Supporting Information

Design and synthesis of novel monoterpenoidindole alkaloids-like analogues and their antitumour activities *in vitro*

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The preparation of genipin (G)

Genipin (**G**) was obtained by the enzymatic hydrolysis (emulsin) of geniposide that was isolated from *Gardenia jasminoides* Ellis. **G** was unsteady in aqueous solution and could be isomerized to form a couple of epimers[1] that can be observed by the NMR. These two epimers were unable to be separated by conventional methods.

^{1}H-NMR ($CDCl_3$, 400 MHz) for **G** δ (ppm): 7.53 (d, J = 0.8 Hz, 1H), 5.88 (d, J = 0.8 Hz, 1H), 4.80 (d, J = 7.2 Hz, 1H), 4.33 (d, J = 13.2 Hz, 1H), 4.28 (d, J = 13.2 Hz, 1H), 3.74 (s, 3H), 3.21 (m, 1H), 2.88 (m, 1H), 2.53 (ddd, J = 8.2, 8.2, 1.6 Hz, 1H), 2.06 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) for **G** δ (ppm): 168.0, 152.6, 142.0, 130.9, 110.7, 96.3, 61.2, 51.3, 48.1, 39.0, 36.7. ESI-MS *m/z*: 249.1 $[M + Na]^+$.

The preparation of G_1

According to the reported procedure[2], several drops of HCl were added to the solution of **G** (500 mg) in methanol (or ethanol), and stirred at 60℃ for 6 h. The solution was treated with $NaHCO_3$, then extracted three times with EtOAc, the combined organic phases were evaporated at reduced pressure. The residue was purified by silica gel column chromatography eluting with a gradient of petroleum ether and EtOAc (1:1) to afford $\mathbf{G_1}$. When R^1 was CH_3, $\mathbf{G_{1\text{-}1}}$ was obtained (the ESI-MS *m/z*: 263.0 $[M + Na]^+$), when R^1 was CH_3CH_2, $\mathbf{G_{1\text{-}2}}$ was obtained (ESI-MS *m/z*: 277.1 $[M + Na]^+$).

The preparation of G_{6a} and G_{6b}

Dess-Martin periodinane (DMP, 883 mg, 2.08 mmol) was added to the solution of $\mathbf{G_{1\text{-}1}}$ (500 mg, 2.08 mmol) in the dry dichloromethane, stirred at room temperature for 1h. The saturated solutions of $NaHCO_3$ and $Na_2S_2O_3$ were added progressively to the

mixture, then extracted three times with dichloromethane, after distillation of the dichloromethane, the residue was purified by silica gel column chromatography (petroleum ether:EtOAc = 8:1) to give **G_{6a-1}** and **G_{6b-1}**. **G_{6a-2}** and **G_{6b-2}** can be prepared in the same way. Intermediates **G_{6a}** and **G_{6b}** were a pair of epimer that were able to be separated by silica gel column chromatography.

^{1}H-NMR ($CDCl_3$, 400 MHz) for **G_{6a-1}** δ (ppm): 9.77 (s, 1H), 7.47 (d, *J* = 1.0 Hz, 1H), 6.98 (d, *J* = 1.7 Hz, 1H), 5.29 (d, *J* = 4.1 Hz, 1H), 3.73 (s, 3H), 3.48 (s, 3H), 3.34 (ddd, *J* = 7.8, 4.1, 1.0 Hz, 1H), 3.29 (dt, *J* = 3.9, 2.0 Hz, 1H), 3.01 (m, 1H), 2.57 (dddd, *J* = 19.5, 4.4, 2.8, 1.8 Hz, 1H). When R^1 was CH_3, **G_{6a-1}** was obtained (ESI-MS *m/z*: 261.1 $[M + Na]^+$; **G_{6b-1}** was obtained (ESI-MS *m/z*: 261.1 $[M + Na]^+$). When R^1 was CH_3CH_2, **G_{6a-2}** was obtained (ESI-MS *m/z*: 275.0 $[M + Na]^+$); **G_{6b-2}** was obtained (ESI-MS *m/z*: 275.0 $[M + Na]^+$).

The preparation of G_{1a} and G_{1b}

G_{6a-2} (546 mg, 2.16 mmol) was dissolved in MeOH, then $NaBH_4$ (90 mg, 2.38 mmol) was added to the solution and stirred at room temperature for 30 minutes, then extracted three times with EtOAc, the combined organic phases were evaporated at reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether: EtOAc = 4:1) to give **G_{1a-2}**. And other intermediates **G_{1a-1}**, **G_{1b-1}** and **G_{1b-2}** can be got in the same way.

^{1}H-NMR ($CDCl_3$, 400 MHz) for **G_{1a-2}** δ (ppm): 7.52 (s, 1H), 5.84 (s, 1H), 4.55 (d, *J* = 8.4 Hz, 1H), 4.26 (s, 2H), 4.14 (m, 1H), 3.73 (s, 3H), 3.64 (m, 1H), 3.22 (d, *J* = 8.6 Hz, 1H), 3.18 (d, *J* = 8.6 Hz, 1H)， 2.88 (m, 1H), 2.68 (br s, 1H), 2.59 (t, *J* = 8.2 Hz, 1H), 2.07 (m, 1H), 1.80 (t, *J* = 6.8 Hz, 3H). ESI-MS *m/z*: 277.1 $[M + Na]^+$.

^{1}H-NMR ($CDCl_3$, 400 MHz) for $\mathbf{G_{1b\text{-}2}}$ δ (ppm): 7.46 (s, 1H), 5.76 (s, 1H), 5.11 (d, *J* = 2.8 Hz, 1H), 4.26 (d, *J* = 13.2 Hz, 1H), 4.18 (d, *J* = 13.2 Hz, 1H), 3.88 (m, 1H), 3.72(s, 1H), 3.57 (s, 1H), 3.15 (m, 2H), 2.75 (m, 1H), 2.36 (br s, 1H), 2.25 (m, 1H), 1.21 (t, *J* = 7.0 Hz, 3H); ESI-MS *m/z*: 277.1 $[M + Na]^+$.

The preparation of G_2

G (501 mg, 2.21 mmol), imidazole (301 mg, 4.43 mmol) were added into a flask in dry THF under the condition of ice-bath, the solution of TBS-Cl in dry THF was injected slowly into the mixture, then stirred at room temperature, monitored by TLC. The residue was obtained after distillation under reduced pressure, then purified by silica gel column chromatography (petroleum ether:EtOAc = 10:1) to give $\mathbf{G_{2m}}$ (ESI-MS m/z: 363.2 [M + Na]+). Dess-Martin periodinane (451 mg, 1.06 mmol) was added to the solution of $\mathbf{G_{2m}}$ (181 mg, 0.532 mmol) in dry dichloromethane, stirred at room temperature, monitored by TLC[6]. The saturated solution of $Na_2S_2O_3$ was added progressively to the mixture, then extracted three times with diethyl ether, the combined organic phases were evaporated at reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether:EtOAc = 10:1) to offer $\mathbf{G_2}$ (ESI-MS m/z: 361.1 $[M + Na]^+$).

The preparation of G_3

$\mathbf{G_{1a\text{-}1}}$ (200 mg, 0.832 mmol) and Ph_3P (251 mg, 0.957 mmol) were added into a flask in dry dichloromethane, the solution of CBr_4 (317 mg, 0.957 mmol) in dry dichloromethane[3] was injected into the flask and stirred at room temperature under N_2 atmosphere, monitored by TLC. The residue was obtained after distillation under reduced pressure, then purified by silica gel column chromatography (petroleum ether:EtOAc = 10:1) to give $\mathbf{G_3}$.

The preparation of G_4

G_{1a-1} (50 mg, 0.222 mmol) and triethylamine (37 μL, 0.266 mmol) were added into a flask in dry THF, and acrylylchloride (18 μL, 0.224 mmol) was added and stirred at room temperature for 4h[4]. Then extracted three times with EtOAc, the combined organic phases were evaporated at reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether:EtOAc = 4:1) to offer **G_4**.

G_4: ESI-MS *m/z*: 317.0 $[M+Na]^+$.

The preparation of G_5

G_{1a-1} (140 mg, 0.588 mmol), phthalimide (111 mg, 0.756 mmol), Ph_3P (196 mg, 0.756 mmol) were added into a flask in dry THF. Diisopropyl azodiformate (153μL, 1.164 mmol) was injected into the solution and stirred at room temperature for 1h[5], then extracted three times with EtOAc, the combined organic phases were evaporated at reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether:EtOAc = 8:1) to give **G_{5m}**. 80% hydrazinehydrate (127 μL) was added to the solution of **G_{5m}** (130 mg, 0.548 mmol) in EtOH and stirred overnight. After filtration and distillation under reduced pressure, the residue was purified with preparative TLC (EtOAc:MeOH:Et_2NH = 60:5:1) to provide **G_{5-1}** (ESI-MS *m/z*: 240.1 $[M+H]^+$). **G_{5-2}** can be obtained in the same way by using **G_{1a-2}**.

The preparation of G_{7a}

The aqueous solution of NaOH (1.5 mL, 1M) was added to the solution of **G_{1a-2}** (30 mg) in THF, stirred at room temperature for 24 h. The pH of the solution was adjusted to around 5 by progressively adding 10% HCl, then extracted three times with ethyl

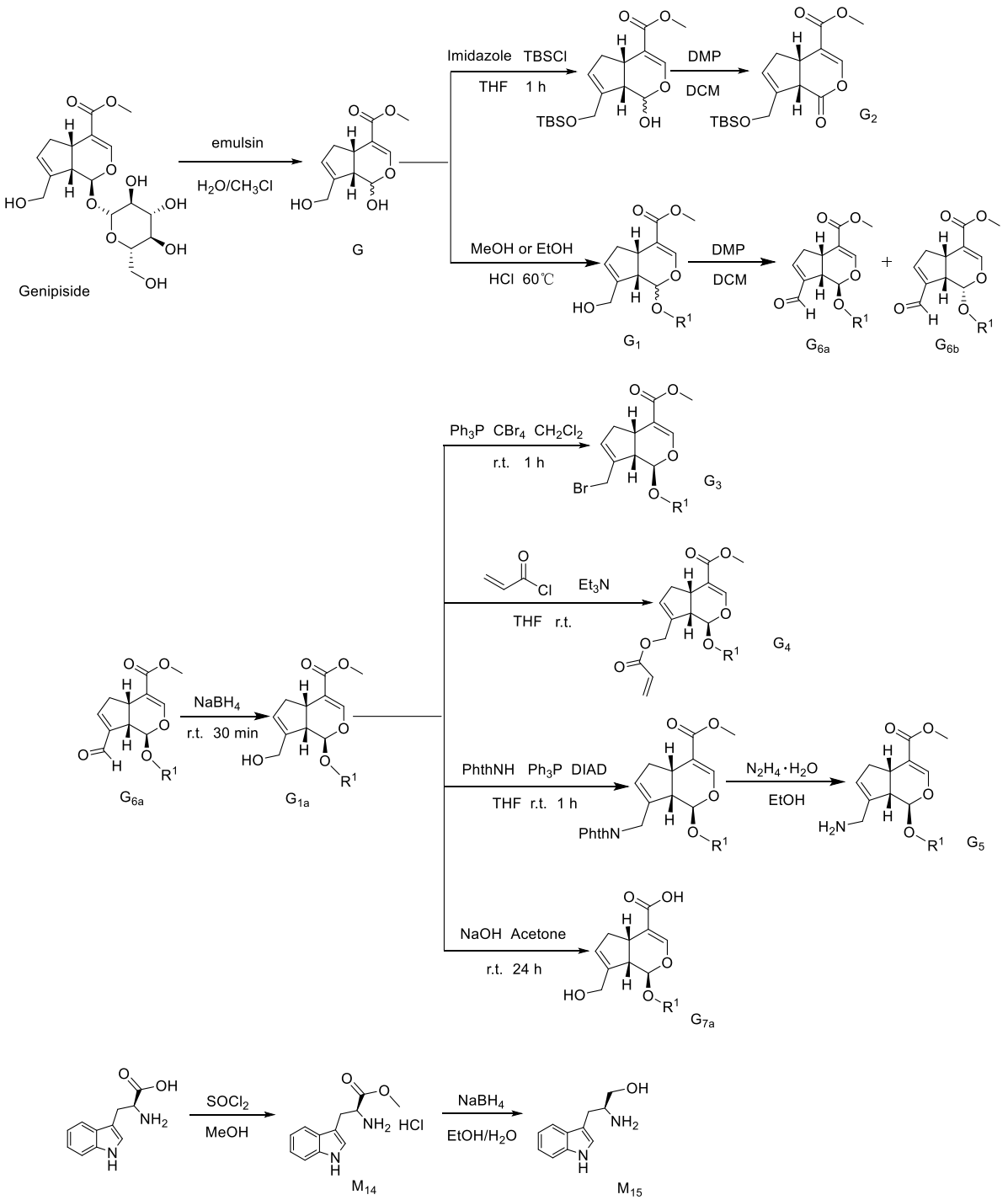
acetate. The combined organic phases were evaporated at reduced pressure. The residue was purified with silica gel column chromatography (petroleum ether:EtOAc AcOH = 100:50:3) to give **G_{7a}**.

The preparation of M_{14}

Thionyl chloride (180 μL, 0.297 mmol) was added dropwisely to the solution of tryptophan (200 mg, 0.979 mmol) in dry MeOH under the condition of ice-bath, then heated to reflux, monitored by TLC. **M_{14}** was obtained after distillation under reduced pressure (**M_{14}**: ESI-MS *m/z*: 219.1 $[M + H]^+$).

The preparation of M_{15}

$NaBH_4$ (600 mg, 15.9 mmol) was added gradually to the solution of **M_{14}** (300 mg, 1.18 mmol) in EtOH/H_2O (V/V = 1:1), stirred at room temperature for 11h, then extracted three times with $CHCl_3$. The combined organic phases were evaporated at reduced pressure to give **M_{15}** (ESI-MS *m/z*: 189.1 $[M - H]^-$)



Scheme 1. Synthesis routes of intermediates.

References

[1] Yang Yi-Shun, Zhang Tong, Yu Shai-Cheng, Transformation of geniposide into genipin by immobilized β-glucosidase in a two-phase aqueous-organic system, *Molecules*. 2011, 16(5): 4295 - 4304.

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[4] Takayoshi Arai, Tetuya Sekiguti, Kazuhiro Otsuki, "Catalyst Analogue": A Concept for Constructing Multicomponent Asymmetric Catalysts (MAC) by Using a Polymer Support, *Angew. Chem. Int. Ed*. 2003(42):2144-2147.

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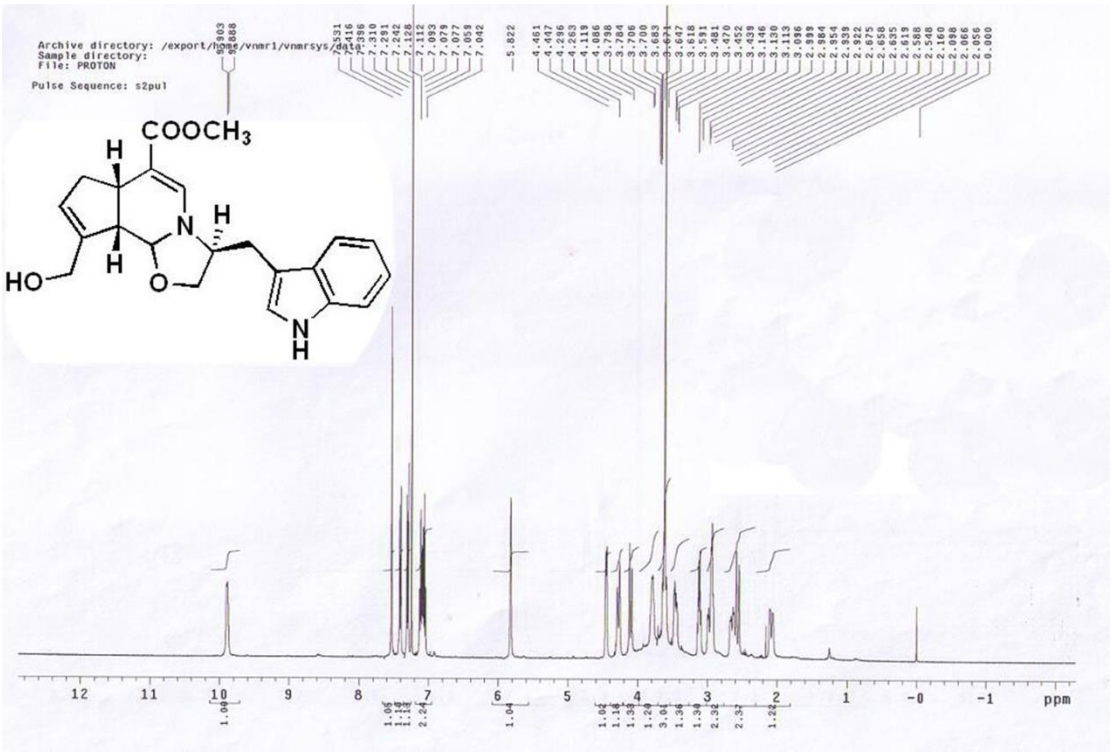
[6] Miura, Okajima, Hondo, Acid-catalyzed cyclization of vinylsilanes bearing a hydroxy group: A new method for stereoselective synthesis of disubstituted tetrahydrofurans, *J. Am. Chem. Soc*. 2000, 122(46): 11348 - 11357.

^{1}H and ^{13}C-NMR, and HR-MS spectra for compounds 1−34.

^{1}H-NMR of compound **1**



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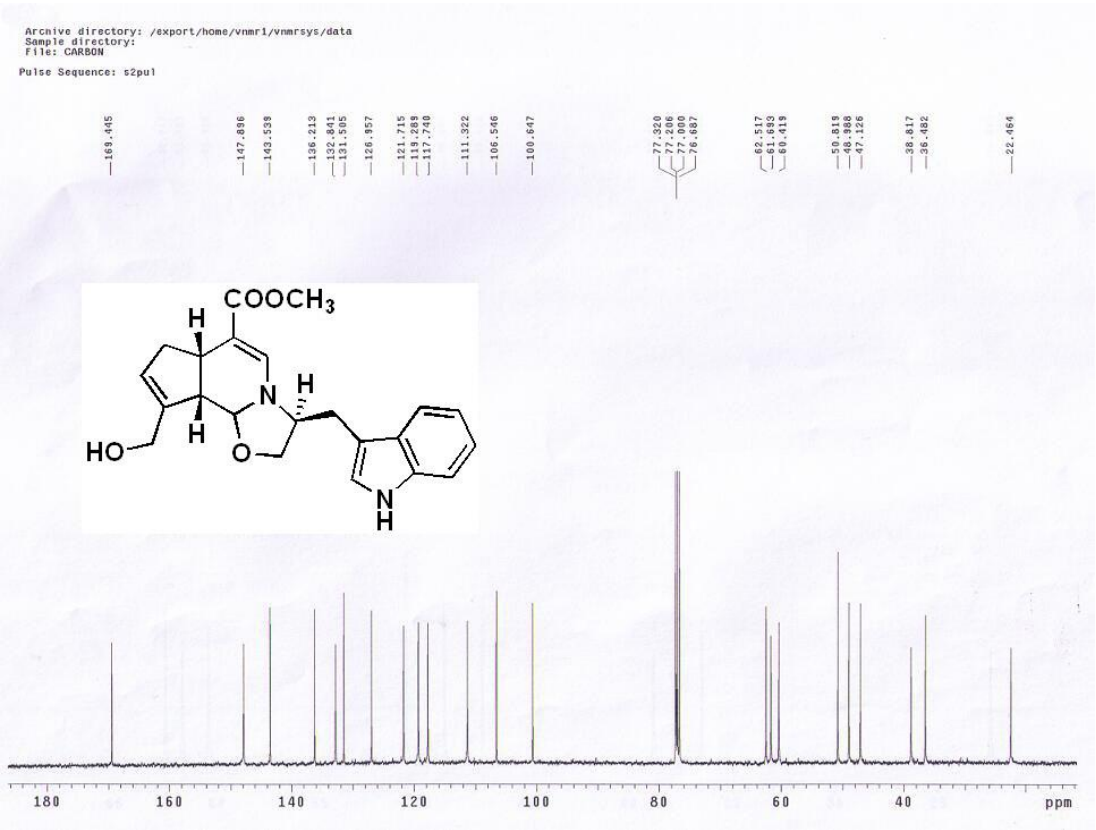

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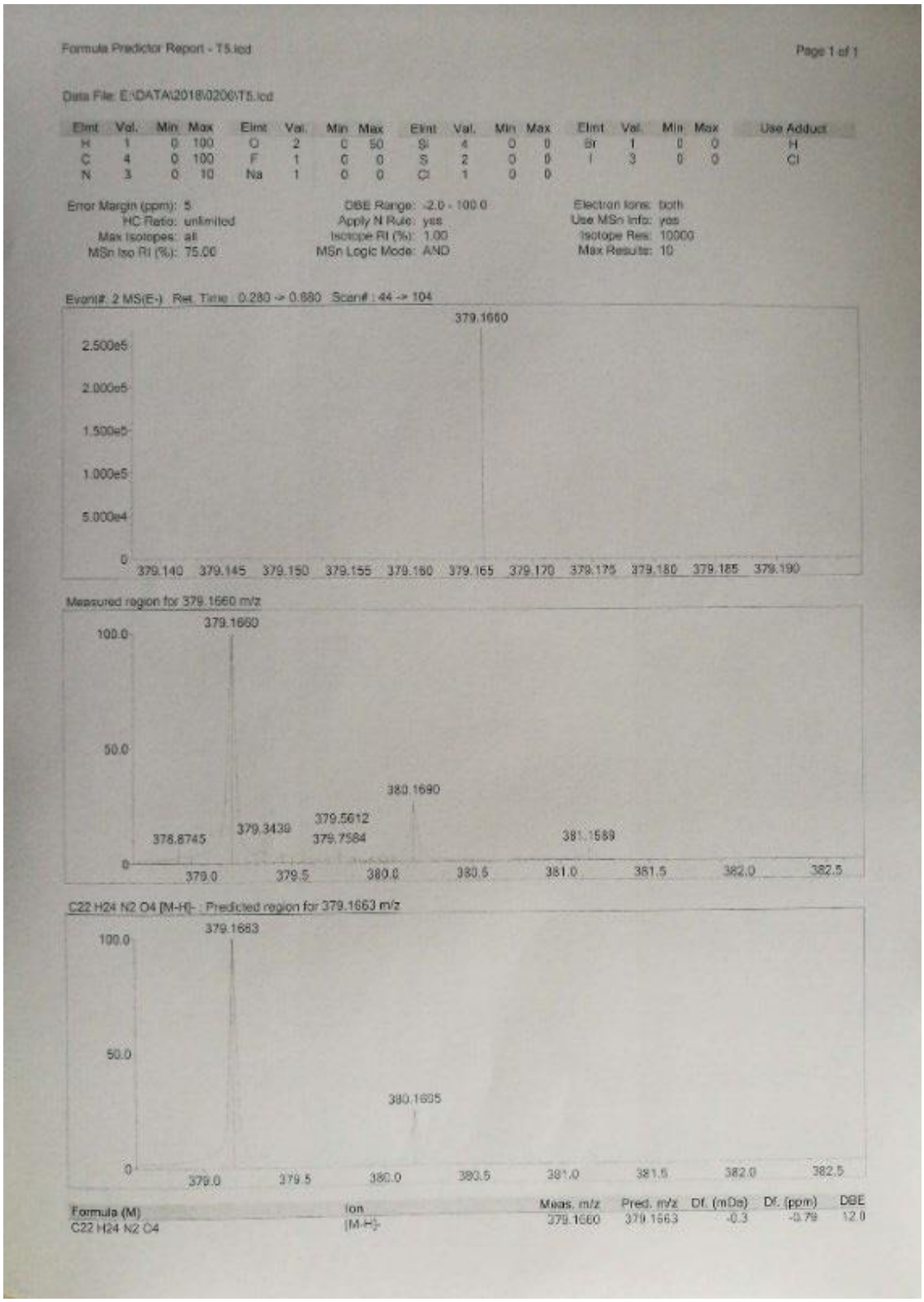

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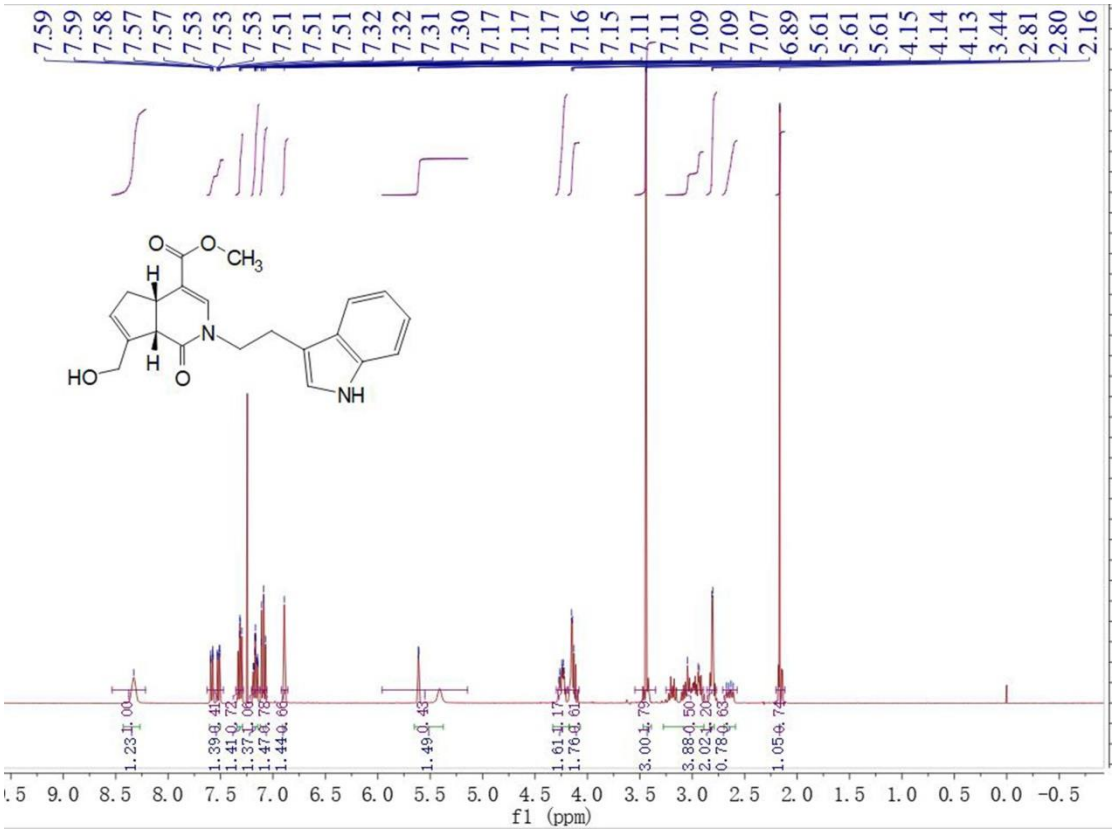

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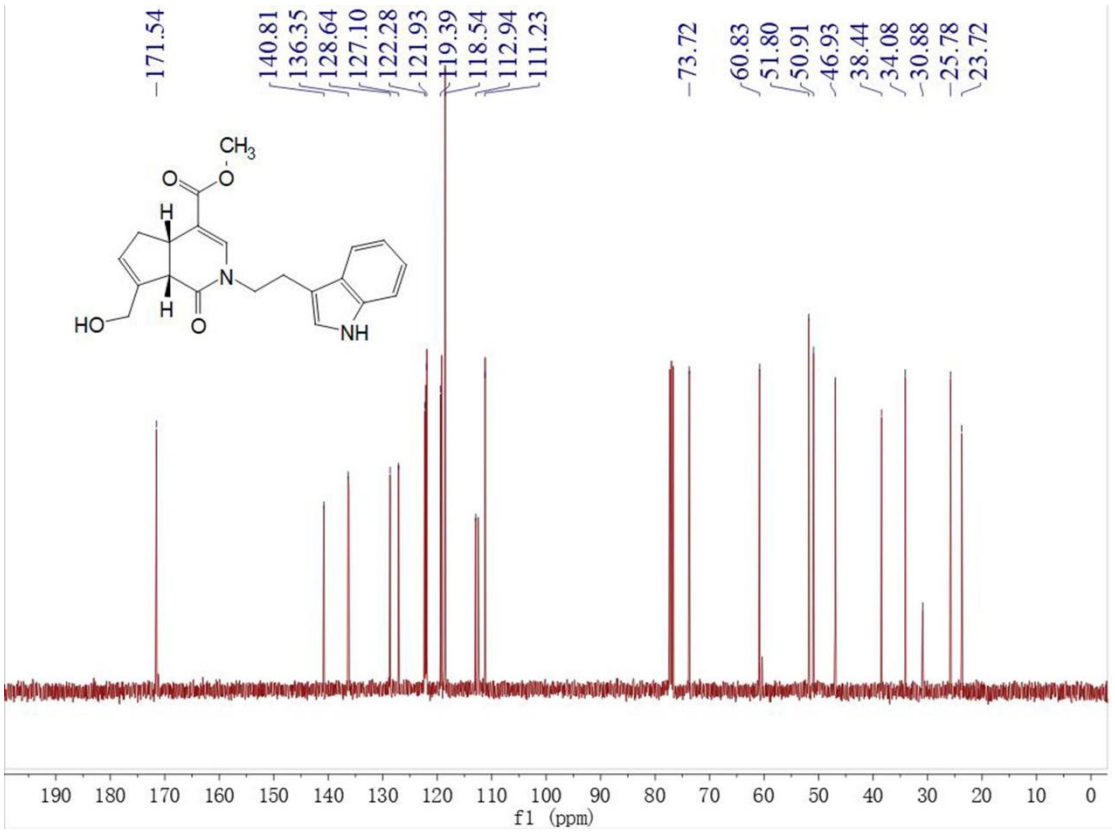

HR-EI-MS of compound **2**

Elemental Composition Report **Page 1**

Single Mass Analysis
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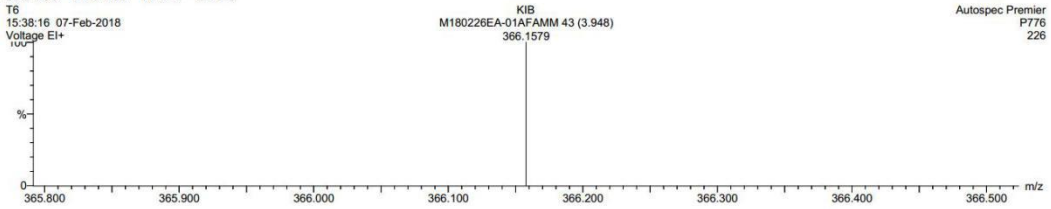
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
16 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 N: 2-2 O: 3-5



Minimum:				-10.0		
Maximum:		200.0	10.0	120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
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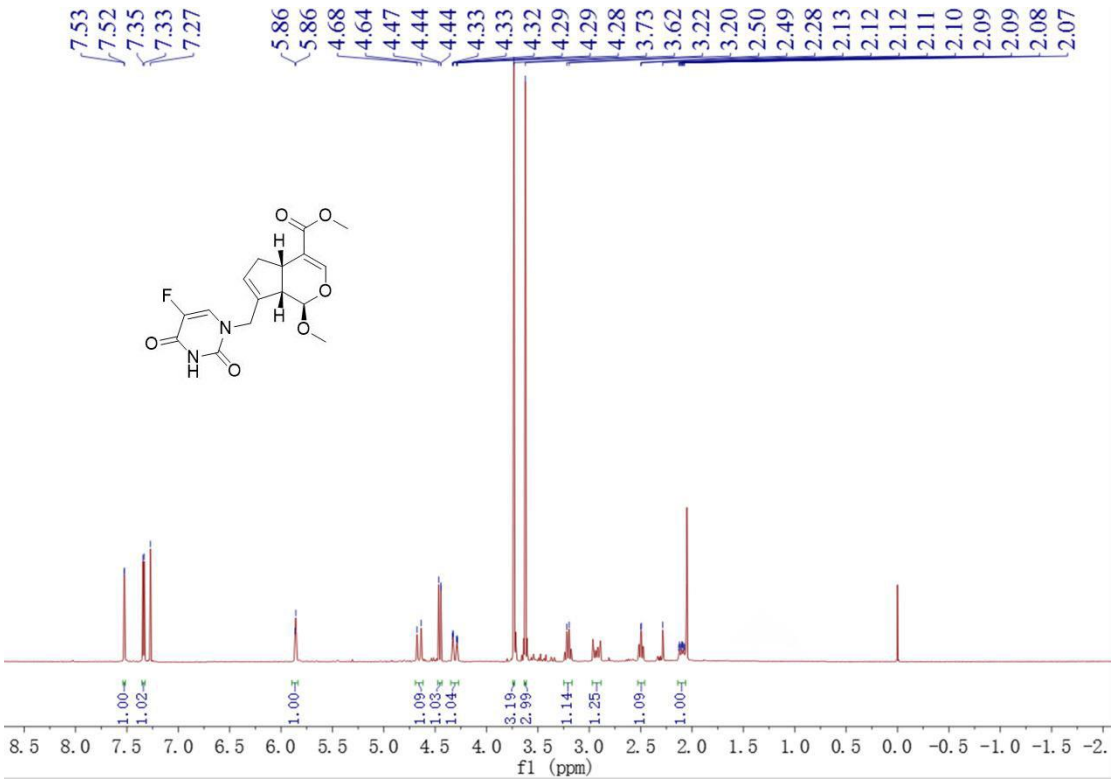
^{1}H-NMR of compound **3**



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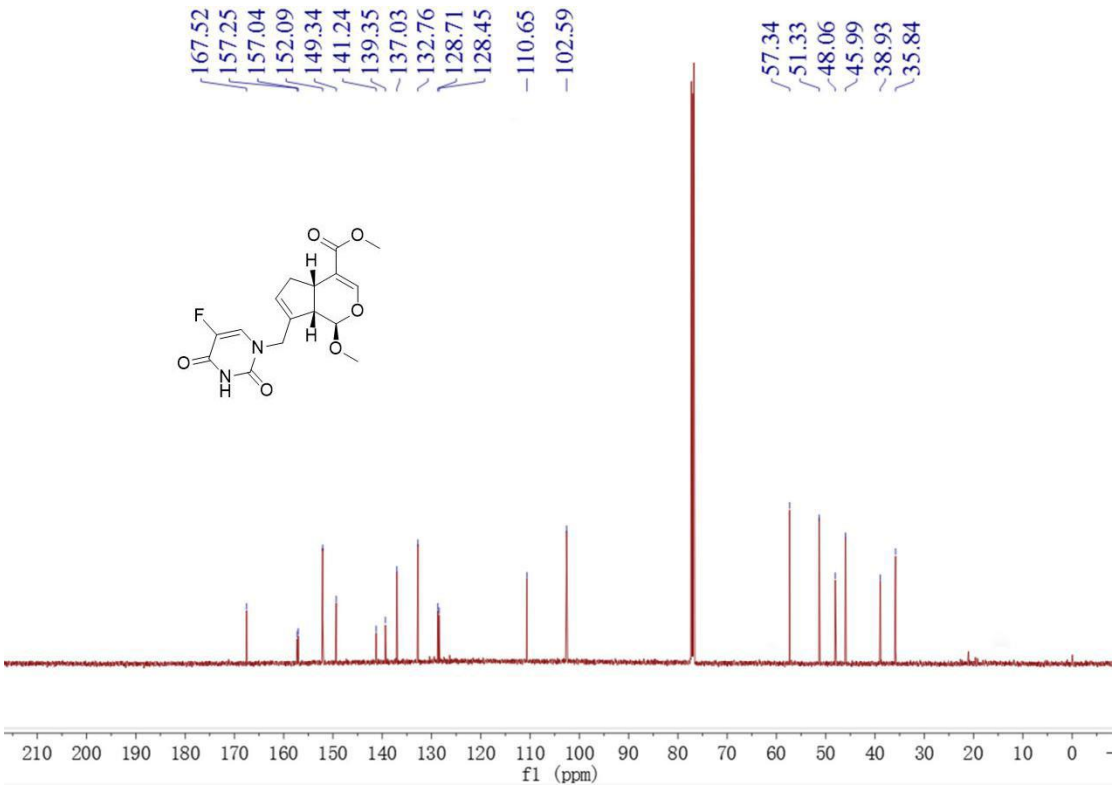
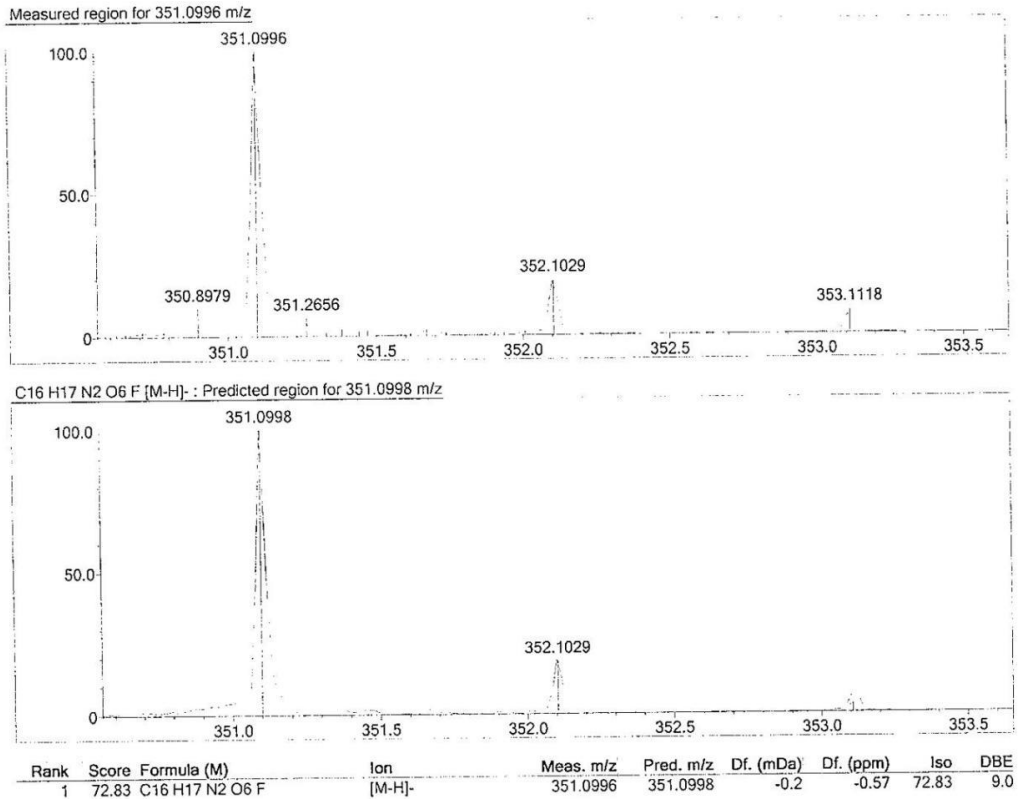
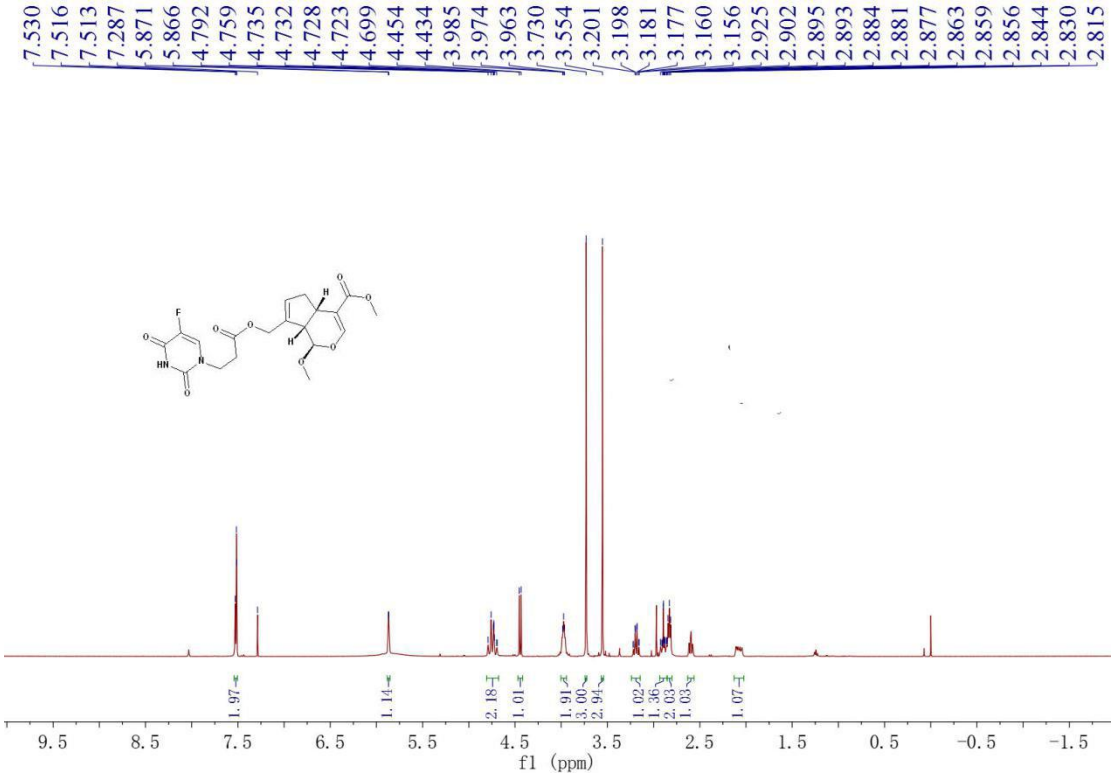


HR-EI-MS of compound **3**



Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	72.83	C16 H17 N2 O6 F	[M-H]-	351.0996	351.0998	-0.2	-0.57	72.83	9.0

^{1}H-NMR of compound **4**



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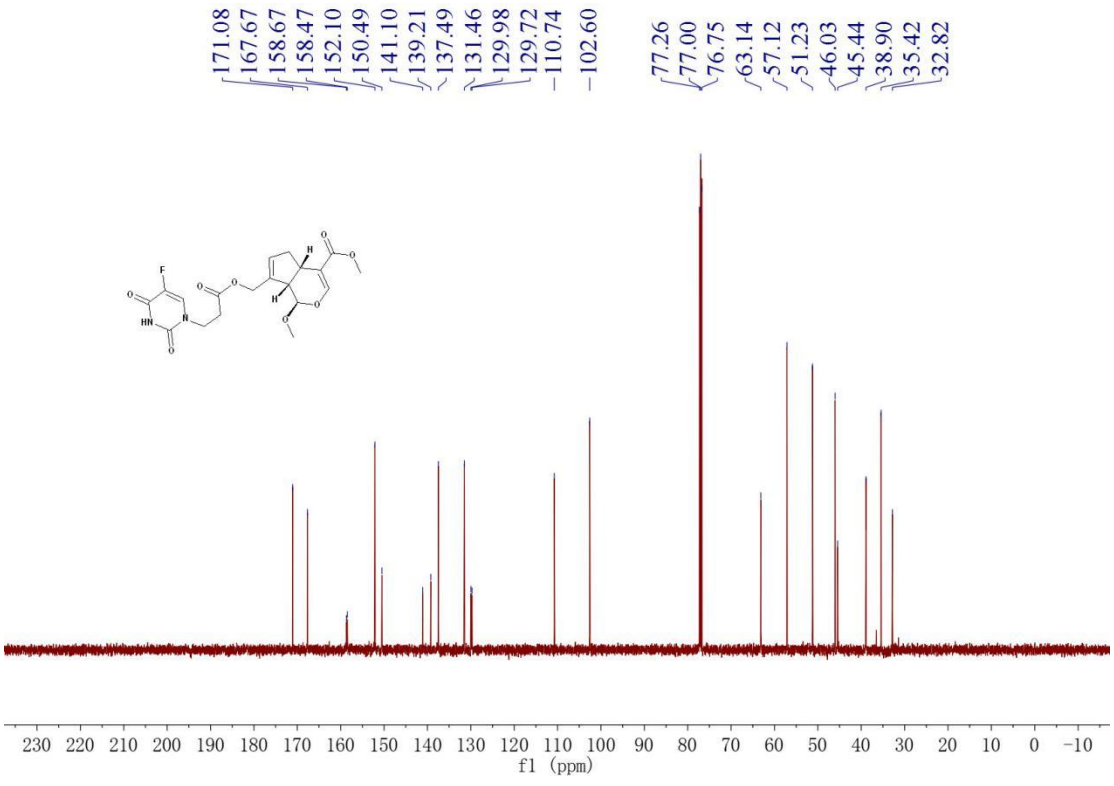

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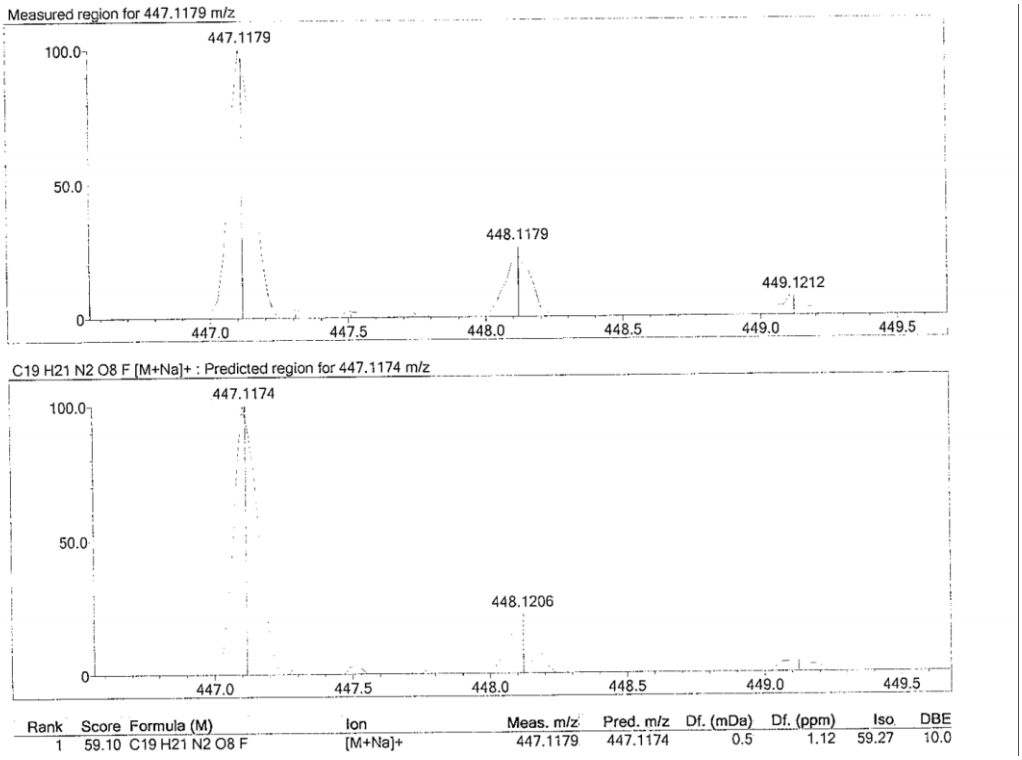
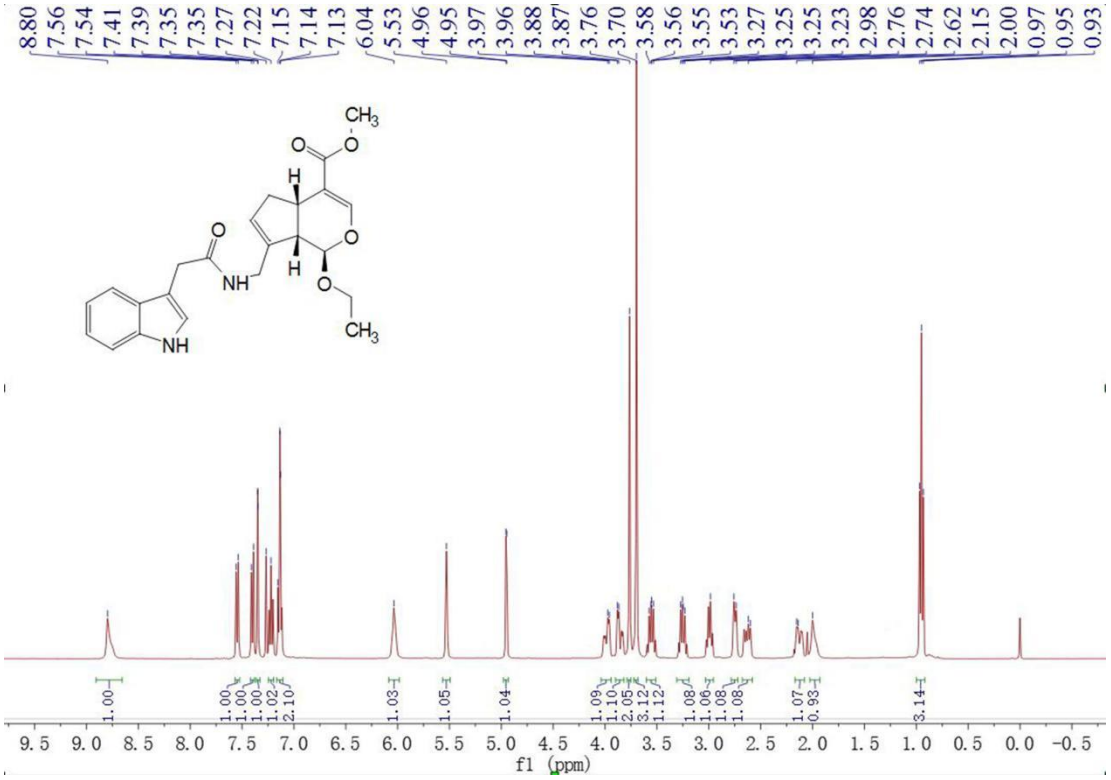


Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	59.10	C19 H21 N2 O8 F	[M+Na]+	447.1179	447.1174	0.5	1.12	59.27	10.0

^{1}H-NMR of compound **5**



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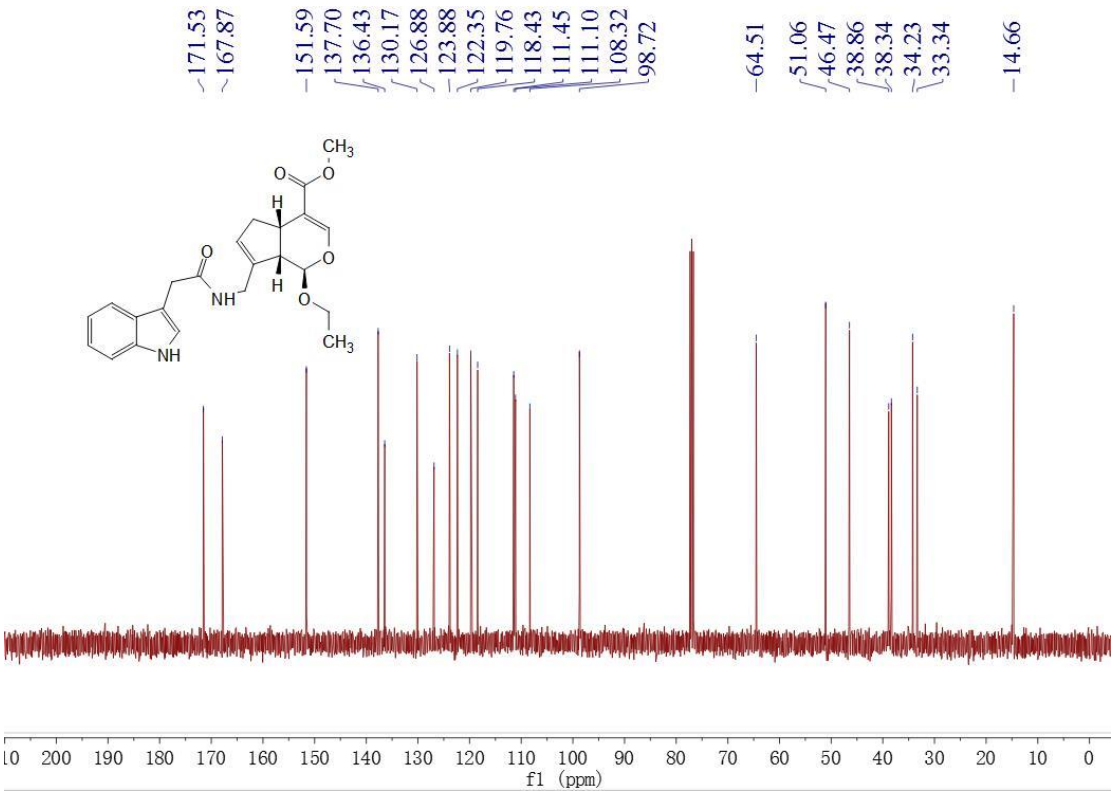

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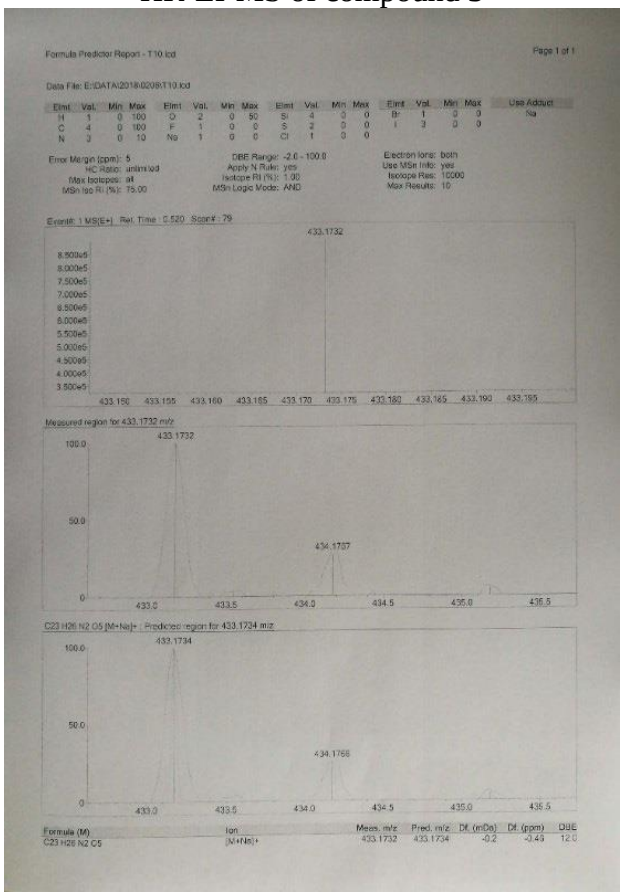

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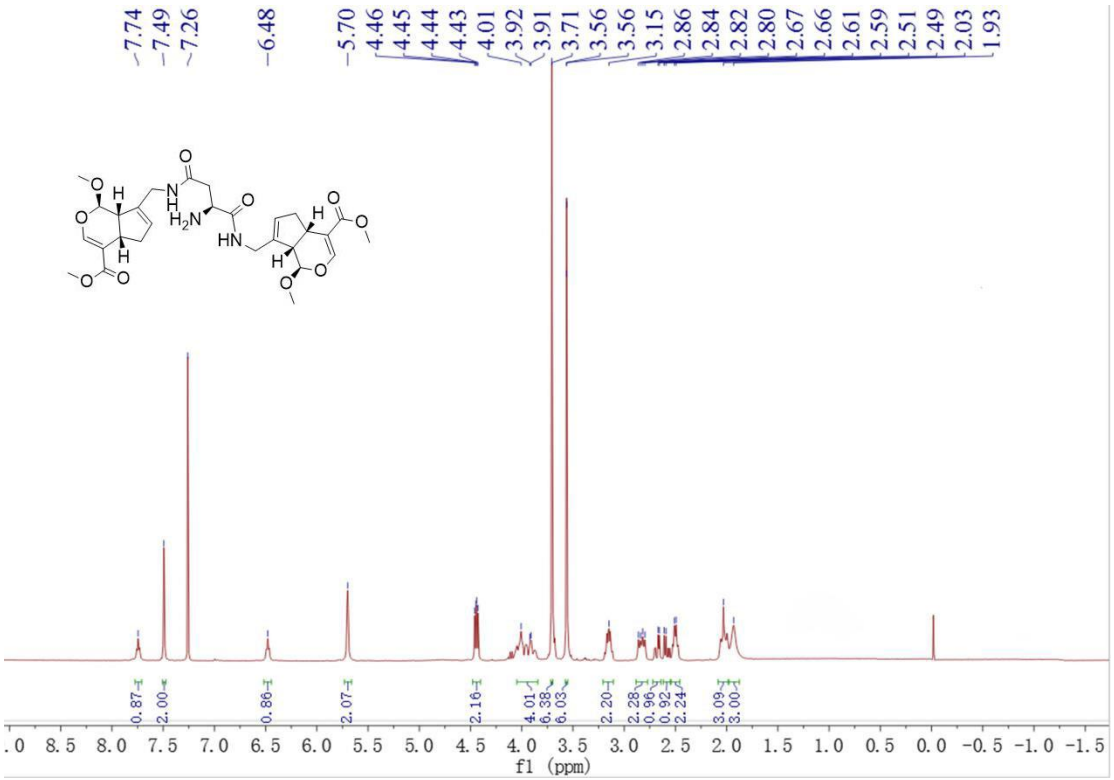

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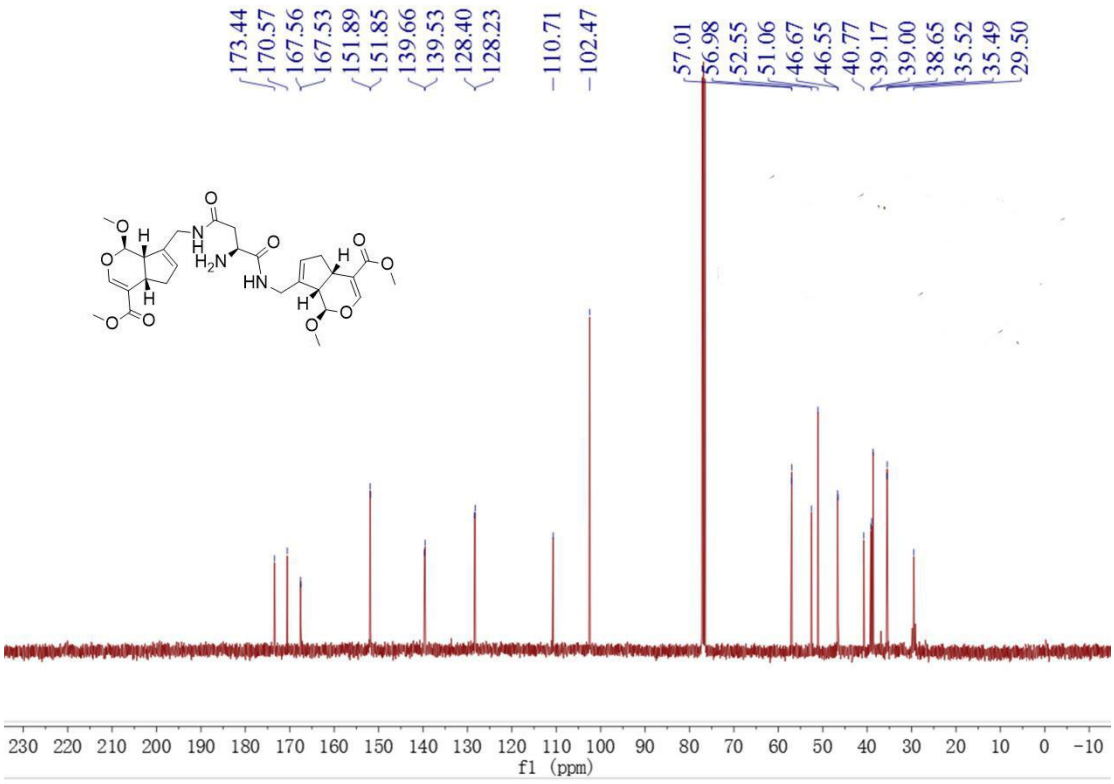

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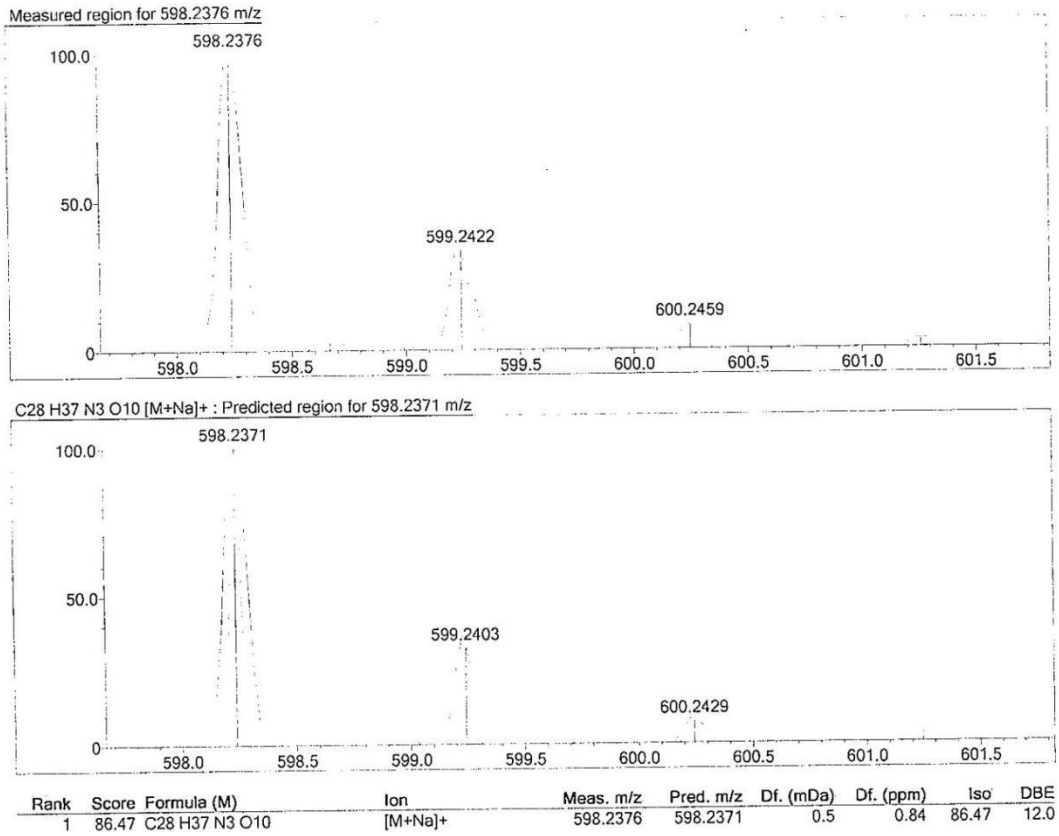
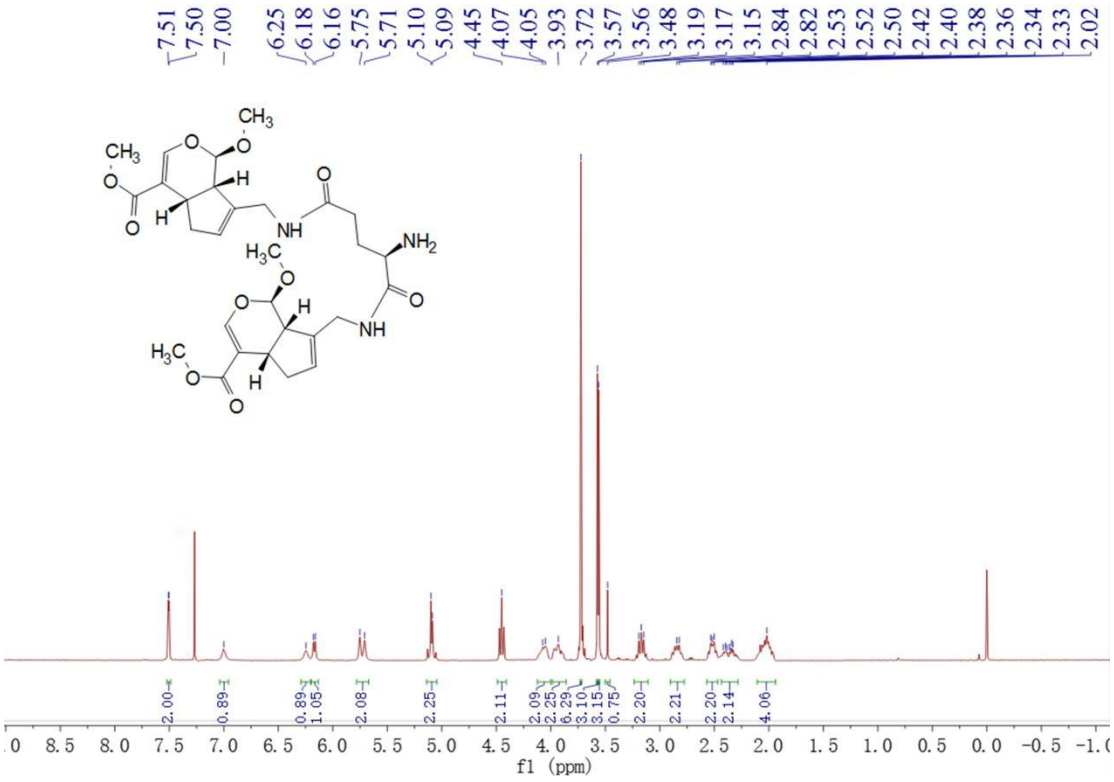


Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	86.47	C28 H37 N3 O10	[M+Na]+	598.2376	598.2371	0.5	0.84	86.47	12.0

^{1}H-NMR of compound **7**



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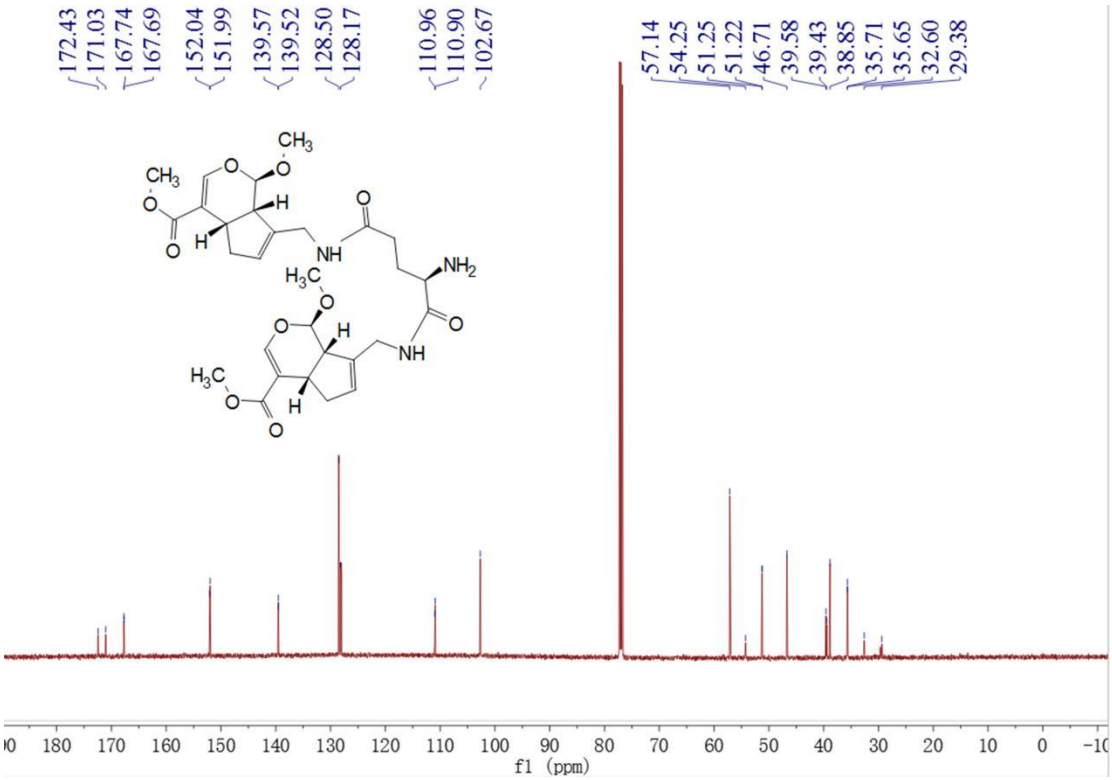

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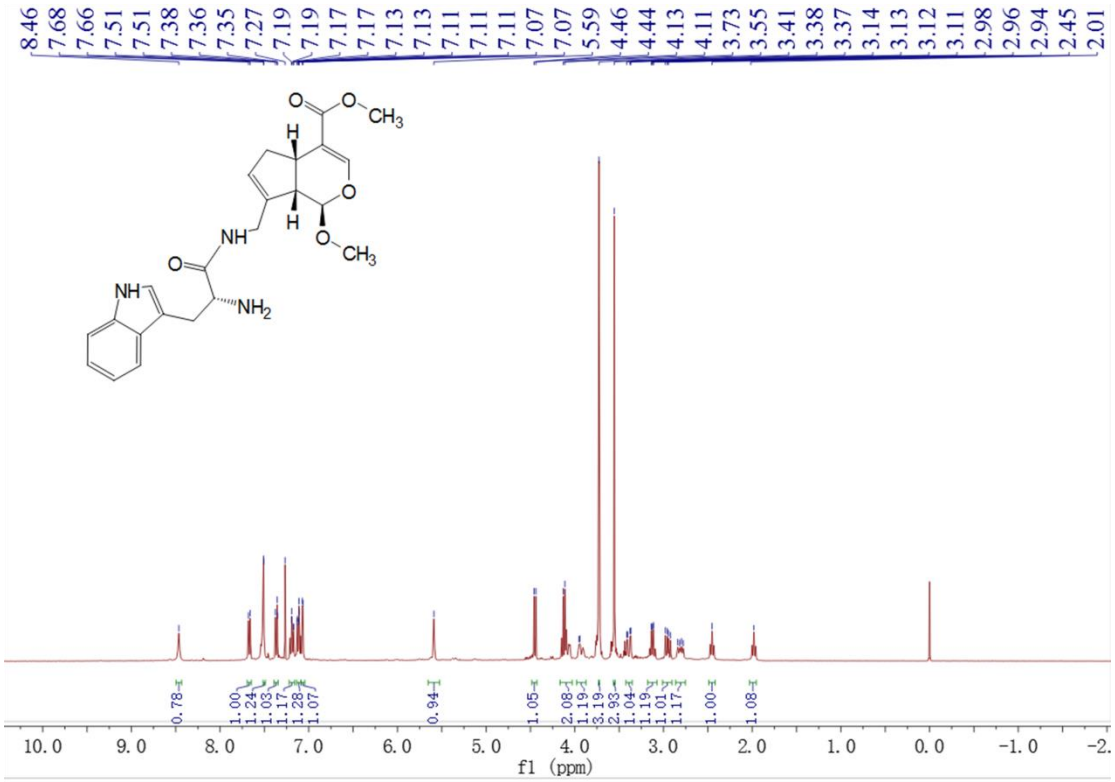

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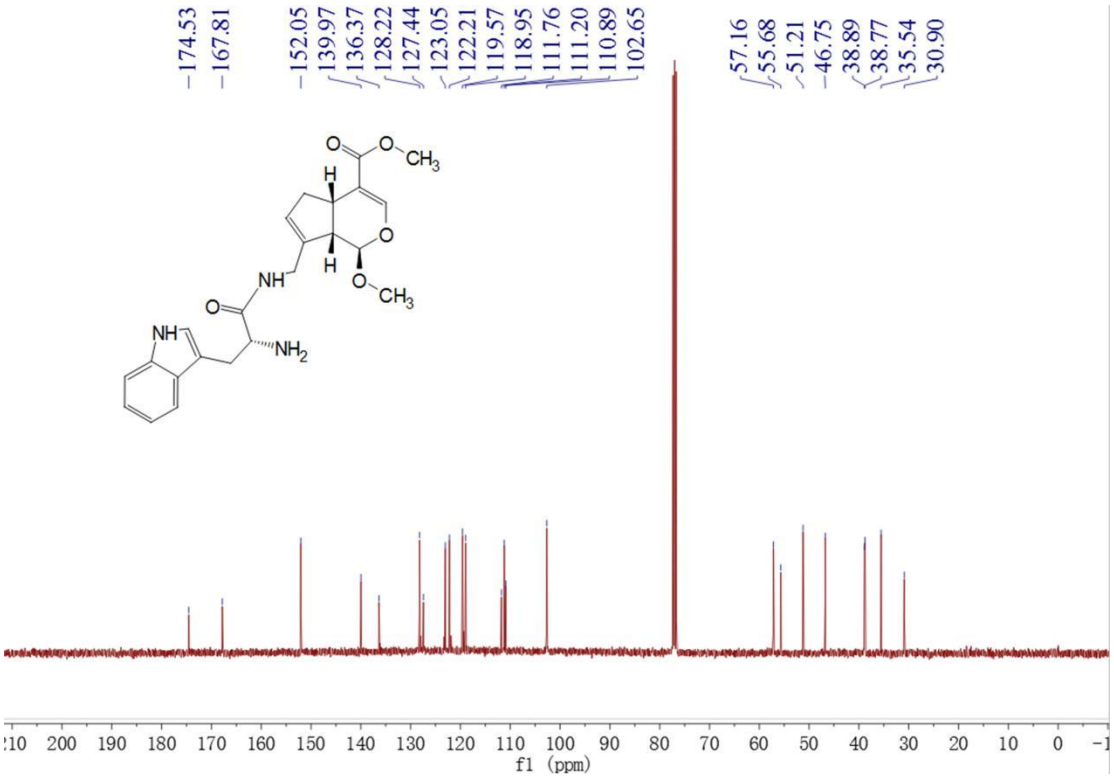

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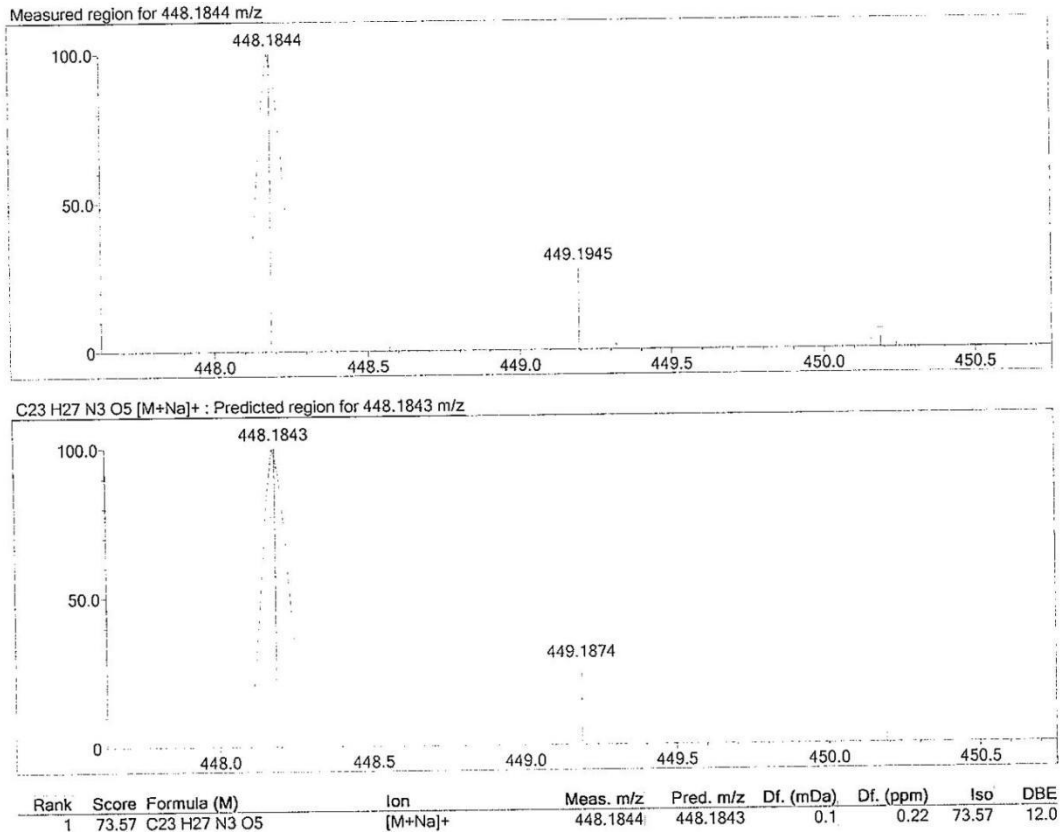

Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	73.57	C23 H27 N3 O5	[M+Na]+	448.1844	448.1843	0.1	0.22	73.57	12.0

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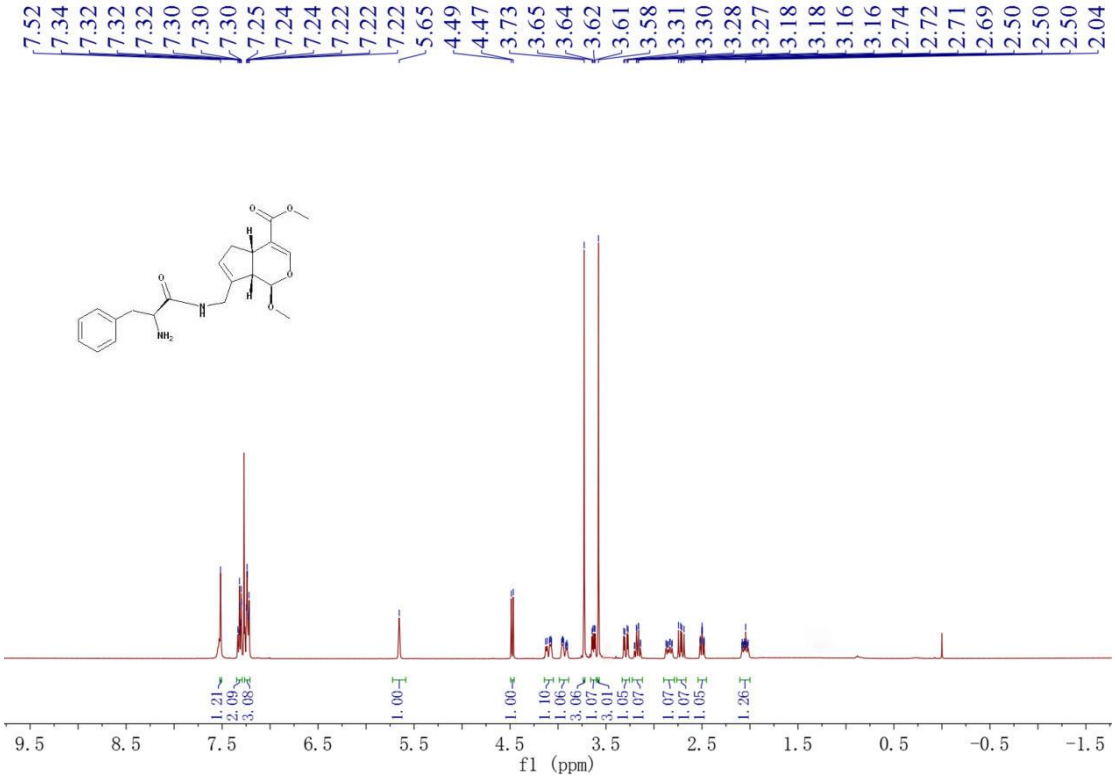
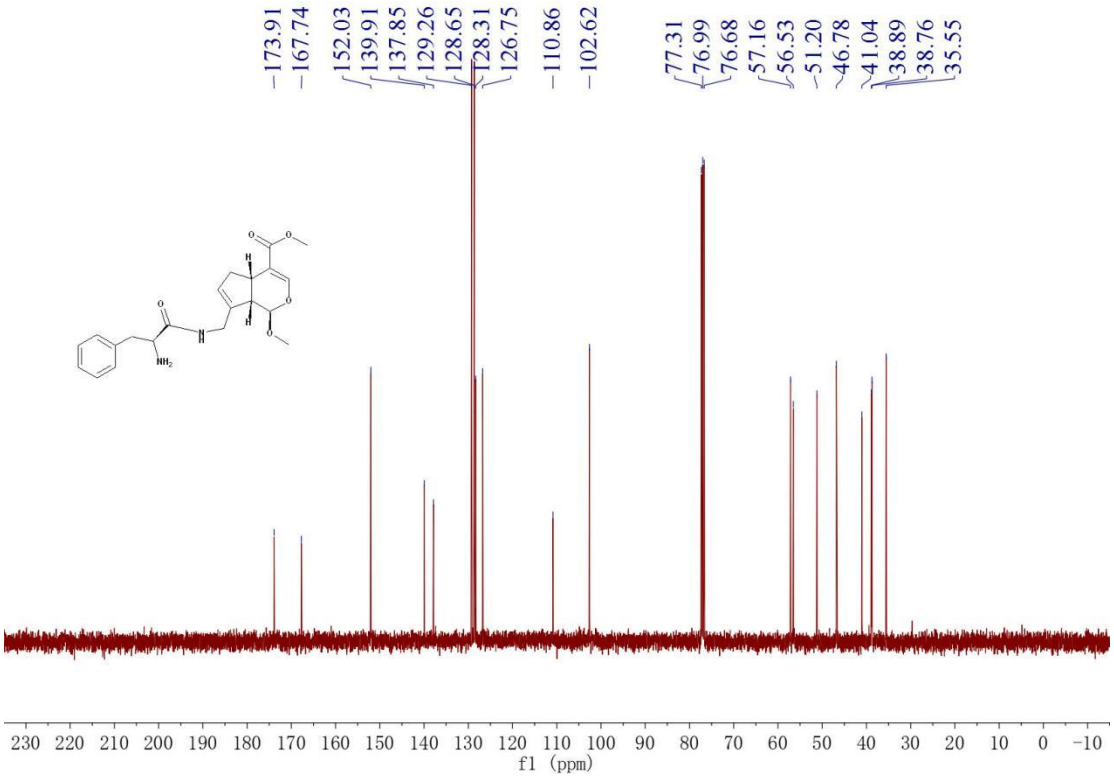
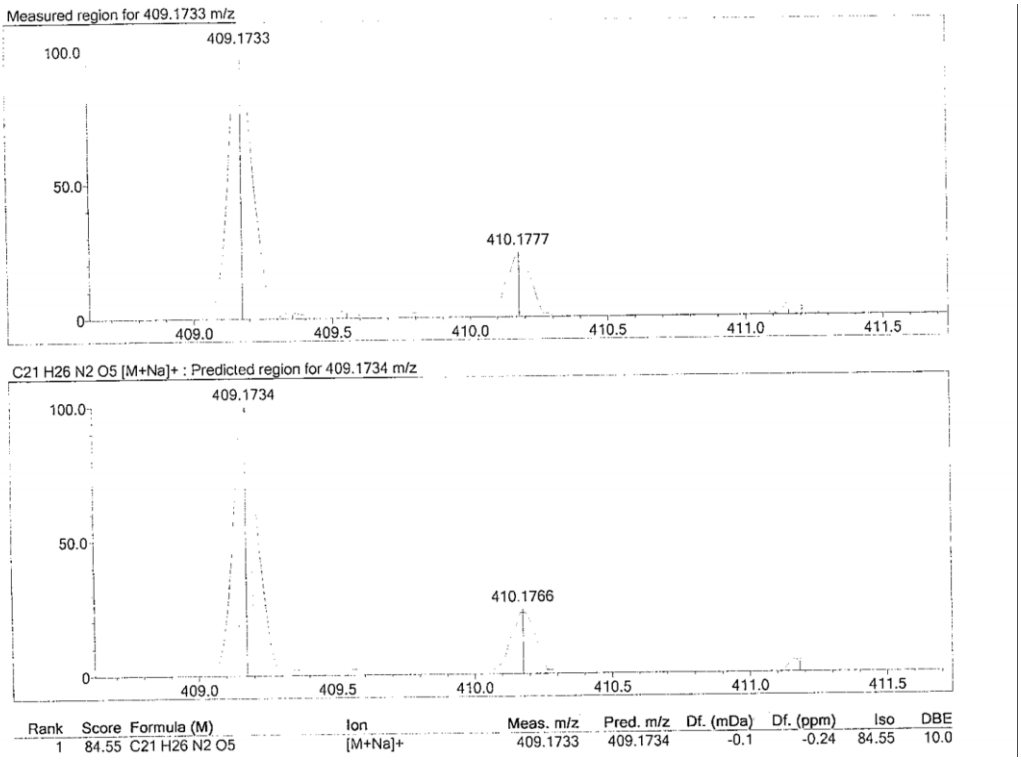


^{13}C-NMR of compound **9**

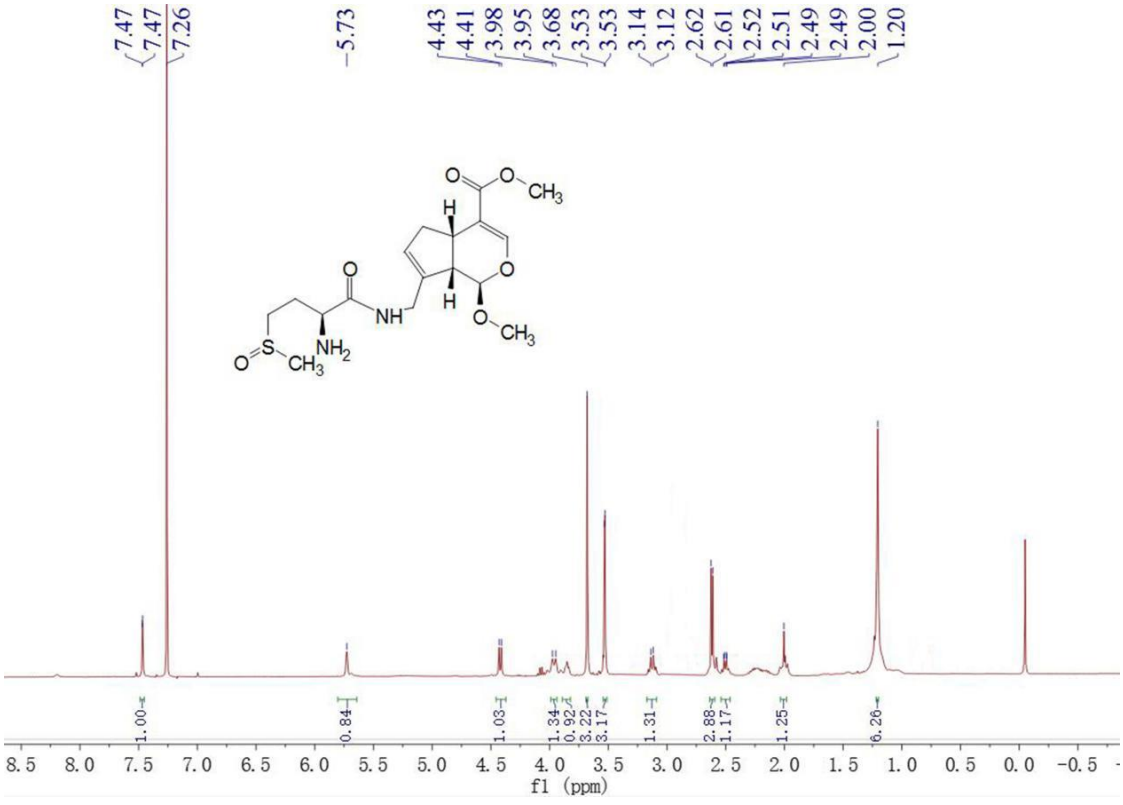


HR-EI-MS of compound **9**

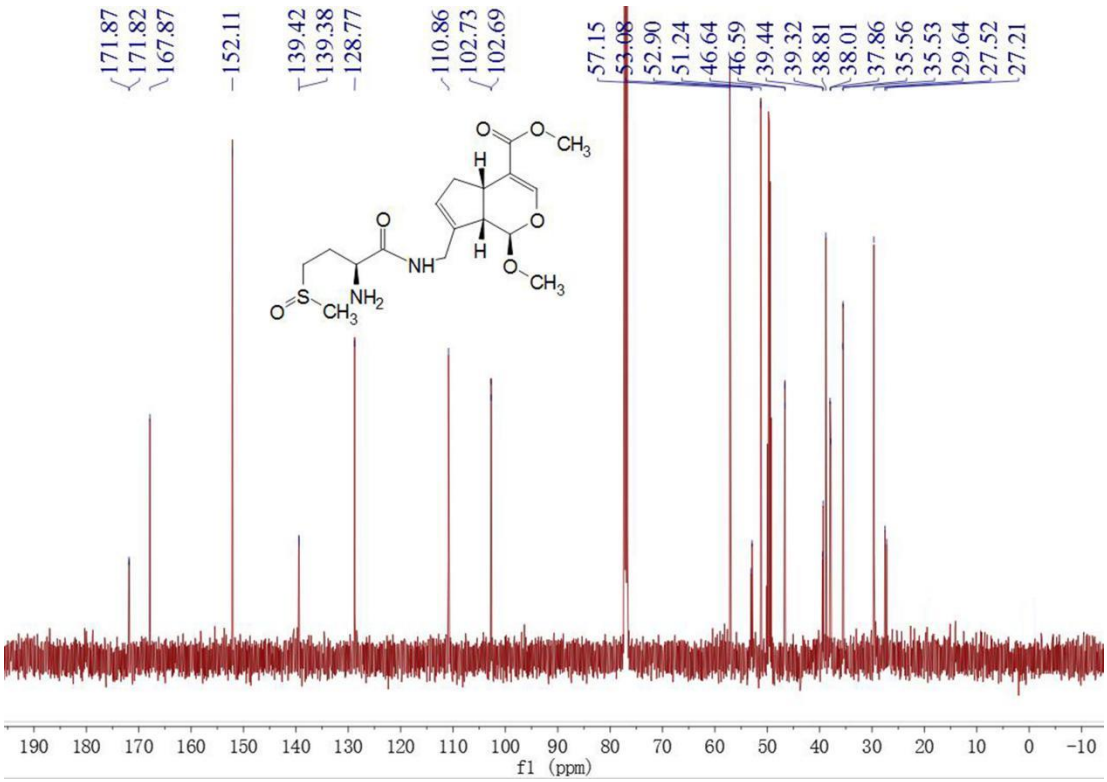


Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	84.55	C21 H26 N2 O5	[M+Na]+	409.1733	409.1734	-0.1	-0.24	84.55	10.0

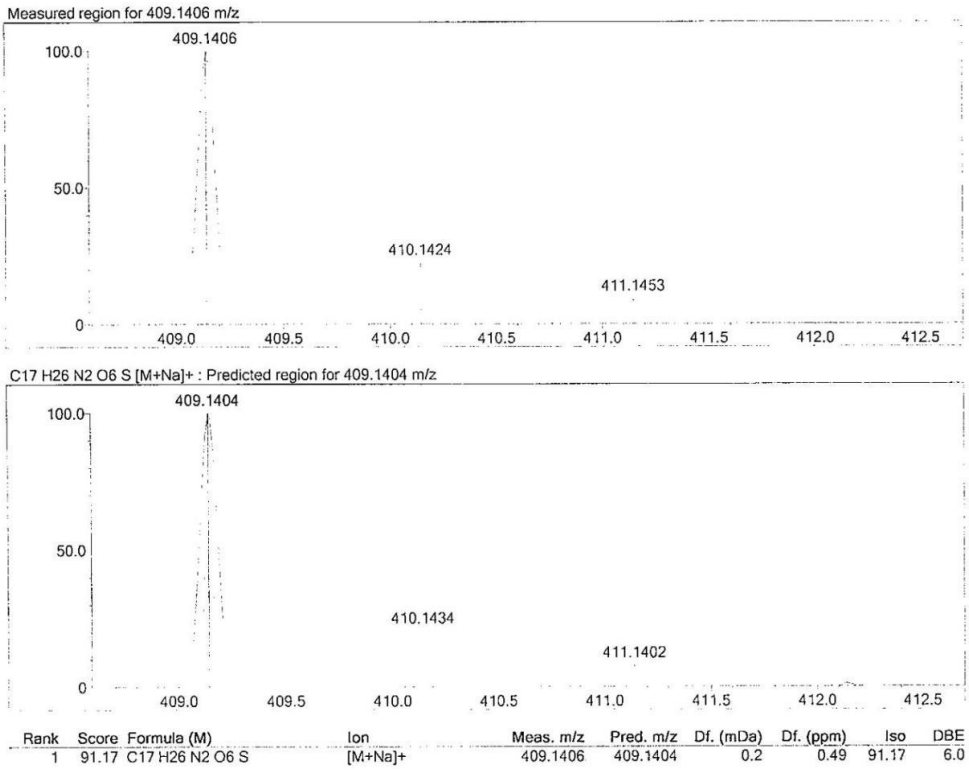
^{1}H-NMR of compound **10**



^{13}C-NMR of compound **10**

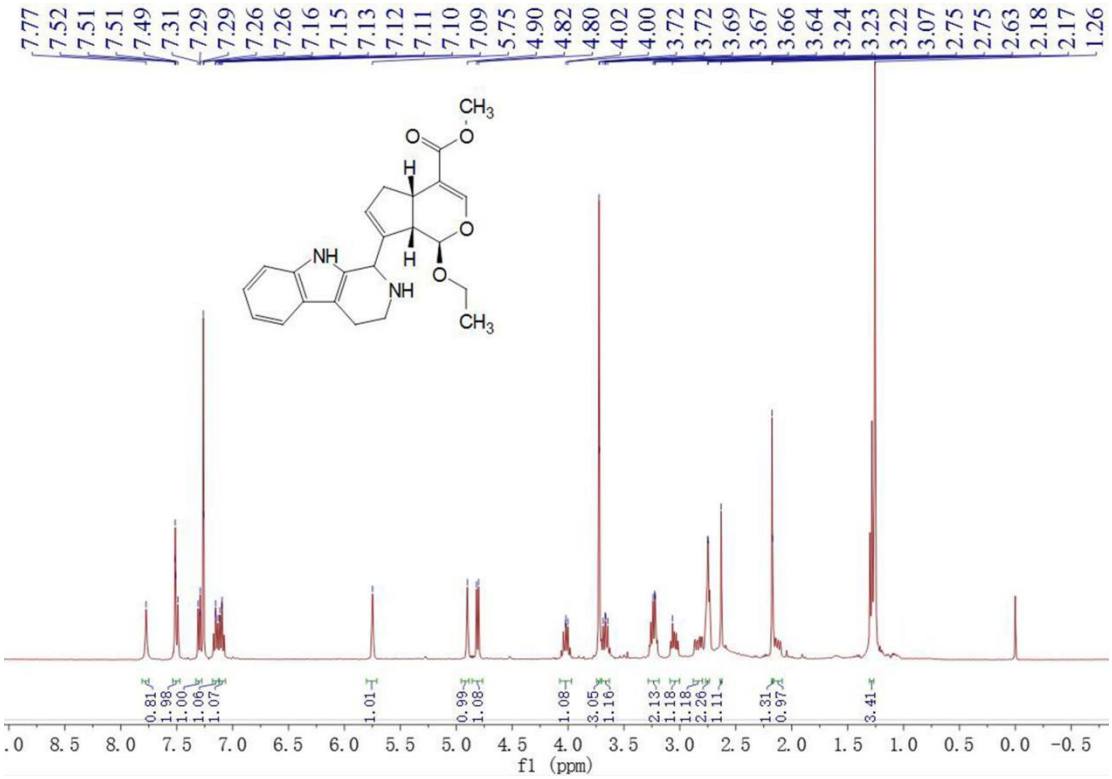


HR-EI-MS of compound **10**

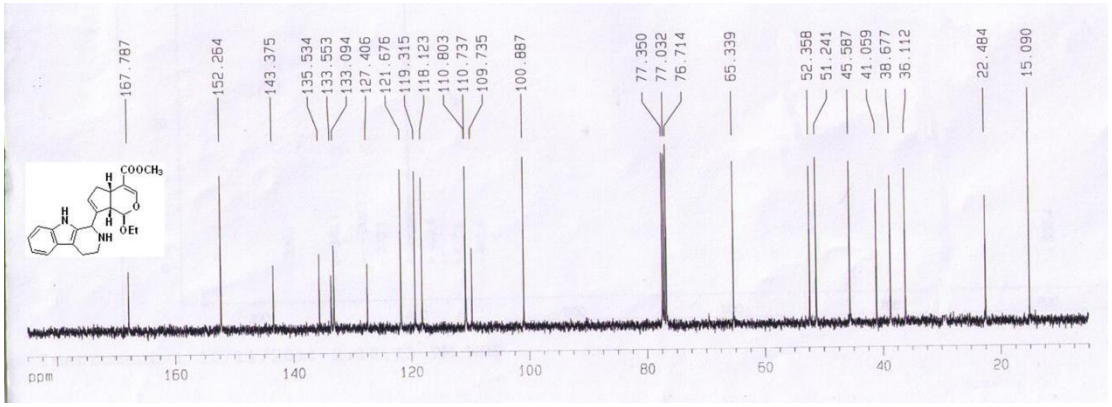


Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	91.17	C17 H26 N2 O6 S	[M+Na]+	409.1406	409.1404	0.2	0.49	91.17	6.0

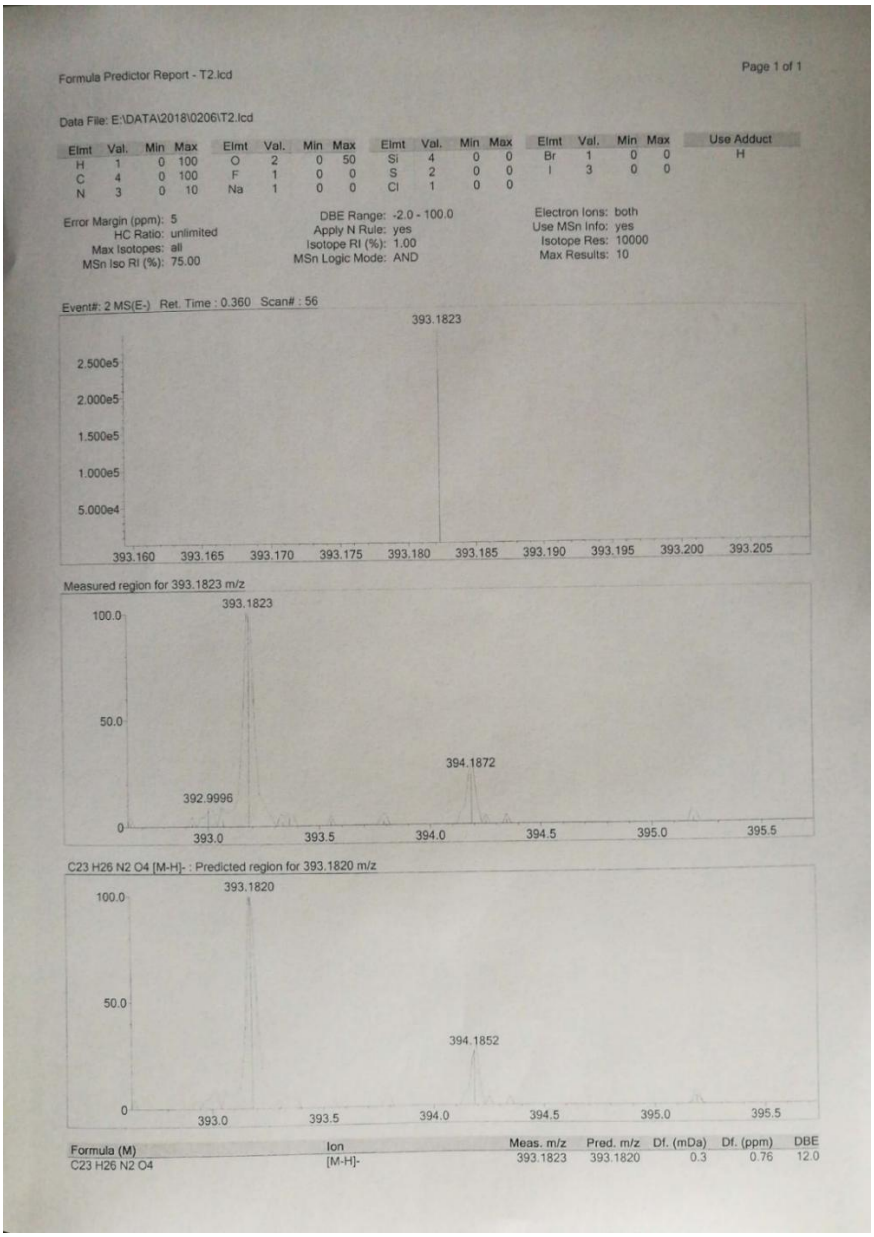
^{1}H-NMR of compound **11**



^{13}C-NMR of compound**11**



HR-EI-MS of compound **11**



Formula Predictor Report - T2.lcd

Page 1 of 1

Data File: E:\DATA\2018\0206\T2.lcd

Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Use Adduct
H	1	0	100	O	2	0	50	Si	4	0	0	Br	1	0	0	H
C	4	0	100	F	1	0	0	S	2	0	0	I	3	0	0	
N	3	0	10	Na	1	0	0	Cl	1	0	0					

Error Margin (ppm): 5
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

DBE Range: -2.0 - 100.0
Apply N Rule: yes
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: both
Use MSn Info: yes
Isotope Res: 10000
Max Results: 10

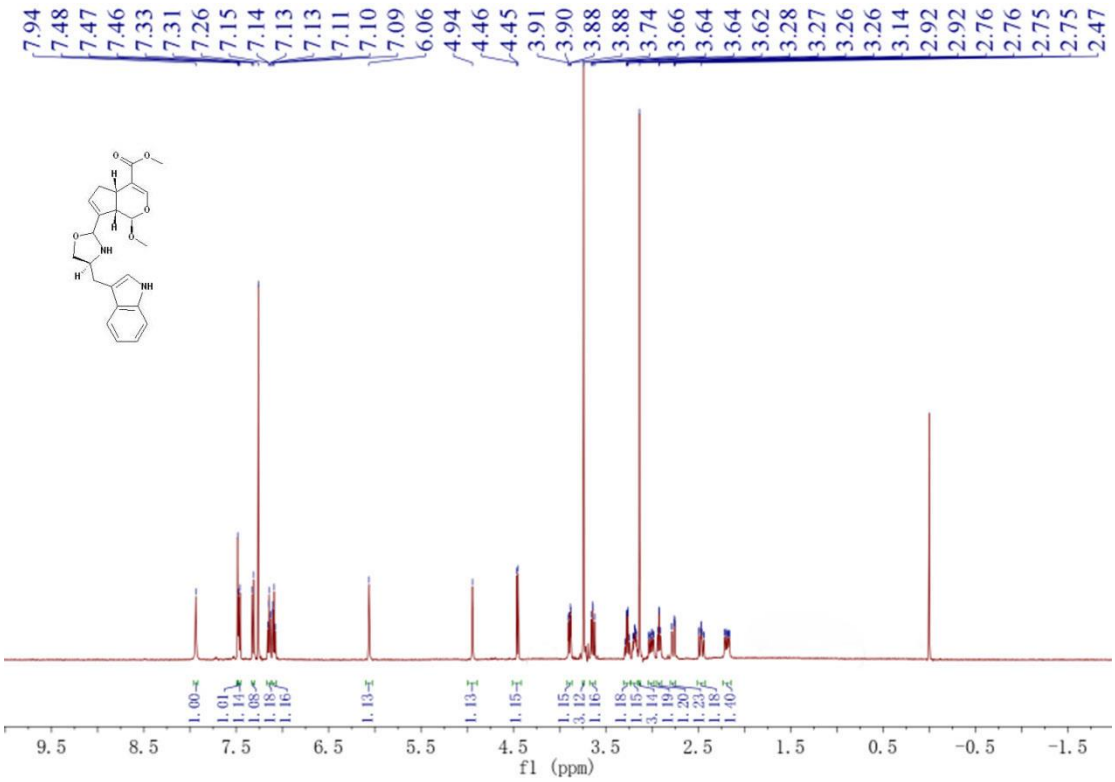
Event#: 2 MS(E-) Ret. Time : 0.360 Scan# : 56

Measured region for 393.1823 m/z

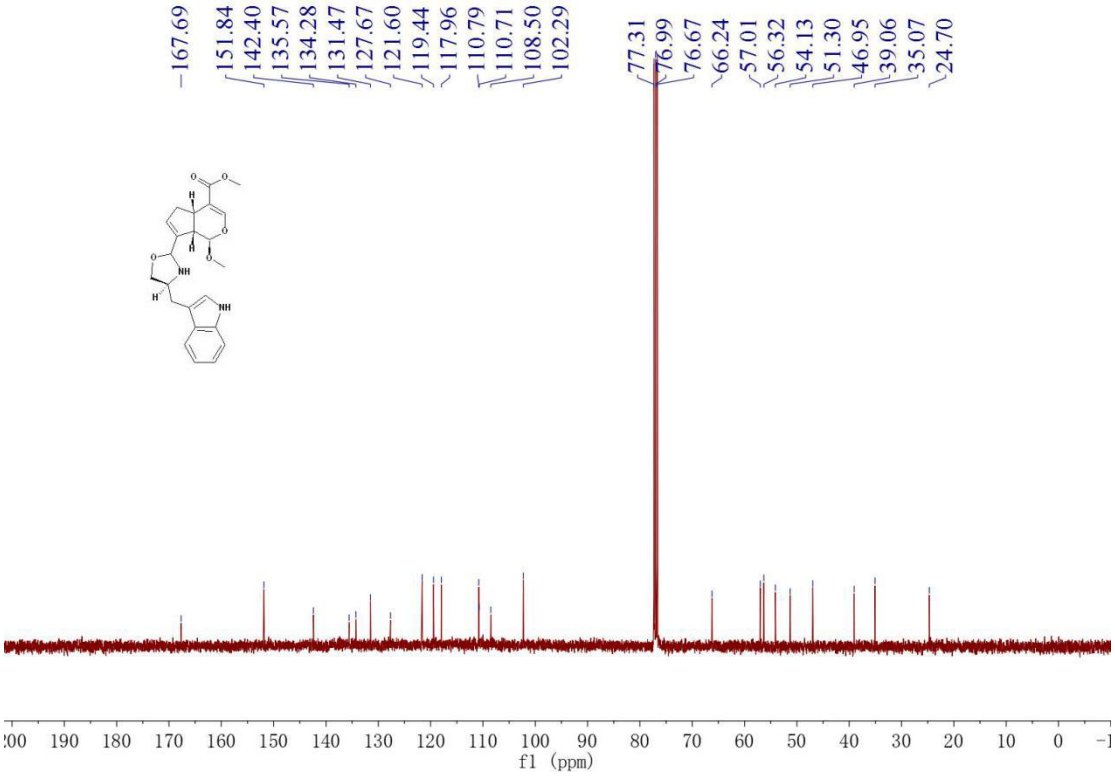
C23 H26 N2 O4 [M-H]- : Predicted region for 393.1820 m/z

Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	DBE
C23 H26 N2 O4	[M-H]-	393.1823	393.1820	0.3	0.76	12.0

^{1}H-NMR of compound **12**



^{13}C-NMR of compound **12**



HR-EI-MS of compound **12**

Elemental Composition Report **Page 1**

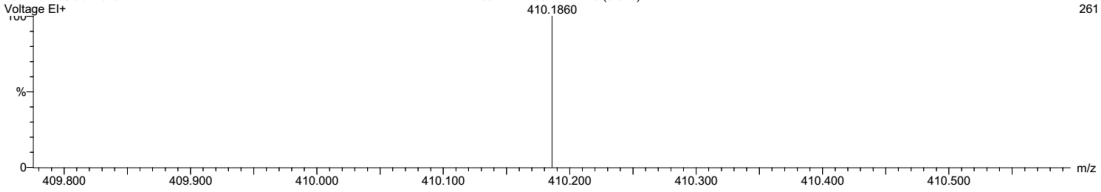
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
22 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 N: 2-2 O: 4-7

PMF7
13:44:57 08-Jul-2016
Voltage EI+

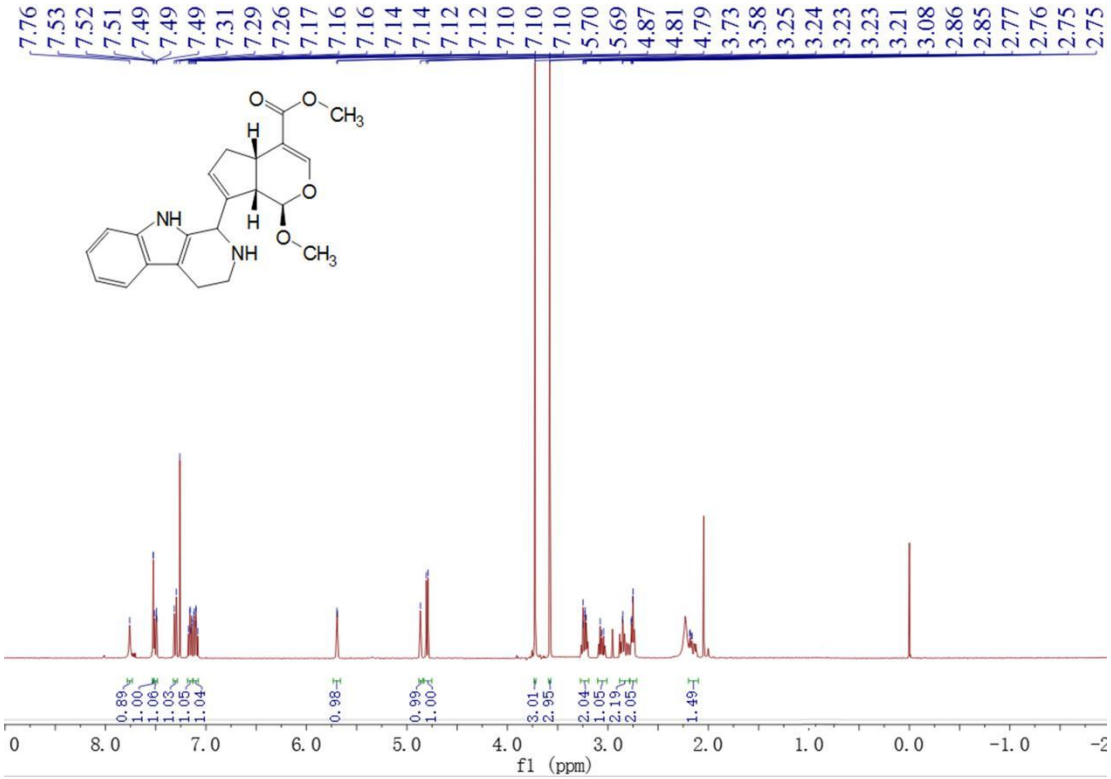
KIB
M160711EA-05AFAMM 9 (0.826)
410.1860

Autospec Premier
P776
261

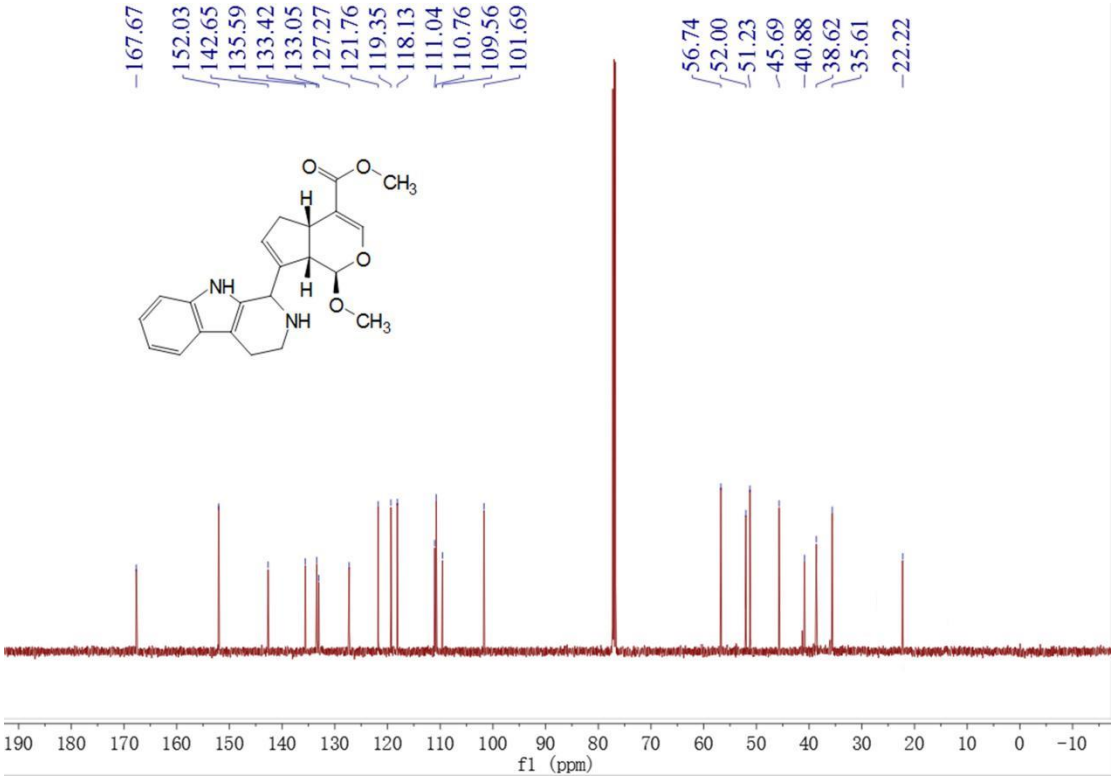


Minimum:				-10.0		
Maximum:		200.0	10.0	120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
410.1860	410.1842	1.8	4.4	12.0	5546145.5	C23 H26 N2 O5

^{1}H-NMR of compound **13**



^{13}C-NMR of compound **13**

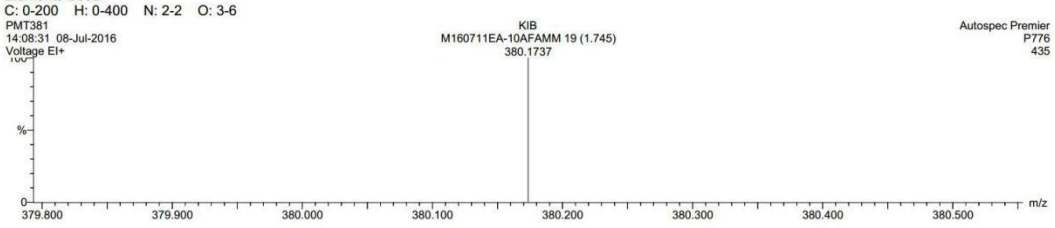


HR-EI-MS of compound **13**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
22 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 N: 2-2 O: 3-6



Minimum:				-10.0		
Maximum:		200.0	10.0	120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
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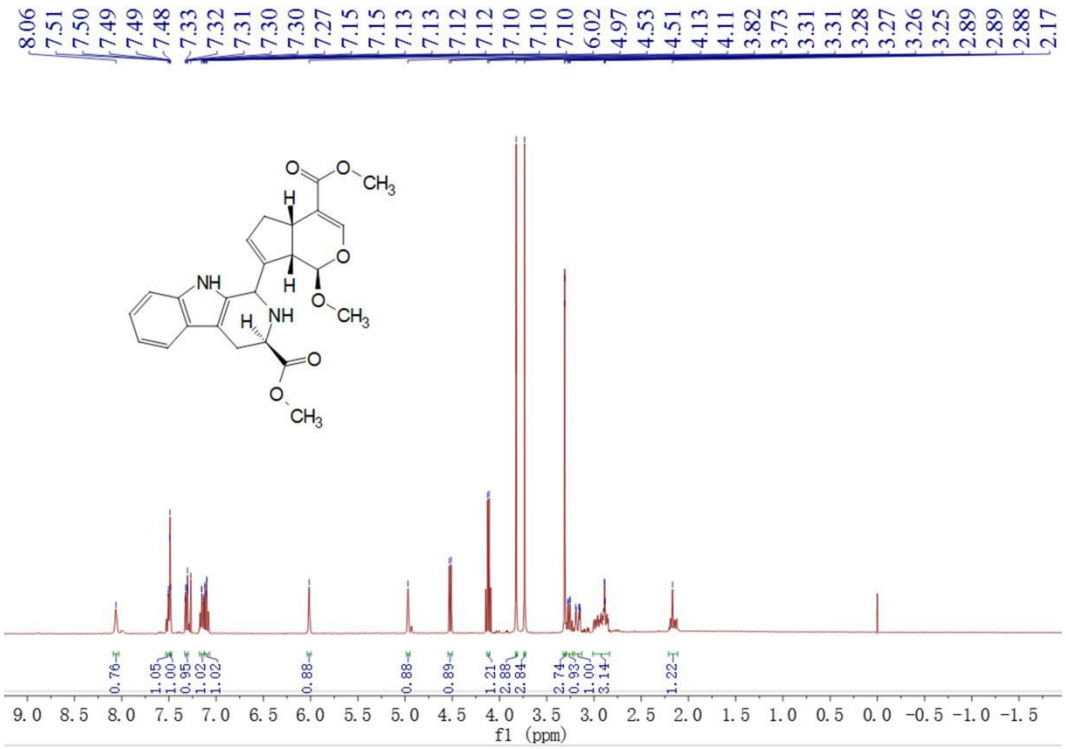
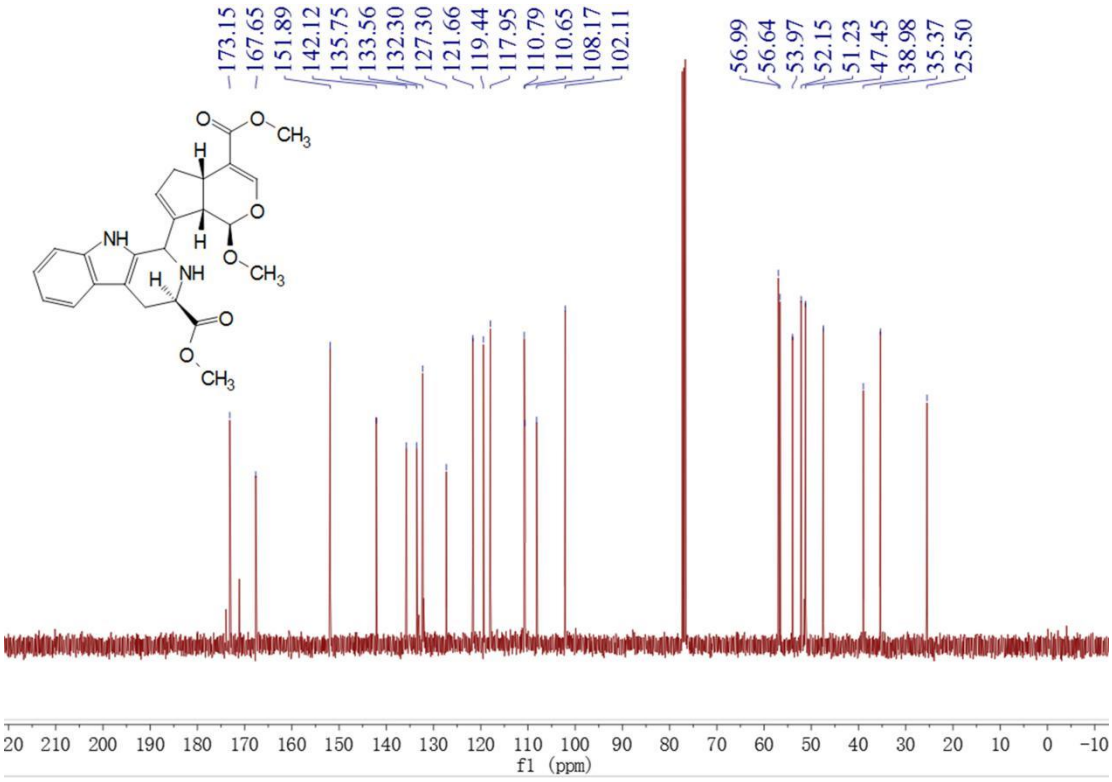
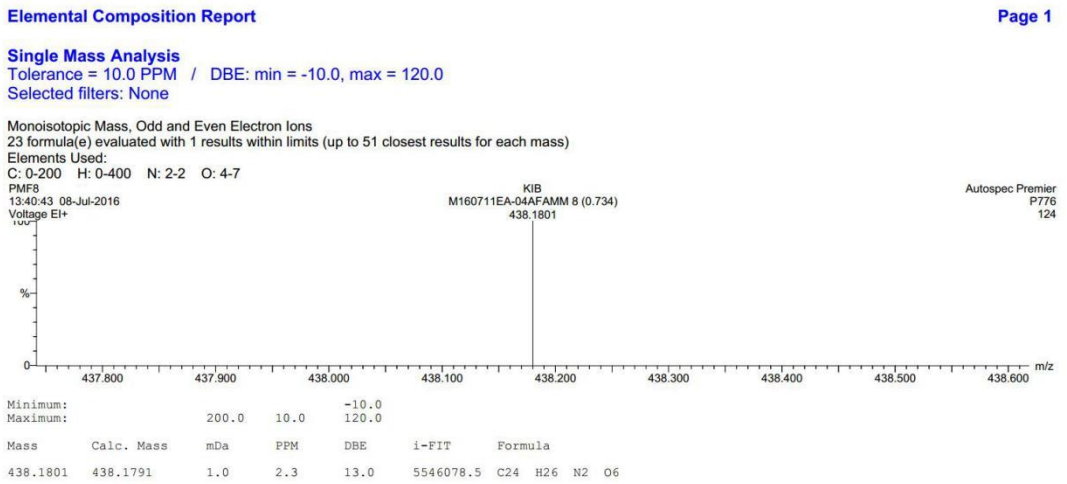
^{1}H-NMR of compound **14**



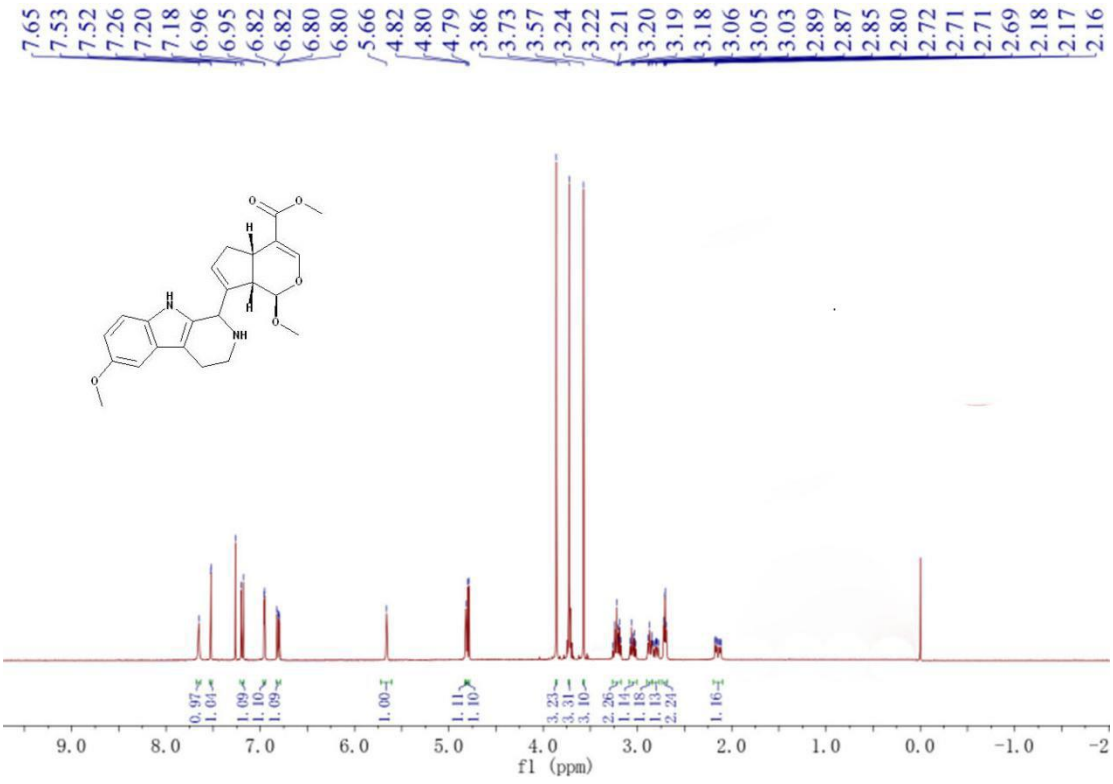
^{13}C-NMR of compound **14**



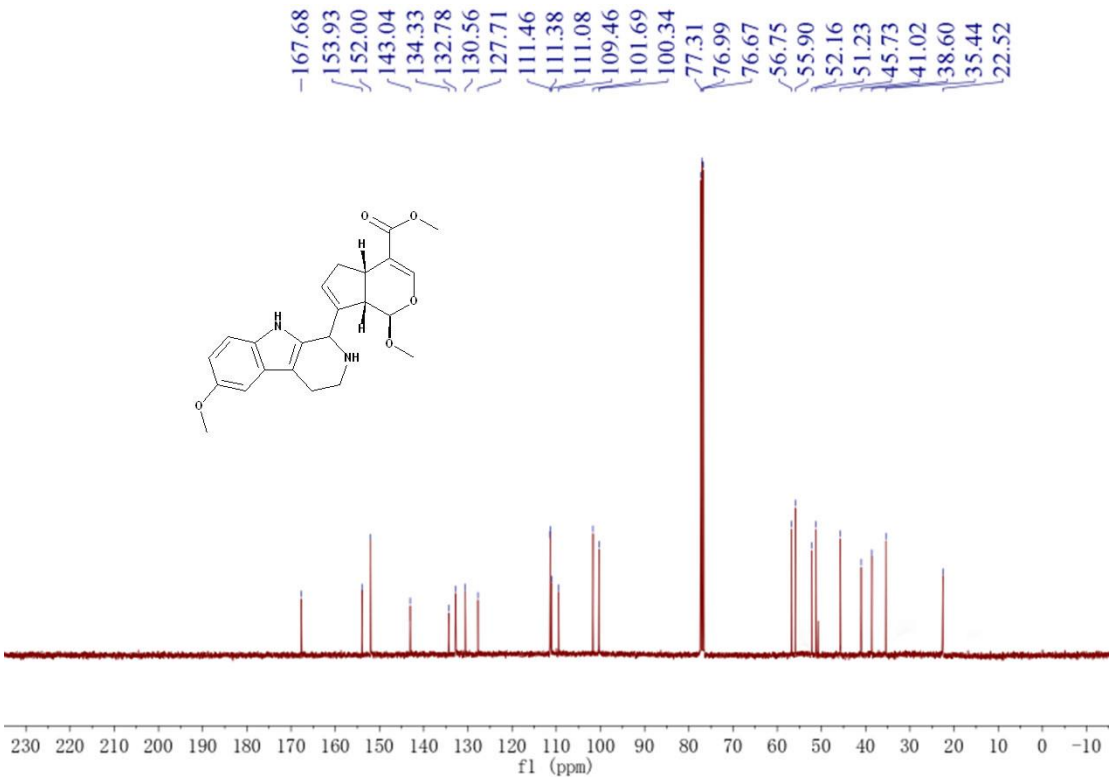
HR-EI-MS of compound **14**



^{1}H-NMR of compound **15**



^{13}C-NMR of compound **15**

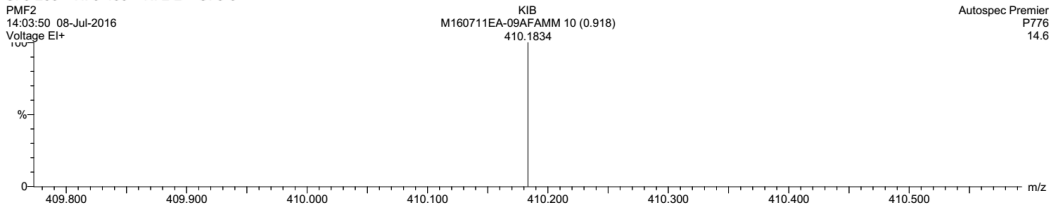


HR-EI-MS of compound **15**

Elemental Composition Report **Page 1**

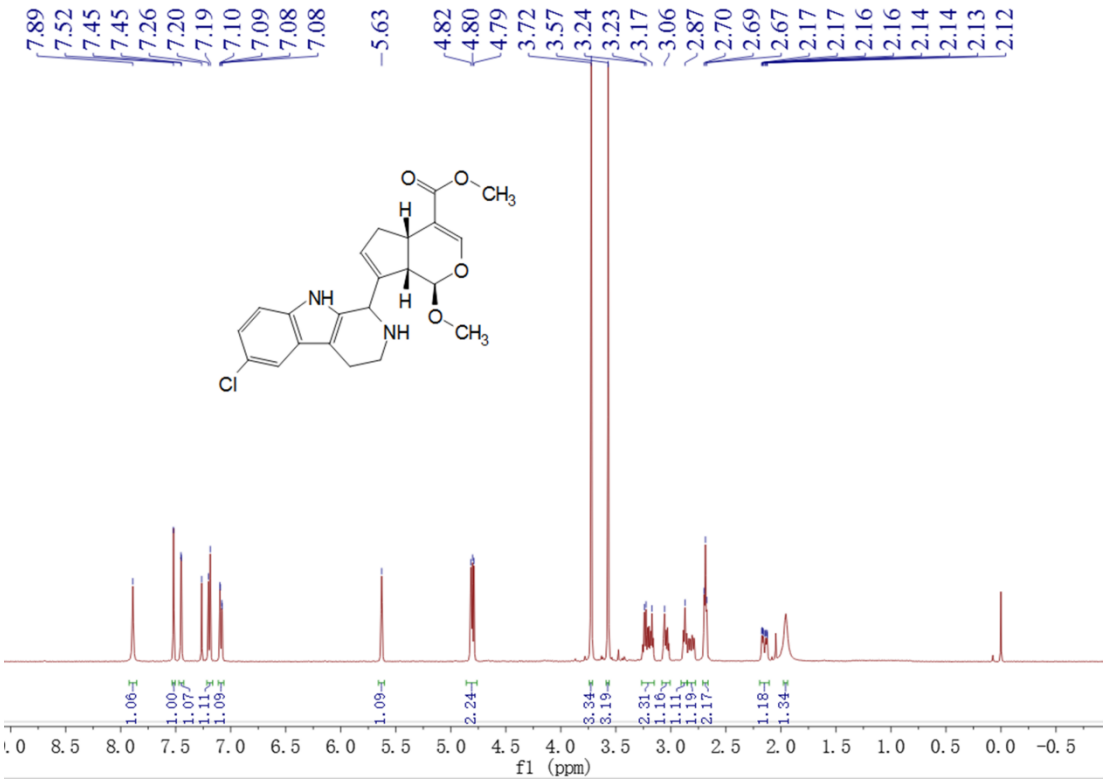
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
23 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 N: 2-2 O: 3-6

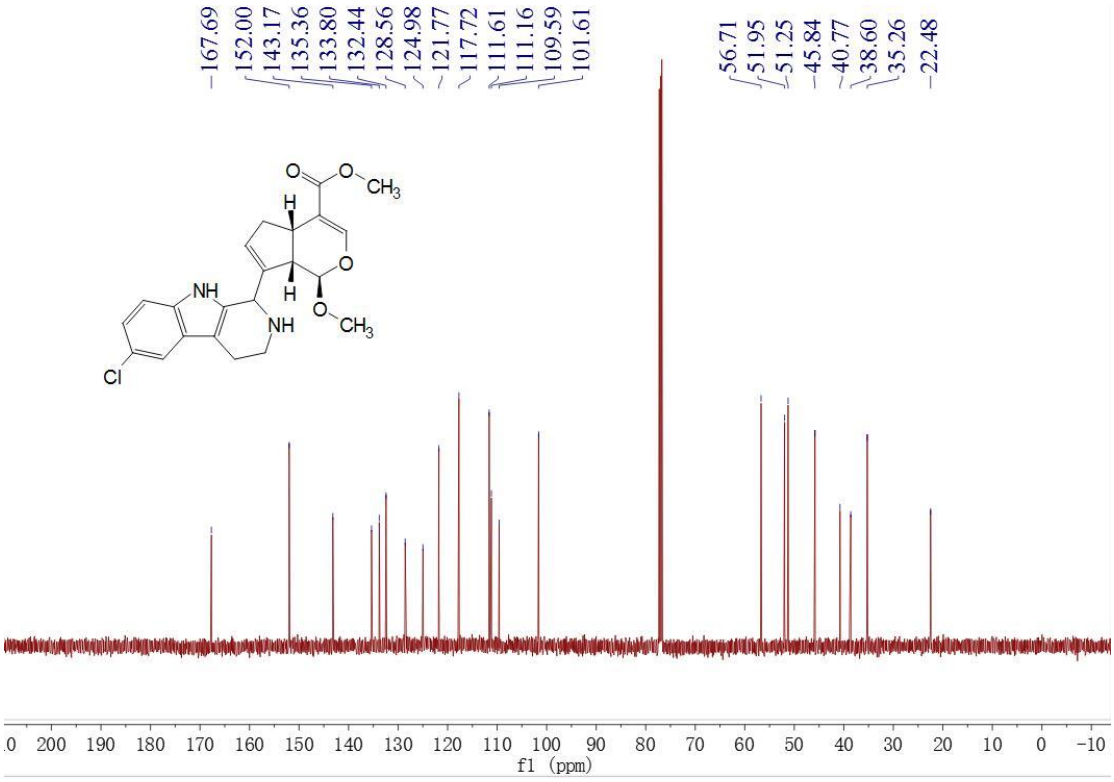


Minimum:				-10.0		
Maximum:		200.0	10.0	120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
410.1834	410.1842	-0.8	-2.0	12.0	5546027.0	C23 H26 N2 O5

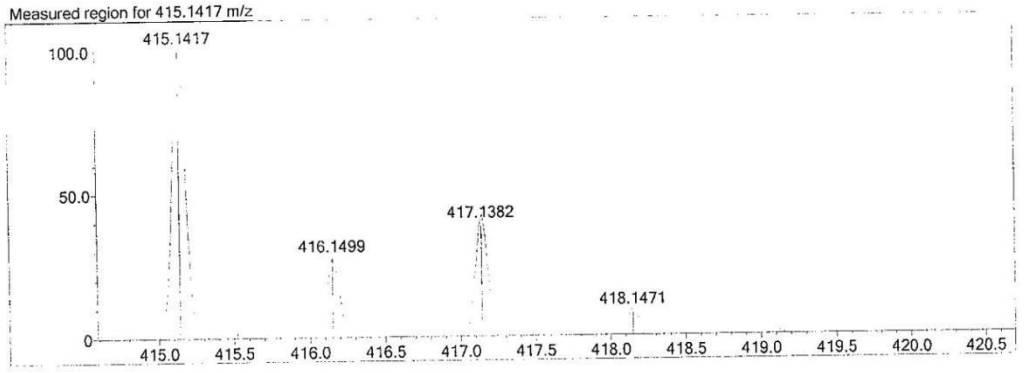
^{1}H-NMR of compound **16**

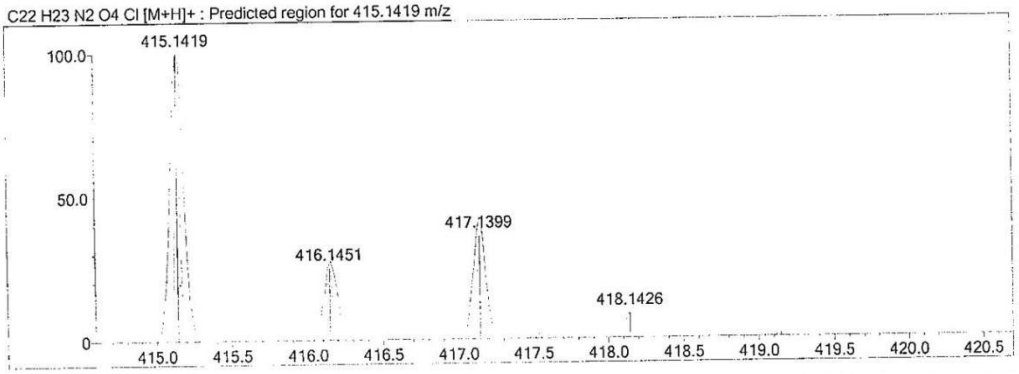


^{13}C-NMR of compound **16**



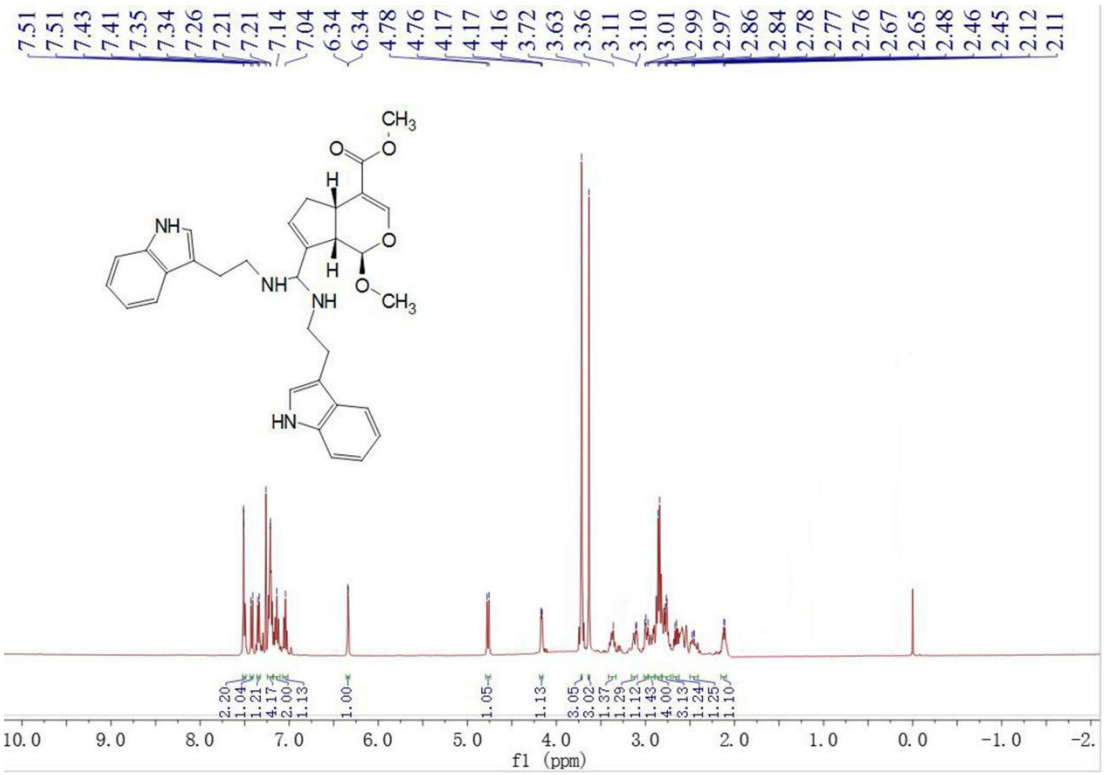
HR-EI-MS of compound **16**



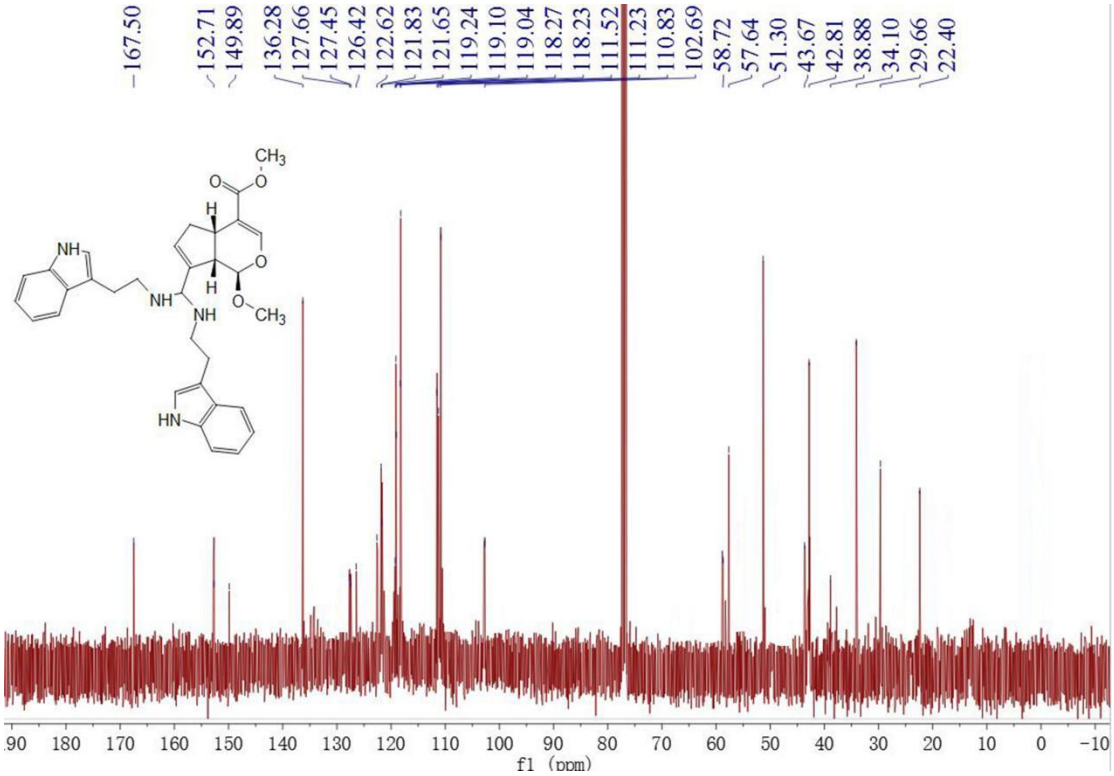


Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	81.62	C22 H23 N2 O4 Cl	[M+H]+	415.1417	415.1419	-0.2	-0.48	81.62	12.0

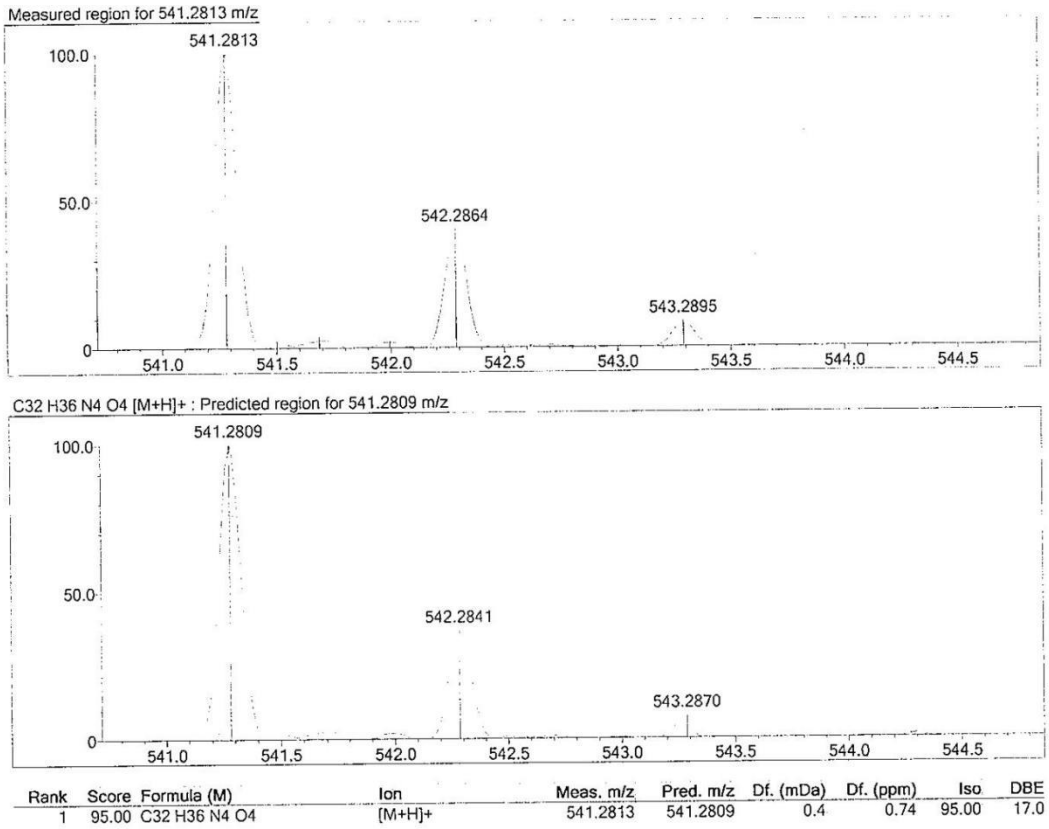
^{1}H-NMR of compound **17**



^{13}C-NMR of compound **17**

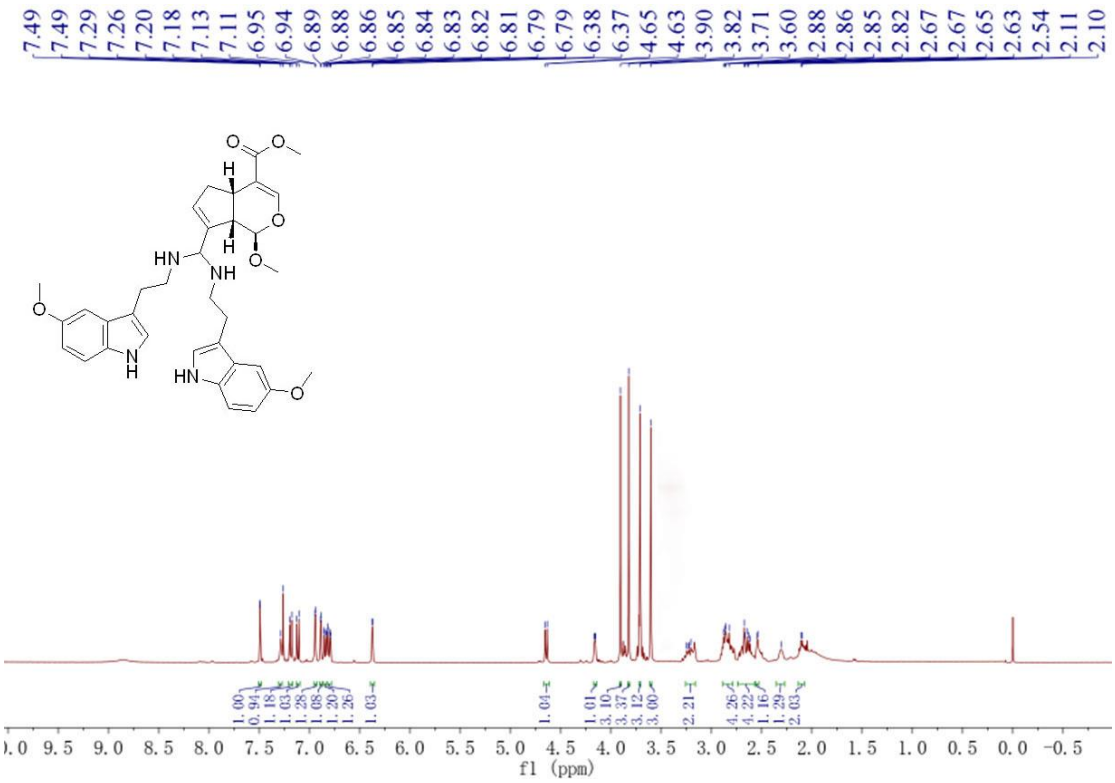


HR-EI-MS of compound **17**

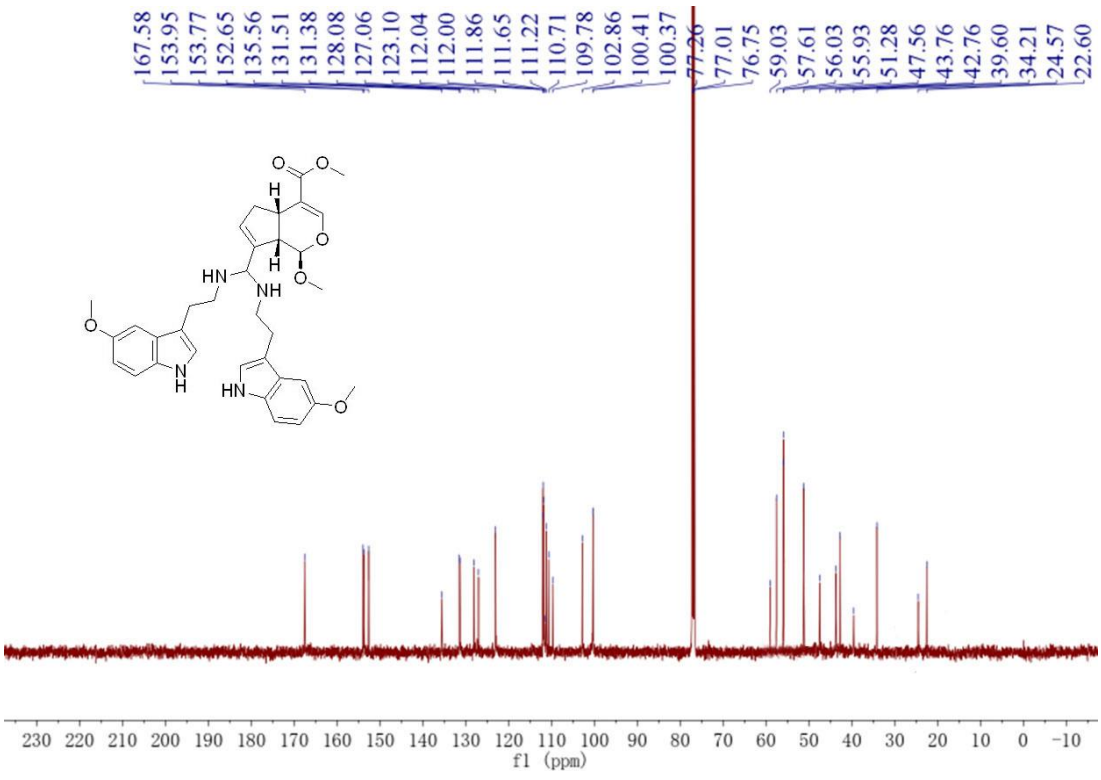


Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	95.00	C32 H36 N4 O4	[M+H]+	541.2813	541.2809	0.4	0.74	95.00	17.0

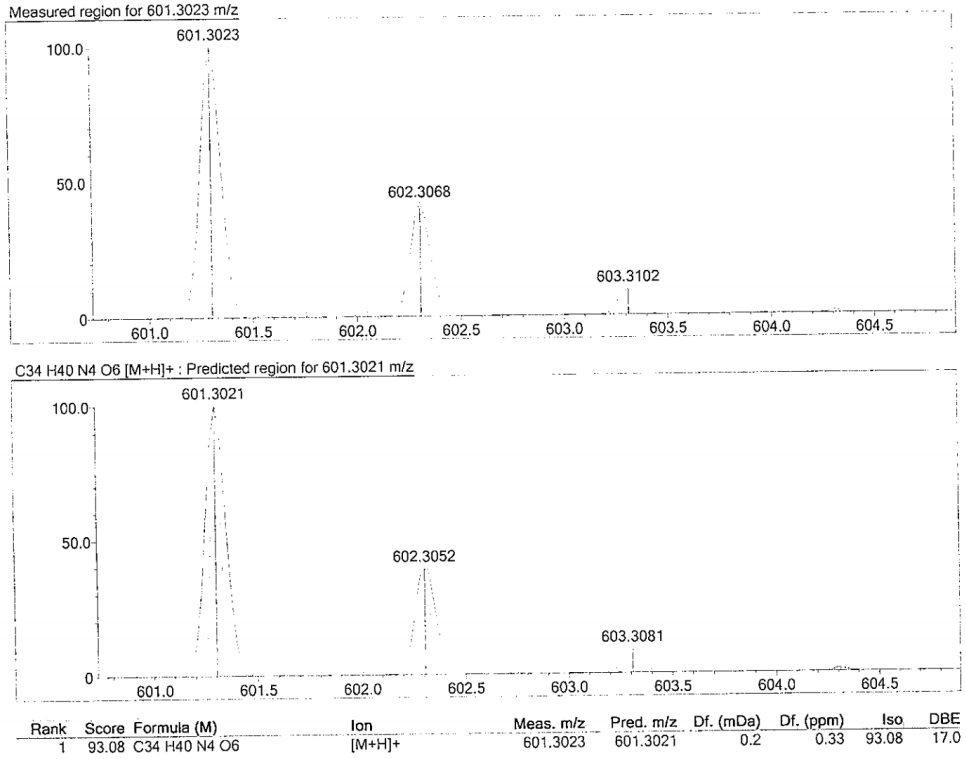
^{1}H-NMR of compound **18**



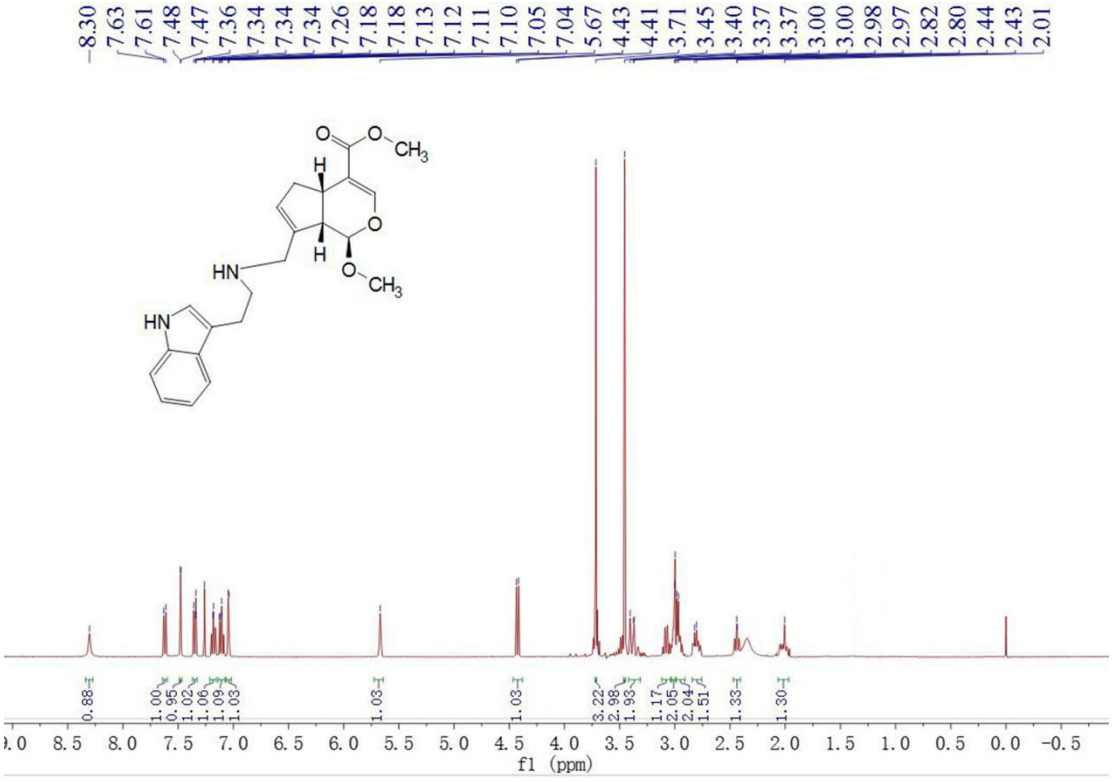
^{13}C-NMR of compound **18**



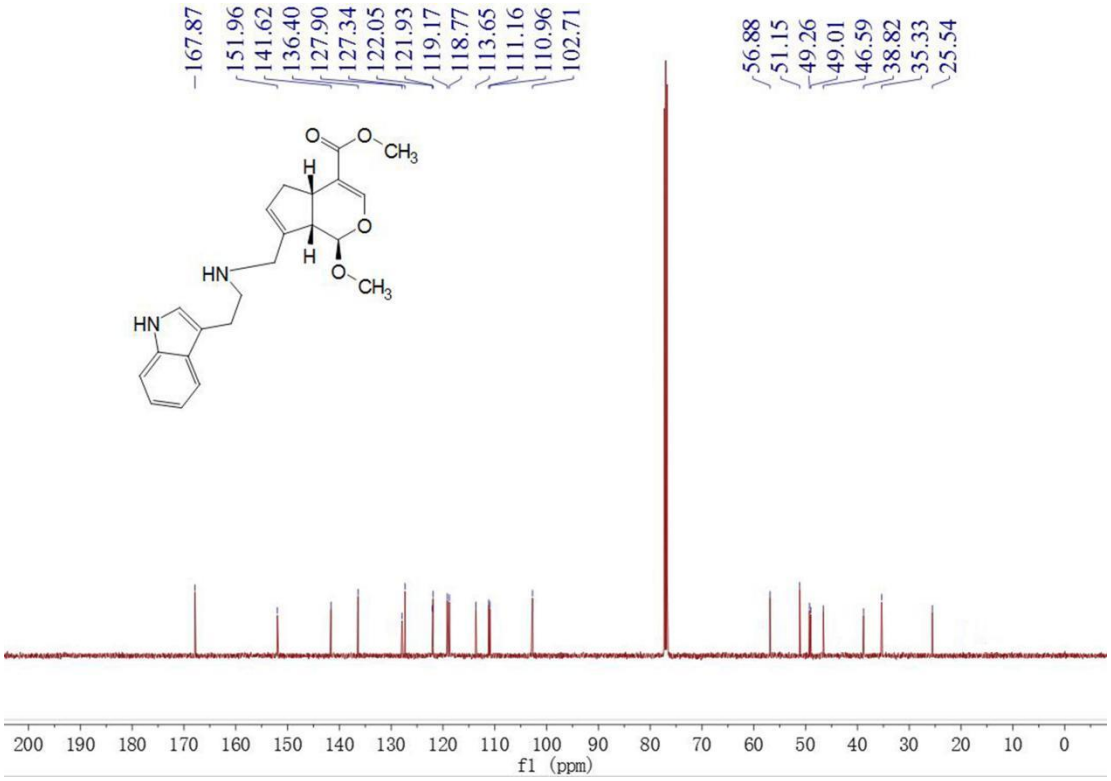
HR-EI-MS of compound **18**



^{1}H-NMR of compound **19**



^{13}C-NMR of compound **19**

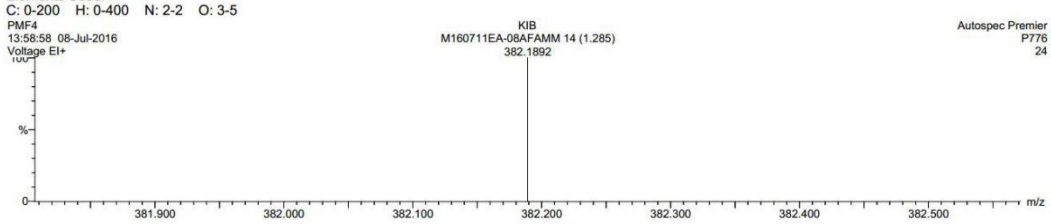


HR-EI-MS of compound **19**

Elemental Composition Report **Page 1**

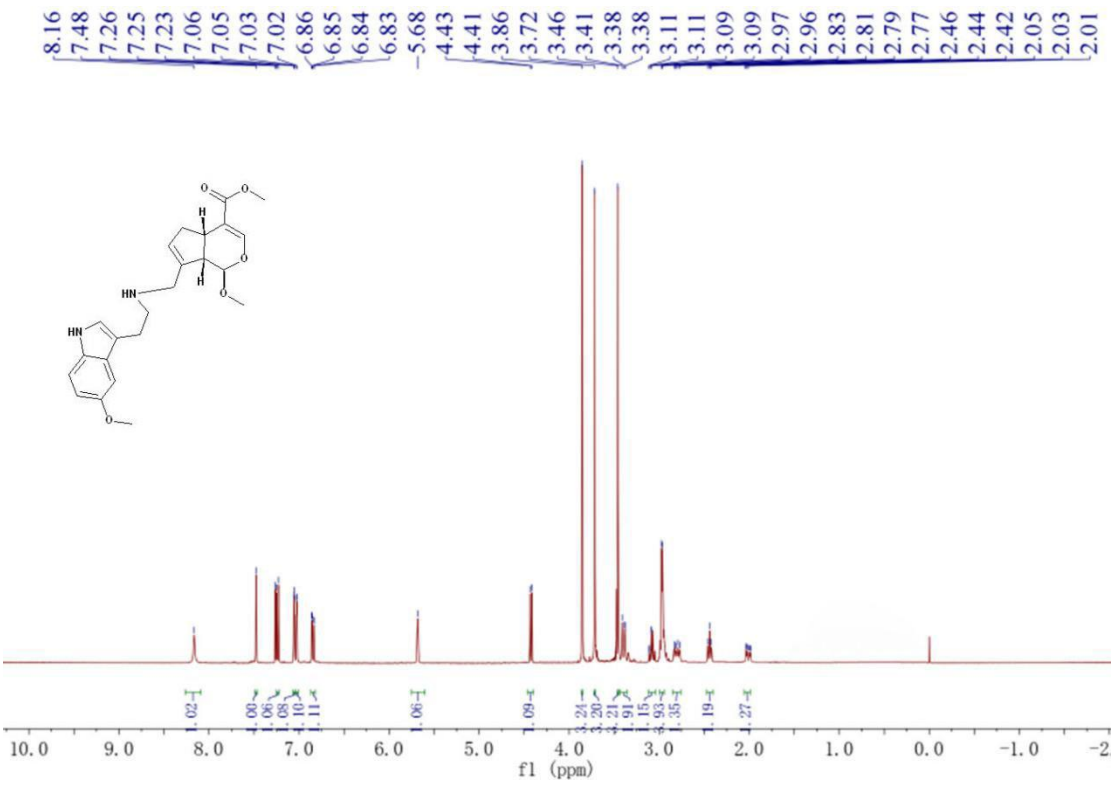
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
17 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 N: 2-2 O: 3-5

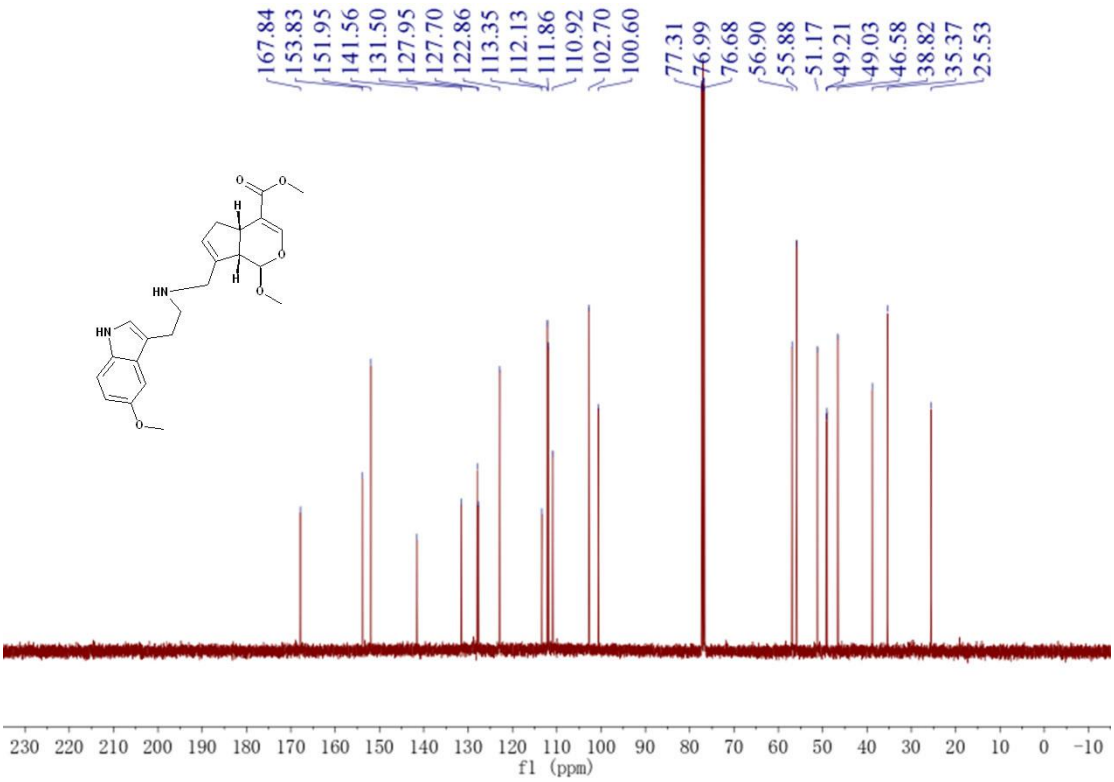


Minimum:				-10.0		
Maximum:		200.0	10.0	120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
382.1892	382.1893	-0.1	-0.3	11.0	5546030.5	C22 H26 N2 O4

^{1}H-NMR of compound **20**



^{13}C-NMR of compound **20**

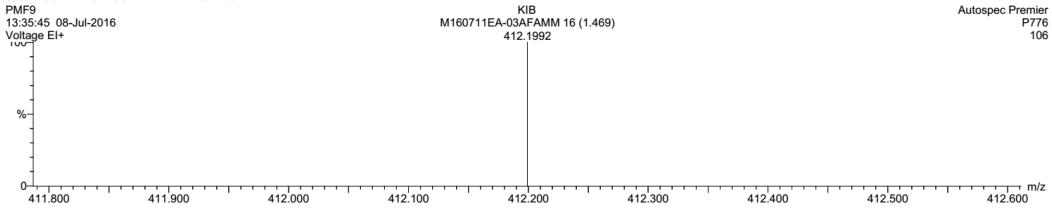


HR-EI-MS of compound **20**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
18 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 N: 2-2 O: 4-6



Minimum:				-10.0		
Maximum:		200.0	10.0	120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
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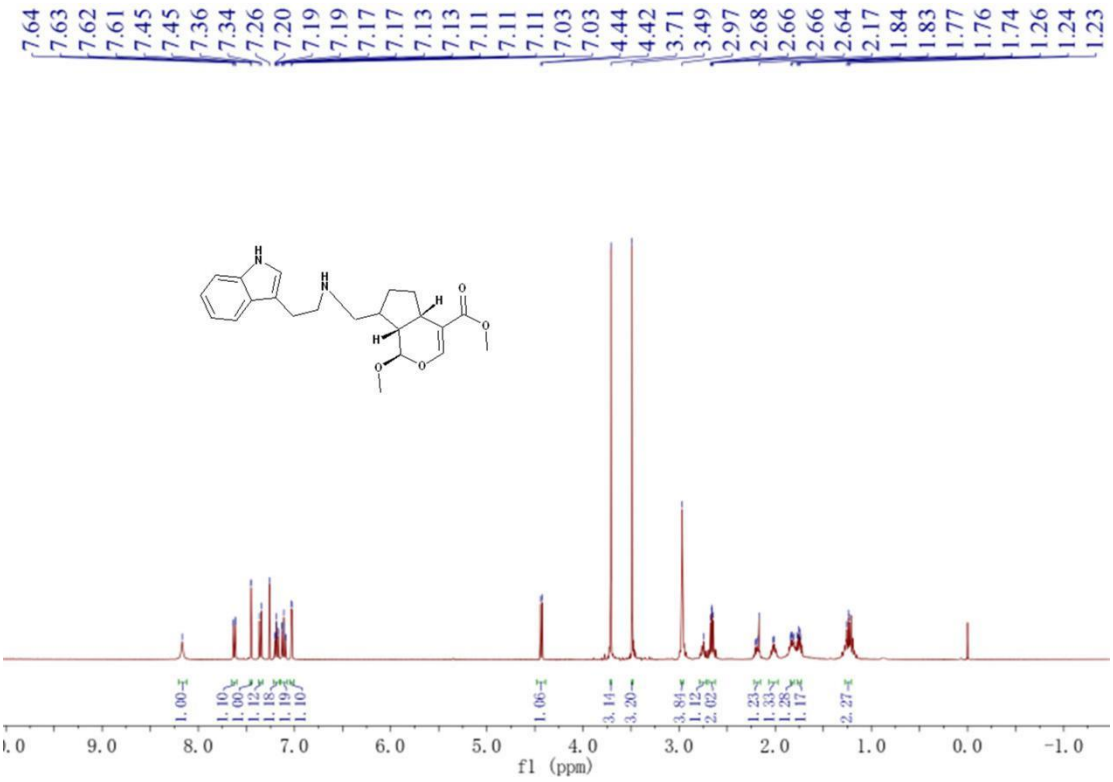
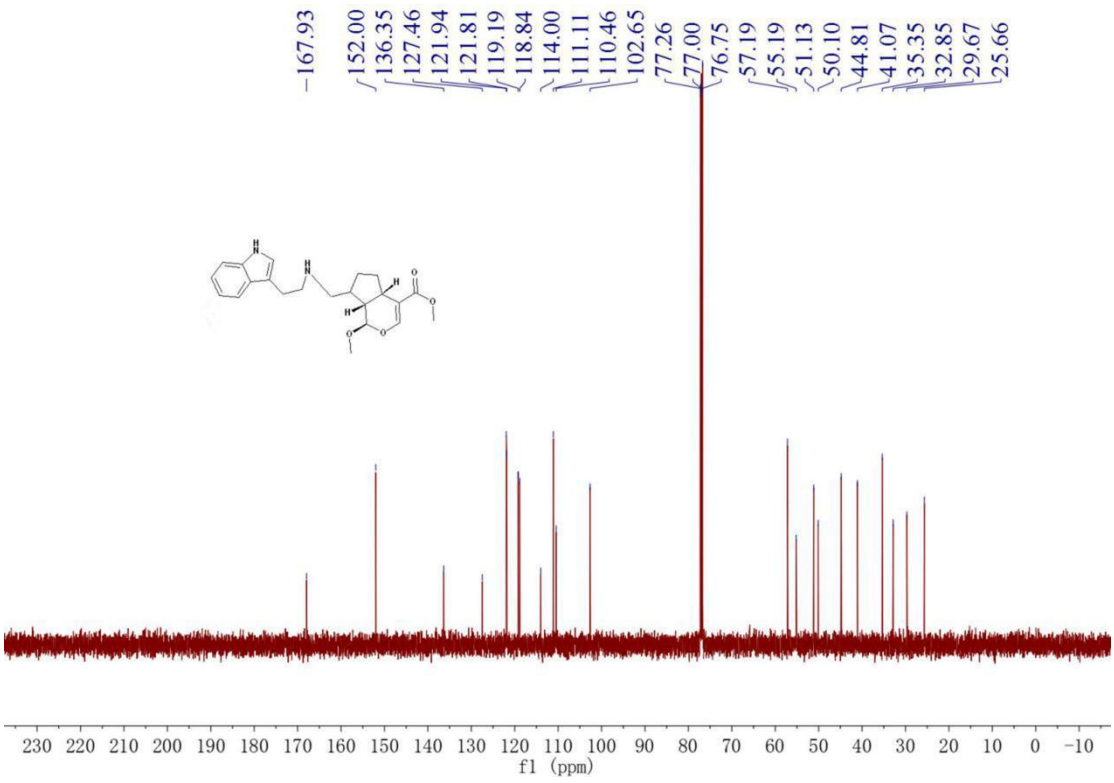
^{1}H-NMR of compound **21**



^{13}C-NMR of compound **21**



HR-EI-MS of compound **21**

Elemental Composition Report **Page 1**

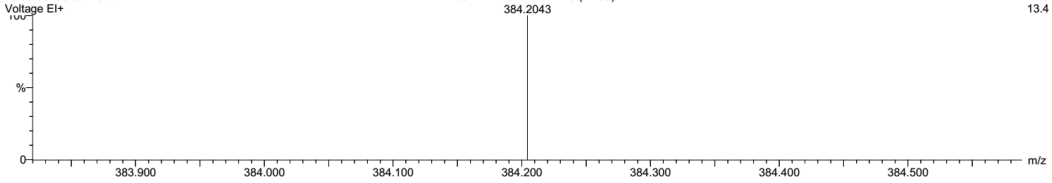
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
18 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 N: 2-2 O: 3-5

PMF5
13:53:53 08-Jul-2016
Voltage EI+

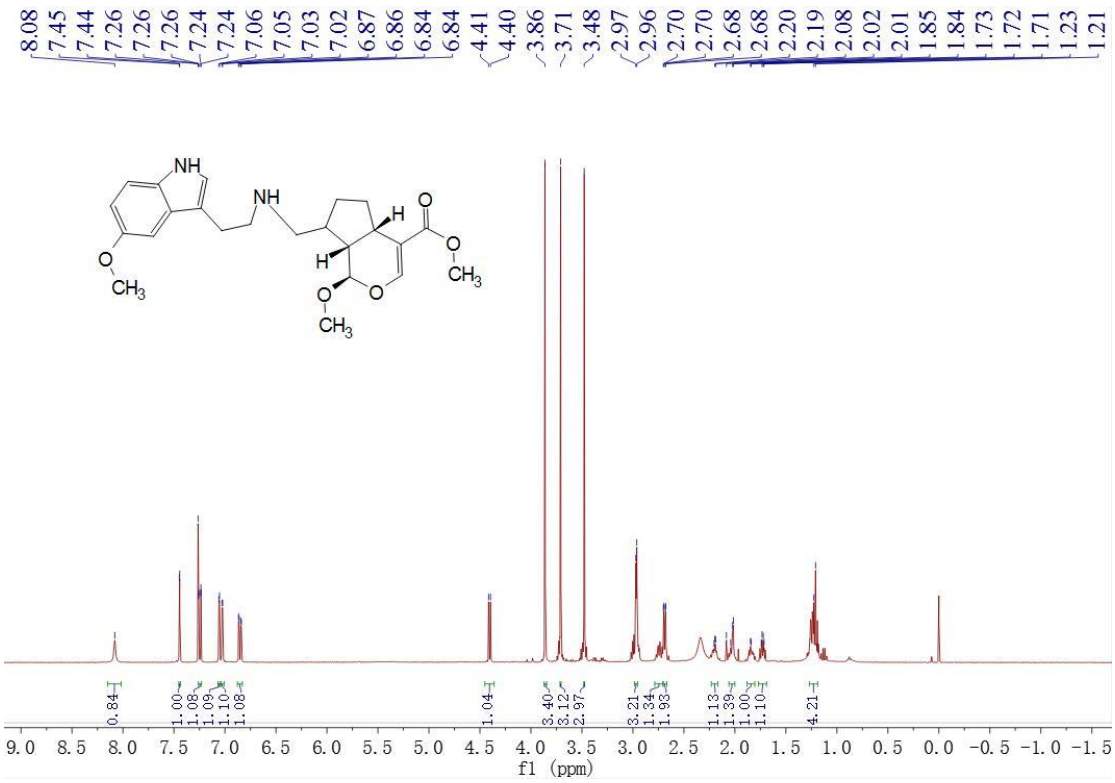
KIB
M160711EA-07AFAMM 13 (1.193)
384.2043

Autospec Premier
P776
13.4

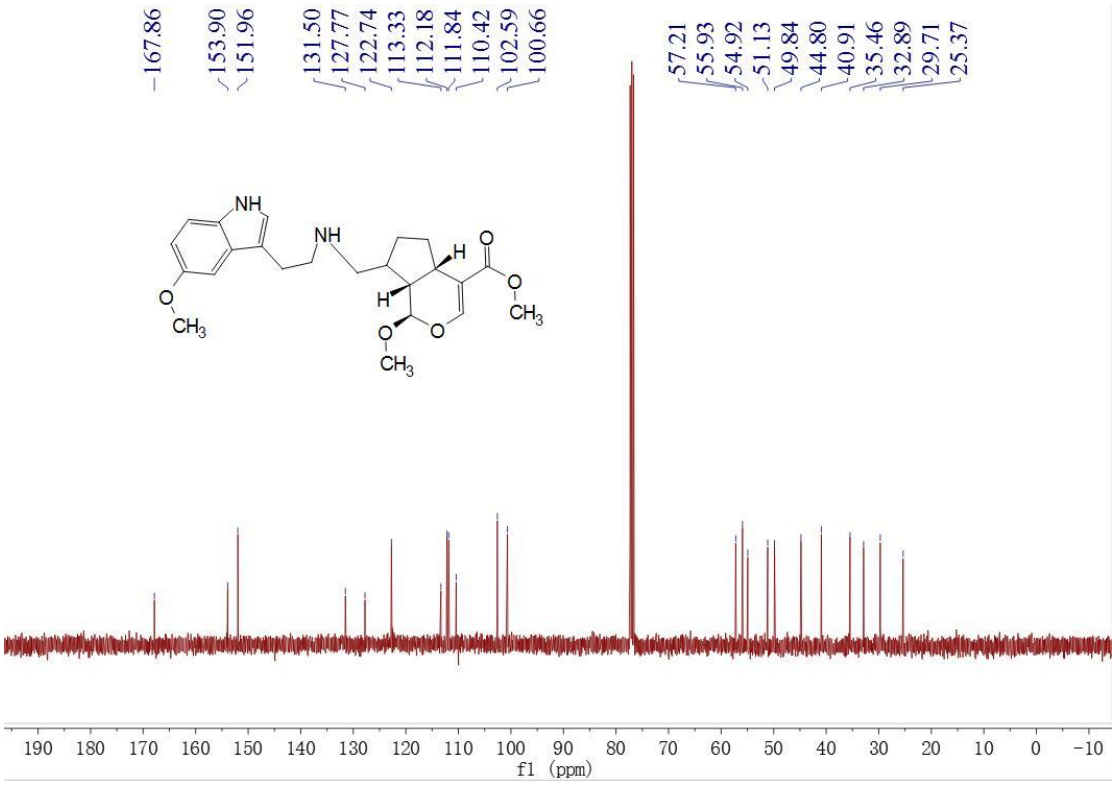


Minimum:				-10.0		
Maximum:		200.0	10.0	120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
384.2043	384.2049	-0.6	-1.6	10.0	5546027.0	C22 H28 N2 O4

^{1}H-NMR of compound **22**



^{13}C-NMR of compound **22**



HR-EI-MS of compound **22**

Elemental Composition Report **Page 1**

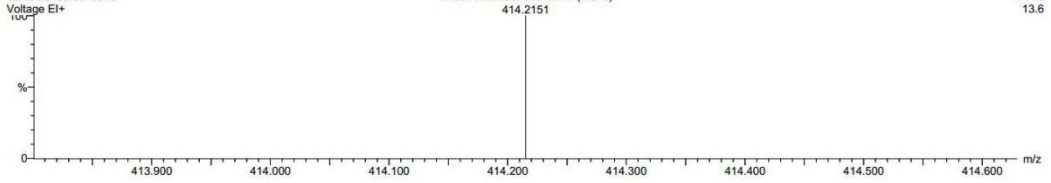
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
23 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 N: 2-2 O: 4-7

PMF6
13:49:20 08-Jul-2016
Voltage EI+

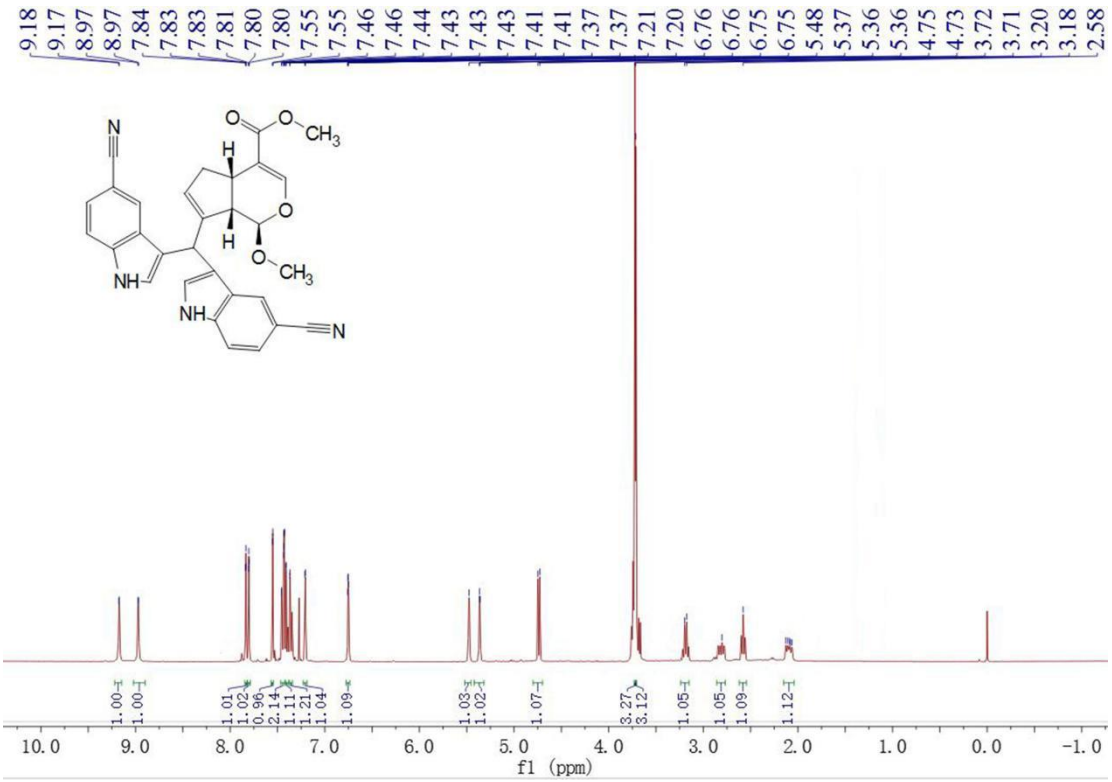
KIB
M160711EA-06AFAMM 11 (1.010)
414.2151

Autospec Premier
P776
13.6

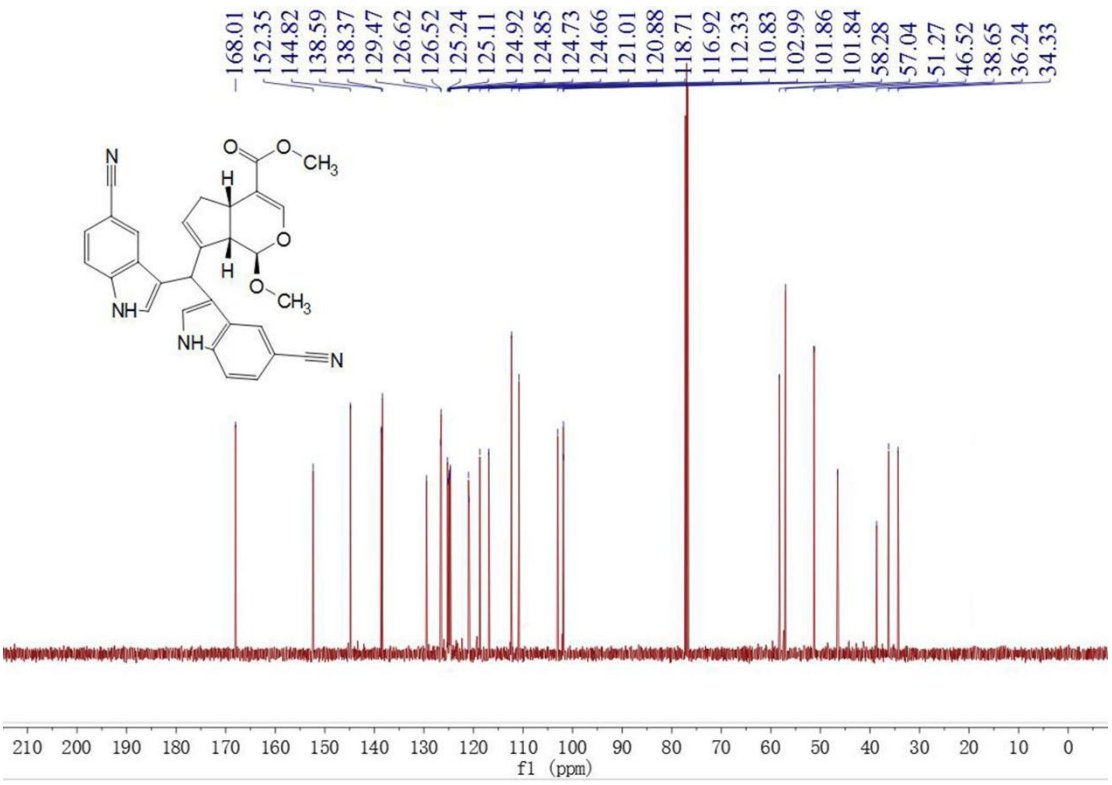


Minimum:				-10.0		
Maximum:		200.0	10.0	120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
414.2151	414.2155	-0.4	-1.0	10.0	5546027.0	C23 H30 N2 O5

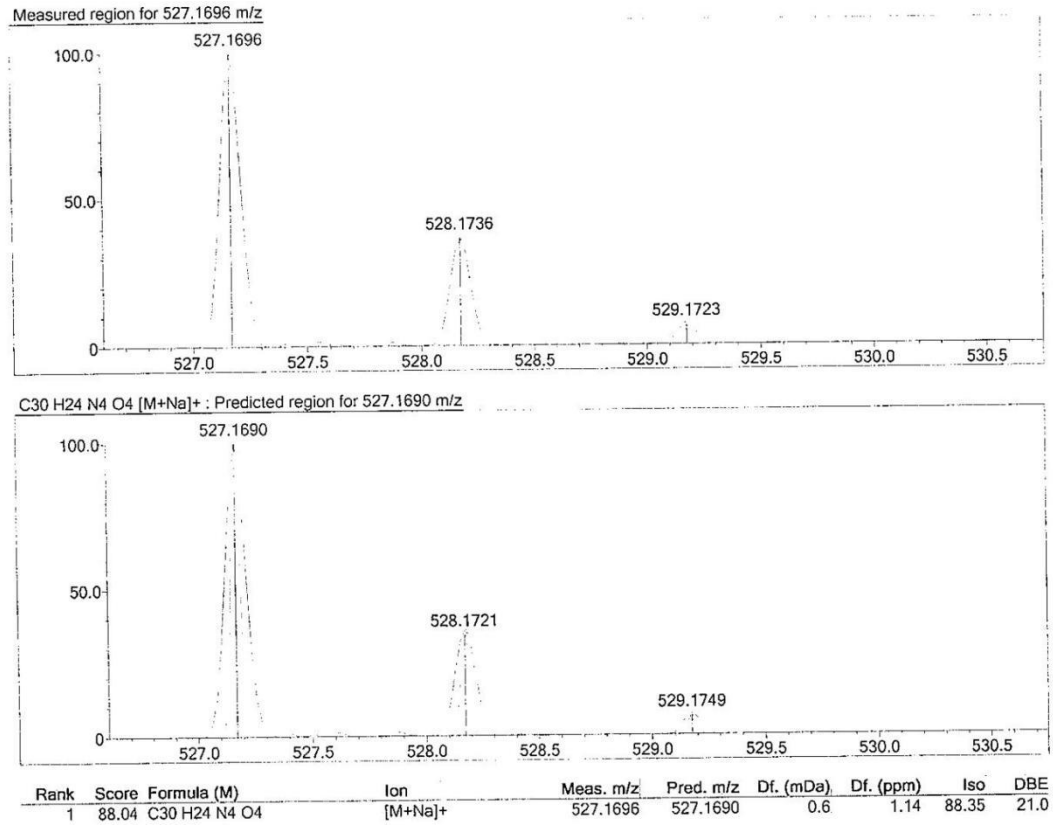
^{1}H-NMR of compound **23**



^{13}C-NMR of compound **23**

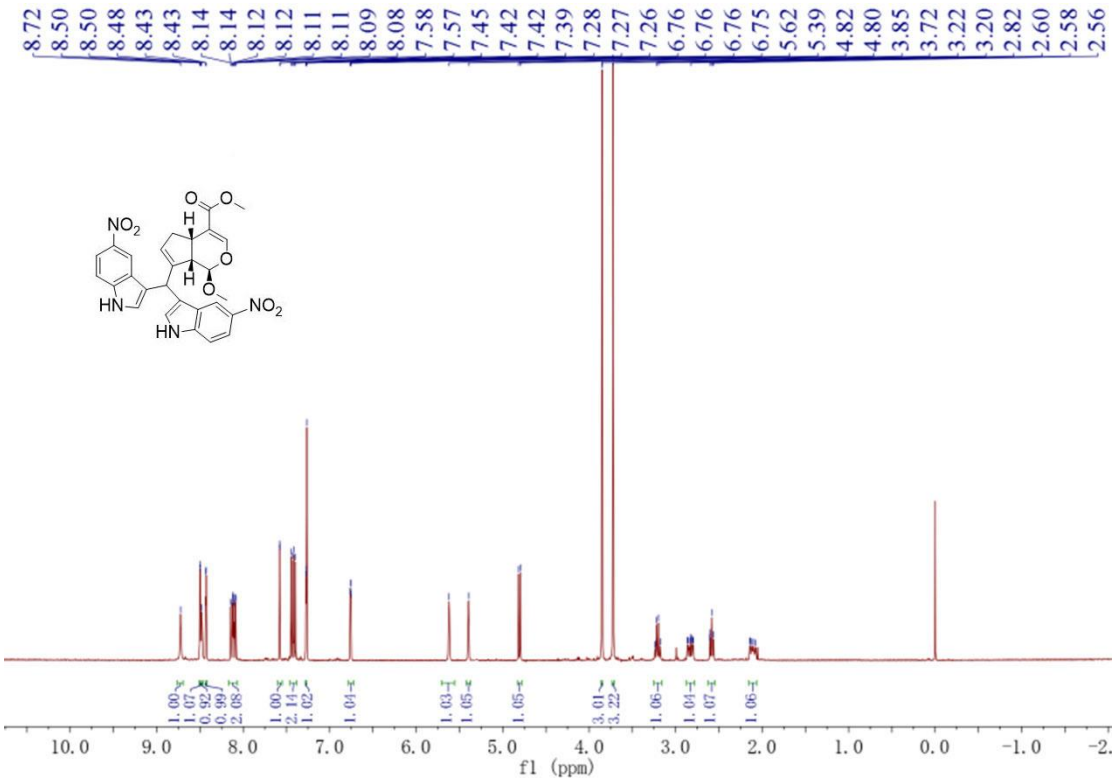


HR-EI-MS of compound **23**

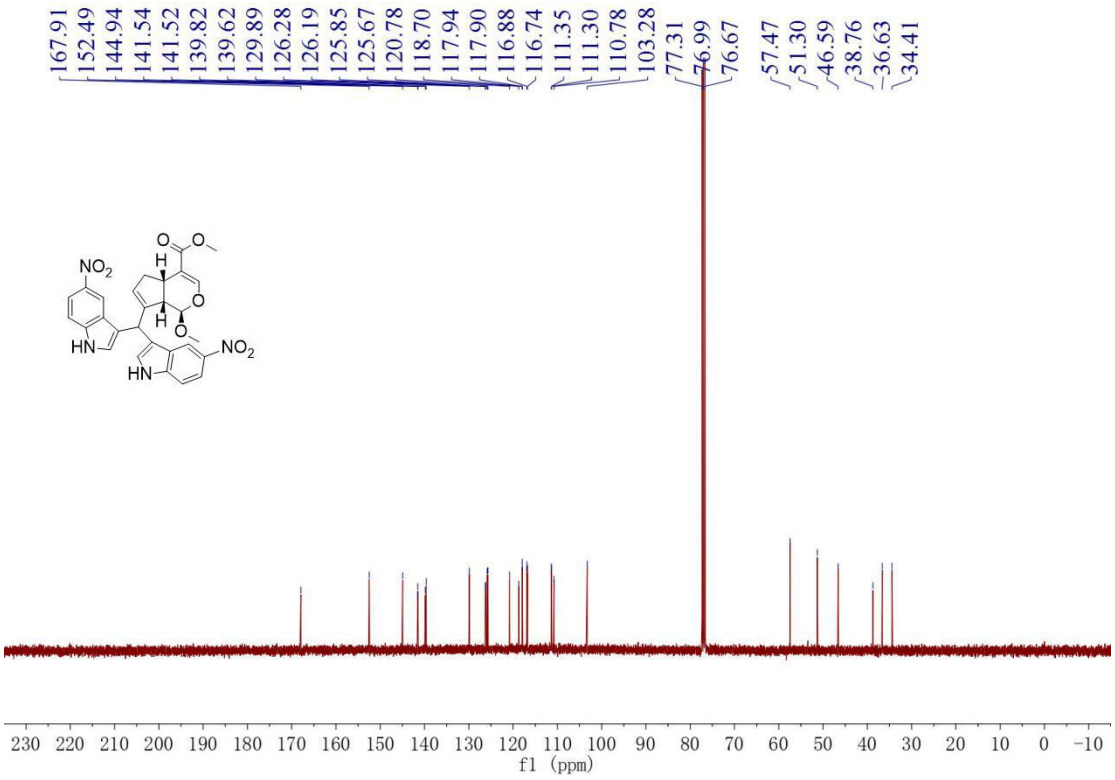


Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	88.04	C30 H24 N4 O4	[M+Na]+	527.1696	527.1690	0.6	1.14	88.35	21.0

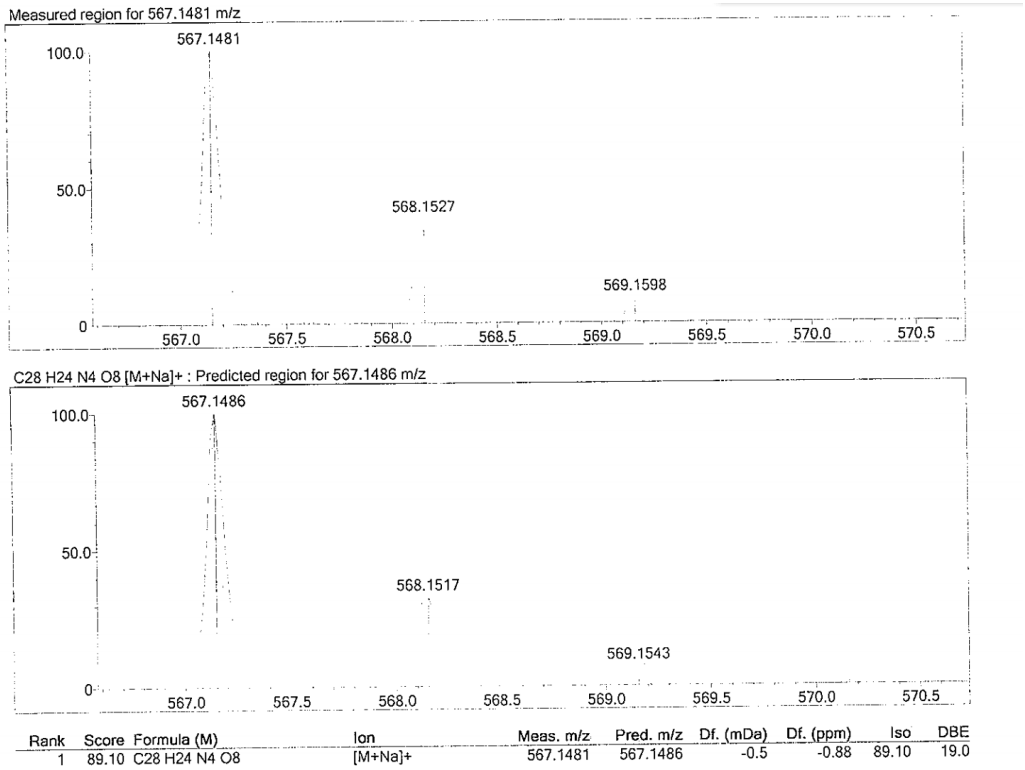
^{1}H-NMR of compound **24**



^{13}C-NMR of compound **24**

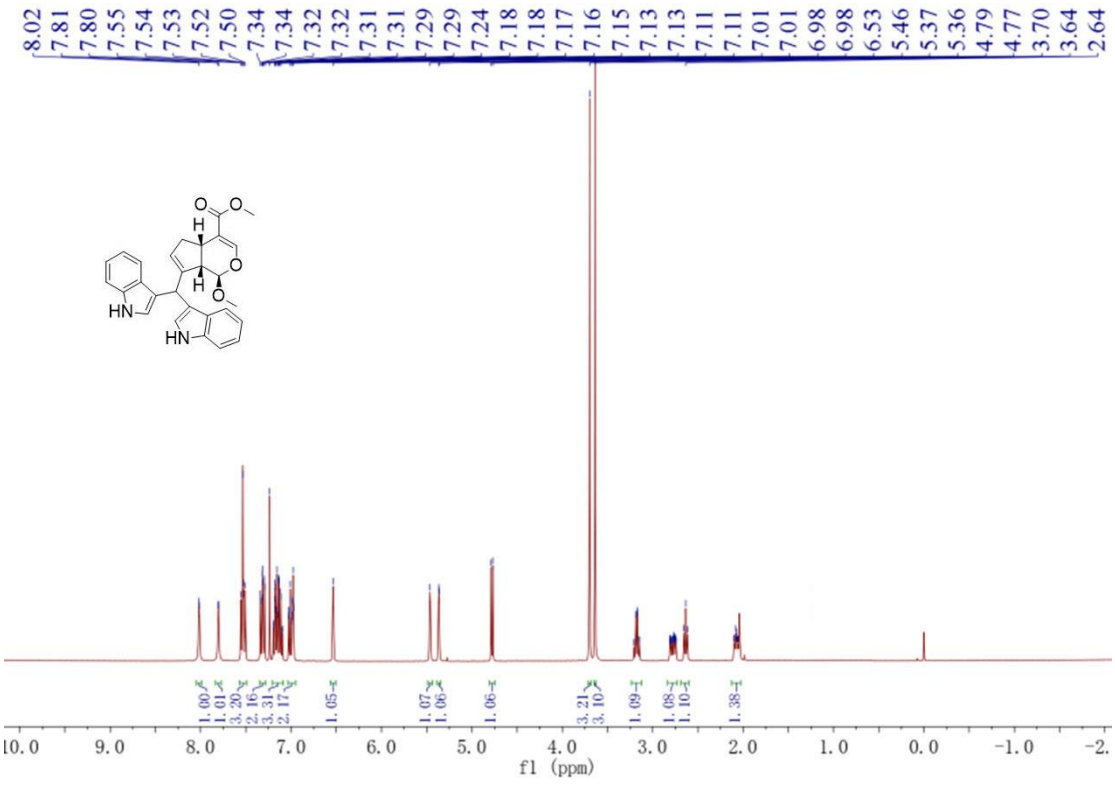


HR-EI-MS of compound **24**

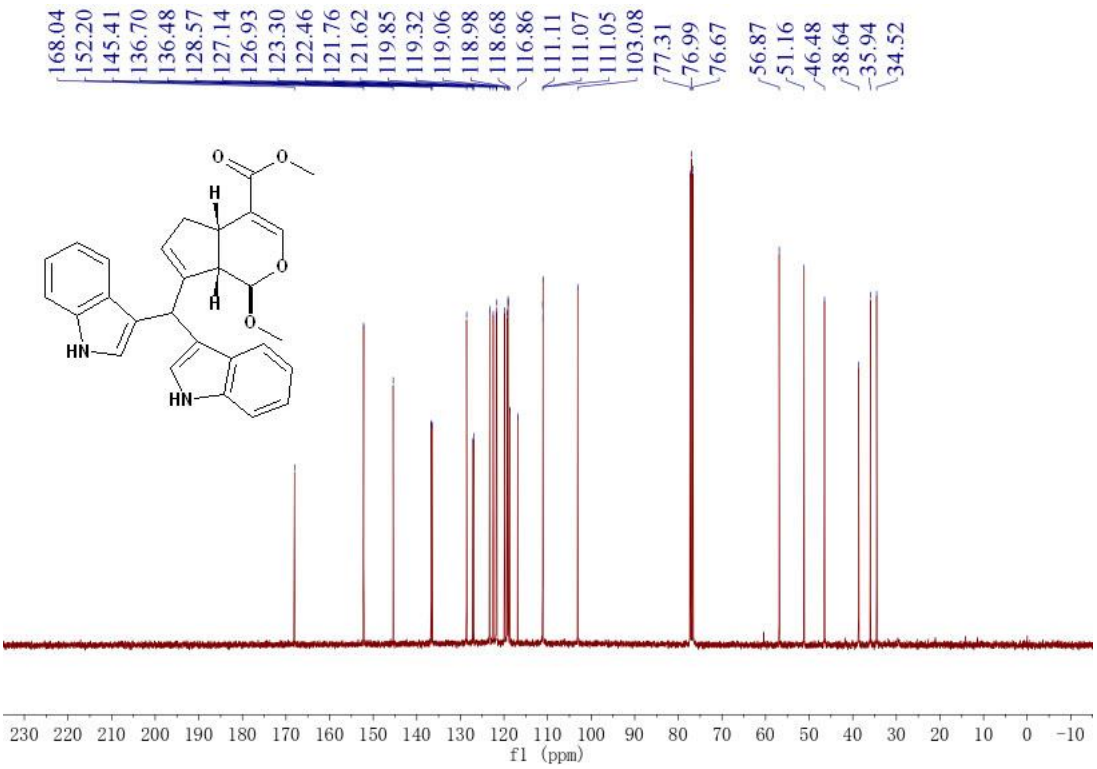


Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	89.10	C28 H24 N4 O8	[M+Na]+	567.1481	567.1486	-0.5	-0.88	89.10	19.0

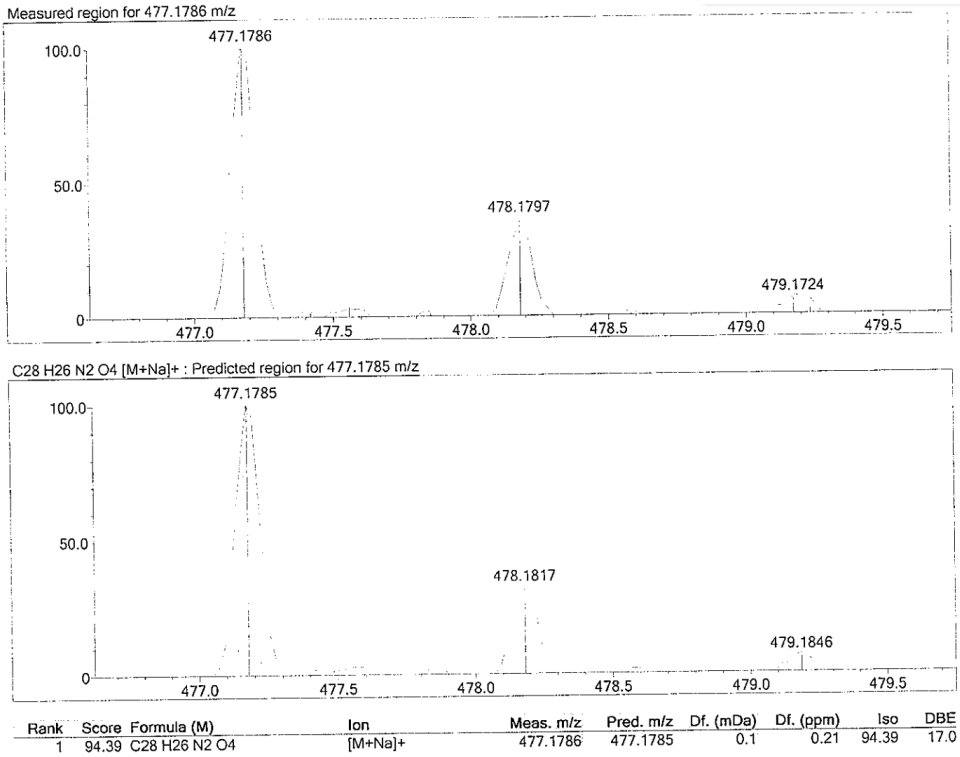
^{1}H-NMR of compound **25**



^{13}C-NMR of compound **25**

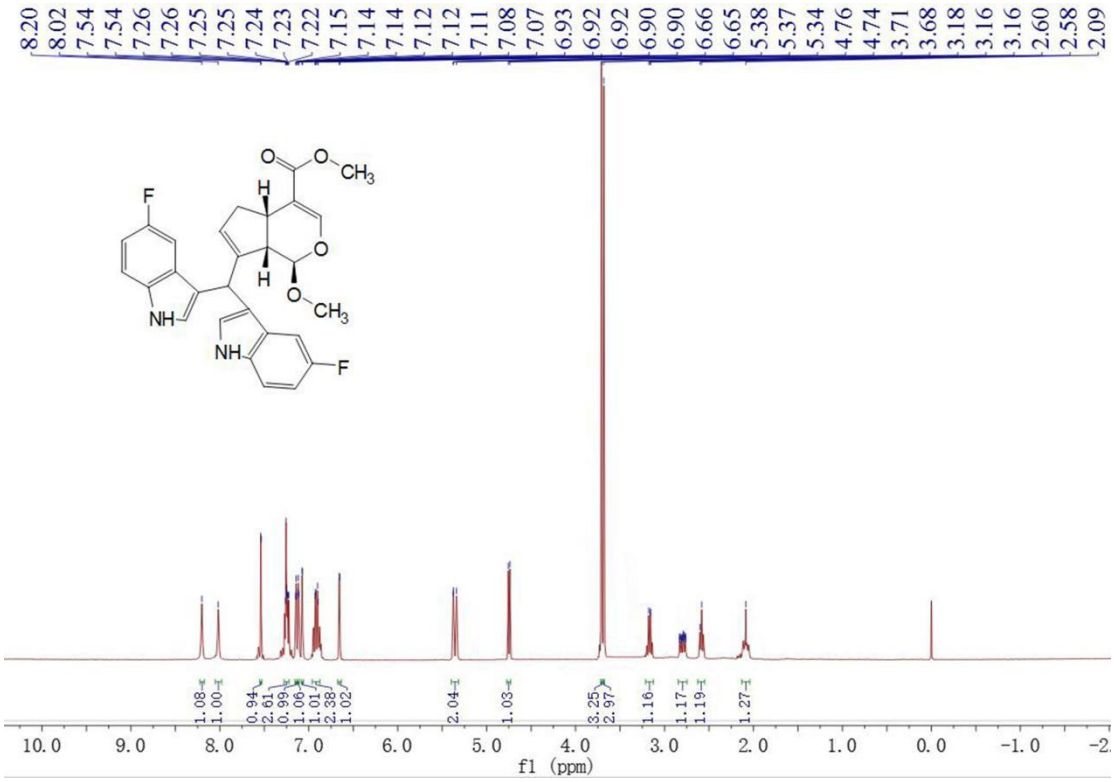


HR-EI-MS of compound **25**

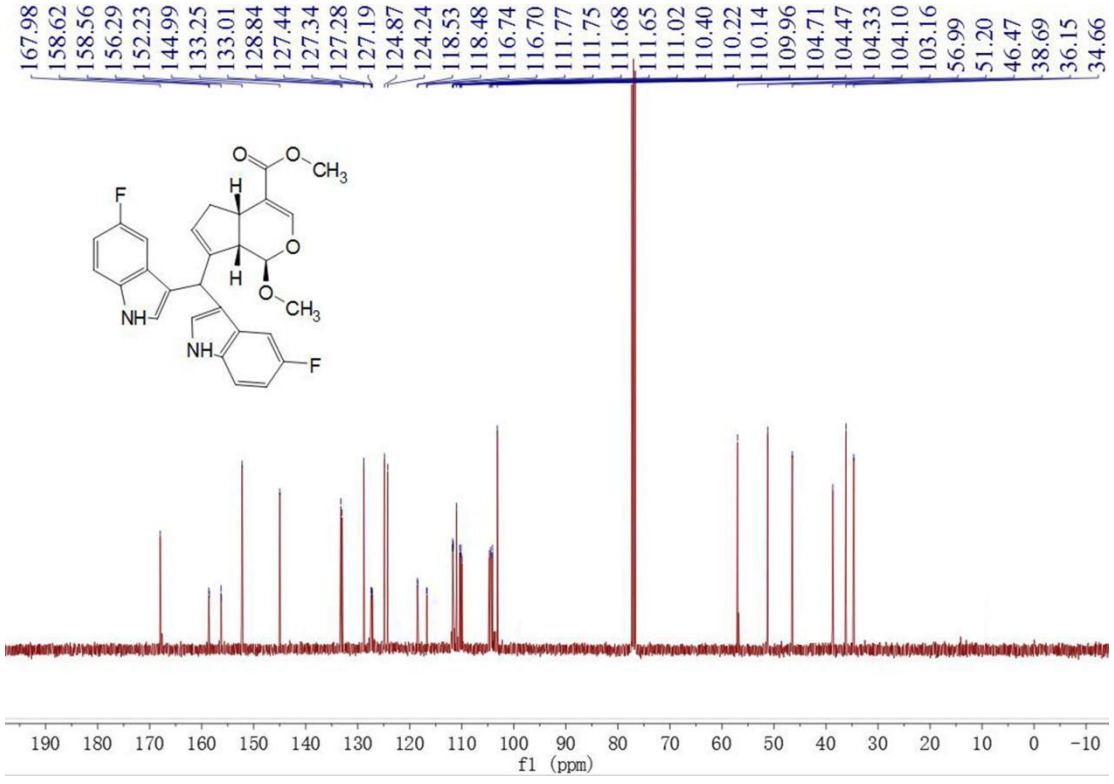


Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	94.39	C28 H26 N2 O4	[M+Na]+	477.1786	477.1785	0.1	0.21	94.39	17.0

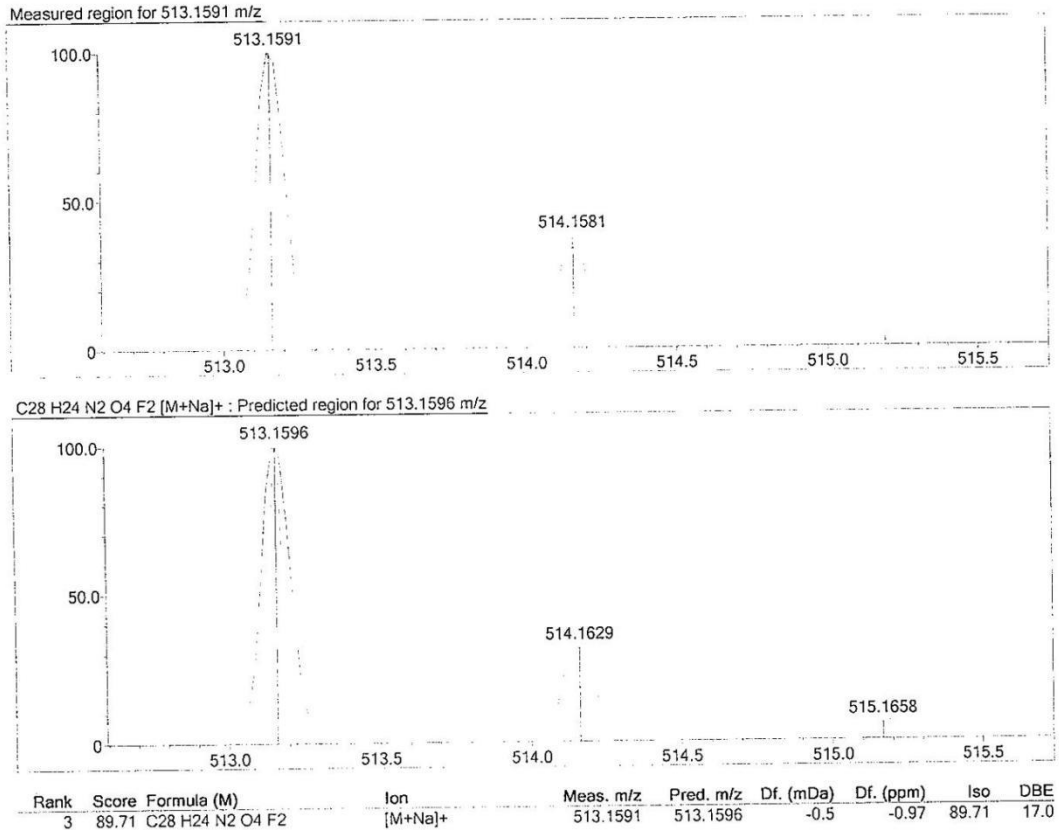
^{1}H-NMR of compound **26**



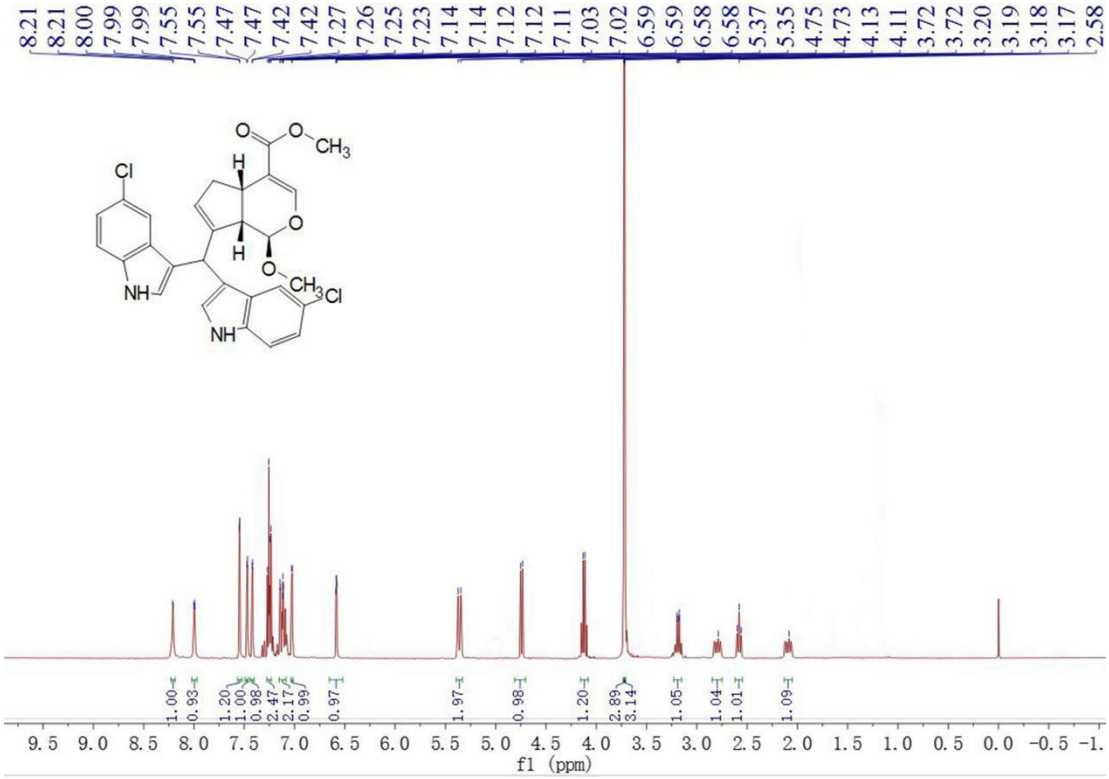
^{13}C-NMR of compound **26**



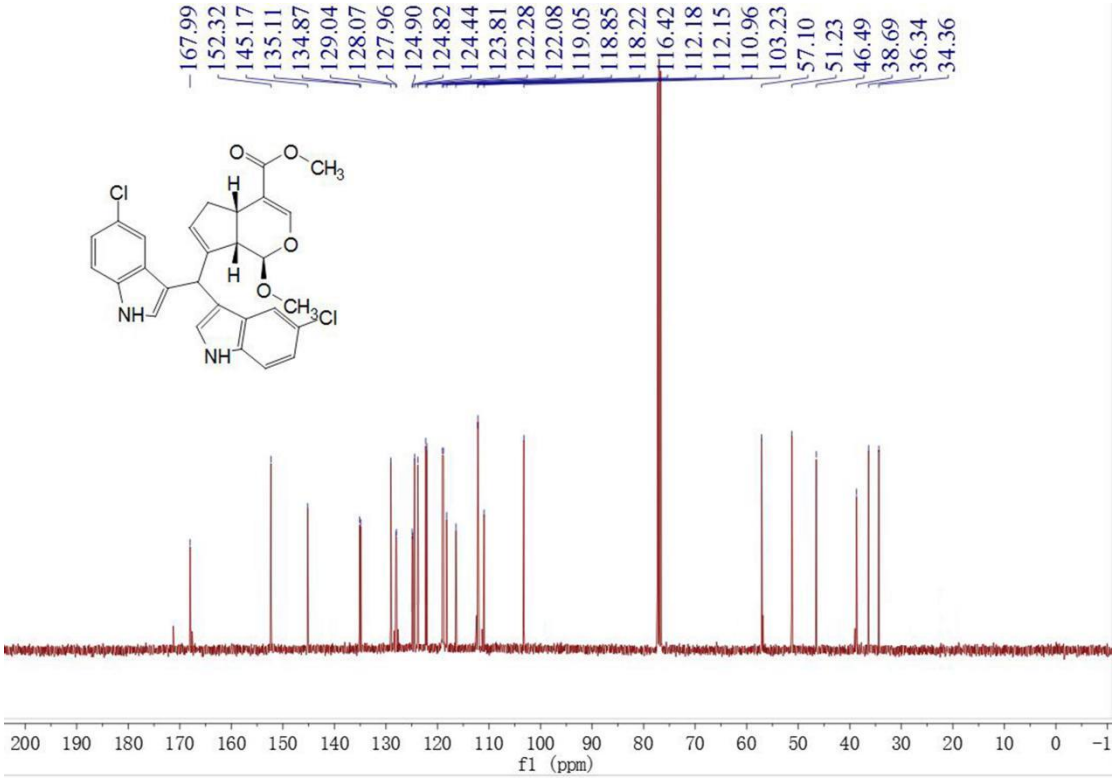
HR-EI-MS of compound **26**



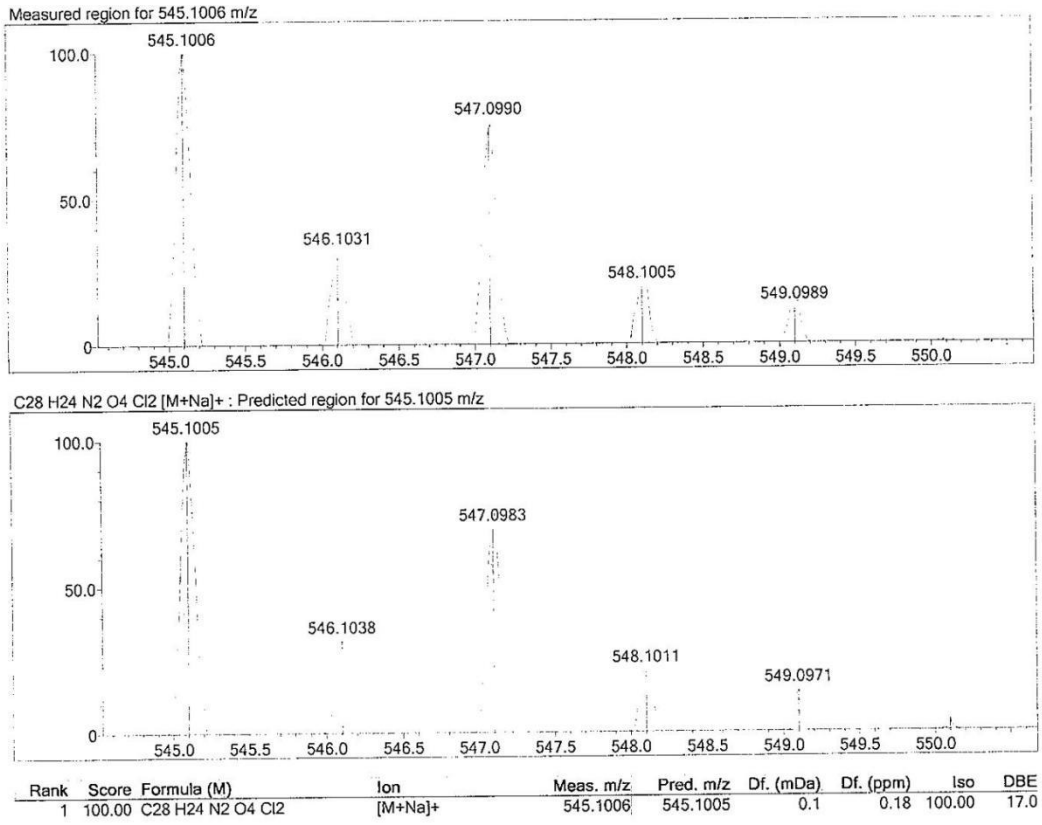
^{1}H-NMR of compound **27**



^{13}C-NMR of compound **27**

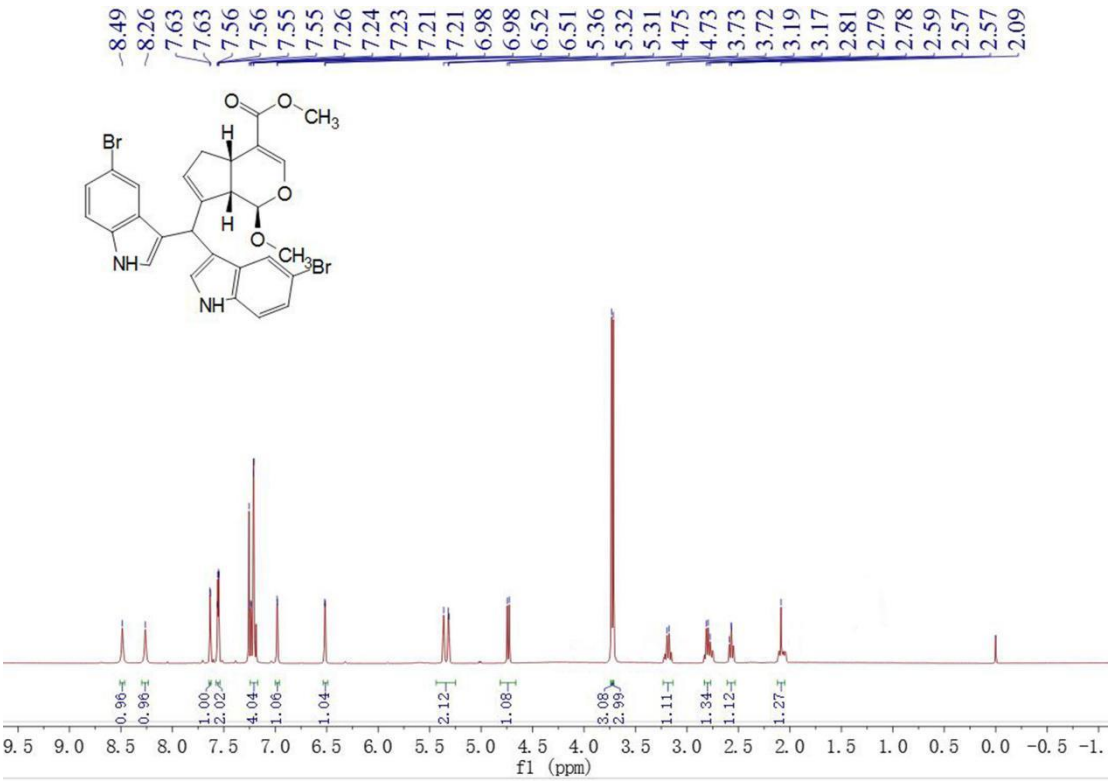


HR-EI-MS of compound **27**

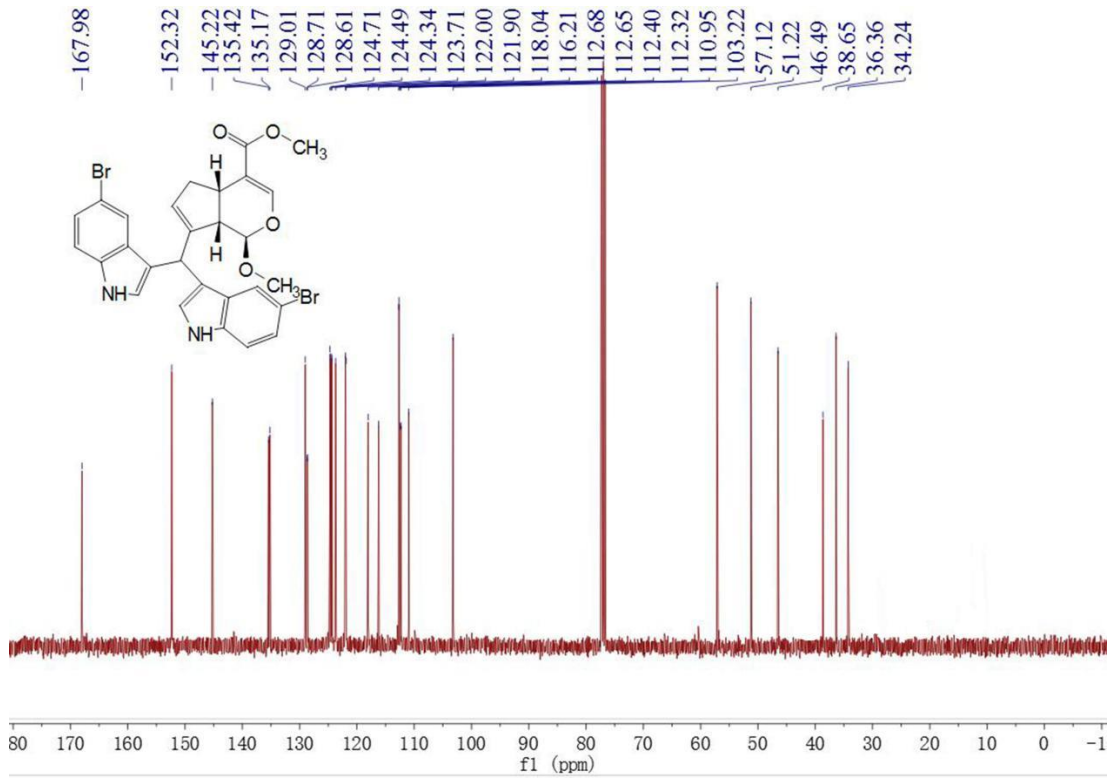


Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	100.00	C28 H24 N2 O4 Cl2	[M+Na]+	545.1006	545.1005	0.1	0.18	100.00	17.0

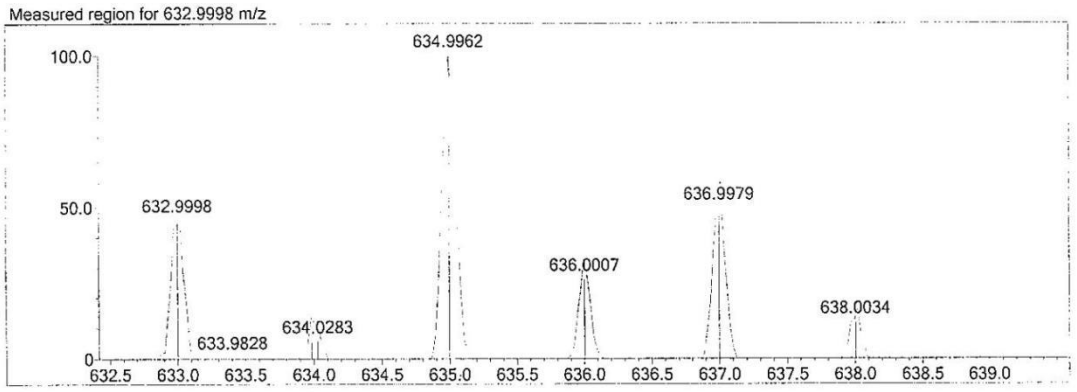
^{1}H-NMR of compound **28**



^{13}C-NMR of compound **28**

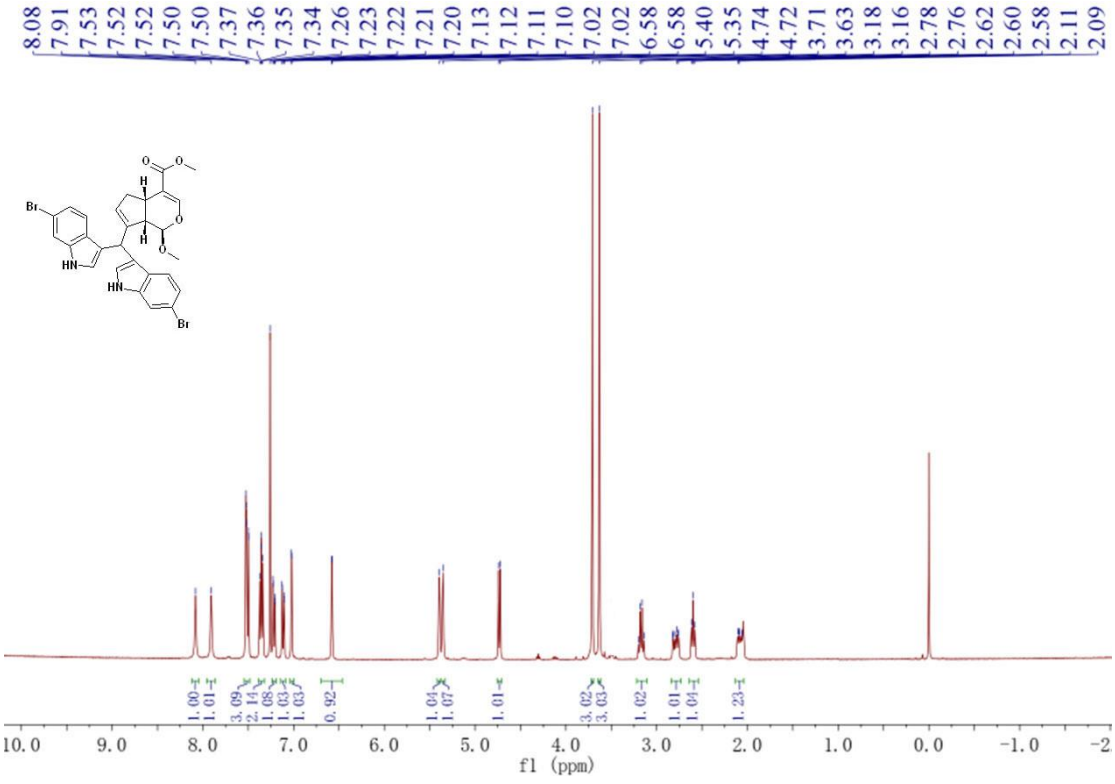


HR-EI-MS of compound **28**

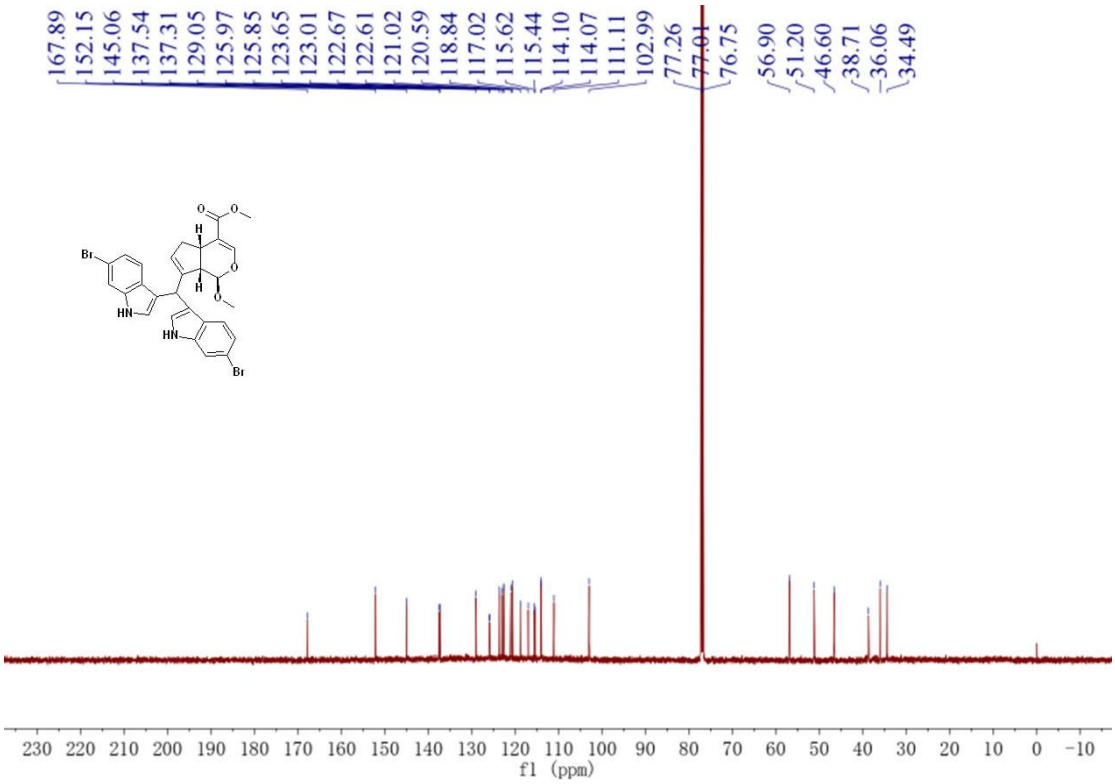


Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
5	79.14	C28 H24 N2 O4 Br2	[M+Na]+	632.9998	632.9995	0.3	0.47	79.14	17.0

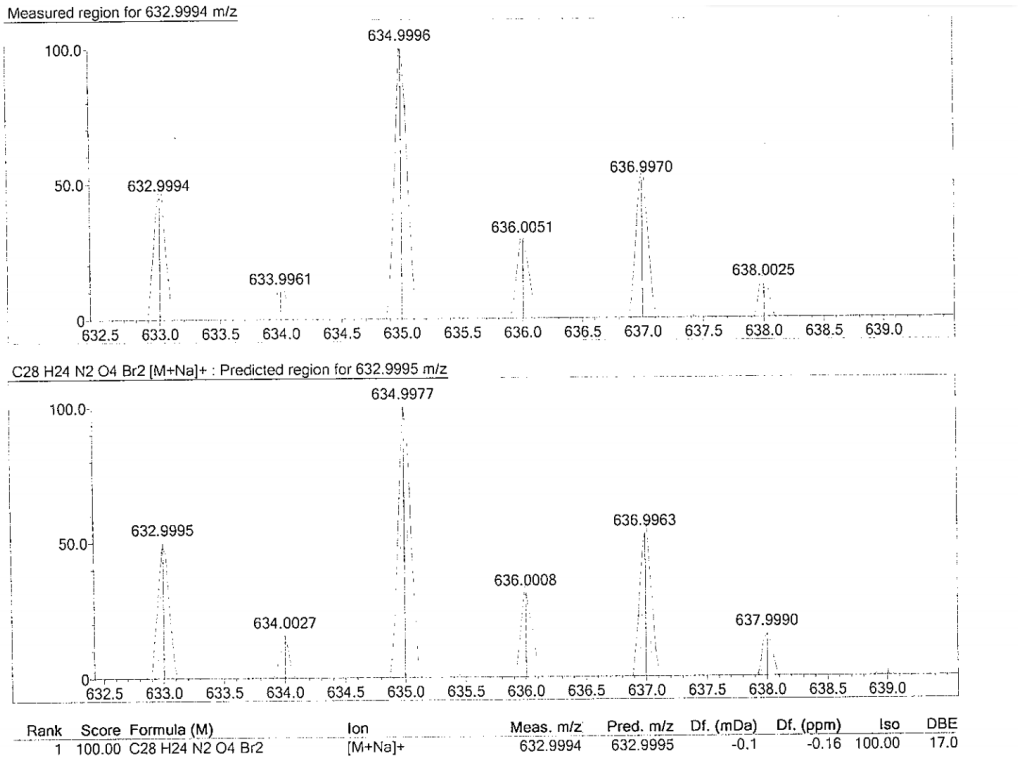
^{1}H-NMR of compound **29**



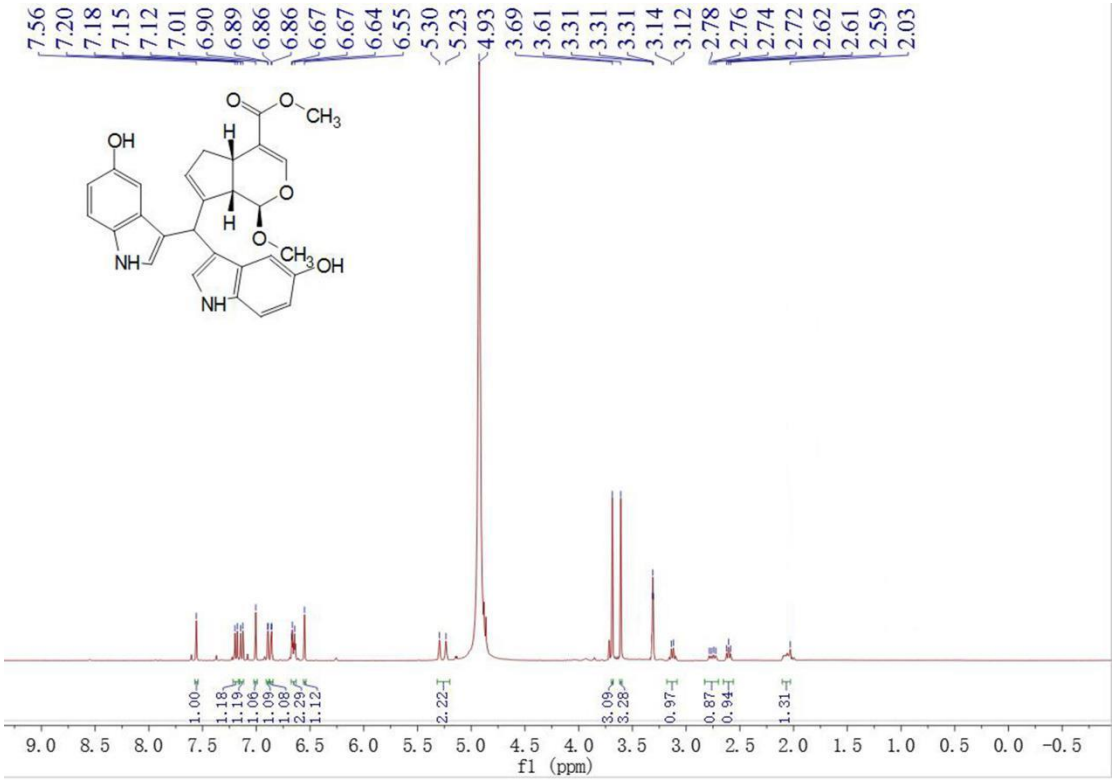
^{13}C-NMR of compound **29**



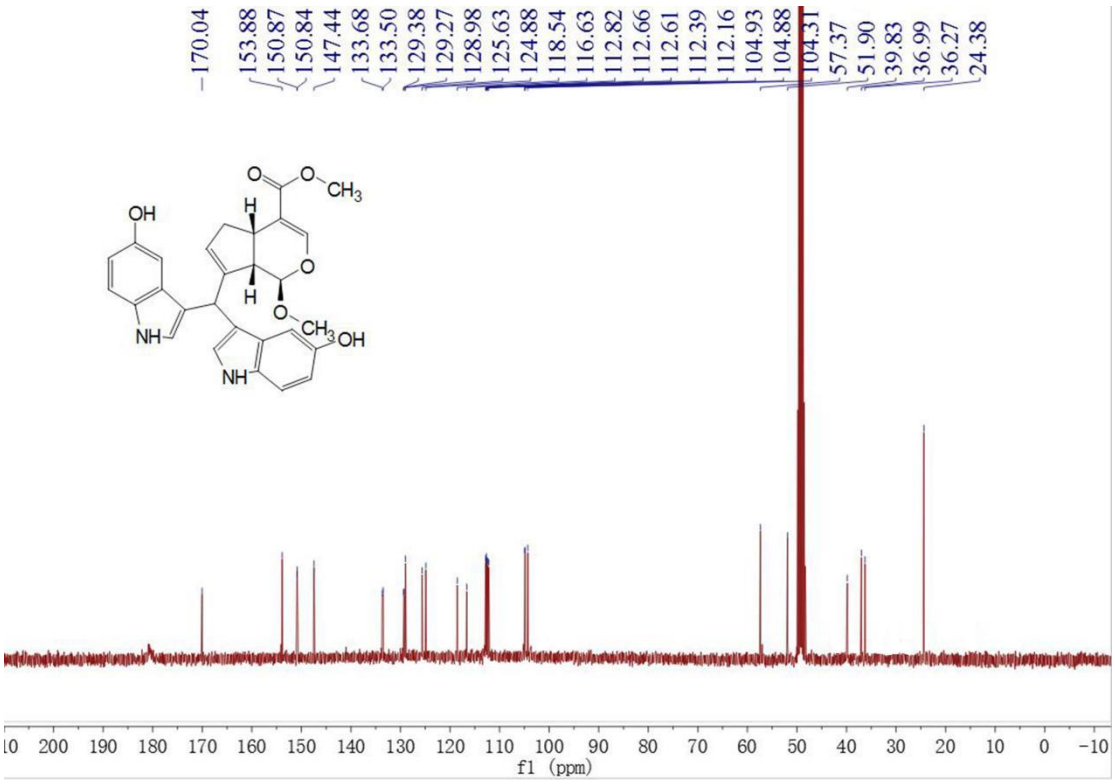
HR-EI-MS of compound **29**



^{1}H-NMR of compound **30**



^{13}C-NMR of compound **30**



HR-EI-MS of compound **30**

Formula Predictor Report - F21.lcd

Page 1 of 1

Data File: E:\DATA\2018\0206\F21.lcd

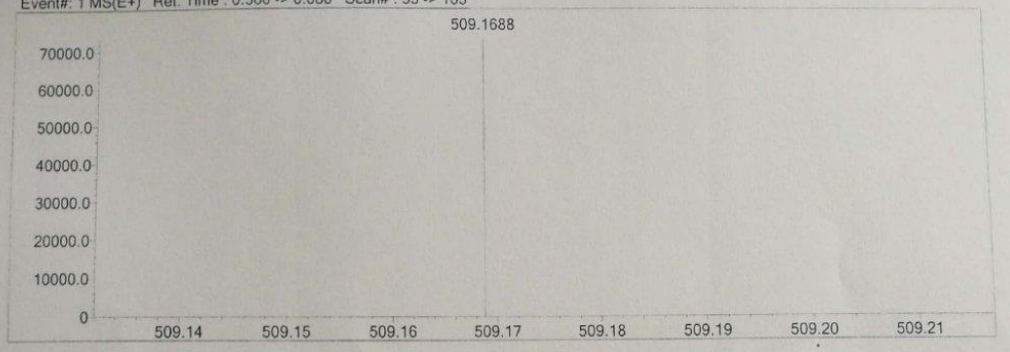
Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Use Adduct
H	1	0	100	O	2	0	50	Si	4	0	0	Br	1	0	0	Na
C	4	0	100	F	1	0	0	S	2	0	0	I	3	0	0	
N	3	0	10	Na	1	0	0	Cl	1	0	0					

Error Margin (ppm): 5
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

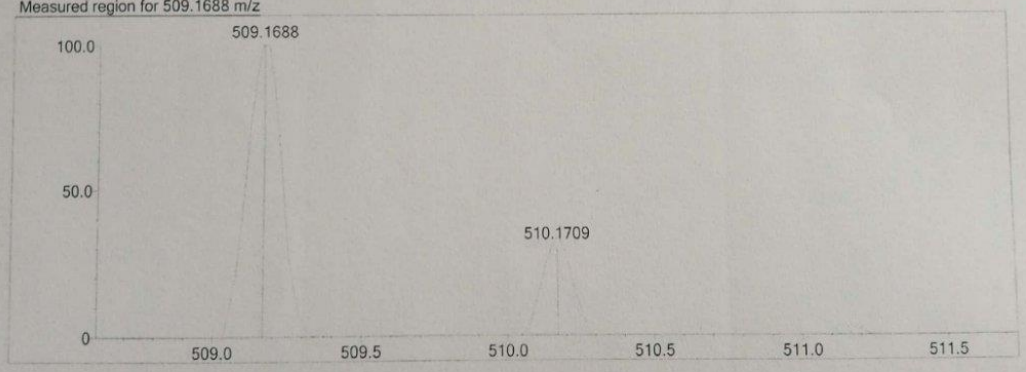
DBE Range: -2.0 - 100.0
Apply N Rule: yes
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: both
Use MSn Info: yes
Isotope Res: 10000
Max Results: 10

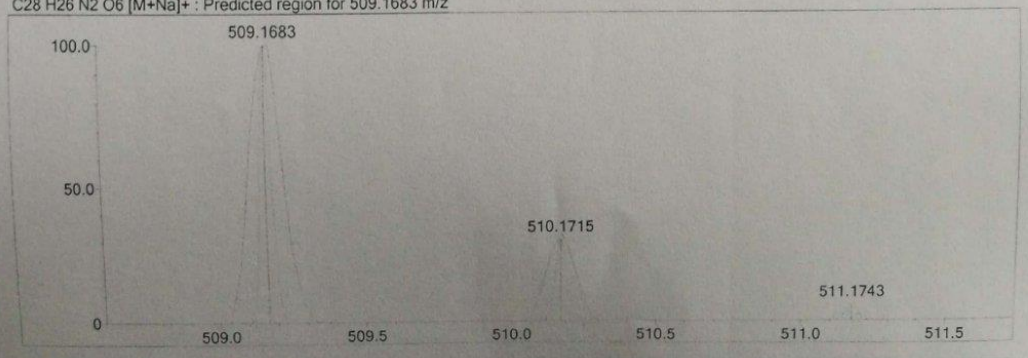
Event#: 1 MS(E+) Ret. Time : 0.360 -> 0.680 Scan# : 55 -> 103



Measured region for 509.1688 m/z

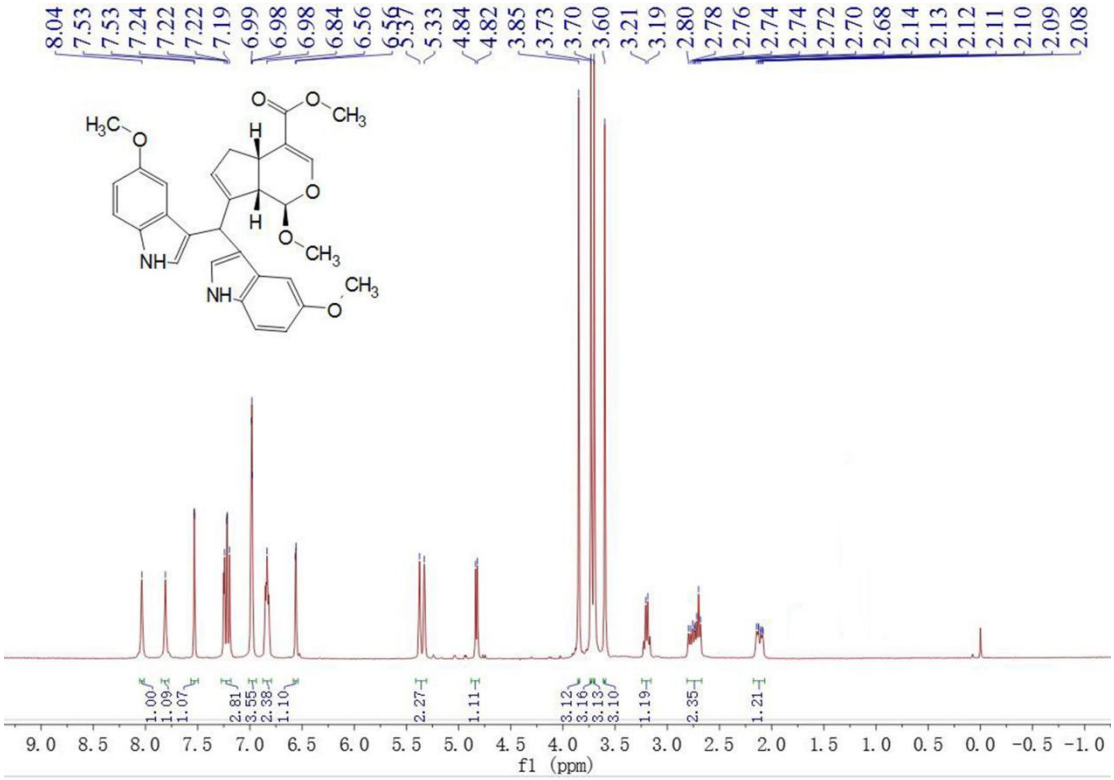


C28 H26 N2 O6 [M+Na]+ : Predicted region for 509.1683 m/z

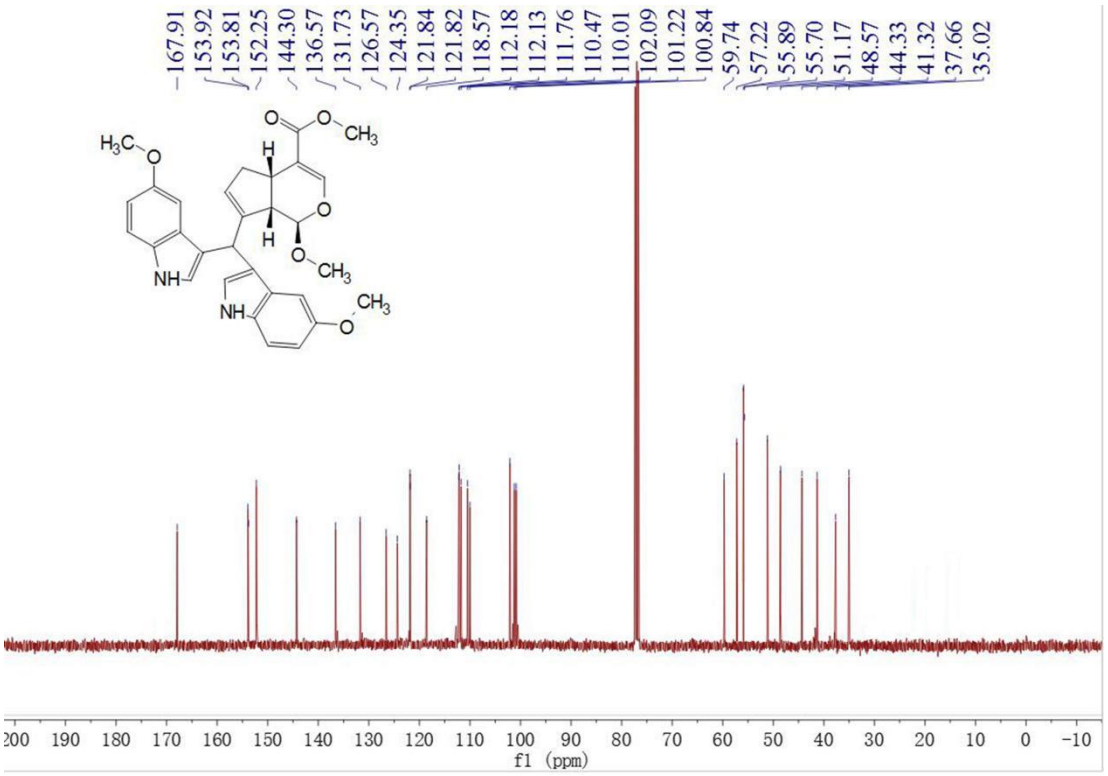


Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	DBE
C28 H26 N2 O6	[M+Na]+	509.1688	509.1683	0.5	0.98	17.0

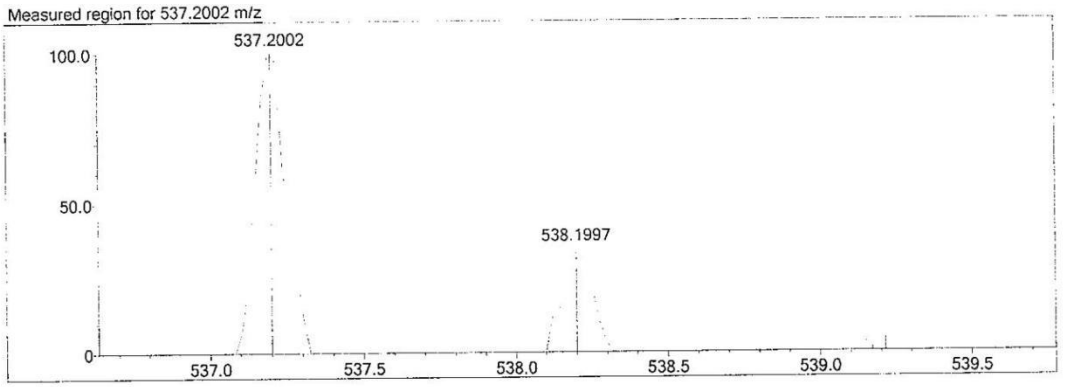
^{1}H-NMR of compound **31**

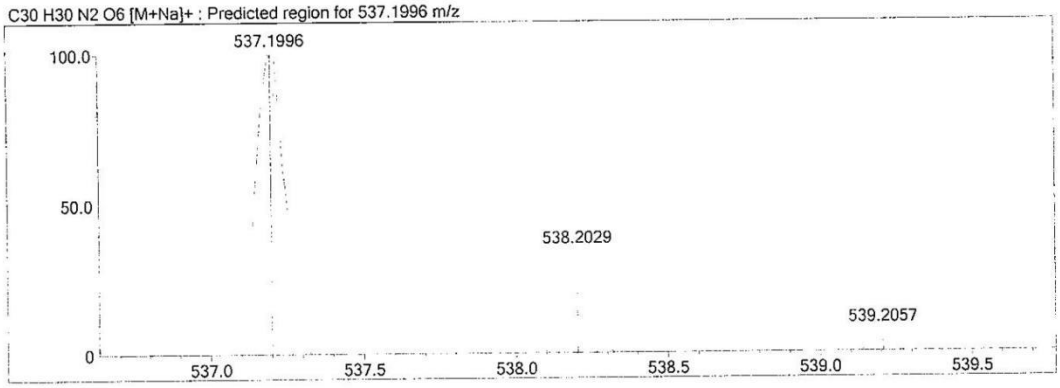


^{13}C-NMR of compound **31**



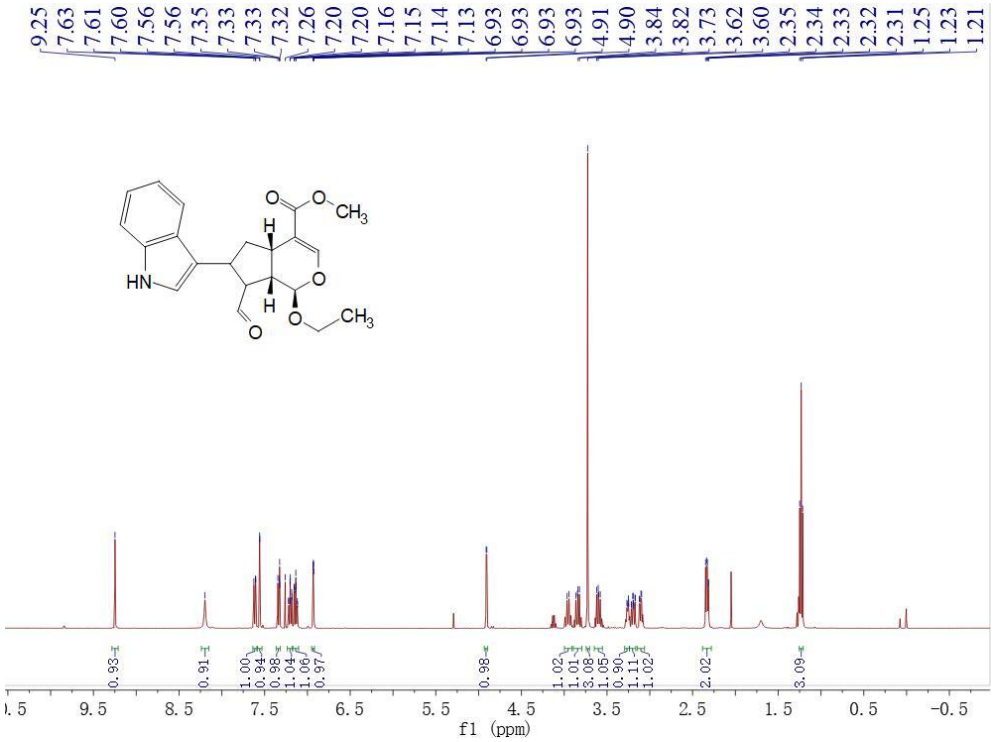
HR-EI-MS of compound **31**



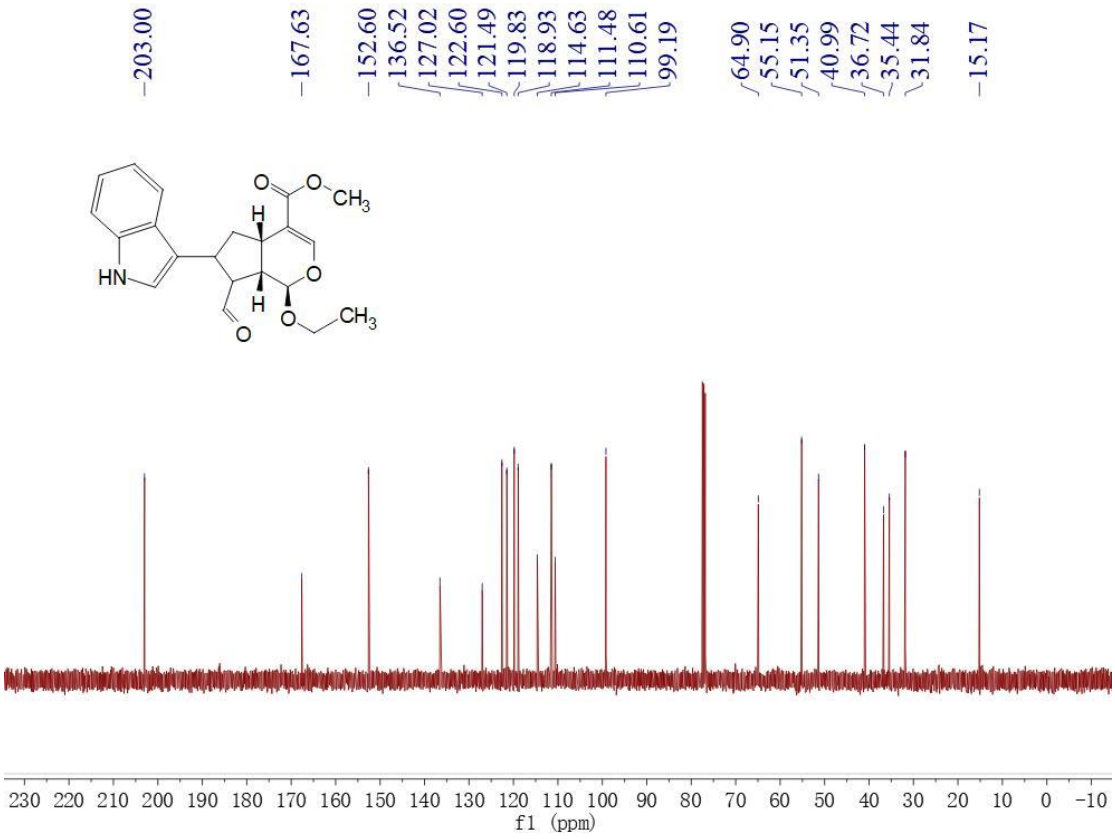


Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	77.57	C30 H30 N2 O6	[M+Na]+	537.2002	537.1996	0.6	1.12	77.80	17.0

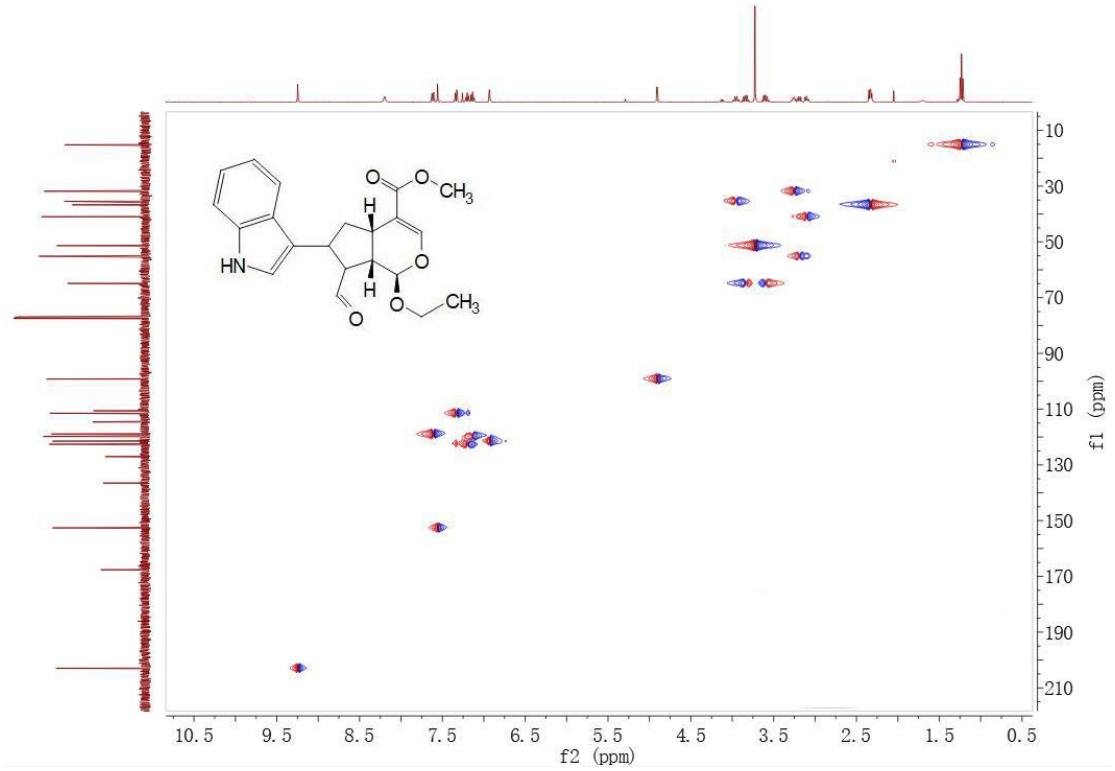
^{1}H-NMR of compound **32**



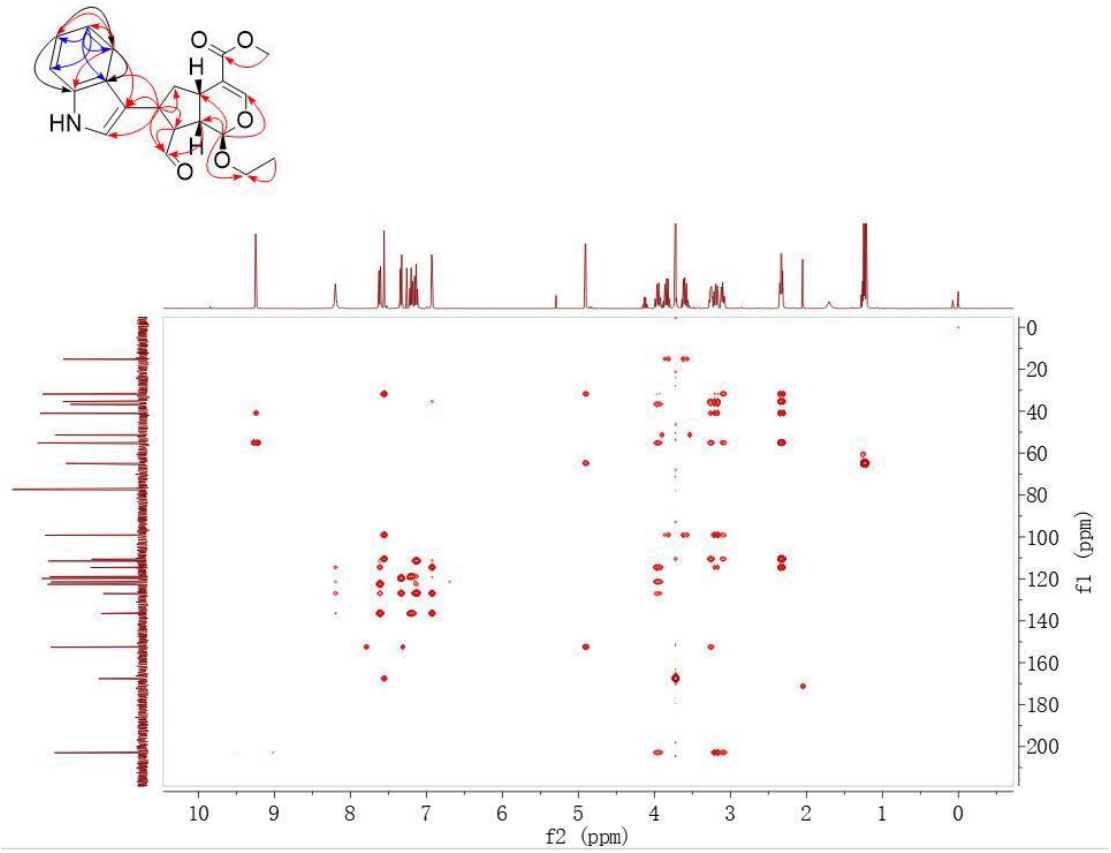
^{13}C-NMR of compound **32**



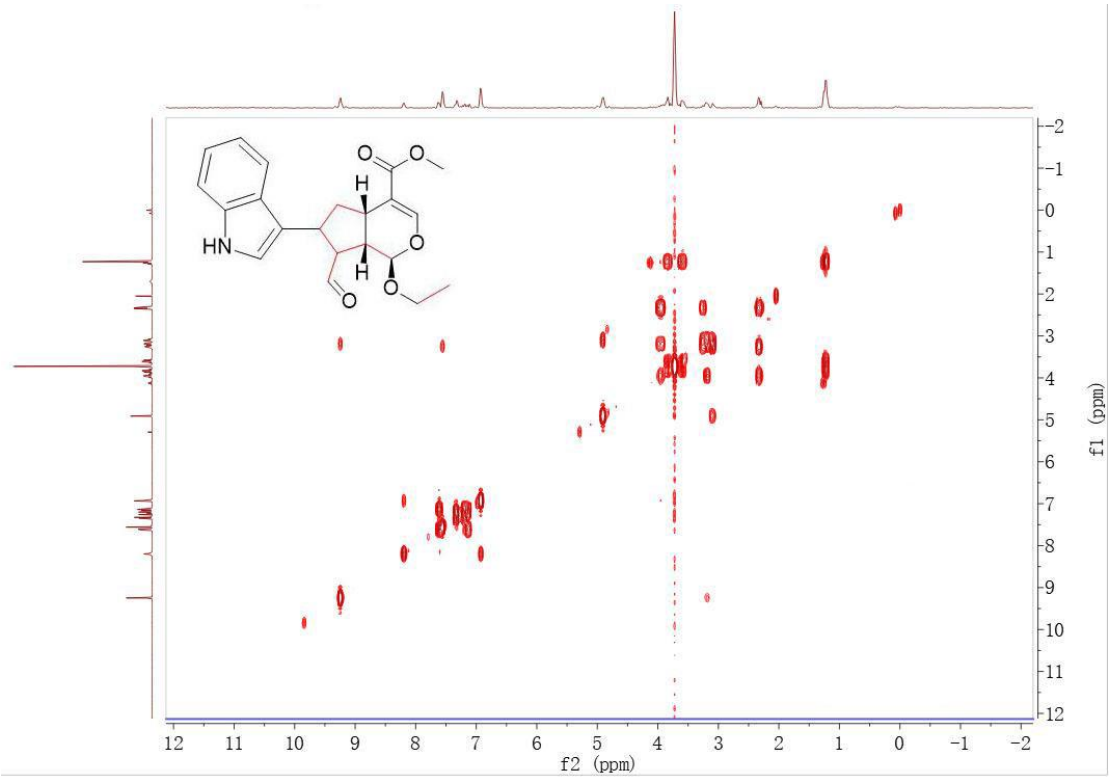
HSQC of compound **32**



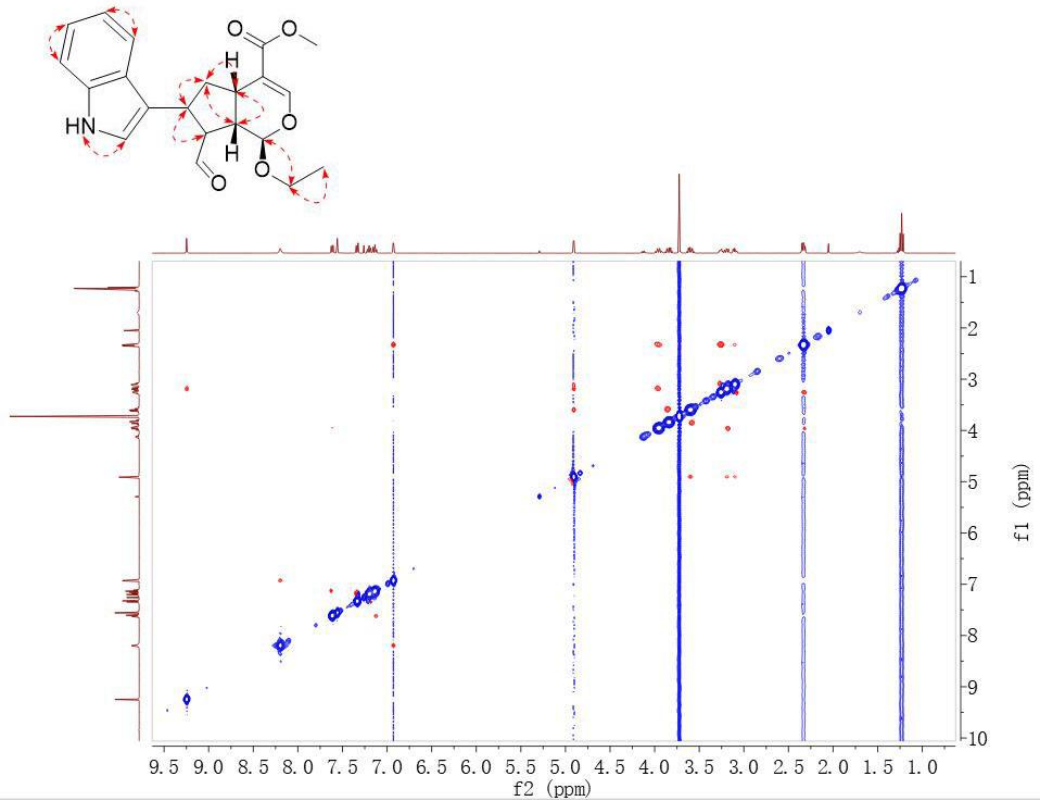
HMBC of compound **32**



H-H COSY of compound **32**



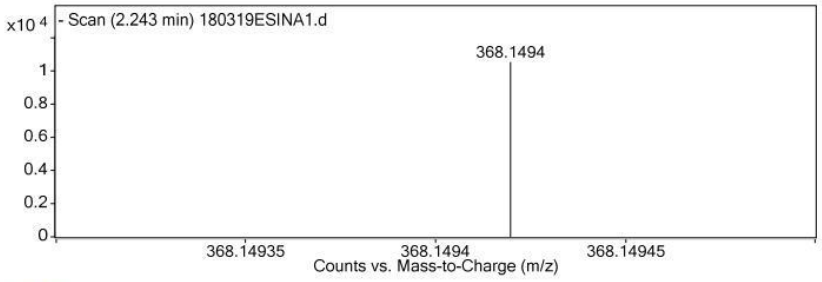
ROESY of compound **32**



HR-ESI-MS of compound **32**

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
360	0	ESI



Peak List

m/z	z	Abund
101.0211	1	361176.84
116.9073		106036.91
118.9044		101976.38
123.1034	1	280366.63
126.9049		74298.16
127.0538	1	121464.89
127.0981	1	287931.06
152.8841		125120.5
154.8811		157801.22
186.9071	1	82006.05

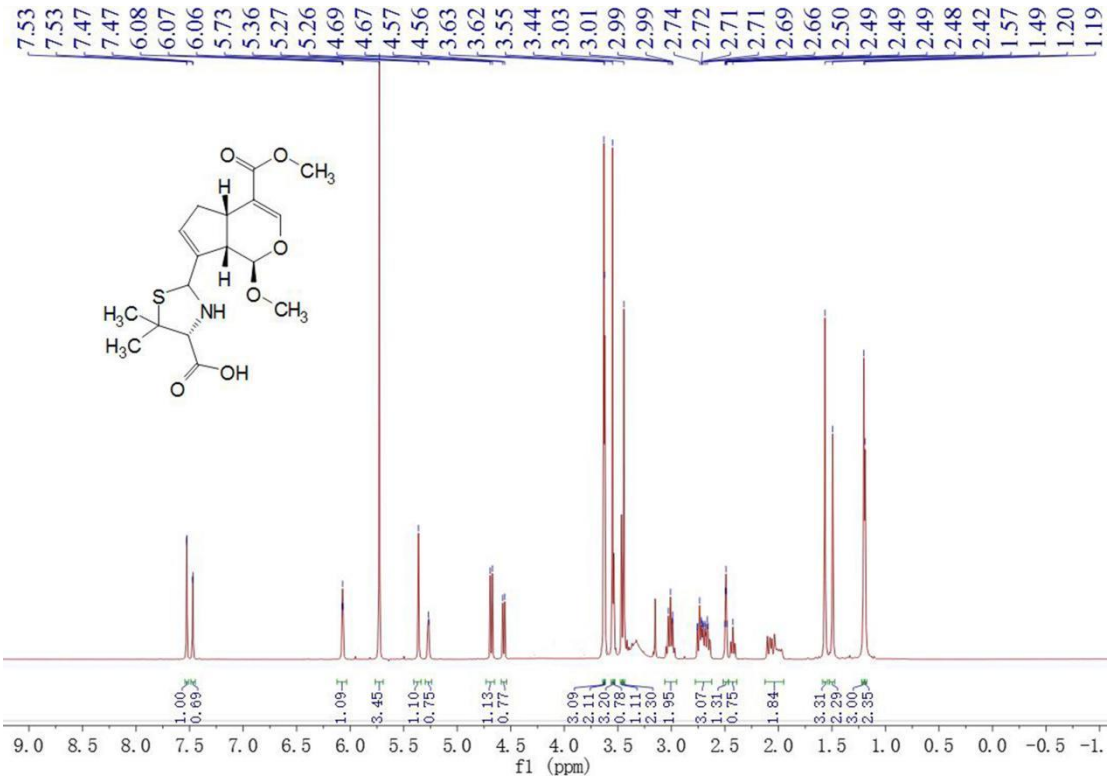
Formula Calculator Element Limits

Element	Min	Max
C	0	200
H	0	400
O	0	10
N	1	1

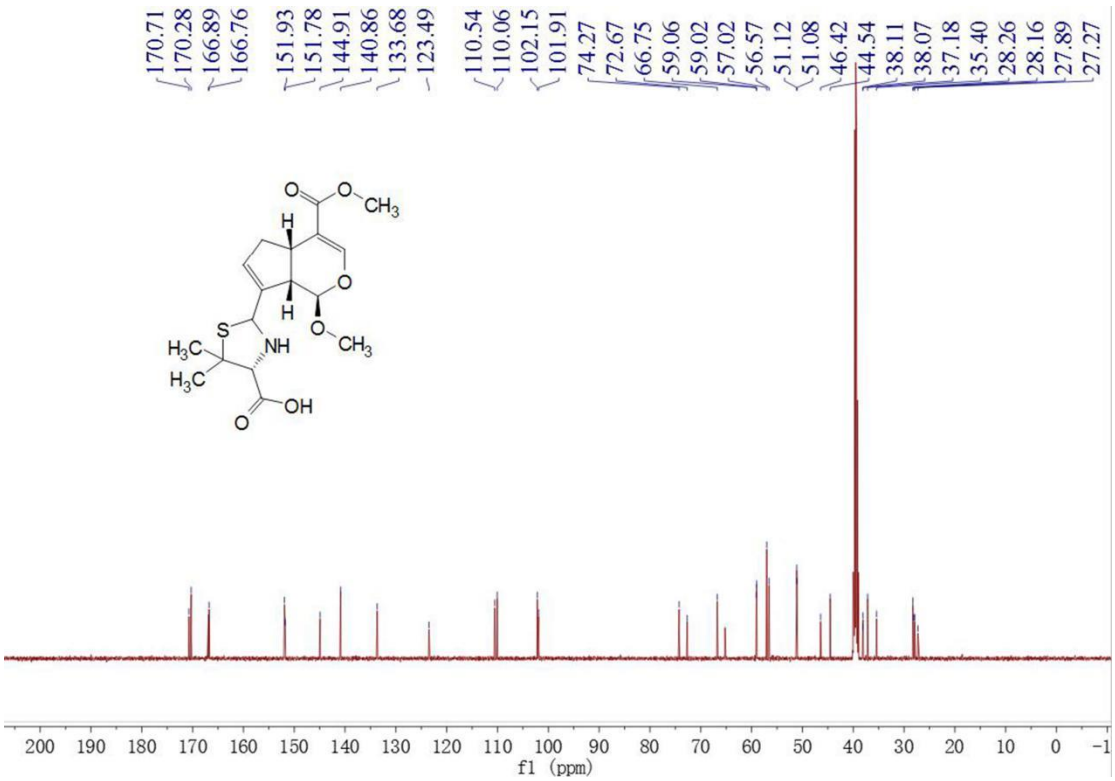
Formula Calculator Results

Formula	CalculatedMass	Mz	Diff.(mDa)	Diff. (ppm)	DBE
C21 H22 N O5	368.1498	368.1494	0.4	1.1	11.5

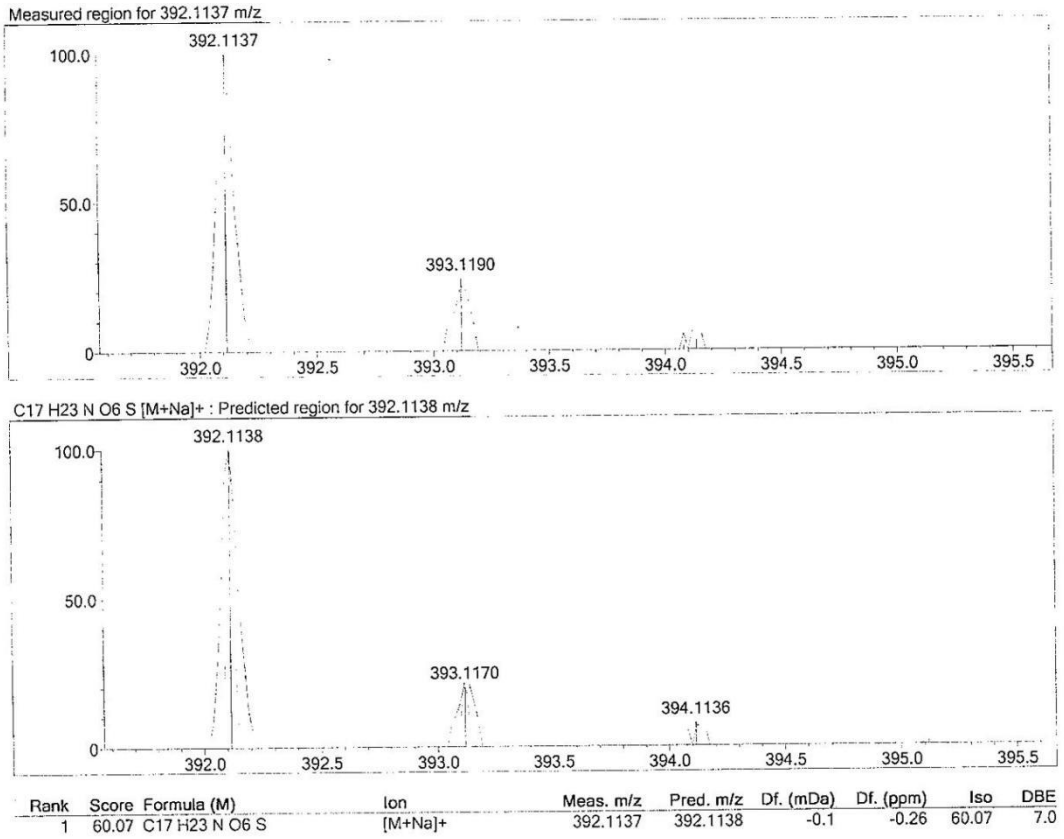
^{1}H-NMR of compound **33**



^{13}C-NMR of compound **33**

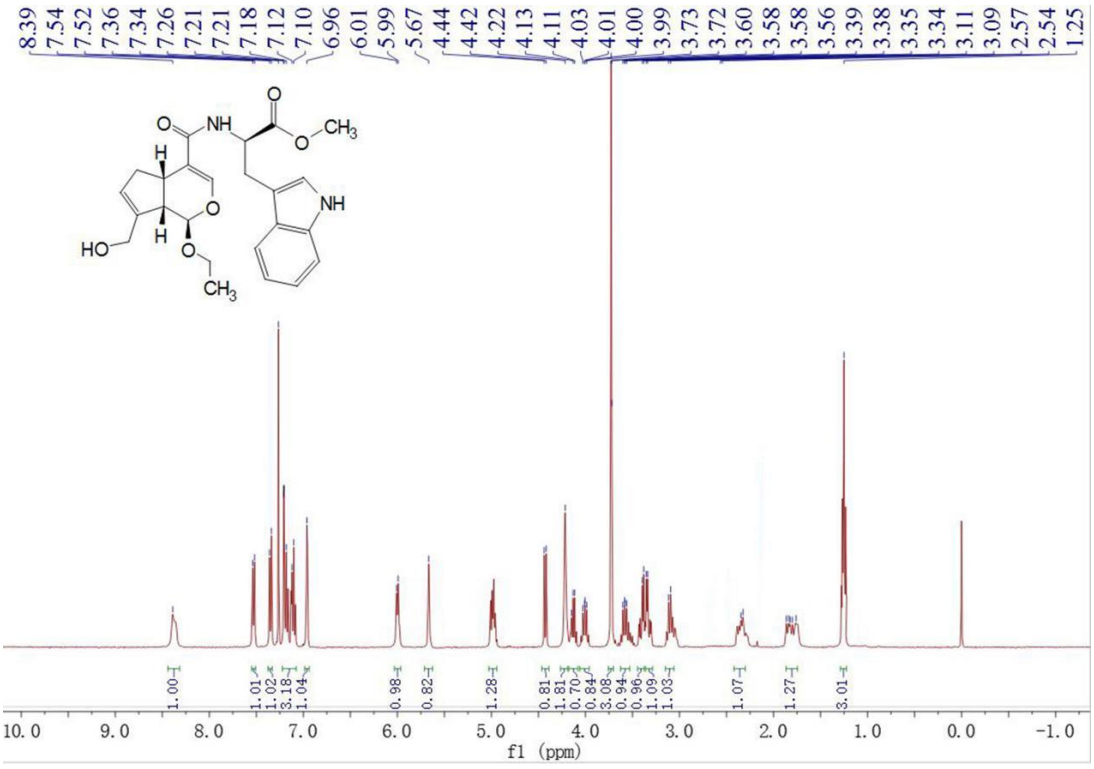


HR-EI-MS of compound **33**

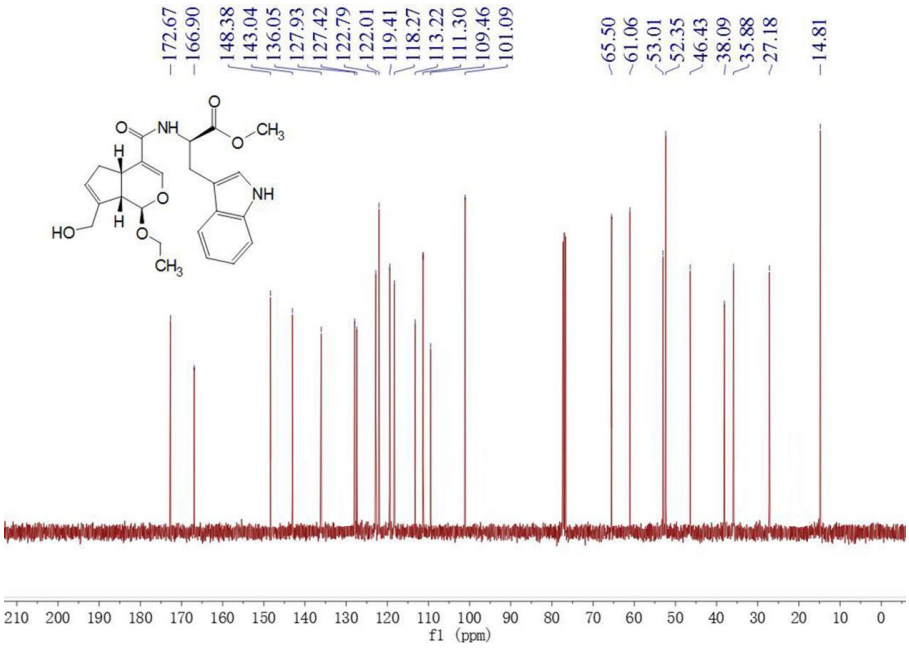


Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	60.07	C17 H23 N O6 S	[M+Na]+	392.1137	392.1138	-0.1	-0.26	60.07	7.0

^{1}H-NMR of compound **34**



^{13}C-NMR of compound **34**



HR-EI-MS of compound **34**