Supporting Information for

Chemoselective Asymmetric Dearomative [3+2] Cycloaddition Reactions of Purines with Aminocyclopropanes

Er-Jun Hao,[a] Dan-Dan Fu,[a] Dong-Chao Wang,*[a] Tao Zhang,[b] Gui-Rong Qu,[a] Gong-Xin Li,[a] Yu Lan,*[b,c] and Hai-Ming Guo*[a]

[a]Henan Key Laboratory of Organic Functional Molecules and Drugs Innovation, Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China. E-mail: wangdc@htu.edu.cn; ghm@htu.edu.cn

[b]School of Chemistry and Chemical Engineering Chongqing University, Chongqing 400030, China. E-mail: lanyu@cqu.edu.cn

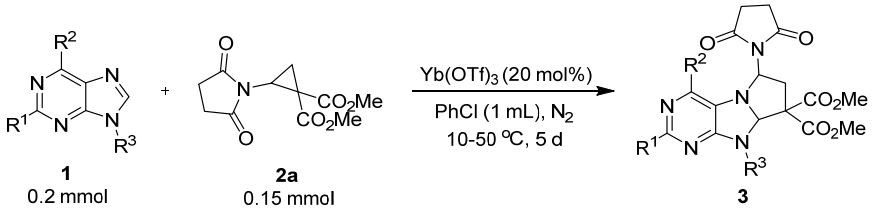
[c]College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, China. E-mail: lanyu@cqu.edu.cn

Table of contents

1.General

All reactions were carried out in oven-dried Schlenk tube filled nitrogen, and monitored by thin layer chromatography (TLC). All reagents were reagent grade quality and purchased from commercial sources unless otherwise indicated. NMR spectra were recorded with a 600 MHz or 400 MHz spectrometer for ^{1}H NMR, 151MHz or 101MHz for ^{13}C NMR. Chemical shifts δ are given in ppm relative to the residual proton signals of the deuterated solvent $CDCl_3$ for ^{1}H and ^{13}C NMR. Multiplicities are reported as follows: singlet, doublet (d), doublet of doublets (dd), triplet (t), quartet (q), multiplet (m). High resolution mass spectra were recorded on a 3000 mass spectrometer. For column chromatography silica gel (200-300 mesh) was used as the stationary phase. PhCl, $ClCH_2CH_2Cl$, CH_2Cl_2 and $CHCl_3$ were distilled from CaH_2 under N_2 prior to use. Substrates **1** were prepared according to the reported method.[i]

2. General procedure for the preparation of racemic dearomatized products (3a was used as a representative example)



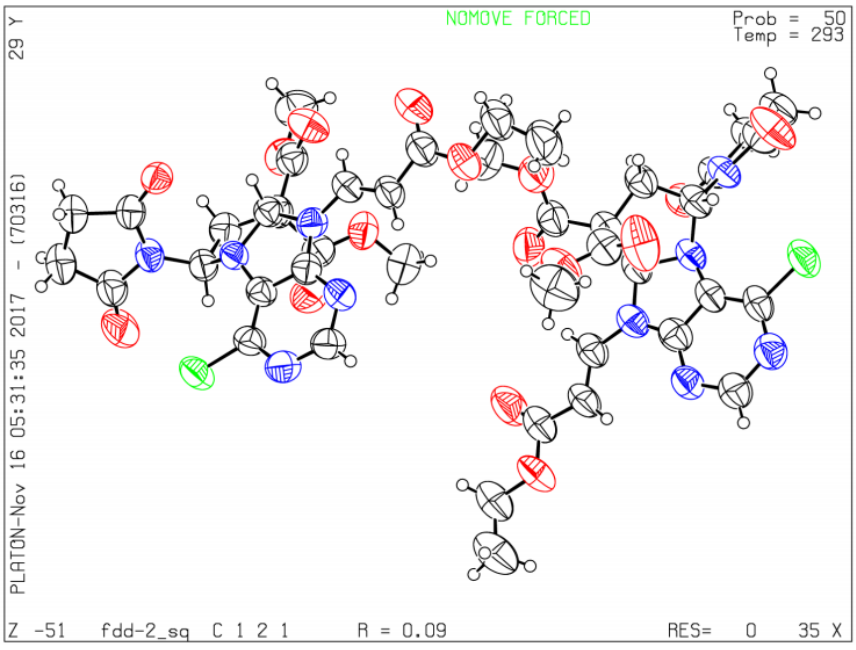
To a Schlenk tube equipped with a magnetic stir bar, purine **1a** (50.4 mg, 0.2 mmol, 1.3 equiv), cyclopropane **2a** (38.5 mg, 0.15 mmol, 1.0 equiv) and $Yb(OTf)_3$ (18.6 mg, 0.03 mmol, 20 mol%) were added. The tube was sealed with threaded rubber stopper, evacuated and backfilled with N_2 (this process was repeated for 3 times). PhCl (1.0 mL) was then added via syringe. The mixture was stirred at 10 – 50 ℃ for 5 days. Upon completion, the contents of the tube were passed through a short silica gel pad using CH_2Cl_2 as the mobile phase and then concentrated to give the crude products, which were then purified by preparative thin layer chromatography using ethyl acetate/petroleum ether system (petroleum ether/ethyl acetate = 2/1 to 1/2).

3. General procedure for the enantioselective preparation of dearomatized products

To a Schlenk tube equipped with a magnetic stir bar, $Cu(OTf)_2$ (3.6 mg, 0.01 mmol, 20 mol%), **L5** (8.0 mg, 0.012 mmol, 24 mol%), and activated 4 Å MS (40 mg) were added. The tube was sealed with threaded rubber stopper, evacuated and backfilled with N_2 (this process was repeated for 3 times). The tube was then charged with PhCl (0.5 mL) via syringe and was allowed to stir at room temperature until a bright green complex was formed (about 0.5 h). To this complex, a solution of the purine **1** (0.05 mmol, 1 equiv) and aminocyclopropane **2a** (51.0 mg, 0.2 mmol, 4 equiv) in PhCl (0.5 mL) was added at 0 ^{o}C. The complex was allowed to proceed until the disappearance of the starting material was confirmed by TLC analysis. Upon completion, the complex was passed through a short silica gel pad using CH_2Cl_2 as the mobile phase and was concentrated in vacuo to give the crude products, which were then purified by preparative thin layer chromatography using ethyl acetate/petroleum ether system (petroleum ether/ethyl acetate = 2/1 to 1/2).

4. The X-ray crystallographic data for compounds 3a, *rac*-3a' and *rac*-4

Recrystallization in a mixture of CH_2Cl_2/petroleum ether/ethyl acetate/ ethyl ether afforded crystals of **3a** suitable for X-ray analysis.



Bond precision: C-C = 0.0073 A Wavelength=1.54184

Cell: a=25.9456(5) b=8.8451(3) c=23.3704(7)
alpha=90 beta=101.146(3) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	5262.1(3)	5262.1(3)
Space group	C 2	C 1 2 1
Hall group	C 2y	C 2y
Moiety formula	C21 H22 Cl N5 O8 [+ solvent]	C21 H22 Cl N5 O8
Sum formula	C21 H22 Cl N5 O8 [+ solvent]	C21 H22 Cl N5 O8
Mr	507.89	507.89
Dx,g cm-3	1.282	1.282
Z	8	8
Mu (mm-1)	1.739	1.739
F000	2112.0	2112.0
F000'	2121.97	
h,k,lmax	30,10,27	30,10,27
Nref	9412[5040]	8872
Tmin,Tmax	0.585,0.855	0.053,1.000
Tmin'	0.413	

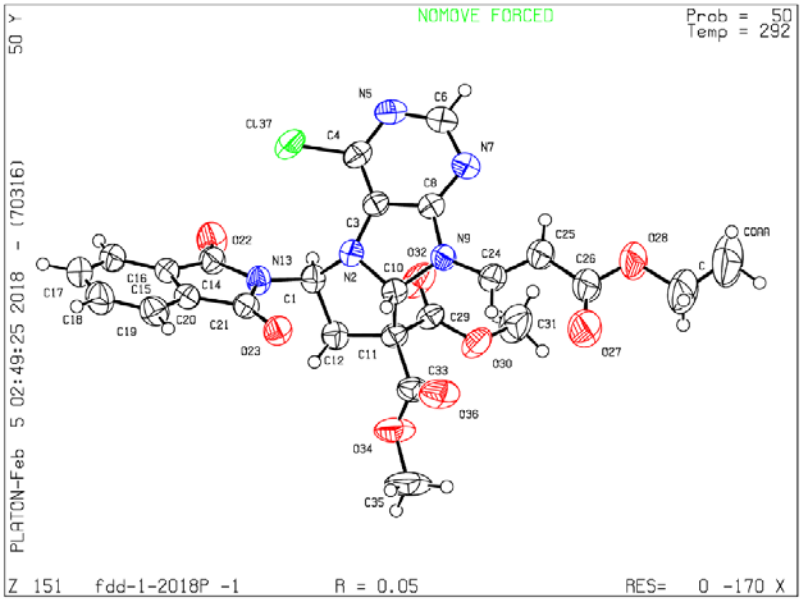
Correction method= # Reported T Limits: Tmin=0.053 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.76/0.94 Theta(max)= 67.063

R(reflections)= 0.0641(8381) wR2(reflections)= 0.1781(8872)

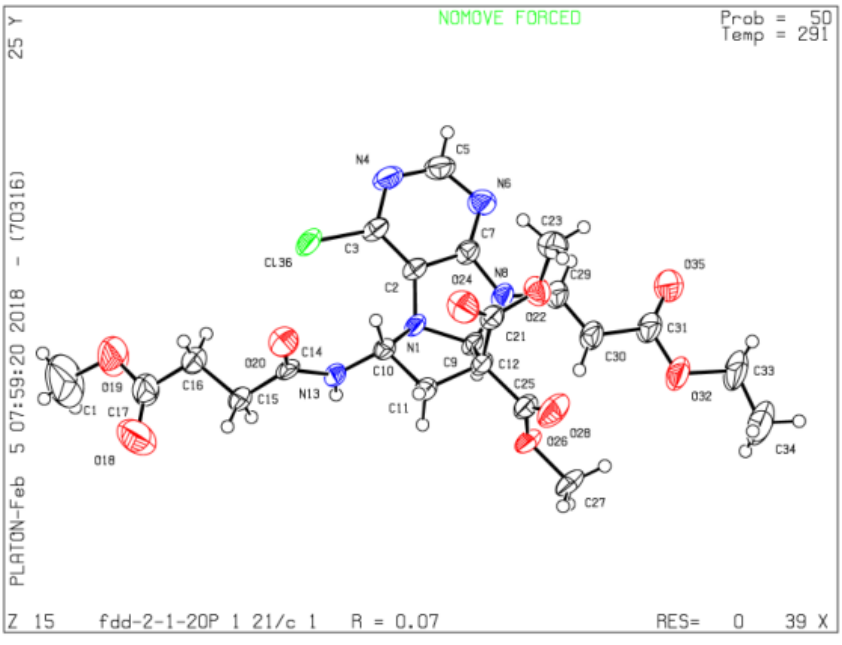
S = 1.052 Npar= 637

Recrystallization in a mixture of CH_2Cl_2/petroleum ether/ethyl acetate/ ethyl ether afforded crystals *rac*-**3a'** suitable for X-ray analysis.



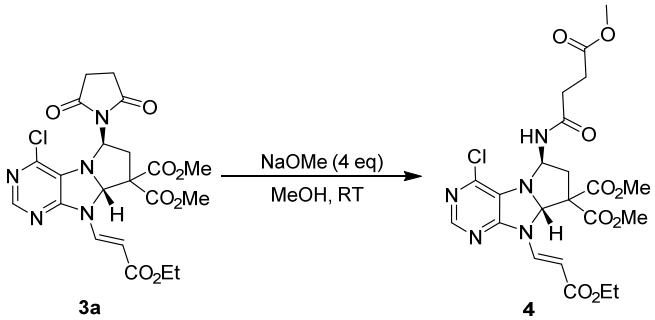
```
Bond precision:  C-C = 0.0034 A          Wavelength=0.71073

Cell:          a=8.9522(4)        b=12.3288(5)      c=12.6211(5)
               alpha=103.938(3)   beta=101.104(4)   gamma=102.417(4)
Temperature:   292 K

                 Calculated                Reported
Volume           1275.71(10)               1275.71(10)
Space group      P -1                      P -1
Hall group       -P 1                      -P 1
Moiety formula   C25 H22 Cl N5 O8          C25 H22 Cl N5 O8
Sum formula      C25 H22 Cl N5 O8          C25 H22 Cl N5 O8
Mr               555.93                    555.92
Dx,g cm-3        1.447                     1.447
Z                2                         2
Mu (mm-1)        0.210                     0.210
F000             576.0                     576.0
F000'            576.59
h,k,lmax         10,14,15                  10,14,15
Nref             4487                      4475
Tmin,Tmax        0.910,0.949               0.845,1.000
Tmin'            0.910

Correction method= # Reported T Limits: Tmin=0.845 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.997          Theta(max)= 25.000

R(reflections)= 0.0503( 3674)     wR2(reflections)= 0.1314( 4475)

S = 1.058                 Npar= 355
```

Recrystallization in a mixture of CH_2Cl_2/petroleum ether/ethyl acetate/ethyl ether afforded crystals of *rac*-**4** suitable for X-ray analysis.



```
Bond precision:  C-C = 0.0037 A          Wavelength=1.54184

Cell:            a=14.6444(2)     b=19.0270(3)        c=9.2992(1)
                 alpha=90         beta=98.115(1)      gamma=90
Temperature:     291 K

                 Calculated                Reported
Volume           2565.17(6)                2565.17(6)
Space group      P 21/c                    P 1 21/c 1
Hall group       -P 2ybc                   -P 2ybc
Moiety formula   C22 H26 Cl N5 O9          C22 H26 Cl N5 O9
Sum formula      C22 H26 Cl N5 O9          C22 H26 Cl N5 O9
Mr               539.93                    539.93
Dx,g cm-3        1.398                     1.398
Z                4                         4
Mu (mm-1)        1.846                     1.846
F000             1128.0                    1128.0
F000'            1133.25
h,k,lmax         18,23,11                  18,23,11
Nref             5089                      5015
Tmin,Tmax        0.590,0.946               0.403,1.000
Tmin'            0.518

Correction method= # Reported T Limits: Tmin=0.403 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.985          Theta(max)= 72.482

R(reflections)= 0.0664( 4205)     wR2(reflections)= 0.1976( 5015)

S = 1.048                 Npar= 338
```

5. Synthesis procedure of compounds 4 and 5

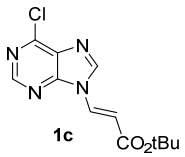


A reaction tube equipped with a magnetic stir bar was charged with **3a** (50.8 mg, 0.1 mmol, 1.0 equiv), $NaOCH_3$ (21.6 mg, 0.4 mmol, 4 equiv) and MeOH (1.0 mL). The mixture was stirred at room temperature for 1.5 h. Upon completion, the reaction mixture was then purified by preparative thin layer chromatography using ethyl acetate/petroleum ether system (petroleum ether/ethyl acetate = 1/1).

A Schlenk tube equipped with a magnetic stir bar was charged with **3a** (50.8 mg, 0.1 mmol, 1.0 equiv), $Cu(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol%) and DCE (1.0 mL). The tube was sealed with threaded rubber stopper. The mixture was stirred at 80 °C for 6 h. The complex was passed through a short silica gel column using CH_2Cl_2 as the mobile phase. The crude product was then purified by preparative thin layer chromatography using ethyl acetate/petroleum ether system (petroleum ether/ethyl acetate = 1/1).

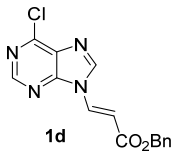
6. The analytical and spectral characterization data for the products

tert-Butyl (*E*)-3-(6-chloro-9*H*-purin-9-yl)acrylate 1c



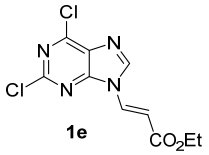
Yellow solid, m.p. = 181-182 °C. 2.33 g, 83% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.31 (s, 1H), 8.07 (d, *J* = 14.4 Hz, 1H), 7.01 (d, *J* = 14.4 Hz, 1H), 1.55 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 153.3, 152.1, 151.3, 143.6, 132.8, 132.2, 113.7, 82.1, 28.3. HRMS (ESI): exact mass calcd for $C_{12}H_{14}ClN_4O_2$ $(M+H)^+$ requires m/z 281.0800, found m/z 281.0800.

Benzyl (*E*)-3-(6-chloro-9*H*-purin-9-yl)acrylate 1d



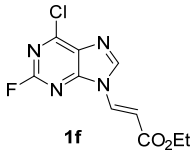
Yellow solid, m.p. = 163-164 °C. 2.39 g, 76% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.30 (s, 1H), 8.19 (d, *J* = 14.4 Hz, 1H), 7.40 (m, 5H), 7.19 (d, *J* = 14.4 Hz, 1H), 5.30 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 153.4, 152.3, 151.3, 143.6, 135.5, 133.4, 132.9, 128.9, 128.7, 128.6, 111.5, 67.2. HRMS (ESI): exact mass calcd for $C_{15}H_{12}ClN_4O_2$ $(M+H)^+$ requires m/z 315.0643, found m/z 315.0639.

Ethyl (*E*)-3-(2,6-dichloro-9*H*-purin-9-yl)acrylate 1e



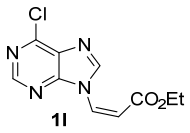
Yellow solid, m.p. = 142-143 °C. 1.69 g, 59% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.11 (d, *J* = 14.4 Hz, 1H), 7.00 (d, *J* = 14.4 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 154.6, 153.0, 152.4, 143.9, 132.5, 131.9, 112.4, 61.6, 14.4. HRMS (ESI): exact mass calcd for $C_{10}H_9Cl_2N_4O_2$ $(M+H)^+$ requires m/z 287.0097, found m/z 287.0096.

Ethyl (*E*)-3-(6-chloro-2-fluoro-9*H*-purin-9-yl)acrylate 1f



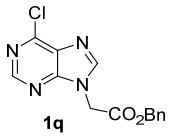
Yellow solid, m.p. = 139-140 °C. 1.057 g, 39% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.09 (d, *J* = 14.4 Hz, 1H), 6.99 (d, *J* = 14.4 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 157.9 (*J* = 224.1 Hz), 154.1 (*J* = 17.5 Hz), 152.9, 144.1 (*J* = 3.5 Hz), 132.5, 131.6, 112.3, 61.6, 14.4. HRMS (ESI): exact mass calcd for $C_{10}H_9ClFN_4O_2$ $(M+H)^+$ requires m/z 271.0393, found m/z 271.0400.

Ethyl (*Z*)-3-(6-chloro-9*H*-purin-9-yl)acrylate 1l



White solid, m.p. = 151-152 °C. 1.92 g, 76% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.80 (s, 1H), 7.54 (d, *J* = 10.2 Hz, 1H), 5.92 (d, *J* = 10.2 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 152.8, 151.7, 146.4, 131.1, 128.0, 109.8, 61.5, 14.2. HRMS (ESI): exact mass calcd for $C_{10}H_{10}ClN_4O_2$ $(M+H)^+$ requires m/z 253.0487, found m/z 253.0486.

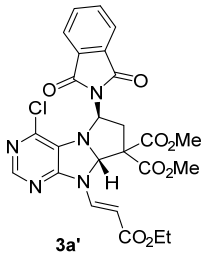
Benzyl 2-(6-chloro-9*H*-purin-9-yl)acetate 1q



1q

White solid, m.p. = 163-164 °C. 2.31 g, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.19 (s, 1H), 7.42 – 7.29 (m, 5H), 5.24 (s, 2H), 5.10 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 152.4, 152.1, 151.5, 145.5, 134.5, 131.4, 129.1, 128.9, 128.8, 68.5, 44.7. HRMS (ESI): exact mass calcd for $C_{14}H_{12}ClN_4O_2$ $(M+H)^+$ requires m/z 303.0643, found m/z 303.0649.

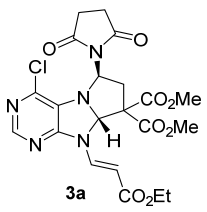
Dimethyl(6*S*,8a*S*)-4-chloro-6-(1,3-dioxoisoindolin-2-yl)-9-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3a'



3a'

Pale yellow solid, m.p. = 223-224 °C. 13.9 mg, 50% yield, 78% *ee*. HPLC CHIRALCEL OD-H, n-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 17.401 min (minor), 30.199 min (major). $[\alpha]_D^{20}$ = -215.79 (c 0.247, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.06 (d, *J* = 14.3 Hz, 1H), 7.90 (m, 2H), 7.78 (m, 2H), 6.69 (s, 1H), 6.54 – 6.43 (m, 2H), 4.23 (m, 2H), 3.89 (s, 3H), 3.60 (s, 3H), 3.16 (dd, *J* = 14.0, 8.4 Hz, 1H), 2.65 (dd, *J* = 14.0, 6.8 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5, 168.3, 167.6, 167.1, 155.7, 151.1, 136.6, 136.1, 134.7, 131.8, 129.4, 123.9, 103.0, 100.1, 85.3, 67.0, 65.6, 60.3, 53.7, 53.6, 37.9, 14.5. HRMS (ESI): exact mass calcd for $C_{25}H_{22}ClN_5NaO_8$ $(M+Na)^+$ requires m/z 578.1049, found m/z 578.1054.

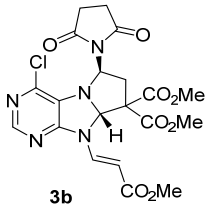
Dimethyl(6*S*,8a*S*)-4-chloro-6-(2,5-dioxopyrrolidin-1-yl)-9-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3a



3a

White solid, m.p. = 117-118 °C. 23.1 mg, 91% yield, 96% *ee*. HPLC CHIRALCEL IA, n-hexane/2-propanol = 60/40, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 11.629 min (minor), 50.577 min (major). $[\alpha]_D^{20}$ = -175.00 (c 0.080, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.01 (d, *J* = 14.4 Hz, 1H), 6.56 (s, 1H), 6.47 (d, *J* = 14.4 Hz, 1H), 6.31 (t, *J* = 7.5 Hz, 1H), 4.21 (dd, *J* = 13.2, 6.6 Hz, 2H), 3.87 (s, 3H), 3.56 (s, 3H), 3.04 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.79 – 2.74 (m, 4H), 2.53 (dd, *J* = 14.1, 6.3 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 168.4, 168.1, 167.6, 155.7, 151.1, 136.5, 135.9, 129.2, 103.1, 85.6, 67.5, 65.7, 60.3, 53.7, 53.6, 37.0, 28.4, 14.5. HRMS (ESI): exact mass calcd for $C_{21}H_{23}ClN_5O_8$ $(M+H)^+$ requires m/z 508.1230, found m/z 508.1231.

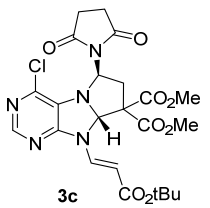
Dimethyl(6*S*,8a*S*)-4-chloro-6-(2,5-dioxopyrrolidin-1-yl)-9-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3b



3b

Colorless oil, 23.2 mg, 94% yield, 96% *ee*. HPLC CHIRALCEL IA, n-hexane/2-propanol = 60/40, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 12.638 min (minor), 54.334 min (major). $[\alpha]_D^{20}$ = -262.22 (c 0.270, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.00 (d, *J* = 14.0 Hz, 1H), 6.55 (s, 1H), 6.45 (d, *J* = 13.6 Hz, 1H), 6.30 (dd, *J* = 8.4, 6.4 Hz, 1H), 3.85 (s, 3H), 3.74 (s, 3H), 3.54 (s, 3H), 3.03 (dd, *J* = 14.0, 8.8 Hz, 1H), 2.75 (s, 4H), 2.51 (dd, *J* = 14.0, 6.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 168.4, 168.1, 167.9, 155.7, 151.1, 136.6, 136.0, 129.2, 102.6, 85.5, 67.5, 65.6, 53.7, 53.5, 51.5, 37.0, 28.4. HRMS (ESI): exact mass calcd for $C_{20}H_{21}ClN_5O_8$ (M+H)+ requires m/z 494.1073, found m/z 494.1074.

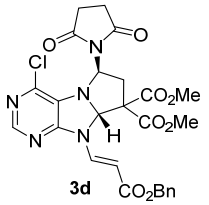
Dimethyl(6*S*,8a*S*)-9-((*E*)-3-(tert-butoxy)-3-oxoprop-1-en-1-yl)-4-chloro-6-(2,5-dioxopyrrolidin-1-yl)-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3c



3c

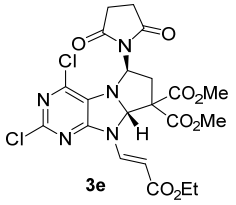
Colorless oil, 24.9 mg, 93% yield, 97% *ee*. HPLC CHIRALCEL IA, n-hexane/2-propanol = 60/40, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 8.640 min (minor), 31.775 min (major). $[\alpha]_D^{20}$ = -148.32 (c 0.258, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.90 (d, *J* = 13.8 Hz, 1H), 6.54 (s, 1H), 6.40 (d, *J* = 14.4 Hz, 1H), 6.31 (dd, *J* = 8.4, 6.6 Hz, 1H), 3.88 (s, 3H), 3.56 (s, 3H), 3.03 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.80 – 2.74 (m, 4H), 2.53 (dd, *J* = 13.8, 6.6 Hz, 1H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 168.4, 168.1, 166.9, 155.9, 151.1, 135.9, 135.7, 129.2, 105.1, 85.7, 80.2, 67.6, 65.7, 53.7, 53.6, 37.0, 28.4, 28.4. HRMS (ESI): exact mass calcd for $C_{23}H_{27}ClN_5O_8$ $(M+H)^+$ requires m/z 536.1543, found m/z 536.1550.

Dimethyl(6*S*,8a*S*)-9-((*E*)-3-(benzyloxy)-3-oxoprop-1-en-1-yl)-4-chloro-6-(2,5-dioxopyrrolidin-1-yl)-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3d



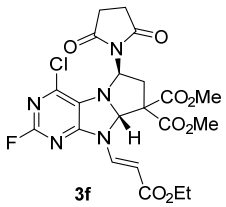
Colorless oil, 24.0 mg, 84% yield, 97% *ee*. HPLC CHIRALCEL IA, n-hexane/2-propanol = 60/40, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 16.391 min (minor), 78.350 min (major). $[\alpha]_D^{20}$ = -122.81 (c 0.320, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.05 (d, *J* = 14.4 Hz, 1H), 7.43 – 7.35 (m, 4H), 7.32 (t, *J* = 6.9 Hz, 1H), 6.56 (d, *J* = 14.4 Hz, 2H), 6.31 (t, *J* = 7.5 Hz, 1H), 5.22 (s, 2H), 3.83 (s, 3H), 3.55 (s, 3H), 3.04 (dd, *J* = 14.1, 8.7 Hz, 1H), 2.80 – 2.70 (m, 4H), 2.52 (dd, *J* = 14.1, 6.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.9, 168.4, 168.1, 167.4, 155.7, 151.1, 137.1, 136.5, 136.0, 129.3, 128.6, 128.2, 128.2, 102.7, 85.6, 67.5, 66.1, 65.7, 53.7, 53.6, 36.9, 31.1, 28.4. HRMS (ESI): exact mass calcd for $C_{26}H_{25}ClN_5O_8$ $(M+H)^+$ requires m/z 570.1386, found m/z 570.1382.

Dimethyl(6*S*,8a*S*)-2,4-dichloro-6-(2,5-dioxopyrrolidin-1-yl)-9-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3e



Colorless oil, 14.2 mg, 53% yield, 95% *ee*. HPLC CHIRALCEL AD, n-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 10.342 min (minor), 25.327 min (major). $[\alpha]_D^{20}$ = -143.64 (c 0.236, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 14.4 Hz, 1H), 6.58 (s, 1H), 6.46 (d, *J* = 14.4 Hz, 1H), 6.28 (dd, *J* = 8.7, 6.3 Hz, 1H), 4.29 – 4.18 (m, 2H), 3.88 (s, 3H), 3.61 (s, 3H), 3.05 (dd, *J* = 14.1, 8.7 Hz, 1H), 2.80 – 2.73 (m, 4H), 2.54 (dd, *J* = 14.1, 6.3 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 168.4, 168.0, 167.2, 157.3, 151.1, 135.8, 135.7, 128.4, 104.6, 86.4, 67.4, 65.7, 60.5, 53.8, 53.8, 37.1, 28.4, 14.5. HRMS (ESI): exact mass calcd for $C_{21}H_{21}Cl_2N_5NaO_8$ $(M+Na)^+$ requires m/z 564.0659, found m/z 564.0657.

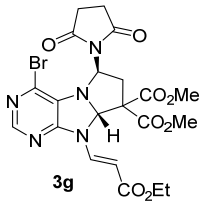
Dimethyl(6*S*,8a*S*)-4-chloro-6-(2,5-dioxopyrrolidin-1-yl)-9-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)-2-fluoro-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3f



3f

Colorless oil, 22.4 mg, 86% yield, 98% *ee*. HPLC CHIRALCEL ID, n-hexane/2-propanol = 40/60, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 14.330 min (minor), 20.123 min (major). $[\alpha]_D^{20}$ = -167.10 (c 0.386, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 13.8 Hz, 1H), 6.59 (s, 1H), 6.46 (d, *J* = 14.4 Hz, 1H), 6.26 (dd, *J* = 8.4, 6.6 Hz, 1H), 4.27 – 4.18 (m, 2H), 3.87 (s, 3H), 3.60 (s, 3H), 3.04 (dd, *J* = 14.4, 8.4 Hz, 1H), 2.82 – 2.74 (m, 4H), 2.55 (dd, *J* = 14.4, 6.6 Hz, 1H), 1.31 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 168.4, 168.0, 167.1, 158.7 (*J* = 17.2 Hz), 156.2 (*J* = 219.4 Hz), 135.8, 135.6, 127.5 (*J* = 6.0 Hz), 104.9, 87.0, 67.7, 65.8, 60.5, 53.8, 53.7, 37.0, 28.4, 14.5. HRMS (ESI): exact mass calcd for $C_{21}H_{22}ClFN_5O_8$ $(M+H)^+$ requires m/z 526.1135, found m/z 526.1142.

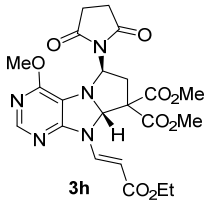
Dimethyl(6*S*,8a*S*)-4-bromo-6-(2,5-dioxopyrrolidin-1-yl)-9-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3g



3g

Colorless oil, 18.4 mg, 67% yield, 93% *ee*. HPLC CHIRALCEL IA, n-hexane/2-propanol = 60/40, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 12.563 min (minor), 74.230 min (major). $[\alpha]_D^{20}$ = -230.99 (c 0.327, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.00 (d, *J* = 13.8 Hz, 1H), 6.57 (s, 1H), 6.46 (d, *J* = 14.4 Hz, 1H), 6.31 (t, *J* = 6.9 Hz, 1H), 4.29 – 4.14 (m, 2H), 3.87 (s, 3H), 3.56 (s, 3H), 3.06 (dd, *J* = 13.5, 8.7 Hz, 1H), 2.79 – 2.72 (m, 4H), 2.47 (dd, *J* = 14.1, 6.3 Hz, 1H), 1.30 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 168.4, 168.1, 167.6, 155.0, 151.0, 136.5, 131.7, 125.9, 103.2, 85.5, 67.7, 65.5, 60.3, 53.7, 53.6, 37.3, 28.4, 14.5. HRMS (ESI): exact mass calcd for $C_{21}H_{22}BrN_5NaO_8$ $(M+Na)^+$ requires m/z 574.0544, found m/z 574.0546.

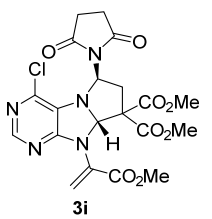
Dimethyl(6*S*,8a*S*)-6-(2,5-dioxopyrrolidin-1-yl)-9-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)-4-methoxy-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3h



3h

Colorless oil, 25.5 mg, 98% yield, 99% *ee*. HPLC CHIRALCEL IE, n-hexane/2-propanol = 60/40, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 42.047 min (minor), 44.320 min (major). $[\alpha]_D^{20}$ = -103.17(c 0.400, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 – 7.98 (m, 2H), 6.44 (s, 1H), 6.20 (d, *J* = 14.4 Hz, 1H), 6.14 (t, *J* = 7.8 Hz, 1H), 4.25 – 4.14 (m, 2H), 3.92 (s, 3H), 3.86 (s, 3H), 3.54 (s, 3H), 2.93 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.79 – 2.71 (m, 4H), 2.63 (dd, *J* = 13.8, 6.6 Hz, 1H), 1.29 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.0, 168.7, 168.5, 168.1, 154.6, 154.3, 151.1, 137.5, 116.8, 99.9, 85.8, 68.6, 66.2, 60.0, 54.0, 53.5, 53.4, 36.1, 31.0, 28.3, 14.5. HRMS (ESI): exact mass calcd for $C_{22}H_{26}N_5O_9$ $(M+H)^+$ requires m/z 504.1725, found m/z 504.1724.

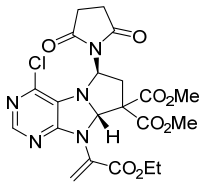
Dimethyl(6*S*,8a*S*)-4-chloro-6-(2,5-dioxopyrrolidin-1-yl)-9-(3-methoxy-3-oxoprop-1-en-2-yl)-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3i



3i

Colorless oil, 15.5 mg, 63% yield, 95% *ee*. HPLC CHIRALCEL IE, n-hexane/2-propanol = 50/50, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 24.778 min (minor), 41.063 min (major). $[\alpha]_D^{20}$ = -128.18 (c 0.194, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 6.58 (s, 1H), 6.50 (s, 1H), 6.31 (t, *J* = 7.5 Hz, 1H), 5.91 (s, 1H), 3.86 (s, 3H), 3.76 (s, 3H), 3.60 (s, 3H), 2.85 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.81 – 2.70 (m, 4H), 2.57 (dd, *J* = 14.4, 7.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.0, 168.9, 168.3, 163.2, 158.9, 150.7, 134.2, 132.4, 128.6, 124.8, 84.9, 67.7, 65.8, 53.3, 53.3, 52.9, 35.5, 31.1, 28.4. HRMS (ESI): exact mass calcd for $C_{20}H_{21}ClN_5O_8$ $(M+H)^+$ requires m/z 494.1073, found m/z 494.1072.

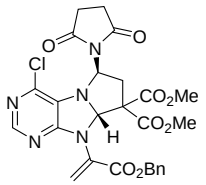
Dimethyl(6*S*,8a*S*)-4-chloro-6-(2,5-dioxopyrrolidin-1-yl)-9-(3-ethoxy-3-oxoprop-1-en-2-yl)-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3j



3j

Colorless oil, 13.7 mg, 54% yield, 95% *ee*. HPLC CHIRALCEL IE, n-hexane/2-propanol = 50/50, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 22.962 min (minor), 39.258 min (major). $[\alpha]_D^{20}$ = -124.34 (c 0.226, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 6.61 (s, 1H), 6.51 (s, 1H), 6.32 (t, *J* = 7.8 Hz, 1H), 5.89 (s, 1H), 4.41 – 4.32 (m, 1H), 4.31 – 4.22 (m, 1H), 3.76 (s, 3H), 3.59 (s, 3H), 2.86 (dd, *J* = 14.4, 8.4 Hz, 1H), 2.80 – 2.70 (m, 4H), 2.55 (dd, *J* = 13.8, 7.2 Hz, 1H), 1.34 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.9, 168.9, 168.2, 162.6, 158.9, 150.7, 134.1, 132.7, 128.6, 124.7, 85.0, 67.7, 65.8, 62.1, 53.3, 53.2, 35.5, 31.1, 28.4, 14.3. HRMS (ESI): exact mass calcd for $C_{21}H_{23}ClN_5O_8$ $(M+H)^+$ requires m/z 508.1230, found m/z 508.1230.

Dimethyl(6*S*,8a*S*)-9-(3-(benzyloxy)-3-oxoprop-1-en-2-yl)-4-chloro-6-(2,5-dioxopyrrolidin-1-yl)-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3k

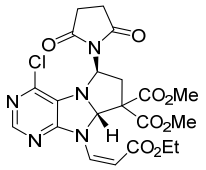


3k

Colorless oil, 14.7 mg, 52% yield, 95% *ee*. HPLC CHIRALCEL IE, n-hexane/2-propanol = 50/50, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 29.837 min (minor), 49.909 min (major). $[\alpha]_D^{20}$ = -

110.34 (c 0.232, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.44 – 7.29 (m, 5H), 6.62 (s, 1H), 6.53 (s, 1H), 6.30 (t, *J* = 7.8 Hz, 1H), 5.91 (s, 1H), 5.27 (dd, *J* = 33.6, 12.0 Hz, 2H), 3.65 (s, 3H), 3.57 (s, 3H), 2.85 (dd, *J* = 14.1, 8.1 Hz, 1H), 2.80 – 2.70 (m, 4H), 2.57 (dd, *J* = 13.8, 7.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.9, 168.9, 168.2, 162.5, 159.0, 150.7, 135.3, 134.2, 132.6, 128.7, 128.7, 128.6, 128.6, 125.2, 85.0, 67.8, 67.7, 65.8, 53.3, 53.1, 35.5, 31.1, 28.4. HRMS (ESI): exact mass calcd for $C_{26}H_{25}ClN_5O_8$ $(M+H)^+$ requires m/z 570.1386, found m/z 570.1386.

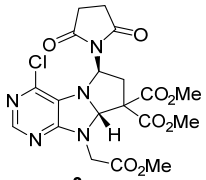
Dimethyl(6*S*,8a*S*)-4-chloro-6-(2,5-dioxopyrrolidin-1-yl)-9-((*Z*)-3-ethoxy-3-oxoprop-1-en-1-yl)-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3l



3l

Colorless oil, 19.1 mg, 75% yield, 94% *ee*. HPLC CHIRALCEL IA, n-hexane/2-propanol = 60/40, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 14.380 min (minor), 27.550 min (major). $[\alpha]_D^{20}$ = -169.96 (c 0.294, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 6.83 (s, 1H), 6.71 (d, *J* = 14.4 Hz, 1H), 6.29 (t, *J* = 11.7 Hz, 1H), 5.57 (d, *J* = 14.4 Hz, 1H), 4.18 (dd, *J* = 10.5,6.9 Hz, 2H), 3.76 (s, 3H), 3.61 (s, 3H), 2.91 (dd, *J* = 20.7, 12.3 Hz, 1H), 2.79 – 2.71 (m, 4H), 2.57 (dd, *J* = 20.7, 11.1 Hz, 1H), 1.24 (t, *J* = 10.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 168.4, 168.1, 165.2, 156.3, 150.5, 134.9, 130.4, 128.5, 109.1, 85.4, 67.3, 65.6, 60.6, 53.8, 53.3, 36.0, 28.3, 14.3. HRMS (ESI): exact mass calcd for $C_{21}H_{22}ClN_5NaO_8$ $(M+Na)^+$ requires m/z 530.1049, found m/z 530.1050.

Dimethyl(6*S*,8a*S*)-4-chloro-6-(2,5-dioxopyrrolidin-1-yl)-9-(2-methoxy-2-oxoethyl)-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3m

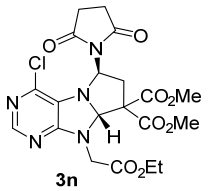


3m

Colorless oil, 16.9 mg, 70% yield, 96% *ee*. HPLC CHIRALCEL IA, n-hexane/2-propanol = 60/40, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 16.364 min (minor), 25.611 min (major). $[\alpha]_D^{20}$ = -286.21 (c 0.174, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 1H), 6.26 (t, *J* = 7.8 Hz, 1H), 6.23 (s,

1H), 4.55 (d, *J* = 18.0 Hz, 1H), 4.23 (d, *J* = 18.0 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.60 (s, 3H), 2.87 (dd, *J* = 14.1, 8.1 Hz, 1H), 2.78 – 2.69 (m, 4H), 2.56 (dd, *J* = 13.8, 7.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 168.8, 168.7, 168.7, 160.1, 151.0, 133.0, 128.0, 85.7, 67.9, 66.3, 53.5, 53.4, 52.6, 43.6, 35.1, 28.4. HRMS (ESI): exact mass calcd for $C_{19}H_{21}ClN_5O_8$ $(M+H)^+$ requires m/z 482.1073, found m/z 482.1068.

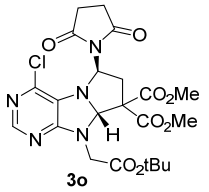
Dimethyl(6*S*,8a*S*)-4-chloro-6-(2,5-dioxopyrrolidin-1-yl)-9-(2-ethoxy-2-oxoethyl)-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3n



3n

Colorless oil, 14.4 mg, 58% yield, 96% *ee*. HPLC CHIRALCEL IA, n-hexane/2-propanol = 60/40, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 17.056 min (minor), 23.721 min (major). $[\alpha]_D^{20}$ = -216.11 (c 0.060, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 1H), 6.26 (d, *J* = 8.4 Hz, 1H), 6.25 (s, 1H), 4.54 (d, *J* = 18.0 Hz, 1H), 4.23 (m, 2H), 4.20 (m, 1H), 3.80 (s, 3H), 3.59 (s, 3H), 2.87 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.78 – 2.69 (m, 4H), 2.55 (dd, *J* = 13.8, 7.2 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 168.8, 168.7, 168.1, 160.2, 150.9, 133.0, 128.0, 85.7, 67.9, 66.3, 61.8, 53.5, 53.4, 43.8, 35.2, 28.4, 14.3. HRMS (ESI): exact mass calcd for $C_{20}H_{23}ClN_5O_8$ $(M+H)^+$ requires m/z 496.1230, found m/z 496.1233.

Dimethyl(6*S*,8a*S*)-9-(2-(tert-butoxy)-2-oxoethyl)-4-chloro-6-(2,5-dioxopyrrolidin-1-yl)-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3o

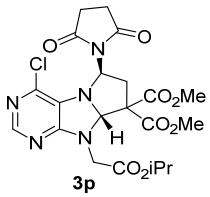


3o

Colorless oil, 21.2 mg, 81% yield, 96% *ee*. HPLC CHIRALCEL IA, n-hexane/2-propanol = 60/40, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 11.292 min (minor), 18.224 min (major). $[\alpha]_D^{20}$ = -178.68 (c 0.272, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (s, 1H), 6.29 – 6.22 (m, 2H), 4.45 (d, *J* = 18.0 Hz, 1H), 4.07 (d, *J* = 18.0 Hz, 1H), 3.80 (s, 3H), 3.59 (s, 3H), 2.87 (dd, *J* = 14.1, 8.1 Hz, 1H), 2.73 (m, 4H), 2.53 (dd, *J* = 13.8, 7.2 Hz, 1H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 168.9,

168.7, 167.1, 160.4, 150.9, 132.9, 128.0, 85.8, 82.8, 67.9, 66.3, 53.4, 53.4, 44.5, 35.3, 31.0, 28.4, 28.1. HRMS (ESI): exact mass calcd for $C_{22}H_{27}ClN_5O_8$ $(M+H)^+$ requires m/z 524.1543, found m/z 524.1537.

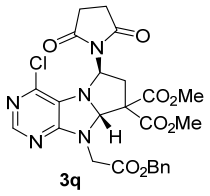
Dimethyl(6*S*,8a*S*)-4-chloro-6-(2,5-dioxopyrrolidin-1-yl)-9-(2-isopropoxy-2-oxoethyl)-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3p



3p

Colorless oil, 20.3 mg, 80% yield, 95% *ee*. HPLC CHIRALCEL IA, n-hexane/2-propanol = 60/40, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 14.305 min (minor), 20.448 min (major). $[\alpha]_D^{20}$ = -158.45 (c 0.284, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (s, 1H), 6.31 – 6.23 (m, 2H), 5.16 – 5.05 (m, 1H), 4.52 (d, *J* = 18.0 Hz, 1H), 4.16 (d, *J* = 17.4 Hz, 1H), 3.81 (s, 3H), 3.60 (s, 3H), 2.88 (dd, *J* = 14.1, 8.1 Hz, 1H), 2.79 – 2.69 (m, 4H), 2.55 (dd, *J* = 13.8, 7.2 Hz, 1H), 1.26 (d, *J* = 6.0 Hz, 7H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 176.0, 168.8, 168.7, 167.6, 160.2, 150.9, 132.9, 128.0, 85.7, 69.7, 67.8, 66.3, 53.5, 53.4, 44.0, 35.2, 28.4, 21.9, 21.9. HRMS (ESI): exact mass calcd for $C_{21}H_{25}ClN_5O_8$ $(M+H)^+$ requires m/z 510.1386, found m/z 510.1386.

Dimethyl(6*S*,8a*S*)-9-(2-(benzyloxy)-2-oxoethyl)-4-chloro-6-(2,5-dioxopyrrolidin-1-yl)-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3q

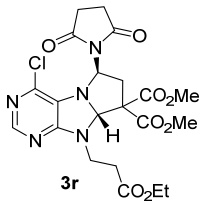


3q

Colorless oil, 21.2 mg, 76% yield, >99% *ee*. HPLC CHIRALCEL IA, n-hexane/2-propanol = 60/40, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 28.371 min (minor), 32.867 min (major). $[\alpha]_D^{20}$ = -153.24 (c 0.278, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.40 – 7.30 (m, 5H), 6.30 – 6.22 (m, 2H), 5.20 (s, 2H), 4.60 (d, *J* = 18.0 Hz, 1H), 4.27 (d, *J* = 18.0 Hz, 1H), 3.75 (s, 3H), 3.59 (s, 3H), 2.87 (dd, *J* = 14.1, 8.1Hz, 1H), 2.80 – 2.68 (m, 4H), 2.56 (dd, *J* = 14.4, 7.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.0, 168.8, 168.7, 168.1, 160.2, 150.9, 135.3, 133.1, 128.7, 128.5, 128.0, 85.8, 67.9,

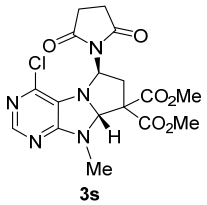
67.4, 66.3, 53.5, 53.4, 43.9, 35.2, 31.0, 28.4. HRMS (ESI): exact mass calcd for $C_{25}H_{25}ClN_5O_8$ $(M+H)^+$ requires m/z 558.1386, found m/z 558.1385.

Dimethyl(6*S*,8a*S*)-4-chloro-6-(2,5-dioxopyrrolidin-1-yl)-9-(3-ethoxy-3-oxopropyl)-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3r



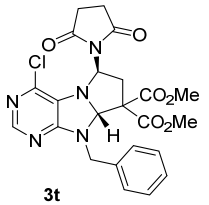
Colorless oil, 12.7 mg, 50% yield, 98% *ee*. HPLC CHIRALCEL ID, n-hexane/2-propanol = 40/60, flow rate = 0.7 mL/min, λ = 254 nm, retention time: 26.803 min (minor), 62.237 min (major). $[\alpha]_D^{20}$ = -185.80 (c 0.162, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (s, 1H), 6.28 – 6.22 (m, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 4.03 (m, 1H), 3.83 (s, 3H), 3.81 – 3.76 (m, 1H), 3.59 (s, 3H), 2.90 – 2.84(dd, *J* = 13.8, 7.8 Hz, 1H), 2.81 (m, 1H), 2.75 (m, 4H), 2.67 (m, 1H), 2.50 (dd, *J* = 13.8, 7.2 Hz, 1H), 1.22 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.0, 171.2, 168.8, 168.6, 159.3, 151.3, 132.6, 128.1, 85.6, 68.0, 66.4, 60.9, 53.5, 53.4, 38.9, 35.3, 31.7, 28.4, 14.2. HRMS (ESI): exact mass calcd for $C_{21}H_{25}ClN_5O_8$ $(M+H)^+$ requires m/z 510.1386, found m/z 510.1379.

Dimethyl(6*S*,8a*S*)-4-chloro-6-(2,5-dioxopyrrolidin-1-yl)-9-methyl-6,7,8a,9-tetrahydro-*8H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3s



Colorless oil, 12.4 mg, 59% yield, 97% *ee*. HPLC CHIRALCEL IE, n-hexane/2-propanol = 60/40, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 32.904 min (minor), 80.125 min (major). $[\alpha]_D^{20}$ = -262.18 (c 0.156, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (s, 1H), 6.25 (t, *J* = 7.8 Hz, 1H), 6.12 (s, 1H), 3.83 (s, 3H), 3.59 (s, 3H), 3.13 (s, 3H), 2.89 (dd, *J* = 12.6, 8.4 Hz, 1H), 2.78 – 2.70 (m, 4H), 2.49 (dd, *J* = 13.8, 7.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1, 168.8, 168.5, 159.9, 151.4, 132.3, 127.9, 87.34, 68.1, 66.1, 53.4, 53.3, 35.4, 28.4. HRMS (ESI): exact mass calcd for $C_{17}H_{19}ClN_5O_6$ $(M+H)^+$ requires m/z 424.1018, found m/z 424.1022.

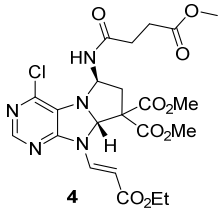
Dimethyl(6*S*,8a*S*)-9-benzyl-4-chloro-6-(2,5-dioxopyrrolidin-1-yl)-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 3t



3t

Colorless oil, 14.2 mg, 57% yield, 97% *ee*. HPLC CHIRALCEL IA, n-hexane/2-propanol = 60/40, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 17.833 min (minor), 22.044 min (major). $[\alpha]_D^{20}$ = -162.29 (c 0.236, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 1H), 6.24 (t, *J* = 7.8 Hz, 1H), 6.15 (s, 1H), 5.11 (d, *J* = 15.6 Hz, 1H), 4.46 (d, *J* = 15.6 Hz, 1H), 3.82 (s, 3H), 3.60 (s, 3H), 2.88 (dd, *J* = 13.8, 8.1 Hz, 1H), 2.74 – 2.67 (m, 4H), 2.48 (dd, *J* = 14.1, 7.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 169.0, 168.7, 159.7, 151.4, 135.8, 132.8, 128.9, 128.6, 128.1, 128.0, 84.7, 68.2, 66.5, 53.5, 53.4, 45.6, 35.3, 28.3. HRMS (ESI): exact mass calcd for $C_{23}H_{23}ClN_5O_8$ $(M+H)^+$ requires m/z 500.1331, found m/z 500.1334.

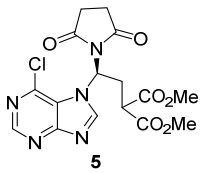
Dimethyl(6*R*,8a*S*)-4-chloro-9-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)-6-((*E*)-4-methoxy-4-oxobut-2-enamido)-6,7,8a,9-tetrahydro-8*H*-pyrrolo[2,1-*f*]purine-8,8-dicarboxylate 4



4

White solid, m.p. = 173-175 ^{o}C. 38.3 mg, 71% yield, 98% *ee*. HPLC CHIRALCEL AD, n-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 15.090 min (minor), 51.240 min (major). $[\alpha]_D^{20}$ = 36.30 (c 0.707, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.88 (d, *J* = 14.4 Hz, 1H), 6.65 (d, *J* = 5.4 Hz, 1H), 6.29 (s, 1H), 6.14 (d, *J* = 13.8 Hz, 1H), 5.60 (dd, *J* = 12.6, 6.6 Hz, 1H), 4.10 (m, 2H), 3.74 (s, 3H), 3.58 (s, 3H), 3.44 (s, 3H), 2.91 (dd, *J* = 14.1, 7.5 Hz, 1H), 2.57 (t, *J* = 6.6 Hz, 2H), 2.50 (dd, *J* = 14.1, 6.3 Hz, 1H), 2.42 (m, 2H), 1.19 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.5, 171.7, 168.9, 168.2, 167.5, 156.0, 151.1, 136.4, 136.3, 129.5, 102.6, 84.9, 69.8, 64.8, 60.4, 53.7, 53.5, 52.1, 39.2, 31.1, 29.0, 14.5. HRMS (ESI): exact mass calcd for $C_{22}H_{27}ClN_5O_9$ $(M+H)^+$ requires m/z 540.1492, found m/z 540.1498.

Dimethyl (*S*)-2-(2-(6-chloro-7*H*-purin-7-yl)-2-(2,5-dioxopyrrolidin-1-yl)ethyl)malonate 5



5

Colorless oil, 20.9 mg, 51% yield, 99% *ee*. HPLC CHIRALCEL IE, n-hexane/2-propanol = 60/40, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 70.313 min (minor), 86.827 min (major). $[\alpha]_D^{20} = 39.56$ (c 0.150, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.86 (s, 1H), 7.28 (d, *J* = 7.2 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 3.37 (t, *J* = 6.9 Hz, 1H), 3.27 – 3.15 (m, 2H), 2.78 (s, 4H). ^{13}C NMR (151 MHz, MeOD) δ 178.7, 169.9, 169.9, 162.1, 153.3, 151.7, 144.6, 123.3, 61.3, 53.5, 53.4, 31.7, 29.1. HRMS (ESI): exact mass calcd for $C_{16}H_{16}ClN_5O_6$ $(M+H)^+$ requires m/z 432.0681, found m/z 432.0689.

7. Complete reference for Gaussian 09

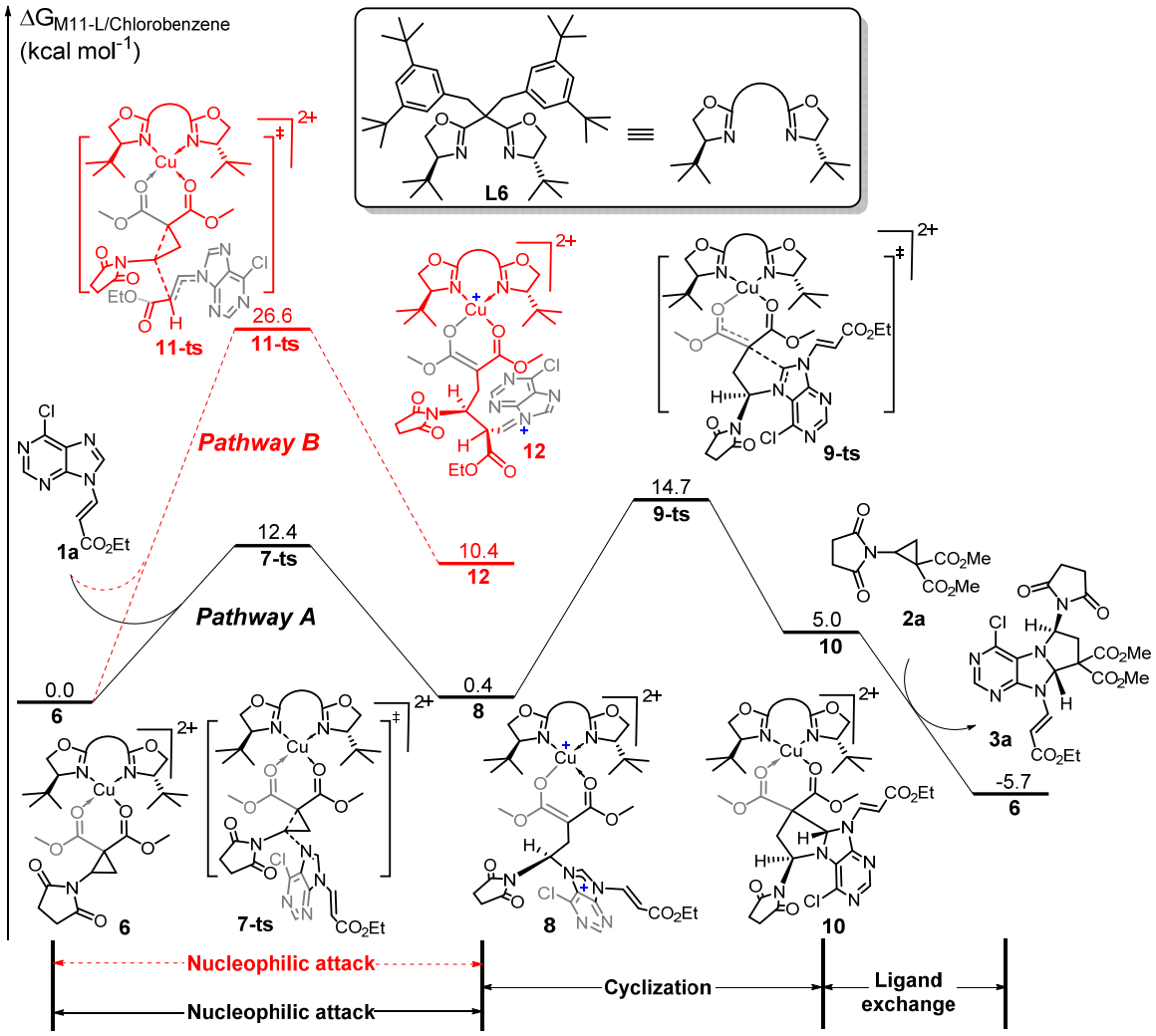
Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; and Fox, D. J. Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, CT, **2013**.

8. Computational methods.

All of the DFT calculations were carried out with the Gaussian 09 series of programs. The B3-LYP[ii] functional with the standard 6-31G(d) basis set was used for geometry optimizations. Harmonic vibrational frequency calculations were performed for all stationary points to determine whether they are local minima or transition structure and to derive thermochemical corrections for the enthalpies and

free energies. The M11-L functional[iii] proposed by Truhlar et al. with the 6-311+g(d) basis set was used to calculate the single point energies, because it is expected that this strategy will provide greater accuracy with regard to the energetic information.[iv] The solvent effects were considered by single-point calculations of the gas-phase stationary points with the SMD continuum model.[v] The energies reported in this paper are the M11-L calculated Gibbs free energies in chlorobenzene solvent based on B3LYP calculated geometries with thermodynamic corrections calculated at the same level.

9. Free energy profiles for [3+2] cycloaddition of purine 1a.



10. B3-LYP and M11-L absolute calculation energies, enthalpies, and free energies.

Geometry	$E_{(elec\text{-}B3\text{-}LYP)}$[1]	$H_{(corr\text{-}B3\text{-}LYP)}$[2]	$G_{(corr\text{-}B3\text{-}LYP)}$[3]	$E_{(solv\text{-}M11\text{-}L)}$[4]	IF[5]
1a	-1216.120600	0.206760	0.146471	-1216.160923	-
2a	-933.0929729	0.259962	0.193192	-933.1421045	
3a	-2149.239784	0.471092	0.367707	-2149.340116	
6	-3146.950614	1.393417	1.203375	-3147.453430	-

7-ts	-4363.085342	1.601020	1.367124	-4363.611875	-57.9
8	-4363.119608	1.604432	1.374758	-4363.638584	
9-ts	-4363.075120	1.603558	1.379627	-4363.620700	-220.6
10	-4363.080390	1.604330	1.377367	-4363.633884	
11-ts	-4363.066320	1.600985	1.370740	-4363.592797	-275.1
12	-4363.074403	1.602878	1.372678	-4363.620673	

[1]The electronic energy calculated by B3-LYP in gas phase. [2]The thermal correction to enthalpy calculated by B3-LYP in gas phase. [3]The thermal correction to Gibbs free energy calculated by B3-LYP in gas phase. [4]The electronic energy calculated by M11-L in chlorobenzene solvent. [5]The B3-LYP calculated imaginary frequencies for the transition states.

11. B3-LYP geometries for all the optimized compounds and transition states.

1a

C	-1.20891500	-0.05356500	-0.00033600
C	-2.53994700	0.41679600	-0.00023900
C	-3.51265100	-0.58637800	-0.00023800
C	-1.86045600	-2.17205400	-0.00053500
C	-1.32767500	2.15336000	-0.00057700
H	-1.62218900	-3.23197100	-0.00035700
H	-0.96701700	3.17465100	-0.00058400
N	-3.16961600	-1.86427300	-0.00031800
N	-0.82434500	-1.32688800	-0.00043900
N	-0.42174800	1.09202200	-0.00013800
N	-2.58157800	1.79927800	0.00004500
C	0.96837100	1.23173200	0.00012200
H	1.30659800	2.26386700	0.00003500
C	1.86499000	0.23530700	0.00040600
H	1.57967700	-0.80856300	0.00051000
C	3.29963200	0.59763000	0.00059700
O	3.74067800	1.73305400	0.00010100
O	4.07025000	-0.50992800	0.00049700
C	5.49836200	-0.28398700	0.00025500
H	5.75994700	0.30789400	-0.88293600
H	5.76022200	0.30800900	0.88328800
C	6.17514300	-1.64182800	0.00023700
H	7.26303200	-1.51339800	0.00006100
H	5.89633200	-2.21855000	0.88801700
H	5.89605800	-2.21866800	-0.88737900
Cl	-5.20707100	-0.18419600	0.00013800

2a

C	-3.28744900	0.97983400	0.93704800
C	-3.88935000	-0.04415900	-0.03590900
H	-3.76498900	0.98084200	1.92201500
H	-3.31948200	2.00730100	0.56247400
H	-4.72676600	-0.61059300	0.38263200
H	-4.23949300	0.40304900	-0.97146700
N	-1.61021400	-0.57183000	0.32166100
C	-2.75556800	-1.01181800	-0.36222700
C	-1.82765500	0.57132000	1.09947300
O	-2.80918000	-1.99060200	-1.07237400
O	-0.97717600	1.11925400	1.76778900
C	-0.34305600	-1.23671500	0.24011300
C	0.19664000	-1.61069200	-1.09107200
C	0.88896400	-0.49451300	-0.30864000
H	-0.10557600	-1.87518700	1.08586500
H	-0.35439200	-1.28654500	-1.96586300
H	0.71962100	-2.55741600	-1.17523400
C	0.65409200	0.90946800	-0.79048300
O	-0.22750500	1.20696200	-1.57436200
O	1.46939600	1.79705100	-0.20703500
C	1.20563900	3.17426600	-0.51721400
H	0.22918100	3.46519000	-0.12084800
H	1.99921700	3.73831700	-0.02694600
H	1.22347500	3.33739900	-1.59756600
C	2.18535900	-0.90288900	0.34111000
O	2.27265600	-1.76445700	1.19297600
O	3.24521800	-0.28520900	-0.20472100
C	4.52255000	-0.66812900	0.33238400
H	5.25563600	-0.07381300	-0.21329800
H	4.56829400	-0.44945500	1.40226400
H	4.69850400	-1.73611500	0.17866800

3a

C	-0.64364600	-1.66781500	-0.00635900
C	0.77238200	-1.68745600	-0.02394600
C	1.34324300	-2.91929400	0.23329100
C	-0.71981200	-3.84587300	0.50764800
C	0.09634800	0.48279200	-0.51315700
H	-1.31276400	-4.72911300	0.72884500
N	0.59735600	-3.99590500	0.50861700
N	-1.40868100	-2.71233800	0.25909300
N	-1.07400000	-0.38954100	-0.32647600
N	1.24928700	-0.42675300	-0.38098100
C	-2.36299600	0.05044800	-0.59820600
H	-2.40871300	1.09018500	-0.90863200
C	-3.49918600	-0.66882200	-0.51112400
H	-3.51881700	-1.70107800	-0.19317200
C	-4.76575400	-0.00677300	-0.86223000
O	-4.90090300	1.14265800	-1.24447100
O	-5.80861100	-0.86313800	-0.70452700
C	-7.10819200	-0.32706200	-1.01861600
H	-7.29904800	0.54263700	-0.38056100
H	-7.10866100	0.02363200	-2.05628900
C	-8.12461300	-1.43178300	-0.79167300
H	-9.13197900	-1.06498300	-1.01810200
H	-7.91753200	-2.29197800	-1.43674000
H	-8.10688400	-1.77131700	0.24916700
Cl	3.08242900	-3.14401400	0.21185900
C	2.38892300	0.24216800	0.24176000

C	5.77077600	0.05390000	-1.43028000
C	4.89490300	0.60256500	-2.56796300
H	6.59139800	0.72194700	-1.15104300
H	6.21370600	-0.92211700	-1.65093700
H	5.23808800	1.56156400	-2.96710600
H	4.80867100	-0.08461000	-3.41595900
N	3.55158600	0.29507500	-0.64843900
C	4.83310200	-0.09689000	-0.23592300
C	3.51019600	0.78739200	-1.95438000
O	2.53162500	1.28330500	-2.47564800
O	5.11205800	-0.46594300	0.88352500
H	2.72806100	-0.30466200	1.12198000
C	1.88401000	1.66299000	0.60933300
H	2.25994200	1.97334600	1.58513300
H	2.23481400	2.38071500	-0.13442700
C	0.33616300	1.60141600	0.56250600
C	-0.28330000	2.93226900	0.12982200
O	-1.05717800	3.06624800	-0.79192400
C	-0.29431800	1.20860900	1.90319500
O	-1.32924900	1.66566400	2.32986000
O	0.16465100	3.93665400	0.89692100
O	0.43352000	0.26345500	2.52883700
C	-0.40633700	5.23138600	0.61875300
H	0.05416900	5.91017600	1.33622600
H	-0.17827500	5.53534900	-0.40571300
H	-1.48970700	5.19895300	0.75460900
C	-0.11798300	-0.22778800	3.76943400
H	0.58907100	-0.97790800	4.12218700
H	-0.21110600	0.58909800	4.48859800
H	-1.10094200	-0.67056000	3.59390500
H	0.06562300	0.95568600	-1.49815900

6

Cu	-0.02515000	0.64461800	0.42995600
C	0.12451300	7.08943900	-2.27934000
C	-0.38828300	8.20516600	-1.35179500
H	1.07758100	7.33564200	-2.75974600
H	-0.57195200	6.82754700	-3.08137700
H	0.24306300	9.09879300	-1.35167900
H	-1.40316100	8.53721600	-1.59237900
N	0.06958500	6.25971700	-0.07181900
C	-0.38811400	7.60804500	0.04627100
C	0.33879600	5.87915800	-1.38535800
O	-0.70038400	8.10939300	1.09527400
O	0.65412700	4.74872200	-1.71339900
C	0.31931500	5.47814600	1.09385300
C	-0.76745500	5.21747200	2.04761700
C	-0.22123600	4.00652700	1.23585000
H	1.32525700	5.57702900	1.49186200
H	-1.76694400	5.53693800	1.77764500
H	-0.53717600	5.21614900	3.10683200
C	-1.04923300	3.42645900	0.14096000
O	-0.90666100	2.28729800	-0.33871400
O	-1.98676600	4.23649600	-0.28562100
C	-2.79836000	3.82069300	-1.42159400
H	-3.32243800	2.89489800	-1.18409500
H	-3.50103400	4.63796400	-1.57181500
H	-2.15206000	3.68766000	-2.29051900
C	0.65830400	3.06928400	1.99544400
O	0.65419300	1.82808400	1.90678900
O	1.44050000	3.68343900	2.85122100
C	2.33300000	2.89403400	3.69252400
H	2.87686700	3.63053600	4.28019100
H	1.74262600	2.23902600	4.33468500
H	3.00860800	2.31098300	3.06573300
C	0.07312800	-2.66789500	-0.47294200
C	1.33259000	-3.63770100	-0.47475100
H	1.09459100	-4.40961400	0.26415900
H	1.31961300	-4.12652100	-1.45217500
C	-1.12428800	-3.58035200	-0.98149200
H	-0.87379300	-3.82523200	-2.01847900
H	-1.04636300	-4.50949200	-0.41213700
C	2.72345400	-3.09172000	-0.21896700
C	3.06219200	-2.42379000	0.96643200
C	3.72970900	-3.38318600	-1.14798000
C	4.38266700	-2.03640300	1.23091100
H	2.29609700	-2.24118500	1.71113700
C	5.06739400	-3.03003900	-0.91959800
H	3.46013800	-3.91750200	-2.05262100
C	5.35735200	-2.34984000	0.27132500
H	6.38734700	-2.07117100	0.46891400
C	-2.54965400	-3.07413300	-0.89653900
C	-2.99120600	-1.97231300	-1.64263900
C	-3.47759800	-3.81025400	-0.15010000
C	-4.33998800	-1.59211500	-1.64699400
H	-2.28226700	-1.43788900	-2.26559900
C	-4.84012300	-3.47875400	-0.13859600
H	-3.12777100	-4.67602500	0.40229300
C	-5.23442600	-2.36021000	-0.88572100
H	-6.28596100	-2.09251800	-0.89600800
C	-0.22292800	-2.20519500	0.93477100
C	-0.72144100	-1.11026600	2.87505600
C	-0.47738900	-2.61581000	3.13741000
H	-1.30330900	-3.13032200	3.62423300
O	-0.33811100	-3.19670000	1.80657300
N	-0.38879200	-1.00933200	1.41460300
C	0.31915800	-1.53883500	-1.44269300
C	0.78741000	0.42810100	-2.49838100
C	0.51989900	-0.69685600	-3.52198100
H	1.30368400	-0.83845300	-4.26295000
N	0.42665700	-0.26617200	-1.22039700
O	0.46833000	-1.91272300	-2.70667100
H	0.45126900	-2.82249200	3.67396800
H	0.01207900	-0.50523400	3.41696900
H	0.08118200	1.25140500	-2.63515300
H	-0.44930900	-0.61174800	-4.01973800
C	6.20233200	-3.38921700	-1.89782700
C	5.68101900	-4.07932300	-3.17298500
H	5.18037600	-5.02892100	-2.95252700
H	4.98377600	-3.44170300	-3.73023900
H	6.52084500	-4.30351900	-3.83838400
C	7.18519400	-4.35576300	-1.19171300
H	8.00185000	-4.62504100	-1.87082100
H	7.63142400	-3.90573300	-0.29857000
H	6.68033700	-5.27903200	-0.88663100
C	6.96128600	-2.10796400	-2.31800900
H	7.77652300	-2.36259200	-3.00411300
H	6.29700800	-1.40361600	-2.83264600
H	7.40477800	-1.58981600	-1.46125500
C	4.79925200	-1.31950400	2.53009800
C	3.61262900	-1.09784000	3.48834500
H	2.82926600	-0.47538500	3.03443000
H	3.16243300	-2.04649600	3.80423100
H	3.96178900	-0.58869800	4.39349300

C	5.85673500	-2.16833100	3.27715000
H	5.45592200	-3.15337400	3.53997000
H	6.75586600	-2.32451800	2.67395700
H	6.16251000	-1.66729600	4.20283600
C	5.40326900	0.06225000	2.18324000
H	6.27946600	-0.02682300	1.53418300
H	4.67046800	0.69275000	1.66134900
H	5.72074100	0.58170700	3.09547900
C	2.23407900	1.02079600	-2.52257600
C	2.33828900	1.88980600	-3.79479400
H	1.63280200	2.72836700	-3.76465600
H	3.34719200	2.30620200	-3.88008300
H	2.15132100	1.31324000	-4.70874700
C	2.46507700	1.91756800	-1.29161500
H	1.72544000	2.72033100	-1.22463600
H	2.46905900	1.32996700	-0.36320600
H	3.45110900	2.38987000	-1.36472900
C	3.31606000	-0.07194200	-2.53470900
H	3.26699000	-0.70829200	-1.64698800
H	3.26512200	-0.71544700	-3.41980800
H	4.30536300	0.39756100	-2.54475900
C	-2.14755000	-0.60885900	3.26938500
C	-3.25831800	-1.39751300	2.55608200
H	-3.21396900	-1.28012300	1.46887200
H	-3.22549100	-2.46887200	2.77885000
H	-4.23687900	-1.03504600	2.88820600
C	-2.30809600	0.88458900	2.93260400
H	-2.27014700	1.06319800	1.85030500
H	-3.28501700	1.23900700	3.27801500
H	-1.54062000	1.49405600	3.42255700
C	-2.27914700	-0.77063700	4.80122500
H	-1.49789700	-0.21640800	5.33611500
H	-3.24723200	-0.38345400	5.13463200
H	-2.22847900	-1.81720500	5.12058700
C	-4.87113800	-0.40680600	-2.47618900
C	-5.91344500	-0.91594900	-3.50150400
H	-6.76513300	-1.39826500	-3.01258400
H	-6.30197500	-0.08160900	-4.09674700
H	-5.46610500	-1.64350700	-4.18744500
C	-3.75319200	0.31175800	-3.25639400
H	-2.97716400	0.70939500	-2.58812100
H	-3.27421400	-0.35309900	-3.98475100
H	-4.17640300	1.15253200	-3.81704500
C	-5.54149300	0.62076100	-1.53347900
H	-6.38144900	0.18578600	-0.98358900
H	-4.82622900	1.00090100	-0.79118100
H	-5.93029000	1.47046300	-2.10735500
C	-5.89537800	-4.31278000	0.61355500
C	-6.88865600	-4.90857900	-0.41467700
H	-7.64309200	-5.51560600	0.09797700
H	-7.41535900	-4.12829800	-0.97422200
H	-6.37191400	-5.54999900	-1.13699800
C	-5.26780300	-5.47622400	1.40514400
H	-4.75182700	-6.18815800	0.75106800
H	-4.55555900	-5.12390700	2.16170100
H	-6.05313000	-6.02912900	1.93043800
C	-6.66898800	-3.41411400	1.60755500
H	-7.17330600	-2.58097500	1.10685100
H	-7.43752700	-3.99992900	2.12365900
H	-5.99956100	-2.99556800	2.36861500

7-ts

Cu	1.49486400	0.13753400	-0.22993400
C	-4.45346300	-4.13956000	-1.74502100
C	-3.97883900	-4.56556900	-0.34546200
H	-5.48510900	-4.42483600	-1.96837800
H	-3.83271200	-4.55456300	-2.54720500
H	-4.79704800	-4.93939000	0.28065700
H	-3.20838700	-5.34160700	-0.35152000
N	-3.68309500	-2.20594800	-0.58499100
C	-3.42868800	-3.31385600	0.30511400
C	-4.34451100	-2.62531800	-1.79388300
O	-2.86374500	-3.17394100	1.35773900
O	-4.74390900	-1.86980600	-2.64114800
C	-3.50757300	-0.93175300	-0.16088200
C	-3.33006200	0.23971900	-1.01437400
C	-1.83766500	0.09111400	-0.71276800
H	-3.44053000	-0.82018000	0.91507600
H	-3.75081000	1.15003800	-0.59475300
H	-3.58391100	0.09918200	-2.05961600
C	-1.28492700	0.75935900	0.44074300
O	-0.07414100	0.79167800	0.78611500
O	-2.19570800	1.36857300	1.18802700
C	-1.76834100	2.05287000	2.39317800
H	-1.05376200	2.83867100	2.14375000
H	-2.68119400	2.47187800	2.81206800
H	-1.32073000	1.33932800	3.08735600
C	-0.97223100	-0.59143300	-1.63656400
O	0.28762000	-0.61343100	-1.61036500
O	-1.61445300	-1.23507500	-2.60520500
C	-0.83546900	-1.89778800	-3.63128700
H	-1.57445200	-2.34595600	-4.29350900
H	-0.23366000	-1.16653900	-4.17401800
H	-0.18991400	-2.65808100	-3.18782900
C	-8.14677500	0.27548000	1.26863000
C	-6.81029500	-0.11667000	1.50246000
C	-6.42090900	-0.05704500	2.84206400
C	-8.50371700	0.68652000	3.42131600
C	-7.12055500	-0.30169300	-0.59464500
H	-9.15950900	1.00601000	4.22519800
H	-6.98915700	-0.48720000	-1.65330200
N	-7.25077500	0.33903800	3.78120400
N	-9.01647000	0.67796500	2.18892000
N	-8.33000100	0.14686700	-0.10300000
N	-6.19021900	-0.47406300	0.31802100
C	-9.46725600	0.39846400	-0.89573500
H	-9.31430300	0.21425200	-1.95490900
C	-10.65517600	0.82489400	-0.45557100
H	-10.86683000	1.02429400	0.58710800
C	-11.72612900	1.02745000	-1.47107300
O	-11.58369600	0.83688300	-2.66453200
O	-12.85570100	1.44471100	-0.88580200
C	-13.98856700	1.67928900	-1.76789400
H	-13.70159400	2.44178500	-2.49839600
H	-14.19585300	0.75378800	-2.31341100
C	-15.15582500	2.11579500	-0.90494600
H	-16.02980100	2.30074800	-1.53813400
H	-15.41722400	1.34179800	-0.17667100
H	-14.92242400	3.03818700	-0.36400200
Cl	-4.79392000	-0.52146600	3.32183400
C	4.90984300	0.26231200	0.20553500
C	5.92948300	-0.94871100	0.07273700
H	6.58162600	-0.67928200	-0.76388500
H	6.54554400	-0.91349800	0.97488100

C	5.82140500	1.50999000	0.57460100
H	6.22226400	1.28856600	1.56868200
H	6.66525100	1.47233800	-0.11853200
C	5.41078600	-2.36076000	-0.11444300
C	4.68136800	-2.73917000	-1.25055700
C	5.78271800	-3.34016000	0.81399700
C	4.30900800	-4.07267000	-1.46481200
H	4.44273400	-1.99205200	-1.99871900
C	5.45055400	-4.69047400	0.63193700
H	6.36673000	-3.03874800	1.67704600
C	4.70529900	-5.02021000	-0.50853100
H	4.44384000	-6.06078600	-0.67164900
C	5.23155700	2.90613300	0.54844800
C	4.16698200	3.28304900	1.37914200
C	5.84837200	3.87546400	-0.25146000
C	3.70142100	4.60440800	1.41058800
H	3.72216900	2.54641500	2.03846300
C	5.43266900	5.21450400	-0.23648000
H	6.68551000	3.57643400	-0.87312900
C	4.35069800	5.54171400	0.59253700
H	4.01357900	6.57277400	0.61886300
C	4.24012900	0.52388600	-1.12195700
C	2.85521700	0.96818200	-2.87409700
C	4.31485900	0.79271800	-3.35752500
H	4.71224500	1.63731200	-3.91691100
O	5.09175600	0.69004900	-2.12729900
N	2.98296000	0.62360300	-1.42079100
C	3.94582800	-0.02648500	1.33219700
C	2.19515000	-0.53395300	2.69950200
C	3.46914500	-0.23486100	3.52447000
H	3.76531700	-1.02832400	4.20749900
N	2.66310800	-0.21291900	1.31104200
O	4.52474100	-0.11399700	2.52435100
H	4.48201400	-0.13003300	-3.91820500
H	2.20693200	0.21380200	-3.32895300
H	1.40238400	0.17818900	2.94438500
H	3.42945500	0.71573600	4.06165100
C	5.90892500	-5.79869000	1.60028500
C	6.64215100	-5.23451700	2.83225400
H	7.55846300	-4.70037300	2.55742600
H	6.00649200	-4.55486400	3.41324400
H	6.93251700	-6.05625800	3.49486800
C	6.87928900	-6.74477200	0.85066100
H	7.22225200	-7.54238500	1.51939400
H	6.40167100	-7.21794900	-0.01389400
H	7.76056200	-6.20158800	0.49195600
C	4.68824800	-6.60975500	2.09609600
H	5.01620100	-7.40390600	2.77596600
H	3.98227200	-5.97190500	2.64088300
H	4.14617800	-7.08698400	1.27307600
C	3.52476900	-4.53118500	-2.70983200
C	3.20734800	-3.36772700	-3.66920300
H	2.59277500	-2.59573700	-3.18670800
H	4.11976500	-2.89610400	-4.05298600
H	2.65126800	-3.74558700	-4.53426100
C	4.35546800	-5.57772000	-3.49176800
H	5.31111200	-5.15457600	-3.81984900
H	4.57330500	-6.46263100	-2.88633400
H	3.80816500	-5.91145000	-4.38099500
C	2.18520300	-5.16673800	-2.26669700
H	2.33911800	-6.02580700	-1.60633200
H	1.56617200	-4.43872000	-1.72520200
H	1.62221300	-5.51855400	-3.13980900
C	1.62413600	-1.97537400	2.89235500
C	1.15353400	-2.08393900	4.36037600
H	0.40102800	-1.32268500	4.60100500
H	0.69826000	-3.06425600	4.53371700
H	1.97670400	-1.98227900	5.07641700
C	0.40469500	-2.20395600	1.98161000
H	-0.38352300	-1.46746500	2.16430300
H	0.67731500	-2.17324100	0.91866900
H	-0.02490900	-3.19231300	2.17301500
C	2.67402000	-3.05782400	2.59330300
H	3.01379100	-3.02290500	1.55427600
H	3.55580300	-2.98158200	3.23875100
H	2.23919100	-4.04804400	2.76598700
C	2.24174400	2.37422800	-3.17306800
C	3.09293800	3.51447300	-2.59065500
H	3.15310900	3.46554300	-1.49953600
H	4.11474500	3.52264200	-2.98427300
H	2.64448300	4.47833600	-2.85337200
C	0.81598000	2.48129300	-2.60095300
H	0.80707000	2.42516400	-1.50527400
H	0.38250100	3.44952900	-2.87284500
H	0.15986400	1.70067800	-3.00014700
C	2.15153600	2.51058500	-4.70983100
H	1.54394600	1.71086600	-5.15179900
H	1.68375800	3.46484900	-4.97254400
H	3.13406100	2.49325500	-5.19442400
C	2.54339000	5.06107500	2.31900500
C	3.04663100	6.15657900	3.29011200
H	3.42092100	7.03473800	2.75547200
H	2.23216800	6.48942600	3.94382300
H	3.85818200	5.77982200	3.92227600
C	1.96739000	3.90796300	3.16374800
H	1.57195200	3.09850700	2.53551400
H	2.71723700	3.48515700	3.84331200
H	1.14510600	4.28226900	3.78363500
C	1.40093100	5.63426900	1.44666400
H	1.73395500	6.48468600	0.84383300
H	1.01020800	4.87303300	0.75871100
H	0.57493400	5.98254600	2.07820800
C	6.13172400	6.31453500	-1.05921700
C	6.71657500	7.37267000	-0.09146400
H	7.22028400	8.16370600	-0.65809600
H	5.93872300	7.84533400	0.51735300
H	7.44916800	6.92351700	0.58810800
C	7.28551100	5.76115100	-1.91769100
H	8.07172700	5.30628200	-1.30460100
H	6.93973400	5.01547900	-2.64411700
H	7.74566000	6.57748000	-2.48378200
C	5.11054100	6.99494600	-2.00171900
H	4.27867000	7.44675400	-1.45149300
H	5.59911100	7.79197300	-2.57327300
H	4.69161000	6.27712000	-2.71688800

8

Cu	1.34063100	0.12412800	-0.17459500
C	-4.02799900	-4.18921100	-1.23761300
C	-3.35228900	-4.44620000	0.11959400
H	-4.89414100	-4.82954400	-1.42896900
H	-3.34907600	-4.31427400	-2.08716800
H	-3.88922900	-5.17557700	0.73524200
H	-2.32006400	-4.79866500	0.04018800

N	-4.08615200	-2.19327200	0.02902100
C	-3.36598000	-3.10700100	0.83863200
C	-4.48082900	-2.73963800	-1.19795600
O	-2.86898000	-2.81157400	1.90014900
O	-5.09398700	-2.12893100	-2.05314900
C	-4.23936400	-0.80406200	0.42238300
C	-3.48804300	0.20166600	-0.48437200
C	-1.98387100	0.08838200	-0.35966000
H	-3.84208900	-0.73940800	1.43294000
H	-3.80882300	1.20335900	-0.18020400
H	-3.78220800	0.05056300	-1.52390500
C	-1.34134000	0.65506000	0.76717000
O	-0.09773200	0.69508000	1.02500500
O	-2.18504300	1.19834900	1.66306400
C	-1.62166600	1.83395700	2.82871000
H	-0.93688700	2.63312400	2.53838500
H	-2.47565000	2.24092800	3.36934200
H	-1.09652300	1.10234100	3.44698400
C	-1.21587800	-0.52290100	-1.37709000
O	0.05258500	-0.57404000	-1.47016000
O	-1.93572300	-1.10023500	-2.35585300
C	-1.23510700	-1.64753300	-3.48987400
H	-2.01636200	-2.05019700	-4.13414400
H	-0.68327800	-0.86426700	-4.01503000
H	-0.54520000	-2.43464800	-3.17821700
C	-7.74430000	0.15672600	1.26585400
C	-6.46036700	-0.22829500	1.69131700
C	-6.29134900	-0.29828800	3.08636800
C	-8.48247200	0.35746700	3.34719800
C	-6.48670800	-0.19510000	-0.51621700
H	-9.27698800	0.58936400	4.04938600
H	-6.17452100	-0.33333700	-1.54066300
N	-7.30138600	-0.00308800	3.87847700
N	-8.76979200	0.45446300	2.04734300
N	-7.72472100	0.16279400	-0.13559800
N	-5.69385600	-0.44170700	0.53638700
C	-8.76326000	0.46621600	-1.05864100
H	-8.46074300	0.38283700	-2.09773100
C	-10.00861300	0.82396800	-0.73924400
H	-10.36668900	0.92103300	0.27736100
C	-10.94207300	1.10018200	-1.87790600
O	-10.61559200	1.02470400	-3.04601900
O	-12.14808900	1.43116500	-1.41825800
C	-13.16669400	1.72711600	-2.42327300
H	-12.80171300	2.55449500	-3.03868400
H	-13.27137800	0.84780900	-3.06531600
C	-14.44692600	2.06803200	-1.68884800
H	-15.23222700	2.29586500	-2.41688300
H	-14.78417000	1.22875600	-1.07294000
H	-14.31215700	2.94306100	-1.04565800
Cl	-4.80312300	-0.77926500	3.82825800
C	4.79886000	0.30866300	-0.04479000
C	5.71552000	1.56220300	0.28388300
H	6.23519200	1.30272400	1.21149600
H	6.47267800	1.58688000	-0.50361300
C	5.82644200	-0.87115300	-0.31208300
H	6.38623600	-0.56644800	-1.20209100
H	6.52954100	-0.84349800	0.52404800
C	5.09523900	2.94012500	0.40735700
C	4.13792700	3.24187100	1.38603100
C	5.58476900	3.96883000	-0.40630200
C	3.65222400	4.54571200	1.55153900
H	3.79834800	2.45829100	2.05295800
C	5.14566000	5.29258200	-0.26244500
H	6.34276700	3.72803200	-1.14409500
C	4.17201900	5.54424000	0.71397200
H	3.81917700	6.56259800	0.84130300
C	5.32624900	-2.29254800	-0.48279900
C	4.44440100	-2.65635400	-1.50987200
C	5.86247100	-3.29094500	0.33927700
C	4.08187600	-3.99374000	-1.71808600
H	4.06648400	-1.89234200	-2.17870800
C	5.54608100	-4.64434800	0.15539900
H	6.55879700	-2.99941600	1.11805800
C	4.64605700	-4.96014100	-0.87184100
H	4.39089700	-6.00278600	-1.03231900
C	3.94704300	-0.04214300	1.15279400
C	2.34481200	-0.64803800	2.64710600
C	3.67727600	-0.33822500	3.36845100
H	4.05283200	-1.14225400	3.99837200
O	4.63703700	-0.15694600	2.28559900
N	2.67417500	-0.25885000	1.23824000
C	4.00504200	0.59974000	-1.29694800
C	2.46603100	1.07315700	-2.90144300
C	3.87652400	0.92791600	-3.52075300
H	4.21222300	1.78754400	-4.09761800
N	2.72653600	0.68554600	-1.47792100
O	4.76367900	0.81162200	-2.37006500
H	3.65843900	0.59449200	3.93783200
H	1.55404800	0.02498000	2.98860300
H	1.78300700	0.32756100	-3.31733600
H	4.00086400	0.01833500	-4.11373900
C	5.71786500	6.45561300	-1.09662300
C	6.72767300	5.97658800	-2.15716300
H	7.60018400	5.49079500	-1.70611700
H	6.27369200	5.27752500	-2.87029900
H	7.09406600	6.83514600	-2.72940800
C	6.44503200	7.44052400	-0.14803800
H	6.86521200	8.27556300	-0.72013600
H	5.76753600	7.85982700	0.60325300
H	7.26649300	6.94443900	0.38075800
C	4.57352700	7.19993400	-1.82449000
H	4.97812500	8.04160100	-2.39771900
H	4.05173800	6.53642800	-2.52417200
H	3.83292600	7.60455200	-1.12677500
C	2.60842600	4.91781500	2.62303100
C	2.17703200	3.70469700	3.46979300
H	1.72505400	2.91686400	2.85319500
H	3.02047800	3.27385000	4.02262400
H	1.43204800	4.01891400	4.20931100
C	3.20110200	5.97957800	3.58089200
H	4.09792100	5.59971400	4.08255400
H	3.47782600	6.89749100	3.05348900
H	2.46853900	6.24826500	4.35088400
C	1.34812800	5.49465100	1.93502500
H	1.57833300	6.38345900	1.33945500
H	0.89134500	4.75492300	1.26493500
H	0.60314700	5.78422800	2.68602700
C	1.81762600	2.48174500	-3.09757500
C	1.59438200	2.67218800	-4.61491400
H	0.96085900	1.87962300	-5.03276400
H	1.09445500	3.62827000	-4.80112800
H	2.53222600	2.68697600	-5.18107100
C	0.44617700	2.55297100	-2.40062200

H	-0.23478800	1.77801800	-2.76656900
H	0.53273900	2.45494900	-1.31209500
H	-0.01698000	3.52574500	-2.59898200
C	2.70764200	3.60992800	-2.55032400
H	2.85109800	3.52897300	-1.46905600
H	3.69706900	3.63454800	-3.01956100
H	2.23719200	4.57888400	-2.74880400
C	1.83727300	-2.11516100	2.82857100
C	2.89415500	-3.15055900	2.40922900
H	3.14810800	-3.06824800	1.34876700
H	3.82182900	-3.06757300	2.98612200
H	2.50515100	-4.16055700	2.57751300
C	0.55705600	-2.35388400	2.00797100
H	0.74395300	-2.28115500	0.92933600
H	0.17578300	-3.36171300	2.20305300
H	-0.23642200	-1.64943000	2.27199200
C	1.48895800	-2.29168900	4.32368000
H	0.72613400	-1.57251900	4.64707200
H	1.09080500	-3.29664900	4.49737300
H	2.36063200	-2.17516800	4.97749100
C	3.12667600	-4.43195800	-2.84532000
C	3.85271200	-5.42230200	-3.78767000
H	4.18174900	-6.32251300	-3.25977300
H	3.18417600	-5.73886000	-4.59692200
H	4.73662500	-4.95879400	-4.23938600
C	2.63531800	-3.24372800	-3.69512900
H	2.08863800	-2.50738000	-3.09188500
H	3.46570500	-2.73400000	-4.19831600
H	1.95807400	-3.60630000	-4.47670900
C	1.88818900	-5.12544700	-2.22887600
H	2.16387700	-6.00722400	-1.64214600
H	1.34521900	-4.43994900	-1.56521200
H	1.20339100	-5.45535600	-3.01984200
C	6.16942500	-5.76919100	1.00495300
C	6.99395800	-6.69894000	0.08075600
H	7.45051200	-7.50505600	0.66621400
H	6.37216700	-7.16126800	-0.69290100
H	7.79699300	-6.14644600	-0.41951300
C	7.10739900	-5.22705300	2.10063500
H	7.95626200	-4.67609600	1.68016900
H	6.58193200	-4.56828400	2.80259900
H	7.51655000	-6.06181400	2.67908100
C	5.05292100	-6.59194500	1.69066700
H	4.36395000	-7.03858500	0.96600500
H	5.49222400	-7.40938000	2.27341600
H	4.46569100	-5.96849000	2.37521800

9-ts

Cu	0.38453100	0.03731100	-0.75016400
C	-3.93499600	-2.81671700	1.59215200
C	-4.90223600	-2.84291500	0.56855500
C	-5.47252100	-4.08713800	0.32662900
C	-4.17686300	-4.99499400	1.98542100
C	-4.08123700	-0.72825400	0.69088000
H	-3.90614300	-5.87999700	2.55279200
N	-5.09813900	-5.14875500	1.03691800
N	-3.54534100	-3.84922100	2.31261200
N	-3.47841600	-1.49619000	1.70776300
N	-5.07466400	-1.53535600	0.09961600
C	-2.68223600	-0.91107600	2.69036000
H	-2.44336300	0.12916600	2.49248600
C	-2.20623600	-1.47348600	3.81204800
H	-2.41886900	-2.49212300	4.10839100
C	-1.36379700	-0.61649900	4.68054500
O	-0.89792900	0.46517900	4.34067200
O	-1.16447200	-1.19763900	5.86831300
C	-0.40696700	-0.45837100	6.86961300
H	0.03408500	-1.23859300	7.49259600
H	0.38406900	0.10009100	6.36400000
C	-1.31694100	0.45693000	7.67236100
H	-0.73958000	0.93991600	8.46818800
H	-1.74481100	1.23853000	7.03744700
H	-2.12952700	-0.11015800	8.13620100
Cl	-6.68566600	-4.31023000	-0.89778100
C	-5.46955500	-1.07001400	-1.23128000
C	-9.06100400	-0.17537900	-1.89865100
C	-8.71054200	0.79480800	-0.75514800
H	-9.37412800	0.32865000	-2.81798500
H	-9.85527000	-0.88265000	-1.64015700
H	-8.83471000	1.84878300	-1.02211700
H	-9.30158900	0.62752400	0.15102300
N	-6.80599400	-0.50368600	-1.25974300
C	-7.78567500	-0.95648800	-2.17541200
C	-7.24651100	0.53475200	-0.43533000
O	-6.53855700	1.10282800	0.37587000
O	-7.57375100	-1.80367900	-3.01062500
H	-5.50163800	-1.91267400	-1.92119000
C	-4.38390600	-0.01879100	-1.65147700
H	-4.18548800	-0.11352500	-2.72199700
H	-4.76535900	0.98345000	-1.46320300
C	-3.10853400	-0.22160900	-0.80403200
C	-2.38562100	0.98394900	-0.32677300
O	-1.19646900	1.01097800	0.06420900
C	-2.22243100	-1.28814600	-1.35304700
O	-0.98042500	-1.26113800	-1.47252800
O	-3.16472100	2.03296600	-0.18717900
O	-2.90470400	-2.33503200	-1.77541100
C	-2.62213100	3.23281800	0.43753600
H	-3.43323800	3.95605000	0.38602000
H	-2.35534400	3.01553900	1.47195900
H	-1.74522000	3.57826900	-0.10994400
C	-2.18372100	-3.46073000	-2.35272200
H	-2.95665500	-4.18242800	-2.60894900
H	-1.64456600	-3.13466200	-3.24340400
H	-1.49050900	-3.87082700	-1.61685200
H	-4.41261400	0.26693000	0.98677800
C	3.51921400	1.34088600	-0.77695800
C	5.04105200	0.89235200	-0.88056000
H	5.41816700	1.33844200	-1.80497500
H	5.54836900	1.39898600	-0.05796100
C	3.57780600	2.93241300	-0.63125100
H	4.39511100	3.10870900	0.07390100
H	3.92326500	3.30246600	-1.60125600
C	5.40197200	-0.58123000	-0.81646300
C	5.06491000	-1.48830400	-1.83087300
C	6.19806100	-1.01923100	0.24963800
C	5.49481700	-2.82194900	-1.78910500
H	4.49999000	-1.13943500	-2.68571800
C	6.67158100	-2.33658600	0.32250600
H	6.47277800	-0.30345200	1.01670900
C	6.29296400	-3.21337400	-0.70363800
H	6.65204700	-4.23682700	-0.66767400
C	2.37829000	3.73895200	-0.16854700
C	2.03634700	3.77702800	1.19312500
C	1.74995200	4.62533600	-1.05355800

C	1.07252800	4.66771000	1.68275500
H	2.59089100	3.15500100	1.88582800
C	0.78386500	5.54246300	-0.60951400
H	2.07749700	4.64555600	-2.08731400
C	0.45163700	5.51896300	0.75335700
H	-0.27486300	6.23817500	1.11823200
C	2.78973400	0.97030400	-2.05430900
C	1.35434000	0.35047200	-3.72076900
C	2.78520600	0.55051100	-4.26887800
H	2.86066100	1.24398600	-5.10324300
O	3.51400600	1.14048300	-3.15399700
N	1.57925500	0.53265500	-2.24233400
C	2.91364300	0.71257800	0.45197600
C	1.71619700	-0.49611800	1.97238800
C	2.90453400	0.22334300	2.65228700
H	3.59702800	-0.43893500	3.16867400
N	1.80053300	0.06236200	0.58097800
O	3.64877900	0.82777100	1.54698100
H	3.29046900	-0.38402500	-4.52220900
H	1.02502000	-0.68249800	-3.87113000
H	0.77225000	-0.16834800	2.41927700
H	2.59917100	1.03393200	3.31551400
C	7.60166800	-2.82679200	1.44954700
C	7.87042600	-1.73736500	2.50556300
H	8.37131400	-0.86211000	2.07699600
H	6.94734300	-1.40140200	2.99470800
H	8.52574000	-2.13697800	3.28628300
C	8.95904900	-3.24626700	0.83333500
H	9.63931000	-3.59474100	1.61867400
H	8.84552300	-4.05904800	0.10843000
H	9.43648700	-2.40369700	0.32097000
C	6.96695400	-4.04373500	2.16347600
H	7.63278000	-4.40600800	2.95467400
H	6.00885800	-3.77759100	2.62623000
H	6.78818200	-4.87780300	1.47724200
C	5.15013200	-3.84653200	-2.88790600
C	4.27650700	-3.24296100	-4.00468800
H	3.31773800	-2.87336200	-3.61589000
H	4.78694800	-2.42204600	-4.52328800
H	4.05263900	-4.01001000	-4.75338400
C	6.45448600	-4.37167900	-3.53595200
H	7.02712300	-3.55469600	-3.98867300
H	7.10107700	-4.86821300	-2.80605600
H	6.22176400	-5.10005400	-4.32114600
C	4.37508700	-5.03025000	-2.26168100
H	4.95948200	-5.53729500	-1.48757700
H	3.43822000	-4.68913900	-1.80351300
H	4.12877500	-5.77282800	-3.02935200
C	1.78123700	-2.05767300	2.02068600
C	1.70752100	-2.49052500	3.50210700
H	0.79303000	-2.13999100	3.99062900
H	1.71735100	-3.58356900	3.56562600
H	2.56233200	-2.13126800	4.08594800
C	0.57293700	-2.65385000	1.27616400
H	-0.37552500	-2.26798600	1.66596000
H	0.62436100	-2.46030700	0.19793800
H	0.55904900	-3.74241200	1.40014800
C	3.07229700	-2.60566400	1.39134800
H	3.15890500	-2.34735400	0.33125200
H	3.97456200	-2.24592800	1.89501900
H	3.08097400	-3.69825400	1.46562500
C	0.30074100	1.29489300	-4.38236200
C	0.68819800	2.77683100	-4.24418000
H	0.72802900	3.08376600	-3.19426800
H	1.65397200	3.00870700	-4.70663700
H	-0.05898700	3.40241000	-4.74388600
C	-1.08838600	1.08796200	-3.75772500
H	-1.10246100	1.39644900	-2.70683800
H	-1.82777000	1.69989900	-4.28535800
H	-1.40741600	0.04232300	-3.82837800
C	0.21335200	0.90354500	-5.87586500
H	-0.06604600	-0.14971600	-6.00129200
H	-0.54951100	1.51051400	-6.37386500
H	1.15226600	1.06865100	-6.41478700
C	0.76227500	4.82260300	3.18653300
C	1.16013300	6.25305100	3.62982600
H	0.59263100	7.02105700	3.09477000
H	0.96763200	6.38391900	4.70054700
H	2.22494500	6.43848100	3.45133400
C	1.53738000	3.81917300	4.06212000
H	1.25305300	2.78331100	3.83836300
H	2.62262000	3.92677900	3.95345100
H	1.29922100	3.99609200	5.11607000
C	-0.74575300	4.60638500	3.45354700
H	-1.37246300	5.27253900	2.85075800
H	-1.03430500	3.56783300	3.24881900
H	-0.97473900	4.80747000	4.50601600
C	0.15070000	6.60486400	-1.53227000
C	0.44153900	8.01596700	-0.96328100
H	0.01283400	8.78120100	-1.61992400
H	0.01097200	8.15902700	0.03290300
H	1.51944200	8.19685700	-0.89191100
C	0.71288100	6.55269000	-2.96549900
H	1.79397000	6.72986900	-2.98655300
H	0.50989600	5.59375700	-3.45571700
H	0.24351700	7.33408900	-3.57196900
C	-1.37972100	6.39165600	-1.60277100
H	-1.84685800	6.45043500	-0.61331300
H	-1.84239700	7.16145600	-2.23046800
H	-1.62335800	5.41441300	-2.03960200

10

Cu	-0.66430200	-0.13820400	0.01145800
C	5.33732300	1.00216800	-0.49721000
C	5.75270900	-0.24268100	-1.00762200
C	6.68918500	-0.17893700	-2.02868200
C	6.67120200	2.10606200	-1.90489600
C	4.18451400	-0.65079400	0.63401700
H	7.06183200	3.04866400	-2.27583000
N	7.13428600	0.99816300	-2.47191300
N	5.75844900	2.17927200	-0.91168300
N	4.41768900	0.76724400	0.53341000
N	5.12981500	-1.25797700	-0.27395400
C	4.05614500	1.63125200	1.56579300
H	3.49209400	1.15076200	2.36044800
C	4.34785900	2.93672700	1.68897200
H	4.93057300	3.48462000	0.96113000
C	3.87529500	3.62626500	2.91180800
O	3.10368800	3.13924000	3.72775200
O	4.40009800	4.85597500	2.99113300
C	4.07906400	5.65151600	4.16648500
H	4.17284000	6.68240000	3.81945900
H	3.04264600	5.45293000	4.44916200
C	5.03785900	5.35252900	5.30774200

H	4.82454300	6.01988600	6.14990500
H	4.92494800	4.32044200	5.65243300
H	6.07500400	5.51374800	4.99820900
Cl	7.32594900	-1.61694900	-2.77718400
C	4.68006900	-2.55055000	-0.76945800
C	6.88054000	-5.57866000	-0.38554700
C	6.74117700	-5.11032500	1.07530200
H	6.52391400	-6.59941000	-0.55300500
H	7.90914900	-5.53828000	-0.75744300
H	6.32139300	-5.86997000	1.74157800
H	7.69039000	-4.79164700	1.51825300
N	5.49931800	-3.66065400	-0.31034600
C	6.03104400	-4.61756100	-1.20392400
C	5.80217800	-3.91403900	1.02991800
O	5.35126500	-3.26908700	1.95825600
O	5.79629200	-4.62418600	-2.38979200
H	4.73963400	-2.58636100	-1.85847400
C	3.20859700	-2.69270600	-0.26503500
H	2.58173300	-3.14927400	-1.03363200
H	3.19221600	-3.33092500	0.61742600
C	2.70055300	-1.27291400	0.15297100
C	1.75487300	-1.33670800	1.33758800
O	0.60112300	-0.87397100	1.41613200
C	2.11466600	-0.54417500	-1.04167000
O	0.96125900	-0.09794800	-1.17049100
O	2.31437400	-1.93088700	2.36272500
O	2.98240800	-0.43819700	-2.01834500
C	1.57835000	-2.06416400	3.61259500
H	2.24994600	-2.61907600	4.26411700
H	1.36960600	-1.07314500	4.01895100
H	0.65163000	-2.61222600	3.43755500
C	2.60818400	0.27330000	-3.23537300
H	3.51726000	0.28931000	-3.83260600
H	1.81465900	-0.27355500	-3.74641400
H	2.28075900	1.28265200	-2.98396400
H	4.29056700	-1.02058800	1.65637200
C	-4.03190700	0.52986200	-0.23068700
C	-4.68777800	1.85978900	-0.80673300
H	-5.27170800	1.53183000	-1.67262600
H	-5.40662200	2.18122100	-0.04863500
C	-5.27076700	-0.37424500	0.18577000
H	-5.75870200	0.17012700	1.00038200
H	-5.95511000	-0.34383100	-0.66518900
C	-3.81502800	3.03846100	-1.19075300
C	-2.84977200	2.95368300	-2.20495900
C	-4.07527100	4.28142200	-0.60086600
C	-2.13061100	4.08145300	-2.62179600
H	-2.69146300	2.00738900	-2.70878900
C	-3.39783800	5.44234700	-1.00186800
H	-4.84035900	4.34073400	0.16609700
C	-2.42534300	5.30519200	-2.00187000
H	-1.89081100	6.19151300	-2.32761600
C	-5.05262300	-1.82042700	0.58561000
C	-4.26129000	-2.18142000	1.68527000
C	-5.76508300	-2.81337100	-0.09741600
C	-4.16257000	-3.51542600	2.10346400
H	-3.75290000	-1.40762400	2.24881800
C	-5.71334200	-4.15814900	0.29637100
H	-6.39100500	-2.51887000	-0.93298500
C	-4.89500200	-4.47599000	1.38932300
H	-4.84447600	-5.51069000	1.71210600
C	-3.25336900	-0.17387400	-1.31500500
C	-1.78936100	-1.31307600	-2.63817000
C	-3.05749300	-0.92246500	-3.43023000
H	-3.56991800	-1.75461900	-3.90827300
O	-3.95928900	-0.38937500	-2.41673400
N	-2.02845000	-0.60765400	-1.33273000
C	-3.20799200	0.86730100	0.98643400
C	-1.60309700	1.31990700	2.54020700
C	-3.01392000	1.44435100	3.15480100
H	-3.21583400	2.39499200	3.64358600
N	-1.92911300	0.76985100	1.18146500
O	-3.90967800	1.34989900	2.00311400
H	-2.88968600	-0.12638300	-4.15939200
H	-0.90170600	-0.86460400	-3.09389400
H	-1.01835000	0.56047500	3.06638700
H	-3.27464300	0.62172400	3.82527400
C	-3.71220000	6.83400400	-0.41951400
C	-4.74602900	6.77197500	0.72115800
H	-5.71140300	6.38013500	0.38167200
H	-4.39688100	6.15490200	1.55822400
H	-4.92452200	7.77962100	1.11015300
C	-4.28712500	7.72726800	-1.54680100
H	-4.52552700	8.72245200	-1.15493300
H	-3.57526200	7.85576800	-2.36896200
H	-5.20577900	7.29779200	-1.96162900
C	-2.42087500	7.48103000	0.13487000
H	-2.64272700	8.47650700	0.53491800
H	-1.99320800	6.88044000	0.94639800
H	-1.65298700	7.60217200	-0.63618200
C	-1.06936600	4.03189600	-3.73828200
C	-0.90389500	2.61977800	-4.33323400
H	-0.58876300	1.89128200	-3.57333300
H	-1.83096900	2.26154400	-4.79688200
H	-0.13740400	2.63820200	-5.11576700
C	-1.47742900	4.98477000	-4.88812400
H	-2.44568600	4.69740900	-5.31232500
H	-1.55596300	6.02234700	-4.55033100
H	-0.73152100	4.95411600	-5.69064400
C	0.29872700	4.47433600	-3.16606500
H	0.26132500	5.48732800	-2.75398500
H	0.62626800	3.80219500	-2.36167600
H	1.06218500	4.46734600	-3.95320900
C	-0.77764300	2.64341000	2.52398500
C	-0.39089400	2.95050500	3.98720600
H	0.19877000	2.13900500	4.42893000
H	0.22768700	3.85108800	4.03106500
H	-1.26949100	3.12176800	4.62059000
C	0.50548000	2.45319200	1.70018700
H	1.11261100	1.63013500	2.08619700
H	0.28425900	2.27818400	0.63785400
H	1.12180000	3.35336300	1.75507500
C	-1.56881100	3.81908500	1.92736000
H	-1.86298900	3.63238100	0.89092800
H	-2.47168200	4.05994100	2.49937900
H	-0.94307500	4.71761400	1.93356300
C	-1.55360300	-2.85358500	-2.52654900
C	-2.75145000	-3.58182200	-1.89558200
H	-2.93262100	-3.25850500	-0.86634500
H	-3.67754600	-3.43865000	-2.46162100
H	-2.55690700	-4.65921300	-1.87408000
C	-0.29975200	-3.14309300	-1.68398400
H	-0.41321000	-2.79875500	-0.64821400
H	-0.11867800	-4.22259200	-1.64562900

H	0.58724000	-2.67375900	-2.12440800
C	-1.29958900	-3.38496100	-3.95556400
H	-0.45393300	-2.87571800	-4.43477500
H	-1.06406900	-4.45338000	-3.91837200
H	-2.17211300	-3.27466500	-4.60794900
C	-3.32268200	-3.95095900	3.31982000
C	-4.23933700	-4.62394100	4.37045800
H	-4.73573200	-5.51283600	3.96997700
H	-3.65349200	-4.93727400	5.24225700
H	-5.01742100	-3.93355900	4.71403200
C	-2.61499200	-2.76490900	4.00356300
H	-1.92661100	-2.24935200	3.31971500
H	-3.33169100	-2.03149700	4.39190900
H	-2.03073200	-3.12787800	4.85642200
C	-2.23959800	-4.95762700	2.86384300
H	-2.67662800	-5.84737800	2.40057100
H	-1.56224700	-4.50091200	2.12965300
H	-1.64282900	-5.29222600	3.72081100
C	-6.53556900	-5.26294800	-0.39539300
C	-7.52459600	-5.87000500	0.63027000
H	-8.12387500	-6.65486700	0.15556100
H	-7.00521300	-6.31903900	1.48328700
H	-8.20967000	-5.10758600	1.01702800
C	-7.34938400	-4.72812200	-1.58952500
H	-8.08080500	-3.97147400	-1.28391700
H	-6.70641700	-4.29341800	-2.36485300
H	-7.90658700	-5.54964200	-2.05121700
C	-5.59257800	-6.37522400	-0.91318700
H	-5.00185000	-6.82480100	-0.10819300
H	-6.17755300	-7.17644500	-1.37797900
H	-4.89705200	-5.98721500	-1.66707300

11-ts

Cu	1.00089800	0.07041800	-0.09633400
C	-4.55901700	-4.59697600	-1.47825500
C	-4.10573000	-5.02587300	-0.07341200
H	-5.52937800	-5.01286000	-1.76251400
H	-3.84789800	-4.87138900	-2.26442000
H	-4.85347100	-5.63478900	0.44323100
H	-3.16650500	-5.58738000	-0.06336800
N	-4.23224100	-2.64091800	-0.15309300
C	-3.92972600	-3.74798700	0.71621100
C	-4.68910700	-3.08655800	-1.44283600
O	-3.58776400	-3.59084000	1.86215600
O	-5.11542700	-2.34268600	-2.28784100
C	-4.29748600	-1.36501000	0.33686600
C	-3.82825400	-0.18014600	-0.48182400
C	-2.31614800	-0.15029400	-0.34455400
H	-4.02878400	-1.34511800	1.39080000
H	-4.25176300	0.73220800	-0.06105800
H	-4.13821800	-0.27471200	-1.51984300
C	-1.72967500	0.42610100	0.81072000
O	-0.49564700	0.54569300	1.08025100
O	-2.61601700	0.87967300	1.71609600
C	-2.09728100	1.52237400	2.90014900
H	-1.47133500	2.37572200	2.63257300
H	-2.97700400	1.85361900	3.45129900
H	-1.52082400	0.81380500	3.49893500
C	-1.49289800	-0.68849100	-1.37086200
O	-0.22696500	-0.63194900	-1.45353200
O	-2.16339400	-1.29830100	-2.35398800
C	-1.42480800	-1.79476100	-3.48961900
H	-2.17948600	-2.23302900	-4.14156000
H	-0.91412600	-0.97527800	-4.00015200
H	-0.69569700	-2.54517700	-3.17704600
C	-7.04321000	1.60527800	-0.75474800
C	-7.32978200	2.97509900	-0.77124800
C	-7.56290300	3.51451700	-2.04258500
C	-7.22550900	1.42830200	-2.95075900
C	-7.05333100	2.52408100	1.29667700
H	-7.19689900	0.82390900	-3.85215300
H	-6.97775300	2.56180600	2.37674900
N	-7.50491200	2.72749200	-3.11139800
N	-6.97297600	0.79106100	-1.79264600
N	-6.85207000	1.28786300	0.61128500
N	-7.32325600	3.51240900	0.51719600
C	-6.62045600	0.09824000	1.20844400
H	-6.62831800	0.13642100	2.29476700
C	-6.69818800	-2.37335000	1.33715800
O	-6.73862900	-3.45778100	0.78512600
O	-6.87930600	-2.16582000	2.64168300
C	-7.13832400	-3.34823800	3.47162600
H	-7.95535100	-3.90800900	3.01063700
H	-6.23575800	-3.96564500	3.45163900
C	-7.47762700	-2.86251400	4.86501100
H	-7.66858200	-3.72630600	5.50985900
H	-6.65144400	-2.29082300	5.29952400
H	-8.37662900	-2.23866900	4.85938700
Cl	-7.92280000	5.18457400	-2.25565800
C	-6.39610800	-1.11824500	0.57035200
H	-6.58222700	-1.17726500	-0.49924400
C	4.43549400	0.32660200	0.13777200
C	5.50856500	-0.78574800	-0.22735200
H	6.07954900	-0.36867000	-1.06281800
H	6.18884900	-0.82951000	0.62683700
C	5.29921300	1.56596300	0.62662500
H	5.79354000	1.22923200	1.54296900
H	6.08234900	1.69273500	-0.12481200
C	5.05110100	-2.19100700	-0.56550300
C	4.24933300	-2.46024900	-1.68351900
C	5.54335200	-3.25964400	0.19312700
C	3.92324700	-3.77362400	-2.04600500
H	3.90961000	-1.63716500	-2.30129500
C	5.26217200	-4.59149600	-0.14386500
H	6.18025400	-3.03934600	1.04308600
C	4.44266300	-4.81304400	-1.25946500
H	4.21843500	-5.83696100	-1.54068200
C	4.62684600	2.90365000	0.86269800
C	3.66147300	3.08207300	1.86341300
C	5.07299200	4.01562600	0.13893000
C	3.13023000	4.34779300	2.14350600
H	3.35470000	2.23050000	2.45988900
C	4.58650000	5.30494700	0.39822700
H	5.83575000	3.86646800	-0.61777300
C	3.61049900	5.43423300	1.39597700
H	3.22562600	6.42454200	1.61701000
C	3.66492000	0.72859700	-1.09711500
C	2.14591300	1.31158400	-2.68765700
C	3.58310300	1.34050000	-3.26488400
H	3.88237800	2.29805600	-3.68704500
O	4.44161600	1.09558000	-2.11243500
N	2.38912500	0.78184000	-1.30795800
C	3.57081800	-0.17868300	1.26894200
C	1.95340200	-0.96600000	2.66227200

C	3.28607700	-0.76571800	3.42567300
H	3.66272000	-1.65705800	3.92401600
N	2.29979600	-0.42068300	1.31058600
O	4.24821800	-0.41844900	2.38844500
H	3.78085100	0.54459200	-3.98666600
H	1.53535900	0.57138000	-3.21315800
H	1.17229700	-0.32274700	3.07777900
H	3.26313900	0.06648900	4.13317800
C	5.84733200	-5.78915000	0.63014800
C	6.66397900	-5.35120900	1.86109200
H	7.52936300	-4.73857400	1.58495100
H	6.05569300	-4.78620800	2.57813900
H	7.04542900	-6.23590400	2.38129100
C	6.78311300	-6.58480300	-0.31322300
H	7.20796700	-7.44658000	0.21389500
H	6.25012100	-6.96150800	-1.19251500
H	7.61184600	-5.96063500	-0.66543500
C	4.70623200	-6.71478400	1.11443800
H	5.12165000	-7.57520200	1.65106400
H	4.03110400	-6.18615100	1.79767300
H	4.10914900	-7.10403100	0.28334200
C	3.05488100	-4.10802500	-3.27414900
C	2.60482700	-2.84711800	-4.03781200
H	2.00659300	-2.17807000	-3.40544000
H	3.45948800	-2.28330600	-4.43047200
H	1.98794400	-3.13632900	-4.89584800
C	3.85711300	-4.99687800	-4.25504300
H	4.76148700	-4.48354900	-4.59937600
H	4.16439200	-5.94096100	-3.79494900
H	3.24867200	-5.23976700	-5.13403200
C	1.78788400	-4.86795700	-2.81299600
H	2.03589800	-5.80100700	-2.29718500
H	1.19271600	-4.25475900	-2.12326400
H	1.16173000	-5.12508900	-3.67613700
C	1.42315100	-2.43635200	2.67306700
C	1.11896200	-2.80025900	4.14397400
H	0.39483200	-2.10673100	4.58946700
H	0.68864600	-3.80561000	4.19660200
H	2.01505500	-2.80319600	4.77406100
C	0.11019000	-2.55278900	1.87707500
H	-0.65662400	-1.87083300	2.25766300
H	0.25797800	-2.35247000	0.80924000
H	-0.28350700	-3.57139500	1.96364600
C	2.44814500	-3.42024300	2.08531500
H	2.65967000	-3.20970000	1.03257800
H	3.40016700	-3.41090000	2.62660100
H	2.05691500	-4.44146600	2.14726600
C	1.39820700	2.68331200	-2.75185000
C	2.16729700	3.79380500	-2.01749000
H	2.26411900	3.58600800	-0.94740600
H	3.17340100	3.94847900	-2.42083500
H	1.63245600	4.74376100	-2.12309800
C	-0.00906000	2.56771500	-2.13842100
H	0.02732500	2.35481500	-1.06362200
H	-0.54033300	3.51838300	-2.25775100
H	-0.60292300	1.78962700	-2.62900700
C	1.23920200	3.04548400	-4.24592600
H	0.70347000	2.26251700	-4.79701300
H	0.66421900	3.97195200	-4.34461200
H	2.19996800	3.21211400	-4.74508700
C	2.08222700	4.58865300	3.24717100
C	2.64679100	5.58206000	4.29145200
H	2.89360700	6.54950300	3.84392600
H	1.91032500	5.76201400	5.08332500
H	3.55680300	5.18773500	4.75681700
C	1.69661300	3.29308800	3.98780800
H	1.26375100	2.54703200	3.30828200
H	2.55740700	2.84288300	4.49664700
H	0.94880600	3.51859200	4.75625800
C	0.79894900	5.18103100	2.61707600
H	0.99502100	6.12570900	2.10050200
H	0.36353700	4.48757900	1.88561100
H	0.04936700	5.37942500	3.39268600
C	5.11308200	6.55666700	-0.33106700
C	5.81898300	7.47359400	0.69851800
H	6.20421700	8.37196100	0.20297500
H	5.13649500	7.79797400	1.49125200
H	6.66275300	6.95922600	1.17173100
C	6.12694000	6.20751000	-1.43772900
H	7.01838500	5.71144900	-1.03797500
H	5.68892500	5.56104600	-2.20832100
H	6.46064600	7.12526700	-1.93282000
C	3.93957800	7.32876500	-0.97904600
H	3.20083900	7.65488800	-0.23984500
H	4.31449800	8.22515100	-1.48553600
H	3.42264700	6.71282400	-1.72422900

12

Cu	-1.00730600	0.02328000	-0.39020400
C	4.42249600	4.25490100	-1.03345900
C	4.29282000	3.98045600	0.47296000
H	5.27403300	4.89124100	-1.29190600
H	3.53369200	4.72663800	-1.46428500
H	5.10873200	4.41237900	1.06184300
H	3.35993600	4.34831400	0.91018600
N	4.55815100	1.91691500	-0.66987300
C	4.34246000	2.46753300	0.61266200
C	4.61288200	2.89226500	-1.68468000
O	4.21726400	1.80165000	1.61766700
O	4.78734200	2.64898100	-2.85792100
C	4.64757800	0.48554700	-0.84938800
C	3.61505700	-0.11710500	-1.82936200
C	2.19422500	-0.00895200	-1.32759000
H	4.47690700	0.08079500	0.15010400
H	3.87694300	-1.17705900	-1.95142500
H	3.71243700	0.34708400	-2.80908700
C	1.74701900	-0.86027600	-0.29069500
O	0.59066900	-0.92455500	0.23353700
O	2.68988700	-1.70070300	0.18968300
C	2.29282700	-2.62126400	1.22496900
H	1.46645100	-3.25133300	0.89003000
H	3.17563500	-3.23122100	1.41918700
H	2.00179100	-2.08179100	2.12923100
C	1.28092900	0.89129600	-1.93796500
O	0.03303400	1.00494800	-1.71459200
O	1.82370600	1.69228300	-2.86094800
C	0.96979000	2.59383900	-3.59040600
H	1.64586800	3.15514500	-4.23419900
H	0.24984900	2.03510700	-4.19346100
H	0.43810800	3.26104400	-2.90863100
C	6.78045700	-1.59047500	1.36613400
C	6.96977900	-2.74515500	2.12515700
C	7.22365600	-2.52519400	3.48467300
C	7.06584900	-0.25873700	3.10291900

C	6.62431700	-3.50522000	0.14760100
H	7.10711700	0.73983200	3.52554500
H	6.48661000	-4.11945500	-0.73440000
N	7.26118200	-1.27671400	3.94529800
N	6.81701600	-0.34234900	1.77867600
N	6.54133500	-2.06061000	0.03354900
N	6.86117700	-3.90356000	1.34003600
C	6.30049100	-1.39734300	-1.07746400
H	6.17926200	-1.99839600	-1.97905200
C	6.18182100	0.05453000	-1.20077700
H	6.78854800	0.56167500	-0.44790300
C	6.59824800	0.41031300	-2.64419800
O	6.25446200	-0.26847000	-3.58912200
O	7.39287300	1.46453600	-2.65542700
C	7.80961900	1.95301600	-3.97952000
H	8.25432700	1.11287300	-4.51848600
H	6.90240200	2.26784100	-4.49975200
C	8.78456600	3.08903300	-3.75780900
H	9.11103900	3.47576600	-4.72863400
H	8.31669000	3.90930100	-3.20479100
H	9.67011300	2.75340800	-3.20961100
Cl	7.48451800	-3.82509400	4.57416200
C	-4.35351300	-0.03592500	0.49144600
C	-5.28691400	1.22345500	0.74769700
H	-6.05818800	1.16708300	-0.02686400
H	-5.78522400	1.03017800	1.70095800
C	-5.30490300	-1.28477900	0.72743700
H	-5.58973900	-1.23449500	1.78284500
H	-6.20844600	-1.07912900	0.14834600
C	-4.69323100	2.61824000	0.77944100
C	-4.06440500	3.18470600	-0.33802800
C	-4.89587900	3.40608500	1.91898400
C	-3.62463600	4.51493200	-0.32910000
H	-3.95406800	2.59344300	-1.23941300
C	-4.49077600	4.74755800	1.96737500
H	-5.40453900	2.96393700	2.76889100
C	-3.84864500	5.26634200	0.83455400
H	-3.53147700	6.30423500	0.85049300
C	-4.81481900	-2.67944900	0.39143500
C	-3.74023100	-3.27096100	1.06985600
C	-5.53449200	-3.43897300	-0.53846800
C	-3.36736800	-4.59903600	0.82551200
H	-3.21866800	-2.70151700	1.82990800
C	-5.21352500	-4.77894500	-0.79904300
H	-6.37611600	-2.97610000	-1.04233900
C	-4.12068600	-5.32384900	-0.11062400
H	-3.85980600	-6.36127600	-0.29368000
C	-3.88158300	-0.04655300	-0.94358300
C	-2.77688100	-0.16673100	-2.92718300
C	-4.27588100	0.14995800	-3.15273900
H	-4.79677400	-0.55236500	-3.80082000
O	-4.87272200	0.03293200	-1.82824700
N	-2.68666500	-0.13079100	-1.43242700
C	-3.23462200	-0.03680800	1.50675800
C	-1.29598200	0.08934400	2.68818500
C	-2.47492100	-0.30582700	3.60993200
H	-2.62100700	0.34656200	4.46863100
N	-1.95657700	0.08431300	1.34431100
O	-3.65362500	-0.17043700	2.76356200
H	-4.45920300	1.17047800	-3.49758800
H	-2.15063600	0.64568800	-3.30633600
H	-0.53512700	-0.69589900	2.67547800
H	-2.43778400	-1.34604700	3.94267500
C	-4.75781000	5.65638700	3.18340100
C	-5.43611300	4.90133700	4.34266400
H	-6.41501000	4.50145600	4.05540400
H	-4.81894600	4.07237000	4.71019300
H	-5.59787100	5.58560600	5.18198900
C	-5.69002500	6.81451300	2.75005700
H	-5.89537300	7.47333900	3.60140500
H	-5.24263900	7.42421100	1.95805300
H	-6.64732500	6.43208500	2.37894500
C	-3.42438000	6.24257900	3.70529300
H	-3.61116900	6.90139900	4.56080200
H	-2.74539600	5.44741500	4.03542800
H	-2.90658900	6.83334300	2.94246500
C	-2.94866600	5.17722700	-1.54529200
C	-2.82075500	4.21675400	-2.74358600
H	-2.21742700	3.33348400	-2.49653800
H	-3.80108100	3.88010600	-3.10155300
H	-2.33250800	4.73281300	-3.57774700
C	-3.78224900	6.39869400	-2.00237000
H	-4.79604800	6.09701100	-2.28755500
H	-3.86819000	7.15377900	-1.21512000
H	-3.31338700	6.87726800	-2.87014200
C	-1.52684400	5.64417000	-1.15176800
H	-1.54724700	6.36170100	-0.32560900
H	-0.90772500	4.79303800	-0.83932400
H	-1.03679600	6.13339900	-2.00233300
C	-0.59630900	1.43069700	3.08051700
C	0.05337500	1.21541100	4.46598700
H	0.77682400	0.39079400	4.44727800
H	0.59095400	2.11954500	4.76970900
H	-0.68147300	1.00191100	5.25018800
C	0.52110700	1.78139100	2.08061700
H	1.26756600	0.98535700	2.00373700
H	0.12410700	1.98867300	1.07958300
H	1.03923700	2.68647500	2.41644200
C	-1.59021600	2.60275000	3.13963600
H	-2.03981600	2.80590500	2.16345700
H	-2.40278900	2.43483700	3.85491000
H	-1.06882900	3.51159200	3.45919000
C	-2.29253900	-1.49696600	-3.59043100
C	-3.10637500	-2.71045800	-3.11175100
H	-2.99066700	-2.88252800	-2.03748500
H	-4.17660200	-2.61211700	-3.32252500
H	-2.76168900	-3.61190300	-3.62984500
C	-0.80420500	-1.75015100	-3.28729800
H	-0.62522500	-1.92208300	-2.21946000
H	-0.47006200	-2.64918400	-3.81676600
H	-0.17538000	-0.91697600	-3.61658700
C	-2.44477200	-1.32581600	-5.11877300
H	-1.87527100	-0.46344400	-5.48711900
H	-2.06603500	-2.21572500	-5.63202000
H	-3.48777500	-1.19863500	-5.42908700
C	-2.20233400	-5.28711300	1.56290600
C	-2.73493700	-6.50815100	2.35124900
H	-3.20160800	-7.24743500	1.69321100
H	-1.91521200	-7.00715600	2.88142600
H	-3.48236900	-6.20243800	3.09167300
C	-1.50170900	-4.34681500	2.56296600
H	-1.07942800	-3.46392700	2.06521300
H	-2.18522000	-4.00854100	3.35094600
H	-0.67977200	-4.87880900	3.05489300

C	-1.14977200	-5.76136200	0.53243000
H	-1.57360400	-6.46543400	-0.19028200
H	-0.74193000	-4.91288000	-0.03233100
H	-0.32048900	-6.26901500	1.03987100
C	-6.03444700	-5.66068400	-1.76045200
C	-6.70306400	-6.79706200	-0.94794200
H	-7.29135000	-7.44067100	-1.61199200
H	-5.96321300	-7.42726900	-0.44322700
H	-7.37604900	-6.39241400	-0.18388800
C	-7.14274700	-4.86901400	-2.48126100
H	-7.87506200	-4.45332000	-1.78018600
H	-6.73560700	-4.04671800	-3.08255400
H	-7.68549700	-5.53383000	-3.16102000
C	-5.10968000	-6.28012700	-2.83509000
H	-4.32216000	-6.90094300	-2.39563100
H	-5.69172500	-6.91858100	-3.50907300
H	-4.62822200	-5.50307400	-3.44033900

12. Reference

i. (a) Xie, M.-S.; Wang, Y.; Li, J.-P.; Du, C.; Zhang, Y.-Y.; Hao, E.-J.; Zhang, Y.-M.; Qu, G.-R.; Guo, H.-M. *Chem. Commun.* **2015**, *51*, 12451−12454. (b) Yang, Q.-L.; Xie, M.-S.; Xia, C.; Sun, H.-L.; D.-Zhang, J.; Huang, K.-X.; Guo, Z.; Qu, G.-R.; Guo, H.-M. *Chem. Commun*. **2014**, *50*, 14809−14812.

ii. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

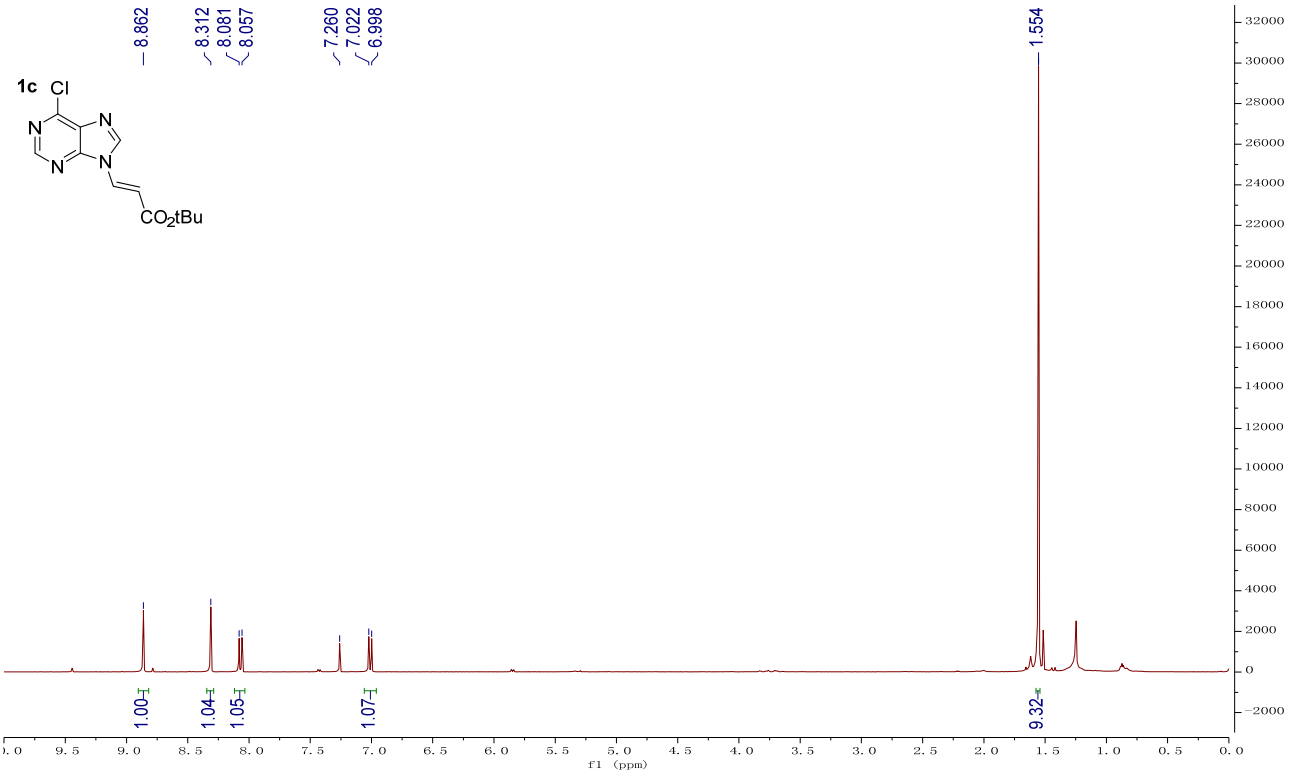
iii. Peverati, R.; Truhlar, D. G. *J. Phys. Chem. Lett.* **2011**, *2*, 2810−2817.

iv. (a) Peverati, R.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2012**, *14*, 11363−11370. (b) Lin, Y.-S.; Tsai, C.-W.; Li, G.-D.; Chai, J.-D. *J. Chem. Phys.* **2012**, *136*, 154109. (c) Steckel, J. A. *J. Phys. Chem. A* **2012**, *116*, 11643−11650. (d) Zhao, Y.; Ng, H. T.; Peverati, R.; Truhlar, D. G. *J. Chem. Theory Comput.* **2012**, *8*, 2824−2834. (e) Yu, Z. Y.; Lan, Y. *J. Org. Chem.* **2013**, *78*, 11501−11507. (f) Liu, S.; Lei, Y.; Qi, X.; Lan, Y. *J. Phys. Chem. A* **2014**, *118*, 2638−2645. (g) Xi, Y.; Su, Y.; Yu, Z.; Dong, B.; McClain, E. J. Lan, Y.; Shi, X. *Angew. Chem. Int. Ed.* **2014**, *53*, 9817−9821. (h) Long, R.; Huang, J.; Shao, W.; Liu, S.; Lan, Y.; Gong, J.; Yang, Z. *Nature Comm.* **2014**, *5*, 5707. (I) Qi, X.; Zhang, H.; Shao, A.; Zhu, L.; Xu, T.; Gao, M.; Liu, C.; Lan, Y. *ACS Catal.* **2015**, *5*, 6640−6647. (j) Fu, J.; Gu, Y.; Yuan, H.; Luo, T.; Liu, S.; Lan, Y.; Gong, J.; Yang, Z. *Nature Comm.* **2015**, *6*, 8617.

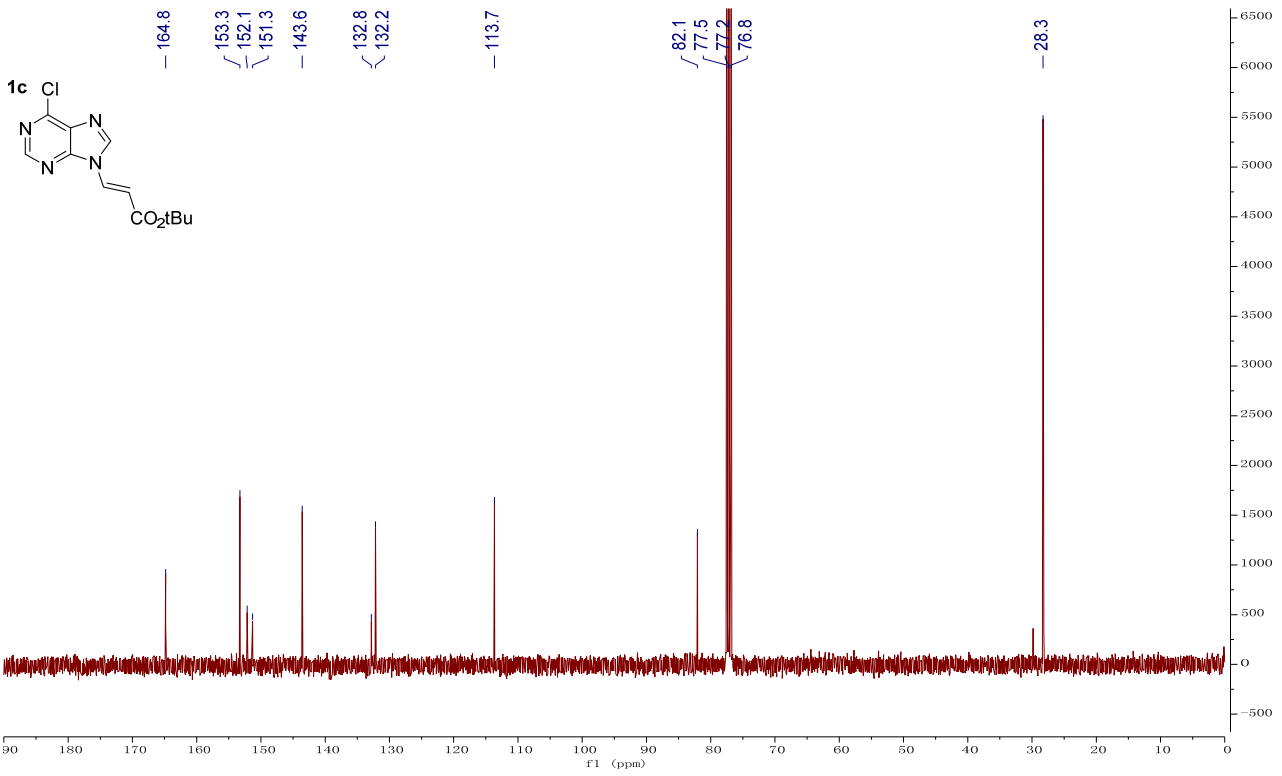
v. (a) Cances, E.; Mennunci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032–3041. (b) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *J. Chem. Phys. Lett.* **1996**, *255*, 327–335. (c) Barone, V.; Cossi, M.; Tomasi, J. *J. Comput. Chem.* **1998** *19*, 404–417.

13. Copies of NMR spectra of products

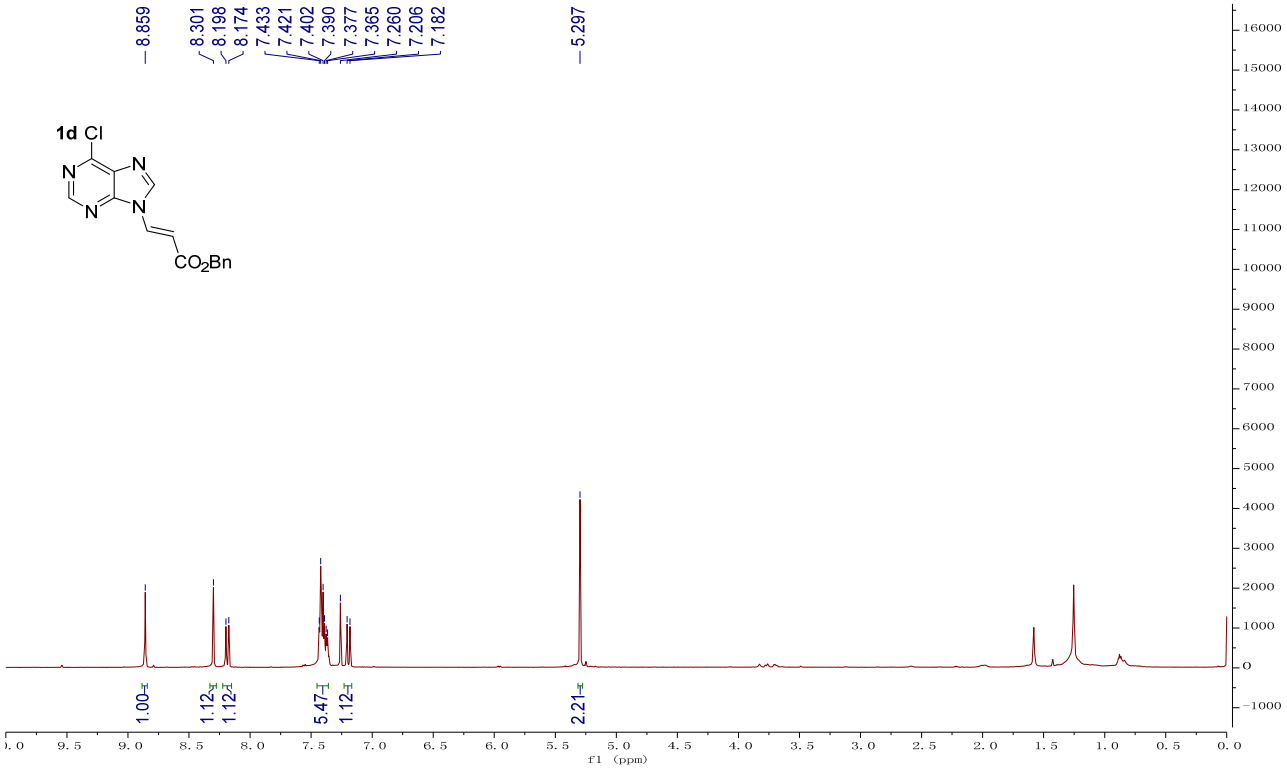
^{1}H-NMR of 1c



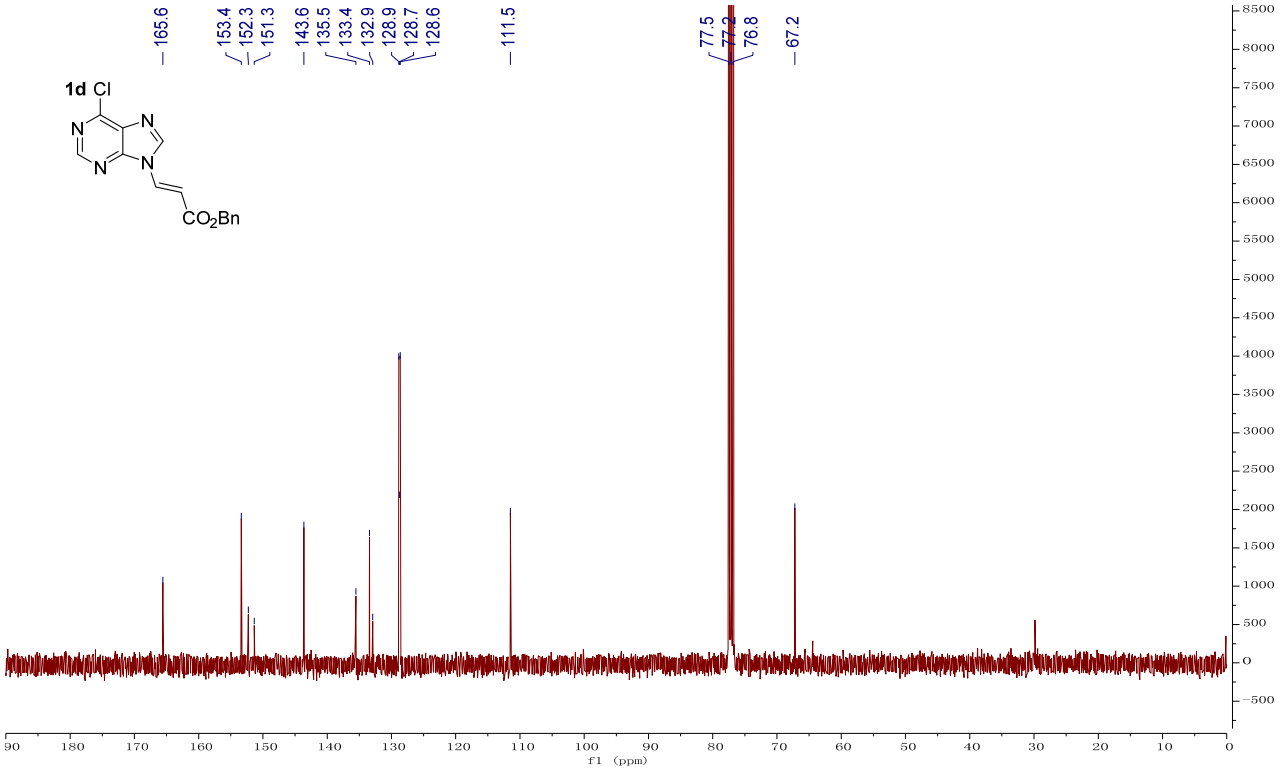
^{13}C-NMR of 1c



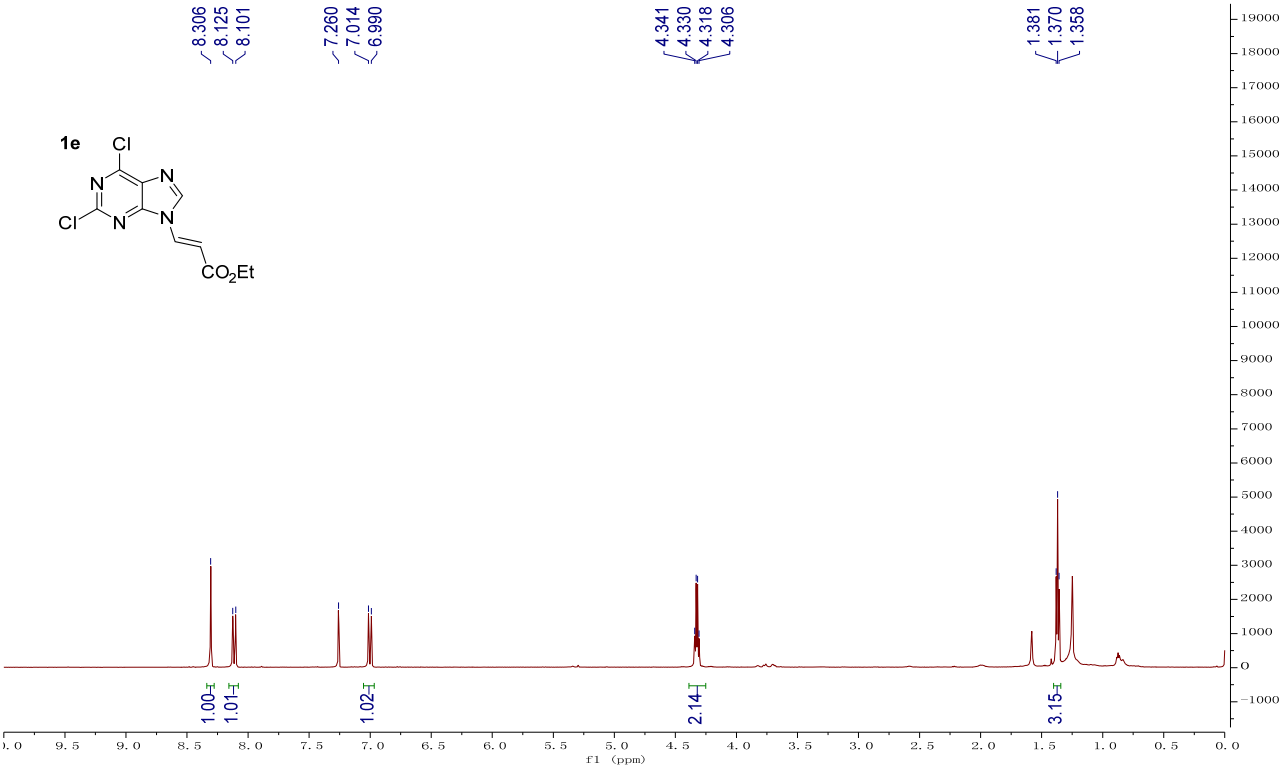
^{1}H-NMR of 1d



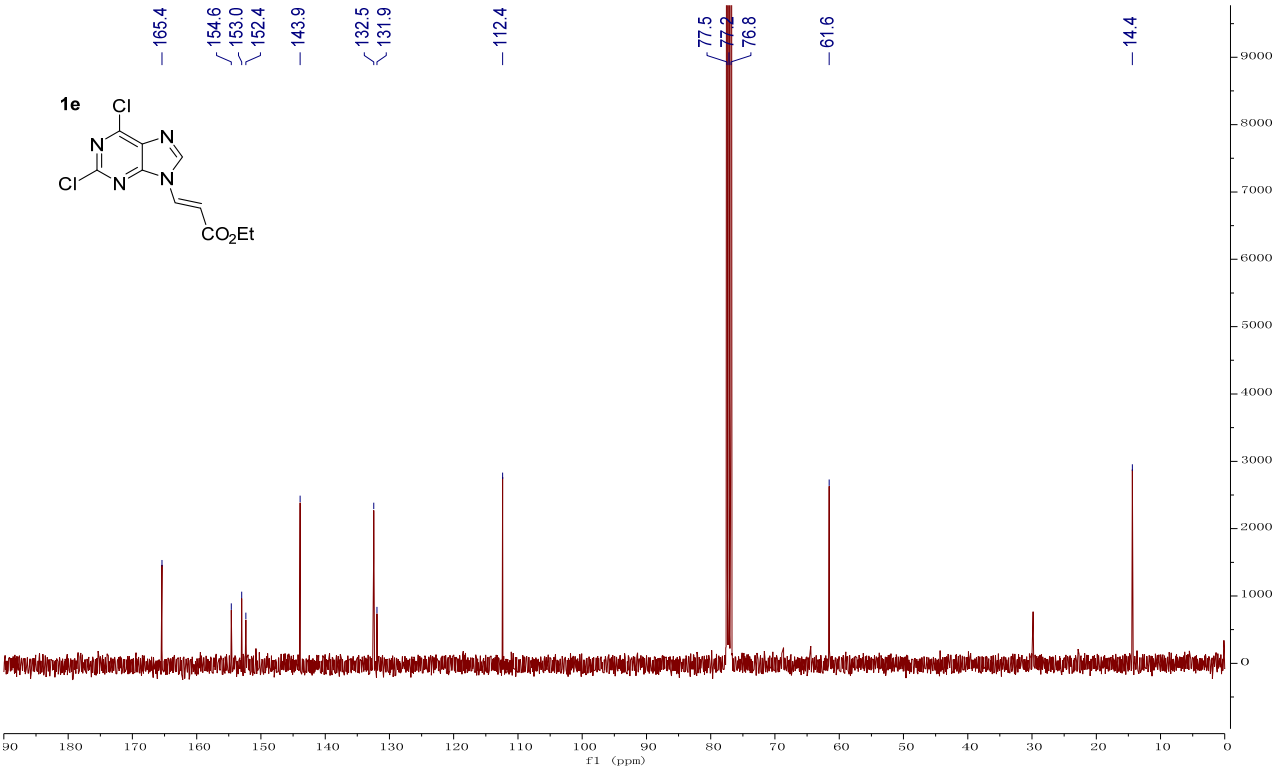
^{13}C-NMR of 1d



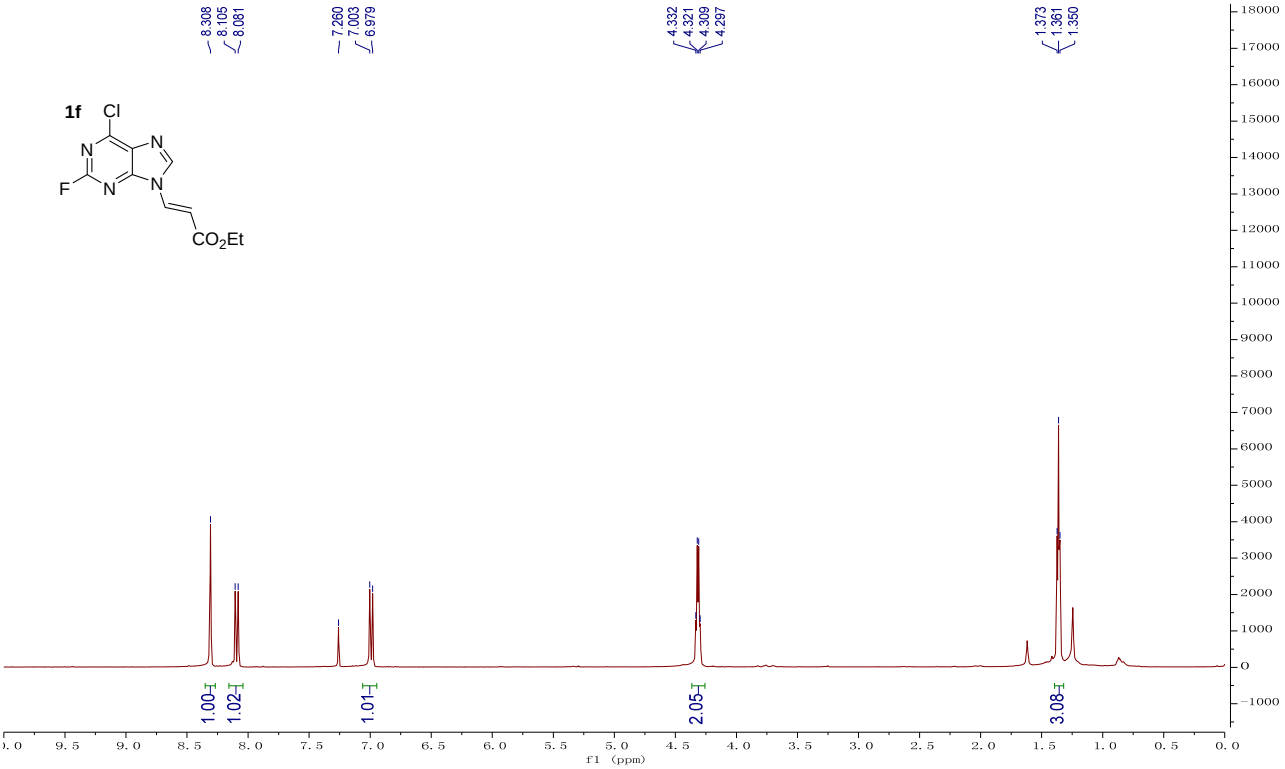
^{1}H-NMR of 1e



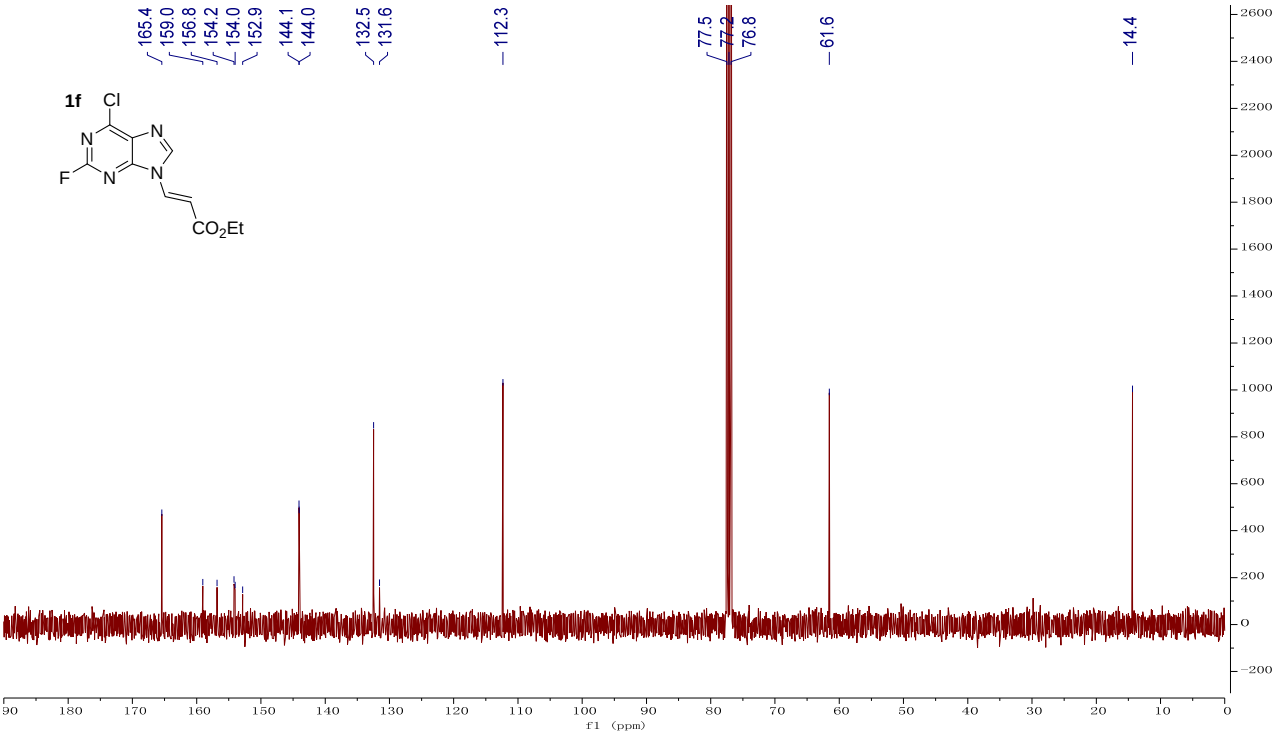
^{13}C-NMR of 1e



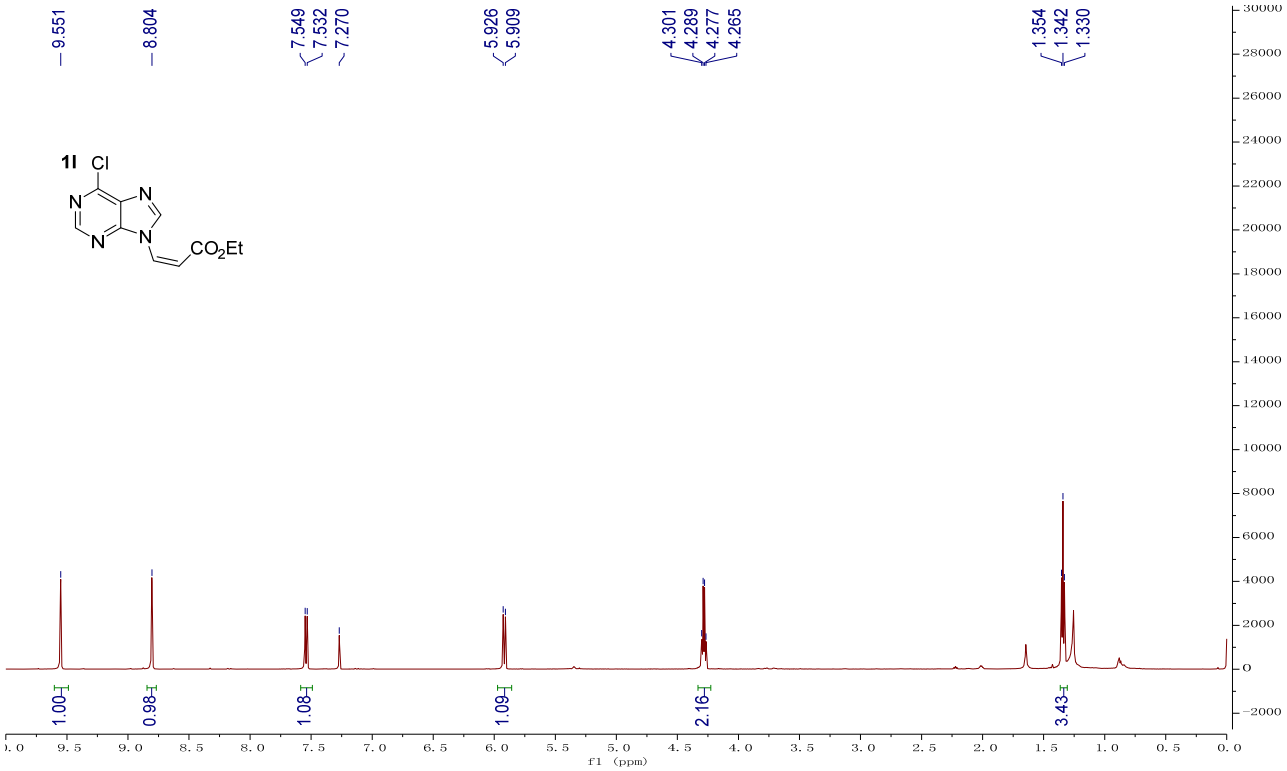
^{1}H-NMR of 1f



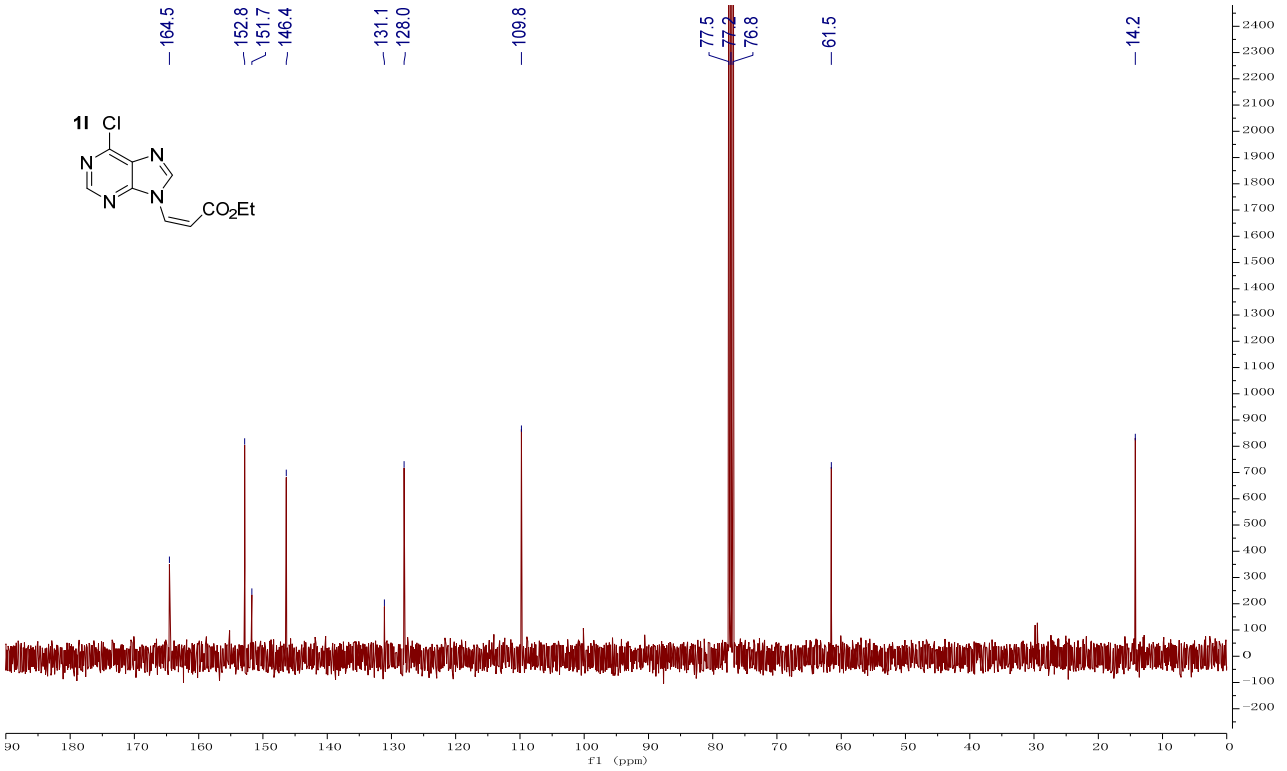
^{13}C-NMR of 1f



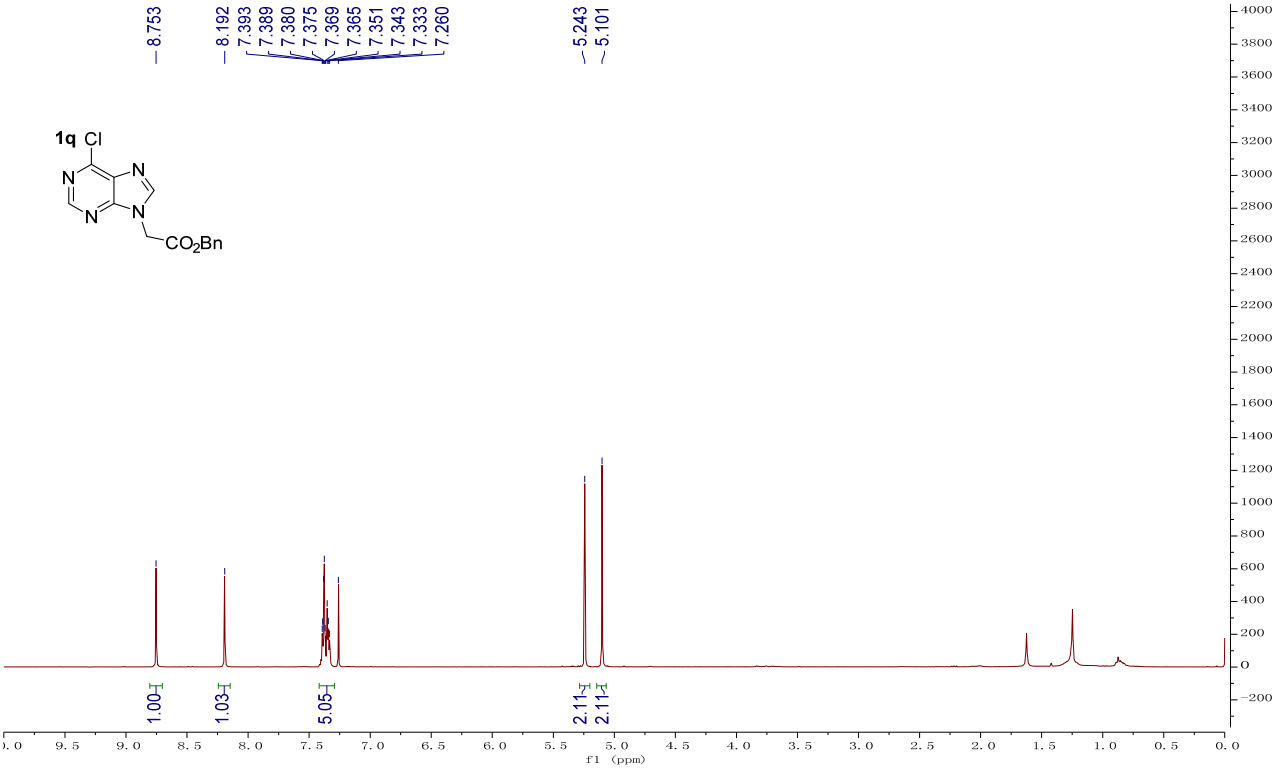
^{1}H-NMR of 1l



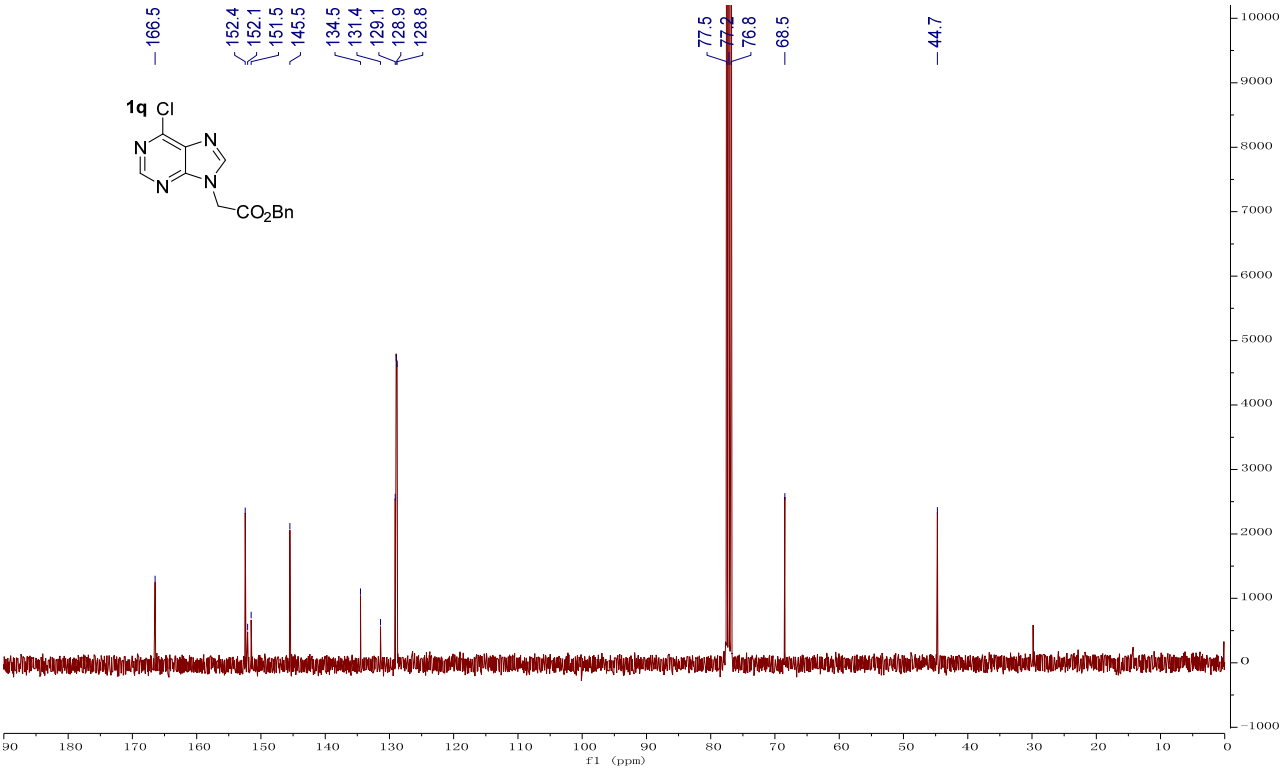
^{13}C-NMR of 1l



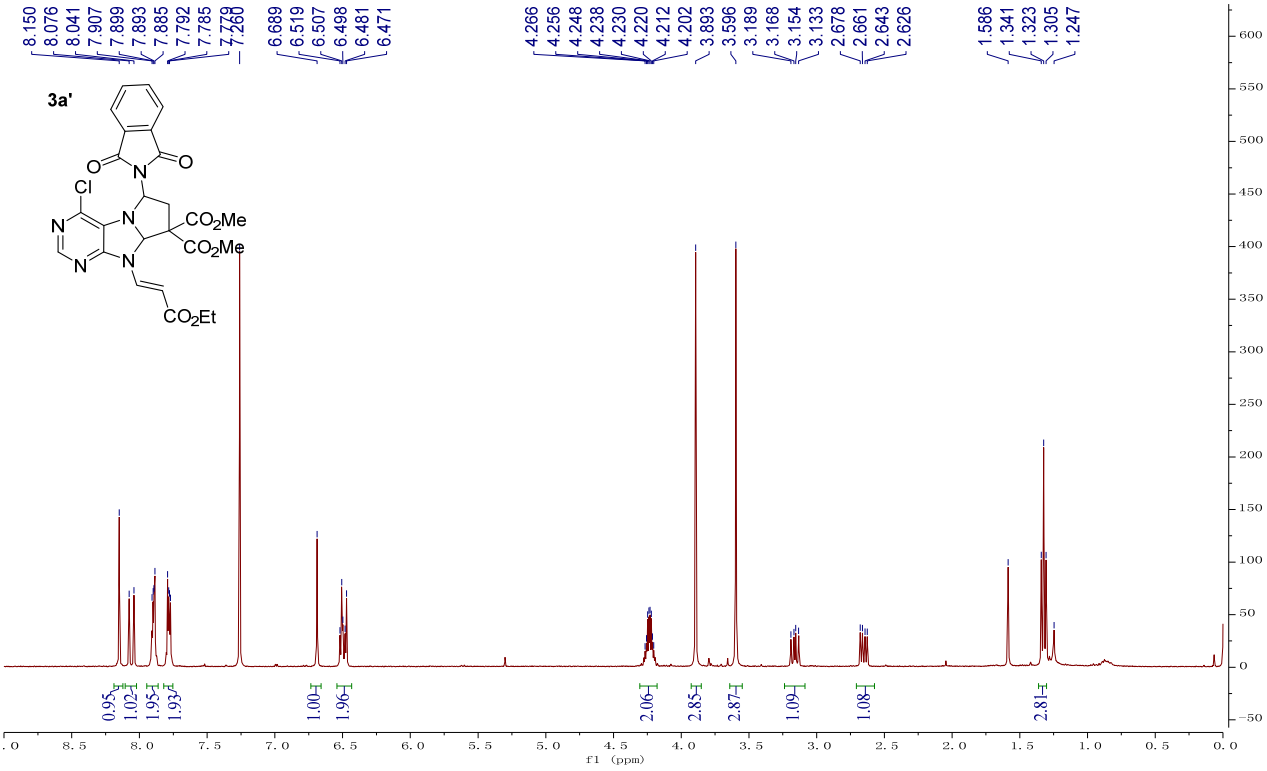
^{1}H-NMR of 1q



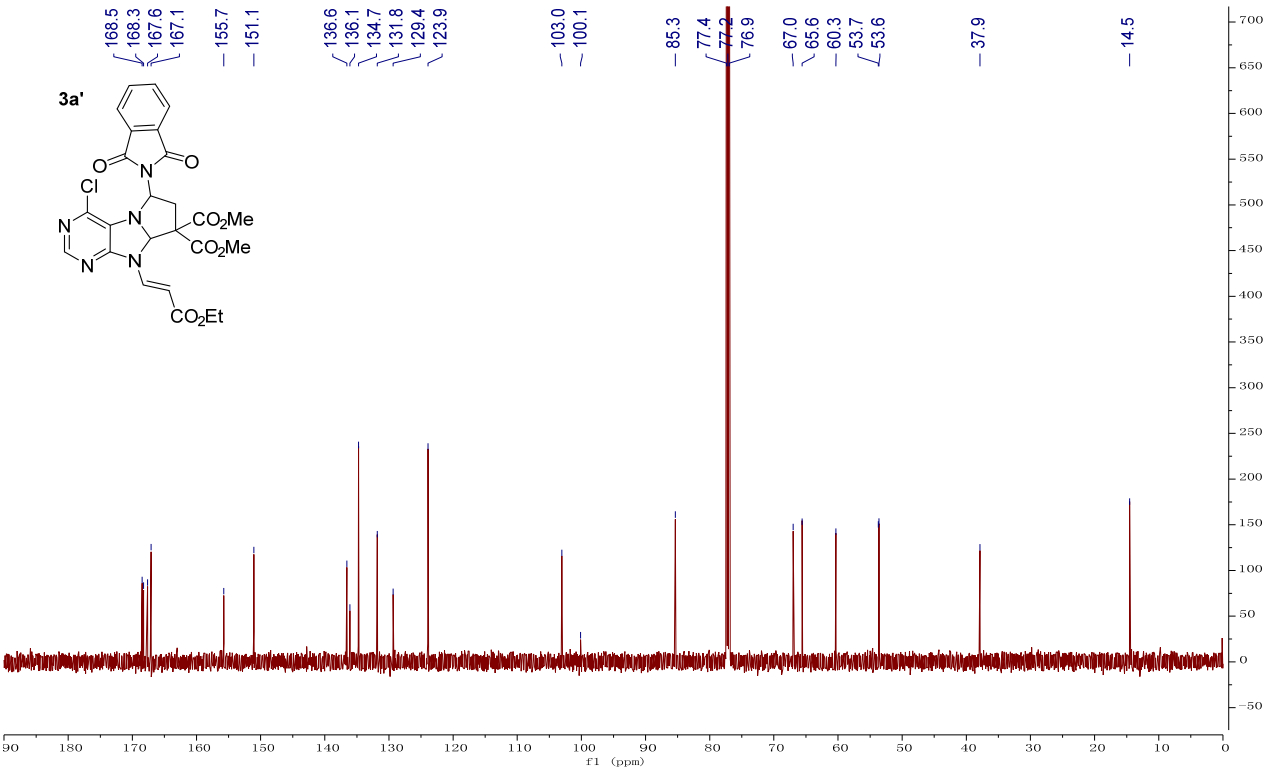
^{13}C-NMR of 1q



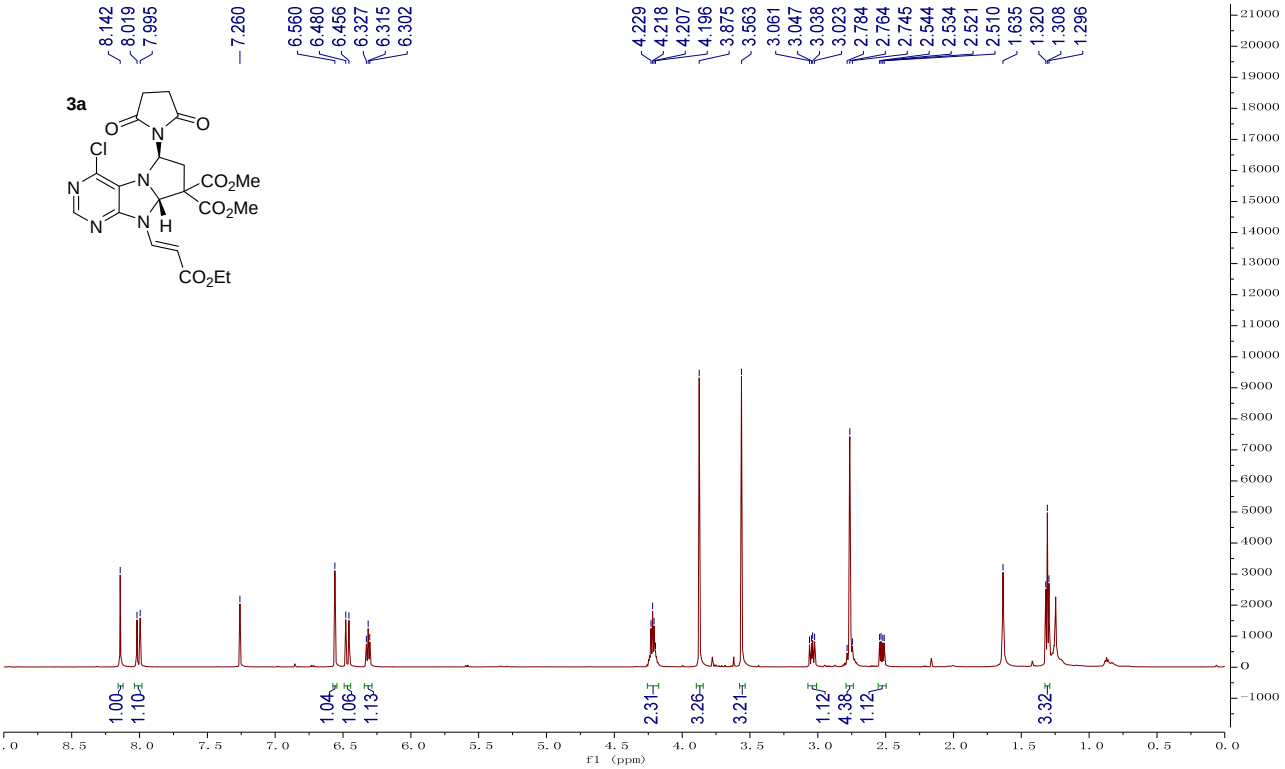
^{1}H-NMR of 3a'



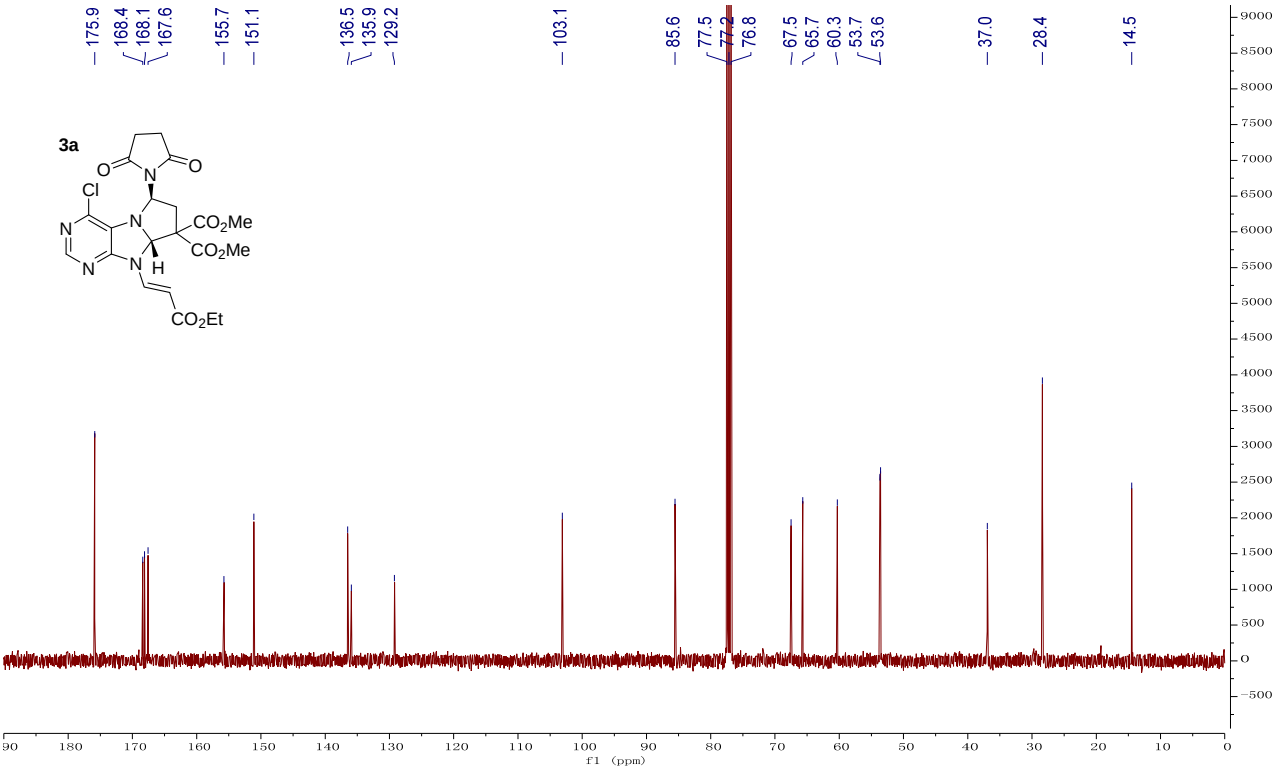
^{13}C-NMR of 3a'



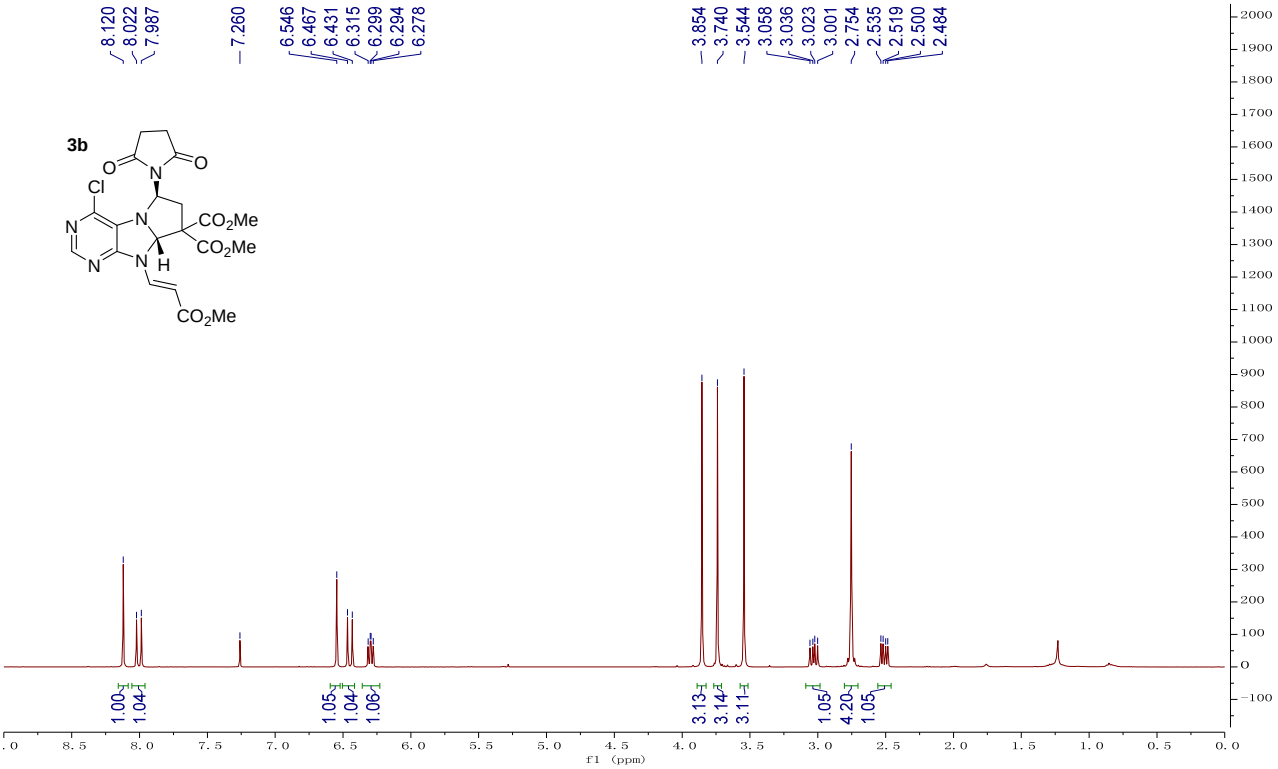
^{1}H-NMR of 3a



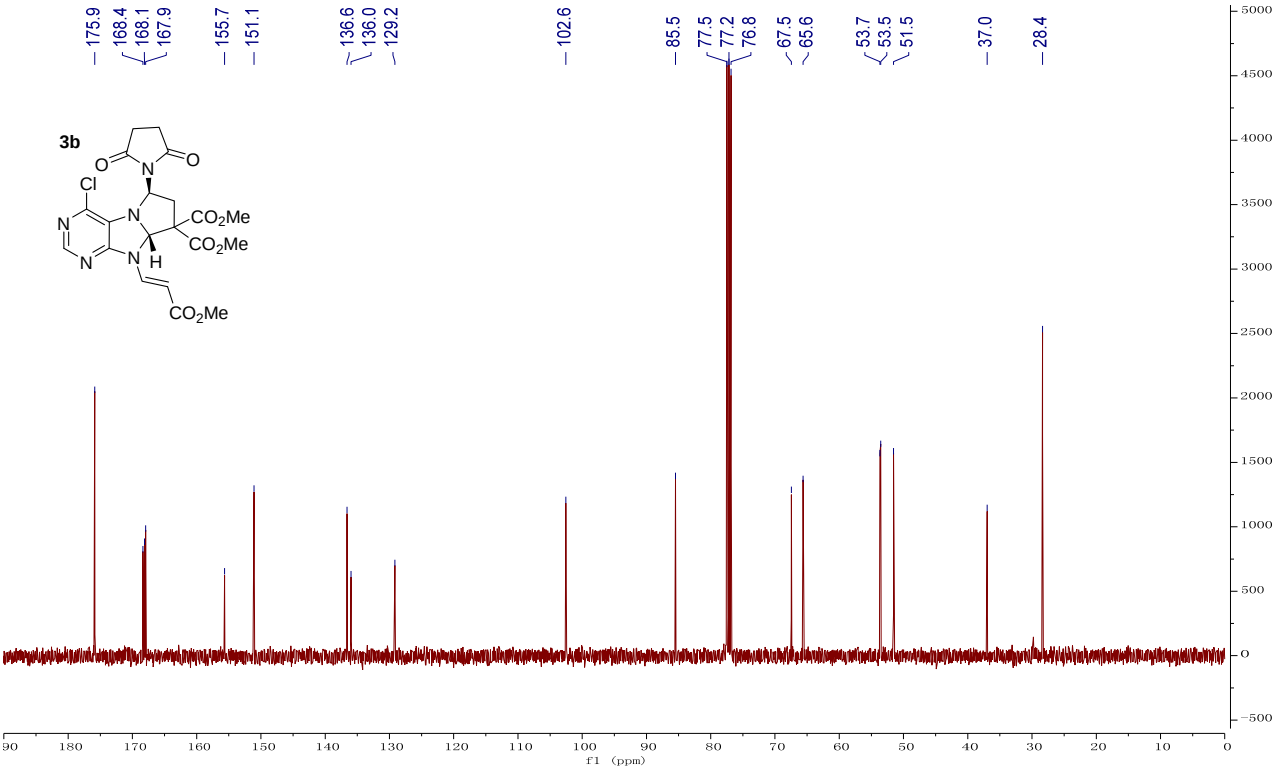
^{13}C-NMR of 3a



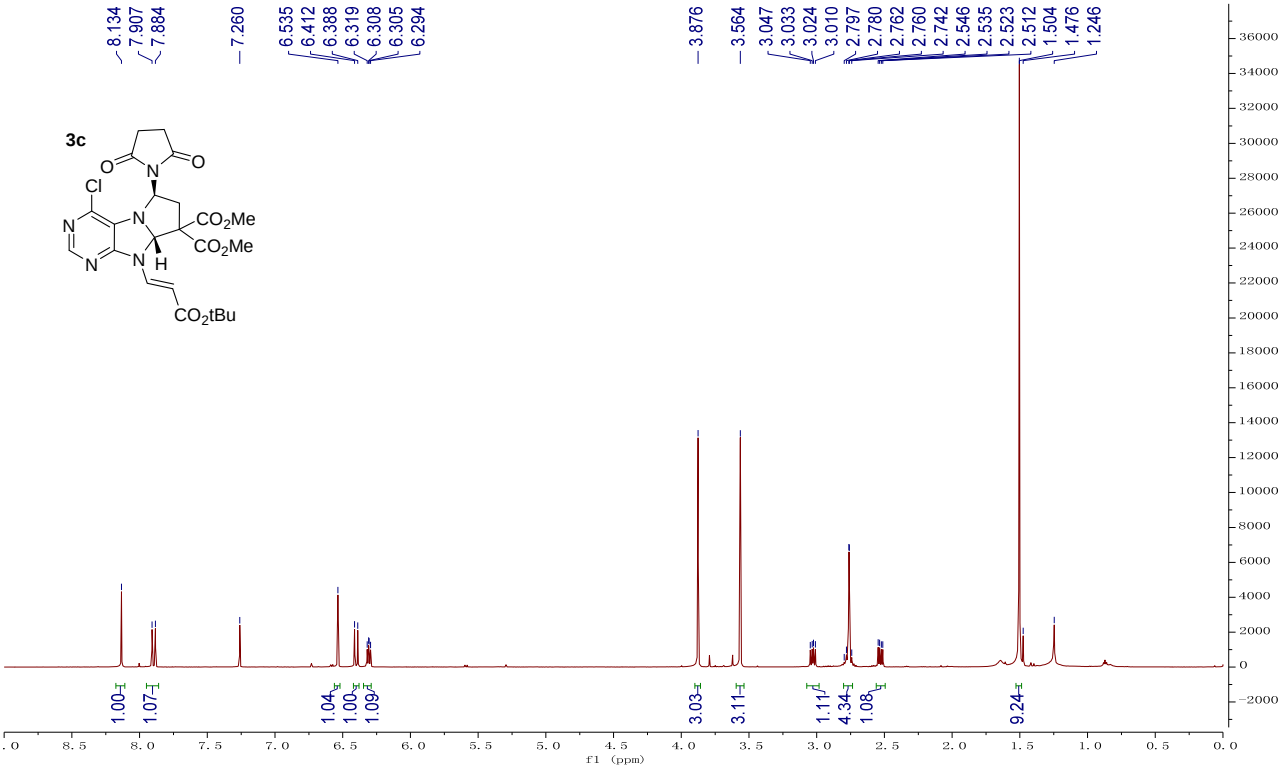
^{1}H-NMR of 3b



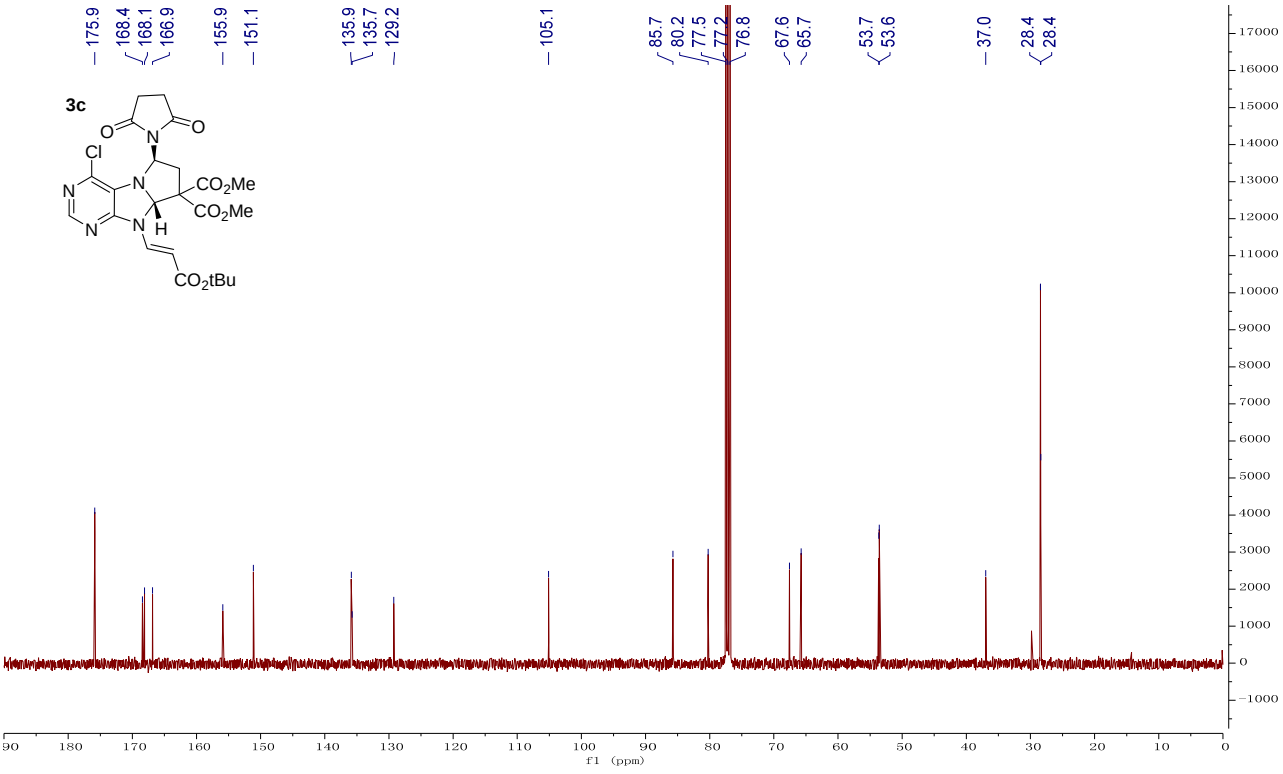
^{13}C-NMR of 3b



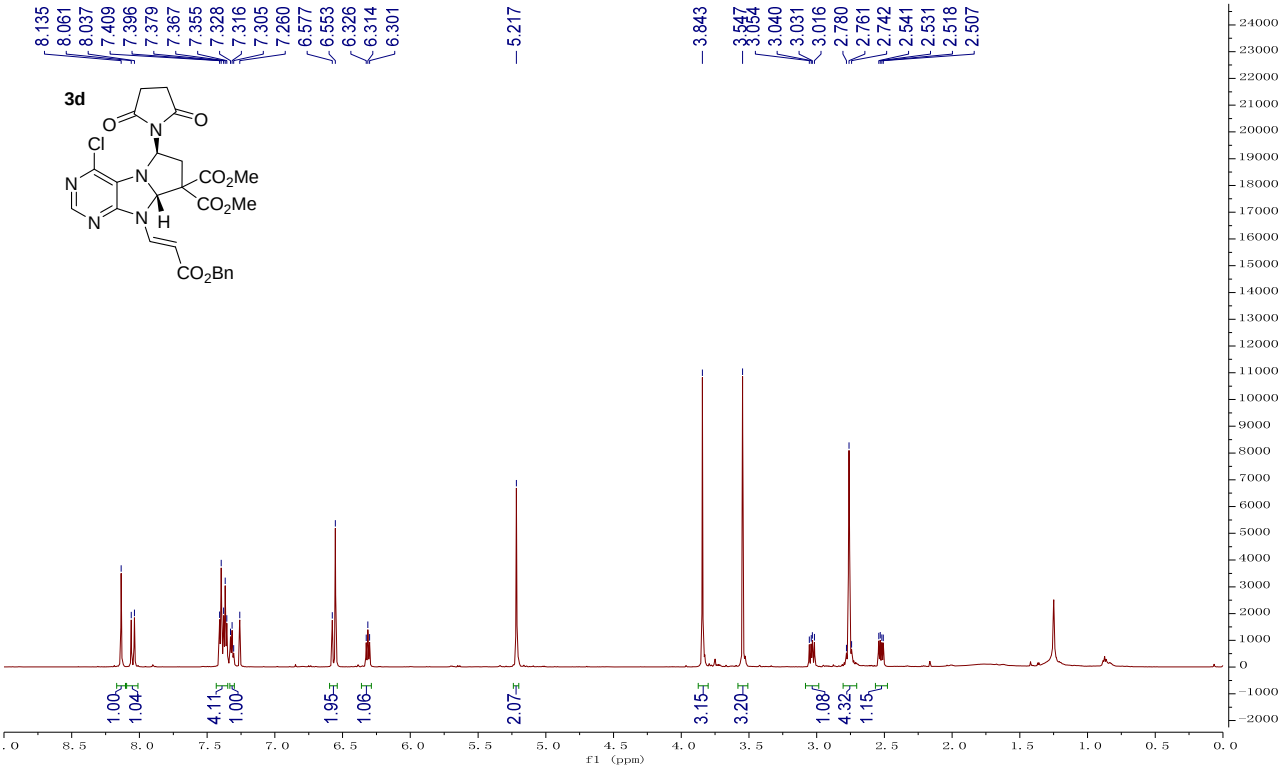
^{1}H-NMR of 3c



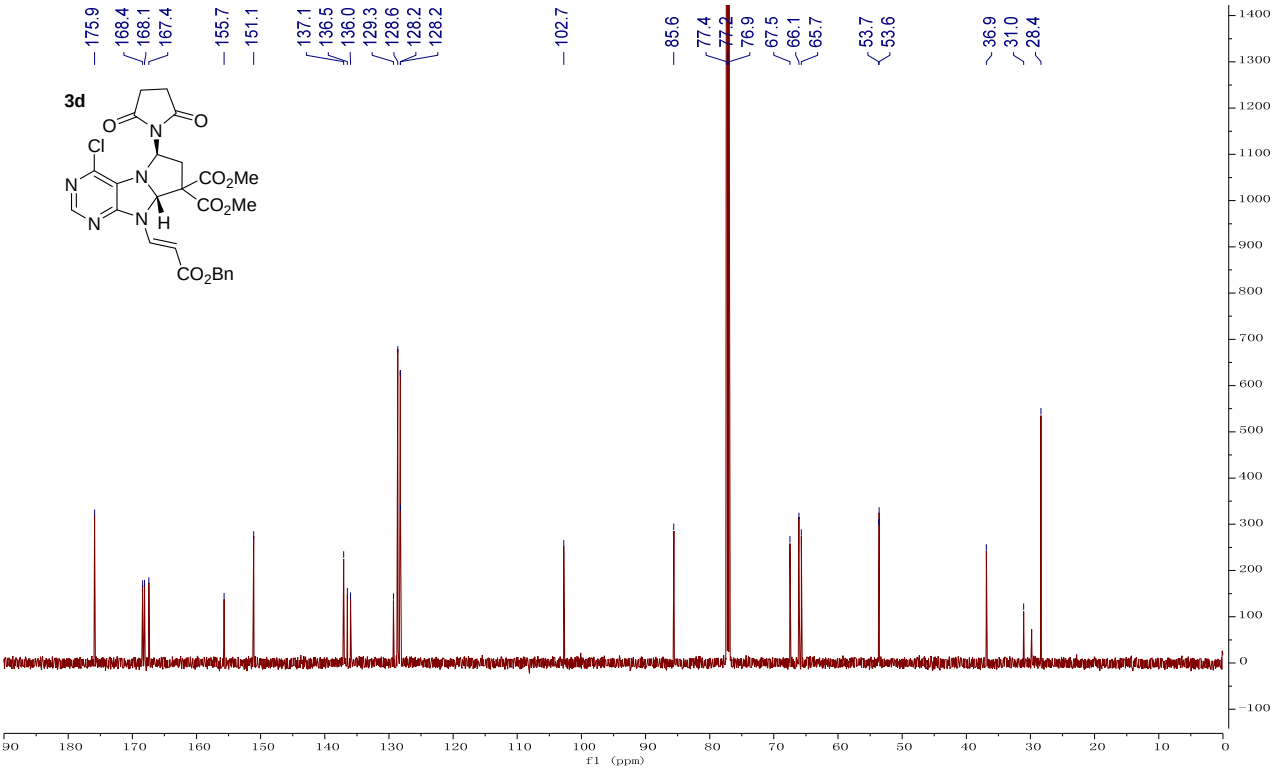
^{13}C-NMR of 3c



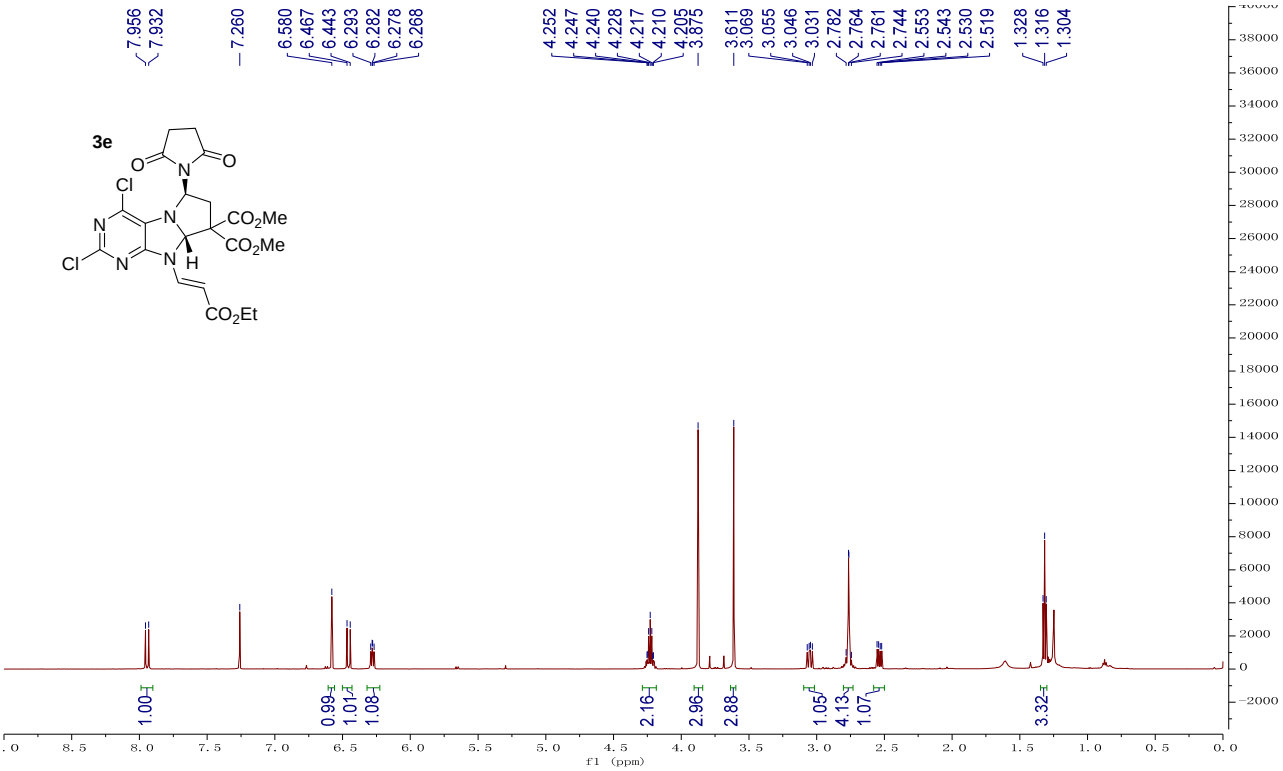
^{1}H-NMR of 3d



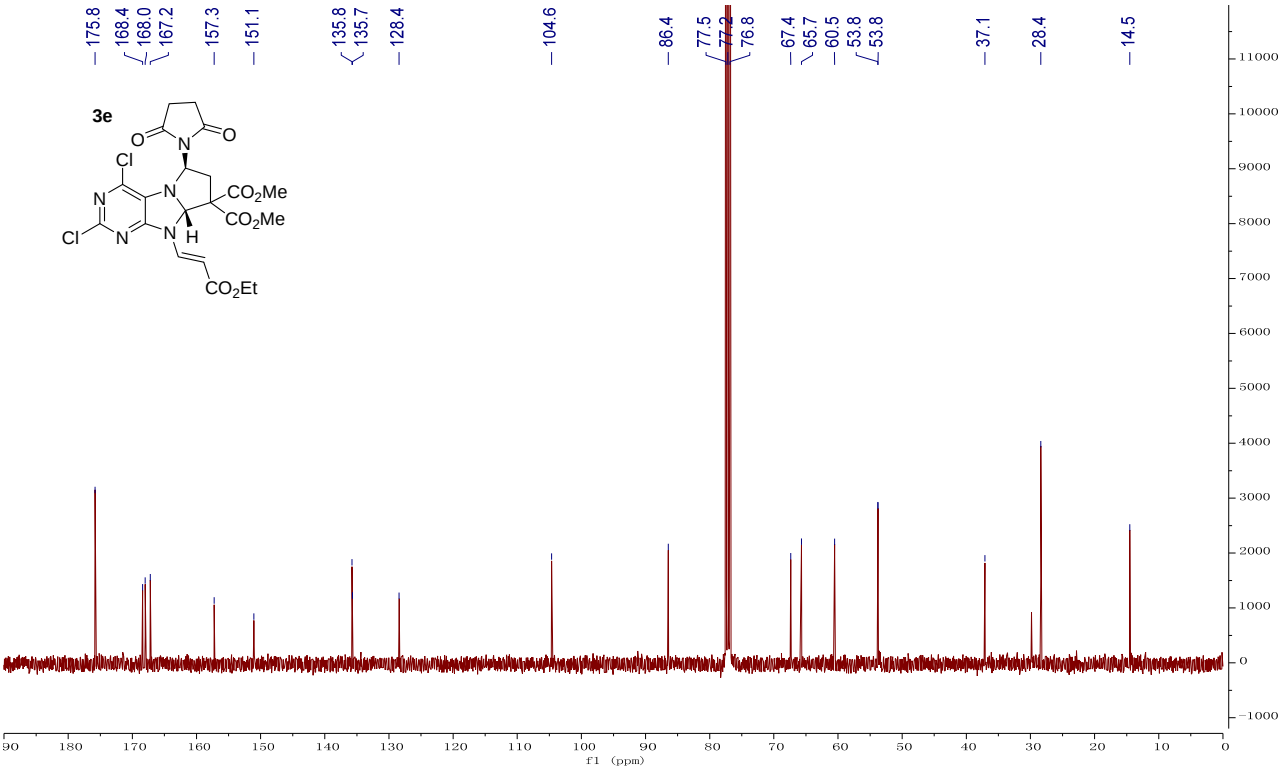
^{13}C-NMR of 3d



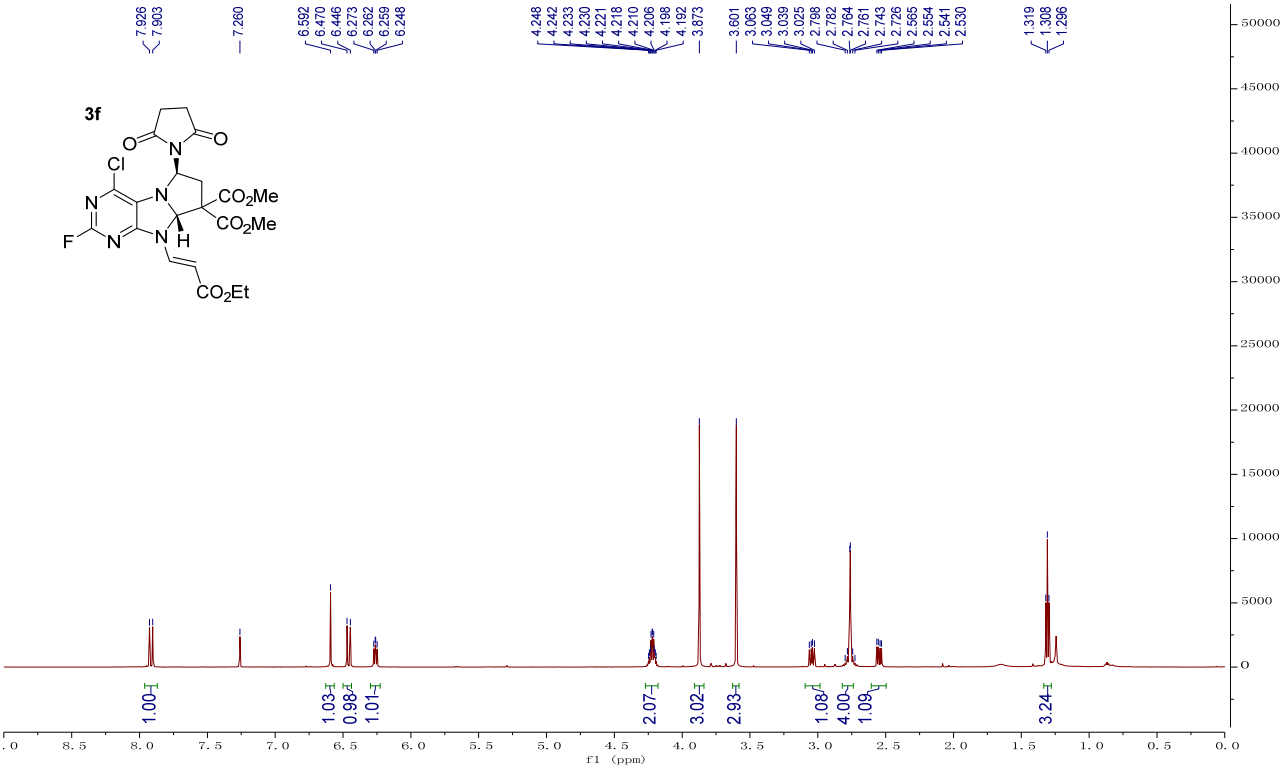
^{1}H-NMR of 3e



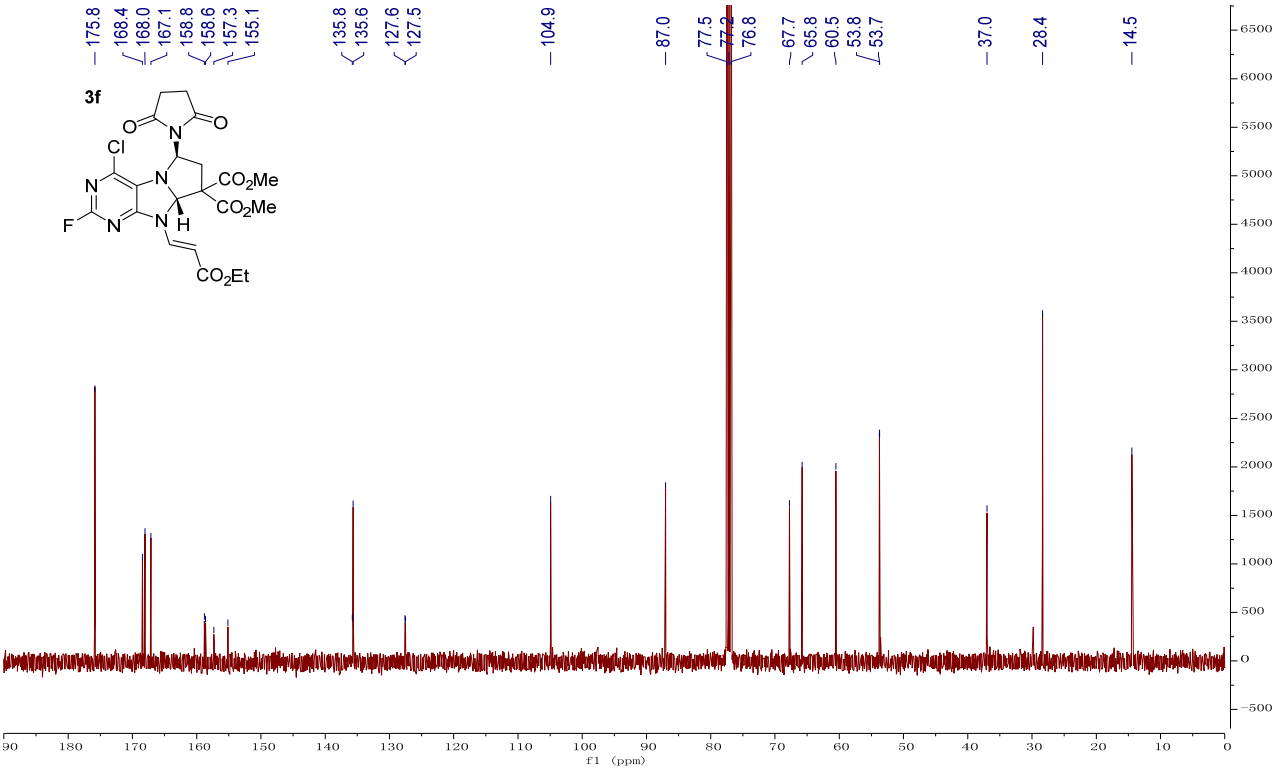
^{13}C-NMR of 3e



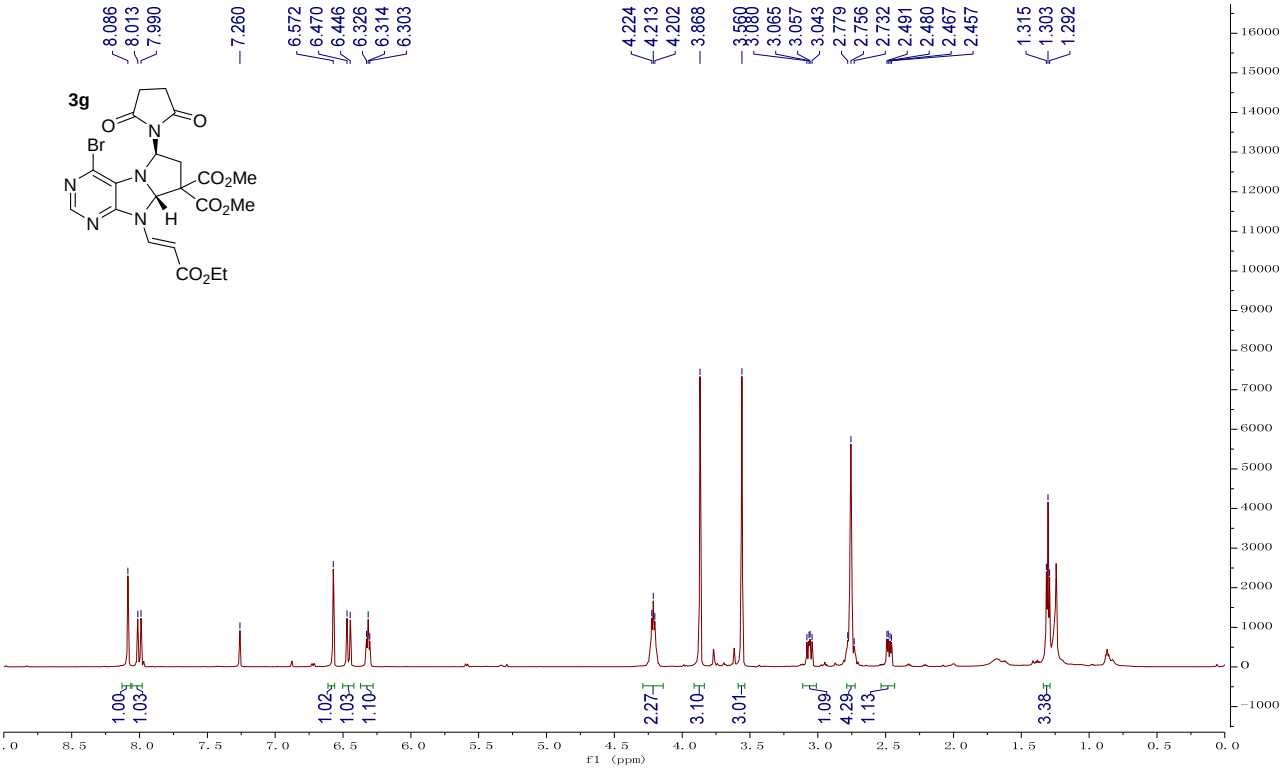
^{1}H-NMR of 3f



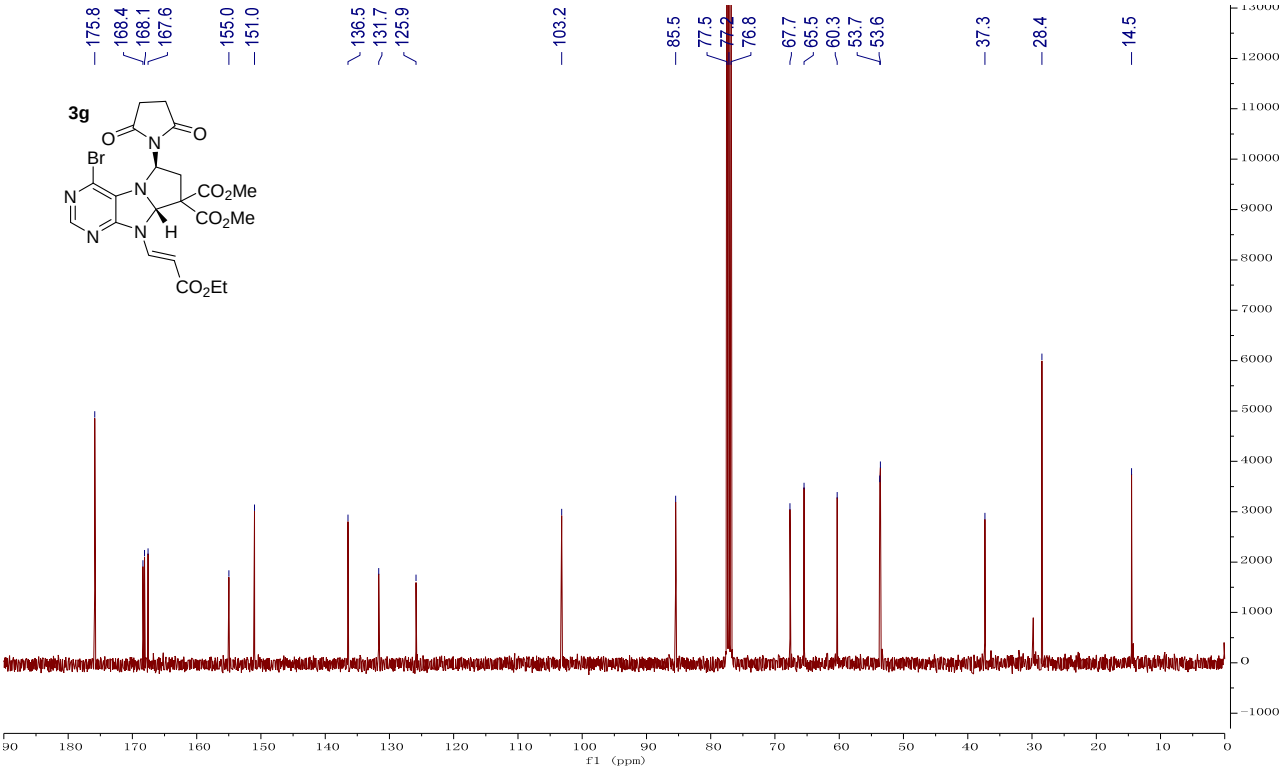
^{13}C-NMR of 3f



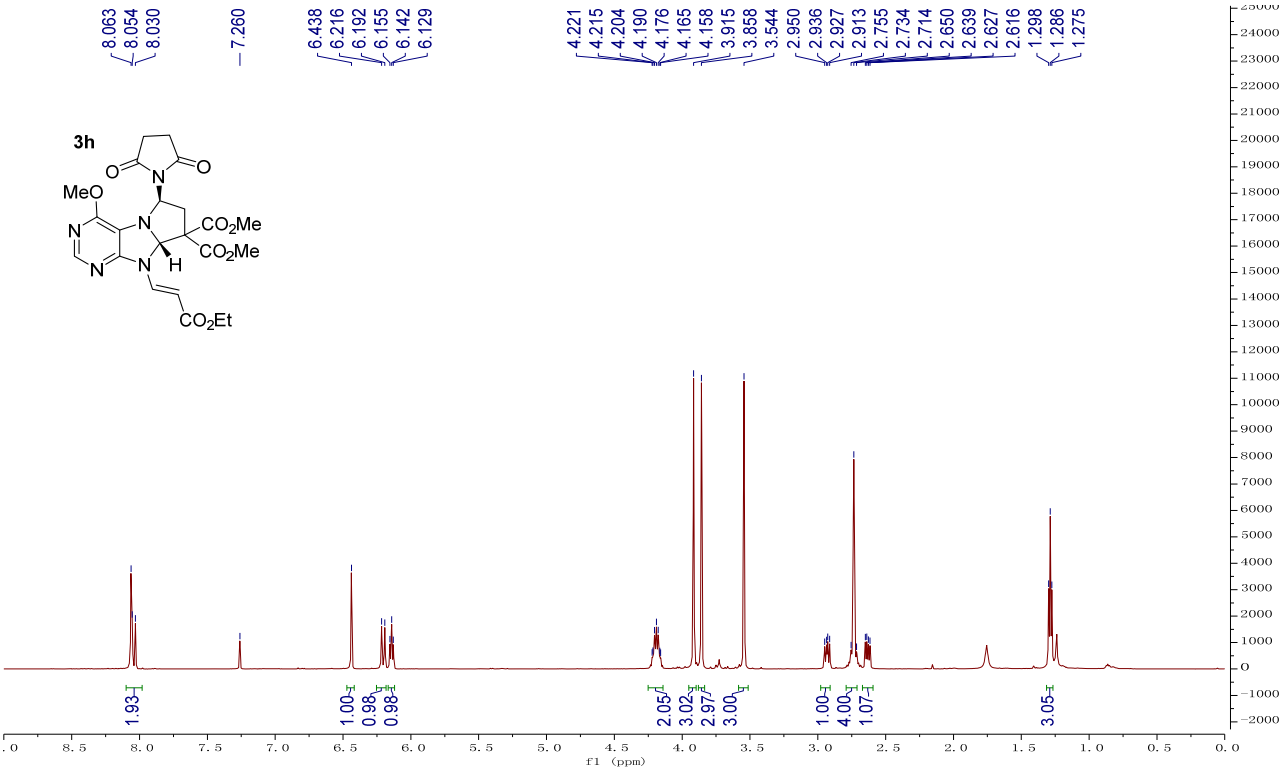
^{1}H-NMR of 3g



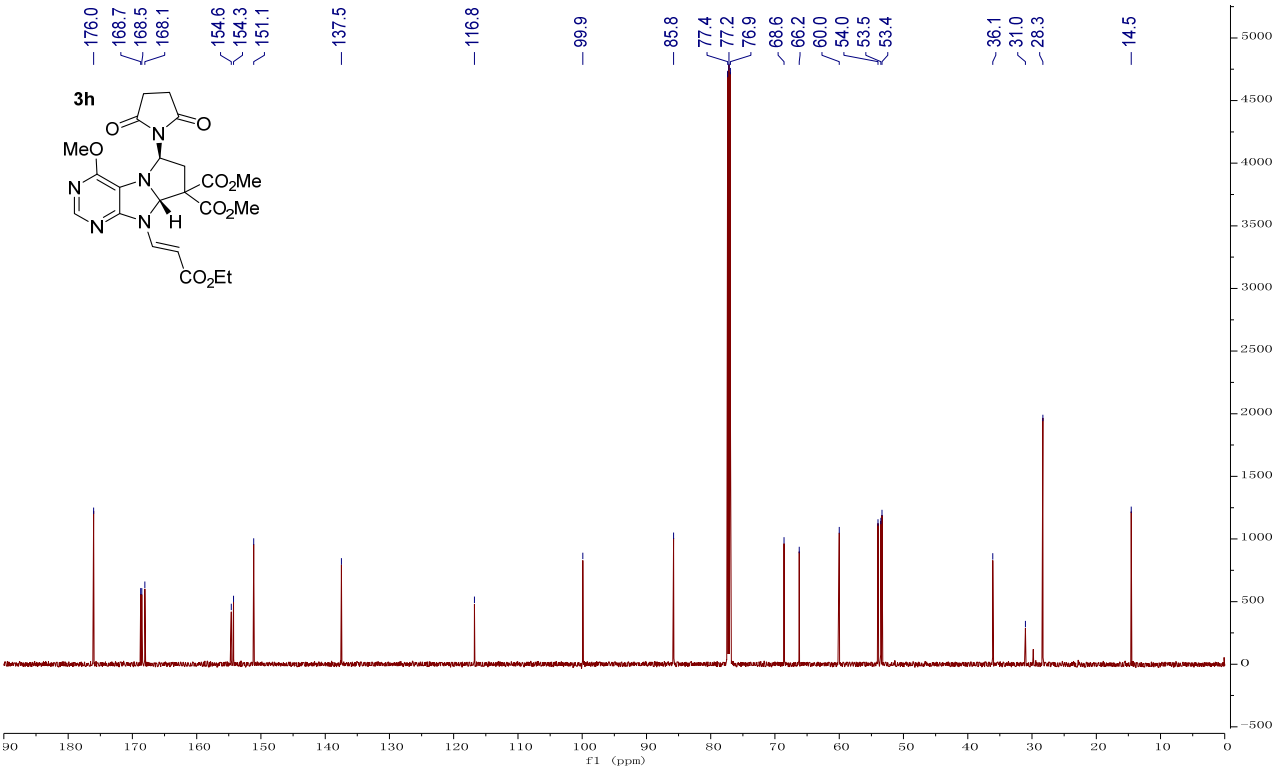
^{13}C-NMR of 3g



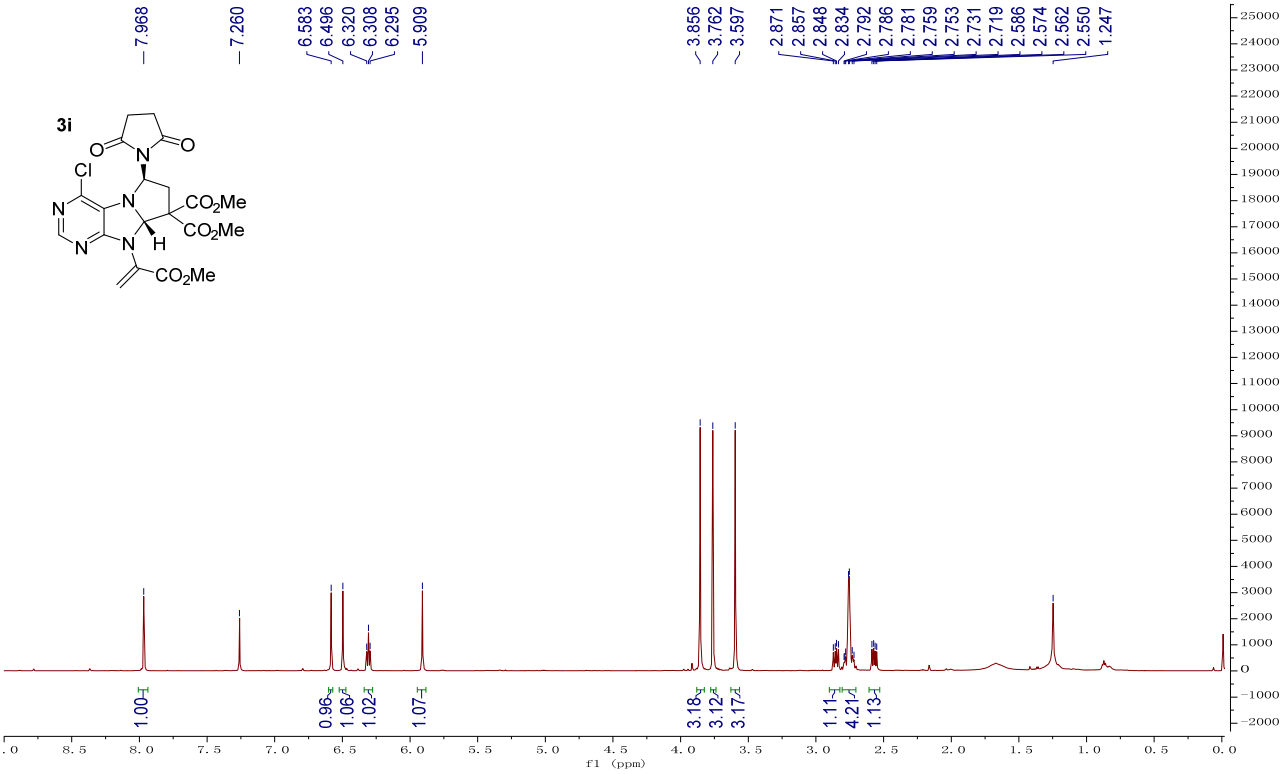
^{1}H-NMR of 3h



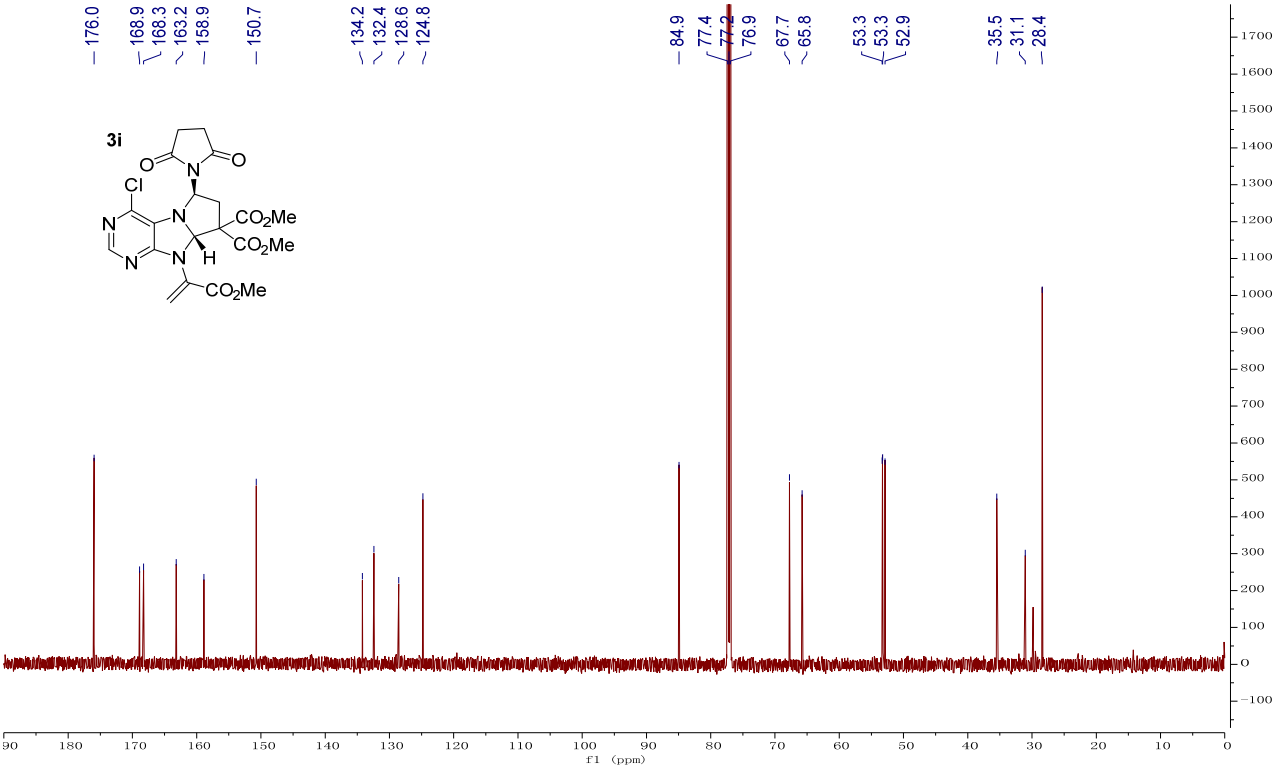
^{13}C-NMR of 3h



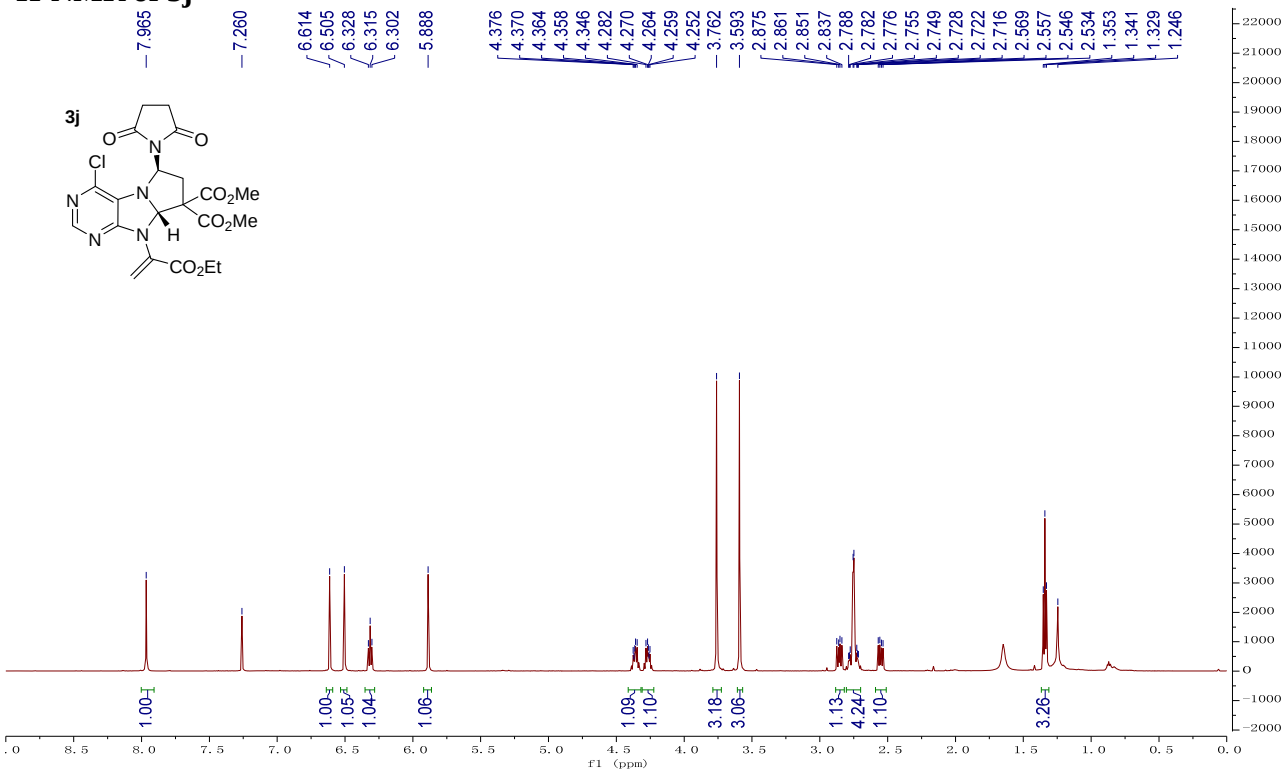
^{1}H-NMR of 3i



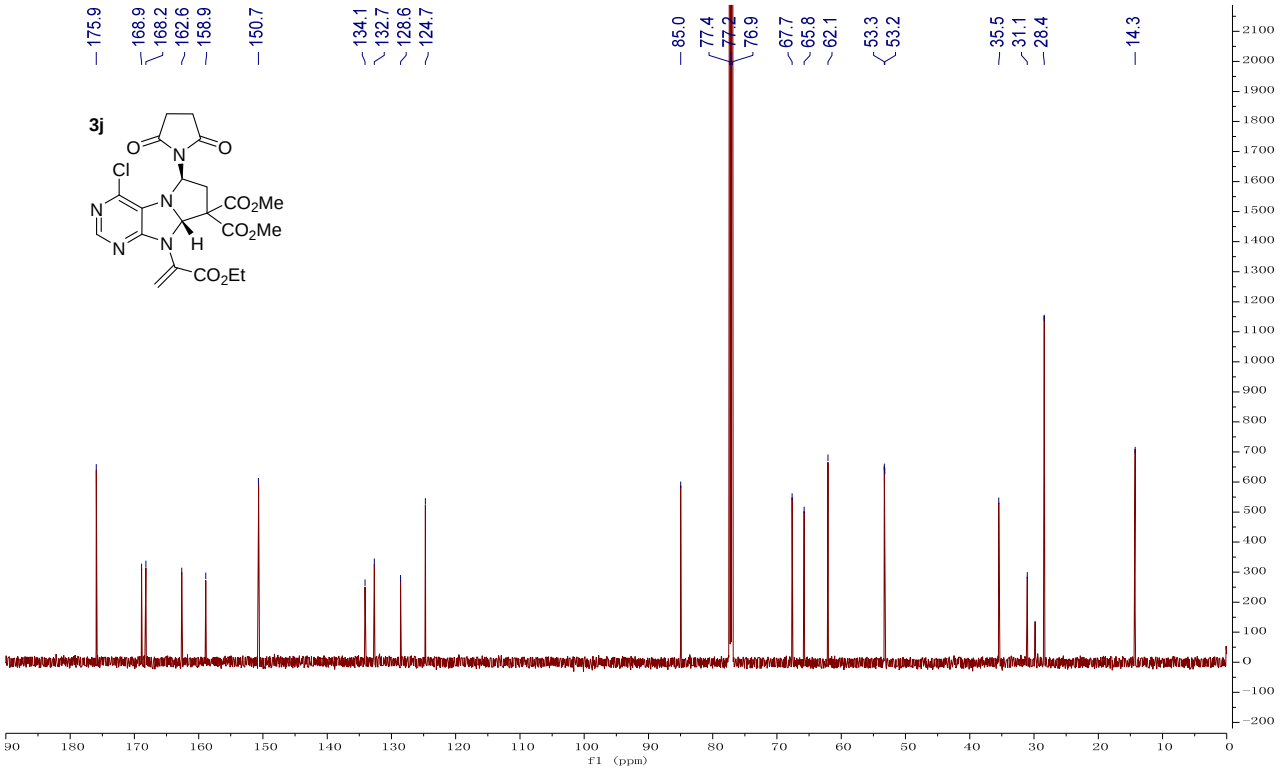
^{13}C-NMR of 3i



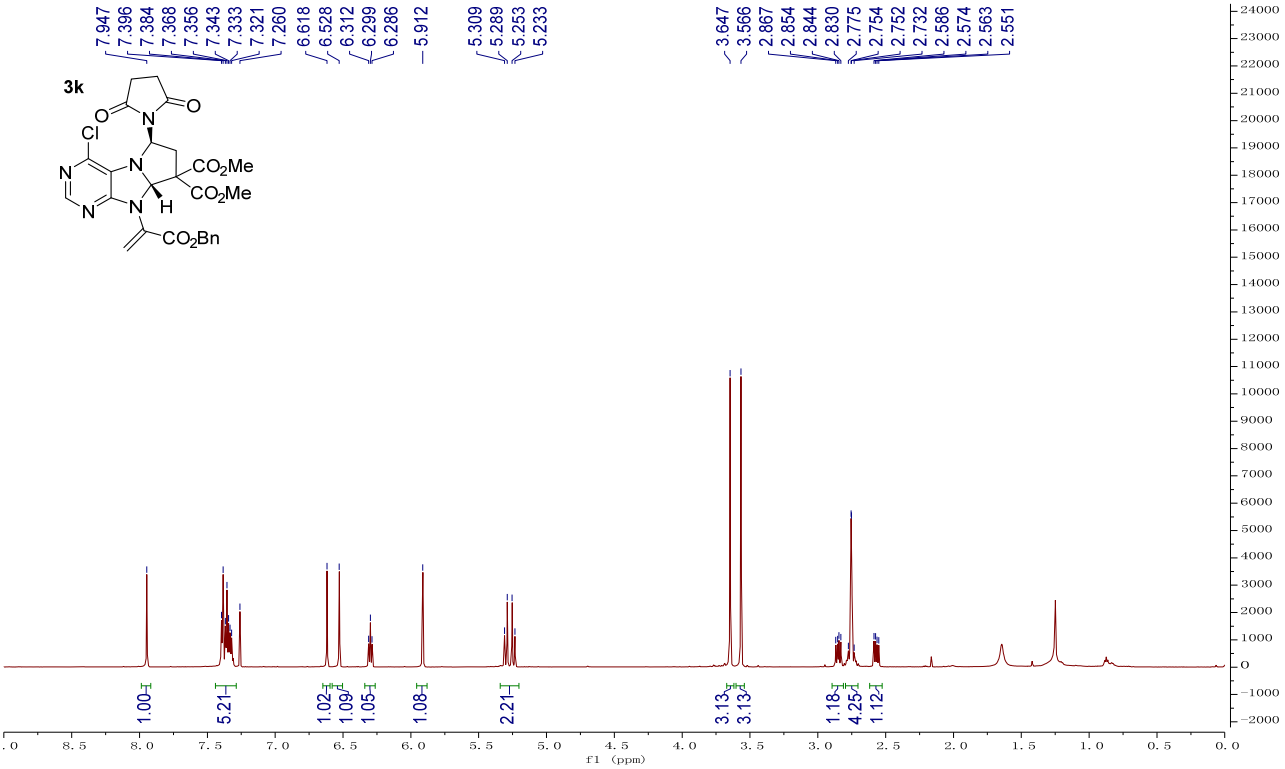
^{1}H-NMR of 3j



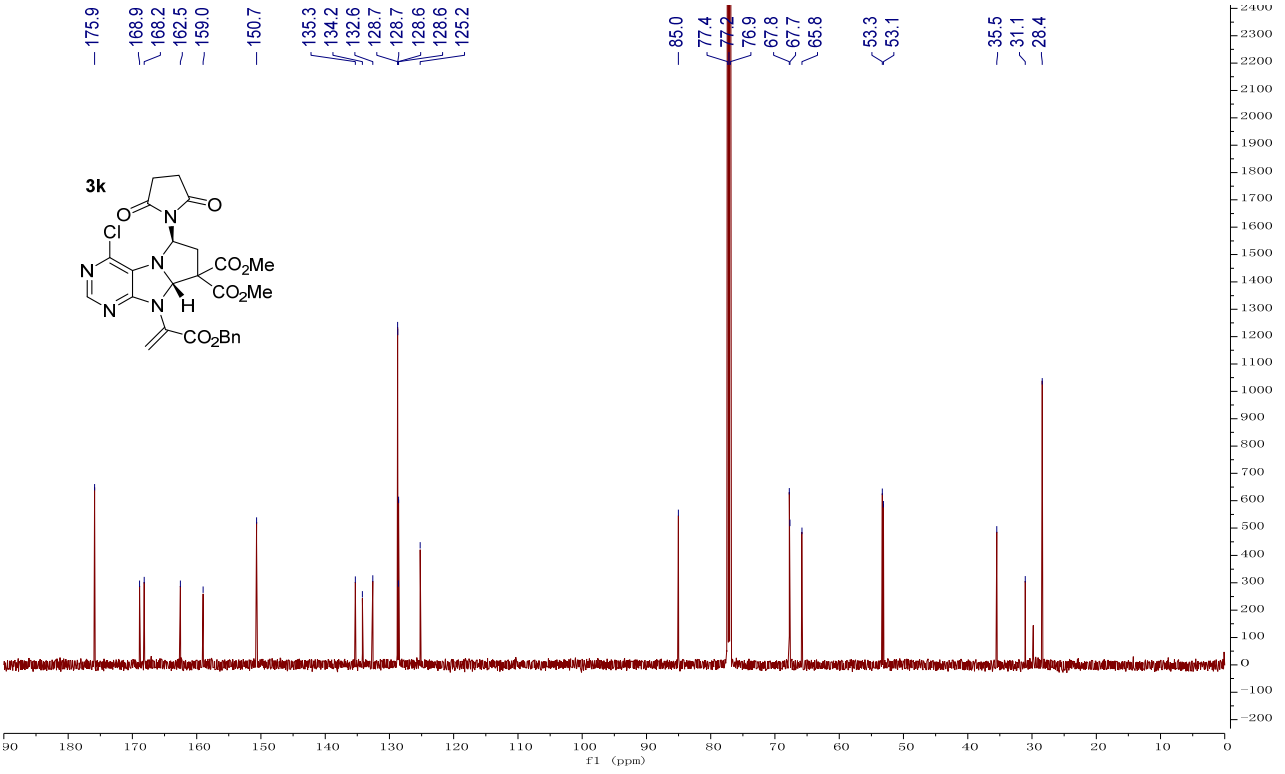
^{13}C-NMR of 3j



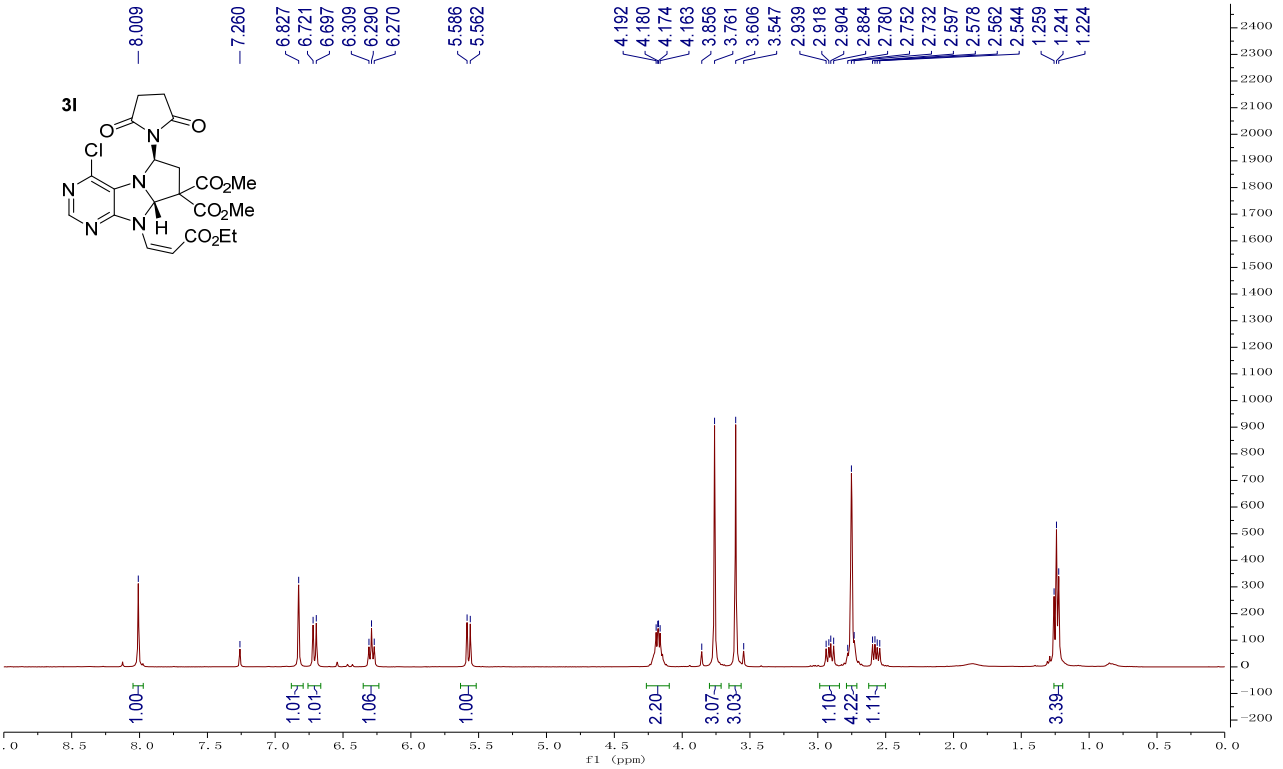
^{1}H-NMR of 3k



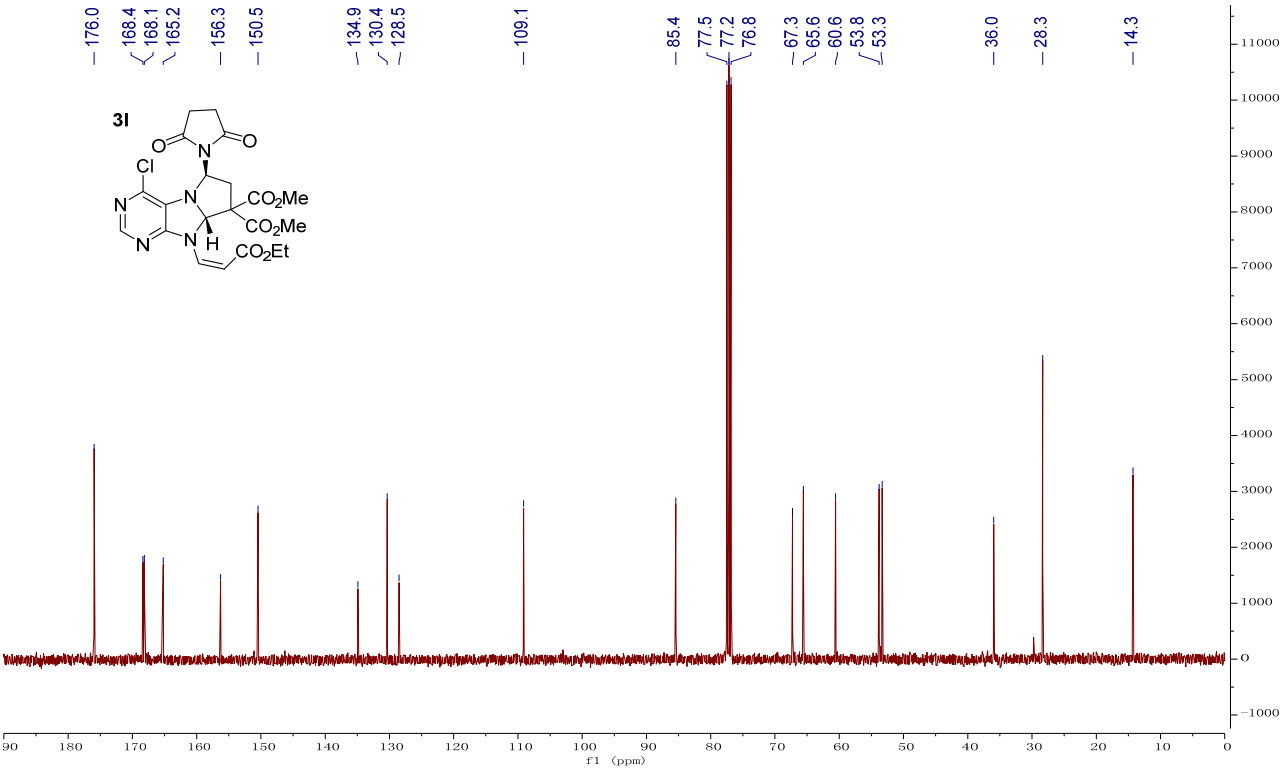
^{13}C-NMR of 3k



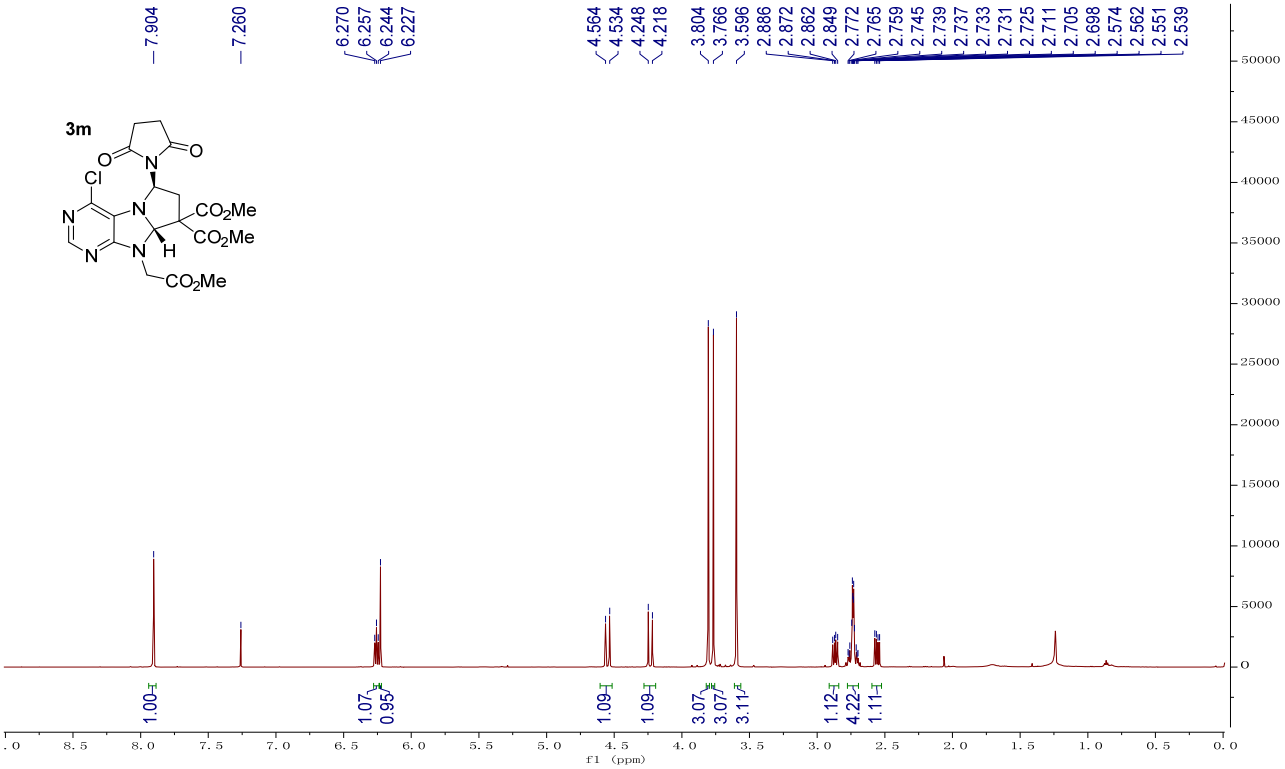
^{1}H-NMR of 3l



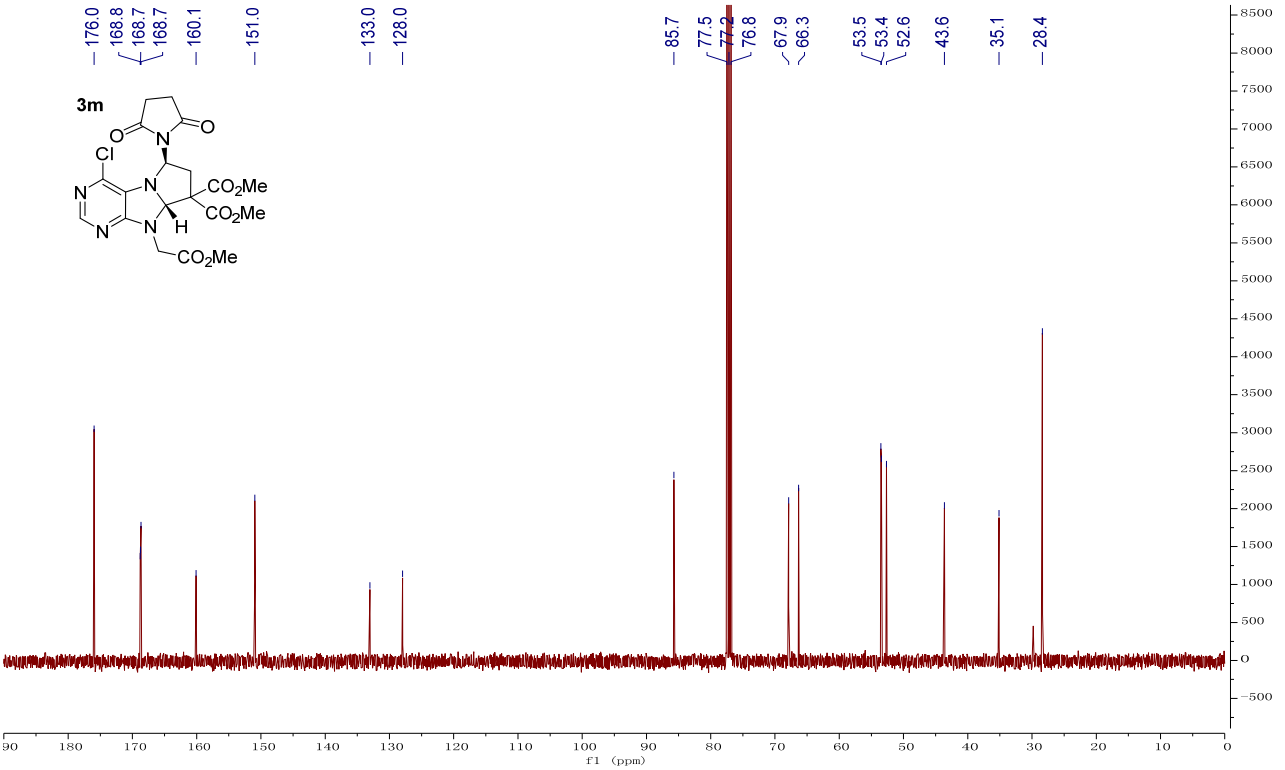
^{13}C-NMR of 3l



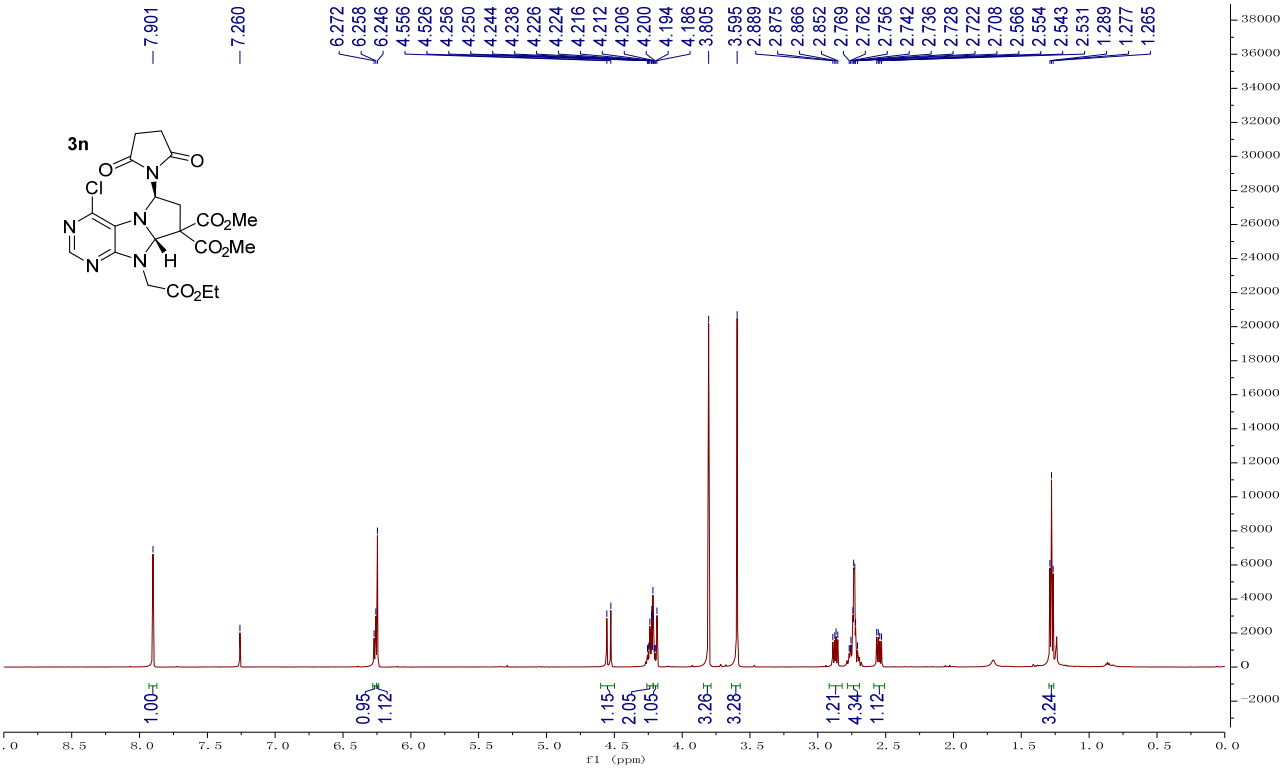
^{1}H-NMR of 3m



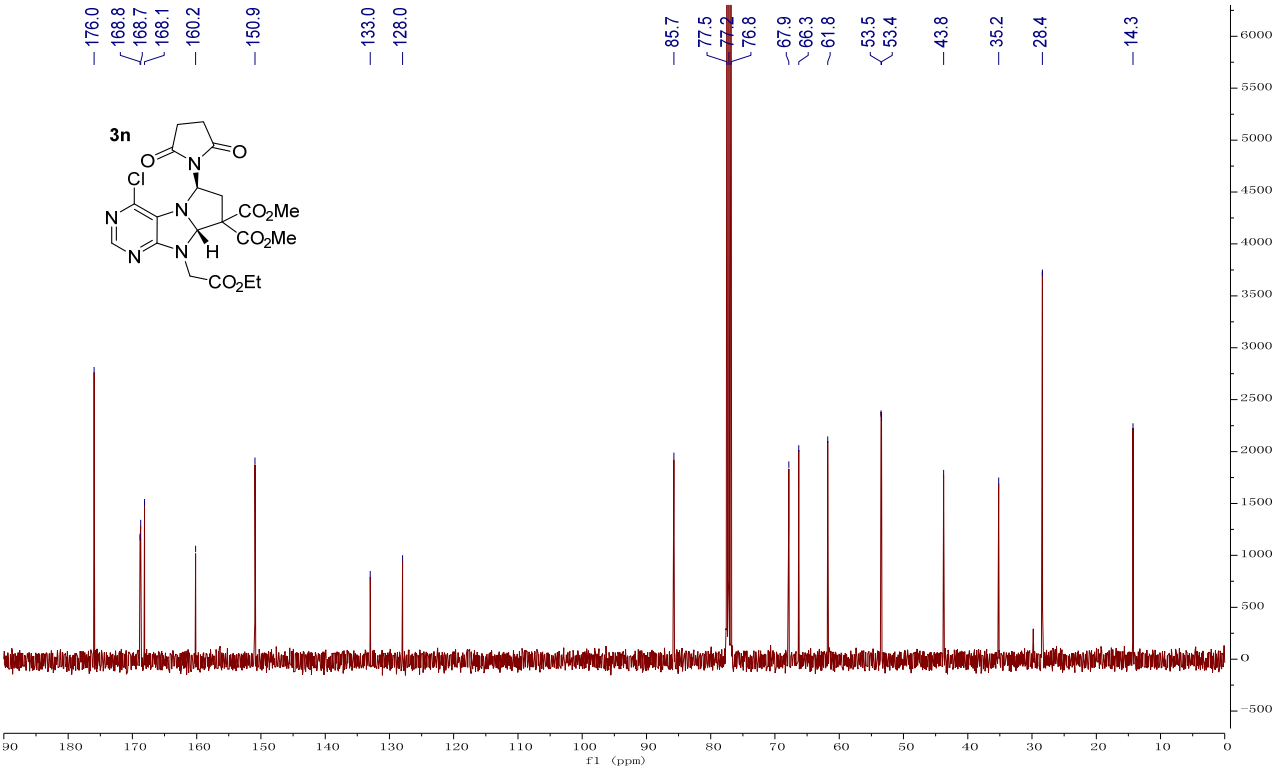
^{13}C-NMR of 3m



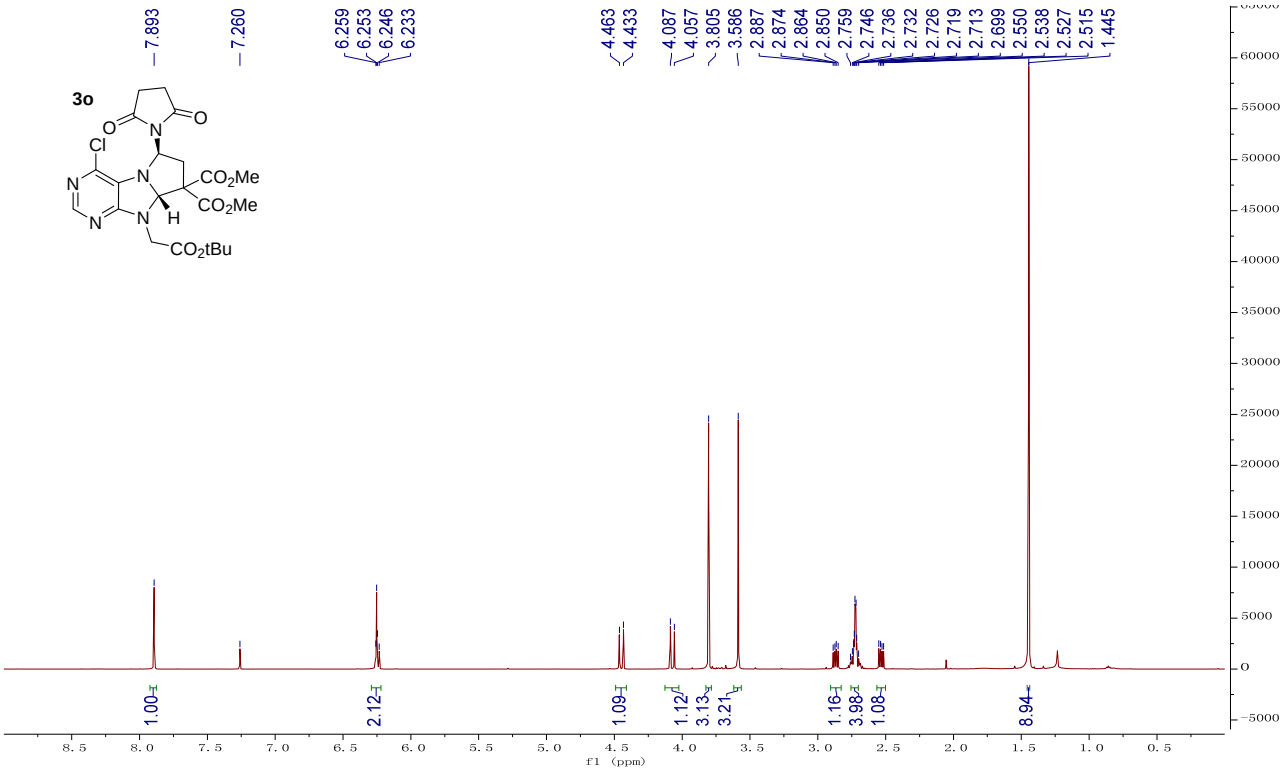
^{1}H-NMR of 3n



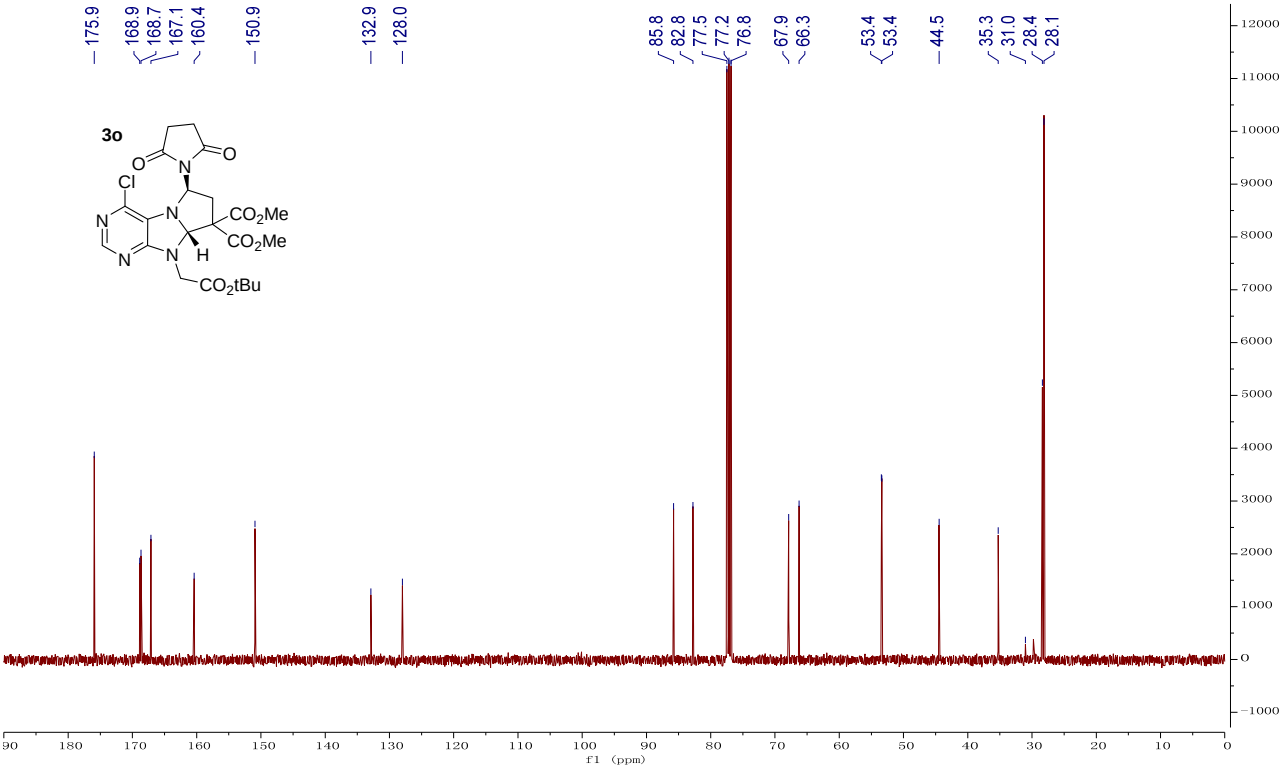
^{13}C-NMR of 3n



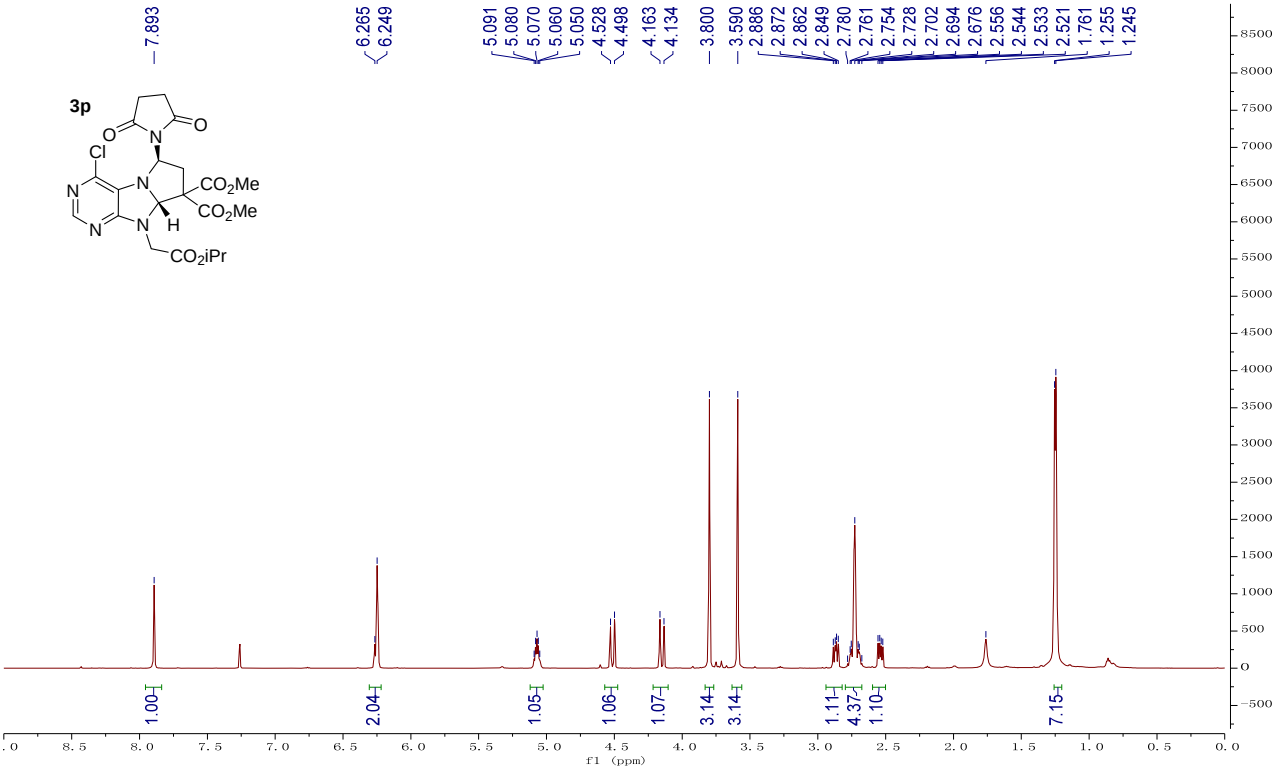
^{1}H-NMR of 3o



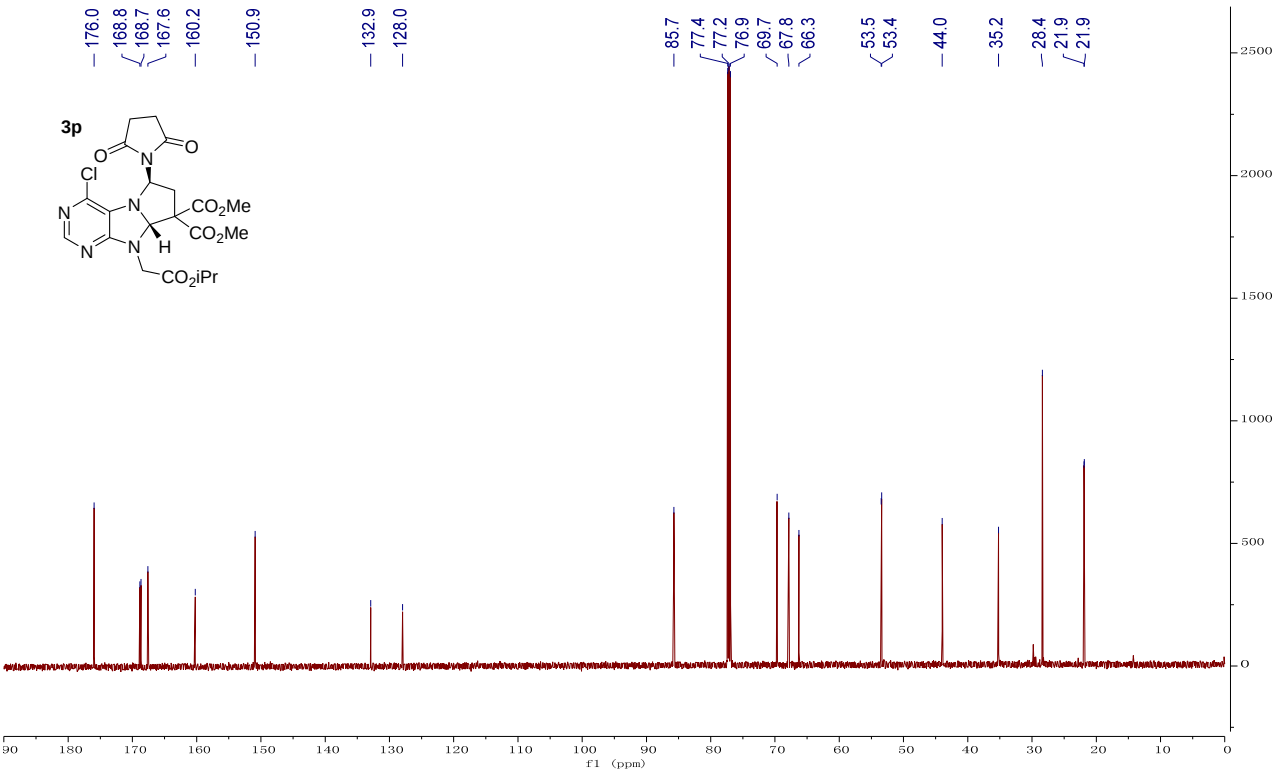
^{13}C-NMR of 3o



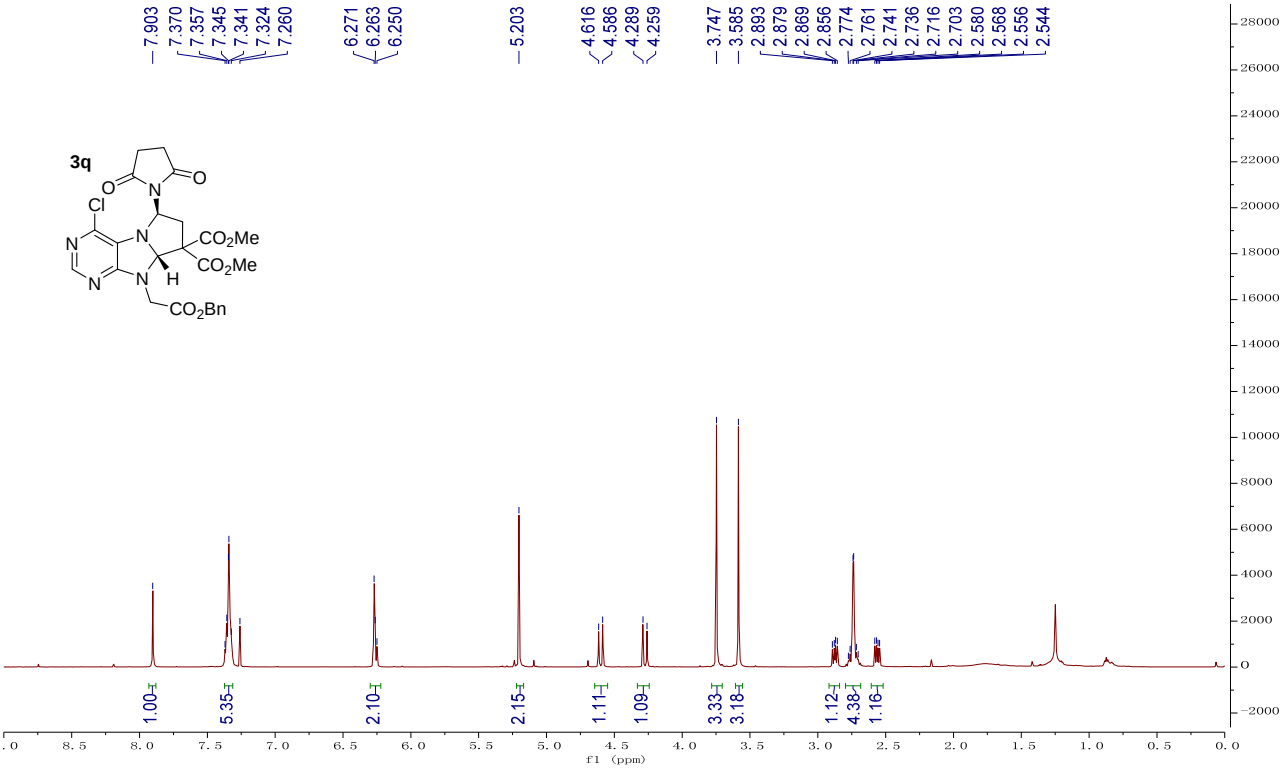
^{1}H-NMR of 3p



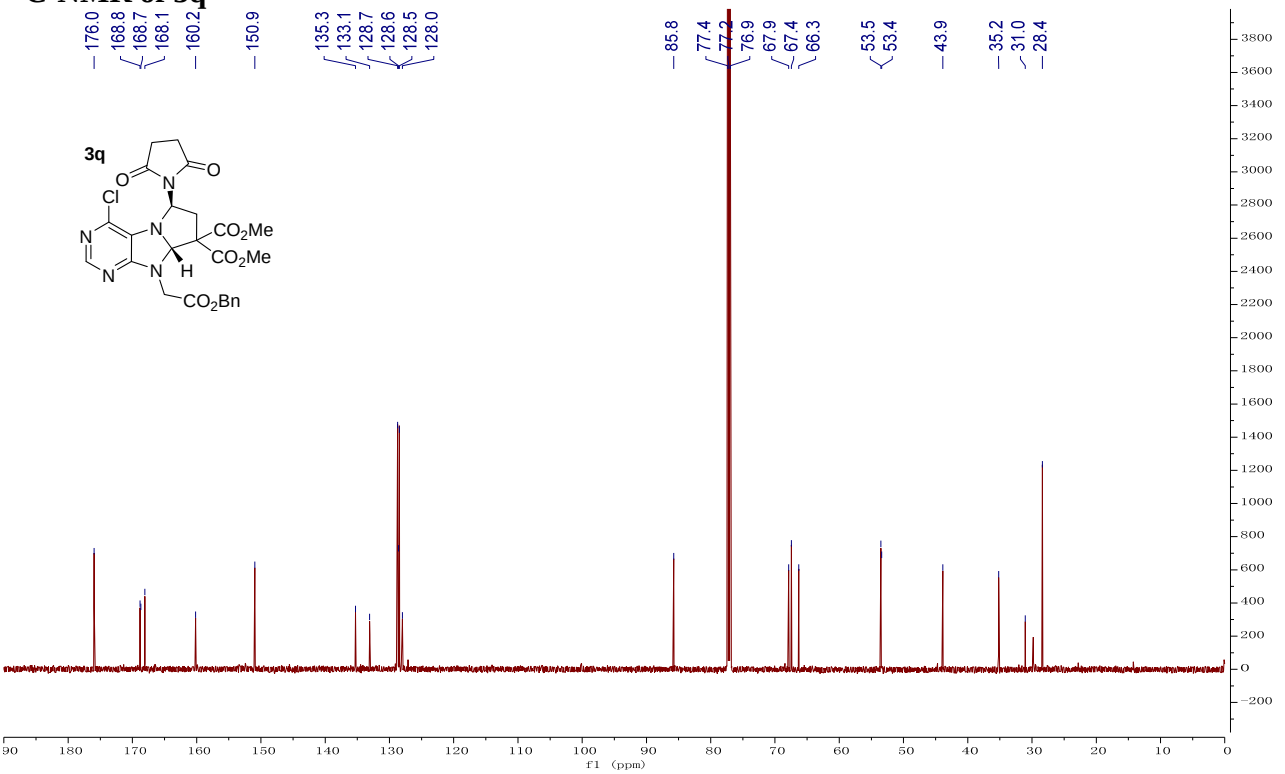
^{13}C-NMR of 3p



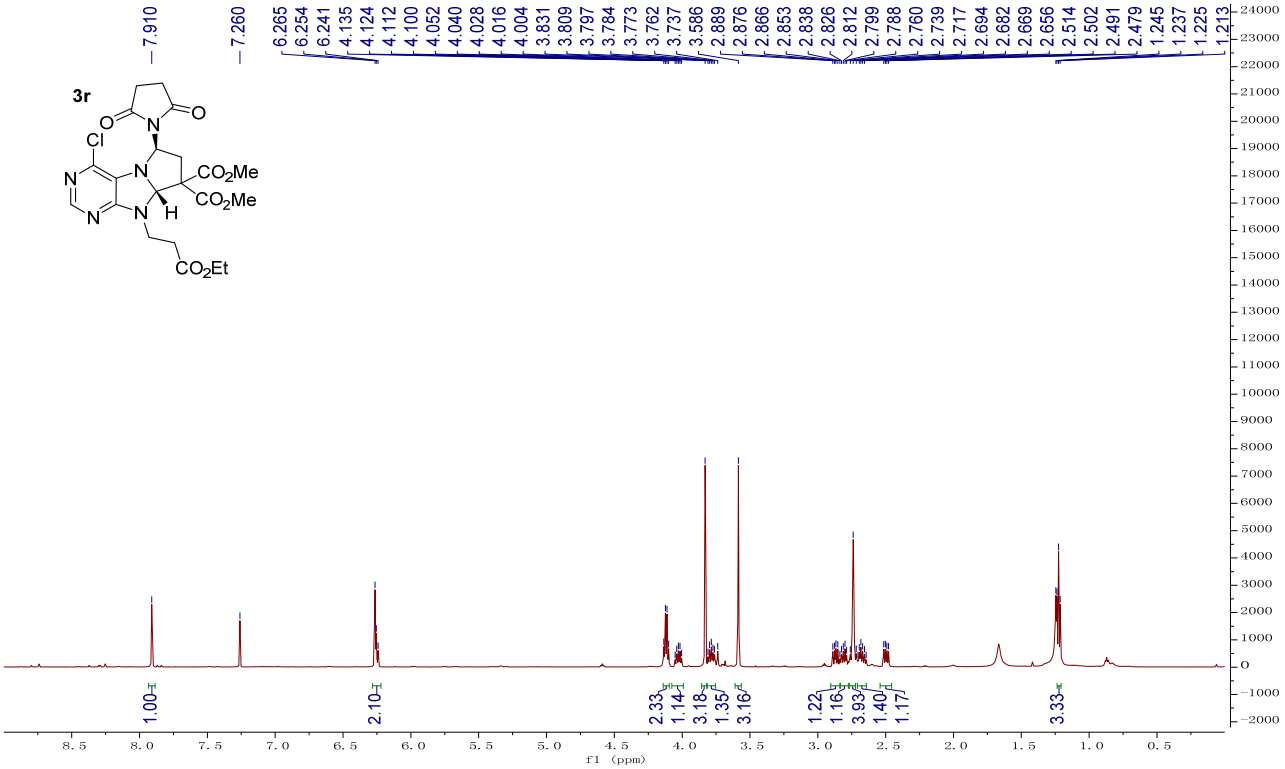
^{1}H-NMR of 3q



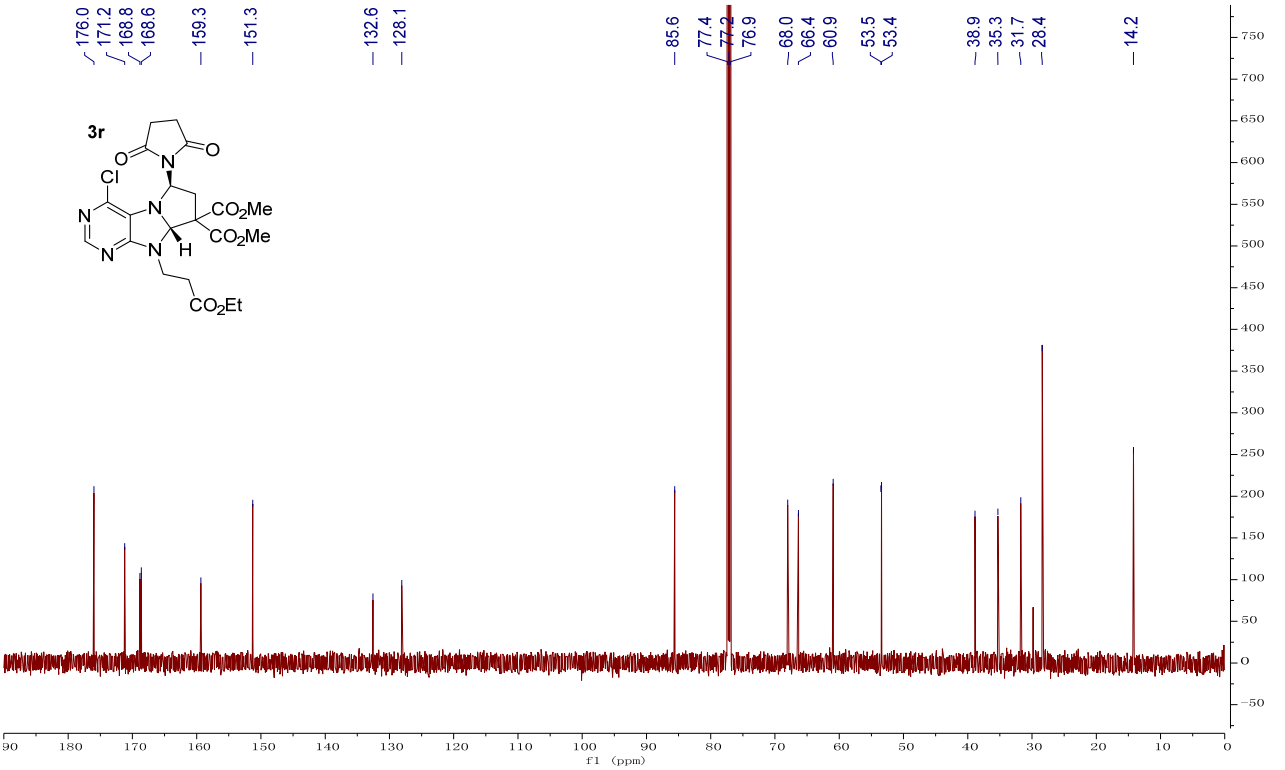
^{13}C-NMR of 3q



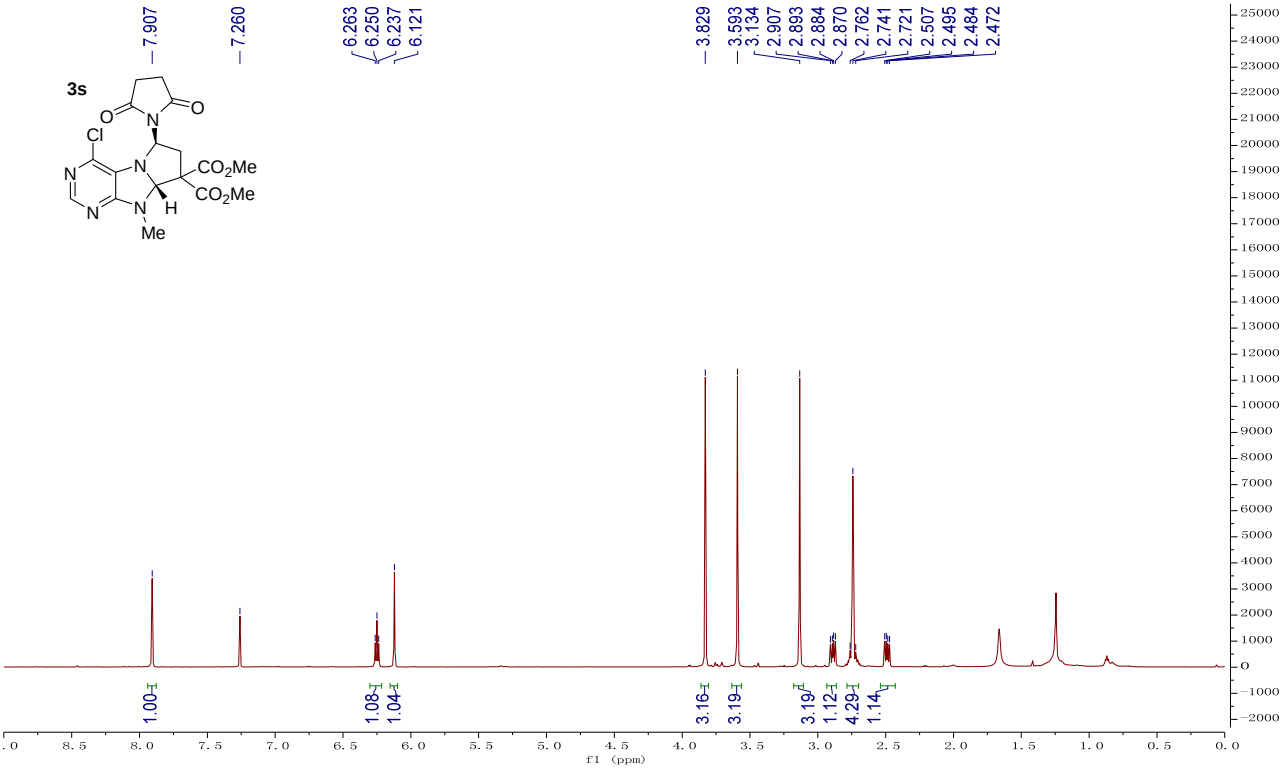
^{1}H-NMR of 3r



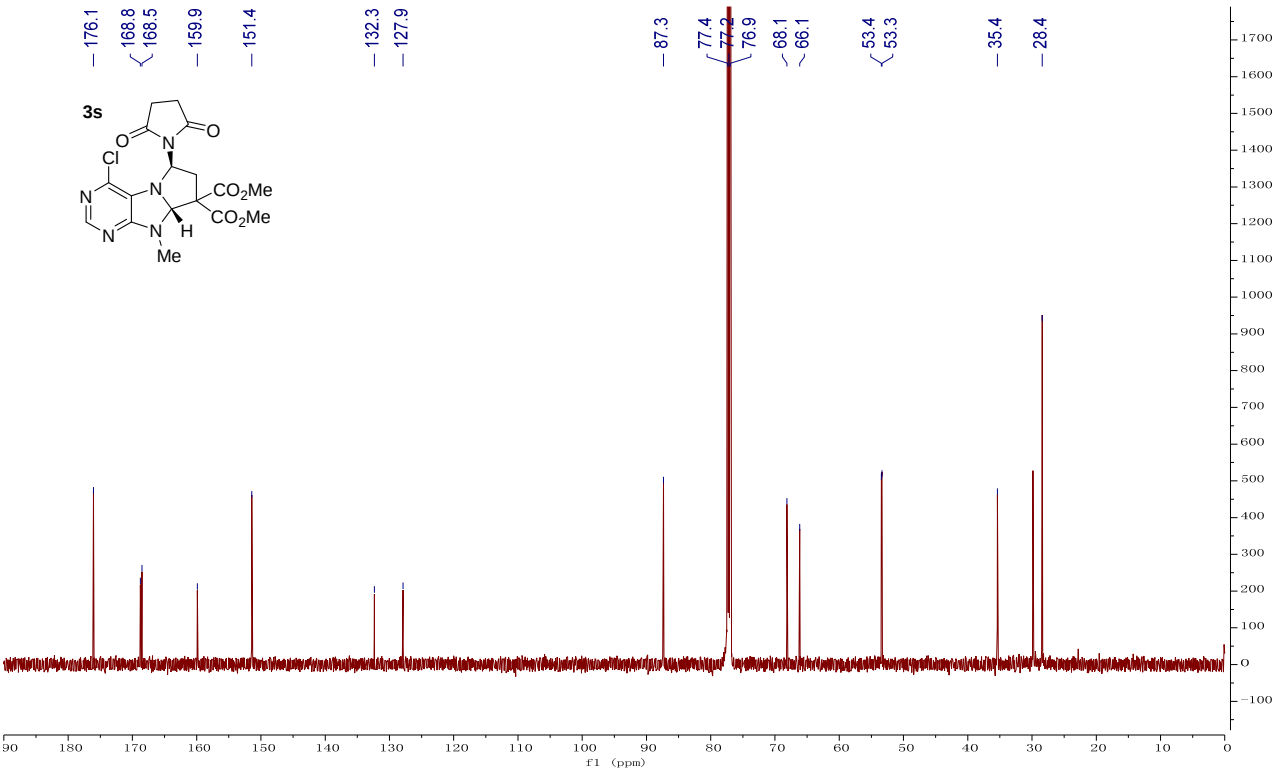
^{13}C-NMR of 3r



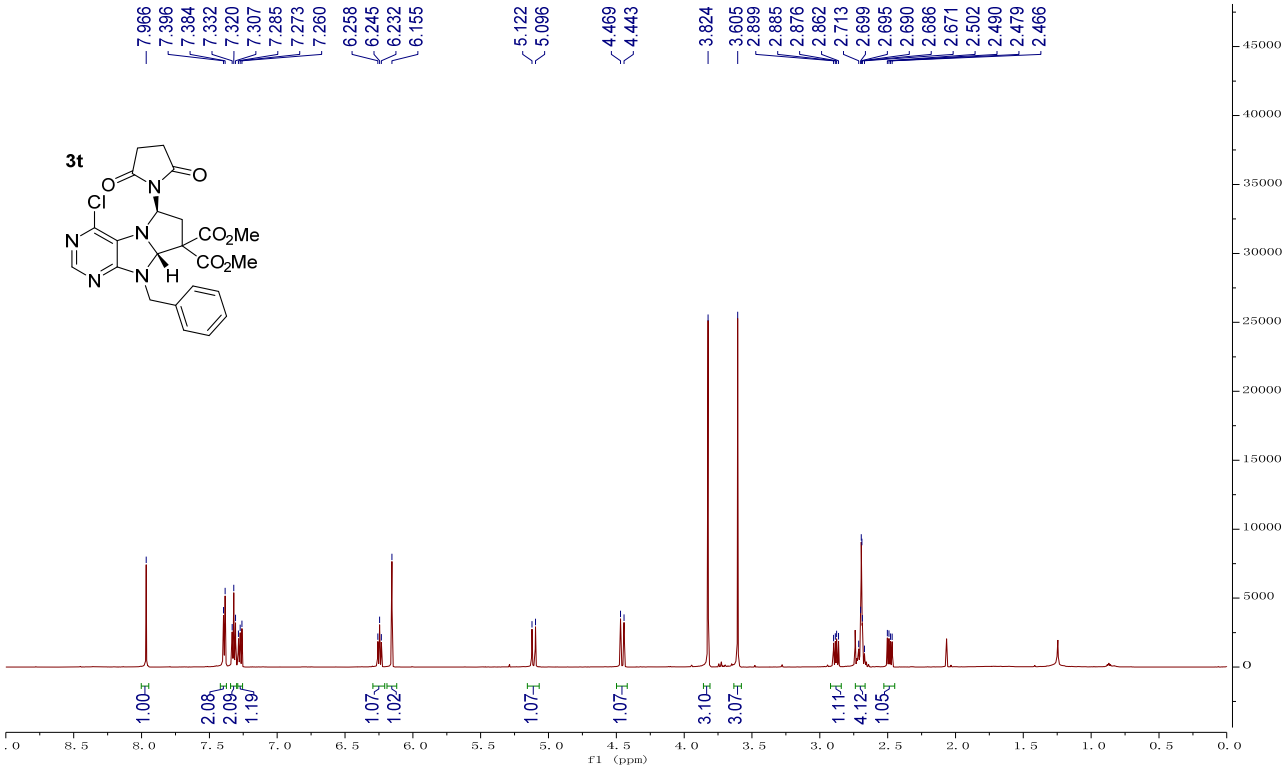
^{1}H-NMR of 3s



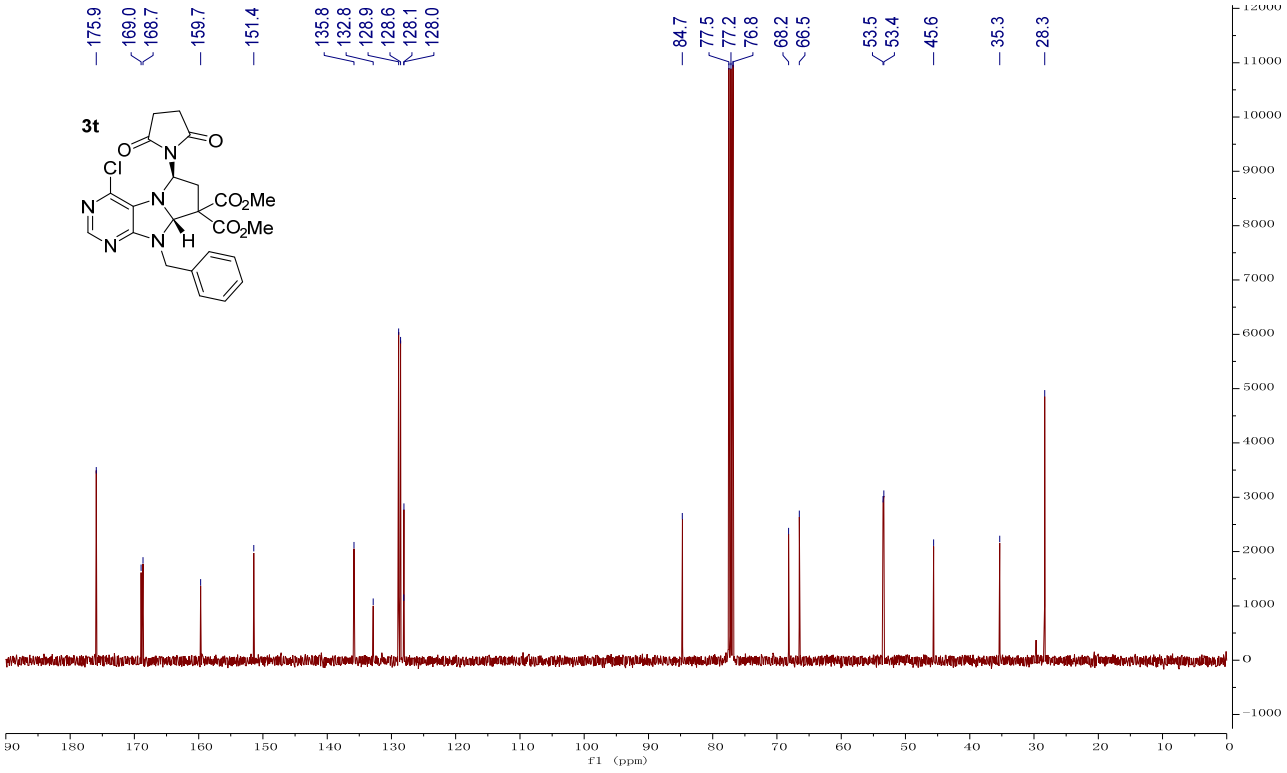
^{13}C-NMR of 3s



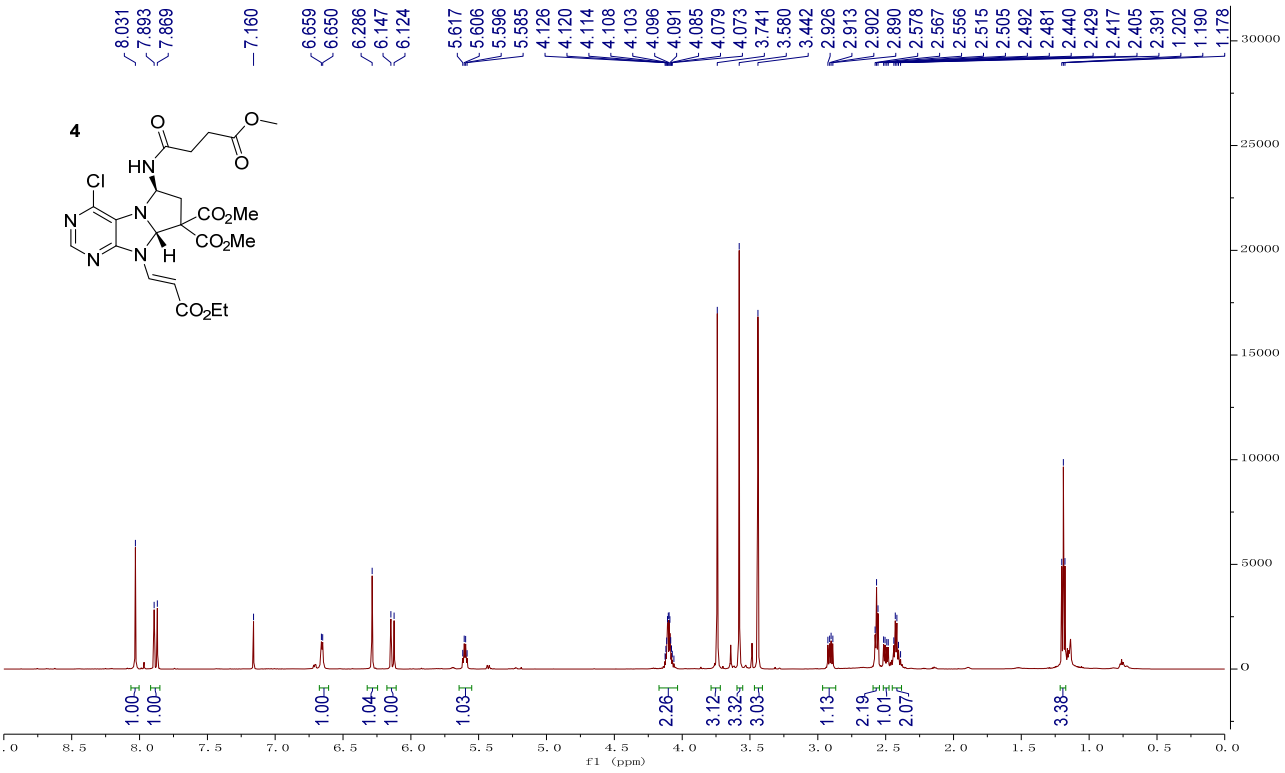
^{1}H-NMR of 3t



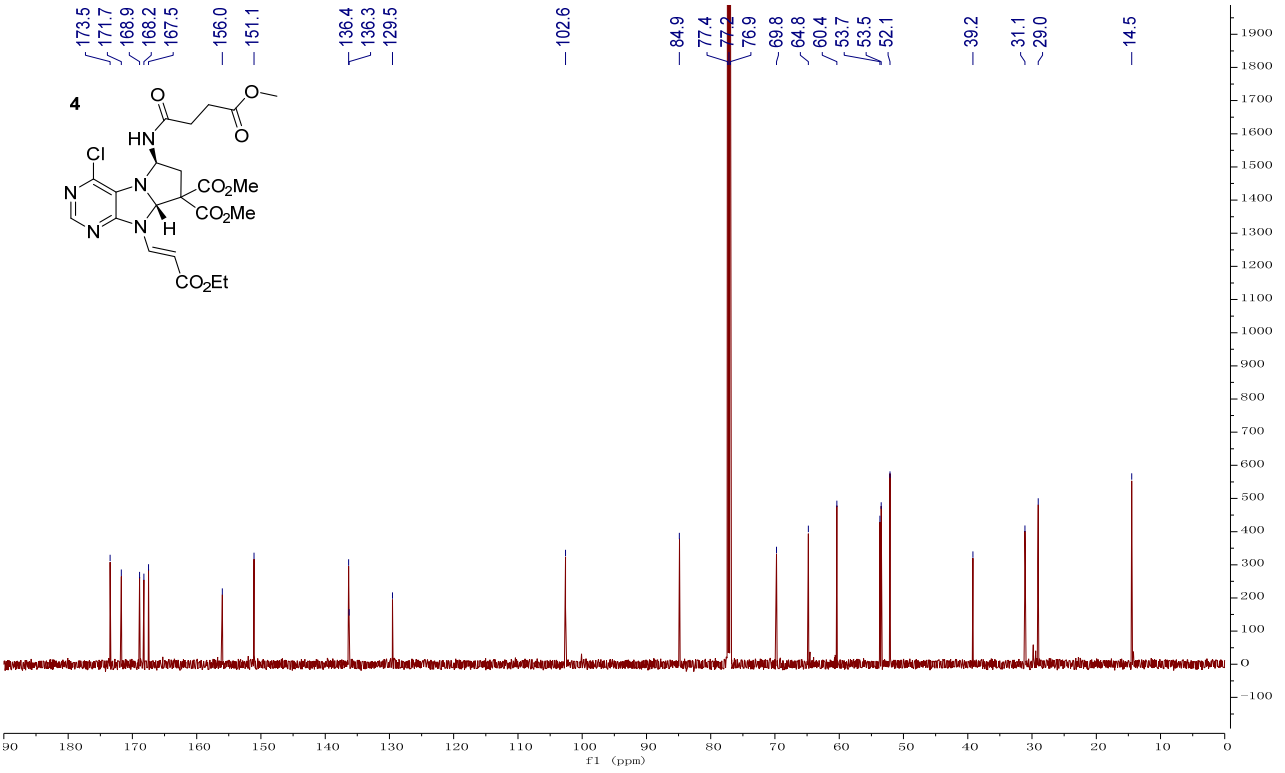
^{13}C-NMR of 3t



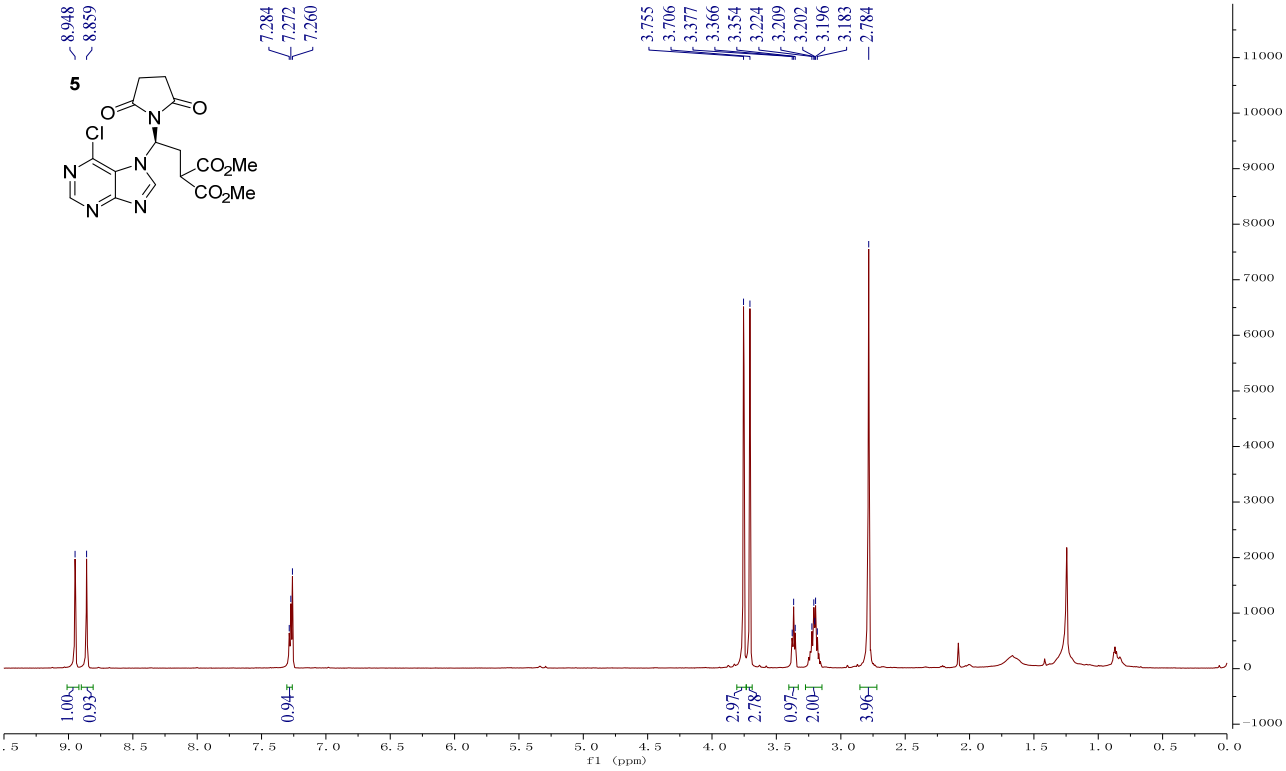
^{1}H-NMR of 4



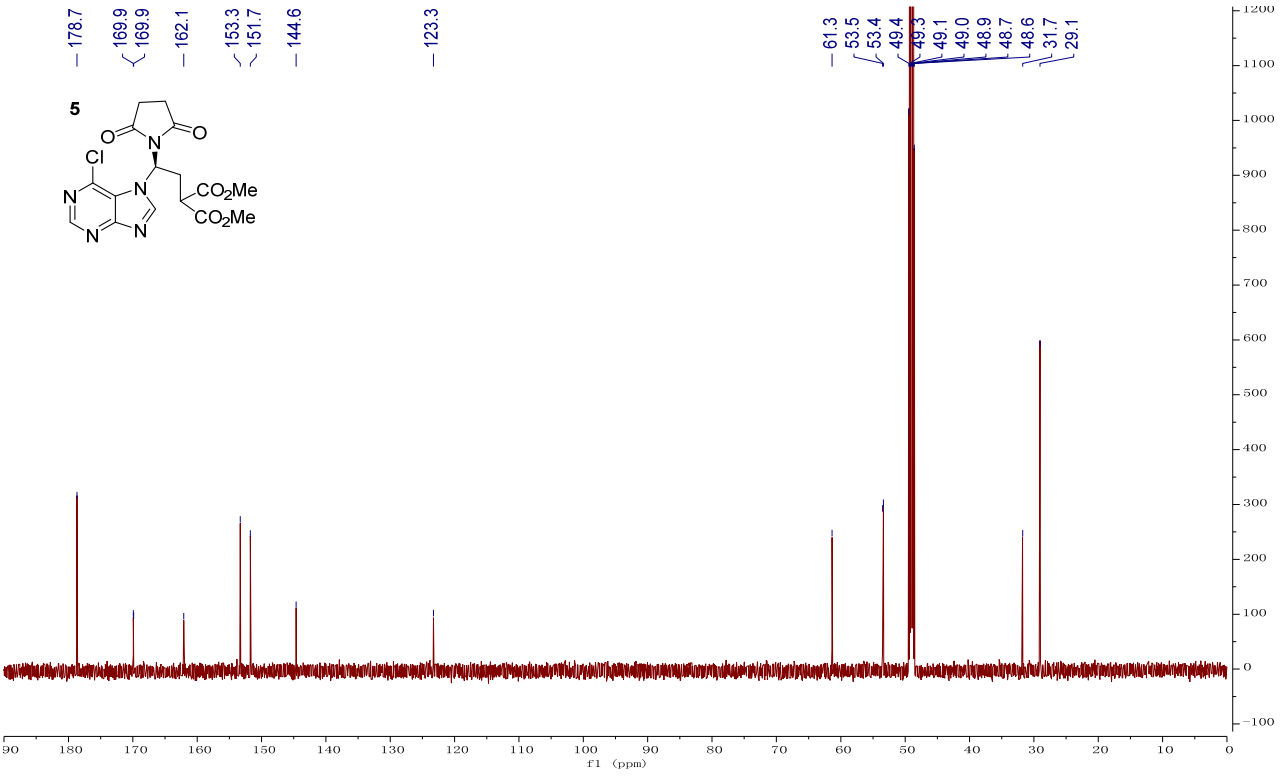
^{13}C-NMR of 4



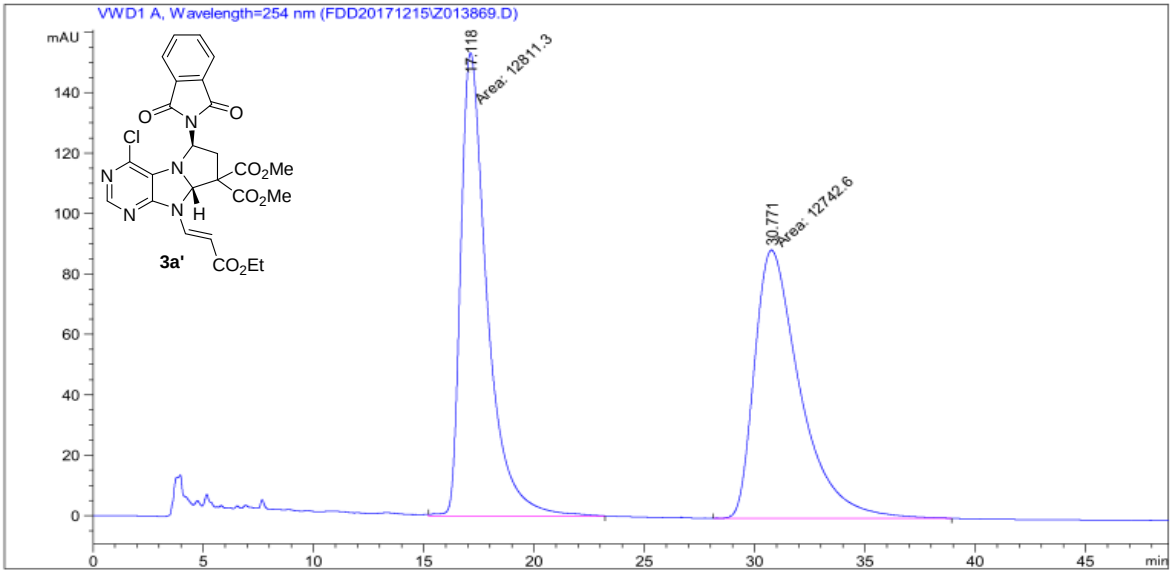
^{1}H-NMR of 5



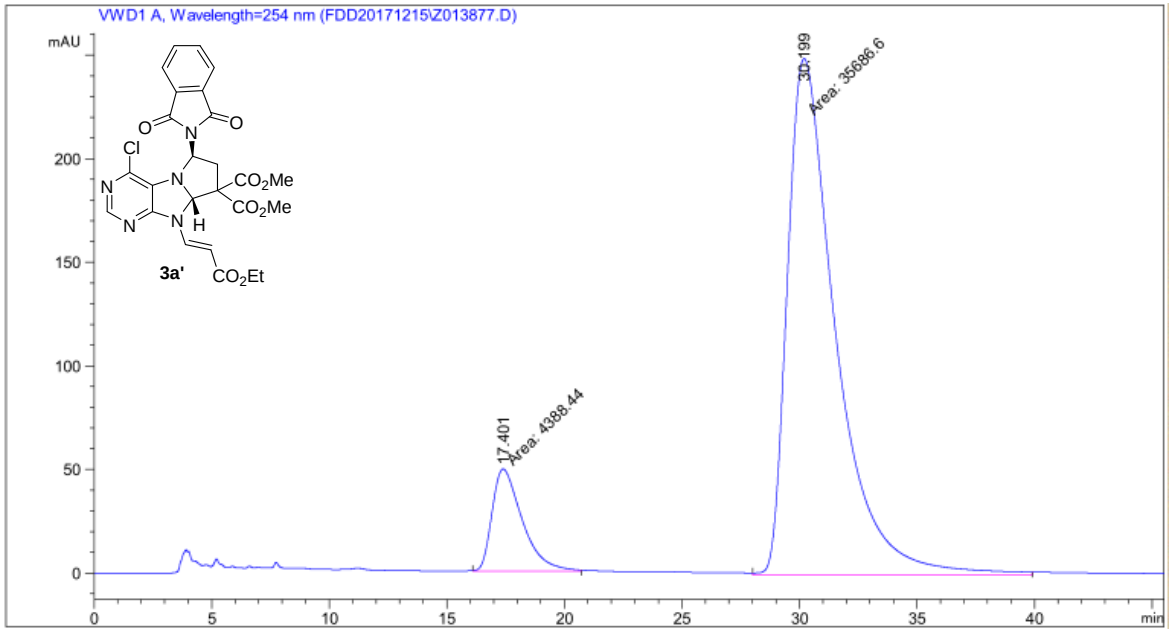
^{13}C-NMR of 5



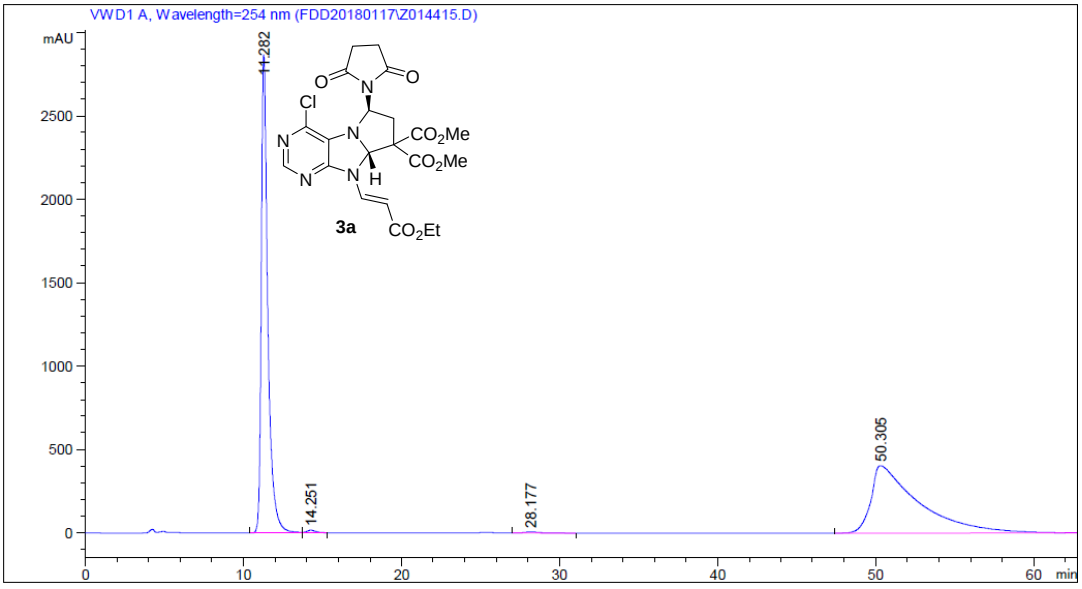
14. Copies of HPLC chromatographs



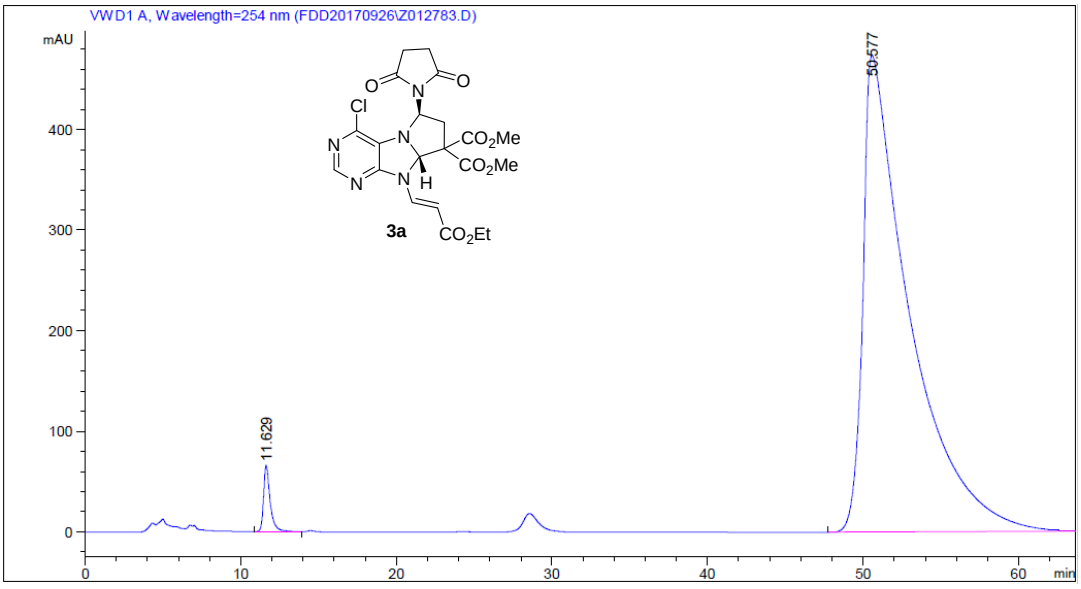
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.118	MM	1.3919	1.28113e4	153.40114	50.1344
2	30.771	MM	2.3905	1.27426e4	88.84343	49.8656



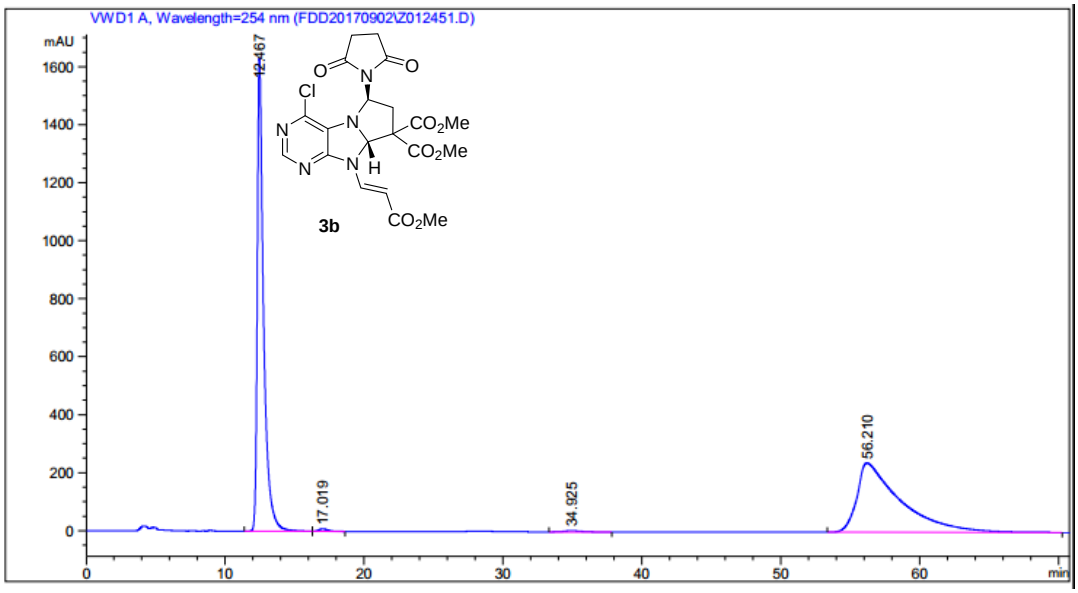
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.401	MM	1.4846	4388.44336	49.26699	10.9506
2	30.199	MM	2.3850	3.56866e4	249.38617	89.0494



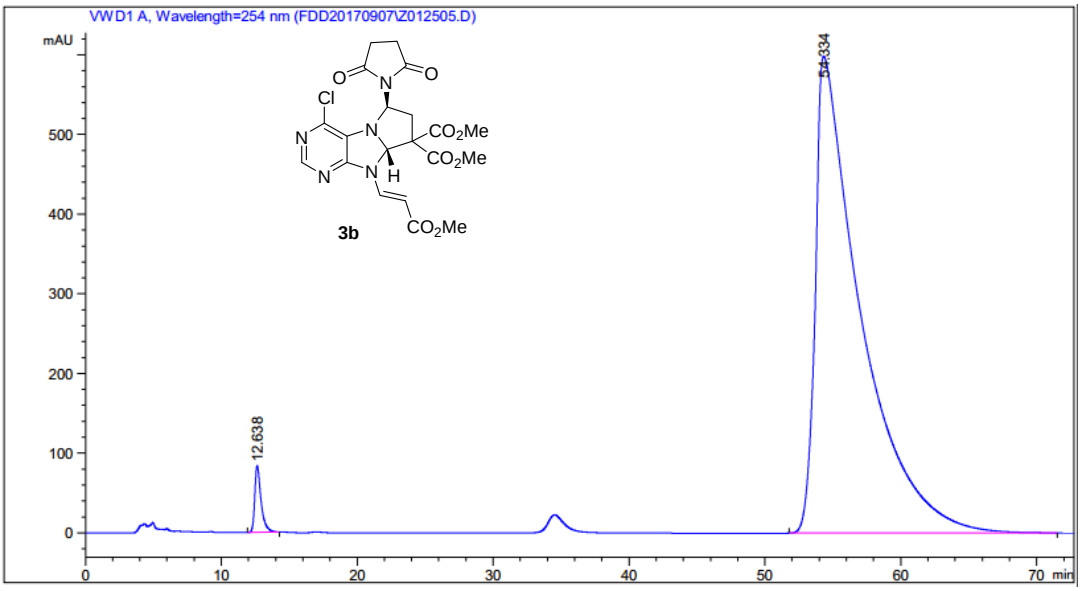
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.282	BV	0.4265	8.29913e4	2867.39111	49.2501
2	14.251	VB	0.5360	575.66101	15.79156	0.3416
3	28.177	BB	0.9175	478.11774	6.92608	0.2837
4	50.305	BBA	2.7411	8.44648e4	404.14551	50.1245



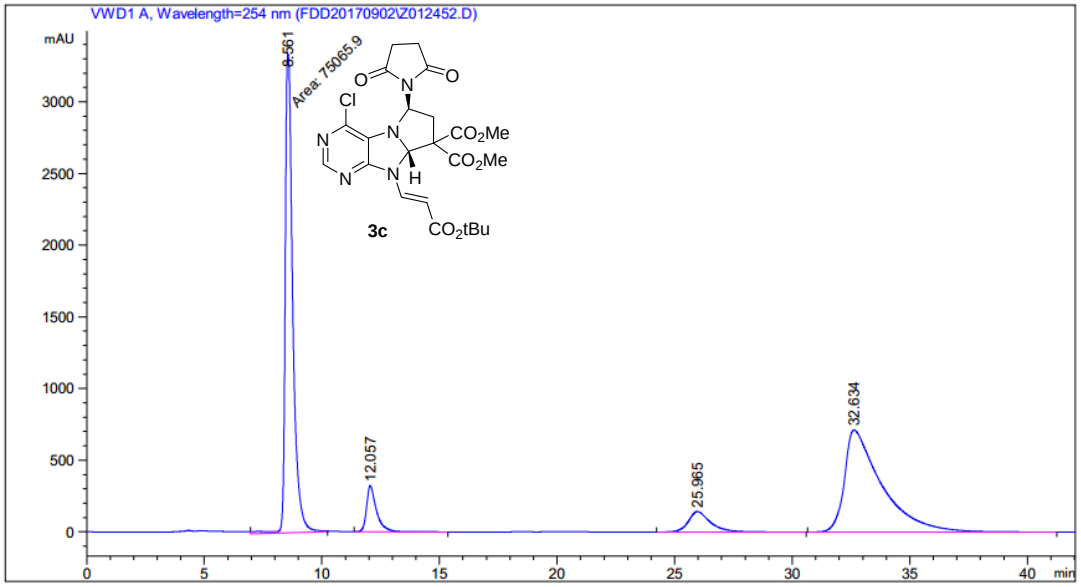
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.629	BB	0.4343	1951.69983	65.91686	1.9466
2	50.577	BBA	2.7818	9.83083e4	473.79288	98.0534



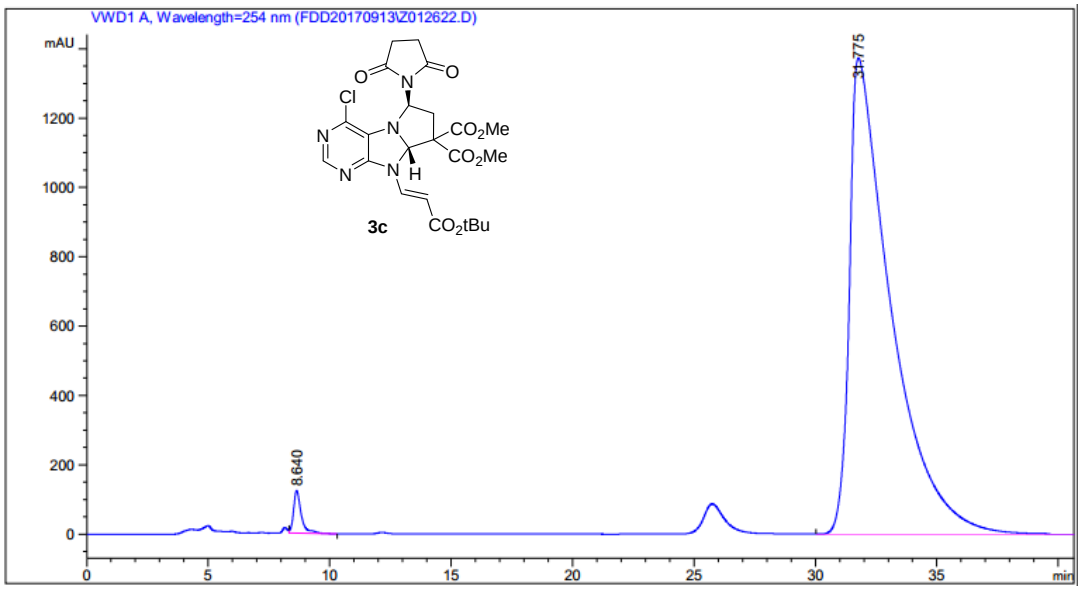
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.467	BB	0.4574	5.17677e4	1632.19702	49.6695
2	17.019	BB	0.6126	356.98615	8.59583	0.3425
3	34.925	BB	1.0287	351.87985	4.22379	0.3376
4	56.210	BB	2.8373	5.17478e4	238.75270	49.6504



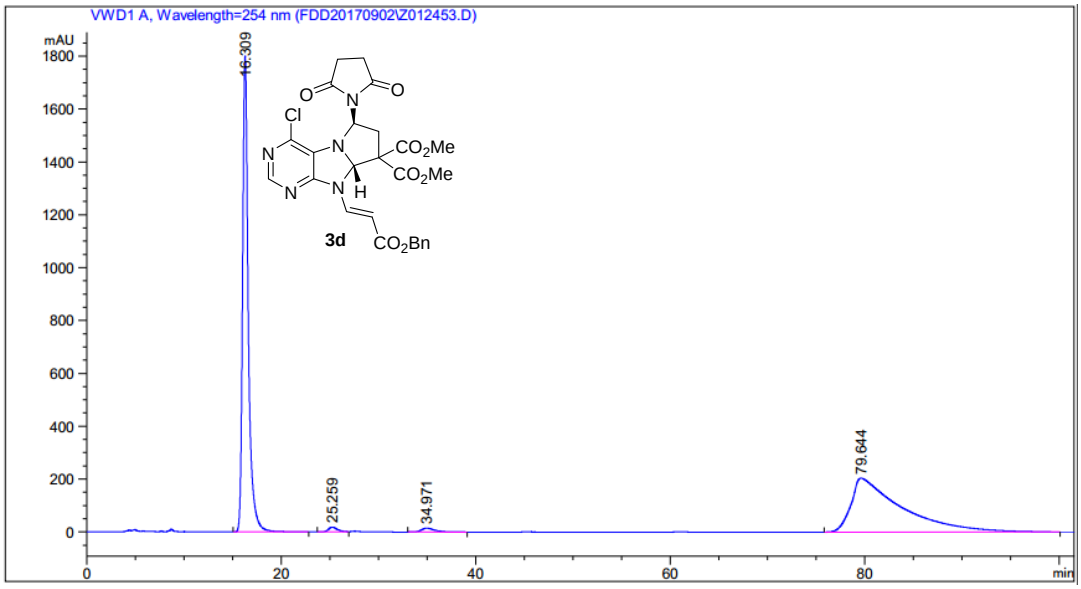
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.638	BB	0.4788	2717.19531	84.11488	1.9311
2	54.334	BB	3.0091	1.37993e5	598.42914	98.0689



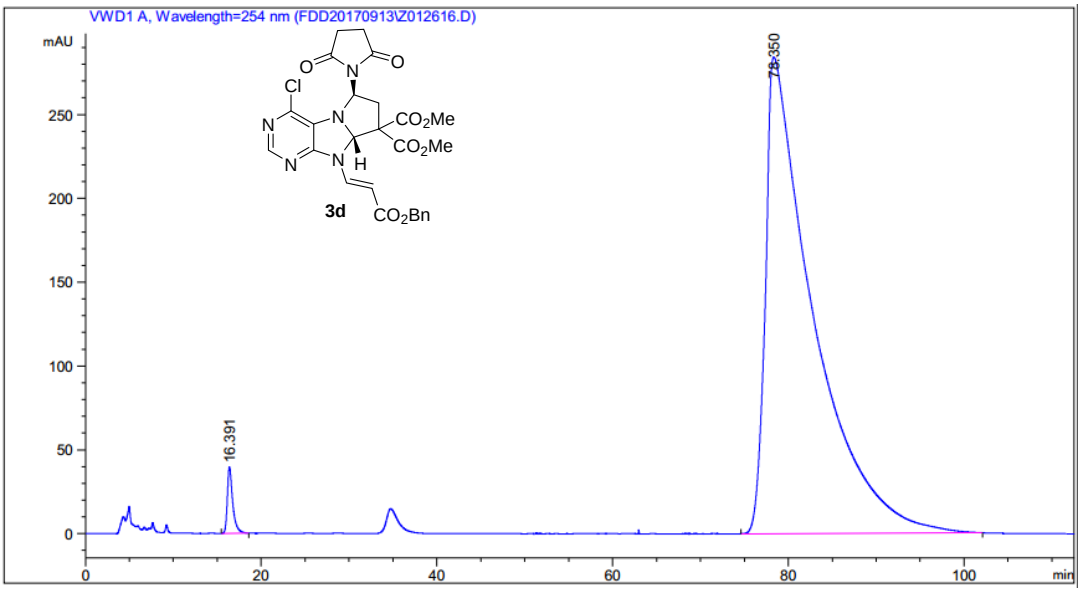
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.561	MM	0.3749	7.50659e4	3337.26758	43.6504
2	12.057	VB	0.4318	9506.60938	321.97870	5.5280
3	25.965	BB	0.9666	9355.62305	142.81801	5.4402
4	32.634	BB	1.5366	7.80425e4	711.14026	45.3813



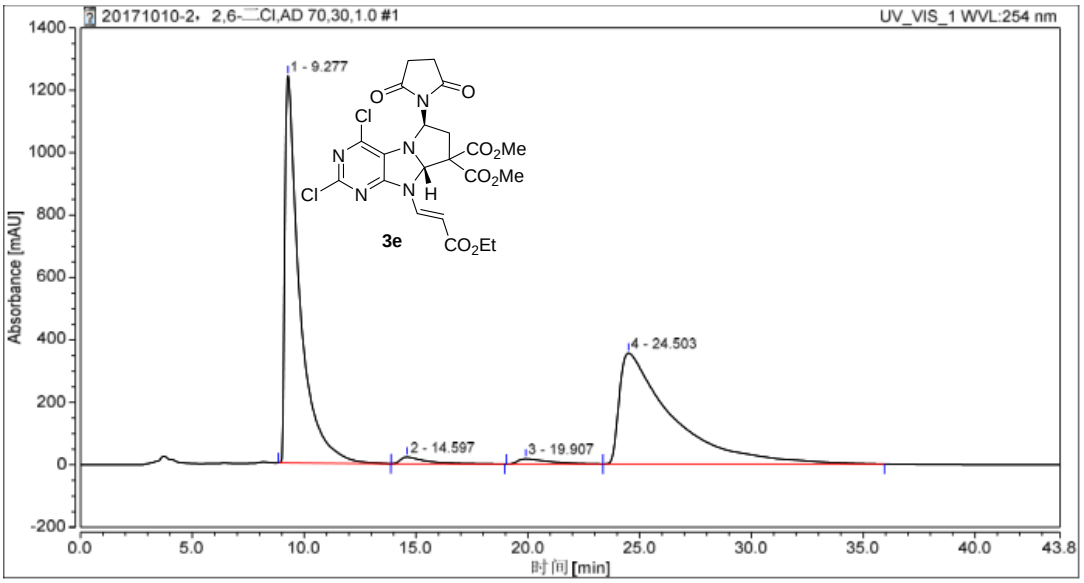
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.640	VB	0.3252	2737.41235	123.67494	1.6533
2	31.775	BBA	1.6139	1.62833e5	1372.78552	98.3467



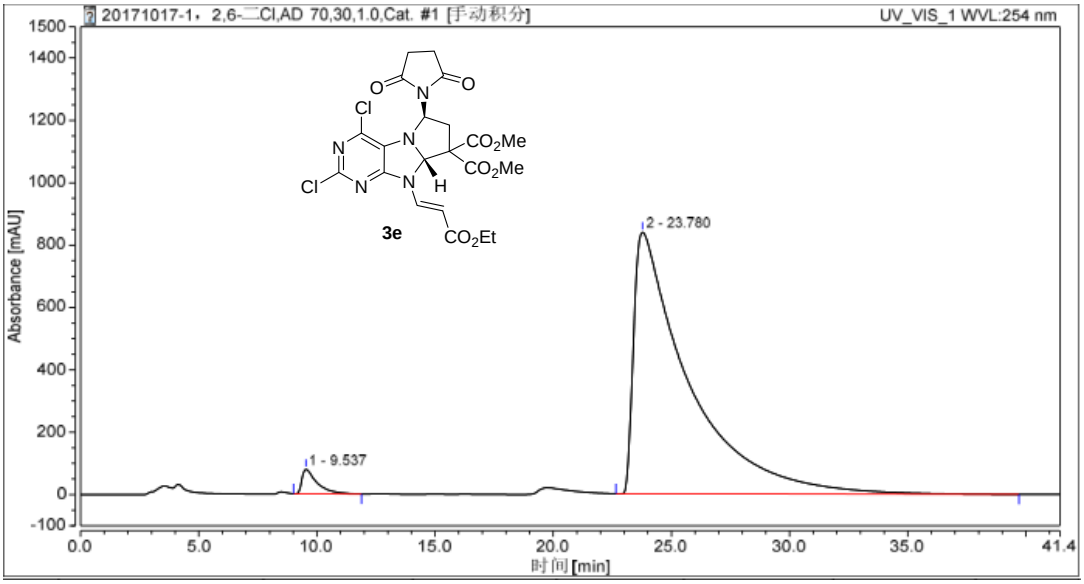
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.309	BB	0.6161	7.37668e4	1801.37878	49.3265
2	25.259	BB	0.9095	1102.10876	17.88805	0.7370
3	34.971	BB	1.3667	1450.32544	14.79138	0.9698
4	79.644	BB	4.5176	7.32288e4	204.04202	48.9668



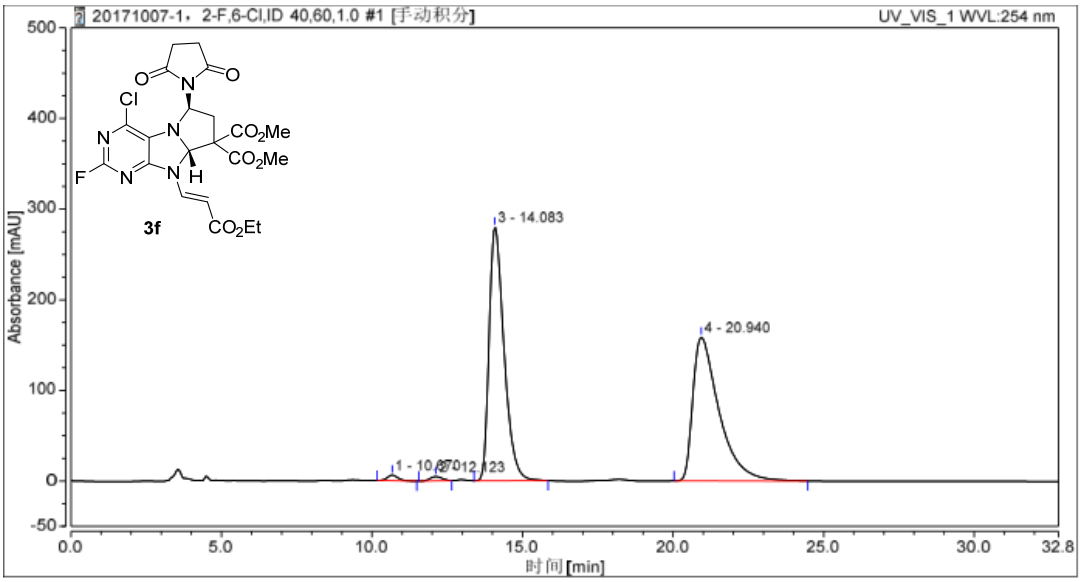
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.391	BB	0.6271	1683.62891	39.59789	1.5567
2	78.350	BB	4.7312	1.06469e5	284.23679	98.4433



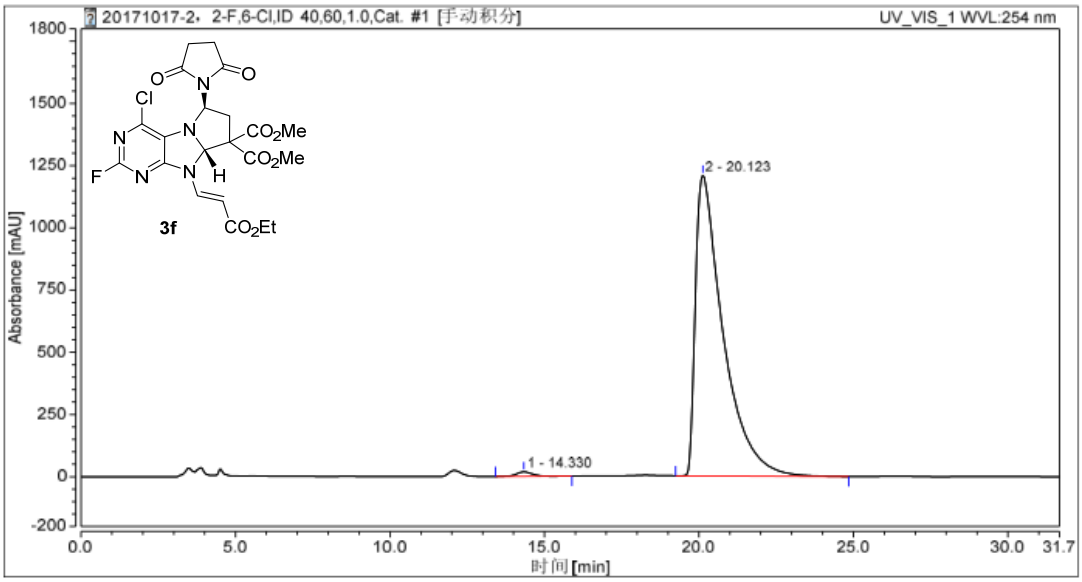
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.277	957.581	1241.095	48.28	75.91
2	14.597	28.621	21.695	1.44	1.33
3	19.907	26.862	16.411	1.35	1.00
4	24.503	970.180	355.670	48.92	21.76



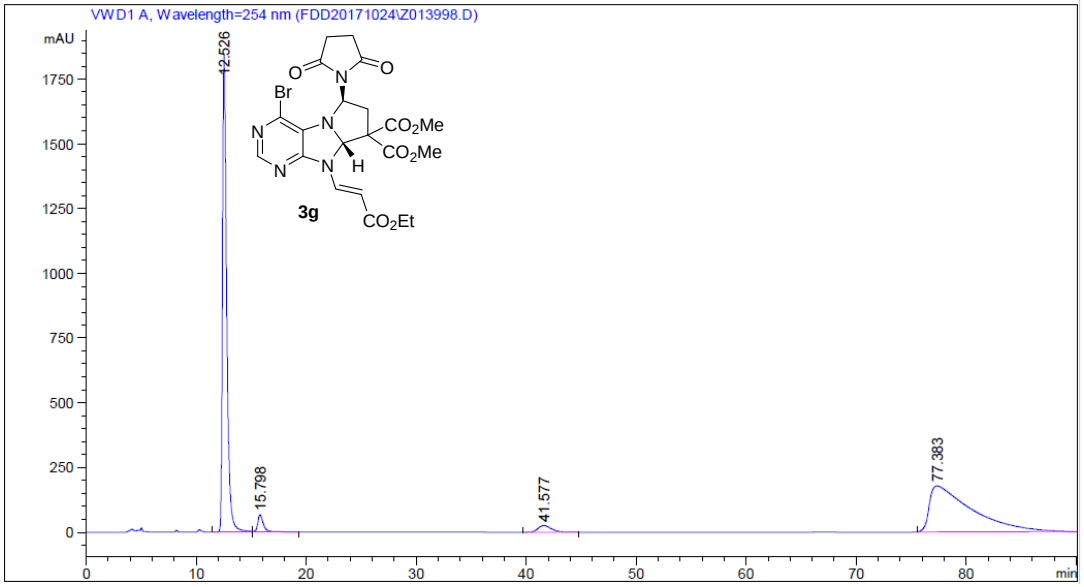
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.537	58.344	78.909	2.52	8.60
2	23.780	2255.651	839.066	97.48	91.40



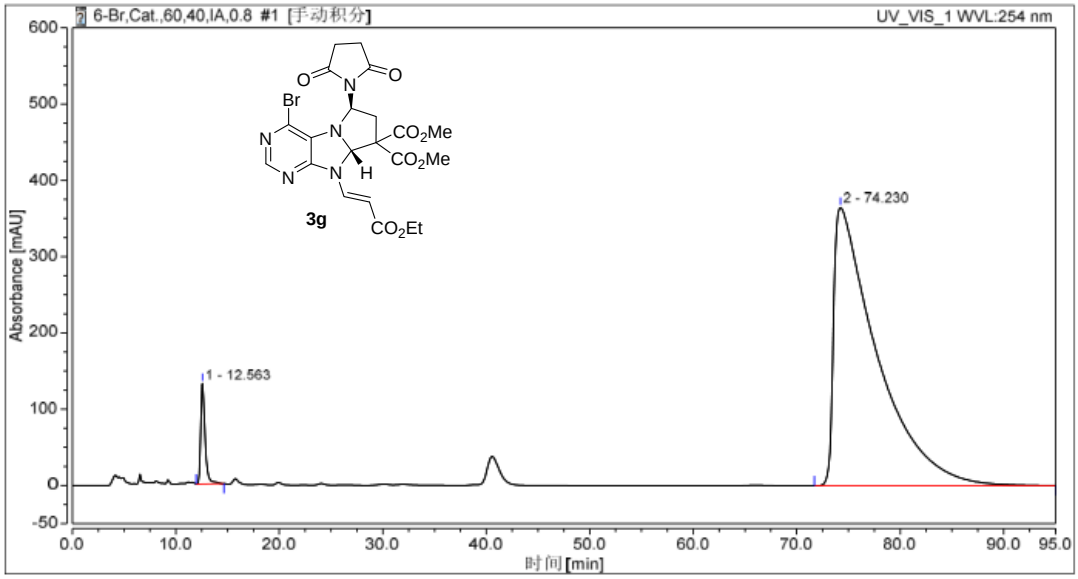
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.670	2.483	6.053	0.76	1.35
2	12.123	2.127	4.662	0.65	1.04
3	14.083	160.786	279.839	49.32	62.29
4	20.940	160.618	158.672	49.27	35.32



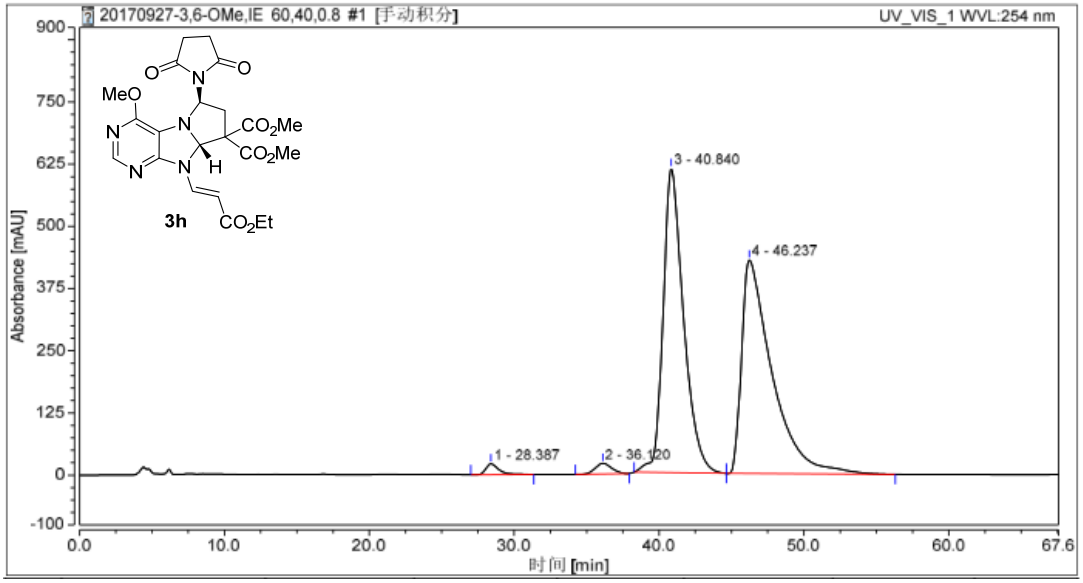
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	14.330	10.613	17.992	0.84	1.47
2	20.123	1252.312	1208.357	99.16	98.53



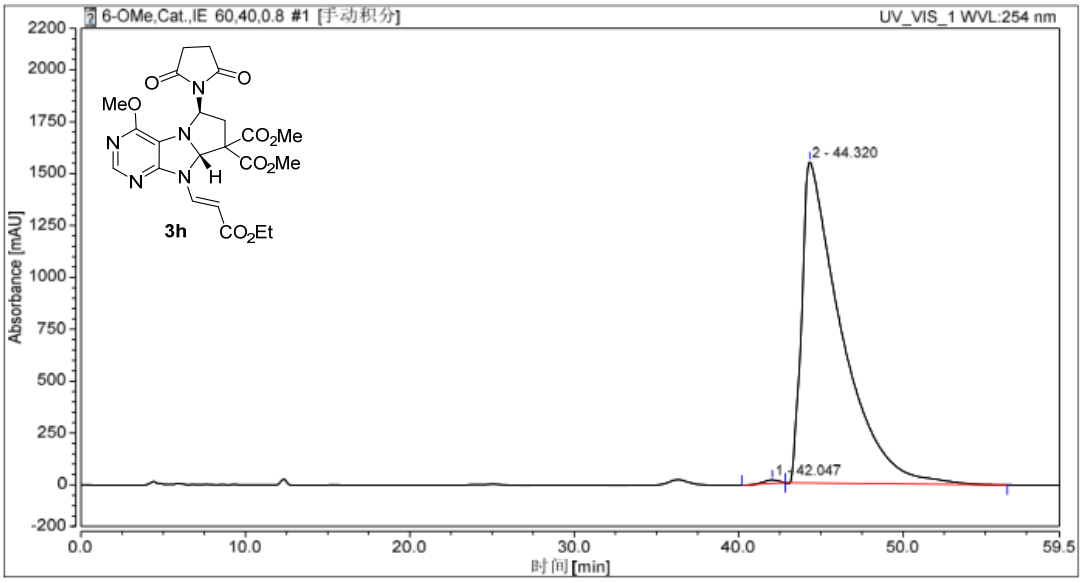
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.526	BV	0.3986	4.91999e4	1844.24573	48.4071
2	15.798	VB	0.5538	2510.99316	66.99063	2.4705
3	41.577	BB	1.2509	2203.05884	26.03034	2.1676
4	77.383	BBA	3.3556	4.77238e4	177.31058	46.9548



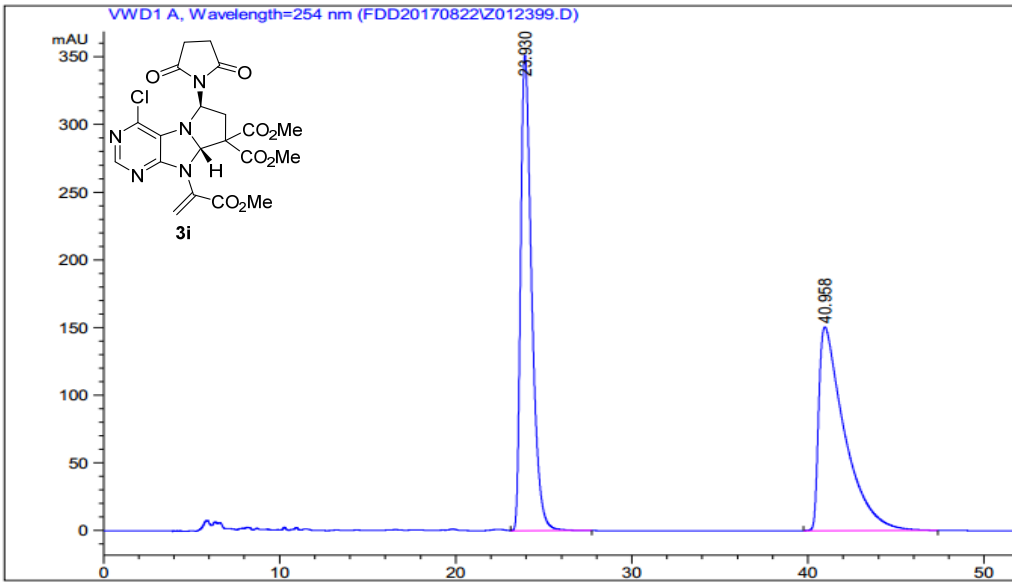
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.563	62.460	131.774	3.42	26.53
2	74.230	1762.465	365.002	96.58	73.47



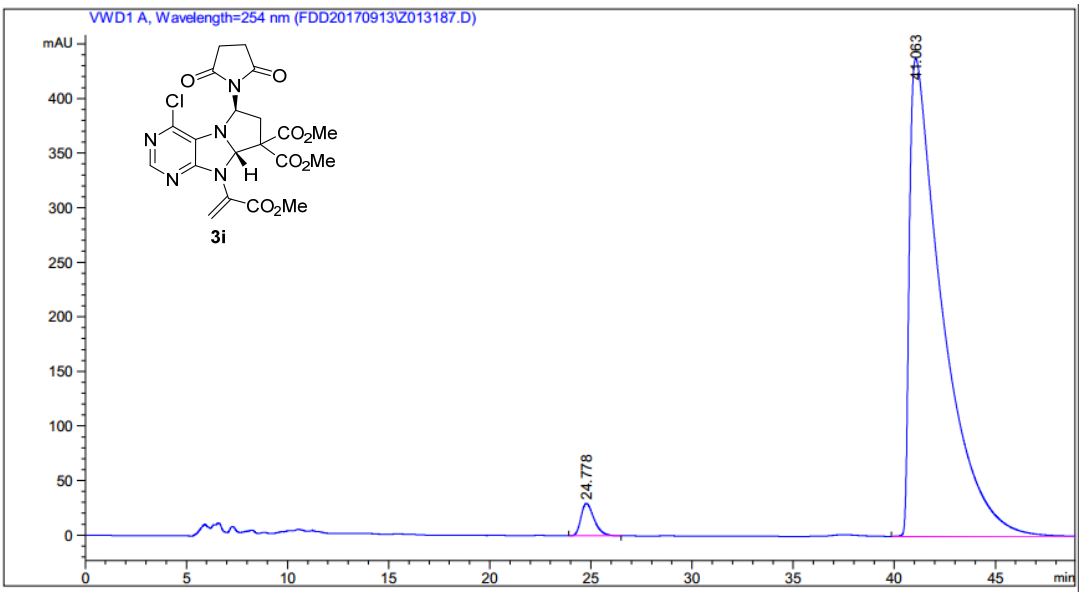
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	28.387	22.760	21.841	1.09	2.02
2	36.120	27.690	21.288	1.32	1.96
3	40.840	1002.602	611.242	47.95	56.41
4	46.237	1037.771	429.145	49.63	39.61



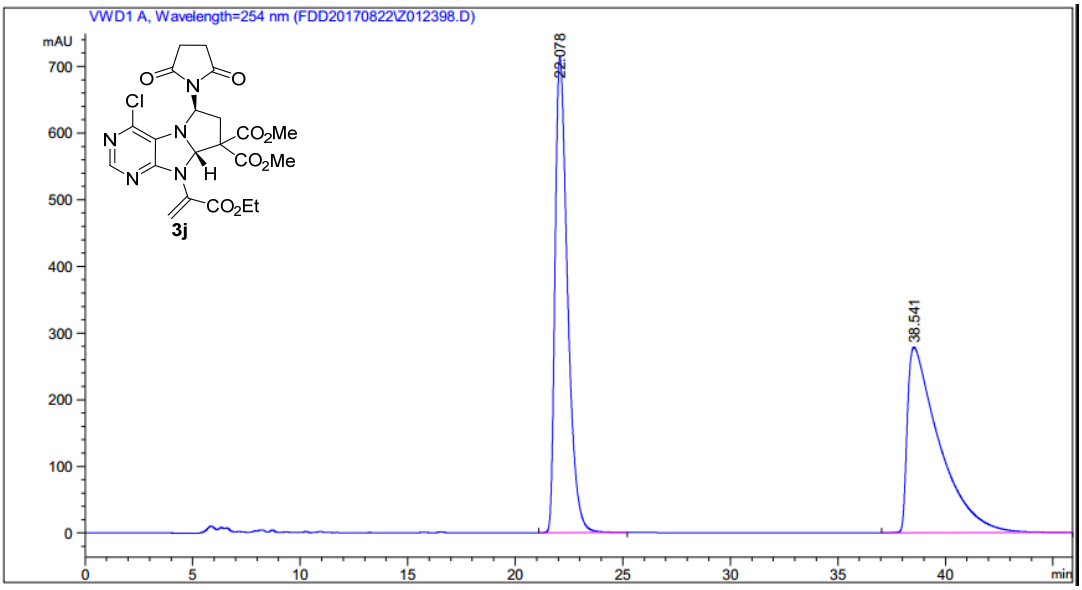
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	42.047	17.865	17.130	0.41	1.09
2	44.320	4295.947	1548.022	99.59	98.91



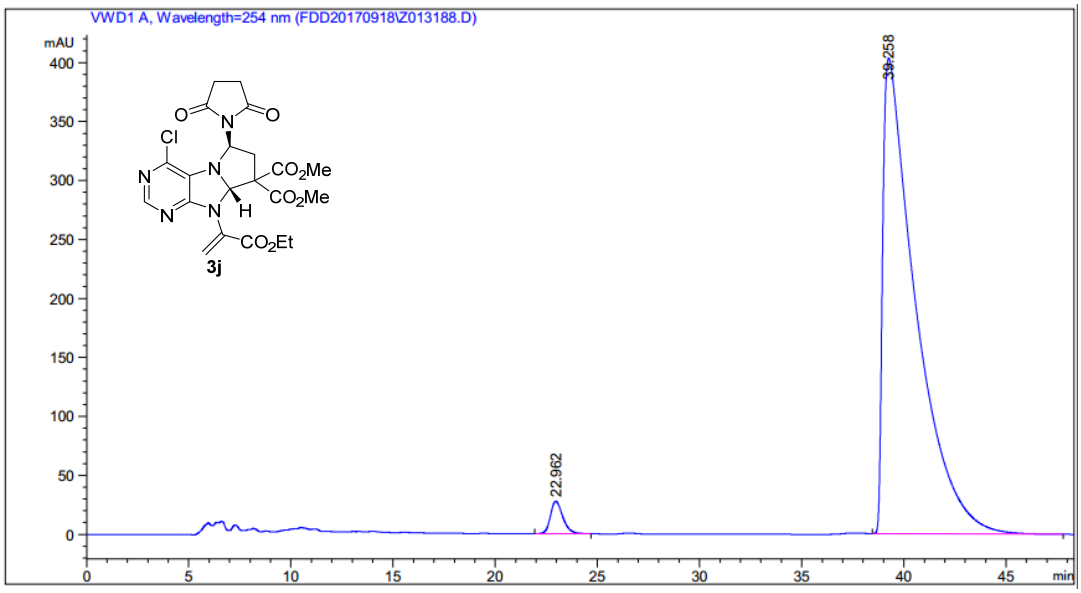
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.930	BB	0.6660	1.53201e4	351.33084	49.9979
2	40.958	BB	1.4136	1.53213e4	150.46886	50.0021



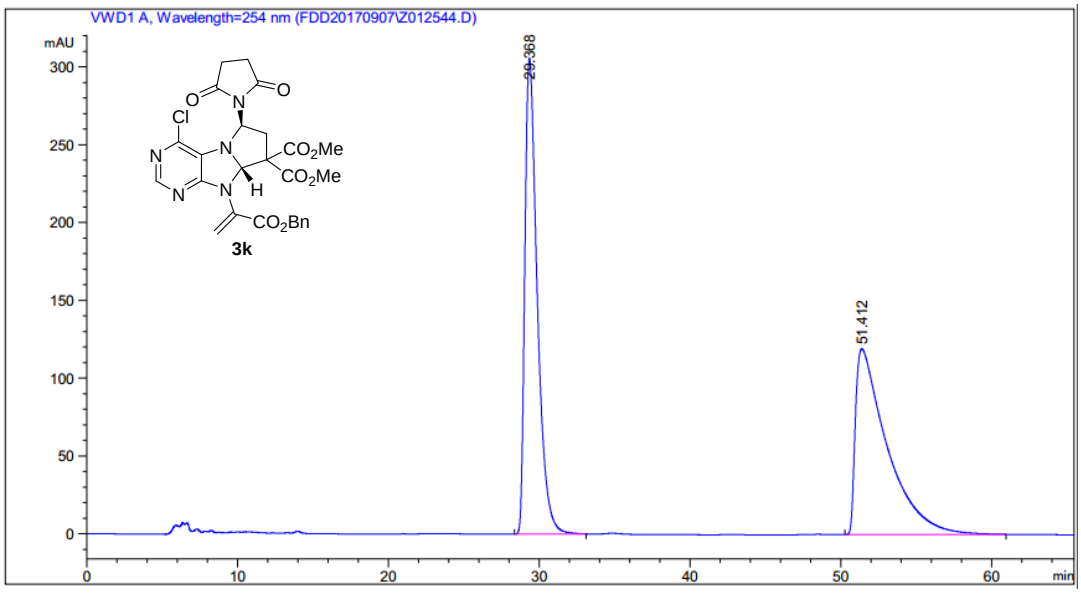
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.778	BB	0.6928	1344.13647	29.76685	2.6599
2	41.063	BBA	1.5568	4.91898e4	437.84448	97.3401



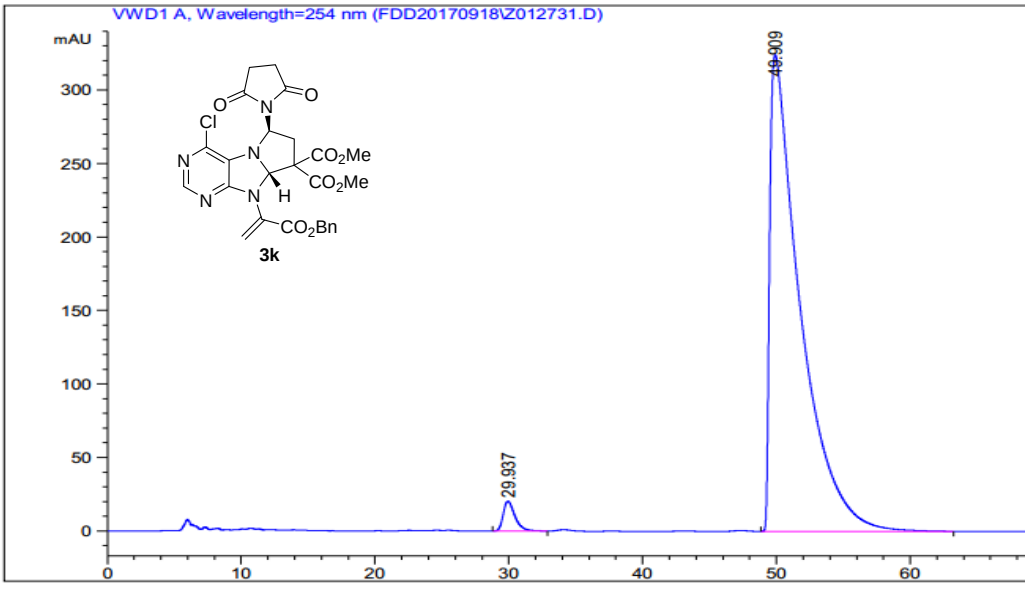
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.078	BB	0.6174	2.87691e4	713.60956	49.8940
2	38.541	BBA	1.4443	2.88914e4	278.26584	50.1060



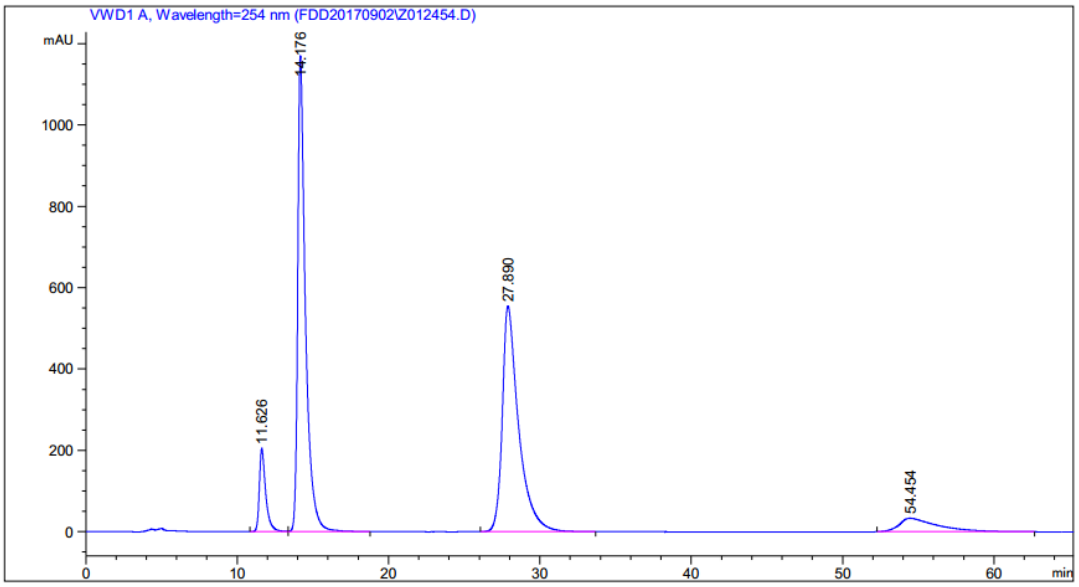
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.962	BB	0.6439	1163.39795	27.56215	2.5155
2	39.258	BB	1.5264	4.50858e4	403.04953	97.4845



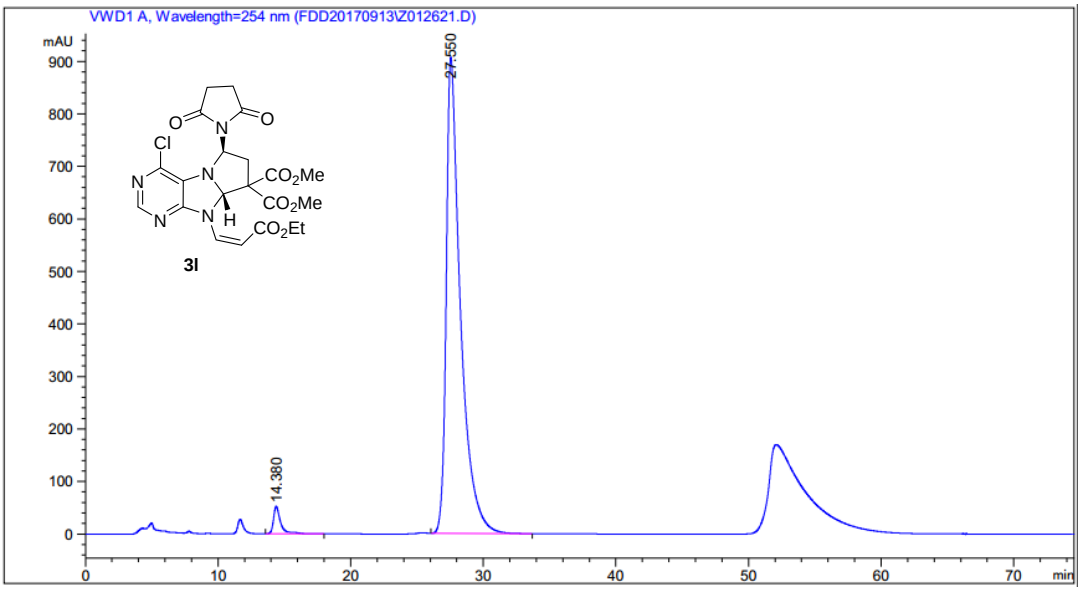
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.368	BV	0.8617	1.74730e4	305.81113	50.0411
2	51.412	BB	1.9943	1.74443e4	119.39934	49.9589



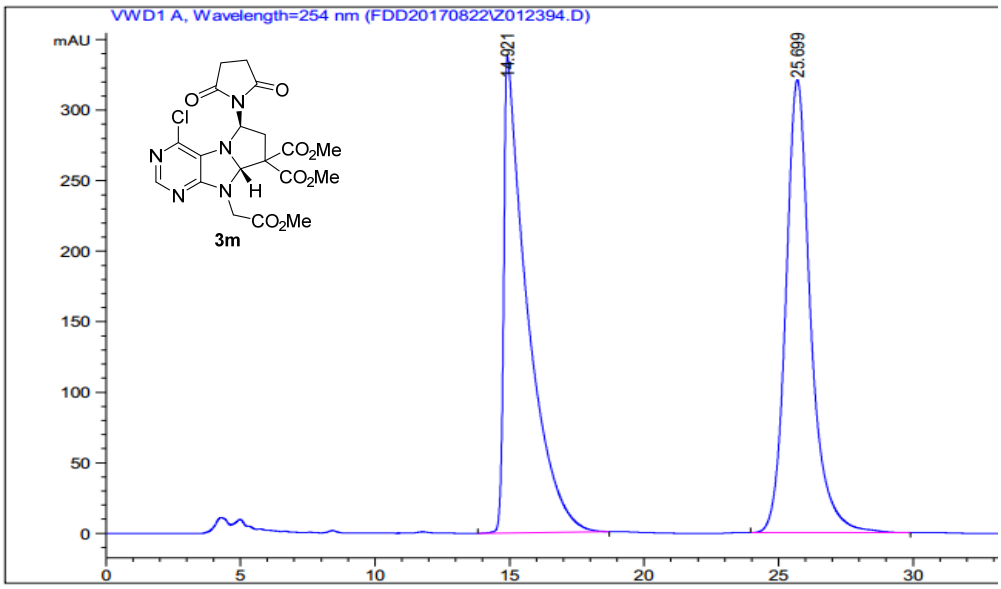
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.937	BB	0.9090	1236.09680	20.32577	2.3606
2	49.909	BB	2.1151	5.11269e4	324.19052	97.6394



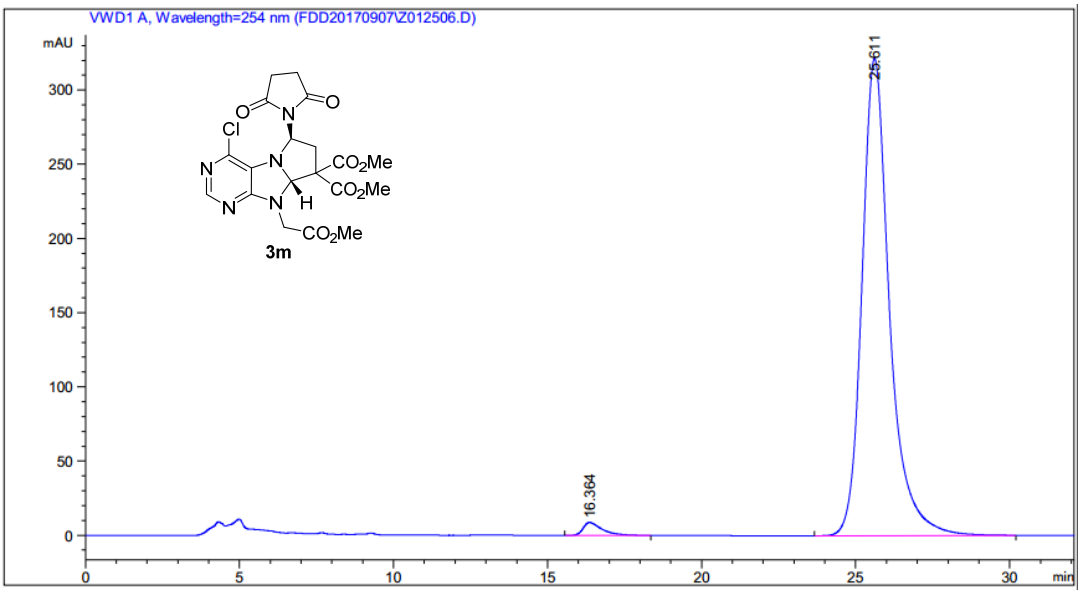
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.626	BV	0.4315	6024.08301	205.10414	6.3403
2	14.176	VB	0.5115	4.16727e4	1170.37280	43.8600
3	27.890	BB	1.0675	4.14900e4	553.94476	43.6677
4	54.454	BB	2.2304	5826.26221	33.15990	6.1321



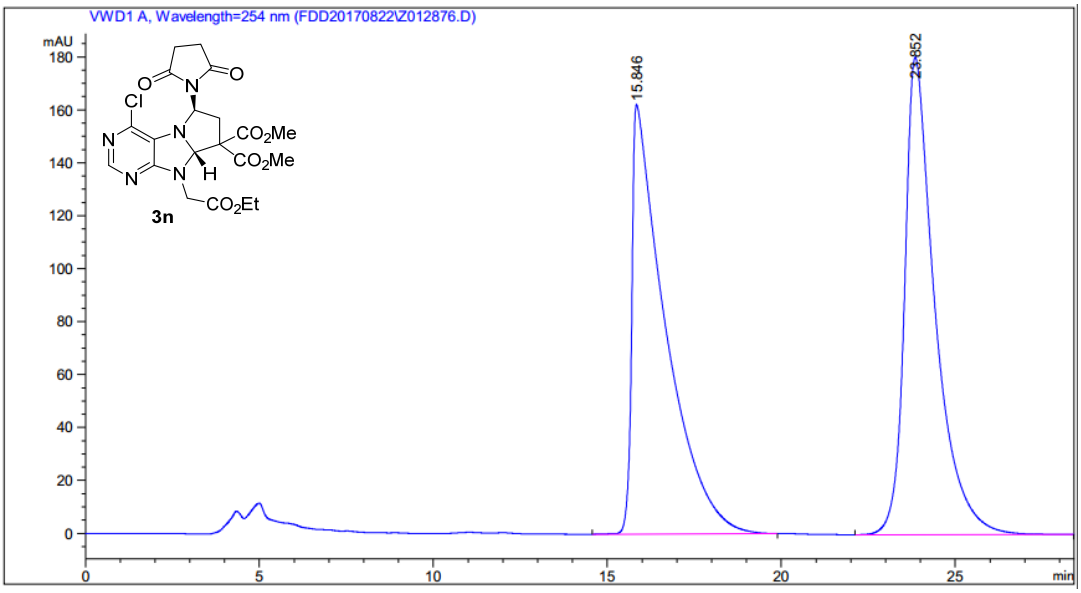
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.380	BB	0.5468	1977.03894	52.52897	2.8448
2	27.550	BB	1.0696	6.75194e4	906.84064	97.1552



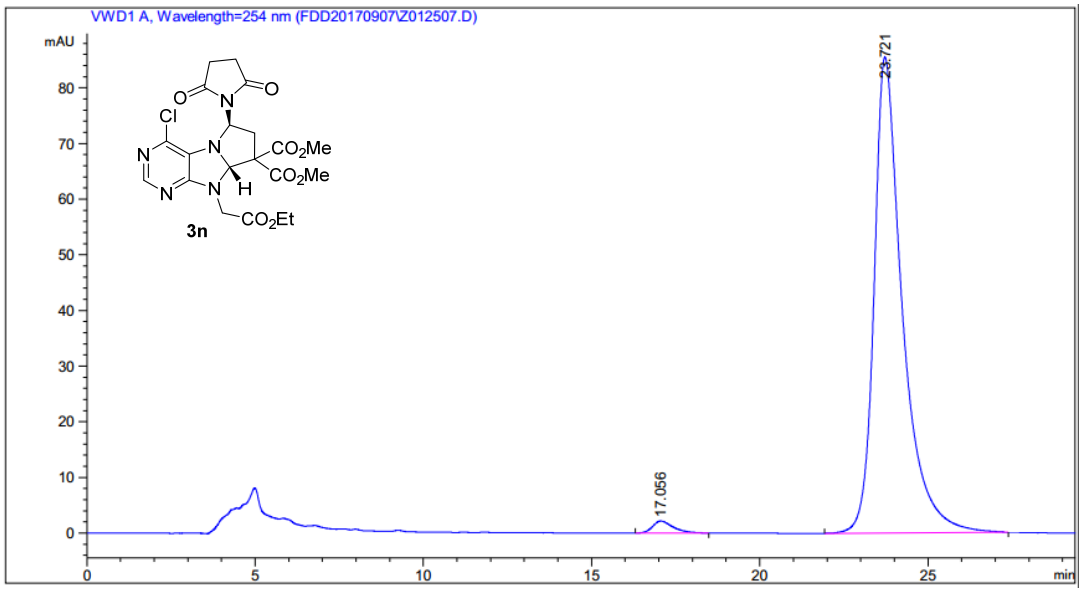
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.921	BB	0.7980	2.04085e4	337.83157	49.8896
2	25.699	BB	0.9648	2.04988e4	321.05212	50.1104



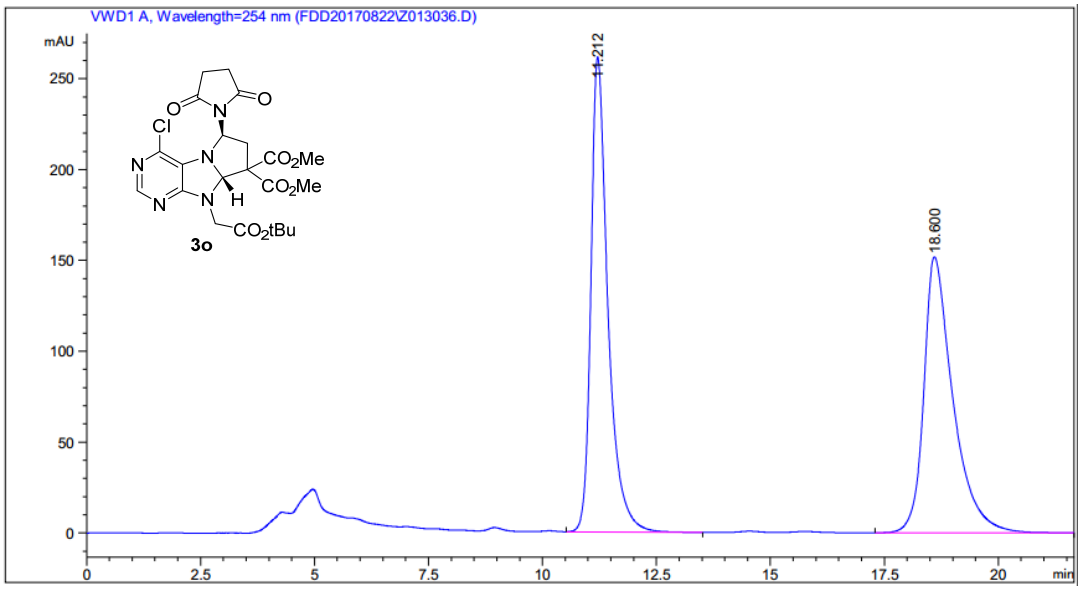
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.364	BB	0.6211	383.05377	8.80459	1.8836
2	25.611	BB	0.9322	1.99530e4	321.51828	98.1164



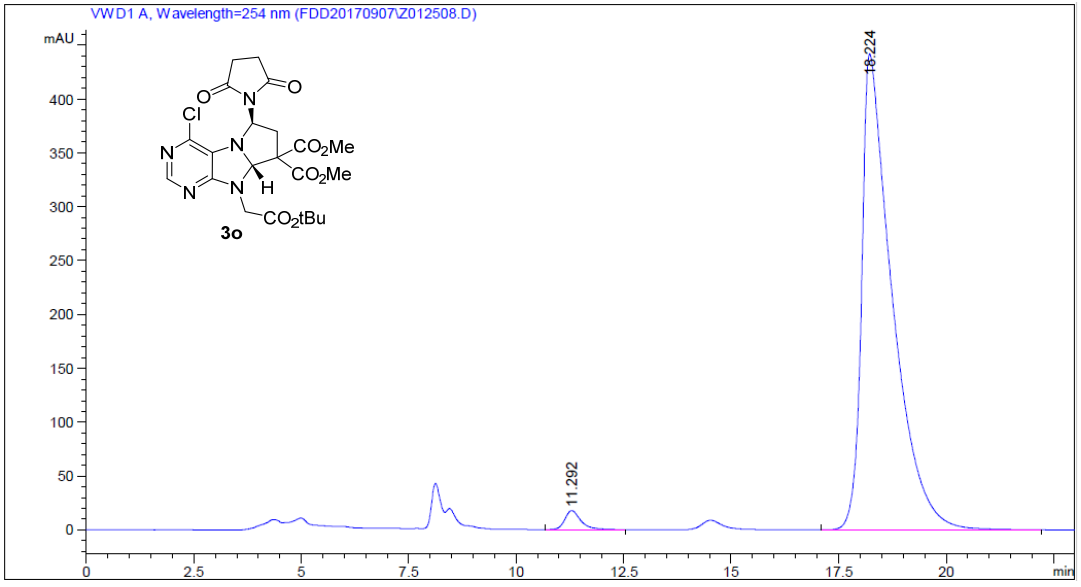
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.846	BB	0.9005	1.08602e4	162.20413	49.7828
2	23.852	BB	0.8833	1.09550e4	180.37910	50.2172



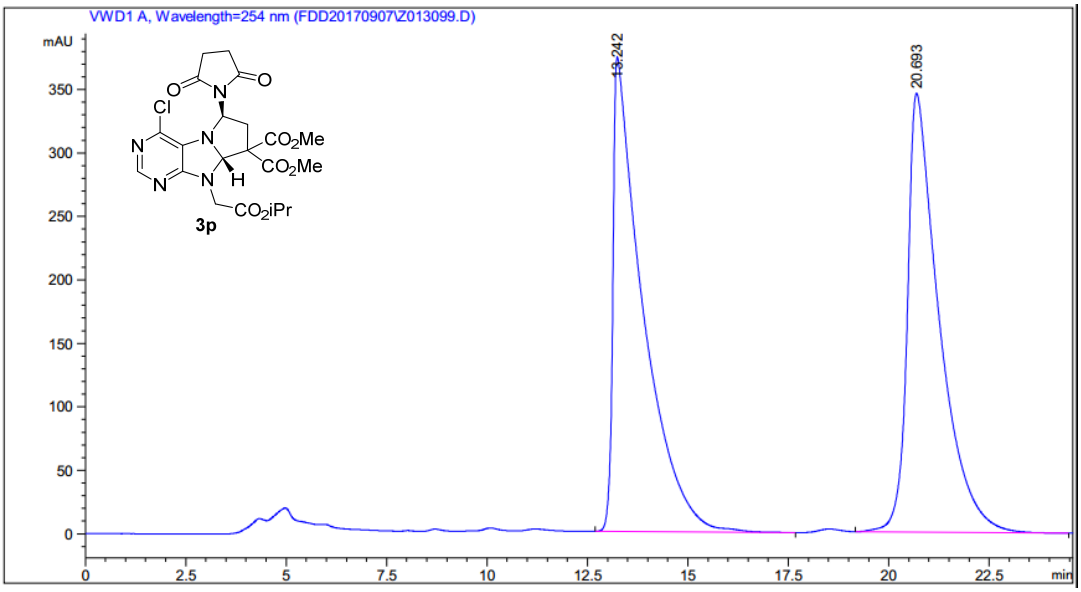
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.056	BB	0.5968	93.23322	2.17259	1.8320
2	23.721	BB	0.8579	4995.84717	85.49332	98.1680



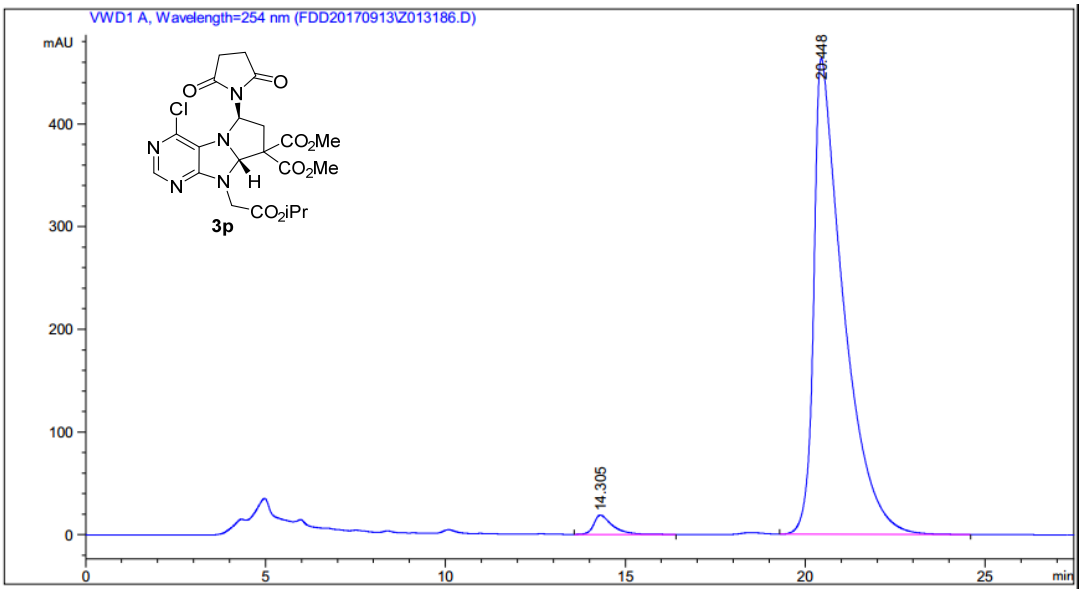
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.212	BB	0.3841	6777.31982	261.33749	50.0277
2	18.600	BBA	0.6481	6769.81787	151.88316	49.9723



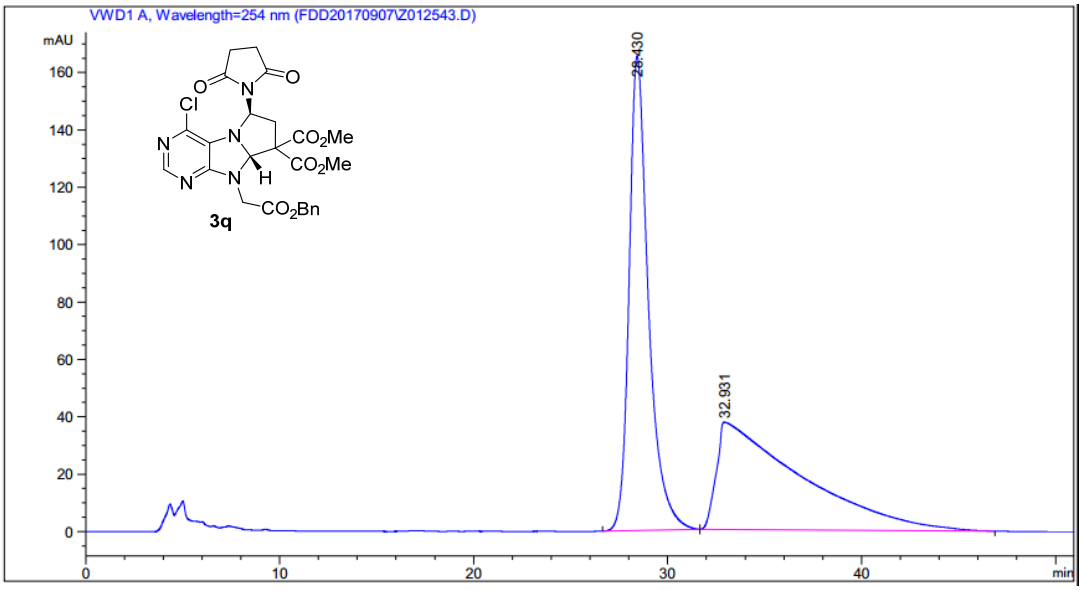
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.292	BB	0.3845	452.41599	17.58976	2.0316
2	18.224	BB	0.6879	2.18162e4	442.06607	97.9684



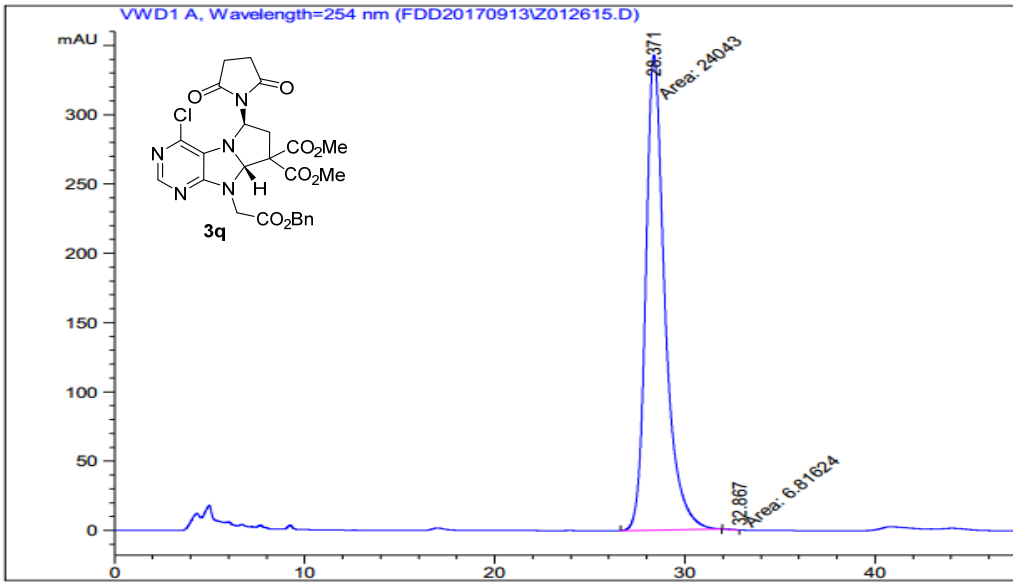
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.242	BB	0.6845	1.92711e4	373.75186	50.2570
2	20.693	BBA	0.7804	1.90740e4	345.76801	49.7430



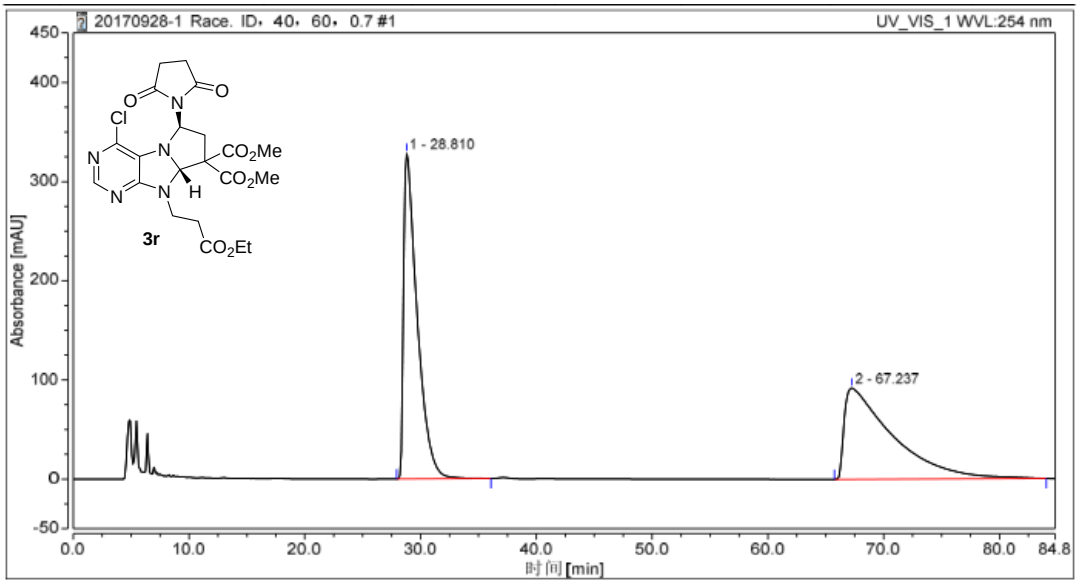
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.305	BB	0.5240	677.44885	18.72689	2.4926
2	20.448	BB	0.7999	2.65005e4	463.24219	97.5074



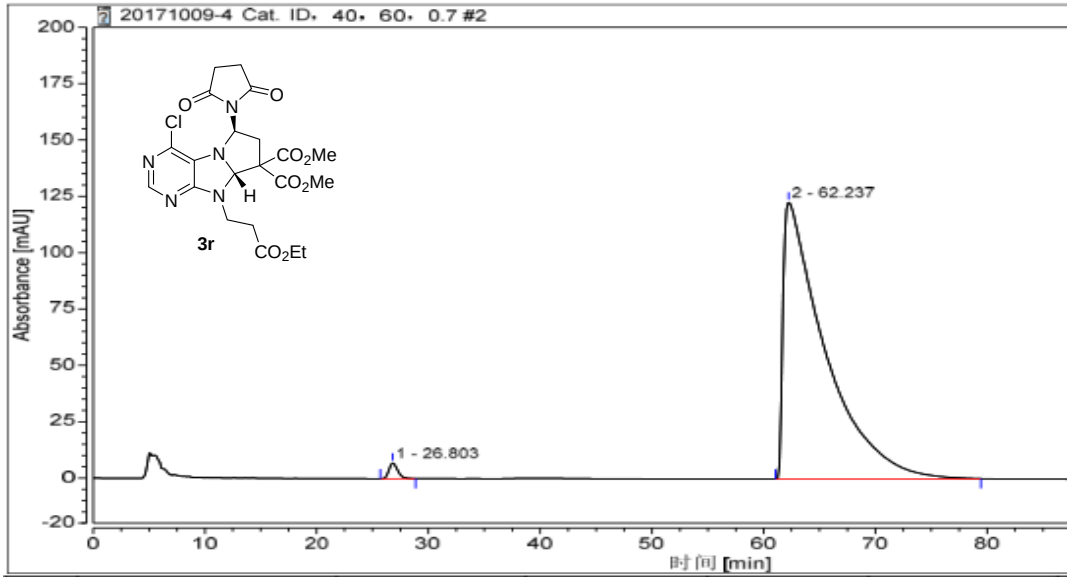
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.430	BB	1.0332	1.14733e4	165.46866	50.3755
2	32.931	BB	3.6101	1.13022e4	37.38475	49.6245



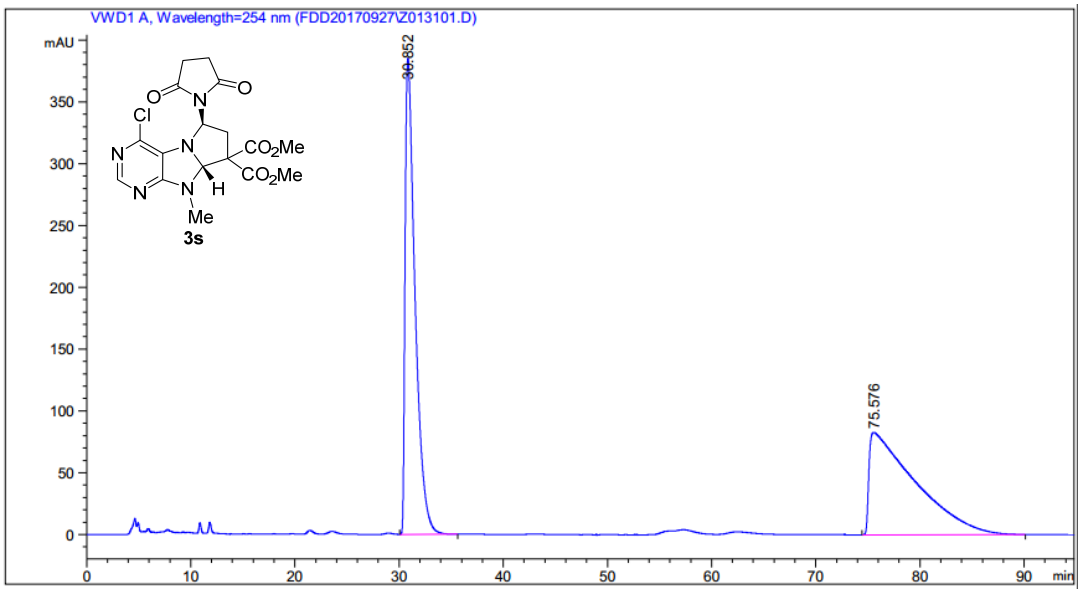
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.371	MM	1.1687	2.40430e4	342.86447	99.9717
2	32.867	MM	0.4739	6.81624	2.39746e-1	0.0283



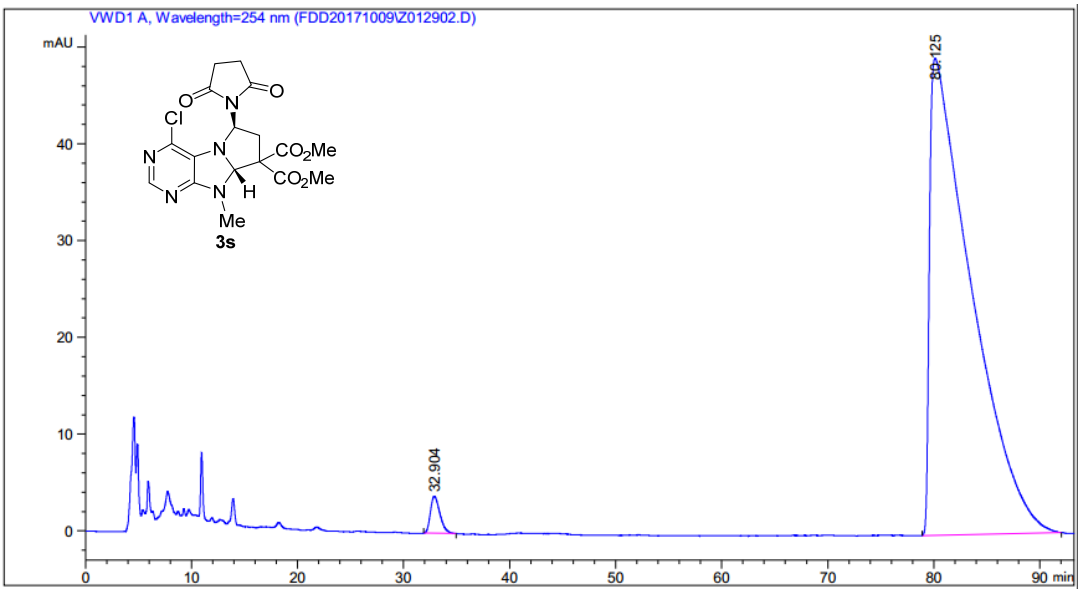
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	28.810	447.722	328.180	50.10	78.13
2	67.237	445.907	91.888	49.90	21.87



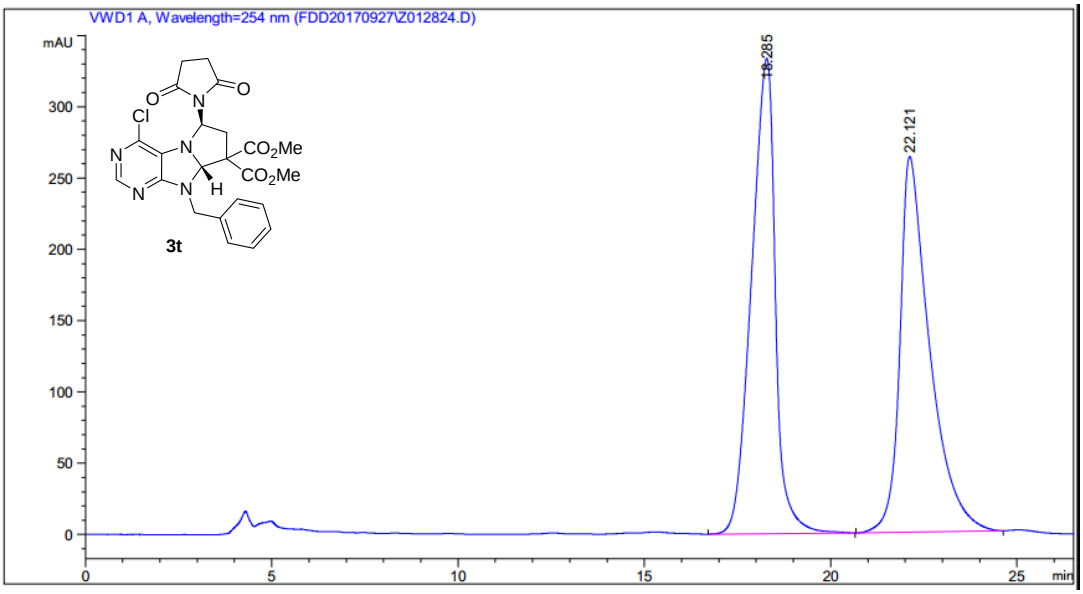
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	26.803	6.347	6.977	1.18	5.37
2	62.237	532.630	122.944	98.82	94.63



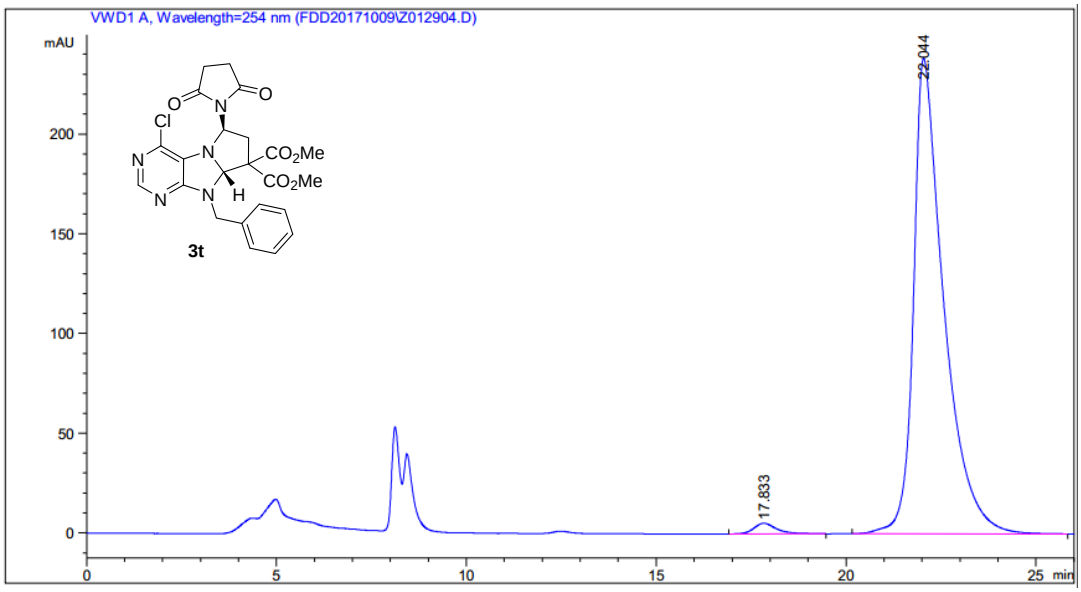
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.852	BB	0.9702	2.55802e4	385.02731	50.0164
2	75.576	BB	3.8320	2.55634e4	82.83260	49.9836



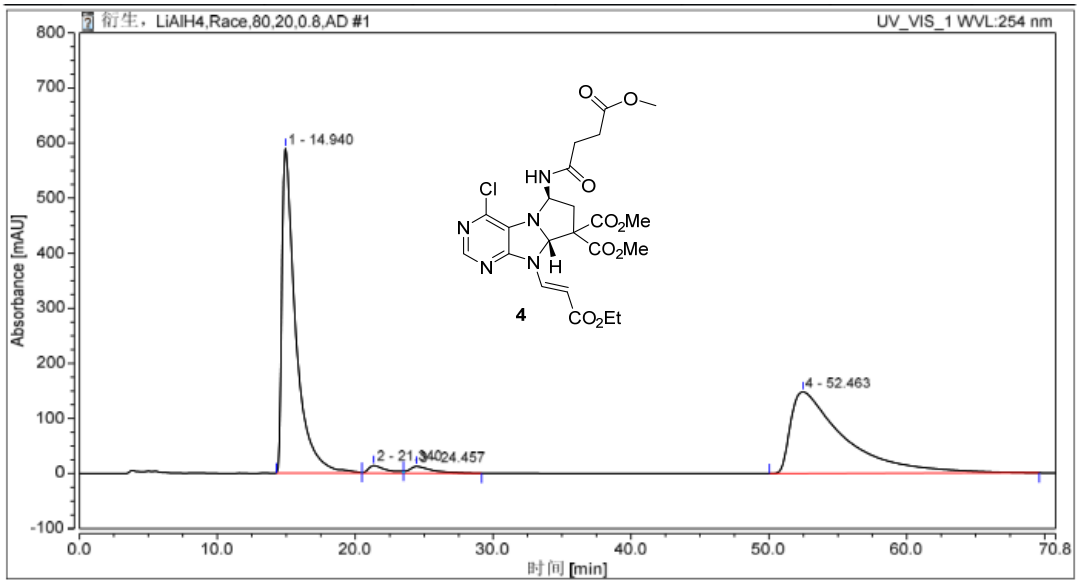
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.904	BB	0.7488	238.33664	3.83260	1.7420
2	80.125	BB	3.4038	1.34432e4	49.25832	98.2580



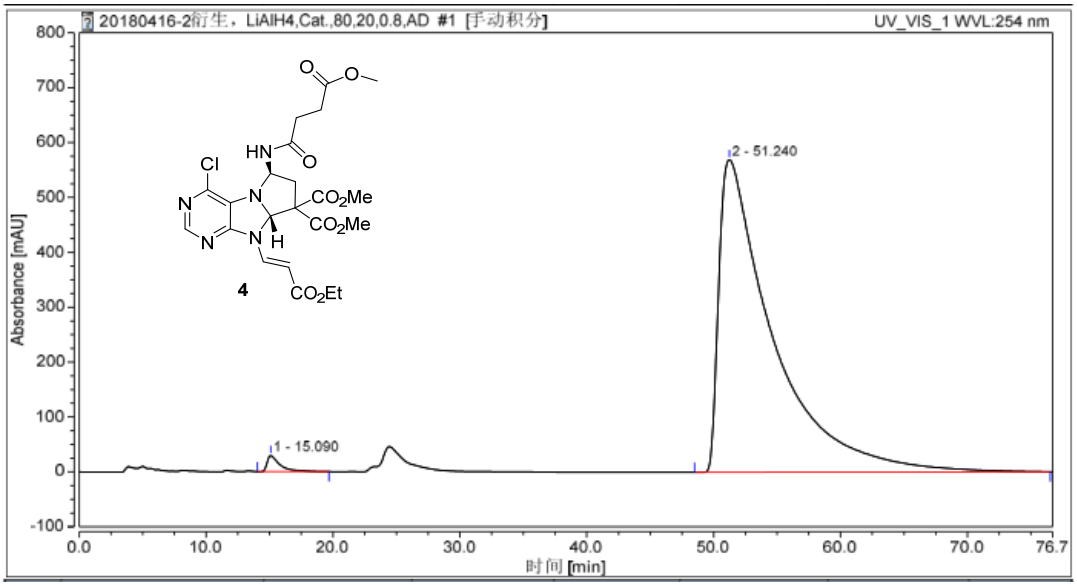
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.285	BB	0.6859	1.48558e4	333.36523	50.2943
2	22.121	BB	0.7955	1.46819e4	263.55215	49.7057



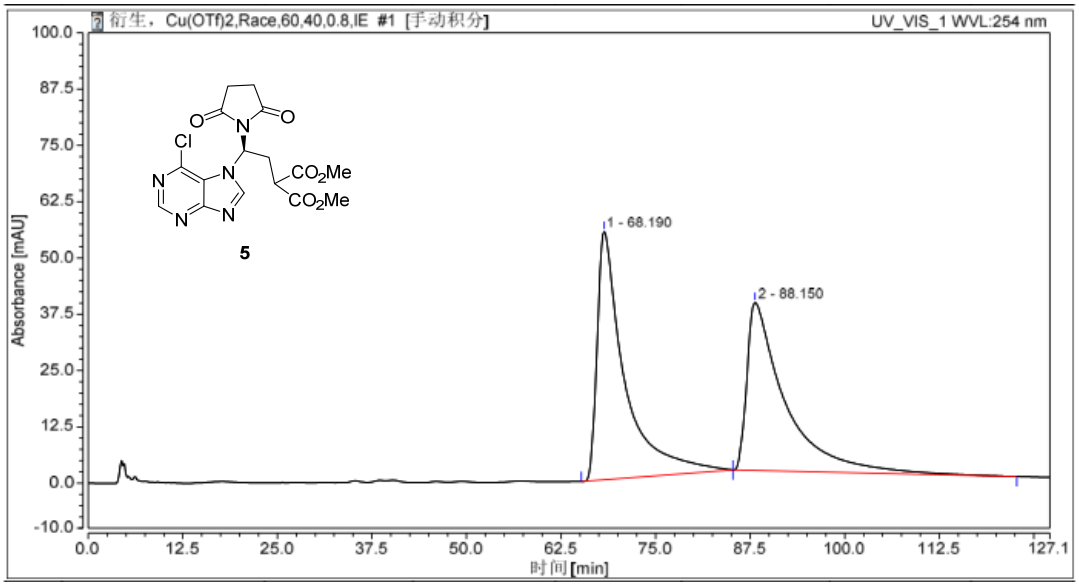
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.833	BB	0.6058	224.09444	5.34278	1.6636
2	22.044	BB	0.7952	1.32466e4	238.42441	98.3364



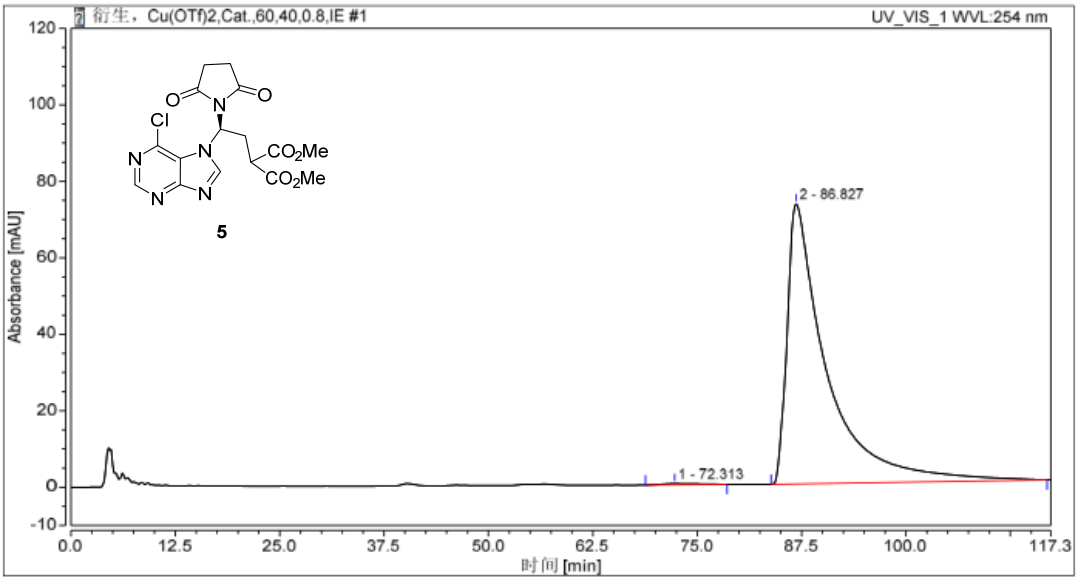
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	14.940	681.844	589.112	48.86	77.17
2	21.340	20.453	13.647	1.47	1.79
3	24.457	23.237	12.335	1.67	1.62
4	52.463	669.948	148.300	48.01	19.43



Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	15.090	34.956	29.483	1.23	4.92
2	51.240	2797.968	569.533	98.77	95.08



Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	68.190	231.948	55.167	51.52	59.64
2	88.150	218.296	37.332	48.48	40.36



Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	72.313	1.469	0.302	0.36	0.41
2	86.827	402.076	73.227	99.64	99.59