Combination of $RuCl_3.{}_XH_2O$ with PEG-A simple and Recyclable Catalytic System for Direct Arylations of Heteroarenes via C-H Bond Activation

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Supplementary Material

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EXPERIMENTAL SECTION

General methods. All the chemicals were purchased from commercial supplier and used as received without any further purification. All reactions were performed in oven-dried schlenk tube under air. Column chromatography was performed on silica gel (300-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance II-400 MHz in $CDCl_3$ or DMSO with TMS as internal standard. HPLC chromatograph analysis was conducted on an YOUNFLIN INSTRUMENT UV730D with an SP-120-5-ODS-AP column of 4.6 mm ID × 150 mm. Mass Spectra (MS) were performed on a Waters Q-TOF Premier mass spectrometer.

Typical experimental procedure for direct arylation of 2-phenylpyridine under air: An oven-dried and clean round-bottom flask was charged with $RuCl_3.xH_2O$ (104 mg, 0.5 mmol) and PEG-400 (10 ml). The mixture was stirred at room temperature until $RuCl_3.xH_2O$ was dispersed in PEG-400 completely. 2-phenylpyridine (**1a**, 1 mmol), 1-chloro-3-fluorobenzene (**2a**, 2.3 mmol), $LiOH.H_2O$ (126 mg, 3 mmol) and PEG-400 (1 mL) containing $RuCl_3.xH_2O$ (0.05 mmol) were added to a schlenk tube, respectively. The mixture solution was stirred at 120 °C under air for 24 h. After cooled to room temperature, the reaction mixture was diluted with 10 mL of water. The aqueous layer was extracted with Et_2O (20 mL) and EtOAc (30 mL), respectively. The combined organic phase was washed with H_2O (20 mL), brine (20 mL), dried it with Na_2SO_4 and concentrated under reduced pressure. The resulting residue was separated through a flash silica gel column chromatography (petroleum ether/EtOAc = 16:1) to give arylated products (306 mg, 95%). The ratio of mono- to diarylated

product was determined by 1H NMR spectroscopy. The arylated products were separated by a silica gel column chromatography (petroleum ether/CH_2Cl_2 = 1:16) to afford target products **3aa** and **4aa**, respectively. The product was characterized by ^1H and ^{13}C NMR spectroscopy.

Recycling experimental procedures: In a reaction tube, 2-phenylpyridine (**1a**, 1mmol), 1-chloro-3-fluorobenzene (**2a**, 2.3 mmol), $LiOH.H_2O$ (126 mg, 3 mmol) and PEG-400 (1 mL) containing $RuCl_3.xH_2O$ (0.05 mmol) were stirred at 120 °C under air for 24 h. At the end of reaction, the reaction mixture was cooled to room temperature and extracted by employing Et_2O (50 ml). And then, 2-phenylpyridine (**1a**, 1 mmol), 1-chloro- 3-fluorobenzene (**2a**, 2.3 mmol), $LiOH.H_2O$ (126 mg, 3 mmol) was added to the PEG solution again, and the reaction and operation were repeated with the above-mentioned process.

Table S1. Effect of the ratio of the substrates on arylation of 2-phenylpyridine with 1-chloro-3-fluorobenzene

Entry	A : B (mmol)	conversion[%]	Yield [%]	3aa/4aa [%]
1[a]	1:2.3	98	94	66:34
2[a]	1:1.2	93	91	77:23
3[a]	1.2:1	96	93	84:16
4[b]	1:2.3	>99	98	17:83
5[b]	1:3	>99	97	20:80

Reaction conditions: [a] 2-phenylpyridine (A), 3-fluoro-chlorobenzene (B), PEG-400 as reaction medium (1 ml), $RuCl_3.xH_2O$ (5 mol-%), and CH_3COOK (2 equiv) and the reaction mixture was heated to 120℃ and 1 h under air, the ratio of mono- and diarylated product determined by HPLC. [b] $LiOH.H_2O$ (3 equiv) and 24 h.

Table S2. Effect of ratio of substrate to catalyst on direct arylation of 2-phenylpyridine with 1-chloro-3-fluorobenzene.

entry	S/C	Time(h)	Yield[%]	3aa/4aa [%]
1	20	24	98	17:83
2	80	24	76	62:38
3	100	24	55	58:42
		48	58	58:42

Reaction conditions: 2-phenylpyridine (n mmol), 3-fluoro-chlorobenzene (2n+0.3 mmol), PEG-400 as reaction medium (1 ml), $RuCl_3.xH_2O$ (0.05 mmol), and $LiOH.xH_2O$ (3 equiv) and the reaction mixture was heated to 120 ^oC under air, the ratio of mono- and diarylated product determined by HPLC.

Table S3-a. Effect of the reaction temperature on direct arylation of 2-phenylpyridine with 1-chloro-3-fluorobenzene.

Entry	T[^{o}C]	Time(h)	Yield[%]	3aa/4aa [%]
1	90	1	2	\
		24	22	87:13
2	120	1	91	77:23
3	150	1	79	78:22

Reaction conditions: 2-phenylpyridine (1 mmol), 3-fluoro-chlorobenzene (1.2 mmol), PEG-400 as reaction medium (1 ml), $RuCl_3.xH_2O$ (5 mol-%), and CH_3COOK (2 equiv) and the reaction mixture was heated under air, the ratio of mono- and diarylated product determined by HPLC.

Table S3-b. Effect of the reaction temperature on direct arylation of 2-phenylpyridine with 1-chloro-3-fluorobenzene.

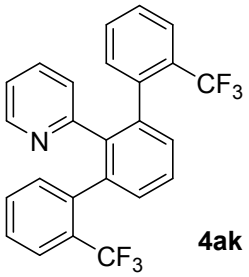
Entry	T[°C]	Time(h)	Yield[%]	3aa/4aa [%]
1	90	5	8	\
		24	13	\
2	120	5	96	25:75
		24	97	15:85
3	150	5	99	44:56
		24	99	40:60

Reaction conditions: 2-phenylpyridine (1 mmol), 3-fluoro-chlorobenzene (2.3 mmol), PEG-400 as reaction medium (1 ml), $RuCl_3.xH_2O$ (5 mol-%), and $LiOH.xH_2O$ (3 equiv) and the reaction mixture was heated under air, the ratio of mono- and diarylated product determined by HPLC.

Table S4. Recyclability of the catalyst for direct the arylation of 2-phenylpyridine with 1-chloro-3-fluorobenzene.

entry	run	Time[h]	yield [%]	ratio(3aa/4aa)
1	1	1	91	77:23
2	2	2	25	84:16
3	3	5	6	50:50
4	4	5	\	\

Reaction conditions: 2-phenylpyridine (1 mmol), 3-fluoro-chlorobenzene (1.2 mmol), PEG-400 as reaction medium (1 ml), $RuCl_3.xH_2O$ (5 mol-%), and CH_3COOK (2 equiv) and the reaction mixture was heated to 120 ^oC under air, the ratio determined by HPLC and every circulation needing to add equivalent base.



4ak

2-Di[2-(2-trifluoromethylphenyl)]phenylpyridine(4ak).

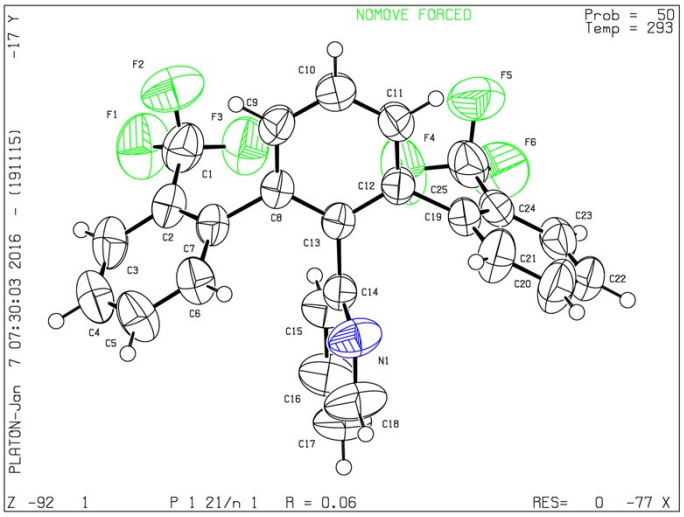


Table 1 Crystal data and structure refinement for 1.

CCDC number	1481843
Identification code	1
Empirical formula	$C_{25}H_{15}F_6N$
Formula weight	443.38
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.6865(3)
b/Å	11.0532(4)
c/Å	22.5491(8)
α/°	90
β/°	95.493(3)
γ/°	90
Volume/Å^3	2155.09(14)
Z	4
ρ_{calc}g/cm^3	1.367
μ/mm^{-1}	1.006
F(000)	904.0
Crystal size/mm^3	0.36 × 0.28 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.606 to 134.084
Index ranges	$-9 \le h \le 10$, $-13 \le k \le 8$, $-26 \le l \le 26$
Reflections collected	11668

Independent reflections	3844 [R_{int} = 0.0307, R_{sigma} = 0.0225]
Data/restraints/parameters	3844/0/289
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0605, wR_2 = 0.1720
Final R indexes [all data]	R_1 = 0.0696, wR_2 = 0.1835
Largest diff. peak/hole / e $Å^{-3}$	0.34/-0.26

2-[2-phenyl]phenylpyridine (3ab). Pale yellow solid.Mp =89°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.9 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.49 – 7.42 (m, 3H), 7.38 (m, 1H), 7.25 – 7.21 (m, 3H), 7.16 (m, 2H), 7.13 – 7.08 (m, 1H), 6.89 (d, *J* = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.19, 148.32, 140.31, 139.61, 138.37, 134.23, 129.47, 128.68, 127.52, 127.03, 126.63, 125.68, 124.41, 120.33. HRMS (ESI): Calc'd for $C_{17}H_{14}N$ ($[M+H]^+$) : 232.1126; found, 232.1097. $C_{17}H_{13}N$ (231.1048).

2-Di[2-phenyl]phenylpyridine (4ab). Pale yellow solid.Mp =135°C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.28 (m, 1H), 7.51 (dd, *J* = 8.6, 6.4 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.28 (td, *J* = 7.7, 1.8 Hz, 1H), 7.16 – 7.07 (m, 10H), 6.89 (ddd, *J* = 13.7, 8.0, 4.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.87, 147.43, 140.81, 140.54, 137.43, 133.86, 128.60, 128.43, 127.15, 126.60, 125.77, 125.24, 119.85. HRMS (ESI): Calc' d for $C_{23}H_{18}N$ ($[M+H]^+$) : 308.1439; found, 308.1405. $C_{23}H_{17}N$ (307.1361).

2-[2-(2-quinolinyl)]phenylpyridine (3ap). Yellow oil (103mg, 37%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (m, 1H), 8.11 (d, *J* = 8.6 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.84 – 7.80 (m, 1H), 7.74 (m, 2H), 7.69 (m, 1H), 7.58 – 7.53 (m, 2H), 7.50 (m, 1H), 7.37 (td, *J* = 7.7, 1.8 Hz, 1H), 7.10 (m, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 7.01 (dt, *J* = 7.9, 1.0

Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.60, 158.86, 149.38, 148.01, 139.79, 139.66, 135.79, 135.36, 130.72, 130.42, 129.55, 129.46, 129.06, 128.94, 127.49, 126.65, 126.47, 125.33, 123.28, 121.67. HRMS (ESI): Calc'd for $C_{20}H_{15}N_2$ ([M+H])$^+$: 283.1235; found, 283.1218. $C_{20}H_{14}N_2$ (282.1157).

2-Di[2-(2quinolinyl)]phenylpyridine (4ap). Light green solid. Mp=160-161^{o}C. (143mg, 35%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.18 (m, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 7.7 Hz, 2H), 7.84 (dd, *J* = 8.5, 4.0 Hz, 2H), 7.72 (m, 3H), 7.69 – 7.64 (m, 2H), 7.52 – 7.45 (m, 2H), 7.29 (dd, *J* = 7.4, 6.1 Hz, 1H), 7.13 – 7.01 (m, 3H), 6.95 – 6.88 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.41, 158.27, 148.33, 147.85, 141.15, 141.11, 135.61, 135.15, 131.02, 129.49, 129.39, 129.02, 127.41, 127.22, 126.45, 126.37, 122.90, 121.32. HRMS (ESI): Calc'd for $C_{29}H_{20}N_3$ ([M+H])$^+$: 410.1657; found, 410.1652. $C_{29}H_{19}N_3$ (409.1579).

2-[2-(2-thiophenyl)]phenylpyridine (3aq). White solid. Mp=196^{o}C. ^{1}H NMR (400 MHz, DMSO) δ 8.61 (m, 1H), 7.69 (td, *J* = 7.7, 1.8 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.53 – 7.46 (m, 3H), 7.45 (m, 1H), 7.32 (m, 1H), 7.21 – 7.17 (d, *J* = 8.0Hz,1H), 6.95 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.78 (dd, *J* = 3.5, 1.2 Hz, 1H).^{13}C NMR (101 MHz, DMSO) δ 158.99, 149.60, 142.65, 139.90, 136.63, 133.03, 130.94, 130.70, 129.14, 128.35, 127.76, 127.25, 127.15, 125.12, 122.81. HRMS (ESI): Calc'd for $C_{15}H_{12}NS$ ([M+H])$^+$: 238.0690; found, 238.0658. $C_{15}H_{11}NS$ (237.0612).

2-Di[2-(2-thiophenyl)]phenylpyridine (4aq). Yellow oil. ^{1}H NMR (400 MHz, DMSO) δ 8.55 (d, *J* = 4.2 Hz, 1H), 7.66 – 7.54 (m, 4H), 7.39 (dd, *J* = 5.1, 1.1 Hz, 2H), 7.30 (m, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 6.88 (dd, *J* = 5.1, 3.6 Hz, 2H), 6.72 (dd, *J* =

3.6, 1.1 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 158.18, 149.27, 142.41, 138.33, 136.66, 134.56, 129.86, 129.19, 127.57, 127.41, 127.35, 126.75, 123.36. HRMS (ESI): Calc'd for $C_{19}H_{14}NS_2$ $([M+H])^+$: 320.0568; found, 320.0538. $C_{19}H_{13}NS_2$ (319.0489).

2-[2-(3-thiophenyl)]phenylpyridine (3ar). White solid. Mp=197-198°C. ^{1}H NMR (400 MHz, DMSO) δ 8.60 (d, *J* = 4.9 Hz, 1H), 7.63 (m, 1H), 7.56 – 7.44 (m, 4H), 7.39 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.06 (m, 1H), 6.63 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 159.25, 149.71, 141.78, 139.73, 136.30, 135.25, 130.76, 130.48, 129.08, 128.98, 127.87, 126.19, 124.94, 123.67, 122.47. HRMS (ESI): Calc'd for $C_{15}H_{12}NS$ $([M+H])^+$: 238.0690; found, 238.0660. $C_{15}H_{11}NS$ (237.0612).

2-Di[2-(3-thiophenyl)]phenylpyridine (4ar). Yellow oil. ^{1}H NMR (400 MHz, DMSO) δ 8.48 (d, *J* = 4.8 Hz, 1H), 7.57 – 7.47 (m, 4H), 7.31 (m , 2H), 7.20 (m, 1H), 7.08 (dt, *J* = 5.9, 2.9 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 5.0 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 159.12, 148.97, 141.76, 138.52, 136.51, 136.24, 129.26, 129.04, 128.81, 126.35, 125.62, 123.77, 122.52. HRMS (ESI): Calc'd for $C_{19}H_{14}NS_2$ $([M+H])^+$: 320.0568; found, 320.0538. $C_{19}H_{13}NS_2$ (319.0489).

2-[2-(4-Methoxylphenyl)]phenylpyridine (3ah). Light yellow oil. (63mg, 24%): NMR data were consistent with reported data.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.8 Hz, 1H), 7.70 – 7.65 (m, 1H), 7.42 (m, 4H), 7.12 – 7.05 (m, 3H), 6.89 (d, *J* = 8.0H), 6.78 (d, *J* = 8.8H), 3.78 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.44, 158.53, 149.41, 140.20, 139.33, 135.29, 133.71, 130.78, 130.51, 130.45, 128.54, 127.32, 125.46, 121.30, 113.55, 55.21.

2-Di[2-(4-Methoxylphenyl)]phenylpyridine (4ah). White solid. Mp =162-163 °C. (244mg, 66%)**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 4.6 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.40 (d, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 4H), 6.97 – 6.91 (m, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 8.6 Hz, 4H), 3.74 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.25, 157.03, 147.53, 140.38, 137.42, 133.98, 133.04, 129.64, 128.15, 127.09, 125.76, 119.77, 112.07, 54.08. HRMS (ESI): Calc'd for $C_{25}H_{22}NO_2$ $([M+H])^+$: 368.1651; found, 368.1621. $C_{25}H_{21}NO_2$ (367.1572).

2-[2-(4-acetylphenyl)]phenylpyridine (3ao). Yellow oil. (80mg, 29%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 – 8.58 (m, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.73 – 7.67 (m, 1H), 7.54 – 7.47 (m, 2H), 7.46 – 7.39 (m, 2H), 7.25 (d, *J* =8.8Hz,2H), 7.15 – 7.10 (m, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 2.57 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 197.83, 158.85, 149.49, 146.44, 139.57, 139.50, 135.60, 135.36, 130.65, 130.32, 129.88, 128.69, 128.33, 128.16, 125.23, 121.63, 26.60. HRMS (ESI): Calc'd for $C_{19}H_{16}NO$ $([M+H])^+$: 274.1232; found, 274.1202. $C_{19}H_{15}NO$ (273.1154).

2-Di[2-(4-acetylphenyl)]phenylpyridine (4ao). Light green solid. Mp = 198 °C. (242mg, 62%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 – 8.29 (d, *J* =5.6Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 4H), 7.58 (m, 1H), 7.52 – 7.46 (m, 2H), 7.33 (m, 1H), 7.19 (d, *J* = 8.4 Hz, 4H), 6.99 – 6.94 (m, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 2.55 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 197.83, 157.93, 148.74, 146.32, 140.99, 138.30, 135.42, 135.16, 129.90, 129.79, 128.56, 127.84, 126.73, 121.53, 26.56. HRMS (ESI): Calc'd for $C_{27}H_{22}NO_2$ $([M+H])^+$: 392.1651; found, 392.1629. $C_{27}H_{21}NO_2$ (391.1572).

2-[2-(4-Methylphenyl)]phenylpyridine (3ae). Colorless oil. (80mg, 33%): NMR data were consistent with reported data.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.8 Hz, 1H), 7.71 – 7.65 (m, 1H), 7.47 – 7.41 (m, 3H), 7.41 – 7.35 (m, 1H), 7.09 (dd, *J* = 7.3, 5.1 Hz, 1H), 7.04 (s, 4H), 6.90 (d, *J* = 7.9 Hz, 1H), 2.31 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.43, 149.41, 140.57, 139.41, 138.38, 136.39, 135.25, 130.54, 130.52, 129.59, 128.84, 128.54, 127.45, 125.46, 121.32, 21.14.

2-Di[2-(4-Methylphenyl)]phenylpyridine (4ae). White soild. Mp =148 °C. (171mg, 51%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 4.8 Hz, 1H), 7.49 (m, 1H), 7.43 – 7.39 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 4.2 Hz, 1H), 6.95 (m, 8H), 6.90 (d, *J* = 7.8 Hz, 1H), 2.26 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.26, 148.52, 141.77, 138.74, 138.45, 135.82, 134.96, 129.50, 129.38, 128.39, 128.17, 126.82, 120.83, 21.08. HRMS (ESI): Calc'd for $C_{25}H_{22}N$ $([M+H])^+$: 336.1752; found, 336.1724. $C_{25}H_{21}N$ (335.1674).

2-[2-(3-Methoxylphenyl)]phenylpyridine (3ag). White solid. Mp = 80 °C. (60mg, 23%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 4.8 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.50 – 7.44 (m, 3H), 7.40 (td, *J* = 7.7, 1.7 Hz, 1H), 7.17 – 7.08 (m, 2H), 6.92 (d, *J* = 7.9 Hz, 1H), 6.77 (m, 2H), 6.70 – 6.65 (s, 1H), 3.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.24, 158.15, 148.31, 141.65, 139.43, 138.42, 134.27, 129.40, 129.30, 128.04, 127.50, 126.70, 124.34, 121.15, 120.33, 113.87, 111.86, 54.06. HRMS (ESI): Calc'd for $C_{18}H_{16}NO$ $([M+H])^+$: 262.1232; found, 262.1205. $C_{18}H_{15}NO$ (261.1154).

2-Di[2-(3-Methoxylphenyl)]phenylpyridine (4ag). White solid. Mp =181 °C. (198mg, 54%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 4.7 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.32 (t, *J* = 6.9 Hz, 1H), 7.08 (t, *J* = 7.9 Hz, 2H), 6.93 (m, 2H), 6.74 (d, *J* = 7.5 Hz, 2H), 6.69 (m, 2H), 6.60 (d, J = 1.5 Hz, 2H), 3.56 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.07, 157.81, 147.48, 141.83, 140.66, 137.31, 134.04, 128.41, 127.65, 127.19, 125.69, 121.08, 119.94, 113.63, 111.86, 54.01. HRMS (ESI): Calc'd for $C_{25}H_{22}NO_2$ $([M+H])^+$: 368.1651; found, 368.1620. $C_{25}H_{21}NO_2$ (367.1572).

2-[2-(3-acetylphenyl)]phenylpyridine (3an). White solid. Mp = 105-106 °C. (145mg, 53%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 – 8.59 (d, *J* = 4.4 Hz, 1H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.75 (t, *J* = 1.4 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.53 – 7.46 (m, 3H), 7.46 – 7.40 (m, 1H), 7.38 – 7.30 (m, 2H), 7.12 (m, 1H), 6.93 (d, *J* = 7.9 Hz, 1H), 2.44 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 197.94, 159.09, 149.45, 141.68, 139.58, 139.54, 136.94, 135.57, 134.26, 130.56, 130.36, 129.93, 128.78, 128.40, 128.13, 126.42, 125.32, 121.57, 26.56. HRMS (ESI): Calc'd for $C_{19}H_{16}NO$ $([M+H])^+$: 274.1232; found, 274.1203. $C_{19}H_{15}NO$ (273.1154).

2-Di[2-(3-acetylphenyl)]phenylpyridine (4an). White solid. Mp = 86 °C. (152mg, 39%): NMR data were consistent with reported data.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 – 8.33 (d, *J* = 4.6Hz, 1H), 7.79 – 7.74 (d, *J* = 8.0Hz, 2H), 7.68 (t, *J* = 1.5 Hz, 2H), 7.58 (m, 1H), 7.53 – 7.49 (m, 2H), 7.39 – 7.31 (m, 3H), 7.28 (t, *J* = 7.7 Hz, 2H), 6.97 – 6.89 (m, 2H), 2.40 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 197.84, 158.45, 148.71, 141.58, 140.94, 138.50, 136.54, 135.44, 134.10, 129.99, 129.78, 128.70, 128.17, 126.88, 126.20, 121.39, 26.54.

2-[2-(3-Methylphenyl)]phenylpyridine (3ad). White solid, Mp = 90 °C. NMR data were consistent with reported data.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.8 Hz, 1H), 7.69 (m, 1H), 7.43 (m, 4H), 7.11 (m, 2H), 7.02 (d, *J* =10.8 Hz, 2H), 6.91 (d, *J* = 7.9 Hz, 2H), 2.26 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.29, 148.27, 140.19, 139.68, 138.37, 136.60, 134.12, 129.41, 129.39, 129.36, 127.43, 126.81, 126.49, 126.38, 125.83, 124.36, 120.25, 20.32.

2-Di[2-(3-Methylphenyl)]phenylpyridine (4ad). Pale yellow solid. Mp = 91 °C. NMR data were consistent with reported data.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.28 (d, *J* = 4.4Hz, 1H), 7.48 (m, 1H), 7.44 – 7.40 (m, 2H), 7.28 (td, *J* = 7.7, 1.8 Hz, 1H), 6.99 (m, 4H), 6.93 (d, *J* = 7.5 Hz, 2H), 6.90 – 6.83 (m, 4H), 2.19 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.95, 147.11, 140.81, 140.38, 137.22, 136.07, 133.90, 129.45, 128.24, 127.09, 126.38, 125.93, 125.76, 125.61, 119.77, 20.22.

2-[2-(2-Methoxylphenyl)]phenylpyridine (3af). White solid. Mp = 75-76 °C. (45mg, 17%): NMR data were consistent with reported data.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 – 8.64 (m, 1H), 7.79 (m, 1H), 7.45 (m, 4H), 7.25 – 7.21 (m, 2H), 7.16 (d, *J* = 8.5 Hz, 1H), 6.97 (m, 2H), 6.71 (d, *J* = 8.2 Hz, 1H), 3.36 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.35, 156.06, 148.70, 139.82, 137.07, 135.44, 131.47, 131.06, 130.31, 129.68, 128.82, 128.51, 127.77, 123.82, 121.26, 120.72, 110.69, 54.92.

2-Di[2-(2-Methoxylphenyl)]phenylpyridine (4af). White solid. Mp = 186-187 °C. (99mg, 27%): NMR data were consistent with reported data.[1] ^{1}H NMR (400 MHz, DMSO) δ 8.07 (s, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 3H), 7.13 (t, *J* = 7.6 Hz, 2H), 6.97 (s, 2H), 6.87 (s, 1H), 6.77 (d, *J* = 7.4 Hz, 5H), 3.37 (s, 6H).^{13}C

NMR (101 MHz, $CDCl_3$) δ 158.31, 154.93, 146.11, 138.86, 136.94, 132.87, 130.91, 129.64, 129.02, 127.20, 126.67, 124.74, 119.36, 119.11, 109.01, 53.83.

2-[2-(2-Methylphenyl)]phenylpyridine (3ac). white solid. Mp = 54 °C (54mg, 22%): NMR data were consistent with reported data.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.9Hz, 1H), 7.80 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.45 (m, 2H), 7.30 – 7.25 (m, 2H), 7.18 – 7.11 (m, 3H), 7.04 (m, 2H), 6.79 (d, *J* = 8.0 Hz, 1H), 1.88 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.69, 149.43, 141.13, 140.15, 139.76, 135.96, 135.17, 130.59, 130.41, 130.04, 129.97, 128.35, 127.77, 127.30, 125.62, 124.58, 121.34, 20.04.

2-Di[2-(2-Methylphenyl)]phenylpyridine (4ac). white solid. Mp = 130-131 °C. (63mg, 19%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.13 (d,*J* = 4.8 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.20 – 7.15 (m, 1H), 7.14 – 7.11 (m, 1H), 7.07 – 6.97 (m, 7H), 6.75 (m, 2H), 2.10 (s, 3H), 2.02 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.37, 146.91, 140.25, 140.07, 134.89, 133.27, 129.56, 129.19, 128.30, 128.02, 126.43, 125.70, 124.67, 123.71, 119.59, 19.39. HRMS (ESI): Calc'd for $C_{25}H_{22}N$ $([M+H])^+$: 336.1752; found, 336.1722. $C_{25}H_{21}N$ (335.1674).

2-[2-(4-fluorophenyl)]phenylpyridine (3aj). white solid. Mp = 84 °C. (94mg, 38%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.7 Hz, 1H), 7.69 (m, 1H), 7.50 – 7.39 (m, 4H), 7.17 – 7.08 (m, 3H), 6.97 – 6.89 (m, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 161.88(d, *J* =246.9Hz), 159.10, 149.44, 139.56, 139.45, 137.33, 135.46, 131.21(d, *J* =8.0Hz), 130.53, 130.42, 128.63, 127.80, 125.33, 121.47, 115.03(d, *J* =21.5Hz). HRMS (ESI): Calc'd for $C_{17}H_{13}FN$ $([M+H])^+$: 250.1032; found, 250.0998. $C_{17}H_{12}FN$ (249.0954).

2-Di[2-(4-fluorophenyl)]phenylpyridine (4aj). White solid. Mp = 102 °C. (172mg, 50%): NMR data were consistent with reported data.[1] ^{1}H NMR (400 MHz, DMSO) δ 8.32 (d, *J* = 4.7 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.48 – 7.41 (m, 3H), 7.06 (m, 5H), 7.00 (t, *J* = 8.9 Hz, 4H), 6.92 (d, *J* = 7.8 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 161.48(d, *J*=246.7Hz), 158.60, 148.68, 140.90, 138.56, 137.41, 135.22, 131.15(d, *J*=8.1Hz), 129.52, 128.31, 126.71, 121.12, 114.72(d, *J*=21.4Hz).

2-[2-(3-fluorophenyl)]phenylpyridine (3aa). White solid. Mp = 90 °C. ^{1}H NMR (400 MHz, CDCl3) δ 8.65 – 8.60 (d, *J* = 4.6 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.52 – 7.40 (m, 4H), 7.21 – 7.11 (m, 2H), 6.95 – 6.86 (m, 4H). ^{13}C NMR (101 MHz, CDCl3) δ 162.51 (d, *J*=246.5Hz), 158.89, 149.45, 143.68, 139.46, 139.39, 135.50, 130.57, 130.34, 129.53, 128.65, 128.01, 125.55, 125.24, 121.59, 116.54 (d, *J*=21.8Hz), 113.61 (d, *J*=21.2Hz).HRMS (ESI): Calc'd for $C_{17}H_{13}FN$ $([M+H])^+$: 250.1032; found, 250.1001. $C_{17}H_{12}FN$ (249.0954).

2-Di[2-(3-fluorophenyl)]phenylpyridine (4aa). White solid. Mp = 112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 4.6 Hz, 1H), 7.53 (m, 1H), 7.47 – 7.43 (m, 2H), 7.35 (m, 1H), 7.11 (td, *J* = 7.9, 6.1 Hz, 2H), 6.97 (dd, *J* = 7.5, 4.9 Hz, 1H), 6.84 (m, 7H). ^{13}C NMR (101 MHz, CDCl3) δ 162.27 (d, *J*=246.6Hz), 158.16, 148.73, 143.63, 140.72, 138.42, 135.25, 129.71, 129.07, 128.40, 126.58, 125.41, 121.36, 116.53(d, *J*=22.0Hz), 113.34(d, *J*=21.0Hz). HRMS (ESI): Calc' d for $C_{23}H_{16}F_2N$ $([M+H])^+$: 344.1251; found, 344.1232. $C_{23}H_{15}F_2N$ (343.1173).

2-[2-(4-trifluoromethylphenyl)]phenylpyridine. (3am). Light yellow solid. Mp = 89 °C. (30mg, 10%): NMR data were consistent with reported data.[1] ^{1}H NMR (400

MHz, DMSO) δ 8.55 – 8.50 (d,*J* = 4.8 Hz, 1H), 7.67 – 7.59 (m, 4H), 7.58 – 7.54 (m, 2H), 7.51 – 7.47 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.10 (d, *J* = 7.9 Hz, 1H).^{13}C NMR (101 MHz, DMSO) δ 158.13, 149.20, 145.23, 139.35, 138.69, 136.10, 130.50, 130.38, 130.01, 128.73, 128.26, 127.12 (q, *J*=32.0Hz), 124.91 (q, *J*=37.0Hz), 124.73, 124.27 (q, *J*=273.1Hz), 122.01.

2-Di[2-(4-trifluoromethylphenyl)]phenylpyridine (4am). White solid. Mp = 138 ^{o}C. (354mg, 80%): ^{1}H NMR (400 MHz, DMSO) δ 8.31 (d, *J* = 4.8 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.59 – 7.53 (m, 6H), 7.48 (m, 1H), 7.26 (d, *J* = 8.1 Hz, 4H), 7.09 (dd, *J* = 7.5, 4.9 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H).^{13}C NMR (101 MHz, DMSO) δ 157.68, 149.05, 145.60, 140.52, 138.86, 136.03, 130.52, 130.40, 129.18, 127.51(q, *J*=31.92), 127.11, 125.05(q, *J*=3.74HZ), 124.69(q, *J*=273), 122.35. HRMS (ESI): Calc'd for $C_{25}H_{16}F_6N$ $([M+H])^+$: 444.1187; found, 444.1158. $C_{25}H_{15}F_6N$ (443.1109).

2-[2-(3-trifluoromethylphenyl)]phenylpyridine (3al). Light yellow solid. Mp = 88 ^{o}C. (84mg, 28%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.3 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.52 – 7.49 (m, 2H), 7.46 (m, 3H), 7.43 – 7.41 (m, 1H), 7.34 – 7.30 (m, 2H), 7.12 (m, 1H), 6.92 (d, *J* = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.76, 148.45, 141.01, 138.62, 138.05, 134.56, 131.94, 129.55, 129.39, 129.30, 127.75, 127.43, 127.26, 125.44 (q, *J*=3.7Hz), 124.13, 122.96(q, *J*=243.5Hz), 122.38 (q, *J*=3.8Hz), 120.60. HRMS (ESI): Calc'd for $C_{18}H_{13}F_3N$ $([M+H])^+$: 300.1000; found, 300.0978. $C_{18}H_{12}F_3N$ (299.0922).

2-Di[2-(3-trifluoromethylphenyl)]phenylpyridine (4al). Colorless oil. (292mg, 66%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (m, 1H), 7.57 (m, 1H), 7.52 – 7.48 (m, 2H),

7.40 (d, *J* = 7.5 Hz, 2H), 7.32 (m, 7H), 6.95 (m, 1H), 6.85 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.81, 147.79, 140.88, 139.53, 137.69, 134.37, 131.75, 129.05(q, *J* =32.3Hz), 128.82, 127.67, 127.21, 125.61, 125.52(q, *J*=3.8Hz), 122.92(q, *J* =273.4Hz), 122.20(q, *J* =4.0Hz), 120.41. HRMS (ESI): Calc'd for $C_{25}H_{16}F_6N$ $([M+H])^+$: 444.1187; found, 444.1158. $C_{25}H_{15}F_6N$ (443.1109).

2-[2-(2-trifluoromethylphenyl)]phenylpyridine (3ak). light yellow solid. Mp = 110 ^{o}C. (48mg, 16%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.3 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.52 (m, 1H), 7.43 (m, 1H), 7.38 – 7.31 (m, 4H), 7.09 – 7.01 (m, 2H), 6.89 (d, *J* = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.41, 148.21, 139.19, 138.60, 136.73, 134.33, 132.07, 129.86, 129.40(q, *J* =1.9Hz), 128.96, 127.73(q, *J* =29.8Hz), 127.29, 126.58, 126.12, 125.13(q, *J* =5.2Hz), 123.31, 123.16 (q, *J* =275.1Hz), 120.32. HRMS (ESI) : Calc'd for $C_{18}H_{13}F_3N$ $([M+H])^+$: 300.1000; found, 300.0984. $C_{18}H_{12}F_3N$ (299.0922).

2-Di[2-(2-trifluoromethylphenyl)]phenylpyridine(4ak). White solid. Mp =109-110 ^{o}C. (80mg, 18%):HRMS (ESI) : Calc'd for $C_{25}H_{16}F_6N$ $([M+H])^+$: 444.1187; found, 444.1157. $C_{25}H_{15}F_6N$ (443.1109).

1-[2-(4-trifluoromethylphenyl)]phenylpyrazol (3bm). Light yellow oil. (120mg, 42%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 2H), 7.51 (m, 4H), 7.47 (m, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 2.3 Hz, 1H), 6.23 (t, *J* = 2.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.20, 139.53, 137.55, 134.50, 130.18, 129.86, 128.44 (q, *J*=32.6Hz), 128.10, 127.76, 127.57, 125.82, 124.34 (q, *J*=3.7Hz), 123.06 (q,

J=273.1Hz), 105.79. HRMS (ESI): Calc'd for $C_{16}H_{12}F_3N_2$ $([M+H])^+$: 289.0953; found, 289.0941. $C_{16}H_{11}F_3N_2$ (288.0874).

1-Di[2-(4-trifluoromethylphenyl)]phenylpyrazol (4bm). White solid. Mp = 132°C . (130mg, 30%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (m, 1H), 7.54 (s, 1H), 7.53 – 7.51 (m, 1H), 7.50 (d, *J* = 8.3 Hz, 4H), 7.39 (d, *J* = 1.8 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 4H), 7.06 (d, *J* = 2.4 Hz, 1H), 6.09 (t, *J* = 2.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.01, 138.98, 138.20, 135.43, 131.34, 129.63, 128.52, 128.43 (q, *J*=32.6Hz), 127.54, 124.08 (q, *J*=3.7Hz), 123.07 (q, *J*=273.1Hz), 105.80. HRMS (ESI): Calc'd for $C_{23}H_{15}F_6N_2$ $([M+H])^+$: 433.1139; found, 433.1120. $C_{23}H_{14}F_6N_2$ (432.1061).

2-[2-(4-trifluoromethylphenyl)]phenyl-2-oxazoline (3cm). (128mg, 44%): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.53 – 7.41 (m, 4H), 7.36 (d, *J* = 7.6 Hz, 1H), 4.17 – 4.09 (m, 2H), 3.91 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.38, 143.99, 139.43, 129.70, 129.27, 128.24(q, *J*=32.3Hz), 128.05, 127.69, 126.86, 126.46, 123.92(q, *J* =3.7Hz), 123.26(q, *J* =272.7Hz), 66.78, 54.03. HRMS (ESI): Calc'd for $C_{16}H_{13}F_3NO$ $([M+H])^+$: 292.0949; found, 292.0934. $C_{16}H_{12}F_3NO$ (291.0871).

2-Di[2-(4-trifluoromethylphenyl)]phenyl-2-oxazoline (4cm). White solid. Sublimation. (57mg, 13%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 4H), 7.61 – 7.53 (m, 5H), 7.42 (d, *J* = 7.7 Hz, 2H), 3.90 (t, *J* = 9.5 Hz, 2H), 3.61 (t, *J* = 9.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.27, 143.21, 143.19, 140.13, 129.01, 128.61 (q, *J*=32.6Hz), 128.39, 127.88, 126.49, 124.05 (q, *J*=3.7Hz), 123.19 (q,

J=273.1Hz), 66.50, 54.06. HRMS (ESI): Calc'd for $C_{23}H_{16}F_6NO$ $([M+H])^+$: 436.1136; found, 436.1120. $C_{23}H_{15}F_6NO$ (435.1058).

2-[2-(4-trifluoromethylphenyl)]phenyl-beta-picoline (3fm). Yellow oil. (238mg, 76%): NMR data were consistent with reported data.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 4.0 Hz, 1H), 7.51 – 7.40 (m, 6H), 7.34 (d, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.12 (m, 1H), 1.78 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.76, 145.62, 143.71, 138.39, 138.20, 136.76, 130.50, 129.01, 128.65, 128.45, 127.67 (q, *J*=32.6Hz), 127.54, 127.20, 123.70 (q, *J*=3.7Hz), 123.16 (q, *J*=273.1Hz), 121.40, 17.79.

2-Di[2-(4-trifluoromethylphenyl)]phenyl-beta-picoline (4fm). (18mg, 4%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 3.8 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.48 (d, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 4H), 7.26 – 7.19 (m, 5H), 6.98 (m, 1H), 1.78 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 155.90, 145.00, 143.59, 139.46, 136.64, 128.88, 128.77, 128.52, 127.86, 127.69, 127.54, 123.59 (q, *J*=3.7Hz), 123.09 (q, *J*=273.1Hz), 121.46, 17.68. HRMS (ESI): Calc'd for $C_{26}H_{18}F_6N$ $([M+H])^+$: 458.1343; found, 458.1314. $C_{26}H_{17}F_6N$ (457.1265).

2-[(2-(4-trifluoromethylphenyl)-4-methoxyl]phenyl)pyridine (3dm). White solid. Mp = 93-94 ^{o}C. (66mg, 20%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.8 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.40 (m, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.12 – 7.07 (m, 1H), 7.05 (m, 1H), 6.94 (d, *J* = 2.6 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.73, 157.40, 148.40, 144.09, 139.48, 134.48, 131.25, 131.08, 128.84, 127.92(q, *J*=32.5Hz), 124.14, 124.02(q,

J=3.7Hz), 123.18(q, *J*=273.1Hz), 120.22, 114.82, 112.71, 54.43. HRMS (ESI): Calc'd for $C_{19}H_{15}F_3NO$ $([M+H])^+$: 330.1106; found, 330.1074. $C_{19}H_{14}F_3NO$ (329.1027).

2-[2,2'-di(4-trifluoromethylphenyl)-4-methoxyl]phenylpyridine (4dm). pale yellow solid. Mp =176 °C. (340mg, 72%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 4.2 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 4H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 4H), 7.00 (s, 2H), 6.99 – 6.93 (m, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 3.92 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.11, 156.64, 147.76, 143.98, 141.11, 134.33, 130.36, 128.74, 127.72 (q, *J*=32.5Hz), 125.98, 123.65 (q, *J*=3.7Hz), 123.16 (q, *J*=273.1Hz), 120.29, 114.35, 54.55. HRMS (ESI): Calc'd for $C_{26}H_{18}F_6NO$ $([M+H])^+$: 474.1293; found, 474.1275. $C_{26}H_{17}F_6NO$ (473.1214).

2-[(2-(4-trifluoromethylphenyl)-4-trifluoromethyl]phenylpyridine (3em). White solid. Mp = 40.5-41 °C. (191mg, 52%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.8Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.76 (s, 1H), 7.70 (s, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.48 (m, 1H), 7.32 – 7.27 (m, 2H), 7.18 (m, 1H), 6.96 (d, *J* = 7.9 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 156.36, 148.74, 142.71, 141.90, 138.89, 134.89, 130.30, 129.83 (q, *J*=32.6Hz), 128.86, 128.55 (q, *J*=32.6Hz), 126.20 (q, *J*=3.6Hz), 124.23 (q, *J*=3.7Hz), 124.08, 123.97 (q, *J*=3.7Hz), 123.06 (q, *J*=273.0Hz), 122.94 (q, *J*=273.1Hz), 121.34. HRMS (ESI): Calc'd for $C_{19}H_{12}F_6N$ $([M+H])^+$: 368.0874; found, 368.0846. $C_{19}H_{11}F_6N$ (367.0796).

2-[2,2'-di(4-trifluoromethylphenyl)-4-Trifluoromethyl]phenylpyridine (4em). White solid. Mp = 130-131 °C. (164mg, 32%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 4.4 Hz, 1H), 7.74 (s, 2H), 7.46 (d, *J* = 8.2 Hz, 4H), 7.39 (m, 1H), 7.23 (d, *J* = 8.1

Hz, 4H), 7.06 – 7.00 (m, 1H), 6.87 (d, *J* = 7.8 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 155.49, 148.06, 142.52, 140.70, 140.64, 134.72, 129.87 (q, *J*=33.0Hz), 128.74, 128.37 (q, *J*=32.7Hz), 125.56 (q, *J*=3.6Hz), 125.34, 123.92 (q, *J*=3.6Hz), 122.95 (q, *J*=273.1Hz), 122.68 (q, *J*=273.6Hz), 121.13. HRMS (ESI): Calc'd for $C_{26}H_{15}F_9N$ $([M+H])^+$: 512.1061; found, 512.1033. $C_{26}H_{14}F_9N$ (511.0983).

2,2'-di(pyridin-2-yl)-1,1'-biphenyl: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 4.7 Hz, 2H), 7.55 – 7.52 (m, 2H), 7.45 – 7.39 (m, 6H), 7.33 (td, *J* = 7.8, 1.7 Hz, 2H), 7.05 – 7.00 (m, 2H), 6.76 (d, *J* = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.78, 147.76, 138.73, 138.56, 134.44, 130.27, 129.01, 127.65, 126.79, 123.47, 120.27. HRMS (ESI): Calc'd for $C_{22}H_{17}N_2$ $([M+H])^+$: 309.1392; found, 309.1381. $C_{22}H_{16}N_2$ (308.1313).

2'-(pyridin-2-yl)-[1,1'-biphenyl]-4-carbonitrile (3au). White solid. Mp = 118 ^{o}C. (140mg, 55%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.8 Hz, 1H), 7.72 – 7.65 (m, 1H), 7.57 – 7.46 (m, 5H), 7.41 (m, 1H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.19 – 7.12 (m, 1H), 6.96 (d, *J* = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.55, 148.55, 145.33, 138.58, 137.76, 134.75, 130.82, 129.68, 129.30, 129.20, 127.79, 127.68, 124.02, 120.77, 117.89, 109.41. HRMS (ESI): Calc' d for $C_{18}H_{13}N_2$ $([M+H])^+$: 257.1079; found, 257.1064. $C_{18}H_{12}N_2$ (256.1000).

2'-(pyridin-2-yl)-[1,1':3',1''-terphenyl]-4,4''-dicarbonitrile (4au). White solid. Mp =166 ^{o}C. (35mg, 10%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.30 (d, *J* = 4.8 Hz, 1H), 7.60 (m, 1H), 7.50 – 7.44 (m, 6H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.21 – 7.16 (m, 4H), 7.02 (m, 1H), 6.86 – 6.81 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.32,

148.04, 144.94, 139.34, 137.30, 134.57, 130.59, 129.19, 129.07, 127.81, 125.60, 120.78, 117.75, 109.46. HRMS (ESI): Calc’d for $C_{25}H_{15}N_3Na$ $([M+Na])^+$: 380.1164; found, 380.1165. $C_{25}H_{15}N_3$ (357.1266).

2-(5-methyl-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)pyridine (3gm). Colorless oil. (187mg, 60%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.3 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.41 (td, *J* = 7.7, 1.8 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.29 – 7.21 (m, 3H), 7.09 (m, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.74, 148.45, 144.26, 138.01, 137.57, 135.83, 134.47, 130.08, 129.61, 128.88, 128.04, 127.69 (q, *J*=32.5HZ）, 124.15, 123.93(q, *J*=3.8HZ), 123.23(q, *J*=273.1HZ), 120.40, 20.15. HRMS (ESI): Calc’d for $C_{19}H_{15}F_3N$ $([M+H])^+$: 314.1157; found, 314.1142. $C_{19}H_{14}F_3N$ (313.1078).

2-(5'-methyl-4,4''-bis(trifluoromethyl)-[1,1':3',1''-terphenyl]-2'-yl)pyridine (4gm). White solid. Mp = 145-146 ^{o}C. (90mg, 20%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 4.3 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 4H), 7.36 – 7.28 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 4H), 6.99 – 6.93 (m, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.87, 147.80, 144.09, 139.61, 137.40, 134.76, 134.33, 129.66, 128.79, 127.54（q, *J*=32.5HZ）, 125.76, 123.59(q, *J*=3.7HZ), 123.16(q, *J*=273.0HZ), 120.37, 20.19. HRMS (ESI): Calc’d for $C_{26}H_{18}F_6N$ $([M+H])^+$: 458.1343; found, 458.1245. $C_{26}H_{17}F_6N$ (457.1265).

2-(3,5-difluoro-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)pyridine (hm). Colorless oil. (105mg, 32%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.8 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.22 – 7.16 (m, 3H), 7.12 (d, *J* = 7.8 Hz,

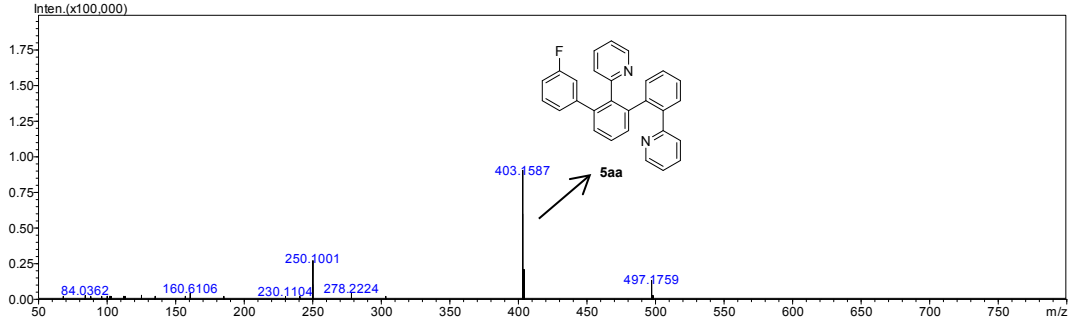
1H), 7.03 – 6.94 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.72 (dd, *J* = 164.0, 13.0 Hz), 159.31(dd, *J* = 163.7, 13.0 Hz), 151.72, 148.48, 142.12(dd, *J* = 9.5, 4.4 Hz), 141.72, 135.08, 128.58, 128.47 (q, *J* = 32.5 Hz), 125.20, 123.97 (q, *J* = 3.7 Hz), 123.19(dd, *J* = 15.9, 3.8 Hz), 122.95(q, *J* = 273.2 Hz), 121.44, 111.99(dd, *J* = 22.0, 3.5 Hz), 102.75(dd, *J* = 26.8, 25.2 Hz). HRMS (ESI): Calc'd for $C_{18}H_{11}F_5N$ $([M+H])^+$: 336.0812; found, 336.0791. $C_{18}H_{10}F_5N$ (335.0733).

[1] J. Zhang, Q. Yang, Z. Zhu, M. L. Yuan, H. Y. Fu, X. L. Zheng, H. Chen, R. X. Li, *Eur. J. Org. Chem*, **201**2, *34*, 6702-6706.

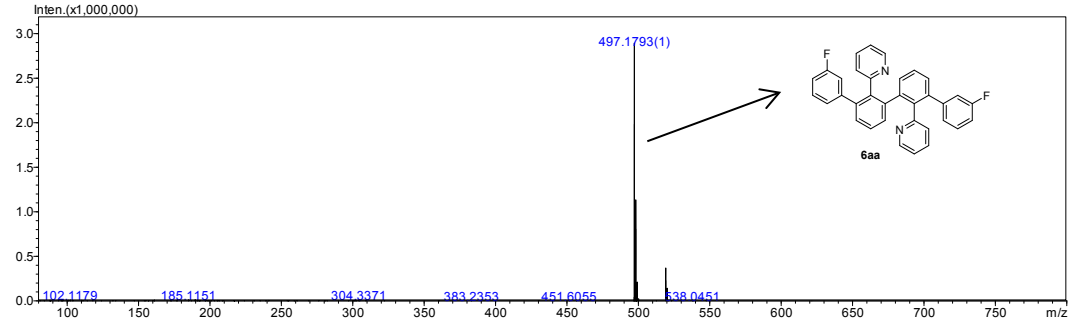
[2] D. Kalyani, N. R. Deprez, L. V. Desai, M. S. Sanford. *J. Am. Chem. Soc*. **2005**, *127*, 7330-7331.

Mass Spectrum of the dehydrogentive cross-coupling products of 3aa:

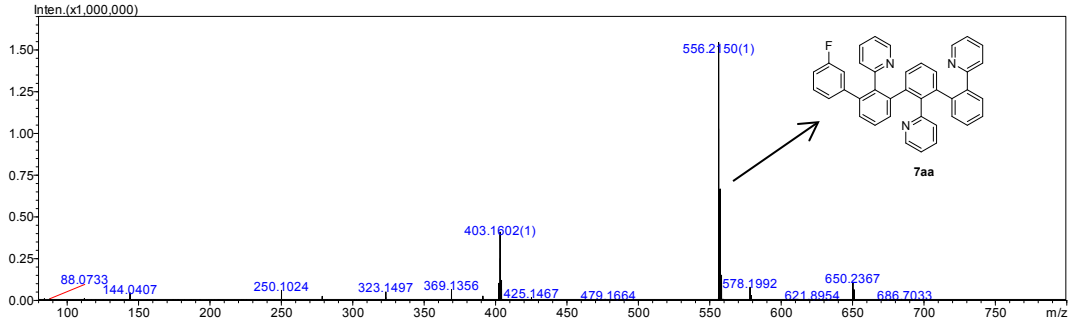
(1) DCCP - 5aa MS(E+)



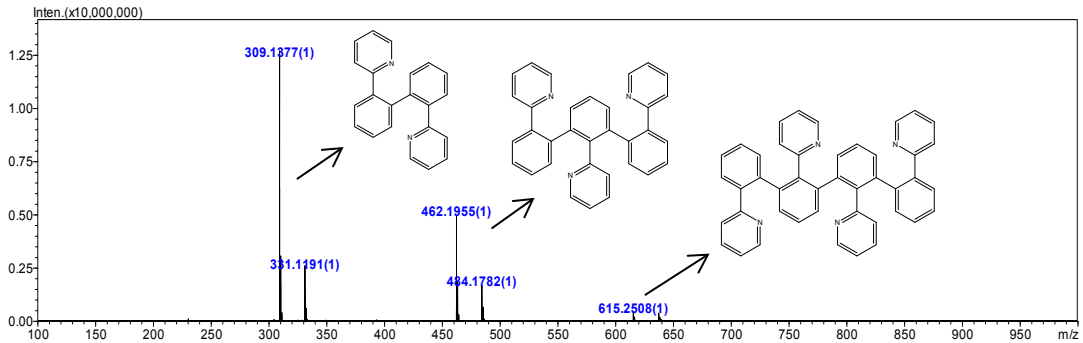
(2) DCCP - 6aa MS(E+)



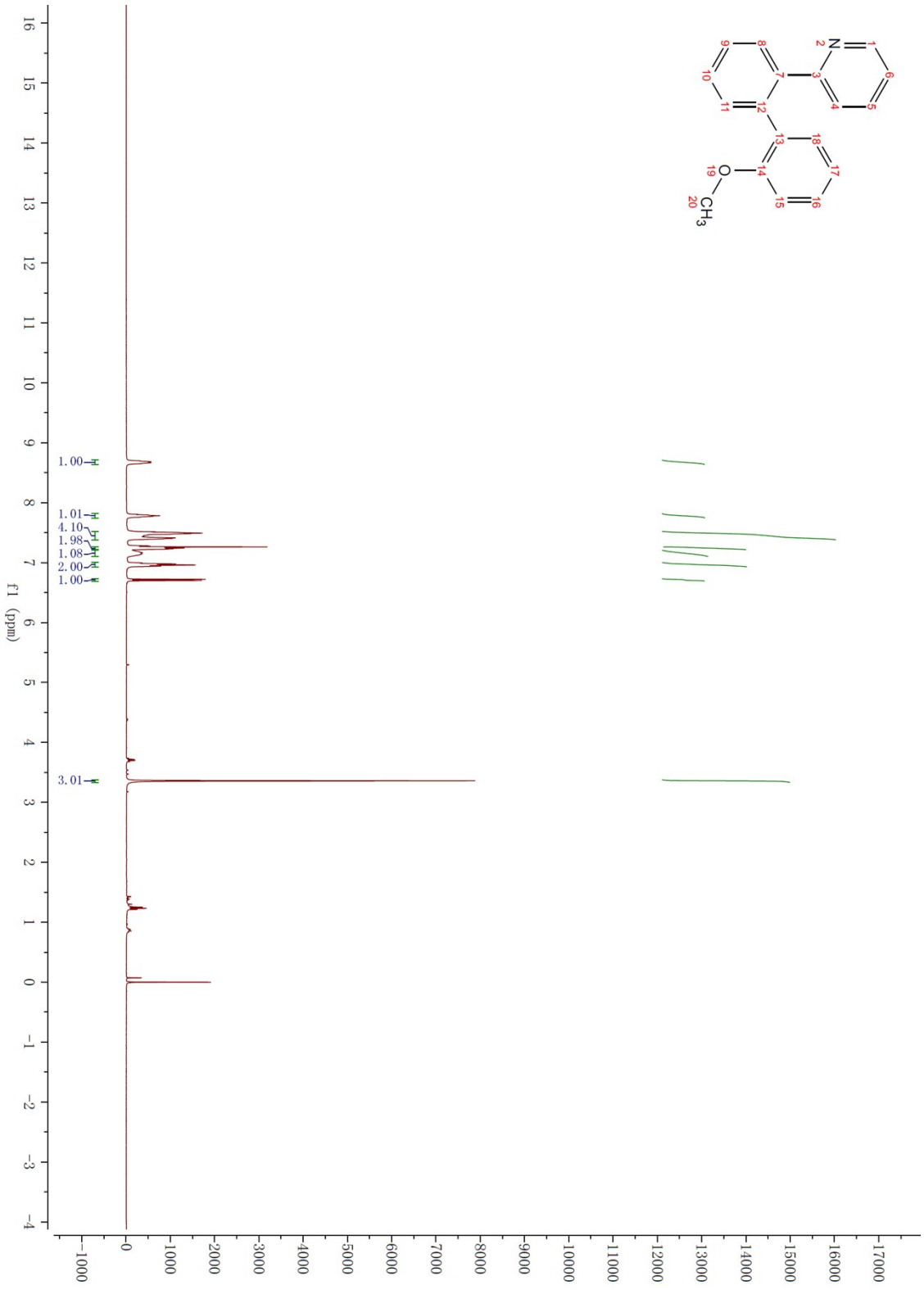
(3) DCCP - 7aa MS(E+)



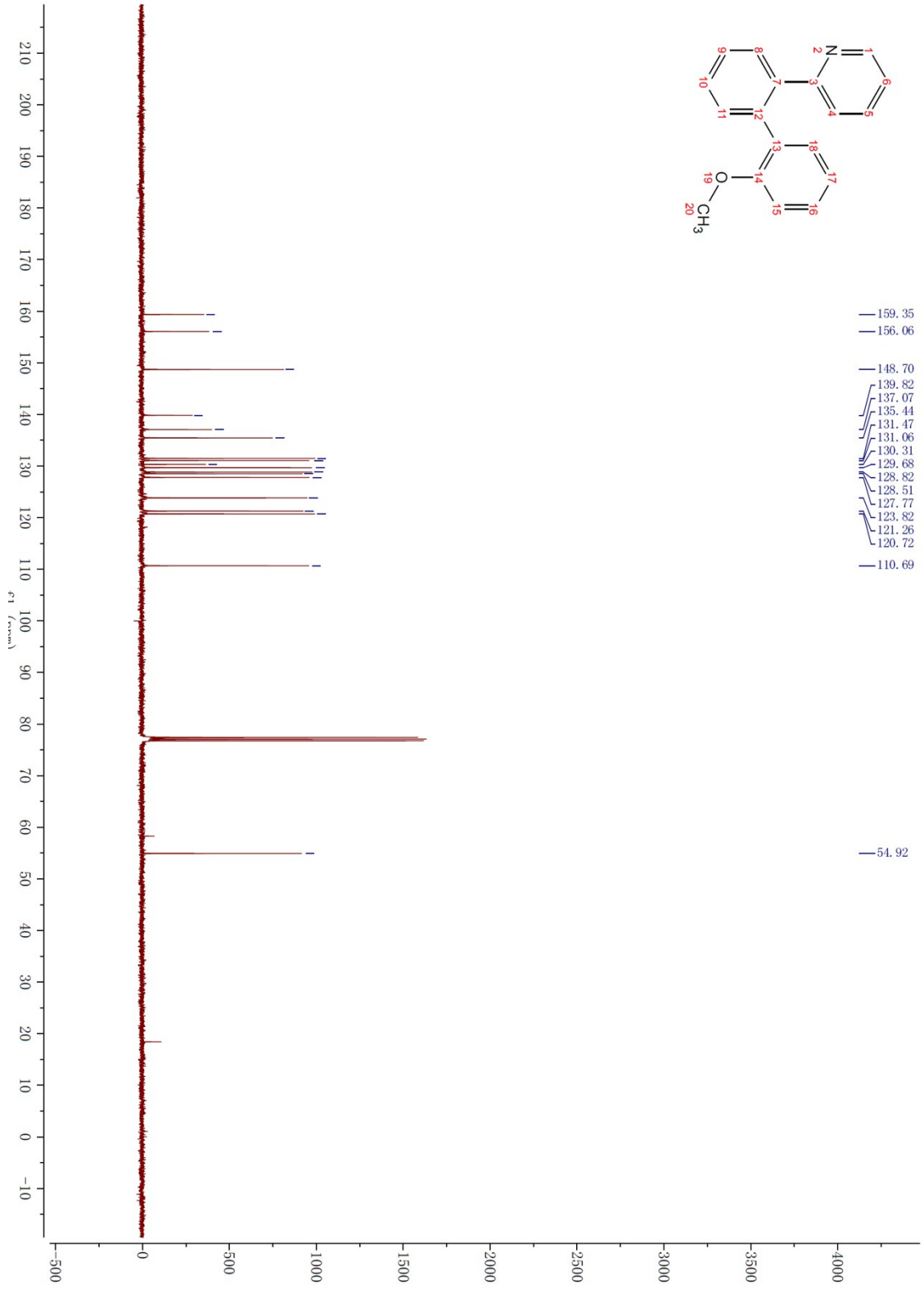
Mass Spectrum of the the oligomerizations of 2-phenylpyridine



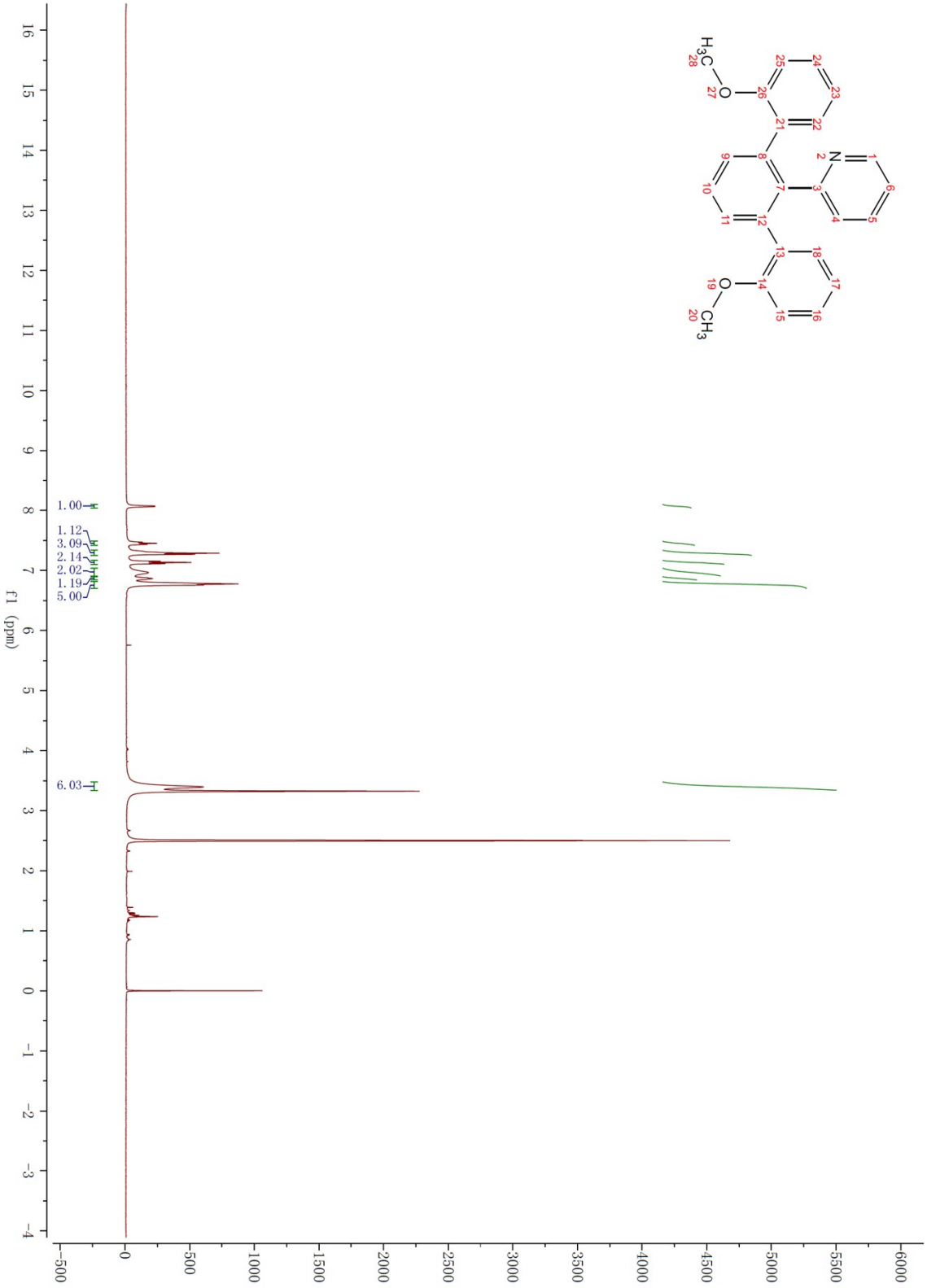
^{1}H NMR Spectrum of the Compound 3af



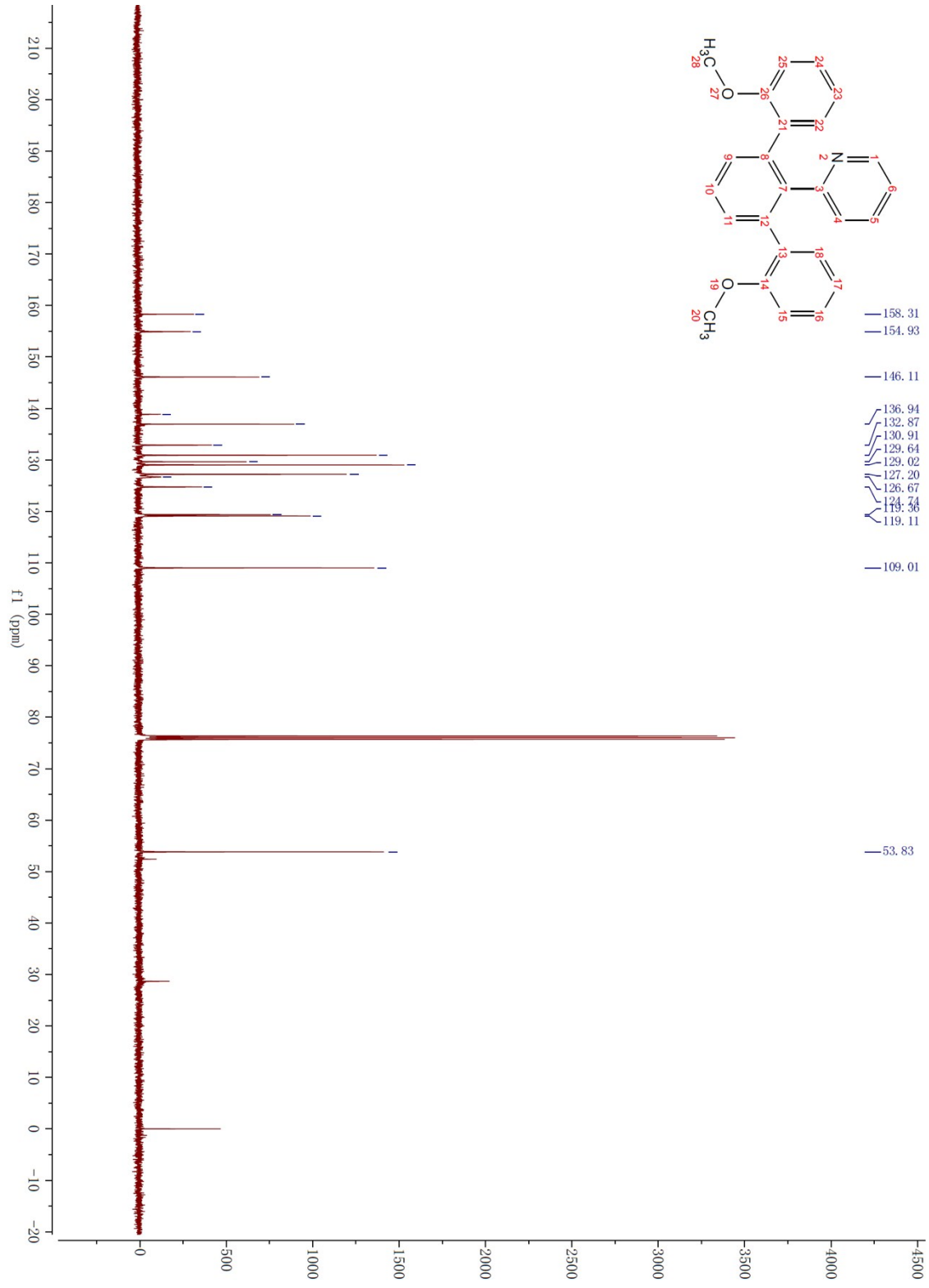
^{13}C NMR Spectrum of the Compound 3af



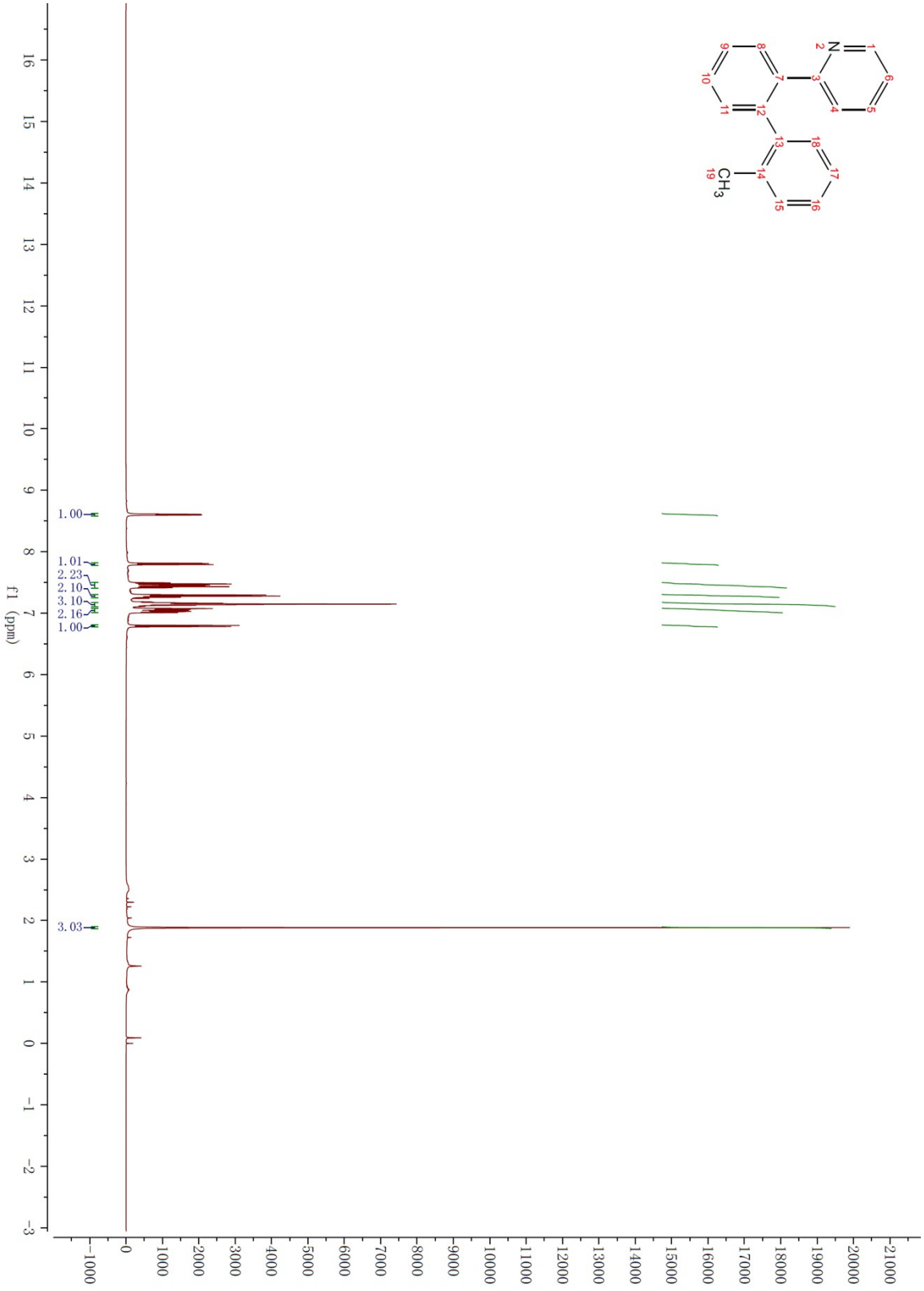
^{1}H NMR Spectrum of the Compound 4af



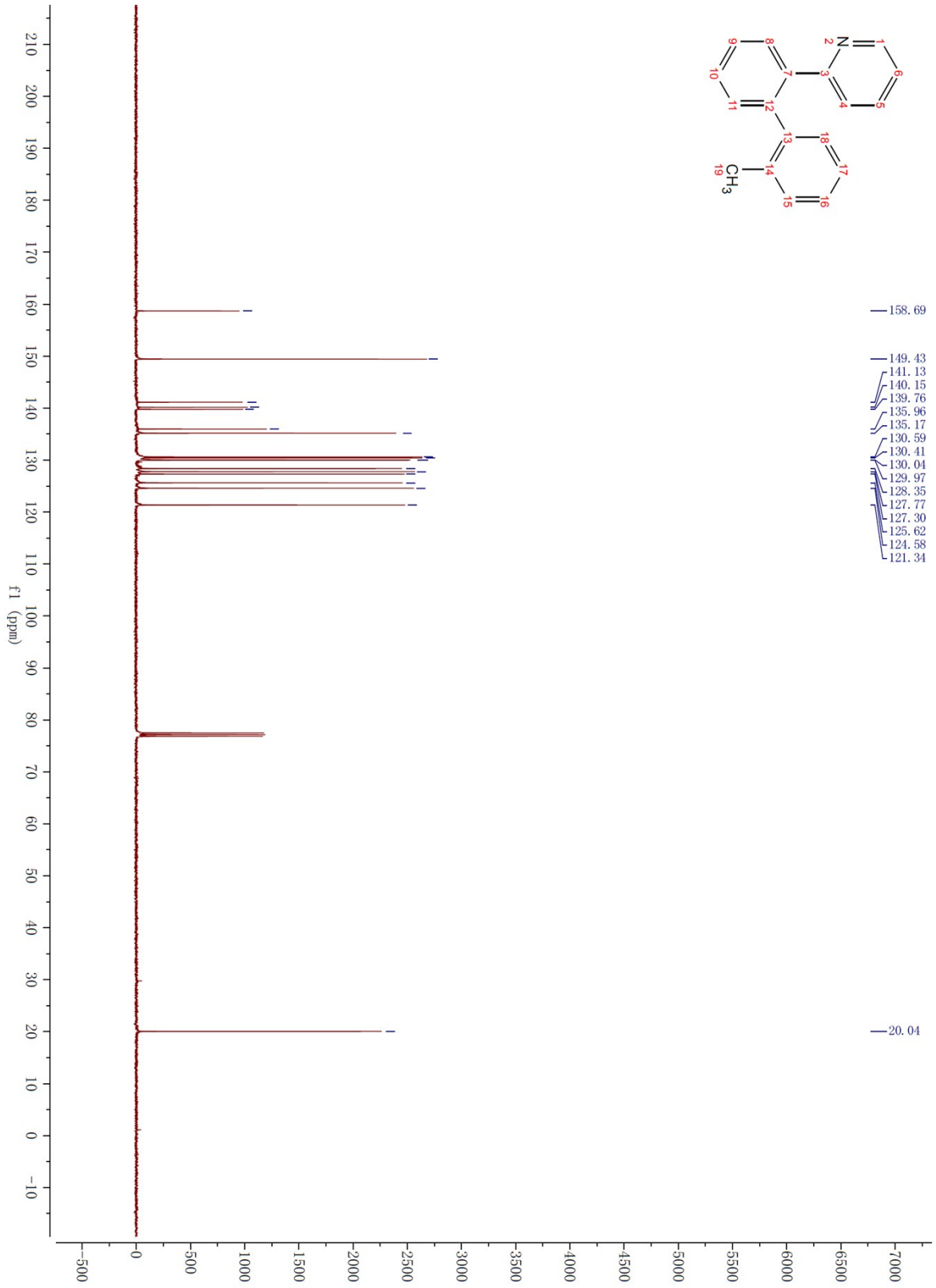
^{13}C NMR Spectrum of the Compound 4af



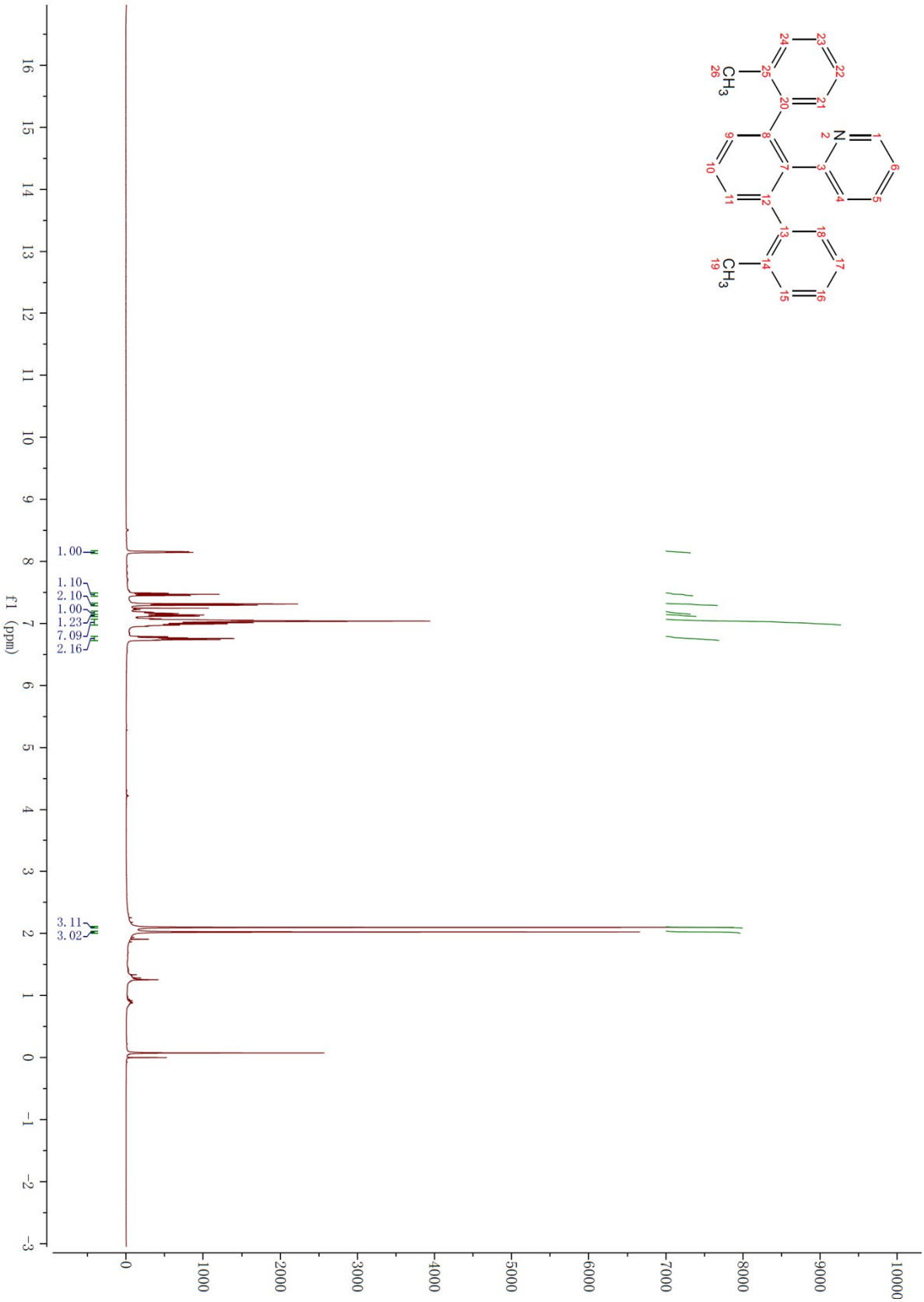
^{1}H NMR Spectrum of the Compound 3ac



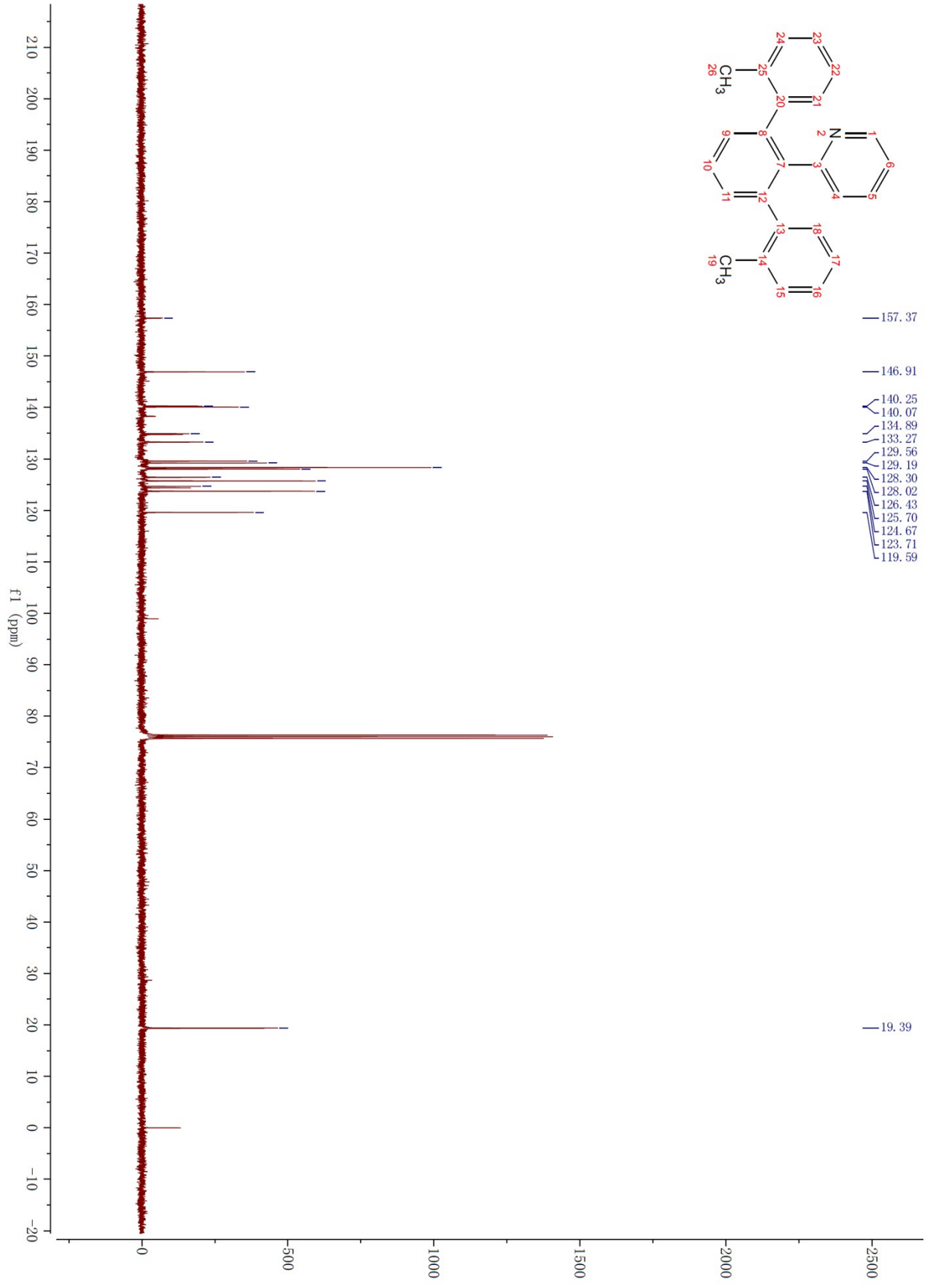
^{13}C NMR Spectrum of the Compound 3ac



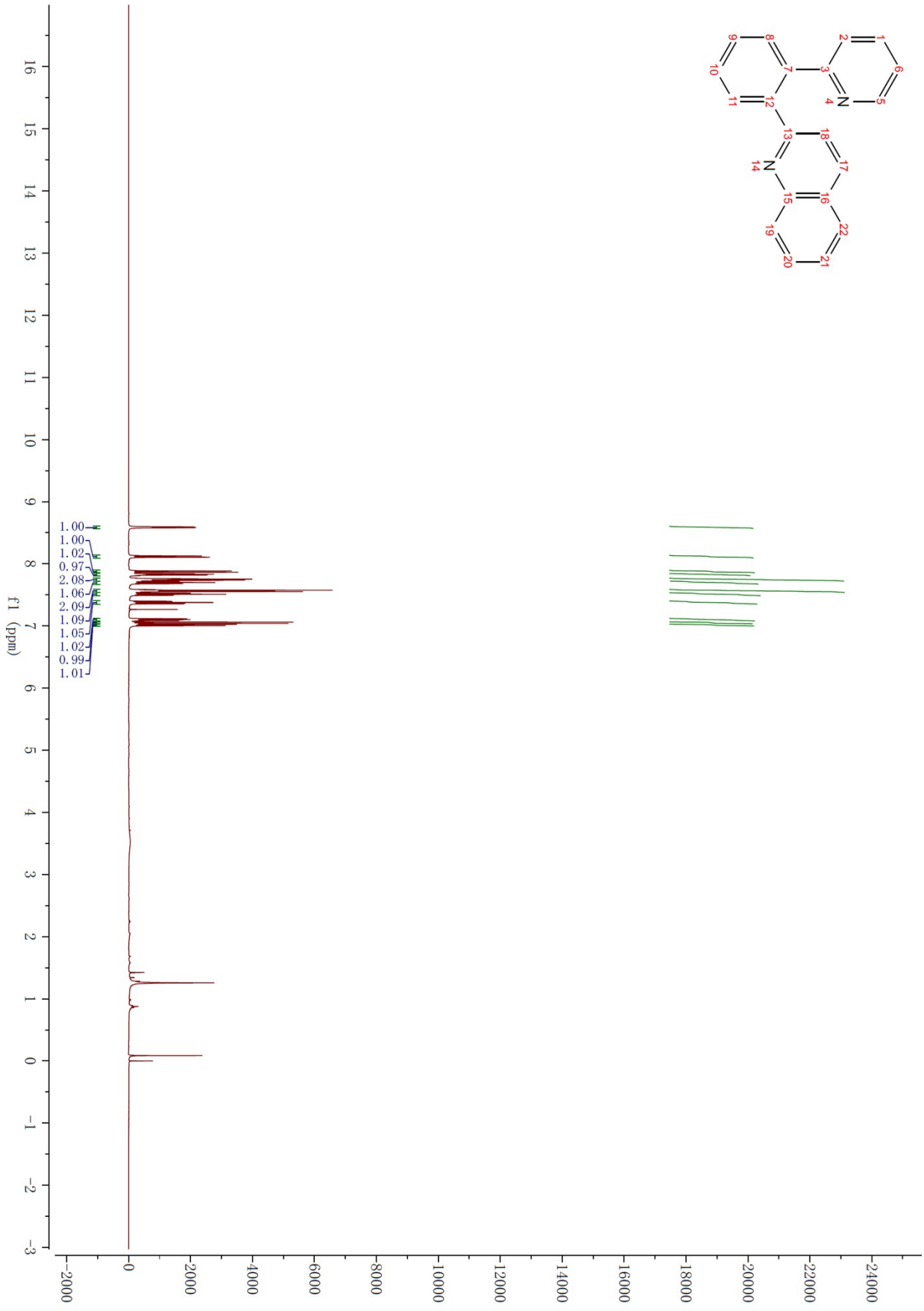
^{1}H NMR Spectrum of the Compound 4ac



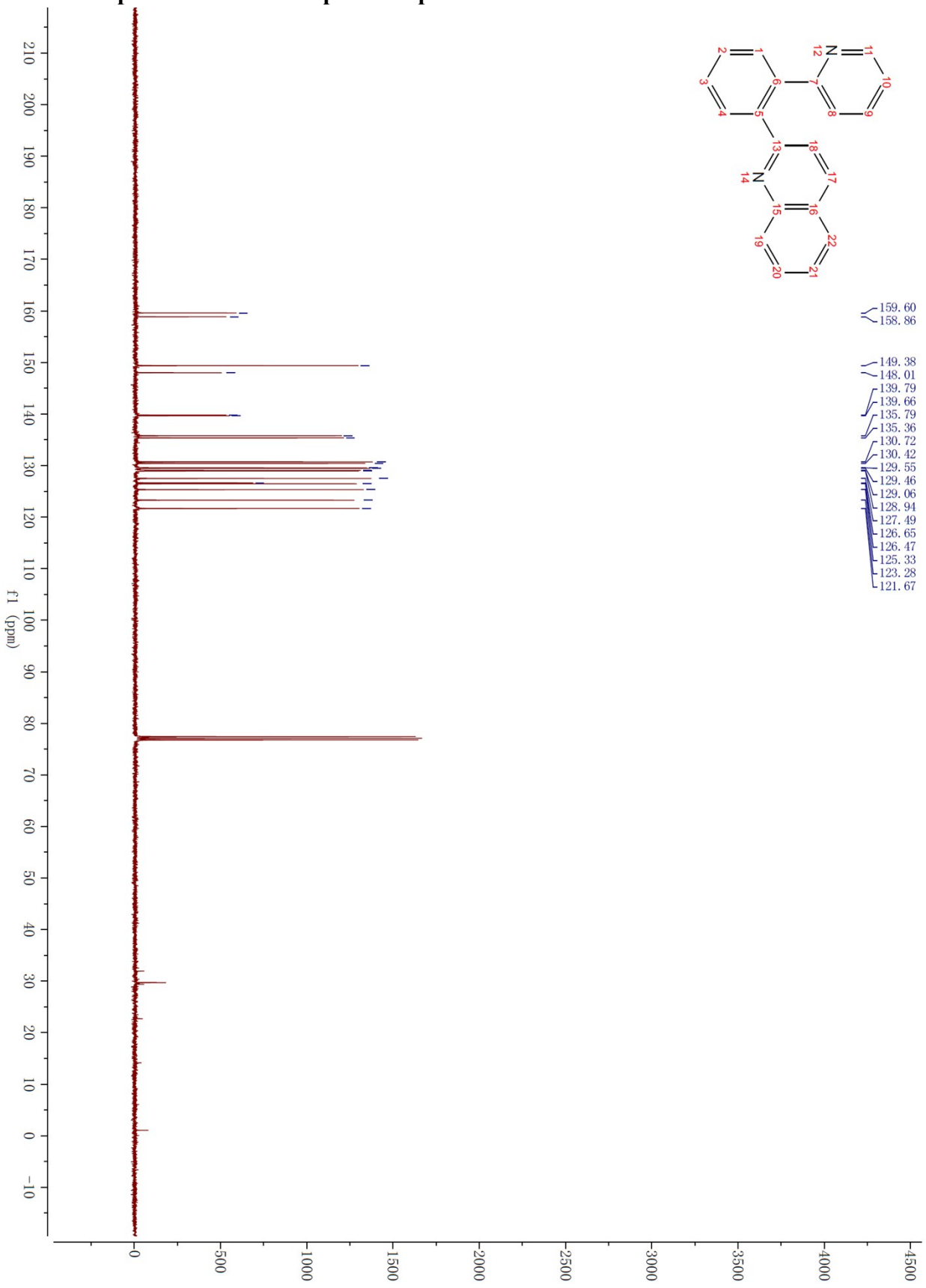
^{13}C NMR Spectrum of the Compound 4ac



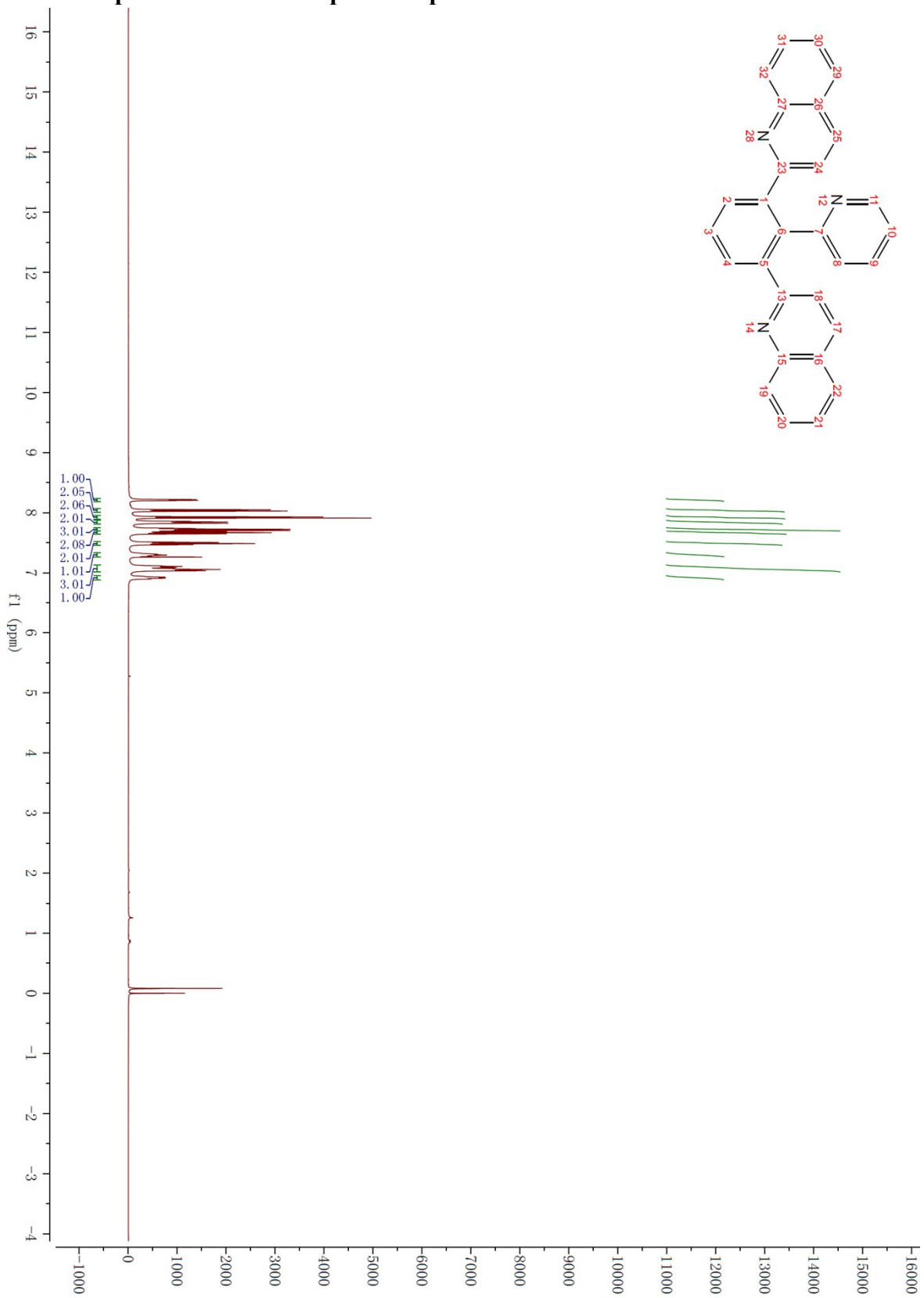
^{1}H NMR Spectrum of the Compound 3ap



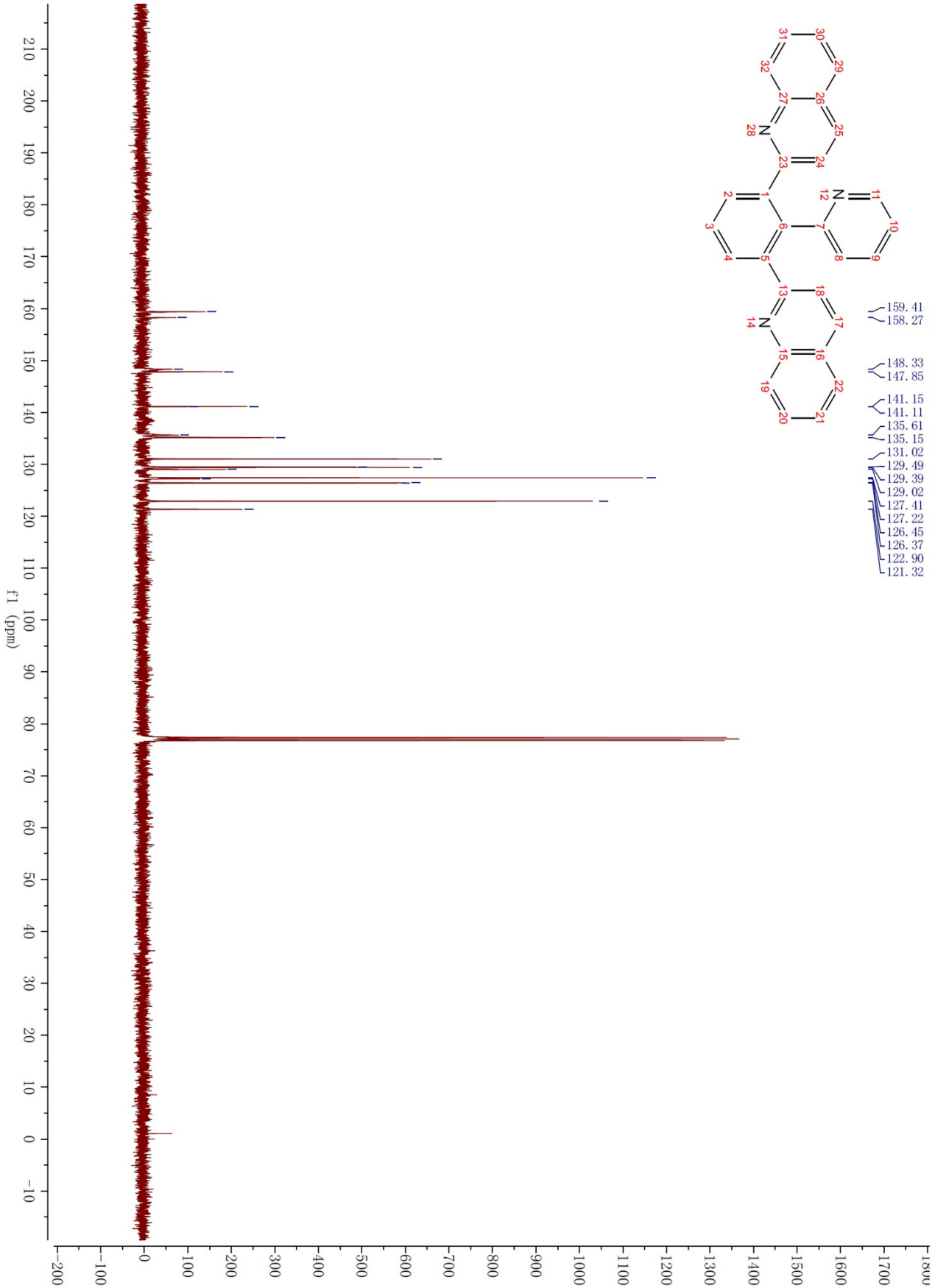
^{13}C NMR Spectrum of the Compound 3ap



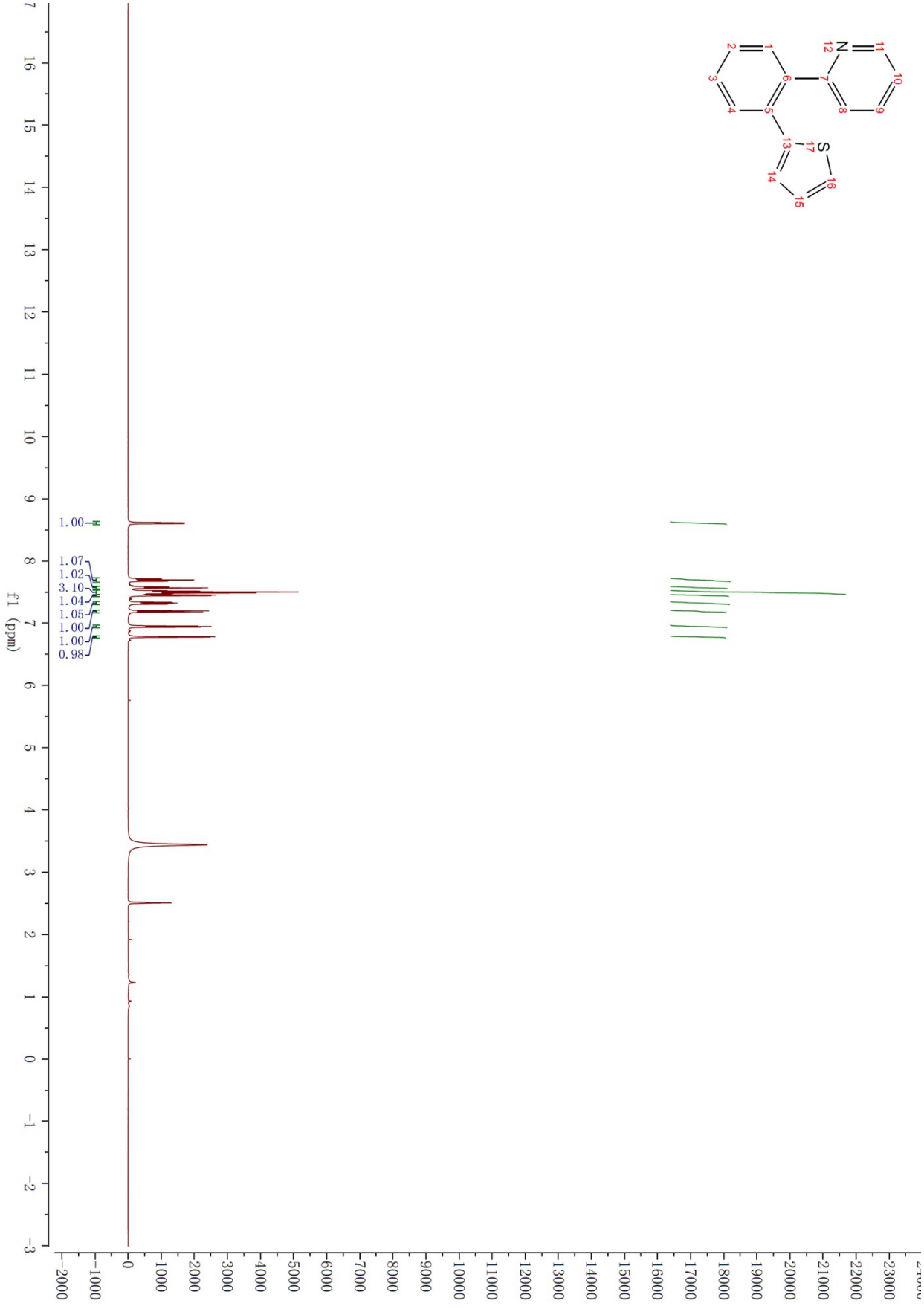
^{1}H NMR Spectrum of the Compound 4ap



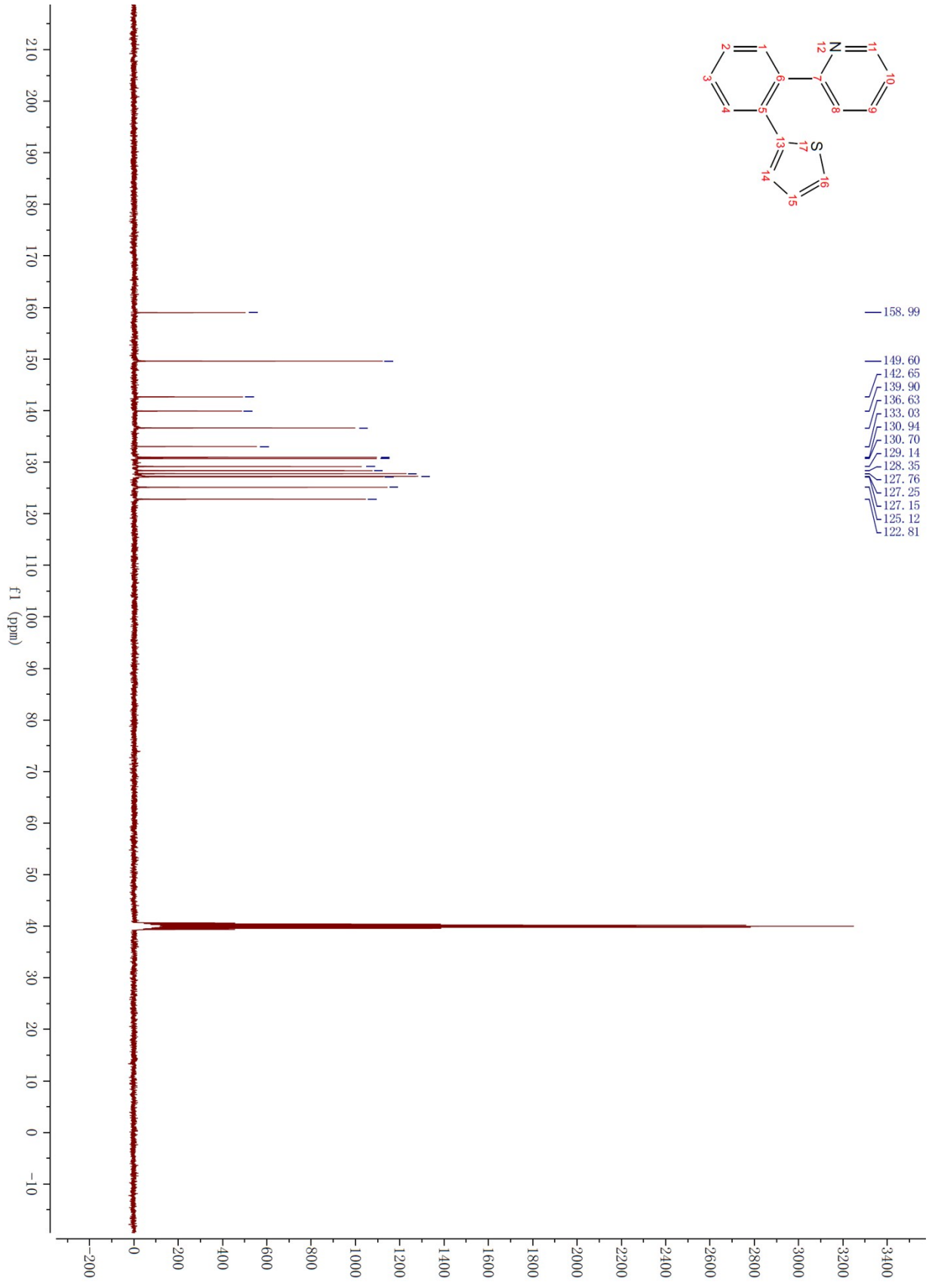
^{13}C NMR Spectrum of the Compound 4ap



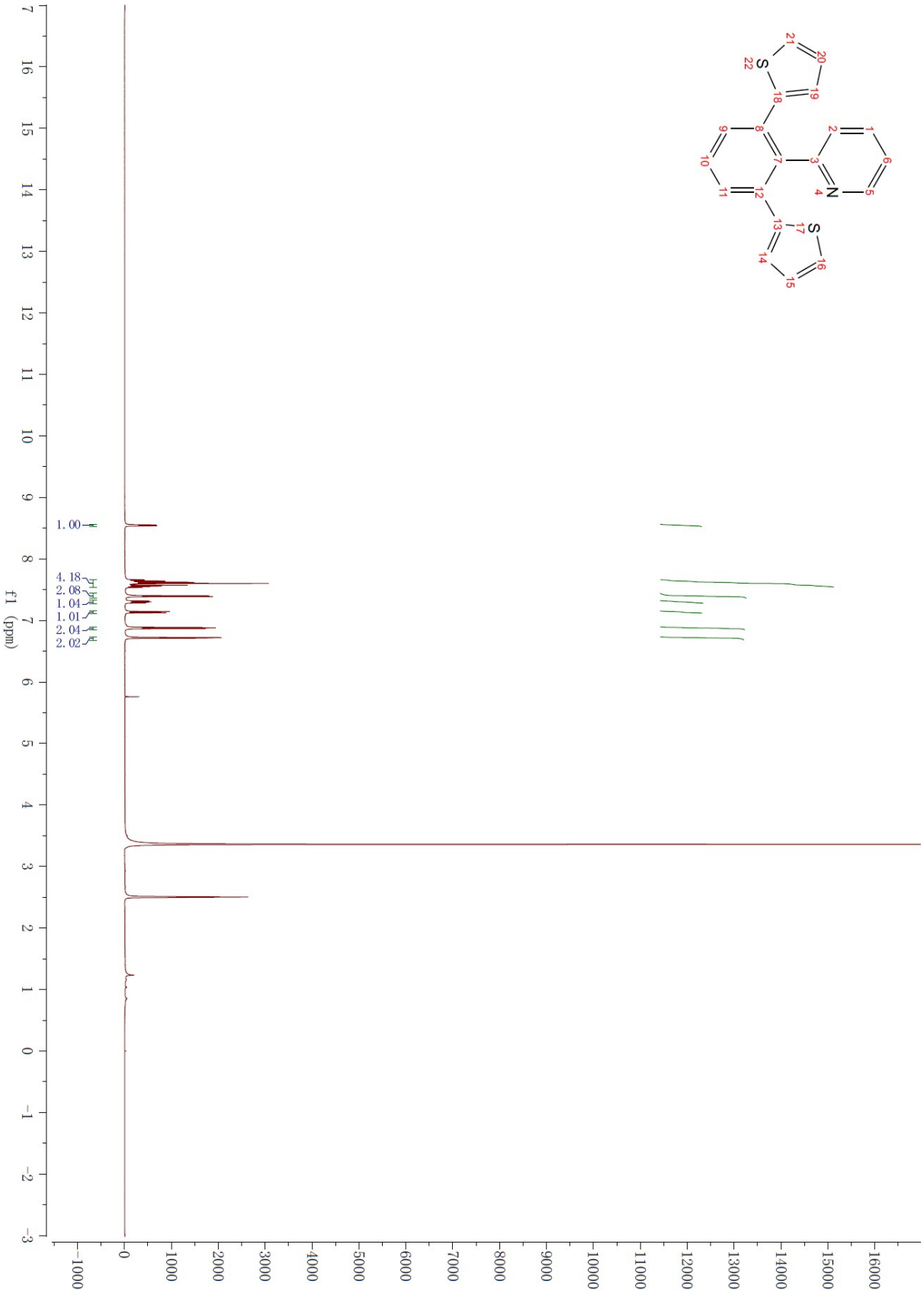
^{1}H NMR Spectrum of the Compound 3aq



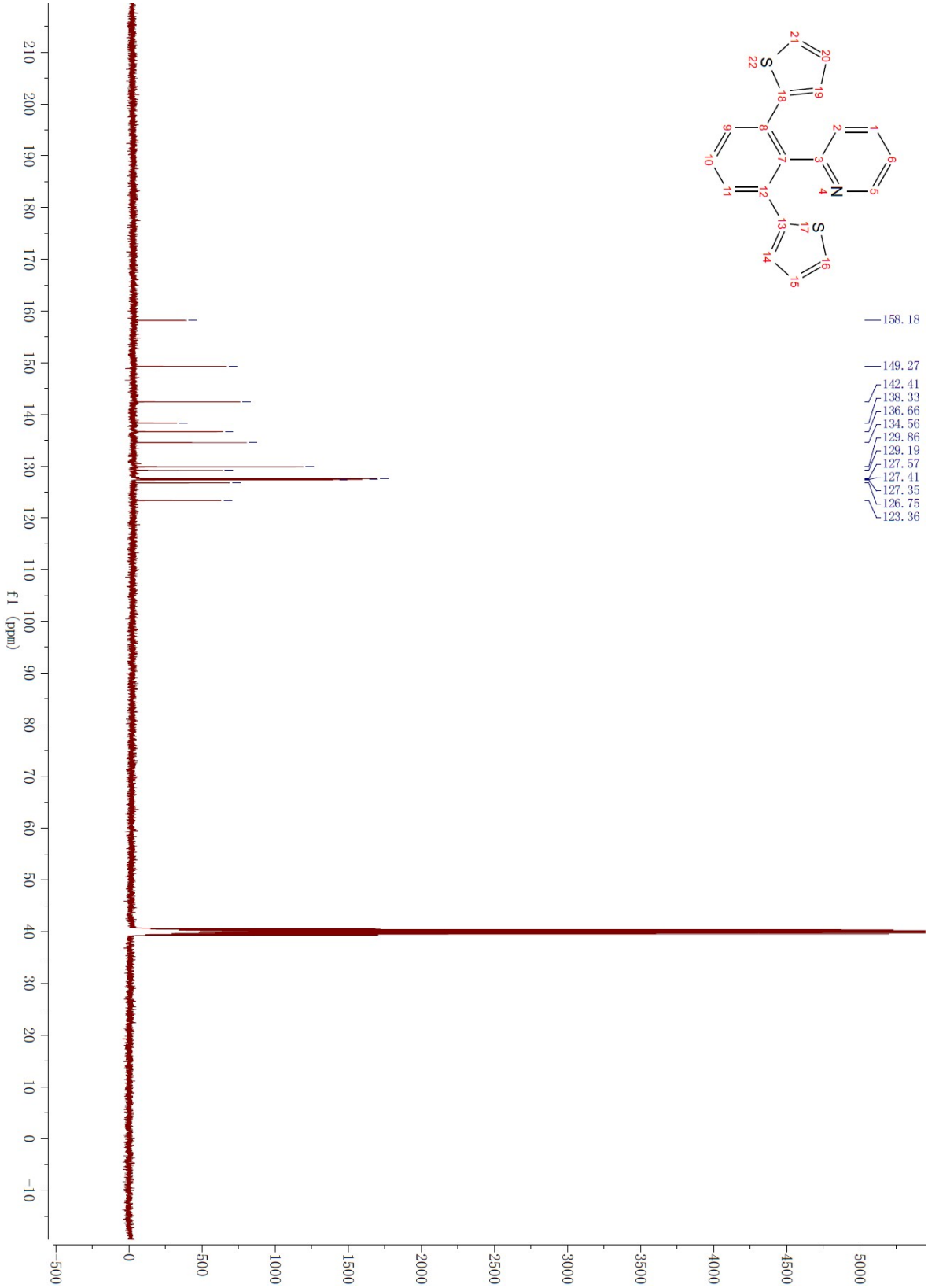
^{13}C NMR Spectrum of the Compound 3aq



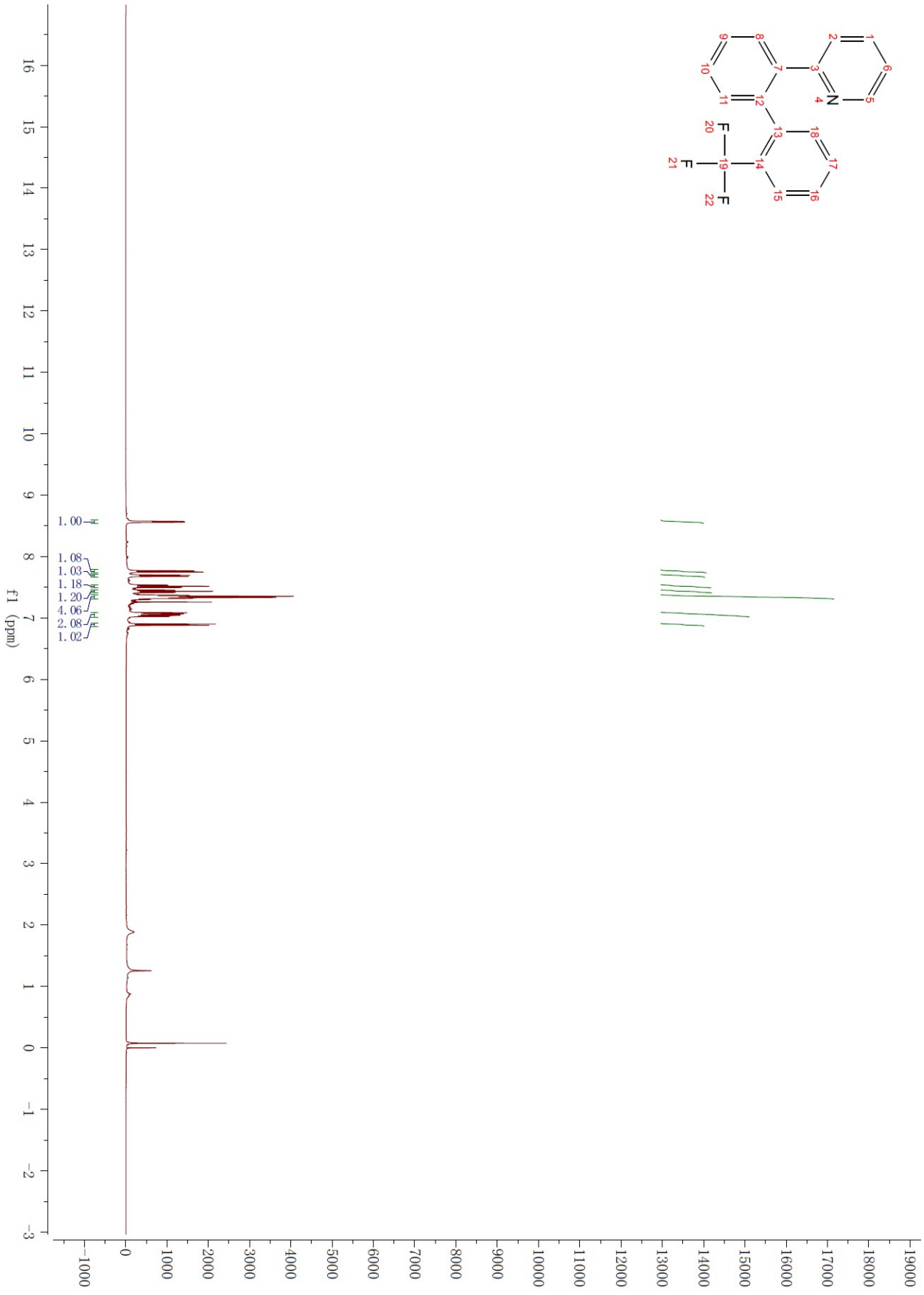
^{1}H NMR Spectrum of the Compound 4aq



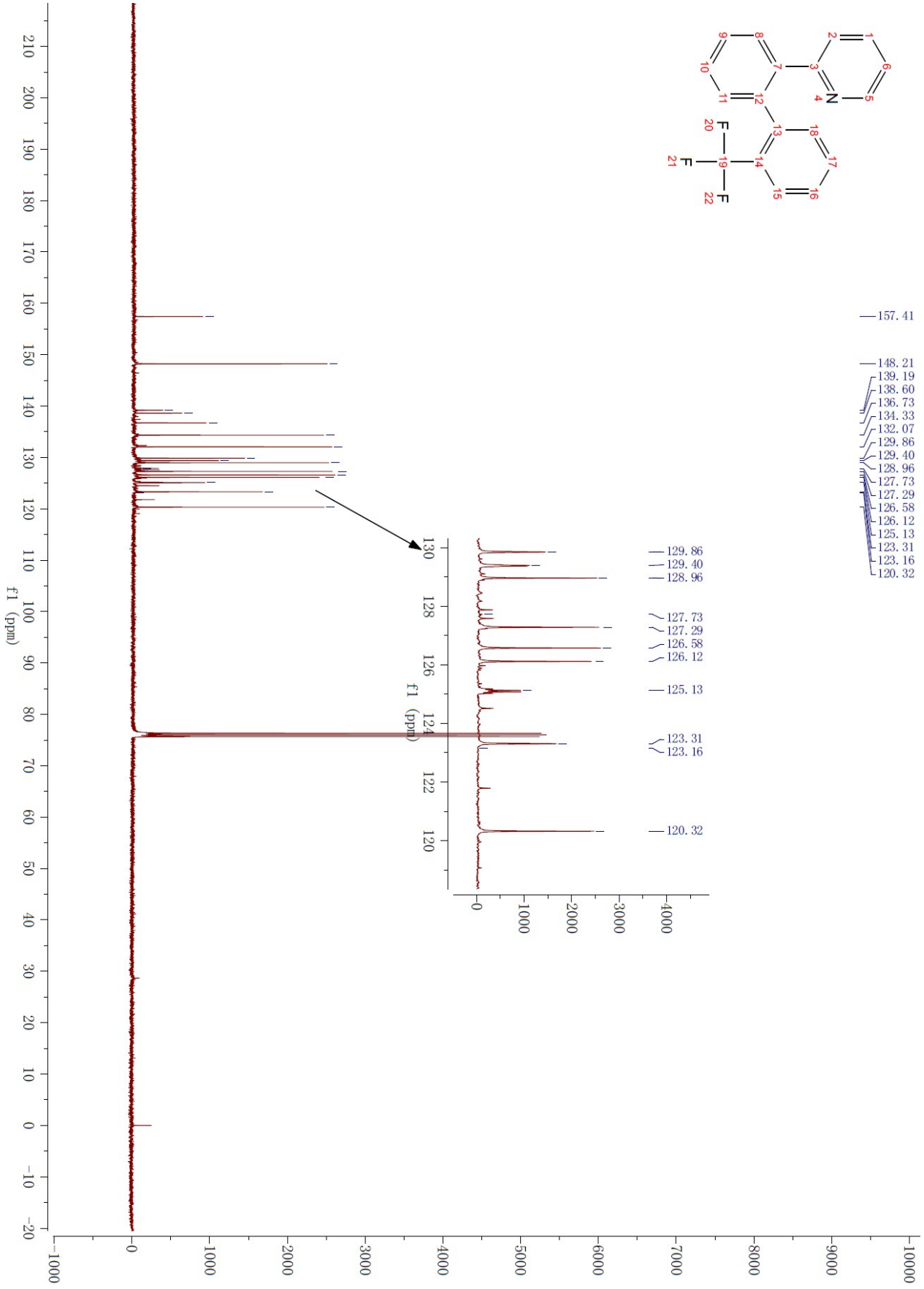
^{13}C NMR Spectrum of the Compound 4aq



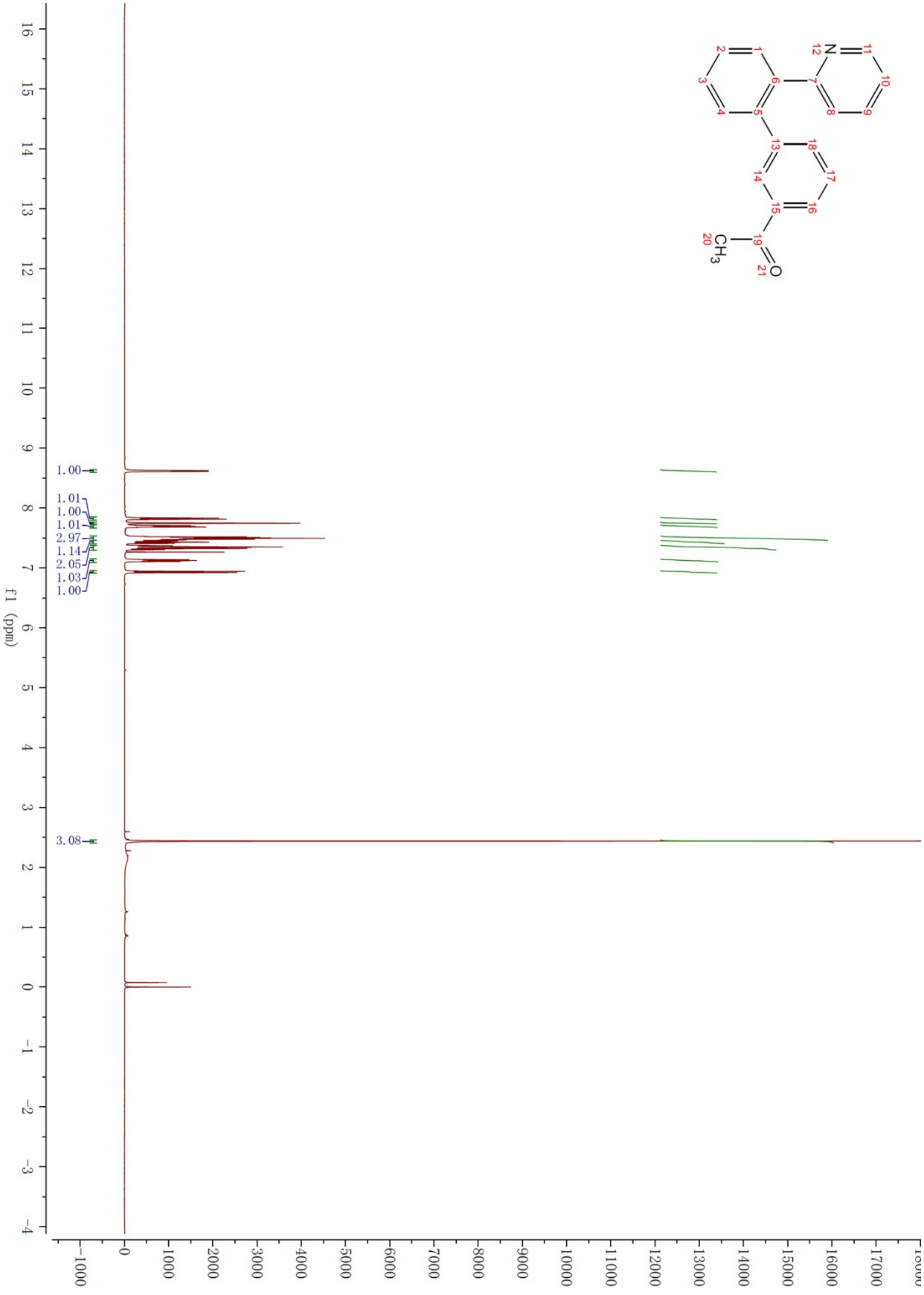
^{1}H NMR Spectrum of the Compound 3ak



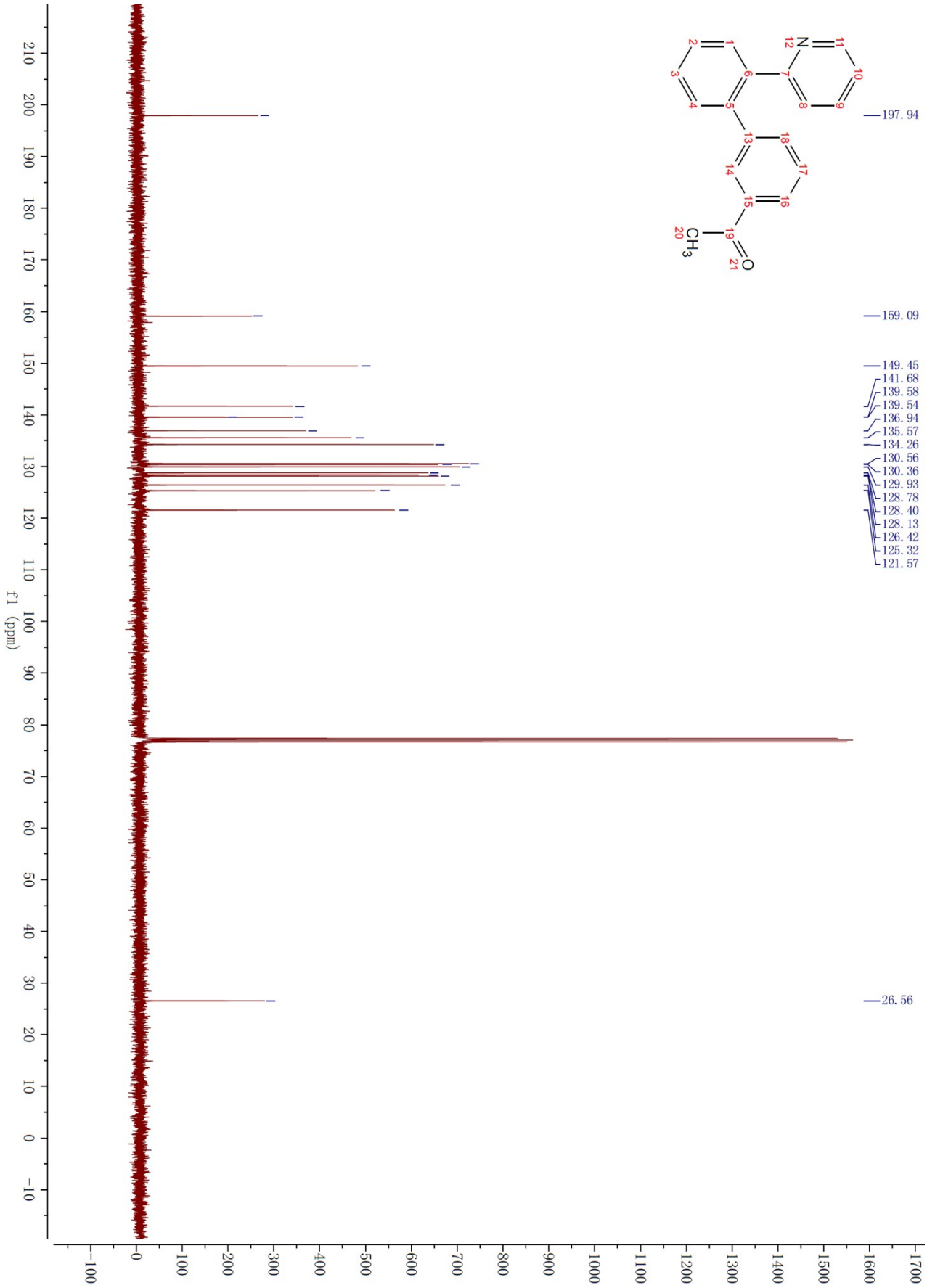
^{13}C NMR Spectrum of the Compound 3ak



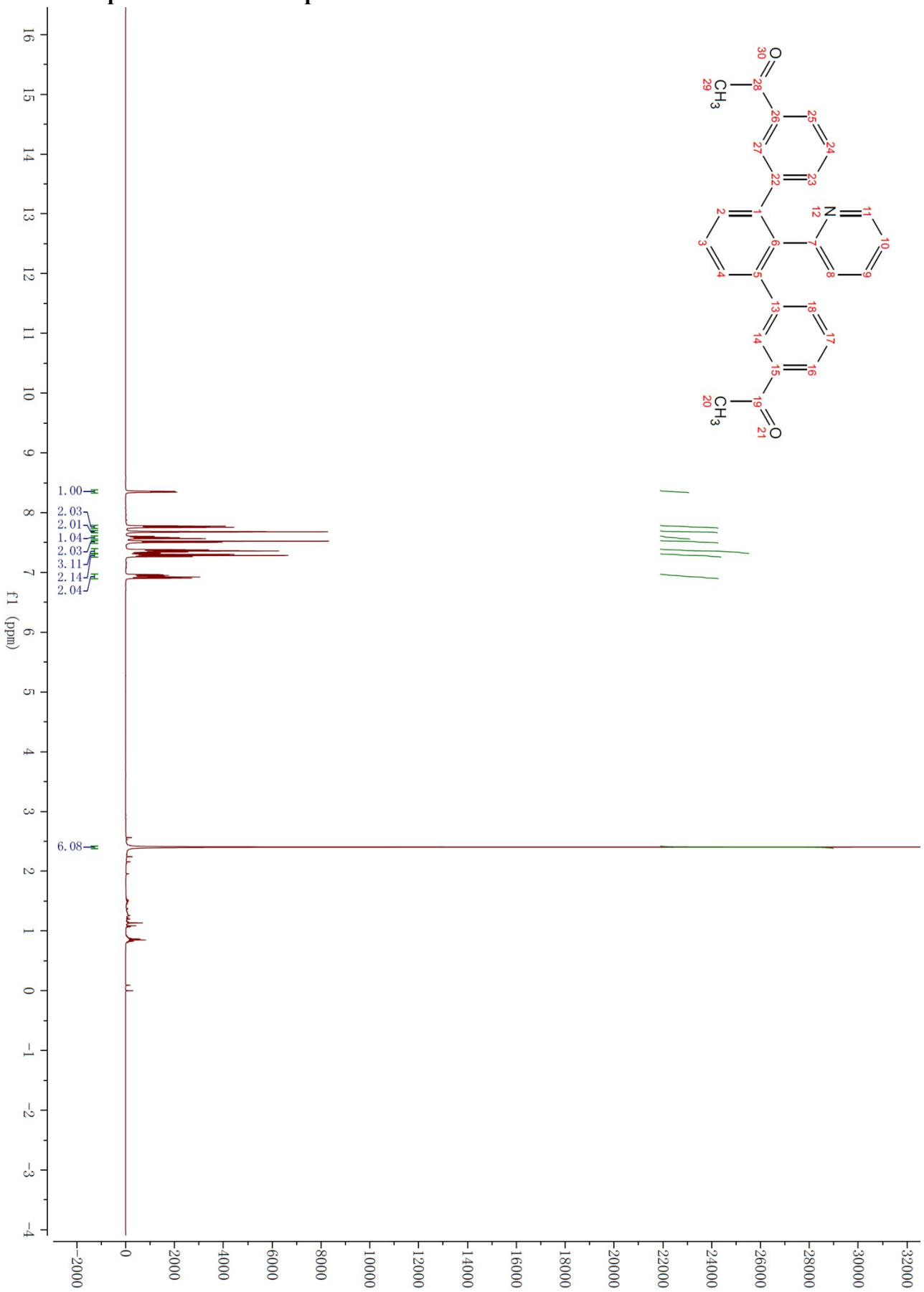
^{1}H NMR Spectrum of the Compound 3an



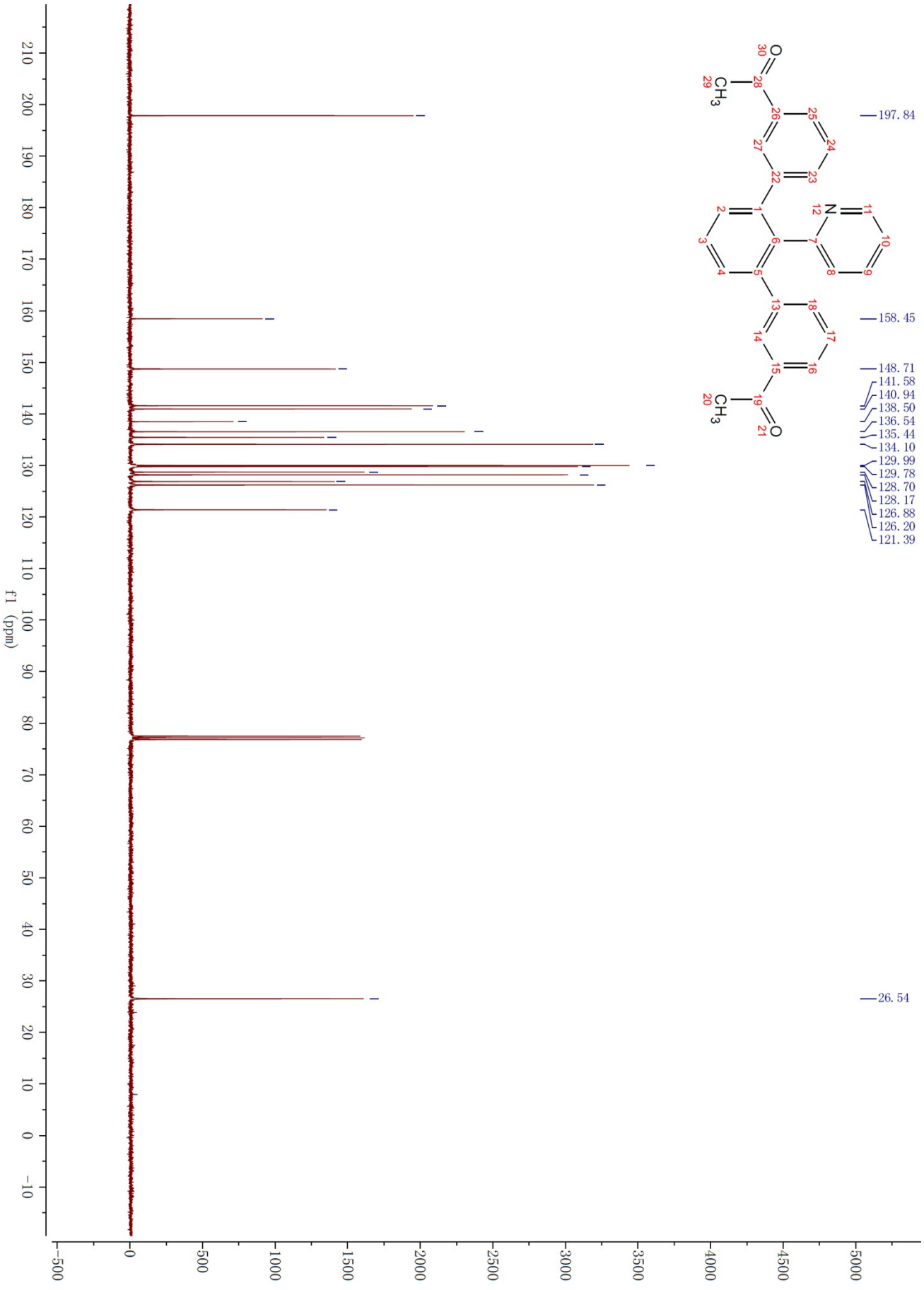
^{13}C NMR Spectrum of the Compound 3an



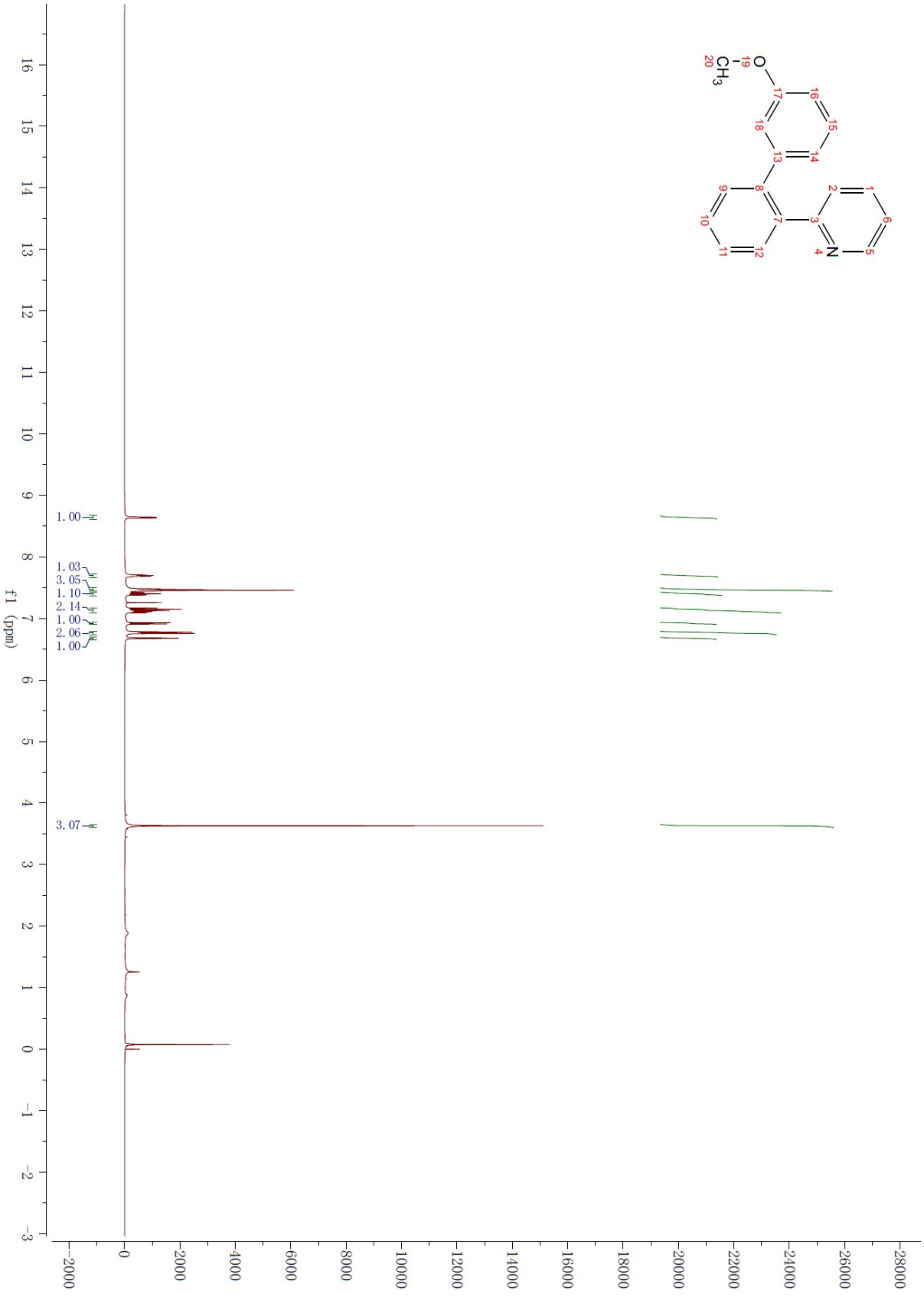
^{1}H NMR Spectrum of the Compound 4an



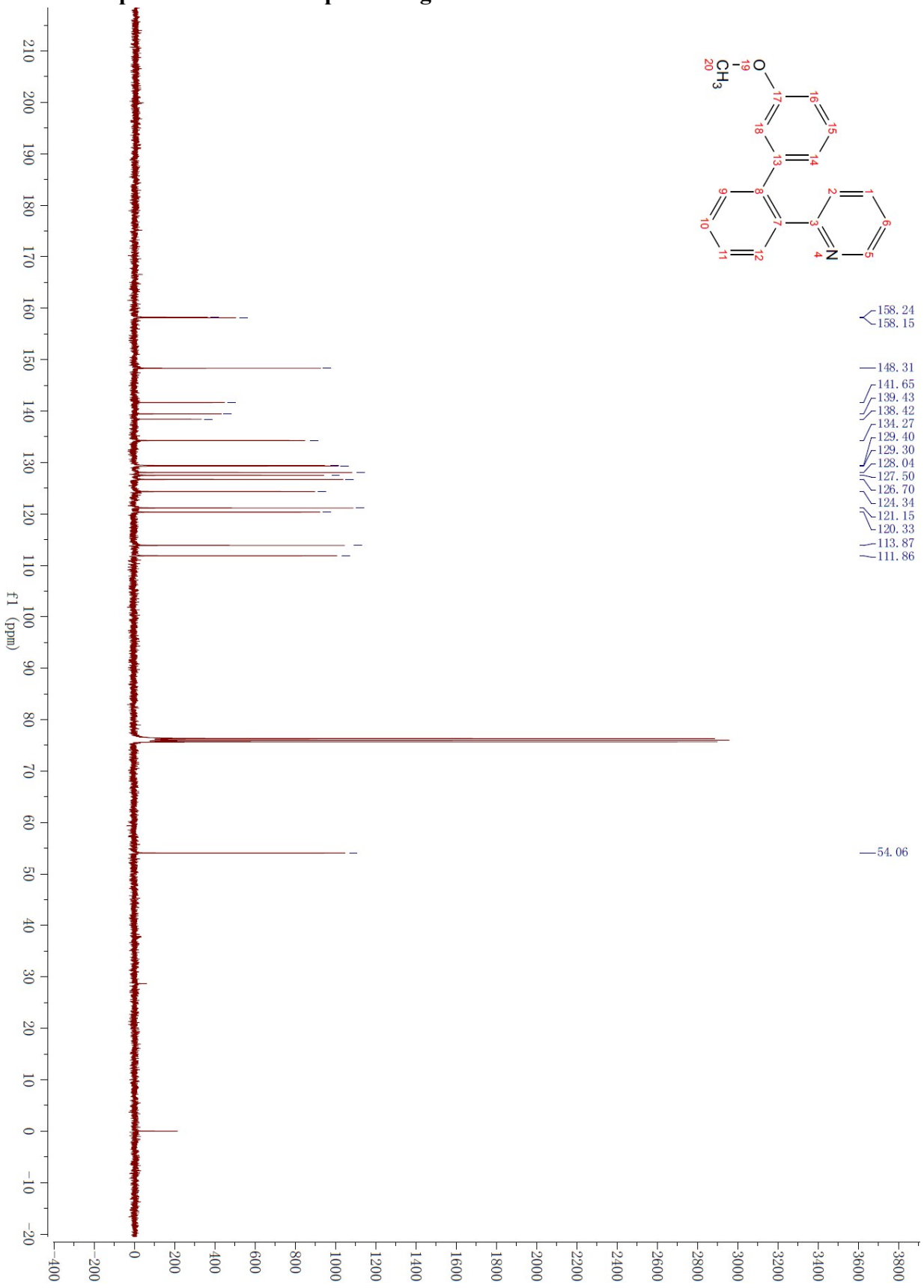
^{13}C NMR Spectrum of the Compound 4an



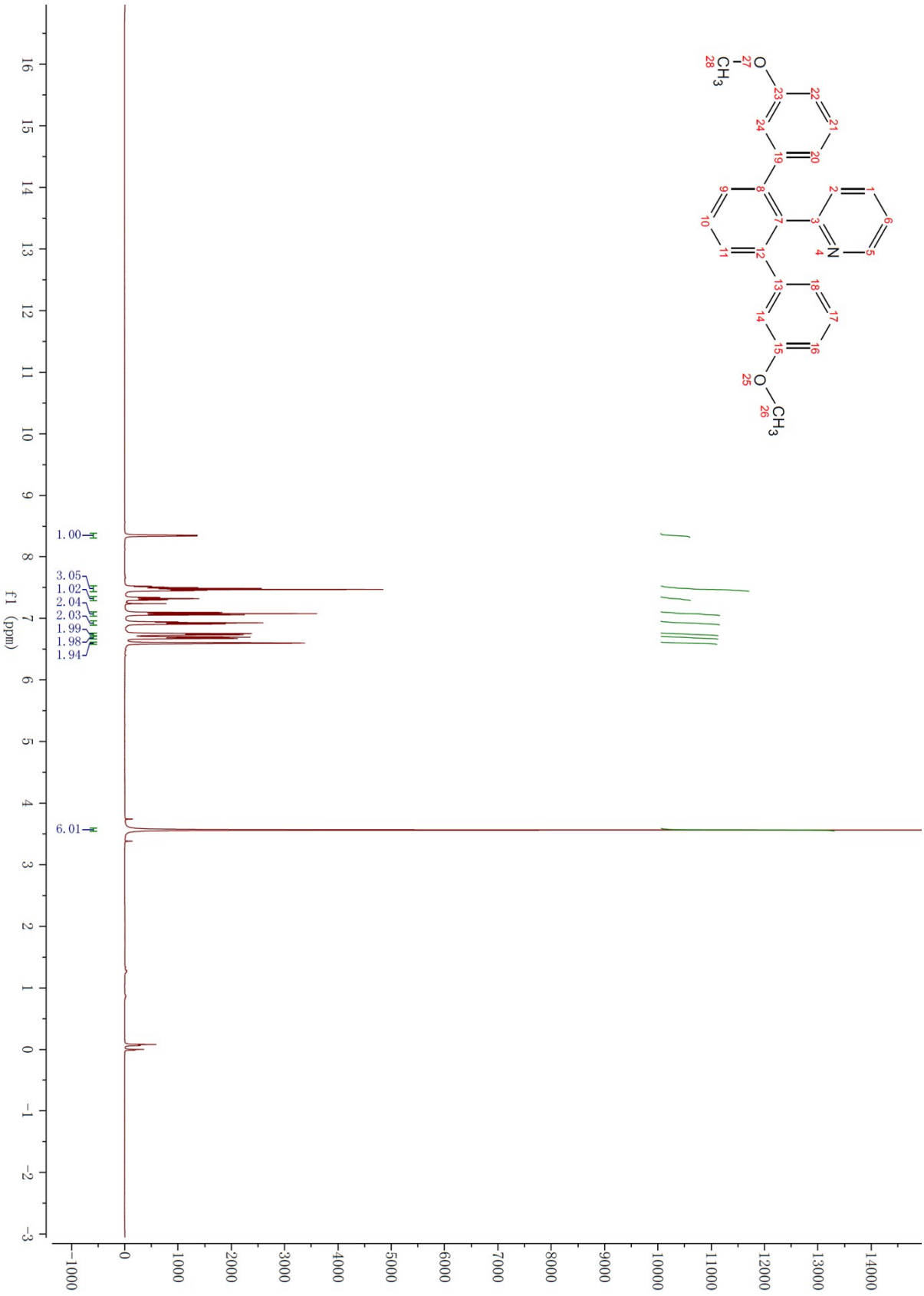
^{1}H NMR Spectrum of the Compound 3ag



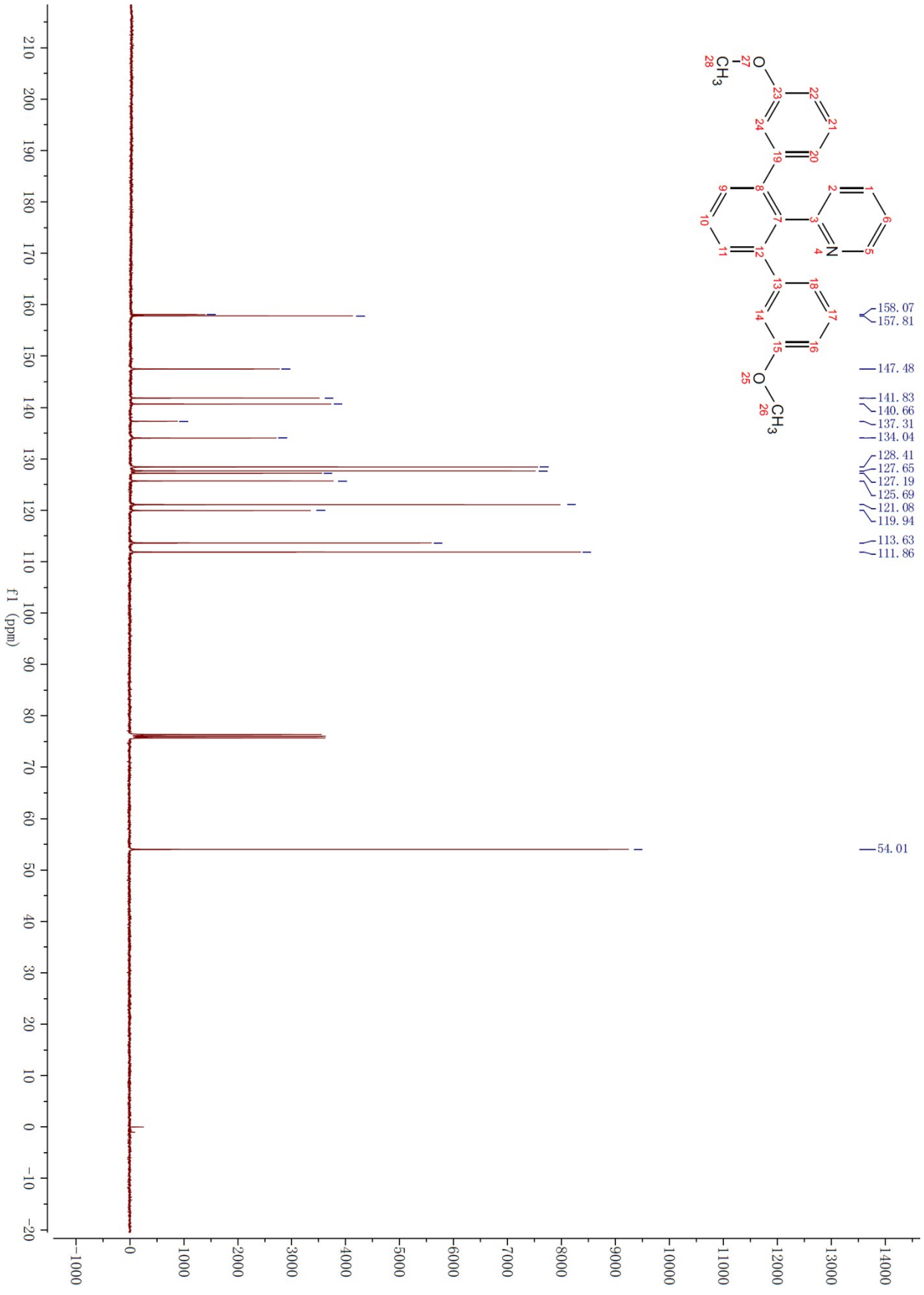
^{13}C NMR Spectrum of the Compound 3ag



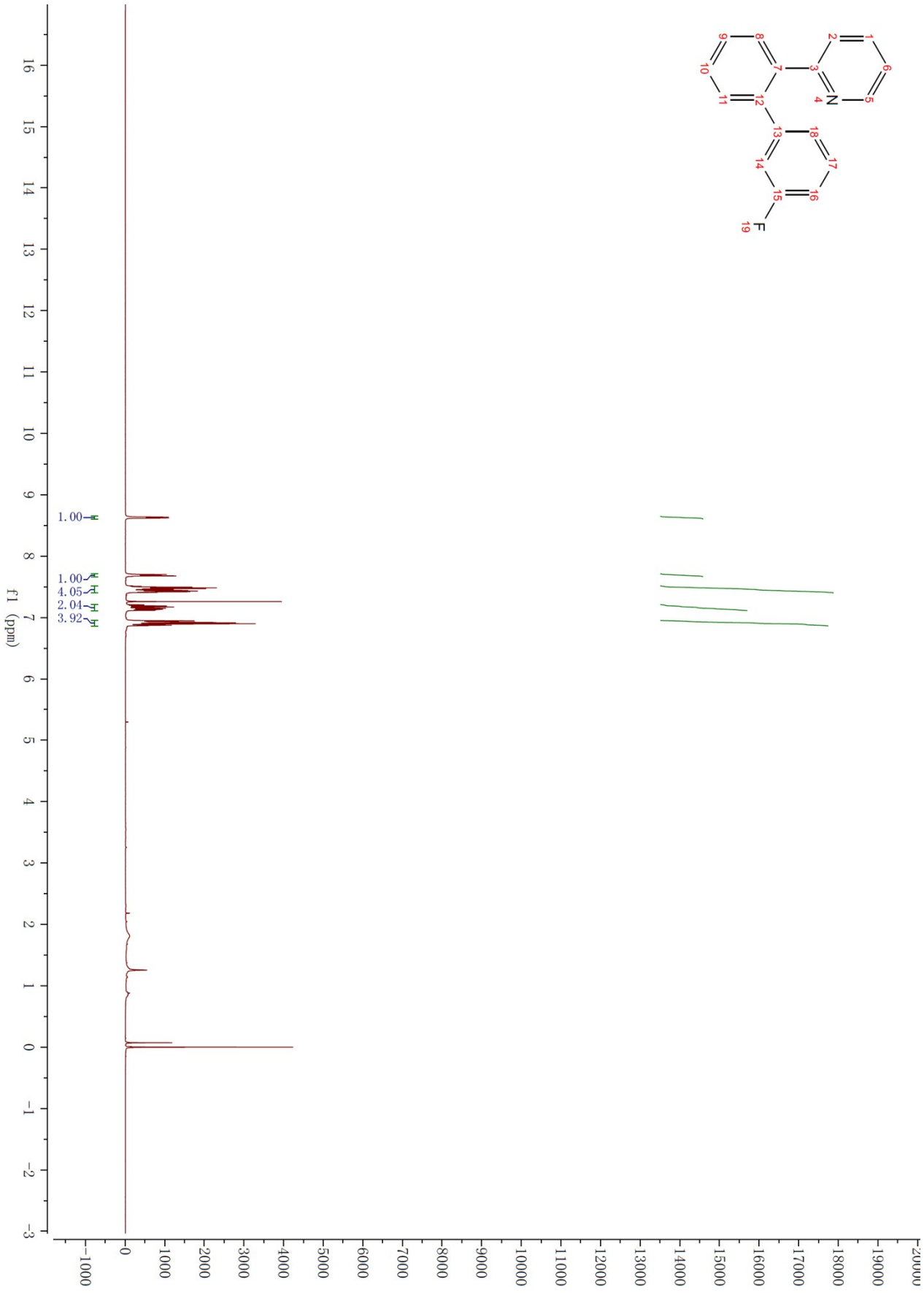
^{1}H NMR Spectrum of the Compound 4ag



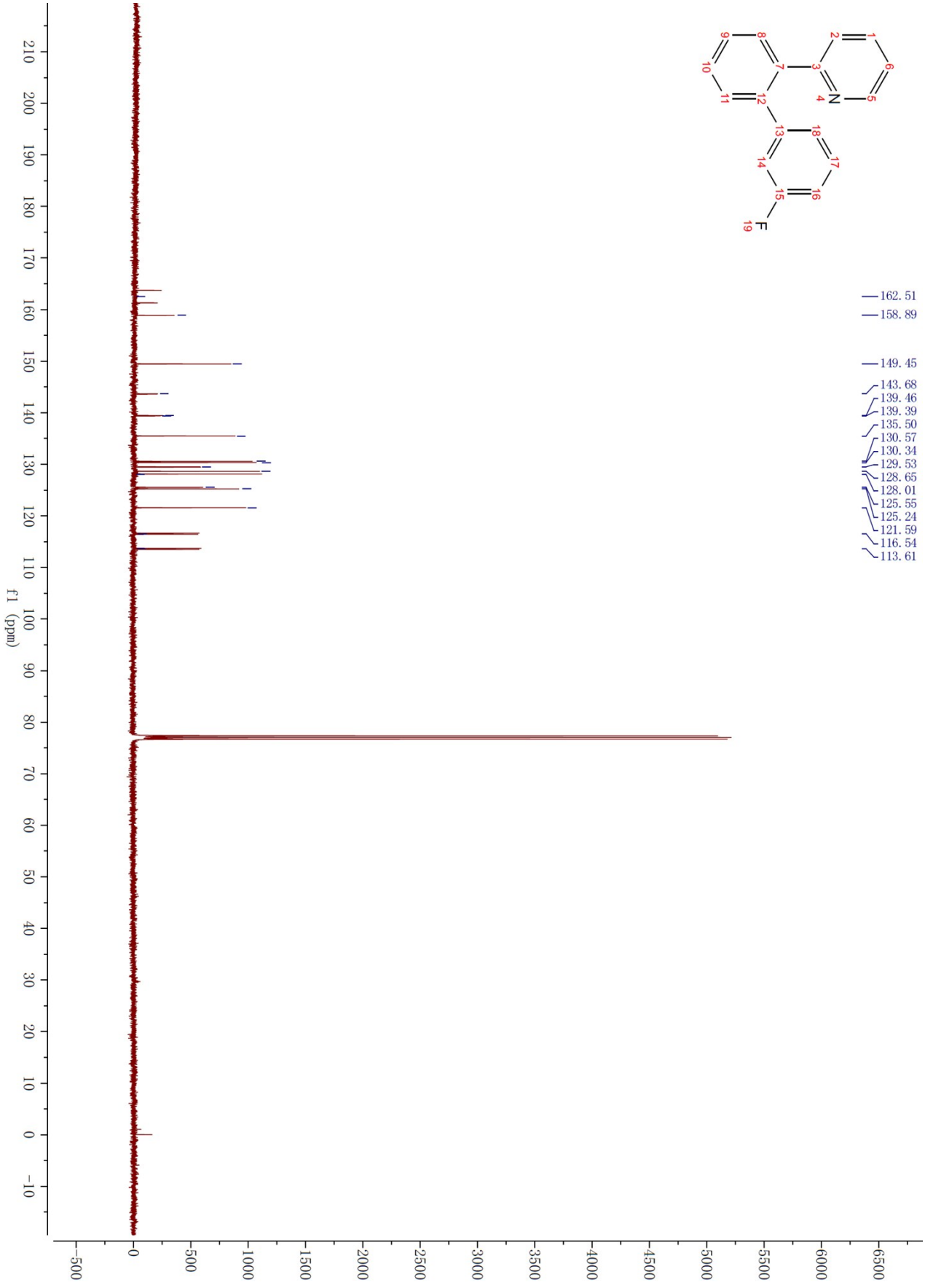
^{13}C NMR Spectrum of the Compound 4ag



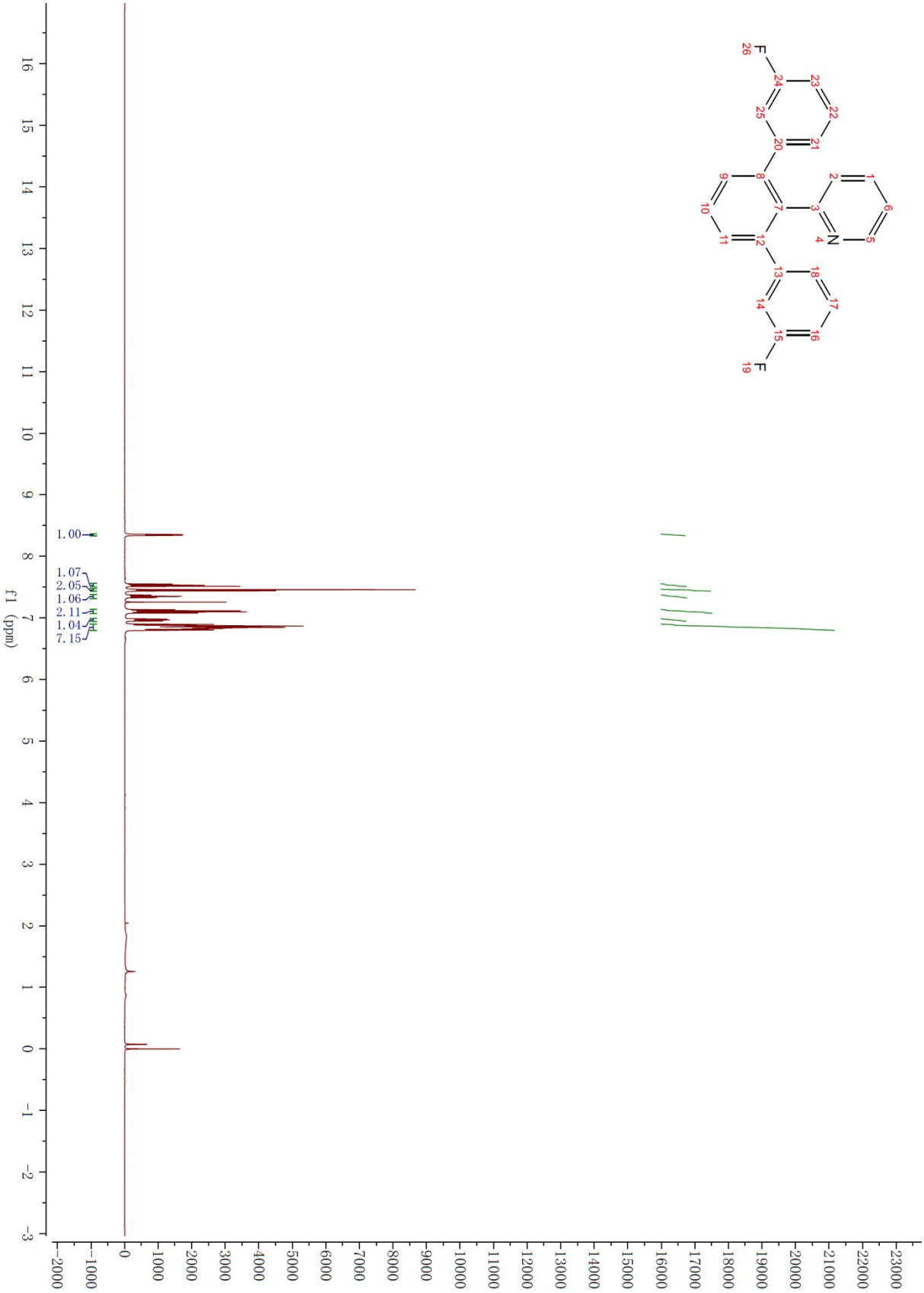
^{1}H NMR Spectrum of the Compound 3aa



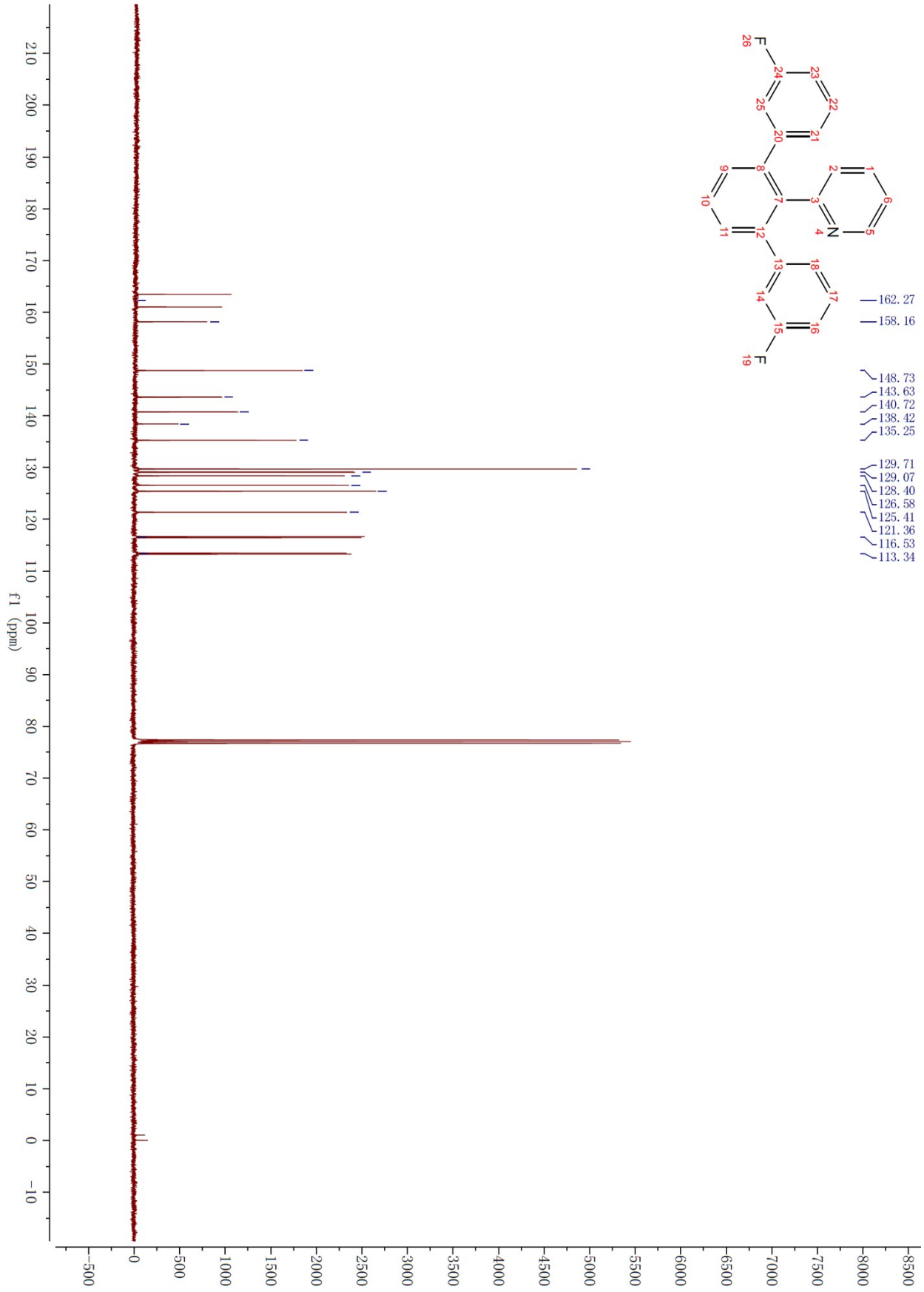
^{13}C NMR Spectrum of the Compound 3aa



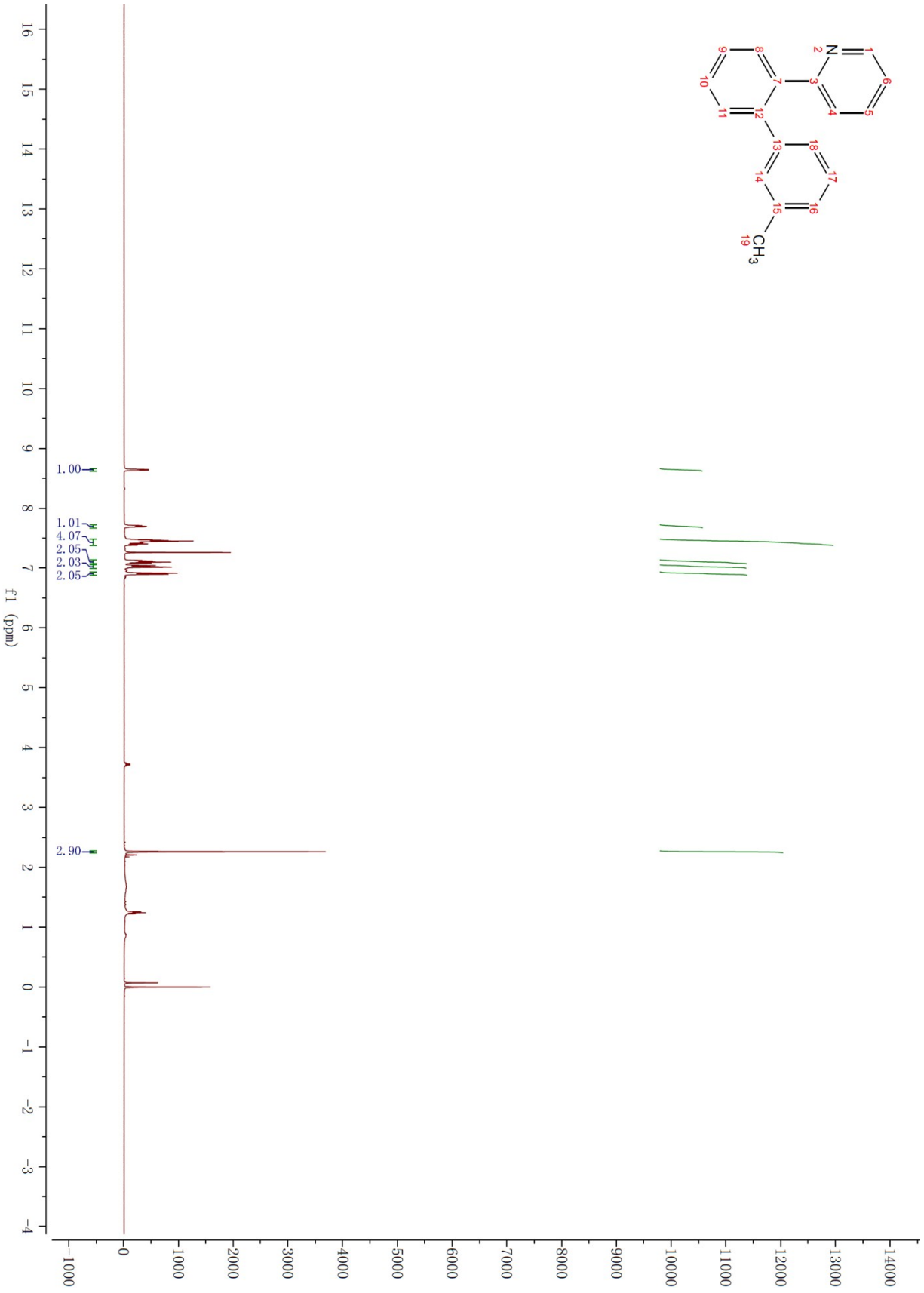
^{1}H NMR Spectrum of the Compound 4aa



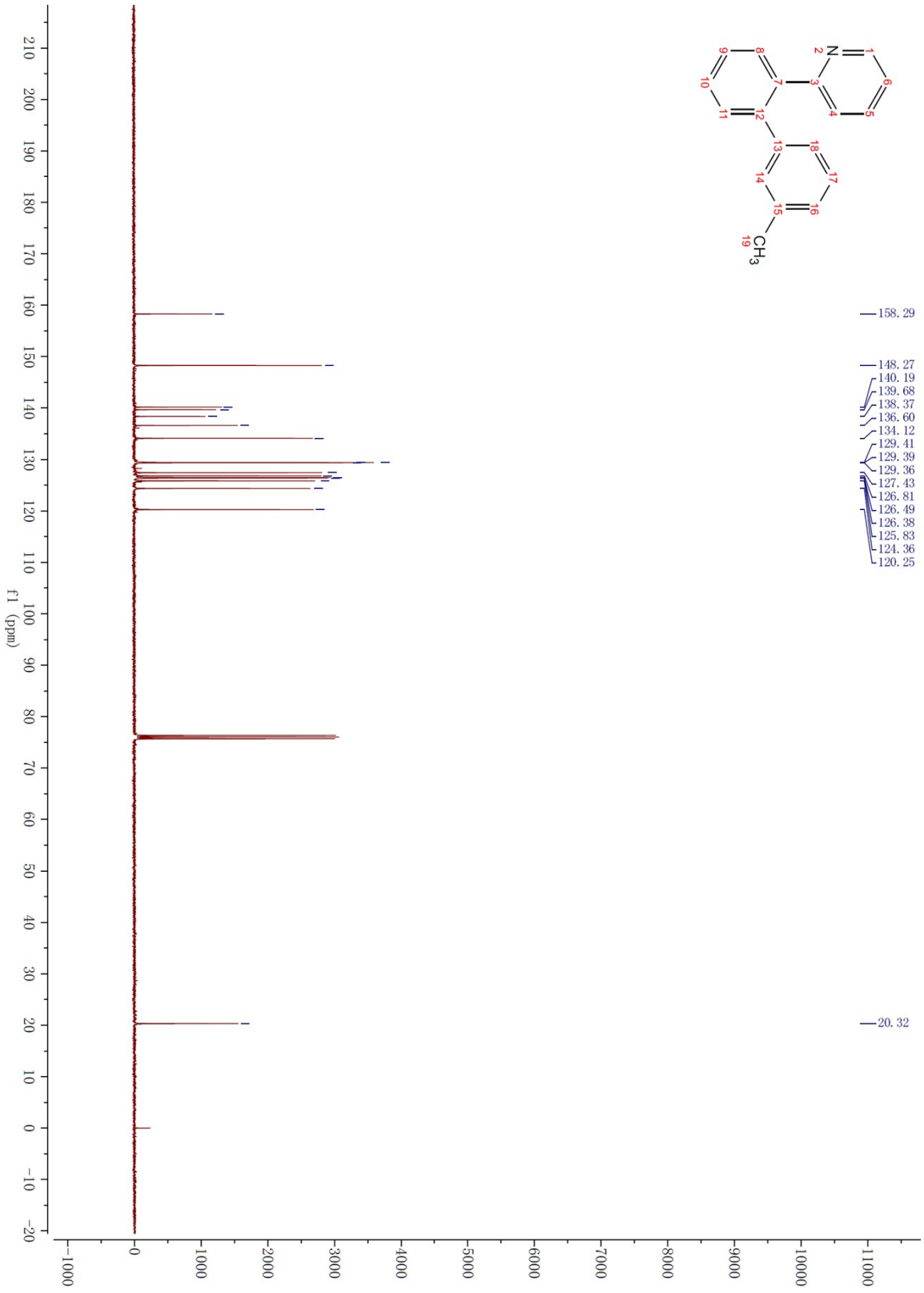
^{13}C NMR Spectrum of the Compound 4aa



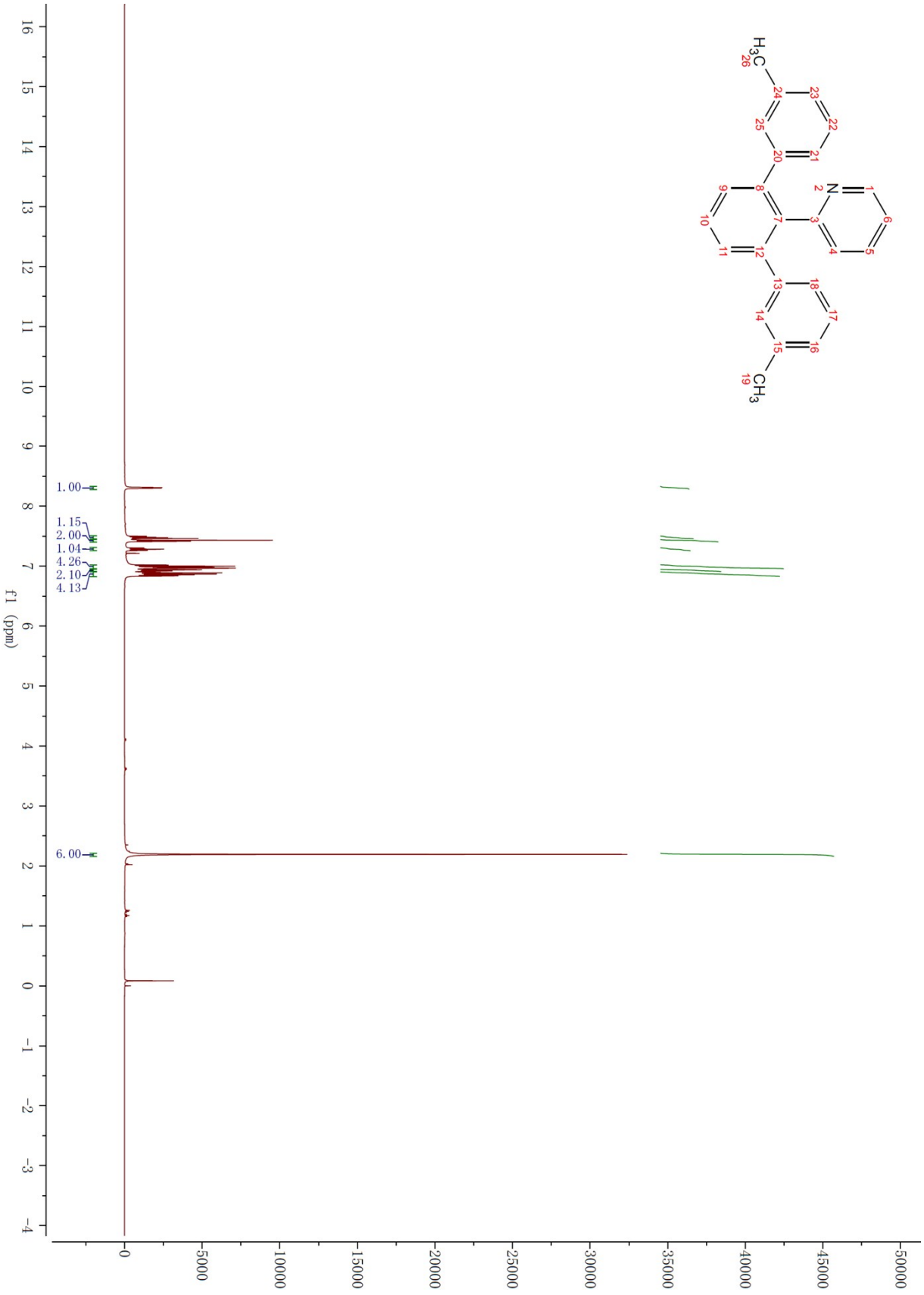
^{1}H NMR Spectrum of the Compound 3ad



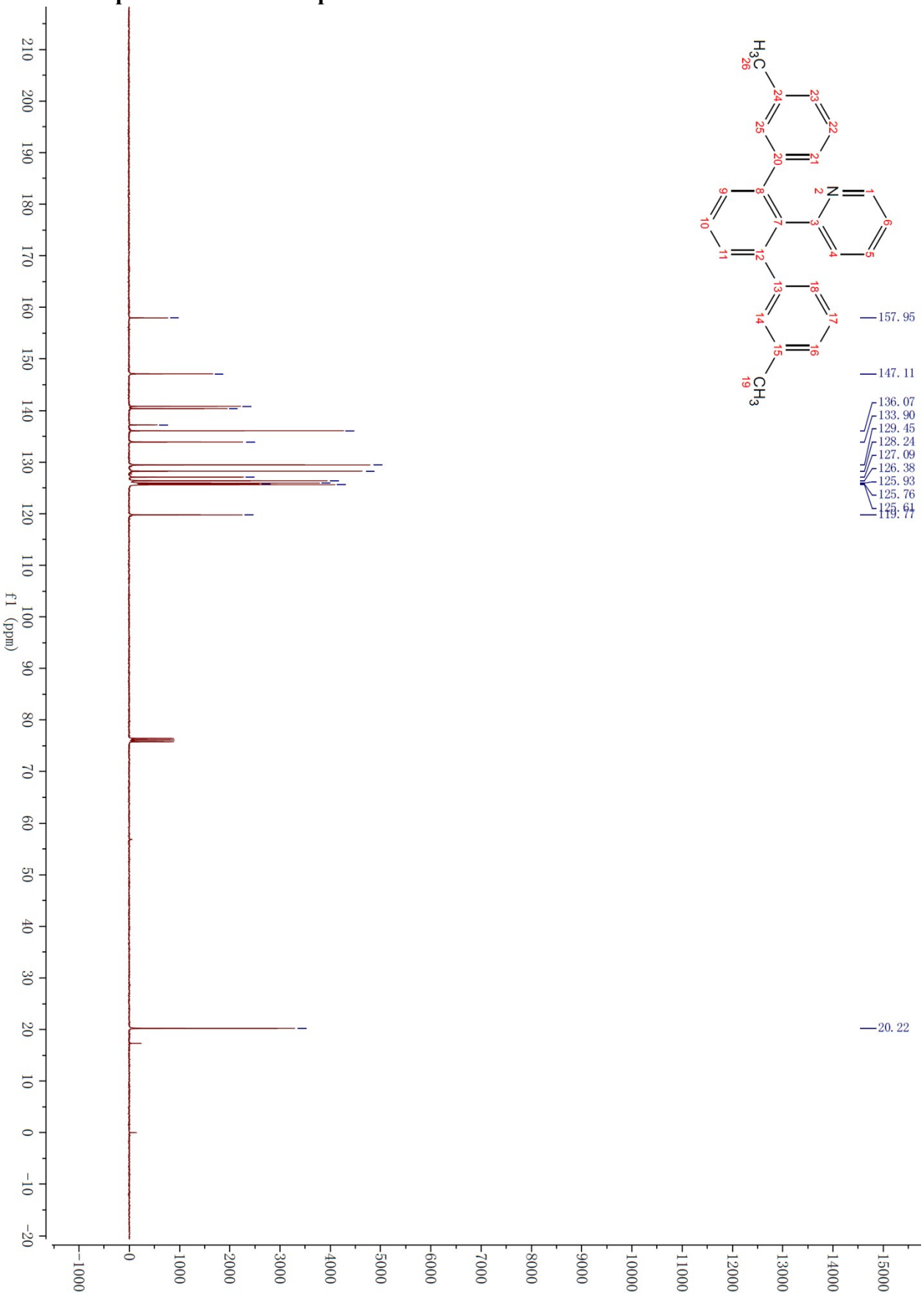
^{13}C NMR Spectrum of the Compound 3ad



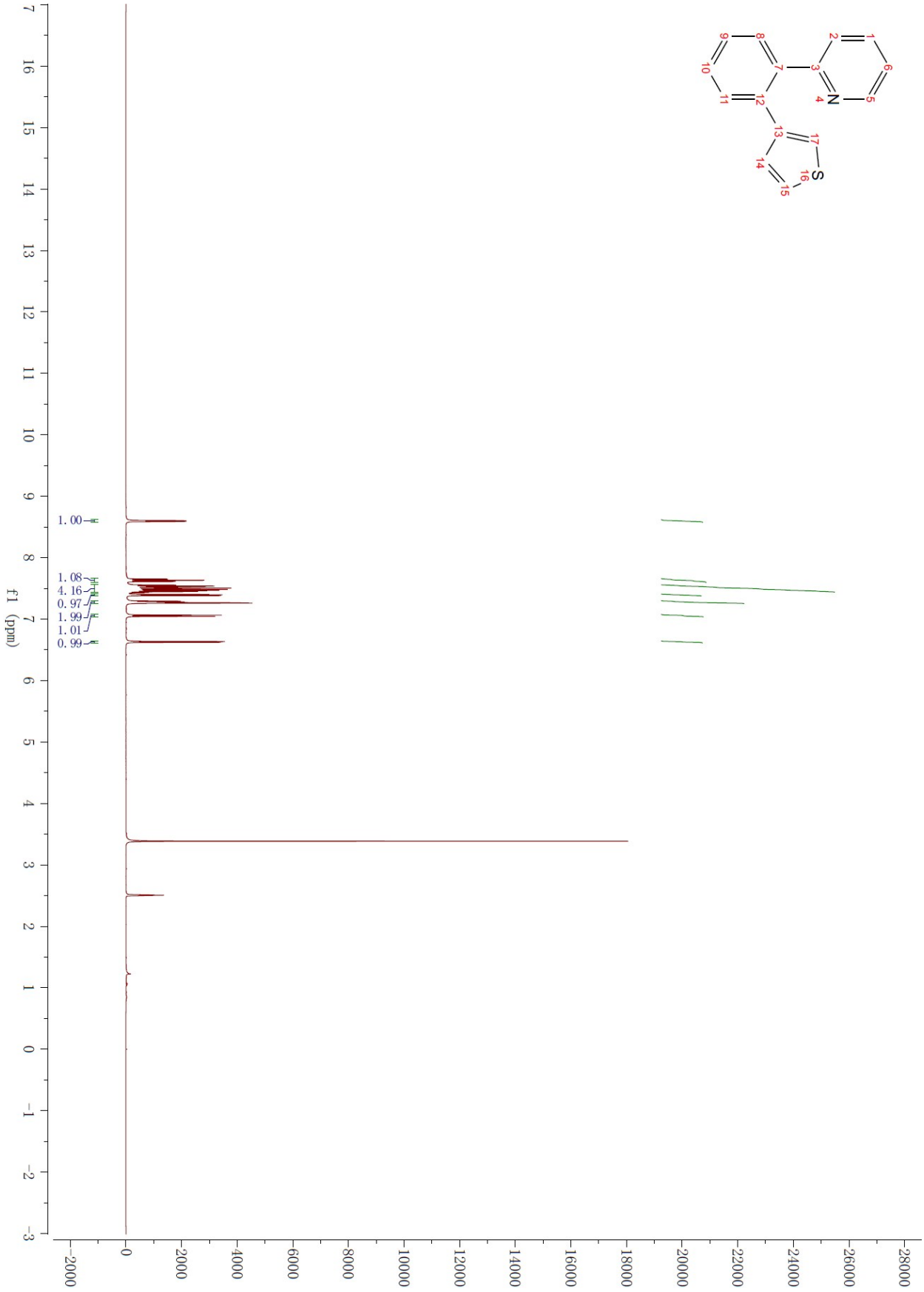
^{1}H NMR Spectrum of the Compound 4ad



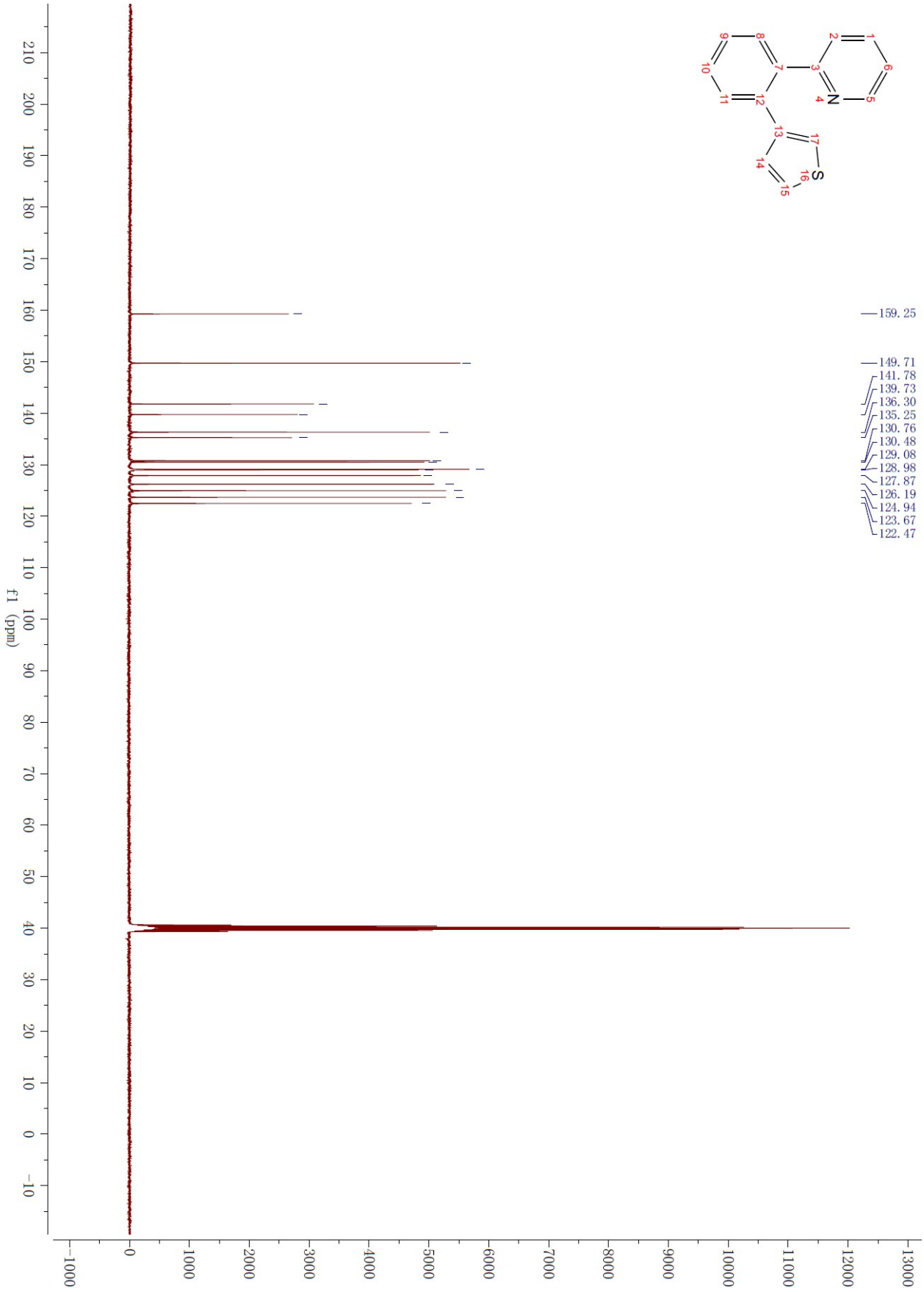
^{13}C NMR Spectrum of the Compound 4ad



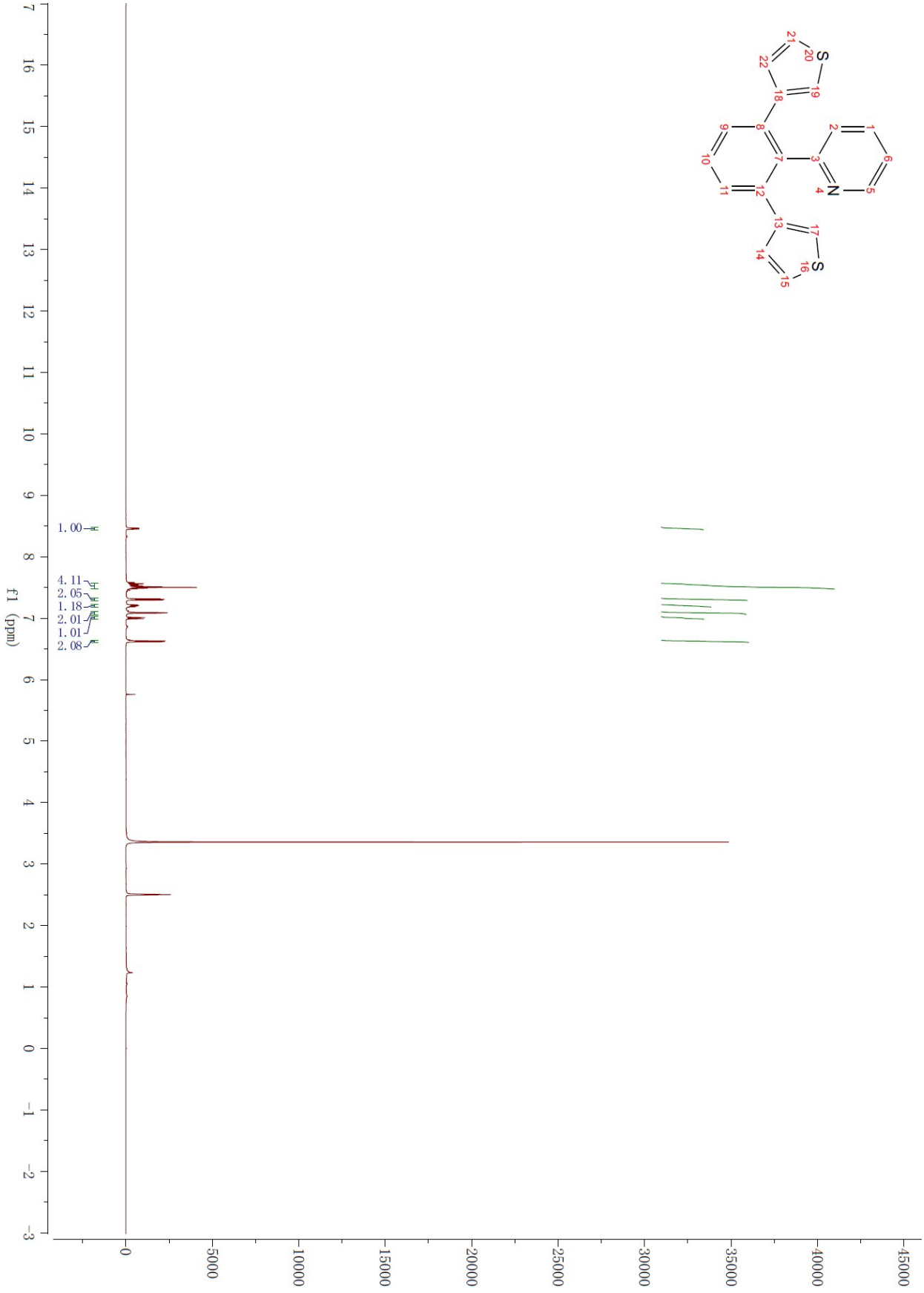
^{1}H NMR Spectrum of the Compound 3ar



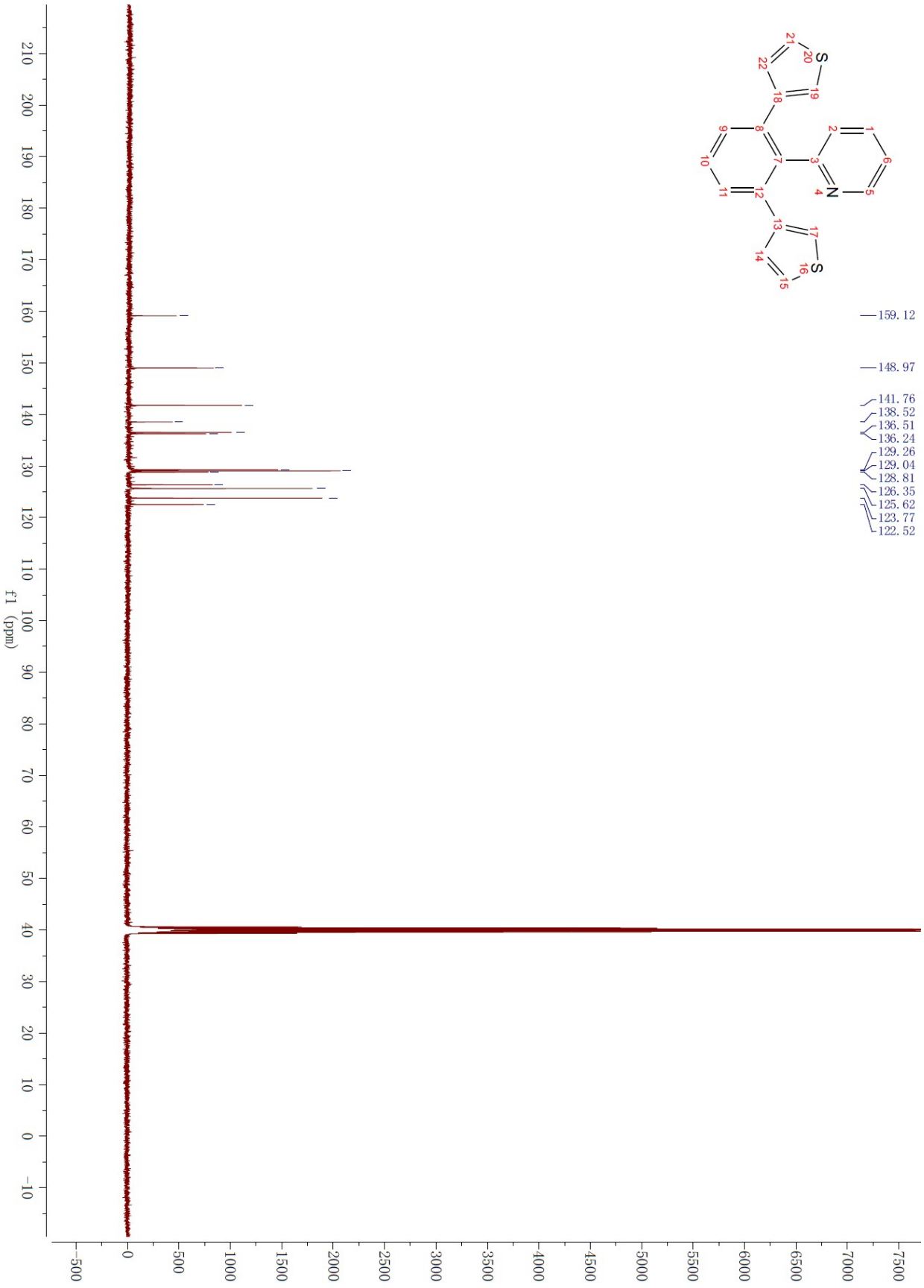
^{13}C NMR Spectrum of the Compound 3ar



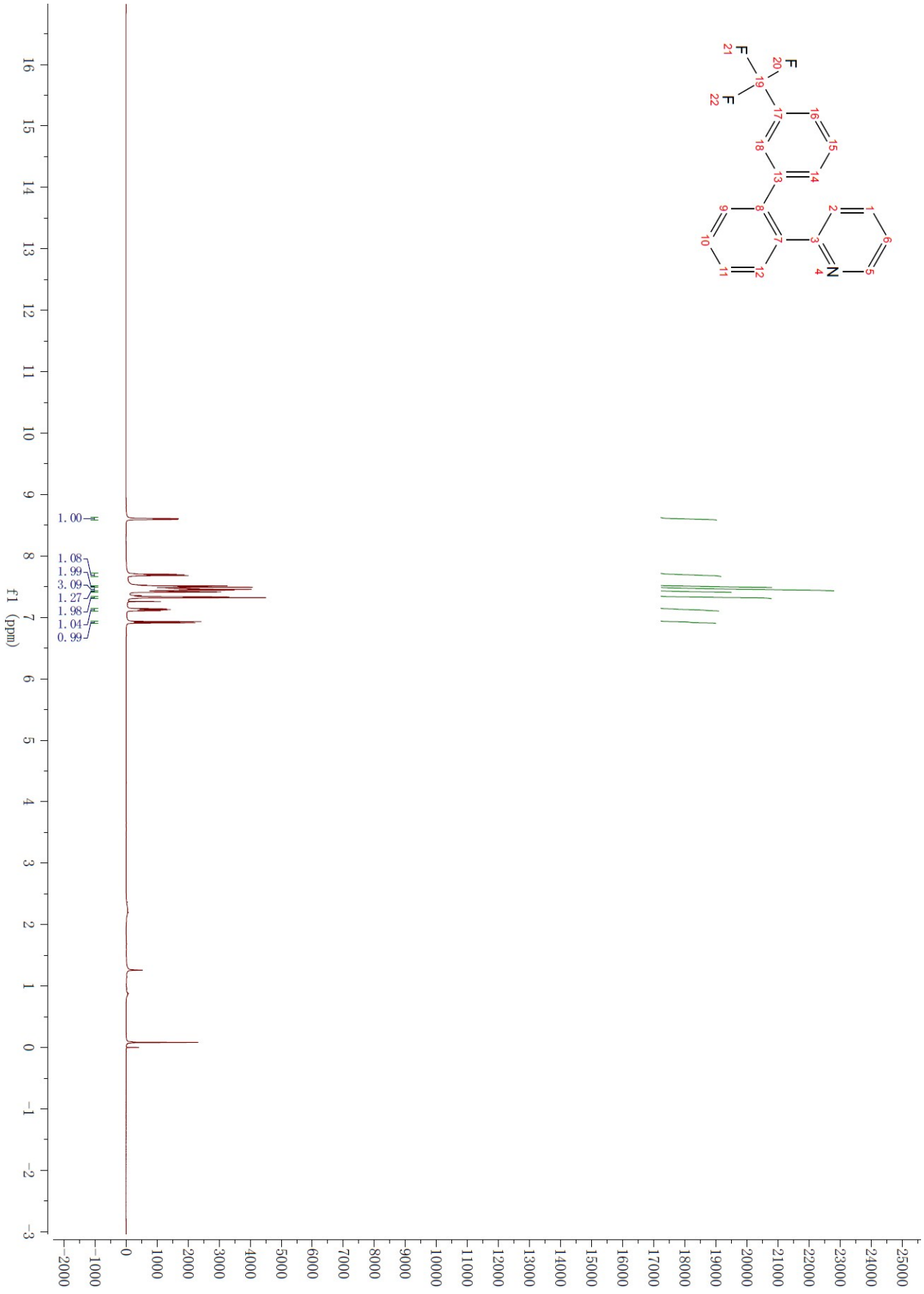
^{1}H NMR Spectrum of the Compound 4ar



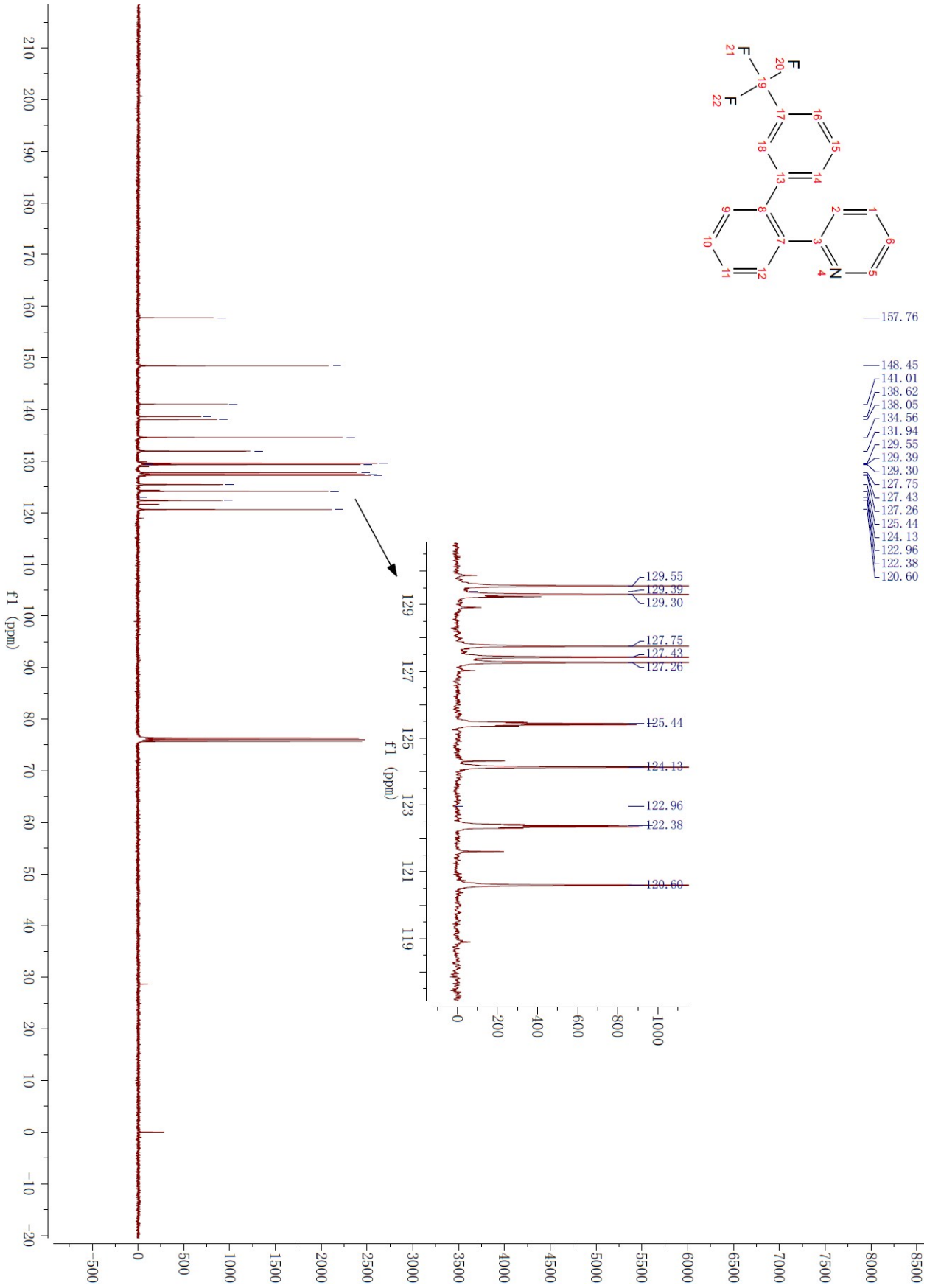
^{13}C NMR Spectrum of the Compound 4ar



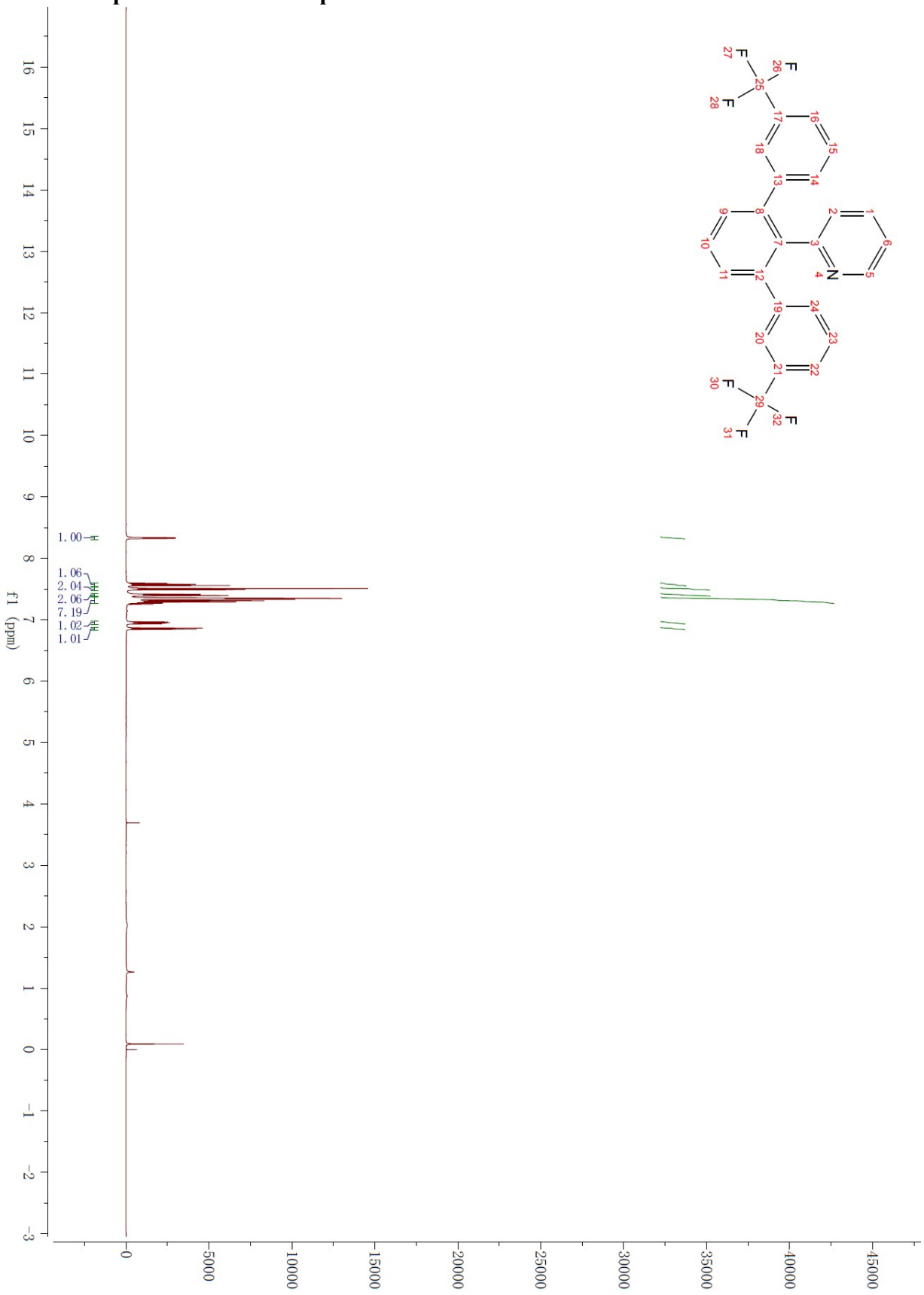
^{1}H NMR Spectrum of the Compound 3al



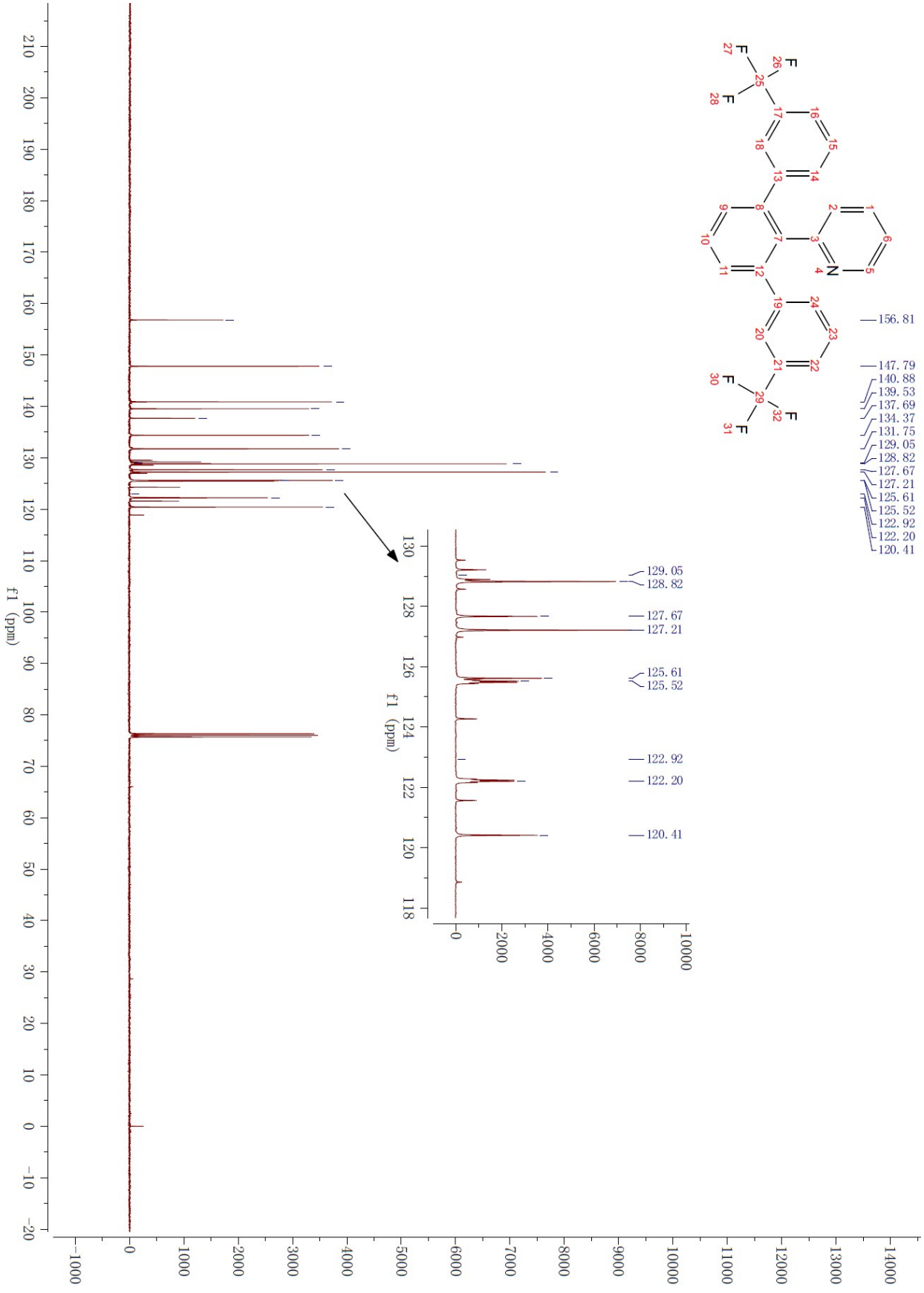
^{13}C NMR Spectrum of the Compound 3al



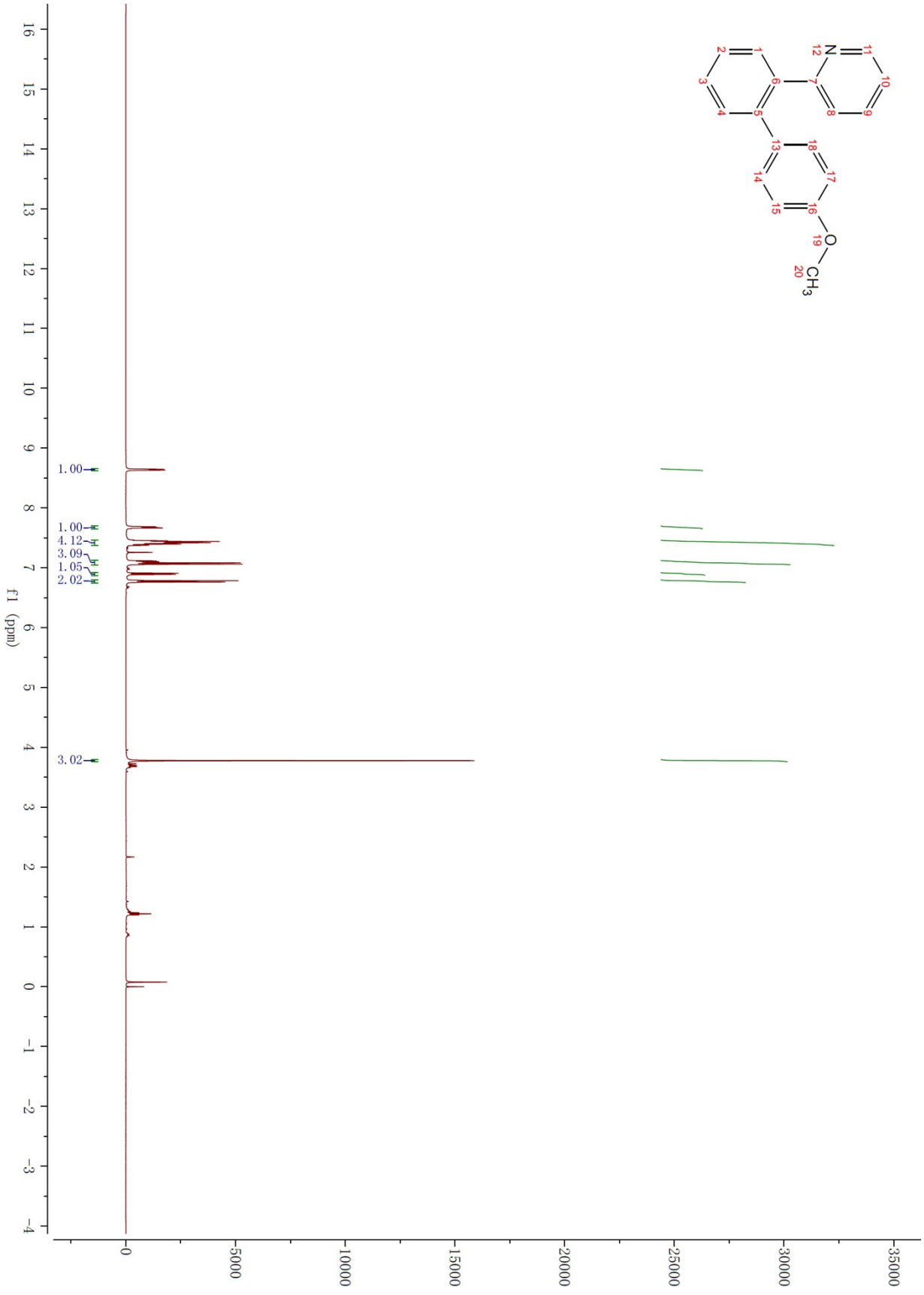
^{1}H NMR Spectrum of the Compound 4al



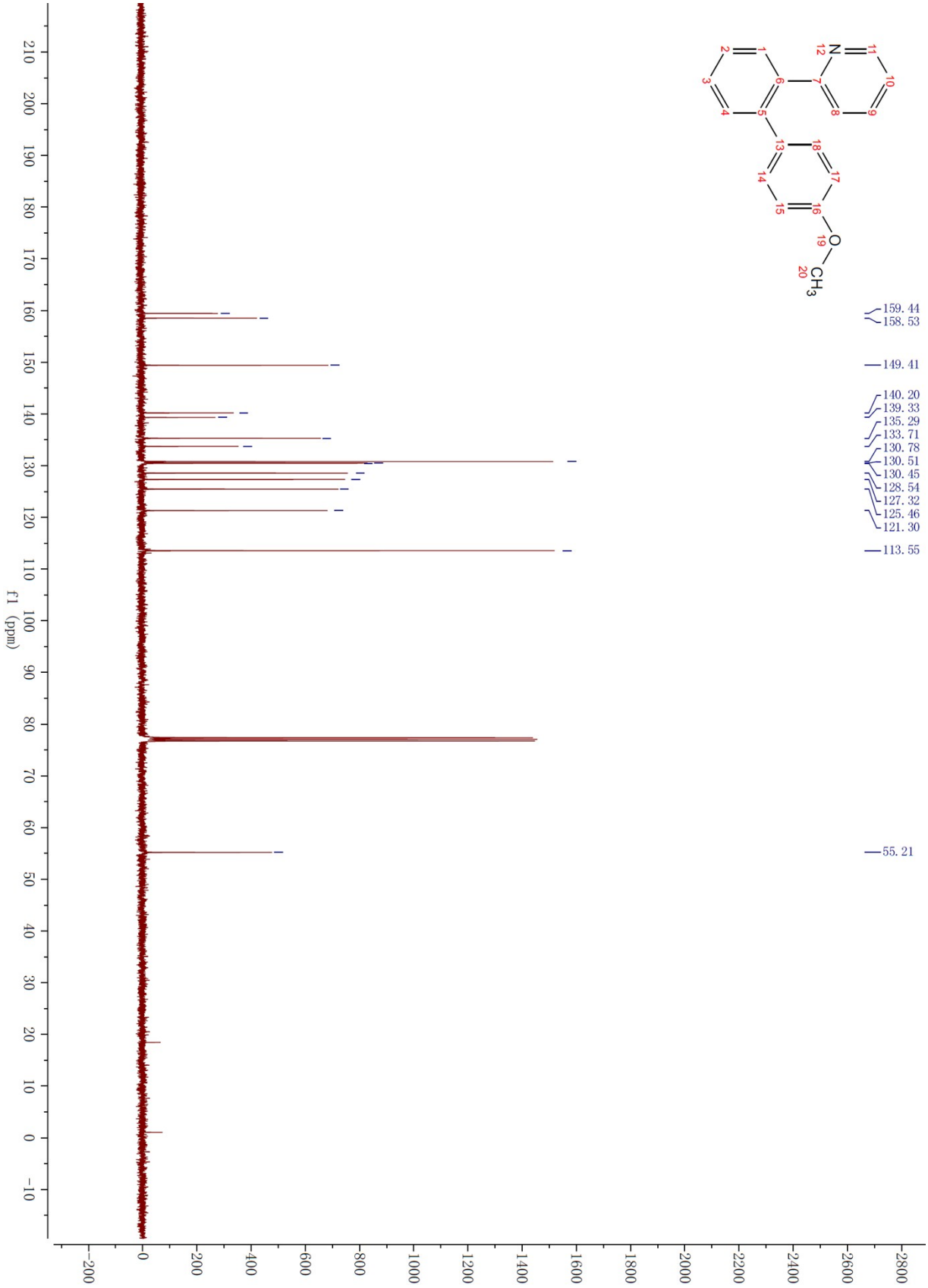
^{13}C NMR Spectrum of the Compound 4al



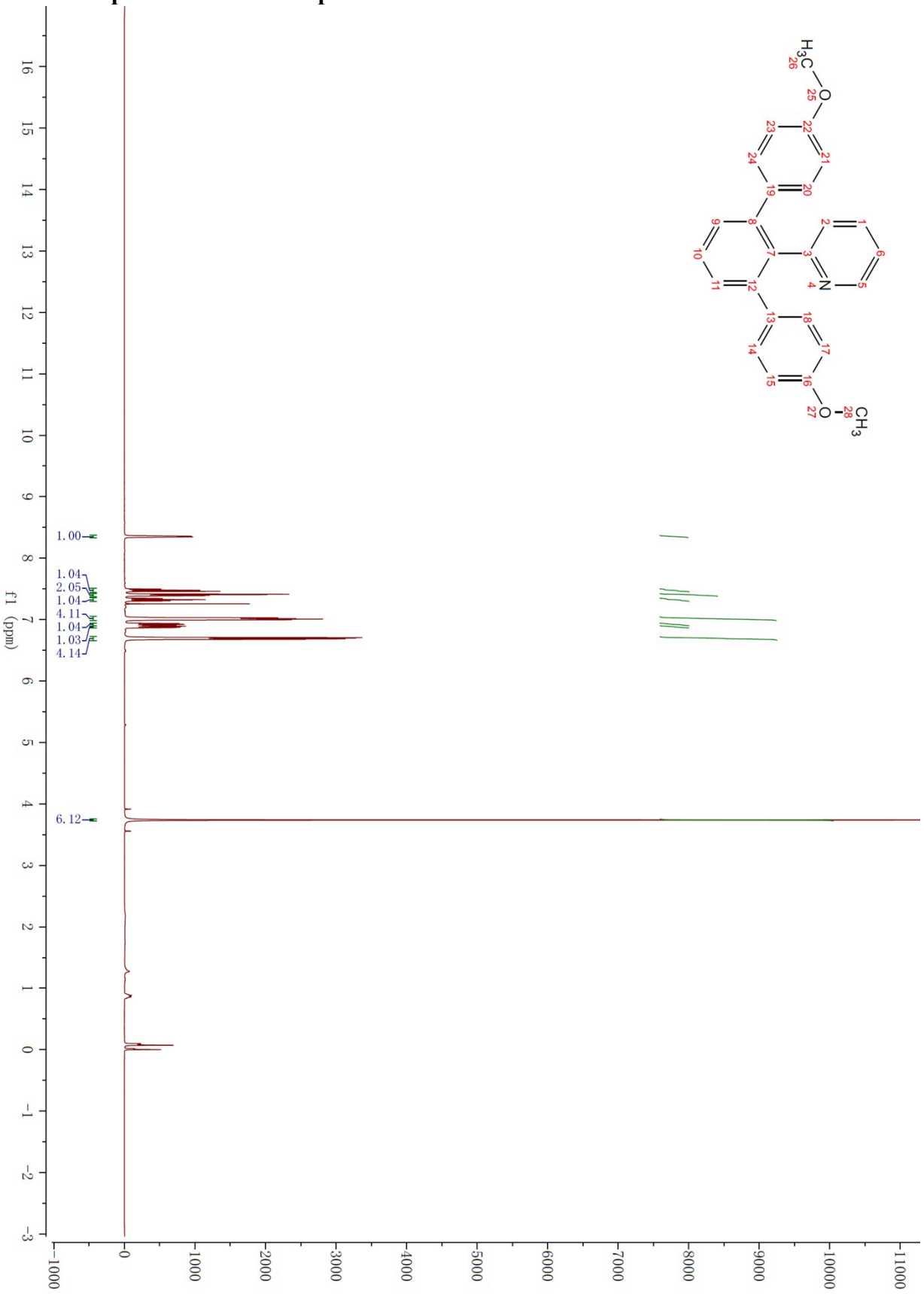
^{1}H NMR Spectrum of the Compound 3ah



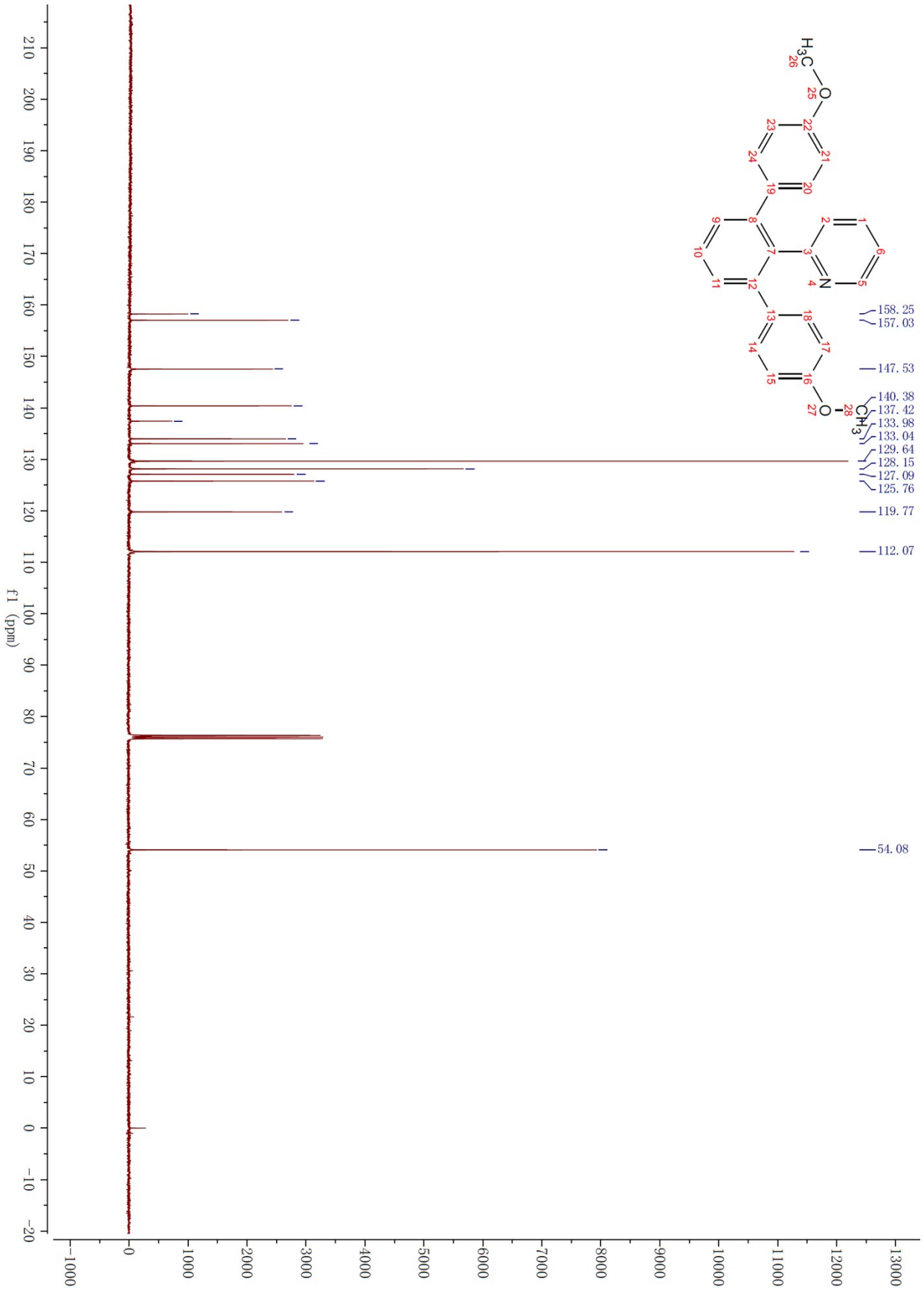
^{13}C NMR Spectrum of the Compound 3ah



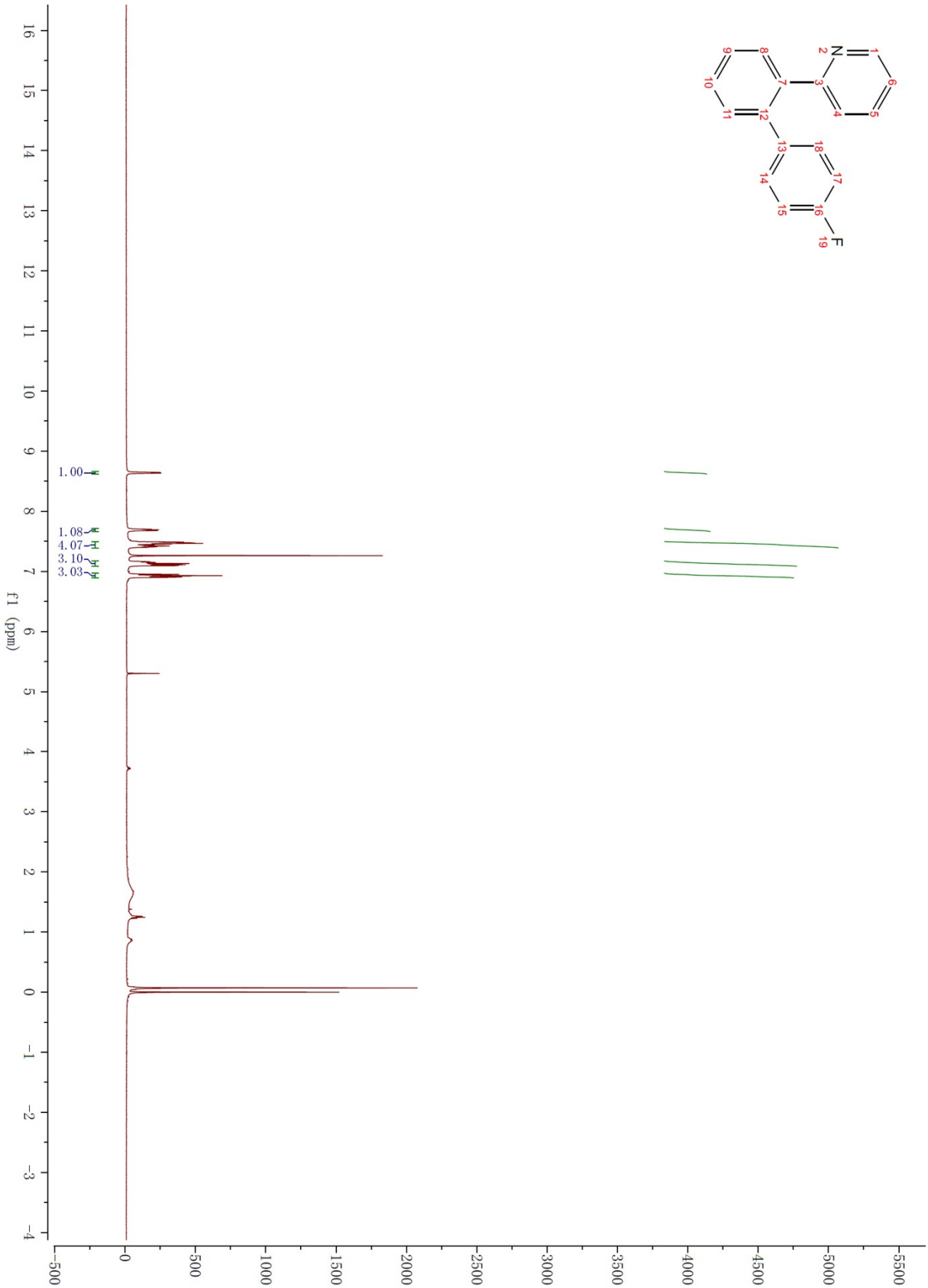
^{1}H NMR Spectrum of the Compound 4ah



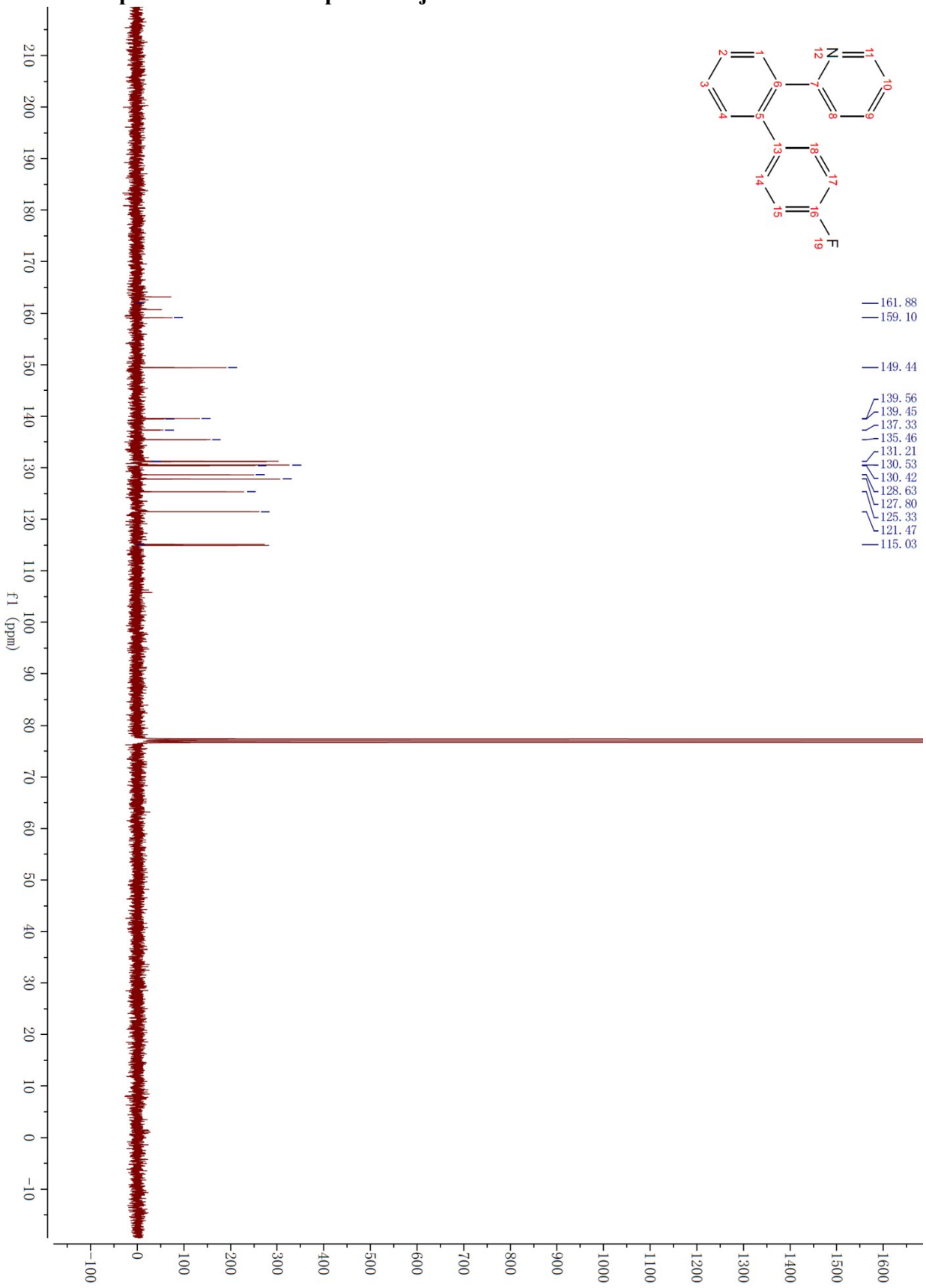
^{13}C NMR Spectrum of the Compound 4ah



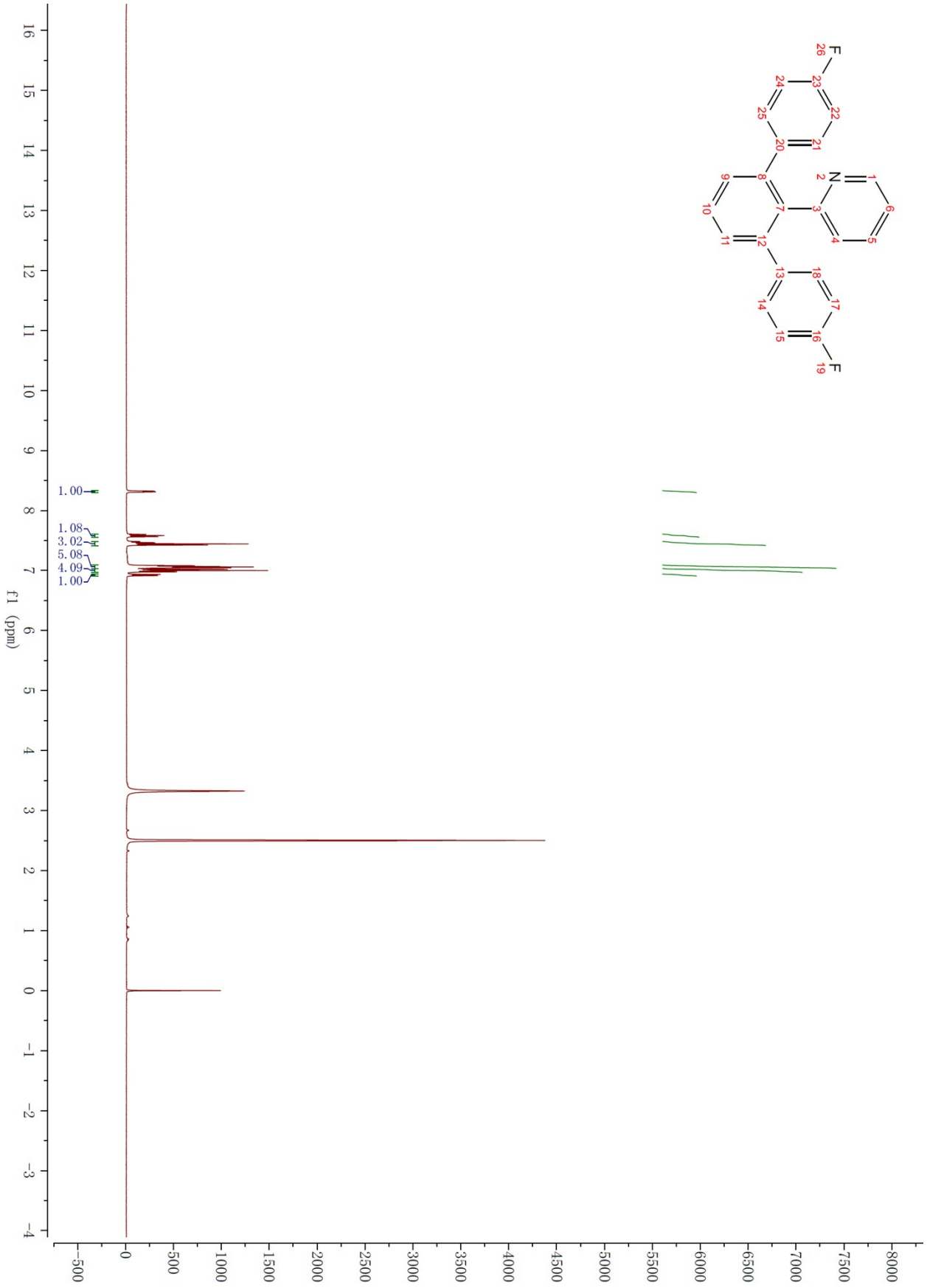
^{1}H NMR Spectrum of the Compound 3aj



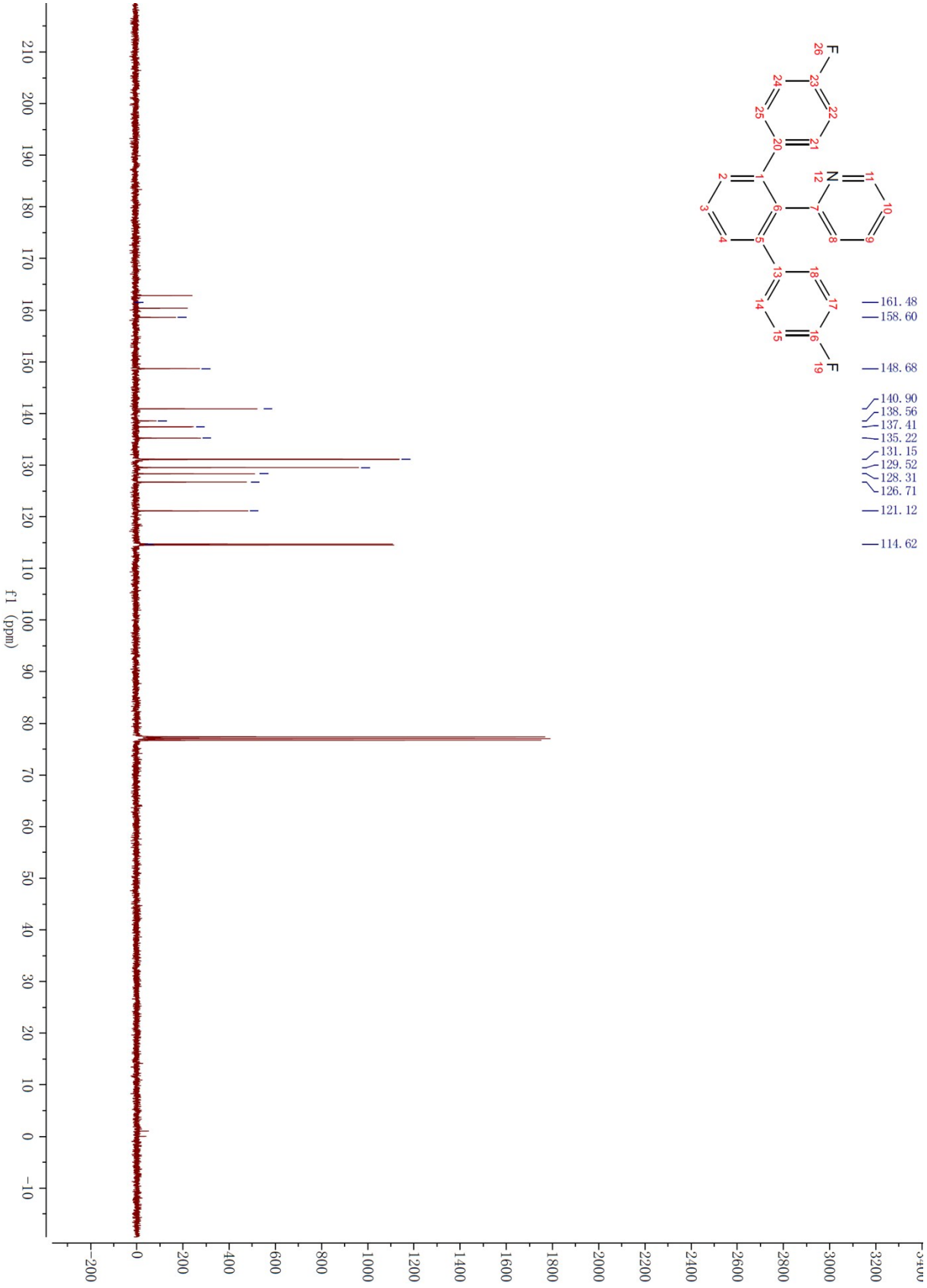
^{13}C NMR Spectrum of the Compound 3aj



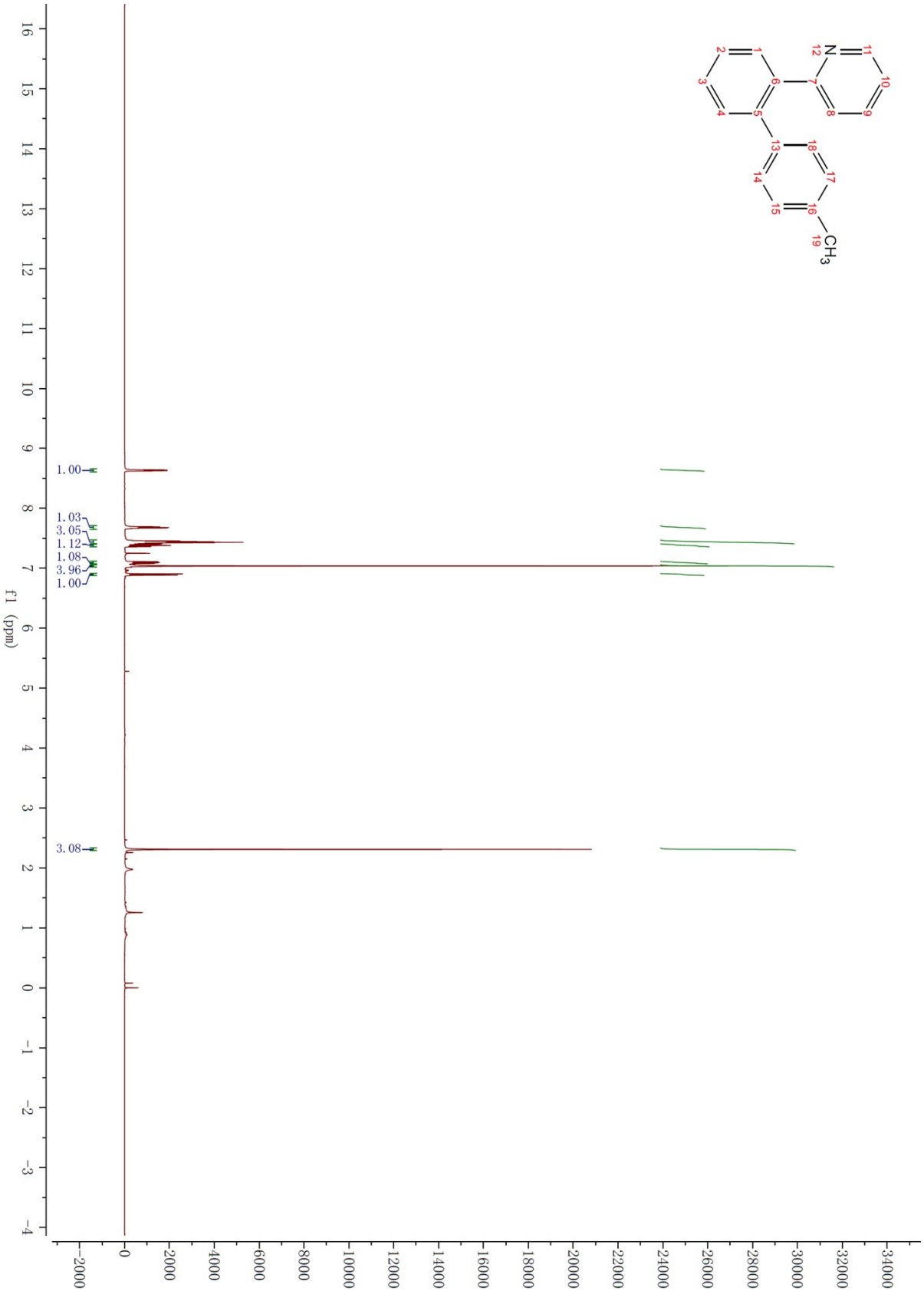
^{1}H NMR Spectrum of the Compound 4aj



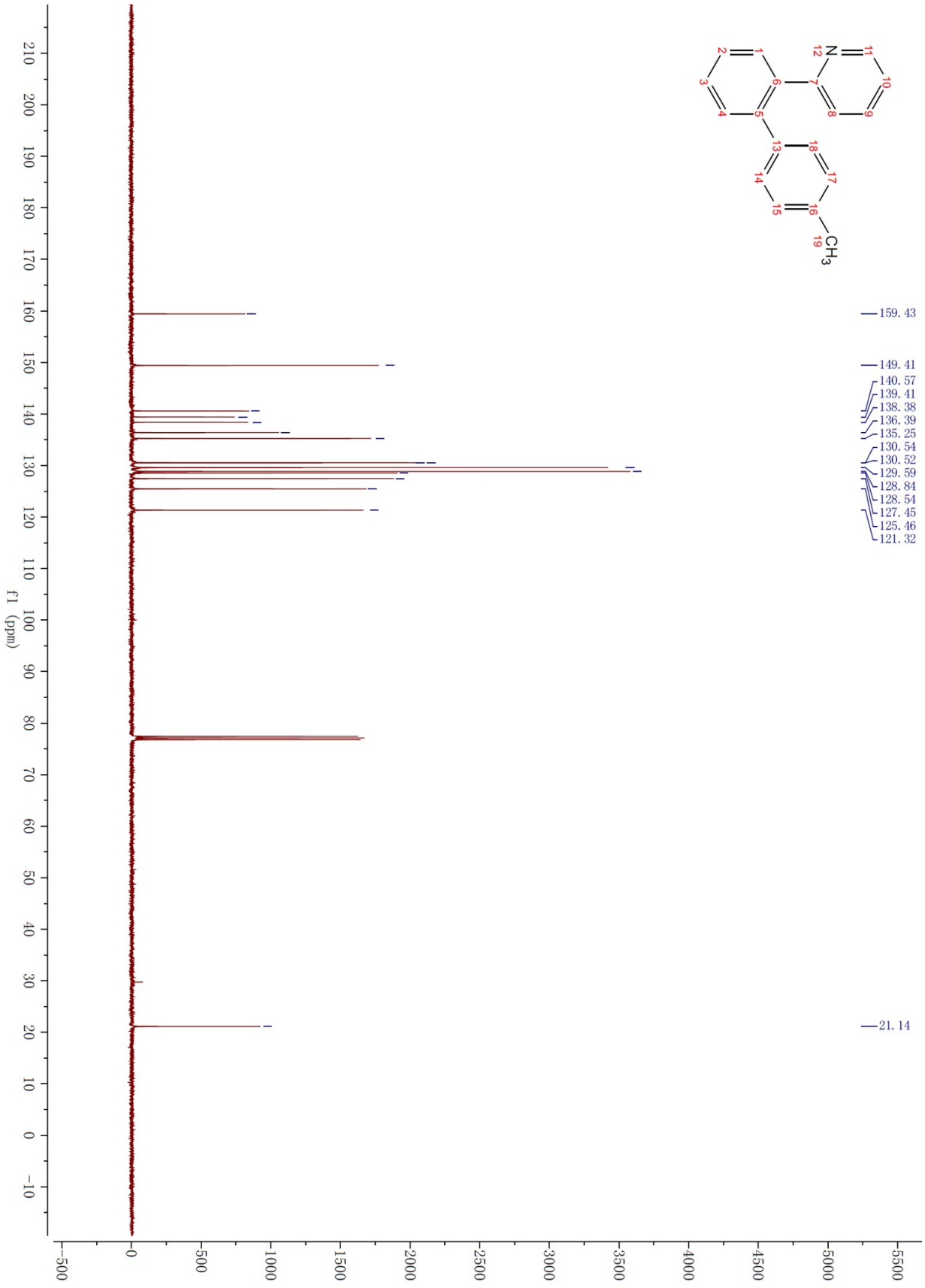
^{13}C NMR Spectrum of the Compound 4aj



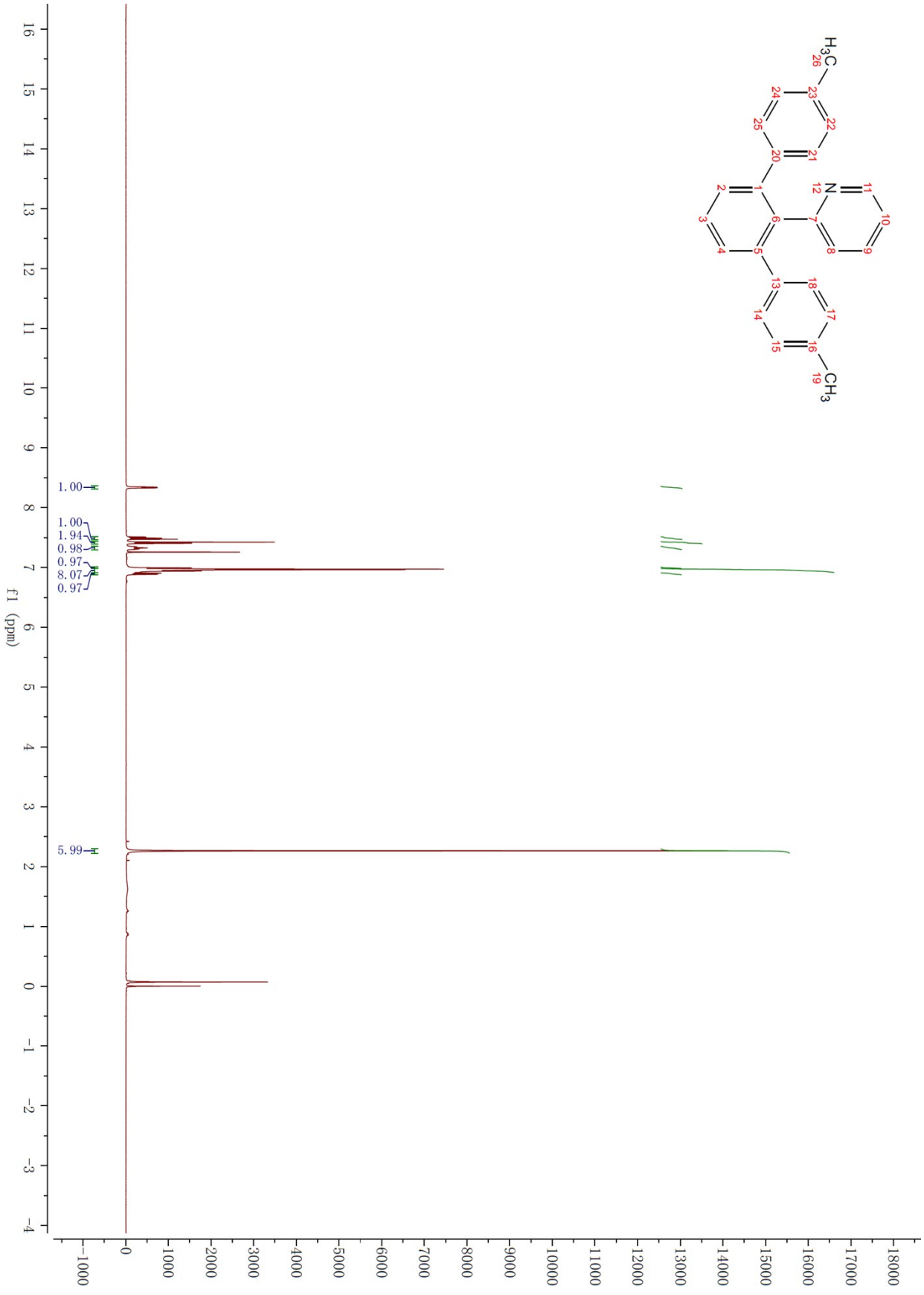
^{1}H NMR Spectrum of the Compound 3ae



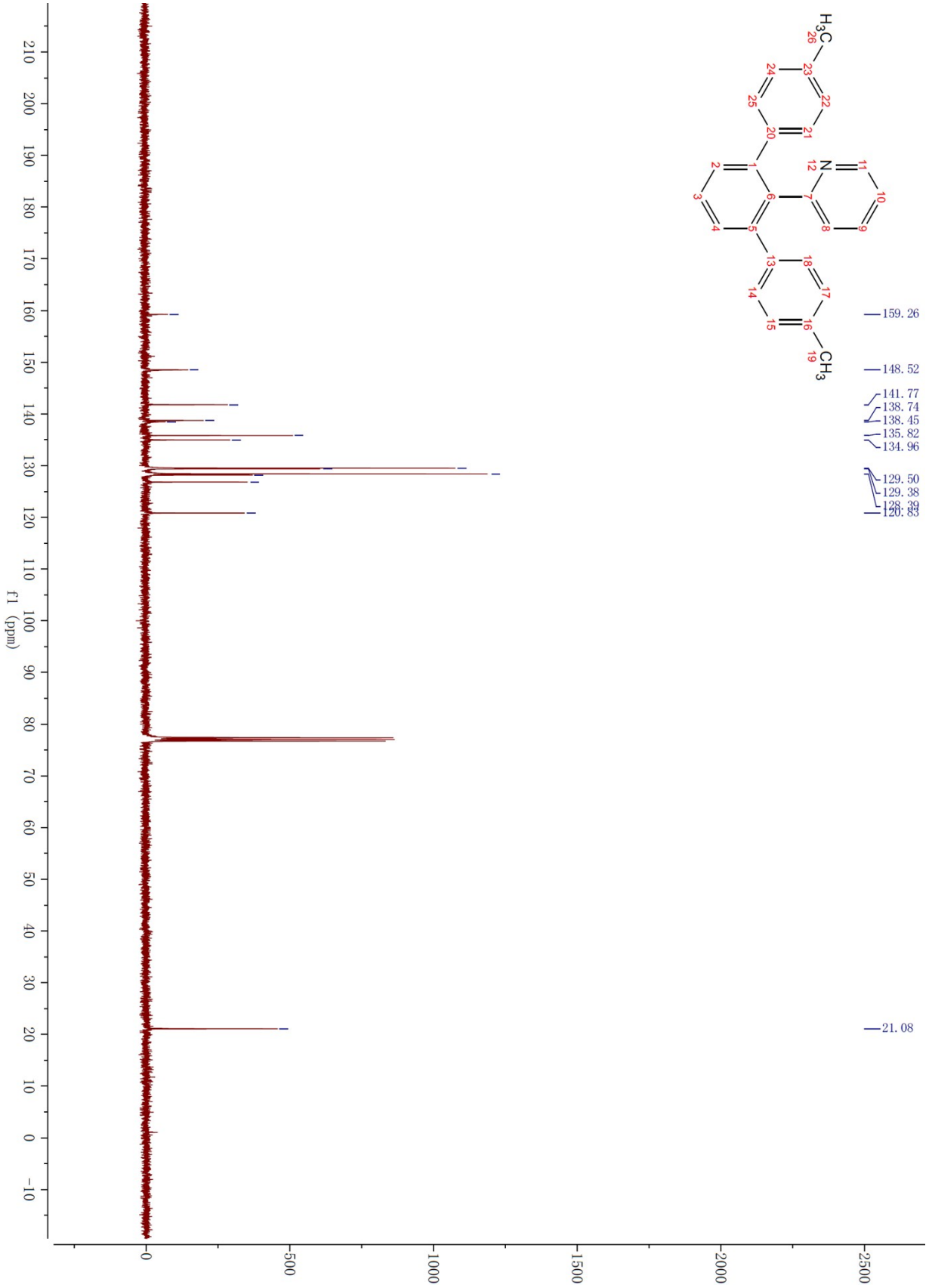
^{13}C NMR Spectrum of the Compound 3ae



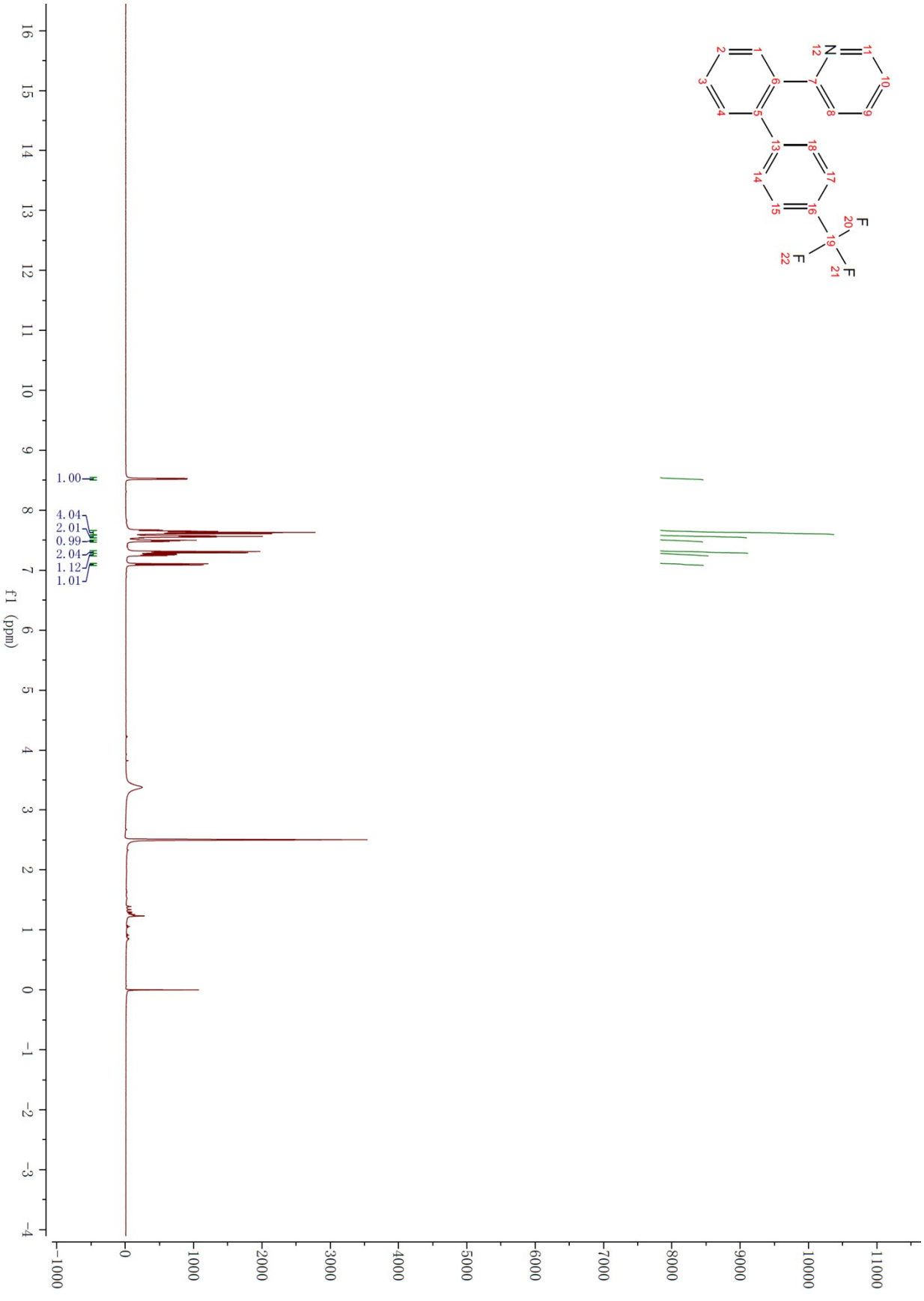
^{1}H NMR Spectrum of the Compound 4ae



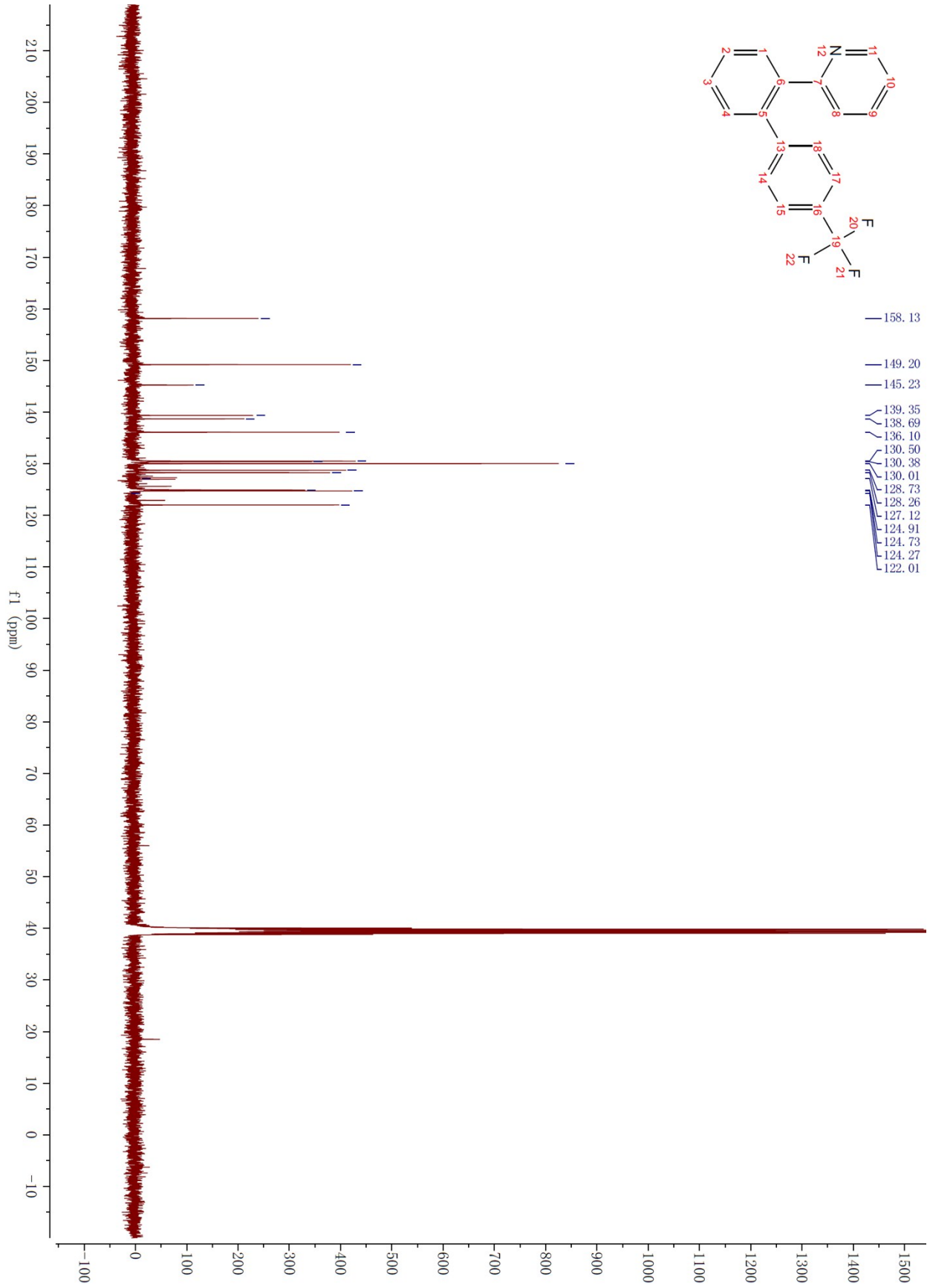
^{13}C NMR Spectrum of the Compound 4ae



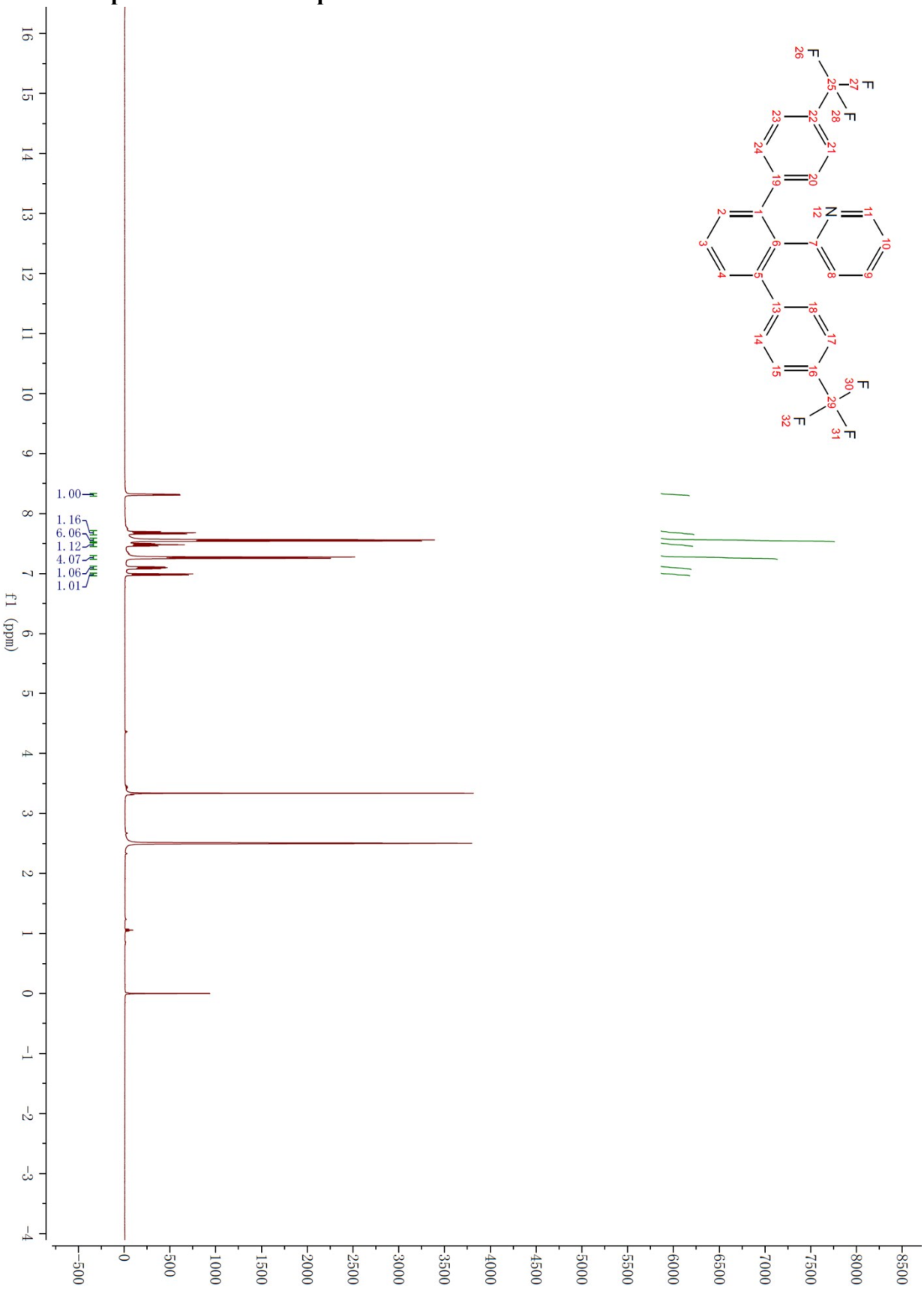
^{1}H NMR Spectrum of the Compound 3am



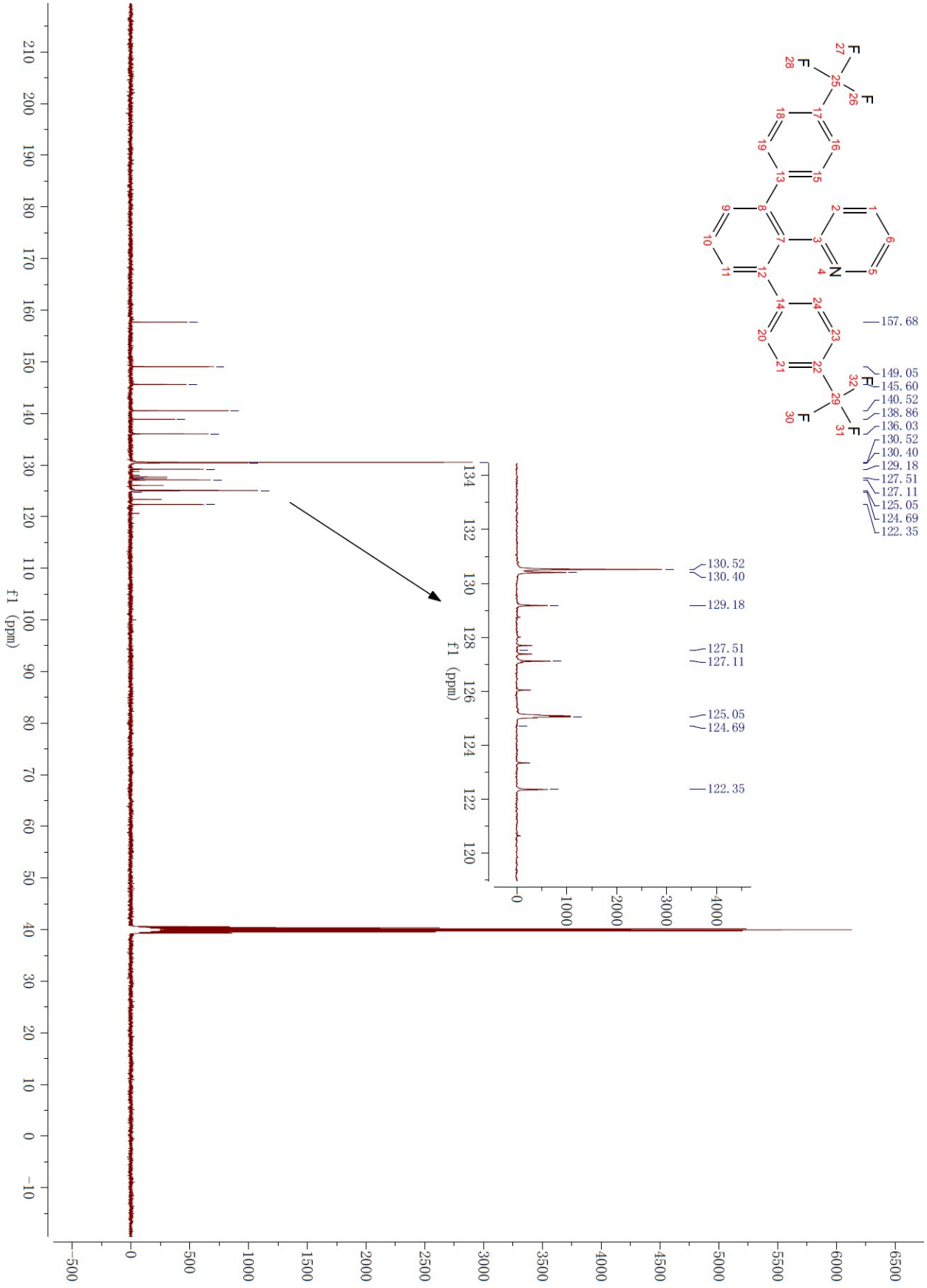
^{13}C NMR Spectrum of the Compound 3am



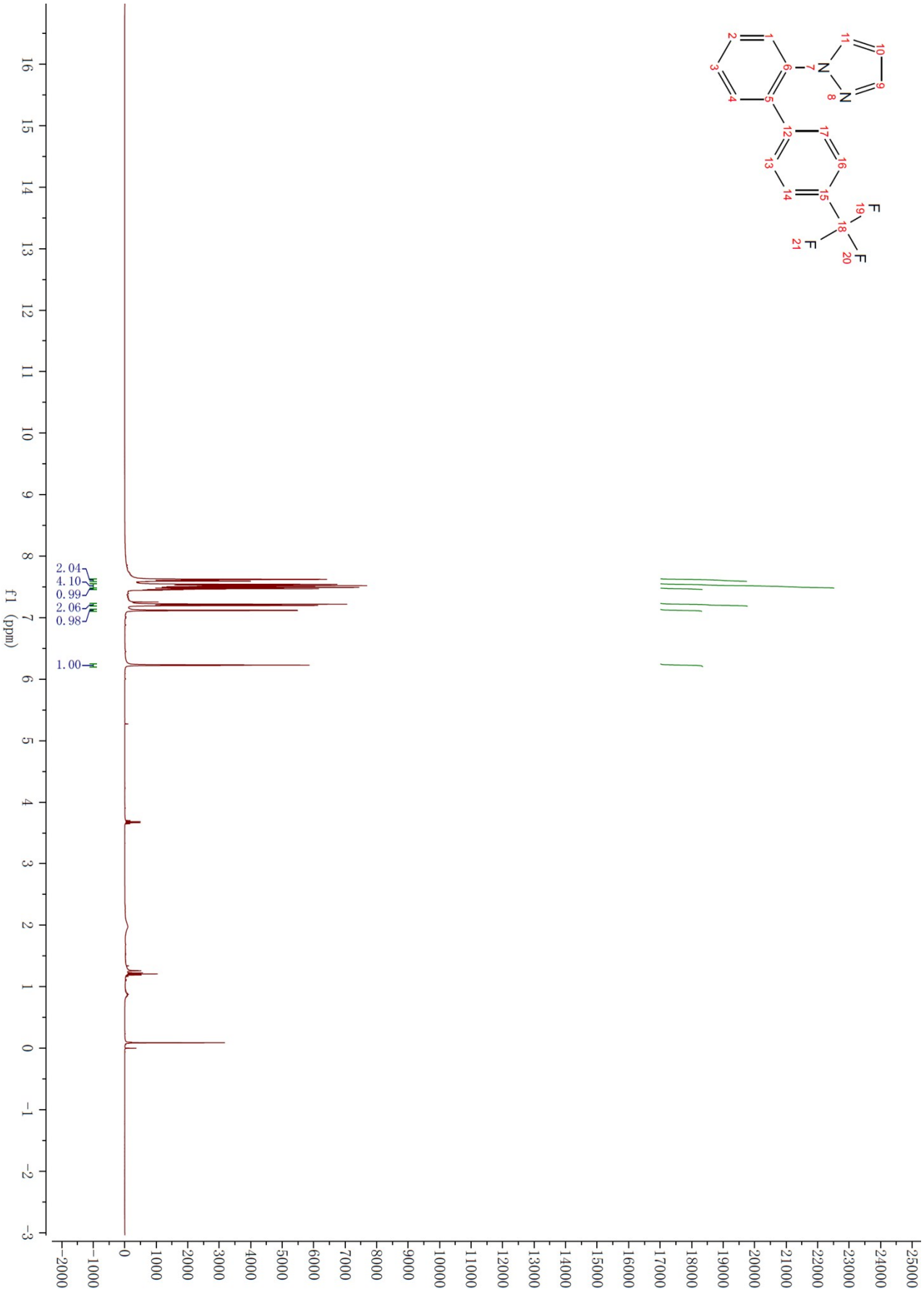
^{1}H NMR Spectrum of the Compound 4am



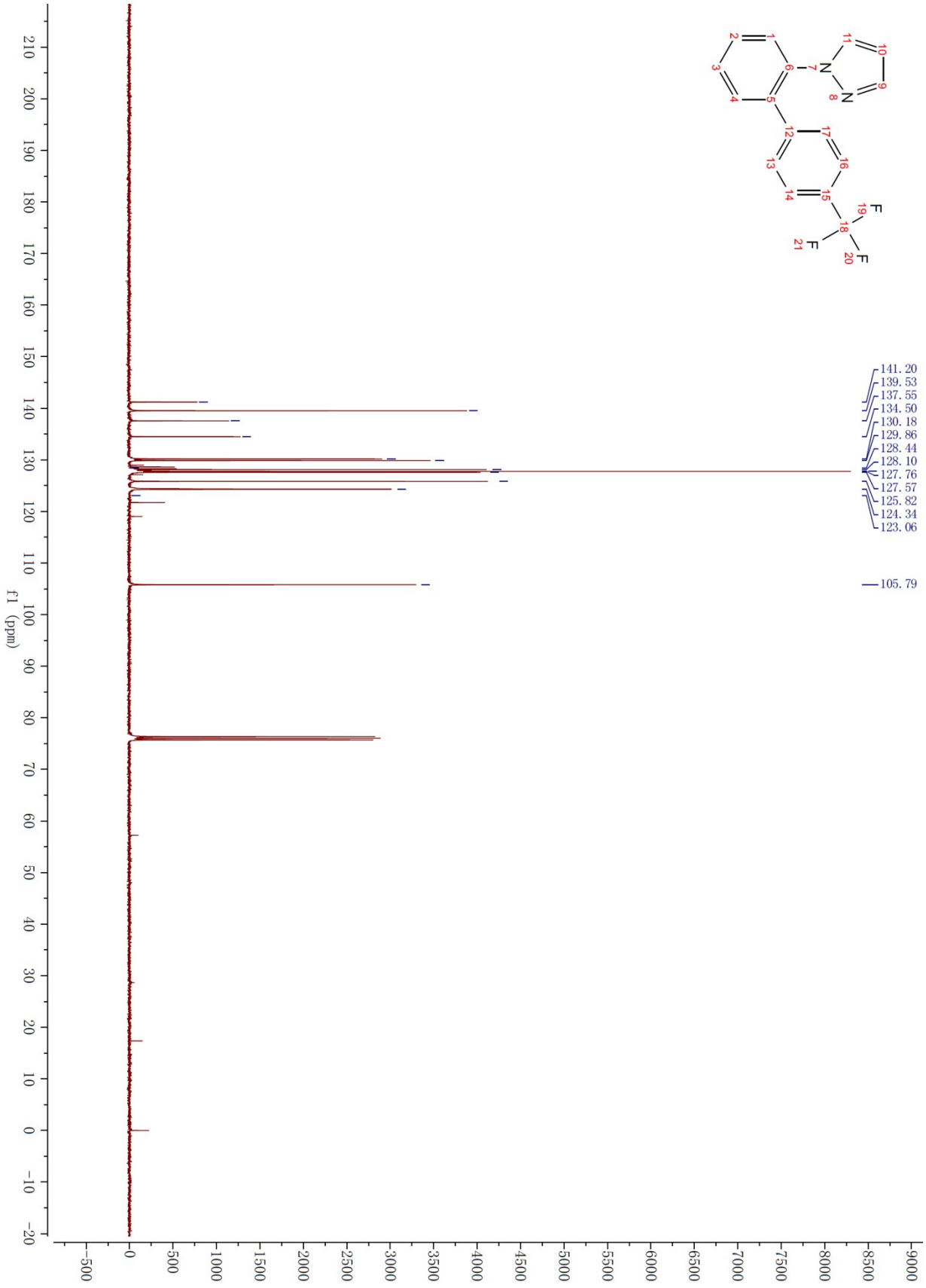
^{13}C NMR Spectrum of the Compound 4am



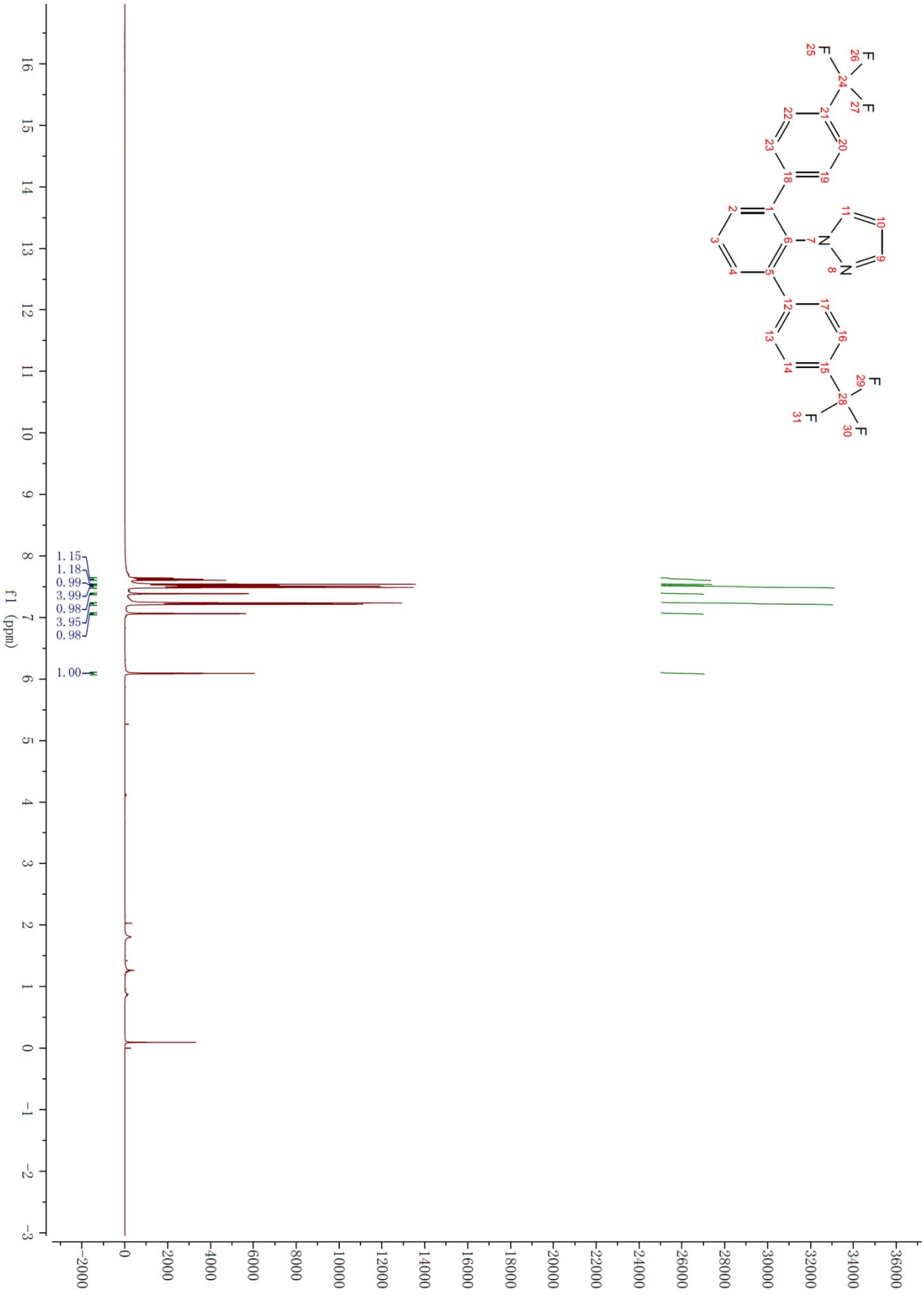
^{1}H NMR Spectrum of the Compound 3bm



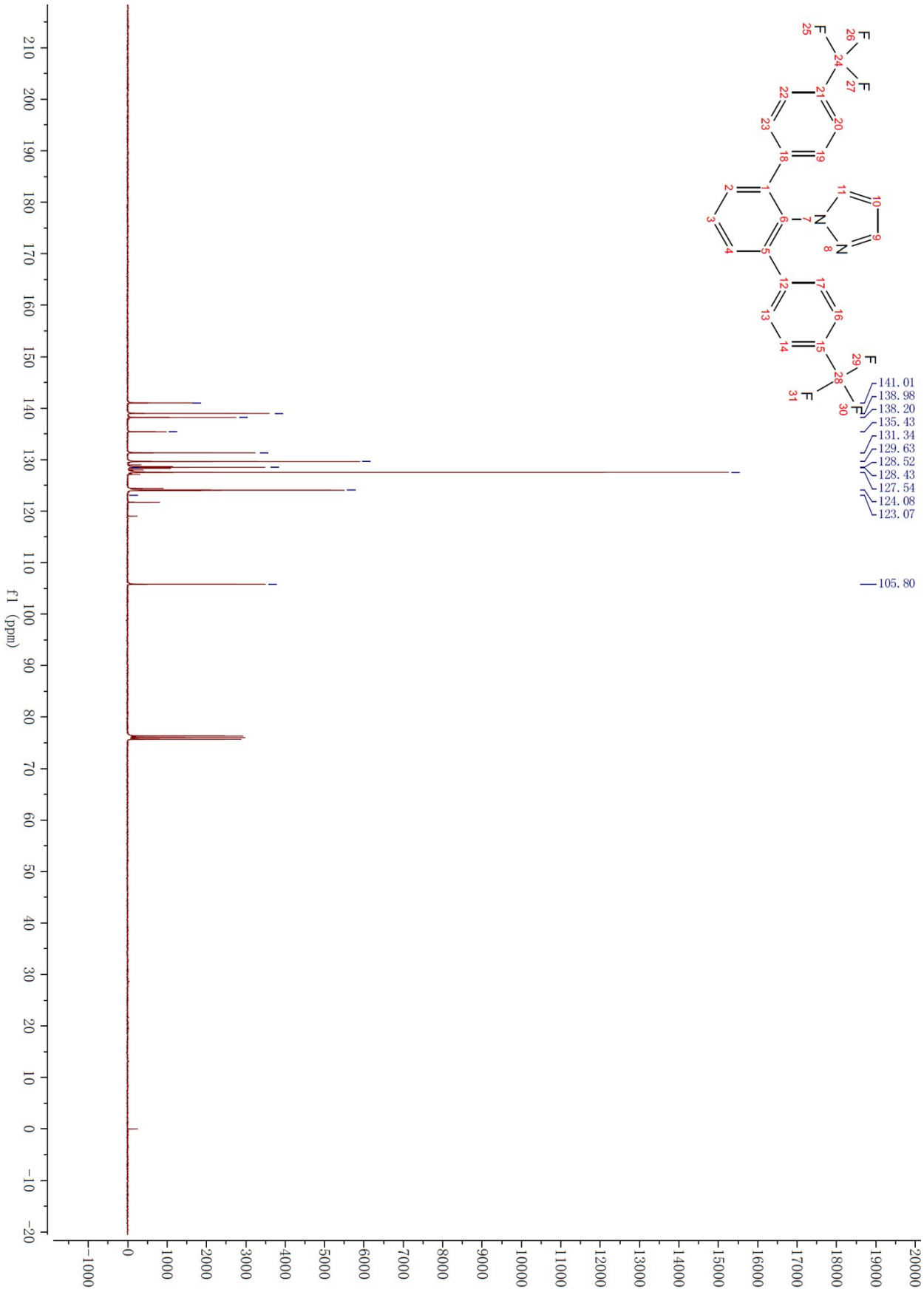
^{13}C NMR Spectrum of the Compound 3bm



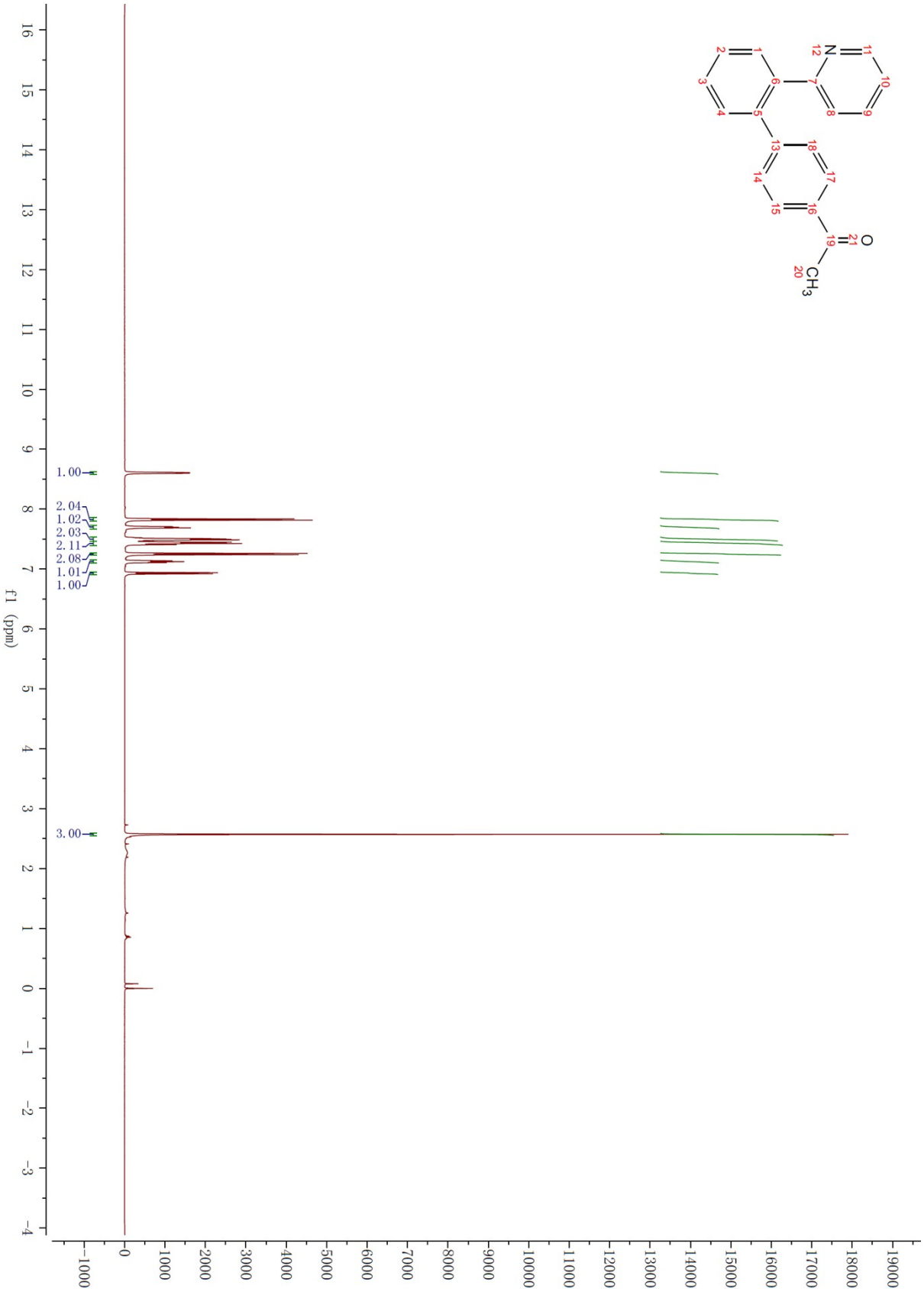
^{1}H NMR Spectrum of the Compound 4bm



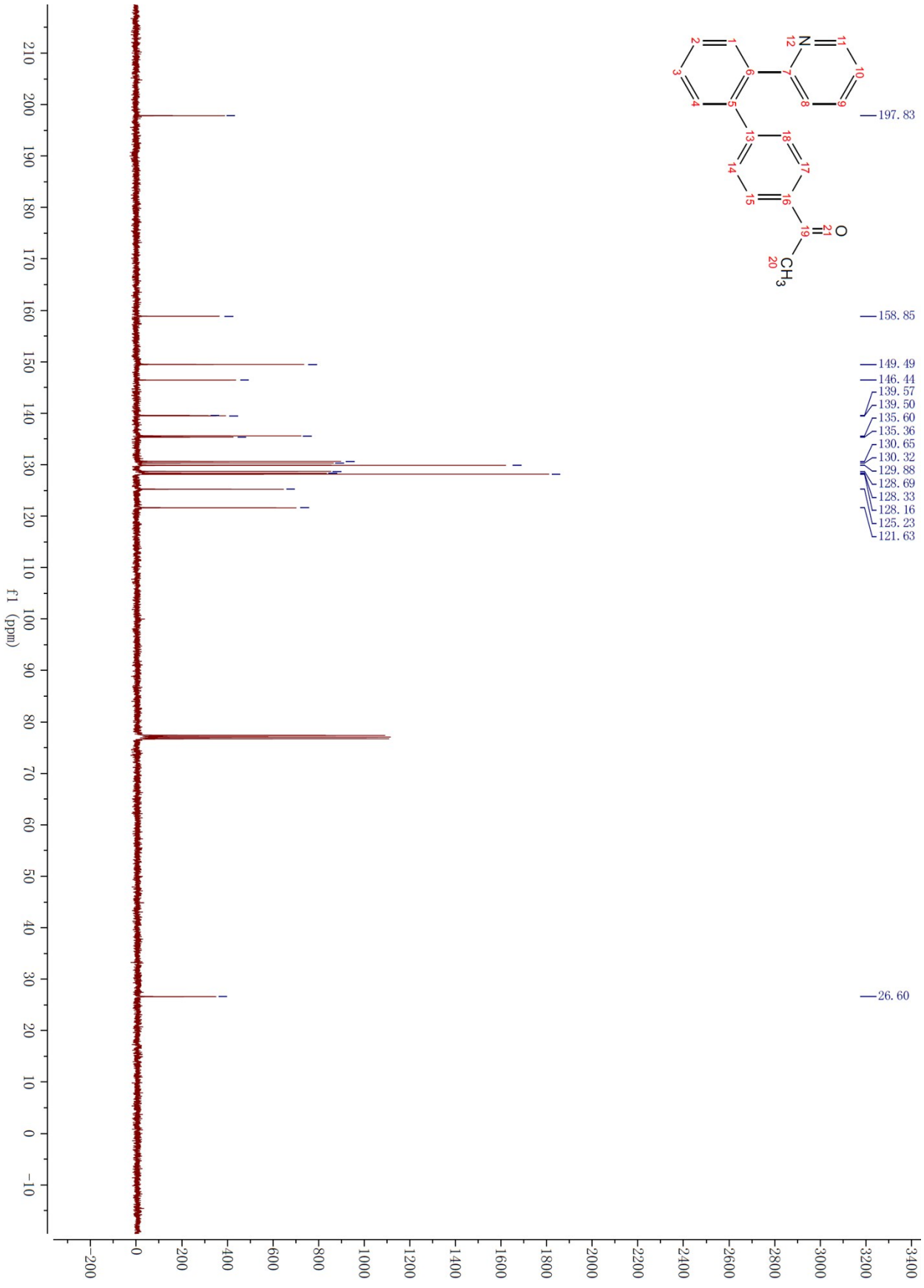
^{13}C NMR Spectrum of the Compound 4bm



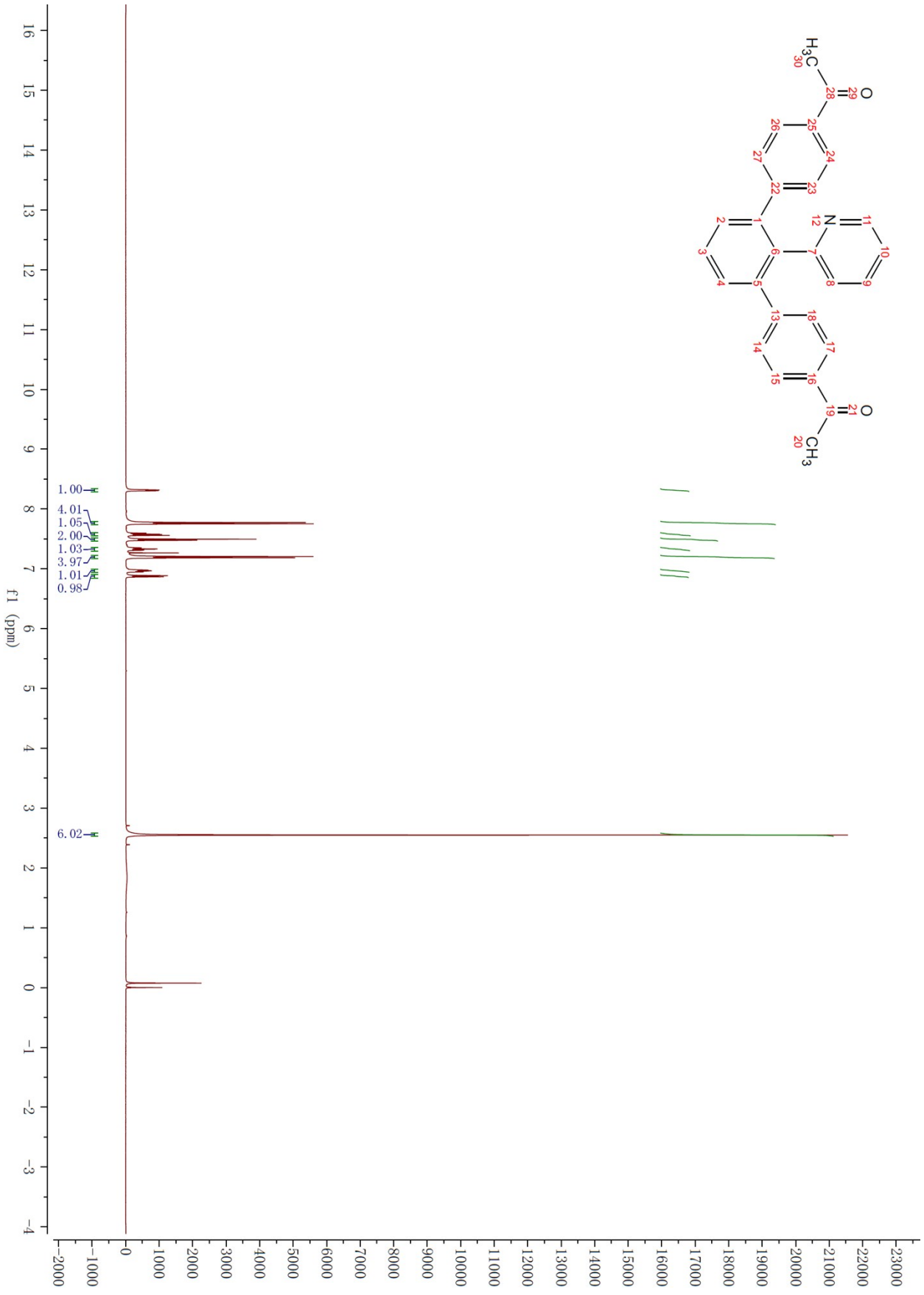
^{1}H NMR Spectrum of the Compound 3ao



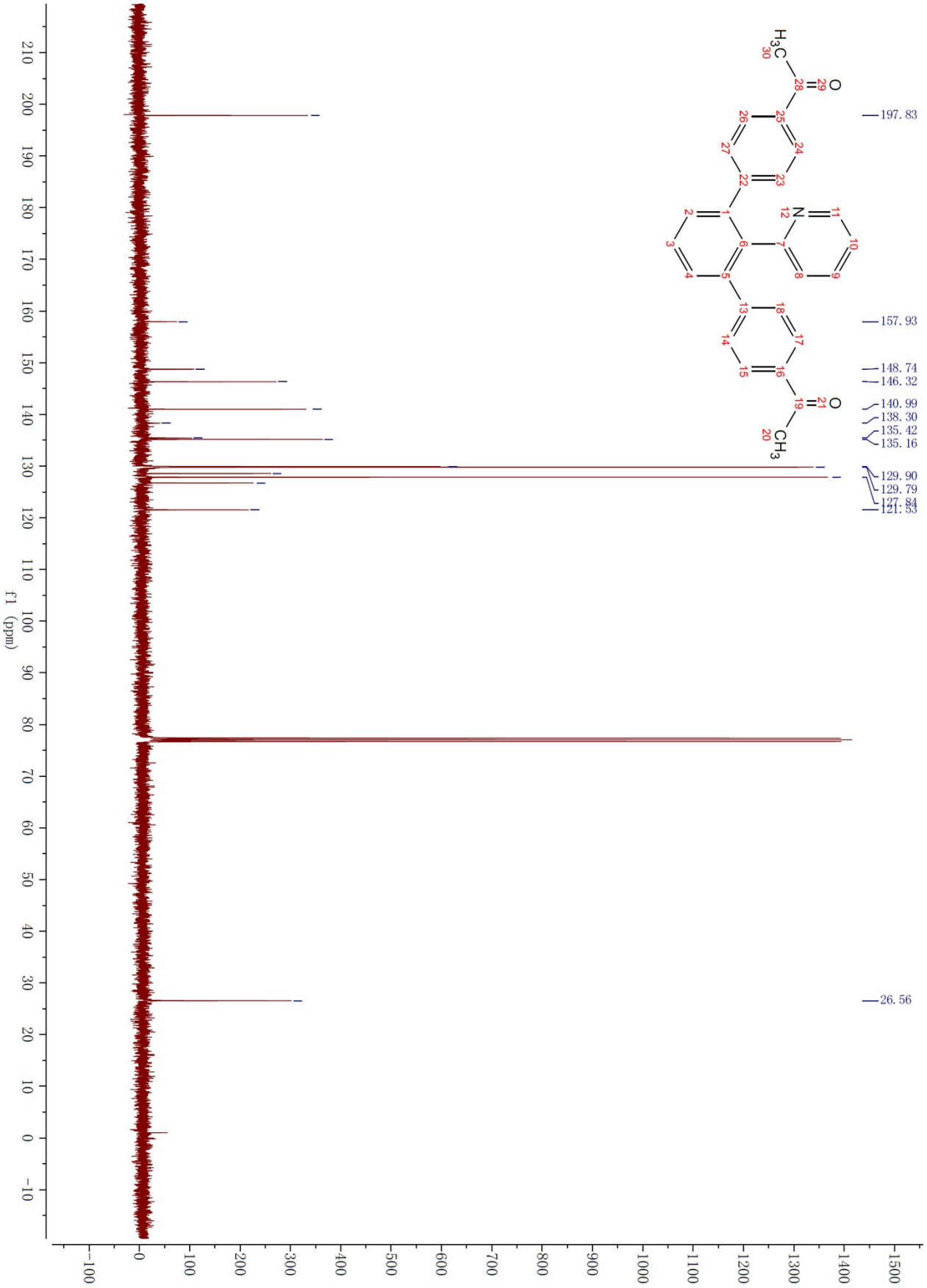
^{13}C NMR Spectrum of the Compound 3ao



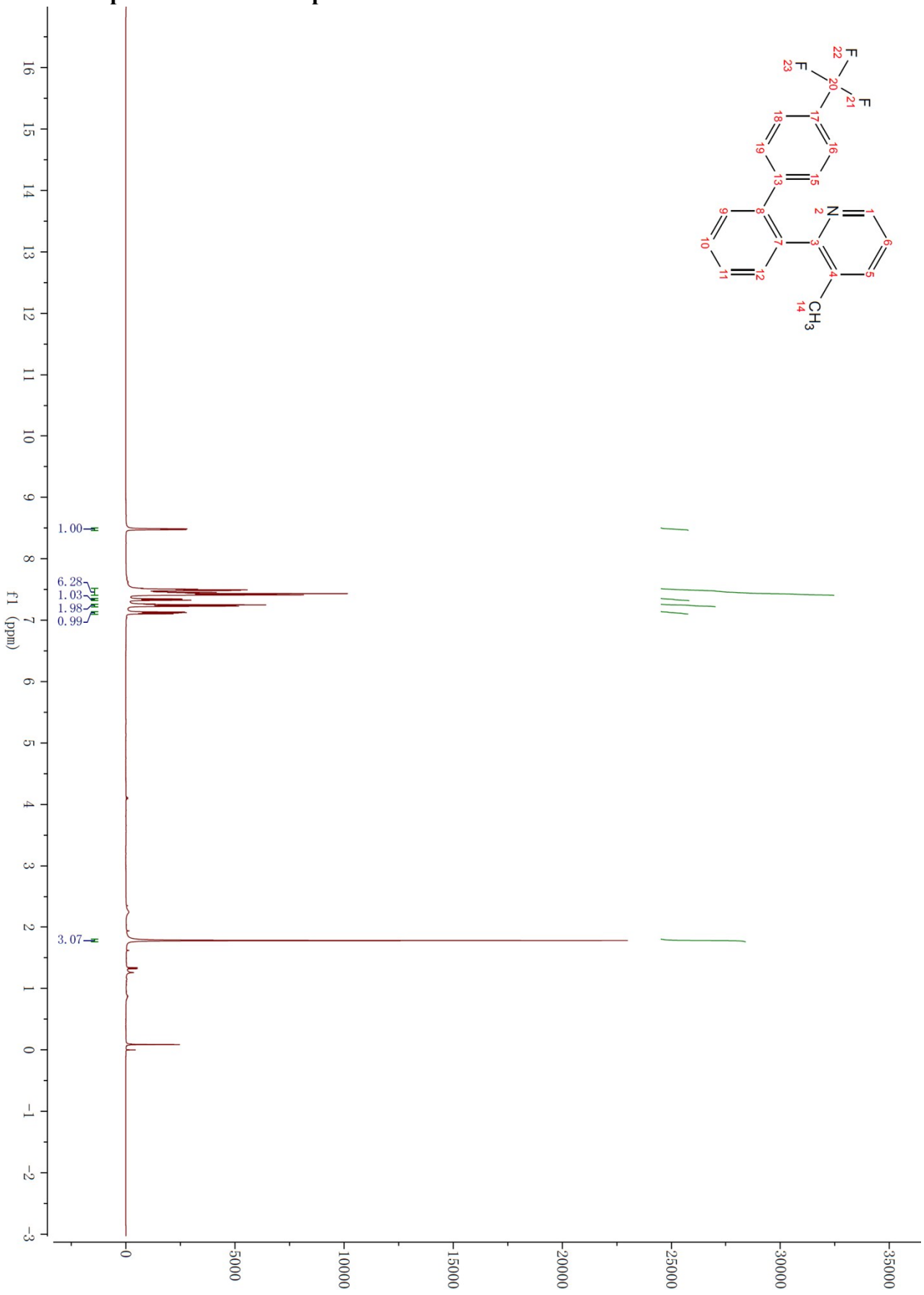
^{1}H NMR Spectrum of the Compound 4ao



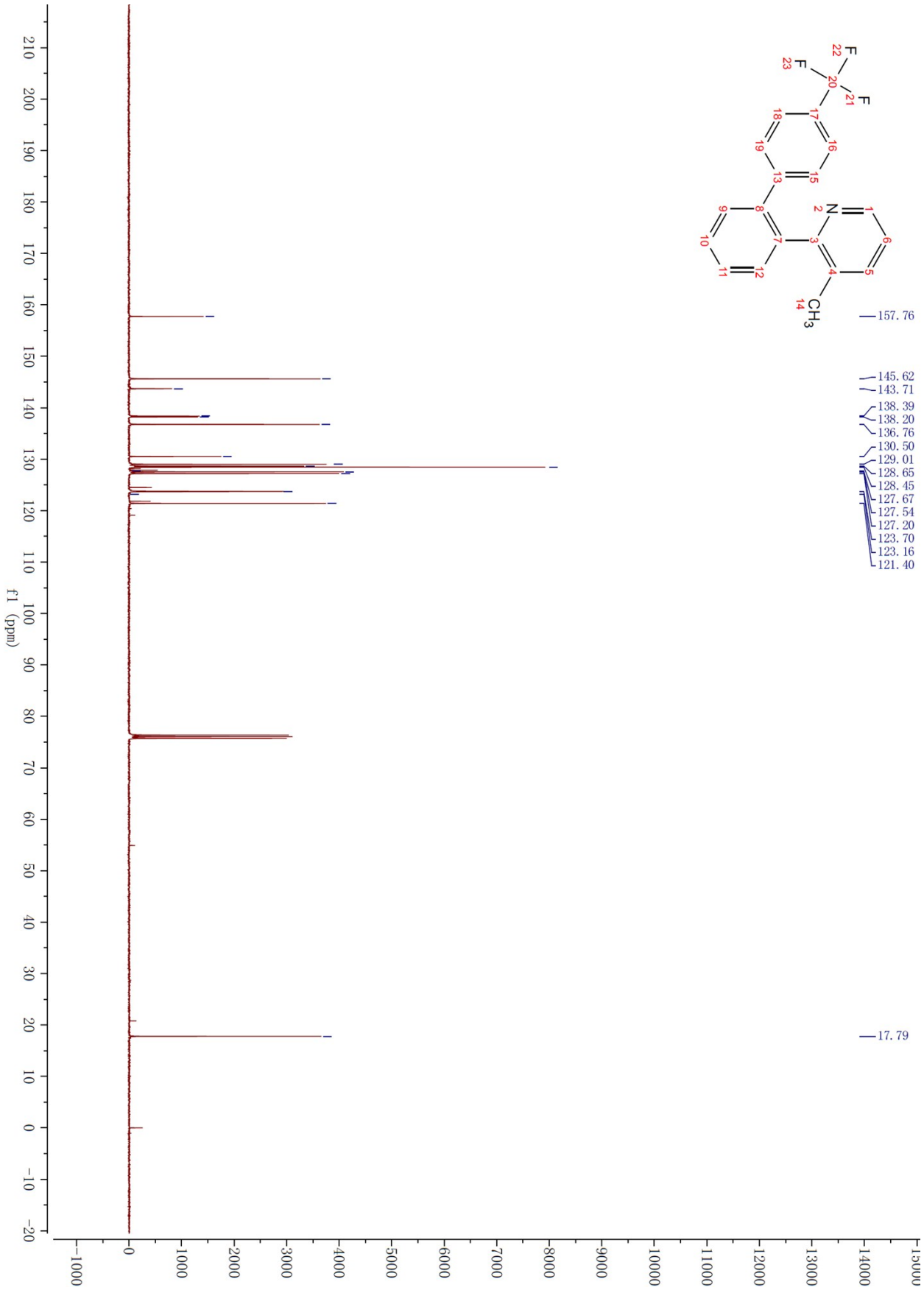
^{13}C NMR Spectrum of the Compound 4ao



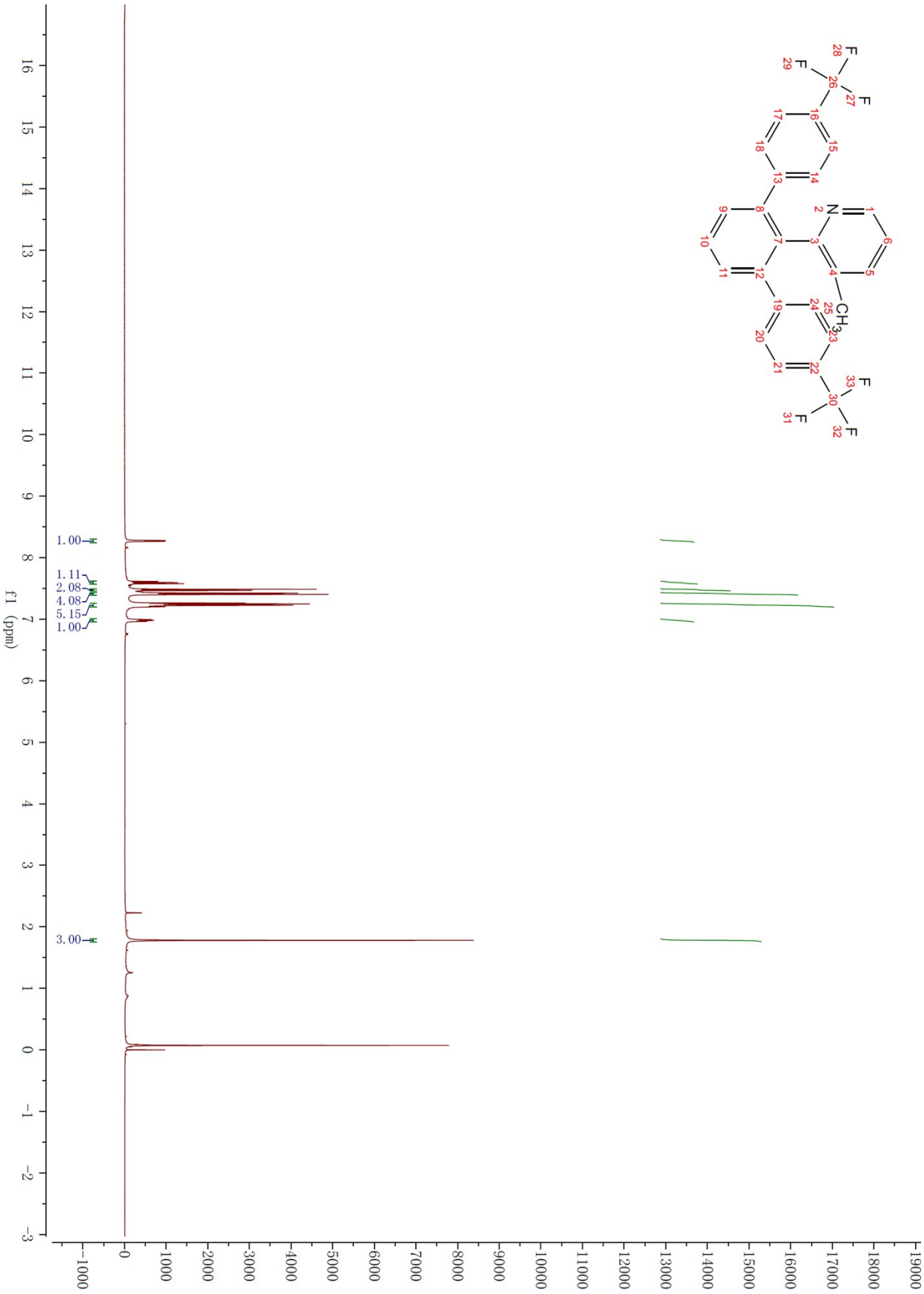
^{1}H NMR Spectrum of the Compound 3fm



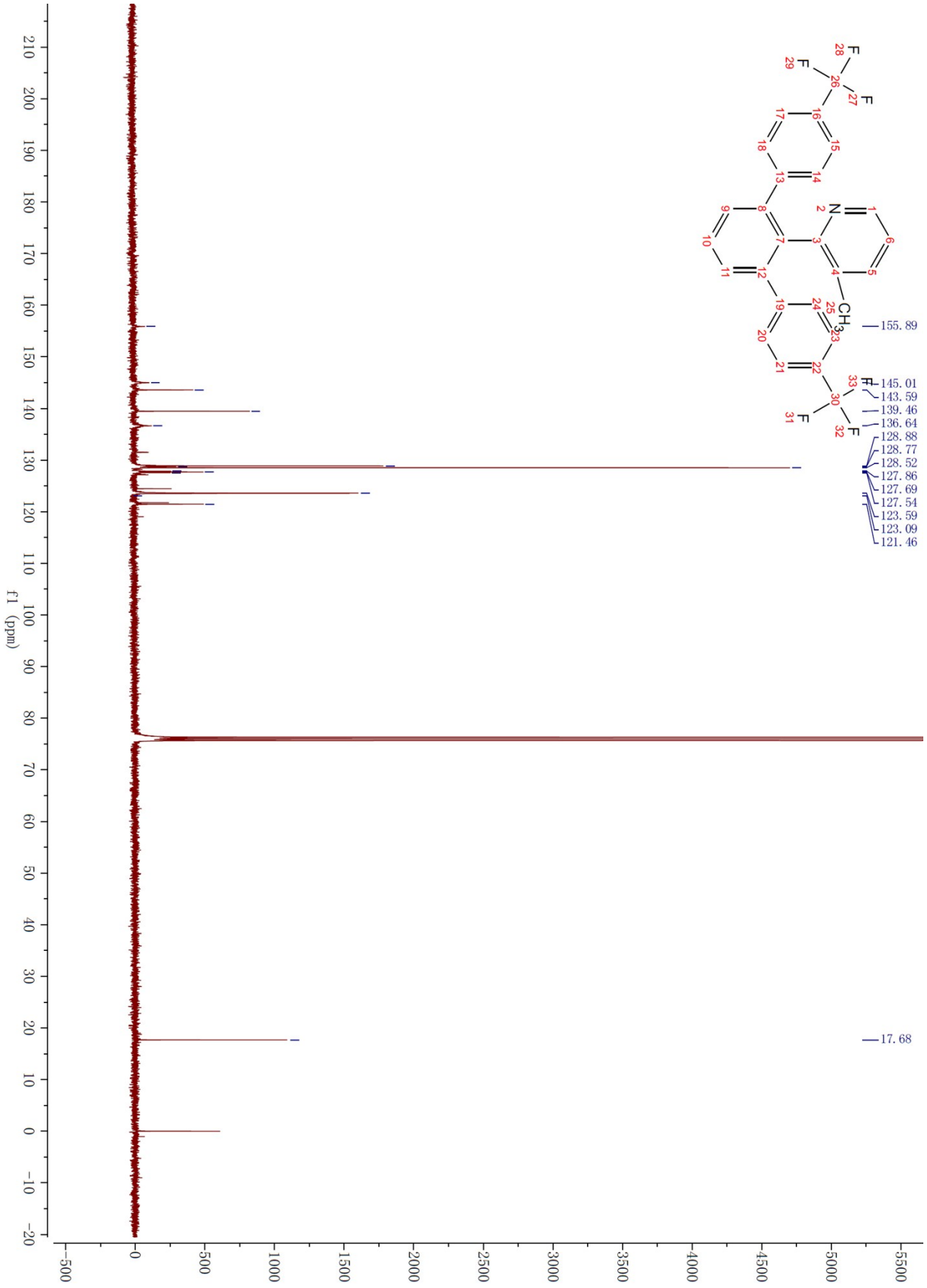
^{13}C NMR Spectrum of the Compound 3fm



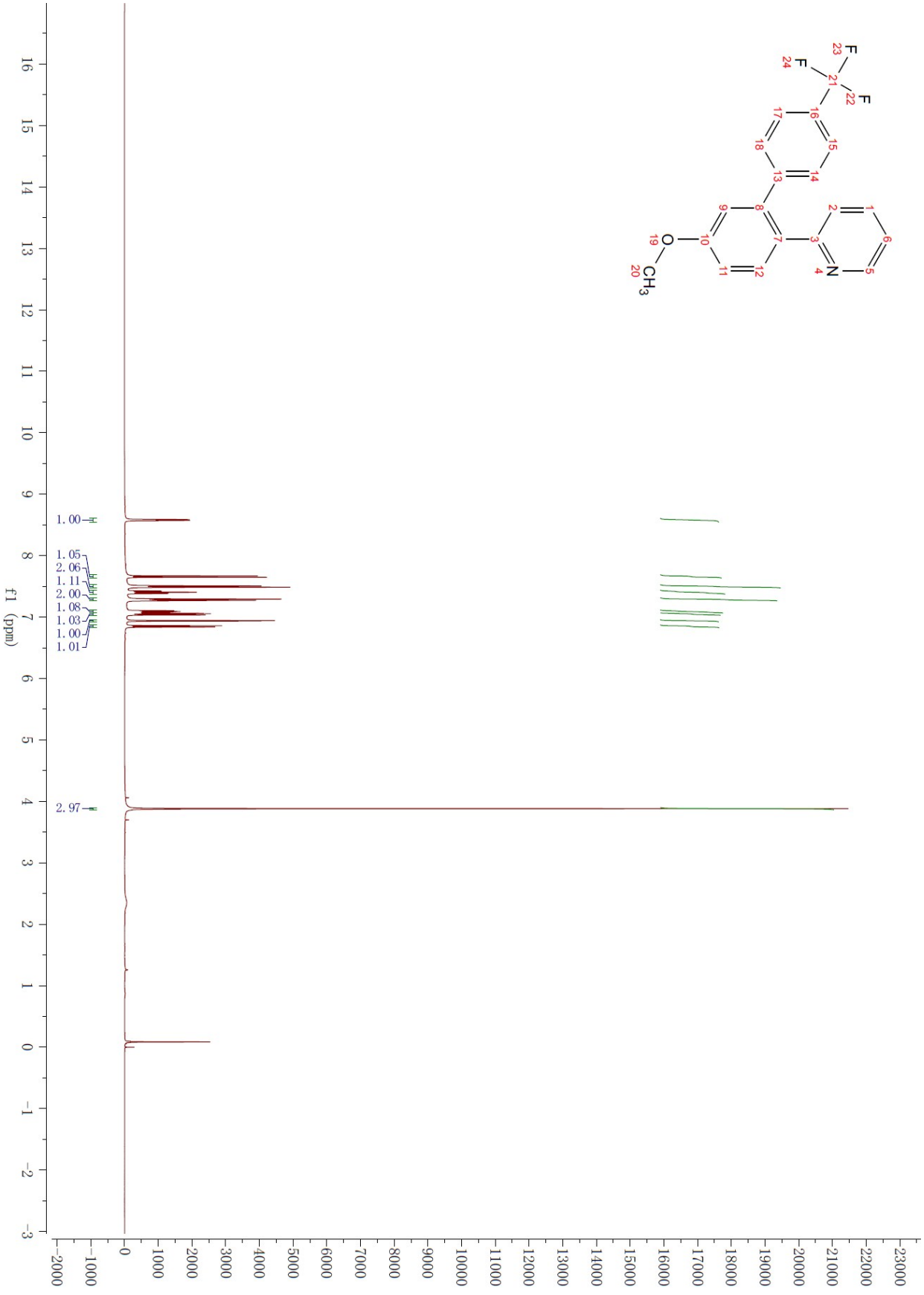
^{1}H NMR Spectrum of the Compound 4fm



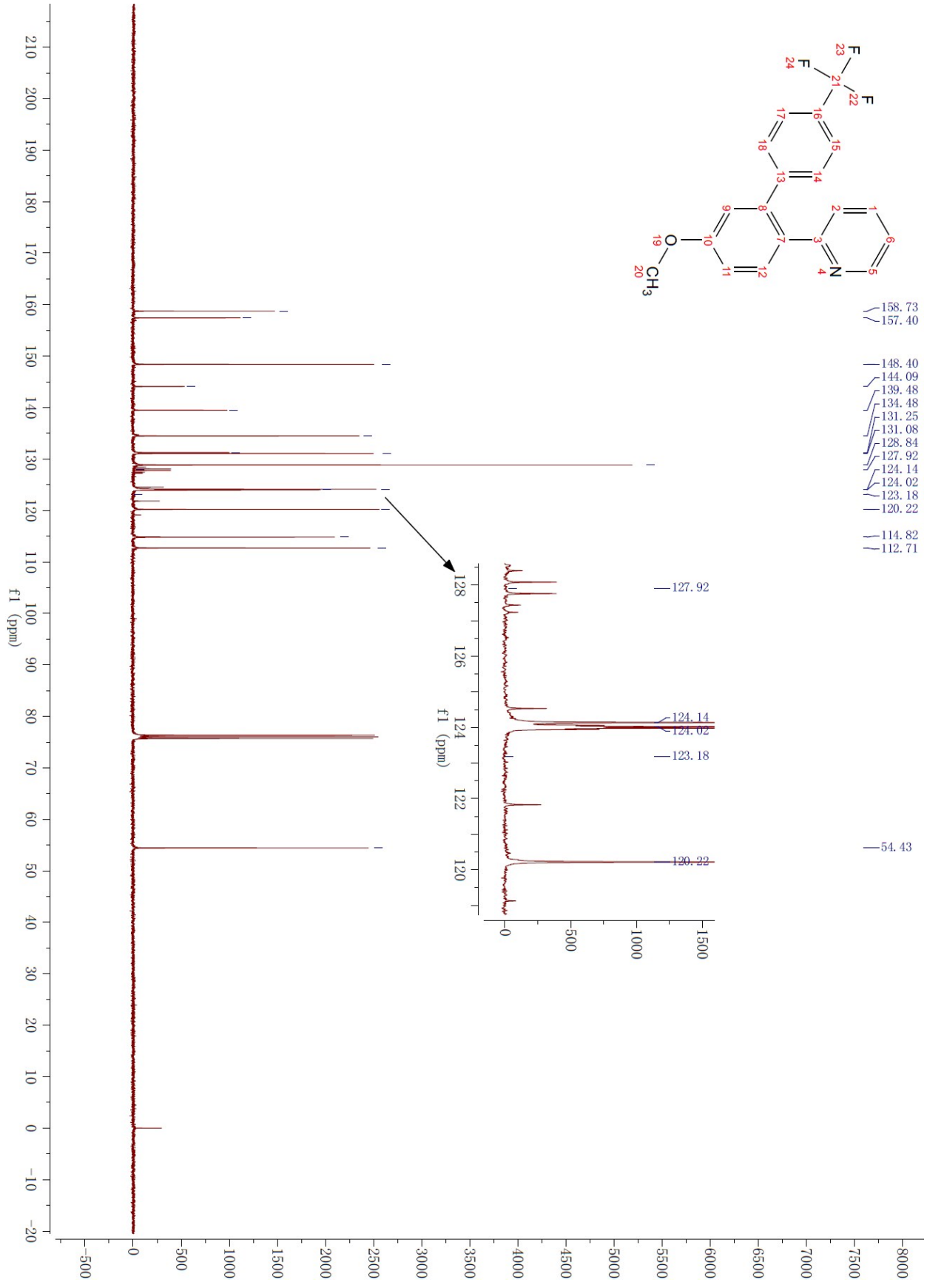
^{13}C NMR Spectrum of the Compound 4fm



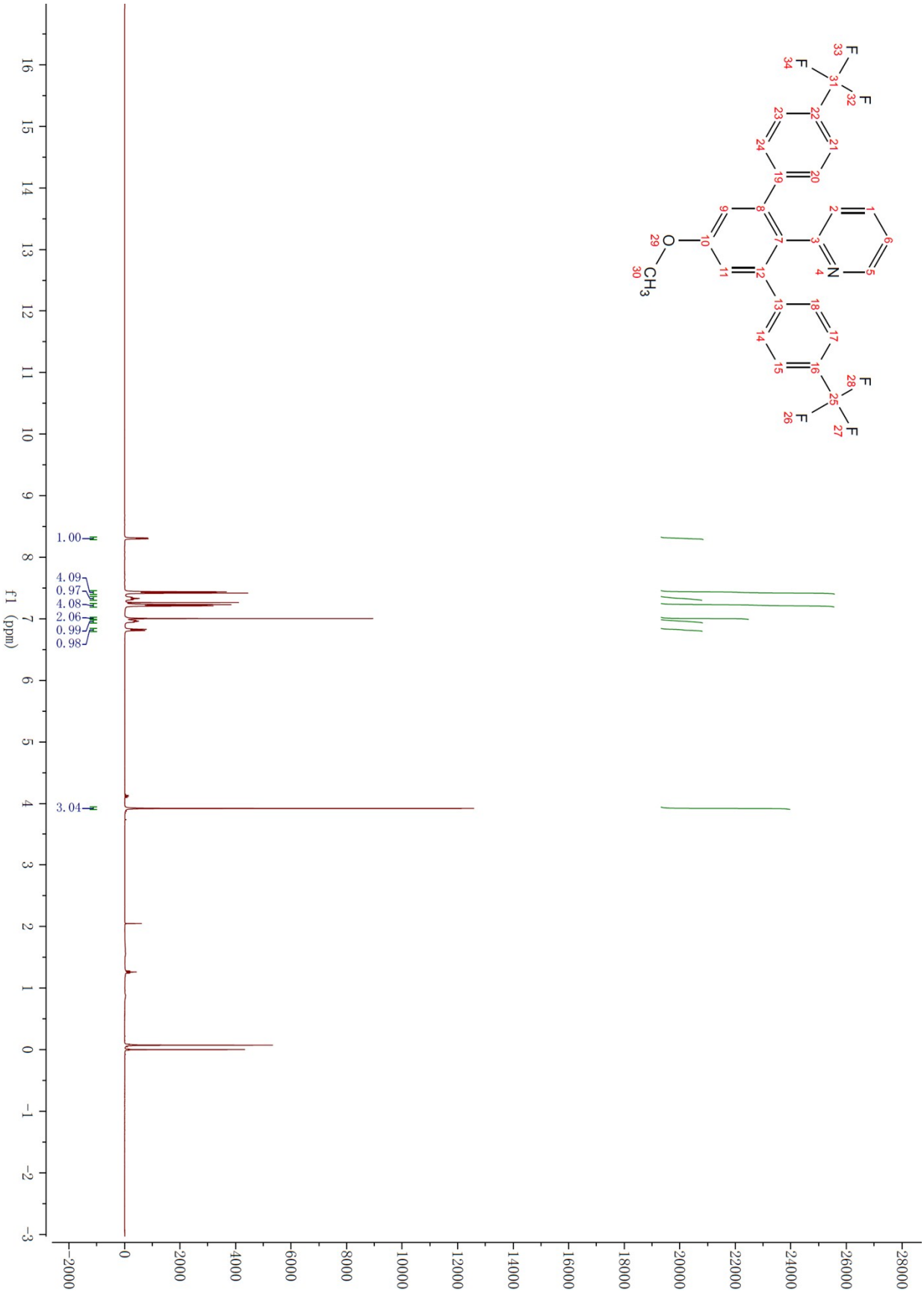
^{1}H NMR Spectrum of the Compound 3dm



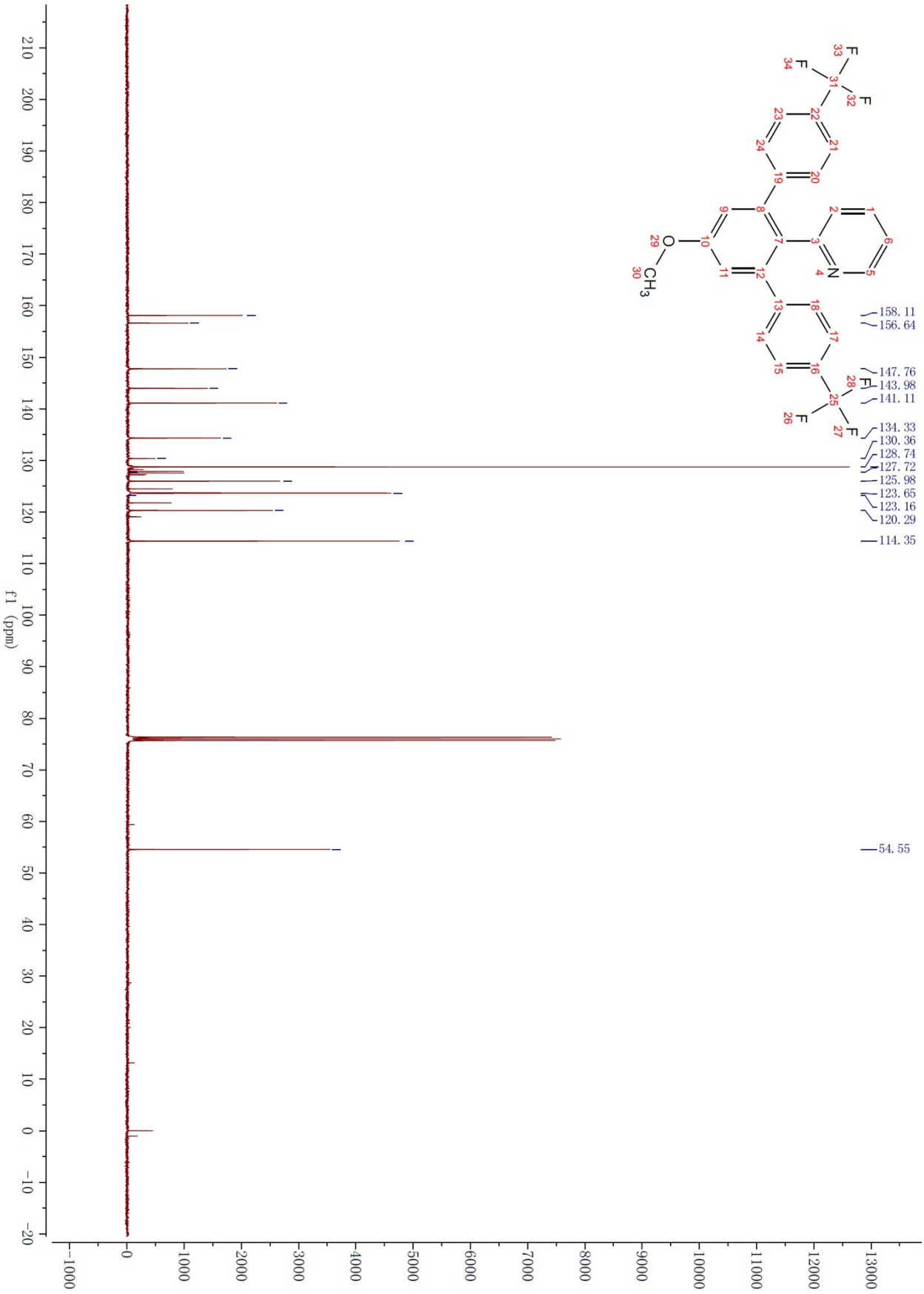
^{13}C NMR Spectrum of the Compound 3dm



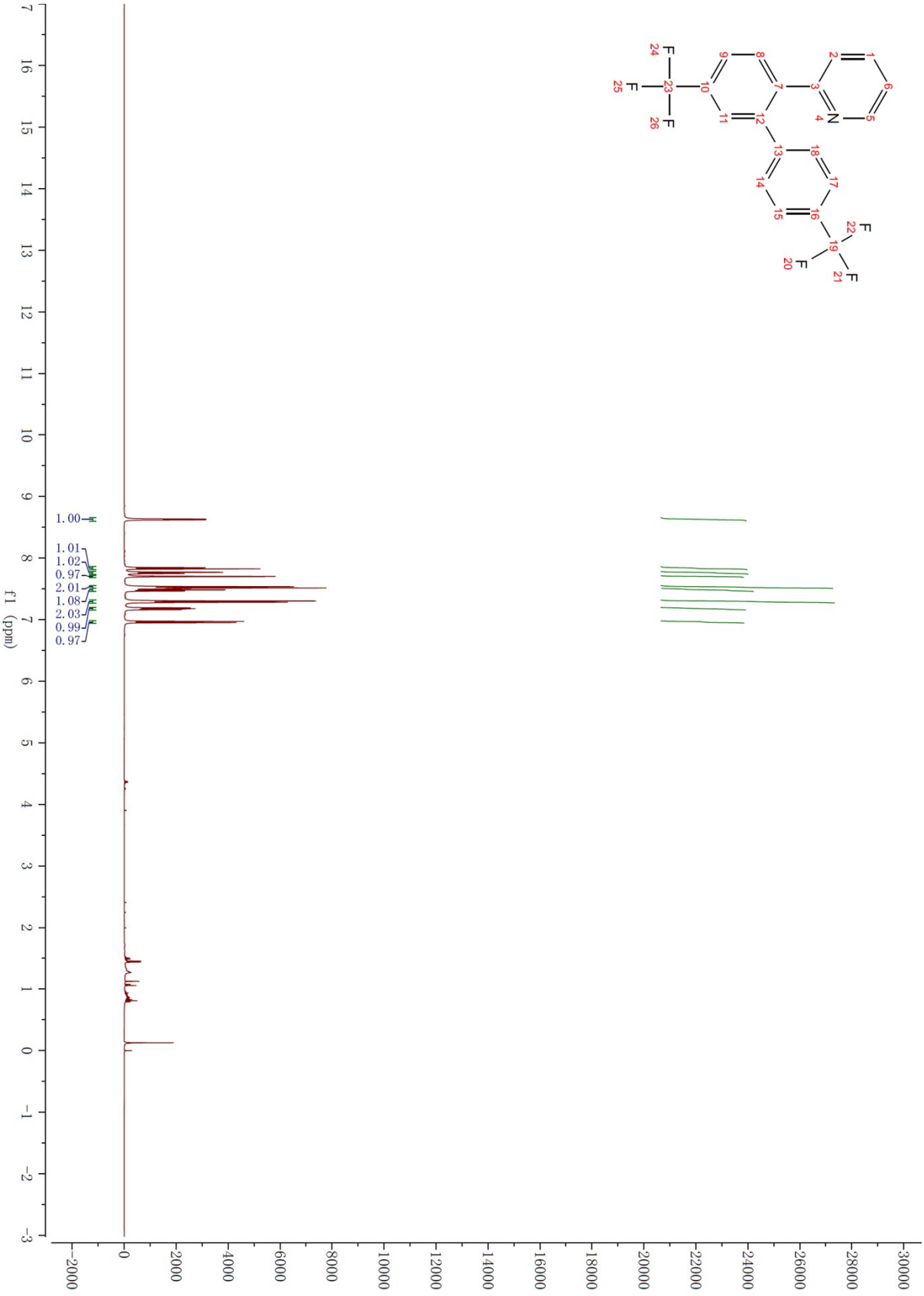
^{1}H NMR Spectrum of the Compound 4dm



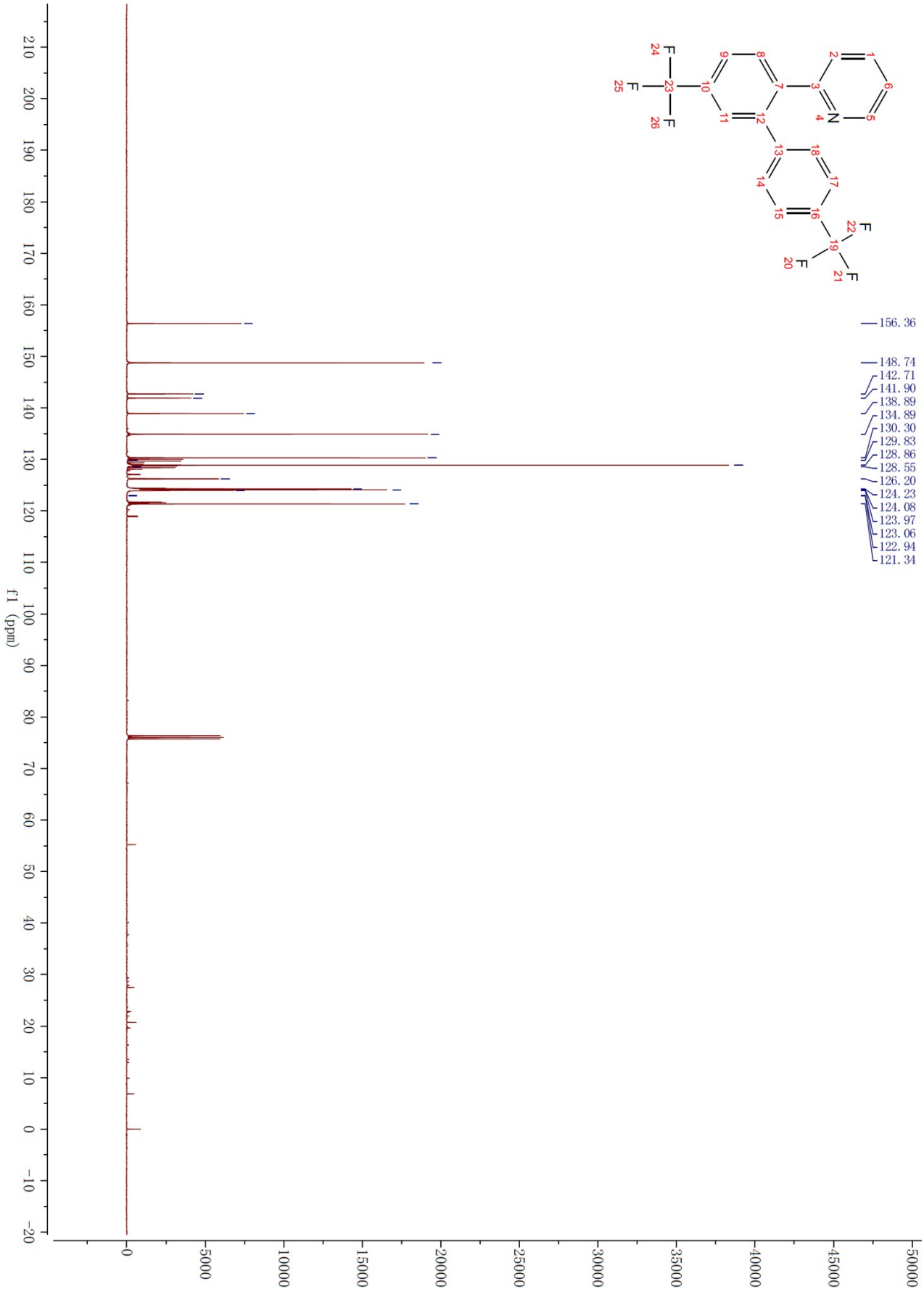
^{13}C NMR Spectrum of the Compound 4dm



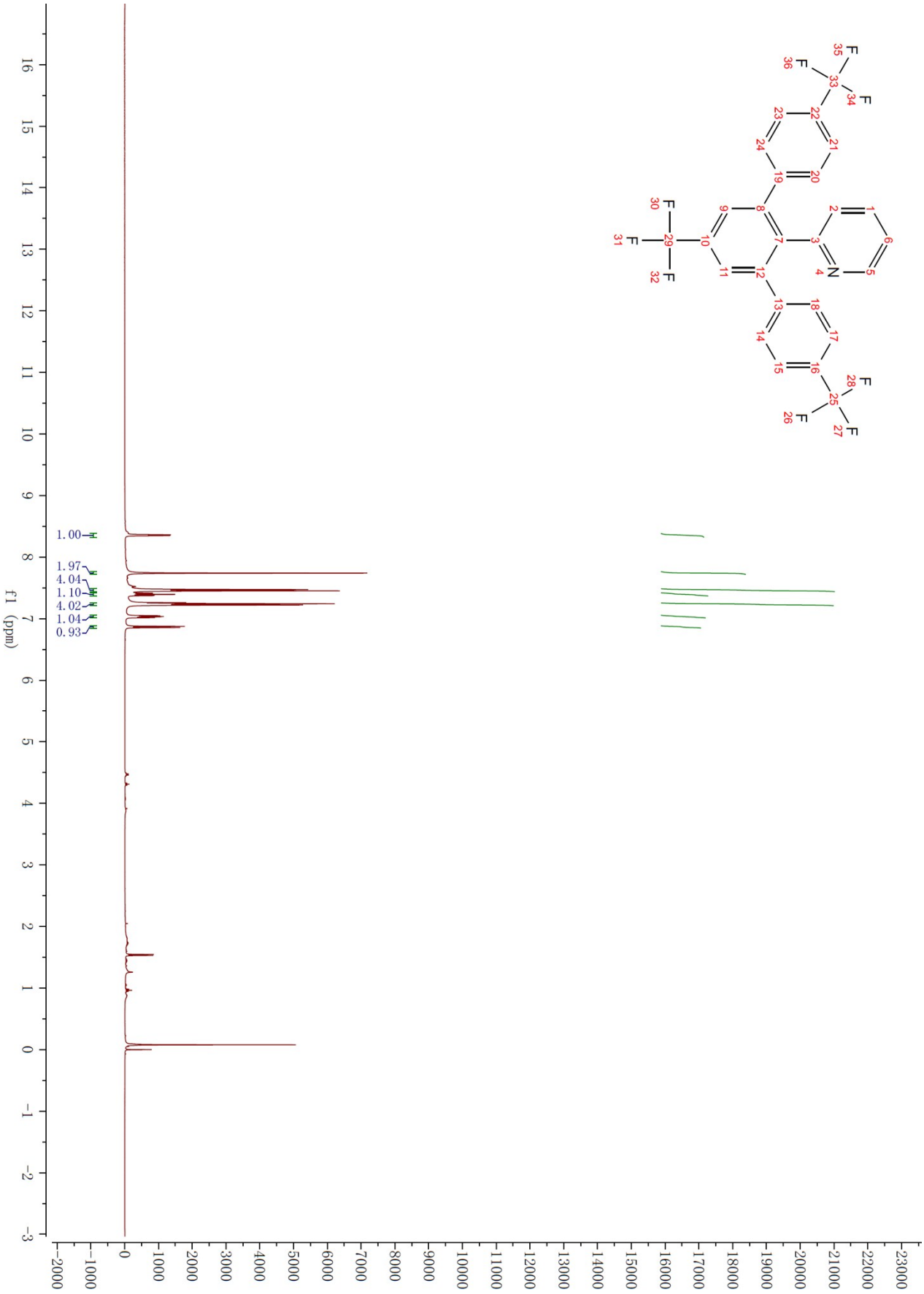
^{1}H NMR Spectrum of the Compound 3em



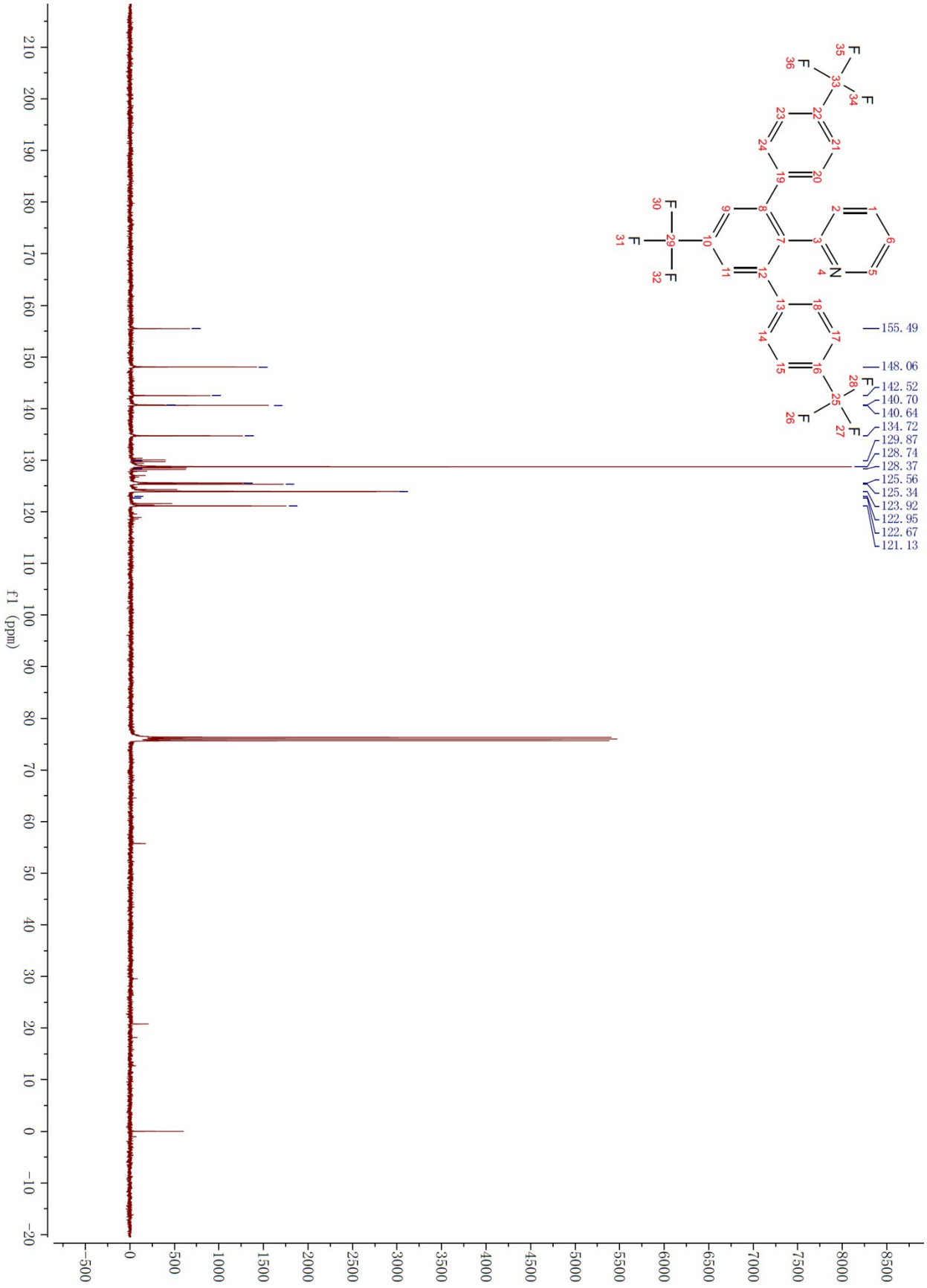
^{13}C NMR Spectrum of the Compound 3em



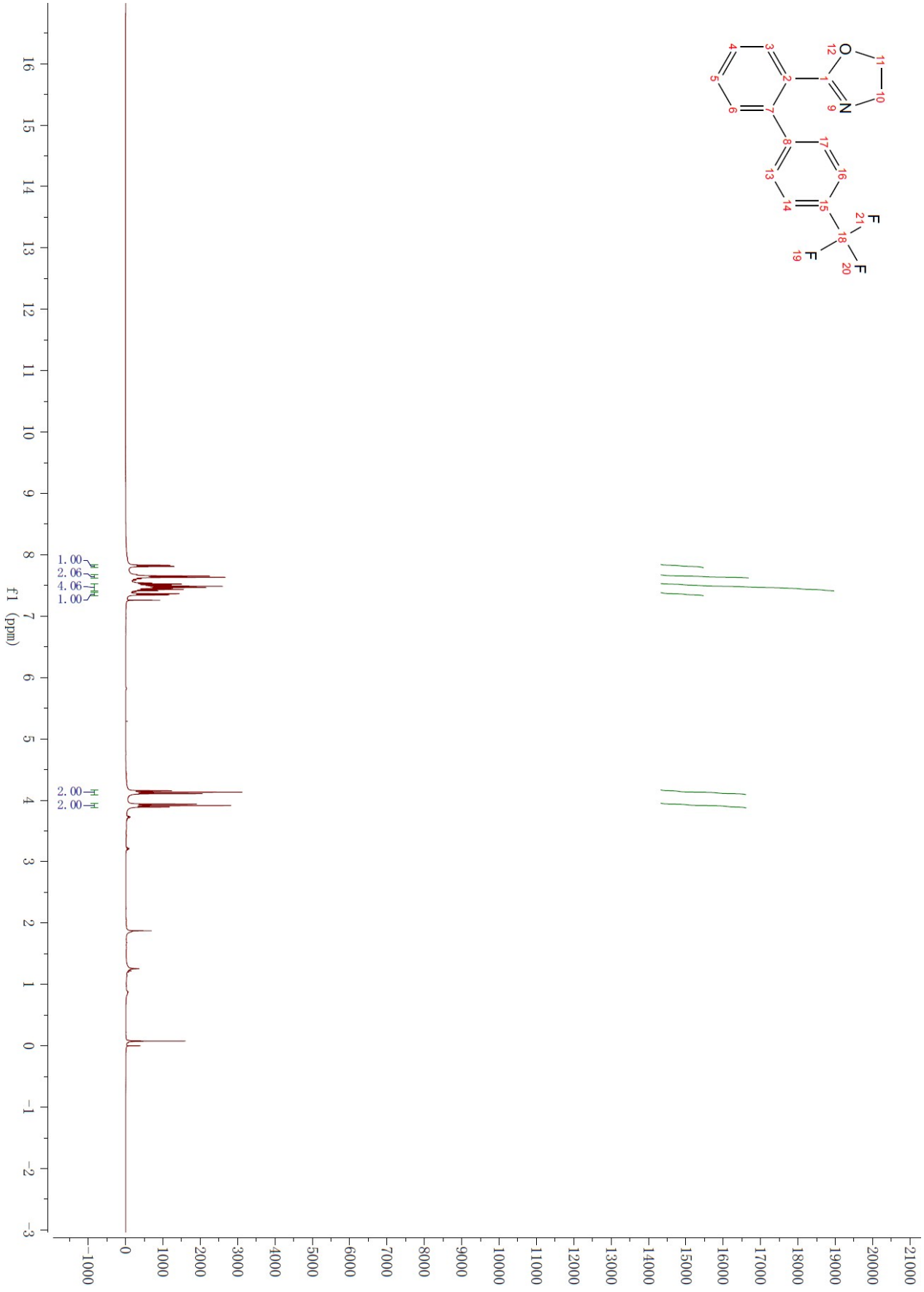
^{1}H NMR Spectrum of the Compound 4em



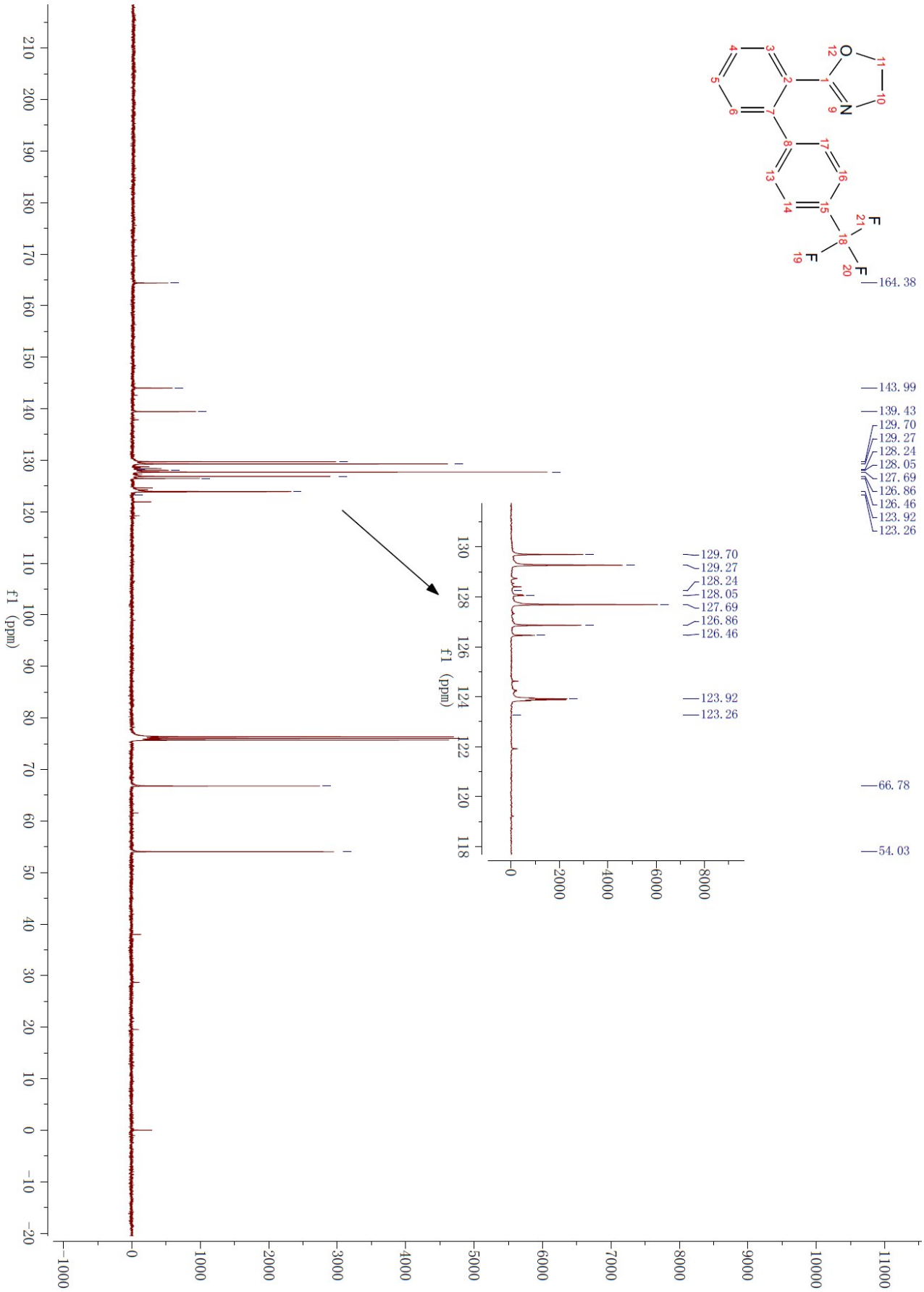
^{13}C NMR Spectrum of the Compound 4em



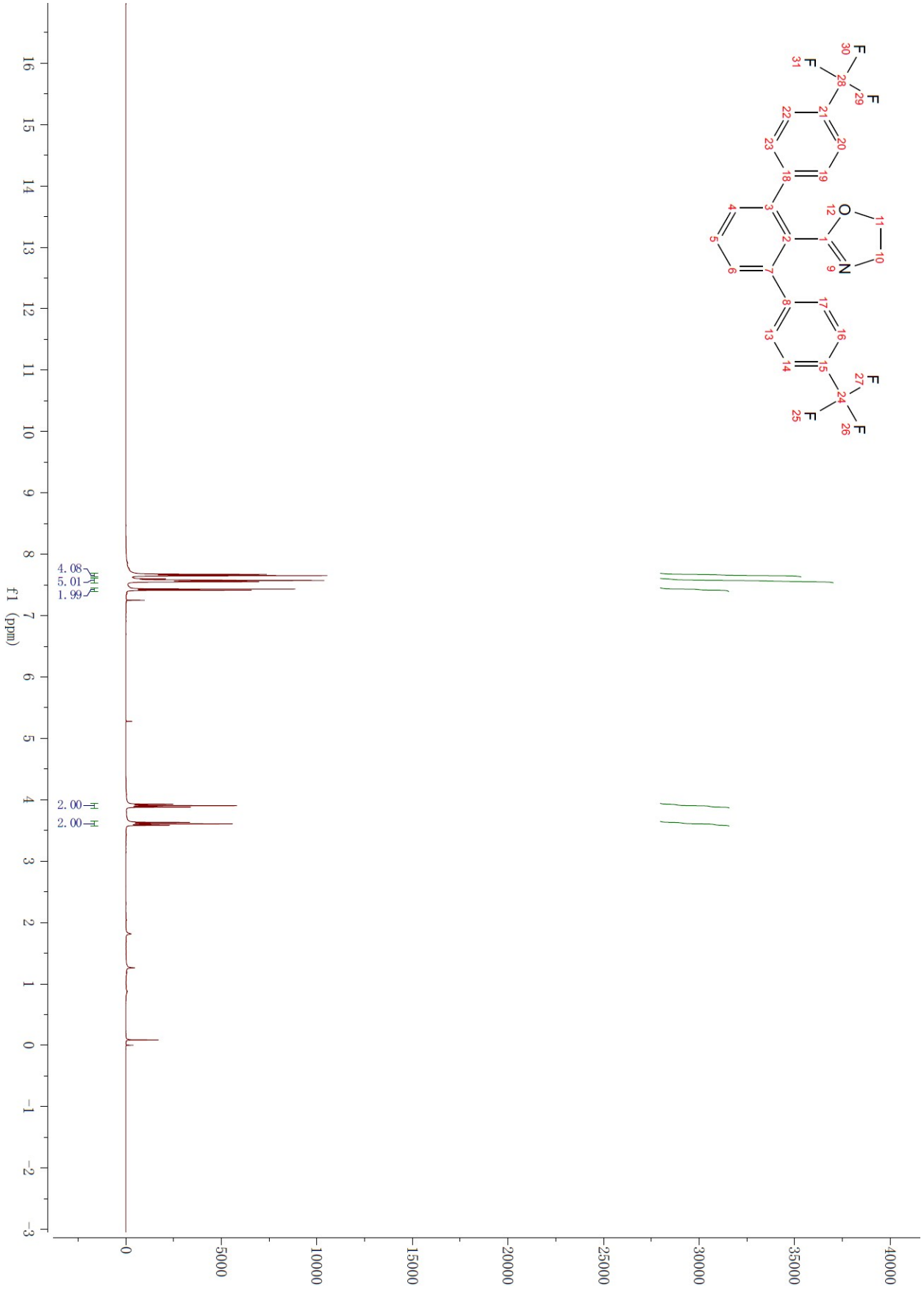
^{1}H NMR Spectrum of the Compound 3cm



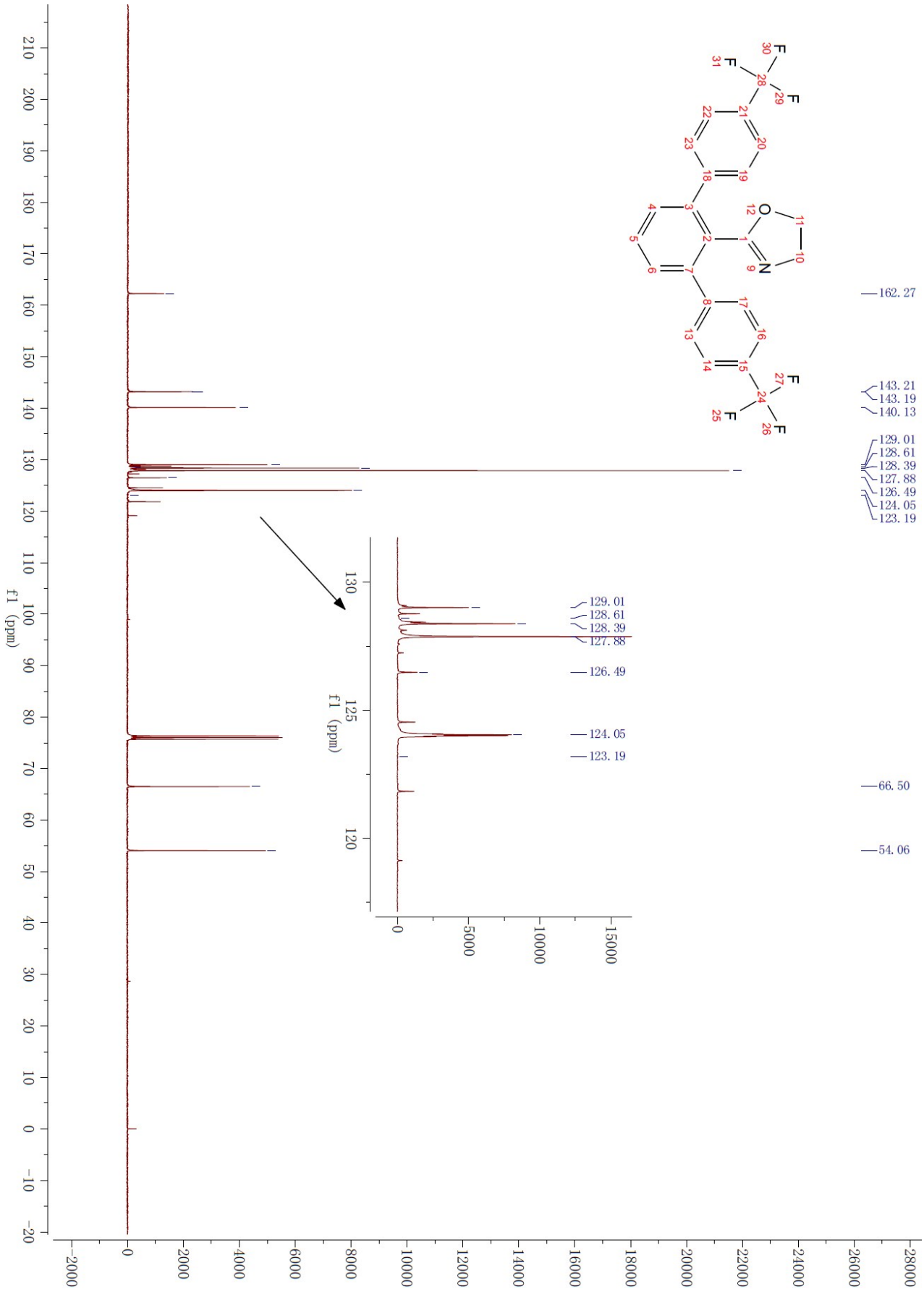
^{13}C NMR Spectrum of the Compound 3cm



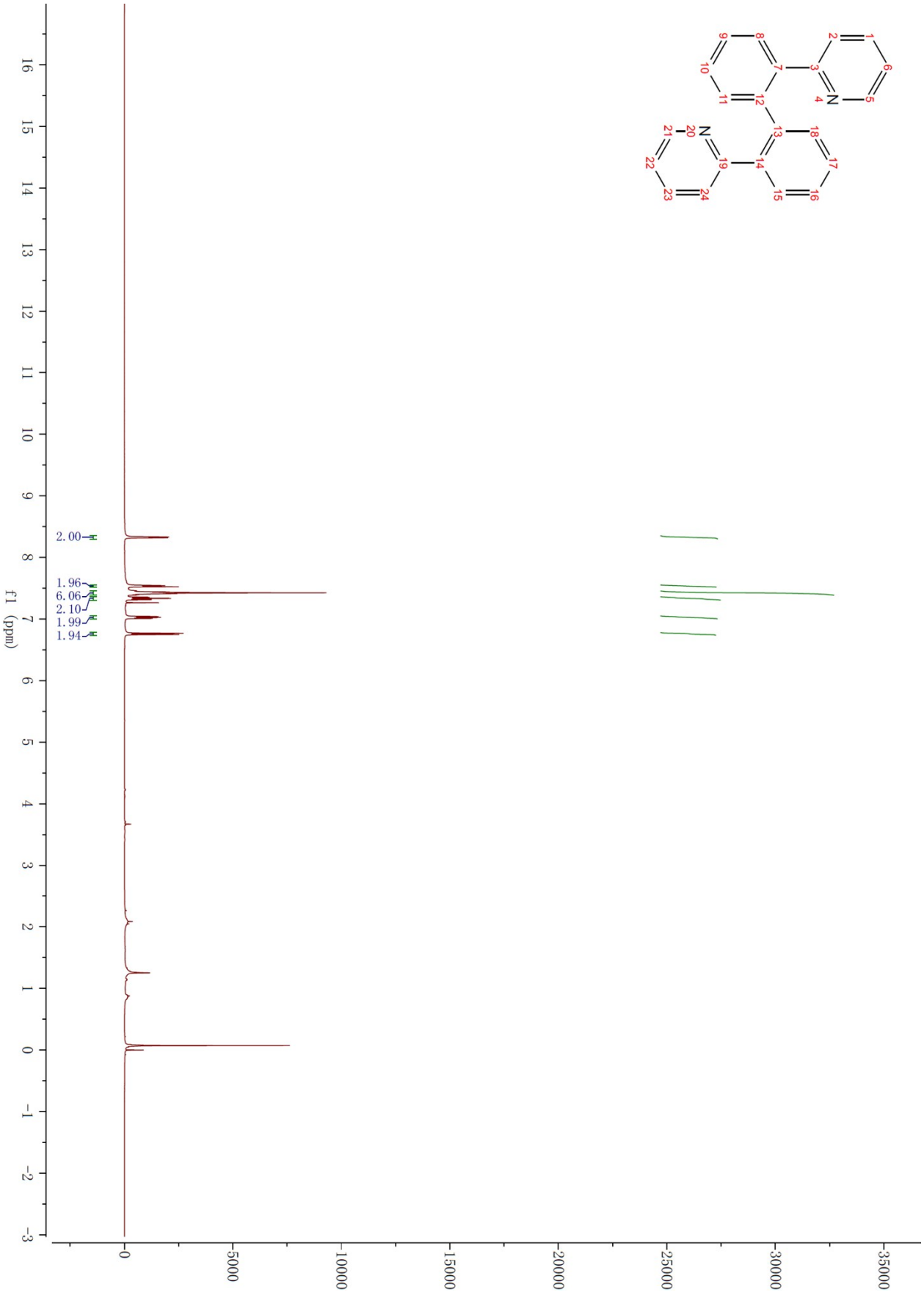
^{1}H NMR Spectrum of the Compound 4cm



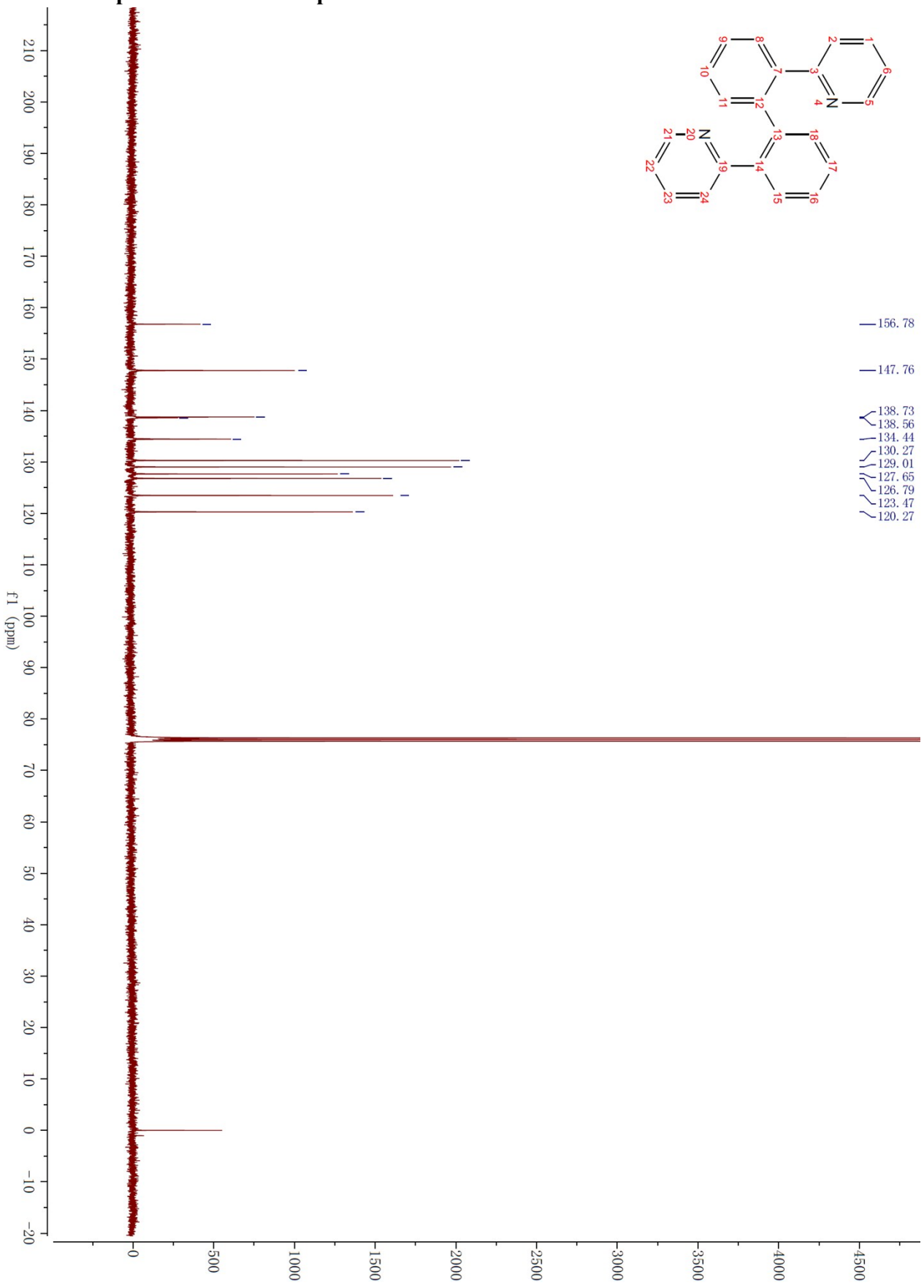
^{13}C NMR Spectrum of the Compound 4cm



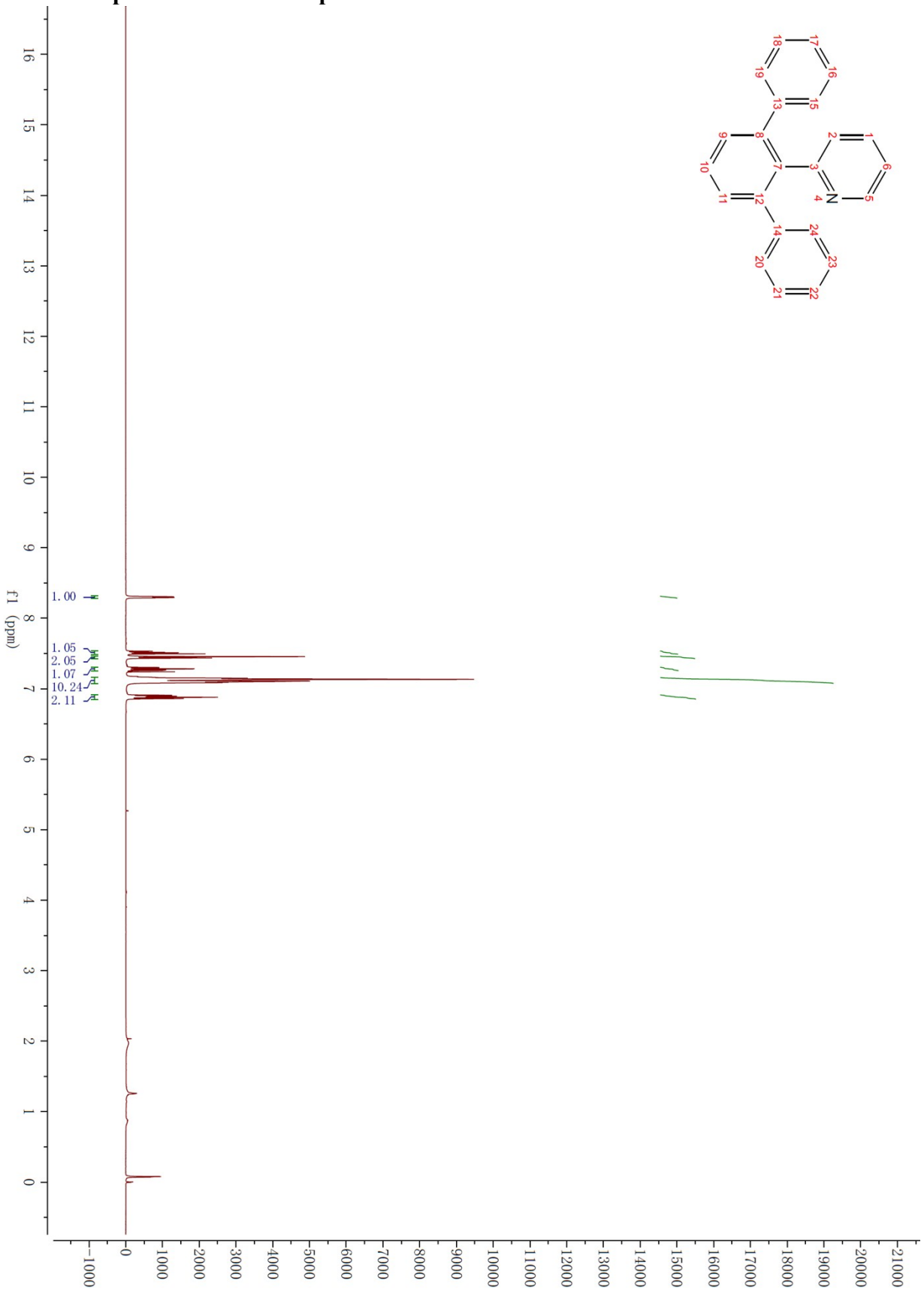
^{1}H NMR Spectrum of the Compound 8



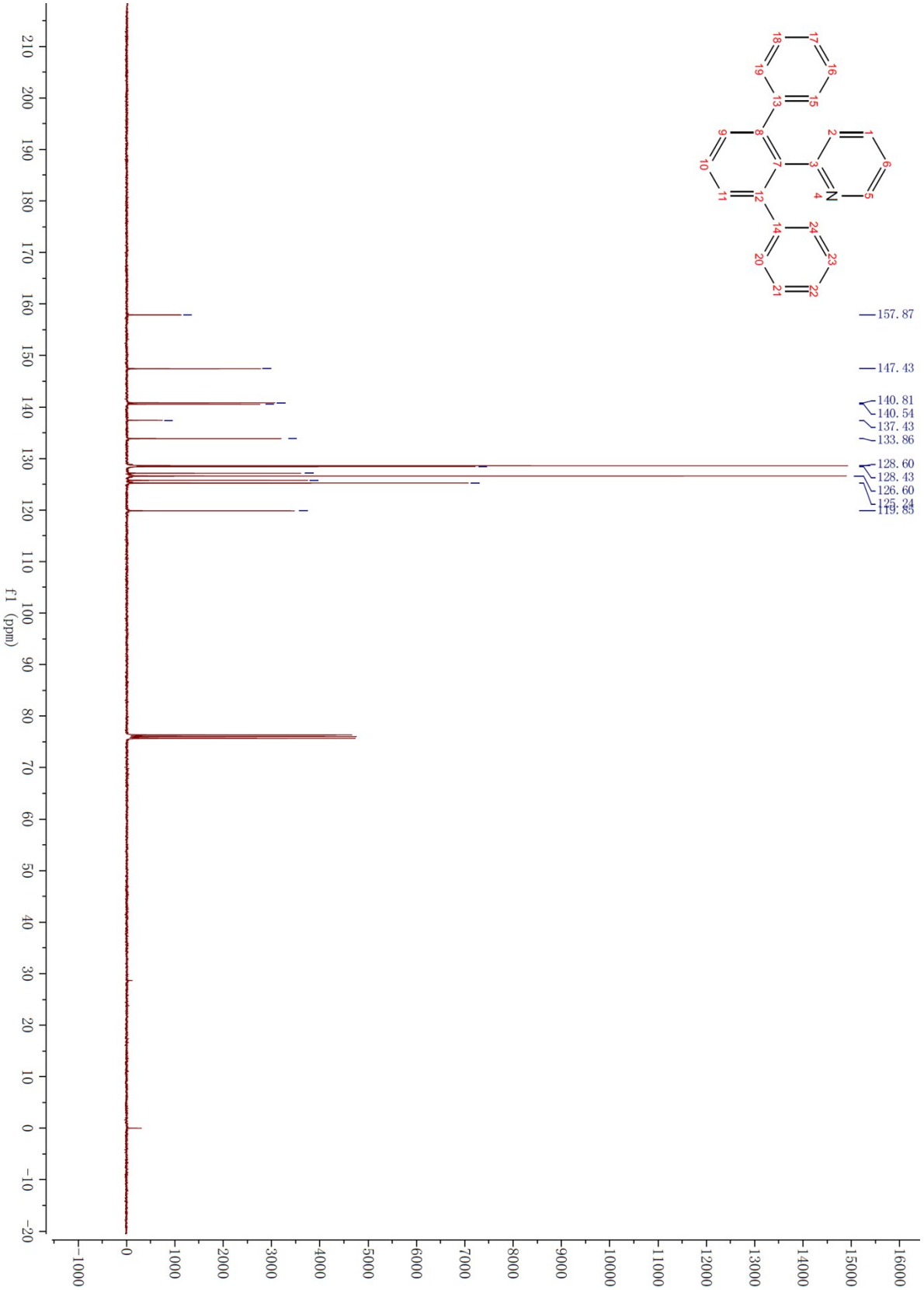
^{13}C NMR Spectrum of the Compound 8



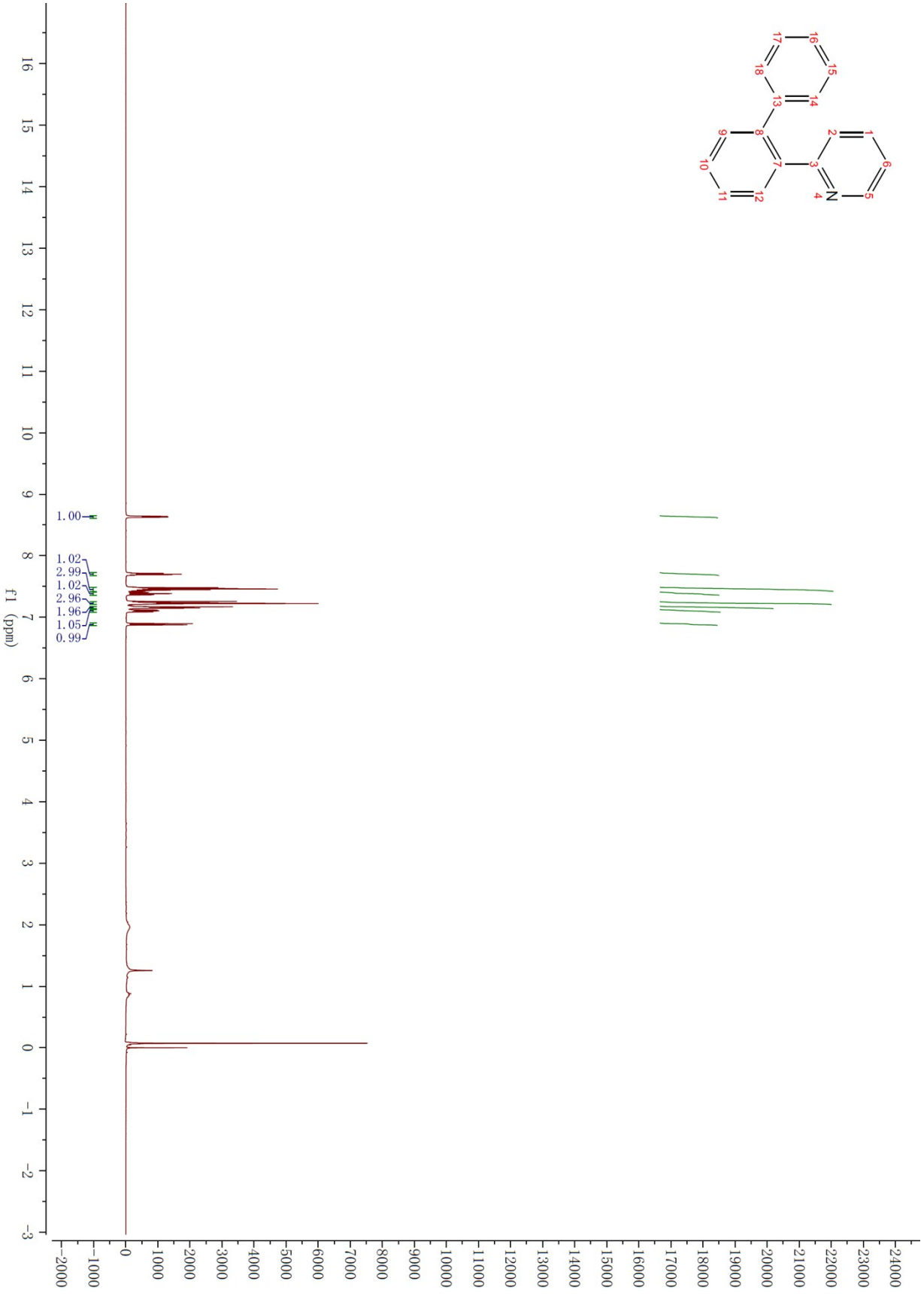
^{1}H NMR Spectrum of the Compound 4ab



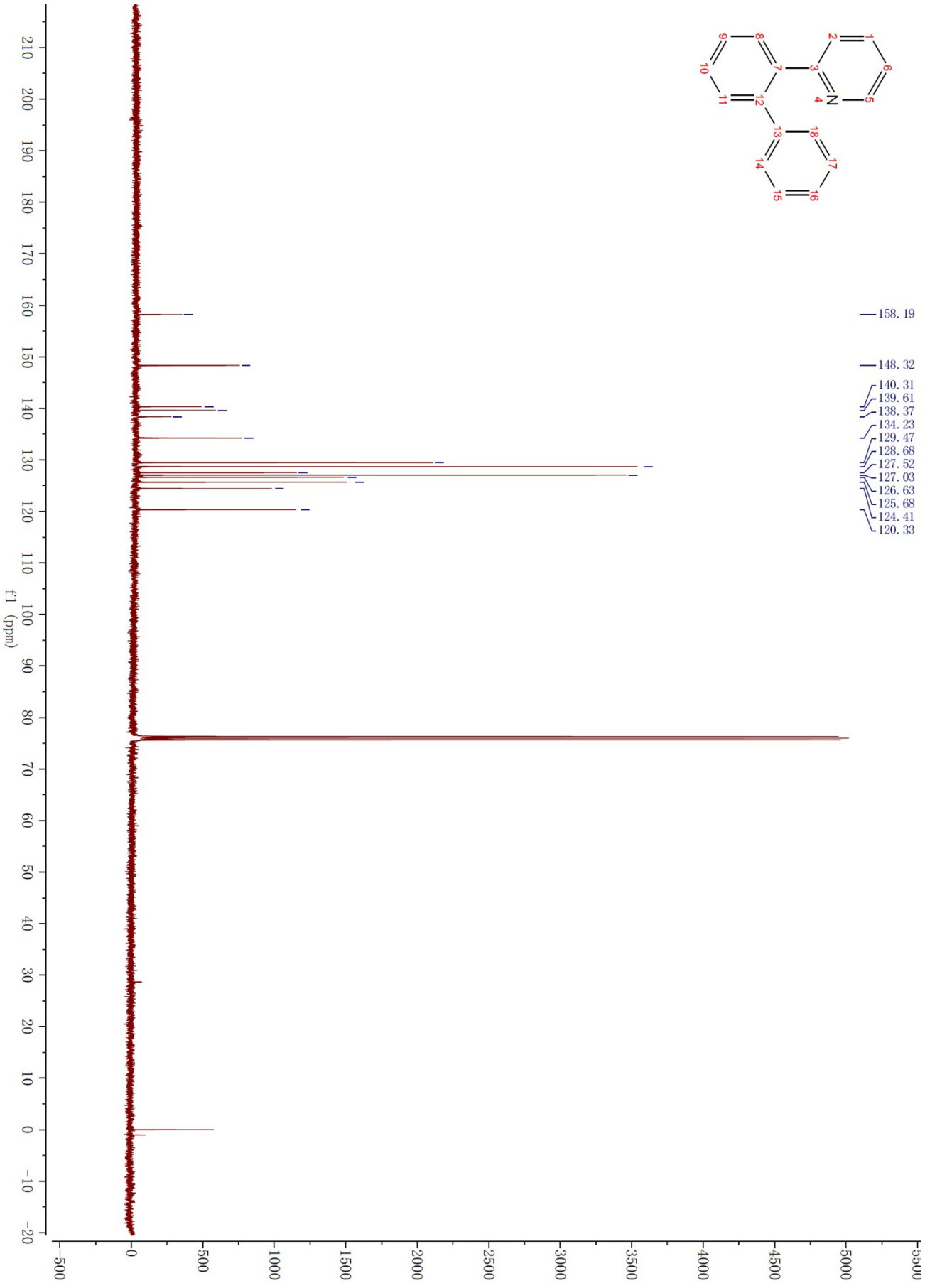
^{13}C NMR Spectrum of the Compound 4ab



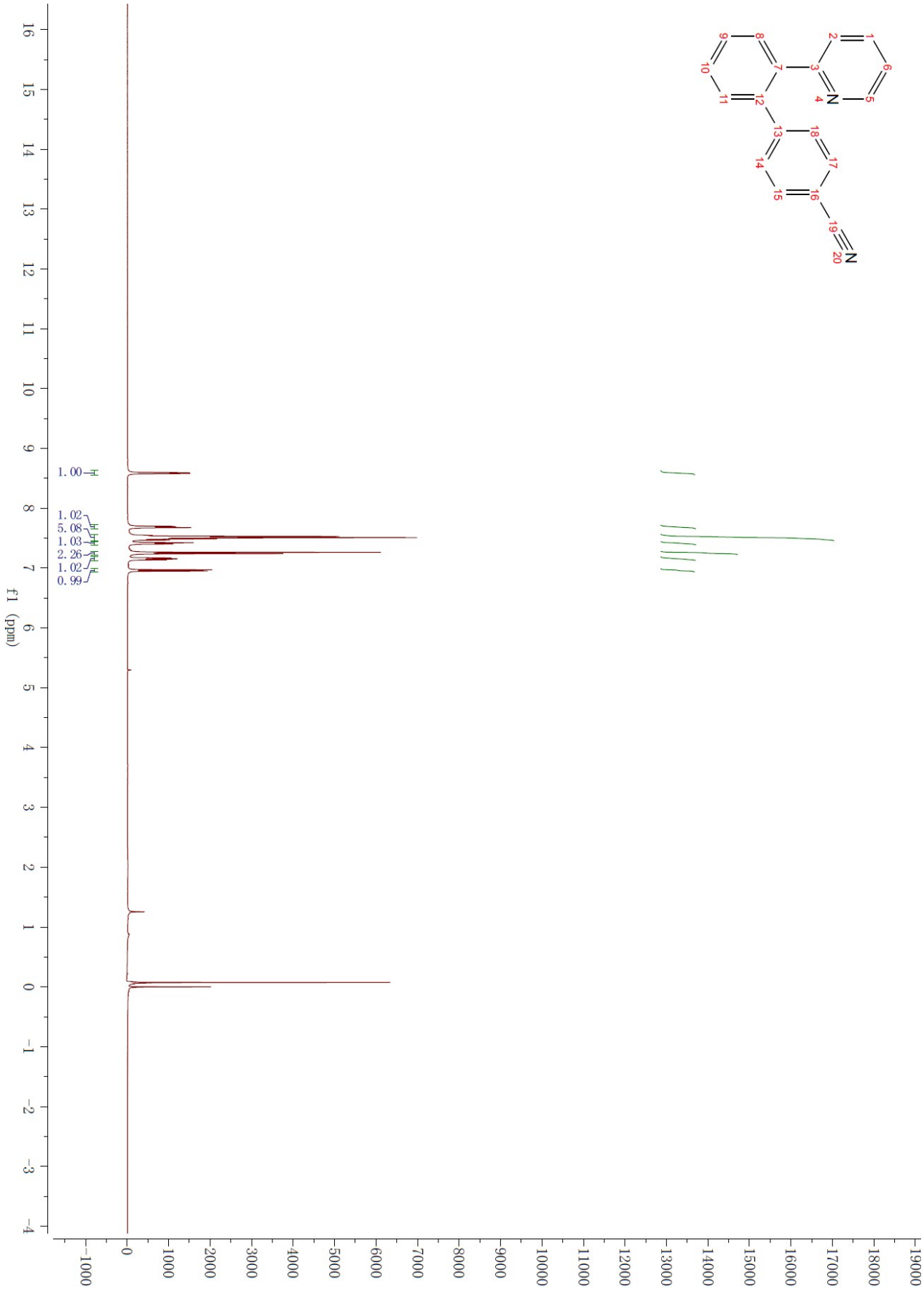
^{1}H NMR Spectrum of the Compound 3ab



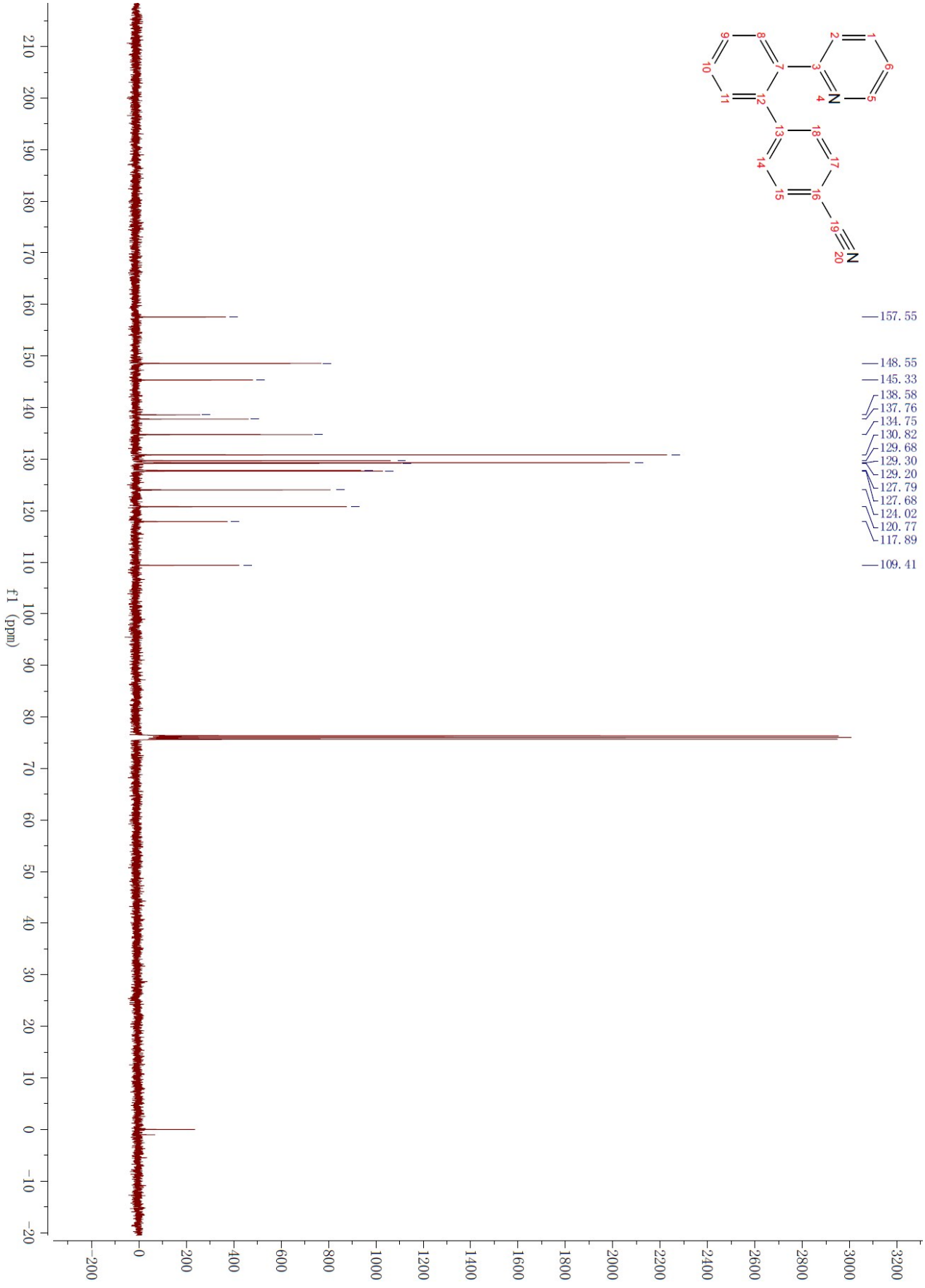
^{13}C NMR Spectrum of the Compound 3ab



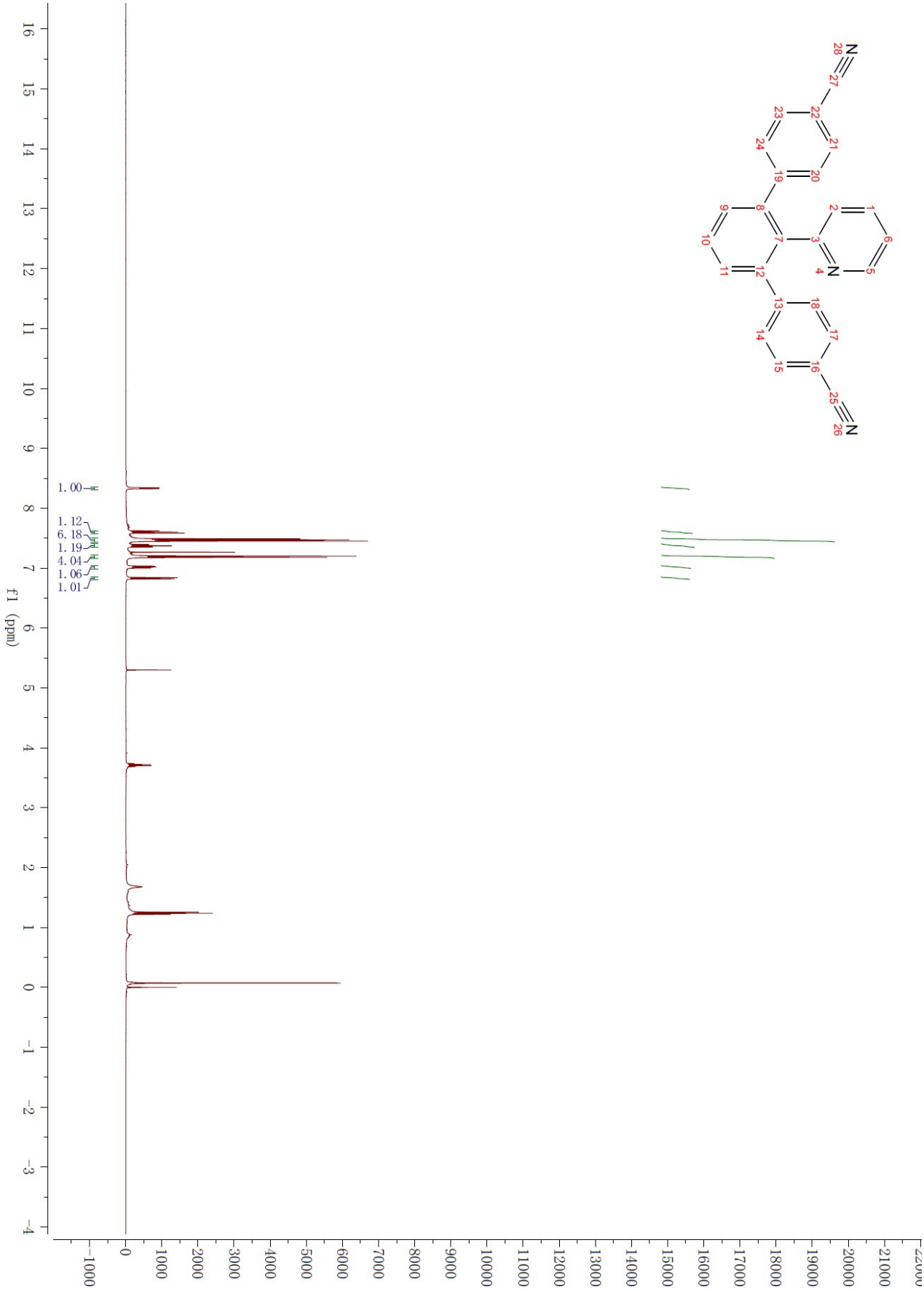
^{1}H NMR Spectrum of the Compound 3au



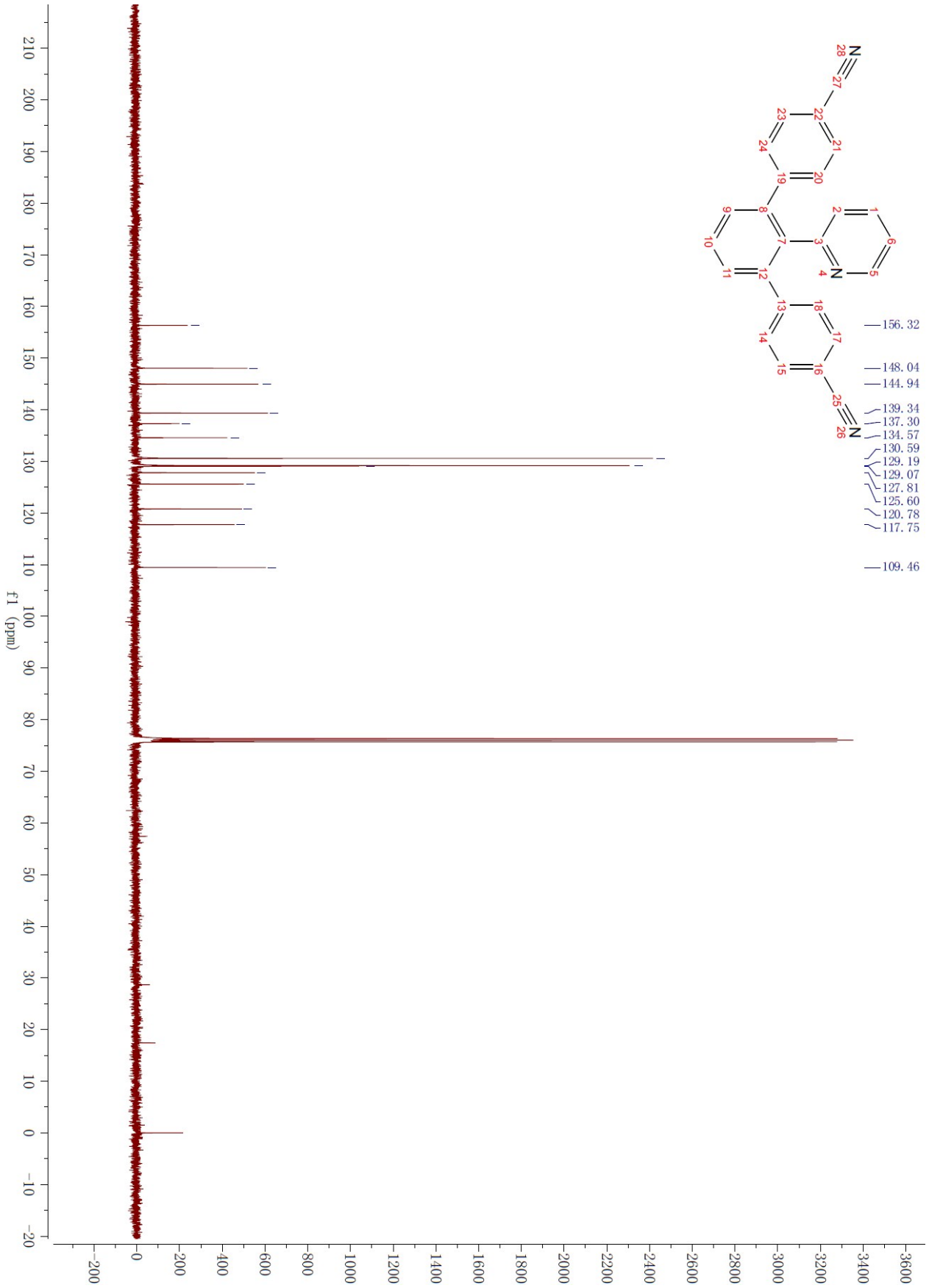
^{13}C NMR Spectrum of the Compound 3au



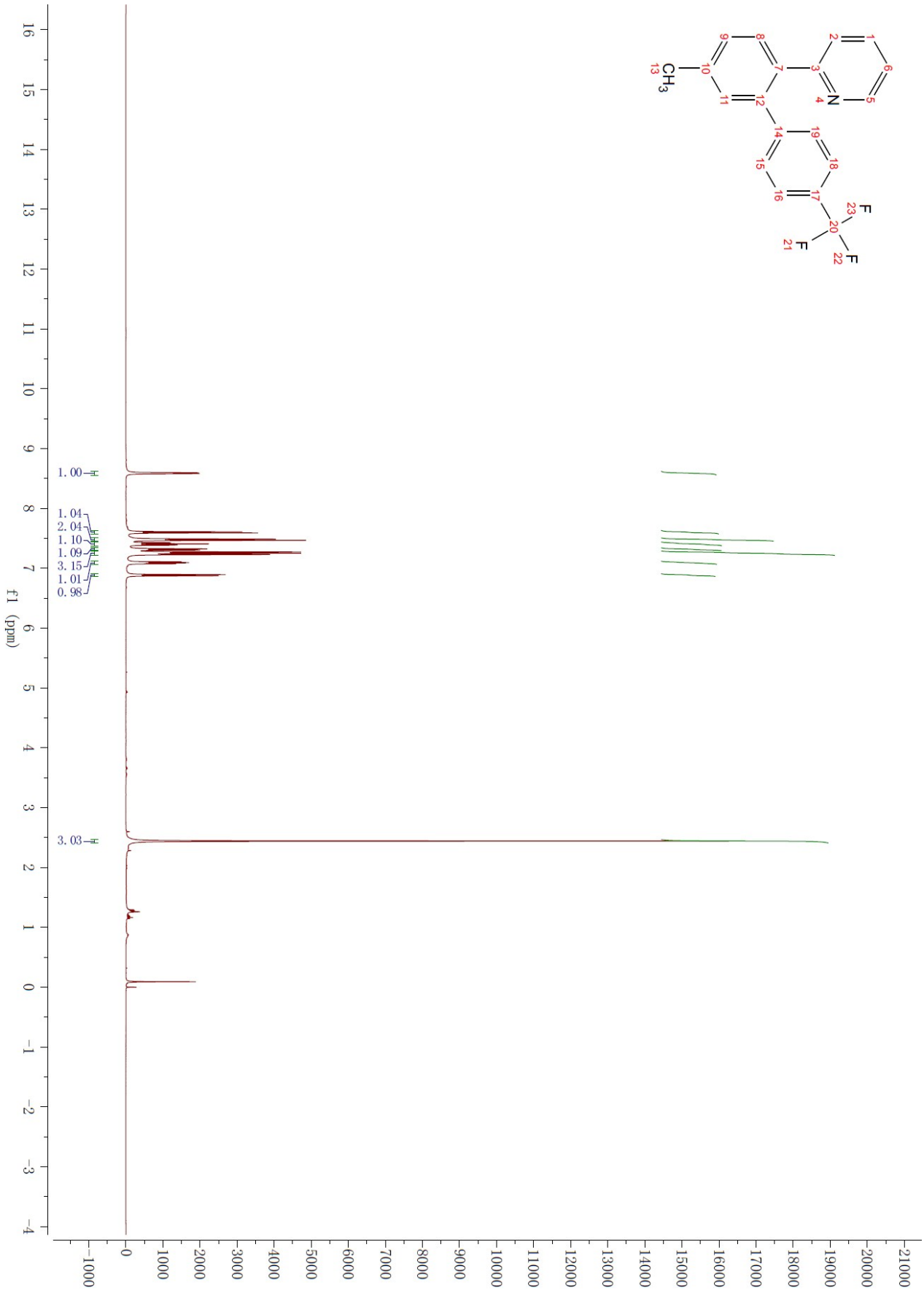
^{1}H NMR Spectrum of the Compound 4au



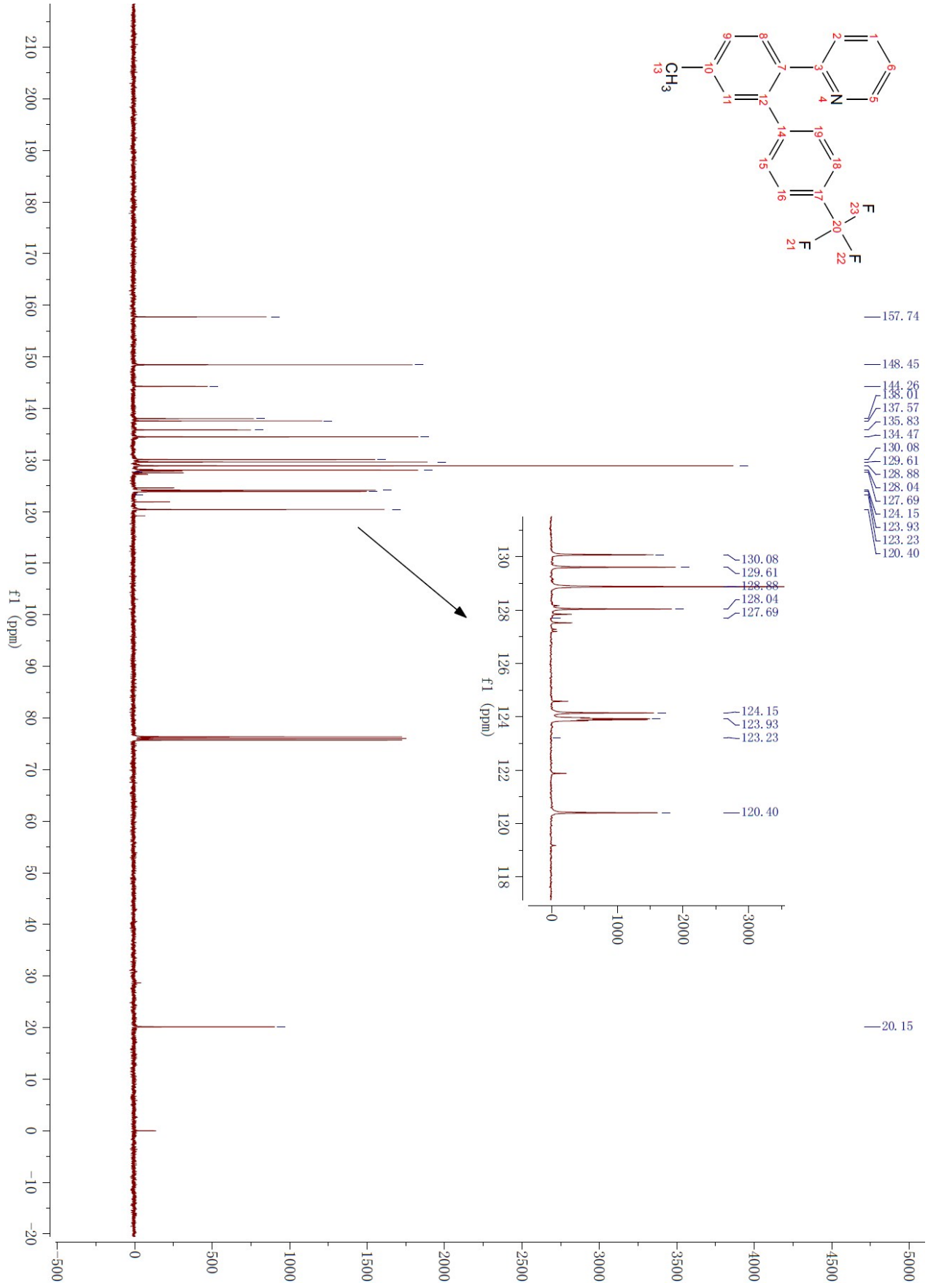
^{13}C NMR Spectrum of the Compound 4au



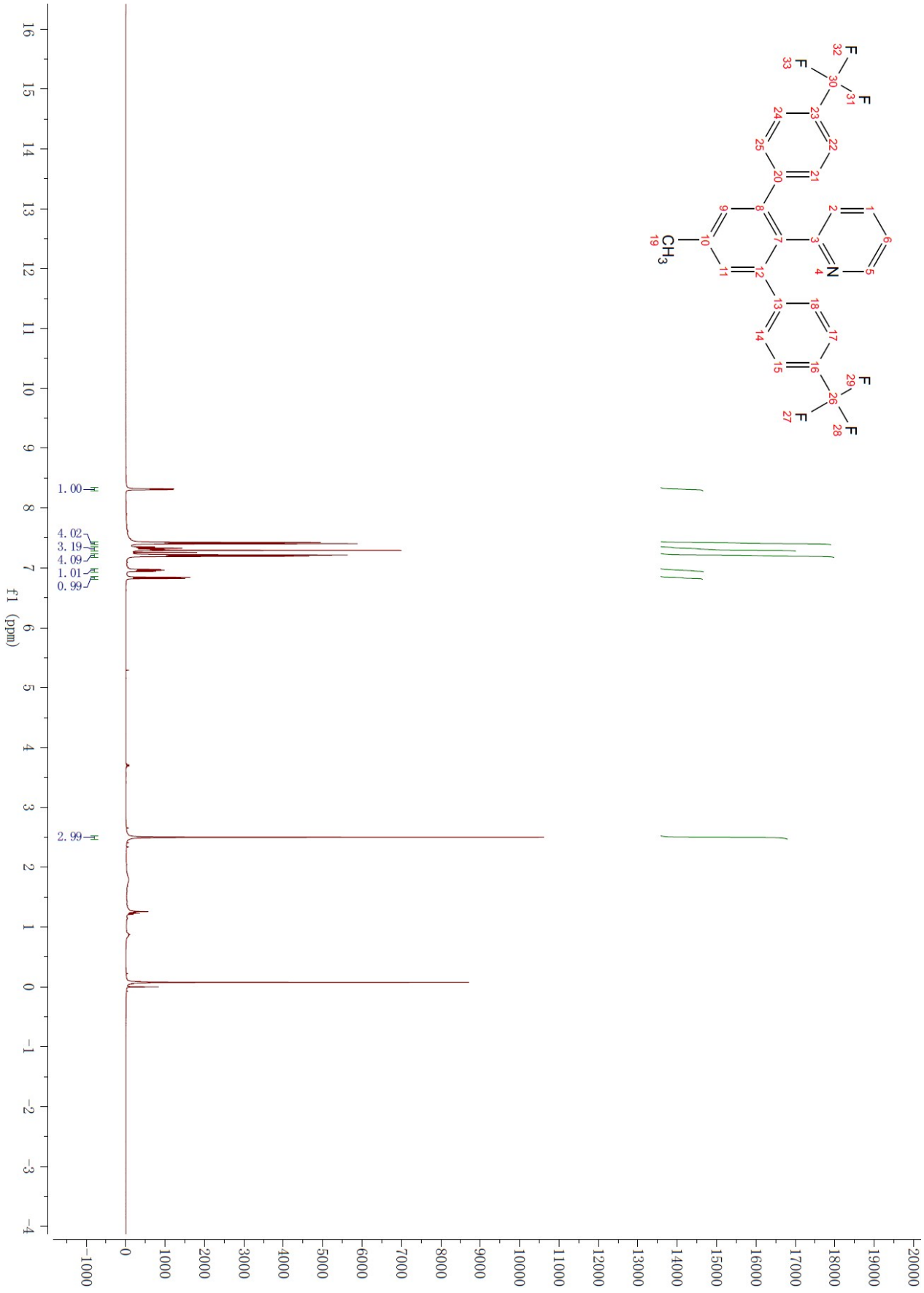
^{1}H NMR Spectrum of the Compound 3gm



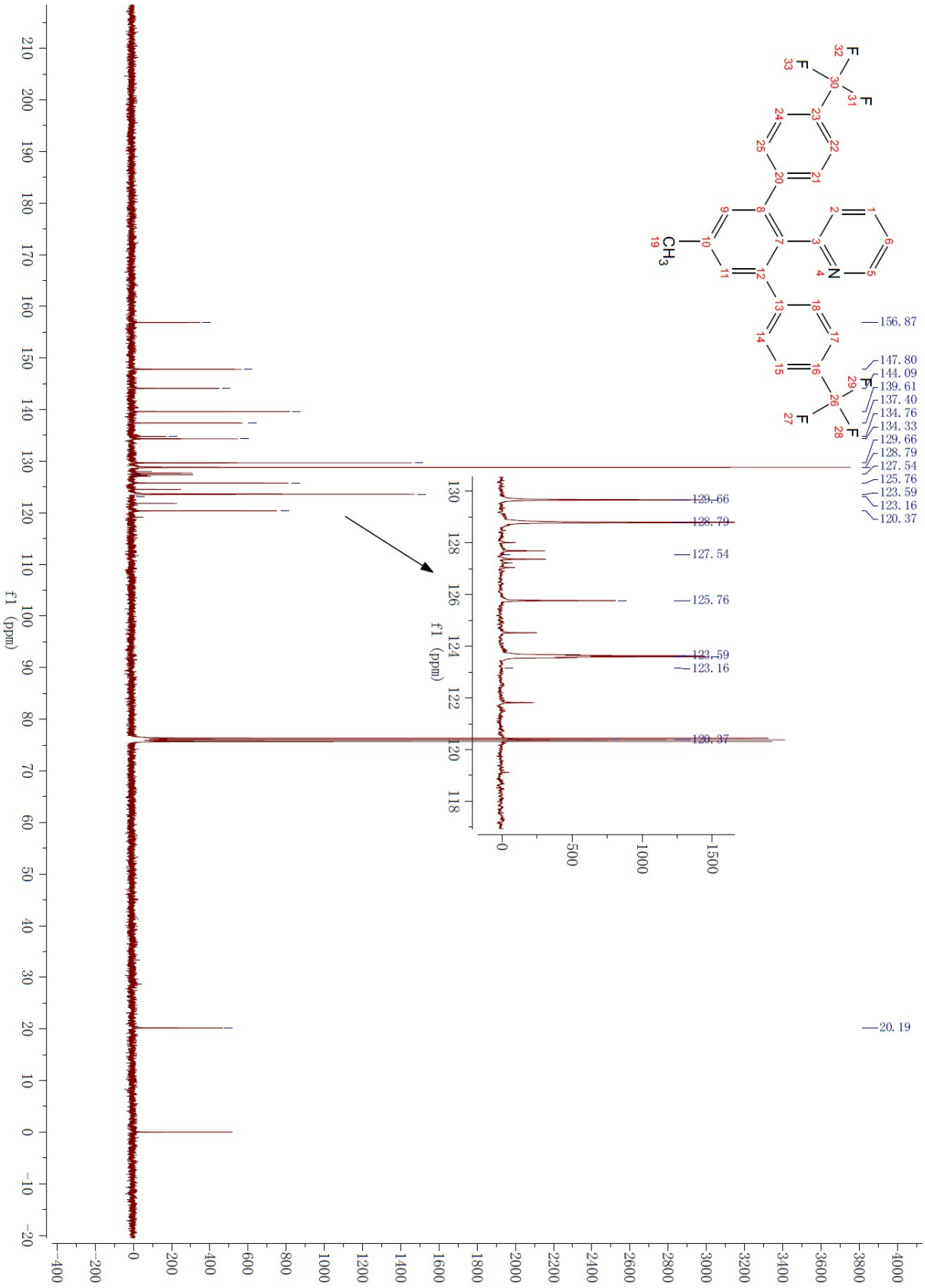
^{13}C NMR Spectrum of the Compound 3gm



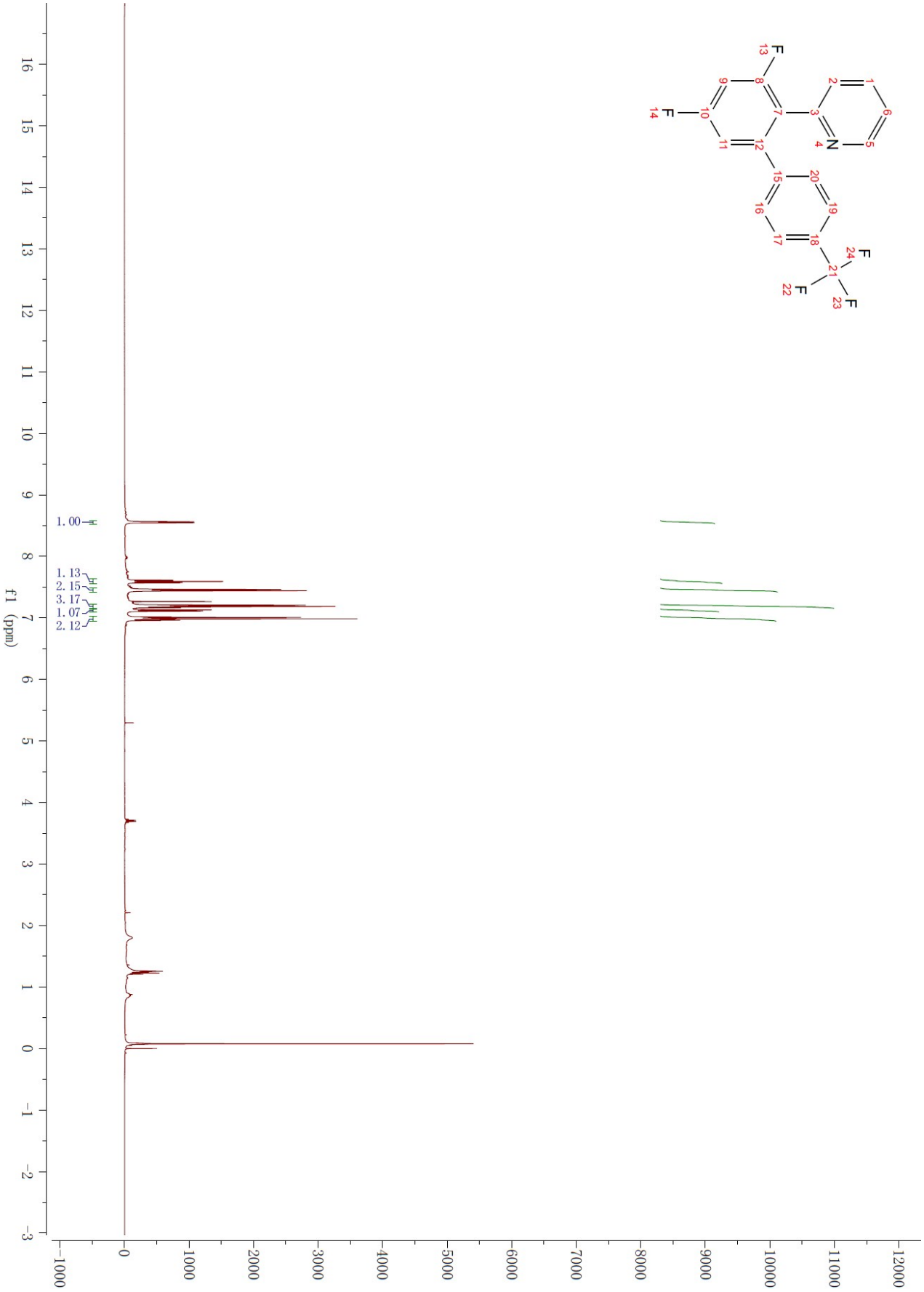
^{1}H NMR Spectrum of the Compound 4gm



^{13}C NMR Spectrum of the Compound 4gm



^{1}H NMR Spectrum of the Compound hm



^{13}C NMR Spectrum of the Compound hm