Supporting Information

Halogen Atom Transfer-Induced Radical Cascades Cyclization of *N*-(*o*-Cyanobiaryl)acrylamides with Alkyl Halides *via* Boryl Radical-Mediated

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1. General Information

Unless otherwise stated, all commercial reagents were used as received. All reagents and solvents were commercially available and used without any further purification unless specified. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (0.25mm, 300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25mm 300-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). All reactions were carried out with magnetic stirring and in dried glassware.Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz, 376 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quated in Hz. The solvent peak was used as a reference value, for ^{1}H NMR: TMS = 0.00 ppm, for ^{13}C NMR: $CDCl_3$ = 77.00 ppm. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, td = triplet of doublet, q = quartet, m = multiplet, and br = broad. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

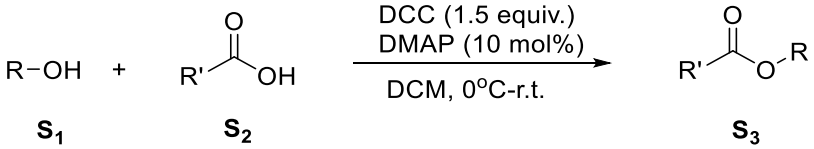
2 Experiment Section

2.1. Starting Material Synthesis

General procedure for synthesis of 1a

N-(*o*-Cyanobiaryl)acrylamides **1a**[1] was synthesized according to the known methods.

General procedure for synthesis of 2x-2ac[2]



General procedure for the synthesis of 1-6: In a 50 mL round-bottom flask equipped with a magnetic stirring bar, **S$_1$** (1.0 equiv.), **S$_2$** (1.2 equiv.), DCC (1.5

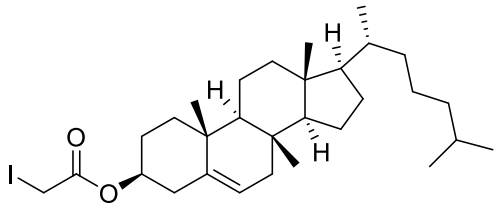
equiv.), DMAP (10 mol%), DCM (10 mL) were charged sequentially under the conditions of an ice bath (0 ^{o}C). The mixture was then allowed to stir for 2 h at room temperature. After the reaction was completed, the residue obtained after treatment was purified by silica gel column chromatography to obtain **S_3**.

2-Iodoethyl 2-(4-isobutylphenyl)propanoate (2x): Prepared according to general substrate synthesis procedure using 2-iodoethanol (1.0 equiv), ibuprofen (1.2 equiv.), DCC (1.5 equiv.), DMAP (10 mol%), DCM (10 mL), The reaction was purified by chromatography to afford the title compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.22 - 7.19 (m, 2H), 7.10 - 7.08 (m, 2H), 4.33 - 4.24 (m, 2H), 3.74 - 3.68 (m, 1H), 3.24 - 3.15 (m, 2H), 2.45 - 2.43 (m, 2H), 1.89 - 1.80 (m, 1H), 1.51 - 1.49 (m, 3H), 0.90 - 0.88 (m, 6H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 173.8, 140.4, 137.2, 129.2 (2C), 127.1 (2C), 64.5, 44.9, 30.0 (2C), 22.3, 22.3, 18.3, 0.2; HRMS (ESI-TOF) *m/z*: $C_{15}H_{22}IO_2^+$ $(M + H)^+$ calcd for 361.0659, found 361.0655.

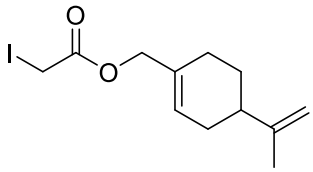
3,7-Dimethyloct-6-en-1-yl 2-iodoacetate (2y): Prepared according to general substrate synthesis procedure using citronellol (1.0 equiv.), iodoacetic acid (1.2 equiv.), DCC (1.5 equiv.), DMAP (10 mol%), DCM (10 mL), The reaction was purified by chromatography to afford the title compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 5.13 - 5.05 (m, 1H), 4.23 - 4.13 (m, 2H), 3.68 (s, 2H), 2.05 - 1.93 (m, 2H), 1.69 (s, 3H), 1.61 (s, 3H), 1.58 (s, 2H), 1.50 - 1.42 (m, 1H), 1.39 - 1.31 (m, 1H), 1.24 - 1.14 (m, 1H), 0.92 (d, *J* = 6.6 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 168.9, 131.4, 124.5, 64.7, 36.9, 35.1, 29.3, 25.7, 25.4, 19.3, 17.7, -5.3; HRMS (ESI-TOF) *m/z*: $C_{12}H_{22}IO_2^+$ $(M + H)^+$ calcd for 325.0659, found 325.0652.

(E)-3,7-Dimethylocta-2,6-dien-1-yl 2-iodoacetate (2z): Prepared according to general substrate synthesis procedure using geraniol (1.0 equiv.), iodoacetic acid (1.2 equiv.), DCC (1.5 equiv.), DMAP (10 mol%), DCM (10 mL), The reaction was purified by chromatography to afford the title compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 5.38 -

5.31 (m, 1H), 5.15 - 5.01 (m, 1H), 4.65 (d, *J* = 7.2 Hz, 2H), 3.69 (t, *J* = 2.4 Hz, 2H), 2.14 - 2.02 (m, 4H), 1.70 (d, *J* = 14.0 Hz, 6H), 1.61 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 168.7, 143.3, 131.8, 123.6, 117.3, 62.9, 39.4, 26.2, 25.6, 17.6, 16.5, -5.2; HRMS (ESI-TOF) *m/z*: $C_{12}H_{20}IO_2^+$ $(M + H)^+$ calcd for 323.0502, found 323.0506.

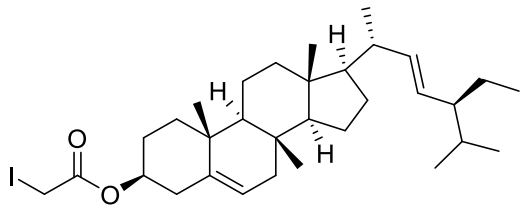
(3*S*,8*S*,9*S*,10*R*,13*R*,14*R*,17*R*)-8,10,13-Trimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 2-iodoacetate (2aa): 

Prepared according to general substrate synthesis procedure using cholesterol (1.0 equiv.), iodoacetic acid (1.2 equiv.), DCC (1.5 equiv.), DMAP (10 mol%), DCM (10 mL), The reaction was purified by chromatography to afford the title compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 5.40 - 5.38 (m, 1H), 4.68 - 4.60 (m, 1H), 3.66 (s, 2H), 2.34 (d, *J* = 7.6 Hz, 2H), 2.04 - 1.94 (m, 2H), 1.91 - 1.80 (m, 3H), 1.71 - 1.42 (m, 8H), 1.40 - 1.23 (m, 4H), 1.23 - 1.07 (m, 7H), 1.02 (s, 7H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.88 - 0.85 (m, 6H), 0.68 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 168.2, 139.2, 123.0, 75.7, 56.6, 56.1, 49.9, 42.3, 39.7, 39.5, 37.5, 36.8, 36.5, 36.1, 35.8, 31.9, 31.8, 28.2, 28.0, 27.3, 24.2, 23.8 (2C), 22.8, 22.5, 21.0, 19.3, 18.7, 11.8, -4.5; HRMS (ESI-TOF) *m/z*: $C_{30}H_{50}IO_2^+$ $(M + H)^+$ calcd for 569.2850, found 569.2855.

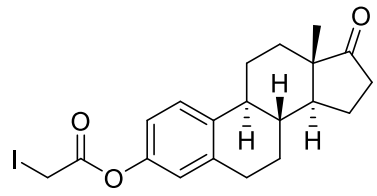
(4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl 2-iodoacetate (2ab): Prepared 

according to general substrate synthesis procedure using Perillyl alcohol (1.0 equiv.), iodoacetic acid (1.2 equiv.), DCC (1.5 equiv.), DMAP (10 mol%), DCM (10 mL), The reaction was purified by chromatography to afford the title compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 - 5.76 (m, 1H), 4.76 - 4.69 (m, 2H), 4.58 - 4.48 (m, 2H), 3.71 (s, 2H), 2.20 - 2.09 (m, 4H), 2.03 - 1.92 (m, 1H), 1.89 - 1.83(m, 1H), 1.74 (s, 3H), 1.56 - 1.45 (m, 1H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 168.5, 149.3, 132.0, 126.6, 108.8, 77.3, 77.0, 76.7, 69.9, 40.6, 30.4, 27.1, 26.2, 20.7, -5.4; HRMS (ESI-TOF) *m/z*: $C_{12}H_{18}IO_2^+$ $(M + H)^+$ calcd for 321.346, found 321.0348.

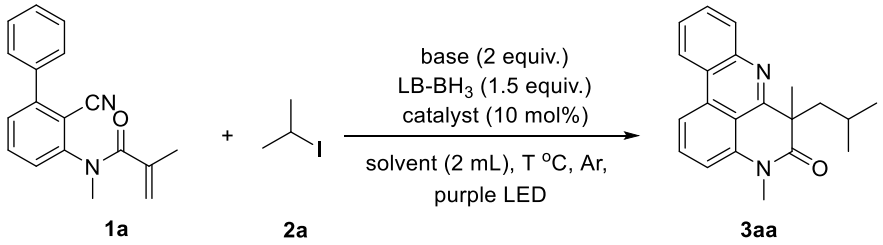
(3*S*,8*S*,9*S*,10*R*,13*R*,14*R*,17*R*)-17-((2*R*,5*S*,*E*)-5-Ethyl-6-methylhept-3-en-2-yl)-8,10,13-trimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 2-iodoacetate (2ac): Prepared according to general substrate synthesis procedure using stigmasterol (1.0 equiv.), iodoacetic acid (1.2 equiv.), DCC (1.5 equiv.), DMAP (10 mol%), DCM (10 mL), The reaction was purified by chromatography to afford the title compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 5.39 (d, *J* = 3.2 Hz, 1H), 5.18 - 5.12 (m, 1H), 5.04 - 5.00 (m, 1H), 4.67 - 4.61 (m, 1H), 3.66 (s, 2H), 2.34 (d, *J* = 8.0 Hz, 2H), 2.08 - 1.94 (m, 3H), 1.91 - 1.83 (m, 2H), 1.73 - 1.66 (m, 1H), 1.62 - 1.39 (m, 9H), 1.34 - 1.10 (m, 6H), 1.10 - 0.91 (m, 10H), 0.86 - 0.77 (m, 9H), 0.70 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 168.2, 139.2, 138.3, 129.2, 123.0, 75.7, 56.7, 55.9, 51.2, 50.0, 42.2, 40.5, 39.6, 37.5, 36.8, 36.5, 31.8 (2C), 31.7, 28.9, 27.3, 25.4, 24.3, 21.2, 21.1 (2C), 21.0, 19.3, 19.0, 12.2, 12.0, -4.6; HRMS (ESI-TOF) *m/z*: $C_{32}H_{52}IO_2^+$ $(M + H)^+$ calcd for 595.3007, found 595.3012.



(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[*a*]phenanthren-3-yl 2-iodoacetate (2ad): Prepared according to general substrate synthesis procedure using estrone (1.0 equiv.), iodoacetic acid (1.2 equiv.), DCC (1.5 equiv.), DMAP (10 mol%), DCM (10 mL), The reaction was purified by chromatography to afford the title compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.30 (d, *J* = 9.6 Hz, 1H), 6.88 (d, *J* = 11.2 Hz, 1H), 6.84 (s, 1H), 3.89 (s, 2H), 2.94 - 2.85 (m, 3H), 2.55 - 2.47 (m, 1H), 2.42 - 2.25 (m, 1H), 2.18 - 1.94 (m, 6H), 1.65 - 1.43 (m, 5H), 0.91 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 221.0, 167.8, 148.3, 138.1, 137.8, 126.4, 120.9, 118.1, 50.3, 47.9, 44.1, 38.3, 37.9, 35.8, 31.4, 29.3, 26.2, 25.7, 21.5, 13.8.; HRMS (ESI-TOF) *m/z*: $C_{20}H_{24}IO_3^+$ $(M + H)^+$ calcd for 435.0765, found 435.0769.



2.2 Screening of the Optimal Reaction Conditions



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

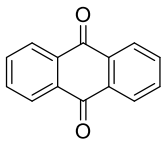
To a Schlenk tube were added **1a** (0.2 mmol), **2a** (0.4 mmol), 2-Br AQ (10 mol %), base (2 equiv.), LB-BH_3 (1.5 equiv.), solvent (2 mL; 0.1 M) at 55 ^{o}C under an argon atmosphere. The mixture was placed from the 390 nm purple LEDs. The LEDs were switched on and the mixture was stirred under irradiation with a fan for 24 hours. Until complete consumption of the starting material was observed by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture removal of the solvent, the crude product was purified by column chromatography to provide the desired products. The residue was dissolved in $CDCl_3$ and analysed by ^{1}H NMR spectroscopy to obtain the NMR yield.

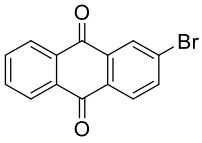
Table S1. Reaction optimization

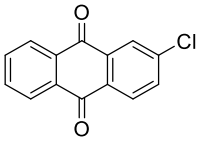
Entry	Catalyst	LB-BH_3	Base	Solvent	Temperature	Yield (%)
Base screening						
1	2-Br AQ	Me_3N-BH_3	K_3PO_4	EtOAc	r.t.	31
2			K_2CO_3			48
3			Na_2CO_3			21
4			Cs_2CO_3			52
5			TMG			34
6			DBU			30
7			$^{i}Pr_2NEt$			41
8			Et_3N			37
9			pyridine			30
10			2,6-lutidine			21

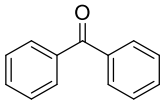
Solvent screening						
11	2-Br AQ	Me_3N-BH_3	Cs_2CO_3	EtOAc	r.t.	52
12				THF		40
13				acetone		35
14				DMF		26
15				$PhCF_3$		64
16				DCE		56
17				CH_3CN		42
18				CH_2Cl_2		38
Catalyst screening						
19	AQ	Me_3N-BH_3	Cs_2CO_3	$PhCF_3$	r.t.	32
20	2-Cl-AQ					41
21	2-Br-AQ					64
22	BP1					15
23	BP2					20
24	4-CzIPN					25
25	$Ir(ppy)_3$					35
LB-BH_3 screening						
26	2-Br AQ	Me_3N-BH_3	Cs_2CO_3	$PhCF_3$	r.t.	64
27		Ph_3P-BH_3				60
28		Pyr-BH_3				22
29		2-MePyr-BH_3				14
30		Me_2NH-BH_3				49
31		^{t}BuNH$_2$-BH_3				34

32		4-MeMorpholine-BH_3				39
Temperature screening						
33	2-Br AQ	Me_3N-BH_3	Cs_2CO_3	$PhCF_3$	40	59
34					55	79
35					70	72
36					80	64


AQ


2-Br-AQ


2-Cl-AQ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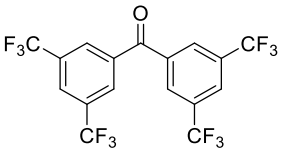
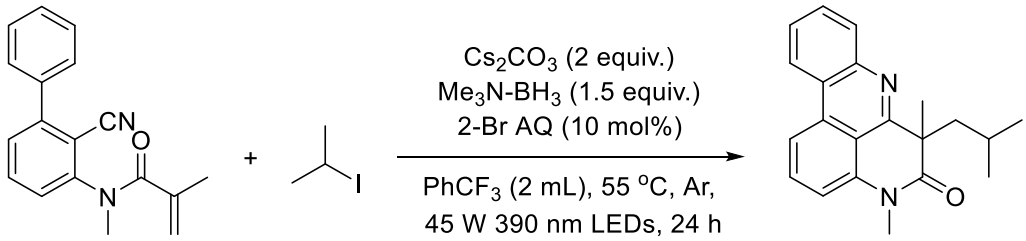

BP2

2.3 The Light on/off Experiments



Time (h)	0	6 (on)	12 (off)	18 (on)	24 (off)	36 (on)
Yield (%)	0	33%	33%	54%	54%	72%

The above depicted reaction was performed according to the general protocol established. The reaction was irradiated with 45 W 390 nm LEDs for 6 hours and then stirred in the dark for 6 hours. This procedure was repeated for 42 hours, and the yield of the product was determined by ^{1}H NMR with dibromomethane as an internal standard at each point the light was turned off or on. The results are shown in the graph above. This result shows that constant light irradiation is needed to progress the reaction.

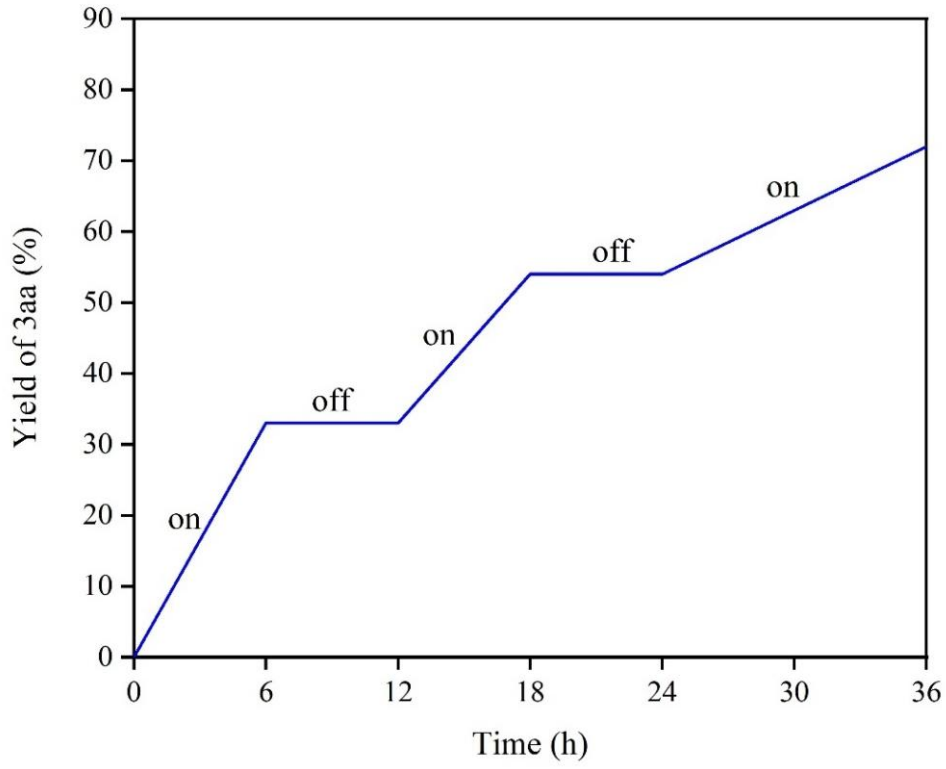


Figure S1 The light on/off Experiments

2.4 Quantum yield determination

Determination of the light intensity at 390 nm: According to the procedure of Yoon[2] the photon flux of the blue LED (λmax = 390 nm) was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 3.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at λ = 390 nm with an emission slit width at 10.0 nm. After irradiation, 0.53 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A nonirradiated sample was also prepared and the absorbance at 390 nm measured. Conversion was calculated using eq 1.

$$mol\ of\ Fe^{2+} = \frac{V \cdot \Delta A_{510\,nm}}{l \cdot \varepsilon} \qquad (1)$$

$$mol\ of\ Fe^{2+} = \frac{(0.00353\ L) \cdot (3.831 - 0.845)}{(1.00\ cm) \cdot (11100 \frac{L}{mol} cm^{-1})} = 9.49 \times 10^{-7}$$

Where V is the total volume (0.00353 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.00 cm), and ε is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11,100 L mol^{-1} cm^{-1}).[3] The photon flux can be calculated using eq 2.

$$Photo\ flux = \frac{mol\ of\ Fe^{2+}}{\emptyset \cdot t \cdot f} \qquad (2)$$

$$Photo\ flux = \frac{9.49 \times 10^{-7}}{(32.3) \cdot (90s) \cdot (0.999)} = 3.26 \times 10^{-10}\ einstein/s$$

Where Φ is the quantum yield for the ferrioxalate actinometer (32.3 at λ = 390 nm), t is the time (90.0 s), and f is the fraction of light absorbed at 390 nm by the ferrioxalate actinometer. This value is calculated using eq 3 where A390 nm is the absorbance of the ferrioxalate solution at 390 nm. An absorption spectrum gave an A390 nm value of > 3, indicating that the fraction of absorbed light (f) is > 0.999.

$$f = 1 - 10^{-A_{390\,nm}}$$

The photon flux was thus calculated to be 3.26×10^{-10}einsteins s^{-1}

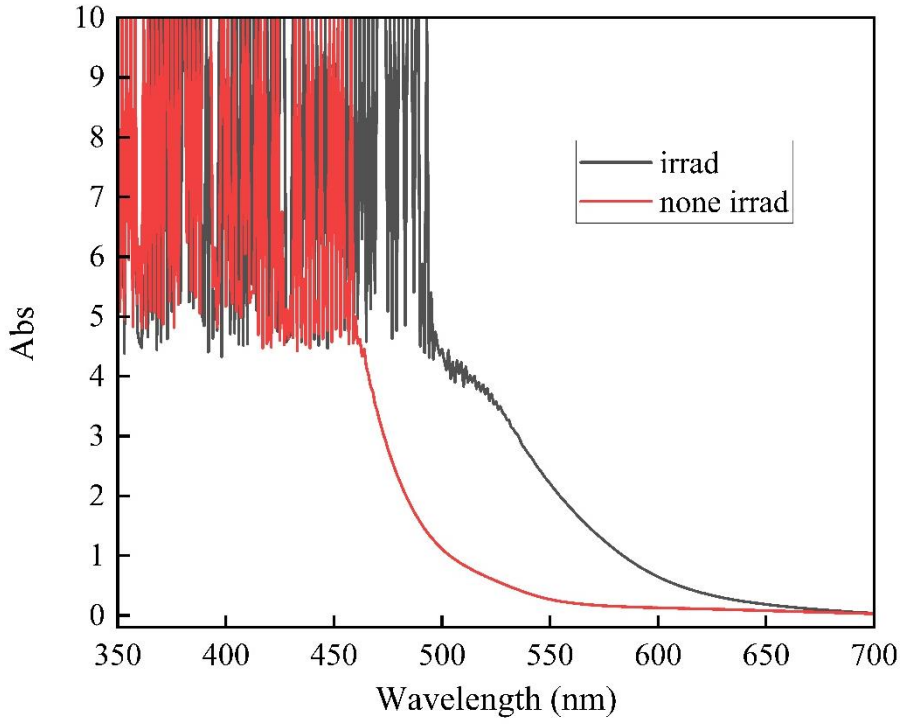
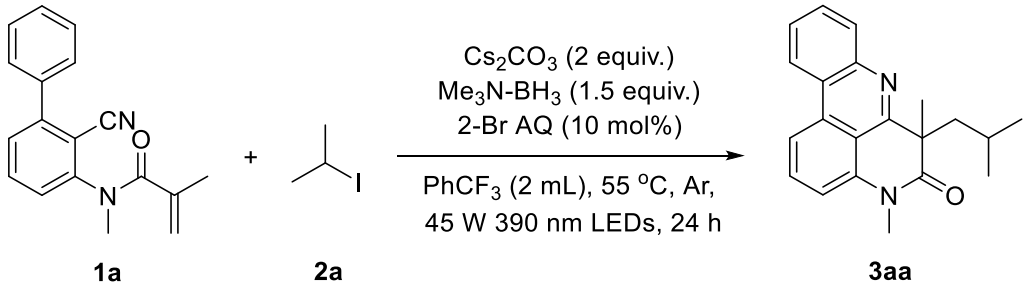


Figure S2 Absorbance of the ferrioxalate actinometer solution

Determination of the reaction quantum yield



A cuvette was charged with 1a (0.2 mmol), 2a (2 equiv), 2-Br AQ (10 mol %), Cs_2CO_3 (2 equiv.), LB-BH_3 (1.5 equiv.), $PhCF_3$ (2 mL; 0.1 M) at 55 ^{o}C under an argon atmosphere. The mixture was placed from the 390 nm purple LEDs. The LEDs were switched on and the mixture was stirred under irradiation with a fan for 2 h (7200s). The solvent was removed in vacuo and the yield of formed product was determined by ^{1}H NMR based on dibromomethane as internal standard. The quantum yield was determined using eq 4.

$$\emptyset = \frac{mol\ of\ product}{flux \cdot t \cdot f} \qquad (4)$$

$$\emptyset = \frac{2.1 \times 10^{-6}}{3.26 \times 10^{-10}\ einstein/s \cdot 7200s \cdot 0.989} = 0.90 < 1$$

The photon flux is $3.26 \times 10^{-10}\ einstein/s$, t is the reaction time (7200 s). f is the fraction of incident light absorbed by the catalyst, determined using eq 3. An absorption spectrum of the catalyst (0.001 M) gave an absorbance value of 0.806 at 390 nm (figure S6), indicating that the fraction of light absorbed by the photocatalyst (f) is 0.989.

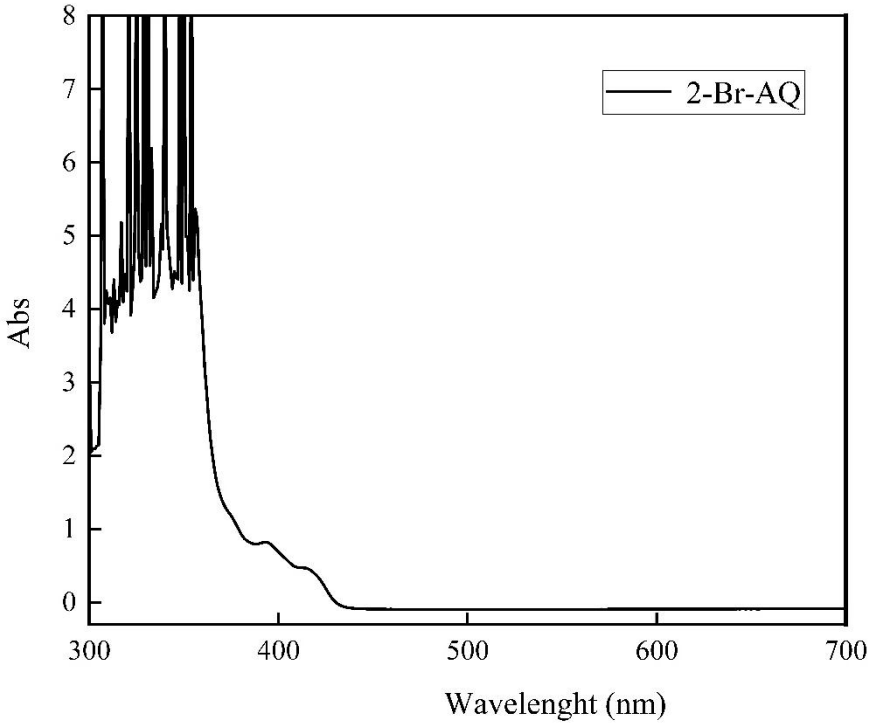


Figure S3 Absorption spectrum of 2-Br-AQ [0.001 M] in $PhCF_3$

2.5 Stern-Volmer quenching experiments

Formulation solution:

Me_3N-BH_3 was dissolved in $PhCF_3$ in a 5 mL volumetric flask to set the concentration to be 0.01 M. 2-Iodopropane 2a was dissolved in $PhCF_3$ in a 5 mL volumetric flask to set the S2 concentration to be 0.01 M and 2-Br AQ were dissolved in $PhCF_3$(5.0 mL) to set the concentration to be 0.01 M.

Additional experimental details:

The samples were prepared by 2-Br AQ (5×10^{-4} M) with different amount of quencher in $PhCF_3$ in a light path quartz fluorescence cuvette. The concentration of quencher is 0.01 M in $PhCF_3$. For each S3 quenching experiment, 3 μl of quencher solution was separately titrated to the 2-Br AQ (3.0 mL).

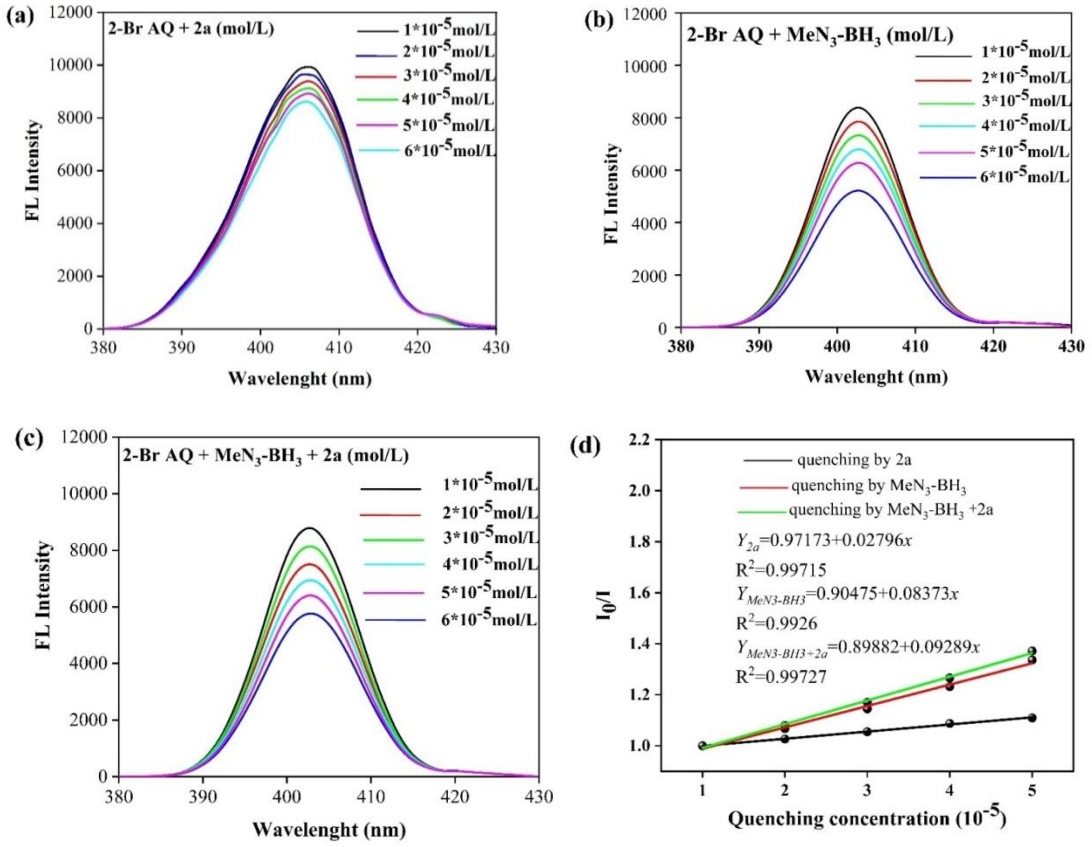


Figure S4 Stern-Volmer Quenching Experiments: (a) 2-Br AQquenched by 2a in $PhCF_3$; (b) 2-Br AQ quenched by Me_3N-BH_3 in $PhCF_3$; (c) 2-Br AQ quenched by Me_3N-BH_3 and 2a in $PhCF_3$, (d) Stern-Volmer plot of photocatalyst at different concentration.

The resulting mixture was sparged with nitrogen for 3 minutes and then irradiated at 400 nm. Fluorescence emission spectra were recorded (3 trials per sample). Into this solution, 3.0 μL of 2a and Me_3N-BH_3 solution was successively added and uniformly stirred, and the resulting mixture was bubbled with nitrogen for 3 minutes and irradiated at 400 nm. Fluorescence emission spectra of 0 μL, 3.0 μL, 6.0 μL, 9.0 μL, 12.0 μL, 15.0 μL fluorescence intensity. Follow this method and make changes to the amount to obtain the Stern-Volmer relationship in turn. Compared the figure S2 (a) (b) of Stern-Volmer quenching experiments results, the emission intensity of the 2-Br AQ solution strongly affected by the gradual increase of the amount of 2a and Me_3N-BH_3, and the influence is not observed to 2a. These indicated that the single electron transfer (SET) process occured in catalyst and 2-Iodopropane.

2.6 UV-Vis Absorption Experiments

UV-visible spectroscopy of reaction solution was recorded on a UV-2600 UV-Vis spectrophotometer. The sample was prepared by N-(2-cyano-[1,1'-biphenyl]-3-yl)-N-methylmethacrylamide **1a** (10^{-4} M), 2-Iodopropane **2a** (10^{-4} M), 2-Br AQ (10^{-4} M) in $PhCF_3$. The absorption was collected and the result was listed in Figure S5.

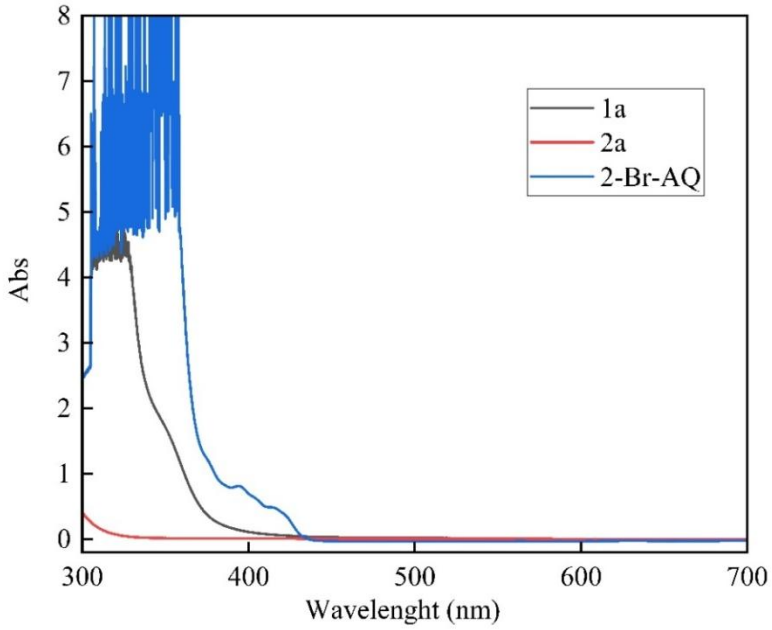
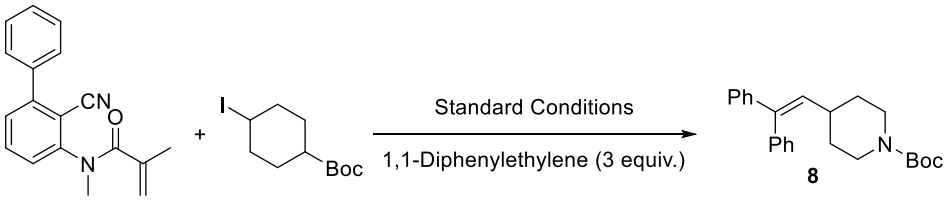


Figure S5 UV-Vis absorption experiments

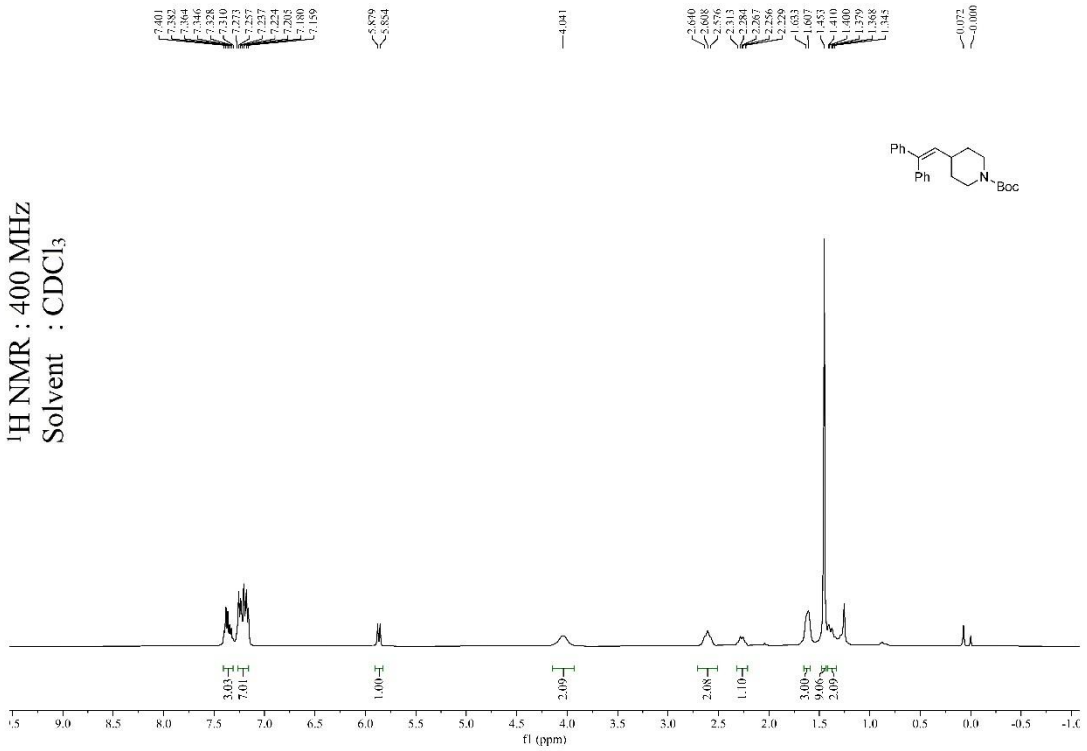
2.7 Control Experiments

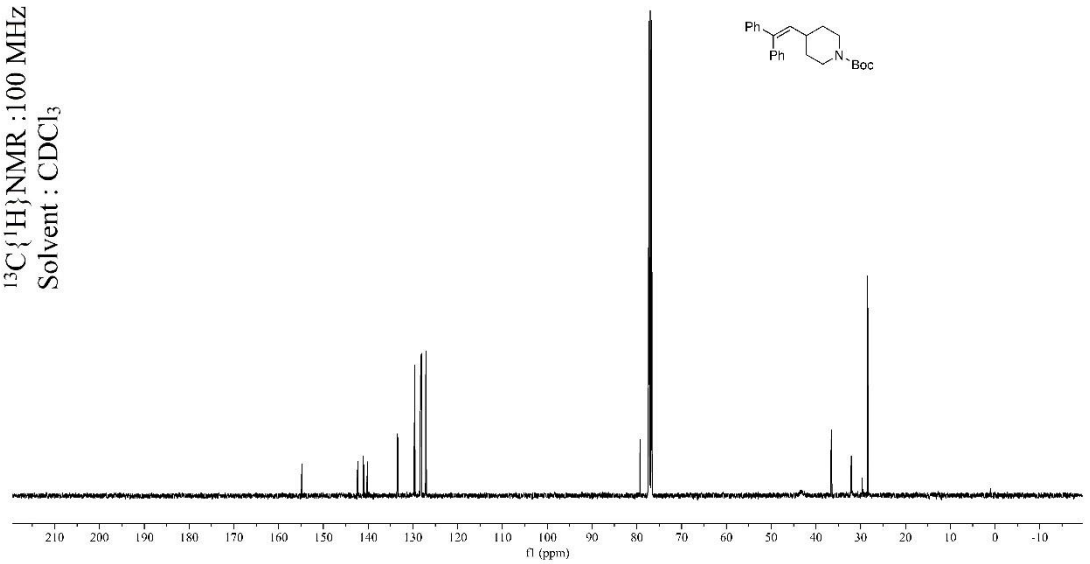
2.7.1 NMR Analysis of Raw Reaction Mixture by Using 1,1-diphenylethen as Radical Inhibito



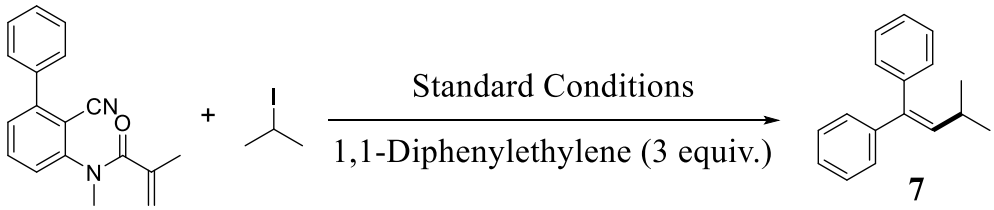
Tert-butyl 4-(2,2-diphenylvinyl)piperidine-1-carboxylate : The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate to afford a White liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.31 (m, 3H), 7.26 - 7.16 (m, 7H), 5.87 (d, *J* = 10.0 Hz, 1H), 4.04 (s, 2H), 2.61 (t, *J* = 12.8 Hz, 2H), 2.31 - 2.23 (m, 1H), 1.63 (d, *J* = 10.4

Hz, 3H), 1.45 (s, 9H), 1.41 - 1.37 (m, 2H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 154.8, 142.3, 141.0, 140.1, 133.4, 129.6 (2C), 128.3 (2C), 128.1 (2C), 127.1 (2C), 127.0 (2C), 79.3, 36.5 (2C), 32.1 (2C), 29.7, 28.4 (3C); HRMS (ESI-TOF) *m/z*: $C_{24}H_{30}NO_2^+$ $(M + H)^+$ calcd for 364.2271, found 364.2274.





2.7.2 GC-MS Analysis of Raw Reaction Mixture by Using 1,1-diphenylethen as Radical Inhibito

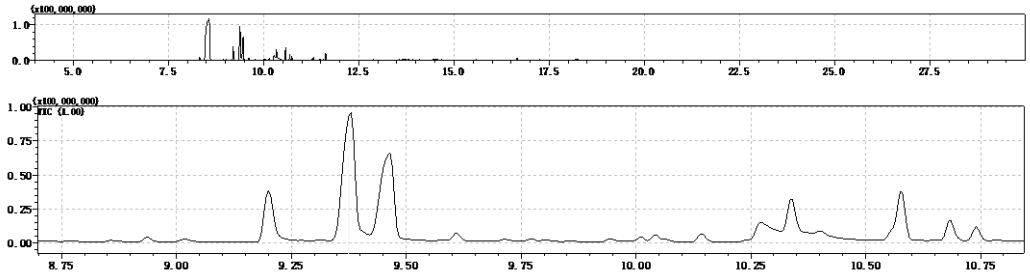


7

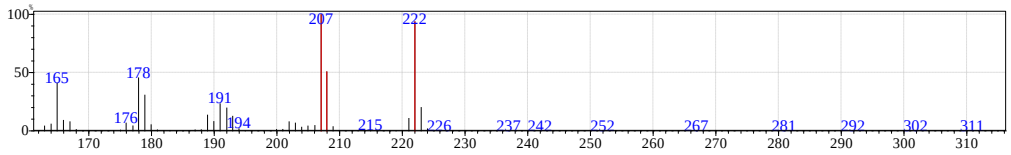
Chemical Formula: $C_{17}H_{18}$

Exact Mass: 222.1409

Spectra of GC-MS



MS spectra of the peak at 9.378 min



[MS Spectrum]

# of Peaks 525

Raw Spectrum 9.375 (scan : 1076)

Background No Background Spectrum

Base Peak m/z 129.15 (Inten : 8,391,213)

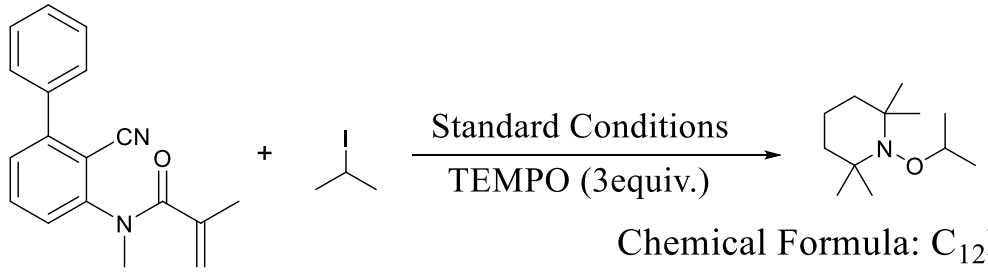
Event# 1

m/z	Absolute Intensity	Relative Intensit						
50.00	153937	1.83	56.45	4791	0.06	62.00	85119	1.01
51.00	726430	8.66	57.50	12153	0.14	63.00	414462	4.94
52.00	141558	1.69	58.45	2003	0.02	64.00	73409	0.87
53.05	110329	1.31	58.95	967	0.01	65.00	463647	5.53
54.05	7039	0.08	60.05	852	0.01	66.00	34514	0.41
55.05	38516	0.46	61.05	12411	0.15	67.05	45556	0.54

68.55	10835	0.13	96.95	57885	0.69	126.05	244897	2.92
69.50	93207	1.11	97.95	37185	0.44	127.05	1228233	14.64
70.45	18212	0.22	99.00	44708	0.53	128.05	3276911	39.05
70.90	17418	0.21	100.05	149200	1.78	129.15	8391213	100.00
71.85	2398	0.03	101.05	669839	7.98	130.05	1949548	23.23
73.05	6133	0.07	102.00	571353	6.81	131.05	515213	6.14
74.00	119346	1.42	103.05	850959	10.14	132.05	49105	0.59
75.00	253967	3.03	103.95	160357	1.91	133.00	3460	0.04
76.05	692862	8.26	105.05	2244375	26.75	134.00	2191	0.03
77.00	1476842	17.60	106.05	209423	2.50	134.95	2626	0.03
78.00	393607	4.69	107.10	32348	0.39	136.05	1316	0.02
79.05	435779	5.19	108.05	19683	0.23	137.00	36943	0.44
80.35	21895	0.26	109.00	12121	0.14	138.05	36556	0.44
81.45	185168	2.21	110.00	18430	0.22	139.00	365390	4.35
82.40	496954	5.92	111.00	38532	0.46	140.00	52182	0.62
83.35	121048	1.44	112.00	10209	0.12	141.00	223839	2.67
84.35	3374	0.04	113.00	118167	1.41	142.05	81495	0.97
85.05	6422	0.08	114.05	81255	0.97	143.00	1089329	12.98
86.00	52961	0.63	115.00	1614294	19.24	144.05	556034	6.63
87.00	142278	1.70	116.05	299801	3.57	145.05	794956	9.47
88.05	394790	4.70	117.05	514695	6.13	146.00	91103	1.09
89.05	1290369	15.38	118.05	83021	0.99	147.00	5852	0.07
89.95	237496	2.83	119.05	145332	1.73	148.05	1094	0.01
91.05	6952109	82.85	120.05	15218	0.18	149.00	20372	0.24
92.00	545319	6.50	121.00	5570	0.07	150.00	15729	1.87
92.60	69878	0.83	122.00	6649	0.08	151.00	34843	4.15
93.65	136948	1.63	123.05	5776	0.07	152.00	10758	12.82
94.60	677716	8.08	124.05	5018	0.06	153.00	22399	2.67
95.95	471297	5.62	125.05	29244	0.35	154.00	41079	0.49

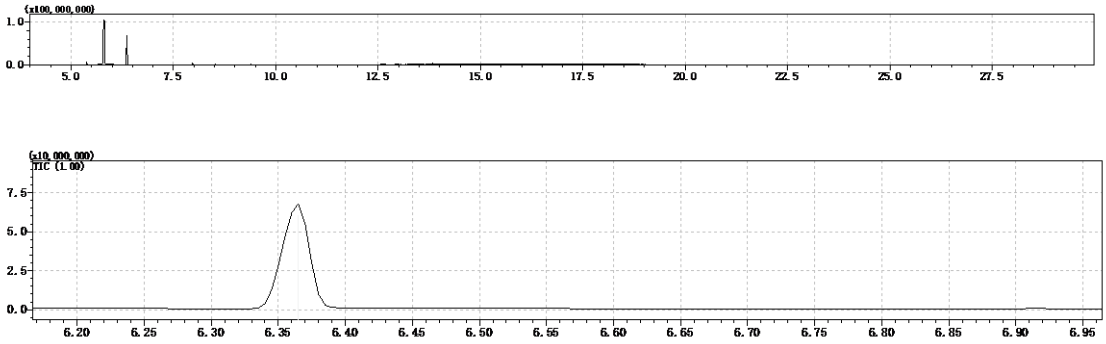
155.00	20183	0.24	179.95	444902	5.30	204.95	34969	4.17
156.00	8350	0.10	180.95	71097	0.85	206.05	39153	4.67
157.00	1570	0.02	181.95	26508	0.32	207.05	83855	99.93
158.00	329	0.00	182.95	33881	0.40	207.95	42583	50.75
158.90	401	0.00	183.95	4643	0.06	208.95	30551	3.64
160.05	372	0.00	184.95	1861	0.02	209.95	15969	0.19
160.95	11468	0.14	185.95	4859	0.06	210.90	2615	0.03
162.05	41183	0.49	186.95	69566	0.83	211.95	16110.02	
162.95	35236	4.20	187.95	84620	1.01	212.95	16529	0.20
164.00	492754	5.87	188.95	113629	13.54	213.95	9033	0.11
164.95	34528	41.15	189.95	67828	8.08	214.95	36494	0.43
165.95	76041	9.06	190.95	19576	23.33	215.95	11721	0.14
167.00	66084	7.88	192.00	16486	19.65	216.95	9368	0.11
168.00	10220	1.22	192.95	105811	12.61	217.95	4144	0.05
169.00	8393	0.10	193.95	15933	1.90	219.00	15111	0.18
169.95	642	0.01	194.95	16047	0.19	220.05	26020	0.31
171.00	81	0.00	195.90	1586	0.02	**221.05**	**90330**	**10.76**
172.00	153	0.00	196.95	858	0.01	**222.00**	**78645**	**93.72**
173.05	1868	0.02	197.90	14903	0.18	**223.00**	**16837**	**20.07**
173.95	28371	0.34	198.95	10630	0.13	224.00	15028	1.79
175.05	54984	0.66	199.95	98521	1.17	224.95	8599	0.10
175.95	56707	6.76	200.95	114035	1.36	225.95	445	0.01
177.05	36144	4.31	201.95	66273	7.90	227.00	100	0.00
177.95	38183	45.50	202.95	56888	6.78	228.00	70	0.00
178.95	2580995	30.76	203.95	27213	3.24			

2.7.3 GC-MS Analysis of Raw Reaction Mixture by Using TEMPO as Radical Inhibitor

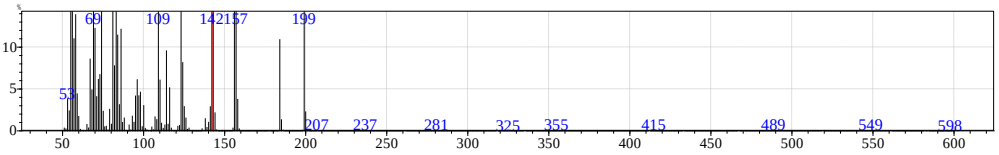


Chemical Formula: $C_{12}H_{25}NO$
Exact Mass: 199.1936

Spectra of GC-MS



MS spectra of the peak at 6.364 min



[MS Spectrum]

# of Peaks 540 Raw Spectrum 6.365 (scan : 474)

Background No Background Spectrum

Base Peak m/z 142.15 (Inten : 8,382,632) Event# 1

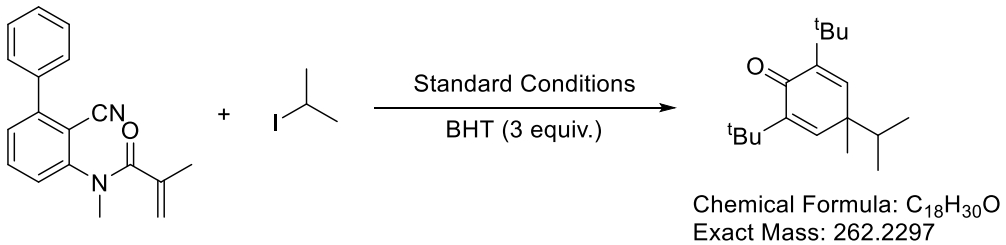
m/z Absolute Intensity Relative Intensity

50.00	5577	0.07	54.15	200654	2.39	58.05	1164478	13.89
51.00	28231	0.34	55.05	371388	44.30	59.05	371487	4.43
52.05	21101	0.25	56.05	248340	29.63	60.00	146286	1.75
53.05	320622	3.82	57.05	922500	11.00	61.00	15407	0.18

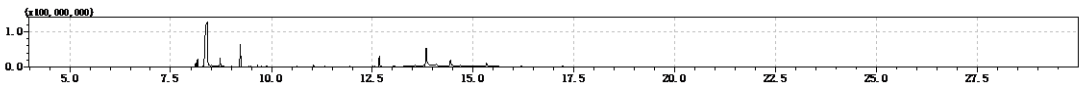
61.95	2167	0.03	91.05	59933	0.71	120.15	2602	0.03
62.90	4729	0.06	92.05	9155	0.11	121.10	46529	0.56
64.00	2278	0.03	93.05	148141	1.77	122.15	53746	0.64
65.00	63998	0.76	94.05	86063	1.03	123.10	298434	35.60
66.05	29952	0.36	95.05	349739	4.17	124.10	684908	8.17
67.05	719013	8.58	96.05	513294	6.12	125.10	243919	2.91
68.10	411657	4.91	97.05	351428	4.19	126.10	128902	1.54
69.05	606662	72.37	98.05	387966	4.63	127.10	15001	0.18
70.05	102679	12.25	99.10	42332	0.50	128.05	28731	0.34
71.05	343504	4.10	100.05	254489	3.04	129.10	2593	0.03
72.05	516270	6.16	101.05	25228	0.30	130.05	795	0.01
73.05	564403	6.73	102.10	10738	0.13	131.10	150	0.00
74.05	369498	44.08	103.05	2016	0.02	132.10	129	0.00
75.05	196924	2.35	104.15	907	0.01	133.05	842	0.01
76.05	41670	0.50	105.05	38556	0.46	134.05	363	0.00
77.00	46094	0.55	106.05	11729	0.14	135.05	1283	0.02
78.05	8826	0.11	107.05	140994	1.68	136.05	22296	0.27
79.05	216638	2.58	108.15	113768	1.36	137.15	3740	0.04
80.15	66546	0.79	109.10	4011974	47.86	138.10	122212	1.46
81.05	208109	24.83	110.10	508567	6.07	139.10	34726	0.41
82.05	651870	7.78	111.10	77654	0.93	140.10	86911	1.04
83.05	169384	20.21	112.10	26266	0.31	141.15	241734	2.88
84.05	959696	11.45	113.10	59543	0.71	142.15	838263	100.00
85.05	263277	3.14	114.05	801916	9.57	143.05	684019	81.60
86.05	101797	12.14	115.10	66862	0.80	144.10	181474	2.16
87.05	84926	1.01	116.10	432303	5.16	145.05	8984	0.11
88.05	129030	1.54	117.10	28839	0.34	146.15	520	0.01
89.05	6835	0.08	118.10	1894	0.02	147.00	921	0.01
90.05	1024	0.01	119.10	5271	0.06	148.00	234	0.00

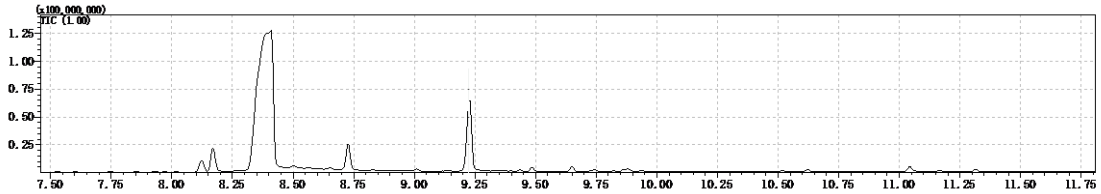
148.95	604	0.01	167.00	644	0.01	185.05	112721	1.34
150.00	137	0.00	168.05	664	0.01	186.05	7950	0.09
151.00	145	0.00	169.10	180	0.00	187.00	460	0.01
152.00	175	0.00	170.10	95	0.00	188.00	65	0.00
153.10	103	0.00	171.10	106	0.00	189.00	148	0.00
154.05	1675	0.02	172.10	30	0.00	190.00	84	0.00
155.15	28211	0.34	173.10	62	0.00	191.00	327	0.00
156.05	279759	33.37	174.10	58	0.00	191.90	209	0.00
157.05	322431	38.46	174.90	143	0.00	192.90	1609	0.02
158.05	316206	3.77	175.90	780	0.01	193.95	505	0.01
159.05	20047	0.24	176.95	2496	0.03	194.90	794	0.01
160.00	11880	0.01	177.95	561	0.01	195.90	110	0.00
161.00	246	0.00	179.00	322	0.00	196.90	70	0.00
162.00	98	0.00	179.90	409	0.00	**198.05**	**5824**	**0.07**
163.00	167	0.00	180.90	110	0.00	**199.05**	**132437**	**15.80**
164.00	156	0.00	182.00	732	0.01	**200.05**	**191295**	**2.28**
164.85	500	0.01	183.05	4310	0.05	201.00	16727	0.20
165.80	194	0.00	184.05	913638	10.90	202.05	11230	0.01

2.7.4 GC-MS Analysis of Raw Reaction Mixture by Using BHT as Radical Inhibitor

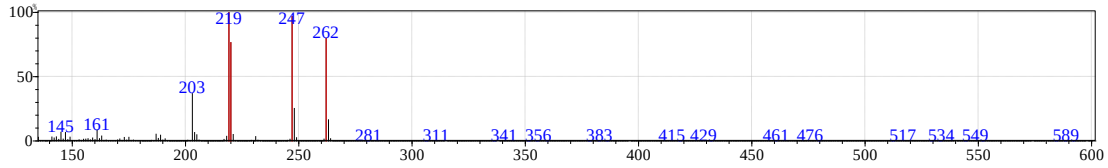


Spectra of GC-MS





MS spectra of the peak at 9.225 min



[MS Spectrum]

# of Peaks 544

Raw Spectrum 9.225 (scan : 1046)

Background No Background Spectrum

Base Peak m/z 219.15 (Inten : 8,382,472)

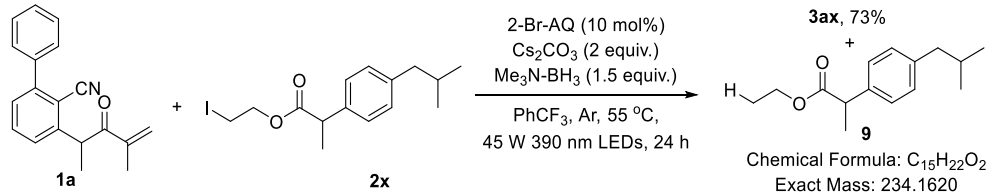
Event# 1

m/z	Absolute Intensity	Relative Intensity						
50.05	8655	0.10	65.00	209204	2.50	80.05	491502	5.86
51.00	74964	0.89	66.00	54839	0.65	81.00	184340	2.20
52.05	33086	0.39	67.00	218012	2.60	82.00	20154	0.24
53.05	189366	2.26	68.00	16977	0.20	83.05	105814	1.26
54.15	22852	0.27	69.05	397795	4.75	84.00	13924	0.17
55.05	781012	9.32	70.05	49128	0.59	85.05	21301	0.25
56.15	89963	1.07	71.00	73289	0.87	86.05	35181	0.42
57.10	4211327	50.24	72.00	44734	0.53	87.00	45962	0.55
58.05	247712	2.96	73.00	58010	0.69	87.95	20890	0.25
59.05	35665	0.43	73.95	21138	0.25	89.00	34940	0.42
60.05	4802	0.06	74.95	10950	0.13	90.05	16742	0.20
61.00	5894	0.07	76.05	28508	0.34	91.00	898295	10.72
62.00	3818	0.05	77.00	365228	4.36	92.05	98345	1.17
63.05	33754	0.40	78.05	108759	1.30	93.05	243616	2.91
64.05	85611	1.02	79.05	377246	4.50	94.05	315420	3.76

95.00	204690	2.44	124.05	12559	0.15	153.00	83129	0.99
96.00	16281	0.19	125.05	3142	0.04	154.00	49159	0.59
97.05	24404	0.29	126.05	8147	0.10	155.00	121662	1.45
98.05	3332	0.04	127.05	150575	1.80	156.00	125169	1.49
99.05	2436	0.03	128.05	524357	6.26	157.00	155121	1.85
100.05	3337	0.04	129.05	531840	6.34	158.00	70492	0.84
101.05	26996	0.32	130.05	199503	2.38	159.00	201052	2.40
102.05	83073	0.99	131.05	744001	8.88	160.05	92328	1.10
103.00	138628	1.65	132.05	126861	1.51	161.00	718046	8.57
104.05	56366	0.67	133.05	493747	5.89	162.00	152633	1.82
105.05	699573	8.35	134.05	101725	1.21	163.00	331572	3.96
106.05	90355	1.08	135.05	244773	2.92	164.00	42385	0.51
107.05	317613	3.79	136.05	28829	0.34	165.00	63425	0.76
108.00	55257	0.66	137.05	38995	0.47	166.00	16695	0.20
109.05	80675	0.96	138.05	6251	0.07	167.00	27895	0.33
110.05	8649	0.10	139.00	16868	0.20	168.00	14209	0.17
111.05	11449	0.14	140.05	71180.08		169.00	32353	0.39
112.05	1020	0.01	141.00	268422	3.20	170.00	70046	0.84
113.05	2828	0.03	142.00	200444	2.39	171.00	138839	1.66
114.05	71190.08		143.00	275854	3.29	172.00	48414	0.58
115.00	471748	5.63	144.05	107314	1.28	173.00	233434	2.78
116.05	200334	2.39	145.00	571521	6.82	174.00	68116	0.81
117.05	416062	4.96	146.00	124436	1.48	175.00	243673	2.91
118.05	70524	0.84	147.00	555486	6.63	176.00	43655	0.52
119.05	649134	7.74	148.05	88413	1.05	177.00	62802	0.75
120.10	102650	1.22	149.00	257874	3.08	178.00	14474	0.17
121.05	581034	6.93	150.05	31726	0.38	179.00	17894	0.21
122.10	63959	0.76	151.00	17522	0.21	180.00	29814	0.36
123.05	91364	1.09	152.00	39639	0.47	181.00	8212	0.10

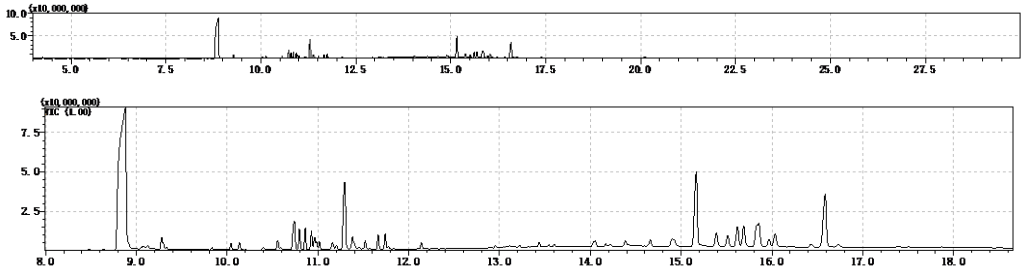
181.95	4466	0.05	211.00	647	0.01	240.00	46	0.00
183.00	11770	0.14	211.95	355	0.00	241.00	230	0.00
184.05	6307	0.08	213.00	2706	0.03	242.00	63	0.00
185.00	48212	0.58	214.05	2059	0.02	243.05	1374	0.02
186.05	16951	0.20	215.00	9358	0.11	244.15	930	0.01
187.00	444041	5.30	216.05	2999	0.04	245.05	46023	0.55
188.00	176953	2.11	217.00	108788	1.30	246.15	121613	1.45
189.00	387615	4.62	218.15	310575	3.71	247.05	8130316	96.99
190.00	60026	0.72	219.15	8382472	100.00	248.05	2129591	25.41
191.00	144254	1.72	220.05	6414975	76.53	249.05	218420	2.61
192.00	21228	0.25	221.05	425715	5.08	250.00	16206	0.19
193.00	7492	0.09	222.00	30705	0.37	250.95	1707	0.02
193.95	1662	0.02	222.95	1981	0.02	251.95	527	0.01
194.95	2721	0.03	224.00	226	0.00	253.00	265	0.00
196.00	951	0.01	225.00	270	0.00	254.00	102	0.00
197.00	2289	0.03	226.00	132	0.00	255.00	30	0.00
198.00	1598	0.02	226.95	482	0.01	256.00	169	0.00
199.00	6874	0.08	228.05	541	0.01	257.00	63	0.00
200.05	3613	0.04	229.05	41252	0.49	258.00	150	0.00
201.00	57430	0.69	230.05	9230	0.11	259.15	368	0.00
202.05	34393	0.41	231.00	288908	3.45	260.15	7307	0.09
203.00	3092116	36.89	232.00	52993	0.63	**261.15**	**131761**	**1.57**
204.00	558809	6.67	233.05	26078	0.31	**262.10**	**6705353**	**79.99**
205.00	413457	4.93	234.05	4842	0.06	**263.10**	**1391158**	**16.60**
206.00	64678	0.77	235.05	1984	0.02	264.05	151566	1.81
207.00	12594	0.15	236.05	10539	0.13	265.05	11896	0.14
208.05	2646	0.03	237.00	3786	0.05	265.95	1295	0.02
208.95	2159	0.03	238.00	750	0.01	266.90	1266	0.02
209.85	655	0.01	239.00	246	0.00			

2.7.5 GC-MS Analysis of Intermediate 9

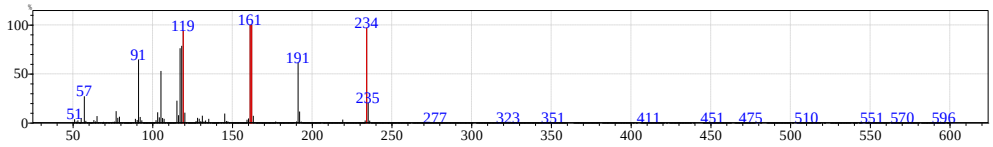


To a Schlenk tube were added **1a** (0.2 mmol), **2x** (0.4 mmol), 2-Br AQ (10 mol %), Cs_2CO_3 (2 equiv.), Me_3N-BH_3 (1.5 equiv.), solvent (2 mL; 0.1 M) at 55 ^oC under an argon atmosphere. The mixture was placed from the 390 nm purple LEDs. The LEDs were switched on and the mixture was stirred under irradiation with a fan for 6 hours. After the reaction was completed, the intermediate **9** was monitored by GC-MS.

Spectra of GC-MS



MS spectra of the peak at 8.859 min



[MS Spectrum]
# of Peaks 506
Raw Spectrum 8.860 (scan : 973)
Background No Background Spectrum
Base Peak m/z 161.05 (Inten : 8,391,542)
Event# 1

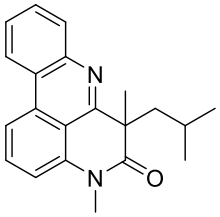
m/z	Absolute Intensity	Relative Intensity						
50.00	67442	0.80	56.15	55601	0.66	62.00	35481	0.42
51.00	297599	3.55	57.05	2266336	27.01	63.00	224130	2.67
52.00	97324	1.16	58.00	159986	1.91	64.05	107476	1.28
53.00	208614	2.49	59.00	33863	0.40	65.00	567020	6.76
54.05	16052	0.19	59.95	2099	0.03	66.00	57982	0.69
55.05	414072	4.93	61.05	4607	0.05	67.00	50473	0.60

68.15	4632	0.06	97.05	568	0.01	126.15	15364	0.18
69.05	77751	0.93	98.05	1994	0.02	127.10	137004	1.63
70.05	21542	0.26	99.05	2539	0.03	128.10	418756	4.99
71.05	69174	0.82	100.15	2092	0.02	129.10	340932	4.06
72.05	49473	0.59	101.10	35730	0.43	130.10	141060	1.68
73.00	44950	0.54	102.05	216566	2.58	131.10	607986	7.25
74.00	28636	0.34	103.05	892735	10.64	132.10	112969	1.35
75.00	73212	0.87	104.10	466546	5.56	133.10	194502	2.32
76.05	92888	1.11	105.10	4440802	52.92	134.15	39652	0.47
77.00	995945	11.87	106.10	409727	4.88	135.10	333161	3.97
78.05	421170	5.02	107.05	339522	4.05	136.10	33116	0.39
79.05	513190	6.12	108.05	26679	0.32	137.10	2359	0.03
80.05	39434	0.47	109.10	2047	0.02	138.15	722	0.01
81.05	18377	0.22	110.10	370	0.00	139.05	11655	0.14
82.05	2242	0.03	111.05	607	0.01	140.15	4681	0.06
83.10	9986	0.12	112.15	959	0.01	141.10	61943	0.74
84.05	1119	0.01	113.10	13846	0.16	142.10	26145	0.31
85.00	2242	0.03	114.15	44619	0.53	143.10	58422	0.70
86.00	6417	0.08	115.10	1892562	22.55	144.15	39241	0.47
87.05	17232	0.21	116.15	649439	7.74	145.10	791418	9.43
88.05	17207	0.21	117.10	6381982	76.05	146.10	149793	1.79
89.05	333933	3.98	118.10	6582559	78.44	147.10	115895	1.38
90.15	240346	2.86	119.10	7873146	93.82	148.10	18172	0.22
91.05	5423380	64.63	120.10	864716	10.30	149.05	30802	0.37
92.10	500550	5.96	121.10	59778	0.71	150.05	6603	0.08
93.10	201977	2.41	122.15	3209	0.04	151.10	2266	0.03
94.10	15414	0.18	123.20	431	0.01	152.05	3233	0.04
95.05	4224	0.05	124.10	212	0.00	153.05	3055	0.04
96.05	467	0.01	125.15	1260	0.02	154.10	1700	0.02

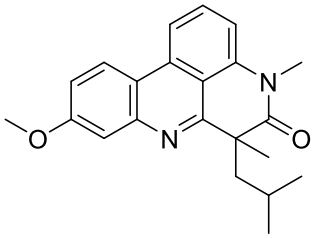
155.10	2607	0.03	183.00	194	0.00	211.10	706	0.01
156.15	1579	0.02	184.10	180	0.00	212.10	281	0.00
157.10	8265	0.10	185.05	798	0.01	213.05	318	0.00
158.05	7128	0.08	186.15	982	0.01	214.05	11970	0.01
159.05	254006	3.03	187.15	11645	0.14	215.05	3521	0.04
160.05	364821	4.35	188.10	43649	0.52	215.95	836	0.01
161.05	8391542	100.00	189.10	34169	0.41	217.10	622	0.01
162.00	8382638	99.89	190.15	111325	1.33	218.15	5349	0.06
163.05	592707	7.06	191.10	5153050	61.41	219.10	269121	3.21
164.05	58895	0.70	192.05	962011	11.46	220.05	43507	0.52
165.00	5495	0.07	193.05	101148	1.21	221.05	4585	0.05
165.95	433	0.01	193.95	8056	0.10	222.05	518	0.01
167.00	177	0.00	195.05	1250	0.01	223.10	702	0.01
168.15	427	0.01	196.10	201	0.00	224.10	134	0.00
169.10	686	0.01	197.10	170	0.00	225.10	825	0.01
170.15	294	0.00	198.10	55	0.00	226.10	175	0.00
171.10	927	0.01	199.10	11910	0.01	227.10	66	0.00
172.15	1329	0.02	200.10	252	0.00	228.10	50	0.00
173.10	11833	0.14	201.10	8639	0.10	229.10	327	0.00
174.10	4282	0.05	202.05	1665	0.02	230.10	158	0.00
175.10	5471	0.07	203.05	2134	0.03	231.10	334	0.00
176.15	6108	0.07	204.15	2856	0.03	232.15	2845	0.03
177.10	109364	1.30	205.10	61114	0.73	**233.15**	**192932**	**2.30**
178.10	34282	0.41	206.10	23945	0.29	**234.10**	**8132567**	**96.91**
179.05	5684	0.07	207.05	5262	0.06	**235.10**	**1701257**	**20.27**
180.05	636	0.01	208.00	722	0.01	236.05	186783	2.23
181.05	985	0.01	209.10	418	0.00	237.05	15959	0.19
182.00	271	0.00	210.10	166	0.00	238.05	1015	0.01

3. Characterization Data for All Products

6-Isobutyl-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3aa): Yield: 44.5 mg, 79%; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.53 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.81 (t, *J* = 8.0 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 3.58 (s, 3H), 2.53 - 2.48 (m, 1H), 2.35 - 2.30 (m, 1H), 1.77 (s, 3H), 1.48 - 1.41 (m, 1H), 0.69 (d, *J* = 6.8 Hz, 3H), 0.51 (d, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ : 174.5, 160.1, 144.9, 138.8, 133.2, 131.6, 129.7, 129.0, 126.4, 122.5, 122.5, 116.0, 112.3, 110.6, 51.1, 50.6, 30.9, 29.7, 25.6, 23.7, 22.9; HRMS (ESI-TOF) *m/z*: $C_{21}H_{23}N_2O^+$ $(M + H)^+$ calcd for 319.1805, found 319.1801.



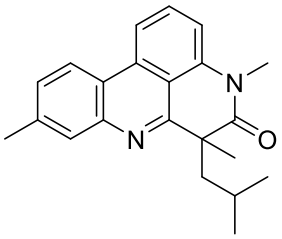
6-Isobutyl-9-methoxy-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ba): Yield: 38.3 mg, 55%; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.40 (d, *J* = 8.8 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.77 (t, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 2.4 Hz, 1H), 7.28 - 7.25 (m, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 4.01 (s, 3H), 3.57 (s, 3H), 2.50 - 2.45 (m, 1H), 2.34 - 2.23 (m, 1H), 1.76 (s, 3H), 1.49 - 1.34 (m, 1H), 0.69 (d, *J* = 6.4 Hz, 3H), 0.51 (d, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ : 174.5, 160.6, 160.4, 146.6, 138.8, 133.3, 131.7, 123.7, 117.9, 116.6, 115.5, 111.5, 109.4, 109.1, 55.6, 51.2, 50.5, 30.9, 29.6, 25.6, 23.7, 22.9; HRMS (ESI-TOF) *m/z*: $C_{22}H_{25}N_2O_2^+$ $(M + H)^+$ calcd for 349.1911, found 349.1915.



9-(*Tert*-butyl)-6-isobutyl-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ca): Yield: 49.4 mg, 66%; white oily; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.46 (d, *J* = 8.8 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 2.0 Hz, 1H), 7.80 (t, *J* = 8.4 Hz, 1H), 7.74 - 7.71 (m, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 3.58 (s, 3H), 2.53 - 2.48 (m, 1H), 2.35 - 2.30 (m, 1H), 1.77 (s, 3H), 1.64 - 1.59 (m, 1H), 1.49 (s, 9H), 0.69 (d, *J* = 6.4 Hz, 3H), 0.53 (d, *J* = 6.4 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ : 174.6, 159.9, 152.5, 144.9, 138.8, 133.1, 131.5, 125.5, 124.9, 122.2, 120.2,

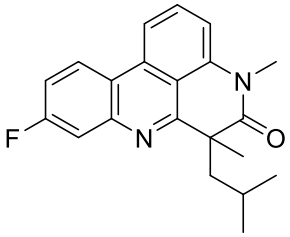
115.9, 112.1, 110.1, 51.1, 50.5, 35.1, 31.3 (2C), 31.0, 29.7, 25.6, 23.8, 22.8; HRMS (ESI-TOF) *m/z*: $C_{25}H_{31}N_2O^+$ $(M + H)^+$ calcd for 375.2431, found 375.2427.

6-Isobutyl-4,6,9-trimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3da):



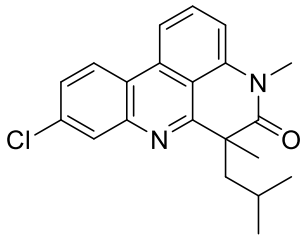
Yield: 37.2 mg, 56%; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.4 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.95 (s, 1H), 7.79 (t, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 3.58 (s, 3H), 2.60 (s, 3H), 2.51 - 2.47 (m, 1H), 2.34 - 2.29 (m, 1H), 1.76 (s, 3H), 1.49 - 1.39 (m, 1H), 0.69 (d, *J* = 6.8 Hz, 3H), 0.50 (d, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ : 174.5, 160.0, 144.9, 139.3, 138.8, 133.2, 131.6, 129.2, 128.2, 122.3, 120.2, 115.8, 112.0, 110.1, 51.1, 50.5, 30.9, 29.7, 25.7, 23.8, 22.9, 21.5; HRMS (ESI-TOF) *m/z*: $C_{22}H_{25}N_2O^+$ $(M + H)^+$ calcd for 333.1961, found 333.1967.

9-Fluoro-6-isobutyl-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one



(3ea): Yield: 34.2 mg, 51%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.52 - 8.48 (m, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.83 (t, *J* = 8.0 Hz, 1H), 7.80 - 7.76 (m, 1H), 7.42 - 7.37 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 3.59 (s, 3H), 2.50 - 2.46 (m, 1H), 2.35 - 2.30 (m, 1H), 1.75 (s, 3H), 1.47 - 1.37 (m, 1H), 0.69 (d, *J* = 6.8 Hz, 3H), 0.50 (d, *J* = 6.8 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: -111.6 (s, 1F); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ : 174.3, 162.9 (d, $J_{C\text{-}F}$ = 247.0 Hz, 1C), 161.6, 146.3 (d, $J_{C\text{-}F}$ = 12.0 Hz, 1C), 139.0, 133.0, 132.1, 124.6 (d, $J_{C\text{-}F}$ = 9.7 Hz, 1C), 119.3 (d, $J_{C\text{-}F}$ = 1.9 Hz, 1C), 115.8 (d, $J_{C\text{-}F}$ = 2.1 Hz, 1C), 115.5, 114.1 (d, $J_{C\text{-}F}$ = 20.2 Hz, 1C), 111.9, 110.4, 51.1, 50.6, 31.0, 29.7, 25.7, 23.7, 22.9; HRMS (ESI-TOF) *m/z*: $C_{21}H_{22}FN_2O^+$ $(M + H)^+$ calcd for 337.1711, found 337.1704.

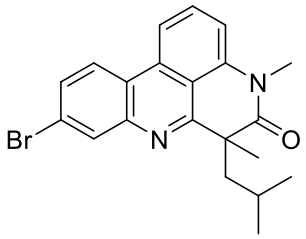
9-Chloro-6-isobutyl-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one



(3fa): Yield: 40.8 mg, 58%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.44 (d, *J* = 8.8 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 8.14 (s, 1H), 7.84 (t, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 3.59 (s, 3H), 2.50 -

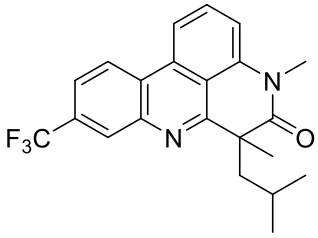
2.45 (m, 1H), 2.35 - 2.29 (m, 1H), 1.75 (s, 3H), 1.45 - 1.34 (m, 1H), 0.70 - 0.68 (m, 3H), 0.51 - 0.49 (m, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 174.3, 161.6, 145.5, 139.0, 134.8, 132.8, 132.2, 128.8, 127.0, 123.9, 121.0, 115.8, 112.2, 110.8, 51.1, 50.7, 31.0, 29.7, 25.7, 23.7, 22.9; HRMS (ESI-TOF) *m/z*: $C_{21}H_{22}ClN_2O^+$ $(M + H)^+$ calcd for 353.1415, found 353.1410.

9-Bromo-6-isobutyl-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one



(3ga): Yield: 41.9 mg, 53%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.38 (d, *J* = 8.8 Hz, 1H), 8.32 (d, *J* = 2.0 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.84 (t, *J* = 8.0 Hz, 1H), 7.73 - 7.71 (m, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 3.58 (s, 3H), 2.50 - 2.45(m, 1H), 2.35 – 2.29 (m, 1H), 1.74 (s, 3H), 1.47 - 1.37(m, 1H), 0.69 (d, *J* = 6.8 Hz, 3H), 0.50 (d, *J* = 6.8 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 174.3, 161.6, 145.7, 139.0, 132.8, 132.2, 132.1, 129.6, 124.0, 122.9, 121.4, 115.8, 112.3, 110.9, 51.1, 50.7, 31.0, 29.7, 25.7, 23.7, 22.9; HRMS (ESI-TOF) *m/z*: $C_{21}H_{22}BrN_2O^+$ $(M + H)^+$ calcd for 397.0910, found 397.0916.

6-Isobutyl-4,6-dimethyl-9-(trifluoromethyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-

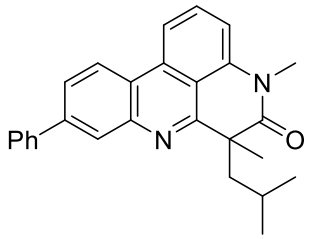


5(6*H*)-one (3ha): Yield: 41.6 mg, 54%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.63 (d, *J* = 8.8 Hz, 1H), 8.44 (s, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 7.90 (t, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 3.60 (s, 3H), 2.53 - 2.48 (m, 1H), 2.37 - 2.32 (m, 1H), 1.77 (s, 3H), 1.47 - 1.41 (m, 1H), 0.70 (d, *J* = 6.4 Hz, 3H), 0.51 (d, *J* = 6.8 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: -62.2 (s, 3F); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 174.2, 162.0, 144.2, 139.1, 132.5, 132.4 (2C), 131.4 (q, J_{C-F} = 32.4 Hz, 1C), 127.3 (q, J_{C-F} = 4.3 Hz, 1C), 125.4 (dd, J_{C-F} = 60.3, J_{C-F} = 91.2 Hz, 1C), 123.6, 122.2(q, J_{C-F} = 3.5 Hz, 1C), 116.2, 112.8, 111.7 , 51.1, 50.7, 31.0, 29.8, 25.7, 23.7, 22.9; HRMS (ESI-TOF) *m/z*: $C_{22}H_{22}F_3N_2O^+$ $(M + H)^+$ calcd for 387.1679, found 387.1672.

6-Isobutyl-4,6-dimethyl-9-phenyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one

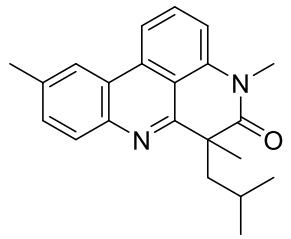
(3ia): Yield: 40.9 mg, 52%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.57 (d, *J* =

8.4 Hz, 1H), 8.39 (d, *J* = 2.0 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 7.91 - 7.89 (m, 1H),



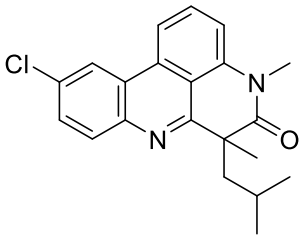
7.84 - 7.80 (m, 3H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 3.59 (s, 3H), 2.55 - 2.50(m, 1H), 2.37 - 2.32 (m, 1H), 1.79 (s, 3H), 1.50 - 1.43 (m, 1H), 0.70 (d, *J* = 6.8 Hz, 3H), 0.53 (d, *J* = 6.8 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 174.5, 160.6, 145.2, 141.8, 140.2, 138.9, 133.0, 131.8, 128.9, 127.8, 127.5, 127.4, 125.6, 123.1, 121.6, 116.0, 112.3, 110.6, 51.1, 50.6, 31.0, 29.7, 25.7, 23.8, 22.9; HRMS (ESI-TOF) *m/z*: $C_{27}H_{27}N_2O^+$ $(M + H)^+$ calcd for 395.2118, found 395.2122.

6-Isobutyl-4,6,10-trimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ja):

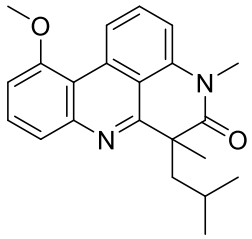


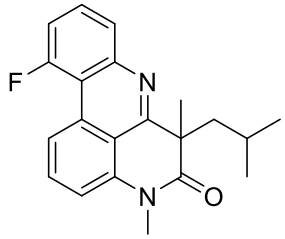
Yield: 19.9 mg, 30%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.31 (s, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.80 (t, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 10.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 3.58 (s, 3H), 2.63 (s, 3H), 2.50 - 2.45 (m, 1H), 2.33 - 2.28 (m, 1H), 1.76 (s, 3H), 1.46 - 1.39 (m, 1H), 0.68 (d, *J* = 6.8 Hz, 3H), 0.49 (d, *J* = 6.8 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 174.6, 159.0, 143.2, 138.8, 136.3, 132.9, 131.4, 130.8, 129.4, 122.4, 122.0, 116.0, 112.4, 110.4, 51.2, 50.4, 30.9, 29.7, 25.6, 23.7, 22.9, 21.9; HRMS (ESI-TOF) *m/z*: $C_{22}H_{25}N_2O^+$ $(M + H)^+$ calcd for 333.1961, found 333.1964.

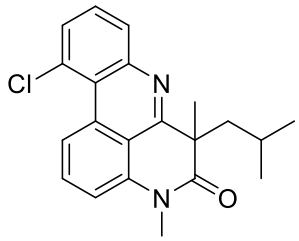
10-Chloro-6-isobutyl-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one



(3ka): Yield: 30.3 mg, 43%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.48 (d, *J* = 2.0 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.8 Hz, 1H), 7.84 (t, *J* = 8.0 Hz, 1H), 7.70 - 7.67 (m, 1H), 7.25 (d, *J* = 9.2 Hz, 1H), 3.59 (s, 3H), 2.49 - 2.44(m, 1H), 2.34 - 2.23(m, 1H), 1.75 (s, 3H), 1.45 - 1.38 (m, 1H), 0.69 (d, *J* = 6.8 Hz, 3H), 0.49 (d, *J* = 6.4 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 174.3, 160.5, 143.3, 138.9, 132.2, 132.2, 132.0, 131.2, 129.6, 123.6, 122.1, 115.9, 112.4, 111.2, 51.1, 50.6, 30.9, 29.7, 25.6, 23.7, 22.9; HRMS (ESI-TOF) *m/z*: $C_{21}H_{22}ClN_2O^+$ $(M + H)^+$ calcd for 353.1415, found 353.1417.

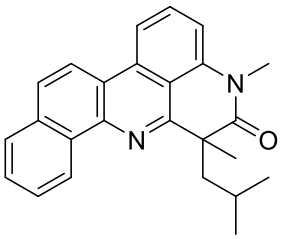
6-Isobutyl-11-methoxy-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3la):  Yield: 47.3 mg, 68%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 9.25 (d, *J* = 7.6 Hz, 1H), 7.80 - 7.76 (m, 2H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 6.8 Hz, 1H), 4.12 (s, 3H), 3.58 (s, 3H), 2.50 - 2.45(m, 1H), 2.30 - 2.27(m, 7.1 Hz, 1H), 1.76 (s, 3H), 1.48 - 1.39(m, 1H), 0.69 (d, *J* = 6.8 Hz, 3H), 0.50 (d, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ : 174.3, 160.3, 158.2, 146.8, 138.2, 133.1, 131.3, 128.5, 122.5, 122.0, 113.5, 112.7, 110.4, 107.3 , 55.8, 51.1, 50.2, 30.7, 29.7, 25.6, 23.7, 22.9; HRMS (ESI-TOF) *m/z*: $C_{22}H_{25}N_2O_2^+$ $(M + H)^+$ calcd for 349.1911, found 349.1908.

11-Fluoro-6-isobutyl-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ma):  Yield: 39.6 mg, 59%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.85 (t, *J* = 8.4 Hz, 1H), 7.69 - 7.64 (m, 1H), 7.37 - 7.31 (m, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 3.59 (s, 3H), 2.51 - 2.46(m, 1H), 2.34 - 2.29 (m, 1H), 1.76 (s, 3H), 1.49 - 1.39 (m, 1H), 0.69 (d, *J* = 6.8 Hz, 3H), 0.51 (d, *J* = 6.4 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: -110.6 (s, 1F); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ : 174.2, 161.2, 160.5 (d, $J_{C\text{-}F}$ = 253.5 Hz, 1C), 146.7 (d, $J_{C\text{-}F}$ = 2.7 Hz, 1C), 138.6, 132.2 (d, $J_{C\text{-}F}$ = 2.2 Hz, 1C), 131.2, 131.1, 128.5 (d, $J_{C\text{-}F}$ = 10.8 Hz, 1C), 125.7 (d, $J_{C\text{-}F}$ = 3.4 Hz, 1C), 121.1 (d, $J_{C\text{-}F}$ = 23.0 Hz, 1C) 112.8 (d, $J_{C\text{-}F}$ = 23.9 Hz, 1C), 112.7, 111.3, 51.1, 50.5, 30.8, 29.8, 25.6, 23.7, 22.9; HRMS (ESI-TOF) *m/z*: $C_{21}H_{22}FN_2O^+$ $(M + H)^+$ calcd for 337.1711, found 337.1715.

11-Chloro-6-isobutyl-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3na):  Yield: 28.2 mg, 40%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 9.57 (d, *J* = 8.8 Hz, 1H), 8.08 (d, *J* = 9.6 Hz, 1H), 7.84 (t, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.0f Hz, 1H), 3.60 (s, 3H), 2.49 - 2.44 (m, 1H), 2.33 - 2.23 (m, 1H), 1.75 (s, 3H), 1.47 - 1.40 (m, 1H), 0.69 (d, *J* = 6.8 Hz, 3H), 0.51 (d, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ :

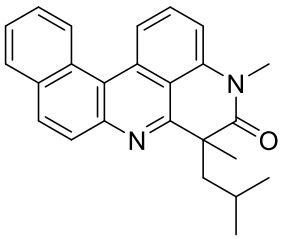
174.0, 160.7, 146.9, 138.6, 132.5, 131.1, 130.8, 130.2, 129.5, 128.3, 120.5, 120.4, 113.2, 111.5, 51.0, 50.3, 30.7, 29.9, 25.6, 23.7, 22.9; HRMS (ESI-TOF) *m/z*: $C_{21}H_{22}ClN_2O^+$ $(M + H)^+$ calcd for 353.1415, found 353.1419.

6-Isobutyl-4,6-dimethyl-4*H*-benzo[*c*]pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one



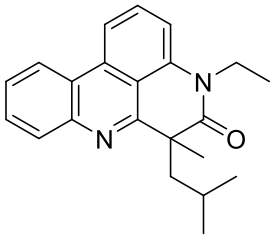
(3oa): Yield: 36.1 mg, 49%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 9.46 (d, *J* = 6.8 Hz, 1H), 8.48 (d, *J* = 9.2 Hz, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 8.00 - 7.96 (m, 2H), 7.83 (t, *J* = 8.0 Hz, 1H), 7.77 (t, *J* = 6.8 Hz, 1H), 7.71 (t, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 3.61 (s, 3H), 2.70 - 2.65 (m, 1H), 2.45 - 2.40 (m, 1H), 1.86 (s, 3H), 1.51 - 1.34 (m, 1H), 0.71 (d, *J* = 6.8 Hz, 3H), 0.49 (d, *J* = 6.4 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ : 174.6, 158.8, 141.9, 138.9, 133.4, 133.4, 131.7, 131.5, 127.6, 127.5, 127.2, 126.8, 125.0, 120.2, 119.2, 116.3, 112.9, 109.8, 51.5, 50.8, 31.7, 29.6, 25.8, 23.9, 23.0; HRMS (ESI-TOF) *m/z*: $C_{25}H_{25}N_2O^+$ $(M + H)^+$ calcd for 369.1961, found 369.1968.

6-Isobutyl-4,6-dimethyl-4*H*-benzo[*a*]pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one



(3pa): Yield: 25.7 mg, 35%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 9.06 (d, *J* = 8.4 Hz, 1H), 8.77 (d, *J* = 8.4 Hz, 1H), 8.08 - 8.02 (m, 3H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 3.63 (s, 3H), 2.53 - 2.48 (m, 1H), 2.37 - 2.32 (m, 1H), 1.82 (s, 3H), 1.46 - 1.34 (m, 1H), 0.70 (d, *J* = 6.8 Hz, 3H), 0.48 (d, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ : 174.5, 159.4, 144.9, 138.7, 133.2, 133.0, 131.3, 130.0, 129.8, 128.8, 128.3, 127.5, 126.6, 126.2, 120.8, 119.0, 113.7, 109.7, 51.3, 50.4, 30.8, 29.8, 25.7, 23.8, 22.9; HRMS (ESI-TOF) *m/z*: $C_{25}H_{25}N_2O^+$ $(M + H)^+$ calcd for 369.1961, found 369.1963.

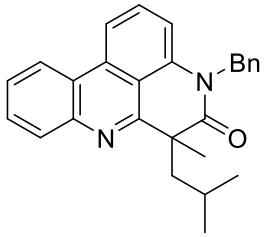
4-Ethyl-6-isobutyl-6-methyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3qa):



Yield: 35.2 mg, 53%; yellow oily; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.53 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.81 (t, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 4.38 -

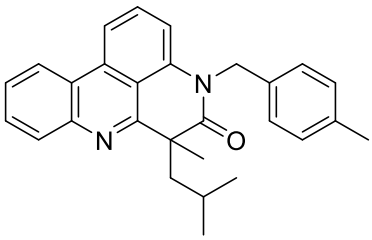
4.30 (m, 1H), 4.18 - 4.09 (m, 1H), 2.52 - 2.47 (m, 1H), 2.35 - 2.30 (m, 1H), 1.75 (s, 3H), 1.51 - 1.42 (m, 1H), 1.36 (t, *J* = 7.2 Hz, 3H), 0.69 (d, *J* = 6.4 Hz, 3H), 0.53 (d, *J* = 6.4 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 174.0, 160.1, 144.8, 137.6, 133.5, 131.7, 129.7, 129.0, 126.4, 122.6, 122.5, 115.7, 112.6, 110.5, 50.8, 50.3, 37.3, 31.1, 25.6, 23.7, 22.9, 11.8; HRMS (ESI-TOF) *m/z*: $C_{22}H_{25}N_2O^+$ $(M + H)^+$ calcd for 333.1961, found 333.1967.

4-Benzyl-6-isobutyl-6-methyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ra):



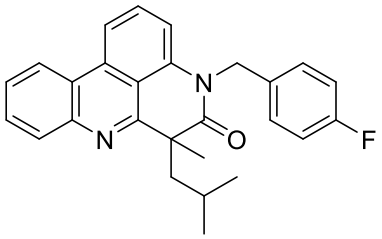
Yield: 33.1mg, 42%; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.51 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.75 (t, *J* = 7.2 Hz, 1H), 7.68 - 7.61 (m, 2H), 7.35 - 7.31 (m, 4H), 7.28 - 24 (m, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 5.57 - 5.22 (m, 2H), 2.62 - 2.57 (m, 1H), 2.44 - 2.39 (m, 1H), 1.83 (s, 3H), 1.66 - 1.60 (m, 1H), 0.77 (d, *J* = 6.8 Hz, 3H), 0.54 (d, *J* = 6.8 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 174.8, 159.9, 144.8, 137.9, 136.4, 133.3, 131.6, 129.7, 129.1, 128.8 (2C), 127.2, 126.5, 126.5 (2C), 122.6, 122.5, 116.1, 112.5, 111.8, 50.9, 50.3, 46.2, 31.6, 25.8, 23.6, 23.3; HRMS (ESI-TOF) *m/z*: $C_{27}H_{27}N_2O^+$ $(M + H)^+$ calcd for 395.2118, found 395.2112.

6-Isobutyl-6-methyl-4-(4-methylbenzyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3sa):



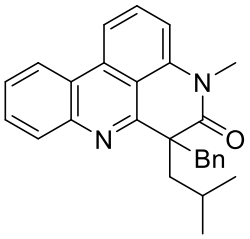
Yield: 45.6 mg, 56%; white oily; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.51 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.69 - 7.61 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.15 - 7.12 (m, 3H), 5.51 - 5.20 (m, 2H), 2.62 - 2.57 (m, 1H), 2.43 - 2.38 (m, 1H), 2.31 (s, 3H), 1.82 (s, 3H), 1.64 (t, *J* = 6.8 Hz, 1H), 0.76 (d, *J* = 6.8 Hz, 3H), 0.53 (d, *J* = 6.8 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 174.7, 160.0, 144.8, 138.0, 136.9, 133.3 (2C), 131.6, 129.7, 129.5 (2C), 129.0, 126.5 (3C), 122.6, 122.5, 116.0, 112.5, 111.8, 50.9, 50.3, 46.0, 31.5, 25.8, 23.6, 23.3, 21.1; HRMS (ESI-TOF) *m/z*: $C_{28}H_{29}N_2O^+$ $(M + H)^+$ calcd for 409.2274, found 409.2278.

4-(4-Fluorobenzyl)-6-isobutyl-6-methyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)



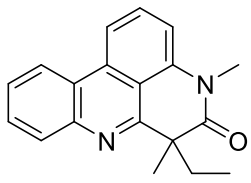
- one (3ta): Yield: 33.1mg, 42%; white oily; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.50 (d, *J* = 7.2 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.31 - 7.25 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 8.8 Hz, 2H), 5.51 - 5.27 (m, 2H), 2.62 - 2.57 (m, 1H), 2.43 - (m, 1H), 1.82 (s, 3H), 1.64 - 1.57 (m, 1H), 0.75 (d, *J* = 6.8 Hz, 3H), 0.53 (d, *J* = 6.8 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: -115.2 (s, 1F); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ : 174.8, 163.2 (d, J_{C-F} = 244.0 Hz, 1C), 159.7, 144.7, 137.7, 133.4, 132.1 (d, J_{C-F} = 3.3 Hz, 1C), 131.5, 129.7, 129.1, 128.2, 128.2, 126.5, 122.5, 122.5, 116.2, 115.8, 115.6, 112.4, 111.5, 50.8, 50.2, 45.6, 31.5, 25.7, 23.6, 23.3; HRMS (ESI-TOF) *m/z*: $C_{27}H_{26}FN_2O^+$ $(M + H)^+$ calcd for 413.2024, found 413.2021.

6-Benzyl-6-isobutyl-4-methyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one



(3wa): Yield: 42.5 mg, 54%; yellow oily; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.51 (d, *J* = 8.4 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.81 (t, *J* = 7.2 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 6.85 - 6.80 (m, 2H), 6.73 (t, *J* = 8.0 Hz, 2H), 6.49 (d, *J* = 9.2 Hz, 2H), 3.55 - 3.46 (m, 2H), 3.35 (s, 3H), 2.80 - 2.75 (m, 1H), 2.56 - 2.51 (m, 1H), 1.55 - 1.46 (m, 1H), 0.72 (d, *J* = 6.8 Hz, 3H), 0.56 (d, *J* = 6.4 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ : 173.0, 158.9, 144.7, 138.2, 136.5, 132.3, 131.4, 129.8, 129.2 (2C), 129.0, 127.2 (2C), 126.5, 126.2, 122.6, 122.5, 115.7, 113.8, 110.1, 57.1, 52.3, 49.8, 29.2, 25.7, 23.8, 22.8.; HRMS (ESI-TOF) *m/z*: $C_{27}H_{27}N_2O^+$ $(M + H)^+$ calcd for 395.2118, found 395.2113.

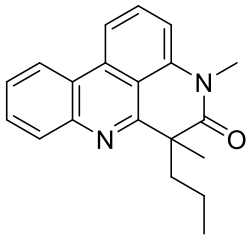
6-Ethyl-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ab): Yield:



23.2 mg, 40%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.54 (d, *J* = 6.8 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 9.6 Hz, 1H), 7.82 (t, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 7.2 Hz, 1H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 3.60 (s, 3H),

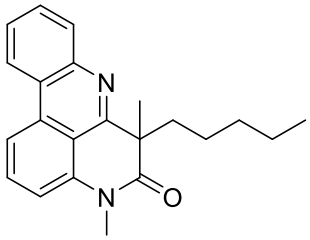
2.46 - 2.37 (m, 1H), 2.34 - 2.26 (m, 1H), 1.81 (s, 3H), 0.65 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 174.3, 159.9, 145.0, 139.0, 133.1, 131.7, 129.8, 129.1, 126.5, 122.6, 122.5, 116.0, 112.6, 110.6, 52.0, 36.4, 29.7, 27.8, 9.8; HRMS (ESI-TOF) *m/z*: $C_{19}H_{19}N_2O^+$ $(M + H)^+$ calcd for 291.1492, found 291.1496.

4,6-Dimethyl-6-propyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ac): Yield:



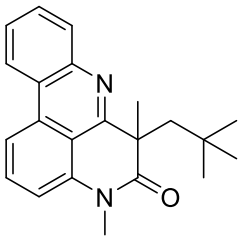
32.8 mg, 54%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.54 (d, *J* = 9.6 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.82 (t, *J* = 8.4 Hz, 1H), 7.76 (t, *J* = 6.8 Hz, 1H), 7.65 (t, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 3.59 (s, 3H), 2.38 - 2.31 (m, 1H), 2.26 - 2.19 (m, 1H), 1.82 (s, 3H), 1.19 - 1.04 (m, 1H), 0.91 - 0.83 (m, 1H), 0.74 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 174.4, 160.0, 145.0, 138.9, 133.0, 131.7, 129.8, 129.1, 126.5, 122.6, 122.5, 116.0, 112.5, 110.6, 51.4, 45.9, 29.6, 28.1, 18.6, 14.2; HRMS (ESI-TOF) *m/z*: $C_{20}H_{21}N_2O^+$ $(M + H)^+$ calcd for 305.1648, found 305.1641.

4,6-Dimethyl-6-pentyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ad): Yield:



(41.8 mg, 63%)[a]; (32.8 mg, 31.8%)[b]; white oily; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.54 (d, *J* = 8.4 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 9.6 Hz, 1H), 7.82 (t, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 3.59 (s, 3H), 2.43 - 2.35 (m, 1H), 2.31 - 2.21 (m, 1H), 1.80 (s, 3H), 1.17 - 1.06 (m, 5H), 0.88 - 0.81 (m, 1H), 0.72 (t, *J* = 6.4 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 174.4, 160.1, 145.0, 138.9, 133.1, 131.6, 129.8, 129.0, 126.4, 122.6, 122.5, 116.0, 112.4, 110.6, 51.4, 43.3, 31.9, 29.7, 28.4, 25.0, 22.2, 13.9; HRMS (ESI-TOF) *m/z*: $C_{22}H_{25}N_2O^+$ $(M + H)^+$ calcd for 333.1961, found 333.1969.

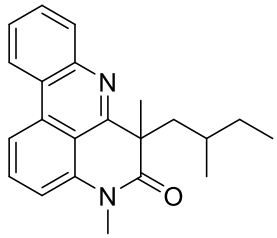
4,6-Dimethyl-6-neopentyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ae):



Yield: 50.4 mg, 76%; white oily; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.53 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 9.6 Hz, 1H), 7.82 (t, *J* = 8.0 Hz, 1H), 7.75 (t, *J* = 7.0 Hz, 1H), 7.63 (t, *J* = 6.8 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 3.57 (s, 3H),

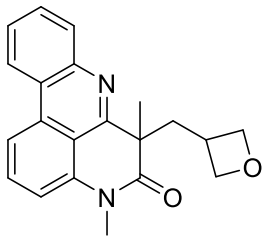
2.63 (d, *J* = 13.6 Hz, 1H), 2.52 (d, *J* = 13.7 Hz, 1H), 1.82 (s, 3H), 0.52 (s, 9H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 174.5, 159.9, 144.6, 138.7, 133.2, 131.7, 129.6, 129.1, 126.4, 122.6, 122.5, 116.0, 112.4, 110.6, 56.2, 49.5, 33.1, 31.8, 30.9 (3C), 29.6; HRMS (ESI-TOF) *m/z*: $C_{22}H_{25}N_2O^+$ $(M + H)^+$ calcd for 333.1961, found 333.1967.

4,6-Dimethyl-6-(2-methylbutyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one



(3af): dr=1:1; Yield: 43.8 mg, 66%; yellow oily; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.53 (d, *J* = 8.4 Hz, 1H), 8.27 (d, *J* = 6.4 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.82 (t, *J* = 8.0 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 3.59 (s, 3H), 2.59 - 2.54 (m, 0.5H), 2.43 - 2.33 (m, 1H), 2.26 - 2.20 (m, 1H), 1.79 (d, *J* = 4.0 Hz, 3H), 1.32 - 1.22 (m, 0.5H), 1.19 - 1.13 (m, 1H), 1.06 - 0.98 (m, 1H), 0.93 - 0.84 (m, 0.5H), 0.69 (t, *J* = 7.4 Hz, 2H), 0.63 - 0.58 (m, 3H), 0.33 (d, *J* = 6.8 Hz, 2H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 174.7, 174.3, 160.3, 159.9, 144.9, 144.8, 138.9, 133.2, 133.1, 131.6, 131.6, 129.7, 129.0, 126.4, 122.6, 122.5, 122.5, 116.0, 112.3, 112.3, 110.6, 110.6, 50.7, 50.4, 49.8, 49.0, 31.9, 31.6, 30.6, 30.4, 30.2, 30.1, 29.7, 29.6, 20.0, 19.4, 11.1, 10.9; HRMS (ESI-TOF) *m/z*: $C_{22}H_{25}N_2O^+$ $(M + H)^+$ calcd for 333.1961, found 333.1969.

4,6-Dimethyl-6-(oxetan-3-ylmethyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-on

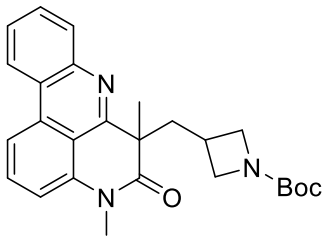


e (3ag): Yield: 43.8 mg, 66%; yellow solid;^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.53 (d, *J* = 7.6 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.82 (t, *J* = 8.8 Hz, 1H), 7.86 (t, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 4.53 (t, *J* = 7.0 Hz, 1H), 4.27 (t, *J* = 6.6 Hz, 1H), 4.01 (d, *J* = 8.4 Hz, 2H), 3.57 (s, 3H), 2.94 - 2.87 (m, 1H), 2.69 - 2.64 (m, 1H), 2.56 - 2.51 (m, 1H), 1.84 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 173.6, 158.7, 144.6, 138.5, 133.2, 131.9, 129.7, 129.3, 126.8, 122.6, 122.5, 116.2, 112.0, 110.8, 77.5 (2C) 50.5, 46.5, 32.7, 29.8, 26.8; HRMS (ESI-TOF) *m/z*: $C_{21}H_{21}N_2O_2^+$ $(M + H)^+$ calcd for 333.1598, found 333.1595.

***Tert*-butyl**

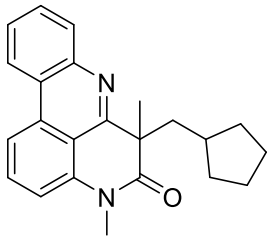
3-((4,6-dimethyl-5-oxo-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*]phenanthridin-

6-yl)methyl)azetidine-1-carboxylate (3ah): Yield: 65.5 mg, 76%; yellow solid; ^{1}H



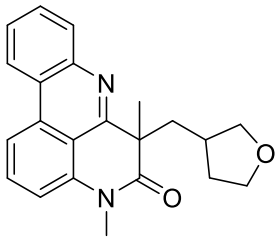
NMR (400 MHz, $CDCl_3$) δ : 8.53 (d, *J* = 8.0 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.83 (t, *J* = 8.6 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 3.69 (t, *J* = 8.4 Hz, 1H), 3.58 (s, 3H), 3.38 (d, *J* = 22.4 Hz, 2H), 3.15 (s, 1H), 2.55 - 2.46 (m, 2H), 2.38 - 2.31 (m, 1H), 1.87 (s, 3H), 1.32 (s, 9H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ : 173.6, 158.7, 156.0, 144.7, 138.5, 133.2, 131.9, 129.8, 129.3, 126.8, 122.6 (2C), 116.3, 112.1, 110.7, 79.1, 60.4, 50.6, 47.7, 29.8, 28.3 (3C), 26.2, 21.0, 14.2; HRMS (ESI-TOF) *m/z*: $C_{26}H_{30}N_3O_3^+$ $(M + H)^+$ calcd for 432.2282, found 432.2286.

6-(Cyclopentylmethyl)-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-on



e (3ai): Yield: 53.6 mg, 78%; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.54 (d, *J* = 8.4 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.82 (t, *J* = 8.2 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 6.8 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 3.59 (s, 3H), 2.57 - 2.52 (m, 1H), 2.43 - 2.38 (m, 1H), 1.82 (s, 3H), 1.47 - 1.40 (m, 2H), 1.33 - 1.01 (m, 6H), 0.73 - 0.64 (m, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ : 174.5, 160.2, 144.8, 138.9, 133.1, 131.6, 129.7, 129.0, 126.4, 122.6, 122.5, 116.0, 112.4, 110.5, 51.1, 49.6, 37.7, 33.4, 32.8, 29.7, 29.7, 24.9, 24.8; HRMS (ESI-TOF) *m/z*: $C_{23}H_{25}N_2O^+$ $(M + H)^+$ calcd for 345.1961, found 345.1967.

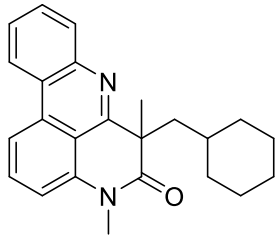
4,6-Dimethyl-6-((tetrahydrofuran-3-yl)methyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3aj): dr=1:1; Yield: 53.6 mg, 78%; yellow oily; ^{1}H



NMR (400 MHz, $CDCl_3$) δ : 8.54 (d, *J* = 8.4 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.13 (t, *J* = 9.2 Hz, 1H), 7.83 (t, *J* = 8.2 Hz, 1H), 7.82 - 7.73 (m, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 3.65 (t, *J* = 8.0 Hz, 1H), 3.6. - 3.51 (m, 4H), 3.49 - 3.42 (m, 0.5H), 3.38 - 3.31 (m, 0.5H), 3.16 (t, *J* = 8.6 Hz, 0.5H), 3.03 (t, *J* = 7.8 Hz, 0.5H), 2.81 (t, *J* = 9.4 Hz, 0.5H), 2.66 - 2.61 (m, 0.5H), 2.56 - 2.54 (m, 1H), 2.43 - 2.38 (m, 0.5H), 1.92 - 1.84 (m, 1H), 1.81 (s, 3H), 1.54 - 1.45 (m, 0.5H), 1.35 - 1.27

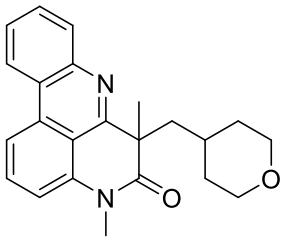
(m, 0.5H), 1.20 - 1.10 (m, 0.5H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 174.0, 173.9, 159.4, 159.1, 144.7, 144.7, 138.6, 133.3, 133.2, 131.8, 129.7, 129.2, 129.2, 126.7, 126.7, 122.6, 122.5, 116.3, 116.2, 112.2, 112.1, 110.8, 110.7, 73.3, 73.1, 67.6, 67.4, 51.0, 50.9, 45.4, 45.2, 37.1, 36.9, 33.0, 32.9, 29.8, 29.5; HRMS (ESI-TOF) *m/z*: $C_{22}H_{23}N_2O_2^+$ $(M + H)^+$ calcd for 347.1754, found 347.1759.

6-(Cyclohexylmethyl)-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one



(3ak): Yield: (54.4 mg, 76%)[a], (53.6 mg, 73%)[b]; white oily; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.54 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 9.6 Hz, 1H), 7.82 (t, *J* = 8.0 Hz, 1H), 7.77 - 7.73 (m, 1H), 7.66 - 7.62 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 3.59 (s, 3H), 2.54 - 2.49 (m, 1H), 2.32 - 2.27 (m, 1H), 1.73 (s, 3H), 1.49 - 1.46 (m, 1H), 1.42 - 1.31 (m, 3H), 1.22 - 1.16 (m, 1H), 1.12 - 1.08 (m, 1H), 0.97 - 0.79 (m, 4H), 0.72 - 0.63 (m, 1H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 174.5, 160.1, 144.8, 138.8, 133.2, 131.6, 129.7, 129.0, 126.4, 122.6, 122.5, 116.0, 112.2, 110.6, 50.3, 49.4, 34.9, 33.9, 33.5, 31.0, 29.7, 26.1, 26.1, 26.0; HRMS (ESI-TOF) *m/z*: $C_{24}H_{27}N_2O^+$ $(M + H)^+$ calcd for 359.2118, found 359.2115.

4,6-Dimethyl-6-((tetrahydro-2*H*-pyran-4-yl)methyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3al):

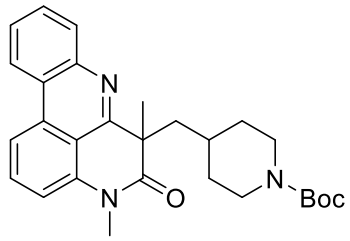


Yield: 61.9 mg, 86%; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.54 (d, *J* = 9.6 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.83 (t, *J* = 8.2 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 3.75 - 3.70 (m, 1H), 3.60 - 3.56 (m, 4H), 3.08 - 2.95 (m, 2H), 2.65 - 2.60 (m, 1H), 2.39 - 2.34 (m, 1H), 1.72 (s, 3H), 1.45 - 1.38 (m, 1H), 1.33 - 1.27 (m, 2H), 1.12 - 1.01 (m, 1H), 0.98 - 0.93 (m, 1H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 174.1, 159.6, 144.7, 138.6, 133.3, 131.7, 129.7, 129.1, 126.6, 122.5 (2C), 116.1, 112.0, 110.7, 67.7 (2C), 50.2, 48.0, 33.5, 33.3, 32.4, 31.5, 29.7; HRMS (ESI-TOF) *m/z*: $C_{23}H_{25}N_2O_2^+$ $(M + H)^+$ calcd for 361.1911, found 361.1913.

***Tert*-butyl**

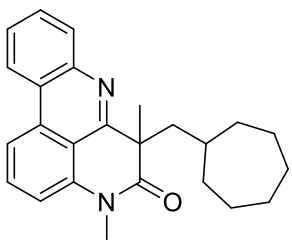
4-((4,6-dimethyl-5-oxo-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*]phenanthridin-6-yl)meth

yl)piperidine-1-carboxylate (3am): Yield: 78.0 mg, 85%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.55 (d, *J* = 8.0 Hz, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.84 (t, *J* = 8.2 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 6.6 Hz, 1H), 3.85 - 3.60 (m, 2H), 3.60 (s, 3H), 2.65 - 2.60 (m, 1H), 2.39 - 2.29 (m, 3H), 1.71 (s, 3H), 1.36 (s, 10H), 1.15 - 1.04 (m, 2H), 0.92 - 0.85 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ : 174.2, 159.6, 154.7, 144.8, 138.7, 133.4, 131.8, 129.8, 129.2, 126.7, 122.7, 122.6, 116.2, 112.1, 110.8, 79.1, 50.4, 47.5 (2C), 33.5, 32.7, 31.6, 29.8, 29.7 (2C), 28.4 (3C); HRMS (ESI-TOF) *m/z*: $C_{28}H_{34}N_3O_3^+$ $(M + H)^+$ calcd for 460.2595, found 460.2590.



6-(Cycloheptylmethyl)-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-on

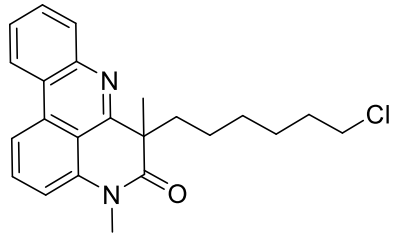
e (3an): Yield: 32.7 mg, 44%; white oily; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.54 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.83 (t, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 3.59 (s, 3H), 2.47 - 2.42 (m, 1H), 2.32 - 2.28 (m, 1H), 1.78 (s, 3H), 1.40 - 1.36 (m, 3H), 1.33 - 1.24 (m, 5H), 1.14 - 1.07 (m, 3H), 0.97 - 0.84 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ : 174.5, 160.2, 144.9, 138.9, 133.1, 131.6, 129.8, 129.0, 126.4, 122.6, 122.5, 116.0, 112.4, 110.5, 50.8, 50.7, 36.3, 35.2, 34.7, 29.9, 29.7, 28.4, 28.3, 25.9, 25.7; HRMS (ESI-TOF) *m/z*: $C_{25}H_{29}N_2O^+$ $(M + H)^+$ calcd for 373.2274, found 373.2275.



6-(((*3r,5r,7r*)-Adamantan-1-yl)methyl)-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ao): Yield: 53.3 mg, 65%; white oily; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.54 (d, *J* = 8.4 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.83 (t, *J* = 8.2 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 3.58 (s, 3H), 2.55 (d, *J* = 14.0 Hz, 1H), 2.37 (d, *J* = 13.3 Hz, 1H), 1.78 (s, 3H), 1.59 (s, 3H), 1.40 (d, *J* = 11.6 Hz, 3H), 1.28 - 1.24 (m, 3H), 1.19 - 1.14 (m, 3H), 1.07 - 1.03 (m, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ : 174.6,

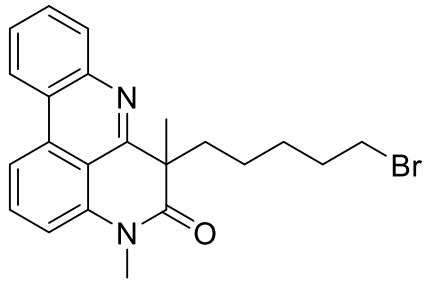
160.1, 144.6, 138.7, 133.2, 131.6, 129.7, 129.1, 126.3, 122.6, 122.6, 116.0, 112.3, 110.6, 57.6, 48.7, 43.4 (3C), 36.6 (3C), 34.0, 33.4, 29.7, 28.5 (3C); HRMS (ESI-TOF) *m/z*: $C_{28}H_{31}N_2O^+$ $(M + H)^+$ calcd for 411.2431, found 411.2433.

6-(6-Chlorohexyl)-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one



(3ap): Yield: 44.8 mg, 59%; yellow oily; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.54 (d, *J* = 8.4 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.82 (t, *J* = 8.2 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 3.59 (s, 3H), 3.39 (t, *J* = 6.6 Hz, 2H), 2.46 - 2.38 (m, 1H), 2.30 - 2.22 (m, 1H), 1.79 (s, 3H), 1.62 - 1.55 (m, 2H), 1.28 - 1.08 (m, 5H), 0.92 - 0.84 (m, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ : 174.3, 159.9, 145.0, 138.9, 133.1, 131.7, 129.8, 129.1, 126.5, 122.6, 122.5, 116.0, 112.4, 110.6, 51.4, 45.0, 42.8, 32.4, 29.7, 28.9, 28.7, 26.4, 25.1; HRMS (ESI-TOF) *m/z*: $C_{23}H_{26}ClN_2O^+$ $(M + H)^+$ calcd for 381.1728, found 381.1724.

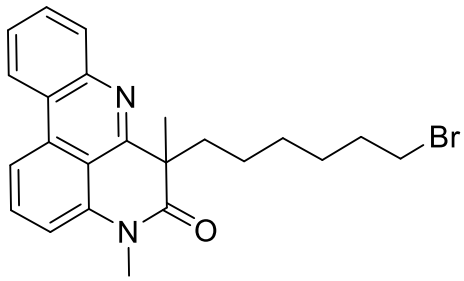
6-(5-Bromopentyl)-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one



(3aq): Yield: 56.6 mg, 69%; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.83 (t, *J* = 8.1 Hz, 1H), 7.82 - 7.41 (m, 1H), 7.67-7.63 (m, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 3.59 (s, 3H), 3.26 - 3.22(m, 2H), 2.49 - 2.41 (m, 1H), 2.32 - 2.24 (m, 1H), 1.77 (s, 3H), 1.72 - 1.65 (m, 2H), 1.34 - 1.25 (m, 2H), 1.17 - 1.25 (m, 1H), 0.94 - 0.89 (m, 1H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 174.2, 159.7, 145.0, 138.8, 133.1, 131.7, 129.8, 129.1, 126.5, 122.6, 122.5, 116.1, 112.4, 110.7, 51.4, 42.2, 33.7, 32.3, 29.7, 28.9, 28.2, 24.4.; HRMS (ESI-TOF) *m/z*: $C_{22}H_{24}BrN_2O^+$ $(M + H)^+$ calcd for 411.1067, found 411.1062.

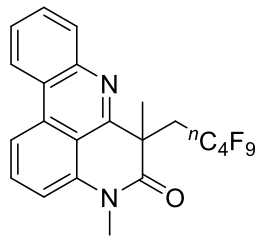
6-(6-Bromohexyl)-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one

(3ar): Yield: 55.9 mg, 66%; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.54 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.82 (t, *J* = 8.2 Hz,



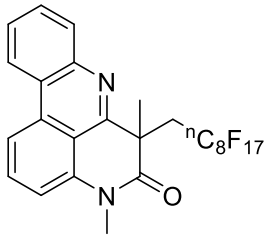
1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 3.59 (s, 3H), 3.26 (t, *J* = 6.8 Hz, 2H), 2.46 - 2.39 (m, 1H), 2.30 - 2.23 (m, 1H), 1.78 (s, 3H), 1.70 - 1.63 (m, 2H), 1.26 - 1.14 (m, 5H), 0.90 - 0.85 (m, 1H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 174.3, 159.9, 145.0, 138.8, 133.1, 131.7, 129.8, 129.1, 126.5, 122.6, 122.5, 116.0, 112.4, 110.7, 51.4, 42.7, 33.9, 32.6, 29.7, 28.8, 28.7, 27.7, 25.1; HRMS (ESI-TOF) *m/z*: $C_{23}H_{26}BrN_2O^+$ $(M + H)^+$ calcd for 425.1223, found 425.1229.

4,6-Dimethyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3as): Yield: 40.5 mg, 41%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$)



δ : 8.55 (d, *J* = 8.4 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 9.6 Hz, 1H), 7.85 (t, *J* = 8.2 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.67 (t, *J* = 8.4 Hz, 1H), 7.27 (t, *J* = 4.0 Hz, 2H), 3.66 - 3.53 (m, 4H), 3.45 - 3.28 (m, 1H), 1.83 (s, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: -81.05 - -81.11 (m, 3F), -108.31 (t, *J* = 11.4 Hz, 1H), -109.05 (t, *J* = 10.1 Hz, 1H), -109.81 (t, *J* = 10.0 Hz, 1H), -110.53 (t, *J* = 10.0 Hz, 1H), -124.74 - -124.82 (m, 1F), -125.89 - -126.01 (m, 1F); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 172.0, 157.0, 144.5, 138.3, 133.5, 131.9, 129.7, 129.2, 126.9, 122.8, 122.6, 116.4, 111.5, 111.0, 46.9, 40.5 (t, J_{C-F} = 22.9 Hz), 31.7, 29.9; HRMS (ESI-TOF) *m/z*: $C_{22}H_{16}F_9N_2O^+$ $(M + H)^+$ calcd for 495.1113, found 495.1115

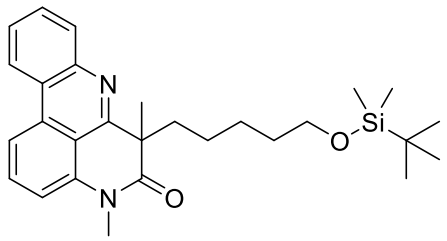
6-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl)-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3at): Yield: 83.2 mg, 60%; white solid; ^{1}H



NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.4 Hz, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.84 (t, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.2 Hz, 1H), 3.66 - 3.53 (m, 4H), 3.41 - 3.29 (m, 1H), 1.83 (s, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ : -80.80 (t, *J* = 7.4 Hz, 3F), -108.05 (t, *J* = 10.9 Hz, 1F), -108.77 (t, *J* = 10.9 Hz, 1F), -109.49 (t, *J* = 10.5 Hz, 1F), -110.21 (t, *J* =

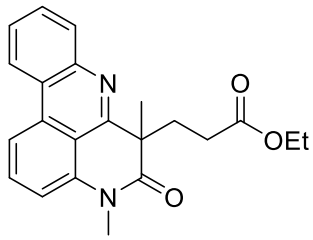
10.5 Hz, 1F), -121.57 (s, 2F), -121.97 (s, 2F), -122.76 (s, 2F), -123.86 (s, 2F), -126.13 (s, 2F); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 172.0, 157.1, 144.5, 138.3, 133.5, 131.9, 129.7, 129.2, 126.9, 122.8, 122.6, 116.4, 111.5, 111.0, 46.9, 40.4, 31.7, 29.9; HRMS (ESI-TOF) *m/z*: $C_{26}H_{16}F_{17}N_2O^+$ $(M + H)^+$ calcd for 695.0986, found 695.0980.

6-(5-((Tert-butyldimethylsilyl)oxy)pentyl)-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3au): Yield: 38.6 mg, 46%; yellow oily; ^{1}H NMR



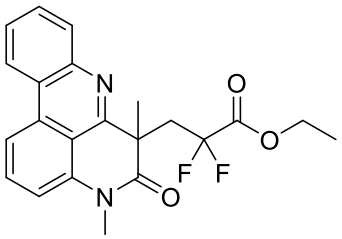
(400 MHz, $CDCl_3$) δ : 8.53 (d, *J* = 8.4 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.82 (t, *J* = 8.2 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 3.59 (s, 3H), 3.41 (t, *J* = 6.6 Hz, 2H), 2.43 - 2.36 (m, 1H), 2.31 - 2.22 (m, 1H), 1.80 (s, 3H), 1.34 - 1.28 (m, 3H), 1.22 - 1.12 (m, 3H), 0.79 (s, 9H), -0.08 (s, 6H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 174.3, 160.0, 145.0, 138.9, 133.1, 131.7, 129.8, 129.0, 126.5, 122.6, 122.5, 116.0, 112.5, 110.6, 63.0, 51.4, 43.3, 32.4, 29.7, 28.4, 25.9, 25.9 (3C), 25.1, 18.3, -5.4 (2C); HRMS (ESI-TOF) *m/z*: $C_{28}H_{39}N_2O_2Si^+$ $(M + H)^+$ calcd for 463.2775, found 463.2772.

Ethyl 3-(4,6-dimethyl-5-oxo-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanoate (3av): Yield: 51.4 mg, 71%; yellow oily; ^{1}H NMR (400 MHz, $CDCl_3$)



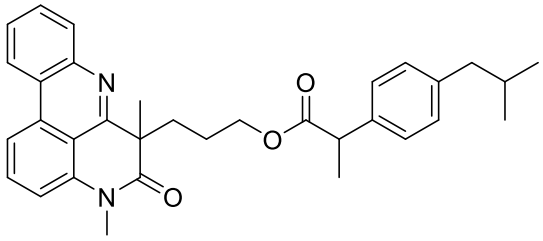
δ : 8.53 (d, *J* = 6.8 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.83 (t, *J* = 8.0 Hz, 1H), 7.75 (t, *J* = 8.4 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 3.94 - 3.88 (m, 2H), 3.59 (s, 3H), 2.81 - 2.75 (m, 1H), 2.64 - 2.57 (m, 1H), 2.26 - 2.18 (m, 1H), 2.11 - 2.03 (m, 1H), 1.79 (s, 3H), 1.10 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 173.5, 172.8, 158.7, 144.8, 138.6, 133.2, 131.8, 129.9, 129.1, 128.6, 126.7, 122.5, 116.1, 112.1, 110.8, 60.2, 50.6, 36.2, 30.4, 29.8, 28.4, 14.0; HRMS (ESI-TOF) *m/z*: $C_{22}H_{23}N_2O_3^+$ $(M + H)^+$ calcd for 363.1703, found 363.1708.

Ethyl 3-(4,6-dimethyl-5-oxo-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*]phenanthridin-6-yl)-2,2-difluoropropanoate (3aw): Yield: 51.4 mg, 42%; yellow oily; ^{1}H NMR (400



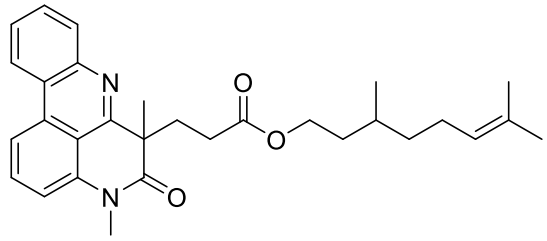
MHz, $CDCl_3$) δ : 8.53 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.84 (t, *J* = 8.2 Hz, 1H), 7.74 (t, *J* = 7.4 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 5.2 Hz, 1H), 3.89 - 3.81 (m, 1H), 3.77 - 3.69 (m, 1H), 3.68 - 3.56 (m, 4H), 3.43 - 3.32 (m, 1H), 1.75 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ : -98.13 (d, *J* = 196.8 Hz, 1F), -104.13 (d, *J* = 197.1 Hz, 1F); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 172.5, 164.2 (t, $J_{C\text{-}F}$ = 32.4 Hz, 1F), 157.7, 144.4, 138.6, 133.4, 132.0, 129.5, 129.1, 126.8, 122.9, 122.6, 117.6, 116.2, 115.1, 115.1, 112.6, 111.8, 111.0, 47.7, 47.7, 47.7, 47.6, 44.0, 43.8, 43.8, 43.6, 31.6, 29.9, 13.5; HRMS (ESI-TOF) *m/z*: $C_{22}H_{21}F_2N_2O_3^+$ $(M + H)^+$ calcd for 399.1515, found 399.1518.

3-(4,6-Dimethyl-5-oxo-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propyl 2-(4-isobutylphenyl)propanoate (3ax): Yield: 74.2 mg, 73%; yellow oily; ^1H NMR



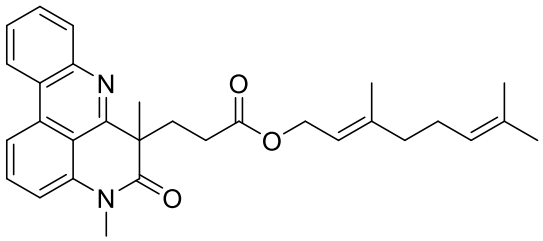
(400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.4 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 7.2 Hz, 1H), 7.82 (t, *J* = 8.2 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 7.6 Hz, 2H), 3.99 - 3.92 (m, 1H), 3.90 - 3.84 (m, 1H), 3.61 - 3.55 (m, 4H), 2.53 - 2.45 (m, 1H), 2.40 (d, *J* = 7.2 Hz, 2H), 2.33 - 2.26 (m, 1H), 1.84 - 1.79 (m, 1H), 1.76 (s, 3H), 1.49 - 1.46 (m, 1H), 1.42 - 1.39 (m, 3H), 1.31 - 1.21(m, 1H), 0.88 - 0.86 (m, 6H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 174.6, 173.8, 159.3, 145.0, 140.3, 138.7, 137.7, 137.7, 133.2, 131.7, 129.8, 129.2, 129.1, 127.1, 126.6, 122.6, 122.5, 116.1, 112.3, 110.7, 64.5, 51.1, 45.0, 45.0, 45.0, 38.4, 38.2, 30.1, 29.7, 28.9, 28.9, 24.7, 24.7, 22.4, 18.4, 18.4; HRMS (ESI-TOF) *m/z*: $C_{33}H_{37}N_2O_3^+$ $(M + H)^+$ calcd for 509.2799, found 509.2796.

3,7-Dimethyloct-6-en-1-yl 3-(4,6-dimethyl-5-oxo-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanoate (3ay): Yield: 57.5 mg, 61 %; yellow oily; ^1H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.15 (d,

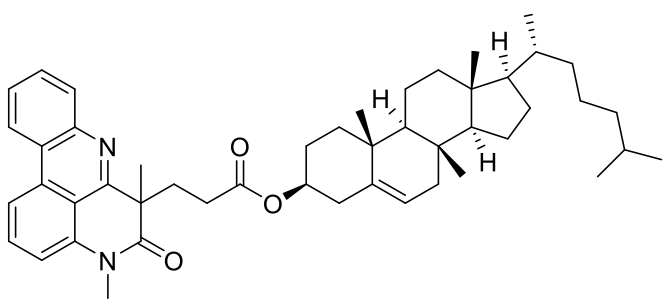


J = 8.0 Hz, 1H), 7.83 (t, *J* = 8.2 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 5.06 - 5.02 (m, 1H), 3.92 - 3.84 (m, 2H), 3.59 (s, 3H), 2.82 - 2.76 (m, 1H), 2.64 - 2.57 (m, 1H), 2.26 - 2.18 (m, 1H), 2.11 - 2.03 (m, 1H), 1.97 - 1.85 (m, 2H), 1.78 (s, 3H), 1.65 (s, 3H), 1.56 (s, 3H), 1.52 - 1.39 (m, 2H), 1.32 - 1.22 (m, 2H), 1.14 - 1.07 (m, 1H), 0.82 (d, J = 6.8 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, CDCl3) δ: 173.5, 172.9, 158.7, 144.9, 138.7, 133.3, 131.8, 131.2, 129.9, 129.1, 126.7, 124.5, 122.7, 122.5, 116.2, 112.2, 110.8, 62.9, 50.7, 36.9, 36.1, 35.2, 30.4, 29.8, 29.3, 28.5, 25.7, 25.3, 19.3, 17.6; HRMS (ESI-TOF) m/z: $C_{30}H_{37}N_2O_3^+$ $(M + H)^+$ calcd for 473.2399, found 473.2395.

***(E)*-3,7-Dimethylocta-2,6-dien-1-yl 3-(4,6-dimethyl-5-oxo-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanoate (3az):** Yield: 62.9 mg, 67%; yellow oily; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.53 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.83 (t, *J* = 8.2 Hz, 1H), 7.75 (t, *J* = 7.4 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 5.17 (t, *J* = 7.0 Hz, 1H), 5.04 (t, *J* = 7.0 Hz, 1H), 4.40 - 4.37 (m, 2H), 3.59 (s, 3H), 2.82 - 2.74 (m, 1H), 2.64 - 2.57 (m, 1H), 2.27 - 2.19 (m, 1H), 2.11 - 2.01 (m, 3H), 1.98 - 1.94 (m, 2H), 1.79 (s, 3H), 1.65 (s, 3H), 1.58 (d, *J* = 12.4 Hz, 6H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 173.5, 172.8, 158.7, 144.9, 142.0, 138.7, 133.2, 131.8, 131.8, 129.9, 129.1, 126.7, 123.7, 122.7, 122.5, 118.1, 116.2, 112.2, 110.8 , 61.2, 50.6, 39.4, 36.4, 30.4, 29.8, 28.3, 26.2, 25.6, 17.6, 16.4; HRMS (ESI-TOF) *m/z*: $C_{30}H_{35}N_2O_3^+$ $(M + H)^+$ calcd for 471.2642, found 471.2645.

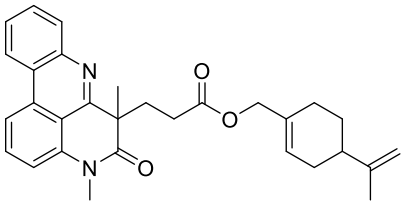


(3*S*,8*S*,9*S*,10*R*,13*R*,14*R*,17*R*)-8,10,13-Trimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 3-(4,6-dimethyl-5-oxo-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanoate (3aaa): Yield: 98.8 mg, 69%; yellow oily; ^{1}H NMR (400 MHz,

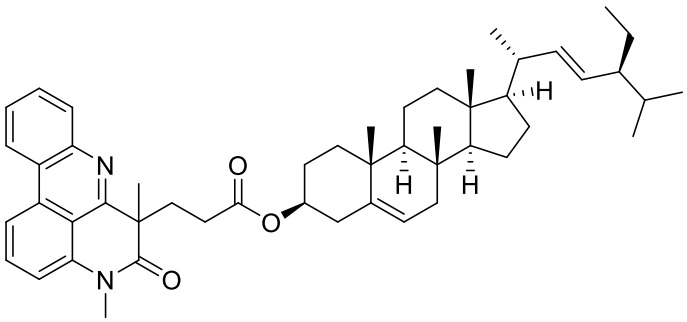


$CDCl_3$) δ : 8.53 (d, *J* = 8.4 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.82 (t, *J* = 8.2 Hz, 1H), 7.75 (t, *J* = 7.4 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 5.32 - 5.24 (m, 1H), 4.49 - 4.38 (m, 1H), 3.59 (s, 3H), 2.80 - 2.73 (m, 1H), 2.63 - 2.55 (m, 1H), 2.19 - 2.13 (m, 3H), 2.06 - 1.89 (m, 4H), 1.80 (s, 3H), 1.71 - 1.67 (m, 1H), 1.54 - 1.48 (m, 3H), 1.45 - 1.40 (m, 4H), 1.38 - 1.31 (m, 4H), 1.28 - 1.22 (s, 3H), 1.16 – 1.06 (m, 7H), 1.02 - 0.98 (m, 3H), 0.94 (s, 2H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.87 - 0.85 (m, 6H), 0.65 (d, *J* = 5.6 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 173.5, 172.1, 158.8, 144.9, 139.6, 138.7, 133.2, 131.8, 129.9, 129.1, 126.7, 122.7, 122.5, 122.4, 116.1, 112.2, 110.7, 73.8, 56.6, 56.0, 50.6, 49.9, 42.2, 39.6, 39.5, 36.9, 36.5, 36.4, 36.1, 35.7, 31.8, 31.8, 30.6, 29.8, 28.3, 28.2, 28.0, 27.6, 27.6, 24.2, 23.8 (2C), 22.8, 22.5, 20.9, 19.2, 18.7, 11.8; HRMS (ESI-TOF) *m/z*: $C_{48}H_{65}N_2O_3^+$ $(M + H)^+$ calcd for 717.4990, found 717.4995.

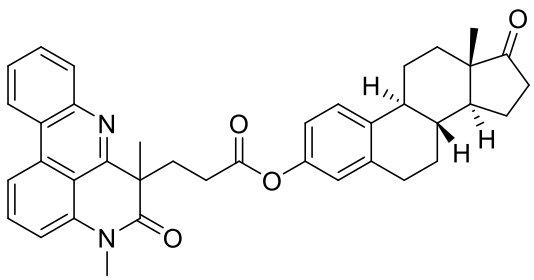
(4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl 3-(4,6-dimethyl-5-oxo-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanoate (3aab): Yield: 53.3 mg, 57%; yellow oily; ^1H NMR (400 MHz, $CDCl_3$) δ : 8.54 (d, *J* = 8.0 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.83 (t, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 5.61 (t, *J* = 2.1 Hz, 1H), 4.69 (d, *J* = 11.2 Hz, 2H), 4.29 - 4.21 (m, 2H), 3.59 (s, 3H), 2.85 - 2.77 (m, 1H), 2.65 - 2.58 (m, 1H), 2.29 - 2.22 (m, 1H), 2.13 - 2.05 (m, 3H), 1.94 (t, *J* = 5.1 Hz, 2H), 1.78 (s, 3H), 1.70 (s, 2H), 1.62 (s, 1H), 1.45 - 1.37 (m, 2H), 1.28 - 1.20 (m, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 173.5, 172.7, 158.7, 149.6, 144.9, 138.7, 133.3, 132.4, 131.8, 129.9, 129.1, 126.7, 125.6, 122.7, 122.5, 116.2, 112.2, 110.8, 108.7, 68.3, 50.7, 40.7, 36.1, 30.4, 30.4, 29.8, 28.6, 27.2, 26.3, 20.7; HRMS (ESI-TOF) *m/z*: $C_{30}H_{33}N_2O_3^+$ $(M + H)^+$ calcd for 469.2486, found 469.2488.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*R*,17*R*)-17-((2*R*,5*S*,*E*)-5-Ethyl-6-methylhept-3-en-2-yl)-8,10,13-trimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 3-(4,6-dimethyl-5-oxo-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanoate (3aac): Yield: 53.3 mg, 57%; yellow oily; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.2 Hz, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.82 (t, *J* = 8.1 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 5.32 – 5.24 (m, 1H), 4.49 – 4.38 (m, 1H), 3.59 (s, 3H), 2.82 – 2.70 (m, 1H), 2.66 – 2.53 (m, 1H), 2.16 (dt, *J* = 13.9, 6.9 Hz, 3H), 2.11 – 1.87 (m, 4H), 1.80 (s, 3H), 1.71 – 1.65 (m, 1H), 1.51 (dt, *J* = 13.4, 6.5 Hz, 3H), 1.43 (q, *J* = 6.0 Hz, 4H), 1.34 (s, 4H), 1.26 (s, 3H), 1.14 – 1.04 (m, 6H), 0.98 (d, *J* = 3.3 Hz, 3H), 0.94 (s, 2H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.87 – 0.85 (m, 6H), 0.65 (d, *J* = 5.6 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 173.5, 172.1, 158.8, 144.9, 139.6, 138.7, 133.2, 131.8(2C), 129.9, 129.1, 126.7, 122.7, 122.5, 122.4(2C), 116.1, 112.2, 110.7, 73.8, 56.6, 56.0, 50.6, 49.9, 42.2, 39.6, 39.5, 36.9, 36.5, 36.4, 36.1, 35.7, 31.8, 31.8, 30.6, 29.8, 28.3, 28.2, 28.0, 27.6, 27.6, 24.2, 23.8, 22.8(2C), 22.5, 20.9, 19.2, 18.7, 11.8; HRMS (ESI-TOF) *m/z*: $C_{50}H_{67}N_2O_3^+$ $(M + H)^+$ calcd for 743.5146, found 743.5149.

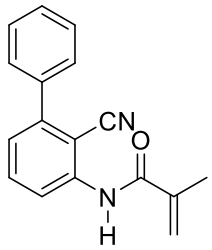


(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[*a*]phenanthren-3-yl 3-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanoate (3aad): Yield: 62.1 mg, 53%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.55 (d, *J* = 9.6 Hz, 1H), 8.29 (d, *J* = 7.6 Hz, 1H), 8.17 (d, *J* = 9.6 Hz, 1H), 7.84 (t, *J* = 8.0 Hz, 1H), 7.77 (t, *J* = 8.2 Hz, 1H), 7.67 (t, *J* = 4.8 Hz, 1H), 7.25 -



7.18 (m, 1H), 6.71 (t, *J* = 8.4 Hz, 1H) 6.64 (t, *J* = 4.2 Hz, 1H), 3.60 (s, 3H), 2.96 - 2.89 (m, 1H), 2.86 - 2.81 (m, 2H), 2.77 - 2.70 (m, 1H), 2.52 - 2.44 (m, 2H), 2.40 - 2.33 (m, 2H), 1.97 - 1.92 (m, 2H), 1.81 (s, 3H), 1.66 - 1.35 (m, 9H), 0.88 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 220.8, 173.4, 171.6, 158.6, 148.4, 144.8, 138.6, 137.7, 137.0, 133.3, 131.8, 129.9, 129.1, 126.7, 126.2, 122.7, 122.5, 121.4, 118.6, 116.2, 112.1, 110.8, 50.6, 50.3, 47.8, 44.0, 37.8, 35.8, 35.6, 31.4, 30.5, 29.8, 29.2, 28.7, 26.2, 25.6, 21.5, 13.7.; HRMS (ESI-TOF) *m/z*: $C_{38}H_{39}N_2O_4^+$ $(M + H)^+$ calcd for 587.2904, found 587.2908.

N-(2-cyano-[1,1'-biphenyl]-3-yl)methacrylamide: Yield: 33.0 mg, 63%; white solid;



^{1}H NMR (400 MHz, $CDCl_3$) δ : ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 9.6 Hz, 1H), 8.27 (s, 1H), 7.64 (t, *J* = 8.2 Hz, 1H), 7.87 - 7.45 (m, 5H), 7.23 (d, *J* = 8.0 Hz, 1H), 5.98 (s, 1H), 5.60 (s, 1H), 2.13 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ : 166.4, 145.8, 141.3, 139.9, 138.0, 133.8, 128.9 (2C), 128.8 (2C), 128.6 (2C), 125.0, 121.9, 119.1, 116.3, 18.5; HRMS (ESI-TOF) *m/z*: $C_{17}H_{15}N_2O^+$ $(M + H)^+$ calcd for 263.1179, found 263.1175.

4. **References**

(1) Chen, M.-L.; Chen, J.-Q.; Chen, Z.-K.; Wu, J. Synthesis of Ester-Containing Phenanthridines *via* Photoredox Catalyzed Radical Cascade Cyclization of *N*-Arylacrylamides with Alkyloxalyl Chlorides. *Org. Chem. Front.* **2023**, *10*, 3995-4001.

(2) Neises, B.; Steglich, W. A Mild Method for the Esterification of Carboxylic Acids. *Angew. Chem. Int. Ed.* **1978**, *17*, 522-524.

5. X-Ray Crystallographic Data

A single crystal of **3ia** suitable for X-ray crystallography was obtained by crystallization via evaporation from its PE/DCM solution.

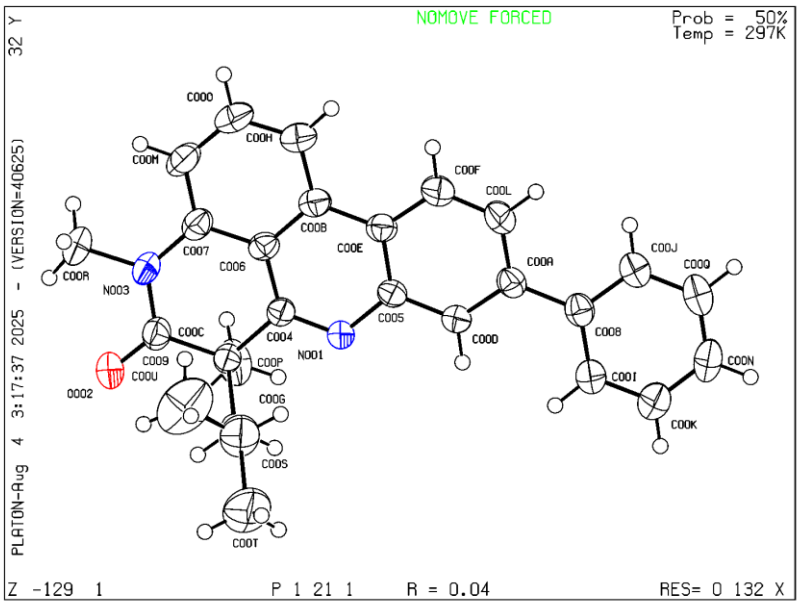


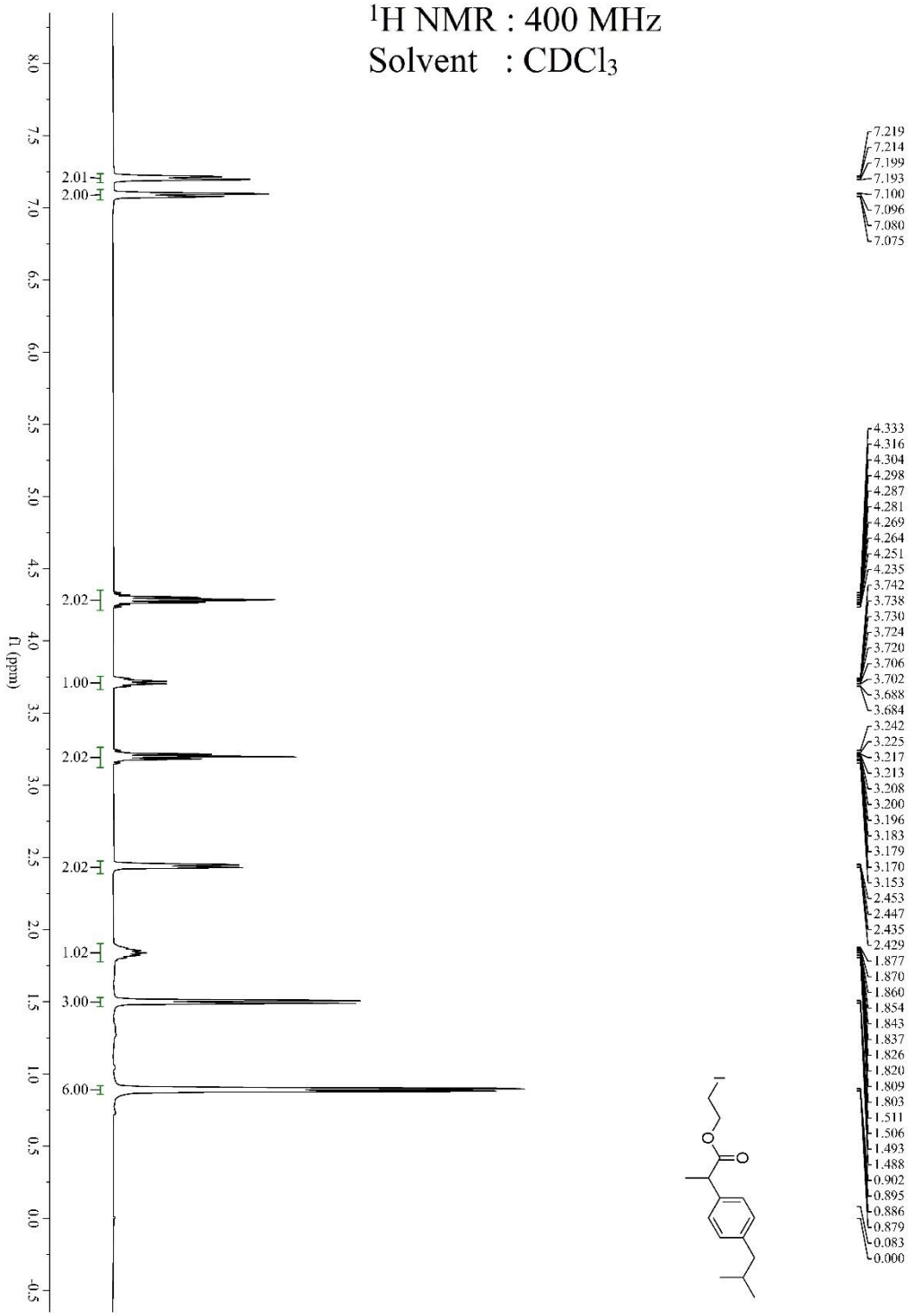
Figure S4. X-Ray crystallographic data of **3ia**. Thermal ellipsoids are shown at the 30% level.

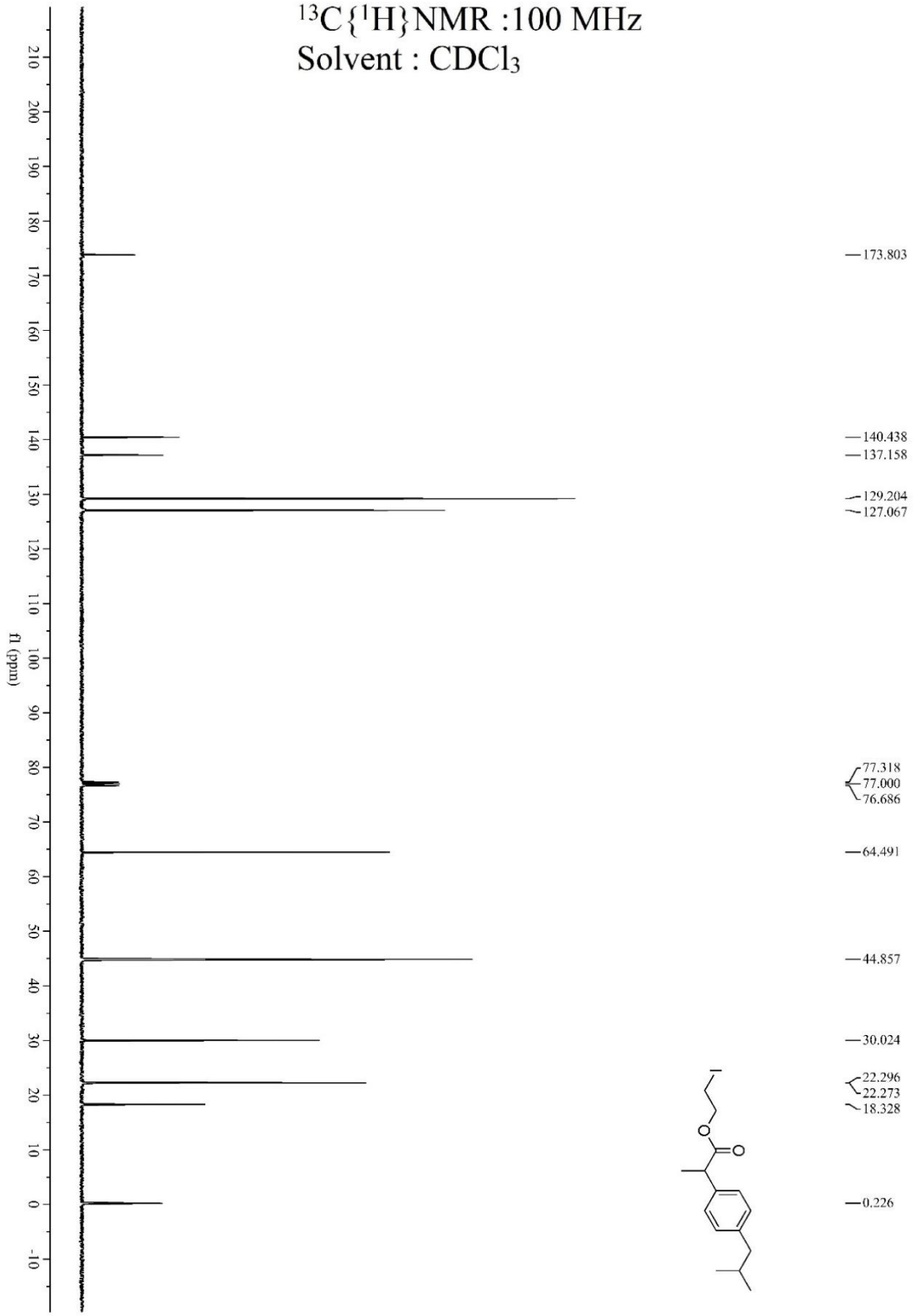
Table S2. Crystal data and structure refinement for **3ia**

Bond precision:	C-C = 0.0039 A	Wavelength =	1.54178
Cell:	a = 8.3509(3)	b = 8.0842(3)	c = 16.1093(6)
	alpha = 90	beta = 97.133(2)	gamma = 90
Temperature: 297 K			
	Calculated		Reported
Volume	1079.13(7)		1079.13(7)
Space group	P 21		P 1 21 1
Hall group	P 2yb		P 2yb
Moiety formula	$C_{27}H_{26}N_2O$		$C_{27}H_{26}N_2O$
Sum formula	$C_{27}H_{26}N_2O$		$C_{27}H_{26}N_2O$
Mr	394.50		396.49
Dx,g cm^{-3}	1.214		1.220
Z	2		2
Mu (mm^{-1})	0.573		0.598
F000	420.0		422.0
F000’	421.13		
h,k,lmax	10, 9, 19		10, 9, 19
Nref	3956 [2130]		3214
Tmin,Tmax	0.931, 0.942		0.606, 0.753
Tmin’	0.931		
Correction method= # Reported T Limits: Tmin = 0.606		Tmax = 0.753	
AbsCorr = NONE			
Data completeness = 1.51/0.81		Theta(max) = 68.494	
R(reflections) = 0.0417(3076)		wR2(reflections) = 0.1193(3214)	
S = 1.028		Npar= 275	

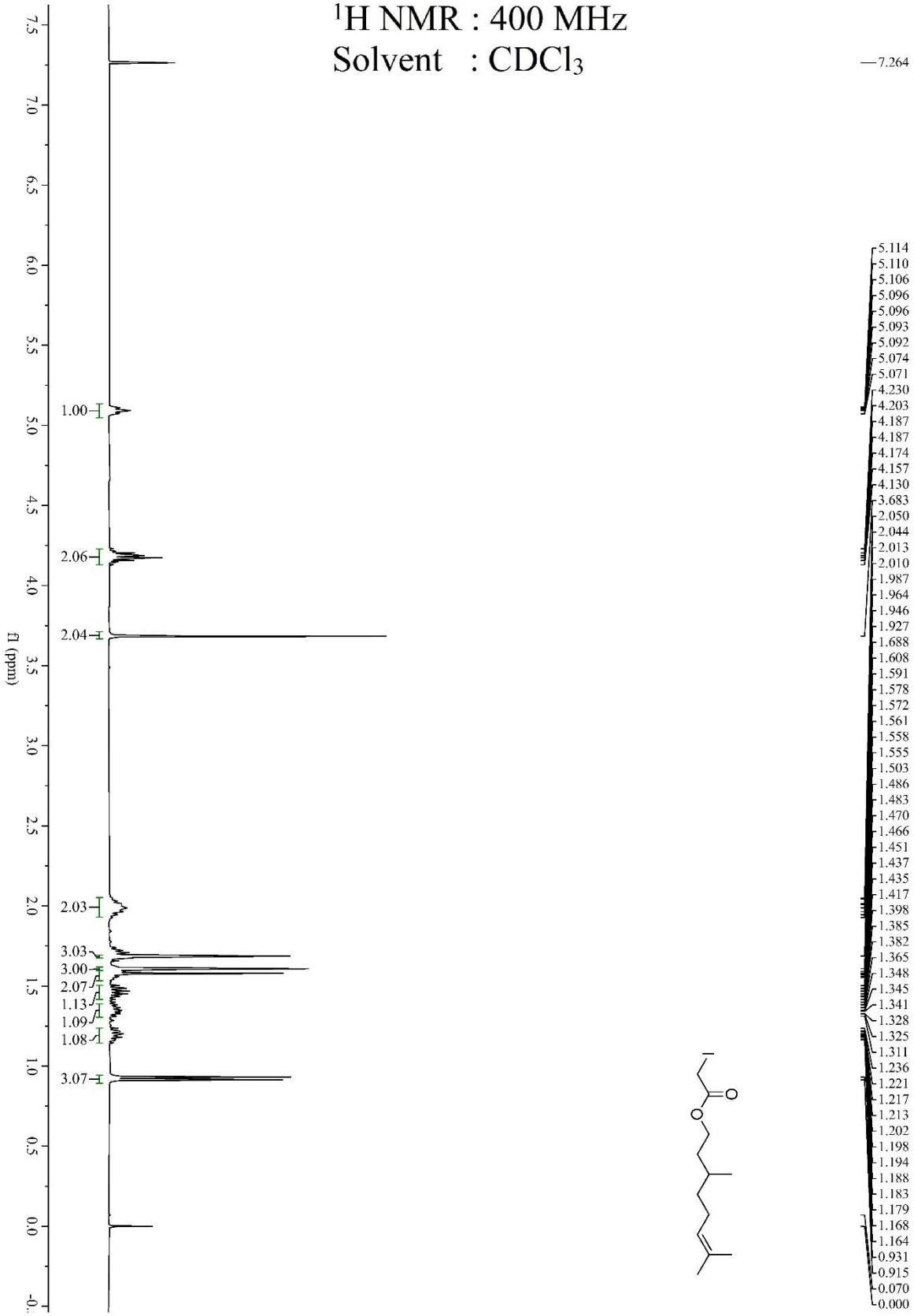
6. Spectra

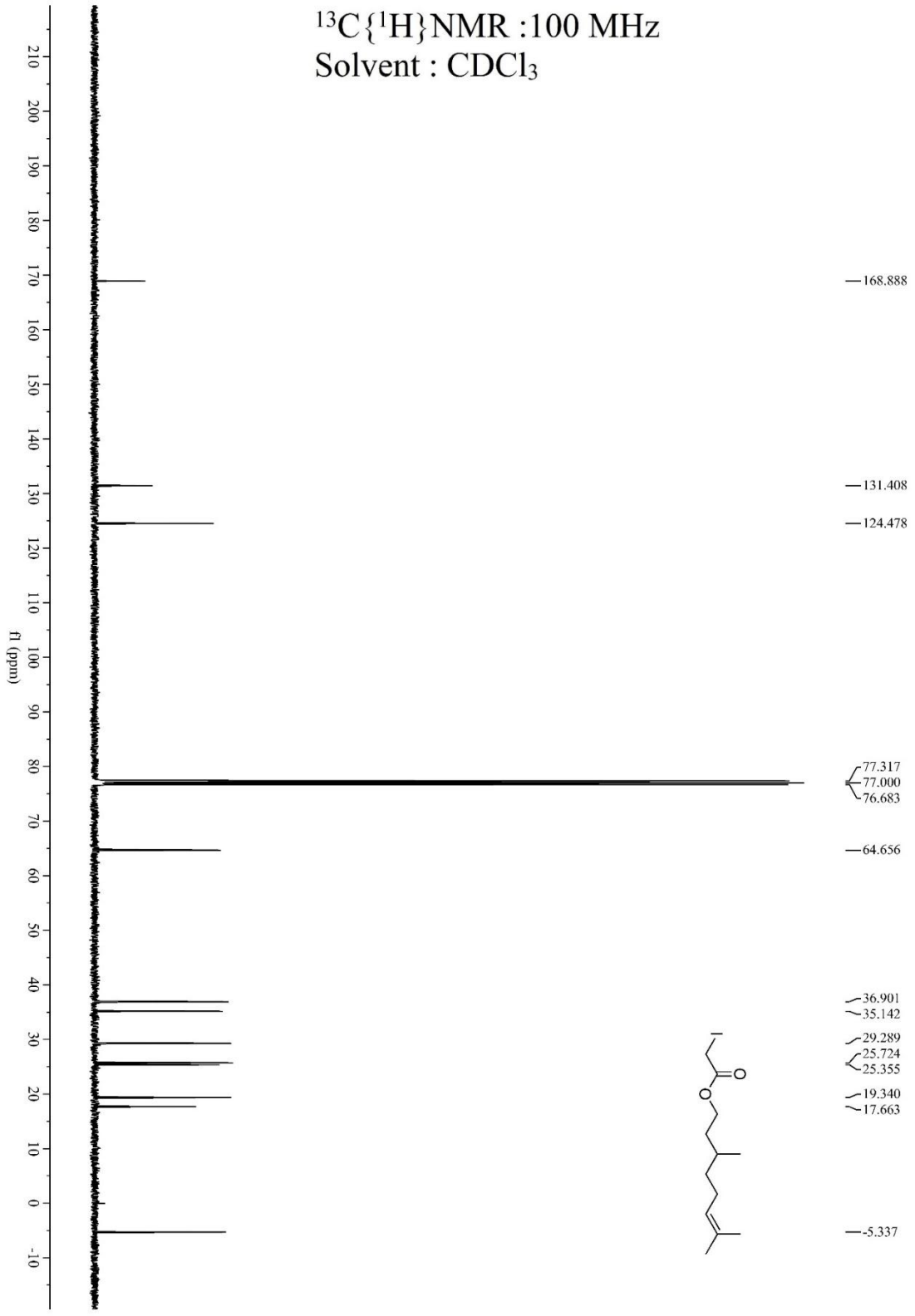
2-Iodoethyl 2-(4-isobutylphenyl)propanoate (2x)



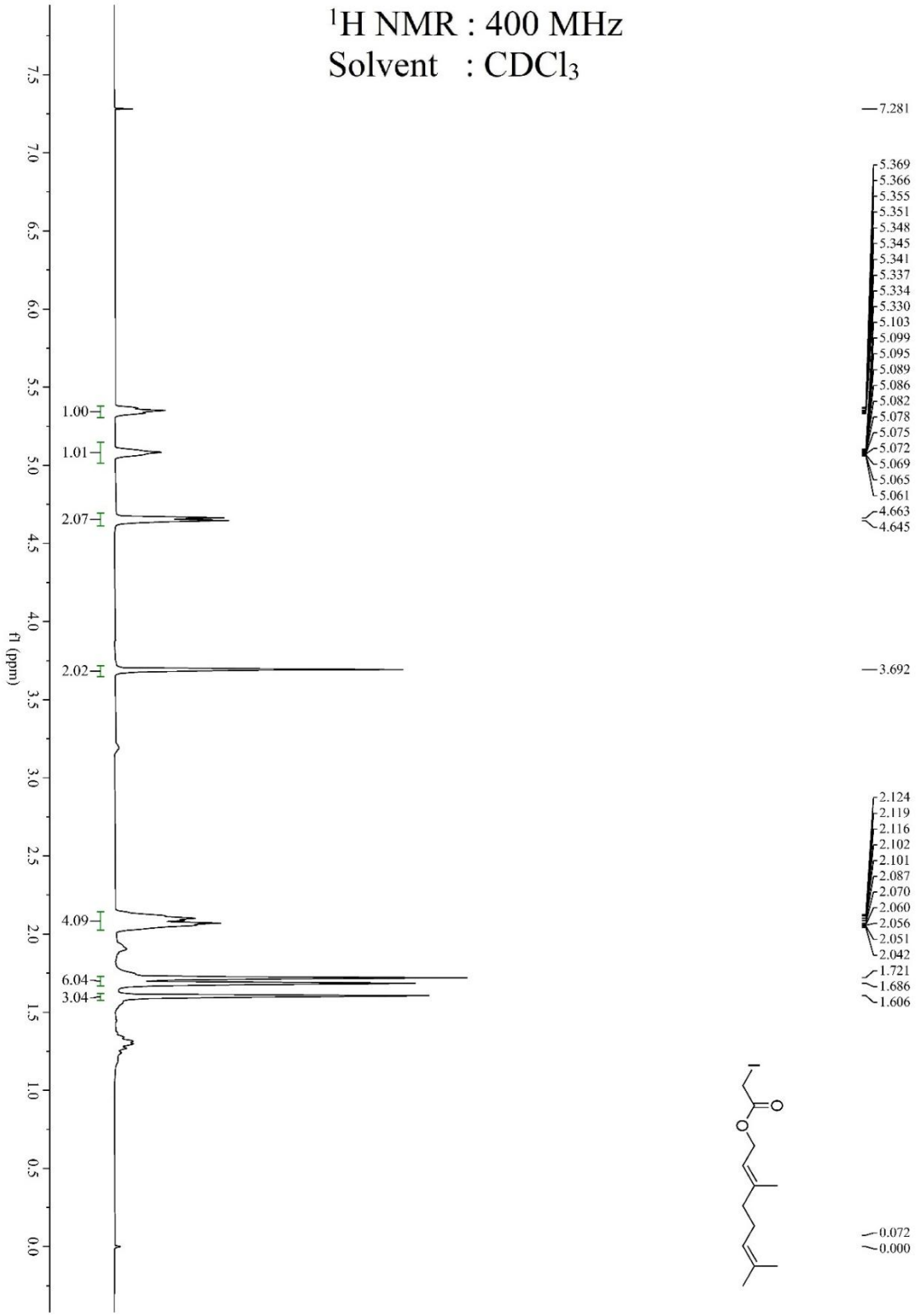

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
173.803
140.438
137.158
129.204
127.067
77.318
77.000
76.686
64.491
44.857
30.024
22.296
22.273
18.328
0.226

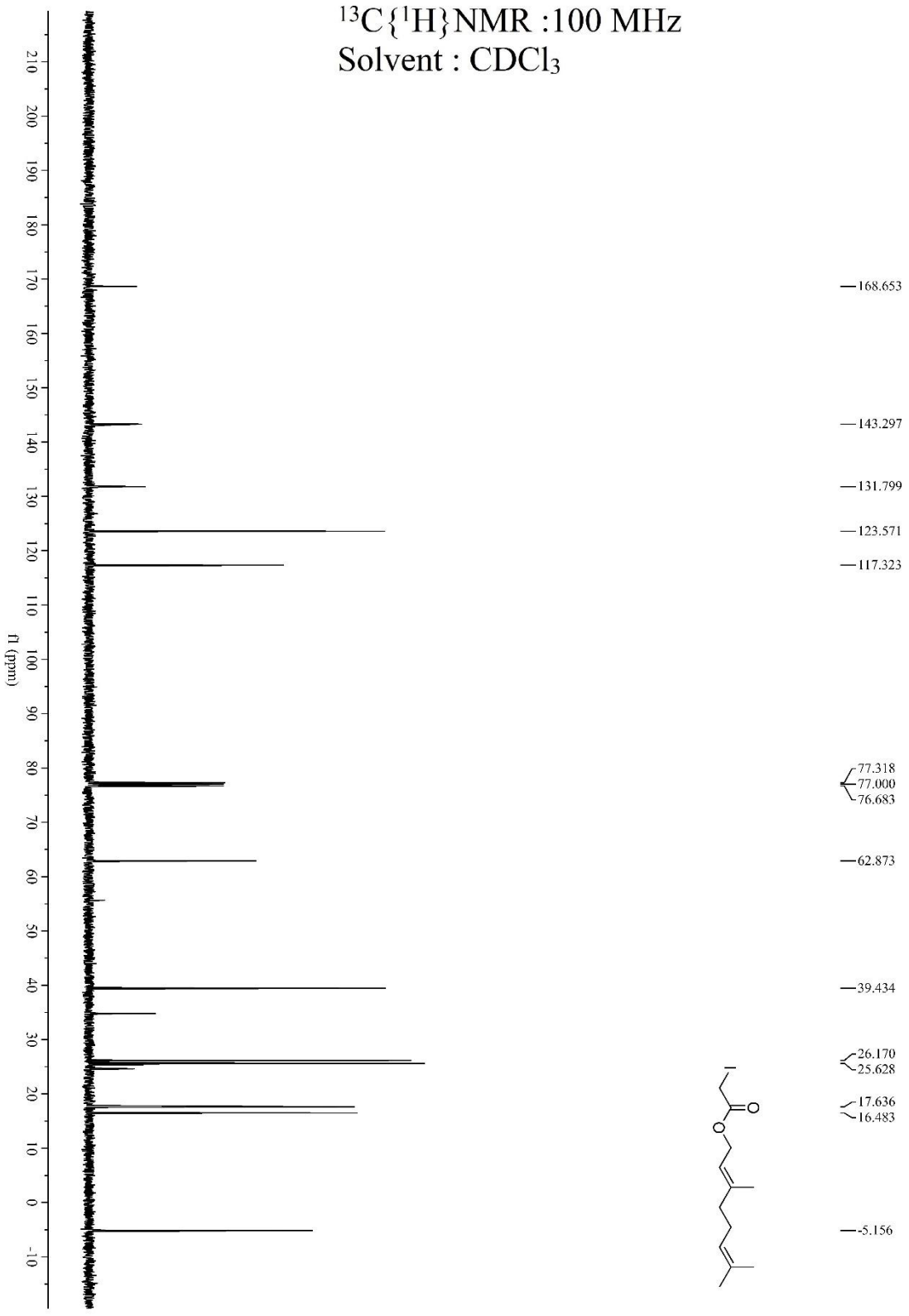
3,7-Dimethyloct-6-en-1-yl 2-iodoacetate (2y)



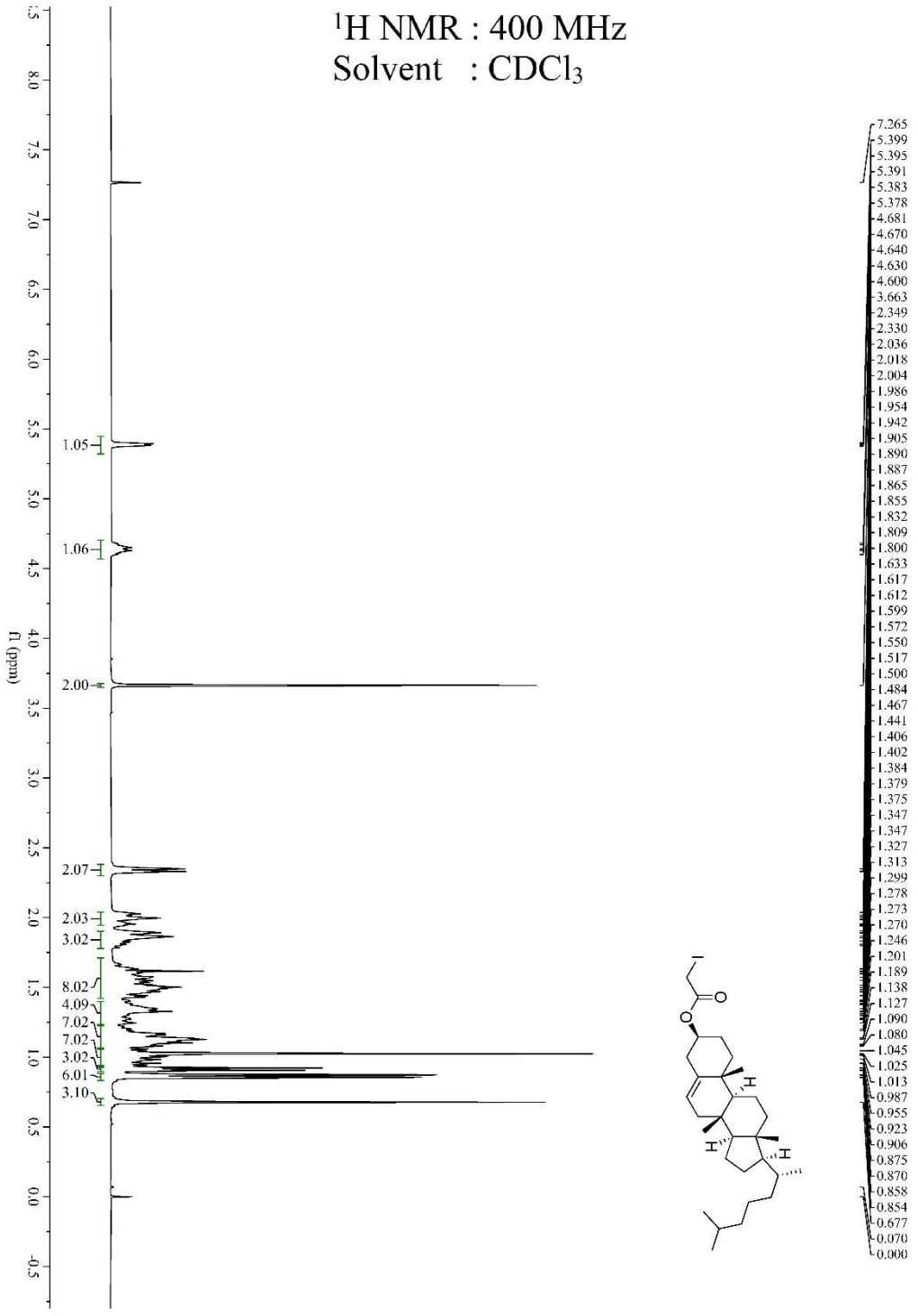

$^{13}C\{^{1}H\}NMR$:100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
168.888
131.408
124.478
77.317
77.000
76.683
64.656
36.901
35.142
29.289
25.724
25.355
19.340
17.663
-5.337
O
O

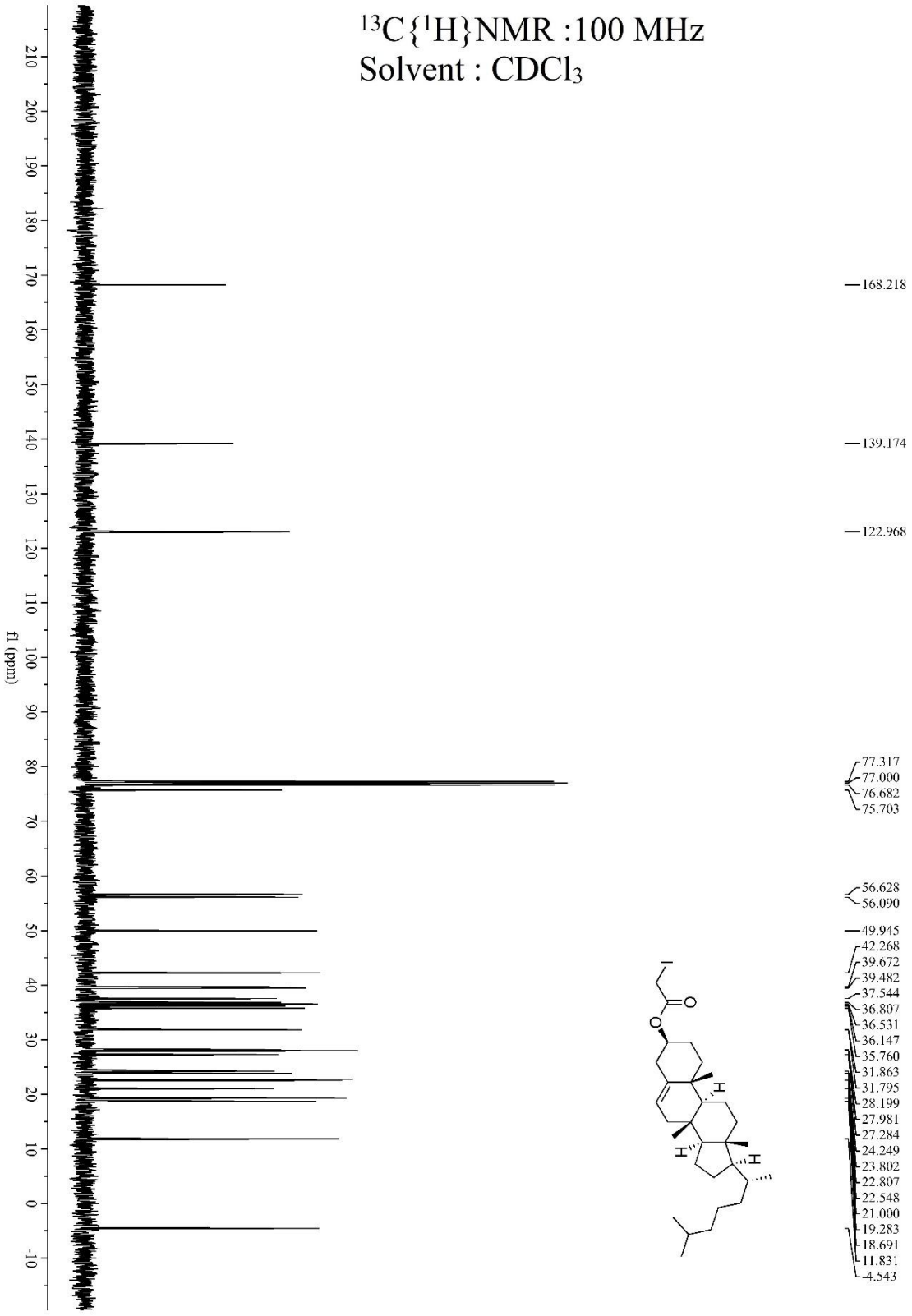
(E)-3,7-Dimethylocta-2,6-dien-1-yl 2-iodoacetate (2z)



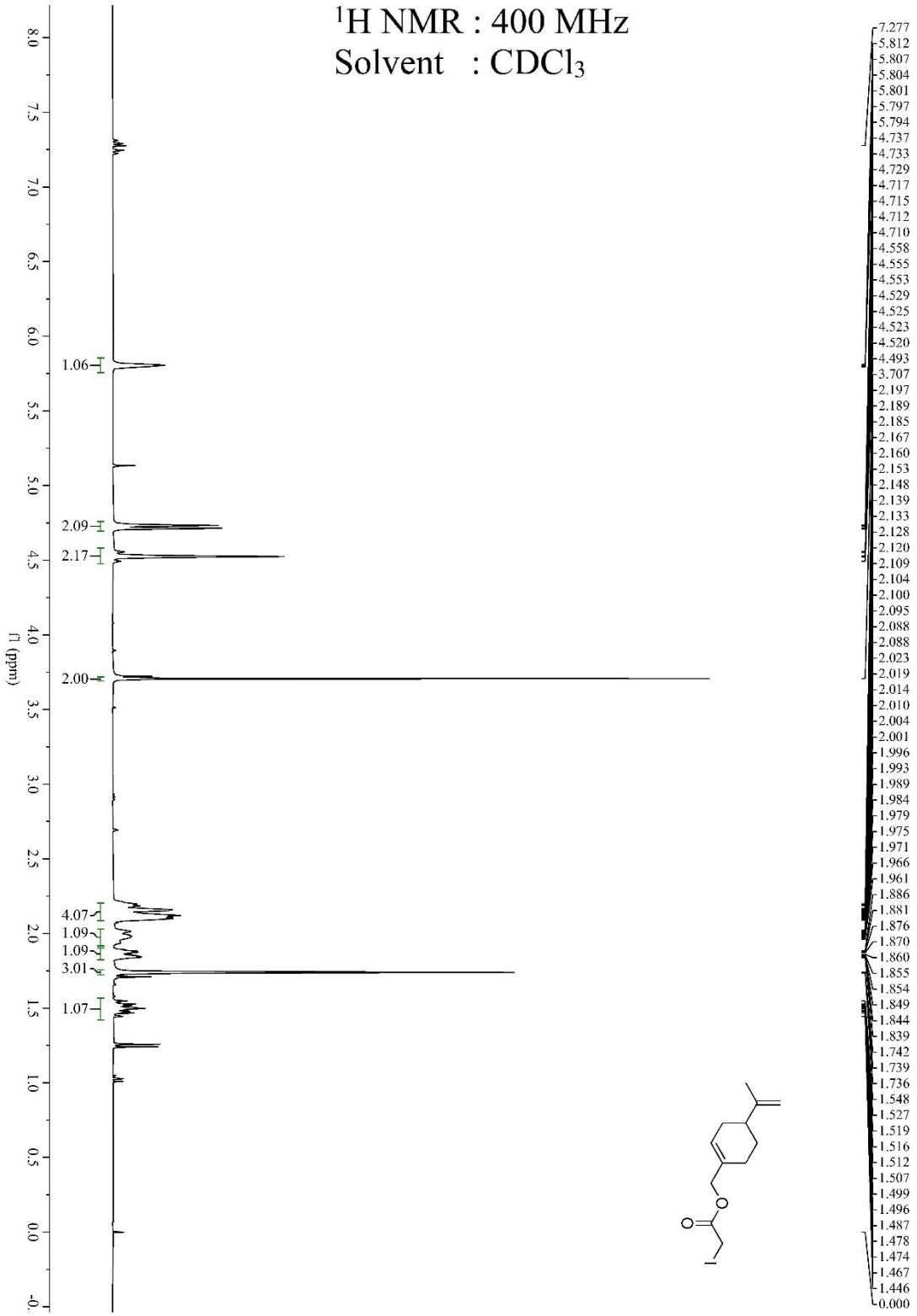

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
168.653
143.297
131.799
123.571
117.323
77.318
77.000
76.683
62.873
39.434
26.170
25.628
17.636
16.483
-5.156

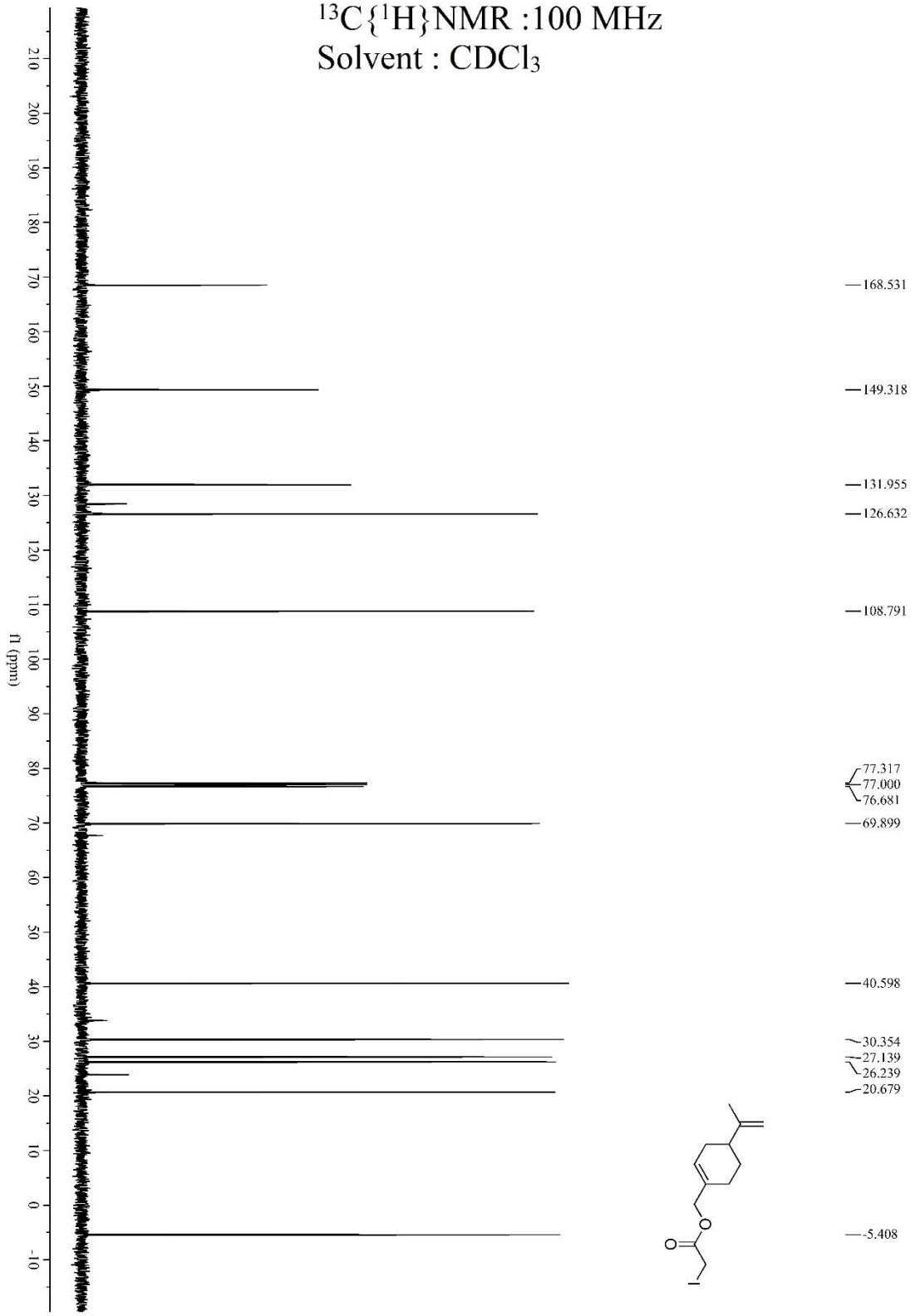
(3*S*,8*S*,9*S*,10*R*,13*R*,14*R*,17*R*)-8,10,13-Trimethyl-17-((*R*)-6-methylhept an-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cy clopenta[*a*]phenanthren-3-yl 2-iodoacetate (2aa)



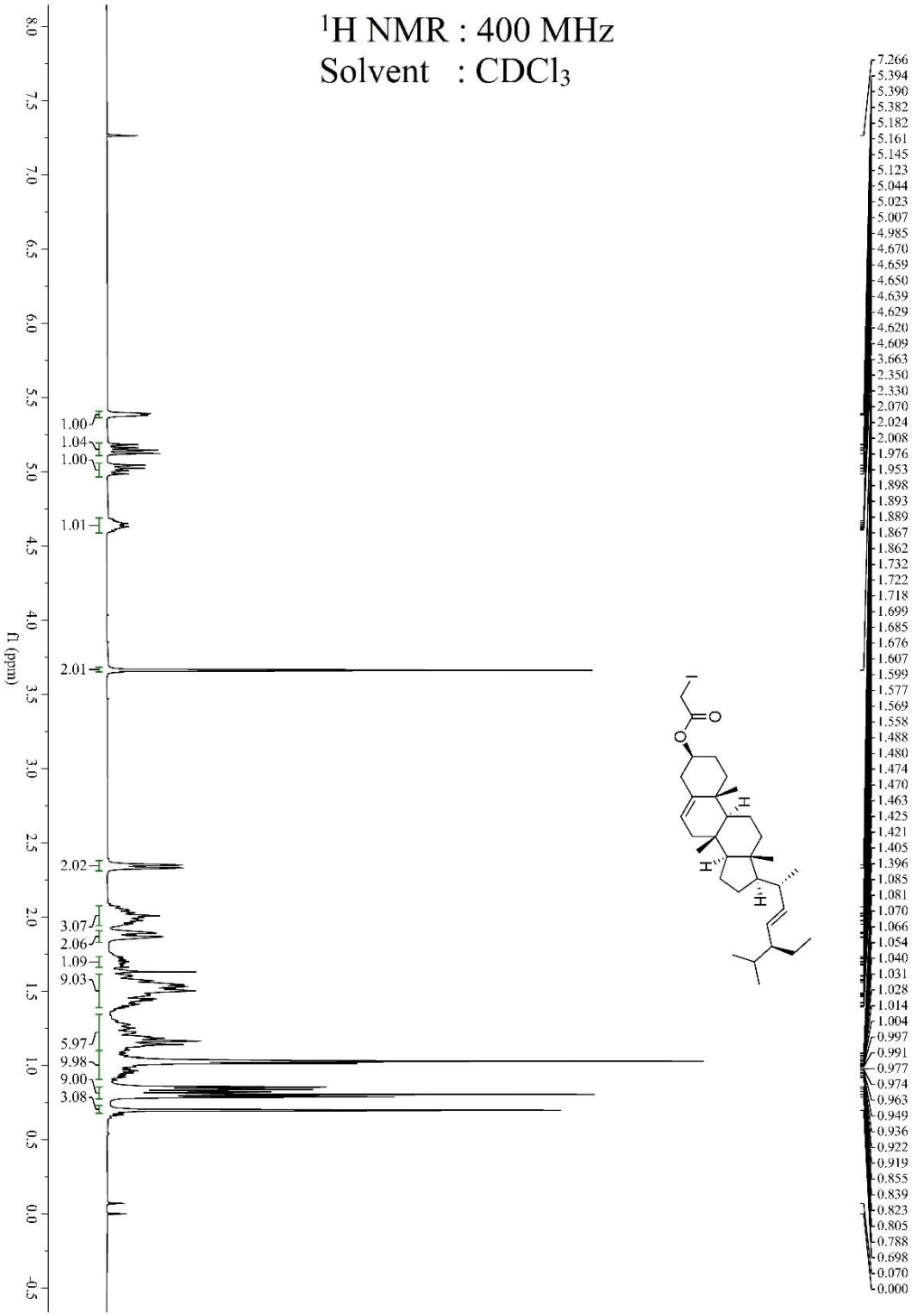

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
168.218
139.174
122.968
77.317
77.000
76.682
75.703
56.628
56.090
49.945
42.268
39.672
39.482
37.544
36.807
36.531
36.147
35.760
31.863
31.795
28.199
27.981
27.284
24.249
23.802
22.807
22.548
21.000
19.283
18.691
11.831
-4.543
O
O
H
H
H

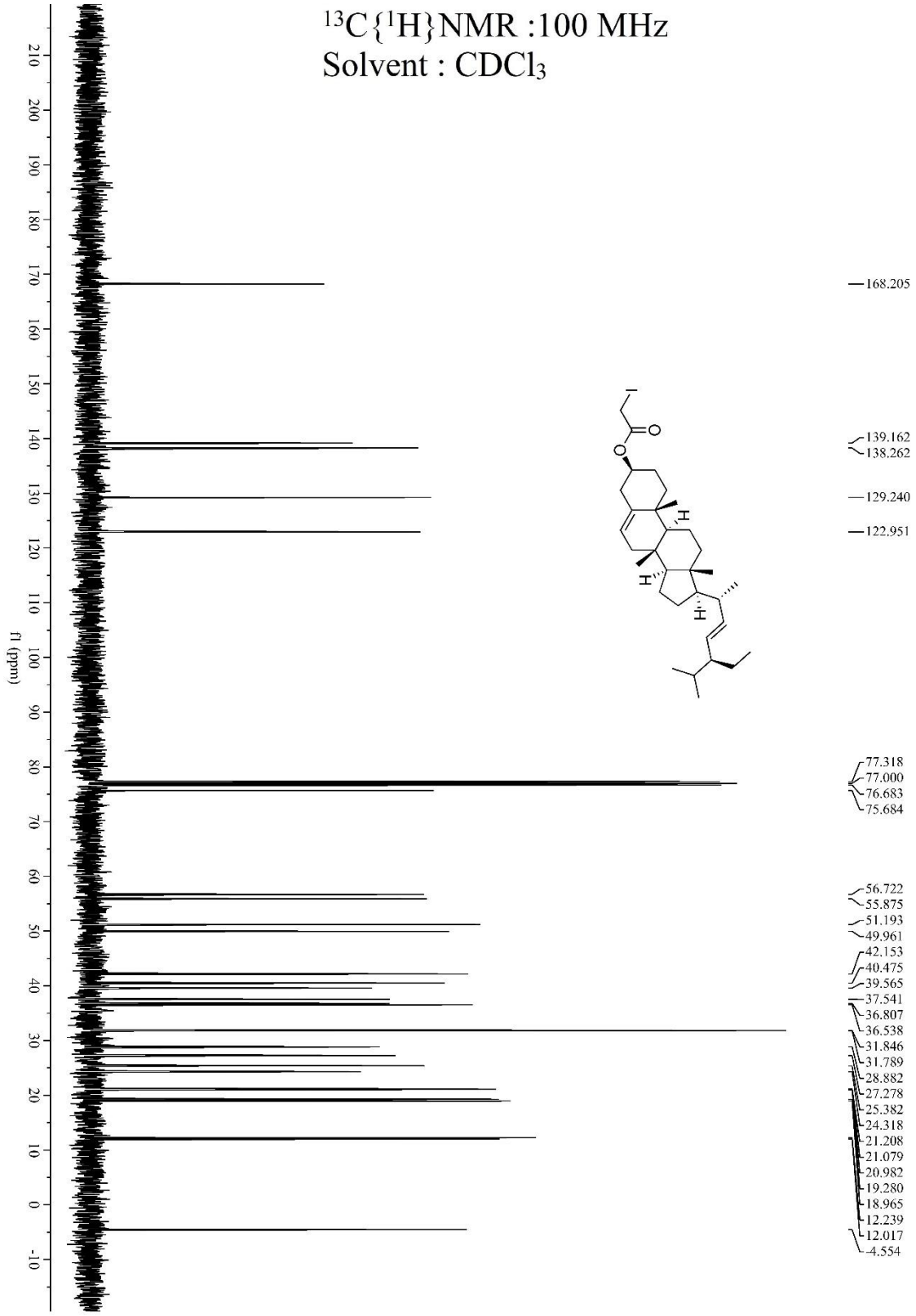
(4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl 2-iodoacetate (2ab)




$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
168.531
149.318
131.955
126.632
108.791
77.317
77.000
76.681
69.899
40.598
30.354
27.139
26.239
20.679
-5.408

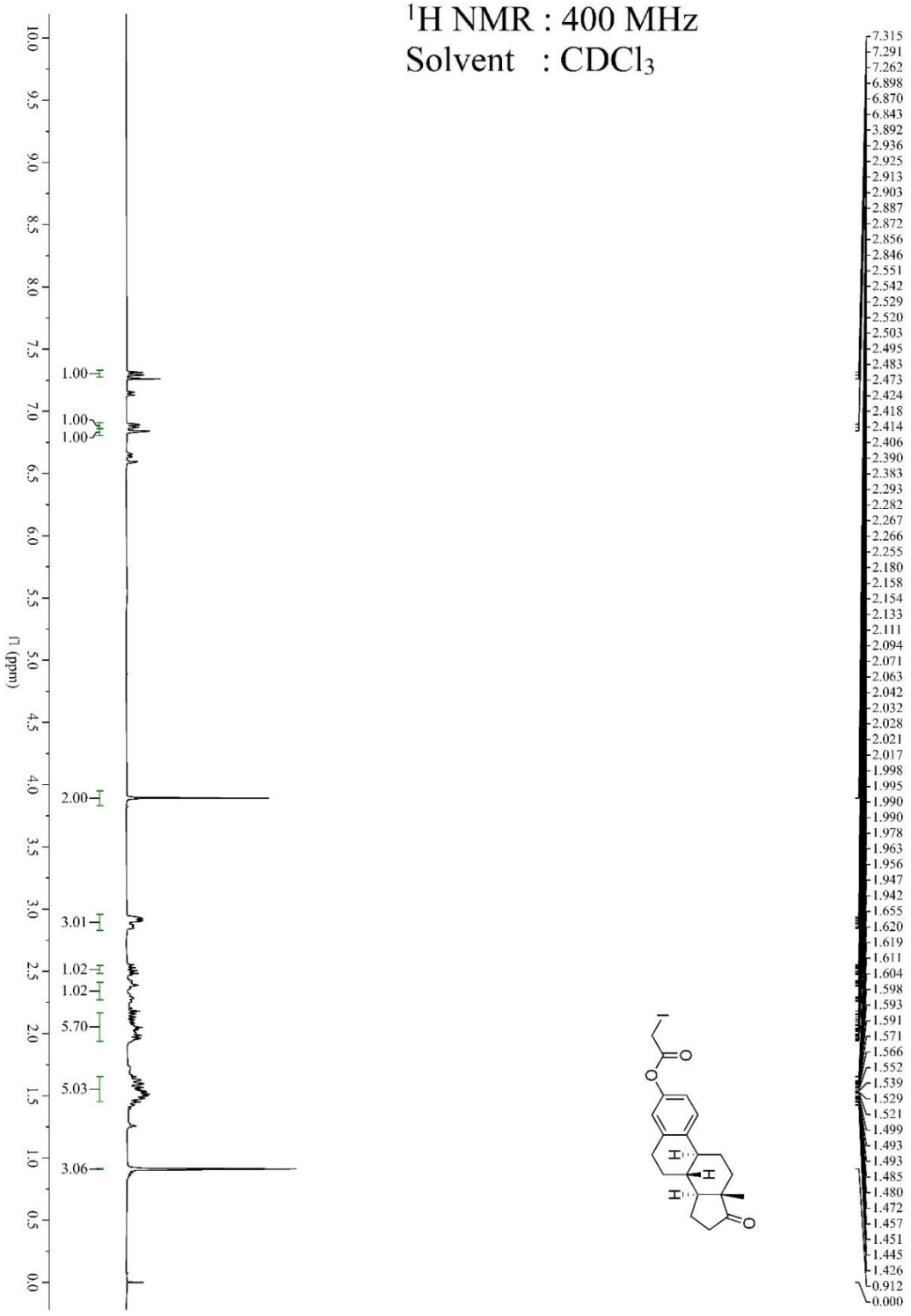
(3*S*,8*S*,9*S*,10*R*,13*R*,14*R*,17*R*)-17-((2*R*,5*S*,*E*)-5-Ethyl-6-methylhept-3-en-2-yl)-8,10,13-trimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 2-iodoacetate (2ac)

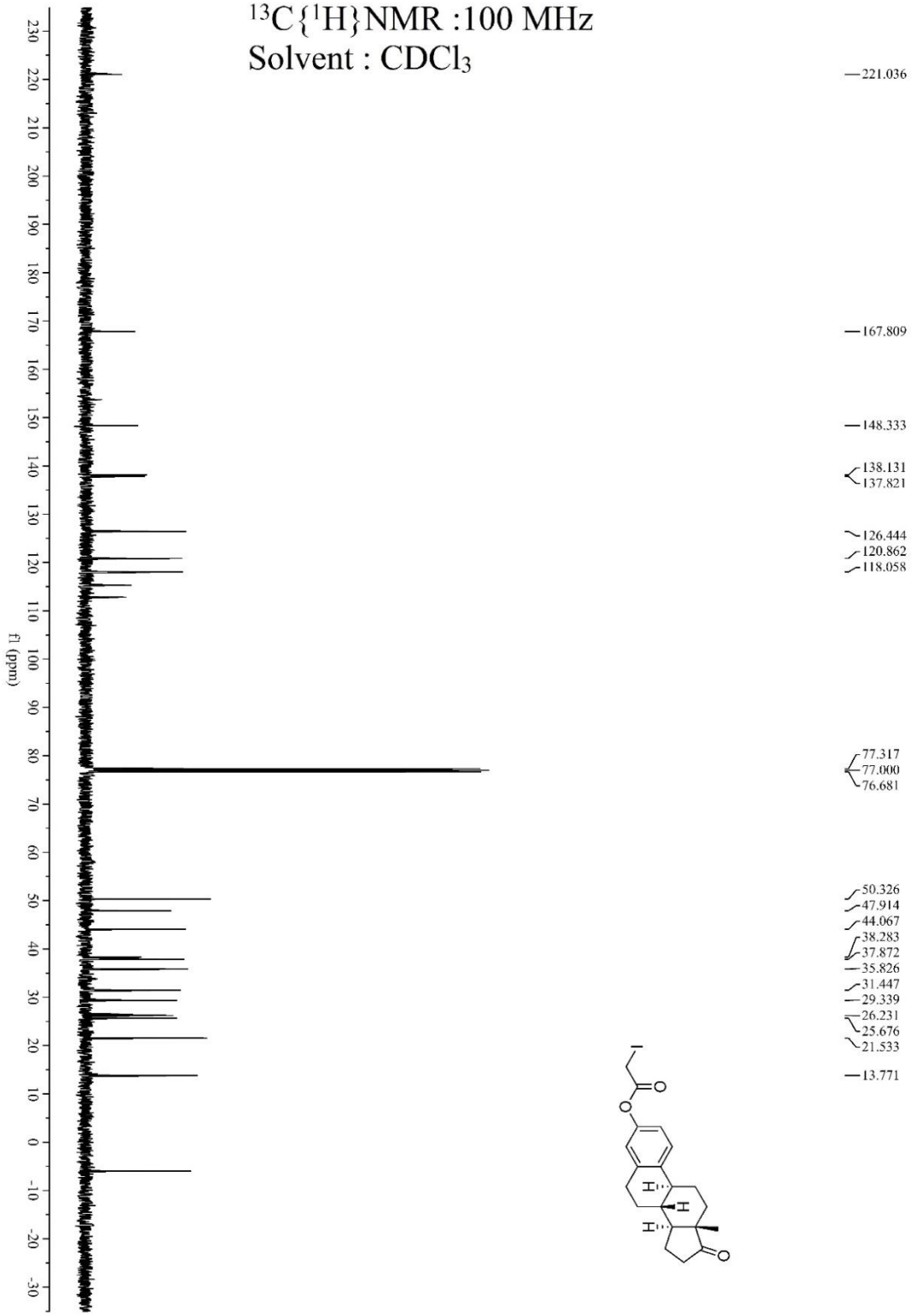



$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
168.205
139.162
138.262
129.240
122.951
77.318
77.000
76.683
75.684
56.722
55.875
51.193
49.961
42.153
40.475
39.565
37.541
36.807
36.538
31.846
31.789
28.882
27.278
25.382
24.318
21.208
21.079
20.982
19.280
18.965
12.239
12.017
-4.554

(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahyd

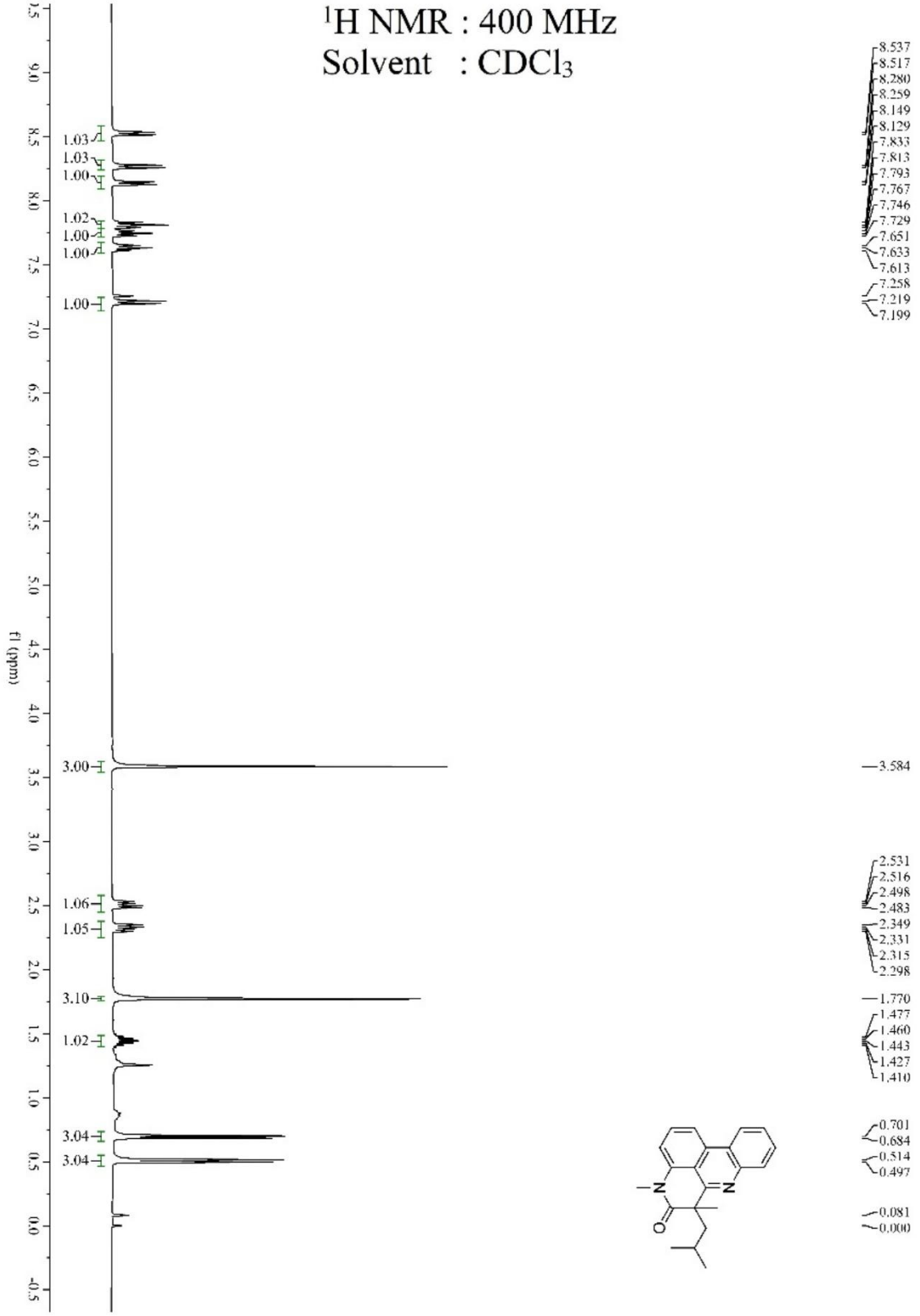
ro-6H- cyclopenta[*a*]phenanthren-3-yl-2-iodoacetate (2ad)

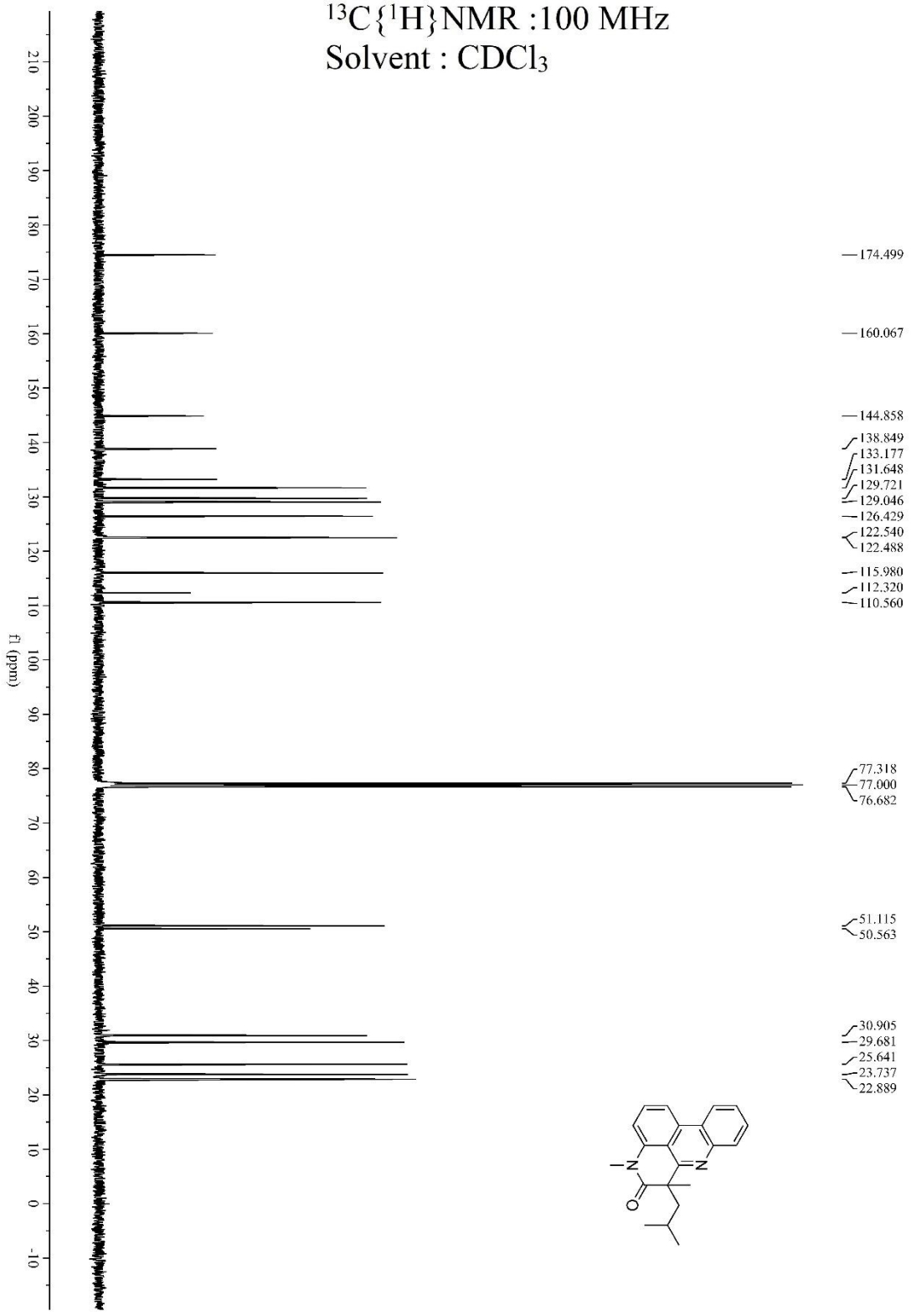



$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
221.036
167.809
148.333
138.131
137.821
126.444
120.862
118.058
77.317
77.000
76.681
50.326
47.914
44.067
38.283
37.872
35.826
31.447
29.339
26.231
25.676
21.533
13.771

6-Isobutyl-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one

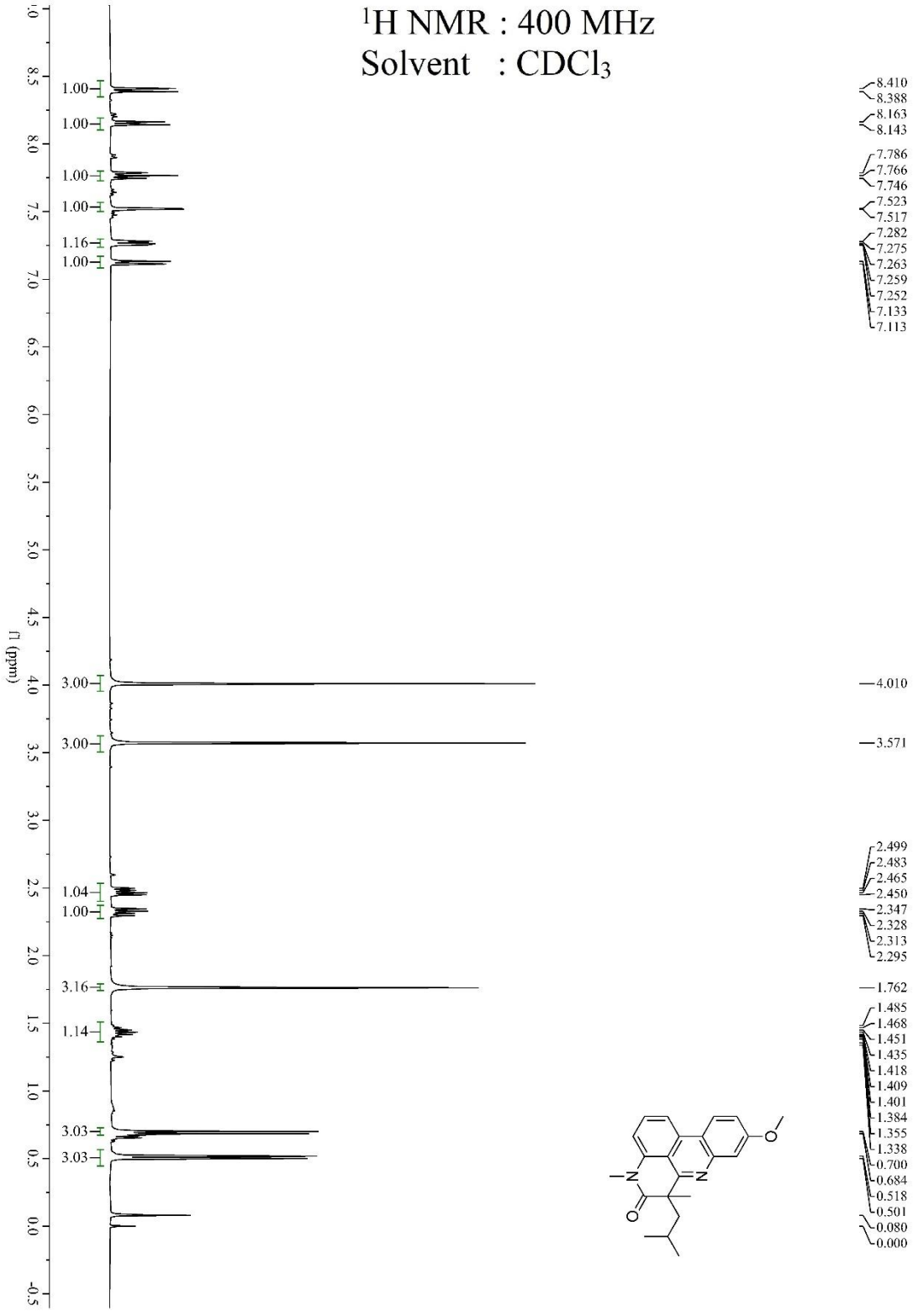
(3aa)

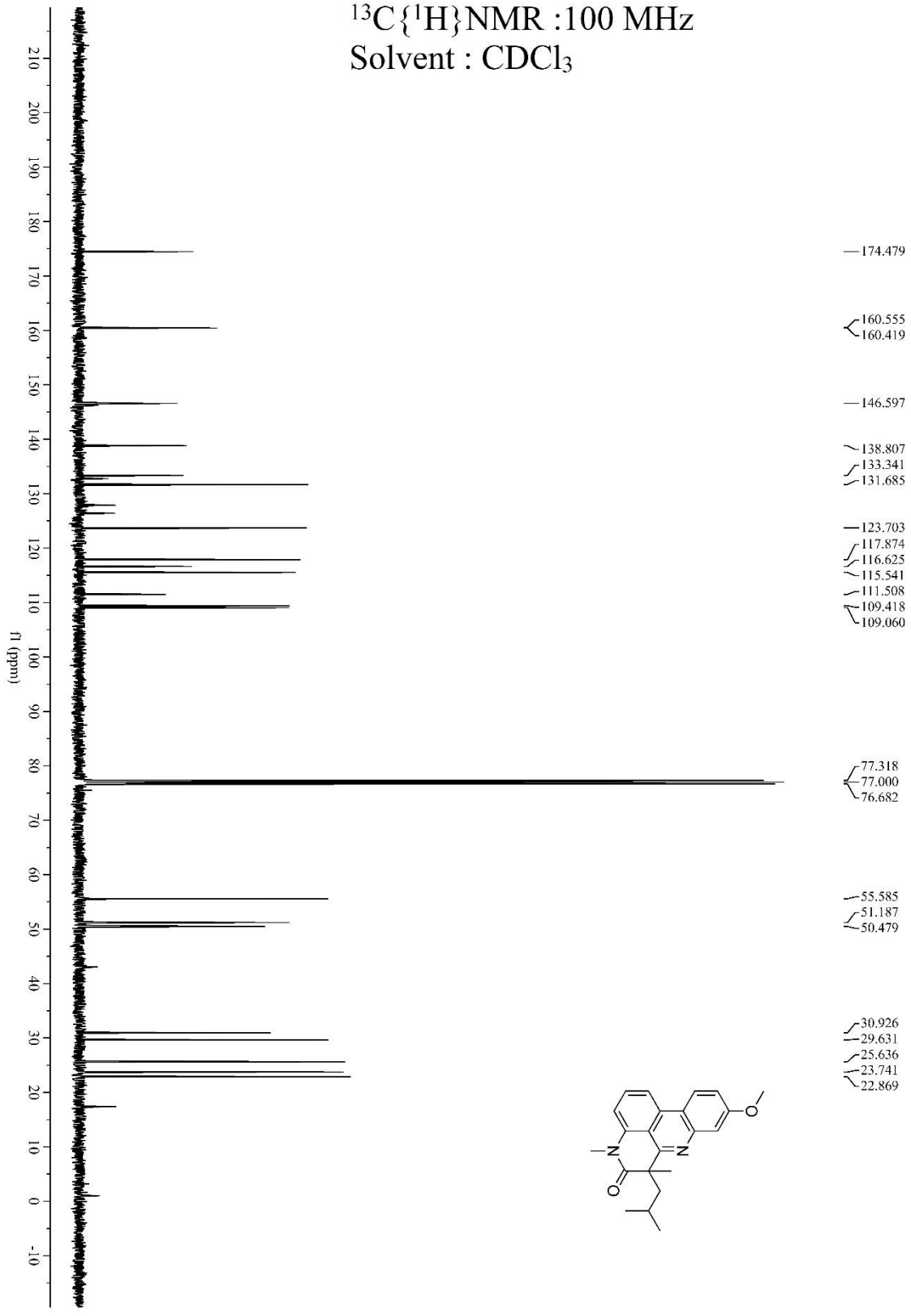



$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.499
160.067
144.858
138.849
133.177
131.648
129.721
129.046
126.429
122.540
122.488
115.980
112.320
110.560
77.318
77.000
76.682
51.115
50.563
30.905
29.681
25.641
23.737
22.889

6-Isobutyl-9-methoxy-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridi

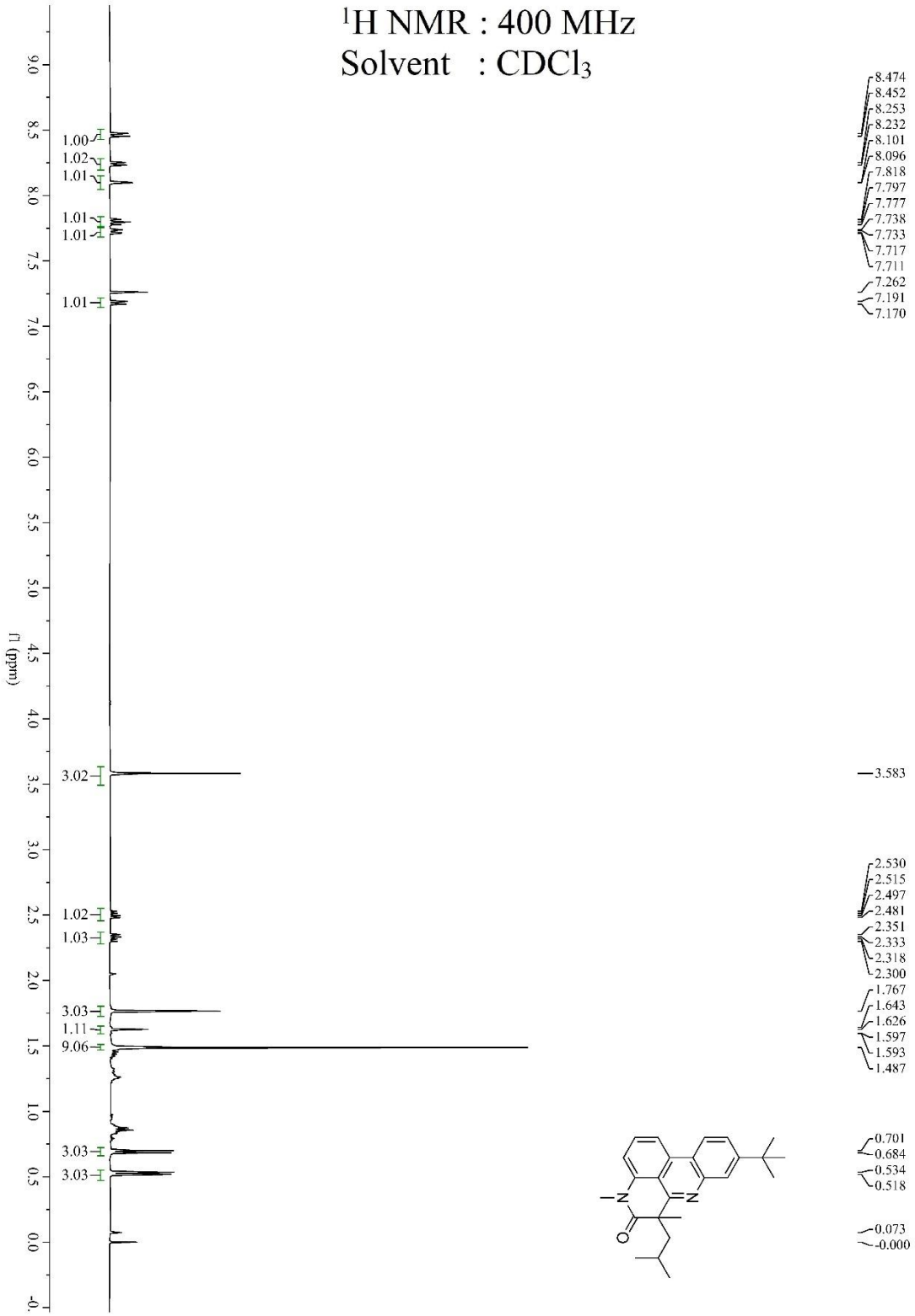
n-5(6*H*)-one (3ba)

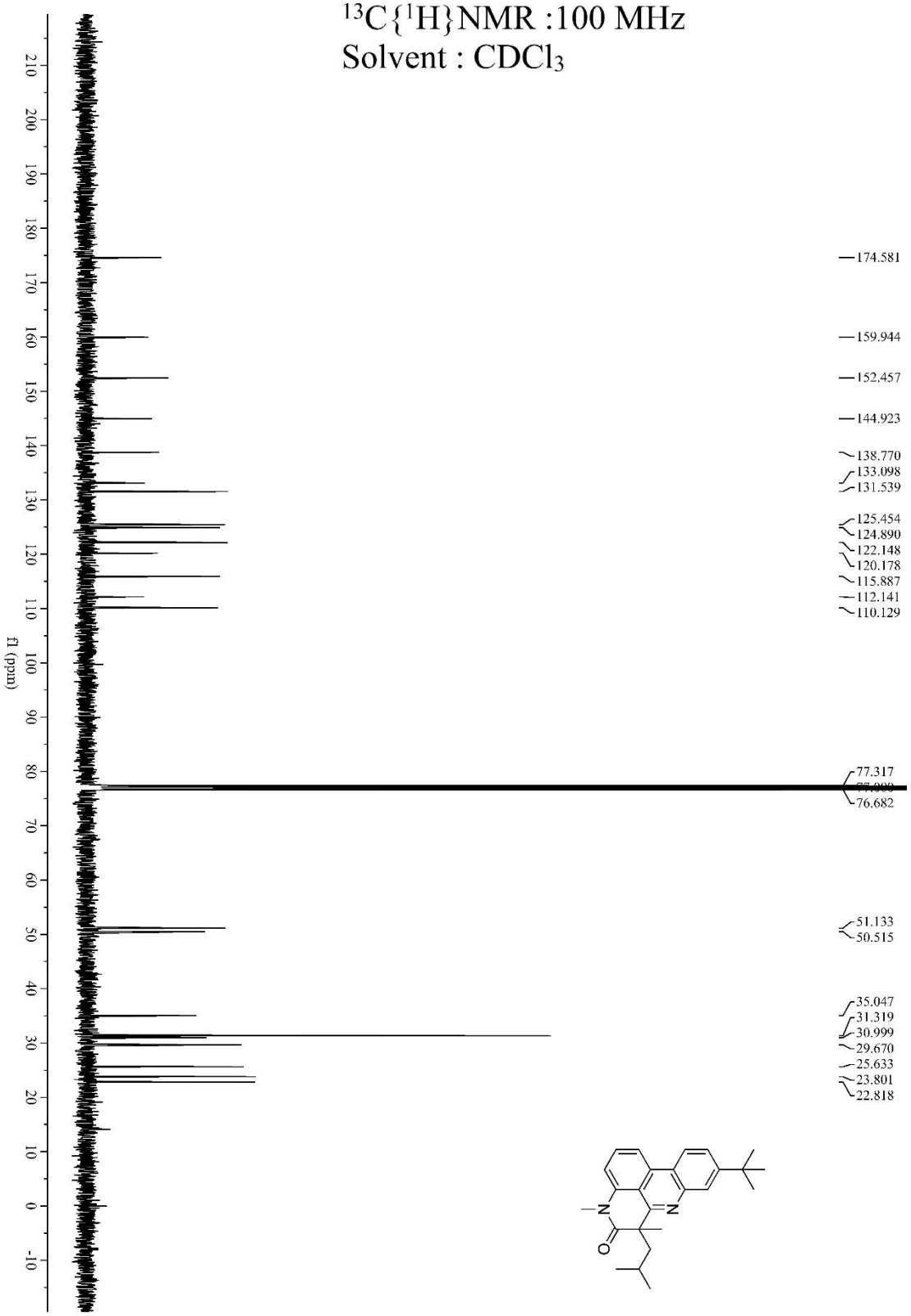



$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.479
160.555
160.419
146.597
138.807
133.341
131.685
123.703
117.874
116.625
115.541
111.508
109.418
109.060
77.318
77.000
76.682
55.585
51.187
50.479
30.926
29.631
25.636
23.741
22.869

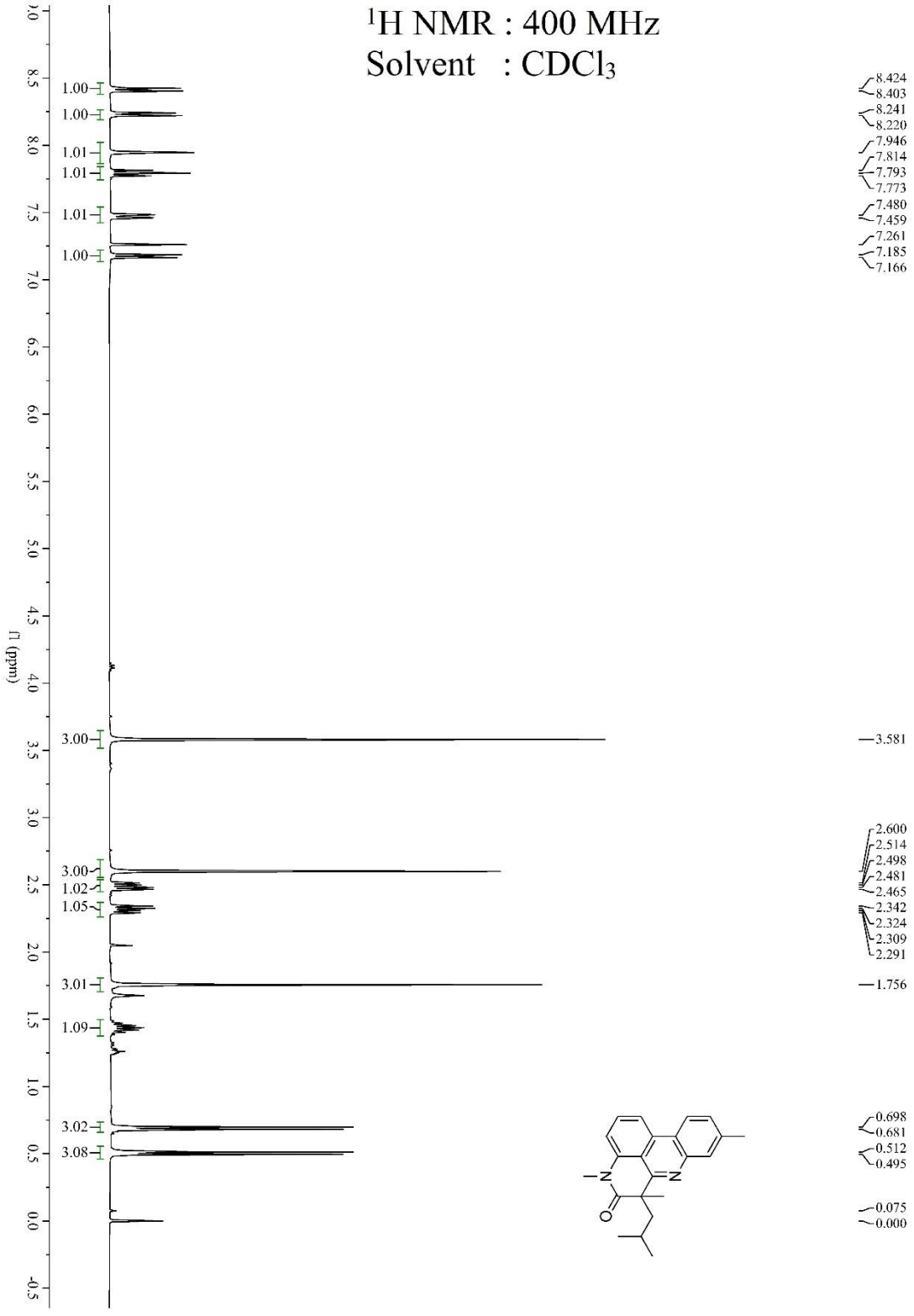
9-(*Tert*-butyl)-6-isobutyl-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthri

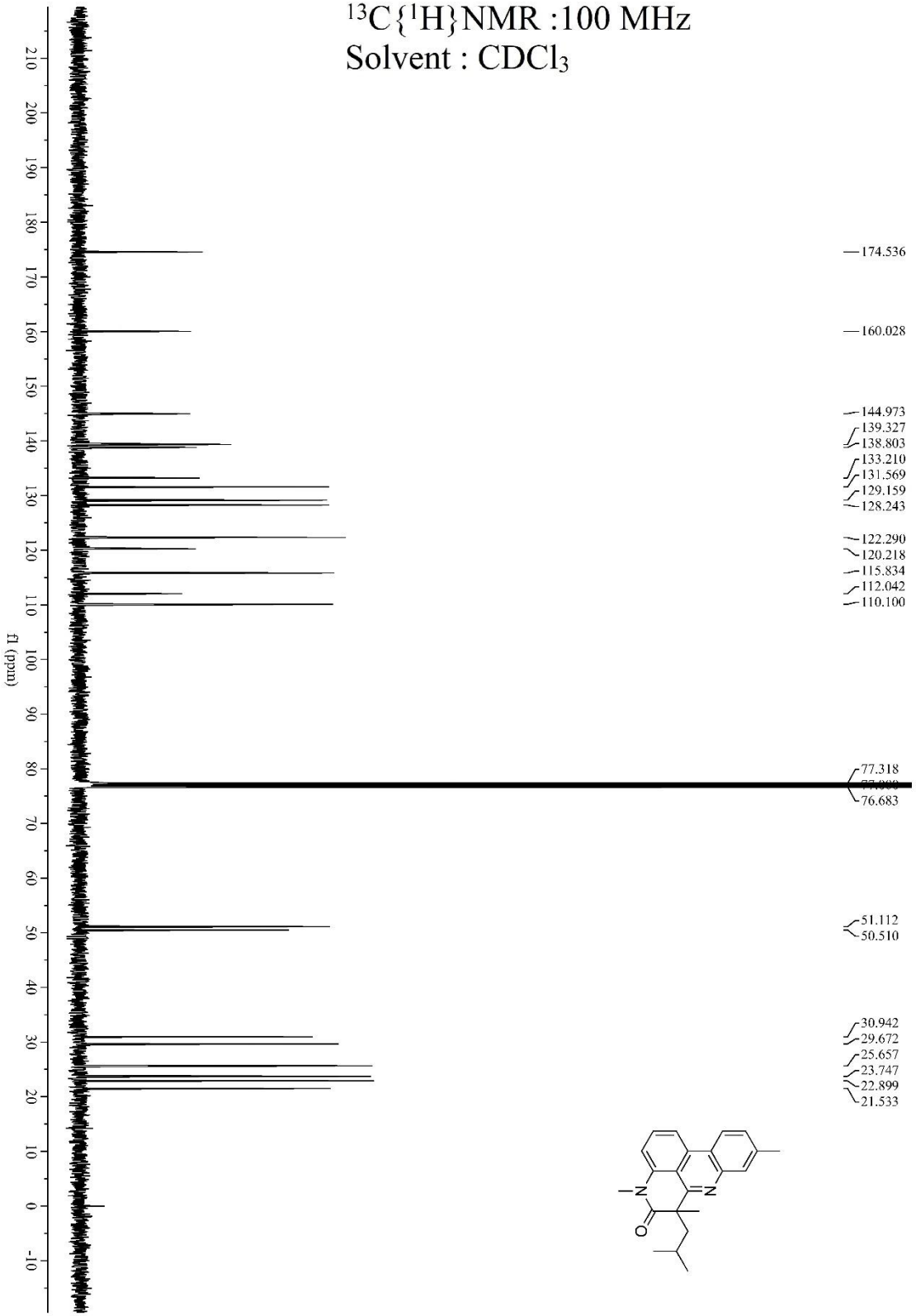
din-5(6*H*)- one (3ca)



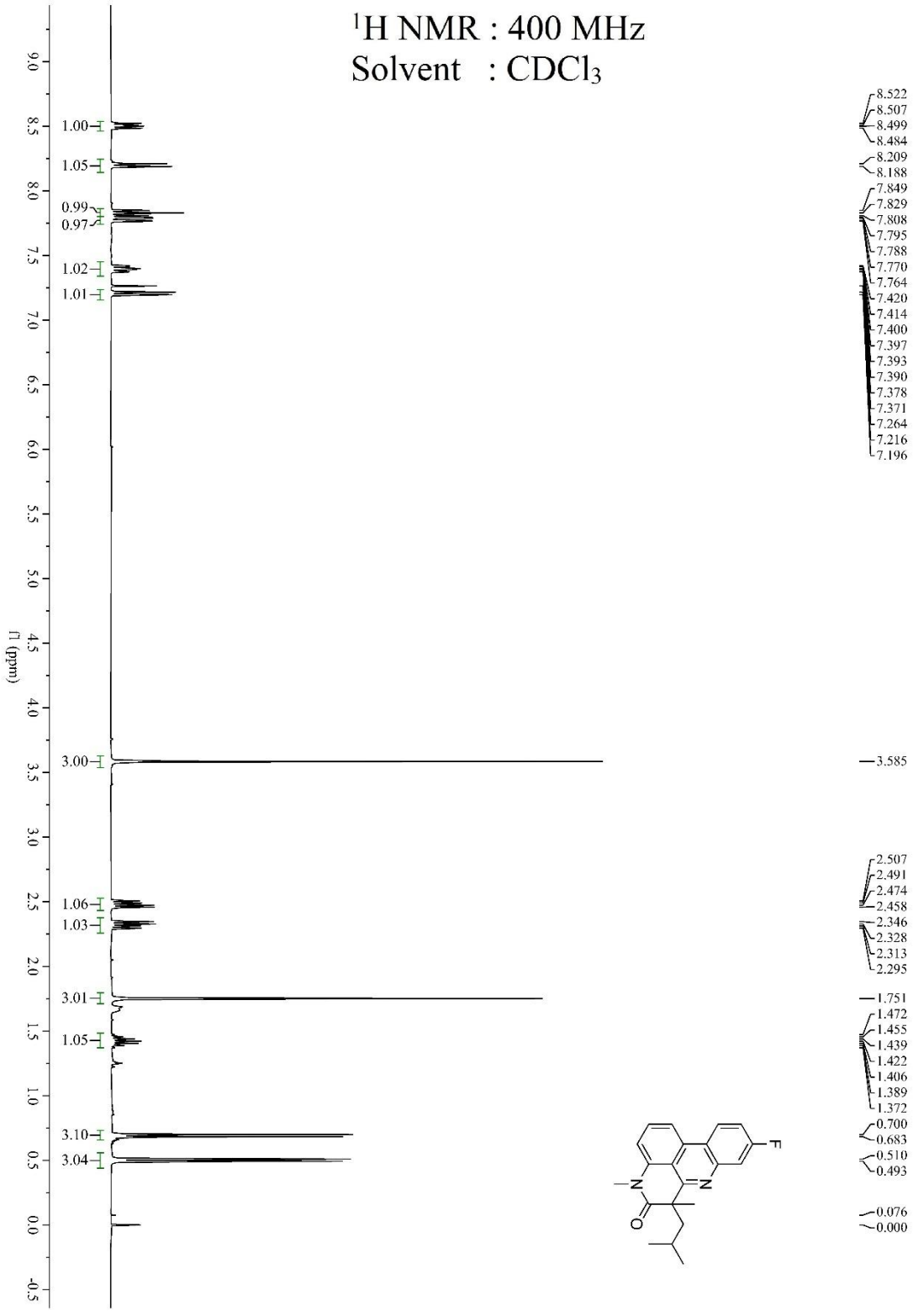

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.581
159.944
152.457
144.923
138.770
133.098
131.539
125.454
124.890
122.148
120.178
115.887
112.141
110.129
77.317
76.682
51.133
50.515
35.047
31.319
30.999
29.670
25.633
23.801
22.818
N
N
O

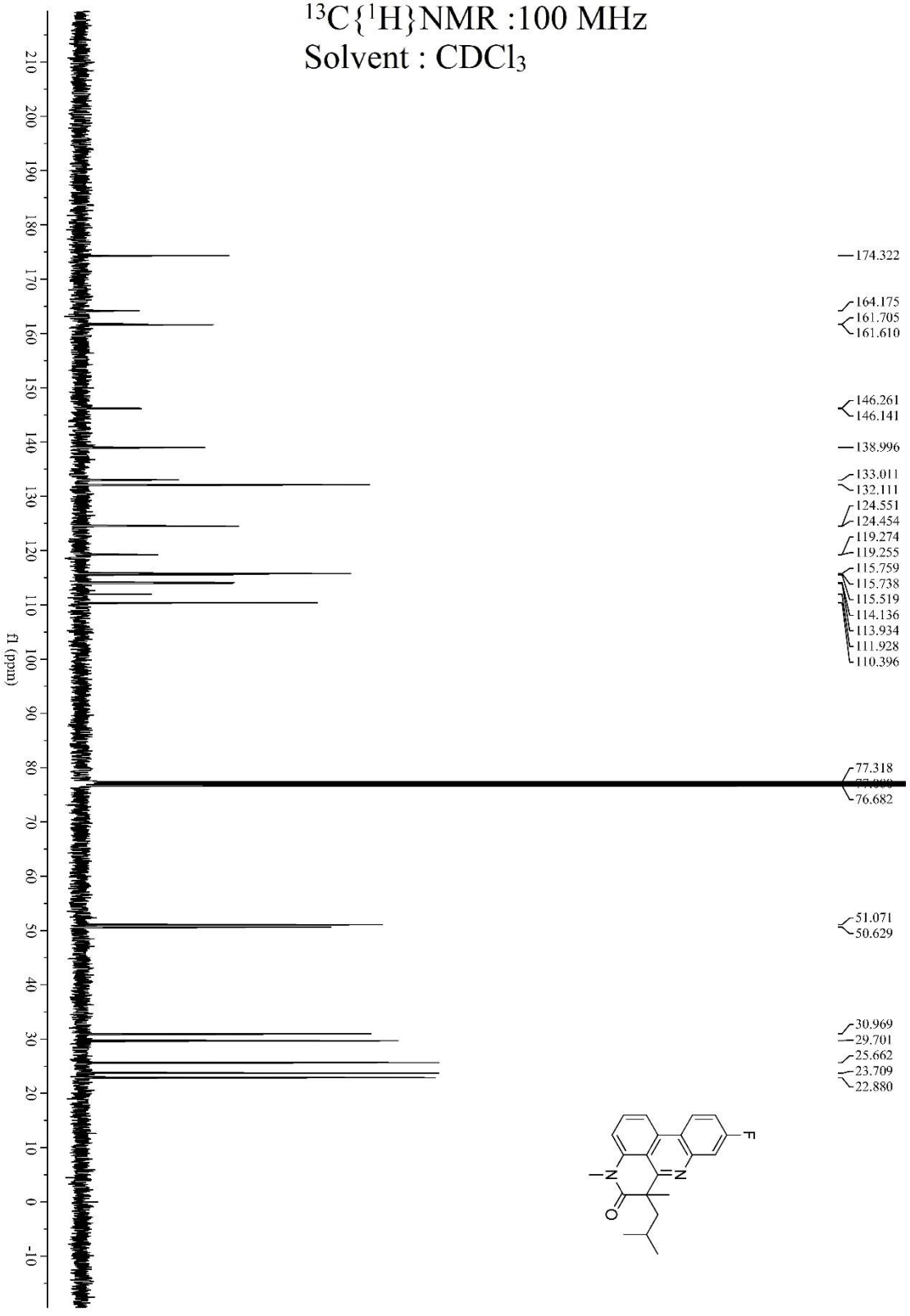
6-Isobutyl-4,6,9-trimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3da)




$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.536
160.028
144.973
139.327
138.803
133.210
131.569
129.159
128.243
122.290
120.218
115.834
112.042
110.100
77.318
76.683
51.112
50.510
30.942
29.672
25.657
23.747
22.899
21.533
N
N
O

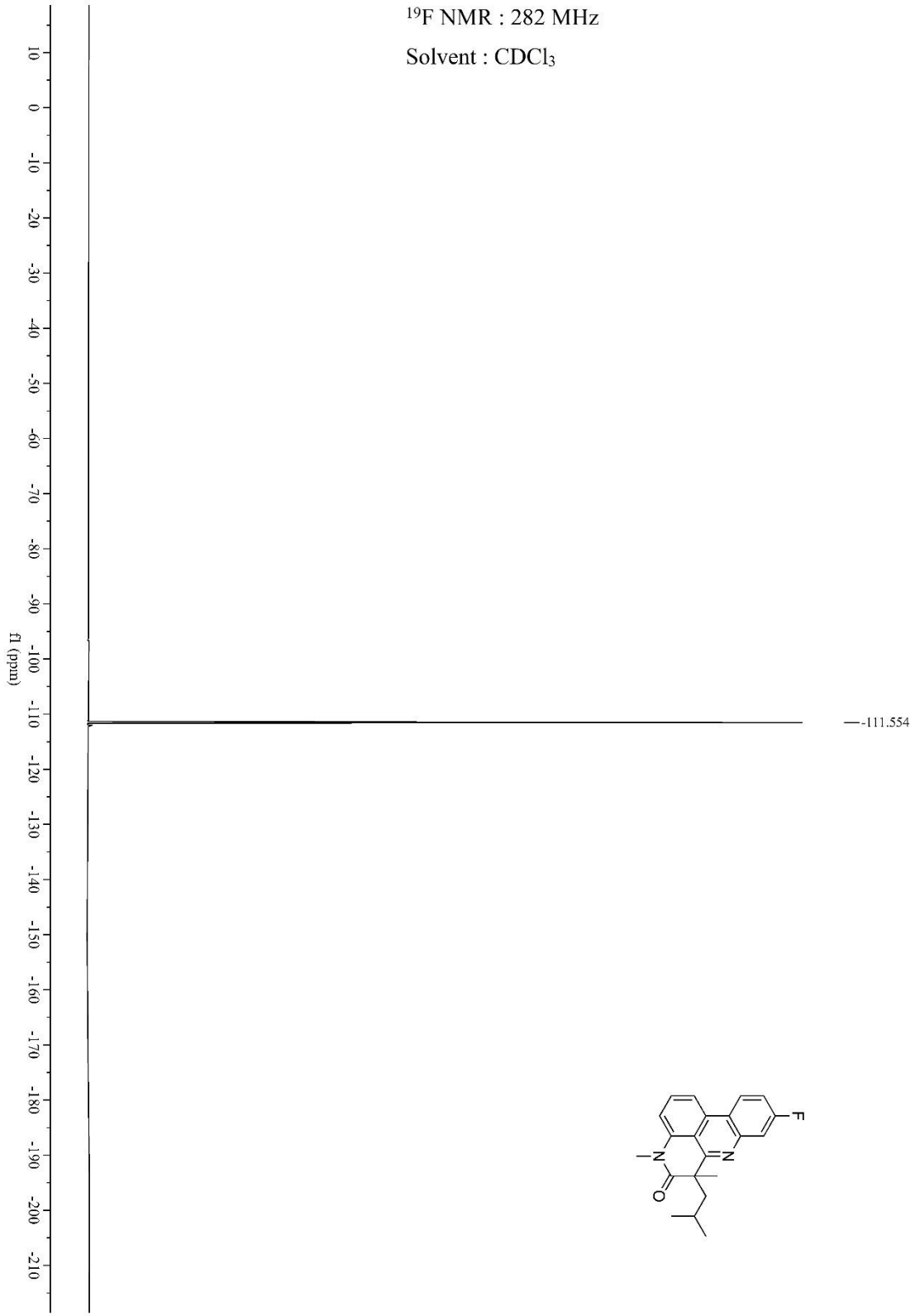
9-Fluoro-6-isobutyl-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ea)



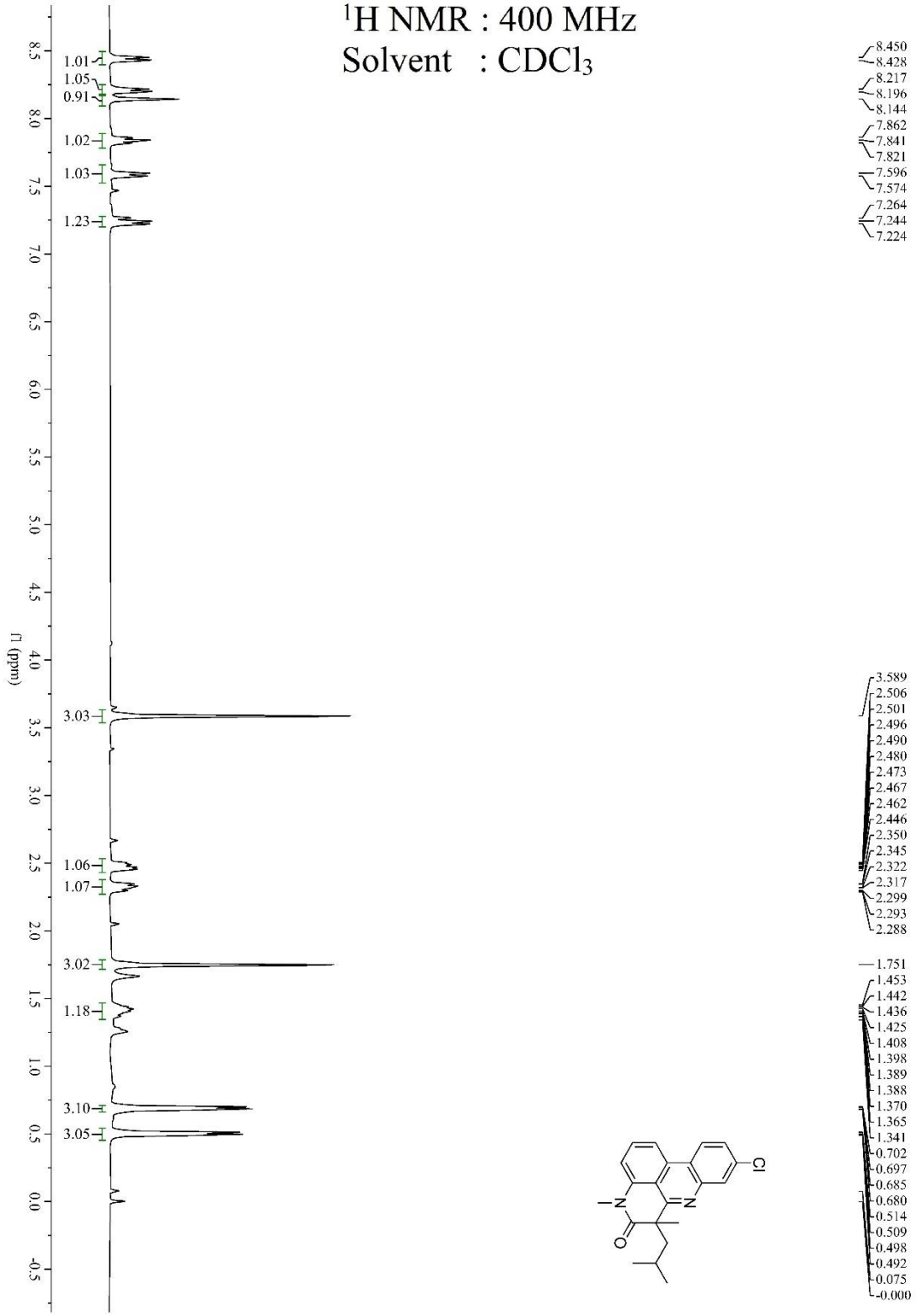

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.322
164.175
161.705
161.610
146.261
146.141
138.996
133.011
132.111
124.551
124.454
119.274
119.255
115.759
115.738
115.519
114.136
113.934
111.928
110.396
77.318
76.682
51.071
50.629
30.969
29.701
25.662
23.709
22.880
F
N
N
O

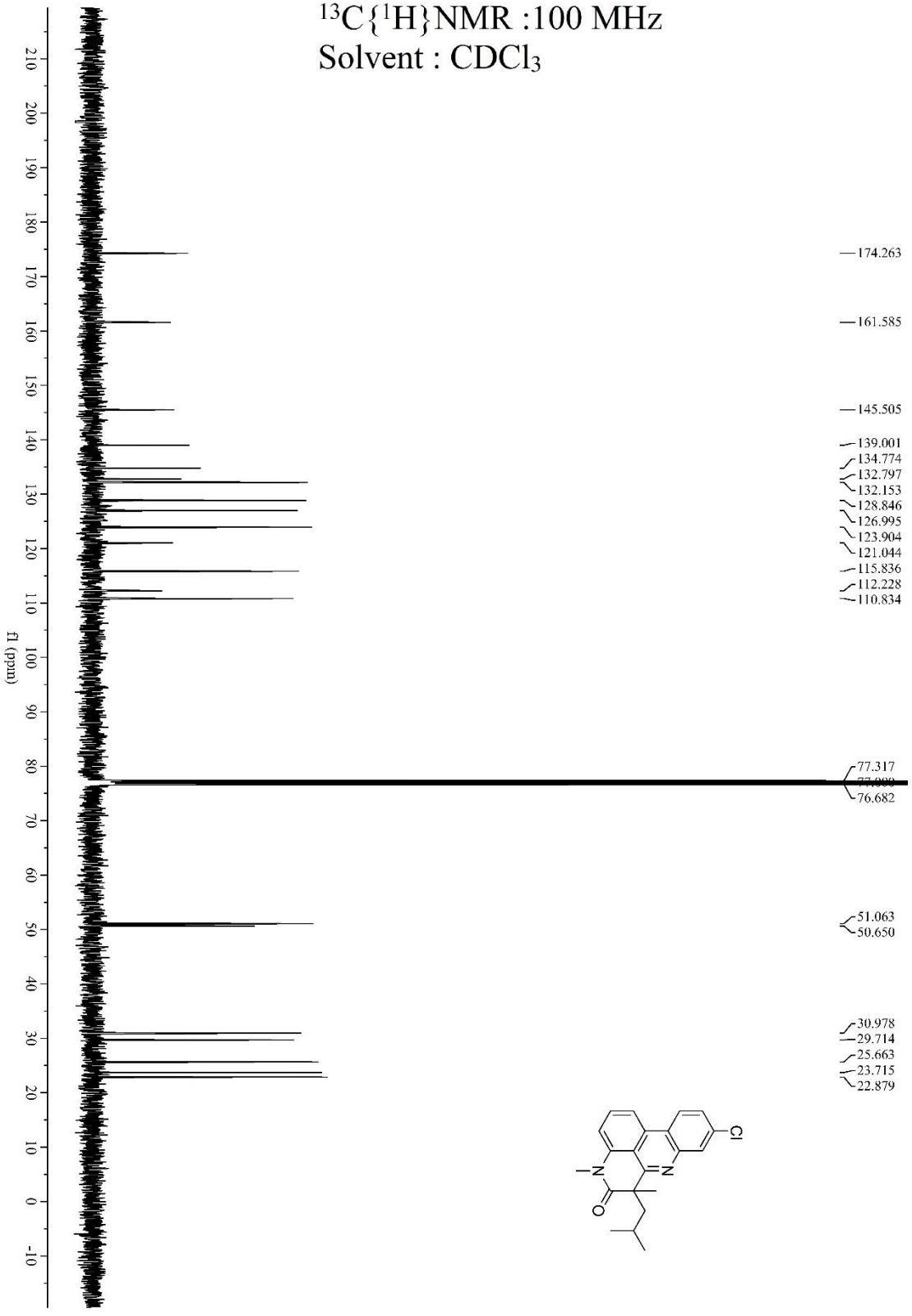
^{19}F NMR : 282 MHz

Solvent : $CDCl_3$

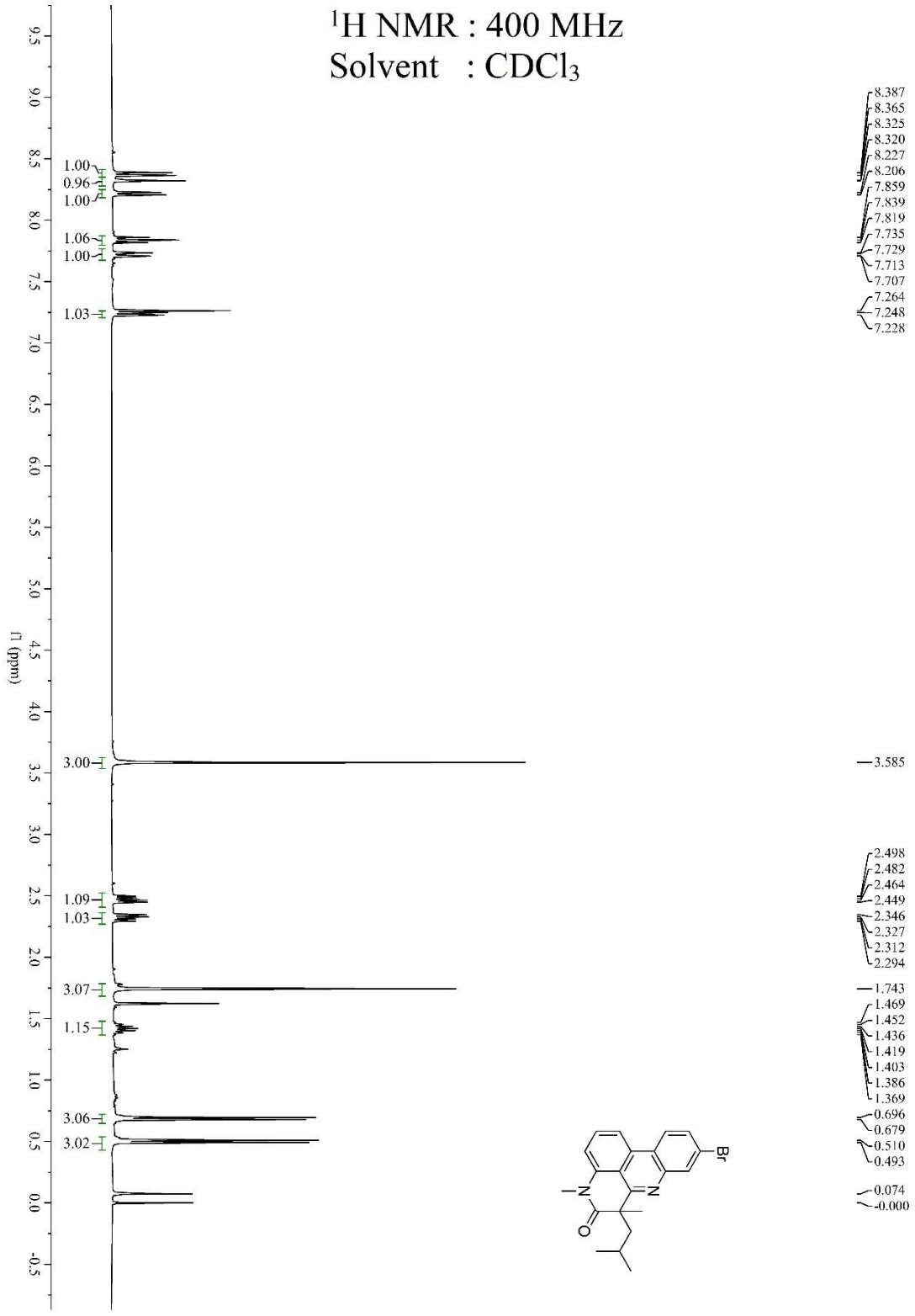


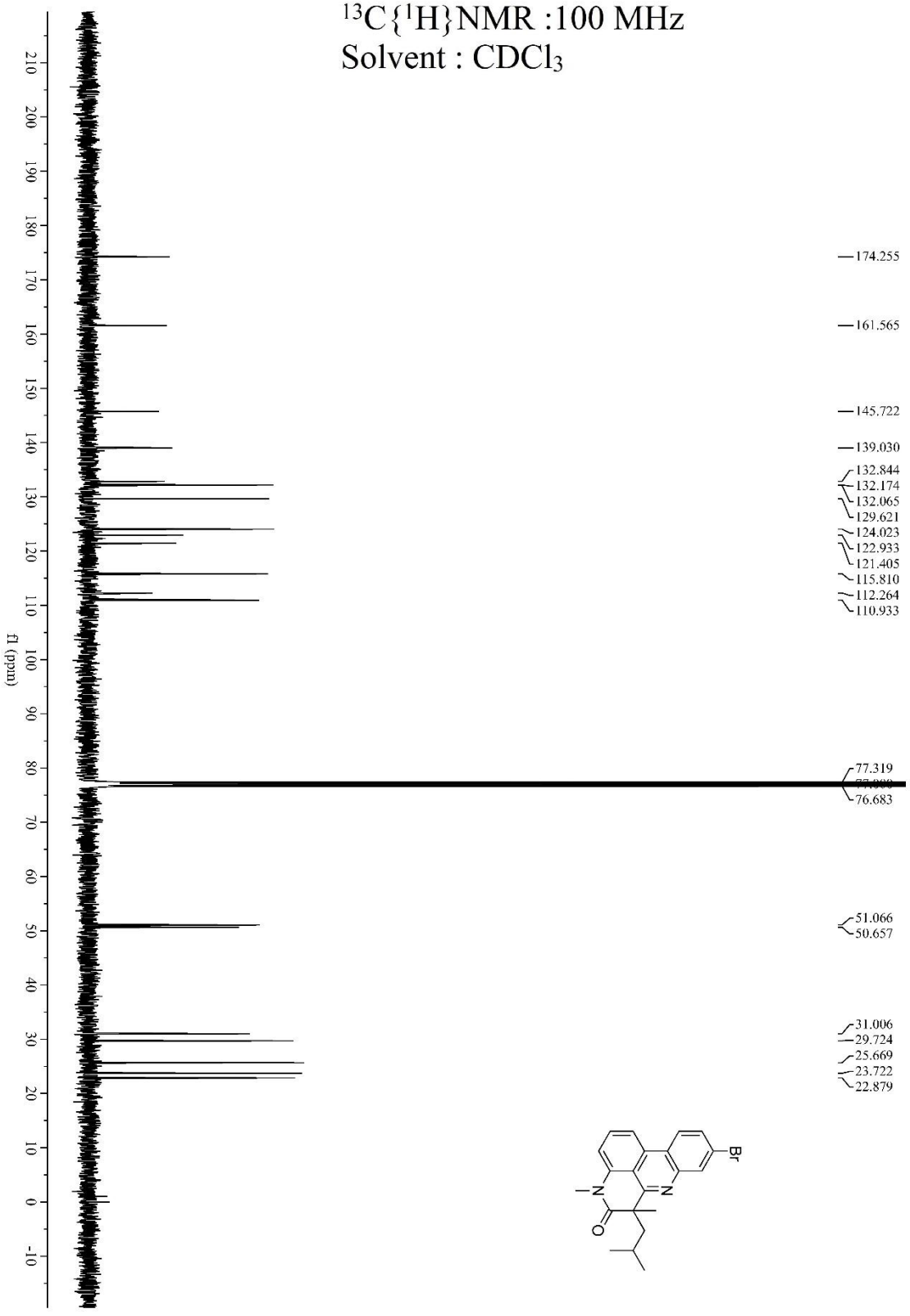
9-Chloro-6-isobutyl-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3fa)




$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
174.263
161.585
145.505
139.001
134.774
132.797
132.153
128.846
126.995
123.904
121.044
115.836
112.228
110.834
77.317
76.682
51.063
50.650
30.978
29.714
25.663
23.715
22.879
Cl
N
N
O

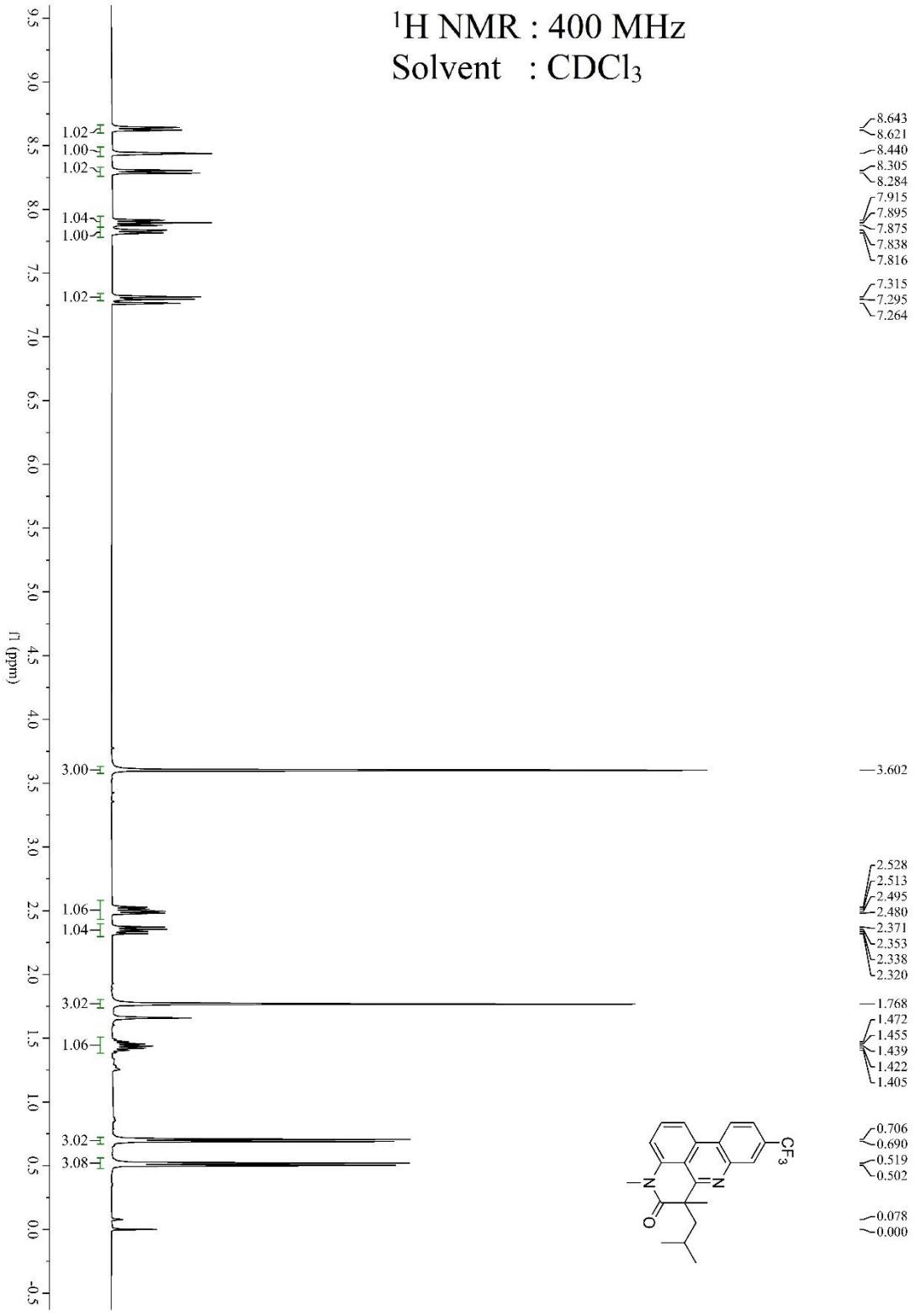
9-Bromo-6-isobutyl-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ga)

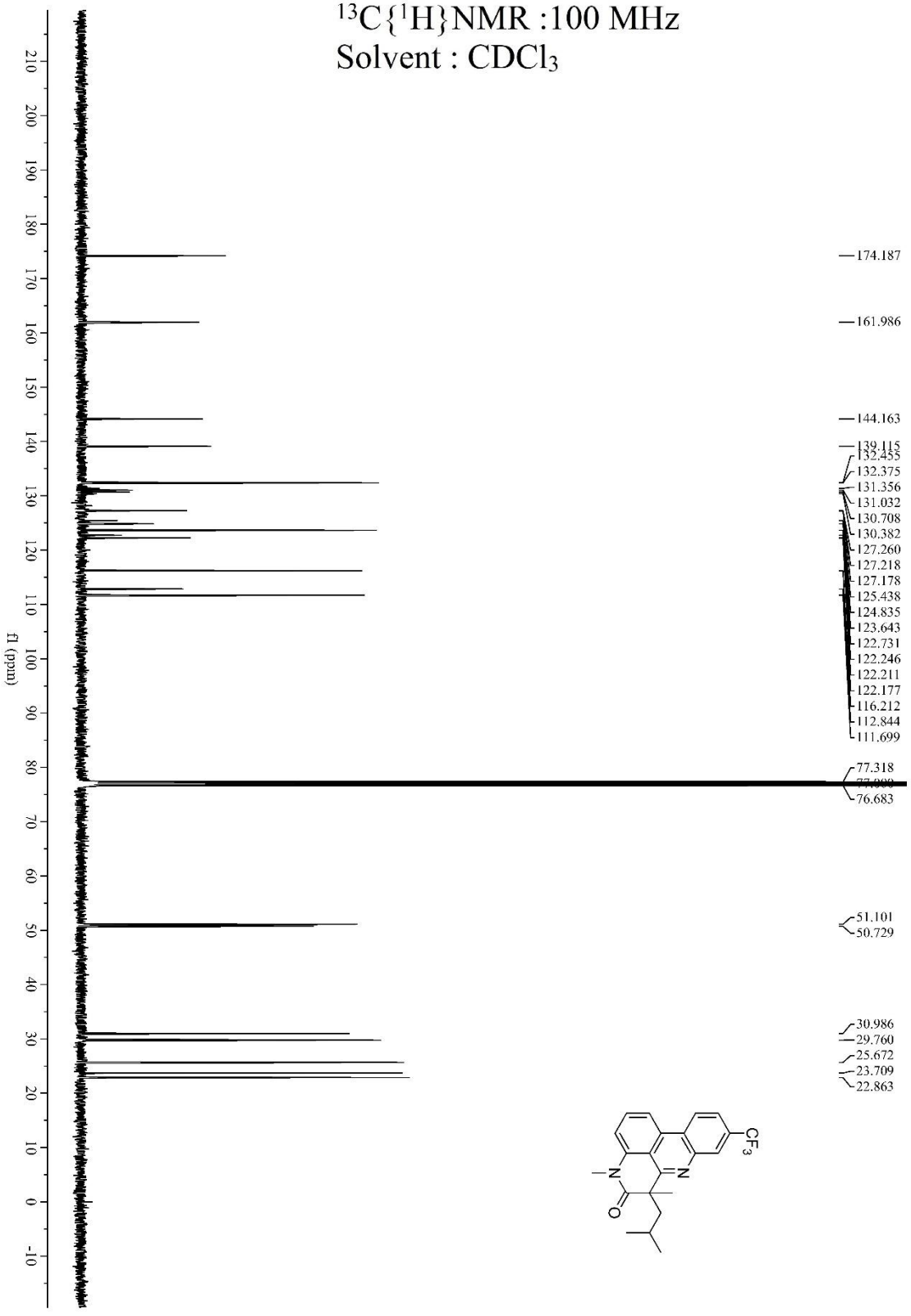



$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.255
161.565
145.722
139.030
132.844
132.174
132.065
129.621
124.023
122.933
121.405
115.810
112.264
110.933
77.319
76.683
51.066
50.657
31.006
29.724
25.669
23.722
22.879
Br
N
N
O

6-Isobutyl-4,6-dimethyl-9-(trifluoromethyl)-4*H*-pyrido[4,3,2-*gh*]phen

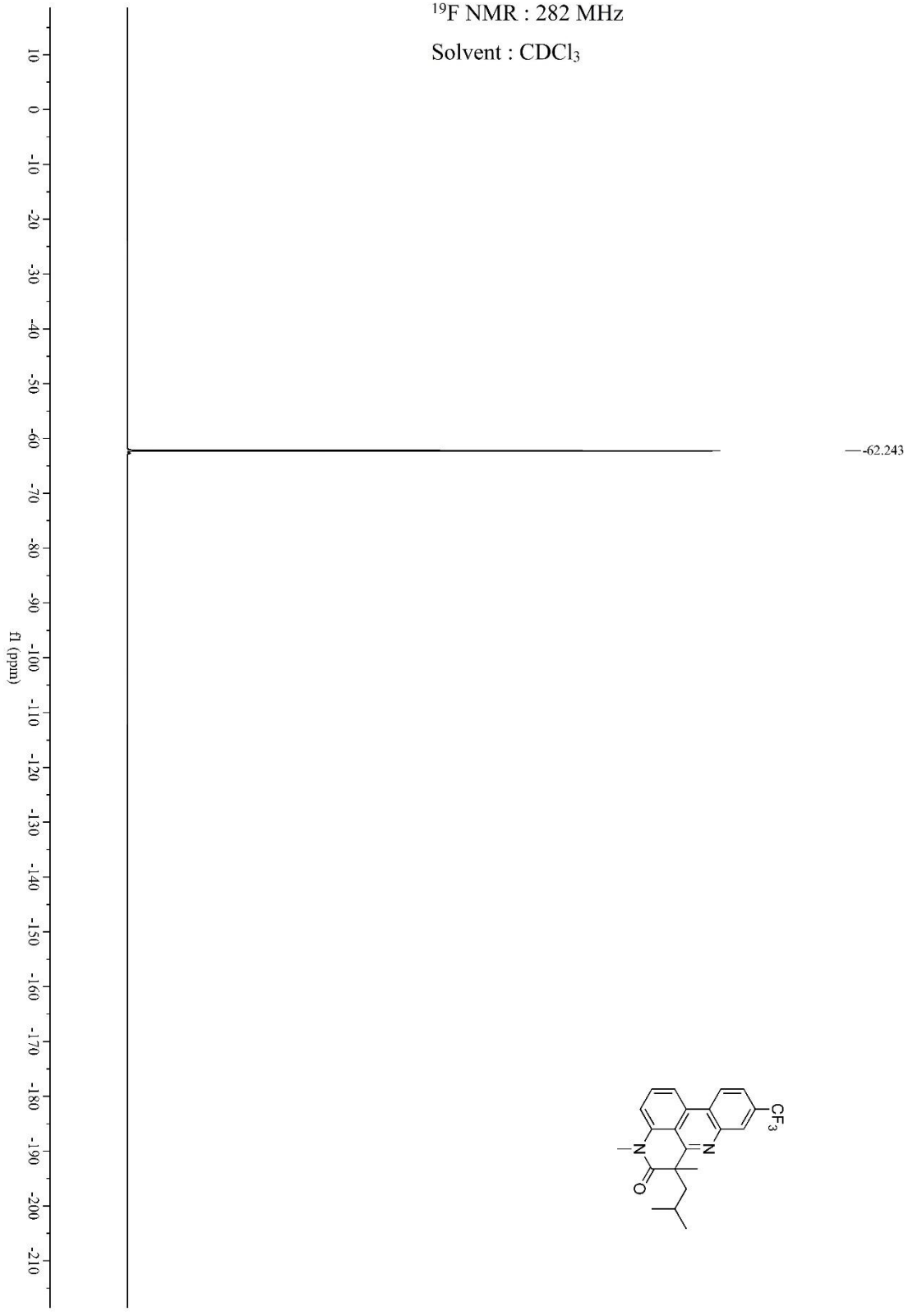
anthridin- 5(6*H*)-one (3ha)



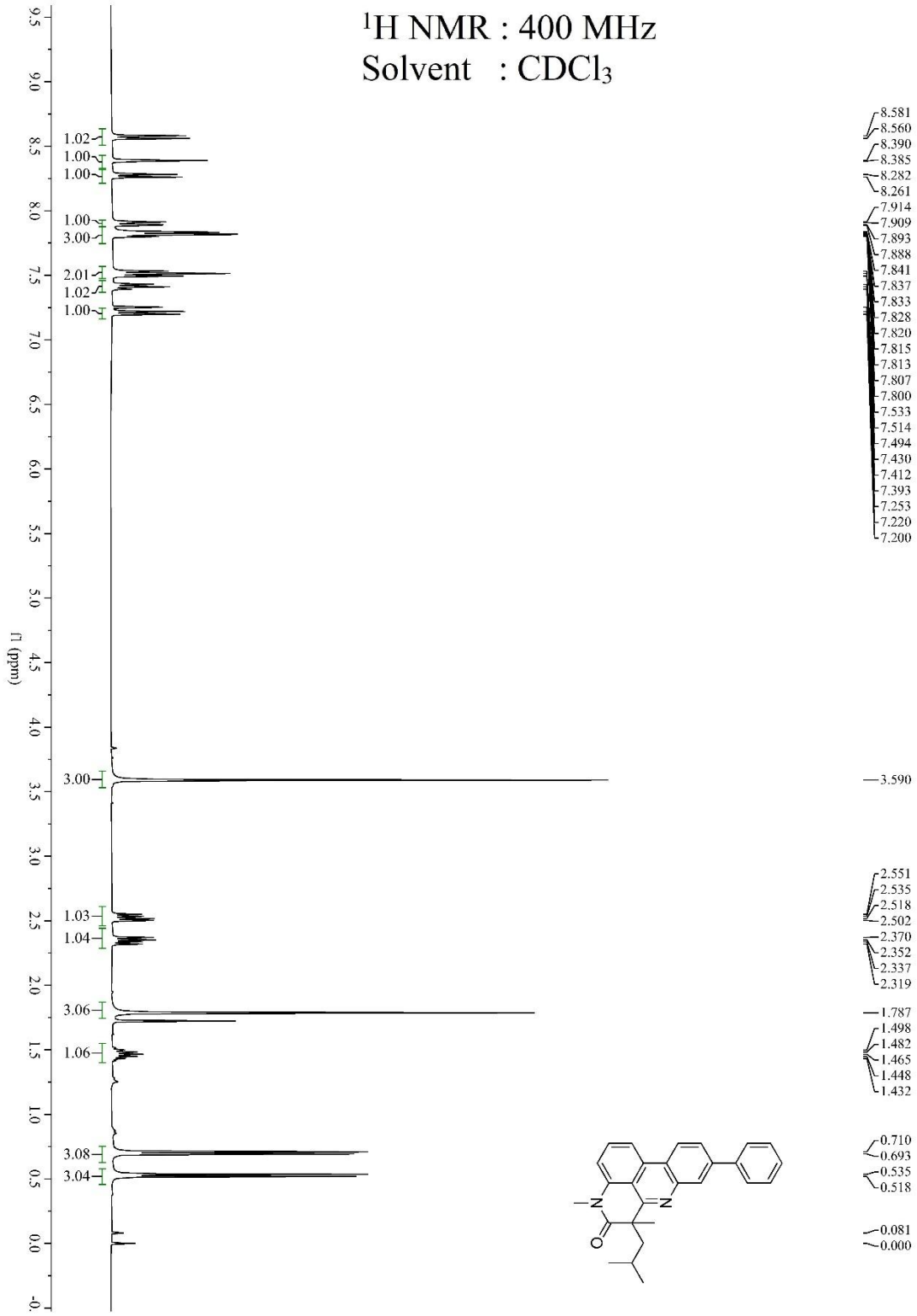

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.187
161.986
144.163
139.115
132.455
132.375
131.356
131.032
130.708
130.382
127.260
127.218
127.178
125.438
124.835
123.643
122.731
122.246
122.211
122.177
116.212
112.844
111.699
77.318
76.683
51.101
50.729
30.986
29.760
25.672
23.709
22.863
CF3
N
N
O

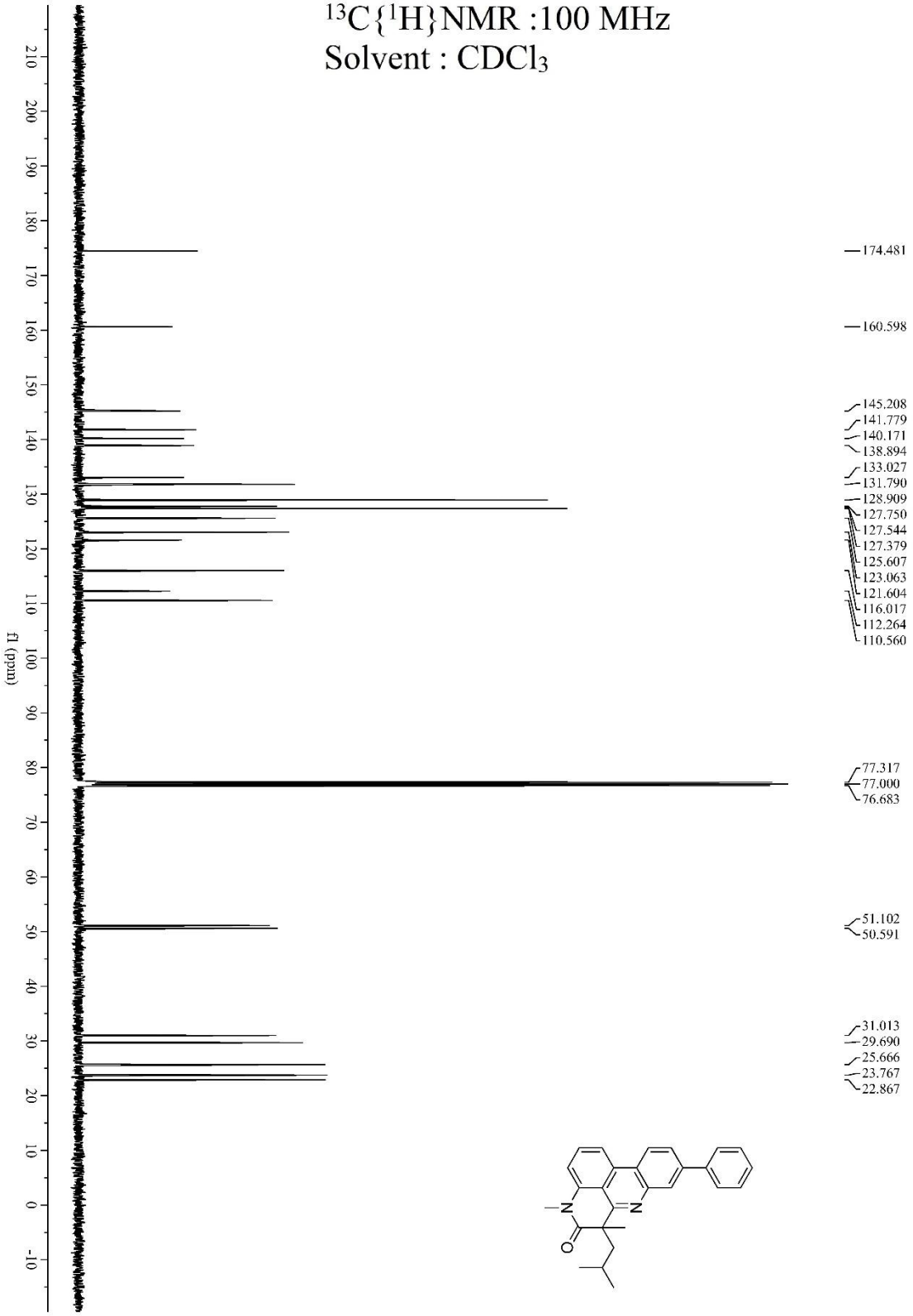
^{19}F NMR : 282 MHz

Solvent : $CDCl_3$

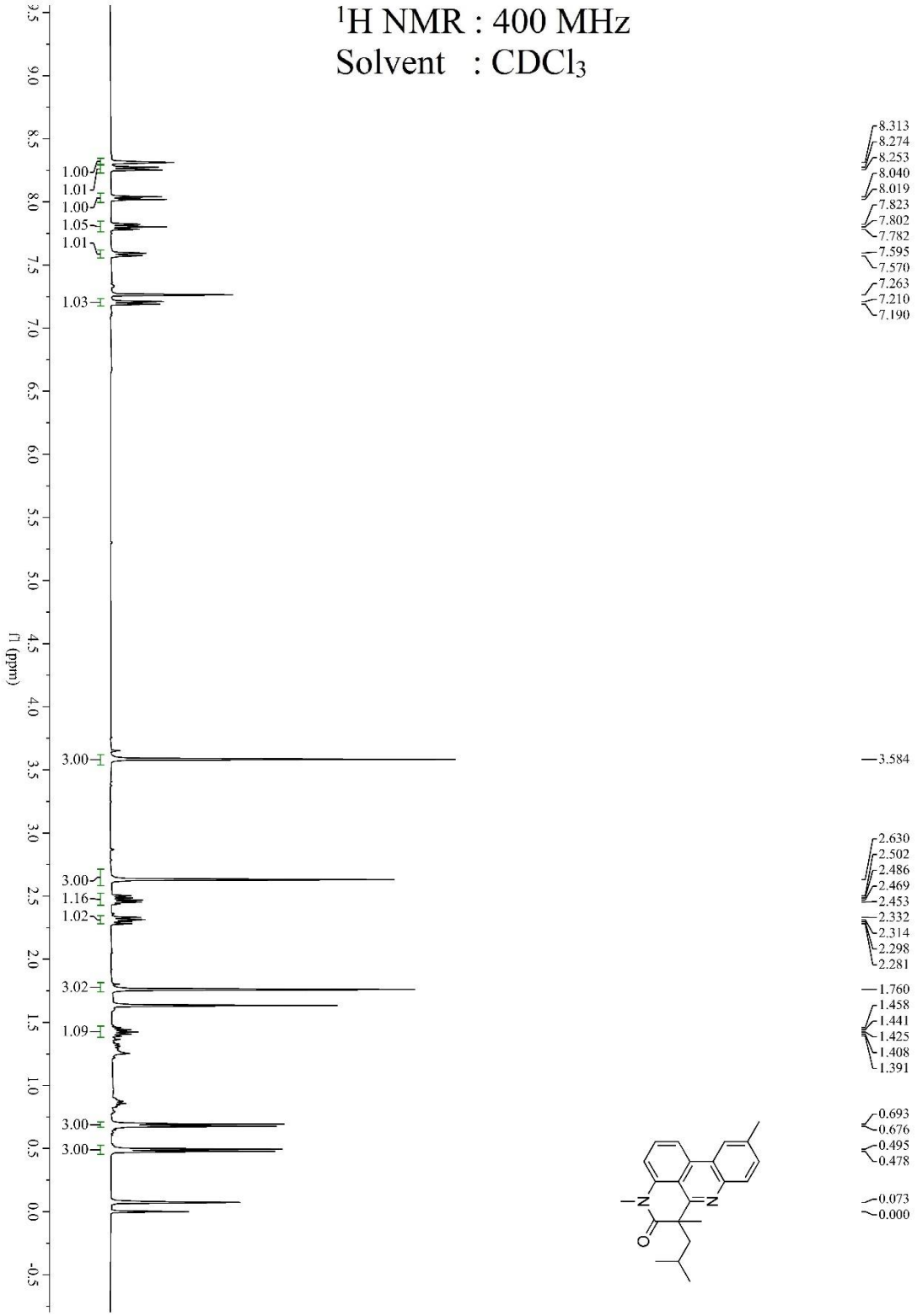


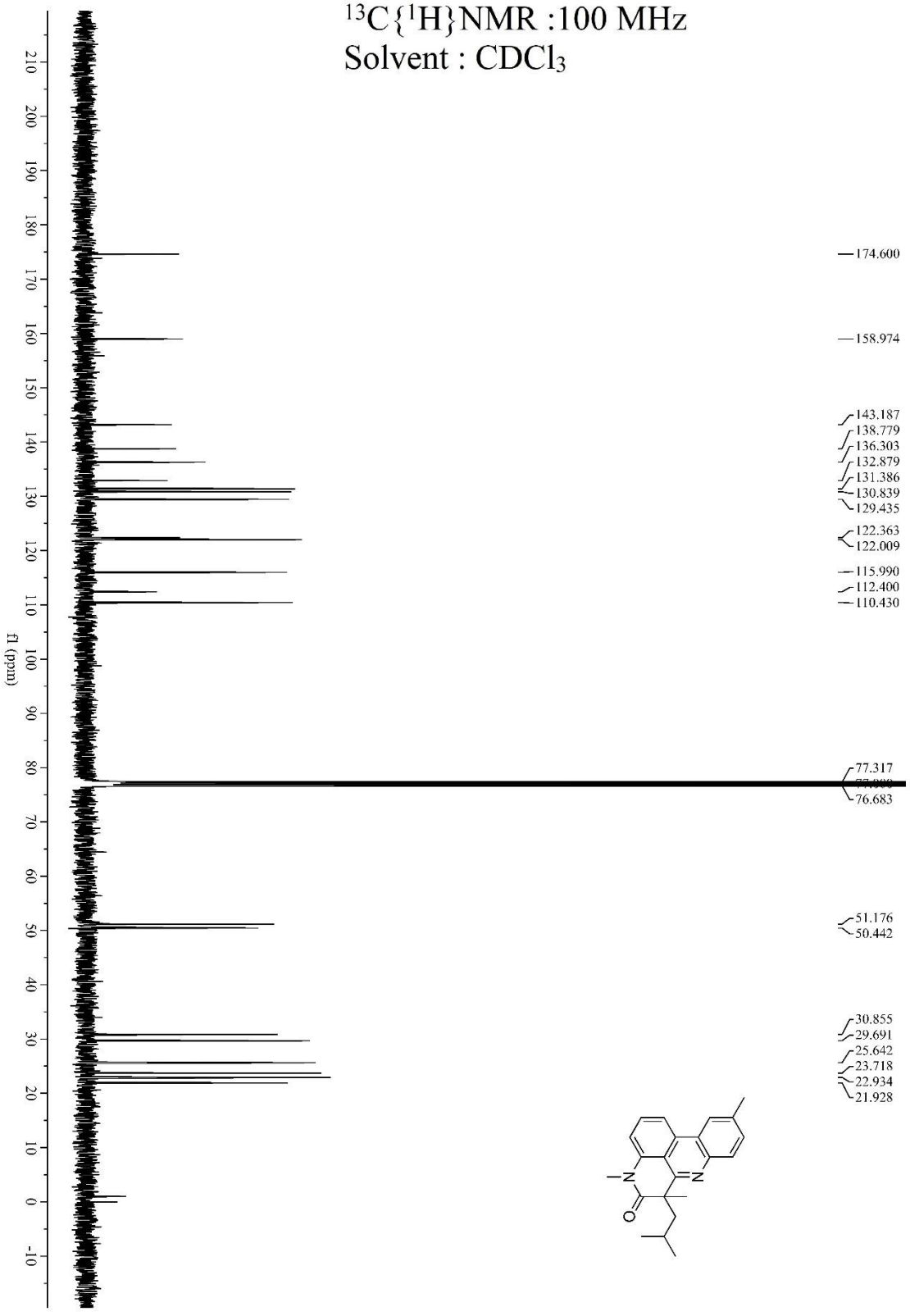
6-Isobutyl-4,6-dimethyl-9-phenyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ia)



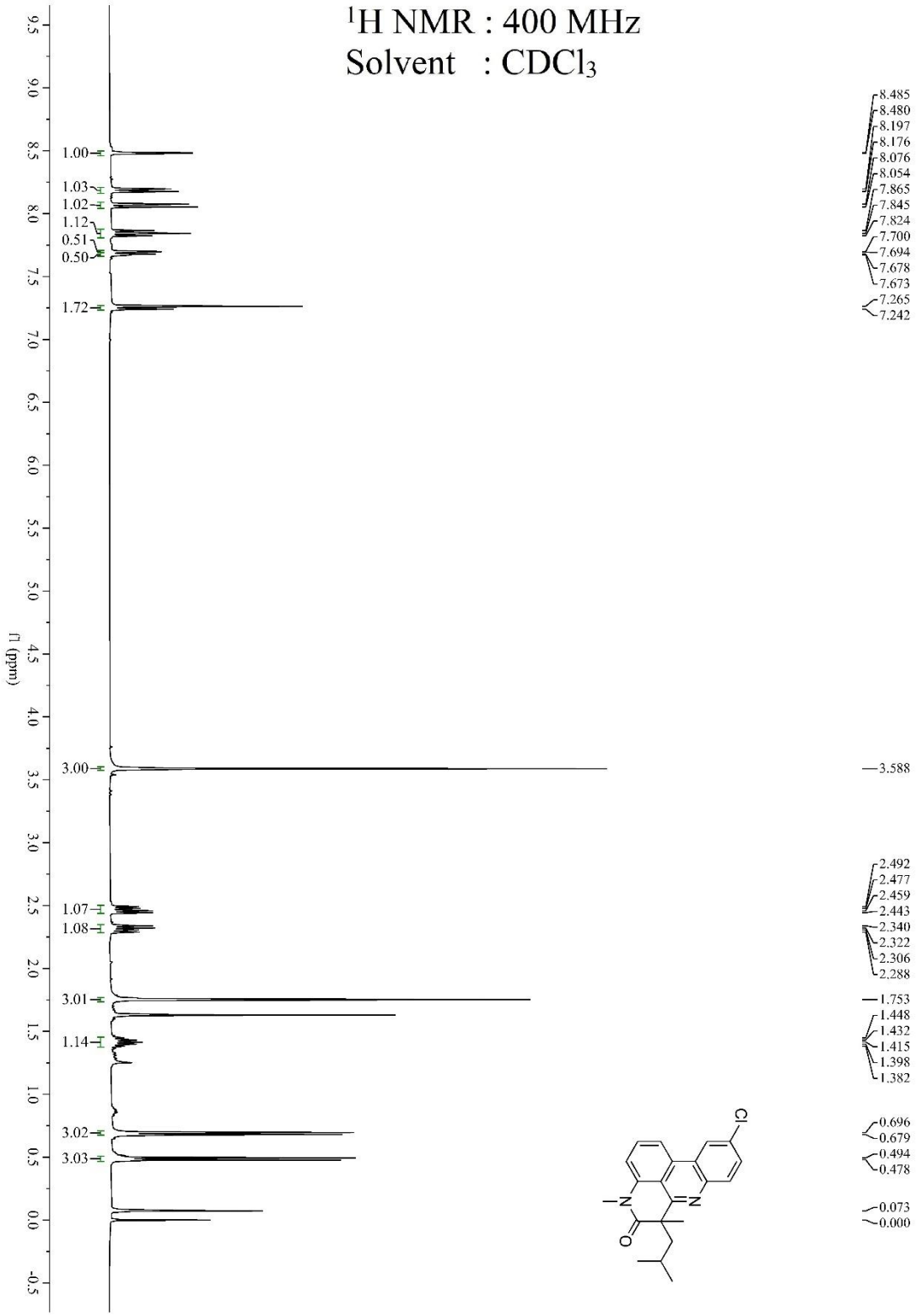

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.481
160.598
145.208
141.779
140.171
138.894
133.027
131.790
128.909
127.750
127.544
127.379
125.607
123.063
121.604
116.017
112.264
110.560
77.317
77.000
76.683
51.102
50.591
31.013
29.690
25.666
23.767
22.867

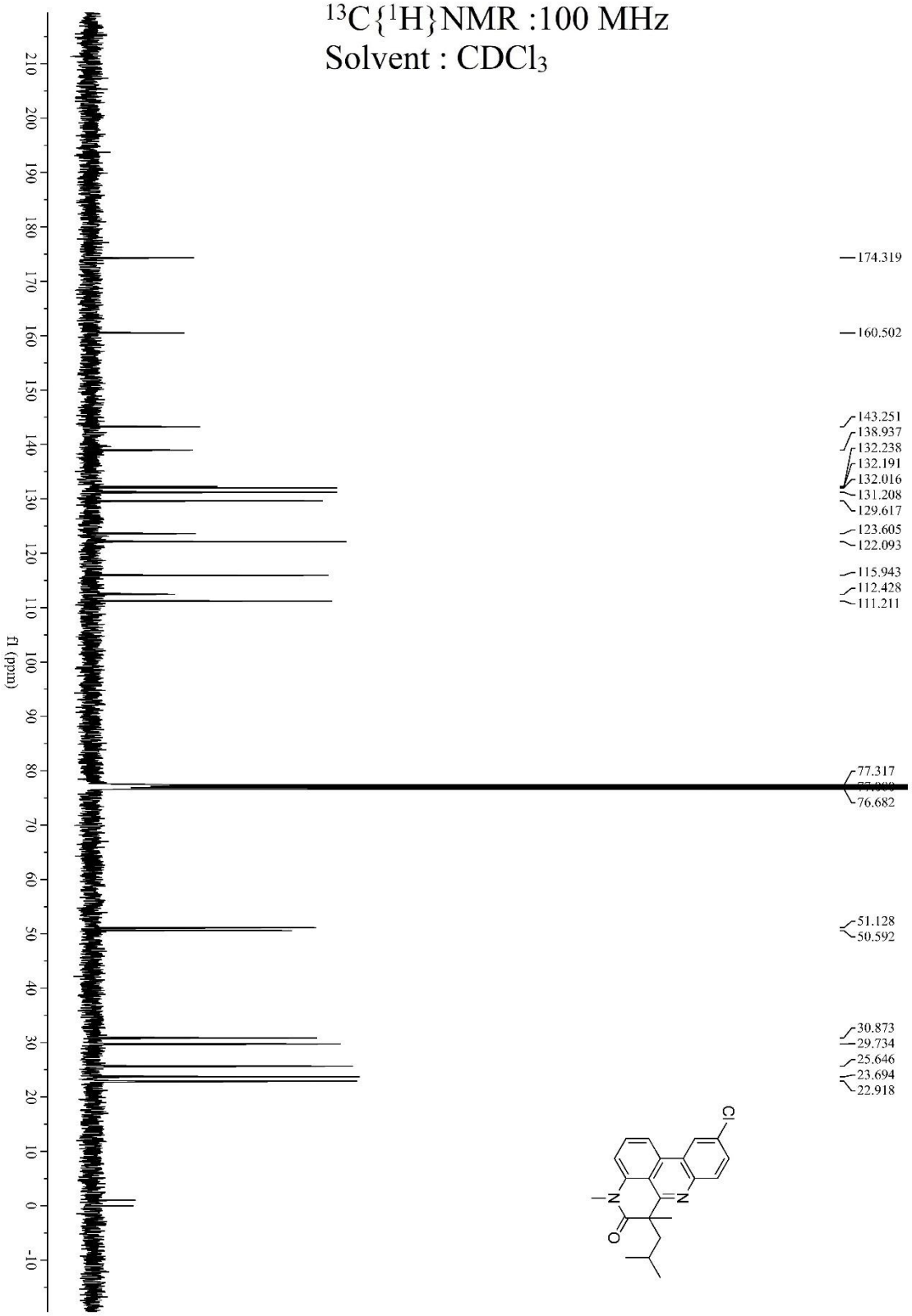
6-Isobutyl-4,6,10-trimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ja : 3ja' =1 : 1)




$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.600
158.974
143.187
138.779
136.303
132.879
131.386
130.839
129.435
122.363
122.009
115.990
112.400
110.430
77.317
76.683
51.176
50.442
30.855
29.691
25.642
23.718
22.934
21.928

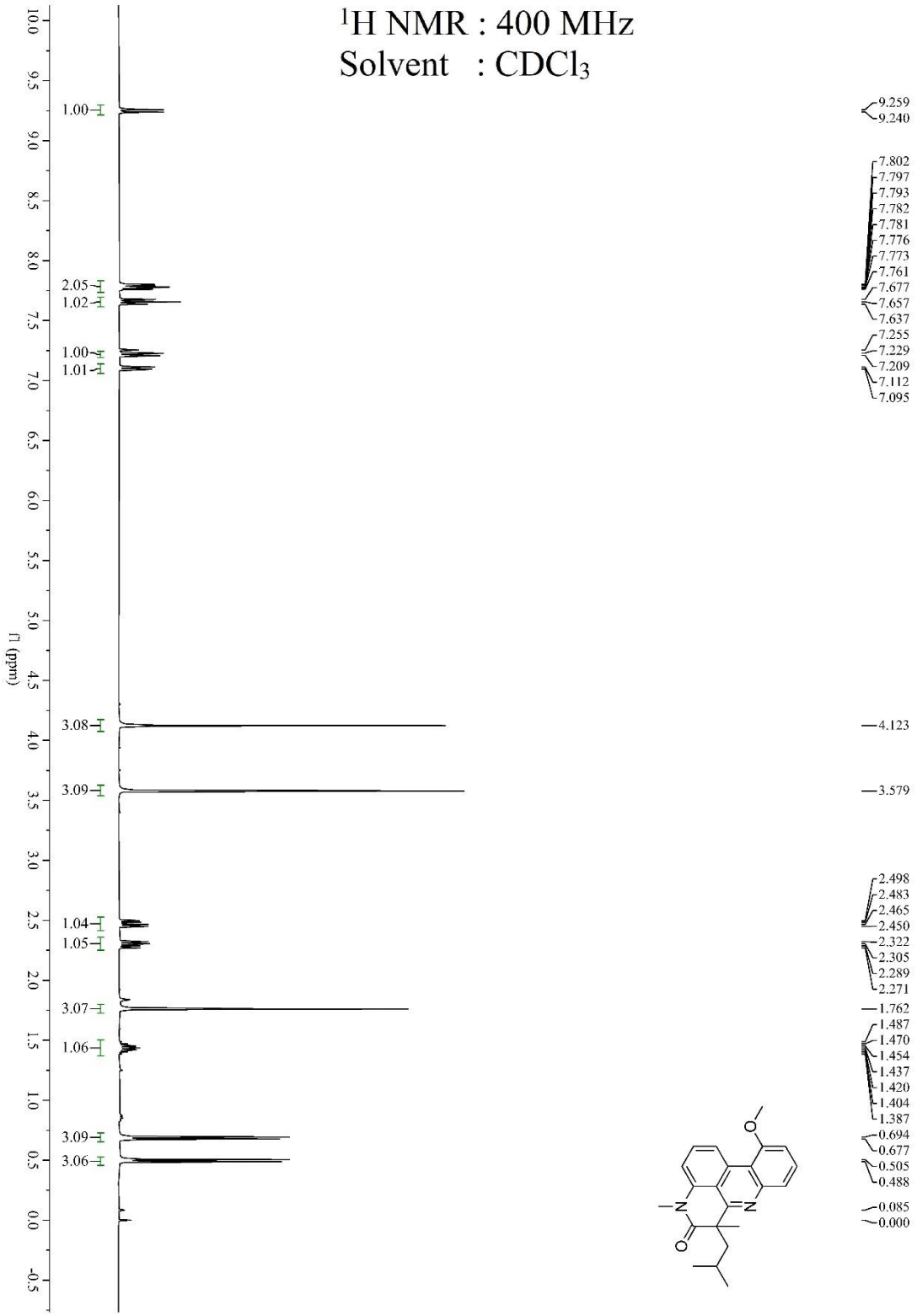
10-Chloro-6-isobutyl-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ka : 3ka' =1 : 1)

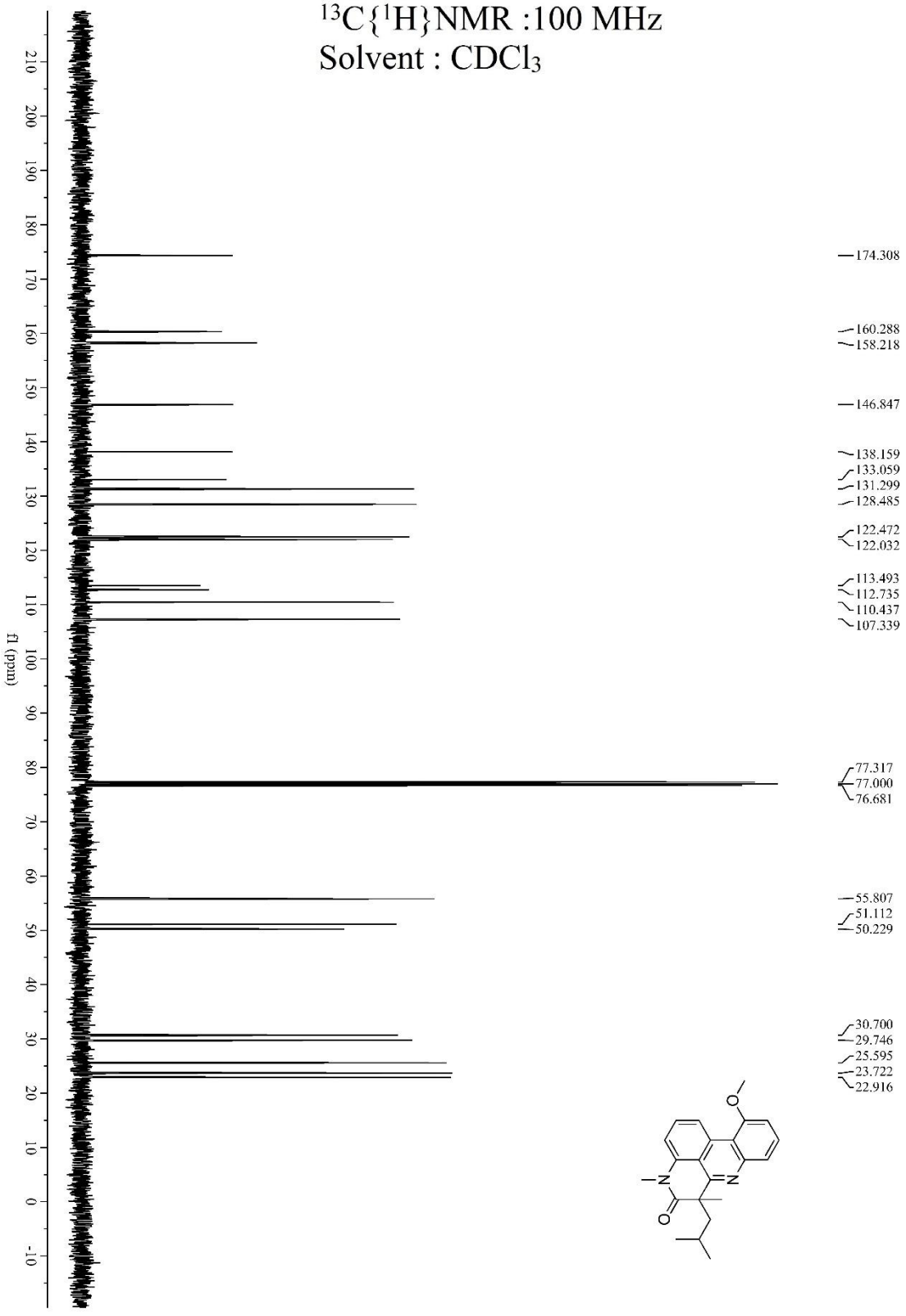



$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.319
160.502
143.251
138.937
132.238
132.191
132.016
131.208
129.617
123.605
122.093
115.943
112.428
111.211
77.317
76.682
51.128
50.592
30.873
29.734
25.646
23.694
22.918
Cl
N
N
O

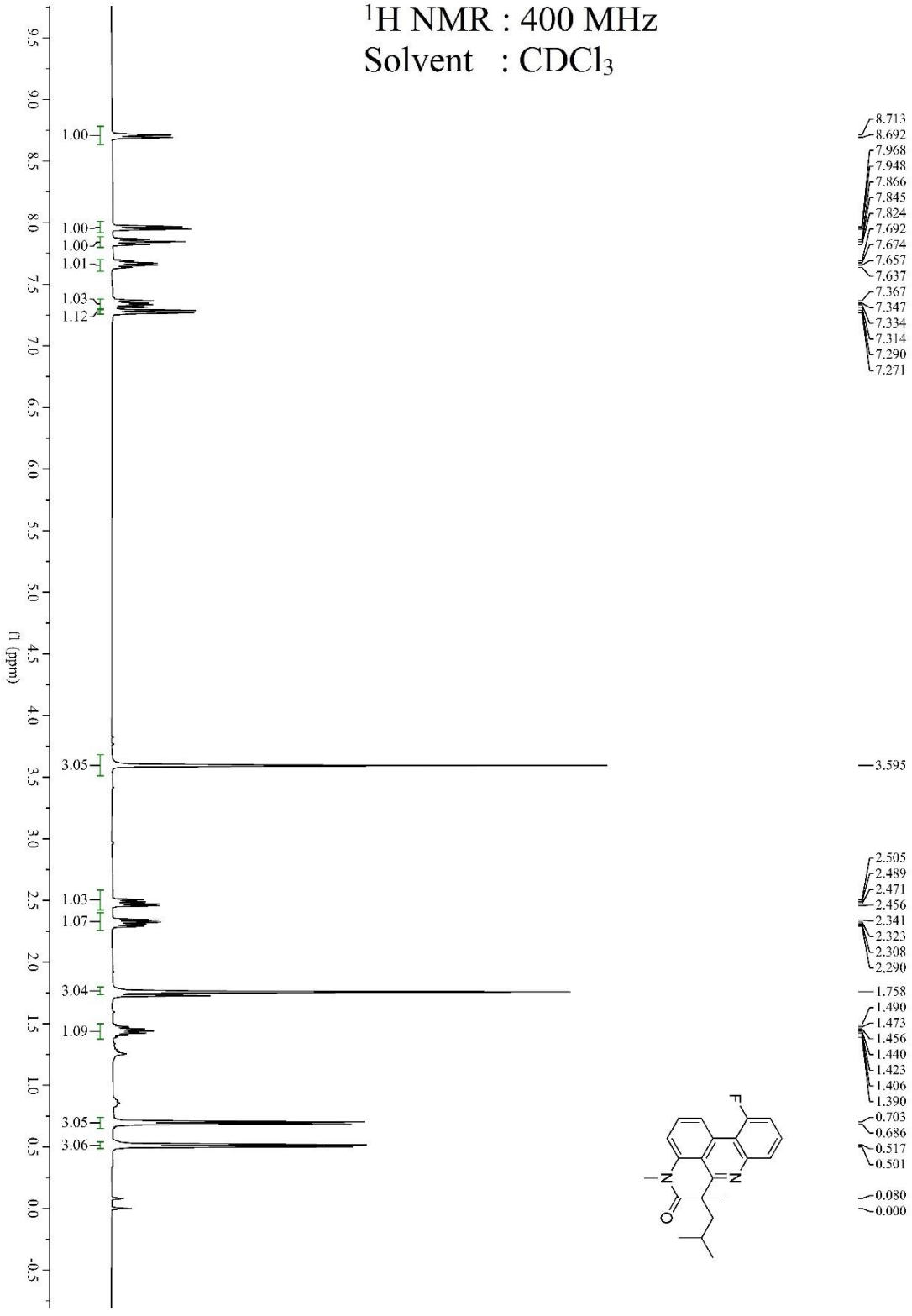
6-Isobutyl-11-methoxy-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthrid

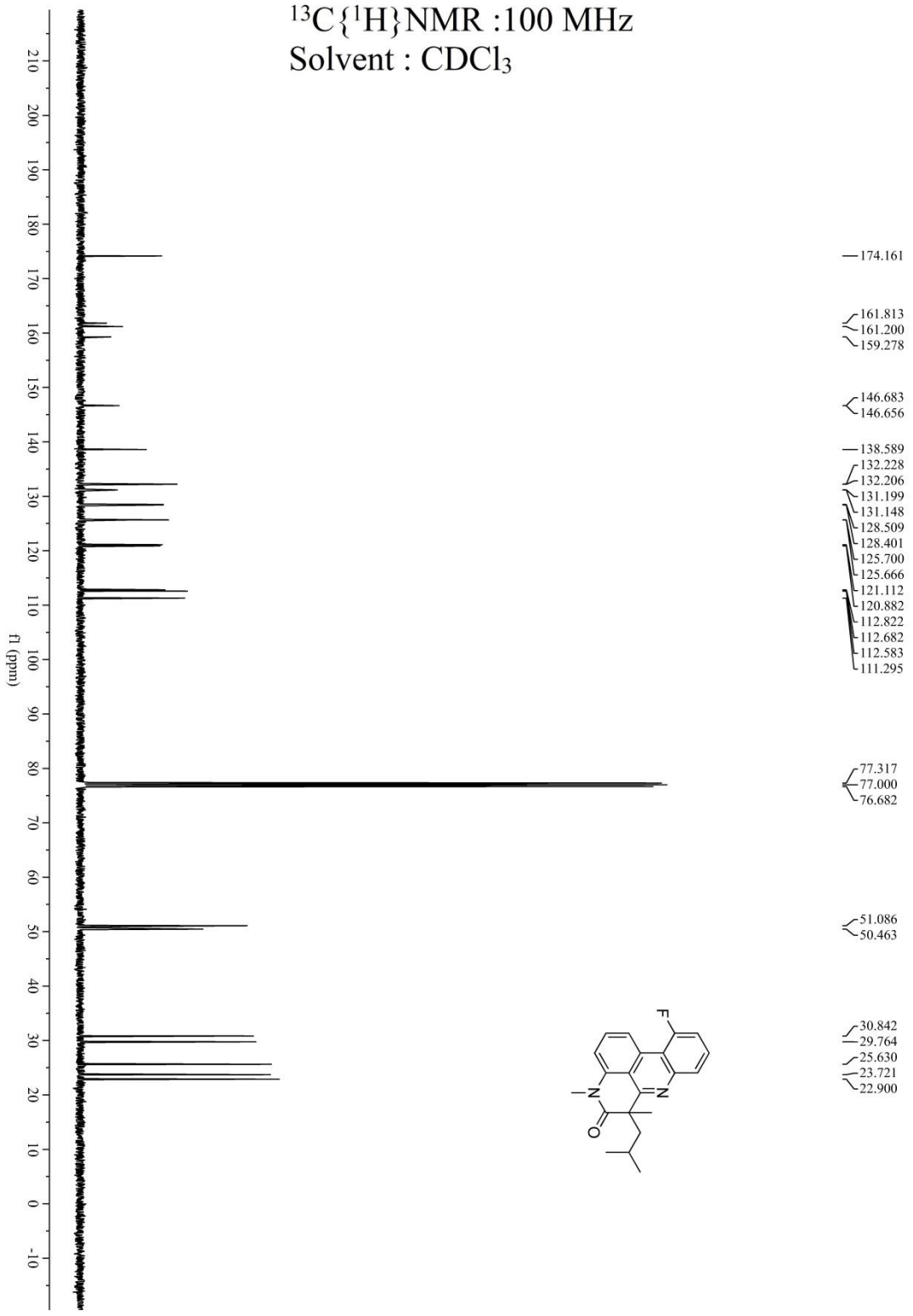
in-5(6*H*)- one (3la)




$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.308
160.288
158.218
146.847
138.159
133.059
131.299
128.485
122.472
122.032
113.493
112.735
110.437
107.339
77.317
77.000
76.681
55.807
51.112
50.229
30.700
29.746
25.595
23.722
22.916

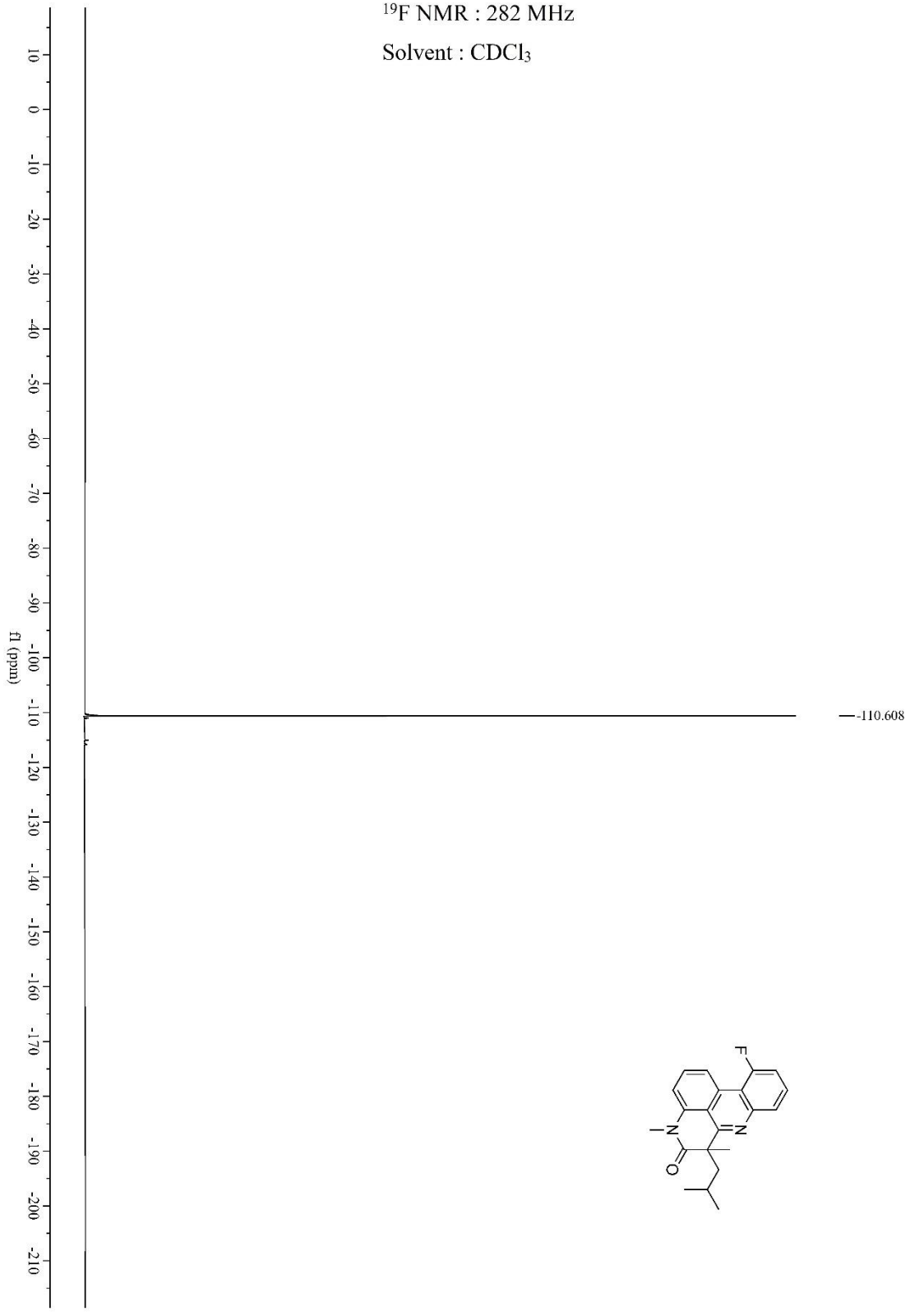
11-Fluoro-6-isobutyl-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ma)



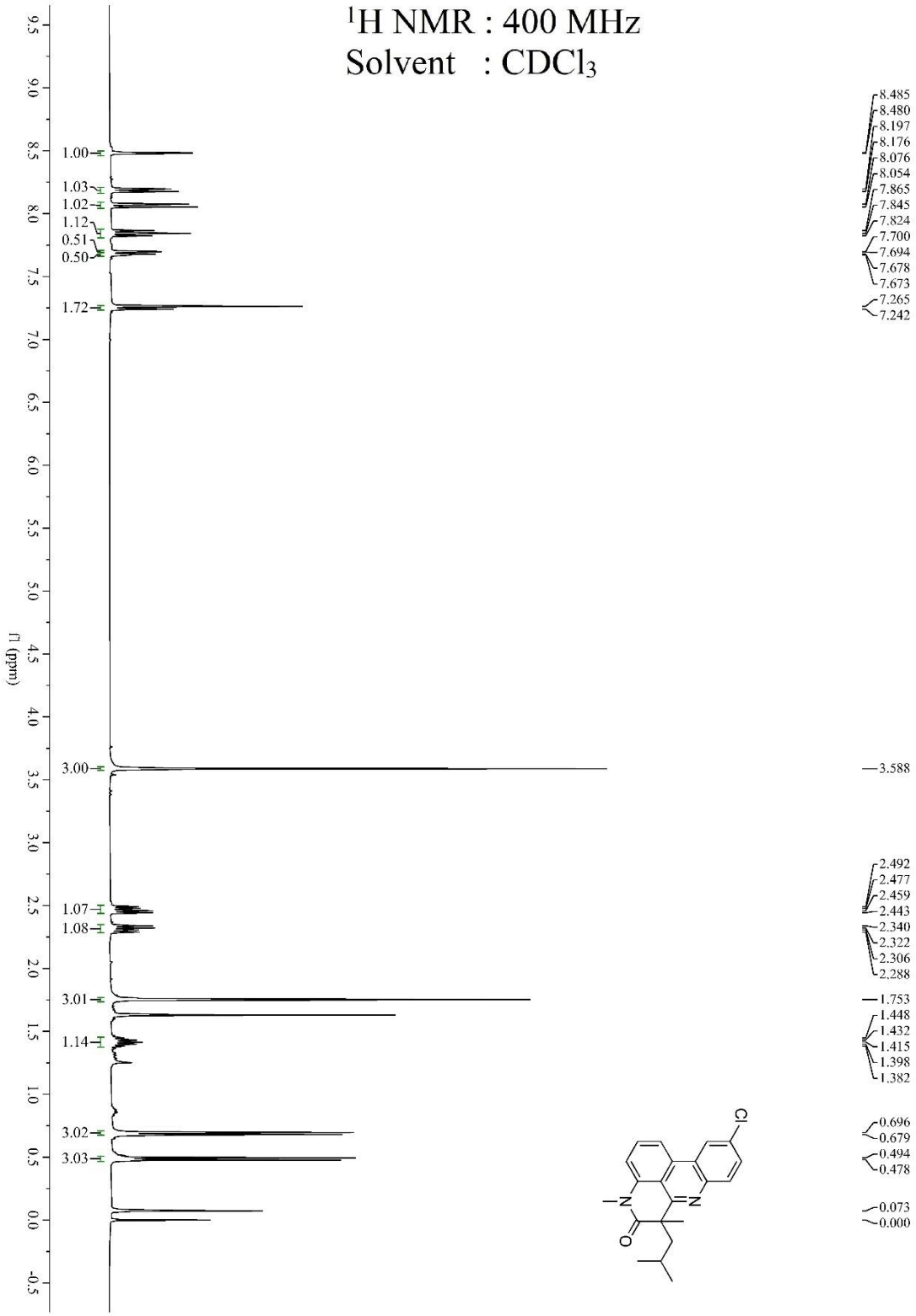

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.161
161.813
161.200
159.278
146.683
146.656
138.589
132.228
132.206
131.199
131.148
128.509
128.401
125.700
125.666
121.112
120.882
112.822
112.682
112.583
111.295
77.317
77.000
76.682
51.086
50.463
30.842
29.764
25.630
23.721
22.900
F
N
N
O

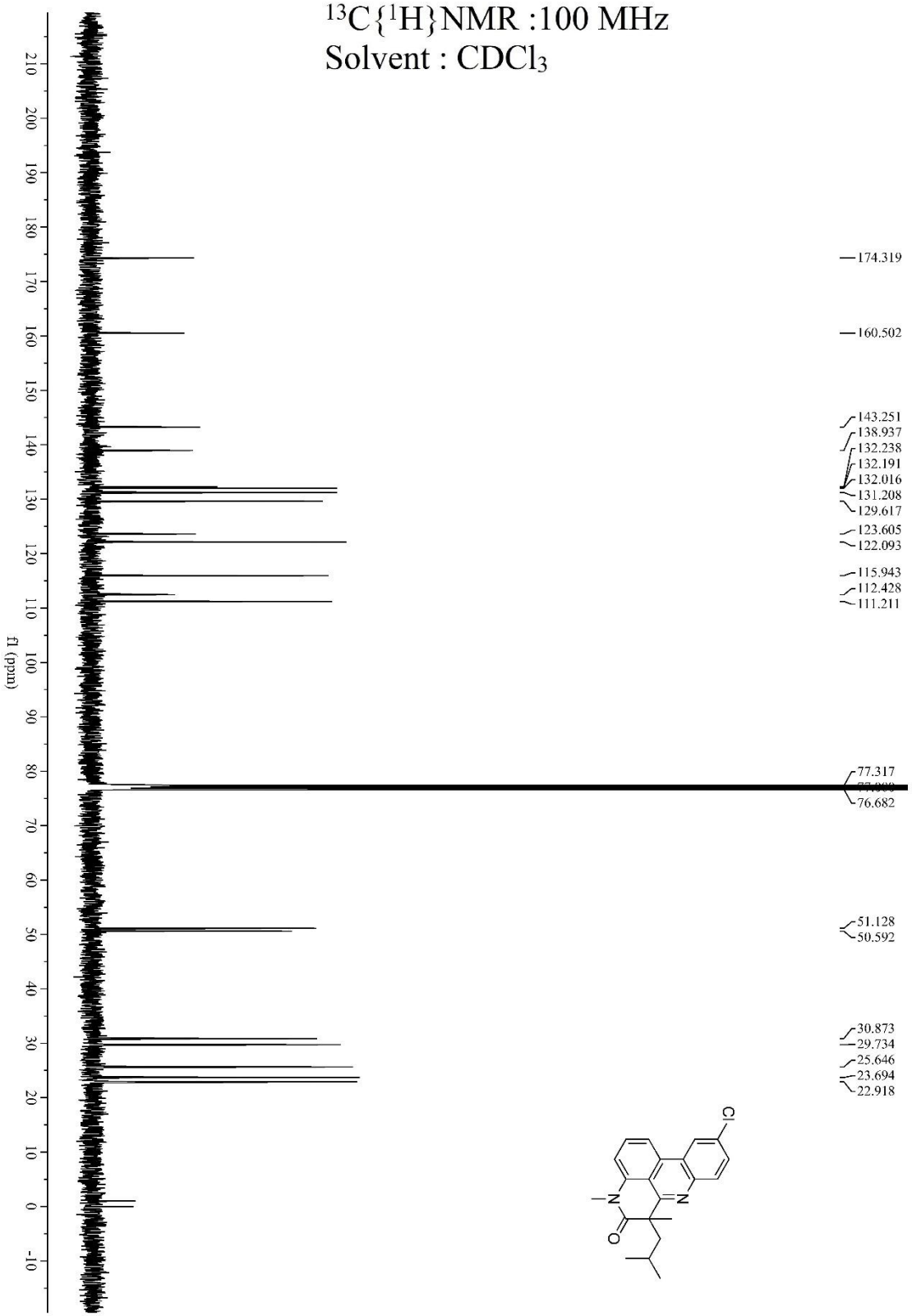
^{19}F NMR : 282 MHz

Solvent : $CDCl_3$

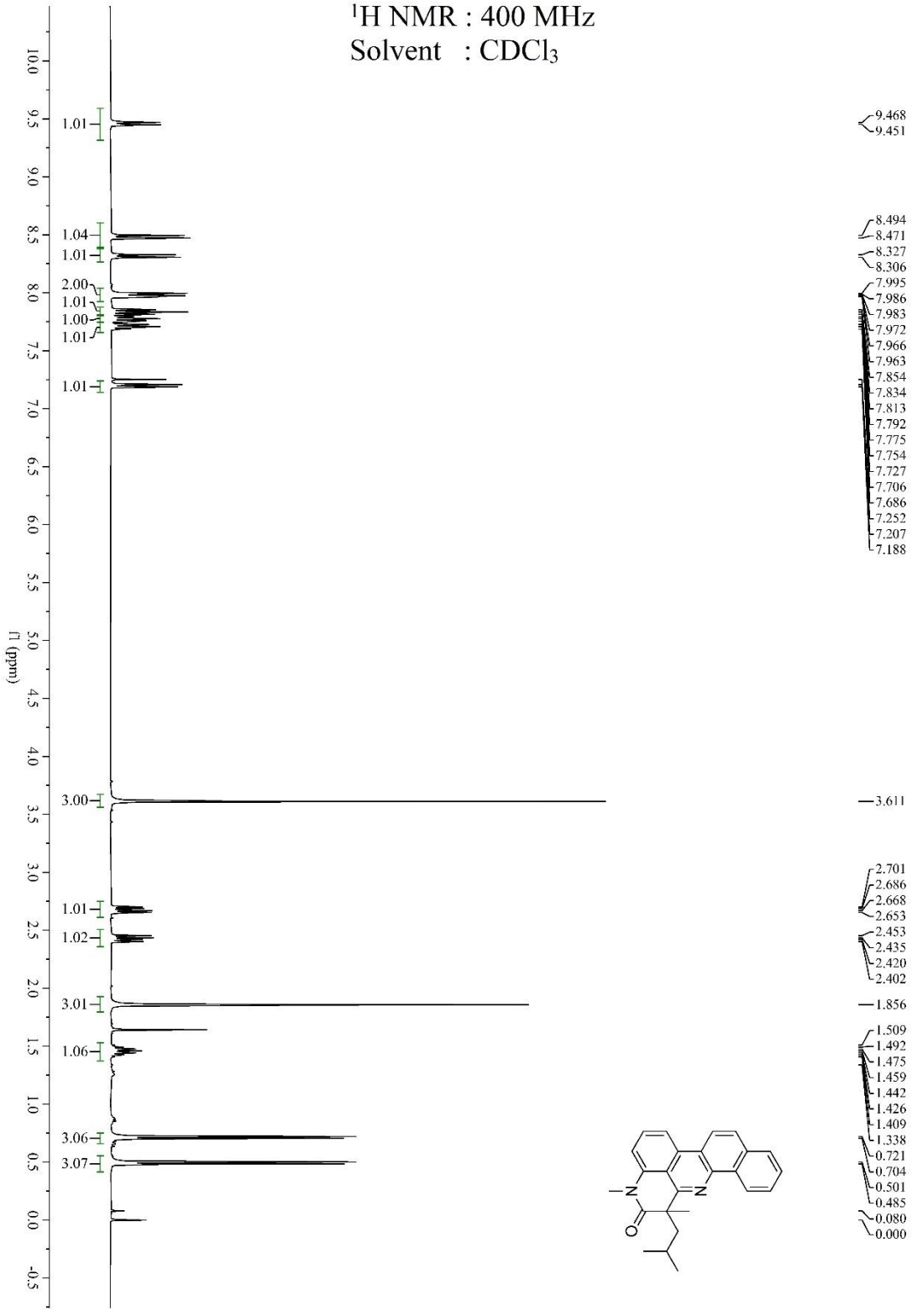


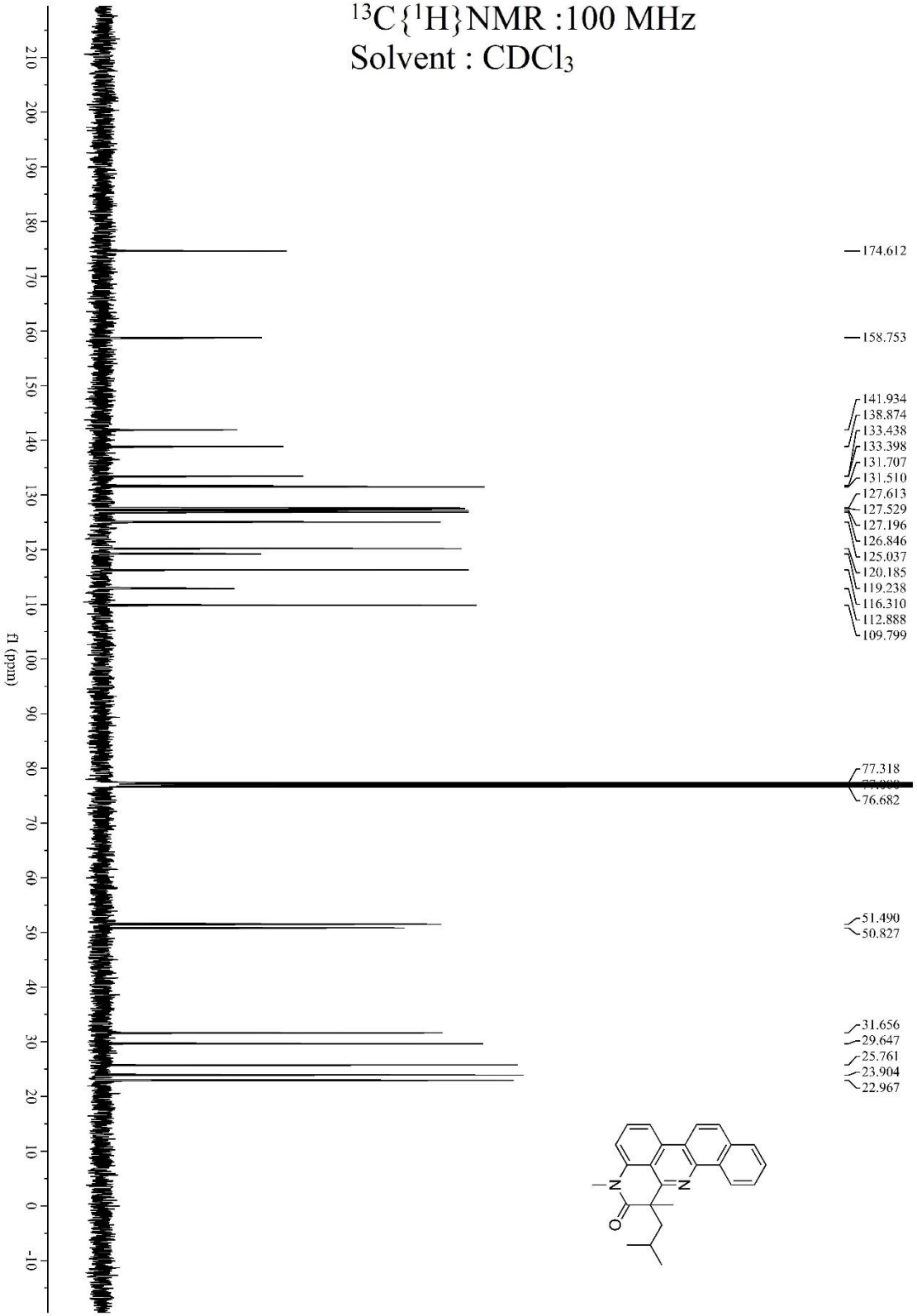
11-Chloro-6-isobutyl-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3na)



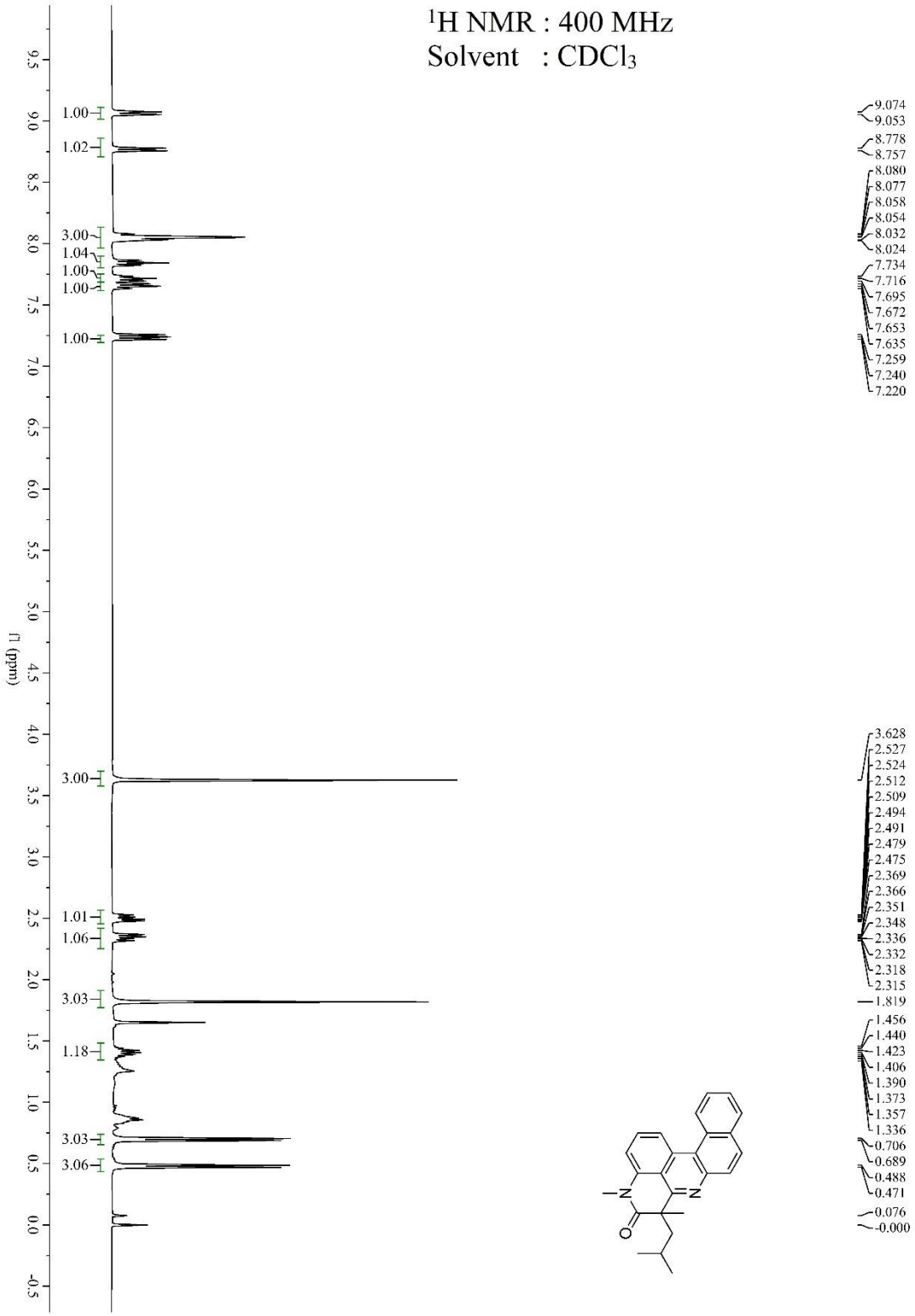

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
174.319
160.502
143.251
138.937
132.238
132.191
132.016
131.208
129.617
123.605
122.093
115.943
112.428
111.211
77.317
76.682
51.128
50.592
30.873
29.734
25.646
23.694
22.918
Cl
N
N
O

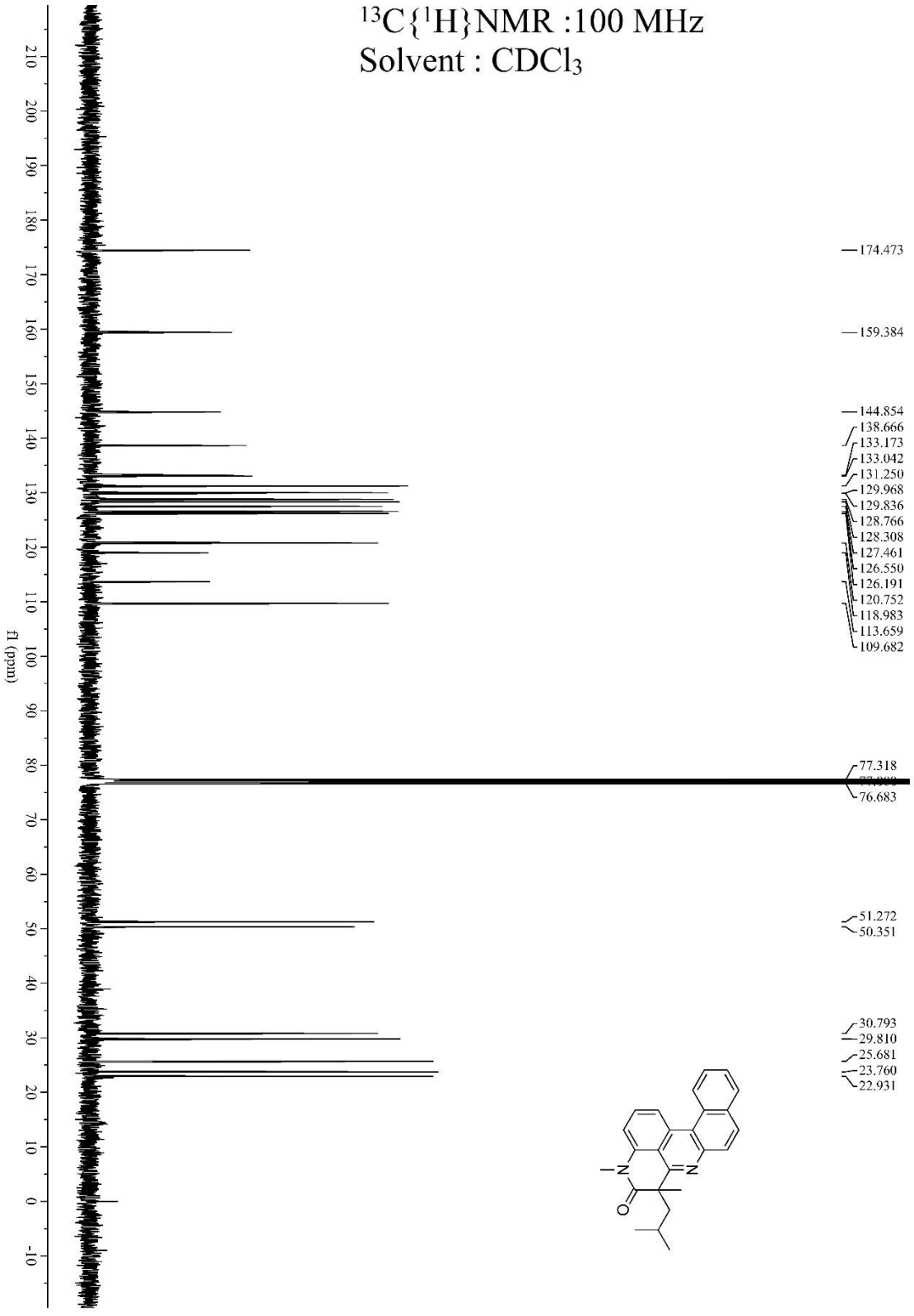
6-Isobutyl-4,6-dimethyl-4*H*-benzo[*c*]pyrido[4,3,2-*gh*]phenanthridin-5 (6*H*)-one (3oa)



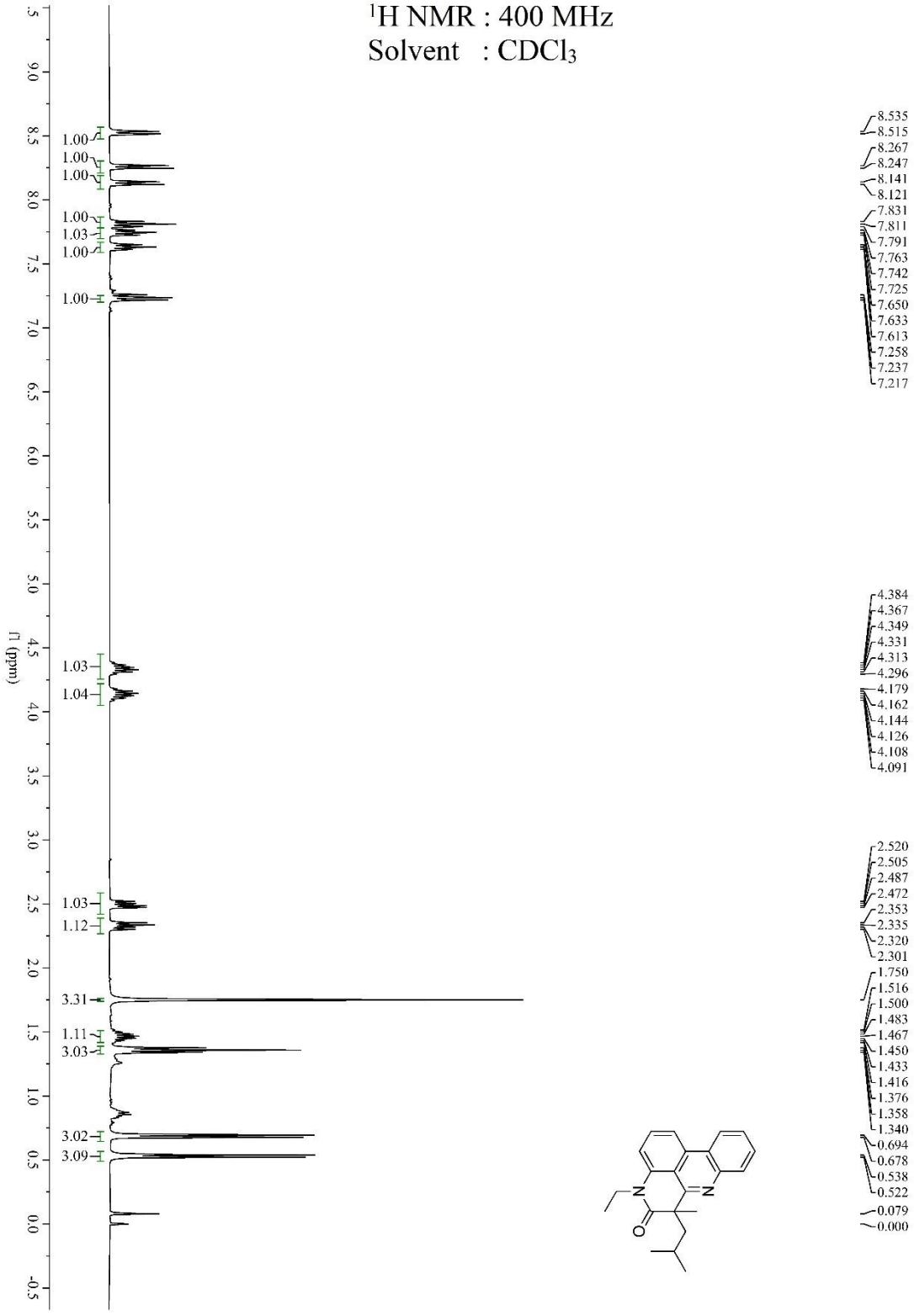

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.612
158.753
141.934
138.874
133.438
133.398
131.707
131.510
127.613
127.529
127.196
126.846
125.037
120.185
119.238
116.310
112.888
109.799
77.318
76.682
51.490
50.827
31.656
29.647
25.761
23.904
22.967
N
N
O

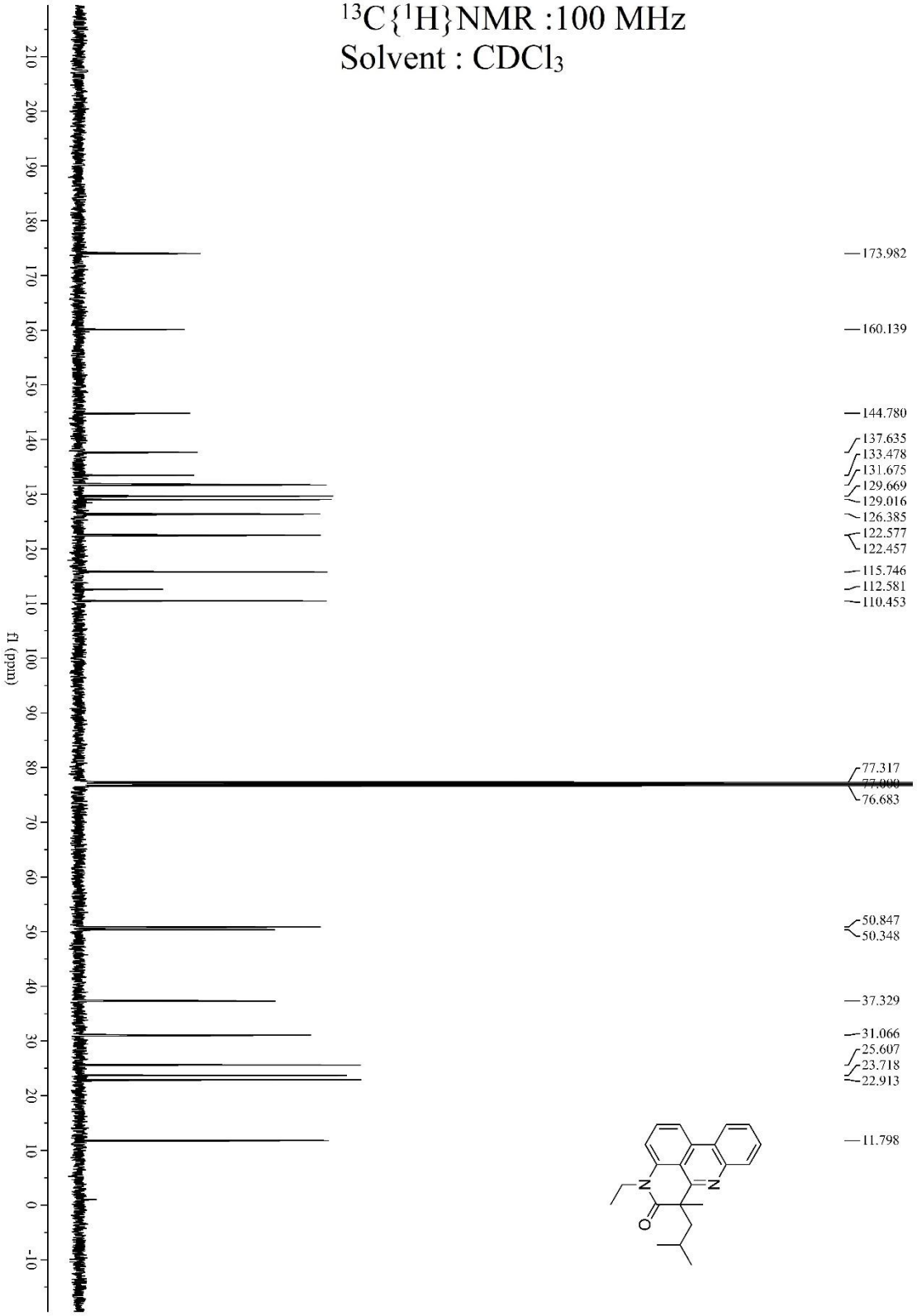
6-Isobutyl-4,6-dimethyl-4*H*-benzo[*a*]pyrido[4,3,2-*gh*]phenanthridin-5 (6*H*)-one (3pa)



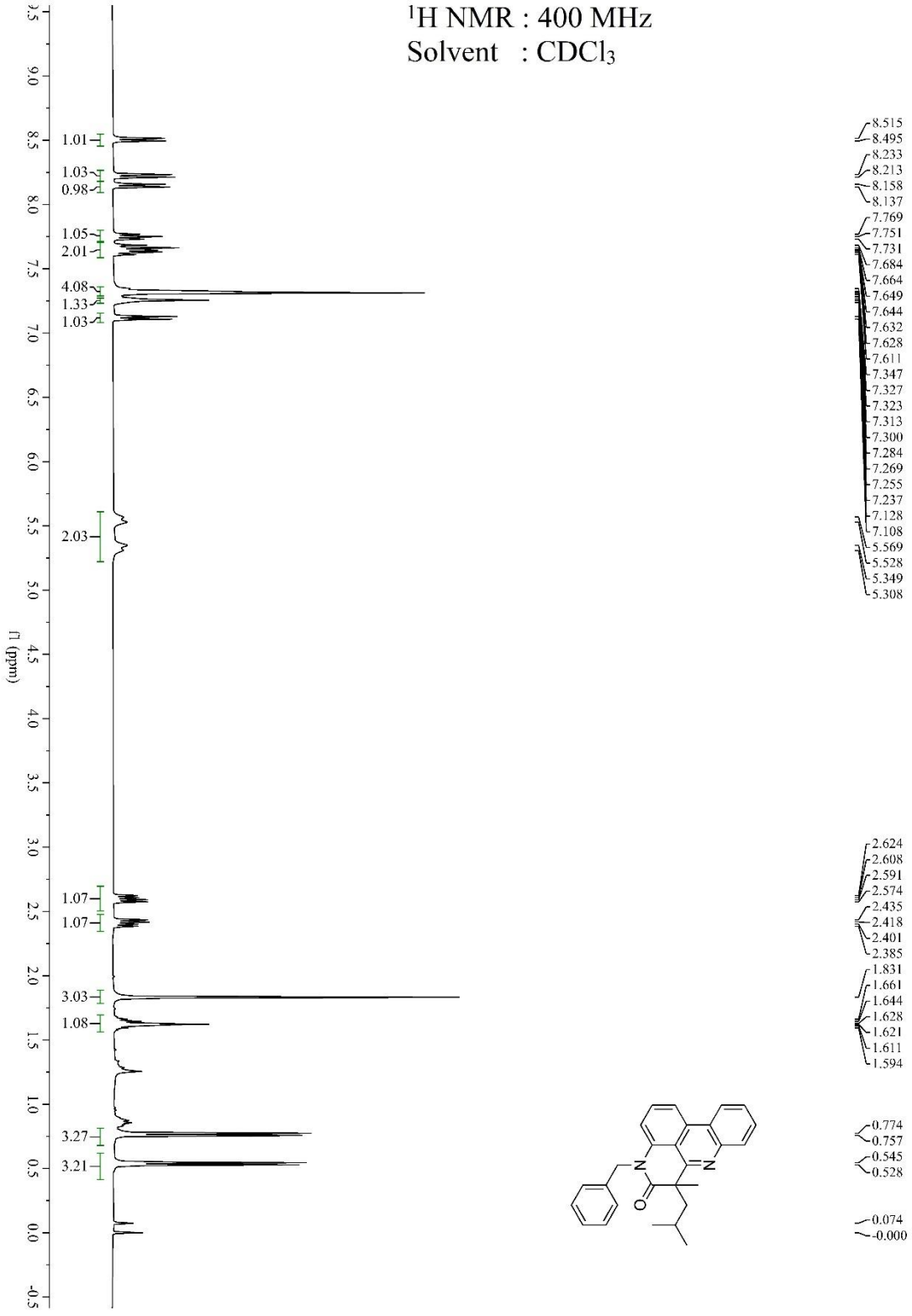

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.473
159.384
144.854
138.666
133.173
133.042
131.250
129.968
129.836
128.766
128.308
127.461
126.550
126.191
120.752
118.983
113.659
109.682
77.318
76.683
51.272
50.351
30.793
29.810
25.681
23.760
22.931

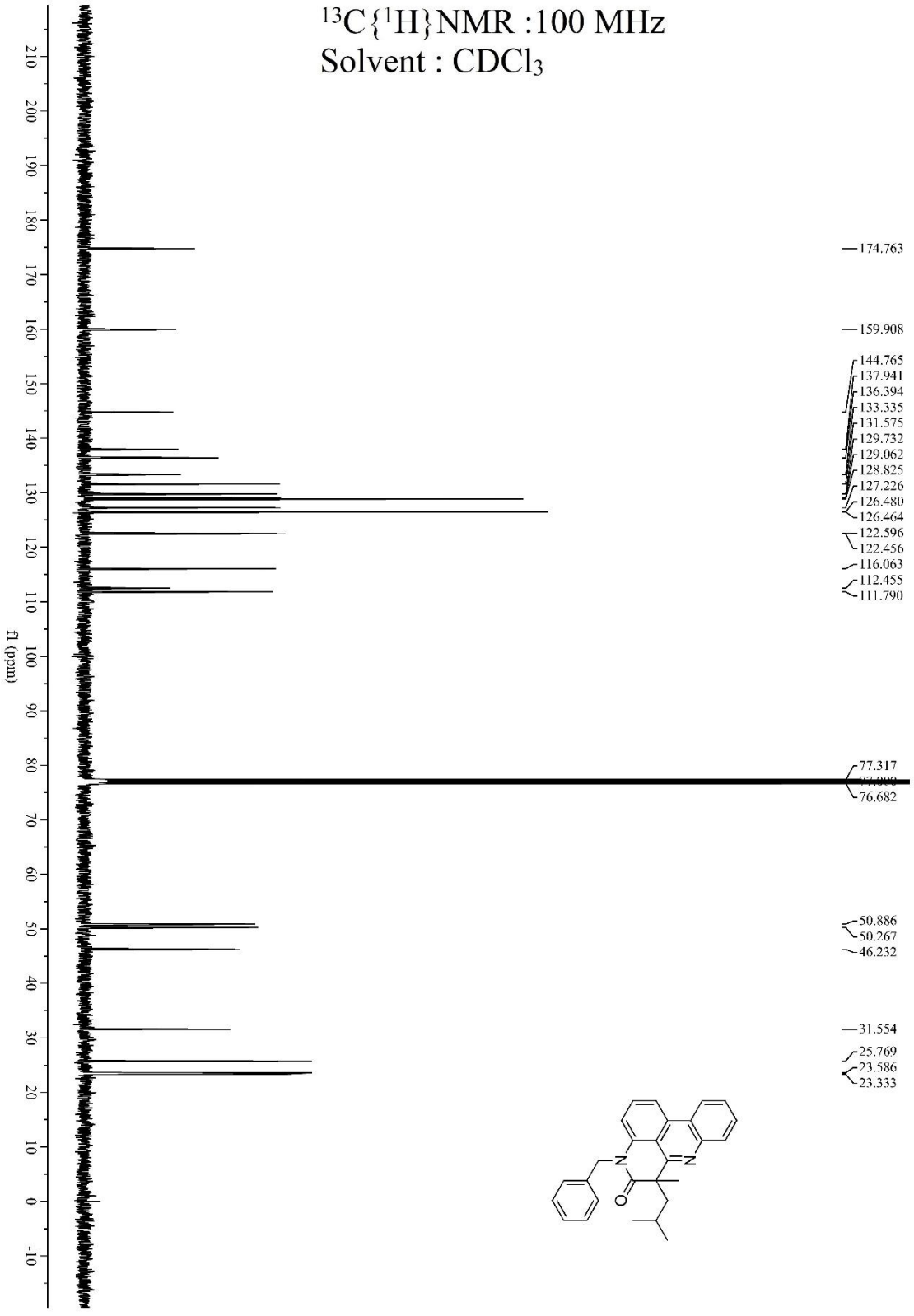
4-Ethyl-6-isobutyl-6-methyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3qa)




$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
173.982
160.139
144.780
137.635
133.478
131.675
129.669
129.016
126.385
122.577
122.457
115.746
112.581
110.453
77.317
77.000
76.683
50.847
50.348
37.329
31.066
25.607
23.718
22.913
11.798

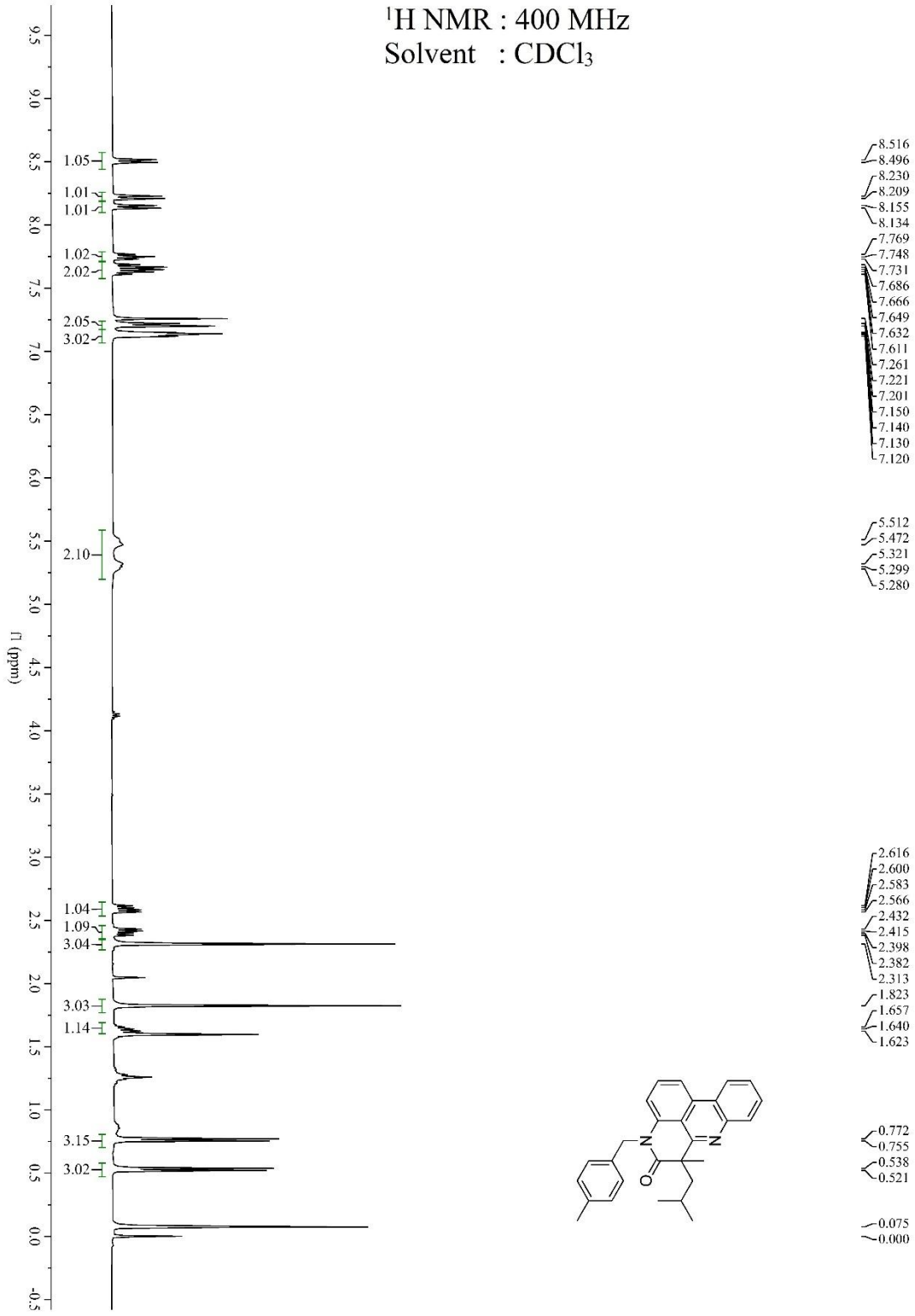
4-Benzyl-6-isobutyl-6-methyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ra)

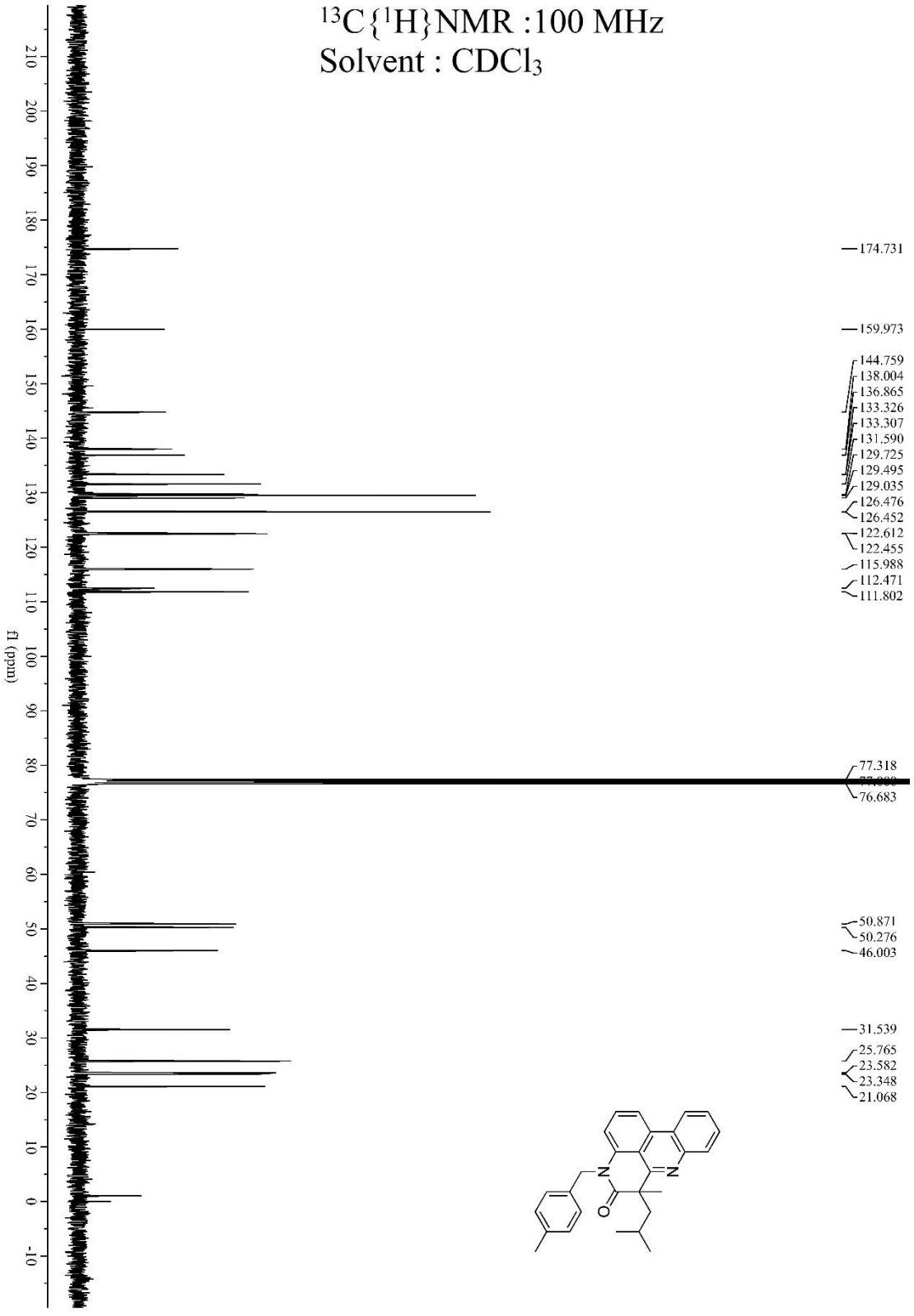



$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.763
159.908
144.765
137.941
136.394
133.335
131.575
129.732
129.062
128.825
127.226
126.480
126.464
122.596
122.456
116.063
112.455
111.790
77.317
76.682
50.886
50.267
46.232
31.554
25.769
23.586
23.333

6-Isobutyl-6-methyl-4-(4-methylbenzyl)-4*H*-pyrido[4,3,2-*gh*]phenant

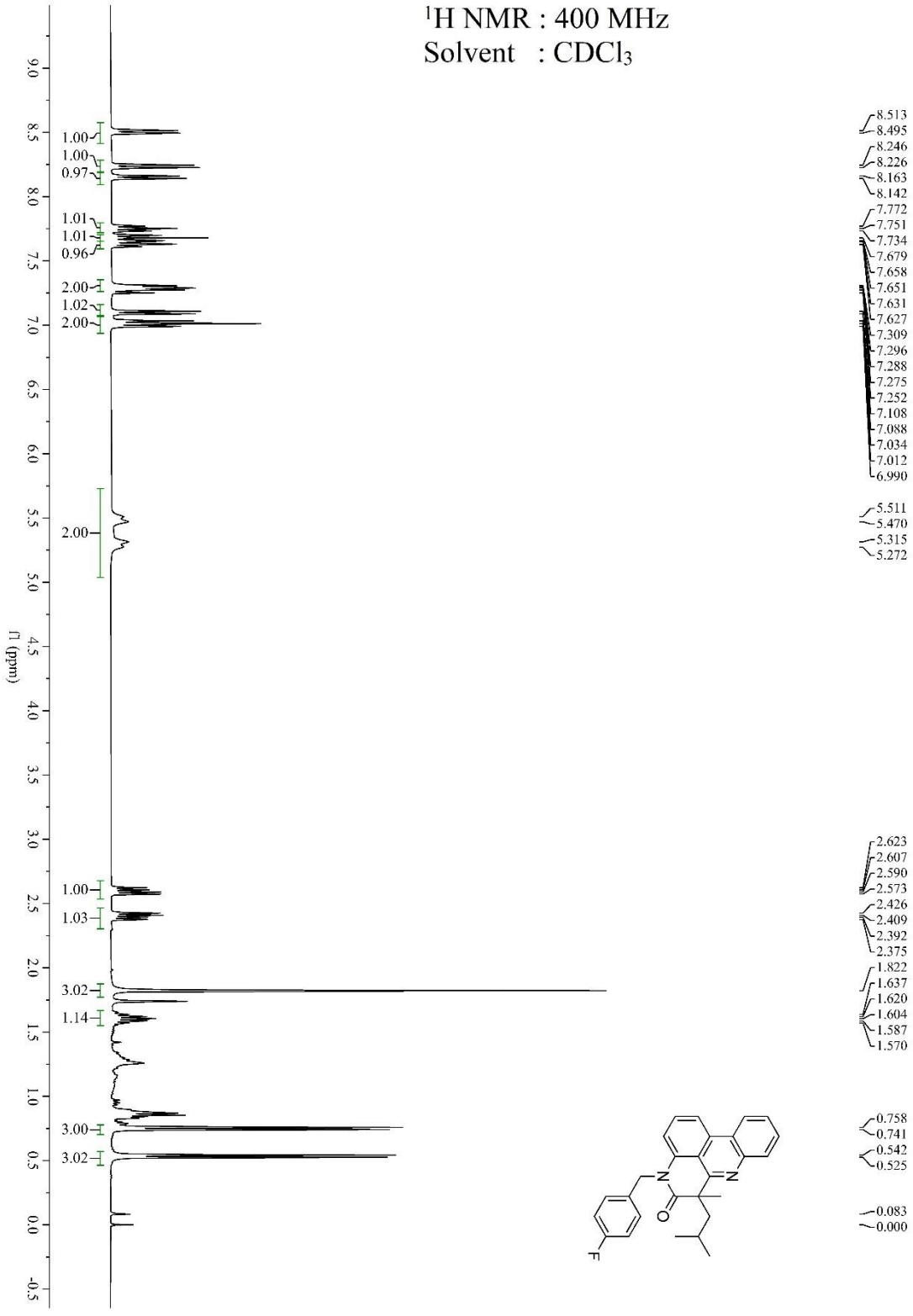
hridin-5(6*H*)-one (3sa)

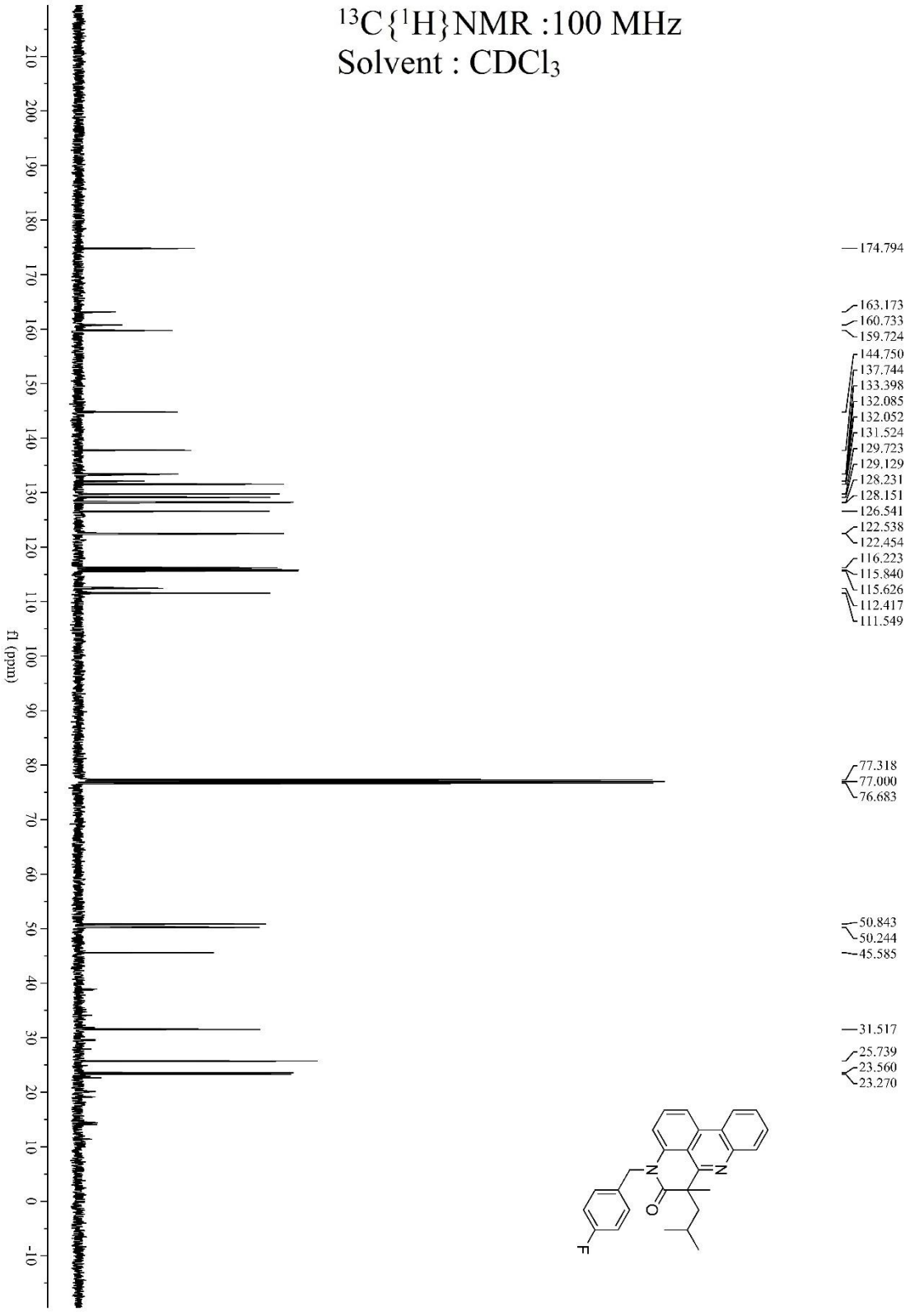



$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.731
159.973
144.759
138.004
136.865
133.326
133.307
131.590
129.725
129.495
129.035
126.476
126.452
122.612
122.455
115.988
112.471
111.802
77.318
76.683
50.871
50.276
46.003
31.539
25.765
23.582
23.348
21.068
N
N
O

4-(4-Fluorobenzyl)-6-isobutyl-6-methyl-4*H*-pyrido[4,3,2-*gh*]phenanth

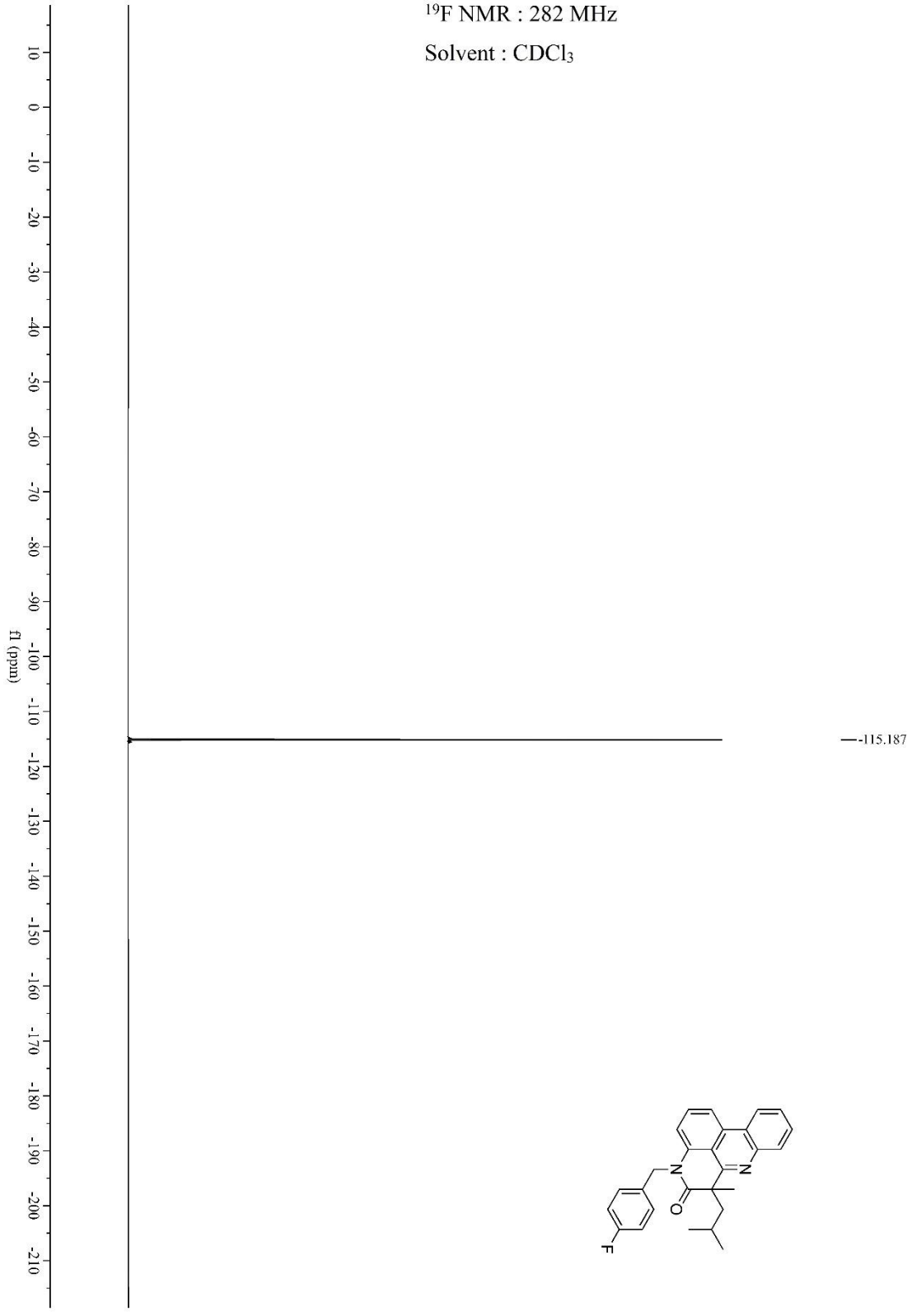
ridin-5(6*H*)- one (3ta)



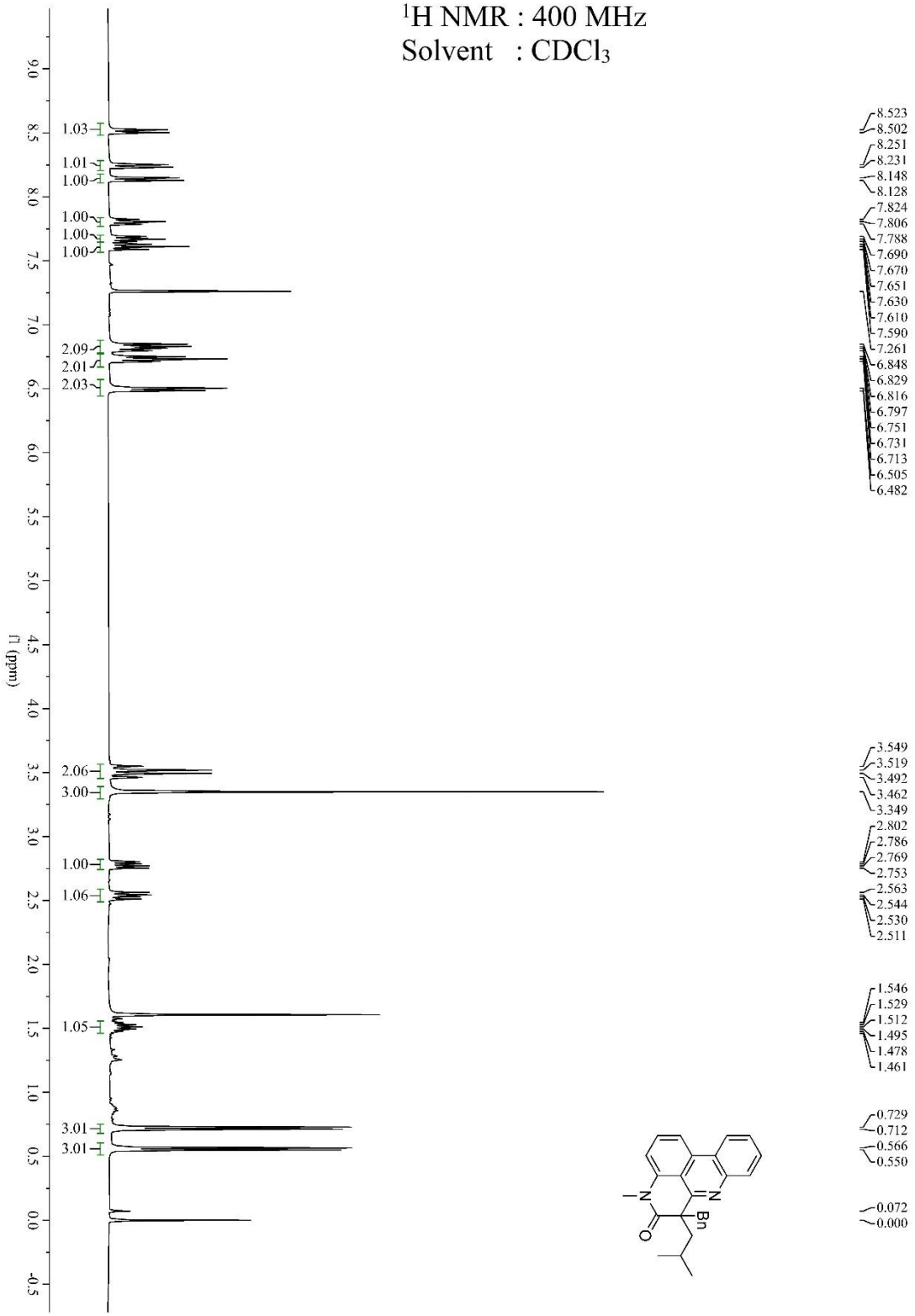

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.794
163.173
160.733
159.724
144.750
137.744
133.398
132.085
132.052
131.524
129.723
129.129
128.231
128.151
126.541
122.538
122.454
116.223
115.840
115.626
112.417
111.549
77.318
77.000
76.683
50.843
50.244
45.585
31.517
25.739
23.560
23.270
N
N
O
F

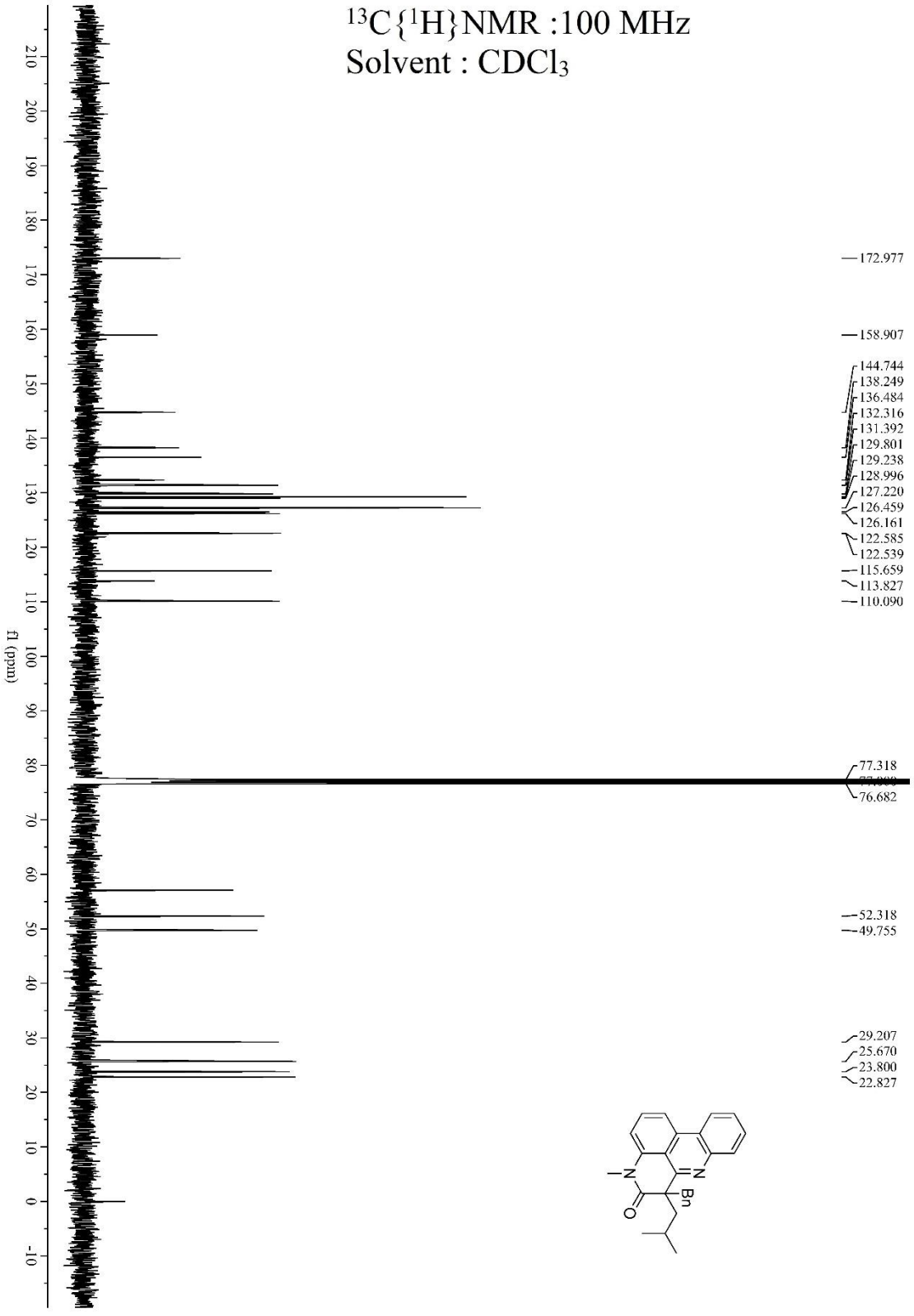
^{19}F NMR : 282 MHz

Solvent : $CDCl_3$



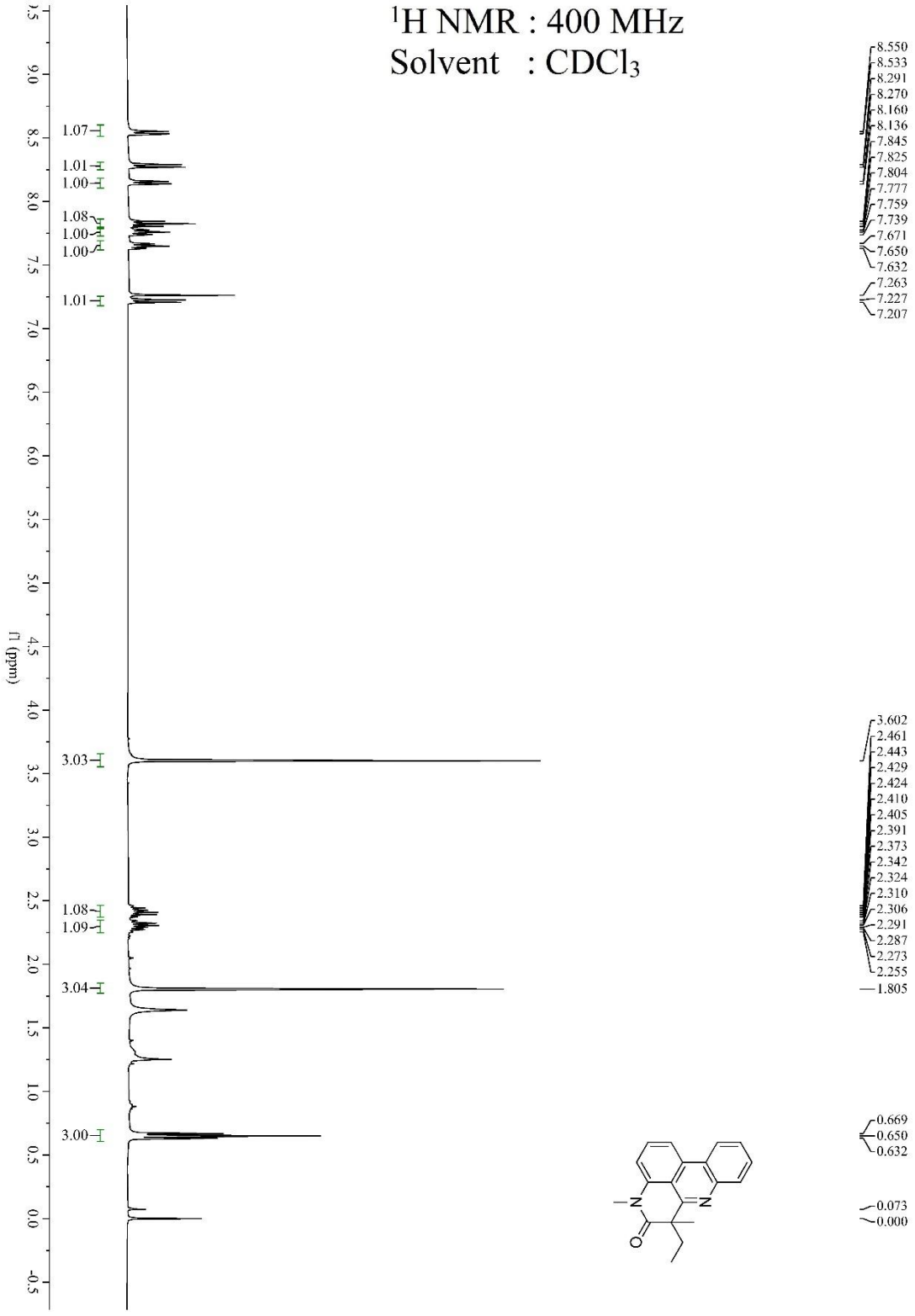
6-Benzyl-6-isobutyl-4-methyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3wa)

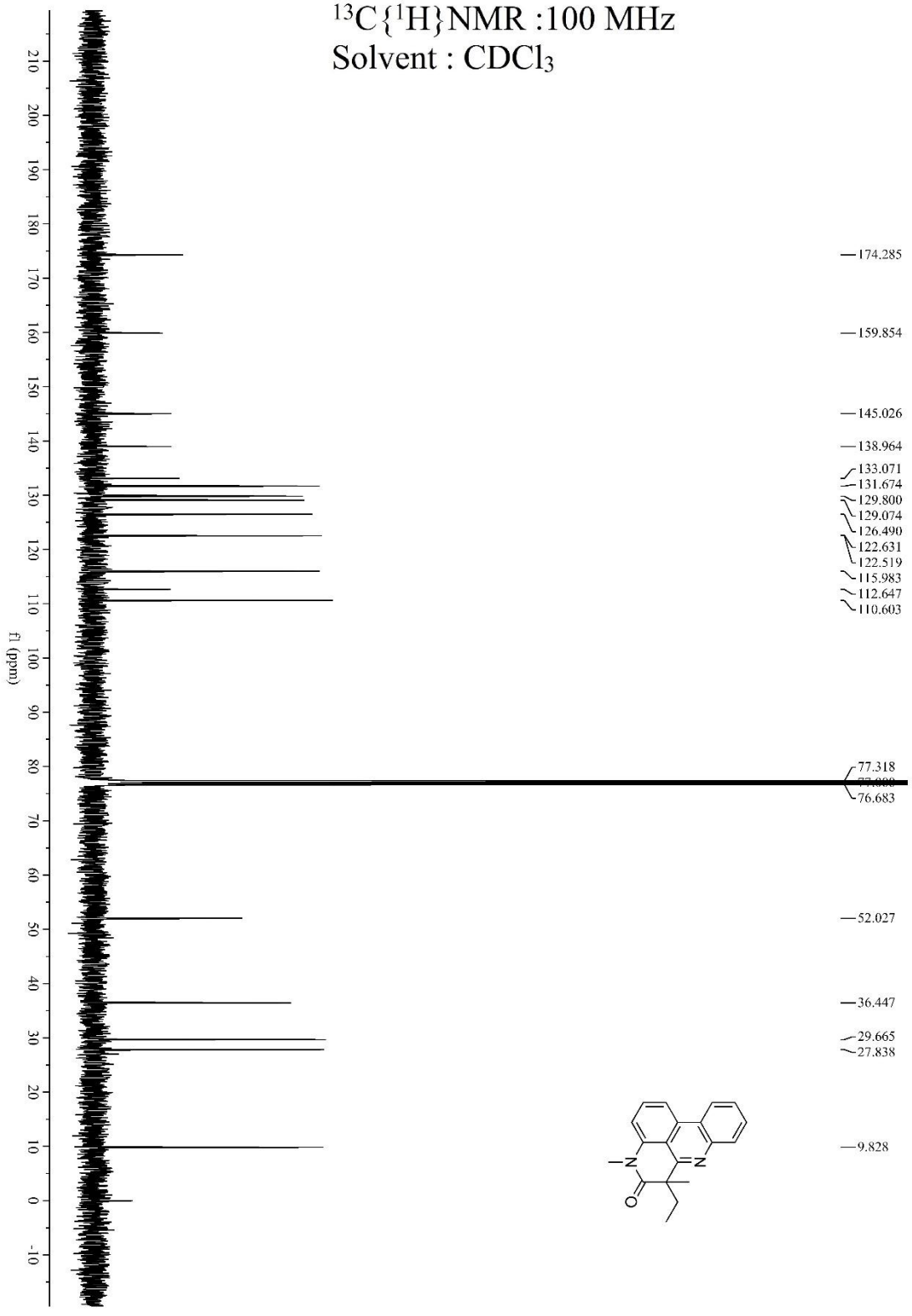



$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
172.977
158.907
144.744
138.249
136.484
132.316
131.392
129.801
129.238
128.996
127.220
126.459
126.161
122.585
122.539
115.659
113.827
110.090
77.318
76.682
52.318
49.755
29.207
25.670
23.800
22.827
N
N
O
Bn

6-Ethyl-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one

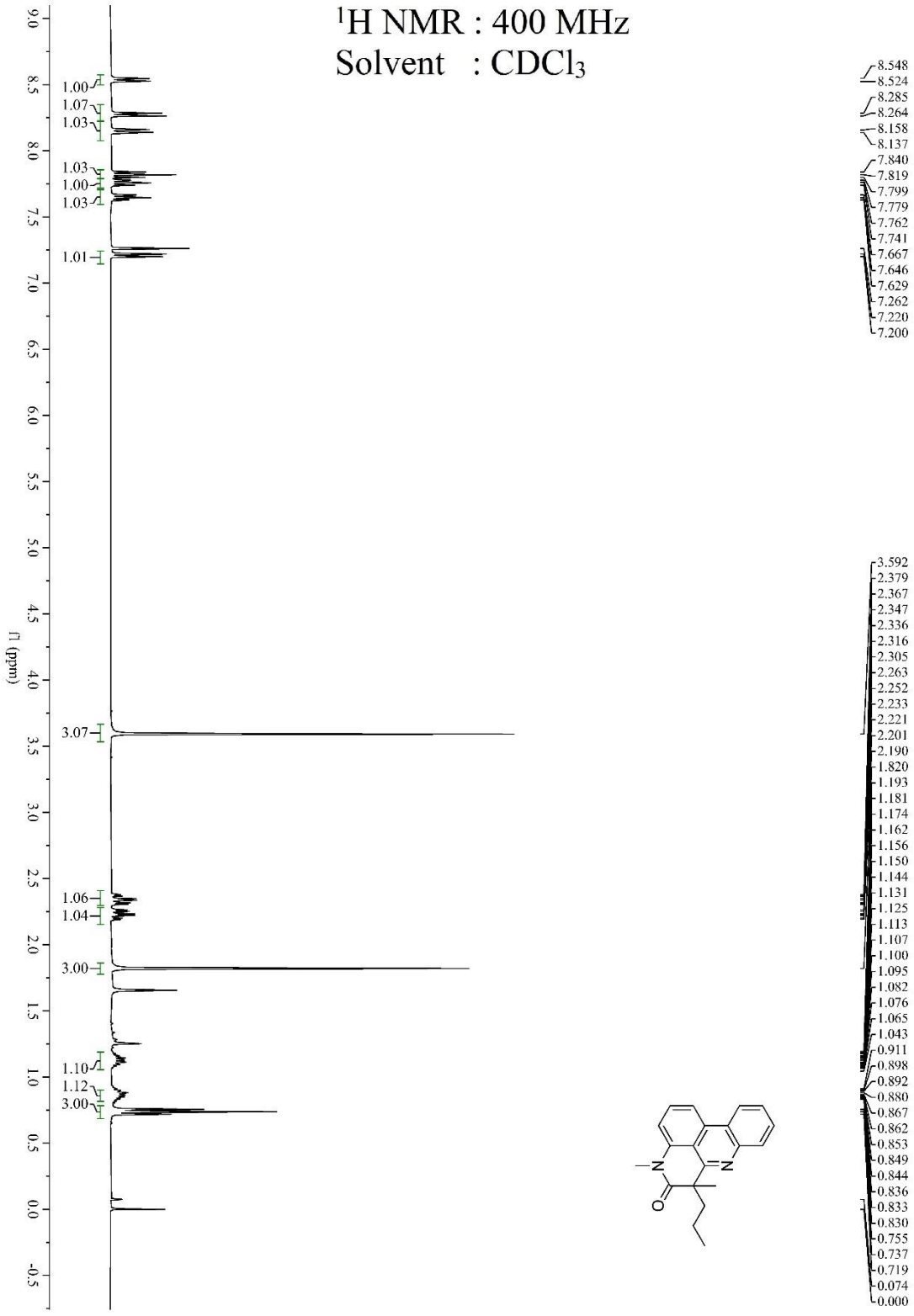
(3ab)

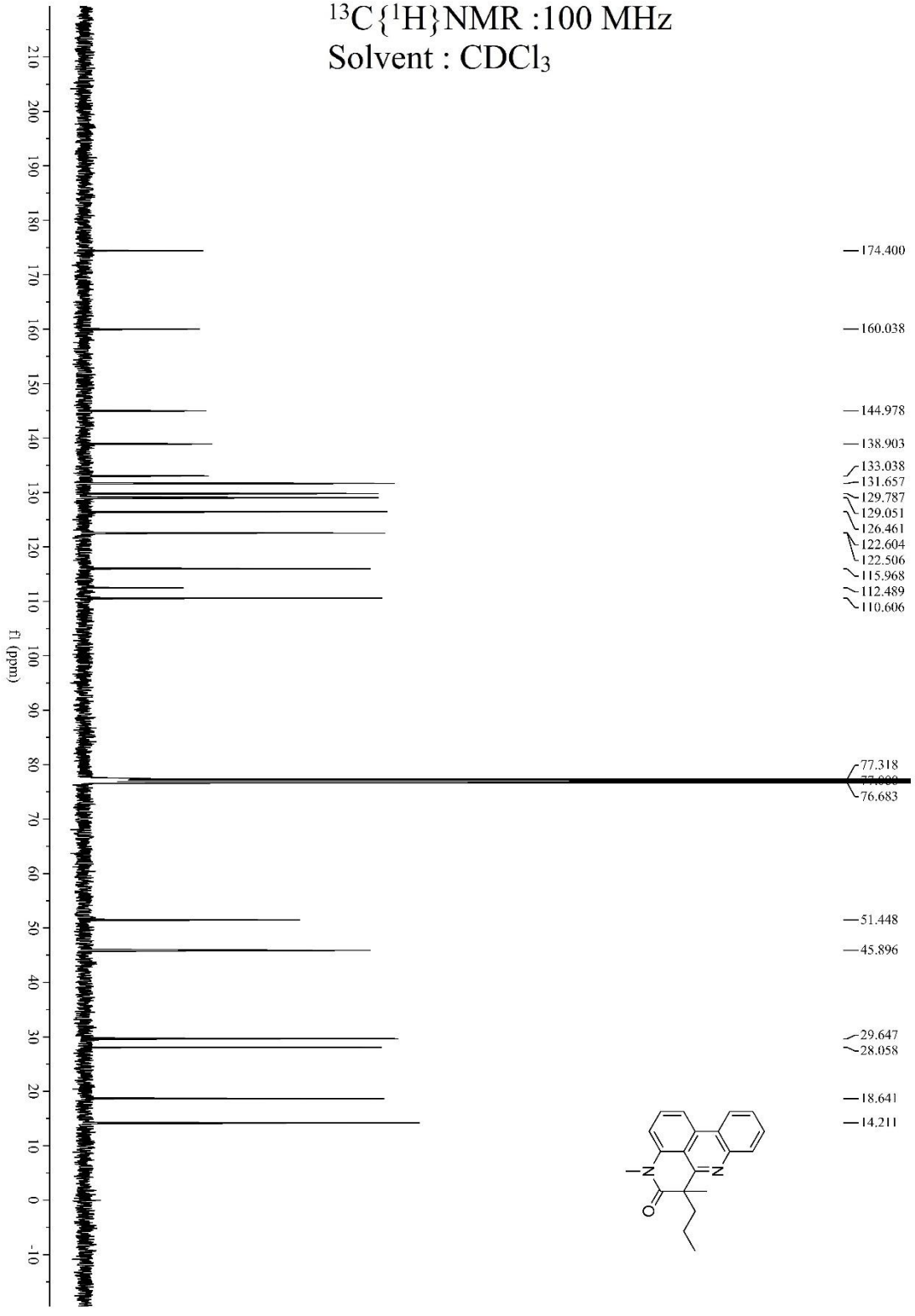



$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.285
159.854
145.026
138.964
133.071
131.674
129.800
129.074
126.490
122.631
122.519
115.983
112.647
110.603
77.318
76.683
52.027
36.447
29.665
27.838
9.828

4,6-Dimethyl-6-propyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one

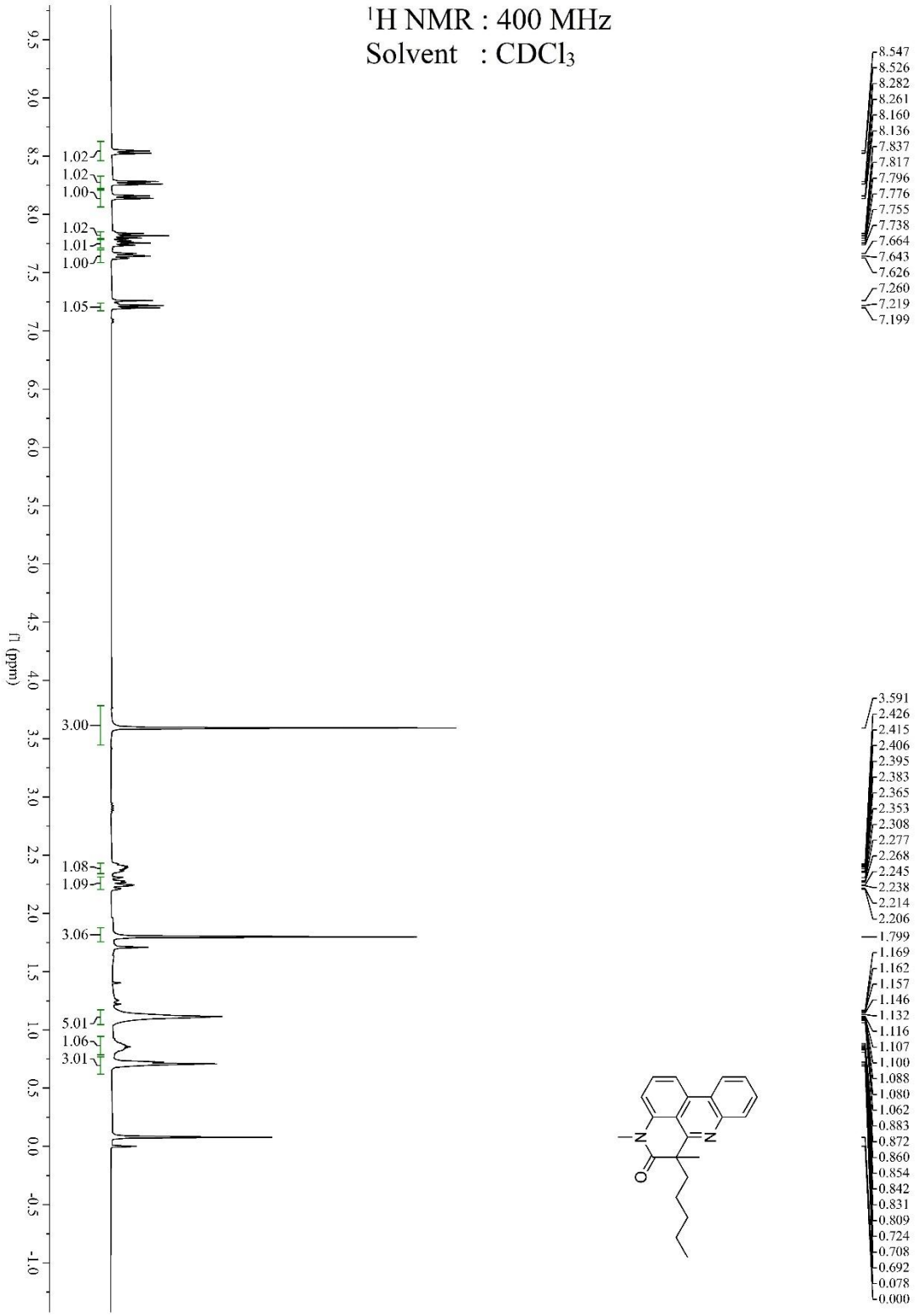
(3ac)

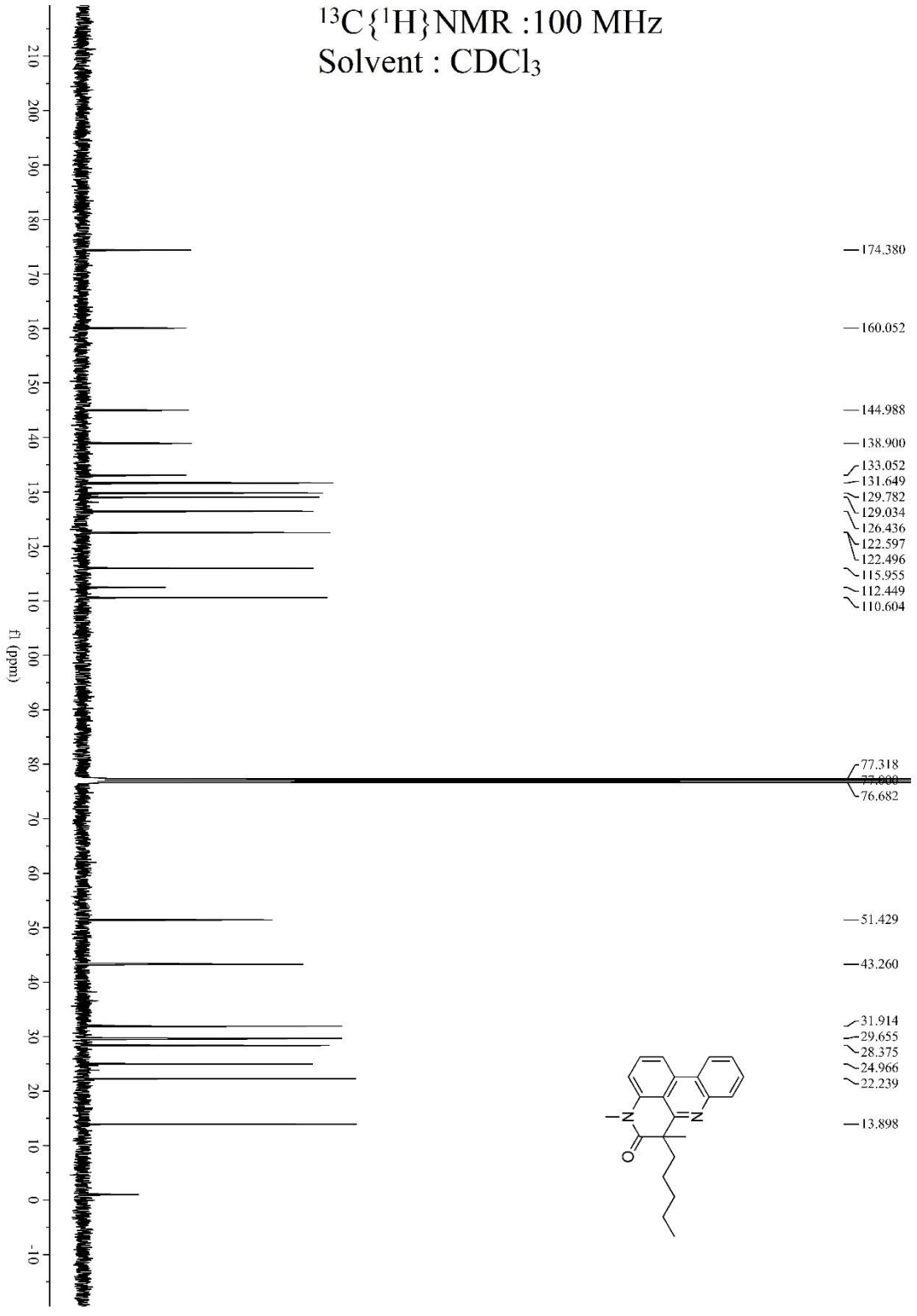



$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.400
160.038
144.978
138.903
133.038
131.657
129.787
129.051
126.461
122.604
122.506
115.968
112.489
110.606
77.318
76.683
51.448
45.896
29.647
28.058
18.641
14.211

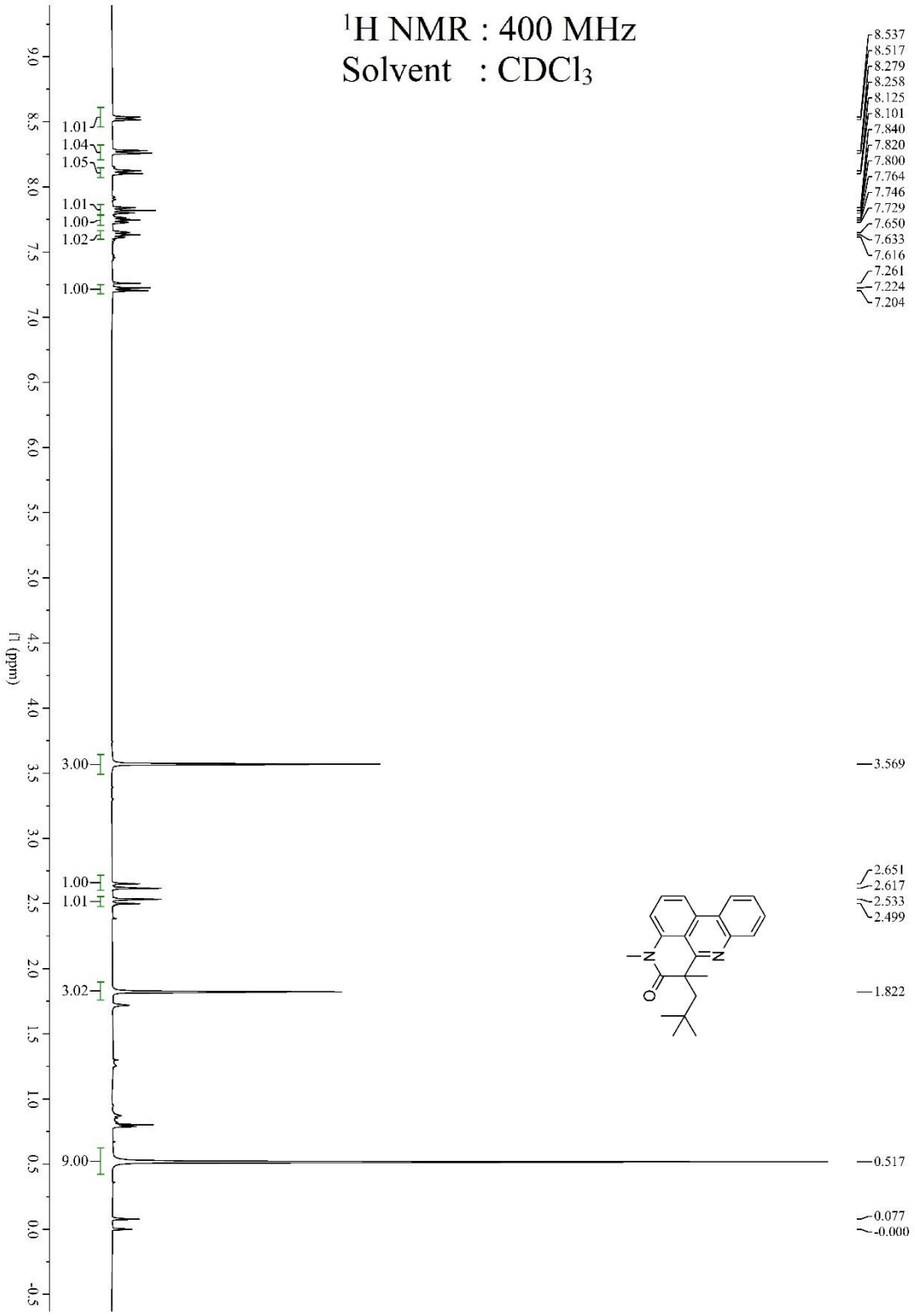
4,6-Dimethyl-6-pentyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one

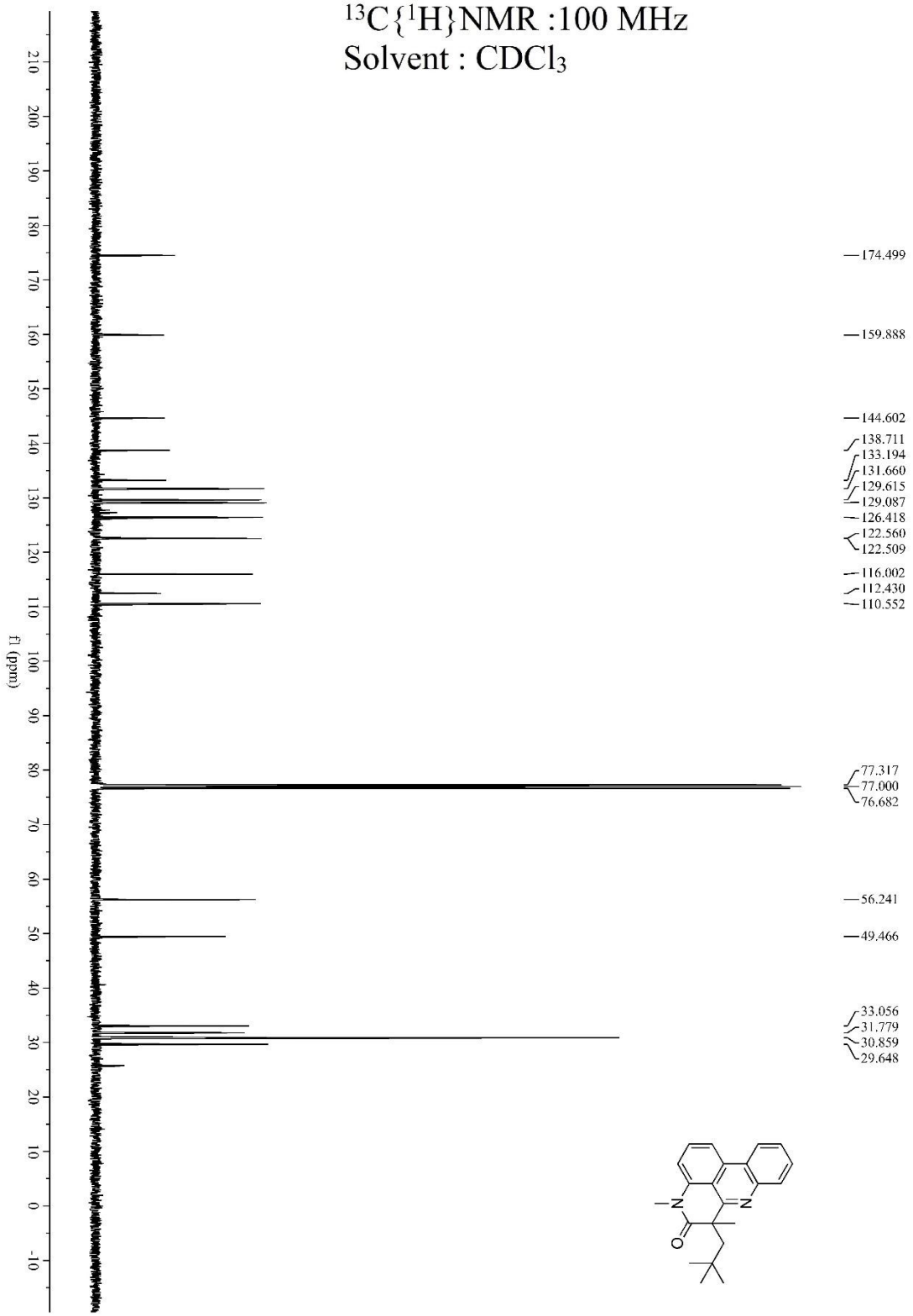
(3ad)



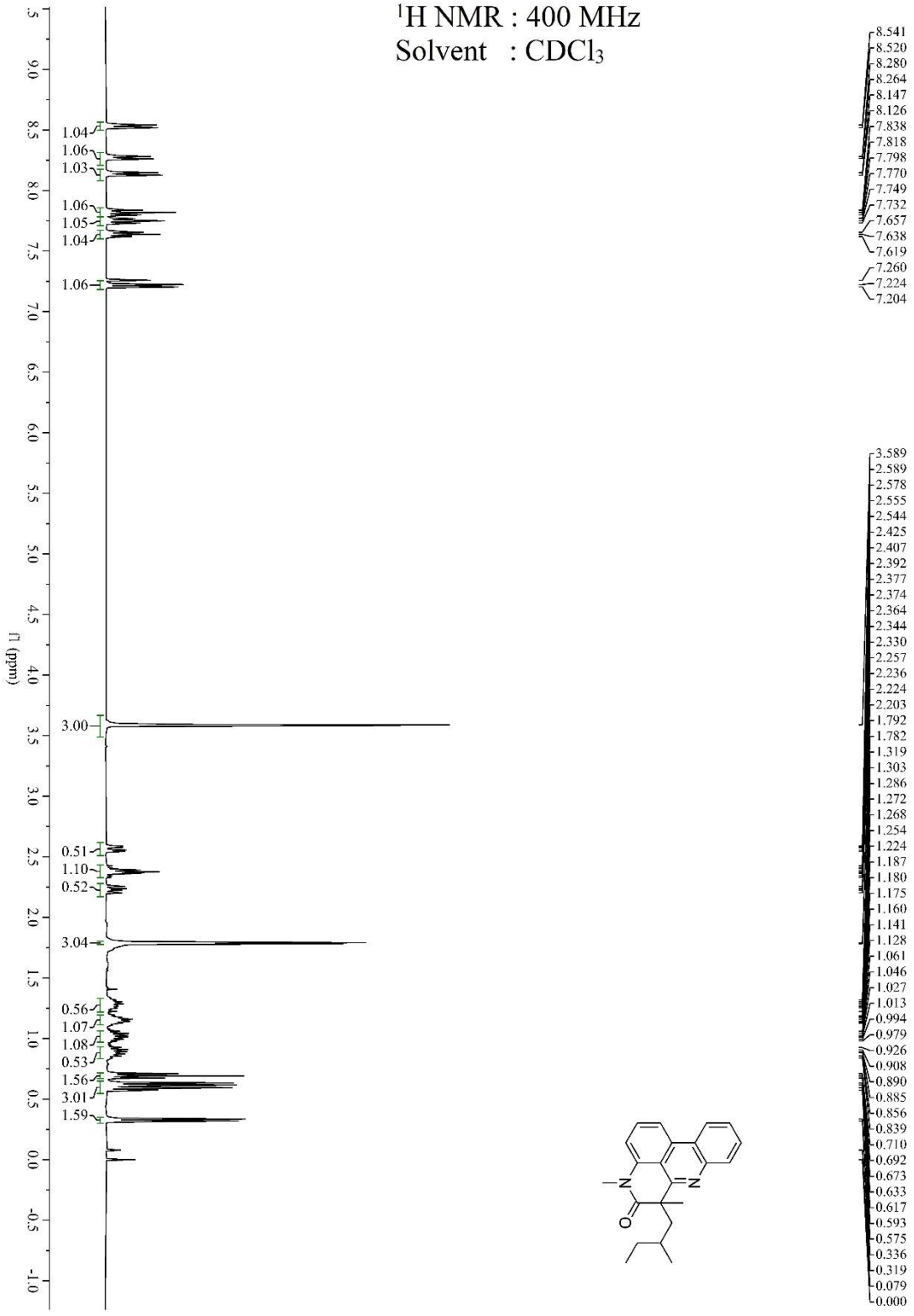

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.380
160.052
144.988
138.900
133.052
131.649
129.782
129.034
126.436
122.597
122.496
115.955
112.449
110.604
77.318
77.000
76.682
51.429
43.260
31.914
29.655
28.375
24.966
22.239
13.898

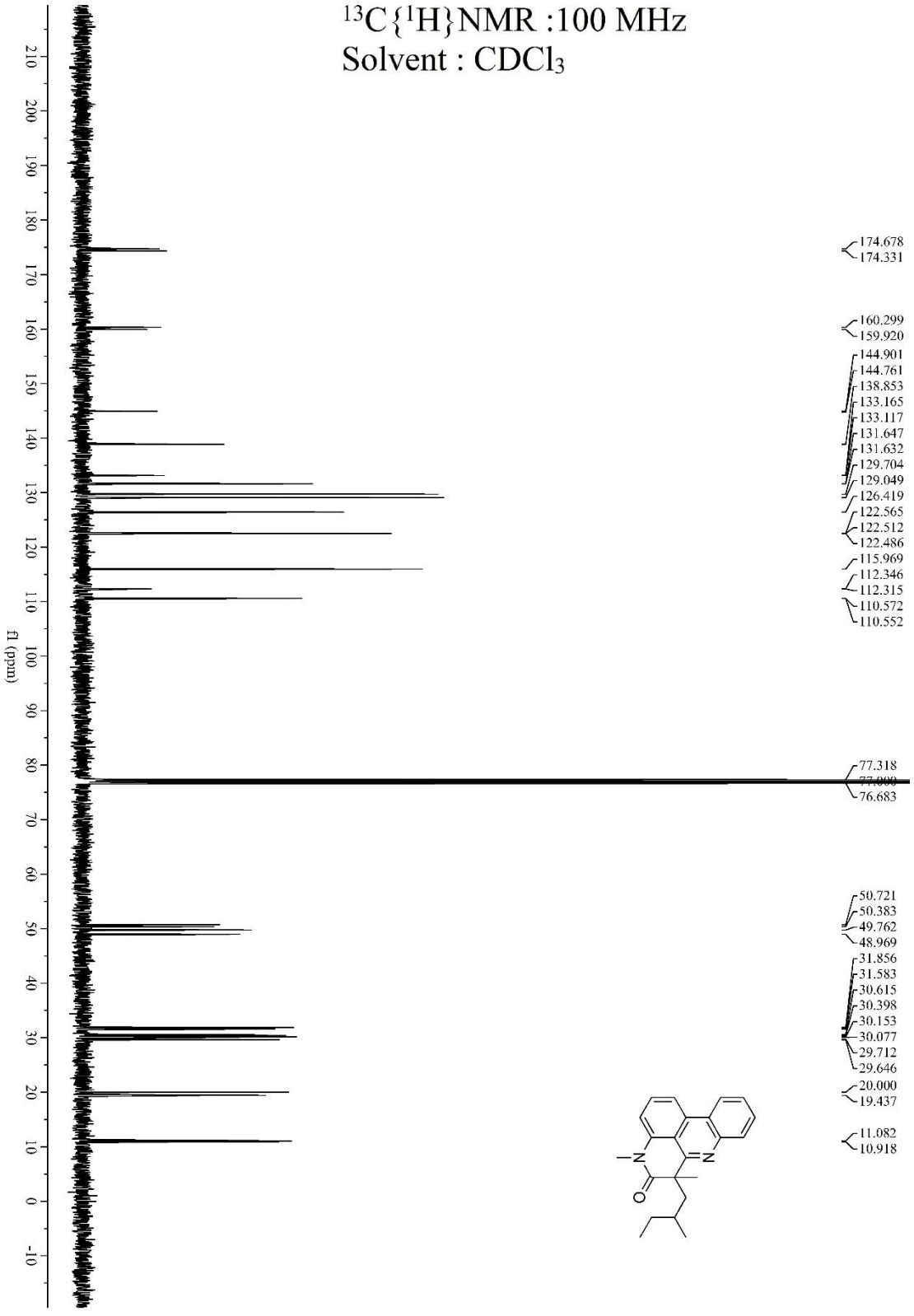
4,6-Dimethyl-6-neopentyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ae)



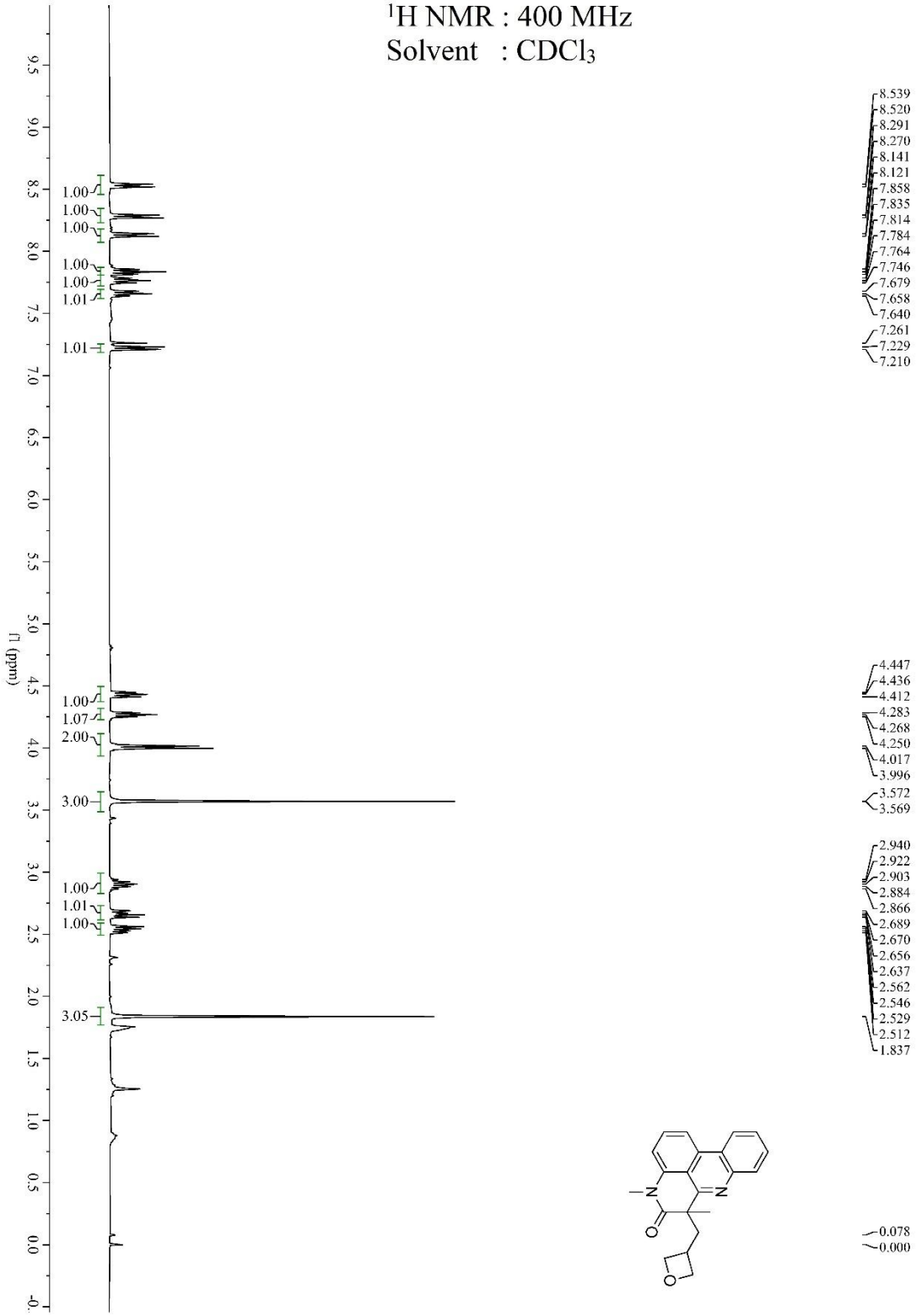

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.499
159.888
144.602
138.711
133.194
131.660
129.615
129.087
126.418
122.560
122.509
116.002
112.430
110.552
77.317
77.000
76.682
56.241
49.466
33.056
31.779
30.859
29.648

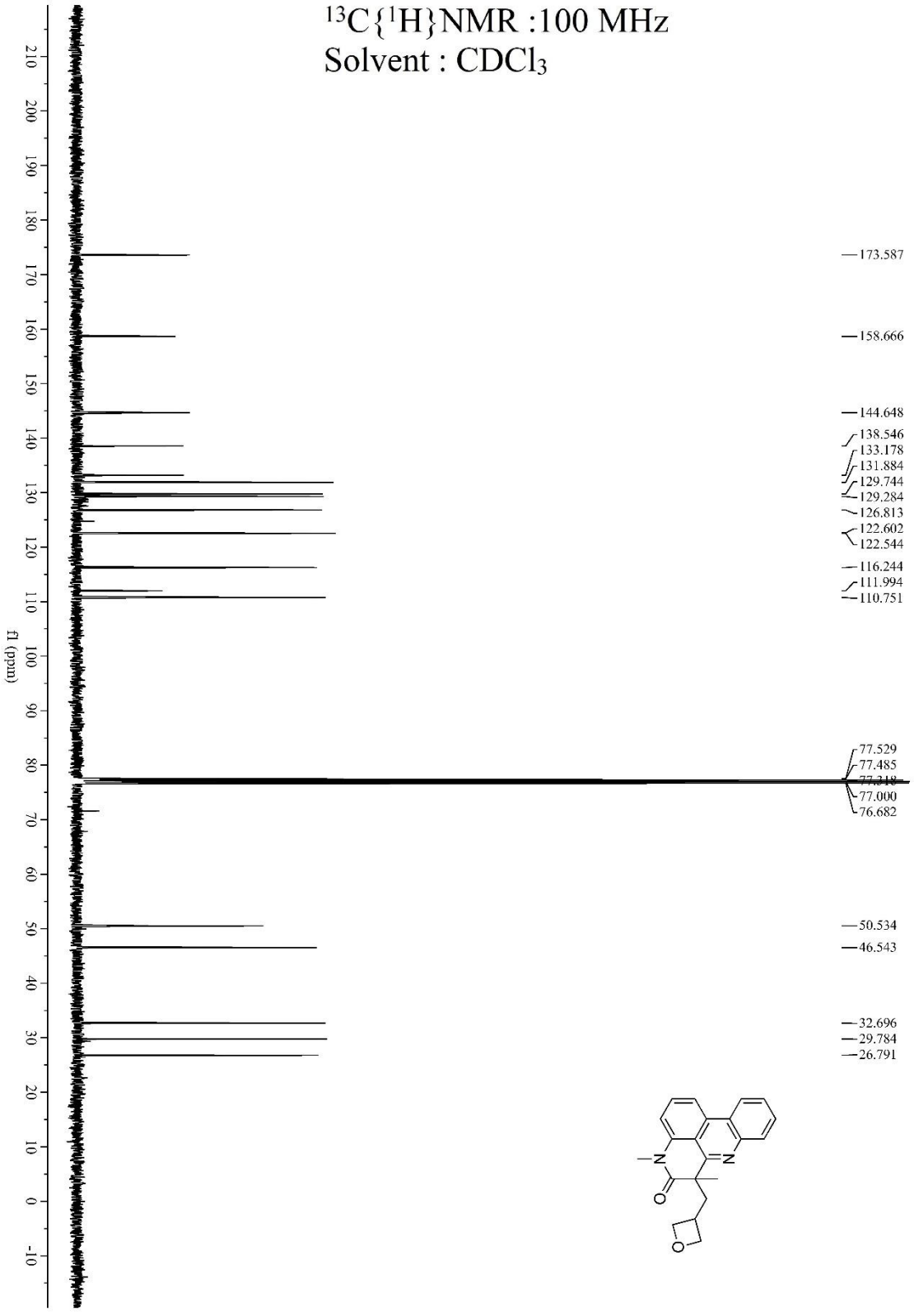
4,6-Dimethyl-6-(2-methylbutyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3af), dr=1:1



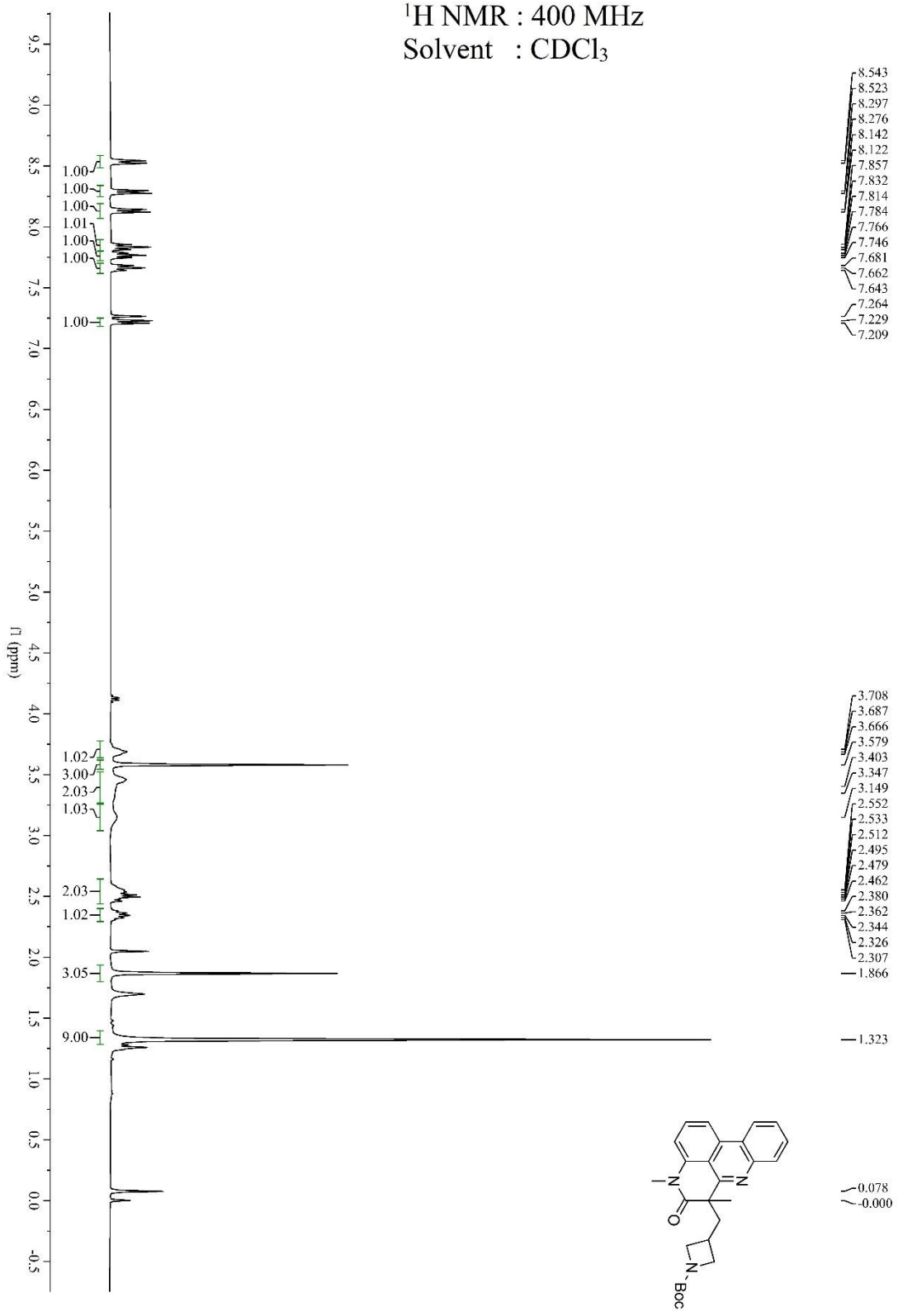

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.678
174.331
160.299
159.920
144.901
144.761
138.853
133.165
133.117
131.647
131.632
129.704
129.049
126.419
122.565
122.512
122.486
115.969
112.346
112.315
110.572
110.552
77.318
77.000
76.683
50.721
50.383
49.762
48.969
31.856
31.583
30.615
30.398
30.153
30.077
29.712
29.646
20.000
19.437
11.082
10.918

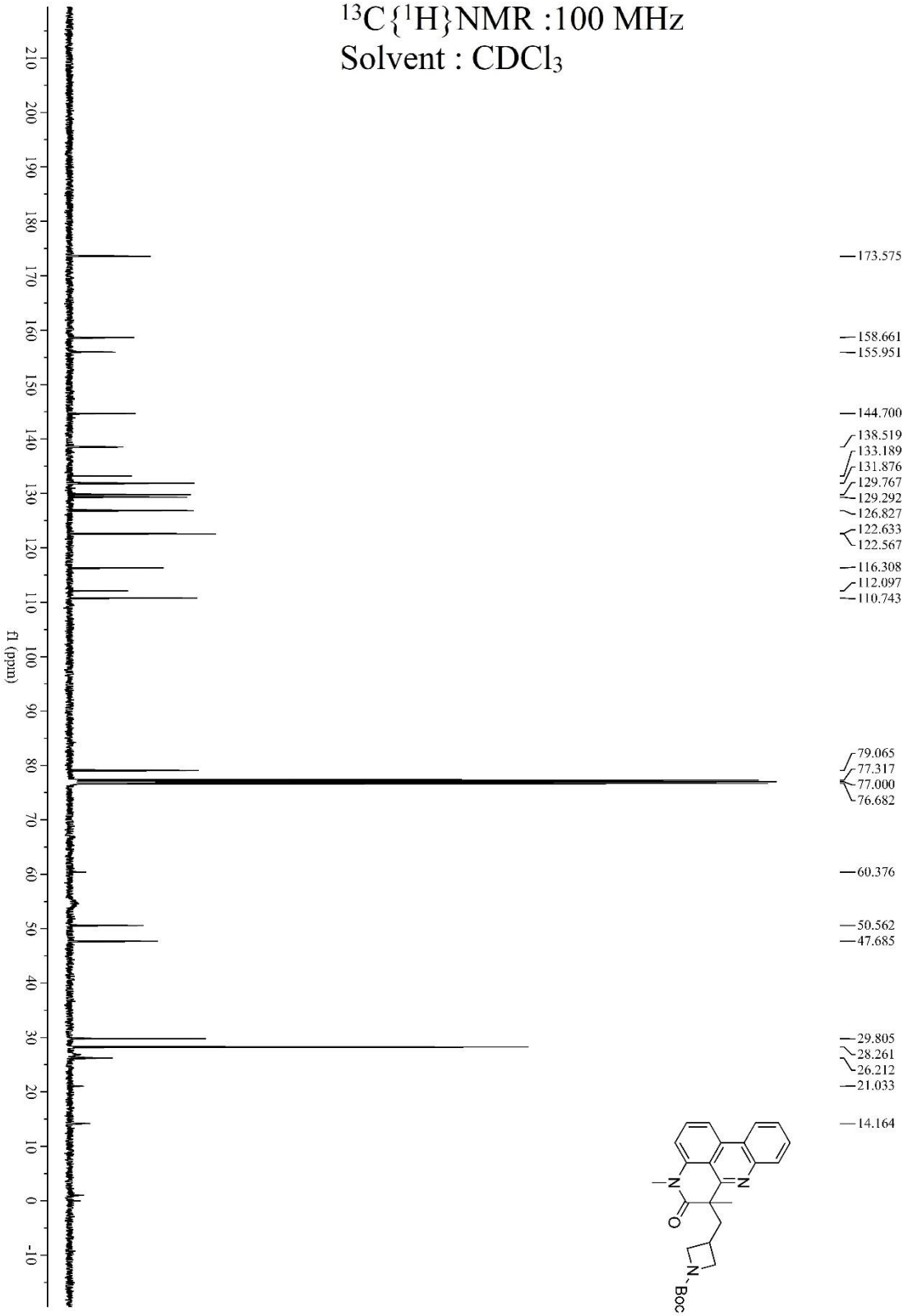
4,6-Dimethyl-6-(oxetan-3-ylmethyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ag)



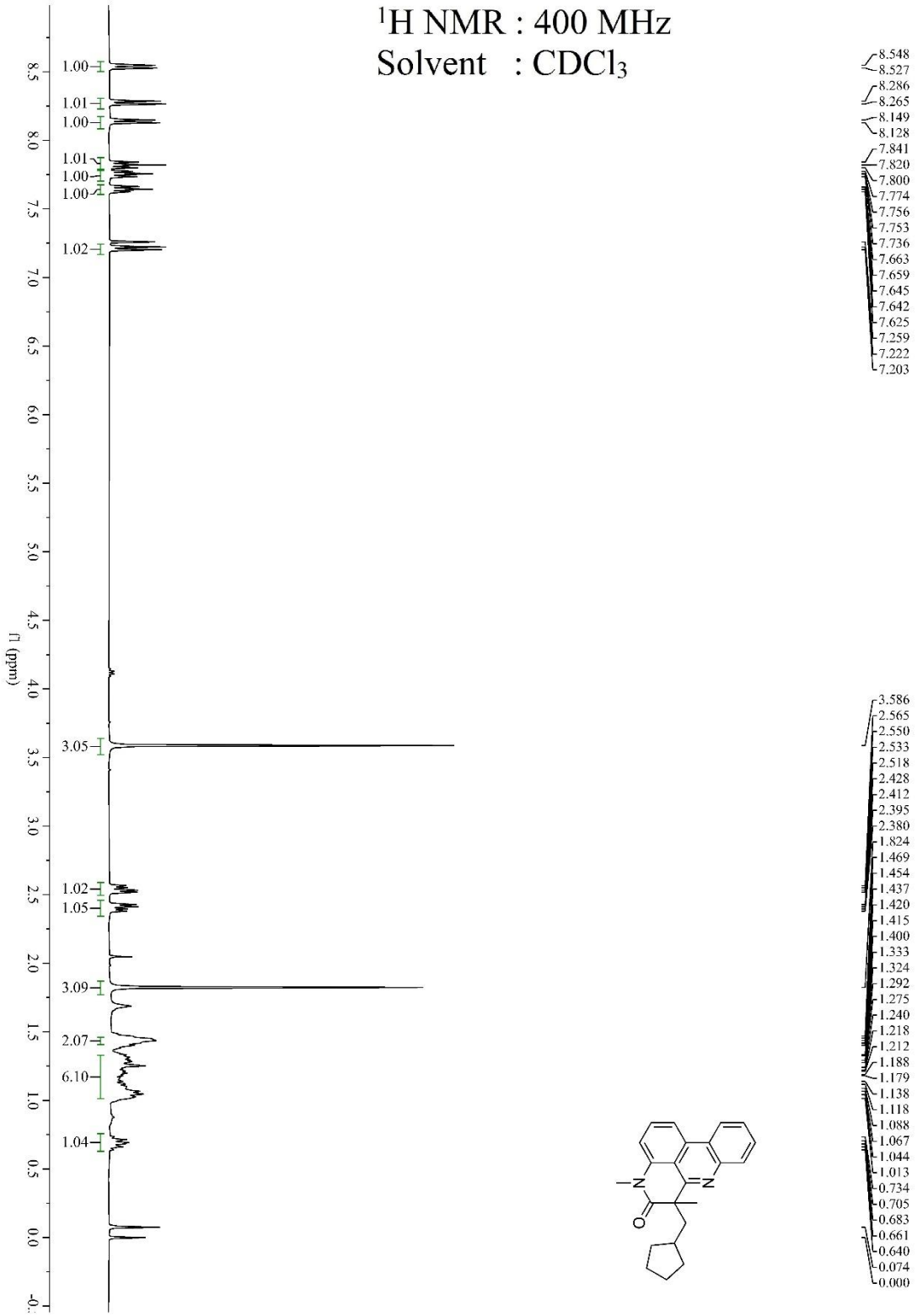

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
173.587
158.666
144.648
138.546
133.178
131.884
129.744
129.284
126.813
122.602
122.544
116.244
111.994
110.751
77.529
77.485
77.318
77.000
76.682
50.534
46.543
32.696
29.784
26.791

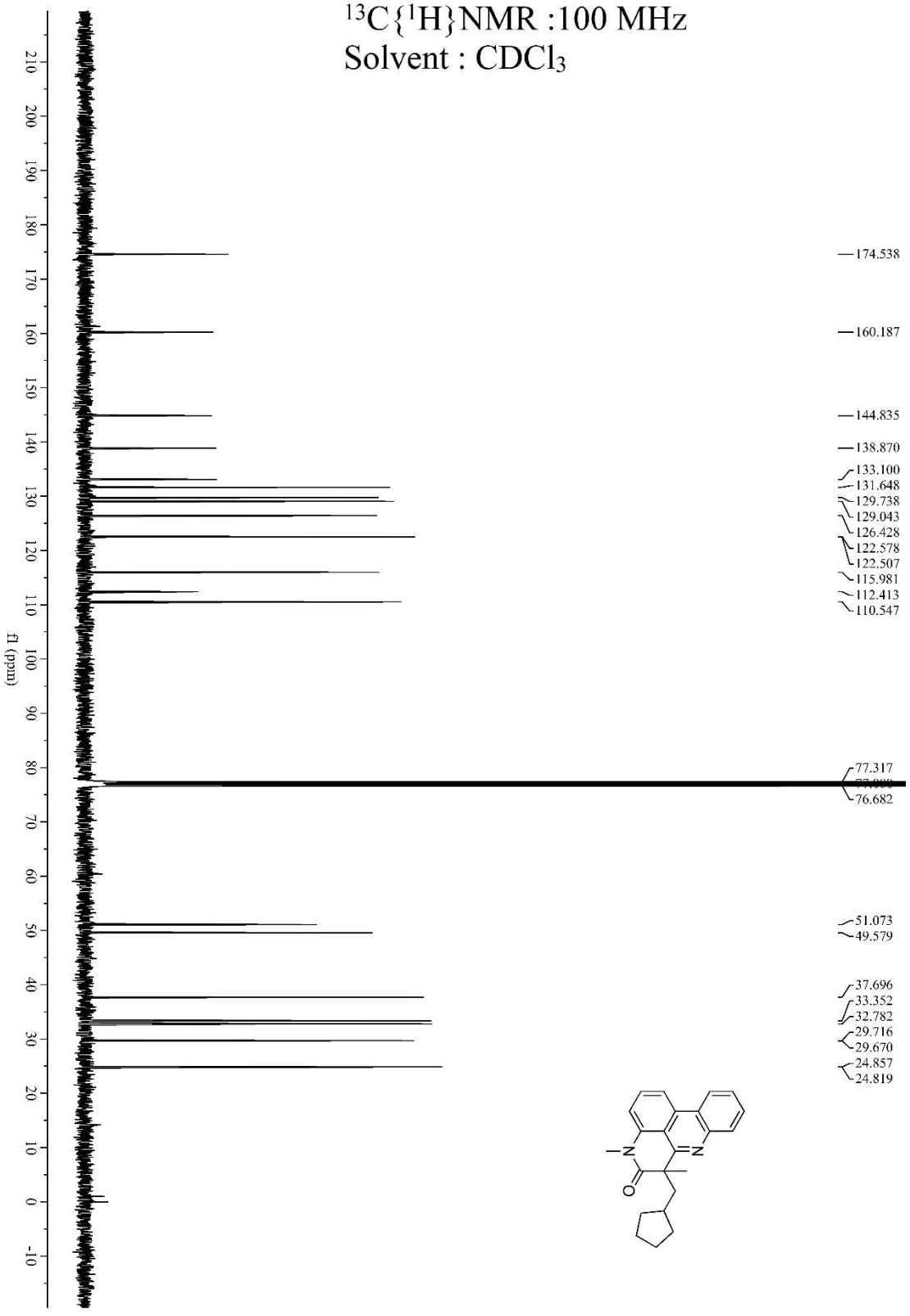
Tert-butyl 3-((4,6-dimethyl-5-oxo-5,6-dihydro-4*H*-pyrido [4,3,2-*gh*]phenanthridin- 6-yl)methyl)azetidine-1-carboxylate (3ah)



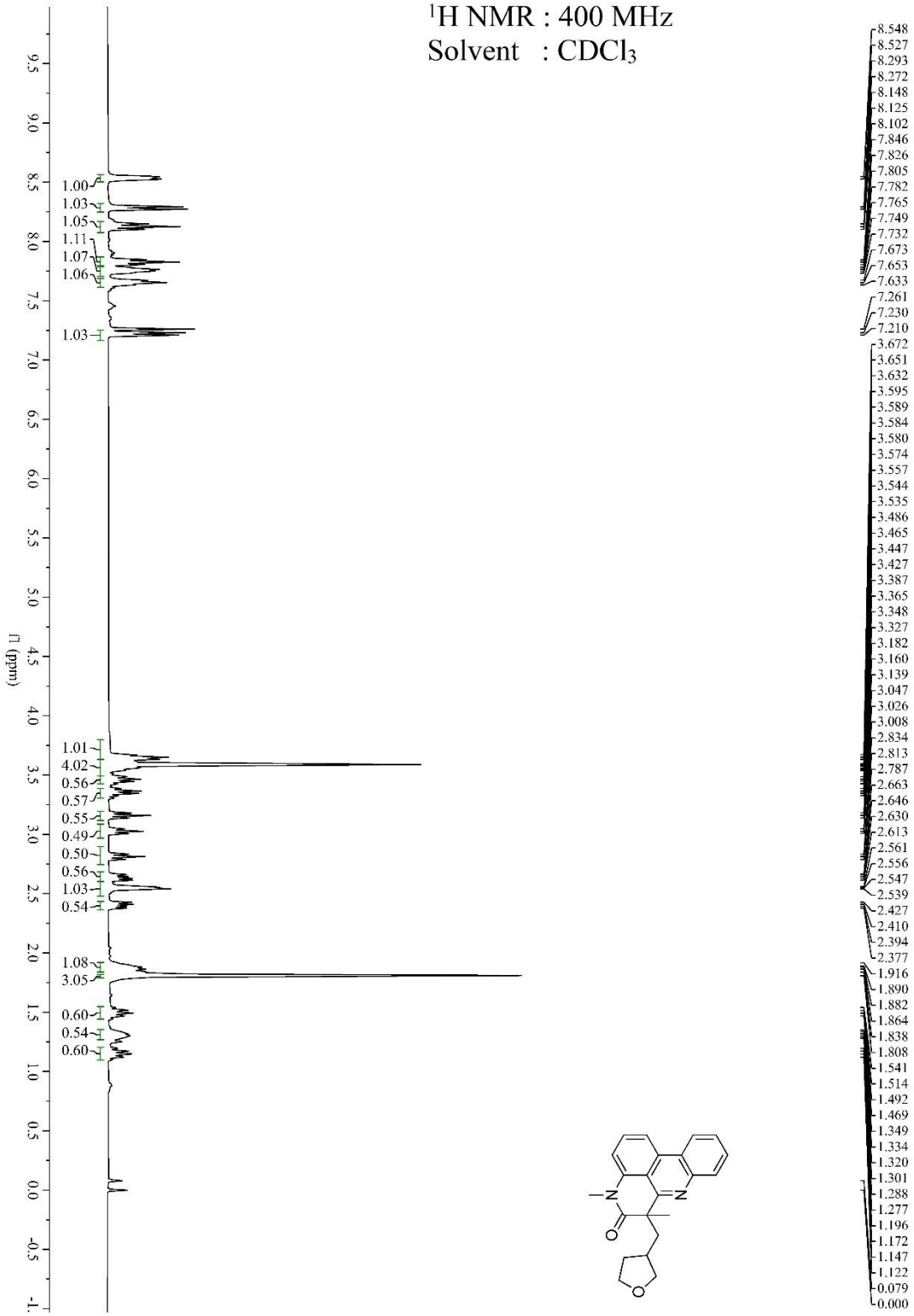

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
173.575
158.661
155.951
144.700
138.519
133.189
131.876
129.767
129.292
126.827
122.633
122.567
116.308
112.097
110.743
79.065
77.317
77.000
76.682
60.376
50.562
47.685
29.805
28.261
26.212
21.033
14.164
N
O
N
Boc

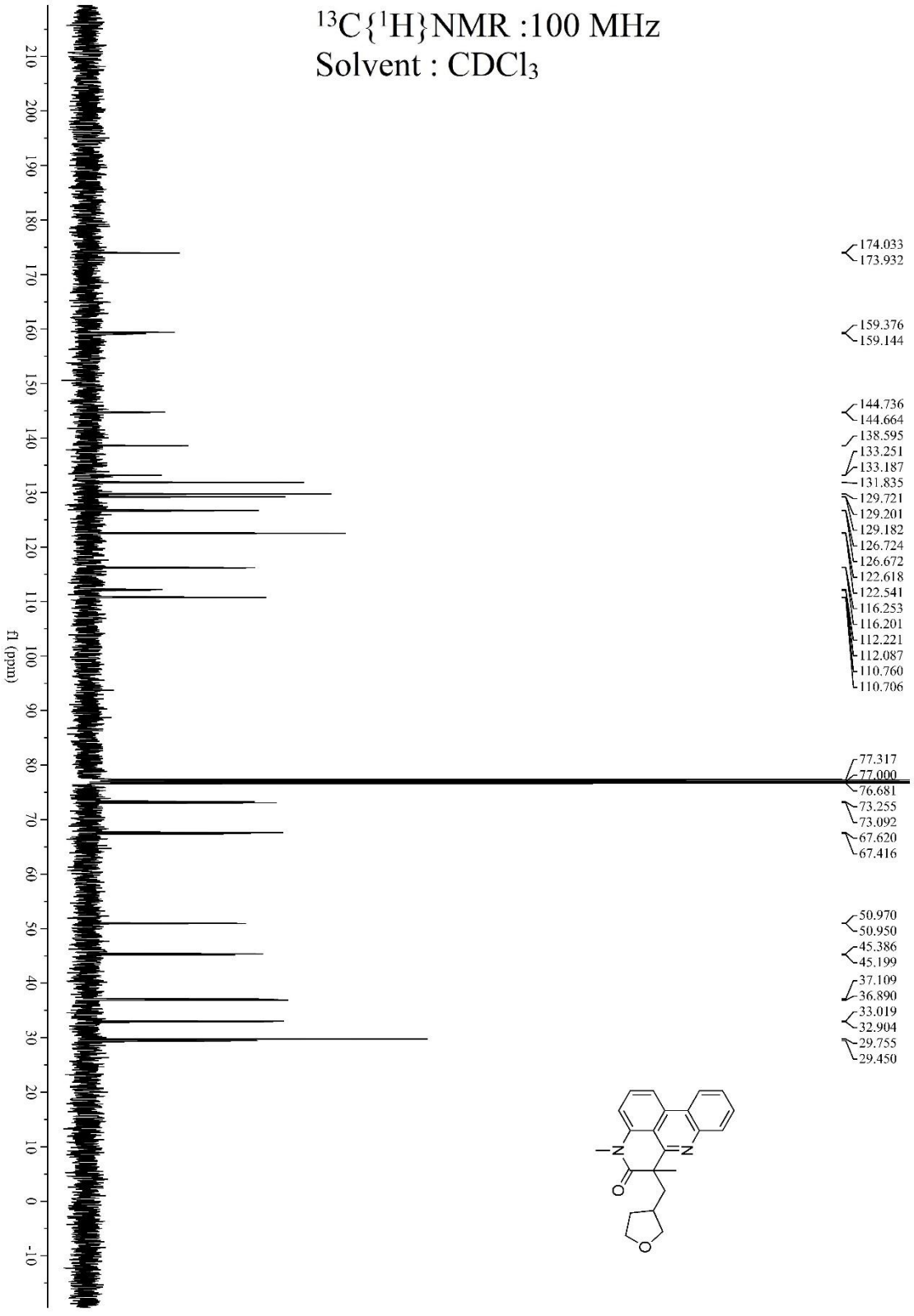
6-(Cyclopentylmethyl)-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ai)




$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.538
160.187
144.835
138.870
133.100
131.648
129.738
129.043
126.428
122.578
122.507
115.981
112.413
110.547
77.317
76.682
51.073
49.579
37.696
33.352
32.782
29.716
29.670
24.857
24.819

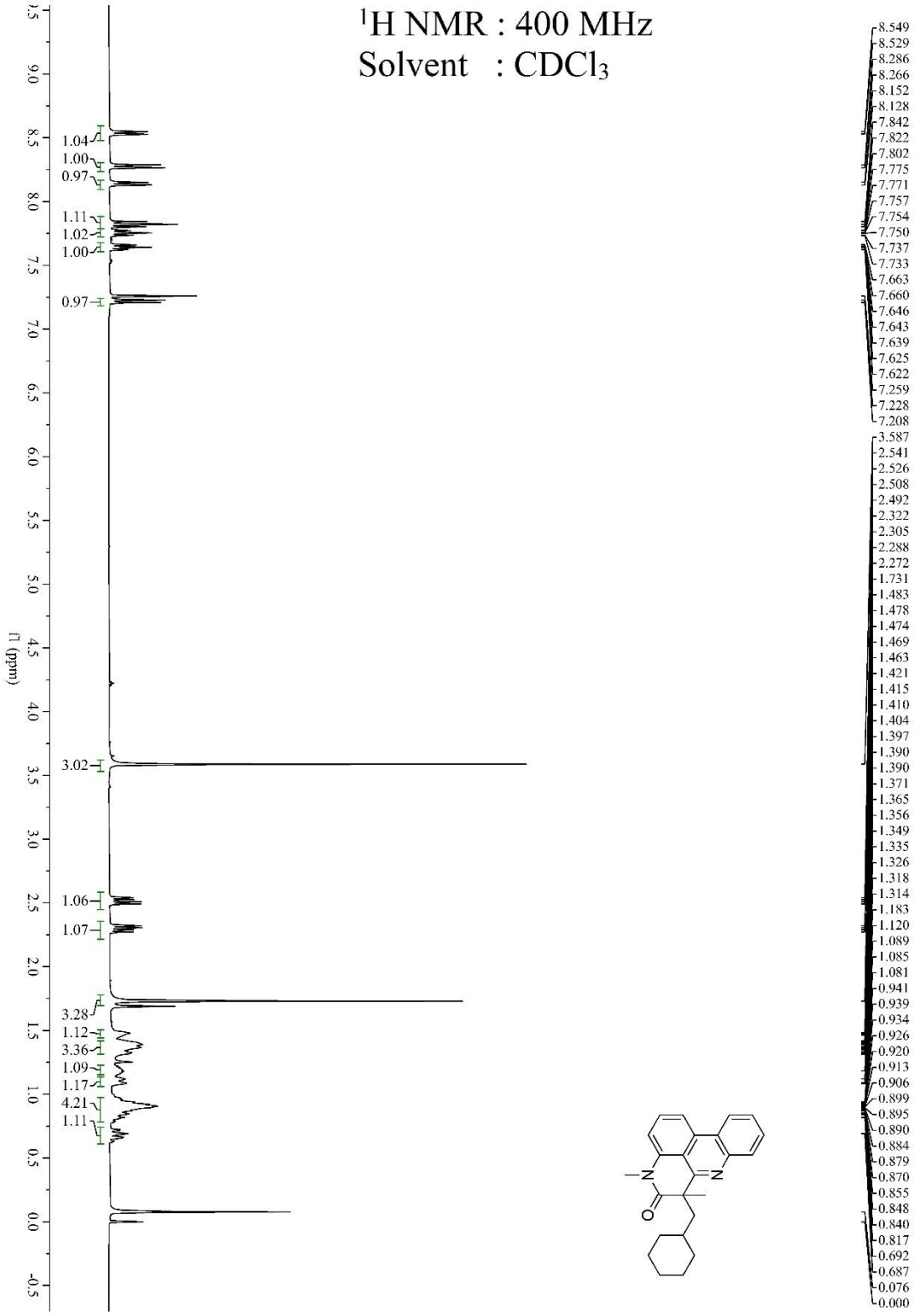
4,6-Dimethyl-6-((tetrahydrofuran-3-yl)methyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3aj), *dr* = 1 : 1

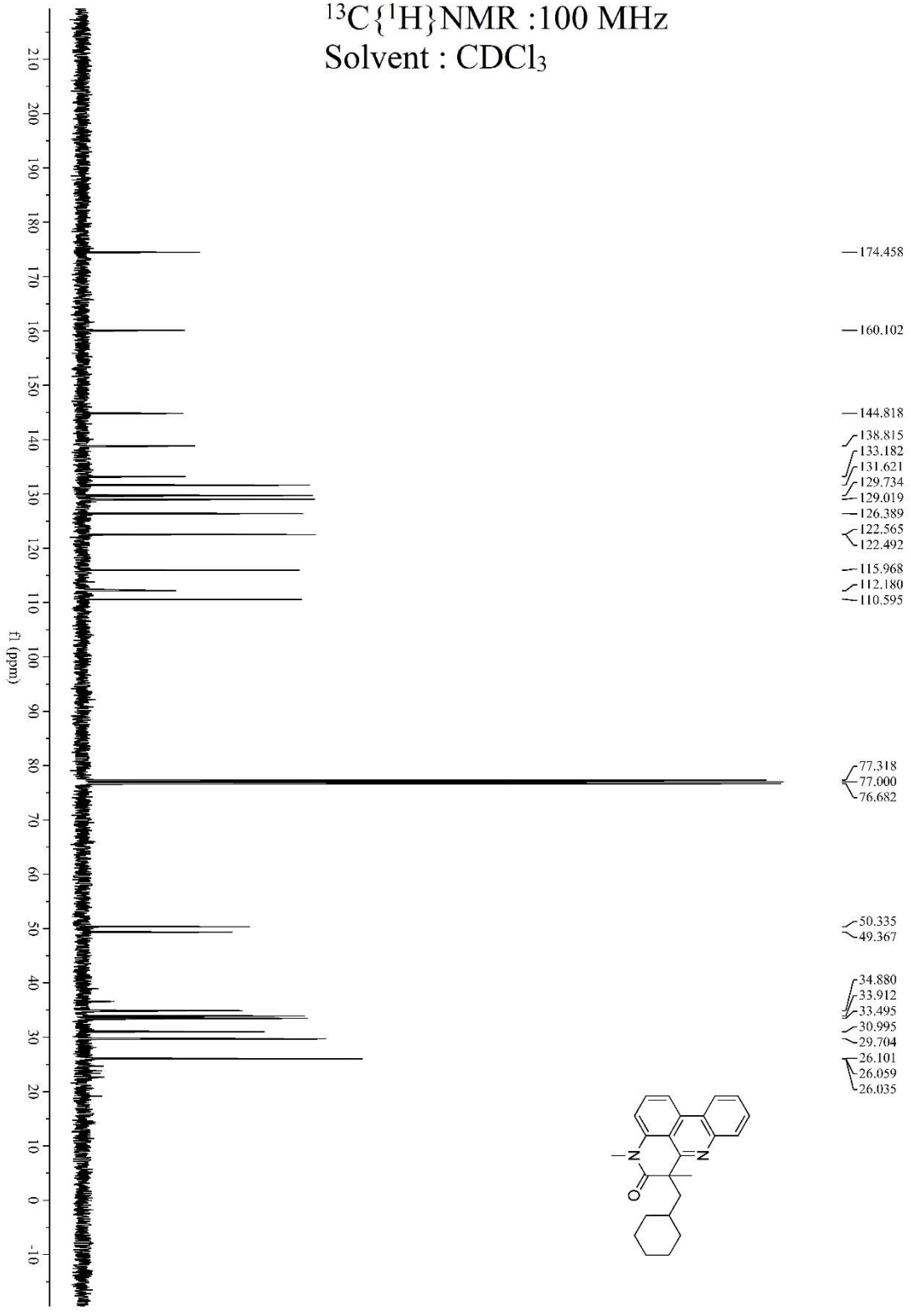



$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.033
173.932
159.376
159.144
144.736
144.664
138.595
133.251
133.187
131.835
129.721
129.201
129.182
126.724
126.672
122.618
122.541
116.253
116.201
112.221
112.087
110.760
110.706
77.317
77.000
76.681
73.255
73.092
67.620
67.416
50.970
50.950
45.386
45.199
37.109
36.890
33.019
32.904
29.755
29.450

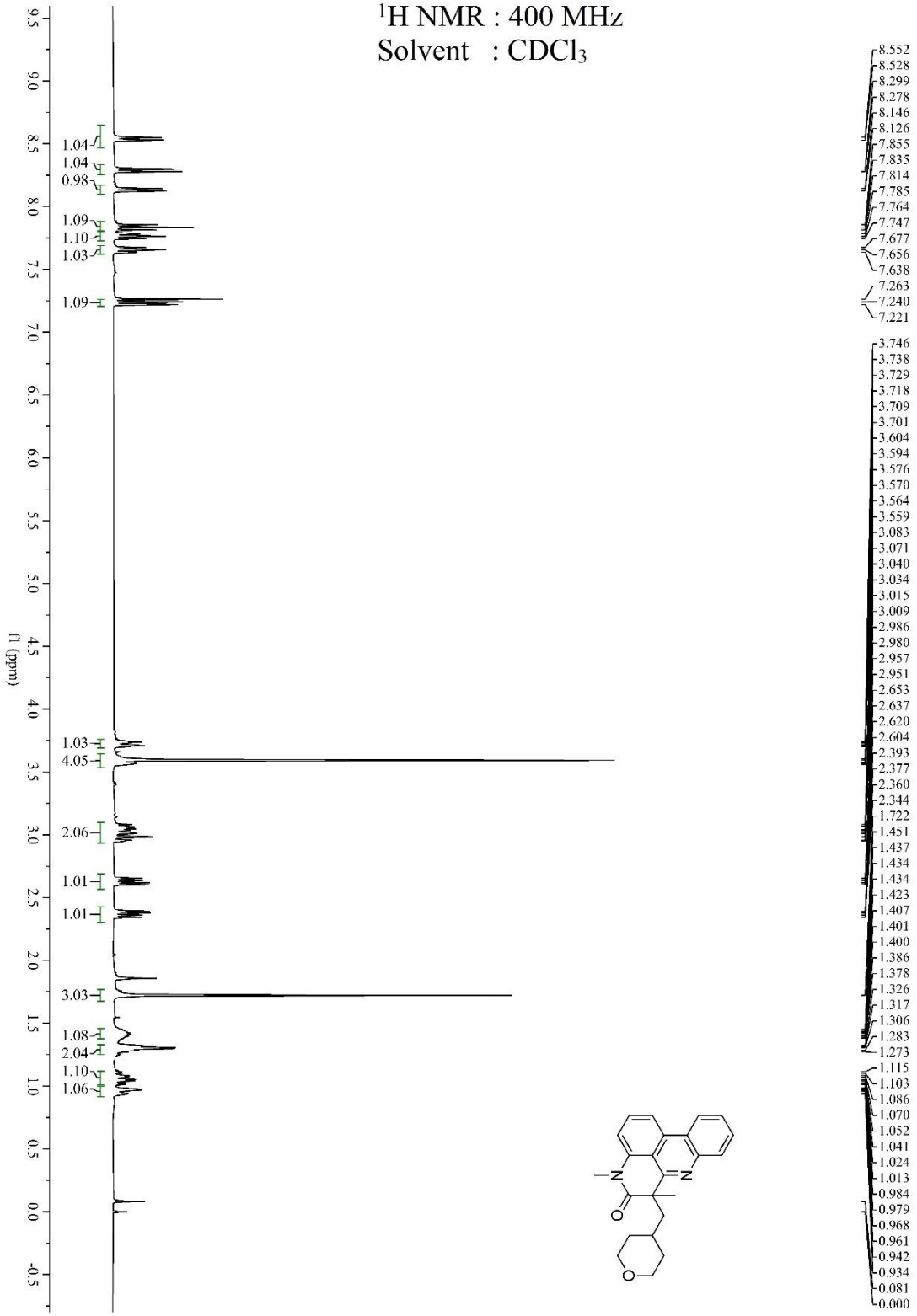
6-(Cyclohexylmethyl)-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridi

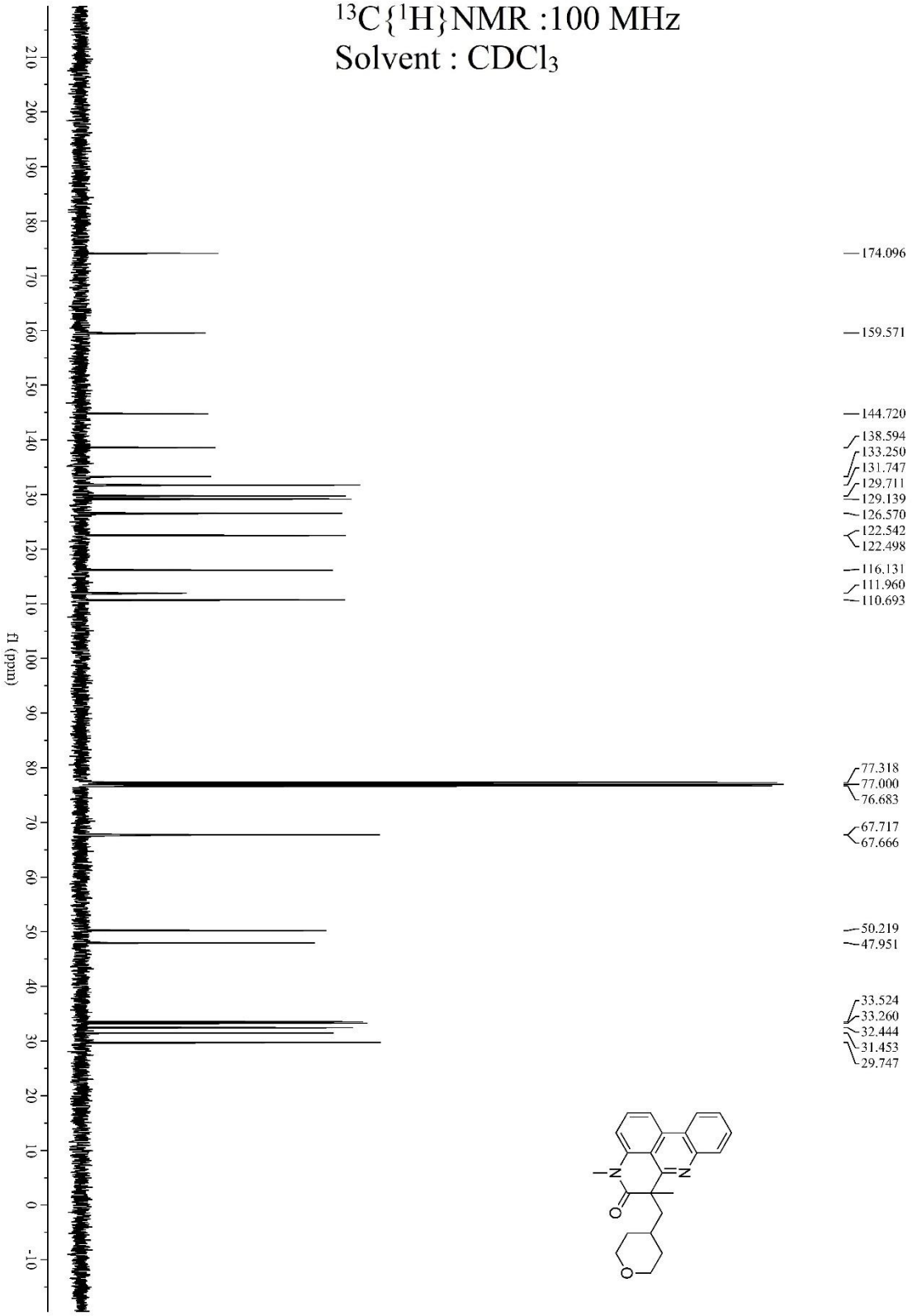
n-5(6*H*)-one (3ak)



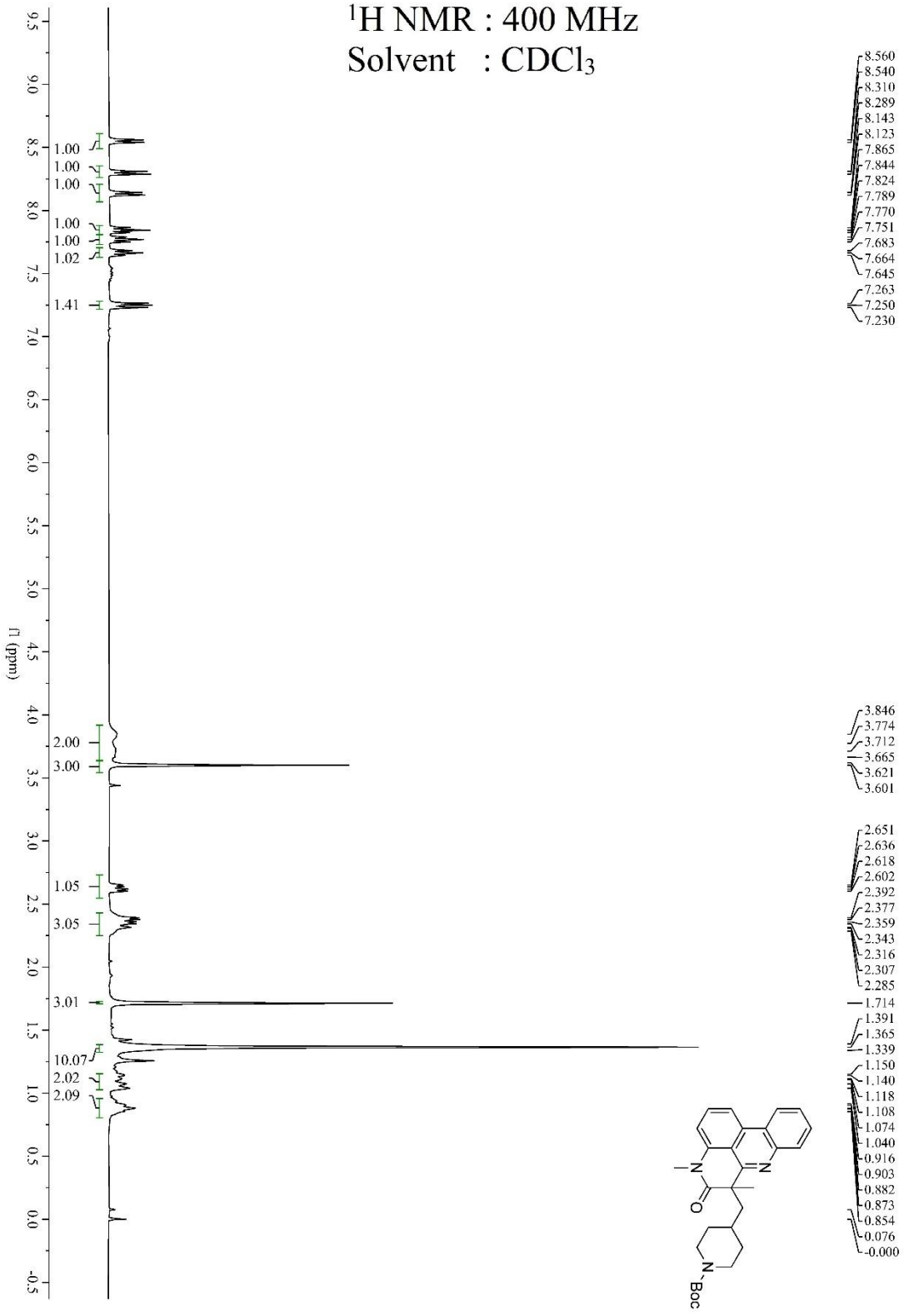

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.458
160.102
144.818
138.815
133.182
131.621
129.734
129.019
126.389
122.565
122.492
115.968
112.180
110.595
77.318
77.000
76.682
50.335
49.367
34.880
33.912
33.495
30.995
29.704
26.101
26.059
26.035

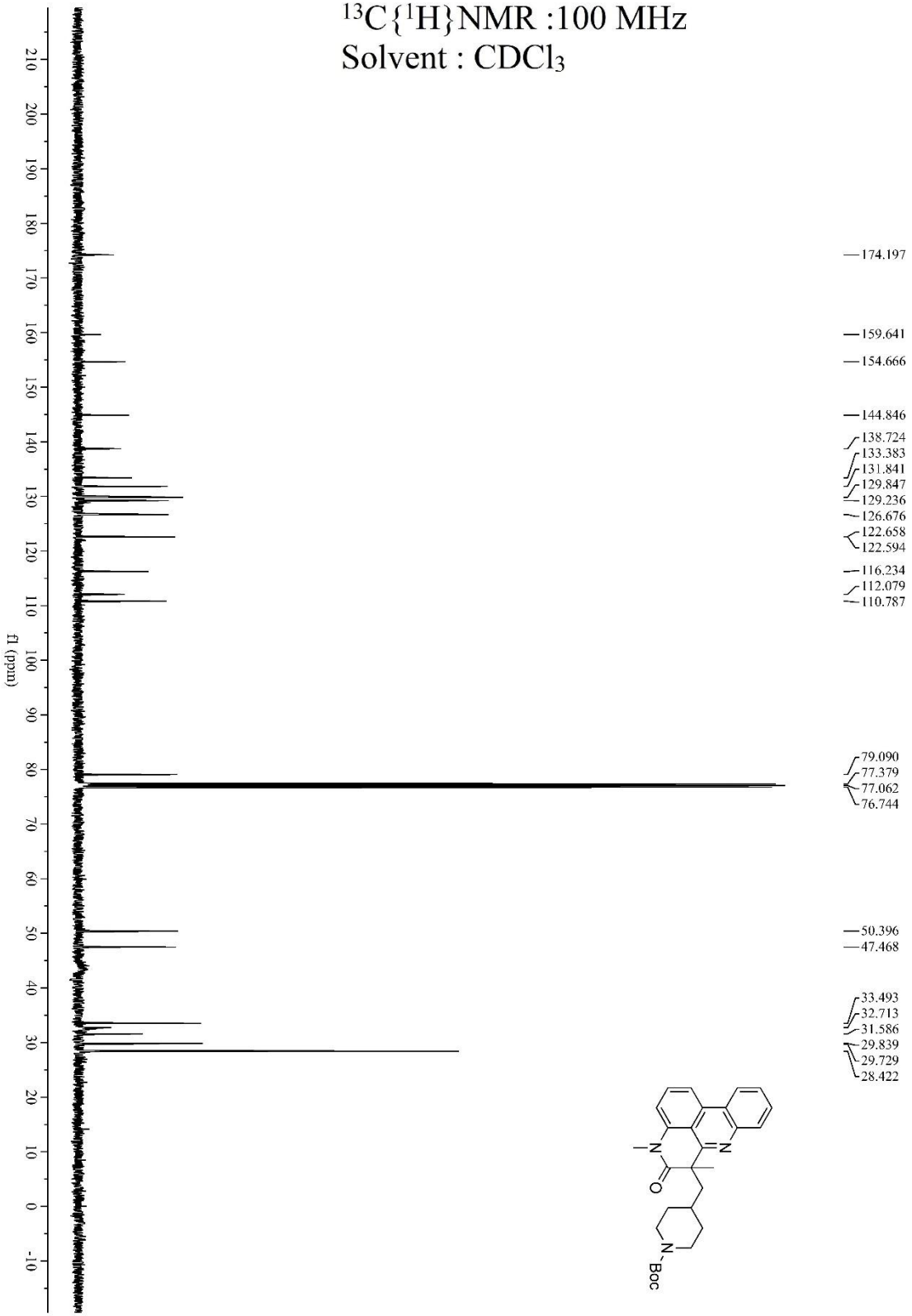
4,6-Dimethyl-6-((tetrahydro-2*H*-pyran-4-yl)methyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3al)



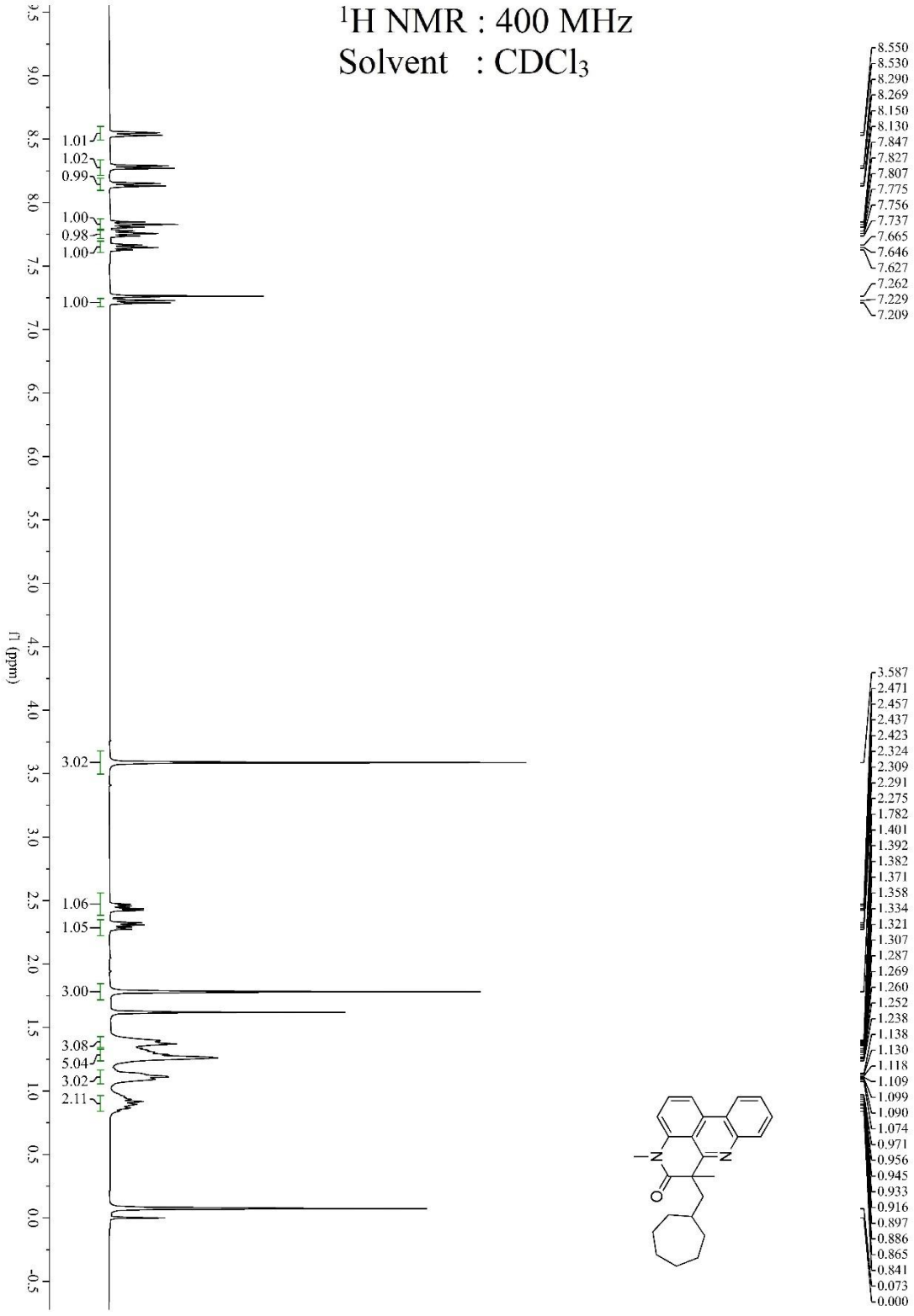

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.096
159.571
144.720
138.594
133.250
131.747
129.711
129.139
126.570
122.542
122.498
116.131
111.960
110.693
77.318
77.000
76.683
67.717
67.666
50.219
47.951
33.524
33.260
32.444
31.453
29.747

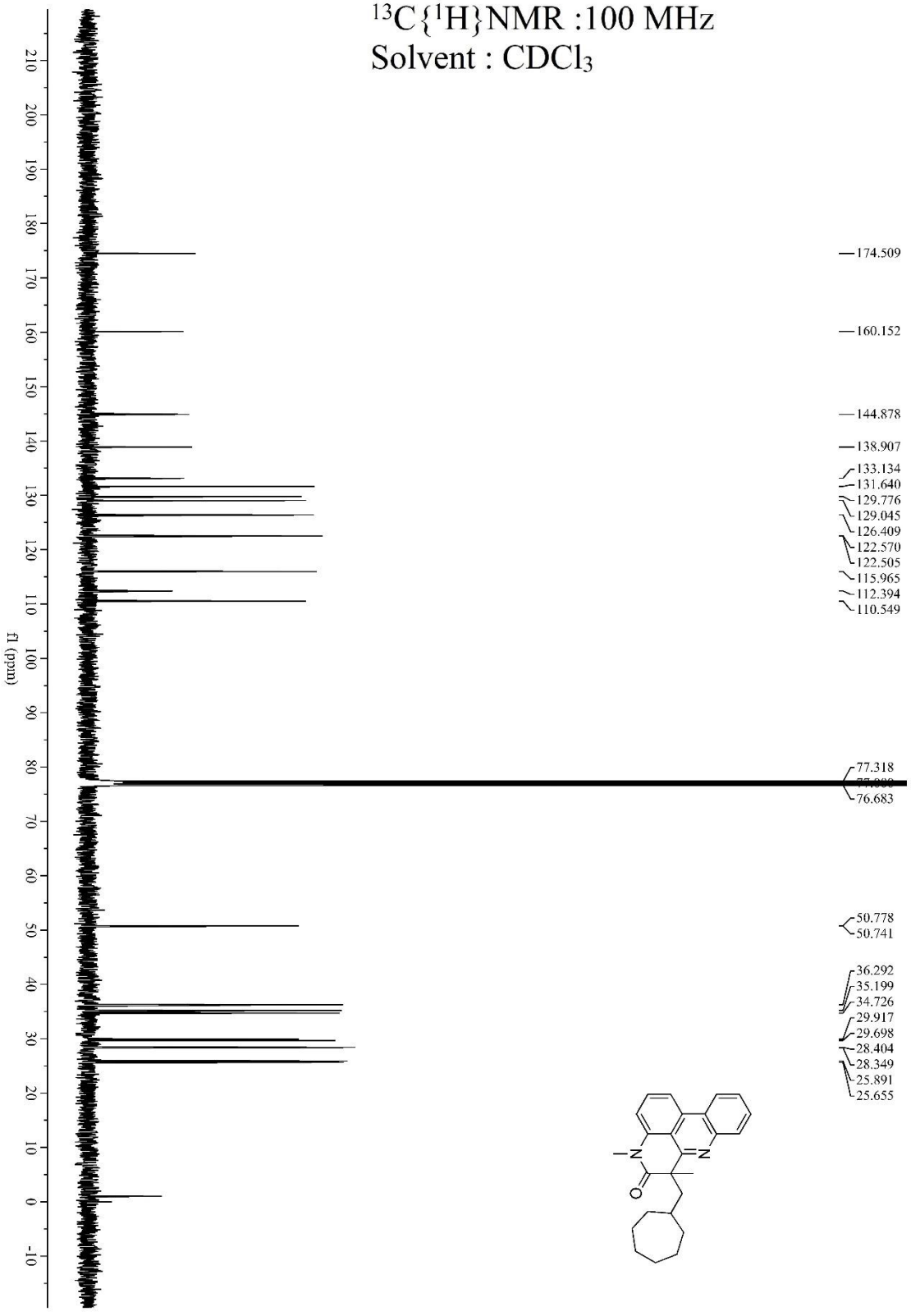
Tert-butyl 4-((4,6-dimethyl-5-oxo-5,6-dihydro-4_H_-pyrido [4,3,2-_gh_]phenanthridin-6-yl)methyl)piperidine-1-carboxylate (3am)



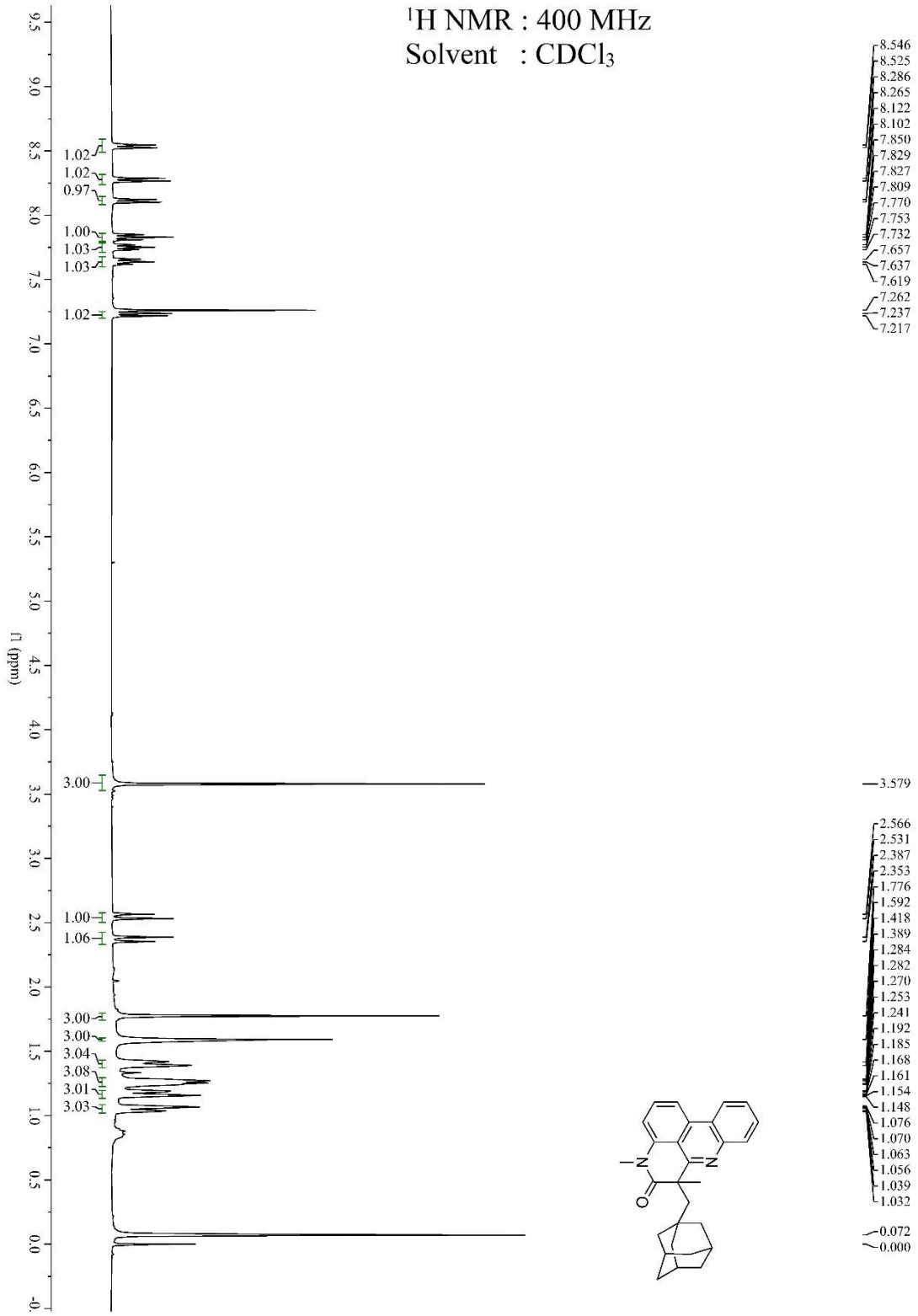

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
174.197
159.641
154.666
144.846
138.724
133.383
131.841
129.847
129.236
126.676
122.658
122.594
116.234
112.079
110.787
79.090
77.379
77.062
76.744
50.396
47.468
33.493
32.713
31.586
29.839
29.729
28.422
N
O
N
N
Boc

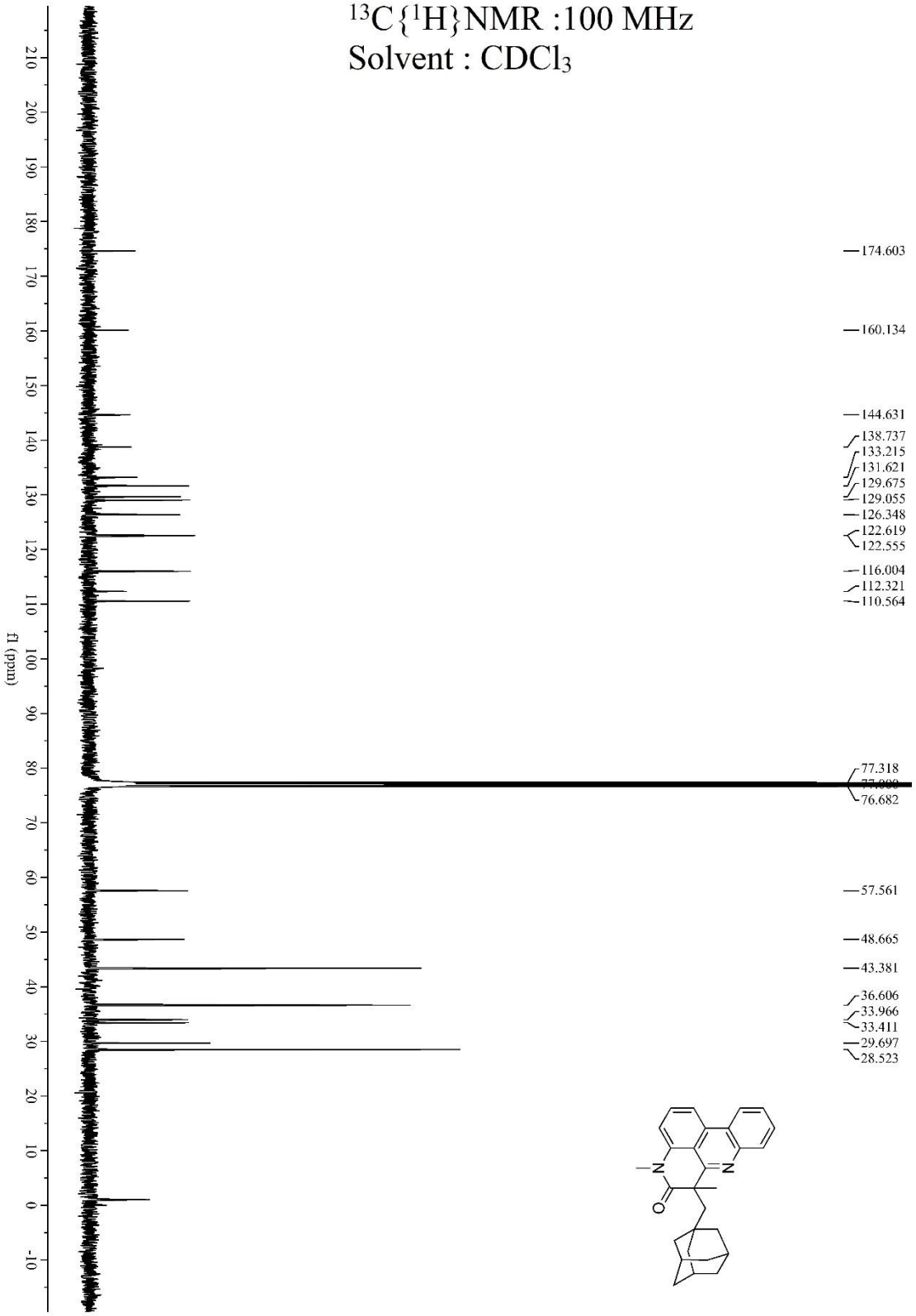
6-(Cycloheptylmethyl)-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3an)



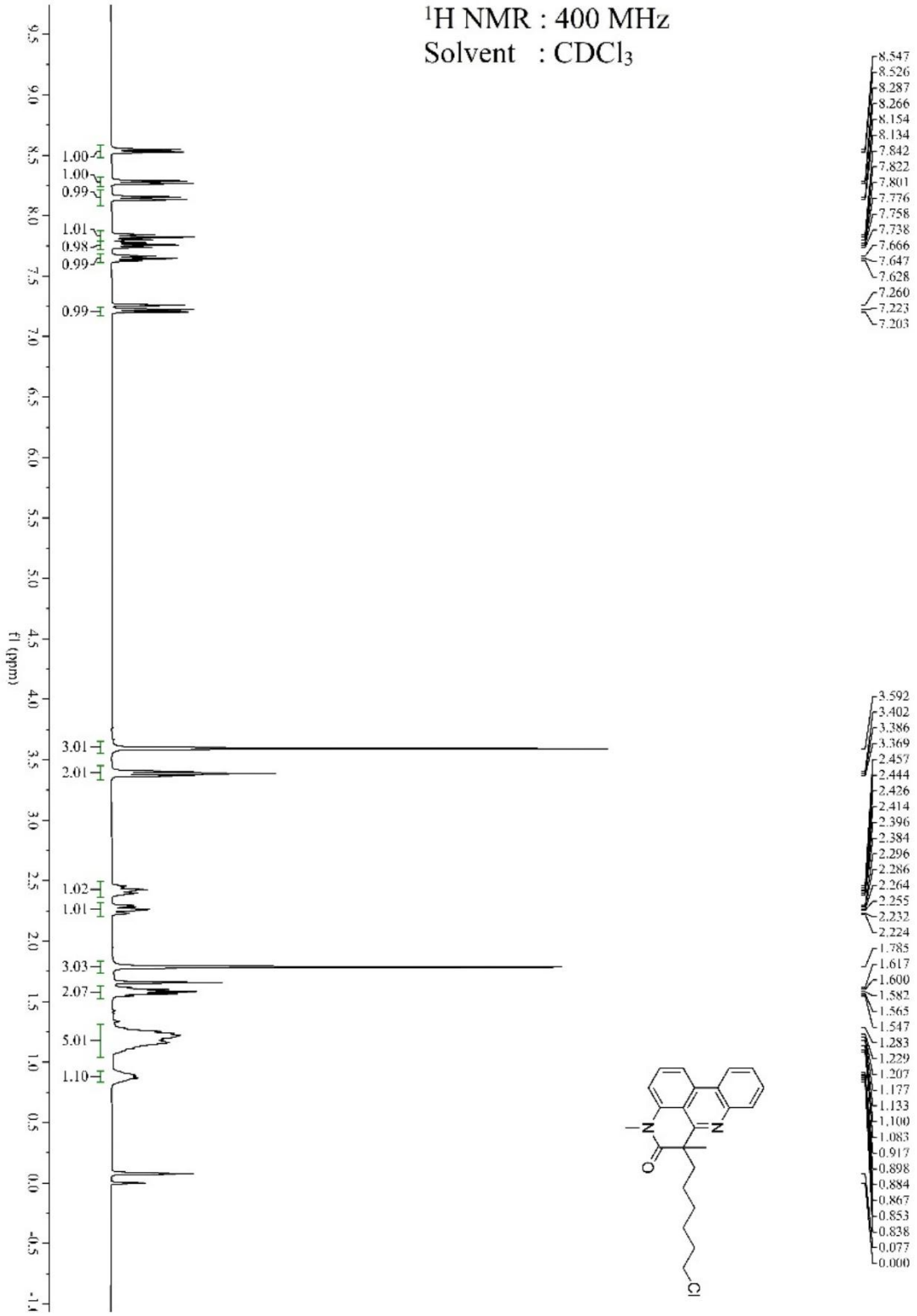

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.509
160.152
144.878
138.907
133.134
131.640
129.776
129.045
126.409
122.570
122.505
115.965
112.394
110.549
77.318
76.683
50.778
50.741
36.292
35.199
34.726
29.917
29.698
28.404
28.349
25.891
25.655
N
N
O

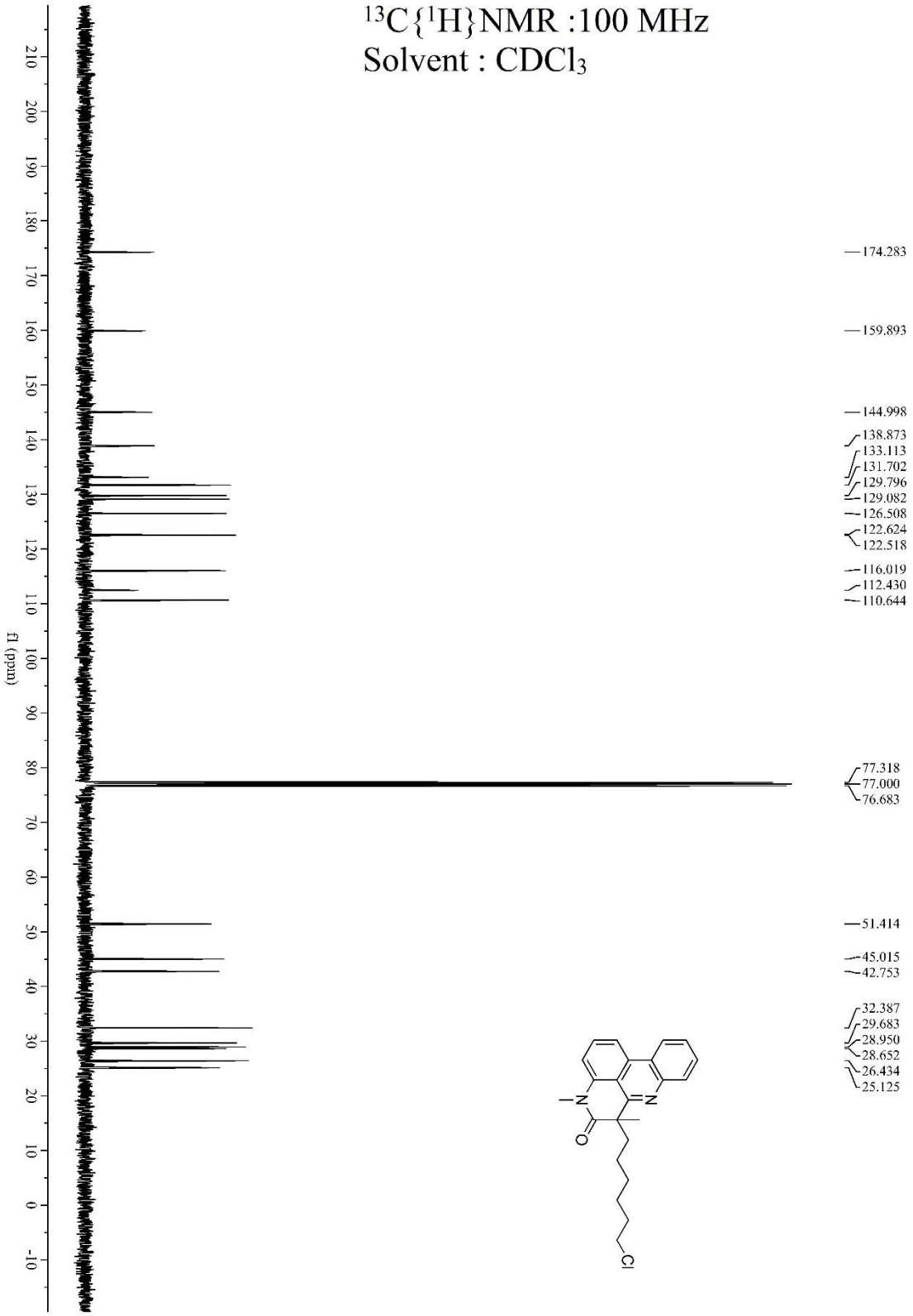
6-(((*3r,5r,7r*)-Adamantan-1-yl)methyl)-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ao)



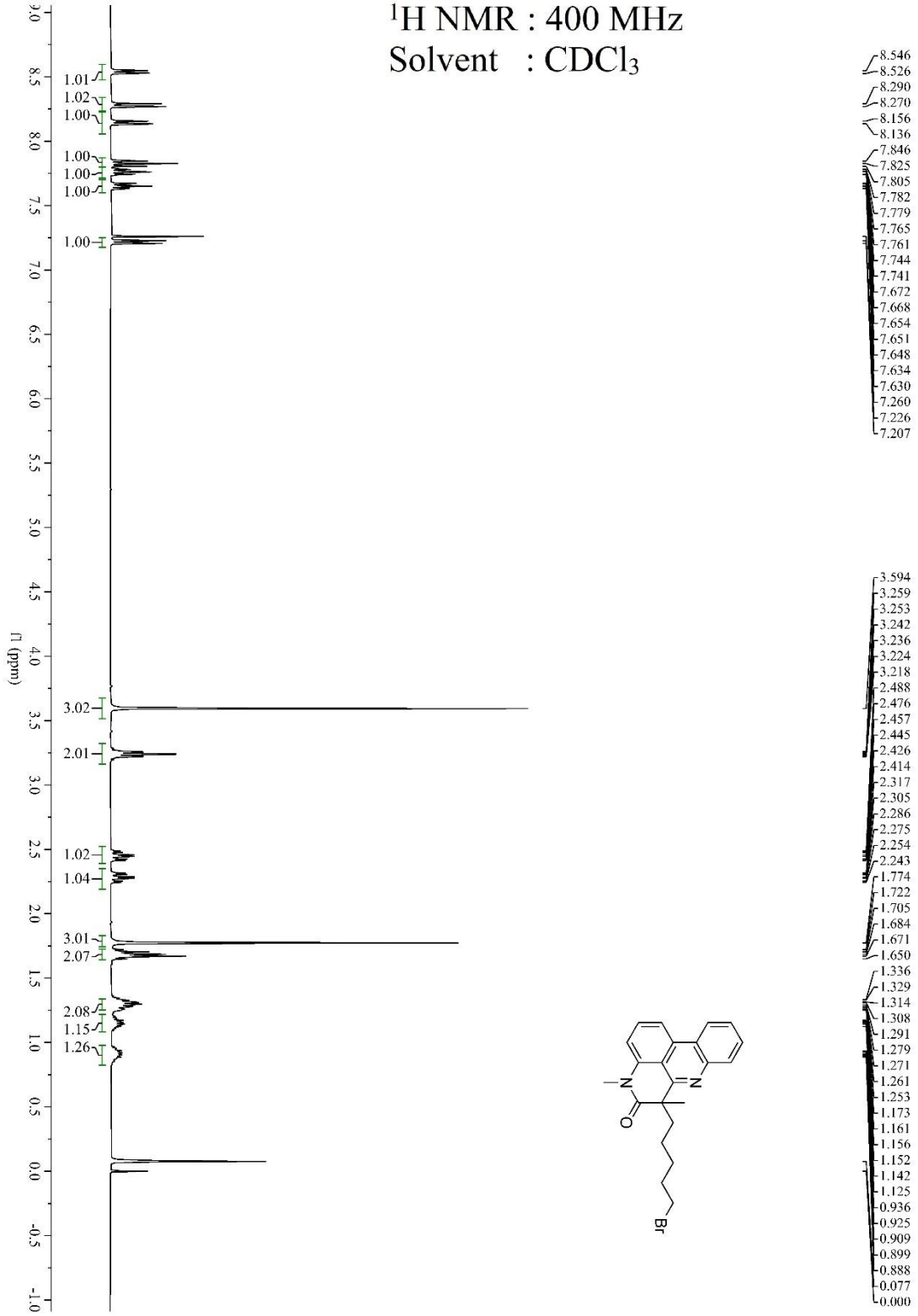

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.603
160.134
144.631
138.737
133.215
131.621
129.675
129.055
126.348
122.619
122.555
116.004
112.321
110.564
77.318
76.682
57.561
48.665
43.381
36.606
33.966
33.411
29.697
28.523

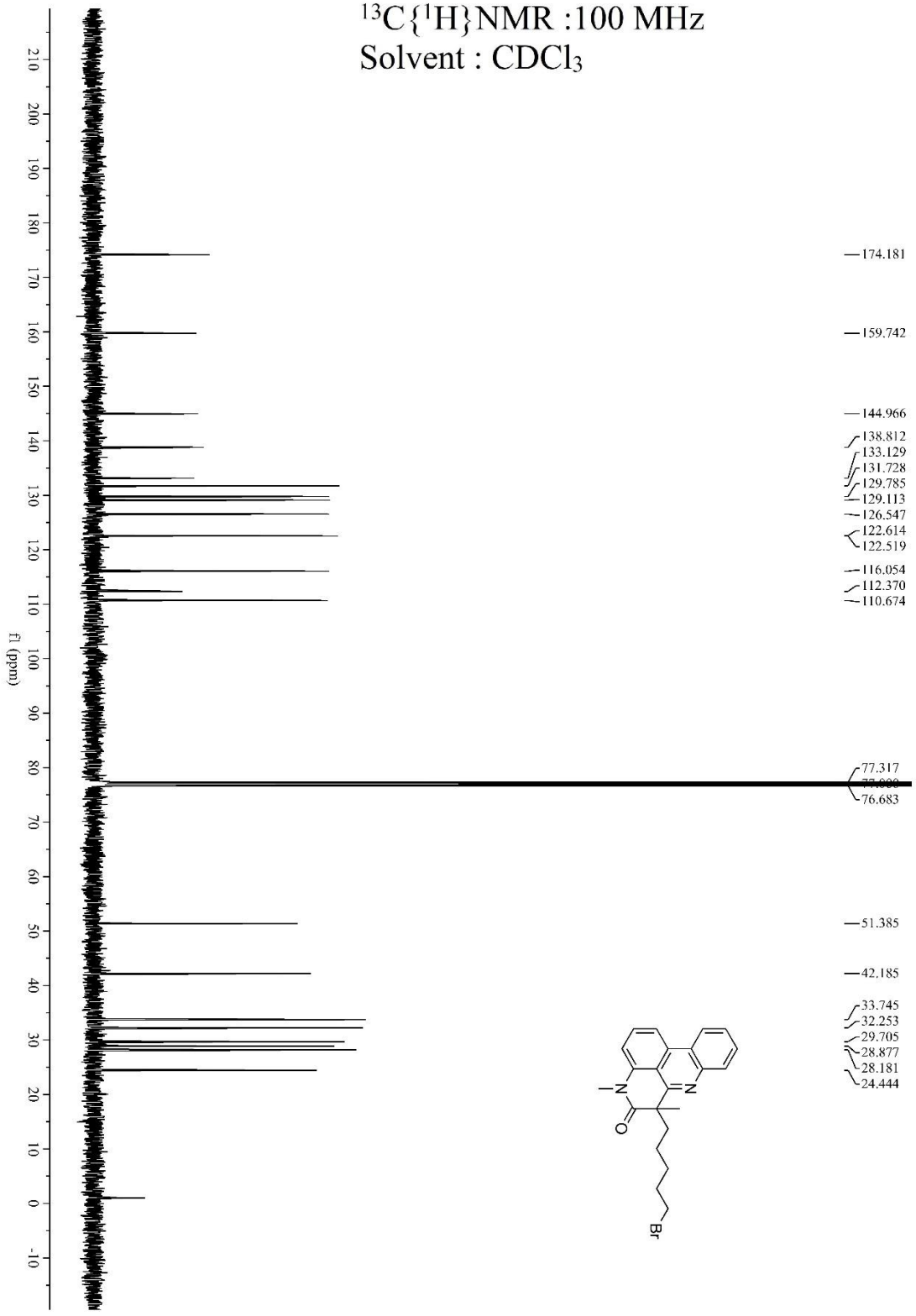
6-(6-Chlorohexyl)-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ap)



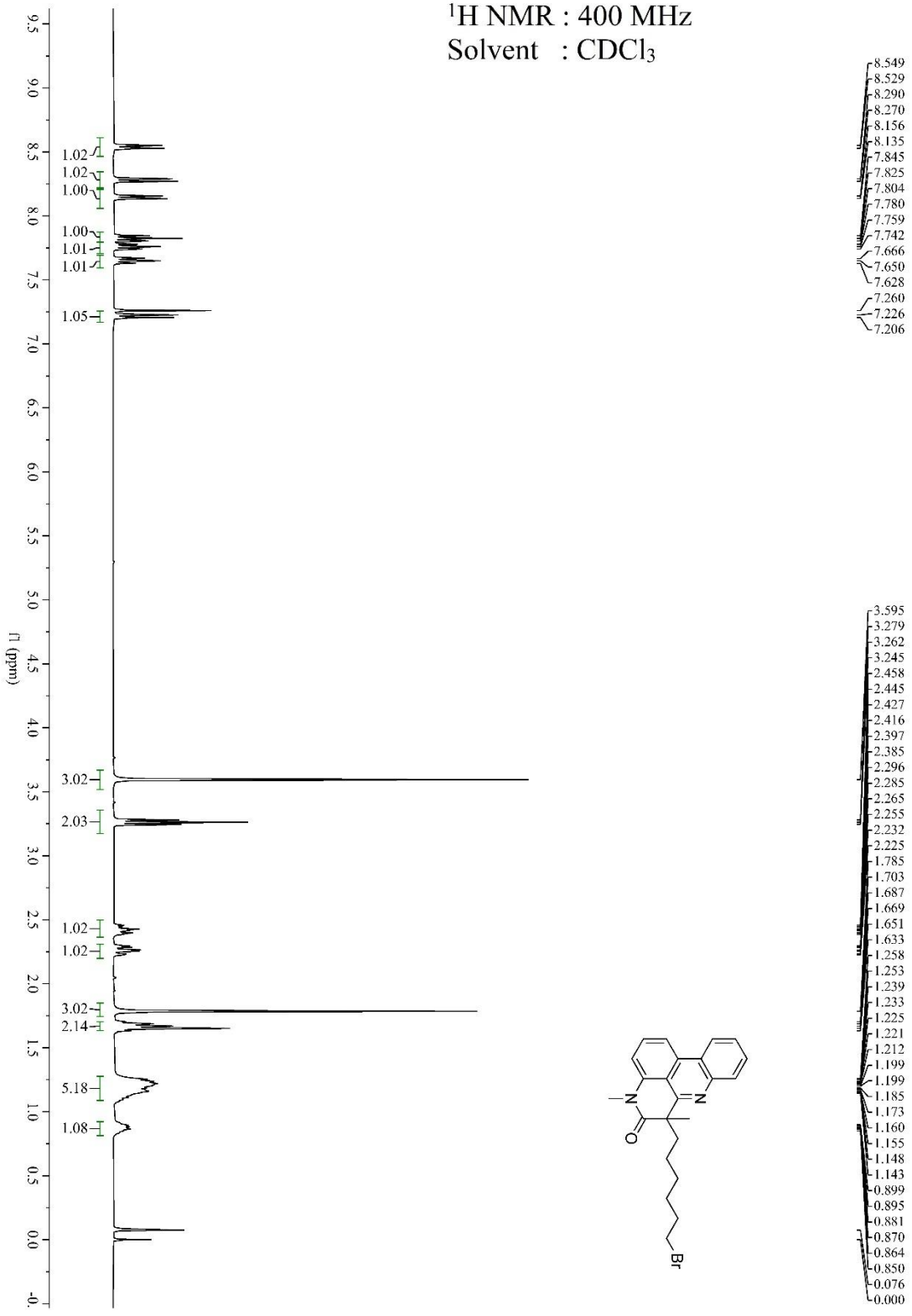

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
174.283
159.893
144.998
138.873
133.113
131.702
129.796
129.082
126.508
122.624
122.518
116.019
112.430
110.644
77.318
77.000
76.683
51.414
45.015
42.753
32.387
29.683
28.950
28.652
26.434
25.125
N
N
O
Cl

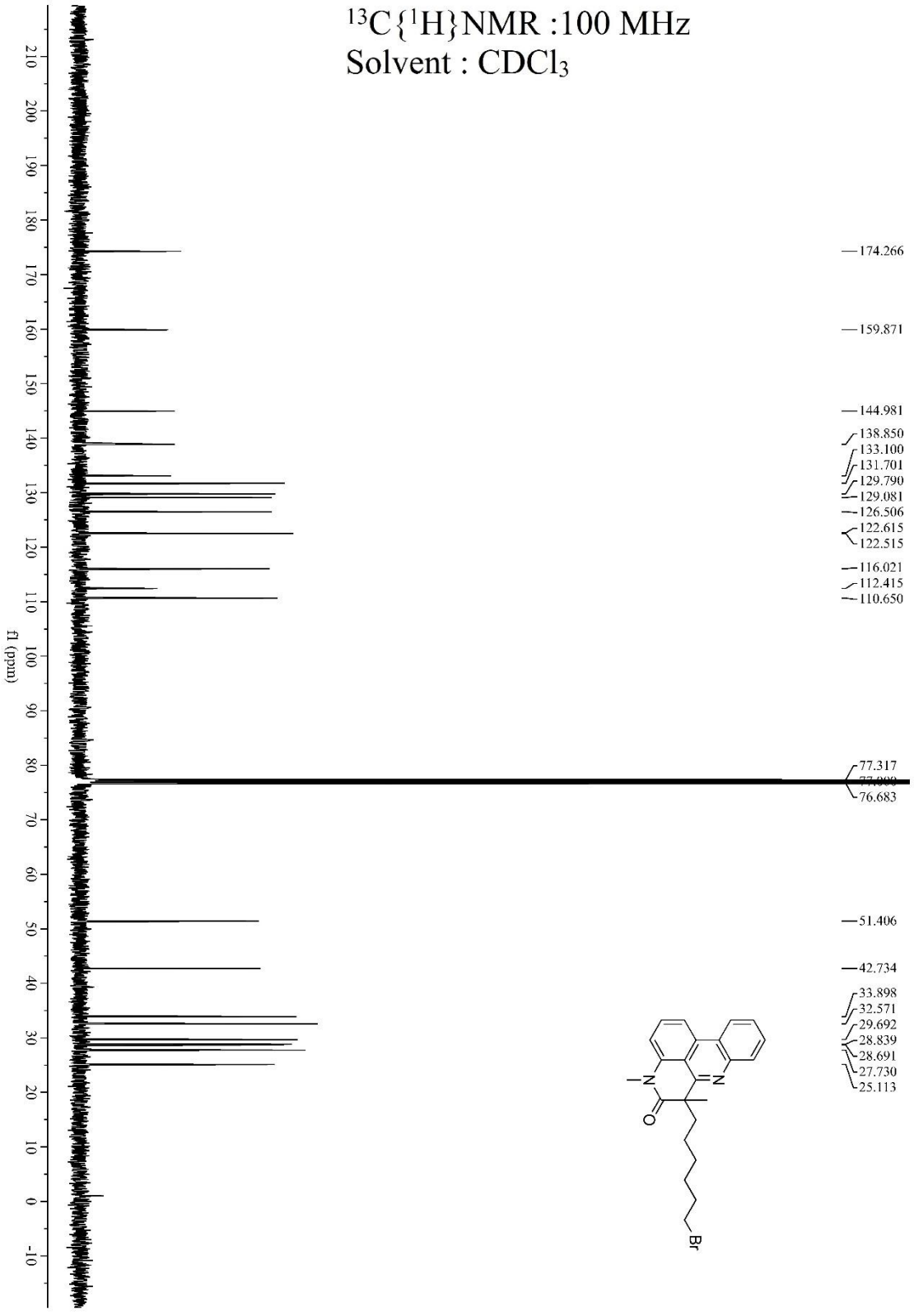
6-(6-Bromohexyl)-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3aq)




$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.181
159.742
144.966
138.812
133.129
131.728
129.785
129.113
126.547
122.614
122.519
116.054
112.370
110.674
77.317
76.683
51.385
42.185
33.745
32.253
29.705
28.877
28.181
24.444
N
N
O
Br

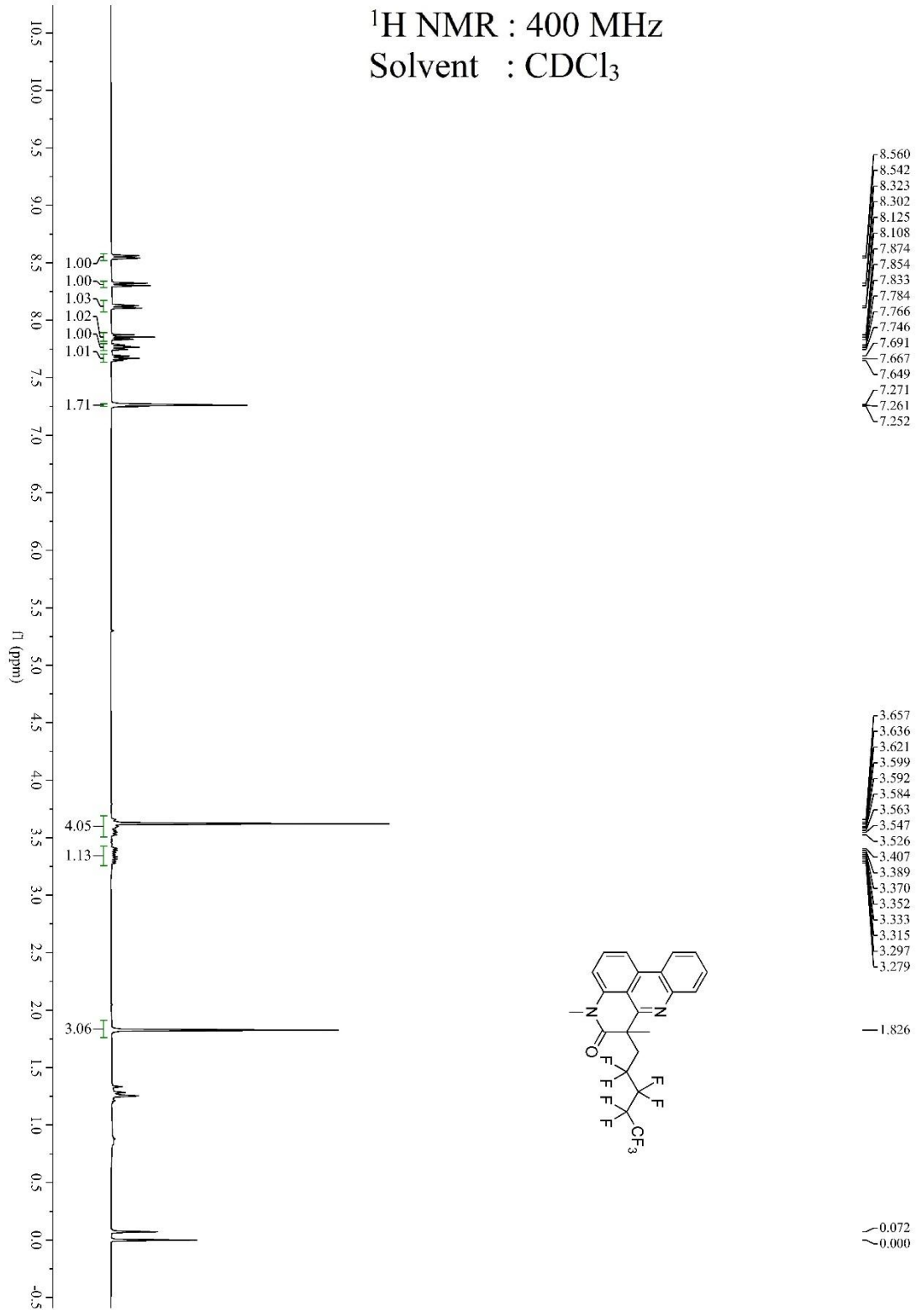
6-(5-Bromopentyl)-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ar)

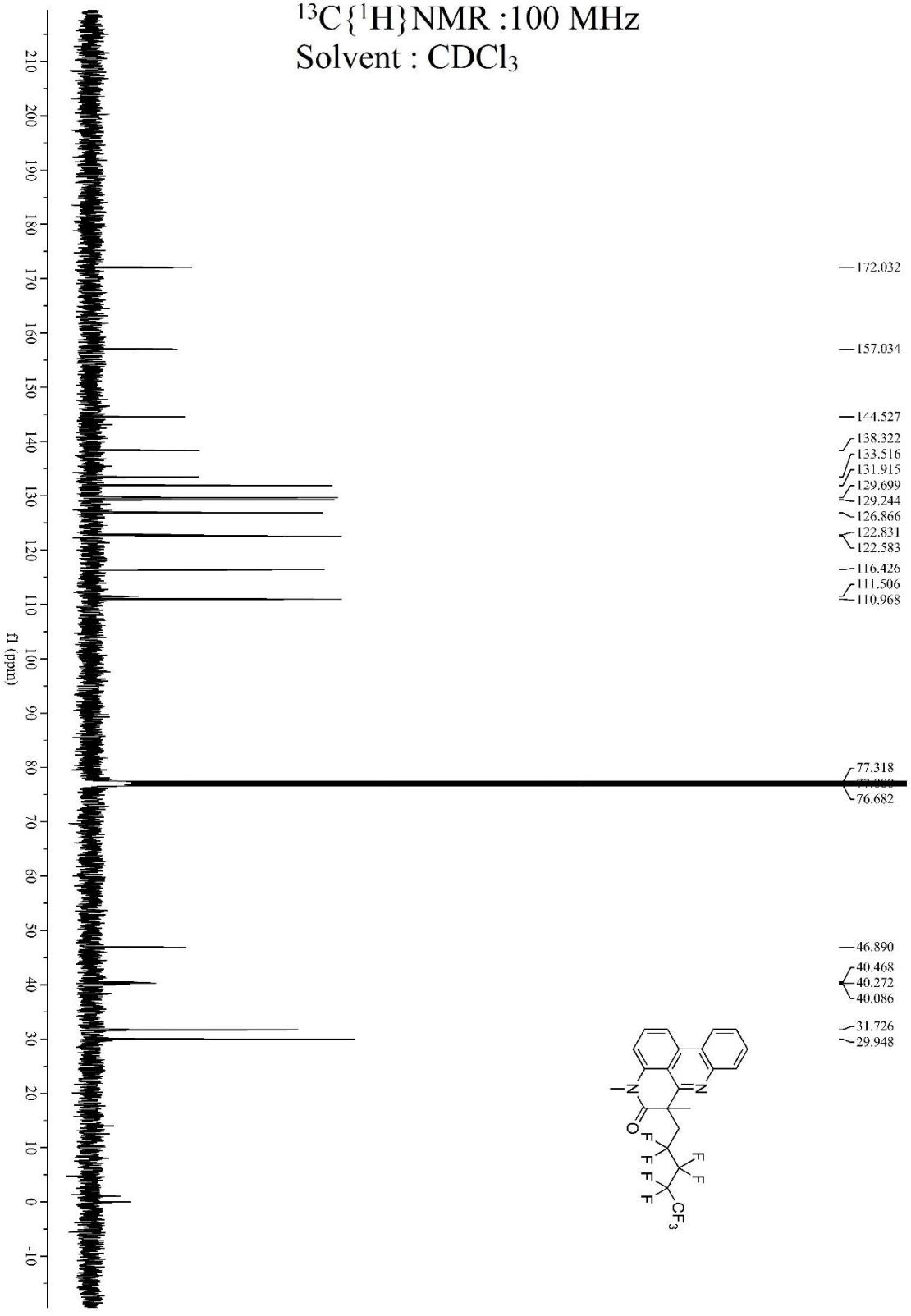



$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.266
159.871
144.981
138.850
133.100
131.701
129.790
129.081
126.506
122.615
122.515
116.021
112.415
110.650
77.317
76.683
51.406
42.734
33.898
32.571
29.692
28.839
28.691
27.730
25.113
N
N
O
Br

**4,6-Dimethyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-4*H*-pyrido[4,3,2-*g*

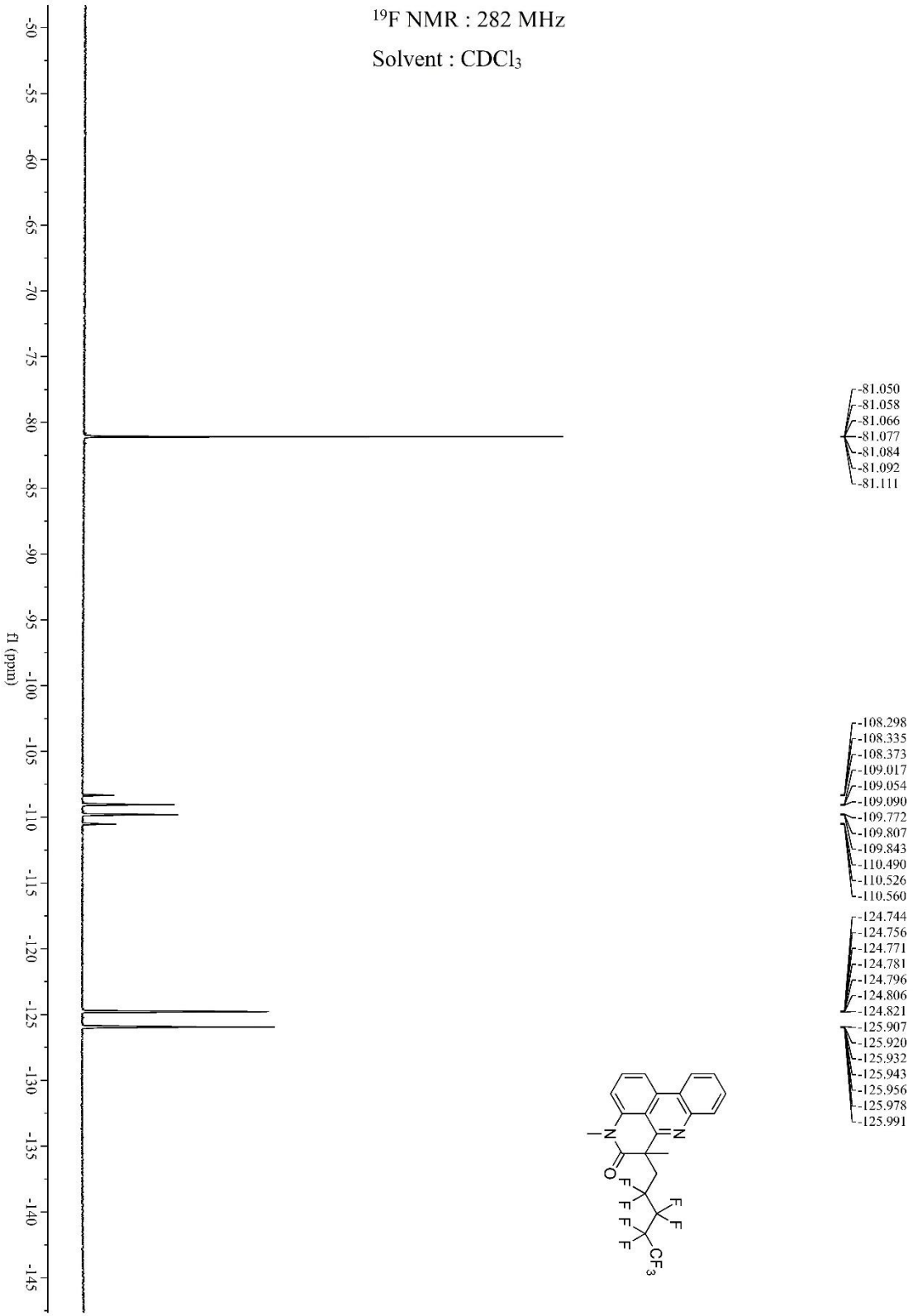
h]phenanthridin-5(6*H*)-one (3as)**



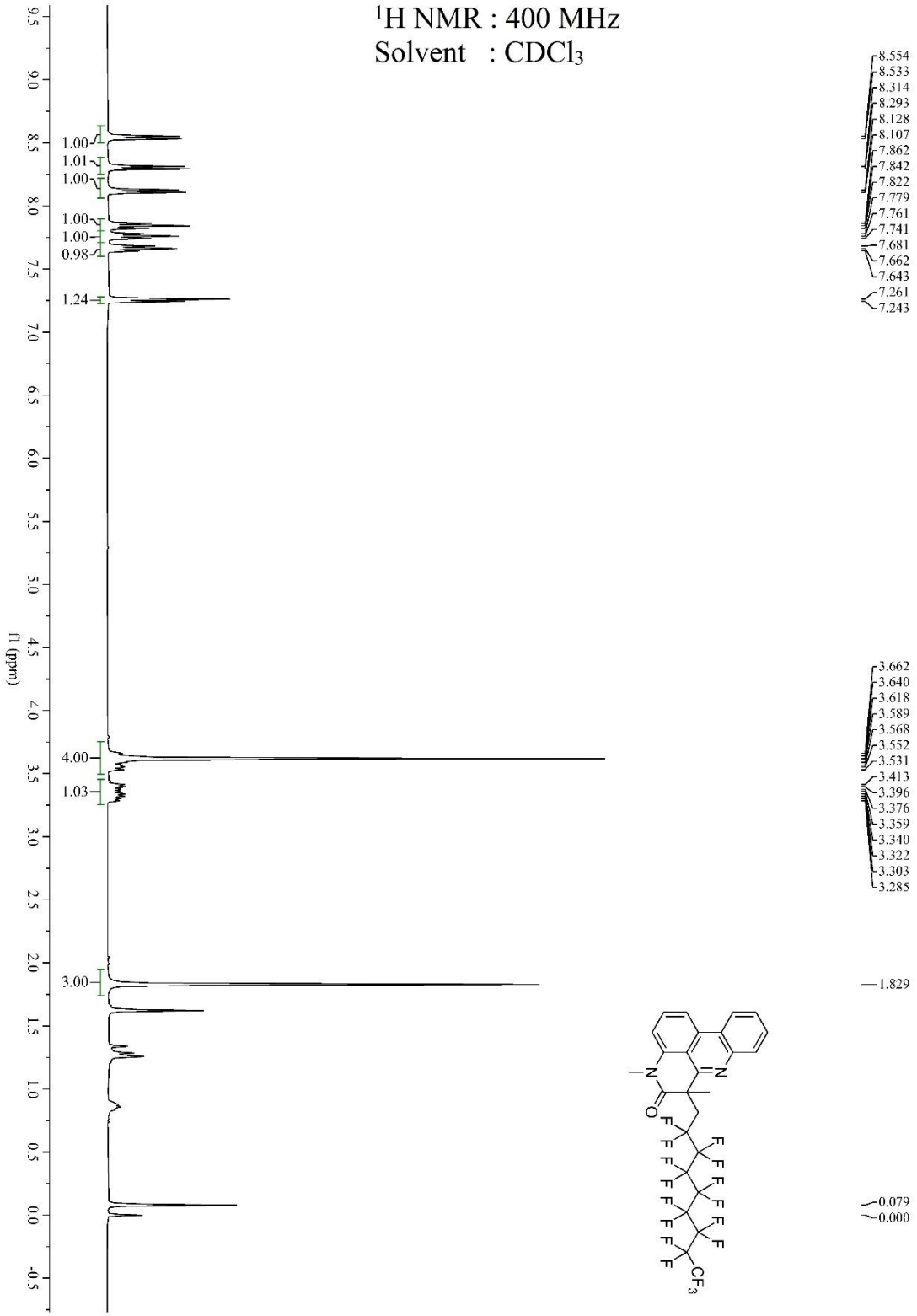

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
172.032
157.034
144.527
138.322
133.516
131.915
129.699
129.244
126.866
122.831
122.583
116.426
111.506
110.968
77.318
76.682
46.890
40.468
40.272
40.086
31.726
29.948

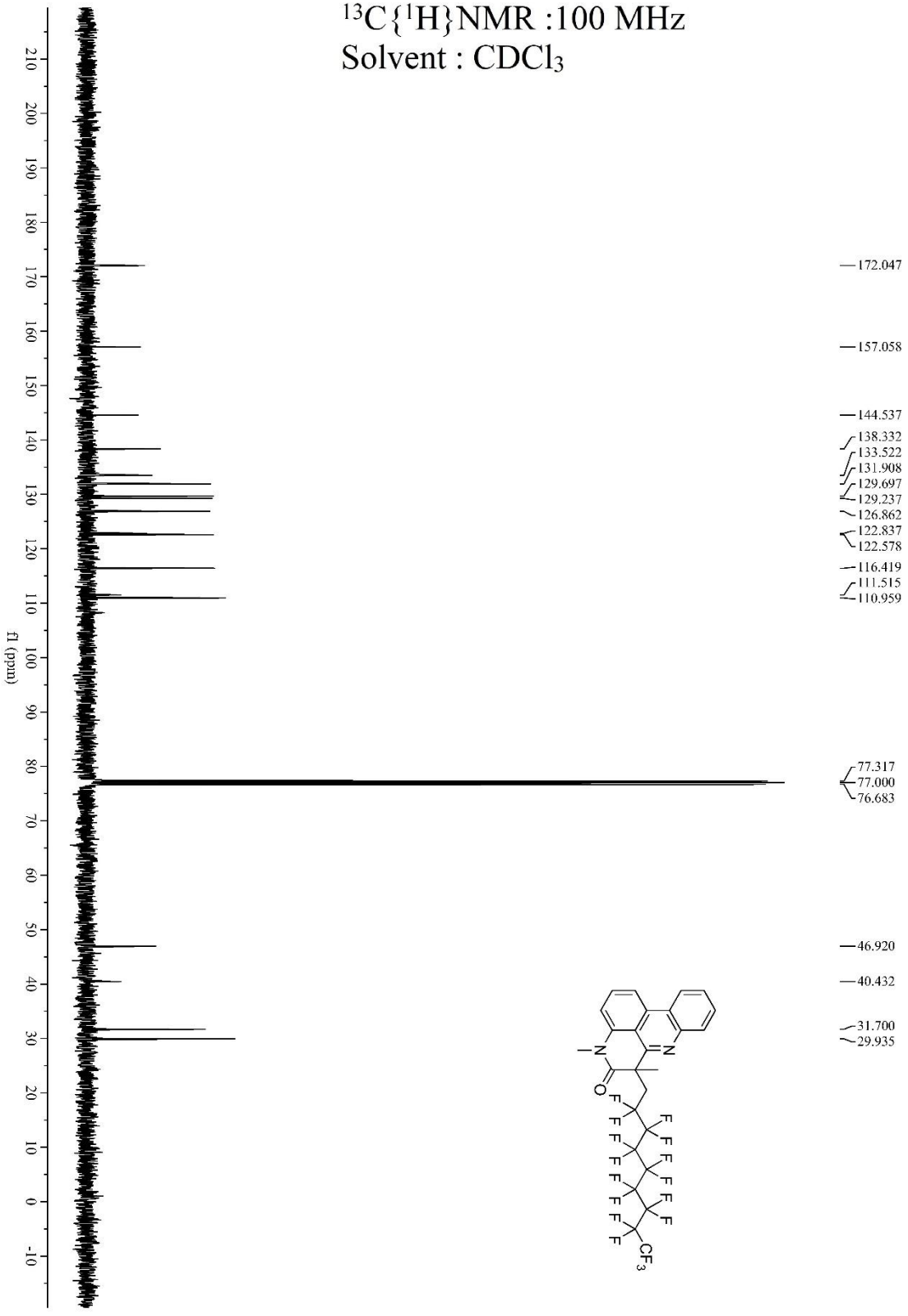
^{19}F NMR : 282 MHz

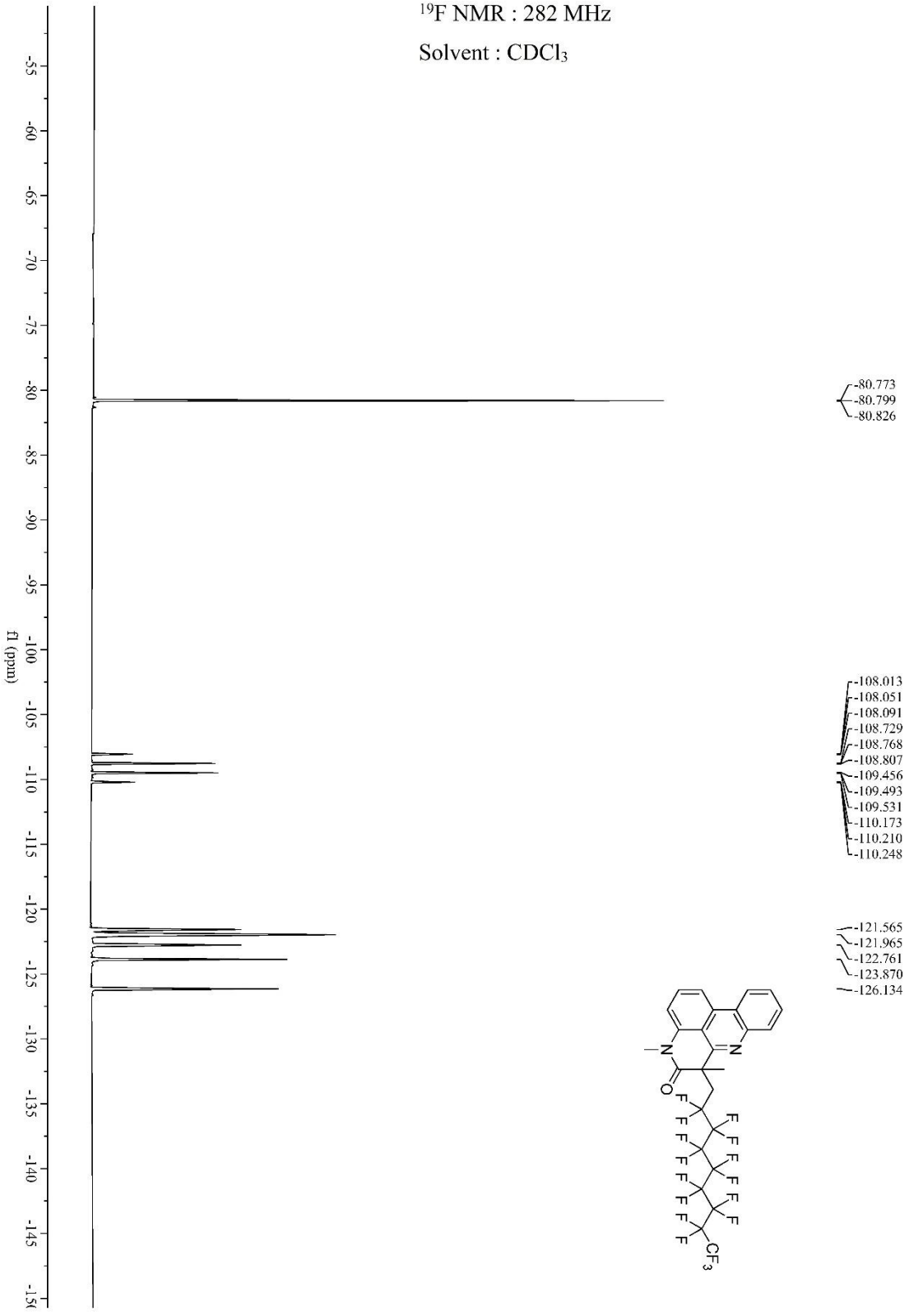
Solvent : $CDCl_3$



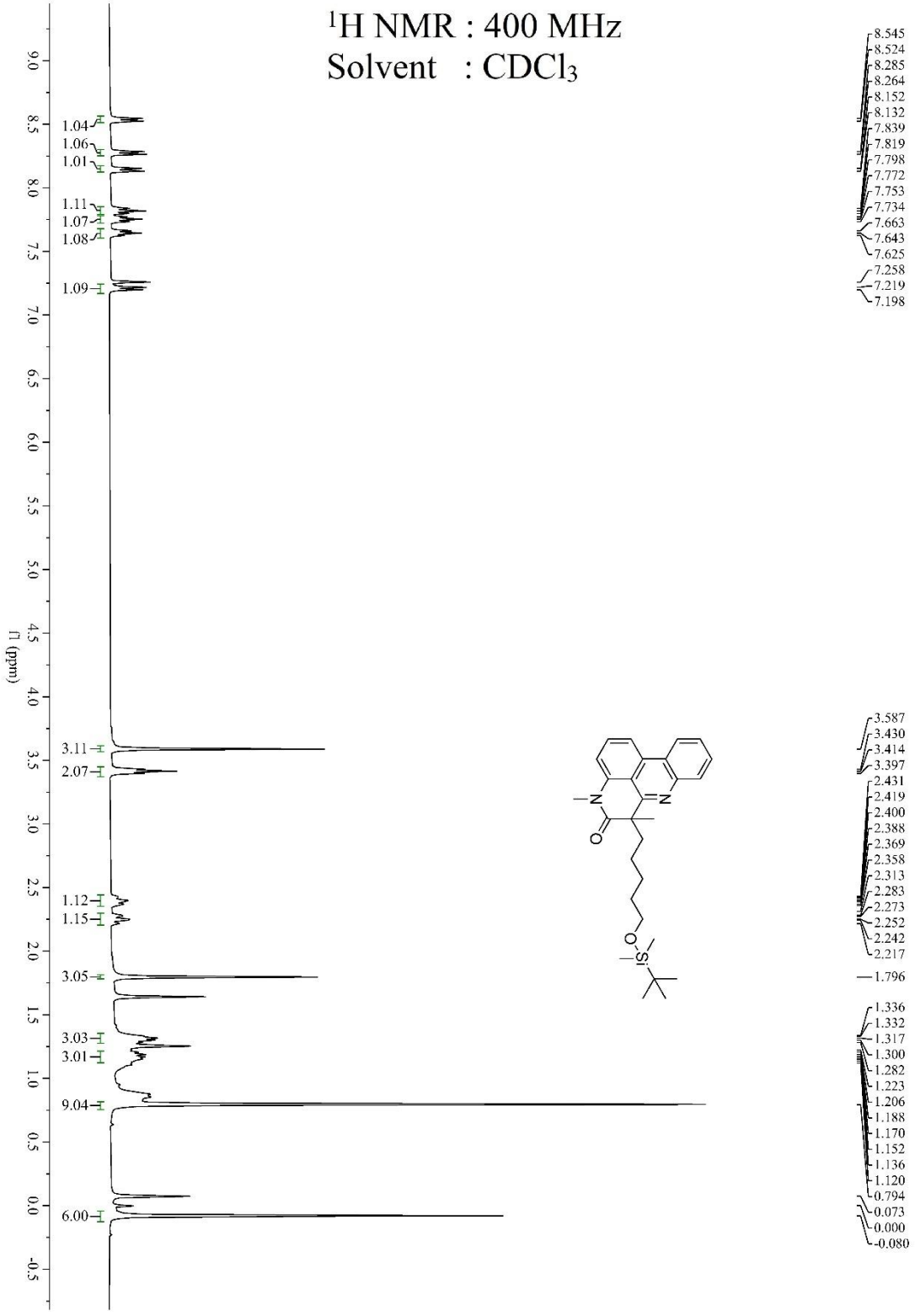
6-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl)-4,6-dimethyl -4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3at)

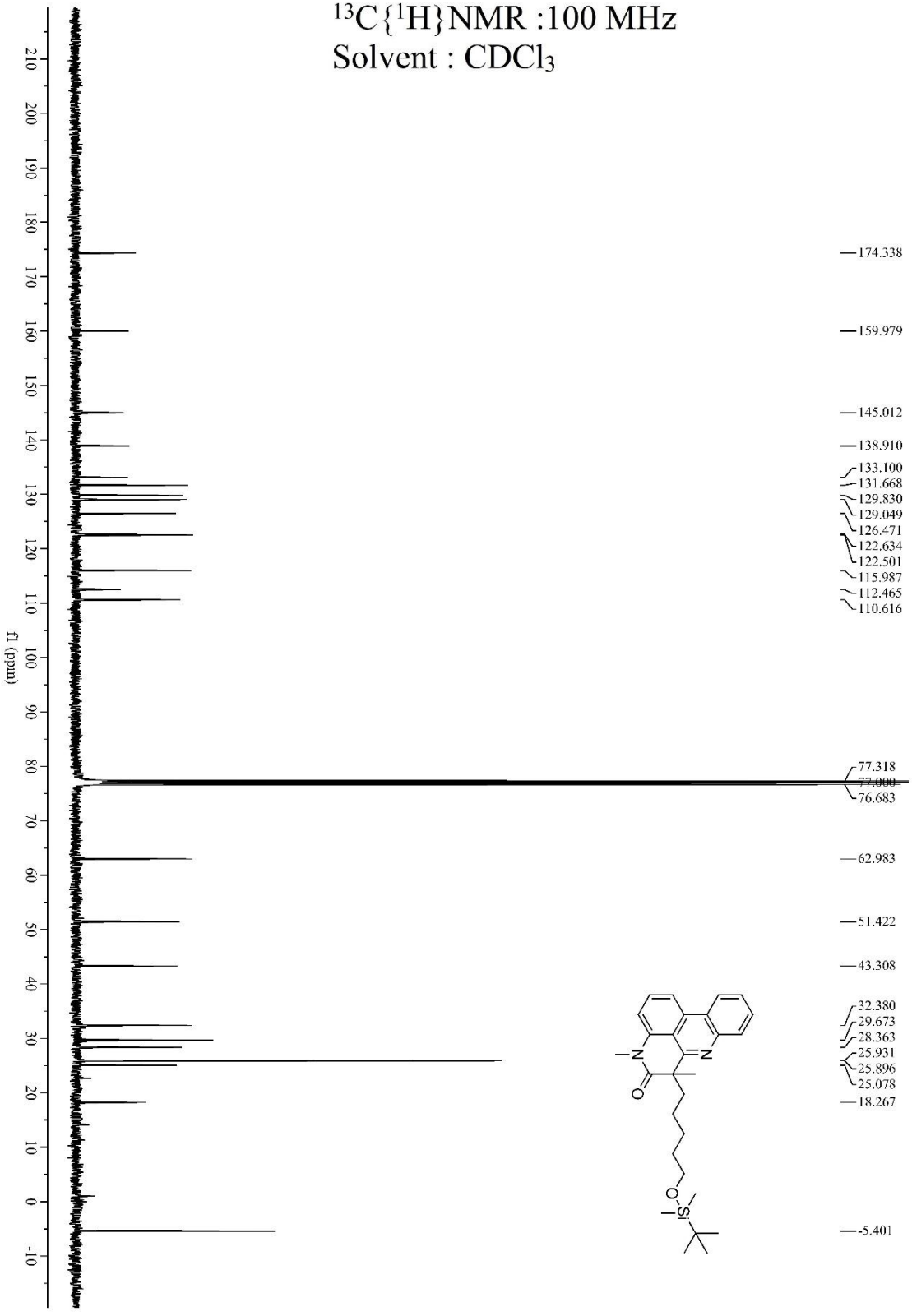



$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
172.047
157.058
144.537
138.332
133.522
131.908
129.697
129.237
126.862
122.837
122.578
116.419
111.515
110.959
77.317
77.000
76.683
46.920
40.432
31.700
29.935

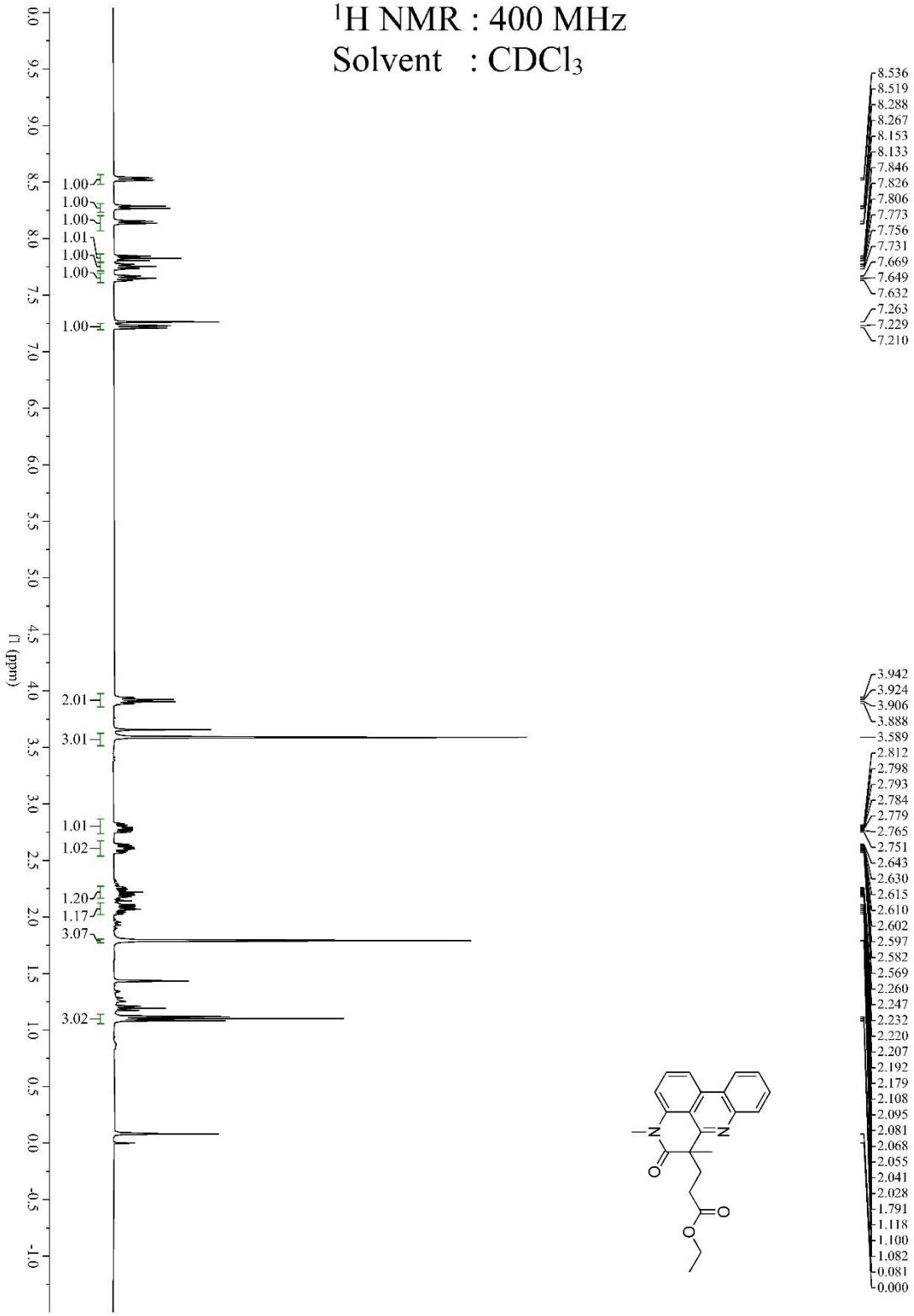

19F NMR : 282 MHz
Solvent : CDCl3
f1 (ppm)
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-80.773
-80.799
-80.826
-108.013
-108.051
-108.091
-108.729
-108.768
-108.807
-109.456
-109.493
-109.531
-110.173
-110.210
-110.248
-121.565
-121.965
-122.761
-123.870
-126.134
N
N
O
F
CF3

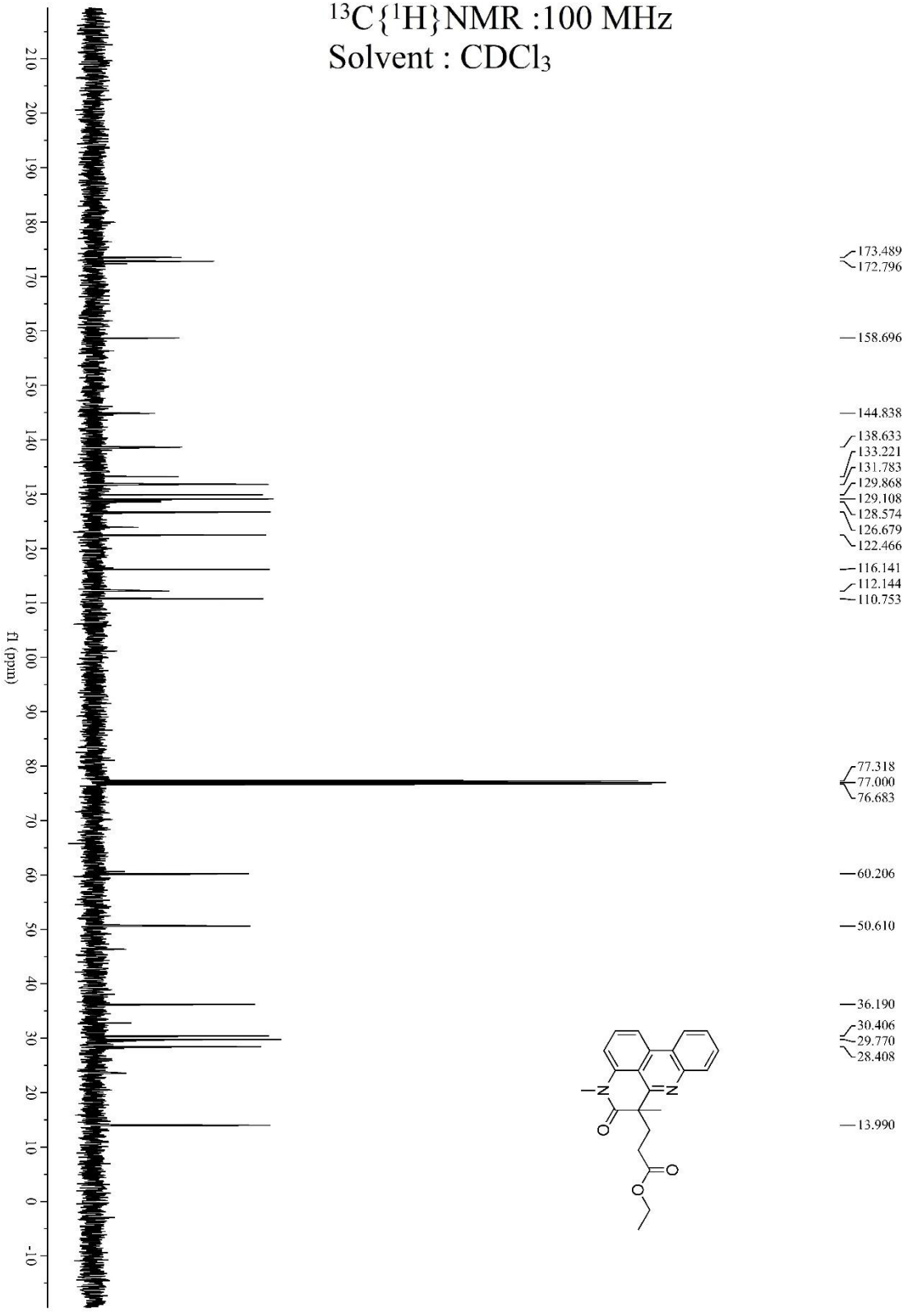
6-(5-((Tert-butyldimethylsilyl)oxy)pentyl)-4,6-dimethyl-4*H*-pyrido[4,3,2- *gh*]phenanthridin-5(6*H*)-one (3au)



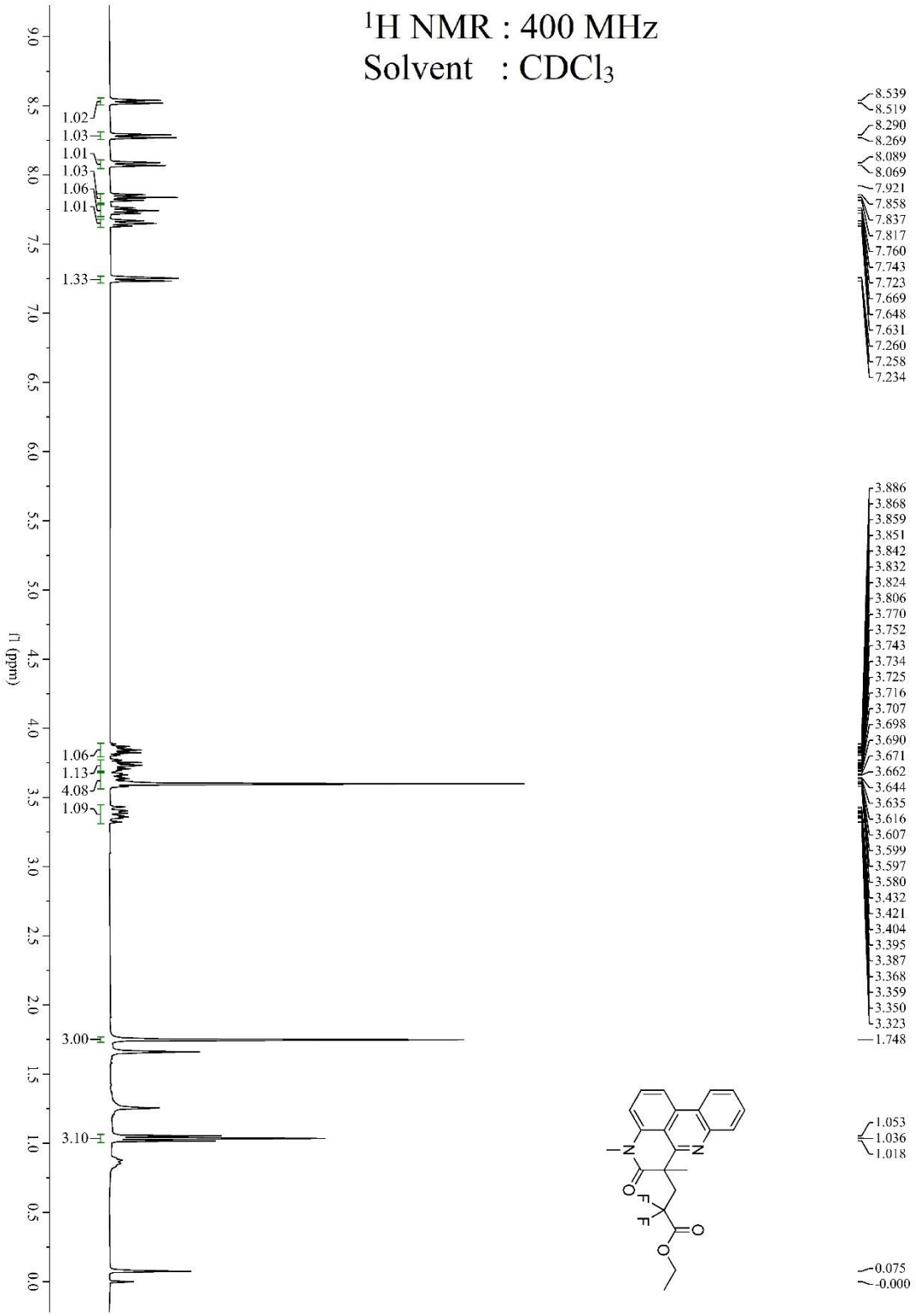

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
174.338
159.979
145.012
138.910
133.100
131.668
129.830
129.049
126.471
122.634
122.501
115.987
112.465
110.616
77.318
77.000
76.683
62.983
51.422
43.308
32.380
29.673
28.363
25.931
25.896
25.078
18.267
-5.401

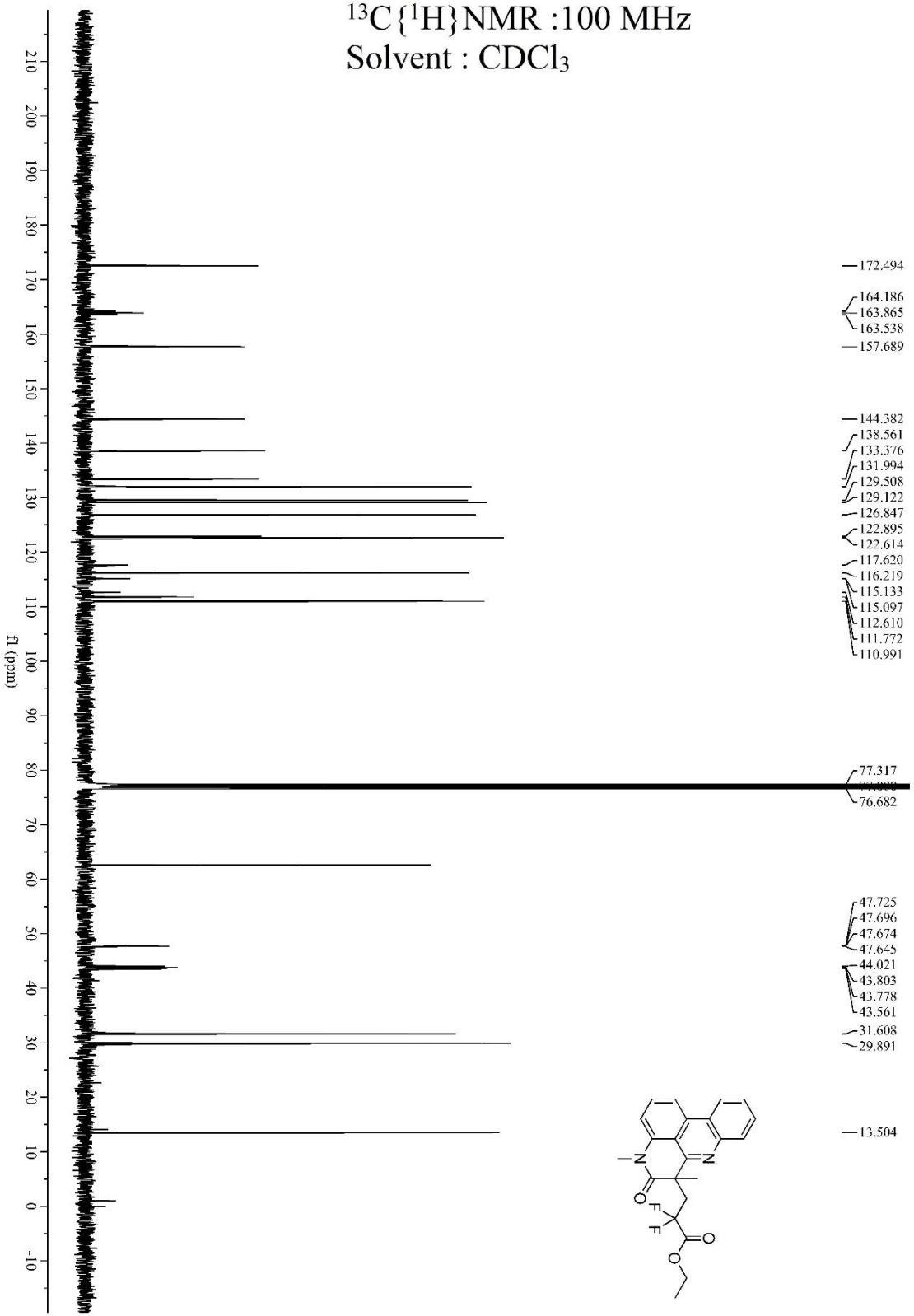
Ethyl 3-(4,6-dimethyl-5-oxo-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanoate (3av)




$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
173.489
172.796
158.696
144.838
138.633
133.221
131.783
129.868
129.108
128.574
126.679
122.466
116.141
112.144
110.753
77.318
77.000
76.683
60.206
50.610
36.190
30.406
29.770
28.408
13.990
N
N
O
O
O

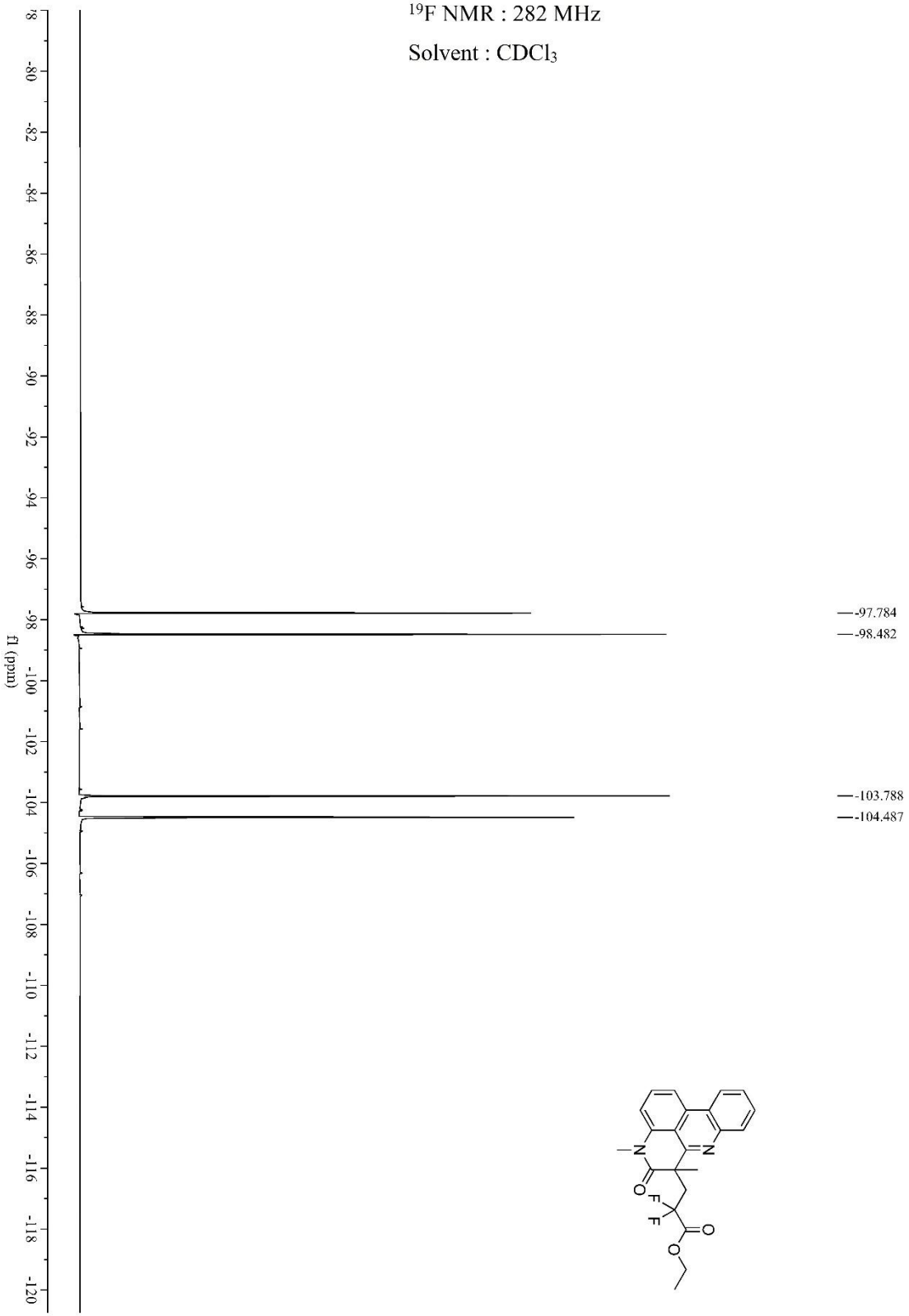
Ethyl 3-(4,6-dimethyl-5-oxo-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*]phenanthridin-6-yl)-2,2-difluoropropanoate (3aw)



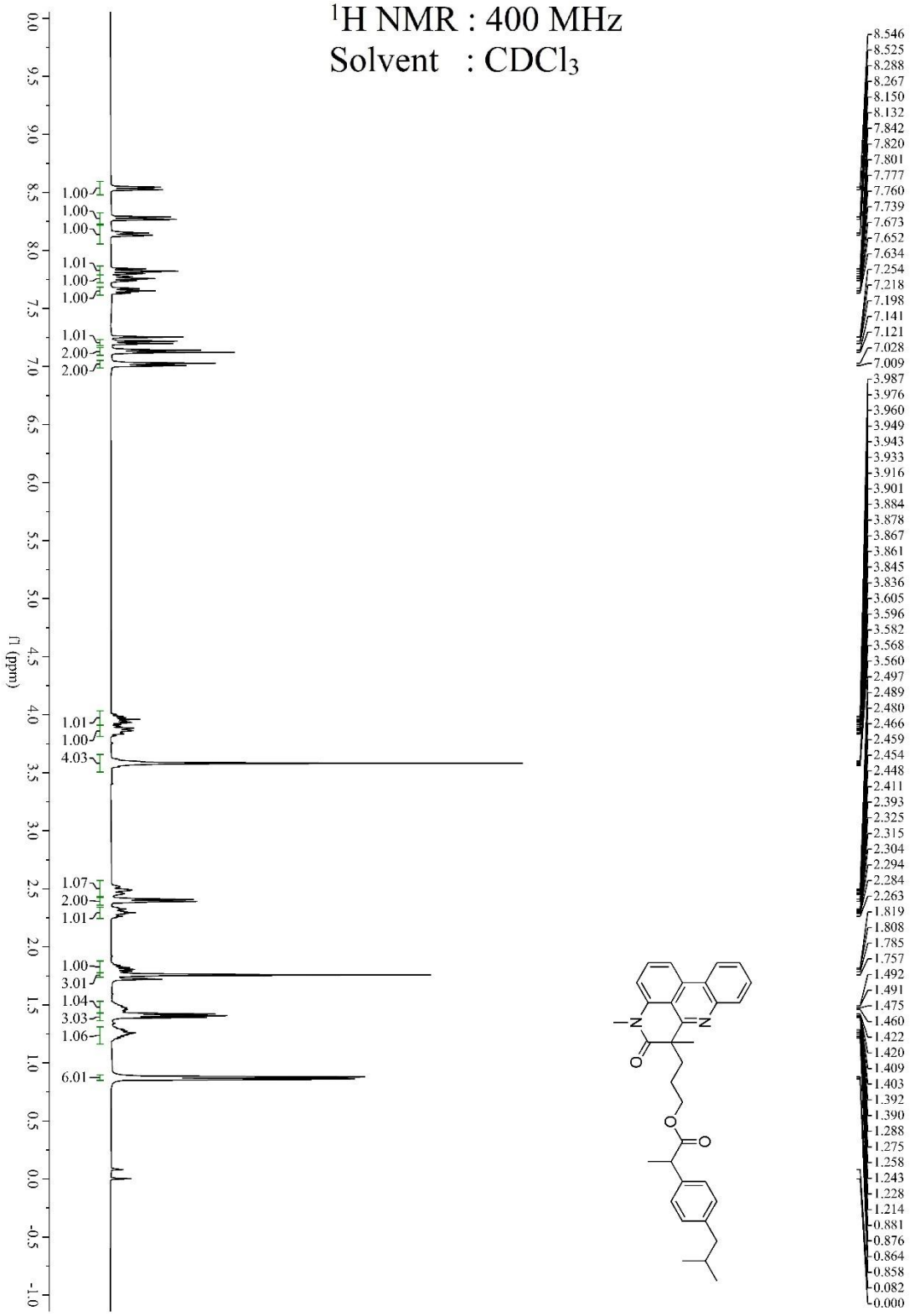

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
172.494
164.186
163.865
163.538
157.689
144.382
138.561
133.376
131.994
129.508
129.122
126.847
122.895
122.614
117.620
116.219
115.133
115.097
112.610
111.772
110.991
77.317
76.682
47.725
47.696
47.674
47.645
44.021
43.803
43.778
43.561
31.608
29.891
13.504

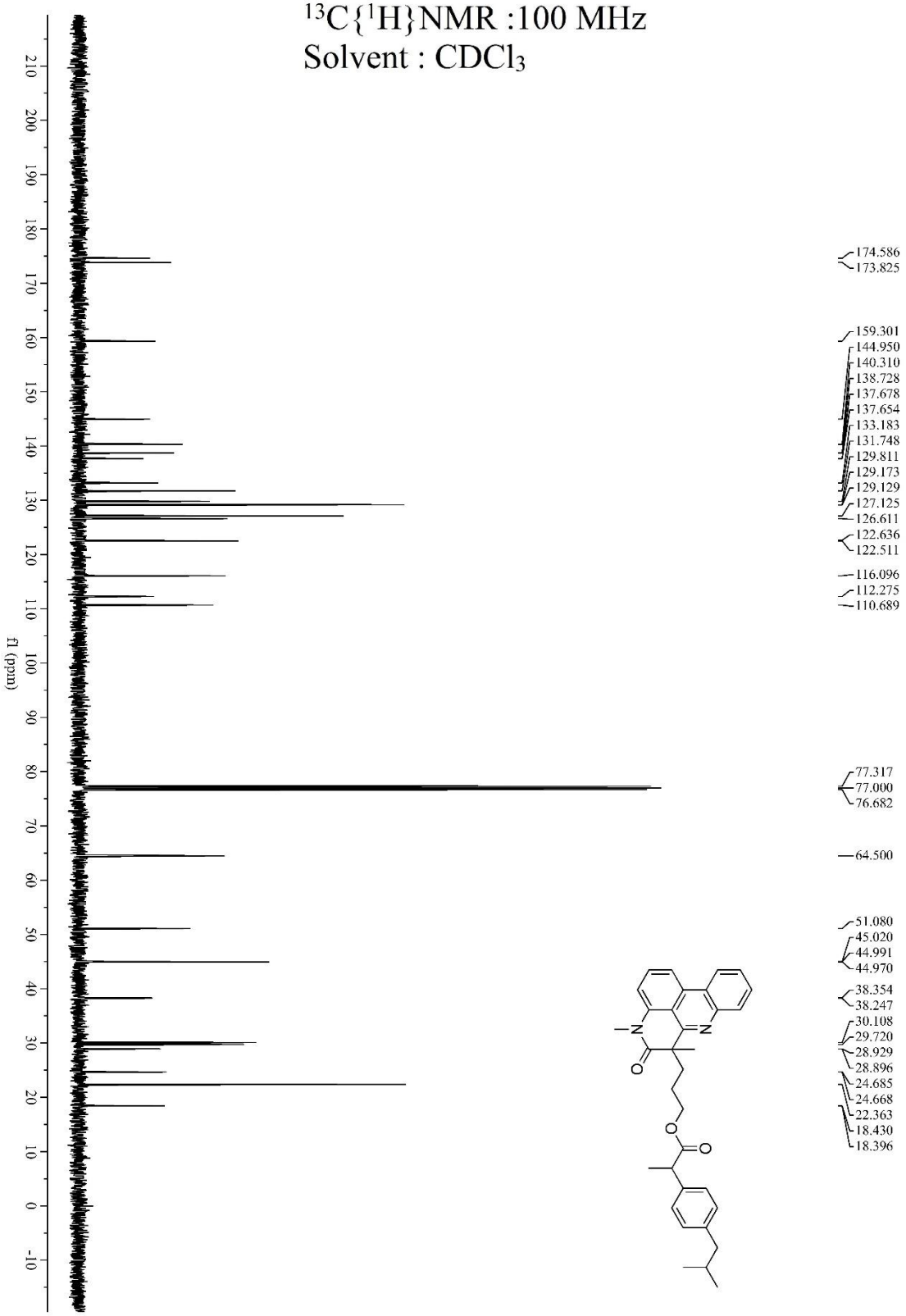
^{19}F NMR : 282 MHz

Solvent : $CDCl_3$

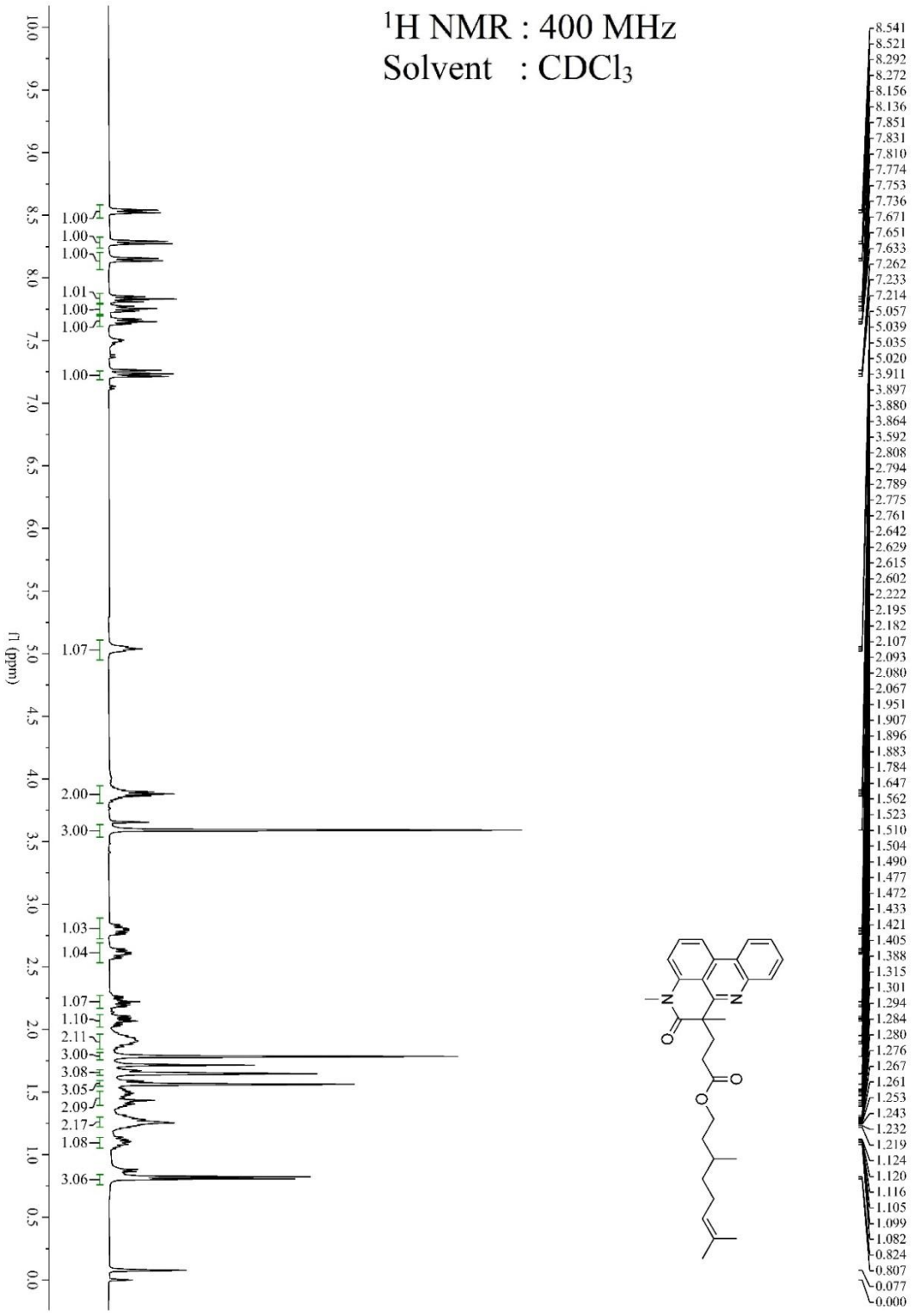


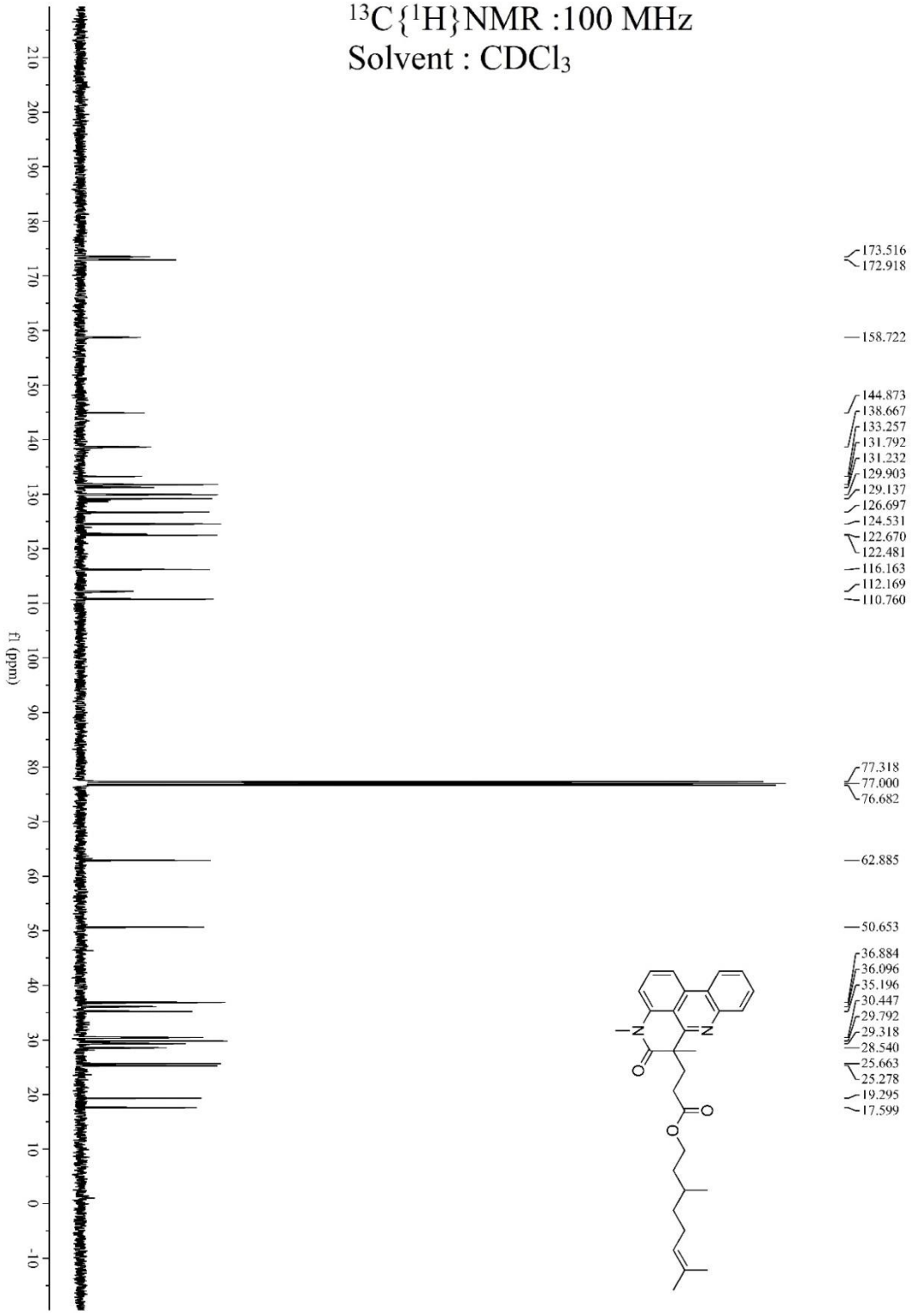
3-(4,6-Dimethyl-5-oxo-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propyl 2-(4-isobutylphenyl)propanoate (3ax)



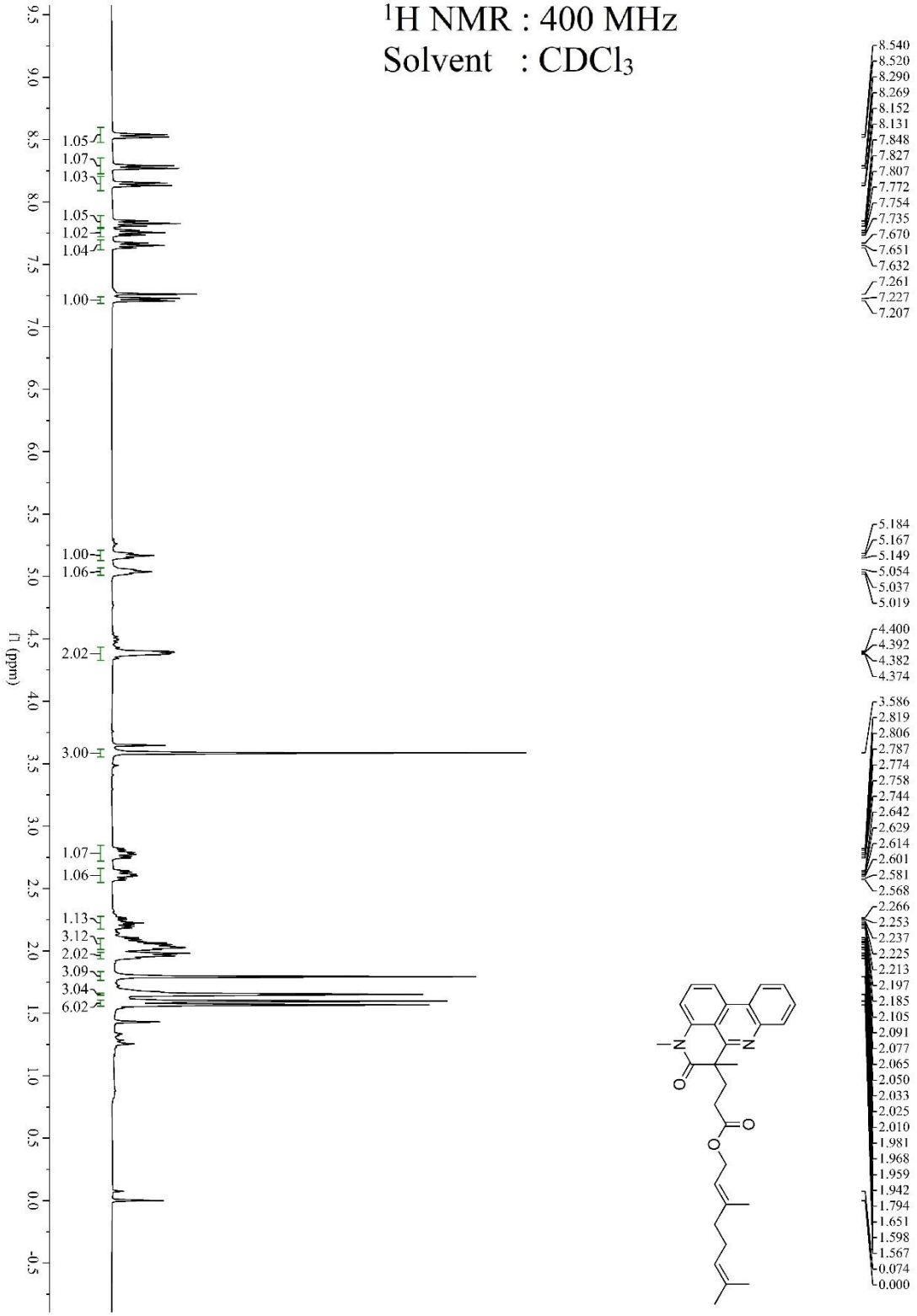

$^{13}C\{^{1}H\}NMR$:100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
174.586
173.825
159.301
144.950
140.310
138.728
137.678
137.654
133.183
131.748
129.811
129.173
129.129
127.125
126.611
122.636
122.511
116.096
112.275
110.689
77.317
77.000
76.682
64.500
51.080
45.020
44.991
44.970
38.354
38.247
30.108
29.720
28.929
28.896
24.685
24.668
22.363
18.430
18.396
N
N
O
O
O

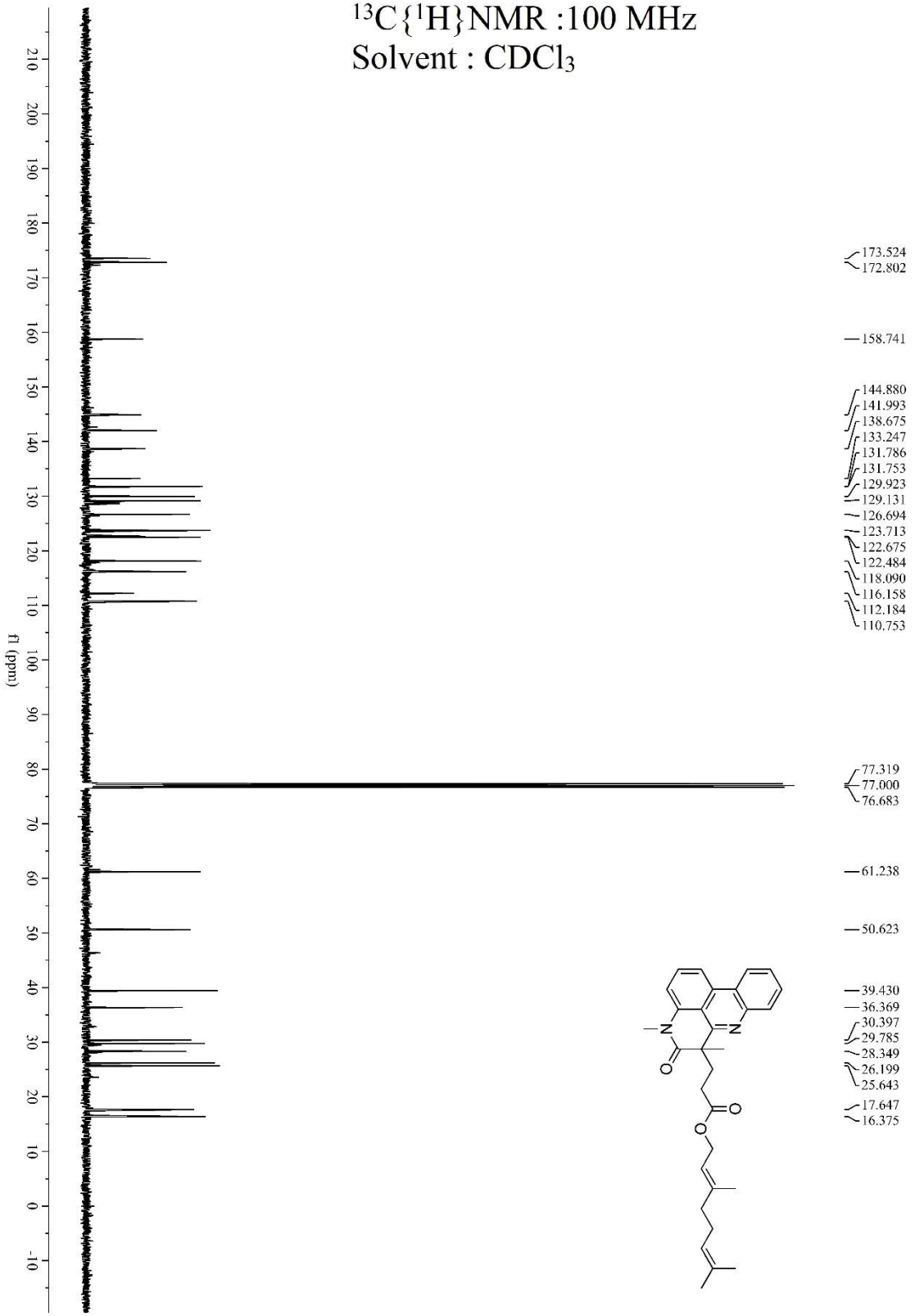
3,7-Dimethyloct-6-en-1-yl 3-(4,6-dimethyl-5-oxo-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanoate (3ay)



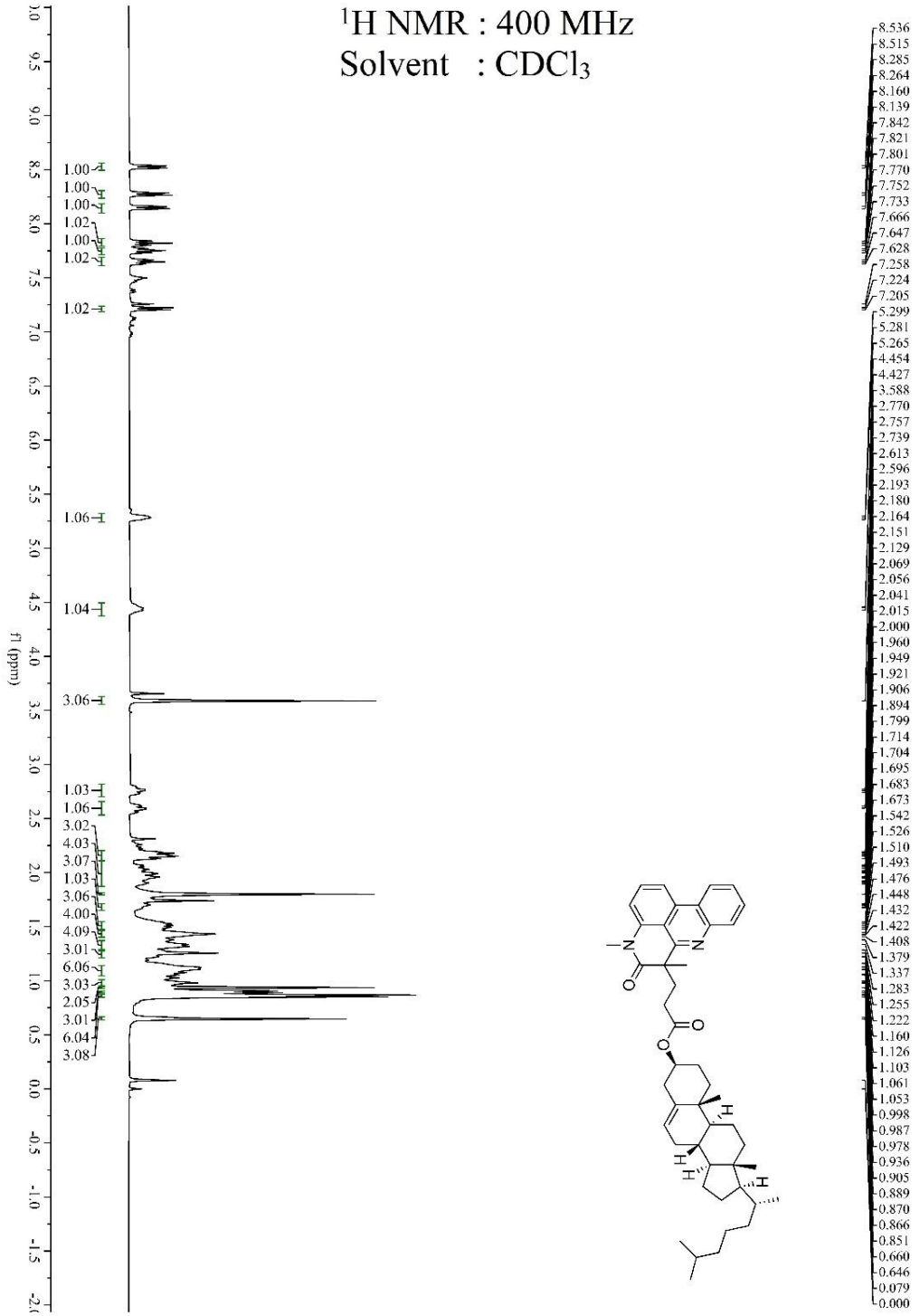

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
173.516
172.918
158.722
144.873
138.667
133.257
131.792
131.232
129.903
129.137
126.697
124.531
122.670
122.481
116.163
112.169
110.760
77.318
77.000
76.682
62.885
50.653
36.884
36.096
35.196
30.447
29.792
29.318
28.540
25.663
25.278
19.295
17.599
N
N
O
O
O

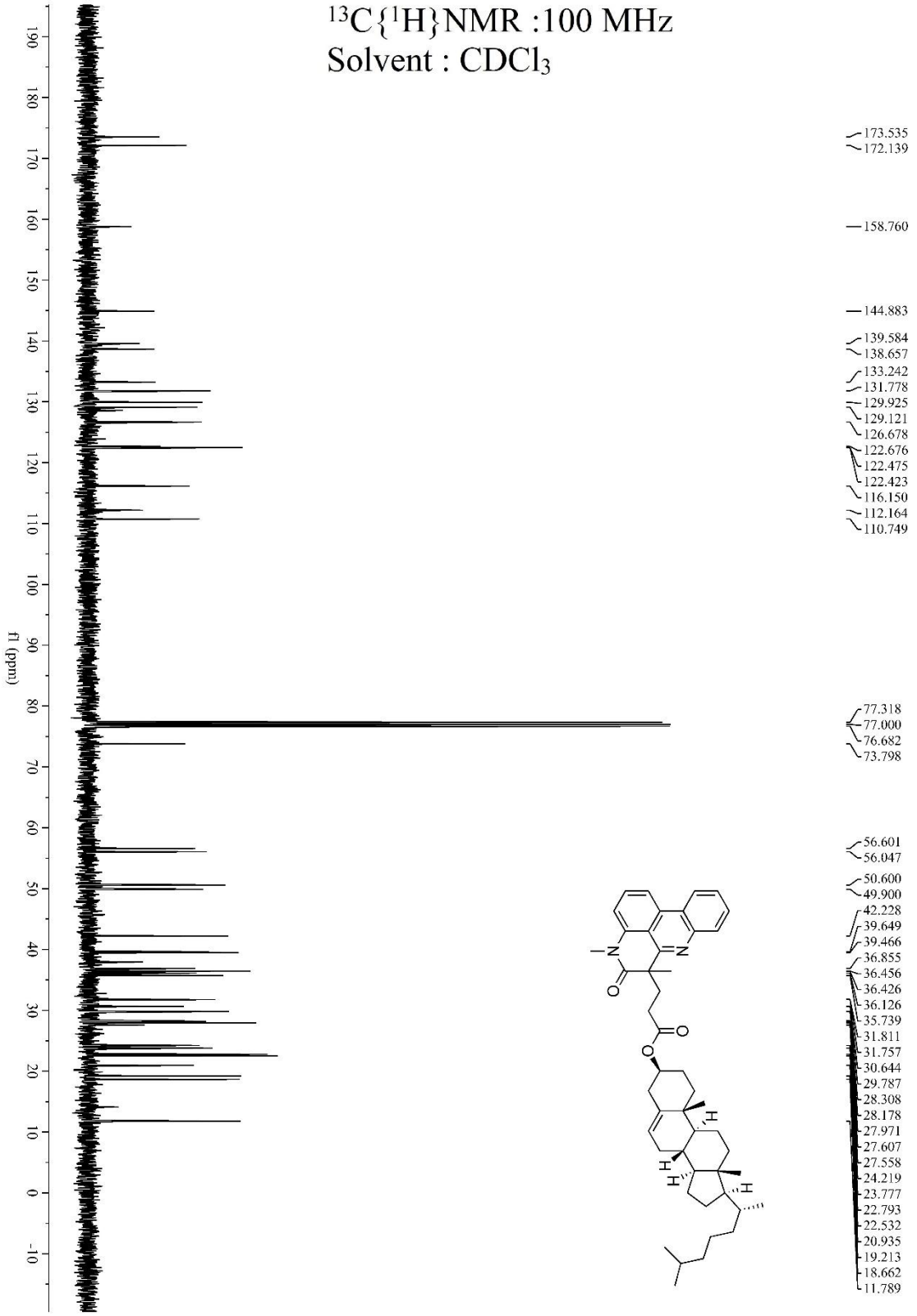
_(E)_-3,7-Dimethylocta-2,6-dien-1-yl 3-(4,6-dimethyl-5-oxo-5,6-dihydro-4_H_-pyrido[4,3,2-_gh_]phenanthridin-6-yl)propanoate (3az)



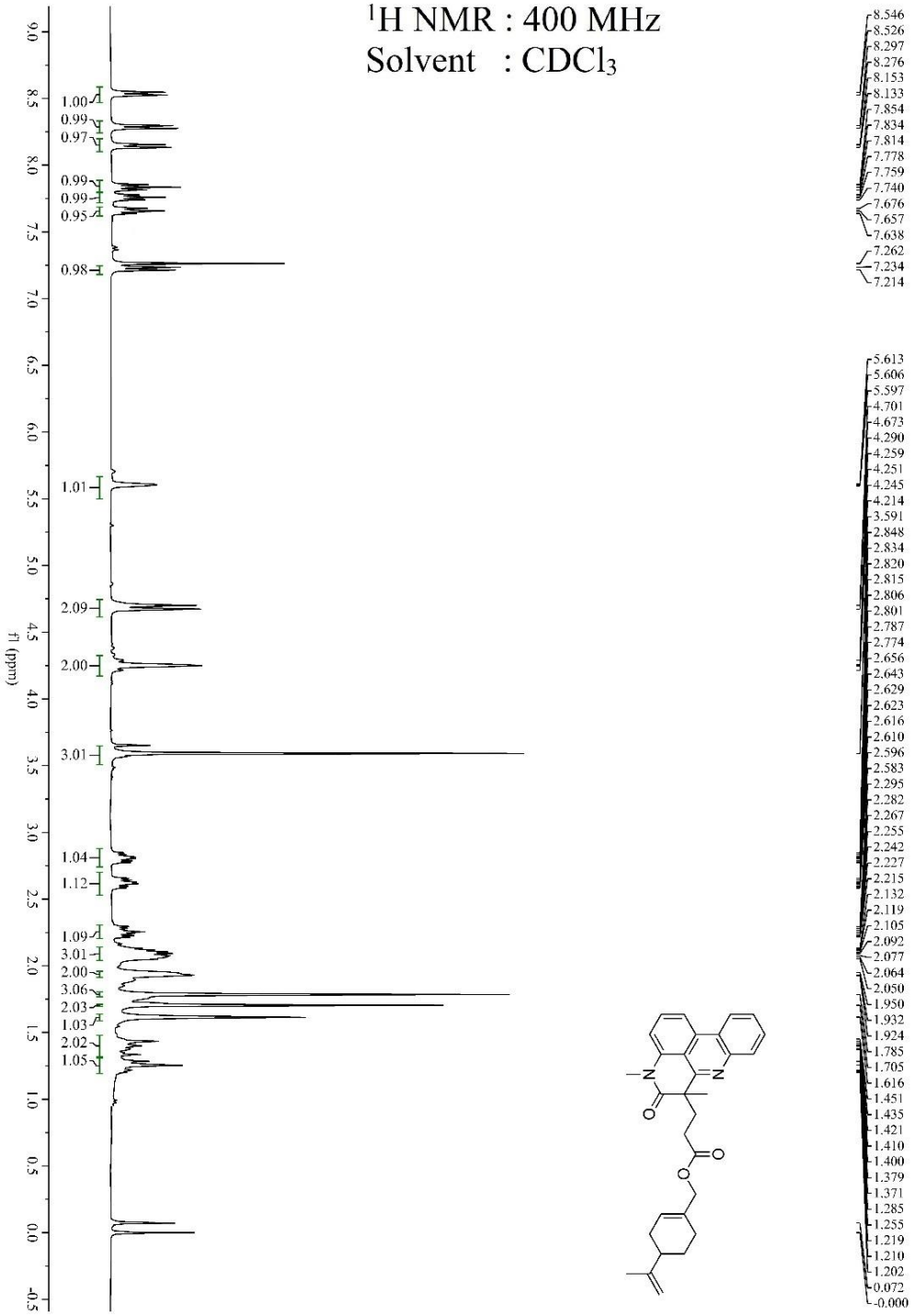

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
173.524
172.802
158.741
144.880
141.993
138.675
133.247
131.786
131.753
129.923
129.131
126.694
123.713
122.675
122.484
118.090
116.158
112.184
110.753
77.319
77.000
76.683
61.238
50.623
39.430
36.369
30.397
29.785
28.349
26.199
25.643
17.647
16.375
N
N
O
O
O

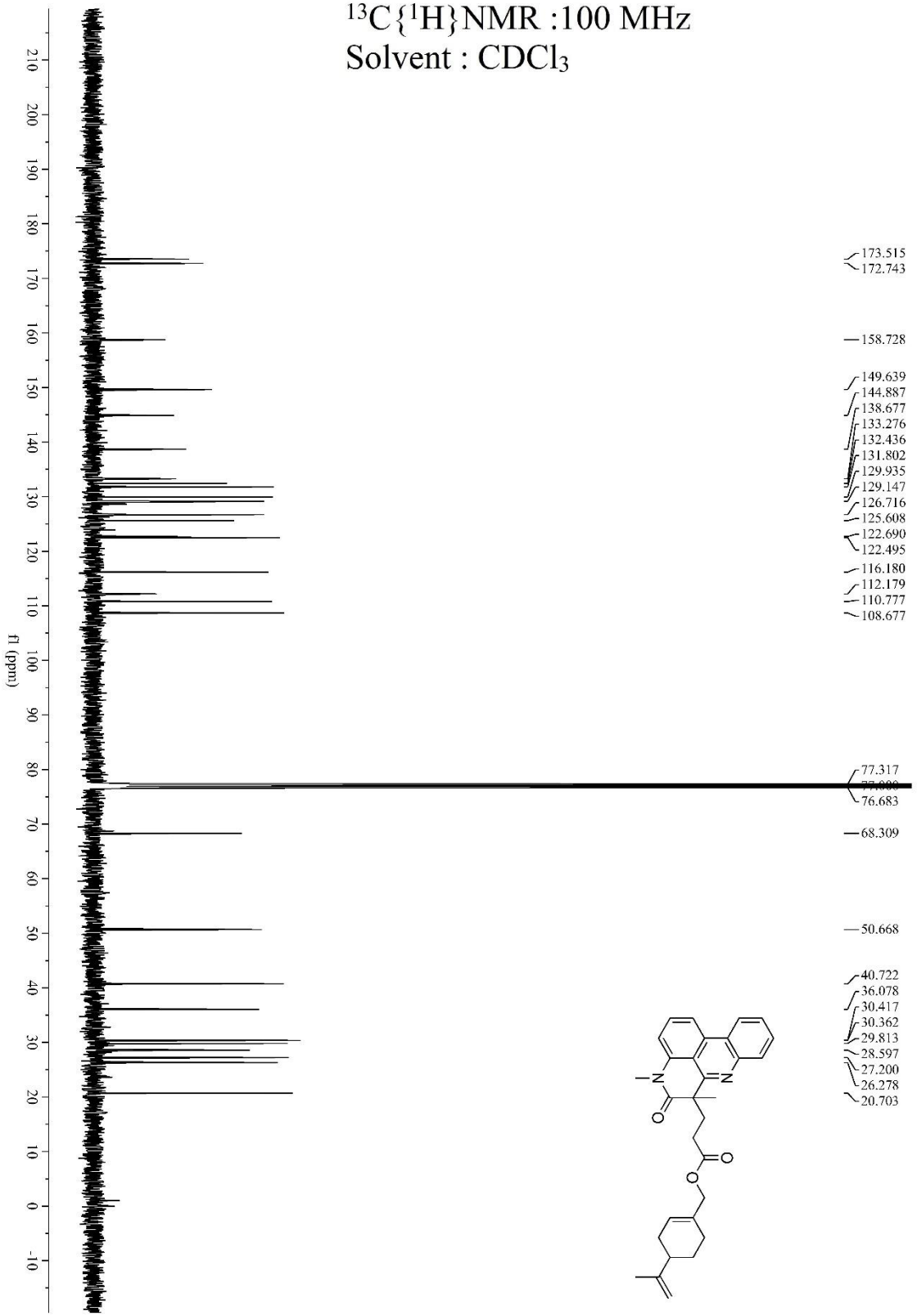
(3*S*,8*S*,9*S*,10*R*,13*R*,14*R*,17*R*)-8,10,13-Trimethyl-17-((*R*)-6-methylhept an-2-yl)- 2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl-3-(4,6-dimethyl-5-oxo-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanoate (3aaa)



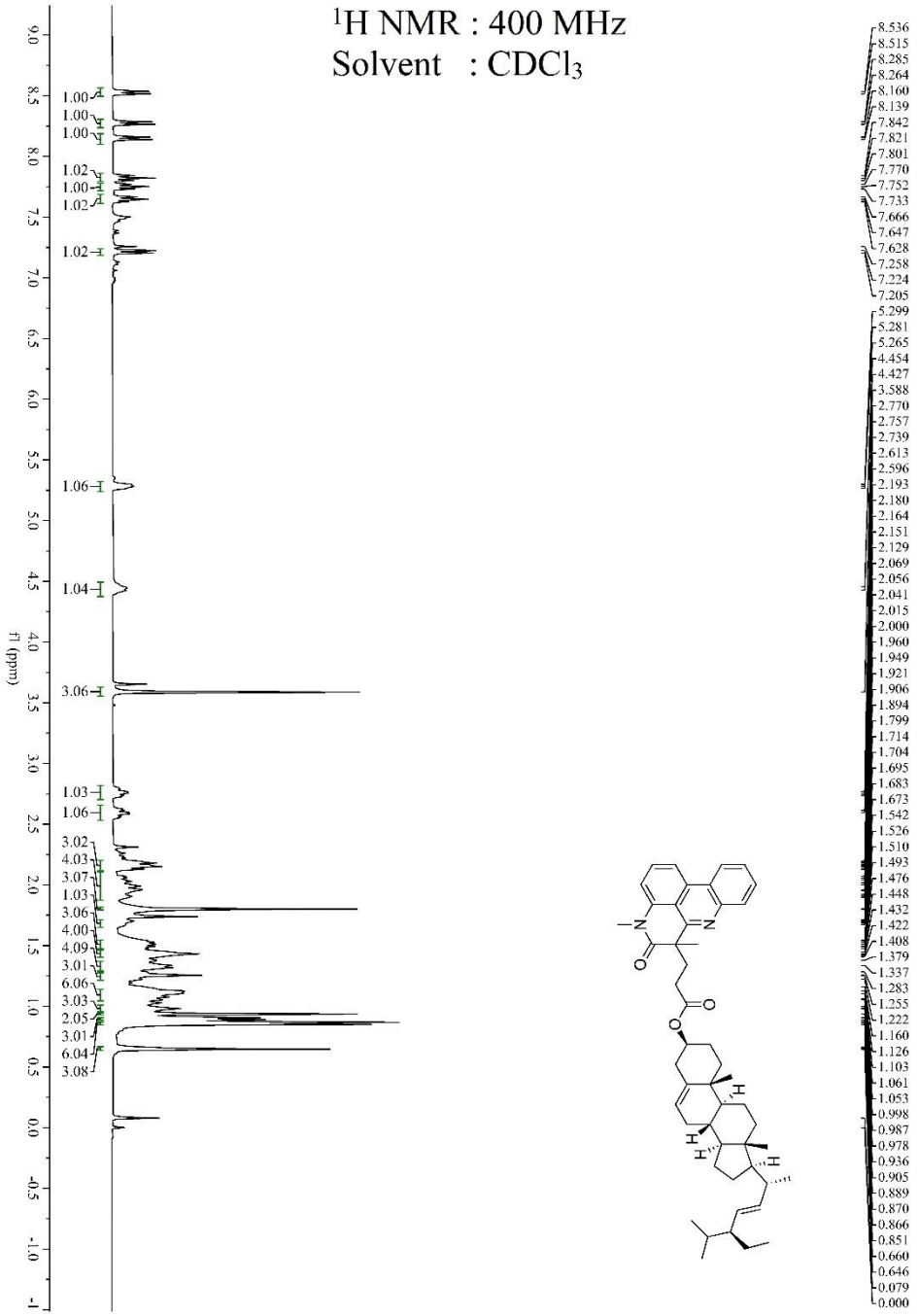

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
173.535
172.139
158.760
144.883
139.584
138.657
133.242
131.778
129.925
129.121
126.678
122.676
122.475
122.423
116.150
112.164
110.749
77.318
77.000
76.682
73.798
56.601
56.047
50.600
49.900
42.228
39.649
39.466
36.855
36.456
36.426
36.126
35.739
31.811
31.757
30.644
29.787
28.308
28.178
27.971
27.607
27.558
24.219
23.777
22.793
22.532
20.935
19.213
18.662
11.789
N
N
O
O
O
H
H
H

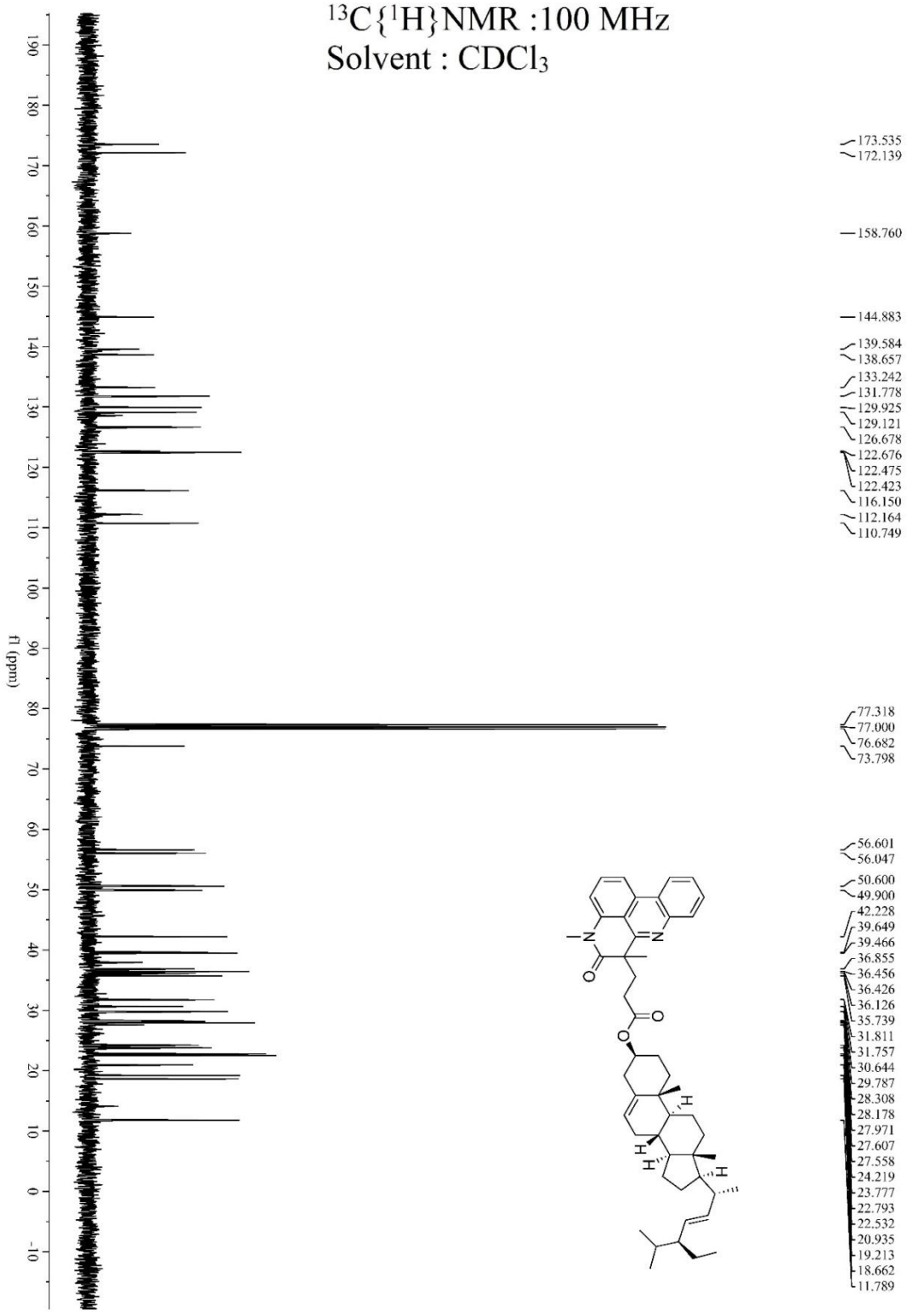
(4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl 3-(4,6-dimethyl-5-oxo-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanoate (3aab)



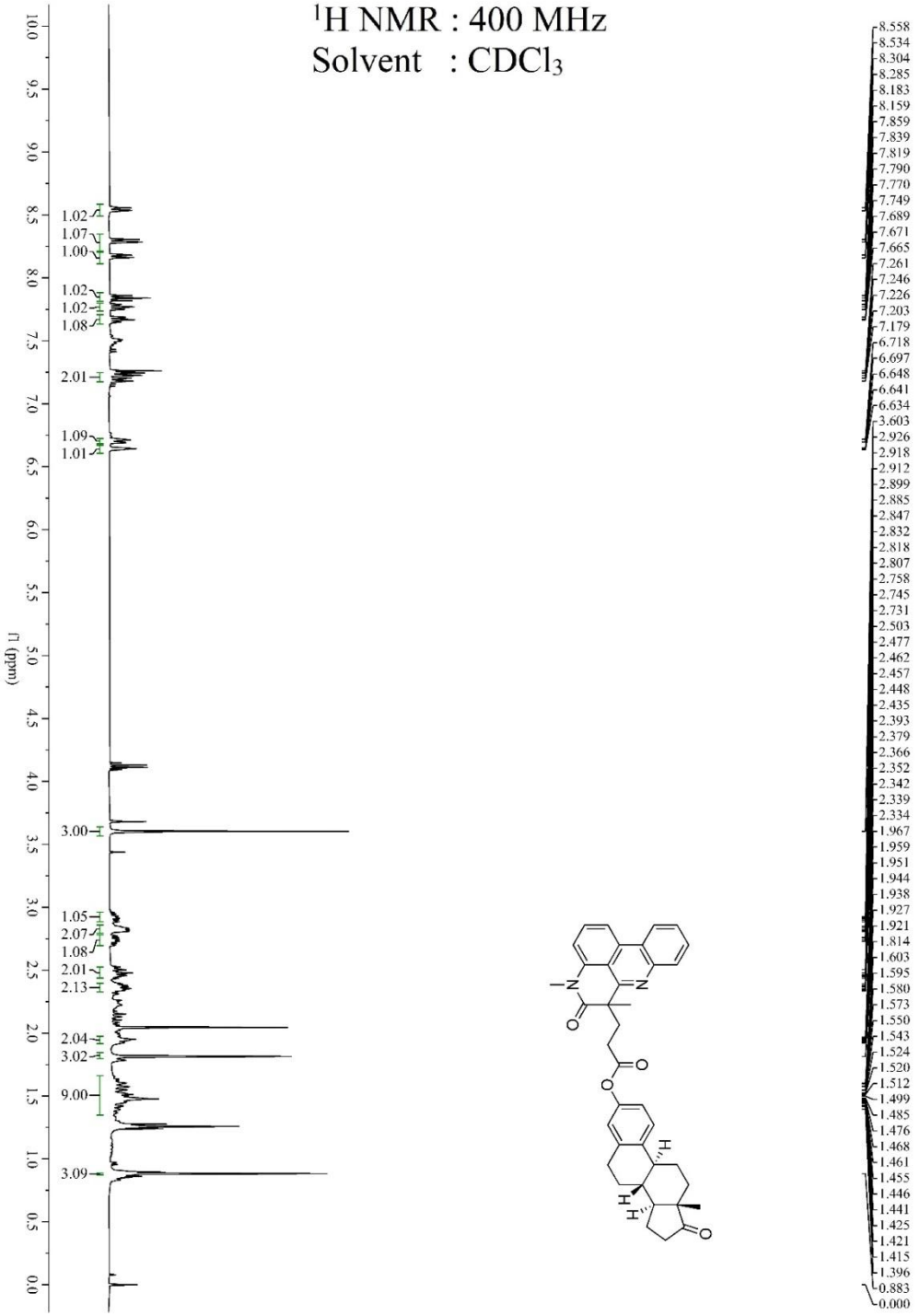

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
173.515
172.743
158.728
149.639
144.887
138.677
133.276
132.436
131.802
129.935
129.147
126.716
125.608
122.690
122.495
116.180
112.179
110.777
108.677
77.317
76.683
68.309
50.668
40.722
36.078
30.417
30.362
29.813
28.597
27.200
26.278
20.703
N
N
O
O
O

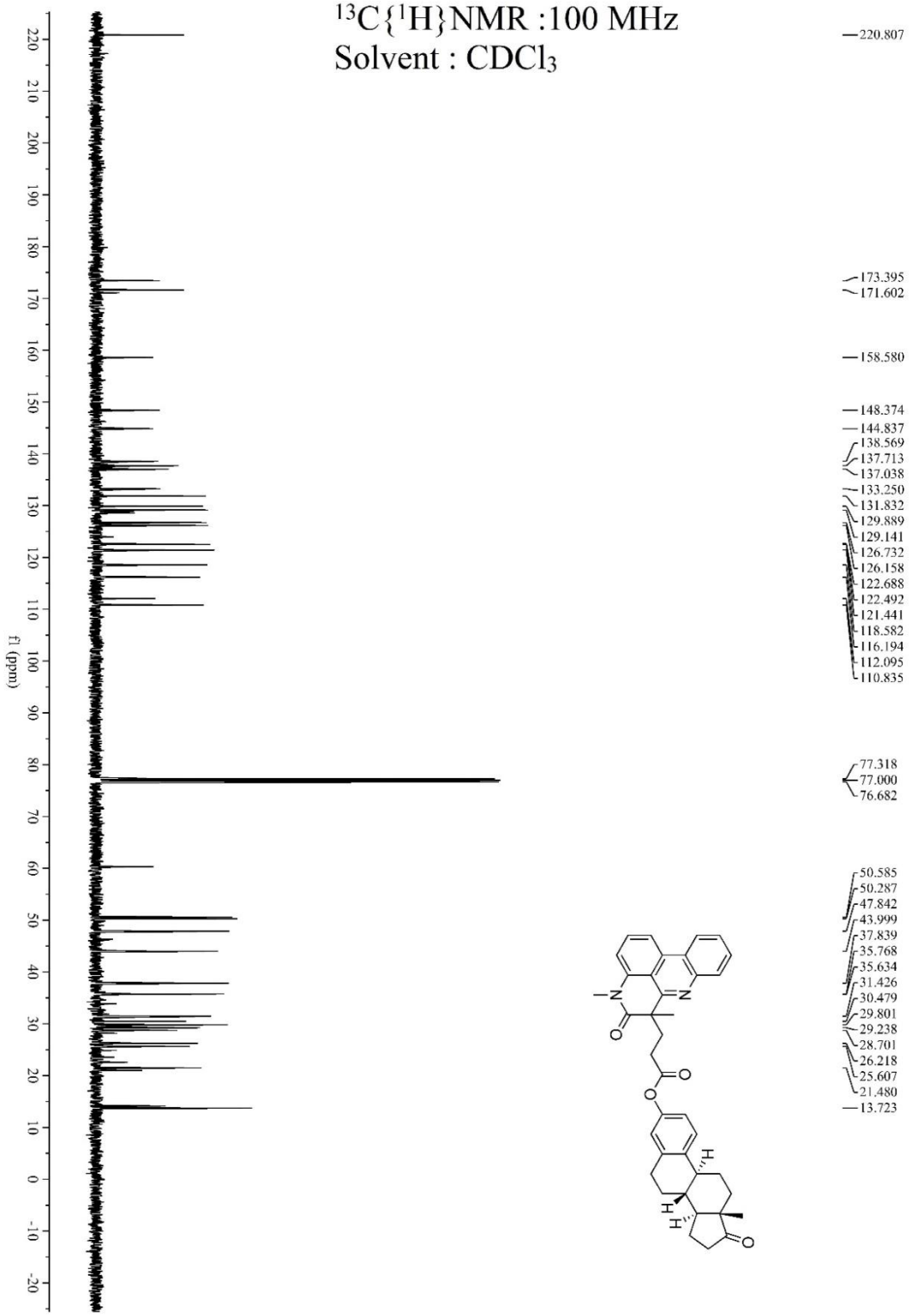
(3*S*,8*S*,9*S*,10*R*,13*R*,14*R*,17*R*)-17-((2*R*,5*S*,*E*)-5-Ethyl-6-methylhept-3-en-2-yl)- 8,10,13-trimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl-3-(4,6-dimethyl-5-oxo-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanoate (3aac)



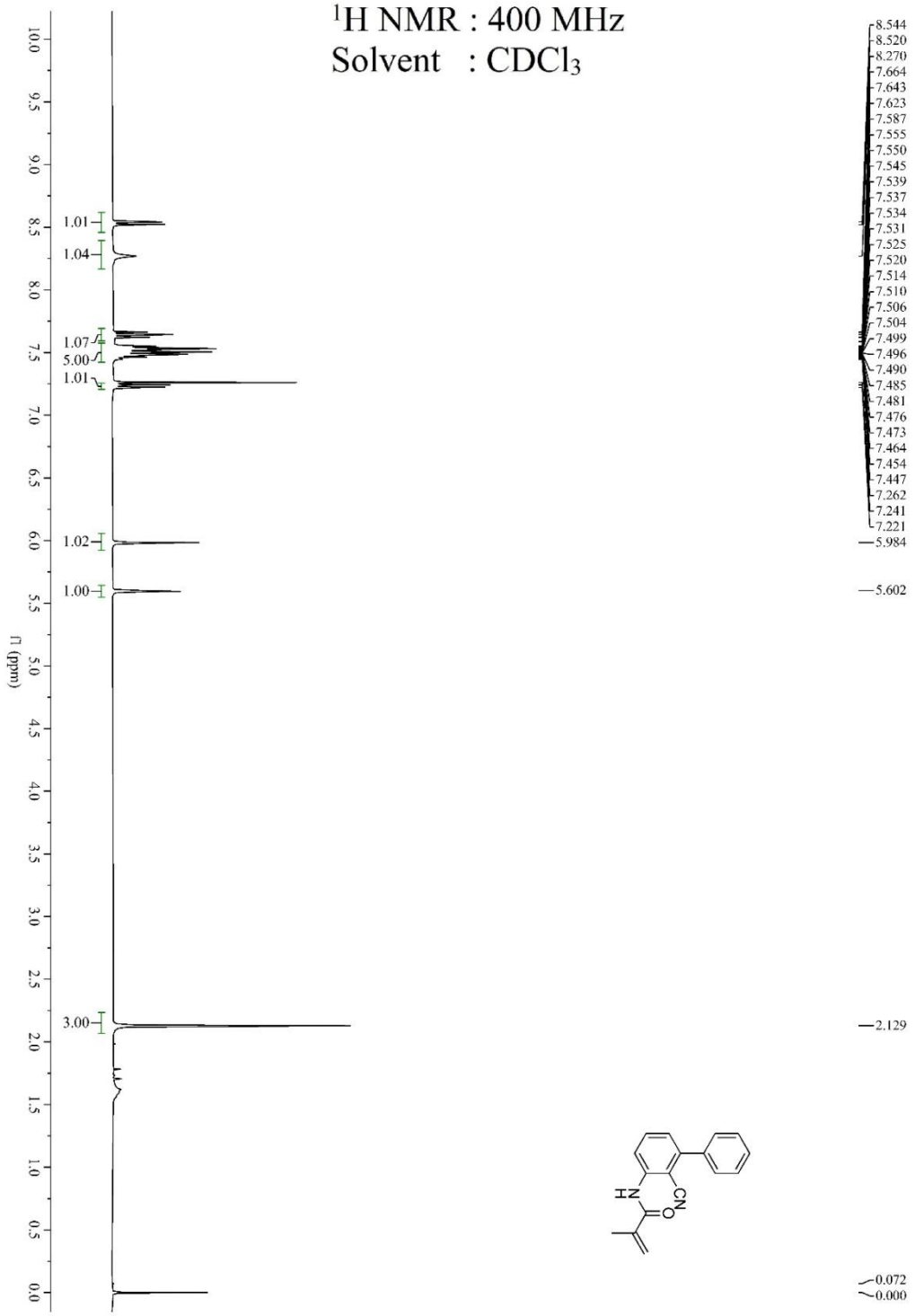

$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
173.535
172.139
158.760
144.883
139.584
138.657
133.242
131.778
129.925
129.121
126.678
122.676
122.475
122.423
116.150
112.164
110.749
77.318
77.000
76.682
73.798
56.601
56.047
50.600
49.900
42.228
39.649
39.466
36.855
36.456
36.426
36.126
35.739
31.811
31.757
30.644
29.787
28.308
28.178
27.971
27.607
27.558
24.219
23.777
22.793
22.532
20.935
19.213
18.662
11.789

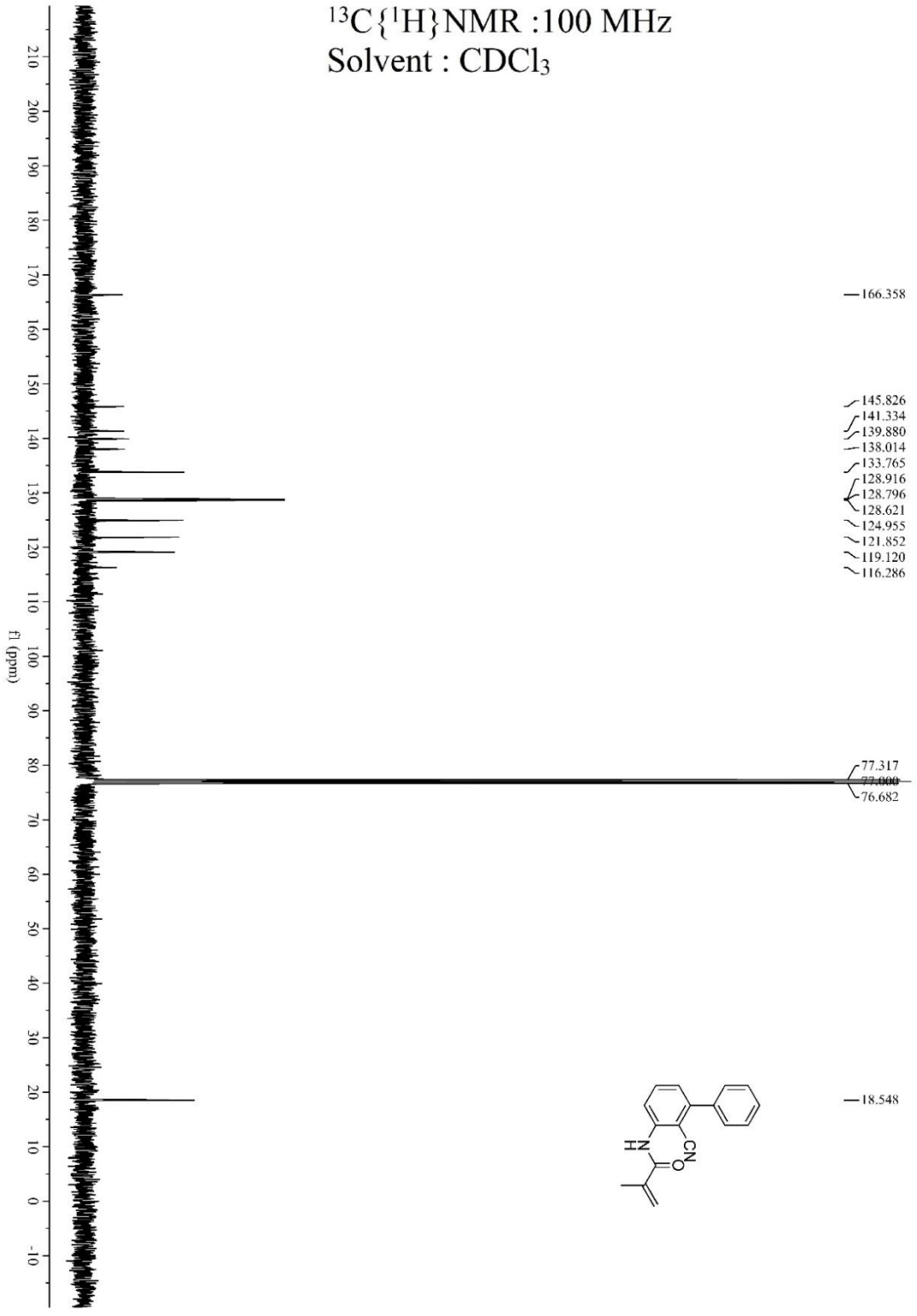
(*8R*,*9S*,*13S*,*14S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-*6H*-cyclopenta[*a*]phenanthren-3-yl-3-(4,6-dimethyl-5-oxo-5,6- dihydro-*4H*-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanoate (3aad)




$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
220.807
173.395
171.602
158.580
148.374
144.837
138.569
137.713
137.038
133.250
131.832
129.889
129.141
126.732
126.158
122.688
122.492
121.441
118.582
116.194
112.095
110.835
77.318
77.000
76.682
50.585
50.287
47.842
43.999
37.839
35.768
35.634
31.426
30.479
29.801
29.238
28.701
26.218
25.607
21.480
13.723

N-(2-cyano-[1,1'-biphenyl]-3-yl)methacrylamide




$^{13}C\{^{1}H\}$NMR :100 MHz
Solvent : $CDCl_3$
f1 (ppm)
166.358
145.826
141.334
139.880
138.014
133.765
128.916
128.796
128.621
124.955
121.852
119.120
116.286
77.317
77.000
76.682
18.548
HN
O
CN