Supporting Information

Photocatalytic Radical Cyclization of *N*-(*o*-Cyanobiaryl)acrylamides with Oxime Esters

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1. General Information

Unless otherwise stated, all commercial reagents were used as received. 2-Bromo-6-aminobenzonitrile (Leyan, 99%), *p*-Tolylbronic acid (Meryer, 98%), 2,3-Butanedione (Macklin, 98%) were used without further treatment. 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, 282 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).

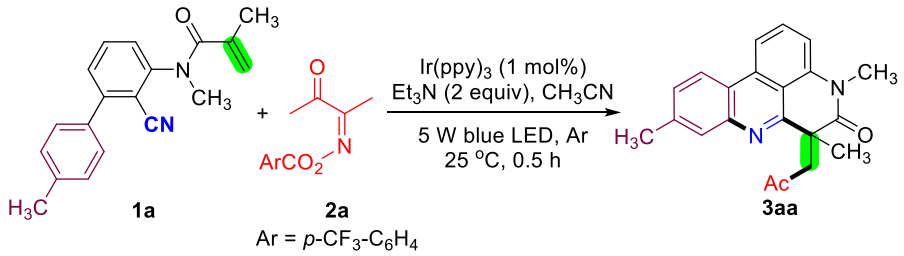
2. Experiment Section

2.1 General Procedure for the Synthesis of Substrates

All of the *N*-(2-cyano-4'-methyl-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide(**1**)[1] and 3-(((4-(trifluoromethyl)benzoyl)oxy)imino)butan-2-one (**2**)[2]-[3] were synthesized according to the known methods.

2.2 Table S1. Screening optimal conditions of 1a and acyl oxime esters 2a [a]

we investigated the optimal reaction conditions of *N*-(2-cyano-4'-methyl-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide (**1a**) and 3-(((4-(trifluoromethyl)benzoyl)oxy)imino)butan-2-one (**2a**) (Table S1, ESI). Pleasingly, the desired **3aa** was produced in 81% yield (Table 1, entry 1). Control experiments revealed that both of photocatalyst and light irradiation were essential for reactivity (entry 2). The absence of base resulted in reduced yield (entry 3). The use of other photocatalyst decreased the yield (entries 4-7). The effect of bases was examined, and the results showed that Et_3N was preferred (entry 1 vs entries 8-11). Other solvents, such as THF (tetrahydrofuran), DMF (*N*,*N*-dimethylformamide), and toluene, could also favor the reaction, albeit with lower reactivity (entry 1 vs entries 12-18).

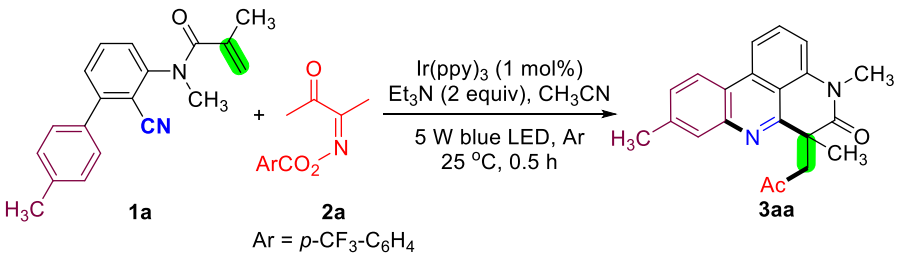


Entry	Variation from the standard conditions	Yield (%)[b]
1	none	81
2	no light	0
3	no PC	17
4	no Et_3N	28
5	$Ru(bpy)_3Cl_2$ instead of $Ir(ppy)_3$	55
6	Eosin Y instead of $Ir(ppy)_3$	28
7	Na_2-Eosin Y instead of $Ir(ppy)_3$	33
8	Eosin B instead of $Ir(ppy)_3$	30
9	2,6-lutidine instead of Et_3N	52
10	DIPEA instead of Et_3N	46
11	DABCO instead of Et_3N	66
12	Na_2CO_3 instead of Et_3N	32
13	THF instead of CH_3CN	51
14	DMF instead of CH_3CN	73
15	toluene instead of CH_3CN	72
16	DCE instead of CH_3CN	70
17	DMSO instead of CH_3CN	62

18	1,4-dioxane instead of CH_3CN	58
19	acetone instead of CH_3CN	56
20[c]	none	72

[a] Standard reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), photocatalyst (2 mol %), base (0.4 mmol, 2.0 equiv), solvent (2.0 mL), 5 W blue LED (λmax = 468 nm), argon, 25 °C, 0.5 h. [b] Yield of isolated 3aa was reported. [c] 1 mmol scale reaction.

2.3 Typical Experimental Procedure



To a Schlenk tube were added *N*-(2-cyano-4'-methyl-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide **1a** (0.2 mmol, 1.0 equiv.), 3-(((4-(trifluoromethyl)benzoyl)oxy)imino)butan-2-one **2a** (0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (1% mol), Et_3N (0.4 mmol, 2.0 equiv), and CH_3CN (2 mL) at 25 °C under an argon atmosphere by 5 W blue LEDs irradiation for 0.5 h. Until completion, consumption of the starting material was observed by TLC and/or GC-MS analysis. After the reaction was finished, the solvent was removed from the reaction mixture and the crude product was purified by column chromatography (petroleum ether/ethyl acetate, 4 : 1) to provide the desired products.

2.4 Details of Visible-Light Source

The light source bought from SANYI (https://item.taobao.com/item.htm?spm=a1z09.2.0.0.42672e8dv2Chsz&id=35497290577&_u=j35sh1qt9325), 5 W blue LED light bulb (E27). The wavelength was about 460-470 nm and the wavelength of peak intensity was about 467.5 nm. The pictures of the visible-light source (Figure S1) was shown as follow:

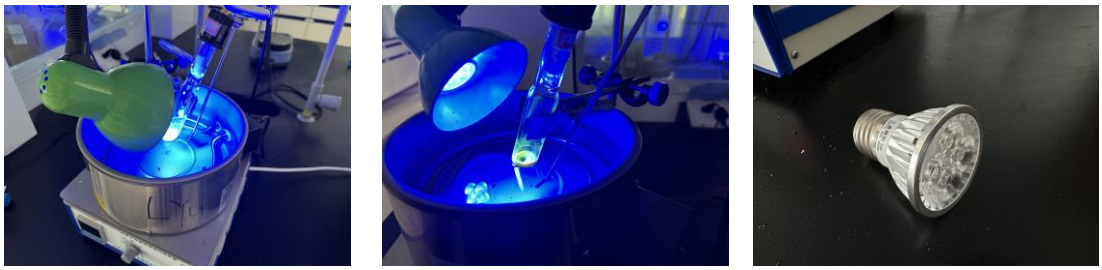
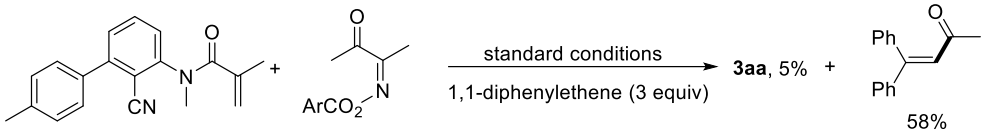


Figure S1. Pictures of Visible-Light Source

2.5 Control Experiments

2.5.1 GC-MS Analysis of trapping product 4

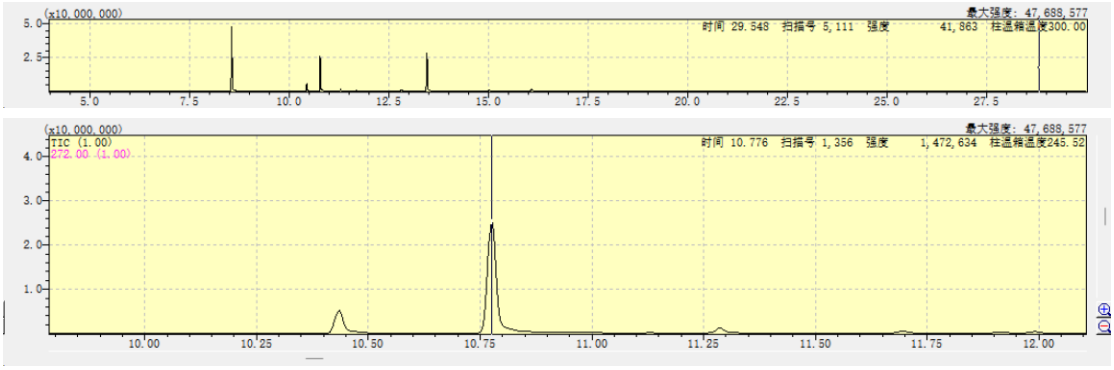


1a

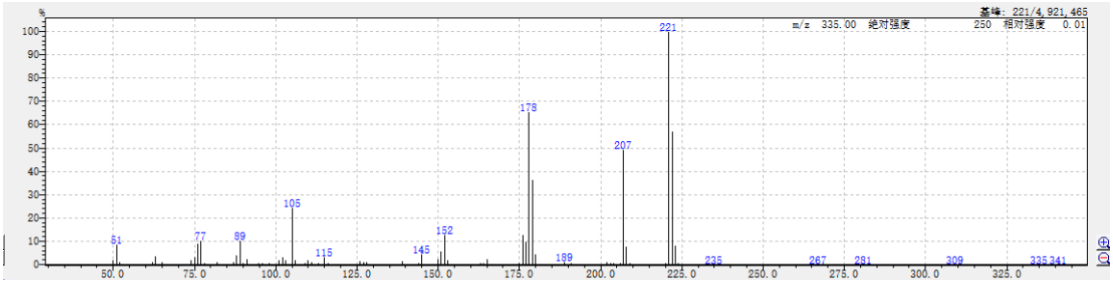
2a
Ar = *p*-CF_3-C_6H_4

4 (Observed by GC-MS analysis)Chemical Formula: $C_{16}H_{14}O$
Exact Mass: 222.1045
Molecular Weight: 222.2870

Spectra of GC-MS



MS spectra of the peak at 10.775 min



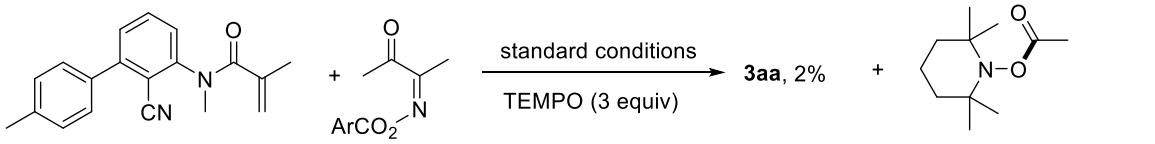
[MS Spectrum]
# of Peaks 457
Raw Spectrum 10.775 (scan : 1356)
Background No Background Spectrum
Base Peak m/z 221.00 (Inten : 4,921,465)
Event# 1

m/z	Absolute Intensity	Relative Intensity						
50.00	98246	2.00	51.00	421742	8.57	52.00	66522	1.35

53.05	14591	0.30	97.05	20100	0.41	141.05	4283	0.09
54.05	1061	0.02	98.00	44311	0.90	142.15	1301	0.03
55.00	3695	0.08	99.05	25050	0.51	143.05	1733	0.04
55.60	700	0.01	100.10	26642	0.54	144.05	31720	0.64
56.65	11660.02		101.05	104478	2.12	145.00	218311	4.44
57.65	2048	0.04	102.05	168463	3.42	146.00	24666	0.50
58.30	594	0.01	103.05	109399	2.22	147.00	2842	0.06
59.30	841	0.02	103.95	16244	0.33	148.05	792	0.02
60.00	294	0.01	105.05	1198170	24.35	149.05	14017	0.28
61.05	7608	0.15	106.05	92984	1.89	150.00	122362	2.49
62.05	51962	1.06	107.05	5696	0.12	151.00	283628	5.76
63.05	182715	3.71	108.00	742	0.02	152.00	635375	12.91
64.05	21035	0.43	109.05	30777	0.63	153.00	104558	2.12
65.05	55691	1.13	110.00	107111	2.18	154.00	8649	0.18
66.05	3896	0.08	111.00	58409	1.19	155.00	11400.02	
67.45	953	0.02	111.95	6828	0.14	156.00	58	0.00
68.55	3344	0.07	113.05	39549	0.80	157.00	148	0.00
69.50	15089	0.31	114.10	15007	0.30	158.00	190	0.00
70.45	2075	0.04	115.05	167081	3.39	159.00	239	0.00
71.00	1682	0.03	116.05	37030	0.75	160.00	14	0.00
72.05	524	0.01	117.05	11424	0.23	161.05	2777	0.06
73.05	4583	0.09	118.10	1412	0.03	162.00	10399	0.21
74.05	92611	1.88	118.90	932	0.02	162.95	49773	1.01
75.05	169922	3.45	119.90	311	0.01	164.00	33898	0.69
76.05	454070	9.23	121.00	590	0.01	165.00	116772	2.37
77.00	520303	10.57	122.05	5319	0.11	166.00	19009	0.39
78.05	48924	0.99	123.00	3710	0.08	167.00	7754	0.16
79.05	3930	0.08	124.00	3386	0.07	168.05	1986	0.04
80.15	643	0.01	125.05	17900	0.36	169.00	1964	0.04
81.15	17028	0.35	126.05	86413	1.76	170.00	198	0.00
82.10	54215	1.10	127.05	68262	1.39	171.00	119	0.00
83.05	28452	0.58	128.05	62420	1.27	172.00	65	0.00
84.05	7793	0.16	129.05	24991	0.51	173.05	1901	0.04
85.05	5813	0.12	130.05	2689	0.05	173.95	19710	0.40
86.05	29213	0.59	131.05	1910	0.04	175.05	43789	0.89
87.05	66359	1.35	132.00	303	0.01	176.00	636905	12.94
88.05	208717	4.24	133.00	750	0.02	177.00	493956	10.04
89.05	517759	10.52	134.00	1282	0.03	178.00	3231591	65.66
90.05	34275	0.70	135.00	1898	0.04	179.00	1802255	36.62
91.05	121034	2.46	136.05	422	0.01	180.00	233553	4.75
92.05	8663	0.18	137.05	15036	0.31	180.95	23797	0.48
93.65	12815	0.26	138.00	13470	0.27	182.00	4060	0.08
94.65	48668	0.99	139.00	80239	1.63	182.90	713	0.01
96.05	31638	0.64	140.00	11471	0.23	183.90	94	0.00

185.05	408	0.01	208.00	393734	8.00	231.00	58	0.00
185.95	820	0.02	209.00	36663	0.74	232.00	74	0.00
187.00	9209	0.19	209.95	2301	0.05	233.00	185	0.00
188.00	7460	0.15	210.90	220	0.00	234.00	194	0.00
189.00	59041	1.20	211.90	68	0.00	234.95	541	0.01
190.00	26148	0.53	212.90	38	0.00	236.00	65	0.00
191.00	39292	0.80	213.90	62	0.00	237.00	13	0.00
192.00	9943	0.20	214.90	46	0.00	238.00	50	0.00
193.00	27570	0.56	215.90	87	0.00	239.00	11	0.00
193.95	65110.13		217.05	303	0.01	242.00	22	0.00
194.95	6902	0.14	217.95	7289	0.15	244.00	36	0.00
195.90	11510.02		219.00	20318	0.41	245.00	36	0.00
196.90	305	0.01	220.05	41841	0.85	246.00	50	0.00
197.90	393	0.01	**221.00**	**4921465**	**100.00**	247.00	65	0.00
198.95	1098	0.02	**222.00**	**2822166**	**57.34**	248.00	62	0.00
199.95	11302	0.23	**223.00**	**417332**	**8.48**	249.00	126	0.00
201.00	14175	0.29	224.00	38826	0.79	250.00	316	0.01
202.00	67217	1.37	224.95	2365	0.05	250.95	440	0.01
203.00	45154	0.92	226.00	238	0.00	251.80	516	0.01
204.00	31284	0.64	227.00	63	0.00	252.80	183	0.00
204.95	25623	0.52	228.00	79	0.00	253.80	266	0.01
206.05	30948	0.63	229.00	90	0.00			
207.00	2428650	49.35	230.00	57	0.00			

2.5.2 GC-MS Analysis of trapping product 5

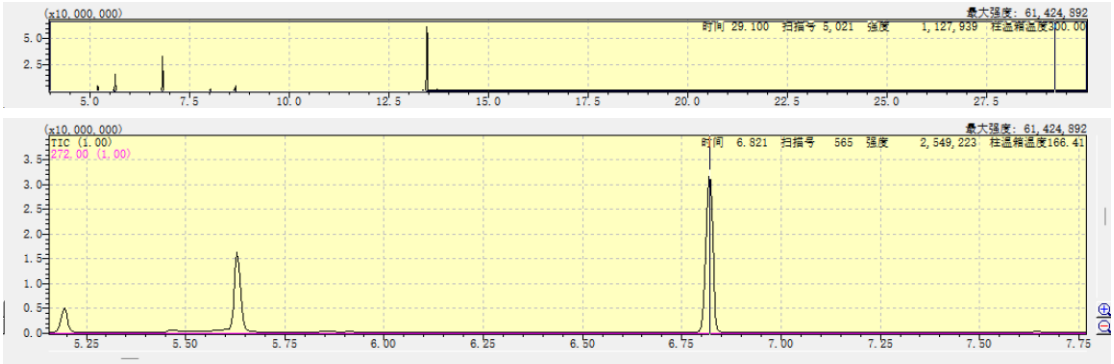


1a

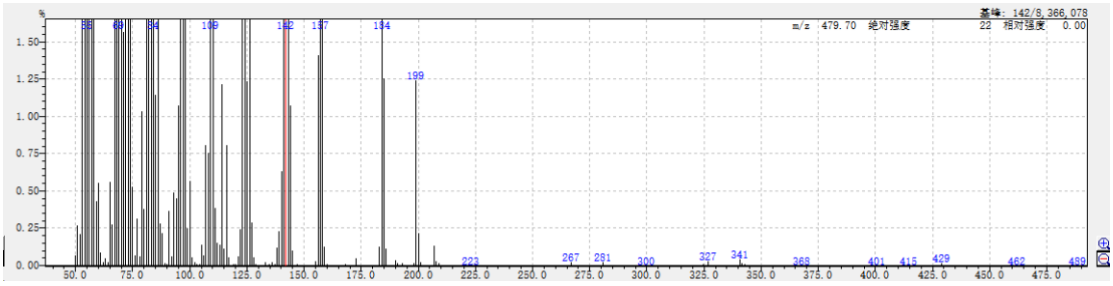
2a
Ar = *p*-CF_3-C_6H_4

5(Observed by GC-MS analysis)
Chemical Formula: $C_{11}H_{21}NO_2$
Exact Mass: 199.1572
Molecular Weight: 199.2940

Spectra of GC-MS



MS spectra of the peak at 6.820 min



[MS Spectrum]

# of Peaks 544

Raw Spectrum 6.820 (scan : 565)

Background No Background Spectrum

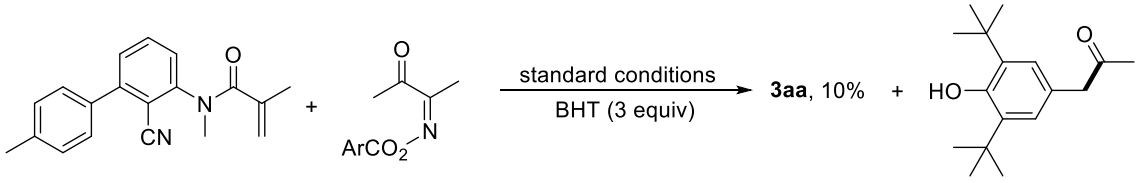
Base Peak m/z 142.10 (Inten : 8,366,078)

Event# 1

m/z	Absolute Intensity	Relative Intensity						
50.00	5748	0.07	80.05	32050	0.38	110.10	230071	2.75
50.95	22756	0.27	81.05	373374	4.46	111.10	32354	0.39
52.05	17958	0.21	82.05	344722	4.12	112.10	13169	0.16
53.00	201458	2.41	83.05	1411824	16.88	113.15	11810	0.14
54.05	153858	1.84	84.05	396255	4.74	114.05	102207	1.22
55.00	4241814	50.70	85.05	96058	1.15	115.05	9913	0.12
56.00	1796764	21.48	86.00	357474	4.27	116.00	67910	0.81
57.05	322629	3.86	87.05	23714	0.28	117.00	4932	0.06
58.00	591054	7.06	88.00	18615	0.22	118.05	719	0.01
59.05	36285	0.43	89.00	1756	0.02	119.05	11880.01	
60.00	46734	0.56	90.05	834	0.01	120.15	1348	0.02
61.00	7324	0.09	91.00	30826	0.37	121.10	5250	0.06
61.95	2050	0.02	92.05	5598	0.07	122.15	20720	0.25
63.00	4138	0.05	93.05	41058	0.49	123.10	176914	2.11
64.05	2441	0.03	94.05	37951	0.45	124.10	289506	3.46
65.00	47231	0.56	95.05	90230	1.08	125.10	103881	1.24
66.05	23476	0.28	96.05	156846	1.87	126.10	252023	3.01
67.05	334082	3.99	97.05	203377	2.43	127.10	24546	0.29
68.05	253423	3.03	98.05	191135	2.28	128.05	4785	0.06
69.05	1991910	23.81	99.05	21092	0.25	129.00	961	0.01
70.05	499011	5.96	100.05	47952	0.57	130.05	536	0.01
71.05	131296	1.57	101.05	4694	0.06	131.00	404	0.00
72.05	178516	2.13	102.05	23110.03		132.00	242	0.00
73.05	147411	1.76	103.05	968	0.01	133.00	2297	0.03
74.05	1050061	12.55	104.15	999	0.01	133.95	672	0.01
75.00	44314	0.53	105.05	12066	0.14	134.95	964	0.01
76.05	6181	0.07	106.15	6099	0.07	136.05	2244	0.03
77.00	26756	0.32	107.05	67703	0.81	137.15	11010.01	
78.05	5425	0.06	108.15	63355	0.76	138.10	10446	0.12
79.00	86682	1.04	109.05	1675304	20.02	139.15	19478	0.23

140.10	52894	0.63	165.05	413	0.00	189.90	3279	0.04
141.15	209881	2.51	166.00	186	0.00	190.80	1548	0.02
142.10	8366078	100.00	167.00	183	0.00	191.85	409	0.00
143.05	1589342	19.00	168.00	978	0.01	192.80	1580	0.02
144.05	89810	1.07	169.00	206	0.00	193.85	465	0.01
145.05	8680	0.10	169.90	49	0.00	194.90	282	0.00
146.05	680	0.01	170.90	476	0.01	195.90	134	0.00
147.00	11830	0.01	172.00	178	0.00	196.90	132	0.00
148.00	382	0.00	172.95	4519	0.05	**198.05**	**1507**	**0.02**
149.00	310	0.00	173.95	550	0.01	**199.00**	**103895**	**1.24**
150.00	148	0.00	175.00	119	0.00	**200.00**	**18180**	**0.22**
151.00	585	0.01	175.90	84	0.00	201.00	2126	0.03
152.00	393	0.00	176.90	550	0.01	202.00	140	0.00
153.00	255	0.00	177.90	215	0.00	203.00	73	0.00
154.10	239	0.00	178.80	386	0.00	204.00	41	0.00
155.15	2544	0.03	179.80	100	0.00	205.00	174	0.00
156.15	118186	1.41	180.80	63	0.00	205.90	162	0.00
157.05	1704179	20.37	182.00	247	0.00	206.95	11128	0.13
158.05	179444	2.14	183.05	11076	0.13	207.90	2534	0.03
158.95	11044	0.13	184.00	904495	10.81	208.85	1798	0.02
160.10	873	0.01	185.00	105033	1.26	209.80	246	0.00
161.10	206	0.00	186.00	9698	0.12	210.90	538	0.01
162.10	202	0.00	186.95	644	0.01	211.90	218	0.00
163.00	500	0.01	188.00	151	0.00	212.90	50	0.00
164.00	175	0.00	188.90	114	0.00			

2.5.3GC-MS Analysis of trapping product 6

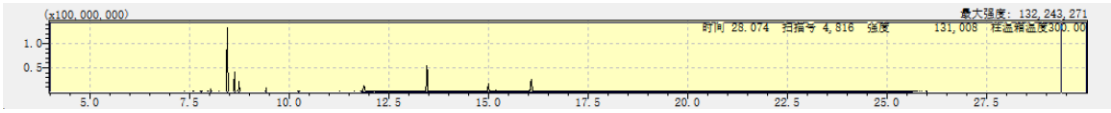


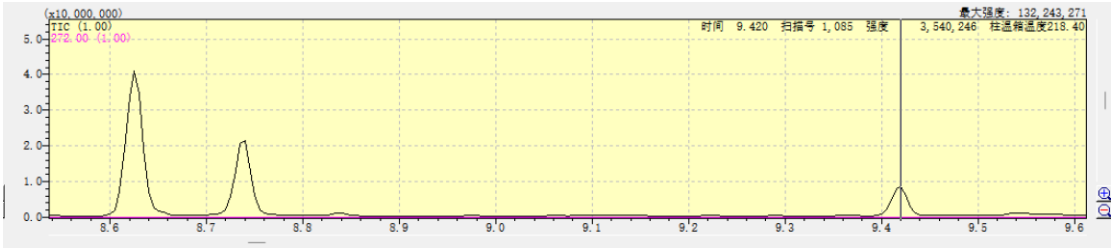
1a

2a
Ar = *p*-CF_3-C_6H_4

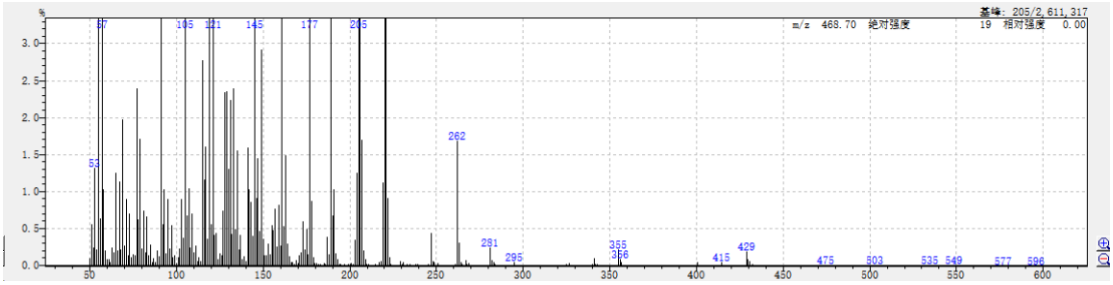
6 (Observed by GC-MS analysis)
Chemical Formula: $C_{17}H_{26}O_2$
Exact Mass: 262.1933
Molecular Weight: 262.3930

Spectra of GC-MS





MS spectra of the peak at 9.420 min



[MS Spectrum]

# of Peaks 545

Raw Spectrum 9.420 (scan : 1085)

Background No Background Spectrum

Base Peak m/z 205.05 (Inten : 2,611,317)

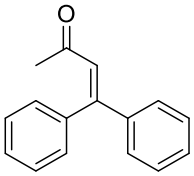
Event# 1

m/z	Absolute Intensity	Relative Intensity						
49.95	2660	0.10	72.05	3741	0.14	94.05	4580	0.18
50.95	14707	0.56	73.00	18658	0.71	95.05	23661	0.91
52.00	6433	0.25	73.95	3190	0.12	96.05	6068	0.23
53.00	34537	1.32	75.00	4178	0.16	97.05	14511	0.56
54.05	5875	0.22	76.05	3818	0.15	98.05	3038	0.12
55.00	128775	4.93	77.00	62708	2.40	99.10	3684	0.14
56.05	16810	0.64	78.05	16479	0.63	100.05	11750.04	
57.05	533012	20.41	79.00	44975	1.72	100.95	3123	0.12
58.05	26916	1.03	80.05	6017	0.23	102.00	6193	0.24
59.00	5388	0.21	81.05	19393	0.74	103.00	23620	0.90
60.00	2346	0.09	82.05	4969	0.19	104.05	9800	0.38
61.00	2390	0.09	83.05	17510	0.67	105.05	156772	6.00
61.95	1404	0.05	84.05	3924	0.15	106.05	17797	0.68
62.95	6620	0.25	85.05	7431	0.28	107.05	27484	1.05
64.05	4734	0.18	86.05	1515	0.06	108.05	6570	0.25
65.00	33004	1.26	86.95	2644	0.10	109.05	18595	0.71
66.00	5554	0.21	88.05	1225	0.05	110.05	4913	0.19
67.05	29824	1.14	88.95	5466	0.21	111.05	7299	0.28
68.00	5842	0.22	90.05	3489	0.13	112.05	1765	0.07
69.05	51688	1.98	91.00	121758	4.66	113.10	2977	0.11
70.05	7186	0.28	92.05	14599	0.56	114.05	1759	0.07
71.05	23592	0.90	93.05	27007	1.03	115.00	72750	2.79

116.00	30364	1.16	160.05	72110.28		204.05	33056	1.27
117.00	42305	1.62	161.00	94812	3.63	205.05	2611317	100.00
118.15	9593	0.37	162.05	14064	0.54	206.00	404124	15.48
119.05	89534	3.43	163.00	38985	1.49	207.00	44658	1.71
120.05	14642	0.56	164.00	7902	0.30	207.95	5420	0.21
121.05	93380	3.58	165.00	3588	0.14	208.90	2290	0.09
122.05	10899	0.42	166.10	1538	0.06	209.95	527	0.02
123.05	11490	0.44	167.00	1281	0.05	210.95	834	0.03
124.05	2541	0.10	168.05	777	0.03	212.00	300	0.01
125.05	4371	0.17	169.00	1956	0.07	212.95	513	0.02
126.05	3630	0.14	170.05	11050.04		214.00	484	0.02
127.00	19561	0.75	171.00	3892	0.15	214.95	750	0.03
128.05	61458	2.35	172.05	4874	0.19	216.15	361	0.01
129.05	61693	2.36	173.00	15636	0.60	217.05	1205	0.05
130.05	34266	1.31	174.00	5879	0.23	218.15	1771	0.07
131.05	58683	2.25	175.00	13121	0.50	219.15	29624	1.13
132.05	11415	0.44	176.05	41180.16		220.05	1505008	57.63
133.05	62869	2.41	177.00	164585	6.30	221.05	251478	9.63
134.05	12998	0.50	178.00	23017	0.88	222.00	24073	0.92
135.05	40666	1.56	179.00	3124	0.12	223.00	3010	0.12
136.05	5895	0.23	179.90	11160.04		223.90	702	0.03
137.05	11073	0.42	181.00	894	0.03	225.10	510	0.02
138.10	2250	0.09	182.05	556	0.02	226.10	185	0.01
139.10	3567	0.14	183.10	630	0.02	227.10	430	0.02
140.05	1685	0.06	184.05	437	0.02	228.15	269	0.01
141.05	41691	1.60	185.05	11000.04		229.10	1751	0.07
142.05	27015	1.03	186.05	849	0.03	230.05	648	0.02
143.05	22491	0.86	187.00	10111	0.39	231.00	1254	0.05
144.05	10578	0.41	188.05	4024	0.15	231.90	444	0.02
145.05	134424	5.15	189.00	99524	3.81	233.10	580	0.02
146.00	23993	0.92	190.00	17807	0.68	233.90	217	0.01
147.00	38020	1.46	191.00	27186	1.04	234.90	654	0.03
148.05	12412	0.48	192.00	4410	0.17	236.10	490	0.02
149.05	76573	2.93	192.95	2552	0.10	237.00	366	0.01
150.00	9598	0.37	193.95	761	0.03	238.05	738	0.03
150.95	3720	0.14	194.95	729	0.03	239.00	780	0.03
152.05	3897	0.15	195.85	421	0.02	240.00	214	0.01
152.95	7749	0.30	197.05	665	0.03	240.95	443	0.02
154.05	4222	0.16	198.05	340	0.01	242.00	170	0.01
155.00	14234	0.55	199.00	641	0.02	242.95	455	0.02
156.00	12735	0.49	200.00	538	0.02	244.05	327	0.01
157.00	20273	0.78	201.00	940	0.04	245.15	515	0.02
158.00	6791	0.26	202.05	824	0.03	246.05	499	0.02
159.00	21750	0.83	203.00	9306	0.36	247.05	11689	0.45

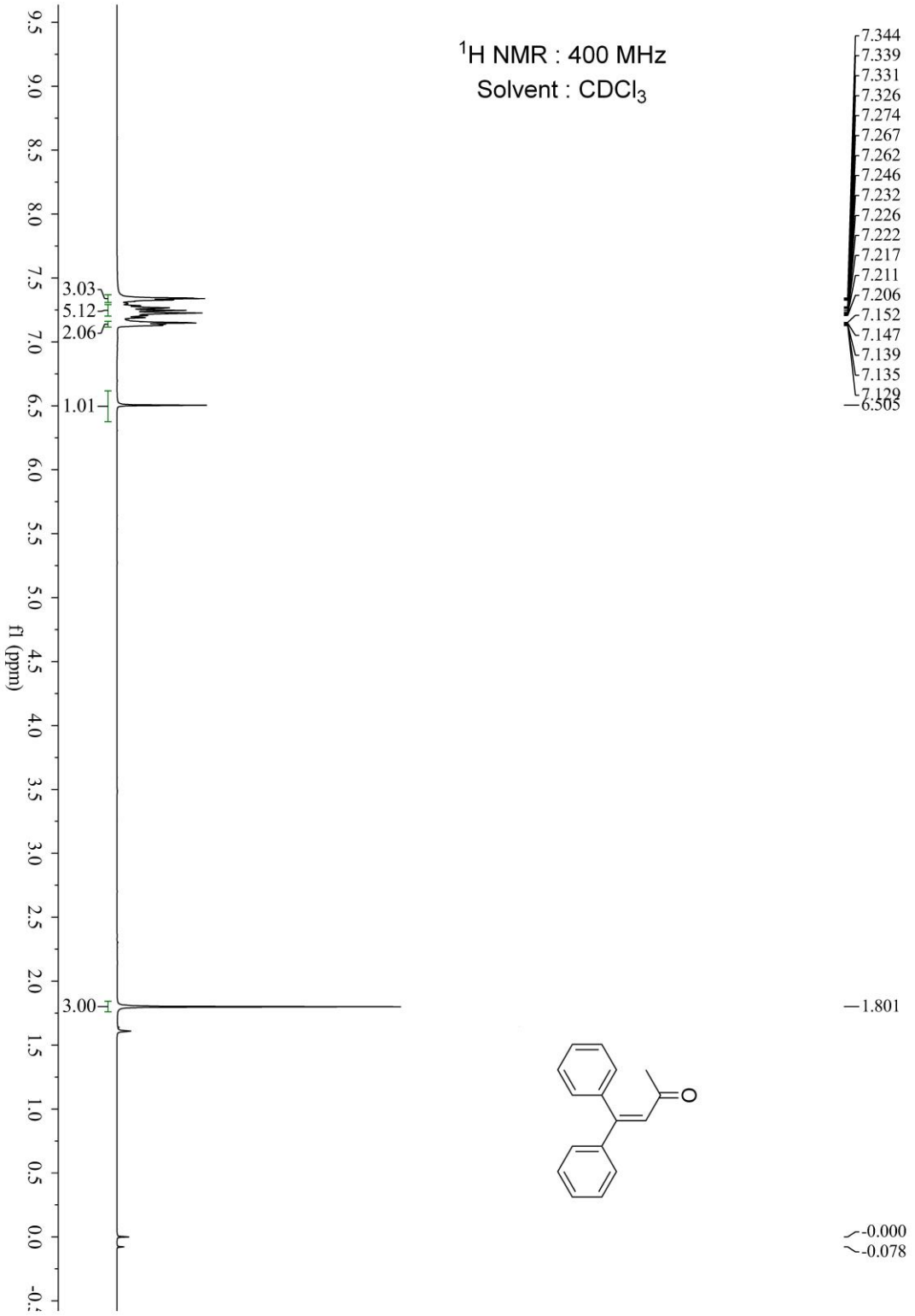
247.95	1817	0.07	270.80	119	0.00	294.00	81	0.00
248.95	1261	0.05	271.80	146	0.01	295.00	1233	0.05
249.70	166	0.01	273.15	386	0.01	295.90	356	0.01
250.75	962	0.04	274.20	223	0.01	296.85	467	0.02
251.80	164	0.01	275.20	223	0.01	297.90	127	0.00
252.80	426	0.02	276.20	148	0.01	298.90	129	0.00
253.80	242	0.01	277.20	161	0.01	299.90	124	0.00
255.00	382	0.01	277.90	110	0.00	300.90	90	0.00
256.00	191	0.01	278.85	482	0.02	301.90	89	0.00
257.00	202	0.01	279.85	323	0.01	302.90	164	0.01
258.00	252	0.01	280.90	6473	0.25	303.90	111	0.00
259.00	284	0.01	281.95	1899	0.07	304.90	82	0.00
260.00	262	0.01	282.95	1481	0.06	305.90	170	0.01
261.15	837	0.03	284.00	754	0.03	306.90	78	0.00
262.05	**44323**	**1.70**	284.95	413	0.02	307.90	110	0.00
263.00	**8334**	**0.32**	286.10	407	0.02	309.00	372	0.01
264.10	**1310**	**0.05**	287.10	162	0.01	310.00	118	0.00
265.05	774	0.03	288.10	262	0.01	311.00	79	0.00
265.85	500	0.02	289.10	218	0.01	312.00	82	0.00
266.80	2218	0.08	290.10	180	0.01	313.00	105	0.00
267.85	713	0.03	291.10	156	0.01			
268.85	11290.04		292.10	218	0.01			
269.80	230	0.01	293.10	127	0.00			

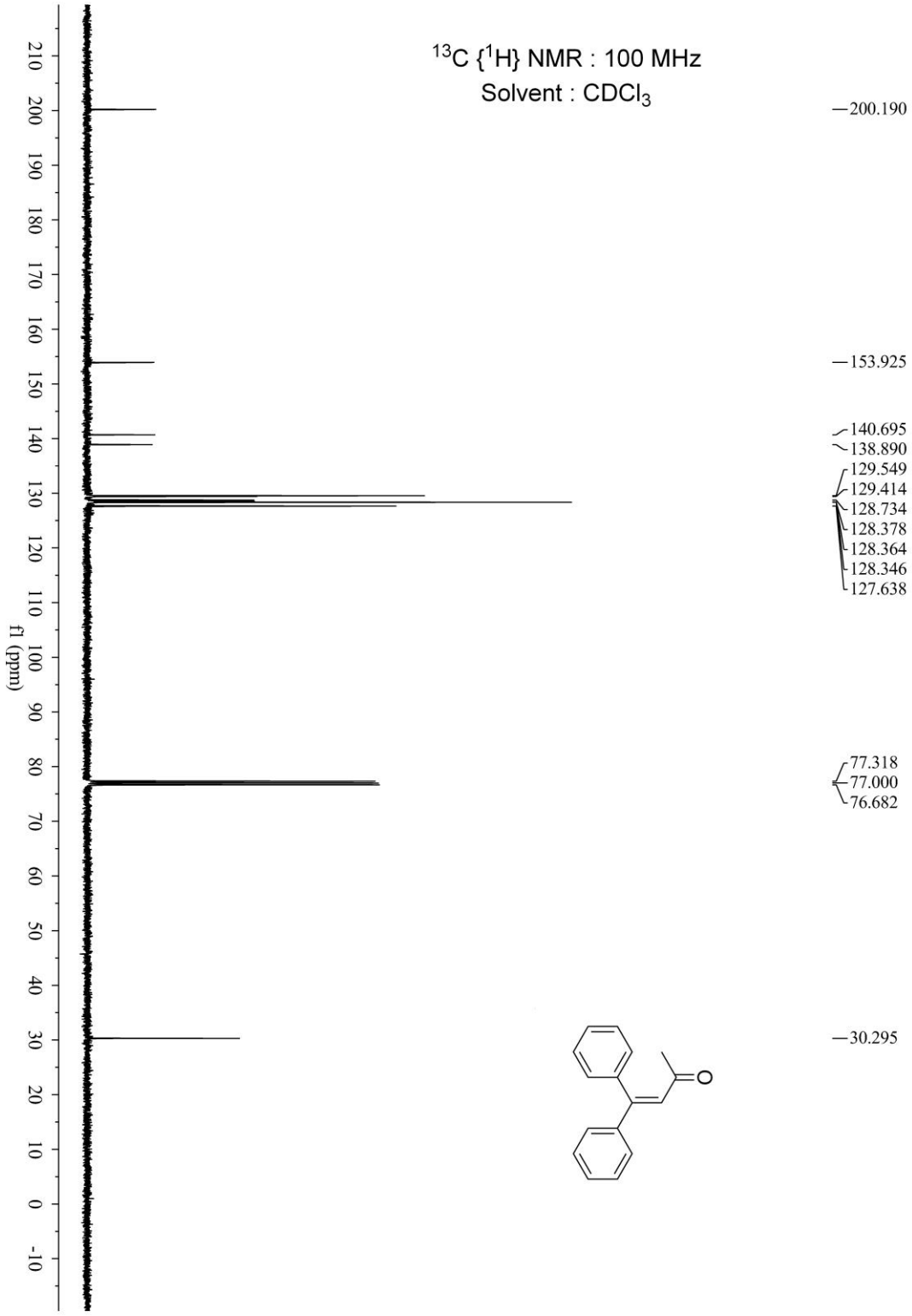
2.5.4 NMR Spectrum Analysis of trapping product 4.



4,4-diphenylbut-3-en-2-one 4: Yield: 25.8 mg, 58%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35-7.32 (m, 3H), 7.28-7.21 (m, 5H), 7.15-7.13 (m, 2H), 6.51 (s, 1H), 1.80 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 200.2, 153.9, 140.7, 138.9, 129.5, 129.4, 128.7, 128.4, 128.4, 128.3, 127.6, 30.3; HRMS (ESI-TOF) *m/z*: $C_{16}H_{15}O$ $(M + H)^+$ calcd for 223.1117, found 223.1121.

The ^{1}H NMR and ^{13}C NMR spectra for 4


^{1}H NMR : 400 MHz
Solvent : $CDCl_3$
7.344
7.339
7.331
7.326
7.274
7.267
7.262
7.246
7.232
7.226
7.222
7.217
7.211
7.206
7.152
7.147
7.139
7.135
7.129
6.505
3.03
5.12
2.06
1.01
3.00
1.801
-0.000
-0.078
f1 (ppm)
O


^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
200.190
153.925
140.695
138.890
129.549
129.414
128.734
128.378
128.364
128.346
127.638
77.318
77.000
76.682
30.295
O
f1 (ppm)

2.6 Stern-Volmer quenching experiments

Formulation solution: *N*-(2-cyano-4'-methyl-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide **1a** (14.5 mg) was dissolved in CH_3CN in a 5 mL volumetric flask to set the concentration to be 0.01 M. 3-(((4-(trifluoromethyl)benzoyl)oxy)imino)butan-2-one **2a** (13.65 mg) was dissolved in CH_3CN in a 5 mL volumetric flask to set the concentration to be 0.01 M.

Additional experimental details: The samples were prepared by the photocatalyst $Ir(ppy)_3$ (5×10^{-4} M) with different amount of quencher **1a** in CH_3CN in a light path quartz fluorescence cuvette. The concentration of quencher **1a** is 0.01 M in CH_3CN. For each S2 quenching experiment, 3 μl of quencher solution was separately titrated to the photocatalyst $Ir(ppy)_3$ (3.0 mL).

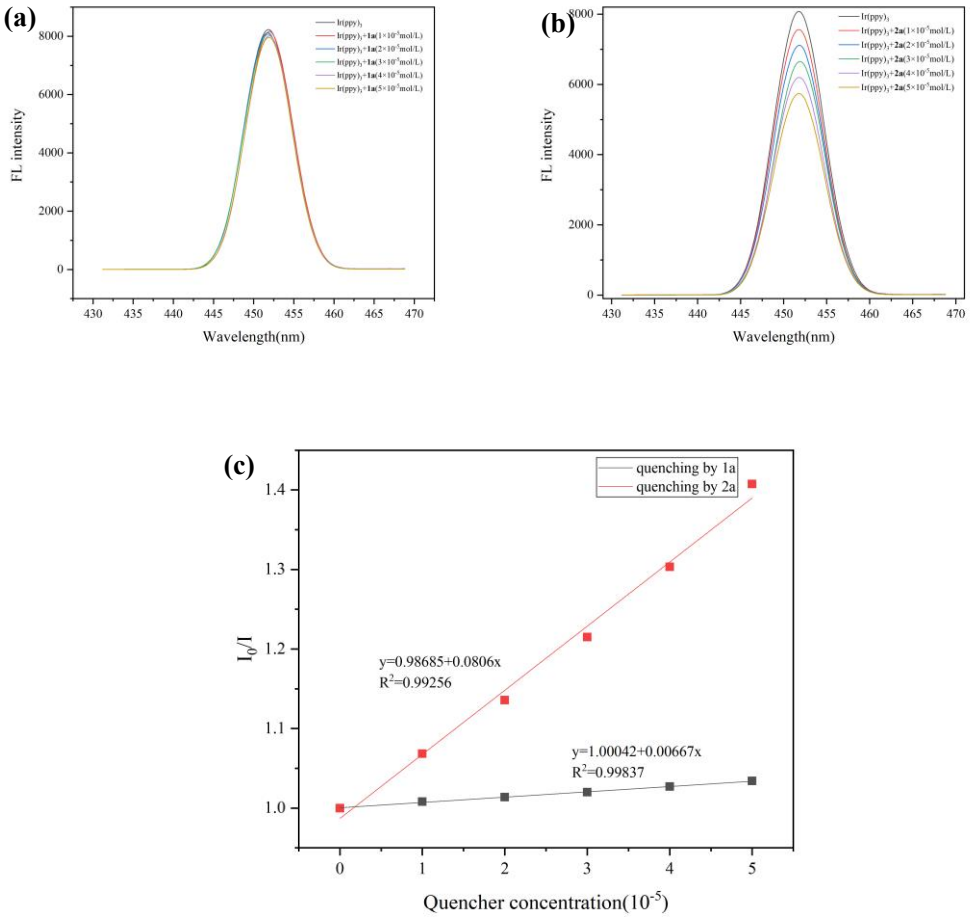


Figure S2 Stern-Volmer Quenching Experiments: (a) $Ir(ppy)_3$ quenched by 1a in CH_3CN; (b) $Ir(ppy)_3$ quenched by 2a in CH_3CN; (c) Stern-Volmer plot of photocatalyst at different concentration.

The resulting mixture was sparged with nitrogen for 3 minutes and then irradiated at 468 nm. Fluorescence emission spectra were recorded (3 trials per sample). Into this solution, 3.0 μL of a *N*-(2-cyano-4'-methyl-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide **1a** solution was successively added and uniformly stirred, and the resulting mixture was bubbled with nitrogen for 3 minutes and irradiated at 468 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)** of Stern-Volmer quenching experiments results, the emission intensity of the photocatalyst $Ir(ppy)_3$ solution strongly affected by the gradual increase of the amount of **2a**, and the influence is not observed to **1a**. These indicated that the single electron transfer (SET) process occured in photocatalyst and 3-(((4-(trifluoromethyl)benzoyl)oxy)imino)butan-2-one.

2.7 Quantum yield determination

Determination of the light intensity at 468 nm:

According to the procedure of Yoon[2] the photon flux of the blue LED (λmax = 468 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, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at λ = 468 nm with an emission slit width at 10.0 nm. After irradiation, 0.35 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 510 nm measured. Conversion was calculated using eq 1.

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

$$mol \text{ of } Fe^{2+} = \frac{(0.00235L) \cdot (2.786)}{(1.00cm) \cdot (11100 \frac{L}{mol} cm^{-1})} = 5.9 \times 10^{-7}$$

Where V is the total volume (0.00235 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 (1.000 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.

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

$$Photo \text{ flux} = \frac{5.9 \times 10^{-7}}{(0.92) \cdot (90s) \cdot (0.998)} = 7.1 \times 10^{-9} einstein / s$$

Where Φ is the quantum yield for the ferrioxalate actinometer (0.92 at λ = 468 nm), t is the time (90.0 s), and f is the fraction of light absorbed at 468 nm by the ferrioxalate actinometer. This value is calculated using eq 3 where A468 nm is the absorbance of the ferrioxalate solution at 468 nm. An absorption spectrum gave an A468 nm value of 2.806 at 468 nm, indicating that the fraction of absorbed light (f) is 0.998.

$$f = 1 - 10^{-A_{468nm}} \qquad (3)$$

The photon flux was thus calculated to be 7.1×10^{-9} einsteins s^{-1}

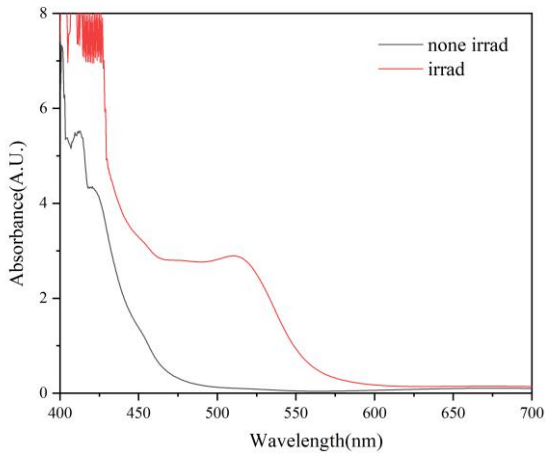
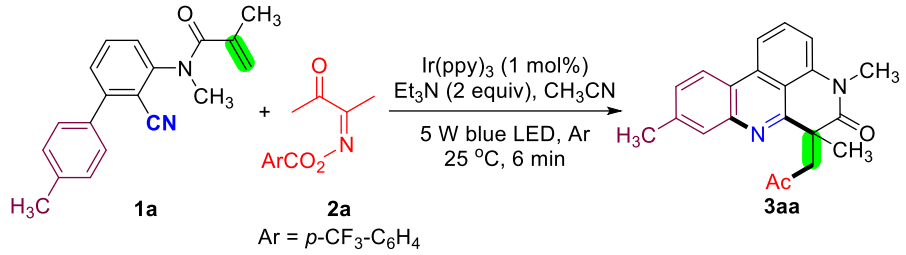


Figure S3. Absorbance of the ferrioxalate actinometer solution.

Determination of the reaction quantum yield.



To a Schlenk tube were added *N*-(2-cyano-4'-methyl-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide **1a** (0.1 mmol, 1.0 equiv.), 3-(((4-(trifluoromethyl)benzoyl)oxy)imino)butan-2-one **2a** (0.15 mmol, 1.5 equiv.), $Ir(ppy)_3$ (1% mol), Et_3N (0.2 mmol, 2.0 equiv), and CH_3CN (1 mL). The reaction mixture was stirred at room temperature (oil bath) for 6 min under blue LED irradiation (λ = 468 nm). The reaction mixture was extracted using EtOAc and saturated brine, and the organic layer was dried with anhydrous Na_2SO_4, filtrated and concentrated in vacuo. The yield was calculated by NMR with 1,3,5-trimethoxybenzene as an internal standard. The quantum yield was determined using eq 4.

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

$$\phi = \frac{3.1\times10^{-5}}{(7.1\times10^{-9}\,einstein/s)\cdot(360s)\cdot(0.78)} = 15.5$$

The photon flux is 7.1×10^{-9} einsteins s^{-1} , t is the reaction time (360 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 0.658 at 468 nm (figure S4), indicating that the fraction of light absorbed by the photocatalyst (f) is 0.78.

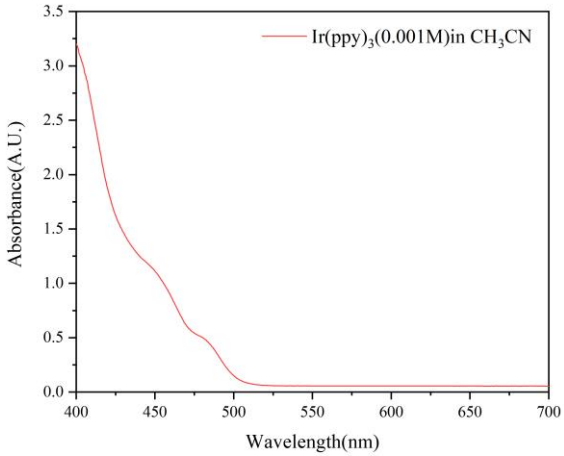


Figure S4. Absorption spectrum of $Ir(ppy)_3$ [0.001 M] in acetonitrile

2.8 UV/vis studies

UV/vis absorption spectra were measured in a 1 cm quartz cuvette using a Shimadzu UV-2600 UV/Vis spectrometer. Absorption spectra of individual reaction components and mixtures thereof were recorded. A bathochromic shift was observed for a mixture of *N*-(2-cyano-4'-methyl-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide **1a**, 3-(((4-(trifluoromethyl)benzoyl)oxy)imino)butan-2-one **2a**, and Et_3N in CH_3CN (0.2 M), which was a visibly in color (Figure S5). This indicates the formation of an electron donor-acceptor (EDA) complex (Figure S6, red band)

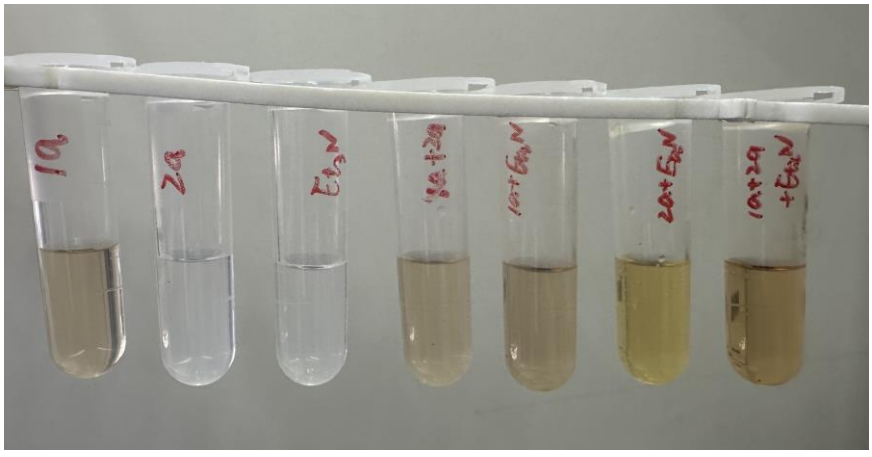


Figure S5. Visual appearance of reaction components and mixtures thereof.

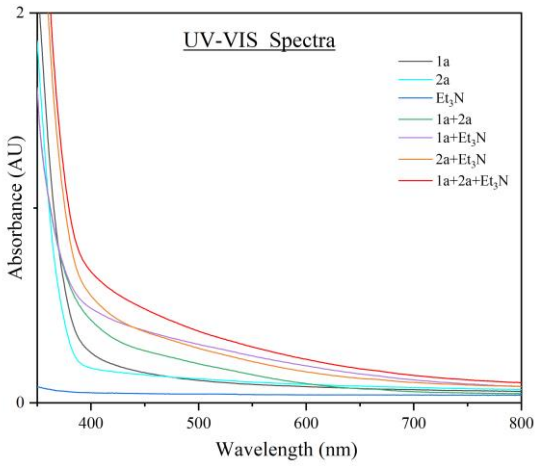


Figure S6. UV/vis absorption spectra of individual reaction components and a combination thereof. All spectra were measured in CH_3CN and with a concentration of 0.1 M *N*-(2-cyano-4'-methyl-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide **1a**, 0.15 M 3-(((4-(trifluoromethyl)benzoyl)oxy)imino)butan-2-one **2a**, 0.2 M Et_3N. The stoichiometry and concentration of samples reflects the used reaction conditions.

Job Plot

Using UV-vis spectroscopy, the absorbance values at 468 nm (corresponding to the EDA complex's absorption) were monitored and plotted as a function of molar fraction of the 3-(((4-(trifluoromethyl)benzoyl)oxy)imino)butan-2-one of **2a**. A parabolic curve with a maximum absorbance value at 50% mol fraction of *N*-(2-cyano-4'-methyl-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide **1a** was obtained, indicating a 1:1 EDA complex between 1a and the conjugated base of **2a**.

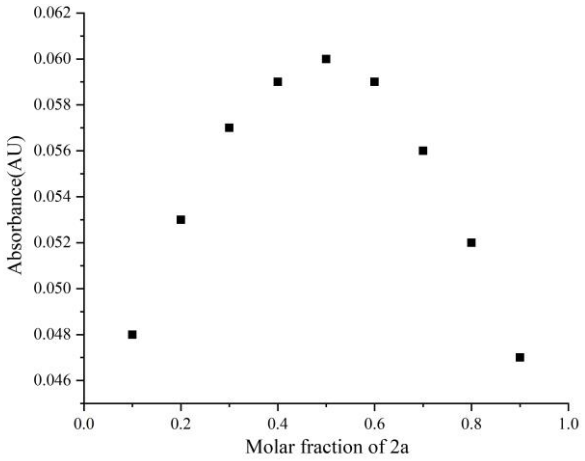


Figure S7. Job Plot of the EDA complex system between **1a** and **2a** at 468 nm.

Benesi–Hildebrand Plot

The absorbance values of five solutions containing a constant value of 0.01 M of *N*-(2-cyano-4'-methyl-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide **1a** and increasing amounts of the 3-(((4-(trifluoromethyl)benzoyl)oxy)imino)butan-2-one of **2a** from 0.01 M to 0.05 M were recorded at 468 nm. Using the Benesi–Hildebrand method, 1/ΔAbsorbance versus 1/[Concentration of **2a**] were plotted and a linear relationship (Figures S8) was observed. Through linear regression, the y-intercept and slope values allowed an estimation of the association constant of the EDA complex (KEDA) as 6.8 in CH_3CN.

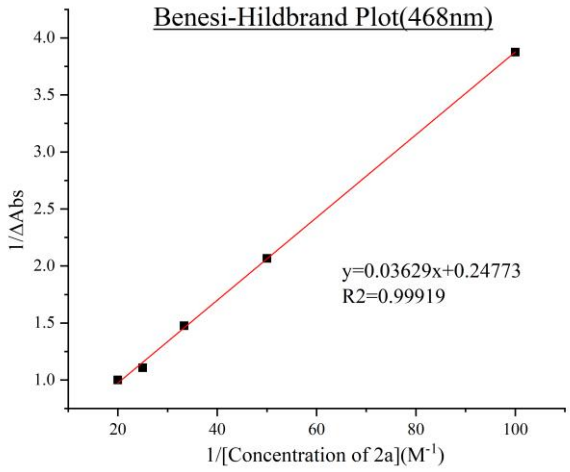
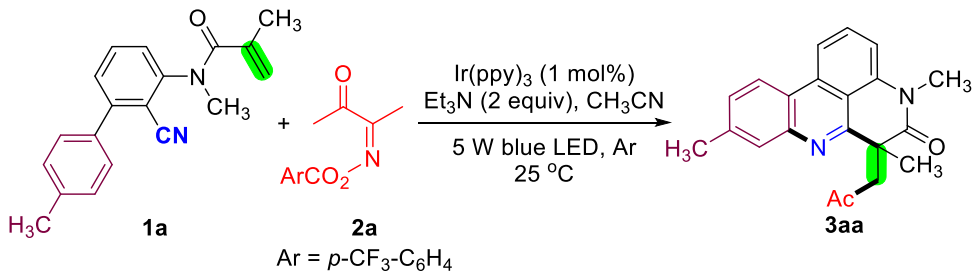


Figure S8. Benesi-Hildebrand Plot of the EDA complex system between **1a** and **2a** at 468 nm.

2.9 The Light on/off Experiments



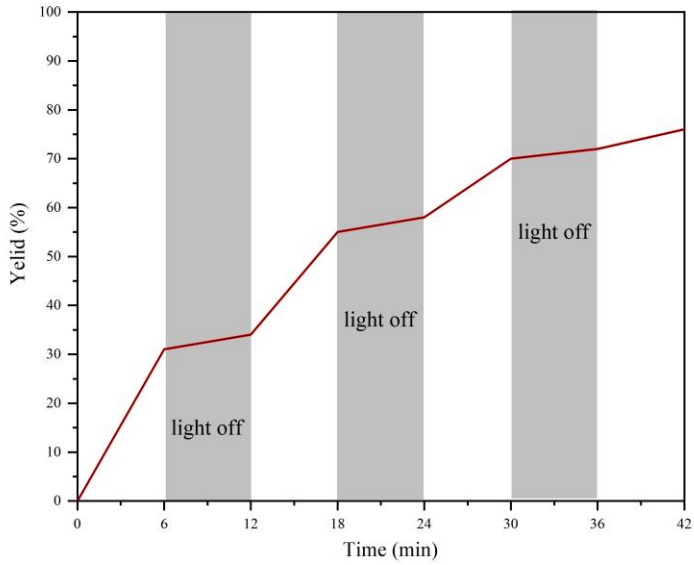


Figure S9 The Light on/off Experiments

2.10 Possible reaction mechanisms involving an EDA process

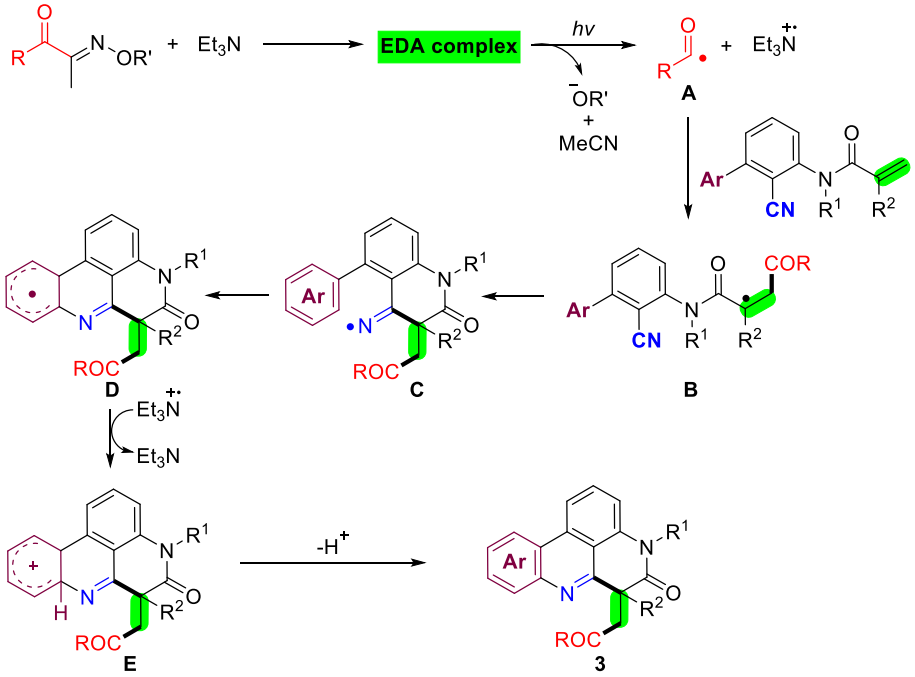


Figure S10 Possible reaction mechanisms involving an EDA process

3. References

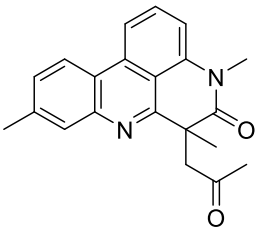
[1] Y.-J. Ma, Z-H Yuan, P Gao, X-H Duan, H Xin, L Liu and L-N Guo, *J. Org. Chem.,* **2023**,88,9927-9940.

[2] P. Chen, J. Xie, Z. Chen, B.-Q. Xiong, Y. Liu, C.-A. Yang and K.-W. Tang, *Adv. Synth. Catal.*, **2021**, 363, 4440.

[3] X. Fan, T. Lei, B. Chen, C.-H. Tung and L.-Z. Wu, *Org. Lett.*, **2019**, 21, 4153

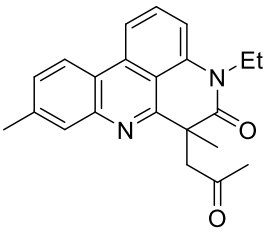
4. Analytical data

4,6,9-Trimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one



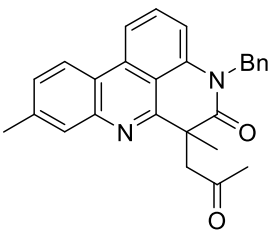
(3aa): Yield: 53.8 mg, 81%; yellow solid; mp 141.5-141.8 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35 (d, *J* = 8.4 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.82 (s, 1H), 7.75 (t, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 4.18 (d, *J* = 18.0 Hz, 1H), 3.73 (d, *J* = 18.0 Hz, 1H), 3.57 (s, 3H), 2.55 (s, 3H), 2.11 (s, 3H), 1.51 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 206.9, 174.1, 160.0, 144.6, 139.0, 139.0, 133.3, 131.6, 128.8, 128.0, 122.3, 120.5, 115.7, 111.6, 110.4, 52.9, 48.1, 29.7, 29.5, 29.4, 21.4; HRMS (ESI-TOF) *m/z*: $C_{21}H_{21}N_2O_2$ $(M + H)^+$ calcd for 333.1598, found 333.1601.

4-Ethyl-6,9-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ba):



Yield: 55.4 mg, 80%; yellow solid; mp 87.3-87.6 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.38 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.82-7.77 (m, 2H), 7.44-7.41 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 4.29-4.15 (m, 3H), 3.72 (d, *J* = 18.0 Hz, 1H), 2.56 (s, 3H), 2.11 (s, 3H), 1.50 (s, 3H), 1.35 (t, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 206.9, 173.6, 160.1, 144.7, 139.0, 137.8, 133.7, 131.6, 128.9, 128.0, 122.3, 120.6, 115.5, 112.0, 110.3, 53.0, 48.0, 37.3, 29.7, 29.5, 21.5, 11.9; HRMS (ESI-TOF) *m/z*: $C_{22}H_{23}N_2O_2$ $(M + H)^+$ calcd for 347.1754, found 347.1751.

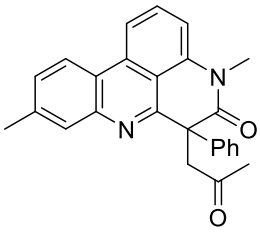
4-Benzyl-6,9-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ca):



Yield: 63.6 mg, 78%; yellow solid; mp 72.1-72.5 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.82 (s, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.39-7.29 (m, 5H), 7.24-7.20 (m, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 5.45-5.35 (m, 2H), 4.26 (d, *J* = 18.0 Hz, 1H), 3.79 (d, *J* = 18.0 Hz, 1H), 2.54 (s, 3H), 2.15 (s, 3H), 1.60 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 206.9, 174.5, 159.9, 144.6, 139.0, 137.8, 136.4, 133.5, 131.5, 128.8, 128.8, 128.0, 127.0, 126.2,

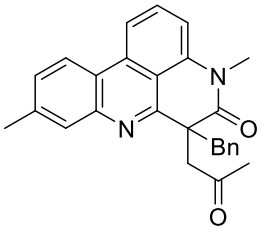
122.3, 120.6, 115.7, 111.8, 111.6, 52.8, 48.3, 46.1, 29.7, 29.5, 21.5; HRMS (ESI-TOF) *m/z*: $C_{27}H_{25}N_2O_2$ $(M + H)^+$ calcd for 409.1911, found 409.1912.

4,9-Dimethyl-6-(2-oxopropyl)-6-phenyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)



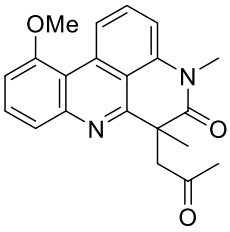
-one (3da): Yield: 59.1 mg, 75%; yellow solid; mp 104.4-104.8 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.39 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.87 (s, 1H), 7.76 (t, *J* = 8.0 Hz, 1H), 7.46-7.44 (m, 1H), 7.18-7.08 (m, 6H), 4.55 (d, *J* = 17.6 Hz, 1H), 4.14 (d, *J* = 18.0 Hz, 1H), 3.59 (s, 3H), 2.56 (s, 3H), 2.20 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 206.6, 171.7, 158.2, 144.6, 141.4, 139.1, 139.0, 133.3, 131.7, 129.3, 128.5, 128.4, 127.2, 126.7, 122.4, 120.7, 115.9, 112.8, 110.7, 56.5, 53.0, 30.2, 29.7, 21.5; HRMS (ESI-TOF) *m/z*: $C_{26}H_{23}N_2O_2$ $(M + H)^+$ calcd for 395.1754, found 395.1752.

6-Benzyl-4,9-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-



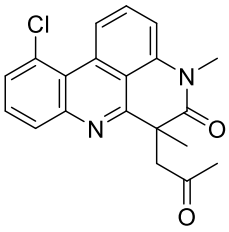
one (3ea): Yield: 62.8 mg, 77%; yellow solid; mp 60.4-60.9 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.91 (s, 1H), 7.53 (t, *J* = 8.4 Hz, 1H), 7.47-7.44 (m, 1H), 6.86-6.82 (m, 1H), 6.74-6.70 (m, 3H), 6.35 (d, *J* = 6.8 Hz, 2H), 4.33 (d, *J* = 18.0 Hz, 1H), 3.86 (d, *J* = 18.0 Hz, 1H), 3.32-3.19 (m, 5H), 2.61 (s, 3H), 2.13 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 206.7, 172.5, 158.7, 144.6, 138.9, 138.4, 134.9, 132.2, 131.2, 129.1, 129.0, 128.1, 127.0, 126.5, 122.4, 120.6, 115.3, 113.7, 109.8, 53.9, 53.5, 50.1, 29.6, 29.2, 21.5; HRMS (ESI-TOF) *m/z*: $C_{27}H_{25}N_2O_2$ $(M + H)^+$ calcd for 409.1911, found 409.1912.

11-Methoxy-4,6-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6

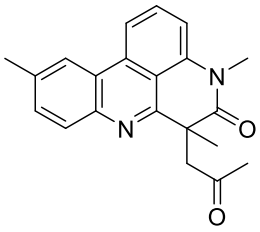


***H*)-one (3fa):** Yield: 49.4 mg, 71%; yellow solid; mp 171.3-171.5 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.22 (d, *J* = 8.8 Hz, 1H), 7.80 (t, *J* = 8.0 Hz, 1H), 7.67-7.58 (m, 2H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 4.18 (d, *J* = 18.0 Hz, 1H), 4.10 (s, 3H), 3.72 (d, *J* = 18.0 Hz, 1H), 3.59 (s, 3H), 2.11 (s, 3H), 1.50 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 206.9, 173.9, 160.3, 158.3, 146.6, 138.4, 133.2, 131.4, 128.3, 122.2, 122.0, 113.9, 112.4, 110.7, 107.4, 55.8, 52.8, 48.0, 29.9, 29.5,

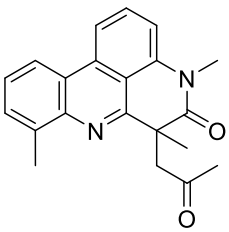
29.5; HRMS (ESI-TOF) *m/z*: $C_{21}H_{21}N_2O_3$ $(M + H)^+$ calcd for 349.1547, found 349.1551.

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

Yield: 57.7 mg, 82%; yellow solid; mp 166.9-167.3 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.54 (d, *J* = 8.8 Hz, 1H), 7.96-7.94 (m, 1H), 7.84 (t, *J* = 8.4 Hz, 1H), 7.67-7.65 (m, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 4.16 (d, *J* = 18.0 Hz, 1H), 3.74 (d, *J* = 18.0 Hz, 1H), 3.60 (s, 3H), 2.12 (s, 3H), 1.50 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 206.9, 173.6, 160.7, 146.7, 138.8, 132.7, 131.1, 130.9, 130.0, 129.2, 128.0, 120.8, 120.5, 112.8, 111.8, 52.8, 48.0, 30.0, 29.4, 29.3; HRMS (ESI-TOF) *m/z*: $C_{20}H_{18}ClN_2O_2$ $(M + H)^+$ calcd for 353.1051, found 353.1053.

4,6,10-Trimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ha): 

Yield: 33.7 mg, 50%; yellow solid; mp 128.2-128.7 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 6.8 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 4.20 (d, *J* = 18.0 Hz, 1H), 3.74 (d, *J* = 18.0 Hz, 1H), 3.59 (s, 3H), 2.78 (s, 3H), 2.11 (s, 3H), 1.51 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 206.9, 174.1, 158.5, 143.1, 139.0, 136.9, 133.6, 131.5, 129.4, 125.9, 122.6, 120.4, 116.1, 111.7, 110.6, 53.0, 48.4, 29.9, 29.8, 29.6, 18.2; HRMS (ESI-TOF) *m/z*: $C_{21}H_{21}N_2O_2$ $(M + H)^+$ calcd for 333.1598, found 333.1601.

4,6,8-Trimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ha'): 

Yield: 16.8 mg, 26%; yellow solid; mp 148.0-148.4 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.80 (t, *J* = 8.0 Hz, 1H), 7.53-7.51 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 4.18 (d, *J* = 18.0 Hz, 1H), 3.72 (d, *J* = 18.0 Hz, 1H), 3.59 (s, 3H), 2.60 (s, 3H), 2.11 (s, 3H), 1.52 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 207.0, 174.2, 159.0, 142.9, 139.0, 136.1, 133.1, 131.4, 130.5, 129.1, 122.7, 122.1, 115.9, 112.1, 110.7, 53.0, 48.1, 29.8, 29.6, 29.5,

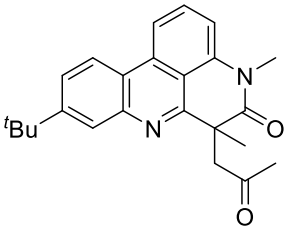
21.9; HRMS (ESI-TOF) *m/z*: $C_{21}H_{21}N_2O_2$ $(M + H)^+$ calcd for 333.1598, found 333.1601.

10-Chloro-4,6-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ia) and 8-chloro-4,6-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ia') mixture : Yield: 44.4 mg, 63%; yellow solid; mp 145.2-145.6 °C (uncorrected); **3ia** : **3ia'** = 7:3; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.42 (d, *J* = 2.0 Hz, 0.3H), 8.39-8.37 (m, 0.7H), 8.18 (d, *J* = 8.4 Hz, 0.7H), 8.11 (d, *J* = 8.0 Hz, 0.3H), 7.93 (d, *J* = 8.8 Hz, 0.3H), 7.83-7.76 (m, 1.7H), 7.63-7.60 (m, 0.3H), 7.47 (t, *J* = 8.0 Hz, 0.7H), 7.26-7.23 (m, 1H), 4.28 (d, *J* = 17.6 Hz, 0.7H), 4.16 (d, *J* = 18.0 Hz, 0.3H), 3.78-3.72 (m, 1H), 3.59-3.58 (m, 3H), 2.15-2.11 (m, 3H), 1.53-1.51 (m, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 207.3, 206.9, 173.9, 173.9, 160.8, 160.5, 143.0, 140.8, 139.3, 139.1, 133.9, 133.1, 132.3, 132.1, 132.0, 130.8, 129.3, 129.1, 126.1, 124.5, 123.9, 122.1, 121.4, 116.0, 115.8, 112.1, 111.9, 111.4, 111.3, 53.0, 52.8, 48.7, 48.2, 29.8, 29.7, 29.5, 29.4; HRMS (ESI-TOF) *m/z*: $C_{20}H_{18}ClN_2O_2$ $(M + H)^+$ calcd for 353.1051, found 353.1053.

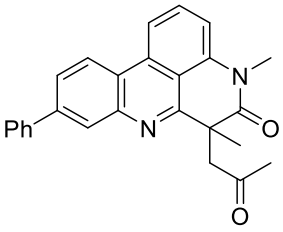
9-Methoxy-4,6-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ja): Yield: 59.9 mg, 86%; yellow solid; mp 192.2-192.5 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36 (d, *J* = 8.8 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.75 (t, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 2.8 Hz, 1H), 7.24-7.21 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 4.17 (d, *J* = 18.0 Hz, 1H), 3.97 (s, 3H), 3.74 (d, *J* = 18.0 Hz, 1H), 3.58 (s, 3H), 2.12 (s, 3H), 1.52 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 206.9, 174.1, 160.5, 160.2, 146.3, 139.1, 133.5, 131.7, 123.8, 117.4, 117.0, 115.4, 111.2, 109.7, 109.1, 55.5, 53.0, 48.2, 29.8, 29.6, 29.5; HRMS (ESI-TOF) *m/z*: $C_{21}H_{21}N_2O_3$ $(M + H)^+$ calcd for 349.1547, found 349.1551.

9-Isopropyl-4,6-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ka): Yield: 56.9 mg, 79%; yellow solid; mp

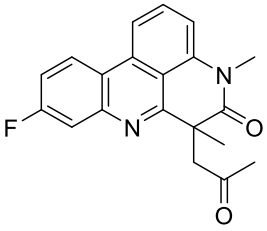
138.8-139.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.59-8.55 (m, 2H), 8.27 (d, *J* = 8.0 Hz, 1H), 8.17-8.15 (m, 1H), 7.87 (t, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 4.21 (d, *J* = 18.0 Hz, 1H), 3.82-3.75 (m, 2H), 3.60 (s, 3H), 2.14 (s, 3H), 1.54 (s, 3H), 1.32-1.30 (m, 6H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 207.0, 173.9, 161.3, 144.3, 139.2, 136.1, 132.7, 132.2, 130.2, 126.2, 125.1, 123.2, 116.3, 112.6, 112.0, 53.2, 48.3, 35.5, 29.9, 29.5, 29.4, 19.3, 19.2; HRMS (ESI-TOF) *m/z*: $C_{23}H_{25}N_2O_2$ $(M + H)^+$ calcd for 361.1911, found 361.1915.

9-(*tert*-Butyl)-4,6-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3la): 

Yield: 62.1 mg, 83%; yellow solid; mp 156.1-156.4 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.42 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 2.4 Hz, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 7.69-7.66 (m, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 4.21 (d, *J* = 18.0 Hz, 1H), 3.74 (d, *J* = 18.0 Hz, 1H), 3.58 (s, 3H), 2.12 (s, 3H), 1.53 (s, 3H), 1.46 (s, 9H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 206.9, 174.2, 159.9, 152.1, 144.6, 139.0, 133.2, 131.6, 125.2, 124.6, 122.2, 120.5, 115.7, 111.8, 110.4, 53.1, 48.1, 34.9, 31.3, 29.8, 29.6, 29.5; HRMS (ESI-TOF) *m/z*: $C_{24}H_{27}N_2O_2$ $(M + H)^+$ calcd for 375.2067, found 375.2071.

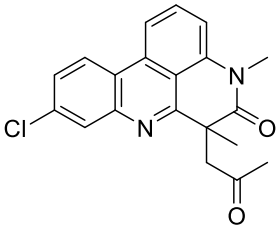
4,6-Dimethyl-6-(2-oxopropyl)-9-phenyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ma): 

Yield: 65.4 mg, 83%; yellow solid; mp 216.2-216.7 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (d, *J* = 8.4 Hz, 1H), 8.26-8.24 (m, 2H), 7.87-7.78 (m, 4H), 7.52-7.48 (m, 2H), 7.42-7.38 (m, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 4.21 (d, *J* = 18.4 Hz, 1H), 3.76 (d, *J* = 18.0 Hz, 1H), 3.60 (s, 3H), 2.12 (s, 3H), 1.55 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 207.0, 174.1, 160.6, 144.9, 141.6, 140.3, 139.2, 133.2, 131.8, 128.9, 127.7, 127.3, 127.3, 125.5, 123.1, 122.0, 115.9, 112.0, 110.9, 53.1, 48.2, 29.8, 29.6, 29.5; HRMS (ESI-TOF) *m/z*: $C_{26}H_{23}N_2O_2$ $(M + H)^+$ calcd for 395.1754, found 395.1752.

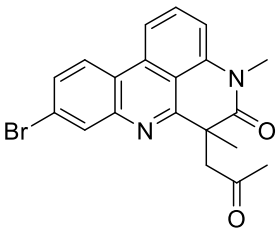
9-Fluoro-4,6-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3na): 

Yield: 52.4 mg, 78%; yellow solid; mp 139.8-140.1

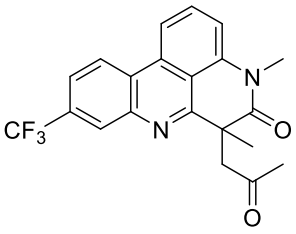
°C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.46-8.42 (m, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.79 (t, *J* = 8.0 Hz, 1H), 7.67-7.64 (m, 1H), 7.36-7.31 (m, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 4.16 (d, *J* = 18.0 Hz, 1H), 3.75 (d, *J* = 18.0 Hz, 1H), 3.58 (s, 3H), 2.12 (s, 3H), 1.52 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 207.0, 173.9, 162.8 (d, *J* = 246.7 Hz, 1C), 161.6, 145.9 (d, *J* = 12.0 Hz, 1C), 139.2, 133.1, 132.1, 124.5 (d, *J* = 9.5 Hz, 1C), 119.6 (d, *J* = 2.0 Hz, 1C), 115.6, 115.3 (d, *J* = 23.6 Hz, 1C), 113.8 (d, *J* = 20.3 Hz, 1C), 111.6, 110.6, 53.0, 48.2, 29.8, 29.5, 29.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ: -111.9 (s, 1F); HRMS (ESI-TOF) *m/z*: $C_{20}H_{18}FN_2O_2$ $(M + H)^+$ calcd for 337.1347, found 337.1345.

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

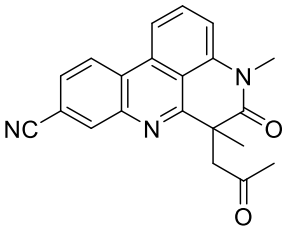
Yield: 56.3 mg, 80%; yellow solid; mp 172.3-172.8 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (d, *J* = 8.8 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 2.0 Hz, 1H), 7.79 (t, *J* = 8.4 Hz, 1H), 7.53-7.50 (m, 1H), 7.23 (d, *J* = 7.2 Hz, 1H), 4.15 (d, *J* = 18.0 Hz, 1H), 3.75 (d, *J* = 18.4 Hz, 1H), 3.58 (s, 3H), 2.12 (s, 3H), 1.51 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 206.9, 173.8, 161.6, 145.2, 139.2, 134.5, 132.9, 132.1, 128.5, 126.8, 123.9, 121.4, 115.7, 111.9, 111.1, 53.0, 48.3, 29.8, 29.4, 29.4; HRMS (ESI-TOF) *m/z*: $C_{20}H_{18}ClN_2O_2$ $(M + H)^+$ calcd for 353.1051, found 353.1053.

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

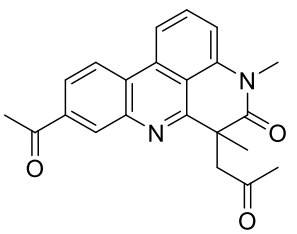
Yield: 61.0 mg, 77%; yellow solid; mp 171.7-172.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (d, *J* = 8.8 Hz, 1H), 8.20-8.16 (m, 2H), 7.82 (t, *J* = 8.0 Hz, 1H), 7.68-7.66 (m, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 4.15 (d, *J* = 18.0 Hz, 1H), 3.75 (d, *J* = 18.0 Hz, 1H), 3.59 (s, 3H), 2.12 (s, 3H), 1.51 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 207.0, 173.9, 161.6, 145.5, 139.3, 133.0, 132.2, 131.8, 129.4, 124.1, 122.6, 121.8, 115.7, 111.9, 111.2, 77.3, 77.0, 76.7, 53.1, 48.3, 29.9, 29.5, 29.4; HRMS (ESI-TOF) *m/z*: $C_{20}H_{18}BrN_2O_2$ $(M + H)^+$ calcd for 397.0546, found 397.0548.

4,6-Dimethyl-6-(2-oxopropyl)-9-(trifluoromethyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3qa): 

Yield: 53.3 mg, 69%; yellow solid; mp 213.7-214.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.57 (d, *J* = 8.4 Hz, 1H), 8.31 (d, *J* = 2.0 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.85 (t, *J* = 8.4 Hz, 1H), 7.78-7.75 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 4.19 (d, *J* = 18.0 Hz, 1H), 3.79 (d, *J* = 18.0 Hz, 1H), 3.59 (s, 3H), 2.13 (s, 3H), 1.53 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 207.0, 173.8, 162.0, 143.9, 139.3, 132.5, 132.3, 130.6 (q, *J* = 32.6 Hz, 1C), 126.9 (q, *J* = 4.2 Hz, 1C), 125.2, 124.1 (q, *J* = 270.7 Hz, 1C), 123.7, 122.0 (q, *J* = 3.5 Hz, 1C), 116.1, 112.5, 112.0, 53.1, 48.3, 29.9, 29.4, 29.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ: -62.3 (s, 3F); HRMS (ESI-TOF) *m/z*: $C_{21}H_{18}F_3N_2O_2$ $(M + H)^+$ calcd for 387.1315, found 387.1317.

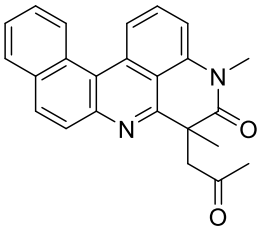
4,6-Dimethyl-5-oxo-6-(2-oxopropyl)-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*]phenanthridine-9-carbonitrile (3ra): 

Yield: 52.8 mg, 77%; yellow solid; mp 150.1-150.6 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (d, *J* = 8.4 Hz, 1H), 8.35 (d, *J* = 2.0 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.89 (t, *J* = 8.0 Hz, 1H), 7.76-7.74 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 4.17 (d, *J* = 18.0 Hz, 1H), 3.79 (d, *J* = 18.4 Hz, 1H), 3.60 (s, 3H), 2.14 (s, 3H), 1.53 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 207.0, 173.6, 162.7, 143.8, 139.4, 134.4, 132.6, 132.2, 127.6, 126.2, 123.9, 118.6, 116.2, 112.6, 112.5, 112.0, 53.1, 48.4, 29.9, 29.4, 29.4; HRMS (ESI-TOF) *m/z*: $C_{21}H_{18}N_3O_2$ $(M + H)^+$ calcd for 344.1394, found 344.1399.

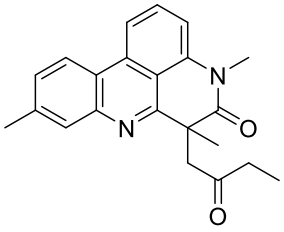
9-Acetyl-4,6-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3sa): 

Yield: 49.7 mg, 69%; yellow solid; mp 66.1-66.5 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.57 (d, *J* = 1.6 Hz, 1H), 8.54 (d, *J* = 8.4 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 8.17-8.14 (m, 1H), 7.86 (t, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 4.20 (d, *J* = 18.0 Hz, 1H), 3.79 (d, *J* = 18.0 Hz, 1H), 3.60 (s, 3H), 2.77 (s, 3H), 2.14 (s, 3H), 1.54 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 206.9, 197.9, 173.8, 161.4, 144.1, 139.2, 136.9, 132.6, 132.2, 130.7, 126.4, 124.6, 123.1, 116.4,

112.6, 112.0, 53.1, 48.3, 29.9, 29.5, 29.4, 26.8; HRMS (ESI-TOF) *m/z*: $C_{22}H_{21}N_2O_3$ $(M + H)^+$ calcd for 361.1547, found 361.1552.

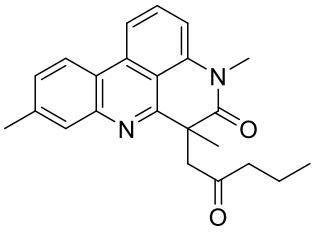
4,6-Dimethyl-6-(2-oxopropyl)-4*H*-benzo[*a*]pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ta):  Yield: 54.5 mg, 74%; yellow solid; mp 221.9-222.3 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.03 (d, *J* = 8.4 Hz, 1H), 8.73 (d, *J* = 8.4 Hz, 1H), 8.01-7.93 (m, 3H), 7.83 (t, *J* = 8.0 Hz, 1H), 7.70-7.66 (m, 1H), 7.64-7.60 (m, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 4.22 (d, *J* = 18.4 Hz, 1H), 3.76 (d, *J* = 18.0 Hz, 1H), 3.62 (s, 3H), 2.13 (s, 3H), 1.55 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 207.0, 174.0, 159.2, 144.5, 138.9, 133.4, 132.9, 131.3, 129.9, 129.7, 128.7, 128.0, 127.4, 126.5, 126.1, 120.7, 119.3, 113.3, 110.0, 52.9, 48.0, 29.9, 29.5, 29.5; HRMS (ESI-TOF) *m/z*: $C_{24}H_{21}N_2O_2$ $(M + H)^+$ calcd for 369.1598, found 369.1603.

4,6,9-Trimethyl-6-(2-oxobutyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one



(3ab): Yield: 56.1 mg, 81%; yellow solid; mp 158.9-159.4 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.81-7.75 (m, 2H), 7.43-7.40 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 4.17 (d, *J* = 17.6 Hz, 1H), 3.70 (d, *J* = 18.0 Hz, 1H), 3.59 (s, 3H), 2.56 (s, 3H), 2.52-2.36 (m, 2H), 1.52 (s, 3H), 0.91 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 209.8, 174.2, 160.1, 144.7, 139.0, 139.0, 133.4, 131.6, 128.8, 128.0, 122.4, 120.6, 115.7, 111.7, 110.4, 51.8, 48.1, 35.3, 29.8, 29.6, 21.5, 7.4; HRMS (ESI-TOF) *m/z*: $C_{22}H_{23}N_2O_2$ $(M + H)^+$ calcd for 347.1754, found 347.1757.

4,6,9-Trimethyl-6-(2-oxopentyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one



(3ac): Yield: 55.4 mg, 77%; yellow solid; mp 138.8-139.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.38 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.81-7.77 (m, 2H), 7.44-7.42 (m, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 4.17 (d, *J* = 17.6 Hz, 1H), 3.70 (d, *J* = 18.0 Hz, 1H), 3.59 (s, 3H), 2.57 (s, 3H), 2.39 (t, *J* = 7.2 Hz, 2H), 1.52 (s, 3H), 1.50-1.44 (m, 2H), 0.80 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 209.5, 174.2, 160.2, 144.7, 139.1, 139.0, 133.4, 131.6, 128.8, 128.0,

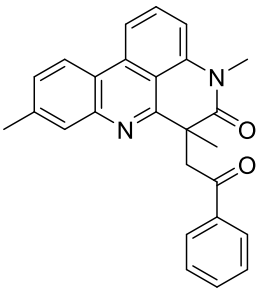
122.4, 120.6, 115.7, 111.7, 110.4, 52.2, 48.1, 44.1, 29.8, 29.6, 21.5, 17.1, 13.6; HRMS (ESI-TOF) *m/z*: $C_{23}H_{25}N_2O_2$ $(M + H)^+$ calcd for 361.1911, found 361.1915.

4,6,9-Trimethyl-6-(3-methyl-2-oxobutyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ad): Yield: 51.1 mg, 71%; yellow solid; mp 146.7-1447.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.40 (d, *J* = 8.4 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.95 (s, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 7.47-7.45 (M, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 3.57 (s, 3H), 2.59 (s, 3H), 2.52-2.47 (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, 145.0, 139.3, 138.8, 133.2, 131.5, 131.5 129.2, 128.2, 122.3, 120.2, 115.8, 112.0, 110.1, 51.1, 50.5, 30.9, 29.6, 25.6, 23.7, 22.9, 21.5; HRMS (ESI-TOF) *m/z*: $C_{23}H_{25}N_2O_2$ $(M + H)^+$ calcd for 361.1911, found 361.1915.

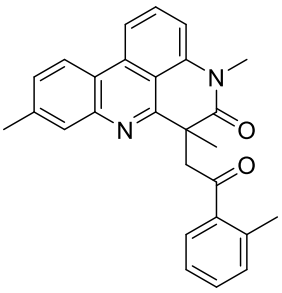
4,6,9-Trimethyl-6-(2-oxohexyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ae): Yield: 59.8 mg, 80%; yellow solid; mp 128.0-128.4 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.81-7.75 (m, 2H), 7.43-7.41 (m, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 4.17 (d, *J* = 18.0 Hz, 1H), 3.70 (d, *J* = 17.6 Hz, 1H), 3.58 (s, 3H), 2.56 (s, 3H), 2.41 (t, *J* = 7.6 Hz, 2H), 1.52 (s, 3H), 1.48-1.40 (m, 2H), 1.23-1.15 (m, 2H), 0.81 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 209.6, 174.2, 160.1, 144.7, 139.0, 139.0, 133.4, 131.6, 128.8, 128.0, 122.3, 120.6, 115.7, 111.7, 110.4, 52.2, 48.1, 41.9, 29.8, 29.5, 25.7, 22.1, 21.5, 13.8; HRMS (ESI-TOF) *m/z*: $C_{24}H_{27}N_2O_2$ $(M + H)^+$ calcd for 375.2067, found 375.2071.

4,6,9-Trimethyl-6-(2-oxoheptyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3af): Yield: 59.0 mg, 76%; yellow solid; mp 90.3-90.7 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.81-7.75 (m, 2H), 7.43-7.40 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 4.17 (d, *J* = 18.0 Hz, 1H), 3.70 (d, *J* = 18.0 Hz, 1H), 3.58 (s, 3H), 2.55 (s, 3H), 2.42-2.37 (m, 2H), 1.52 (s, 3H), 1.47-1.41 (m, 2H), 1.22-1.12 (m, 4H), 0.78 (t, *J*

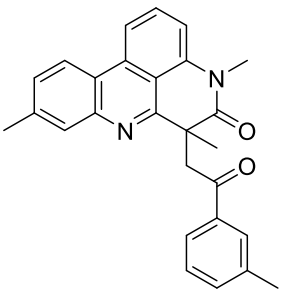
= 6.8 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 209.6, 174.2, 160.2, 144.7, 139.1, 139.0, 133.4, 131.6, 128.8, 128.0, 122.3, 120.6, 115.7, 111.7, 110.4, 52.2, 48.1, 42.2, 31.2, 29.8, 29.5, 23.4, 22.4, 21.5, 13.8; HRMS (ESI-TOF) *m/z*: $C_{25}H_{29}N_2O_2$ $(M + H)^+$ calcd for 389.2224, found 389.2226.

4,6,9-Trimethyl-6-(2-oxo-2-phenylethyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ag): 

Yield: 62.3 mg, 79%; yellow solid; mp 194.5-194.9 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.96-7.94 (m, 2H), 7.80-7.74 (m, 2H), 7.52-7.48 (m, 1H), 7.42-7.36 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 1H), 4.79 (d, *J* = 17.6 Hz, 1H), 4.27 (d, *J* = 18.0 Hz, 1H), 3.62 (s, 3H), 2.49 (s, 3H), 1.65 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 198.2, 174.2, 160.1, 144.7, 139.1, 138.9, 136.2, 133.4, 133.1, 131.6, 128.9, 128.4, 128.2, 127.9, 122.3, 120.5, 115.7, 111.7, 110.4, 48.8, 48.3, 29.8, 29.7, 21.4; HRMS (ESI-TOF) *m/z*: $C_{26}H_{23}N_2O_2$ $(M + H)^+$ calcd for 395.1754, found 395.1759.

4,6,9-Trimethyl-6-(2-oxo-2-(*o*-tolyl)ethyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ah): 

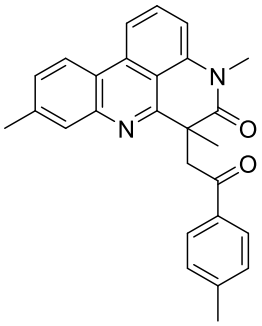
Yield: 57.1 mg, 70%; yellow solid; mp 71.6-72.1 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.39 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.88-7.79 (m, 3H), 7.43-7.41 (m, 1H), 7.35-7.24 (m, 3H), 7.14 (d, *J* = 7.2 Hz, 1H), 4.67 (d, *J* = 17.6 Hz, 1H), 4.16 (d, *J* = 17.6 Hz, 1H), 3.64 (s, 3H), 2.54 (s, 3H), 2.22 (s, 3H), 1.59 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 202.7, 174.2, 160.3, 144.8, 139.2, 139.1, 137.8, 137.7, 133.5, 131.6, 131.5, 131.0, 128.9, 128.5, 128.0, 125.5, 122.4, 120.6, 115.7, 111.8, 110.5, 51.2, 48.7, 29.9, 29.7, 21.5, 20.8; HRMS (ESI-TOF) *m/z*: $C_{27}H_{25}N_2O_2$ $(M + H)^+$ calcd for 409.1911, found 409.1913.

4,6,9-Trimethyl-6-(2-oxo-2-(*m*-tolyl)ethyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ai): 

Yield: 62.0 mg, 76%; yellow solid; mp 81.9-82.4 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.79-7.74

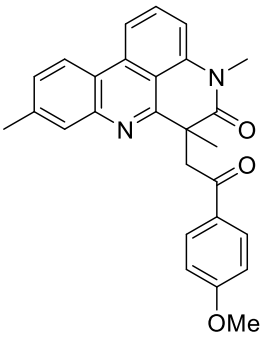
(m, 4H), 7.38-7.35 (m, 1H), 7.32-7.28 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 4.77 (d, *J* = 18.0 Hz, 1H), 4.26 (d, *J* = 17.6 Hz, 1H), 3.61 (s, 3H), 2.48 (s, 3H), 2.33 (s, 3H), 1.65 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 198.4, 174.3, 160.2, 144.7, 139.1, 138.9, 138.1, 136.2, 133.8, 133.4, 131.6, 128.9, 128.7, 128.2, 127.9, 125.4, 122.3, 120.5, 115.7, 111.7, 110.4, 49.0, 48.3, 29.8, 29.7, 21.4, 21.2; HRMS (ESI-TOF) *m/z*: $C_{27}H_{25}N_2O_2$ $(M + H)^+$ calcd for 409.1911, found 409.1913.

4,6,9-Trimethyl-6-(2-oxo-2-(*p*-tolyl)ethyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3aj):



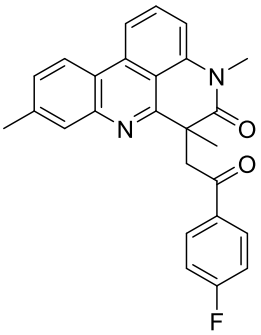
Yield: 64.5 mg, 79%; yellow solid; mp 138.1-138.4 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.85-7.83 (m, 2H), 7.79 (t, *J* = 8.4 Hz, 1H), 7.74 (s, 1H), 7.39-7.36 (m, 1H), 7.24-7.18 (m, 3H), 4.76 (d, *J* = 17.6 Hz, 1H), 4.24 (d, *J* = 18.0 Hz, 1H), 3.62 (s, 3H), 2.49 (s, 3H), 2.36 (s, 3H), 1.64 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 197.8, 174.3, 160.2, 144.7, 143.8, 139.1, 138.9, 133.8, 133.4, 131.6, 129.0, 128.9, 128.3, 127.9, 122.3, 120.6, 115.7, 111.7, 110.4, 48.8, 48.3, 29.8, 29.7, 21.6, 21.4; HRMS (ESI-TOF) *m/z*: $C_{27}H_{25}N_2O_2$ $(M + H)^+$ calcd for 409.1911, found 409.1914.

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



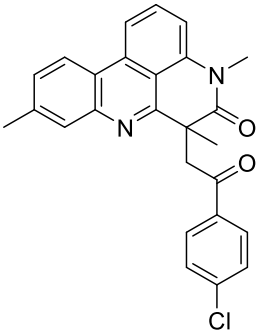
Yield: 62.8 mg, 74%; yellow solid; mp 191.5-191.8 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.94-7.90 (m, 2H), 7.81 (t, *J* = 8.4 Hz, 1H), 7.75 (s, 1H), 7.41-7.38 (m, 1H), 7.25 (d, *J* = 8.8 Hz, 1H), 6.90-6.86 (m, 2H), 4.73 (d, *J* = 17.6 Hz, 1H), 4.22 (d, *J* = 17.6 Hz, 1H), 3.83 (s, 3H), 3.63 (s, 3H), 2.51 (s, 3H), 1.64 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 196.7, 174.4, 163.4, 160.4, 144.8, 139.2, 138.9, 133.5, 131.6, 130.5, 129.6, 129.0, 127.9, 122.3, 120.6, 115.7, 113.5, 111.8, 110.4, 55.4, 48.7, 48.3, 29.9, 29.7, 21.4; HRMS (ESI-TOF) *m/z*: $C_{27}H_{25}N_2O_3$ $(M + H)^+$ calcd for 425.1860, found 425.1862.

6-(2-(4-Fluorophenyl)-2-oxoethyl)-4,6,9-trimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthr



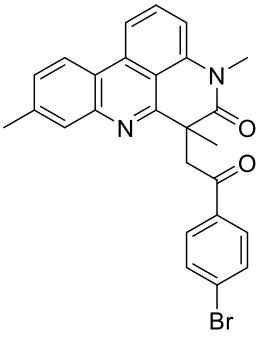
idin-5(6*H*)-one (3al): Yield: 64.3 mg, 78%; yellow solid; mp 184.8-185.3 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.98-7.95 (m, 2H), 7.80 (t, *J* = 8.0 Hz, 1H), 7.75 (s, 1H), 7.40-7.37 (m, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 8.8 Hz, 2H), 4.74 (d, *J* = 17.6 Hz, 1H), 4.23 (d, *J* = 17.6 Hz, 1H), 3.62 (s, 3H), 2.50 (s, 3H), 1.64 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 196.7, 174.2, 165.7 (d, *J* = 253.0 Hz, 1C), 160.0, 144.7, 139.0 (d, *J* = 1.9 Hz, 1C), 133.4, 132.8 (d, *J* = 3.0 Hz, 1C), 131.7, 130.8 (d, *J* = 9.3 Hz, 1C), 128.8, 128.0, 126.6, 122.3, 120.5, 115.6 (d, *J* = 46.0 Hz, 1C), 115.5, 111.7, 110.5, 48.6, 48.3, 29.8, 29.7, 21.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ: -105.2 (s, 1F); HRMS (ESI-TOF) *m/z*: $C_{26}H_{22}FN_2O_2$ $(M + H)^+$ calcd for 413.1660, found 412.1663.

6-(2-(4-Chlorophenyl)-2-oxoethyl)-4,6,9-trimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthr



idin-5(6*H*)-one (3am): Yield: 67.6 mg, 79%; yellow solid; mp 161.2-161.7 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.80 (t, *J* = 8.0 Hz, 1H), 7.74 (s, 1H), 7.40-7.36 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 1H), 4.73 (d, *J* = 17.6 Hz, 1H), 4.22 (d, *J* = 17.6 Hz, 1H), 3.62 (s, 3H), 2.50 (s, 3H), 1.64 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 197.1, 174.1, 160.0, 144.7, 139.5, 139.0, 139.0, 134.6, 133.4, 131.7, 129.6, 128.9, 128.7, 128.0, 122.3, 120.6, 115.8, 111.7, 110.5, 48.6, 48.4, 29.9, 29.7, 21.4; HRMS (ESI-TOF) *m/z*: $C_{26}H_{22}ClN_2O_2$ $(M + H)^+$ calcd for 429.1364, found 429.1361.

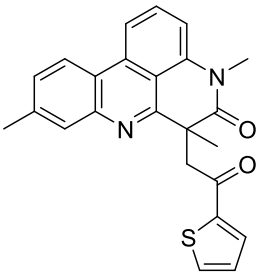
6-(2-(4-Bromophenyl)-2-oxoethyl)-4,6,9-trimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthr



idin-5(6*H*)-one (3an): Yield: 68.9 mg, 73%; yellow solid; mp 137.6-137.9 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.38 (d, *J* = 8.4 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.84-7.79 (m, 3H), 7.74 (s, 1H), 7.57-7.54 (m, 2H), 7.42-7.39 (m, 1H), 7.26 (d,

J = 8.0 Hz, 1H), 4.73 (d, *J* = 17.6 Hz, 1H), 4.21 (d, *J* = 17.6 Hz, 1H), 3.63 (s, 3H), 2.51 (s, 3H), 1.64 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 197.3, 174.1, 160.0, 144.7, 139.1, 139.0, 135.1, 133.5, 131.7, 131.7, 129.7, 128.9, 128.3, 128.1, 122.3, 120.6, 115.8, 111.7, 110.5, 48.6, 48.4, 29.9, 29.7, 21.4; HRMS (ESI-TOF) *m/z*: $C_{26}H_{22}BrN_2O_2$ $(M + H)^+$ calcd for 473.0859, found 473.0864.

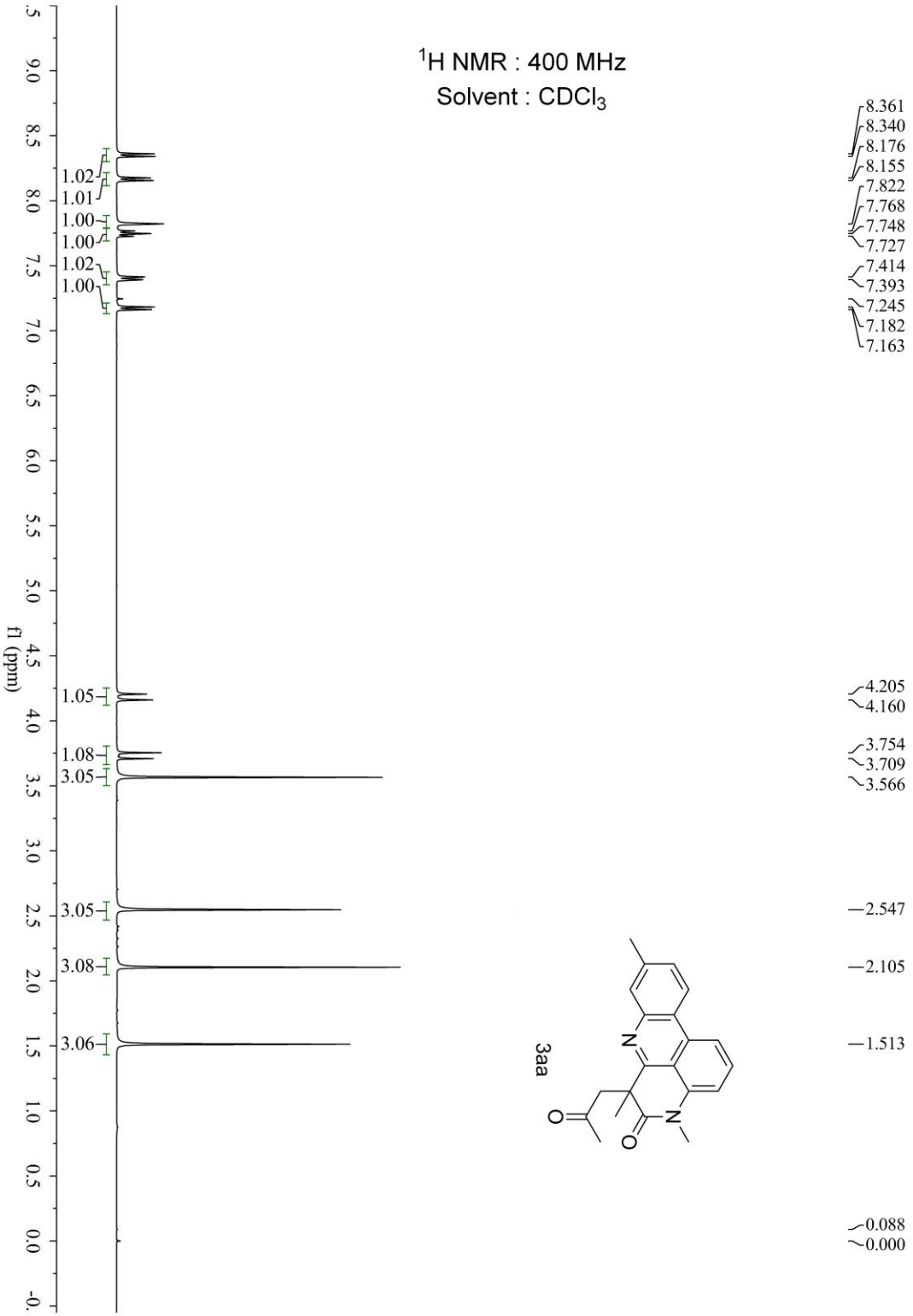
4,6,9-Trimethyl-6-(2-oxo-2-(thiophen-2-yl)ethyl)-4*H*-pyrido[4,3,2-*gh*]phenanthri

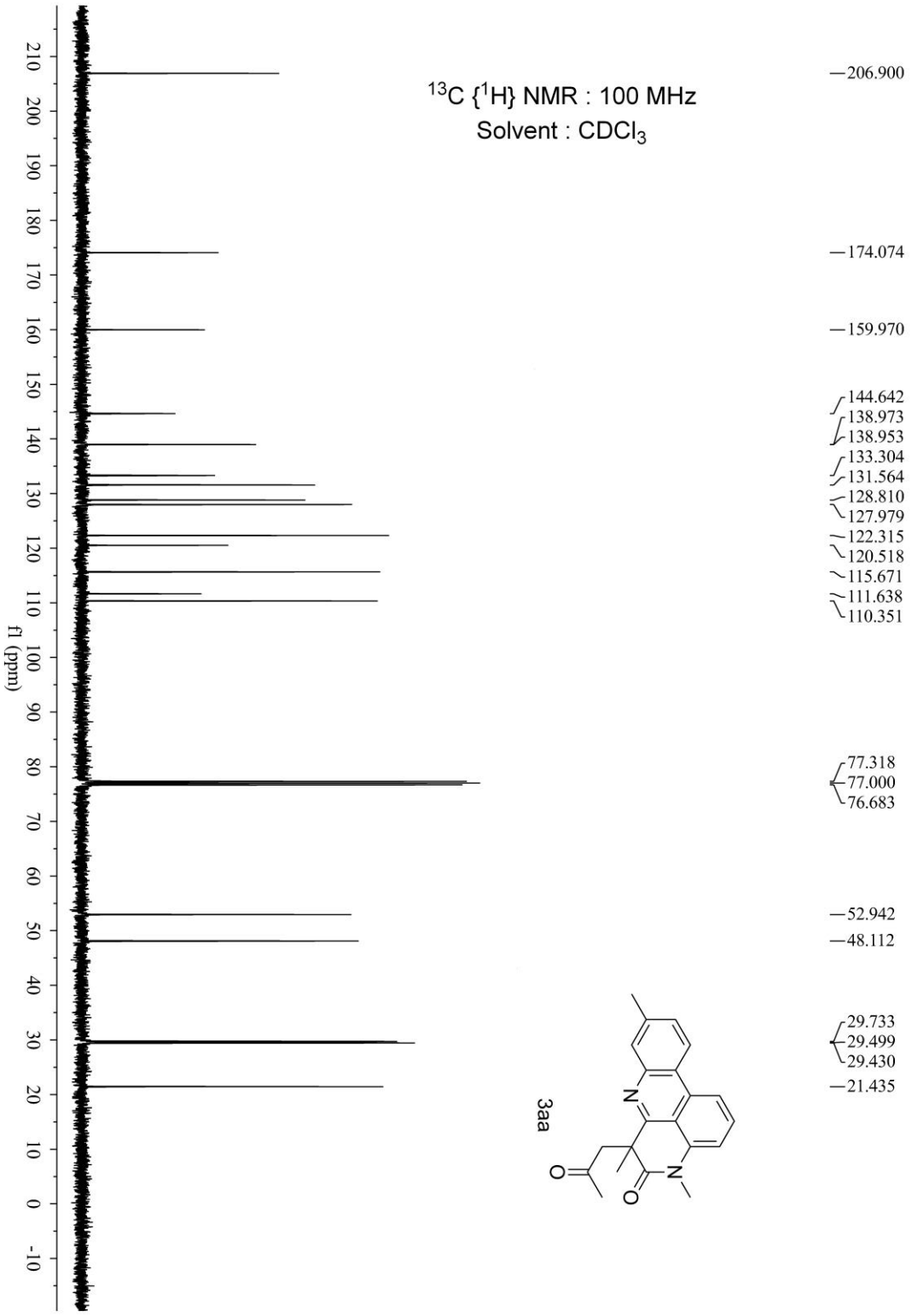


din-5(6*H*)-one (3ao): Yield: 51.2 mg, 64%; yellow solid; mp 143.5-143.8 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.38 (d, *J* = 8.4 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.85-7.77 (m, 3H), 7.56-7.54 (m, 1H), 7.42-7.39 (m, 1H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.12-7.10 (m, 1H), 4.70 (d, *J* = 17.6 Hz, 1H), 4.22 (d, *J* = 17.6 Hz, 1H), 3.62 (s, 3H), 2.52 (s, 3H), 1.64 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 191.1, 174.1, 159.9, 144.7, 143.4, 139.1, 139.0, 133.5, 133.3, 132.1, 131.6, 129.0, 128.0, 127.9, 122.3, 120.6, 115.8, 111.7, 110.5, 49.2, 48.3, 29.9, 29.7, 21.4; HRMS (ESI-TOF) *m/z*: $C_{24}H_{21}N_2O_2S$ $(M + H)^+$ calcd for 401.1318, found 401.1342.

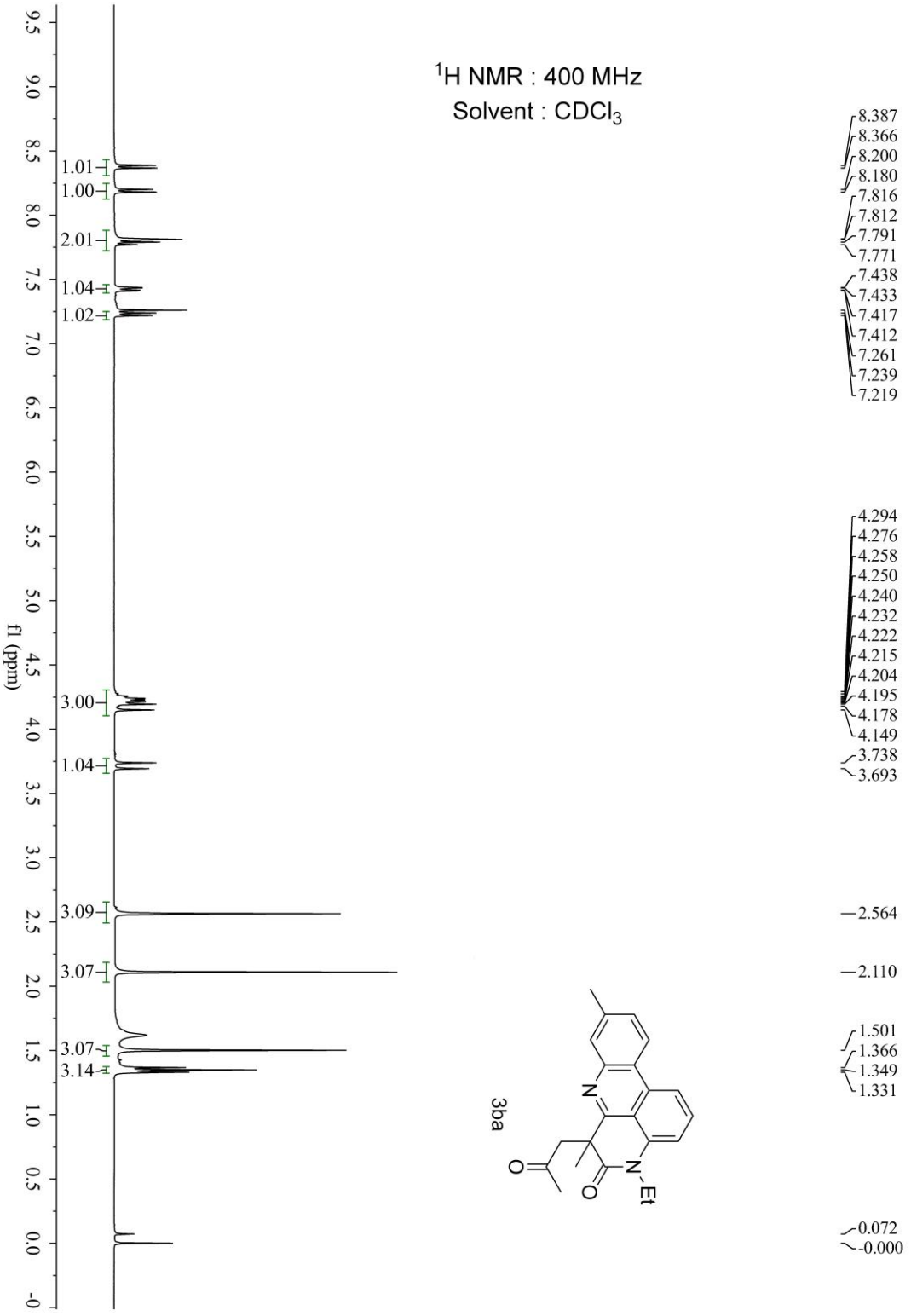
5. The ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra for all compounds

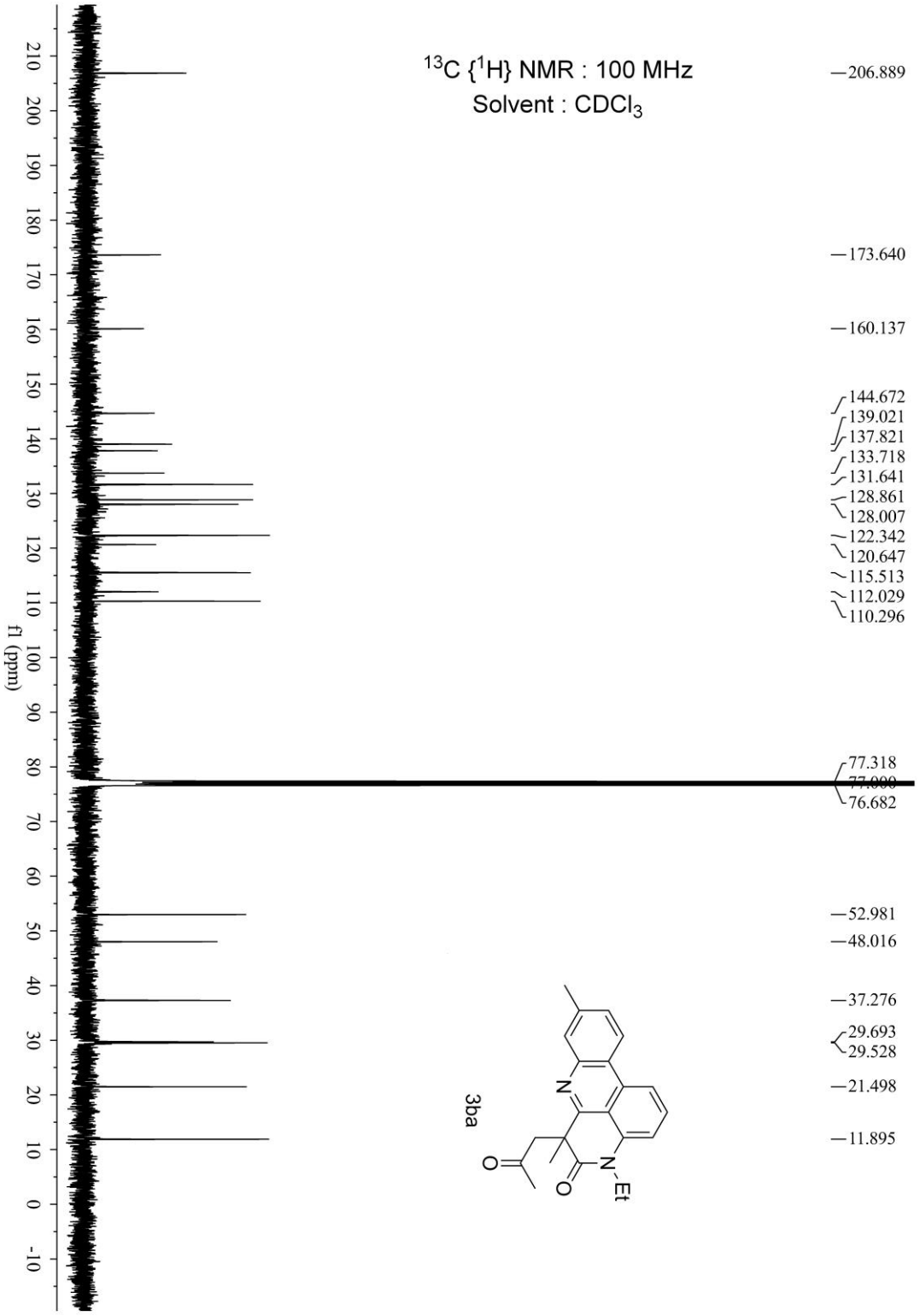
4,6,9-Trimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3aa)



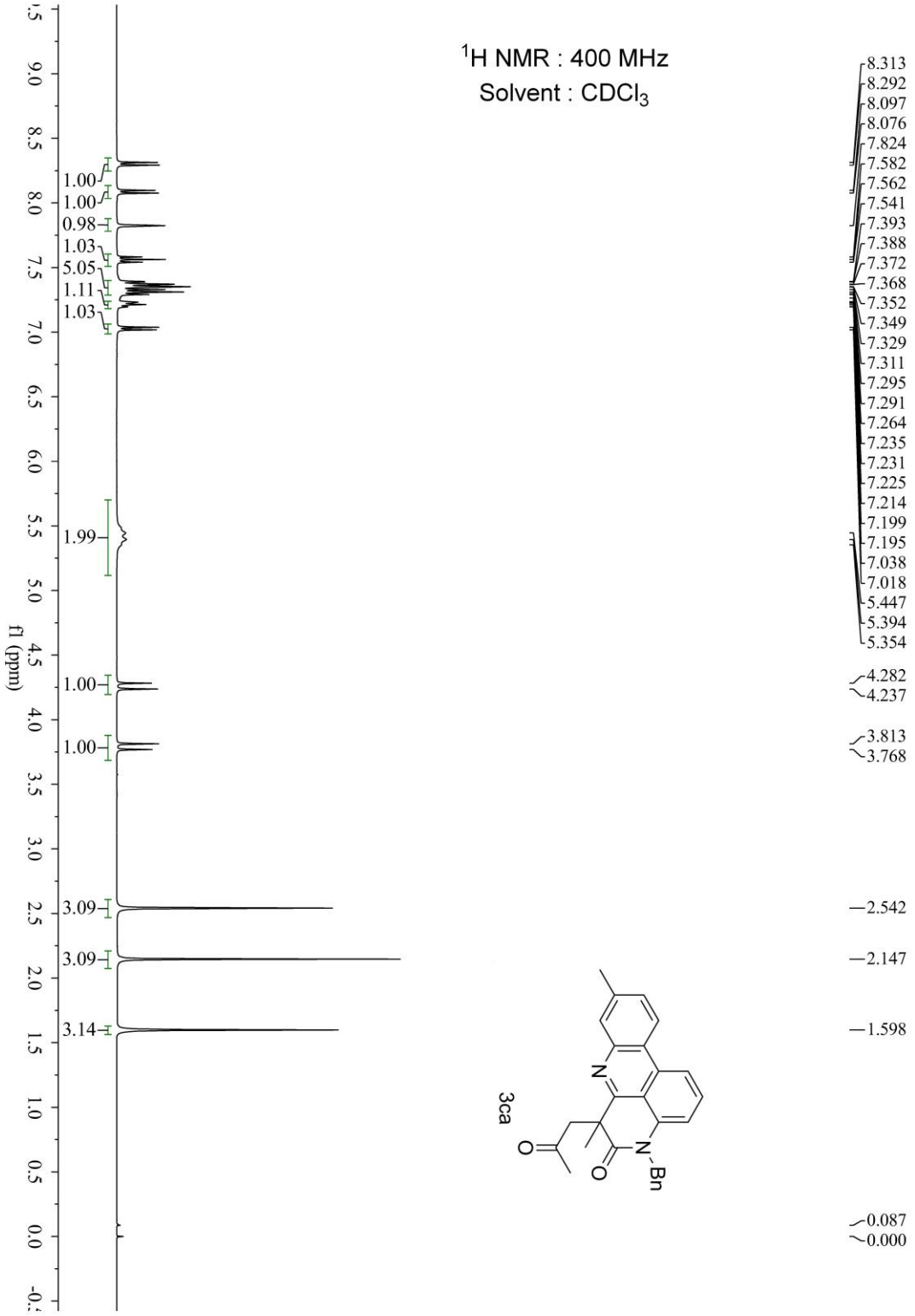

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
206.900
174.074
159.970
144.642
138.973
138.953
133.304
131.564
128.810
127.979
122.315
120.518
115.671
111.638
110.351
77.318
77.000
76.683
52.942
48.112
29.733
29.499
29.430
21.435
3aa
N
O
N
O

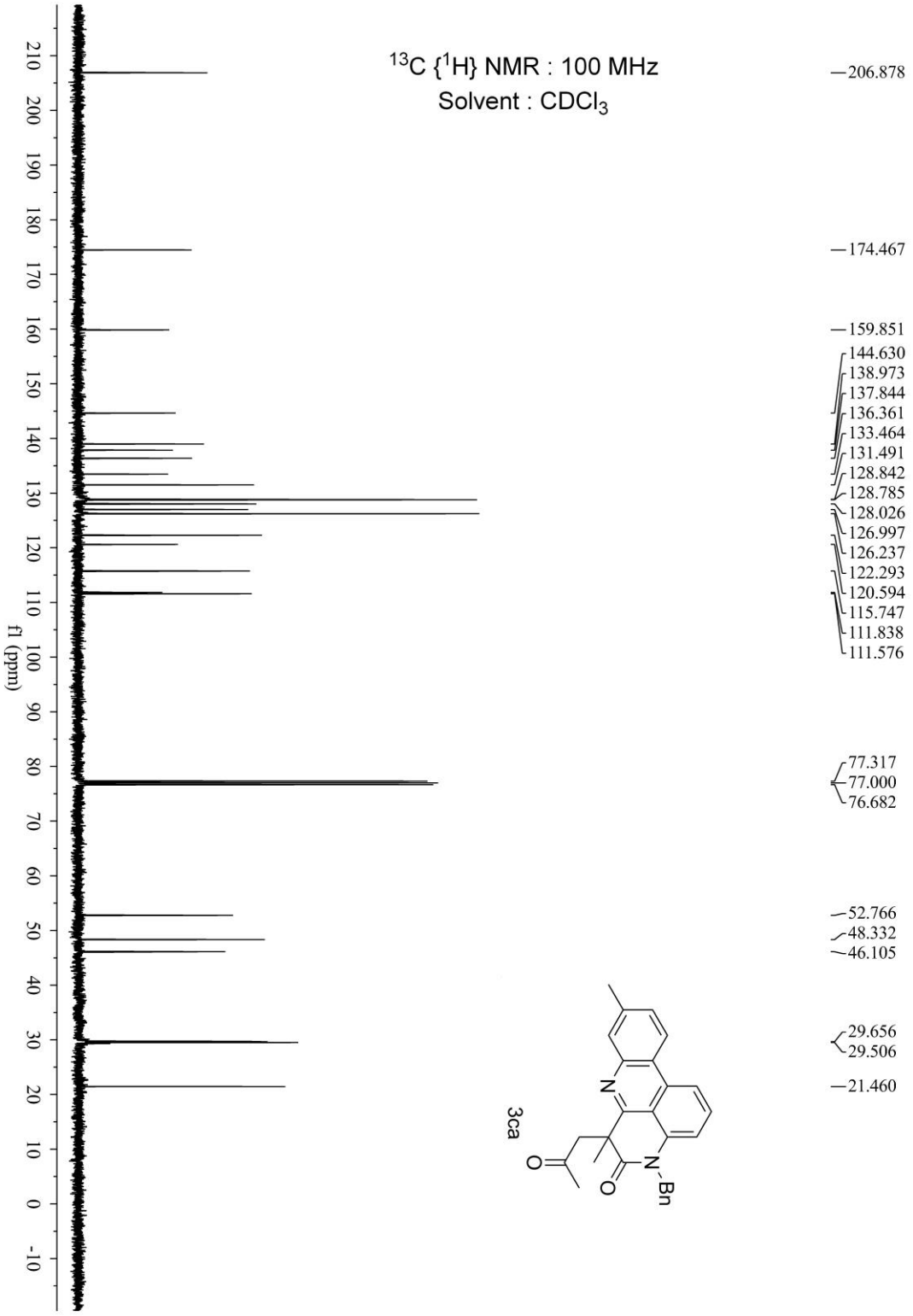
4-Ethyl-6,9-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ba)



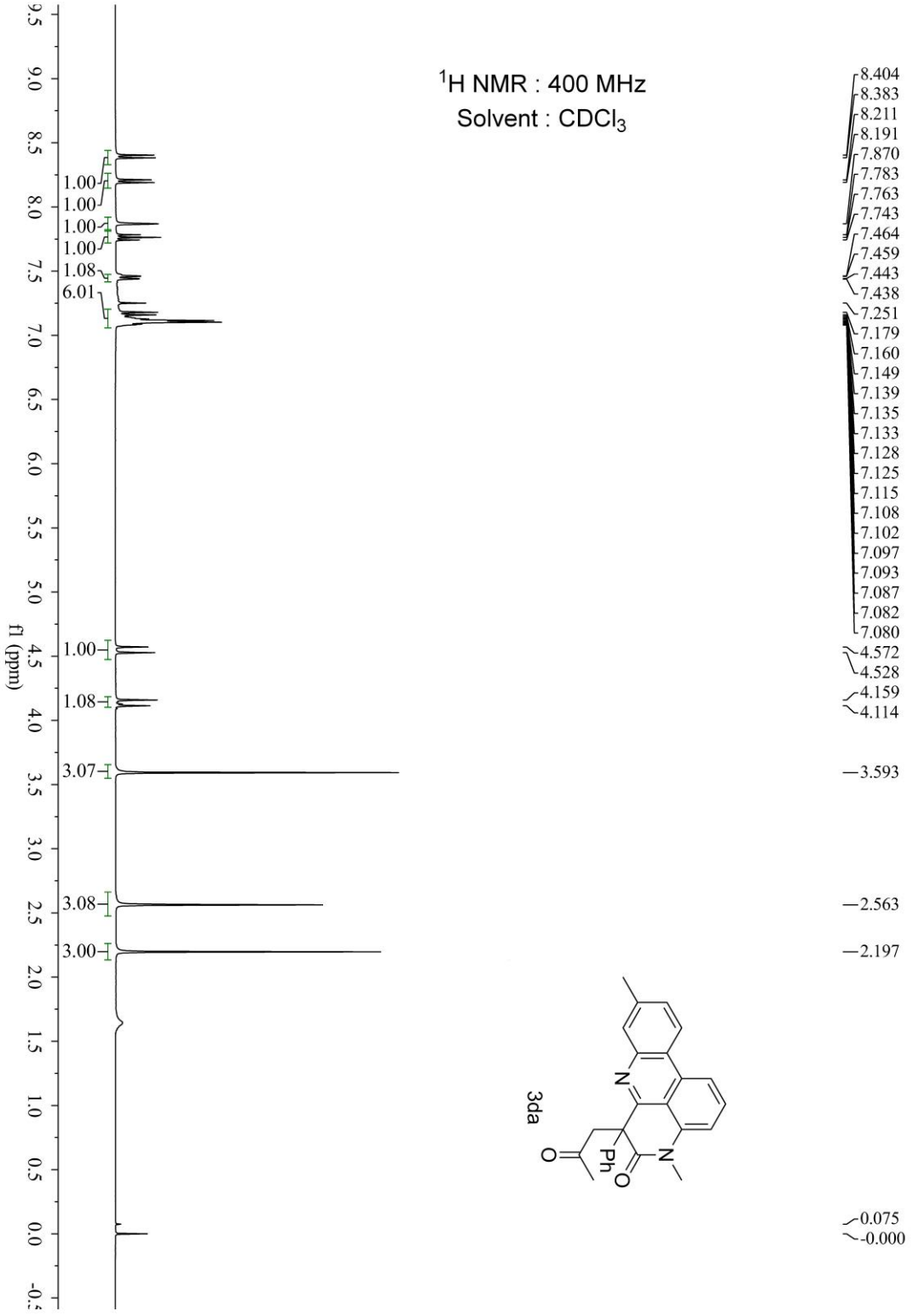

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
206.889
173.640
160.137
144.672
139.021
137.821
133.718
131.641
128.861
128.007
122.342
120.647
115.513
112.029
110.296
77.318
77.000
76.682
52.981
48.016
37.276
29.693
29.528
21.498
11.895
3ba
O
N
O
N
Et

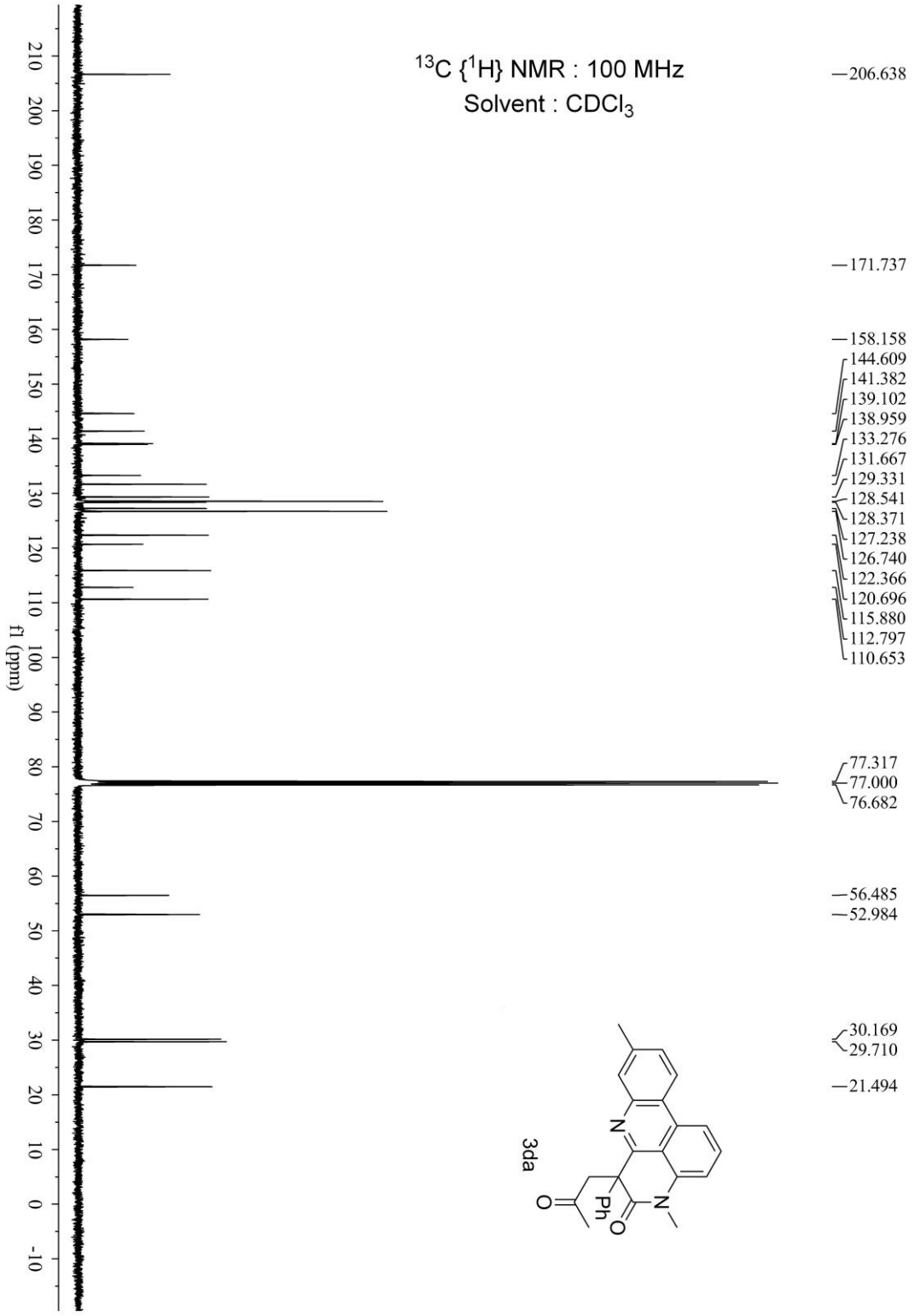
4-Benzyl-6,9-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ca)



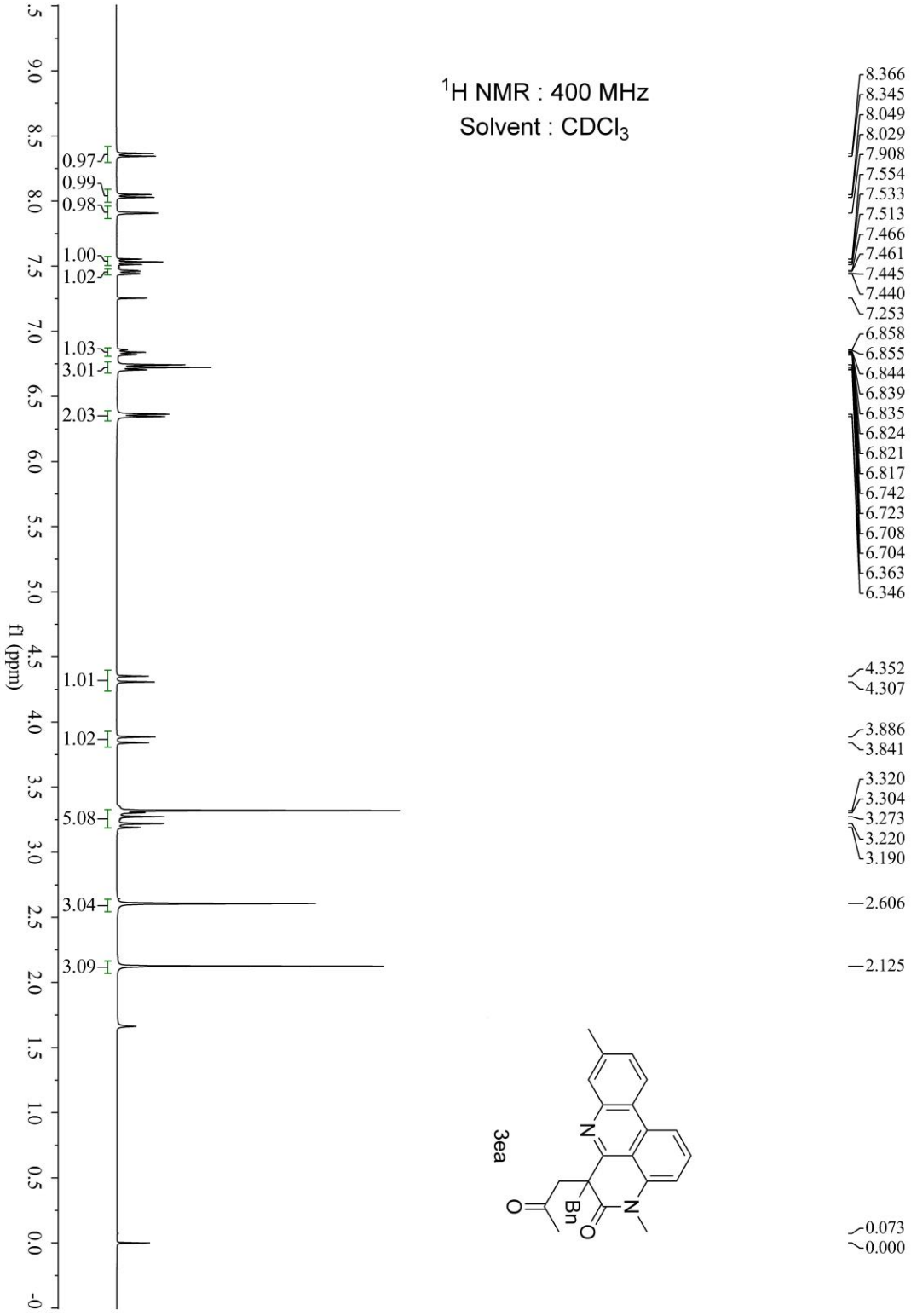

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
206.878
174.467
159.851
144.630
138.973
137.844
136.361
133.464
131.491
128.842
128.785
128.026
126.997
126.237
122.293
120.594
115.747
111.838
111.576
77.317
77.000
76.682
52.766
48.332
46.105
29.656
29.506
21.460
3ca
N
O
O
N
Bn

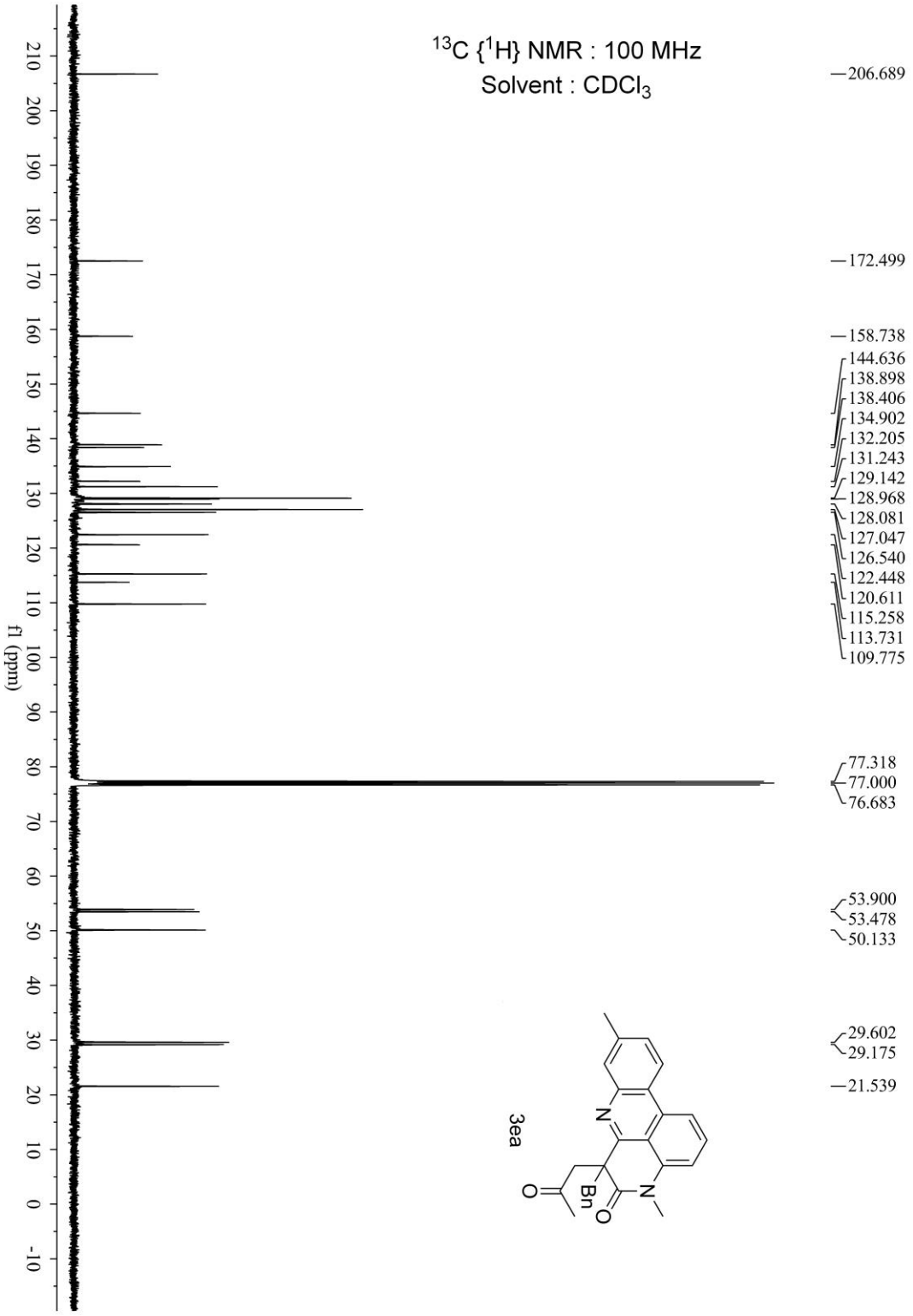
4,9-Dimethyl-6-(2-oxopropyl)-6-phenyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3da)



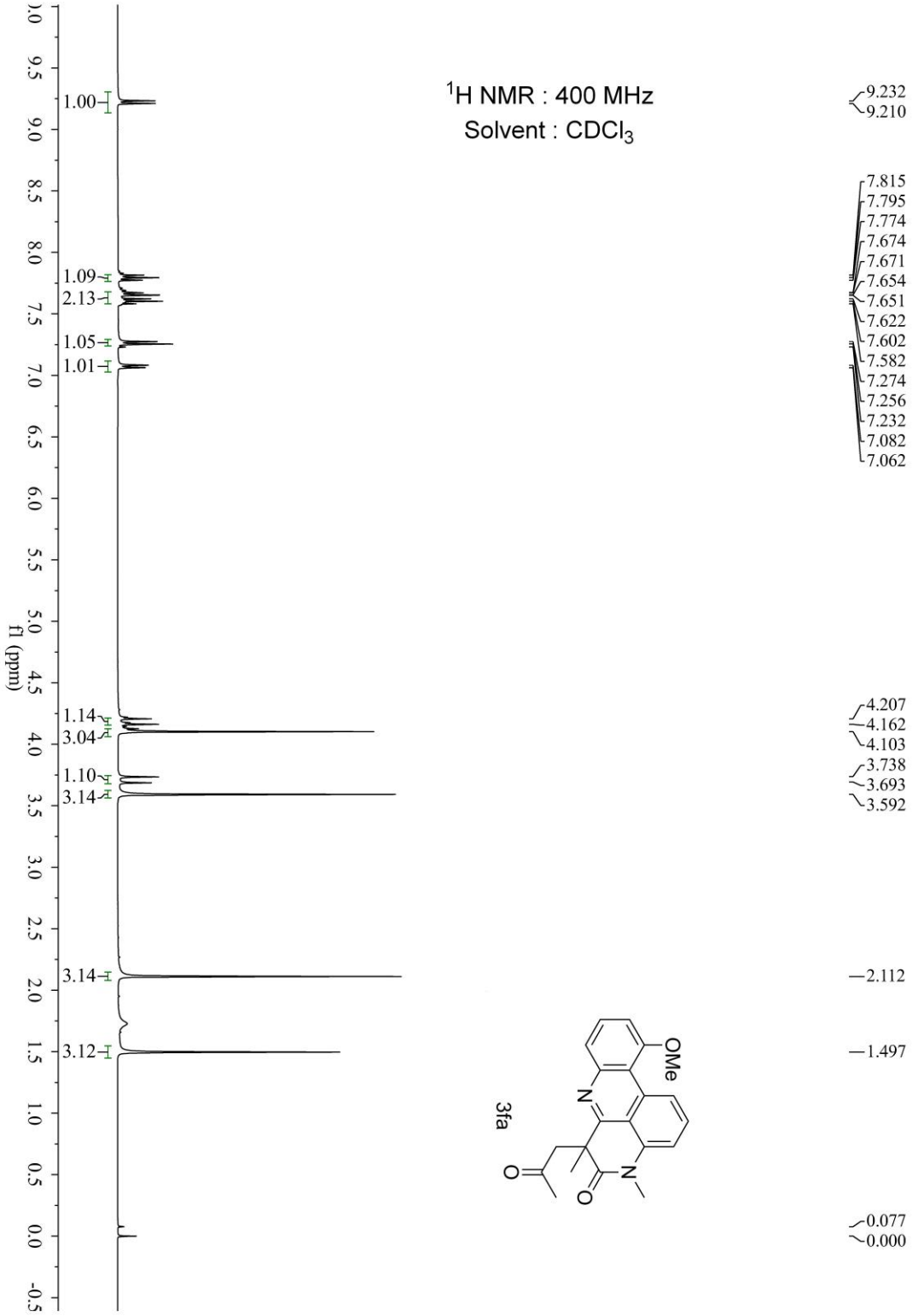

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
f1 (ppm)
206.638
171.737
158.158
144.609
141.382
139.102
138.959
133.276
131.667
129.331
128.541
128.371
127.238
126.740
122.366
120.696
115.880
112.797
110.653
77.317
77.000
76.682
56.485
52.984
30.169
29.710
21.494
3da

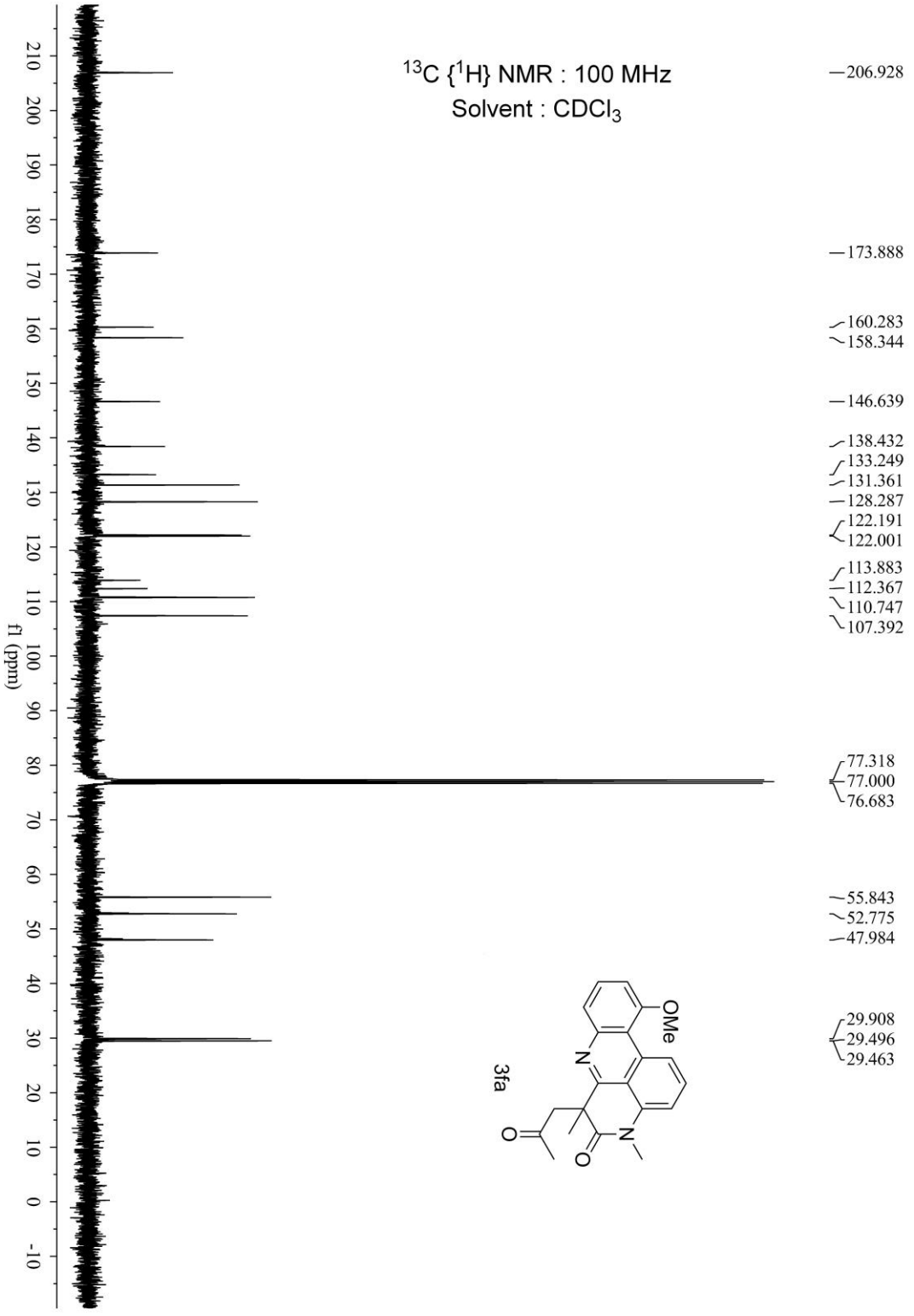
6-Benzyl-4,9-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ea)



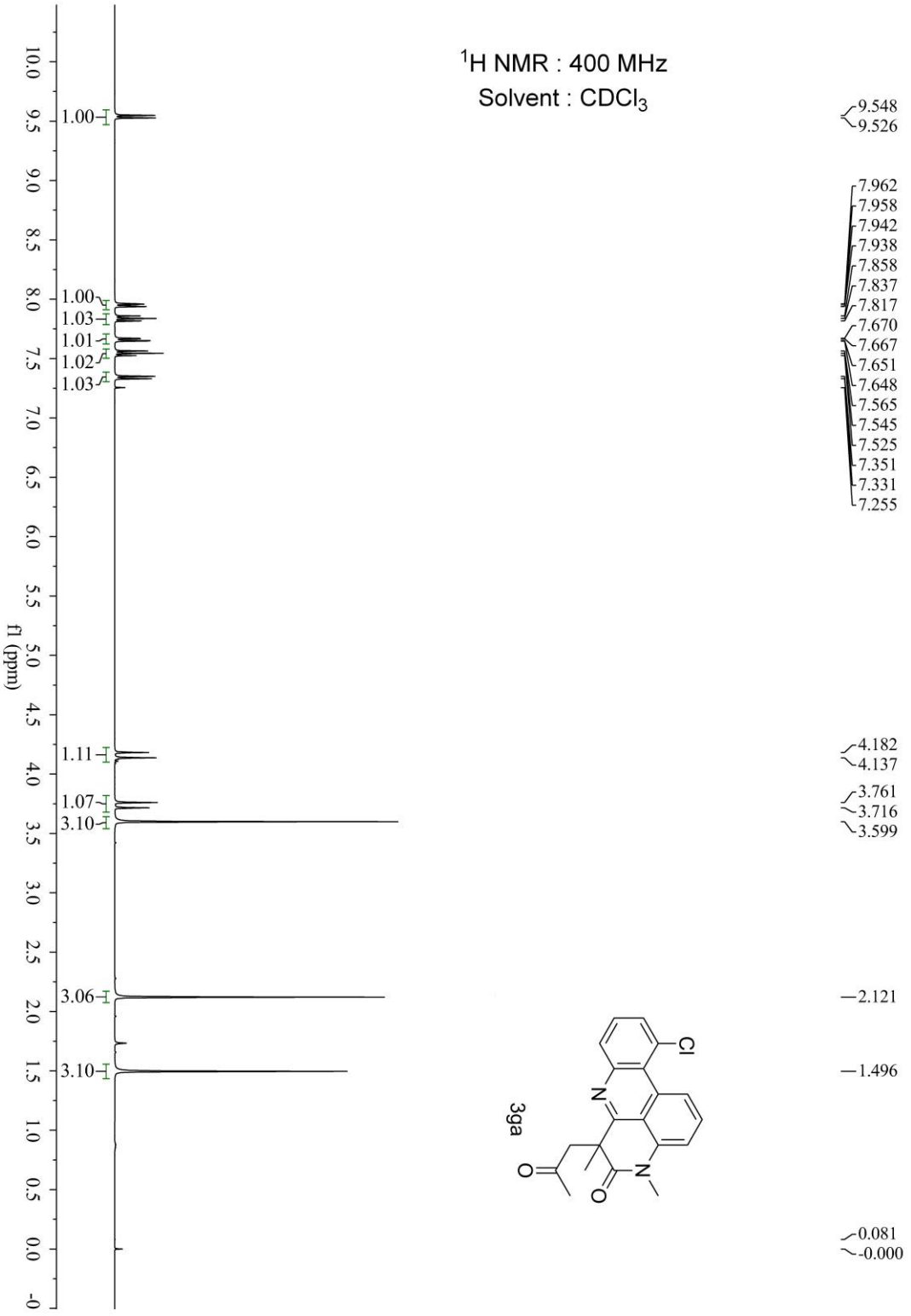

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
206.689
172.499
158.738
144.636
138.898
138.406
134.902
132.205
131.243
129.142
128.968
128.081
127.047
126.540
122.448
120.611
115.258
113.731
109.775
77.318
77.000
76.683
53.900
53.478
50.133
29.602
29.175
21.539
f1 (ppm)
3ea
N
O
Bn
O
N

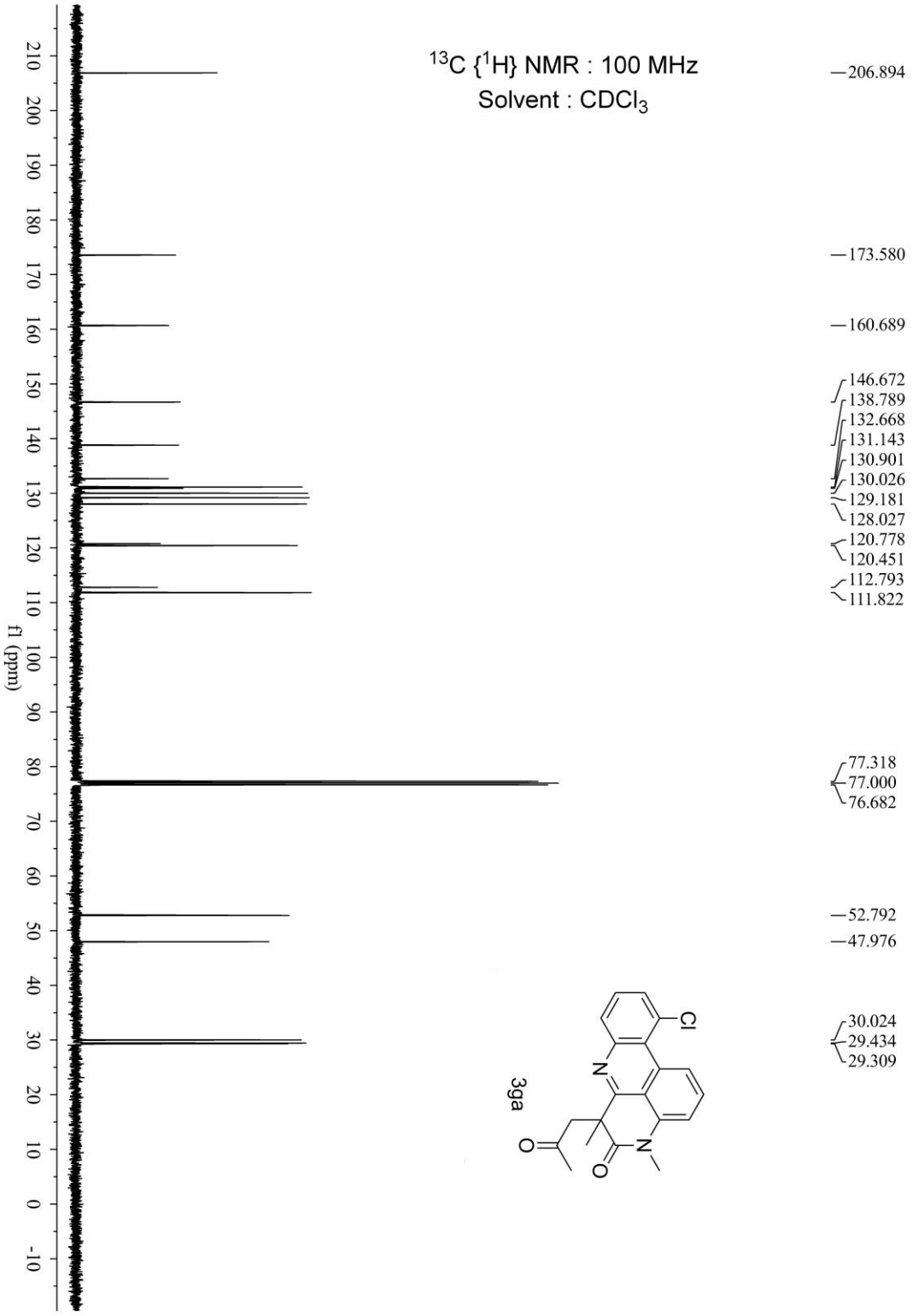
11-Methoxy-4,6-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phena nthridin-5(6*H*)-one (3fa)



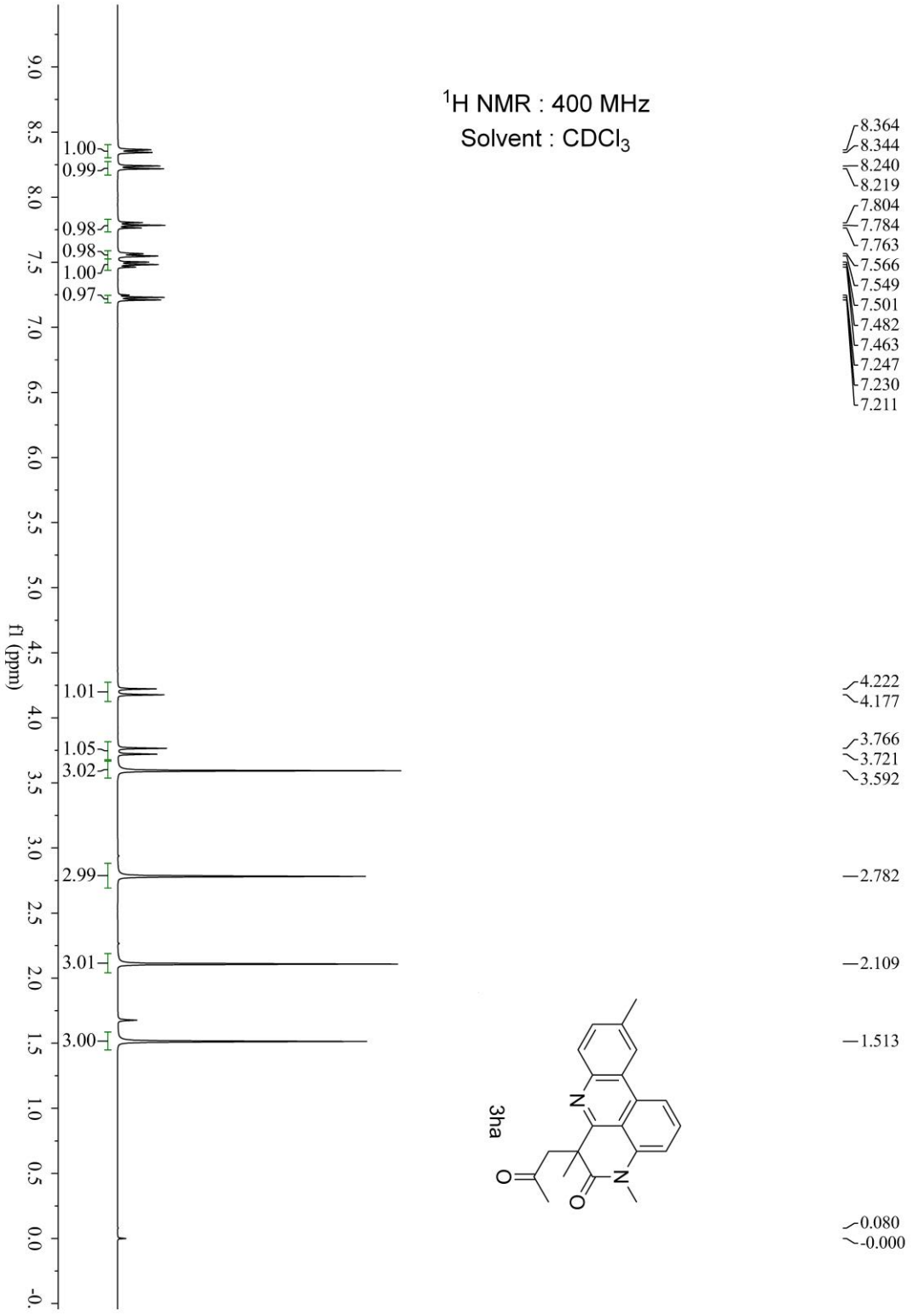

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
206.928
173.888
160.283
158.344
146.639
138.432
133.249
131.361
128.287
122.191
122.001
113.883
112.367
110.747
107.392
77.318
77.000
76.683
55.843
52.775
47.984
29.908
29.496
29.463
f1 (ppm)
OMe
N
O
N
O
3fa

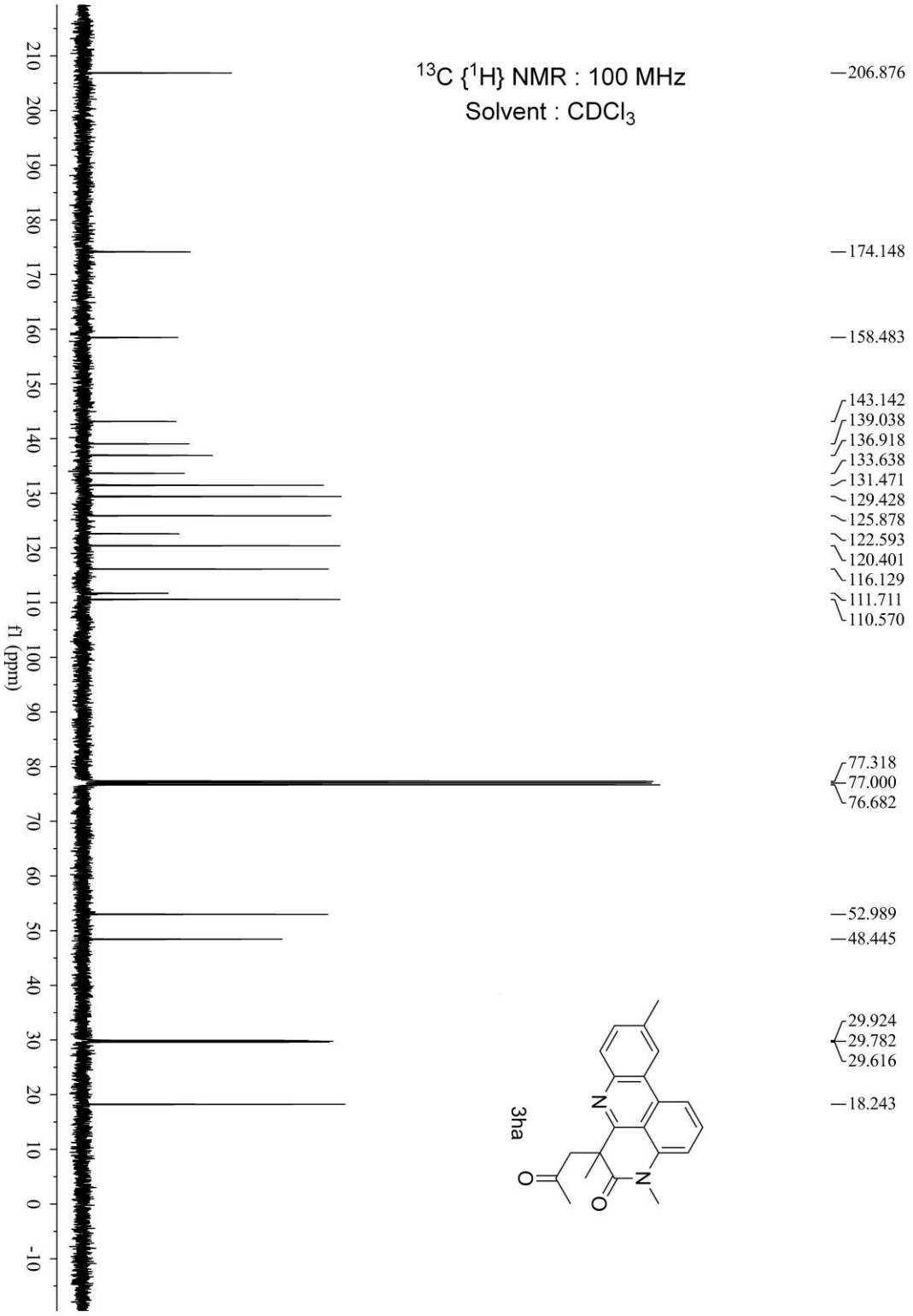
11-Chloro-4,6-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ga)



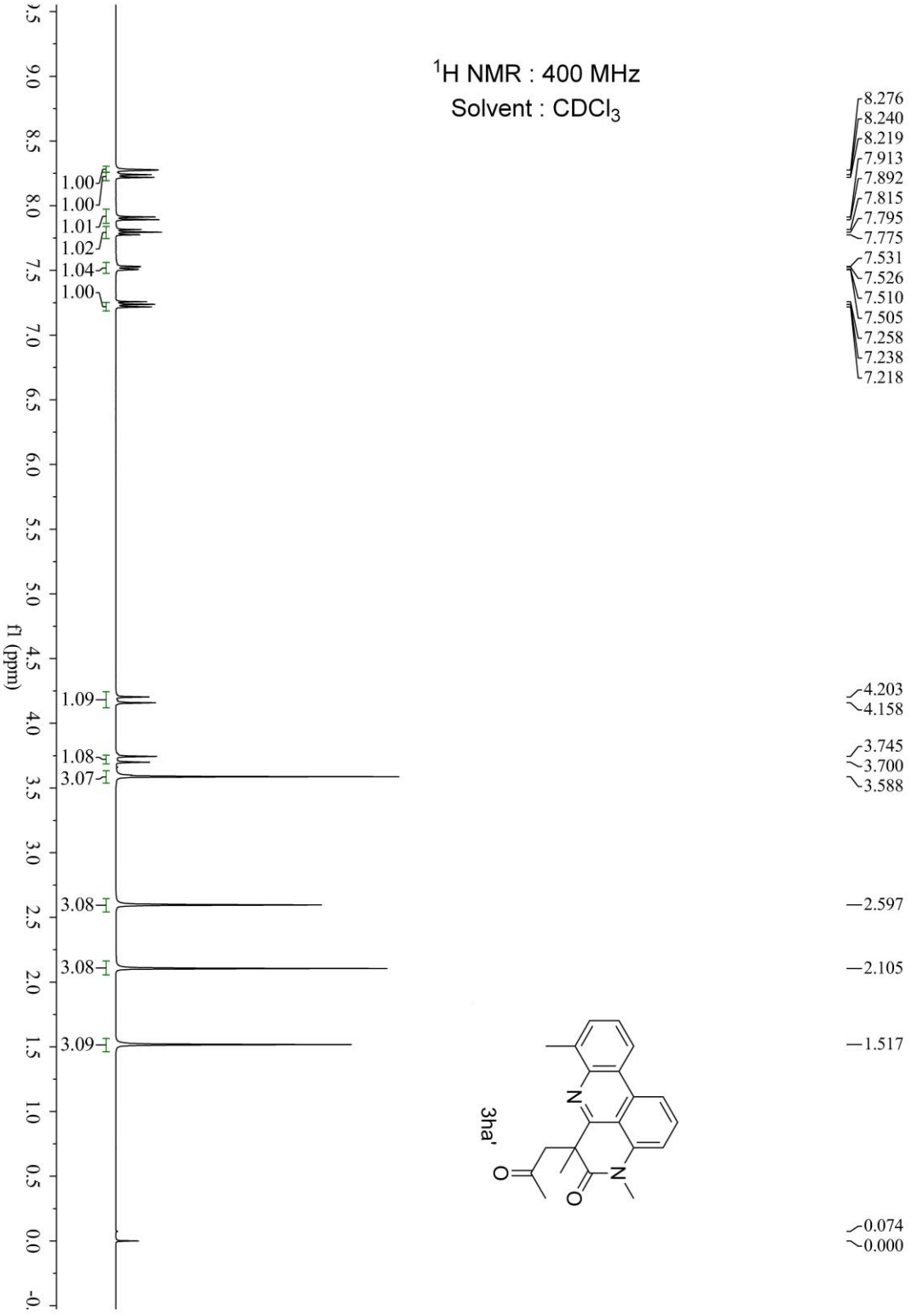

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
206.894
173.580
160.689
146.672
138.789
132.668
131.143
130.901
130.026
129.181
128.027
120.778
120.451
112.793
111.822
77.318
77.000
76.682
52.792
47.976
30.024
29.434
29.309
3ga
Cl
N
O
N
O

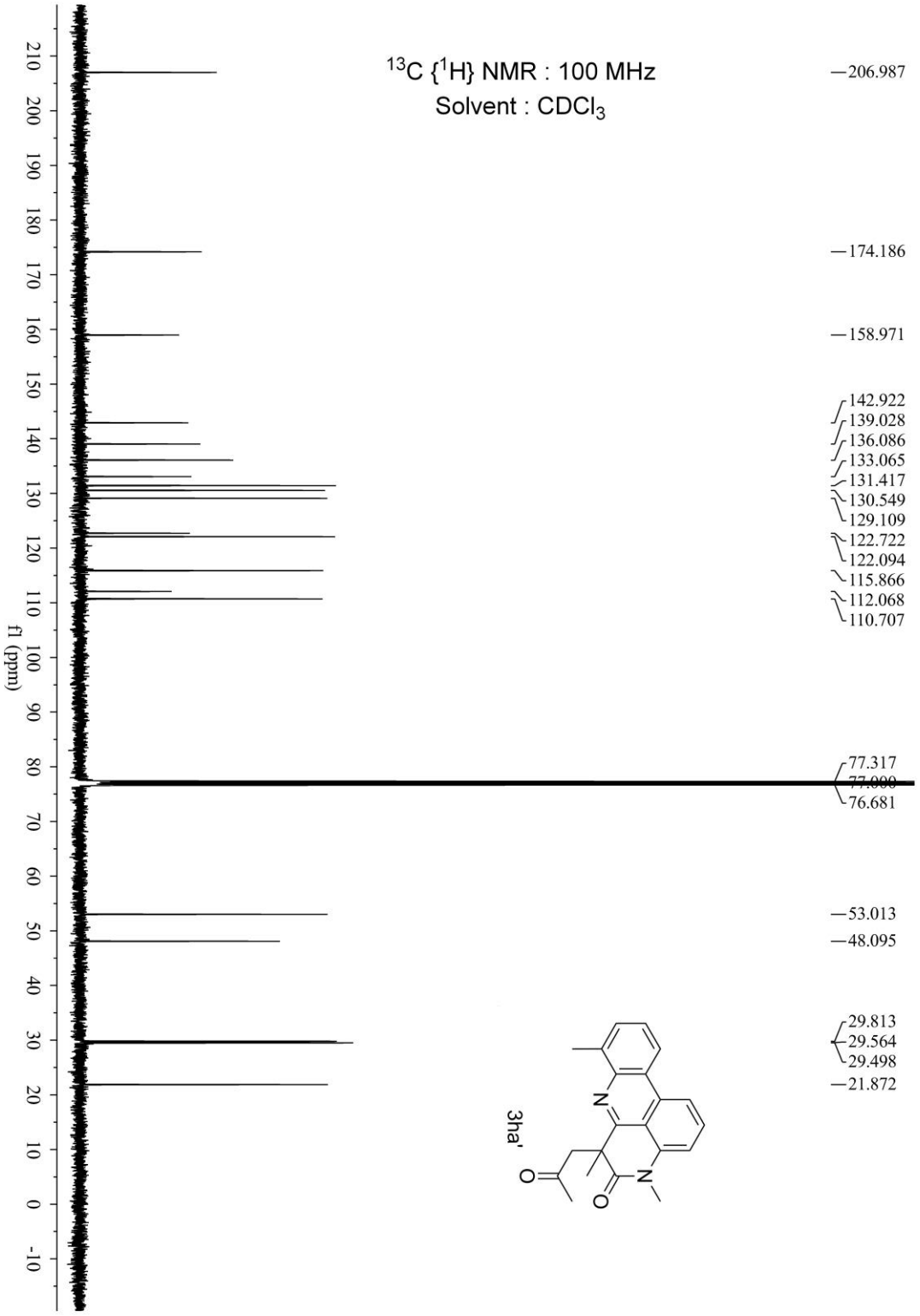
4,6,10-Trimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ha)



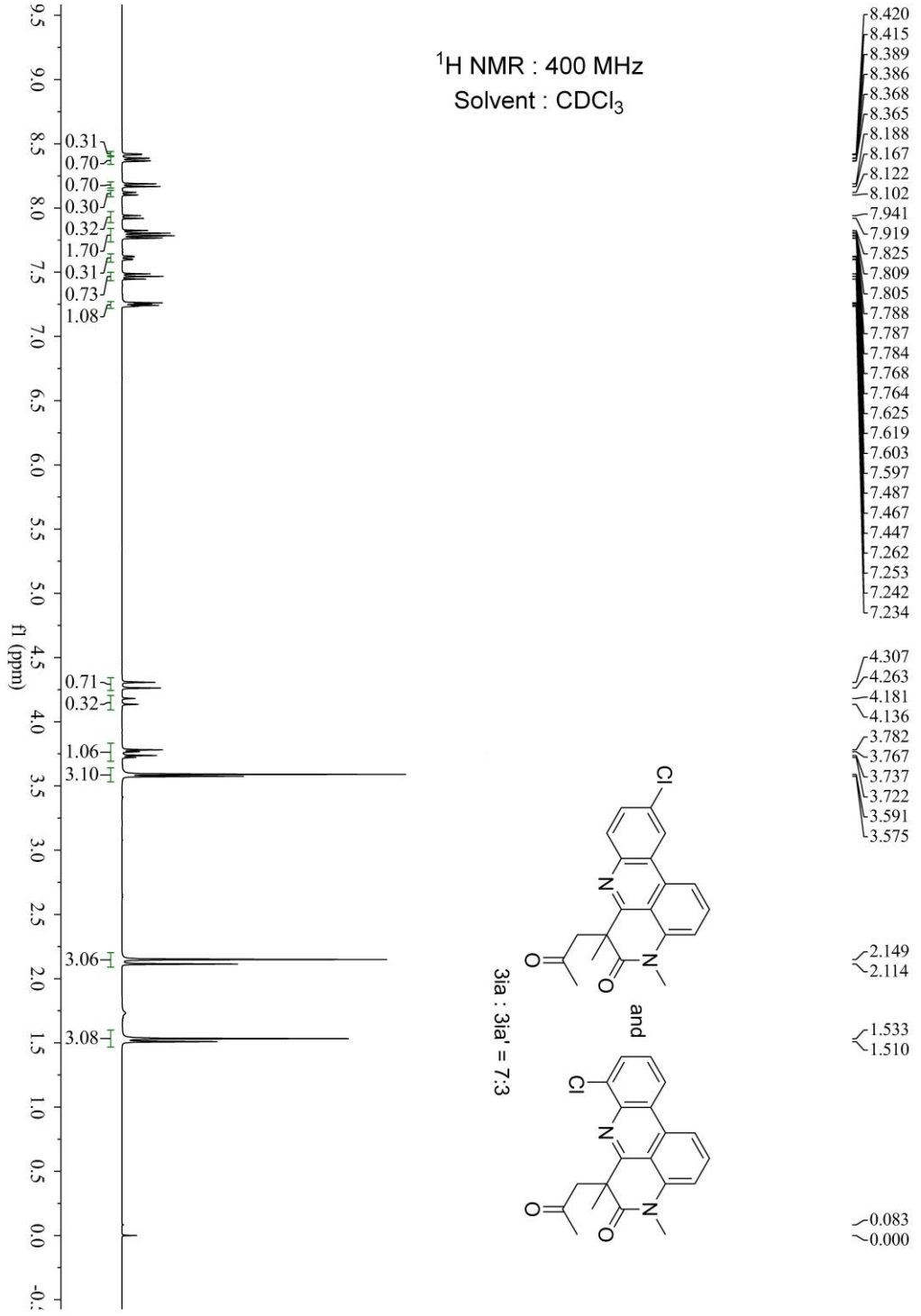

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
206.876
174.148
158.483
143.142
139.038
136.918
133.638
131.471
129.428
125.878
122.593
120.401
116.129
111.711
110.570
77.318
77.000
76.682
52.989
48.445
29.924
29.782
29.616
18.243
3ha
N
O
N
O

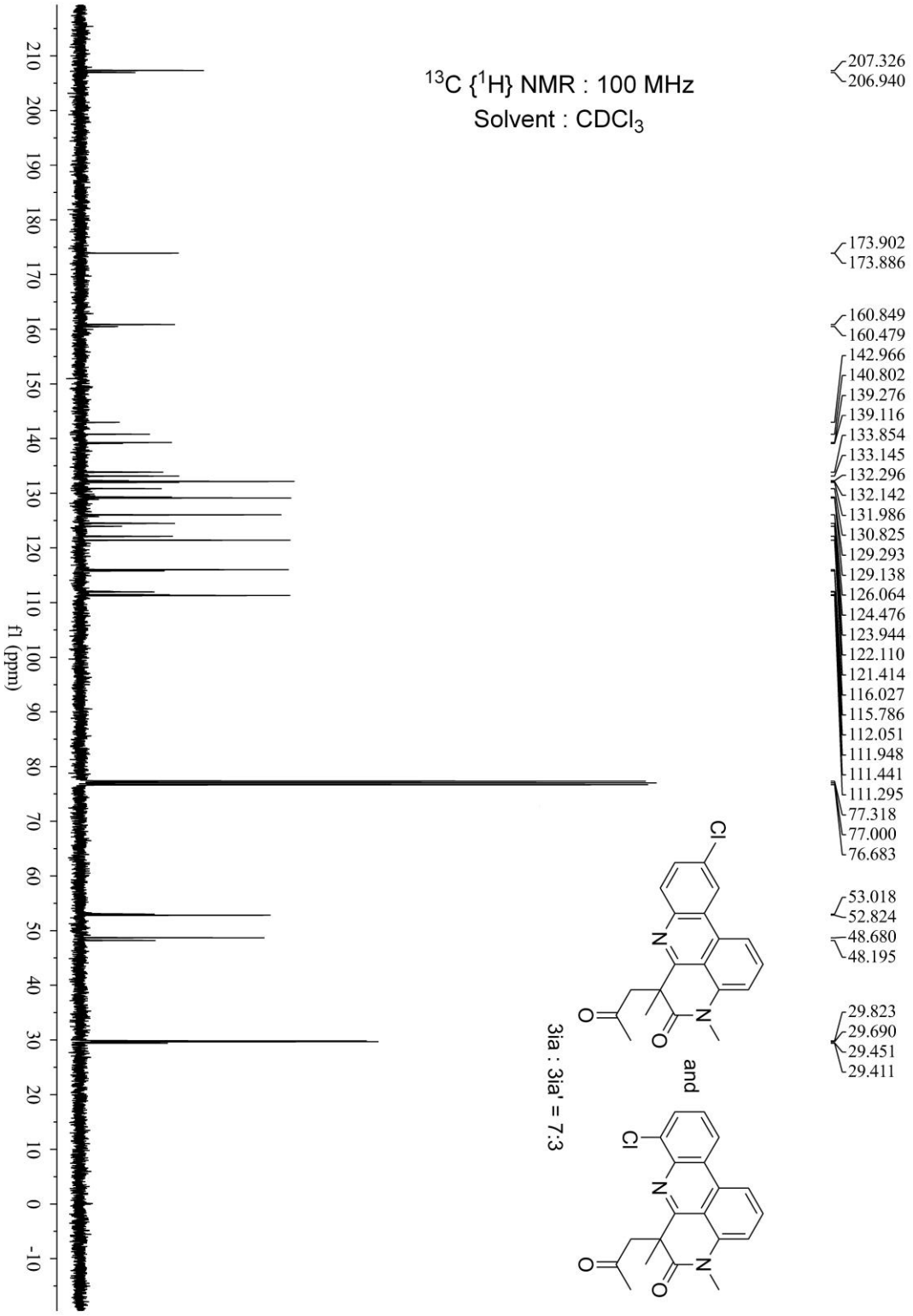
4,6,8-Trimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5 (6*H*)-one (3ha')



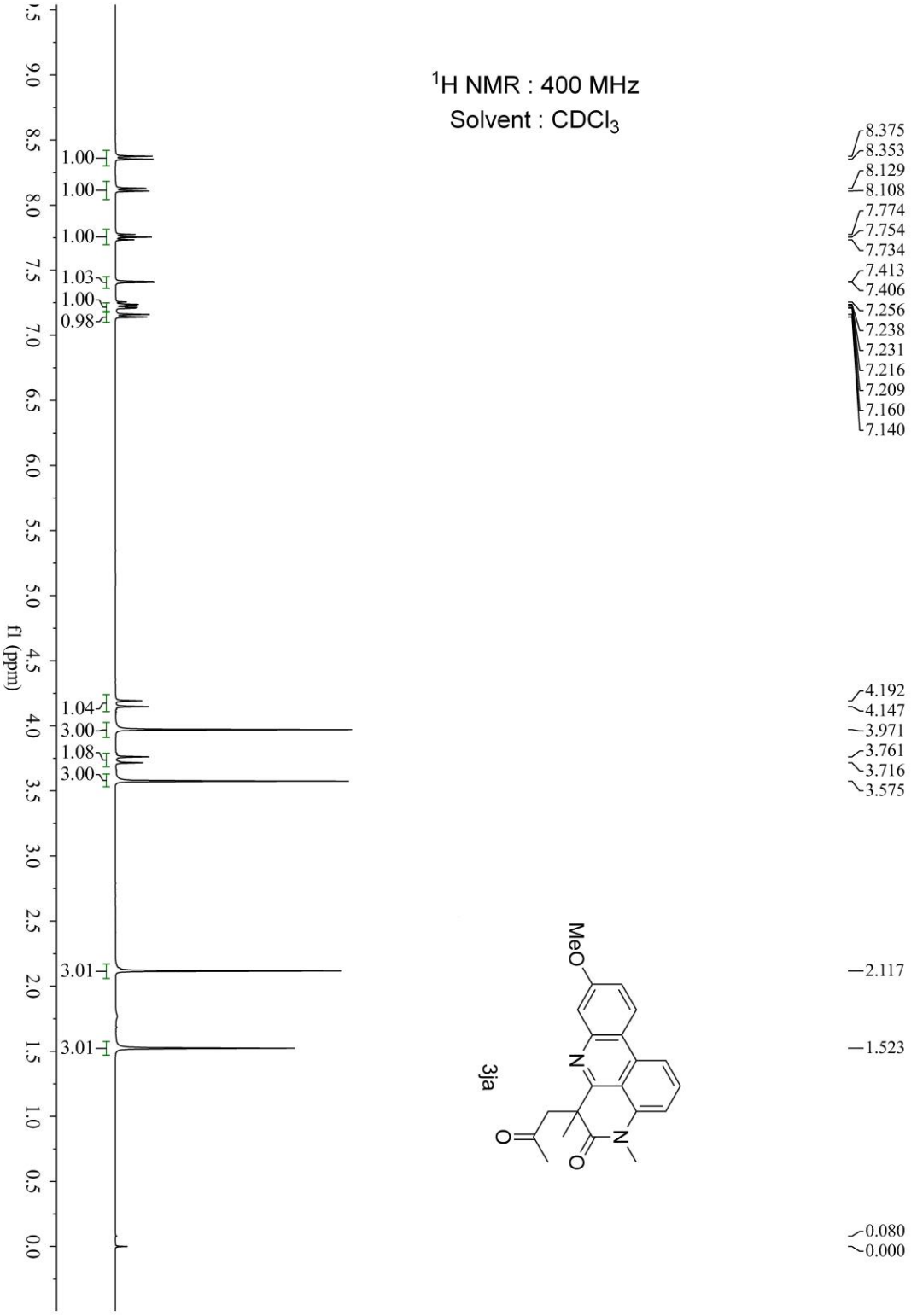

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
206.987
174.186
158.971
142.922
139.028
136.086
133.065
131.417
130.549
129.109
122.722
122.094
115.866
112.068
110.707
77.317
77.000
76.681
53.013
48.095
29.813
29.564
29.498
21.872
f1 (ppm)
3ha'

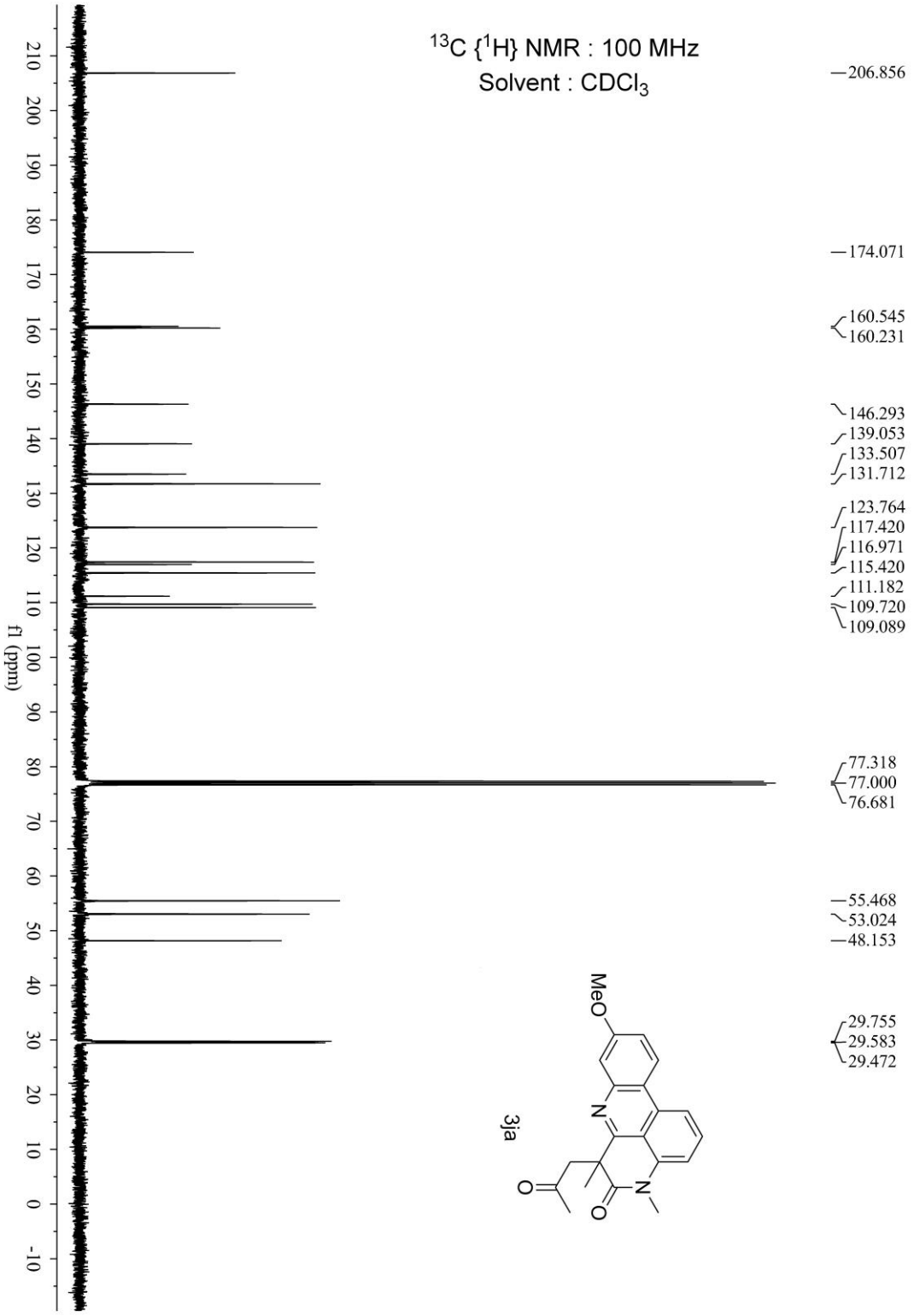
10-Chloro-4,6-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenant hridin-5(6*H*)-one (3ia) and 8-chloro-4,6-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthr idin-5(6*H*)-one (3ia') mixture



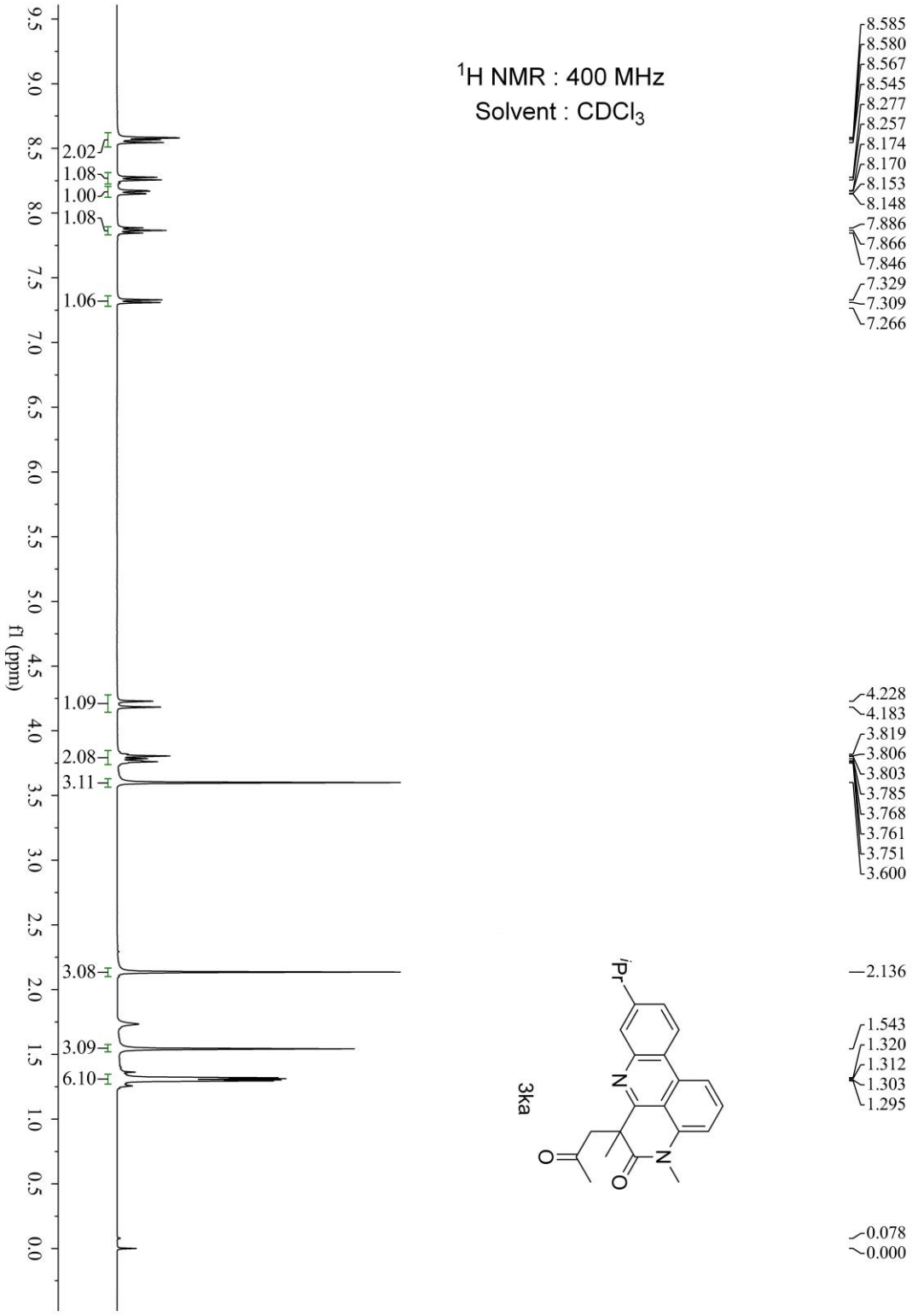

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
f1 (ppm)
207.326
206.940
173.902
173.886
160.849
160.479
142.966
140.802
139.276
139.116
133.854
133.145
132.296
132.142
131.986
130.825
129.293
129.138
126.064
124.476
123.944
122.110
121.414
116.027
115.786
112.051
111.948
111.441
111.295
77.318
77.000
76.683
53.018
52.824
48.680
48.195
29.823
29.690
29.451
29.411
Cl
N
O
N
O
and
3ia : 3ia' = 7:3

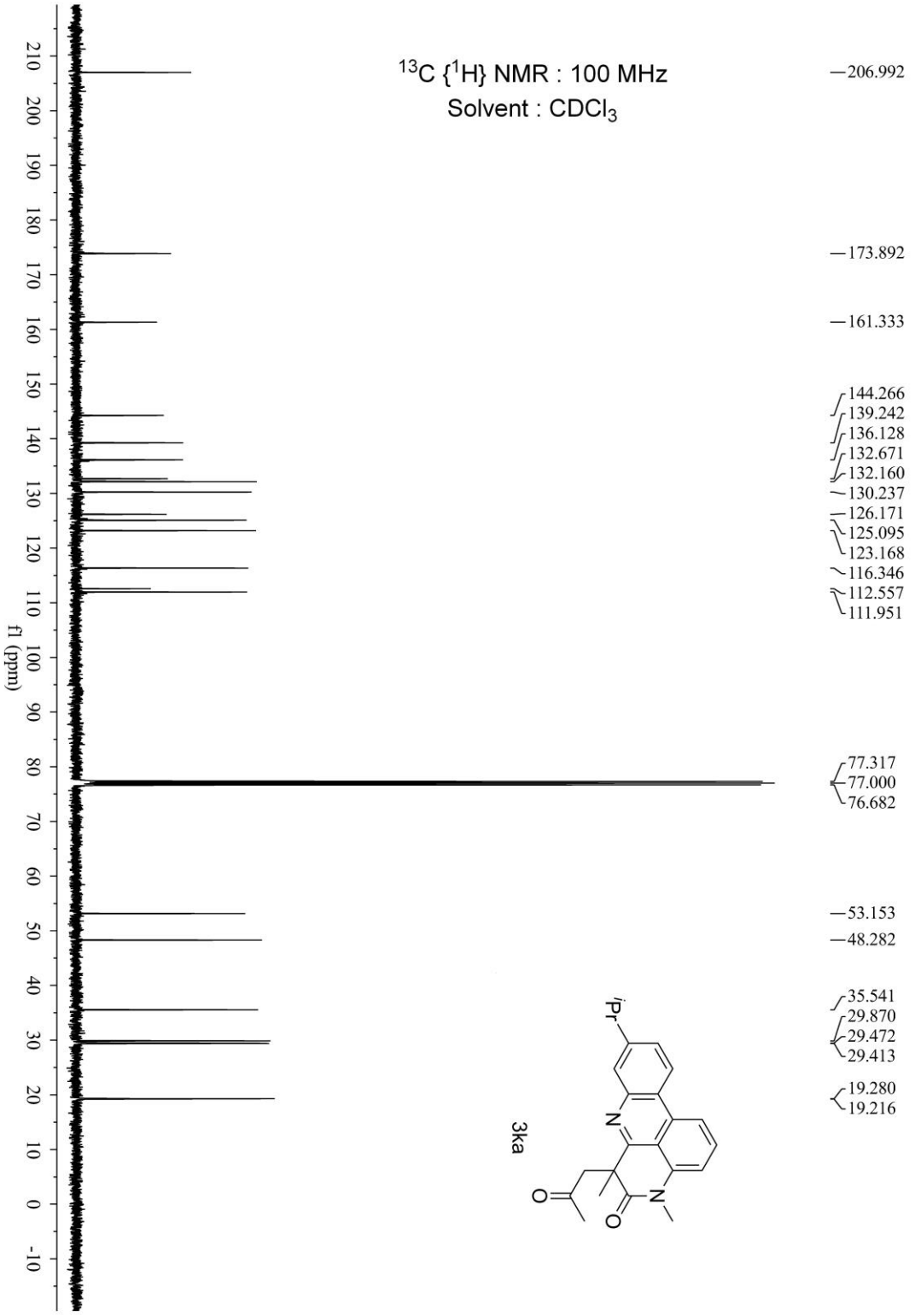
9-Methoxy-4,6-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenant hridin-5(6*H*)-one (3ja)



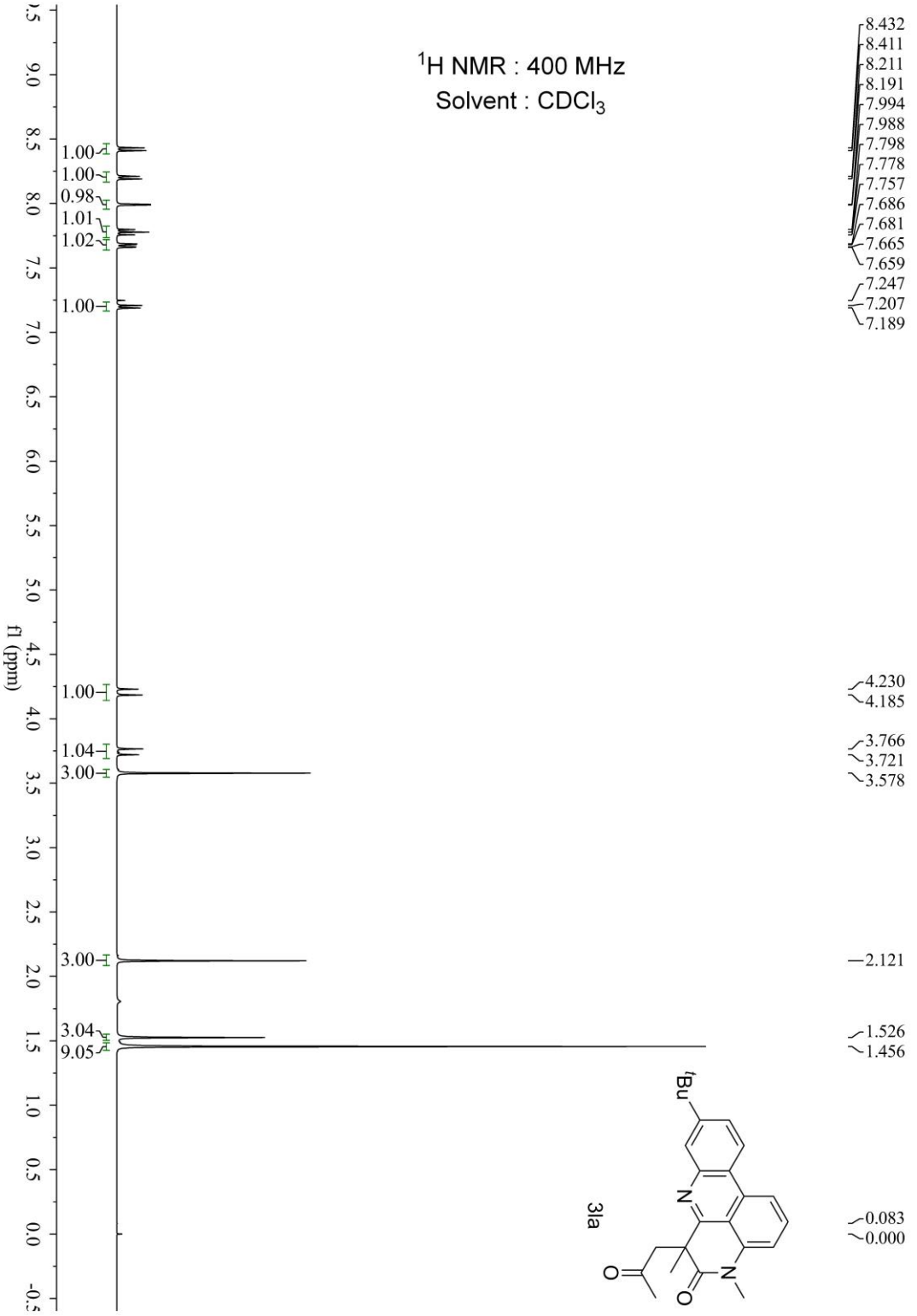

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
f1 (ppm)
206.856
174.071
160.545
160.231
146.293
139.053
133.507
131.712
123.764
117.420
116.971
115.420
111.182
109.720
109.089
77.318
77.000
76.681
55.468
53.024
48.153
29.755
29.583
29.472
MeO
N
O
N
O
3ja

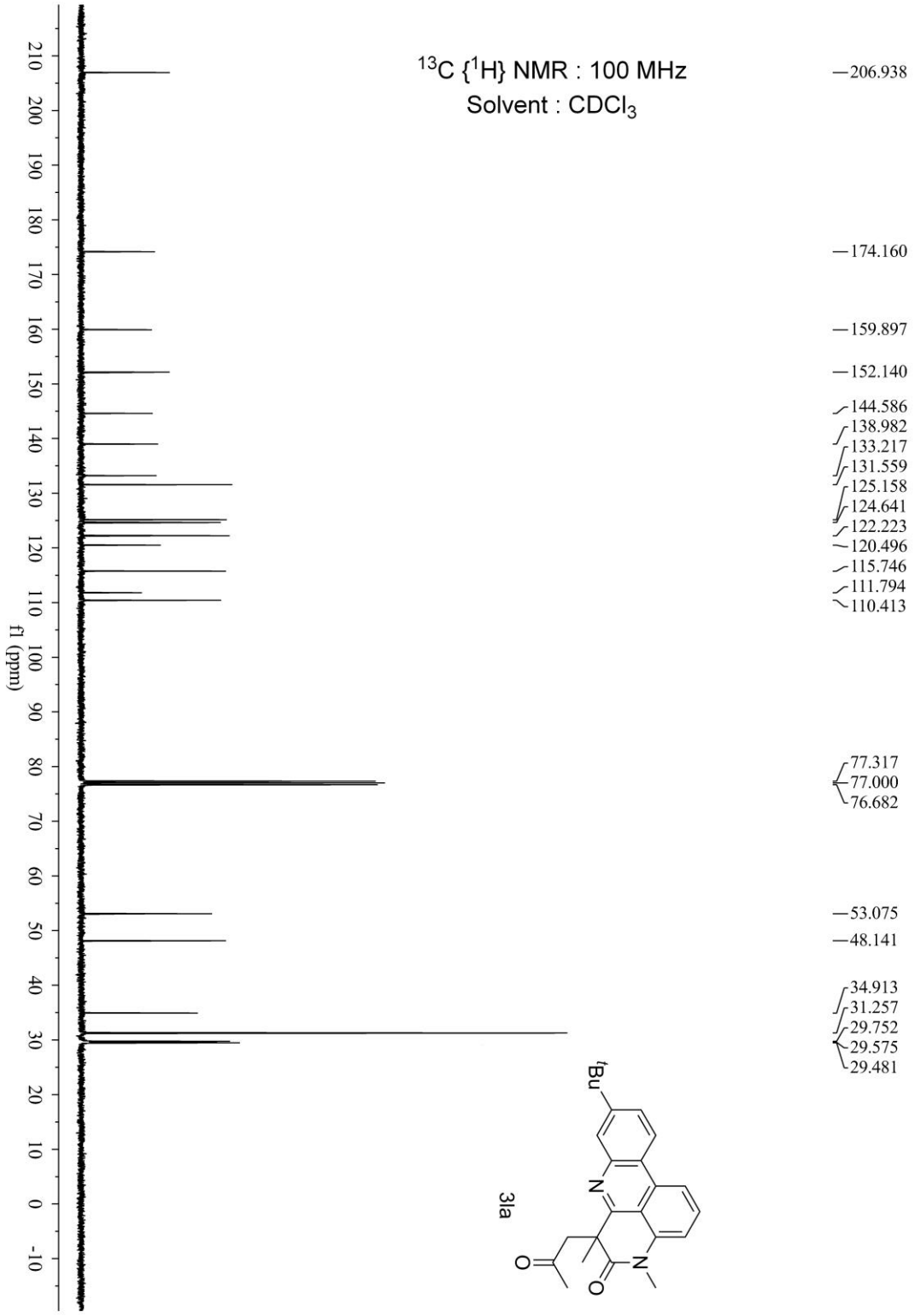
9-Isopropyl-4,6-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ka)



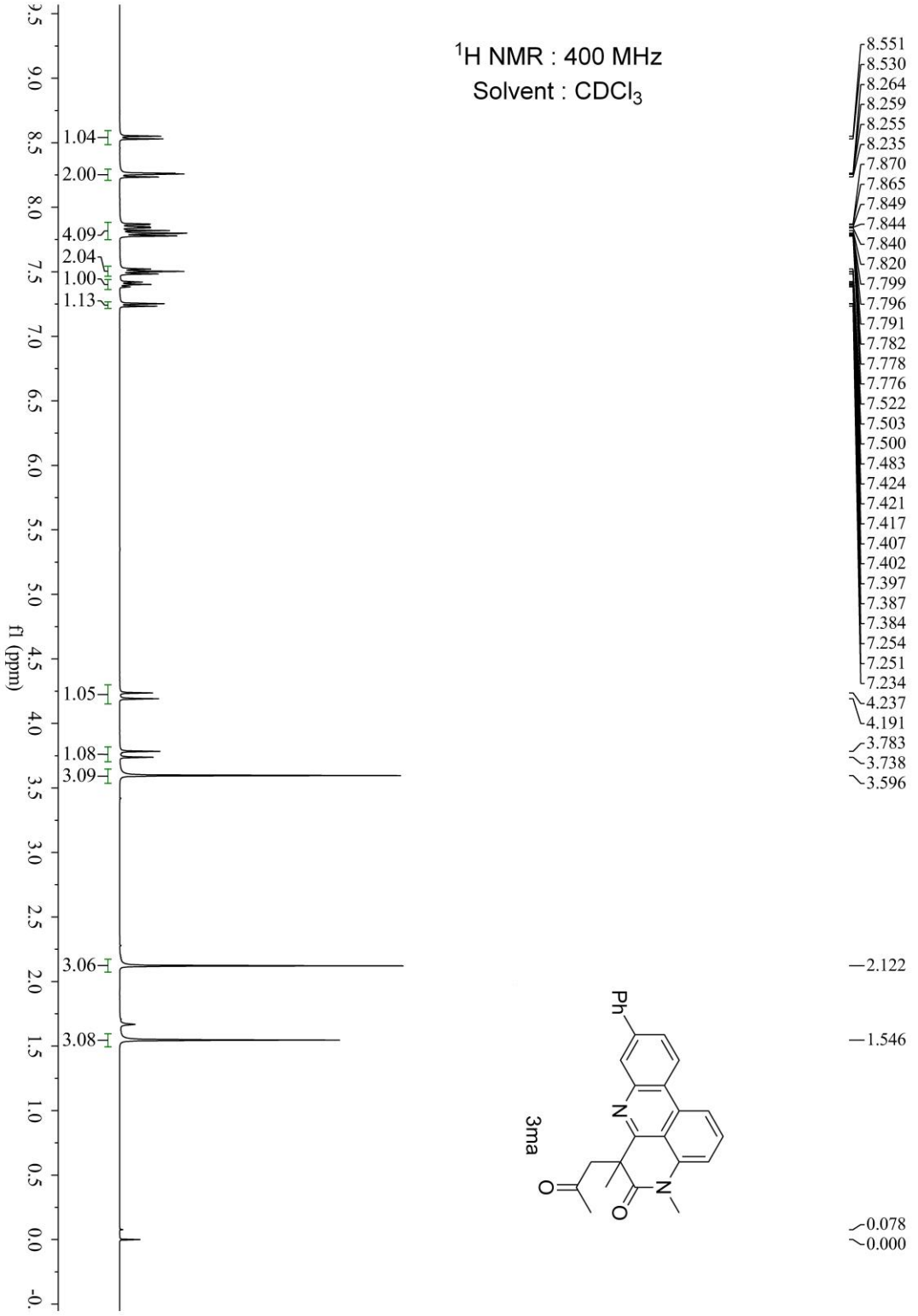

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
206.992
173.892
161.333
144.266
139.242
136.128
132.671
132.160
130.237
126.171
125.095
123.168
116.346
112.557
111.951
77.317
77.000
76.682
53.153
48.282
35.541
29.870
29.472
29.413
19.280
19.216
f1 (ppm)
3ka

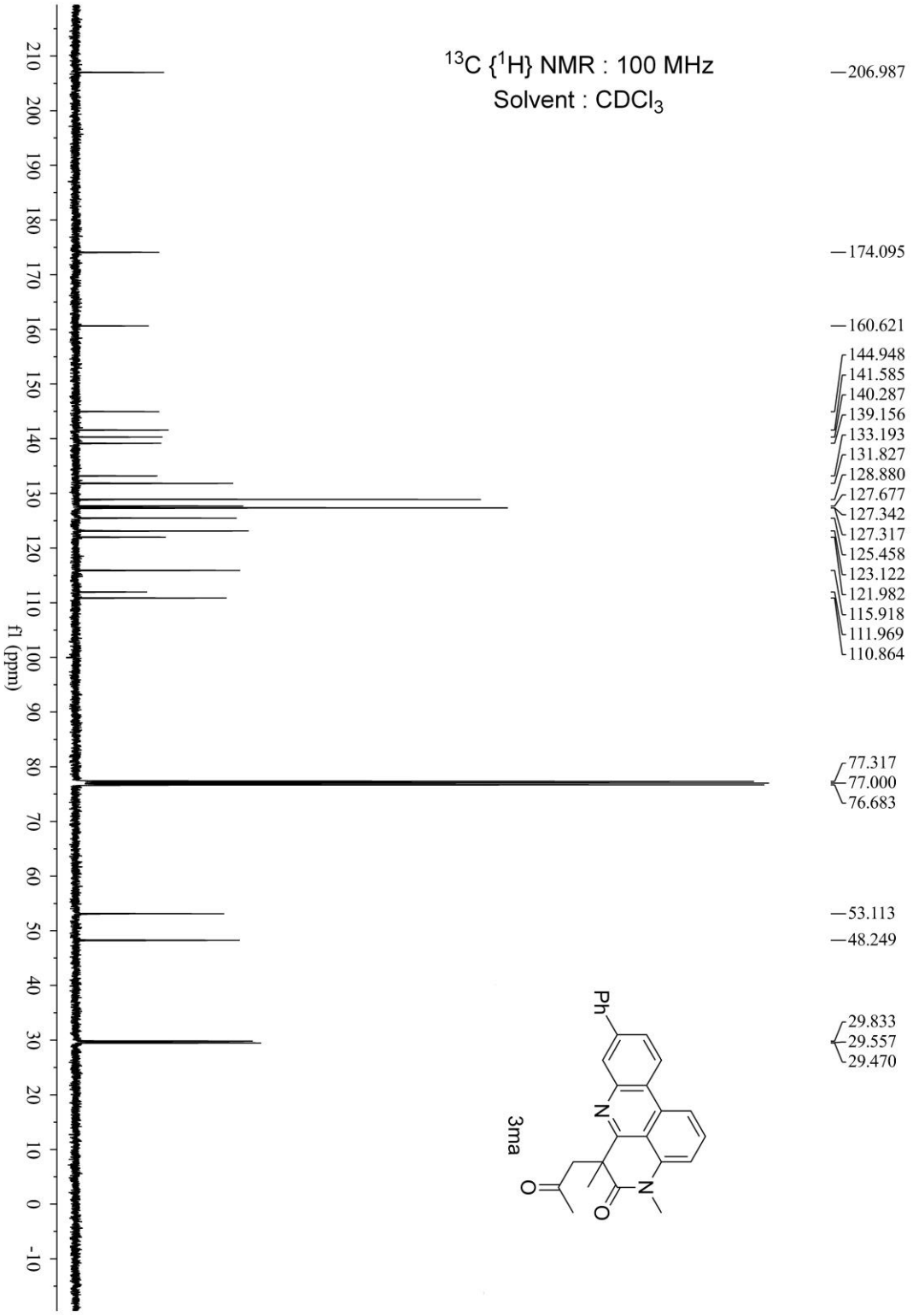
9-(*tert*-Butyl)-4,6-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phen anthridin-5(6*H*)-one (3la)



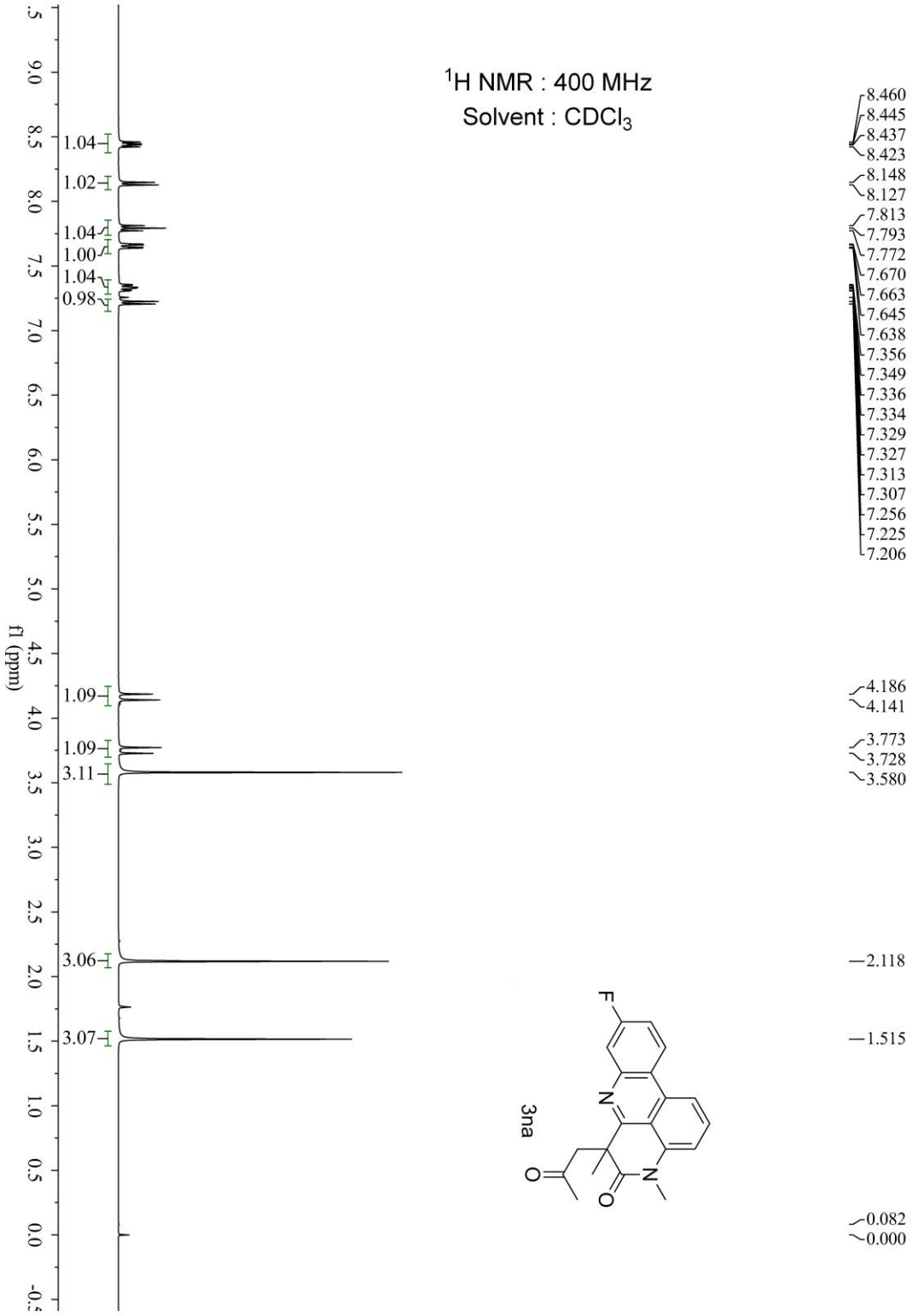

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
f1 (ppm)
206.938
174.160
159.897
152.140
144.586
138.982
133.217
131.559
125.158
124.641
122.223
120.496
115.746
111.794
110.413
77.317
77.000
76.682
53.075
48.141
34.913
31.257
29.752
29.575
29.481
3la
tBu
N
O
N
O

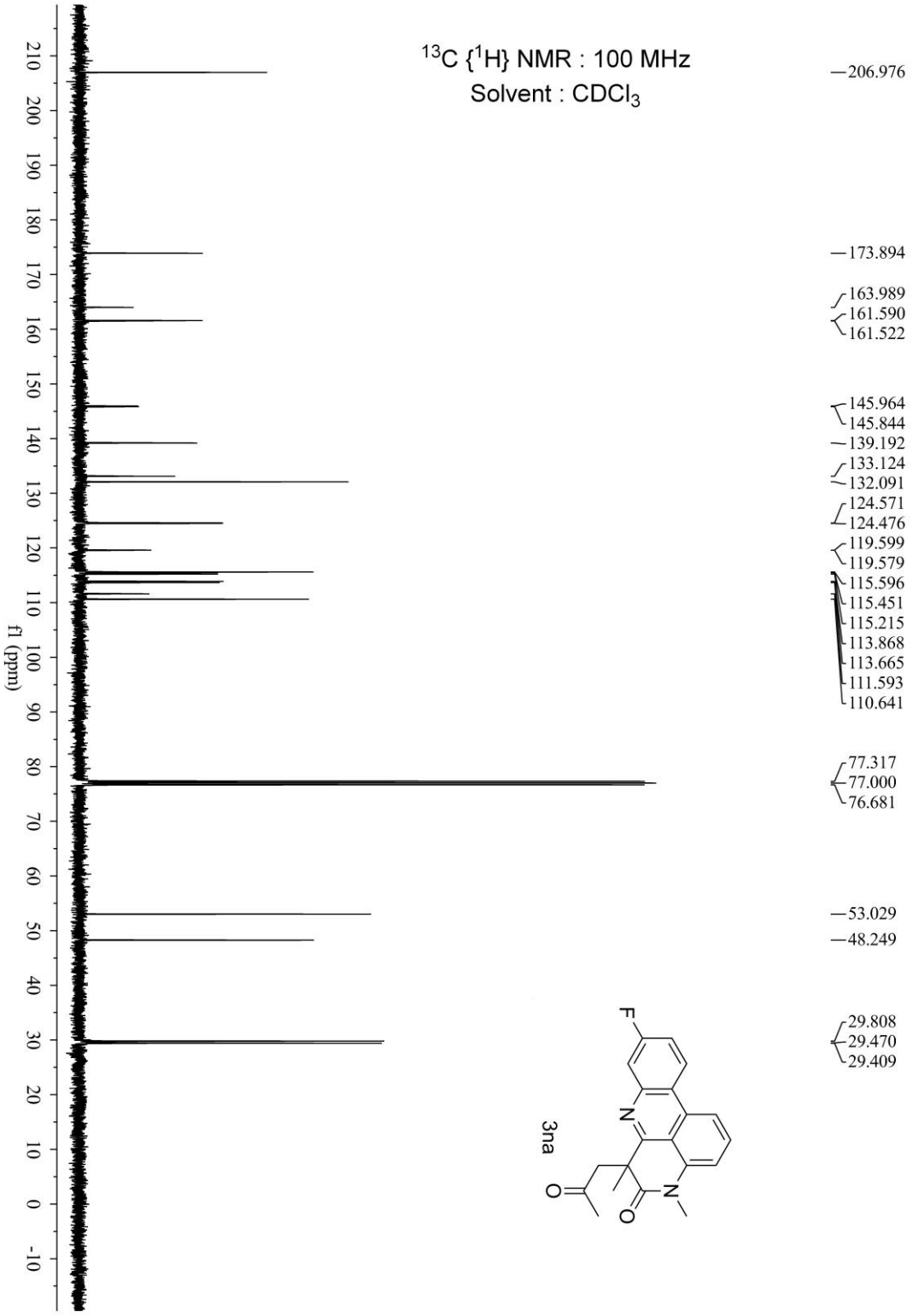
4,6-Dimethyl-6-(2-oxopropyl)-9-phenyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ma)

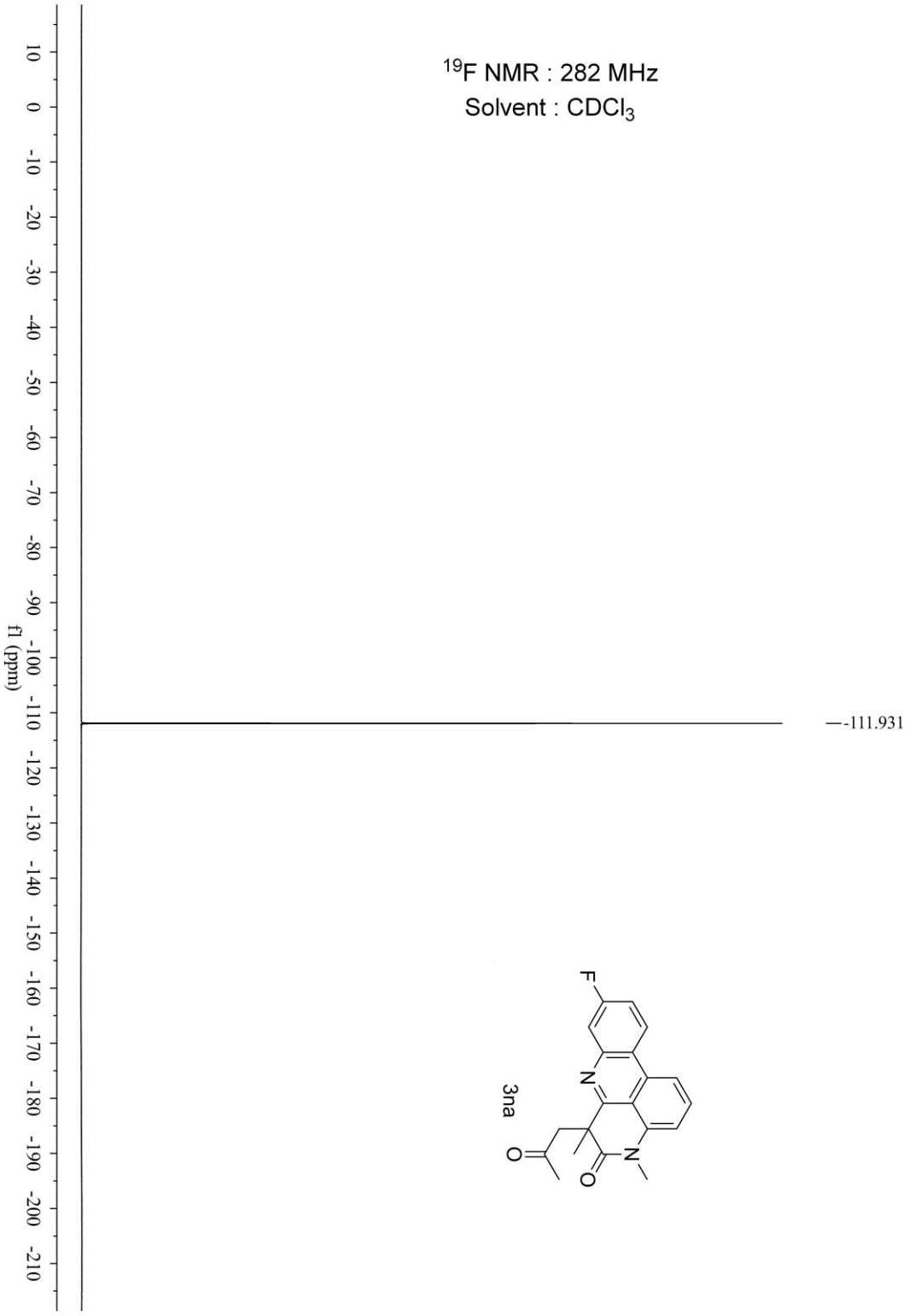



^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
206.987
174.095
160.621
144.948
141.585
140.287
139.156
133.193
131.827
128.880
127.677
127.342
127.317
125.458
123.122
121.982
115.918
111.969
110.864
77.317
77.000
76.683
53.113
48.249
29.833
29.557
29.470
Ph
N
O
N
O
3ma

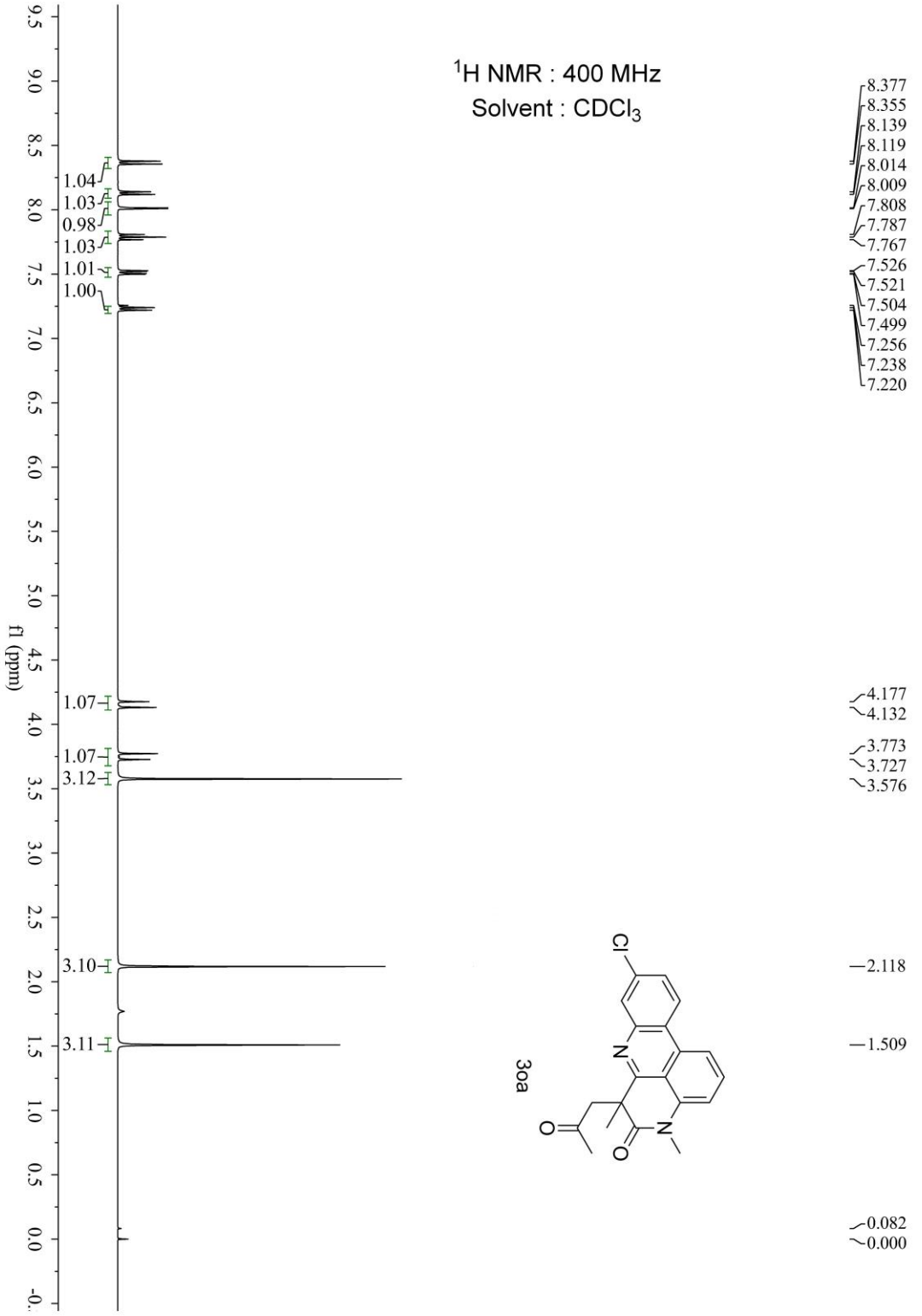
9-Fluoro-4,6-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanth ridin-5(6*H*)-one (3na)

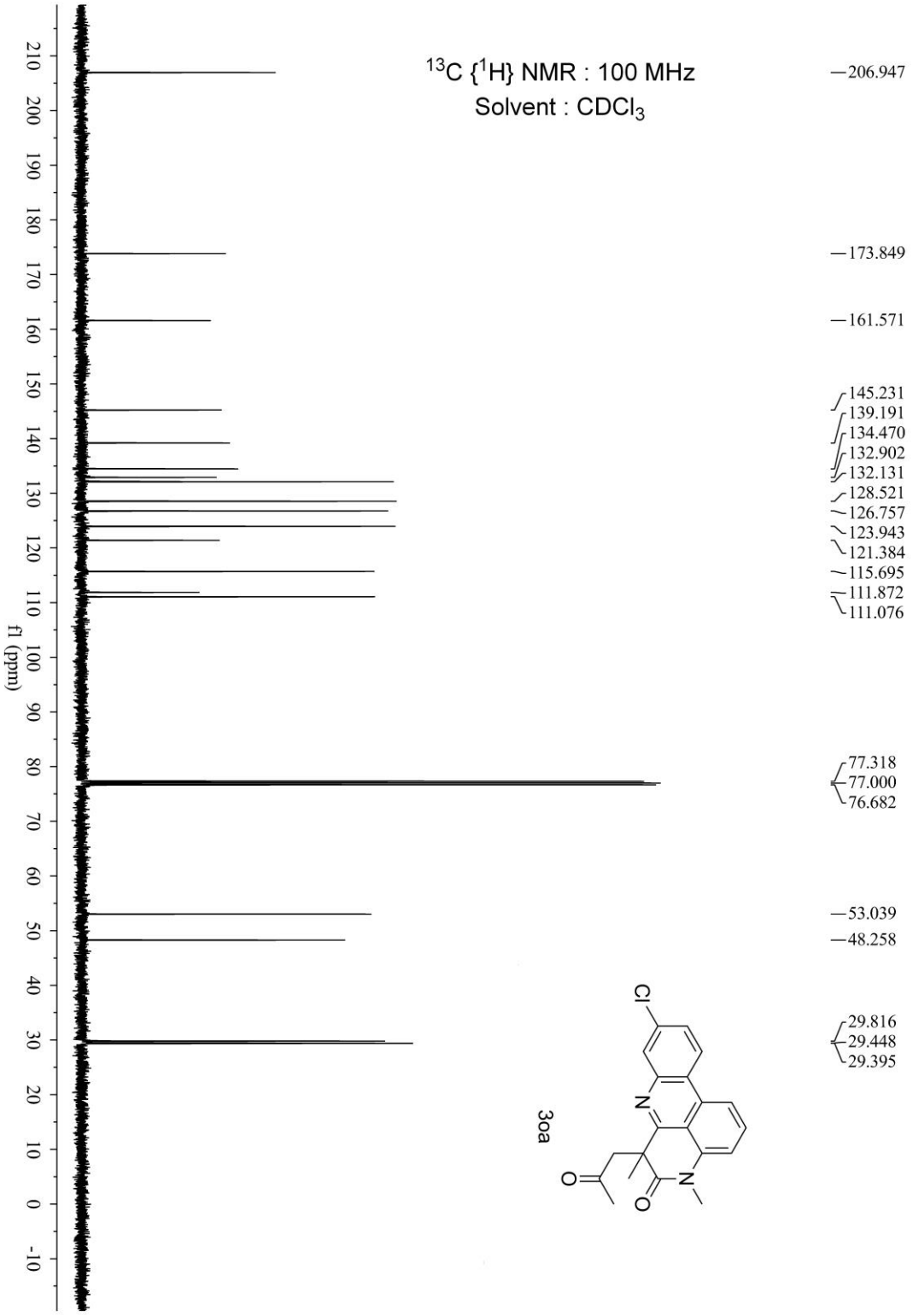



^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
206.976
173.894
163.989
161.590
161.522
145.964
145.844
139.192
133.124
132.091
124.571
124.476
119.599
119.579
115.596
115.451
115.215
113.868
113.665
111.593
110.641
77.317
77.000
76.681
53.029
48.249
29.808
29.470
29.409
f1 (ppm)
3na

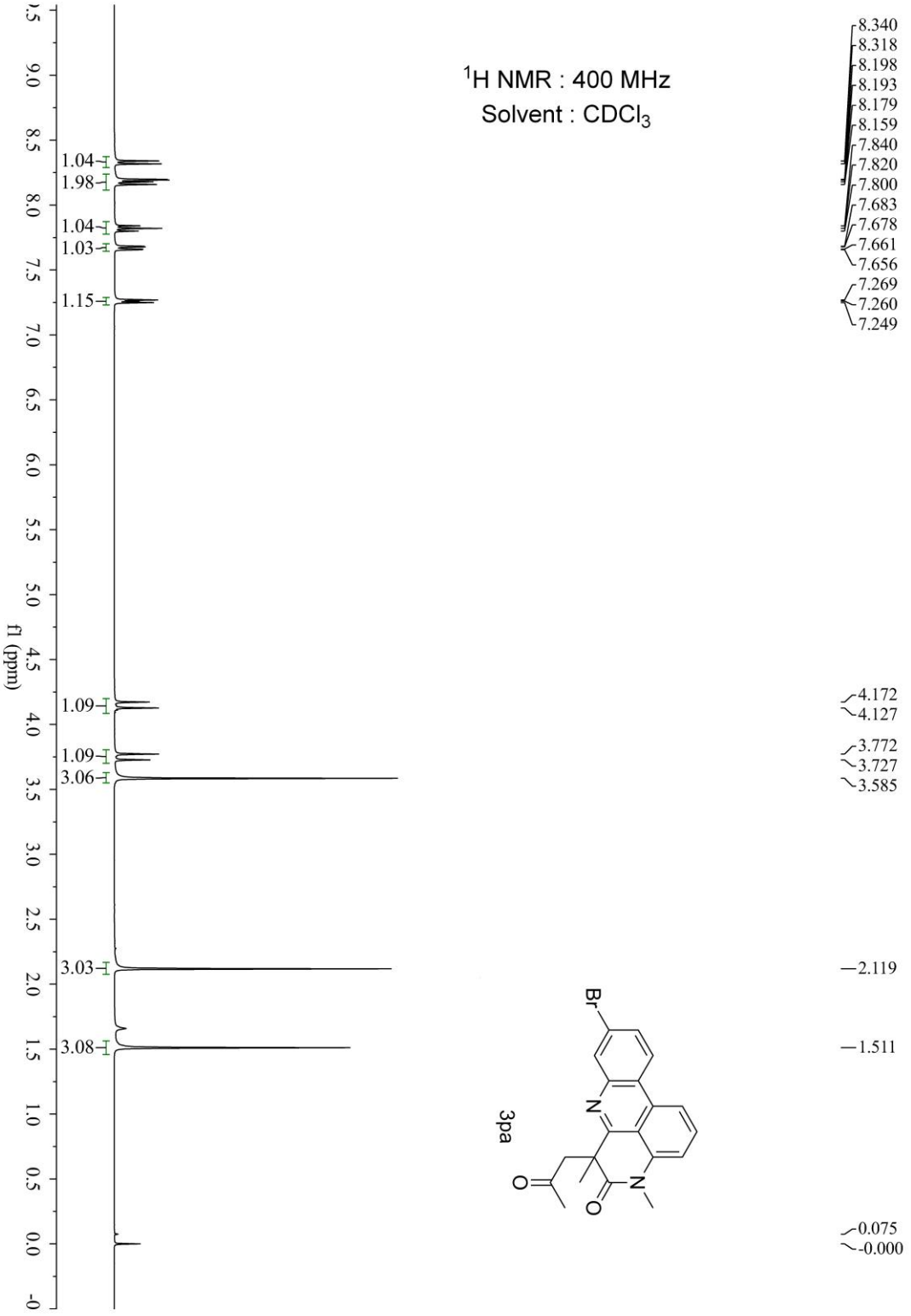

^{19}F NMR : 282 MHz
Solvent : $CDCl_3$
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
—-111.931
3na
F
N
O
N
O

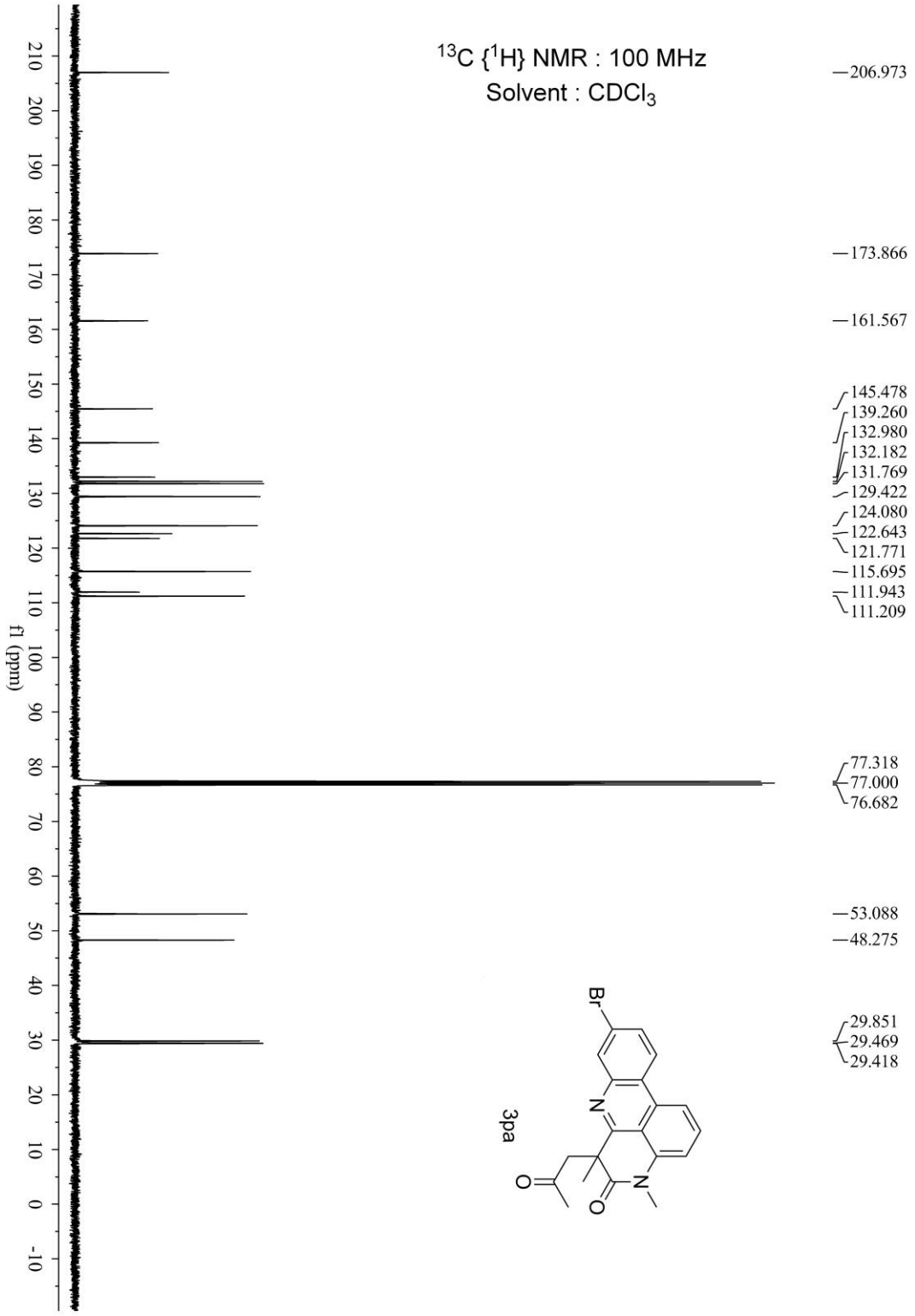
9-Chloro-4,6-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3oa)



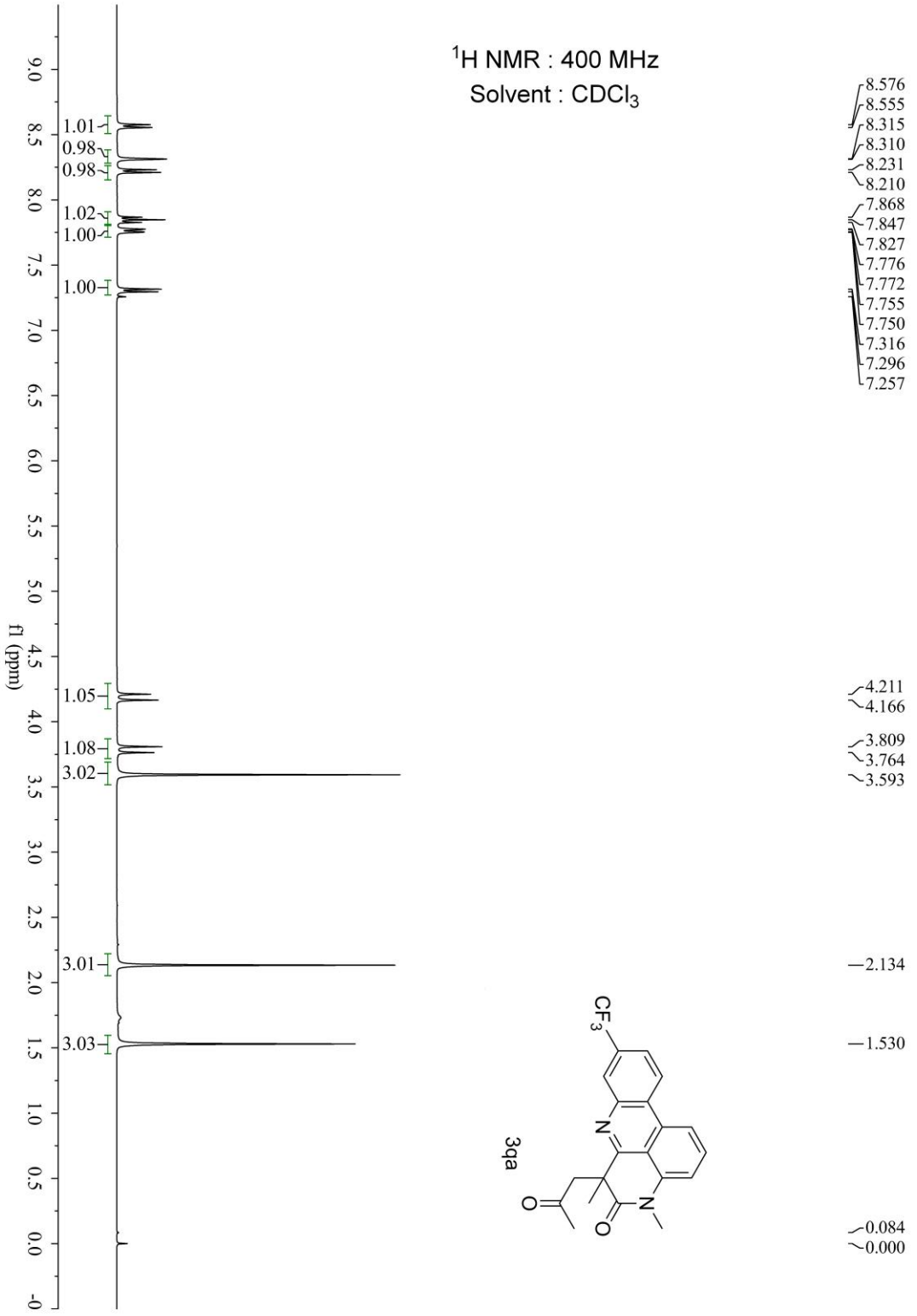

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
206.947
173.849
161.571
145.231
139.191
134.470
132.902
132.131
128.521
126.757
123.943
121.384
115.695
111.872
111.076
77.318
77.000
76.682
53.039
48.258
29.816
29.448
29.395
f1 (ppm)
3oa
Cl
N
O
N
O

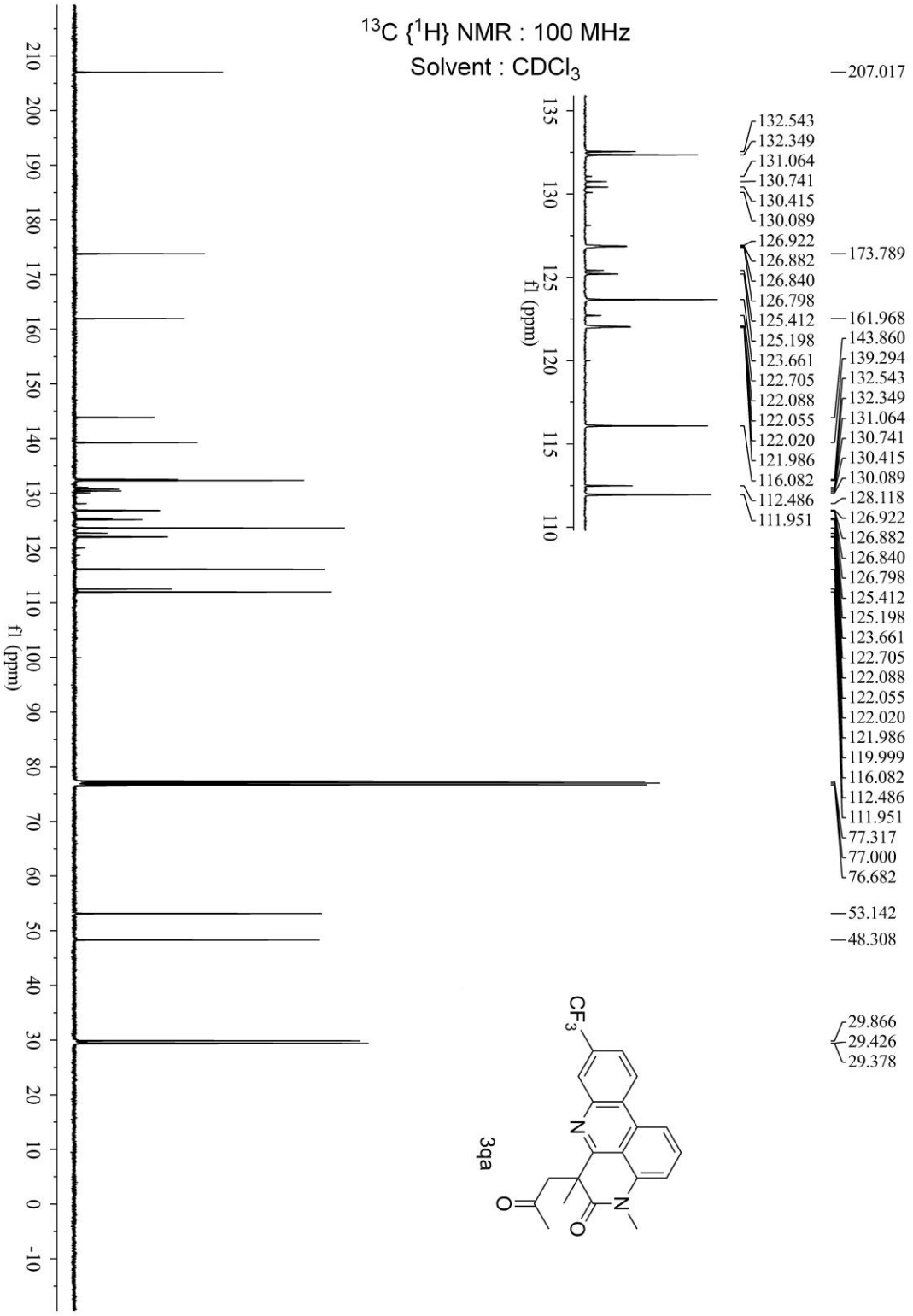
9-Bromo-4,6-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3pa)

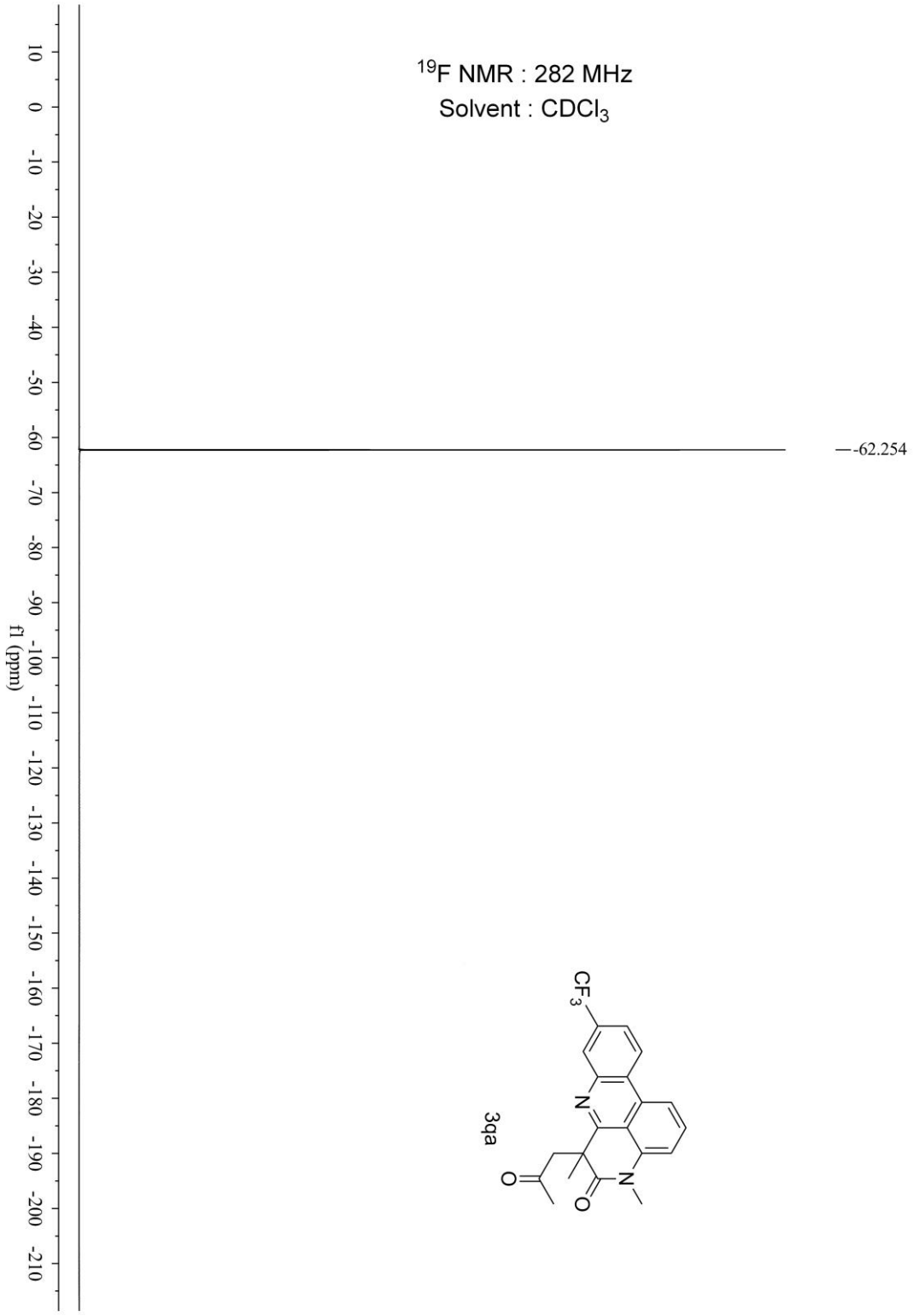



^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
206.973
173.866
161.567
145.478
139.260
132.980
132.182
131.769
129.422
124.080
122.643
121.771
115.695
111.943
111.209
77.318
77.000
76.682
53.088
48.275
29.851
29.469
29.418
f1 (ppm)
3pa
Br
N
O
N
O

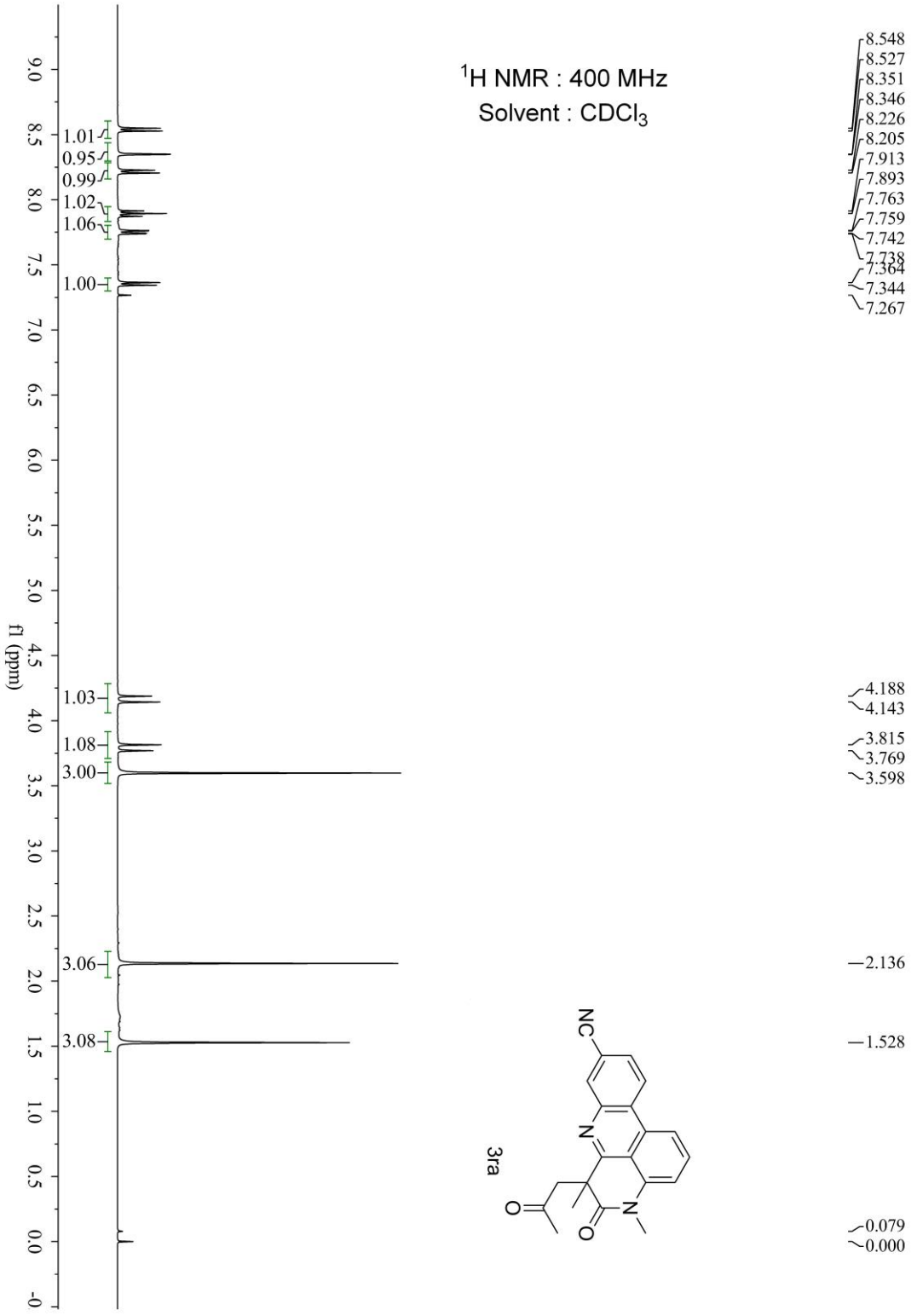
4,6-Dimethyl-6-(2-oxopropyl)-9-(trifluoromethyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3qa)

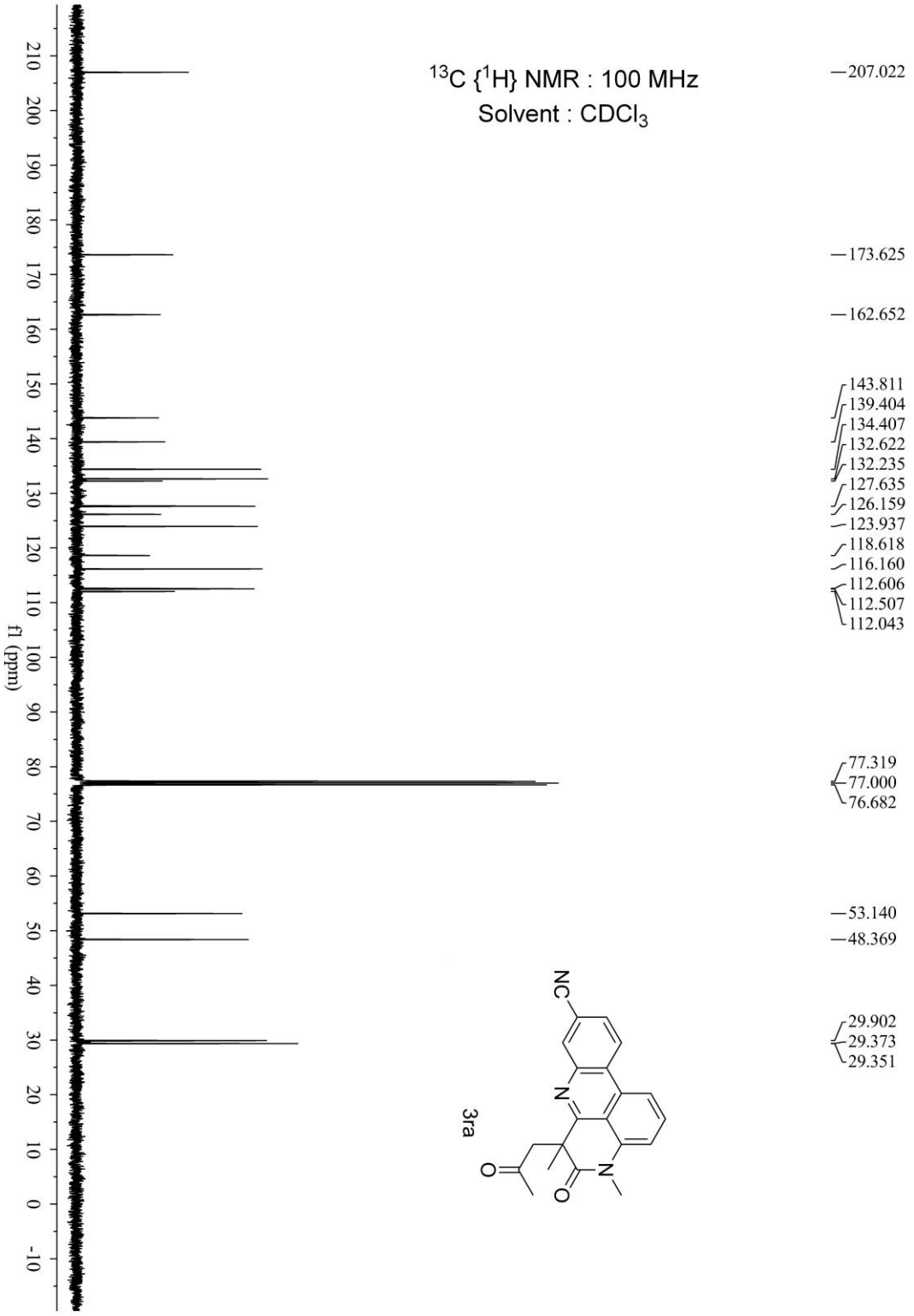



^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
f1 (ppm)
207.017
173.789
161.968
143.860
139.294
132.543
132.349
131.064
130.741
130.415
130.089
128.118
126.922
126.882
126.840
126.798
125.412
125.198
123.661
122.705
122.088
122.055
122.020
121.986
119.999
116.082
112.486
111.951
77.317
77.000
76.682
53.142
48.308
29.866
29.426
29.378
CF_3
N
O
3qa

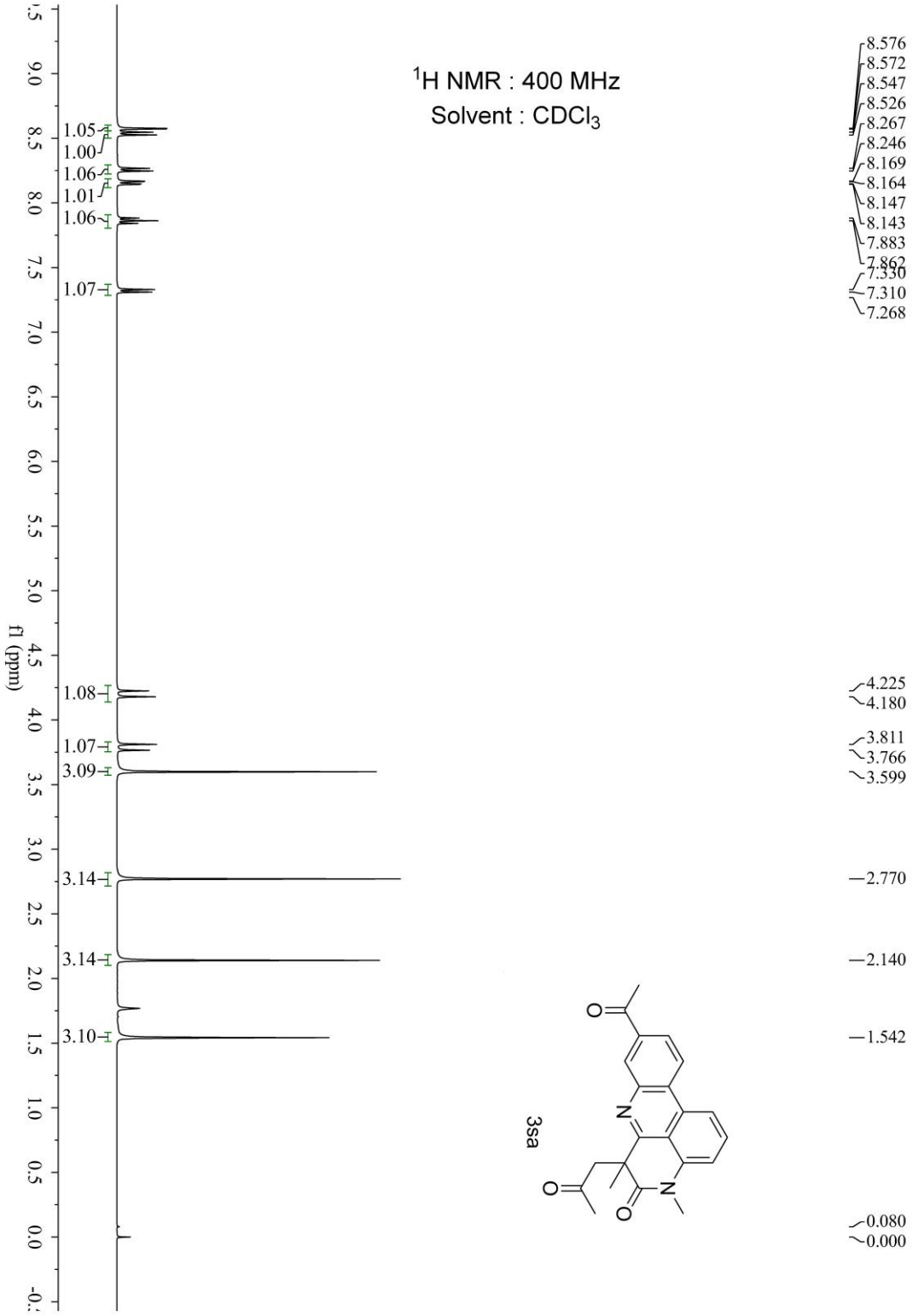

^{19}F NMR : 282 MHz
Solvent : $CDCl_3$
-62.254
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
3qa
CF_3
N
O
N
O

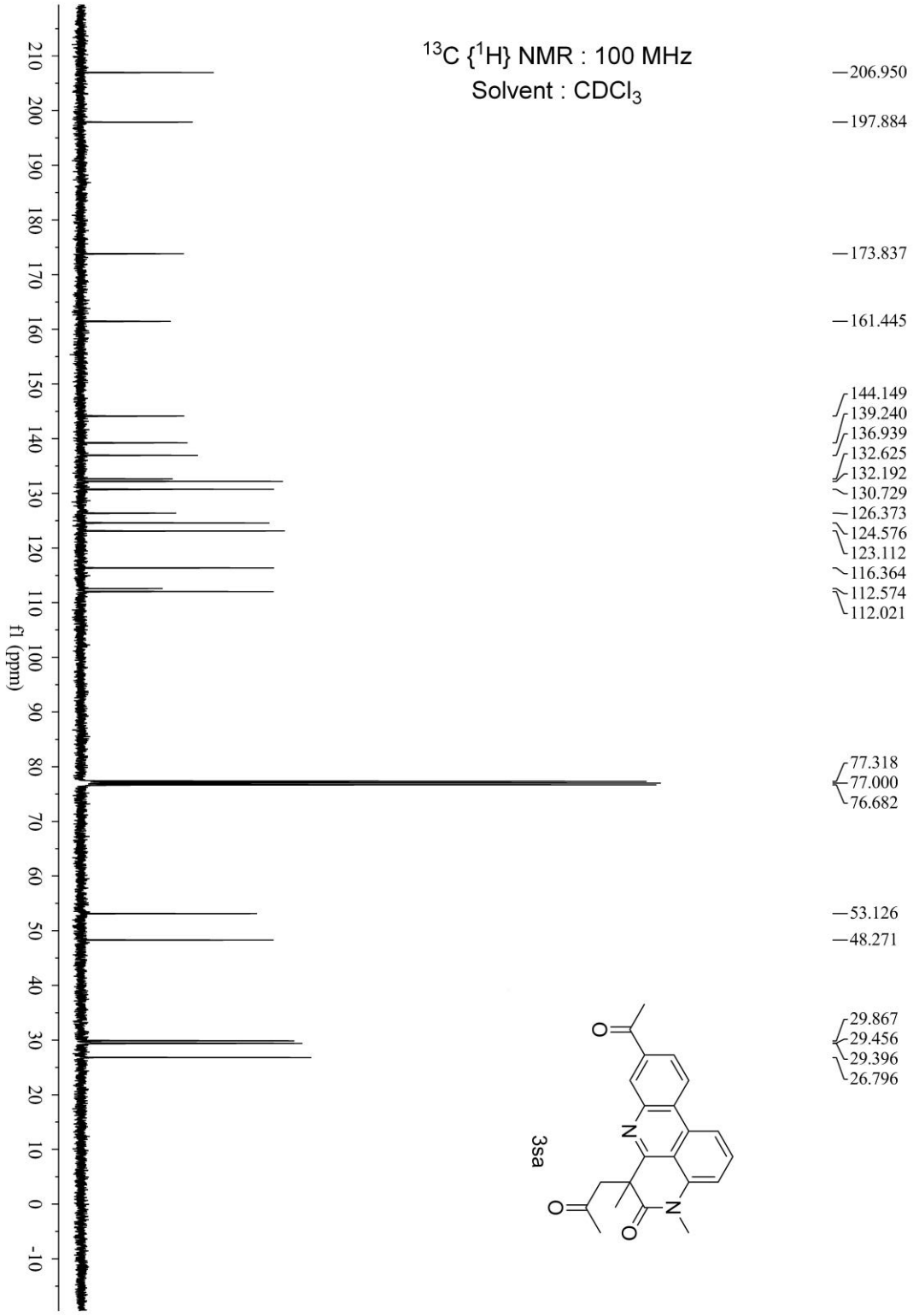
4,6-Dimethyl-5-oxo-6-(2-oxopropyl)-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*] phenanthridine-9-carbonitrile (3ra)




^{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
207.022
173.625
162.652
143.811
139.404
134.407
132.622
132.235
127.635
126.159
123.937
118.618
116.160
112.606
112.507
112.043
77.319
77.000
76.682
53.140
48.369
29.902
29.373
29.351
NC
N
O
N
O
3ra

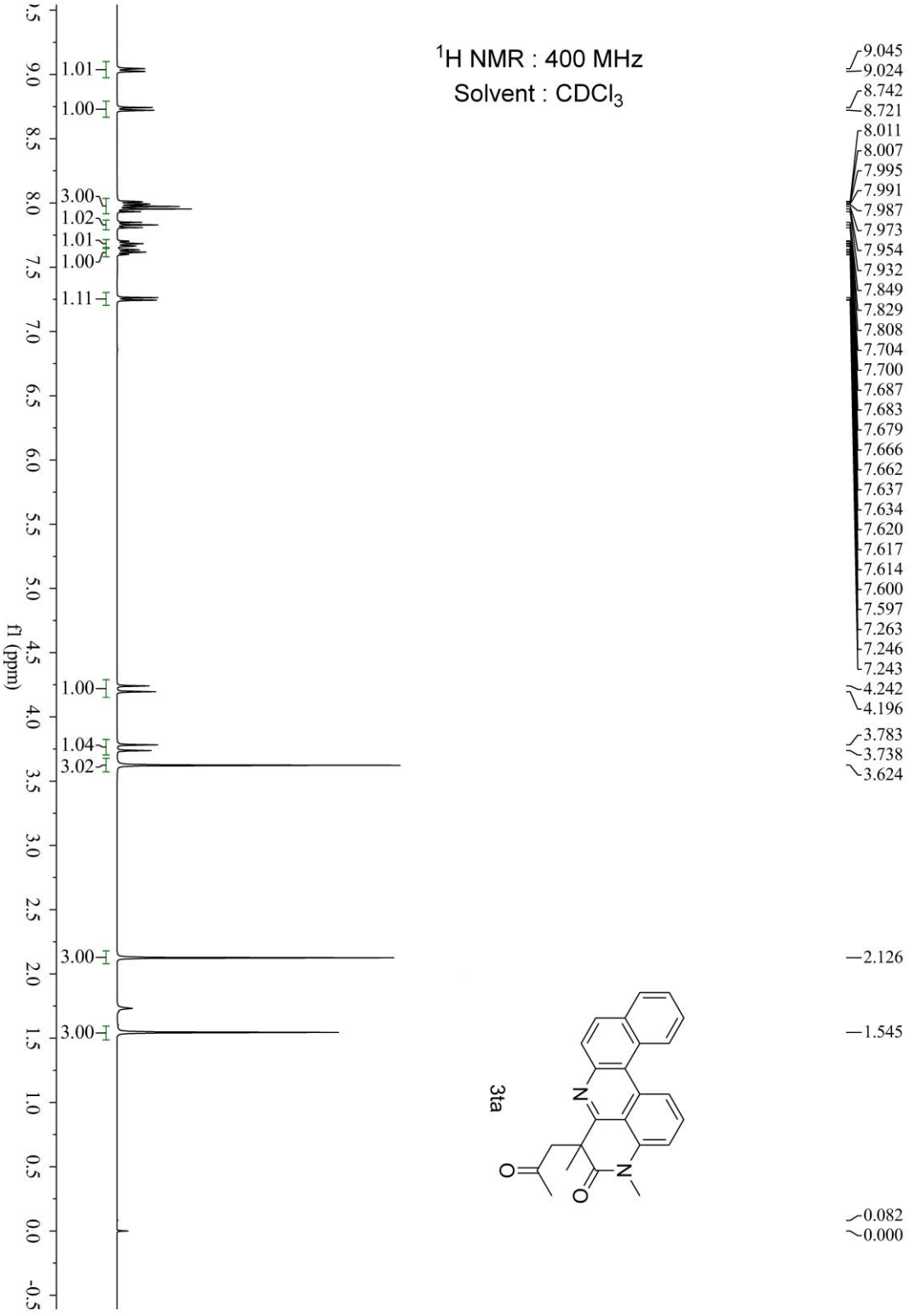
9-Acetyl-4,6-dimethyl-6-(2-oxopropyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3sa)

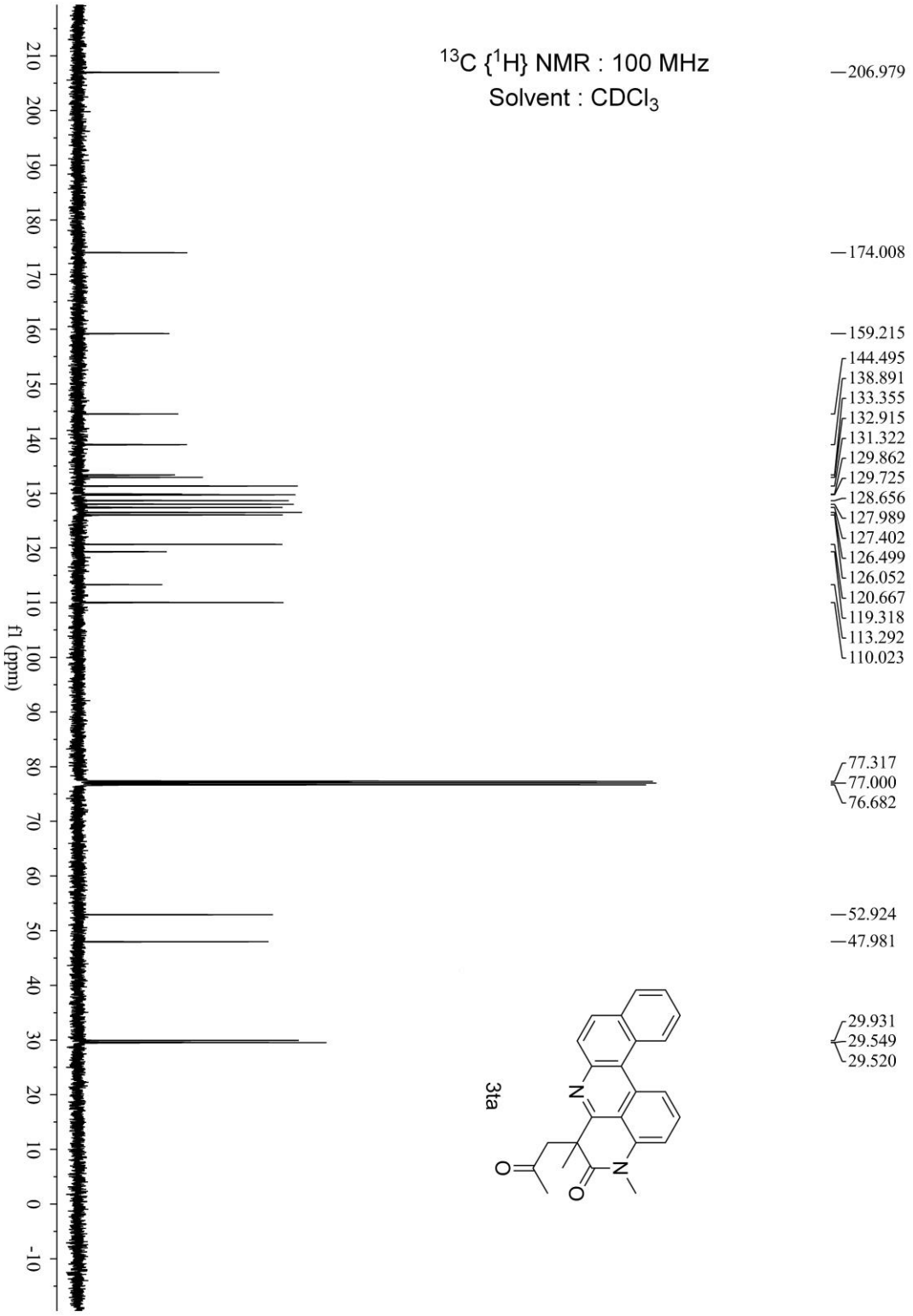



^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
206.950
197.884
173.837
161.445
144.149
139.240
136.939
132.625
132.192
130.729
126.373
124.576
123.112
116.364
112.574
112.021
77.318
77.000
76.682
53.126
48.271
29.867
29.456
29.396
26.796
3sa
O
N
O
O
N

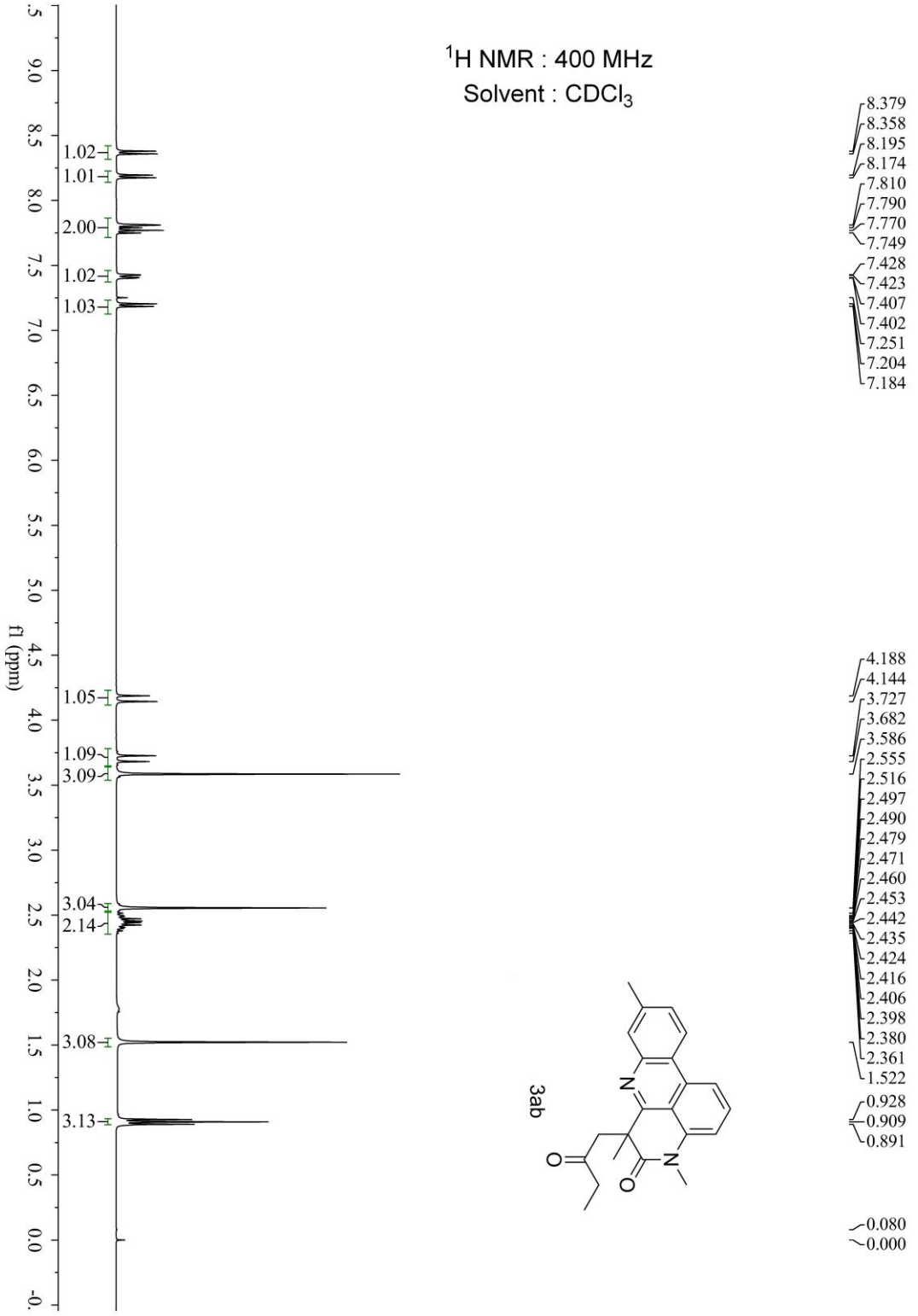
4,6-Dimethyl-6-(2-oxopropyl)-4*H*-benzo[*a*]pyrido[4,3,2-*gh*]phenanthr

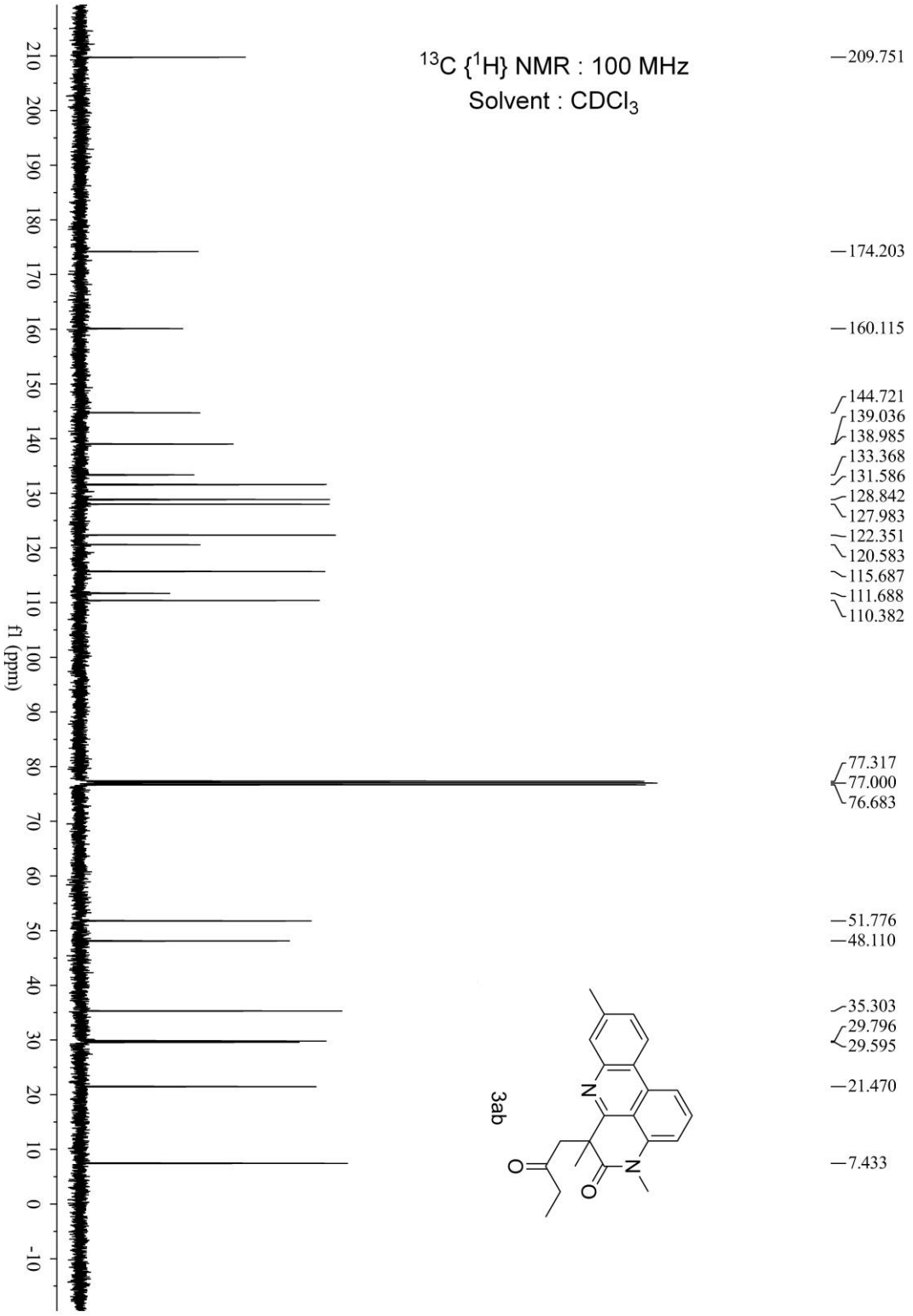
idin-5(6*H*)-one (3ta)



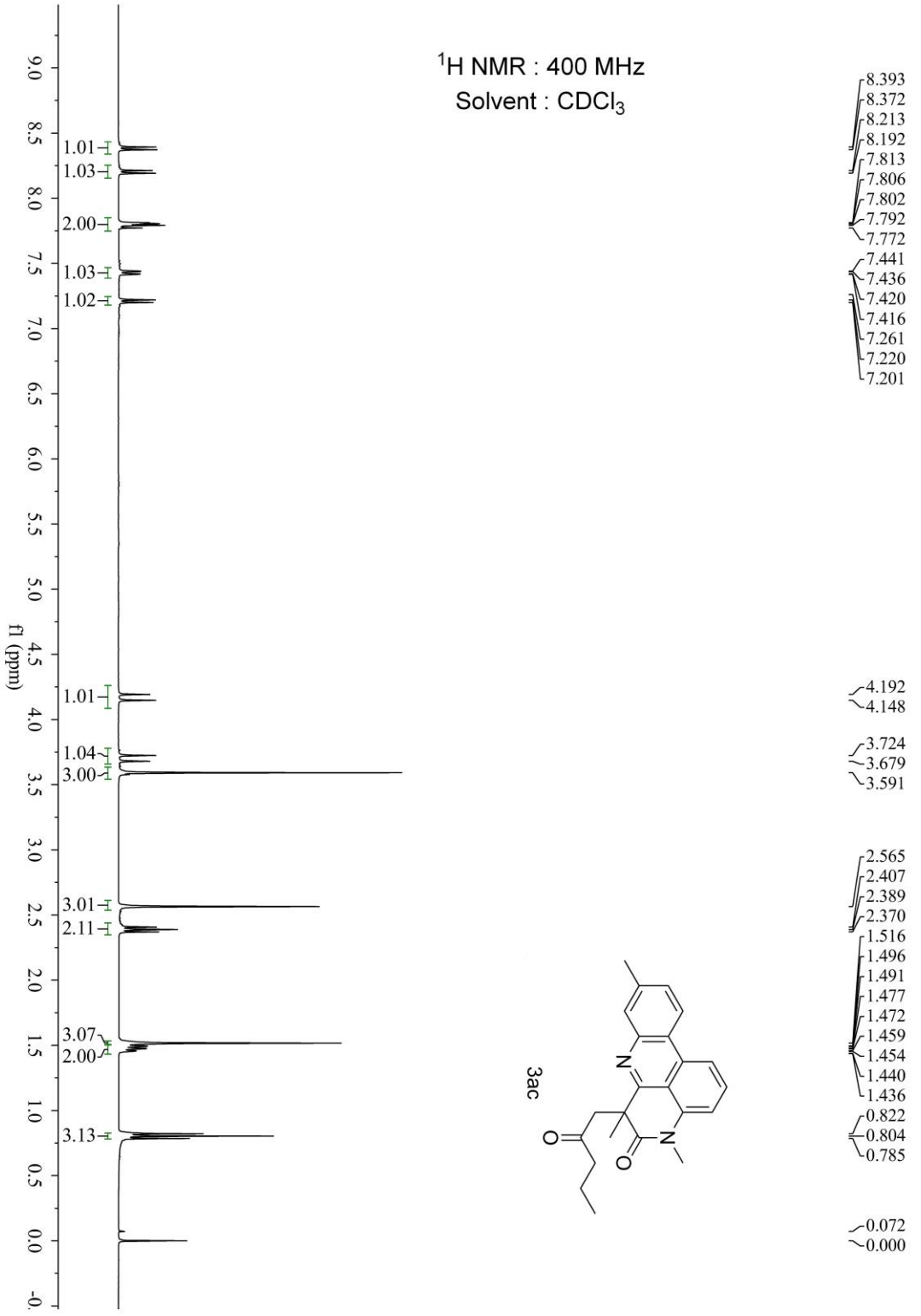

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
206.979
174.008
159.215
144.495
138.891
133.355
132.915
131.322
129.862
129.725
128.656
127.989
127.402
126.499
126.052
120.667
119.318
113.292
110.023
77.317
77.000
76.682
52.924
47.981
29.931
29.549
29.520
f1 (ppm)
3ta

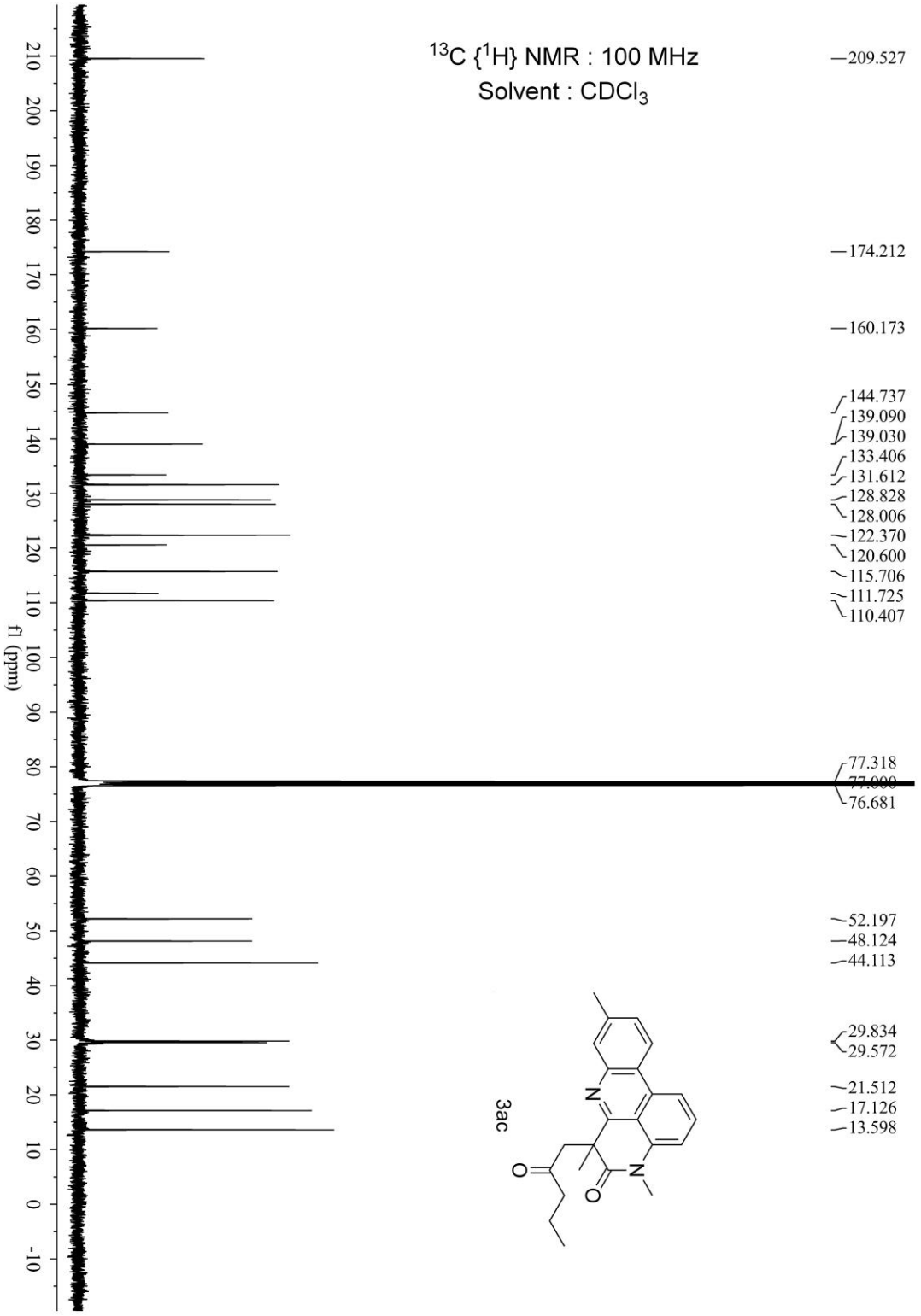
4,6,9-Trimethyl-6-(2-oxobutyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ab)



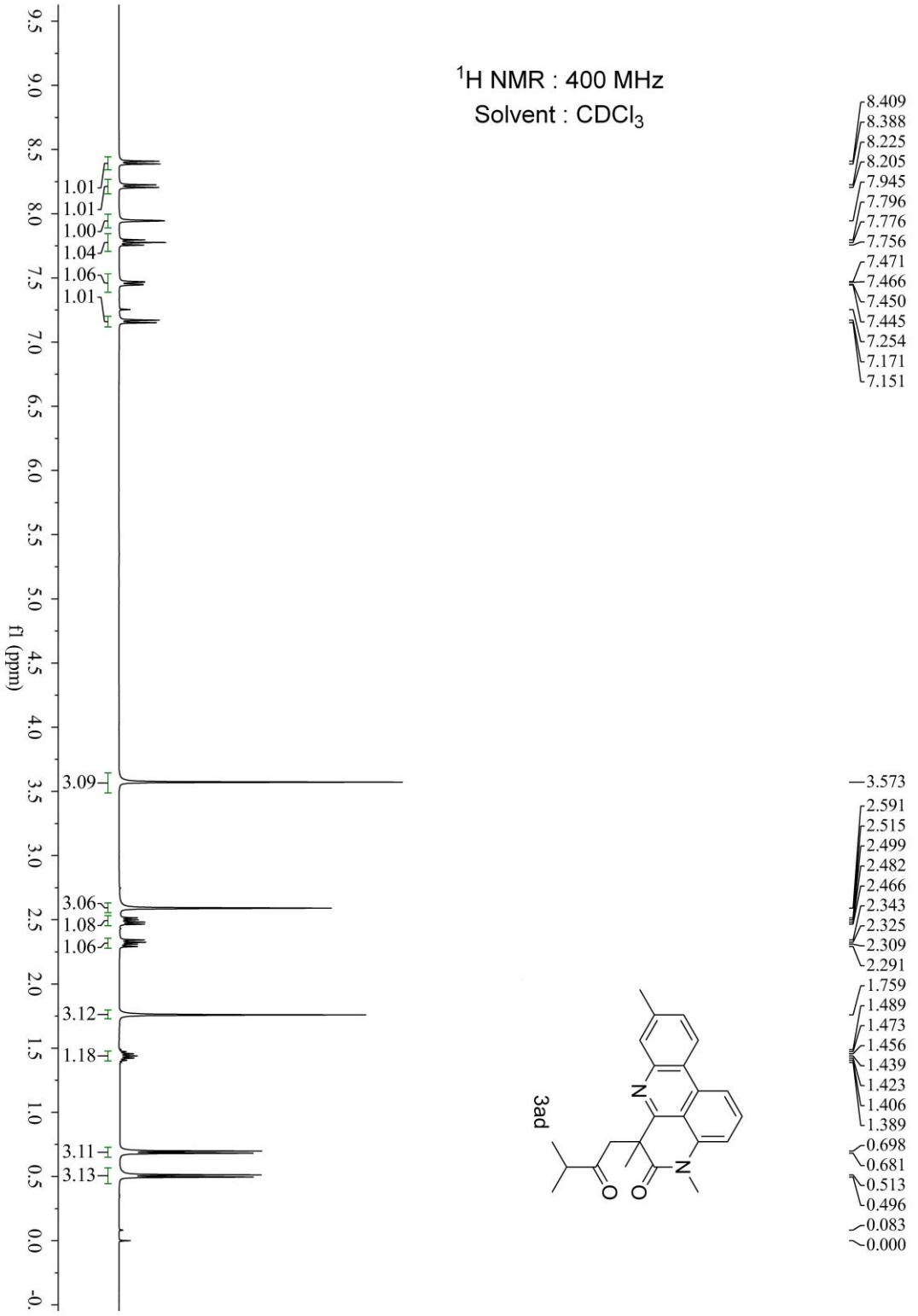

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
209.751
174.203
160.115
144.721
139.036
138.985
133.368
131.586
128.842
127.983
122.351
120.583
115.687
111.688
110.382
77.317
77.000
76.683
51.776
48.110
35.303
29.796
29.595
21.470
7.433
3ab
N
O
N
O

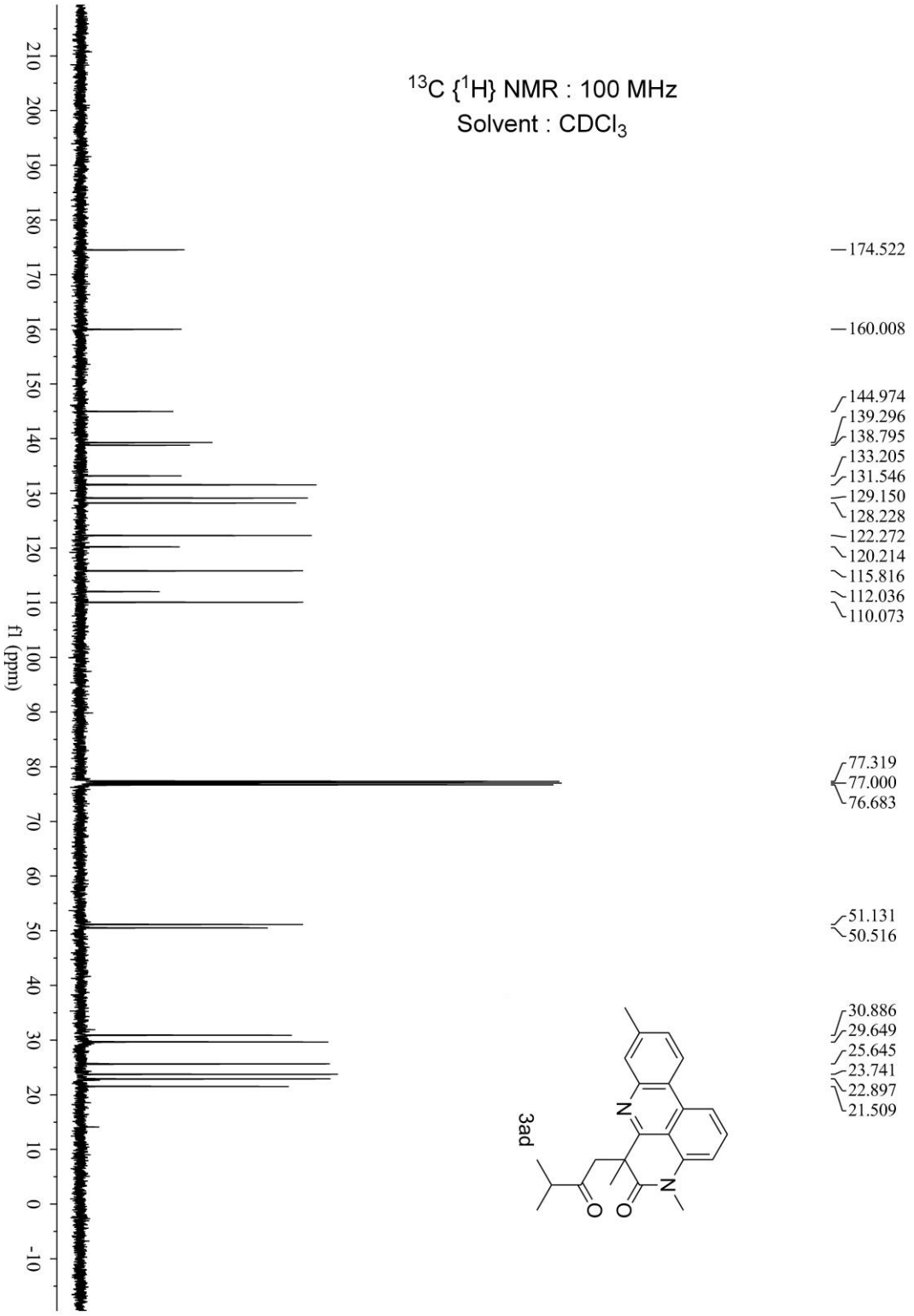
4,6,9-Trimethyl-6-(2-oxopentyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ac)



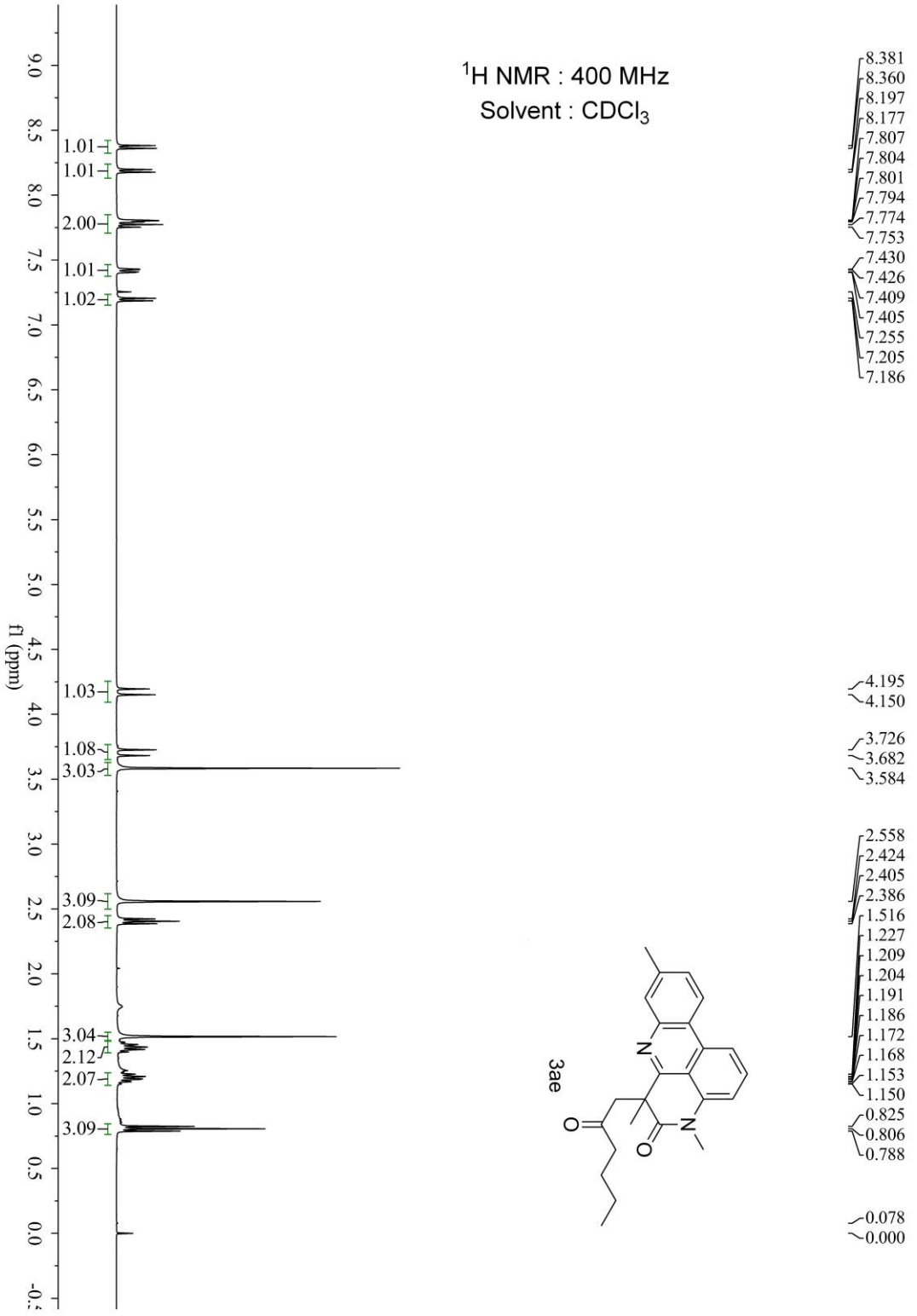

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
209.527
174.212
160.173
144.737
139.090
139.030
133.406
131.612
128.828
128.006
122.370
120.600
115.706
111.725
110.407
77.318
76.681
52.197
48.124
44.113
29.834
29.572
21.512
17.126
13.598
f1 (ppm)
3ac

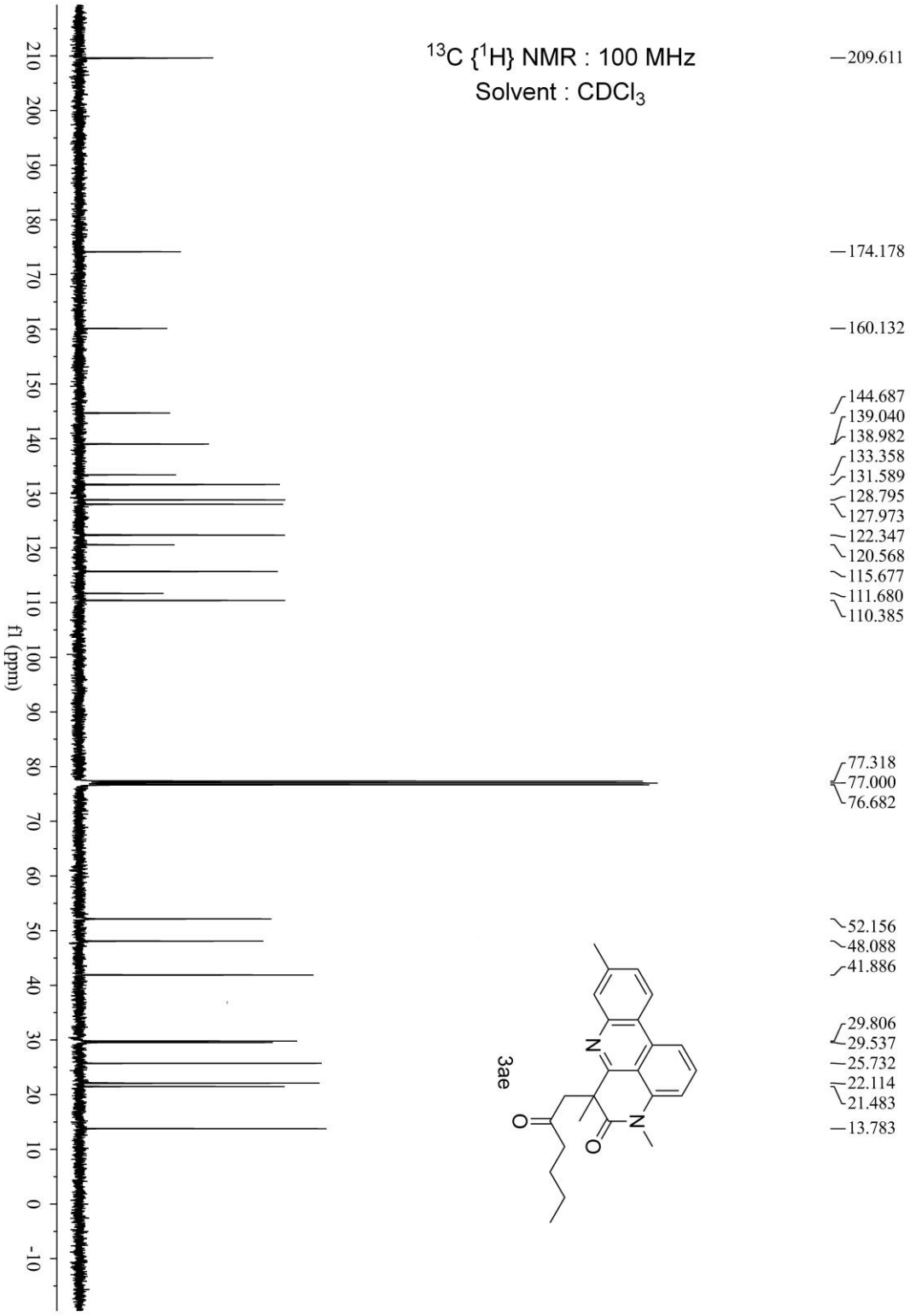
4,6,9-Trimethyl-6-(3-methyl-2-oxobutyl)-4*H*-pyrido[4,3,2-*gh*]phenant hridin-5(6*H*)-one (3ad)



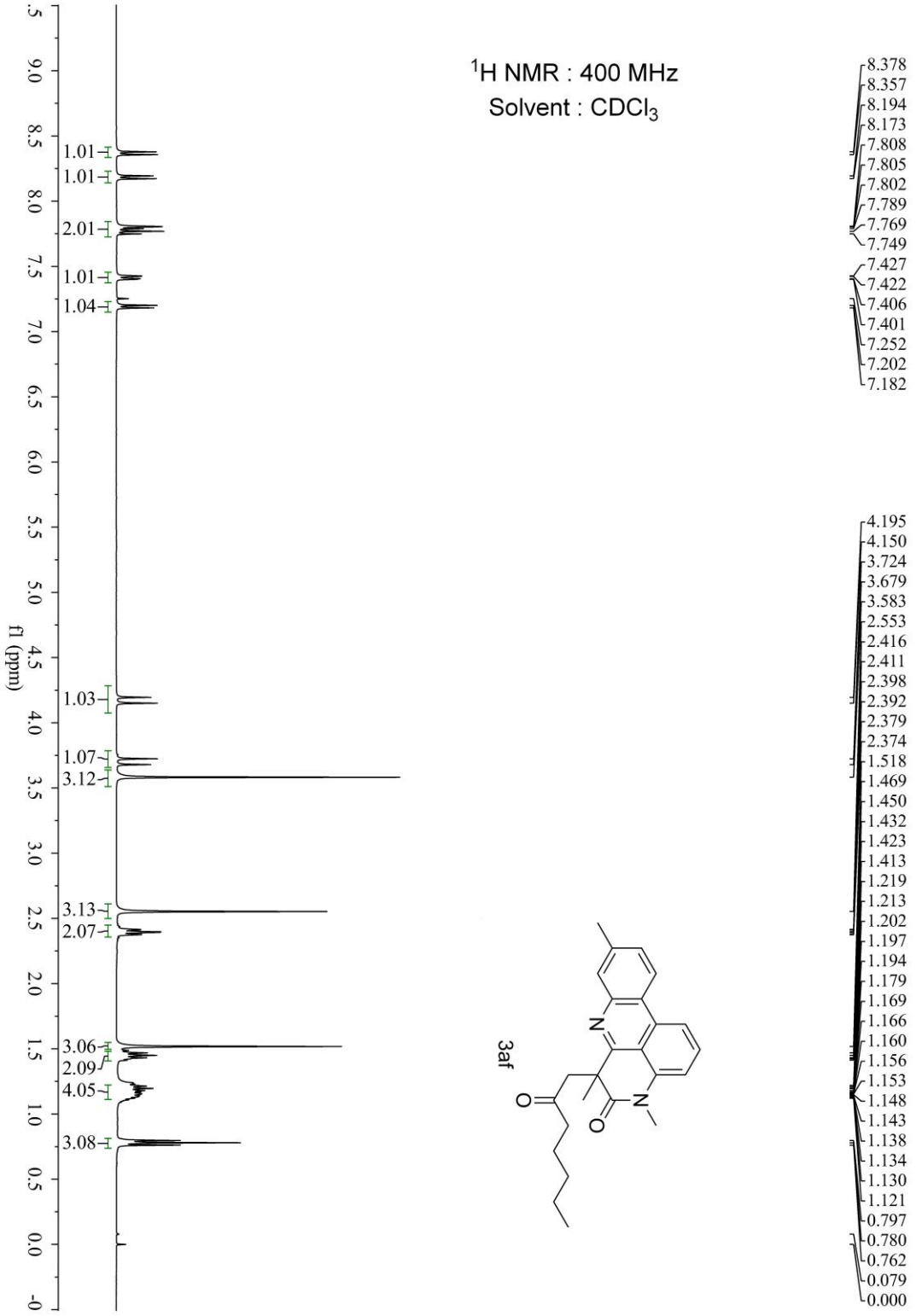

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
174.522
160.008
144.974
139.296
138.795
133.205
131.546
129.150
128.228
122.272
120.214
115.816
112.036
110.073
77.319
77.000
76.683
51.131
50.516
30.886
29.649
25.645
23.741
22.897
21.509
3ad
N
N
O
O

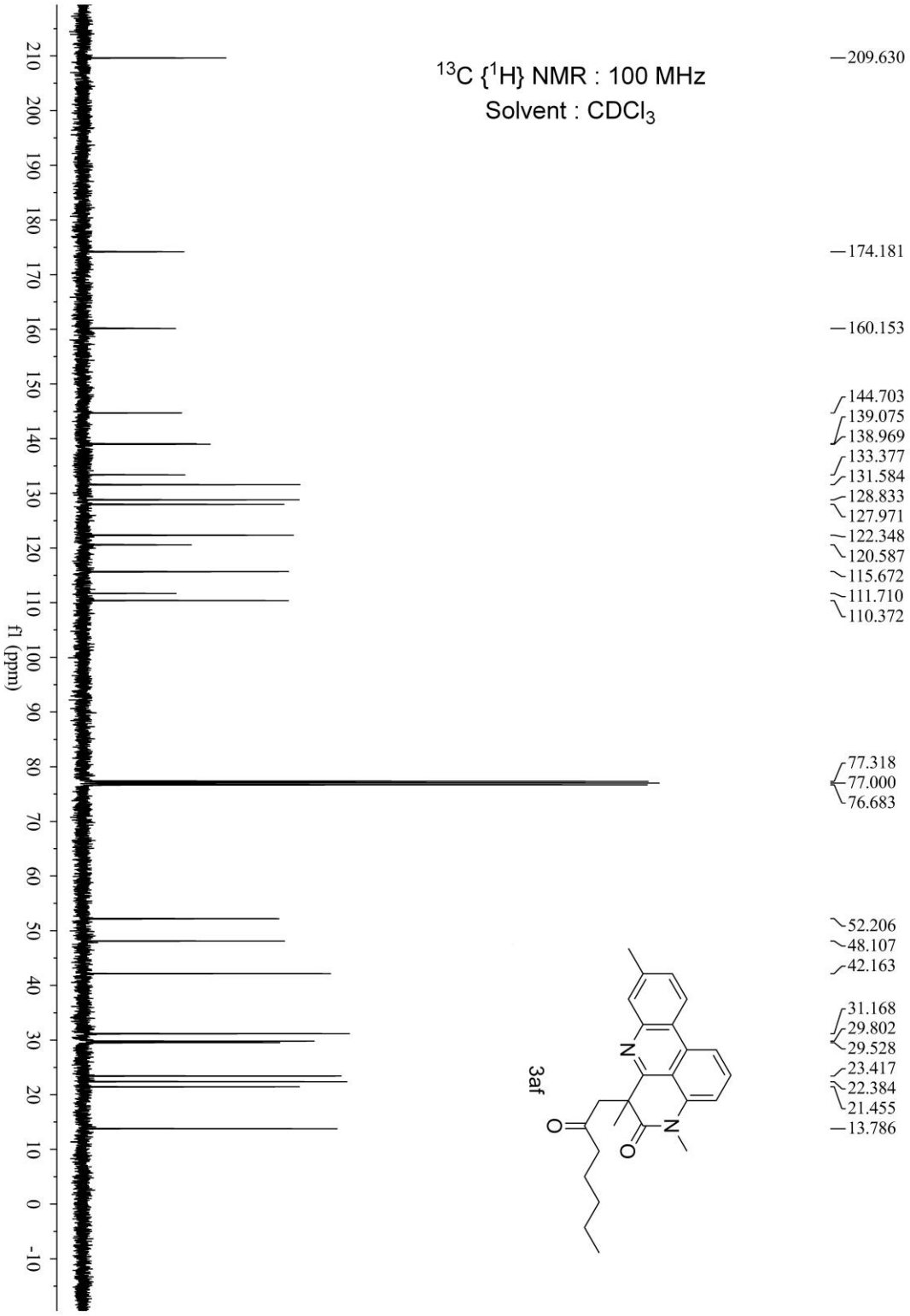
4,6,9-Trimethyl-6-(2-oxohexyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ae)



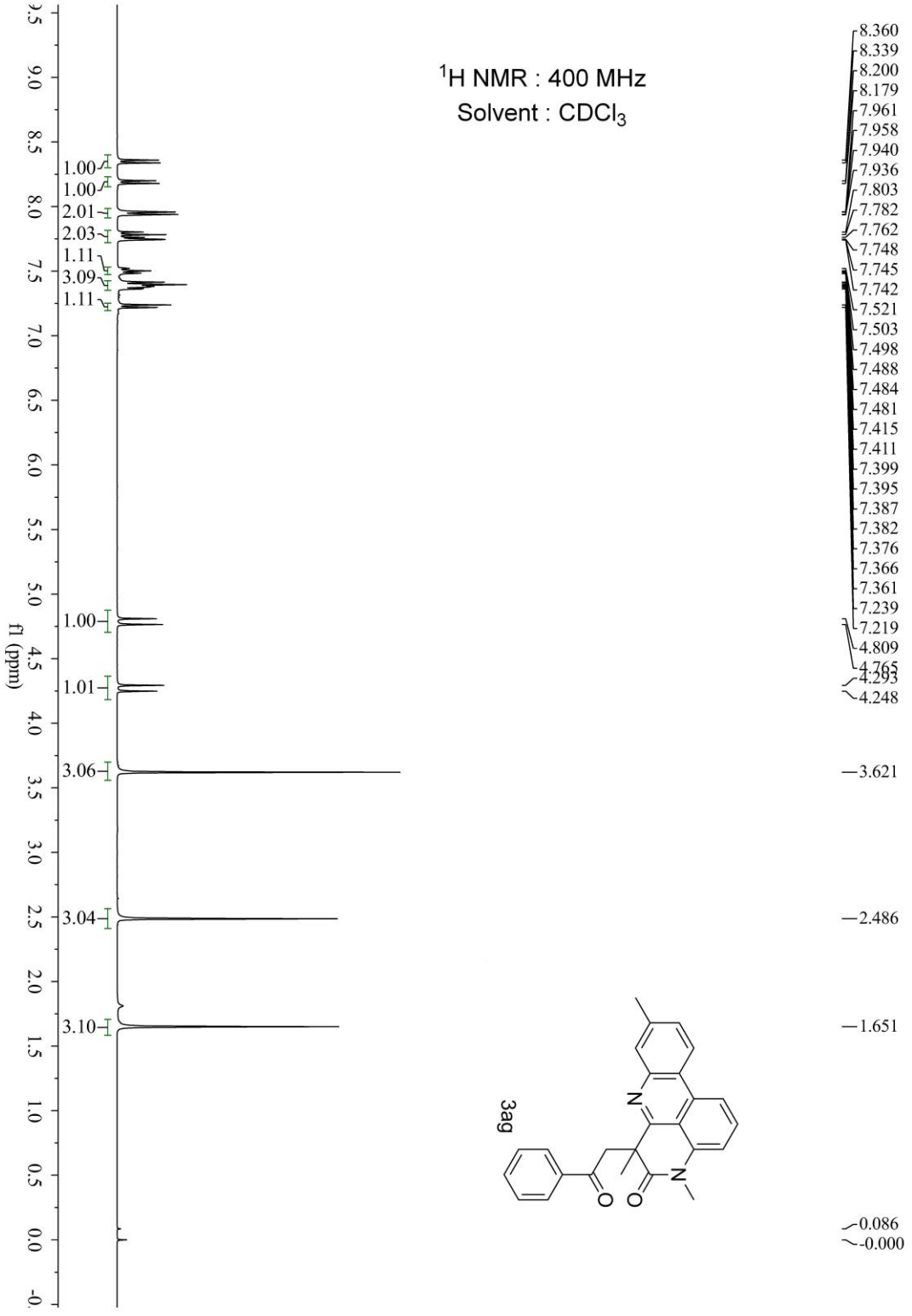

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
209.611
174.178
160.132
144.687
139.040
138.982
133.358
131.589
128.795
127.973
122.347
120.568
115.677
111.680
110.385
77.318
77.000
76.682
52.156
48.088
41.886
29.806
29.537
25.732
22.114
21.483
13.783
f1 (ppm)
3ae

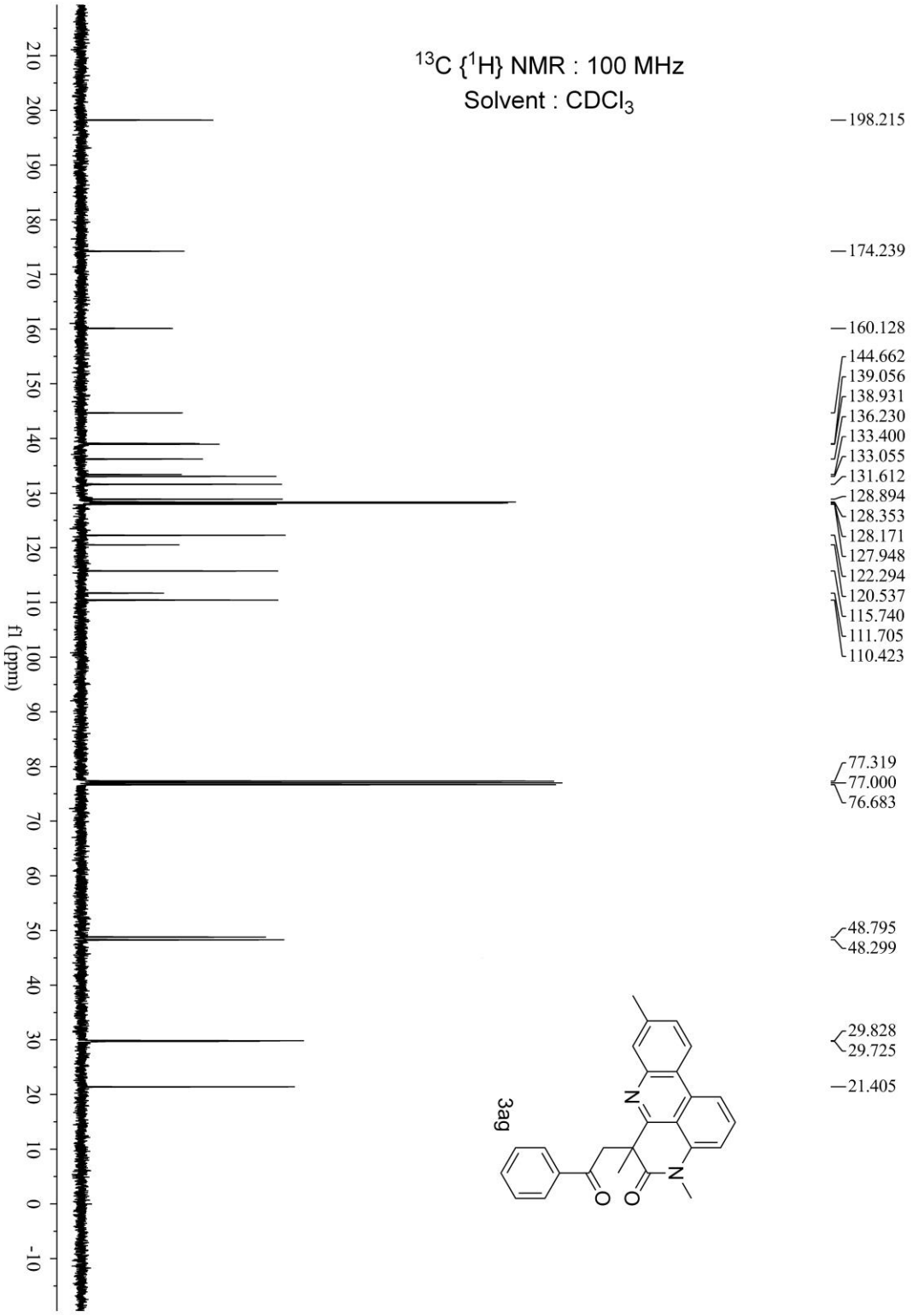
4,6,9-Trimethyl-6-(2-oxoheptyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5 (6*H*)-one (3af)



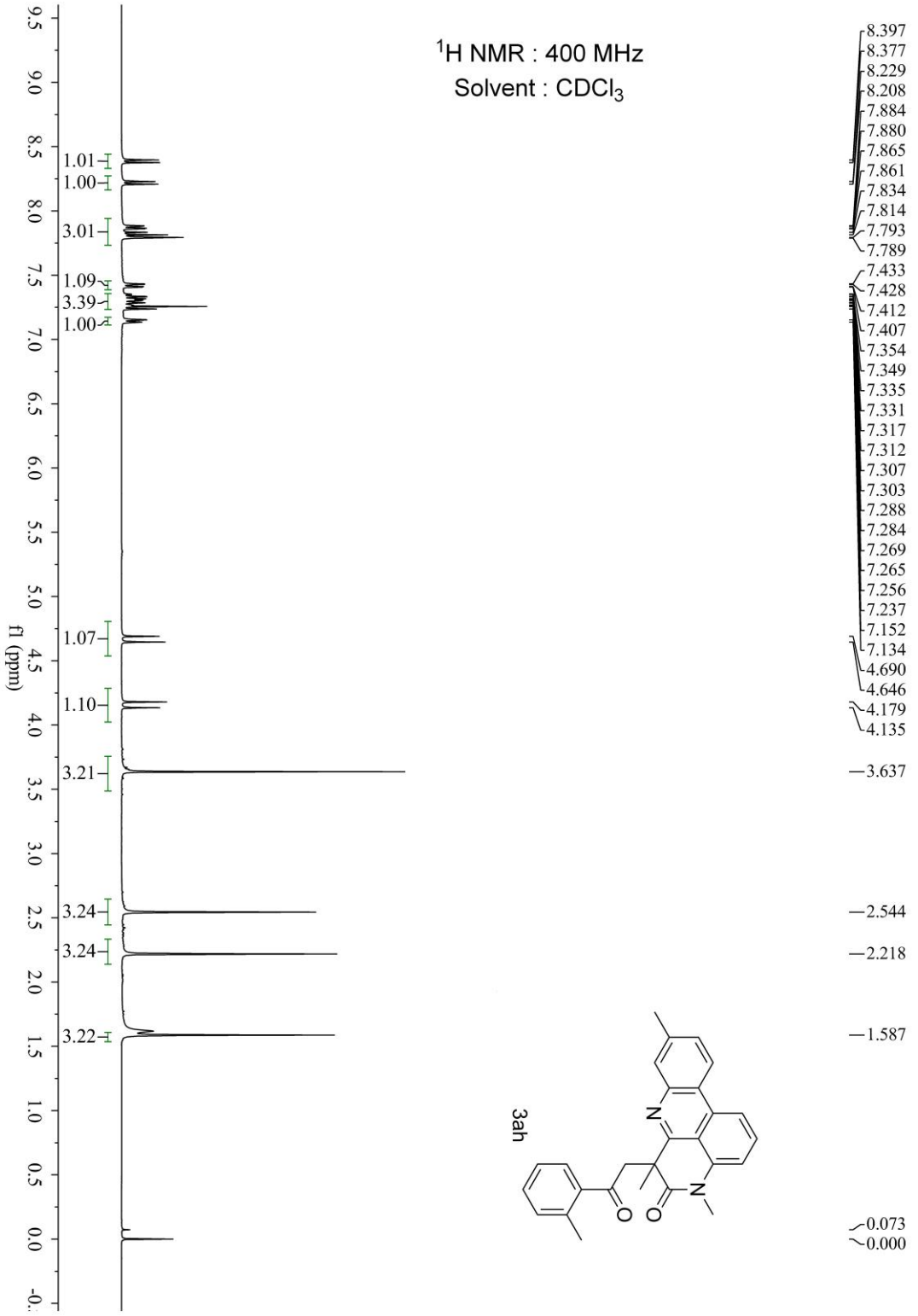

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
209.630
174.181
160.153
144.703
139.075
138.969
133.377
131.584
128.833
127.971
122.348
120.587
115.672
111.710
110.372
77.318
77.000
76.683
52.206
48.107
42.163
31.168
29.802
29.528
23.417
22.384
21.455
13.786
3af
N
O
N
O

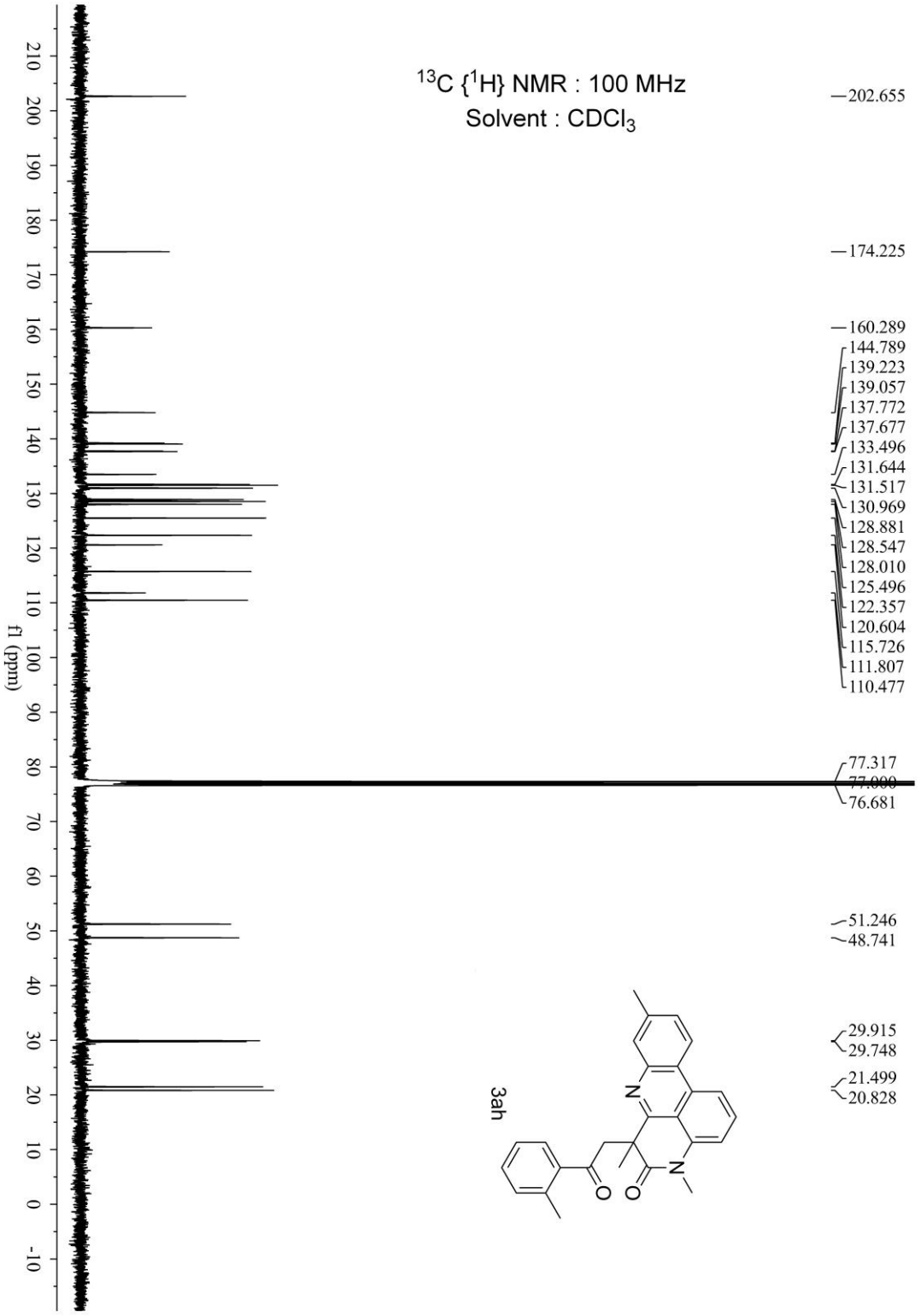
4,6,9-Trimethyl-6-(2-oxo-2-phenylethyl)-4*H*-pyrido[4,3,2-*gh*]phenant hridin-5(6*H*)-one (3ag)



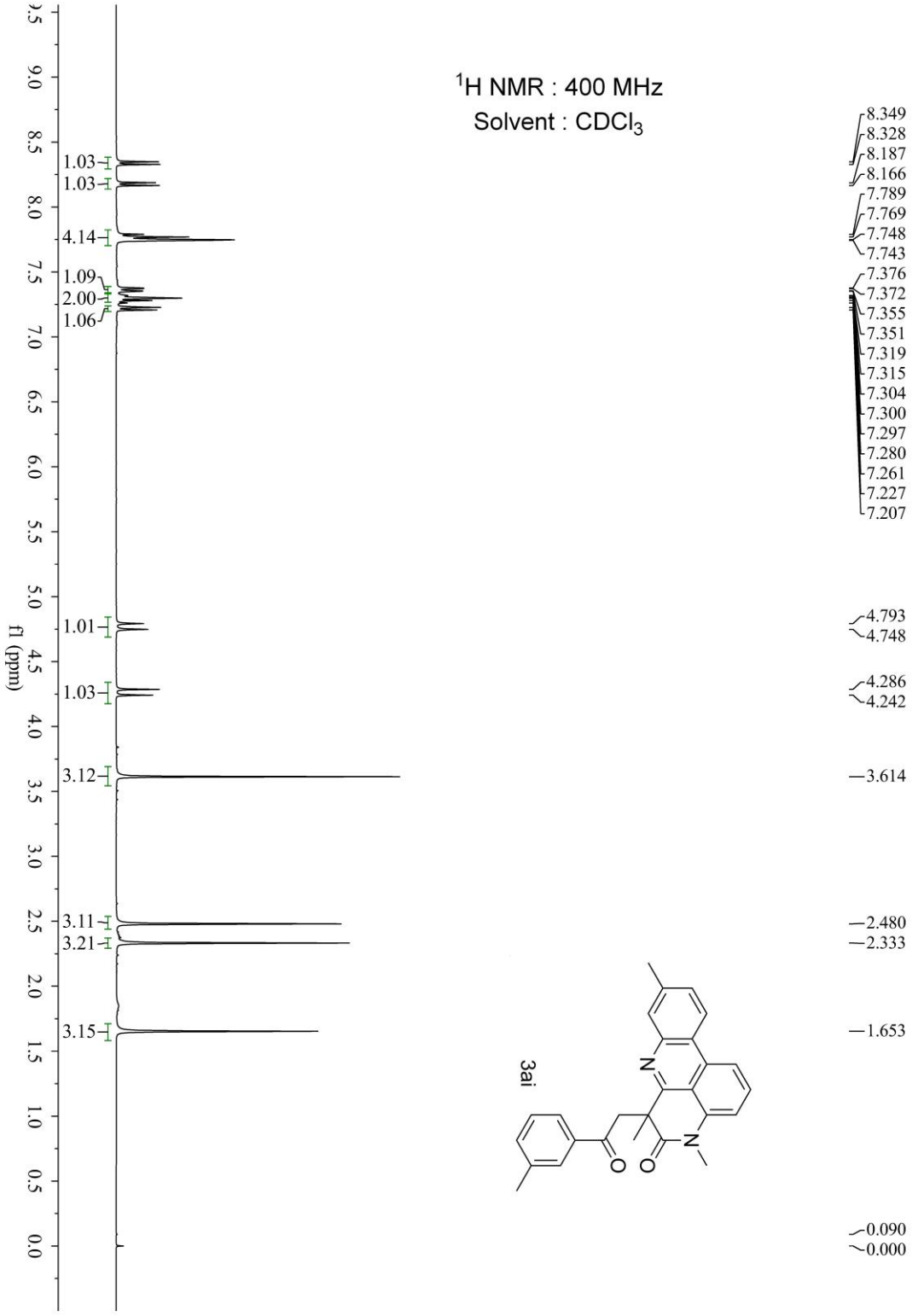

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
198.215
174.239
160.128
144.662
139.056
138.931
136.230
133.400
133.055
131.612
128.894
128.353
128.171
127.948
122.294
120.537
115.740
111.705
110.423
77.319
77.000
76.683
48.795
48.299
29.828
29.725
21.405
f1 (ppm)
3ag
N
O
O
N

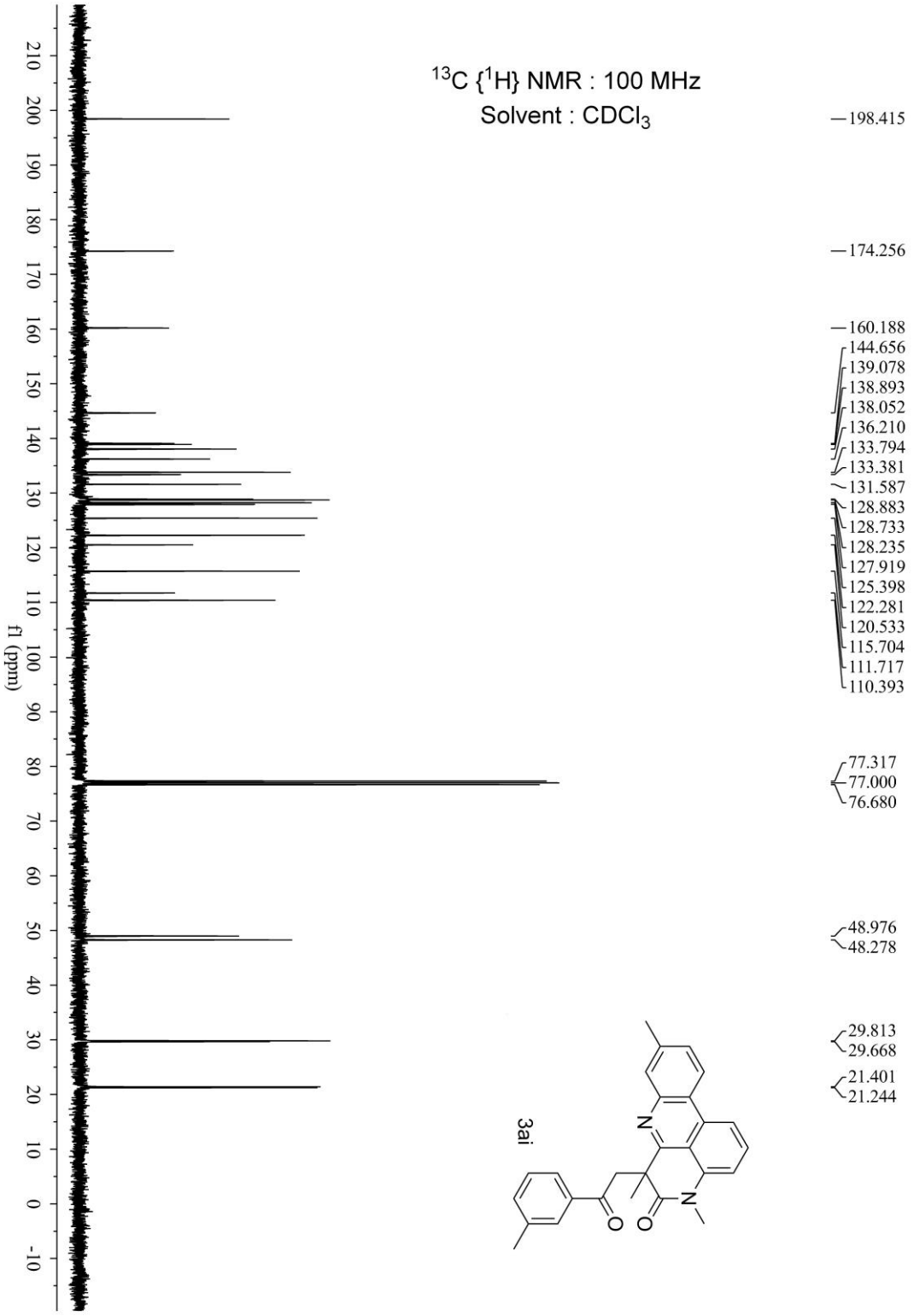
4,6,9-Trimethyl-6-(2-oxo-2-(*o*-tolyl)ethyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ah)



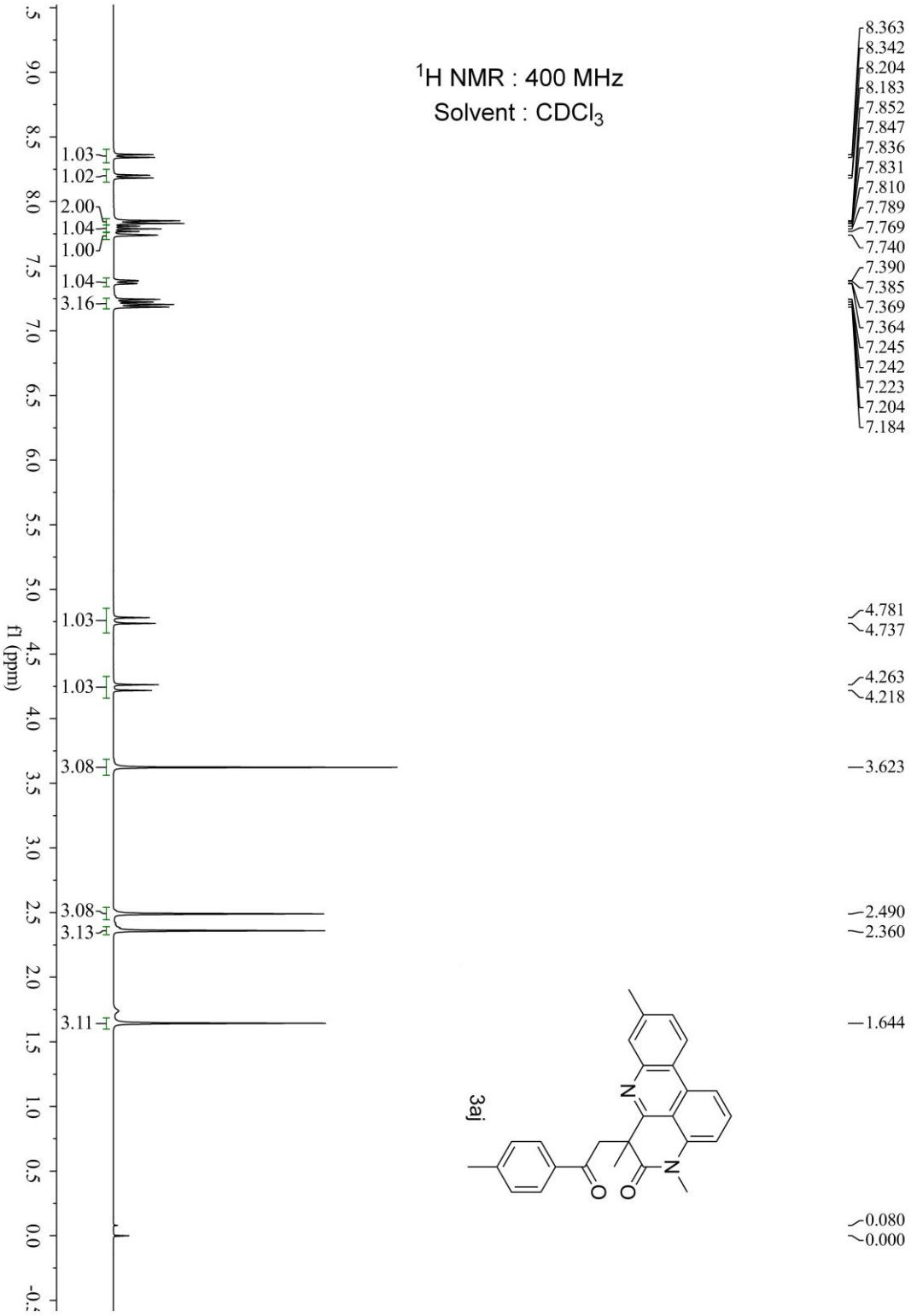

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
202.655
174.225
160.289
144.789
139.223
139.057
137.772
137.677
133.496
131.644
131.517
130.969
128.881
128.547
128.010
125.496
122.357
120.604
115.726
111.807
110.477
77.317
77.000
76.681
51.246
48.741
29.915
29.748
21.499
20.828
3ah
N
O
O
N

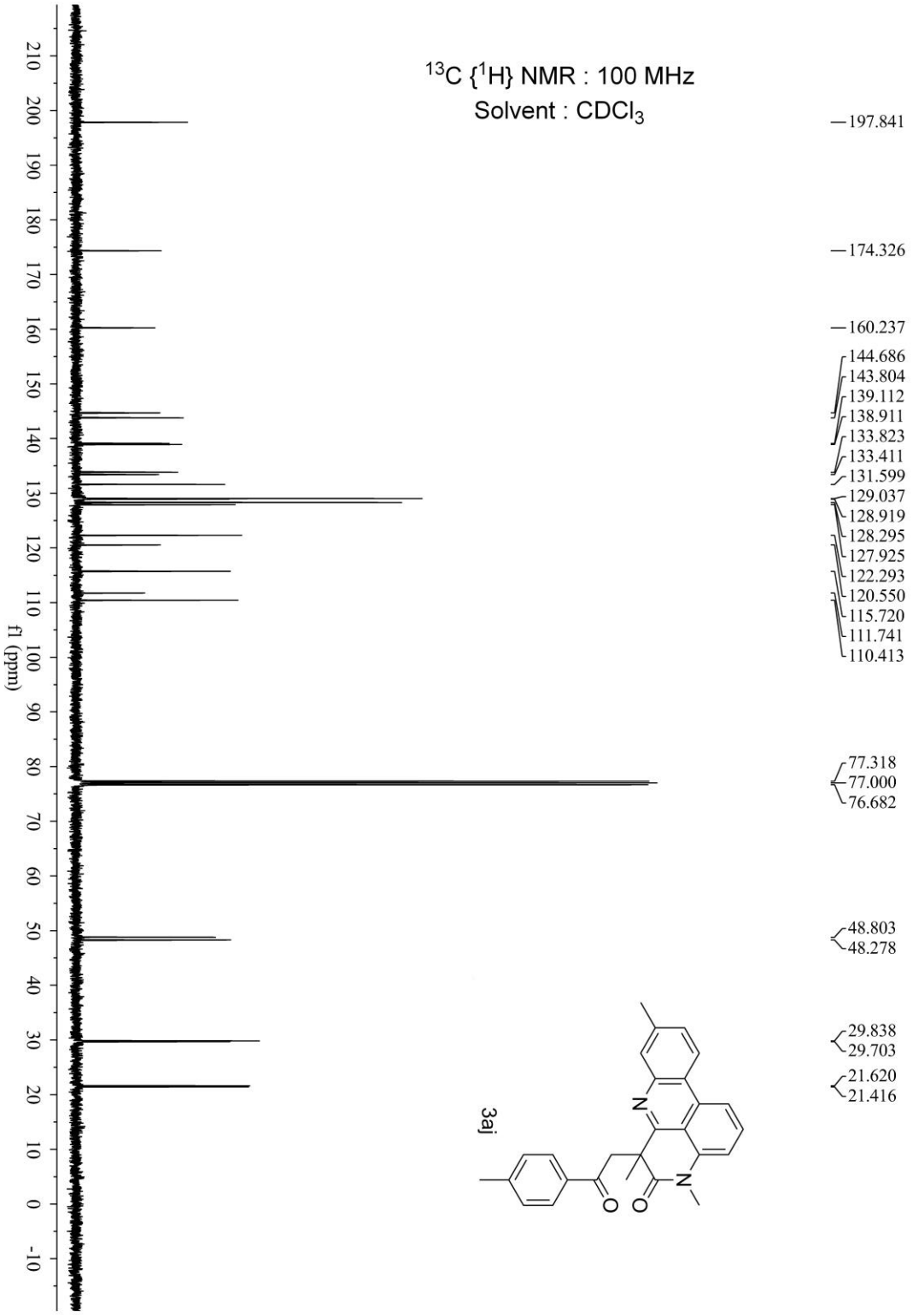
4,6,9-Trimethyl-6-(2-oxo-2-(*m*-tolyl)ethyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ai)



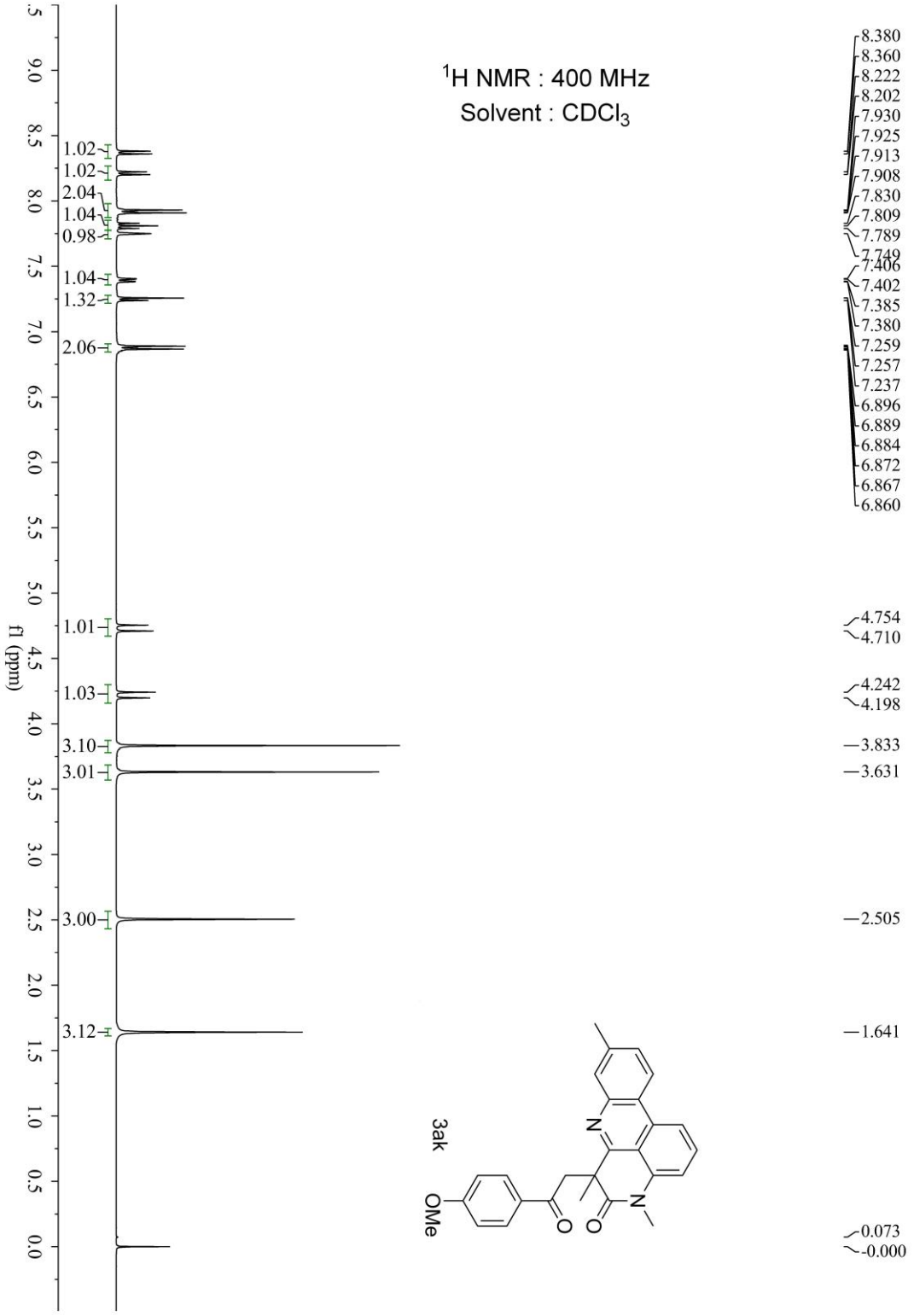

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
f1 (ppm)
198.415
174.256
160.188
144.656
139.078
138.893
138.052
136.210
133.794
133.381
131.587
128.883
128.733
128.235
127.919
125.398
122.281
120.533
115.704
111.717
110.393
77.317
77.000
76.680
48.976
48.278
29.813
29.668
21.401
21.244
3ai

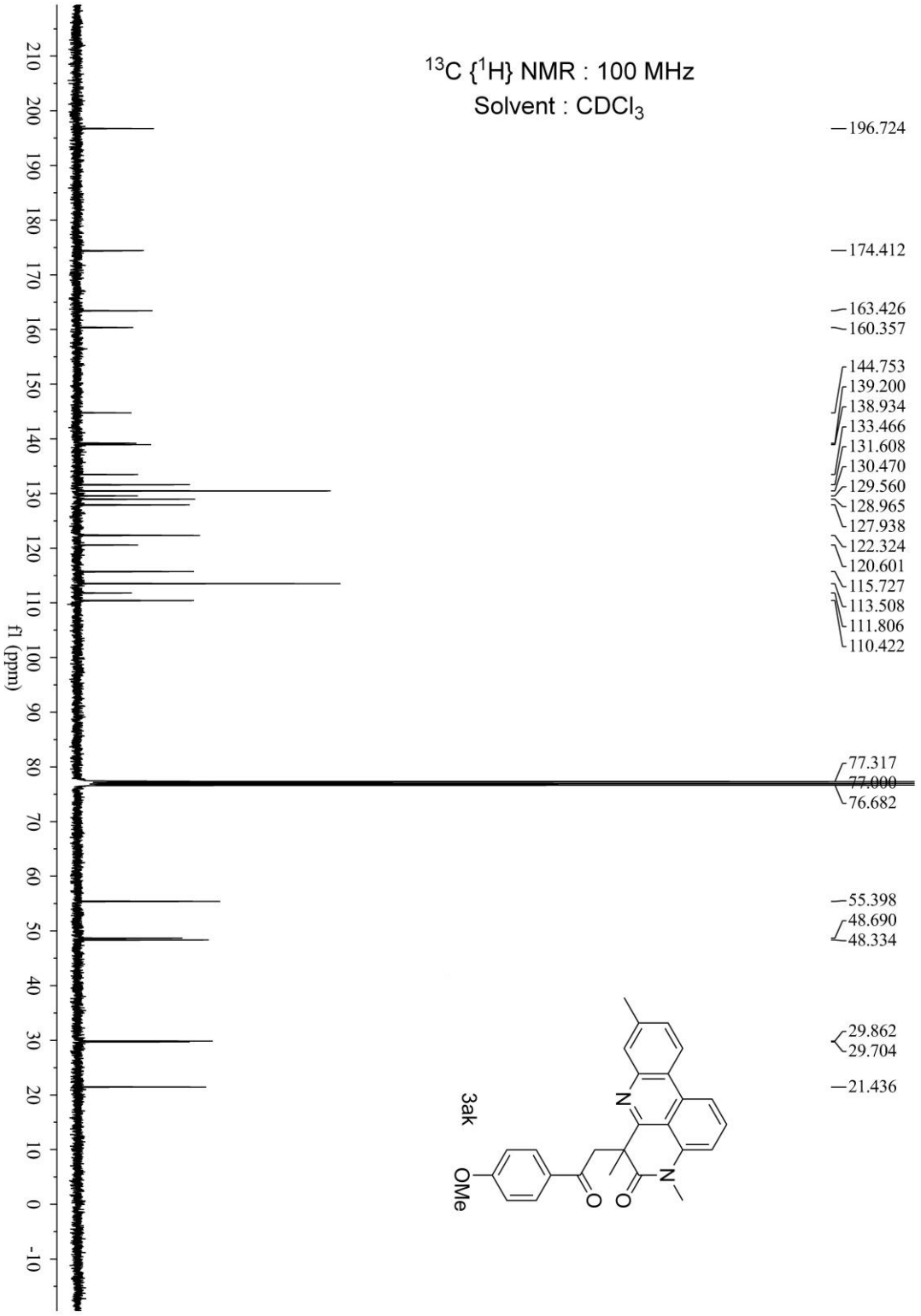
4,6,9-Trimethyl-6-(2-oxo-2-(*p*-tolyl)ethyl)-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3aj)



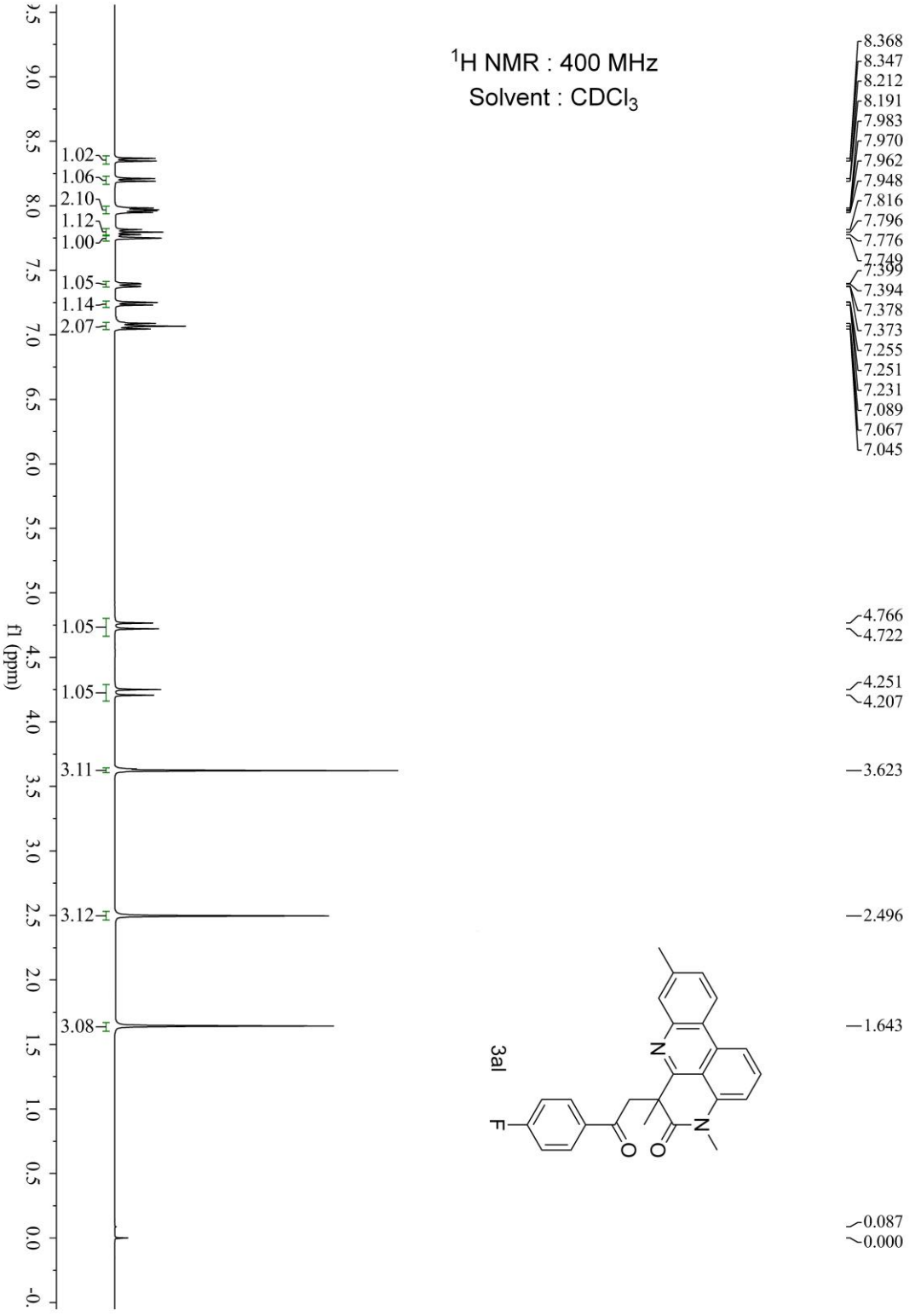

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
197.841
174.326
160.237
144.686
143.804
139.112
138.911
133.823
133.411
131.599
129.037
128.919
128.295
127.925
122.293
120.550
115.720
111.741
110.413
77.318
77.000
76.682
48.803
48.278
29.838
29.703
21.620
21.416
3aj
N
N
O
O

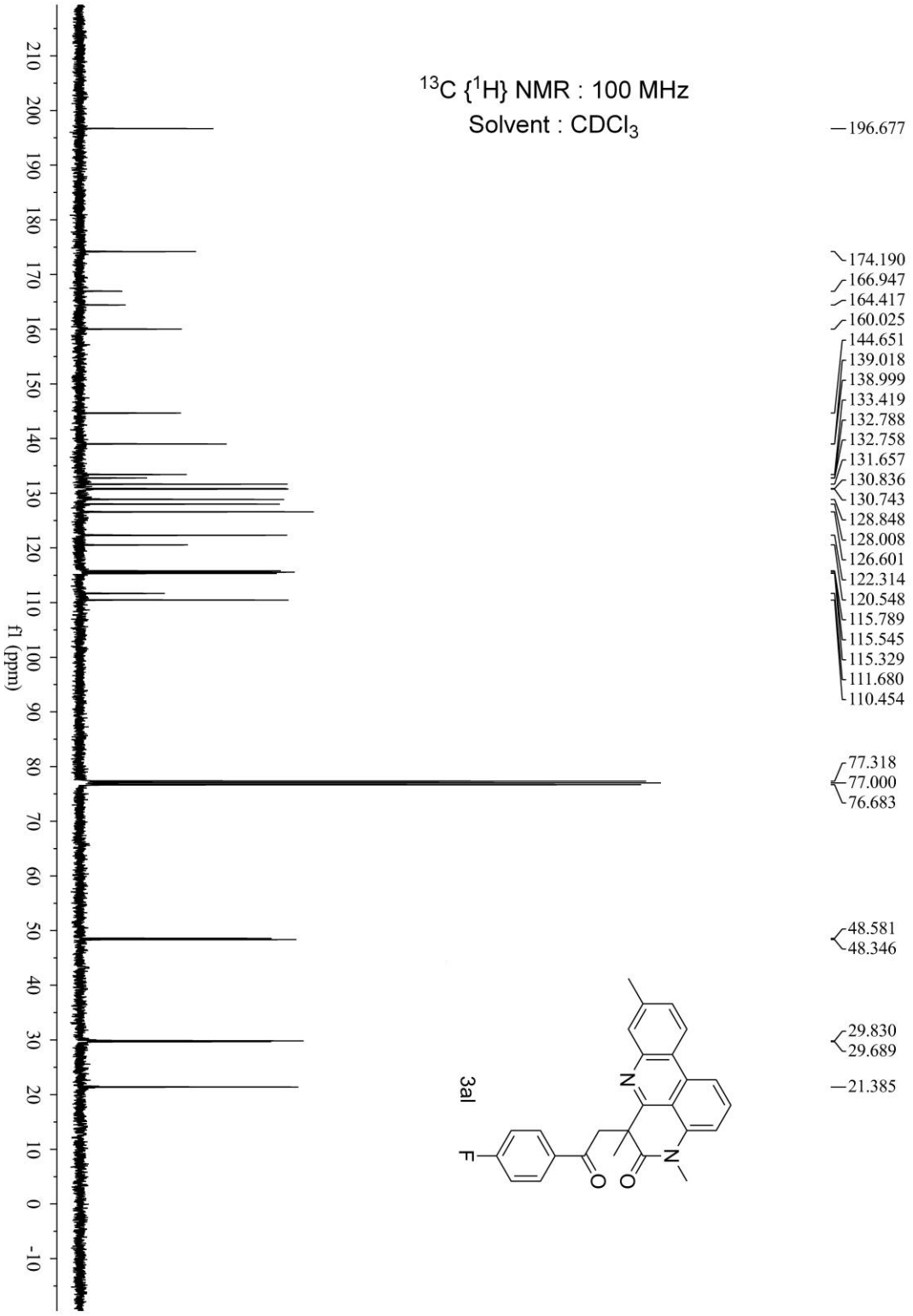
6-(2-(4-Methoxyphenyl)-2-oxoethyl)-4,6,9-trimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ak)

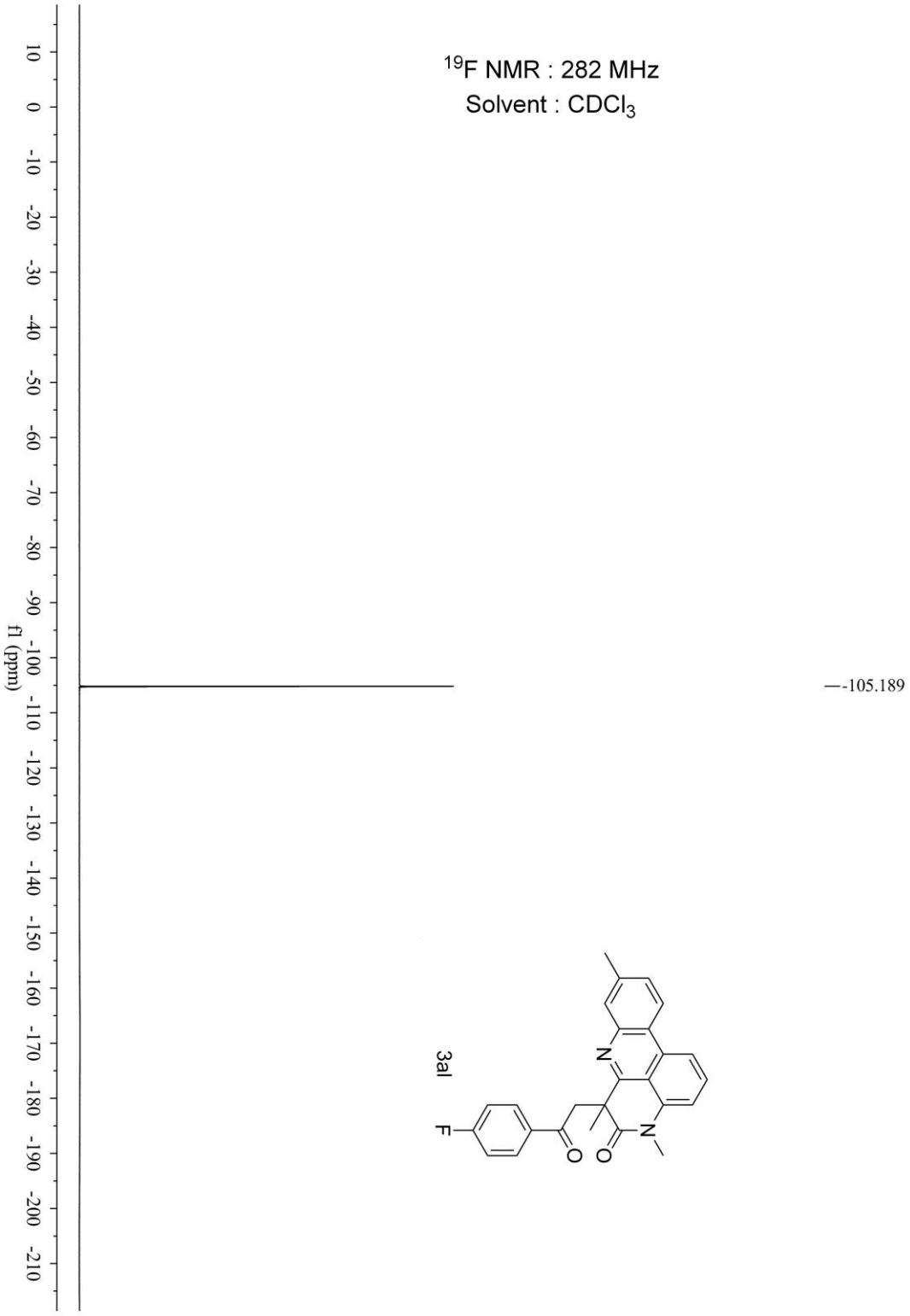



^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
196.724
174.412
163.426
160.357
144.753
139.200
138.934
133.466
131.608
130.470
129.560
128.965
127.938
122.324
120.601
115.727
113.508
111.806
110.422
77.317
77.000
76.682
55.398
48.690
48.334
29.862
29.704
21.436
f1 (ppm)
3ak
OMe
N
N
O
O

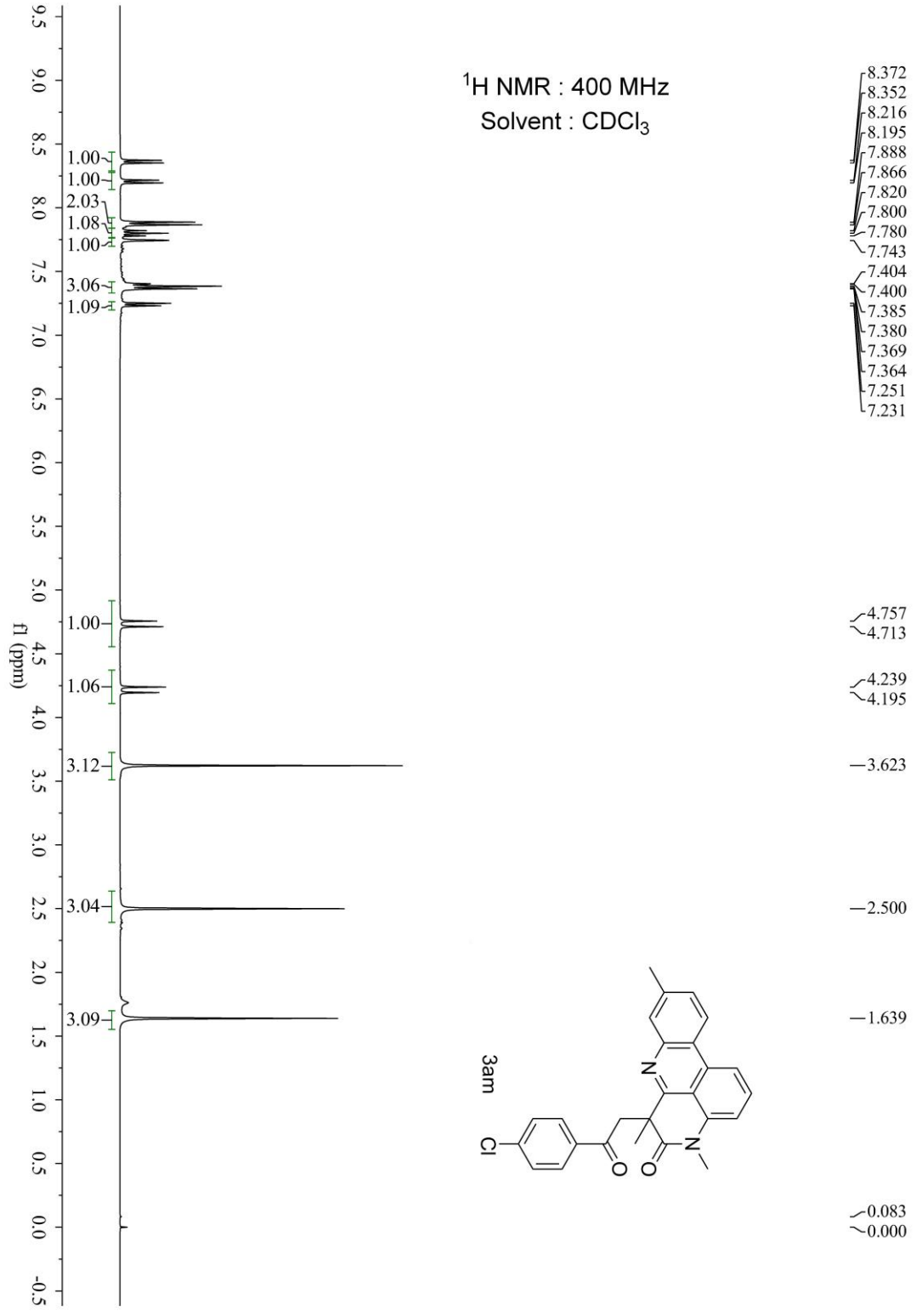
6-(2-(4-Fluorophenyl)-2-oxoethyl)-4,6,9-trimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3al)

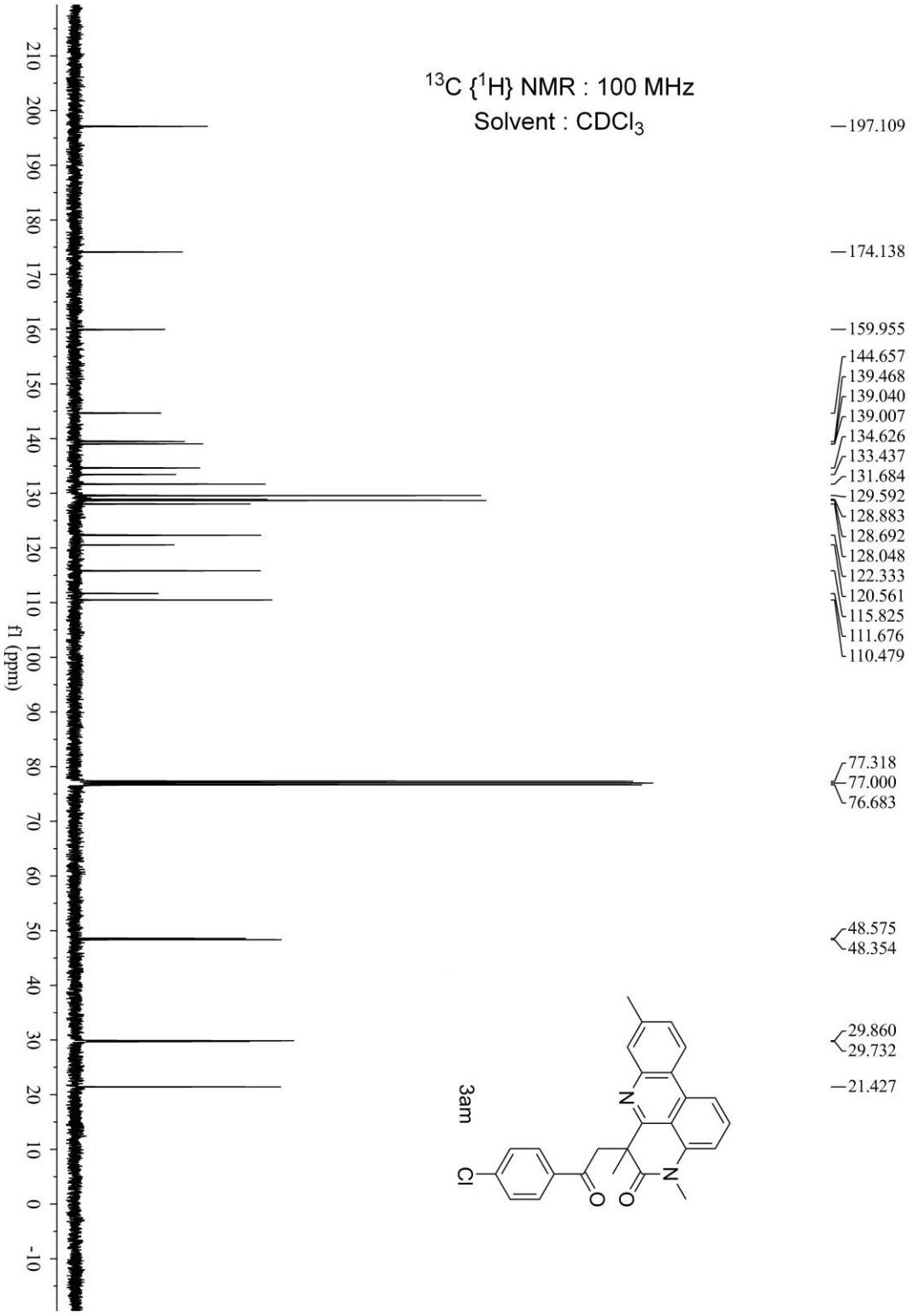



^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
f1 (ppm)
196.677
174.190
166.947
164.417
160.025
144.651
139.018
138.999
133.419
132.788
132.758
131.657
130.836
130.743
128.848
128.008
126.601
122.314
120.548
115.789
115.545
115.329
111.680
110.454
77.318
77.000
76.683
48.581
48.346
29.830
29.689
21.385
3al
F
N
O
O
N

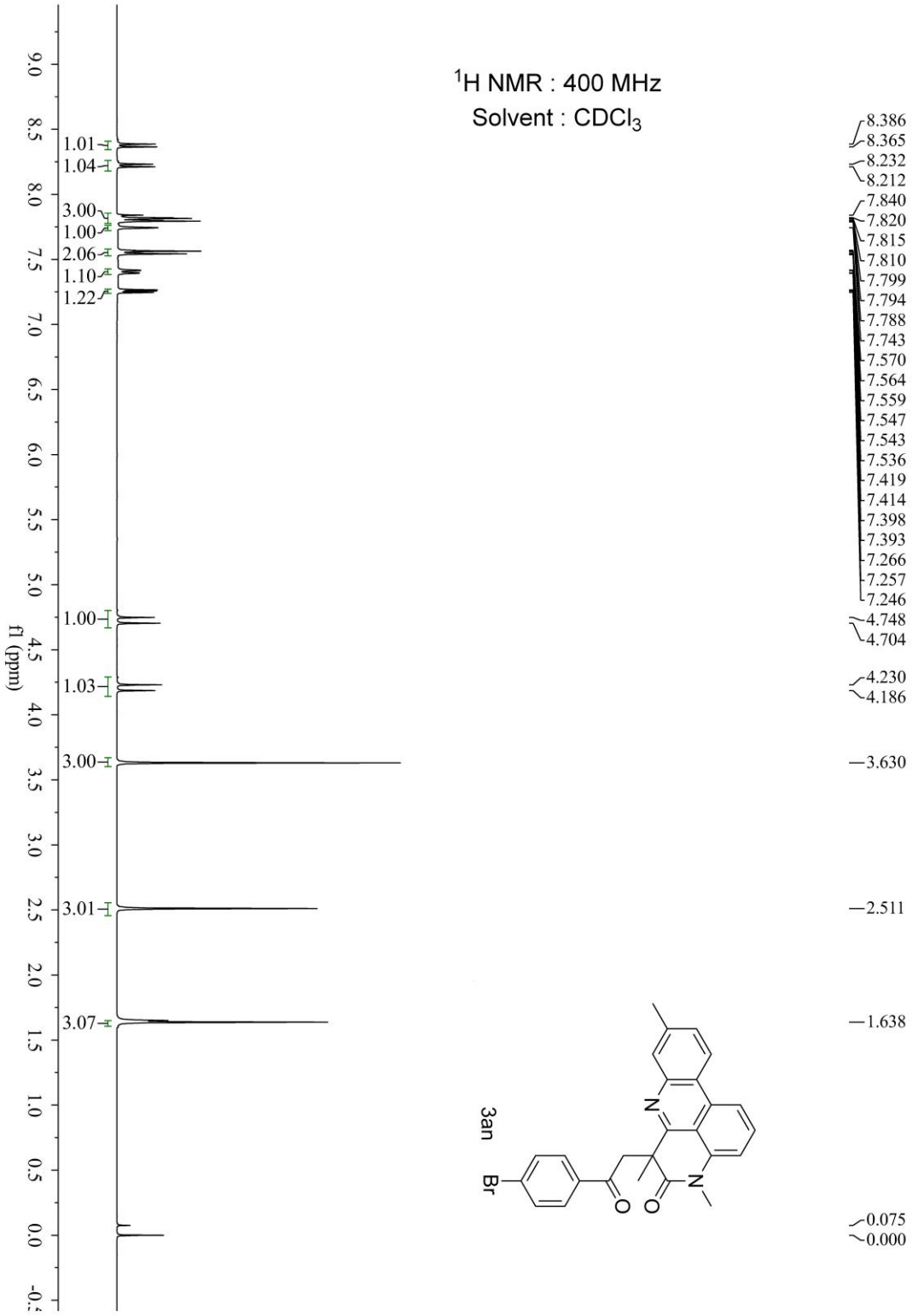

^{19}F NMR : 282 MHz
Solvent : $CDCl_3$
-105.189
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
3al
F
N
O
O
N

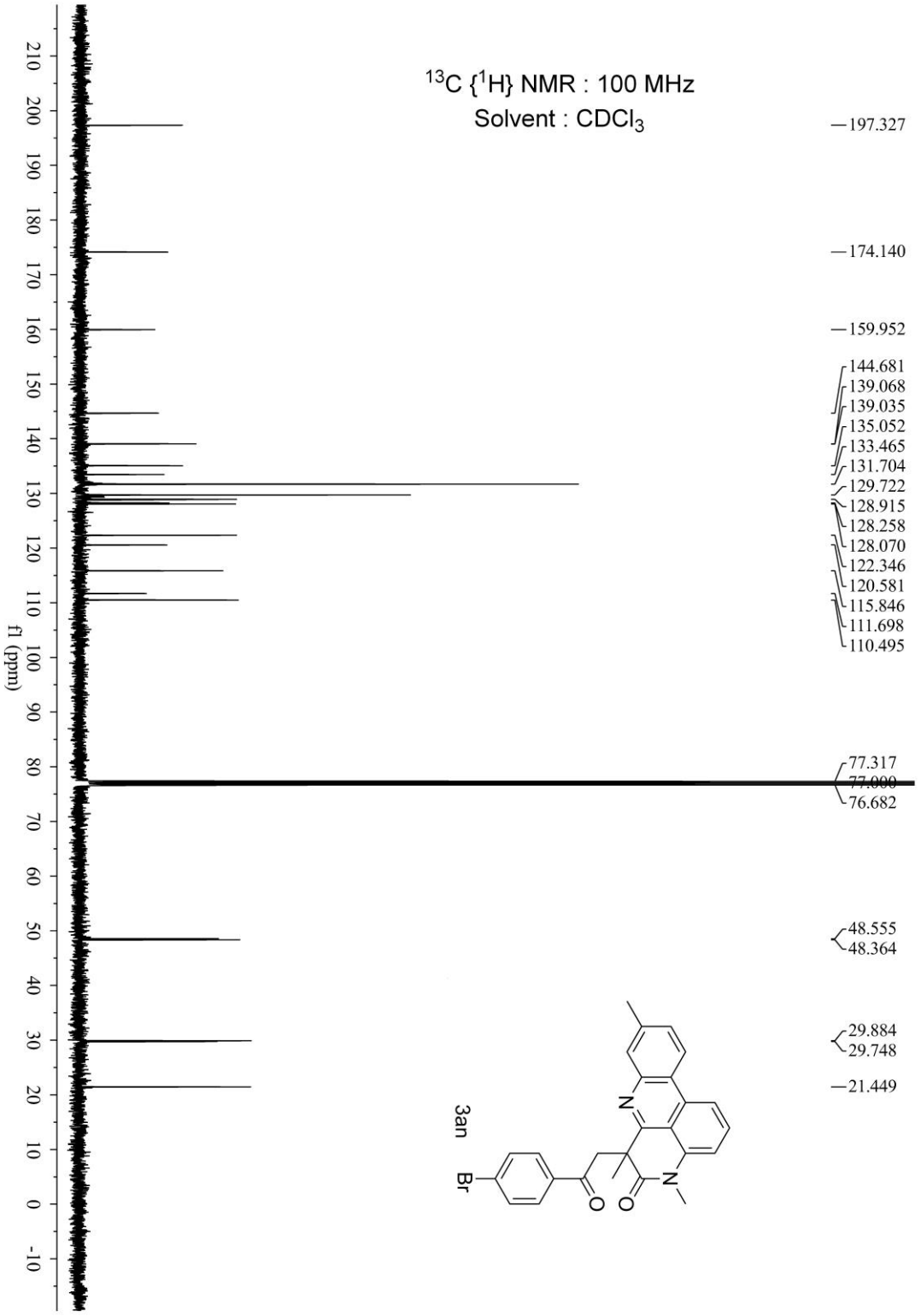
6-(2-(4-Chlorophenyl)-2-oxoethyl)-4,6,9-trimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3am)



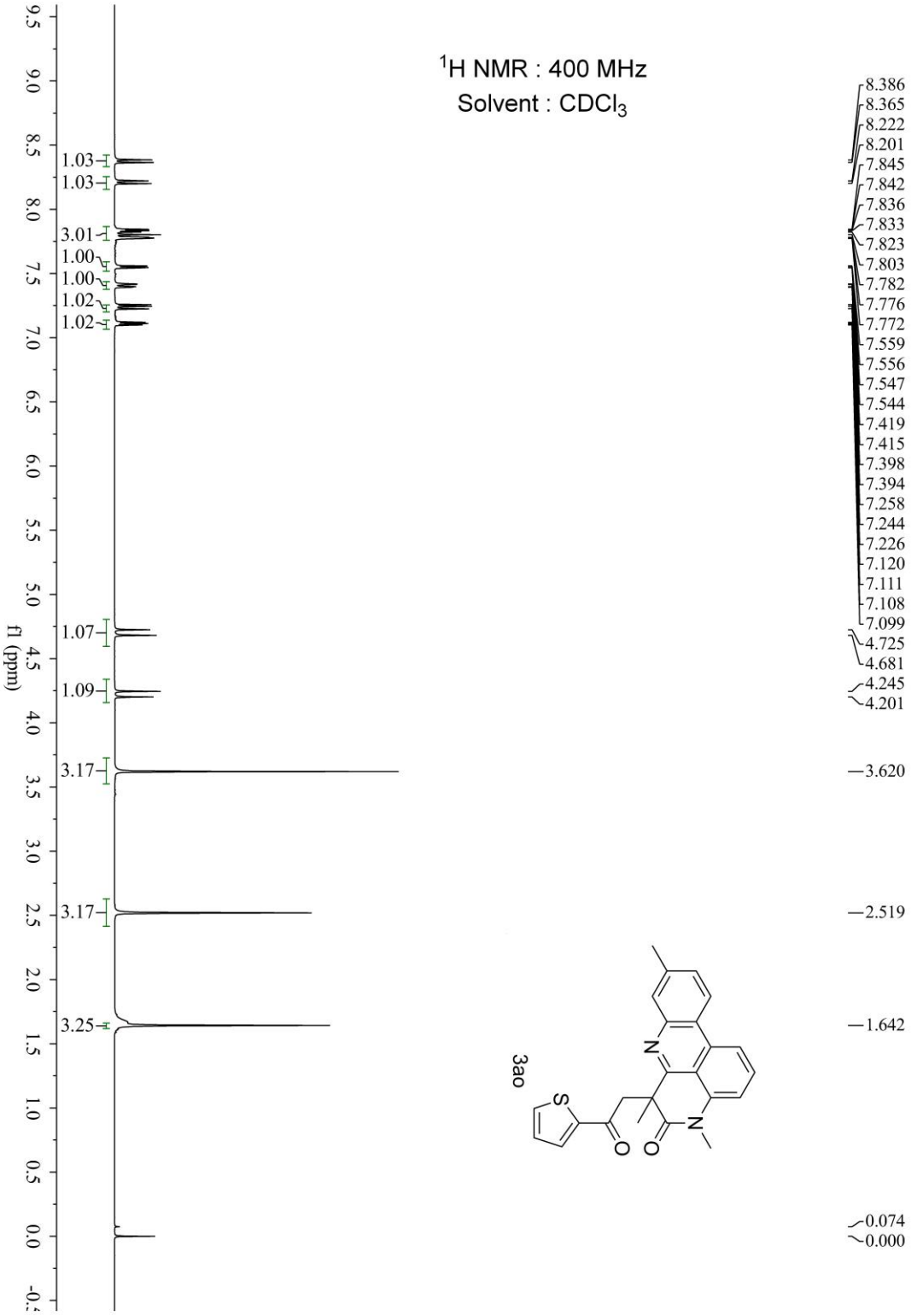

^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
197.109
174.138
159.955
144.657
139.468
139.040
139.007
134.626
133.437
131.684
129.592
128.883
128.692
128.048
122.333
120.561
115.825
111.676
110.479
77.318
77.000
76.683
48.575
48.354
29.860
29.732
21.427
3am
Cl
N
N
O
O

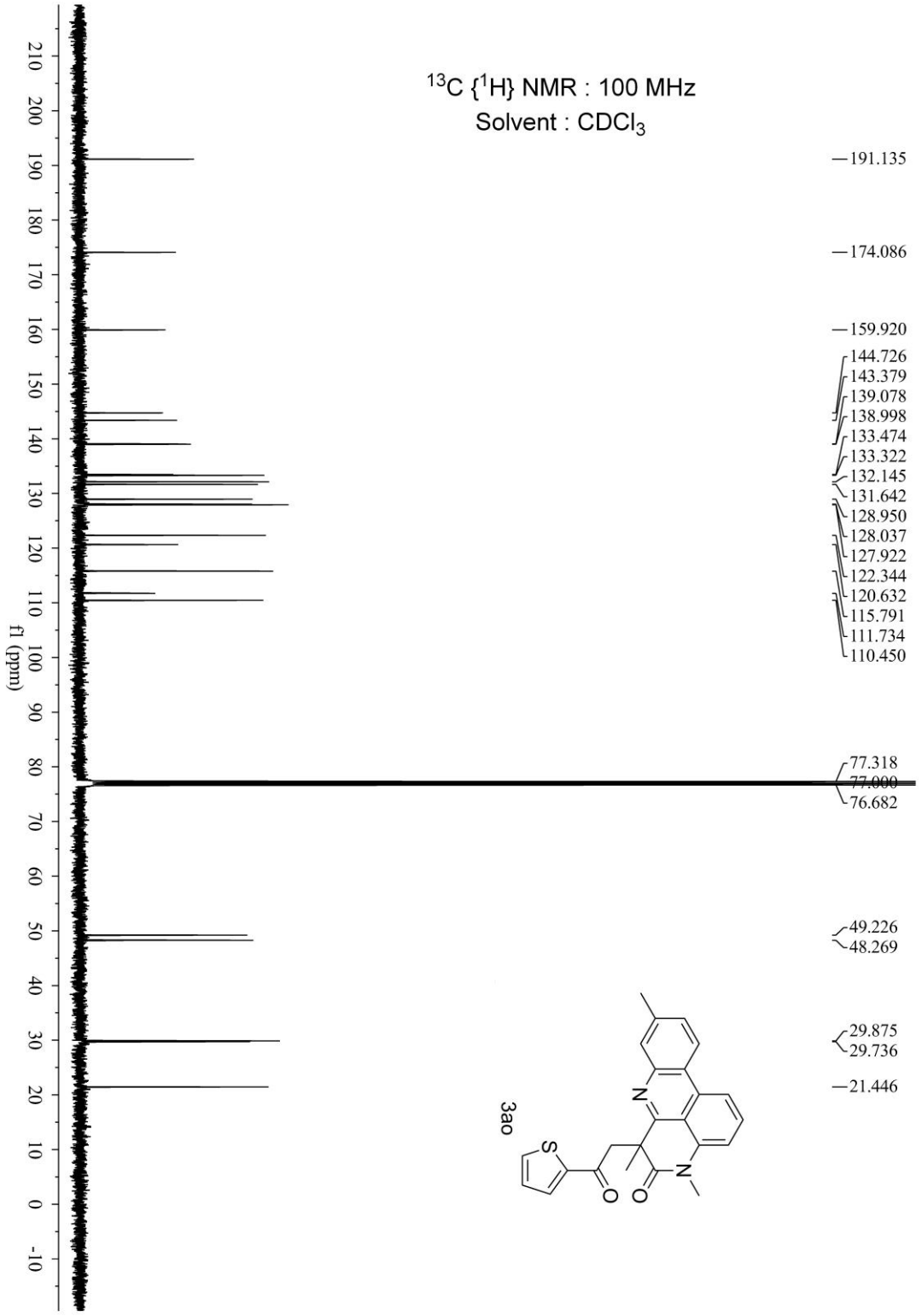
6-(2-(4-Bromophenyl)-2-oxoethyl)-4,6,9-trimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3an)




^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$
197.327
174.140
159.952
144.681
139.068
139.035
135.052
133.465
131.704
129.722
128.915
128.258
128.070
122.346
120.581
115.846
111.698
110.495
77.317
77.000
76.682
48.555
48.364
29.884
29.748
21.449
f1 (ppm)
3an
Br
N
O
O
N

4,6,9-Trimethyl-6-(2-oxo-2-(thiophen-2-yl)ethyl)-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)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
191.135
174.086
159.920
144.726
143.379
139.078
138.998
133.474
133.322
132.145
131.642
128.950
128.037
127.922
122.344
120.632
115.791
111.734
110.450
77.318
77.000
76.682
49.226
48.269
29.875
29.736
21.446
3ao
N
S
O
O
N