SUPPORTING INFORMATION

Microwave Assisted Synthesis of Phenanthridinones and Dihydrophenanthridines by Vasicine/KO*t*Bu Promoted Intramolecular C-H Arylation

Sushila Sharma,[a,b] Manoranjan Kumar, [a,b] Shruti Sharma,[a] Onkar S. Nayal,[a,b] Neeraj Kumar,[$] Bikram Singh* and Upendra Sharma*

[a]Natural Product Chemistry and Process Development Division, CSIR-Institute of Himalayan Bioresource Technology, Palampur, Himachal Pradesh-176 061, India

[b]Academy of Scientific and Innovative Research, Anusandhan Bhawan, 2 Rafi Marg, New Delhi-110001, India

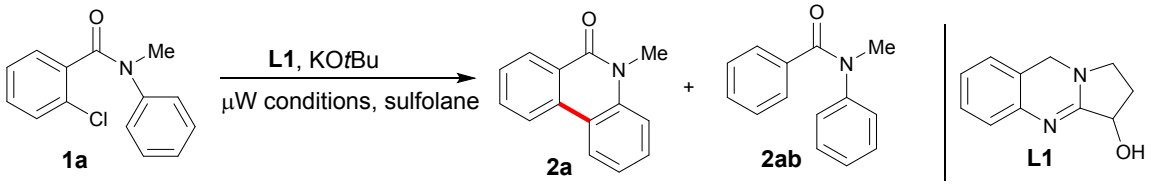
*E-mail: upendra@ihbt.res.in (US); bikramsingh@ihbt.res.in (BS)

[$] Deceased on 28th March 2016

General information

All reagents, high grade solvents and materials were used as received from commercial sources unless otherwise stated. Toluene was distilled from sodium and benzophenone. Column chromatography was carried out with 100-200 mesh silica gel (Merck India). TLC silica gel 60 F_{254} plates and 100-200 mesh silica gel were purchased from Merck India Ltd. 2-Halobenzoic acid, anilines and NMR solvents were purchased from sigma Aldrich. ^{1}H NMR and ^{13}C NMR experiments were performed on Bruker Avance-300 and 600 MHz spectrometer. NMR spectra were recorded in $CDCl_3$. Chemical shifts are reported in parts per million (ppm) downfield from an internal standard. Splitting patterns are given as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; brs, broad singlet; dd, double doublet. All coupling constants are given in Hertz (Hz). All experiments were performed on CEM Discover focused microwave (2450 MHz, 300W). The GC-MS analysis was carried out using DB-5 MS capillary column, (30 m x 0.25 mm i.d., 0.25 µm) on a Shimadzu (QP 2010) series Gas Chromatogram-Mass Spectrometer (Tokyo, Japan) coupled with AOC-20i auto-sampler. The initial temperature of column was 70 °C held for 4 min. and was programmed upto 230 °C at 4°C/min., then held for 15 min. at 230 °C; the sample injection volume was 2 µL in GC grade dichloromethane. Nitrogen was used as carrier gas at a flow rate of 1.1 mL min^{-1} on split mode (1: 50). Mass spectra were recorded on QTOF-Micro of Waters Micromass.

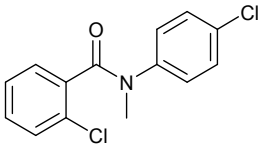
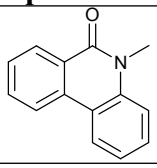
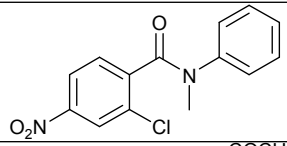
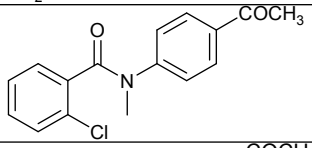
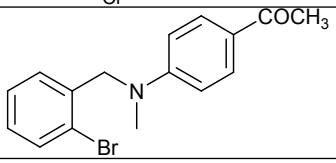
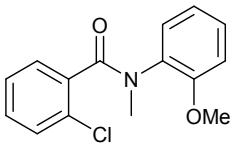
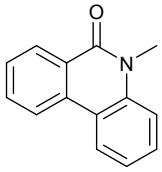
Table S1 Optimization of reaction conditions



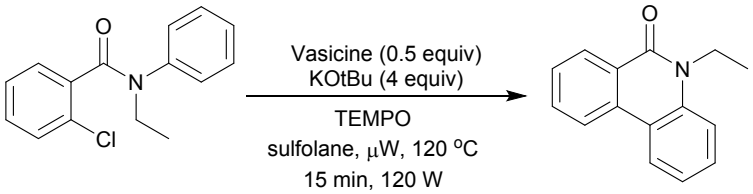
entry	catalyst	base	solvent	Time (min)	Temperature (°C)	conv (%)	yield (%)[b] 2a	2ab
1	**L1**	KO*t*Bu	Sulfolane	15	80	90	35	49
2	**L1**	KO*t*Bu	Sulfolane	5	120	92	38	48
3	**L1**	KO*t*Bu	Sulfolane	10	120	99	45	39
4	**L1**	KO*t*Bu	Sulfolane	15	150	99	50	40
5[c]	**L1**	KO*t*Bu	Sulfolane	30	120	99	48	30

[a] Reaction was carried out with 0.25 mmol of **1a** in the presence of vasicine (50 mol%) and KO*t*Bu (4 equiv) in 0.4 mL of sulfolane under μW. [b] Isolated yield**.** In most cases dechlorination of **1a** yielding corresponding amide and cleavage of **1a**, yielding *N*-methylaniline was observed. [c] *N*-methylaniline (15%) was observed.

Table S2: Other tested amines and amides for intramolecular cylization

entry	substrate	product	Yield (%)
1			58
2		Decomposition was observed	nd
3		Decomposition was observed	traces
4		Decomposition was observed	nd
5			65

Procedure for radical scavenging experiment

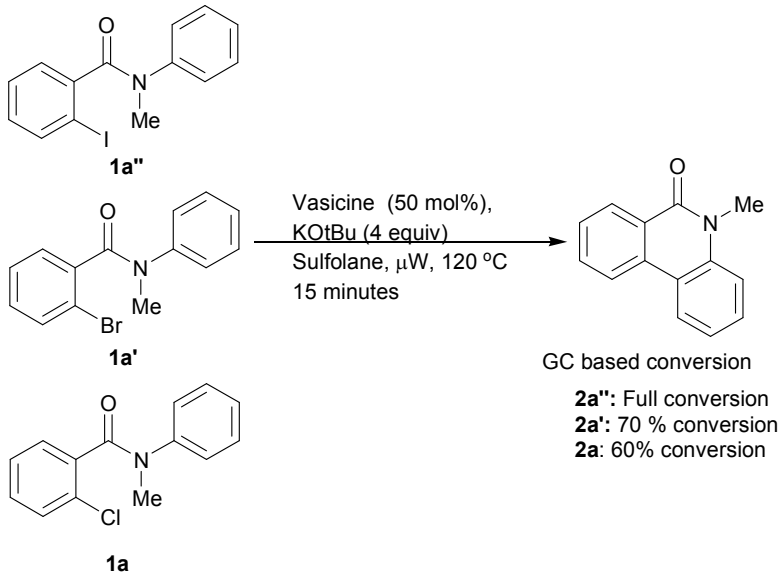


TEMPO (1 equiv); Yield = 30%
TEMPO (3 equiv); Yield = traces

To an oven dried 10 mL glass tube charged with magnetic bar was added 2-chloro-*N*-ethyl-*N*-phenylbenzamide (0.25 mmol), vasicine (0.12 mmol), KO*t*Bu (1 mmol), TEMPO (0.25 mmol) and sulfolane (0.4 mL). The tube was sealed with a septum stirred and placed in the microwave and subjected to microwave irradiation of 120 W. The temperature was ramped from rt to 120 °C and held at 120 °C for 15 min. After the reaction, the reaction mixture was allowed to cool and was diluted with ethyl acetate. The organic layer was then washed with water and the solvent was removed under vacuo. The crude residue was subjected to column chromatography on silica gel using *n*-hexane: EtOAc to afford the cyclized product.

Further, same procedure for the reaction of 2-chloro-*N*-ethyl-*N*-phenylbenzamide (0.25 mmol) in the presence of vasicine (0.12 mmol), KO*t*Bu (1 mmol), and 3 equivalent of TEMPO (0.75 mmol) in sulfolane yielded the cyclised product in trace amount.

Procedure for competition reaction between iodo-, bromo-and chloro-substituted amides

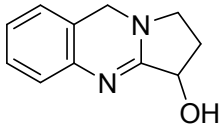


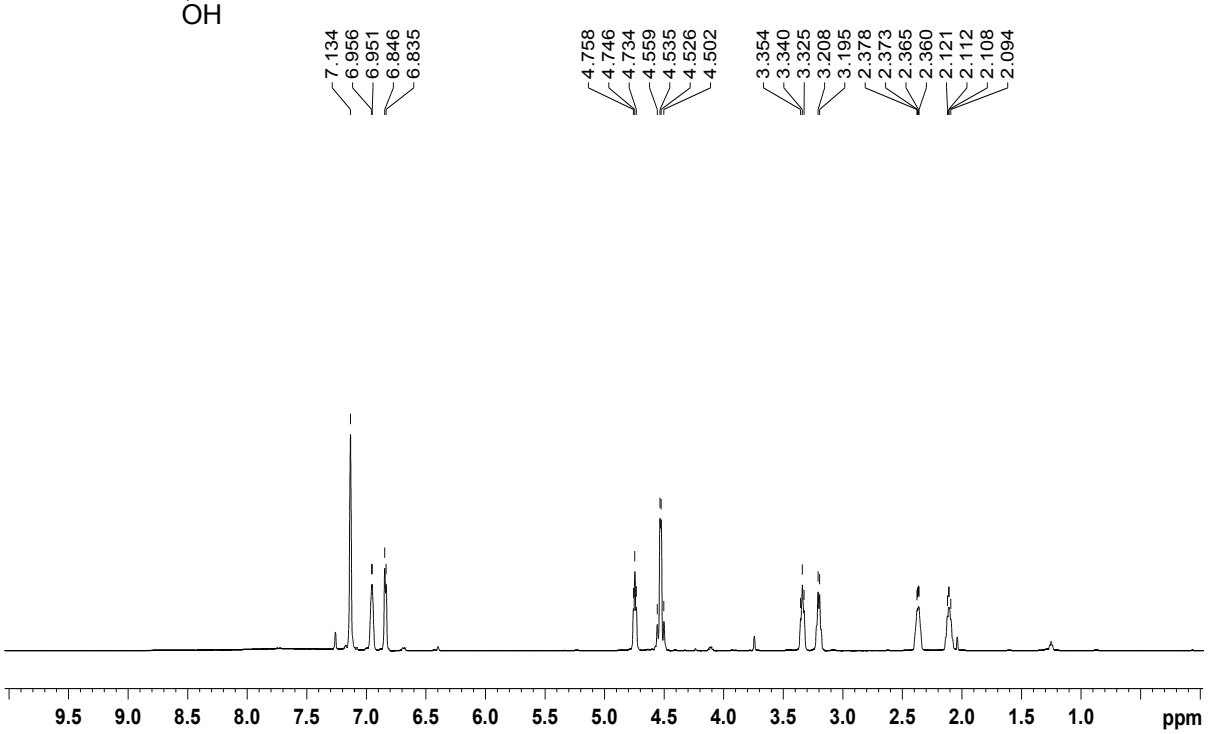
To an oven dried 10 mL glass tube charged with magnetic bar was added 2-iodo-*N*-methyl-*N*-phenylbenzamide (**1a''**, 0.15 mmol), 2-bromo-*N*-methyl-*N*-phenylbenzamide (**1a'**, 0.15 mmol), 2-chloro-*N*-methyl-*N*-phenylbenzamide (**1a**, 0.15 mmol), vasicine (0.075 mmol), KO*t*Bu (0.6 mmol), sulfolane (0.4 mL). The tube was sealed with a septum stirred and placed in the microwave and subjected to microwave irradiation of 120 W. The temperature was ramped from rt to 120 °C and held at 120 °C for 15 min. After the reaction, the reaction mixture was allowed to cool and was diluted with ethyl acetate. The organic layer was then washed with water and the solvent was removed under vacuo. The crude reaction mixture was then analyzed with GC-MS

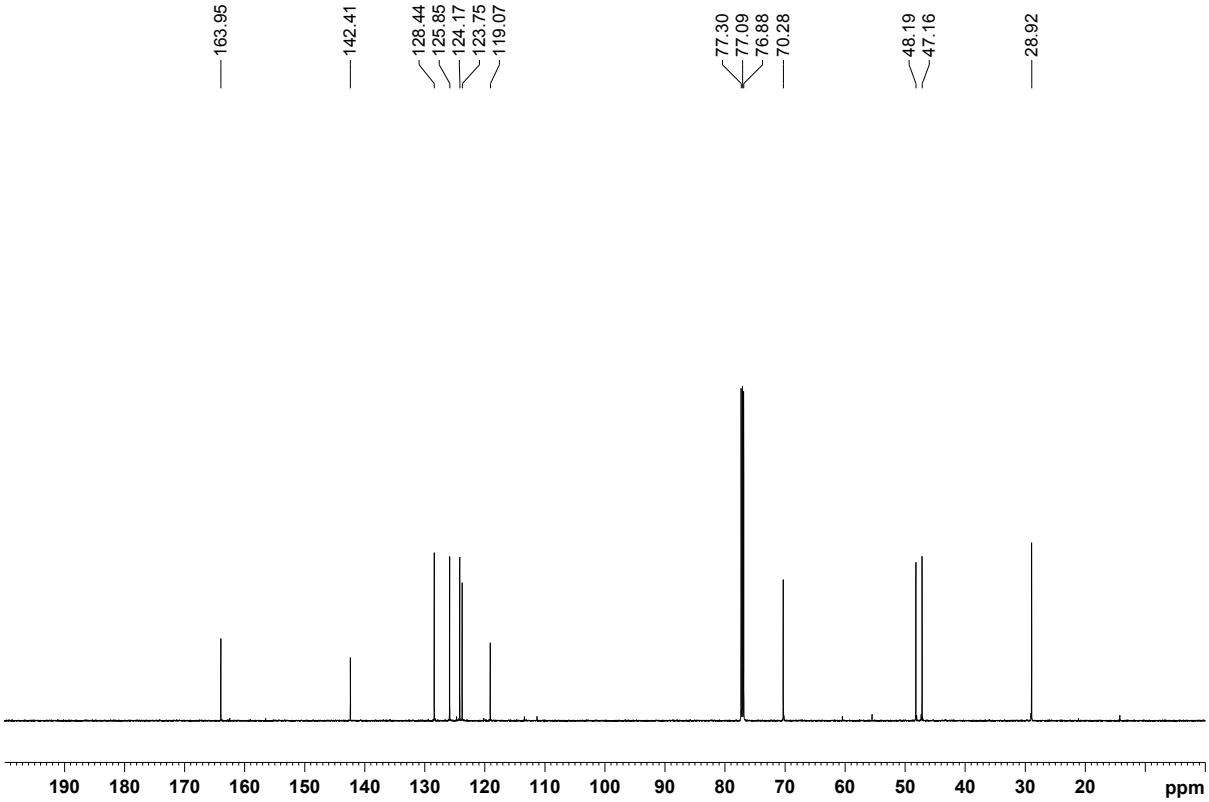
***Cyclization reaction of 3-chloro-N-methyl-N-phenylbenzamide*:** To an oven dried 10 mL glass tube charged with magnetic bar was added 3-chloro-*N*-methyl-*N*-phenylbenzamide (0.15 mmol), vasicine (0.075 mmol), KOtBu (0.6 mmol) and sulfolane (0.4 mL). The tube was sealed with a septum stirred and placed in the microwave and subjected to microwave irradiation of 120 W. The temperature was ramped from rt to 120 °C and held at 120 °C for 15 min. After the reaction, the reaction mixture was allowed to cool and was diluted with ethyl acetate. The organic layer was then washed with water and the solvent was removed under vacuo. No product formation was observed.

^{1}H and ^{13}C NMR Spectra of isolated compounds

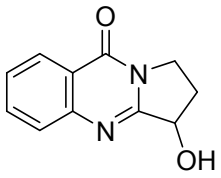
Vasicine

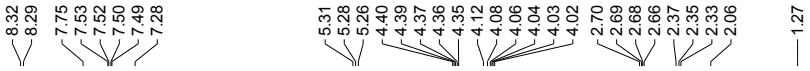






Vasicinone


O
N
N
OH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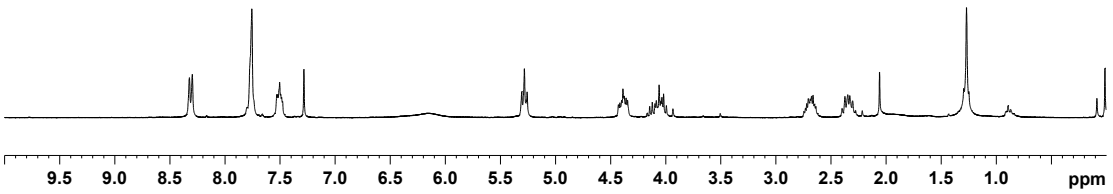
8.29
7.75
7.53
7.52
7.50
7.49
7.28
5.31
5.28
5.26
4.40
4.39
4.37
4.36
4.35
4.12
4.08
4.06
4.04
4.03
4.02
2.70
2.69
2.68
2.66
2.37
2.35
2.33
2.06
1.27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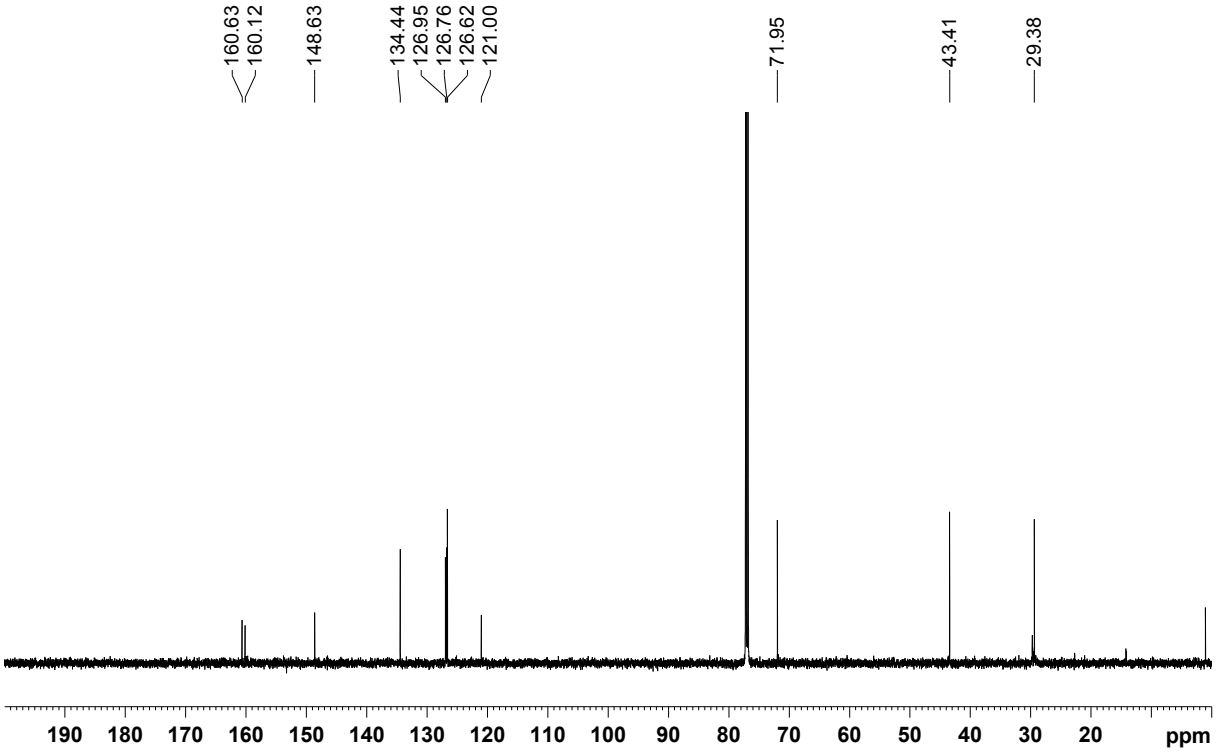
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm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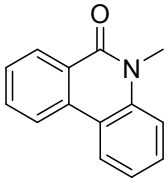
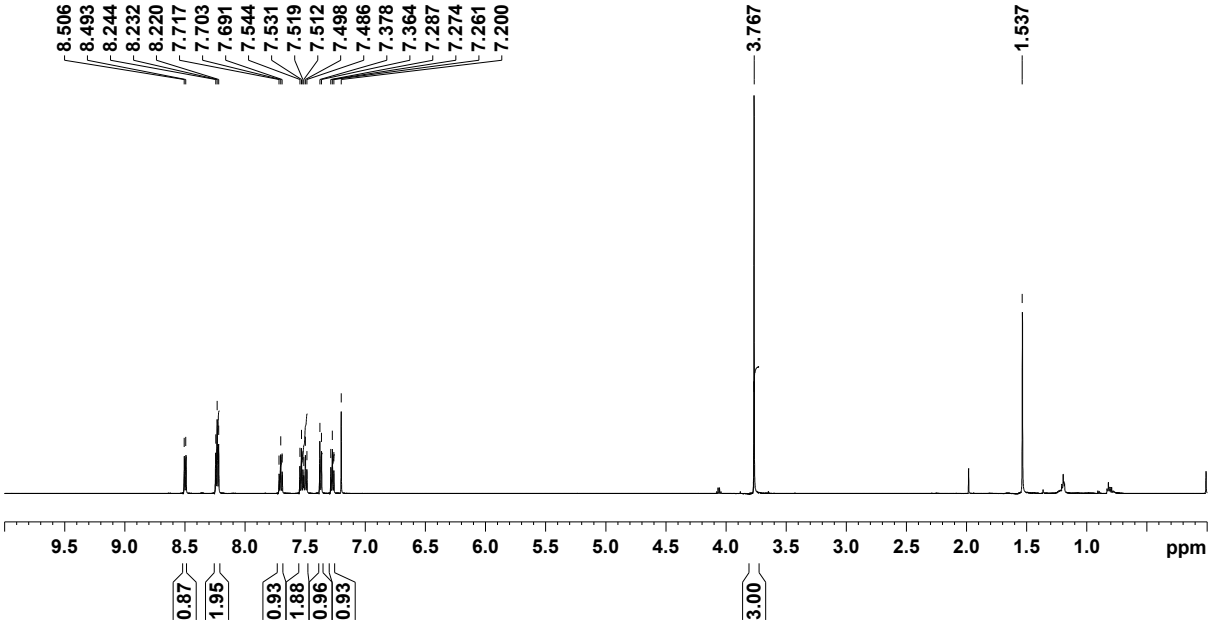
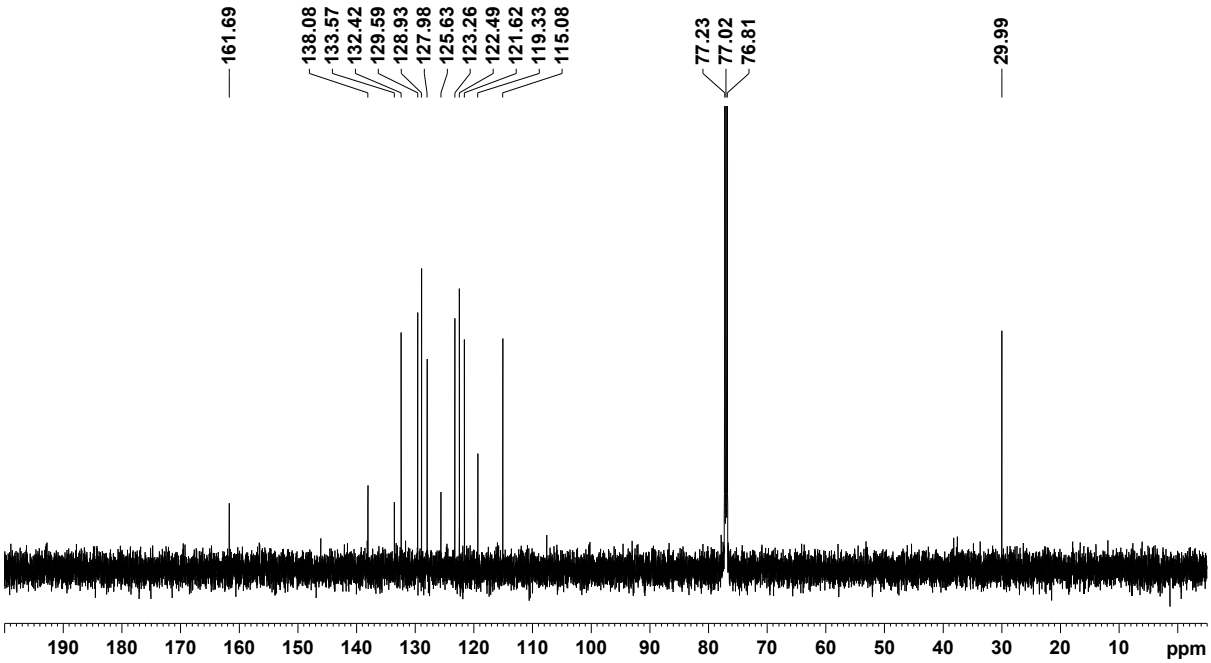
160.12
148.63
134.44
126.95
126.76
126.62
121.00
71.95
43.41
29.38
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

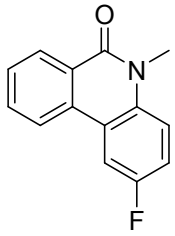
5-methylphenanthridin-6(*5H*)-one (2a)

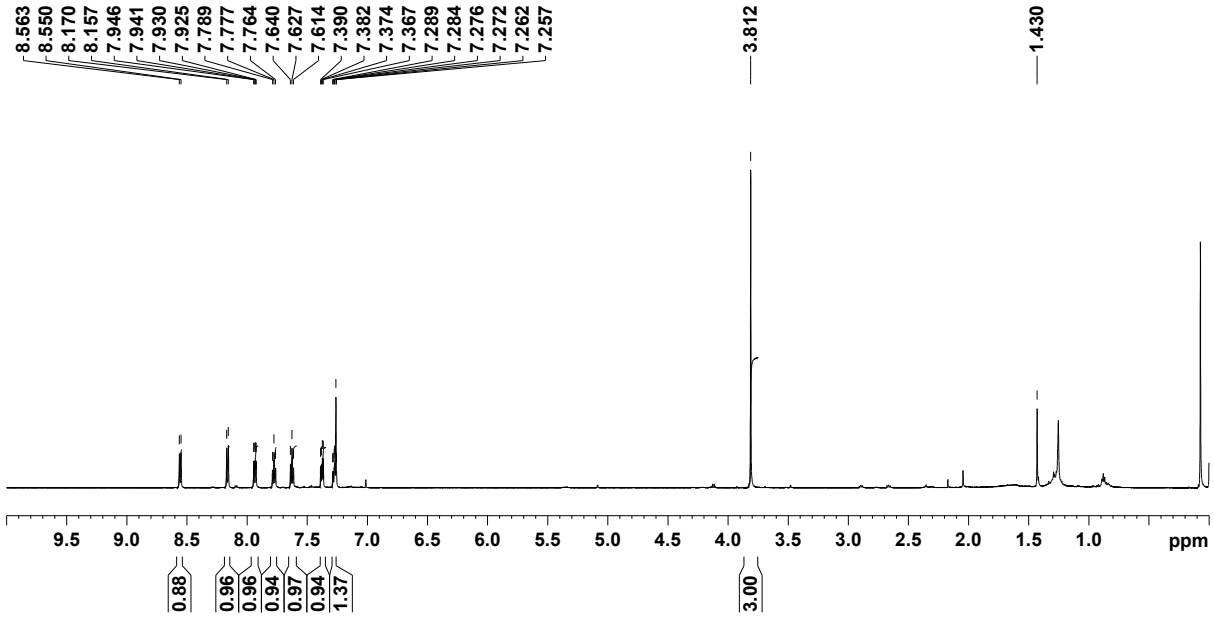


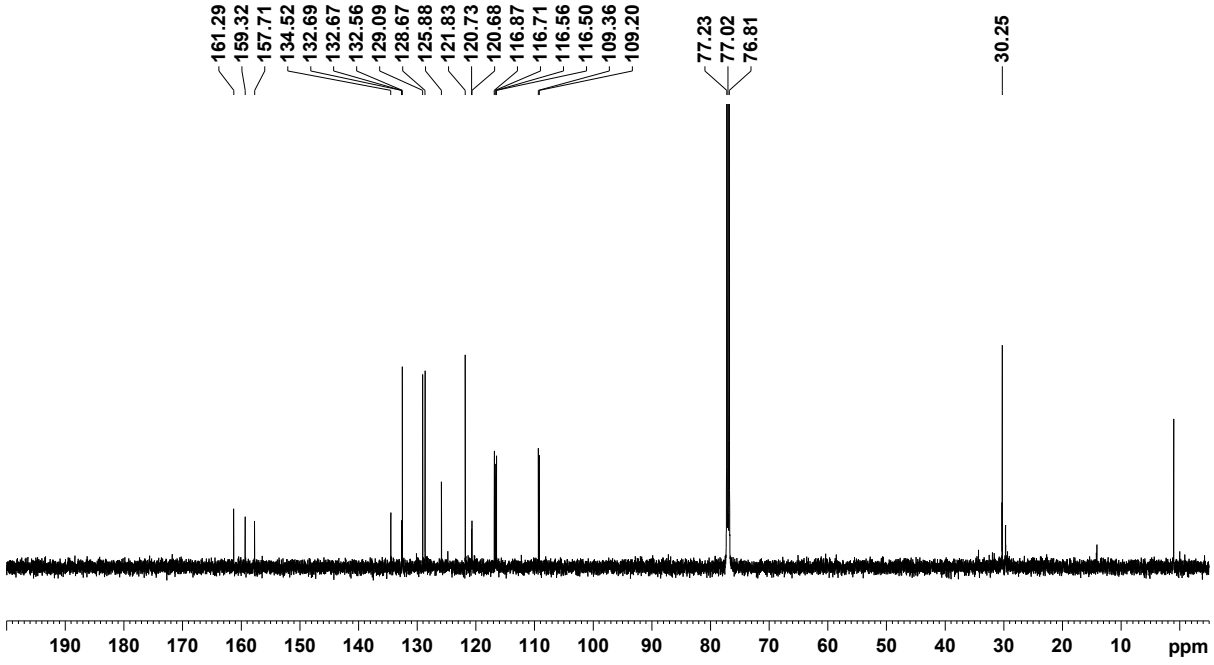




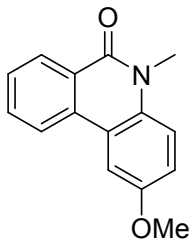
3-Fluoro-5-methylphenanthridin-6(*5H*)-one (2b)

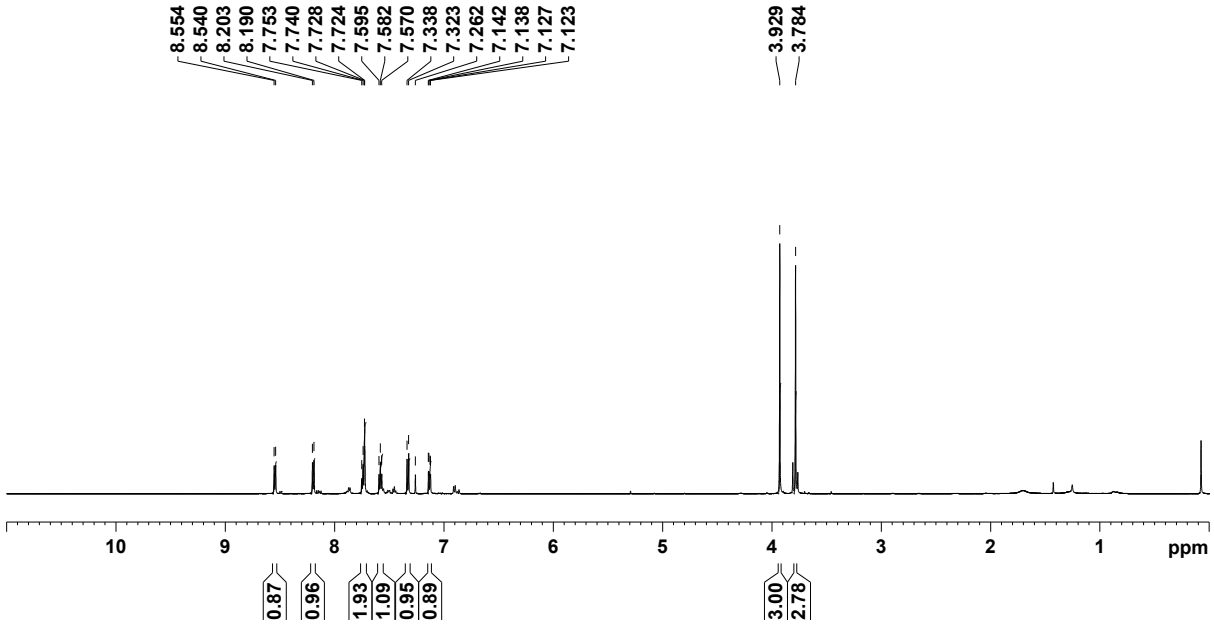


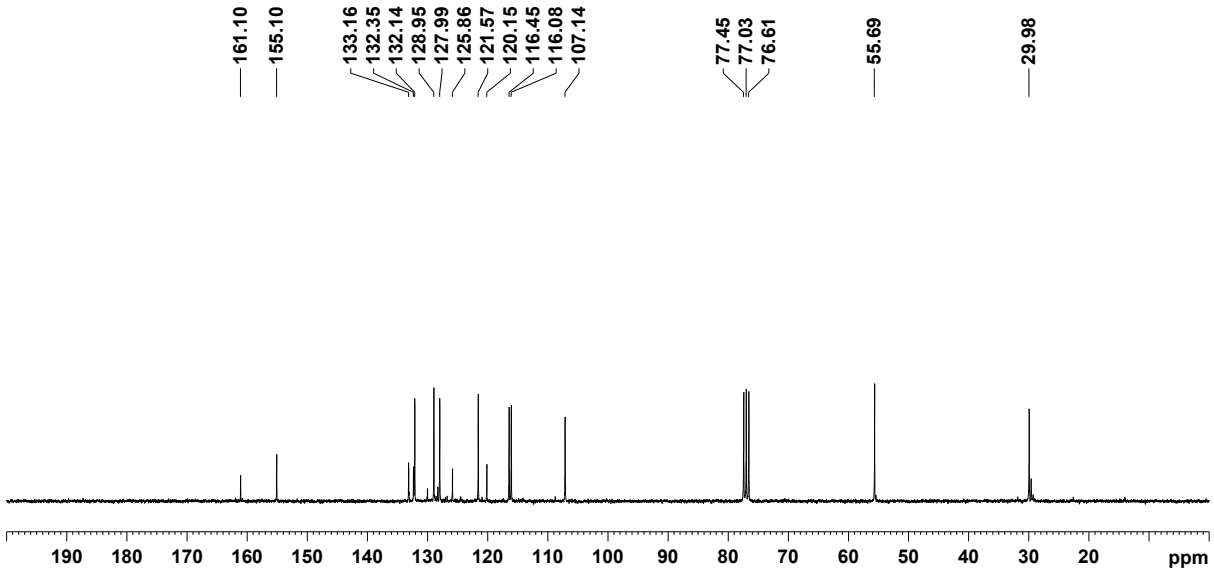




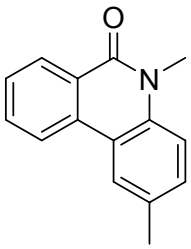
3-Methoxy-5-methylphenanthridin-6(*5H*)-one (2c)

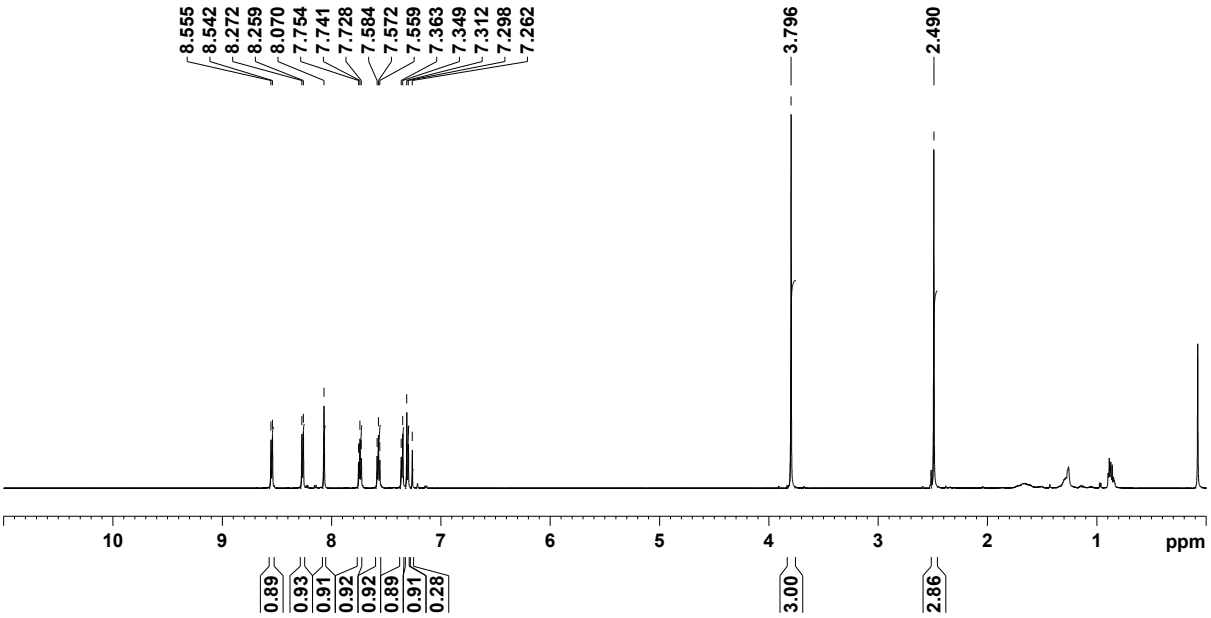


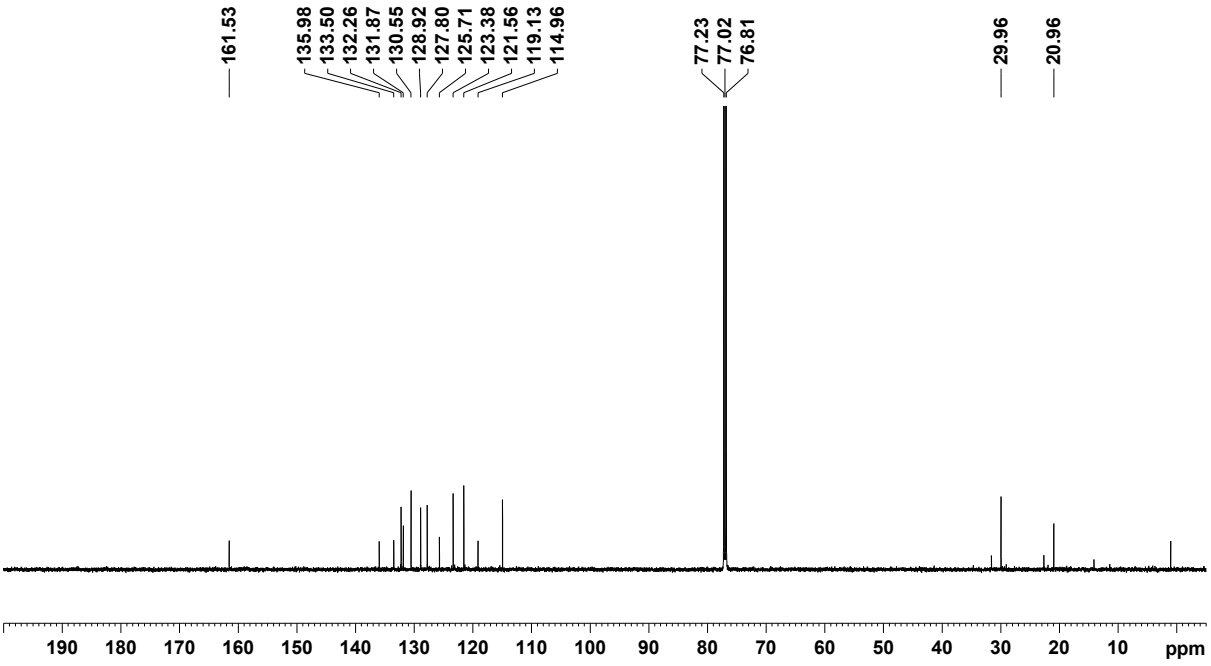




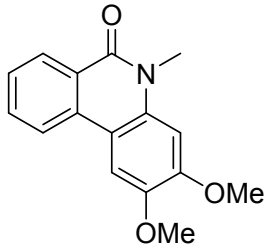
3,5-Dimethylphenanthridin-6(*5H*)-one (2d)

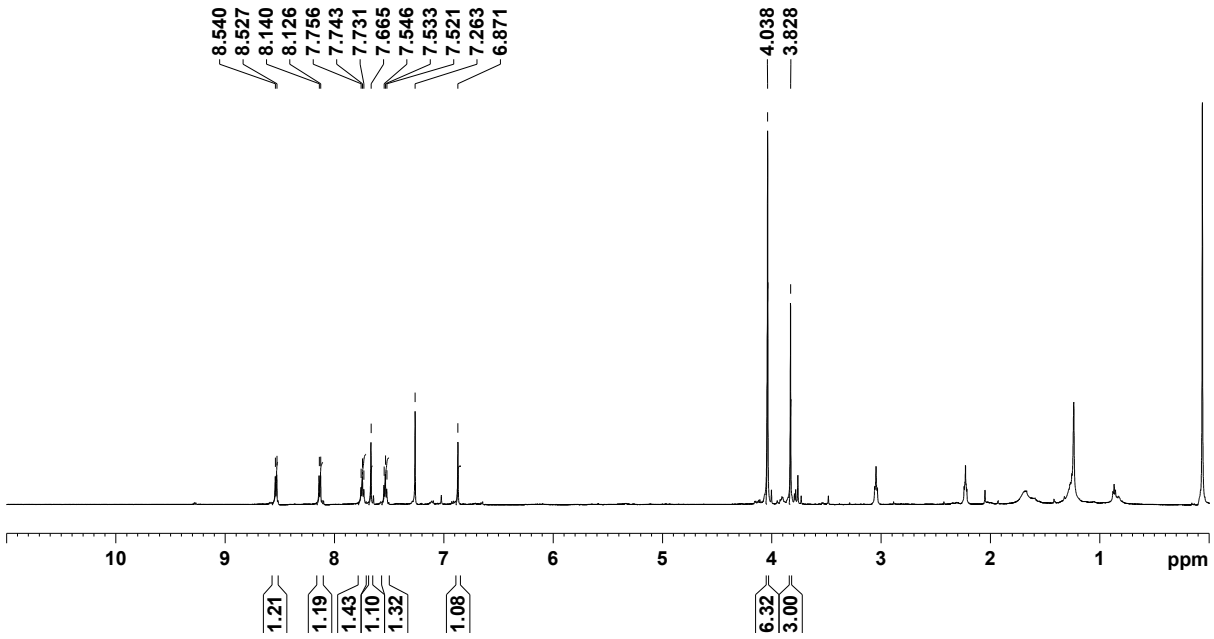


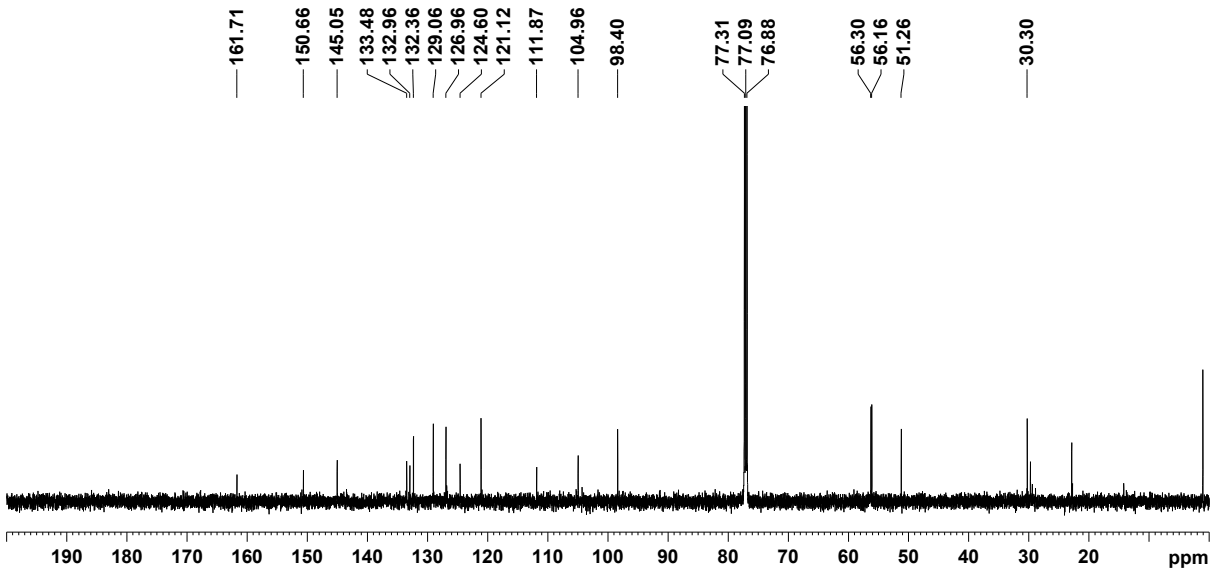




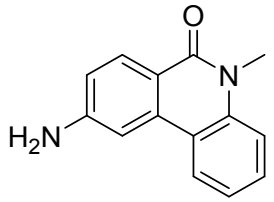
2,3-Dimethoxy-5-methylphenanthridin-6(*5H*)-one (2e)

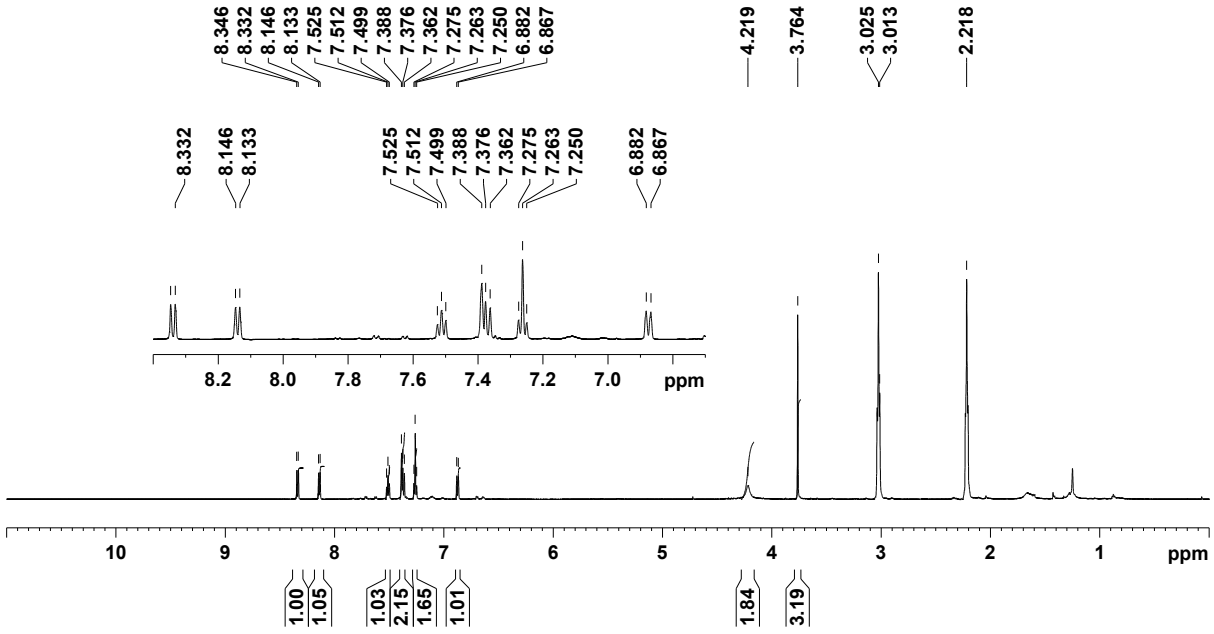


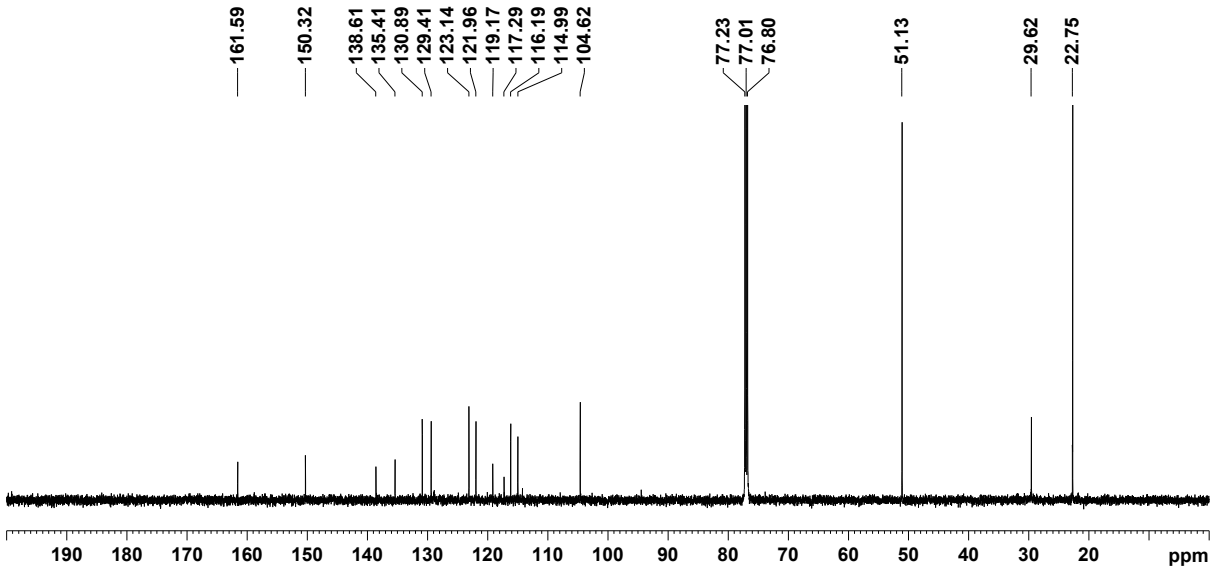




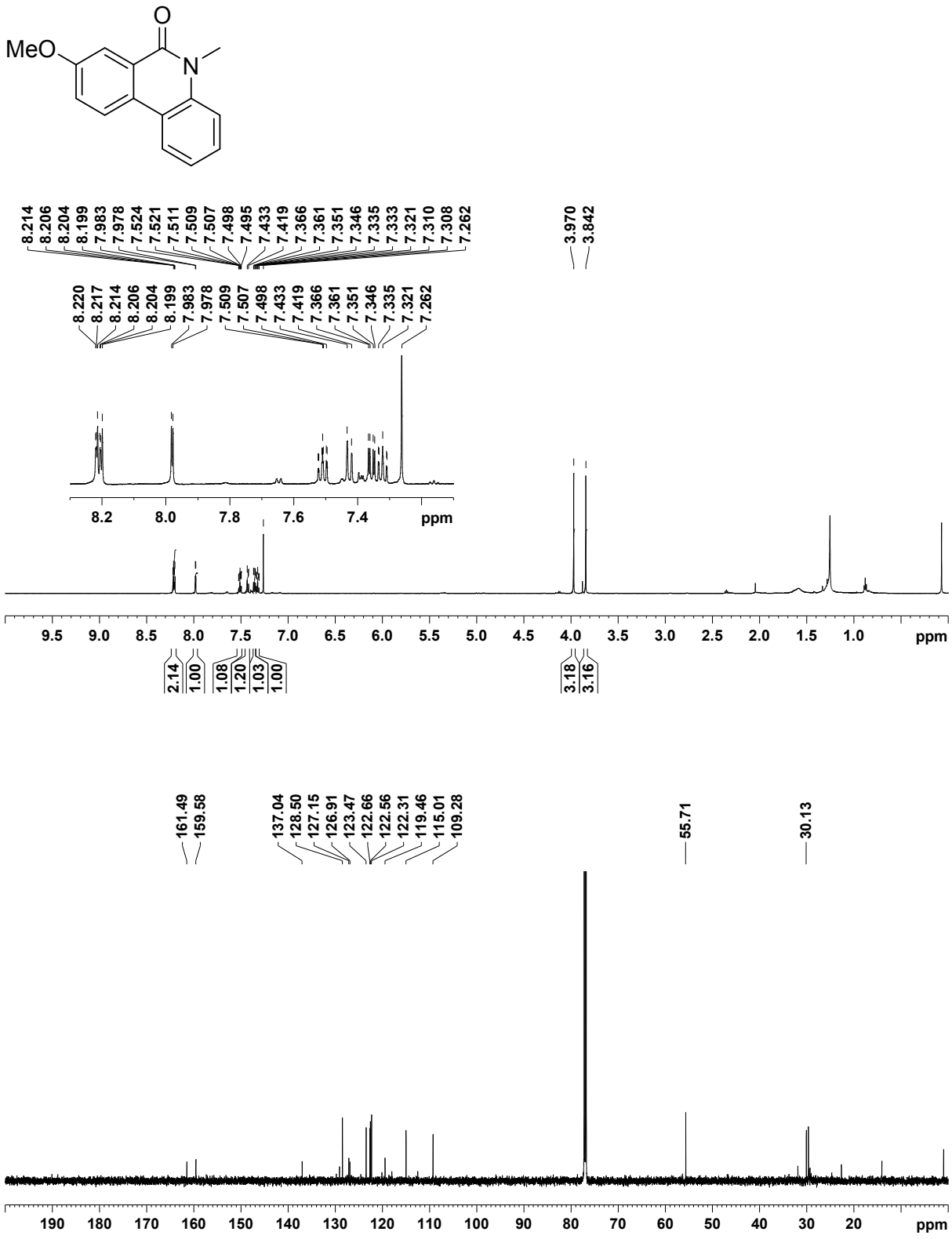
9-Amino-5-methylphenanthridin-6(*5H*)-one (2f)



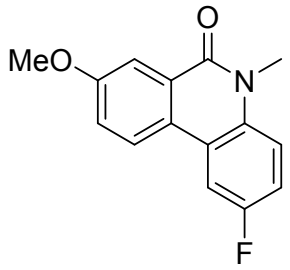


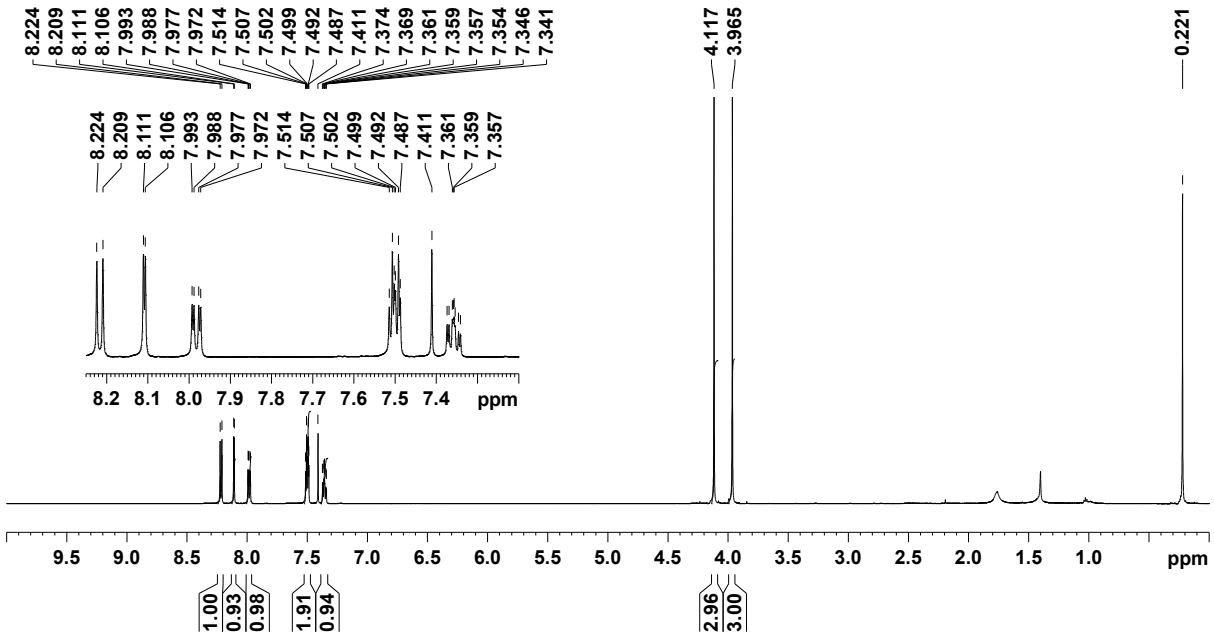


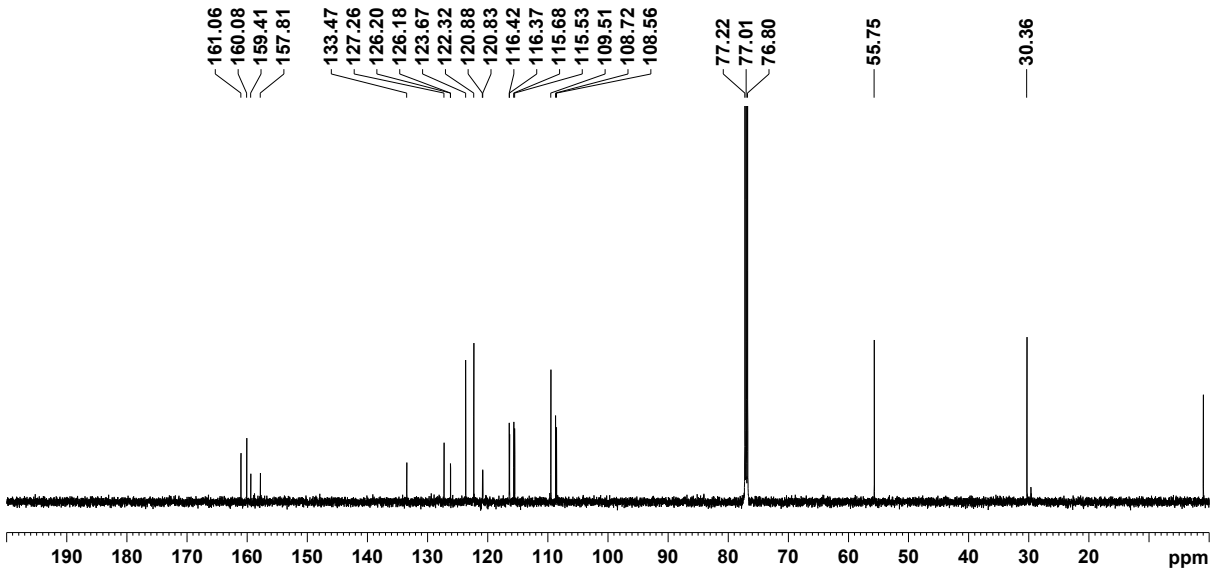
8-Methoxy-5-methylphenanthridin-6(*5H*)-one (2g)



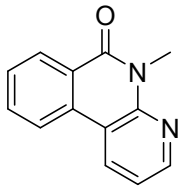
8-Methoxy-2-fluoro-5-methylphenanthridin-6(5*H*)-one (2h)

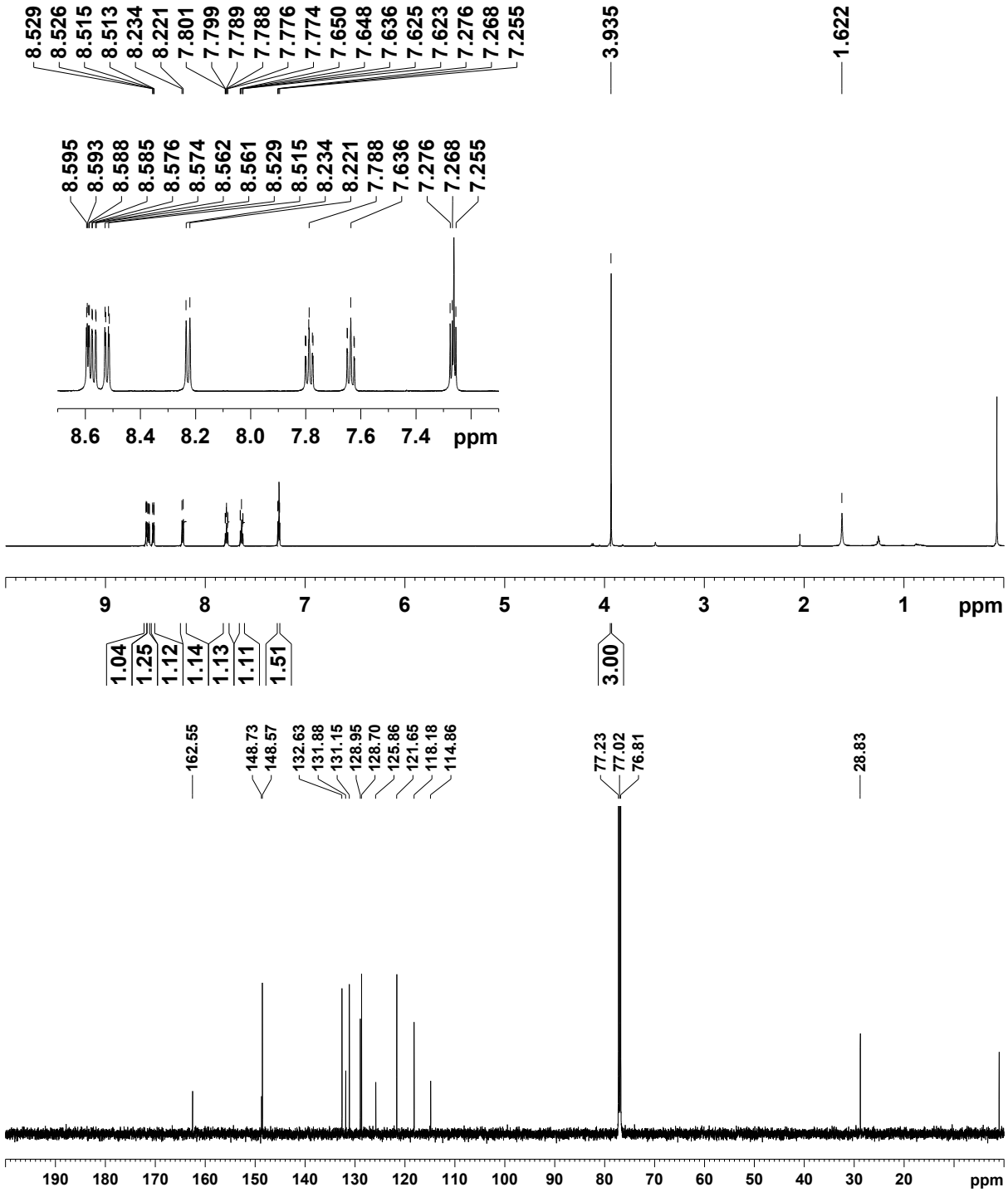




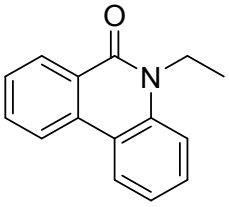


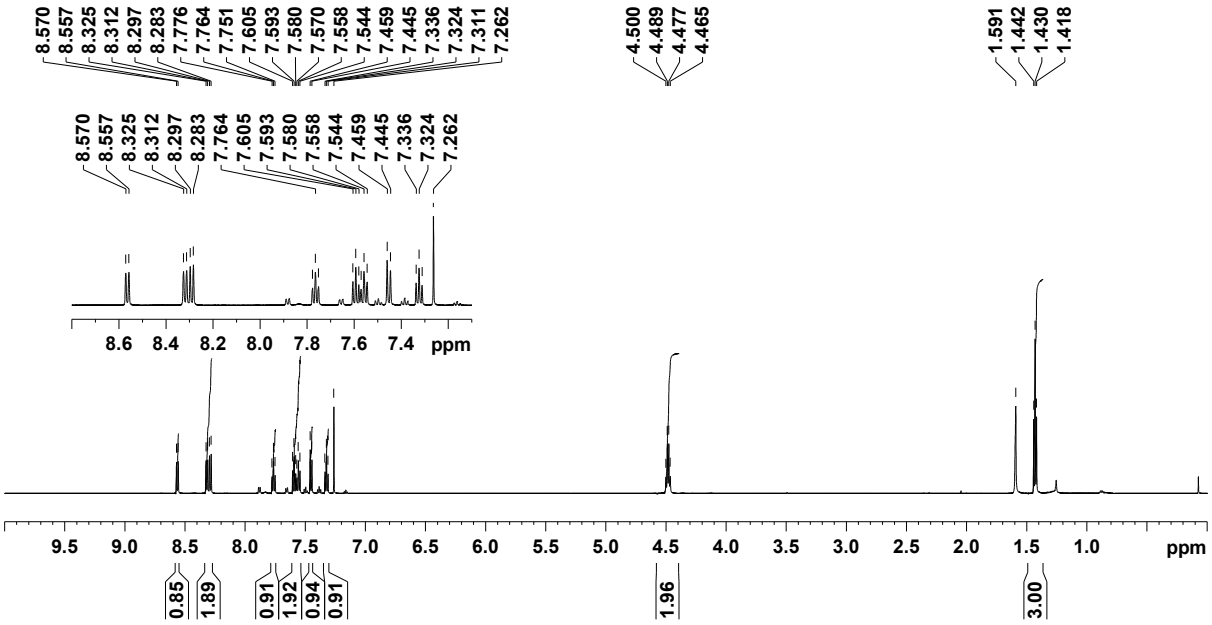
5-methyl-*5H*-benzo[c][1,8]naphthyridin-6-one (2j)

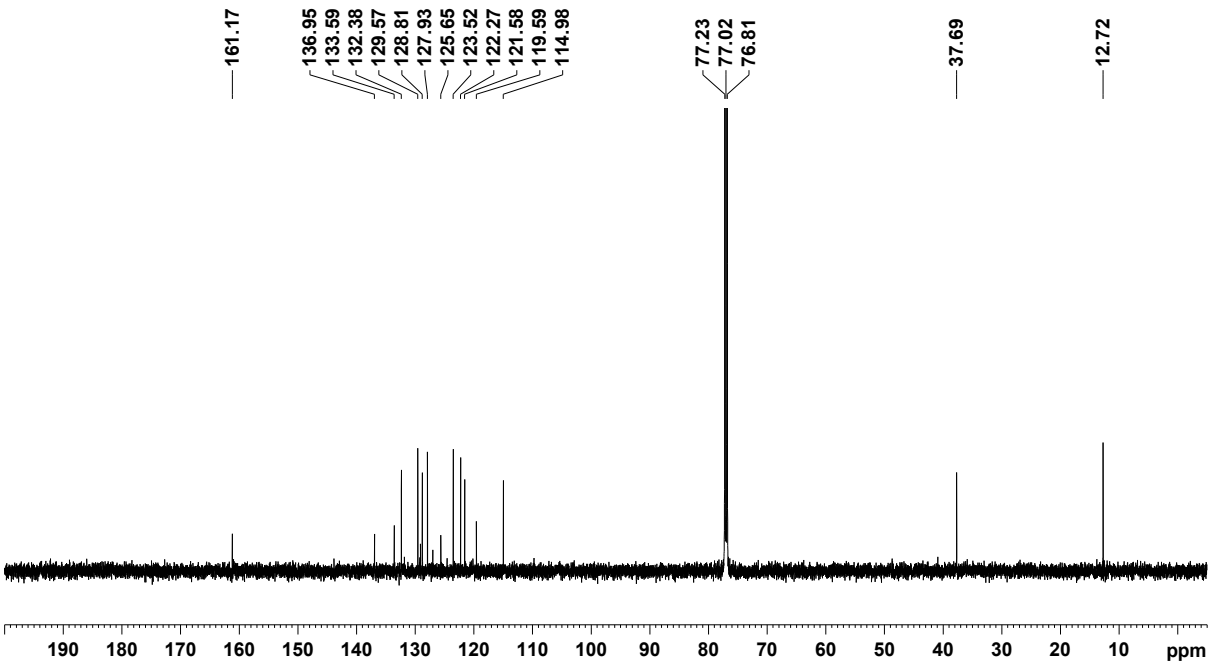




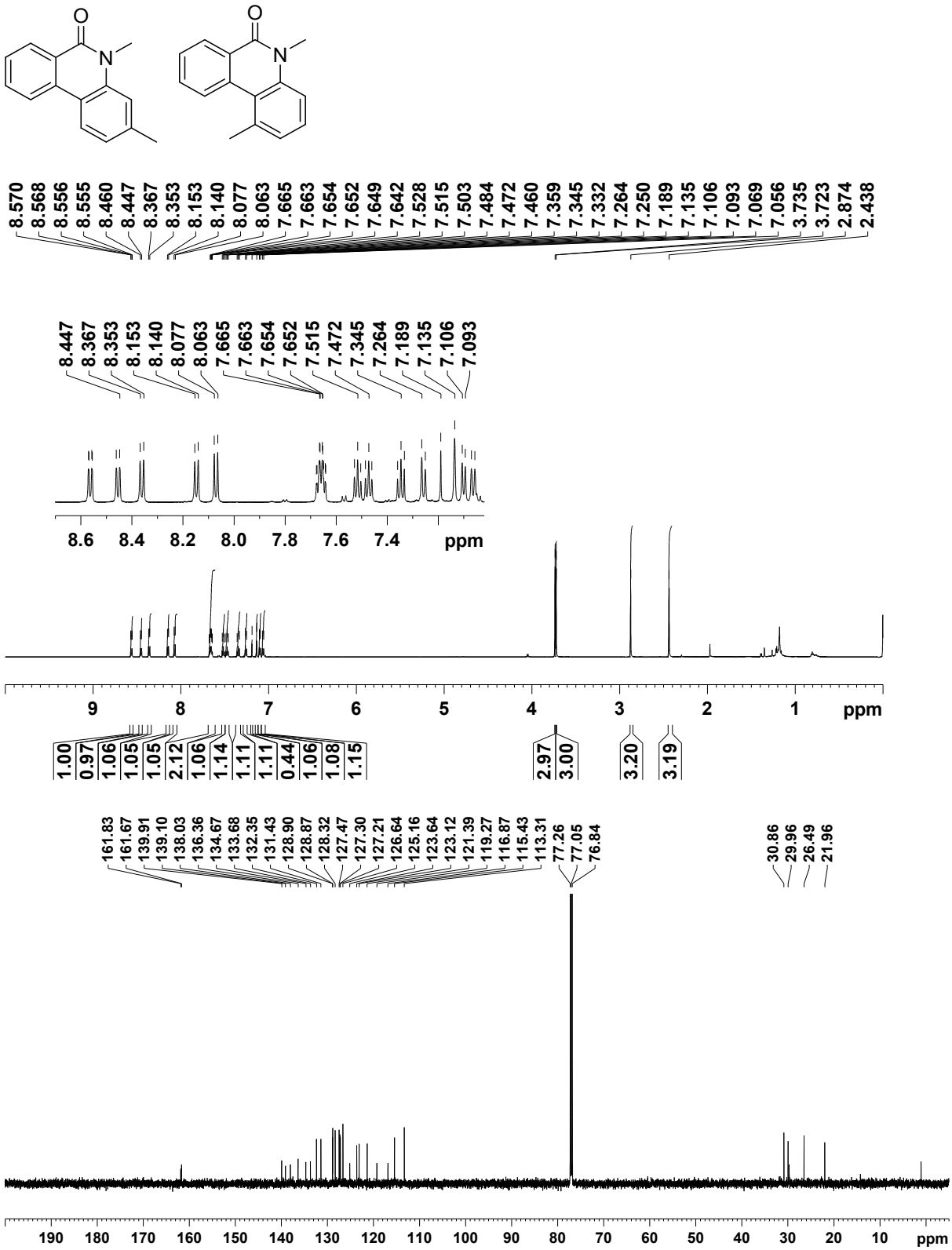
5-Ethylphenanthridin-6(*5H*)-one (2k)



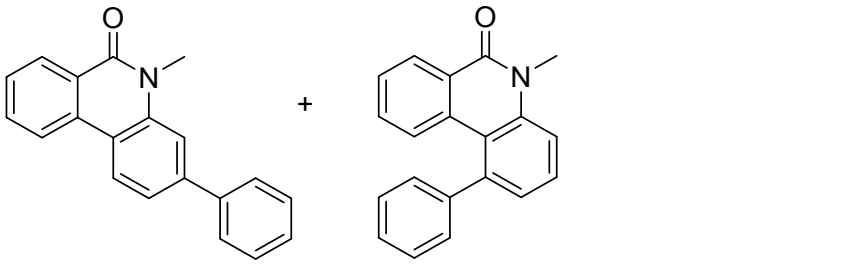


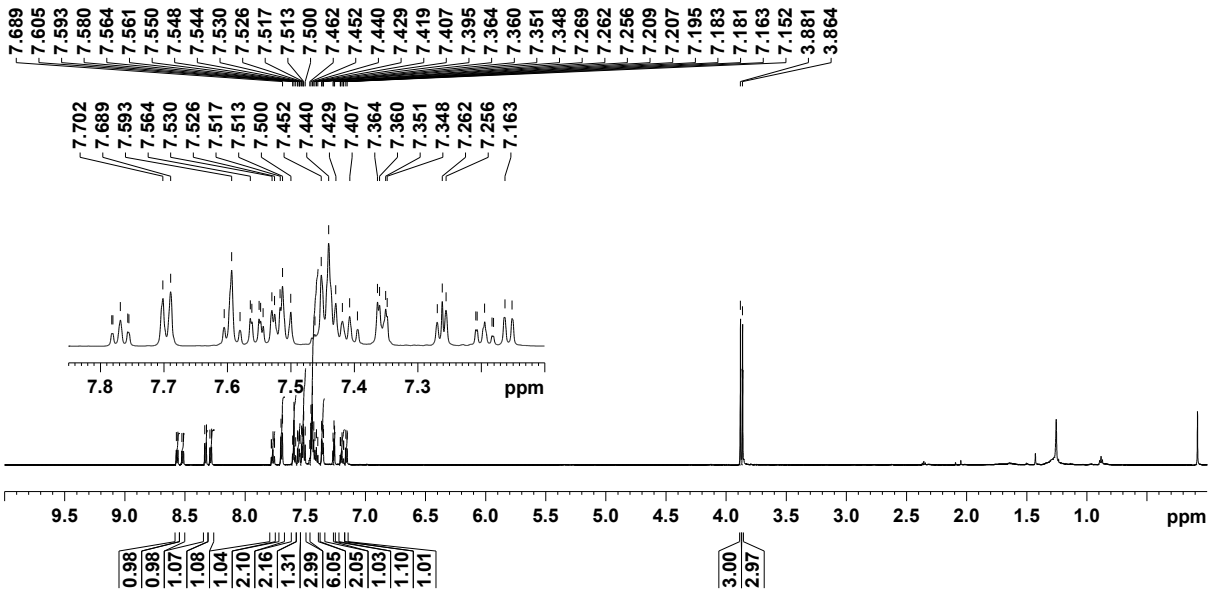


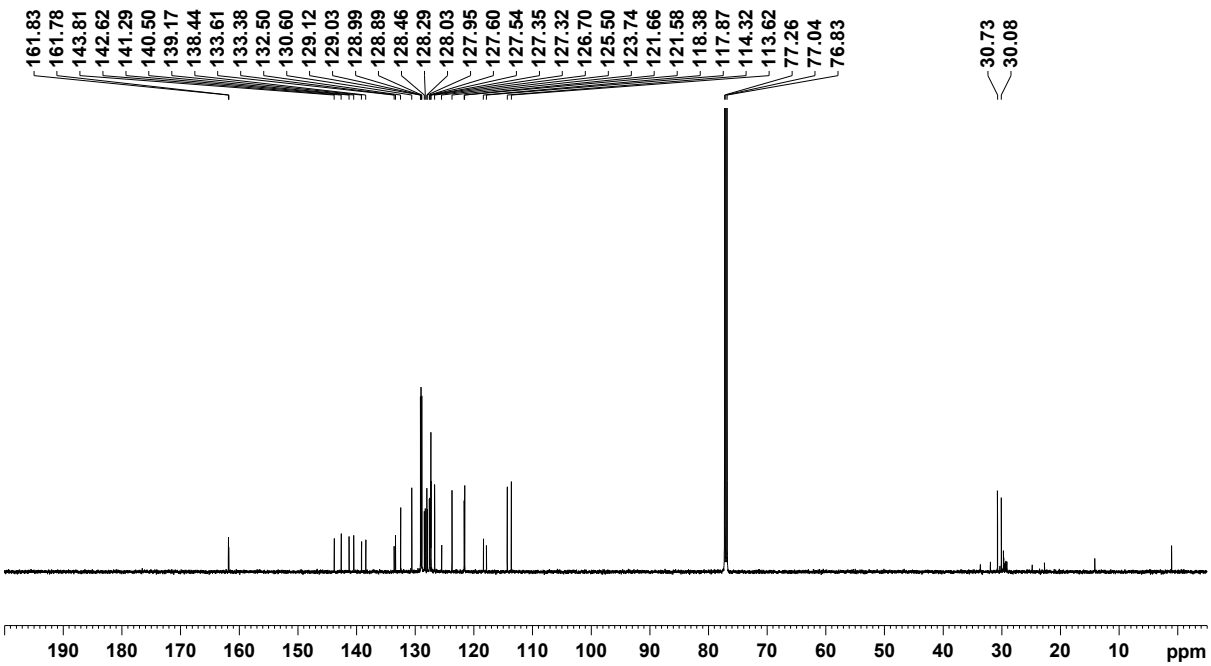
Mixture of 3,5-Dimethylphenanthridin-6(*5H*)-one + 1,5-Dimethylphenanthridin-6(*5H*)-one (2l)



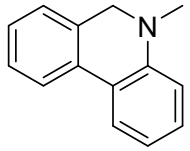
Mixture of 1-phenyl-5-methylphenanthridin-6(*5H*)-one + 5-Methyl-3-phenyl-phenanthridin-6(*5H*)-one (2m)

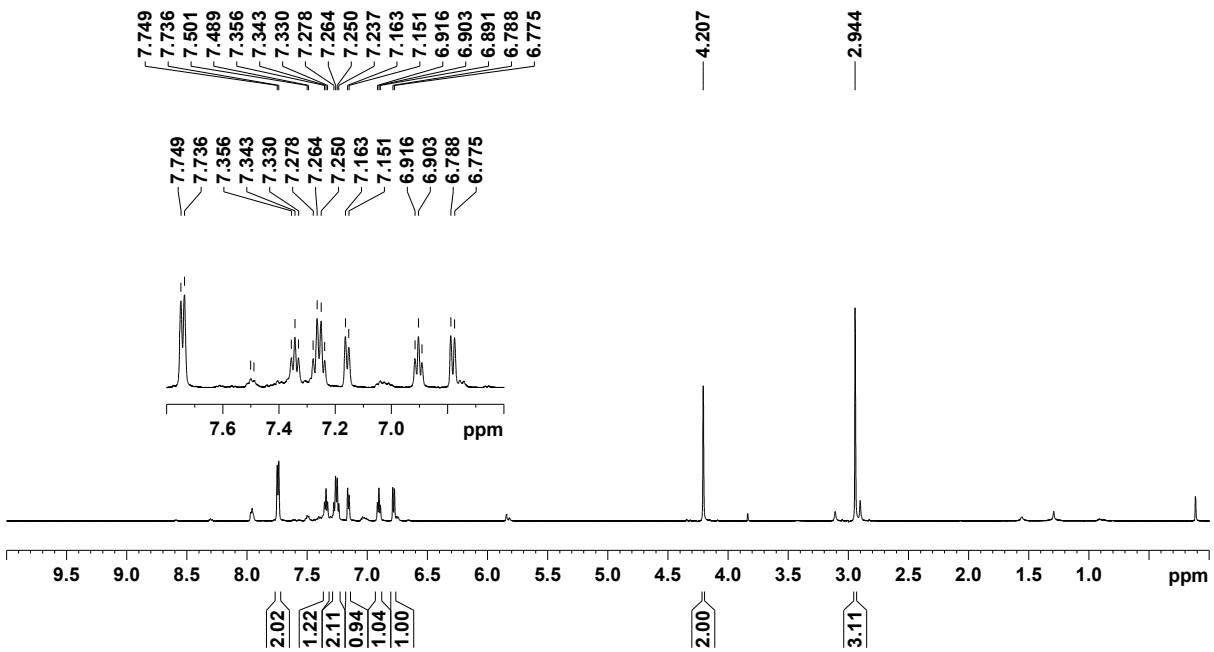


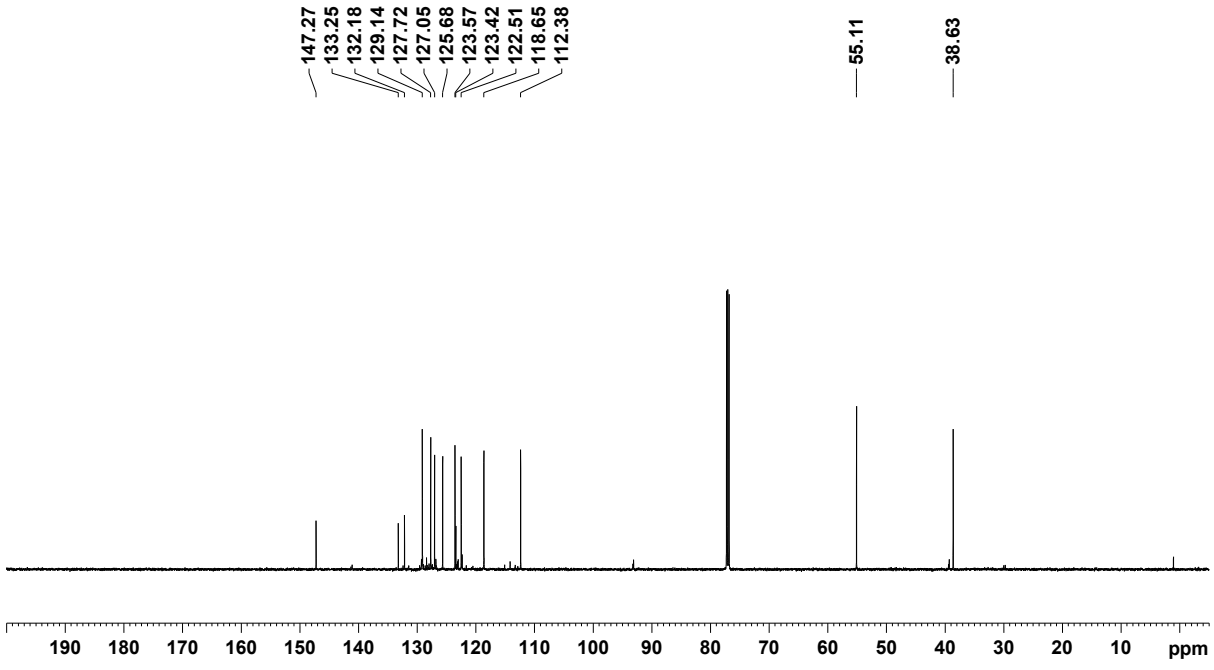




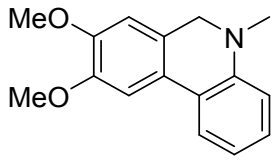
5-Methyl-5,6-dihydrophenanthridine (4a)

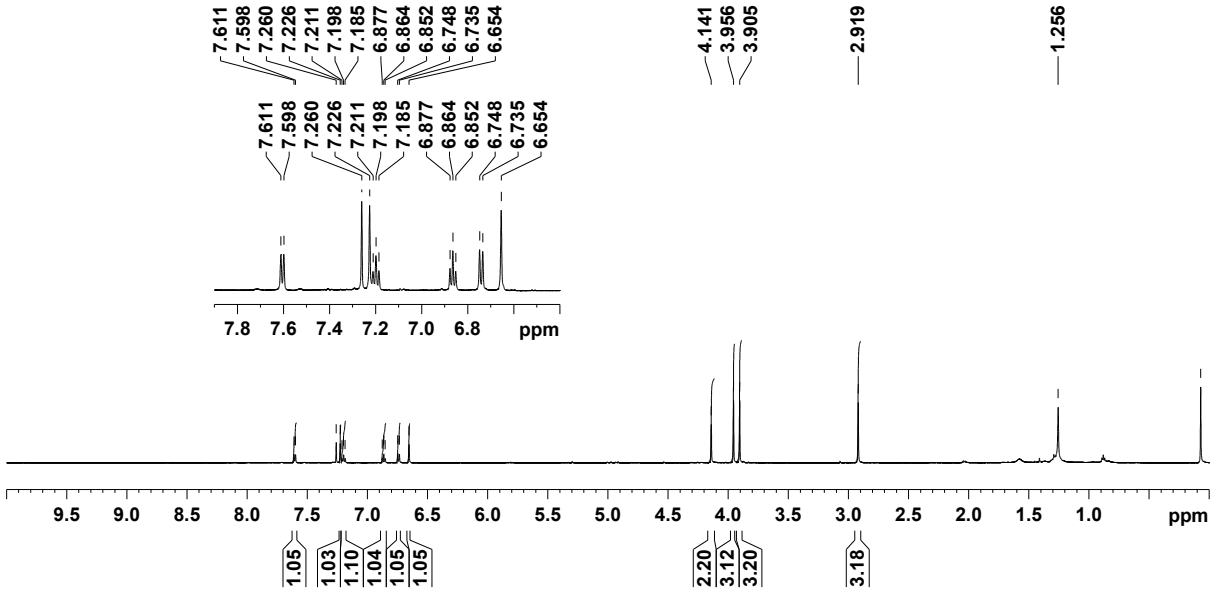


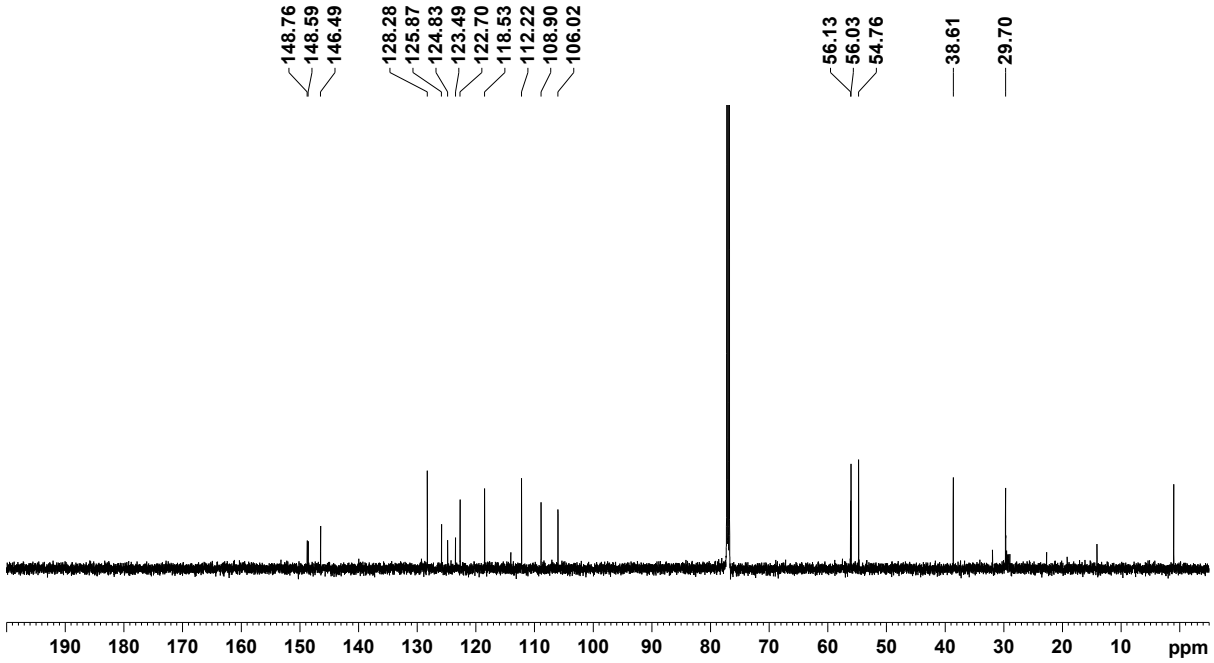




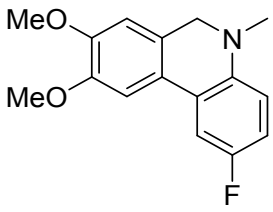
8,9-Dimethoxy-5-methyl-5,6-dihydrophenanthridine (4b)

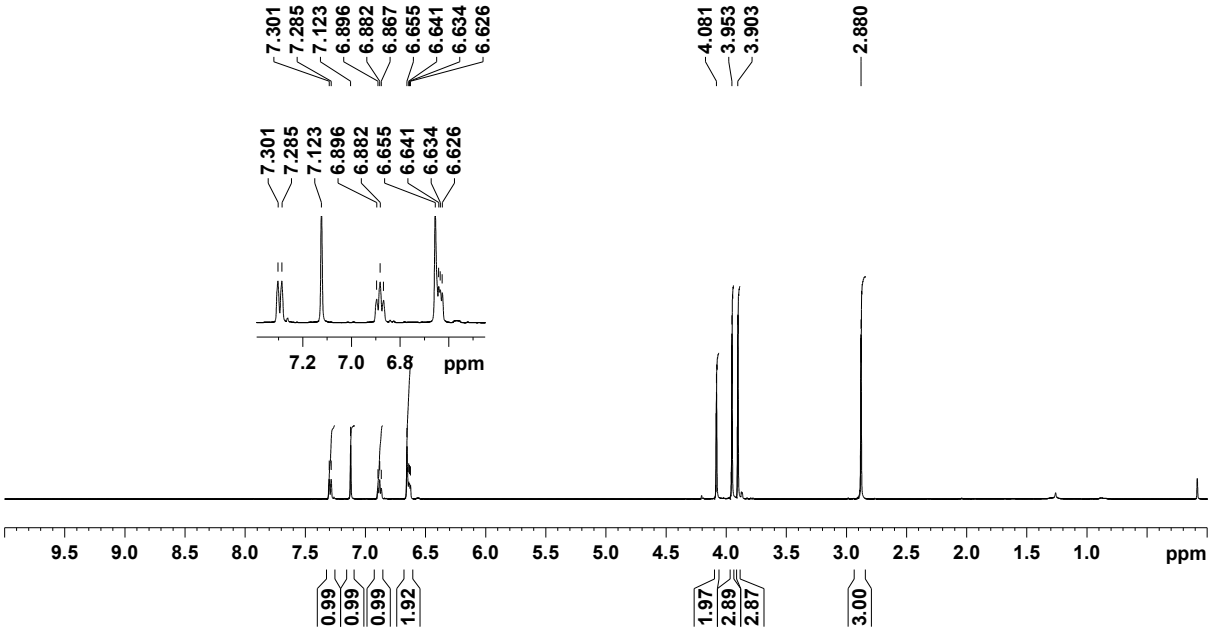


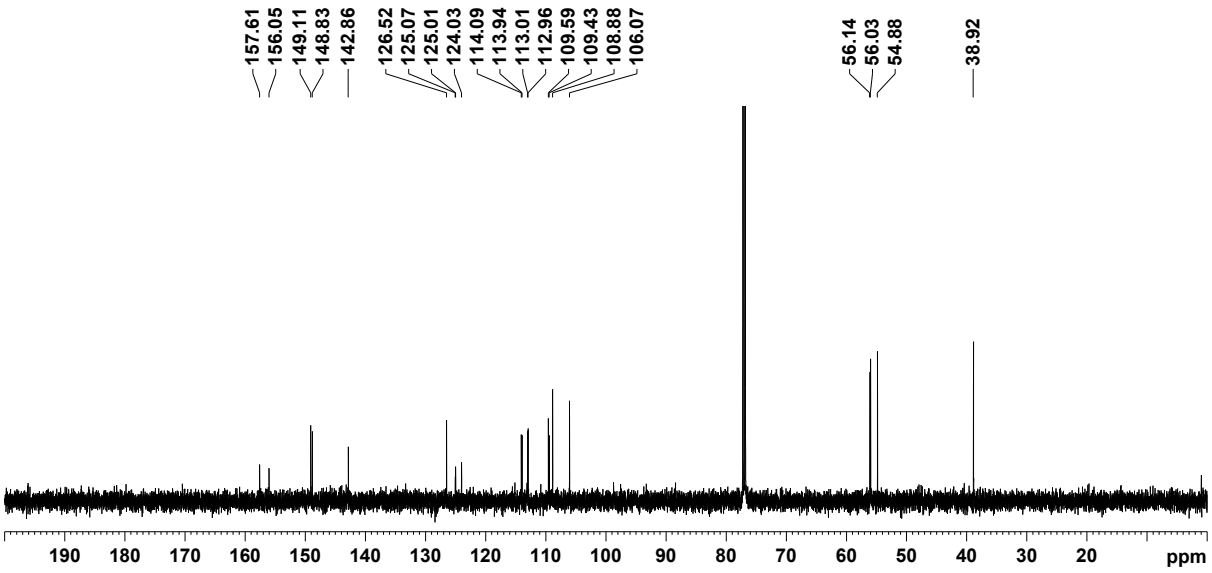




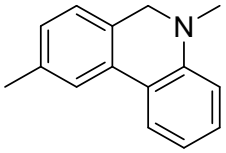
2-Fluoro-8,9-dimethoxy-5-methyl-5,6-dihydrophenanthridine (4c)

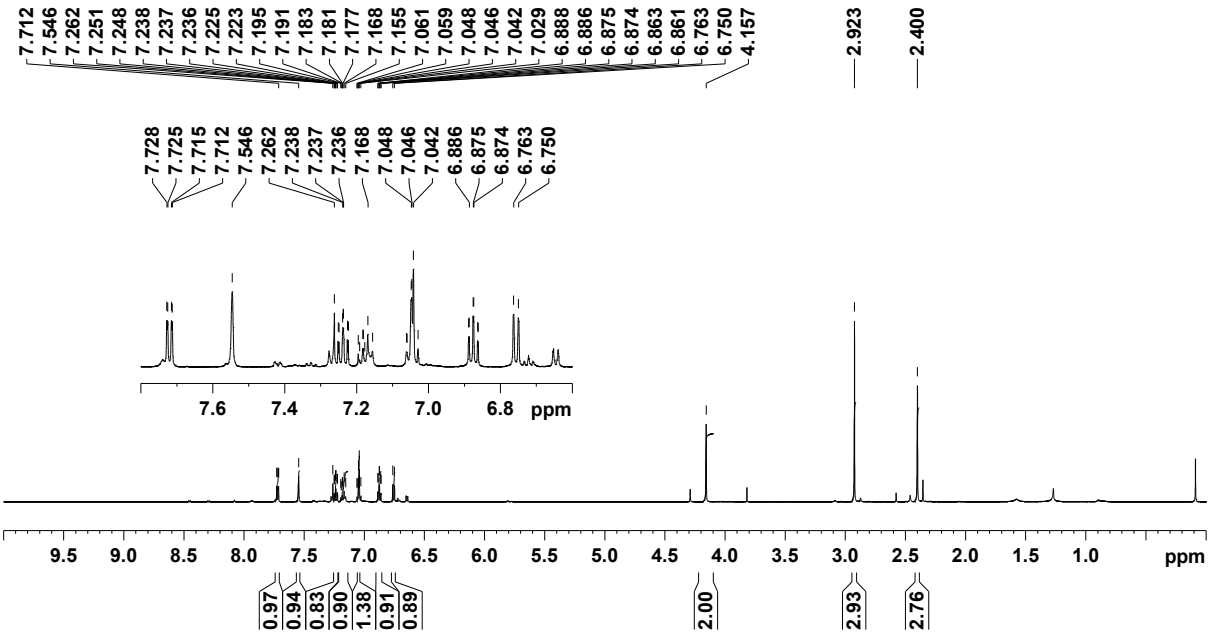


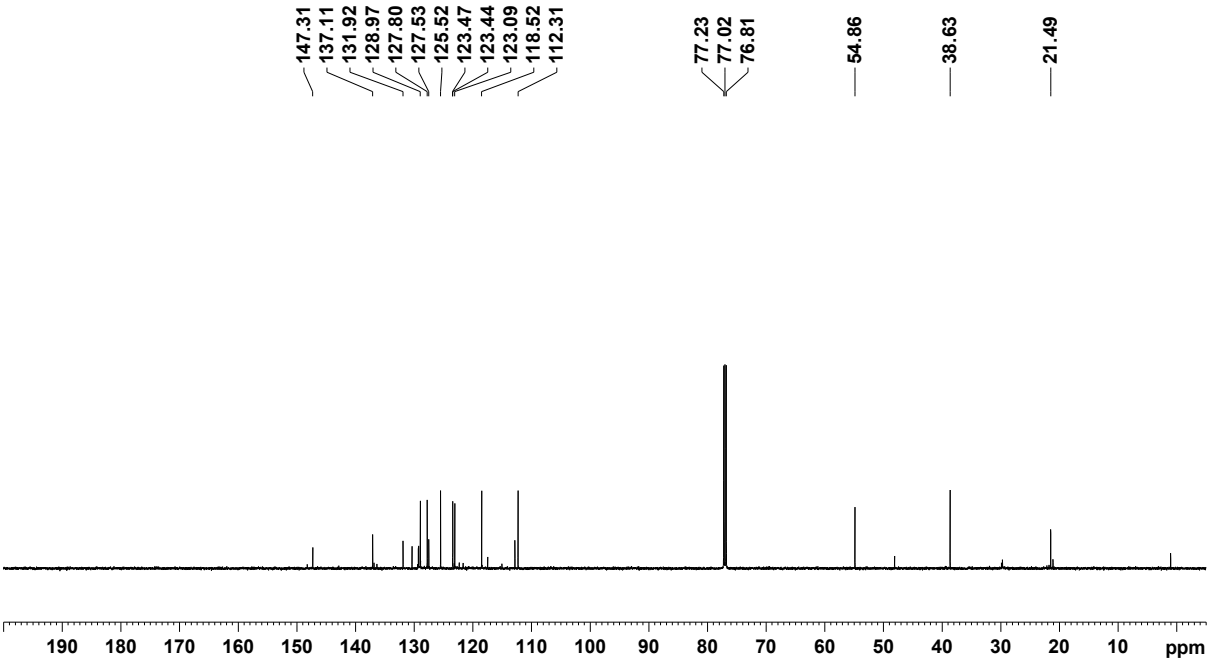




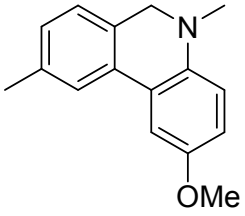
5,9-Dimethyl-5,6-dihydrophenanthridine (4d)

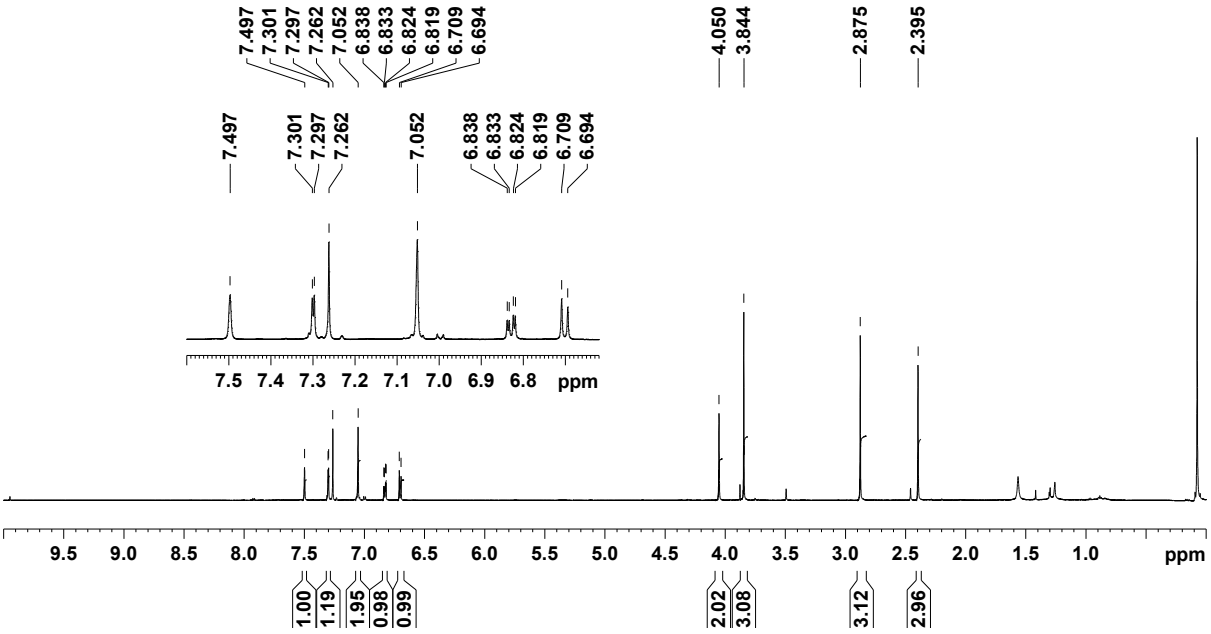


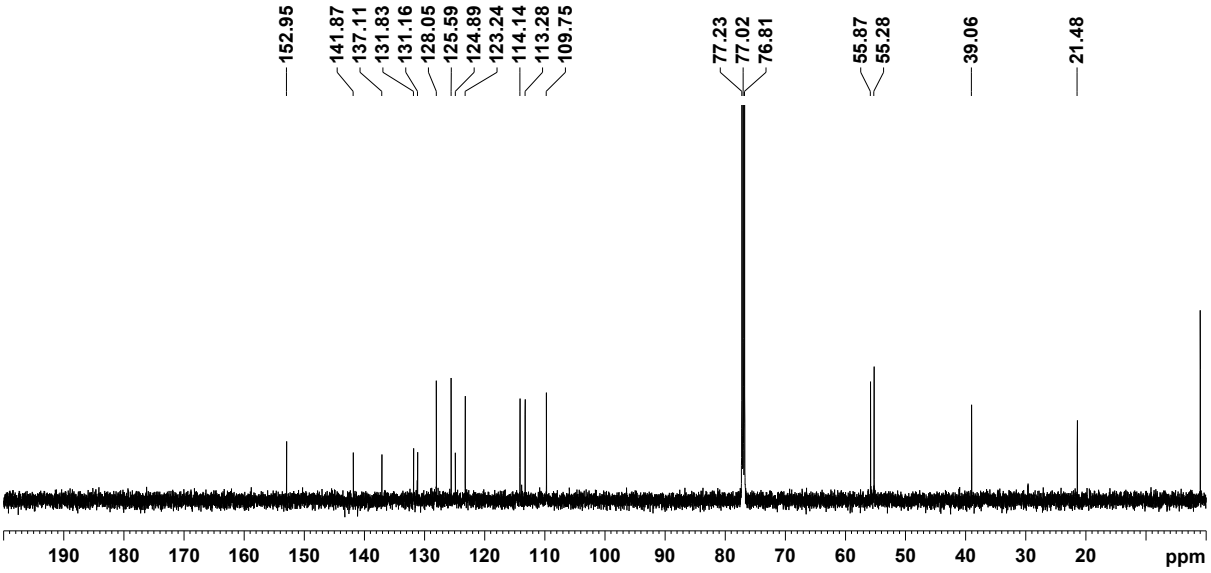




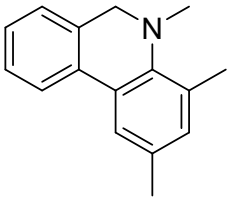
2-Methoxy-5,9-dimethyl-5,6-dihydrophenanthridine (4e)

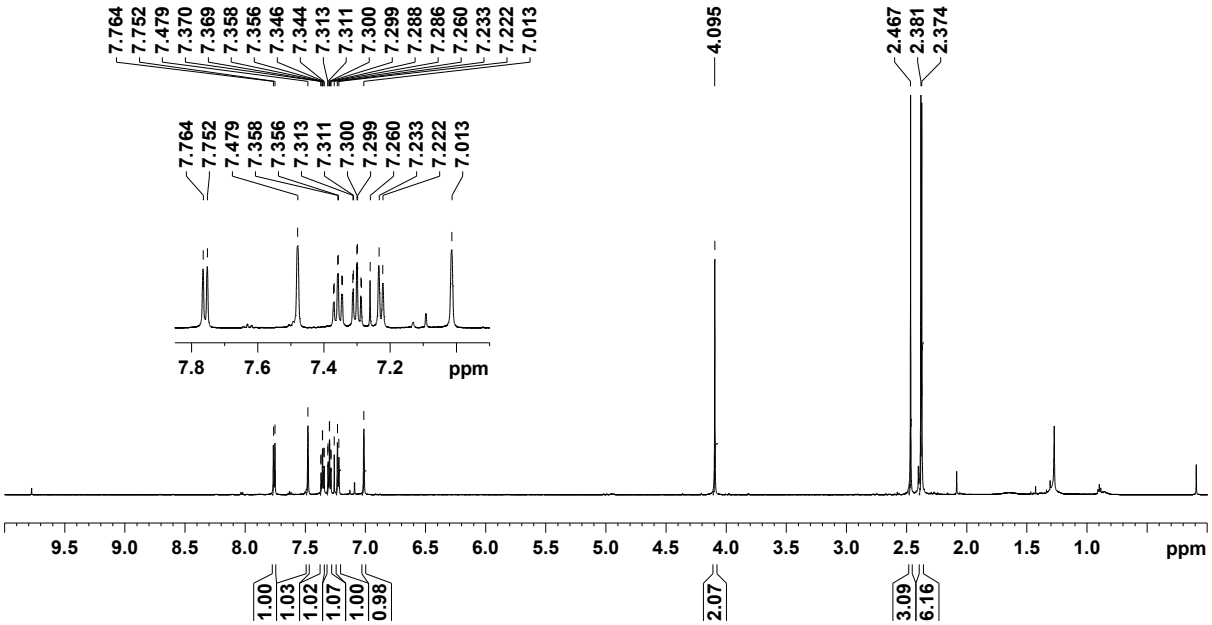


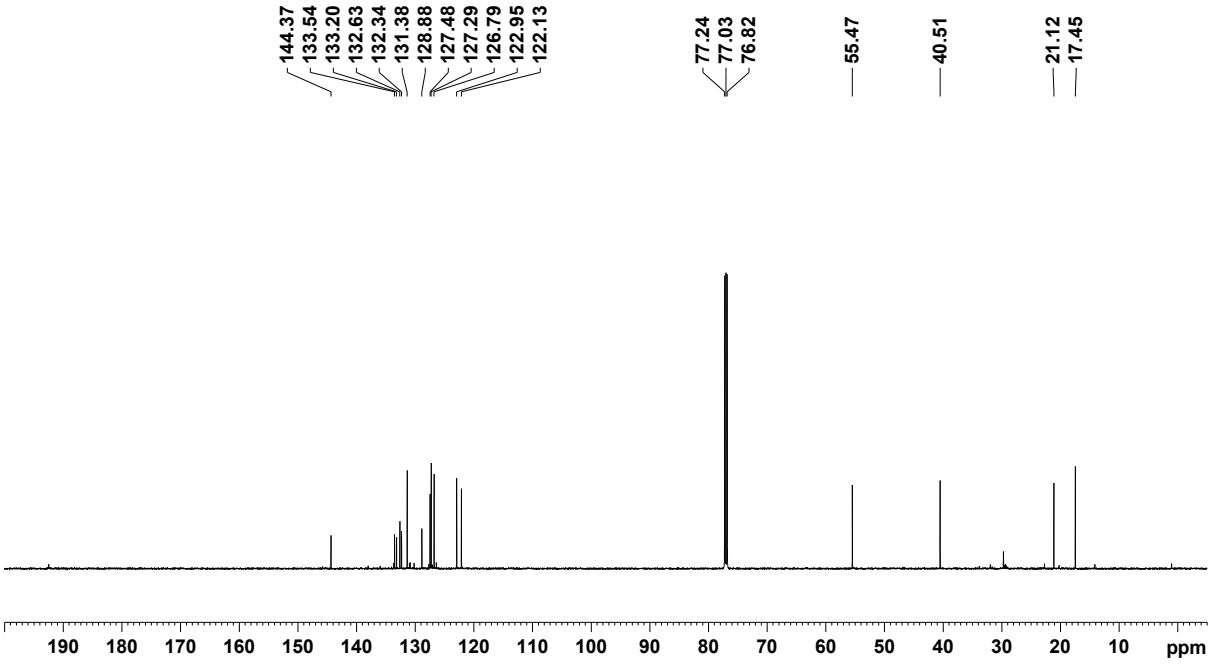




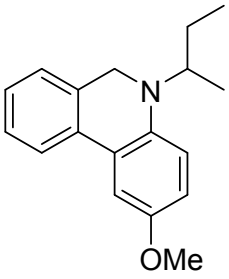
2,4,5-Trimethyl-5,6-dihydrophenanthridine (4f)

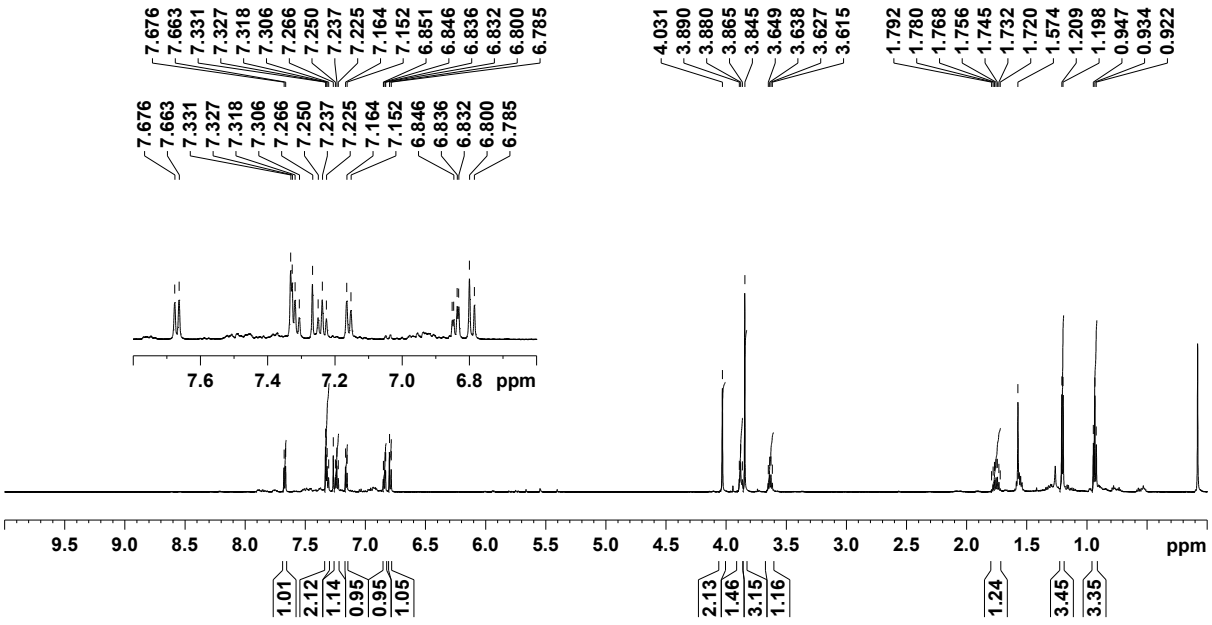


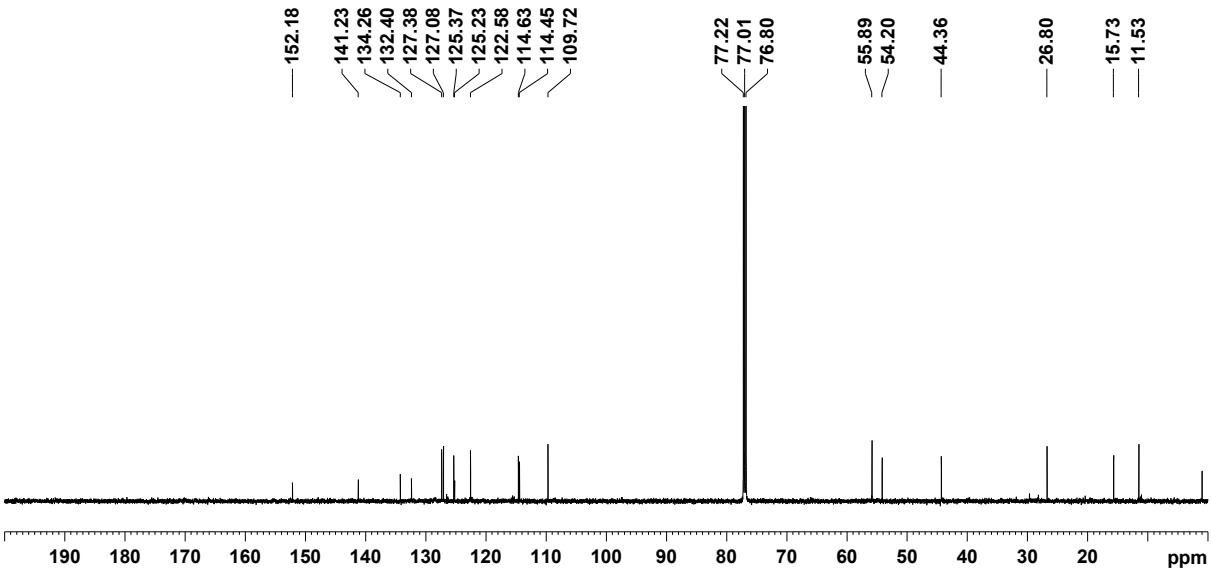




2-Methoxy-5-*sec*-butyl-5,6-dihydrophenanthridine (4g)







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