Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

A Cascade Alkylarylation Reaction of 2-Isocyanobiphenyls with Simple Alkanes for 6-Alkyl Phenanthridines via Dual C(sp^3)-H/C(sp^2)-H Functionalizations

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Supporting Information

Contents

1. General Imformation

Unless otherwise indicated, all reagents were purchased from commercial distributors and used without further purification. ^{1}H and ^{13}C NMR were recorded with ^{1}H at 400 MHz and ^{13}C at 100 MHz, respectively, using tetramethylsilane as an internal reference. Mass spectroscopy data were collected on an HRMS-ESI instrument. Melting points were uncorrected. Flash column chromatography was performed over silica gel 200-300. All 2-isocynobiaryl were prepared according to a reported method.[1]

2. Optimization of the Reaction Conditions

Table S1. Screening of reaction conditions.[a]

Entry	catalyst (mol%)	Oxidant (eq)	Temp	Yield (%)[b]
1	CuCl	TBHP	110	38
2	CuBr	TBHP	110	45
3	CuI	TBHP	110	20
4	Cu_2O	TBHP	110	52
5	$CuBr_2$	TBHP	110	42
6	$Cu(OAc)_2$	TBHP	110	21
7[c]	--	TBHP	110	trace
8	Cu_2O	DTBP	110	63
9	Cu_2O	TBPB	110	58
10	Cu_2O	DCP	110	56
11	Cu_2O	70% TBHP	110	33
12	Cu_2O	$K_2S_2O_8$	110	--
13	Cu_2O	O_2	110	--
14[d]	Cu_2O	DTBP	110	64
15[e]	Cu_2O	DTBP(3)	110	67
16[f]	Cu_2O	DTBP(3.5)	110	73
17[g]	Cu_2O	DTBP(4)	110	75
18	Cu_2O	DTBP(3.5)	90	trace
19	**Cu_2O**	**DTBP(3.5)**	**120**	**82**
20	Cu_2O	DTBP(3.5)	130	80
21[h]	Cu_2O	DTBP(3.5)	120	77
22[c]	--	DTBP(3.5)	120	68

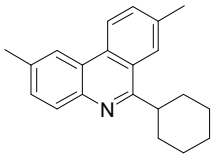
[a] Reaction conditions: The mixture of **1a** (0.2 mmol), **2** (5 ml) and catalyst (0.01 mmol) was stirred at 110 ℃; for 24 h; [b] Isolated yield; [c] In the absence of catalyst; [d] under nitrogen atmosphere. e) 3eq oxidant. f) 3.5 eq oxidant. g) 4 eq oxidant. h) **2a** (4 ml).

3. Experimental Procedure

General procedure of the cascade alkylarylation reaction of 2-isocyanobiaryls **1** with alkanes **2** for the synthesis of 6-alkylated phenanthridines **3**: A mixture of 2-isocynaobiaryl **1** (0.2 mmol), alkane **2** (5 ml), Cu_2O (1.43 mg, 0.01 mmol) and DTBP (105.5 mg, 0.7 mmol) was sealed in a Teflon septum screw-capped tube. Then the reaction mixture was stirred at 120 ℃ for 24 h. After cooling to room temperature, the mixture was concentrated under vacuum, and the residue was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate as eluent) to afford the desired product **3**.

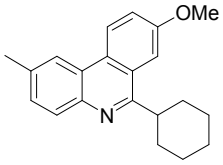
4. Characterization of Alkylarylated Products

6-Cyclohexyl-2,8-dimethylphenanthridine **3aa**



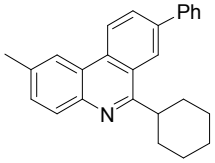
Yield: 82%. White solid. Mp: 135-136℃; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.51 (d, J = 8.4 Hz, 1H), 8.27 (s, 1H), 8.04 (s, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.61 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.48 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 3.60-3.53 (m, 1H), 2.61 (s, 3H), 2.59 (s, 3H), 2.06-1.82 (m, 7H), 1.63-1.52 (m, 2H), 1.48-1.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 164.0, 141.9, 136.7, 135.7, 131.4, 130.7, 129.6, 125.0, 124.9, 123.2, 122.5, 121.3, 41.8, 32.3, 26.9, 26.4, 22.0, 21.9; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{21}H_{23}N$ 289.1830; found 289.1826.

6-Cyclohexyl-8-methoxy-2-methylphenanthridine **3ba**



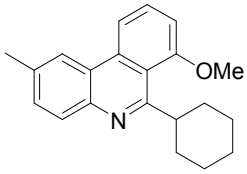
Yield: 71%. White solid. Mp: 130-132℃; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.52 (d, J = 8.8 Hz, 1H), 8.20 (s, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 2.8 Hz, 1H), 7.44 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H), 7.40 (dd, J = 9.2 Hz, J = 2.4 Hz, 1H), 3.98 (s, 3H), 3.51-3.45 (m, 1H), 2.57 (s, 3H), 2.09-1.82 (m, 7H), 1.61-1.51 (m, 2H), 1.47-1.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 163.3, 158.4, 141.4, 135.9, 129.7, 129.1, 127.1, 126.1, 124.2, 123.2, 120.9, 119.5, 106.6, 55.1, 42.1, 32.2, 26.9, 26.4, 21.9; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{21}H_{23}NO$ 305.1780; found 305.1779.

6-Cyclohexyl-2-methyl-8-phenylphenanthridine **3ca**



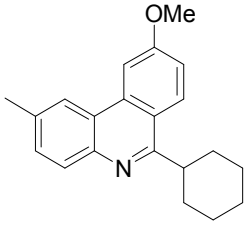
Yield: 72%. White solid. Mp: 146-147℃; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.63 (d, J = 8.4 Hz, 1H), 8.43 (s, 1H), 8.28 (s, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.97 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.72 (d, J = 8.4 Hz, J = 1.6 Hz, 1H), 7.54-7.49 (m, 3H), 7.42 (t, J = 7.4 Hz, 1H), 3.67-3.61 (m, 1H), 2.59 (s, 3H), 2.11-1.82 (m, 7H), 1.62-1.52 (m, 2H), 1.47-1.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 164.3, 142.2, 141.0, 139.8, 136.0, 131.9, 130.1, 129.7, 129.1, 129.0, 127.7, 127.5, 125.1, 123.7, 123.2, 123.0, 121.5, 42.0, 32.4, 26.9, 26.4, 21.9; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{26}H_{25}N$ 351.1987; found 351.1984.

6-Cyclohexyl-7-methoxy-2-methylphenanthridine **3da**



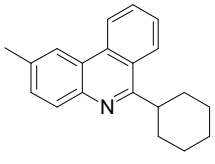
Yield: 47%. White solid. Mp: 139-141℃; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.24 (s, 1H), 8.21 (d, J = 8.0 Hz, 1H), 8.04 (s, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.66 (t, J = 8.2 Hz, 1H), 7.48 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H), 7.06 (d, J = 8.0 Hz, 1H), 4.08-4.03 (m, 1H), 4.02 (s, 3H), 2.58 (s, 3H), 2.08-1.74 (m, 7H), 1.56-1.45 (m, 2H), 1.44-1.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 164.2, 158.4, 142.0, 135.5, 130.2, 129.9, 129.4, 122.5, 121.9, 117.0, 114.8, 108.2, 55.7, 46.4, 33.1, 27.4, 26.7, 21.9; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{21}H_{23}NO$ 305.1780; found 305.1776.

6-Cyclohexyl-9-methoxy-2-methylphenanthridine **3da′**



Yield: 31% yield. White solid. Mp: 144-145℃; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.21 (t, J = 4.4 Hz, 2H), 7.98 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 2.4 Hz, 1H), 7.50 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.25 (dd, J = 9.2 Hz, J = 2.8 Hz, 1H), 4.05 (s, 3H), 3.56-3.48 (m, 1H), 2.60 (s, 3H), 2.59 (s, 3H), 2.05-1.81 (m, 7H), 1.58-1.50 (m, 2H), 1.46-1.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 163.9, 160.6, 142.7, 135.3, 134.9, 130.2, 129.7, 127.5, 123.0, 121.4, 119.8, 117.0, 103.1, 55.5, 42.0, 32.3, 26.9, 26.3, 21.8; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{21}H_{23}NO$ 305.1780; found 305.1778.

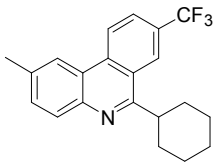
6-Cyclohexyl-2-methylphenanthridine **3ea**[1]



Yield: 74%. White solid. Mp: 115-116℃; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.60 (d, J = 8.0 Hz, 1H), 8.27 (d, J = 8.0 Hz, 2H),

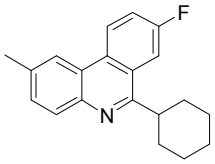
8.01 (d, J = 8.4 Hz, 1H), 7.75 (td, J = 8.0 Hz, J = 1.2 Hz, 1H), 7.63 (td, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.50 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 3.61-3.54 (m, 1H), 2.59 (s, 3H), 2.06-1.82 (m, 7H), 1.61-1.50 (m, 2H), 1.47-1.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 164.2, 142.3, 135.8, 132.8, 130.0, 129.7, 129.6, 126.9, 125.6, 124.8, 123.2, 122.5, 121.5, 42.0, 32.3, 26.9, 26.4, 21.9; MS (EI): *m/z*: 275 $[M]^+$, 220(100), 207, 165, 77.

6-Cyclohexyl-2-methyl-8-trifluoromethylphenanthridine **3fa**



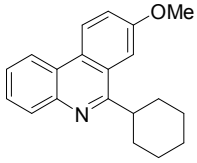
Yield: 75%. White solid. Mp: 117-119℃; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.70 (d, J = 8.8 Hz, 1H), 8.52 (s, 1H), 8.28 (s, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.57 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 3.59-3.54 (m, 1H), 2.61 (s, 3H), 2.06-1.84 (m, 7H), 1.65-1.54 (m, 2H), 1.47-1.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 164.1, 142.9, 136.6, 135.0, 131.3, 129.9, 125.5, 125.4, 124.1, 123.6, 123.0, 122.9, 122.2, 121.8, 41.8, 32.4, 26.8, 26.3, 21.9; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{21}H_{20}F_3N$ 343.1548; found 343.1542.

6-Cyclohexyl-8-fluoro-2-methylphenanthridine **3ga**



Yield: 74%. White solid. Mp: 145-146℃; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.60 (dd, J = 9.2 Hz, J = 5.6 Hz, 1H), 8.24 (s, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.88 (dd, J = 10.4 Hz, J = 2.4 Hz, 1H), 7.55-7.49 (m, 2H), 3.47-3.41 (m, 1H), 2.59 (s, 3H), 2.06-1.83 (m, 7H), 1.62-1.51 (m, 2H), 1.47-1.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 163.4, 163.3, 162.6, 160.2, 141.9, 136.3, 130.0, 129.8, 129.5, 126.2, 126.1, 125.1, 125.0, 122.7, 121.2, 118.9, 118.7, 110.3, 110.1, 42.1, 32.2, 26.8, 26.3, 21.9; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{20}H_{20}FN$ 293.1580; found 293.1584.

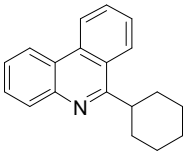
6-Cyclohexyl-8-methoxyphenanthridine **3ha**



Yield: 71%. White solid. Mp: 80-81℃; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.54 (d, J = 9.2 Hz, 1H), 8.42 (d, J = 8.0 Hz, 1H), 8.10 (dd, J = 8.0 Hz, J = 0.8 Hz, 1H), 7.64-7.60 (m, 2H), 7.55 (td, J = 8.0 Hz, J = 1.2 Hz, 1H), 7.43 (dd, J = 8.8 Hz, J = 2.4 Hz, 1H), 3.99 (s, 3H), 3.54-3.47 (m, 1H), 2.09-1.82 (m, 7H), 1.62-1.50 (m, 2H), 1.48-1.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 164.4, 158.6, 143.1, 129.9, 127.4, 127.3, 126.2, 126.1, 124.3, 123.4,

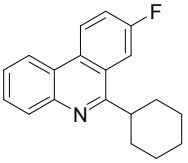
121.3, 119.7, 106.7, 55.5, 42.2, 32.2, 26.9, 26.4; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{20}H_{21}NO$ 291.1623; found 291.1623.

6-Cyclohexylphenanthridine **3ia**[2]



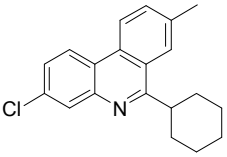
Yield: 73%. Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.63 (d, J = 8.4 Hz, 1H), 8.51 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 8.30 (d, J = 8.4 Hz, 1H), 8.13 (dd, J = 8.0 Hz, J = 0.8 Hz, 1H), 7.78 (td, J = 8.0 Hz, J = 1.2 Hz, 1H), 7.70-7.64 (m, 1H), 3.60-3.53 (m, 2H), 7.58 (td, J = 8.0 Hz, J = 1.2 Hz, 1H), 3.64-3.56 (m, 1H), 2.08-1.82 (m, 7H), 1.62-1.51 (m, 2H), 1.48-1.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 165.3, 144.0, 133.1, 130.0, 129.9, 128.4, 127.0, 126.1, 125.6, 124.8, 123.4, 122.6, 121.8, 42.0, 32.3, 26.9, 26.4; MS (EI): *m/z*: 261 [M]$^+$, 206(100), 151, 109, 77.

6-Cyclohexyl-8-fluorophenanthridine **3ja**



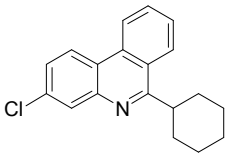
Yield: 74%. White solid. Mp: 93-94℃; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.58 (dd, J = 10.8 Hz, J = 4.2 Hz, 1H), 8.43 (d, J = 7.6 Hz, 1H), 8.12 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.89 (dd, J = 10.4 Hz, J = 2.4 Hz, 1H), 7.67 (td, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.58 (td, J = 8.0 Hz, J = 1.2 Hz, 1H), 7.54-7.49 (m, 1H), 3.48-3.40 (m, 1H), 2.61 (s, 6H), 2.59 (s, 6H), 2.06-1.82 (m, 7H), 1.61-1.50 (m, 2H), 1.47-1.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 164.4, 164.3, 162.7, 160.3, 143.6, 130.1, 129.7, 128.3, 126.5, 126.1, 126.0, 125.1, 125.0, 122.9, 121.6, 119.1, 118.9, 110.4, 110.2, 42.2, 32.2, 26.8, 26.3; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{19}H_{18}FN$ 279.1423; found 279.1422.

3-Chloro-6-cyclohexyl-8-methylphenanthridine **3ka**



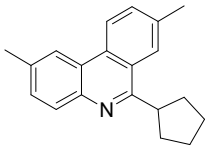
Yield: 72%. Light yellow solid. Mp: 165-168℃; ^{1}H NMR (400 MHz, $CDCl_3$)), δ (ppm): 8.44-8.42 (m, 2H), 8.05 (s, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.58 (dd, J = 8.8 Hz, J = 2.0 Hz, 1H), 7.43 (dd, J = 8.8 Hz, J = 2.4 Hz, 1H), 3.60-3.53 (m, 1H), 2.62 (s, 3H), 2.05-1.83 (m, 7H), 1.63-1.52 (m, 2H), 1.48-1.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 165.3, 142.0, 137.7, 131.9, 131.8, 131.3, 129.9, 128.3, 125.1, 125.0, 124.5, 122.5, 121.3, 41.8, 32.3, 26.8, 26.3, 22.0; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{20}H_{20}ClN$ 309.1284; found 309.1283.

3-Chloro-6-cyclohexylphenanthridine **3la**



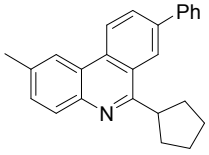
Yield: 73% yield. Light yellow solid. Mp: 105-107℃; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.54 (d, J = 8.0 Hz, 1H), 8.47 (s, 1H), 8.30 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.8 Hz, 1H), 7.81 (t, J = 7.6 Hz, 1H), 7.70 (t, J = 7.8 Hz, 1H), 7.62 (dd, J = 8.8 Hz, J = 2.4 Hz, 1H), 3.62-3.55 (m, 1H), 2.07-1.83 (m, 7H), 1.62-1.51 (m, 2H), 1.47-1.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 165.6, 142.4, 132.0, 131.9, 131.4, 130.2, 128.8, 127.7, 125.7, 124.9, 124.4, 122.6, 121.5, 42.0, 32.3, 26.8, 26.3; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{19}H_{18}ClN$ 295.1128; found 295.1126.

6-Cyclopentyl-2,8-dimethylphenanthridine **3ab**



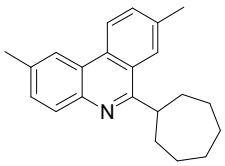
Yield: 76%. White solid. Mp: 110-112℃; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.48 (d, J = 8.4 Hz, 1H), 8.25 (s, 1H), 8.06 (s, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.59 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H), 7.46 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 4.05-3.97 (m, 1H), 2.59 (s, 3H), 2.58 (s, 3H), 2.27-2.12 (m, 4H), 1.97-1.88 (m, 2H), 1.83-1.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 162.8, 141.8, 136.6, 135.7, 131.4, 130.6, 129.6, 129.5, 125.9, 125.7, 123.4, 122.3, 121.3, 43.4, 32.2, 26.0, 21.9, 21.9; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{20}H_{21}N$ 275.1674; found 275.1673.

6-Cyclopentyl-2-methyl-8-phenylphenanthridine **3cb**



Yield: 68%. White solid. Mp: 109-111℃; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.60 (d, J = 8.8 Hz, 1H), 8.45 (s, 1H), 8.26 (s, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.96 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H), 7.71 (d, J = 7.2 Hz, 2H), 7.50 (t, J = 7.8 Hz, 3H), 7.40 (t, J = 7.2 Hz, 1H), 4.12-4.04 (m, 1H), 2.58 (s, 3H), 2.31-2.15 (m, 4H), 1.92-1.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 163.3, 142.1, 140.9, 139.7, 136.0, 130.1, 131.8, 130.1, 129.7, 129.1, 129.0, 127.7, 127.5, 126.0, 124.4, 123.2, 123.0, 121.5, 43.6, 32.3, 26.1, 22.0; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{25}H_{23}N$ 337.1830; found 337.1833.

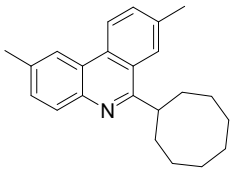
6-Cycloheptyl-2,8-dimethylphenanthridine **3ac**



Yield: 80%. White solid. Mp: 92-94℃; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.48 (d, J = 8.4 Hz, 1H), 8.24 (s, 1H), 8.00 (s, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.58 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H),

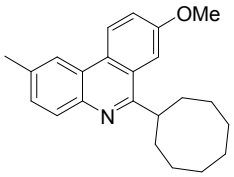
7.46 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H), 3.75-3.71 (m, 1H), 2.59 (s, 3H), 2.57 (s, 3H), 2.15-2.07 (m, 4H), 1.97-1.92 (m, 2H), 1.81-1.67 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 165.3, 141.8, 136.6, 135.7, 131.3, 130.8, 129.6, 125.2, 124.8, 123.2, 122.5, 121.2, 43.4, 34.2, 28.3, 27.6, 22.0, 21.9; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{22}H_{25}N$ 303.1987; found 303.1988.

6-Cyclooctyl-2,8-dimethylphenanthridine **3ad**



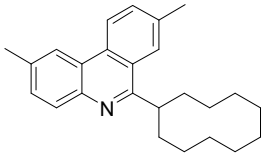
Yield: 78%. Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.48 (d, J = 8.4 Hz, 1H), 8.24 (s, 1H), 8.01 (s, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.58 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.46 (dd, J = 8.4 Hz, J = 2.0 Hz, 1H), 3.86-3.80 (m, 1H), 2.59 (s, 3H), 2.57 (s, 3H), 2.20-2.04 (m, 7H), 1.91-1.89 (m, 2H), 1.80-1.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=165.8, 141.8, 136.6, 135.7, 131.4, 130.9, 129.6, 129.6, 125.3, 124.8, 123.2, 122.5, 121.3, 41.5, 32.6, 27.0, 26.3, 22.1, 21.9; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{23}H_{27}N$ 317.2143; found 317.2145.

6-Cyclooctyl-8-methoxy-2-methylphenanthridine **3bd**



Yield: 70%. Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.51 (d, J = 8.8 Hz, 1H), 8.19 (s, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.59 (d, J = 2.4 Hz, 1H), 7.44 (dd, J = 8.0 Hz, J = 1.2 Hz, 1H), 7.40 (dd, J = 8.8 Hz, J = 2.4 Hz, 1H),3.97 (s, 3H), 3.79-3.73 (m, 1H), 2.57 (s, 3H), 2.21-2.04 (m, 4H), 192-1.91 (m, 2H), 1.79-1.70 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 165.2, 158.4, 141.2, 135.8, 129.6, 129.1, 127.3, 125.9, 124.2, 123.2, 120.9, 119.6, 106.7, 55.5, 41.7, 32.5, 27.1, 26.9, 26.4, 21.9; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{23}H_{27}NO$ 333.2093; found 333.2084.

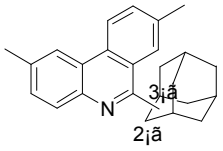
6-Cyclodecyl-2,8-dimethylphenanthridine **3ae**



Yield: 75%. Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.51 (d, J = 8.4 Hz, 1H), 8.26 (s, 1H), 8.07 (s, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.61 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H), 7.47 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 4.06-4.00 (m, 1H), 2.61 (s, 3H), 2.59 (s, 3H), 2.16-2.11 (m, 4H), 1.79-1.51 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 164.6, 141.8, 136.6, 135.7, 131.3, 130.8, 129.6, 129.6, 125.4, 125.2, 123.2, 122.5, 121.2, 39.2, 30.9, 25.5, 25.3, 24.7, 22.0, 21.9; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{25}H_{31}N$

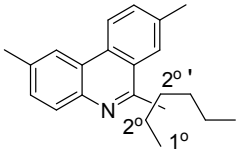
345.2468; found 345.2467.

6-Adamantan-1-yl-2,8-dimethylphenanthridine **3af** *and 6-Adamantan-2-yl-2,8-dimethylphenanthridine* **3af′**



Yield: 51% (**3af**:**3af'** =2:1). White solid. A mixture of regioisomers 2°-C and 3°-C: ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.60 (s, 0.64H), 8.55 (d, J = 8.4 Hz, 0.65H), 8.50 (d, J = 8.4 Hz, 0.33H), 8.26 (s, 0.33H), 8.25 (s, 0.66H), 8.01 (d, J = 8.0 Hz, 0.33H), 7.97 (d, J = 8.0 Hz, 0.66H), 7.88 (s, 0.32H), 7.57 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.47 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 3.93 (s, 0.34H), 2.61 (s, 3H), 2.59 (s, 3H), 2.65 (s, 0.34H), 2.47 (d, J = 2.4 Hz, 4H), 2.23-2.02 (m, 4H), 1.95-1.82 (m, 5H), 1.62-1.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 164.6, 162.6, 141.4, 141.2, 136.4, 136.0, 135.7, 135.1, 131.7, 131.0, 130.6, 130.6, 129.9, 129.6, 129.5, 127.6, 125.6, 125.2, 124.7, 123.2, 123.0, 122.9, 122.5, 121.2, 121.1, 47.5, 42.9, 42.1, 40.2, 38.3, 37.3, 32.7, 29.3, 28.6, 28.1, 22.3, 22.1, 22.0, 21.9; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{25}H_{27}N$ 341.2144; found 341.2141.

6-Hexyl-2,8-dimethylphenanthridine **3ag**, *6-(hexan-2-yl)-2,8-dimethylphenanthridine* **3ag′** *and 6-(hexan-3-yl)-2,8-dimethylphenanthridine* **3ag′′**



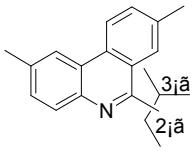
Yield: 62%. Light yellow oil. **3ag**: ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.51 (d, J = 8.4 Hz, 1H), 8.28 (s, 1H), 7.99 (s, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.63 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.49 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H), 3.32 (t, J = 8.0 Hz, 2H), 1.94-1.86 (m, 2H), 1.57-1.50 (m, 2H), 1.42-1.32 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 161.2, 141.7, 136.9, 135.9, 131.8, 130.6, 129.8, 129.2, 125.8, 125.5, 123.6, 122.4, 121.4, 36.4, 31.8, 29.7, 29.6, 22.7, 21.9, 14.1; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{21}H_{25}N$ 291.1987; found 291.1990.

A mixture of **3ag′** and **3ag′′**: ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.52 (d, J = 8.4 Hz, J = 2.0 Hz, 1H), 8.27 (s, 1H), 8.07 (d, J = 11.2 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 3.83-3.74 (m, 0.6), 3.67-3.61 (m, 0.39H), 2.60 (s, 3H), 2.59 (s, 3H), 2.15-2.01 (m, 1H), 1.88-1.72 (m, 1H), 1.45 (d, J = 6.4 Hz, 2H) 1.38-1.32 (m, 3H), 0.89-0.83 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 164.3, 142.0, 141.9, 136.7, 136.6, 135.7, 135.6, 131.4, 130.7, 130.5, 129.6, 126.4, 125.4, 125.2, 125.1, 123.2, 123.1, 122.5, 122.4, 121.3, 37.2, 36.4, 36.0, 30.2,

29.7, 28.0, 23.0, 22.0, 21.9, 21.0, 20.2, 14.4, 14.1, 12.4; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{21}H_{25}N$ 291.1987; found 291.1991.

6-(1,1-Dimethyl-propyl)-2,8-dimethyl-phenanthridine **3ah** *and 6-(1,2-Dimethyl-propyl*

)-2,8-dimethyl-phenanthridine **3ah′**



Yield: 56% (C2°/C3°=1:4). Light yellow oil. **3ah**: ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.55 (d, J = 8.4 Hz, 1H), 8.37 (s, 1H), 8.26 (s, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.58 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.47 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H), 2.59 (s, 6H), 2.19 (q, J = 7.6 Hz, 2H), 1.67 (s, 6H), 0.72 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 164.3, 141.0, 136.0, 135.5, 131.4, 130.7, 130.0, 129.5, 127.2, 125.0, 123.2, 122.8, 121.1, 43.9, 35.5, 29.3, 22.2, 22.0, 9.57; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{20}H_{23}N$ 277.1830; found 277.1835.

3ah′: ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.52 (d, J = 8.4 Hz, 1H), 8.28 (s, 1H), 8.06 (s, 1H), 7.99 (dd, J = 8.4 Hz, J = 3.2 Hz, 1H), 7.61 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.48 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H), 3.60-3.50 (m, 1H), 2.60 (s, 3H), 2.59 (s, 3H), 2.46-2.38 (m, 1H), 1.42 (d, J = 6.8 Hz, 3H), 1.06 (d, J = 6.8 Hz, 3H), 0.86 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 164.4, 141.8, 136.7, 135.7, 131.4, 130.6, 130.0, 129.6, 125.7, 125.2, 123.1, 122.4, 121.3, 43.0, 32.8, 22.1, 22.0, 21.9, 19.7, 17.1; HRMS (TOF MS EI$^+$): *m/z* calcd for $C_{20}H_{23}N$ 277.1830; found 277.1829.

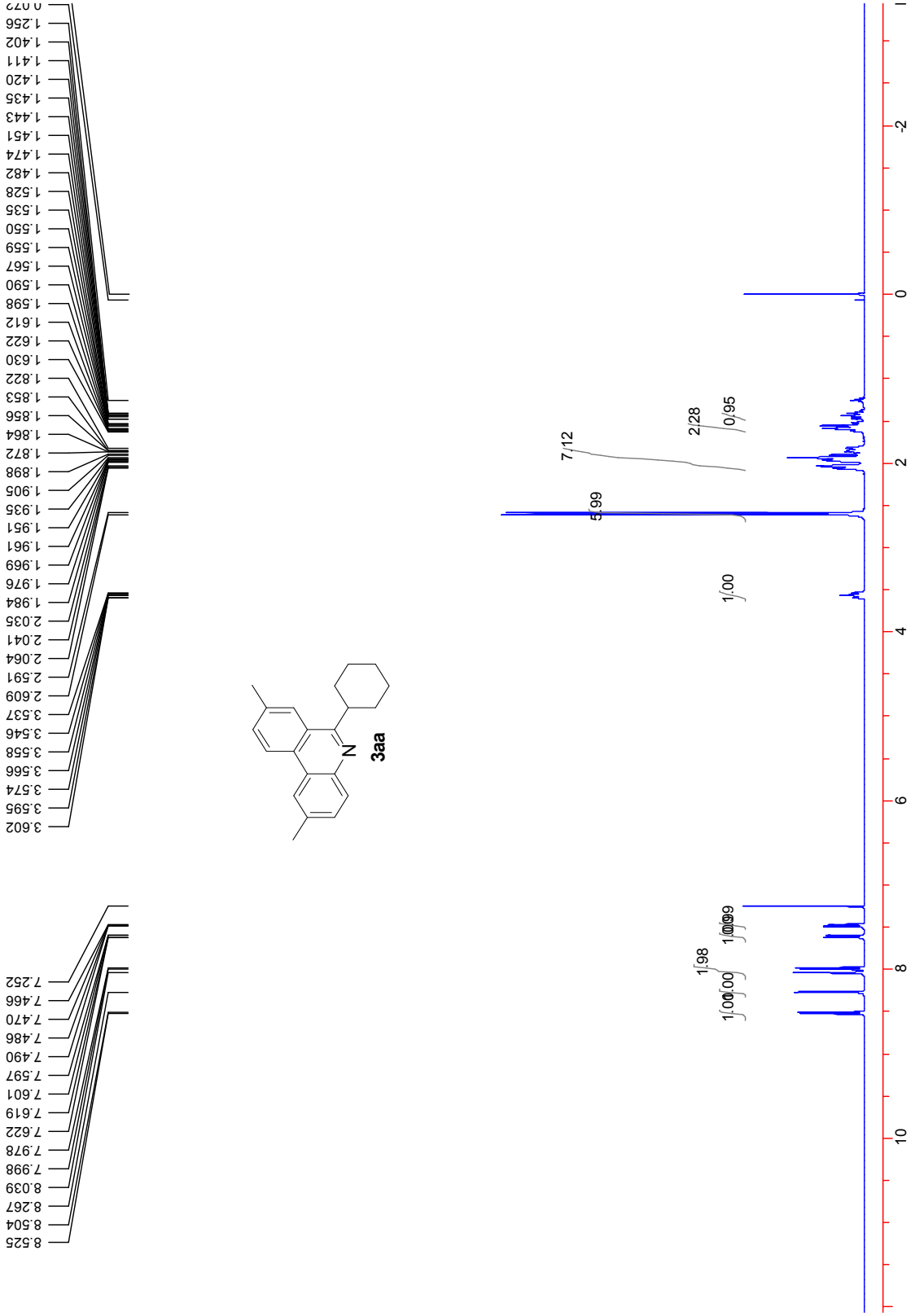
5. References

[1] M. Tobisu, K. Koh, T. Furukawa and N. Chatani, *Angew. Chem., Int. Ed.,* **2012**, *51*, 11363-11366.

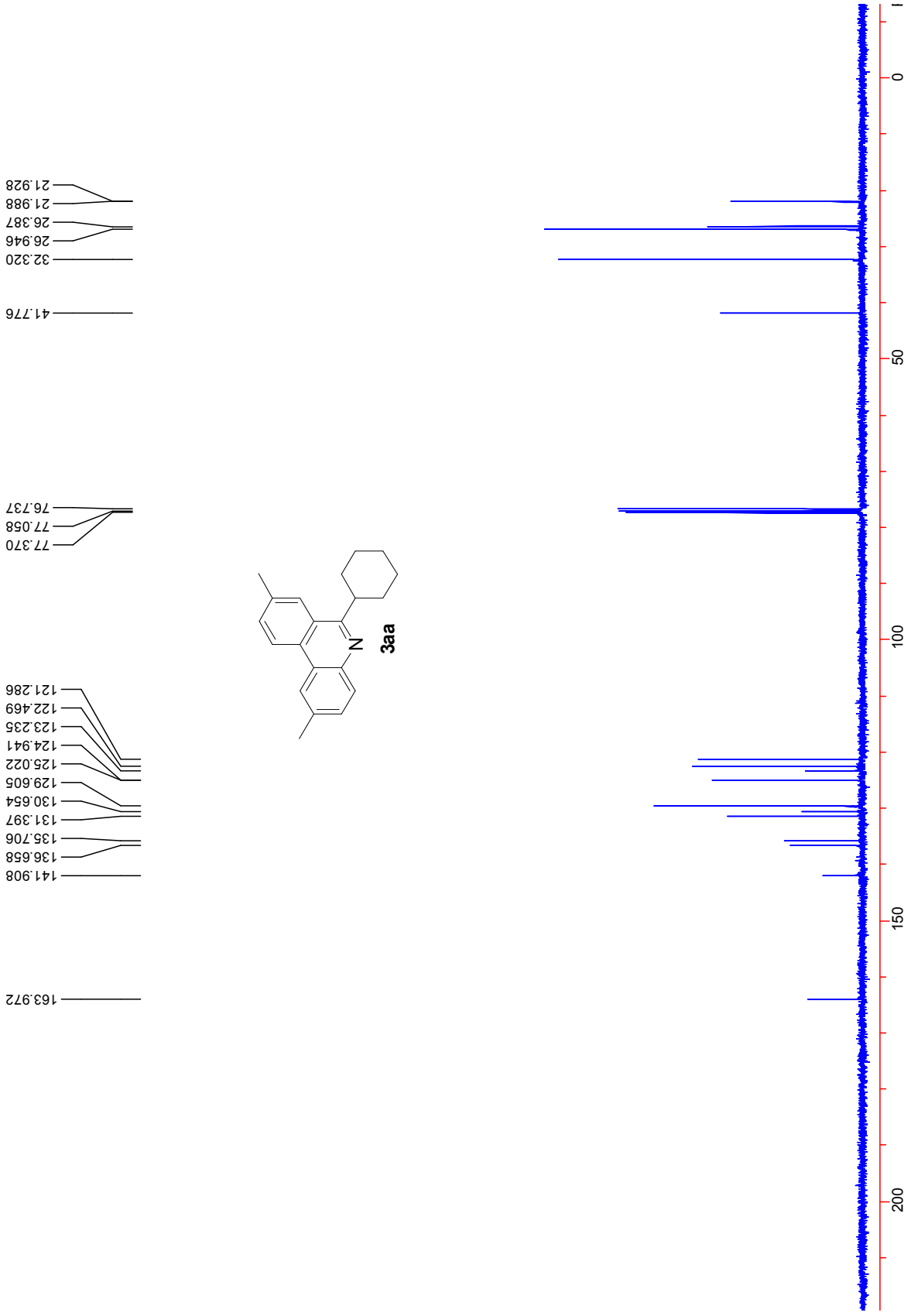
[2] T. Xiao, L. Li, G. Lin, Q. Wang, P. Zhang, Z. Mao, L. Zhou, *Green Chem.* **2014**, doi: 10.1039/c3gc42517g.

6. ^{1}H NMR, ^{13}C NMR and HR-MS Spectra of New Compounds

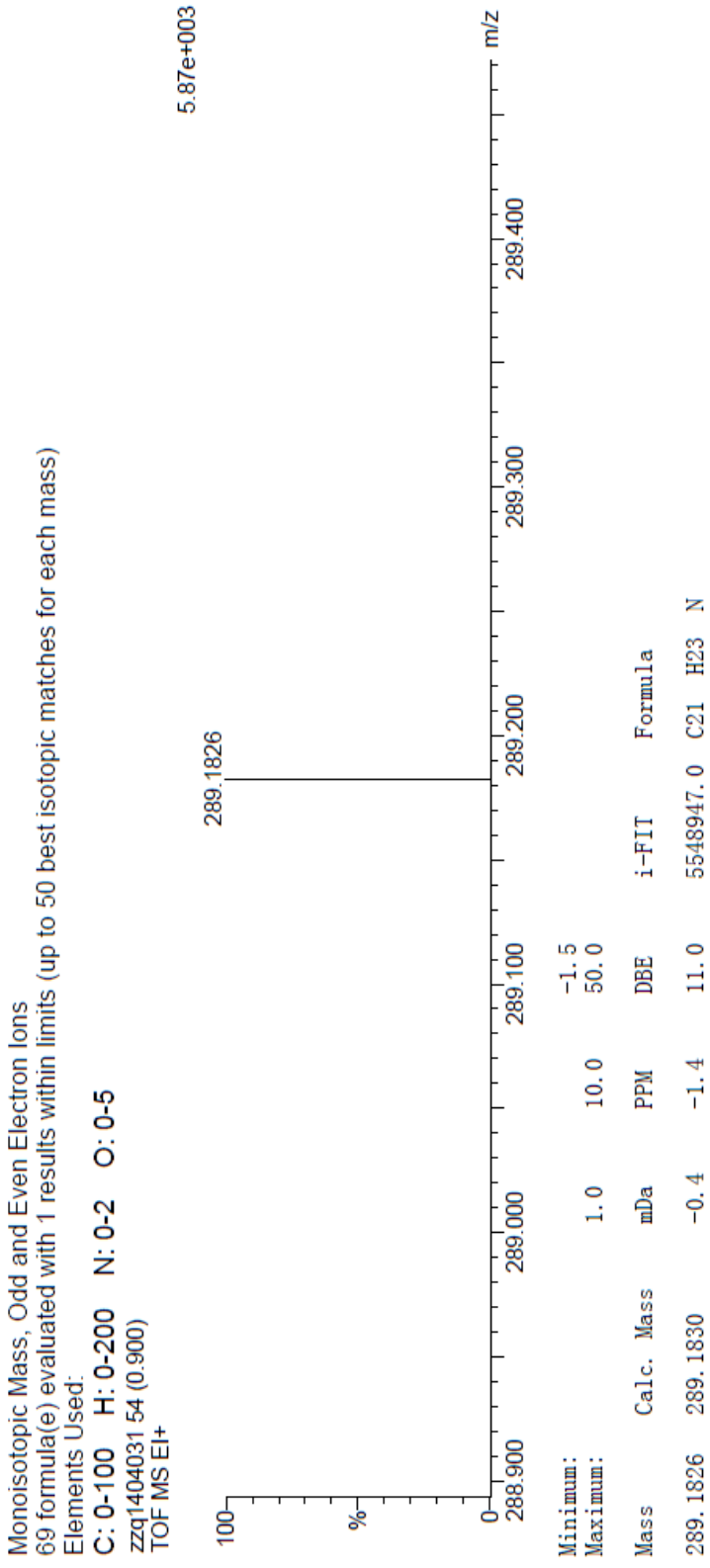
^{1}H NMR spectra of 6-cyclohexyl-2,8-dimethylphenanthridine (**3aa**)



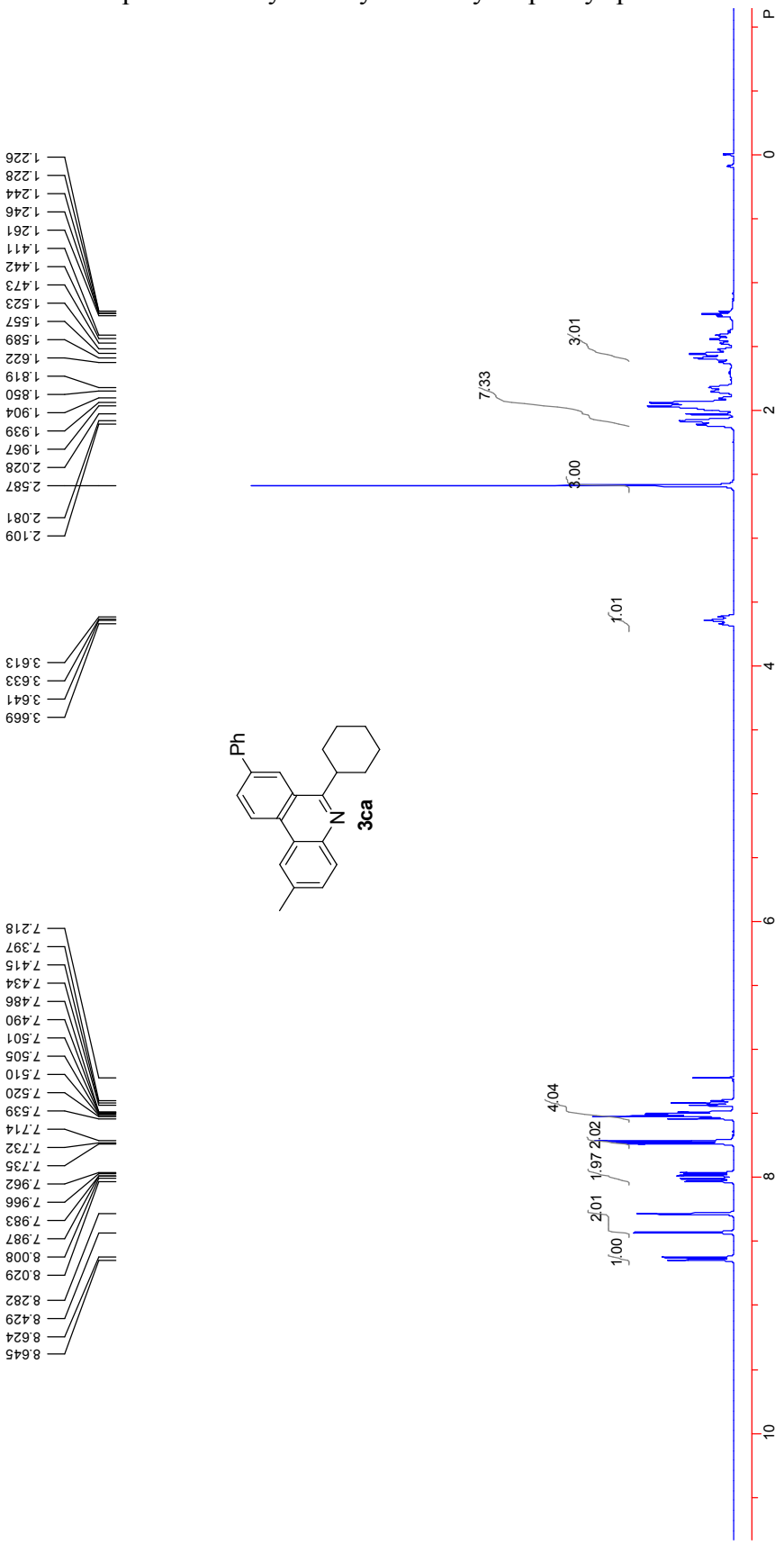
^{13}C NMR spectra of 6-cyclohexyl-2,8-dimethylphenanthridine (**3aa**)



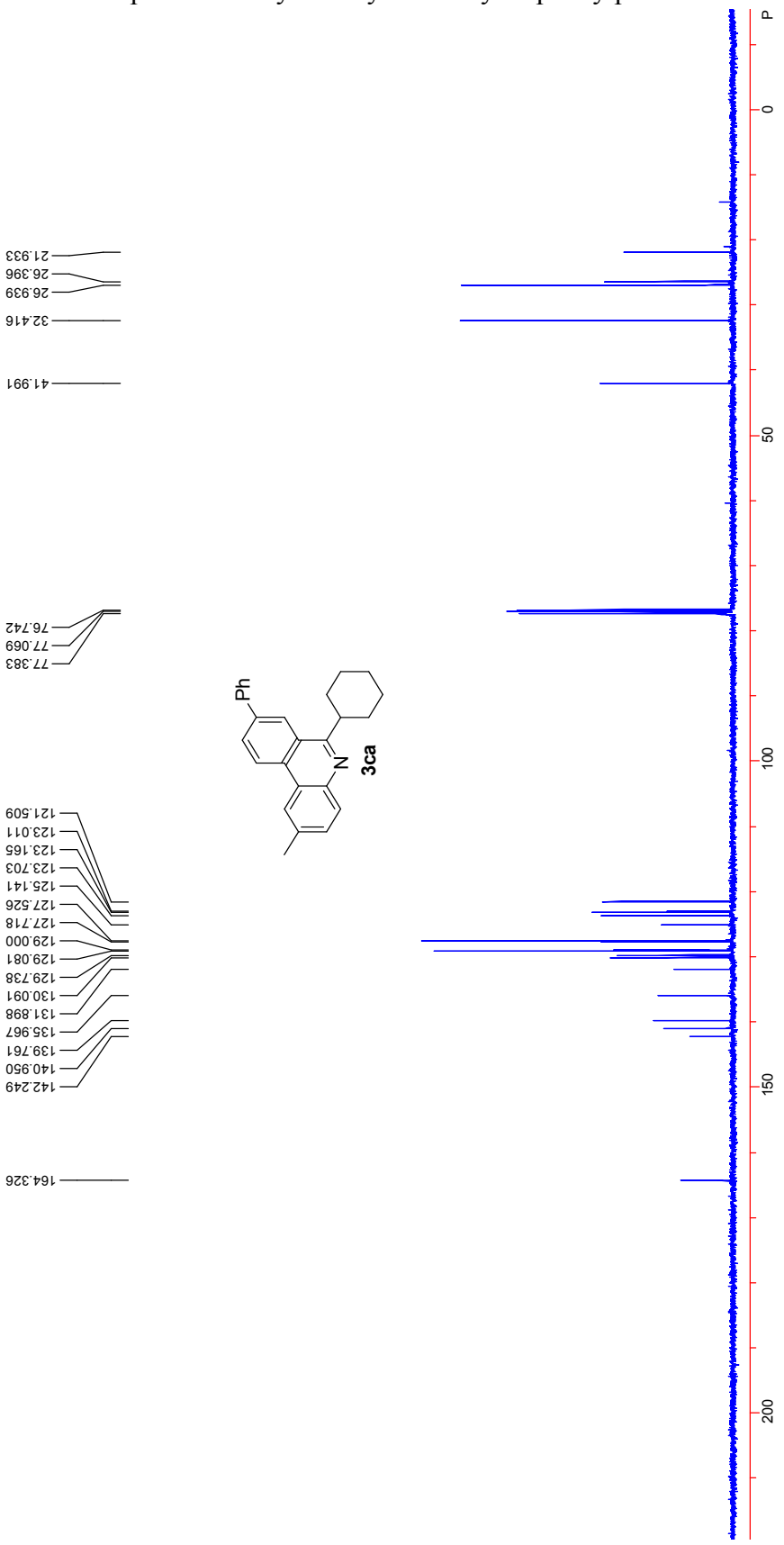
HR-MS spectra of 6-cyclohexyl-2,8-dimethylphenanthridine (**3aa**)



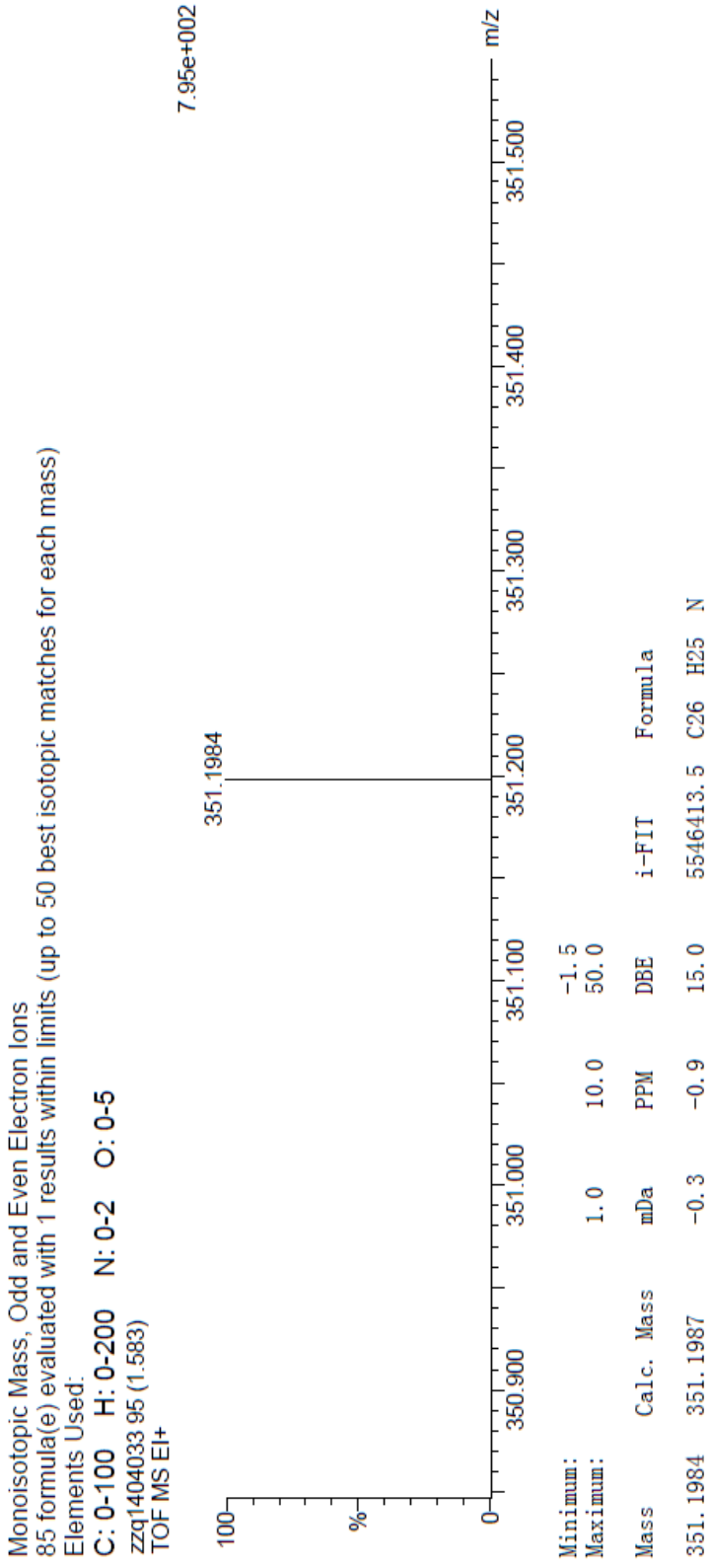
[1]H NMR spectra of 6-cyclohexyl-2-methyl-8-phenyl-phenanthridine (**3ca**)



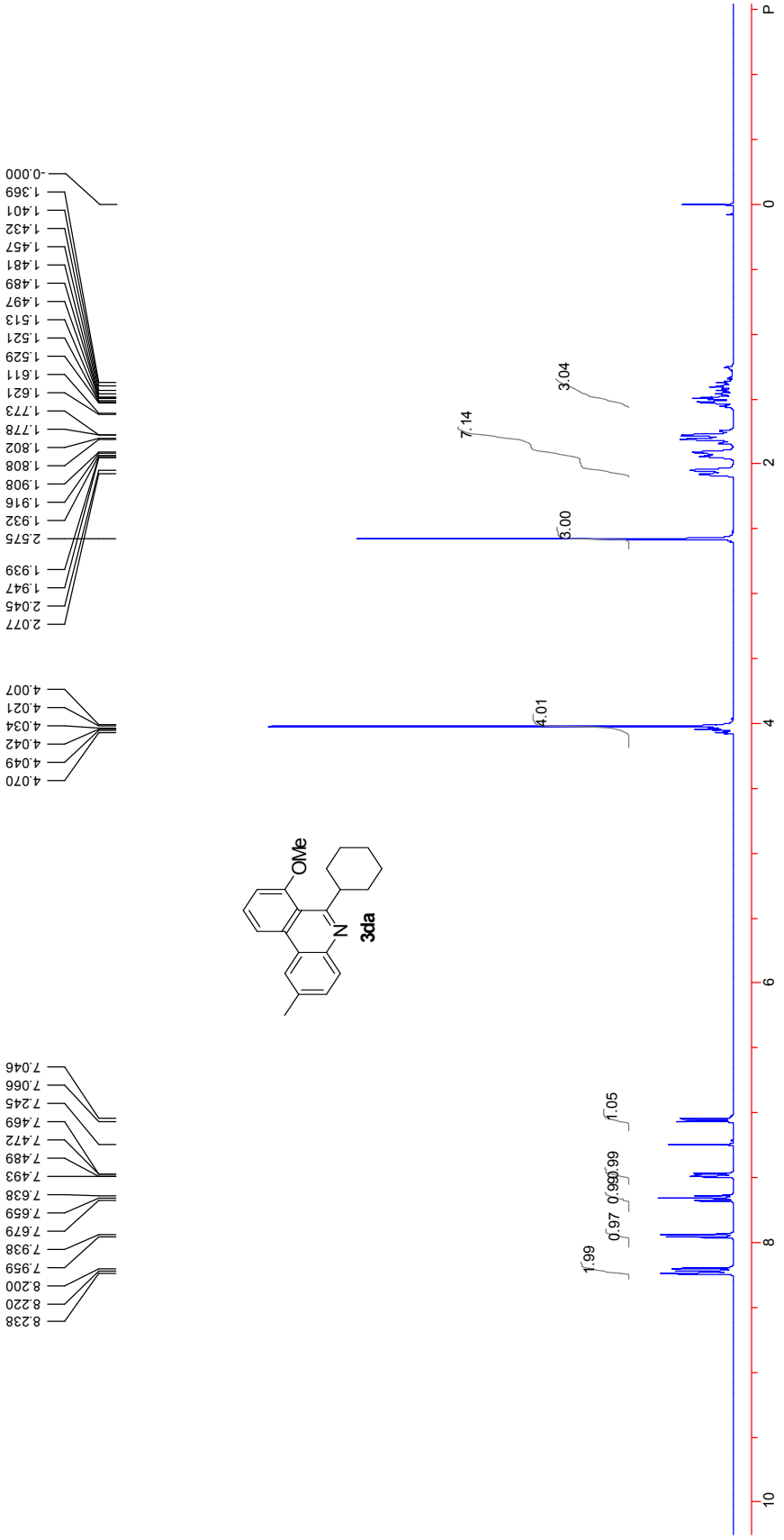
^{13}C NMR spectra of 6-cyclohexyl-2-methyl-8-phenylphenanthridine (**3ca**)



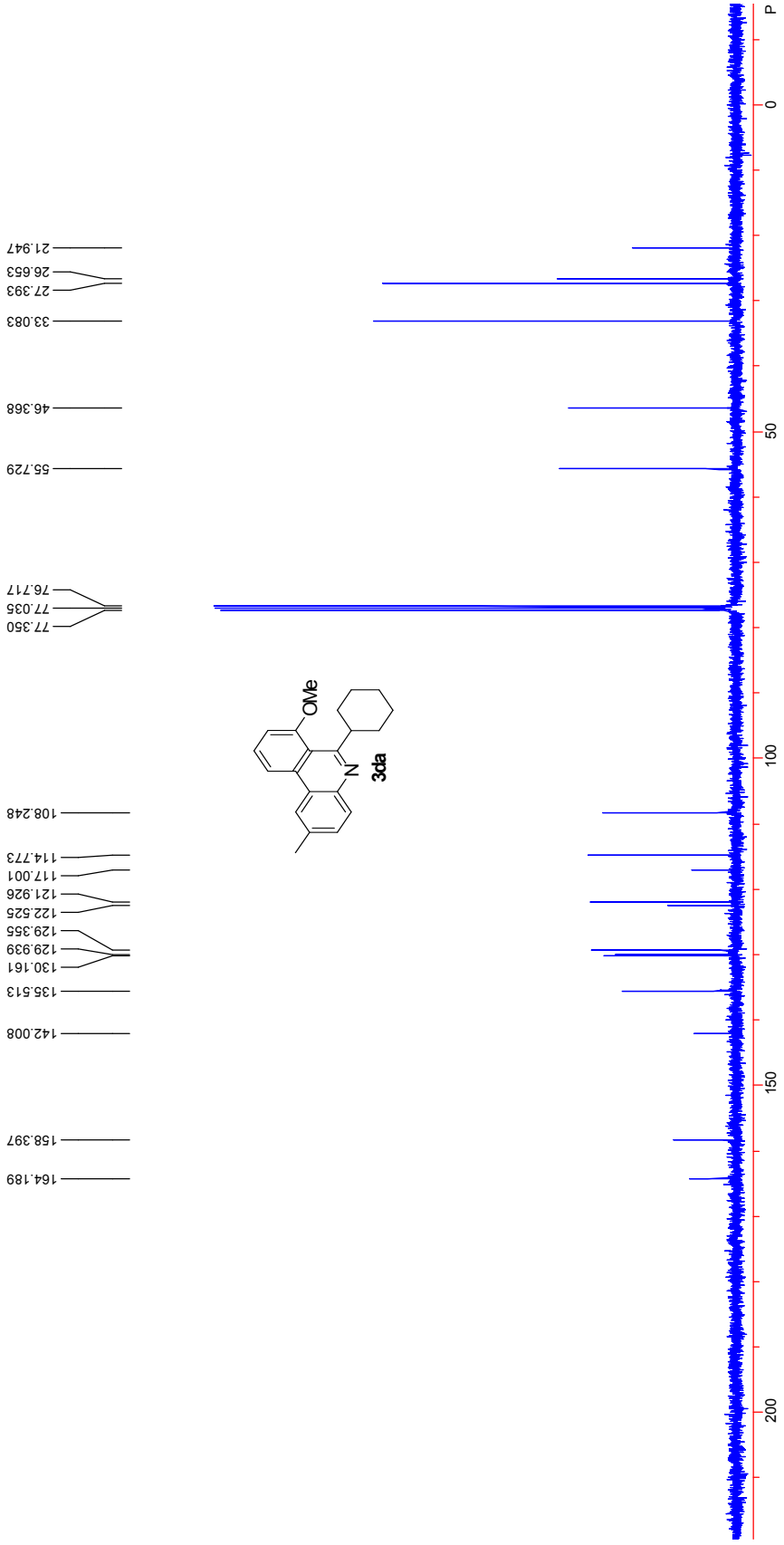
HR-MS spectra of 6-cyclohexyl-2-methyl-8-phenylphenanthridine (**3ca**)



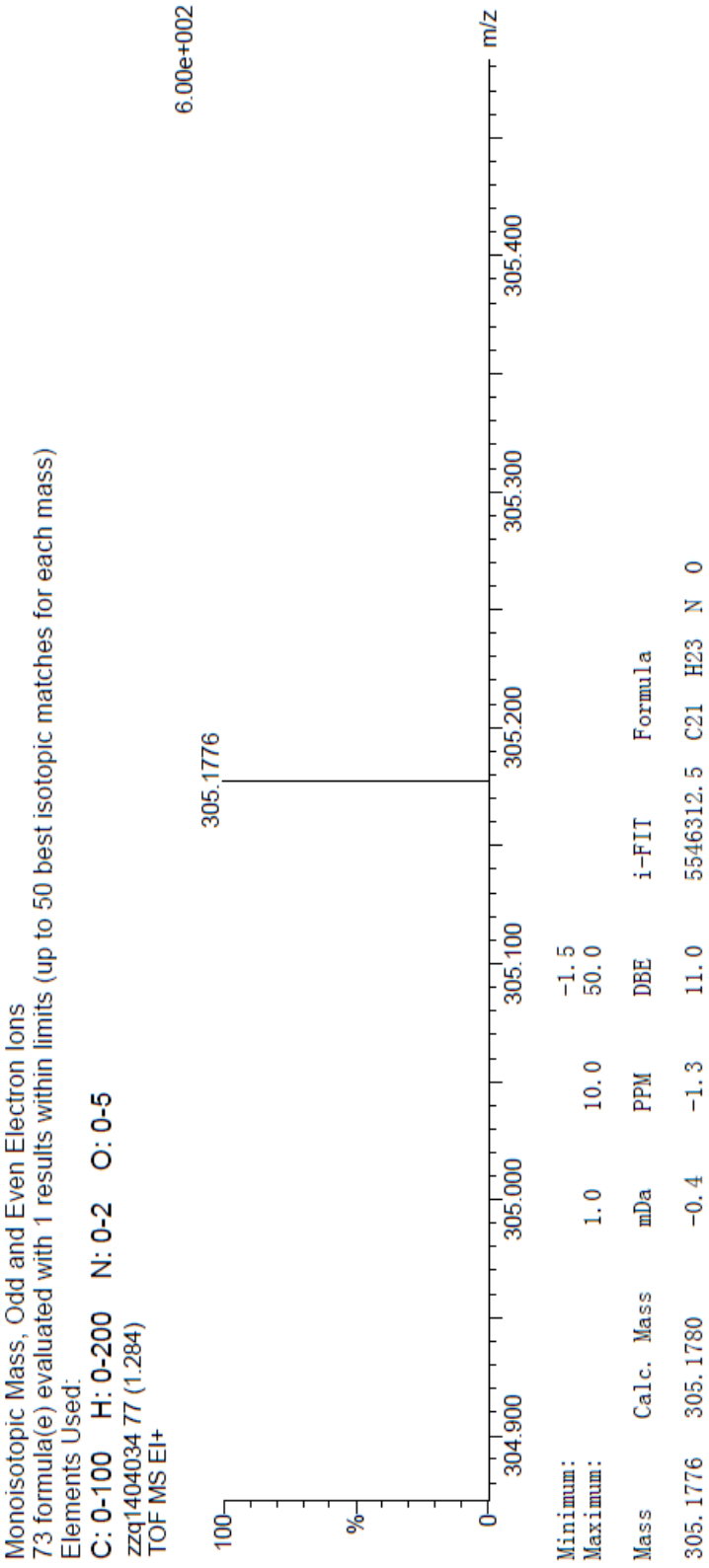
[1]H NMR spectra of 6-cyclohexyl-7-methoxy-2-methylphenanthridine (**3da**)



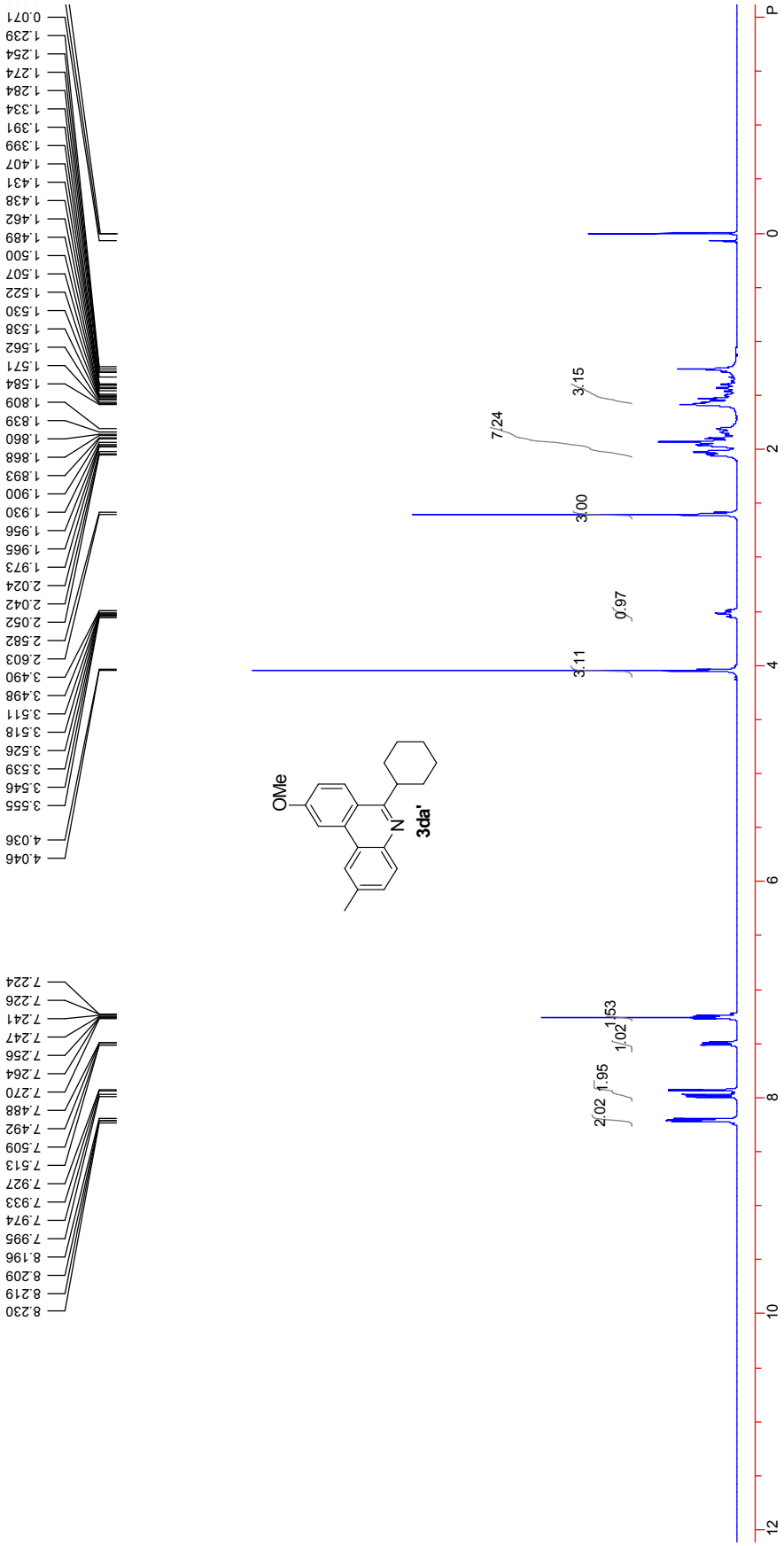
^{13}C NMR spectra of 6-cyclohexyl-7-methoxy-2-methylphenanthridine (**3da**)



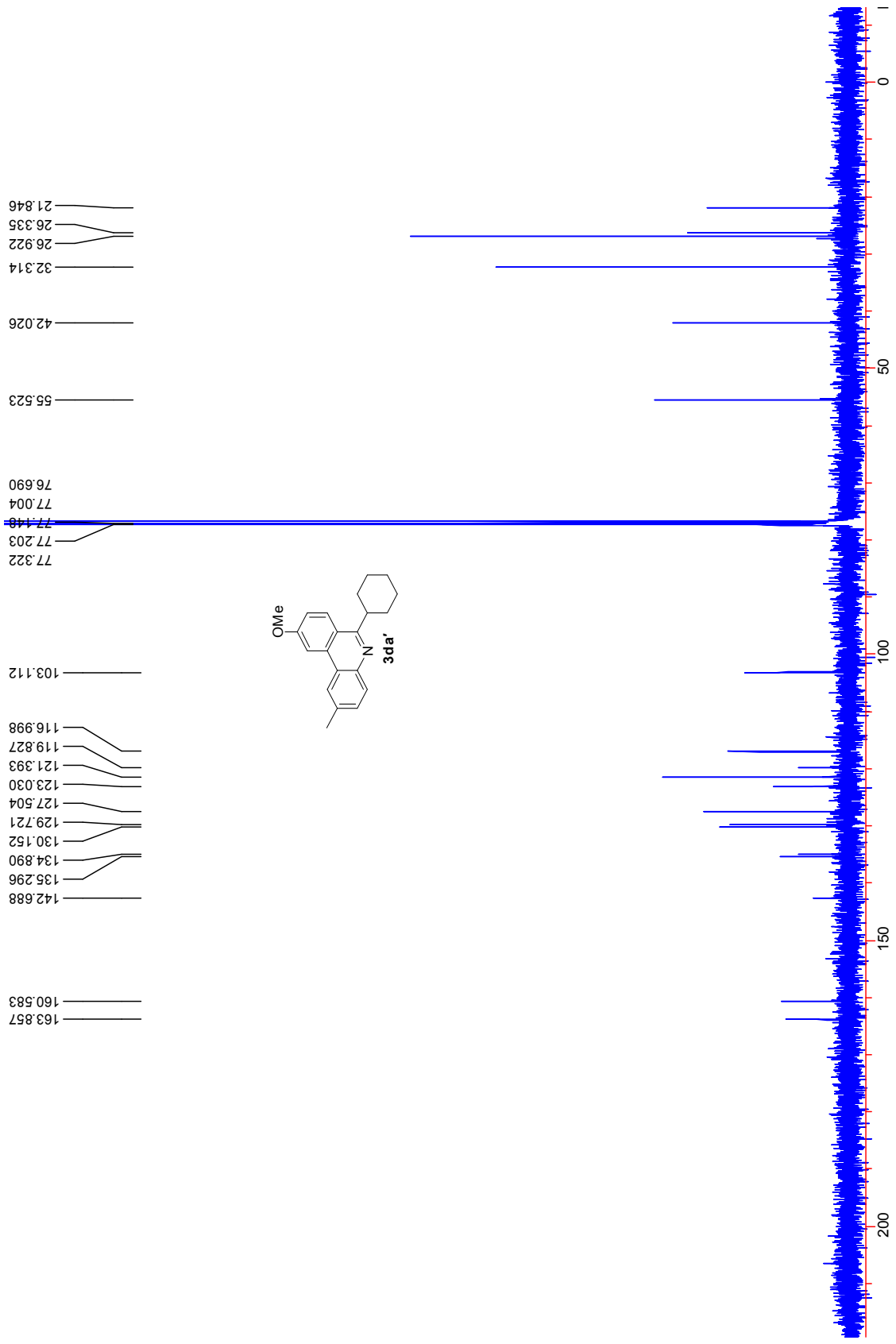
HR-MS spectra of 6-cyclohexyl-7-methoxy-2-methylphenanthridine (**3da**)



^{1}H NMR spectra of 6-cyclohexyl-9-methoxy-2-methylphenanthridine (**3da′**)

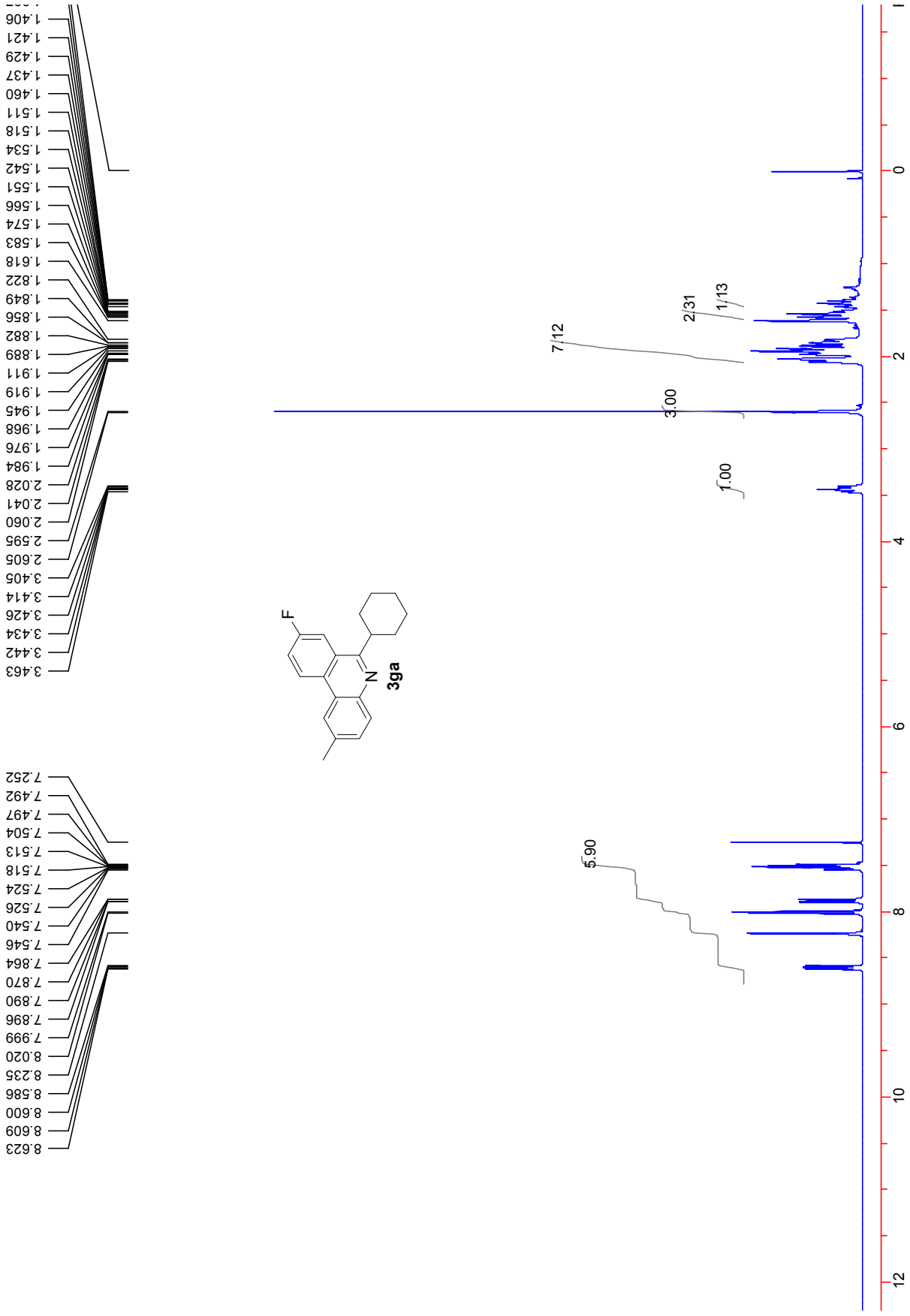


^{13}C NMR spectra of 6-cyclohexyl-9-methoxy-2-methylphenanthridine (**3da′**)

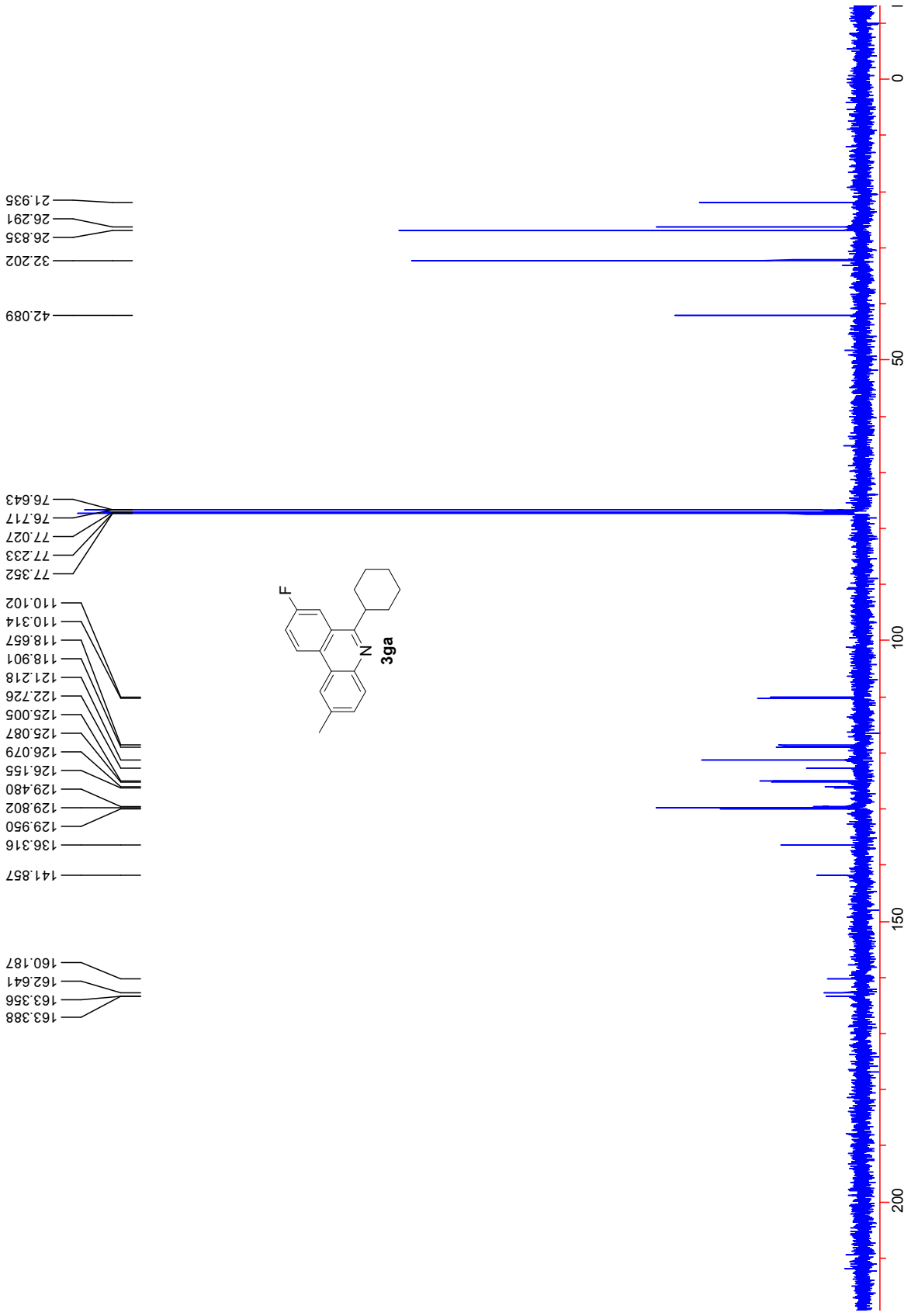


HR-MS spectra of 6-cyclohexyl-7-methoxy-2-methylphenanthridine (**3da′**)

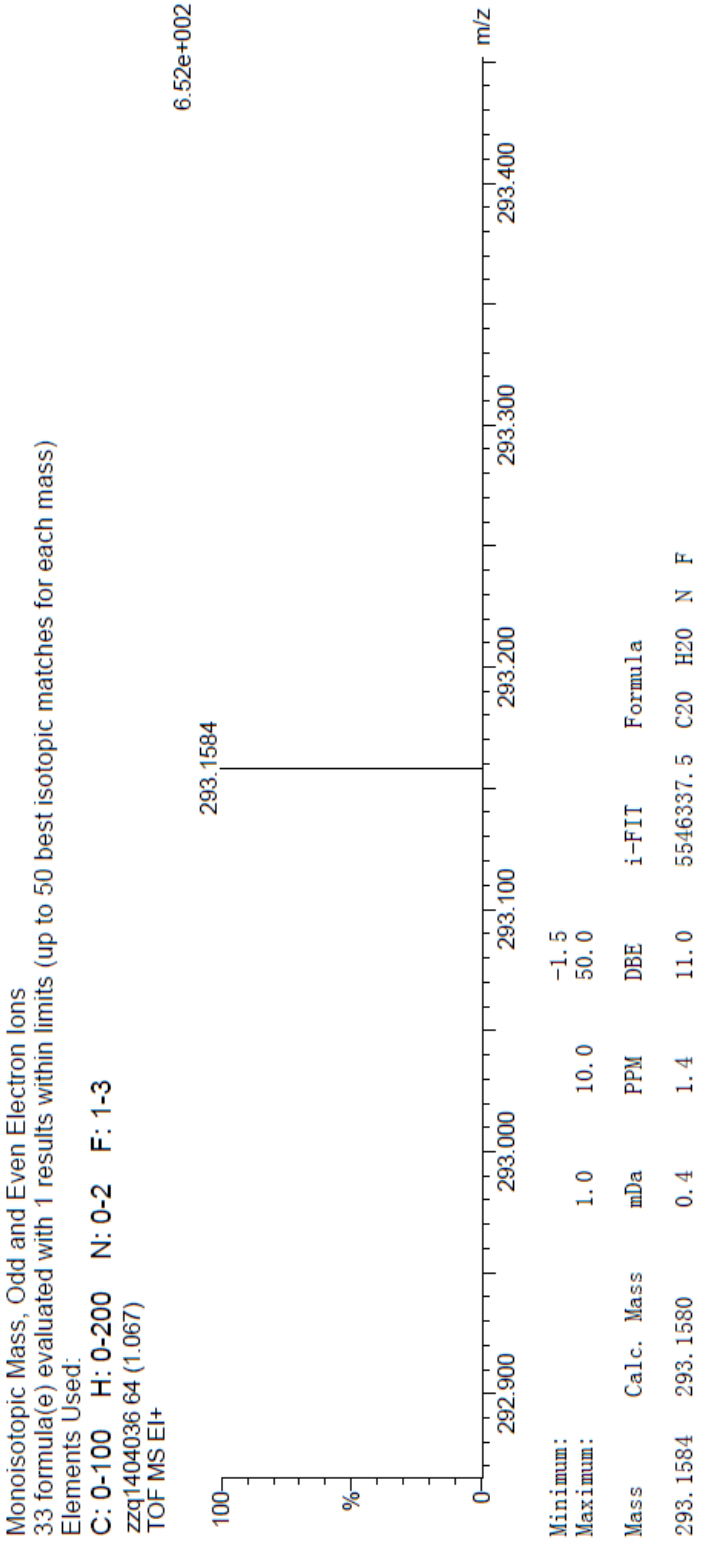
^{1}H NMR spectra of 6-cyclohexyl-8-fluoro-2-methylphenanthridine (**3ga**)



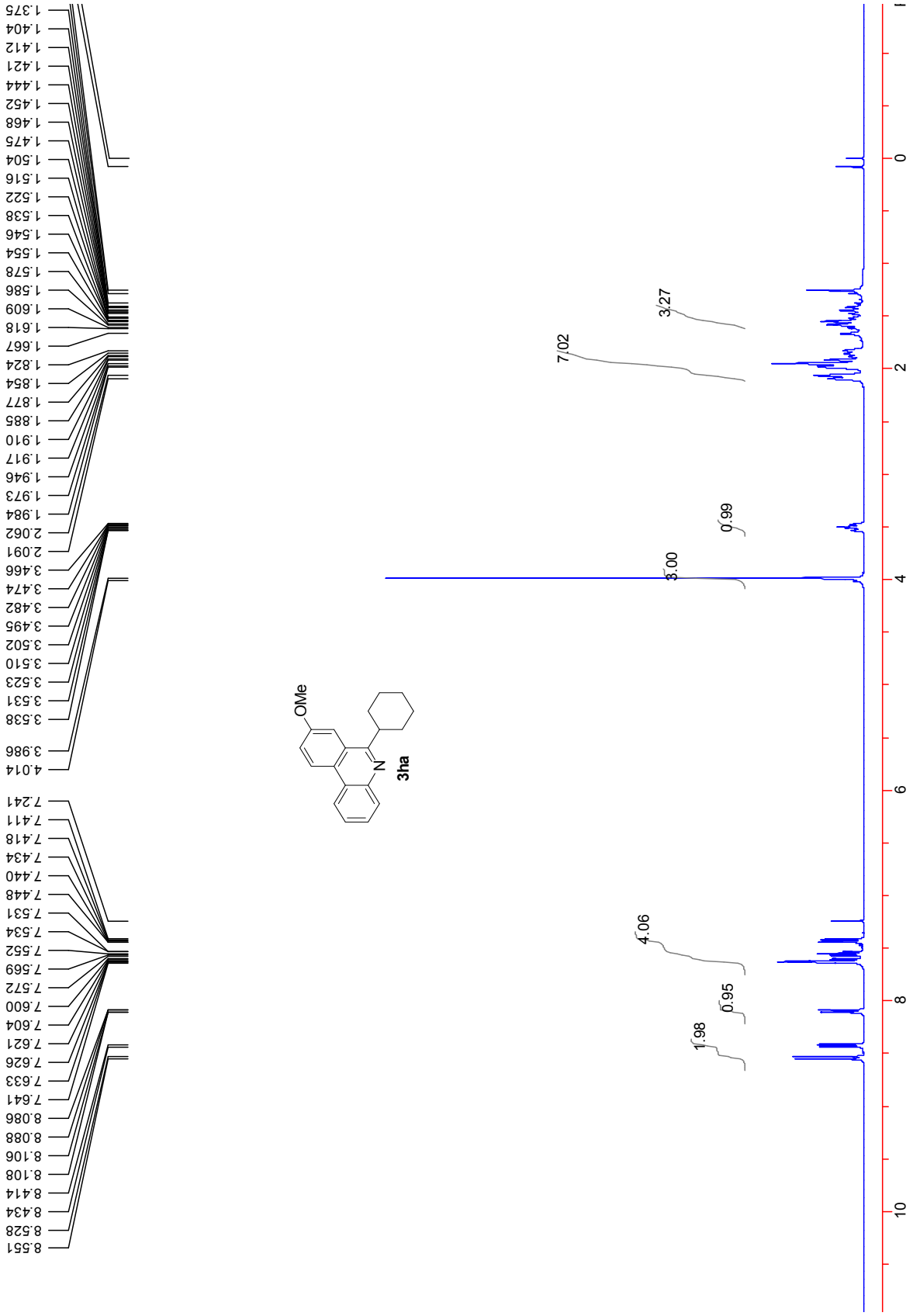
^{13}C NMR spectra of 6-cyclohexyl-8-fluoro-2-methylphenanthridine (**3ga**)



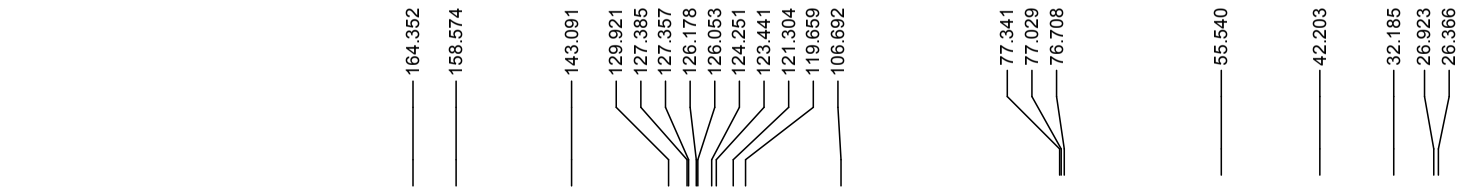
HR-MS spectra of 6-cyclohexyl-8-fluoro-2-methylphenanthridine (**3ga**)

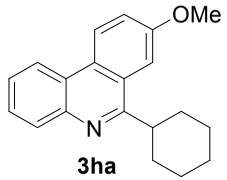


^{1}H NMR spectra of 6-cyclohexyl-8-methoxyphenanthridine (**3ha**)

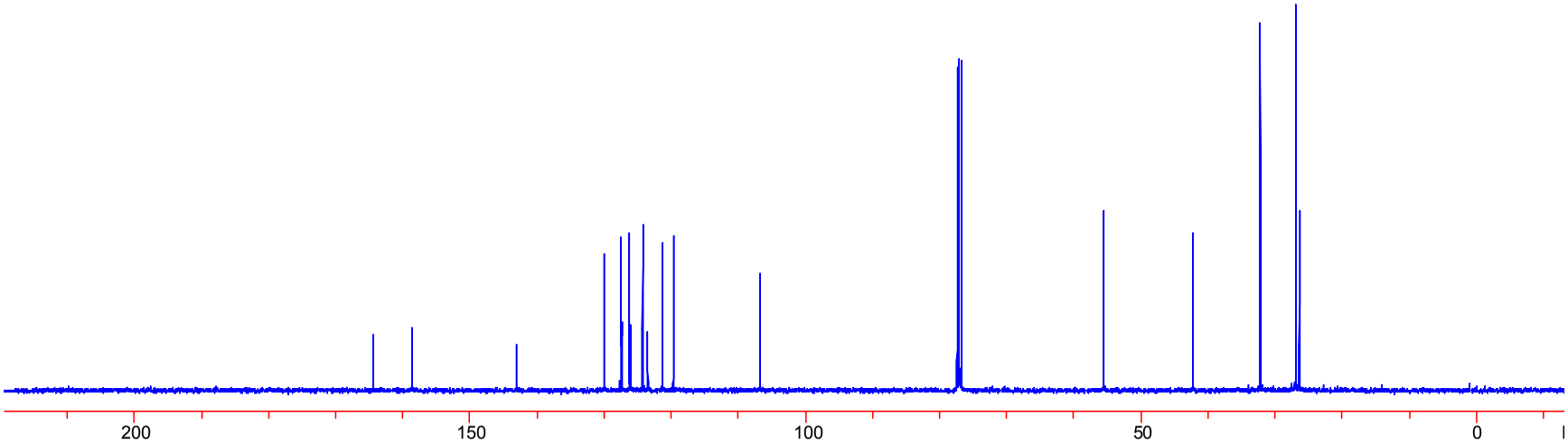


^{13}C NMR spectra of 6-cyclohexyl-8-methoxyphenanthridine (**3ha**)

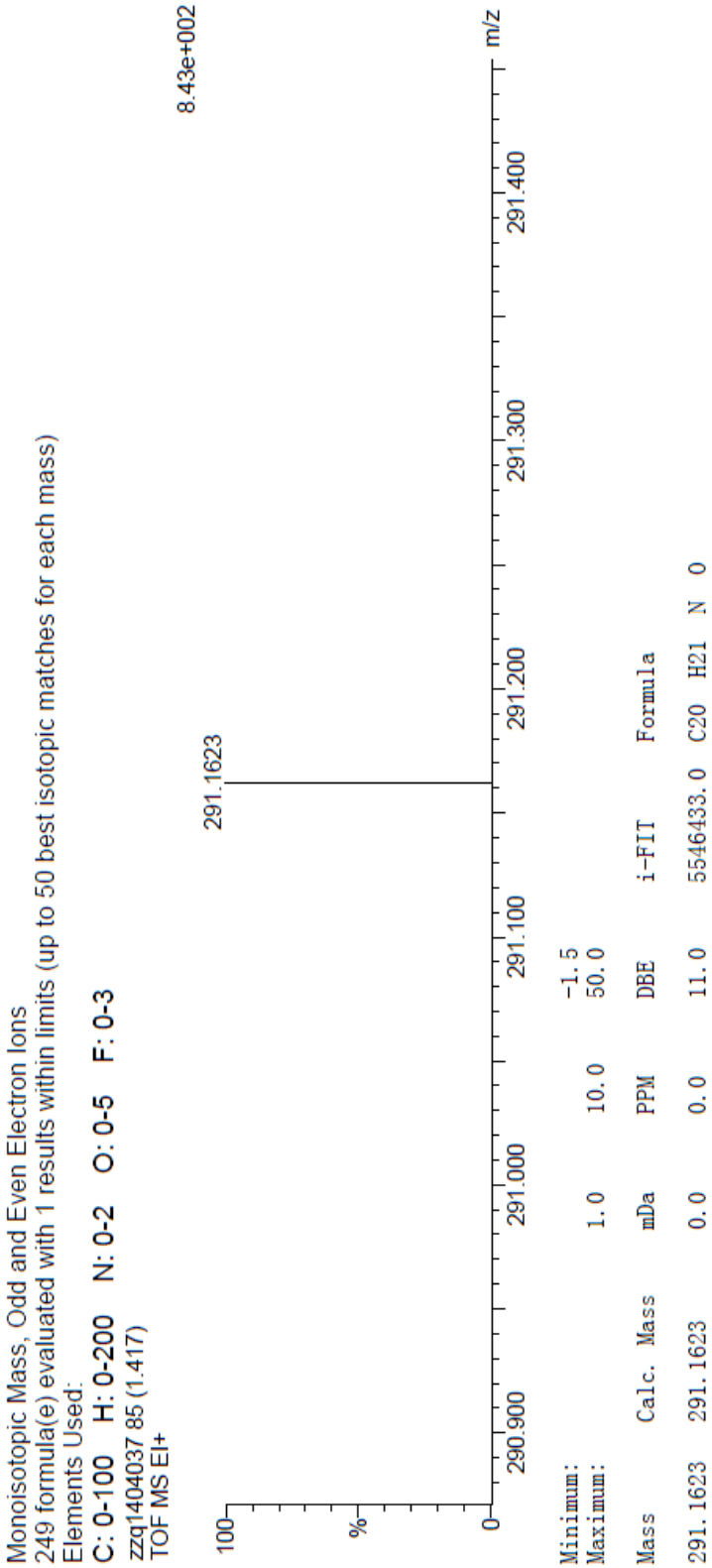

164.352
158.574
143.091
129.921
127.385
127.357
126.178
126.053
124.251
123.441
121.304
119.659
106.692
77.341
77.029
76.708
55.540
42.203
32.185
26.923
26.366


OMe
N

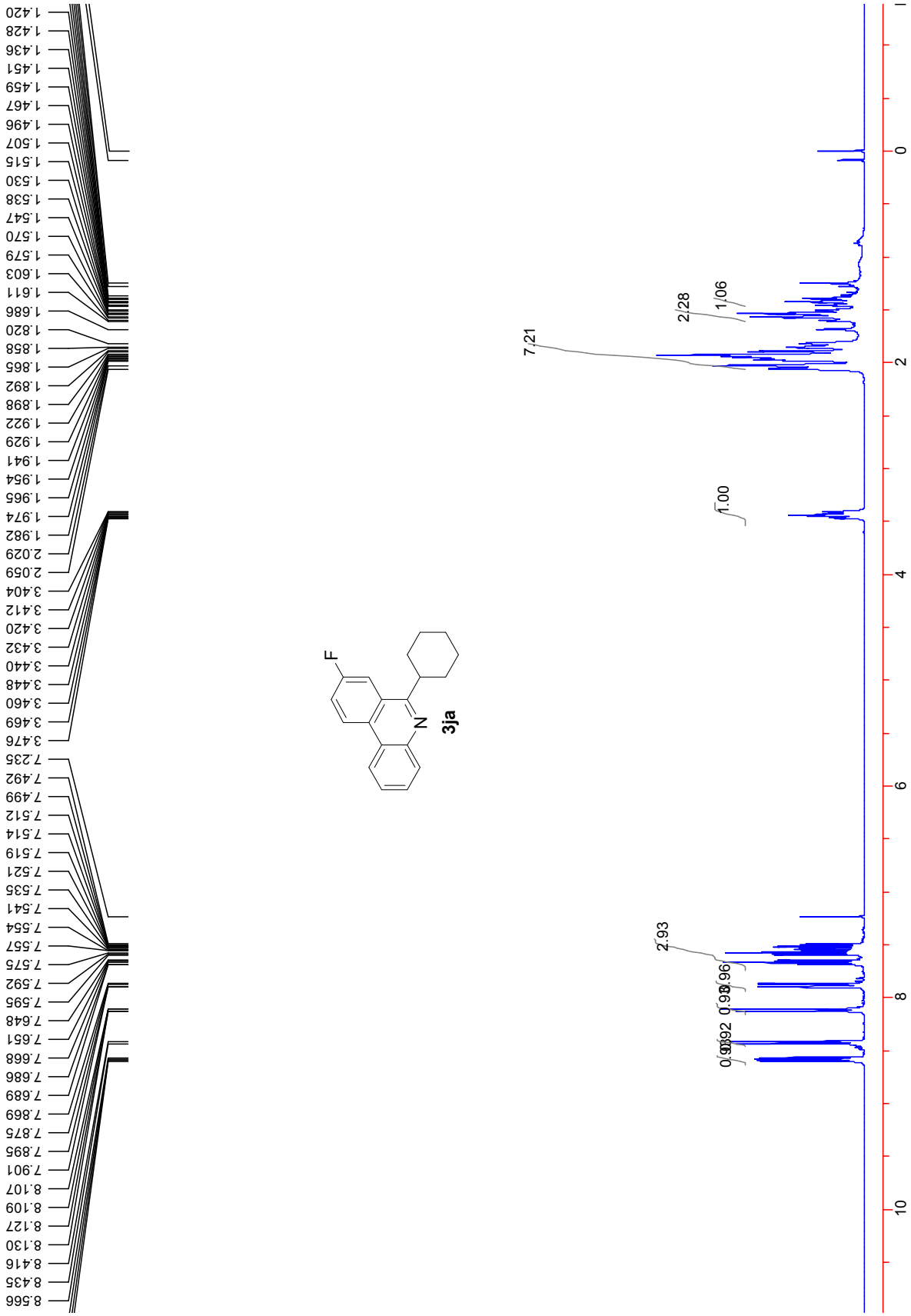
3ha


200
150
100
50
0

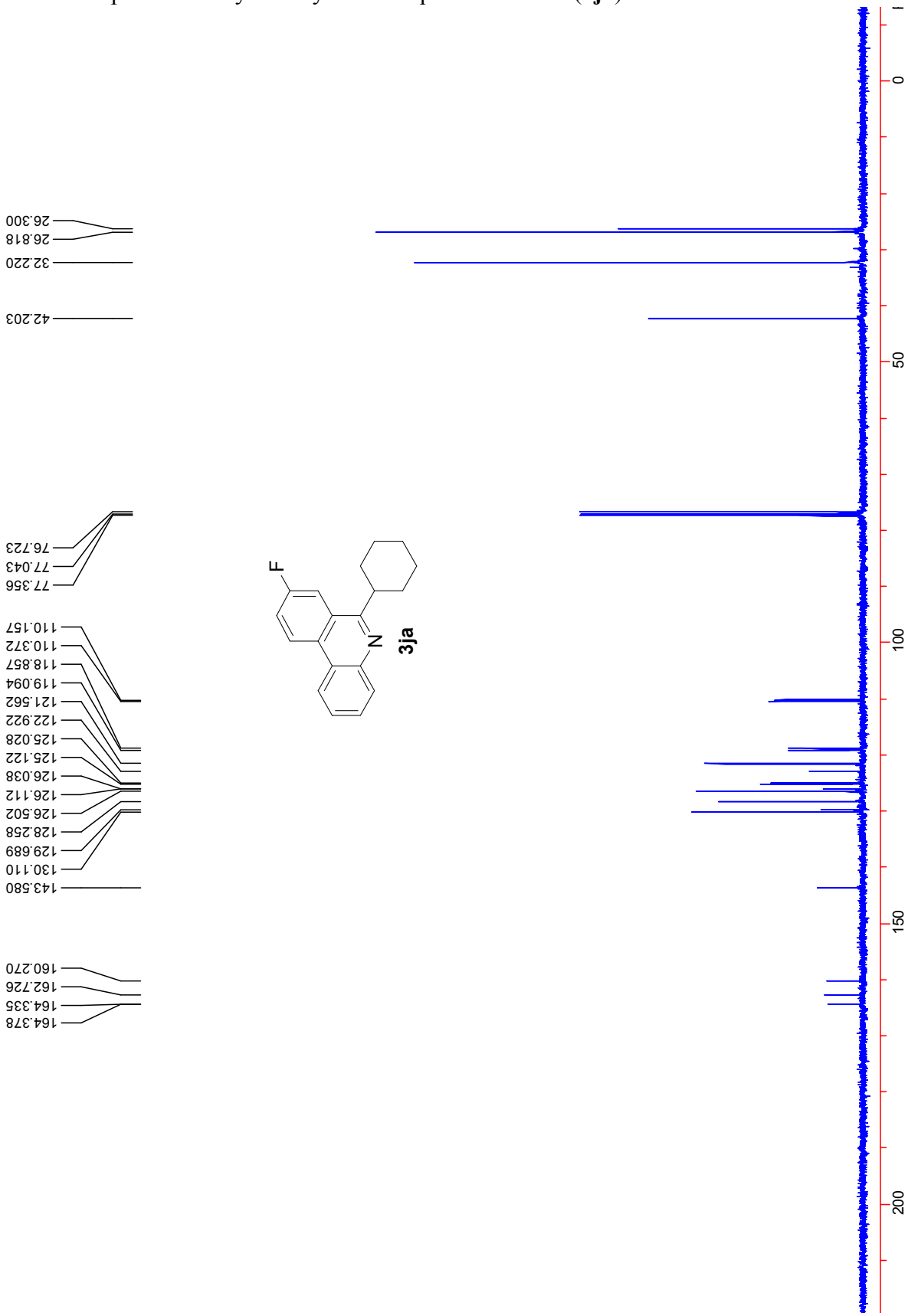
HR-MS spectra of 6-cyclohexyl-8-methoxyphenanthridine (**3ha**)



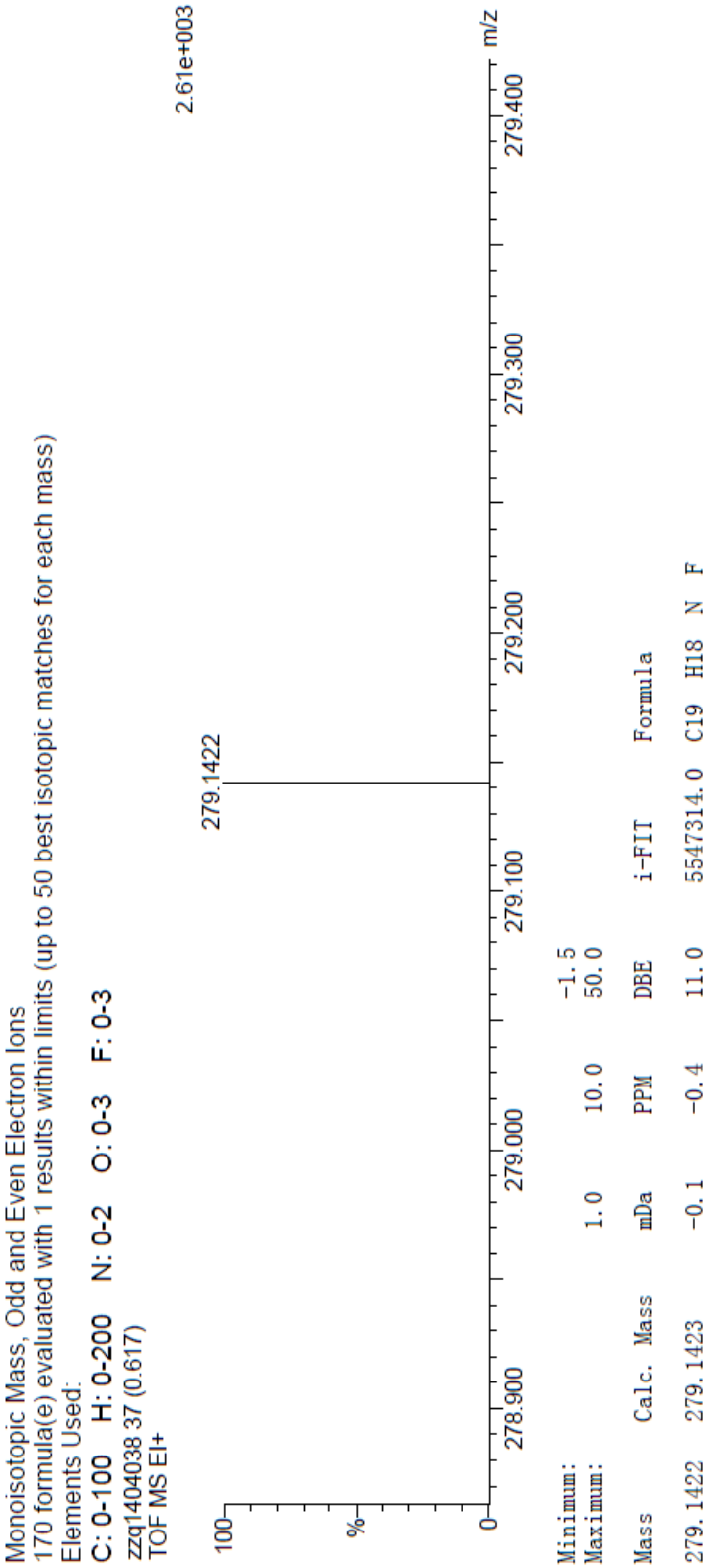
[1]H NMR spectra of 6-cyclohexyl-8-fluorophenanthridine (**3ja**)



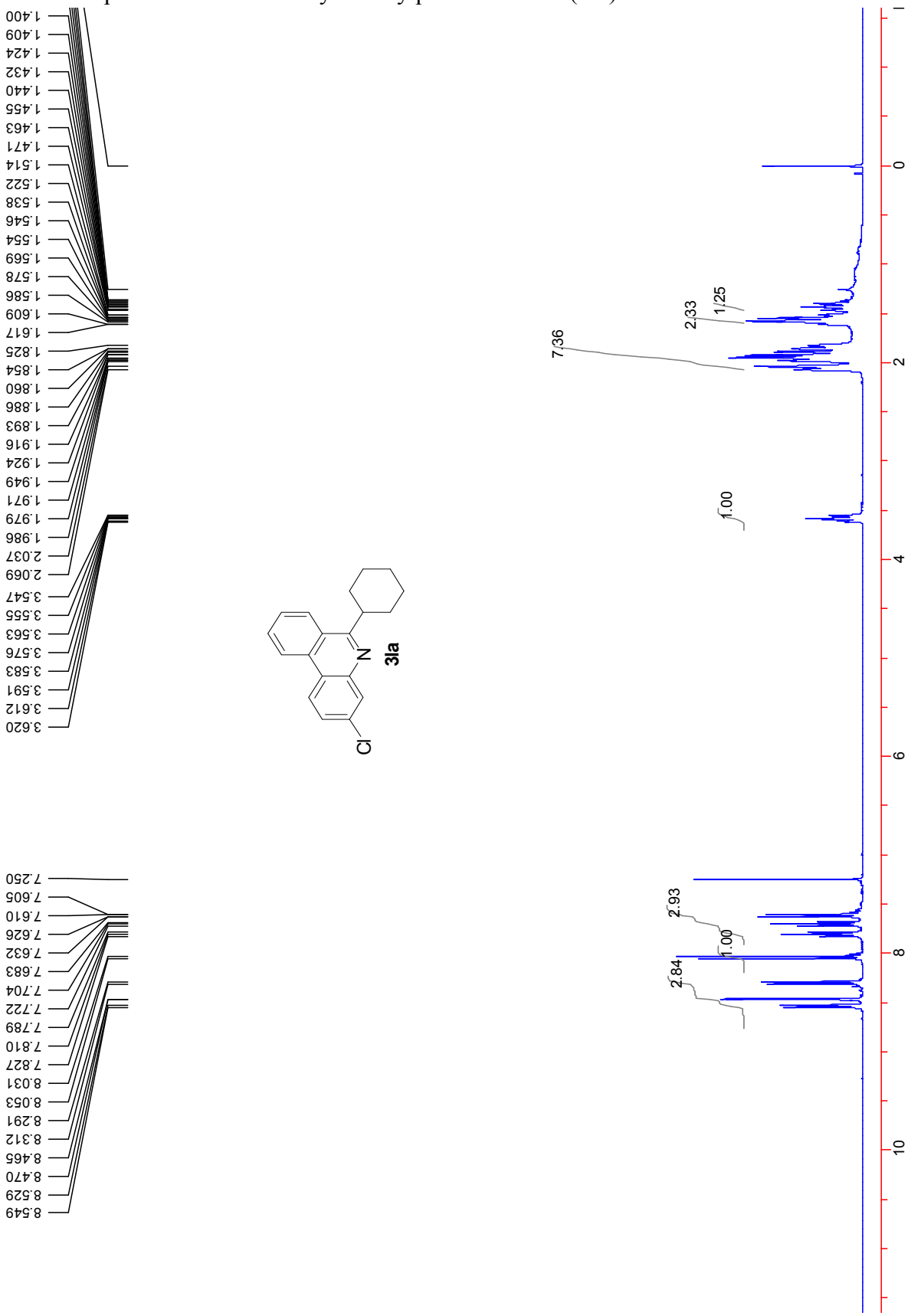
^{13}C NMR spectra of 6-cyclohexyl-8-fluorophenanthridine (**3ja**)



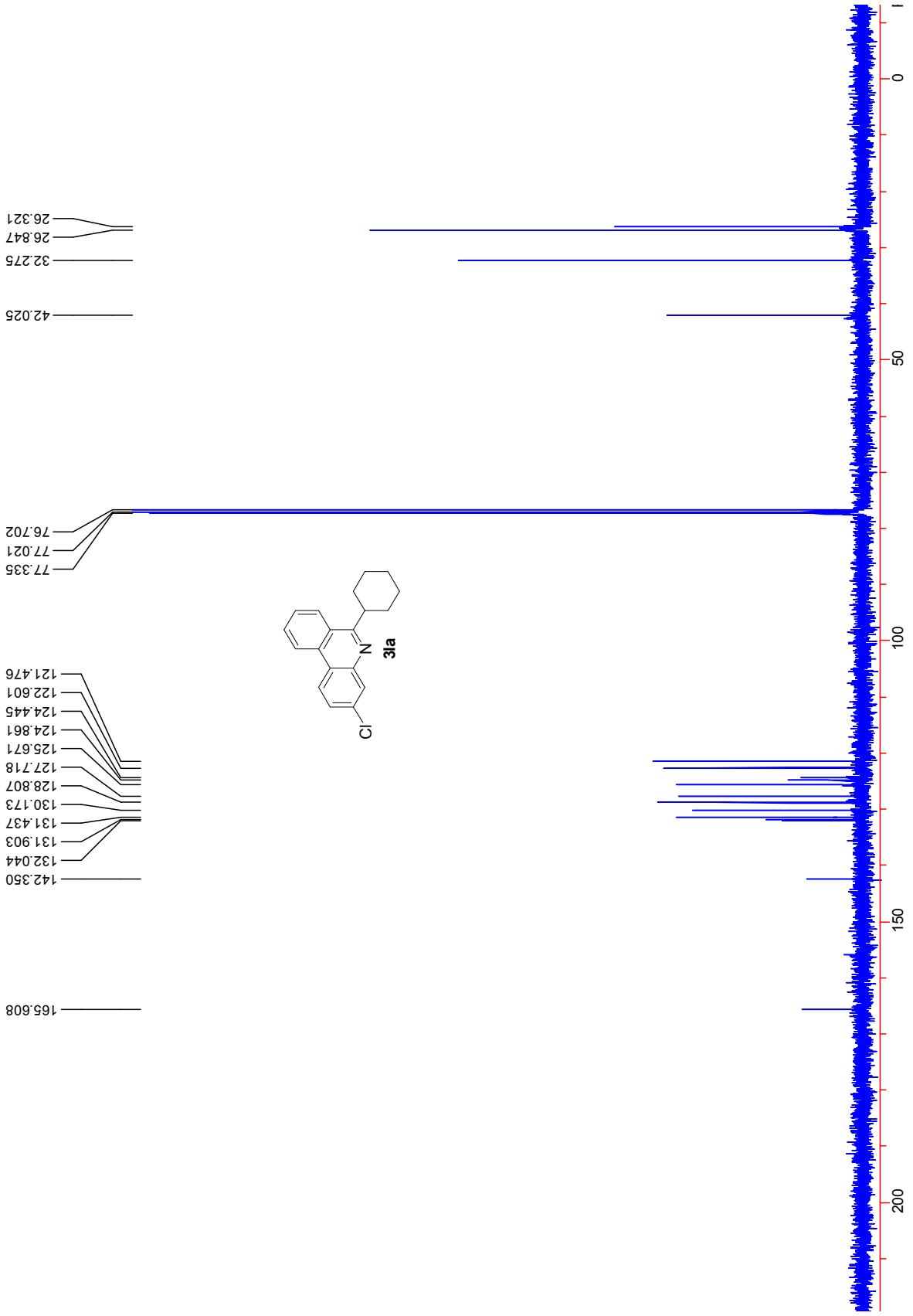
HR-MS spectra of 6-cyclohexyl-8-fluorophenanthridine (**3ja**)



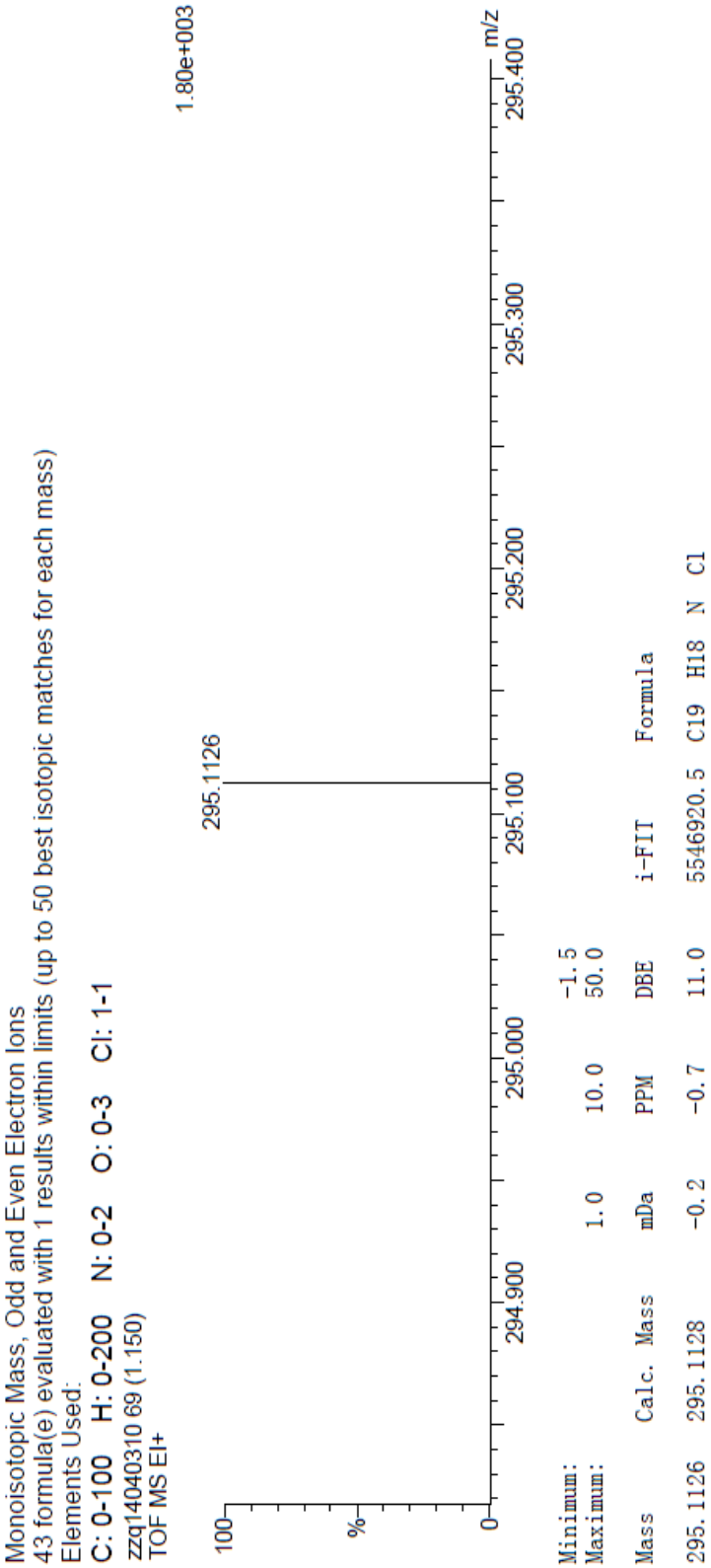
[1]H NMR spectra of 3-chloro-6-cyclohexylphenanthridine (**3la**)



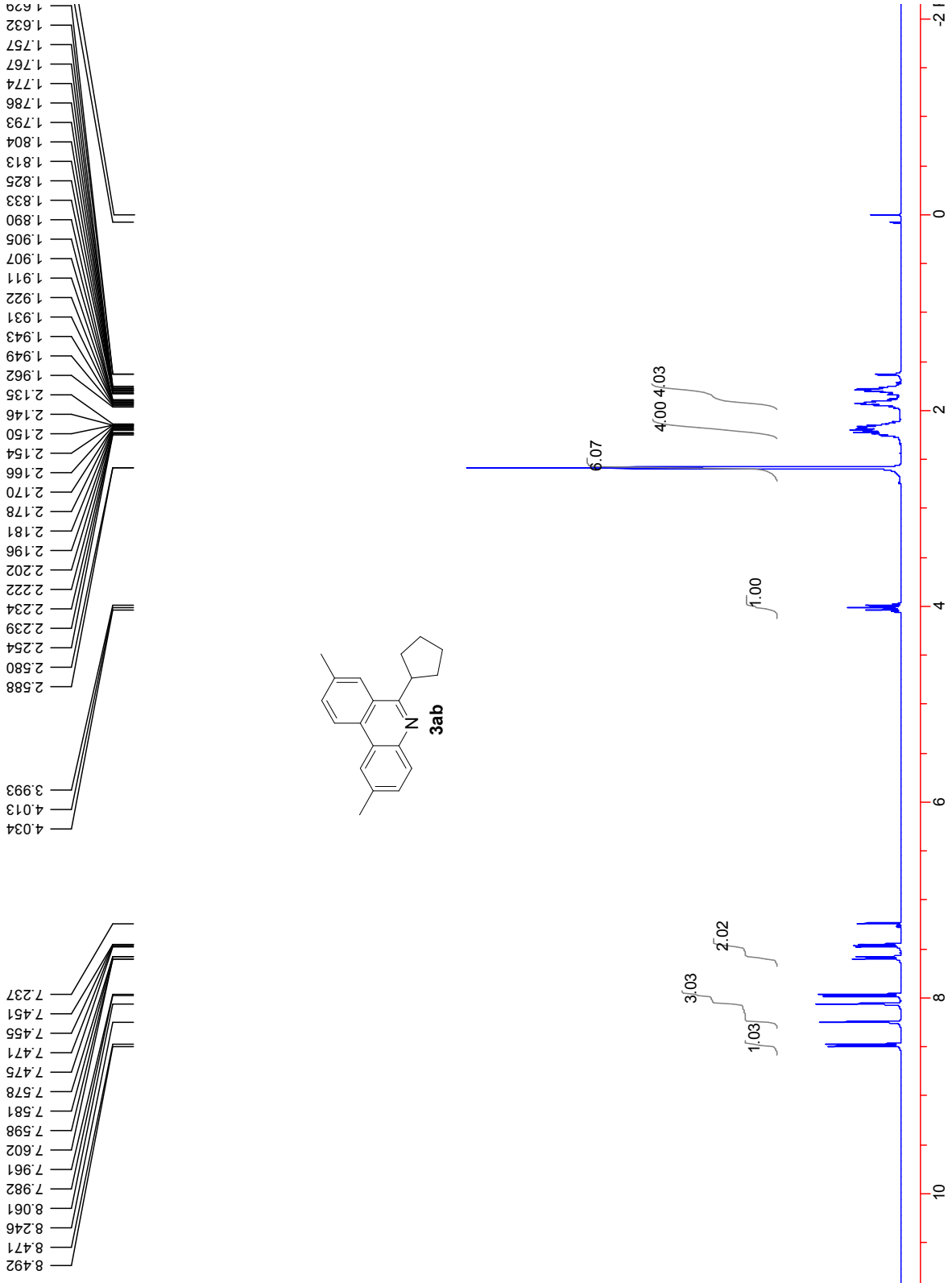
^{13}C NMR spectra of 3-chloro-6-cyclohexylphenanthridine (**3la**)



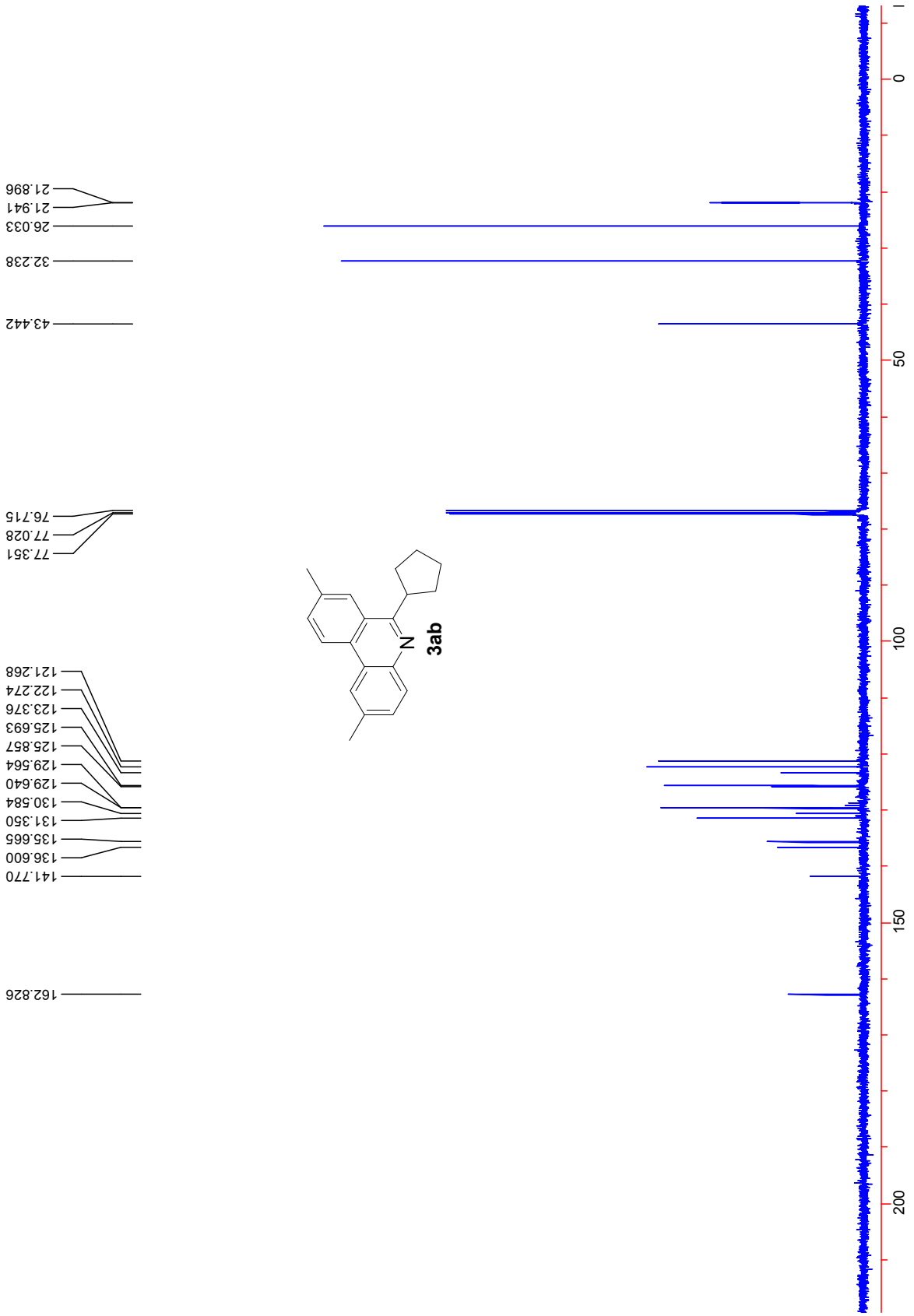
HR-MS spectra of 3-chloro-6-cyclohexylphenanthridine (**3la**)



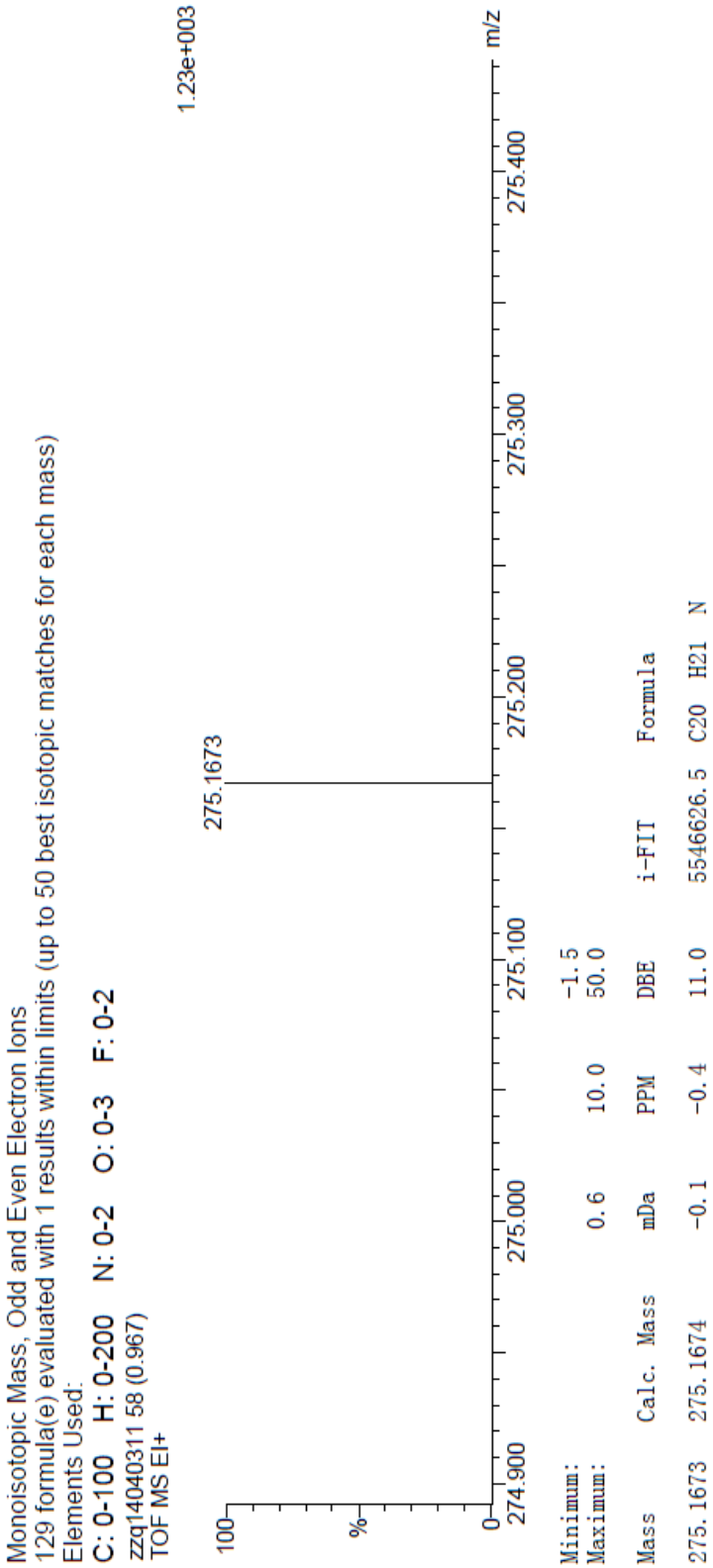
[1]H NMR spectra of 6-cyclopentyl-2,8-dimethylphenanthridine (**3ab**)



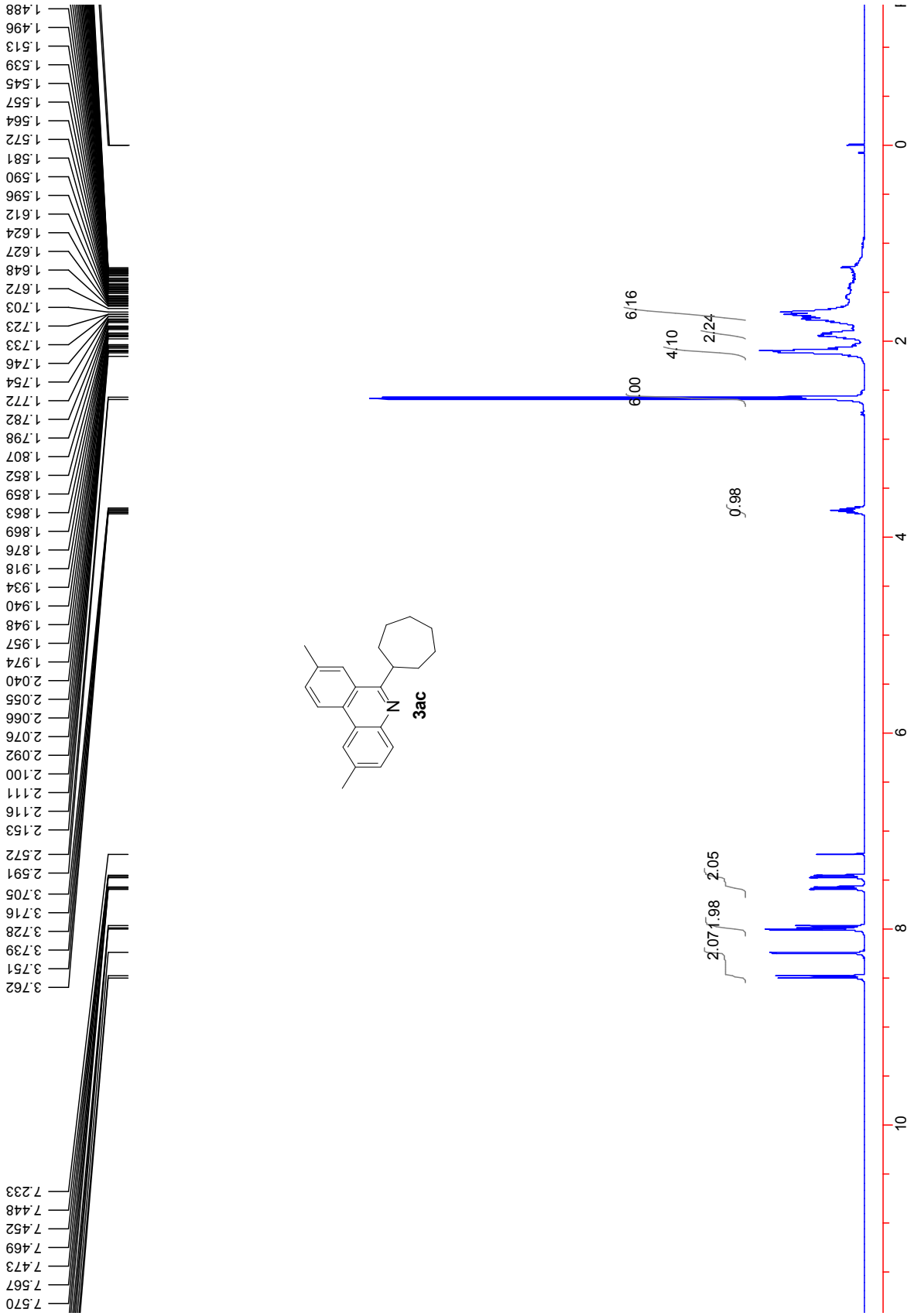
^{13}C NMR spectra of 6-cyclopentyl-2,8-dimethylphenanthridine (**3ab**)



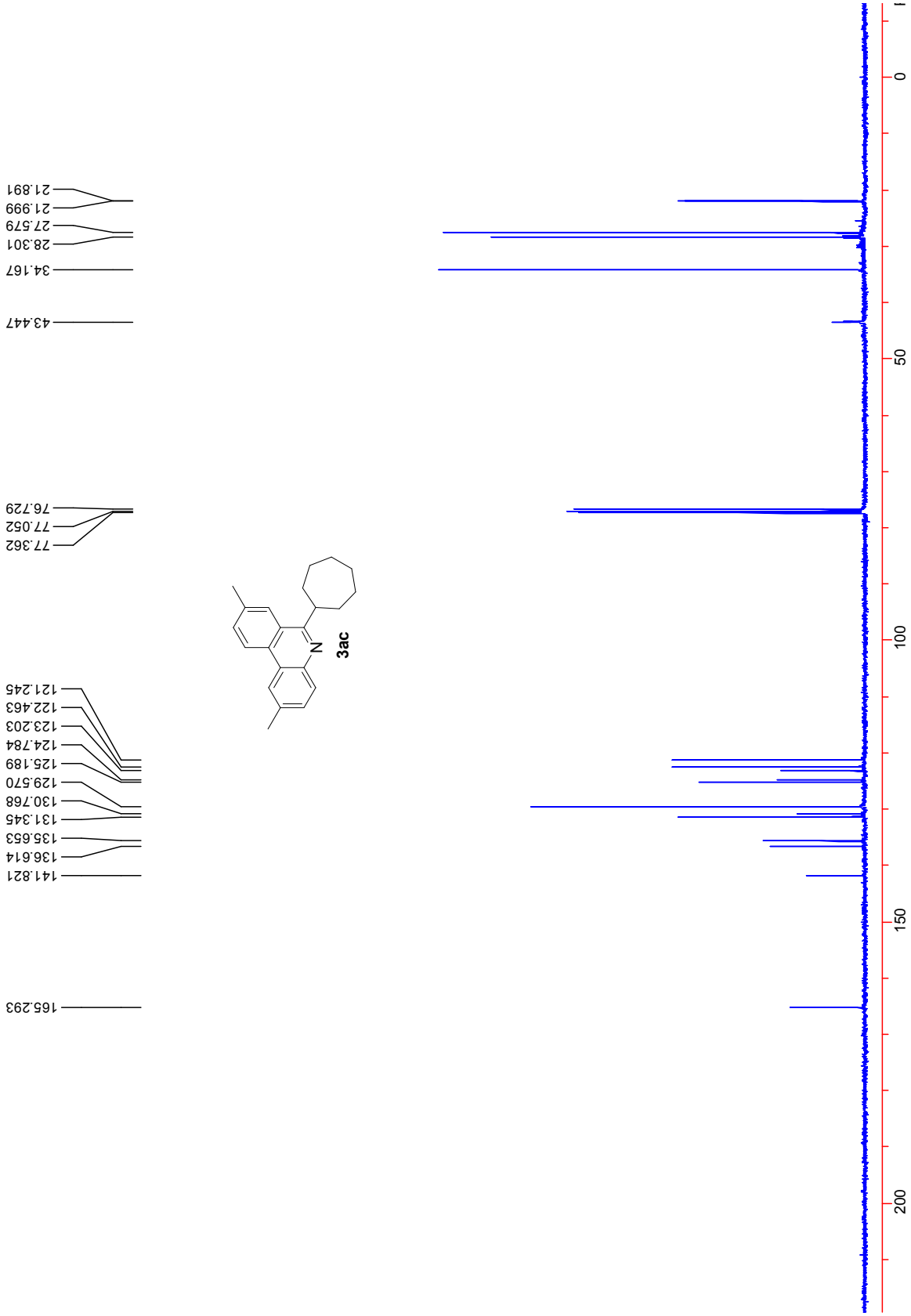
HR-MS spectra of 6-cyclopentyl-2,8-dimethylphenanthridine (**3ab**)



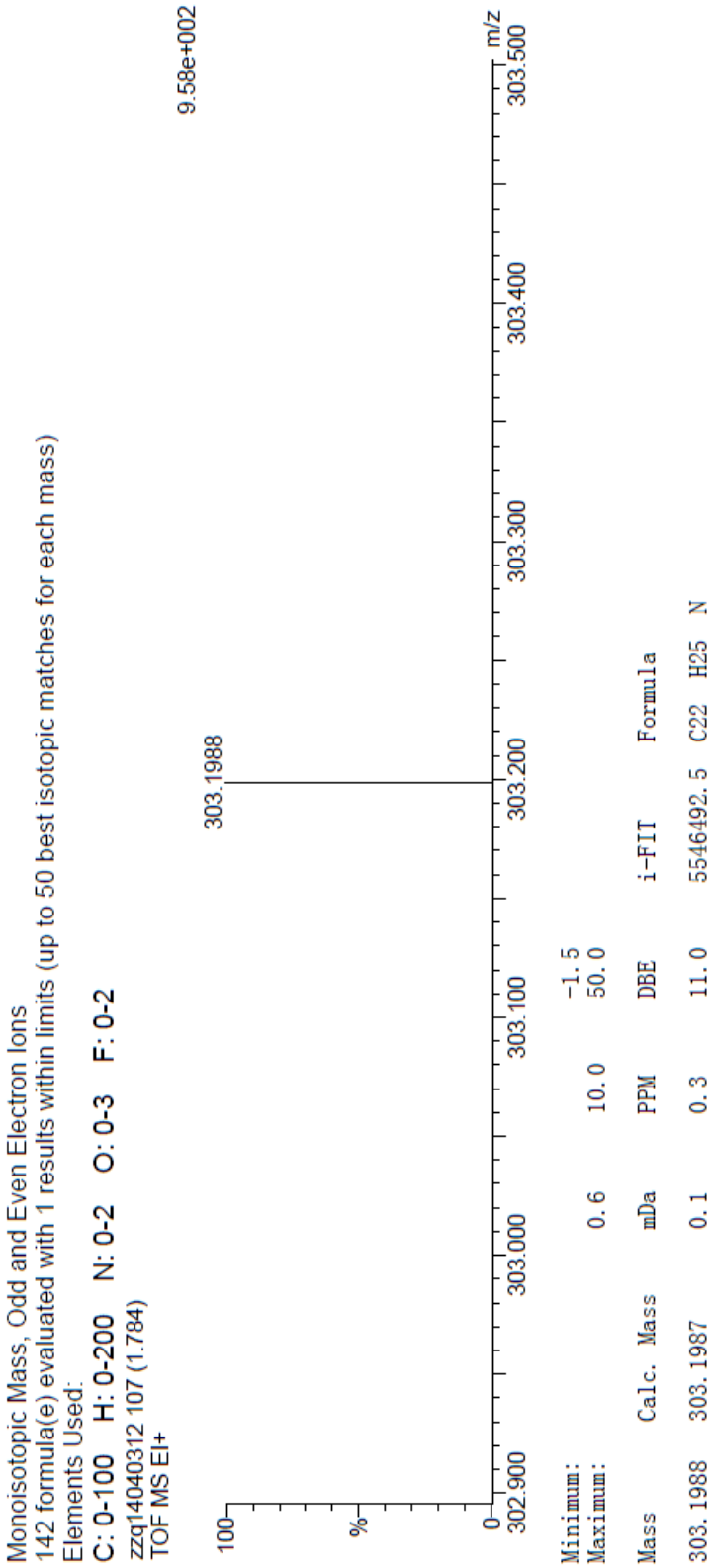
^{1}H NMR spectra of 6-cycloheptyl-2,8-dimethylphenanthridine (**3ac**)



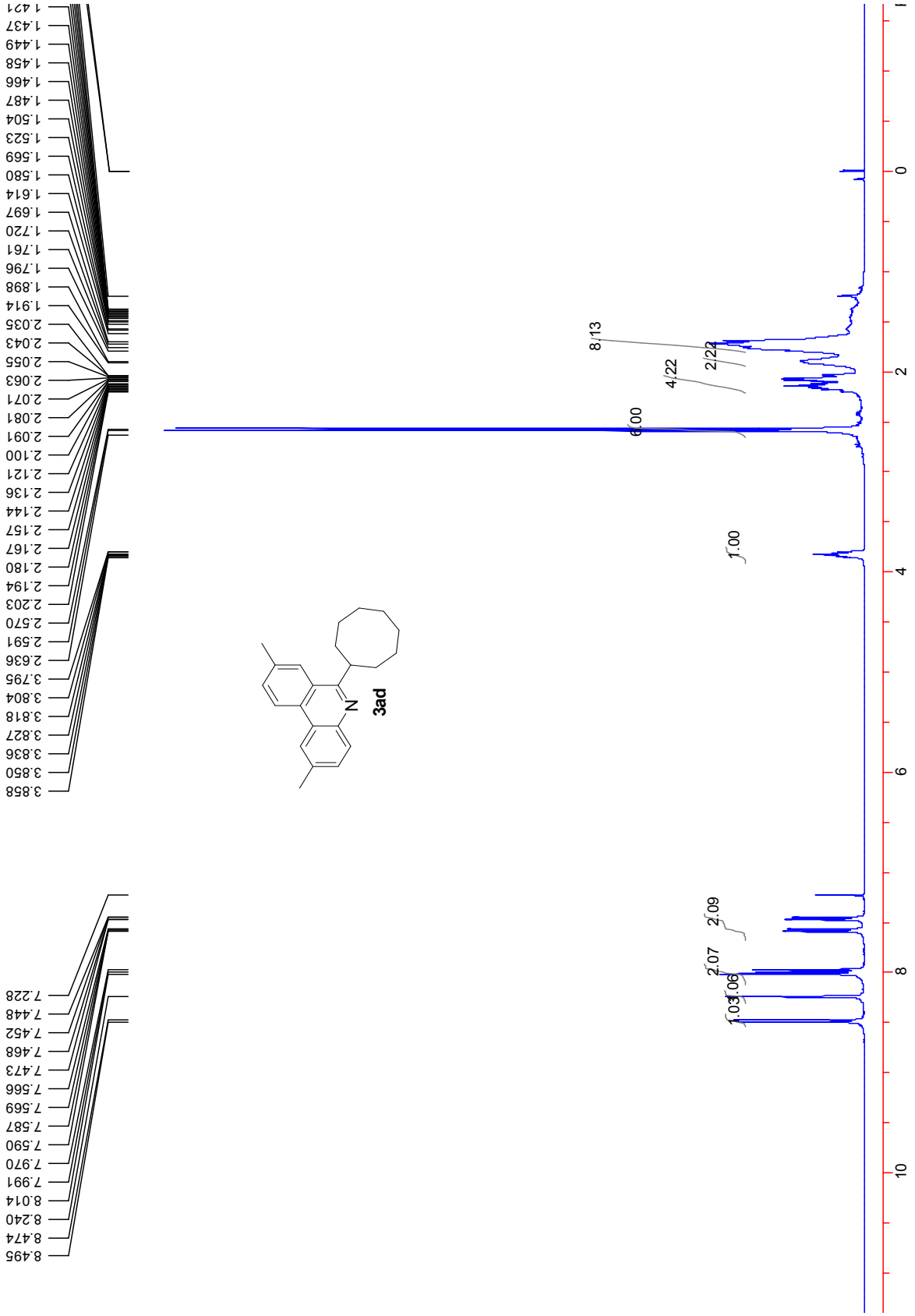
^{13}C NMR spectra of 6-cycloheptyl-2,8-dimethylphenanthridine (**3ac**)



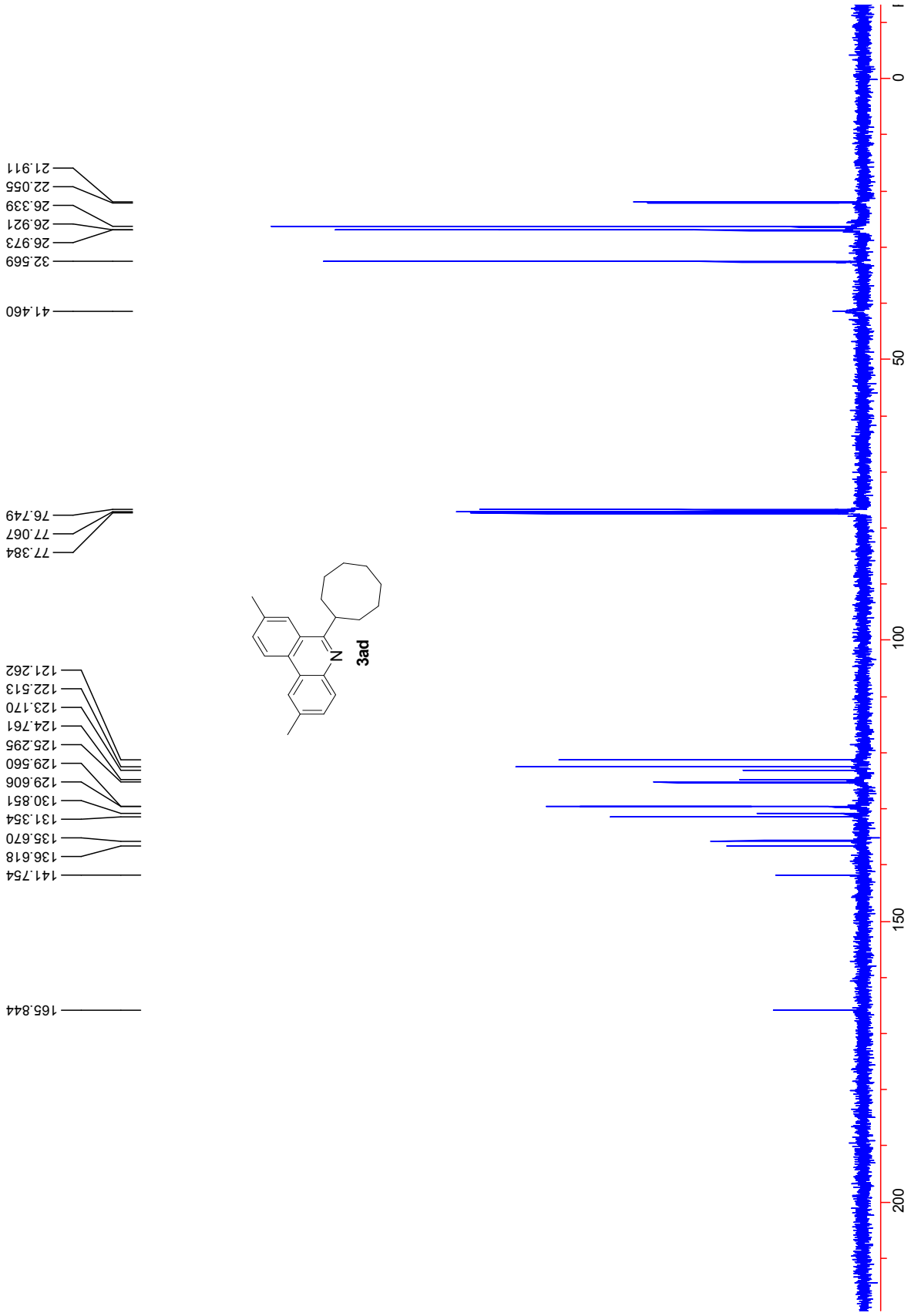
HR-MS spectra of 6-cycloheptyl-2,8-dimethylphenanthridine (**3ac**)



[1]H NMR spectra of 6-cyclooctyl-2,8-dimethylphenanthridine (**3ad**)

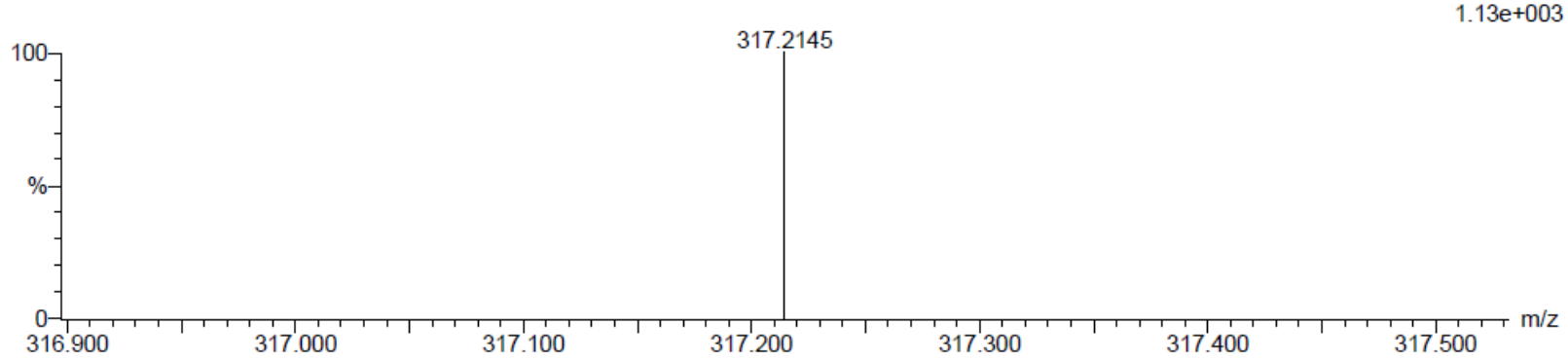


^{13}C NMR spectra of 6-cyclooctyl-2,8-dimethylphenanthridine (**3ad**)



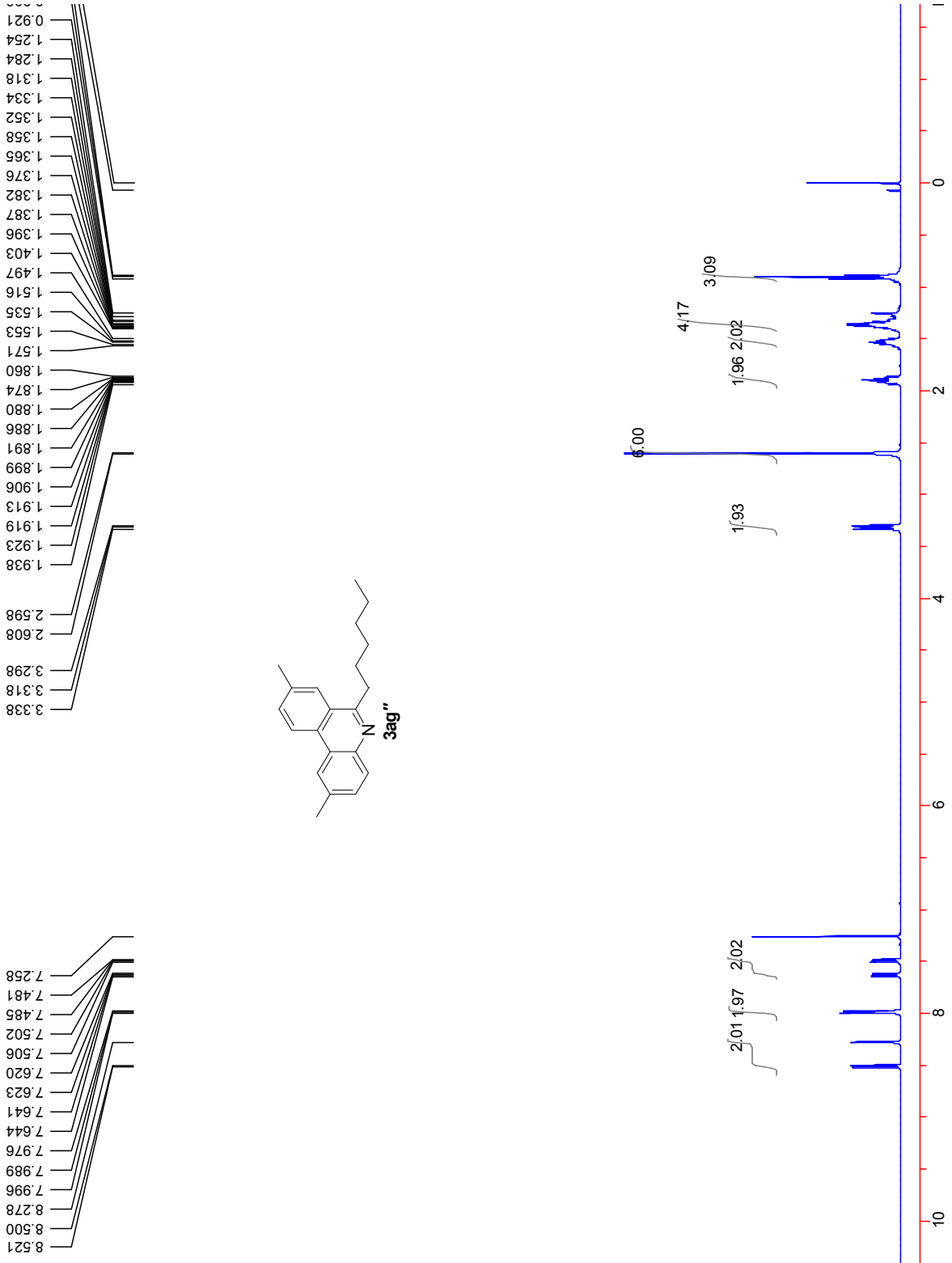
HR-MS spectra of 6-cyclooctyl-2,8-dimethylphenanthridine (**3ad**)

Monoisotopic Mass, Odd and Even Electron Ions
147 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-200 N: 0-2 O: 0-3 F: 0-2
zzq14040314 110 (1.834)
TOF MS EI+

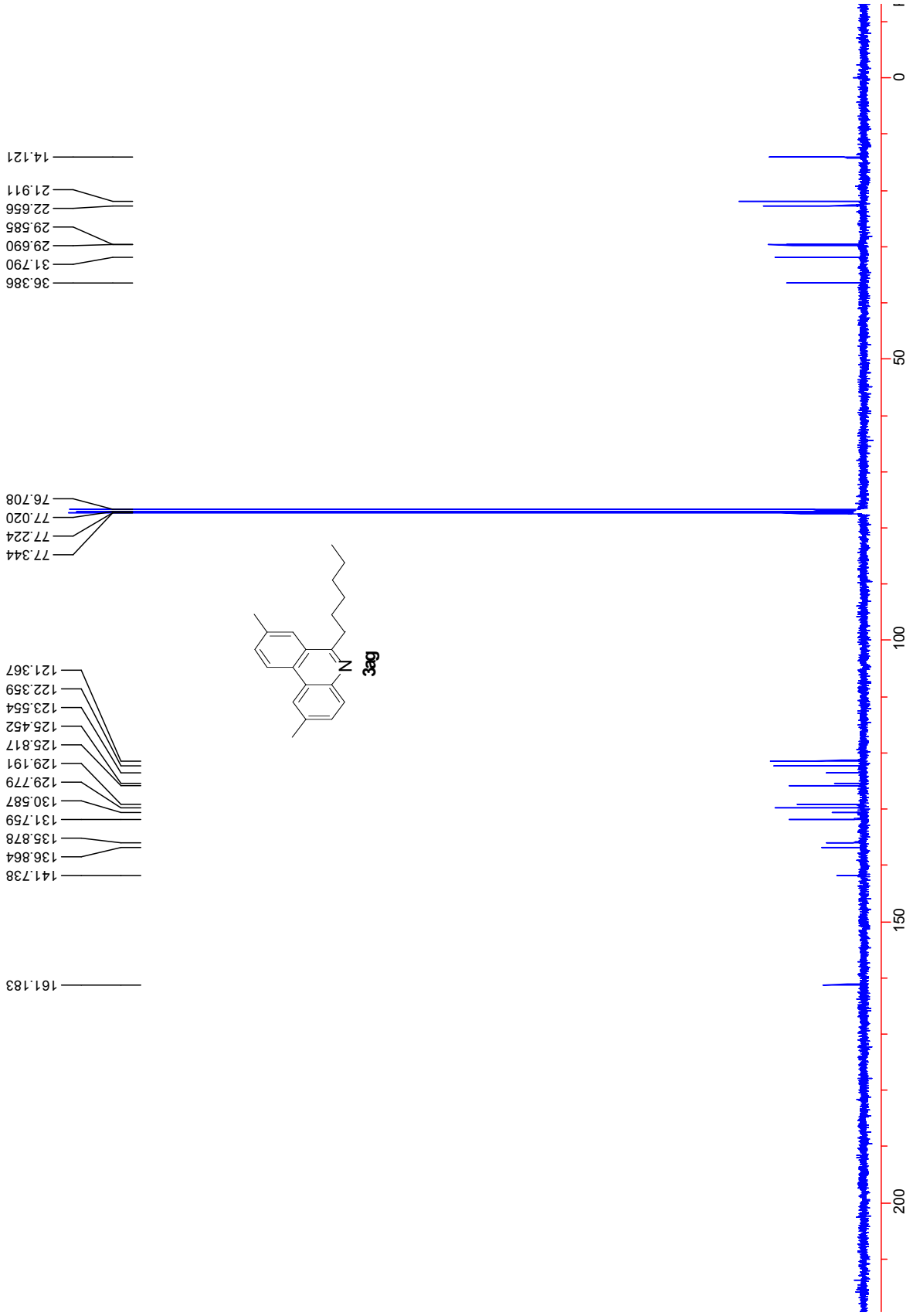


Minimum:				-1.5		
Maximum:		0.9	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
317.2145	317.2144	0.1	0.3	11.0	5546580.0	C23 H27 N

^{1}H NMR spectra of 6-hexyl-2,8-dimethylphenanthridine (**3ag**)



^{13}C NMR spectra of 6-hexyl-2,8-dimethylphenanthridine (**3ag**)



HR-MS spectra of 6-hexyl-2,8-dimethylphenanthridine (**3ag**)