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Supporting Information

Free-radical initiated cascade methylation or trideuteromethylation of isocyanides with dimethyl Sulfoxides

Rui Zhang[†a], Xiaoqian Shi[†a], Qinqin Yan[a], Zejiang Li*[ab], Zheng Wang[a], Haifei Yu[a], Xiaoke Wang[a], Jing Qi*[a], menglu Jiang[a]

[a]College of Chemistry & Environmental Science, Hebei University, Baoding, Hebei; [b]Key Laboratory of Medicinal Chemistry and Molecular Diagnosis of Ministry of Education, Baoding, Hebei, 071002, P. R. China

E-mail: lizejiang898@126.com; qijing634@126.com

General Information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance Ⅲ 600 spectrometer in $CDCl_3$ with TMS as internal standard. Mass spectra were determined on a Hewlett Packard 5988A spectrometer by direct inlet at 70 eV. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II. Element analysis (EA) data were measured on a Vario EL. All products were identified by ^{1}H and ^{13}C NMR, MS, HRMS. The starting materials were purchased from Energy, J&K Chemicals or Aldrich and used without further purification.

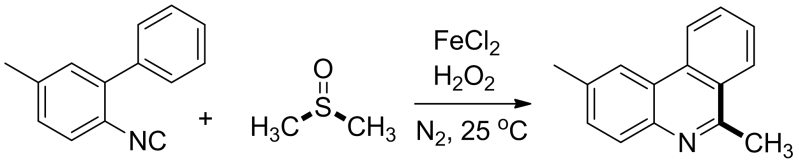
Typical procedure

(1) A mixture of isocyanides (1 equiv., 0.25 mmol), Iron(II) chloride (0.2 equiv., 0.05 mmol), Hydrogen peroxide (3 eq, 0.75 mmol) and DMSO (3 mL) was stirred at 25℃ under nitrogen condition for 6 h in a sealed tube (15 mL). After the reaction finished, the mixture was extracted

with ethyl acetate and water, evaporated under vacuum and purified by column chromatography to afford the desired product.

(2) A mixture of isocyanides (1 equiv., 0.25 mmol), Iron(II) chloride (0.2 equiv., 0.05 mmol), Hydrogen peroxide (3 eq, 0.75 mmol) and DMSO-d^6 (1 mL) was stirred at 20℃ under nitrogen condition for 12 h in a sealed tube (15 mL). After the reaction finished, the mixture was extracted with ethyl acetate and water, evaporated under vacuum and purified by column chromatography to afford the desired product.

The modification of the methylation reaction condition



Entry	Catalyst (equiv)	Hydrogen peroxide (30 %), (equiv)	t/h	Yield (%)[b]
1	$FeCl_2$ (0.5)	3	3	52
2	$FeCl_2$ (0.5)	3	6	55
3	$FeCl_2$ (0.5)	3	10	52
4[c]	$FeCl_2$ (0.5)	3	6	30
5[d]	$FeCl_2$ (0.5)	3	6	40
6[e]	$FeCl_2$ (0.5)	3	6	50
7	-	3	6	n. r.
8	$FeCl_2$ (0.1)	3	6	63
9	$FeCl_2$ (0.2)	3	6	70
10	$FeCl_2$ (0.3)	3	6	55
11	$FeCl_2$ (0.4)	3	6	55
12	$FeCl_2$ (0.2)	1	6	20
13	$FeCl_2$ (0.2)	2	6	36
14	$FeCl_2$ (0.2)	4	6	56
15[f]	$FeCl_2$ (0.2)	3	6	60
16	$CoCl_2$ (0.2)	3	6	n. r.
17	$NiCl_2$ (0.2)	3	6	n. r.
18	CuCl (0.2)	3	6	n. r.
19[g]	$FeCl_2$ (0.2)	3	6	n. r.

20[h]	$FeCl_2$ (0.2)	3	6	n. r.

[a] Reaction conditions: *2*-isocyano-5-methyl-1,1'-biphenyl (1 equiv., 0.25 mmol), DMSO (3 mL), 25 ℃, N_2. [b] Isolated yields. [c] DMSO (1 mL). [d] DMSO (2 mL). [e] DMSO (4 mL). [f]50℃. [g]DMF(3 mL). [h]CH_3CN(3 mL).

Physical data and references for the following products

All known compounds are determined by ^1H NMR and ^{13}C NMR, MS analysis and compared with which were cited in the following references, and the new compounds were further confirmed by HRMS.

References:

1. Z. J. Li, F. H. Fan, J. Yang and Z.-Q. Liu, *Org. Lett.* 2014, **16**, 3396.

2. Z. Xu, C. Yan and Z.-Q. Liu, *Org. Lett.* 2014, **16**, 5670.

3. T. Xiao, L. Li, G. Lin, Q. Wang, P. Zhang, Z.-W. Mao and L. Zhou, *Green Chemistry.* 2014, **16**, 2418.

4. Q. Dai, J. Yu, X. Feng, Y. Jiang, H. Yang and J. Cheng, *Advanced Synthesis & Catalysis.* 2014, **356**, 3341.

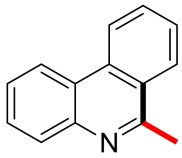
5. R. Caporaso, S. Manna, S. Zinken, A. R. Kochnev, E. R. Lukyanenko, A. V. Kurkin and A. P. Antonchick, *Chem. Commun*. 2016, **52**, 12486.

6. Z.-J. Li, X. Cui, L. Niu, Y. Ren, M. Bian, X. Yang, B. Yang, Q.-Q. Yan and J. Zhao, *Adv. Synth. & Catal*. 2017, **359**, 246.

Physical data for the following products:

1. 6-methylphenanthridine

A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 69-71℃.



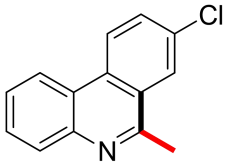
^1H NMR (600 MHz, $CDCl_3$): δ 8.63 (d, J = 8.4 Hz, 1H), 8.54 (dd, J = 8.4, 1.2 Hz, 1H), 8.22 (dd, J = 7.8, 0.6 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.84 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.72 – 7.68 (m, 2H), 7.63 – 7.61 (m, 1H), 3.05 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 158.8, 143.7, 132.6, 130.4, 129.4, 128.6, 127.3, 126.5, 126.3, 125.9, 123.8, 122.3, 121.9, 23.3.

MS(EI): m/z(%): 193(100.0), 178(14.3), 165(14.0).

2. 8-chloro-6-methylphenanthridine

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 105-107℃.



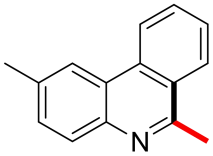
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.50 (d, *J* = 9.0 Hz, 1H), 8.44 (d, *J* = 7.8 Hz, 1H), 8.14 (d, *J* = 1.8 Hz, 1H), 8.08 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.75 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.72 – 7.70 (m, 1H), 7.62 – 7.60 (m, 1H), 2.99 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 157.7, 143.6, 133.1, 130.9, 130.9, 129.5, 128.9, 126.8, 126.7, 125.8, 124.1, 123.1, 121.8, 23.2.

MS(EI): m/z(%): 230(4.9), 229(30.6), 228(16.7), 227(100.0), 192(9.4), 191(7.0), 190(6.2), 165(5.9).

3. 2,6-dimethylphenanthridine

A white soild after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 69-71℃.



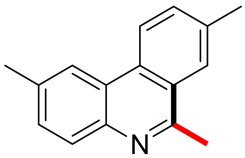
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.61 (d, *J* = 8.4 Hz, 1H), 8.31 (s, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.81 (t, *J* = 8.4 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.53 (dd, *J* = 7.8, 1.8 Hz, 1H), 3.02 (s, 3H), 2.61 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 157.8, 142.0, 136.0, 132.3, 130.3, 130.2, 129.1, 127.1, 126.5, 126.0, 123.6, 122.3, 121.6, 23.3, 21.9.

MS(EI): *m/z*(%): 208(17.6), 207(100.0), 206(35.9), 192(6.9), 190(5.2), 165(8.1).

4. 2,6,8-trimethylphenanthridine

A white soild after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 106-108℃.



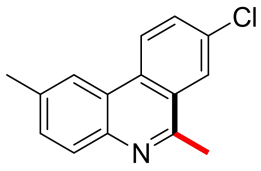
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.50 (d, J = 8.4 Hz, 1H), 8.28 (s, 1H), 7.97 – 7.96 (m, 2H), 7.65 (dd, J = 8.4, 1.8 Hz, 1H), 7.50 (dd, J = 8.4, 1.2 Hz, 1H), 3.00 (s, 3H), 2.60 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 157.5, 141.7, 137.0, 136.0, 131.9, 130.2, 129.8, 129.0, 126.1, 126.0, 123.7, 122.2, 121.4, 23.3, 21.9, 21.8

MS(EI): m/z(%): 222(16.8), 221(100.0), 220(37.1), 206(38.0).

5. 8-chloro-2,6-dimethylphenanthridine

A white soild after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), M. P.: 132-134°C.



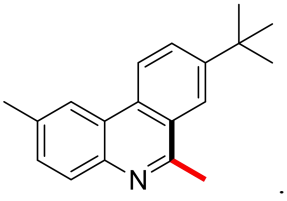
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.51 (dd, J = 8.4, 2.4 Hz, 1H), 8.22 (s, 1H), 8.13 (s, 1H), 7.97 (d, J = 7.8 Hz, 1H), 7.74 (d, J = 9.0, 1H), 7.53 (d, J = 7.8 Hz, 1H), 2.98 (s, 3H), 2.60 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 156.6, 142.0, 136.6, 133.0, 130.7, 130.7, 130.6, 129.2, 126.9, 125.8, 124.0, 122.9, 121.4, 23.2, 21.9.

HRMS (ESI, m/z): Calculated for $C_{15}H_{13}ClN$ $(M+H)^+$ 242.0731, found 242.0733.

6. 8-(tert-butyl)-2,6-dimethylphenanthridine

A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 109-110℃.



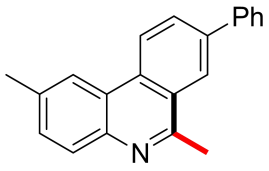
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.54 (d, J = 8.4 Hz, 1H), 8.29 (s, 1H), 8.14 (d, J = 1.8 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.90 (dd, J = 8.4, 1.8 Hz, 1H), 7.50 (dd, J = 8.4, 1.8 Hz, 1H), 3.04 (s, 3H), 2.61 (s, 3H), 1.48 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 157.9, 150.2, 141.8, 135.9, 130.2, 129.9, 128.9, 128.6, 125.9, 123.6, 122.1, 121.9, 121.4, 35.1, 31.4, 23.3, 21.9.

HRMS (ESI, m/z): Calculated for $C_{19}H_{22}N$ $(M+H)^+$ 264.1747, found 264.1751.

7. 2,6-dimethyl-8-phenylphenanthridine

A white soild after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 118-120℃.



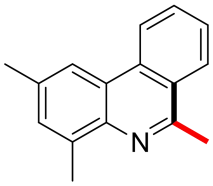
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.66 (d, *J* = 9.0 Hz, 1H), 8.37 (d, *J* = 1.8 Hz, 1H), 8.33 (s, 1H), 8.06 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 3H), 7.44 (t, *J* = 7.2 Hz, 1H), 3.08 (s, 3H), 2.63 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 157.9, 142.0, 140.5, 140.0, 136.2, 131.4, 130.3, 129.5, 129.1, 129.0, 127.8, 127.4, 126.3, 124.6, 123.4, 122.9, 121.6, 23.3, 21.9.

HRMS (ESI, m/z): Calculated for $C_{21}H_{18}N$ $(M+H)^+$ 284.1434, found 284.1438.

8. 2,4,6-trimethylphenanthridine

A white soild after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 99-100℃.



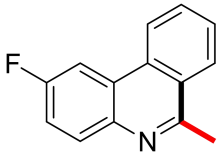
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.61 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 8.4 Hz, 2H), 7.80 – 7.78 (m, 1H), 7.66 (t, J = 7.8 Hz, 1H), 7.41 (s, 1H), 3.04 (s, 3H), 2.84 (s, 3H), 2.57 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 156.2, 140.8, 136.8, 135.3, 132.6, 131.0, 129.8, 126.8, 126.3, 125.7, 123.4, 122.5, 119.4, 23.6, 21.8, 18.2.

HRMS (ESI, m/z): Calculated for $C_{16}H_{16}N$ $(M+H)^+$ 222.1277, found 222.1280.

9. 2-fluoro-6-methylphenanthridine

A yellow soild after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 110-112℃.



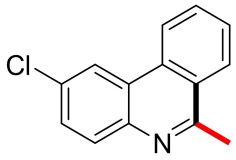
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.50 (d, *J* = 7.8 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.14 (dd, *J* = 10.2, 3.0 Hz, 1H), 8.08 (dd, *J* = 9.0, 6.0 Hz, 1H), 7.86 (t, J = 7.8 Hz, 1H), 7.74 (t, J = 7.8 Hz, 1H), 7.46 – 7.43 (m, 1H), 3.02 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 161.7, 160.1, 158.0, 140.6, 131.5 (d, *J* = 9.0 Hz), 130.5, 127.9, 126.6, 125.9, 125.0 (d, *J* = 9.0 Hz), 122.5, 117.4 (d, *J* = 24.0 Hz), 106.9 (d, *J* = 22.9 Hz), 23.3.

MS(EI): *m/z*(%): 211(100.0), 196(12.0), 183(17.0).

10. 2-chloro-6-methylphenanthridine

A white soild after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 103-105℃.



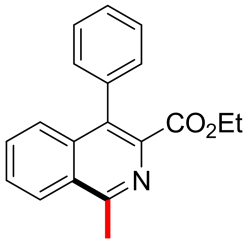
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.49 (d, *J* = 8.4 Hz, 1H), 8.44 (d, *J* = 1.2 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 7.83 (t, *J* = 8.4 Hz, 1H), 7.72 – 7.70 (m, 1H), 7.62 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.00 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 159.1, 142.1, 132.1, 131.5, 130.8, 130.7, 129.0, 127.9, 126.5, 126.0, 124.8, 122.3, 121.6, 23.3.

MS(EI): *m/z*(%): 230(4.9), 229(30.7), 228(17.6), 227(100.0), 192(7.5), 191(6.5), 190(6.1), 165(6.2).

13. ethyl 1-methyl-4-phenylisoquinoline-3-carboxylate

A white soild after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1), m. p. 104-106℃.



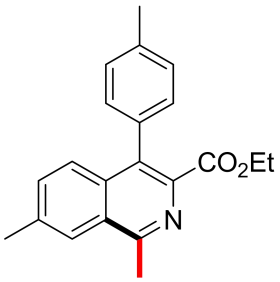
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.67 (ddd, *J* = 8.4, 5.4, 3.0 Hz, 1H), 7.65 – 7.62 (m, 2H), 7.49 – 7.43 (m, 3H), 7.34 (dd, *J* = 7.8, 1.8 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.06 (s, 3H), 0.97 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 167.6, 158.4, 141.4, 136.4, 135.4, 131.9, 130.4, 129.9, 128.1, 128.0, 127.8, 127.7, 126.9, 125.6, 61.2, 22.6, 13.6.

HRMS (ESI, m/z): Calculated for $C_{19}H_{18}NO_2$ $(M+H)^+$ 292.1332, found 292.1331.

14. ethyl 1,7-dimethyl-4-(p-tolyl)isoquinoline-3-carboxylate

A light yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



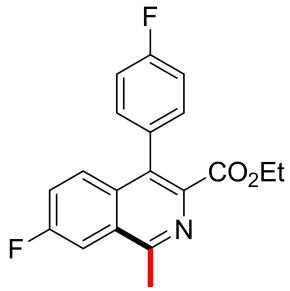
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.45 (dd, J = 9.0, 1.2 Hz, 1H), 7.27 (d, J = 7.8 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 4.14 (q, J = 7.2 Hz, 2H), 3.02 (s, 3H), 2.57 (s, 3H), 2.45 (s, 3H), 1.02 (t, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 167.7, 157.4, 140.6, 138.2, 137.3, 133.7, 133.5, 132.4, 132.0, 129.8, 128.8, 128.0, 126.8, 124.6, 61.1, 22.6, 21.9, 21.3, 13.7.

HRMS (ESI, m/z): Calculated for $C_{21}H_{22}NO_2$ $(M+H)^+$ 320.1645, found 320.1644.

15. ethyl 7-fluoro-4-(4-fluorophenyl)-1-methylisoquinoline-3-carboxylate

A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1), m. p. 130-132℃.



^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79 (dd, J = 9.6, 2.4 Hz, 1H), 7.61 (dd, J = 9.0, 5.4 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.31 – 7.28 (m, 2H), 7.18 (t, J = 8.4 Hz, 2H), 4.15 (q, J = 7.2 Hz, 2H), 3.01 (s, 3H), 1.04 (t, J = 7.2 Hz, 3H).

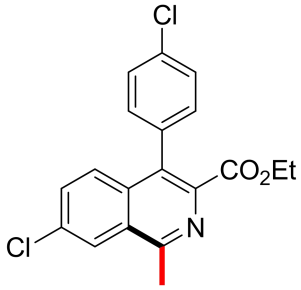
^{13}C NMR (150 MHz, $CDCl_3$): δ 167.2, 162.1 (dd, J = 246.2, 162.6 Hz), 157.9, 141.1, 132.6, 131.9 (d, J = 3.6 Hz), 131.5 (d, J = 8.1 Hz), 130.8, 129.7 (d, J = 8.7 Hz), 129.0

(d, J = 8.3 Hz), 120.8 (d, J = 24.6 Hz), 115.3 (d, J = 21.5 Hz), 109.5 (d, J = 21.1 Hz), 61.4, 22.6, 13.8.

HRMS (ESI, m/z): Calculated for $C_{19}H_{16}F_2NO_2$ $(M+H)^+$ 328.1144, found 328.1146.

16. ethyl 7-chloro-4-(4-chlorophenyl)-1-methylisoquinoline-3-carboxylate

A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1), m. p. 106-108℃.

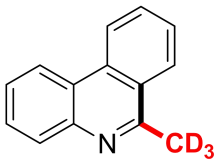


^{1}H NMR (600 MHz, $CDCl_3$): δ 8.18 (d, J = 1.8 Hz, 1H), 7.59 (dd, J = 9.0, 2.4 Hz, 1H), 7.53 (d, J = 9.0 Hz, 1H), 7.47 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 7.8 Hz, 2H), 4.16 (q, J = 7.2 Hz, 2H), 3.03 (s, 3H), 1.06 (t, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 167.0, 158.0, 141.5, 134.5, 134.3, 134.2, 133.7, 131.5, 131.2, 130.6, 128.6, 128.4, 124.8, 61.5, 22.6, 13.7.

HRMS (ESI, m/z): Calculated for $C_{19}H_{16}Cl_2NO_2$ $(M+H)^+$ 360.0553, found 360.0554.

17. A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 75-76℃.

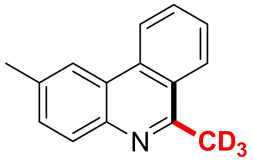


^{1}H NMR (600 MHz, $CDCl_3$): δ 8.63 (d, J = 8.4 Hz, 1H), 8.54 (d, J = 7.8 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.71 (td, J = 8.4, 1.2 Hz, 2H), 7.64 – 7.61 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 158.8, 143.8, 132.6, 130.4, 129.4, 128.6, 127.3, 126.5, 126.3, 125.9, 123.8, 122.3, 121.9, 23.0 – 22.6 (m).

HRMS (ESI, m/z): Calculated for $C_{14}H_9D_3N$ $(M+H)^+$ 197.1199, found 197.1192.

18. A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), m. p. 78-79℃.

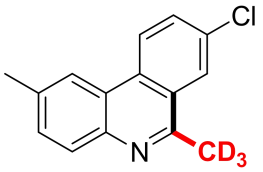


^{1}H NMR (600 MHz, $CDCl_3$): δ 8.61 (d, *J* = 8.4 Hz, 1H), 8.32 (s, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.83 – 7.80 (m, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.53 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.61 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 157.8, 142.0, 136.1, 132.4, 130.3, 130.2, 129.1, 127.1, 126.5, 126.0, 123.6, 122.3, 121.6, 23.0 – 22.5 (m), 21.9.

HRMS (ESI, m/z): Calculated for $C_{15}H_{11}D_3N$ $(M+H)^+$ 211.1356, found 211.1358.

19. A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1), m. p. 135-137℃.

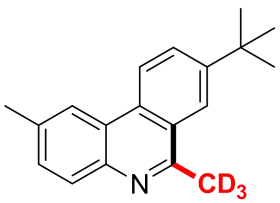


^{1}H NMR (600 MHz, $CDCl_3$): δ 8.49 (d, *J* = 8.4 Hz, 1H), 8.21 (s, 1H), 8.11 (d, *J* = 1.2 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 2.59 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 156.6, 141.9, 136.6, 132.9, 130.7, 130.6, 129.2, 126.8, 125.8, 124.0, 122.9, 121.4, 23.0 – 22.5 (m), 21.9.

HRMS (ESI, m/z): Calculated for $C_{15}H_{10}D_3ClN$ $(M+H)^+$ 245.0919, found 245.0920.

20. A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1), m. p. 110-112℃.

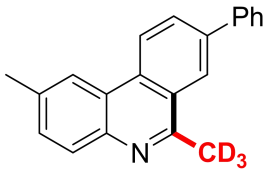


^{1}H NMR (600 MHz, $CDCl_3$): δ 8.54 (d, *J* = 9.0 Hz, 1H), 8.29 (s, 1H), 8.14 (s, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.90 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 2.61 (s, 3H), 1.48 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 157.8, 150.1, 141.8, 135.9, 130.1, 129.9, 128.9, 128.6, 125.9, 123.6, 122.1, 121.9, 121.4, 35.1, 31.3, 23.0 – 22.6 (m), 21.9.

HRMS (ESI, m/z): Calculated for $C_{19}H_{19}D_3N$ $(M+H)^+$ 267.1935, found 267.1932.

21. A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).

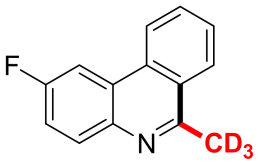


^{1}H NMR (600 MHz, $CDCl_3$): δ 8.66 (d, J = 8.4 Hz, 1H), 8.36 (s, 1H), 8.33 (s, 1H), 8.06 (dd, J = 8.4, 1.8 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 7.8 Hz, 2H), 7.54 (t, J = 7.8 Hz, 3H), 7.44 (t, J = 7.2 Hz, 1H), 2.63 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 157.8, 142.0, 140.5, 140.0, 136.2, 131.4, 130.3, 129.5, 129.1, 129.0, 127.8, 127.4, 126.4, 124.6, 123.4, 122.9, 121.6, 21.9.

HRMS (ESI, m/z): Calculated for $C_{21}H_{15}D_3N$ $(M+H)^+$ 287.1669, found 287.1667.

22. A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1), m. p. 124-126℃.

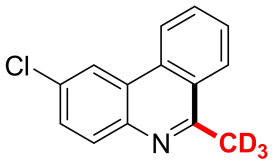


^{1}H NMR (600 MHz, $CDCl_3$): δ 8.49 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 7.8 Hz, 1H), 8.13 (dd, J = 9.6, 2.4 Hz, 1H), 8.08 (dd, J = 9.0, 5.4 Hz, 1H), 7.86 – 7.84 (m, 1H), 7.75 – 7.72 (m, 1H), 7.44 (td, J = 8.4, 2.4 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 160.9 (d, J = 244.3 Hz), 158.0, 140.6, 132.0, 131.5 (d, J = 9.0 Hz), 130.5, 127.9, 126.6, 126.0, 125.0 (d, J = 9.2 Hz), 122.5, 117.4 (d, J = 24.0 Hz), 106.9 (d, J = 23.1 Hz).

HRMS (ESI, m/z): Calculated for $C_{14}H_8D_3FN$ $(M+H)^+$ 215.1105, found 215.1099.

23. A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1), m. p. 109-111℃.

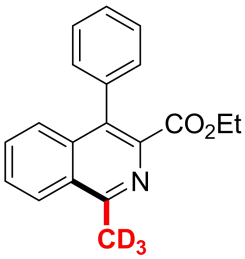


^{1}H NMR (600 MHz, $CDCl_3$): δ 8.52 (d, J = 8.4 Hz, 1H), 8.47 (d, J = 2.4 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 9.0 Hz, 1H), 7.86 – 7.84 (m, 1H), 7.74 – 7.71 (m, 1H), 7.64 (dd, J = 8.4, 2.4 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 159.1, 142.1, 132.1, 131.5, 130.8, 130.7, 129.0, 127.9, 126.6, 126.0, 124.8, 122.3, 121.6, 23.2 – 22.6 (m).

HRMS (ESI, m/z): Calculated for $C_{14}H_8D_3ClN$ $(M+H)^+$ 231.0809, found 231.0807.

24. A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1), m. p. 108-110℃.

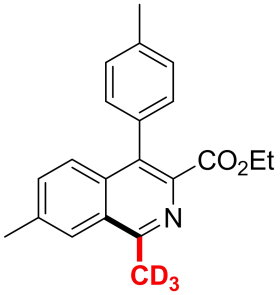


^{1}H NMR (600 MHz, $CDCl_3$): δ 8.20 (d, J = 8.4 Hz, 1H), 7.69 – 7.66 (m, 1H), 7.65 – 7.63 (m, 2H), 7.49 – 7.44 (m, 3H), 7.34 (dd, J = 7.8, 1.8 Hz, 2H), 4.11 (q, J = 7.2 Hz, 2H), 0.97 (t, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 167.6, 158.4, 141.5, 136.4, 135.4, 131.9, 130.4, 130.0, 128.1, 128.1, 127.9, 127.8, 126.9, 125.6, 61.2, 22.1 – 21.7 (m), 13.6.

HRMS (ESI, m/z): Calculated for $C_{19}H_{15}D_3NO_2$ $(M+H)^+$ 295.1567, found 295.1565.

25. A light yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).

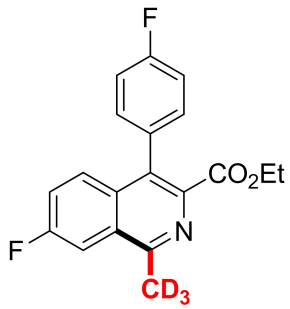


^{1}H NMR (600 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 2.57 (s, 3H), 2.45 (s, 3H), 1.02 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 167.7, 157.3, 140.6, 138.2, 137.3, 133.7, 133.5, 132.4, 132.0, 129.8, 128.7, 128.0, 126.8, 124.6, 61.1, 21.9, 21.3, 13.7.

HRMS (ESI, m/z): Calculated for $C_{21}H_{19}D_3NO_2$ $(M+H)^+$ 323.1880, found 323.1875.

26. A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1), m. p. 138-140℃.

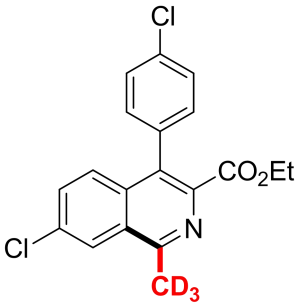


^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79 (dd, *J* = 9.6, 2.4 Hz, 1H), 7.62 (dd, *J* = 9.6, 5.4 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.31 – 7.28 (m, 2H), 7.18 (t, *J* = 8.4 Hz, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 1.05 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 167.2, 162.1 (dd, *J* = 246.2, 162.6 Hz), 157.9, 141.2, 132.6, 131.9 (d, *J* = 3.6 Hz), 131.6 (d, *J* = 8.1 Hz), 130.8, 129.7 (d, *J* = 8.7 Hz), 129.0 (d, *J* = 8.3 Hz), 120.8 (d, *J* = 24.6 Hz), 115.3 (d, *J* = 21.5 Hz), 109.5 (d, *J* = 21.1 Hz), 61.4, 22.1-21.9 (m), 13.8.

HRMS (ESI, m/z): Calculated for $C_{19}H_{13}D_3F_2NO_2$ $(M+H)^+$ 331.1378, found 331.1375.

27. A light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1), m. p. 107-109℃.



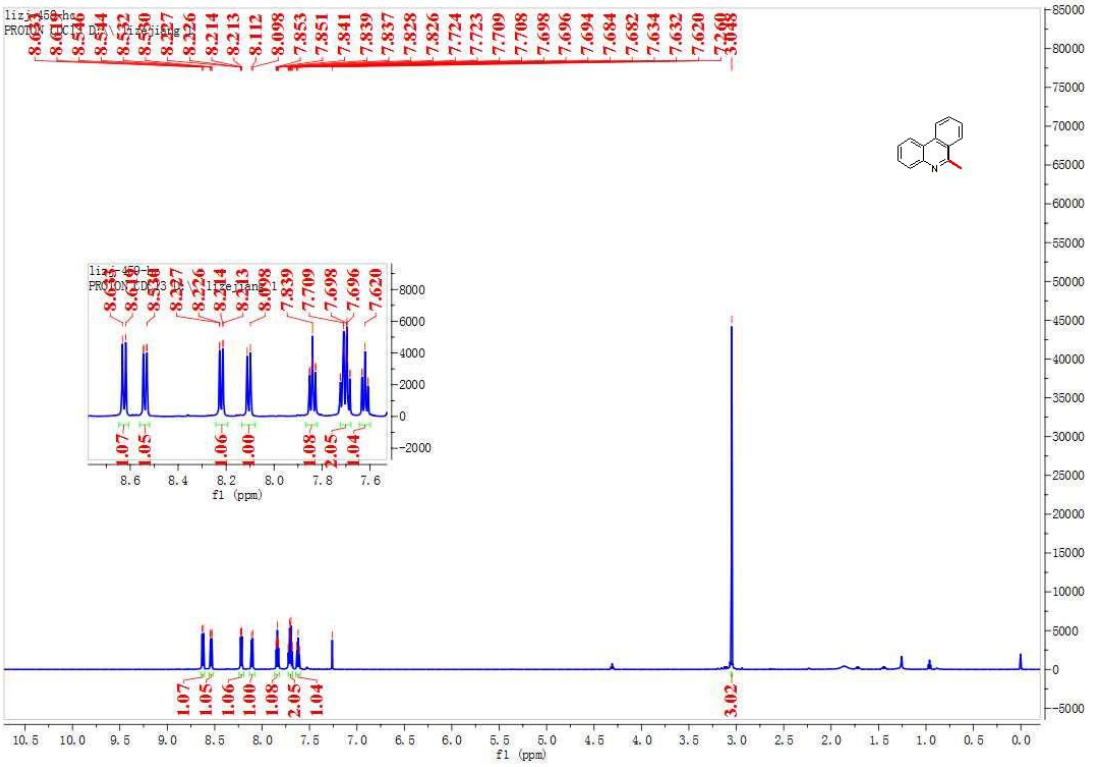
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.18 (d, *J* = 1.8 Hz, 1H), 7.59 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 1.06 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.9, 157.9, 141.6, 134.5, 134.4, 134.3, 133.7, 131.5, 131.2, 130.6, 128.6, 128.4, 124.8, 61.5, 13.8.

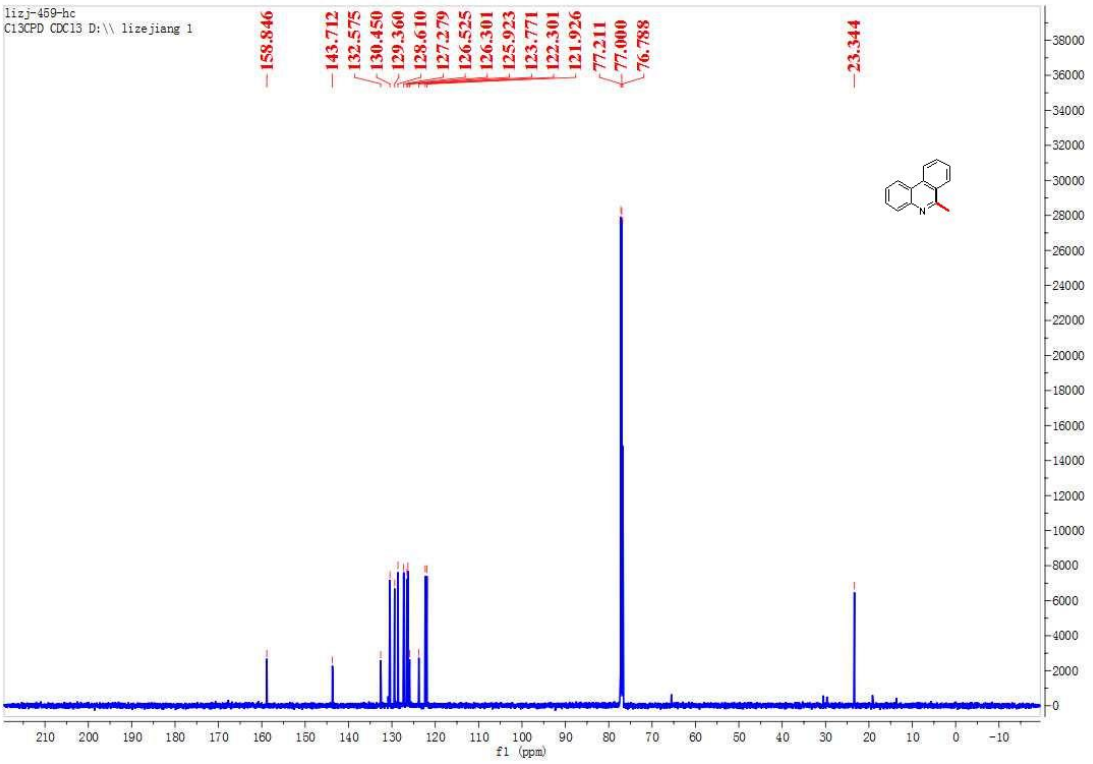
HRMS (ESI, m/z): Calculated for $C_{19}H_{13}D_3Cl_2NO_2$ $(M+H)^+$ 363.0787, found 363.0785.

Copies of the ^{1}H NMR, ^{13}C NMR

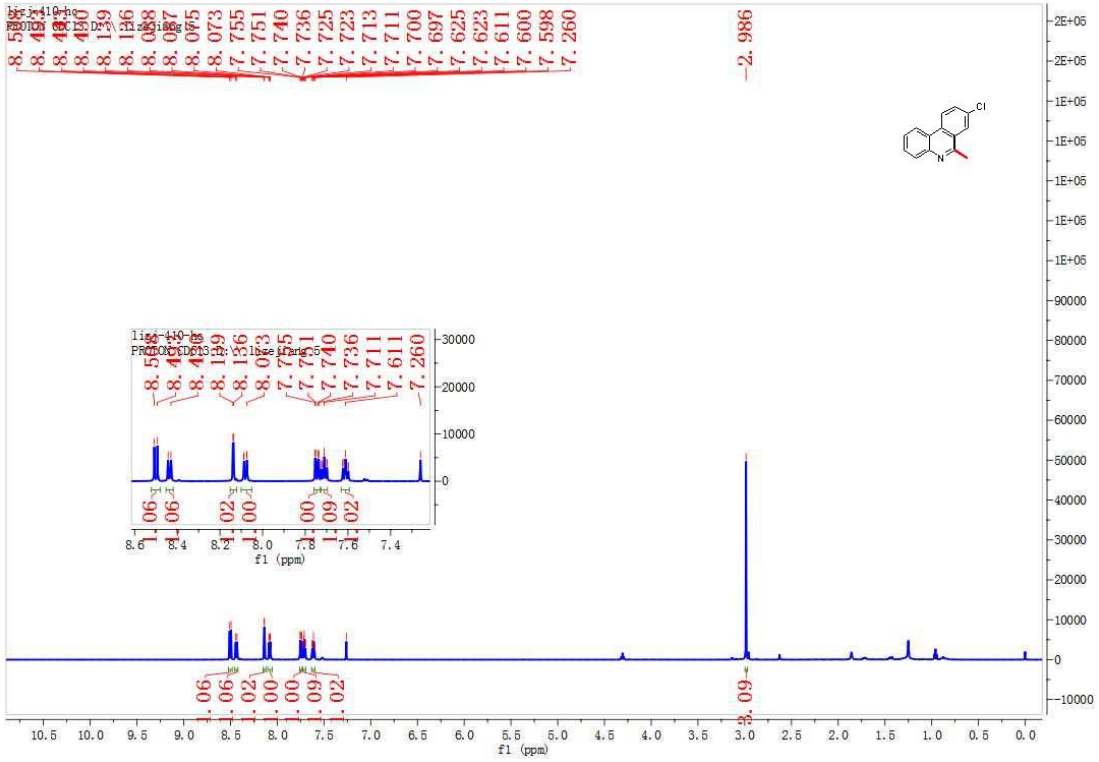
1-^{1}H NMR



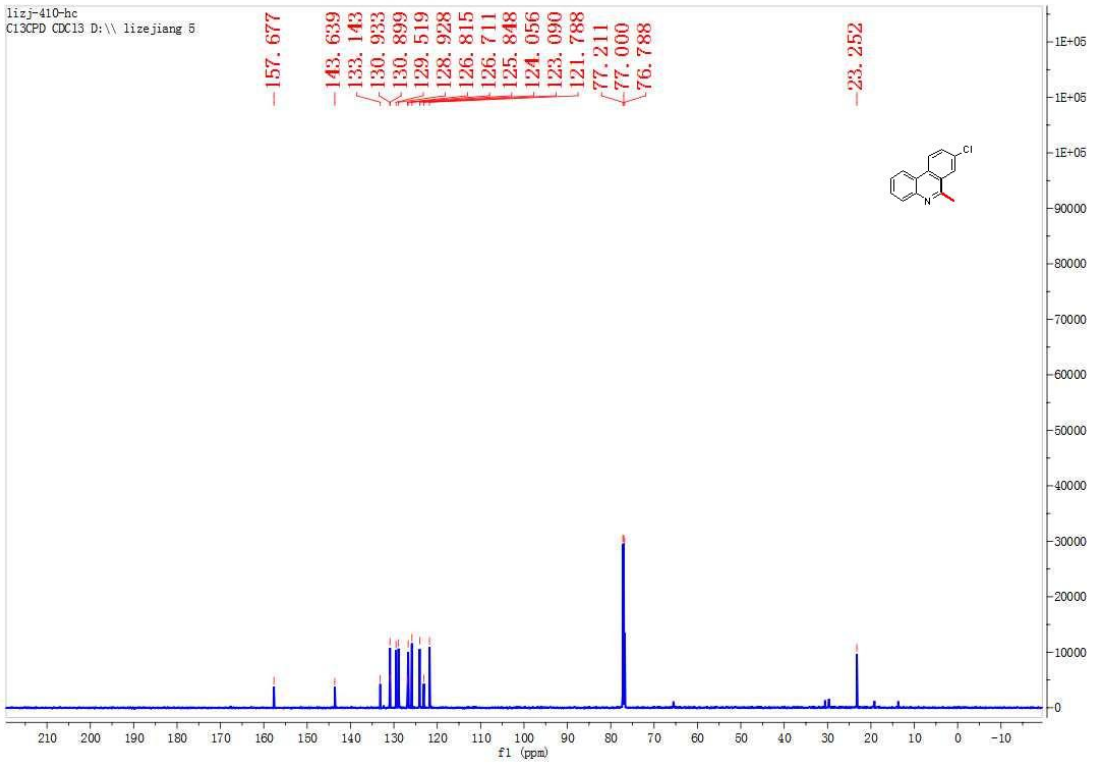
1-^{13}C NMR



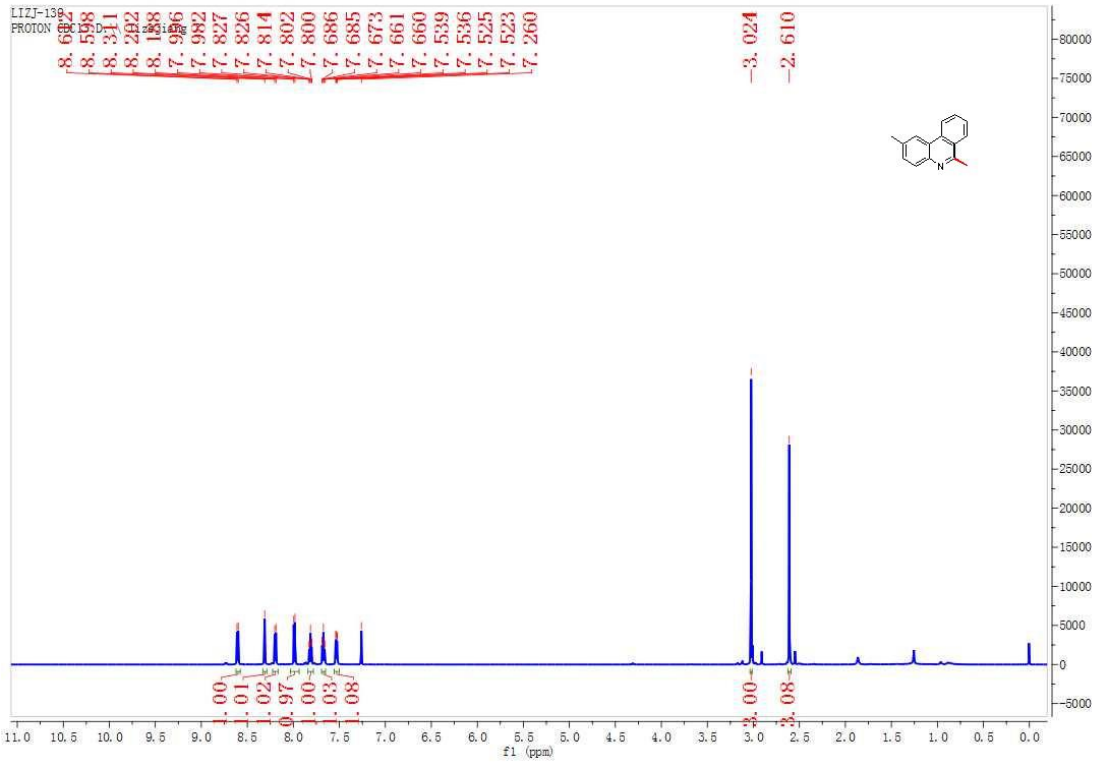
2-^{1}H NMR



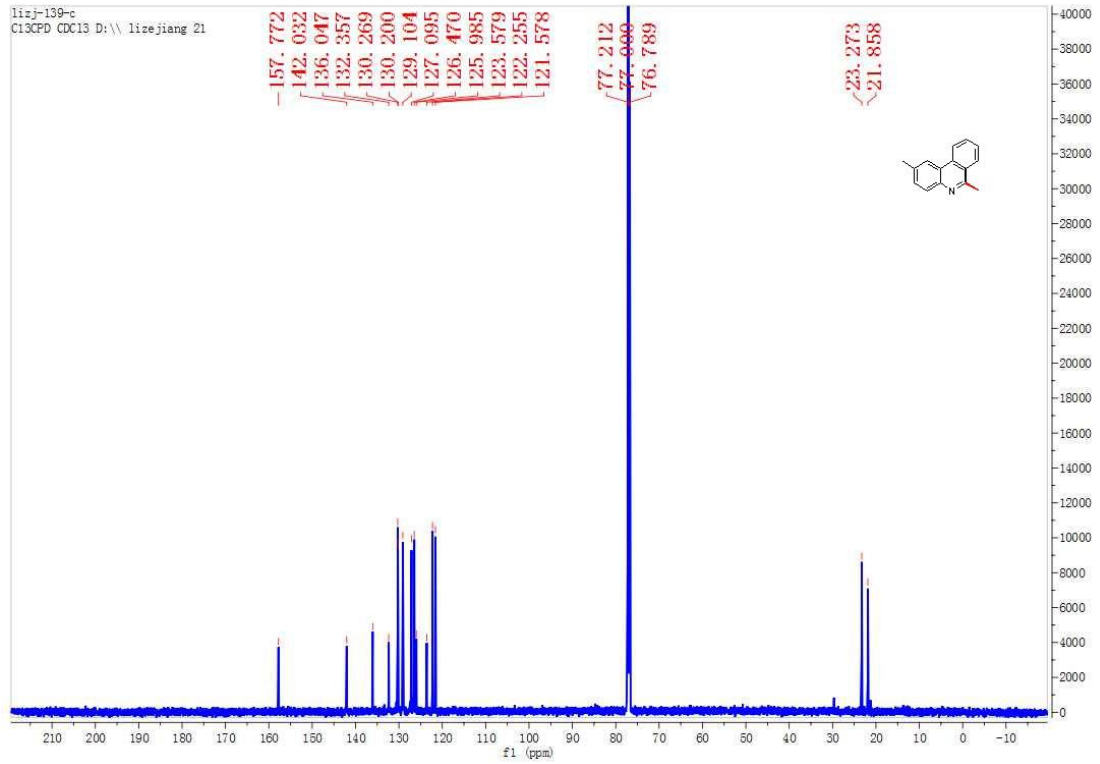
2-^{13}C NMR



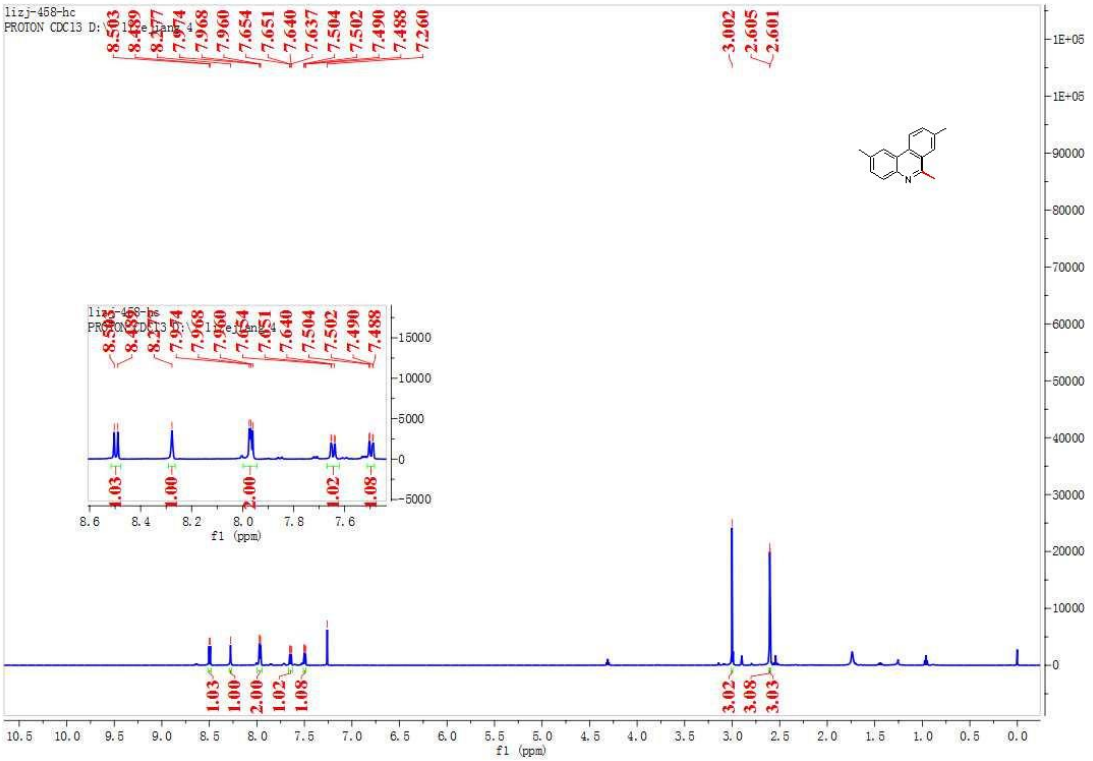
3-^{1}H NMR



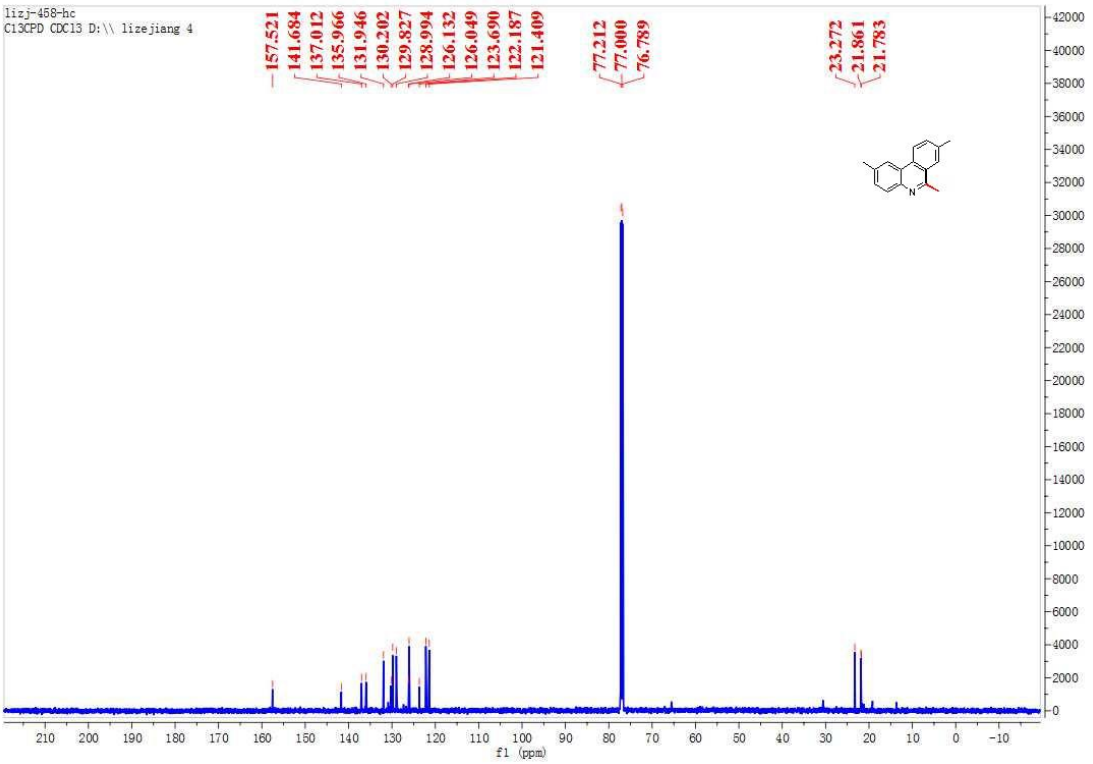
3-^{13}C NMR



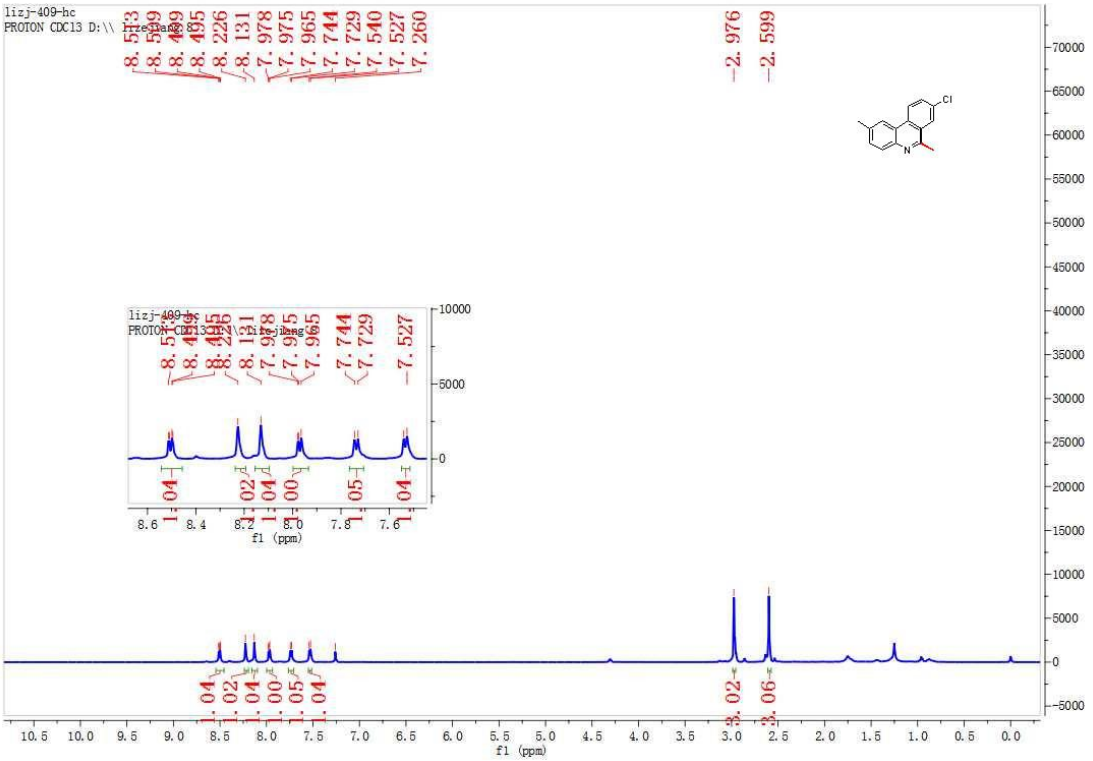
4-^{1}H NMR



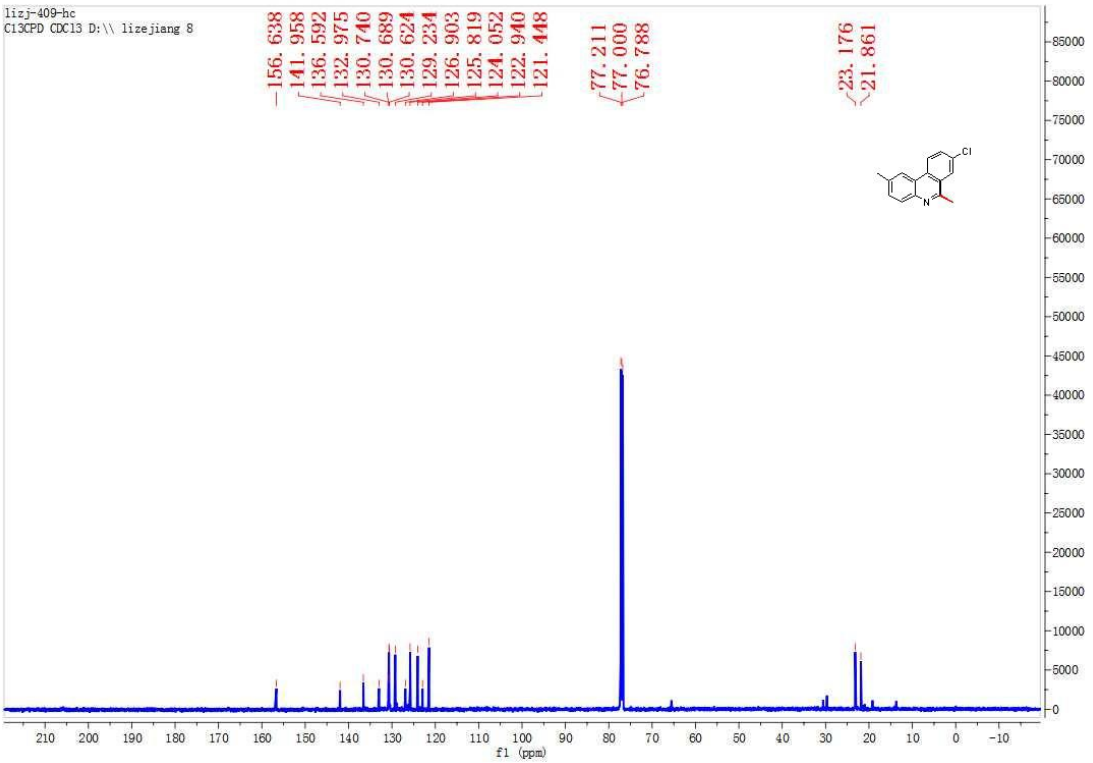
4-^{13}C NMR



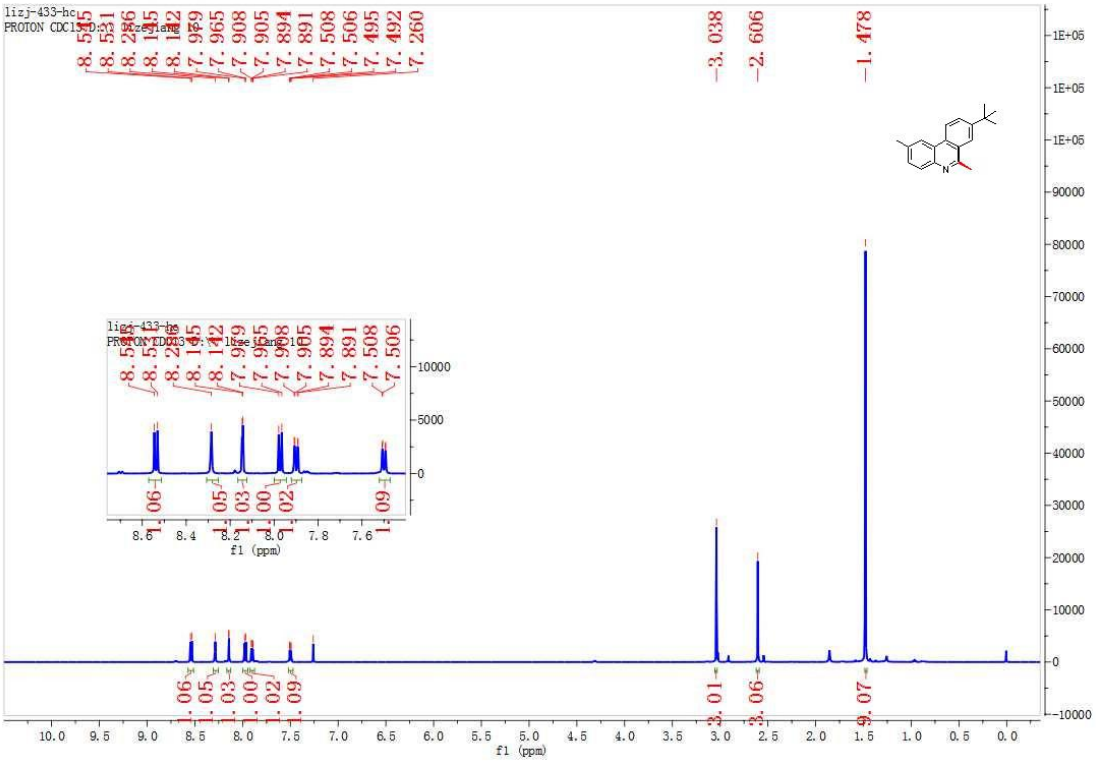
5-^{1}H NMR



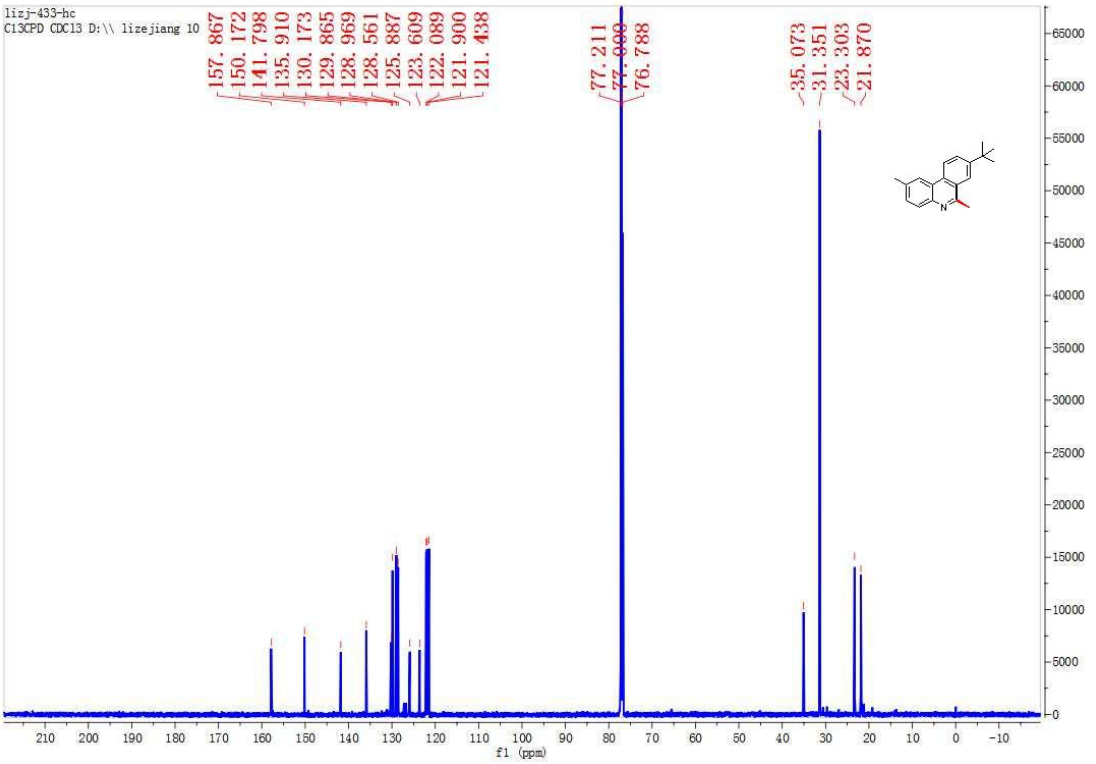
5-^{13}C NMR



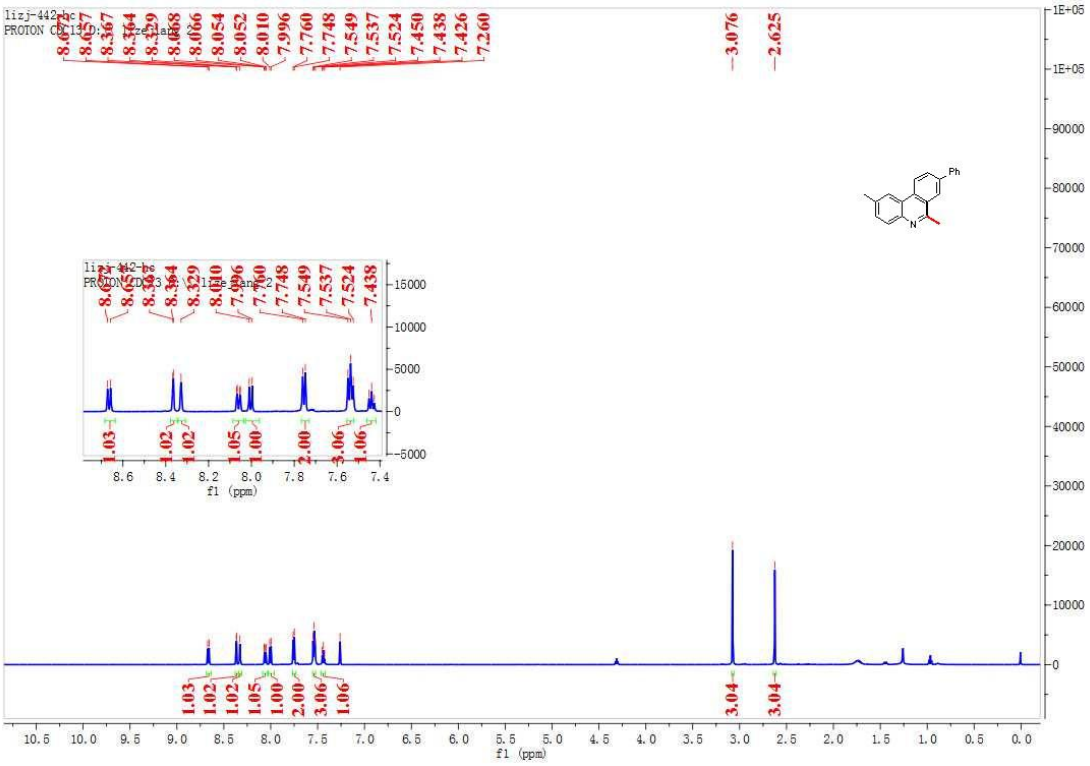
6-^{1}H NMR



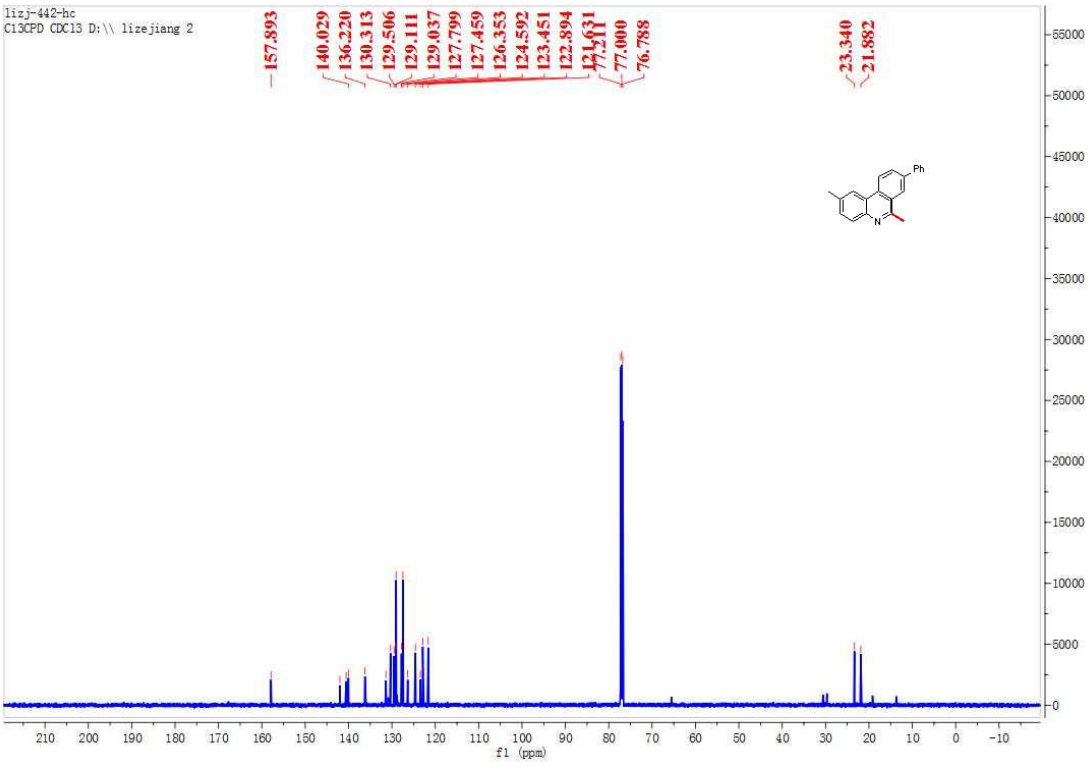
6-^{13}C NMR



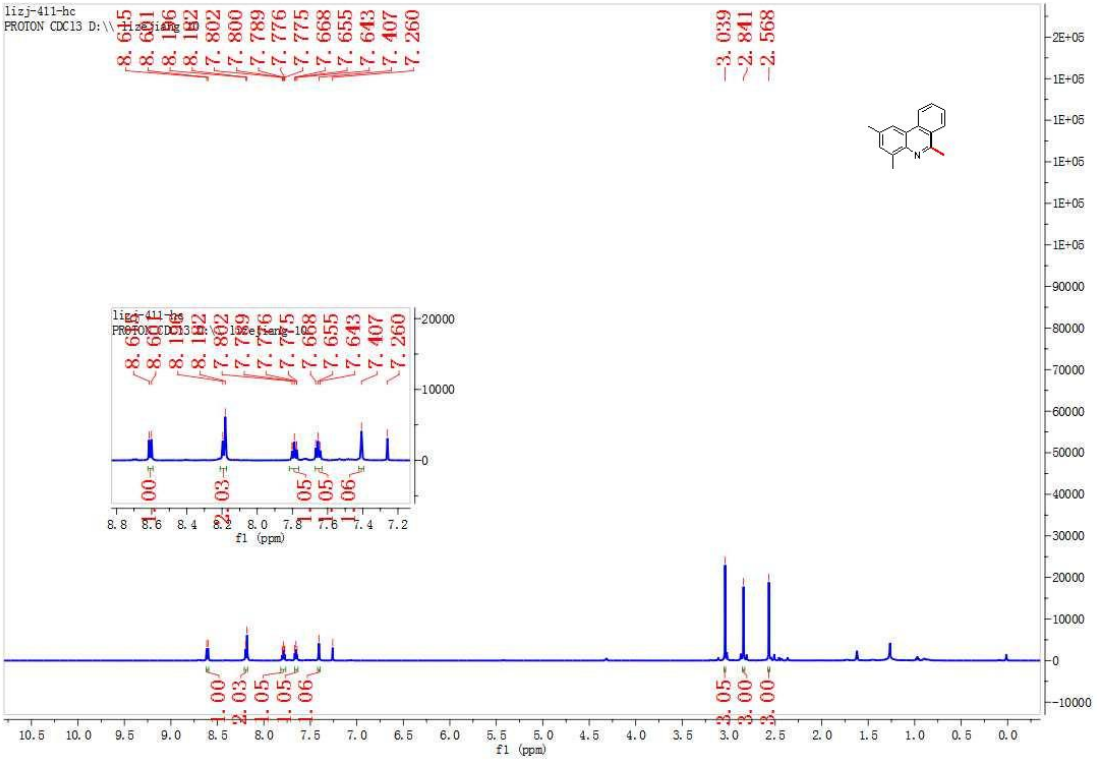
7-^{1}H NMR



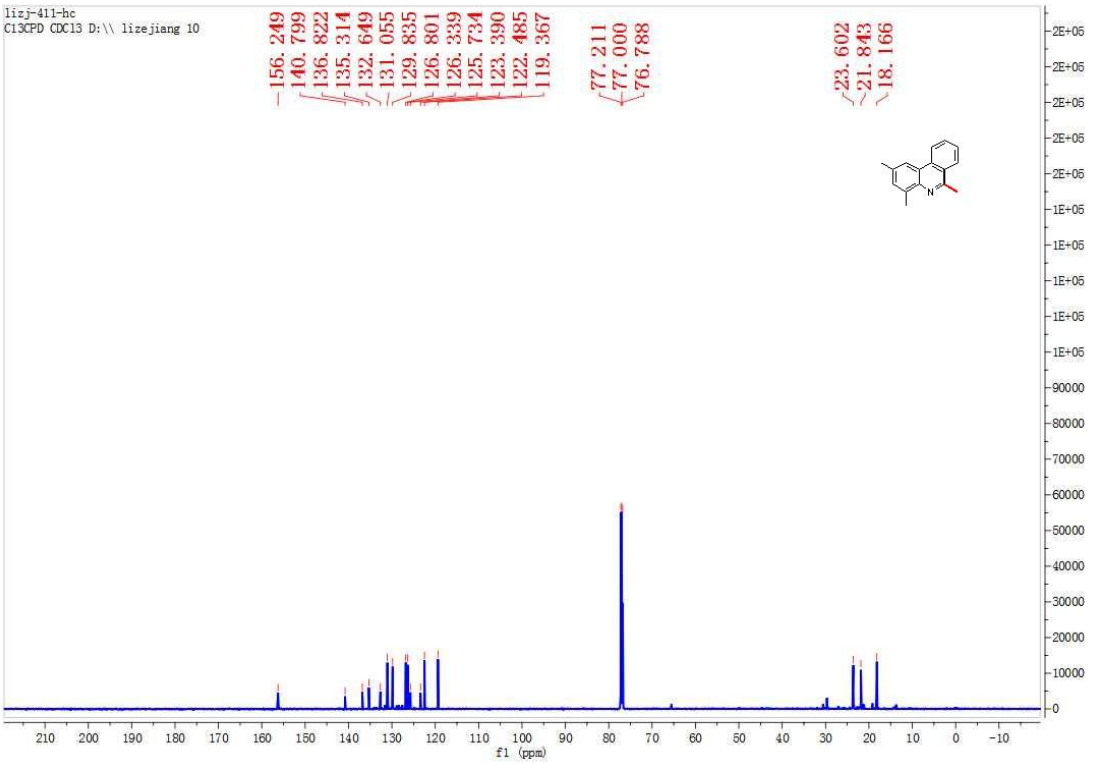
7-^{13}C NMR



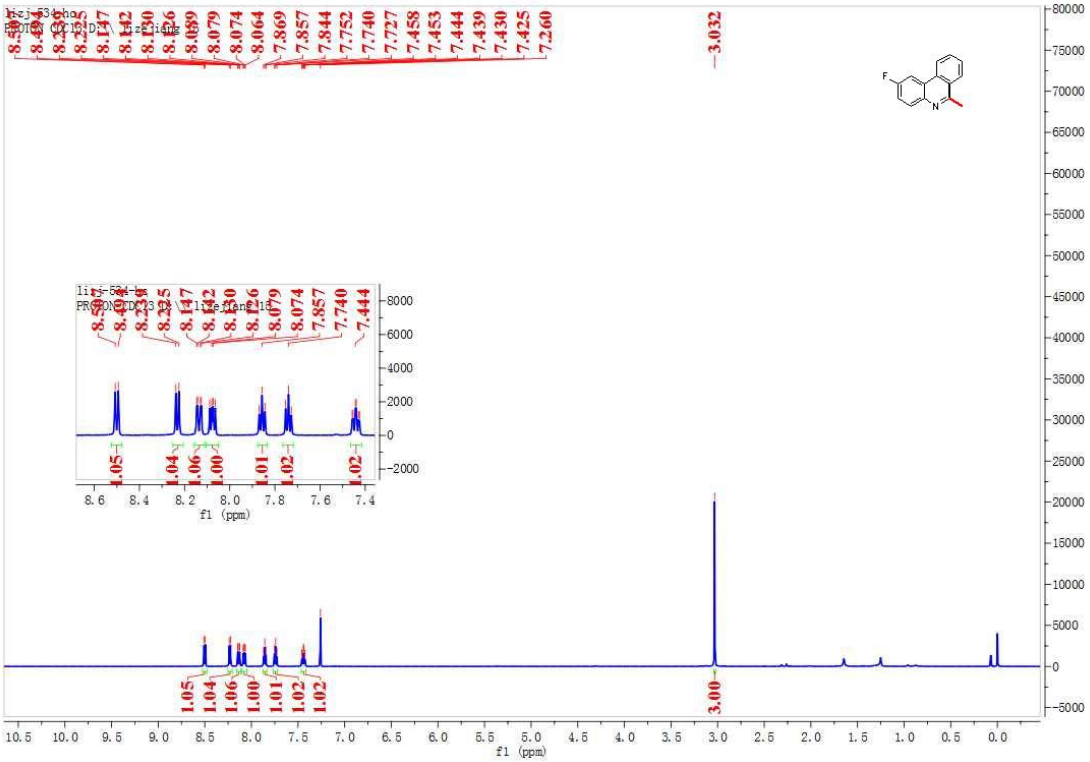
8-^{1}H NMR



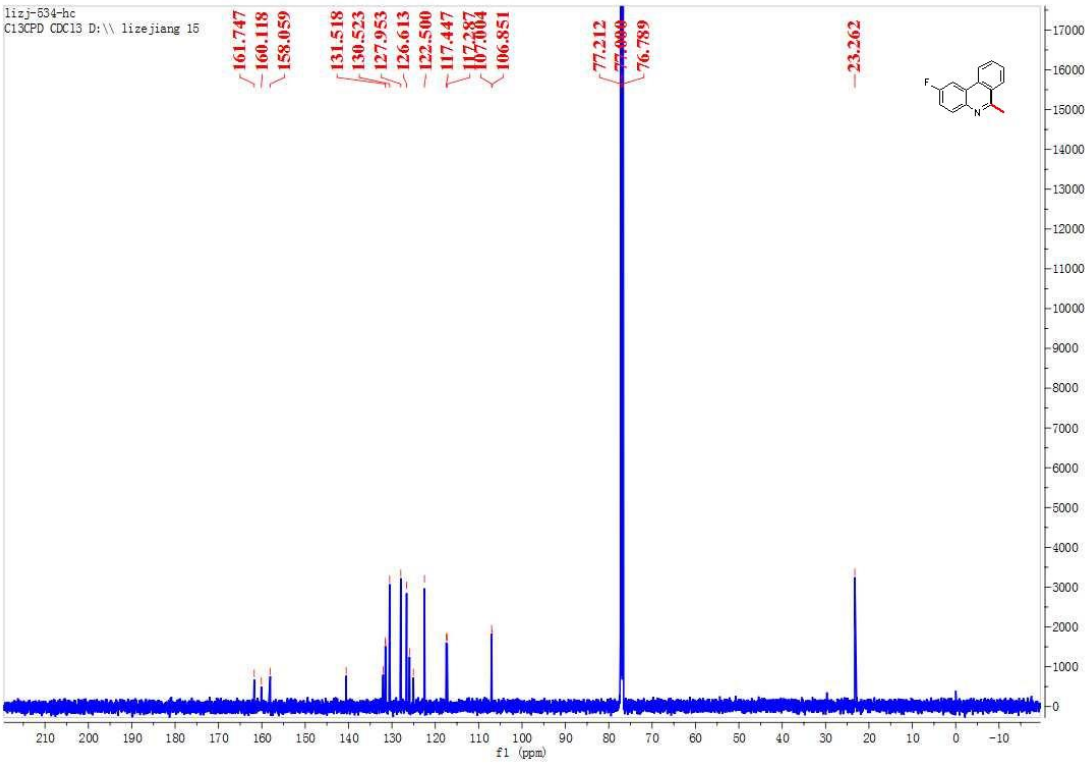
8-^{13}C NMR



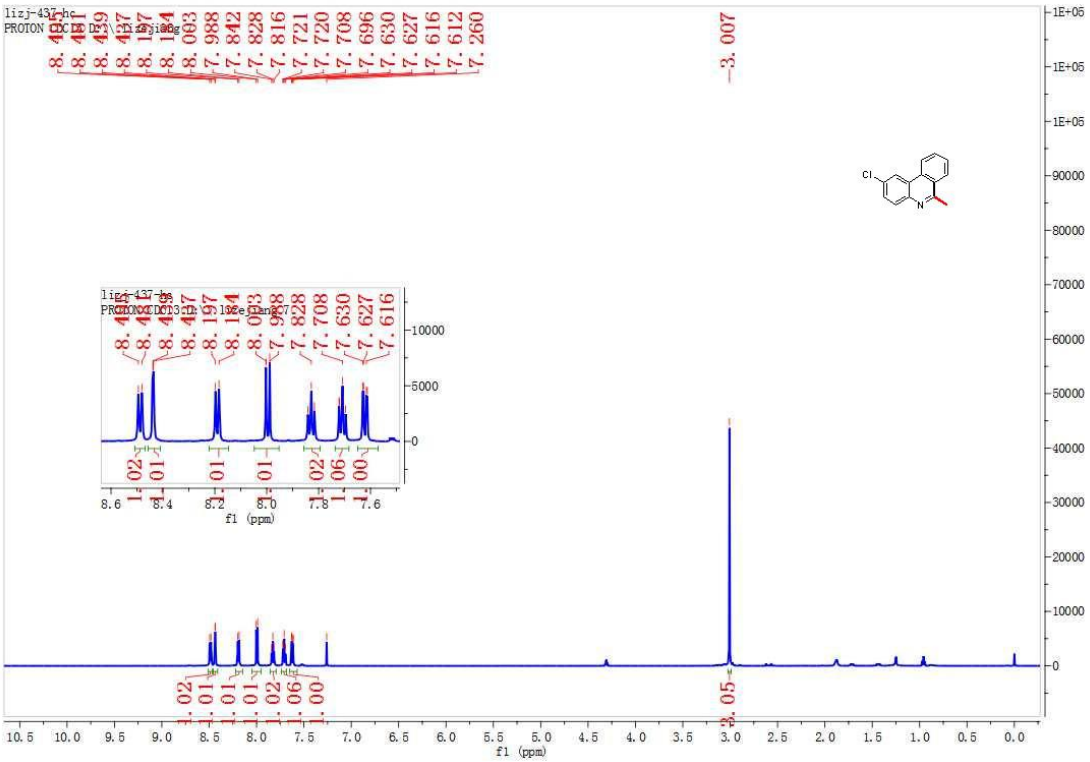
9-^{1}H NMR



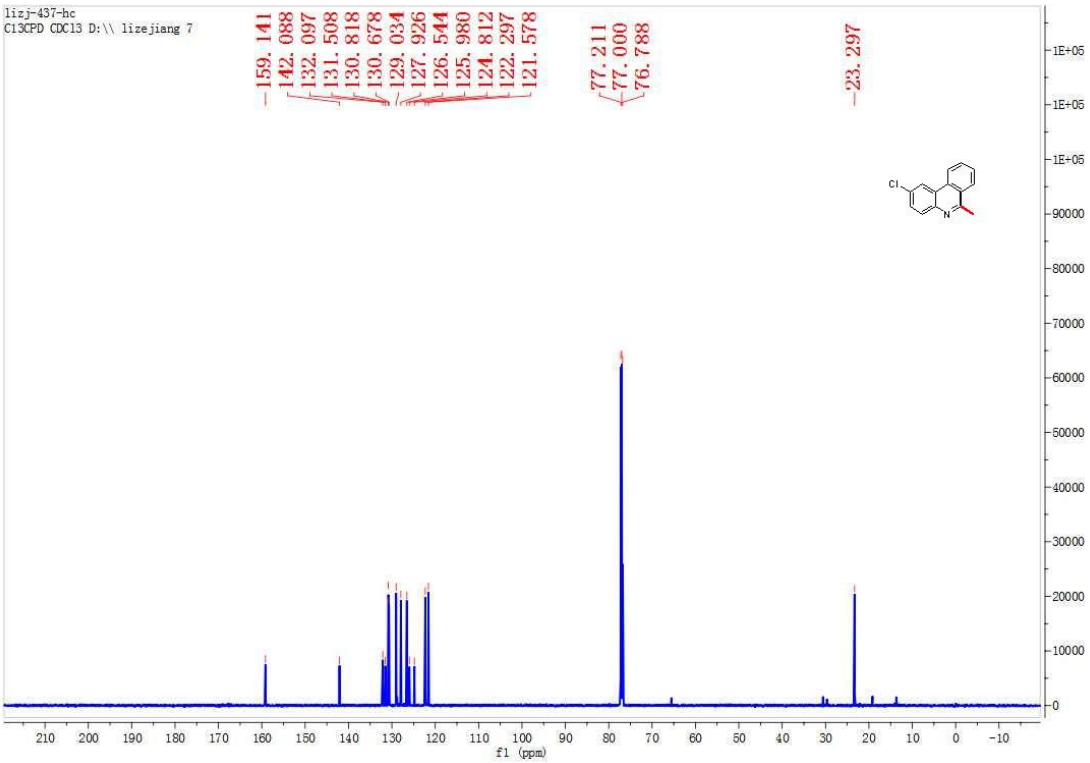
9-^{13}C NMR



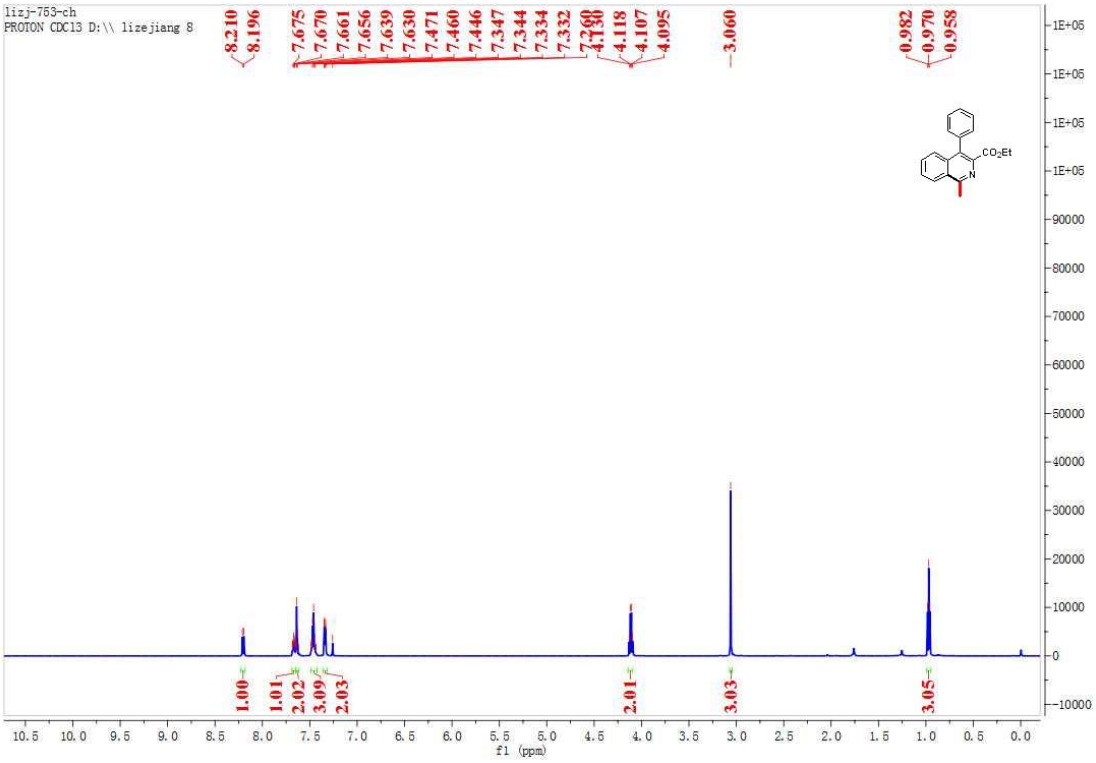
10-^{1}H NMR



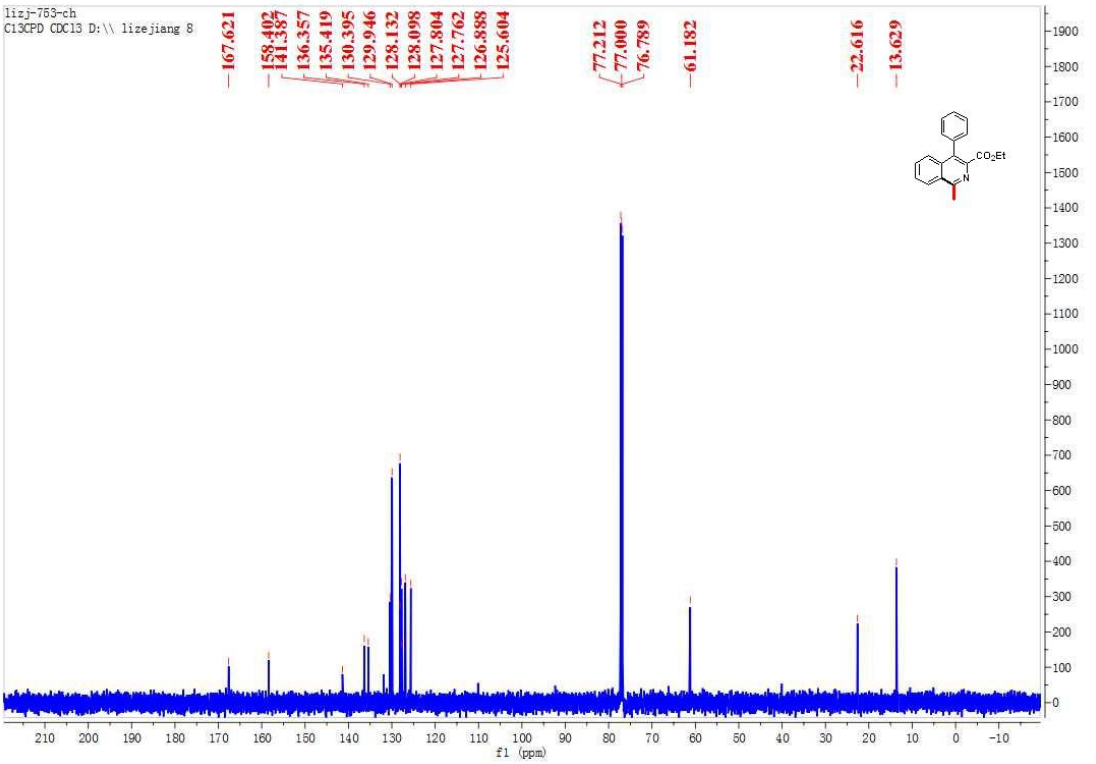
10-^{13}C NMR



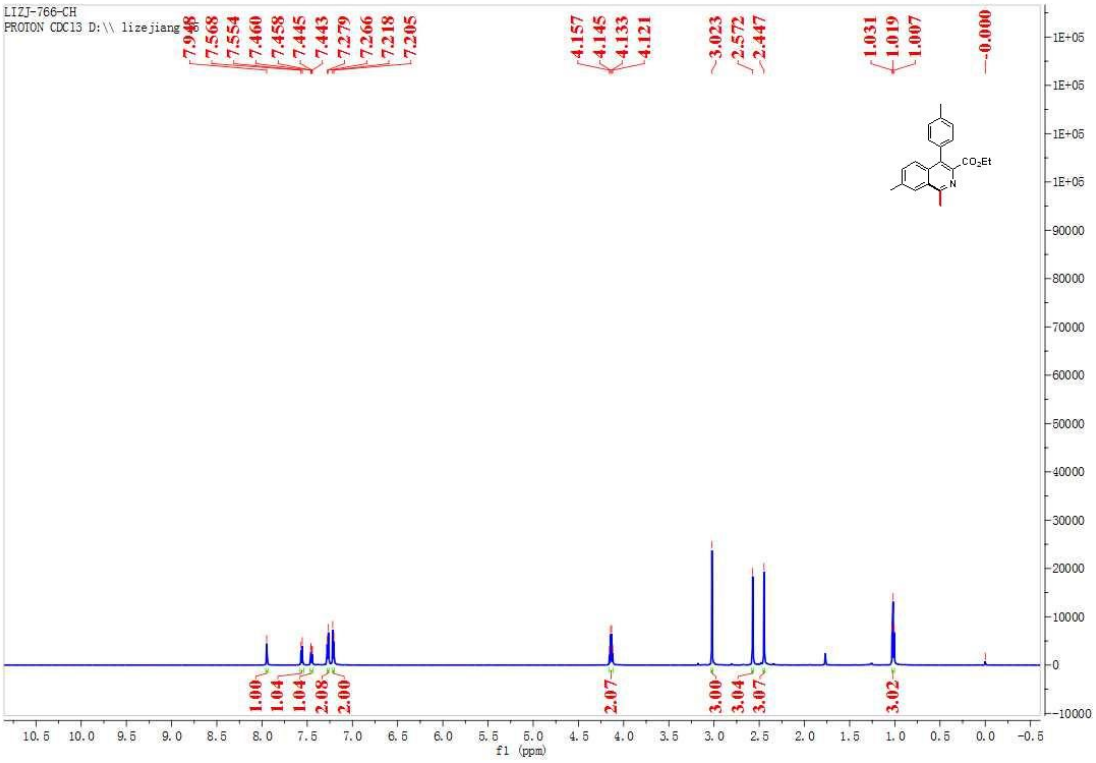
13-^{1}H NMR



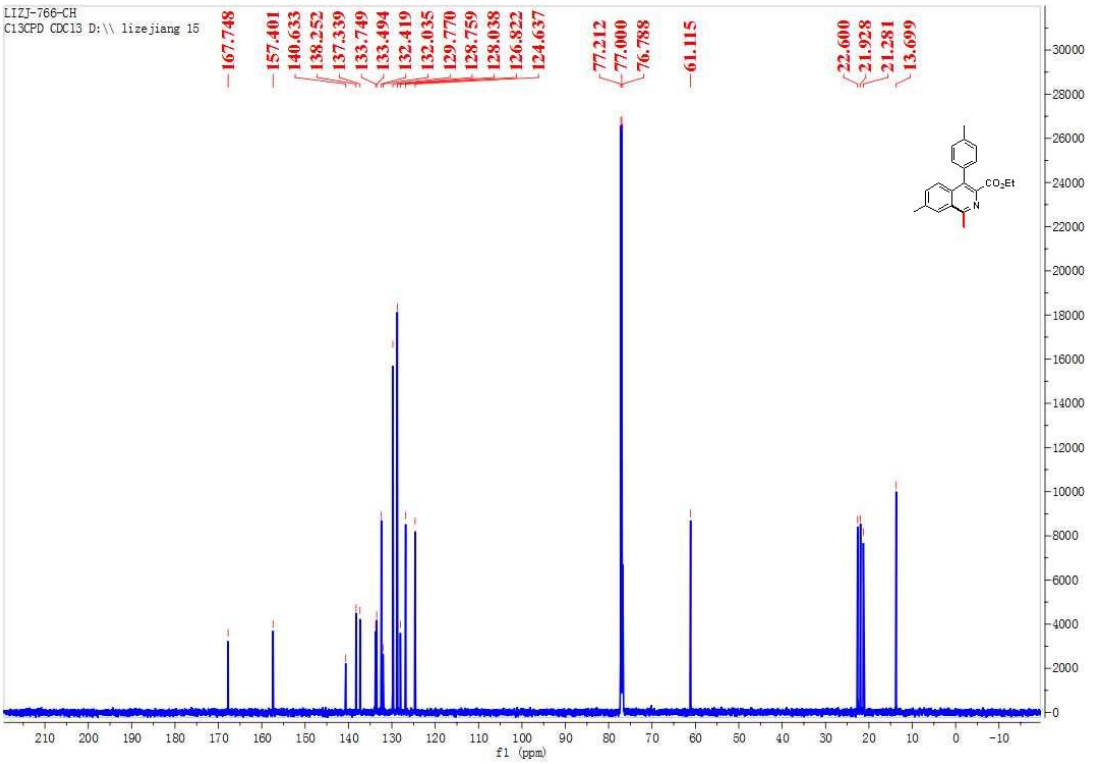
13-^{13}C NMR



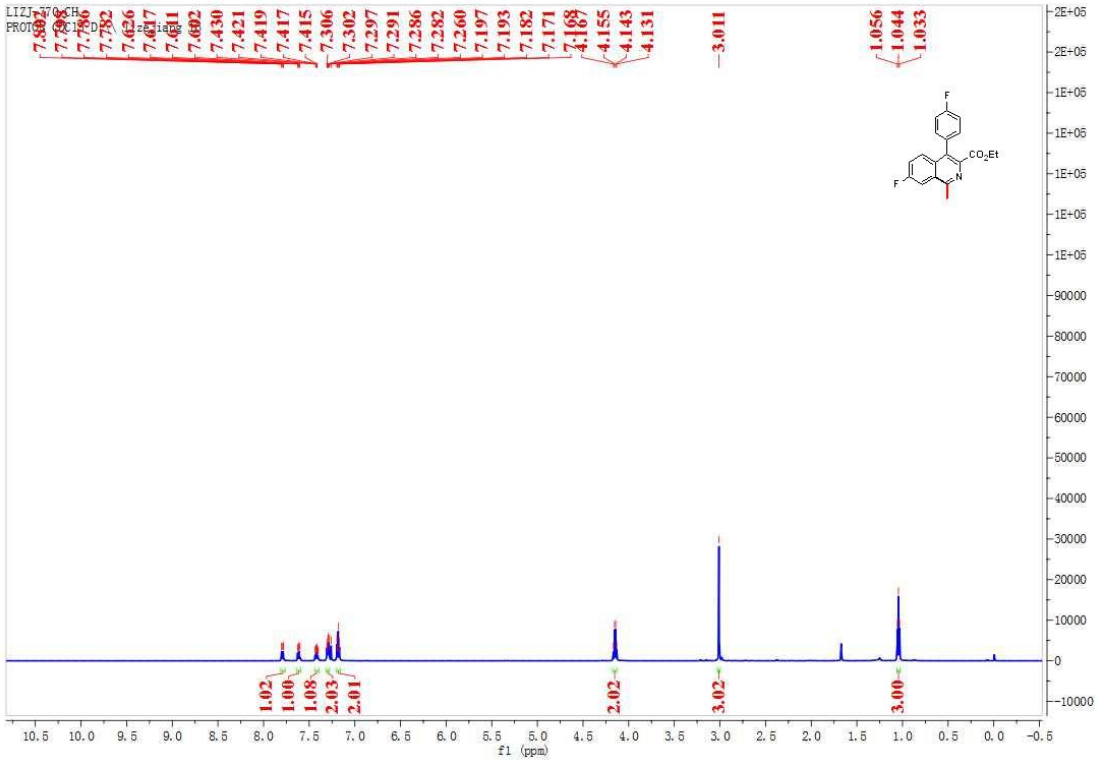
14-^{1}H NMR



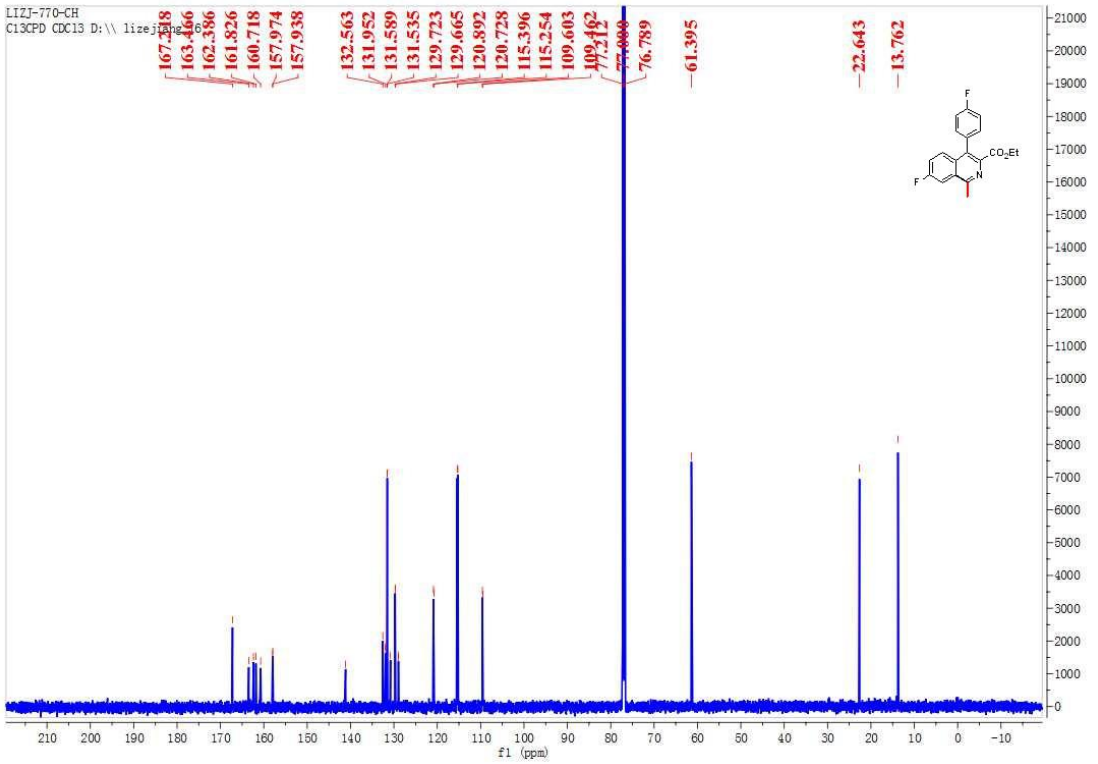
14-^{13}C NMR



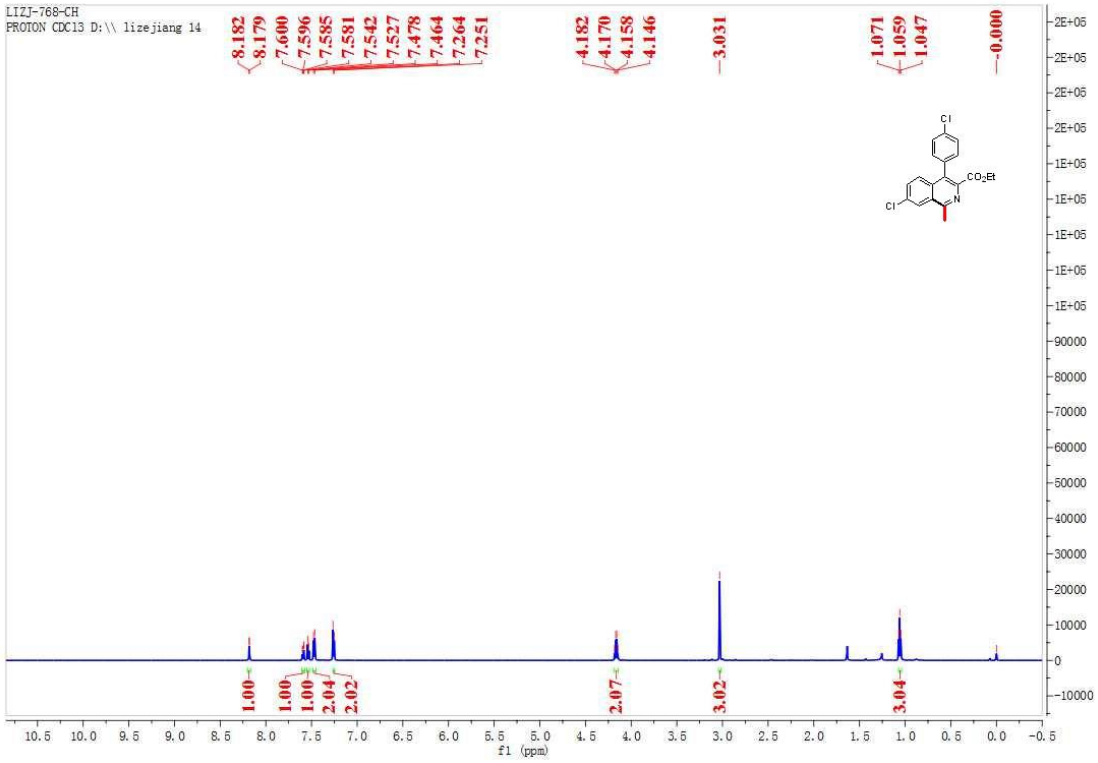
15-^{1}H NMR



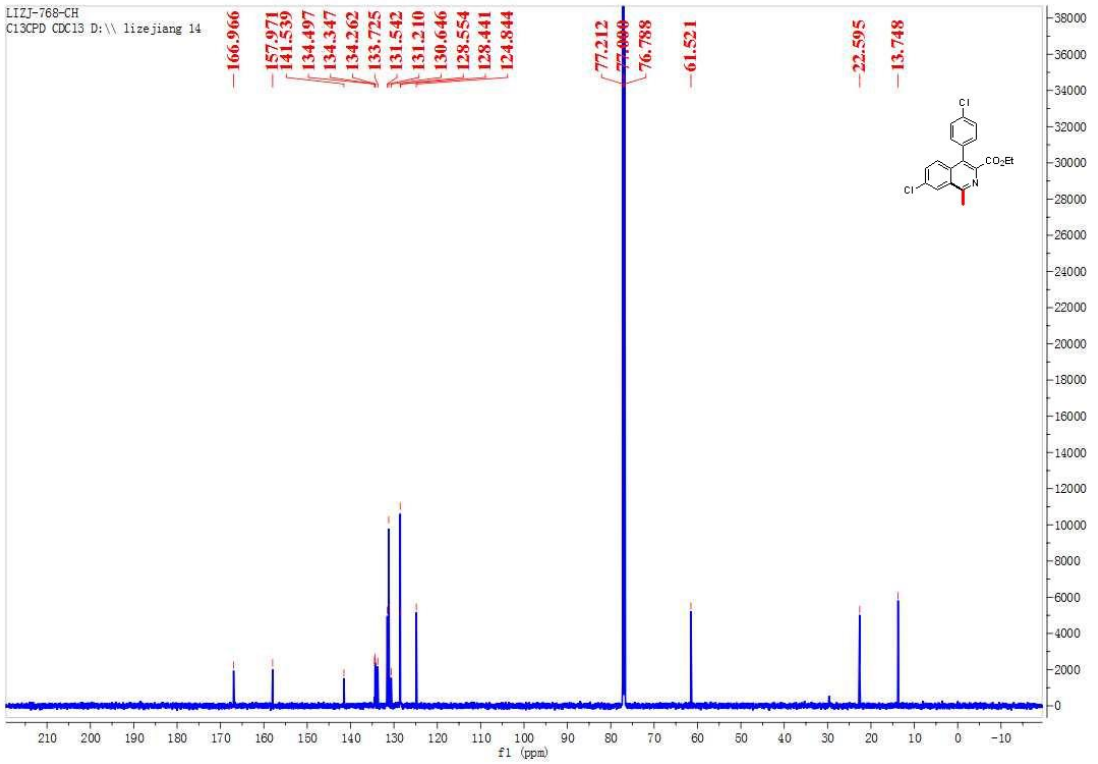
15-^{13}C NMR



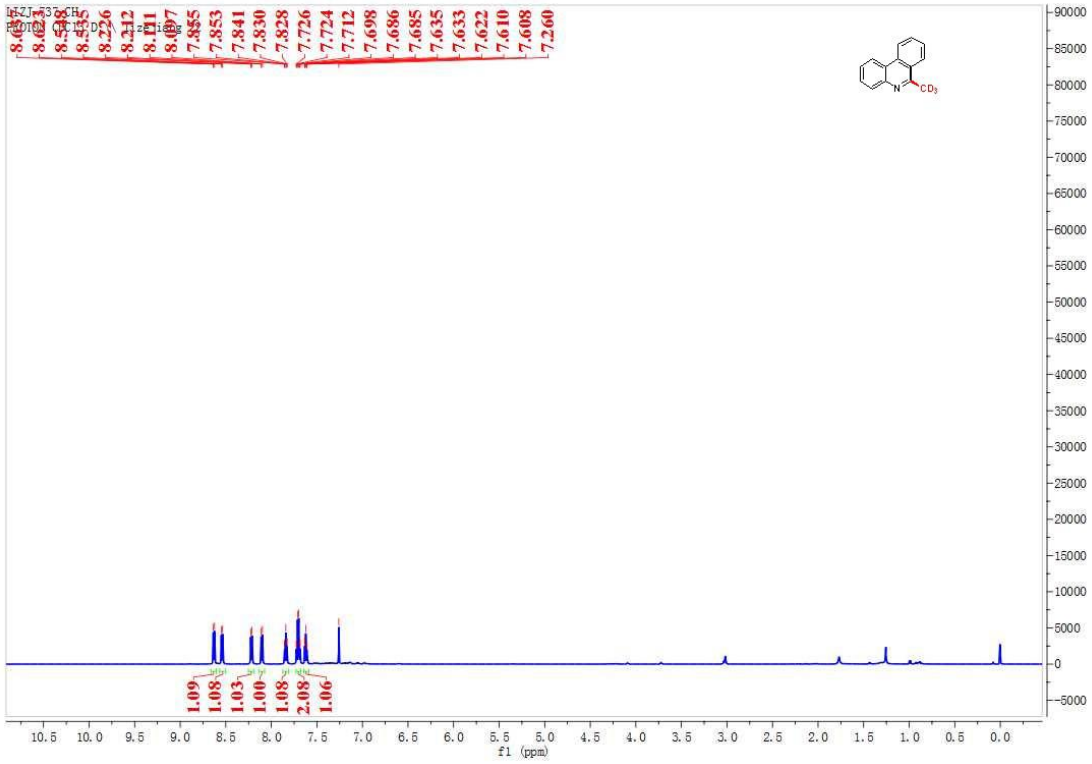
16-^{1}H NMR



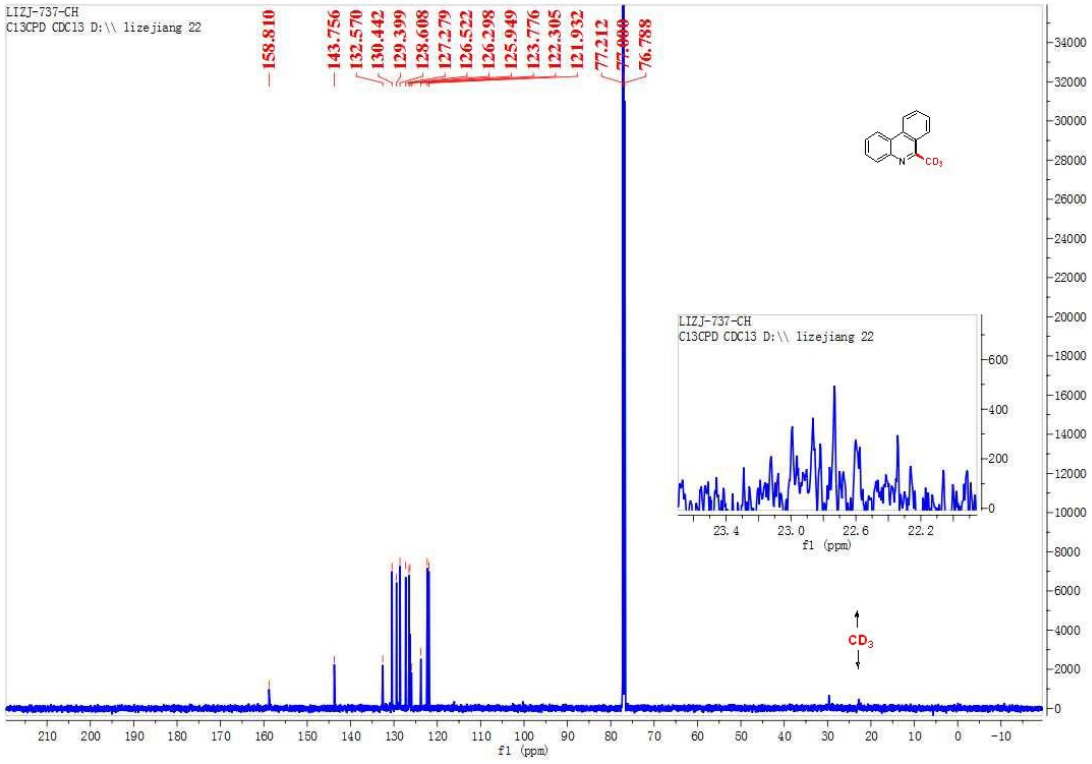
16-^{13}C NMR



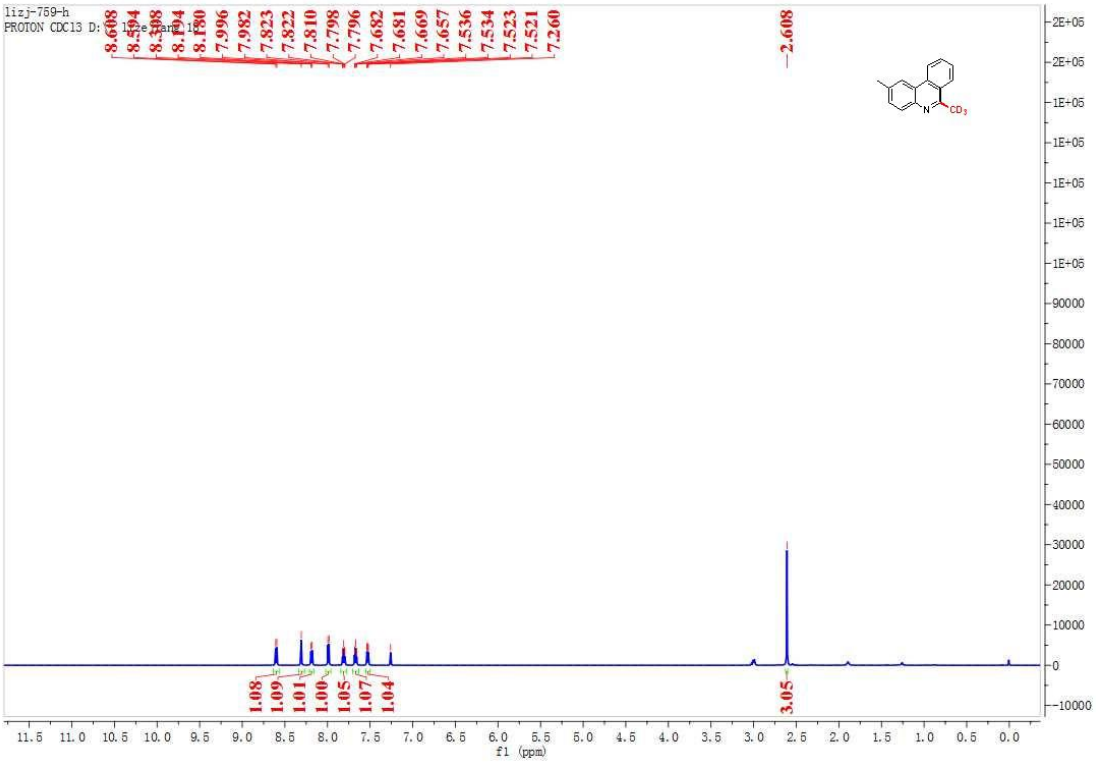
17-^{1}H NMR



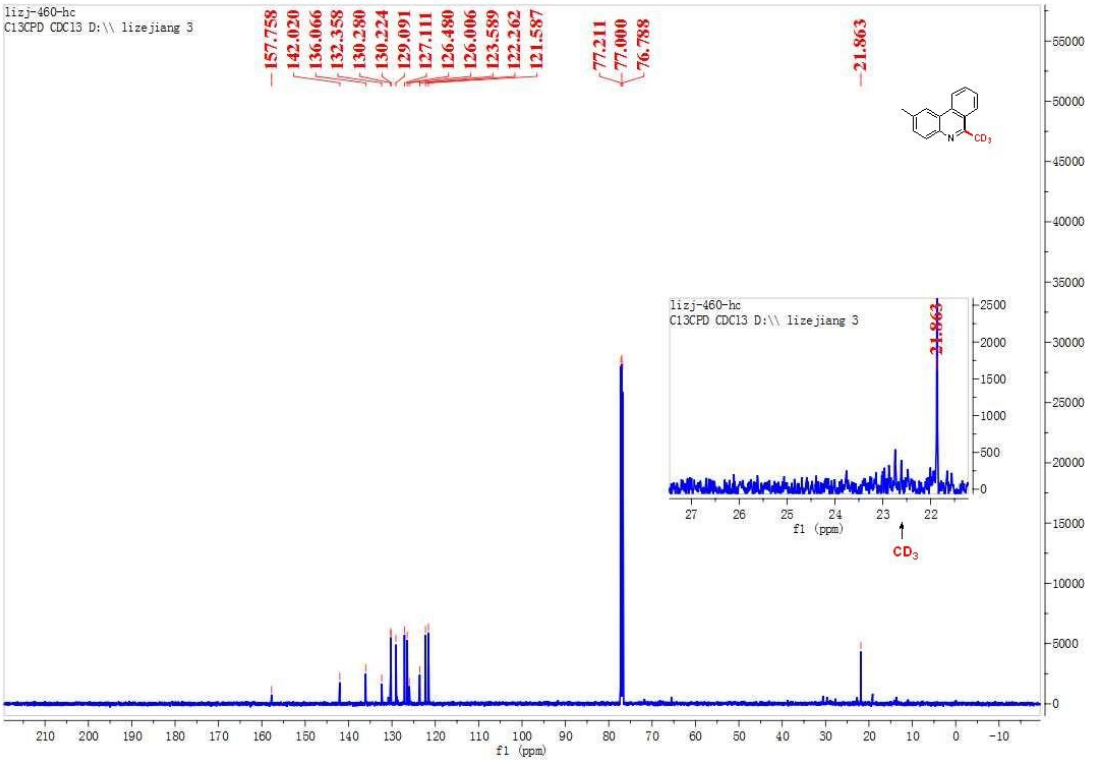
17-^{13}C NMR



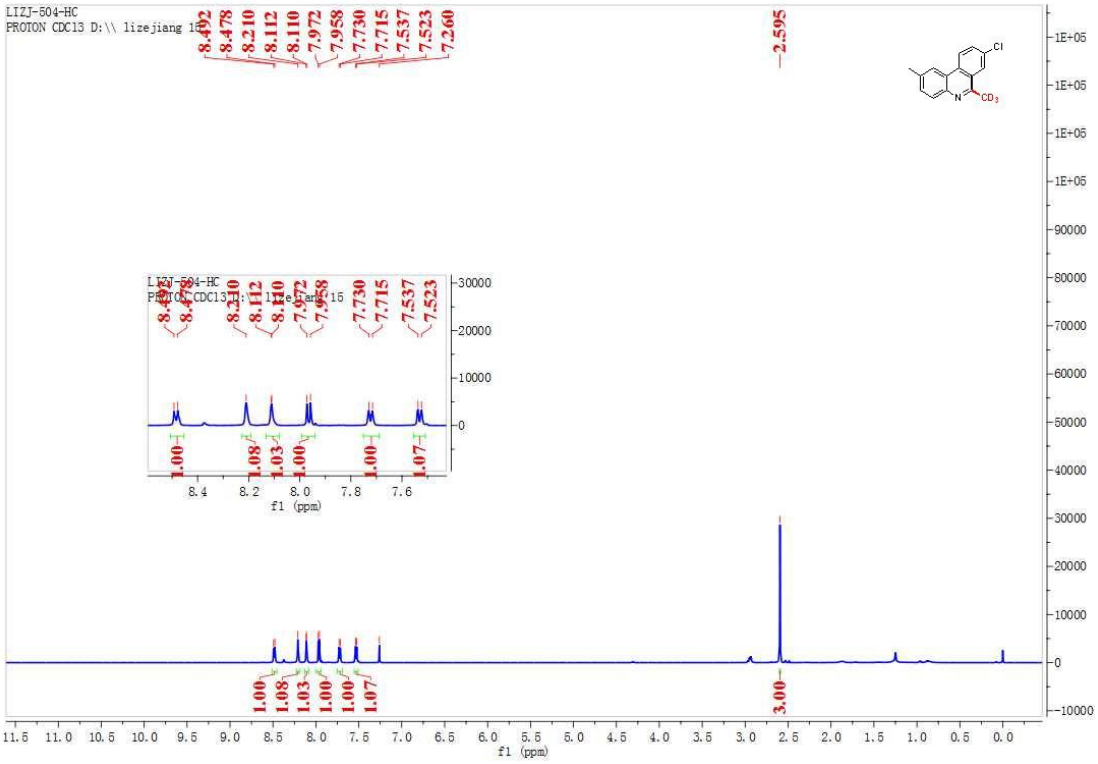
18-^{1}H NMR



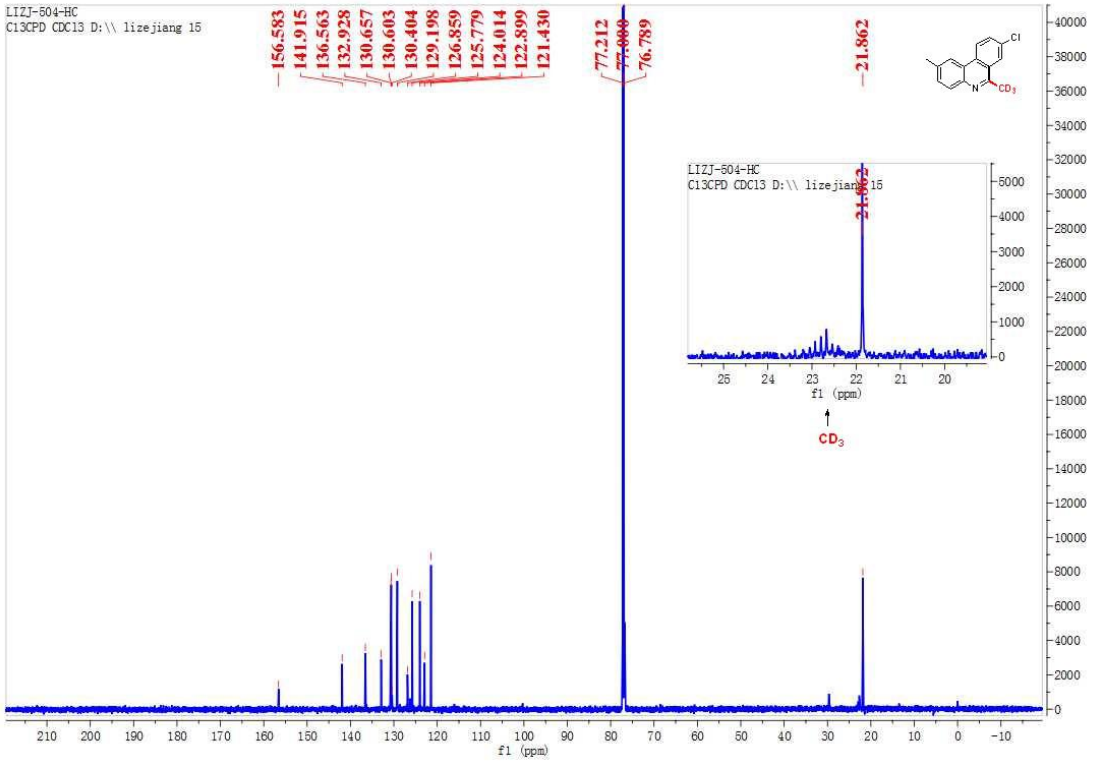
18-^{13}C NMR



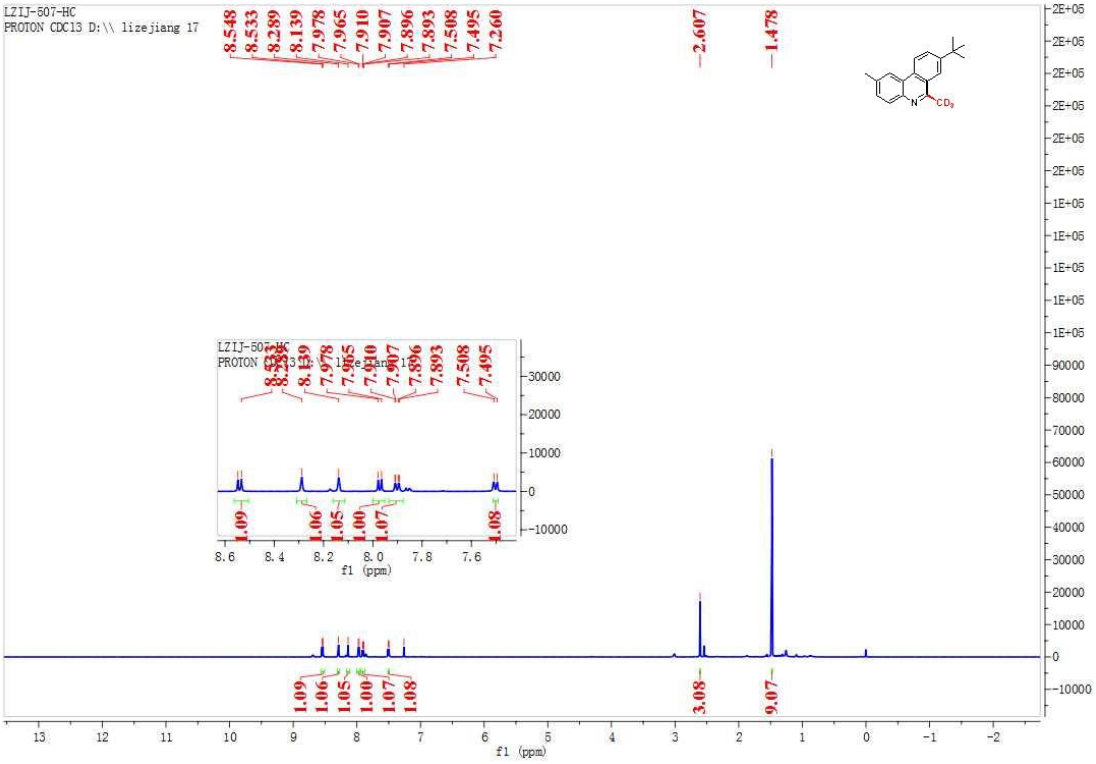
19-^{1}H NMR



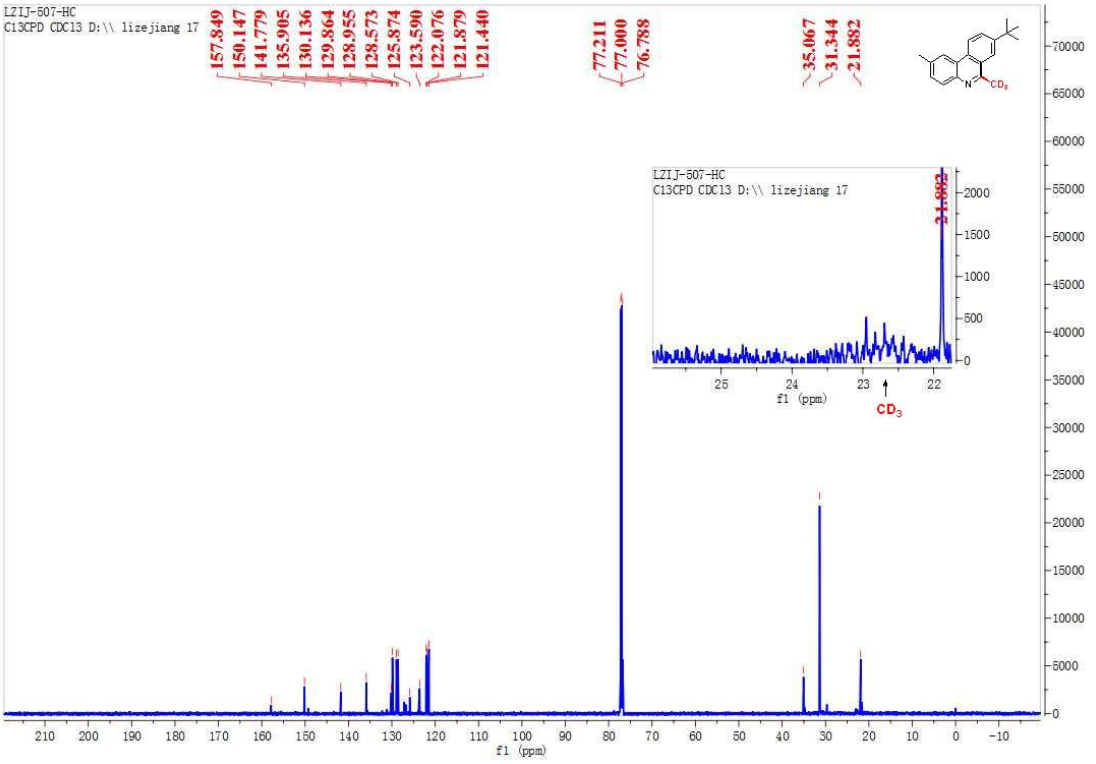
19-^{13}C NMR



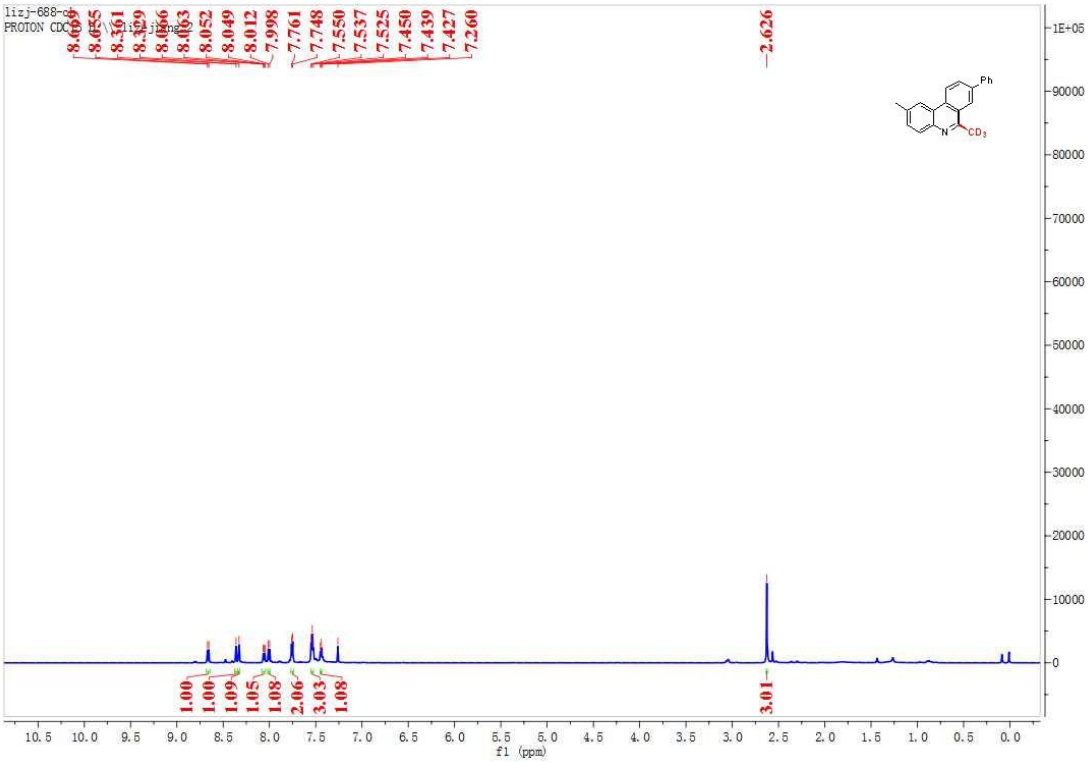
20-^{1}H NMR



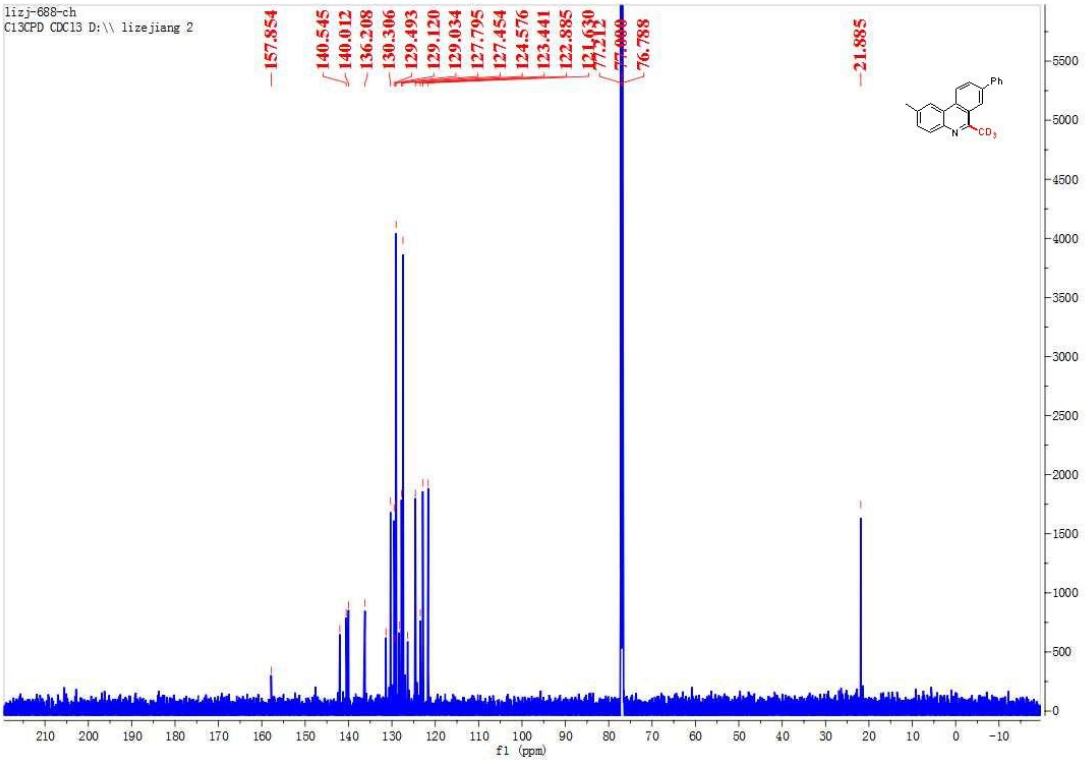
20-^{13}C NMR



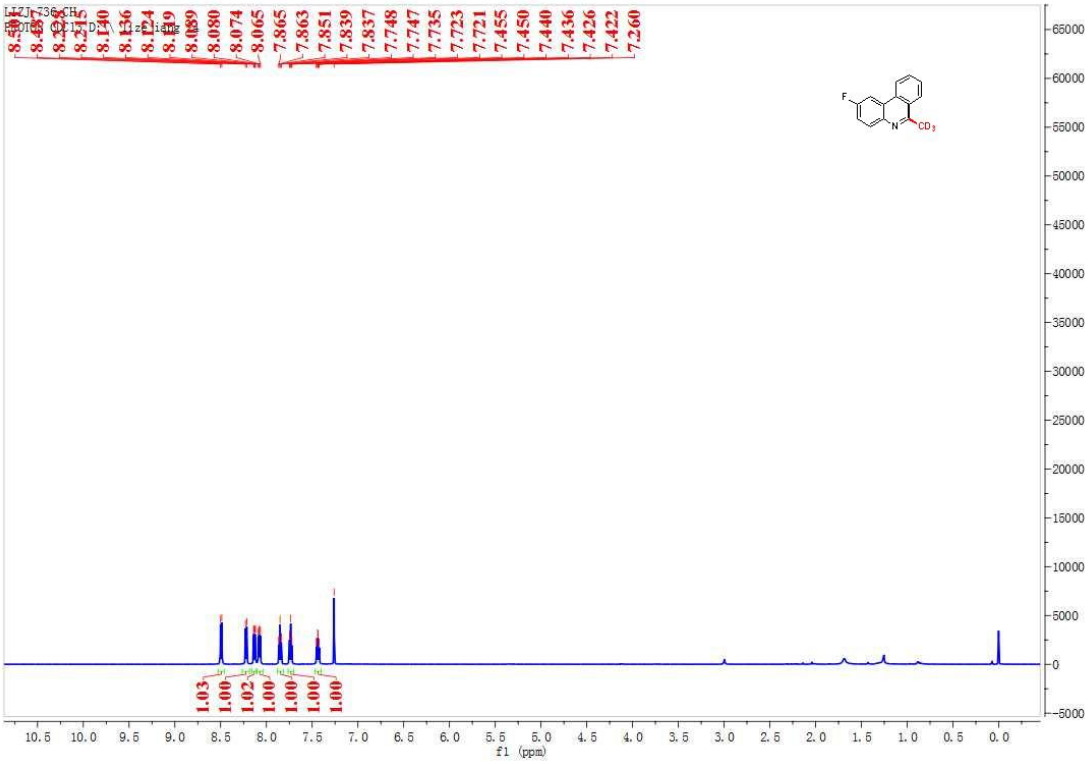
21-^{1}H NMR



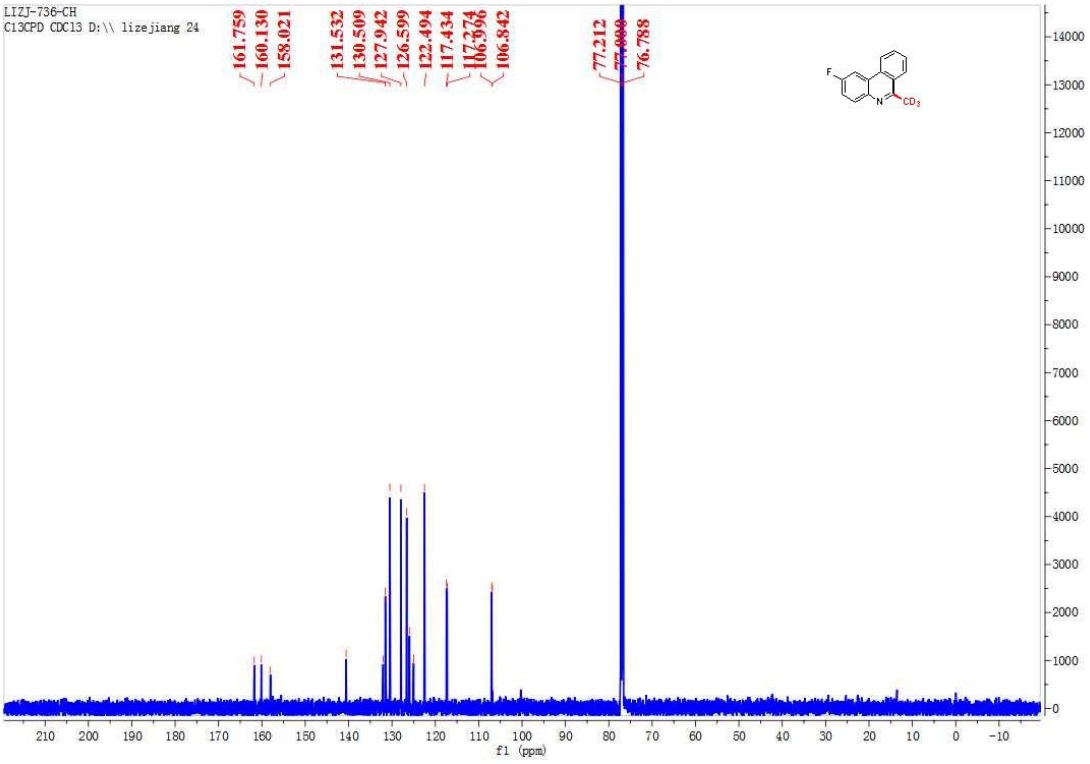
21-^{13}C NMR



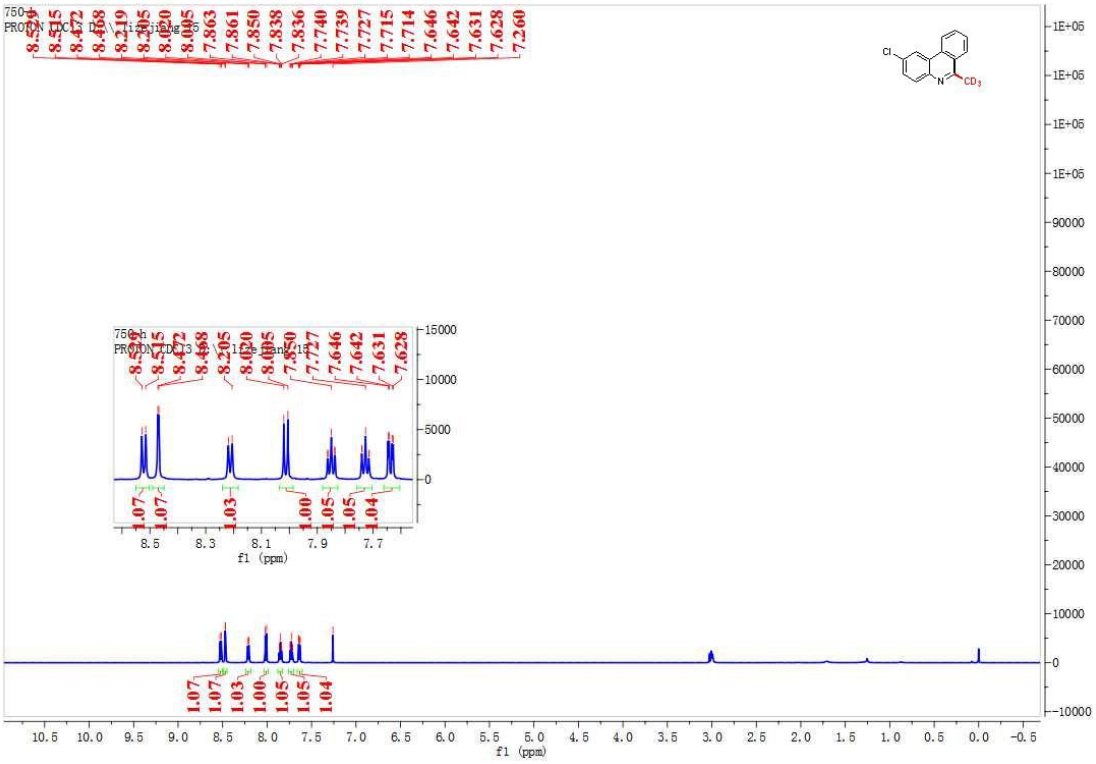
22-^{1}H NMR



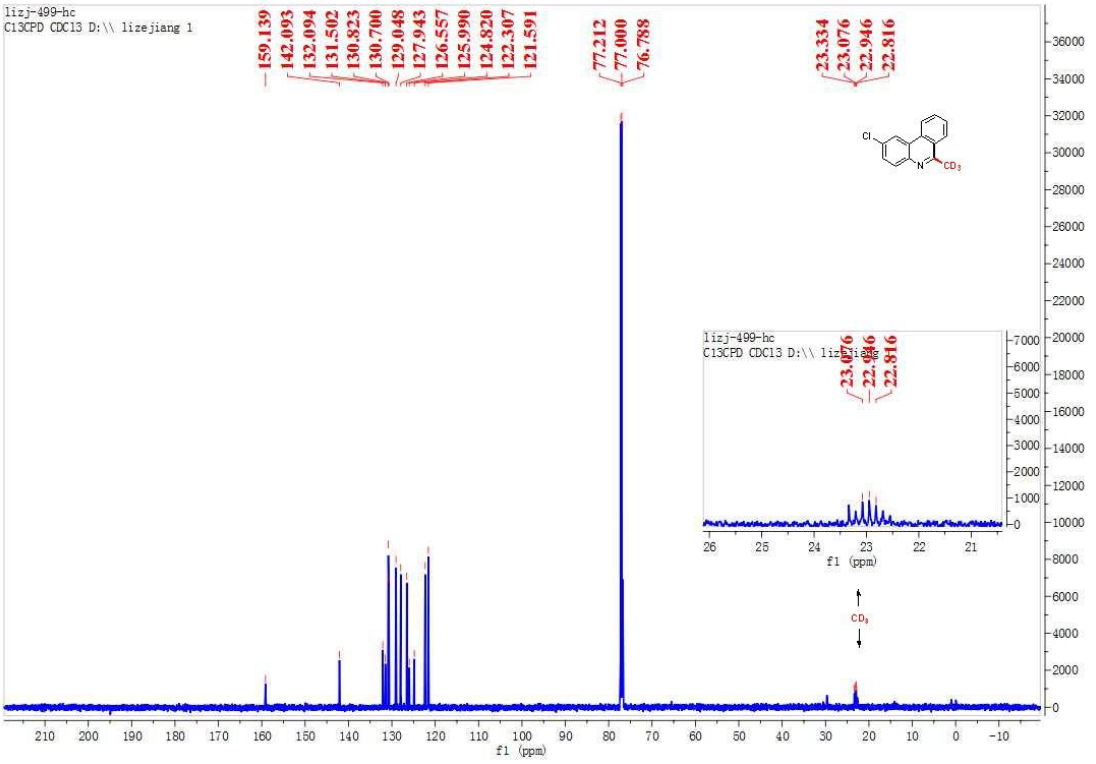
22-^{13}C NMR



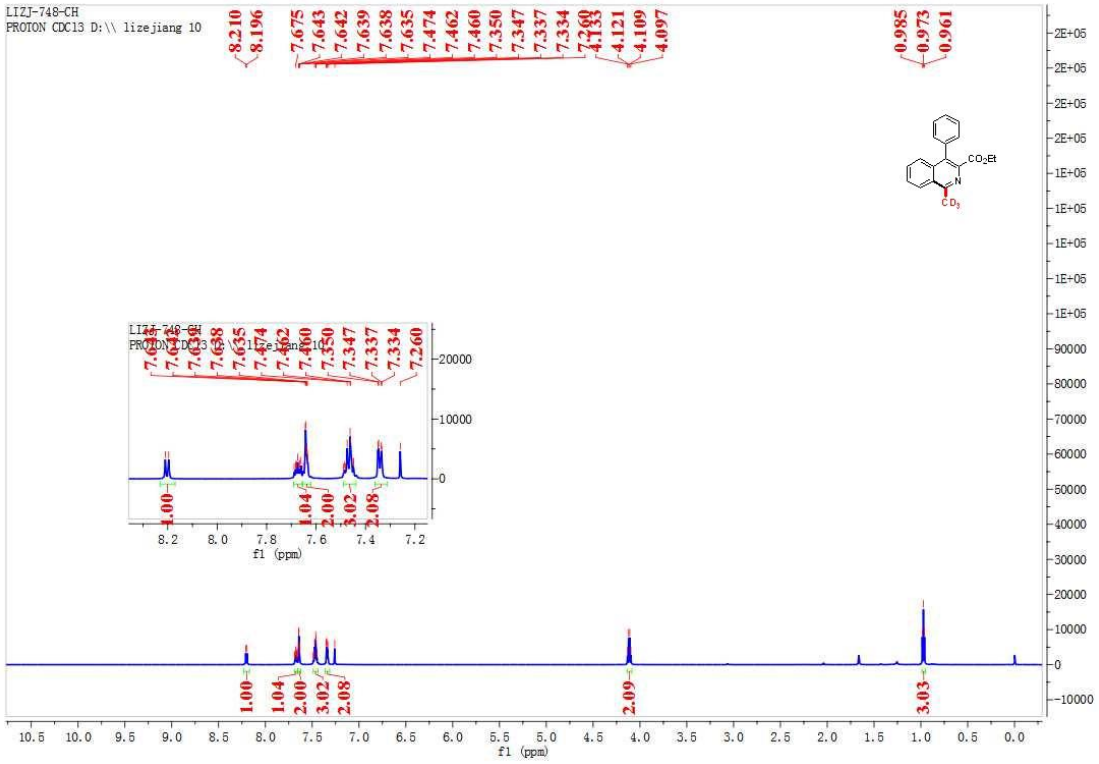
23-^{1}H NMR



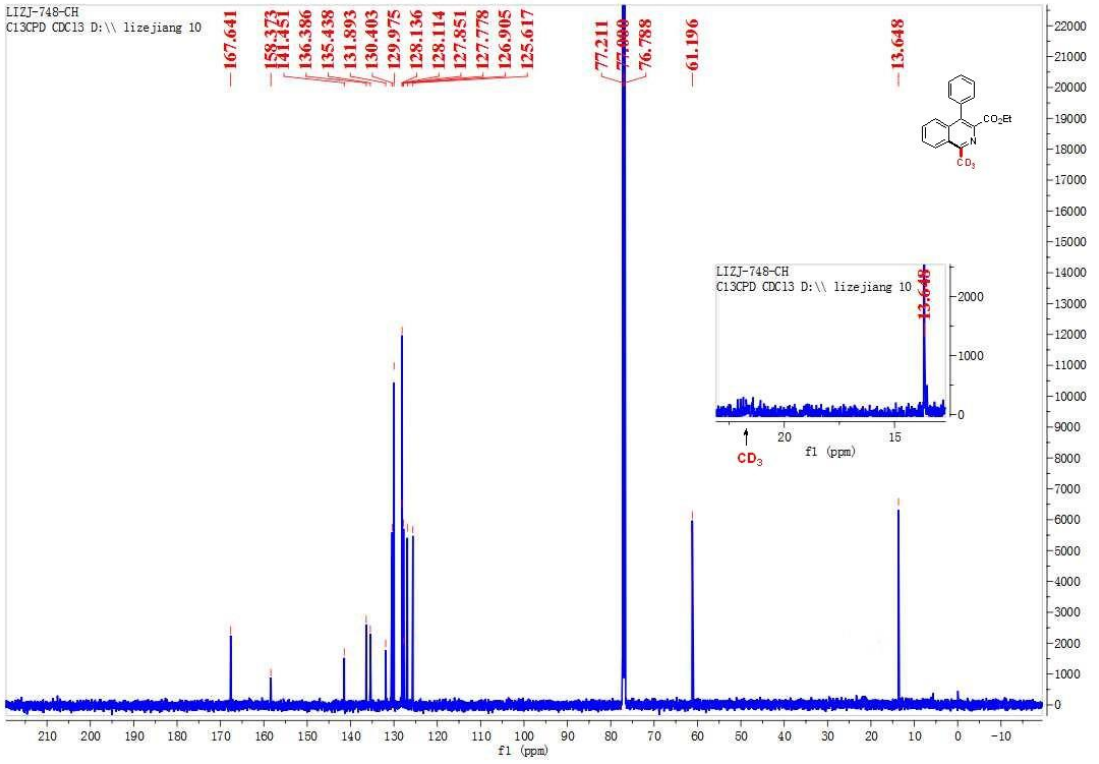
23-^{13}C NMR



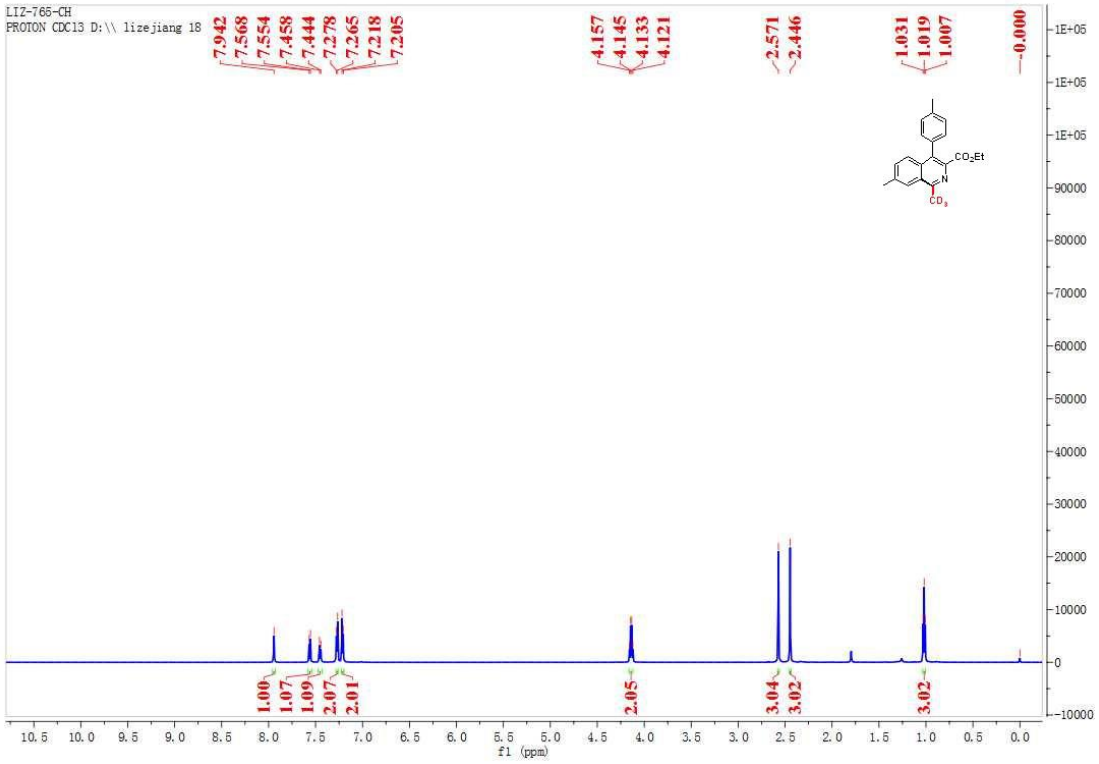
24-^{1}H NMR



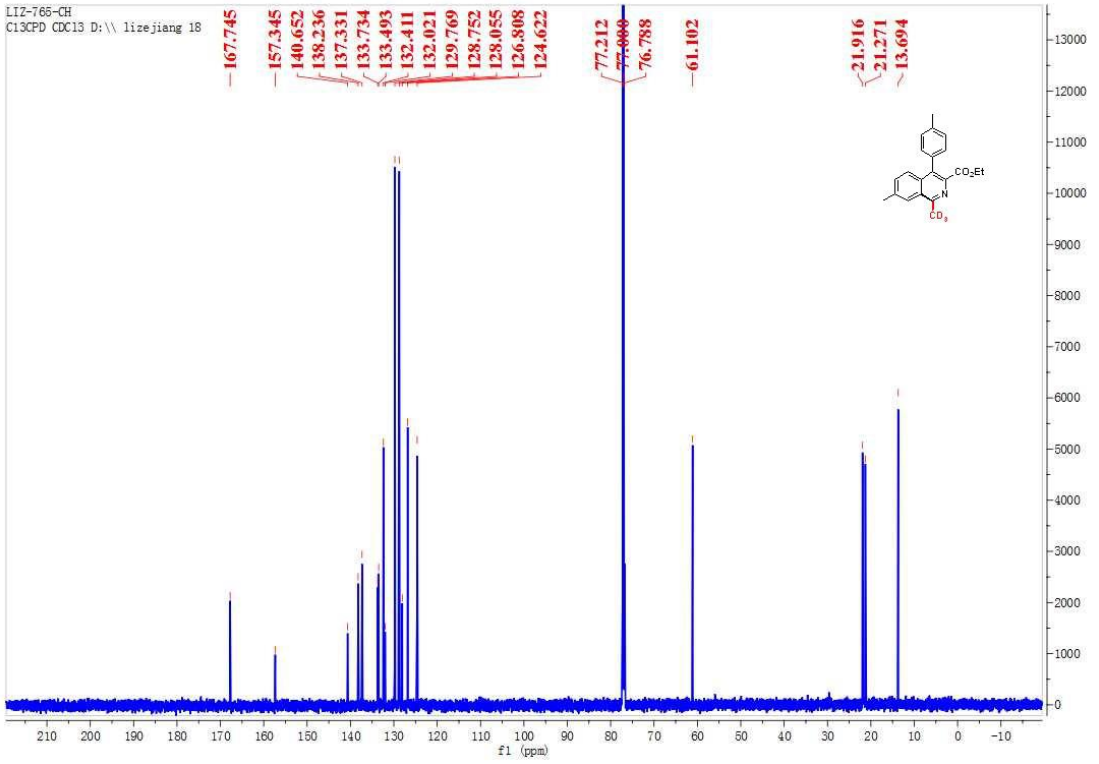
24-^{13}C NMR



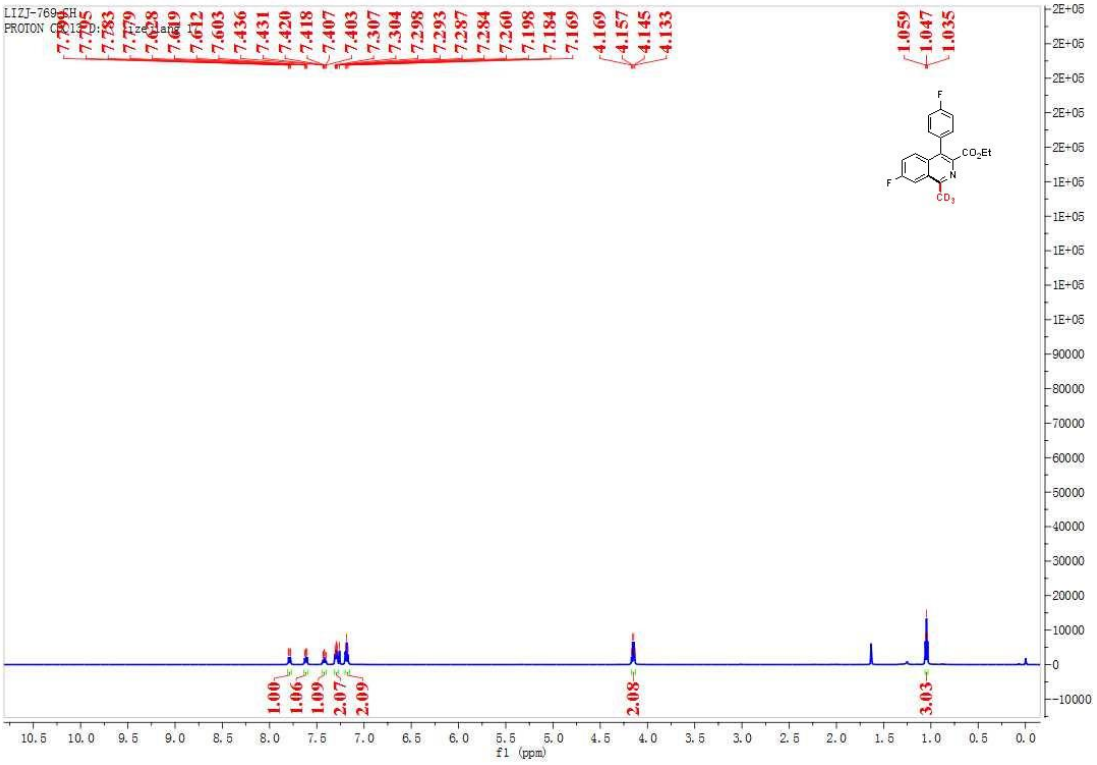
25-^{1}H NMR



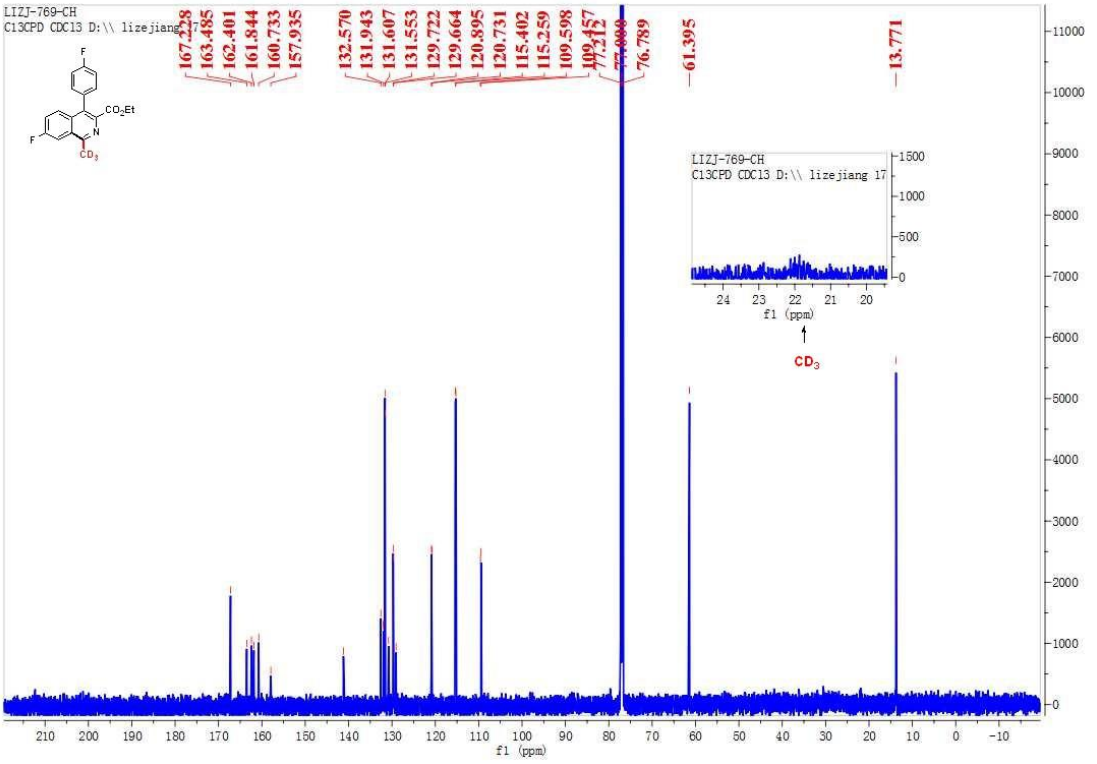
25-^{13}C NMR



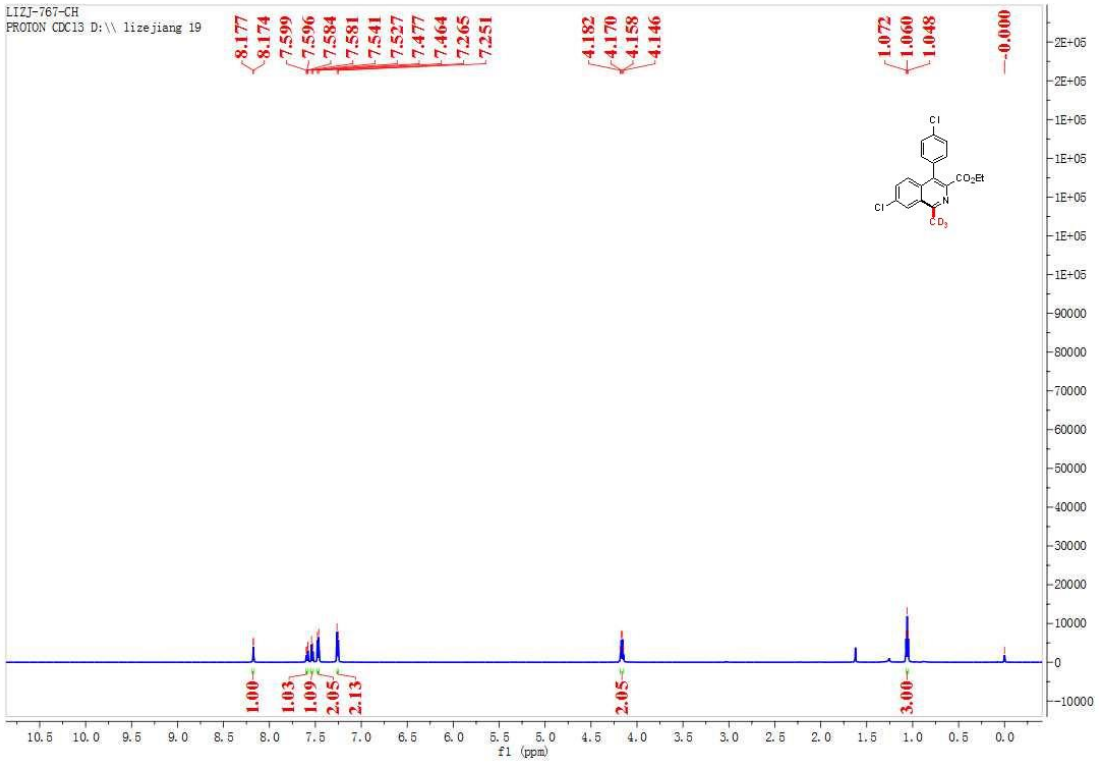
26-^{1}H NMR



26-^{13}C NMR



27-^{1}H NMR



27-^{13}C NMR