Supporting Information

Photo-induced radical cyclization reaction of isocyanides with *α*-carbonyl bromides to access 11-alkyl-substituted 1,4-dibenzodiazepines

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1. General Information

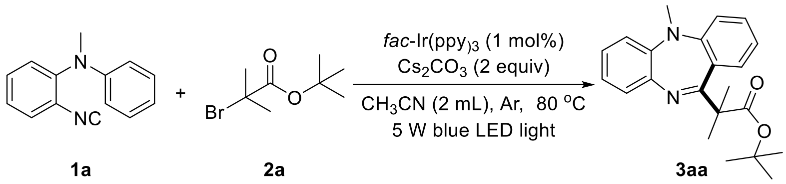
Unless otherwise stated, all commercial reagents were used as received. Aniline (Adamas-beta, 99%), 1-fluoro-2-nitrobenzene (Leyan, 99%), triethylamine (Aladdin, 99%), acetonitrile (Aladdin, 99%), formic acid (Aladdin, 99%) and phosphorus oxychloride (Adamas-beta, 99%) were used without further treatment. All reagents and solvents were commercially available and used without any further purification unless specified. 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 are quoted 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 1

2-Isocyano-*N*-methyl-*N*-phenylaniline **1**[1-2] was synthesized according to the known methods.

2.2 Typical Experimental Procedure



To a schlenk tube were added 2-isocyano-*N*-methyl-*N*-phenylaniline **1a** (0.2 mmol, 41.6 mg), *tert*-butyl 2-bromo-2-methylpropanoate **2a** (2.0 equiv, 0.4 mmol, 88.8 mg), Cs_2CO_3 (2.0 equiv, 0.4 mmol, 130 mg), *fac*-Ir(ppy)$_3$ (1 mol%,0.6 mg), MeCN (2 mL). Then the tube was stirred at 80 °C in an argon atmosphere for the indicated time until complete consumption of the starting material as monitored by TLC analysis. The residue was purified by silica gel flash column chromatography (petroleum ether/ethyl acetate = 90 : 1) to afford the desired products **3aa.**

2.3 Additional Experimental Details

The light source bought from YICAI (https://item.taobao.com/item.htm?_u=u10503hgcbe1&id=597700668537&spm=a1z09.2.0.0.1f8a2e8dVdegb2&skuId=4812351826113), 5 W blue LED light bulb (E27). The wavelength was about 400-500 nm and the wavelength of peak intensity was about 415.0 nm. The pictures of the visible-light source (**Figure S1**) was shown as follow:

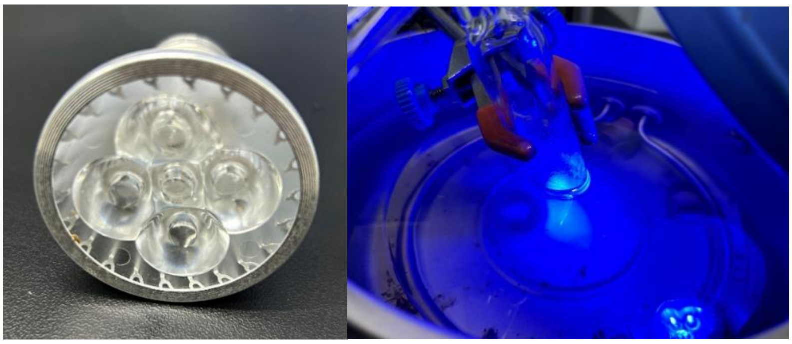
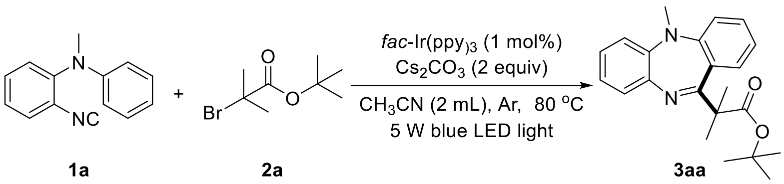


Figure S1. **The light source and photographs of the experimental setup.**

2.4 The Light On/Off Experiments



Time/h	0	6 (on)	12 (off)	18 (on)	24 (off)	30 (on)	36 (off)	42 (on)
Yield/%	0	20	20	40	40	62	62	83

The above-depicted reaction was performed according to the general protocol established. The reaction was irradiated with 5 W blue LEDs for 6 hours and then stirred in the dark for 6 hours. This procedure was repeated for 42 hours, and the yield of the product was determined by ^{1}H NMR with dibromomethane as an internal standard at each point the light was turned off or on. The results are shown in the graph above. This result shows that constant light irradiation is needed to progress the reaction.

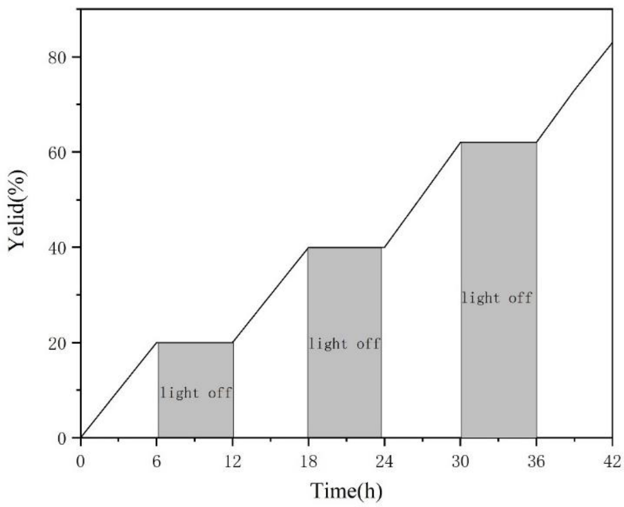


Figure S2 The light on/off Experiments

2.5 Stern-Volmer Quenching Experiments

Formulation solution:

2-isocyano-*N*-methyl-*N*-phenylaniline **1a** (8.2 mg) was dissolved in MeCN in a 4 mL volumetric flask to set the concentration to be 0.01 M. *tert*-butyl 2-bromo-2-methylpropanoate **2a** (8.8 mg) was dissolved in MeCN in a 4mL volumetric flask to set the concentration to be 0.01 M.

Additional experimental details:

The samples were prepared by the copper-based photocatalyst *fac*-Ir(ppy)$_3$ (5×10^{-4} M) with different amounts of quencher **1a** in MeCN in a light path quartz fluorescence cuvette. The concentration of quencher **1a** is 0.01 M in MeCN. For each **S3** quenching experiment, 3 μL of quencher solution was separately titrated to the copper based photocatalyst *fac*-Ir(ppy)$_3$ (3.0 mL).

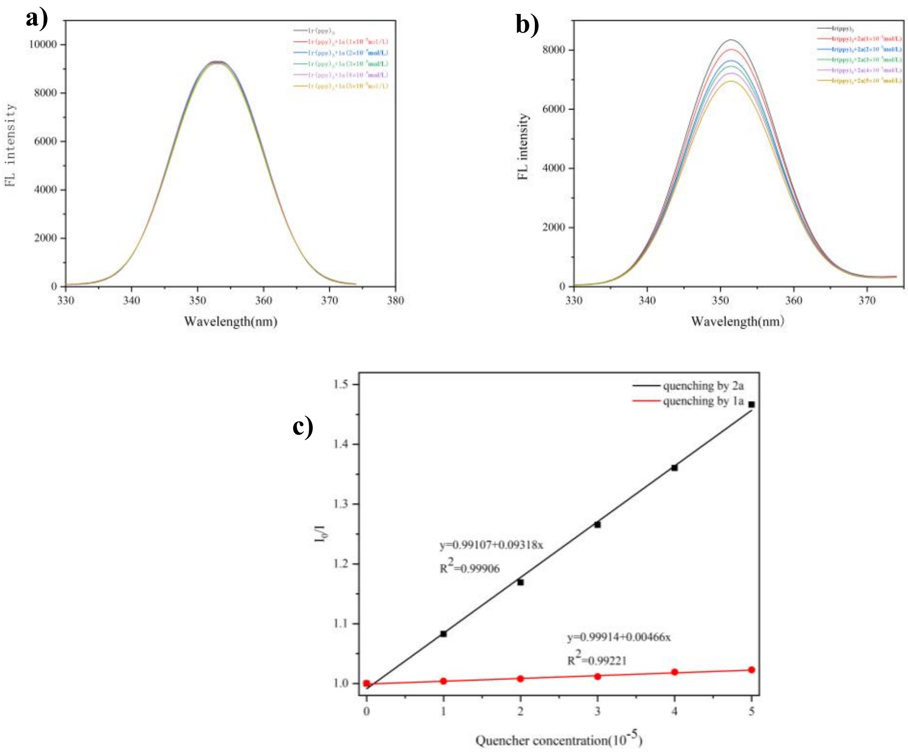


Figure S3 Stern-Volmer Quenching Experiments: (a) *fac*-Ir(ppy)$_3$ quenched by 1a in MeCN; (b) *fac*-Ir(ppy)$_3$ quenched by 2a in MeCN; (c) Stern-Volmer plot of photocatalyst at different concentration.

The resulting mixture was sparged with nitrogen for 3 minutes and then irradiated at 450 nm. Fluorescence emission spectra were recorded (3 trials per sample). Into this solution, 3.0 μL of a 2-isocyano-*N*-methyl-*N*-phenylaniline **1a** solution was successively added and uniformly stirred, and the resulting mixture was bubbled with nitrogen for 3 minutes and irradiated at 450 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 **S3 (a)** of Stern-Volmer quenching experiments results, the emission intensity of the copperbased photocatalyst *fac*-Ir(ppy)$_3$ solution was 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 occurred in photocatalyst and sulfonium salt.

2.7 Quantum Yield Determination

Determination of the light intensity at 415 nm:

According to the procedure of Yoon[2] the photon flux of the blue LED (λ_{max} = 415 nm) was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 3.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at λ = 415 nm with an emission slit width at 10.0 nm. After irradiation, 0.53 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A nonirradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using eq. 1.

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

$$mol \text{ of } \mathrm{Fe}^{2+} = \frac{(0.00353L) \cdot (3.162 - 0.399)}{(1.00cm) \cdot (11100 \frac{L}{mol} cm^{-1})} = 8.80 \times 10^{-7}$$

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

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

$$Photo \text{ flux} = \frac{8.80 \times 10^{-7}}{(1.12) \cdot (90s) \cdot (0.994)} = 8.8 \times 10^{-9} einstein/s$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.12 at λ = 415 nm), t is the time (90.0 s), and f is the fraction of light absorbed at 415 nm by the ferrioxalate actinometer. This value is calculated using eq 3 where $A_{415\text{ nm}}$ is the absorbance of the ferrioxalate solution at 415 nm. An absorption spectrum gave an $A_{415\text{ nm}}$ value of > 3, indicating that the fraction of absorbed light (f) is > 0.999.

$$f = 1 - 10^{-A_{415\text{nm}}} \quad (3)$$

The photon flux was thus calculated to be 8.8 × 10^{-9} einsteins s^{-1}

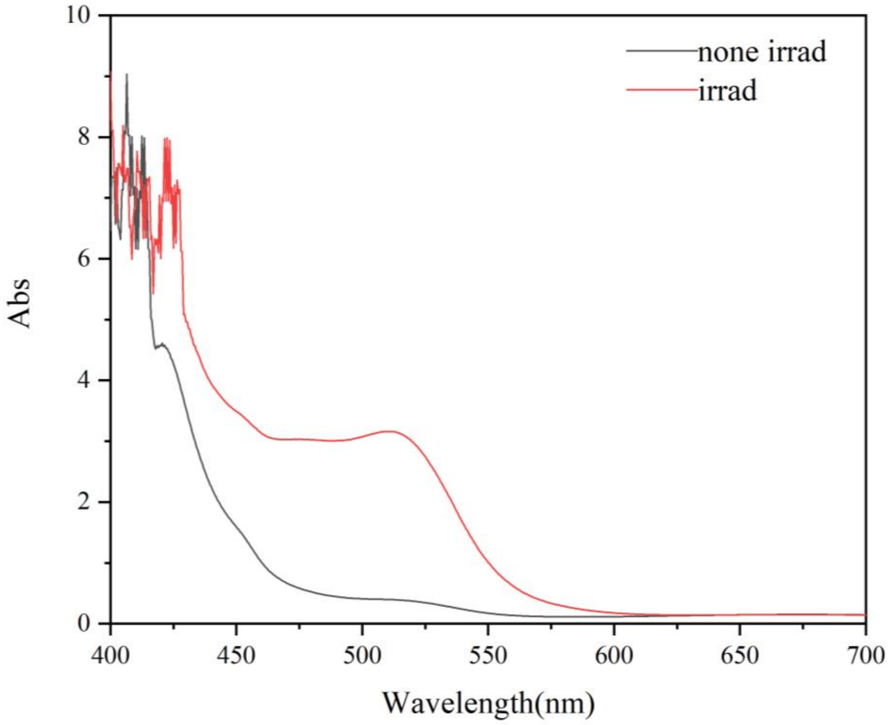
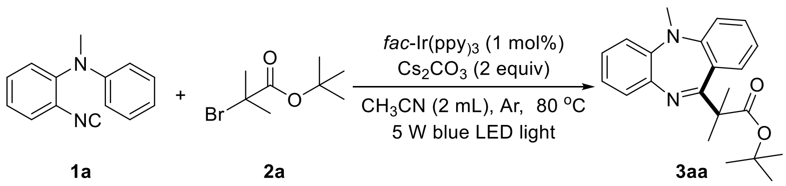


Figure S6 Absorbance of the sulfuric acid solution.

Determination of the reaction quantum yield:



A cuvette was charged with 2-isocyano-*N*-methyl-*N*-phenylaniline **1a** (0.2 mmol, 441.6mg), *tert*-butyl 2-bromo-2-methylpropanoate **2a** (2 equiv., 0.4 mmol, 88.8 mg), Cs_2CO_3 (2 equiv., 0.4 mmol, 130 mg), *fac*-Ir(ppy)$_3$ (1 mol%, 0.6 mg), MeCN (2 mL). The reaction mixture was stirred at room temperature for 2 h (7200 s) under blue LED irradiation (λ = 415 nm). The solvent was removed in vacuo and the yield of formed product was determined by ^{1}H NMR based on dibromomethane as internal standard. The quantum yield was determined using eq. 4.

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

$$\phi = \frac{5.4 \times 10^{-5}}{(8.8 \times 10^{-9} einstein/s) \cdot (3600s) \cdot (0.994)} = 0.17 < 1$$

The photon flux is 8.8 × 10^{-9} einsteins s^{-1}, t is the reaction time (7200 s). *f* is the fraction of incident light absorbed by the catalyst, determined using eq 3. An absorption spectrum of the catalyst (0.001 M) gave an absorbance value of 0.658 at 415 nm (figure **S7**), indicating that the fraction of light absorbed by the photocatalyst (*f*) is 0.994.

Absorbance of catalyst:

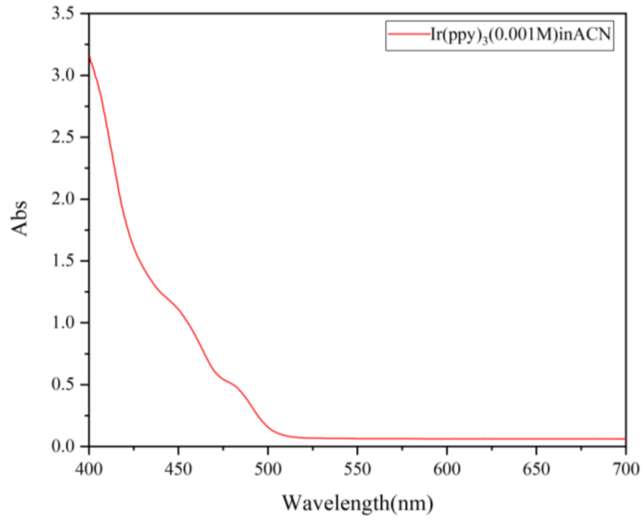
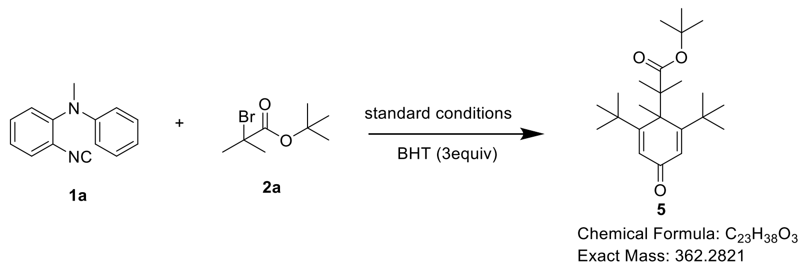
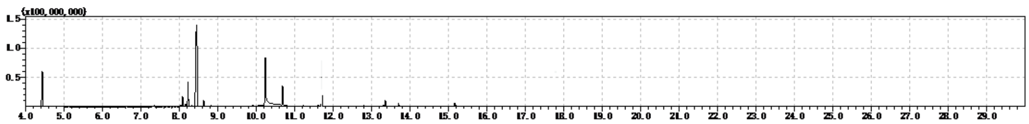


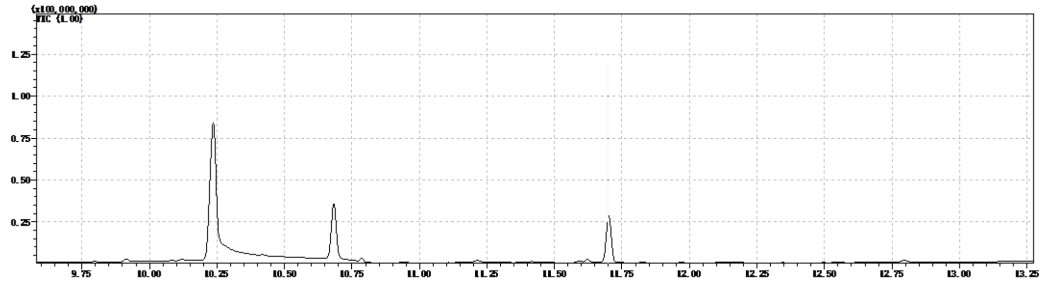
Figure S7 Absorption spectrum of *fac*-Ir(ppy)$_3$ [0.001 M] in MeCN

2.8 Control Experiments

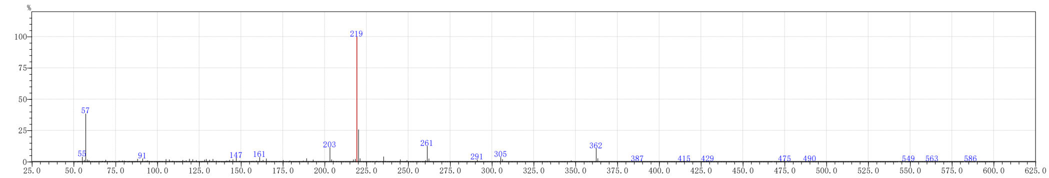
GC-MS Analysis of Raw Reaction Mixture by Using BHT as Radical Inhibitor (1, 2)







MS spectra of the peak at 11.701 min

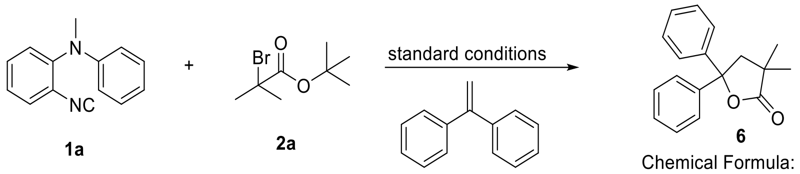


[MS Spectrum]
# of Peaks 546
Raw Spectrum 11.705 (scan : 1542)
Background No Background Spectrum
Base Peak m/z 219.15 (Inten : 7,995,683)
Event# 1

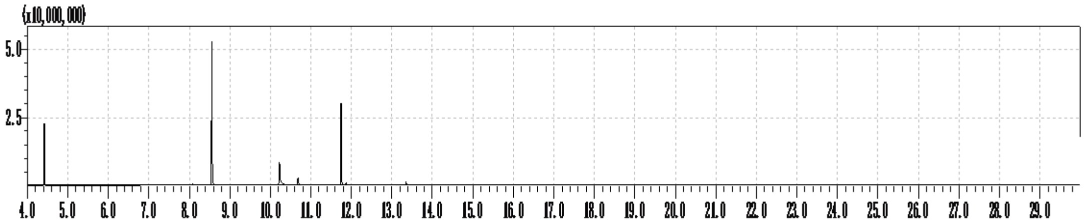
m/z	Absolute Intensity	Relative Intensity				
50.007617	0.10	72.0523450	0.29	94.1088543	1.11	
51.0517812	0.22	73.0542395	0.53	95.1050007	0.63	
52.056513	0.08	74.053961	0.05	96.106708	0.08	
53.0550049	0.63	75.054757	0.06	97.1012660	0.16	
54.1512429	0.16	76.055669	0.07	98.153014	0.04	
55.05322728	4.04	77.0575317	0.94	99.152494	0.03	
56.15124943	1.56	78.1021148	0.26	100.15	4088	0.05
57.103082111	38.55	79.0581221	1.02	101.15	37089	0.46
58.10144641	1.81	80.1075382	0.94	102.10	28558	0.36
59.0599751	1.25	81.0543511	0.54	103.10	31902	0.40
60.056699	0.08	82.156120	0.08	104.15	14577	0.18
61.001636	0.02	83.1038550	0.48	105.10	171983	2.15
62.101420	0.02	84.054912	0.06	106.15	23701	0.30
63.057159	0.09	85.107892	0.10	107.10	151548	1.90
64.0512450	0.16	86.159858	0.12	108.15	16573	0.21
65.0540356	0.50	87.1537228	0.47	109.15	65453	0.82
66.1010089	0.13	88.10188561	2.36	110.05	5786	0.07
67.0560305	0.75	89.0515122	0.19	111.10	4564	0.06
68.157268	0.09	90.158117	0.10	112.15	1856	0.02
69.05128531	1.61	91.10206697	2.59	113.15	2018	0.03
70.0536585	0.46	92.1024401	0.31	114.15	4815	0.06
71.0538354	0.48	93.1064649	0.81	115.10	115442	1.44

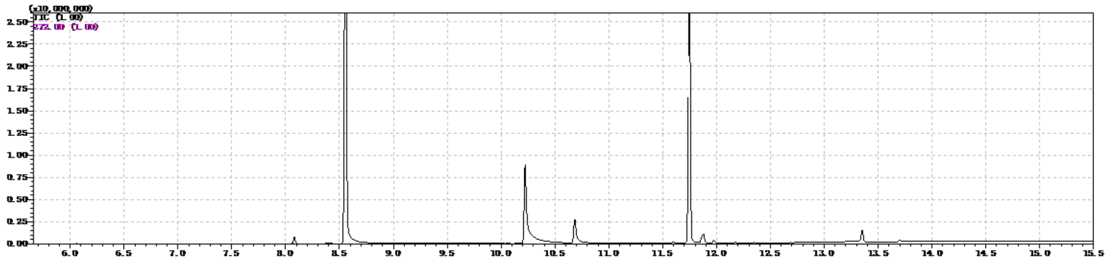
116.10	42196	0.53	160.15	37058	0.46	204.10	151316	1.89
117.10	91676	1.15	161.10	292265	3.66	205.10	69452	0.87
118.15	18513	0.23	162.10	49836	0.62	206.10	13452	0.17
119.10	185663	2.32	163.10	114874	1.44	207.05	39105	0.49
120.15	30587	0.38	164.15	17636	0.22	208.05	15450	0.19
121.10	164722	2.06	165.10	202775	2.54	209.05	5590	0.07
122.15	19349	0.24	166.05	28876	0.36	210.05	1498	0.02
123.15	101284	1.27	167.10	14650	0.18	211.00	1727	0.02
124.05	8974	0.11	168.10	8719	0.11	212.15	1112	0.01
125.15	1859	0.02	169.10	22860	0.29	213.10	3378	0.04
126.15	2672	0.03	170.10	29550	0.37	214.15	1423	0.02
127.15	37841	0.47	171.10	41334	0.52	215.10	11446	0.14
128.10	140361	1.76	172.10	15137	0.19	216.15	3535	0.04
129.10	169294	2.12	173.10	52534	0.66	217.10	147063	1.84
130.15	56428	0.71	174.10	19767	0.25	218.25	184810	2.31
131.15	130950	1.64	175.10	104455	1.31	219.15	7995683	100.00
132.15	29918	0.37	176.10	18263	0.23	220.15	2066319	25.84
133.15	182858	2.29	177.10	15911	0.20	221.10	221756	2.77
134.15	35968	0.45	178.15	5229	0.07	222.10	18423	0.23
135.15	64977	0.81	179.10	71545	0.89	223.10	2447	0.03
136.15	8864	0.11	180.05	11086	0.14	224.05	858	0.01
137.10	29574	0.37	181.05	6429	0.08	225.05	1013	0.01
138.15	3547	0.04	182.10	5007	0.06	226.15	1248	0.02
139.10	5551	0.07	183.10	10970	0.14	227.10	3078	0.04
140.15	3589	0.04	184.15	6720	0.08	228.25	1016	0.01
141.10	77513	0.97	185.10	36486	0.46	229.15	14139	0.18
142.10	66934	0.84	186.15	10234	0.13	230.20	4497	0.06
143.10	120922	1.51	187.10	70980	0.89	231.15	57810	0.72
144.15	45644	0.57	188.10	39818	0.50	232.10	11047	0.14
145.10	152068	1.90	189.10	223390	2.79	233.15	27422	0.34
146.15	38774	0.48	190.10	35497	0.44	234.25	11663	0.15
147.10	234772	2.94	191.10	24495	0.31	235.15	337732	4.22
148.10	34481	0.43	192.15	7657	0.10	236.10	55956	0.70
149.10	66847	0.84	193.05	139097	1.74	237.10	6166	0.08
150.10	9074	0.11	194.10	26116	0.33	238.15	686	0.01
151.10	6343	0.08	195.05	6901	0.09	239.05	913	0.01
152.05	11515	0.14	196.10	1879	0.02	240.10	3158	0.04
153.10	25454	0.32	197.10	6482	0.08	241.05	1301	0.02
154.10	17841	0.22	198.10	3868	0.05	242.05	476	0.01
155.10	44519	0.56	199.10	7734	0.10	243.15	3197	0.04
156.10	40398	0.51	200.15	3420	0.04	244.25	3779	0.05
157.10	58356	0.73	201.10	28761	0.36	245.15	156466	1.96
158.10	22446	0.28	202.15	17182	0.21	246.15	30659	0.38
159.10	70662	0.88	203.10	907796	11.35	247.15	9479	0.12

248.15	2508	0.03
249.10	102081	1.28
250.10	19110	0.24
251.10	5425	0.07
252.05	1025	0.01
252.95	1721	0.02
254.15	942	0.01
255.10	1071	0.01
255.90	254	0.00
256.90	414	0.01
258.25	884	0.01
259.20	11455	0.14
260.25	99241	1.24
261.20	1011318	12.65
262.20	203470	2.54
263.15	33651	0.42
264.10	4510	0.06
265.05	1827	0.02
266.05	632	0.01
267.00	4140	0.05
268.05	1089	0.01
269.10	1428	0.02
270.05	506	0.01
271.00	1066	0.01
272.10	300	0.00
273.15	2222	0.03
274.25	588	0.01
275.15	6343	0.08
276.20	1570	0.02
277.20	3130	0.04
278.15	614	0.01
279.10	425	0.01
280.05	301	0.00
281.05	9258	0.12
282.05	2848	0.04
283.05	3392	0.04
284.05	1010	0.01
285.05	911	0.01
286.00	284	0.00
287.15	1007	0.01
288.25	779	0.01
289.20	19556	0.24
290.25	6051	0.08
291.20	143193	1.79
292.15	29289	0.37
293.15	3871	0.05
294.15	653	0.01
295.15	743	0.01
296.00	142	0.00
297.00	1172	0.01
298.00	215	0.00
299.00	394	0.00
300.00	121	0.00
301.00	151	0.00
302.00	74	0.00
303.05	402	0.01
304.25	3560	0.04
305.20	293572	3.67
306.20	166860	2.09
307.20	31138	0.39
308.20	4695	0.06
309.15	706	0.01
310.20	154	0.00
311.20	334	0.00
312.00	154	0.00
313.00	1055	0.01
314.10	399	0.00
315.10	281	0.00
316.10	300	0.00
317.10	44	0.00
318.10	50	0.00
319.10	87	0.00
320.10	82	0.00
321.10	90	0.00
322.10	76	0.00
323.10	249	0.00
324.10	217	0.00
325.05	980	0.01
326.00	2215	0.03
327.00	3666	0.05
327.95	1088	0.01
329.00	959	0.01
330.00	167	0.00
331.00	182	0.00
332.00	62	0.00
333.00	74	0.00
334.10	145	0.00
335.05	653	0.01
336.10	129	0.00
337.10	190	0.00
338.10	119	0.00
339.10	172	0.00
340.00	385	0.00
341.05	5595	0.07
342.05	2148	0.03
343.05	2356	0.03
343.90	660	0.01
345.10	935	0.01
346.25	873	0.01
347.25	88104	1.10
348.20	20510	0.26
349.20	3463	0.04
350.20	375	0.00
351.20	42	0.00
352.20	62	0.00
353.20	135	0.00
354.10	76	0.00
355.05	5282	0.07
356.00	1679	0.02
357.05	1206	0.02
358.05	690	0.01
359.05	1002	0.01
360.05	326	0.00
361.35	**11494**	**0.14**
362.25	**858878**	**10.74**
363.25	**221507**	**2.77**
364.25	33198	0.42
365.25	3985	0.05
366.15	388	0.00
367.20	201	0.00
368.10	134	0.00

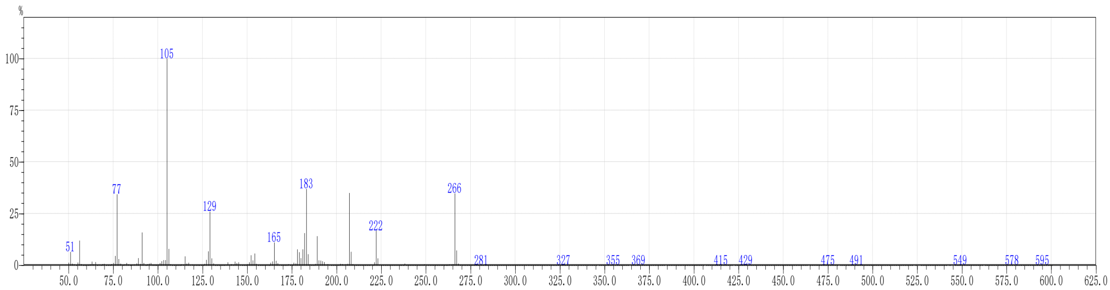


Chemical Formula: $C_{18}H_{18}O_2$
Exact Mass: 266.1307





MS spectra of the peak at 11.749 min



[MS Spectrum]
# of Peaks 537
Raw Spectrum 11.750 (scan : 1551)
Background No Background Spectrum
Base Peak m/z 105.05 (Inten : 5,971,653)
Event# 1

m/z	Absolute Intensity	Relative Intensity			
50.0577445	1.30	59.051562	0.03	68.056108	0.10
51.00393292	6.59	60.053540.01		69.0535882	0.60
52.0550576	0.85	61.052491	0.04	70.0041250	0.69
53.0034466	0.58	62.0522705	0.38	70.953780	0.06
54.1510354	0.17	63.05105790	1.77	72.057980.01	
55.1585048	1.42	64.0530253	0.51	73.056600	0.11
56.05757084	12.68	65.05100354	1.68	74.0036238	0.61
57.0537101	0.62	66.058535	0.14	75.0568312	1.14
58.052121	0.04	67.0511591	0.19	76.05270163	4.52

77.052104186		35.24	121.10	1118	0.02	165.05	576880	9.66
78.05186486	3.12		122.05	1644	0.03	166.05	108960	1.82
79.0556067	0.94		123.00	1250	0.02	167.05	55891	0.94
80.553598	0.06		124.05	1339	0.02	168.10	8321	0.14
81.5528044	0.47		125.10	6210	0.10	169.05	992 0.02	
82.5068313	1.14		126.10	46540	0.78	170.00	193 0.00	
83.4516796	0.28		127.10	152484	2.55	171.00	273 0.00	
84.452176	0.04		128.10	395974	6.63	172.05	400 0.01	
85.051869	0.03		129.10	1495985	25.05	173.05	29741	0.50
86.0511884	0.20		130.10	188775	3.16	174.00	6865	0.11
87.0525985	0.44		131.10	56953	0.95	175.05	6453	0.11
88.1055270	0.93		132.10	6769	0.11	176.05	61939	1.04
89.05198213	3.32		133.10	4318	0.07	177.15	48611	0.81
90.1547538	0.80		134.15	736 0.01		178.05	384464	6.44
91.05976490	16.35		135.05	1679	0.03	179.05	318420	5.33
92.0567315	1.13		136.15	522 0.01		180.05	141423	2.37
93.155869	0.10		137.05	7824	0.13	181.05	415439	6.96
94.1531561	0.53		138.15	9559	0.16	182.05	866211	14.51
95.0548912	0.82		139.10	86817	1.45	183.05	2032609	34.04
96.0572027	1.21		140.10	12686	0.21	184.05	285618	4.78
97.057420	0.12		141.10	30970	0.52	185.00	21593	0.36
98.108575	0.14		142.15	10469	0.18	186.00	1478	0.02
99.058345	0.14		143.10	103559	1.73	187.05	4270	0.07
100.15	15511	0.26	144.10	57927	0.97	188.15	40923	0.69
101.10	65854	1.10	145.10	85289	1.43	189.05	754157	12.63
102.10	112268	1.88	146.10	10190	0.17	190.05	129386	2.17
103.10	147340	2.47	147.05	2037	0.03	191.05	122400	2.05
104.15	152804	2.56	148.15	439 0.01		192.05	100879	1.69
105.05	5971653	100.00	149.10	3185	0.05	193.05	78990	1.32
106.05	463827	7.77	150.10	27090	0.45	194.05	15646	0.26
107.10	30028	0.50	151.10	80762	1.35	195.05	30921	0.52
108.05	4104	0.07	152.05	261494	4.38	196.05	9379	0.16
109.15	2577	0.04	153.10	131265	2.20	197.00	1266	0.02
110.10	5863	0.10	154.10	311713	5.22	198.05	499 0.01	
111.05	5012	0.08	155.10	40558	0.68	199.05	664 0.01	
112.15	2333	0.04	156.05	2911	0.05	200.00	5927	0.10
113.05	26651	0.45	157.10	724 0.01		201.00	7041	0.12
114.15	15955	0.27	158.15	487 0.01		202.05	39705	0.66
115.10	255750	4.28	159.05	6036	0.10	203.05	33960	0.57
116.10	48113	0.81	160.10	2554	0.04	204.00	18479	0.31
117.10	76118	1.27	161.10	13071	0.22	205.05	24522	0.41
118.10	11903	0.20	162.15	8020	0.13	206.15	39956	0.67
119.10	20694	0.35	163.05	69195	1.16	207.10	1849436	30.97
120.05	2699	0.05	164.10	102956	1.72	208.05	328826	5.51

209.05	29460	0.49
210.05	2561	0.04
211.10	358	0.01
212.00	185	0.00
213.00	962	0.02
214.05	384	0.01
215.05	2818	0.05
216.10	924	0.02
217.05	801	0.01
218.05	1636	0.03
219.05	3241	0.05
220.15	4129	0.07
221.15	72453	1.21
222.10	863134	14.45
223.10	168956	2.83
224.05	16098	0.27
225.05	1186	0.02
226.10	84	0.00
228.10	47	0.00
229.10	238	0.00
230.10	46	0.00
231.10	487	0.01
232.05	762	0.01
233.05	2691	0.05
234.05	1577	0.03
235.10	1430	0.02
236.05	1557	0.03
237.15	4990	0.08
238.10	39902	0.67
239.05	7268	0.12
240.05	1511	0.03
241.10	122	0.00
242.10	108	0.00
243.10	16	0.00
244.10	31	0.00
245.10	42	0.00
246.10	74	0.00
247.10	266	0.00
248.10	1023	0.02
249.10	6319	0.11
250.10	2498	0.04
251.05	1165	0.02
252.00	268	0.00
253.00	318	0.01
254.00	63	0.00
255.00	97	0.00
256.00	137	0.00
257.00	36	0.00
258.00	47	0.00
259.00	31	0.00
260.00	18	0.00
261.00	42	0.00
262.10	126	0.00
263.10	5124	0.09
264.15	4914	0.08
265.15	**27727**	**0.46**
266.10	**1657436**	**27.76**
267.10	**335959**	**5.63**
268.05	38532	0.65
269.05	3582	0.06
270.10	305	0.01
271.10	105	0.00
272.10	46	0.00
273.10	19	0.00

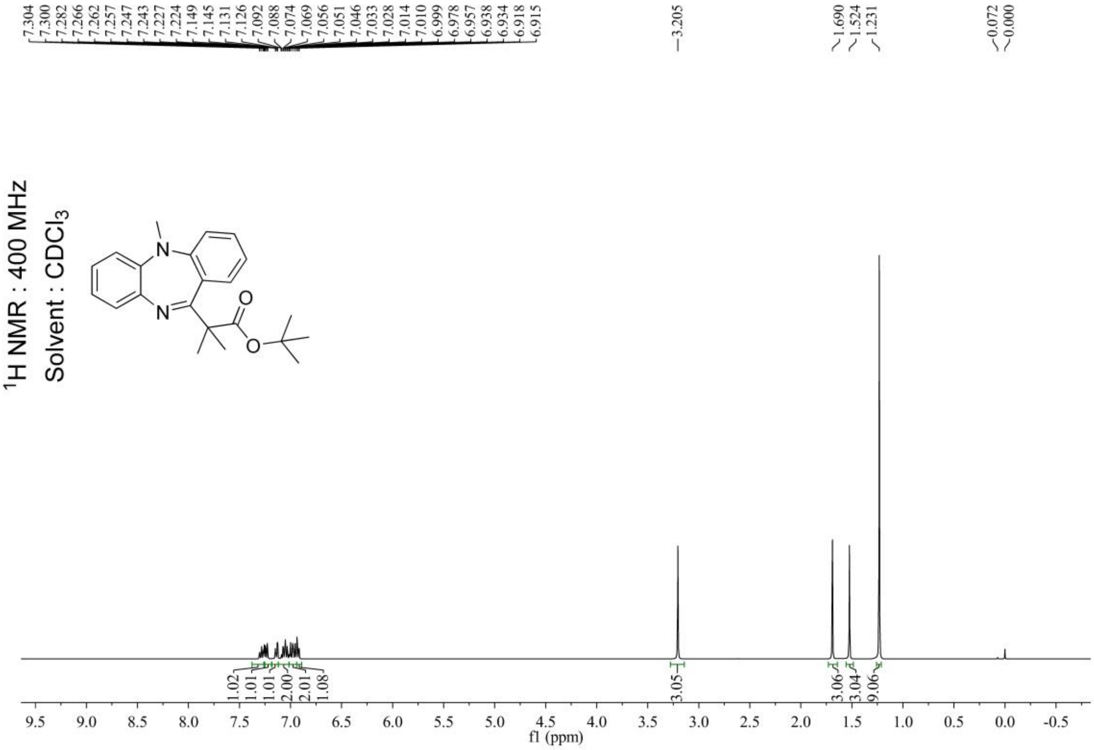
3.Reference

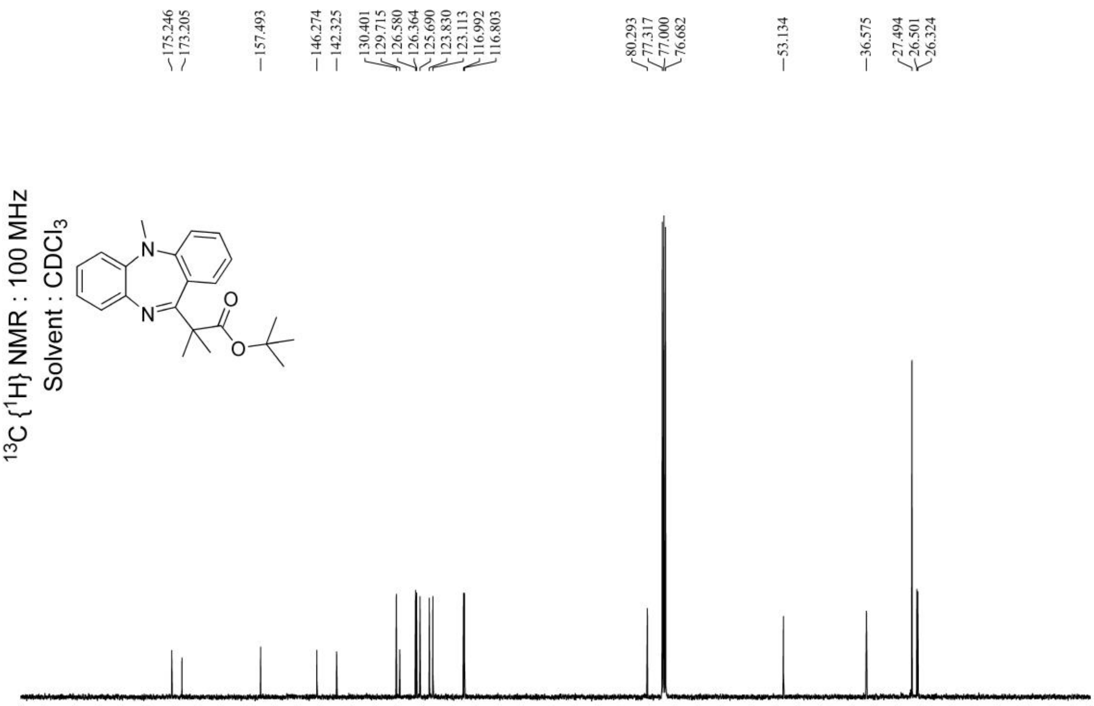
【1】W. Hu, F. Teng, H. Hu, S. Luo and Q. Zhu, *J. Org. Chem.,* **2019**, 84, 6524-6535.

【2】S. Yuan, X. Ye, J. Cai, Z. Song, Y. Tan, Y. Peng and Q. Ding, *J. Org. Chem.,* **2022**, 87, 1485-1492.

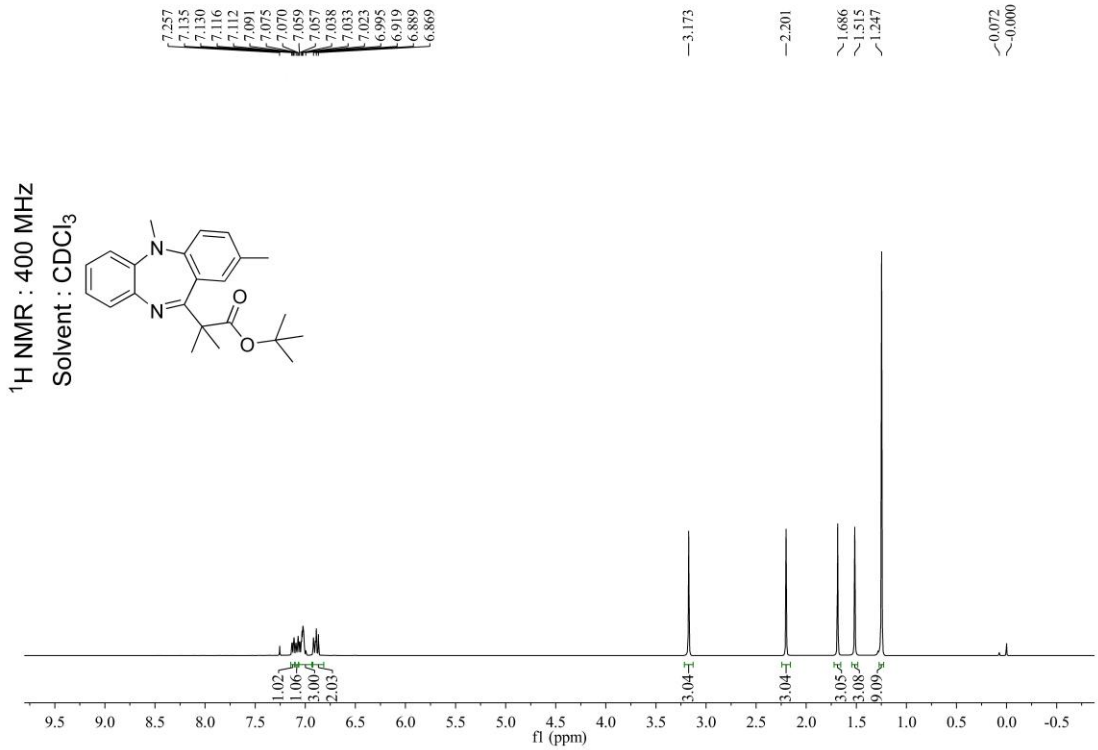
4.Spectra

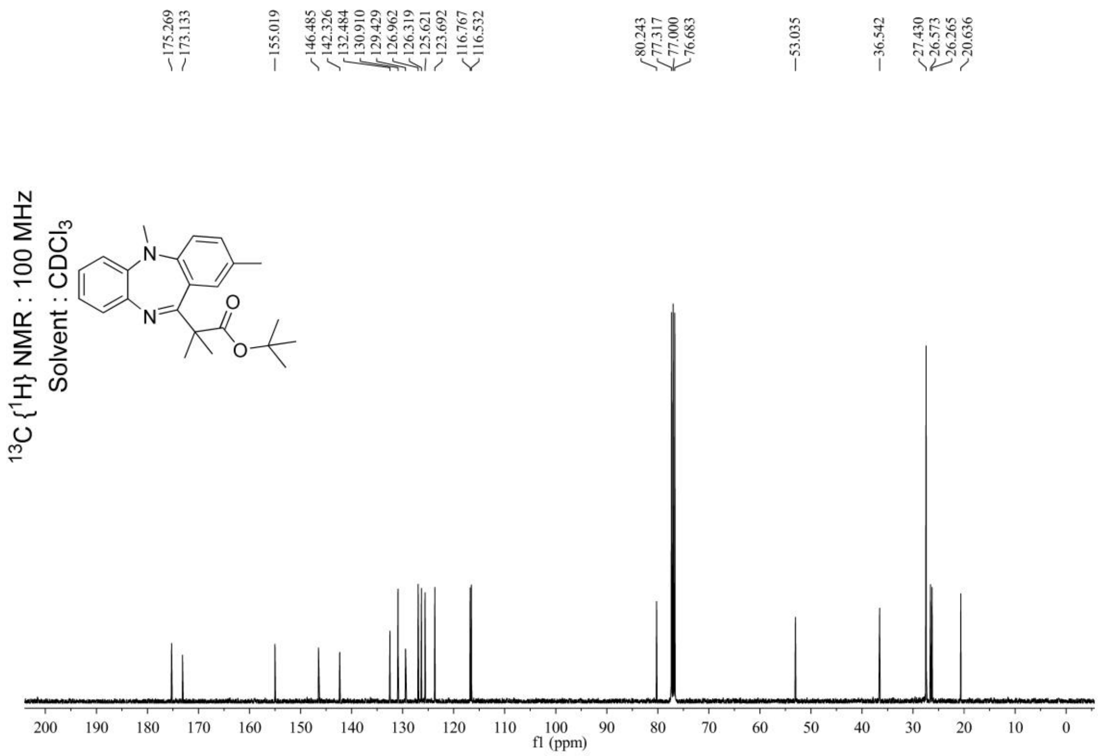
*t*ert-Butyl 2-methyl-2-(5-methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepin-11-yl)propanoate (3aa)



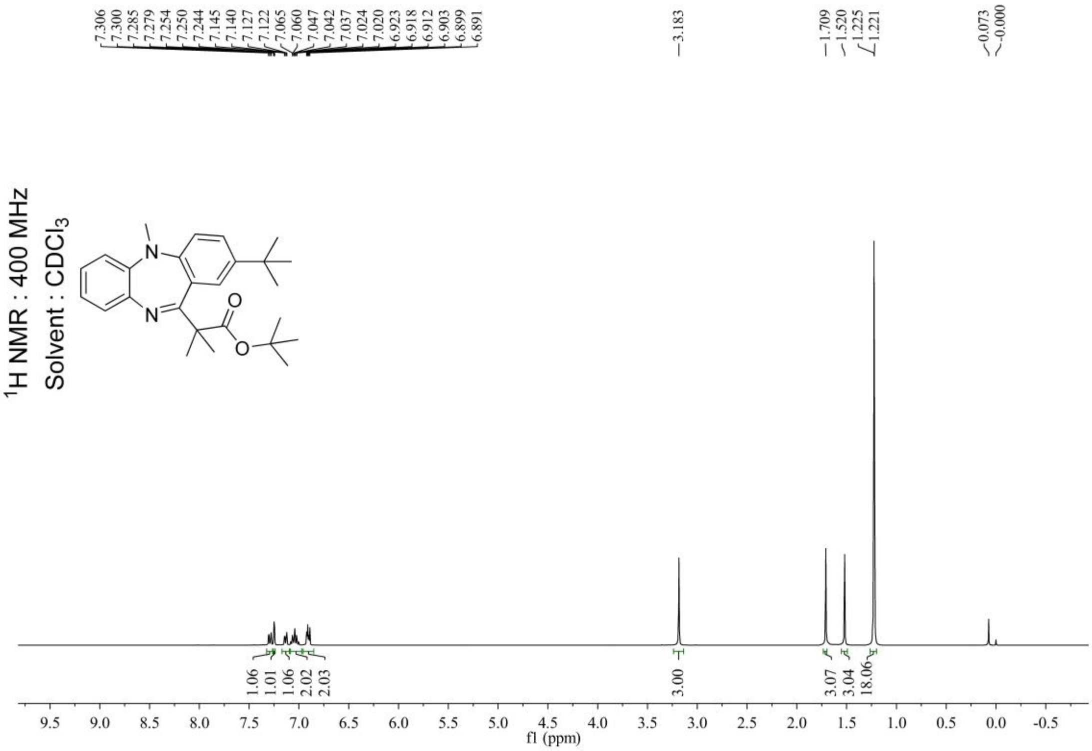


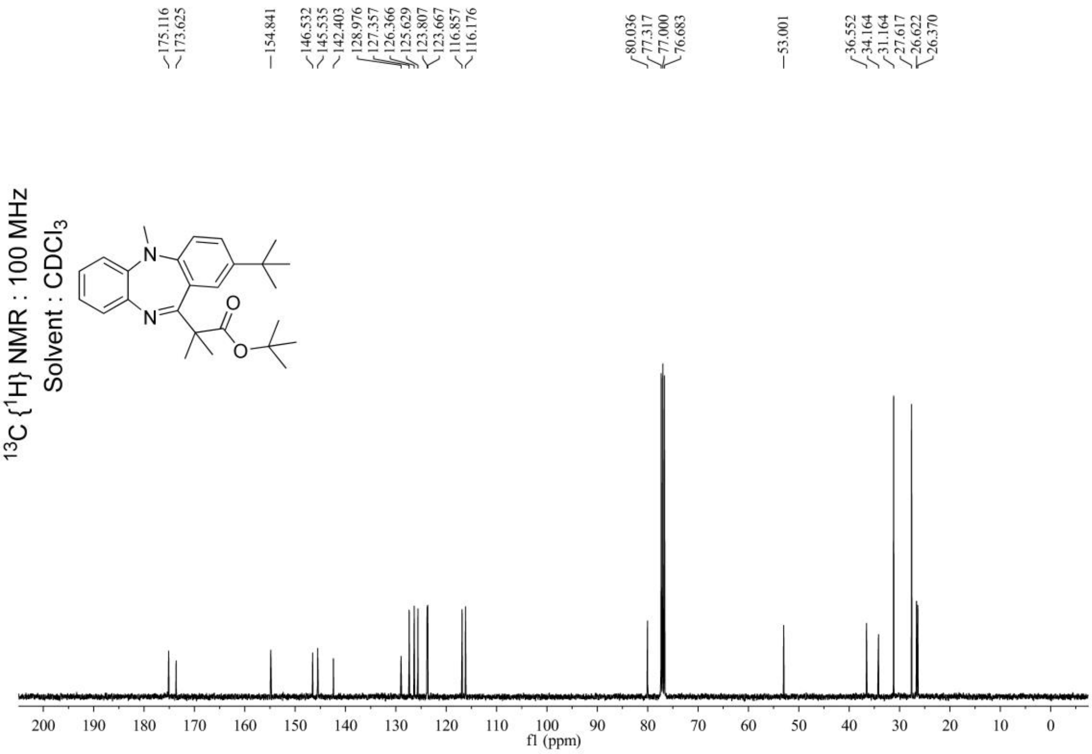
tert-Butyl 2-(2,5-dimethyl-5_H_-dibenzo[_b,e_][1,4]diazepin-11-yl)-2-methylpropanoate(3ba)



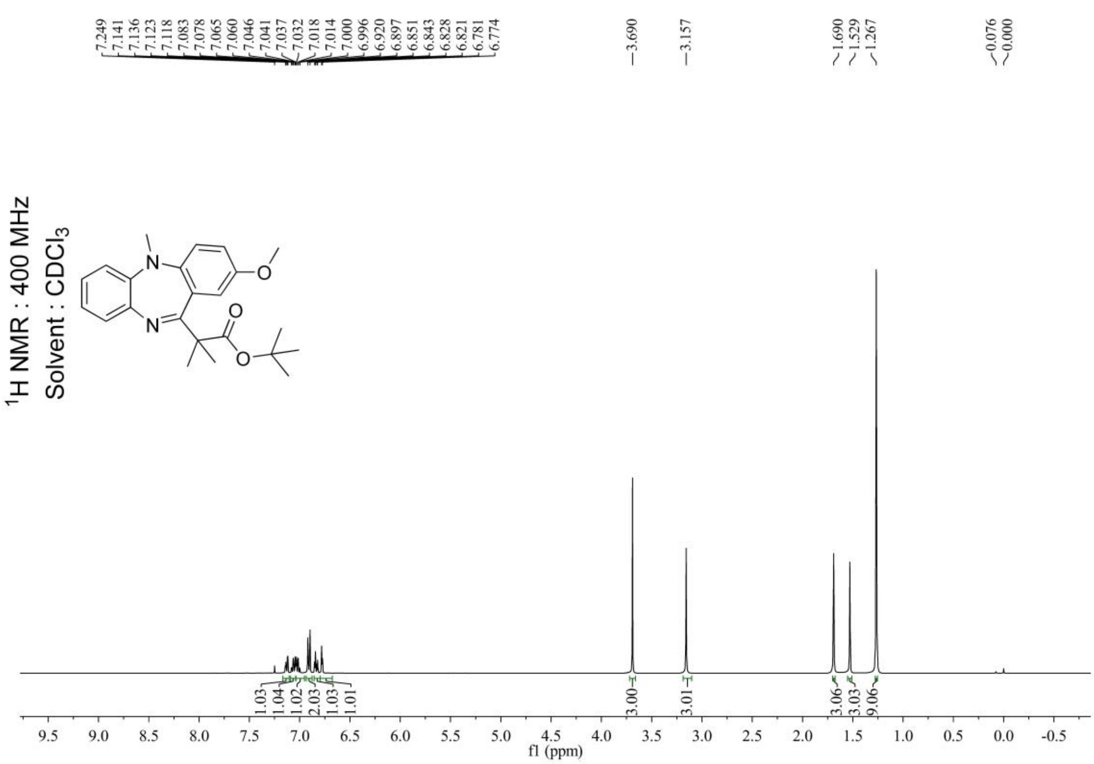


tert-Butyl 2-(2-(tert-butoxy)-5-methyl-5_H_-dibenzo[_b,e_][1,4]diazepin-11-yl)-2-methylpropanoate(3ca)

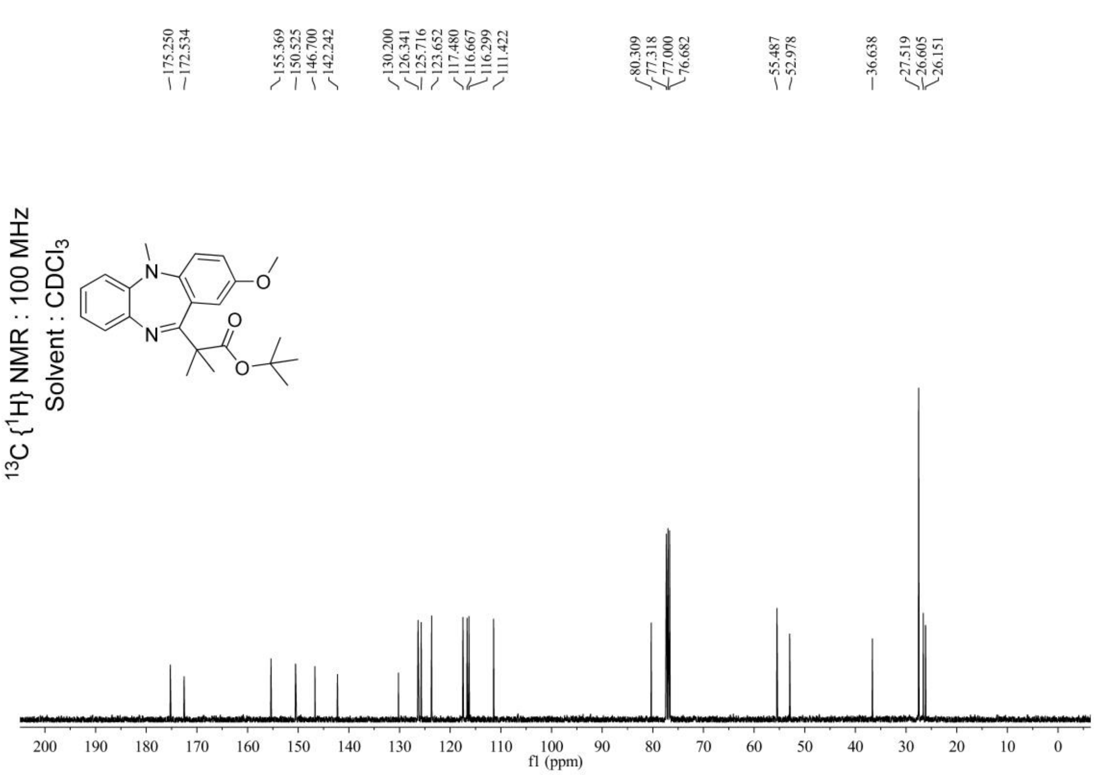




tert-Butyl 2-(2-methoxy-5-methyl-5_H_-dibenzo[_b,e_][1,4]diazepin-11-yl)-2-methylpropanoate(3da)

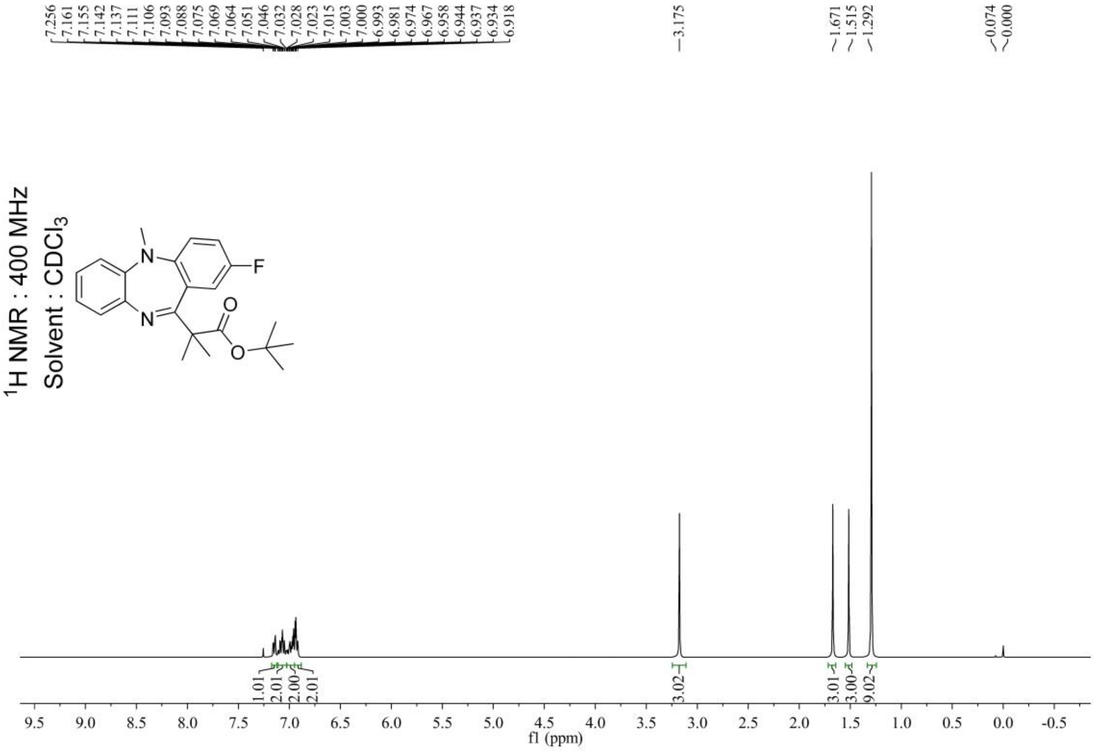


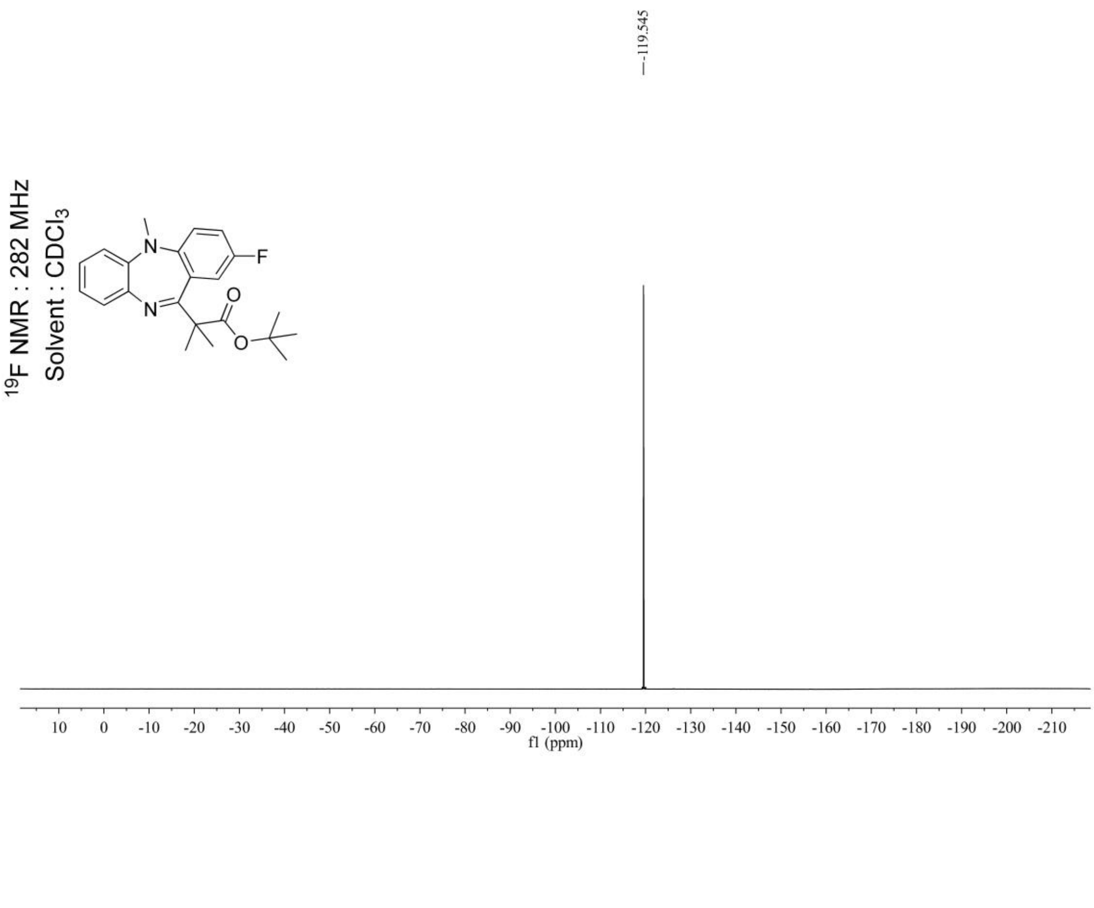
1H NMR : 400 MHz
Solvent : CDCl3
7.249
7.141
7.136
7.123
7.118
7.083
7.078
7.065
7.060
7.046
7.041
7.037
7.032
7.018
7.014
7.000
6.996
6.920
6.897
6.851
6.843
6.828
6.821
6.781
6.774
3.690
3.157
1.690
1.529
1.267
0.076
0.000
1.03
1.04
1.02
2.03
1.03
1.01
3.00
3.01
3.06
3.03
9.06
N
O
f1 (ppm)

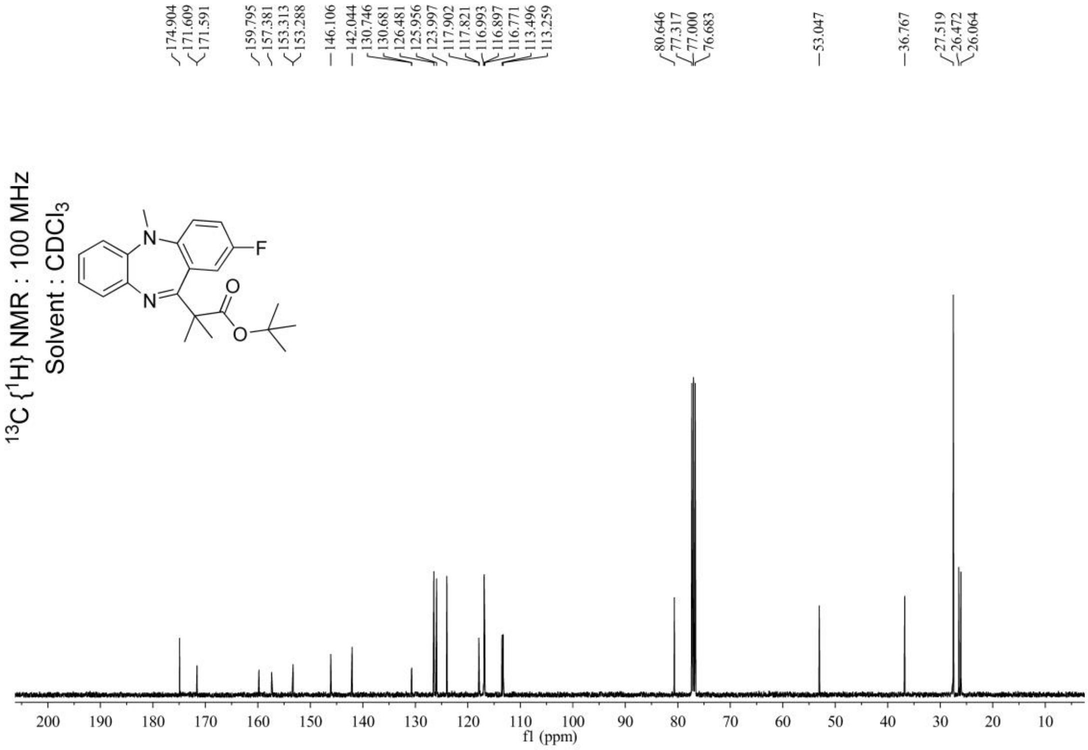


13C {1H} NMR : 100 MHz
Solvent : CDCl3
175.250
172.534
155.369
150.525
146.700
142.242
130.200
126.341
125.716
123.652
117.480
116.667
116.299
111.422
80.309
77.318
77.000
76.682
55.487
52.978
36.638
27.519
26.605
26.151
N
O
f1 (ppm)

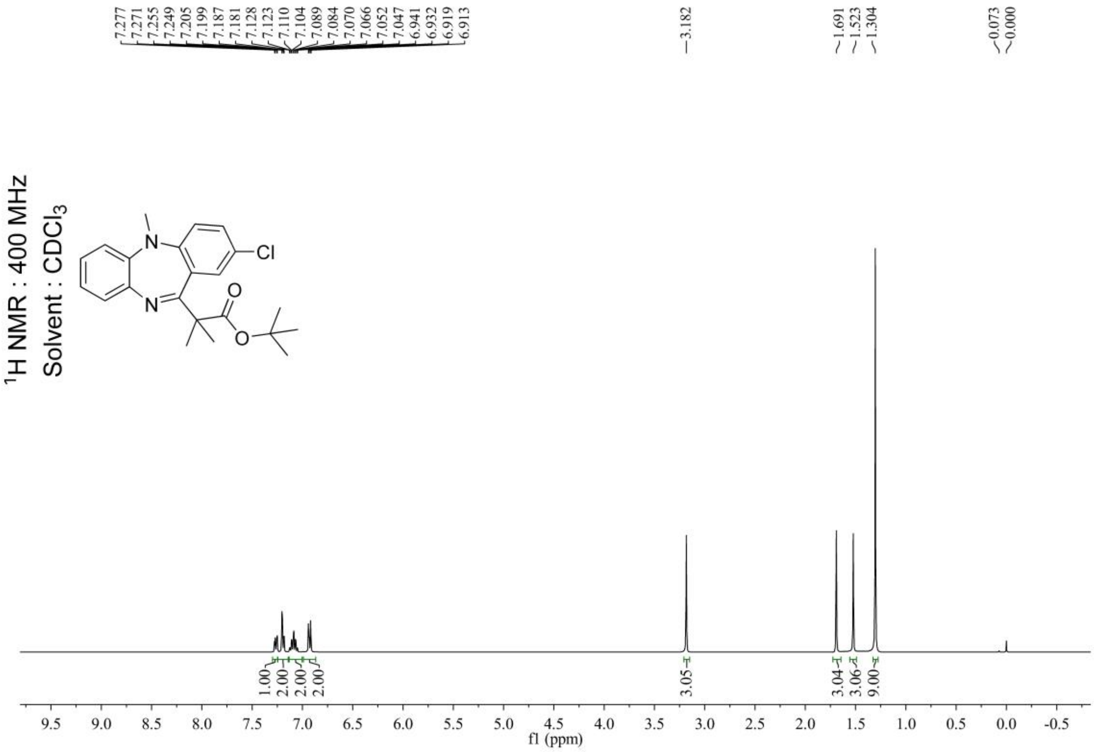
tert-Butyl 2-(2-fluoro-5-methyl-5_H_-dibenzo[_b,e_][1,4]diazepin-11-yl)-2-methylpropanoate(3ea)

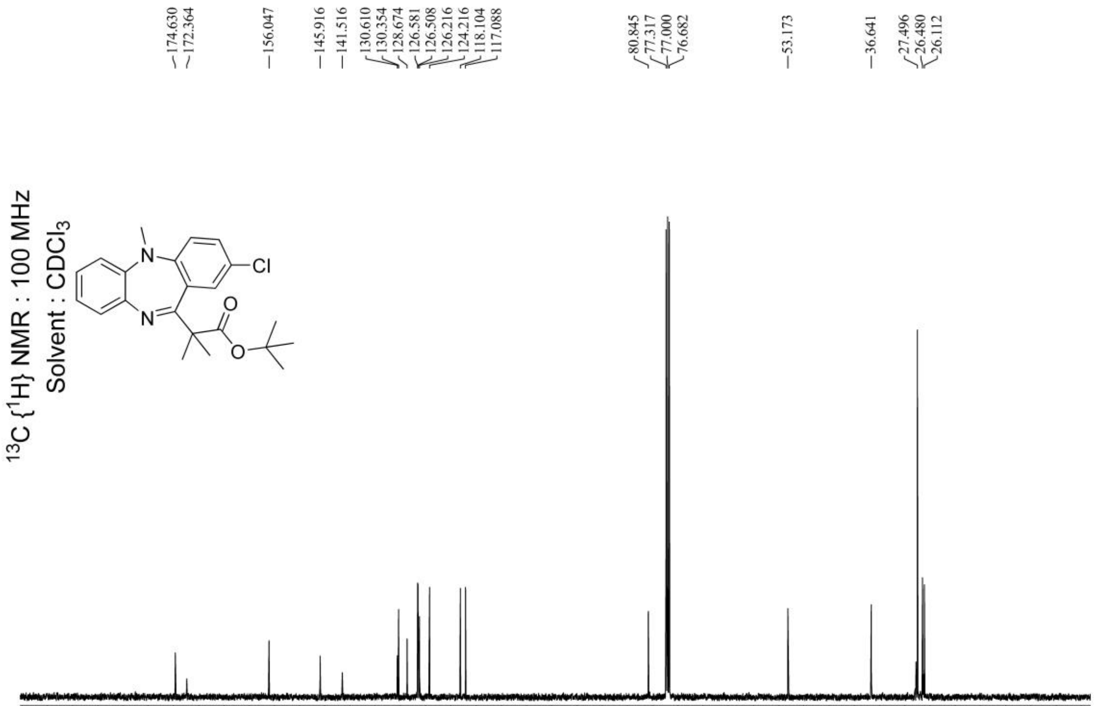




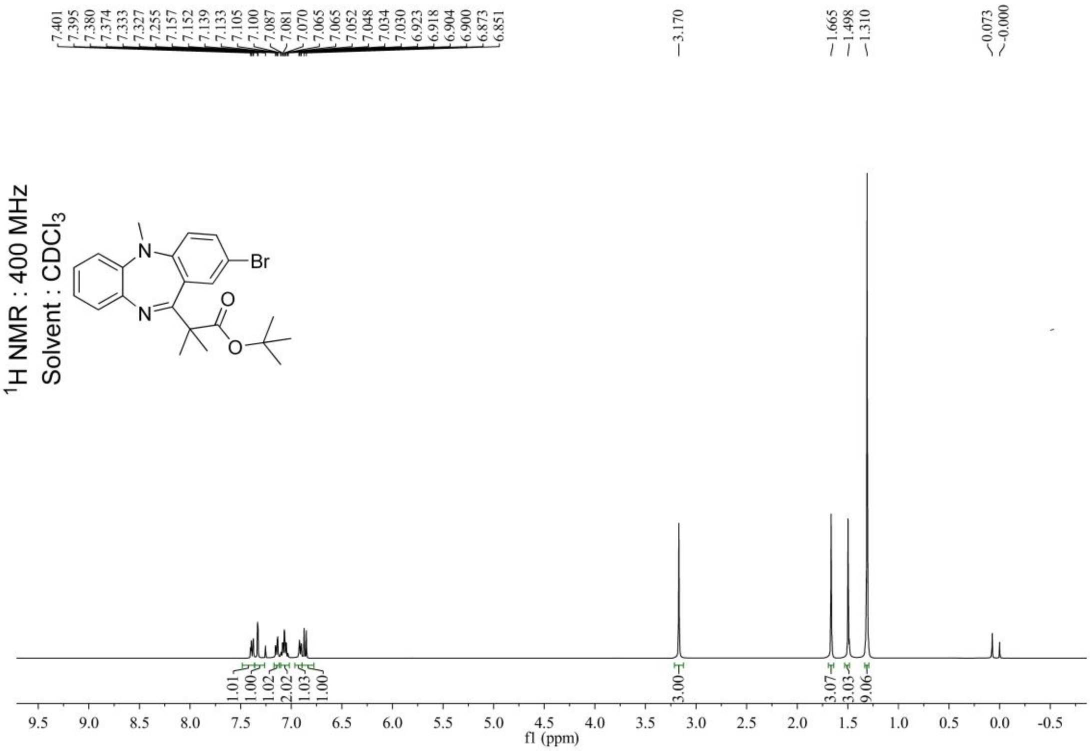

13C {1H} NMR : 100 MHz
Solvent : CDCl3
N
N
F
O
O
174.904
171.609
171.591
159.795
157.381
153.313
153.288
146.106
142.044
130.746
130.681
126.481
125.956
123.997
117.902
117.821
116.993
116.897
116.771
113.496
113.259
80.646
77.317
77.000
76.683
53.047
36.767
27.519
26.472
26.064
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

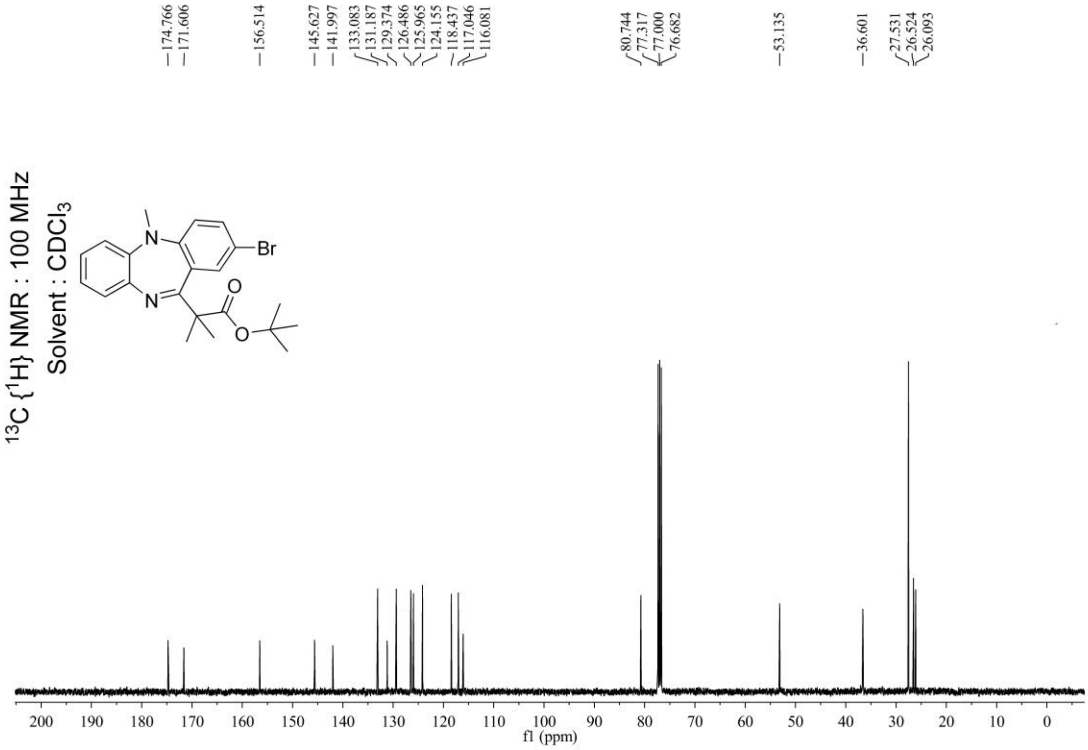
tert-Butyl 2-(2-chloro-5-methyl-5_H_-dibenzo[_b_,_e_][1,4]diazepin-11-yl)-2-methylpropanoate(3fa)



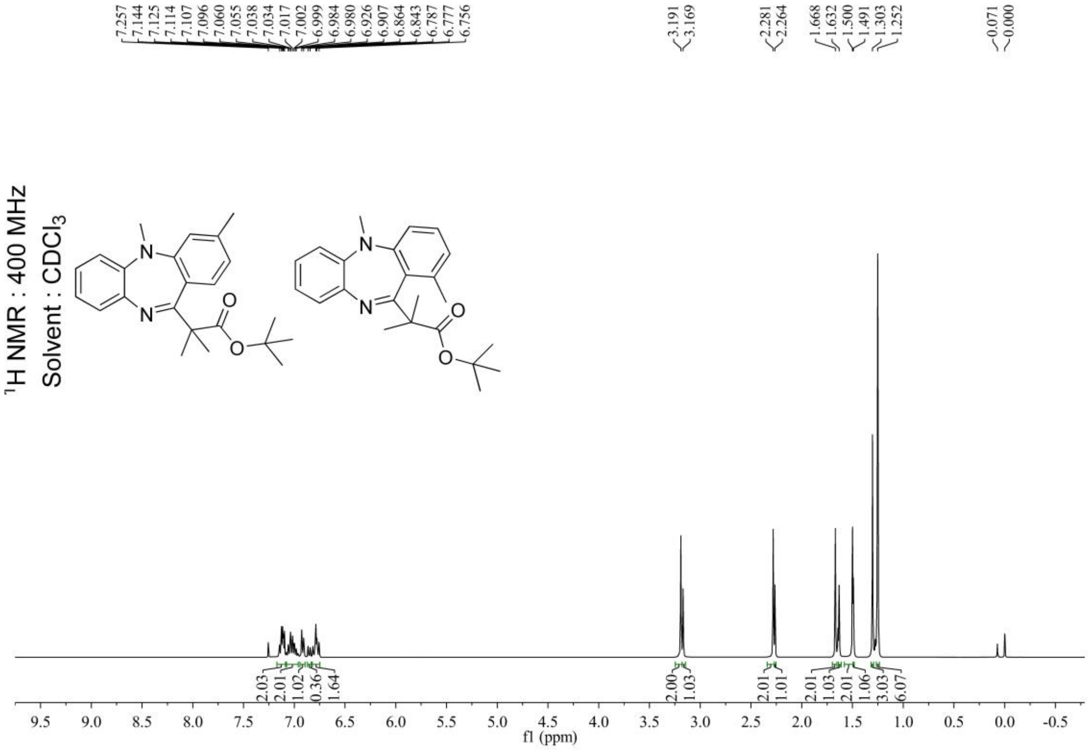


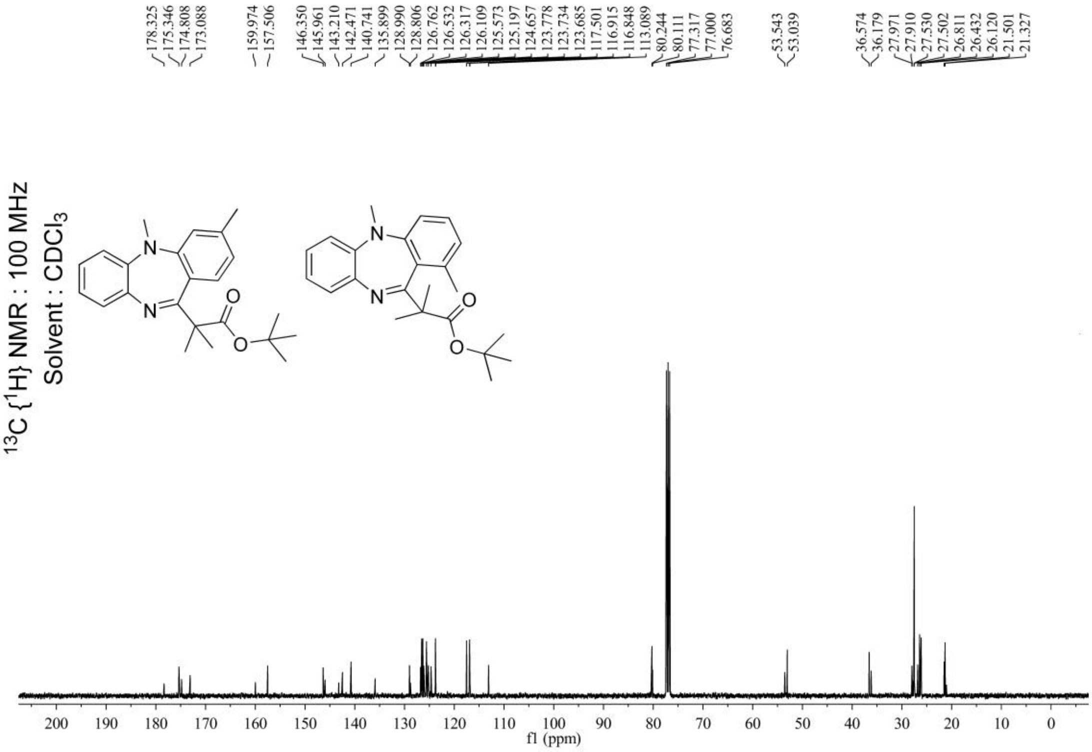
tert-Butyl 2-(2-bromo-5-methyl-5_H_-dibenzo[_b,e_][1,4]diazepin-11-yl)-2-methylpropanoate(3ga)



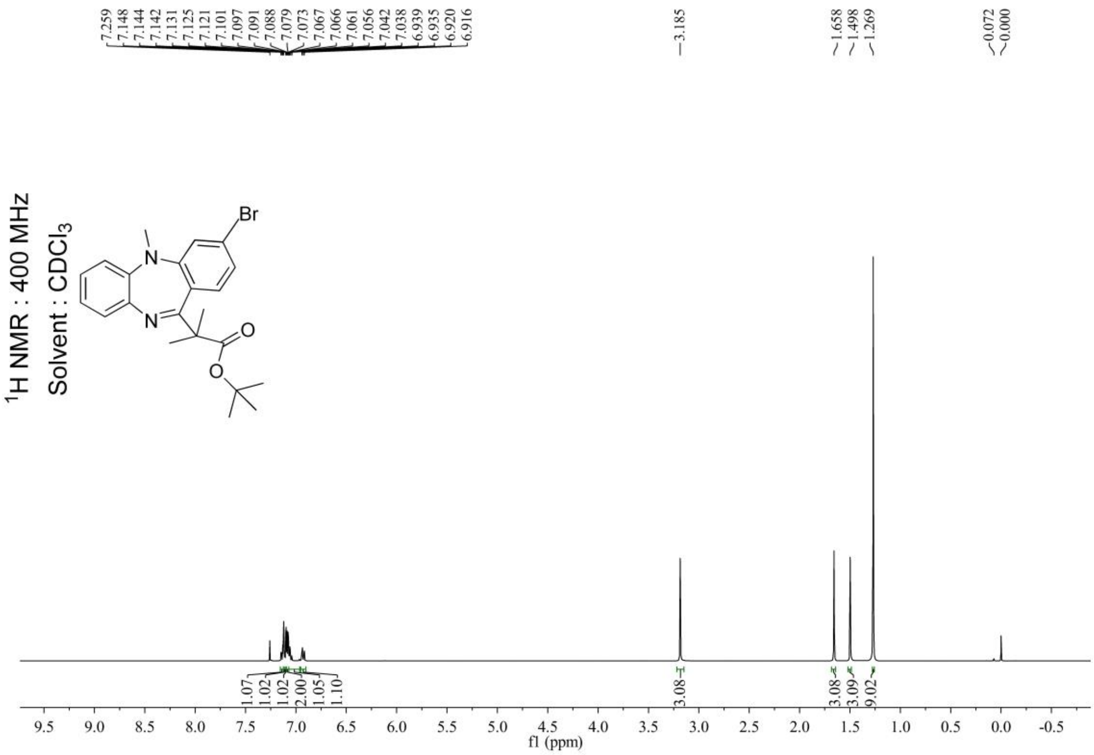


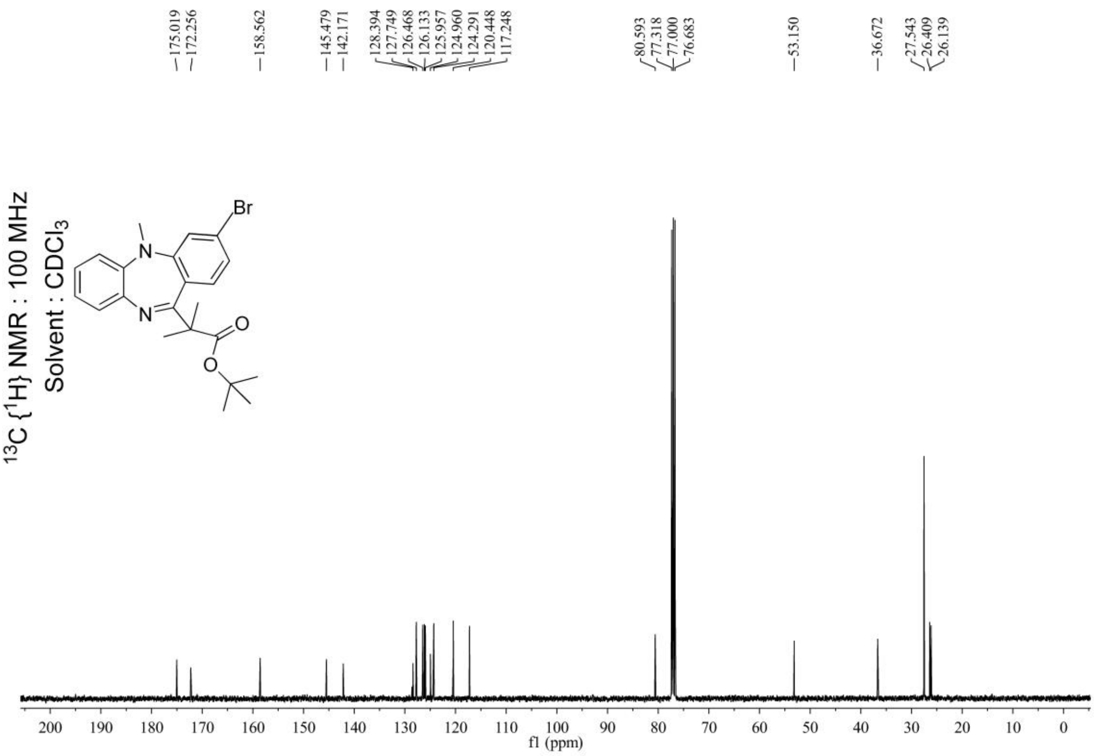
tert-Butyl 2-(3-bromo-5-methyl-5_H_-dibenzo[_b,e_][1,4]diazepin-11-yl)-2-methylpropanoate（3ha）andtert-butyl 2-(1-bromo-5-methyl-5_H_-dibenzo[_b,e_][1,4]diazepin-11-yl)-2-methylpropanoate(3ha')



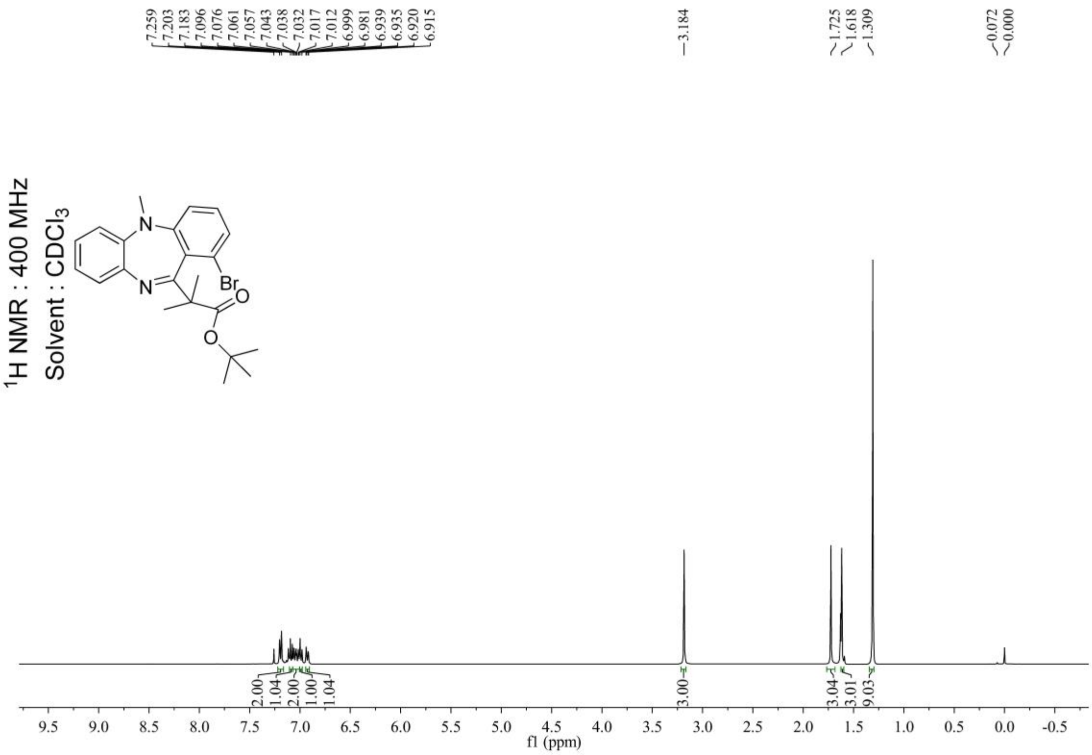


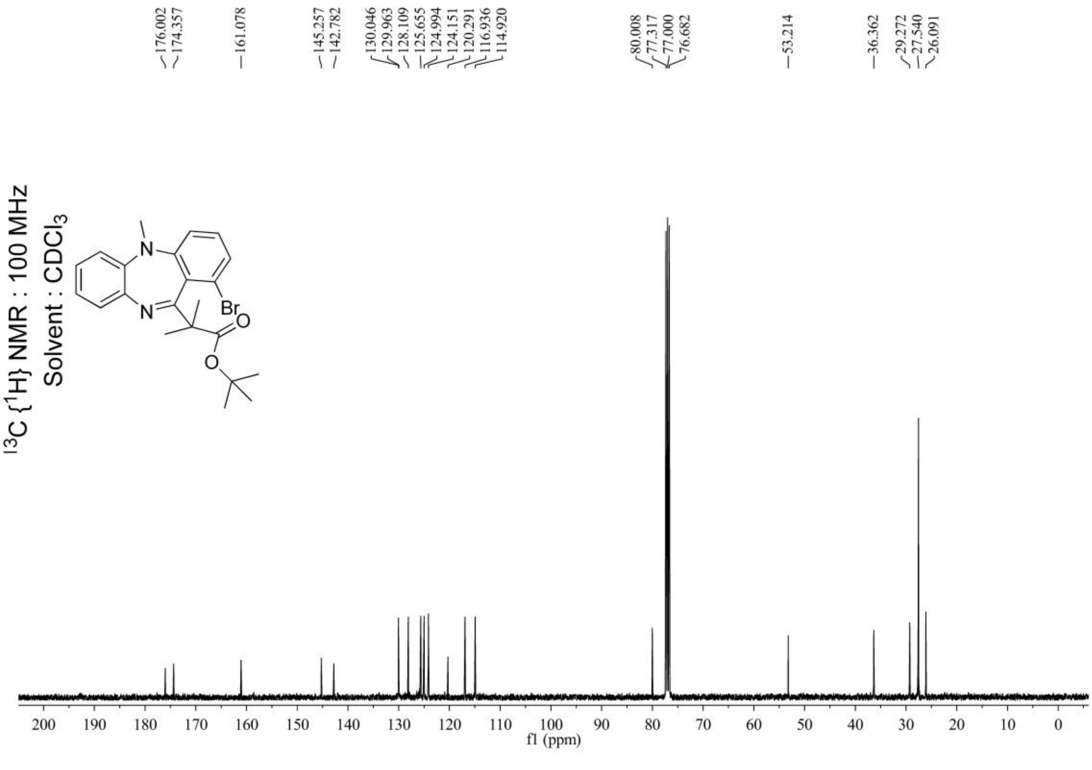
tert-Butyl 2-(3-bromo-5-methyl-5_H_-dibenzo[_b,e_][1,4]diazepin-11-yl)-2-methylpropanoate(3ia)



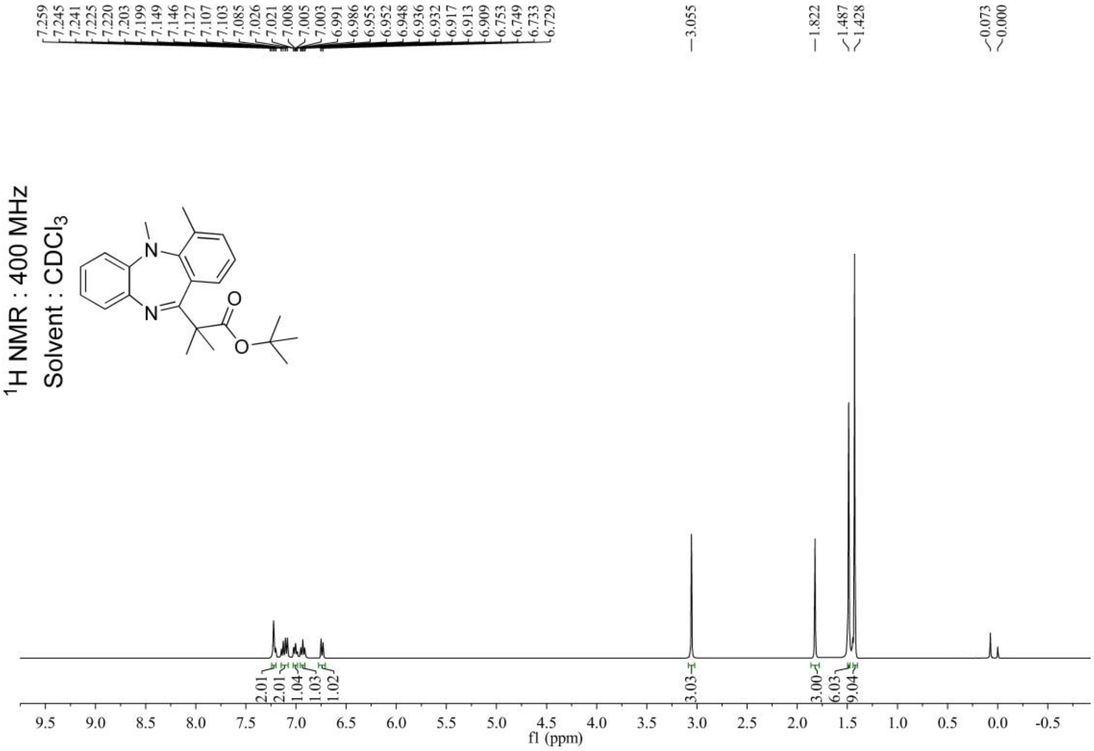


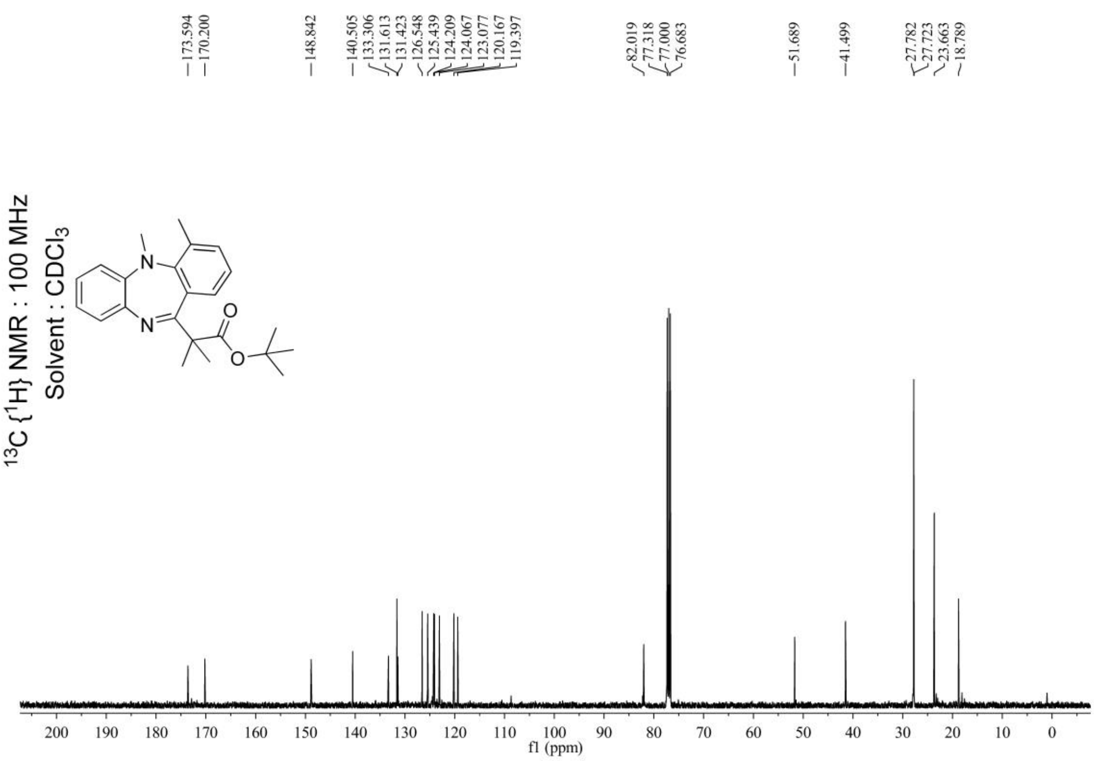
***tert*-Butyl 2-(1-bromo-5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepin-11-yl)-2-methylpropanoate(3ia')**



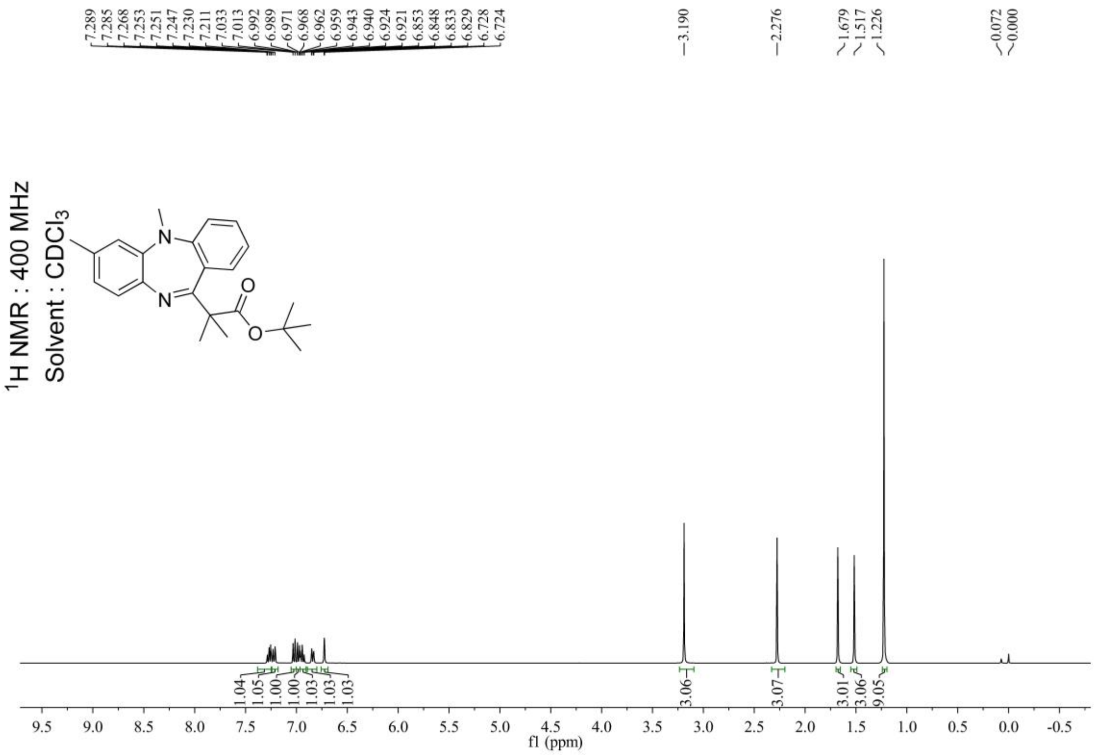


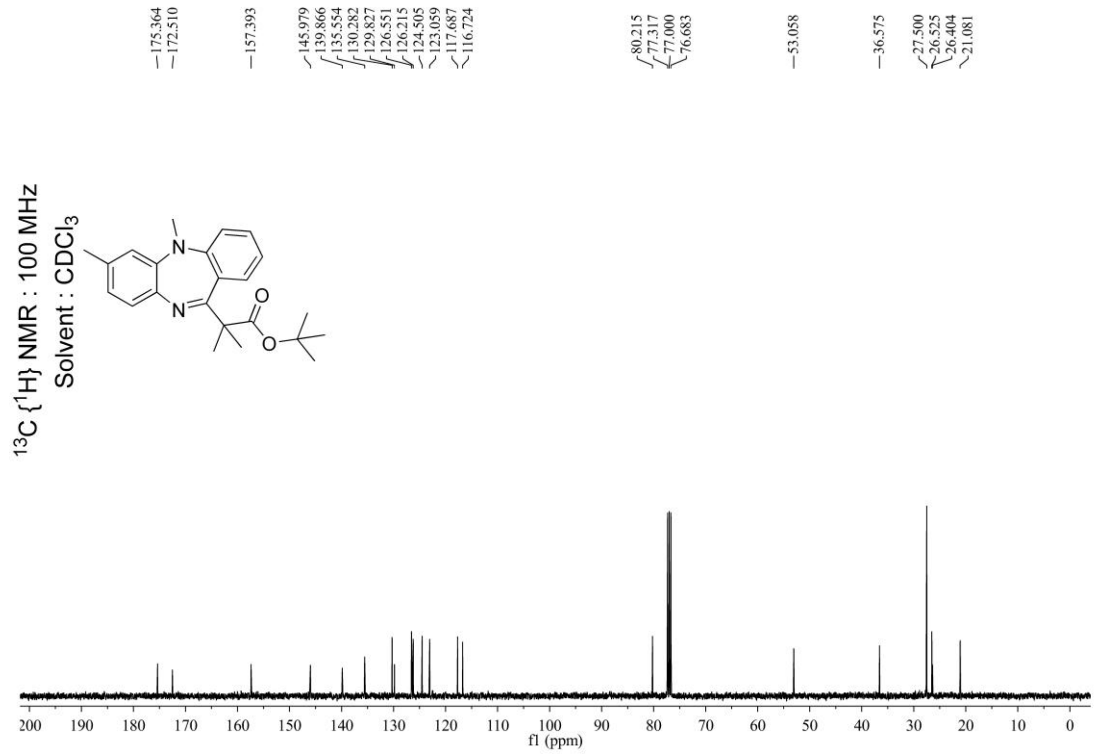
tert-Butyl 2-(4,5-dimethyl-5_H_-dibenzo[_b,e_][1,4]diazepin-11-yl)-2-methylpropanoate(3ja)



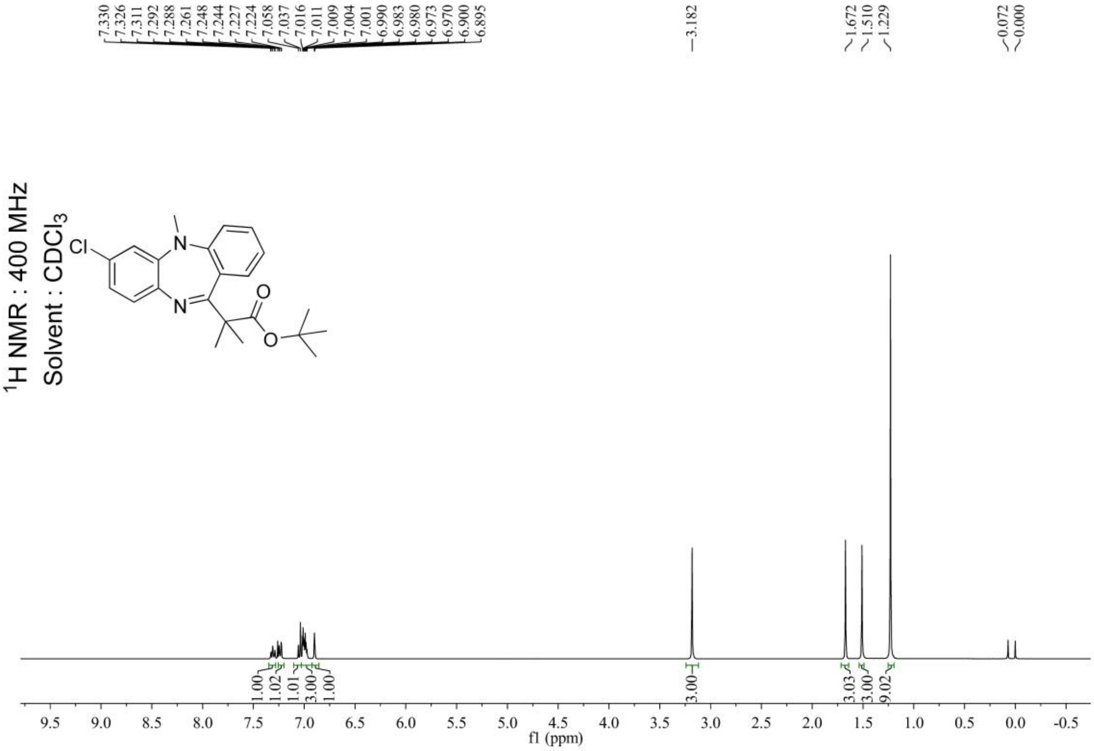


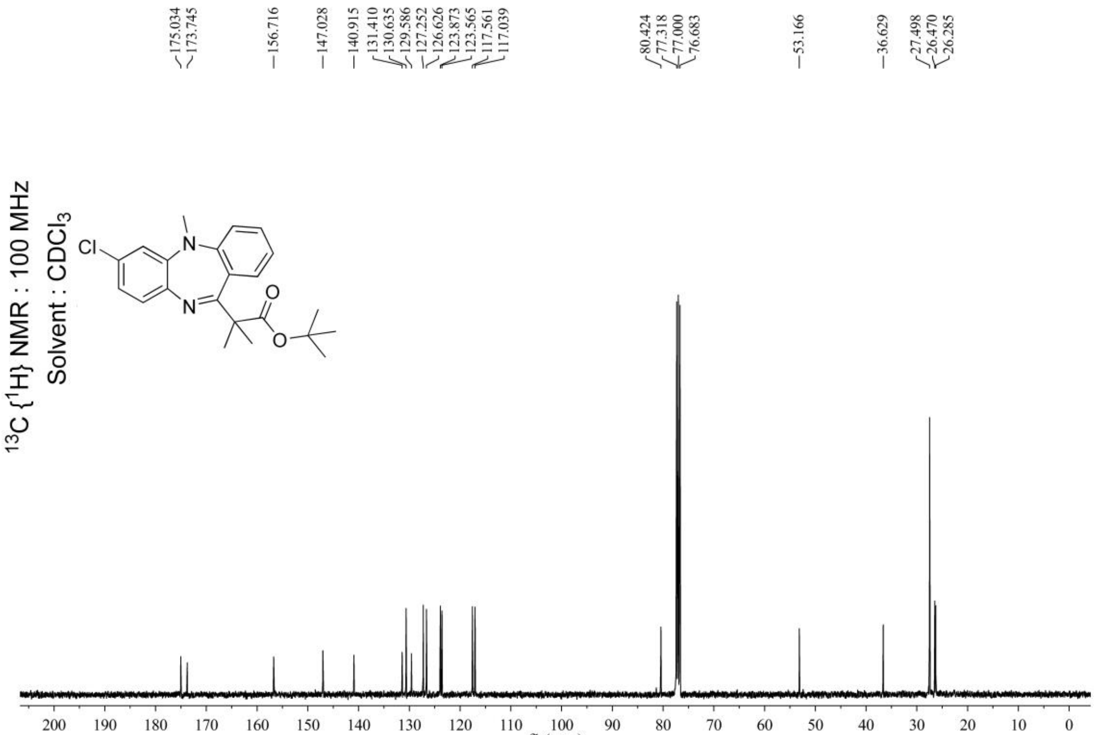
tert-Butyl 2-(5,7-dimethyl-5_H_-dibenzo[_b,e_][1,4]diazepin-11-yl)-2-methylpropanoate(3ka)



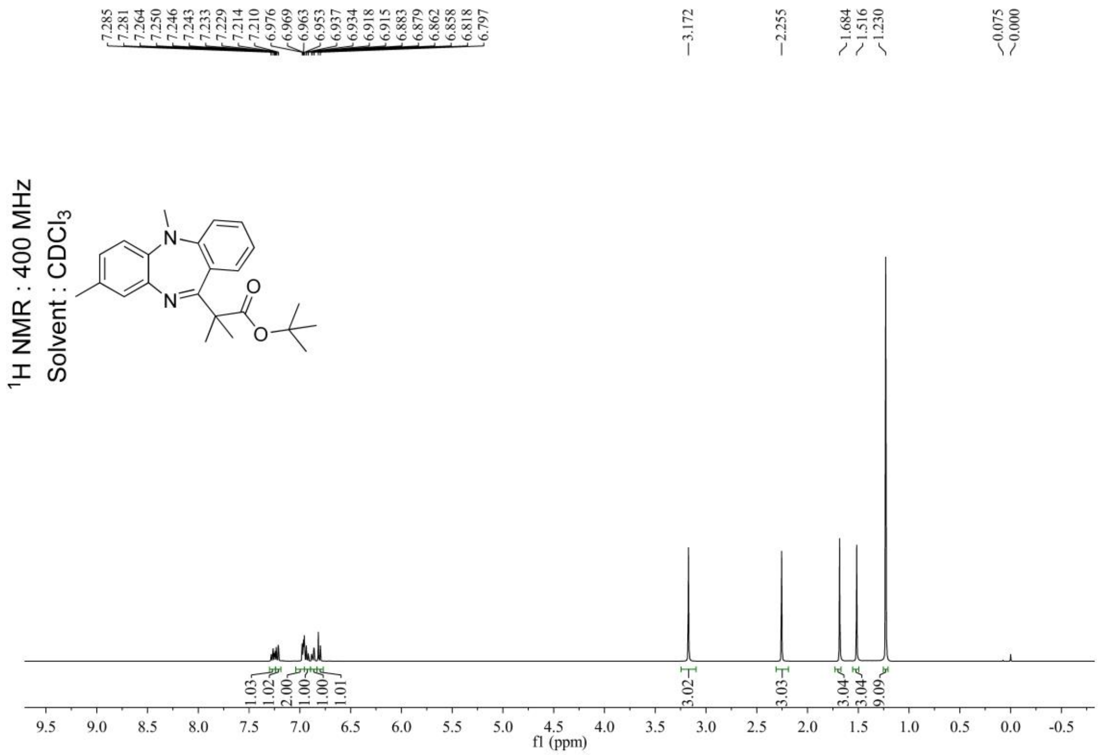


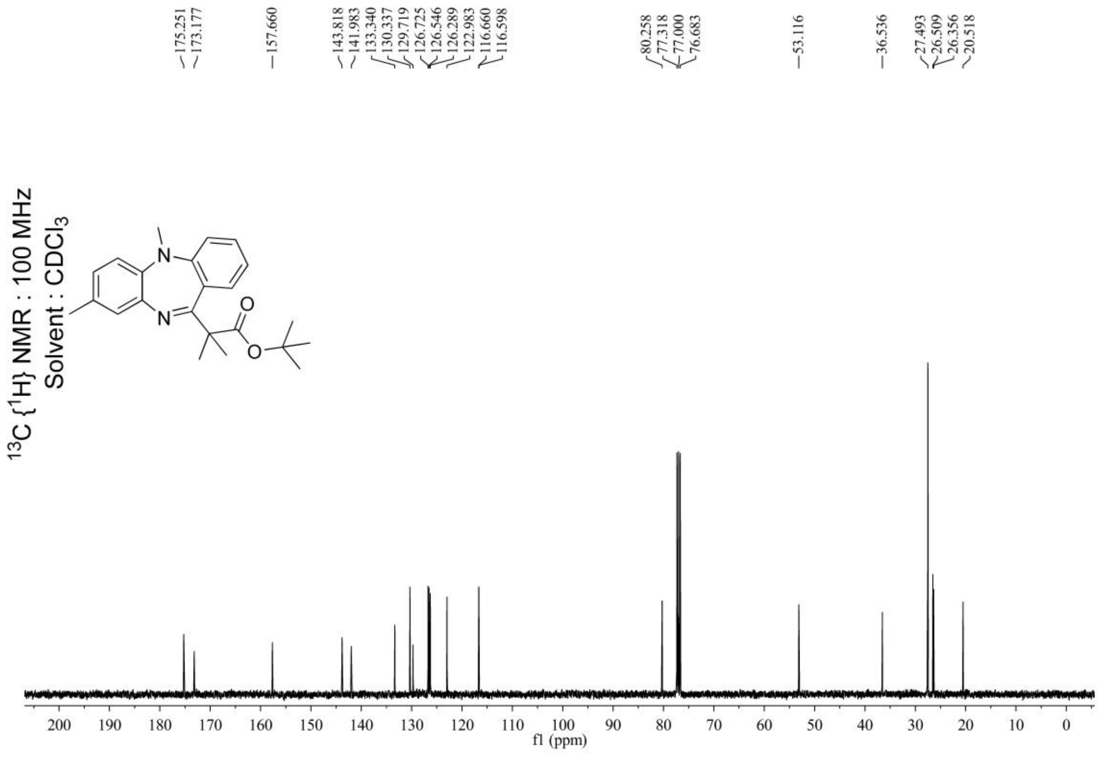
***tert*-Butyl 2-(7-chloro-5-methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepin-11-yl)-2-methylpropanoate(3la)**



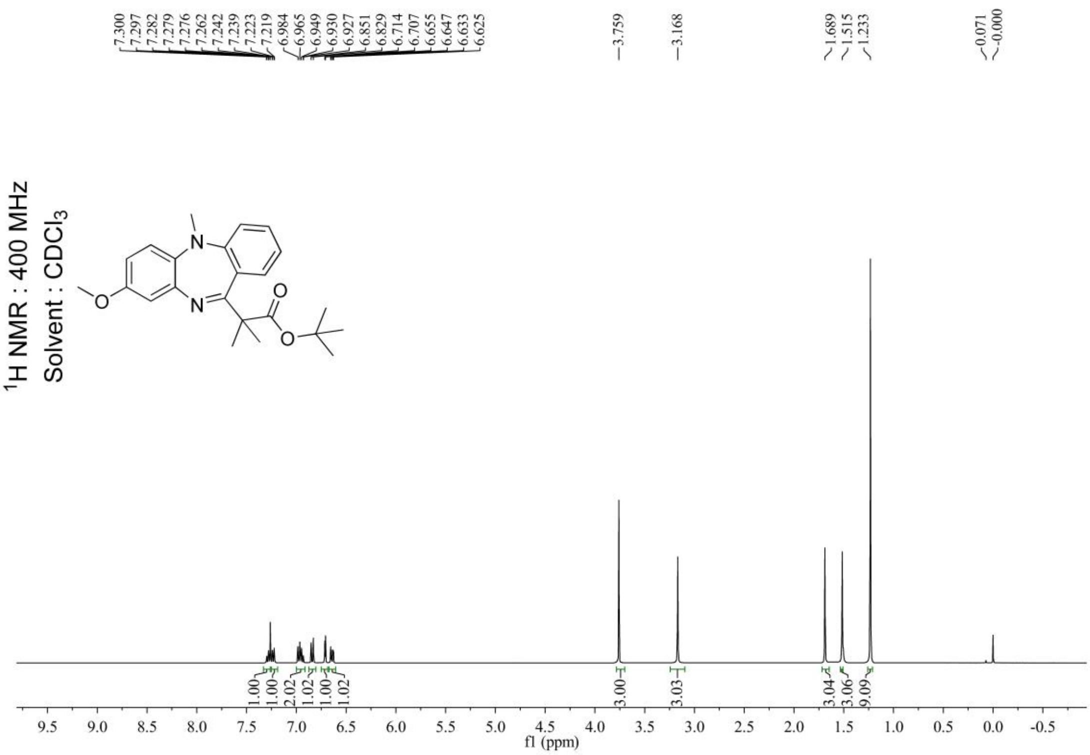


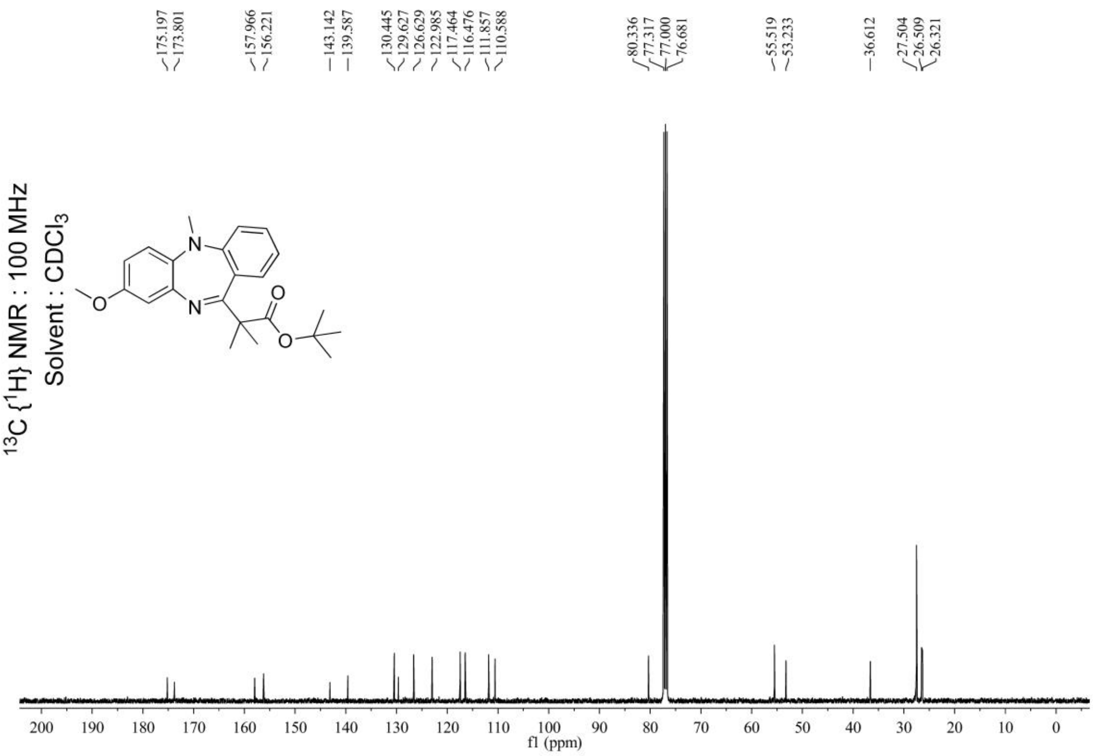
tert-Butyl 2-(5,8-dimethyl-5_H_-dibenzo[_b,e_][1,4]diazepin-11-yl)-2-methylpropanoate(3ma)



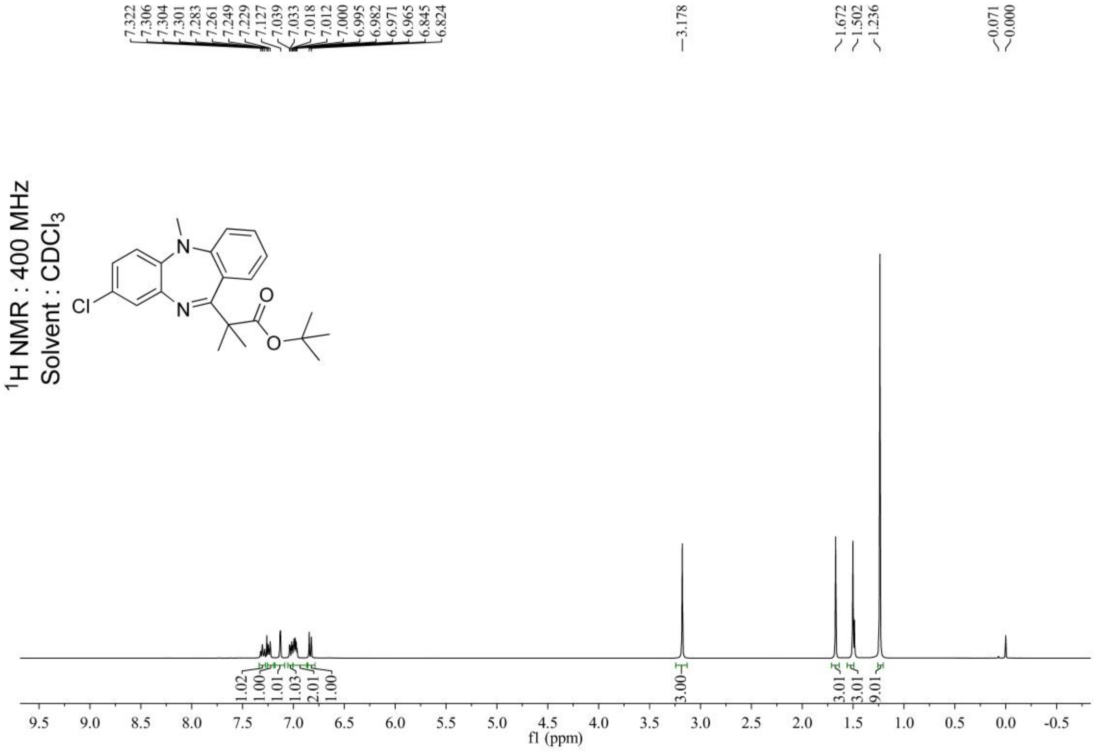


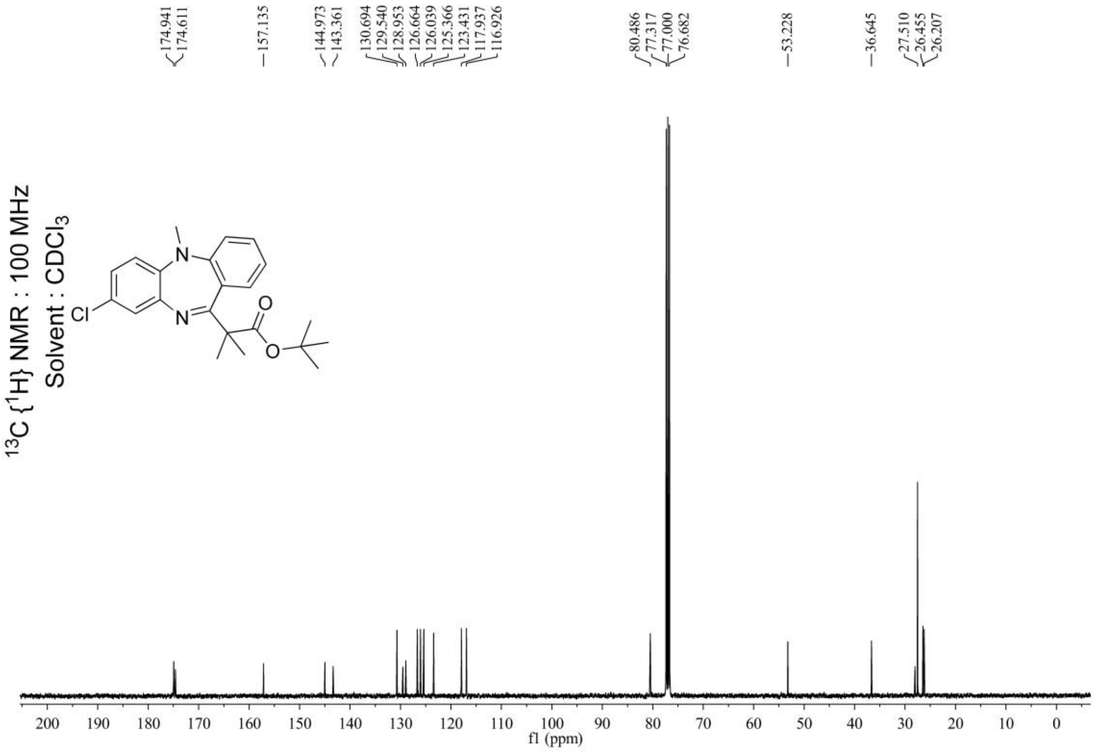
***tert*-Butyl 2-(8-methoxy-5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepin-11-yl)-2-methylpropanoate(3na)**



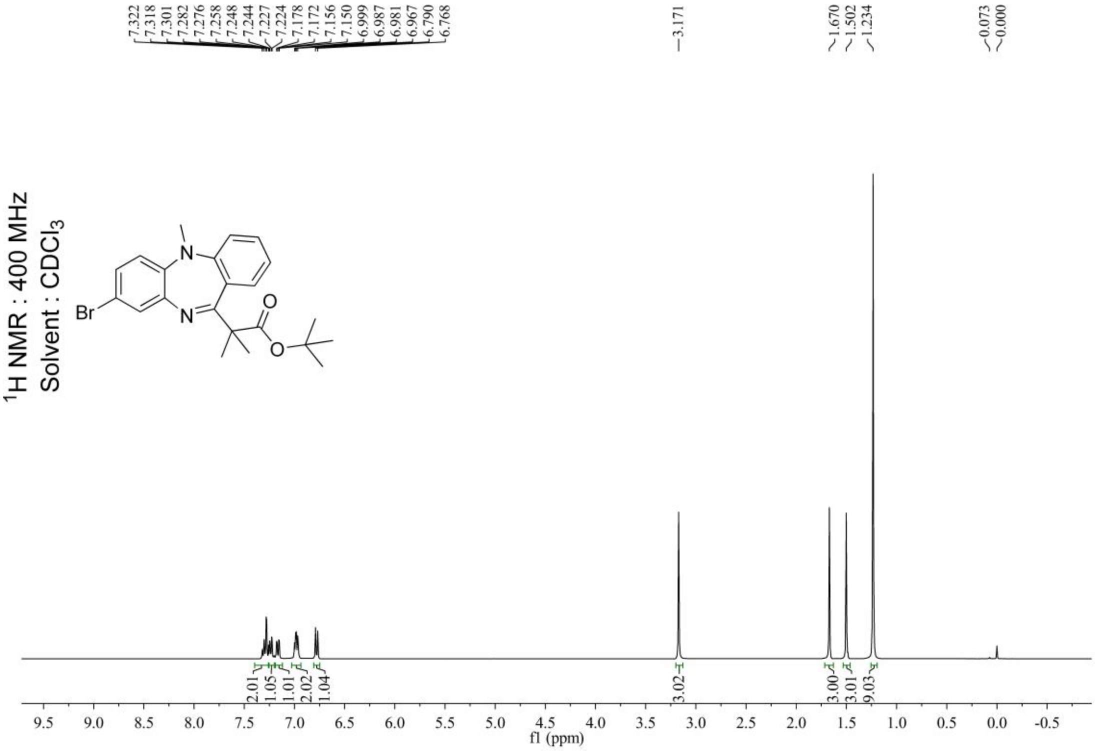


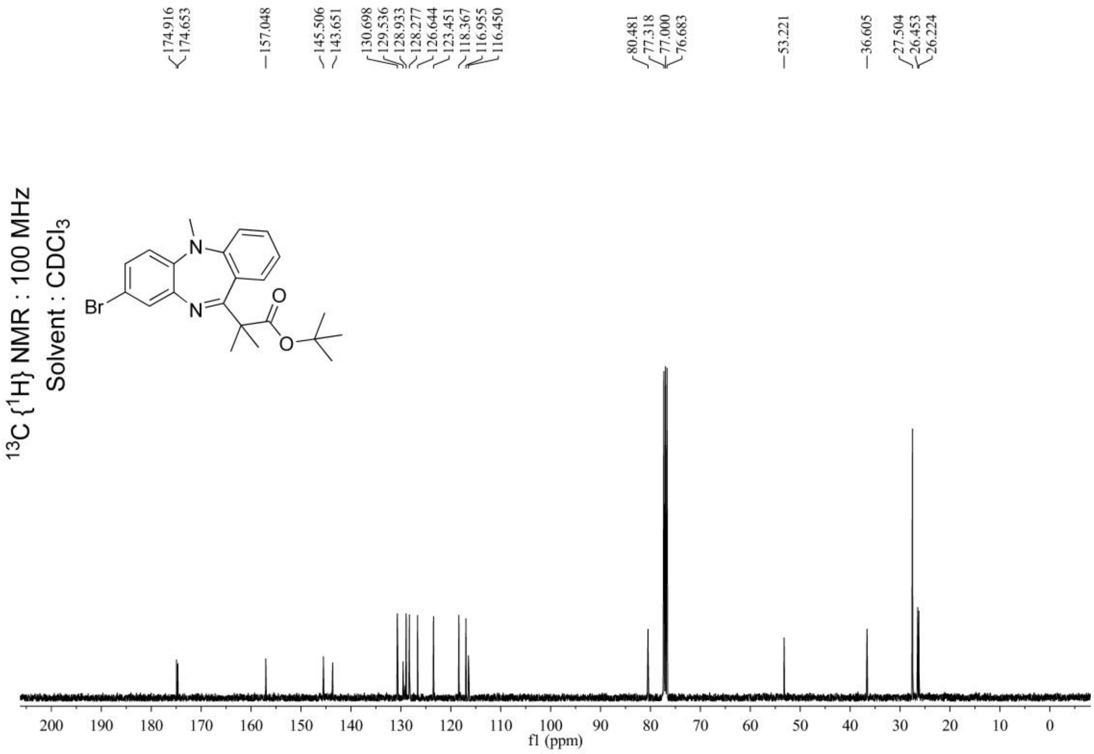
***tert*-Butyl 2-(8-chloro-5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepin-11-yl)-2-methylpropanoate(3oa)**



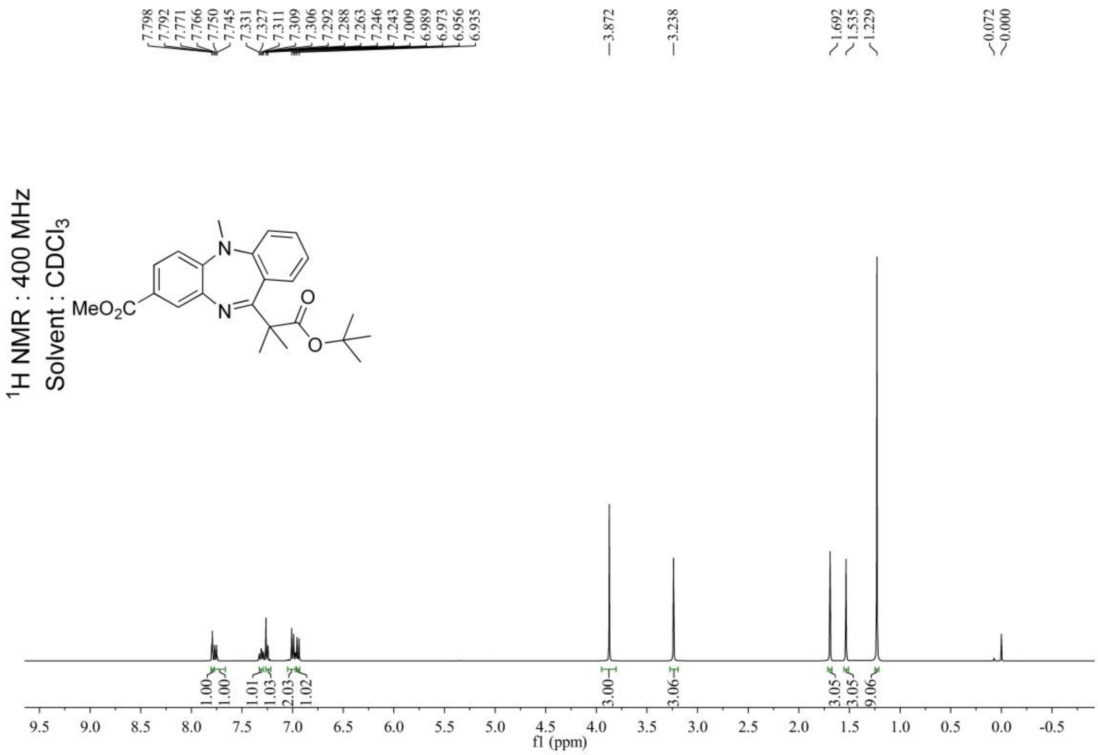


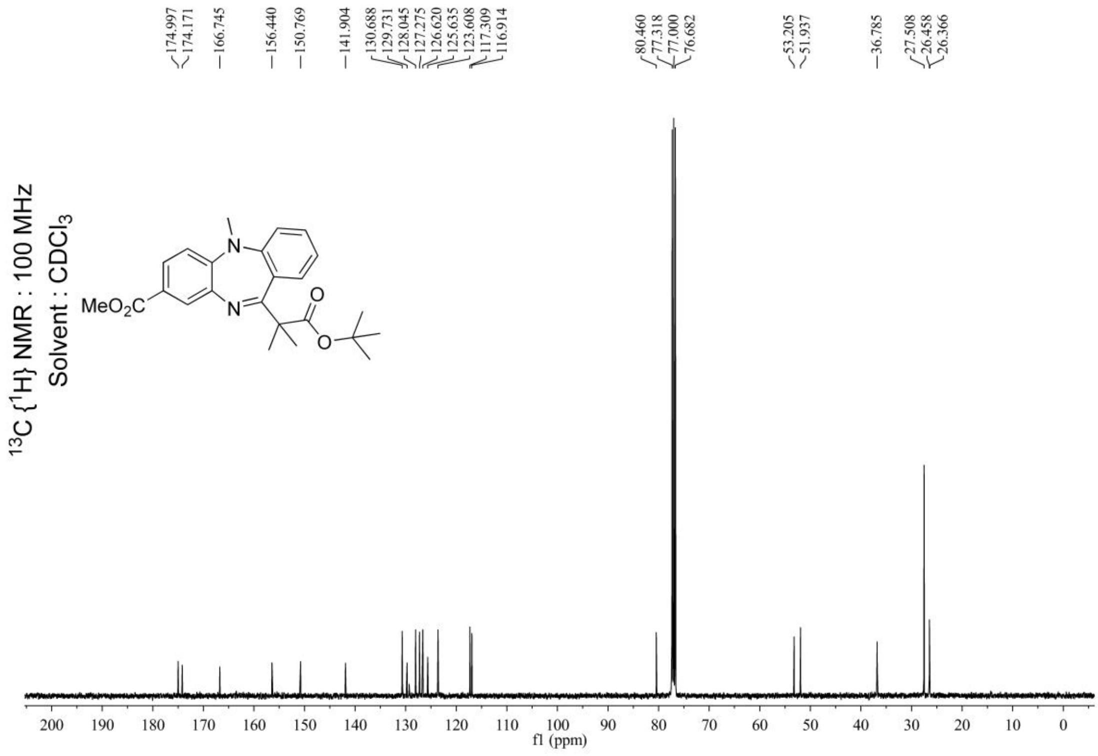
tert-Butyl 2-(8-bromo-5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepin-11-yl)-2-methylpropanoate(3pa)



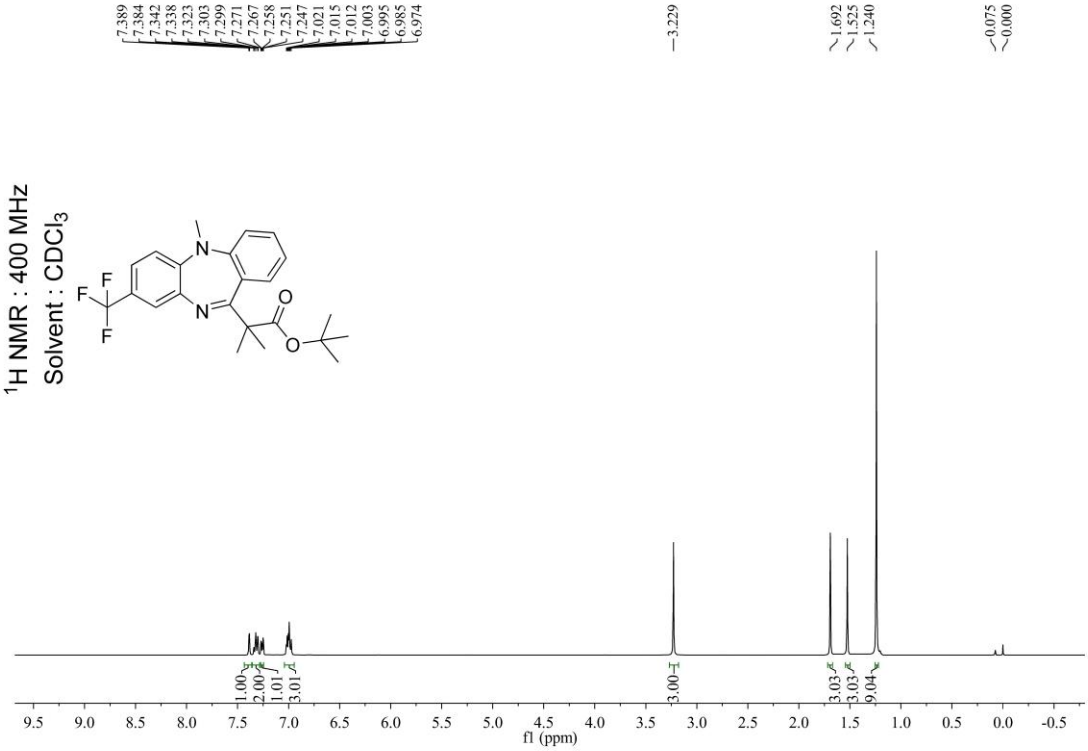


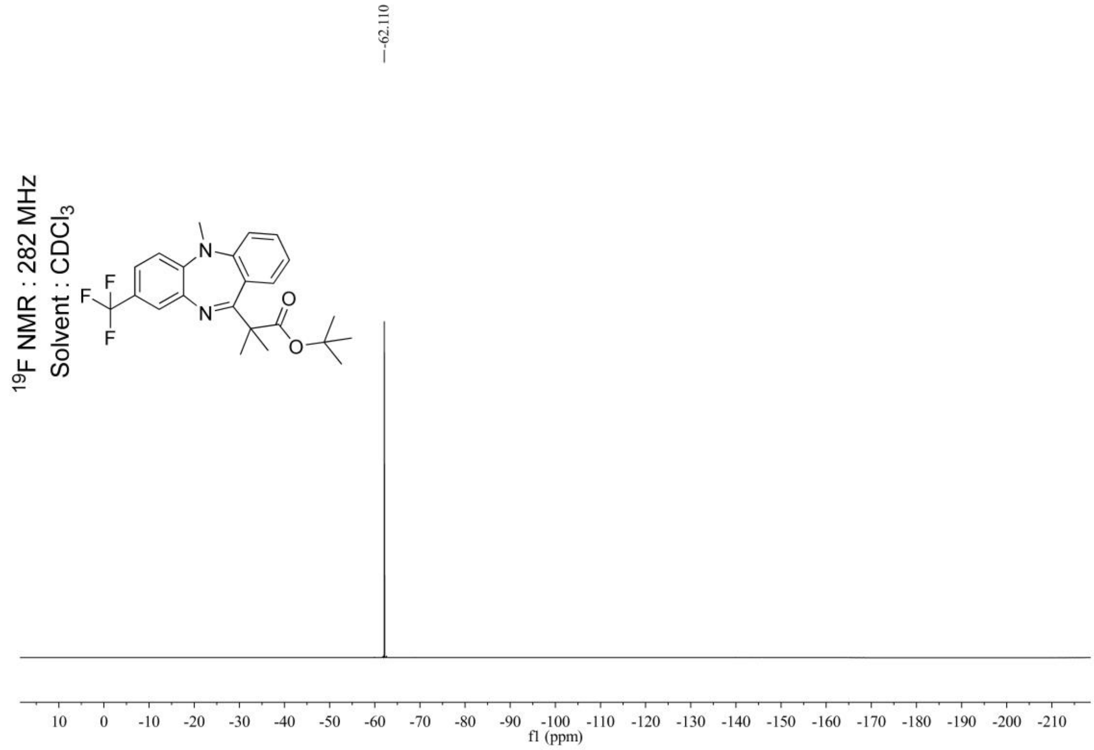
Methyl 11-(1-(*tert*-butoxy)-2-methyl-1-oxopropan-2-yl)-5-methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine-8-carboxylate(3qa)

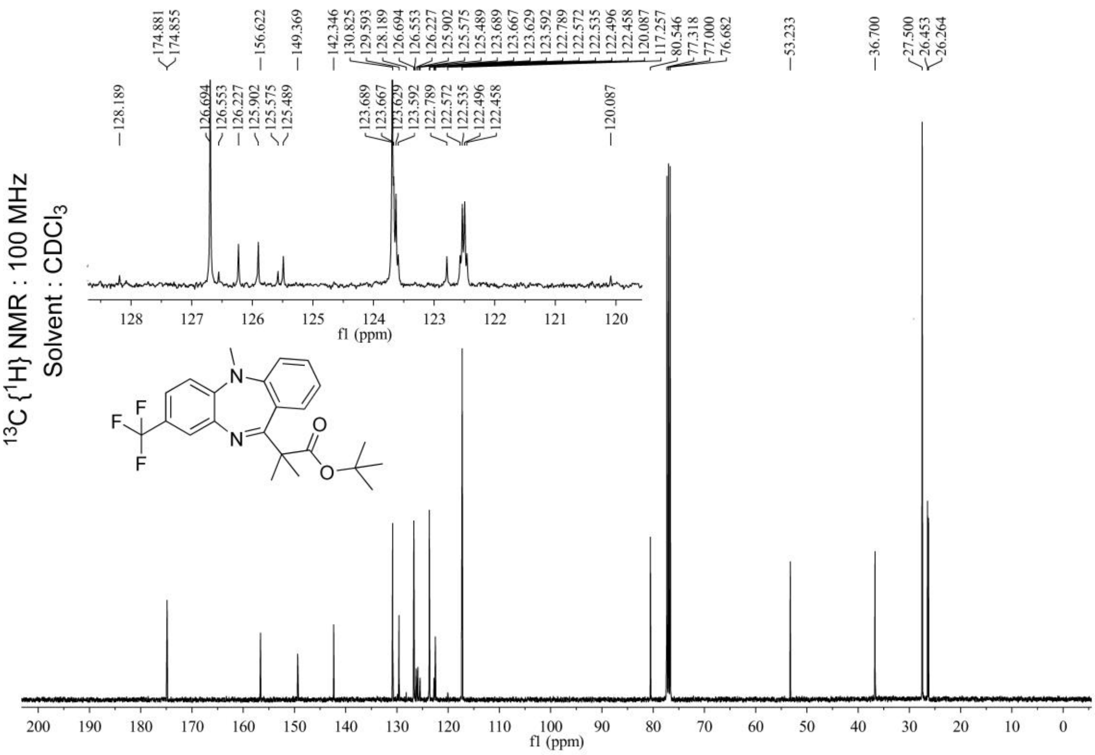




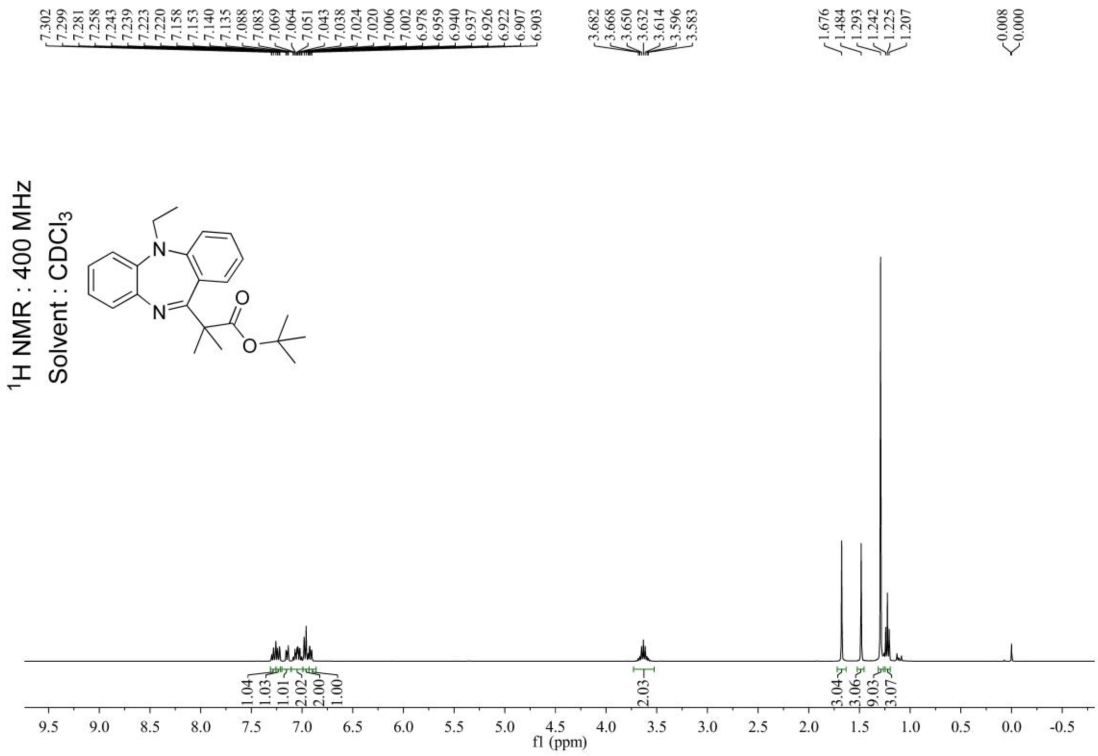
tert-Butyl 2-methyl-2-(5-methyl-8-(trifluoromethyl)-5*H* dibenzo[*b,e*][1,4]diazepin-11-yl)propanoate(3ra)

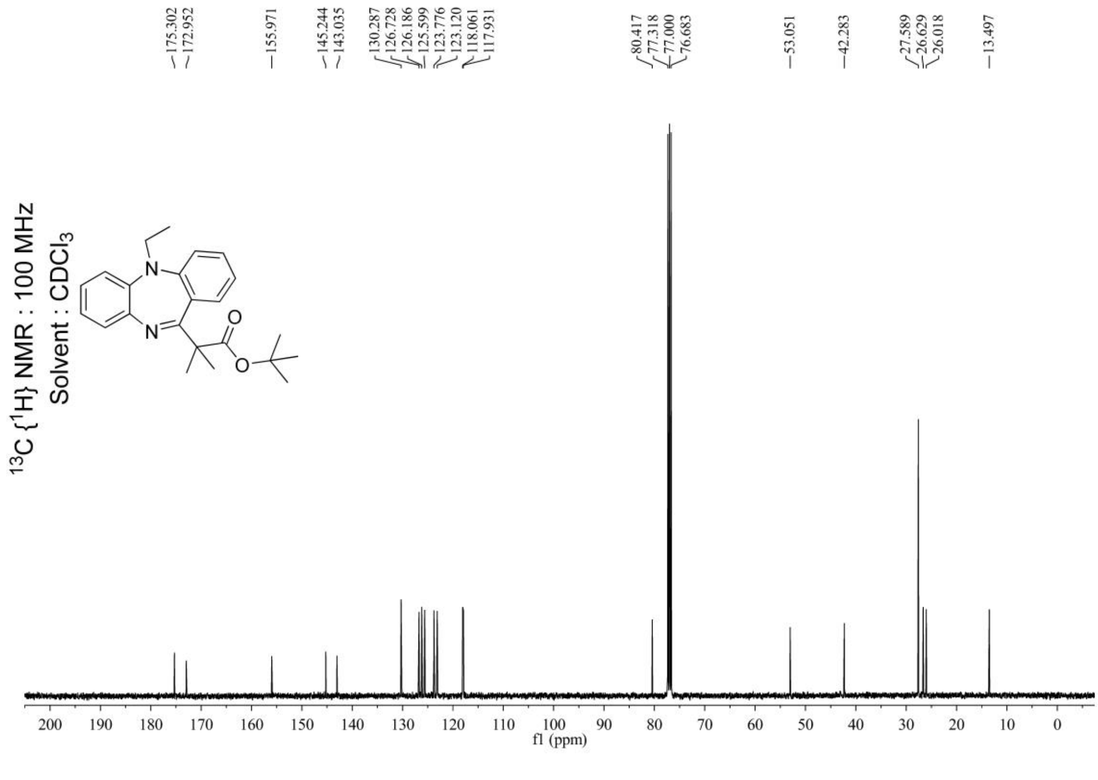



19F NMR : 282 MHz
Solvent : CDCl3
-62.110
f1 (ppm)

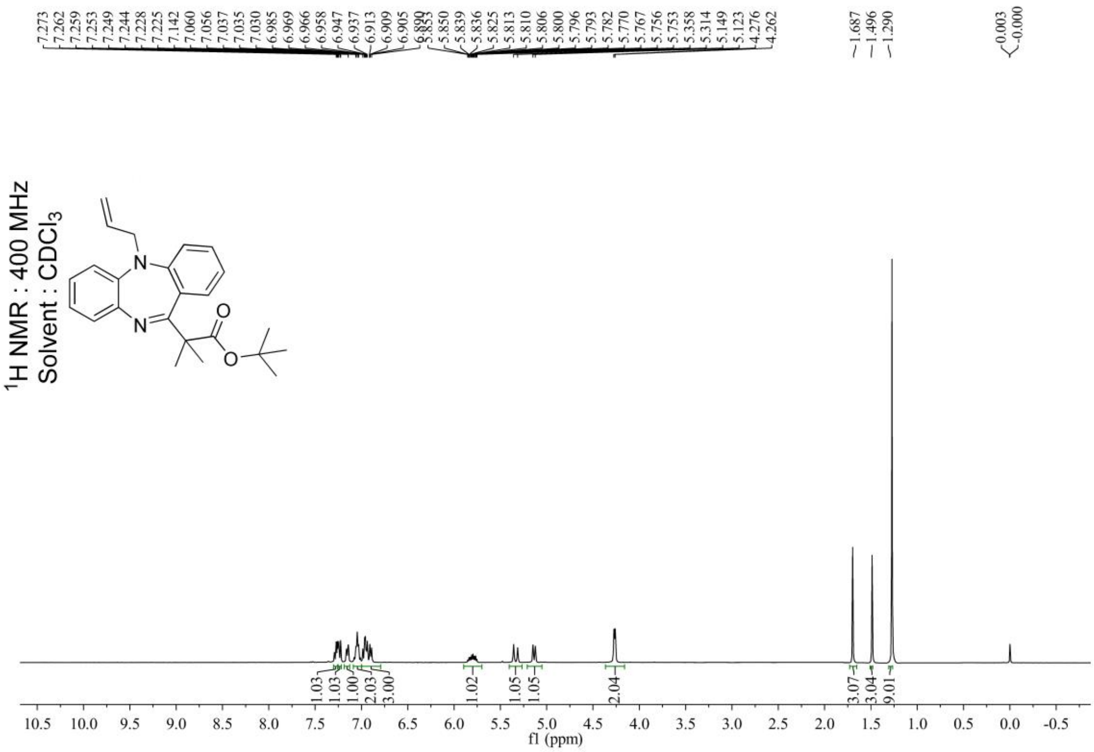

13C {1H} NMR : 100 MHz
Solvent : CDCl3
174.881
174.855
156.622
149.369
142.346
130.825
129.593
128.189
126.694
126.553
126.227
125.902
125.575
125.489
123.689
123.667
123.629
123.592
122.789
122.572
122.535
122.496
122.458
120.087
117.257
80.546
77.318
77.000
76.682
53.233
36.700
27.500
26.453
26.264
f1 (ppm)

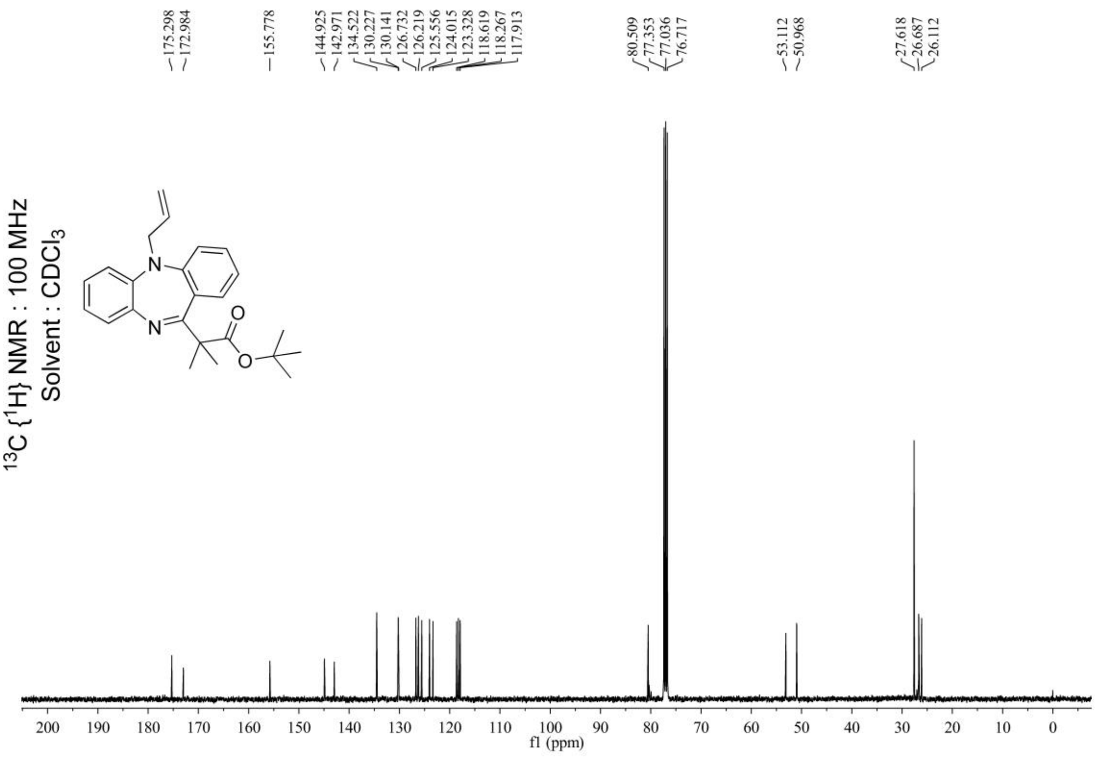
tert-Butyl 2-(5-ethyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-2-methylpropanoate(3sa)



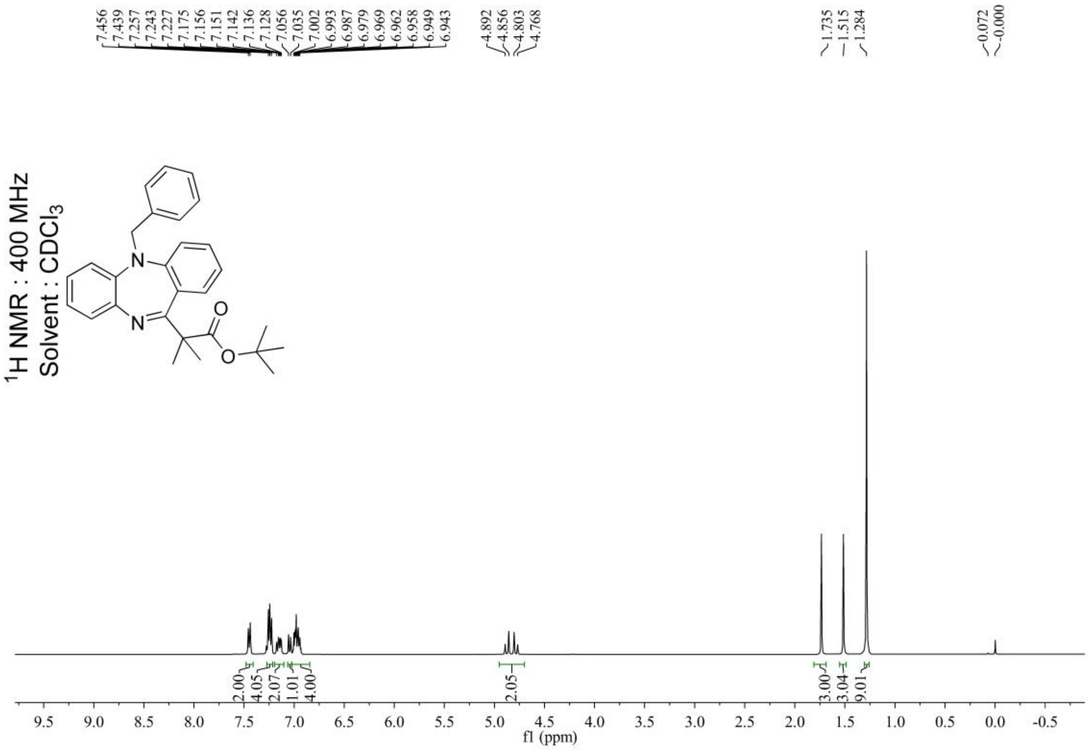


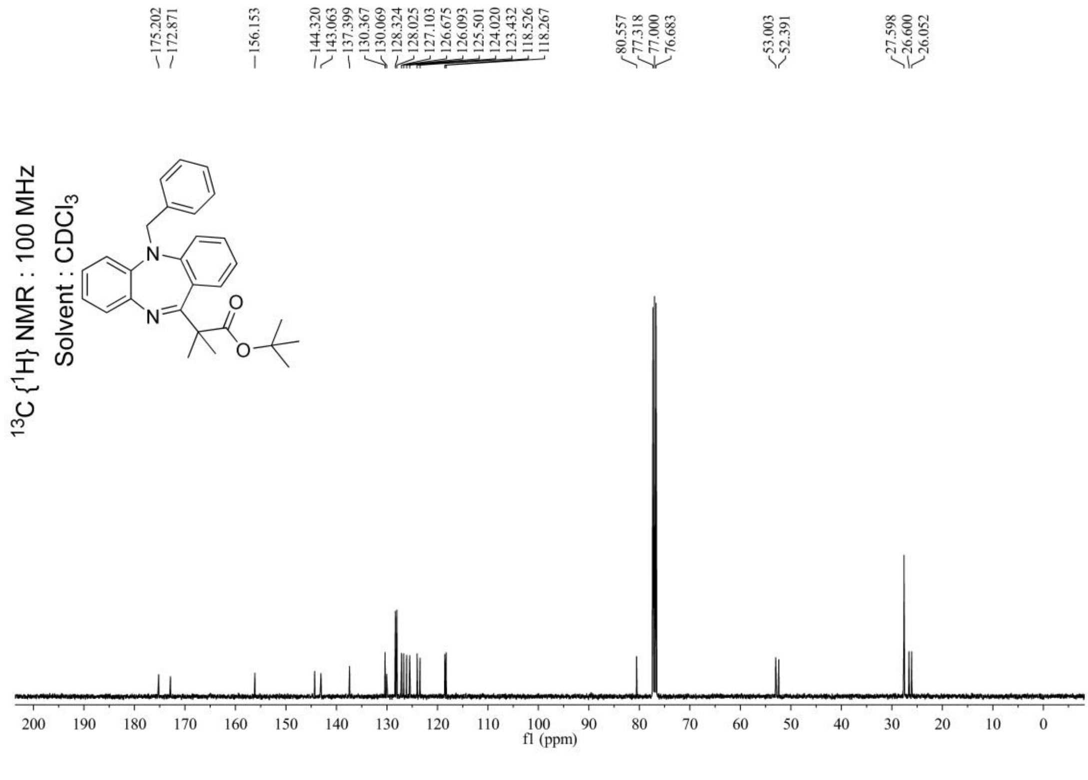
***tert*-Butyl 2-(5-allyl-5H-dibenzo[b,e][1,4]diazepin-11-yl)-2-methylpropanoate(3ta)**



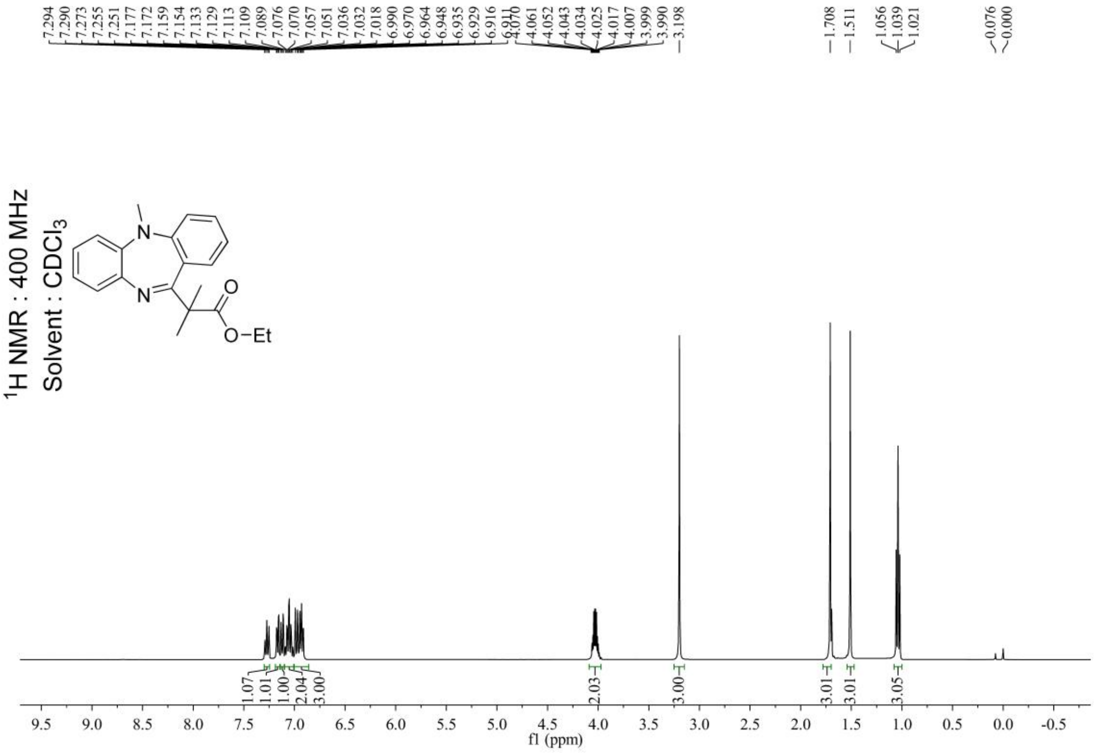


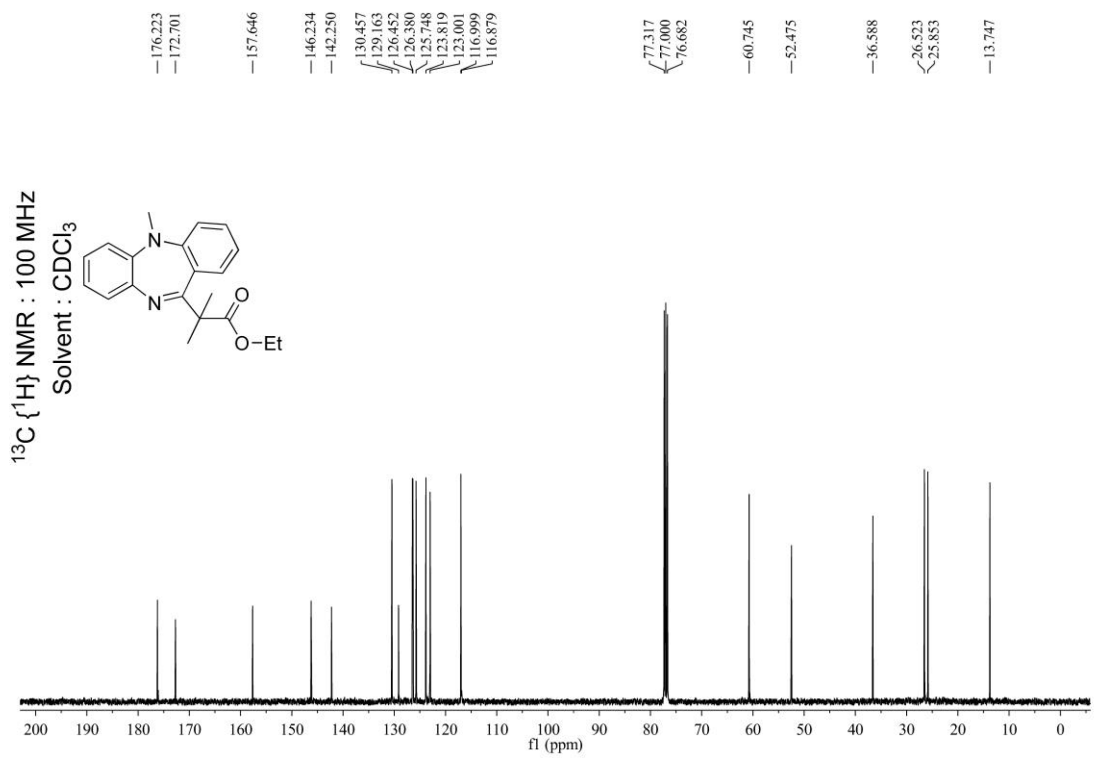
***tert*-butyl 2-(5-benzyl-*5H*-dibenzo[*b,e*][1,4]diazepin-11-yl)-2-methylpropanoate(3ua)**



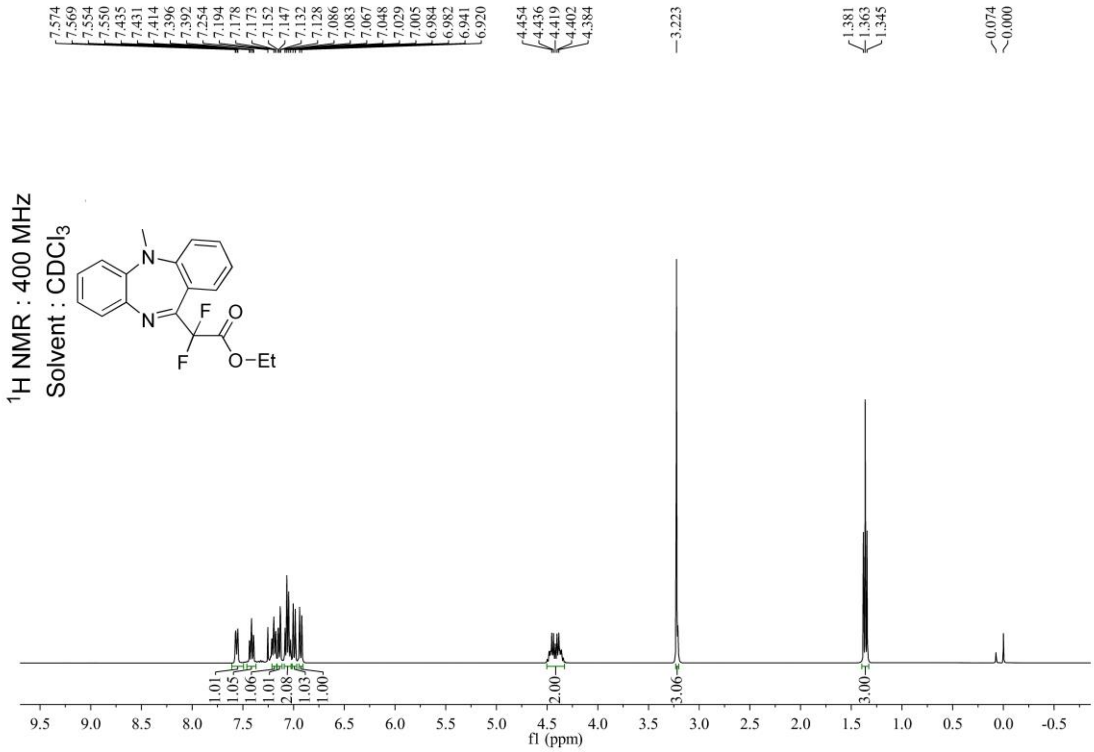


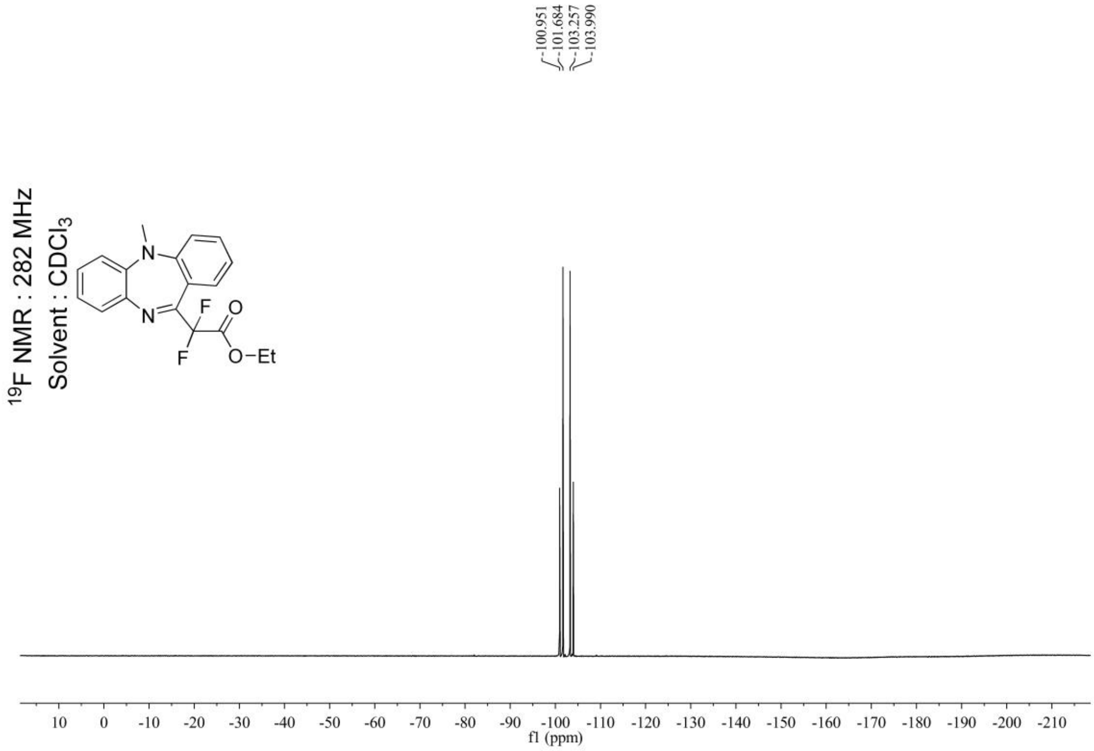
Ethyl 2-methyl-2-(5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepin-11-yl)propanoate (3ab)

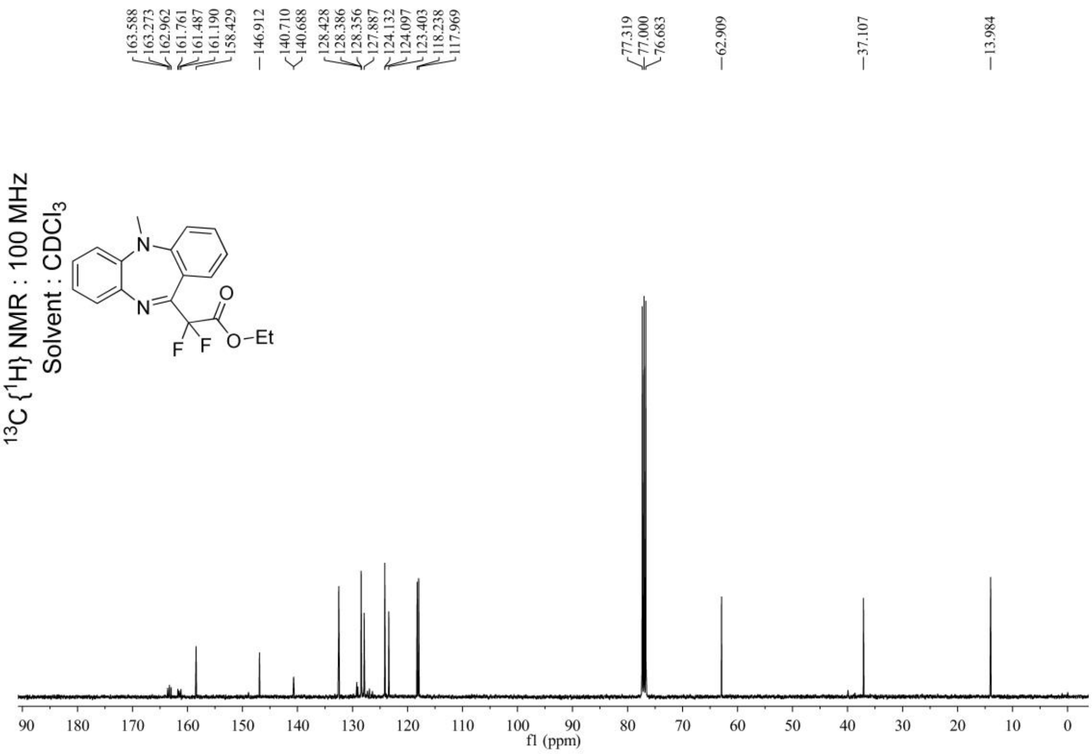




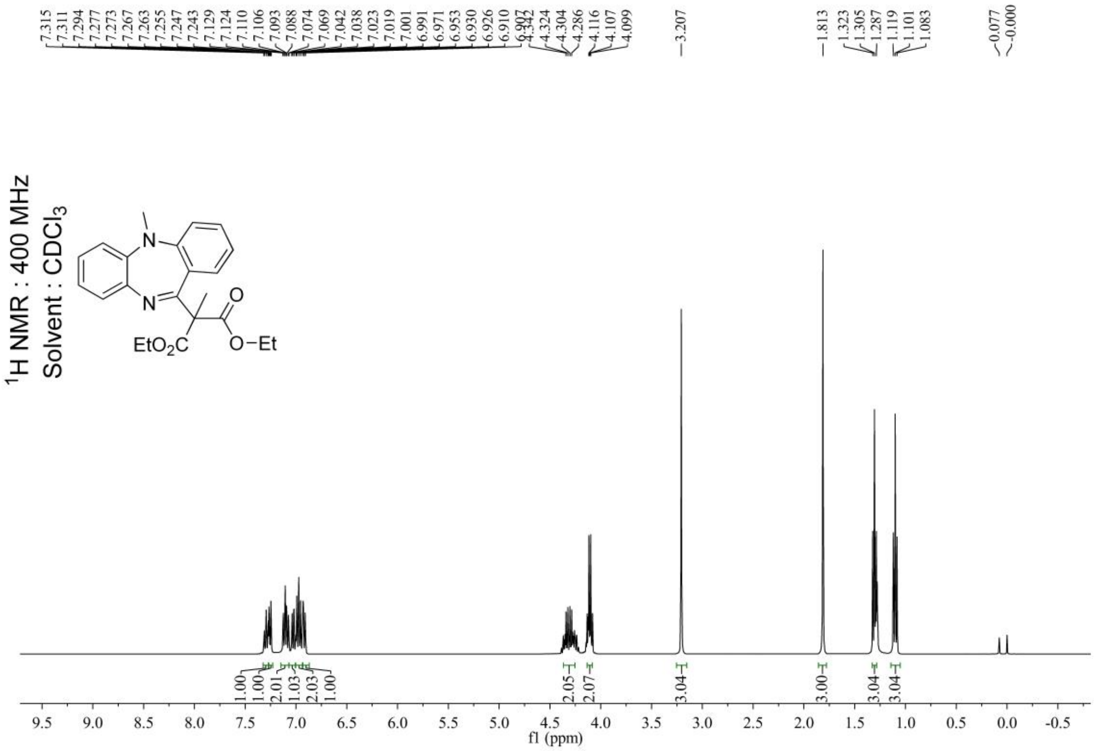
Ethyl 2,2-difluoro-2-(5-methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepin-11-yl)acetate(3ac)

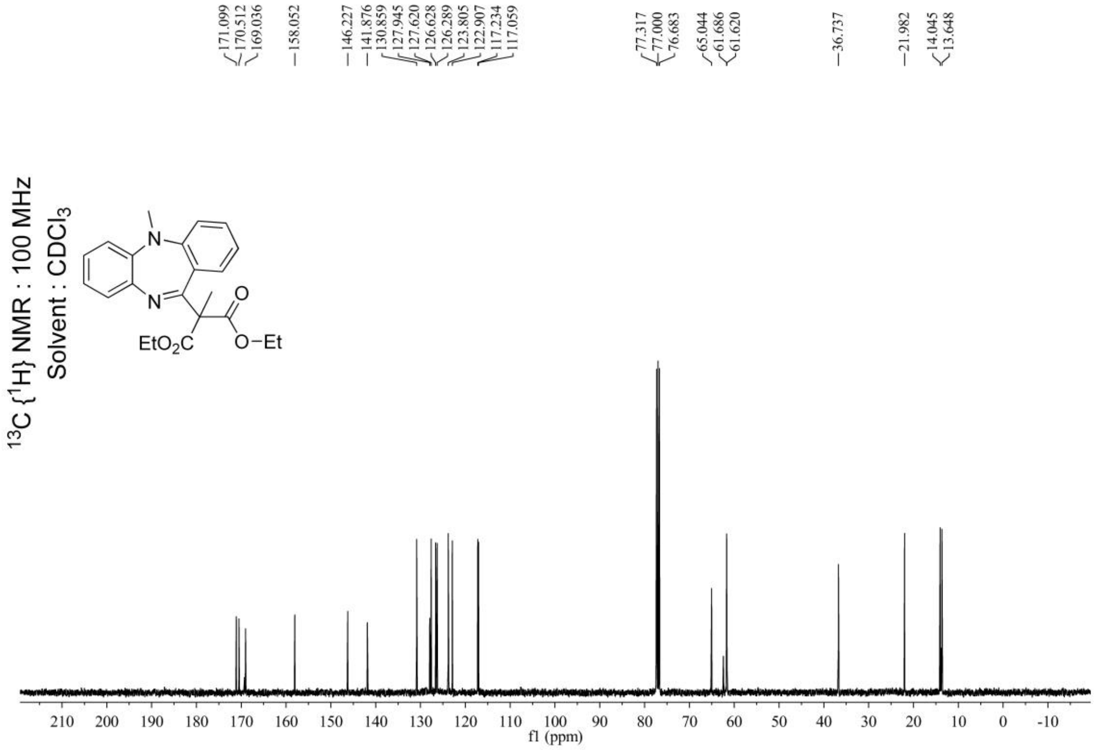




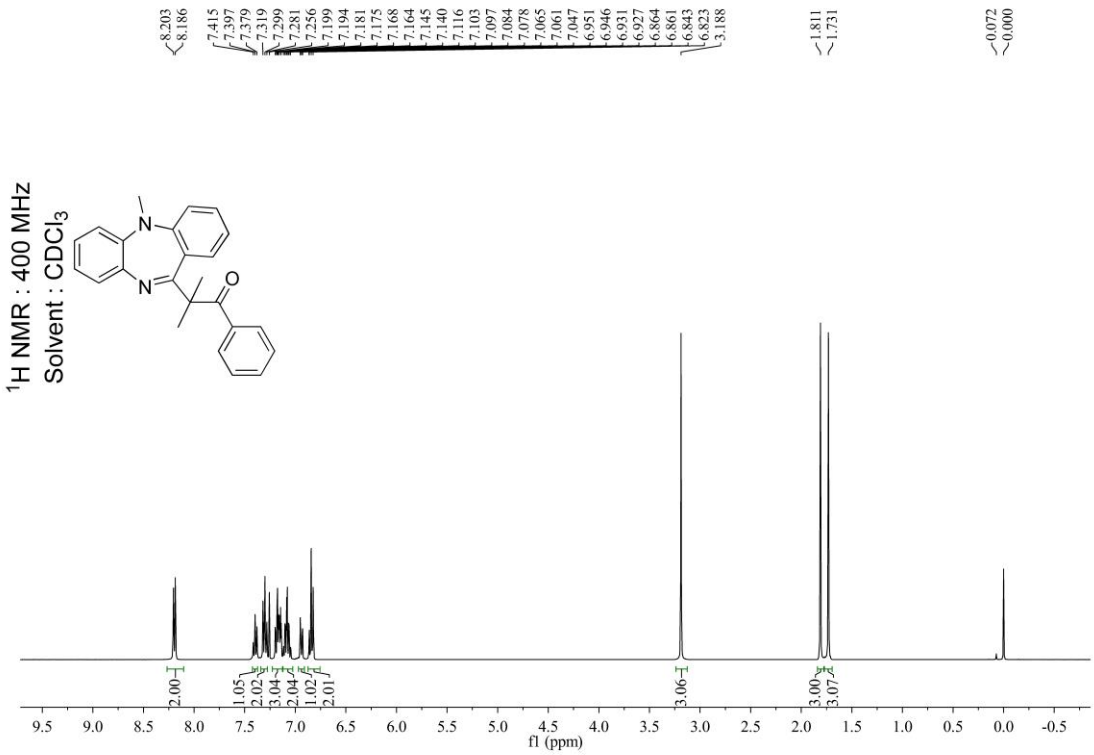

13C {1H} NMR : 100 MHz
Solvent : CDCl3
N
N
O
O–Et
F F
163.588
163.273
162.962
161.761
161.487
161.190
158.429
146.912
140.710
140.688
128.428
128.386
128.356
127.887
124.132
124.097
123.403
118.238
117.969
77.319
77.000
76.683
62.909
37.107
13.984
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

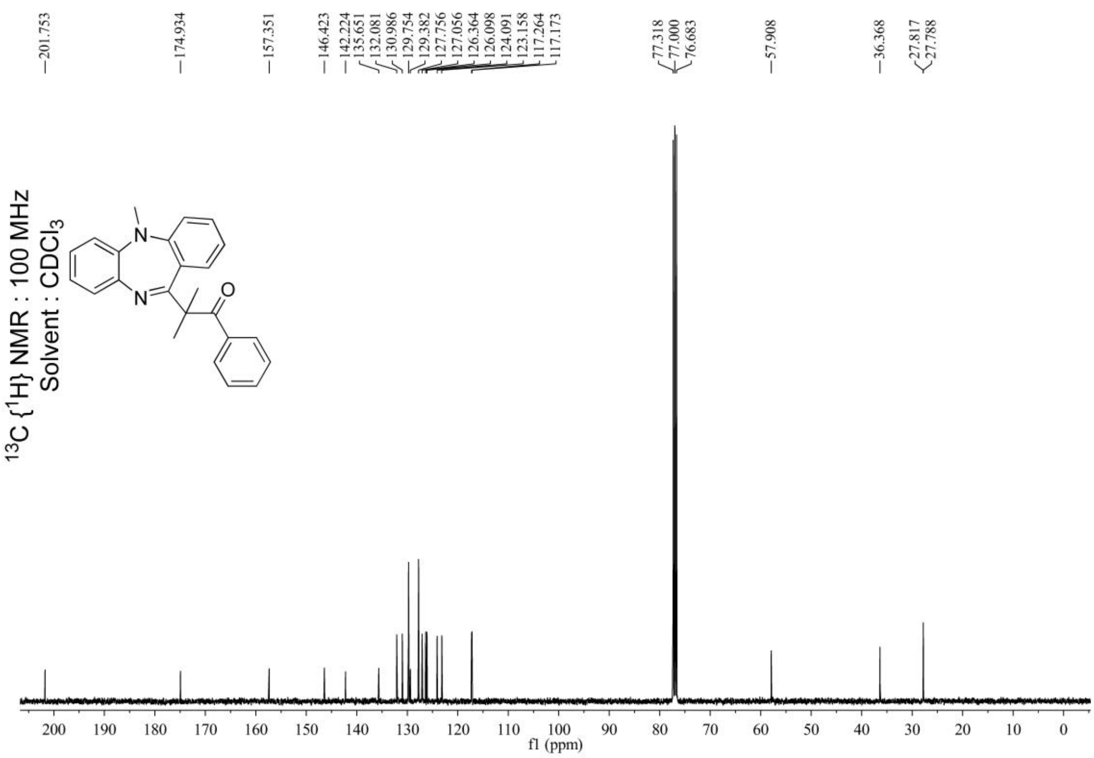
Diethyl 2-methyl-2-(5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepin-11-yl)malonate(3ad)



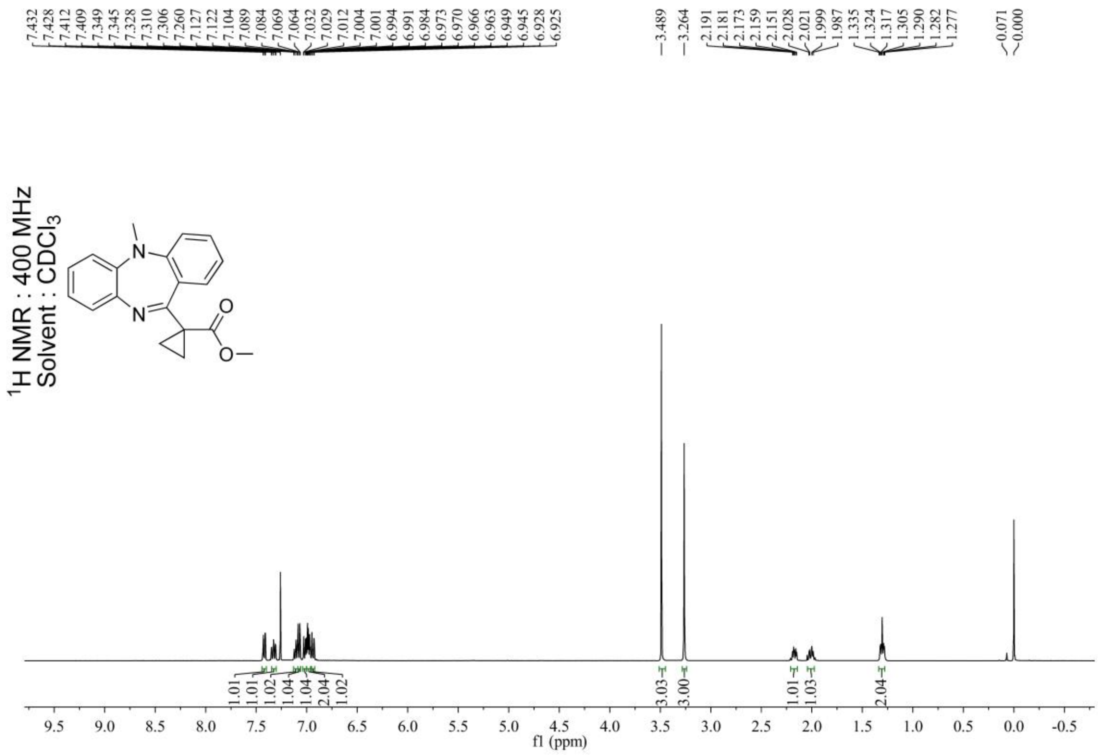


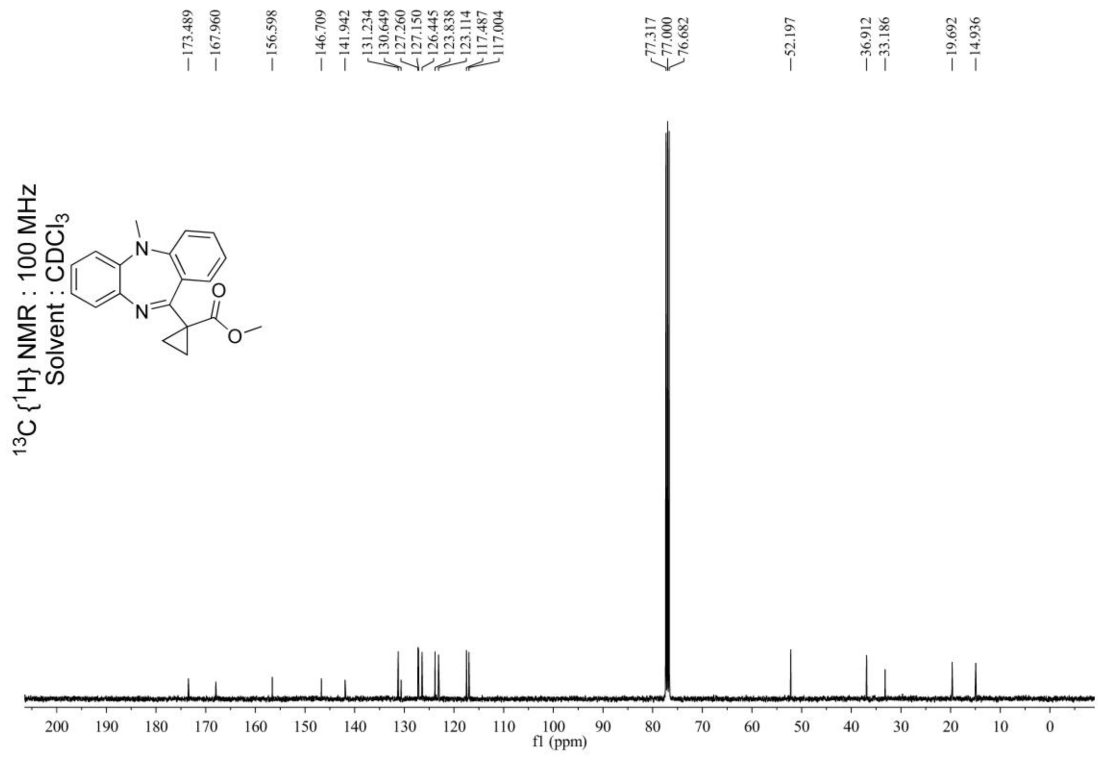
2-*m*ethyl-2-(5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepin-11-yl)-1-phenylpropan-1-one (3ae)



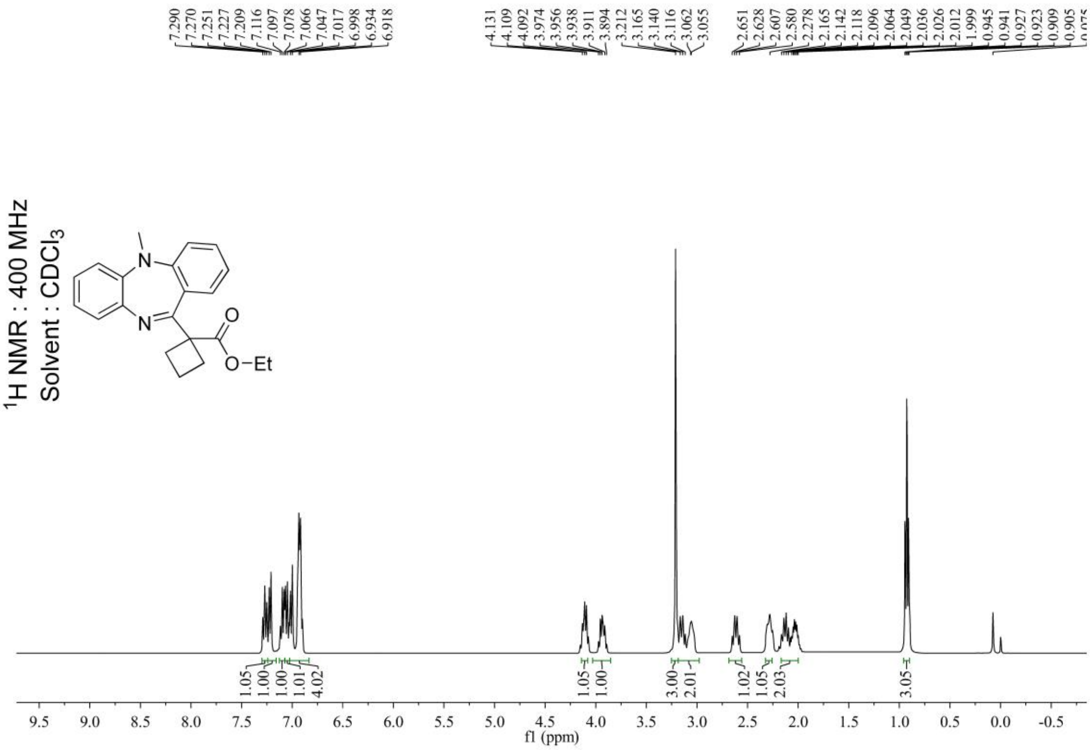


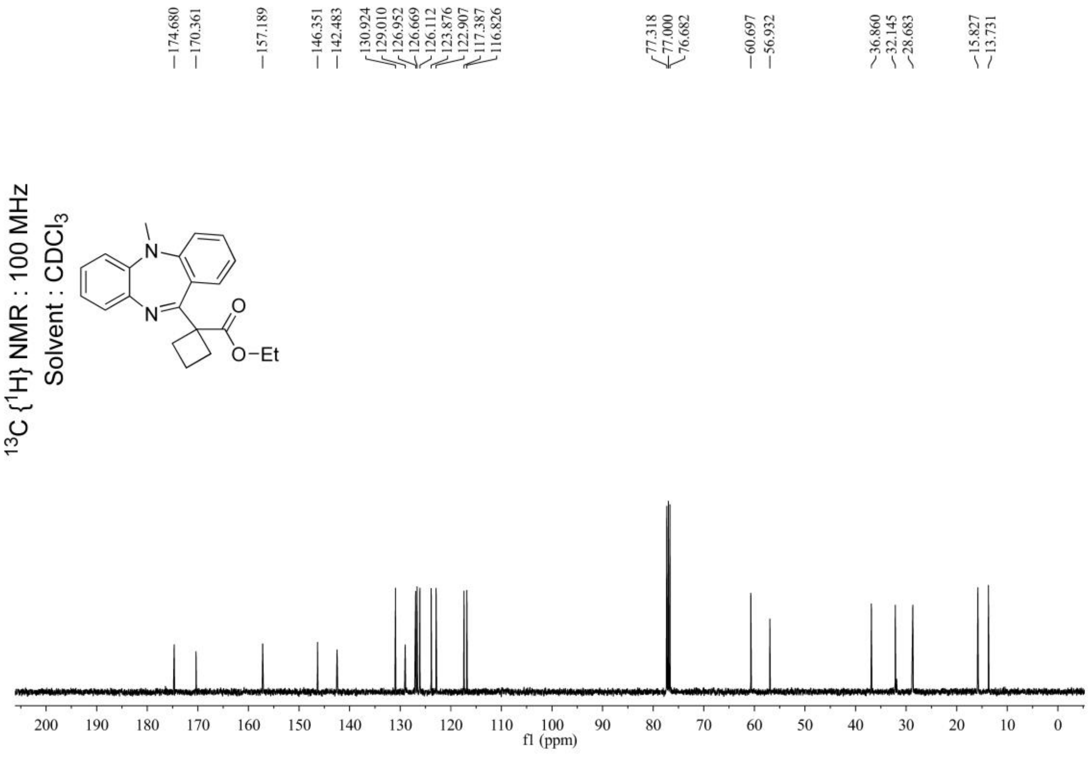
Methyl 1-(5-methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepin-11-yl)cyclopropane-1-carboxylate(3af)



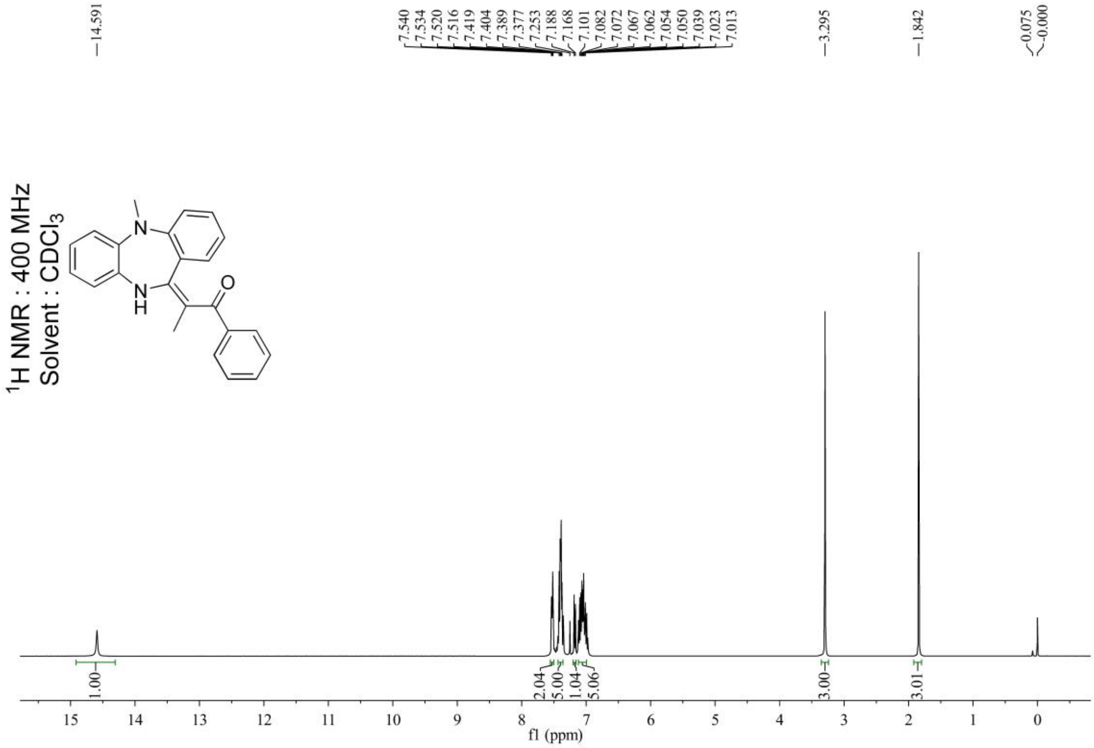


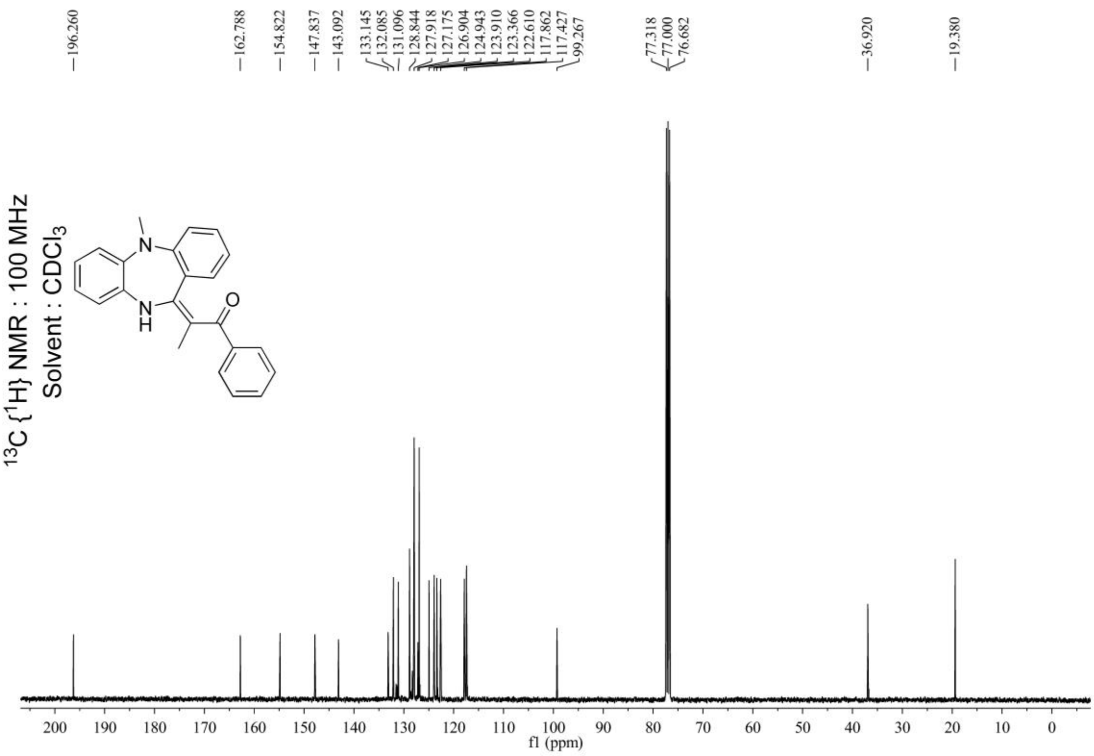
Ethyl 1-(5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepin-11-yl)cyclobutane-1-carboxylate(3ag)



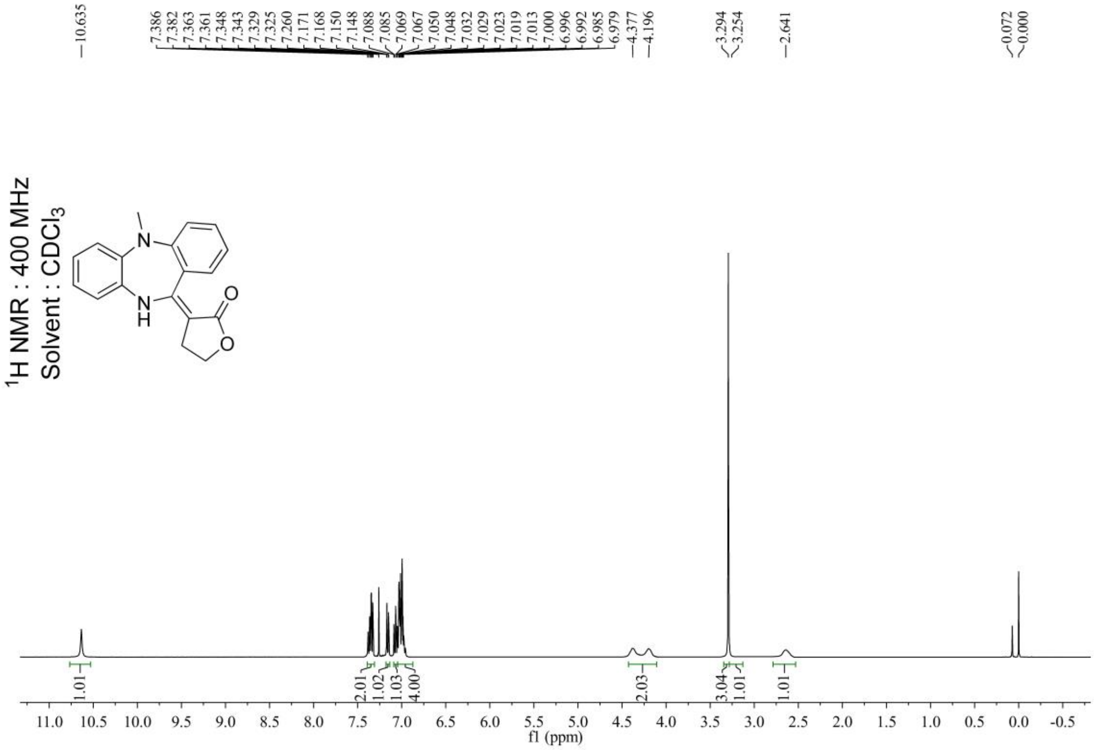


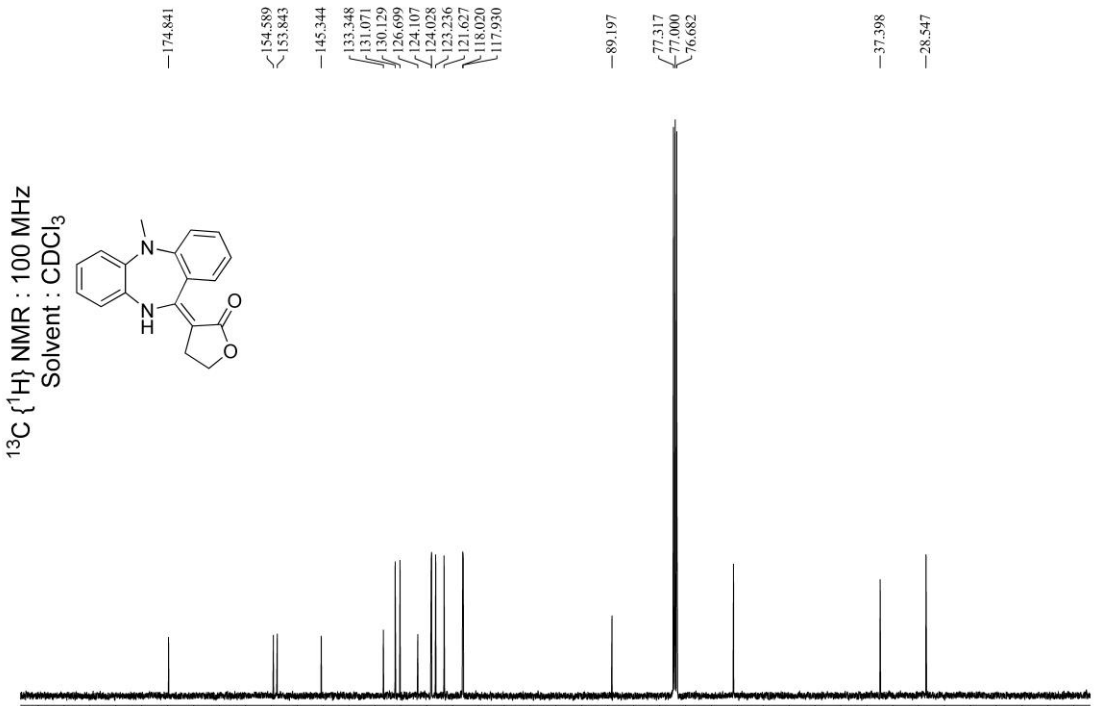
2-(5-methyl-5*H*-dibenzo[*b,e*][1,4]diazepin-11-yl)-1-phenylpropan-1-one（4ah）



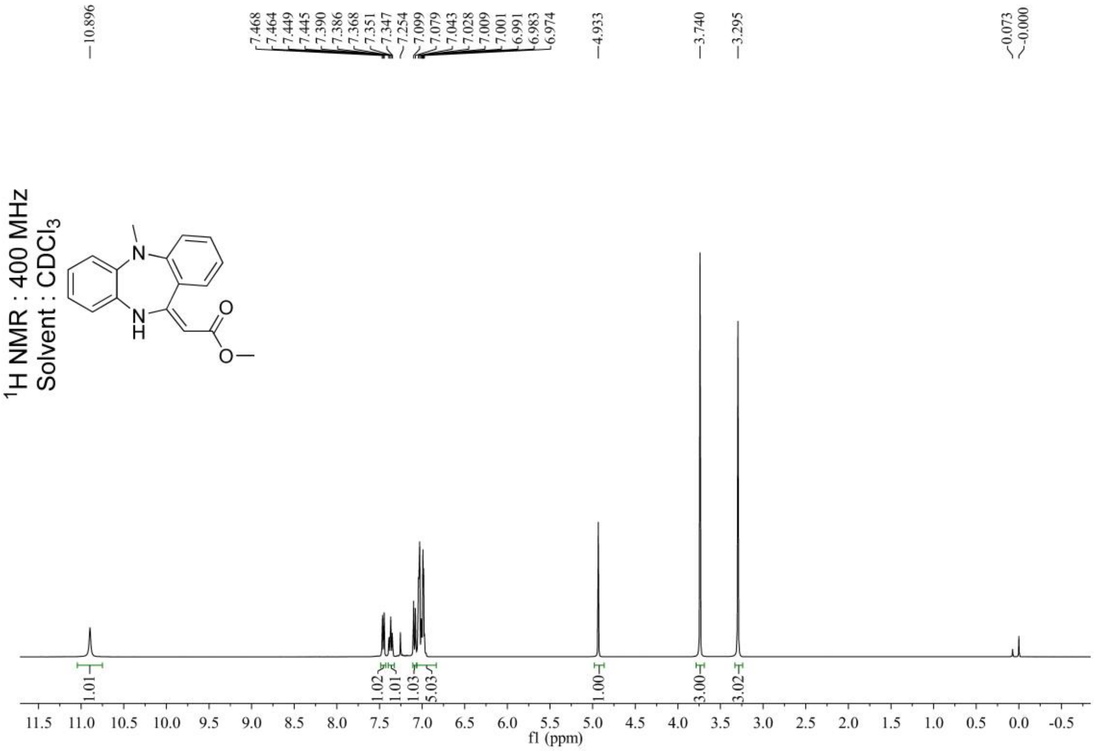


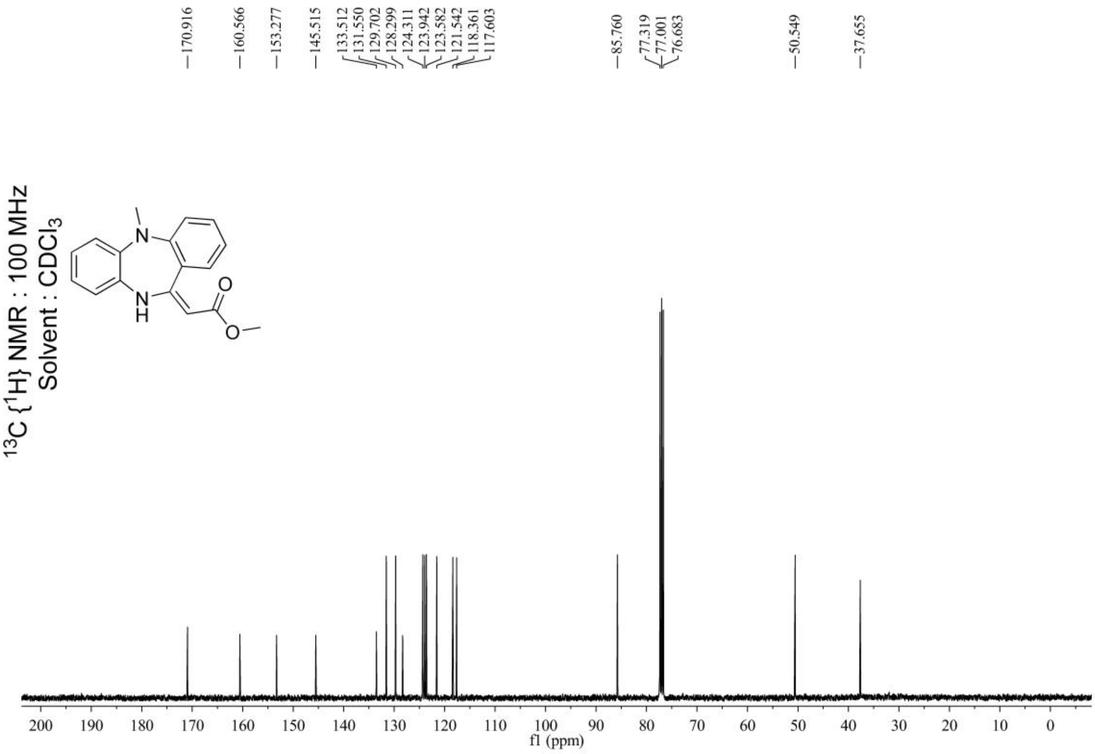
(*E*)-3-(5-methyl-5,10-dihydro-11*H*-dibenzo[*b,e*][1,4]diazepin-11-ylidene)dihydrofuran-2(3H)-one (4ai)



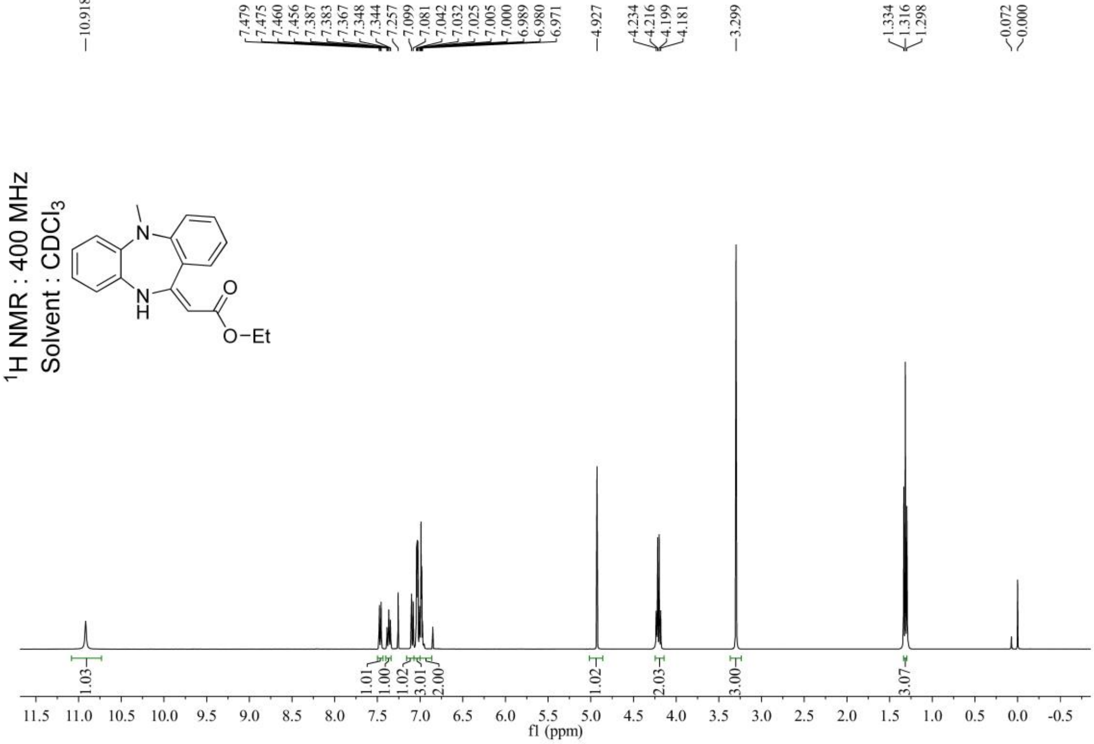


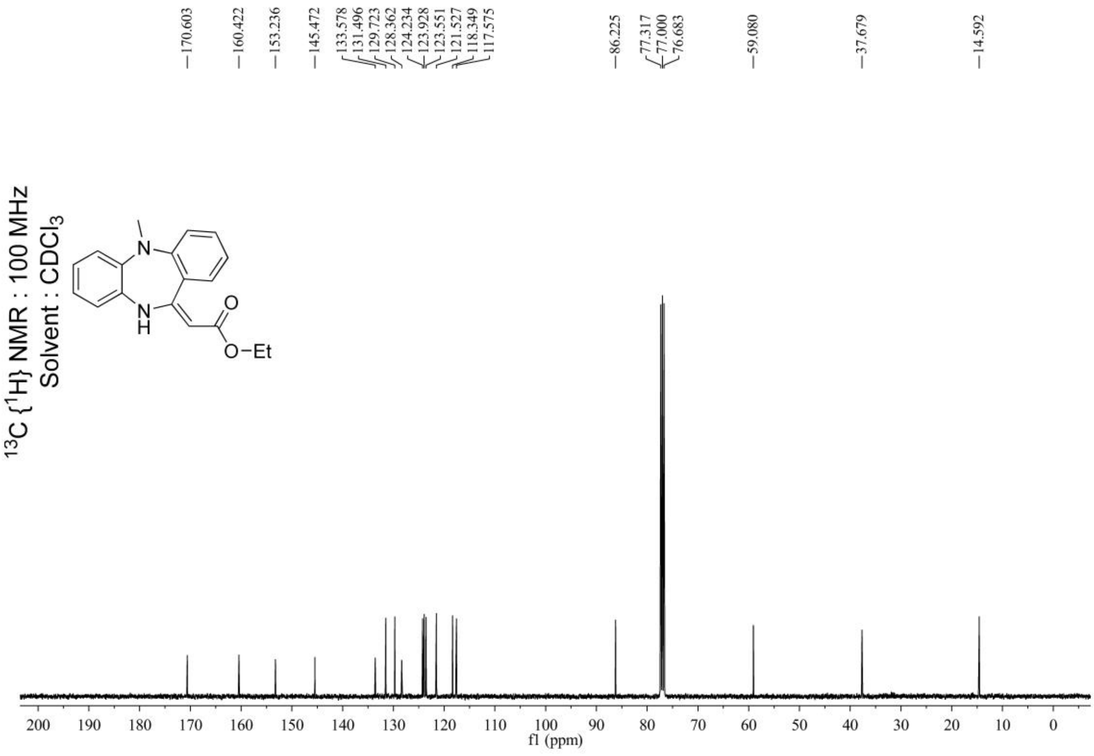
(*E*)-1-(5-methyl-5,10-dihydro-11*H*-dibenzo[*b,e*][1,4]diazepin-11-ylidene)propan-2-one(4aj)



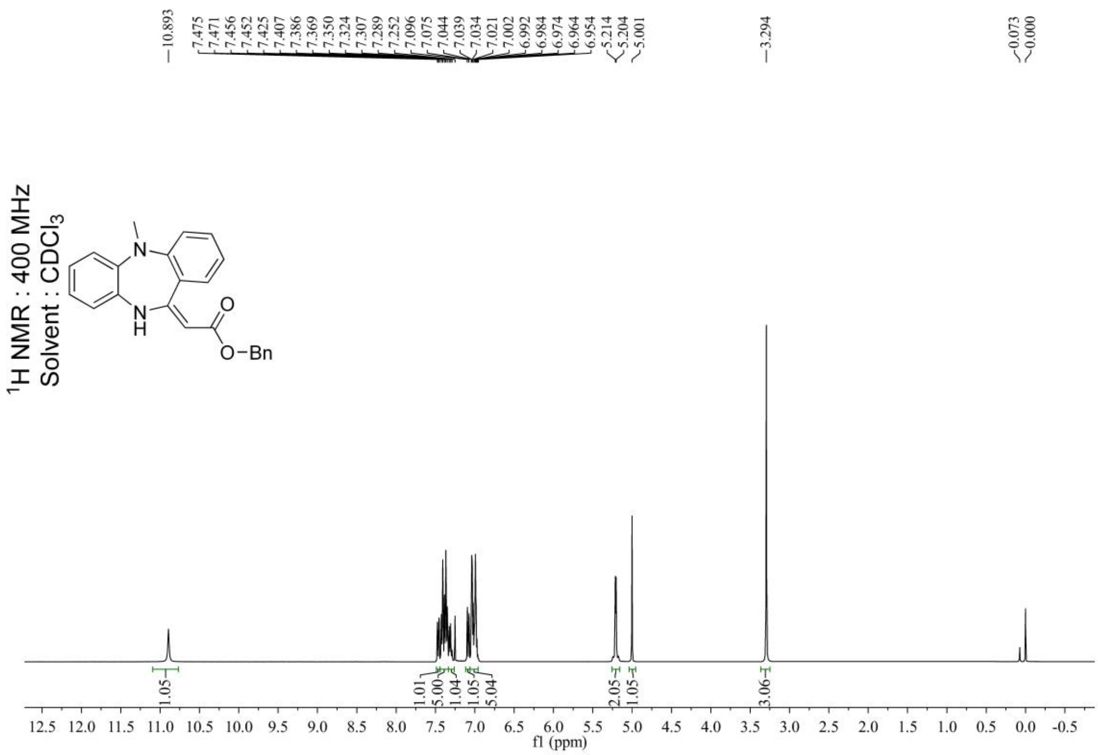


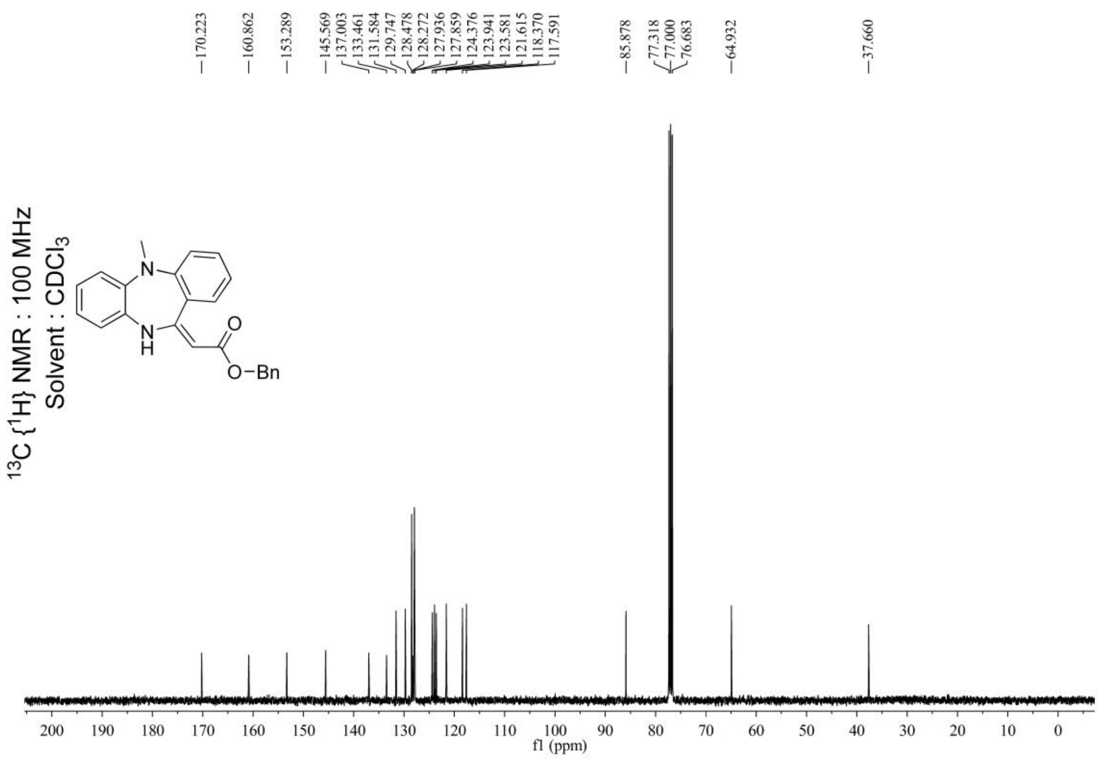
(*E*)-1-(5-methyl-5,10-dihydro-11*H*-dibenzo[*b,e*][1,4]diazepin-11-ylidene)butan-2-one(4ak)



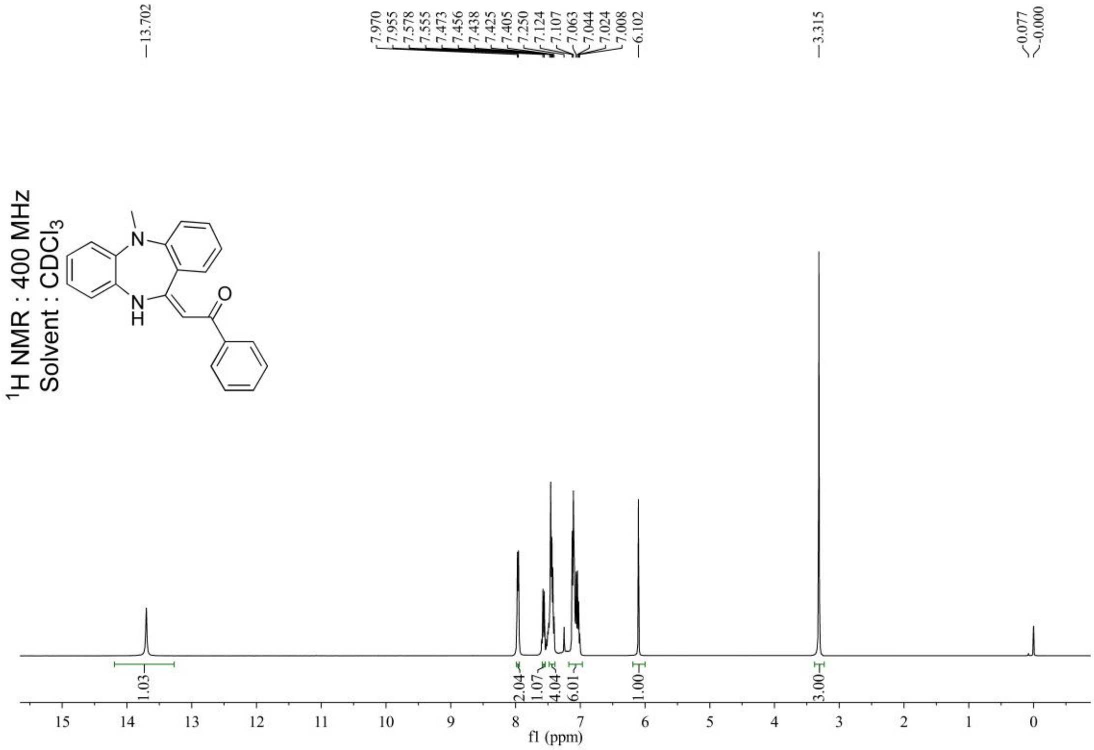


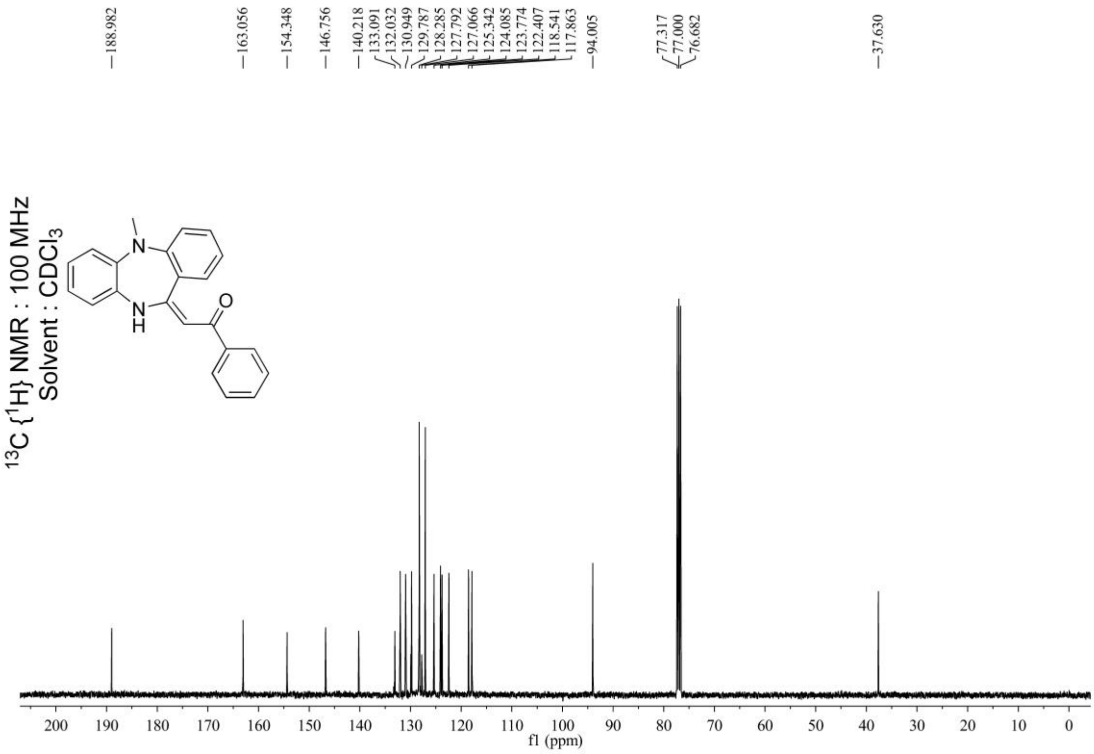
(*E)*-1-(5-methyl-5,10-dihydro-11*H*-dibenzo[*b,e*][1,4]diazepin-11-ylidene)-3-phenylpropan-2-one(4al)



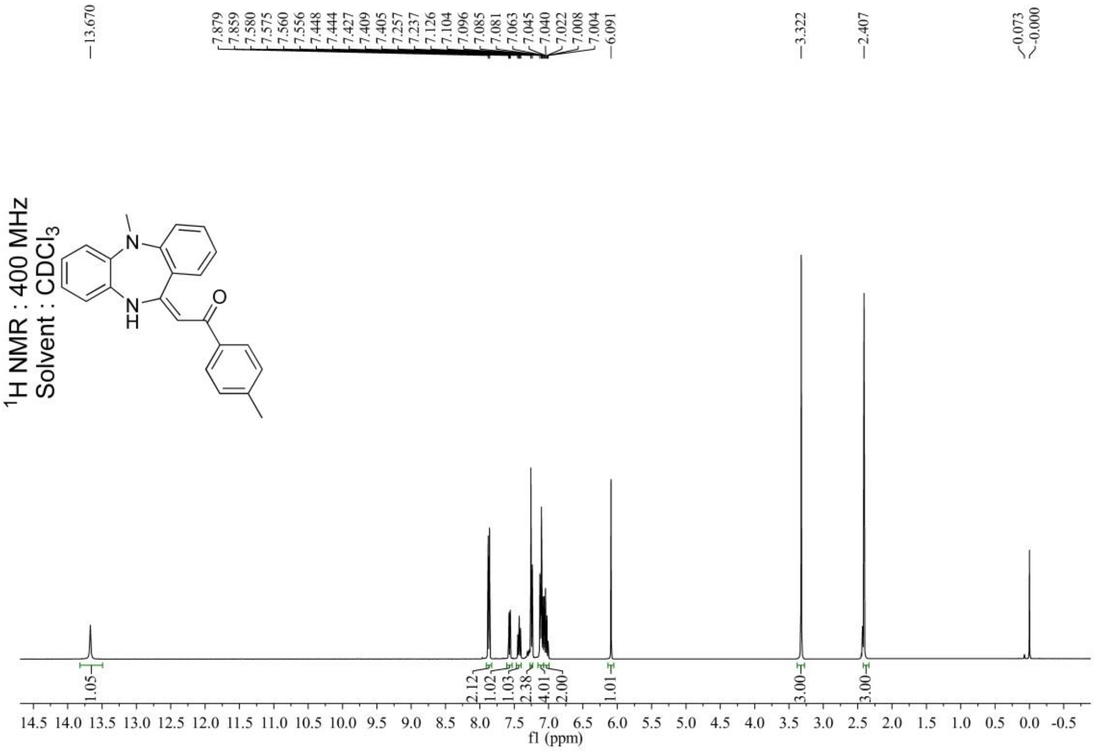


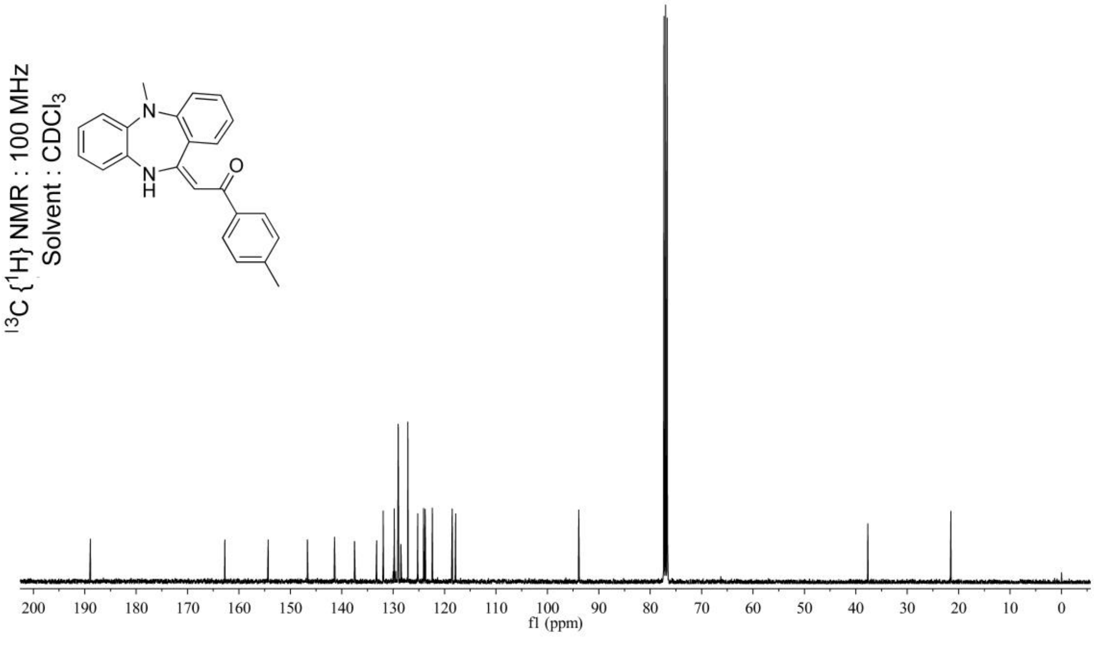
(*E*)-2-(5-methyl-5,10-dihydro-11*H*-dibenzo[*b,e*][1,4]diazepin-11-ylidene)-1-phenylethan-1-one(4am)



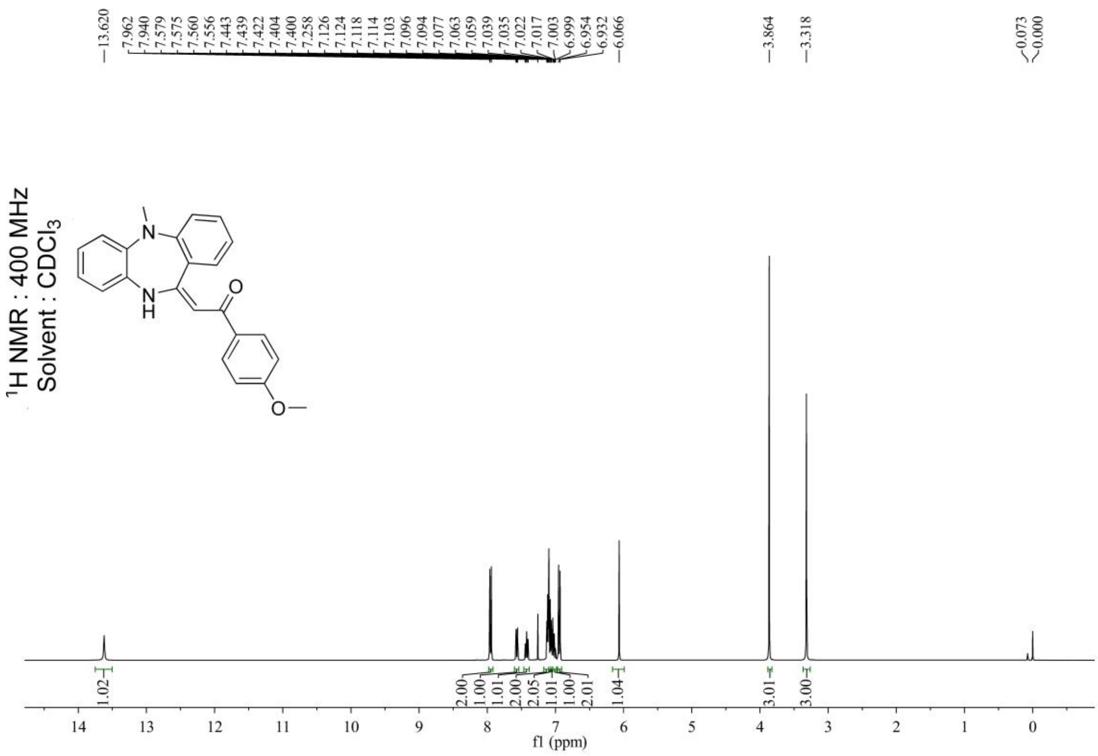


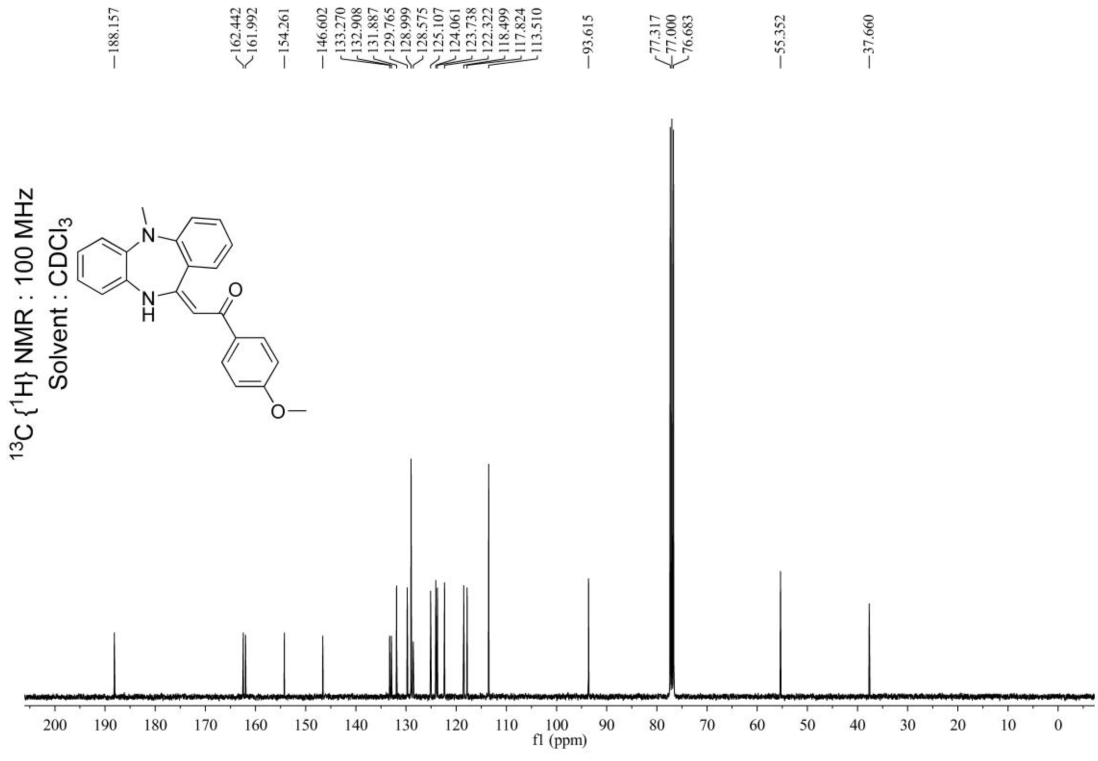
(*Z*)-2-(5-methyl-5,10-dihydro-11*H*-dibenzo*[b,e]*[1,4]diazepin-11-ylidene)-1-(p-tolyl)ethan-1-one(4an)



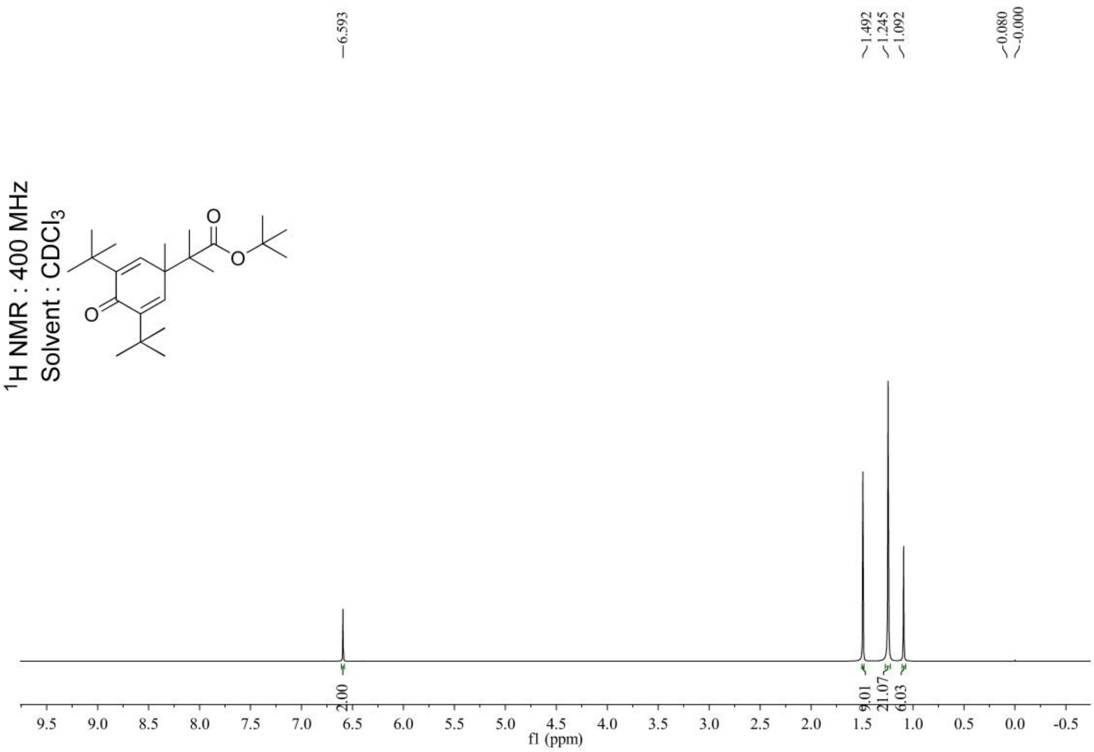


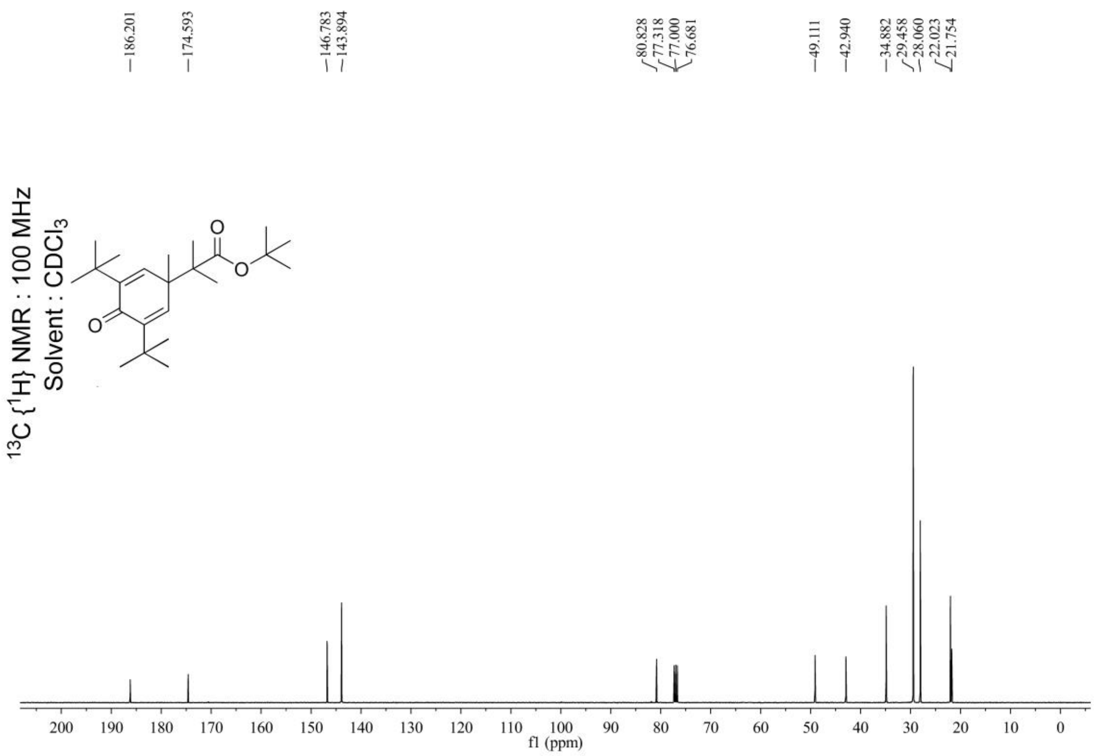
(*E*)-1-(4-methoxyphenyl)-2-(5-methyl-5,10-dihydro-11*H*-dibenzo[*b,e*][1,4]diazepin-11-ylidene)ethan-1-one(4ao)





tert-Butyl 2-(3,5-di-tert-butyl-1-methyl-4-oxo-1l5,4l5-phenyl)-2-methylpropanoate (5)





3,3-Dimethyl-5,5-diphenyldihydrofuran-2(3*H*)-one (6)