Electronic Supplementary Material (ESI) for RSC Advances.

A novel *C-C* radical-radical coupling reaction promoted by visible light: facile synthesis of 6-substituted *N*-methyl 5,6-dihydrobenzophenanthridine alkaloids

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***General*:**

Column chromatography silica gel (200-300 mesh) and TCL plate were purchased from Qingdao Meijin Chemical Inc(Qingdao; China); HRMS data were obtained in the ESI mode on an Agilent 6530 Q-TOF/MS system; GC-MS data were obtained on an Agilent GCMS-QP2010 system. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometer and chemical shifts were given in δ with TMS as an internal reference. Dihydrosanguinarine and dihydrochelerythrine were isolated from *Macleaya Cordata* in our lab.

Representative experimental procedure for visible light promoted synthesis of 6-substituted 5,6-dihydrobenzophenanthridine.

A solution of dihydrosanguinarine **5** (0.2 mmol), 3.0 eq of Na_2HPO_4, $Ir(ppy)_3$ (2 mol%) and 3.0 equiv of $BrCH_2COOEt$ in DMF (2 mL) was firstly bubbled with nitrogen for 10 minutes and then irradiated with 25 W household compact fluorescent lamp under nitrogen atmosphere. After 24 h reaction, the resulting mixture was poured into water (50 mL) and then extracted with EtOAc (20 mL×3). The combined organic solution was then washed with water (20 mL×3). The organic layers were washed with brine and dried over $MgSO_4$. The solvent were removed via vacuo and theresidue was purified by flash column chromatography (SiO_2) with petroleum ether/AcOEt (8:1) to give target compound**14a**.

HPLC-Q-TOF analysis for the crude product from Tabble 1, entry 3 (Na_2CO_3 used as base)

Based on previous literature, if α-bromo carbonyl compounds were used as radical precursor, Na_2HPO_4 was the mostly used deacid reagent along with DMF as solvent (*Angew. Chem. Int. Ed.* 2013, 52, 13289; *Org. Lett*., 2013, 18, 4884; *Angew. Chem. Int. Ed*. 2015, 54, 15545). Based on the reviewer's comments, we analyzed the crude product when Na_2CO_3 was used. After 24 h reaction, HPLC-HRMS analysis (Figure 1s) showed that a major byproduct with m/z value of 405.1435 was detected (peak 2, Figure 1s). Because a positive mode was applied in the MS analysis, peak 2 (m/z = 405.1435) should belong to a byproduct that possessed two nitrogen atoms. Thus we suggested that if Na_2CO_3 was used in the reaction, dihydrosanguinarine would react with solvent DMF. This byproduct was unstable during the silica gel column chromatography isolation process, and we only obtained the byproduct with low purity.

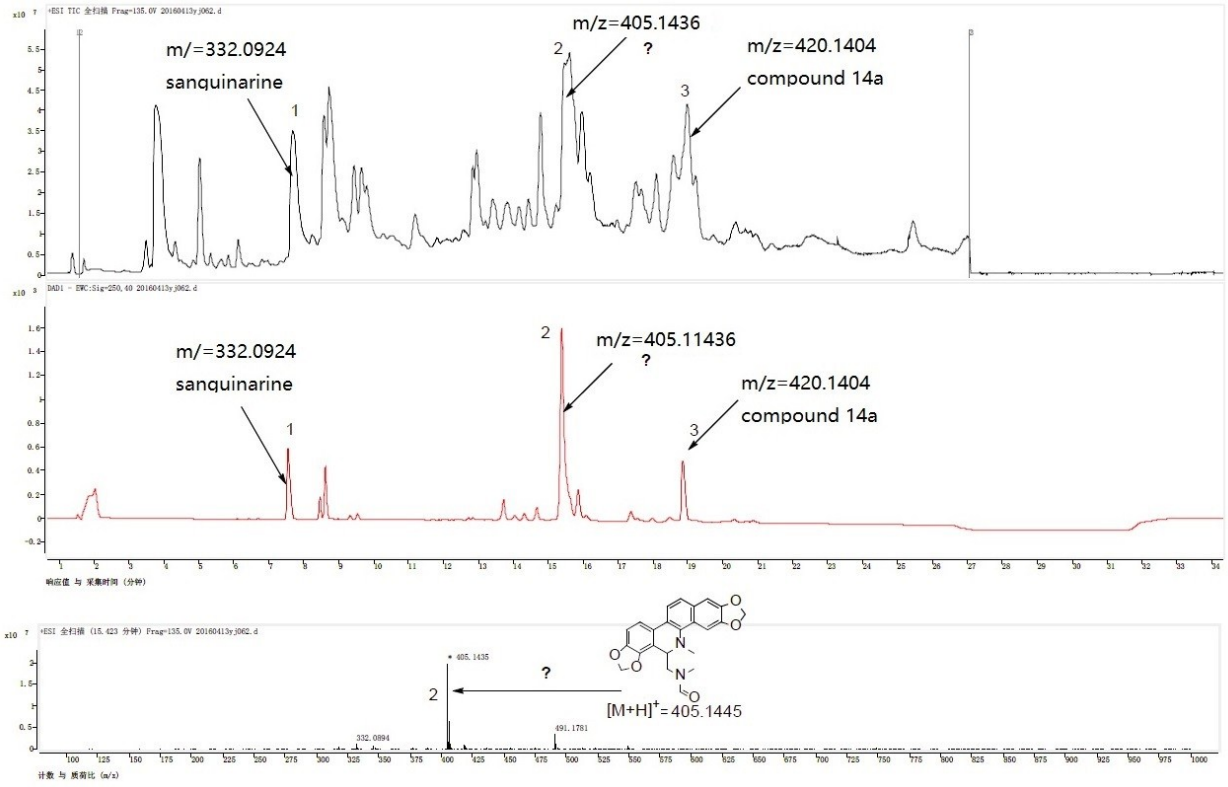


Figure 1s. HPLC-HRMS analysis of crude product using Na_2CO_3 as base

NMR spectra of byproduct from Tabble 1, entry 3

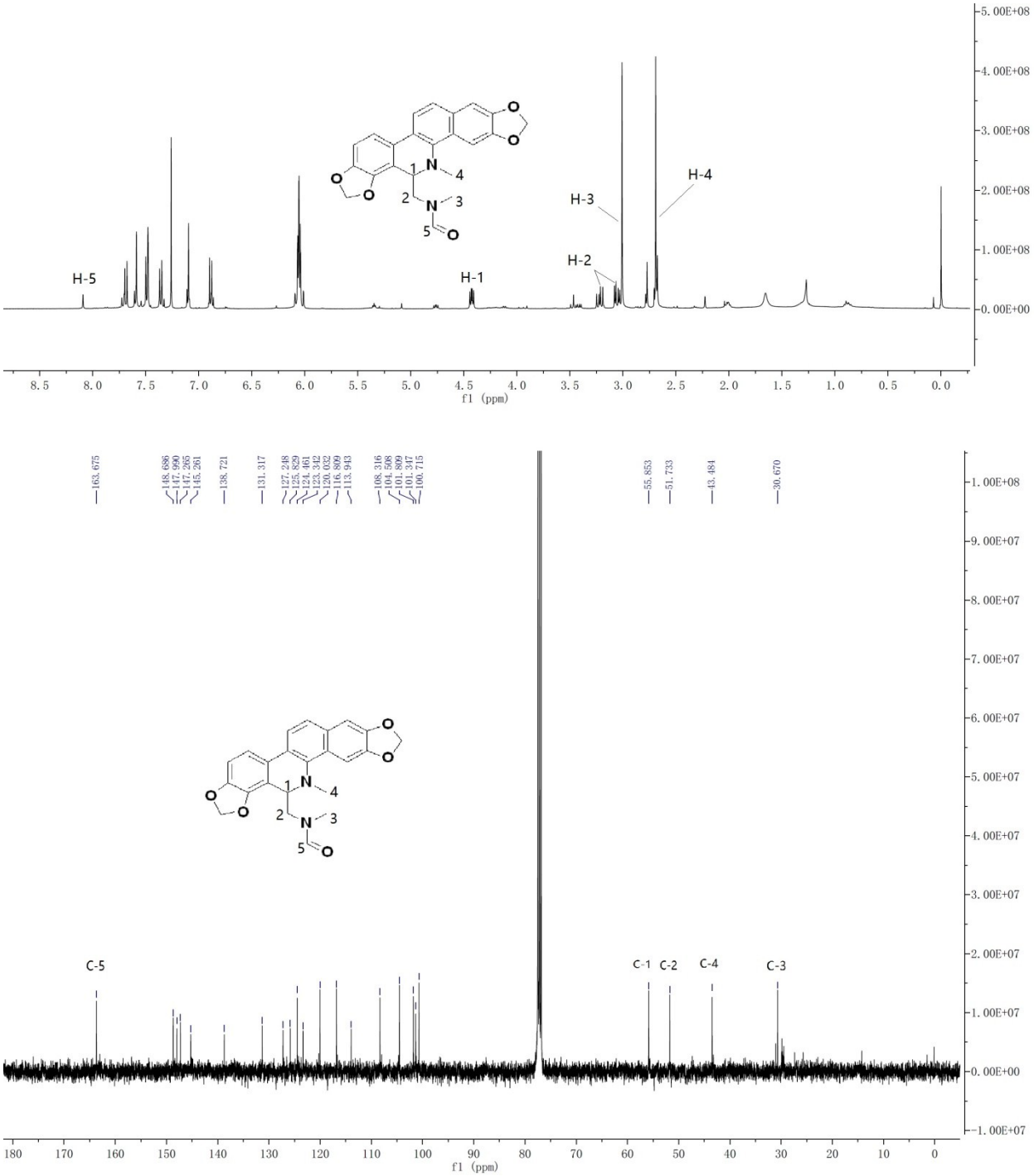


Figure 2s. NMR spectra of byproduct when Na_2CO_3 was used as base

HPLC-Q-TOF analysis for the crude product of compound 14c

We analyzed the crude product of **14c** based on HPLC-HRMS technology (Figure 3s). Interestingly, target compound 14c was detected in moderate HPLC yield. But we didn't isolate compound **14c** after column chromatography at 0.2 mmol scales which indicated that compound **14c** was not stable during purification process. To obtain pure compound **14c**, the coupling reaction was performed in 0.6 mmol scales again, but only isolated in 8% yield.

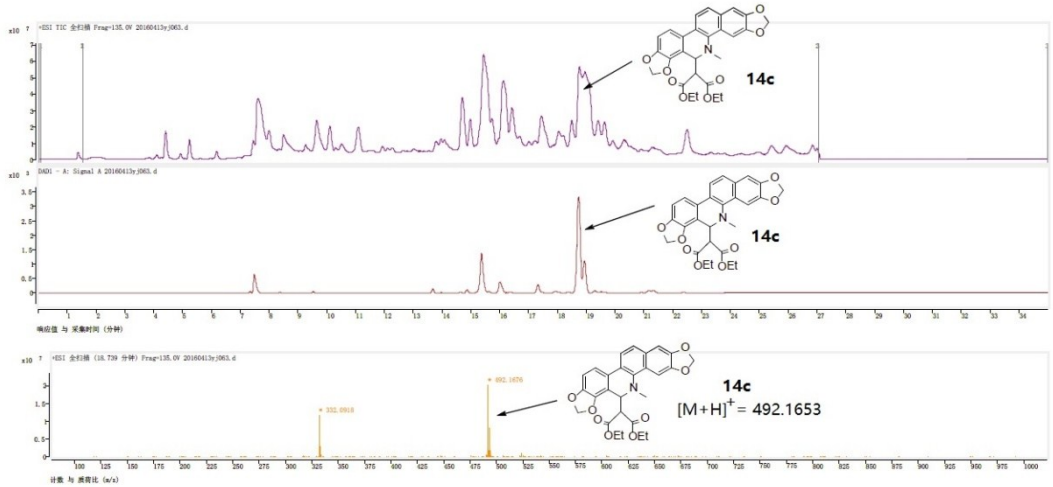


Figure 3s. HPLC-HRMS analysis of crude product **14c**

As shown in Figure 4s, we firstly isolated compound **14c** by column chromatography, but a an impurity generated during the isolation process (Figure 4, **A**). Thus, we purified combined fractions of compound **14c** using preparation TLC again (Figure 4, **B**). But another impurity generated as shown in Figure 4, **B**. Finally, compound **14c** was obtained only in 8% isolated yield. As a result, we thought that it was the poor stability of compound **14c** but not the enolization of diethyl bromomalonate that led to the poor isolated yield.

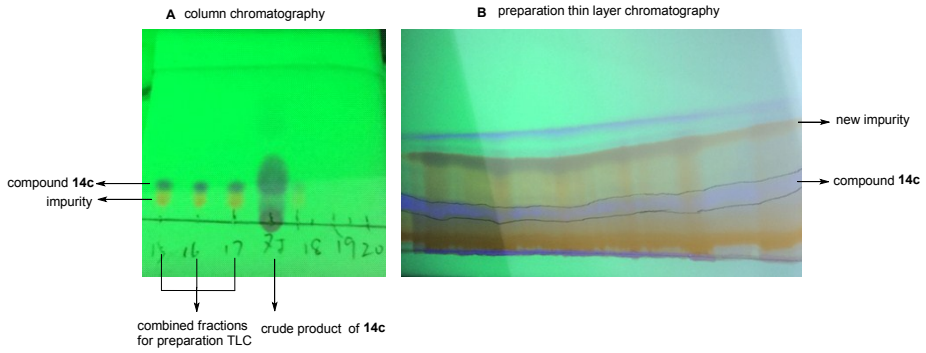


Figure 4s. Column chromatography (**A**) and preparation TLC (**B**) isolation of compound **14c**

HPLC-Q-TOF and GC-MS analysis for the radical trapping experiment

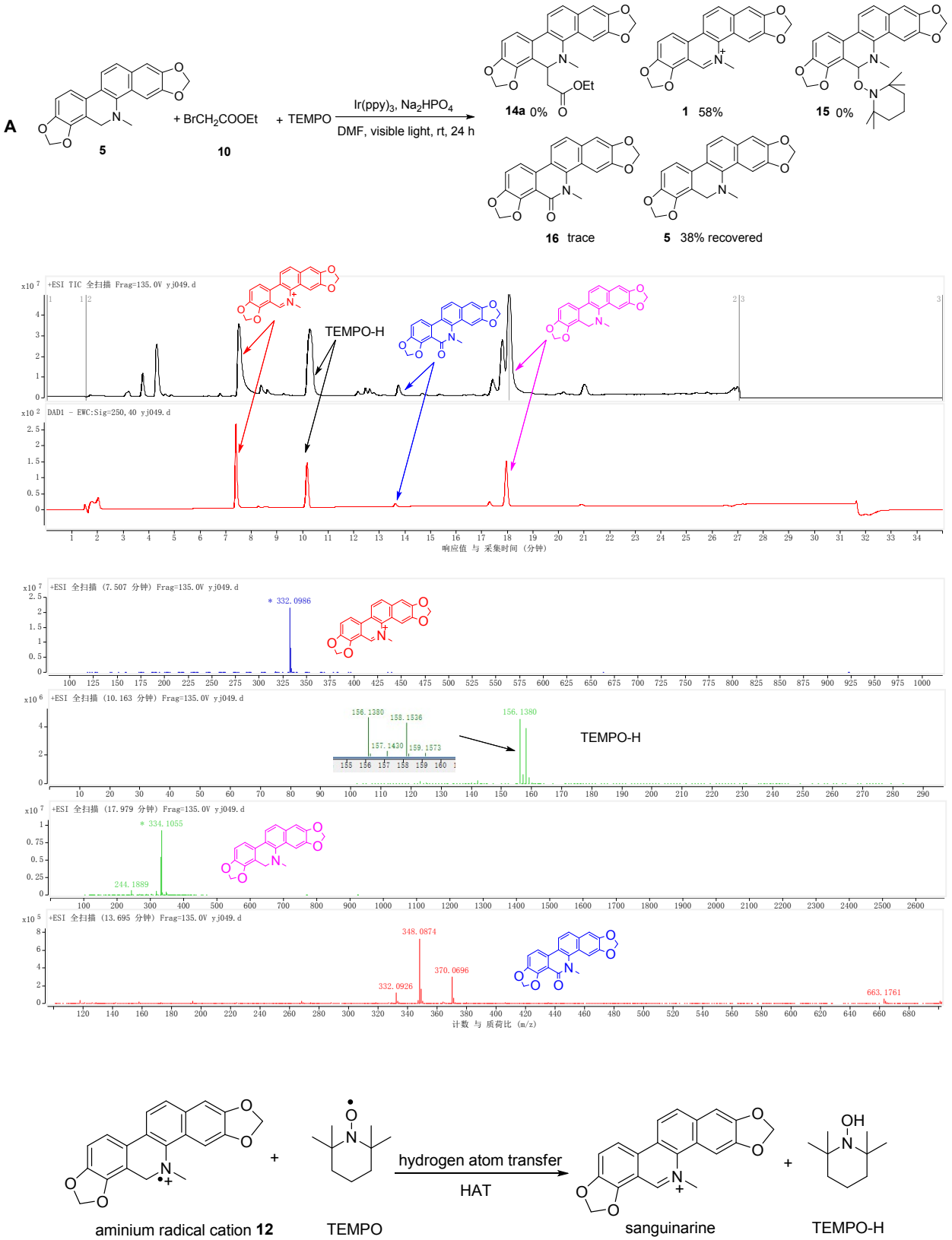


Figure 5s. HPLC-Q-TOF analysis for the radical trapping experiment

We proposed that hydrogen atom transfer (HAT) process existed between aminium radical cation **12** and

TEMPO. This HAT process promote the yield of sanguinarine in the radical trapping experiment

On the other hand, we analyzed the crude product from radical trapping experiment using GC-MS. The coupling product of TEMPO with radical **11** was detected as shown in Figure 6s:

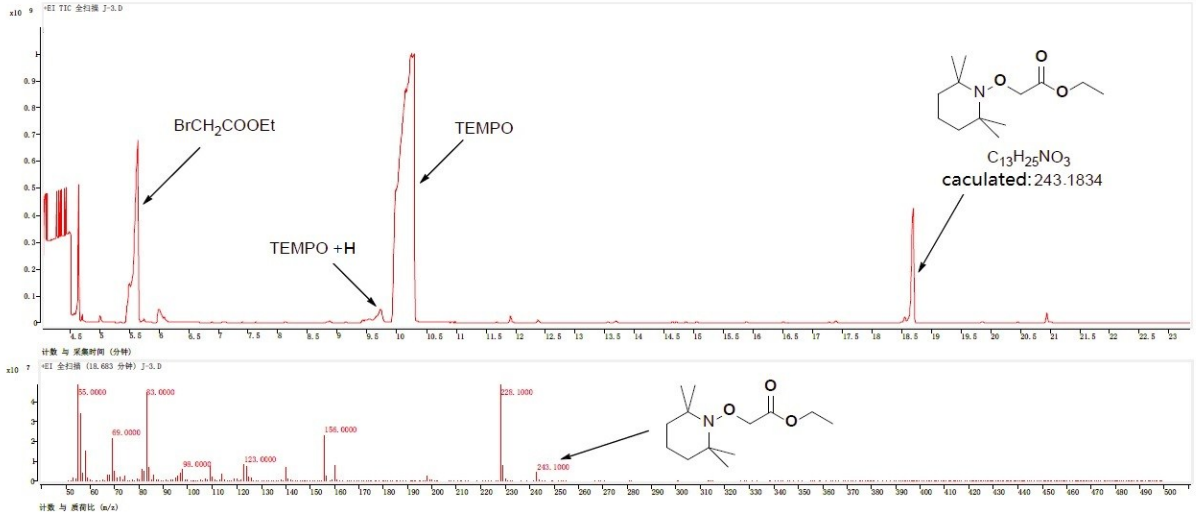
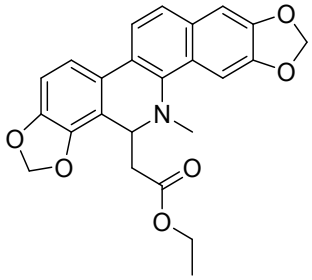
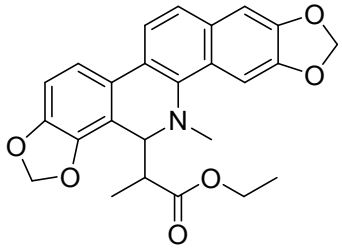


Figure 6s. GC-MS analysis of crude product from radical coupling experiment

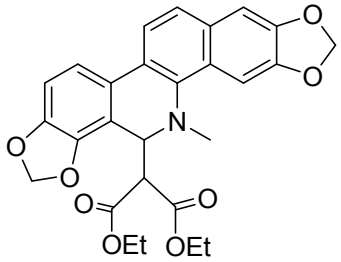
Characterization data of compounds 14



Ethyl 2'-(5,6-dihydrosanguinarine-6-yl)acetate(14a): Obtained as pale yellow amorphous powder, ^{1}H NMR (400MHz, $CDCl_3$): δ 7.68 （d, *J* = 8.4 Hz, 1H）, 7.56 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.09 (s, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.05-6.03 (m, 4H), 4.83 (t, *J* = 8.0 Hz, 1H), 4.16 (m, 2H), 2.66 (s, 3H), 2.39 (d, *J* = 8.0 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$): δ 171.5, 148.2, 147.7,, 147.2, 144.6, 139.4, 131.2, 127.8, 125.9, 124.1, 123.4, 120.1, 116.6, 115.8, 107.8, 104.4, 101.6, 101.1, 101.0, 60.5, 54.9, 43.2, 39.1, 14.4, HRMS (ESI$^+$): calcd 420.1441 for $C_{24}H_{22}NO_6^+$ $[M+H]^+$; found, 420.1450.

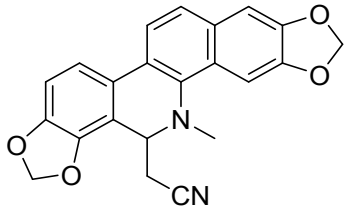


Ethyl 2'-(5,6-dihydrosanguinarine-6-yl) propanoate (14b): Obtained as white amorphous powder, ^{1}H NMR (400MHz, $CDCl_3$): δ 7.16-7.64, 7.48-7.45 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.10 (two s, 1H), 6.90-6.85 (two d, *J* = 8.0 Hz, 1H), 4.51 (d, *J* = 11.2 Hz, 0.5H), 4.46 (d, *J* = 9.2 Hz, 0.5H), 4.18-3.98 (m, 2H), 2.68, 2.62 (two s, 3H), 2.48-2.38 (m, 1H), 1.14-1.05 (m, 6H). ^{13}C NMR (100MHz, $CDCl_3$): δ 175.9, 174.7, 148.3, 148.0, 147.7, 147.6, 147.1, 147.0, 145.0, 139.9, 139.7, 131.2, 131.1, 127.6, 126.2, 124.0, 123.9, 123.5, 120.2, 120.0, 116.9, 116.8, 114.3, 107.9, 107.8, 104.6, 104.4, 101.4, 101.2, 100.8, 60.7, 60.4, 60.3, 60.0, 44.2, 43.7, 43.3, 42.9, 14.3, 14.2, 14.2, 14.1. HRMS (ESI$^+$): calcd 434.1598 for $C_{25}H_{24}NO_6^+$ $[M+H]^+$; found, 434.1597.

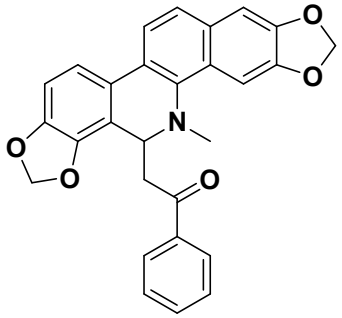


Ethyl 2'-(5,6-dihydrosanguinarine-6-yl) maonlate (14c):Obtained as white amorphous powder, ^{1}H NMR (400MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.42 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.10 (s, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.03-6.00 (m, 4H), 5.10 (d, *J* = 7.2 Hz, 1H), 4.24-4.12 (m, 2H), 4.04-4.00 (m, 2H), 3.41 (d, *J* = 7.2 Hz, 1H), 2.67 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$): δ 167.7, 166.9, 148.2, 147.7, 147.2, 145.5, 138.7, 131.2, 127.4, 126.2, 124.3, 123.6, 120.1, 117.0, 112.7, 108.3, 104.5, 101.6, 101.2, 100.8, 61.4, 61.4, 57.3, 55.5, 42.4, 14.1,

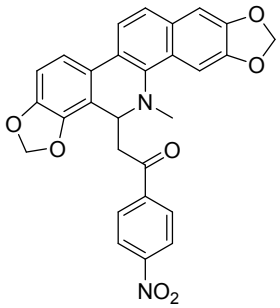
13.9. HRMS (ESI$^+$): calcd 492.1653 for $C_{27}H_{26}NO_8^+$ [M+H]$^+$; found, 492.1649.



6-Nitrilemethyl dihydrosanguinarine(14d): Obtained as pale yellow amorphous powder, ^{1}H NMR (400MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.11 (s, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.08-6.06 (m, 4H), 4.66 (t, *J* = 7.6 Hz, 1H), 2.72 (s, 3H), 2.44 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 148.7, 148.1, 147.5, 145.0, 138.1, 131.4, 127.7, 125.4, 124.7, 122.9, 119.9, 117.8, 116.9, 113.8, 108.6, 104.4, 101.9, 101.3, 101.0, 54.6, 43.2, 22.6. HRMS (ESI$^+$): calcd 373.1183 for $C_{22}H_{17}N_2O_4^+$ [M+H]$^+$; found, 373,1191.

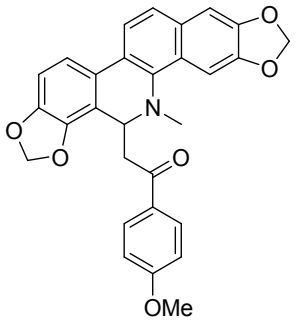


1'-phenyl-2'-(5,6-dihydrosanguinarine-6-yl)ethanone(14e): Obtained as pale yellow amorphous powder, ^{1}H NMR (400MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 8.0Hz, 1H), 7.26-7.20 (m, 3H), 7.06 (s, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.02 (dd, *J* = 1.2, 9.6 Hz, 2H), 5.97 (dd, *J* = 1.2, 8.8 Hz, 2H), 5.04 (dd, *J* = 4.8, 10.0 Hz, 1H), 3.27 (dd, *J* = 10.0, 14.8 Hz, 1H), 2.80-2.76 (m, 1H), 2.63 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$): δ 198.8, 148.0, 147.7, 147.3, 144.5, 137.4, 132.7, 131.1, 128.5, 128.4 (×4), 127.7, 126.0, 124.1, 123.5, 120.1, 116.6, 116.5, 107.7, 104.2, 101.7, 101.1, 101.0, 55.2, 43.2, 42.1. HRMS (ESI$^+$): calcd 452.1492 for $C_{28}H_{22}NO_5^+$ [M+H]$^+$; found,452.1493.

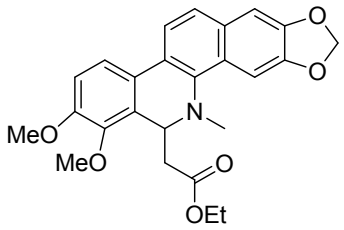


1'-(4-Nitrophenyl)-2'-(5,6-dihydrosanguinarine-6-yl)ethanone(1f): Obtained as light red amorphous powder, ^{1}H NMR (400MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.4Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.03 (s, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.07 (dd, *J* = 1.2, 4.8 Hz, 2H), 5.90 (dd, *J* = 1.2, 16 Hz, 2H), 4.97 (dd, *J* = 4.4, 10.4 Hz, 1H), 3.35 (dd, *J* =12.8, 10.4 Hz, 1H), 2.72 (dd, *J* = 4.4, 12.8 Hz, 1H), 2.56 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$): δ 198.2, 150.0, 147.8, 147.6, 147.4, 144.5, 141.7, 138.8, 131.0, 129.2(×2), 127.4, 125.8, 124.4, 123.6, 123.5(×2), 120.1, 116.8, 115.7, 108.1, 104.3, 101.8, 101.3, 100.4, 56.6, 43.2, 41.7. HRMS (ESI$^+$): calcd 497.1343 for

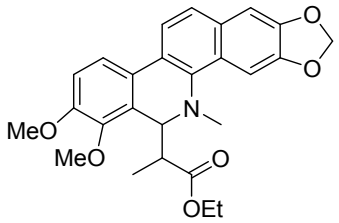
$C_{28}H_{21}N_2O_7^+$ [M+H]$^+$; found, 497.1339.



1'-(4-methoxyphenyl)-2'-(5,6-dihydrosanguinarine-6-yl)ethanone(14g): Obtained as pale yellow amorphous powder, ^{1}H NMR (400MHz, $CDCl_3$): δ 7.75(d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.13 (s, 1H), 7.07 (s, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.06-5.95 (m, 4H), 5.03 (dd, *J* = 10.4, 4.8 Hz, 1H), 3.79 (s, 3H), 3.27 (dd, *J* = 14.4, 10.4 Hz, 1H), 2.67(dd, *J* = 14.4, 4.4 Hz, 1H), 2.63 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$): δ 197.5, 163.3, 147.9, 147.5, 147.3, 144.5, 139.6, 131.0, 130.7, 130.6 (×2), 127.8, 126.0, 124.0, 123.6, 120.1, 116.7, 116.5, 113.4 (×2), 107.7, 104.0, 101.7, 101.2, 101.1, 55.7, 55.4, 43.1, 41.4. HRMS (ESI$^+$): calcd 482.1598 for $C_{29}H_{24}NO_6^+$ [M+H]$^+$; found, 482.1599.

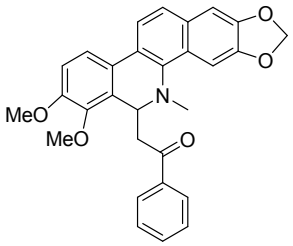


Ethyl 2'-(5,6-dihydrocheletrythrine-6-yl)acetate(14h): Obtained as pale yellow amorphous powder, ^{1}H NMR (400MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.8 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.54 (s, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.10 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 6.03 (s, 2H), 5.00 (dd, *J* = 4.4, 14.4 Hz, 1H), 3.97 (s, 3H), 3.93 (s, 3H), 3.72 (t, *J* = 7.2 Hz, 2H), 2.65 (s, 3H), 2.33 (m, 2H), 1.82 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$): δ 171.8, 152.2, 148.1, 147.6, 145.9, 139.5, 131.2, 128.1, 127.7, 125.1, 123.9, 123.2, 119.9, 118.9, 111.8, 104.4, 101.1, 101.1 (overlapped), 61.2, 60.4, 56.0, 55.2, 43.0, 39.3, 14.4. HRMS (ESI$^+$): calcd 436.1755 for $C_{25}H_{26}NO_6^+$ [M+H]$^+$; found, 436.1750.



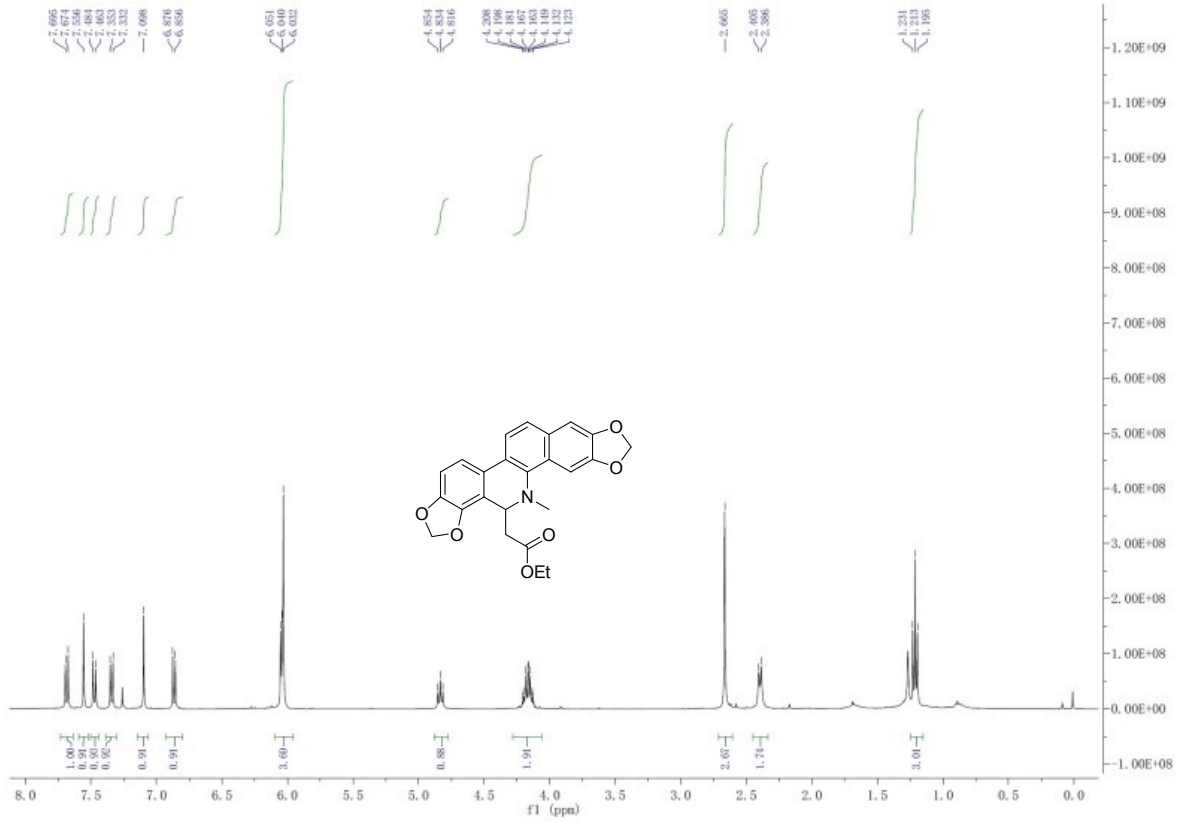
Ethyl 2'-(5,6-dihydrochelerythrine-6-yl) propanoate (14i): Obtained as white amorphous powder, ^{1}H NMR (400MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.62 (s, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.49 (s, 1H), 7.46 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.10 (s, 2H), 6.97 (d, *J* = 8.8 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.04 (s, 2H), 6.02 (s, 2H), 4.71-4.68 (m, 2H), 4.15-4.03 (m, 4H), 3.94 (s, 3H), 3.94 (s, 3H), 3.91 (s, 3H), 3.91 (s, 3H), 2.68 (s, 3H), 2.61 (s, 3H), 2.53-2.49 (m, 1H), 2.36-2.32 (m, 1H), 1.40 (t, *J* = 7.2 Hz, 3H),

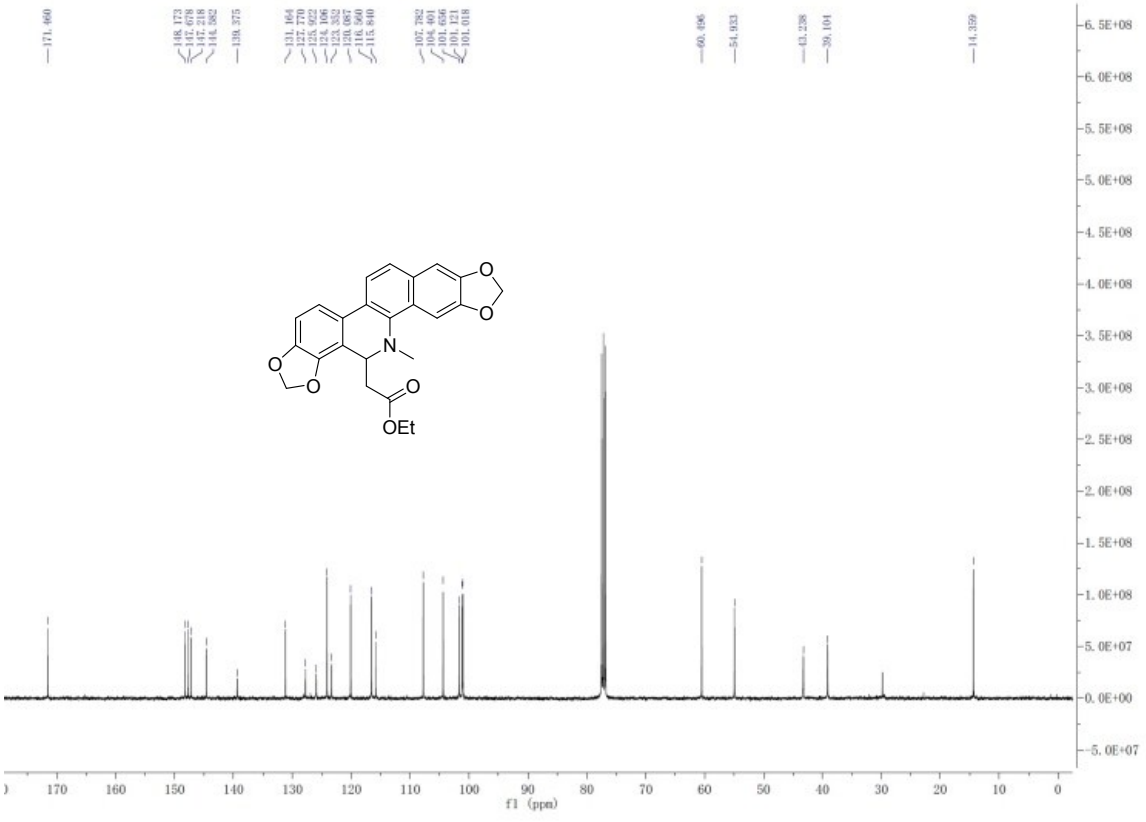
1.07 (t, *J* = 7.2 Hz, 3H), 1.00 (d, *J* = 7.2 Hz, 3H), 0.94 (d, *J* = 7.2 Hz, 3H). ^{3}C NMR (100MHz, $CDCl_3$): δ 176.4, 174.7, 152.1, 152.1, 148.2, 147.9, 147.6, 147.5, 147.2, 146.5, 140.2, 140.0, 131.2, 131.1, 127.4, 127.1, 126.9, 125.9, 125.5, 125.2, 124.1, 123.8, 123.7, 123.4, 119.9, 119.8, 119.2, 118.8, 111.7, 111.7, 104.5, 104.4, 101.1, 101.0, 100.9, 61.0, 61.0, 60.4, 60.4, 60.2, 60.0, 55.9, 55.9, 44.8, 43.5, 43.5, 42.4, 14.4, 14.2, 14.2, 13.2. HRMS (ESI$^+$): calcd 450.1911 for $C_{26}H_{28}NO_6^+$ [M+H]$^+$; found, 450.1912.

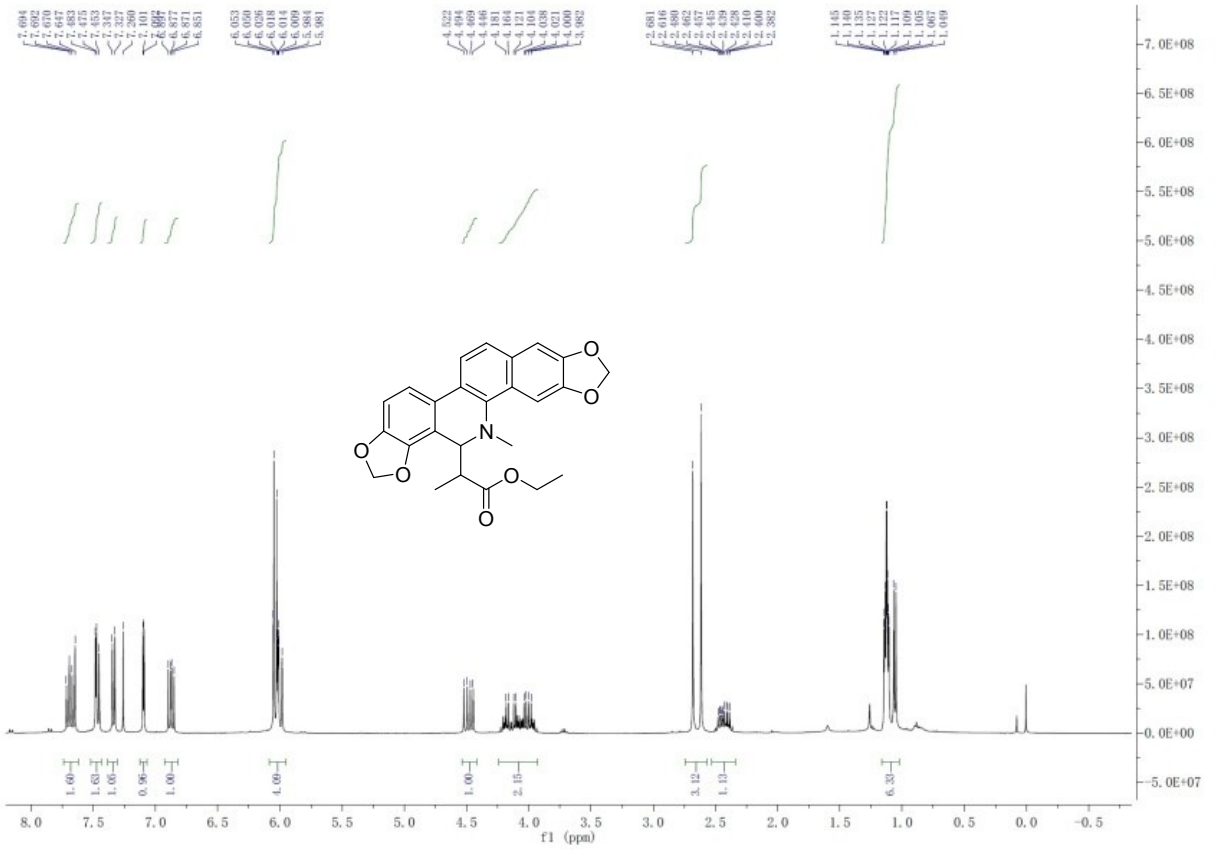


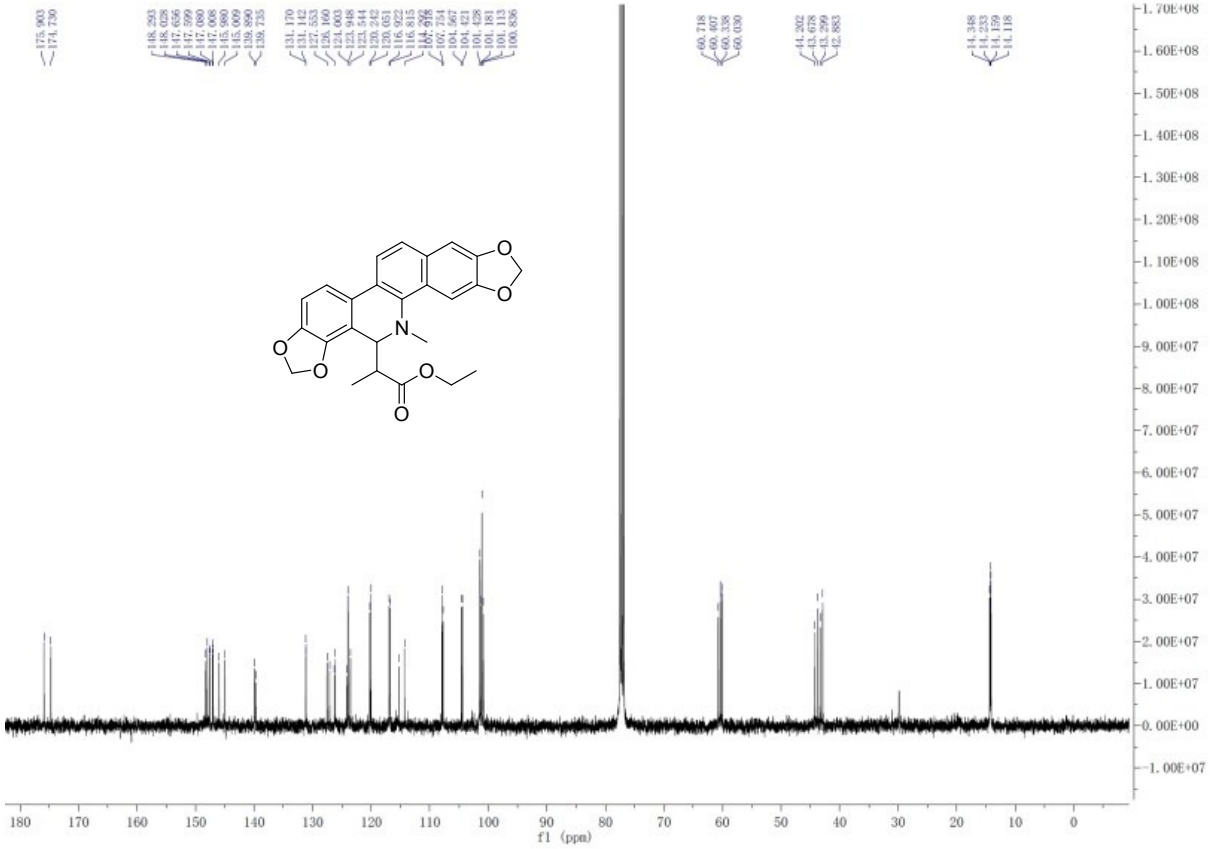
2-(chelerythrine-6-yl)-1-phenylethanone(14j): Obtained as pale yellow amorphous powder, ^{1}H NMR (400MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.8 Hz, 3H), 7.57(d, *J* = 8.8 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.27-7.25 (m, 2H), 7.21 (s, 1H), 7.05 (s, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 5.96 (dd, *J* = 1.2, 9.2 Hz, 2H), 5.20 (dd, *J* = 3.6, 10.8 Hz, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 3.15 (dd, *J* = 11.2, 10.8 Hz, 1H), 2.76 (dd, *J* = 3.6, 10.8 Hz, 1H), 2.59 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$): δ 199.0, 152.3, 147.9, 147.6, 145.7, 139.6, 137.4, 132.6, 131.1, 128.7, 128.4(×2), 128.3(×2), 127.6, 125.2, 123.9, 123.3, 119.8, 118.9, 111.7, 104.2, 101.2, 101.0, 61.1, 56.0, 55.8, 43.0, 42.2. HRMS (ESI$^+$): calcd 468.1805 for $C_{29}H_{26}NO_5^+$ [M+H]$^+$; found,468.1820.

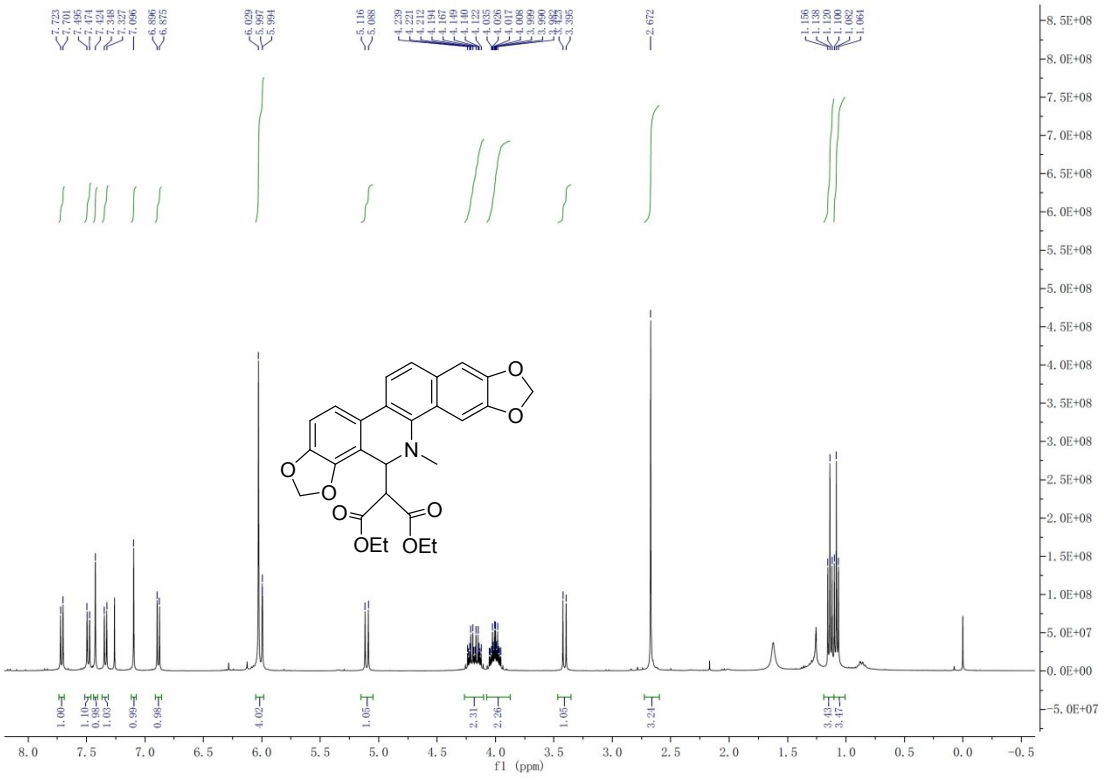
[1]H NMR and [13]C NMR spectra of compounds 14

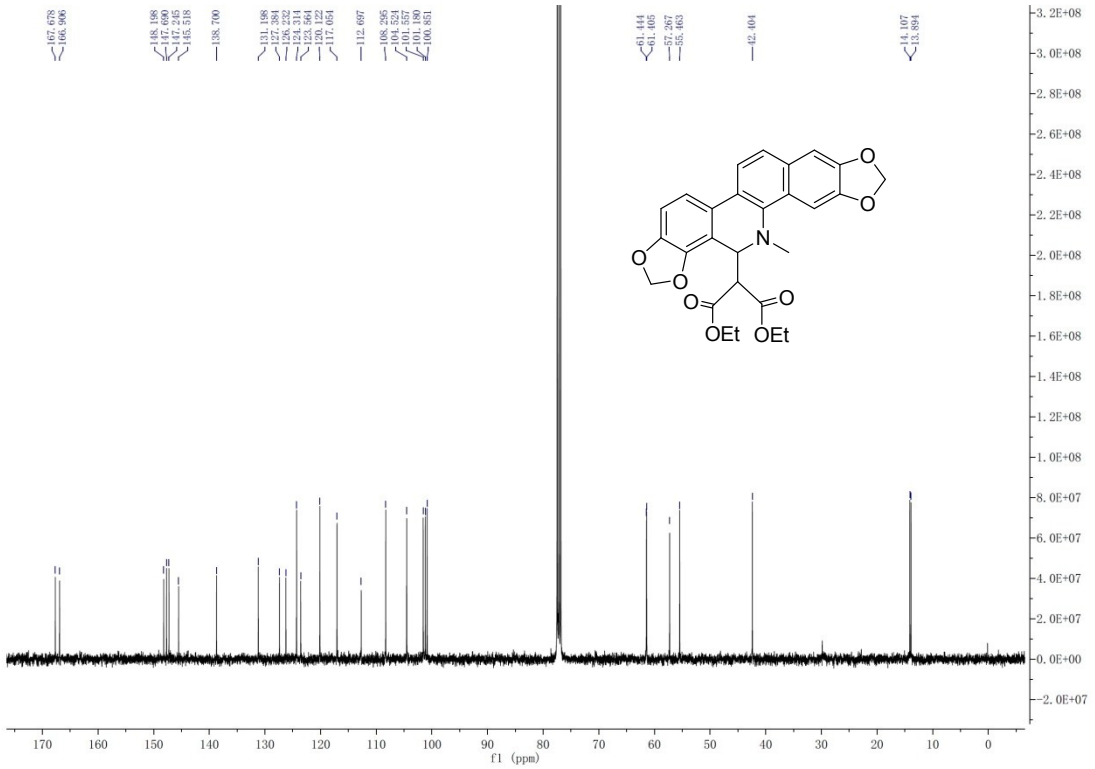





f1 (ppm)



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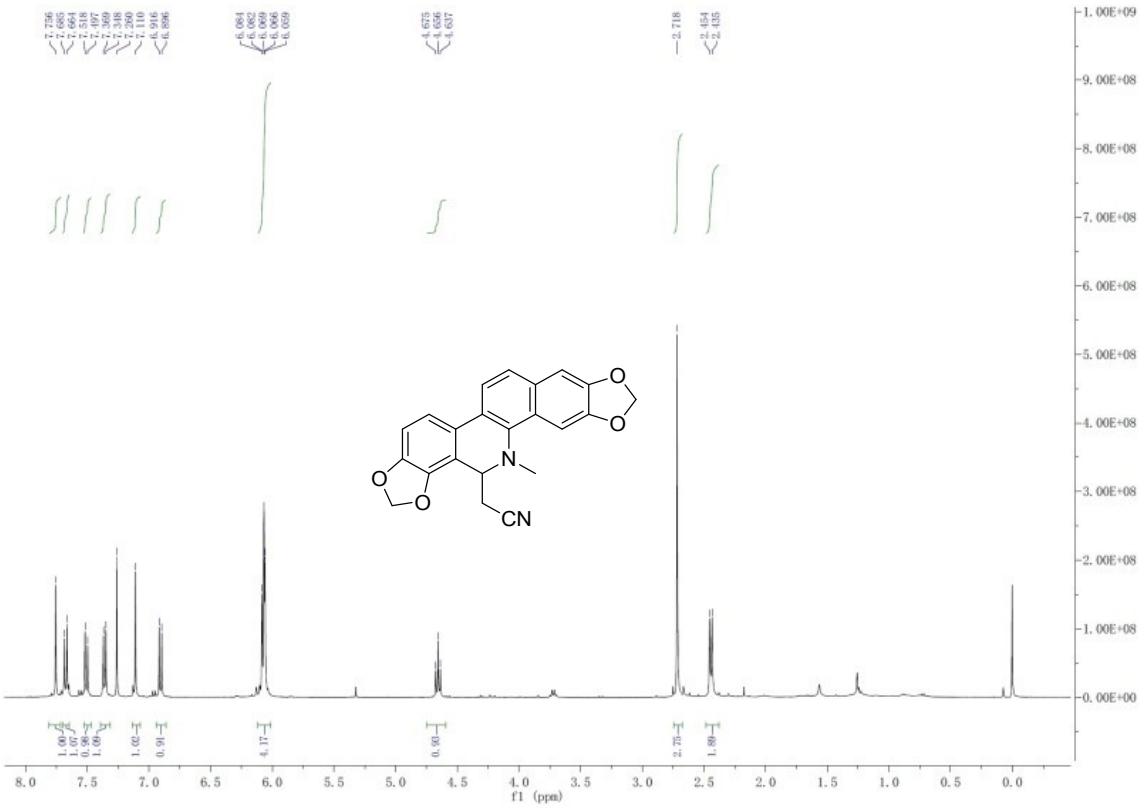
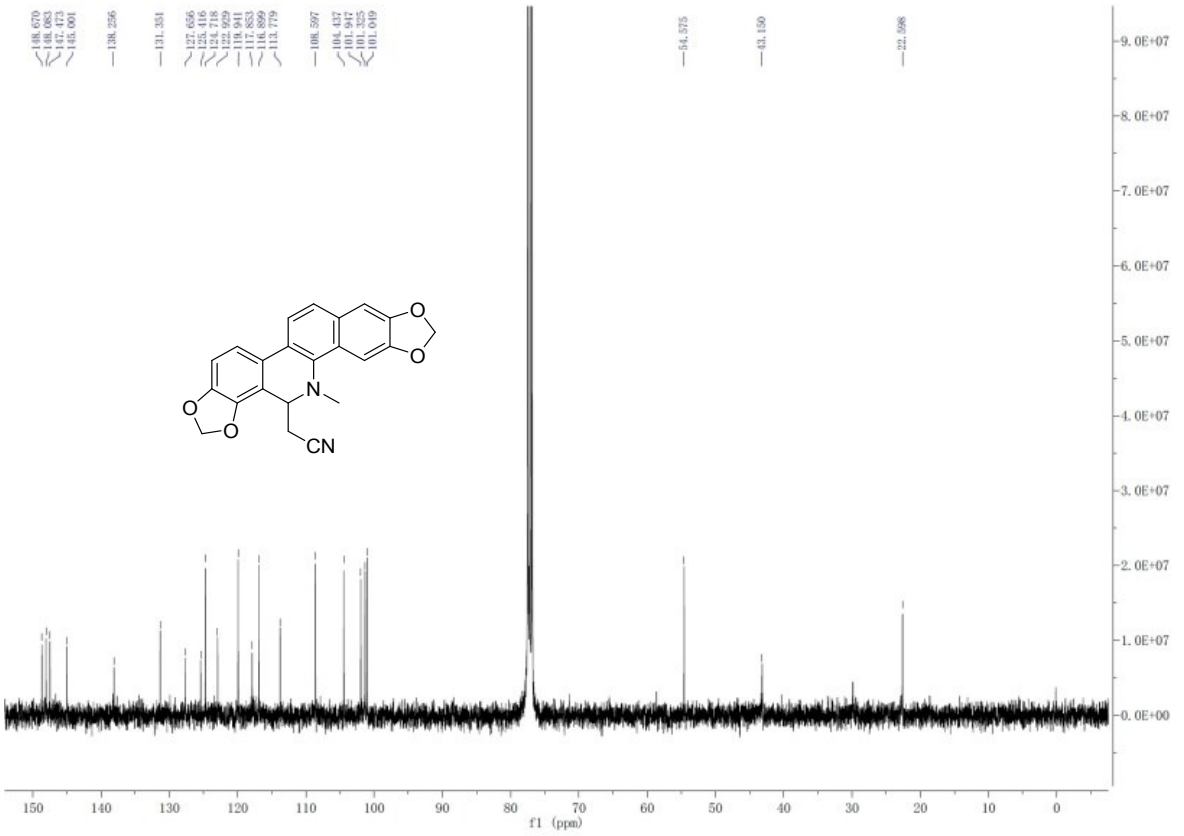
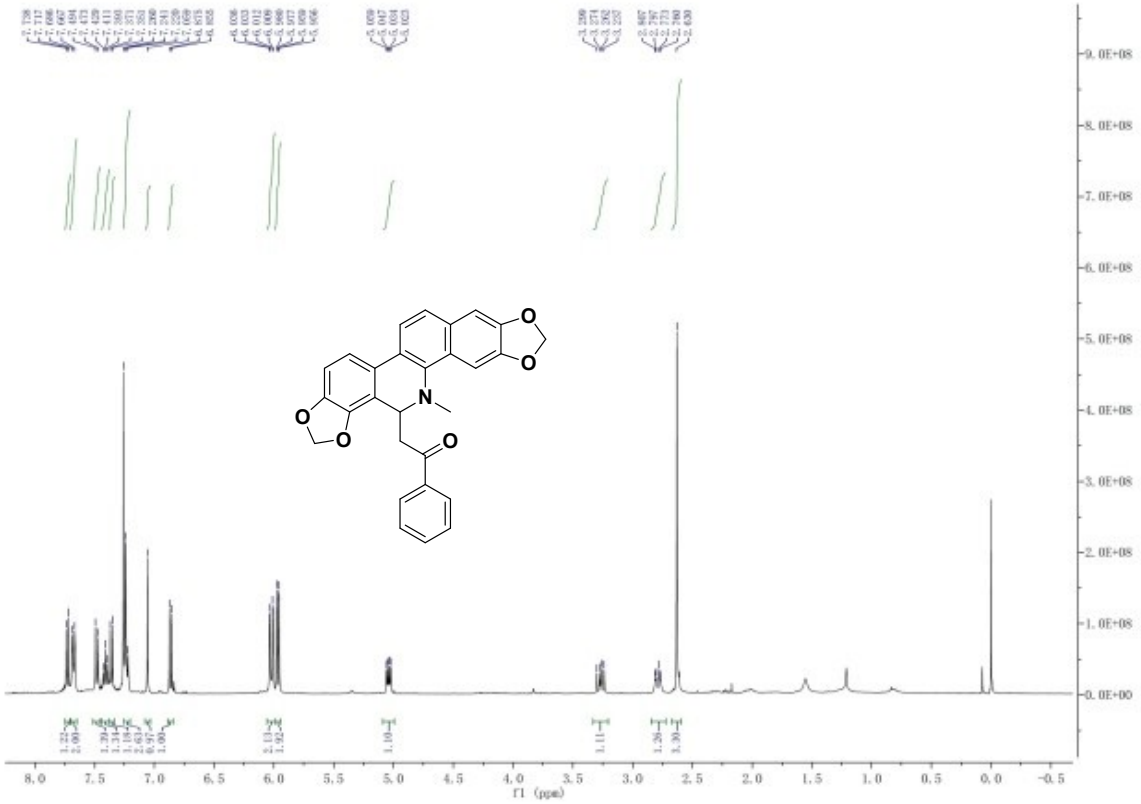
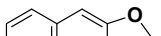
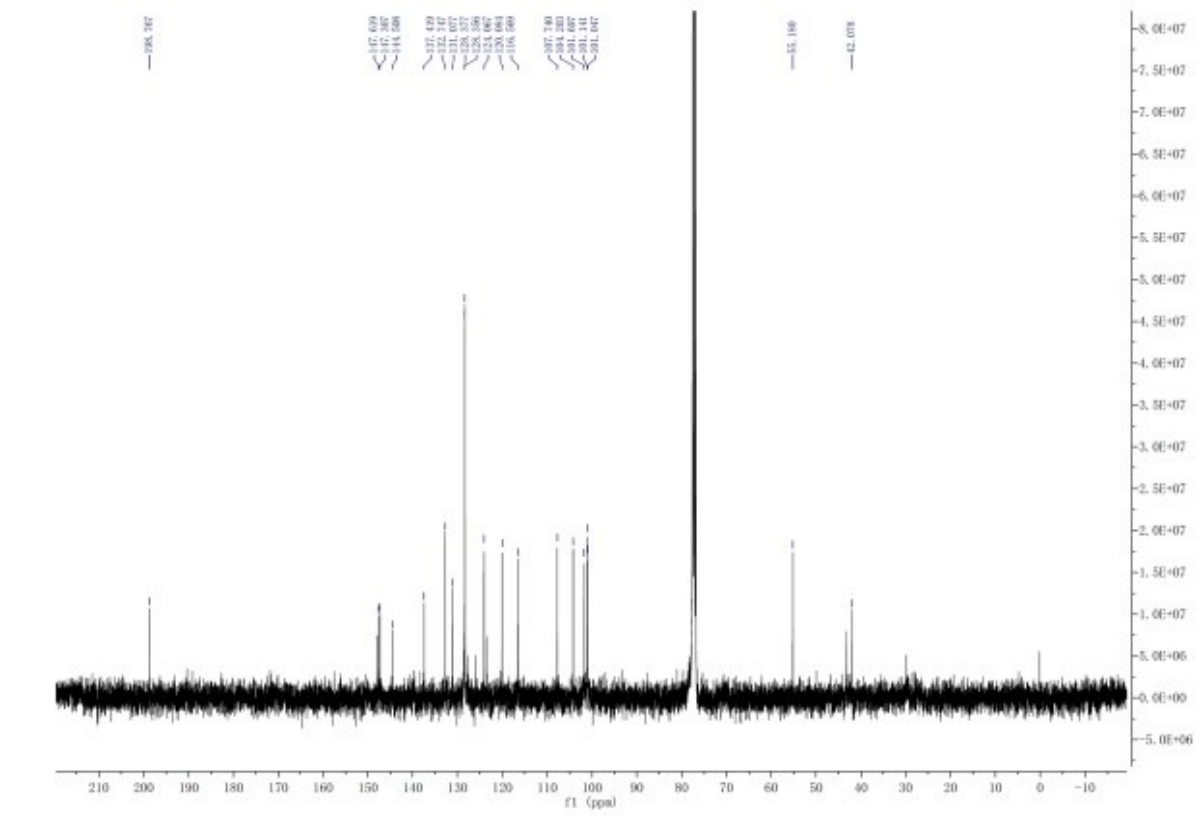
166.906
148.198
147.690
147.245
145.518
138.700
131.188
127.394
126.232
124.314
123.564
120.122
117.664
112.667
108.295
104.524
101.557
101.180
100.851
61.444
61.165
57.267
55.463
42.404
14.107
13.894
O
O
O
O
N
O
O
OEt
OEt
f1 (ppm)

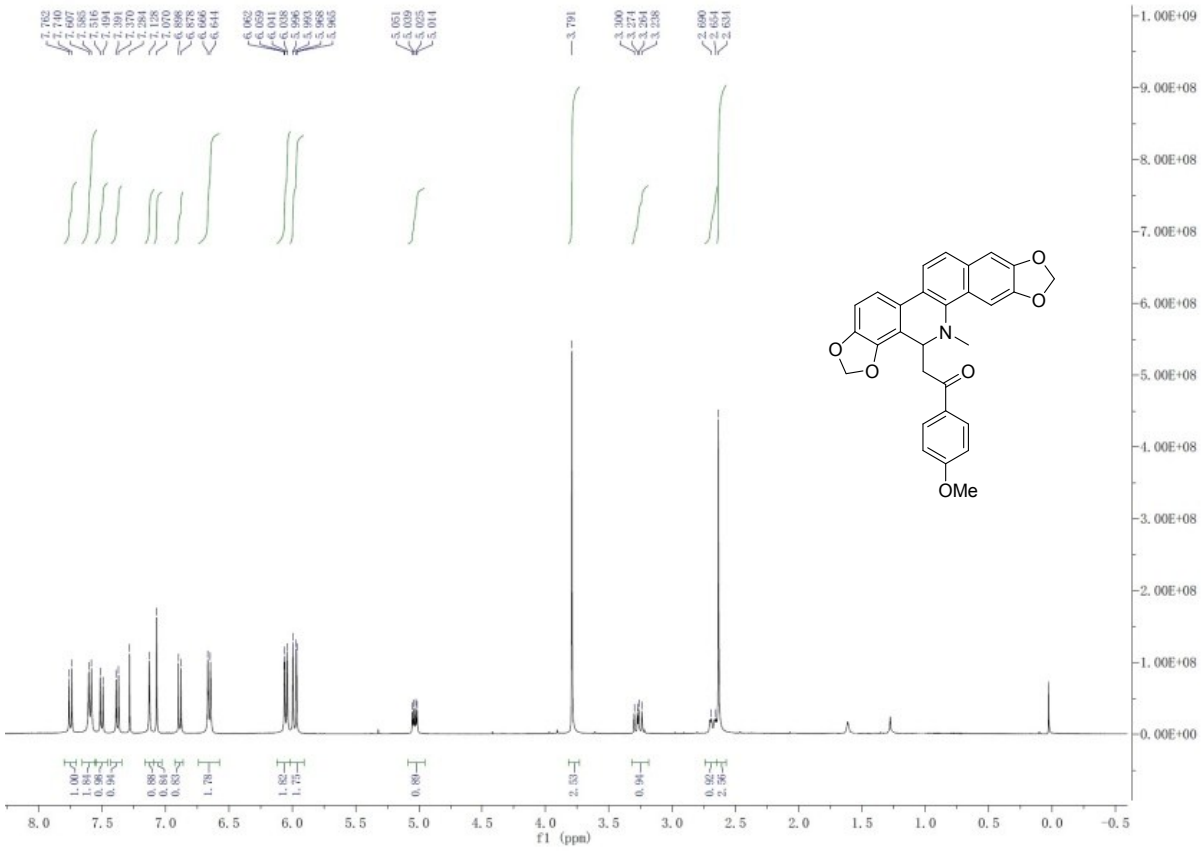

7.736
7.685
7.664
7.518
7.497
7.369
7.348
7.290
7.110
6.916
6.896
6.084
6.069
6.066
6.059
4.675
4.656
4.637
2.718
2.454
2.435
1.00
1.07
0.98
1.08
1.02
0.91
4.17
0.93
2.75
1.89
O
O
O
O
N
CN
f1 (ppm)

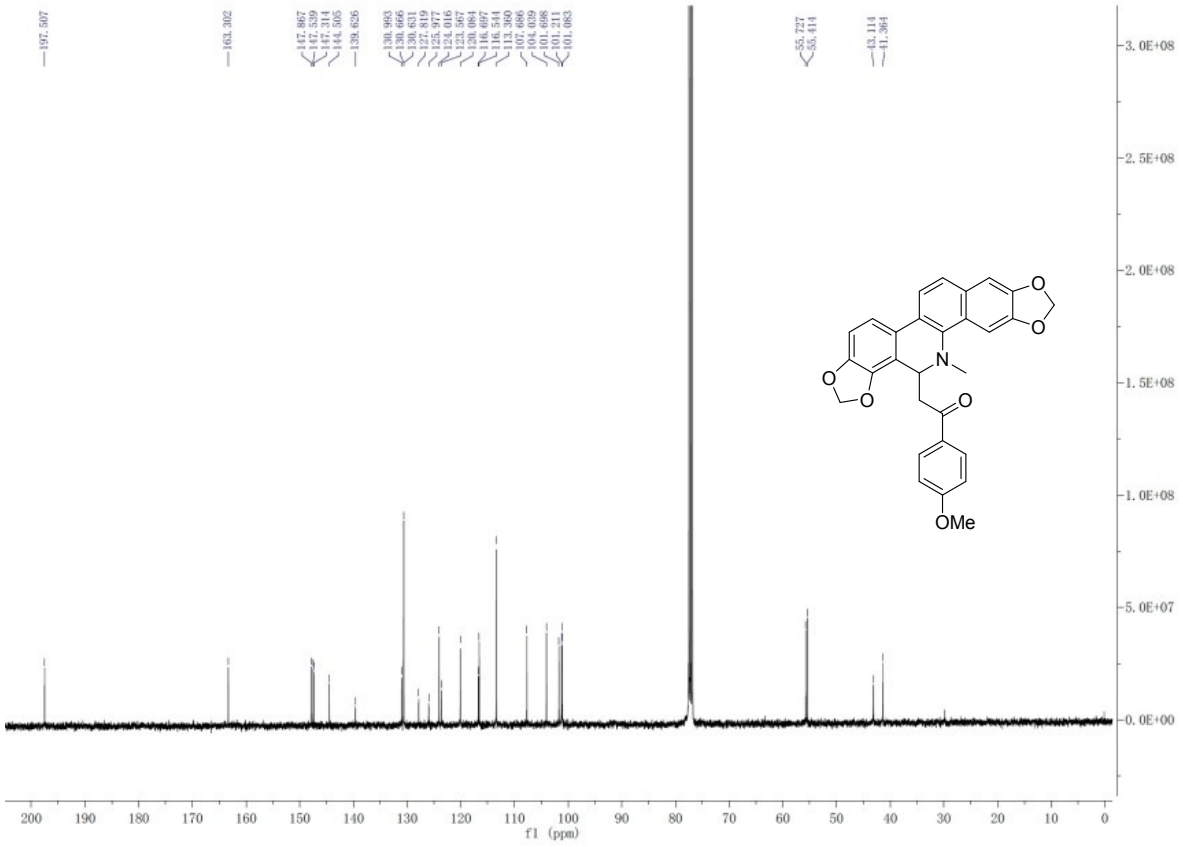

148.670
148.083
147.473
145.001
138.256
131.351
127.656
125.416
124.718
122.959
118.941
117.853
116.899
113.779
108.597
104.437
101.947
101.325
101.049
54.575
43.130
22.598
O
O
O
O
N
CN
9.0E+07
8.0E+07
7.0E+07
6.0E+07
5.0E+07
4.0E+07
3.0E+07
2.0E+07
1.0E+07
0.0E+00
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
O
O
N
O
9.0E+08
8.0E+08
7.0E+08
6.0E+08
5.0E+08
4.0E+08
3.0E+08
2.0E+08
1.0E+08
0.0E+00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


O




OMe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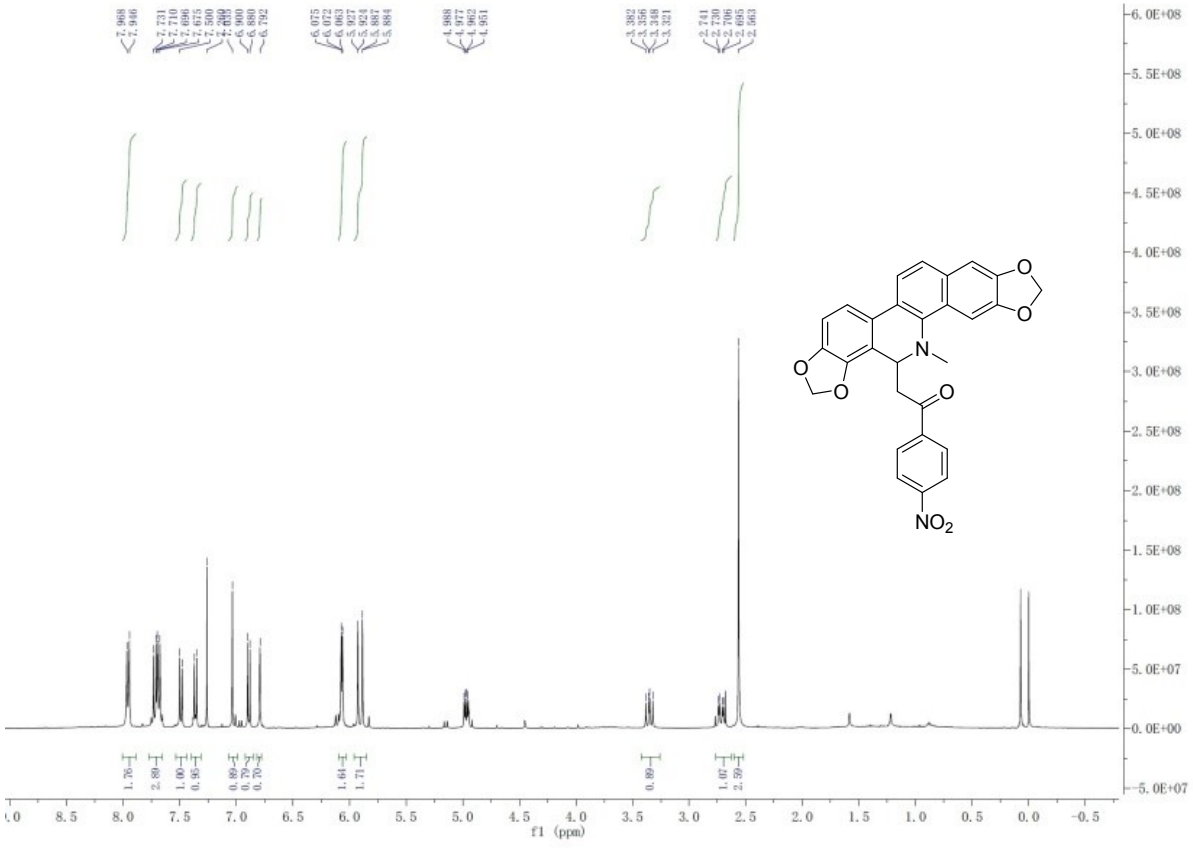
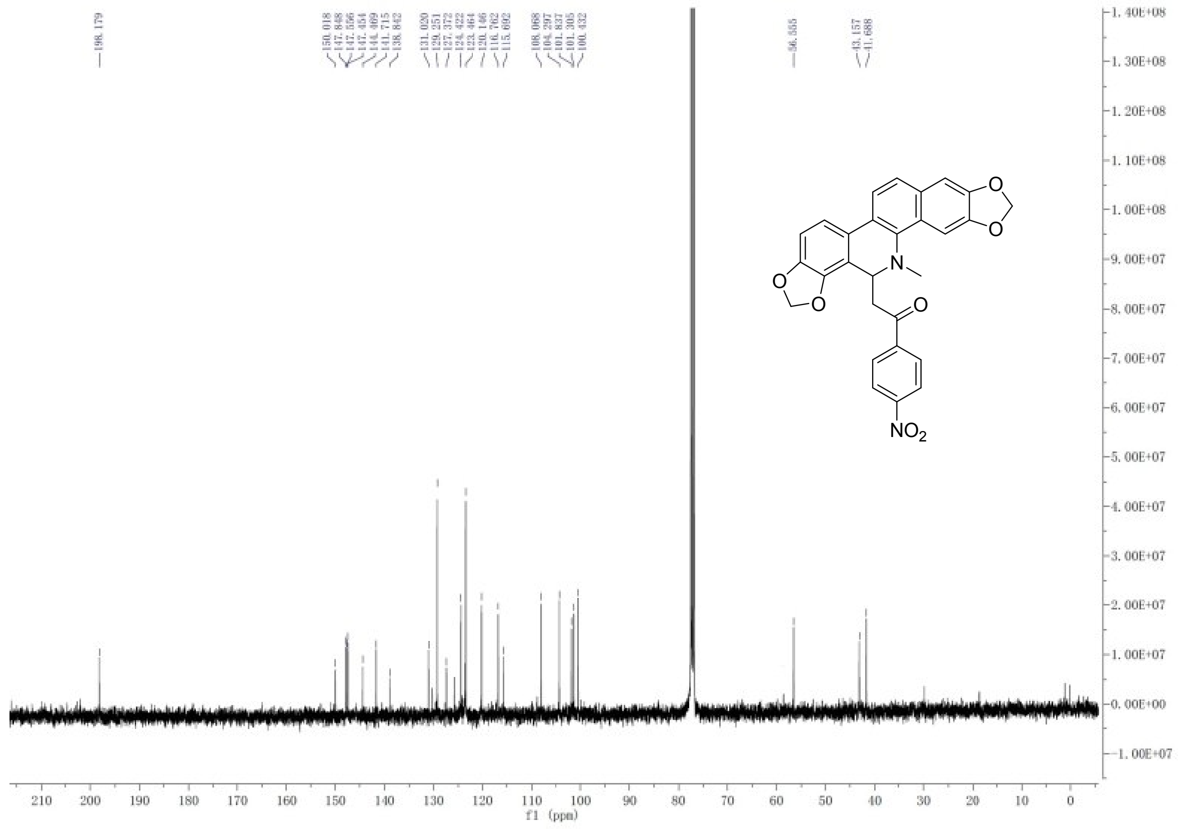
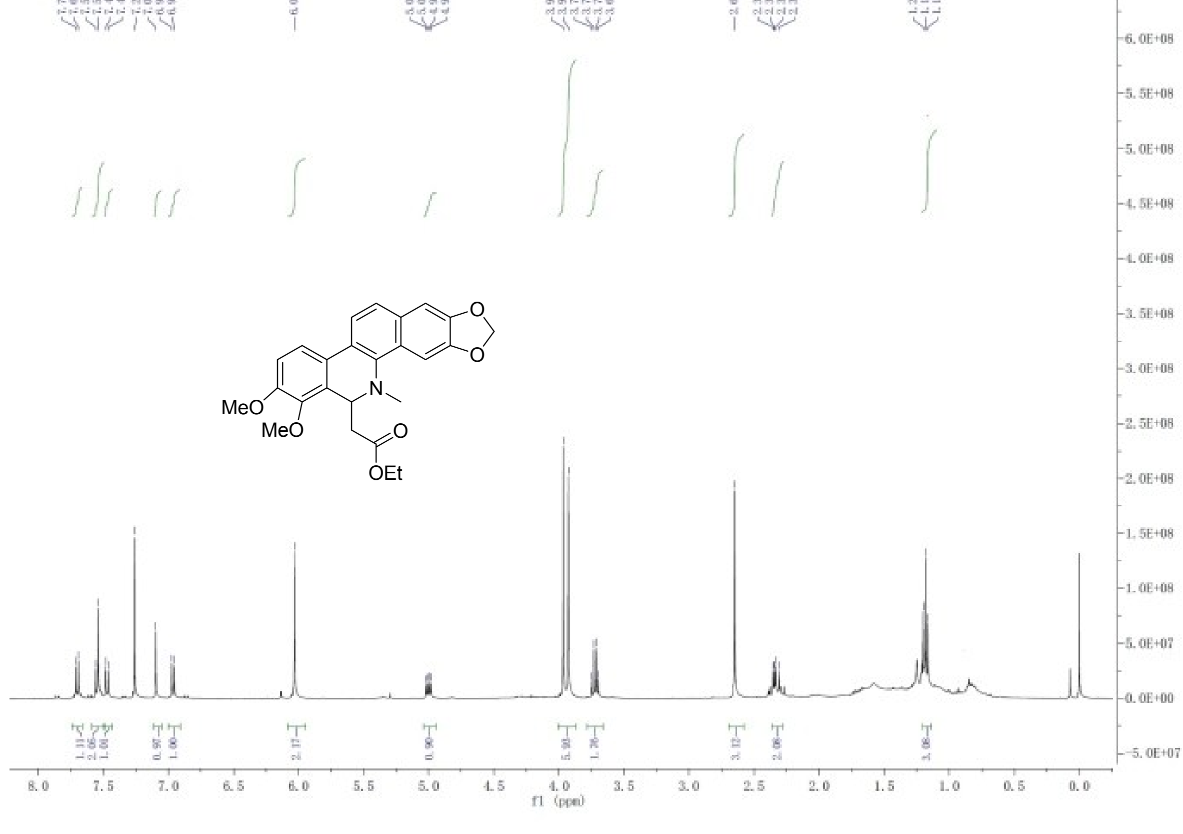
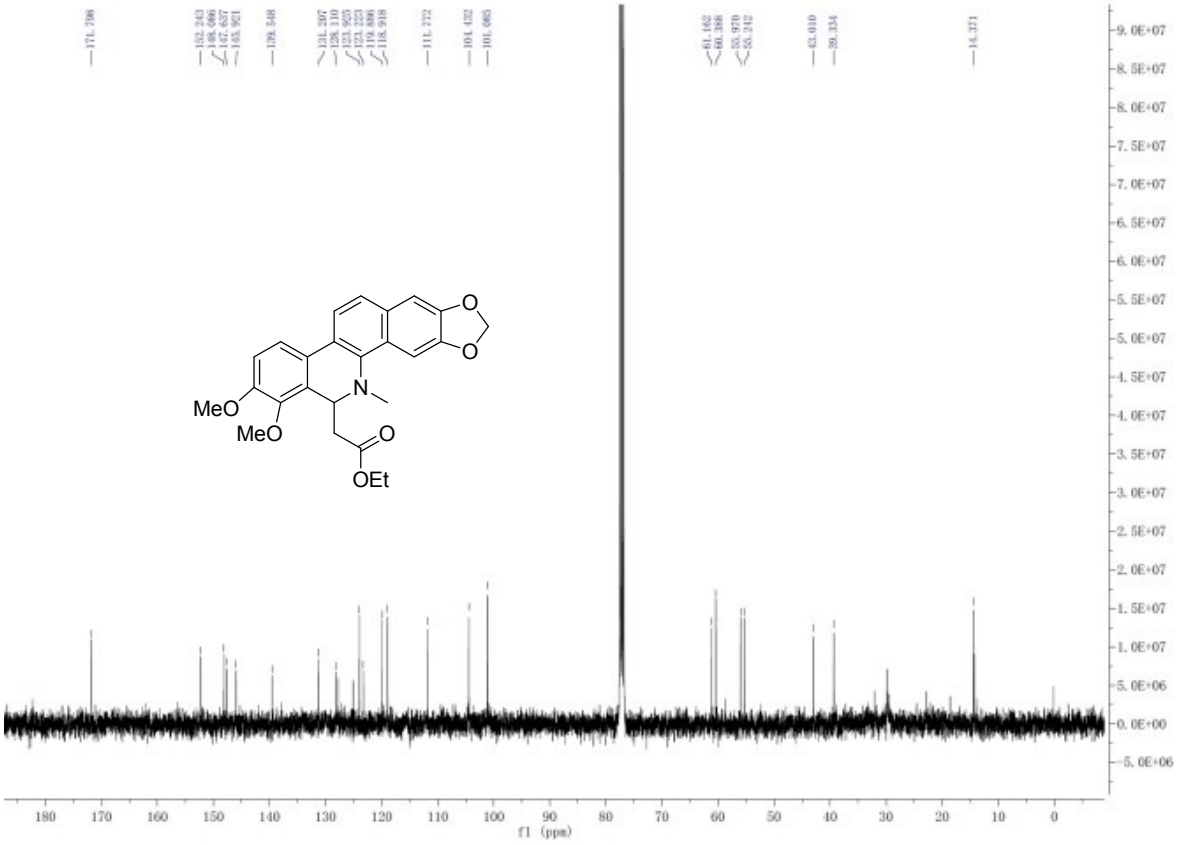
163.302
147.867
147.539
147.314
144.505
139.626
130.993
130.666
130.631
127.819
125.577
124.016
123.567
120.084
116.697
116.544
113.360
107.666
104.039
101.698
101.211
101.083
55.727
55.414
43.114
41.364
OMe
f1 (ppm)


7.968
7.946
7.731
7.710
7.696
7.675
7.500
6.900
6.880
6.792
6.075
6.072
6.053
5.907
5.924
5.887
5.884
4.988
4.977
4.962
4.951
3.382
3.356
3.348
3.321
2.741
2.730
2.706
2.695
2.563
1.76
2.89
1.00
0.95
0.89
0.79
0.70
1.64
1.71
0.89
1.07
2.59
NO2
f1 (ppm)



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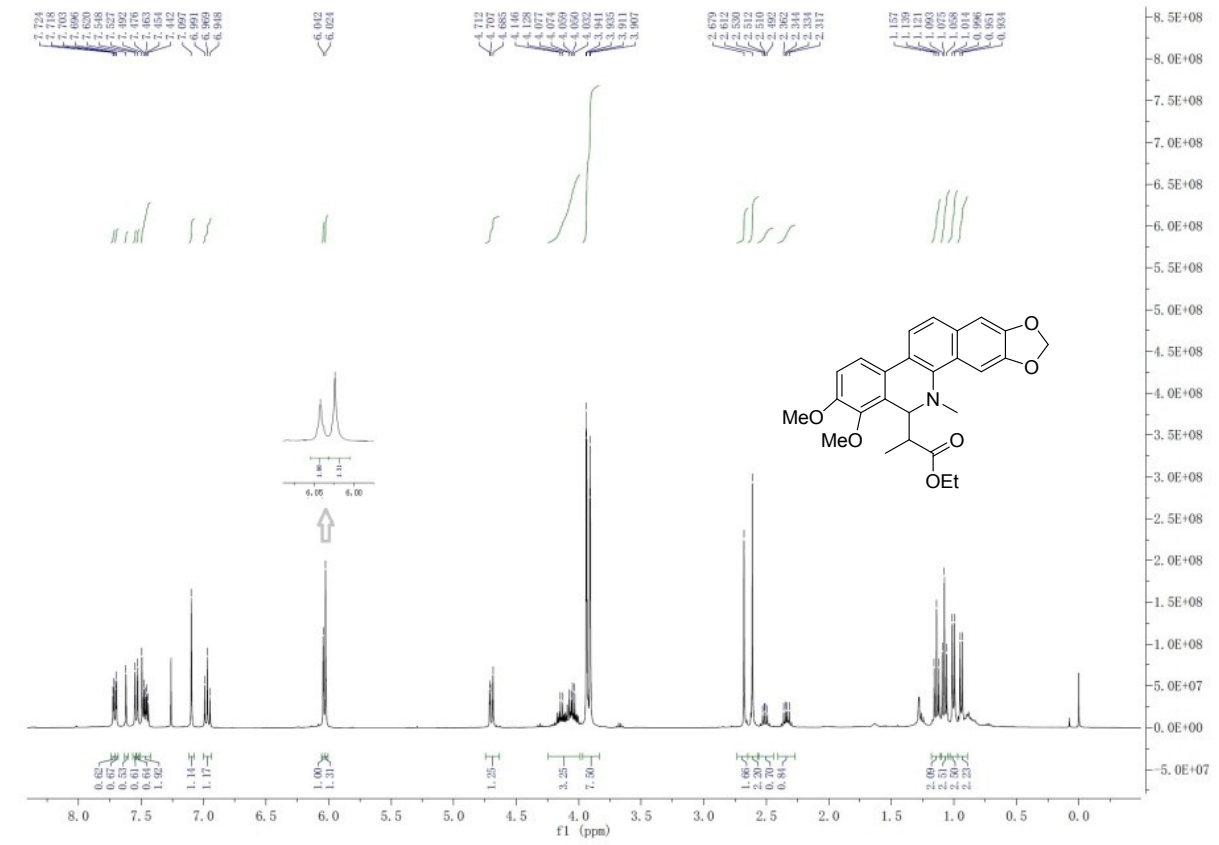
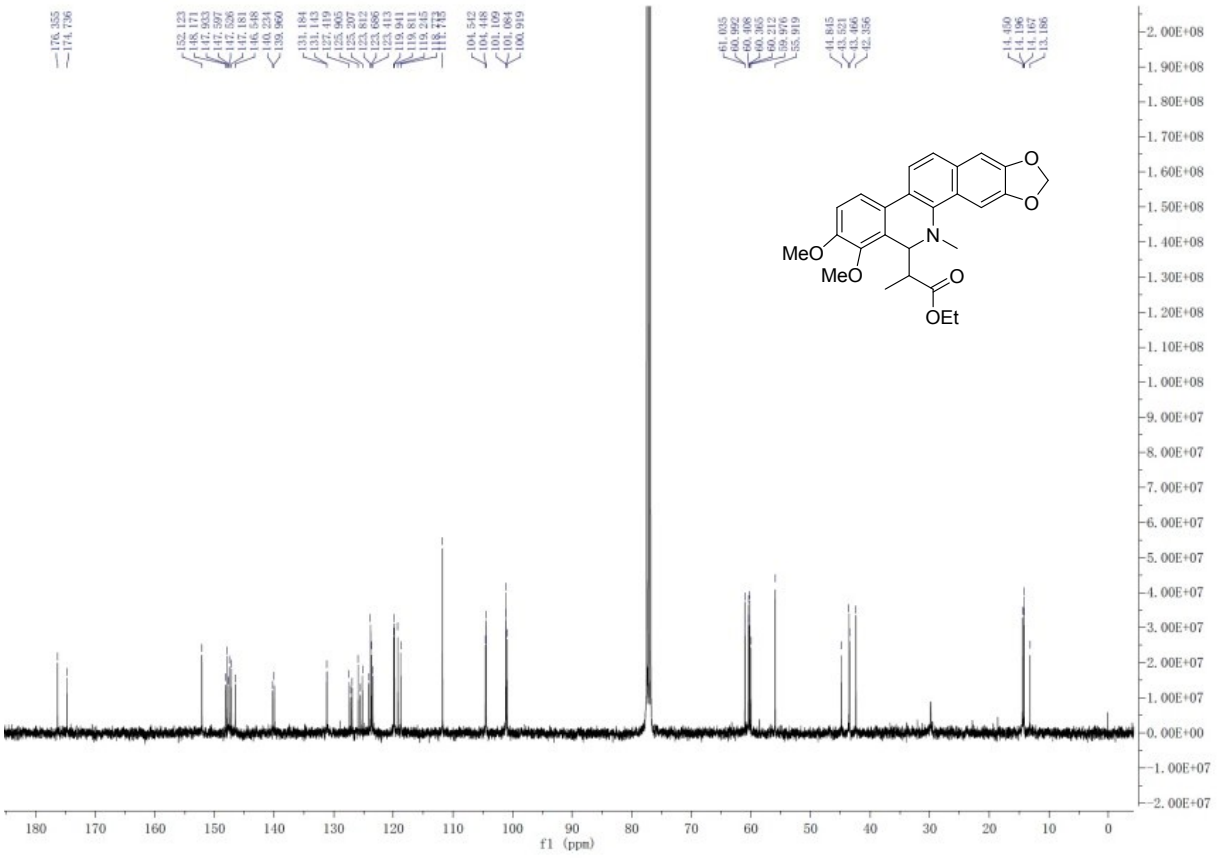
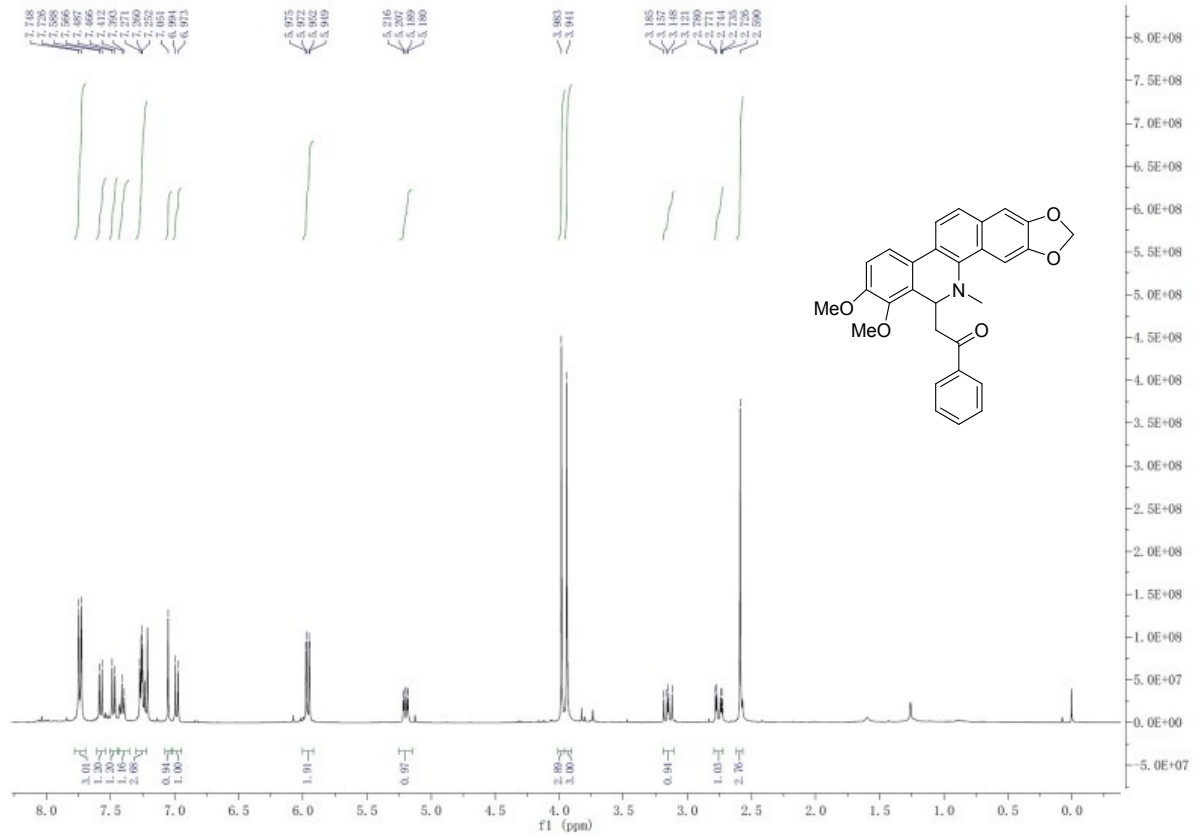
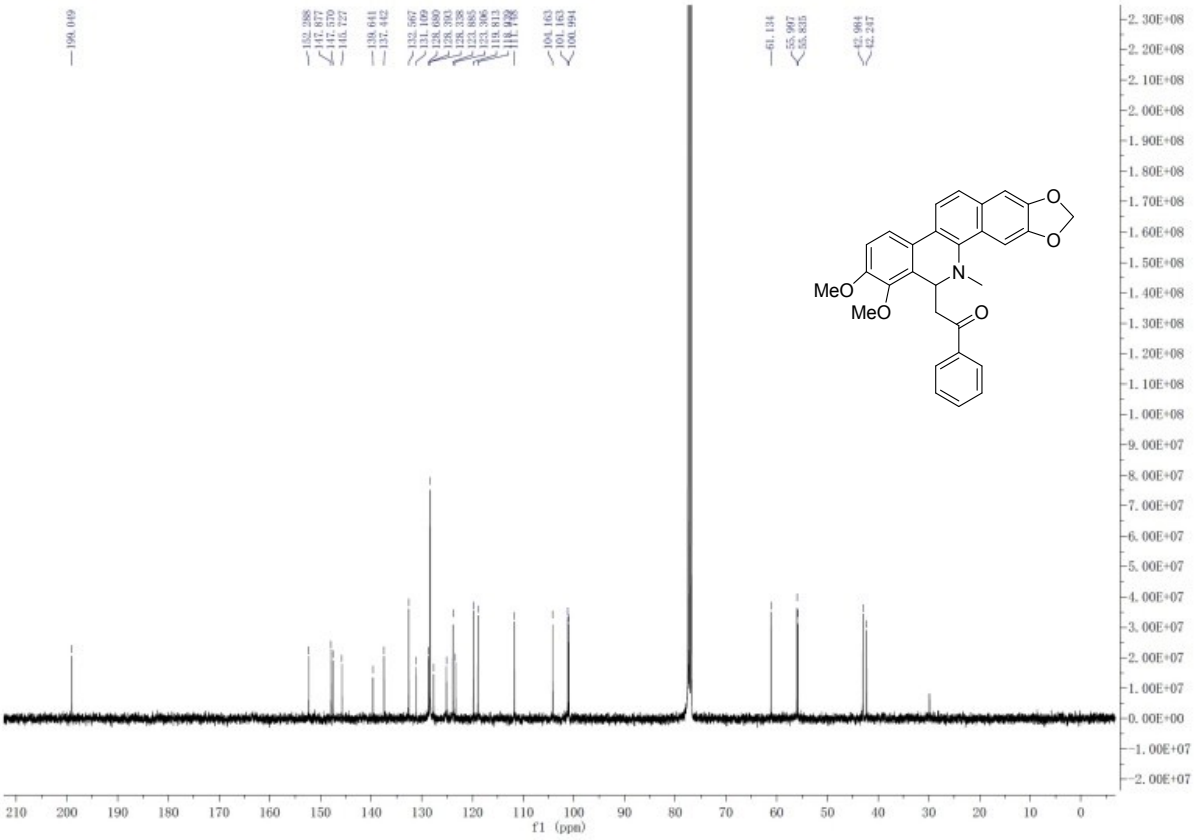
152.243
148.696
147.697
145.921
139.548
131.397
128.110
123.925
121.223
119.896
118.918
111.772
104.432
101.085
61.162
60.388
55.970
55.242
43.010
39.334
14.371
MeO
MeO
N
O
O
O
OEt
9.0E+07
8.5E+07
8.0E+07
7.5E+07
7.0E+07
6.5E+07
6.0E+07
5.5E+07
5.0E+07
4.5E+07
4.0E+07
3.5E+07
3.0E+07
2.5E+07
2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
-5.0E+06
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

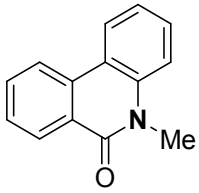

MeO
MeO
O
O
N
O
OEt
f1 (ppm)


MeO
MeO
O
O
N
O
OEt
f1 (ppm)

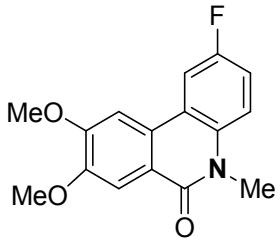

MeO
MeO
N
O
O
O
f1 (ppm)


MeO
MeO
N
O
O
O
f1 (ppm)

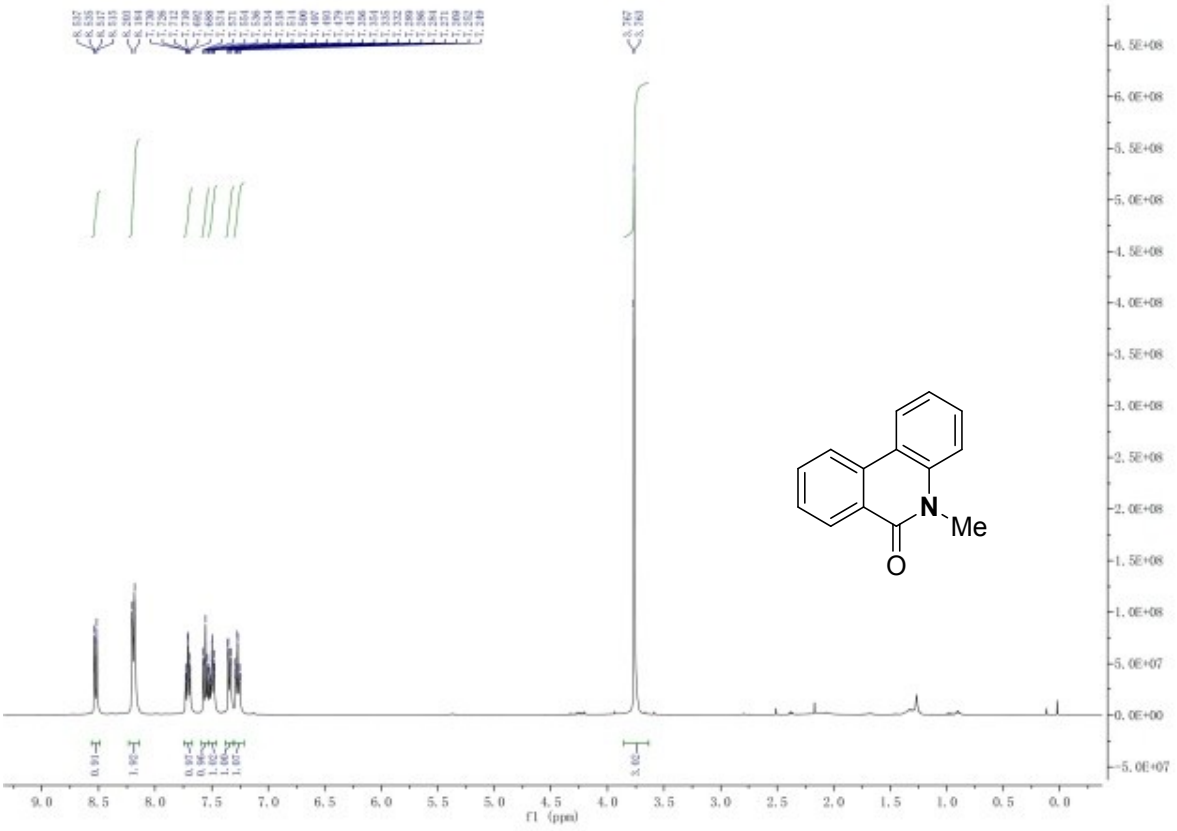
NMR data and spectra of compounds19

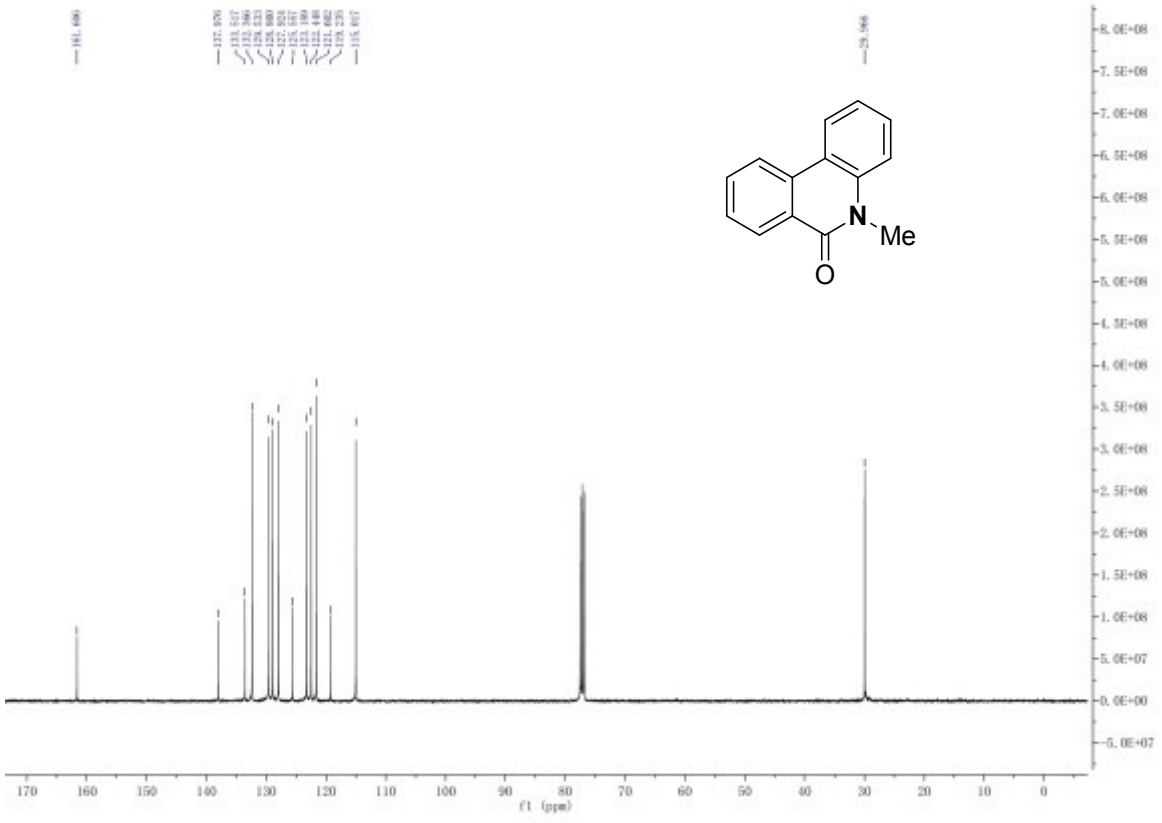


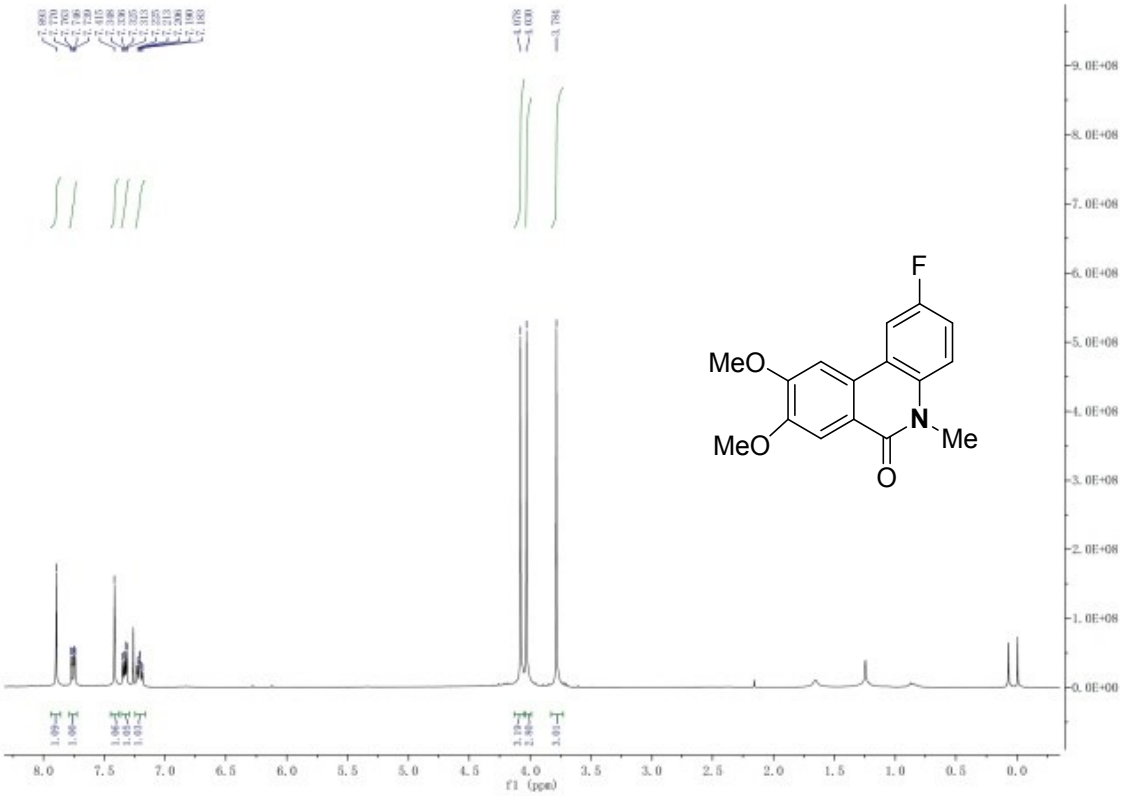
5-methylphenanthridin-6(5H)-one (19a): Obtained as white amorphous powder, ^{1}H NMR (400MHz, $CDCl_3$): δ 8.53 (dd, J = 0.8, 8.0 Hz, 1H), 8.19 (d, J = 7.6 Hz, 2H), 7.71 (brt, J = 7.2 Hz, 1H), 7.55 (brt, J = 7.2 Hz, 1H), 7.49 (brtt, J = 7.6 Hz, 1H), 7.34 (dd, J = 1.2, 8.8 Hz, 1H), 7.25 (brt, J = 7.2 Hz, 1H), 3.76 (brs, 3H). ^{13}C NMR (100MHz, $CDCl_3$): δ 161.6, 138.0, 133.5, 132.4, 129.5, 128.7, 125.6, 123.2, 122.4, 121.6, 119.2, 115.0, 23.0 . HRMS (ESI^+): calcd 210.0913 for $C_{14}H_{12}NO^+$ $[M+H]^+$; found, 210.0917.

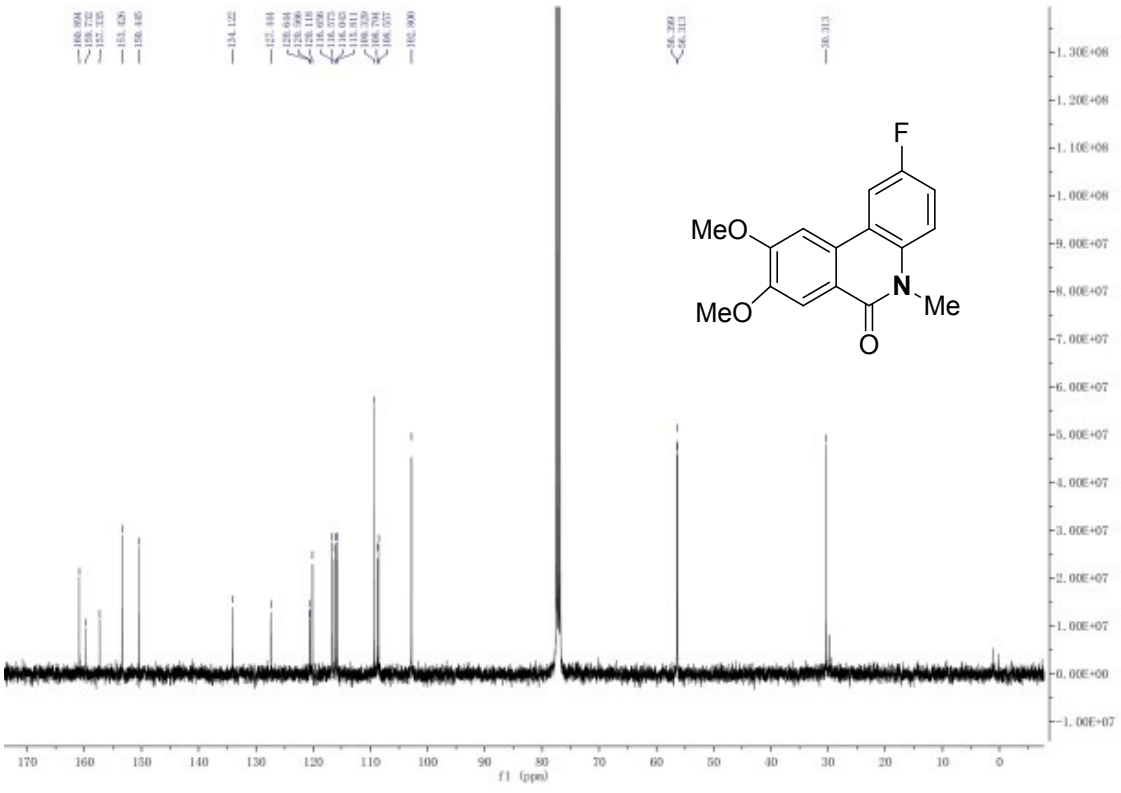


2-fluoro-8,9-dimethoxy-5-methylphenanthridin-6(5H)-one(19b): Obtained as white amorphous powder, ^{1}H NMR (400MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.45 (dd, J = 2.8, 9.6 Hz, 1H), 7.41 (s, 1H), 7.33 (dd, J = 4.8, 9.2 Hz, 1H), 7.22-7.18 (m, 1H), 4.08 (s, 3H), 4.03 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$): δ 160.9, 158.5 (d, $^{1}J_{F-C}$ = 249.9 Hz), 153.4, 150.4, 134.1, 127.4, 120.5 (d, $^{3}J_{F-C}$ = 2.8 Hz), 120.1, 116.6 (d, $^{3}J_{F-C}$ = 8.3 Hz), 115.9 (d, $^{2}J_{F-C}$ =23.2 Hz), 109.3, 108.6 (d, $^{2}J_{F-C}$ = 23.7 Hz), 102.8, 56.4, 56.3, 30.3. HRMS (ESI^+): calcd 288.1030 for $C_{16}H_{15}FNO_3^+$ $[M+H]^+$; found, 288.1023.

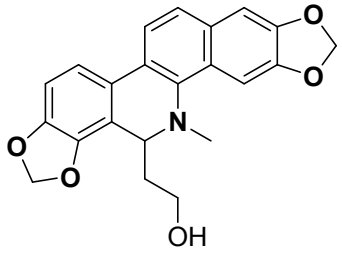

N
Me
O
f1 (ppm)


N
Me
O
f1 (ppm)

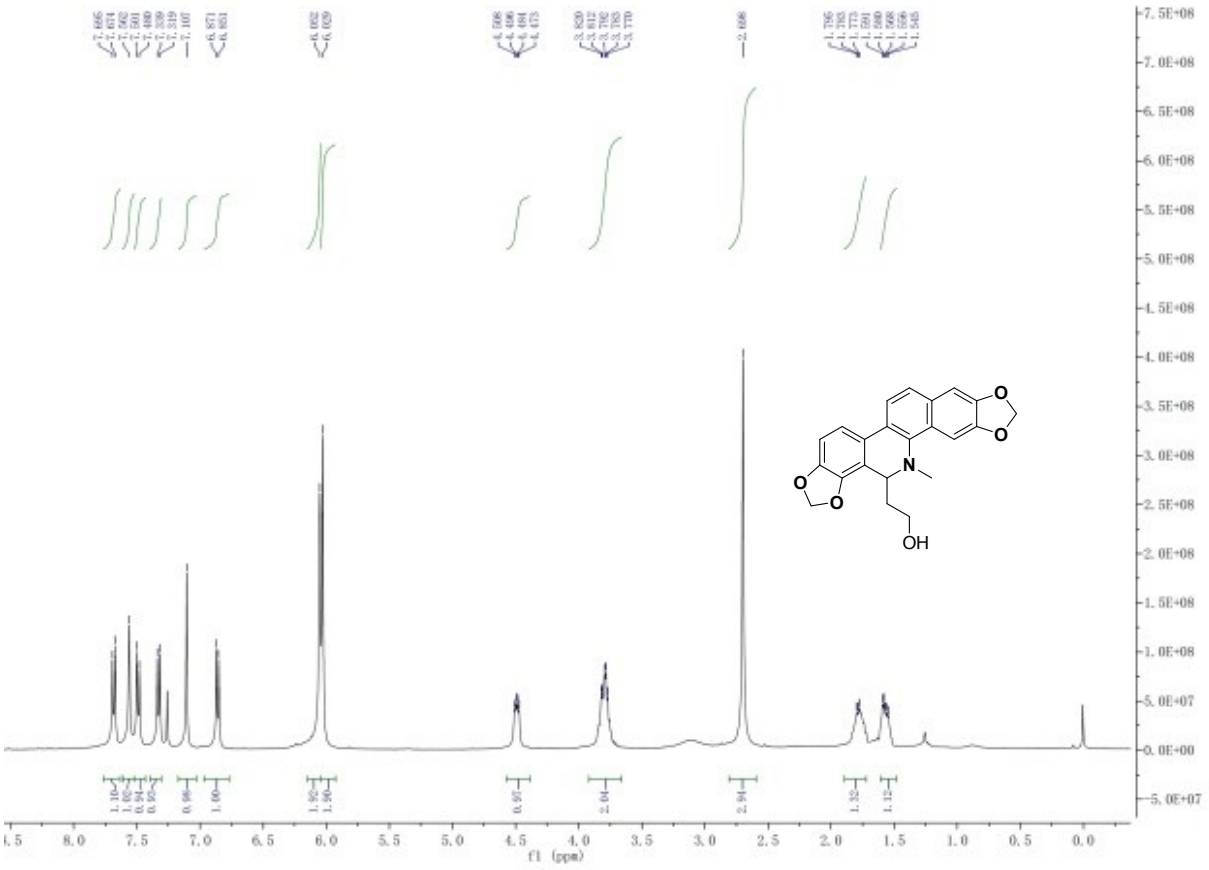

F
MeO
MeO
N
Me
O
f1 (ppm)

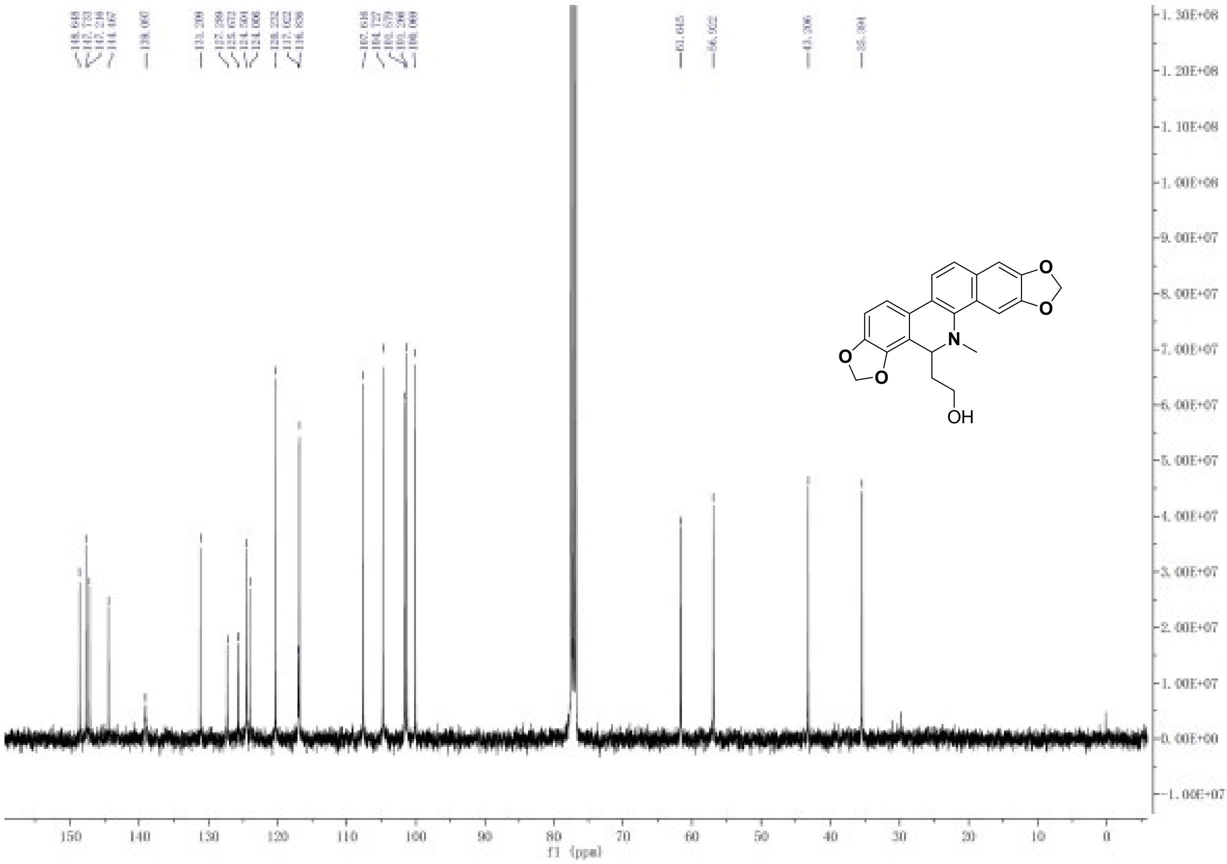

F
MeO
MeO
N
Me
O
f1 (ppm)

NMR data and spectra of synthetic compound 4



6-hydroxyl 5,6-dihydrosnanguinarine(4): Obtained as white amorphous powder, ^{1}H NMR (400MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.6 Hz, 1H), 7.56 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.11 (s, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.05 (s, 2H), 6.03 (s, 2H), 4.51-4.47 (m, 1H), 3.82-3.77 (m, 2H), 2.70 (s, 3H), 1.80-1.77 (m, 1H), 1.59-1.55 (m, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 148.6, 147.7, 147.2, 144.5, 139.1, 131.2, 127.3, 125.6, 124.5, 124.0, 120.2, 117.0, 116.8, 107.6, 104.7, 101.6, 101.3, 100.1, 61.6, 56.9, 43.2, 35.4. HRMS (ESI^{+}): calcd 378.1336 for $C_{22}H_{20}NO_5^{+}$ $[M+H]^{+}$; found, 378.1340.





150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
O
N
O
O
OH