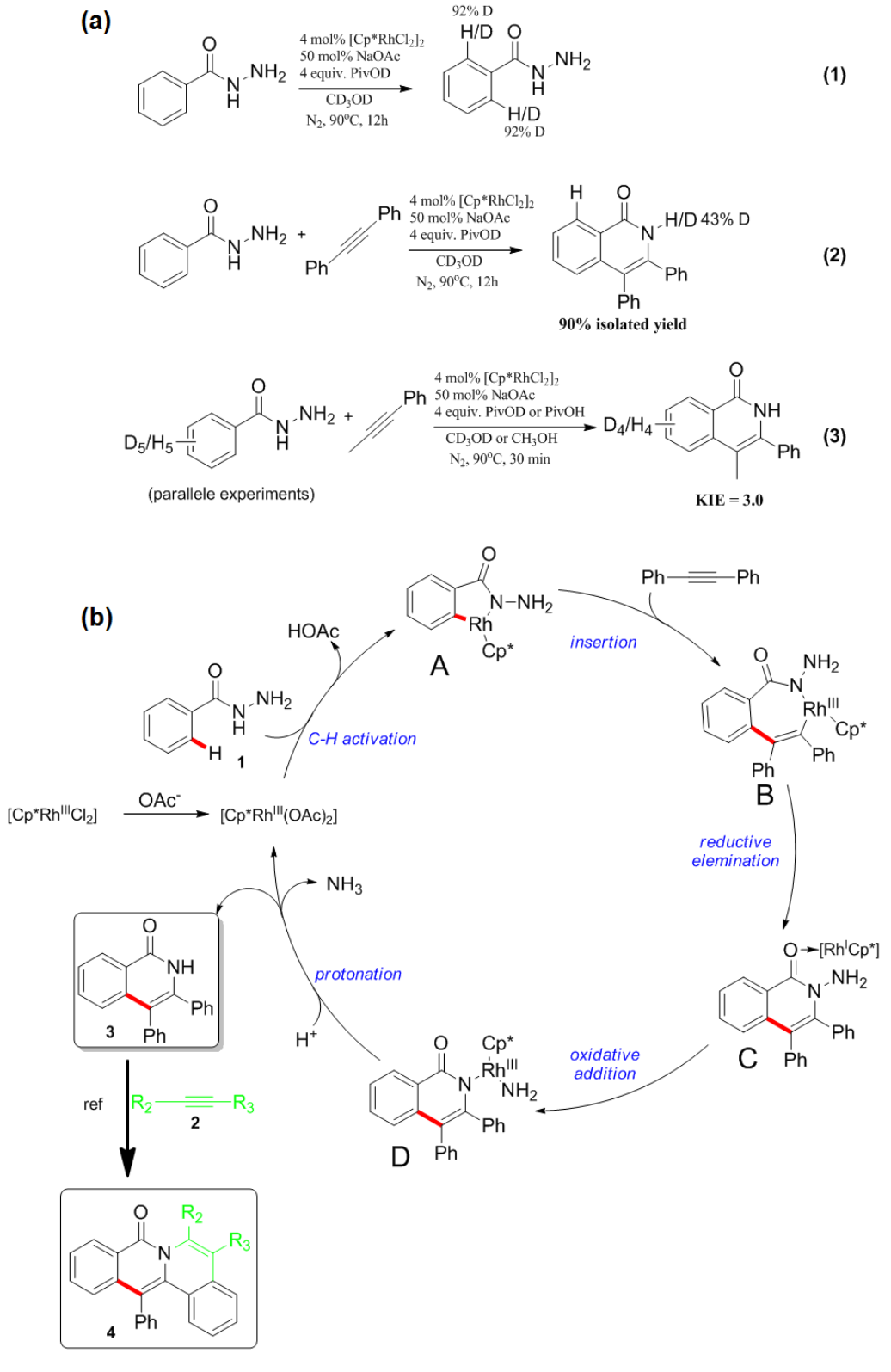


Fig. S1 Mechanistic studies. (a) Deuteration experiments and the study of the kinetic isotope effect (KIE). (b) Proposed mechanism of the hydrazine-directed redox-neutral C–H activation/annulation of benzoylhydrazines and alkynes.

6. Optical properties of compound 3, 4

Table S2 Optical properties of **3** and **4**.

Compound	λ_{abs}/nm[a]	log ε	λ_{em}/nm[b]		ϕ[c]		ϕ_P/ϕ_{Sol}
			THF	**Powders**	**THF**	**Powders**	
3aa	309	4.27	391	412	0.008	0.035	4.4
3ba	314	4.2	393	396	0.007	0.146	20.9
3ca	313	4.26	388	406	0.008	0.078	9.8
3da	312	4.08	415	425	0.006	0.131	21.8
3ea	314	4.20	397	416	0.009	0.027	3
3fa	313	3.58	396	416	0.003	0.003	1
3ga	314	4.31	398	403	0.002	0.003	1.5
3ha	312	4.26	418	415	0.047	0.054	1.1
3ia	308	3.46	391	415	0.008	0.036	4.5
3ja	308	4.15	394	400	0.011	0.028	2.5
3ka	312	4.3	406	427	0.005	0.012	2.4
3la	312	3.73	406	406	0.002	0.002	1
3ma	338	3.91	459	467	0.267	0.123	0.5
3ab	312	4.09	394	435	0.009	0.038	4.2
3ac	314	3.98	393	410	0.008	0.047	5.9
3ad	310	4.08	389	431	0.006	0.026	4.3
3ae	313	4.08	392	437	0.006	0.086	14.3
3af	317	4.35	419	402	0.007	0.077	11
3ag	321	4.36	385	427	0.015	0.019	1.3
3ah	339	3.75	389	424	0.014	0.008	0.6
3ai	305	4.29	389	417	0.011	0.025	2.3
3aj	305	4.24	386	389	0.008	0.023	2.9
3ak	308	4.52	387	414	0.010	0.027	2.7
4aa	301,395	4.43,4.16	520	520	0.003	0.033	11
4ba	300,394	4.46,4.14	500	500	0.003	0.109	36.3
4ca	301,395	4.34,4.02	519	519	0.002	0.041	20.5
4da	303,396	4.27,4.02	525	525	0.002	0.045	22.5
4ea	303,399	4.34,4.06	524	534	0.002	0.025	8.3
4fa	315,403	4.26,3.90	550	550	0.002	0.016	8
4ab	301,395	4.61,4.33	524	524	0.003	0.045	15
4ac	301,394	4.54,4.27	522	522	0.003	0.033	11
4ad	300,394	4.52,4.25	520	520	0.002	0.022	11
4ae	301,394	4.55,4.23	519	519	0.003	0.030	10
4af	298,395	4.29,4.03	517	517	0.002	0.025	12.5
4ag	298,396	4.72,4.40	527	527	0.002	0.027	13.5
4ah	298,394	4.58,4.29	530	530	0.002	0.018	9

4ai	298,395	3.93,3.65	520	520	0.002	0.029	14.5
4aj	299,395	3.96,3.67	526	526	0.002	0.015	7.5

[a] Absorption maximum in THF. [b] Emission maximum excited at 310 nm for **3**, 395 nm for **4**. [c] Absolute quantum yield determined by an integrating sphere system.

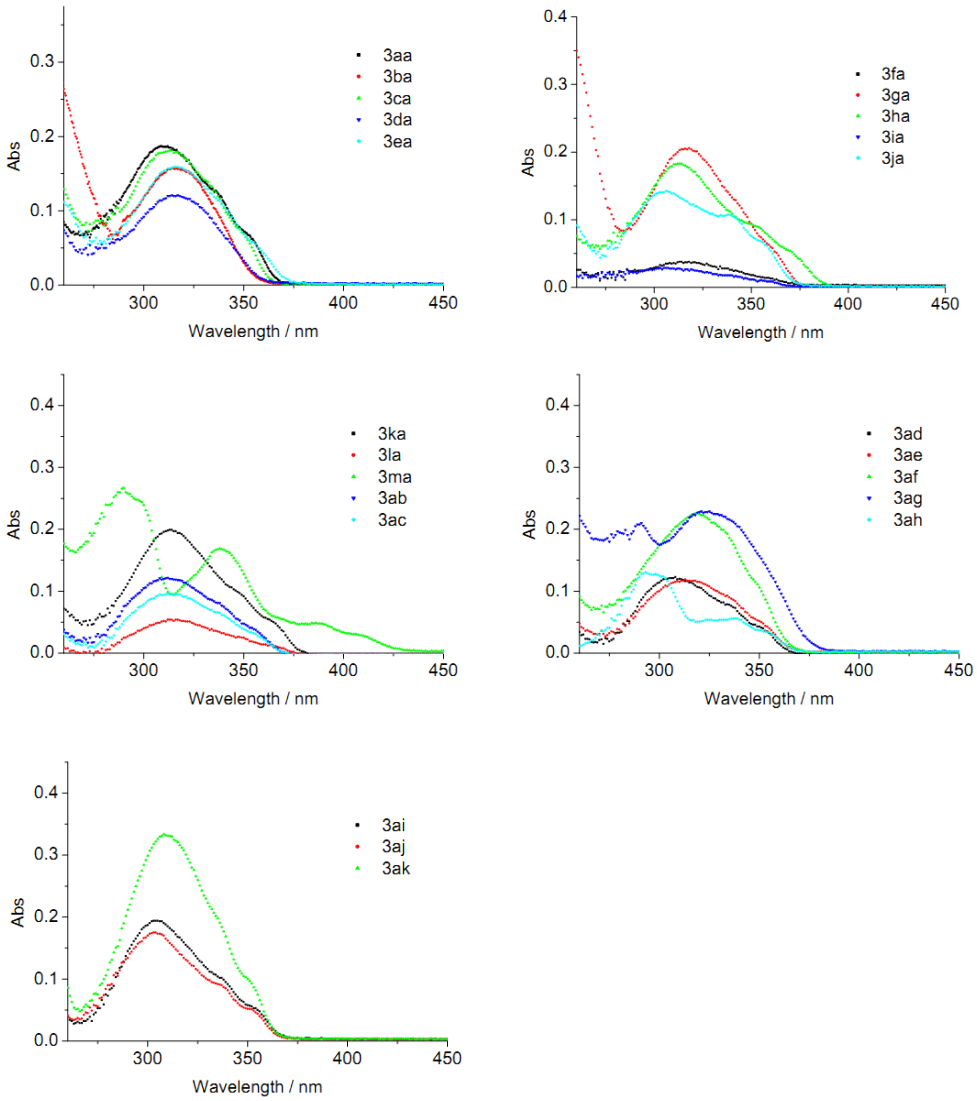


Fig. S2 Absorption spectra of **3** in THF solution (concentration: 10 μM).

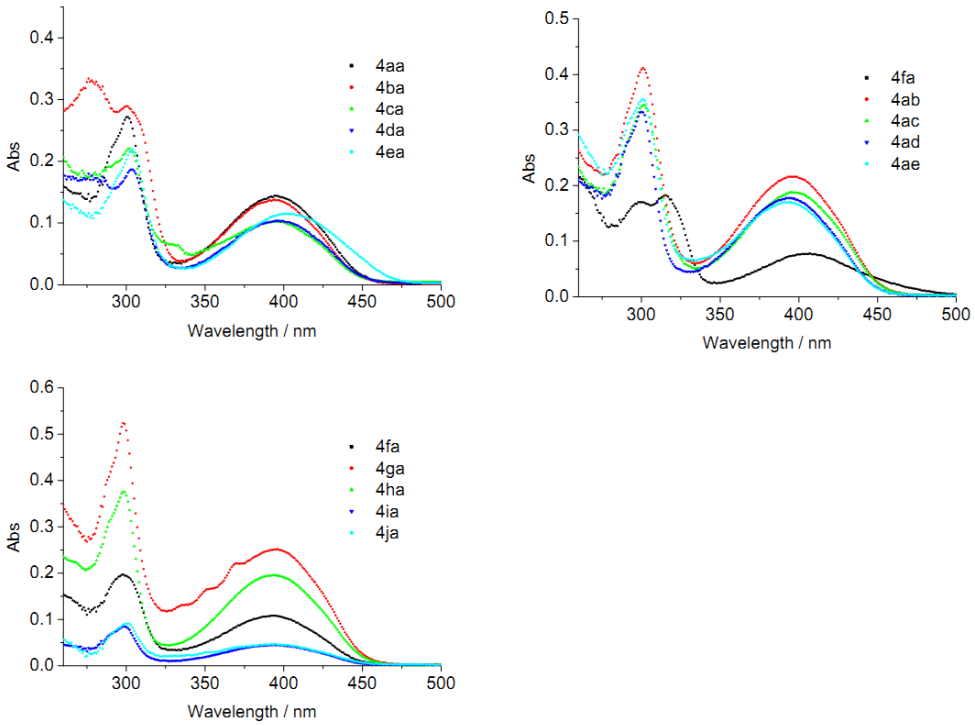
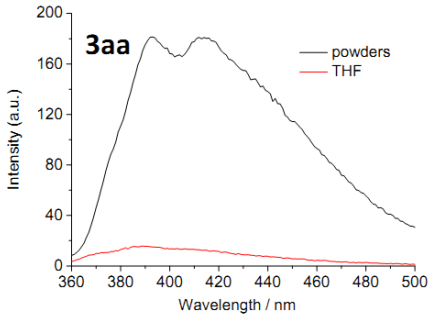
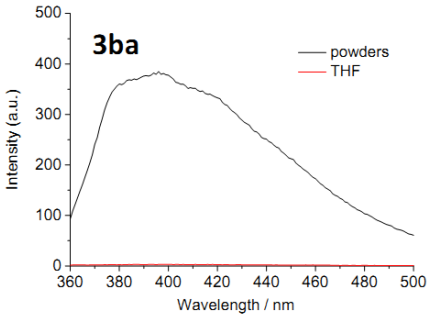
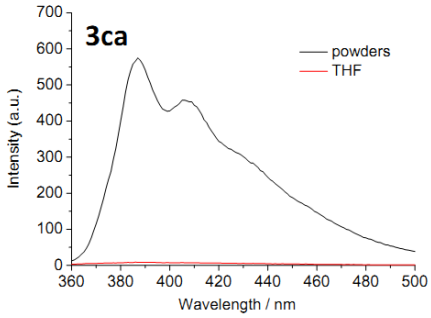
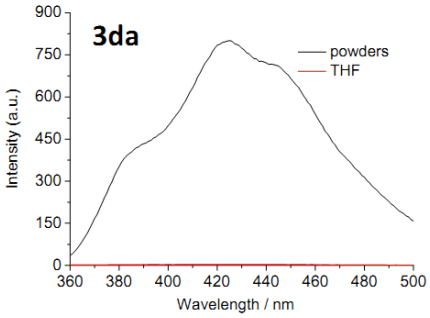


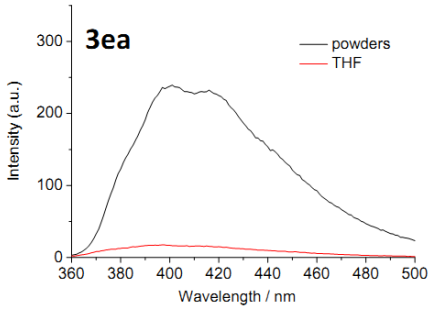
Fig. S3 Absorption spectra of **4** in THF solution (concentration: 10 μM).

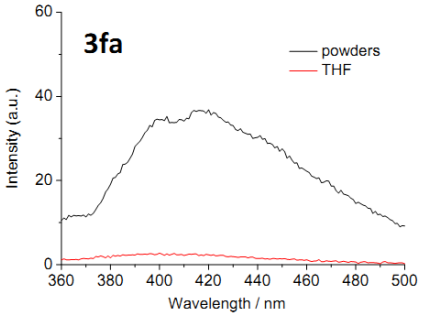

3aa
powders
THF
Intensity (a.u.)
Wavelength / nm

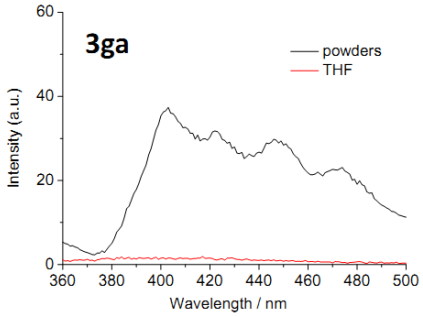

3ba
powders
THF
Intensity (a.u.)
Wavelength / nm

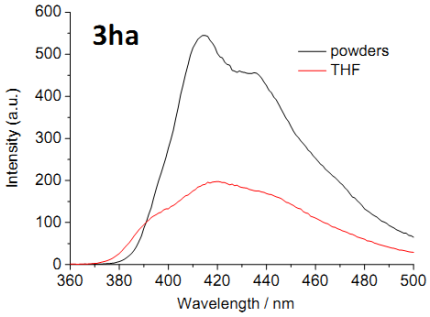

3ca
powders
THF
Intensity (a.u.)
Wavelength / nm

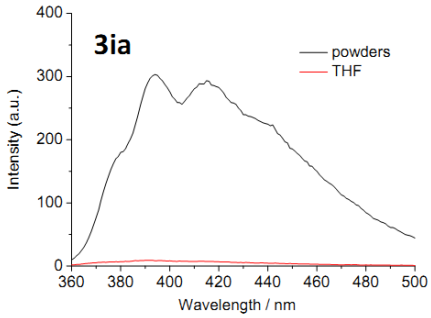

3da
powders
THF
Intensity (a.u.)
Wavelength / nm

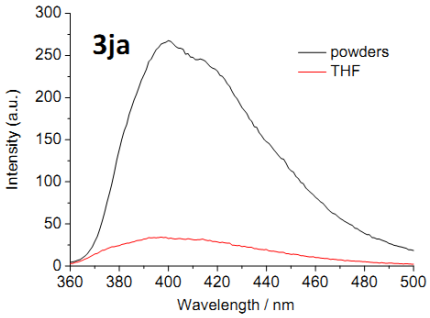

3ea
powders
THF
Intensity (a.u.)
Wavelength / nm

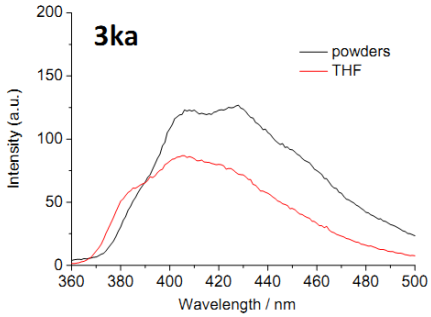

3fa
powders
THF
Intensity (a.u.)
Wavelength / nm

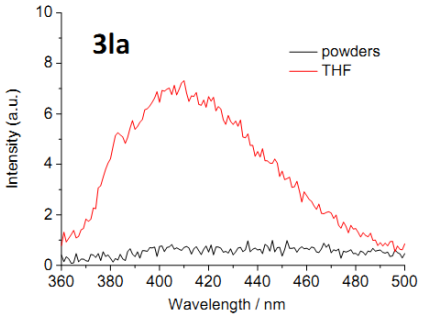

3ga
powders
THF
Intensity (a.u.)
Wavelength / nm

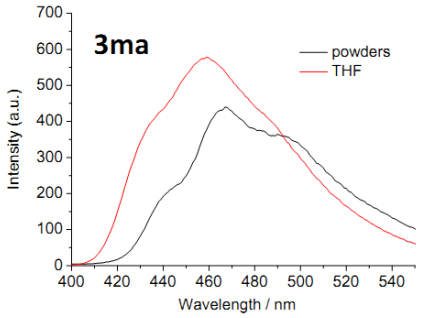

3ha
powders
THF
Intensity (a.u.)
Wavelength / nm

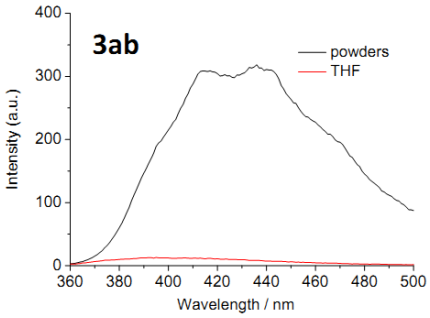

3ia
powders
THF
Intensity (a.u.)
Wavelength / nm

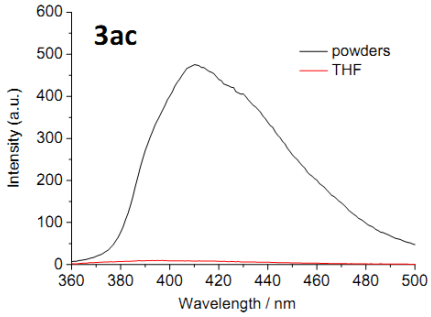

3ja
powders
THF
Intensity (a.u.)
Wavelength / nm

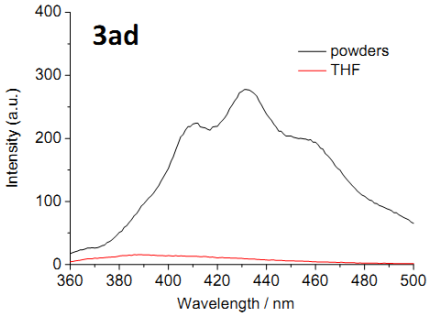

3ka
powders
THF
Intensity (a.u.)
Wavelength / nm


3la
powders
THF
Intensity (a.u.)
Wavelength / nm


3ma
powders
THF
Intensity (a.u.)
Wavelength / nm


3ab
powders
THF
Intensity (a.u.)
Wavelength / nm


3ac
powders
THF
Intensity (a.u.)
Wavelength / nm


3ad
powders
THF
Intensity (a.u.)
Wavelength / nm

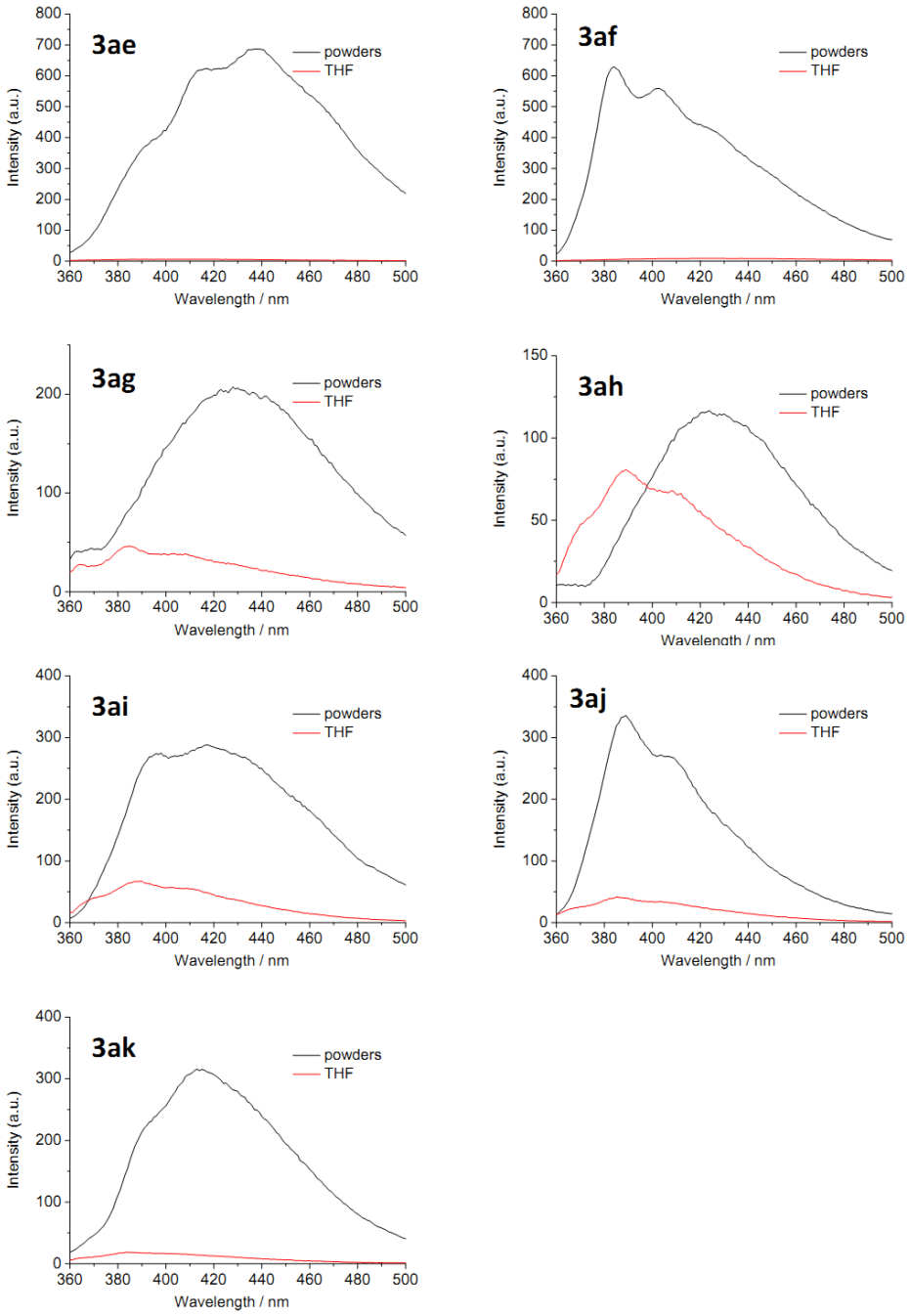
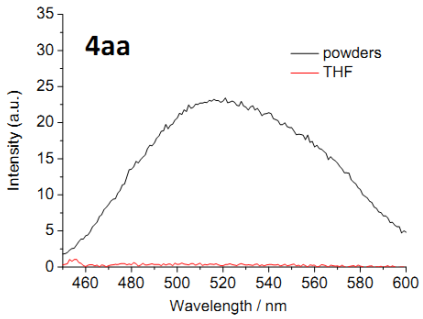
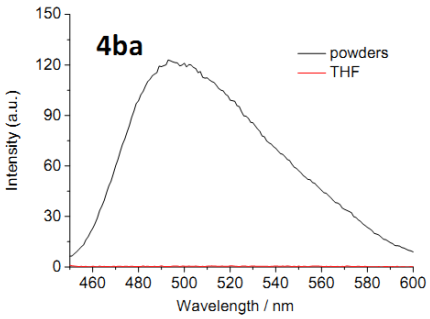
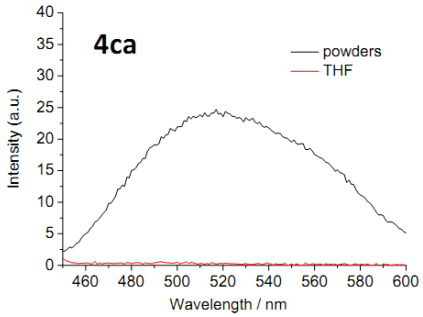
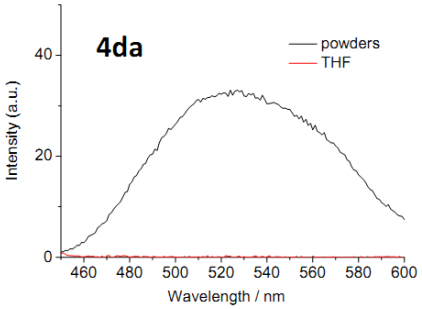


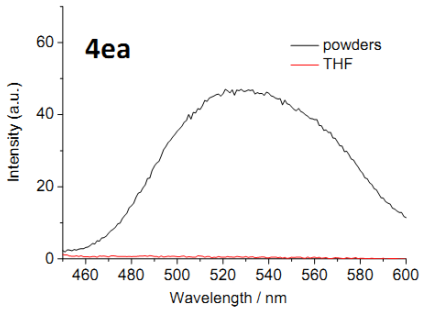
Fig. S4 Emission spectra of **3** in powders and in THF solution with an excitation wavelength of 310 nm (concentration: 10 μM).

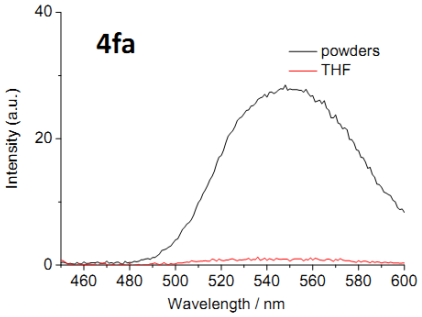

4aa
powders
THF
Intensity (a.u.)
Wavelength / nm

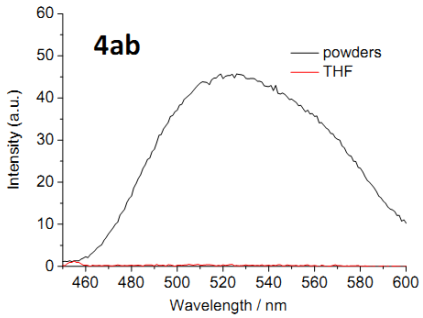

4ba
powders
THF
Intensity (a.u.)
Wavelength / nm

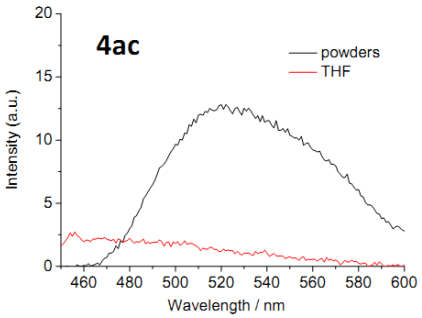

4ca
powders
THF
Intensity (a.u.)
Wavelength / nm


4da
powders
THF
Intensity (a.u.)
Wavelength / nm


4ea
powders
THF
Intensity (a.u.)
Wavelength / nm


4fa
powders
THF
Intensity (a.u.)
Wavelength / nm


4ab
powders
THF
Intensity (a.u.)
Wavelength / nm


4ac
powders
THF
Intensity (a.u.)
Wavelength / nm

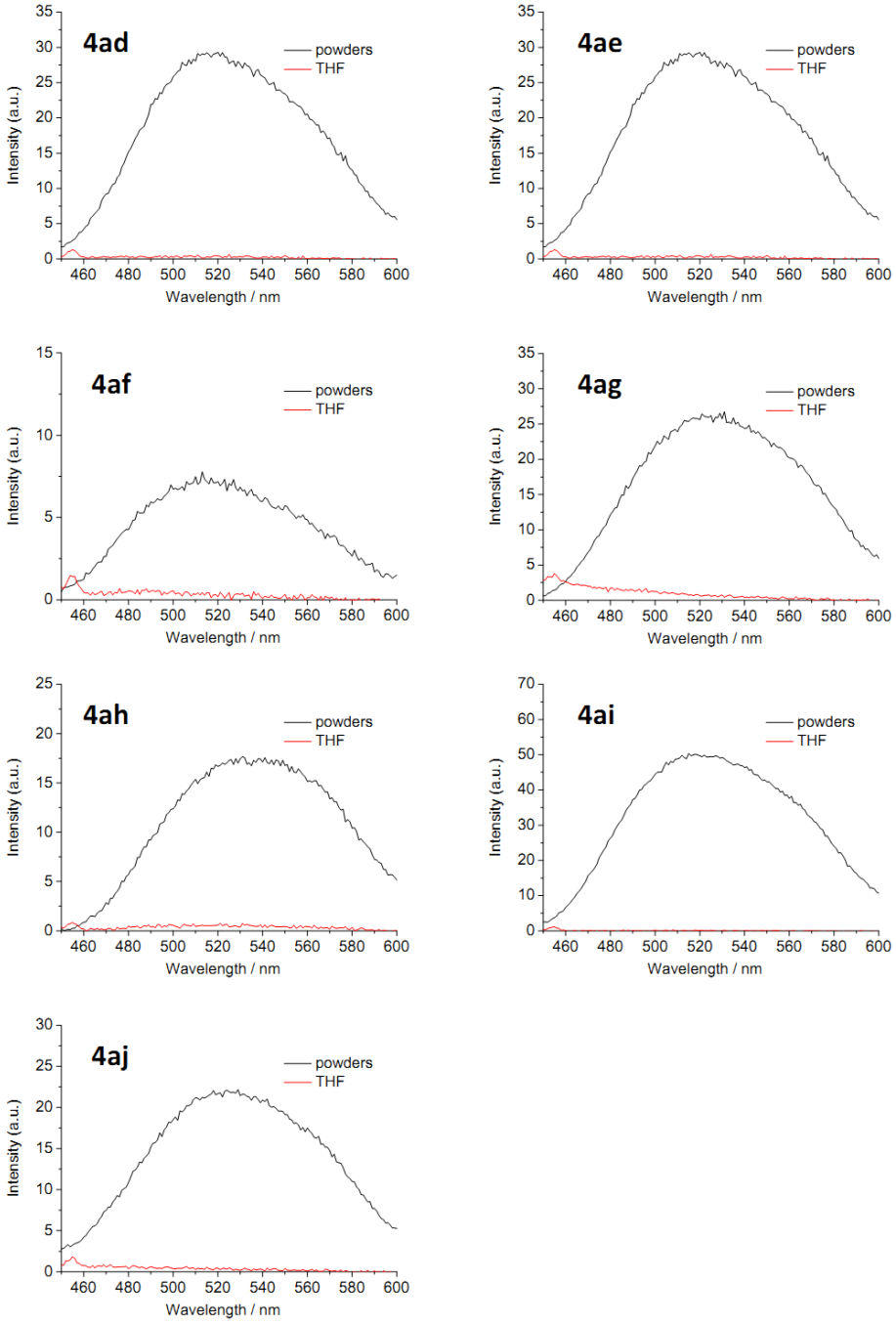


Fig. S5 Emission spectra of **4** in powders and in THF solution with an excitation wavelength of 395 nm (concentration: 10 μM).

7. X-ray Crystallographic Data

Crystal data and structure refinement for **3ak**

Fig. S6

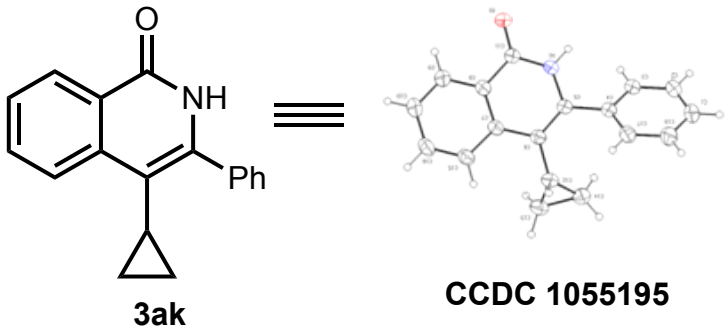


Table S3 Crystal data and structure refinement for d1.

Identification code	shelx	
Empirical formula	C18 H15 N O	
Formula weight	261.31	
Temperature	293(2) K	
Wavelength	1.54187 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 12.7421(2) Å	α= 90°.
	b = 7.51390(10) Å	β= 106.877(8)°.
	c = 14.7733(10) Å	γ = 90°.
Volume	1353.52(11) $Å^3$	
Z	4	
Density (calculated)	1.282 Mg/m^3	
Absorption coefficient	0.622 mm^{-1}	
F(000)	552	
Crystal size	0.20 x 0.20 x 0.20 mm^3	
Theta range for data collection	6.672 to 68.270°.	
Index ranges	-15<=h<=15, -8<=k<=9, -17<=l<=17	
Reflections collected	17762	

Independent reflections	2435 [R(int) = 0.0536]
Completeness to theta = 67.687°	98.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.883 and 0.706
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2435 / 1 / 184
Goodness-of-fit on F^2	1.124
Final R indices [I>2sigma(I)]	R1 = 0.0468, wR2 = 0.1214
R indices (all data)	R1 = 0.0537, wR2 = 0.1303
Extinction coefficient	n/a
Largest diff. peak and hole	0.191 and -0.224 e.$Å^{-3}$

Table S4 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for d1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-967(1)	464(2)	548(1)	66(1)
N(1)	849(1)	757(2)	1272(1)	50(1)
C(1)	4752(1)	1259(3)	1303(1)	76(1)
C(2)	3986(1)	-16(2)	906(1)	68(1)
C(3)	3020(1)	-120(2)	1154(1)	55(1)
C(4)	2814(1)	1053(2)	1812(1)	50(1)
C(5)	1762(1)	976(2)	2056(1)	46(1)
C(6)	1628(1)	1115(2)	2933(1)	46(1)
C(7)	521(1)	1103(2)	3017(1)	45(1)
C(8)	-382(1)	894(2)	2211(1)	45(1)
C(9)	-1453(1)	871(2)	2281(1)	55(1)
C(10)	-1641(1)	1058(2)	3141(1)	63(1)
C(11)	-209(1)	687(2)	1287(1)	49(1)

C(12)	2558(1)	1266(2)	3820(1)	57(1)
C(13)	2764(1)	-191(3)	4545(1)	73(1)
C(14)	3549(1)	109(3)	3989(1)	80(1)
C(15)	296(1)	1300(2)	3891(1)	56(1)
C(16)	-759(1)	1286(2)	3944(1)	63(1)
C(17)	3598(1)	2338(2)	2206(1)	63(1)
C(18)	4559(1)	2433(3)	1951(1)	77(1)

Table S5 Bond lengths [Å] and angles [°] for d1.

O(1)-C(11)	1.2418(16)
N(1)-C(11)	1.3559(17)
N(1)-C(5)	1.3924(16)
N(1)-H(1N)	0.861(14)
C(1)-C(2)	1.372(2)
C(1)-C(18)	1.375(3)
C(1)-H(1)	0.9300
C(2)-C(3)	1.3850(19)
C(2)-H(2)	0.9300
C(3)-C(4)	1.393(2)
C(3)-H(3)	0.9300
C(4)-C(17)	1.3904(19)
C(4)-C(5)	1.4863(17)
C(5)-C(6)	1.3591(19)
C(6)-C(7)	1.4519(18)
C(6)-C(12)	1.4945(18)
C(7)-C(8)	1.4045(18)
C(7)-C(15)	1.4090(19)
C(8)-C(9)	1.3986(18)

C(8)-C(11)	1.4517(18)
C(9)-C(10)	1.366(2)
C(9)-H(9)	0.9300
C(10)-C(16)	1.387(2)
C(10)-H(10)	0.9300
C(12)-C(14)	1.493(2)
C(12)-C(13)	1.501(2)
C(12)-H(12)	0.9800
C(13)-C(14)	1.484(2)
C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(15)-C(16)	1.369(2)
C(15)-H(15)	0.9300
C(16)-H(16)	0.9300
C(17)-C(18)	1.382(2)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300

C(11)-N(1)-C(5)	125.81(12)
C(11)-N(1)-H(1N)	115.2(10)
C(5)-N(1)-H(1N)	118.7(10)
C(2)-C(1)-C(18)	119.82(14)
C(2)-C(1)-H(1)	120.1
C(18)-C(1)-H(1)	120.1
C(1)-C(2)-C(3)	120.18(15)
C(1)-C(2)-H(2)	119.9
C(3)-C(2)-H(2)	119.9
C(2)-C(3)-C(4)	120.75(13)

C(2)-C(3)-H(3)	119.6
C(4)-C(3)-H(3)	119.6
C(17)-C(4)-C(3)	118.23(12)
C(17)-C(4)-C(5)	121.03(12)
C(3)-C(4)-C(5)	120.69(11)
C(6)-C(5)-N(1)	119.73(12)
C(6)-C(5)-C(4)	126.85(11)
N(1)-C(5)-C(4)	113.42(11)
C(5)-C(6)-C(7)	118.42(12)
C(5)-C(6)-C(12)	123.67(12)
C(7)-C(6)-C(12)	117.92(11)
C(8)-C(7)-C(15)	117.09(12)
C(8)-C(7)-C(6)	120.31(12)
C(15)-C(7)-C(6)	122.61(12)
C(9)-C(8)-C(7)	120.96(12)
C(9)-C(8)-C(11)	119.13(12)
C(7)-C(8)-C(11)	119.90(11)
C(10)-C(9)-C(8)	120.41(14)
C(10)-C(9)-H(9)	119.8
C(8)-C(9)-H(9)	119.8
C(9)-C(10)-C(16)	119.38(13)
C(9)-C(10)-H(10)	120.3
C(16)-C(10)-H(10)	120.3
O(1)-C(11)-N(1)	120.90(12)
O(1)-C(11)-C(8)	123.32(12)
N(1)-C(11)-C(8)	115.78(12)
C(14)-C(12)-C(6)	121.32(13)
C(14)-C(12)-C(13)	59.44(11)
C(6)-C(12)-C(13)	120.04(13)
C(14)-C(12)-H(12)	114.9

C(6)-C(12)-H(12)	114.9
C(13)-C(12)-H(12)	114.9
C(14)-C(13)-C(12)	60.03(11)
C(14)-C(13)-H(13A)	117.8
C(12)-C(13)-H(13A)	117.8
C(14)-C(13)-H(13B)	117.8
C(12)-C(13)-H(13B)	117.8
H(13A)-C(13)-H(13B)	114.9
C(13)-C(14)-C(12)	60.53(11)
C(13)-C(14)-H(14A)	117.7
C(12)-C(14)-H(14A)	117.7
C(13)-C(14)-H(14B)	117.7
C(12)-C(14)-H(14B)	117.7
H(14A)-C(14)-H(14B)	114.8
C(16)-C(15)-C(7)	121.00(14)
C(16)-C(15)-H(15)	119.5
C(7)-C(15)-H(15)	119.5
C(15)-C(16)-C(10)	121.16(13)
C(15)-C(16)-H(16)	119.4
C(10)-C(16)-H(16)	119.4
C(18)-C(17)-C(4)	120.55(14)
C(18)-C(17)-H(17)	119.7
C(4)-C(17)-H(17)	119.7
C(1)-C(18)-C(17)	120.48(15)
C(1)-C(18)-H(18)	119.8
C(17)-C(18)-H(18)	119.8

Symmetry transformations used to generate equivalent atoms:

Table S6 Anisotropic displacement parameters ($Å^2 x\ 10^3$)for d1. The anisotropic

displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	48(1)	106(1)	40(1)	-6(1)	7(1)	2(1)
N(1)	47(1)	69(1)	34(1)	-2(1)	13(1)	0(1)
C(1)	57(1)	114(1)	65(1)	-3(1)	30(1)	-13(1)
C(2)	60(1)	99(1)	49(1)	-7(1)	23(1)	1(1)
C(3)	50(1)	73(1)	41(1)	-3(1)	13(1)	-3(1)
C(4)	48(1)	62(1)	38(1)	3(1)	12(1)	-2(1)
C(5)	47(1)	51(1)	38(1)	-1(1)	11(1)	-1(1)
C(6)	50(1)	48(1)	39(1)	-2(1)	12(1)	1(1)
C(7)	54(1)	42(1)	40(1)	0(1)	16(1)	4(1)
C(8)	51(1)	45(1)	42(1)	1(1)	16(1)	3(1)
C(9)	51(1)	62(1)	54(1)	-3(1)	18(1)	0(1)
C(10)	60(1)	71(1)	66(1)	-2(1)	32(1)	4(1)
C(11)	47(1)	59(1)	40(1)	1(1)	11(1)	1(1)
C(12)	56(1)	74(1)	39(1)	-6(1)	8(1)	-1(1)
C(13)	68(1)	109(1)	41(1)	9(1)	12(1)	15(1)
C(14)	56(1)	129(2)	51(1)	12(1)	10(1)	20(1)
C(15)	65(1)	62(1)	42(1)	-3(1)	19(1)	8(1)
C(16)	74(1)	73(1)	52(1)	-1(1)	33(1)	10(1)
C(17)	61(1)	75(1)	55(1)	-7(1)	22(1)	-14(1)
C(18)	66(1)	100(1)	68(1)	-9(1)	26(1)	-28(1)

Table S7 Hydrogen bonds for d1 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

N(1)-H(1N)...O(1)#1	0.861(14)	2.039(14)	2.8855(15)	167.5(15)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z

Crystal data and structure refinement for **4ha**

Fig. S7

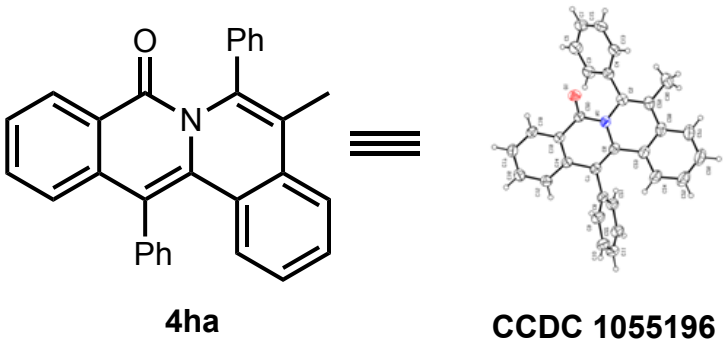


Table S8 Crystal data and structure refinement for b3.

Identification code	shelx	
Empirical formula	C30 H21 N O	
Formula weight	411.48	
Temperature	293(2) K	
Wavelength	1.54187 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 11.1528(2) Å	α= 90°.
	b = 12.1629(2) Å	β= 90°.
	c = 32.522(2) Å	γ = 90°.
Volume	4411.6(3) $Å^3$	
Z	8	

Density (calculated)	1.239 Mg/m^3
Absorption coefficient	0.578 mm^{-1}
F(000)	1728
Crystal size	0.200 x 0.200 x 0.200 mm^3
Theta range for data collection	6.739 to 68.446°.
Index ranges	-12<=h<=13, -14<=k<=14, -39<=l<=38
Reflections collected	51493
Independent reflections	4022 [R(int) = 0.0435]
Completeness to theta = 67.687°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.904 and 0.741
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4022 / 0 / 290
Goodness-of-fit on F^2	1.093
Final R indices [I>2sigma(I)]	R1 = 0.0417, wR2 = 0.1077
R indices (all data)	R1 = 0.0461, wR2 = 0.1112
Extinction coefficient	n/a
Largest diff. peak and hole	0.141 and -0.165 $e.Å^{-3}$

Table S9 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for b3. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-1745(1)	9152(1)	873(1)	58(1)
N(1)	58(1)	9196(1)	1210(1)	47(1)
C(1)	-3412(2)	6702(1)	1570(1)	76(1)
C(2)	-2325(2)	6395(1)	1410(1)	75(1)
C(3)	-1364(1)	7109(1)	1421(1)	63(1)
C(4)	-1483(1)	8148(1)	1594(1)	52(1)

C(5)	-451(1)	8921(1)	1600(1)	50(1)
C(6)	1270(1)	9547(1)	1183(1)	49(1)
C(7)	1889(1)	9370(1)	827(1)	49(1)
C(8)	3188(1)	9635(1)	773(1)	50(1)
C(9)	3542(1)	10488(1)	516(1)	63(1)
C(10)	4737(1)	10705(1)	446(1)	68(1)
C(11)	5602(1)	10064(1)	626(1)	66(1)
C(12)	-3541(1)	7718(1)	1747(1)	70(1)
C(13)	-2583(1)	8440(1)	1762(1)	59(1)
C(14)	1265(1)	8932(1)	471(1)	47(1)
C(15)	1859(1)	8618(1)	106(1)	57(1)
C(16)	1220(1)	8298(1)	-234(1)	64(1)
C(17)	-29(1)	8287(1)	-228(1)	62(1)
C(18)	-629(1)	8570(1)	124(1)	53(1)
C(19)	10(1)	8874(1)	476(1)	45(1)
C(20)	-656(1)	9101(1)	853(1)	45(1)
C(21)	4069(1)	9003(1)	957(1)	56(1)
C(22)	5270(1)	9219(1)	881(1)	65(1)
C(23)	1687(1)	10166(1)	1548(1)	58(1)
C(24)	2606(2)	10944(2)	1526(1)	84(1)
C(25)	2947(2)	11535(2)	1869(1)	108(1)
C(26)	2389(2)	11368(2)	2241(1)	103(1)
C(27)	1468(2)	10636(2)	2267(1)	84(1)
C(28)	1087(1)	10026(1)	1925(1)	61(1)
C(29)	72(1)	9274(1)	1949(1)	60(1)
C(30)	-356(2)	8901(2)	2365(1)	92(1)

Table S10 Bond lengths [Å] and angles [°] for b3.

O(1)-C(20)	1.2184(13)
N(1)-C(20)	1.4128(14)
N(1)-C(6)	1.4191(15)
N(1)-C(5)	1.4285(15)
C(1)-C(2)	1.370(2)
C(1)-C(12)	1.371(2)
C(1)-H(1)	0.9300
C(2)-C(3)	1.380(2)
C(2)-H(2)	0.9300
C(3)-C(4)	1.3894(19)
C(3)-H(3)	0.9300
C(4)-C(13)	1.3885(18)
C(4)-C(5)	1.4866(18)
C(5)-C(29)	1.3477(18)
C(6)-C(7)	1.3651(17)
C(6)-C(23)	1.4800(17)
C(7)-C(14)	1.4540(16)
C(7)-C(8)	1.4939(16)
C(8)-C(21)	1.3839(17)
C(8)-C(9)	1.3902(19)
C(9)-C(10)	1.3780(19)
C(9)-H(9)	0.9300
C(10)-C(11)	1.372(2)
C(10)-H(10)	0.9300
C(11)-C(22)	1.372(2)
C(11)-H(11)	0.9300
C(12)-C(13)	1.385(2)
C(12)-H(12)	0.9300
C(13)-H(13)	0.9300
C(14)-C(19)	1.4015(16)

C(14)-C(15)	1.4109(17)
C(15)-C(16)	1.3708(19)
C(15)-H(15)	0.9300
C(16)-C(17)	1.393(2)
C(16)-H(16)	0.9300
C(17)-C(18)	1.3694(19)
C(17)-H(17)	0.9300
C(18)-C(19)	1.4005(16)
C(18)-H(18)	0.9300
C(19)-C(20)	1.4580(16)
C(21)-C(22)	1.3870(19)
C(21)-H(21)	0.9300
C(22)-H(22)	0.9300
C(23)-C(24)	1.397(2)
C(23)-C(28)	1.408(2)
C(24)-C(25)	1.382(2)
C(24)-H(24)	0.9300
C(25)-C(26)	1.375(3)
C(25)-H(25)	0.9300
C(26)-C(27)	1.362(3)
C(26)-H(26)	0.9300
C(27)-C(28)	1.403(2)
C(27)-H(27)	0.9300
C(28)-C(29)	1.457(2)
C(29)-C(30)	1.505(2)
C(30)-H(30A)	0.9600
C(30)-H(30B)	0.9600
C(30)-H(30C)	0.9600

C(20)-N(1)-C(6)	120.72(10)

C(20)-N(1)-C(5)	119.08(10)
C(6)-N(1)-C(5)	120.20(10)
C(2)-C(1)-C(12)	119.84(15)
C(2)-C(1)-H(1)	120.1
C(12)-C(1)-H(1)	120.1
C(1)-C(2)-C(3)	120.41(15)
C(1)-C(2)-H(2)	119.8
C(3)-C(2)-H(2)	119.8
C(2)-C(3)-C(4)	120.54(14)
C(2)-C(3)-H(3)	119.7
C(4)-C(3)-H(3)	119.7
C(13)-C(4)-C(3)	118.44(13)
C(13)-C(4)-C(5)	121.15(11)
C(3)-C(4)-C(5)	120.41(12)
C(29)-C(5)-N(1)	120.12(12)
C(29)-C(5)-C(4)	123.17(12)
N(1)-C(5)-C(4)	116.40(10)
C(7)-C(6)-N(1)	119.11(10)
C(7)-C(6)-C(23)	126.87(11)
N(1)-C(6)-C(23)	113.80(10)
C(6)-C(7)-C(14)	119.43(11)
C(6)-C(7)-C(8)	123.82(11)
C(14)-C(7)-C(8)	116.71(11)
C(21)-C(8)-C(9)	118.24(11)
C(21)-C(8)-C(7)	121.15(12)
C(9)-C(8)-C(7)	120.50(11)
C(10)-C(9)-C(8)	121.15(13)
C(10)-C(9)-H(9)	119.4
C(8)-C(9)-H(9)	119.4
C(11)-C(10)-C(9)	120.04(14)

C(11)-C(10)-H(10)	120.0
C(9)-C(10)-H(10)	120.0
C(10)-C(11)-C(22)	119.64(13)
C(10)-C(11)-H(11)	120.2
C(22)-C(11)-H(11)	120.2
C(1)-C(12)-C(13)	120.36(14)
C(1)-C(12)-H(12)	119.8
C(13)-C(12)-H(12)	119.8
C(12)-C(13)-C(4)	120.39(13)
C(12)-C(13)-H(13)	119.8
C(4)-C(13)-H(13)	119.8
C(19)-C(14)-C(15)	117.79(11)
C(19)-C(14)-C(7)	119.12(11)
C(15)-C(14)-C(7)	122.99(11)
C(16)-C(15)-C(14)	120.70(12)
C(16)-C(15)-H(15)	119.6
C(14)-C(15)-H(15)	119.6
C(15)-C(16)-C(17)	120.79(13)
C(15)-C(16)-H(16)	119.6
C(17)-C(16)-H(16)	119.6
C(18)-C(17)-C(16)	119.79(12)
C(18)-C(17)-H(17)	120.1
C(16)-C(17)-H(17)	120.1
C(17)-C(18)-C(19)	120.15(12)
C(17)-C(18)-H(18)	119.9
C(19)-C(18)-H(18)	119.9
C(18)-C(19)-C(14)	120.70(11)
C(18)-C(19)-C(20)	118.64(10)
C(14)-C(19)-C(20)	120.64(10)
O(1)-C(20)-N(1)	120.92(11)

O(1)-C(20)-C(19)	124.20(11)
N(1)-C(20)-C(19)	114.77(10)
C(8)-C(21)-C(22)	120.27(13)
C(8)-C(21)-H(21)	119.9
C(22)-C(21)-H(21)	119.9
C(11)-C(22)-C(21)	120.65(13)
C(11)-C(22)-H(22)	119.7
C(21)-C(22)-H(22)	119.7
C(24)-C(23)-C(28)	118.43(13)
C(24)-C(23)-C(6)	122.29(13)
C(28)-C(23)-C(6)	119.13(12)
C(25)-C(24)-C(23)	120.86(18)
C(25)-C(24)-H(24)	119.6
C(23)-C(24)-H(24)	119.6
C(26)-C(25)-C(24)	120.56(18)
C(26)-C(25)-H(25)	119.7
C(24)-C(25)-H(25)	119.7
C(27)-C(26)-C(25)	119.61(16)
C(27)-C(26)-H(26)	120.2
C(25)-C(26)-H(26)	120.2
C(26)-C(27)-C(28)	121.61(17)
C(26)-C(27)-H(27)	119.2
C(28)-C(27)-H(27)	119.2
C(27)-C(28)-C(23)	118.87(15)
C(27)-C(28)-C(29)	121.64(14)
C(23)-C(28)-C(29)	119.48(11)
C(5)-C(29)-C(28)	119.37(12)
C(5)-C(29)-C(30)	121.68(14)
C(28)-C(29)-C(30)	118.95(13)
C(29)-C(30)-H(30A)	109.5

C(29)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(29)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S11 Anisotropic displacement parameters ($Å^2 x\ 10^3$)for b3. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	41(1)	72(1)	62(1)	7(1)	-3(1)	4(1)
N(1)	44(1)	47(1)	49(1)	-3(1)	-3(1)	1(1)
C(1)	86(1)	70(1)	72(1)	4(1)	16(1)	-25(1)
C(2)	96(1)	51(1)	79(1)	-4(1)	16(1)	-12(1)
C(3)	71(1)	51(1)	68(1)	-3(1)	11(1)	2(1)
C(4)	61(1)	47(1)	48(1)	3(1)	3(1)	2(1)
C(5)	54(1)	47(1)	51(1)	2(1)	-1(1)	7(1)
C(6)	43(1)	46(1)	58(1)	-4(1)	-6(1)	1(1)
C(7)	43(1)	47(1)	57(1)	-3(1)	-4(1)	0(1)
C(8)	43(1)	52(1)	55(1)	-3(1)	-4(1)	-2(1)
C(9)	52(1)	61(1)	76(1)	12(1)	-13(1)	-4(1)
C(10)	60(1)	73(1)	71(1)	11(1)	-6(1)	-18(1)
C(11)	44(1)	85(1)	68(1)	-3(1)	-2(1)	-11(1)
C(12)	69(1)	80(1)	62(1)	4(1)	21(1)	-9(1)
C(13)	68(1)	56(1)	54(1)	-1(1)	13(1)	0(1)
C(14)	45(1)	43(1)	53(1)	0(1)	-2(1)	-1(1)
C(15)	51(1)	60(1)	60(1)	-3(1)	4(1)	-2(1)

C(16)	72(1)	66(1)	54(1)	-7(1)	6(1)	-4(1)
C(17)	71(1)	64(1)	51(1)	-3(1)	-10(1)	-8(1)
C(18)	51(1)	53(1)	56(1)	3(1)	-10(1)	-4(1)
C(19)	45(1)	40(1)	50(1)	2(1)	-4(1)	0(1)
C(20)	41(1)	42(1)	53(1)	4(1)	-5(1)	-1(1)
C(21)	50(1)	60(1)	59(1)	4(1)	-6(1)	0(1)
C(22)	45(1)	79(1)	70(1)	0(1)	-12(1)	6(1)
C(23)	50(1)	58(1)	66(1)	-15(1)	-10(1)	4(1)
C(24)	68(1)	89(1)	95(1)	-38(1)	3(1)	-21(1)
C(25)	86(1)	115(2)	122(2)	-62(1)	1(1)	-32(1)
C(26)	87(1)	121(2)	101(1)	-58(1)	-17(1)	-10(1)
C(27)	83(1)	101(1)	68(1)	-29(1)	-15(1)	5(1)
C(28)	60(1)	63(1)	61(1)	-11(1)	-16(1)	9(1)
C(29)	67(1)	61(1)	51(1)	1(1)	-7(1)	9(1)
C(30)	113(1)	113(2)	51(1)	12(1)	-11(1)	-10(1)

Crystal data and structure refinement for **4ia**

Fig. S8

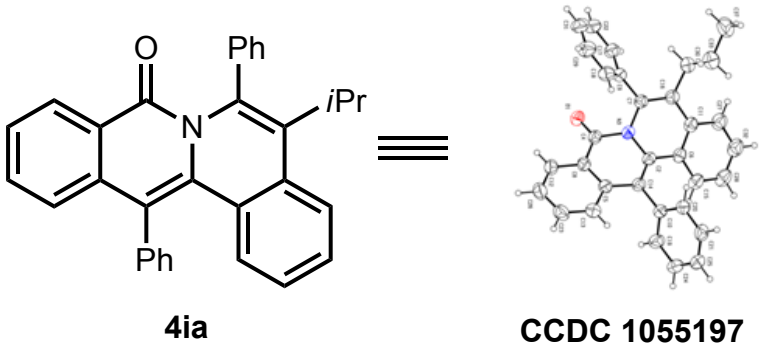


Table S12 Crystal data and structure refinement for b3.

Identification code	shelx
Empirical formula	C32 H25 N O
Formula weight	439.53

Temperature	293(2) K	
Wavelength	1.54187 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 17.0755(12) Å	α= 90°.
	b = 11.3454(2) Å	β= 103.806(7)°.
	c = 12.5168(2) Å	γ = 90°.
Volume	2354.80(19) $Å^3$	
Z	4	
Density (calculated)	1.240 Mg/m^3	
Absorption coefficient	0.572 mm^{-1}	
F(000)	928	
Crystal size	0.200 x 0.200 x 0.200 mm^3	
Theta range for data collection	6.613 to 69.052°.	
Index ranges	-18<=h<=20, -13<=k<=13, -14<=l<=13	
Reflections collected	19430	
Independent reflections	4283 [R(int) = 0.0473]	
Completeness to theta = 67.687°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.894 and 0.743	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4283 / 0 / 308	
Goodness-of-fit on F^2	1.103	
Final R indices [I>2sigma(I)]	R1 = 0.0539, wR2 = 0.1605	
R indices (all data)	R1 = 0.0667, wR2 = 0.1738	
Extinction coefficient	0.0058(7)	
Largest diff. peak and hole	0.404 and -0.150 $e.Å^{-3}$	

Table S13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for b3. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1563(1)	6778(1)	6393(1)	71(1)
N(3)	2241(1)	5031(1)	6457(1)	53(1)
C(2)	2186(1)	3855(2)	6049(2)	54(1)
C(4)	1537(1)	5705(2)	6390(2)	56(1)
C(5)	822(1)	3782(2)	6297(2)	56(1)
C(6)	2873(1)	3523(2)	5587(2)	58(1)
C(7)	3009(1)	5513(2)	6966(2)	55(1)
C(8)	821(1)	5014(2)	6403(1)	56(1)
C(9)	3013(1)	6478(2)	7773(2)	58(1)
C(10)	1445(1)	1929(2)	5748(2)	57(1)
C(11)	3616(1)	4097(2)	5965(2)	62(1)
C(12)	136(1)	5595(2)	6563(2)	67(1)
C(13)	130(1)	3168(2)	6407(2)	70(1)
C(14)	1512(1)	3209(2)	6033(2)	55(1)
C(15)	2784(1)	2722(2)	4710(2)	71(1)
C(16)	3692(1)	5031(2)	6787(2)	62(1)
C(17)	3340(1)	7581(2)	7640(2)	68(1)
C(18)	2699(1)	6304(2)	8672(2)	72(1)
C(19)	919(1)	1524(2)	4794(2)	77(1)
C(20)	1875(1)	1104(2)	6461(2)	63(1)
C(21)	1770(1)	-88(2)	6234(2)	77(1)
C(22)	3350(1)	8466(2)	8391(2)	80(1)
C(23)	-529(1)	3752(2)	6581(2)	81(1)
C(24)	827(2)	342(2)	4566(2)	84(1)
C(25)	1246(1)	-467(2)	5291(2)	79(1)
C(26)	-531(1)	4977(2)	6642(2)	80(1)
C(27)	4256(2)	3806(2)	5488(2)	81(1)

C(28)	3416(2)	2476(2)	4244(2)	86(1)
C(29)	2709(2)	7194(2)	9422(2)	86(1)
C(30)	4520(1)	5422(2)	7405(2)	78(1)
C(31)	3037(2)	8269(2)	9276(2)	88(1)
C(32)	4157(2)	3003(2)	4646(2)	90(1)
C(33)	4963(2)	4551(3)	8213(3)	97(1)
C(37)	5783(2)	5005(4)	8826(4)	158(2)

Table S14 Bond lengths [Å] and angles [°] for b3.

O(1)-C(4)	1.218(2)
N(3)-C(4)	1.411(2)
N(3)-C(7)	1.424(2)
N(3)-C(2)	1.424(2)
C(2)-C(14)	1.360(3)
C(2)-C(6)	1.475(3)
C(4)-C(8)	1.455(3)
C(5)-C(8)	1.404(3)
C(5)-C(13)	1.407(3)
C(5)-C(14)	1.451(3)
C(6)-C(15)	1.404(3)
C(6)-C(11)	1.405(3)
C(7)-C(16)	1.353(3)
C(7)-C(9)	1.489(3)
C(8)-C(12)	1.397(3)
C(9)-C(18)	1.372(3)
C(9)-C(17)	1.396(3)
C(10)-C(20)	1.378(3)
C(10)-C(19)	1.390(3)

C(10)-C(14)	1.493(2)
C(11)-C(27)	1.404(3)
C(11)-C(16)	1.462(3)
C(12)-C(26)	1.362(3)
C(12)-H(12)	0.9300
C(13)-C(23)	1.367(3)
C(13)-H(13)	0.9300
C(15)-C(28)	1.373(3)
C(15)-H(15)	0.9300
C(16)-C(30)	1.508(3)
C(17)-C(22)	1.372(3)
C(17)-H(17)	0.9300
C(18)-C(29)	1.376(3)
C(18)-H(18)	0.9300
C(19)-C(24)	1.372(3)
C(19)-H(19)	0.9300
C(20)-C(21)	1.385(3)
C(20)-H(20)	0.9300
C(21)-C(25)	1.369(3)
C(21)-H(21)	0.9300
C(22)-C(31)	1.358(4)
C(22)-H(22)	0.9300
C(23)-C(26)	1.391(3)
C(23)-H(23)	0.9300
C(24)-C(25)	1.366(3)
C(24)-H(24)	0.9300
C(25)-H(25)	0.9300
C(26)-H(26)	0.9300
C(27)-C(32)	1.373(4)
C(27)-H(27)	0.9300

C(28)-C(32)	1.380(4)
C(28)-H(28)	0.9300
C(29)-C(31)	1.372(4)
C(29)-H(29)	0.9300
C(30)-C(33)	1.486(4)
C(30)-H(30A)	0.9700
C(30)-H(30B)	0.9700
C(31)-H(31)	0.9300
C(32)-H(32)	0.9300
C(33)-C(37)	1.517(4)
C(33)-H(33A)	0.9700
C(33)-H(33B)	0.9700
C(37)-H(37A)	0.9600
C(37)-H(37B)	0.9600
C(37)-H(37C)	0.9600

C(4)-N(3)-C(7)	120.00(14)
C(4)-N(3)-C(2)	120.22(15)
C(7)-N(3)-C(2)	119.75(14)
C(14)-C(2)-N(3)	119.60(16)
C(14)-C(2)-C(6)	127.27(16)
N(3)-C(2)-C(6)	112.88(15)
O(1)-C(4)-N(3)	120.74(17)
O(1)-C(4)-C(8)	124.63(17)
N(3)-C(4)-C(8)	114.47(15)
C(8)-C(5)-C(13)	117.60(17)
C(8)-C(5)-C(14)	119.23(16)
C(13)-C(5)-C(14)	123.11(17)
C(15)-C(6)-C(11)	118.90(18)
C(15)-C(6)-C(2)	121.59(18)

C(11)-C(6)-C(2)	119.26(17)
C(16)-C(7)-N(3)	120.57(16)
C(16)-C(7)-C(9)	123.01(17)
N(3)-C(7)-C(9)	116.14(15)
C(12)-C(8)-C(5)	120.24(18)
C(12)-C(8)-C(4)	118.78(17)
C(5)-C(8)-C(4)	120.94(16)
C(18)-C(9)-C(17)	118.27(18)
C(18)-C(9)-C(7)	120.75(17)
C(17)-C(9)-C(7)	120.98(17)
C(20)-C(10)-C(19)	117.81(18)
C(20)-C(10)-C(14)	120.48(17)
C(19)-C(10)-C(14)	121.62(17)
C(27)-C(11)-C(6)	118.73(19)
C(27)-C(11)-C(16)	121.50(19)
C(6)-C(11)-C(16)	119.65(16)
C(26)-C(12)-C(8)	120.7(2)
C(26)-C(12)-H(12)	119.6
C(8)-C(12)-H(12)	119.6
C(23)-C(13)-C(5)	121.2(2)
C(23)-C(13)-H(13)	119.4
C(5)-C(13)-H(13)	119.4
C(2)-C(14)-C(5)	118.97(16)
C(2)-C(14)-C(10)	122.96(16)
C(5)-C(14)-C(10)	118.07(15)
C(28)-C(15)-C(6)	121.0(2)
C(28)-C(15)-H(15)	119.5
C(6)-C(15)-H(15)	119.5
C(7)-C(16)-C(11)	118.32(17)
C(7)-C(16)-C(30)	122.38(18)

C(11)-C(16)-C(30)	119.30(17)
C(22)-C(17)-C(9)	120.9(2)
C(22)-C(17)-H(17)	119.6
C(9)-C(17)-H(17)	119.6
C(9)-C(18)-C(29)	120.6(2)
C(9)-C(18)-H(18)	119.7
C(29)-C(18)-H(18)	119.7
C(24)-C(19)-C(10)	121.4(2)
C(24)-C(19)-H(19)	119.3
C(10)-C(19)-H(19)	119.3
C(10)-C(20)-C(21)	120.5(2)
C(10)-C(20)-H(20)	119.7
C(21)-C(20)-H(20)	119.7
C(25)-C(21)-C(20)	120.6(2)
C(25)-C(21)-H(21)	119.7
C(20)-C(21)-H(21)	119.7
C(31)-C(22)-C(17)	119.7(2)
C(31)-C(22)-H(22)	120.2
C(17)-C(22)-H(22)	120.2
C(13)-C(23)-C(26)	120.5(2)
C(13)-C(23)-H(23)	119.8
C(26)-C(23)-H(23)	119.8
C(25)-C(24)-C(19)	120.1(2)
C(25)-C(24)-H(24)	119.9
C(19)-C(24)-H(24)	119.9
C(24)-C(25)-C(21)	119.6(2)
C(24)-C(25)-H(25)	120.2
C(21)-C(25)-H(25)	120.2
C(12)-C(26)-C(23)	119.8(2)
C(12)-C(26)-H(26)	120.1

C(23)-C(26)-H(26)	120.1
C(32)-C(27)-C(11)	121.1(2)
C(32)-C(27)-H(27)	119.5
C(11)-C(27)-H(27)	119.5
C(15)-C(28)-C(32)	120.1(2)
C(15)-C(28)-H(28)	120.0
C(32)-C(28)-H(28)	120.0
C(31)-C(29)-C(18)	120.0(2)
C(31)-C(29)-H(29)	120.0
C(18)-C(29)-H(29)	120.0
C(33)-C(30)-C(16)	114.6(2)
C(33)-C(30)-H(30A)	108.6
C(16)-C(30)-H(30A)	108.6
C(33)-C(30)-H(30B)	108.6
C(16)-C(30)-H(30B)	108.6
H(30A)-C(30)-H(30B)	107.6
C(22)-C(31)-C(29)	120.5(2)
C(22)-C(31)-H(31)	119.7
C(29)-C(31)-H(31)	119.7
C(27)-C(32)-C(28)	120.2(2)
C(27)-C(32)-H(32)	119.9
C(28)-C(32)-H(32)	119.9
C(30)-C(33)-C(37)	112.1(3)
C(30)-C(33)-H(33A)	109.2
C(37)-C(33)-H(33A)	109.2
C(30)-C(33)-H(33B)	109.2
C(37)-C(33)-H(33B)	109.2
H(33A)-C(33)-H(33B)	107.9
C(33)-C(37)-H(37A)	109.5
C(33)-C(37)-H(37B)	109.5

H(37A)-C(37)-H(37B)	109.5
C(33)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5

Symmetry transformations used to generate equivalent atoms:

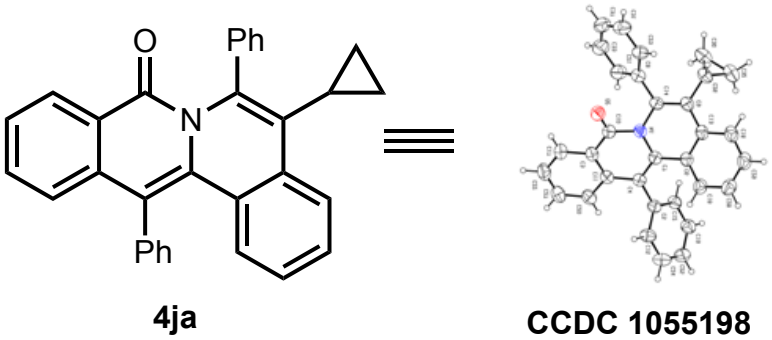
Table S15 Anisotropic displacement parameters ($Å^2 x\ 10^3$)for b3. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	75(1)	46(1)	86(1)	1(1)	9(1)	7(1)
N(3)	57(1)	43(1)	59(1)	-1(1)	14(1)	2(1)
C(2)	62(1)	44(1)	54(1)	0(1)	12(1)	3(1)
C(4)	62(1)	48(1)	54(1)	-1(1)	8(1)	6(1)
C(5)	58(1)	54(1)	56(1)	-1(1)	11(1)	0(1)
C(6)	67(1)	48(1)	62(1)	3(1)	21(1)	4(1)
C(7)	58(1)	47(1)	59(1)	1(1)	13(1)	-2(1)
C(8)	58(1)	58(1)	51(1)	0(1)	8(1)	7(1)
C(9)	56(1)	55(1)	60(1)	-3(1)	11(1)	1(1)
C(10)	58(1)	48(1)	64(1)	-3(1)	12(1)	-1(1)
C(11)	67(1)	53(1)	70(1)	2(1)	26(1)	2(1)
C(12)	64(1)	68(1)	66(1)	-2(1)	11(1)	13(1)
C(13)	64(1)	69(1)	76(1)	-4(1)	15(1)	-6(1)
C(14)	59(1)	48(1)	57(1)	0(1)	11(1)	1(1)
C(15)	83(1)	62(1)	72(1)	-10(1)	27(1)	1(1)
C(16)	61(1)	55(1)	71(1)	0(1)	20(1)	-1(1)
C(17)	72(1)	59(1)	74(1)	-6(1)	19(1)	-7(1)
C(18)	78(1)	71(1)	67(1)	-2(1)	19(1)	-10(1)

C(19)	81(1)	58(1)	77(1)	-4(1)	-7(1)	5(1)
C(20)	59(1)	57(1)	69(1)	1(1)	8(1)	5(1)
C(21)	76(1)	55(1)	98(2)	9(1)	18(1)	14(1)
C(22)	82(1)	63(1)	91(2)	-13(1)	13(1)	-14(1)
C(23)	60(1)	97(2)	89(2)	-6(1)	21(1)	-7(1)
C(24)	82(2)	66(1)	94(2)	-22(1)	1(1)	-2(1)
C(25)	76(1)	51(1)	109(2)	-15(1)	19(1)	-1(1)
C(26)	62(1)	96(2)	81(2)	-5(1)	17(1)	15(1)
C(27)	78(1)	74(1)	101(2)	-8(1)	42(1)	-4(1)
C(28)	107(2)	77(2)	82(2)	-16(1)	41(1)	4(1)
C(29)	95(2)	100(2)	68(1)	-14(1)	28(1)	-11(1)
C(30)	63(1)	79(1)	93(2)	-14(1)	21(1)	2(1)
C(31)	95(2)	88(2)	80(2)	-29(1)	17(1)	-15(1)
C(32)	97(2)	84(2)	107(2)	-13(1)	57(2)	1(1)
C(33)	87(2)	94(2)	104(2)	0(2)	11(2)	12(1)
C(37)	99(2)	196(4)	149(3)	-70(3)	-30(2)	54(2)

Crystal data and structure refinement for **4ja**

Fig. S8



4ja **CCDC 1055198**

Table S16 Crystal data and structure refinement for b3.

Identification code	shelx
Empirical formula	C32 H23 N O

Formula weight	437.51	
Temperature	293(2) K	
Wavelength	1.54187 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.9480(2) Å	α= 88.203(6)°.
	b = 10.1669(2) Å	β= 70.071(5)°.
	c = 12.7171(8) Å	γ = 73.961(5)°.
Volume	1159.31(9) $Å^3$	
Z	2	
Density (calculated)	1.253 Mg/m^3	
Absorption coefficient	0.581 mm^{-1}	
F(000)	460	
Crystal size	0.200 x 0.200 x 0.200 mm^3	
Theta range for data collection	7.130 to 68.249°.	
Index ranges	-11<=h<=11, -12<=k<=12, -15<=l<=15	
Reflections collected	15756	
Independent reflections	4135 [R(int) = 0.0767]	
Completeness to theta = 67.687°	97.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.893 and 0.600	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4135 / 0 / 307	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0550, wR2 = 0.1401	
R indices (all data)	R1 = 0.0931, wR2 = 0.1653	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.173 and -0.180 $e.Å^{-3}$	

Table S17 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)

for b3. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(2)	4000(2)	12144(2)	3608(1)	73(1)
N(1)	3199(2)	10323(2)	3330(1)	56(1)
C(3)	2888(3)	12267(2)	2214(2)	60(1)
C(4)	2747(2)	10042(2)	1624(2)	56(1)
C(5)	2471(3)	9233(2)	805(2)	58(1)
C(6)	3781(3)	7995(2)	2592(2)	59(1)
C(7)	3176(2)	9463(2)	2482(2)	55(1)
C(8)	2382(3)	10992(3)	5352(2)	63(1)
C(9)	3125(3)	8533(3)	4616(2)	60(1)
C(10)	3431(3)	11616(3)	3085(2)	59(1)
C(11)	2490(2)	11508(2)	1526(2)	57(1)
C(12)	1351(3)	8588(3)	1175(2)	62(1)
C(13)	3770(3)	7550(3)	3653(2)	61(1)
C(14)	2953(2)	9878(3)	4446(2)	57(1)
C(15)	3257(3)	9135(3)	-341(2)	72(1)
C(16)	4428(3)	6156(3)	3742(3)	78(1)
C(17)	2749(3)	13657(3)	2100(2)	74(1)
C(18)	4519(3)	7062(3)	1660(2)	70(1)
C(19)	1045(3)	7863(3)	432(2)	73(1)
C(20)	1908(3)	12216(3)	738(2)	72(1)
C(21)	1134(3)	12086(3)	5439(2)	80(1)
C(22)	2195(4)	14307(3)	1309(3)	86(1)
C(23)	3081(3)	10968(3)	6131(2)	71(1)
C(24)	2956(3)	8397(3)	-1076(2)	82(1)
C(25)	1848(3)	7756(3)	-695(2)	78(1)
C(26)	2717(3)	8054(3)	5778(2)	69(1)

C(27)	1775(3)	13585(3)	641(2)	85(1)
C(28)	5175(3)	5704(3)	1775(3)	83(1)
C(29)	5115(3)	5261(3)	2816(3)	85(1)
C(30)	1165(3)	8552(4)	6573(2)	88(1)
C(31)	2572(4)	12036(4)	6938(2)	88(1)
C(32)	1745(3)	7111(4)	6109(2)	87(1)
C(33)	647(4)	13136(3)	6241(3)	96(1)
C(37)	1374(4)	13127(4)	6982(3)	95(1)

Table S18 Bond lengths [Å] and angles [°] for b3.

O(2)-C(10)	1.224(3)
N(1)-C(10)	1.405(3)
N(1)-C(7)	1.419(3)
N(1)-C(14)	1.436(3)
C(3)-C(17)	1.389(3)
C(3)-C(11)	1.402(3)
C(3)-C(10)	1.457(3)
C(4)-C(7)	1.364(3)
C(4)-C(11)	1.450(3)
C(4)-C(5)	1.486(3)
C(5)-C(12)	1.386(3)
C(5)-C(15)	1.391(3)
C(6)-C(18)	1.391(3)
C(6)-C(13)	1.407(3)
C(6)-C(7)	1.468(3)
C(8)-C(23)	1.386(3)
C(8)-C(21)	1.394(4)
C(8)-C(14)	1.488(3)

C(9)-C(14)	1.350(3)
C(9)-C(13)	1.449(3)
C(9)-C(26)	1.497(3)
C(11)-C(20)	1.406(3)
C(12)-C(19)	1.375(3)
C(12)-H(12)	0.9300
C(13)-C(16)	1.406(4)
C(15)-C(24)	1.374(4)
C(15)-H(15)	0.9300
C(16)-C(29)	1.362(4)
C(16)-H(16)	0.9300
C(17)-C(22)	1.374(4)
C(17)-H(17)	0.9300
C(18)-C(28)	1.382(4)
C(18)-H(18)	0.9300
C(19)-C(25)	1.373(4)
C(19)-H(19)	0.9300
C(20)-C(27)	1.367(4)
C(20)-H(20)	0.9300
C(21)-C(33)	1.363(4)
C(21)-H(21)	0.9300
C(22)-C(27)	1.373(4)
C(22)-H(22)	0.9300
C(23)-C(31)	1.379(4)
C(23)-H(23)	0.9300
C(24)-C(25)	1.373(4)
C(24)-H(24)	0.9300
C(25)-H(25)	0.9300
C(26)-C(30)	1.483(4)
C(26)-C(32)	1.497(4)

C(26)-H(26)	0.9800
C(27)-H(27)	0.9300
C(28)-C(29)	1.372(4)
C(28)-H(28)	0.9300
C(29)-H(29)	0.9300
C(30)-C(32)	1.478(4)
C(30)-H(30A)	0.9700
C(30)-H(30B)	0.9700
C(31)-C(37)	1.371(5)
C(31)-H(31)	0.9300
C(32)-H(32A)	0.9700
C(32)-H(32B)	0.9700
C(33)-C(37)	1.369(5)
C(33)-H(33)	0.9300
C(37)-H(37)	0.9300

C(10)-N(1)-C(7)	120.14(17)
C(10)-N(1)-C(14)	120.08(19)
C(7)-N(1)-C(14)	119.76(18)
C(17)-C(3)-C(11)	121.2(2)
C(17)-C(3)-C(10)	118.3(2)
C(11)-C(3)-C(10)	120.5(2)
C(7)-C(4)-C(11)	119.2(2)
C(7)-C(4)-C(5)	122.4(2)
C(11)-C(4)-C(5)	118.35(19)
C(12)-C(5)-C(15)	117.7(2)
C(12)-C(5)-C(4)	119.60(19)
C(15)-C(5)-C(4)	122.6(2)
C(18)-C(6)-C(13)	118.9(2)
C(18)-C(6)-C(7)	121.8(2)

C(13)-C(6)-C(7)	118.8(2)
C(4)-C(7)-N(1)	119.3(2)
C(4)-C(7)-C(6)	126.9(2)
N(1)-C(7)-C(6)	113.47(18)
C(23)-C(8)-C(21)	118.3(3)
C(23)-C(8)-C(14)	120.8(2)
C(21)-C(8)-C(14)	120.9(2)
C(14)-C(9)-C(13)	118.9(2)
C(14)-C(9)-C(26)	120.8(2)
C(13)-C(9)-C(26)	120.3(2)
O(2)-C(10)-N(1)	120.9(2)
O(2)-C(10)-C(3)	124.3(2)
N(1)-C(10)-C(3)	114.7(2)
C(3)-C(11)-C(20)	117.4(2)
C(3)-C(11)-C(4)	119.3(2)
C(20)-C(11)-C(4)	123.3(2)
C(19)-C(12)-C(5)	120.9(2)
C(19)-C(12)-H(12)	119.6
C(5)-C(12)-H(12)	119.6
C(16)-C(13)-C(6)	118.6(2)
C(16)-C(13)-C(9)	121.6(2)
C(6)-C(13)-C(9)	119.7(2)
C(9)-C(14)-N(1)	119.5(2)
C(9)-C(14)-C(8)	124.8(2)
N(1)-C(14)-C(8)	115.5(2)
C(24)-C(15)-C(5)	121.0(2)
C(24)-C(15)-H(15)	119.5
C(5)-C(15)-H(15)	119.5
C(29)-C(16)-C(13)	120.9(2)
C(29)-C(16)-H(16)	119.6

C(13)-C(16)-H(16)	119.6
C(22)-C(17)-C(3)	119.6(3)
C(22)-C(17)-H(17)	120.2
C(3)-C(17)-H(17)	120.2
C(28)-C(18)-C(6)	120.8(2)
C(28)-C(18)-H(18)	119.6
C(6)-C(18)-H(18)	119.6
C(25)-C(19)-C(12)	120.7(2)
C(25)-C(19)-H(19)	119.6
C(12)-C(19)-H(19)	119.6
C(27)-C(20)-C(11)	120.5(3)
C(27)-C(20)-H(20)	119.7
C(11)-C(20)-H(20)	119.7
C(33)-C(21)-C(8)	120.9(3)
C(33)-C(21)-H(21)	119.5
C(8)-C(21)-H(21)	119.5
C(27)-C(22)-C(17)	120.0(3)
C(27)-C(22)-H(22)	120.0
C(17)-C(22)-H(22)	120.0
C(31)-C(23)-C(8)	120.0(3)
C(31)-C(23)-H(23)	120.0
C(8)-C(23)-H(23)	120.0
C(25)-C(24)-C(15)	120.5(2)
C(25)-C(24)-H(24)	119.7
C(15)-C(24)-H(24)	119.7
C(24)-C(25)-C(19)	119.1(2)
C(24)-C(25)-H(25)	120.5
C(19)-C(25)-H(25)	120.5
C(30)-C(26)-C(9)	120.2(2)
C(30)-C(26)-C(32)	59.46(19)

C(9)-C(26)-C(32)	120.0(2)
C(30)-C(26)-H(26)	115.3
C(9)-C(26)-H(26)	115.3
C(32)-C(26)-H(26)	115.3
C(20)-C(27)-C(22)	121.3(3)
C(20)-C(27)-H(27)	119.4
C(22)-C(27)-H(27)	119.4
C(29)-C(28)-C(18)	120.0(3)
C(29)-C(28)-H(28)	120.0
C(18)-C(28)-H(28)	120.0
C(16)-C(29)-C(28)	120.6(3)
C(16)-C(29)-H(29)	119.7
C(28)-C(29)-H(29)	119.7
C(32)-C(30)-C(26)	60.8(2)
C(32)-C(30)-H(30A)	117.7
C(26)-C(30)-H(30A)	117.7
C(32)-C(30)-H(30B)	117.7
C(26)-C(30)-H(30B)	117.7
H(30A)-C(30)-H(30B)	114.8
C(37)-C(31)-C(23)	120.6(3)
C(37)-C(31)-H(31)	119.7
C(23)-C(31)-H(31)	119.7
C(30)-C(32)-C(26)	59.79(19)
C(30)-C(32)-H(32A)	117.8
C(26)-C(32)-H(32A)	117.8
C(30)-C(32)-H(32B)	117.8
C(26)-C(32)-H(32B)	117.8
H(32A)-C(32)-H(32B)	114.9
C(21)-C(33)-C(37)	120.3(3)
C(21)-C(33)-H(33)	119.8

C(37)-C(33)-H(33)	119.8
C(33)-C(37)-C(31)	119.8(3)
C(33)-C(37)-H(37)	120.1
C(31)-C(37)-H(37)	120.1

Symmetry transformations used to generate equivalent atoms:

Table S19 Anisotropic displacement parameters ($Å^2 x\ 10^3$)for b3. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(2)	79(1)	74(1)	75(1)	8(1)	-32(1)	-31(1)
N(1)	61(1)	56(1)	56(1)	9(1)	-26(1)	-16(1)
C(3)	56(1)	57(2)	64(1)	10(1)	-18(1)	-15(1)
C(4)	52(1)	60(2)	54(1)	5(1)	-18(1)	-16(1)
C(5)	54(1)	65(2)	55(1)	6(1)	-21(1)	-13(1)
C(6)	56(1)	56(2)	67(1)	9(1)	-27(1)	-14(1)
C(7)	50(1)	60(2)	56(1)	6(1)	-21(1)	-14(1)
C(8)	60(2)	71(2)	58(1)	9(1)	-21(1)	-20(1)
C(9)	56(1)	64(2)	65(1)	15(1)	-29(1)	-16(1)
C(10)	57(1)	60(2)	62(1)	4(1)	-21(1)	-18(1)
C(11)	50(1)	63(2)	57(1)	10(1)	-17(1)	-14(1)
C(12)	64(2)	69(2)	56(1)	9(1)	-24(1)	-22(1)
C(13)	60(2)	56(2)	73(2)	12(1)	-33(1)	-14(1)
C(14)	53(1)	66(2)	55(1)	8(1)	-24(1)	-17(1)
C(15)	64(2)	91(2)	59(1)	5(1)	-15(1)	-26(1)
C(16)	87(2)	66(2)	89(2)	20(2)	-46(2)	-19(2)
C(17)	82(2)	59(2)	82(2)	11(1)	-29(1)	-22(1)
C(18)	71(2)	58(2)	77(2)	4(1)	-29(1)	-9(1)

C(19)	79(2)	80(2)	73(2)	14(1)	-36(1)	-31(2)
C(20)	72(2)	74(2)	71(2)	17(1)	-32(1)	-16(1)
C(21)	74(2)	82(2)	72(2)	-1(2)	-28(1)	-1(2)
C(22)	98(2)	62(2)	97(2)	23(2)	-35(2)	-17(2)
C(23)	64(2)	90(2)	63(1)	3(1)	-24(1)	-23(2)
C(24)	78(2)	113(2)	53(1)	-3(1)	-19(1)	-27(2)
C(25)	87(2)	88(2)	69(2)	-1(1)	-37(2)	-26(2)
C(26)	66(2)	83(2)	68(2)	25(1)	-33(1)	-25(1)
C(27)	93(2)	76(2)	89(2)	27(2)	-43(2)	-18(2)
C(28)	88(2)	65(2)	96(2)	-2(2)	-38(2)	-12(2)
C(29)	92(2)	60(2)	106(2)	14(2)	-50(2)	-10(2)
C(30)	77(2)	105(3)	77(2)	28(2)	-23(2)	-26(2)
C(31)	86(2)	118(3)	67(2)	-4(2)	-21(2)	-47(2)
C(32)	86(2)	96(2)	95(2)	35(2)	-41(2)	-40(2)
C(33)	95(2)	86(2)	83(2)	-7(2)	-19(2)	0(2)
C(37)	106(3)	93(2)	75(2)	-10(2)	-9(2)	-38(2)

8. References:

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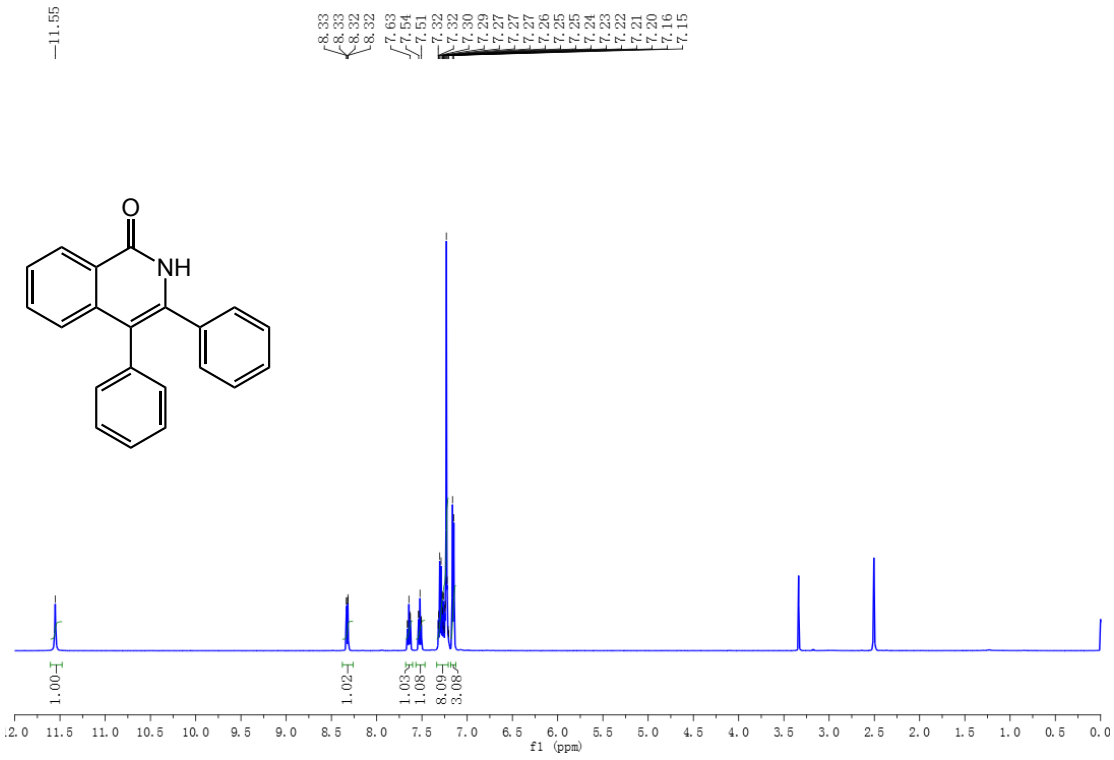
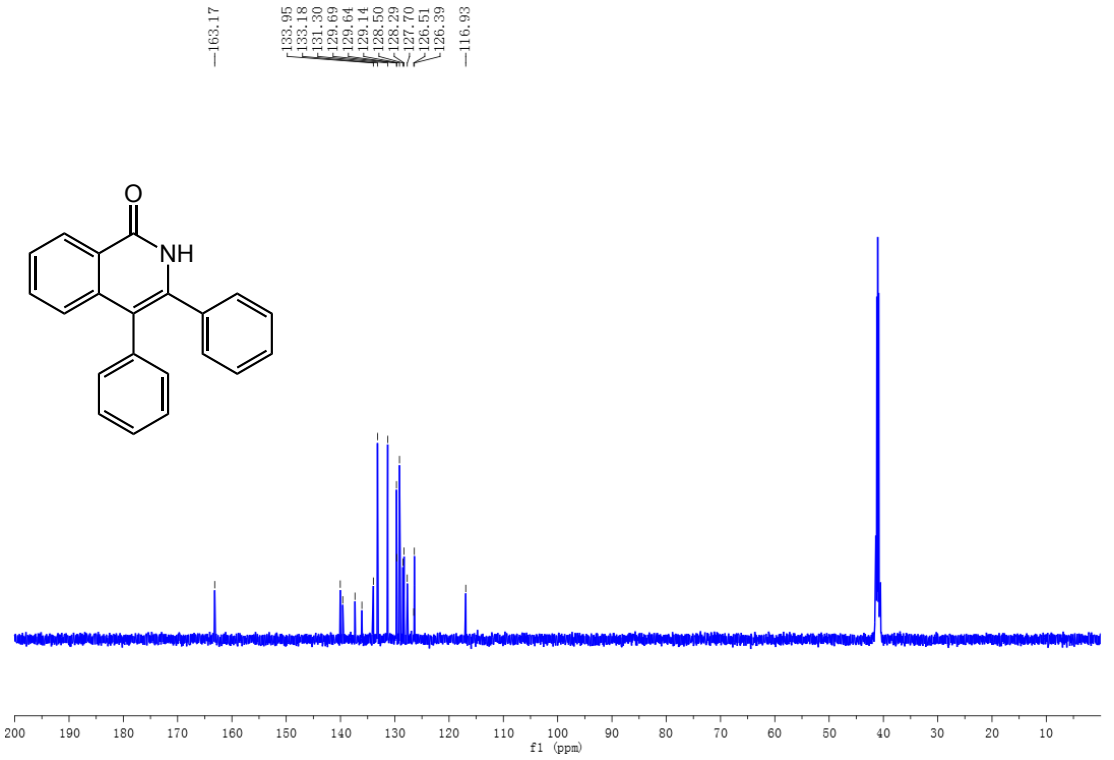
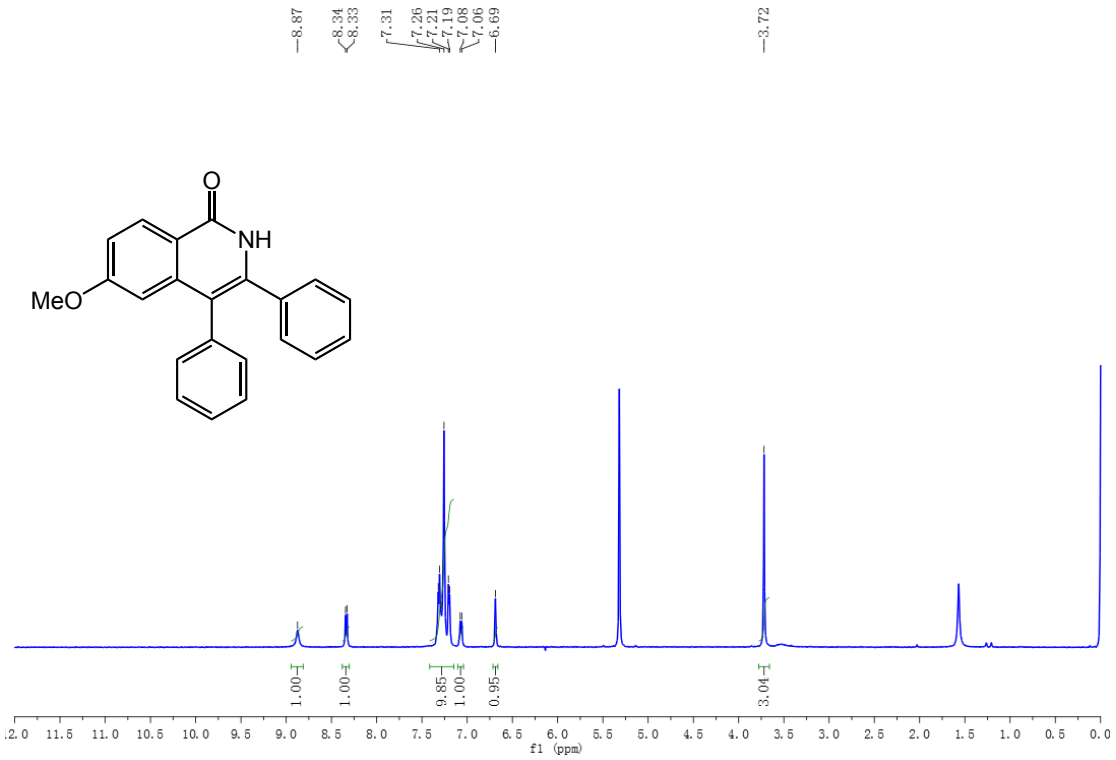
^{1}H NMR and ^{13}C NMR Spectra of products



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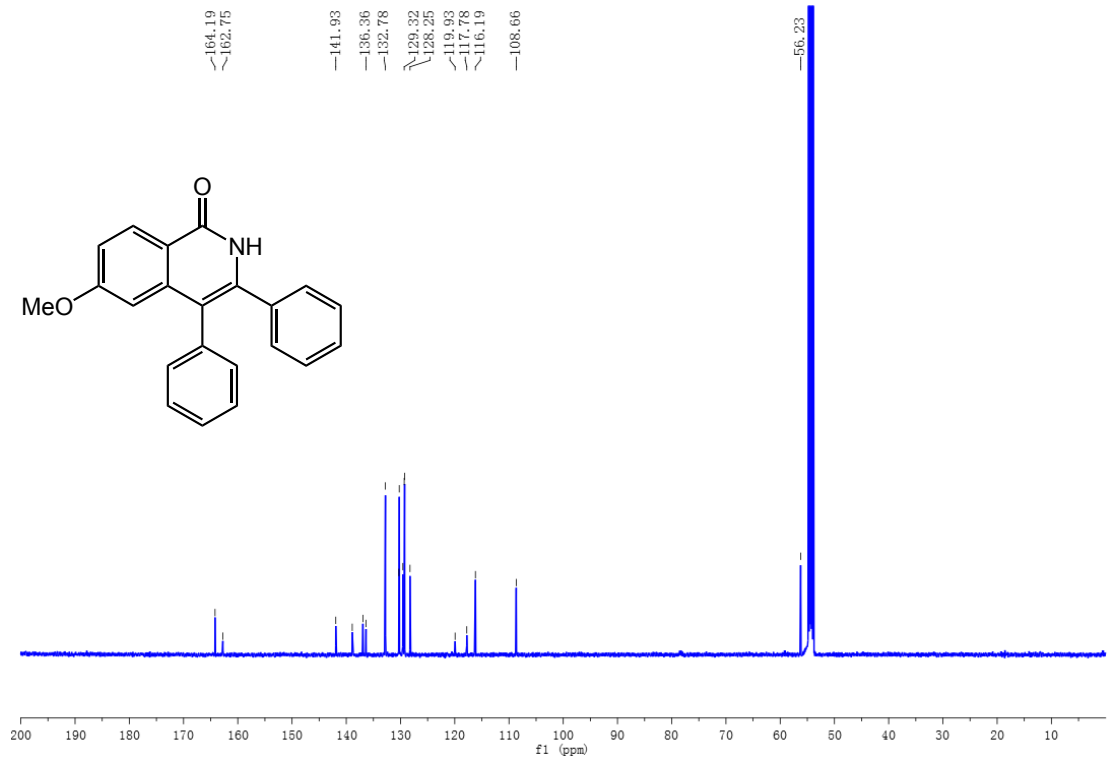
f1 (ppm)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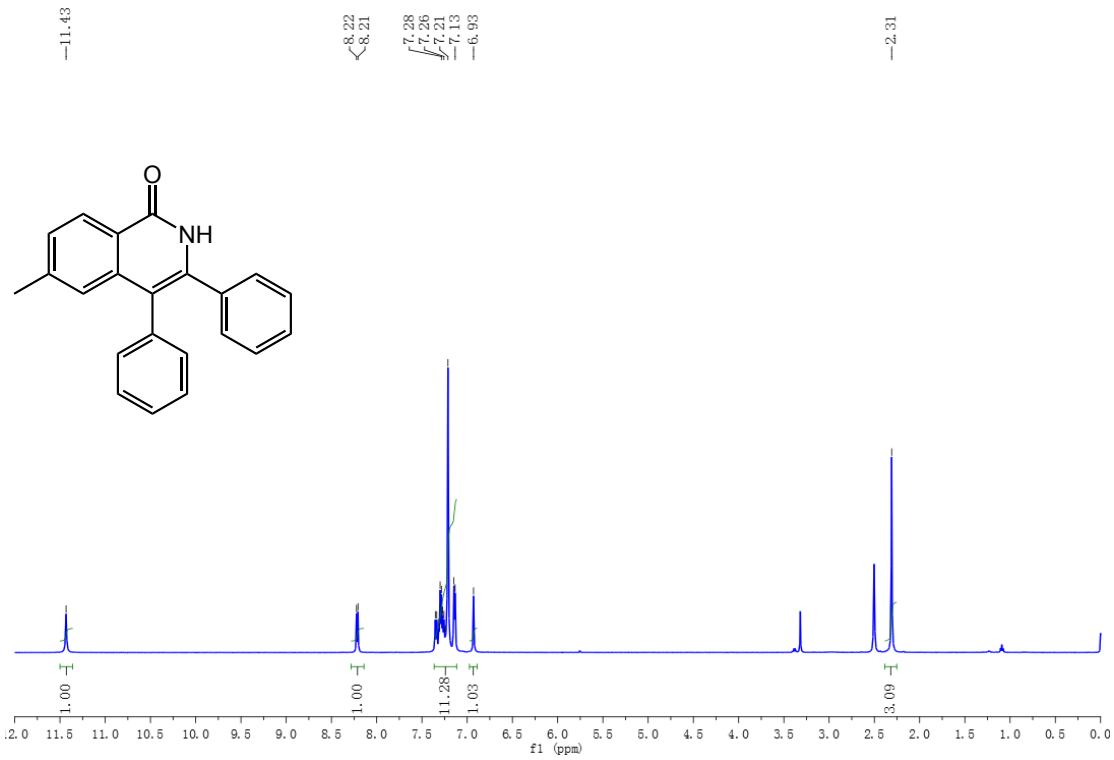
MeO
f1 (ppm)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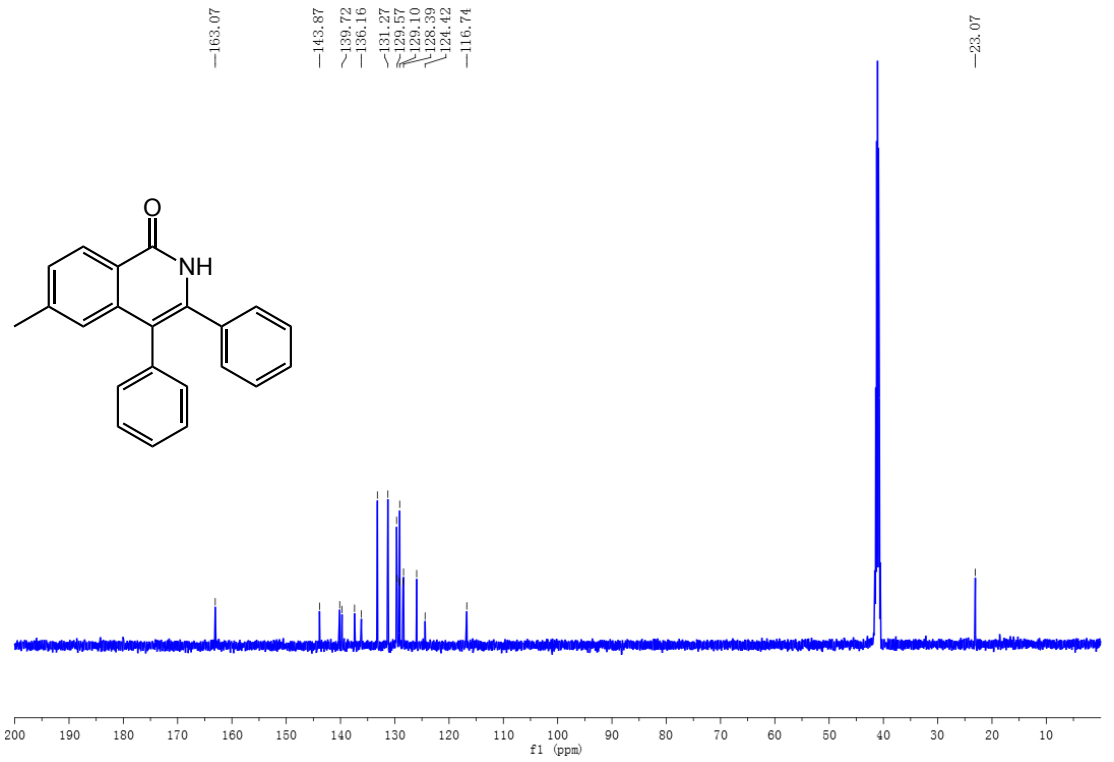
f1 (ppm)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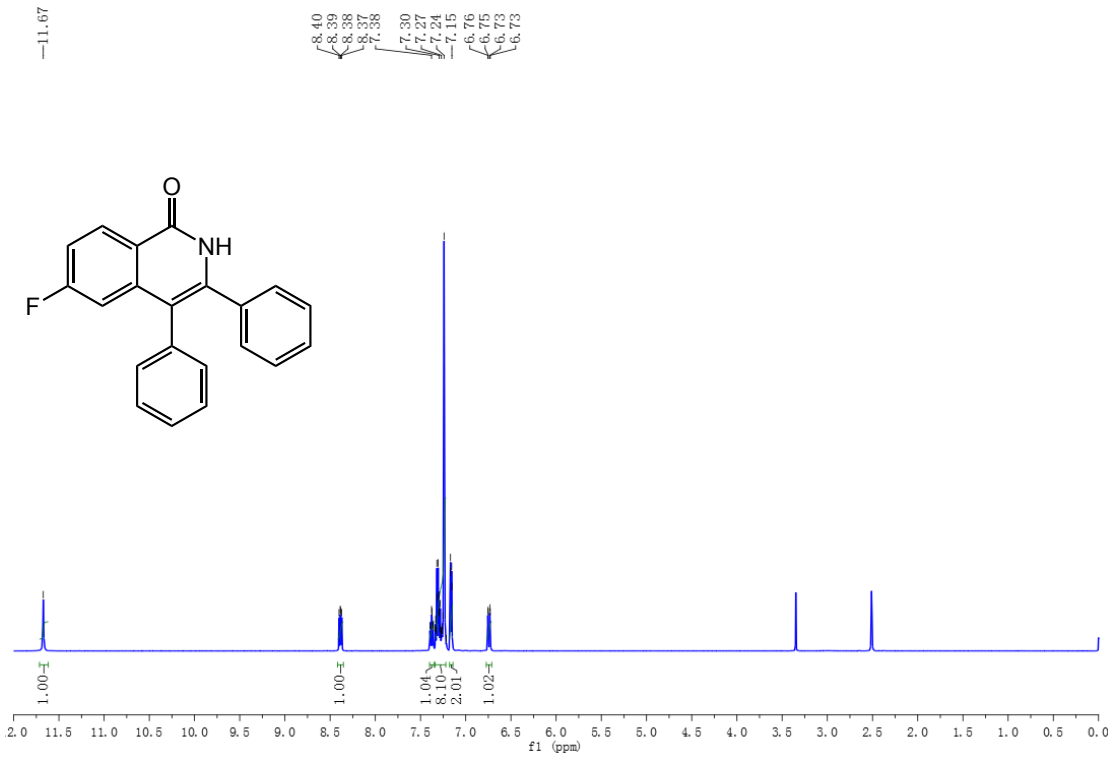
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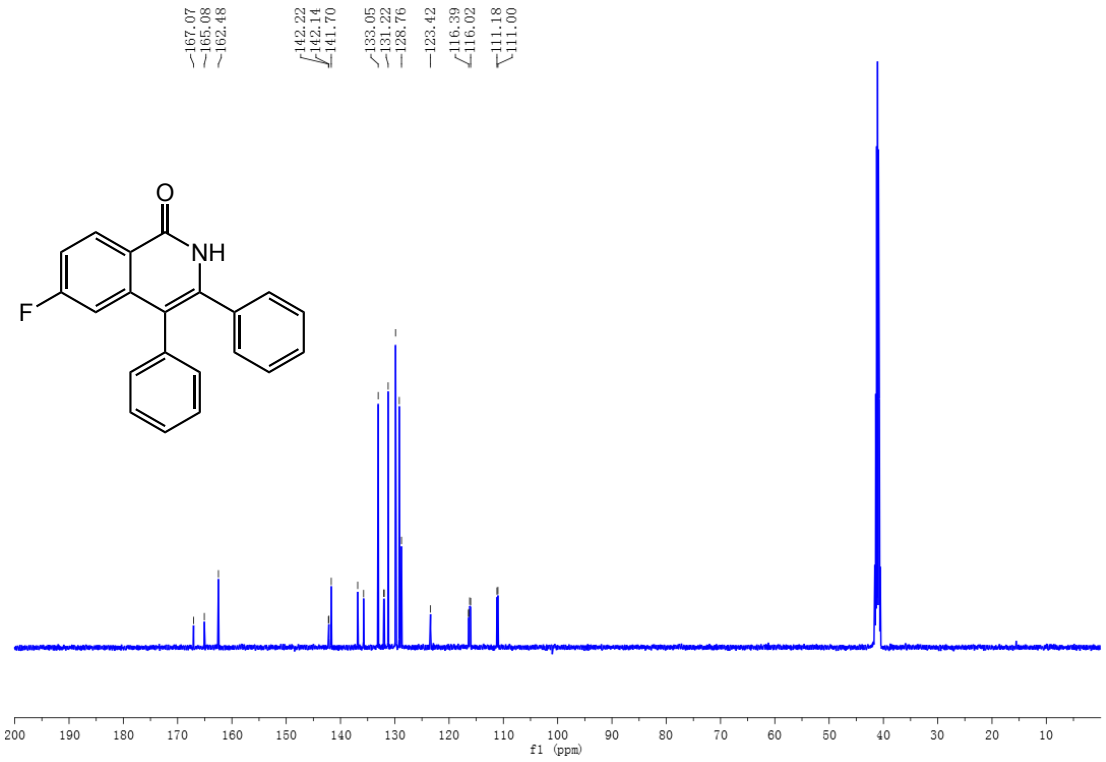
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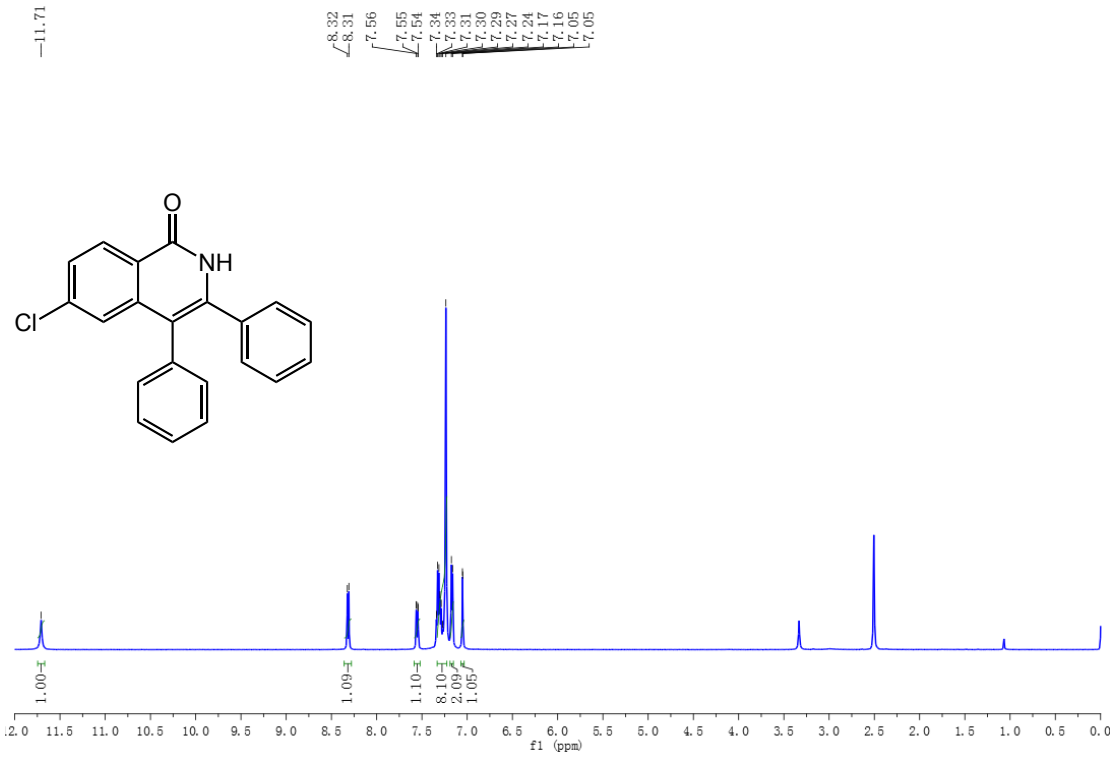
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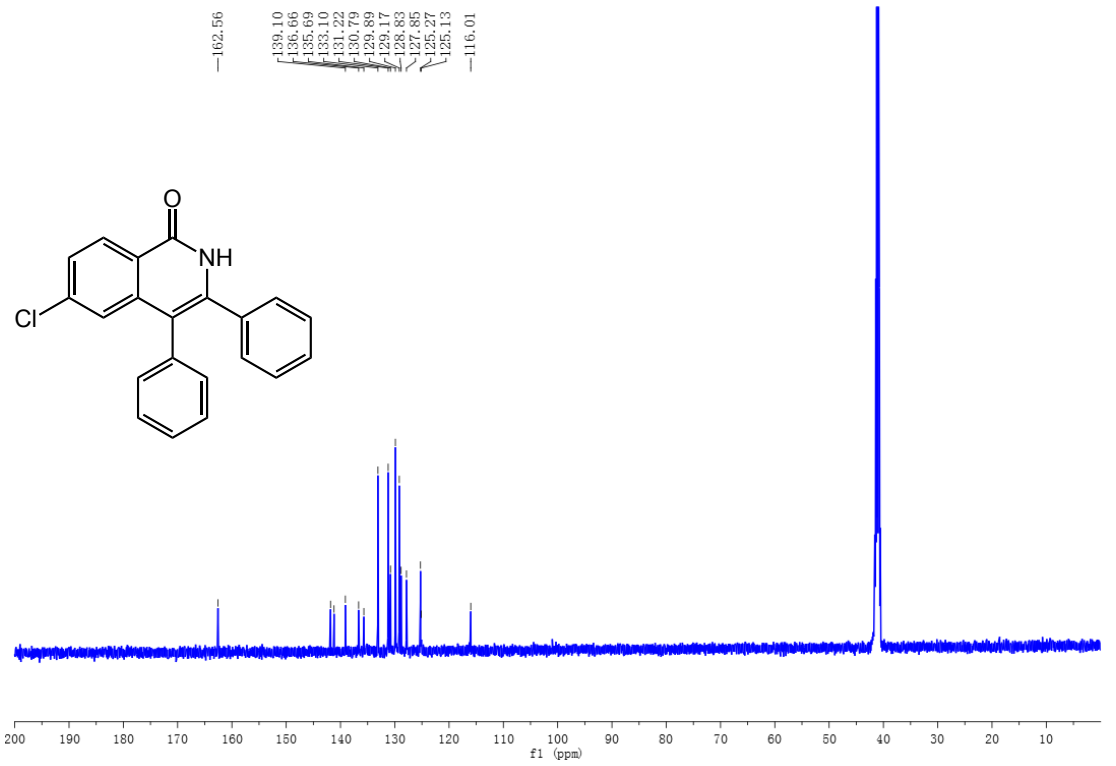
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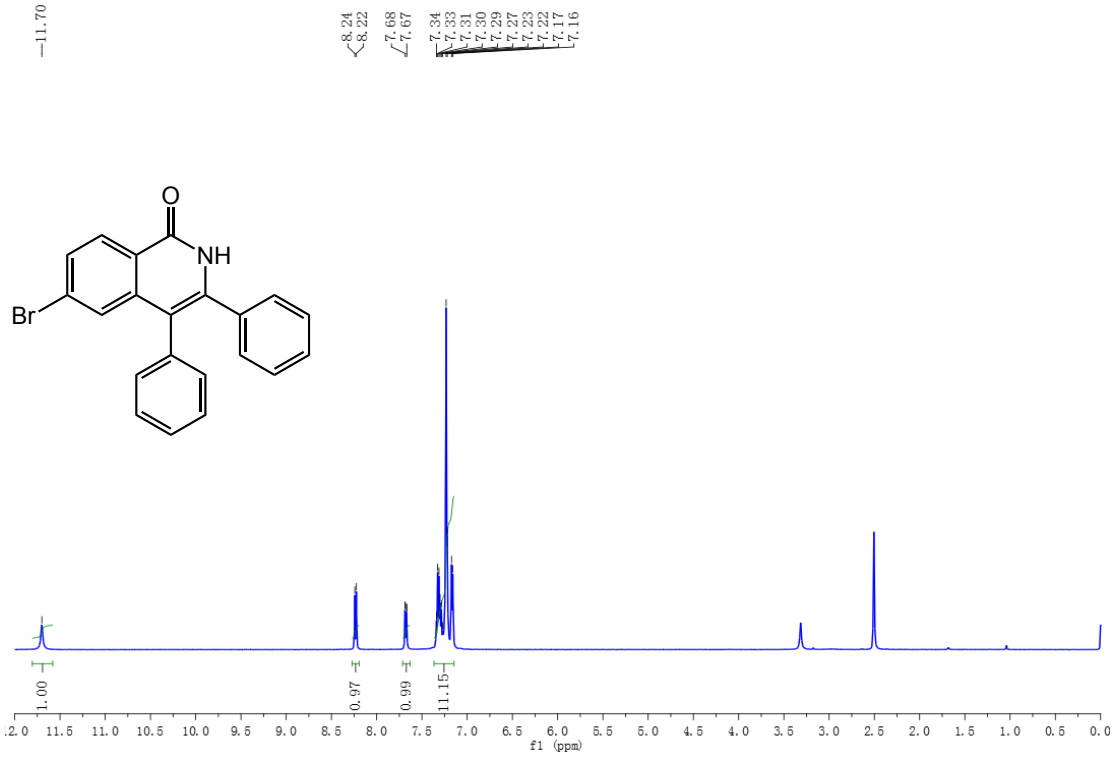
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Br
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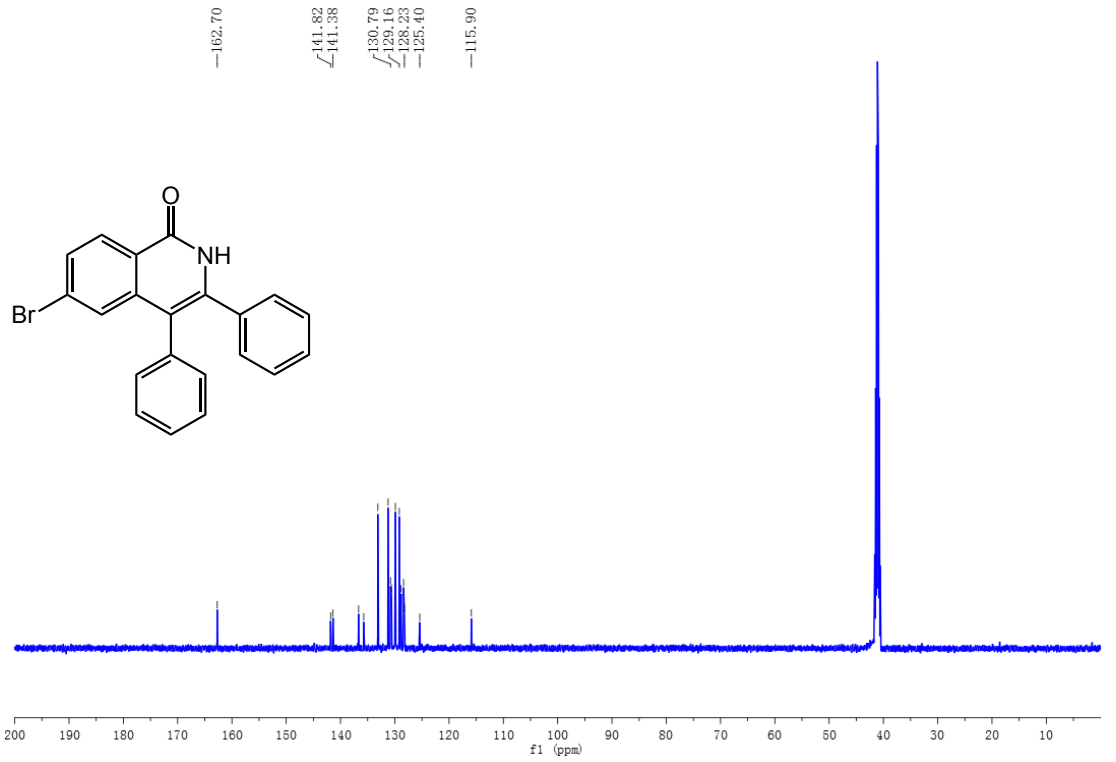
11.15
f1 (ppm)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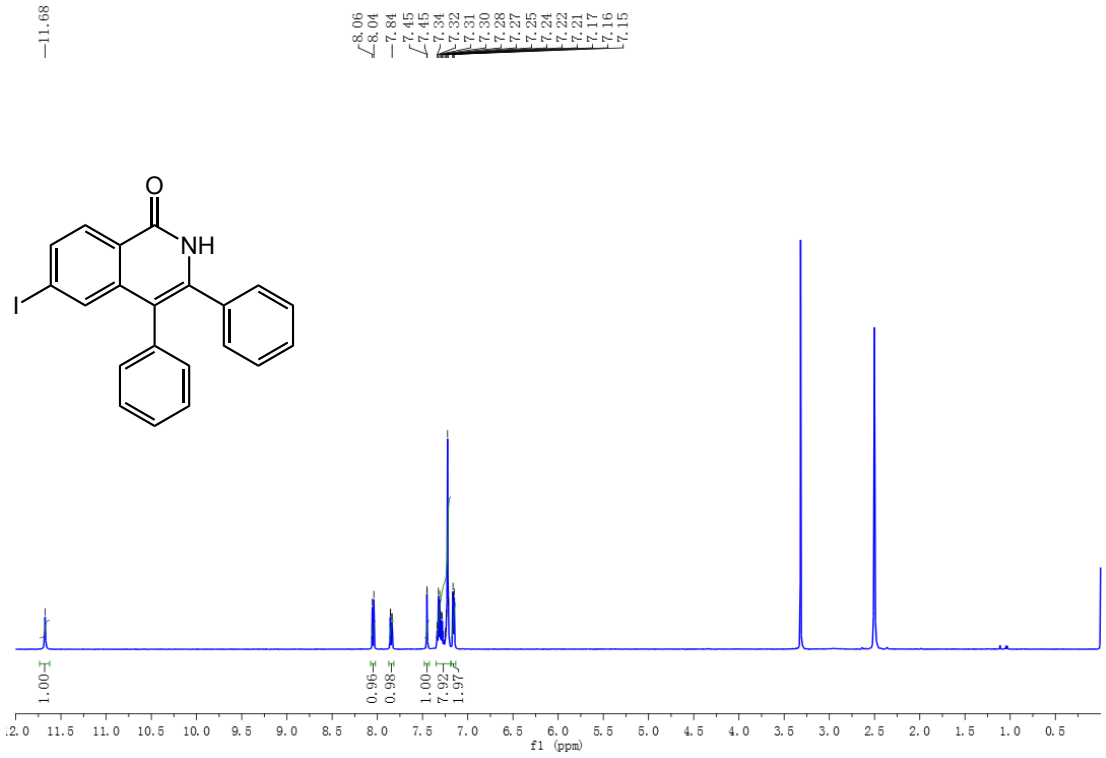
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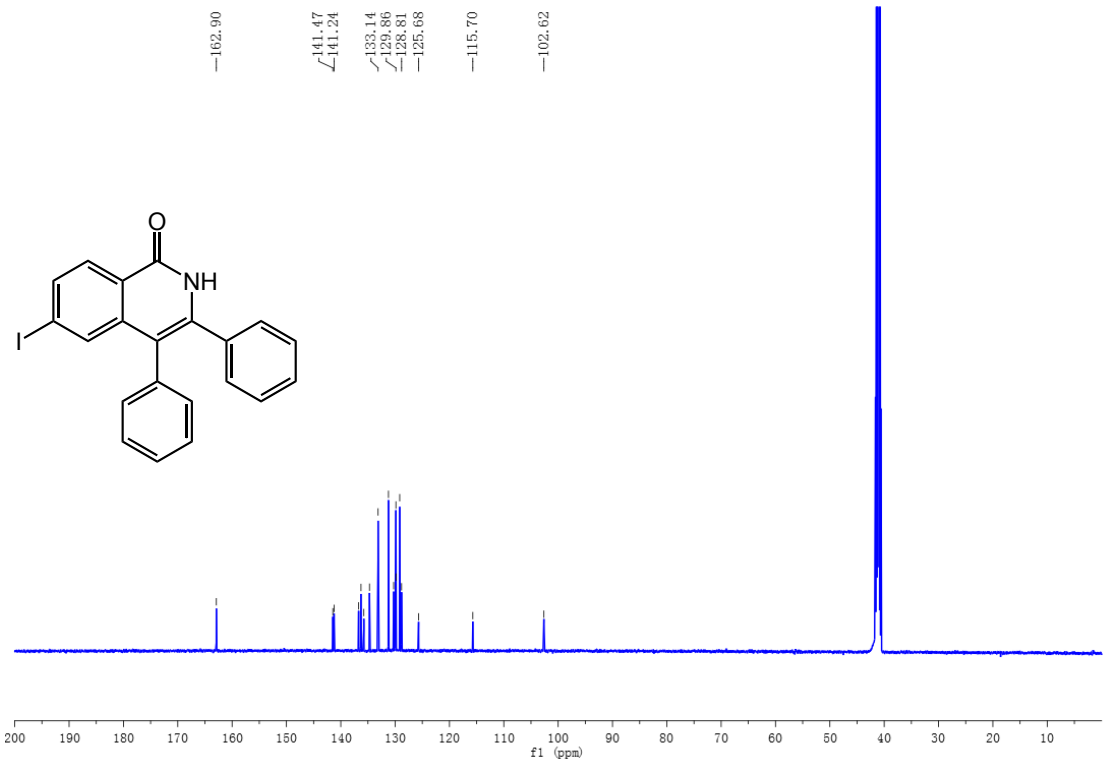
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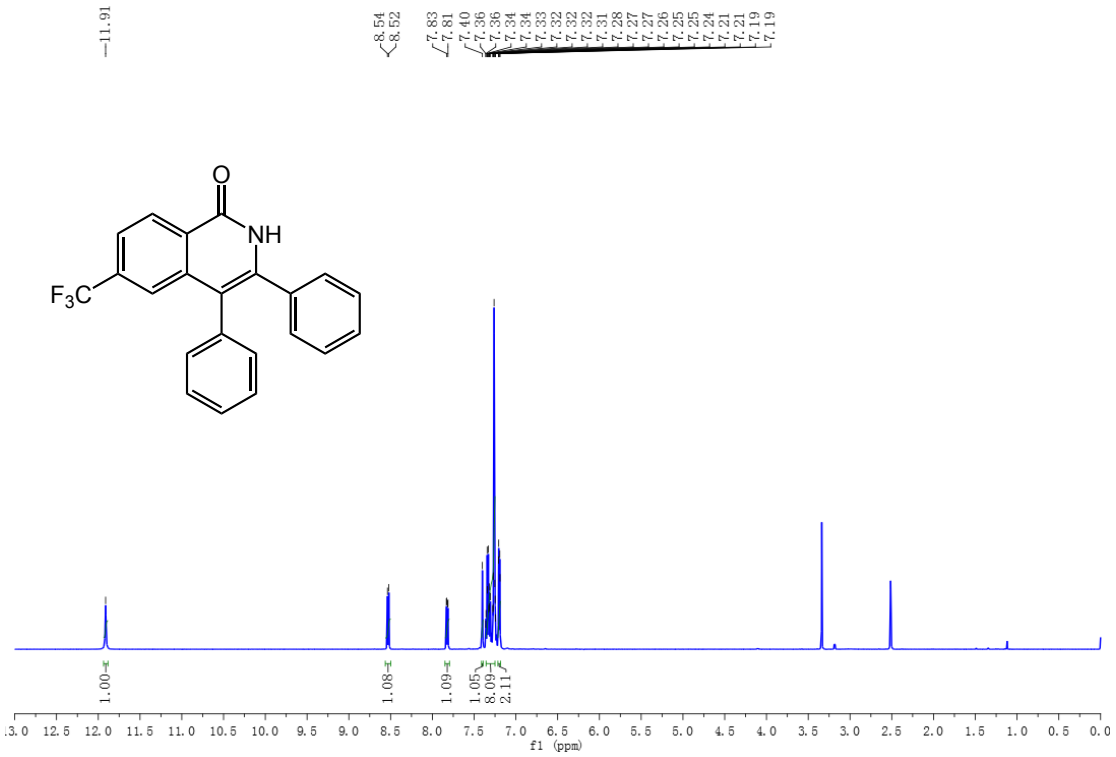
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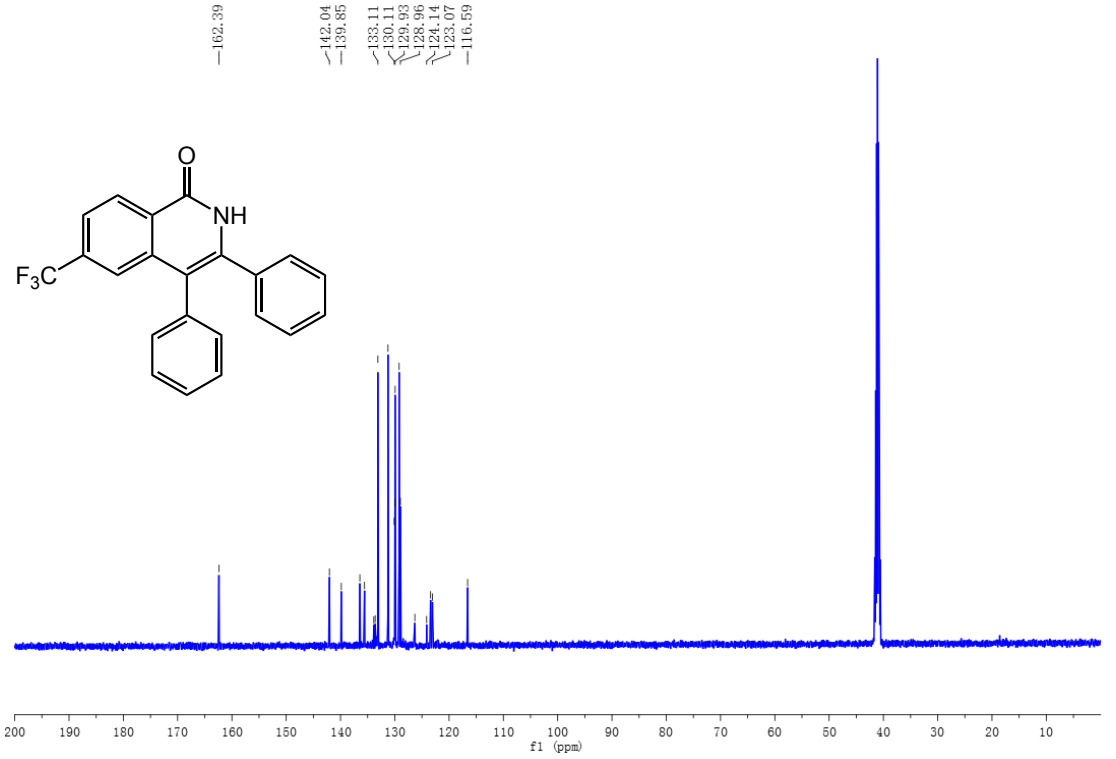
f1 (ppm)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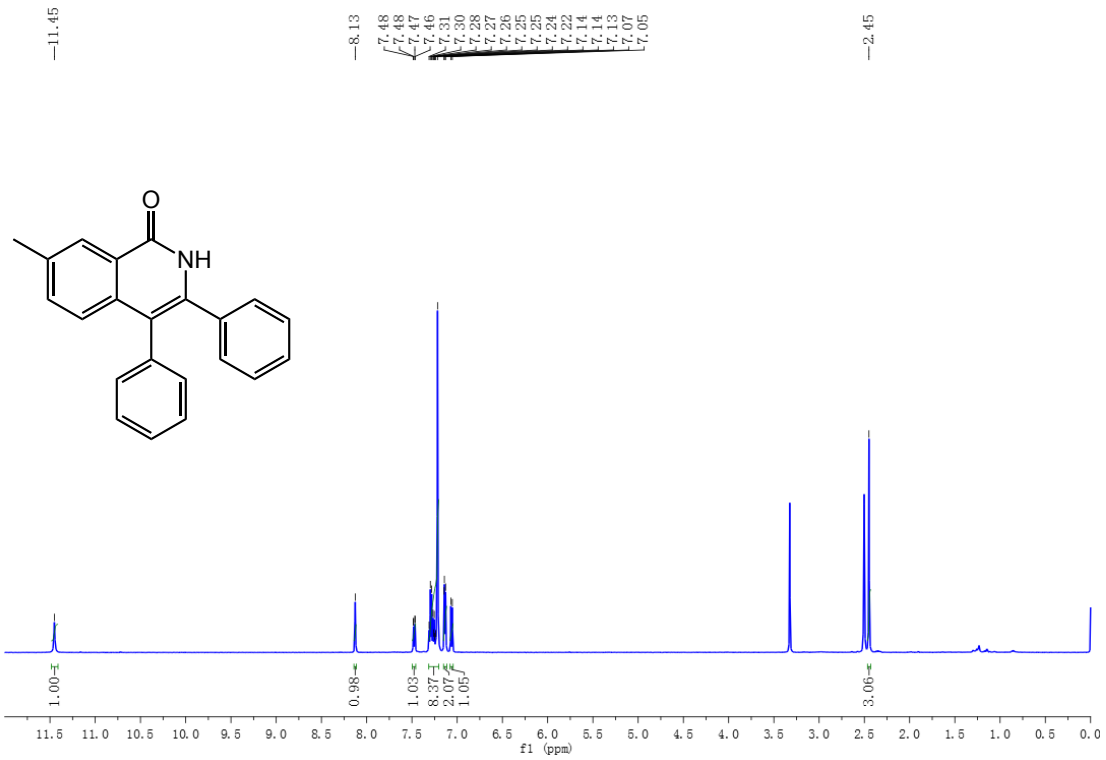
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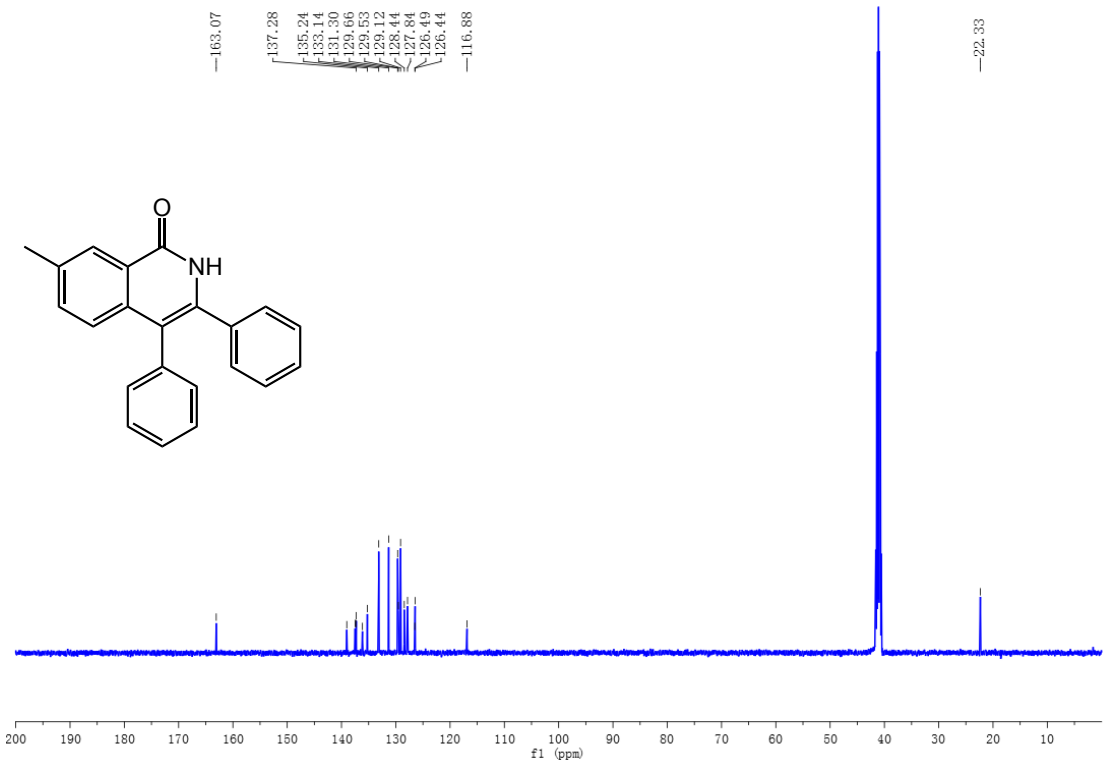
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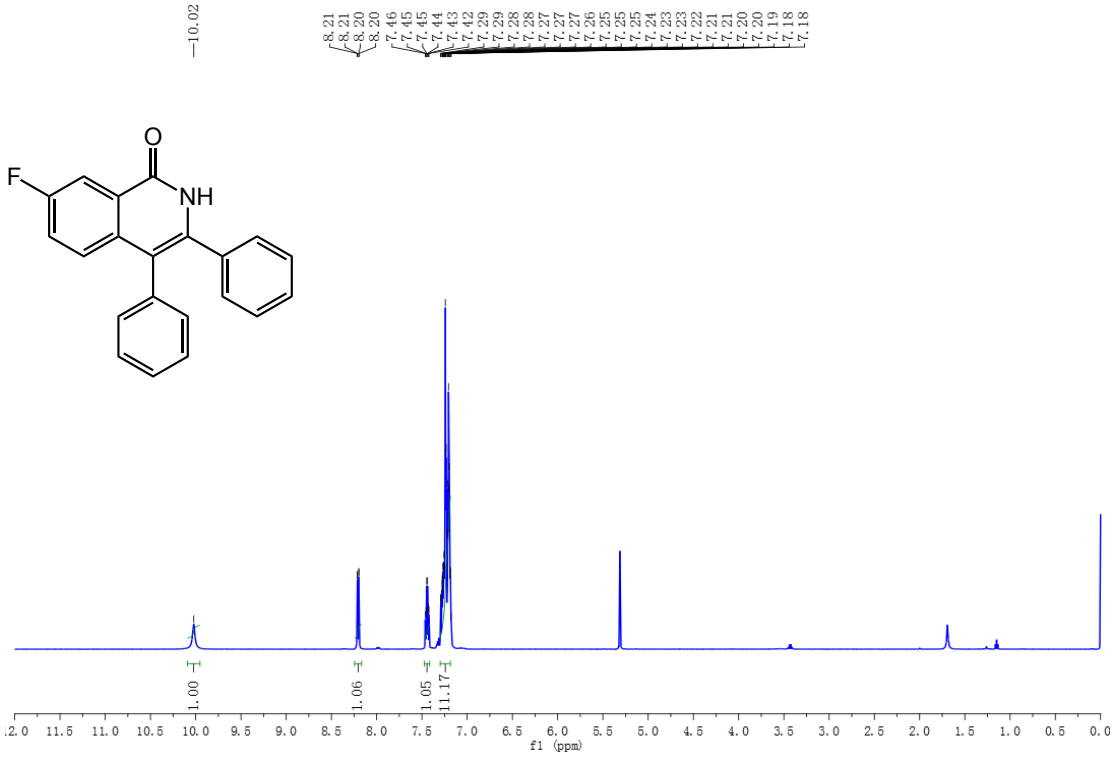
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7.23
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7.21
7.21
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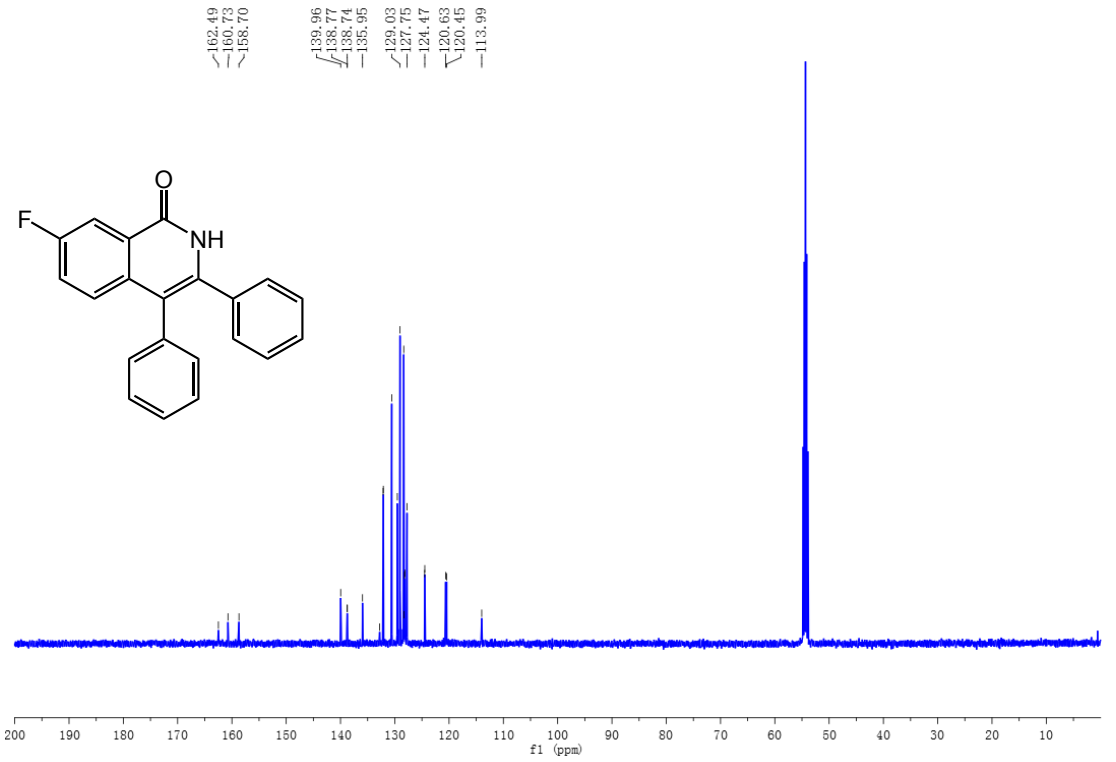
f1 (ppm)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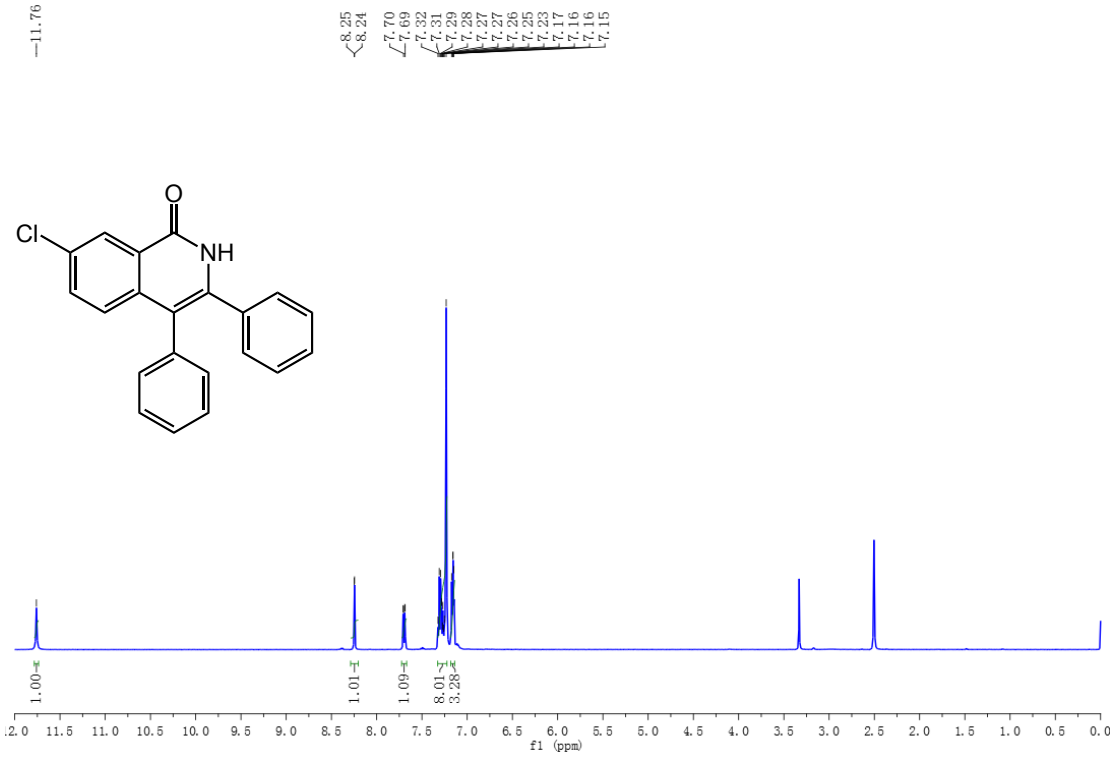
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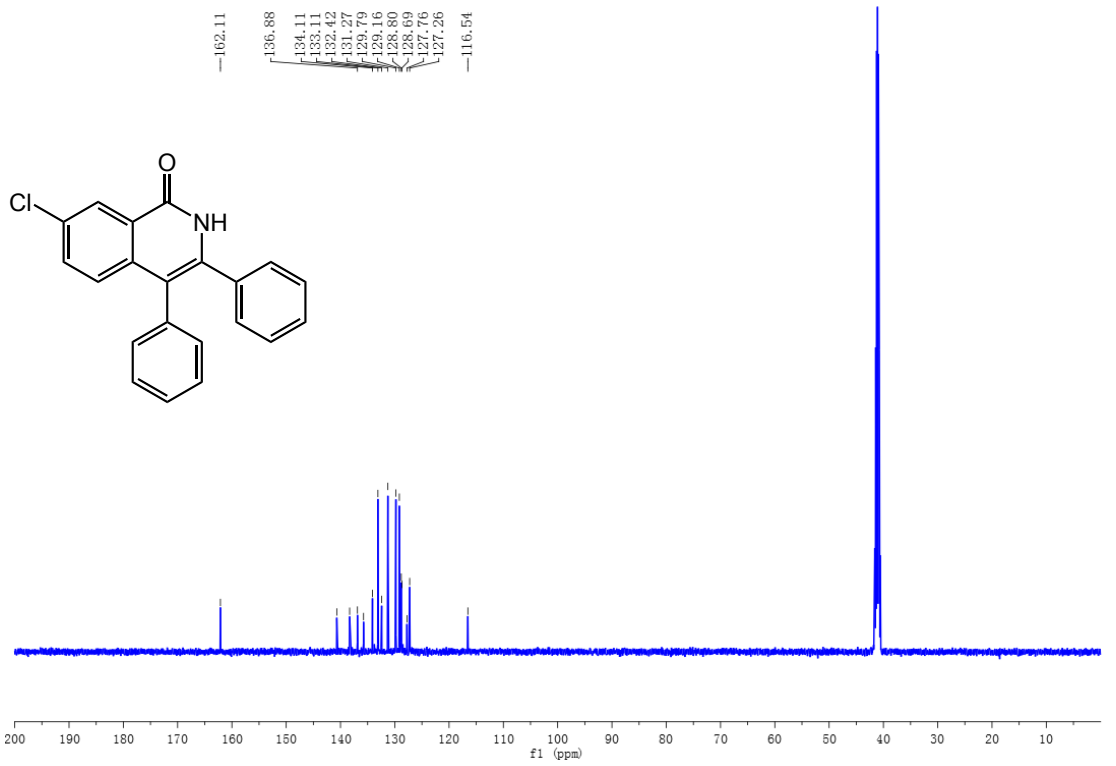
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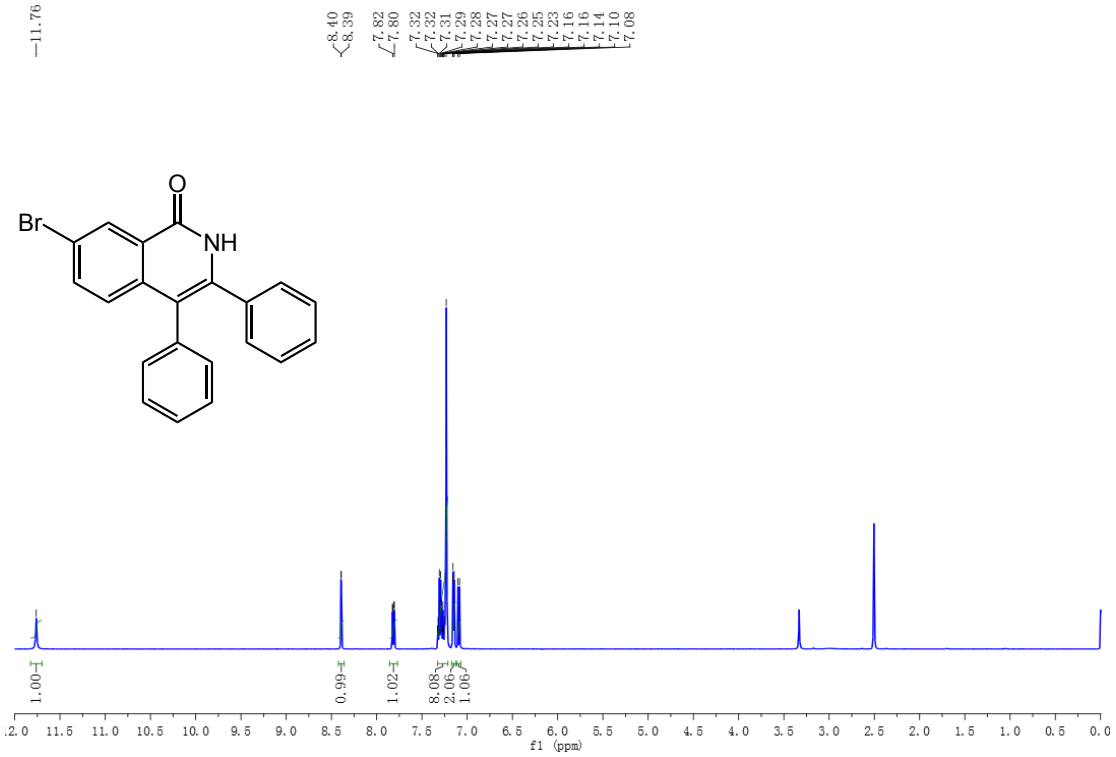
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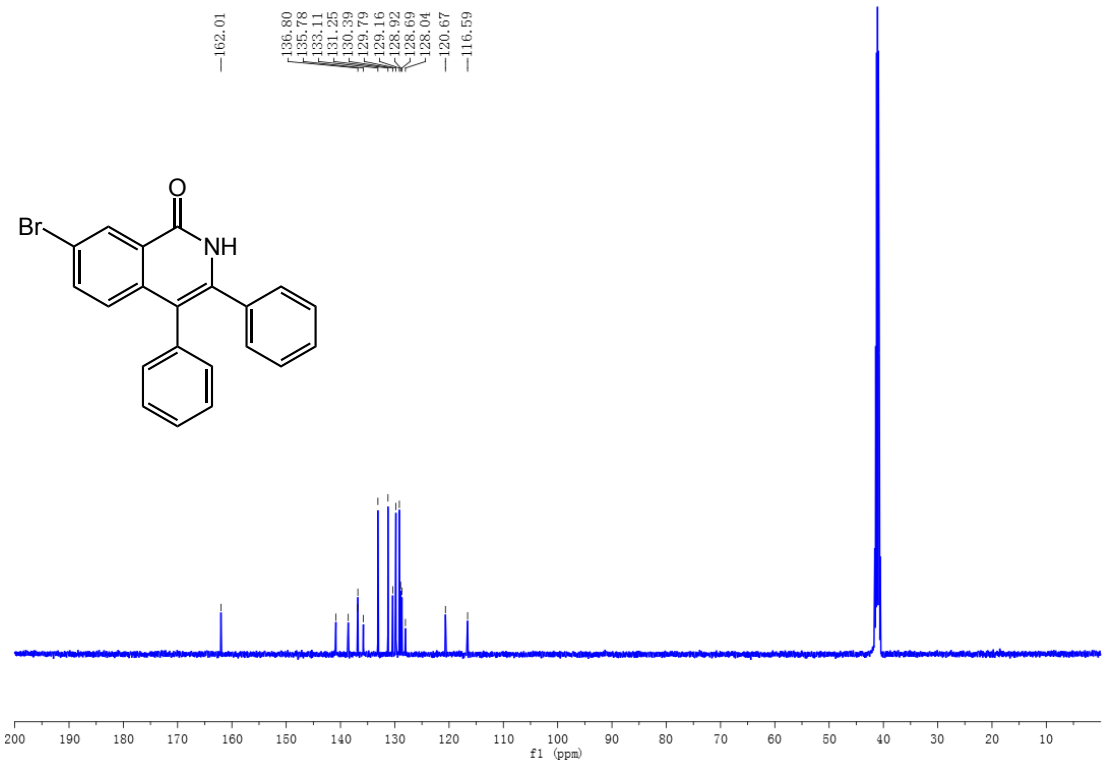
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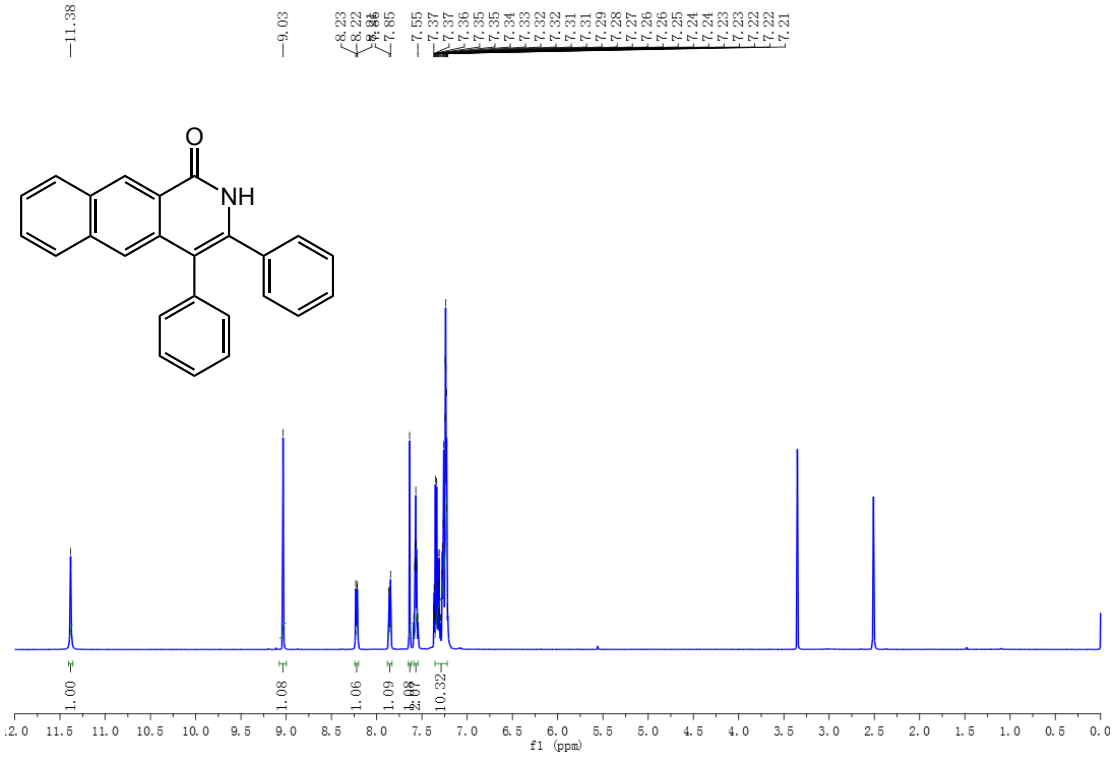
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7.31
7.29
7.28
7.27
7.26
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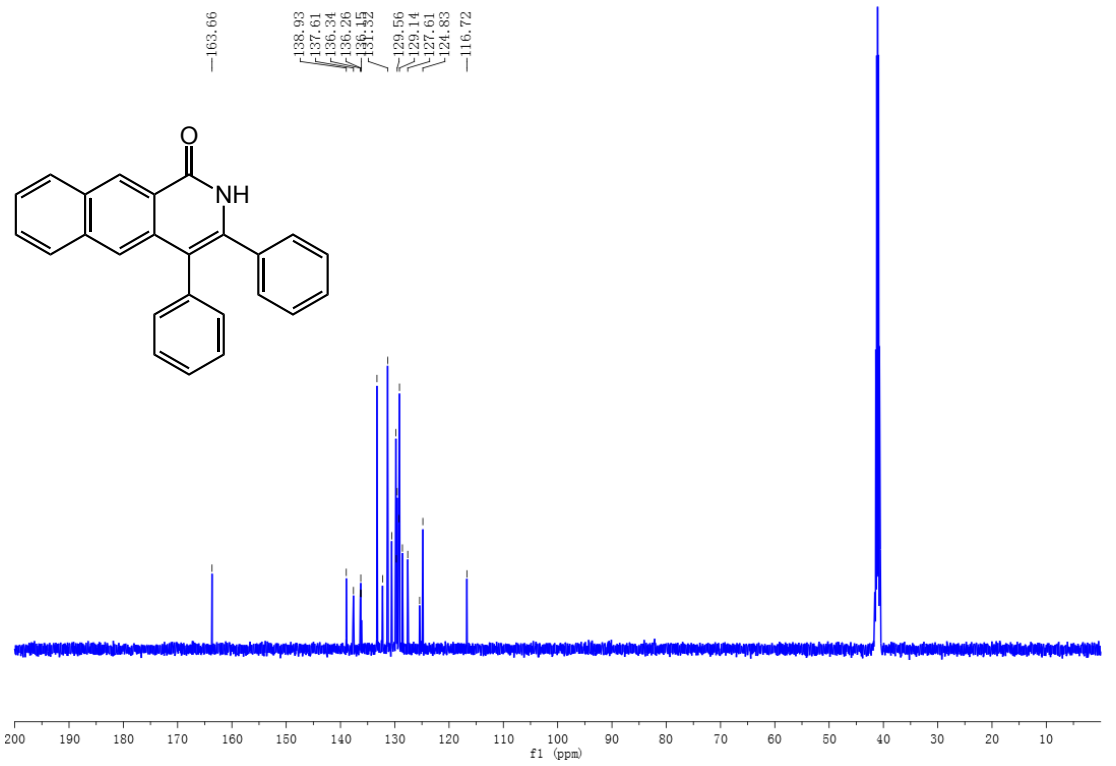
10.32
f1 (ppm)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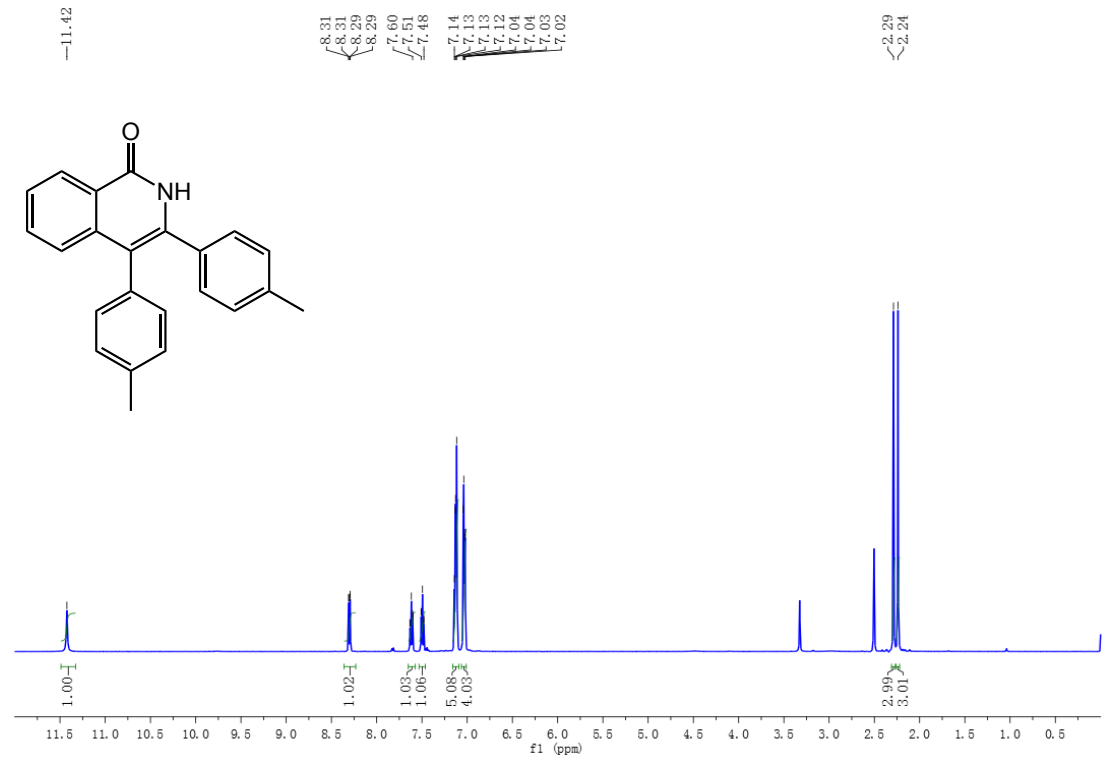
NH
f1 (ppm)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8.31
8.29
8.29
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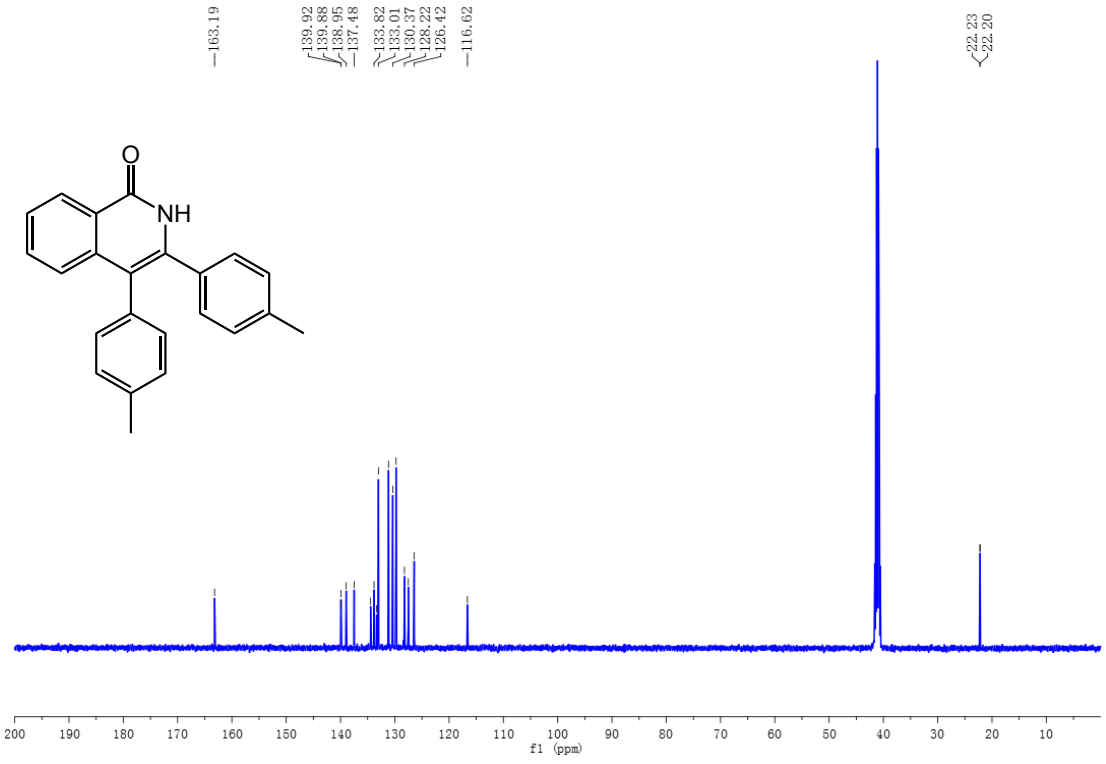
7.51
7.48
7.14
7.13
7.13
7.12
7.04
7.04
7.03
7.02
2.29
2.24
O
NH
1.00
1.02
1.03
1.06
5.08
4.03
2.99
3.01
f1 (ppm)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139.92
139.88
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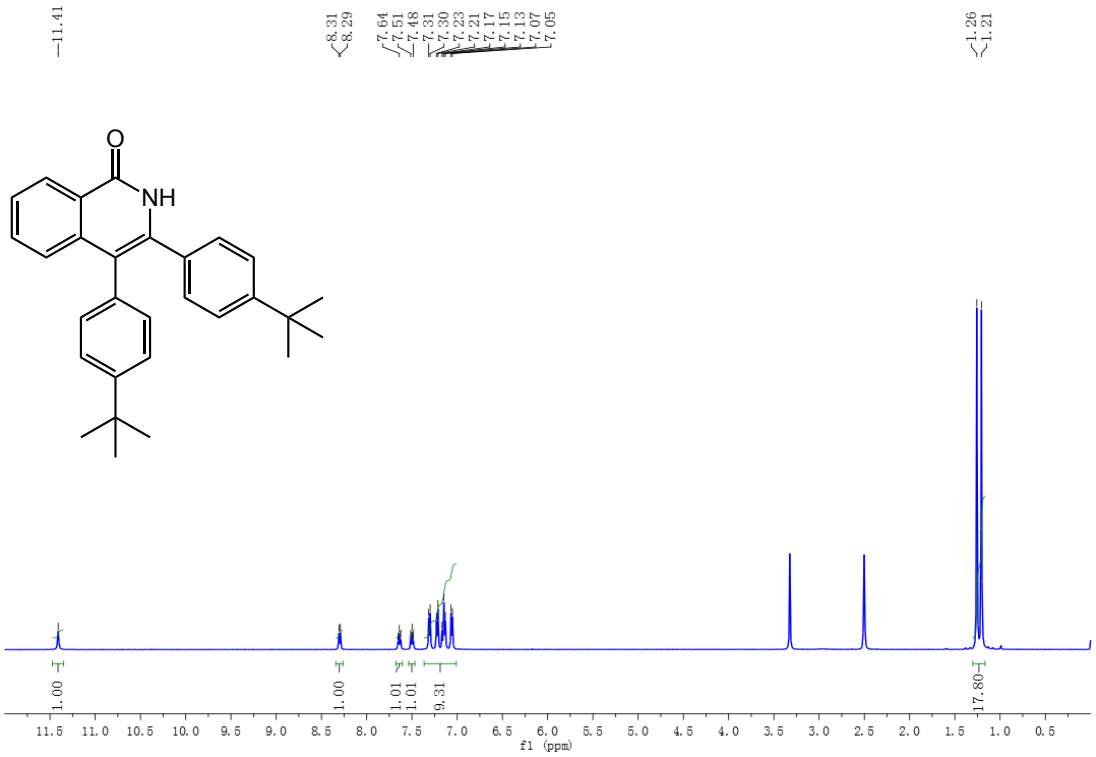
133.01
130.37
128.22
126.42
116.62
22.23
22.20
O
NH
f1 (ppm)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7.31
7.30
7.23
7.21
7.17
7.15
7.13
7.07
7.05
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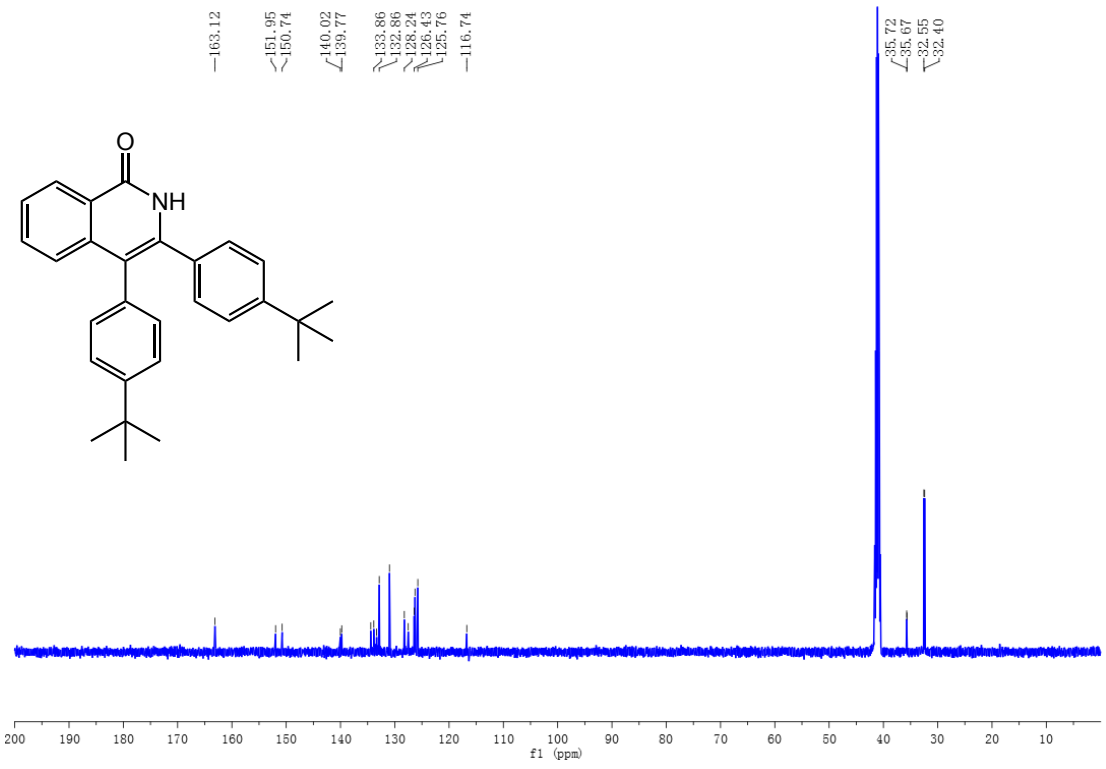
1.21
O
NH
1.00
1.00
1.01
1.01
9.31
17.80
f1 (ppm)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116.74
35.72
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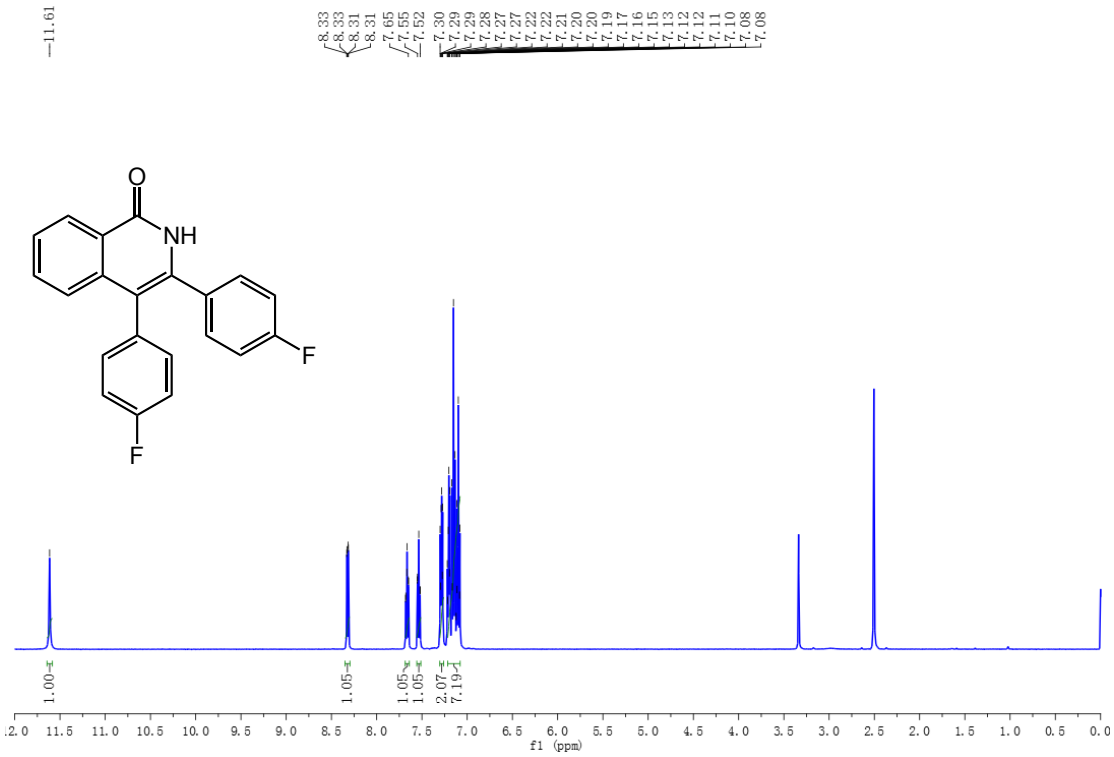
32.55
32.40
O
NH
f1 (ppm)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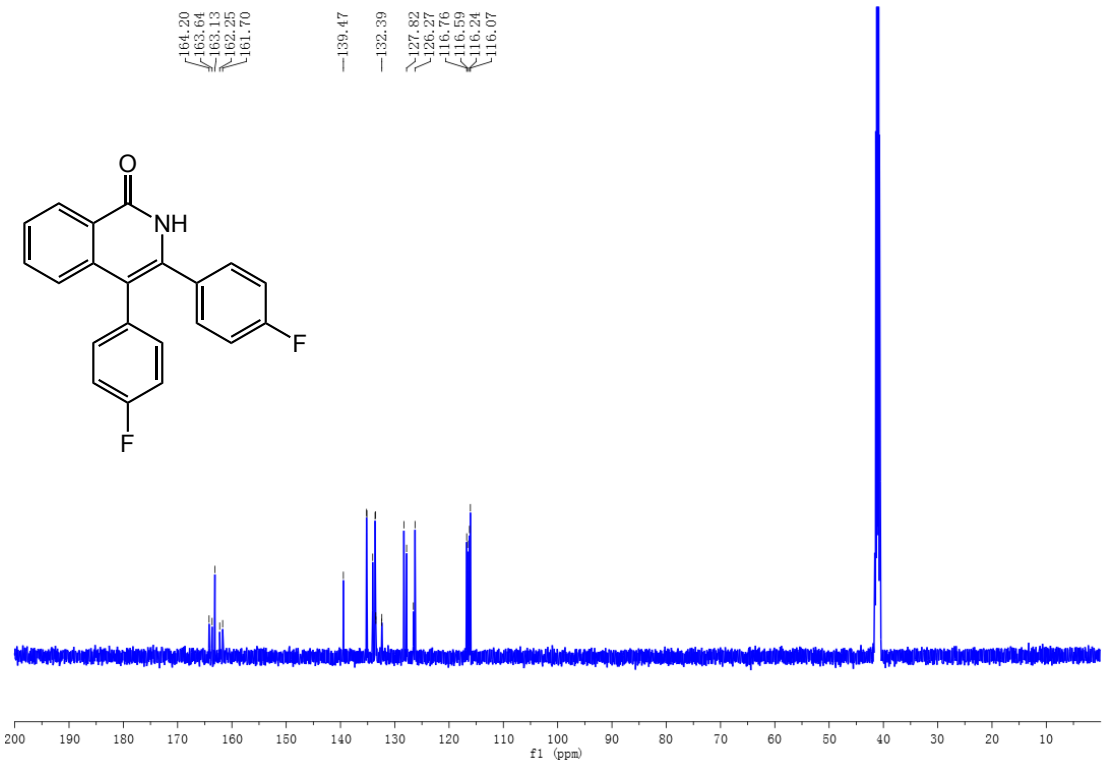
7.27
7.22
7.22
7.21
7.20
7.20
7.19
7.17
7.16
7.15
7.13
7.12
7.12
7.11
7.10
7.08
7.08
O
NH
F
F
1.00
1.05
1.05
1.05
2.07
7.19
f1 (ppm)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163.13
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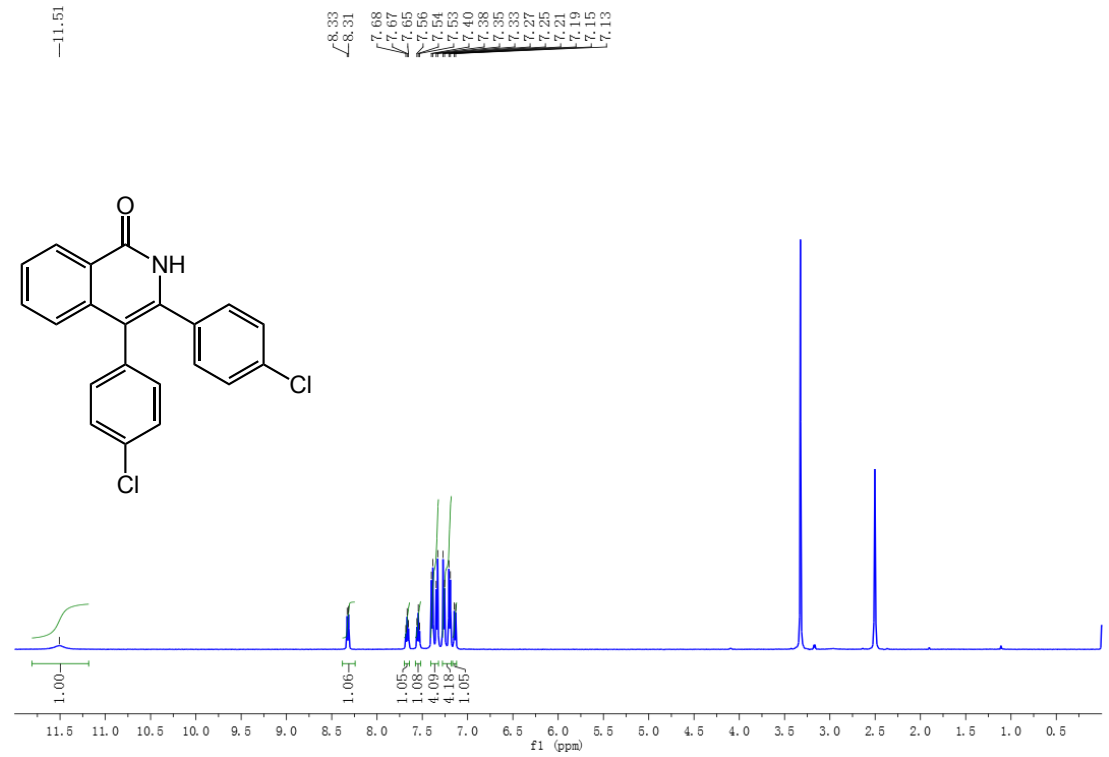
116.59
116.24
116.07
O
NH
F
F
f1 (ppm)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7.35
7.33
7.27
7.25
7.21
7.19
7.15
7.13
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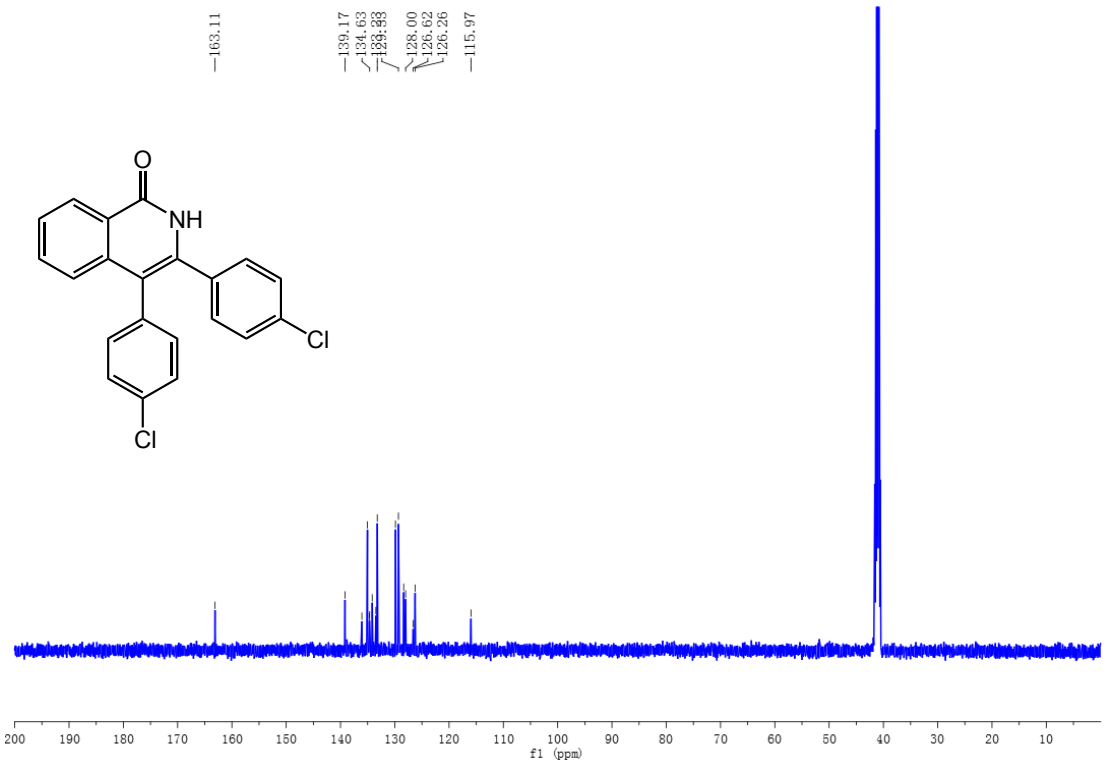
NH
Cl
Cl
1.00
1.06
1.05
1.08
4.09
4.18
1.05
f1 (ppm)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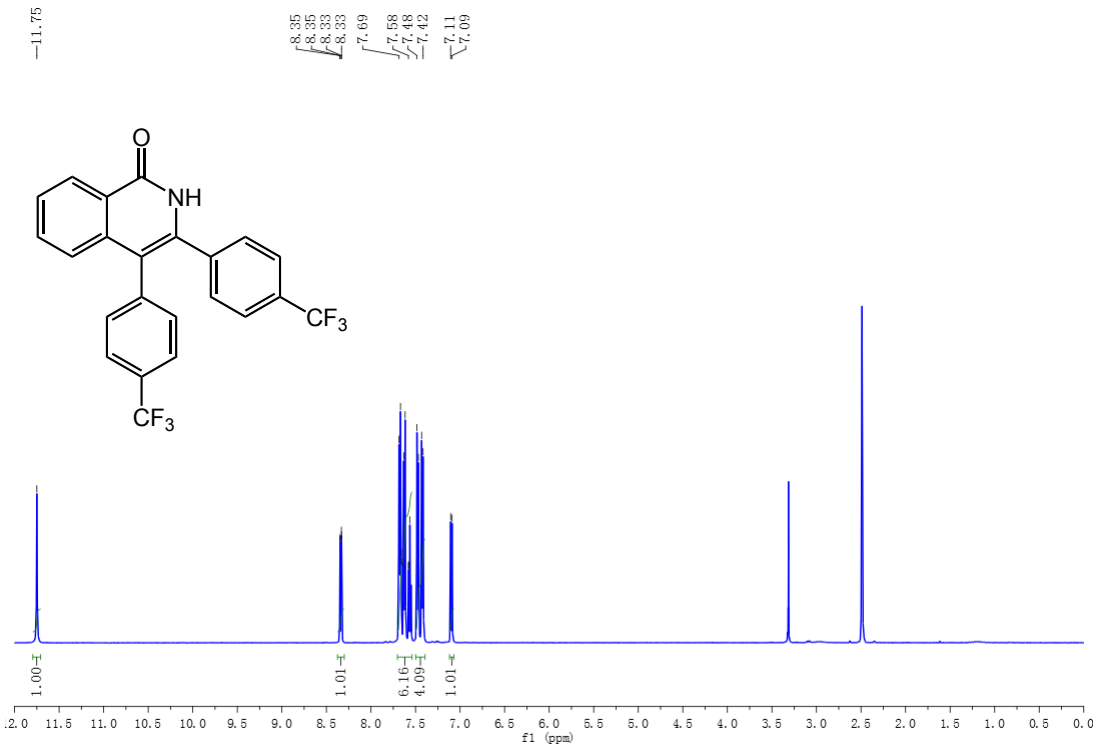
NH
Cl
Cl
f1 (ppm)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7.58
7.48
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7.09
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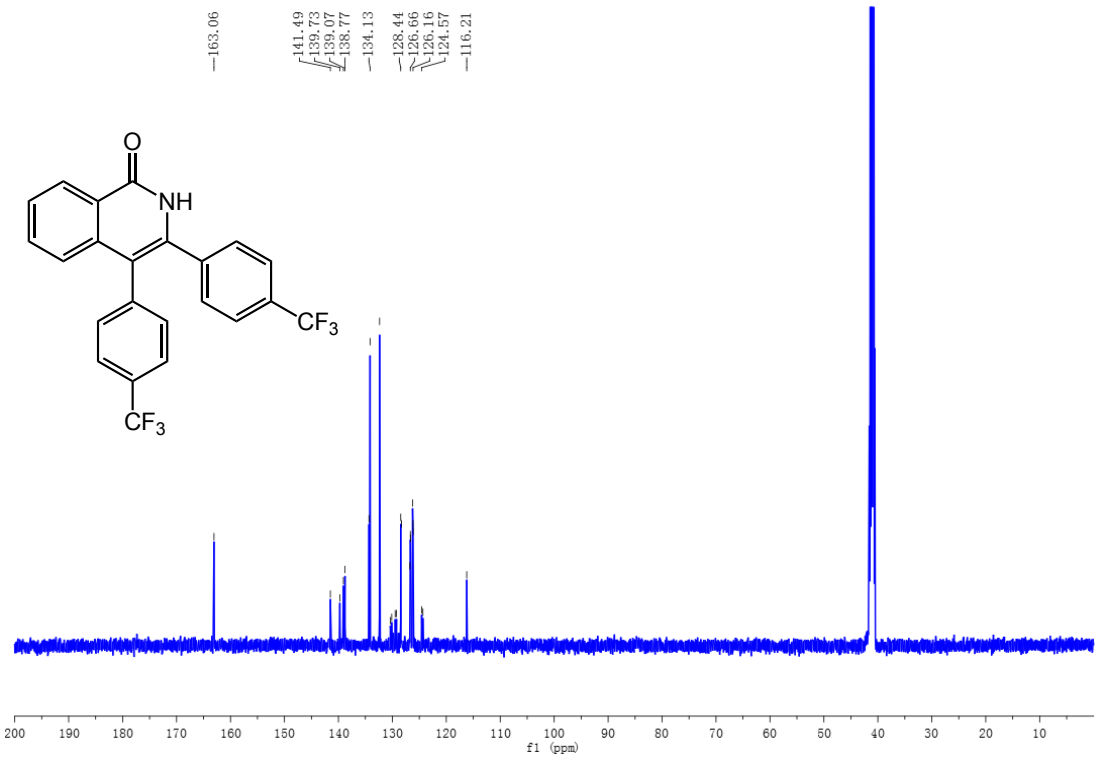
NH
CF3
CF3
1.00
1.01
6.16
4.09
1.01
f1 (ppm)


163.06
141.49
139.73
139.07
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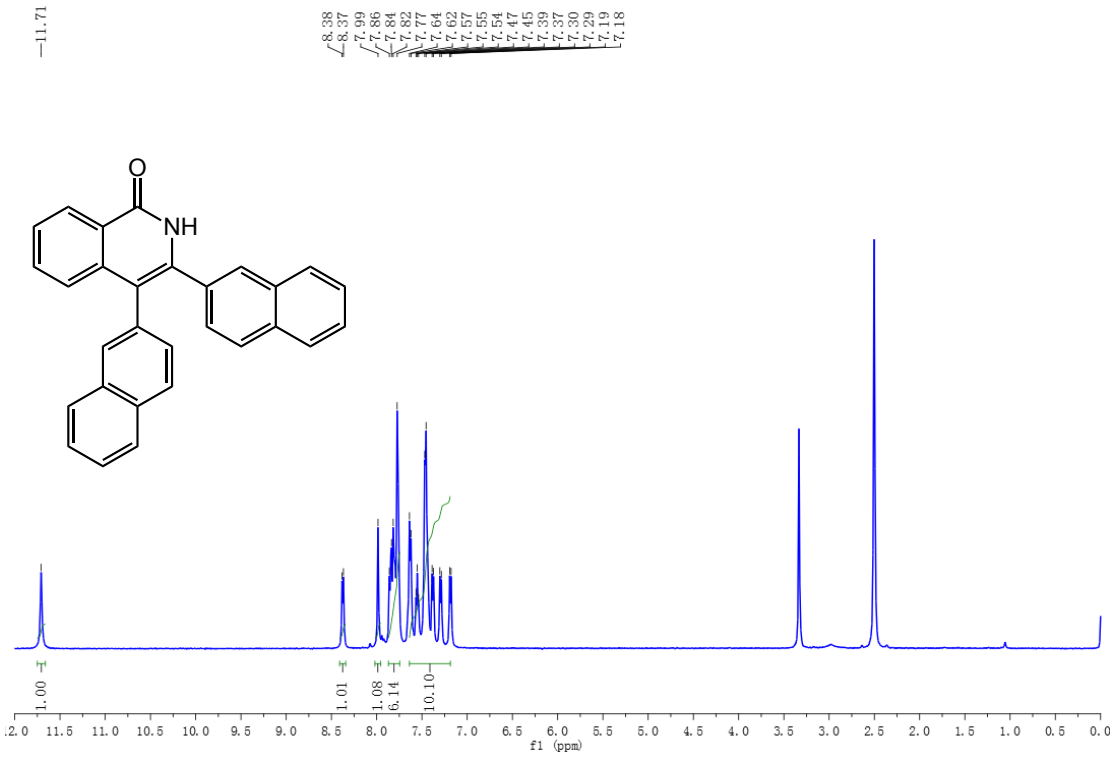
128.44
126.66
126.16
124.57
116.21
O
NH
CF3
CF3
f1 (ppm)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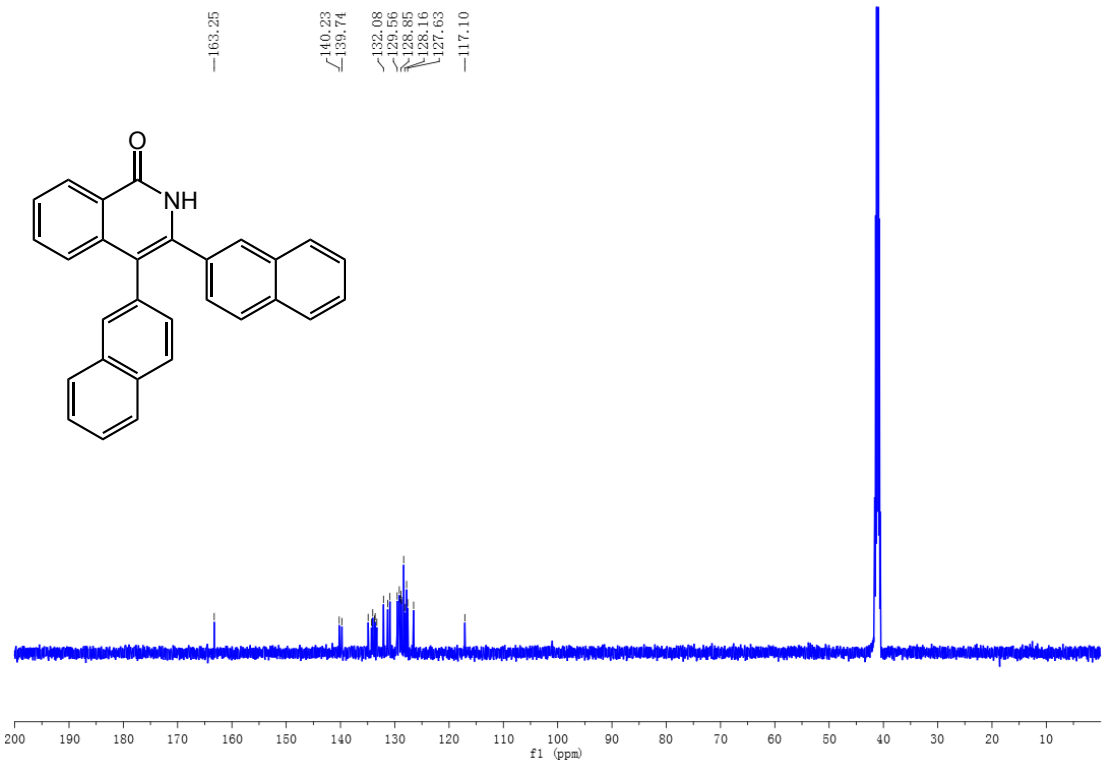
7.82
7.77
7.64
7.62
7.57
7.55
7.54
7.47
7.45
7.39
7.37
7.30
7.29
7.19
7.18
O
NH
1.00
1.01
1.08
6.14
10.10
f1 (ppm)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132.08
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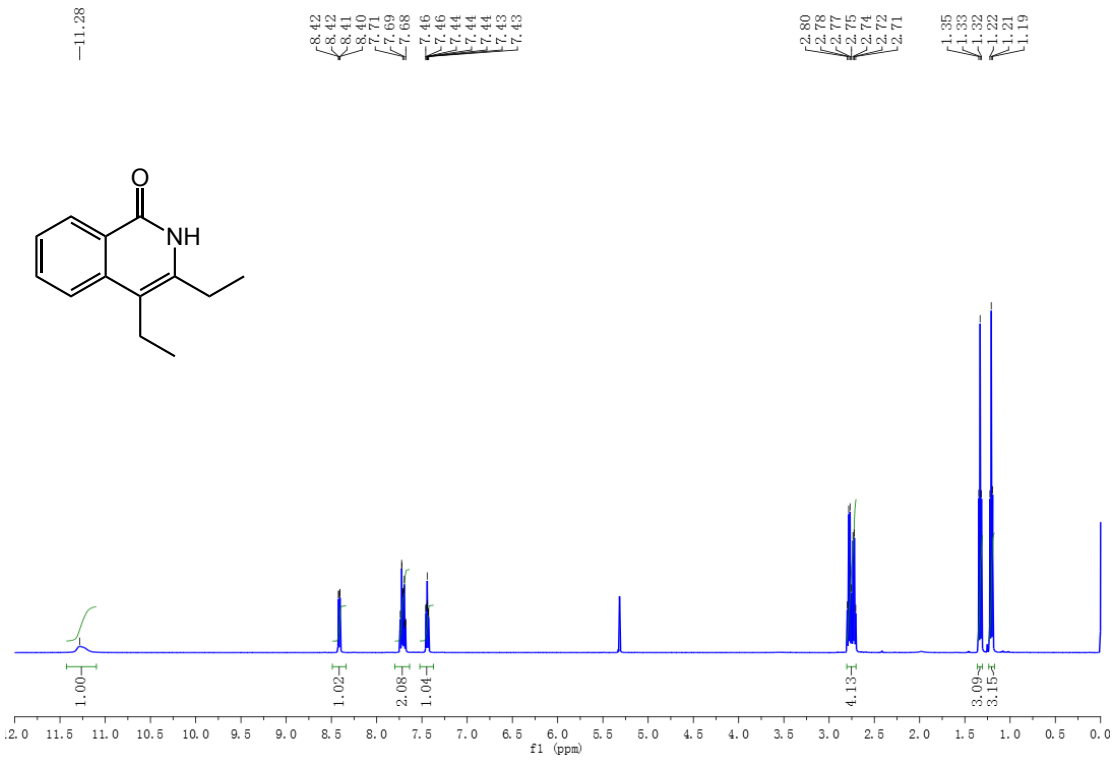
128.85
128.16
127.63
117.10
O
NH
f1 (ppm)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7.46
7.44
7.44
7.44
7.43
7.43
2.80
2.78
2.77
2.75
2.74
2.72
2.71
1.35
1.33
1.32
1.22
1.21
1.19
O
NH
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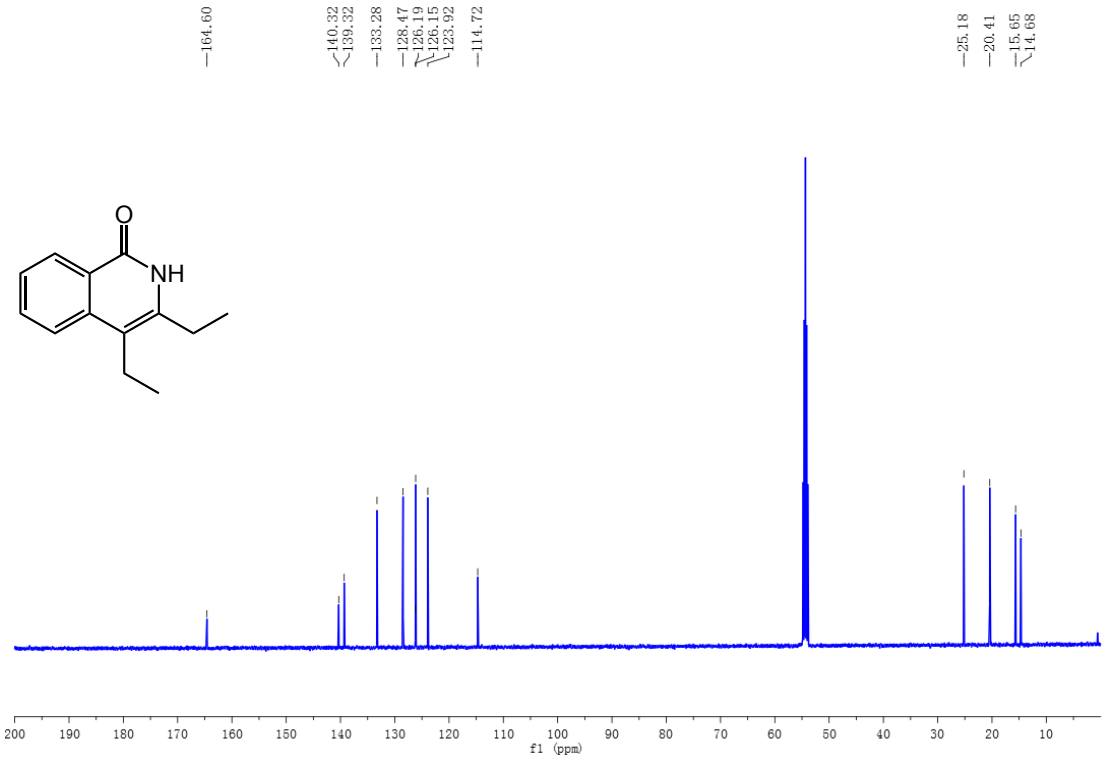
1.02
2.08
1.04
4.13
3.09
3.15
f1 (ppm)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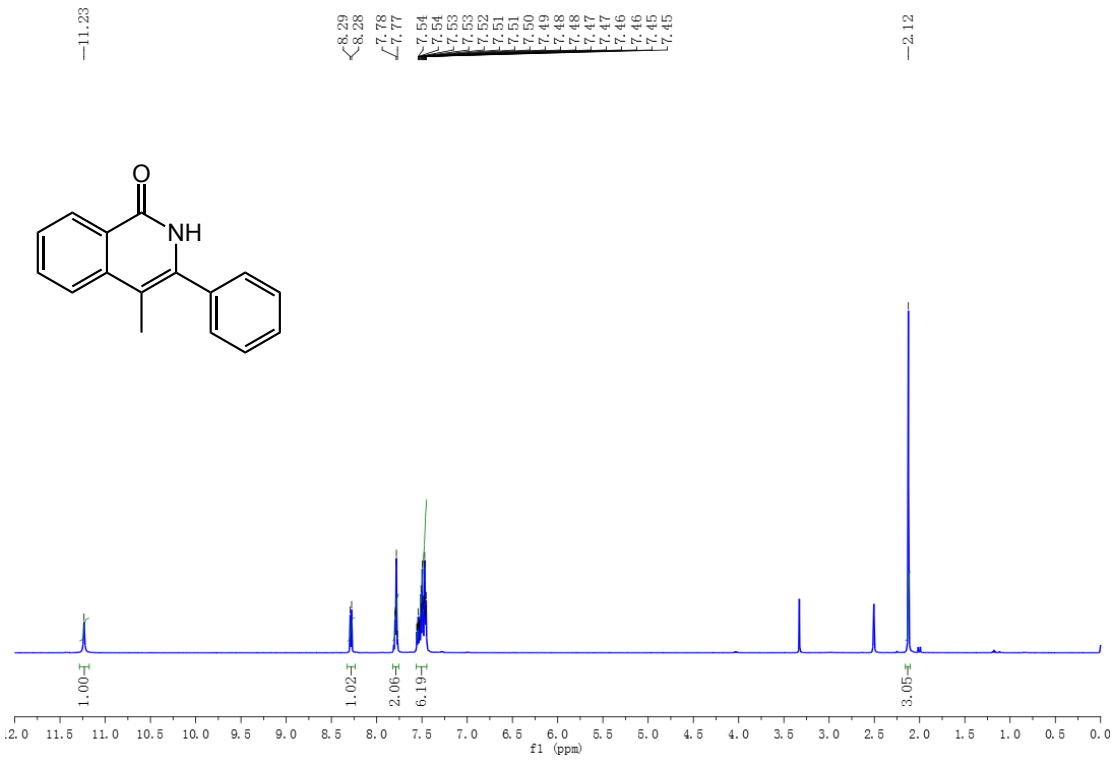
126.15
123.92
114.72
25.18
20.41
15.65
14.68
O
NH
f1 (ppm)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7.54
7.54
7.53
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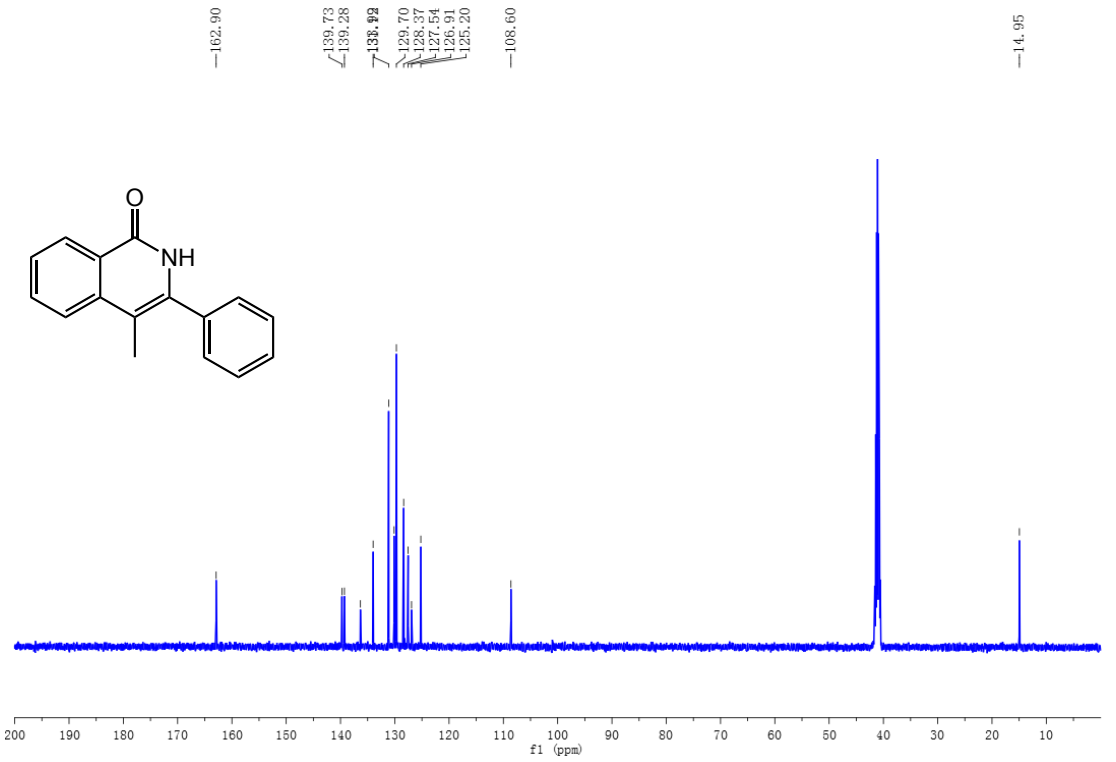
7.52
7.51
7.51
7.50
7.49
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.45
2.12
O
NH
1.00
1.02
2.06
6.19
3.05
f1 (ppm)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126.91
125.20
108.60
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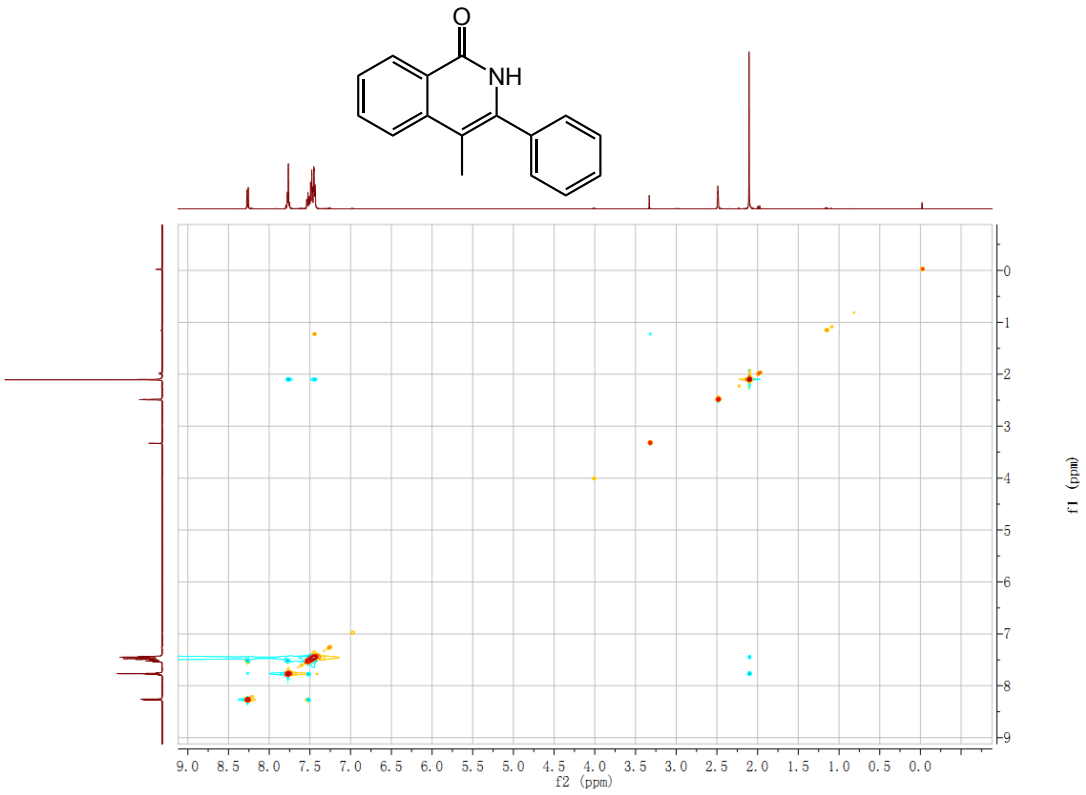
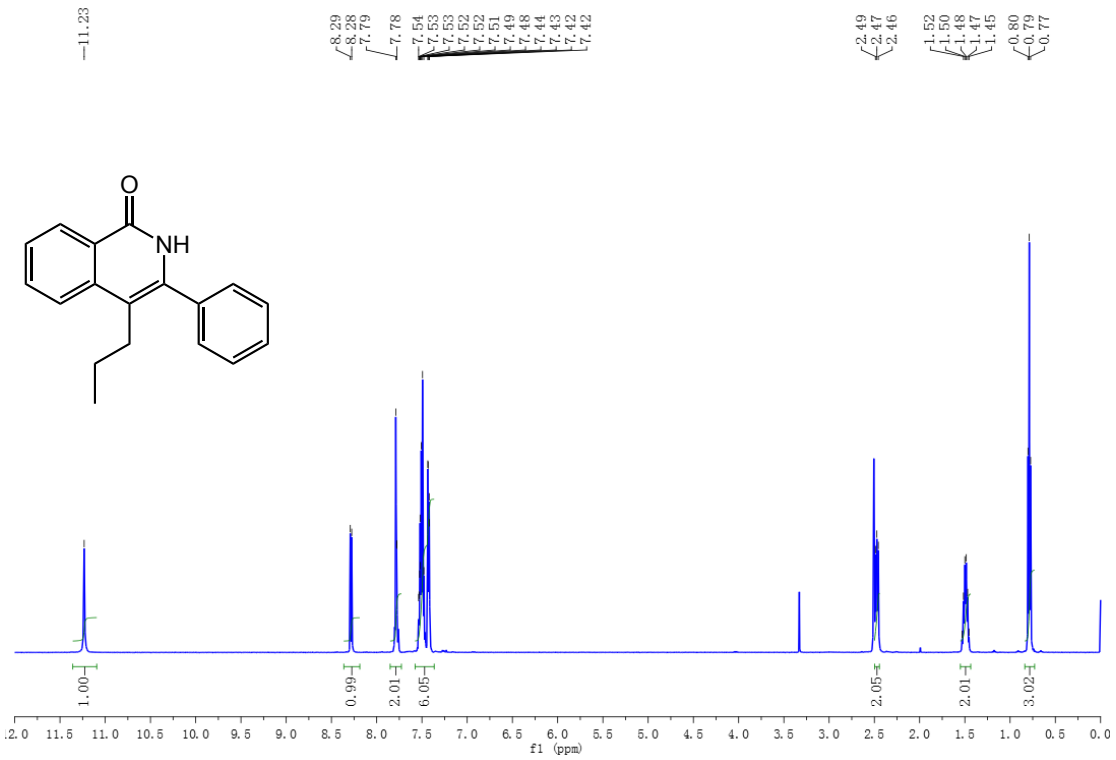
O
NH
f1 (ppm)


O
NH
f1 (ppm)
f2 (ppm)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7.54
7.53
7.53
7.52
7.52
7.51
7.49
7.48
7.44
7.43
7.42
7.42
2.49
2.47
2.46
1.52
1.50
1.48
1.47
1.45
0.80
0.79
0.77
O
NH
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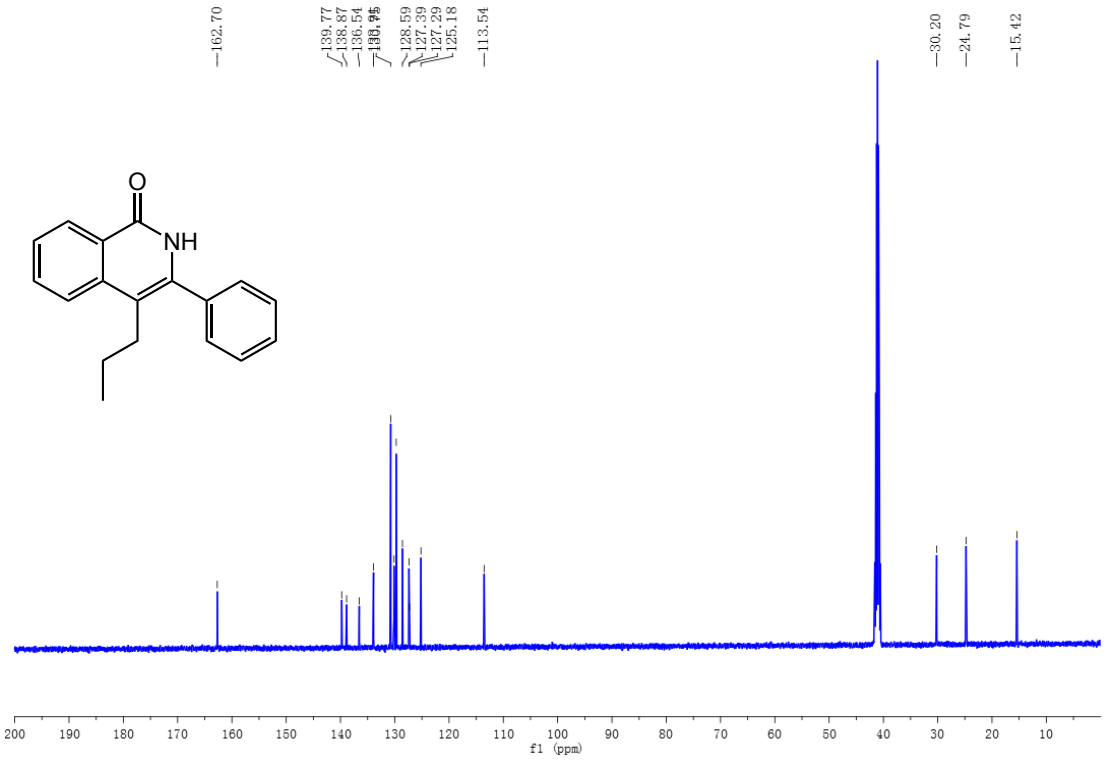
0.99
2.01
6.05
2.05
2.01
3.02
f1 (ppm)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125.18
113.54
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24.79
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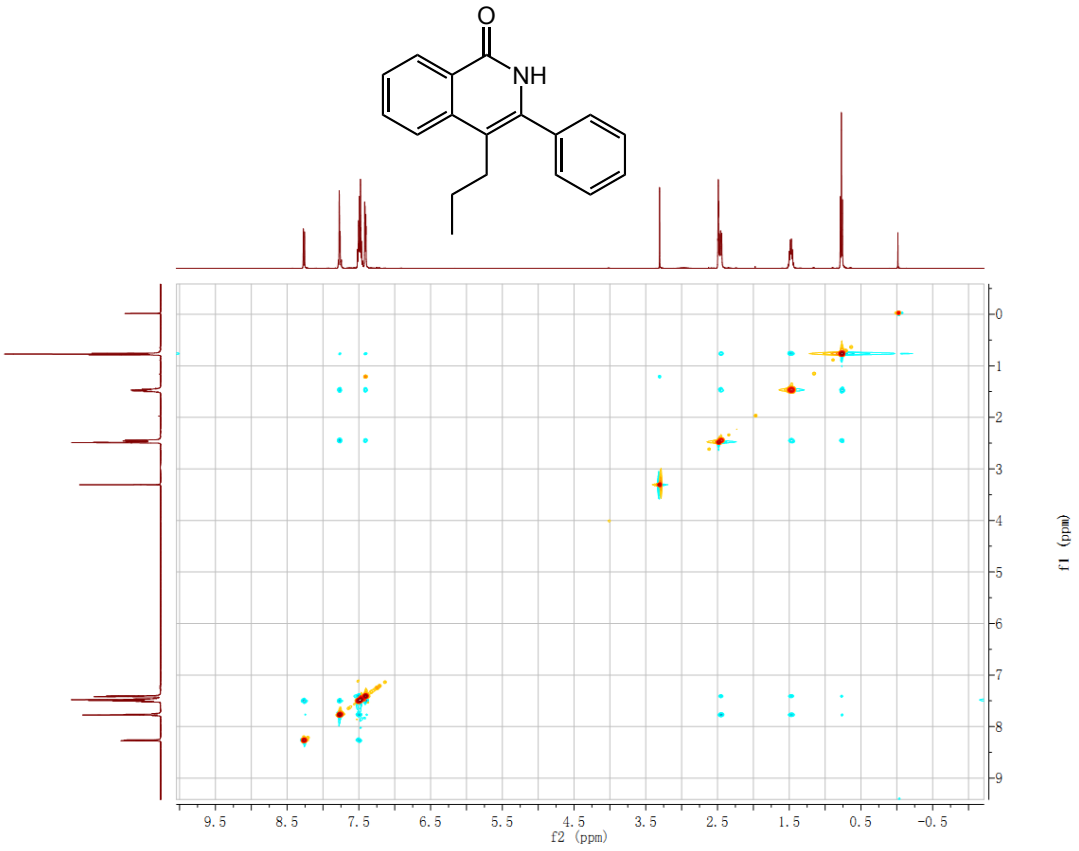
O
NH
f1 (ppm)


O
NH
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
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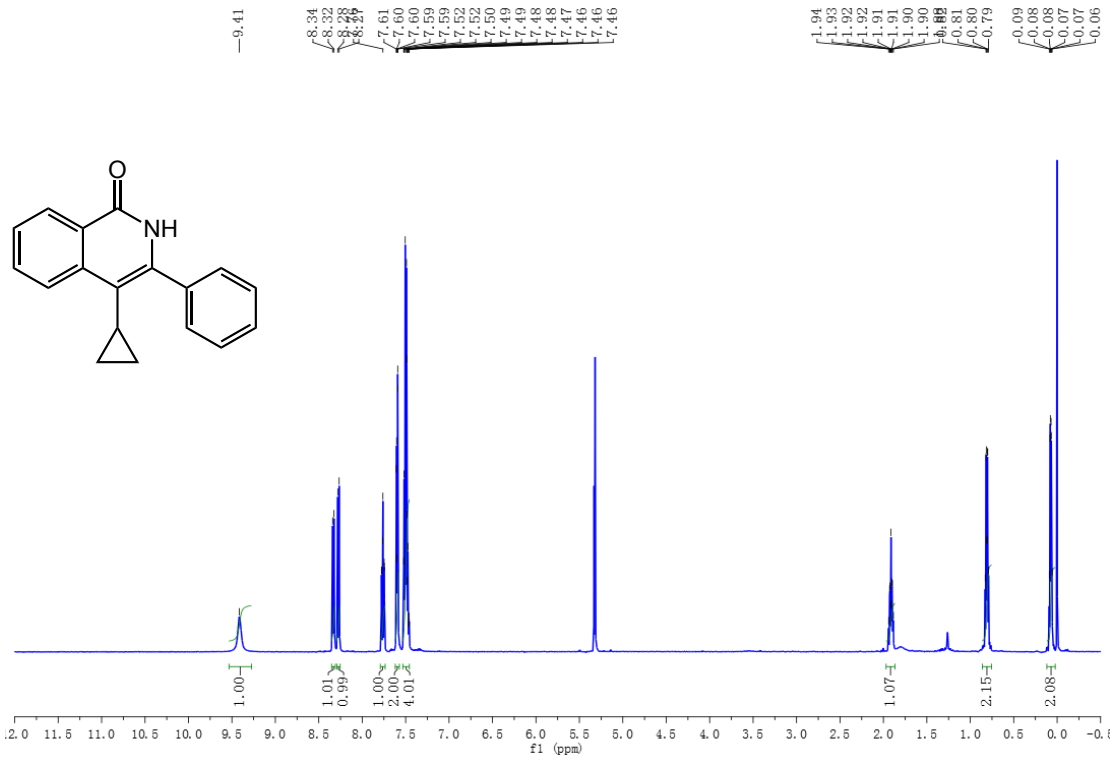
-0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8
9
f1 (ppm)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7.59
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7.49
7.48
7.47
7.46
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1.93
1.92
1.91
1.90
0.81
0.80
0.79
0.09
0.08
0.07
0.06
O
NH
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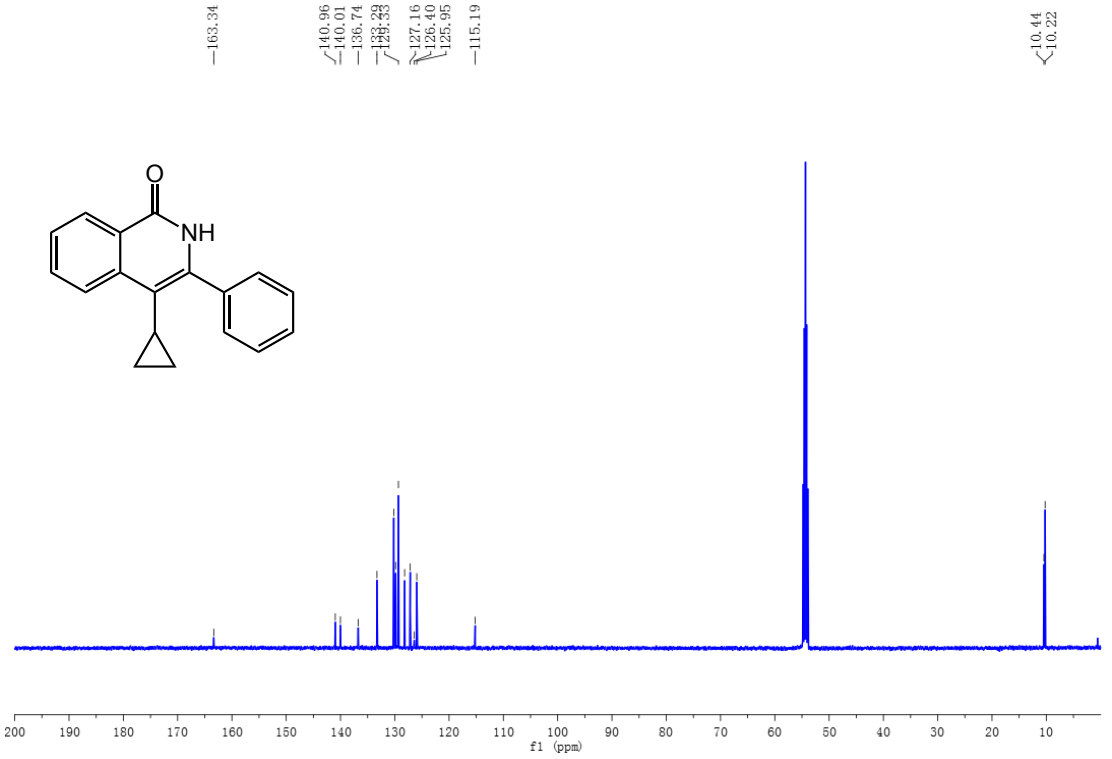
1.01
0.99
1.00
2.00
4.01
1.07
2.15
2.08
f1 (ppm)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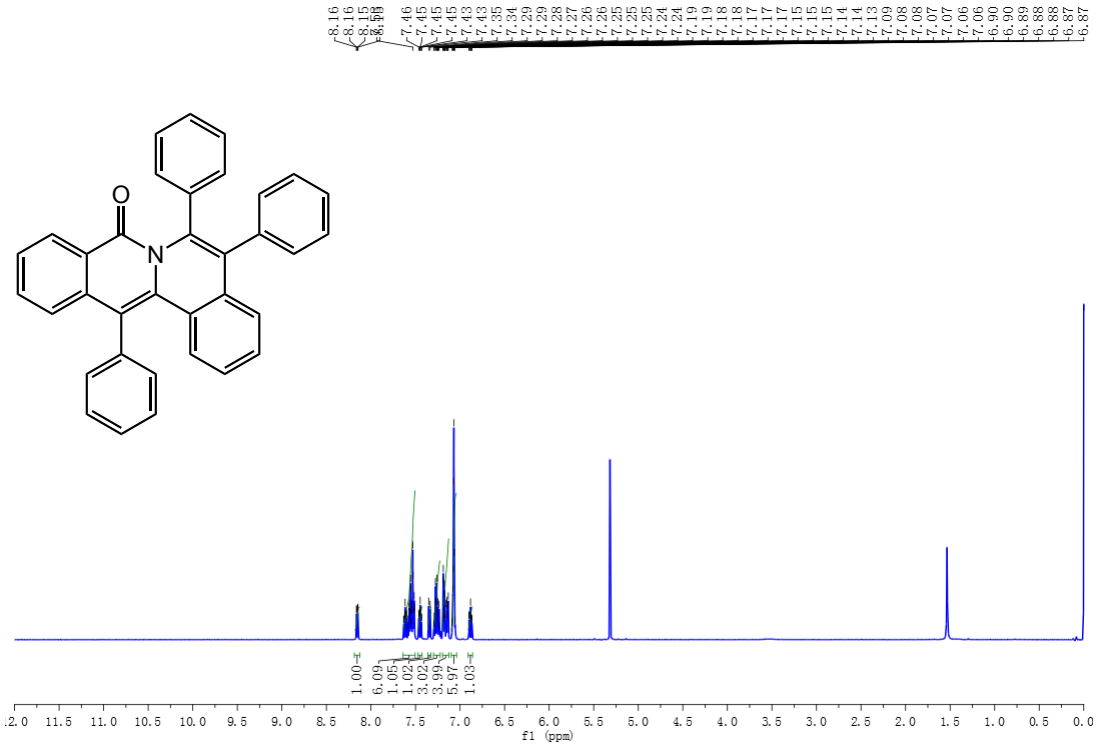
10.44
10.22
O
NH
f1 (ppm)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7.13
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7.08
7.08
7.07
7.07
7.06
7.06
6.90
6.89
6.88
6.88
6.87
6.87
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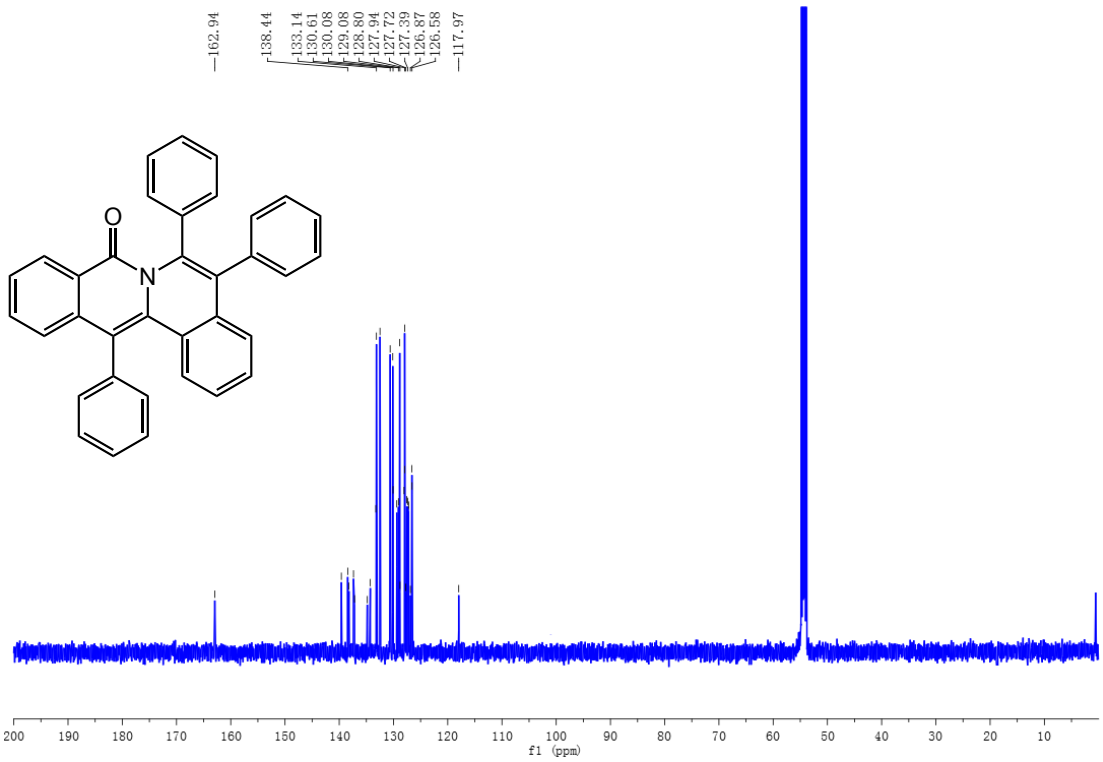
6.09
1.05
1.02
3.02
3.99
5.97
1.03
f1 (ppm)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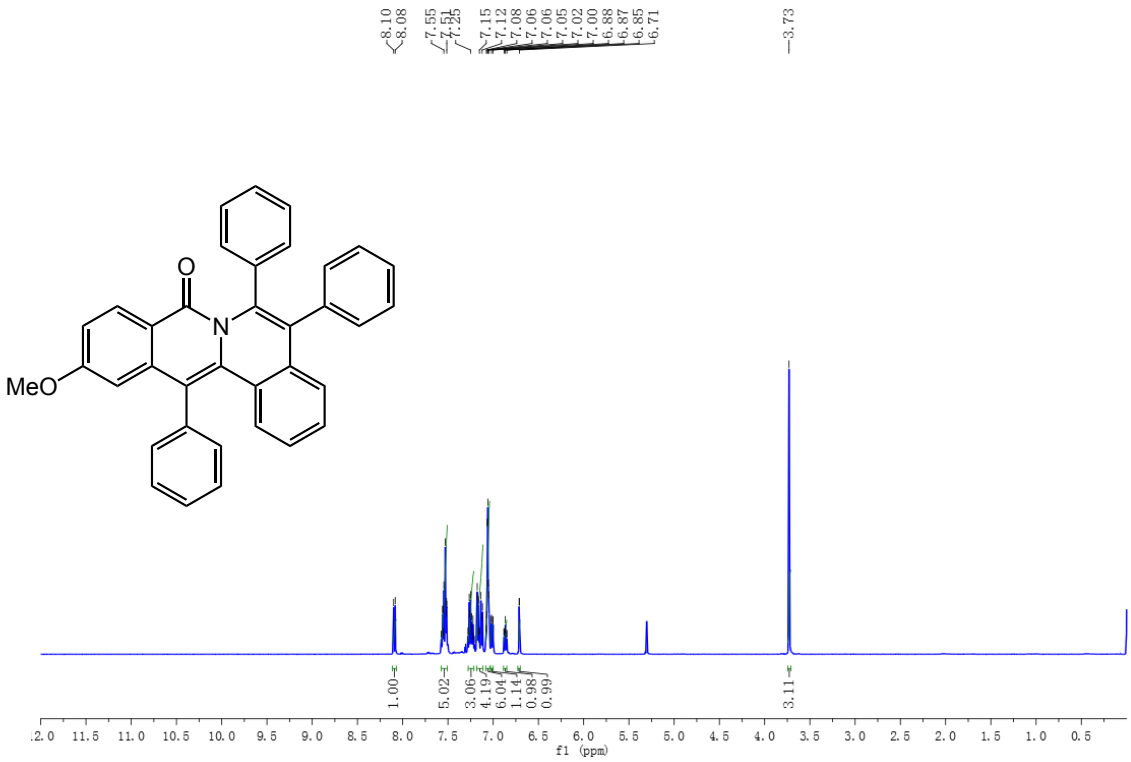
127.39
126.87
126.58
117.97
O
N
f1 (ppm)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7.08
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7.06
7.05
7.02
7.00
6.88
6.87
6.85
6.71
3.73
O
N
MeO
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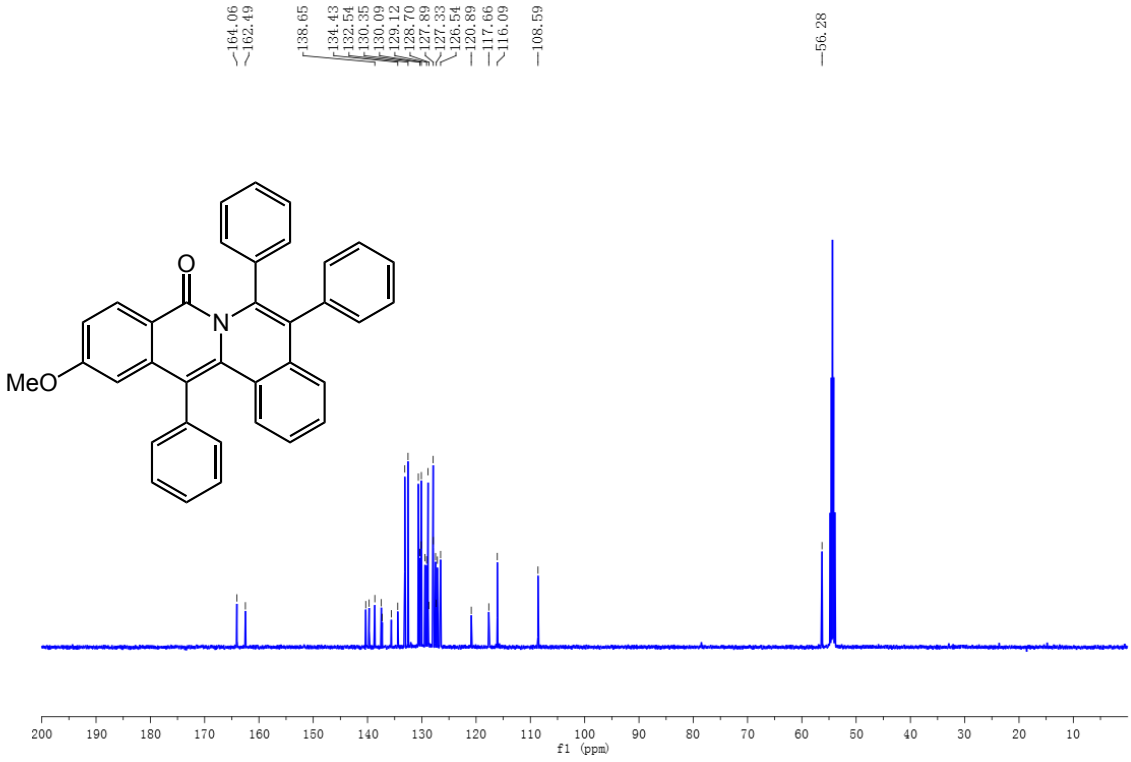
5.02
3.06
4.19
6.04
1.14
0.98
0.99
3.11
f1 (ppm)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116.09
108.59
56.28
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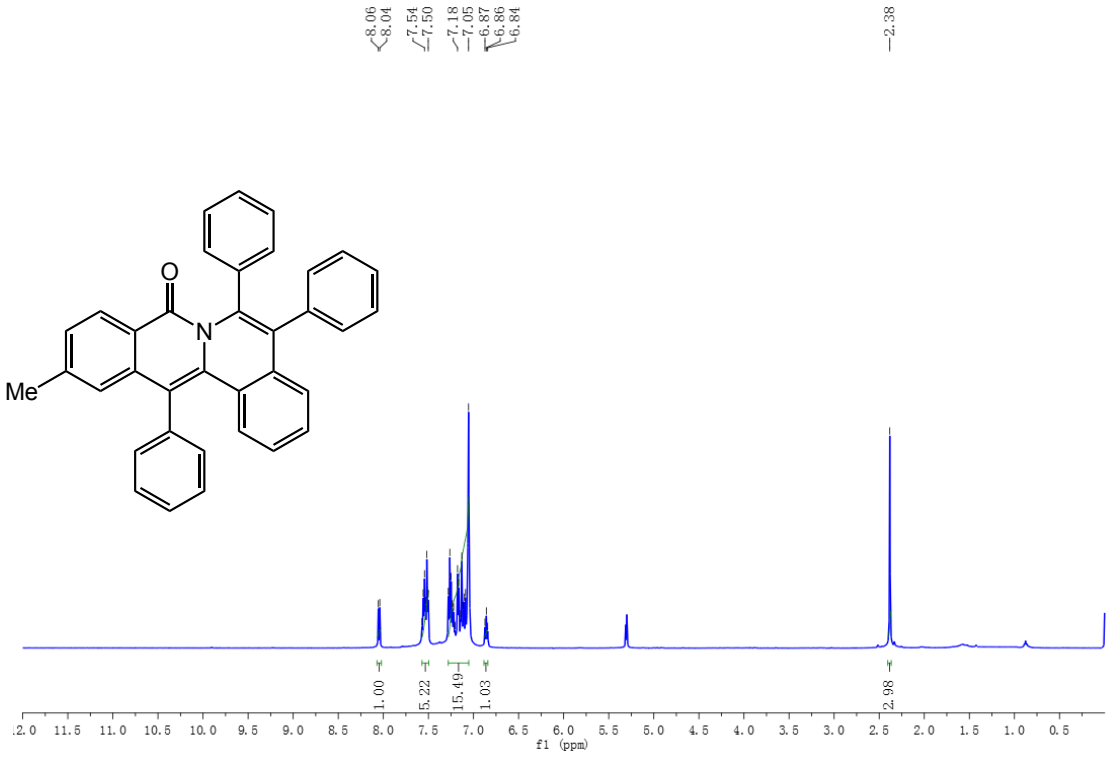
N
MeO
f1 (ppm)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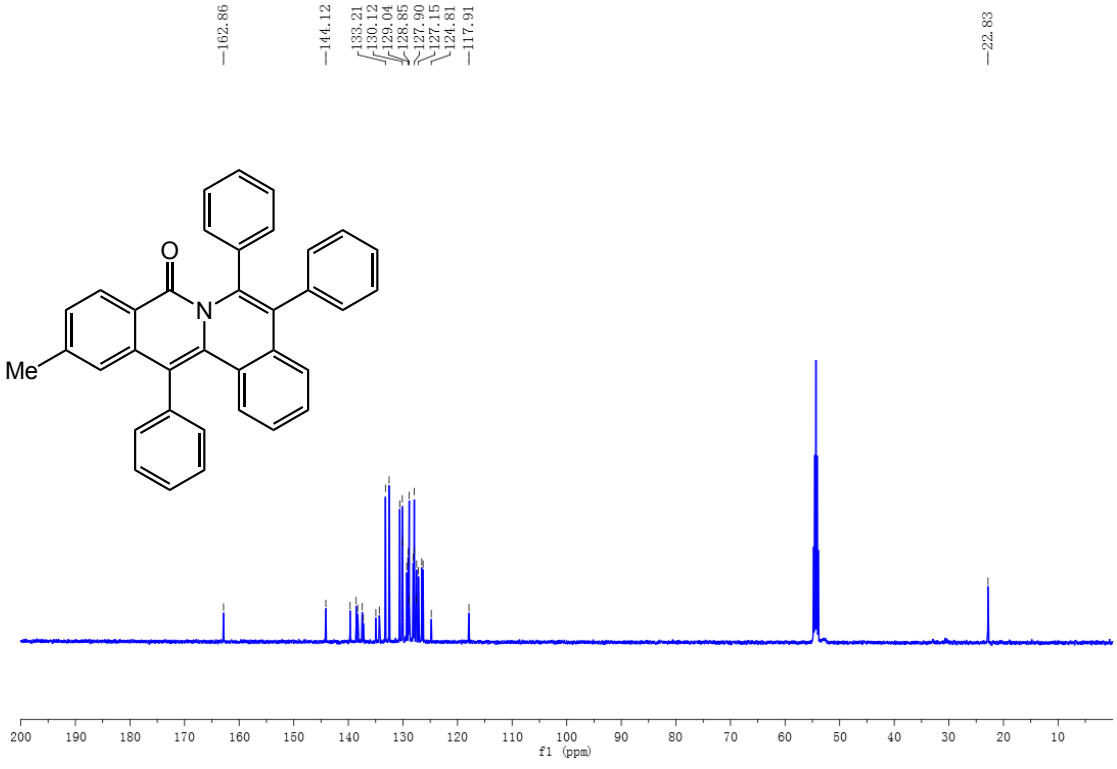
15.49
1.03
2.98
f1 (ppm)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117.91
22.83
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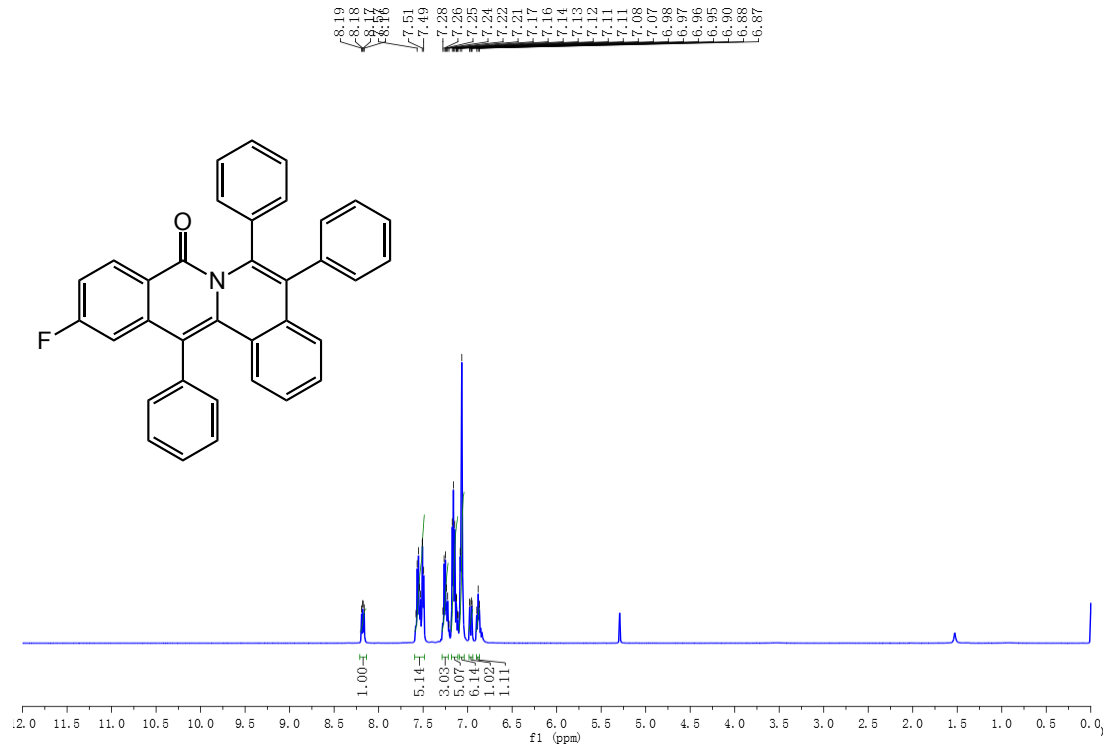
N
Me
f1 (ppm)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7.16
7.14
7.13
7.12
7.11
7.11
7.08
7.07
6.98
6.97
6.96
6.95
6.90
6.88
6.87
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N
F
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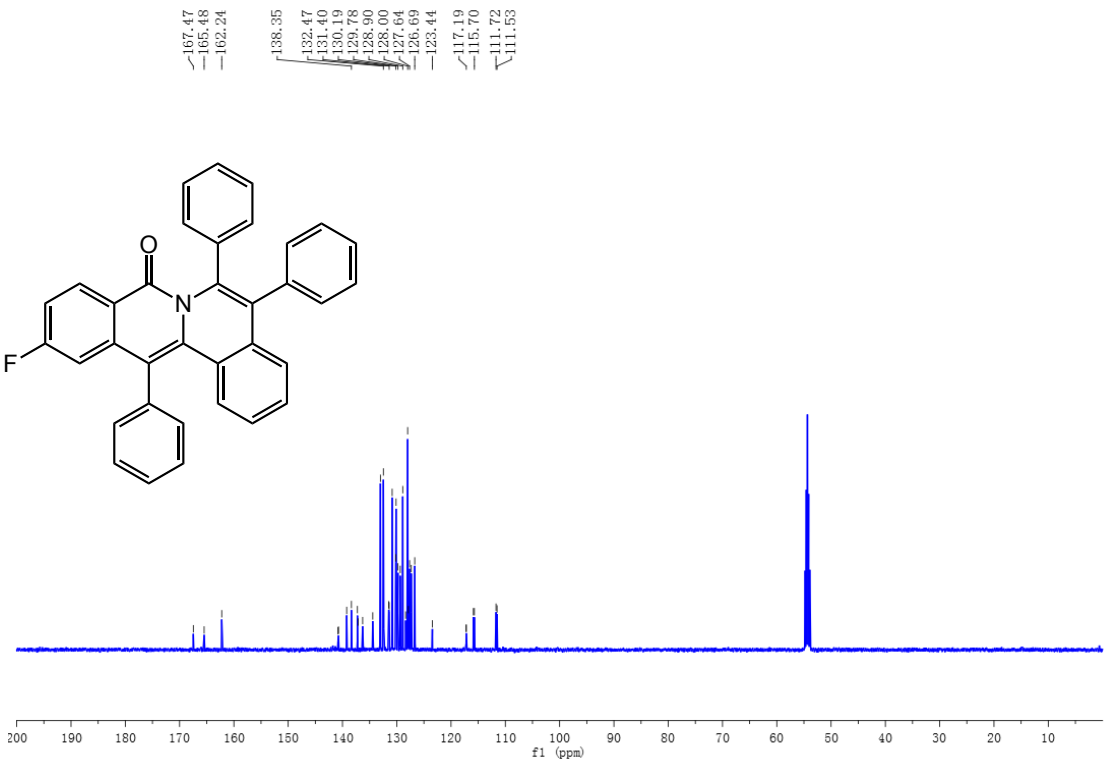
5.14
3.03
5.07
6.14
1.02
1.11
f1 (ppm)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129.78
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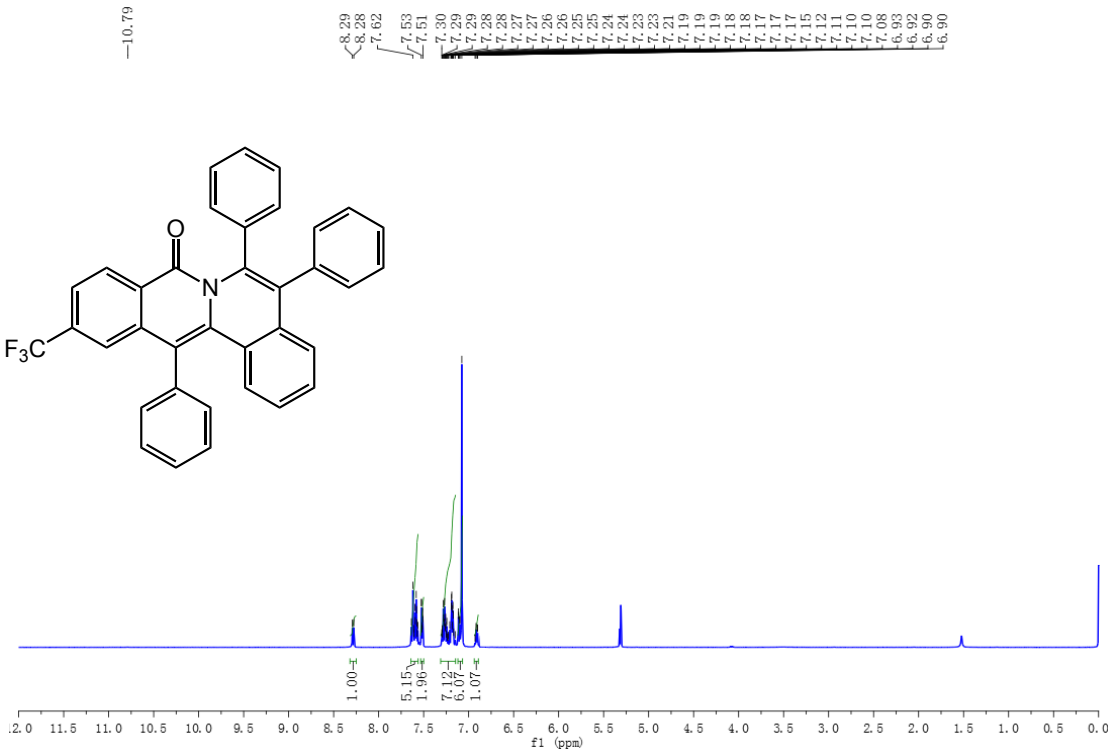
126.69
123.44
117.19
115.70
111.72
111.53
O
N
F
f1 (ppm)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7.17
7.17
7.15
7.12
7.11
7.10
7.10
7.08
6.93
6.92
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O
N
F3C
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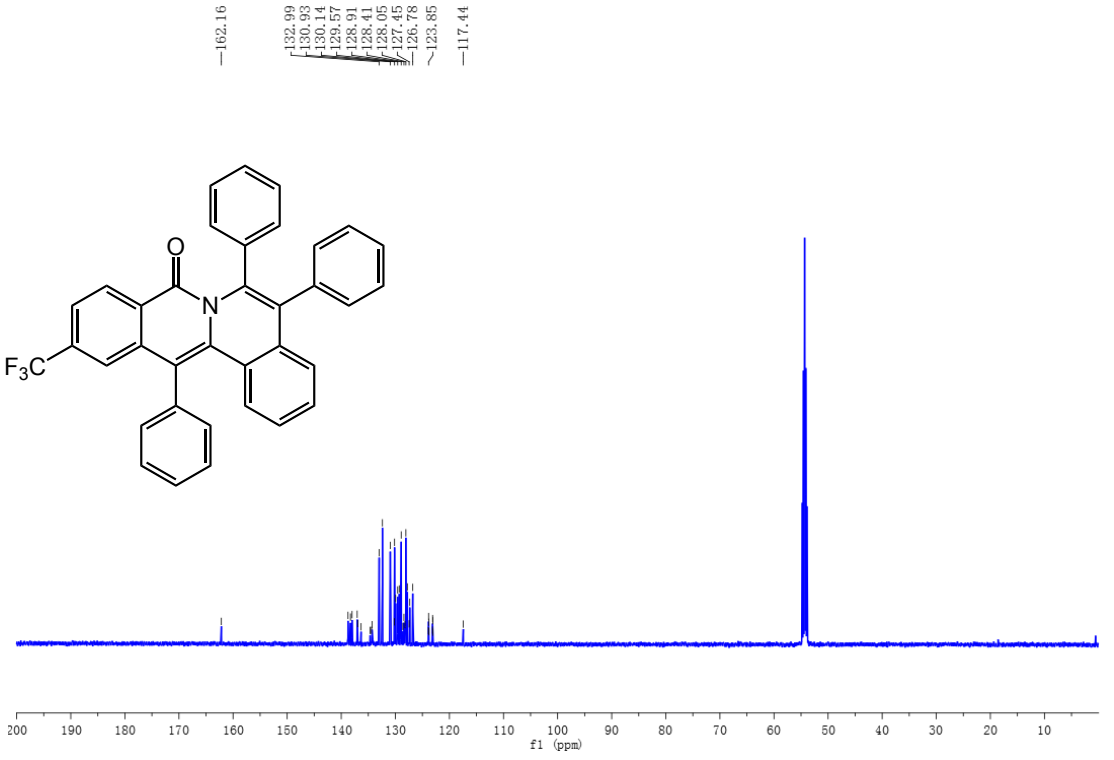
7.12
6.07
1.07
f1 (ppm)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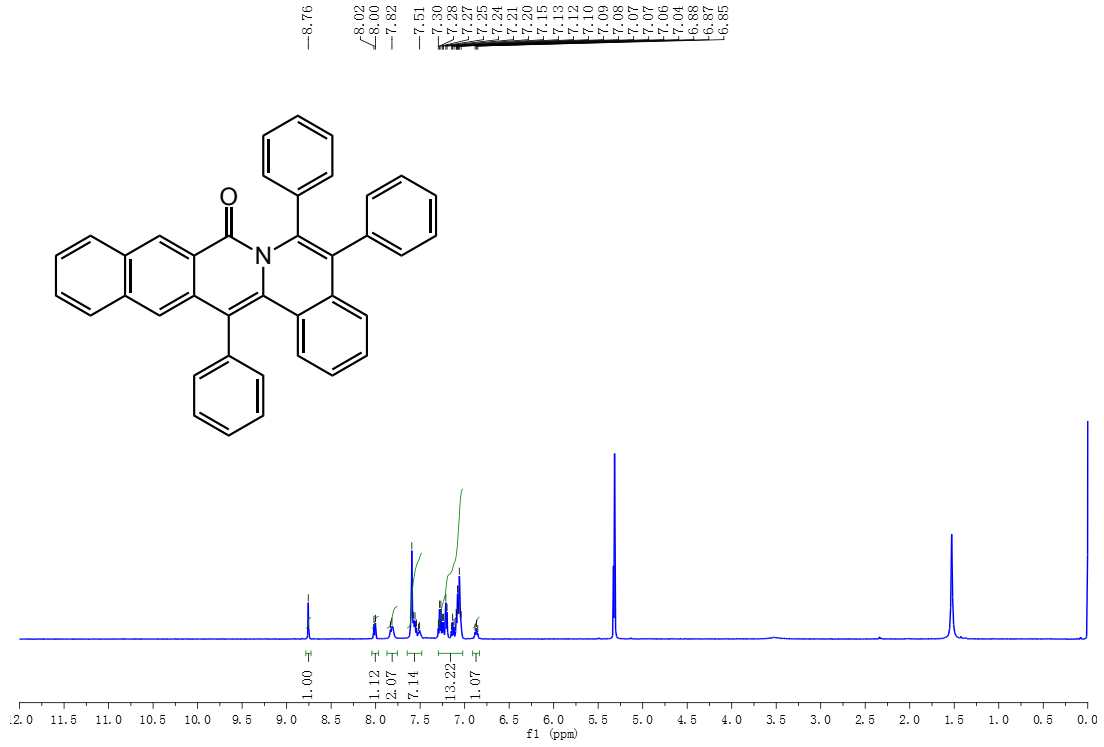
O
N
F3C
f1 (ppm)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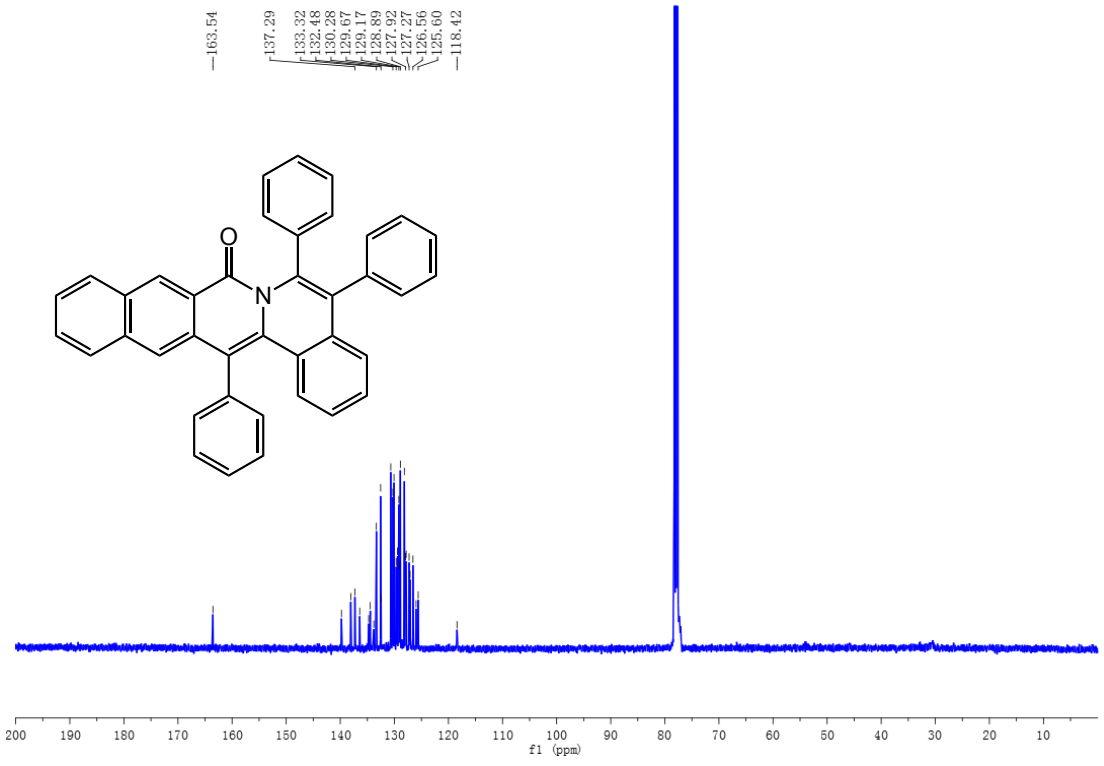
7.30
7.28
7.27
7.25
7.24
7.21
7.20
7.15
7.13
7.12
7.10
7.09
7.08
7.07
7.07
7.06
7.04
6.88
6.87
6.85
O
N
1.00
1.12
2.07
7.14
13.22
1.07
f1 (ppm)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137.29
133.32
132.48
130.28
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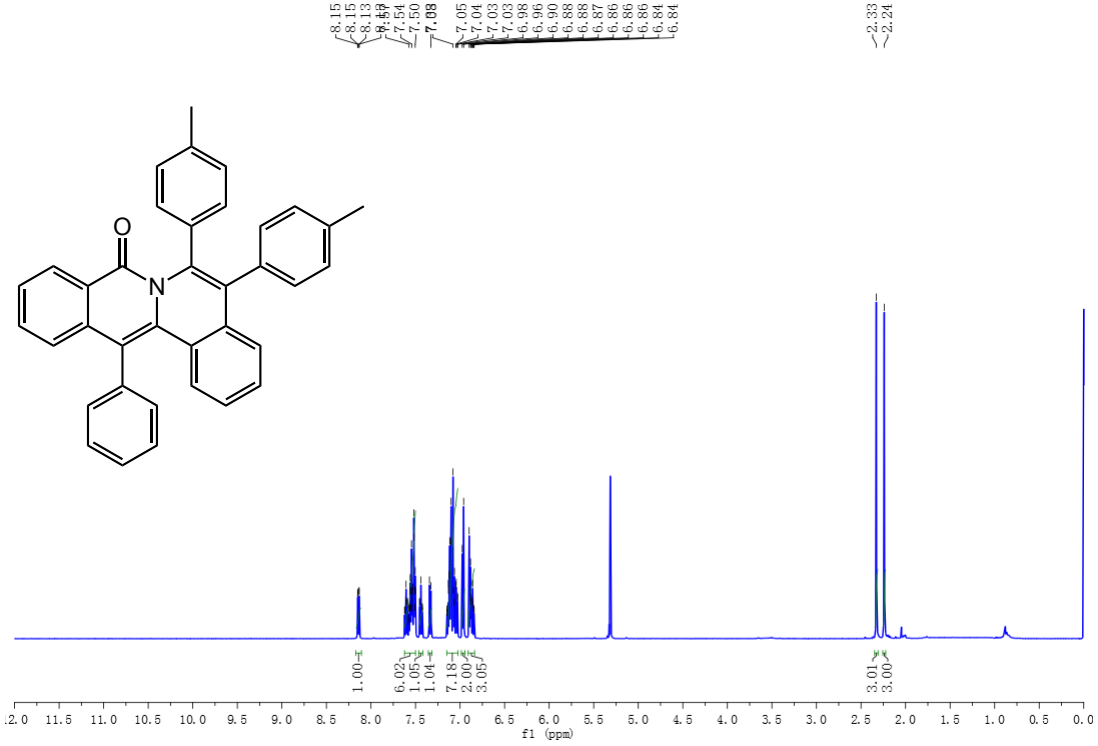
129.17
128.89
127.92
127.27
126.56
125.60
118.42
O
N
f1 (ppm)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8.15
8.13
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7.05
7.04
7.03
7.03
6.98
6.96
6.90
6.88
6.88
6.87
6.86
6.86
6.86
6.84
6.84
2.33
2.24
O
N
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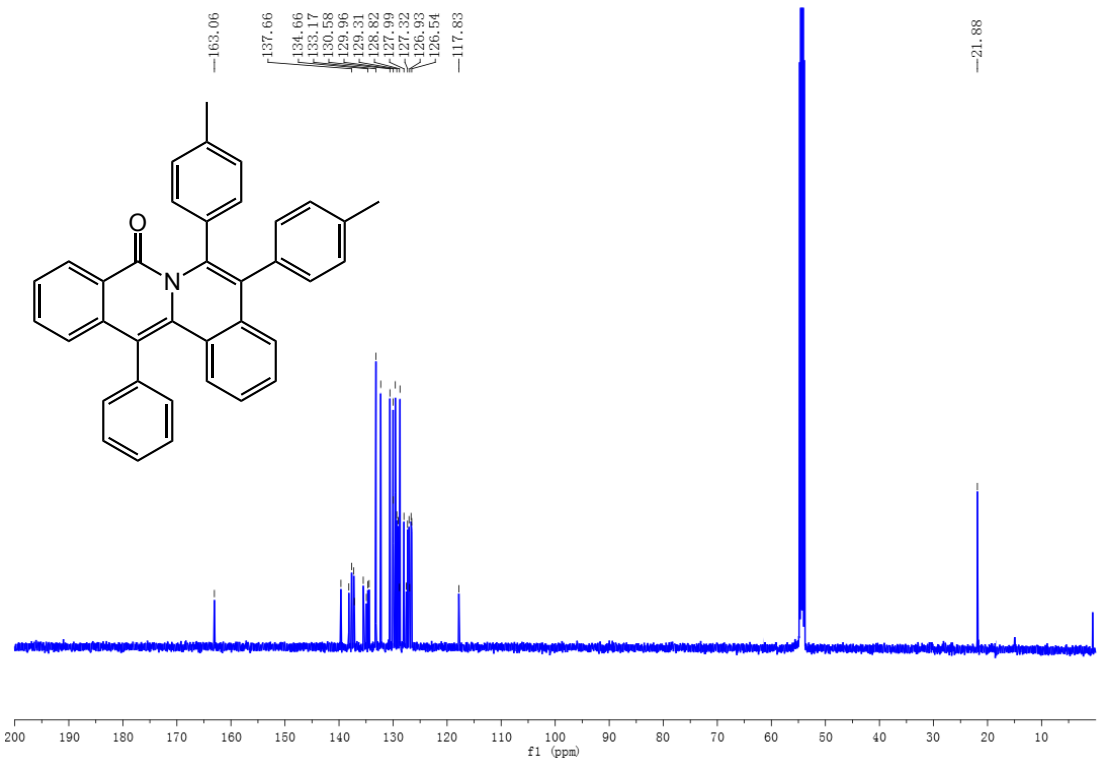
6.02
1.05
1.04
7.18
2.00
3.05
3.01
3.00
f1 (ppm)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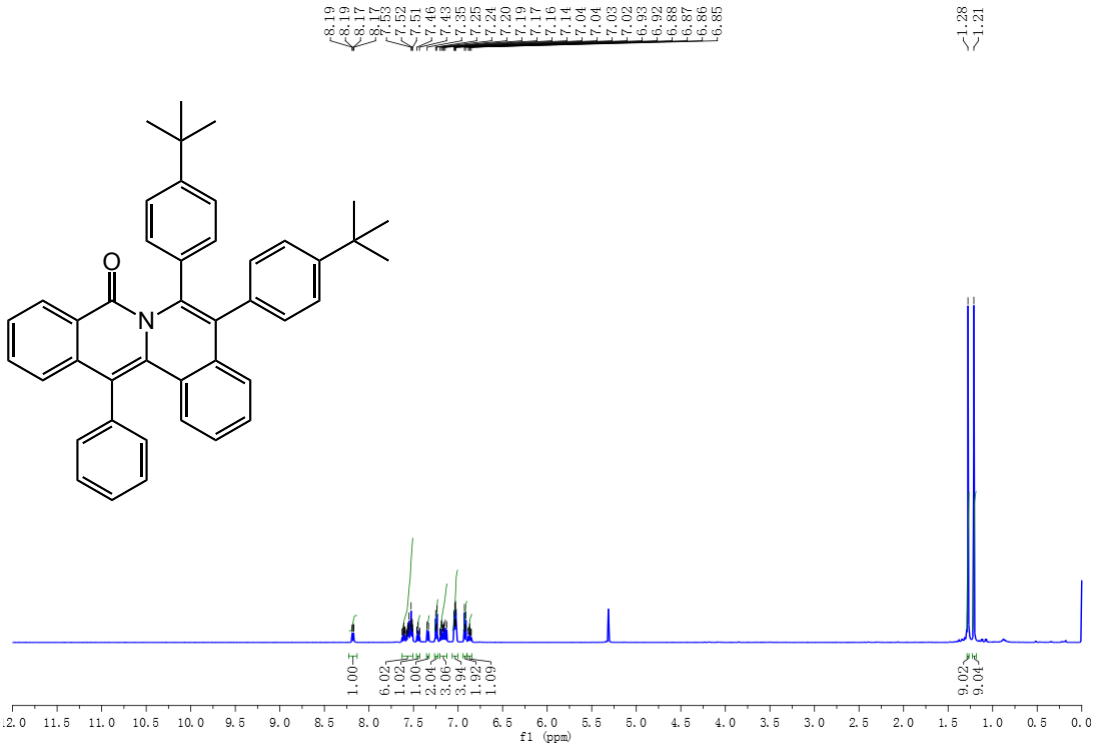
128.82
127.99
127.32
126.93
126.54
117.83
21.88
O
N
f1 (ppm)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8.19
8.17
8.17
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7.52
7.51
7.46
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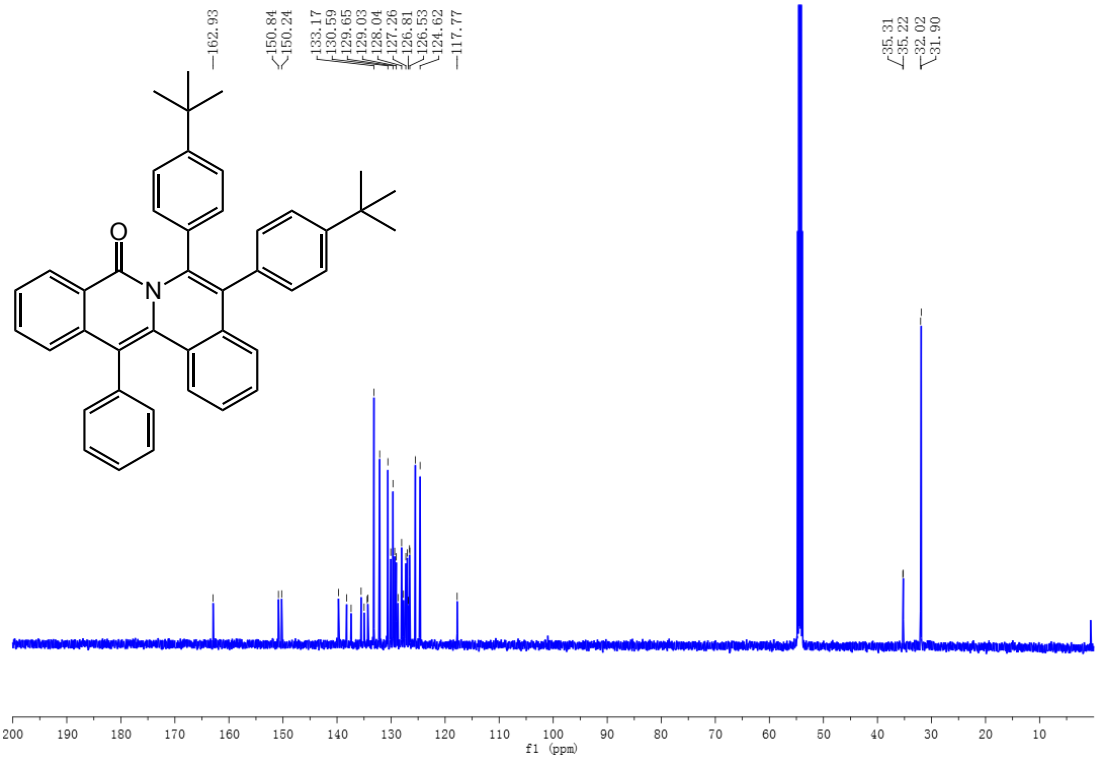
7.35
7.25
7.24
7.20
7.19
7.17
7.16
7.14
7.04
7.04
7.03
7.02
6.93
6.92
6.88
6.87
6.86
6.85
1.28
1.21
O
N
1.00
6.02
1.02
1.00
2.04
3.06
3.94
1.92
1.09
9.02
9.04
f1 (ppm)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150.24
133.17
130.59
129.65
129.03
128.04
127.26
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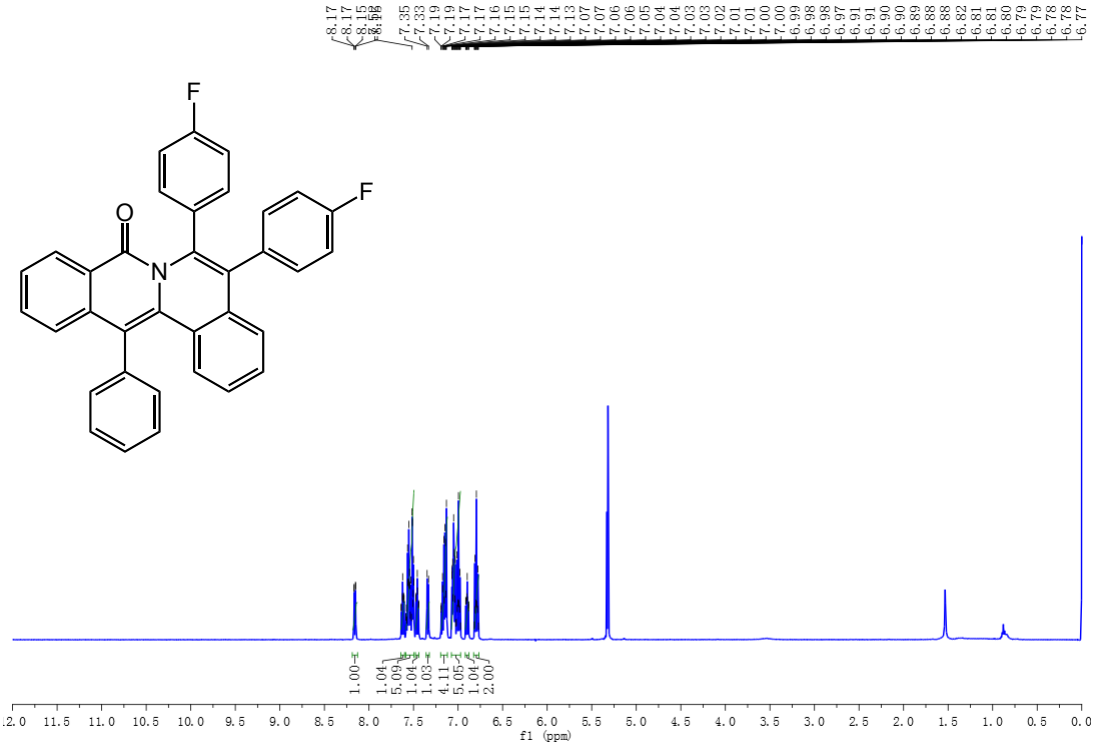
126.53
124.62
117.77
35.31
35.22
32.02
31.90
O
N
f1 (ppm)


F
F
O
N
8.17
8.17
8.15
7.35
7.33
7.19
7.17
7.17
7.16
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7.15
7.14
7.14
7.13
7.07
7.07
7.06
7.06
7.05
7.04
7.04
7.03
7.03
7.02
7.01
7.01
7.00
7.00
6.99
6.98
6.98
6.97
6.91
6.90
6.90
6.89
6.88
6.88
6.82
6.81
6.81
6.80
6.79
6.79
6.78
6.78
6.77
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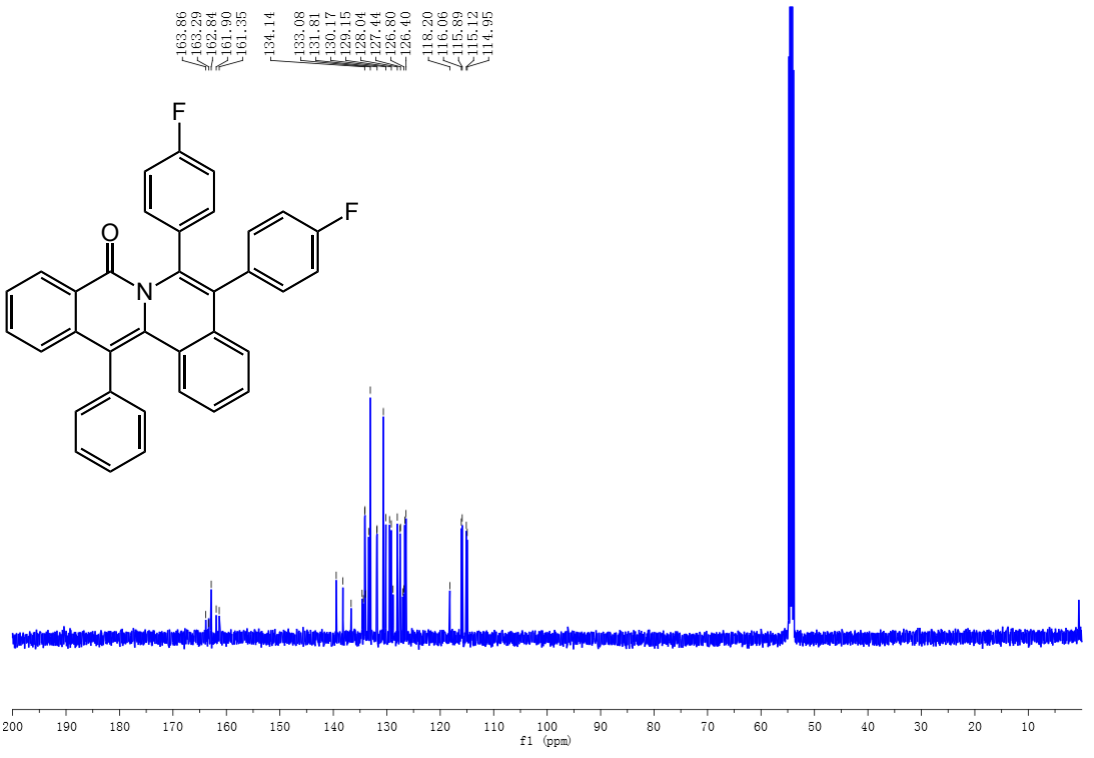
1.04
5.09
1.04
1.03
4.11
5.05
1.04
2.00
f1 (ppm)


F
F
O
N
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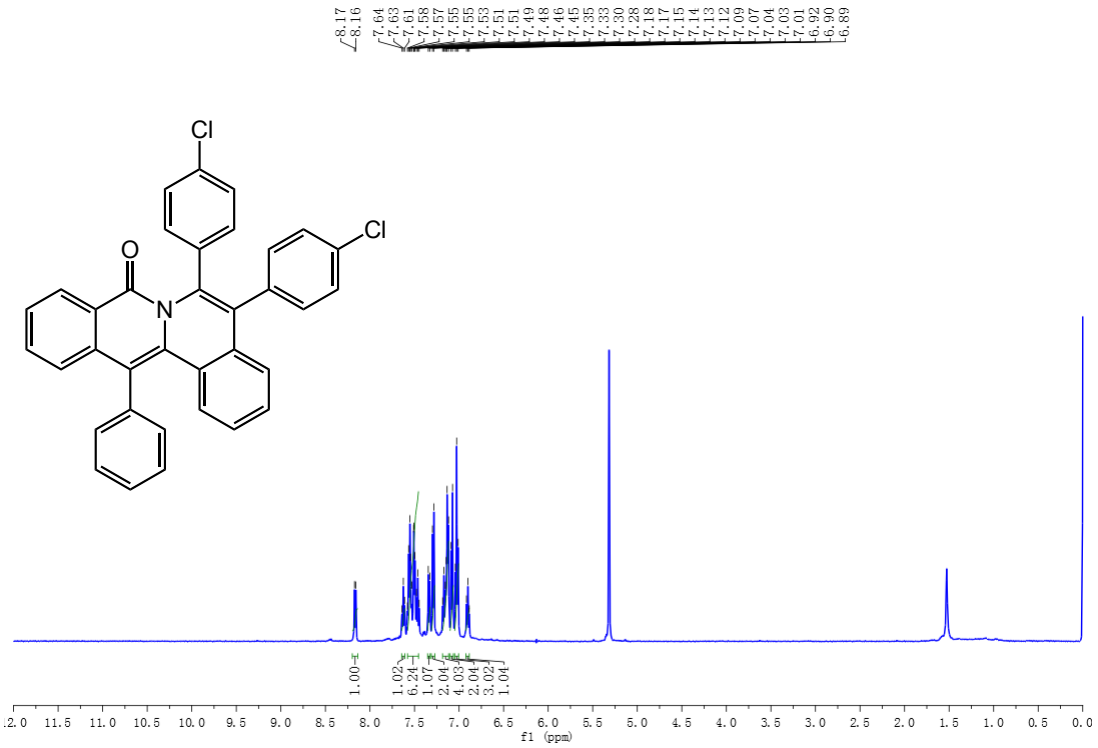
162.84
161.90
161.35
134.14
133.08
131.81
130.17
129.15
128.04
127.44
126.80
126.40
118.20
116.06
115.89
115.12
114.95
f1 (ppm)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8.16
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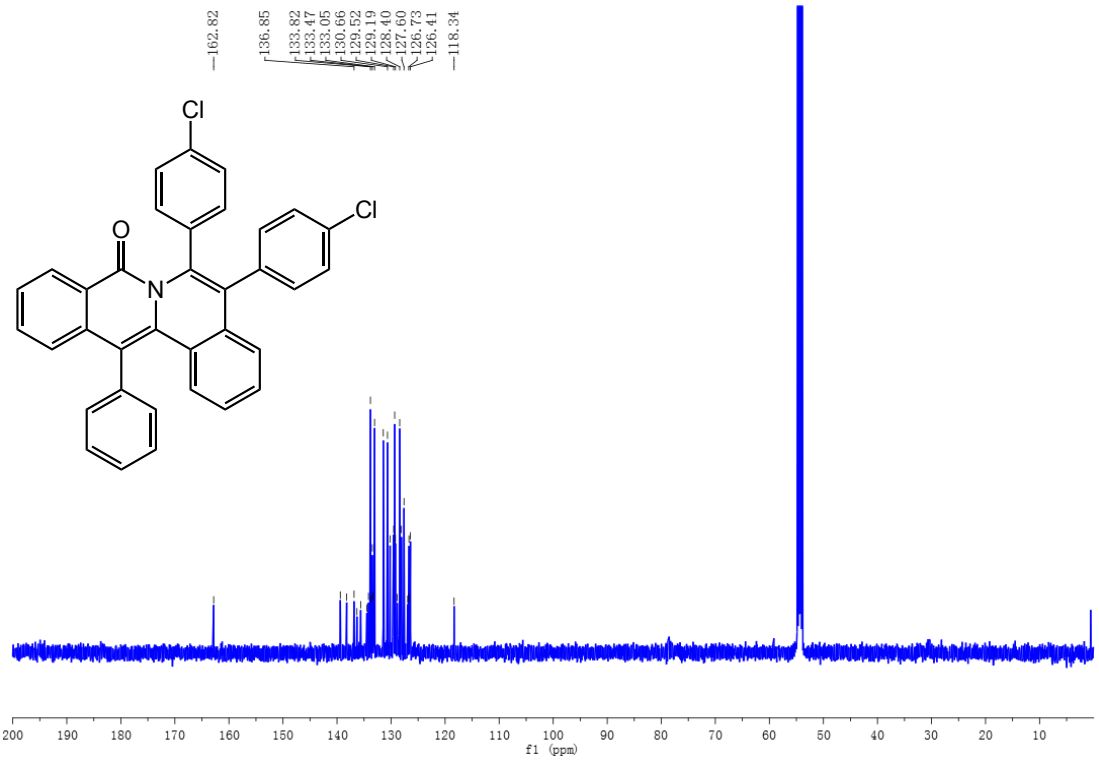
7.63
7.61
7.58
7.57
7.55
7.55
7.53
7.51
7.51
7.49
7.48
7.46
7.45
7.35
7.33
7.30
7.28
7.18
7.17
7.15
7.14
7.13
7.12
7.09
7.07
7.04
7.03
7.01
6.92
6.90
6.89
Cl
Cl
O
N
1.00
1.02
6.24
1.07
2.04
4.03
2.04
3.02
1.04
f1 (ppm)


162.82
136.85
133.82
133.47
133.05
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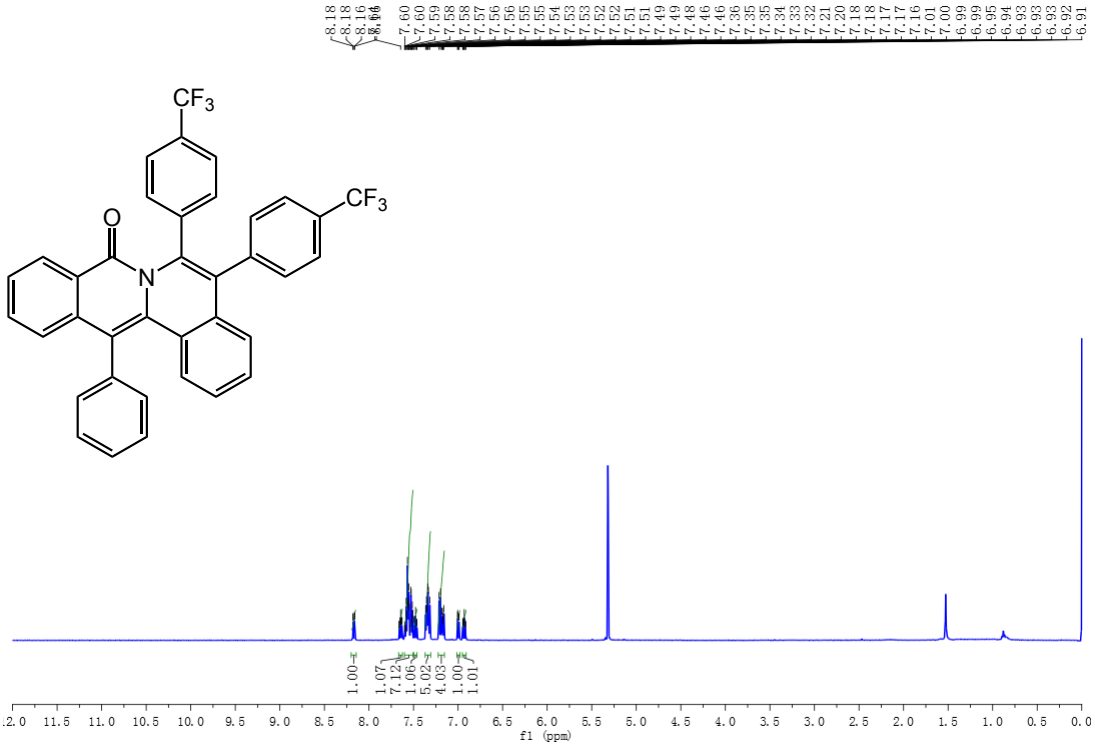
128.40
127.60
126.73
126.41
118.34
Cl
Cl
O
N
f1 (ppm)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8.16
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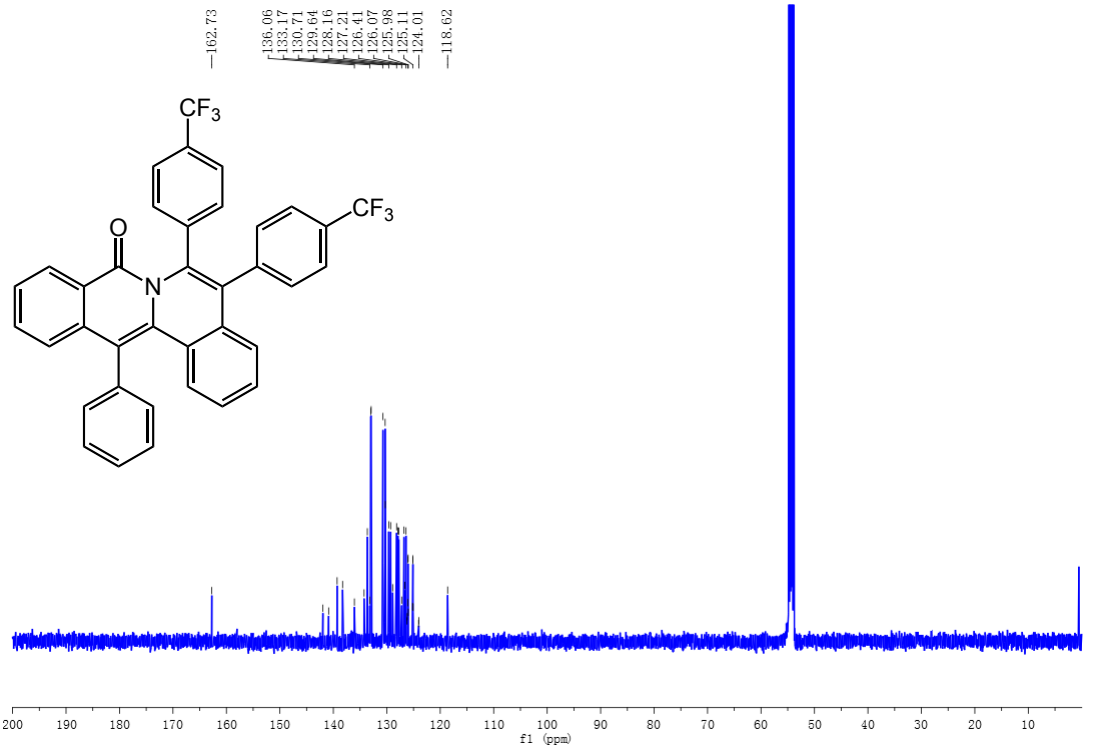
7.59
7.58
7.57
7.56
7.55
7.54
7.53
7.52
7.51
7.49
7.48
7.46
7.36
7.35
7.34
7.33
7.32
7.21
7.20
7.18
7.17
7.16
7.01
7.00
6.99
6.95
6.94
6.93
6.92
6.91
CF3
CF3
O
N
1.00
1.07
7.12
1.06
5.02
4.03
1.00
1.01
f1 (ppm)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136.06
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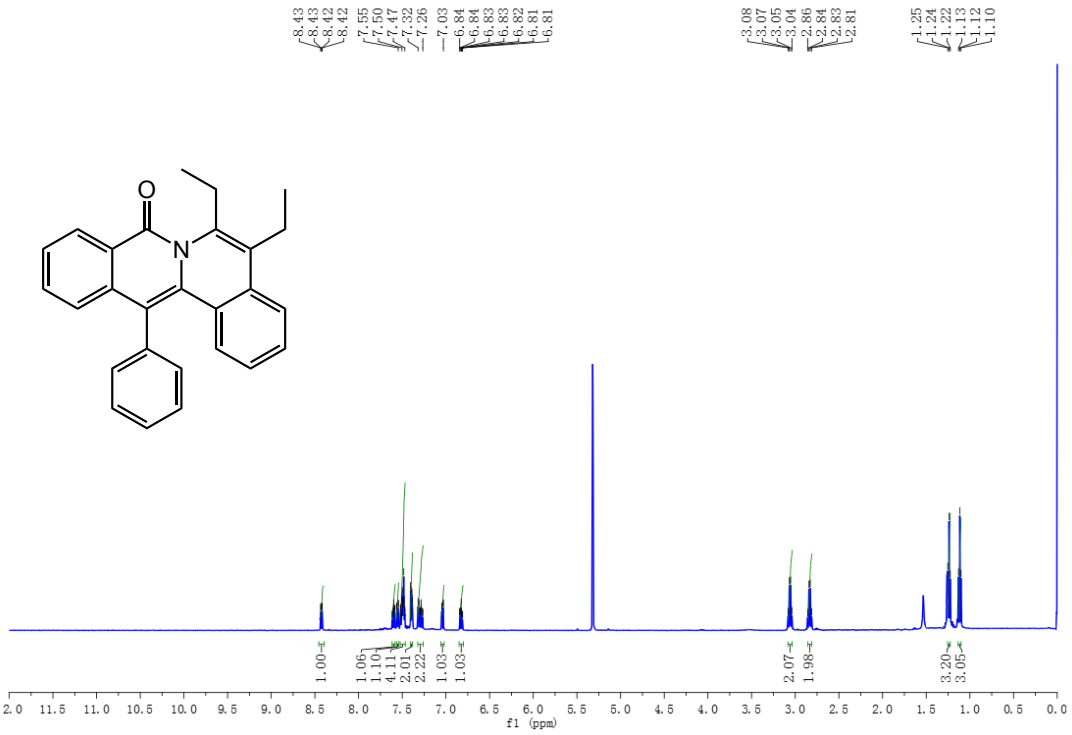
128.16
127.21
126.41
126.07
125.98
125.11
124.01
118.62
CF3
CF3
O
N
f1 (ppm)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7.32
7.26
7.03
6.84
6.84
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6.83
6.82
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6.81
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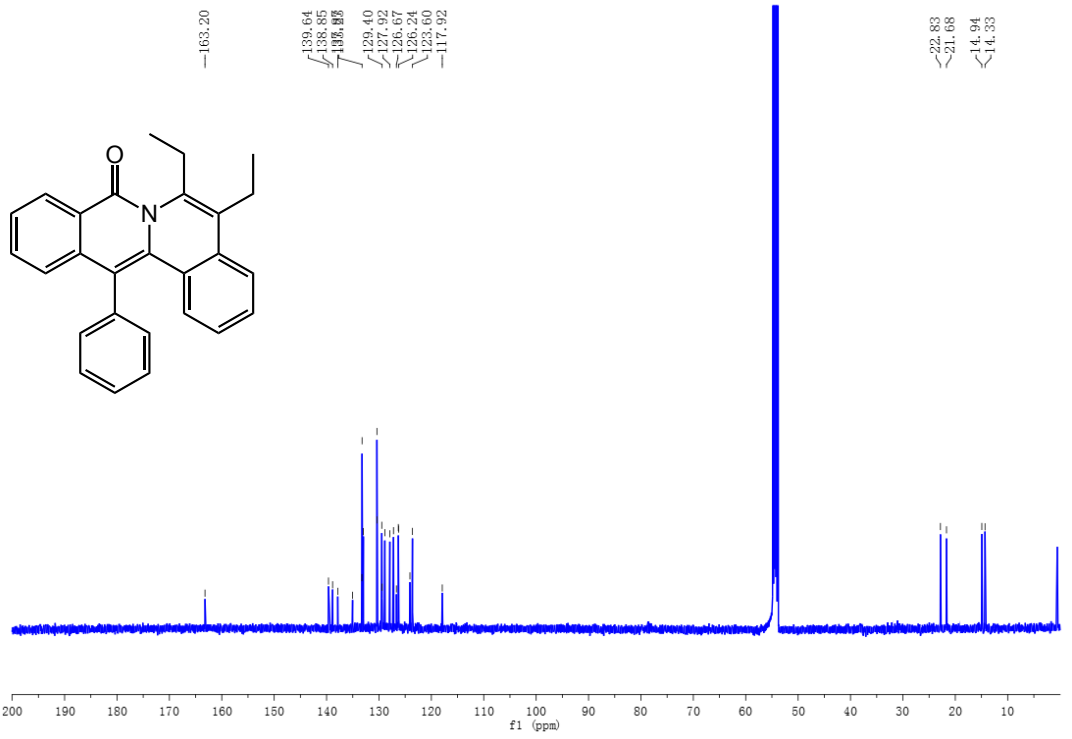
3.07
3.05
3.04
2.86
2.84
2.83
2.81
1.25
1.24
1.22
1.13
1.12
1.10
O
N
1.00
1.06
1.10
4.11
2.01
2.22
1.03
1.03
2.07
1.98
3.20
3.05
f1 (ppm)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138.85
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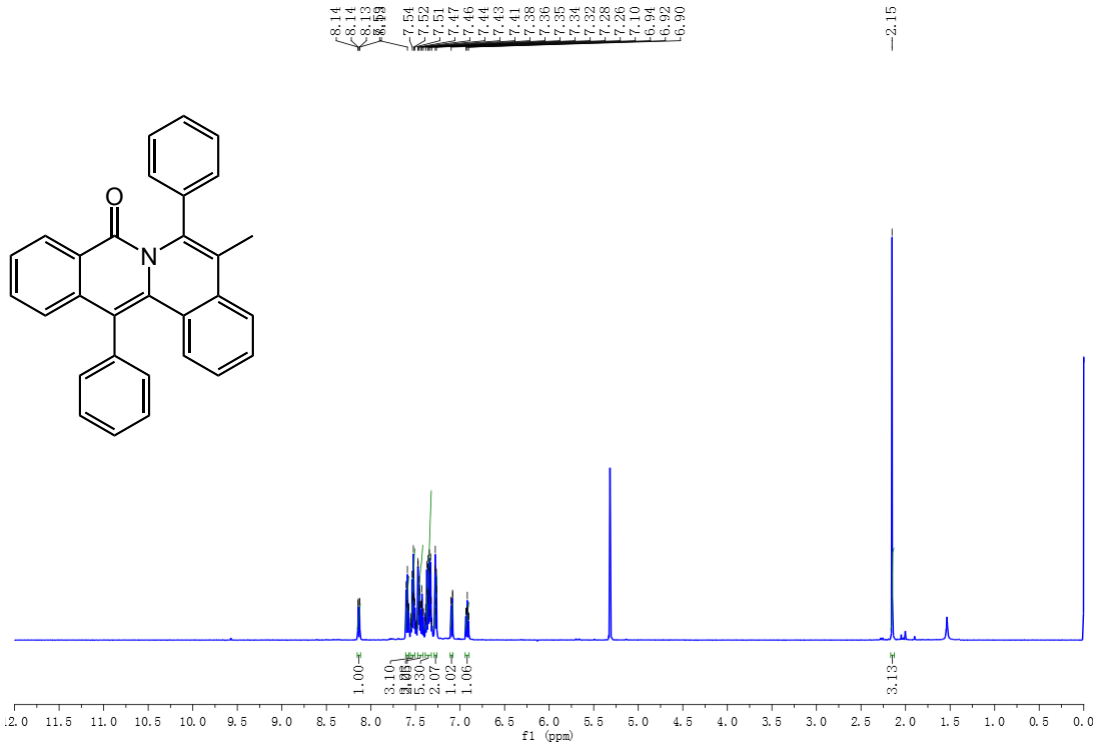
126.24
123.60
117.92
22.83
21.68
14.94
14.33
O
N
f1 (ppm)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8.14
8.13
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7.51
7.47
7.46
7.44
7.43
7.41
7.38
7.36
7.35
7.34
7.32
7.28
7.26
7.10
6.94
6.92
6.90
2.15
O
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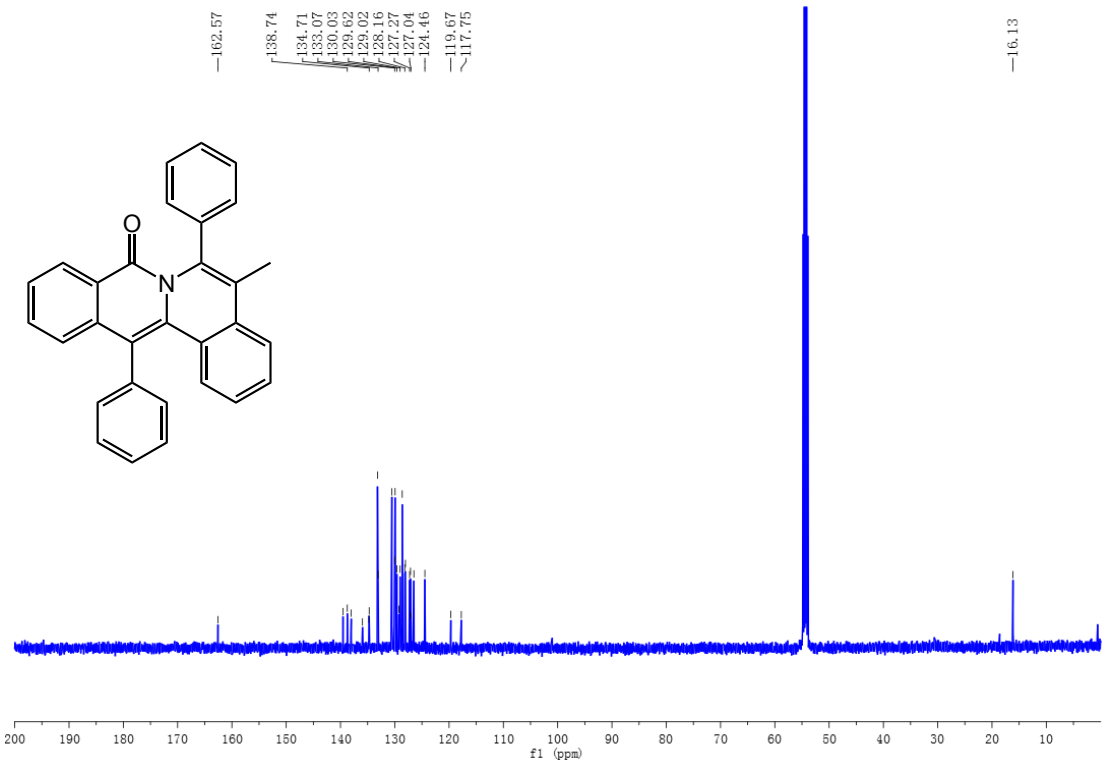
1.00
3.10
2.07
1.02
1.06
3.13
f1 (ppm)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127.27
127.04
124.46
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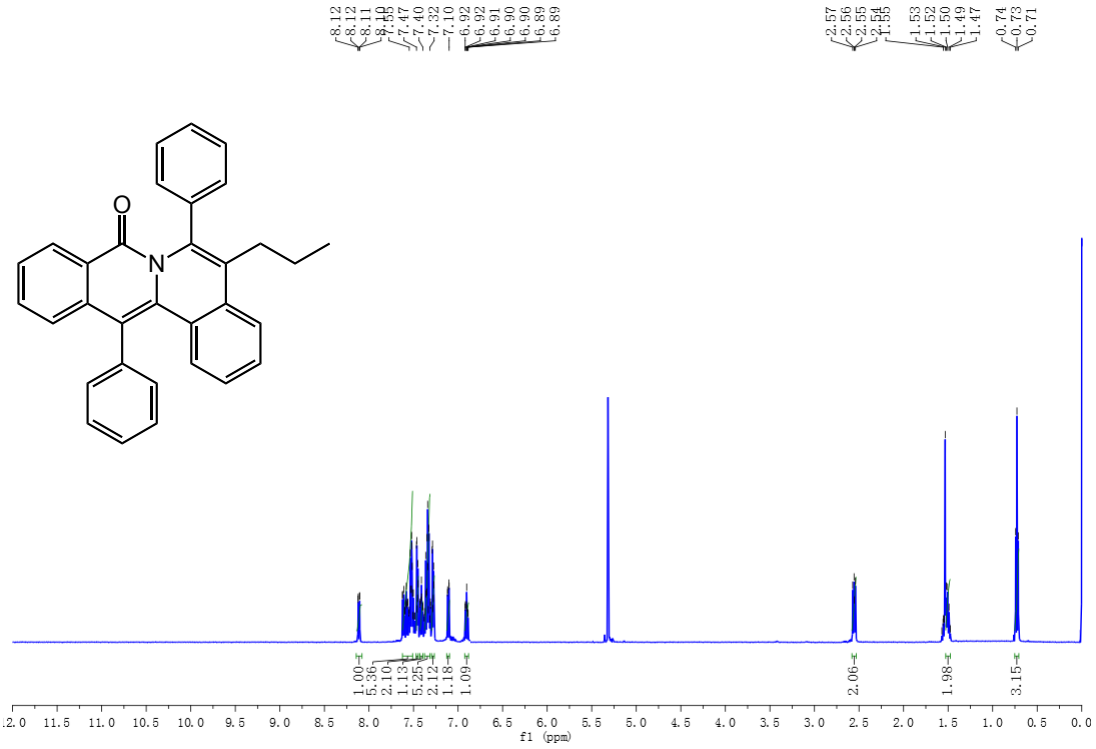
117.75
16.13
O
N
f1 (ppm)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7.10
6.92
6.92
6.91
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6.90
6.89
6.89
2.57
2.56
2.55
2.54
1.55
1.53
1.52
1.50
1.49
1.47
0.74
0.73
0.71
O
N
1.00
5.36
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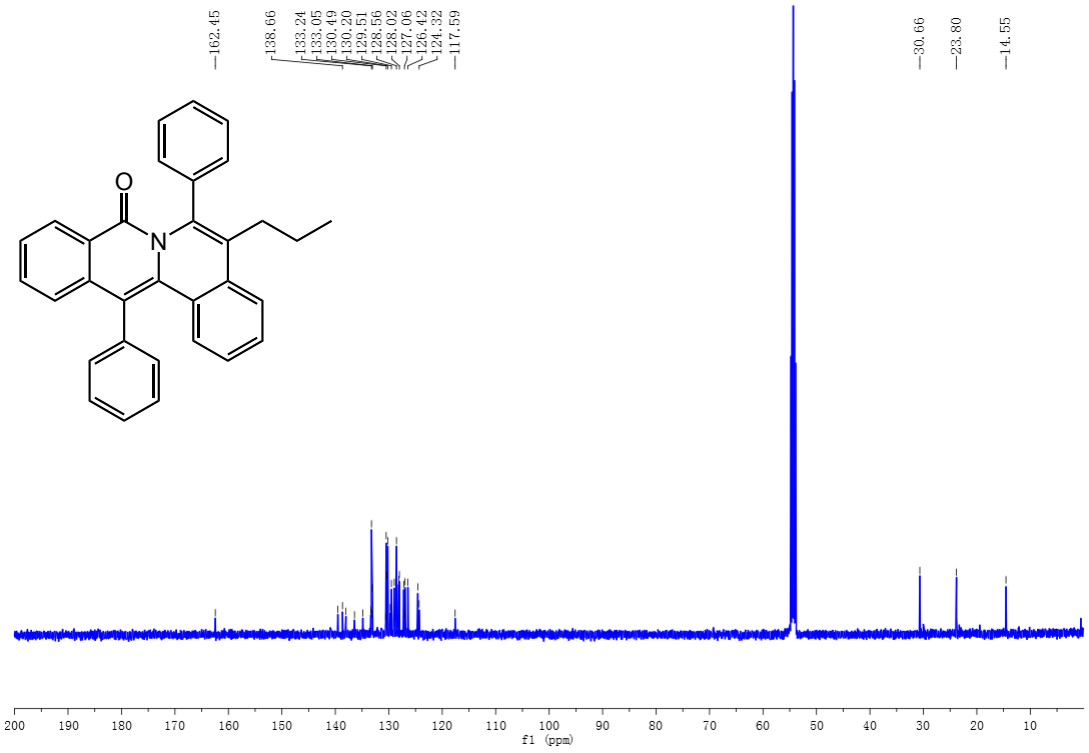
1.13
5.25
2.12
1.18
1.09
2.06
1.98
3.15
f1 (ppm)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124.32
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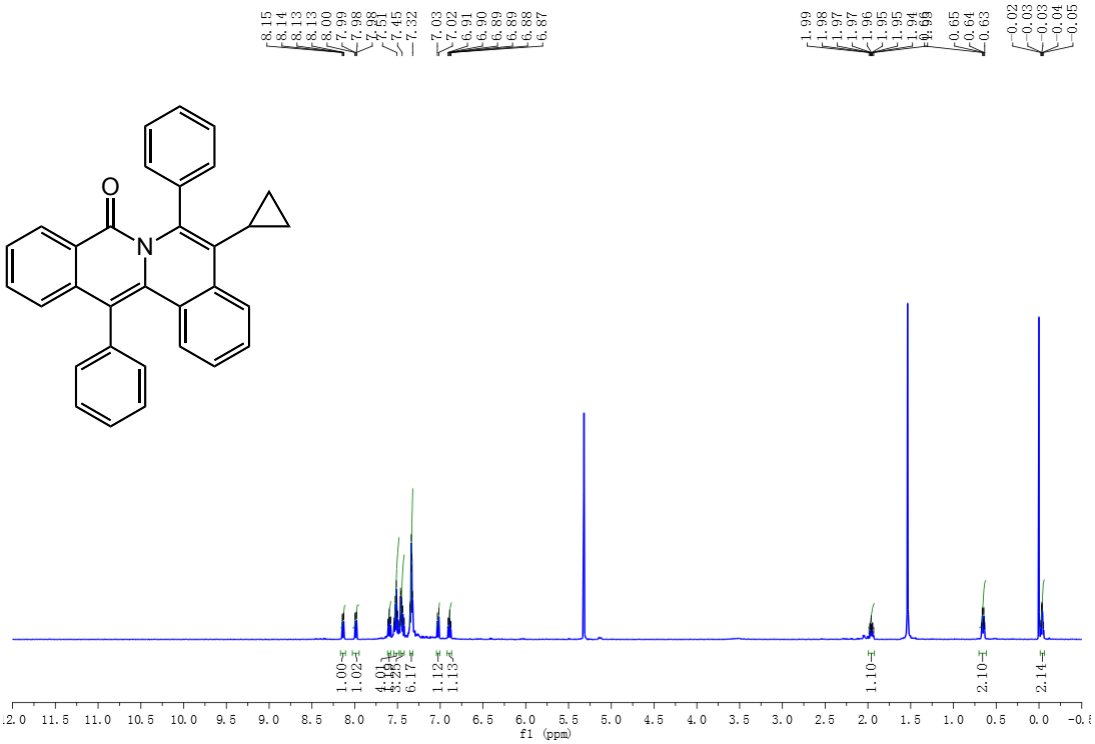
23.80
14.55
O
N
f1 (ppm)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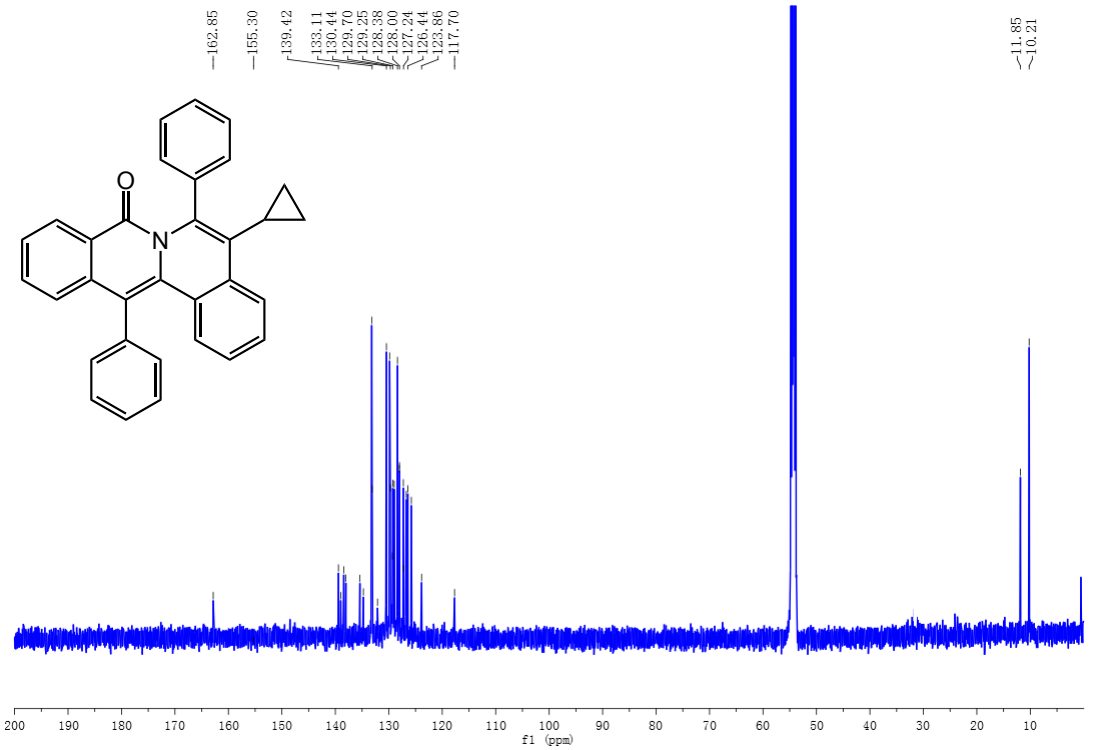
7.45
7.32
7.03
7.02
6.91
6.90
6.89
6.89
6.88
6.87
1.99
1.98
1.97
1.96
1.95
1.95
1.94
0.65
0.64
0.63
0.02
0.03
0.03
0.04
0.05
O
N
1.00
1.02
4.01
3.25
6.17
1.12
1.13
1.10
2.10
2.14
f1 (ppm)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128.38
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127.24
126.44
123.86
117.70
11.85
10.21
O
N
f1 (ppm)