Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Palladium-Catalyzed Decarbonylative Annulation of Phthalimide with Arynes: Direct Construction of Phenanthridinones

Yan-Yu Meng,*[a] Xiao-Ju Si,[b] Yuan-Yuan Song,[b] Hui-Min Zhou,[b] Fen Xu*[b]

[a] Department of College of Science, Henan Agricultural University, Zhengzhou 450002, P. R. China

[b] Department of Material and Chemical Engineering, Zhengzhou University of Light Industry, Zhengzhou 450002, P. R. China.

*E-mail: mengyanyu528@aliyun.com; fenxu_zzuli@163.com

Contents

1. General Information

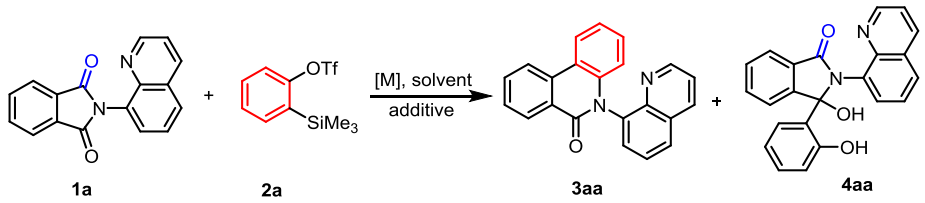
Unless otherwise noted, all the reactions were carried out in a glassware under a nitrogen atmosphere. The commercially available chemicals and solvents were used as received without further purification. Phthalimides **1a**,[S1] **1b**-**1n**,[S2] **1q**[S3] were prepared according to the published procedure.[S4-S5] The reactions were monitored by TLC using UV-light or by staining with iodine. Column chromatography was performed on silica gel (200-300 mesh). Single-crystal X-ray data in this work were collected on an Agilent Technologies SuperNova Single Crystal Diffractometer at different temperatures equipped with graphite-monochromatic Mo Kα or Cu Kα radiation (λ = 0.71073 Å or 1.54184 Å). The structures were solved by SHELXS (direct methods) and refined by SHELXL (full matrix least-squares techniques) in the Olex2 package.[S6] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. ^{1}H, ^{13}C, and ^{19}F NMR were recorded on a 400 MHz Bruker NMR spectrometer in $CDCl_3$ (7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C) using tetramethylsilane (TMS) as the internal standard(s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet). High-resolution mass spectra HRMS data were obtained with Micromass HPLC–Q–TOF mass spectrometer.

2. Optimization of the Reaction Conditions

The reaction of 2-(quinolin-8-yl)isoindoline-1,3-dione **1a** (1 equiv) and Kobayashi benzyne precursor **2a** (2.3 equiv), was systematically examined, and the results were found to be strongly influenced by the solvent, additive, and the loading of catalyst (Table S1). In our initial attempts, the reaction of **1a** with 2- (trimethylsilyl)-phenyl trifluoromethanesulfonate **2a** in the presence of $Pd(PPh_3)_4$ (1.7 mol%), and CsF (2 equiv) in DMF at 140 ℃ failed to provide desired product **3aa** (entry 1, Table S1). To our delight, when PhCl was used as solvent, the reaction produced **3aa** in 19% yield, along with a byproduct **4aa** (entry 2, Table S1). The structure of compound **3aa** and 4aa were unambiguously confirmed by single-crystal X-ray analysis. An increase in the $Pd(PPh_3)_4$ loading (5 mol%) improved the yield of **3aa** (entry 3). Subsequent screening with different solvents revealed that the reaction could achieve higher conversions using PhCl/tert-Amyl alcohol

(1:1) as the mixture solvent (entries 4-7). Further studies have demonstrated that $Pd(PPh_3)_4$ proved to be the best catalyst for this reaction, and other catalytic system such as $dppePdCl_2$, $dpppPdCl_2$, and $(^tBu_3P)_2Pd$, however, were ineffective for this reaction (entries 6 and 8-10). In addition, when 10 mol% of $Pd(PPh_3)_4$ was employed, the yield of **3aa** increased to 58% (entry 11). To our satisfaction, the combination of CsF/KO^{t}Bu gave the corresponding product **3aa** in 63% yield, however, SDS (Sodium dodecyl sulfate) and NH_4PF_6 screened proved futile (entries 13 and 14). When the reaction temperature was decreased to 120 ℃, the isolated yield of **3aa** slightly decreased to 56% (entry 15). To our satisfaction, we found that the ratio of the mixture solvent appeared to tremendously affect the circulation of the reaction. The reaction worked most efficiently in the cosolvent with a 2:1 ratio of PhCl/tert-Amyl alcohol at 120 ^oC, giving rise to the corresponding product **3aa** in 75% yield (entries 15-17). Moreover, reaction of **1a** with **2a** in the present of 18-crown-6, which typically employed for promoting arynes synthesis delivered **3aa** in 68% yield. The results reveal that the decarbonylation is faster than aryne insertion (entry 18).

Table S1. Optimization of the Reaction Conditions[a]



1a **2a** **3aa** **4aa**

Entry	Catalyst	additive	Solvent	yield (%)[b]
1[c]	$Pd(PPh_3)_4$		DMF	N.D
2[c]	$Pd(PPh_3)_4$		PhCl	19
3[d]	$Pd(PPh_3)_4$		PhCl	32
4[e]	$Pd(PPh_3)_4$		PhCl/Trifluorotoluene (1:1)	25
5[e]	$Pd(PPh_3)_4$		PhCl/THF (1:1)	49
6[e]	$Pd(PPh_3)_4$		PhCl/tert-Amyl alcohol (1:1)	54
7[e]	$Pd(PPh_3)_4$		PhCl/2-Methyl-1-phenyl-2-propanol (1:1)	44
8[e]	$dppePdCl_2$		PhCl/tert-Amyl alcohol (1:1)	40
9[e]	$dpppPdCl_2$		PhCl/tert-Amyl alcohol (1:1)	30
10[e]	$(tBu_3P)_2Pd$		PhCl/tert-Amyl alcohol (1:1)	21
11	$Pd(PPh_3)_4$		PhCl/tert-Amyl alcohol (1:1)	58
12	$Pd(PPh_3)_4$	KO^{t}Bu	PhCl/tert-Amyl alcohol (1:1)	63
13	$Pd(PPh_3)_4$	SDS	PhCl/tert-Amyl alcohol (1:1)	39
14	$Pd(PPh_3)_4$	NH_4FP_6	PhCl/tert-Amyl alcohol (1:1)	52
15[f]	$Pd(PPh_3)_4$	KO^{t}Bu	PhCl/tert-Amyl alcohol (1:1)	56
16[f]	$Pd(PPh_3)_4$	KO^{t}Bu	PhCl/tert-Amyl alcohol (2:1)	75

17[f]	$Pd(PPh_3)_4$	KO^{t}Bu	PhCl/tert-Amyl alcohol (1:2)	33
18[f],[g]	$Pd(PPh_3)_4$	KO^{t}Bu	PhCl/tert-Amyl alcohol (2:1)	68

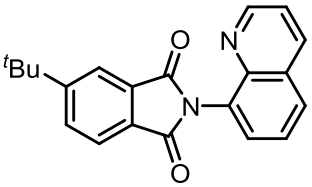
[a] Reaction conditions: Under N_2 atmosphere, **1a** (0.125 mmol), **2a** (2.3 equiv), Catalyst (10 mol%), CsF (4 equiv), and additive (10 mol %) in tert-Amyl alcohol/PhCl (3.0 mL, v/v=1:2) at 140 °C for 36 h. [b] Isolated yields were given. [c] 1.7% $Pd(PPh_3)_4$, CsF (2 equiv), **2a** (1.1 equiv). [d] 5% $Pd(PPh_3)_4$, CsF (2 equiv), **2a** (1.1 equiv). [e] 5% catalyst, CsF (3 equiv), **2a** (1.7 equiv). [f] 120 °C. [g] 18-crown-6 (20 mol%) was added.

3. General Procedure

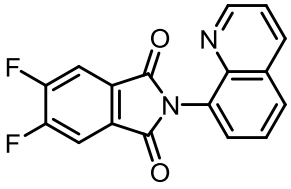
A mixture of $Pd(PPh_3)_4$ (14.4 mg, 10 mol%), CsF (4 equiv), KO^{t}Bu (10 mol%), phthalimide (0.125 mmol), aryne precursor (2.3 equiv), tert-Amyl alcohol/PhCl (3.0 mL, v/v=1:2) was stirred at 120 °C for 36 h. After cooling the reaction to room temperature, the solvent was removed under vacuum and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate = 10:1-4:1 to afford desired products **3aa-3qa** and **3aa-3ag**.

4. Characterization of Phthalimides and Products

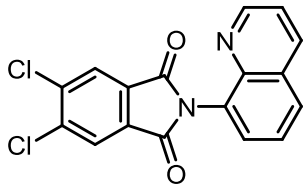
5-(tert-butyl)-2-(quinolin-8-yl)isoindoline-1,3-dione (1d). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.93 – 8.85 (m, 1H), 8.25 (d, *J*=8.3 Hz, 1H), 8.07 (d, *J*=1.3 Hz, 1H), 7.97 (dd, *J*=14.5 Hz, 8.0 Hz, 2H), 7.86 (dd, *J*=7.9 Hz, 1.6 Hz, 1H), 7.77 (dd, *J*=7.3 Hz, 1.4 Hz, 1H), 7.70 (t, *J*=7.7 Hz, 1H), 7.46 (dd, *J*=8.2 Hz, 4.2 Hz, 1H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.4, 168.1, 158.8, 150.9, 144.4, 136.3, 132.6, 131.3, 130.3, 130.0, 129.8, 129.6, 129.3, 126.2, 123.7, 121.9, 121.2, 35.9, 31.2.



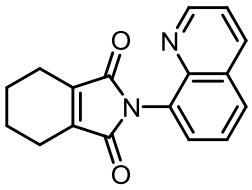
5,6-difluoro-2-(quinolin-8-yl)isoindoline-1,3-dione (1o). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.84 (dd, *J*=4.2 Hz, 1.6 Hz, 1H), 8.24 (dd, *J*=8.3 Hz, 1.6 Hz, 1H), 7.98 (dd, *J*=8.2 Hz, 1.4 Hz, 1H), 7.81 (t, *J*=7.3 Hz, 2H), 7.74 (dd, *J*=7.3 Hz, 1.5 Hz, 1H), 7.72 – 7.64 (m, 1H), 7.46 (dd, *J*=8.3 Hz, 4.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.9, 154.66 (d, *J*=261.2 Hz), 154.55 (d, *J*=261.2 Hz), 150.9, 143.9, 136.4, 130.3, 129.9, 129.4, 129.3, 129.29 (d, *J*=5.6 Hz), 126.2, 122.1, 113.73 (d, *J*=5.9 Hz), 113.68 (d, *J*=46.1 Hz), 113.63 (d, *J*=6.0 Hz).



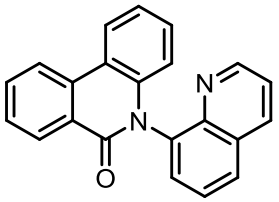
5,6-dichloro-2-(quinolin-8-yl)isoindoline-1,3-dione (1p). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.84 (dd, *J*=4.2 Hz, 1.4 Hz, 1H), 8.26 (d, *J*=8.3 Hz, 1H), 8.08 (s, 2H), 7.99 (d, *J*=8.1 Hz, 1H), 7.75 (dd, *J*=7.3 Hz, 1.3 Hz, 1H), 7.69 (t, *J*=7.7 Hz, 1H), 7.47 (dd, *J*=8.3 Hz, 4.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.0, 150.9, 143.8, 139.2, 136.5, 131.6, 130.3, 129.9, 129.32, 129.27, 126.2, 126.0, 122.0.



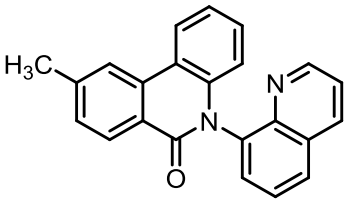
2-(quinolin-8-yl)-4,5,6,7-tetrahydro-1H-isoindole-1,3(2H)-dione (5a). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.89 (dd, *J*=4.2 Hz, 1.6 Hz, 1H), 8.20 (dd, *J*=8.3 Hz, 1.4 Hz, 1H), 7.90 (dd, *J*=6.8 Hz, 2.8 Hz, 1H), 7.68 – 7.57 (m, 2H), 7.43 (dd, *J*=8.3 Hz, 4.2 Hz, 1H), 2.64 – 2.30 (m, 4H), 1.99 – 1.72 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.6, 150.7, 144.5, 142.2, 136.4, 130.4, 129.9, 129.3, 129.2, 126.2, 121.8, 21.4, 20.4.



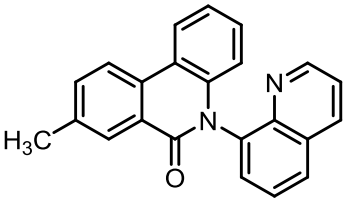
5-(quinolin-8-yl)phenanthridin-6(5H)-one (3aa). m.p. 230.7-232.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.80 (d, *J*=3.3 Hz, 1H), 8.58 (d, *J*=7.9 Hz, 1H), 8.44 – 8.26 (m, 3H), 8.04 (dd, *J*=6.9 Hz, 2.4 Hz, 1H), 7.90 – 7.72 (m, 3H), 7.61 (t, *J*=7.6 Hz, 1H), 7.44 (dd, *J*=8.2 Hz, 4.0 Hz, 1H), 7.33 – 7.23 (m, 1H), 7.19 (t, *J*=7.7 Hz, 1H), 6.49 (d, *J*=8.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.1, 151.3, 144.4, 139.6, 136.6, 136.1, 134.5, 132.8, 130.8, 129.9, 129.5, 129.2, 129.1, 128.0, 126.9, 126.1, 123.1, 122.5, 122.0, 121.9, 119.2, 116.9. HRMS: $[M+H]^+$ Calculated for $C_{22}H_{15}N_2O^+$, 323.1184, found 323.1179.



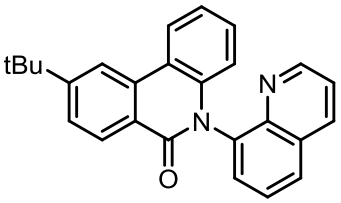
9-methyl-5-(quinolin-8-yl)phenanthridin-6(5H)-one (3ba). m.p. 244.1-245.8. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.80 (dd, *J*=4.2 Hz, 1.6 Hz, 1H), 8.46 (d, *J*=8.1 Hz, 1H), 8.31 (ddd, *J*=18.8 Hz, 8.1 Hz, 1.5 Hz, 2H), 8.17 (s, 1H), 8.03 (dd, *J*=7.0 Hz, 2.6 Hz, 1H), 7.77 (dd, *J*=7.3 Hz, 5.0 Hz, 2H), 7.48 – 7.39 (m, 2H), 7.23 (dd, *J*=7.9 Hz, 1.1 Hz, 1H), 7.20 – 7.14 (m, 1H), 6.47 (dd, *J*=8.3 Hz, 1.0 Hz, 1H), 2.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.1, 151.3, 144.5, 143.3, 139.7, 136.6, 136.2, 134.5, 130.8, 129.8, 129.41, 129.37, 129.2, 128.9, 126.9, 123.8, 123.1, 122.4, 122.0, 121.9, 119.2, 116.9, 22.3. HRMS: $[M+H]^+$ Calculated for $C_{23}H_{17}N_2O^+$, 337.1341, found 337.1346.



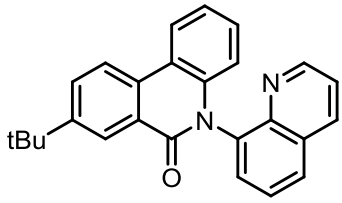
8-methyl-5-(quinolin-8-yl)phenanthridin-6(5H)-one (3ca). m.p. 261.7-263.0. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.79 (dd, *J*=4.1 Hz, 1.0 Hz, 1H), 8.37 (s, 1H), 8.35 – 8.23 (m, 3H), 8.03 (dd, *J*=6.6 Hz, 3.0 Hz, 1H), 7.76 (q, *J*=4.1 Hz, 2H), 7.64 (dd, *J*=8.3 Hz, 1.8 Hz, 1H), 7.42 (dd, *J*=8.3 Hz, 4.2 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.16 (ddd, *J*=8.5 Hz, 7.3 Hz, 1.5 Hz, 1H), 6.47 (d, *J*=8.3 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.1, 151.3, 144.5, 139.2, 138.1, 136.5, 136.2, 134.1, 132.0, 130.7, 129.8, 129.4, 128.9, 128.6, 127.8, 126.9, 125.9, 122.9, 122.5, 121.9, 119.3, 116.8, 21.4. HRMS: $[M+H]^+$ Calculated for $C_{23}H_{17}N_2O^+$, 337.1341, found 337.1337.



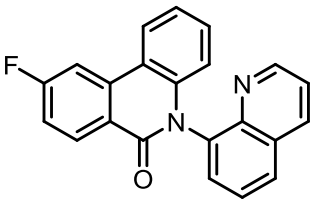
9-(tert-butyl)-5-(quinolin-8-yl)phenanthridin-6(5H)-one (3da). m.p. 238.3-239.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.77 (dd, *J*=4.2 Hz, 1.7 Hz, 1H), 8.50 (d, *J*=8.4 Hz, 1H), 8.38 (td, *J*=3.8 Hz, 1.3 Hz, 2H), 8.27 (dd, *J*=8.3 Hz, 1.7 Hz, 1H), 8.02 (dd, *J*=7.0 Hz, 2.7 Hz, 1H), 7.81 – 7.72 (m, 2H), 7.68 (dd, *J*=8.4 Hz, 1.8 Hz, 1H), 7.41 (dd, *J*=8.3 Hz, 4.2 Hz, 1H), 7.30 – 7.22 (m, 1H), 7.21 – 7.10 (m, 1H), 6.48 (dd, *J*=8.3 Hz, 1.0 Hz, 1H), 1.49 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.0, 156.2, 151.4, 144.7, 139.8, 136.3, 136.3, 134.1, 130.7, 129.8, 129.3, 129.0, 128.8, 126.8, 125.9, 123.8, 122.9, 122.3, 121.9, 119.5, 118.1, 116.9, 35.5, 31.3. HRMS: $[M+H]^+$ Calculated for $C_{26}H_{23}N_2O^+$, 379.1810, found 379.1809.



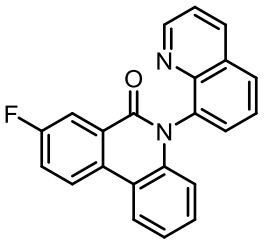
8-(tert-butyl)-5-(quinolin-8-yl)phenanthridin-6(5H)-one (3ea). m.p. 228.1-229.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.79 (dd, *J*=4.2 Hz, 1.7 Hz, 1H), 8.60 (d, *J*=2.2 Hz, 1H), 8.32 (d, *J*=8.6 Hz, 2H), 8.27 (dd, *J*=8.3 Hz, 1.6 Hz, 1H), 8.03 (dd, *J*=6.1 Hz, 3.6 Hz, 1H), 7.88 (dd, *J*=8.6 Hz, 2.2 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.42 (dd, *J*=8.3 Hz, 4.2 Hz, 1H), 7.23 (dd, *J*=10.4 Hz, 3.5 Hz, 2H), 7.20 – 7.12 (m, 1H), 6.49 (dd, *J*=8.3 Hz, 0.9 Hz, 1H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.4, 151.5, 151.3, 144.7, 139.3, 136.4, 136.3, 132.0, 130.58, 130.56, 129.8, 129.4, 128.6, 126.8, 125.6, 125.3, 122.9, 122.4, 121.91, 121.85, 119.3, 116.8, 35.0, 31.3. HRMS: $[M+H]^+$ Calculated for $C_{26}H_{23}N_2O^+$, 379.1810, found 379.1816.



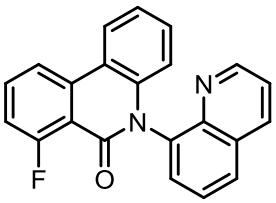
9-fluoro-5-(quinolin-8-yl)phenanthridin-6(5H)-one (3fa). m.p. 237.6-239.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.79 (dd, *J*=4.2 Hz, 1.7 Hz, 1H), 8.38 (dd, *J*=9.0 Hz, 4.9 Hz, 1H), 8.32 – 8.25 (m, 2H), 8.22 (dd, *J*=9.2 Hz, 2.8 Hz, 1H), 8.08 – 8.01 (m, 1H), 7.81 – 7.73 (m, 2H), 7.55 (ddd, *J*=8.9 Hz, 8.1 Hz, 2.9 Hz, 1H), 7.44 (dd, *J*=8.3 Hz, 4.2 Hz, 1H), 7.31 – 7.23 (m, 1H), 7.21 – 7.13 (m, 1H), 6.50 (dd, *J*=8.3 Hz, 0.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.38 (d, *J* = 248.5 Hz), 161.08 (d, *J* = 3.0 Hz), 151.5, 144.5, 139.1, 136.4, 135.9, 130.97 (d, *J* = 2.6 Hz), 130.5, 129.8, 129.6, 129.0, 127.95 (d, *J* = 8.0 Hz), 126.8, 124.5 (d, *J* = 7.9 Hz), 122.9, 122.7, 122.0, 121.12 (d, *J* = 23.3 Hz), 118.6, 117.0, 114.53 (d, *J* = 22.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -112.29. HRMS: $[M+H]^+$ Calculated for $C_{22}H_{14}FN_2O^+$, 341.1090, found 341.1084.



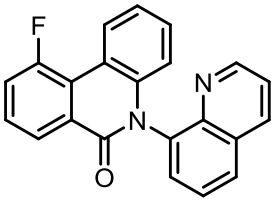
8-fluoro-5-(quinolin-8-yl)phenanthridin-6(5H)-one (3ga). m.p. 223.1-224.9. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.81 (dd, *J*=4.2 Hz, 1.5 Hz, 1H), 8.59 (dd, *J*=8.8 Hz, 6.0 Hz, 1H), 8.31 (dd, *J*=8.3 Hz, 1.4 Hz, 1H), 8.22 (dd, *J*=7.8 Hz, 1.6 Hz, 1H), 8.06 (dd, *J*=5.7 Hz, 4.0 Hz, 1H), 7.99 (dd, *J*=10.4 Hz, 2.4 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.45 (dd, *J*=8.3 Hz, 4.2 Hz, 1H), 7.35 – 7.19 (m, 3H), 6.49 (dd, *J*=8.2 Hz, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.94 (d, *J* = 252.3 Hz), 161.3, 151.4, 144.3, 140.0, 138.5, 137.15 (d, *J* = 9.6 Hz), 136.7, 135.8, 132.40 (d, *J* = 9.9 Hz), 130.7, 129.9, 129.8, 129.6, 126.9, 123.4, 122.7, 122.0, 118.5, 117.1, 116.24 (d, *J* = 22.9 Hz), 107.92 (d, *J* = 23.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -105.50. HRMS: $[M+H]^+$ Calculated for $C_{22}H_{14}FN_2O^+$, 341.1090, found 341.1076.



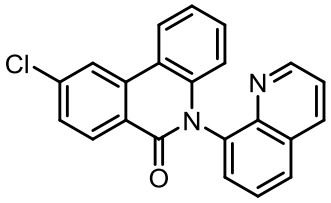
7-fluoro-5-(quinolin-8-yl)phenanthridin-6(5H)-one (3ha). m.p. 221.5-223.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.80 (dd, *J*=4.2 Hz, 1.7 Hz, 1H), 8.33 – 8.24 (m, 2H), 8.19 (d, *J*=8.3 Hz, 1H), 8.04 (dd, *J*=6.4 Hz, 3.3 Hz, 1H), 7.83 – 7.67 (m, 3H), 7.43 (dd, *J*=8.3 Hz, 4.2 Hz, 1H), 7.31 – 7.15 (m, 3H), 6.47 (dd, *J*=8.1 Hz, 1.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.51 (d, *J* = 265.3 Hz), 159.18 (d, *J* = 5.2 Hz), 151.4, 144.6, 139.9, 137.4, 136.4, 135.8, 133.58 (d, *J* = 10.2 Hz), 130.8, 129.82, 129.77, 129.4, 126.8, 123.6, 122.5, 121.9, 118.13 (d, *J* = 2.6 Hz), 117.80 (d, *J* = 4.5 Hz), 116.8, 115.50 (d, *J* = 22.1 Hz), 115.16 (d, *J* = 4.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -108.55. HRMS: $[M+H]^+$ Calculated for $C_{22}H_{14}FN_2O^+$, 341.1090, found 341.1081.



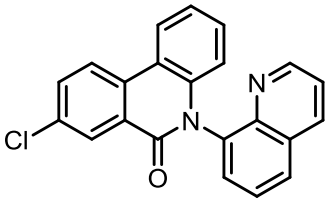
10-fluoro-5-(quinolin-8-yl)phenanthridin-6(5H)-one (3ia). m.p. 225.3-227.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.80 (ddd, *J*=5.9 Hz, 3.8 Hz, 1.6 Hz, 2H), 8.49 – 8.41 (m, 1H), 8.28 (dd, *J*=8.3 Hz, 1.7 Hz, 1H), 8.04 (dd, *J*=5.8 Hz, 3.9 Hz, 1H), 7.80 – 7.73 (m, 2H), 7.60 – 7.52 (m, 2H), 7.43 (dd, *J*=8.3 Hz, 4.2 Hz, 1H), 7.32 – 7.14 (m, 2H), 6.51 (dd, *J*=8.3 Hz, 1.3 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 161.00 (d, *J* = 3.3 Hz), 160.23 (d, *J* = 253.6 Hz), 151.44, 144.36, 139.42, 136.48, 136.01, 130.55, 129.87, 129.55, 129.23 (d, *J* = 2.4 Hz), 128.38 (d, *J* = 3.4 Hz), 128.29 (d, *J* = 9.6 Hz), 128.02 (d, *J* = 24.4 Hz), 126.88, 125.23 (d, *J* = 3.5 Hz), 123.34 (d, *J* = 8.9 Hz), 122.90 (d, *J* = 2.2 Hz), 122.04, 120.24 (d, *J* = 24.4 Hz), 117.00 (d, *J*



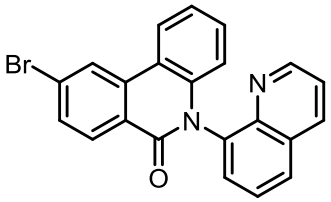
= 5.5 Hz), 116.74. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -111.01. HRMS: $[M+H]^+$ Calculated for $C_{22}H_{14}FN_2O^+$, 341.1090, found 341.1080.



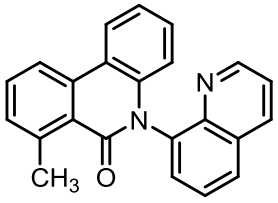
9-chloro-5-(quinolin-8-yl)phenanthridin-6(5H)-one (3ja). m.p. 228.9-230.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.79 (dd, *J*=4.2 Hz, 1.6 Hz, 1H), 8.50 (d, *J*=8.5 Hz, 1H), 8.34 (d, *J*=1.9 Hz, 1H), 8.26 (ddd, *J*=13.3 Hz, 8.0 Hz, 1.5 Hz, 2H), 8.04 (dd, *J*=6.1 Hz, 3.6 Hz, 1H), 7.80 – 7.73 (m, 2H), 7.56 (dd, *J*=8.5 Hz, 1.9 Hz, 1H), 7.43 (dd, *J*=8.3 Hz, 4.2 Hz, 1H), 7.27 – 7.16 (m, 2H), 6.54 – 6.42 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 161.4, 151.5, 144.5, 140.0, 139.6, 136.4, 136.0, 135.8, 131.0, 130.6, 129.9, 129.8, 129.6, 128.4, 126.8, 124.5, 123.2, 122.7, 122.0, 121.9, 118.1, 117.1. HRMS: $[M+H]^+$ Calculated for $C_{22}H_{14}ClN_2O^+$, 357.0795, found 357.0797.



8-chloro-5-(quinolin-8-yl)phenanthridin-6(5H)-one (3ka). m.p. 261.7-263.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.80 (d, *J*=2.9 Hz, 1H), 8.53 (d, *J*=2.3 Hz, 1H), 8.36 – 8.21 (m, 3H), 8.05 (dd, *J*=8.9 Hz, 4.0 Hz, 1H), 7.84 – 7.72 (m, 3H), 7.45 (dd, *J*=8.2 Hz, 4.2 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.24 – 7.17 (m, 1H), 6.49 (d, *J*=8.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.9, 151.4, 144.4, 139.5, 136.5, 135.8, 134.2, 133.1, 133.0, 130.6, 129.9, 129.6, 129.4, 128.7, 127.3, 126.9, 123.7, 123.1, 122.8, 122.1, 118.5, 117.1. HRMS: $[M+H]^+$ Calculated for $C_{22}H_{14}ClN_2O^+$, 357.0795, found 357.0790.

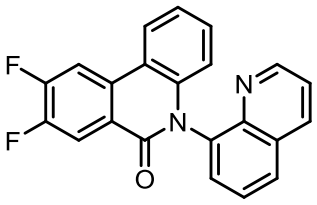


9-bromo-5-(quinolin-8-yl)phenanthridin-6(5H)-one (3la). m.p. 261.5-262.9. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.79 (dd, *J*=4.2 Hz, 1.6 Hz, 1H), 8.52 (d, *J*=1.6 Hz, 1H), 8.42 (d, *J*=8.5 Hz, 1H), 8.27 (ddd, *J*=10.0 Hz, 8.1 Hz, 1.5 Hz, 2H), 8.05 (dd, *J*=5.5 Hz, 4.2 Hz, 1H), 7.78 – 7.73 (m, 2H), 7.71 (dd, *J*=8.5 Hz, 1.8 Hz, 1H), 7.44 (dd, *J*=8.3 Hz, 4.2 Hz, 1H), 7.30 – 7.19 (m, 2H), 6.52 – 6.44 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 161.5, 151.5, 144.5, 140.0, 136.4, 136.1, 135.9, 131.2, 131.0, 130.5, 129.9, 129.8, 129.6, 128.2, 126.8, 125.0, 124.8, 123.2, 122.7, 122.0, 118.0, 117.1. HRMS: $[M+H]^+$ Calculated for $C_{22}H_{14}BrN_2O^+$, 401.0290, found 401.0281.

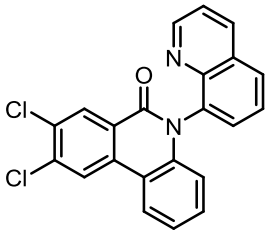


7-methyl-5-(quinolin-8-yl)phenanthridin-6(5H)-one (3na). m.p. 184.2-185.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82 (d, *J*=9.6 Hz, 1H), 7.71 (dd, *J*=7.7 Hz, 1.4 Hz, 1H), 7.54 – 7.45 (m, 2H), 7.39 (d, *J*=7.1 Hz, 1H), 7.34 (t, *J*=7.7 Hz, 1H), 7.22 (dd, *J*=7.7 Hz, 1.5 Hz, 1H), 7.11 (d, *J*=8.5 Hz, 2H), 7.07 – 7.00 (m, 1H), 6.98 (d, *J*=7.3 Hz, 1H), 6.77 (d, *J*=9.5 Hz, 1H), 6.66 (t, *J*=7.5 Hz, 1H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.5, 166.9, 162.8, 140.4, 138.3, 138.0, 137.7, 136.2, 134.1, 133.5, 132.2, 130.8, 129.0, 128.4, 128.0, 128.0, 127.4, 123.1, 123.0, 122.5, 120.8, 118.3, 17.6. HRMS: $[M+H]^+$ Calculated for $C_{23}H_{17}N_2O^+$, 337.1341, found 337.1345.

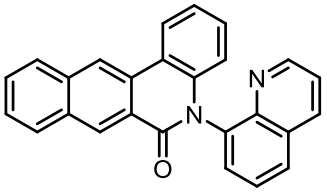
8,9-difluoro-5-(quinolin-8-yl)phenanthridin-6(5H)-one (3oa). m.p. 226.7-228.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.87 – 8.70 (m, 1H), 8.44 – 8.24 (m, 2H), 8.09 (ddd, *J*=23.2 Hz, 10.6 Hz, 5.7 Hz, 3H), 7.75 (t, *J*=6.2 Hz, 2H), 7.44 (dd, *J*=8.3 Hz, 4.2 Hz, 1H), 7.34 – 7.13 (m, 2H), 6.49 (d, *J*=8.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.45 (d, *J* = 2.2 Hz), 154.21 (dd, *J* = 255.3 Hz, 14.2 Hz), 150.50 (dd, *J* = 251.9 Hz, 13.8 Hz), 151.5, 144.4, 139.6, 136.4, 135.6, 132.50 (dd, *J* = 7.8 Hz, 3.1 Hz), 130.5, 129.9, 129.7, 126.8, 123.36 (dd, *J* = 6.0 Hz, 2.4 Hz), 123.2, 122.9, 122.1, 117.9, 117.51 (dd, *J* = 18.7 Hz, 1.7 Hz), 117.19, 110.55 (d, *J* = 19.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -129.26 (d, *J* = 21.8 Hz), -136.06 (d, *J* = 21.8 Hz). HRMS: $[M+H]^+$ Calculated for $C_{22}H_{13}F_2N_2O^+$, 359.0996, found 359.0988.



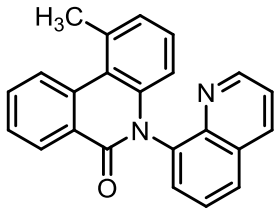
8,9-dichloro-5-(quinolin-8-yl)phenanthridin-6(5H)-one (3pa). m.p. 220.4-222.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.79 (dd, *J*=4.2 Hz, 1.6 Hz, 1H), 8.62 (s, 1H), 8.45 (s, 1H), 8.29 (dd, *J*=8.3 Hz, 1.5 Hz, 1H), 8.21 (dd, *J*=7.8 Hz, 1.4 Hz, 1H), 8.08 – 8.03 (m, 1H), 7.80 – 7.74 (m, 2H), 7.45 (dd, *J*=8.3 Hz, 4.2 Hz, 1H), 7.31 – 7.18 (m, 2H), 6.49 (dd, *J*=8.2 Hz, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.4, 151.5, 144.3, 139.9, 137.8, 136.5, 135.6, 134.1, 132.5, 130.9, 130.5, 130.0, 129.9, 129.7, 126.8, 125.6, 124.1, 123.2, 122.9, 122.1, 117.5, 117.2. HRMS: $[M+H]^+$ Calculated for $C_{22}H_{13}Cl_2N_2O^+$, 391.0405, found 391.0396.



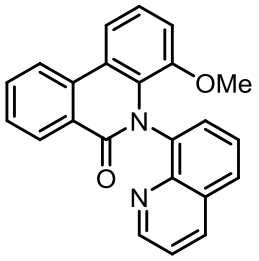
5-(quinolin-8-yl)benzo[j]phenanthridin-6(5H)-one (3qa). m.p. 242.2-243.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.19 (s, 1H), 8.86 (dd, *J*=5.0 Hz, 2.2 Hz, 2H), 8.54 (dd, *J*=8.0 Hz, 1.2 Hz, 1H), 8.36 (d, *J*=7.9 Hz, 1H), 8.10 (dd, *J*=12.7 Hz, 5.3 Hz, 3H), 7.91 – 7.79 (m, 2H), 7.74 – 7.65 (m, 1H), 7.63 – 7.57 (m, 1H), 7.49 (dd, *J*=8.3 Hz, 4.2 Hz, 1H), 7.32 (t, *J*=7.1 Hz, 1H), 7.24 – 7.18 (m, 1H), 6.51 (dd, *J*=8.3 Hz, 0.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.4, 156.9, 151.3, 139.5, 136.7,136.2, 135.5, 132.4, 130.9, 130.6, 130.5, 129.9, 129.5, 129.4, 129.0, 128.4, 128.2, 127.0, 126.5, 124.2, 123.4, 122.7, 122.0, 121.0, 119.6, 117.1. HRMS: $[M+H]^+$ Calculated for $C_{26}H_{17}N_2O^+$, 373.1341, found 373.1347.



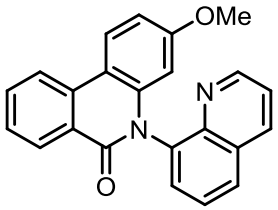
1-methyl-5-(quinolin-8-yl)phenanthridin-6(5H)-one (3ab). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.80 (dd, *J*=4.1 Hz, 1.3 Hz, 1H), 8.66 (dd, *J*=7.9 Hz, 1.4 Hz, 1H), 8.59 (d, *J*=8.5 Hz, 1H), 8.29 (dd, *J*=8.3 Hz, 1.3 Hz, 1H), 8.03 (dd, *J*=5.7 Hz, 4.0 Hz, 1H), 7.86 – 7.72 (m, 3H), 7.62 (t, *J*=7.5 Hz, 1H), 7.43 (dd, *J*=8.3 Hz, 4.2 Hz, 1H), 7.15 – 7.01 (m, 2H), 6.41 (d, *J*=8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 161.9, 151.3, 140.6, 136.8, 136.5, 136.2, 135.7, 131.9, 130.6, 129.8, 129.3, 129.2, 127.8, 127.31, 127.26, 127.0, 126.9, 126.9, 121.9, 119.1, 115.5, 100.0, 26.7. HRMS: $[M+H]^+$ Calculated for $C_{23}H_{17}N_2O^+$, 337.1341, found 337.1336.



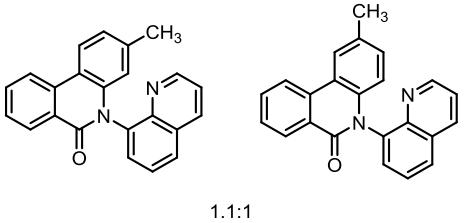
4-methoxy-5-(quinolin-8-yl)phenanthridin-6(5H)-one (3ac). m.p. 214.9-216.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.83 (dd, *J*=4.2 Hz, 1.6 Hz, 1H), 8.53 (dd, *J*=8.0 Hz, 1.1 Hz, 1H), 8.35 (d, *J*=8.2 Hz, 1H), 8.25 (dd, *J*=8.3 Hz, 1.6 Hz, 1H), 8.02 (dd, *J*=8.2 Hz, 1.0 Hz, 1H), 7.89 (dd, *J*=7.2



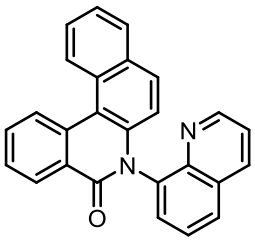
Hz, 2.5 Hz, 1H), 7.84 – 7.76 (m, 1H), 7.65 – 7.55 (m, 3H), 7.40 (dd, *J*=8.3 Hz, 4.2 Hz, 1H), 7.23 (t, *J*=8.1 Hz, 1H), 6.85 (dd, *J*=8.0 Hz, 1.0 Hz, 1H), 2.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.7, 150.5, 148.5, 145.4, 141.4, 138.4, 136.1, 134.6, 132.8, 130.0, 129.1, 128.6, 128.1, 127.5, 126.04, 126.00, 123.0, 122.3, 121.3, 121.2, 116.3, 114.7, 57.0. HRMS: $[M+H]^+$ Calculated for $C_{23}H_{17}N_2O_2^+$, 353.1290, found 353.1285.



3-methoxy-5-(quinolin-8-yl)phenanthridin-6(5H)-one (3ad). m.p. 222.7-224.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.84 (dd, *J*=4.2 Hz, 1.6 Hz, 1H), 8.55 (dd, *J*=8.0 Hz, 1.0 Hz, 1H), 8.30 (ddd, *J*=12.7 Hz, 8.6 Hz, 3.0 Hz, 3H), 8.06 (dd, *J*=7.4 Hz, 2.3 Hz, 1H), 7.86 – 7.72 (m, 3H), 7.62 – 7.53 (m, 1H), 7.46 (dd, *J*=8.3 Hz, 4.2 Hz, 1H), 6.87 (dd, *J*=8.9 Hz, 2.5 Hz, 1H), 6.01 (d, *J*=2.5 Hz, 1H), 3.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.4, 160.3, 151.4, 144.4, 141.0, 136.6, 136.1, 134.7, 132.8, 130.7, 130.7, 129.9, 129.5, 129.1, 126.9, 124.9, 124.6, 122.0, 121.3, 113.1, 108.6, 102.4, 55.24. HRMS: $[M+H]^+$ Calculated for $C_{23}H_{17}N_2O_2^+$, 353.1290, found 353.1283.



3-methyl-5-(quinolin-8-yl)phenanthridin-6(5H)-one (3ae) and 2-methyl-5-(quinolin-8-yl)phenanthridin-6(5H)-one (3af). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.81 (ddd, *J*=7.2 Hz, 4.2 Hz, 1.6 Hz, 2H), 8.61 – 8.51 (m, 2H), 8.40 – 8.27 (m, 4H), 8.22 (d, *J*=8.2 Hz, 1H), 8.14 (s, 1H), 8.03 (ddd, *J*=18.8 Hz, 9.2 Hz, 6.3 Hz, 3H), 7.84 – 7.74 (m, 7H), 7.63 – 7.54 (m, 2H), 7.44 (ddd, *J*=8.4 Hz, 5.3 Hz, 4.4 Hz, 2H), 7.07 (d, *J*=7.3 Hz, 1H), 7.00 (dd, *J*=8.6 Hz, 1.3 Hz, 1H), 6.37 (d, *J*=8.5 Hz, 1H), 2.43 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.2, 161.9, 151.3, 144.4, 144.4, 143.9, 139.6, 139.4, 137.5, 136.7, 136.6, 136.2, 134.6, 134.4, 134.2, 132.7, 132.7, 132.5, 131.9, 130.8, 130.1, 129.8, 129.6, 129.4, 129.4 129.2, 129.1, 127.9, 127.5, 126.9, 126.1, 125.6, 123.9, 123.8, 123.2, 123.0, 121.9, 121.9, 121.9, 121.7, 119.0, 117.0, 116.84, 116.77, 21.7, 21.0. HRMS: $[M+H]^+$ Calculated for $C_{23}H_{17}N_2O^+$, 337.1341, found 337.1346.

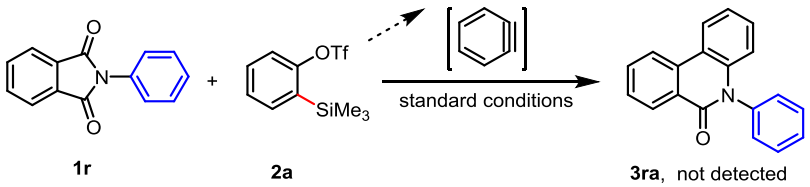


6-(quinolin-8-yl)benzo[a]phenanthridin-5(6H)-one (3ag). m.p. 261.9-263.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.92 (d, *J*=8.7 Hz, 1H), 8.83 (d, *J*=8.3 Hz, 1H), 8.77 (dd, *J*=4.2 Hz, 1.7 Hz, 1H), 8.66 (dd, *J*=7.9 Hz, 1.2 Hz, 1H), 8.30 (dd, *J*=8.3 Hz, 1.6 Hz, 1H), 8.07 (dd, *J*=7.2 Hz, 2.5 Hz, 1H), 7.90 – 7.75 (m, 4H), 7.69 – 7.63 (m, 2H), 7.58 (d, *J*=9.1 Hz, 1H), 7.49 (t, *J*=7.3 Hz, 1H), 7.43 (dd, *J*=8.3 Hz, 4.2 Hz, 1H), 6.68 (d, *J*=9.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.1, 151.5, 144.8, 138.0, 136.37, 136.35, 134.8, 132.0, 130.7, 130.6, 130.06, 129.8, 129.7, 129.5, 129.1, 128.7, 128.1, 127.3, 127.2, 127.1, 126.8, 126.2, 124.7, 122.0, 116.9, 113.8. HRMS: $[M+H]^+$ Calculated for $C_{26}H_{17}N_2O^+$, 373.1341, found 373.1333.

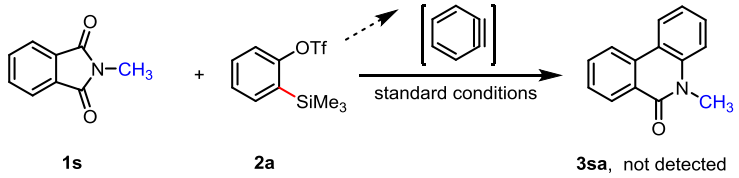
5. Procedures of mechanistic studies

5.1 Control experiments

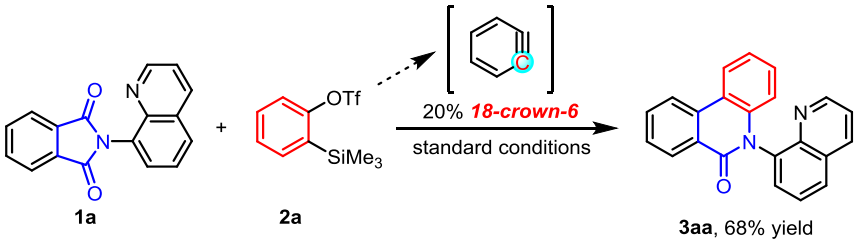
A mixture of $Pd(PPh_3)_4$ (14.4 mg, 10 mol%), CsF (4 equiv), KO^{t}Bu (10 mol%), 2-phenylisoindoline-1,3-dione **1r** (0.125 mmol), **2a** (2.3 equiv), tert-Amyl alcohol/PhCl (3.0 mL, v/v=1:2) was stirred at 120 °C for 36 h. After cooling the reaction to room temperature, no desired product was detected by TLC.



A mixture of $Pd(PPh_3)_4$ (14.4 mg, 10 mol%), CsF (4 equiv), KO^{t}Bu (10 mol%), 2-methylisoindoline-1,3-dione **1s** (0.125 mmol), **2a** (2.3 equiv), tert-Amyl alcohol/PhCl (3.0 mL, v/v=1:2) was stirred at 120 °C for 36 h. After cooling the reaction to room temperature, no desired product was detected by TLC.

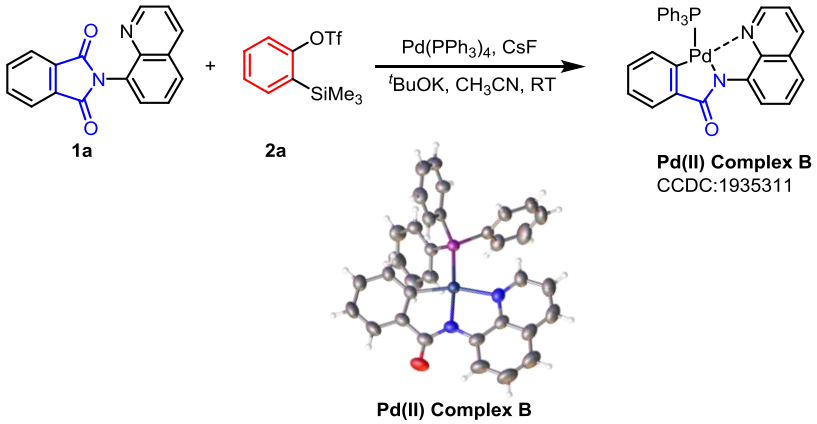


A mixture of $Pd(PPh_3)_4$ (14.4 mg, 10 mol%), CsF (4 equiv), KO^{t}Bu (10 mol%), phthalimide **1a** (0.125 mmol), **2a** (2.3 equiv), 18-crown-6 (20 mol %), tert-Amyl alcohol/PhCl (3.0 mL, v/v=1:2) was stirred at 120 °C for 36 h. After cooling the reaction to room temperature, the solvent was removed under vacuum and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate = 10:1-4:1 to afford desired product **3aa** in 68% yield.



5.2 Synthesis of Pd(II) complex B

$Pd(PPh_3)_4$ (14.4 mg, 0.0125 mmol), phthalimide **1a** (3.4 mg, 0.0125 mmol), **2a** (6.9 uL, 0.0125 mmol), CsF (3.3 mg), ^{t}BuOK (1.4 mg) and CH_3CN (1 mL) were charged into an oven dried reaction tube and then stirred for 5 min at room temperature under air atmosphere. The reaction mixture was recrystallized with *n*-petane to afford the intermediate **Pd(II) complex B**, which further was confirmed by single-crystal X-ray crystallography.



6. References

(S1) L. Zeng, H. Li, S. Tang, X. Gao, Y. Deng, G. Zhang, C.-W. Pao, J.-L. Chen, J.-F. Lee and A. Lei, *ACS Catalysis*, 2018, **8**, 5448.

(S2) N. Barsu, D. Kalsi and B. Sundararaju, *Catal. Sci. Technol.*, 2018, **8**, 5963.

(S3) B. Khan, A. A. Khan, R. Kant and D. Koley, *Adv. Synth. Catal.*, 2016, **358**, 3753.

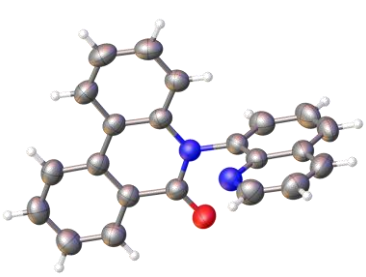
(S4) T. Shiba, T. Kurahashi and S. Matsubara, *J. Am. Chem. Soc.*, 2013, **135**, 13636.

(S5) Y. Kajita, S. Matsubara and T. Kurahashi, *J. Am. Chem. Soc.*, 2008, **130**, 6058.

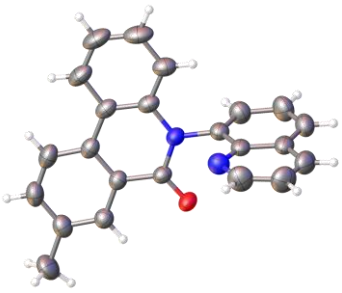
(S6) Sheldrick, G. M. *SHELXTL-97*, *Program for X-ray Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, **1997**.

7. Single-Crystal X-Ray Crystallography

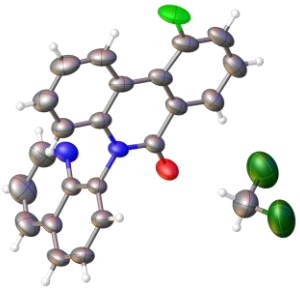
7.1 Crystal structures of targeted phenanthridinone (7 products). The displacement ellipsoids are drawn at the 30% probability.



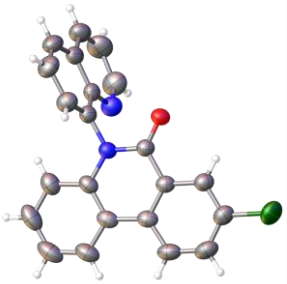
3aa



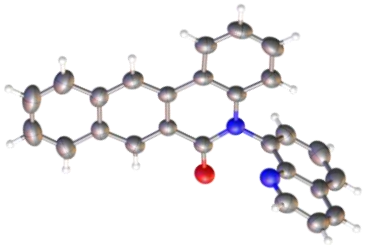
3ca



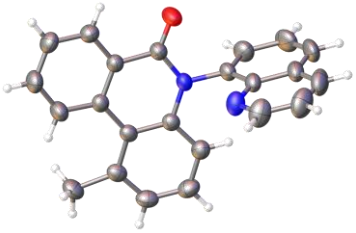
3ia



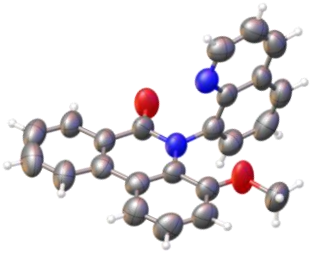
3ka



3qa

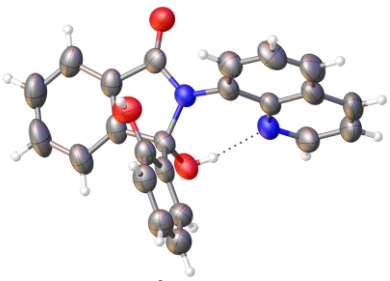


3ab

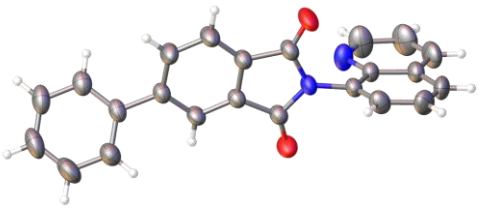


3ac

7.2 Crystal structures of 4aa and 6aa (2 products). The displacement ellipsoids are drawn at the 30% probability.

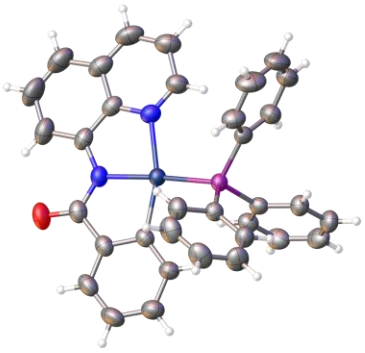


4aa



6aa

7.3 Crystal structures of intermediate Pd(II) Complex B (C: grey; H: white; N: light blue; Pd: navy bule; P: purple; O: red). The displacement ellipsoids are drawn at the 30% probability.



Pd(II) Complex B

Table S2. Crystal data and structure refinement details for targeted phenanthridinones and **Pd(II) Complex B**.

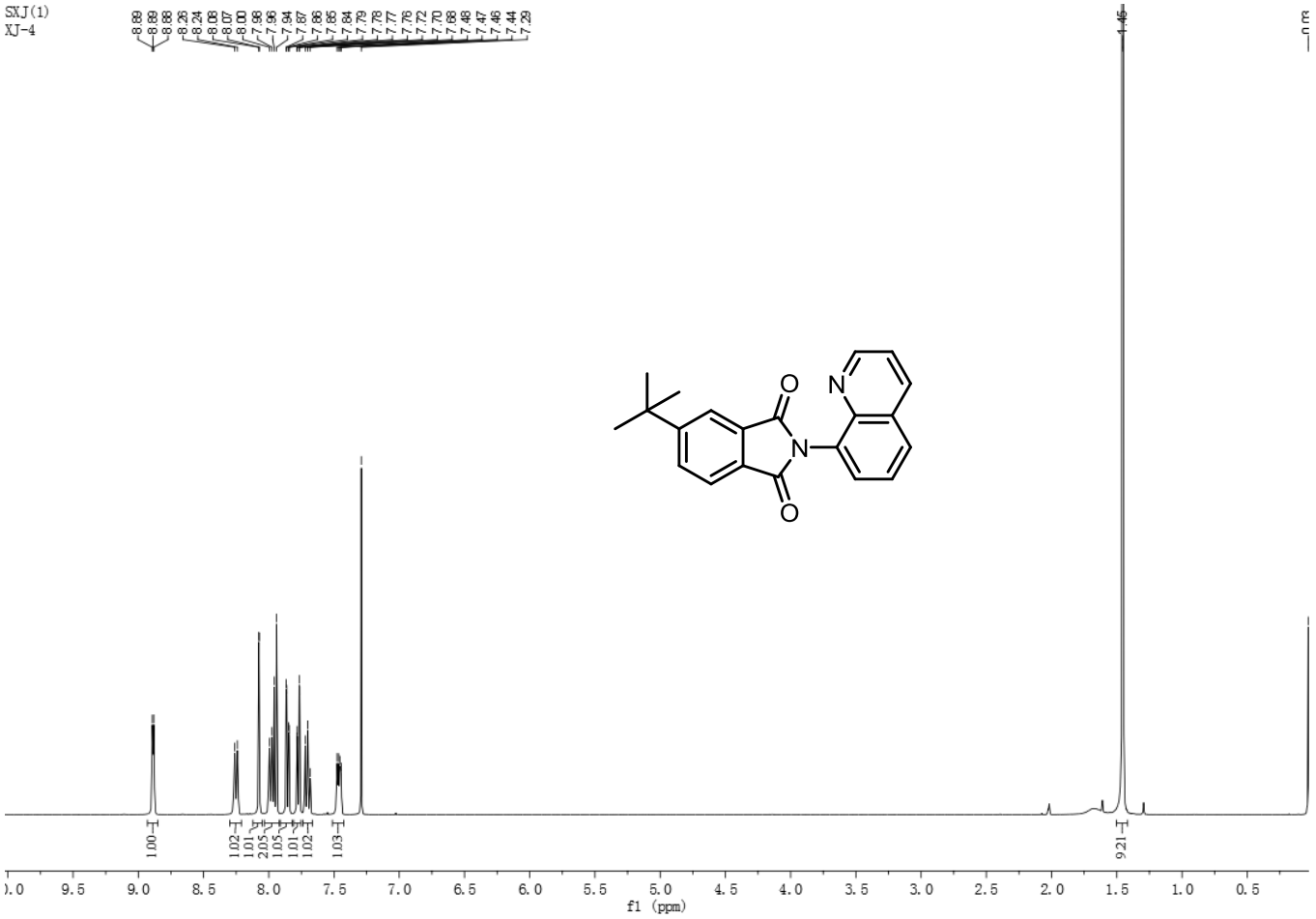
	3aa	**3ca**	**3ia**	**3ka**	**3qa**
Empirical formula	$C_{12.57}H_8N_{1.14}O_{0.57}$	$C_{2.88}H_2N_{0.25}O_{0.13}$	$C_{2.59}H_{1.62}N_{0.22}O_{0.11}Cl_{0.22}F_{0.11}$	$C_{3.67}H_{2.17}N_{0.33}O_{0.17}Cl_{0.17}$	$C_{2.97}H_{1.83}N_{0.23}O_{0.11}$
Formula weight	184.20	42.05	47.27	59.47	42.56
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a / Å	12.4387(7)	11.6498(8)	13.9904(4)	11.6827(13)	7.9197(8)
b / Å	9.6197(5)	11.4654(8)	7.6164(2)	11.2961(12)	11.2944(11)
c / Å	13.4146(9)	12.9919(9)	18.5537(5)	13.0187(12)	21.008(2)
α / °	90	90	90	90	90
β / °	100.572(6)	102.440(7)	99.644(2)	101.779(10)	97.906(9)
γ / °	90	90	90	90	90
Volume / $Å^3$	1577.90(16)	1694.6(2)	1949.07(9)	1681.9(3)	1861.3(3)
Z	7	32	37	24	35
D / g cm^{-3}	1.357	1.318	1.490	1.409	1.329
μ / mm^{-1}	0.668	0.644	3.242	0.240	0.082
F (000)	672.0	704.0	896.0	736.0	776.0
R_{int}	0.0230	0.0356	0.0181	0.0260	0.0310
Goodness-of-fit on F^2	1.051	1.179	1.046	1.060	1.043
$R_1{}^a$ / $wR_2{}^b$ [I >2σ(I)]	0.0441/0.1135	0.0516/0.1512	0.0710/0.2054	0.0647/0.1686	0.0610/0.1346
$R_1{}^a$ / $wR_2{}^b$ (all data)	0.0607/0.1271	0.0667/0.1835	0.0848/0.2230	0.1004/0.1919	0.1149/0.1615
CCDC number	1935307	1935310	1935308	1935312	1935314

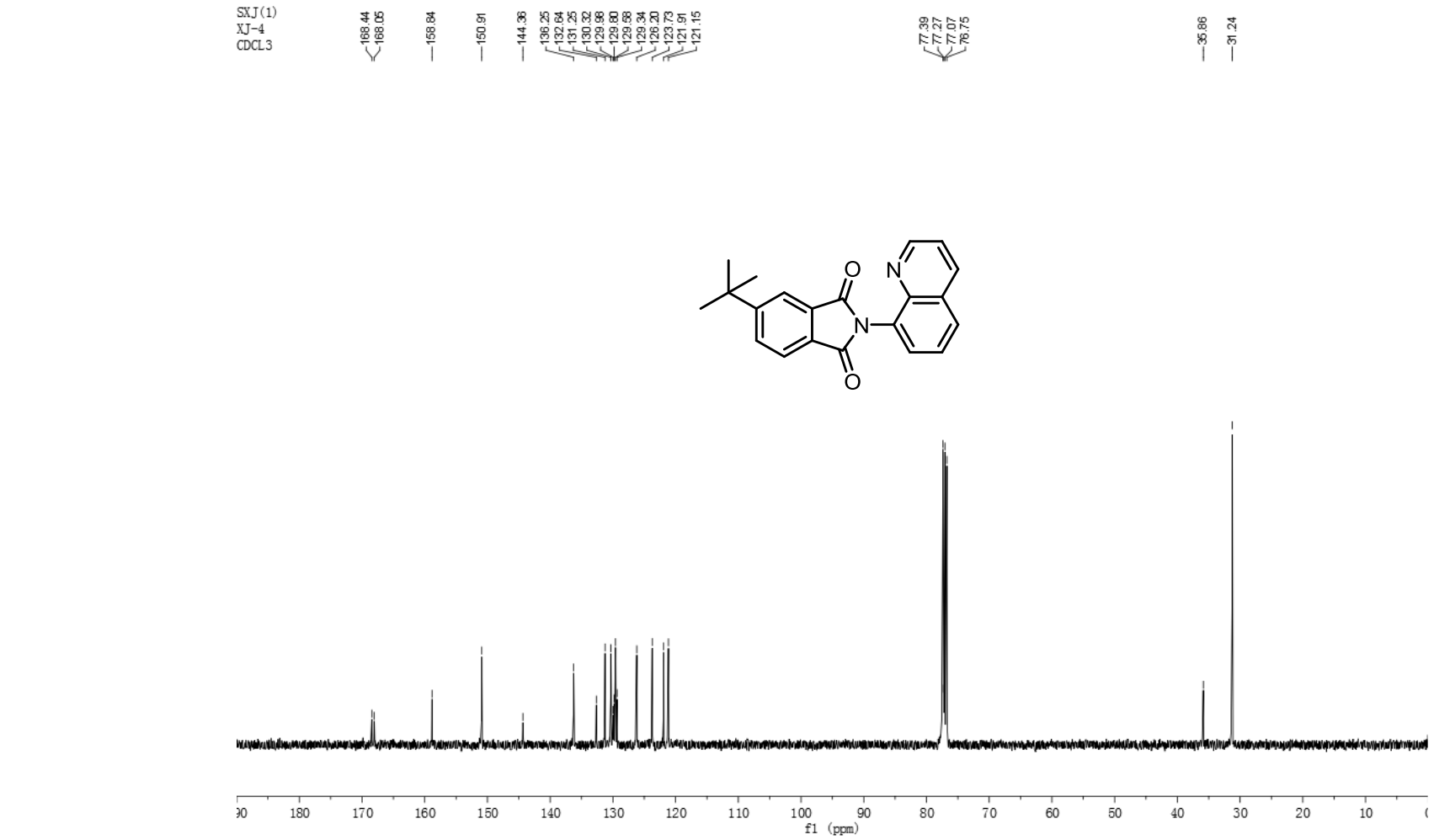
	3ab	3ac	4aa	6aa	Pd(II) Complex B
Empirical formula	$C_{2.97}H_{2.06}N_{0.26}O_{0.13}$	$C_{1.42}H_{0.98}N_{0.12}O_{0.12}$	$C_{3.83}H_{2.67}N_{0.33}O_{0.5}$	$C_{1.42}H_{0.86}N_{0.12}O_{0.12}$	$C_{2.67}H_{1.96}N_{0.16}O_{0.08}P_{0.08}Pd_{0.08}$
Formula weight	43.40	21.68	61.40	21.56	48.23
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	P-1	$P2_1/c$	$P2_1/c$
a / Å	14.7470(4)	10.585(3)	8.3599(9)	13.7590(17)	8.88834(18)
b / Å	7.5124(2)	7.8514(18)	9.1656(18)	9.4936(8)	18.6381(4)
c / Å	15.3583(5)	21.381(4)	12.047(2)	13.7713(15)	16.8048(3)
α / °	90	90	101.840(16)	90	90
β / °	107.412(3)	103.63(2)	102.780(12)	104.908(12)	102.007(2)
γ / °	90	90	93.053(12)	90	90
Volume / $Å^3$	1623.51(9)	1726.9(7)	876.4(3)	1738.3(3)	2723.00(10)
Z	31	65	12	65	51
D / g cm^{-3}	1.376	1.355	1.396	1.339	1.500
μ / mm^{-1}	0.672	0.702	0.761	0.087	6.288
F (000)	704.0	736.0	384.0	728.0	1248.0
R_{int}	0.0125	0.0353	0.0429	0.0189	0.0298
Goodness-of-fit on F^2	1.026	1.118	1.148	1.030	1.054
$R_1{}^a$ / $wR_2{}^b$ [$I > 2\sigma(I)$]	0.0404/0.1068	0.0828/0.2391	0.1106/0.3692	0.0533/0.1251	0.0309/0.0757
$R_1{}^a$ / $wR_2{}^b$ (all data)	0.0461/ 0.1116	0.1217/0.2789	0.1258/0.3836	0.0858/0.1406	0.0353/0.0787
CCDC number	1935309	1935313	1938632	1935306	1935311

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$. $P = (F_o{}^2 + 2F_c{}^2)/3$.

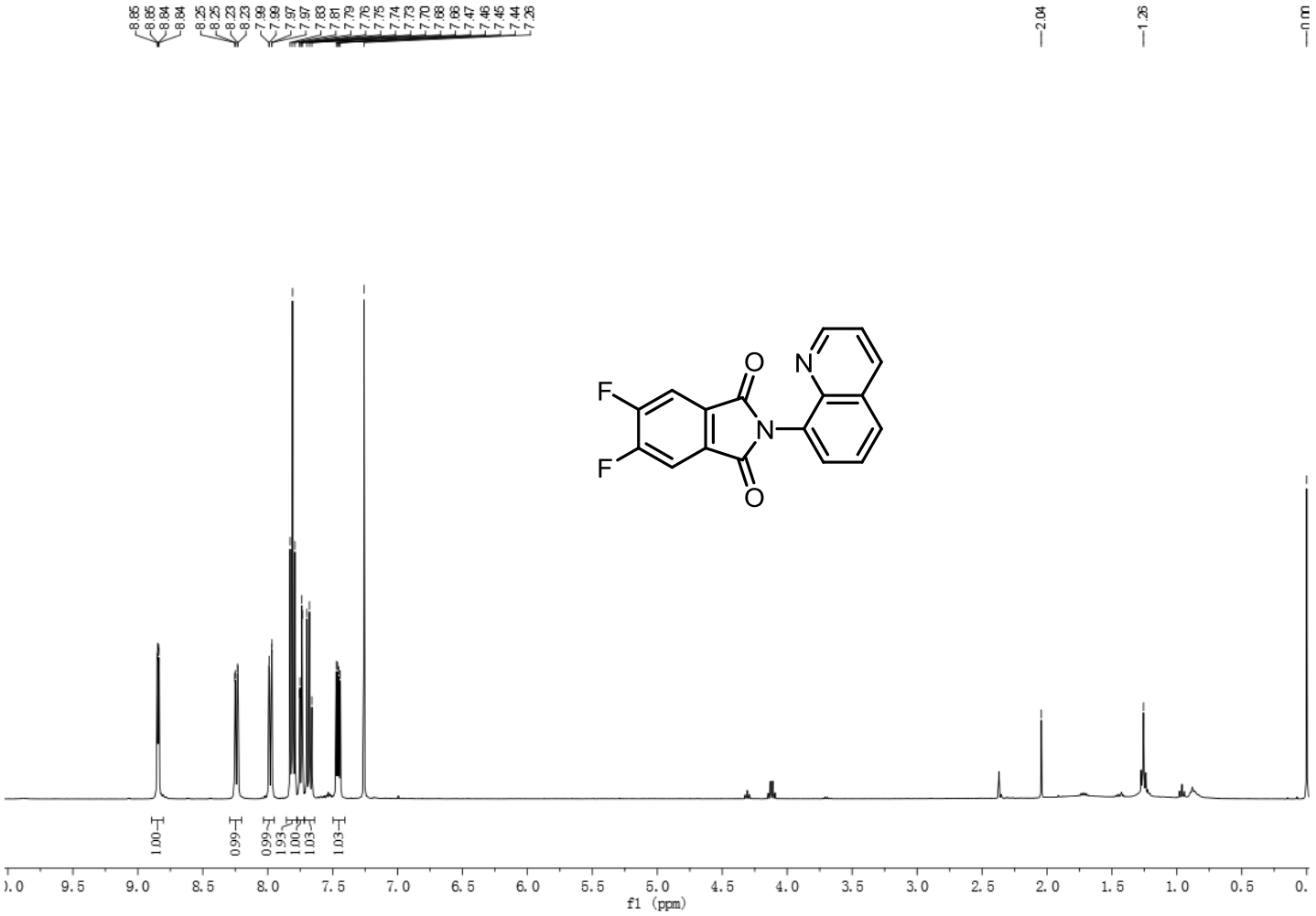
8. Copy of NMR (^{1}H, ^{13}C, ^{19}F) Spectra

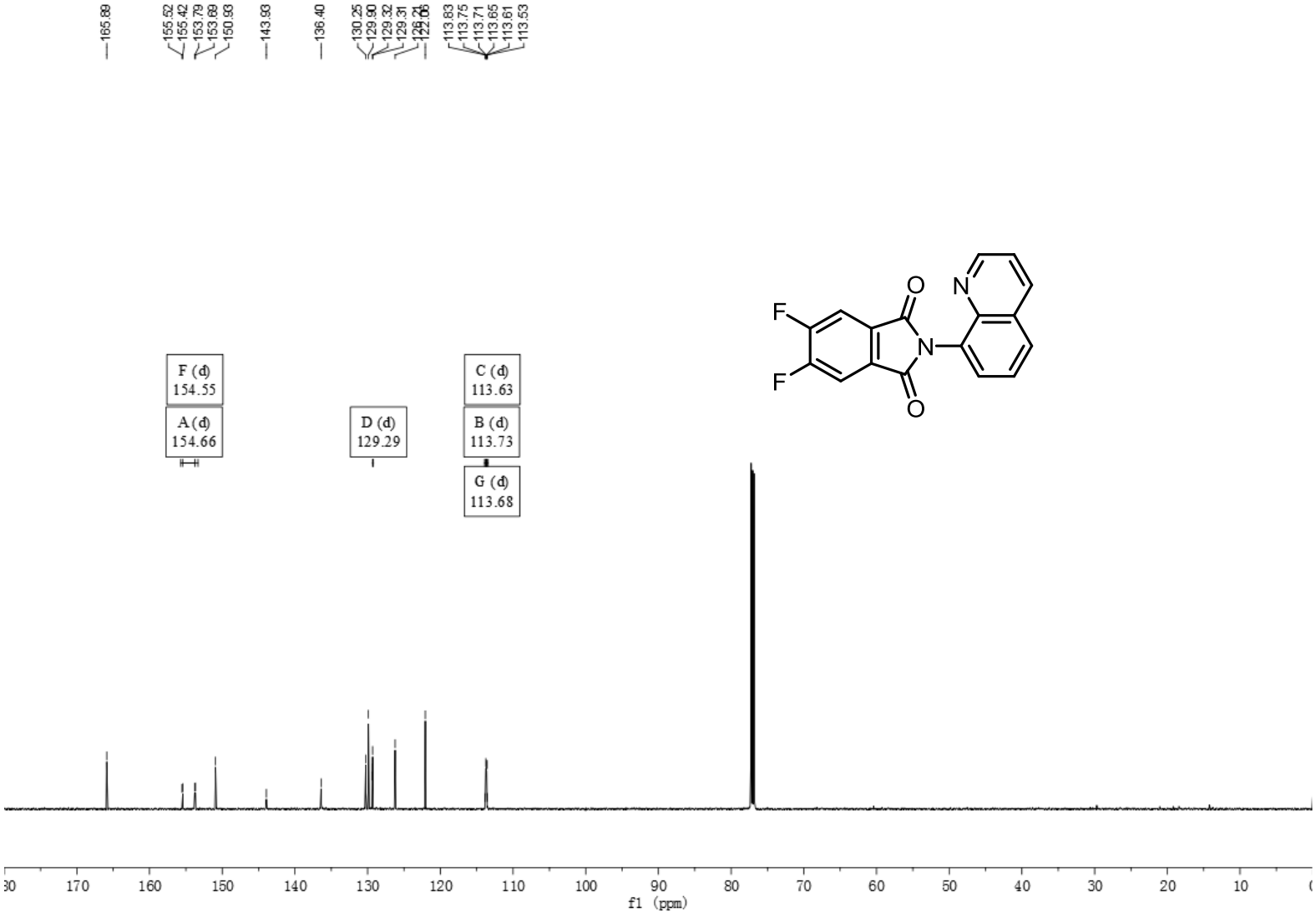
Phthalimides **1d**



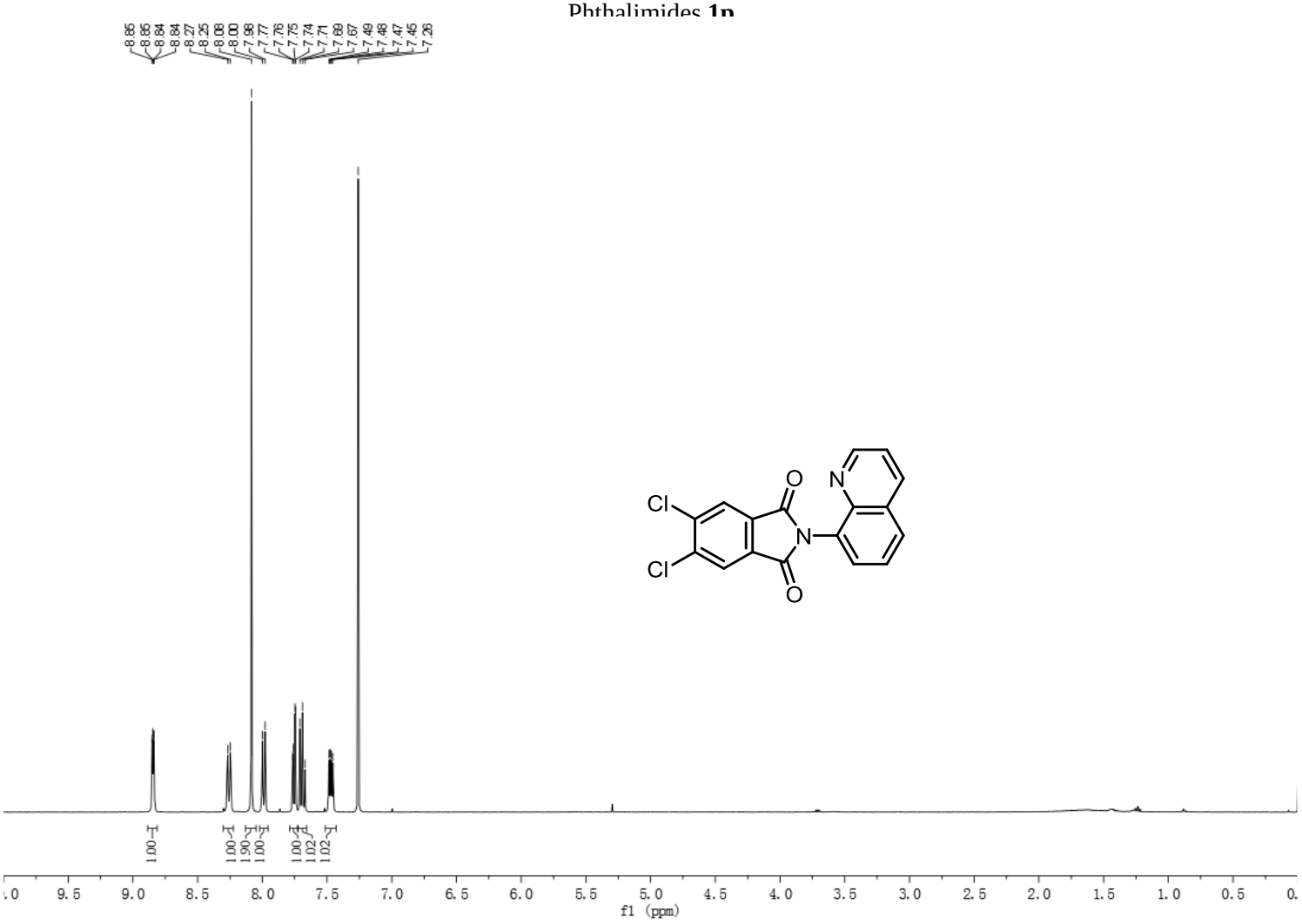

SXJ(1)
XJ-4
CDCL3
168.44
168.05
158.84
150.91
144.36
136.25
132.64
131.25
130.32
129.98
129.80
129.68
129.34
126.20
123.73
121.91
121.15
77.39
77.27
77.07
76.75
35.86
31.24
O
N
O
N
f1 (ppm)

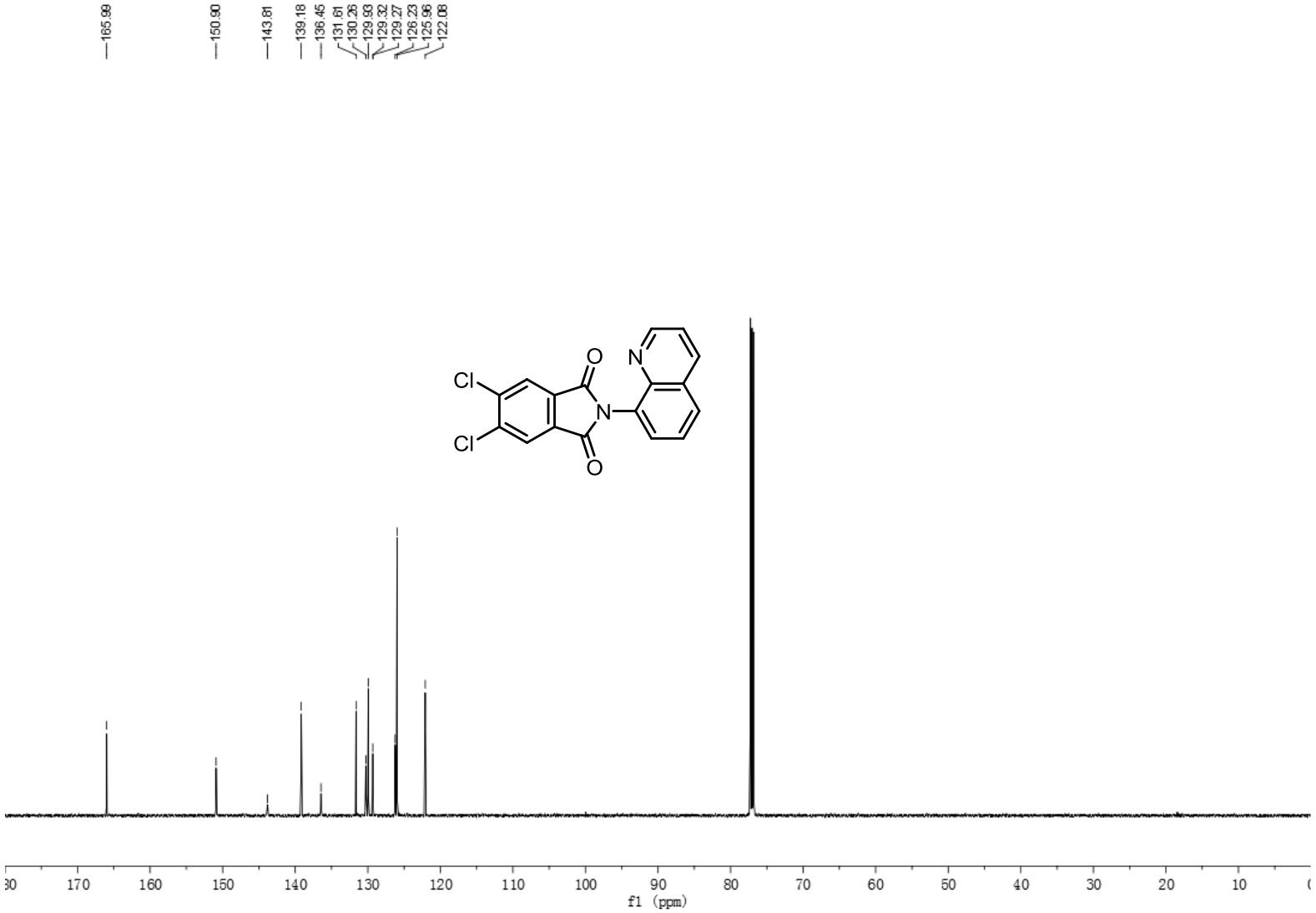
Phthalimides **1o**



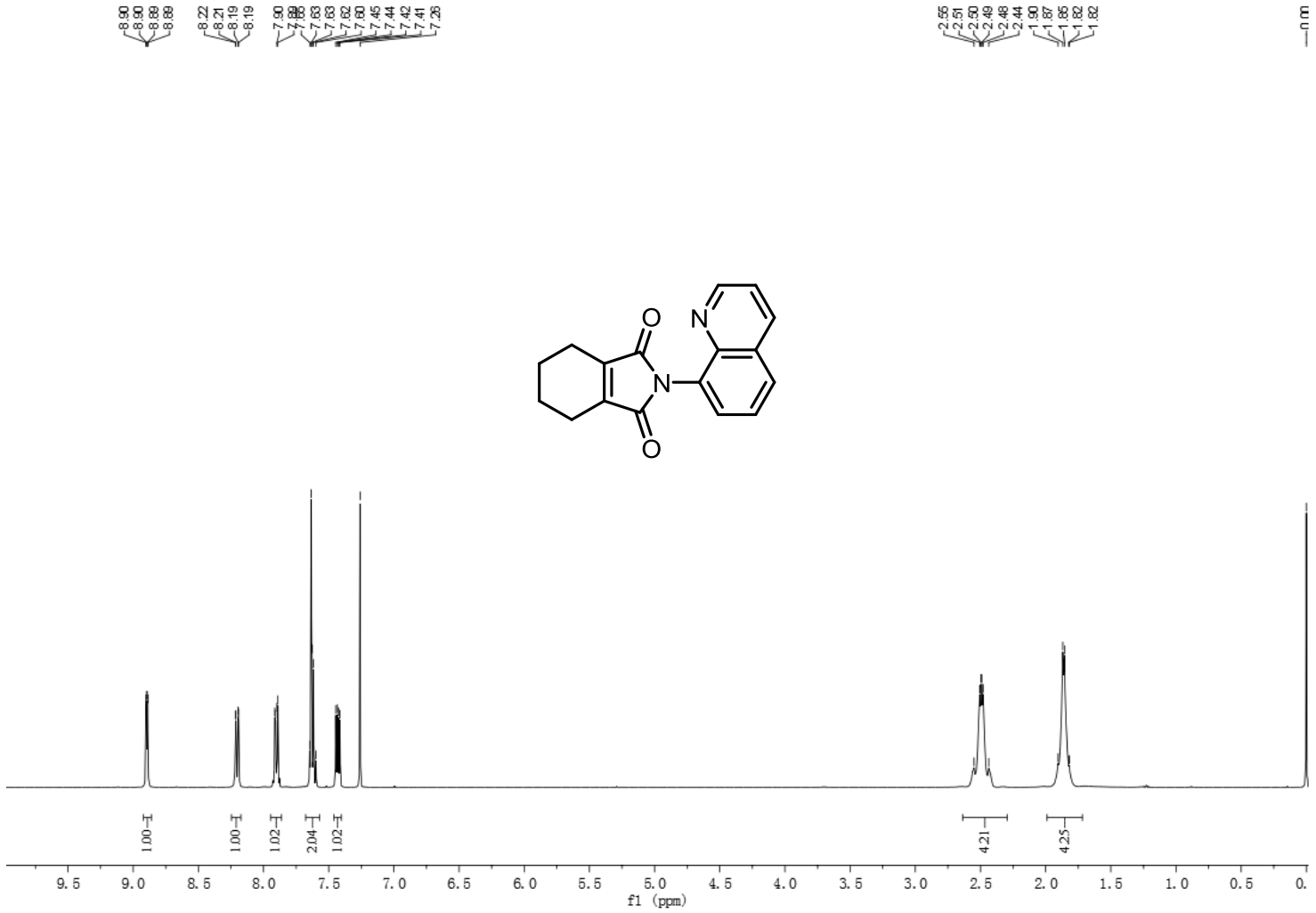

165.89
155.52
155.42
153.79
153.69
150.93
143.93
136.40
130.25
129.90
129.32
129.31
113.83
113.75
113.71
113.65
113.61
113.53
F (d)
154.55
A (d)
154.66
D (d)
129.29
C (d)
113.63
B (d)
113.73
G (d)
113.68
O
N
F
F
O
N
f1 (ppm)

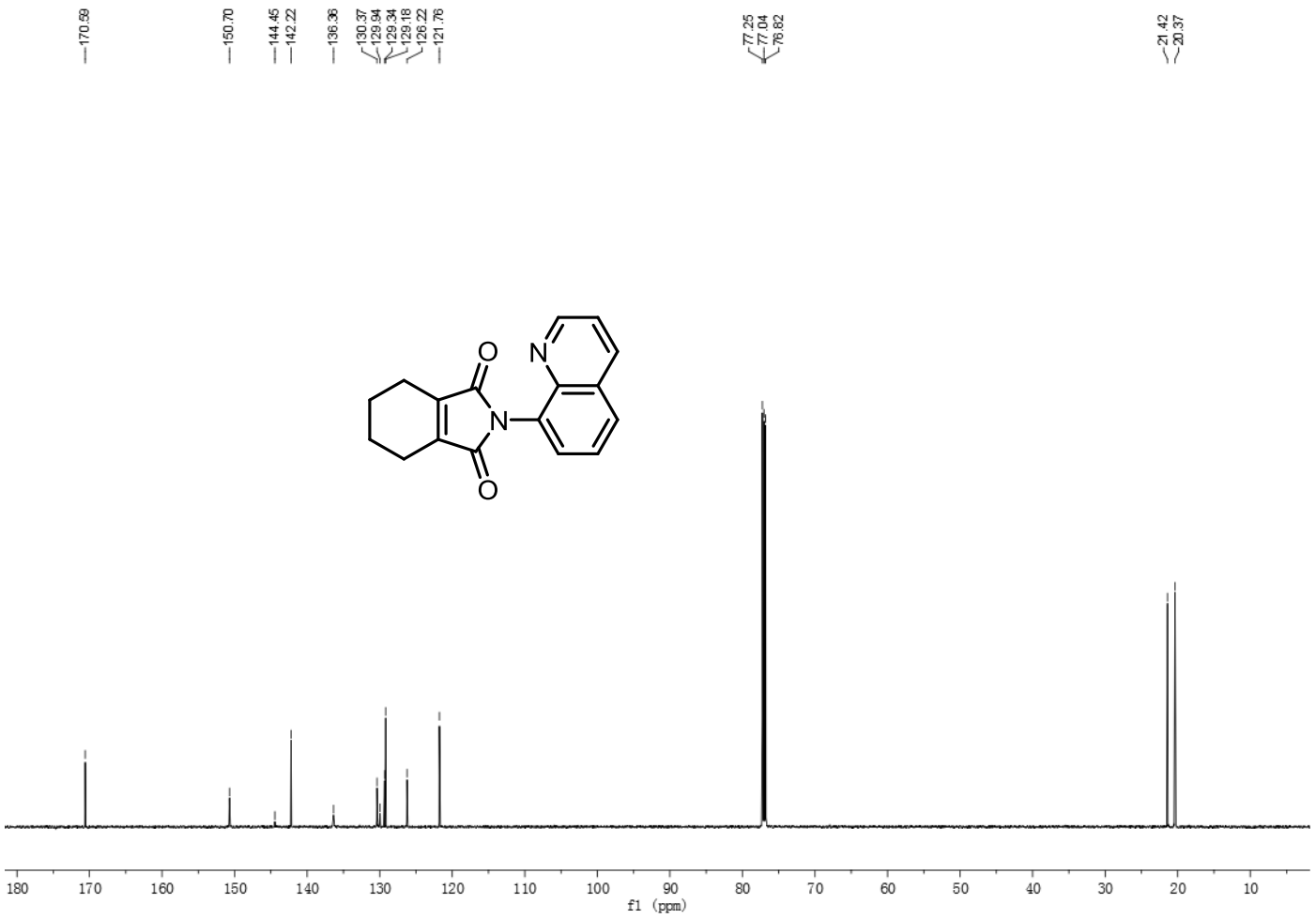
Phthalimides **1p**



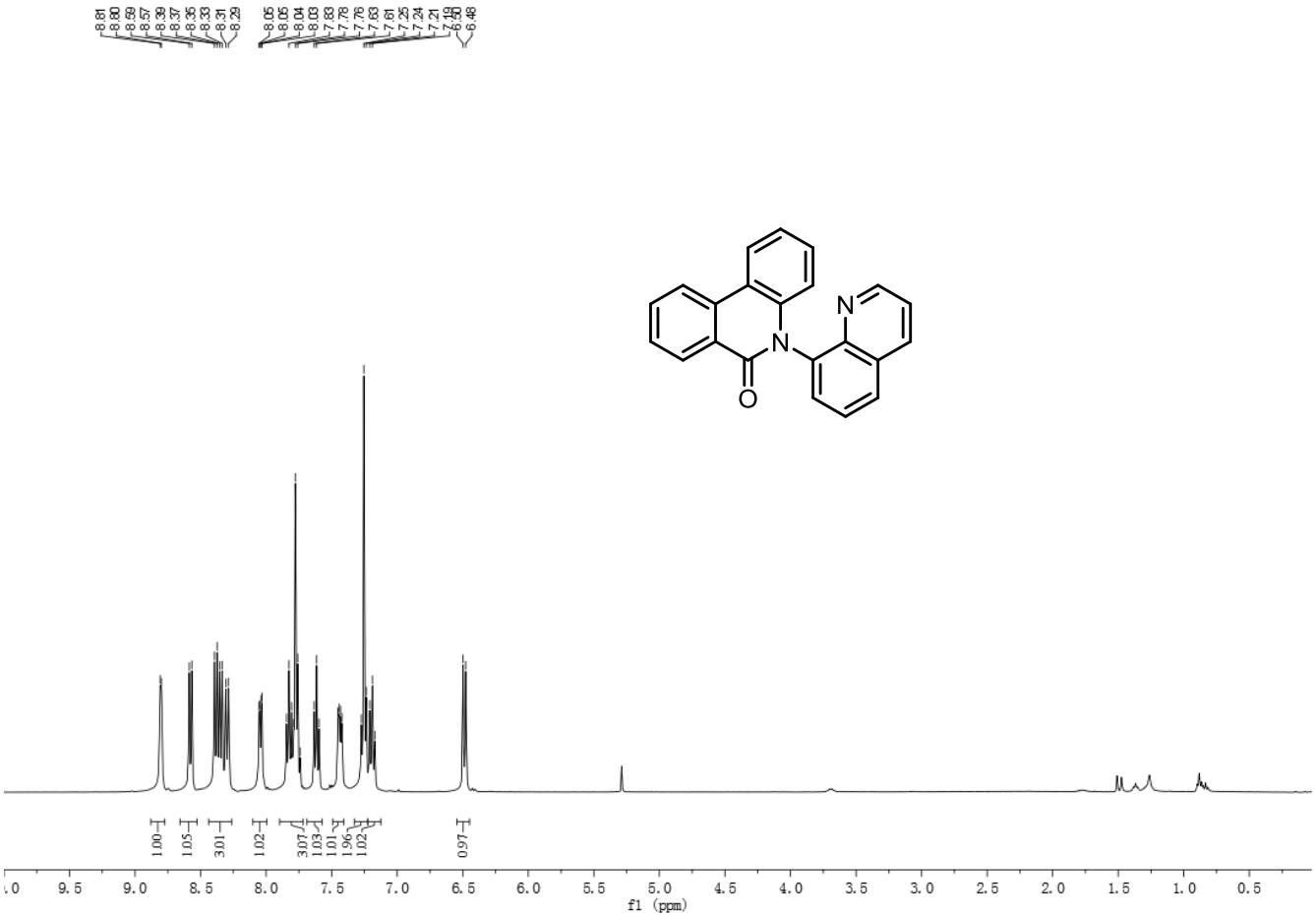

165.99
150.90
143.81
139.18
136.45
131.61
130.26
129.93
129.32
129.27
126.23
125.96
122.08
Cl
Cl
O
O
N
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

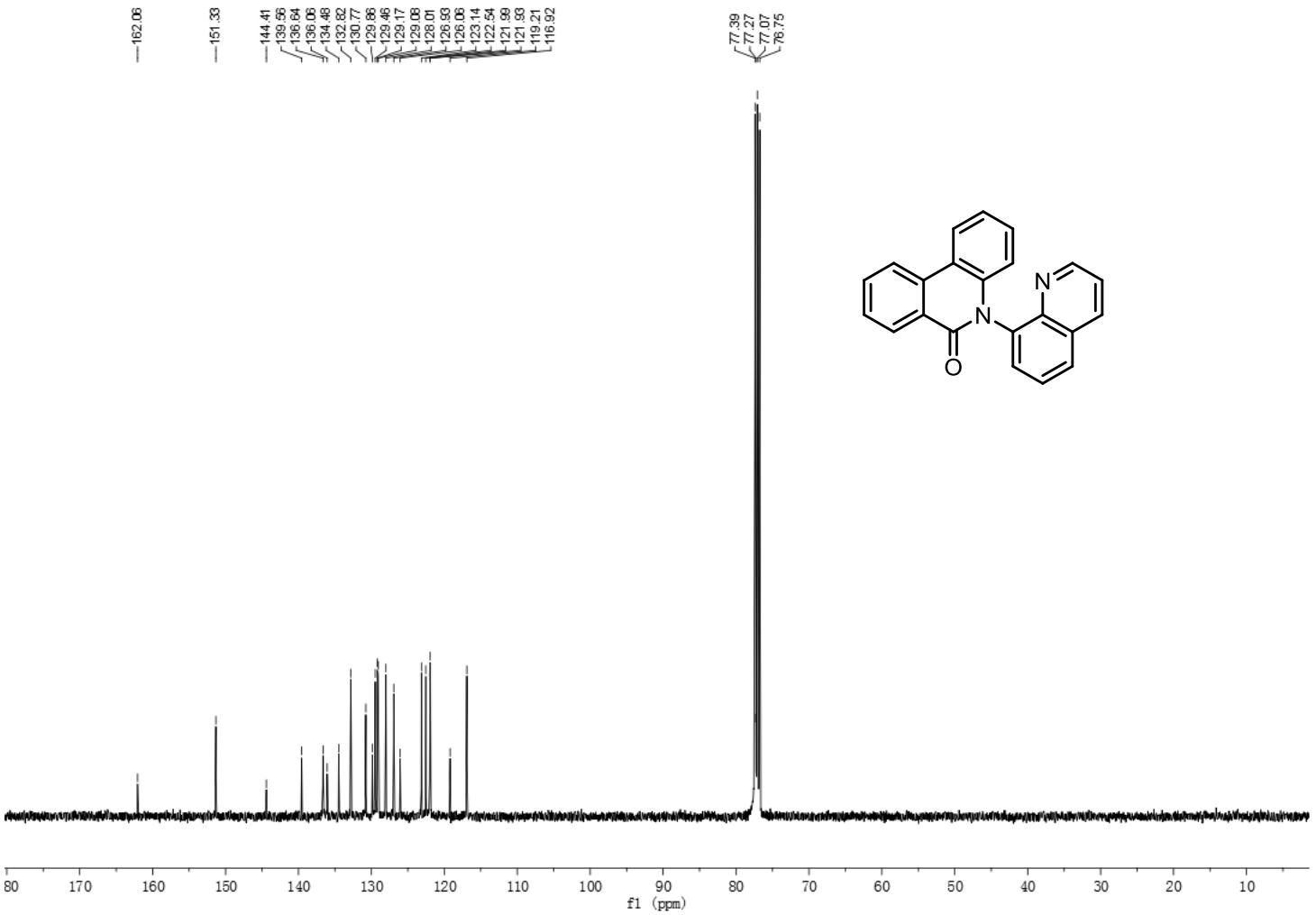
Phthalimides **5a**



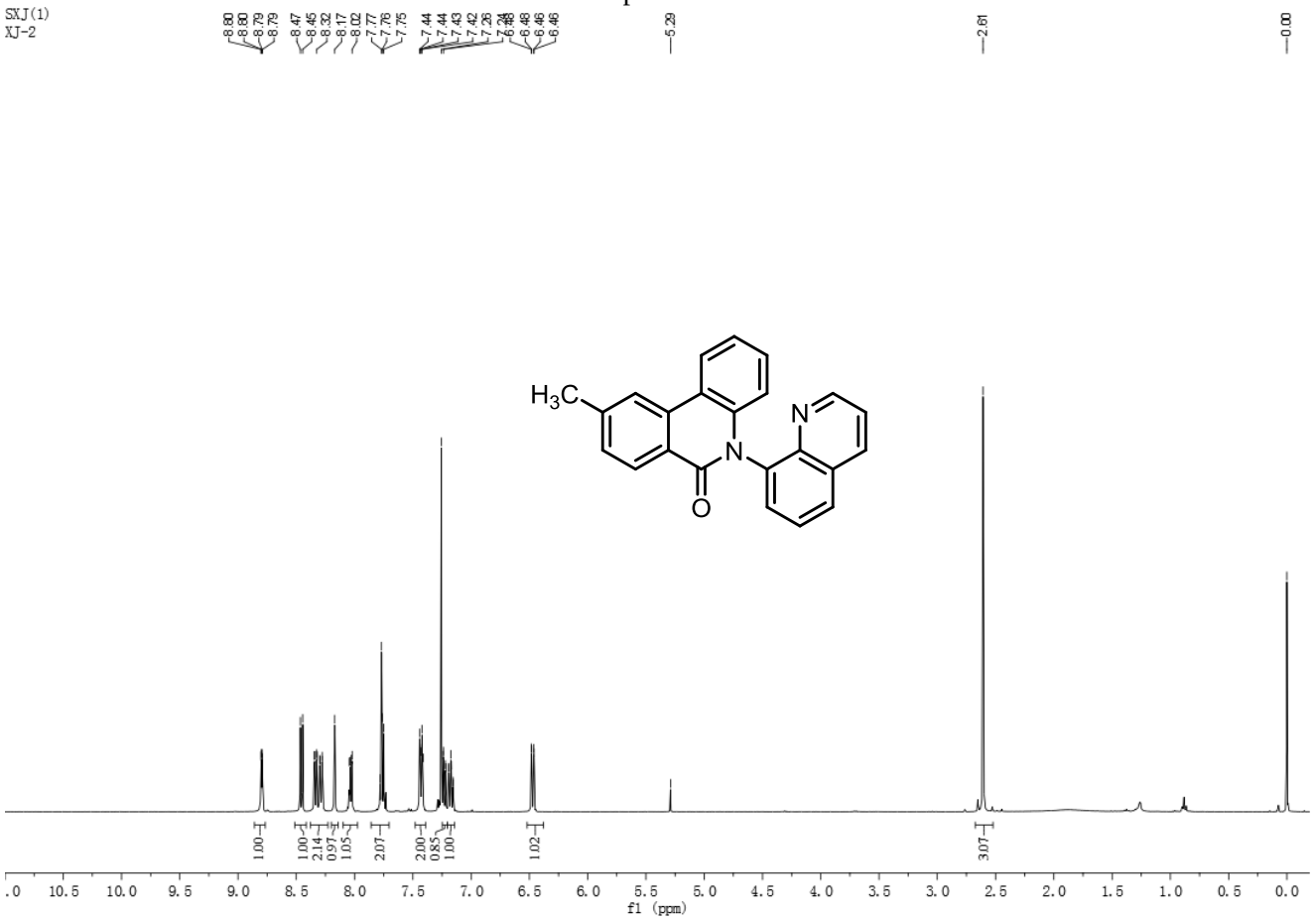

170.59
150.70
144.45
142.22
136.36
130.37
129.94
129.34
129.18
126.22
121.76
77.25
77.04
76.82
21.42
20.37
O
N
N
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

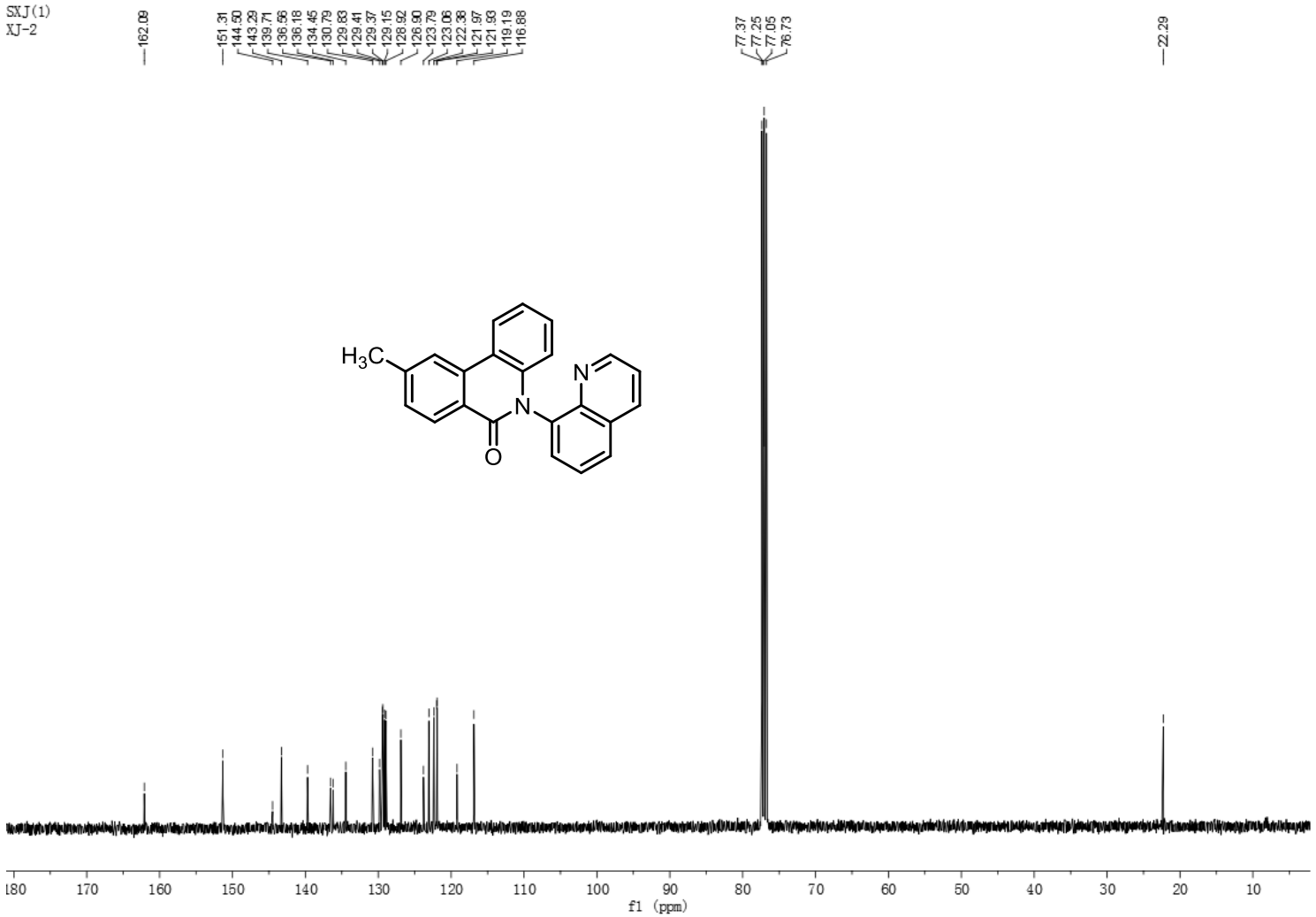
Compound **3aa**



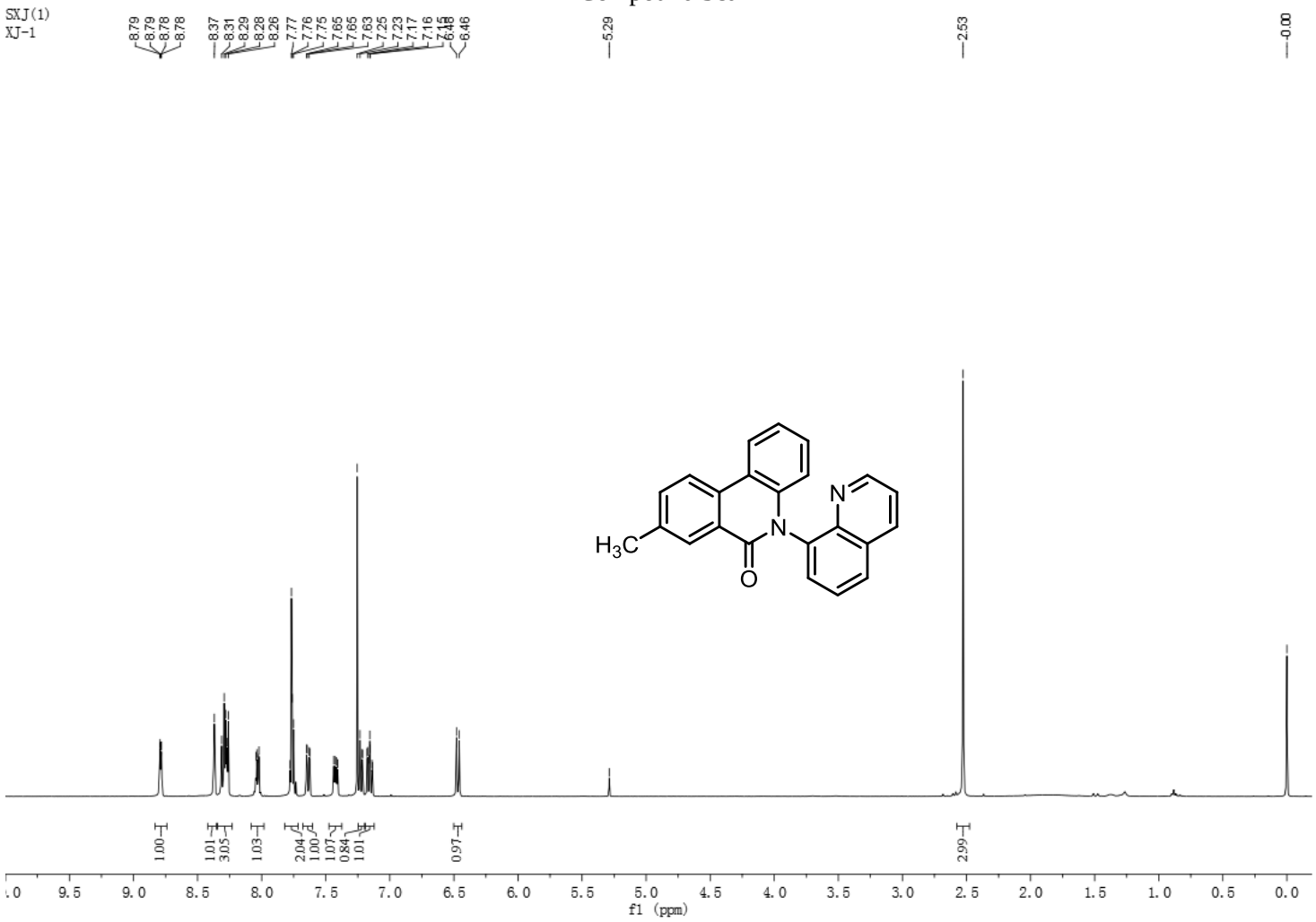

162.06
151.33
144.41
139.56
136.64
136.06
134.48
132.82
130.77
129.86
129.46
129.17
129.08
128.01
126.93
126.06
123.14
122.54
121.99
121.93
119.21
116.92
77.39
77.27
77.07
76.75
N
N
O
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

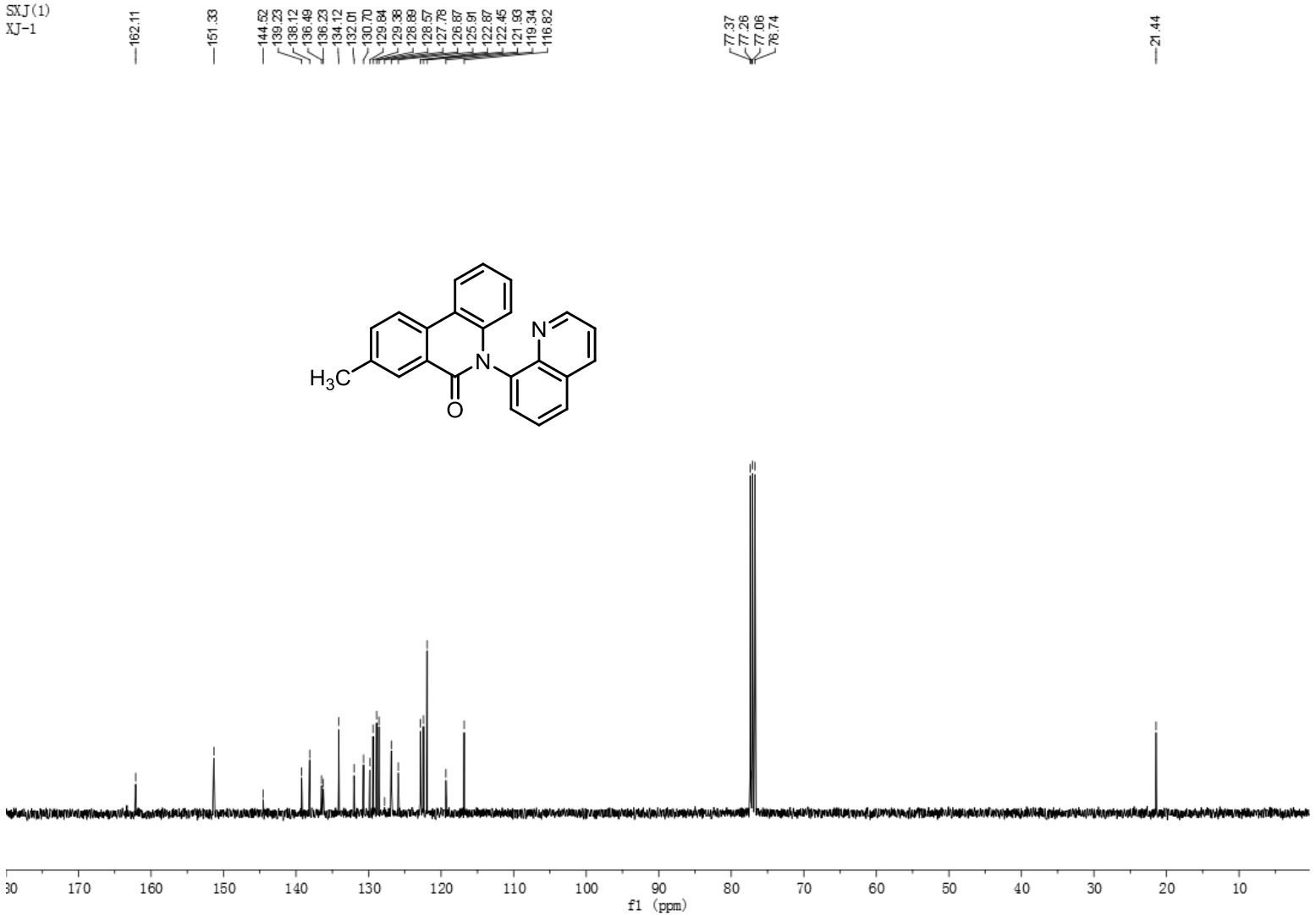
Compound **3ba**



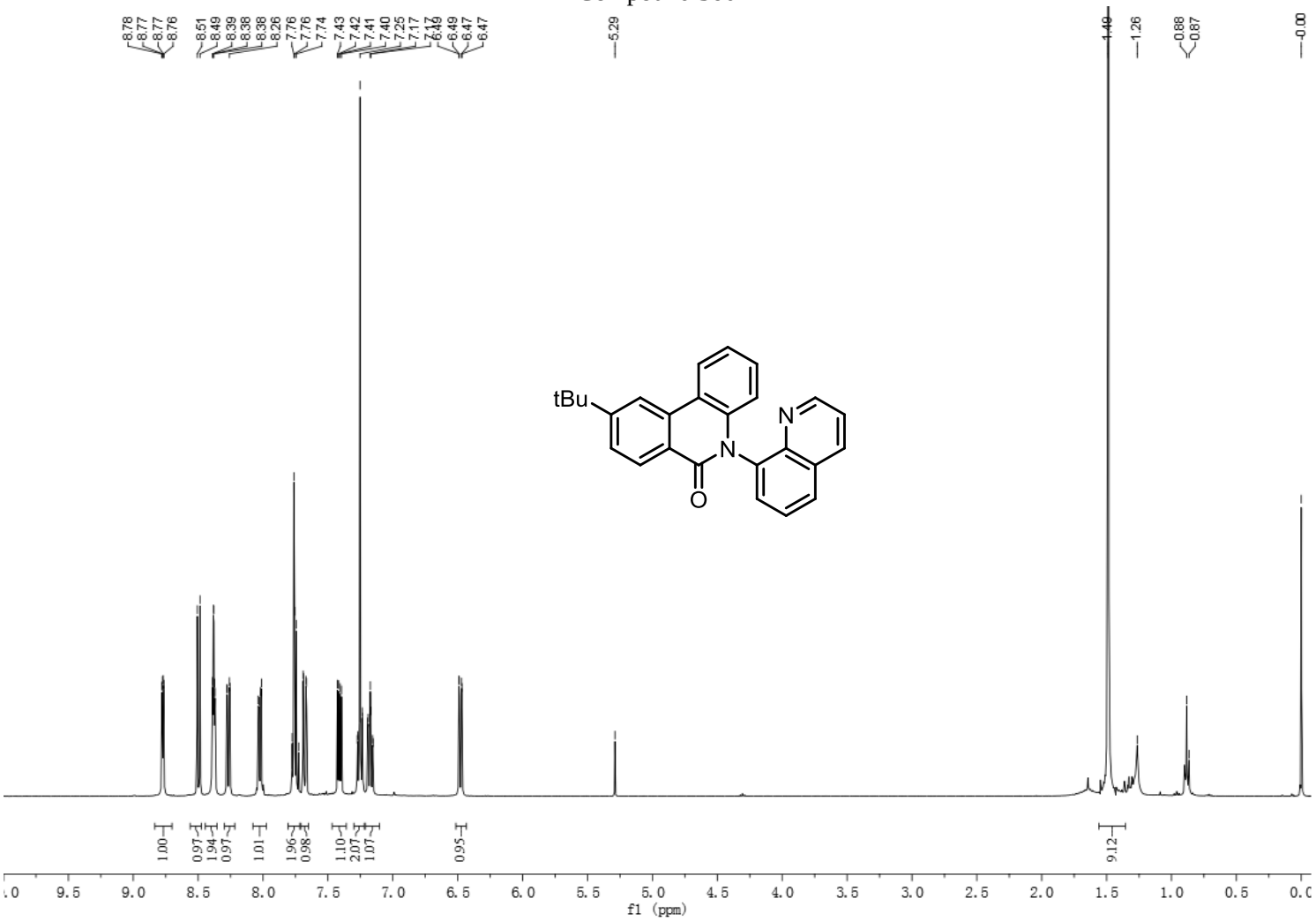

SXJ(1)
XJ-2
162.09
151.31
144.50
143.29
139.71
136.66
136.18
134.45
130.79
129.83
129.41
129.37
129.15
128.92
126.90
123.79
123.06
122.38
121.97
121.93
119.19
116.88
77.37
77.25
77.05
76.73
22.29
H3C
N
N
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

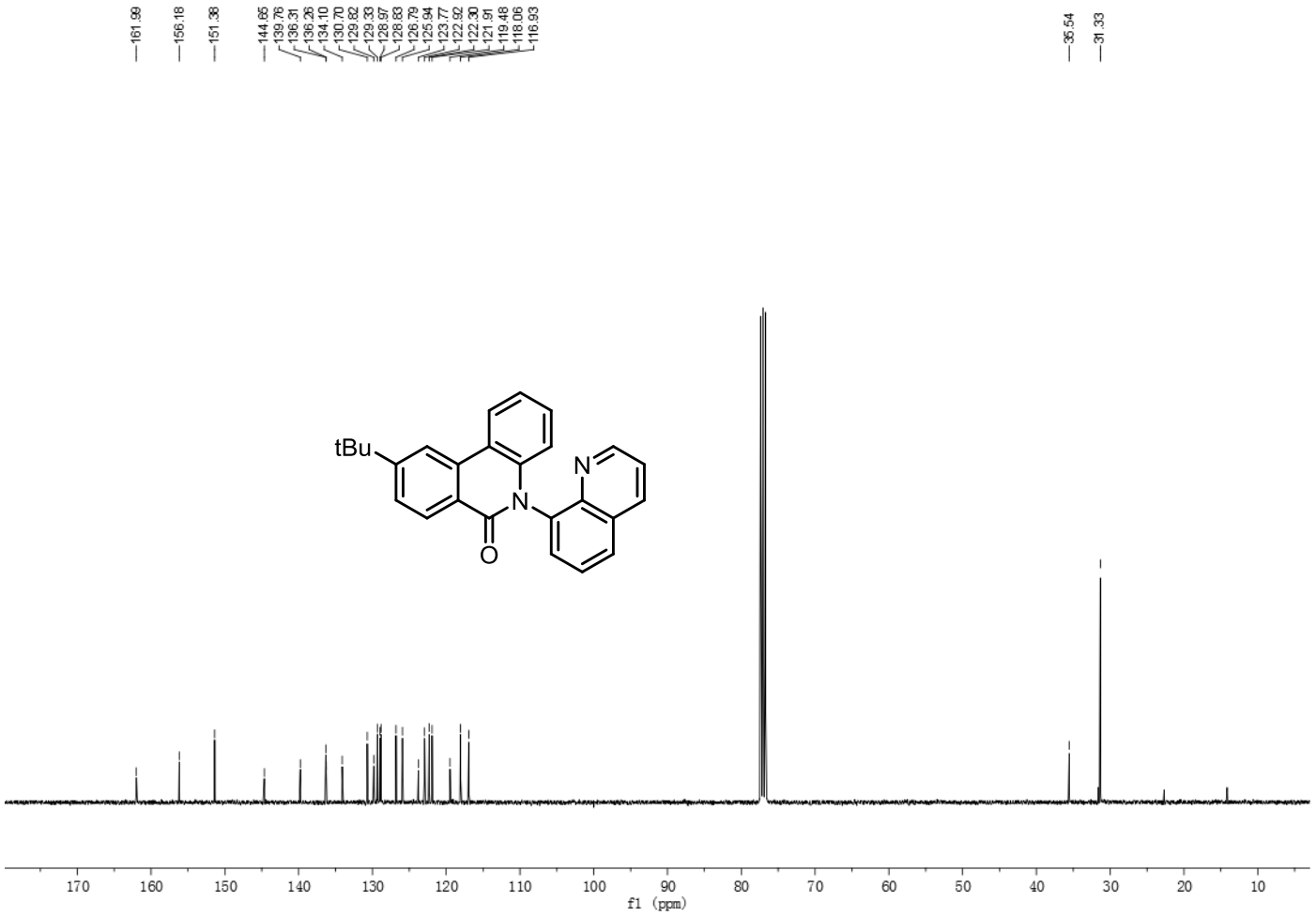
Compound **3ca**



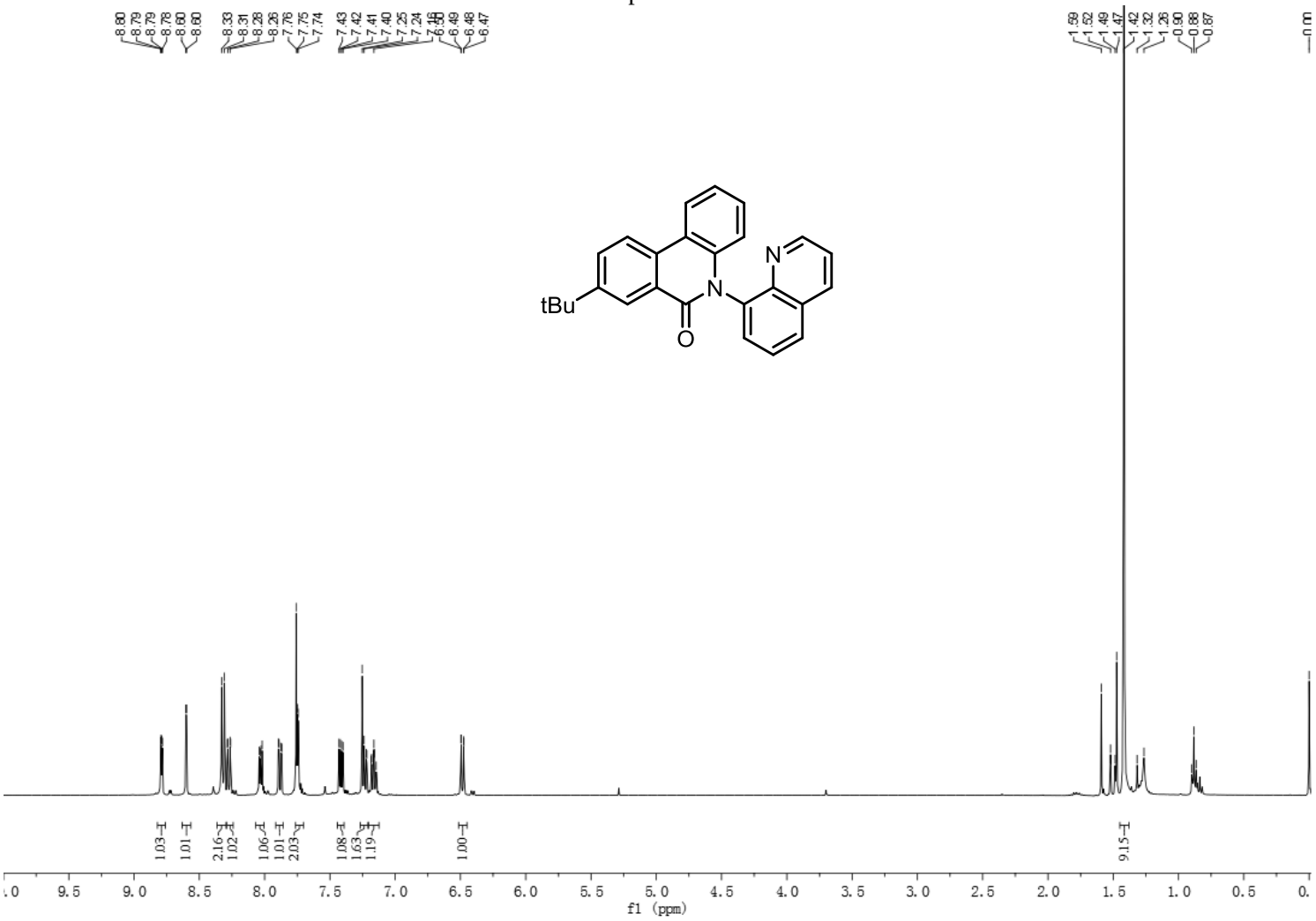

SXJ(1)
XJ-1
162.11
151.33
144.52
139.23
138.12
136.49
136.23
134.12
132.01
130.70
129.84
129.38
128.89
128.57
127.78
126.87
125.91
122.87
122.45
121.93
119.34
116.82
77.37
77.26
77.06
76.74
21.44
H3C
N
N
O
f1 (ppm)

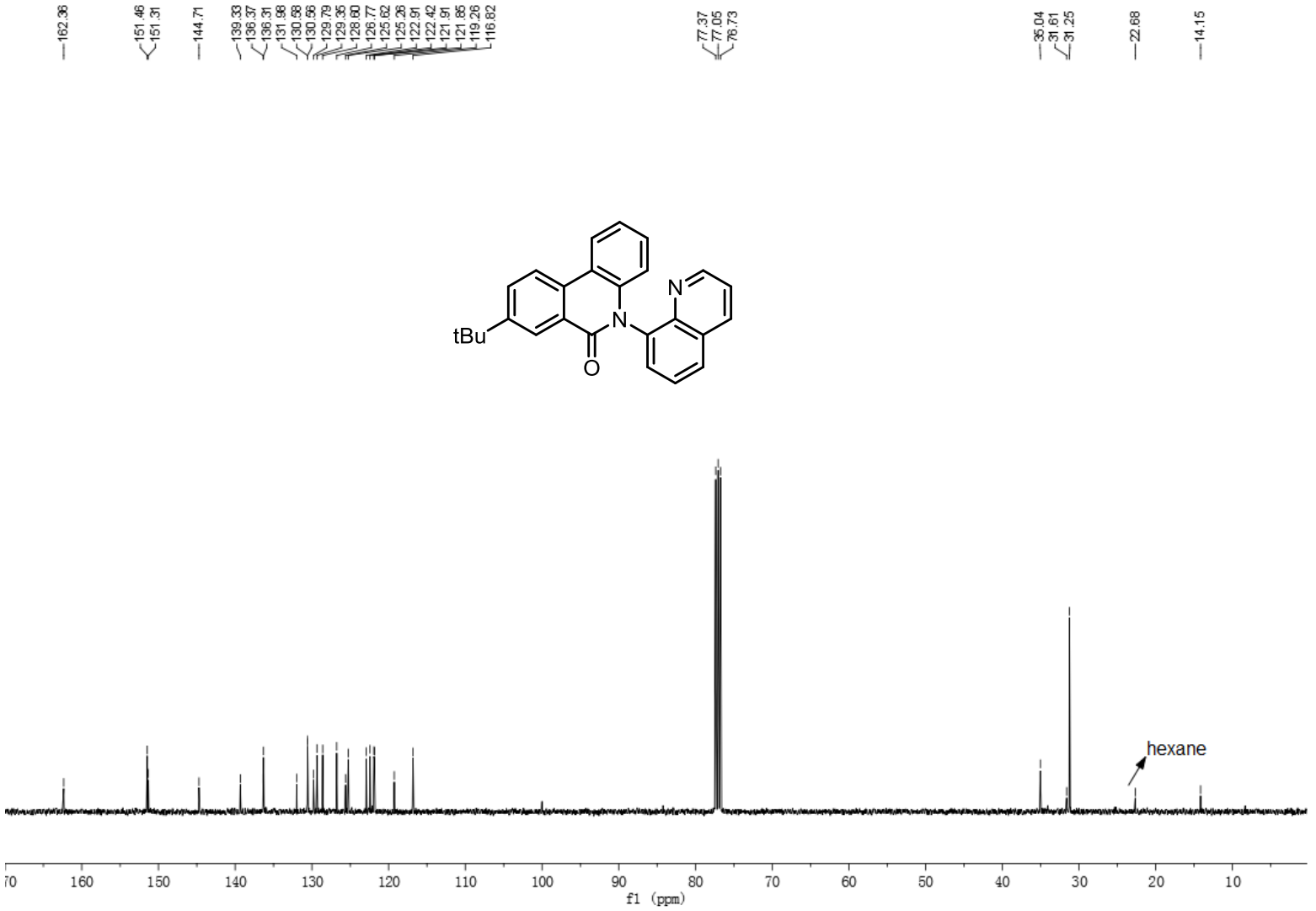
Compound **3da**



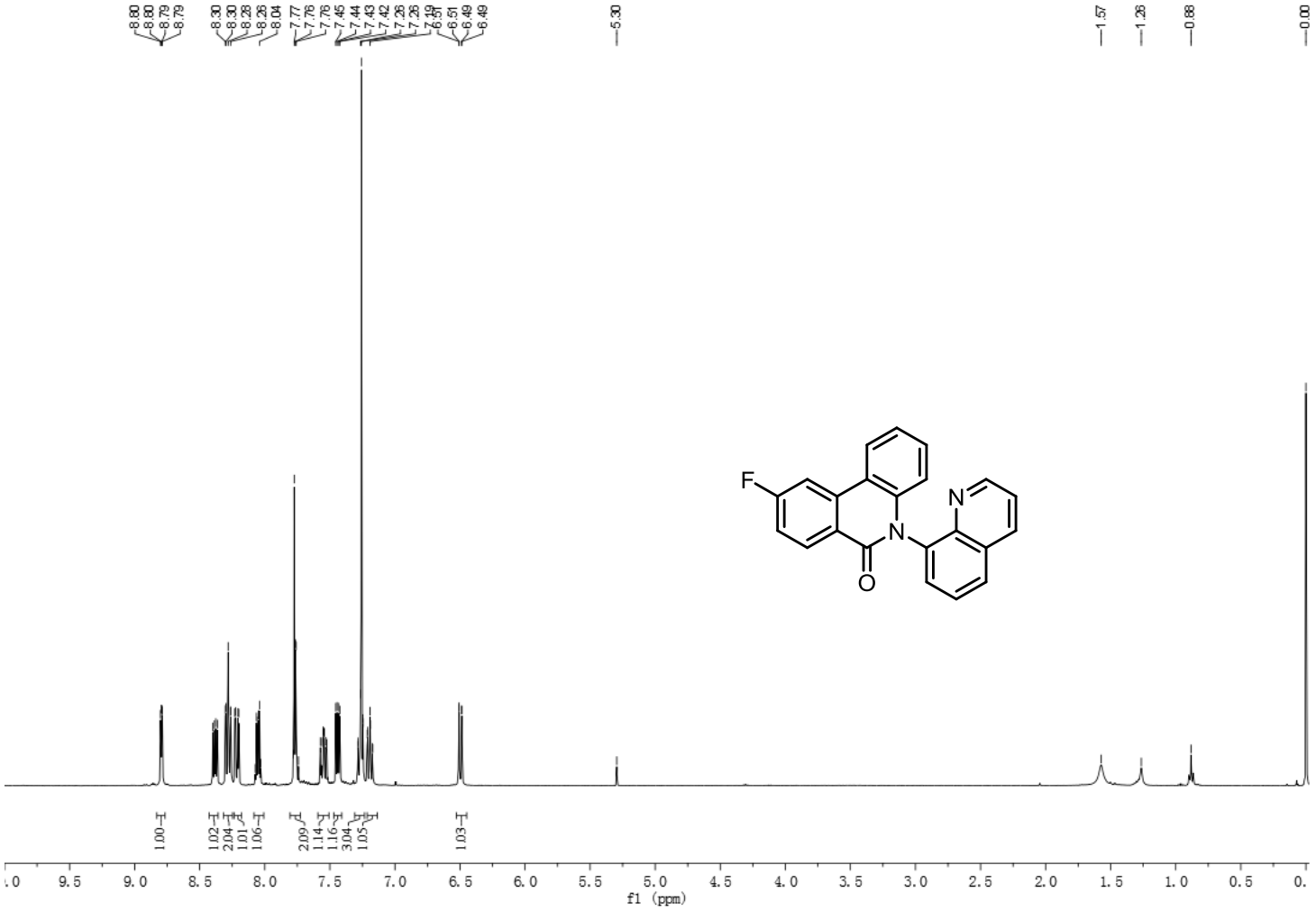

161.99
156.18
151.38
144.65
139.76
136.31
136.26
134.10
130.70
129.82
129.33
128.97
128.83
126.79
125.94
123.77
122.92
122.30
121.91
119.48
118.06
116.93
35.54
31.33
tBu
N
N
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

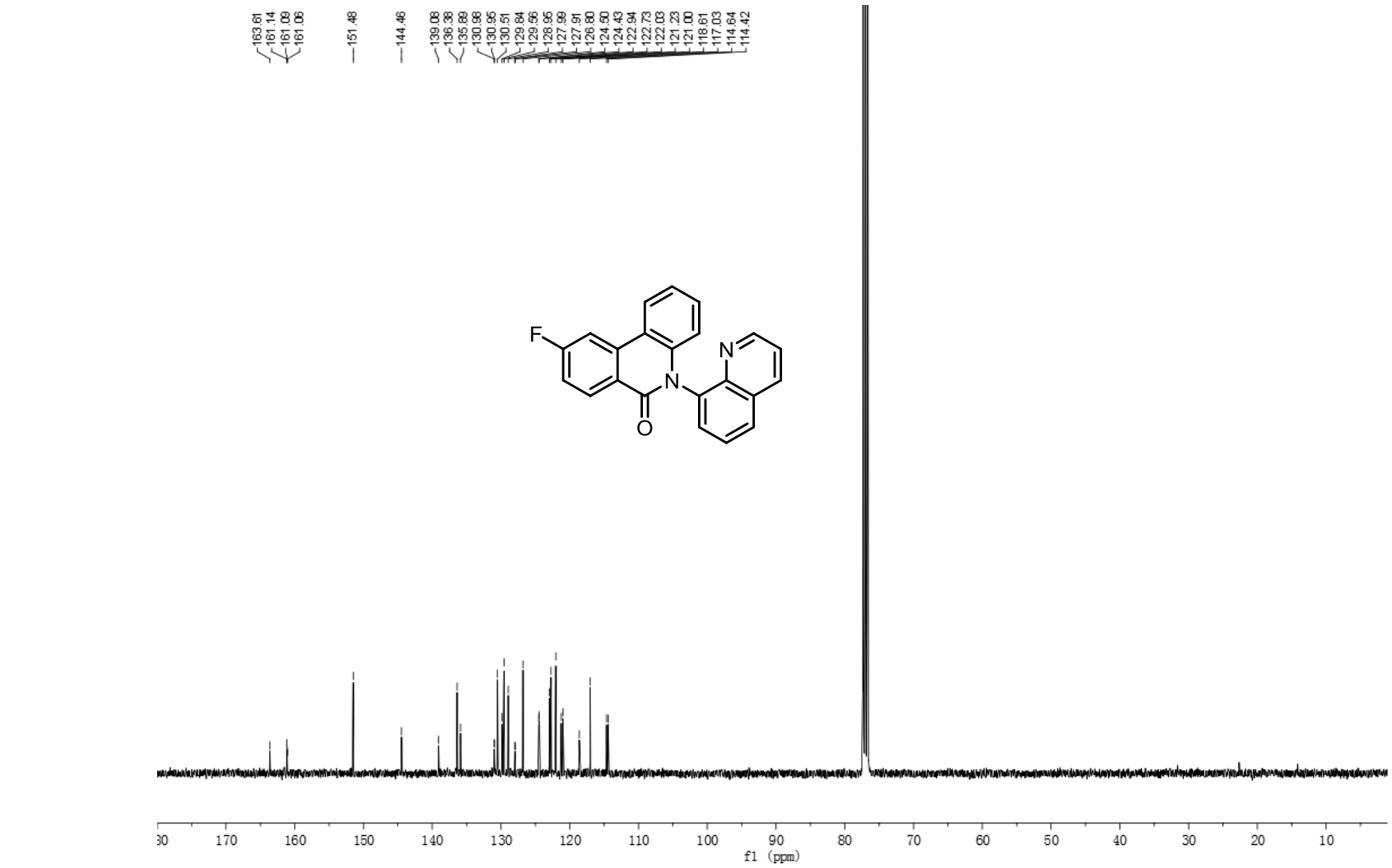
Compound **3ea**

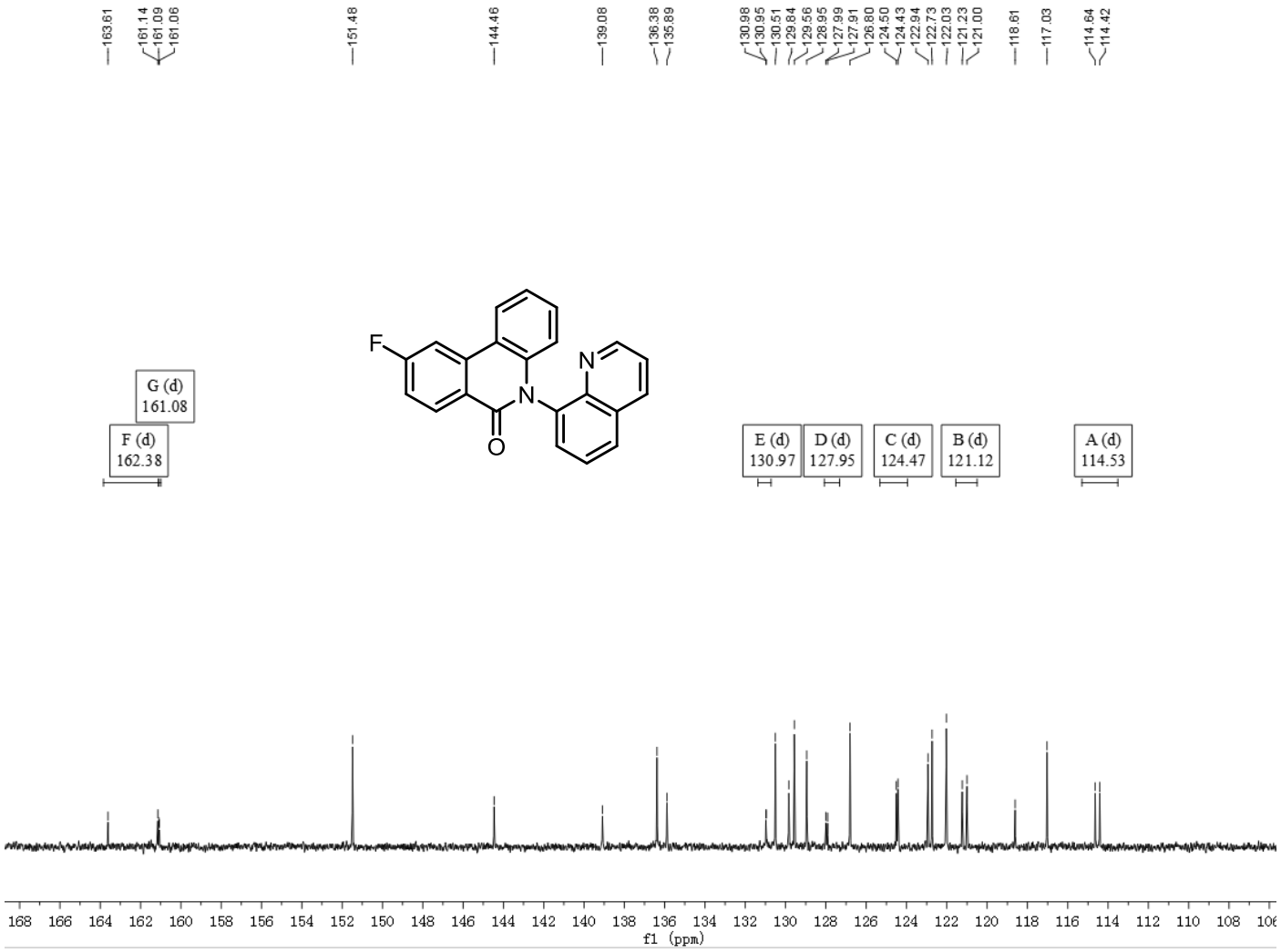


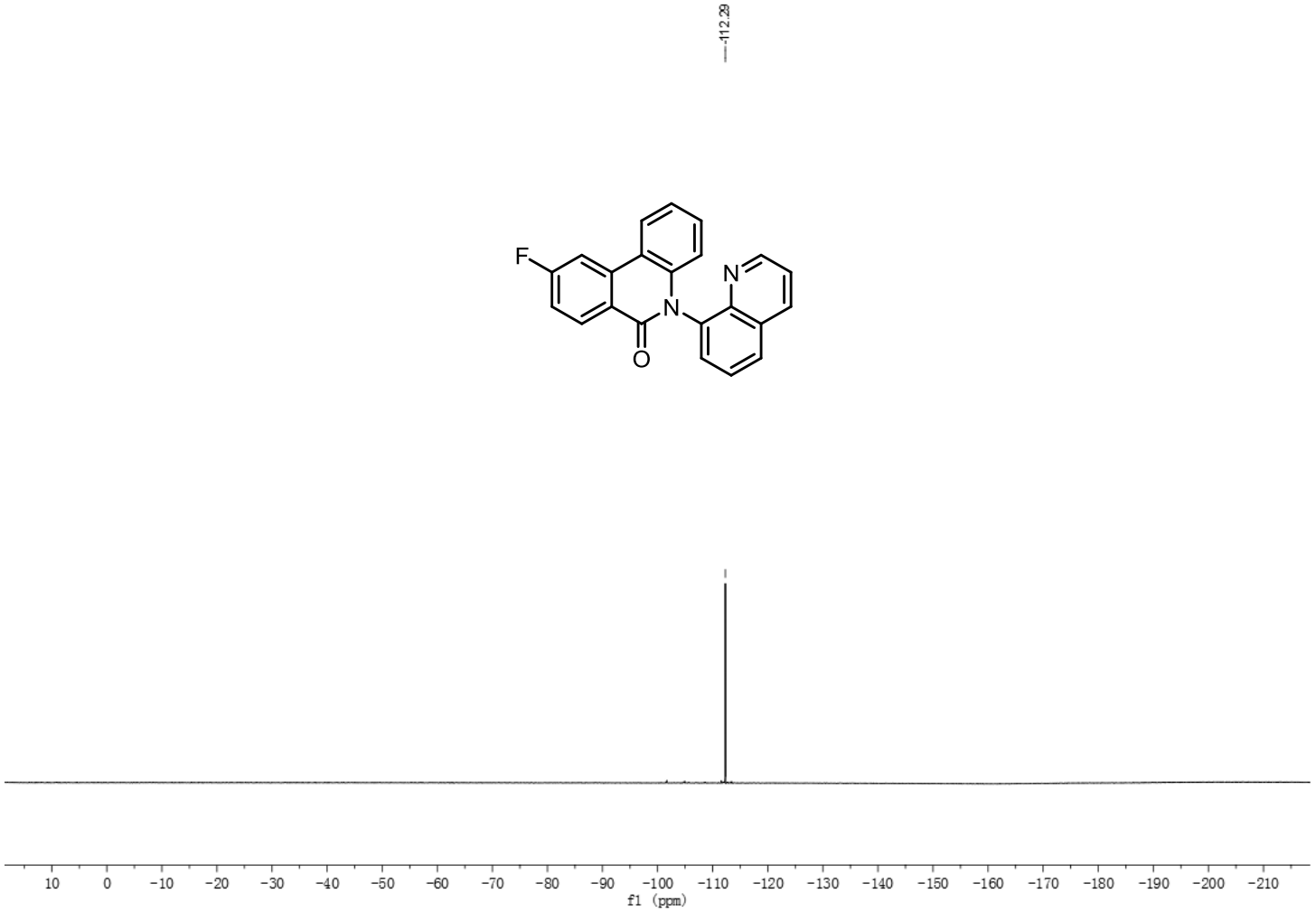

162.36
151.46
151.31
144.71
139.33
136.37
136.31
131.98
130.58
130.56
129.79
129.35
128.60
126.77
125.62
125.26
122.91
122.42
121.91
121.85
119.26
116.82
77.37
77.05
76.73
35.04
31.61
31.25
22.68
14.15
tBu
N
N
O
hexane
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Compound **3fa**

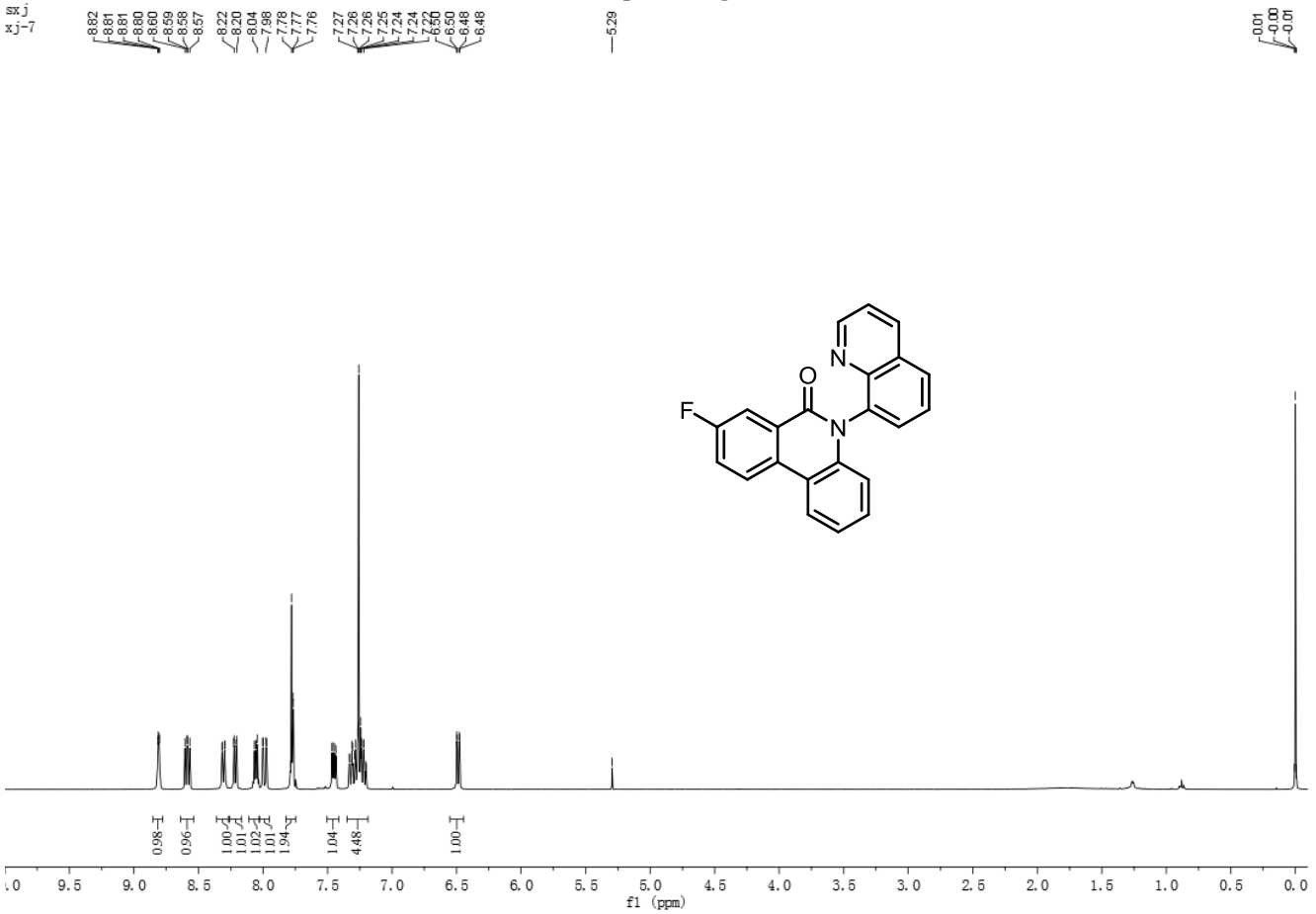


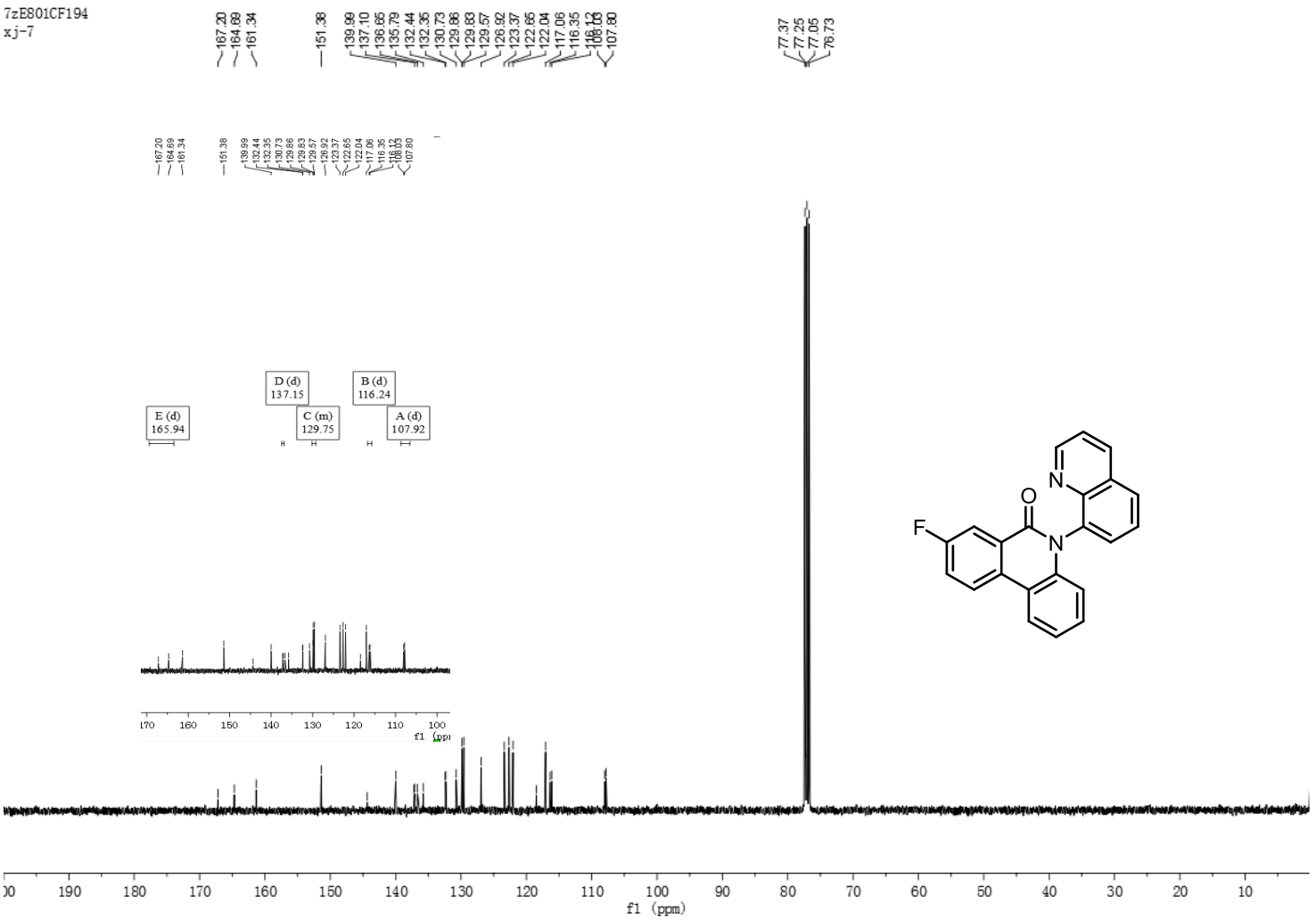

163.61
161.14
161.09
161.06
151.48
144.46
139.08
136.38
135.89
130.98
130.95
130.51
129.84
129.56
128.95
127.99
127.91
126.80
124.50
124.43
122.94
122.73
122.03
121.23
121.00
118.61
117.03
114.64
114.42
F
N
N
O
f1 (ppm)


163.61
161.14
161.09
161.06
151.48
144.46
139.08
136.38
135.89
130.98
130.95
130.51
129.84
129.56
128.95
127.99
127.91
126.80
124.50
124.43
122.94
122.73
122.03
121.23
121.00
118.61
117.03
114.64
114.42
F
N
N
O
G (d)
161.08
F (d)
162.38
E (d)
130.97
D (d)
127.95
C (d)
124.47
B (d)
121.12
A (d)
114.53
168 166 164 162 160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108
f1 (ppm)


-112.29
F
N
N
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

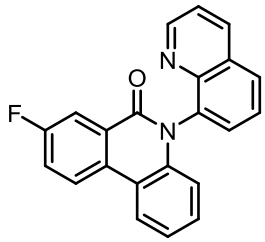
Compound **3ga**

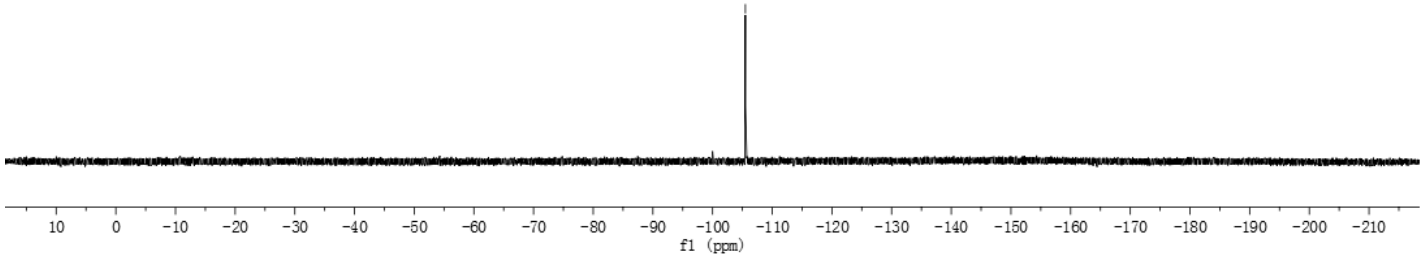



7zE801CF194
xj-7
167.20
164.69
161.34
151.38
139.99
137.10
136.65
135.79
132.44
132.35
130.73
129.86
129.83
129.57
126.92
123.37
122.65
122.04
117.06
116.35
107.80
77.37
77.25
77.05
76.73
E (d)
165.94
D (d)
137.15
C (m)
129.75
B (d)
116.24
A (d)
107.92
F
O
N
N
f1 (ppm)

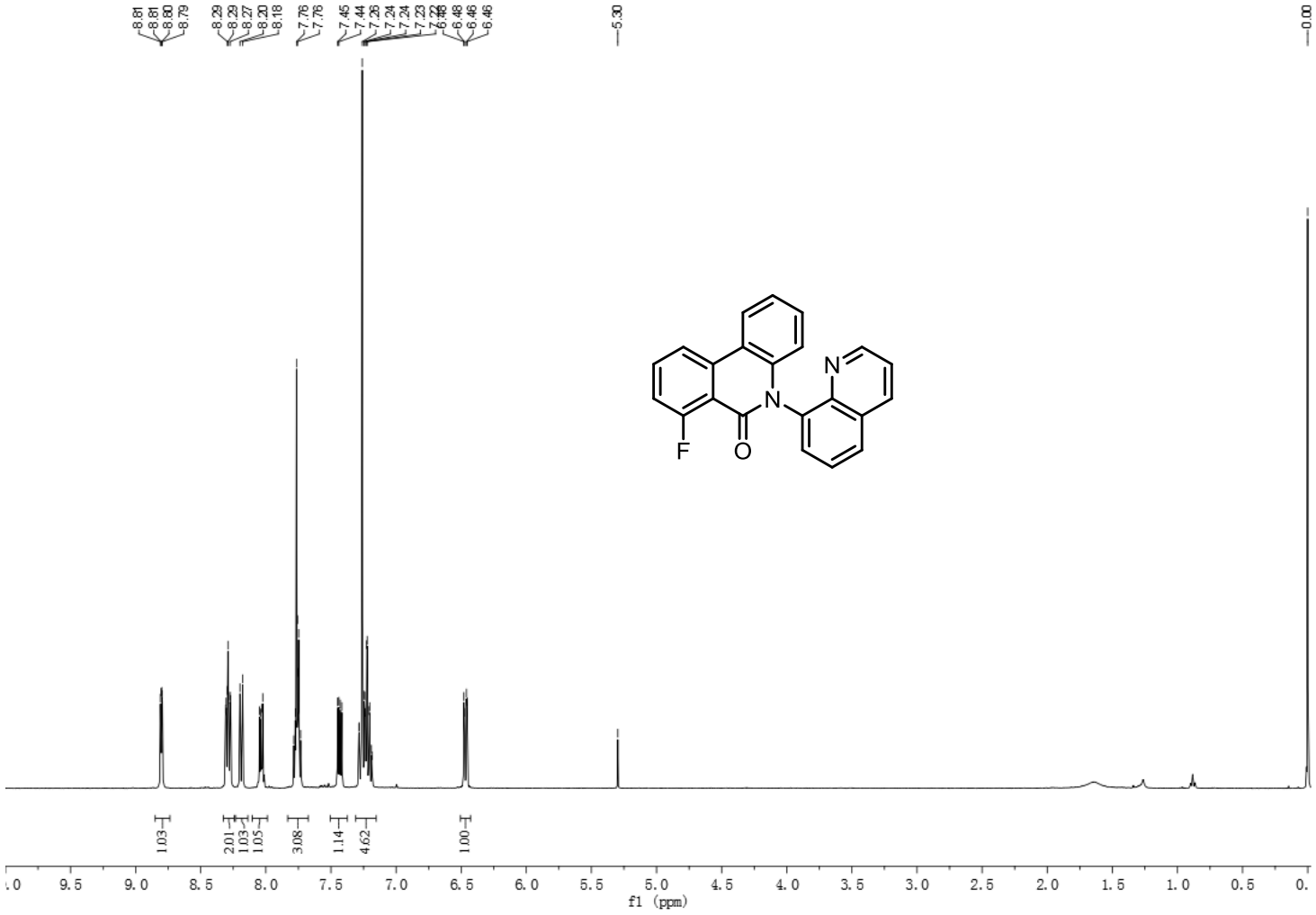
7zE801CF194
xj-7

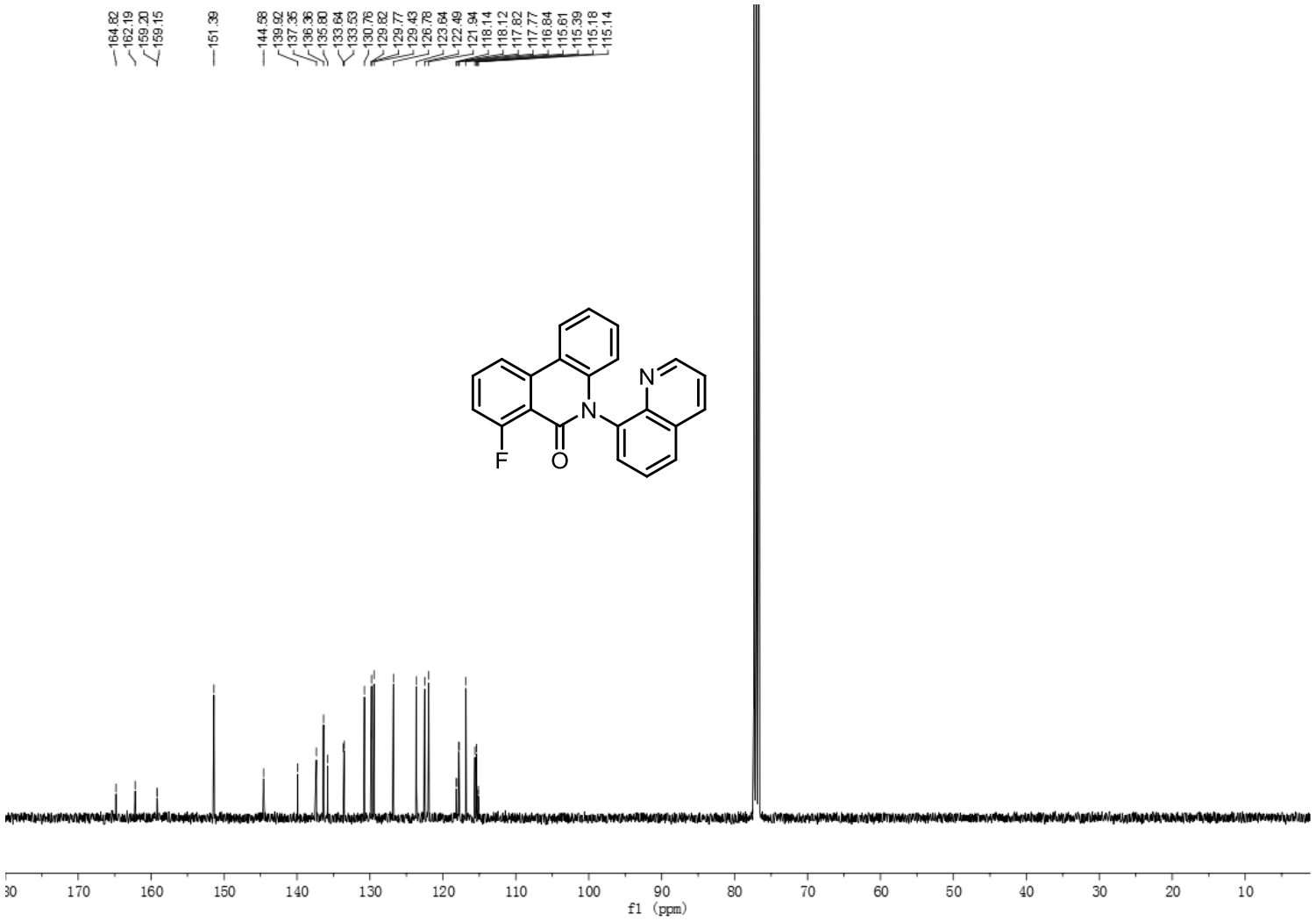
-105.50

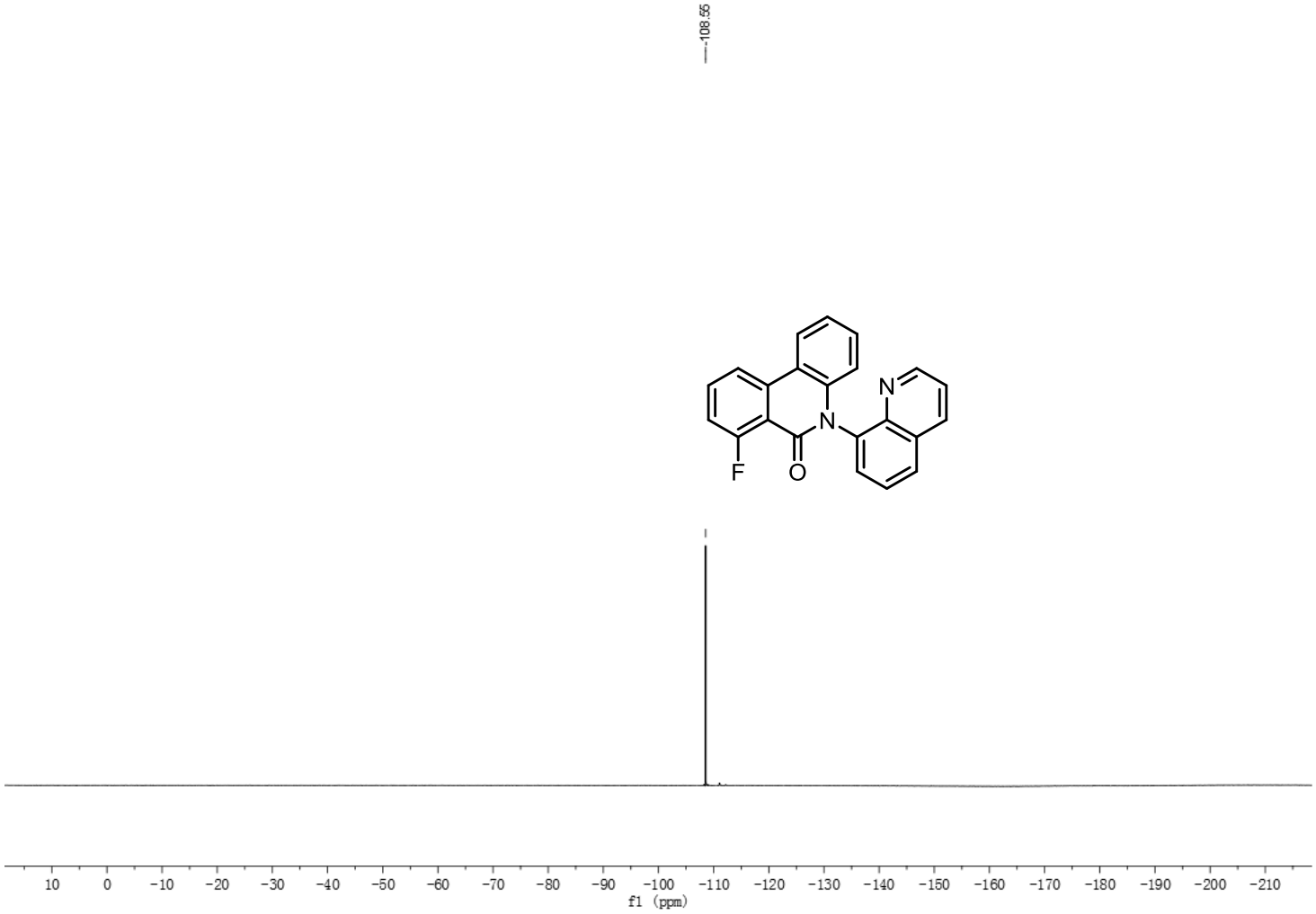




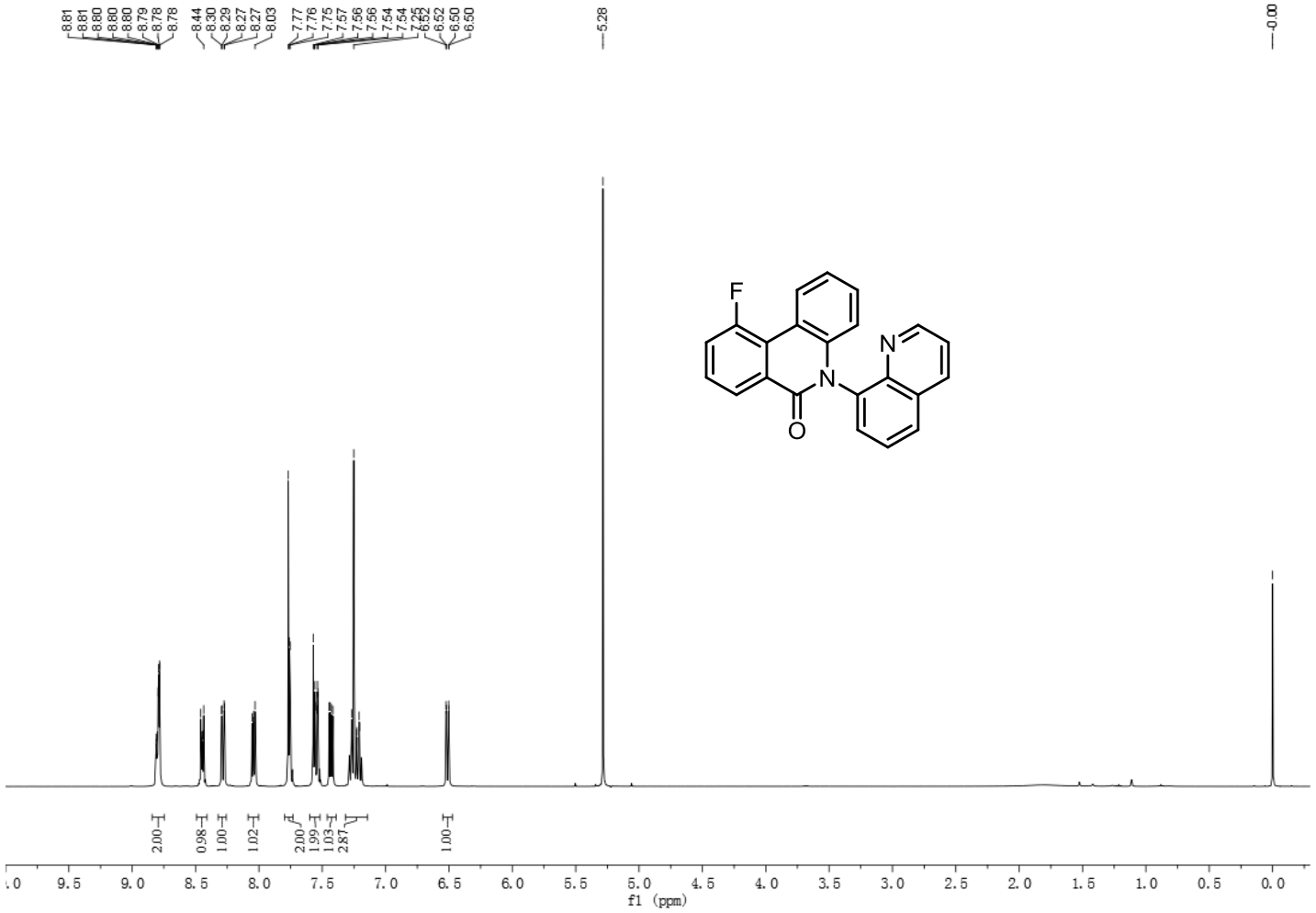
Compound **3ha**

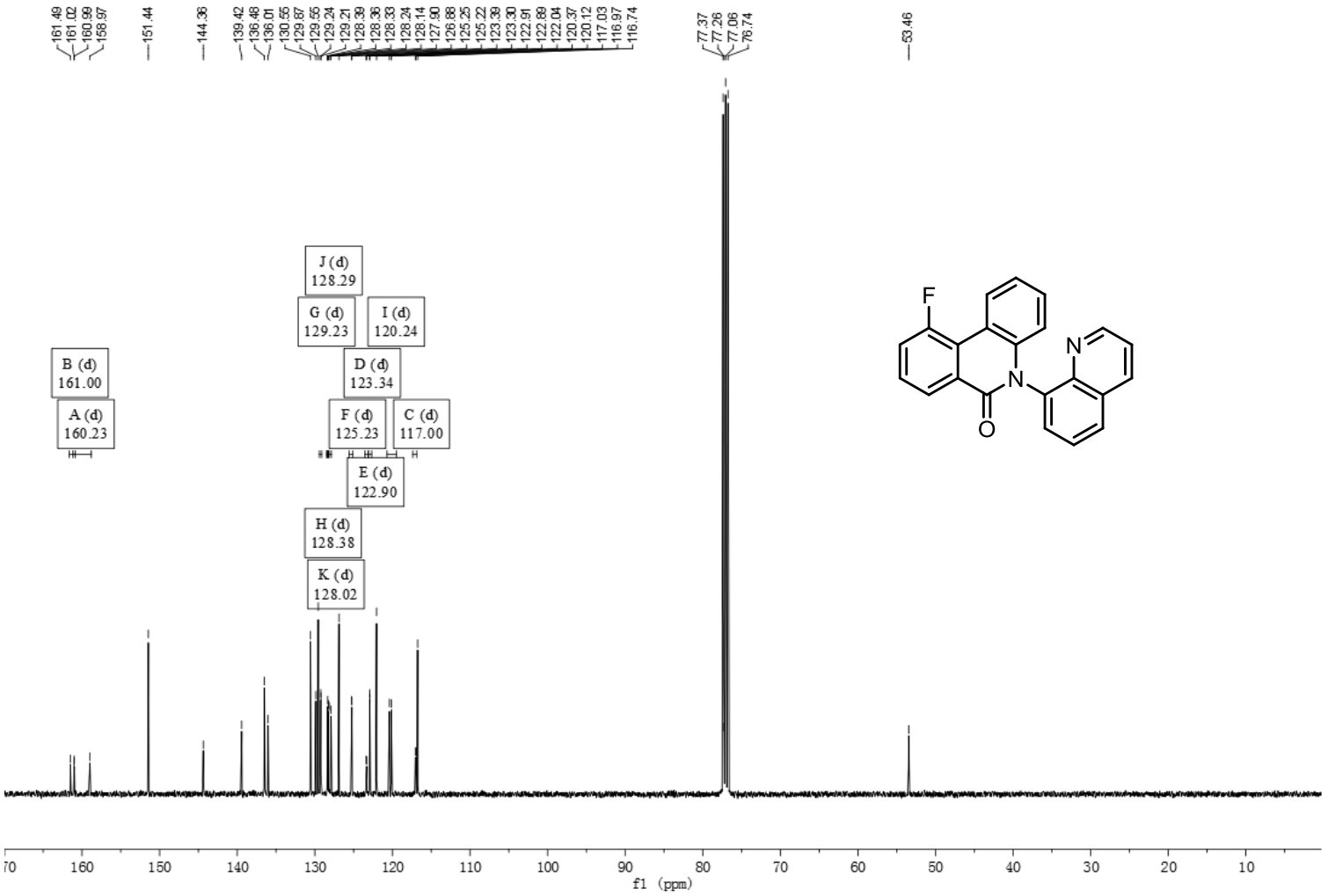


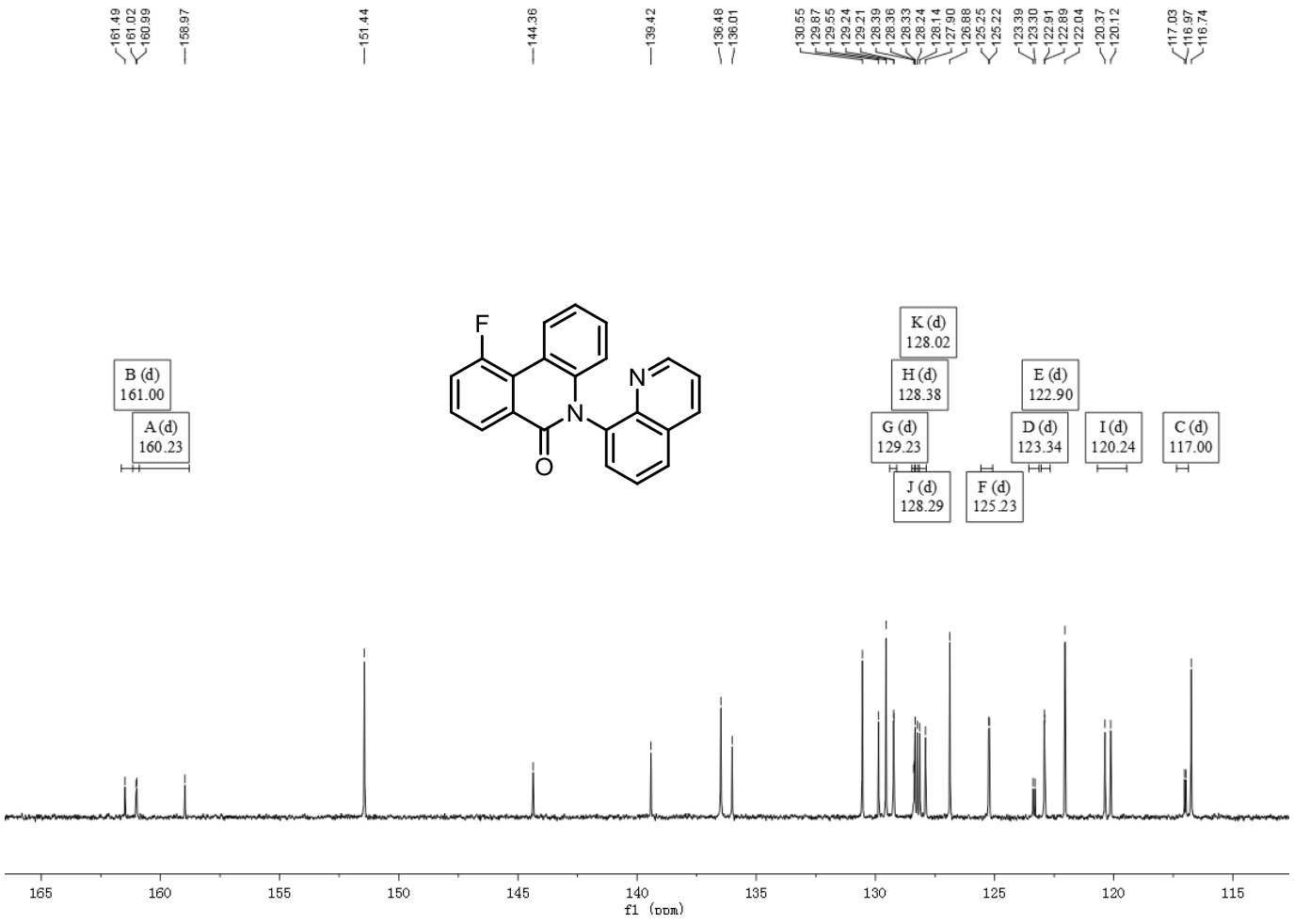

164.82
162.19
159.20
159.15
151.39
144.68
139.92
137.35
136.36
135.80
133.64
133.53
130.76
129.82
129.77
129.43
126.78
123.64
122.49
121.94
118.14
118.12
117.82
117.77
116.84
115.61
115.39
115.18
115.14
N
N
F
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

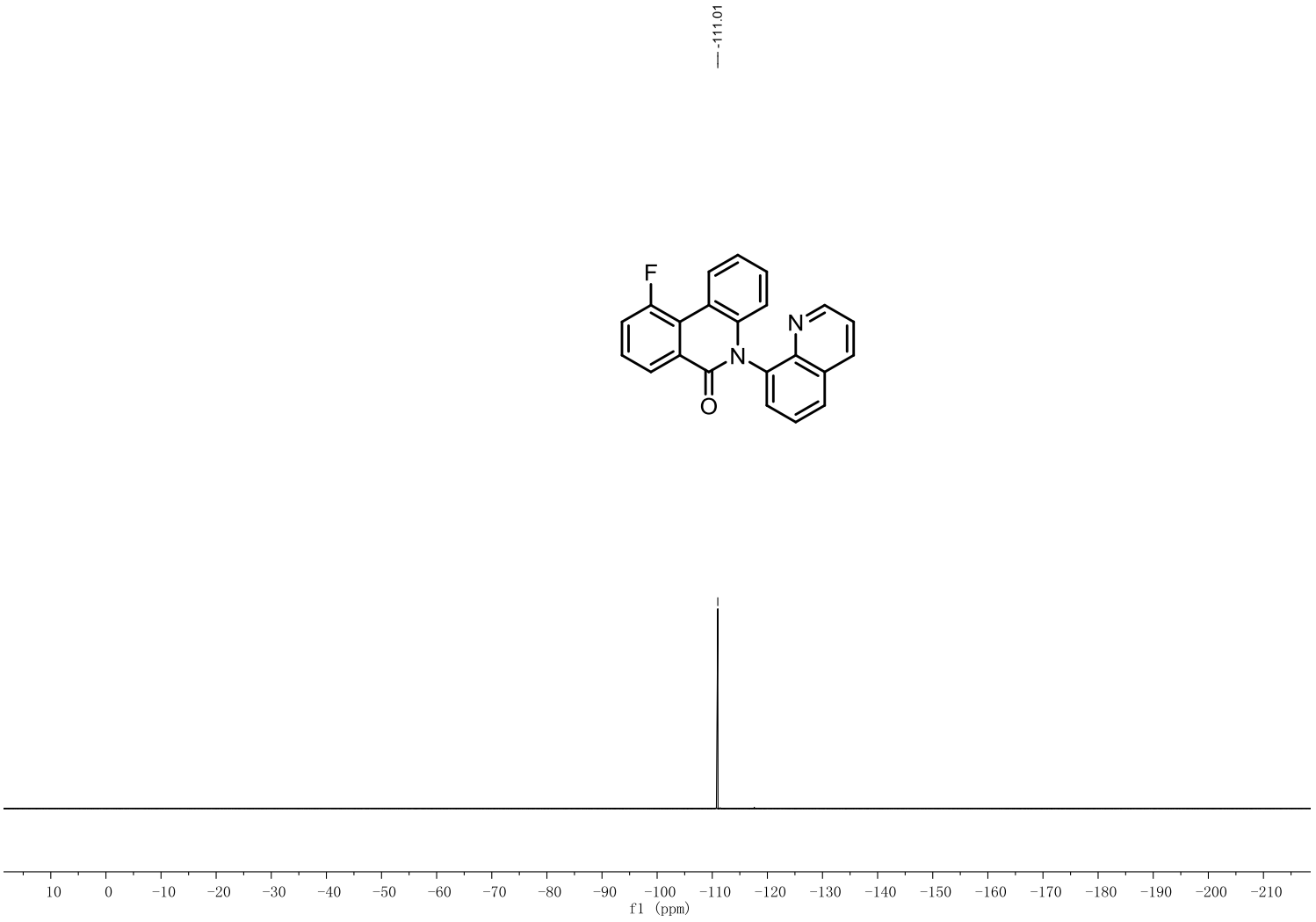

-108.55
N
N
F
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

Compound **3ia**

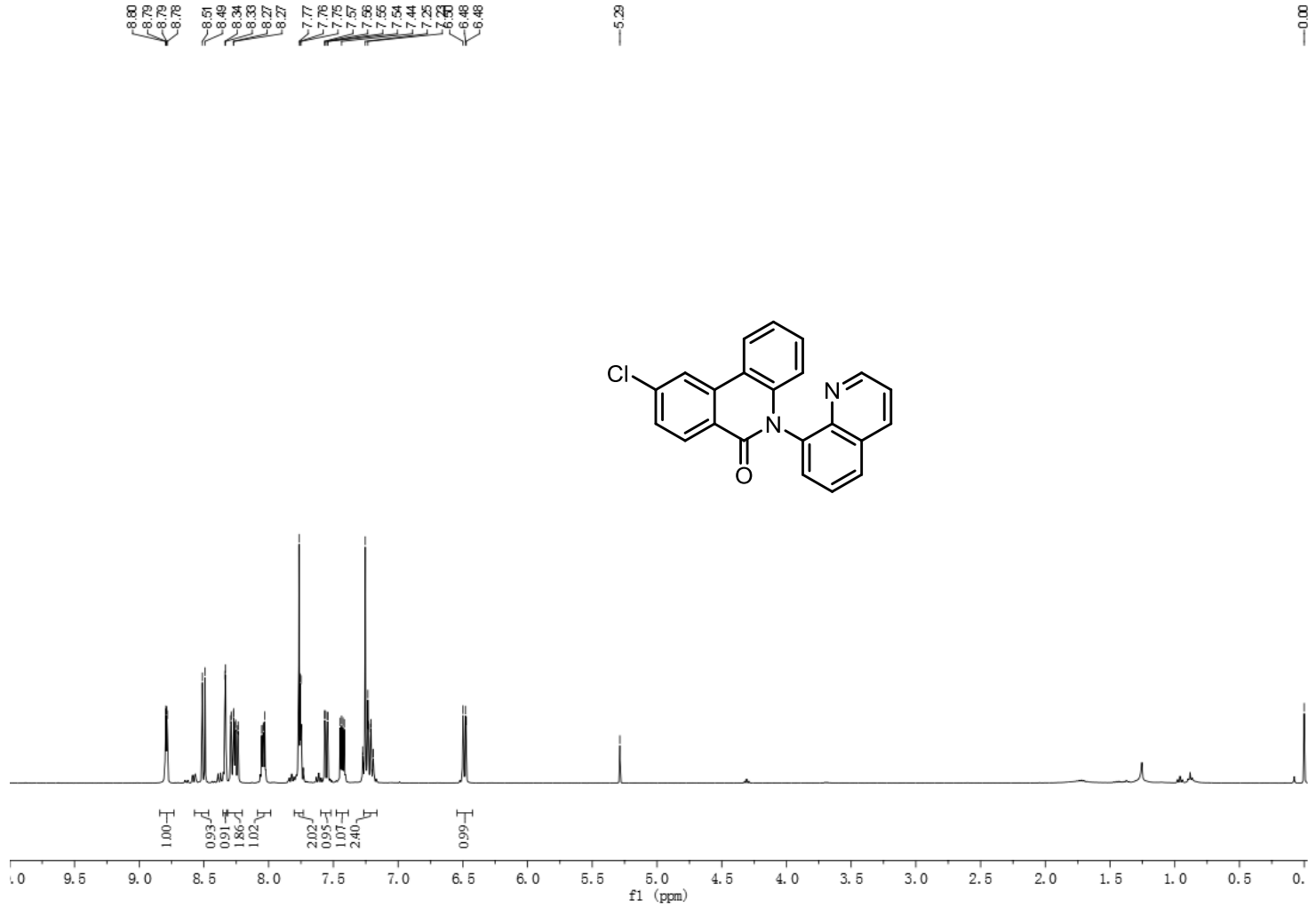


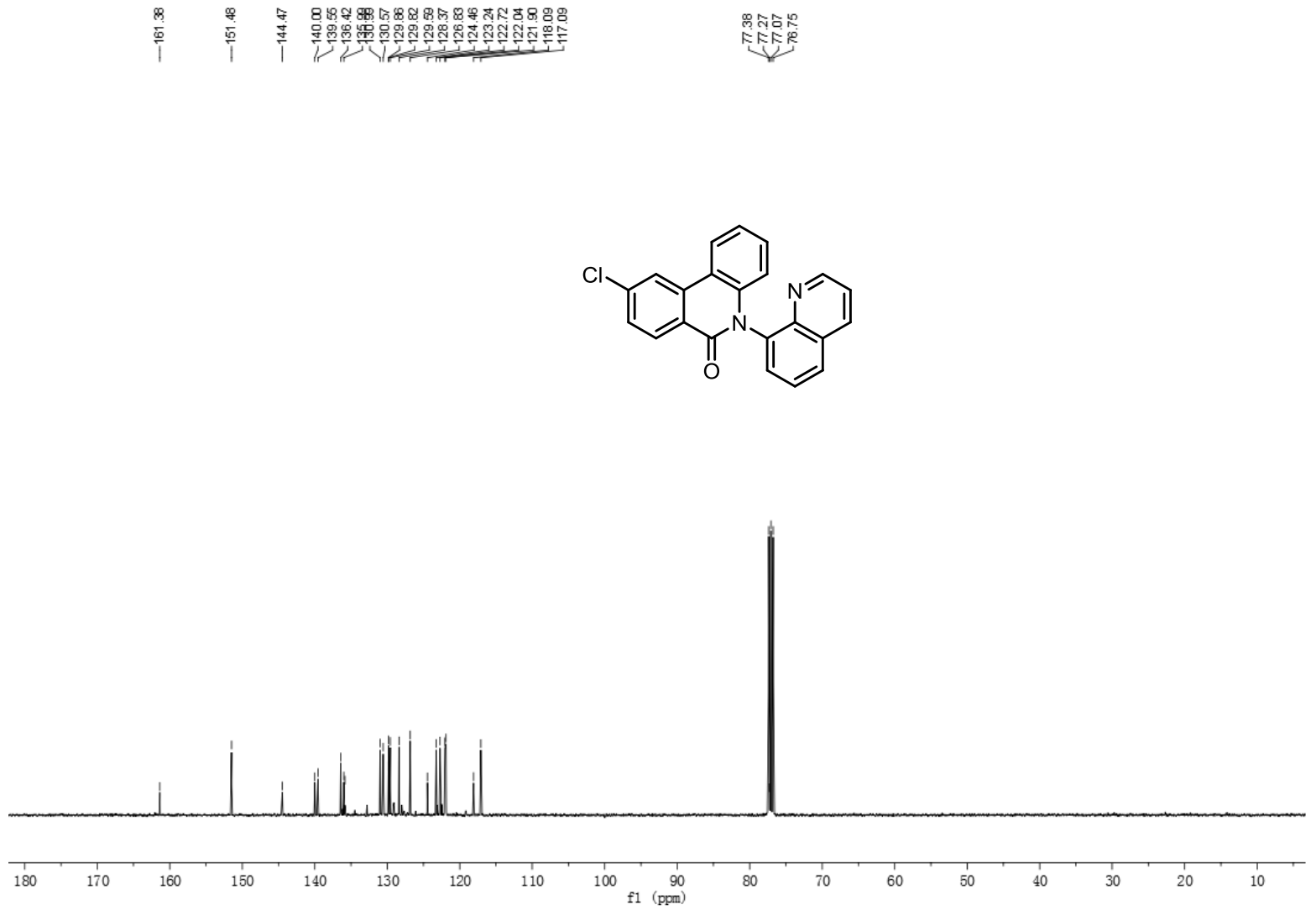

161.49
161.02
160.99
158.97
151.44
144.36
139.42
136.48
136.01
130.55
129.87
129.55
129.24
129.21
128.39
128.36
128.33
128.24
128.14
127.90
126.88
125.25
125.22
123.39
123.30
122.91
122.89
122.04
120.37
120.12
117.03
116.97
116.74
77.37
77.26
77.06
76.74
53.46
J (d)
128.29
G (d)
129.23
I (d)
120.24
B (d)
161.00
D (d)
123.34
A (d)
160.23
F (d)
125.23
C (d)
117.00
E (d)
122.90
H (d)
128.38
K (d)
128.02
F
N
N
O
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


161.49
161.02
160.99
158.97
151.44
144.36
139.42
136.48
136.01
130.55
129.87
129.55
129.24
129.21
128.39
128.36
128.33
128.24
128.14
127.90
126.88
125.25
125.22
123.39
123.30
122.91
122.89
122.04
120.37
120.12
117.03
116.97
116.74
B (d)
161.00
A (d)
160.23
F
N
O
K (d)
128.02
H (d)
128.38
G (d)
129.23
J (d)
128.29
F (d)
125.23
E (d)
122.90
D (d)
123.34
I (d)
120.24
C (d)
117.00
165
160
155
150
145
140
135
130
125
120
115
f1 (ppm)

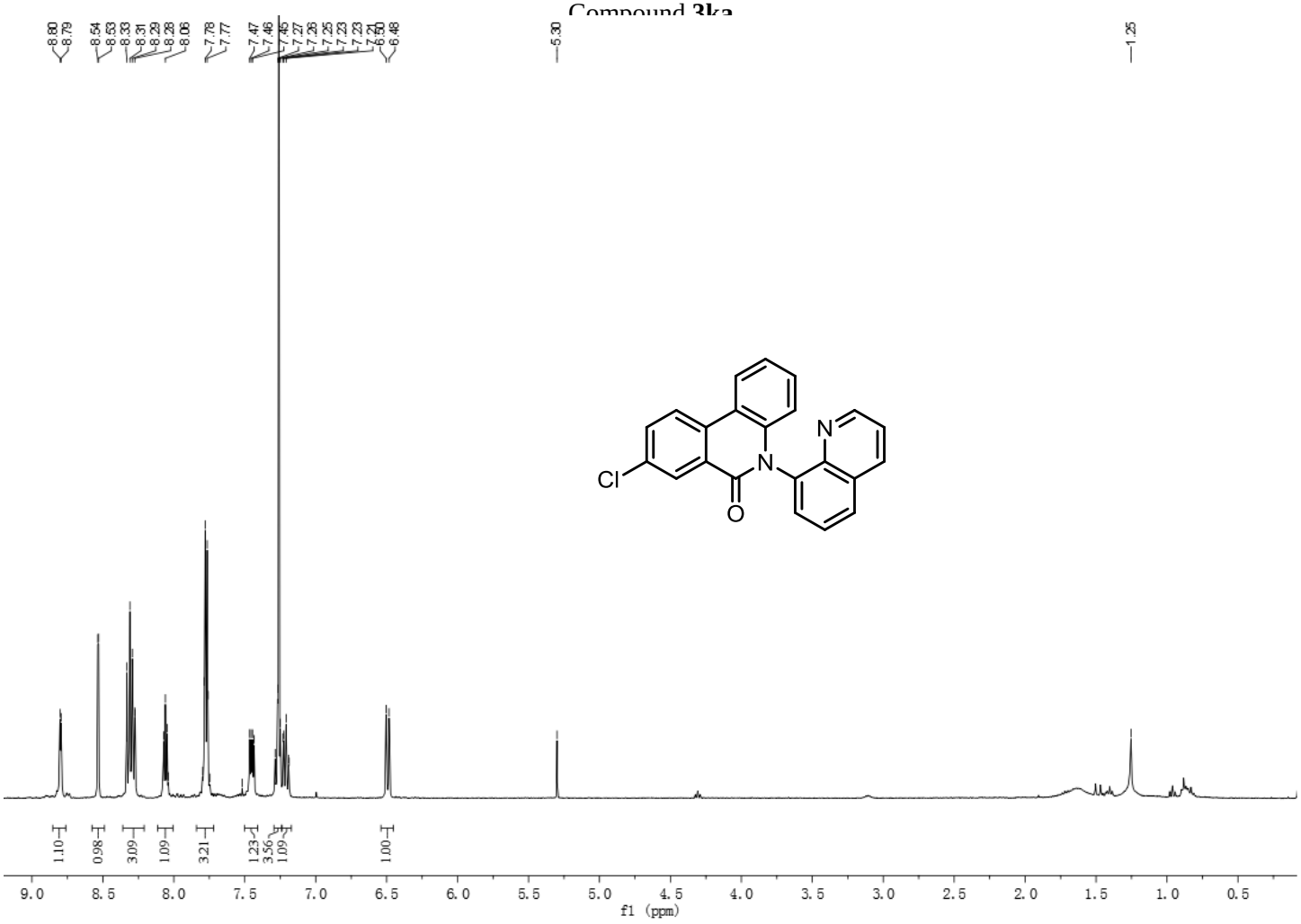

-111.01
F
N
N
O
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

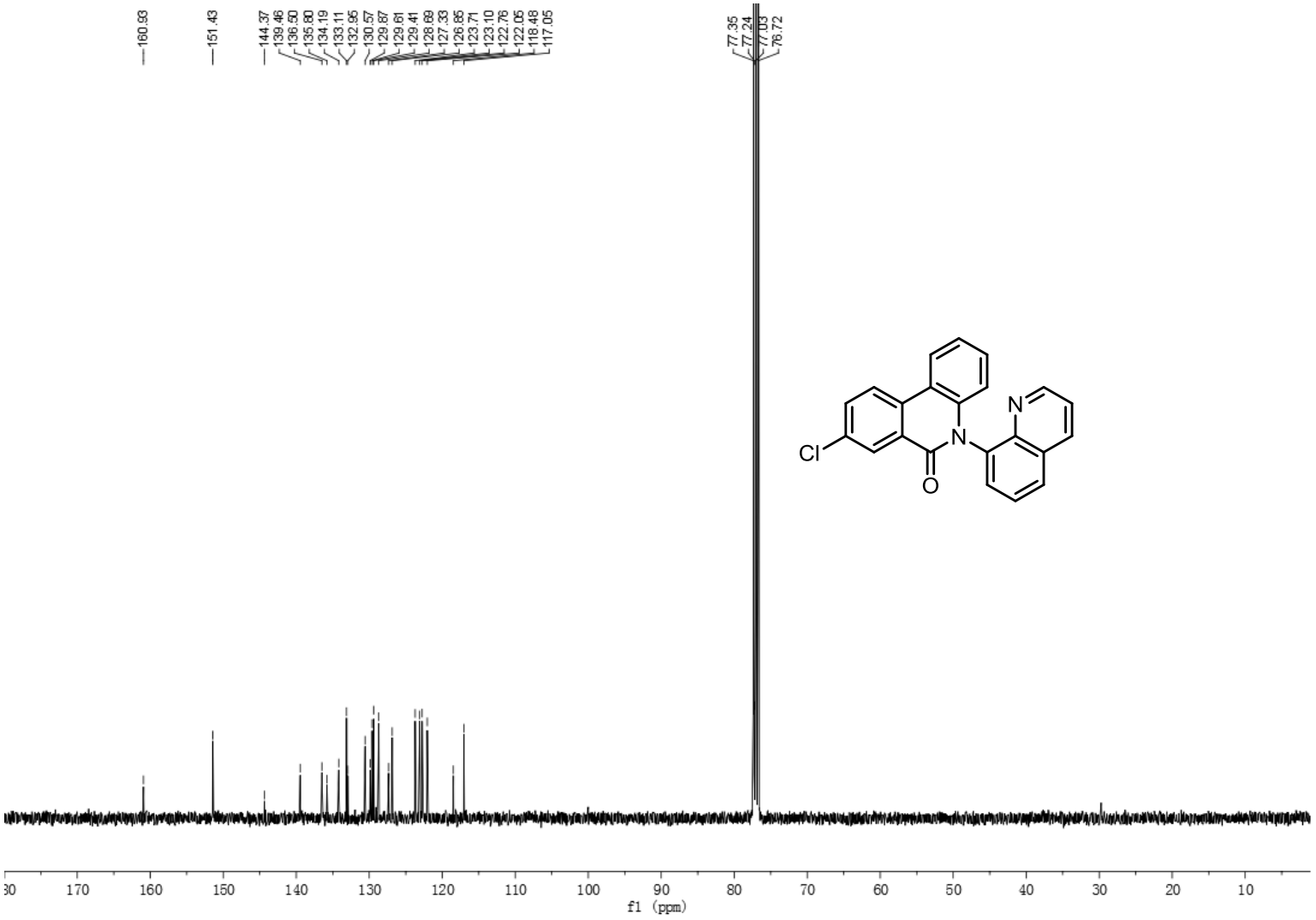
Compound **3ja**



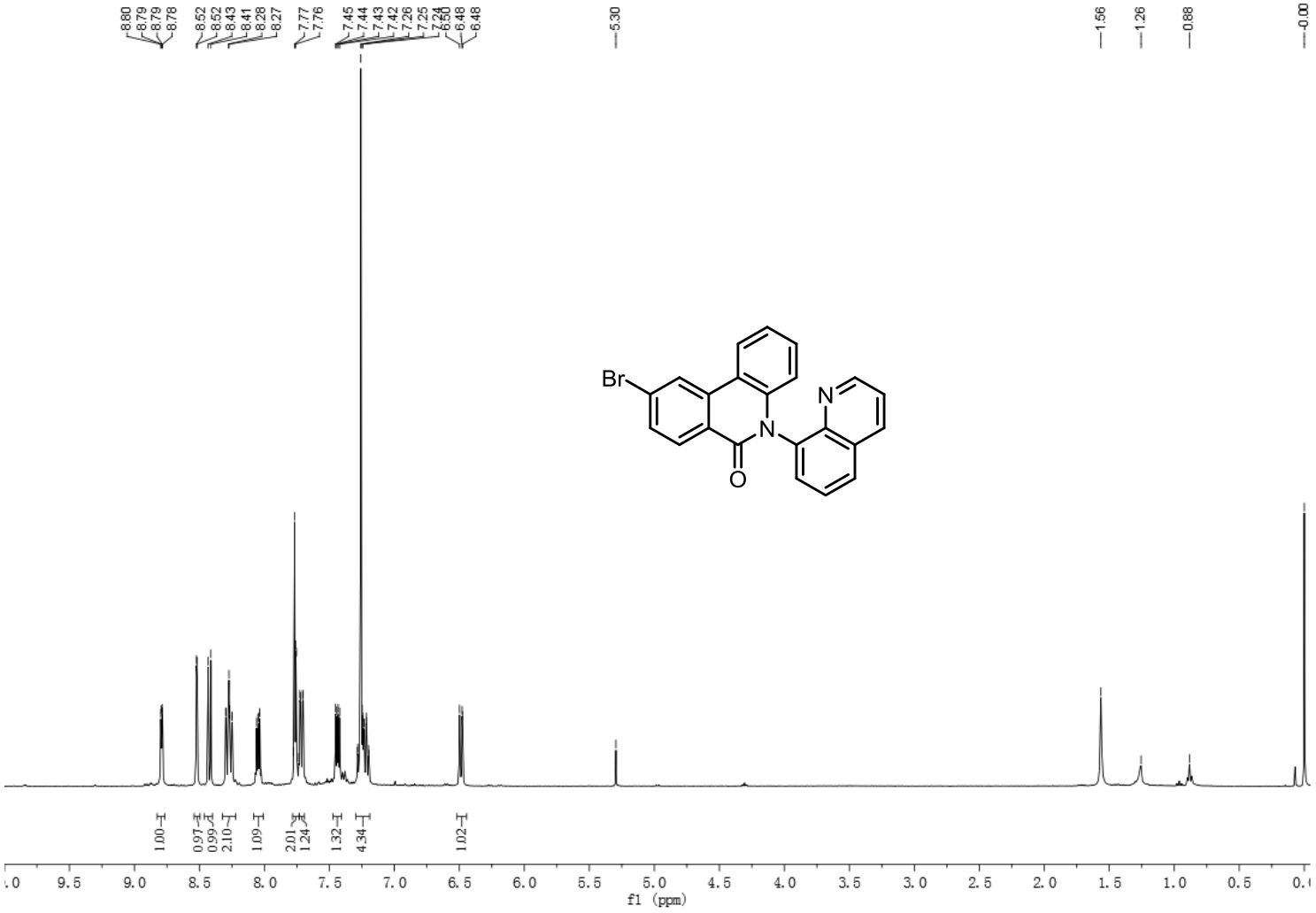

161.38
151.48
144.47
140.00
139.55
136.42
130.57
129.86
129.82
129.59
128.37
126.83
124.46
123.24
122.72
122.04
121.90
118.09
117.09
77.38
77.27
77.07
76.75
Cl
N
N
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

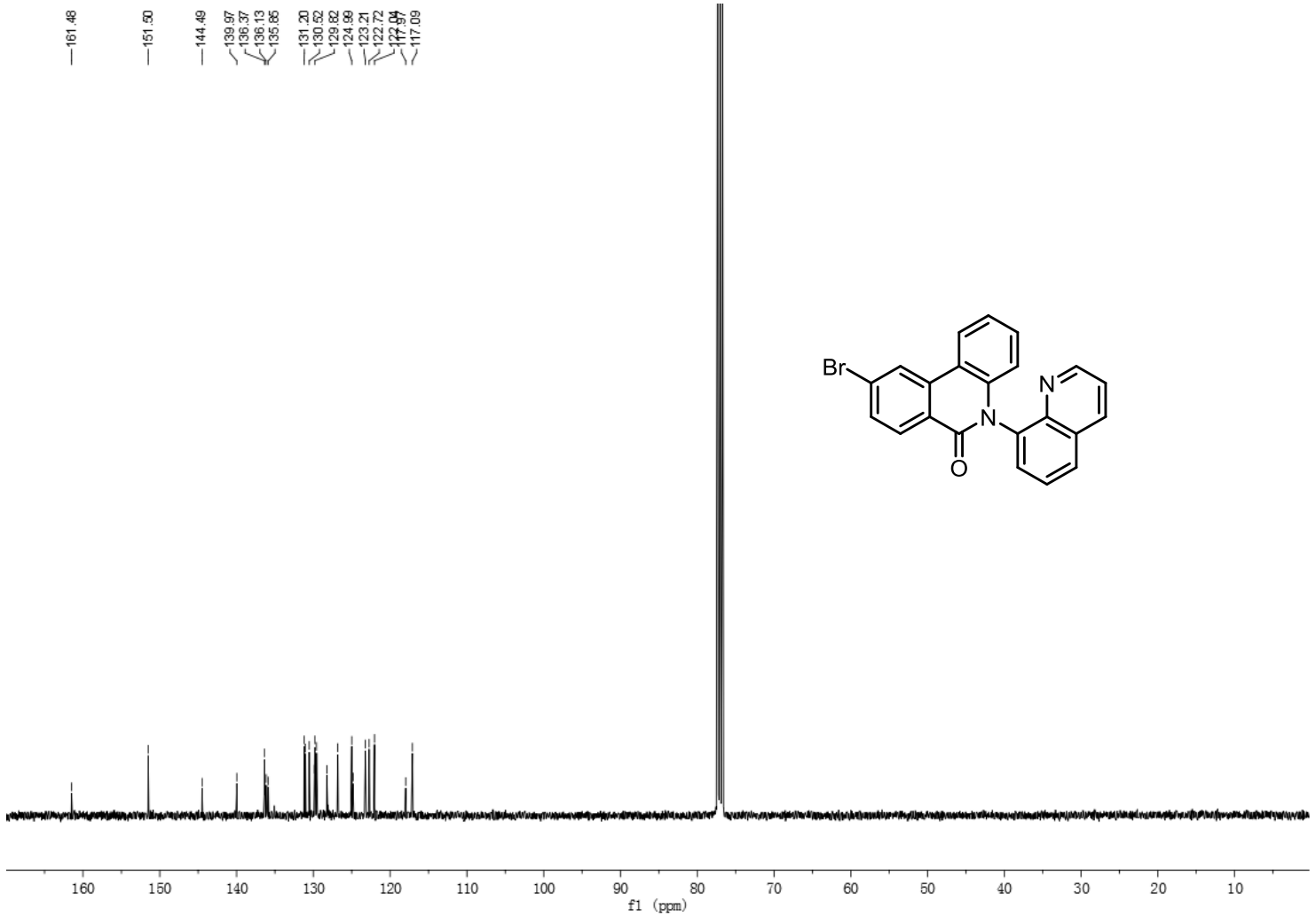
Compound **3ka**



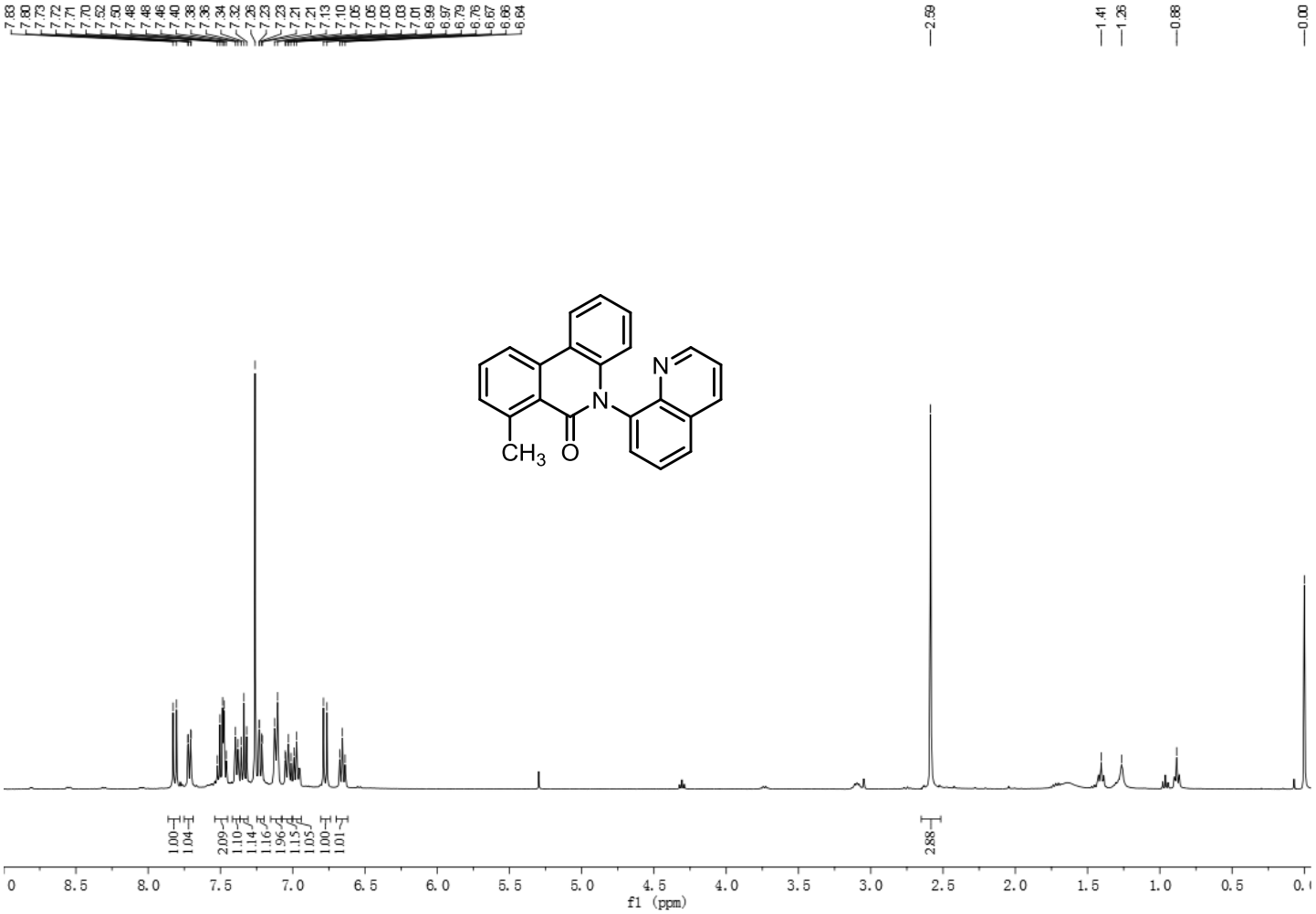

160.93
151.43
144.37
139.46
136.50
135.80
134.19
133.11
132.95
130.57
129.87
129.61
129.41
128.69
127.33
126.85
123.71
123.10
122.76
122.05
118.48
117.05
77.35
77.24
77.03
76.72
Cl
N
N
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

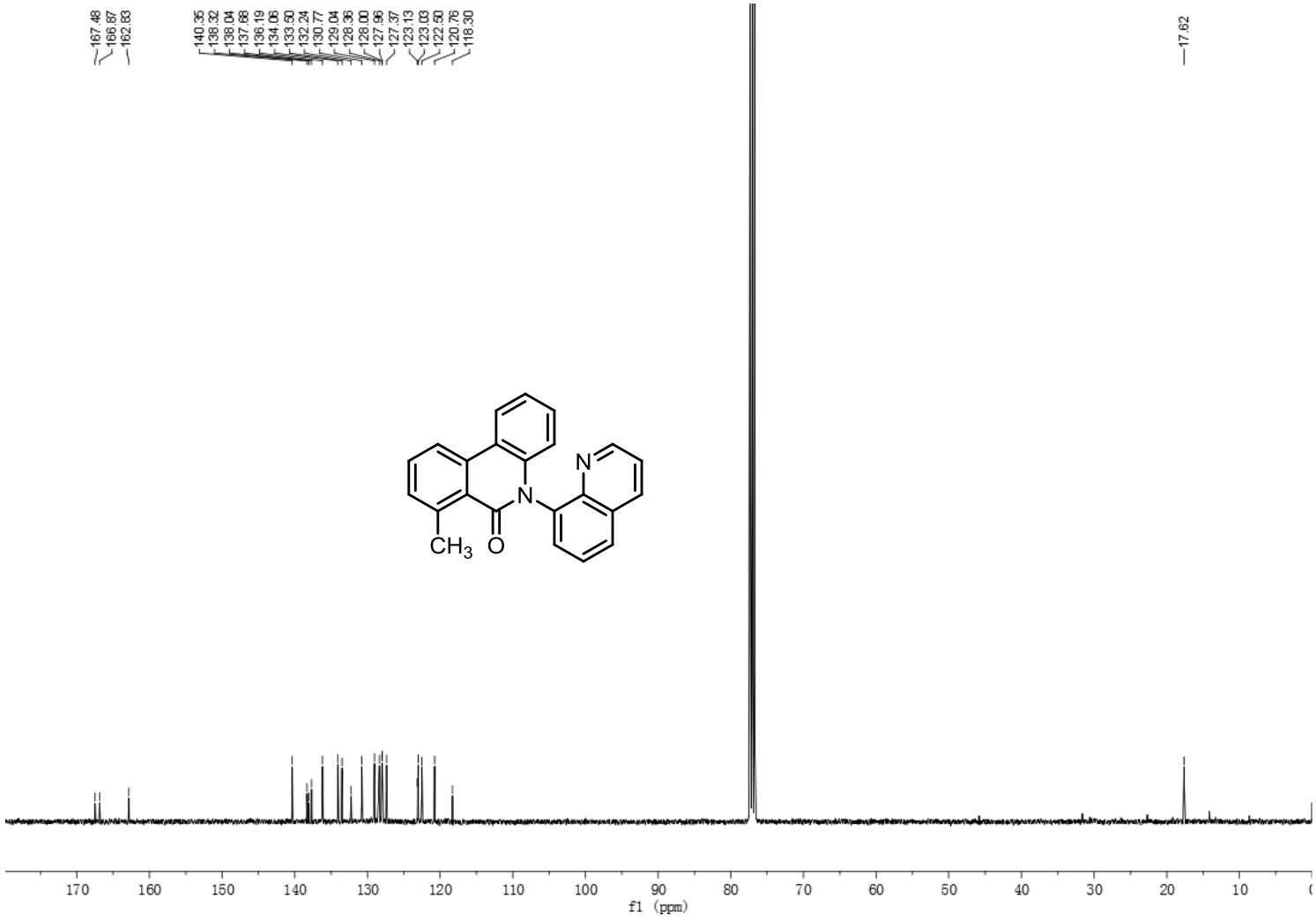
Compound **3la**



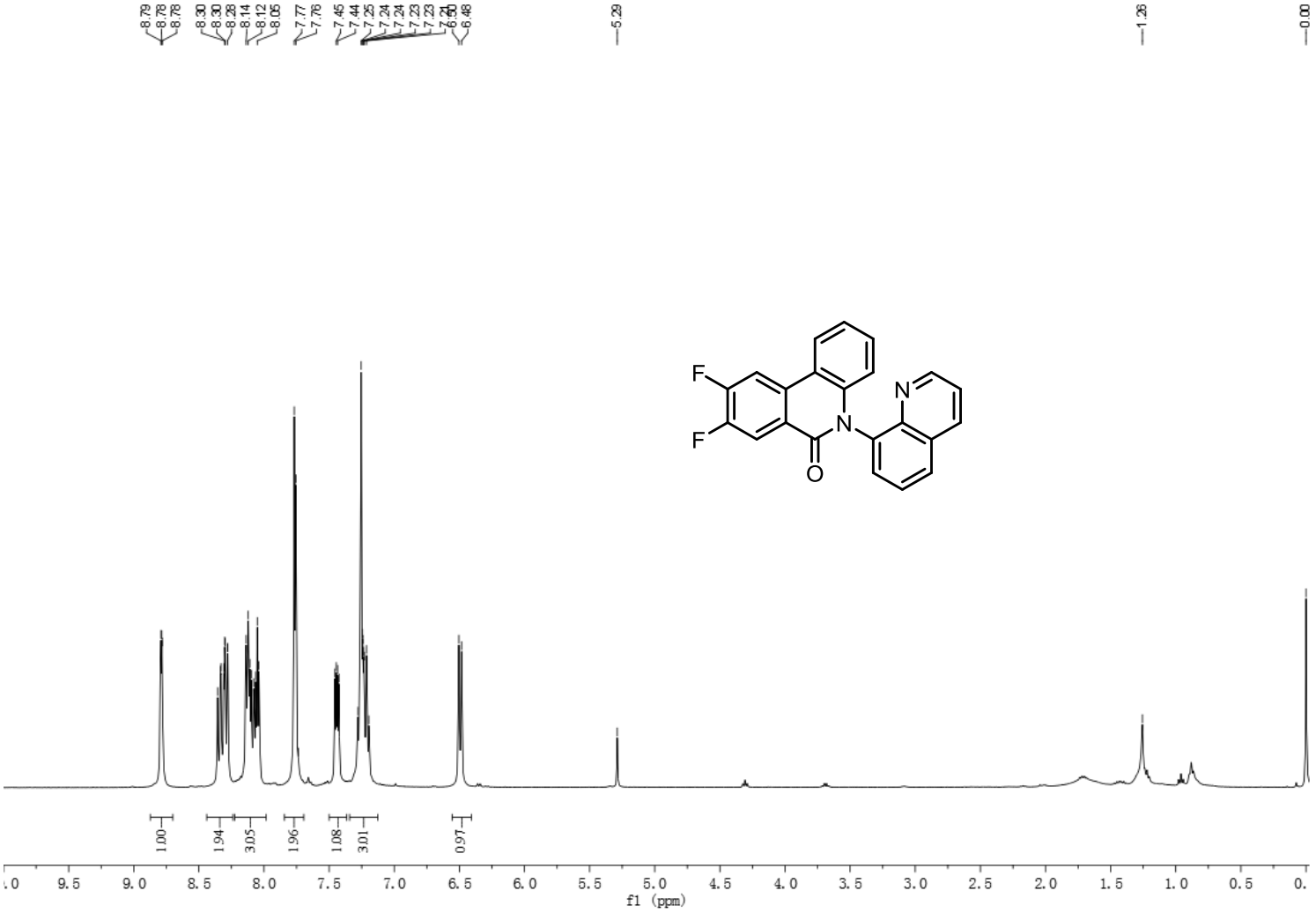

161.48
151.50
144.49
139.97
136.37
136.13
135.85
131.20
130.52
129.82
124.99
123.21
122.72
122.04
117.97
117.09
Br
N
N
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

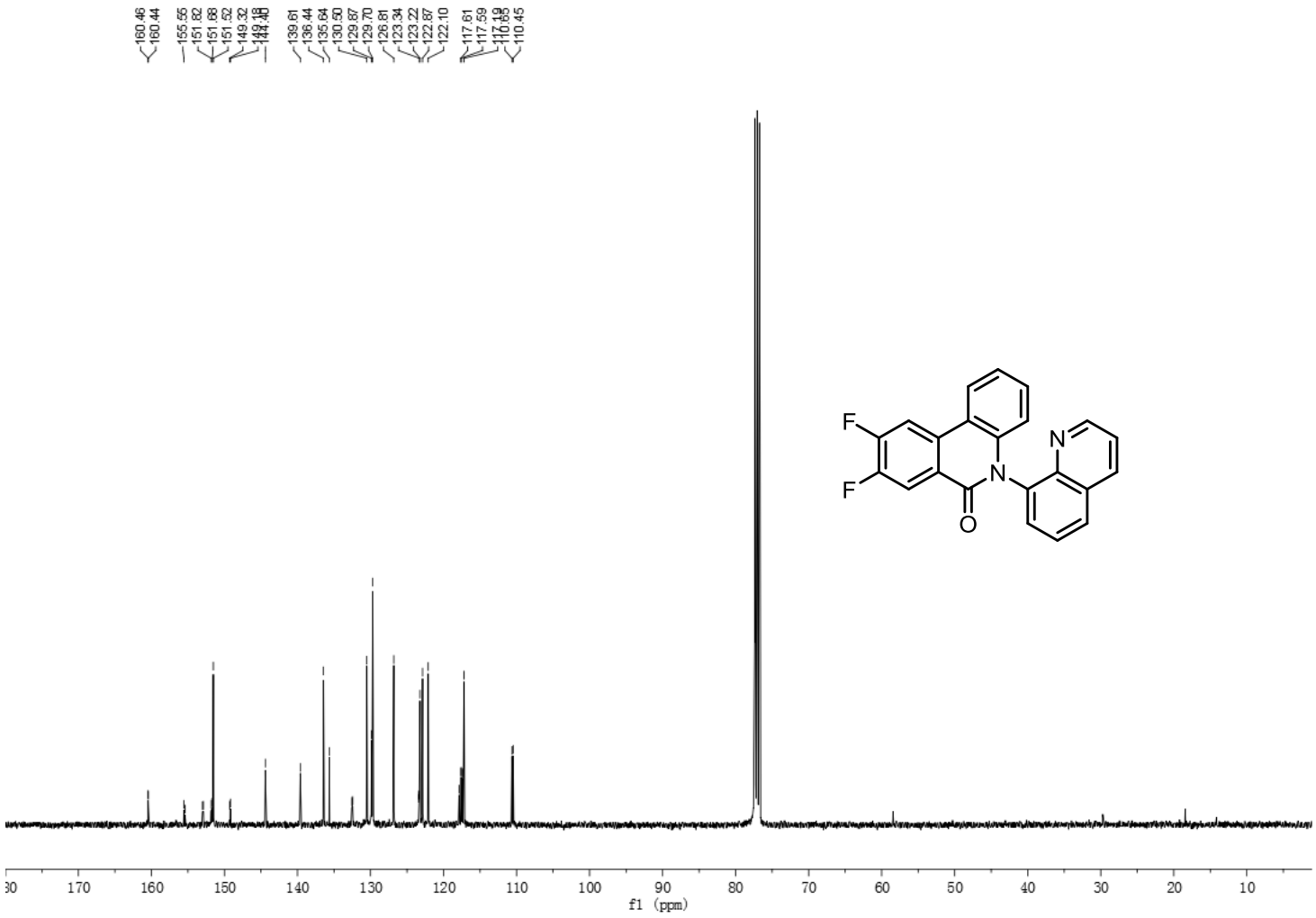
Compound **3na**

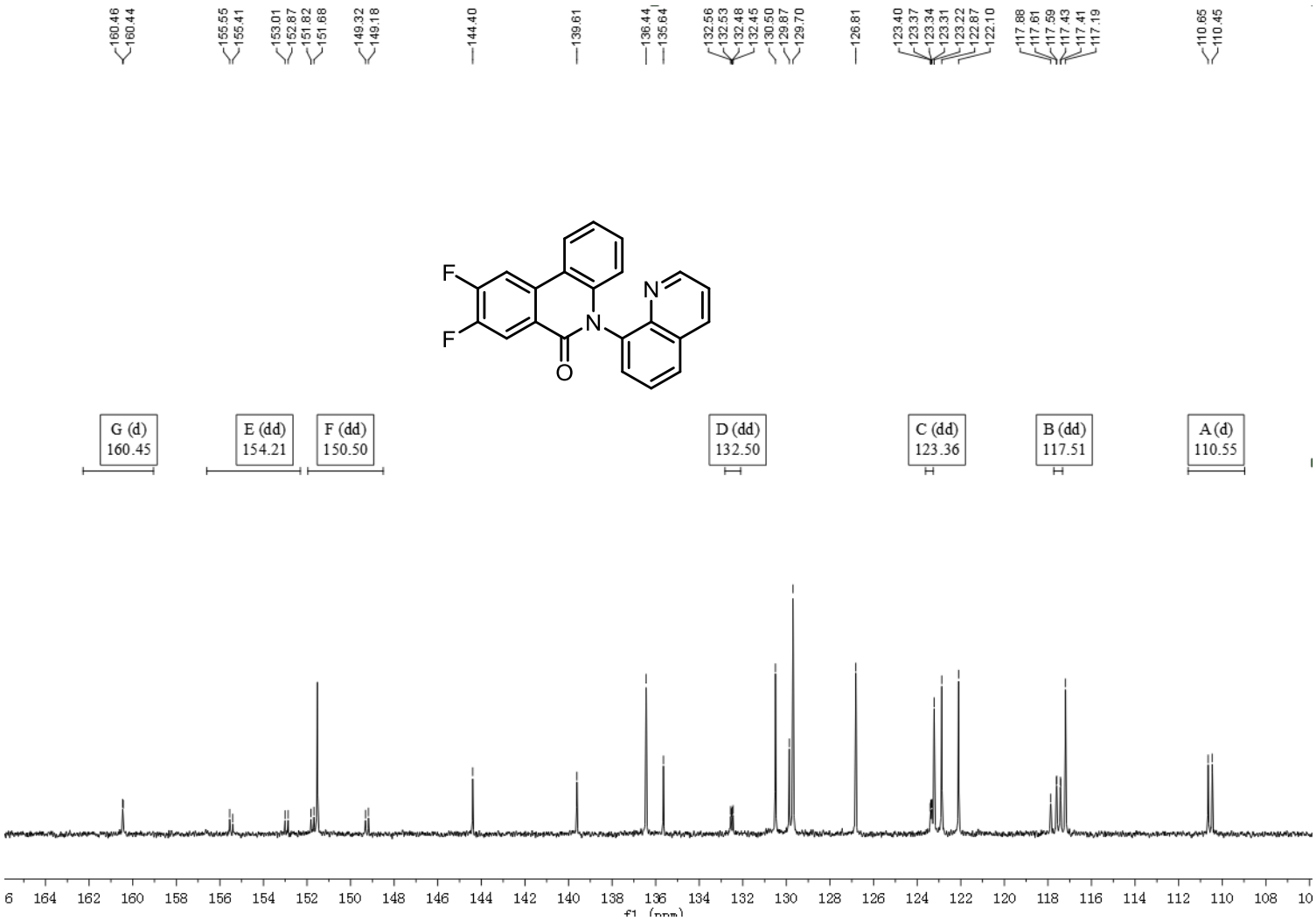



167.48
166.87
162.83
140.35
138.32
138.04
137.68
136.19
134.06
133.50
132.24
130.77
129.04
128.36
128.00
127.96
127.37
123.13
123.03
122.50
120.76
118.30
17.62
N
N
O
CH3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Compound **3oa**

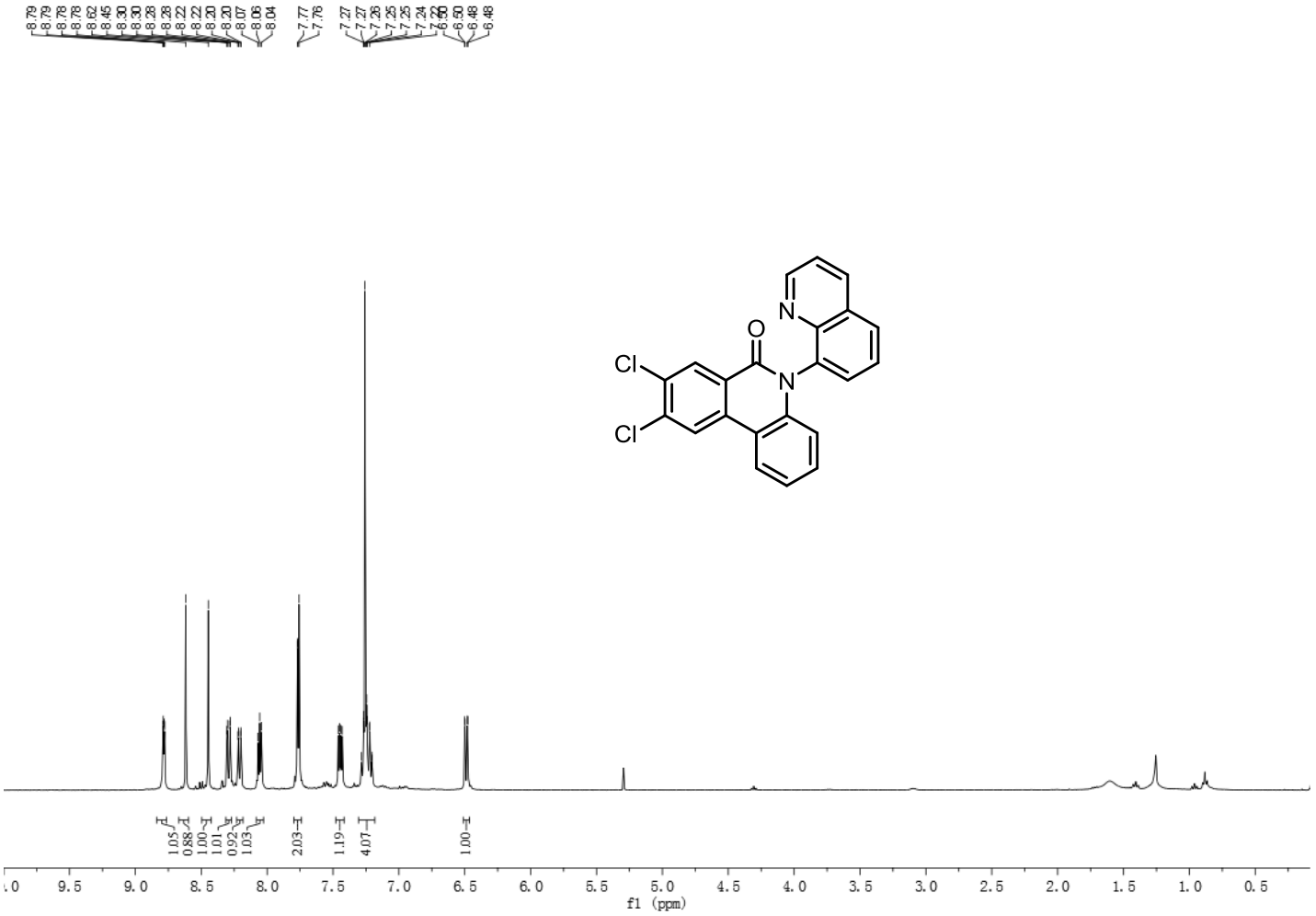


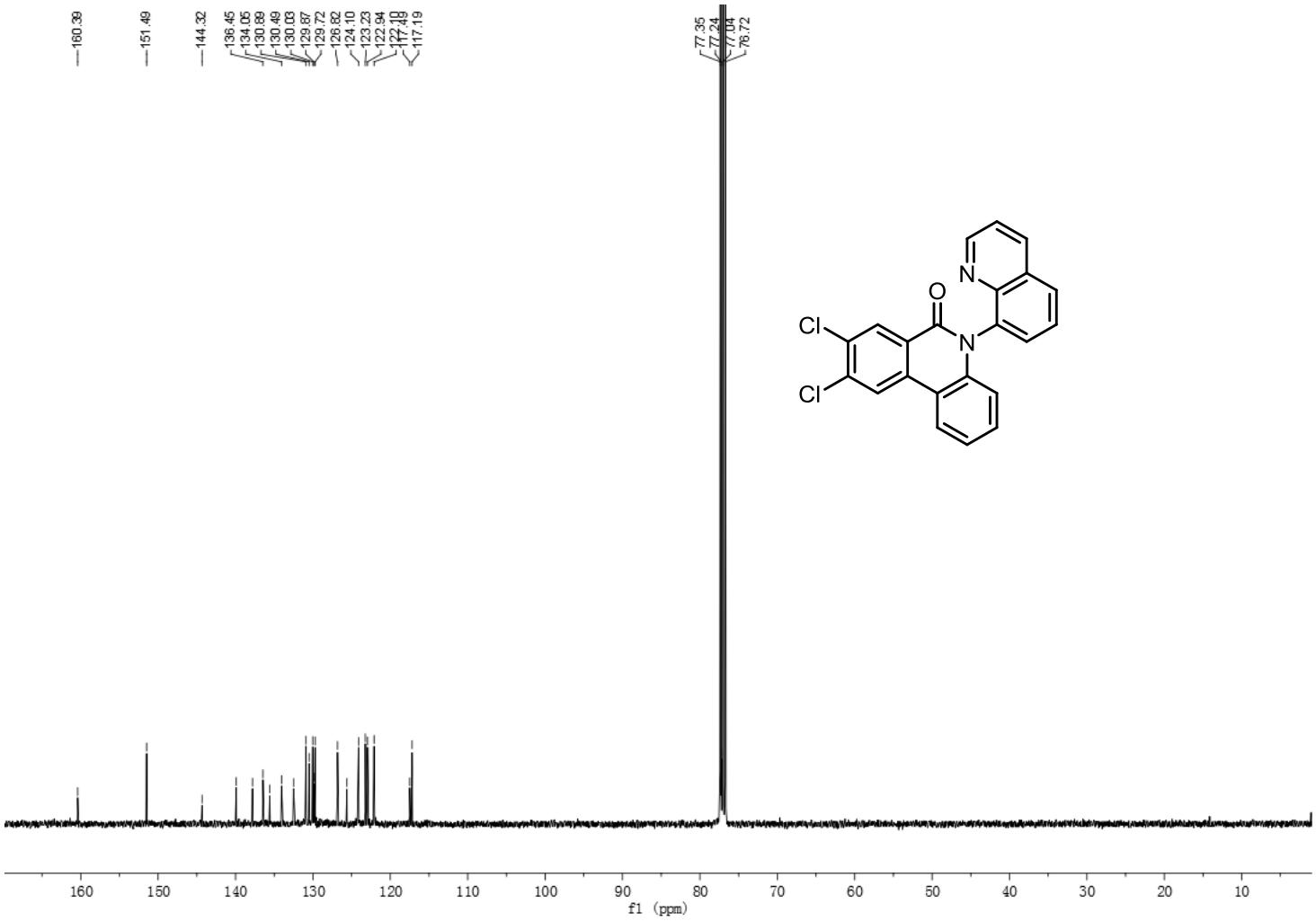

160.46
160.44
155.55
151.82
151.68
151.62
149.32
139.61
136.44
135.64
130.50
129.87
129.70
126.81
123.34
123.22
122.87
122.10
117.61
117.59
110.45
F
F
N
N
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


160.46
160.44
155.55
155.41
153.01
152.87
151.82
151.68
149.32
149.18
144.40
139.61
136.44
135.64
132.56
132.53
132.48
132.45
130.50
129.87
129.70
126.81
123.40
123.37
123.34
123.31
123.22
122.87
122.10
117.88
117.61
117.59
117.43
117.41
117.19
110.65
110.45
F
F
N
N
O
G (d)
160.45
E (dd)
154.21
F (dd)
150.50
D (dd)
132.50
C (dd)
123.36
B (dd)
117.51
A (d)
110.55
6 164 162 160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108 10
f1 (ppm)

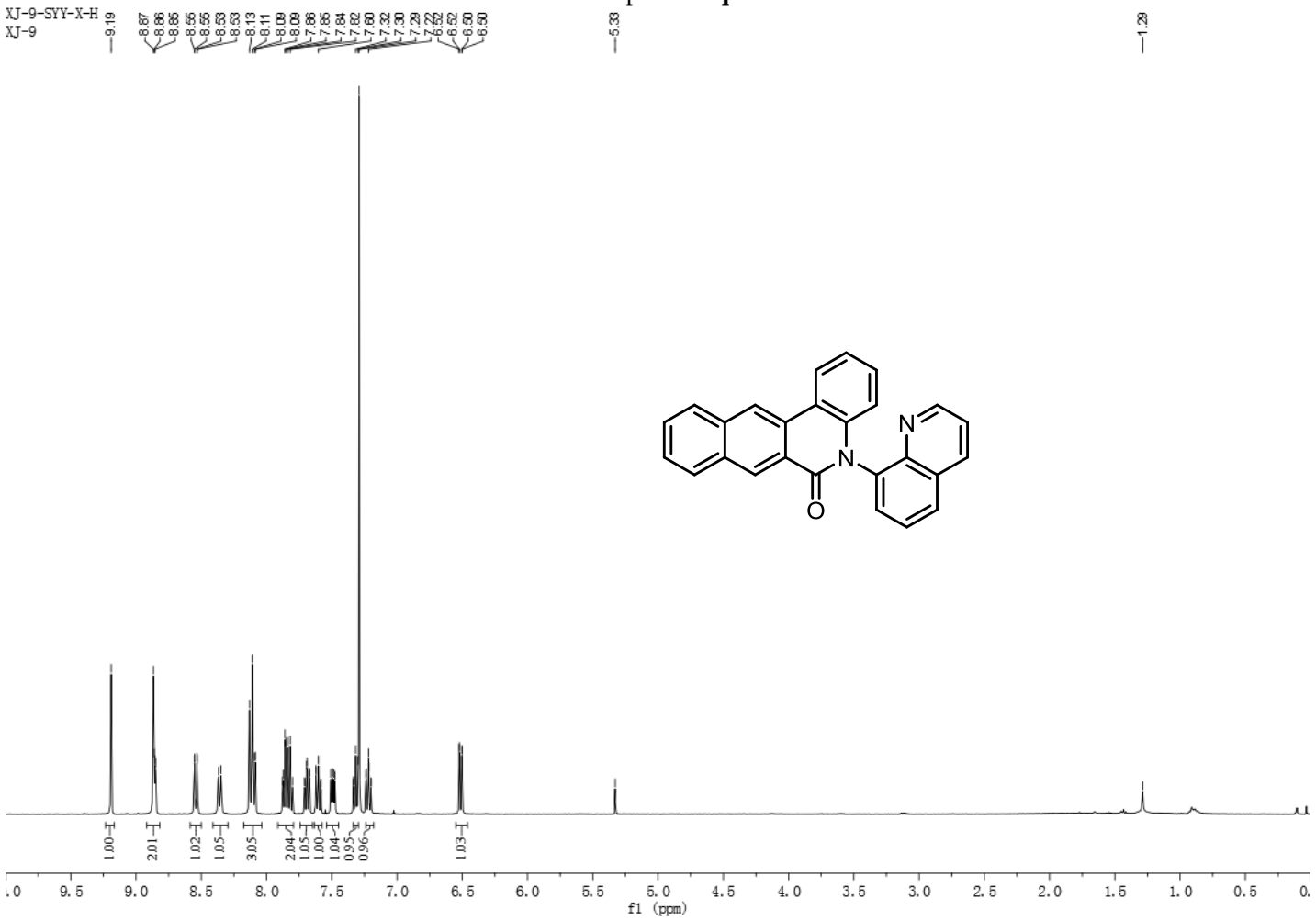

-129.23
-129.29
-136.03
-136.09
F
F
N
N
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

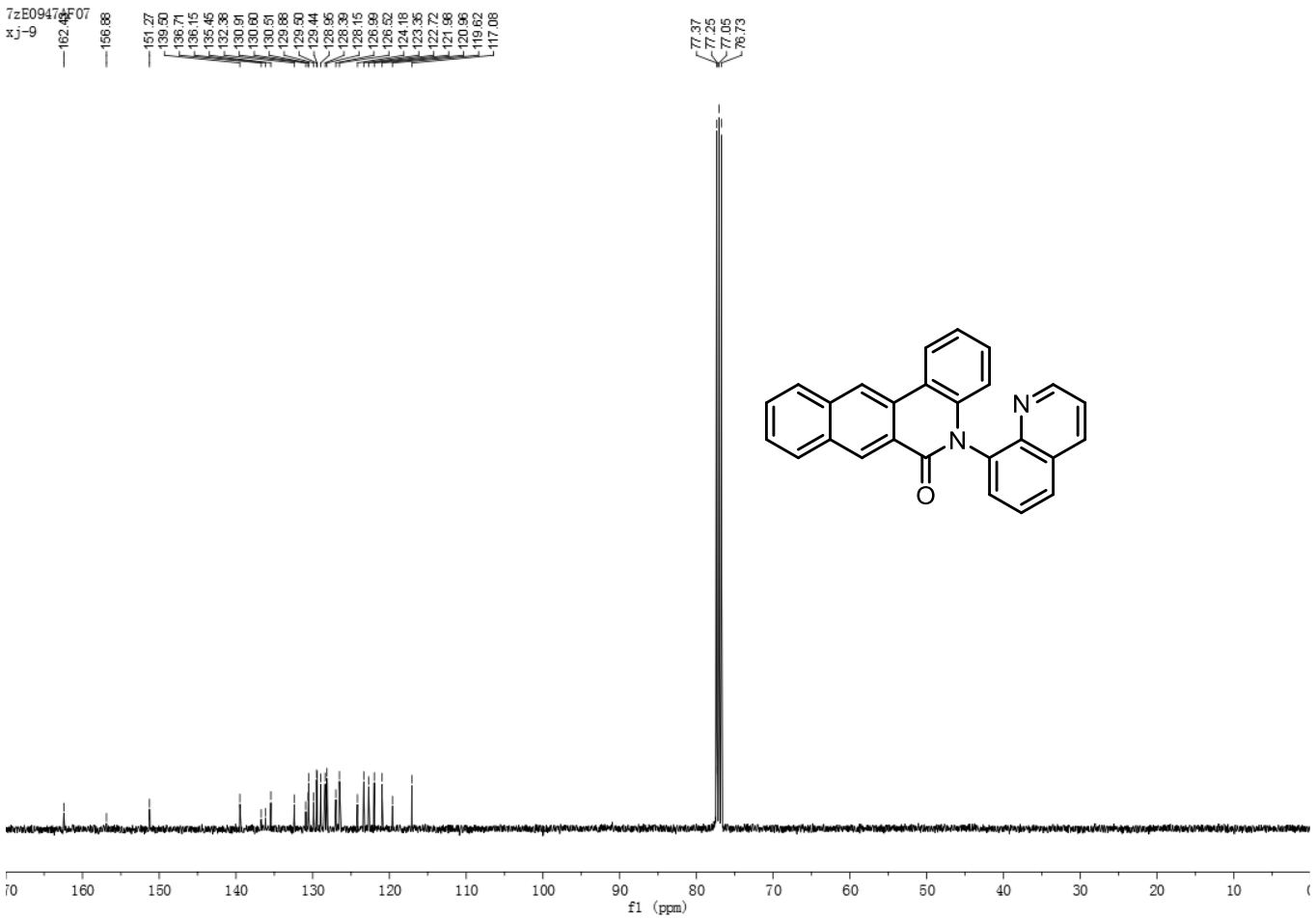
Compound **3pa**



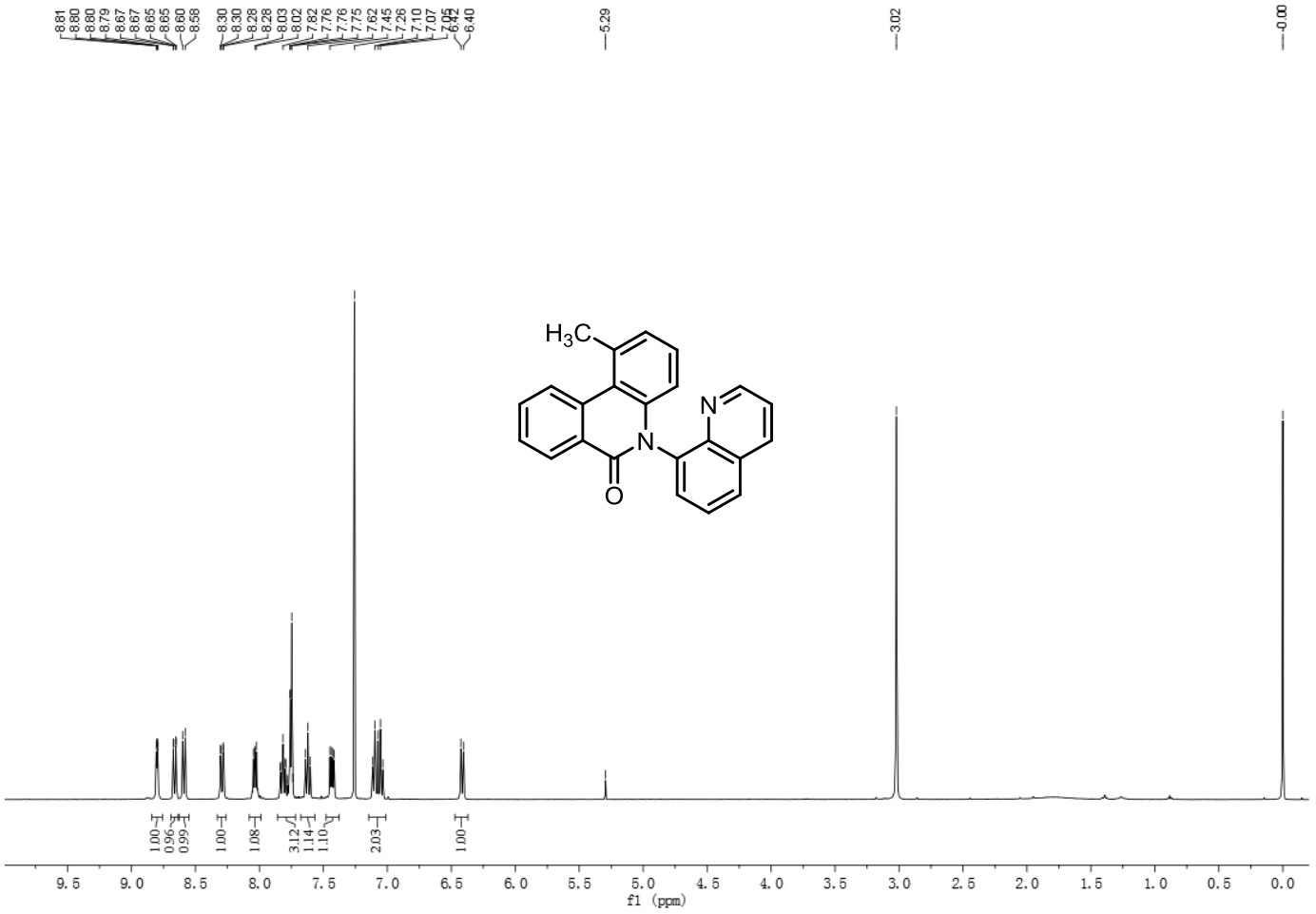

160.39
151.49
144.32
136.45
134.05
130.89
130.49
130.03
129.67
129.72
126.82
124.10
123.23
122.94
117.19
77.35
77.24
77.04
76.72
O
N
N
Cl
Cl
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

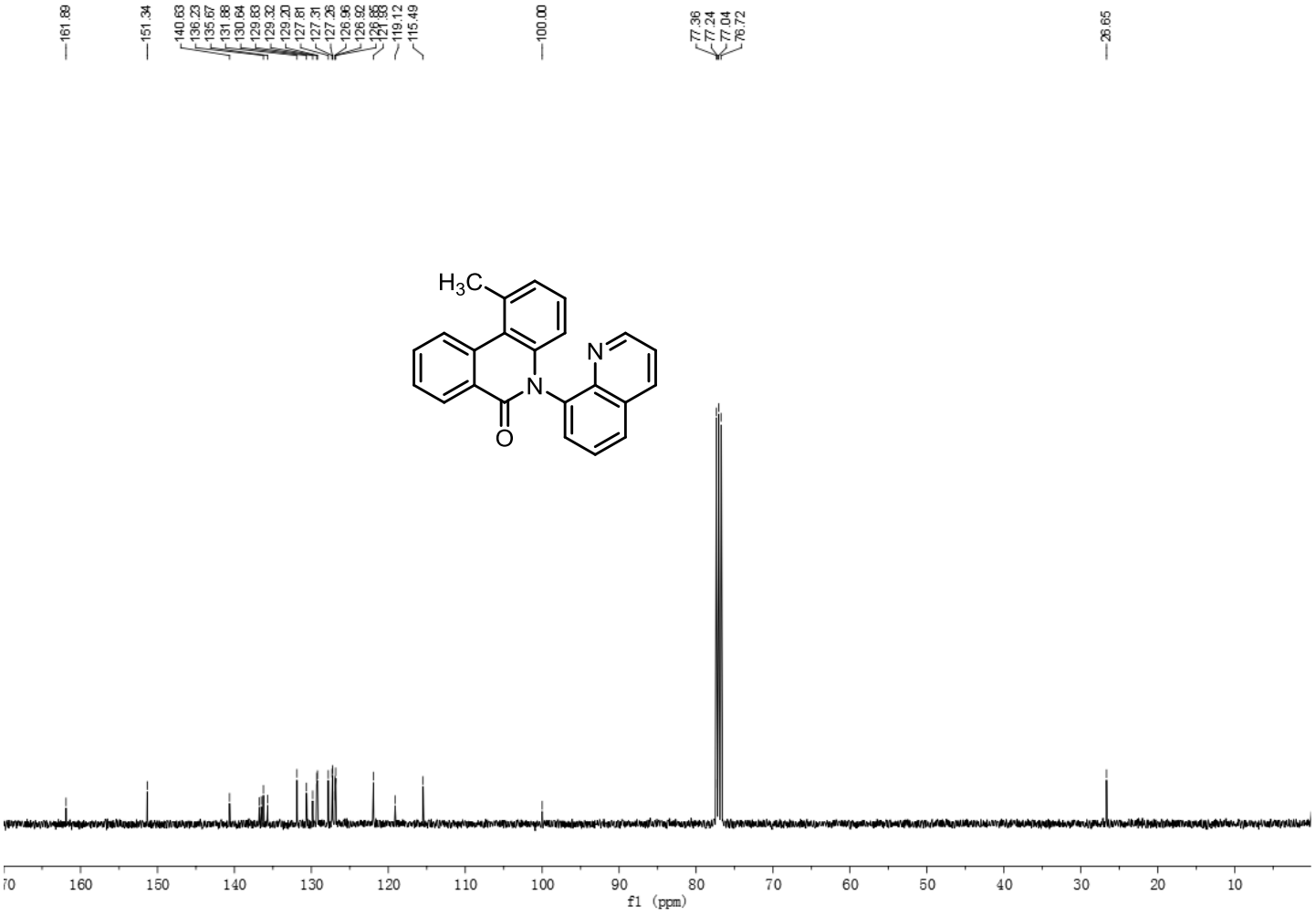
Compound **3qa**



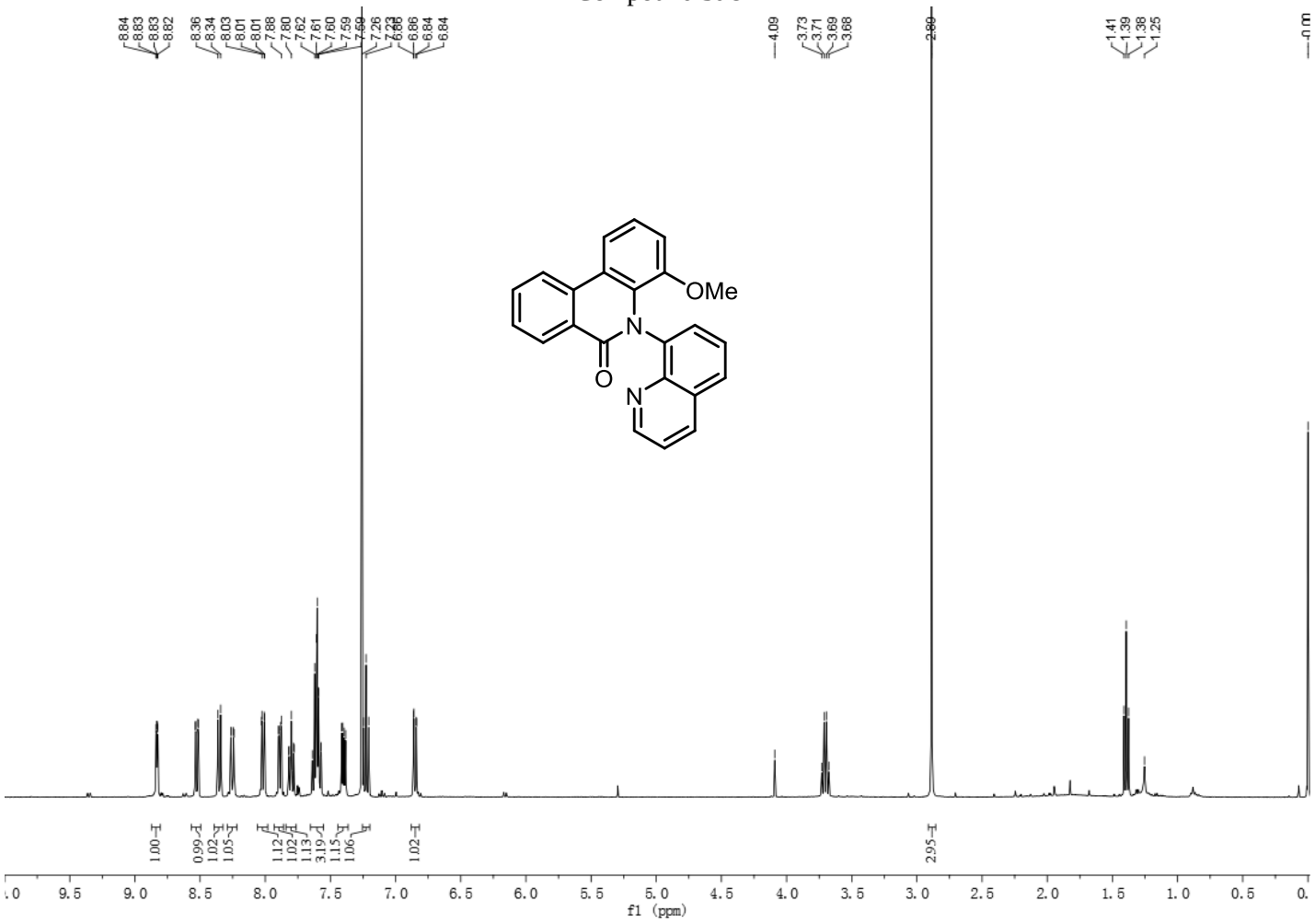

7zE0947-F07
xj-9
162.42
156.88
151.27
139.50
136.71
136.15
135.45
132.38
130.91
130.60
130.51
129.88
129.50
129.44
128.95
128.39
128.15
126.99
126.52
124.18
123.35
122.72
121.98
120.96
119.62
117.06
77.37
77.25
77.05
76.73
N
N
O
f1 (ppm)

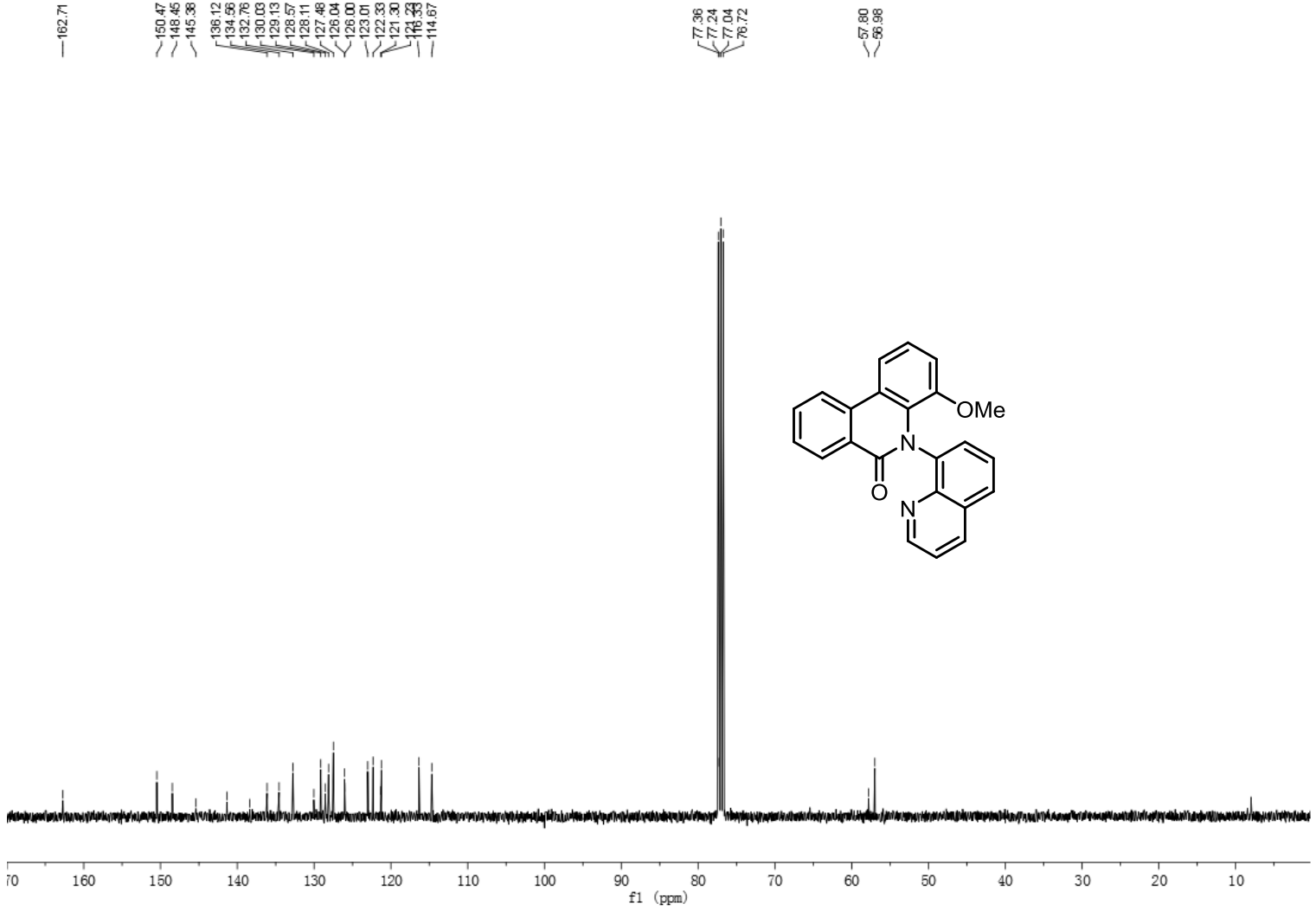
Compound **3ab**



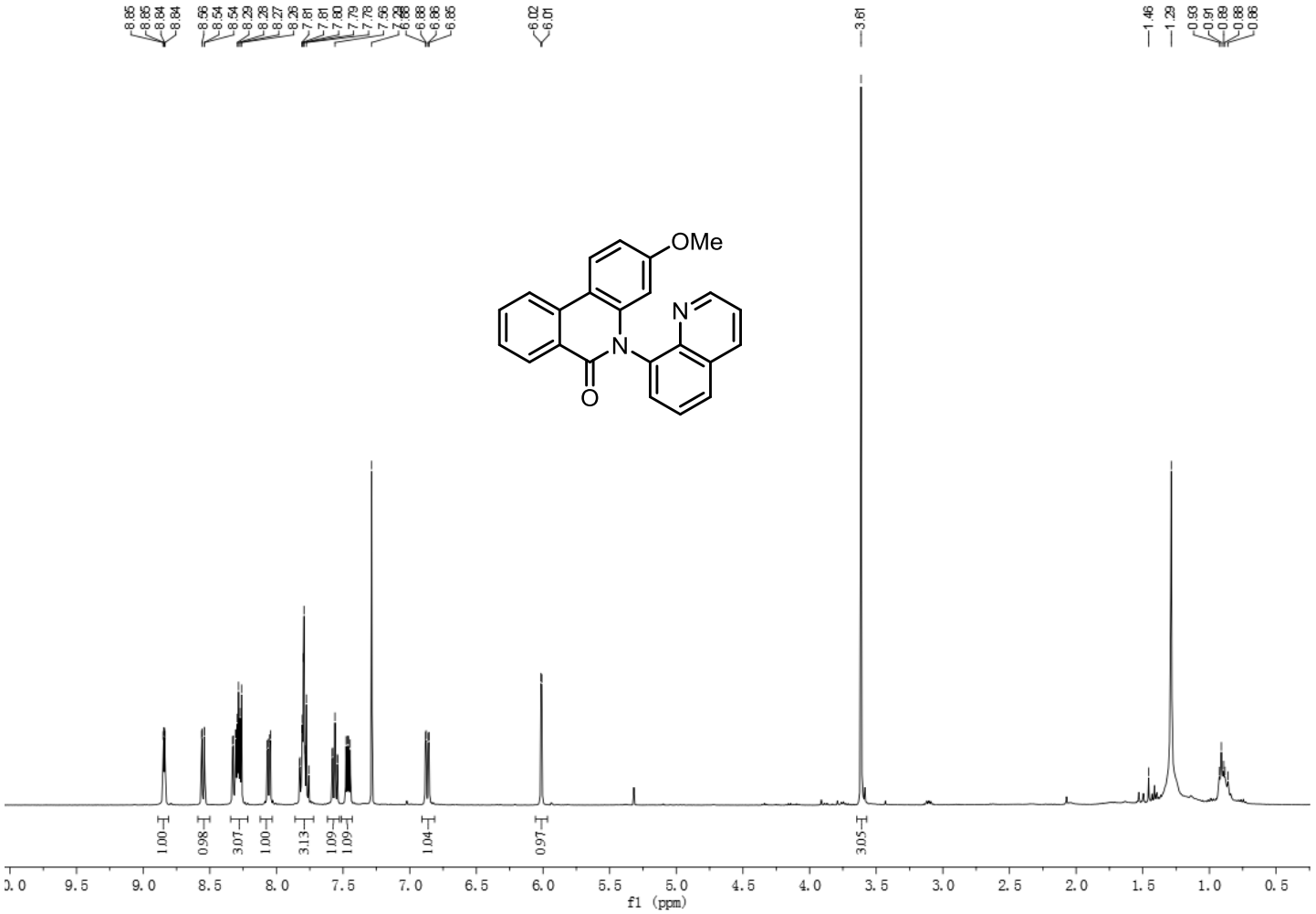

161.89
151.34
140.63
136.23
135.67
131.88
130.64
129.83
129.32
129.20
127.81
127.31
127.26
126.96
126.92
119.12
115.49
100.00
77.36
77.24
77.04
76.72
26.65
H3C
N
N
O
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

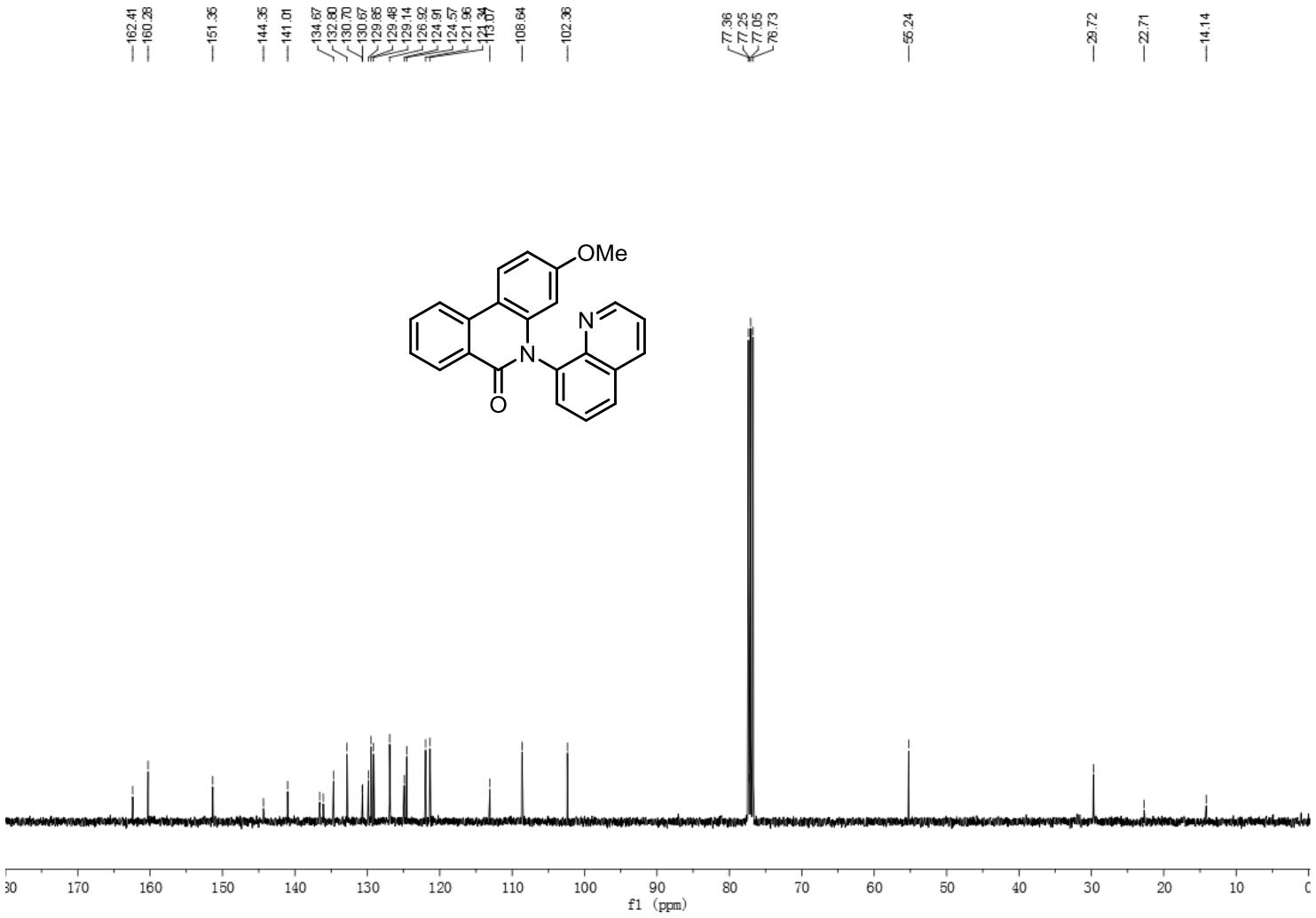
Compound **3ac**



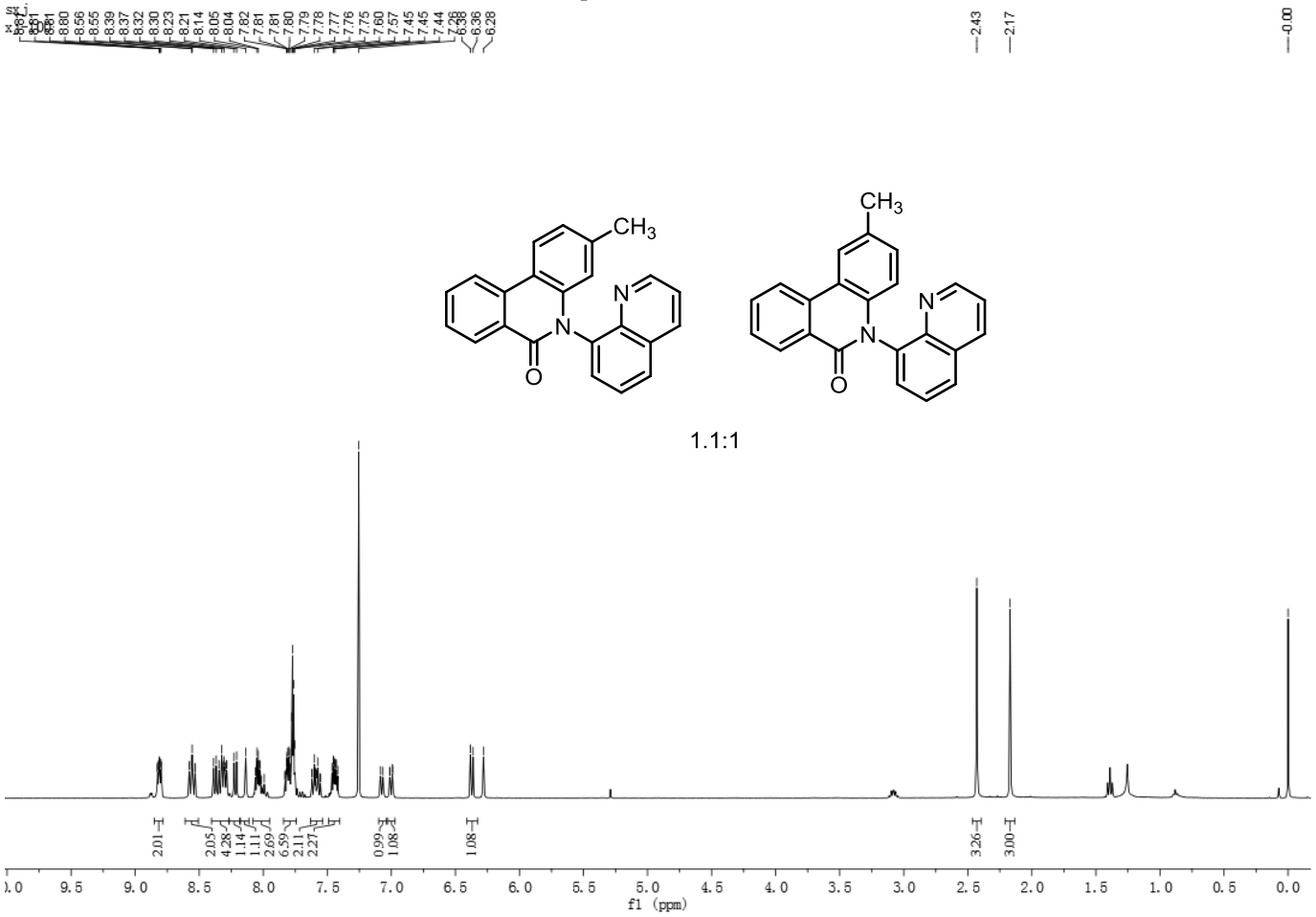

162.71
150.47
148.45
145.38
136.12
134.66
132.76
130.03
129.13
128.57
128.11
127.48
126.04
126.00
123.01
122.33
121.30
121.23
116.33
114.67
77.36
77.24
77.04
76.72
57.80
55.98
OMe
N
O
N
f1 (ppm)

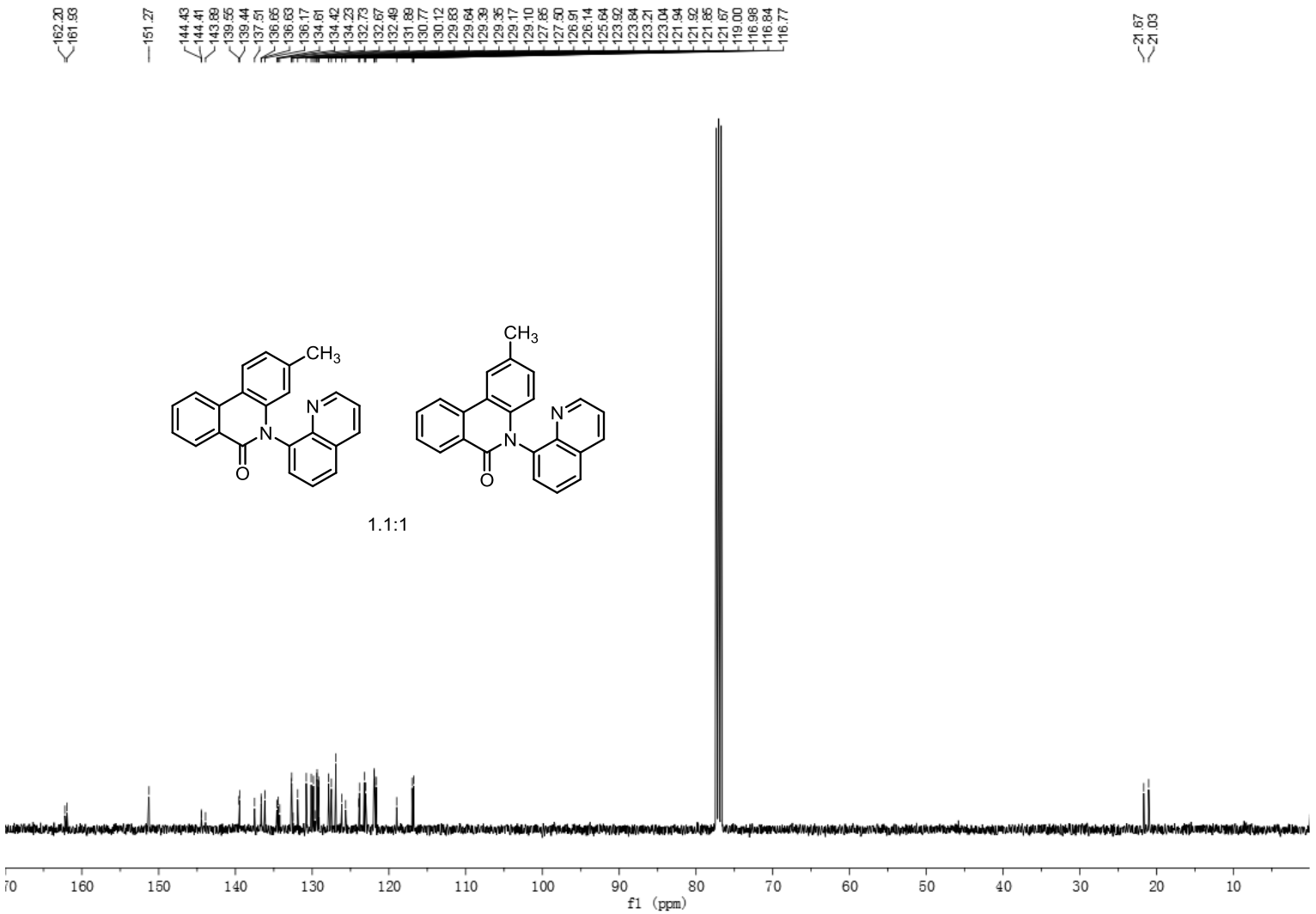
Compound **3ad**



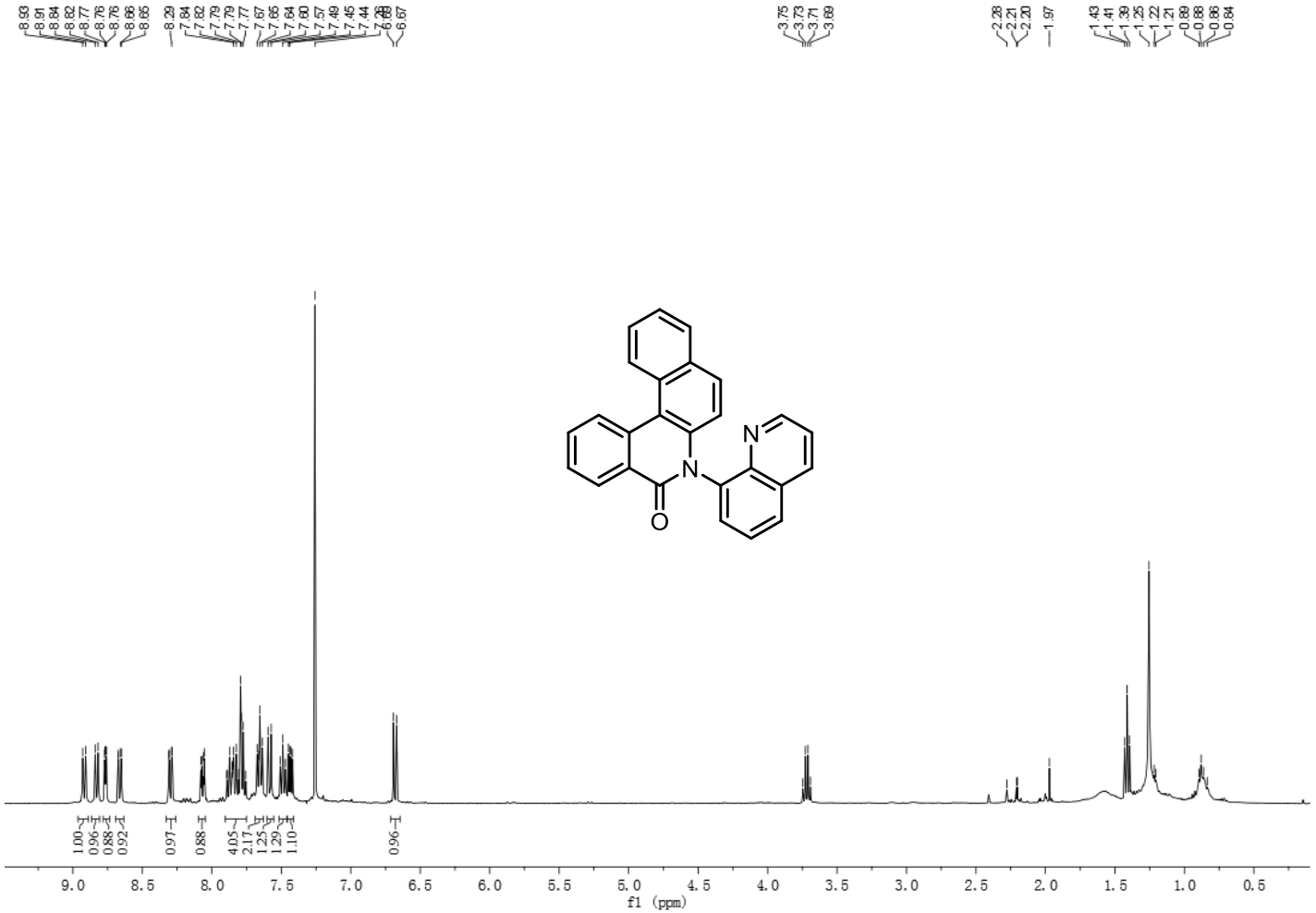

162.41
160.28
151.35
144.35
141.01
134.67
132.80
130.70
130.67
129.85
129.48
129.14
126.92
124.91
124.57
121.96
121.34
113.07
108.64
102.36
77.36
77.25
77.05
76.73
55.24
29.72
22.71
14.14
OMe
N
N
O
f1 (ppm)

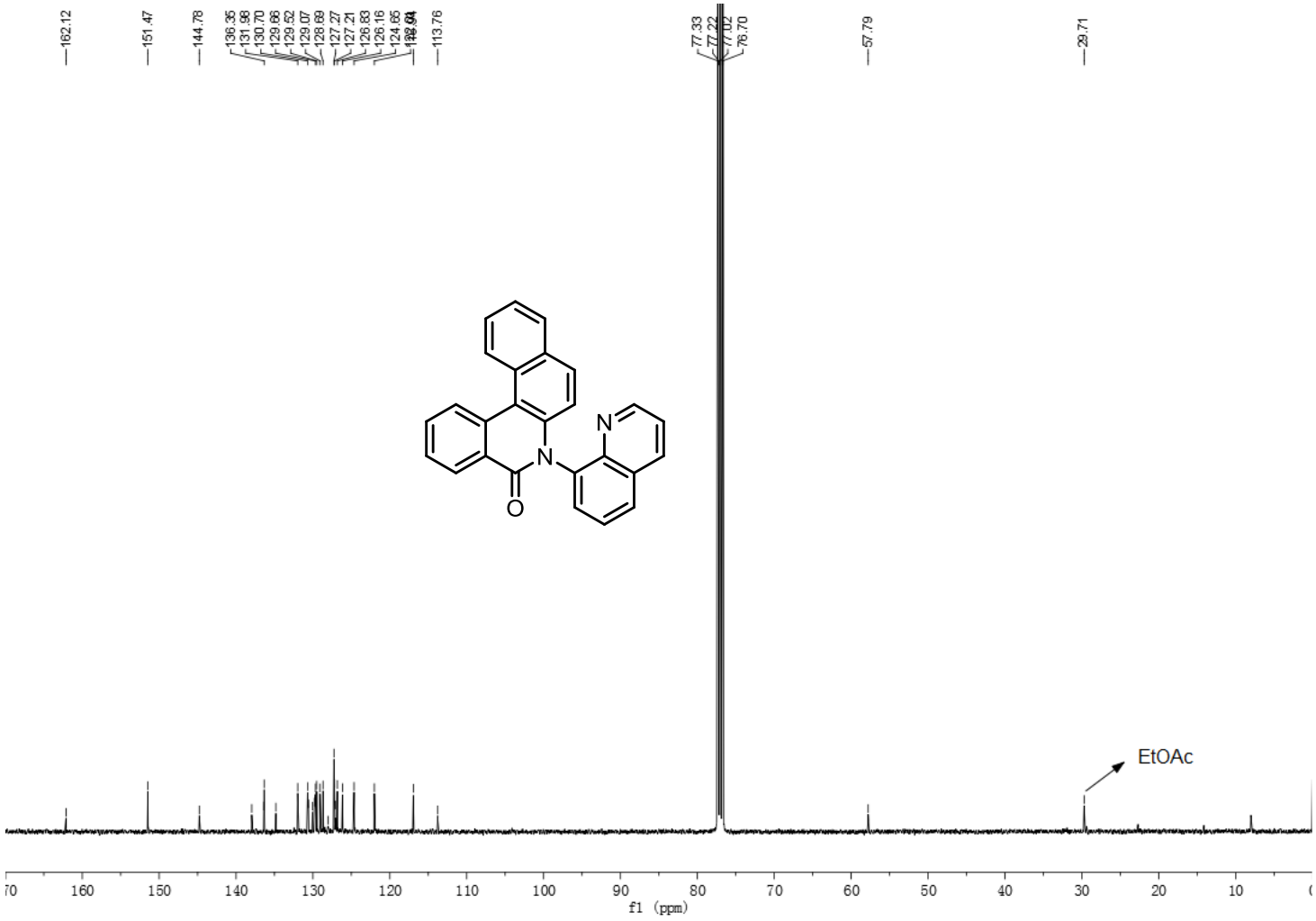
Compound **3ae** and **3af**




162.20
161.93
151.27
144.43
144.41
143.89
139.55
139.44
137.51
136.65
136.63
136.17
134.61
134.42
134.23
132.73
132.67
132.49
131.89
130.77
130.12
129.83
129.64
129.39
129.35
129.17
129.10
127.85
127.50
126.91
126.14
125.64
123.92
123.84
123.21
123.04
121.94
121.92
121.85
121.67
119.00
116.98
116.84
116.77
21.67
21.03
CH3
N
O
CH3
N
O
1.1:1
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

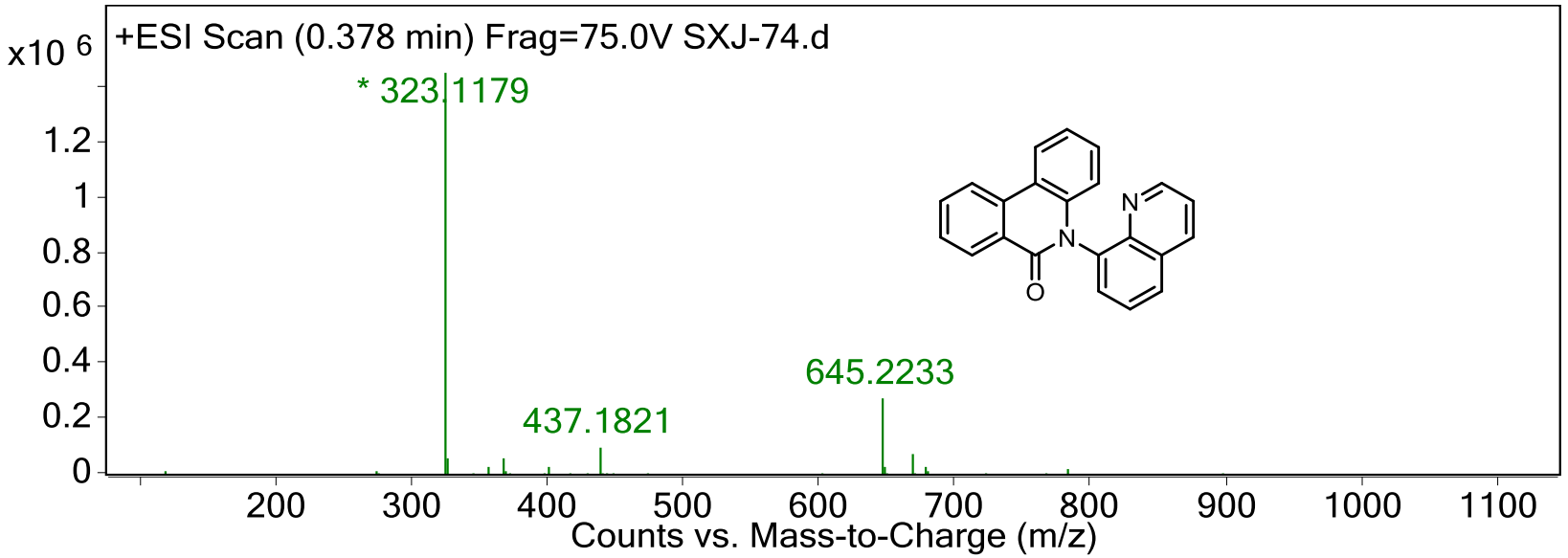
Compound **3ag**



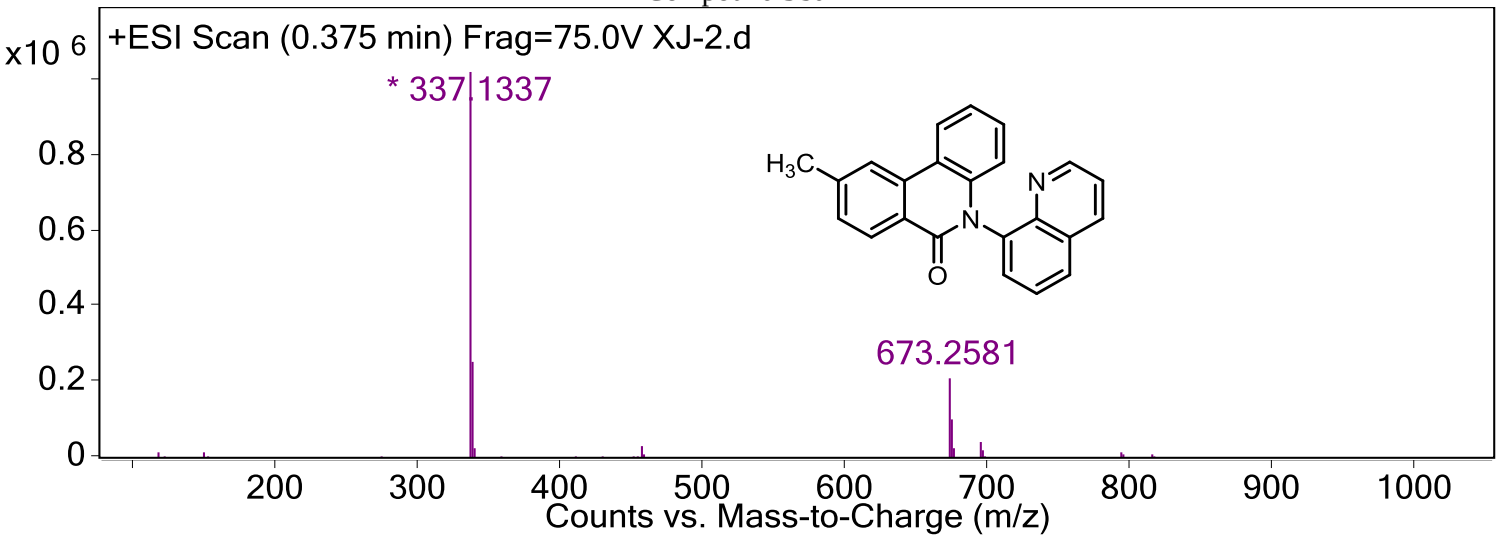

162.12
151.47
144.78
136.35
131.98
130.70
129.66
129.52
129.07
128.69
127.27
127.21
126.83
126.16
124.65
113.76
77.33
77.22
77.02
76.70
57.79
29.71
N
N
O
EtOAc
f1 (ppm)

9. Copy of HRMS Spectra

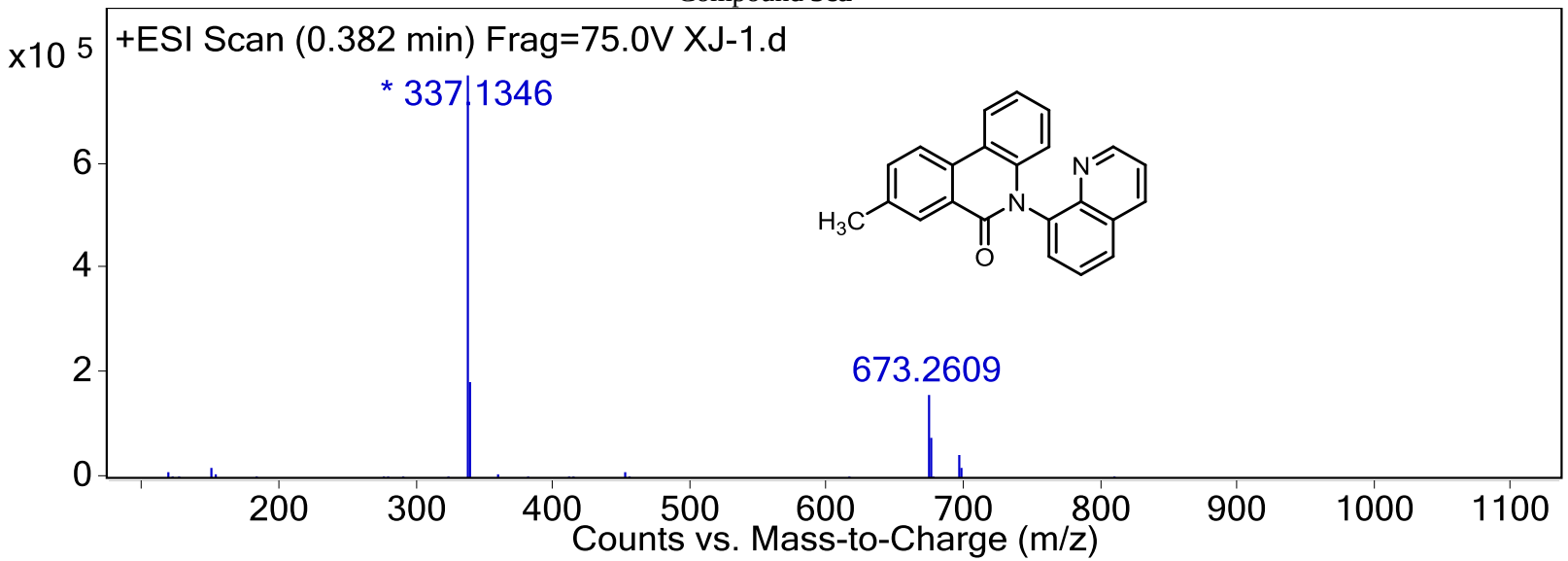
Compound **3aa**



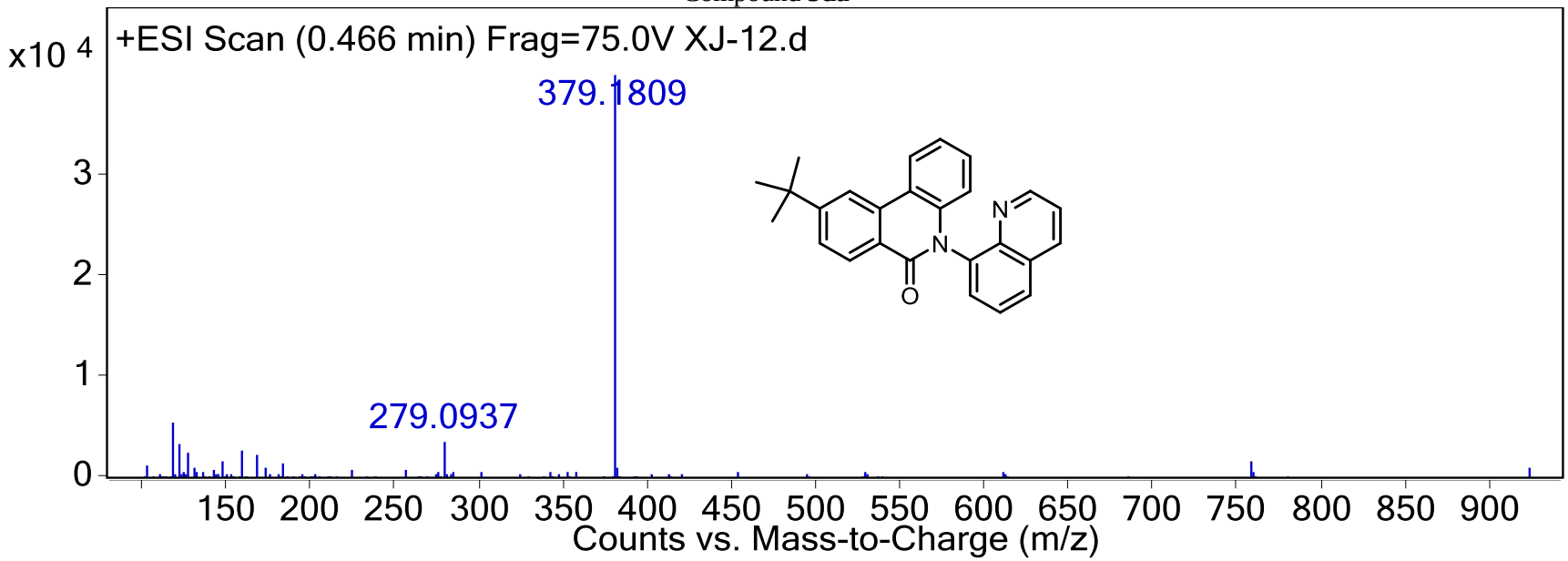
Compound **3ba**



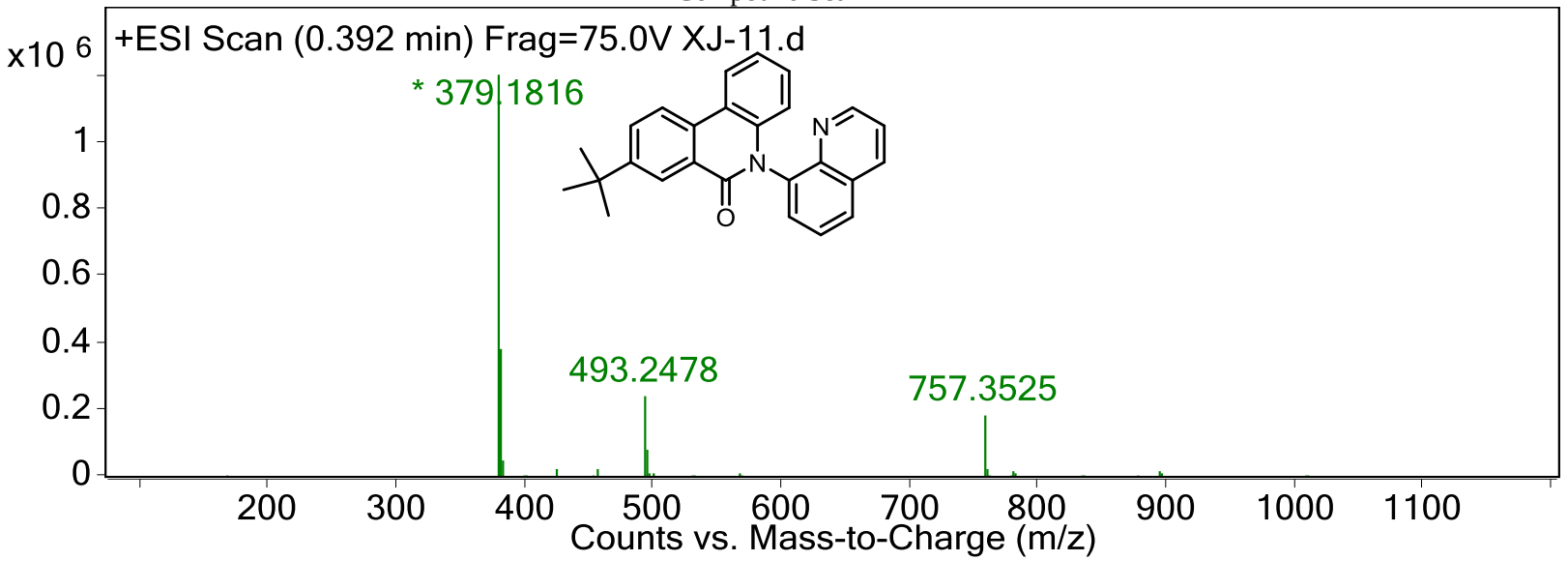
Compound **3ca**



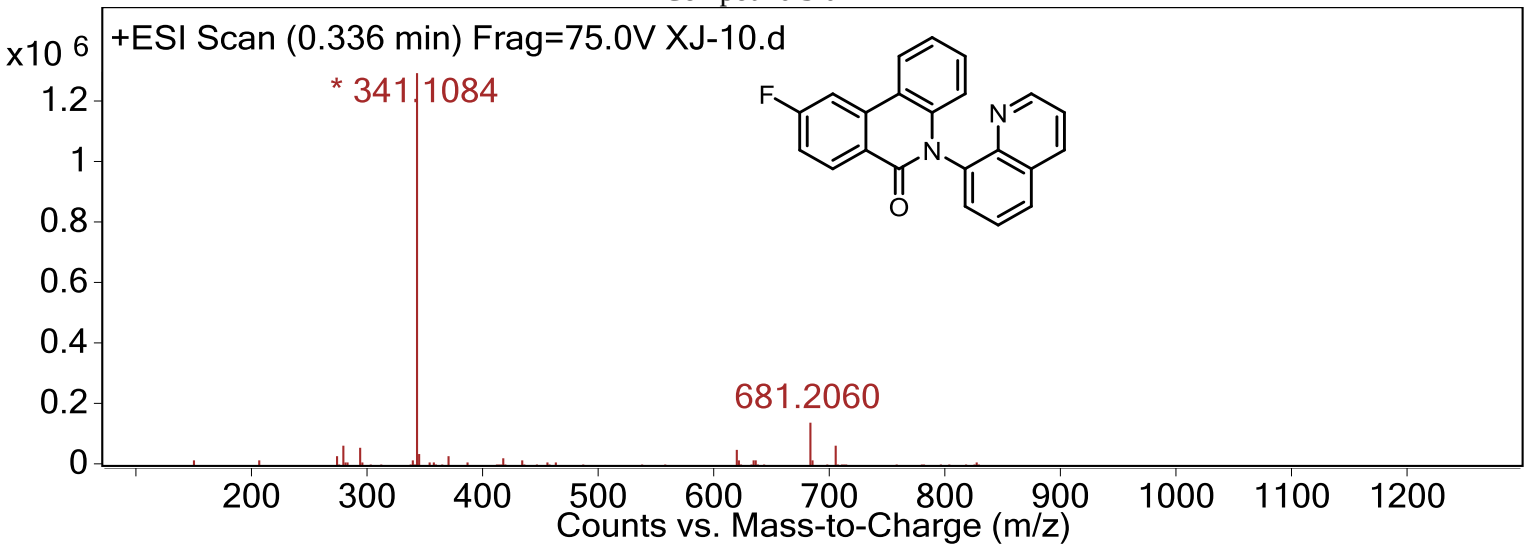
Compound **3da**



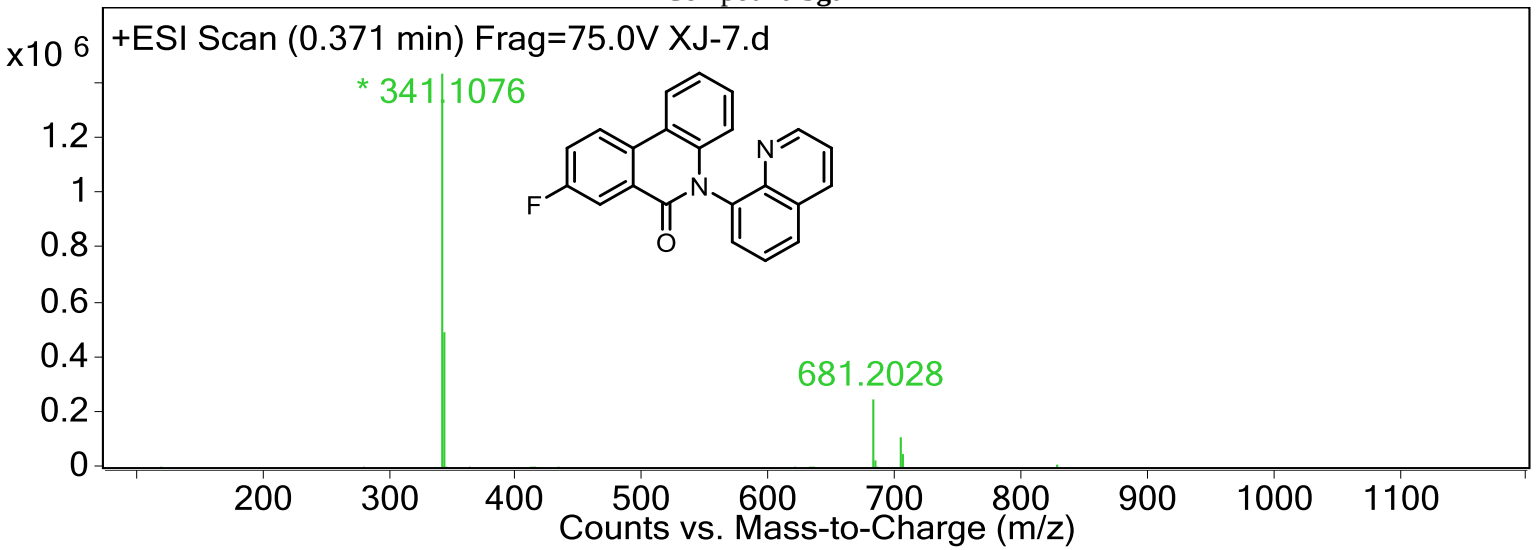
Compound **3ea**



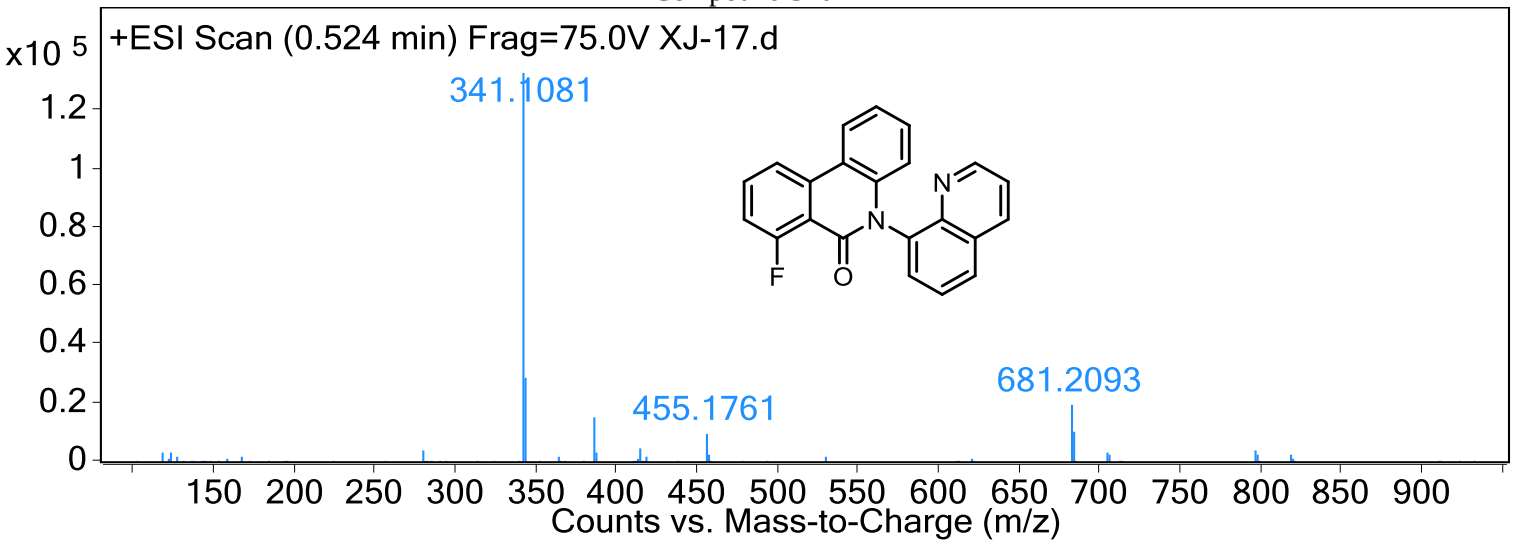
Compound **3fa**



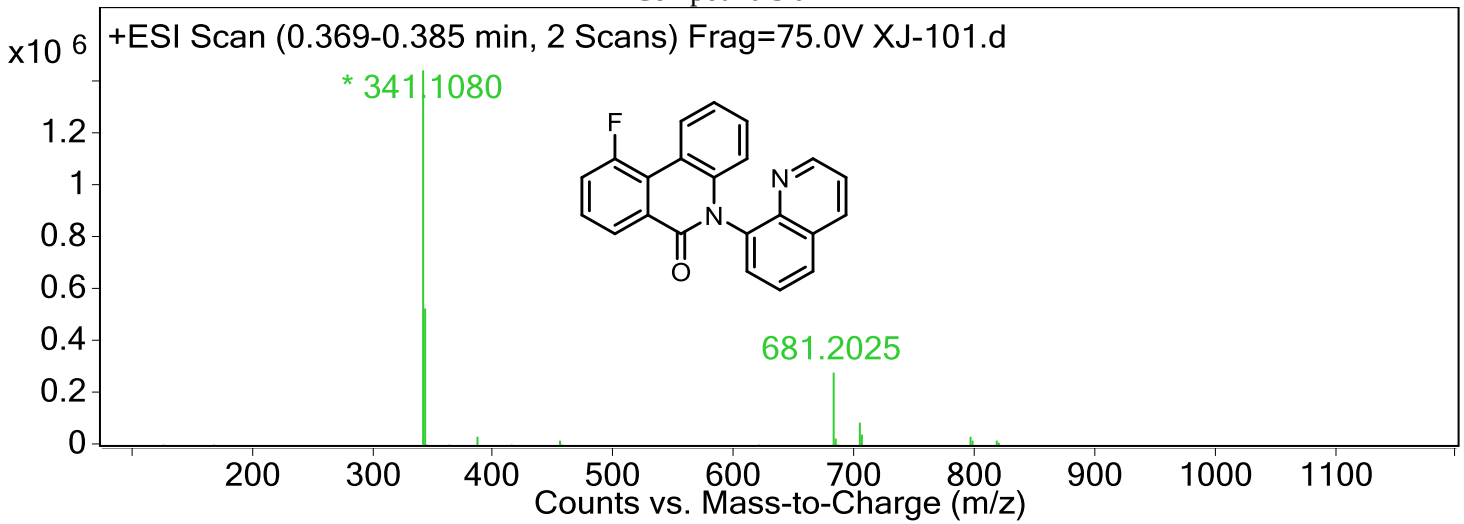
Compound **3ga**



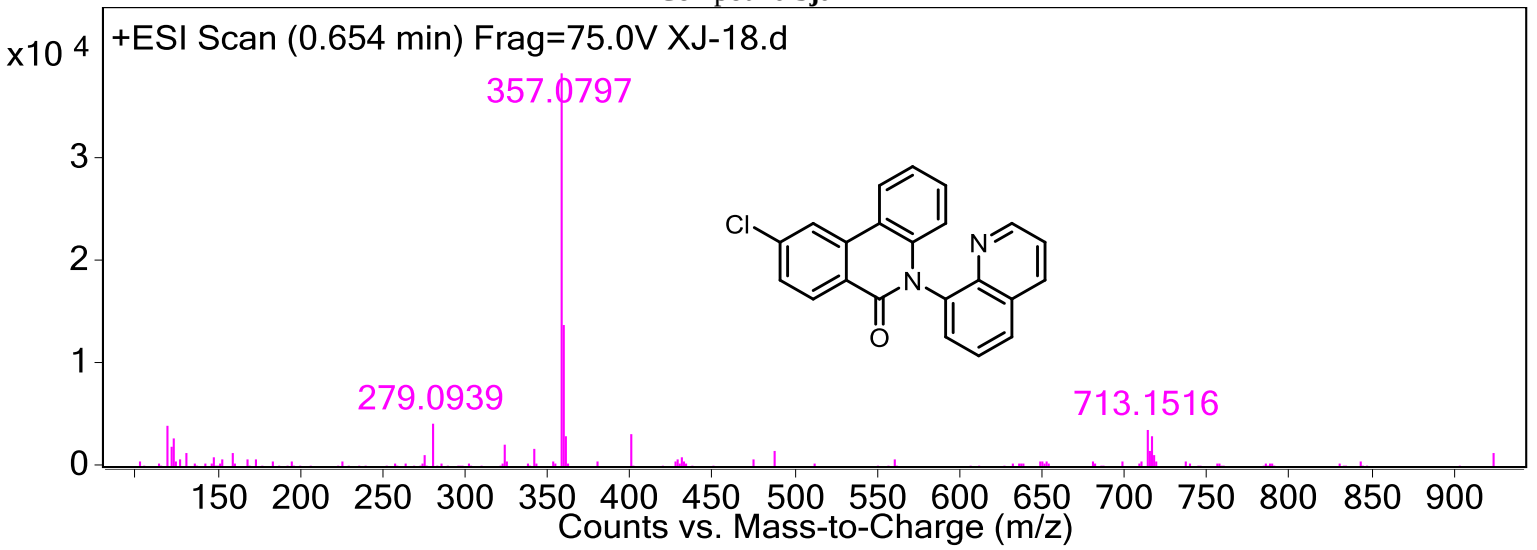
Compound **3ha**



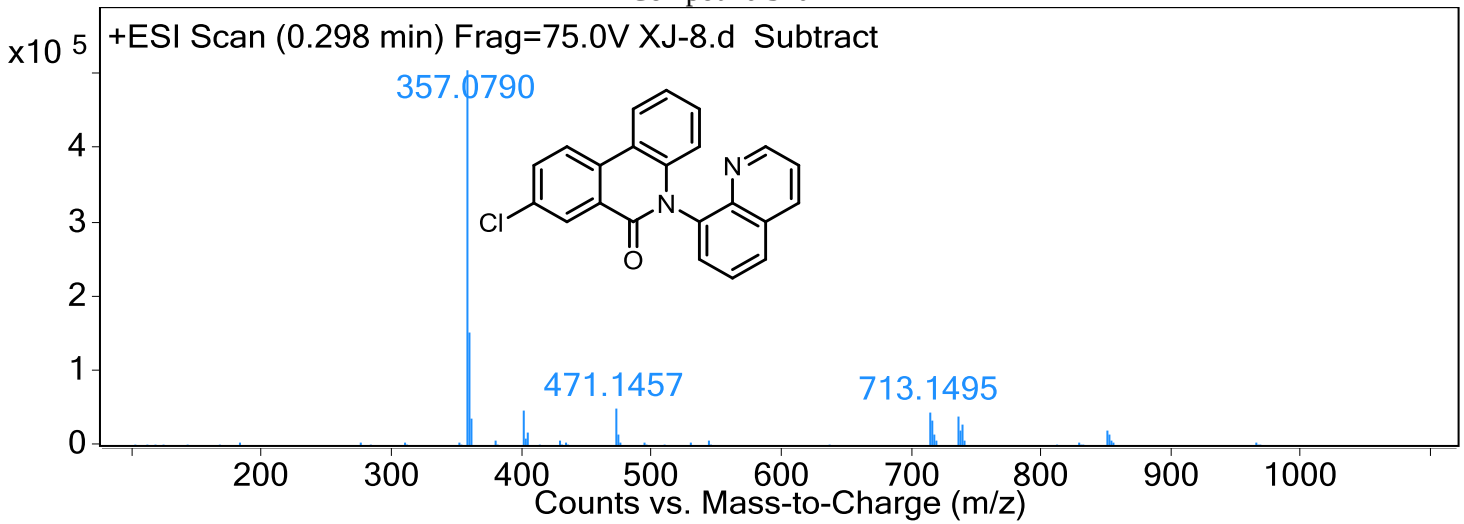
Compound **3ia**



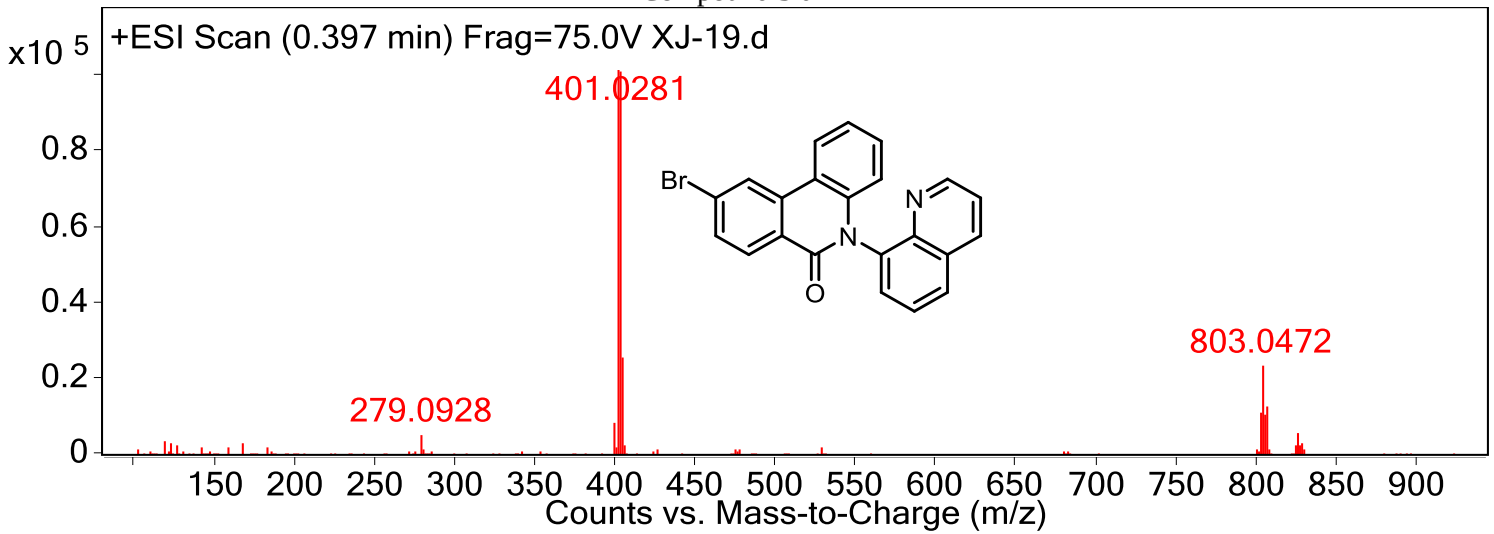
Compound **3ja**



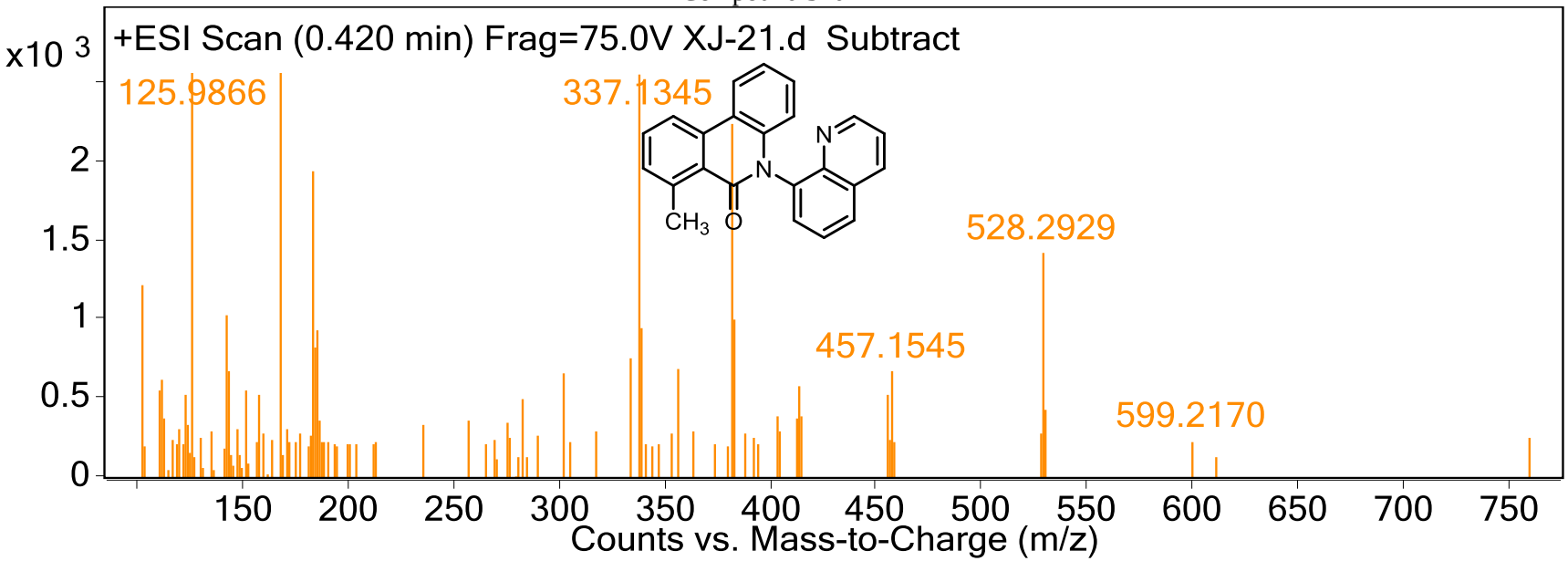
Compound **3ka**



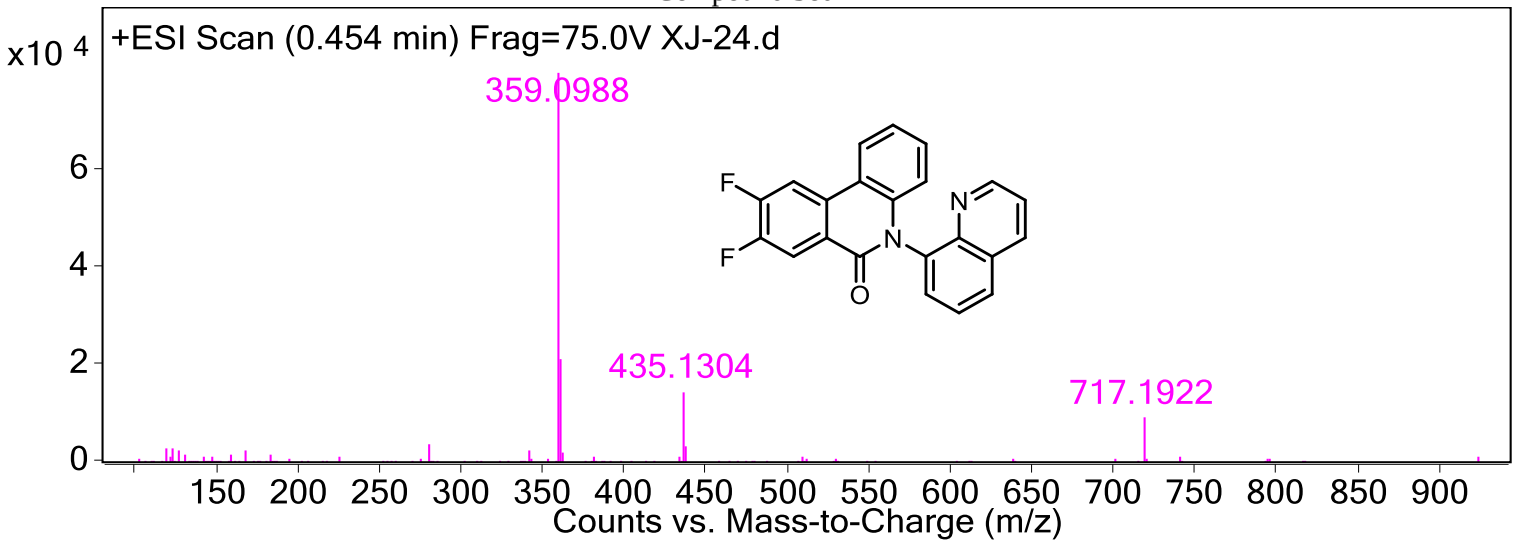
Compound **3la**



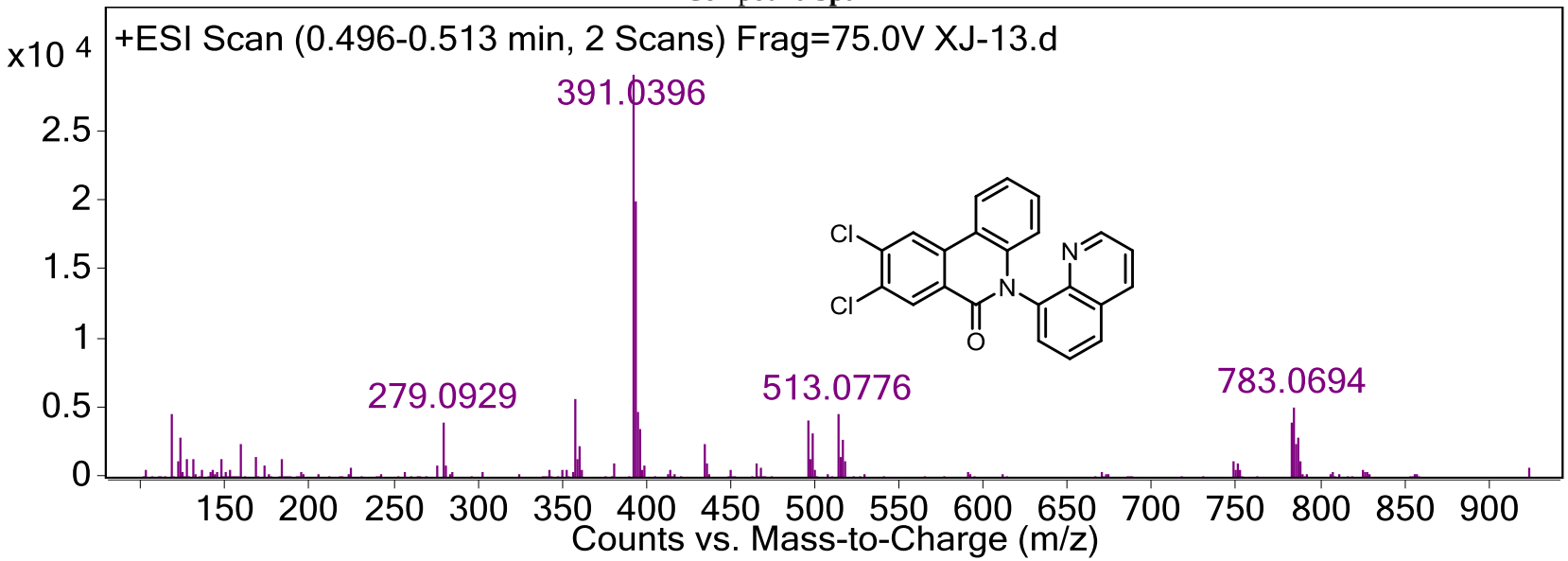
Compound **3na**



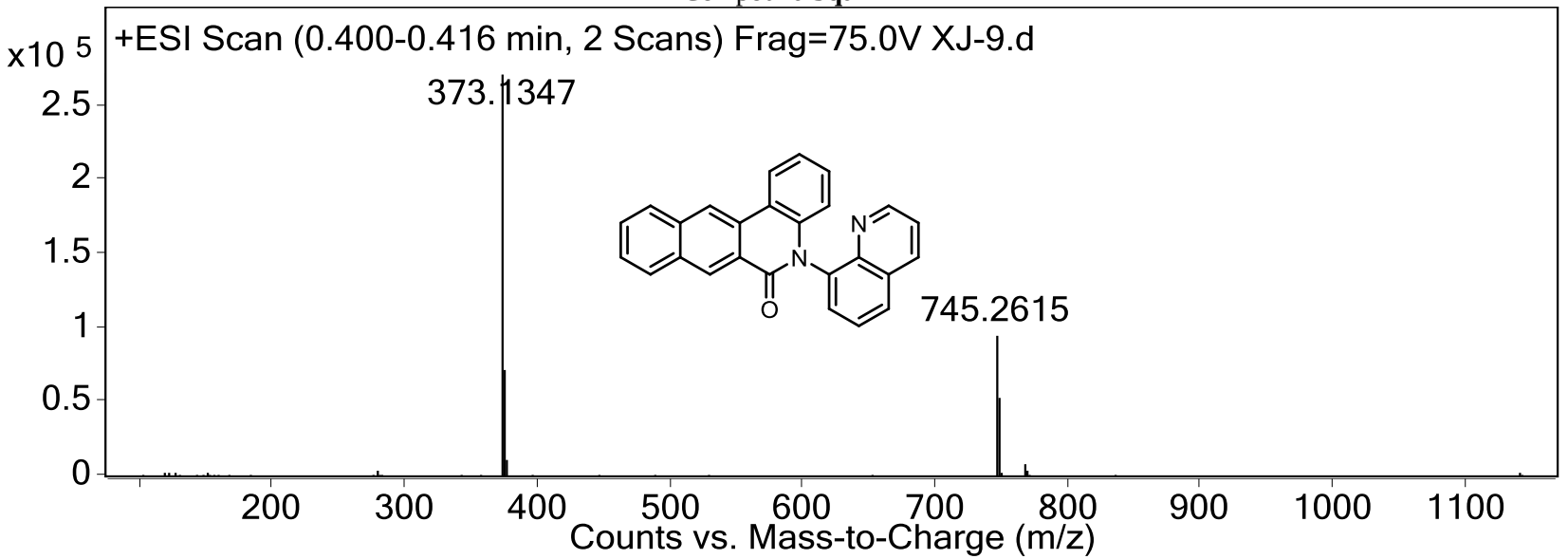
Compound **3oa**



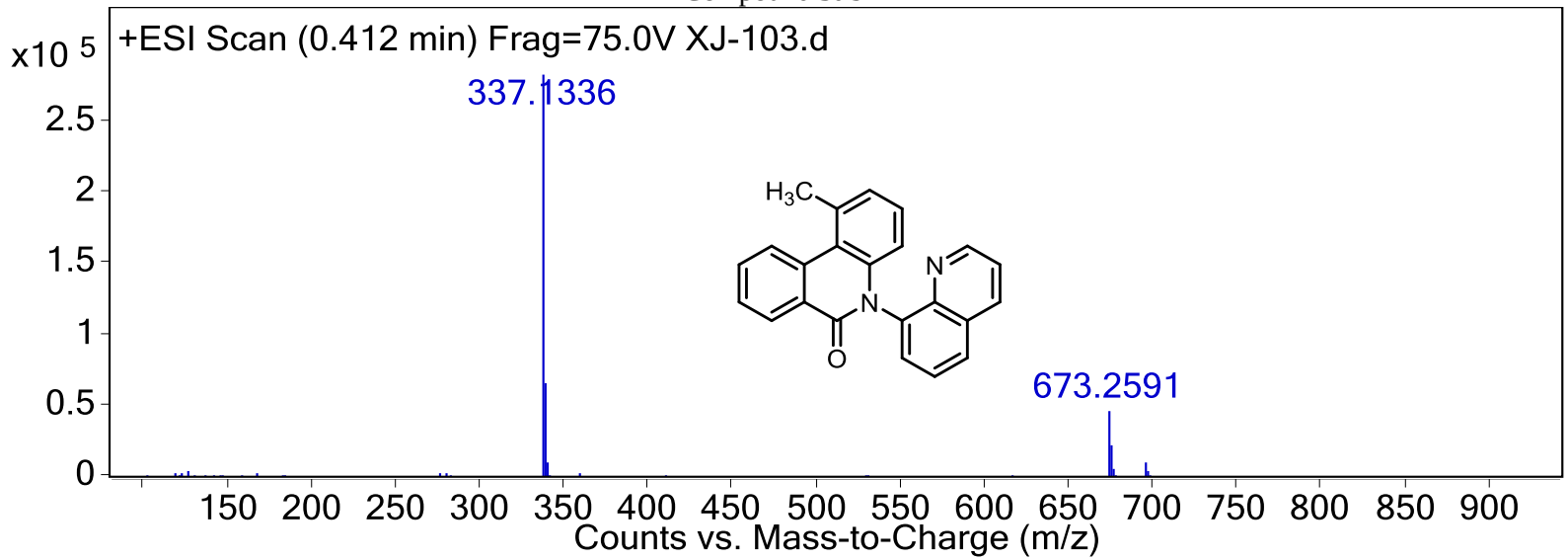
Compound **3pa**



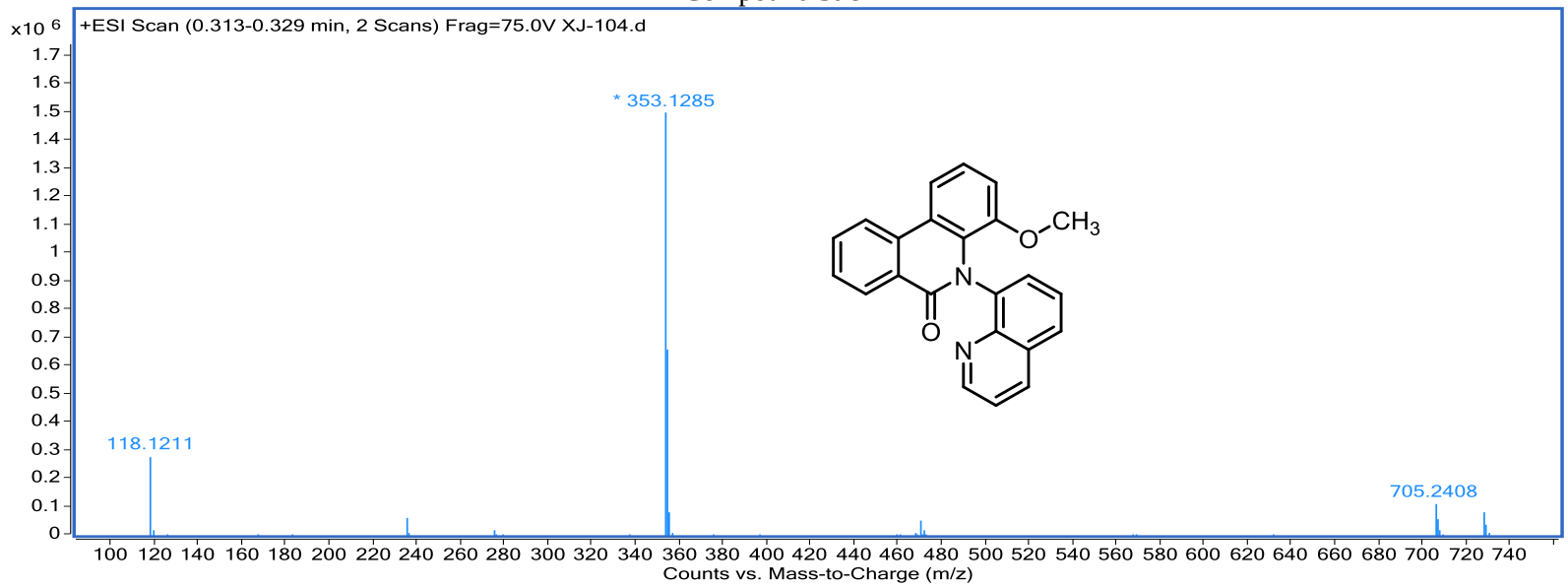
Compound **3qa**



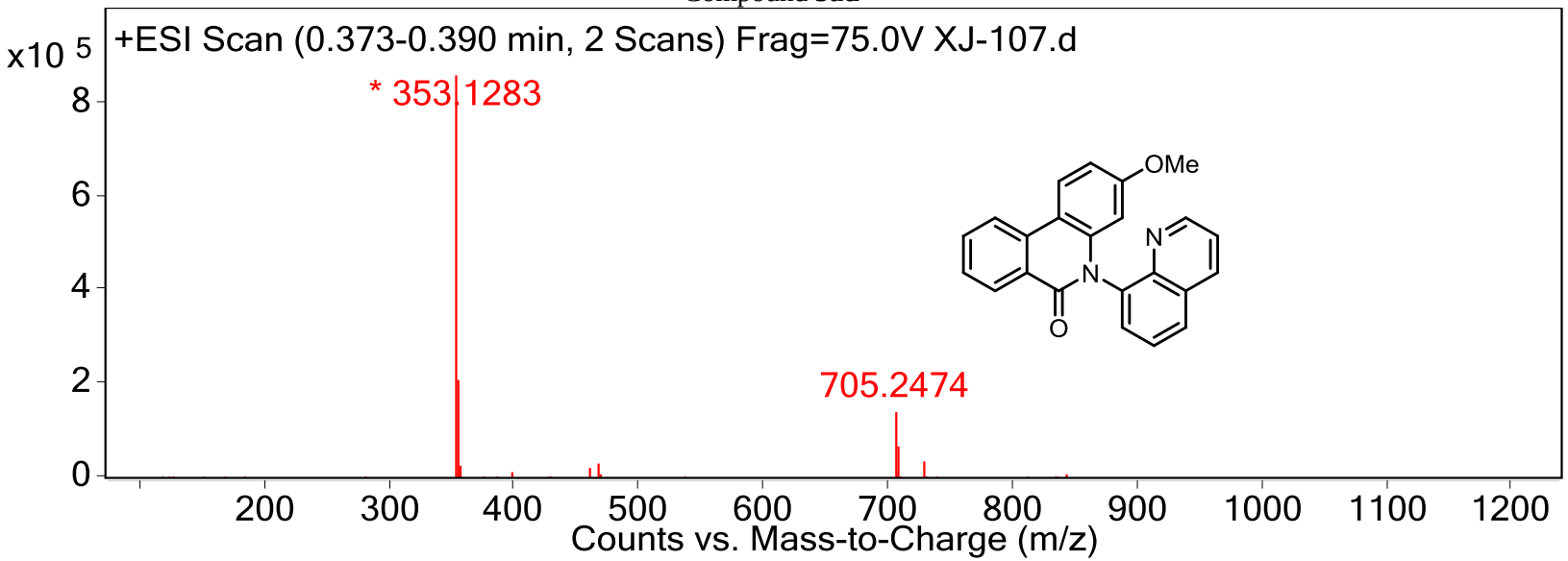
Compound **3ab**



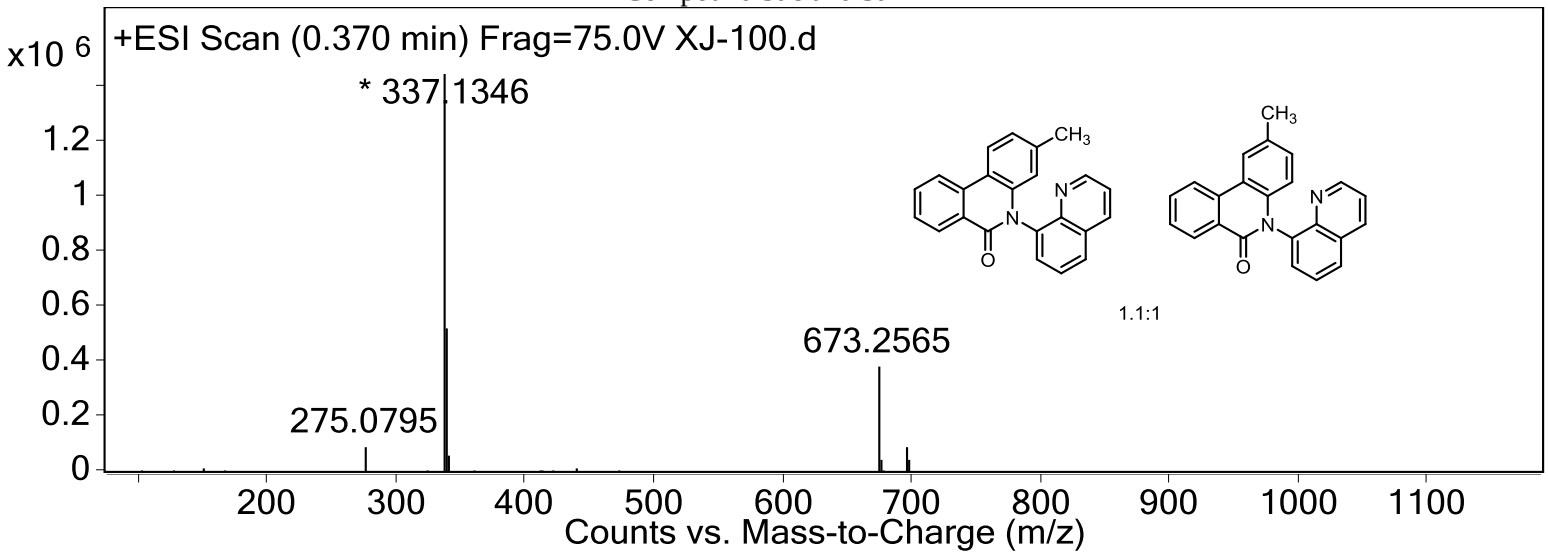
Compound **3ac**



Compound **3ad**



Compound **3ae** and **3af**



Compound **3ag**