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Supporting information:

Synthesis of Nucleosides-substituted Carbonate and Diol Derivatives through the Carbon Dioxide Reaction Using Polyionic Liquid Catalyst

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1. Experiment

1.1. Materials

L1-L4 (99 %), ethylene oxide (99 %), chiral ethylene oxide (99 %) were purchased from Aladdin Chemical Co. Nucleoside 9-epoxy purine was synthesized according to the literature.[1] CO_2 (99.99 %) and N_2 (99.99%) were purchased from Xinxiang special gas company.

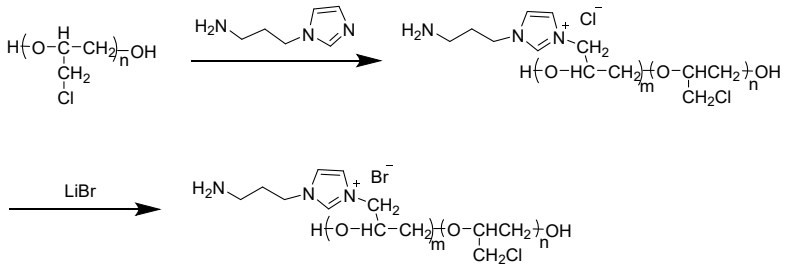
1.2 Methods.

^{1}H NMR spectra were measured on a Bruker 400 MHz NMR spectrometer. A Thermo FLASH 1112 elemental analyzer was used to determine the elemental analysis. The IR measurements were carried out on a Fourier transform infrared spectrometer (Nicolet 94 NEXUS). HPLC method was performed on an Agilent TM 1100. The molecular weight and molecular weight distribution (PDI = Mw/Mn) of the synthesized polymer samples were determined by gel permeation chromatography (GPC) equipped with a Waters 1515 apparatus, DMF was used as eluent, the flow rate was 1.0 mL.min, and polystyrene samples were used as standards. DSC was performed on a custom-made PCT-1A thermal analysis system. The microstructure morphology of the samples were observed by using an Olympus BX51 polarizing optical microscope (POM) equipped with a Linksys 32 THMSE600 hot stage and a digital camera (Micropublisher

5.0 RTV).

1.3 Synthesis of polyionic liquids

Synthesis of P1: Polyepichlorohydrin (PECH) and aminopropyl imidazole were used as raw materials, and PECH with molecular weight of 500 (10 g, 20 mmol) was added into Shrek bottle. After degassing for 30 min, aminopropyl imidazole (6 g, 48 mmol) was added in a syringe drop by drop. After full stirring, the Shrek bottle was sealed and immersed in an oil bath at 80 °C for reaction 10 h. After the reaction, sedimentation in ether, then dissolved with ethanol, and then sedimentation in ether, repeat the above operation, until no small molecule was detected, and vacuum drying at 60 °C for 48 h. 3 g P1 was weighed and dissolved in 30 mL water, and lithium bromide 6 g was dissolved in 10 mL water, then dropped into PIL aqueous solution at room temperature, and then put it into an oil bath at 40 °C for 24 h. It is then put into a dialysis bag with a molecular weight of 500 to dialysis until no chloride ions leak out of the aqueous phase. Freeze-dried products can be obtained. The synthesis of other ionic liquids was similar. The synthesis route is shown in the Scheme. S1.



Scheme S1 Synthesis pathway of polyionic liquids (P1-P5)

1.4 Catalytic reaction

The reaction substrate and catalyst were added into the reactor, CO_2 was introduced, and the reaction was carried out under certain pressure conditions. After the reaction, dichloromethane was added to extract the product, and the product was purified by

column chromatography. Cyclic reaction of catalysts: after the product was extracted by dichloromethane, the polyionic liquid was completely retained, the reaction substrate was added again, mixed, and CO_2 was introduced to continue the reaction.

2. Characterization of polyionic liquids

Table S1 Tg of PILs from DSC results and Cl^- content of PILs from ion chromatography

PIL	P1	P2	P3	P4	P5	P6	P7	P8
Tg (℃)	8.4	44	32	19	5.2	15.6	21.4	-0.9
Graft ratio (%)	45	63	29	42	42	45	13	13
Weight molecular (Mn)	500	500	1000	1000	250	1000	1000	1000

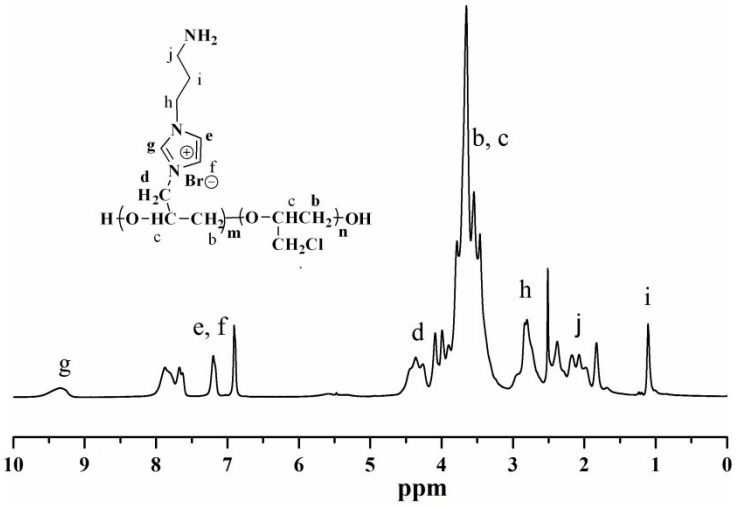
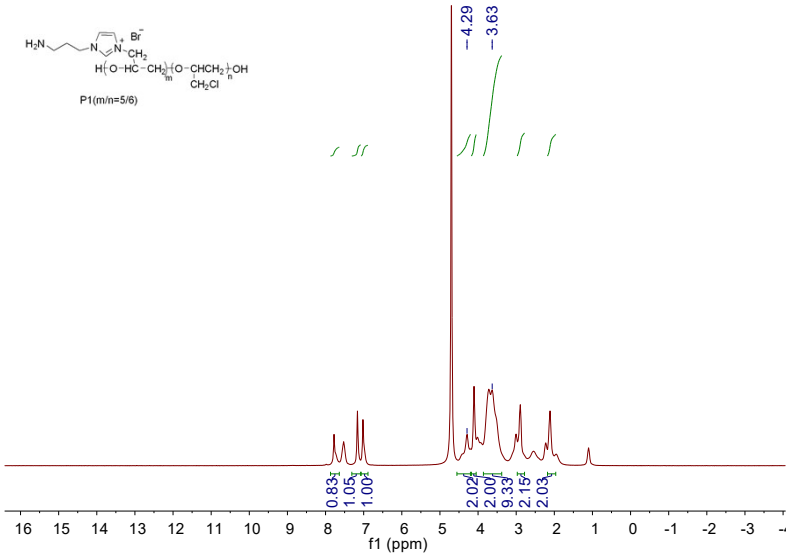


Fig. S1 ^{1}H NMR spectra of P1

2.1 Calculation of grafting rate

Grafting rates were calculted by ^{1}H NMR of polymer. Take P1 as an example, imidazole connected H (δ 4.29) was taken as the standard in NMR, and the corresponding integral of other peaks in imidazole was marked. δ 3.63 was the hydrogen of PECH which not connected to 1H-Imidazole-1-propanamine and PECH without chemical shift. The ratio of the integral H (δ 4.29) and H (δ 3.63) was the graft rate, that is, the graft rate of P1 is 5/11=45%.



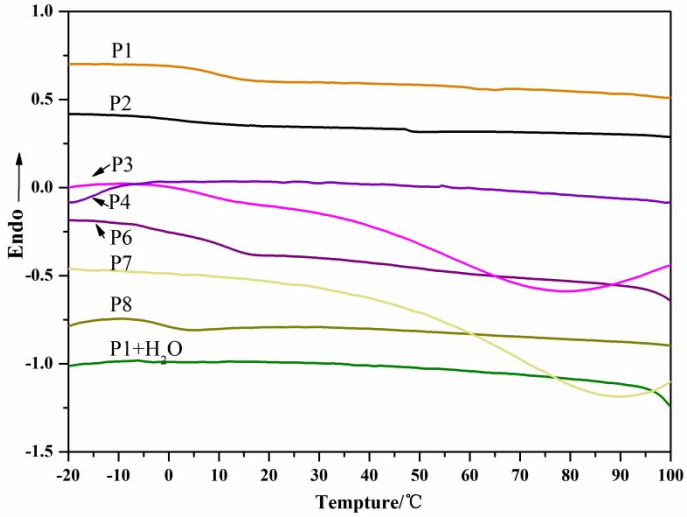


Fig. S2 DSC of polymers.

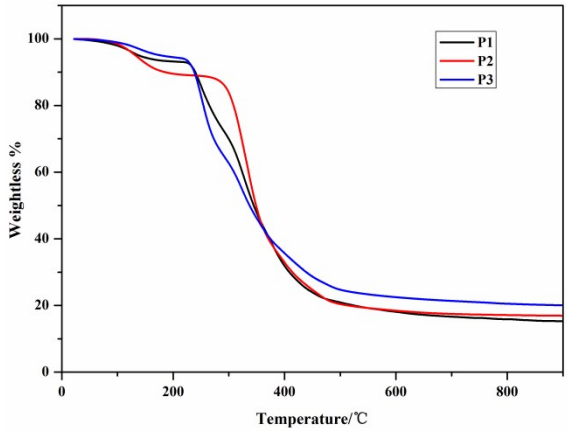


Fig.S3 Tg of polymers.

3. Catalytic properties

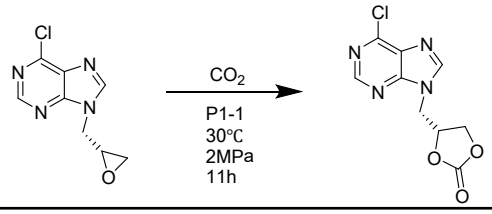
Table S2 P1 catalyzes the cycloaddition of ethylene oxide and previously reported ionic liquid and polyionic liquid catalysis

Catalysts	Catalyst loading (%)	t/h	T/ ℃	Pressure	water	Yield (%) [a]	Reference
P1	2	11	30	2 MPa	/	9	This work
P1	2	11	30	2 MPa	15 eq	16	This work
P1	2	5	60	2 MPa	/	72	This work
P1	2	5	60	2 MPa	/	72	This work
P1	2	11	60	2 MPa	/	91	This work
$[C_1C_4Im][HCO_3]$	6.25	30	60	2 MPa	/	94	2
P(DMAEMA-EtOH)Br	1	3	110	2 MPa	/	99	3
VCEImBr-TMPTA-HMEA	1.5	1.5	120	2 MPa	/	99	4
P(DEMA-EtOH)@SiO_2	0.5	3	120	2.5 MPa	/	91	5
P[EEBVIM]Cl_2-EGDMA	0.9	12	100	1 MPa	/	99	6
[bmim][MET]	0.5	4	120	2 MPa	/	89	7
$[DBUH]_2$[Cys]	25	24	30	0.1 MPa	/	96	8
NMI-OH-	1	4	120	1 MPa	/	80	9

NH_2							
PVIM-Br	5	3	120	2 MPa	/	94	10

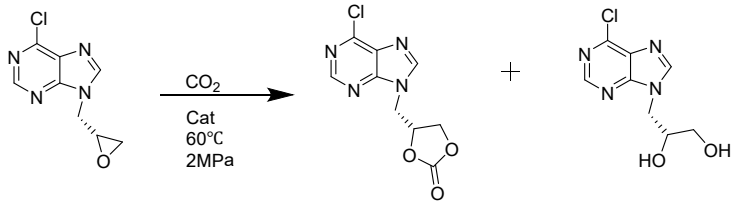
[a] the yield was determined by ^1H NMR.

Table S3 Effects of solvent on the yield of cycloaddition of CO_2



Solvent	PIL: Solvent	Con/%	Yield/%	Mol ratio of PIL: solvent	Con/%	Yield/%
H_2O	1:1	100	94	1:10	100	57
CH_3CN	1:1	55	34	1:10	70	41
MeOH	1:1	35	21	1:10	91	35
DCM	1:1	49	32	1:10	87	36

Table S4 Effects of water on the yield of the product



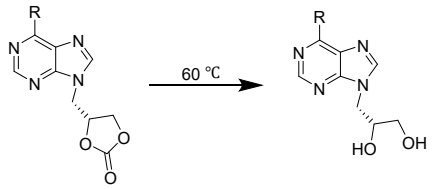
a **b** **c**

Entry	Cat.	$\overline{Mn}$	Grafting ratio (%)	T/H_2O	**Yield (b) (%)**	T/H_2O	**Yield (c) (%)**
1	P1	500	45	30 °C/15 eq	94	60 °C/35 eq	75
2	P1[d]	500	45	30 °C/15 eq	0	60 °C/35 eq	0
3	P2	500	63	30 °C/15 eq	63	60 °C/35 eq	47
4	P3	1000	29	30 °C/15 eq	45	60 °C/35 eq	38
5	P4	1000	42	30 °C/15 eq	51	60 °C/35 eq	59
6	P5	250	42	30 °C/15 eq	86	60 °C/35 eq	43
7	P6	500	45	30 °C/15 eq	41	60 °C/35 eq	5
8	P7	1000	13	30 °C/15 eq	84	60 °C/35 eq	2
9	P8	1000	13	30 °C/15 eq	0	60 °C/35 eq	0

10	L1	30 °C/15 eq	45	60 °C/35 eq	9
11	L2	30 °C/15 eq	0	60 °C/35 eq	0
12	L2	30 °C/15 eq (2h)	52	60 °C/35 eq (6h)	42
13	L3	30 °C/15 eq	95	60 °C/35 eq	0
14	L4	30 °C/15 eq	92	60 °C/35 eq	0

d: The reaction was carried out without CO_2.

Table S5 Ester hydrolysis catalyzed by different catalysts under 60 °C and 200 ul water



Cat	t/h	Conversion (%) [a]	Yield (%) [b]
K_2CO_3	3	100	82
P1	22	100	86
P6	22	100	76
L1	22	100	45
L2	20	100	60

[a] was determined by ^1H NMR, [b] was the isolated yield.

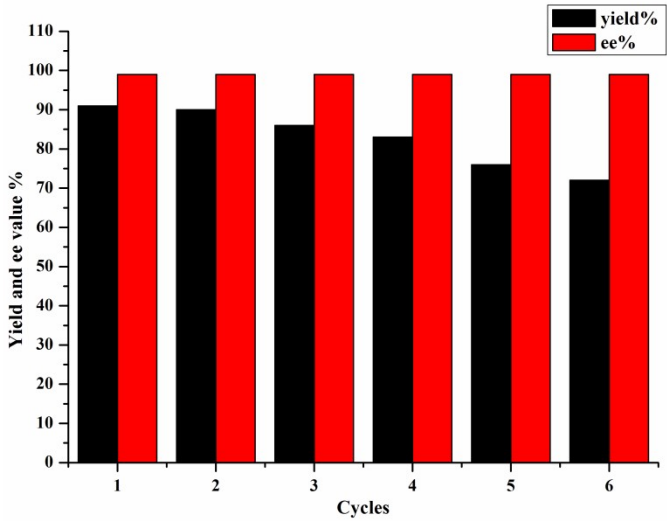


Fig. S4 Cyclic catalytic performance of P1 under the condition:P1/water/epoxy=1/35/1 at 60 °C.

4. Mechanisms

Table S6 pH of different of ionic liquids with the mole ratio of ionic liquid:H_2O=1:1 at 25 °C

P1	P2	P3	P4	P5	P6	P7	P8	L1	L2	L3	L4
8.0	7.2	6.4	6.4	7.2	8.0	6.4	6.4	7.5	9.0	6.2	6.1

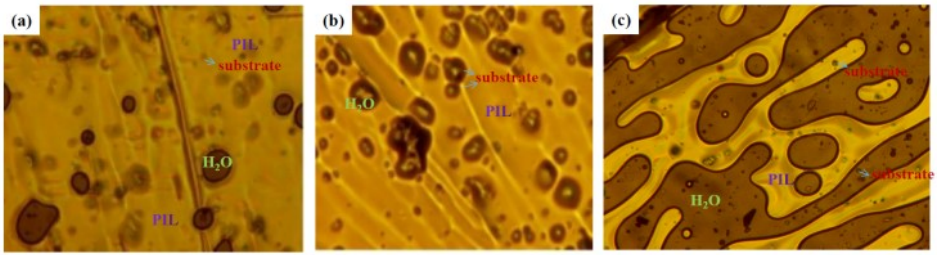


Fig. S5 Image of the phase state for P1, H_2O and solid substrate from POM, P1/water/epoxy=1/15/1 at 25 °C (a), P1/water/epoxy=1/35/1 at 60 °C (b), and P1/water/epoxy=1/70/1 at 60 °C (c).

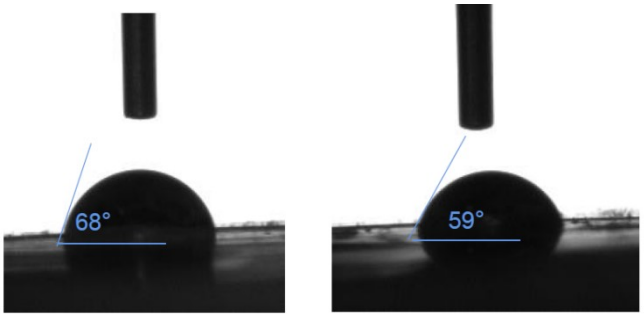


Fig. S6 The contact angle experiment of P1 (left), and P1 after introducing CO_2 (right).

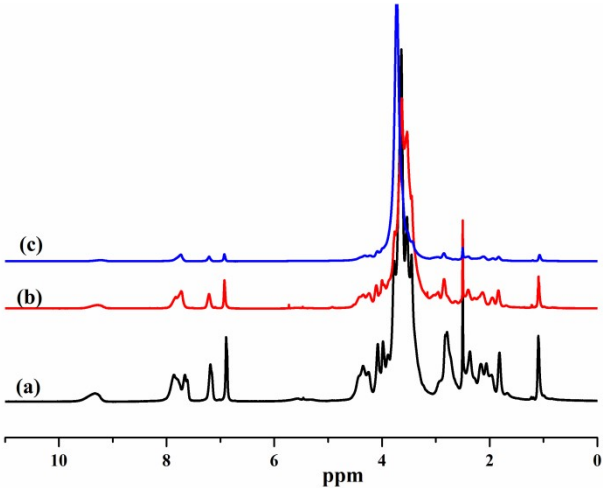


Fig. S7 ^1H NMR spectra of P1 (a), P1 after introducing CO_2 (b), and P1 after introducing CO_2 and H_2O, P1/H_2O=1/15 (c).

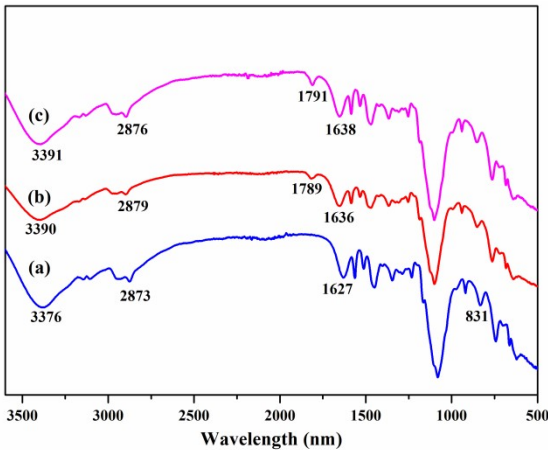
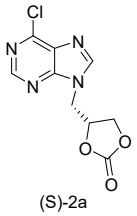


Fig. S8 FTIR of P1 (a), P1 after introducing CO_2 (b), and P1 after introducing CO_2 and H_2O, P1/H_2O=1/15 (c).

5. Characterization of products and raw materials

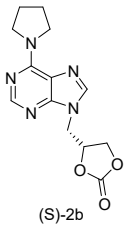
^1H and ^{13}C NMR data



(S)-2a

^1H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.24 (s, 1H), 5.18 (m, 1H), 4.69 (dt, *J* = 11.1, 5.8 Hz, 2H), 4.59 (dd, *J* = 15.1, 6.4 Hz, 1H), 4.36 (dd, *J* = 9.2, 6.5 Hz, 1H).

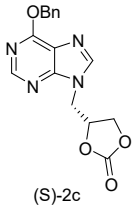
^{13}C NMR (100 MHz, DMSO) δ 154.1, 152.1, 151.8, 149.2, 147.6, 130.7, 74.4, 67.0, 45.5.



(S)-2b

^1H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.85 (s, 1H), 5.26 – 5.07 (m, 1H), 4.68 – 4.51 (m, 3H), 4.41 (dd, *J* = 9.0, 6.6 Hz, 1H), 4.23 (s, 2H), 3.82 (s, 2H), 2.09 (d, *J* = 20.3 Hz, 4H).

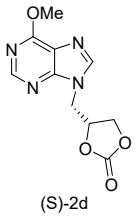
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 153.1, 150.1, 138.8, 119.9, 74.4, 66.5, 44.7.



(S)-2c

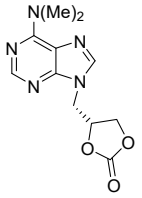
^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.22 (s, 1H), 7.54 (d, *J* = 7.1 Hz, 2H), 7.44 – 7.30 (m, 3H), 5.18 (s, 1H), 4.65 (dd, *J* = 22.3, 12.3 Hz, 3H), 4.46 – 4.30 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 142.3, 135.7, 128.5, 128.4, 128.3, 74.0, 68.8, 66.5.



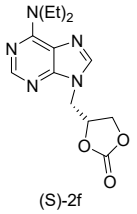
(S)-2d

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.05 (s, 1H), 5.23 – 5.07 (m, 1H), 4.75 – 4.51 (m, 3H), 4.37 (dd, *J* = 9.0, 6.6 Hz, 1H), 4.21 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 153.5, 152.7, 152.1, 142.4, 121.4, 74.3, 66.66, 54.6, 45.4.



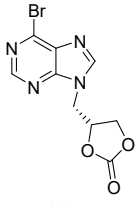
(S)-2e

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.84 (s, 1H), 5.08 – 5.24 (m, 1H), 4.67 (dd, *J* = 20.9, 12.0 Hz, 2H), 4.55 (dd, *J* = 15.4, 6.2 Hz, 1H), 4.36 (dd, *J* = 9.2, 6.5 Hz, 1H), 3.78 – 3.30 (m, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 154.0, 152.8, 151.7, 149.4, 137.4, 118.8, 73.4, 65.5, 64.7, 60.7, 43.8.



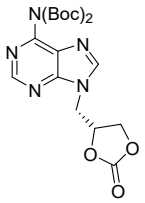
(S)-2f

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.81 (s, 1H), 5.18 – 5.09 (m, 1H), 4.60 (dd, *J* = 11.0, 6.5 Hz, 1H), 4.48-4.56 (m, 2H), 4.37 (dd, *J* = 9.1, 6.6 Hz, 1H), 4.29 – 3.76 (m, 4H), 1.31 (t, *J* = 7.0 Hz, 7H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 153.8, 152.9, 150.5, 138.4, 119.3, 74.4, 66.5, 44.7.



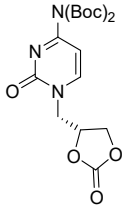
(S)-2g

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.26 (s, 1H), 5.18 (m, 1H), 4.74 – 4.64 (m, 2H), 4.58 (dd, *J* = 15.1, 6.3 Hz, 1H), 4.36 (dd, *J* = 9.2, 6.4 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 153.3, 152.3, 149.8, 145.2, 73.9, 66.4, 45.8.



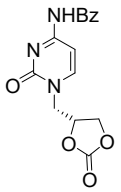
(S)-2h

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.24 (s, 1H), 5.18 (s, 1H), 4.89 – 4.51 (m, 3H), 4.39 (s, 1H), 1.47 (s, 18H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 155.1, 149.3, 148.3, 97.0, 85.3, 74.3, 66.9, 52.3, 27.7.



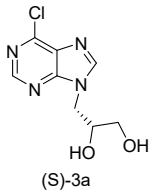
(S)-2i

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.54 (m, 1H), 7.19 – 7.07 (m, 1H), 5.17 – 5.00 (m, 1H), 4.63 (t, *J* = 8.8 Hz, 1H), 4.46 – 4.21 (m, 2H), 3.97 (dd, *J* = 14.3, 7.1 Hz, 1H), 1.56 (s, 18H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 155.1, 149.3, 148.3, 97.0, 85.3, 74.3, 66.9, 52.3, 27.7.



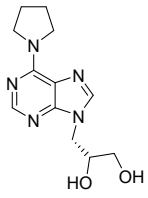
(S)-2j

^{1}H NMR (600 MHz, DMSO) δ 11.24 (s, 1H), 8.13 (d, *J* = 7.3 Hz, 1H), 8.01 (d, *J* = 7.3 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 6.3 Hz, 1H), 5.19 – 5.09 (m, 1H), 4.64 (t, *J* = 8.5 Hz, 1H), 4.36 (dd, *J* = 8.6, 6.3 Hz, 1H), 4.27 (dd, *J* = 14.1, 3.6 Hz, 1H), 4.21 (dd, *J* = 14.2, 7.8 Hz, 1H).
^{13}C NMR (150 MHz, DMSO) δ 164.0, 154.8, 151.2, 133.2, 128.9, 127.9, 96.7, 74.6, 67.6, 66.3, 61.1, 55.4, 51.8.



(S)-3a

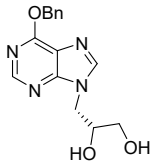
^{1}H NMR (400 MHz, DMSO) δ 8.77 (s, 1H), 8.60 (s, 1H), 5.15 (d, *J* = 4.1 Hz, 1H), 4.88 (t, *J* = 4.8 Hz, 1H), 4.46 (dd, *J* = 13.9, 3.4 Hz, 1H), 4.17 (dd, *J* = 14.0, 8.7 Hz, 1H), 3.90 (s, 1H), 3.45 (d, *J* = 5.0 Hz, 2H).
^{13}C NMR (100 MHz, DMSO) δ 152.7, 151.8, 149.3, 148.7, 131.2, 69.8, 64.0, 47.9.



(S)-3b

^{1}H NMR (400 MHz, DMSO) δ 8.19 (s, 1H), 8.02 (s, 1H), 5.11 (s, 1H), 4.86 (d, *J* = 5.0 Hz, 1H), 4.31 (dd, *J* = 13.9, 3.7 Hz, 1H), 4.02 (dd, *J* = 13.9, 8.0 Hz, 3H), 3.83 (s, 1H), 3.64 (s, 2H), 3.36 – 3.24 (m, 2H), 1.95 (s, 4H).

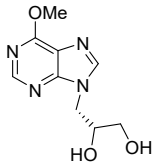
^{13}C NMR (100 MHz, DMSO) δ 153.0, 152.4, 150.5, 141.5, 119.7, 70.1, 63.9, 46.8.



(S)-3c

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.03 (s, 1H), 7.55 (d, *J* = 7.1 Hz, 2H), 7.46 – 7.30 (m, 3H), 5.60 (s, 2H), 4.36 (m, 2H), 4.11 (s, 1H), 3.51 (d, *J* = 3.9 Hz, 2H).

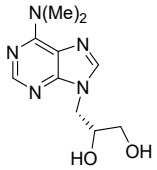
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 151.7, 151.6, 143.6, 135.7, 128.9, 128.9, 128.6, 128.5, 120.5, 69.5, 68.9, 63.4, 47.4.



(S)-3d

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.01 (s, 1H), 4.41 (dd, *J* = 4.9, 2.1 Hz, 2H), 4.20 (s, 3H), 4.14 (t, *J* = 4.0, 1H), 3.57 (*J* = 4.0, 2H).

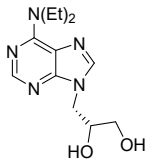
^{13}C NMR (100 MHz, DMSO) δ 151.7, 145.1, 137.0, 124.0, 122.7, 36.3, 31.9, 19.2, 13.7.



(S)-3e

^{1}H NMR (400 MHz, DMSO) δ 8.20 (s, 1H), 8.04 (s, 1H), 5.09 (d, *J* = 5.5 Hz, 1H), 4.83 (t, *J* = 5.7 Hz, 1H), 4.50 – 4.34 (m, 1H), 4.30 (dd, *J* = 13.9, 3.6 Hz, 1H), 4.00 (dd, *J* = 13.9, 8.1 Hz, 1H), 3.88 – 3.73 (m, 1H), 3.55 – 3.41 (m, 4H), 3.30 (d, *J* = 5.8 Hz, 2H).

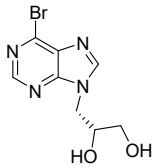
^{13}C NMR (100 MHz, DMSO) δ 154.7, 152.0, 150.9, 141.0, 119.5, 73.0, 70.1, 64.0, 63.6, 46.9.



(S)-3f

^{1}H NMR (400 MHz, DMSO) δ 8.19 (s, 1H), 8.04 (s, 1H), 5.12 – 5.06 (m, 1H), 4.85 (t, *J* = 4.9 Hz, 1H), 4.30 (dd, *J* = 13.9, 3.4 Hz, 1H), 4.00 (dd, *J* = 13.9, 8.1 Hz, 4H), 3.83 (d, *J* = 3.6 Hz, 2H), 1.19 (t, *J* = 6.9 Hz, 7H).

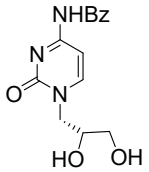
^{13}C NMR (100 MHz, DMSO) δ 153.5, 152.2, 150.9, 141.2, 119.0, 70.1, 64.0, 46.9, 14.0.



(S)-3g

^{1}H NMR (400 MHz, DMSO) δ 8.19 (s, 1H), 8.04 (s, 1H), 5.11 (d, *J* = 4.4 Hz, 1H), 4.87 (s, 1H), 4.30 (dd, *J* = 13.9, 3.5 Hz, 1H), 4.00 (dd, *J* = 13.9, 8.1 Hz, 2H), 3.83 (s, 2H).

^{13}C NMR (100 MHz, DMSO) δ 153.5, 152.2, 150.9, 141.2, 119.0, 70.1, 64.0, 46.9.



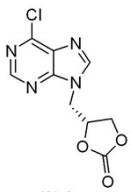
(S)-3j

^{1}H NMR (400 MHz, DMSO) δ 11.13 (s, 1H), 8.11 – 7.94 (m, 3H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 5.3 Hz, 1H), 5.06 (d, *J* = 5.6 Hz, 1H), 4.77 (t, *J* = 5.7 Hz, 1H), 4.16 (dd, *J* = 13.1, 3.2 Hz, 1H), 3.84 – 3.73 (m, 1H), 3.52 (dd, *J* = 13.1, 8.7 Hz, 1H), 3.46 – 3.40 (m, 1H), 3.32 (dd, *J* = 10.2, 4.6 Hz, 1H).

^{13}C NMR (150 MHz, DMSO) δ 167.7, 163.4, 156.0, 152.0, 133.7, 133.1, 128.8,128.8, 95.8, 69.1, 64.22, 53.6.

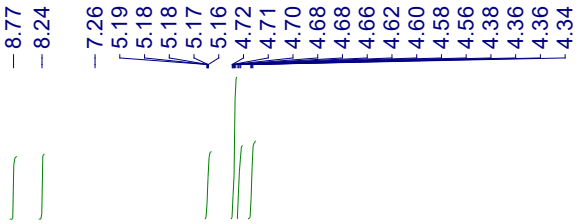
^{1}H data

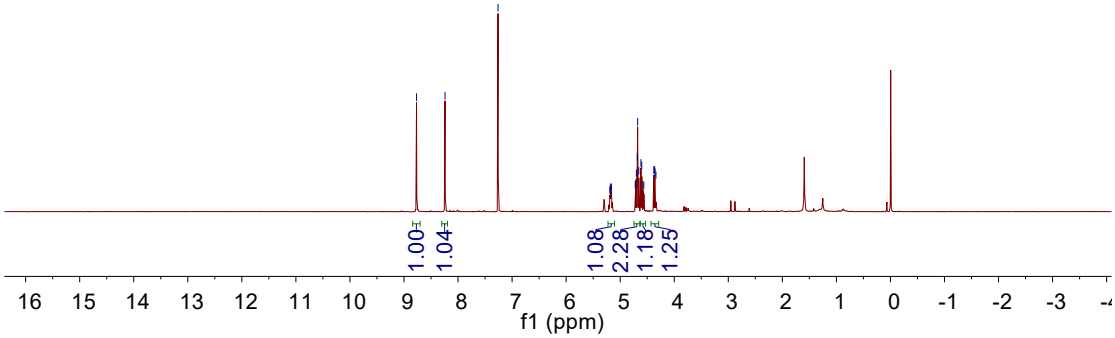
01242021-mxn-6-C1



(S)-2a

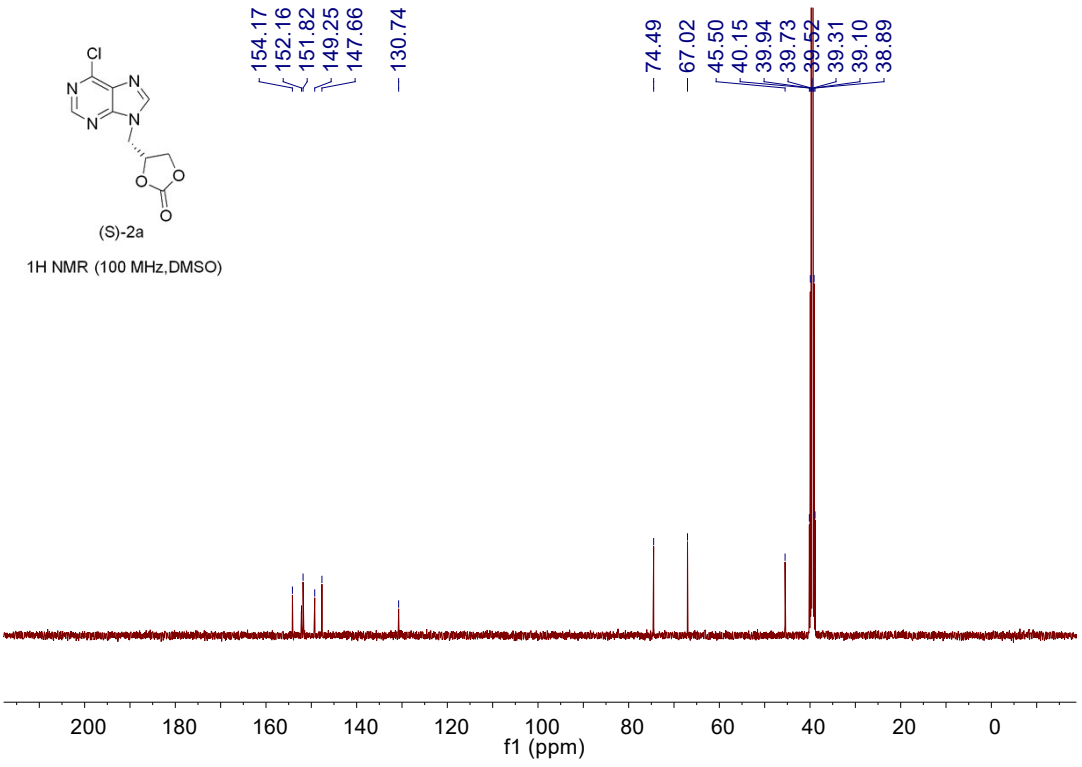
1H NMR (400 MHz, CDCl3)

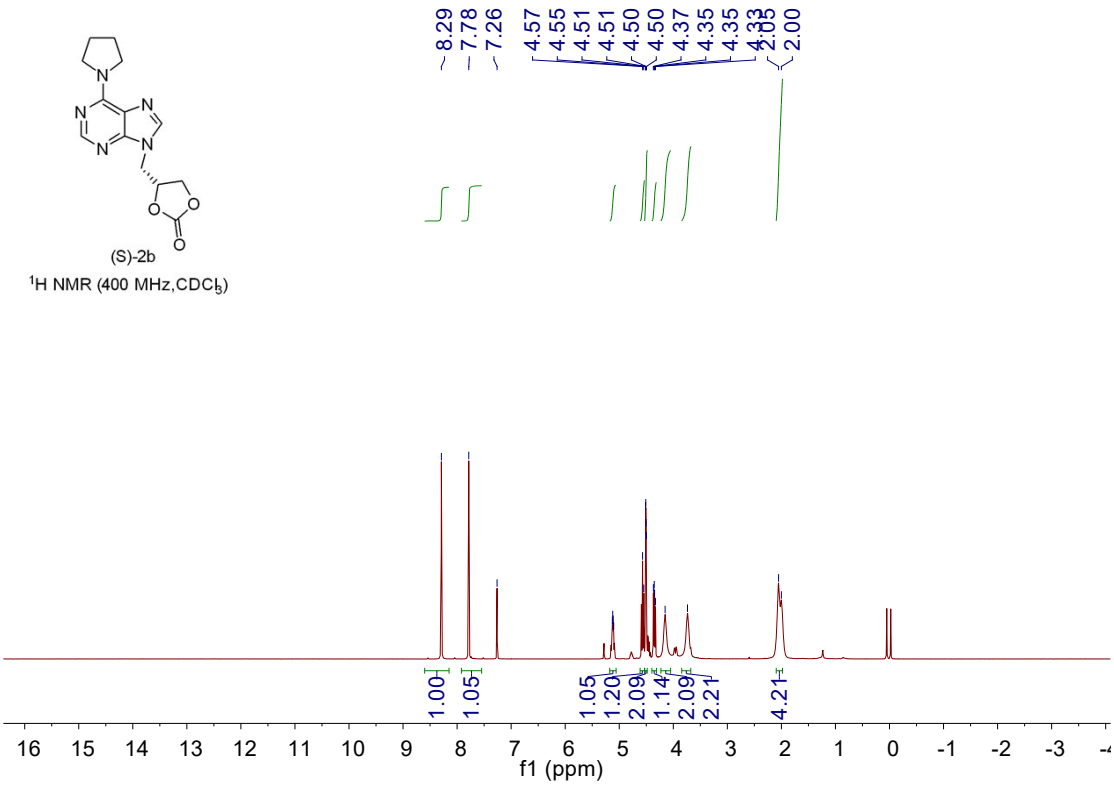




(S)-2a

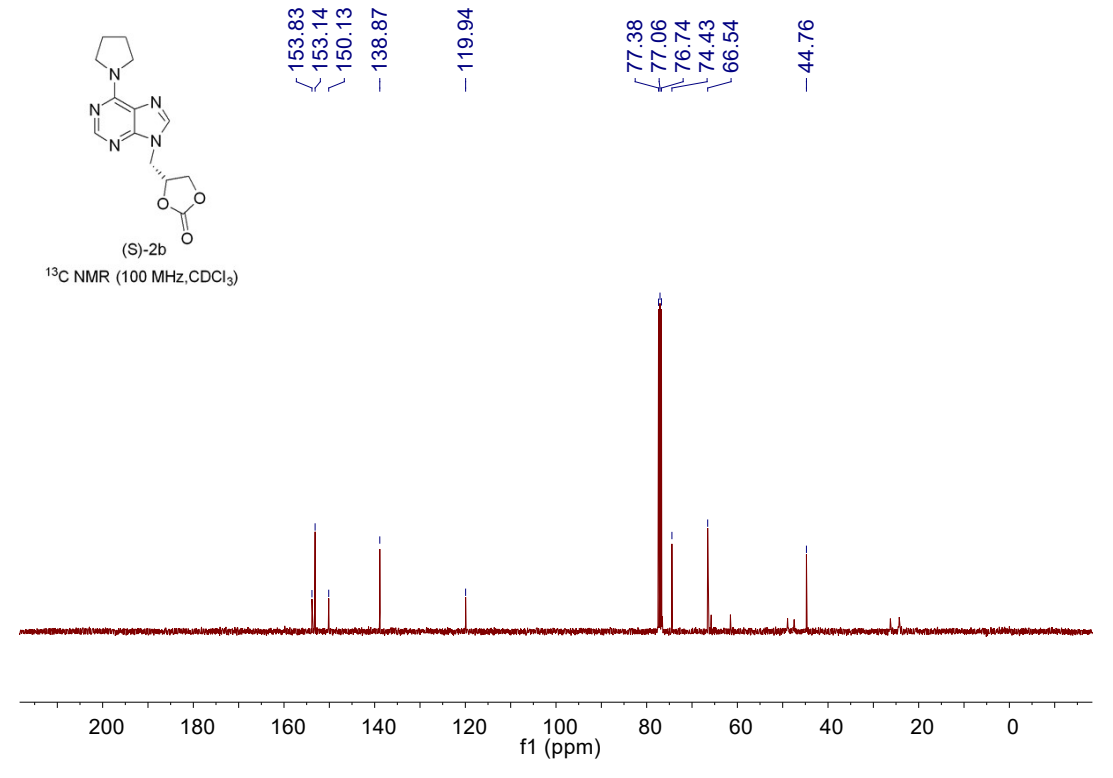
1H NMR (100 MHz,DMSO)





(S)-2b

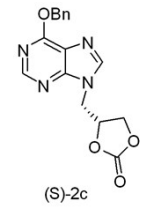
^{1}H NMR (400 MHz,$CDCl_3$)



(S)-2b

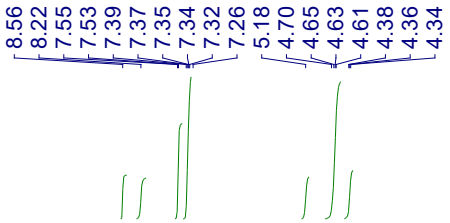
^{13}C NMR (100 MHz,$CDCl_3$)

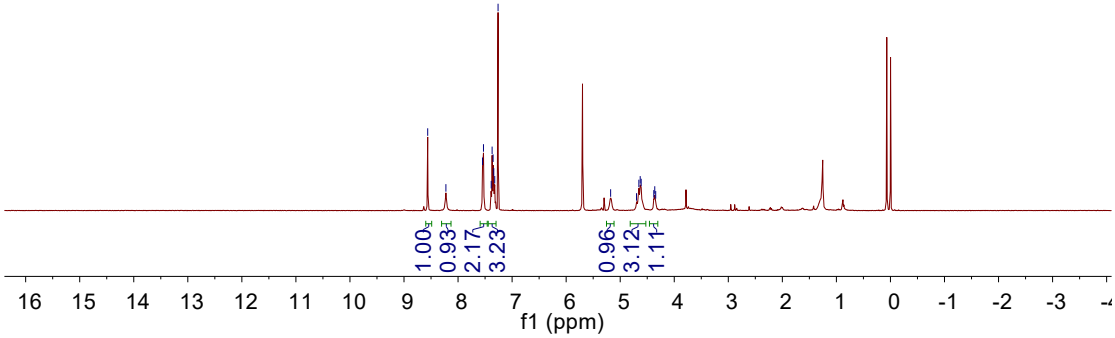
01202021-mxn-OBn

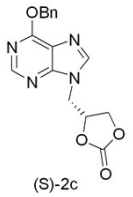


(S)-2c

^{1}H NMR (400 MHz,$CDCl_3$)

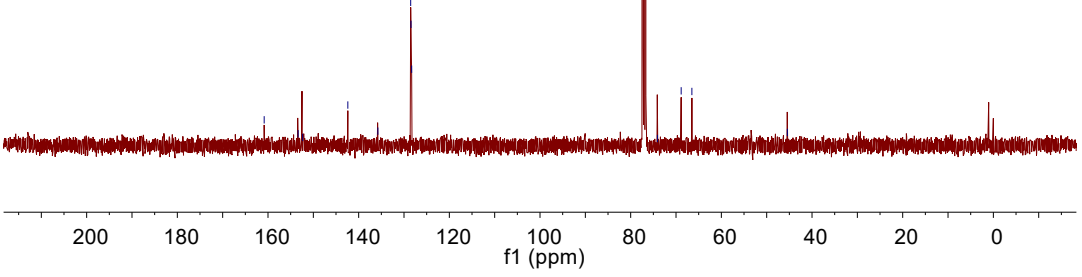


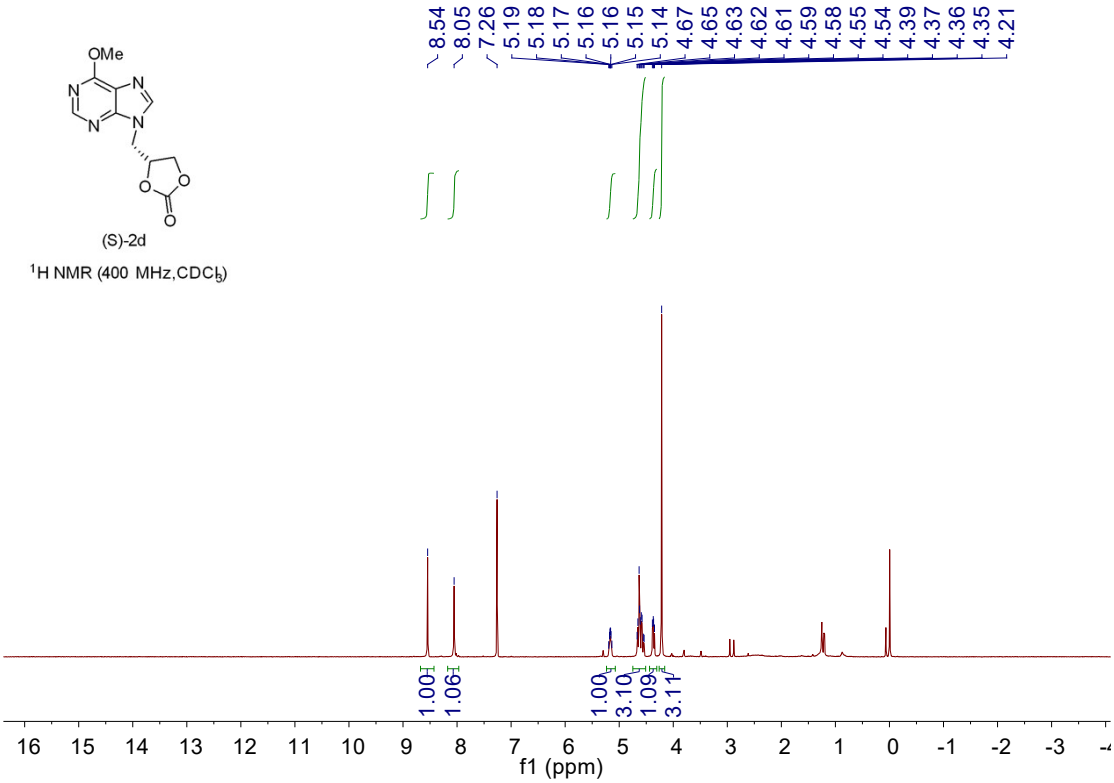


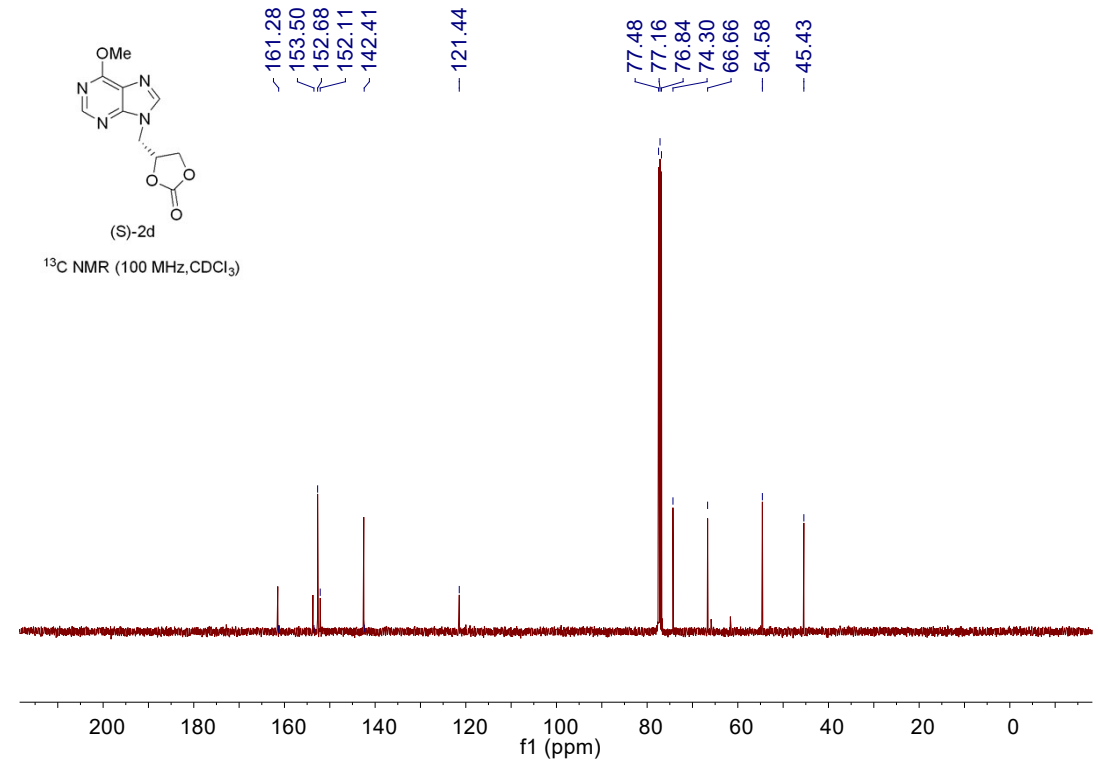


(S)-2c

^{13}C NMR (100 MHz,$CDCl_3$)



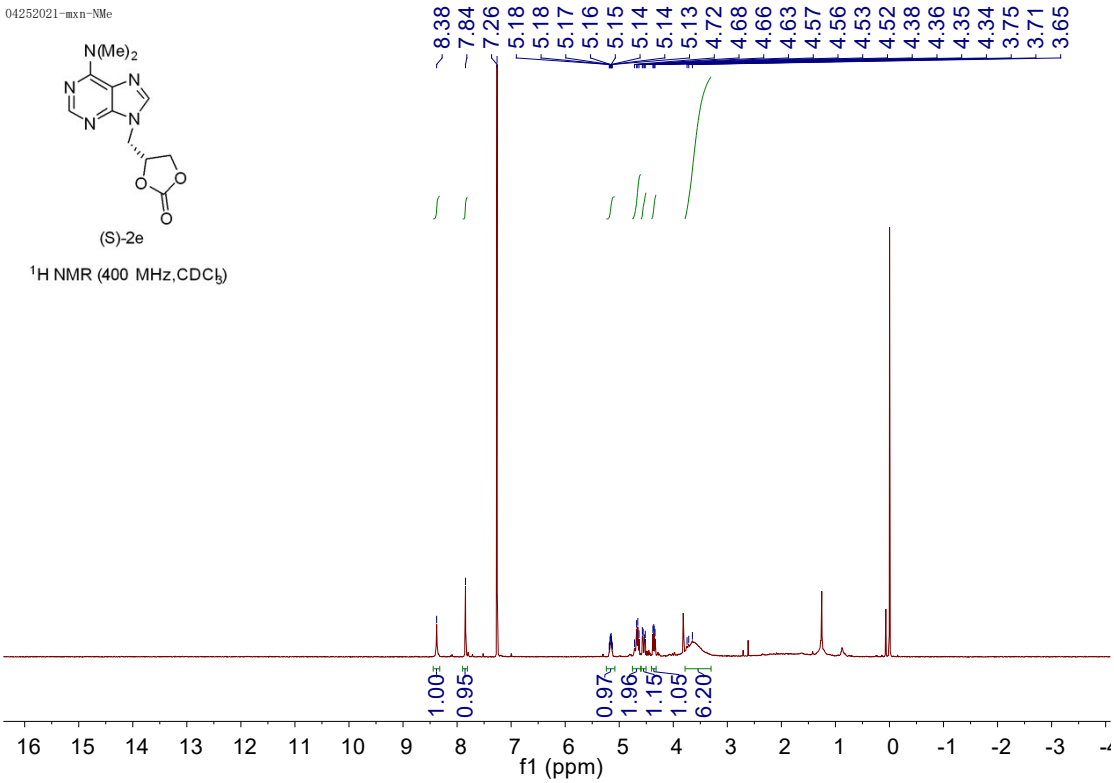

OMe
(S)-2d
^{1}H NMR (400 MHz,CDCl$_3$)
8.54
8.05
7.26
5.19
5.18
5.17
5.16
5.16
5.15
5.14
4.67
4.65
4.63
4.62
4.61
4.59
4.58
4.55
4.54
4.39
4.37
4.36
4.35
4.21
1.00
1.06
1.00
3.10
1.09
3.11
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


OMe
(S)-2d
^{13}C NMR (100 MHz,CDCl$_3$)
161.28
153.50
152.68
152.11
142.41
121.44
77.48
77.16
76.84
74.30
66.66
54.58
45.43
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

04252021-mxn-NMe

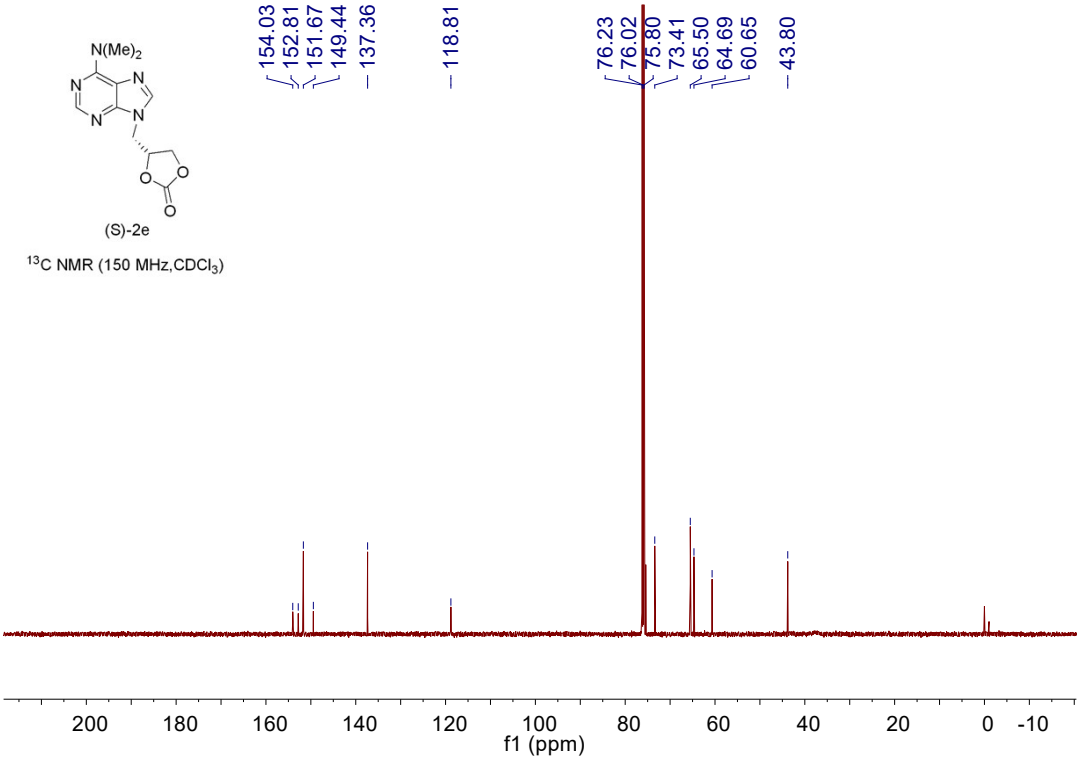
(S)-2e

^{1}H NMR (400 MHz,$CDCl_3$)



(S)-2e

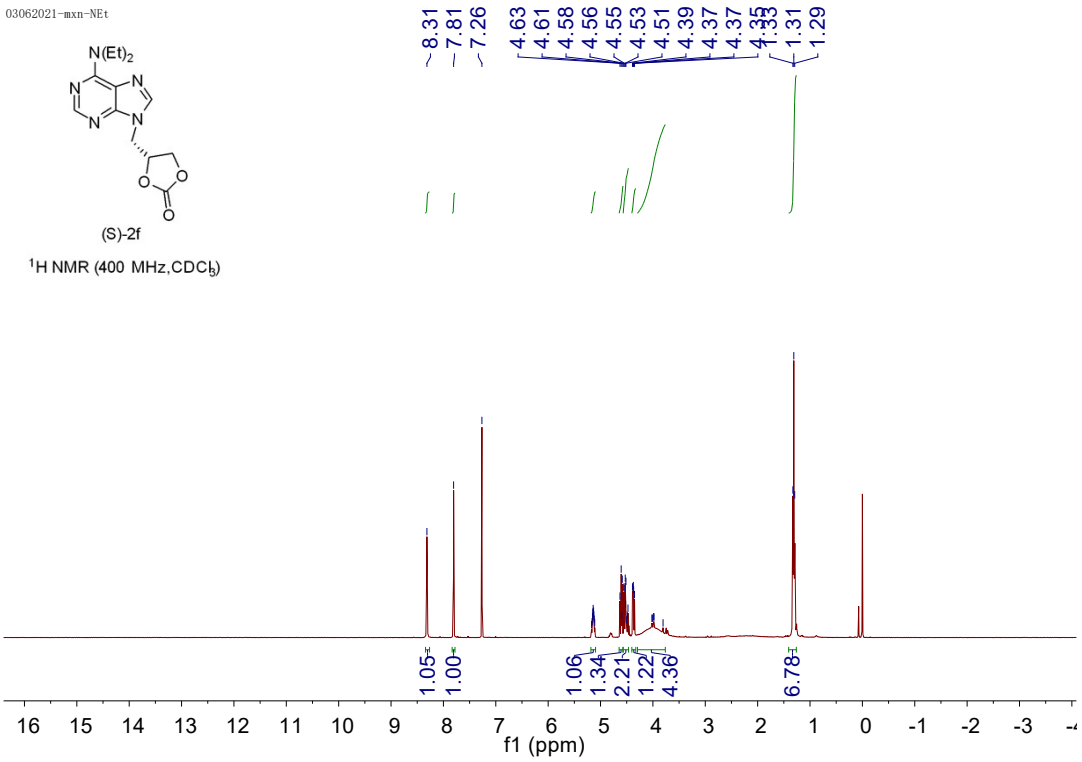
^{13}C NMR (150 MHz,$CDCl_3$)



03062021-mxn-NEt

(S)-2f

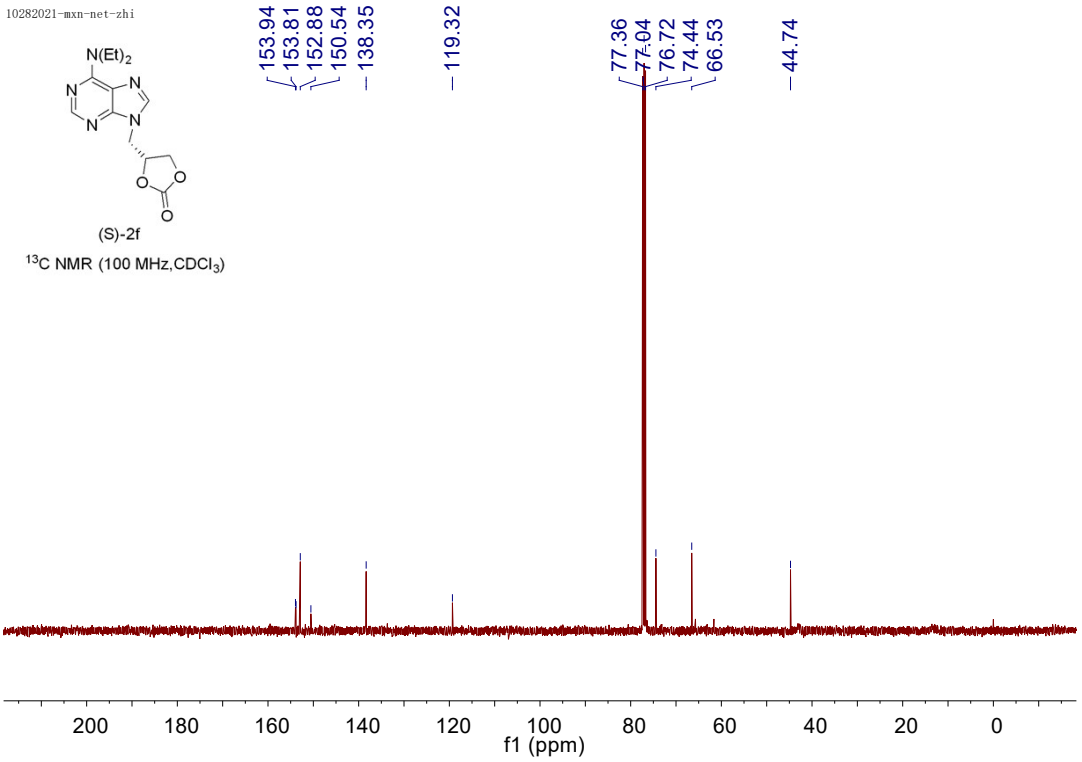
^{1}H NMR (400 MHz,$CDCl_3$)

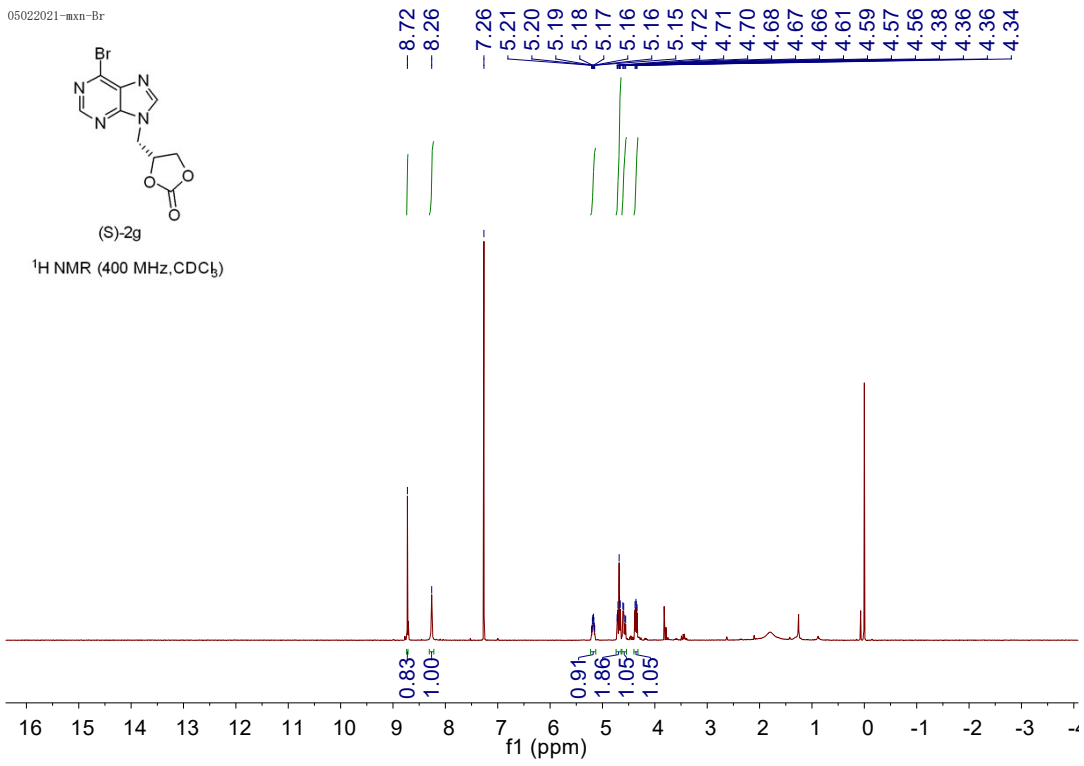


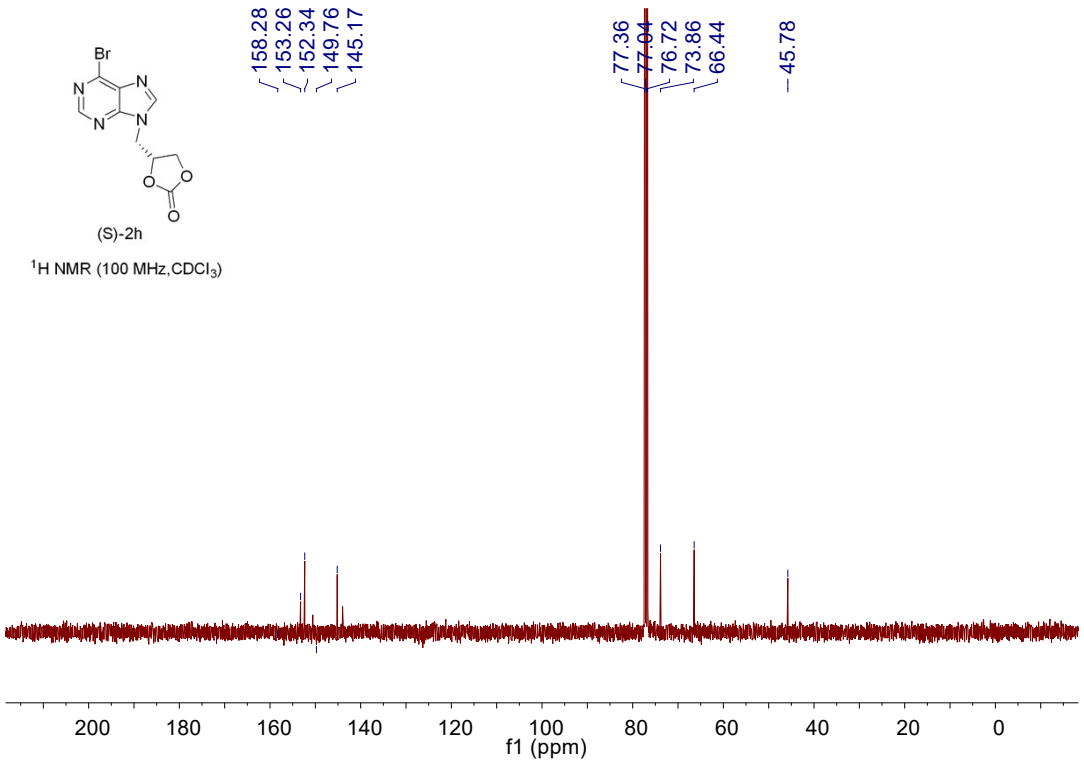
10282021-mxn-net-zhi

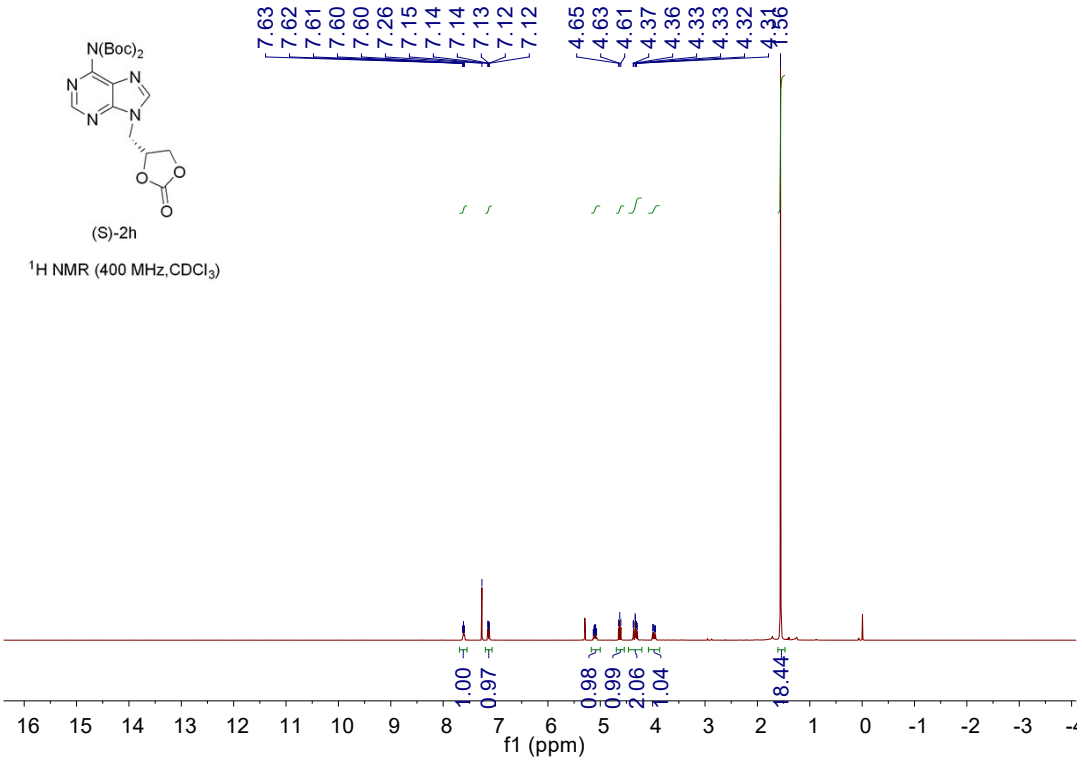
(S)-2f

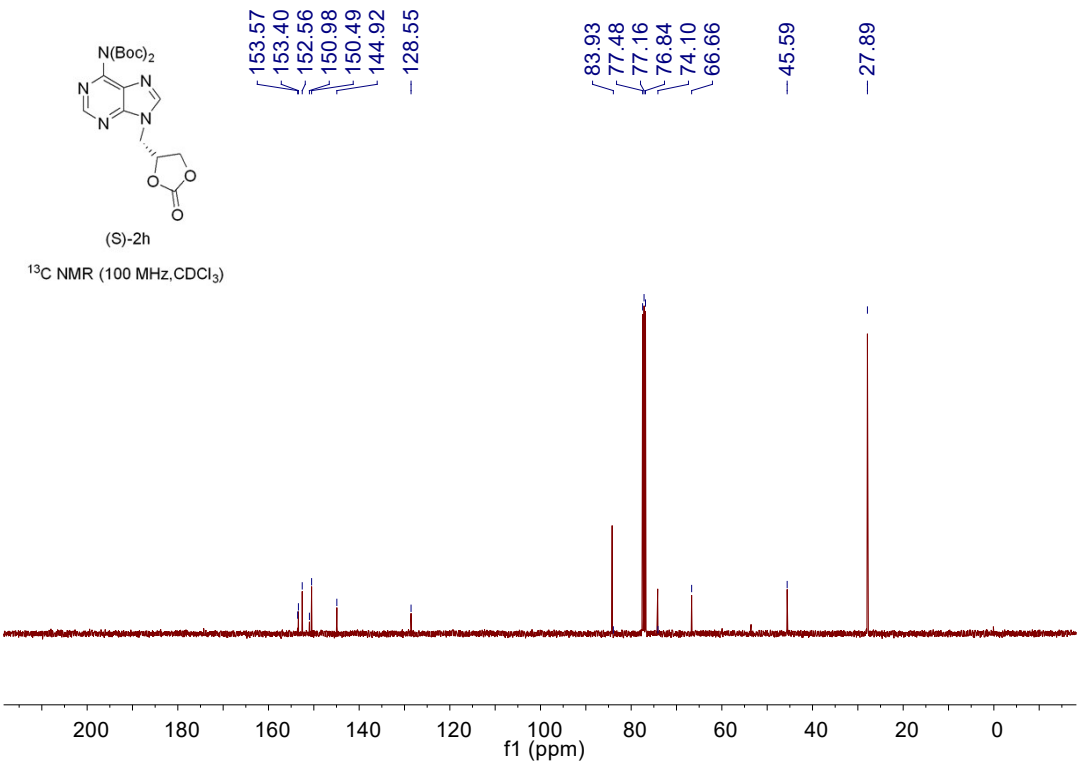
^{13}C NMR (100 MHz,$CDCl_3$)

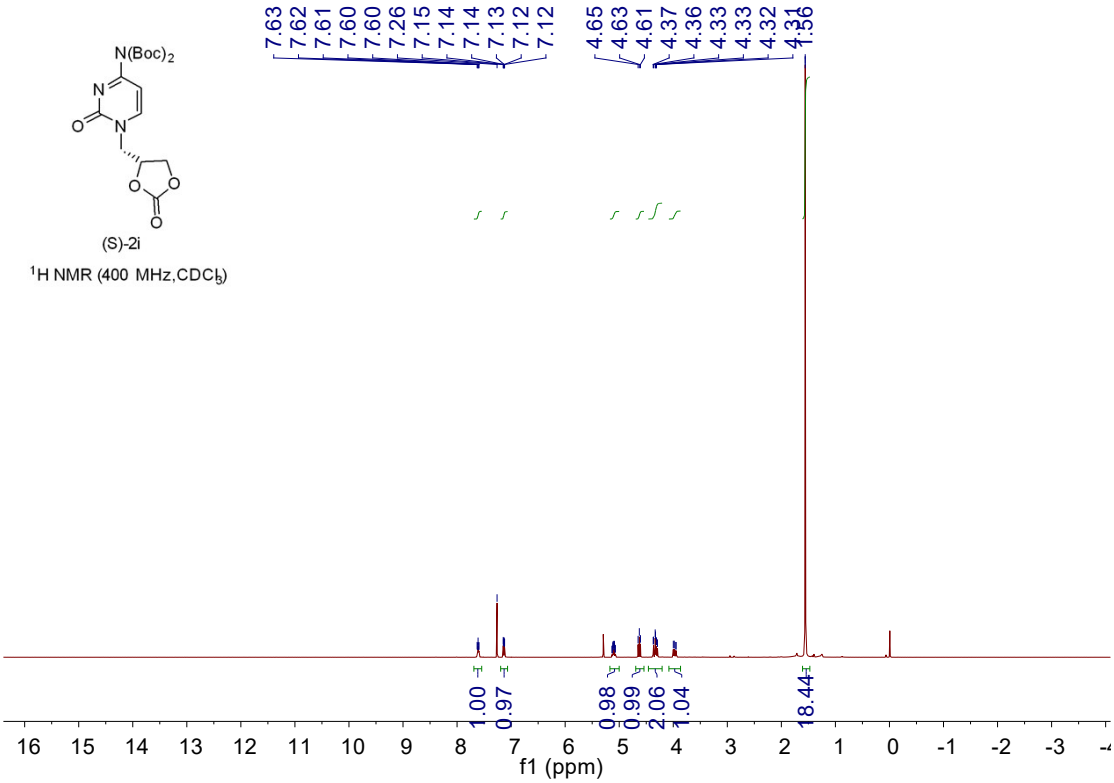


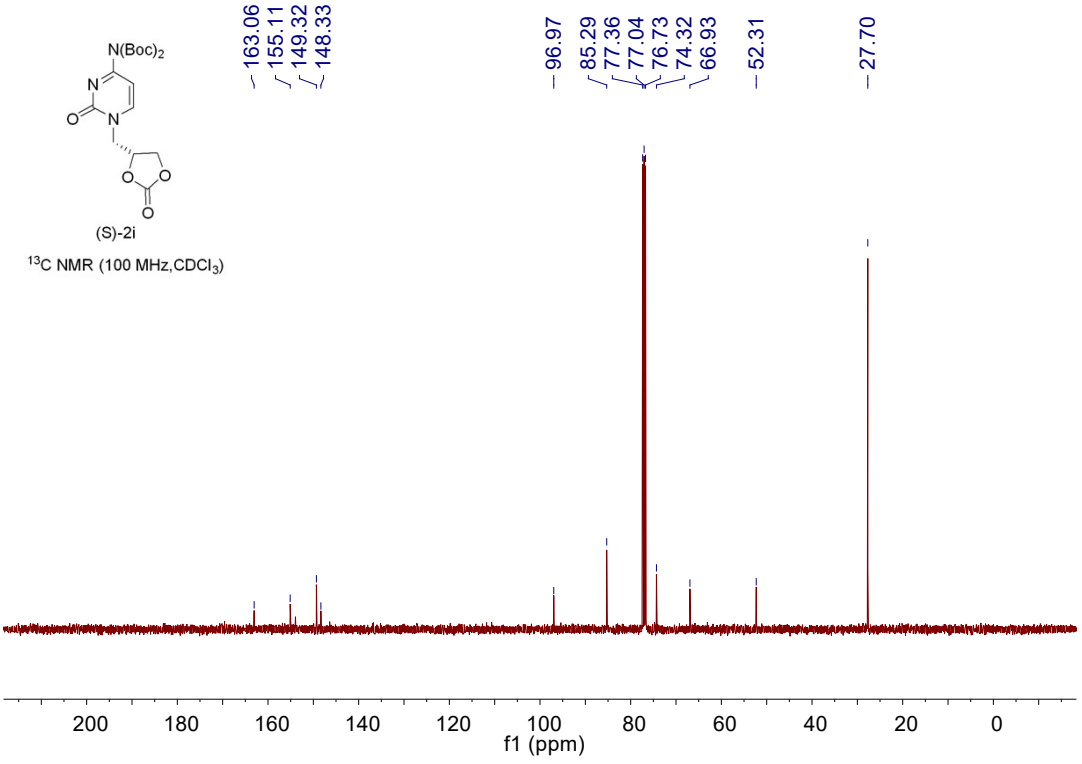

05022021-mxn-Br
Br
N
N
N
N
O
O
O
(S)-2g
1H NMR (400 MHz,CDCl3)
8.72
8.26
7.26
5.21
5.20
5.19
5.18
5.17
5.16
5.16
5.15
4.72
4.71
4.70
4.68
4.67
4.66
4.61
4.59
4.57
4.56
4.38
4.36
4.36
4.34
0.83
1.00
0.91
1.86
1.05
1.05
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

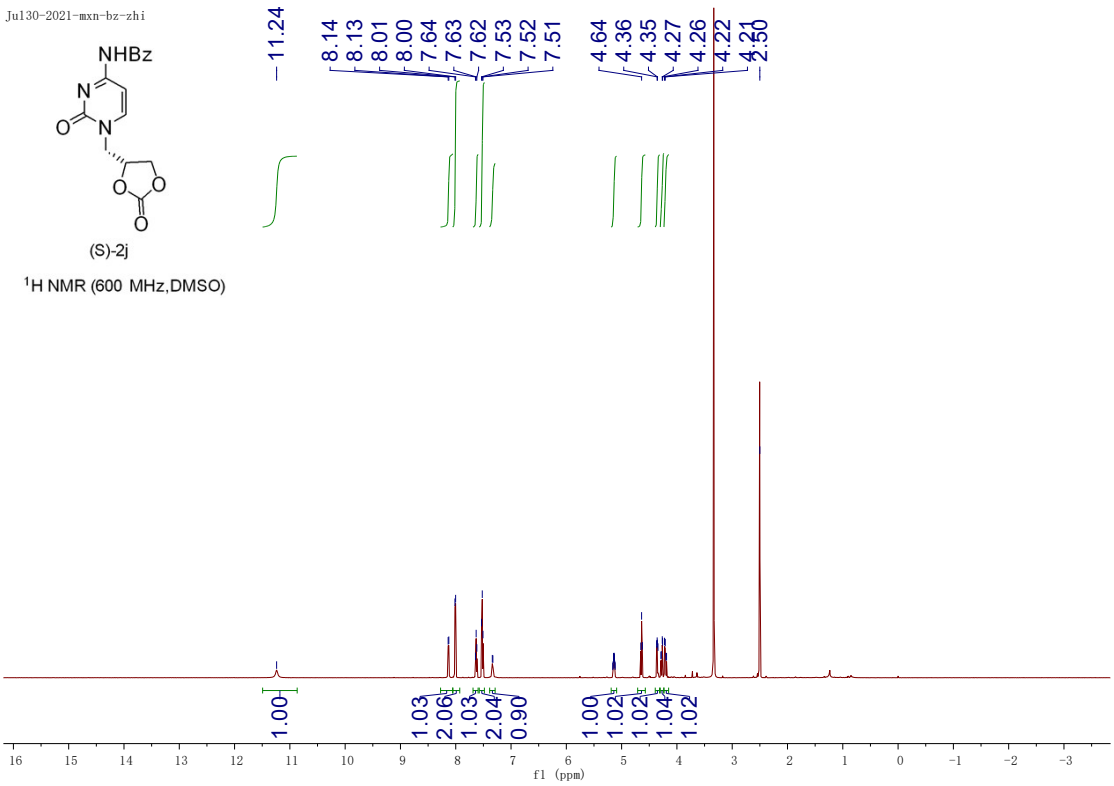

Br
N
N
N
N
O
O
O
(S)-2h
1H NMR (100 MHz,CDCl3)
158.28
153.26
152.34
149.76
145.17
77.36
77.04
76.72
73.86
66.44
45.78
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

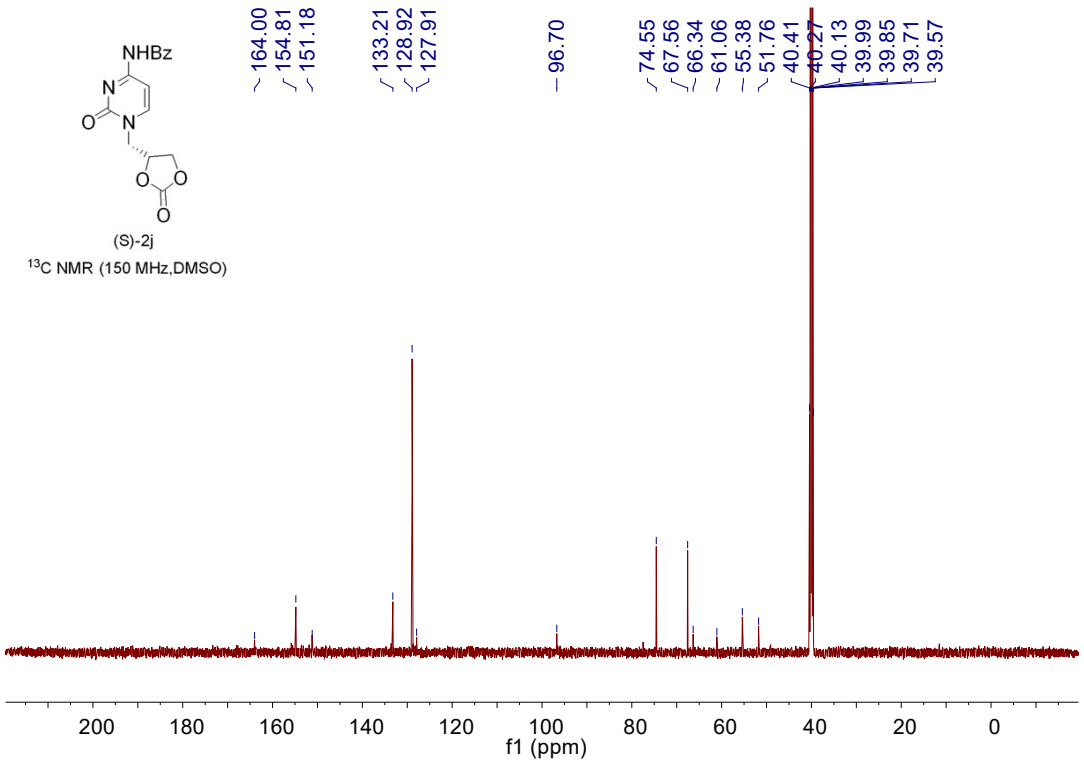

N(Boc)2
(S)-2h
1H NMR (400 MHz,CDCl3)
7.63
7.62
7.61
7.60
7.60
7.26
7.15
7.14
7.14
7.13
7.12
7.12
4.65
4.63
4.61
4.37
4.36
4.33
4.33
4.32
4.31
1.56
1.00
0.97
0.98
0.99
2.06
1.04
18.44
f1 (ppm)

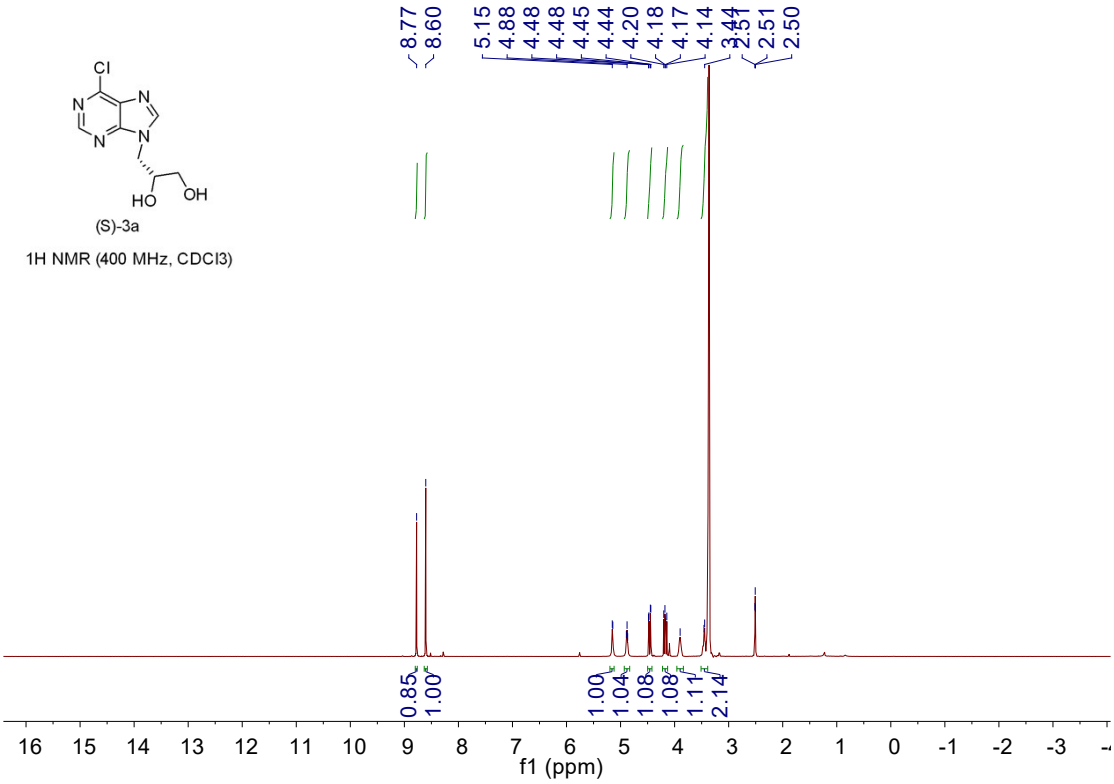

N(Boc)2
(S)-2h
13C NMR (100 MHz,CDCl3)
153.57
153.40
152.56
150.98
150.49
144.92
128.55
83.93
77.48
77.16
76.84
74.10
66.66
45.59
27.89
f1 (ppm)

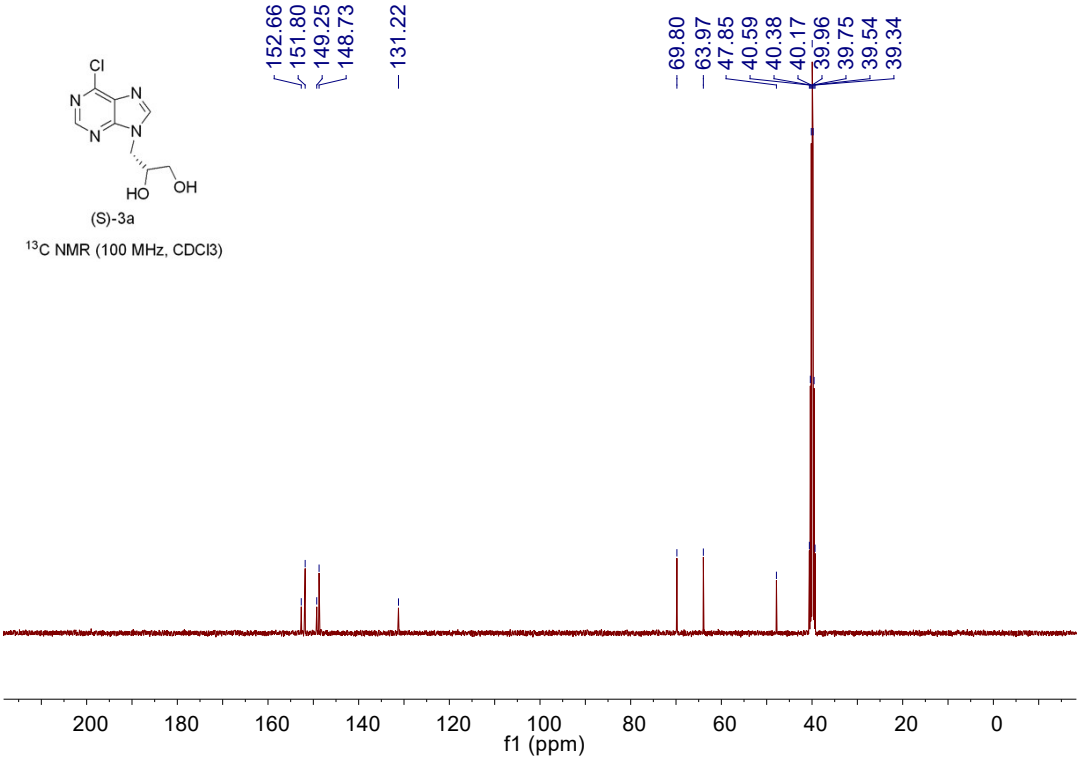

N(Boc)2
(S)-2i
1H NMR (400 MHz,CDCl3)
7.63
7.62
7.61
7.60
7.60
7.26
7.15
7.14
7.14
7.13
7.12
7.12
4.65
4.63
4.61
4.37
4.36
4.33
4.33
4.32
4.31
4.30
1.00
0.97
0.98
0.99
2.06
1.04
18.44
f1 (ppm)

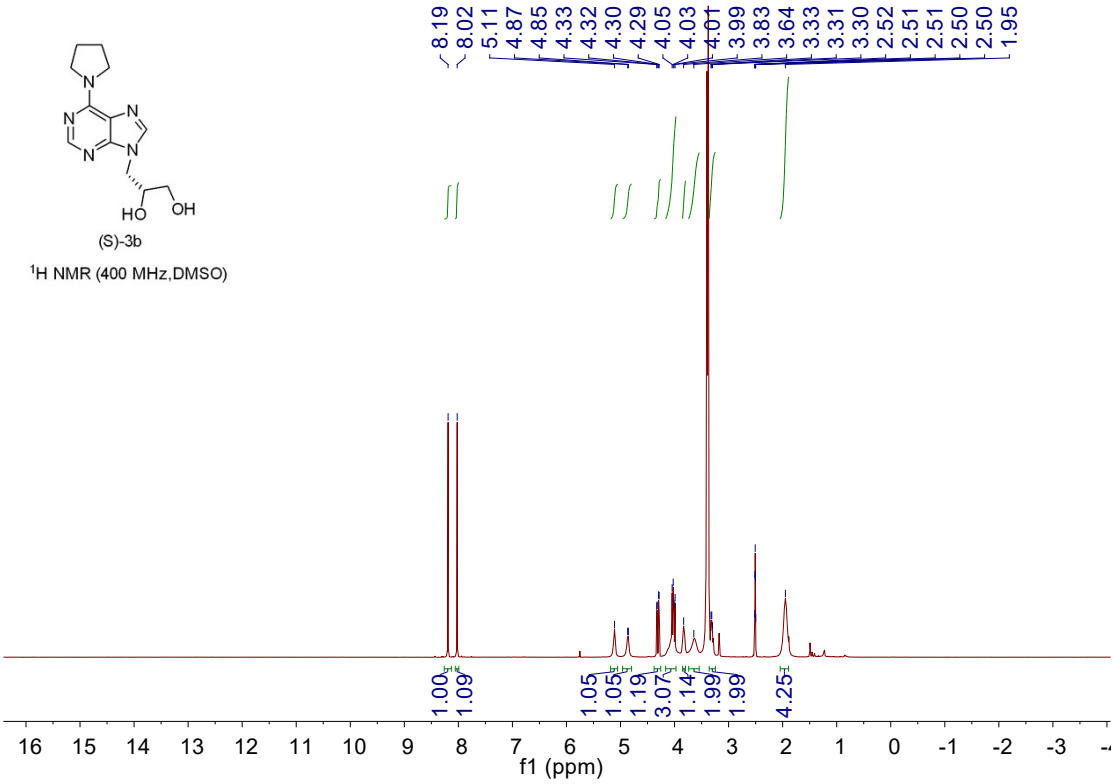

N(Boc)2
(S)-2i
13C NMR (100 MHz,CDCl3)
163.06
155.11
149.32
148.33
96.97
85.29
77.36
77.04
76.73
74.32
66.93
52.31
27.70
f1 (ppm)

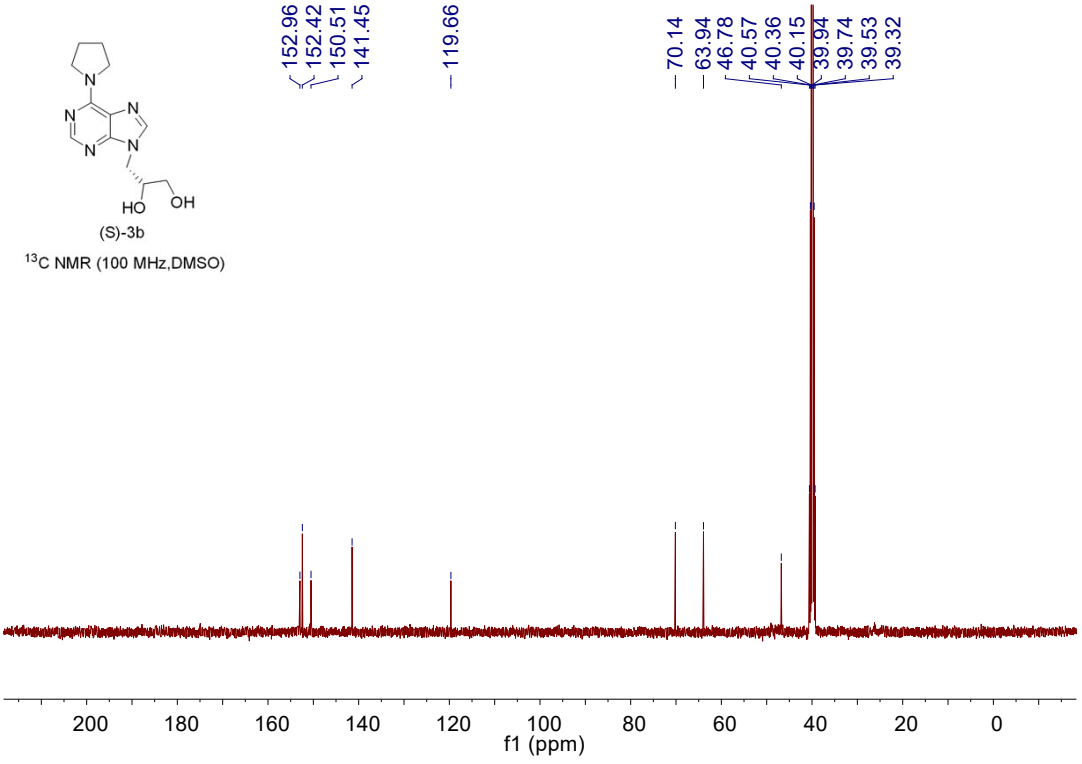

Ju130-2021-mxn-bz-zhi
NHBz
(S)-2j
1H NMR (600 MHz,DMSO)
11.24
8.14
8.13
8.01
8.00
7.64
7.63
7.62
7.53
7.52
7.51
4.64
4.36
4.35
4.27
4.26
4.22
4.21
2.50
1.00
1.03
2.06
1.03
2.04
0.90
1.00
1.02
1.02
1.04
1.02
f1 (ppm)

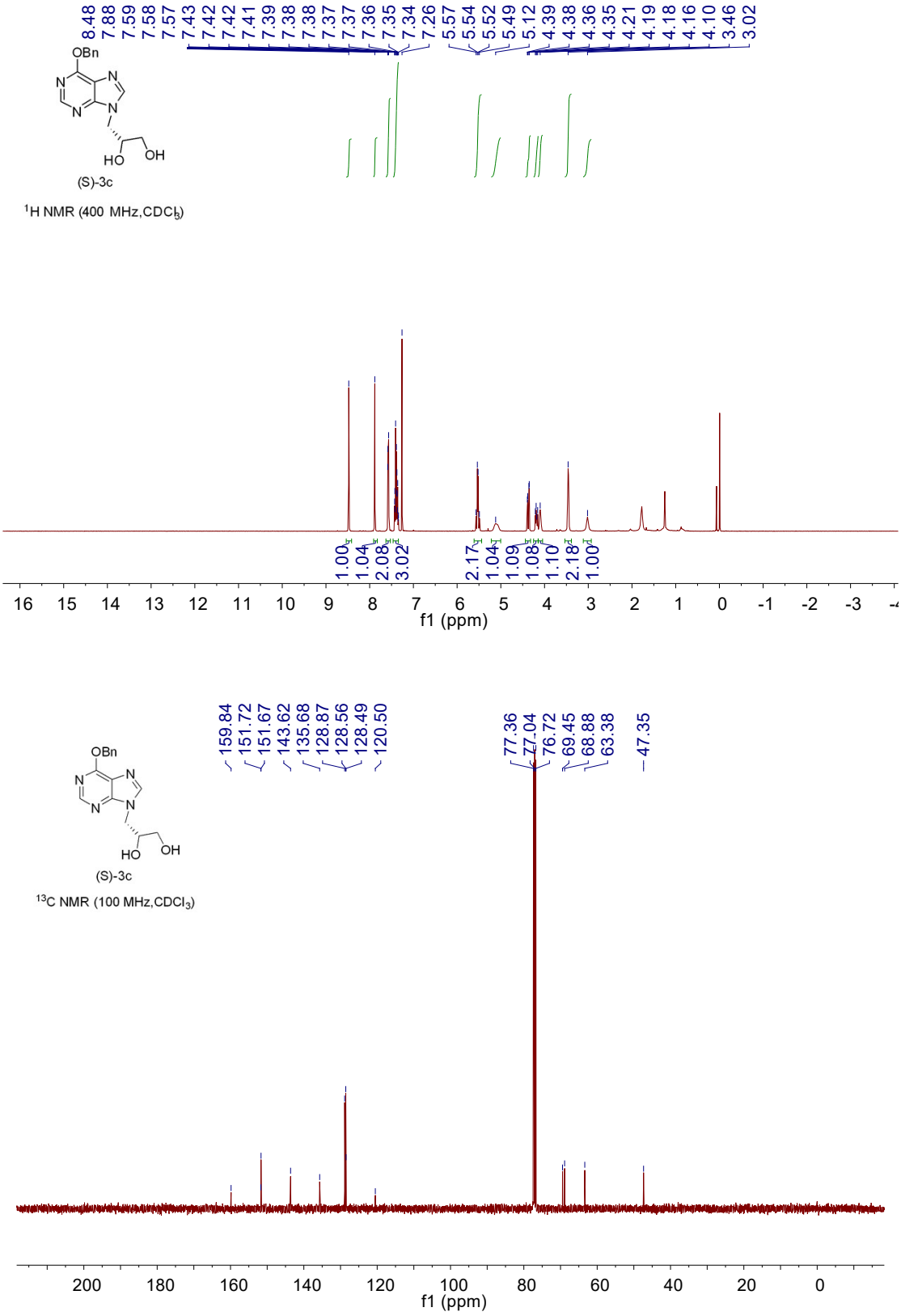

NHBz
(S)-2j
13C NMR (150 MHz,DMSO)
164.00
154.81
151.18
133.21
128.92
127.91
96.70
74.55
67.56
66.34
61.06
55.38
51.76
40.41
40.27
40.13
39.99
39.85
39.71
39.57
f1 (ppm)

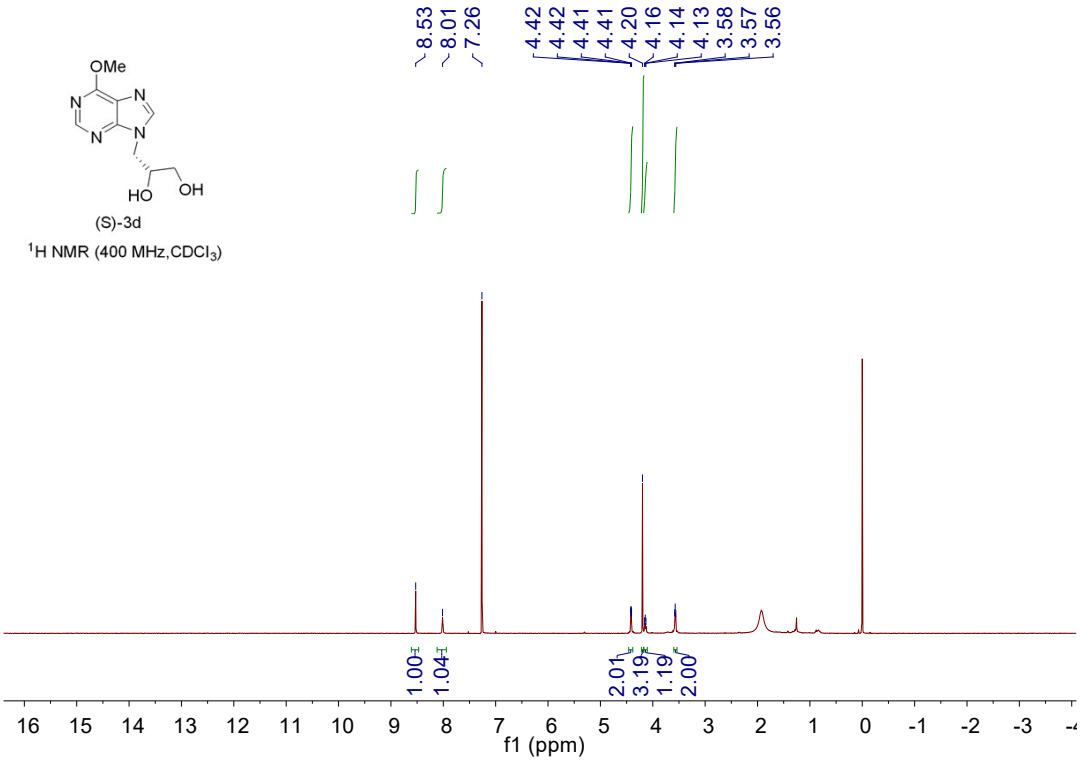

Cl
N
N
N
N
HO
OH
(S)-3a
1H NMR (400 MHz, CDCl3)
8.77
8.60
5.15
4.88
4.48
4.48
4.45
4.44
4.20
4.18
4.17
4.14
3.44
2.51
2.50
0.85
1.00
1.00
1.04
1.08
1.08
1.11
2.14
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

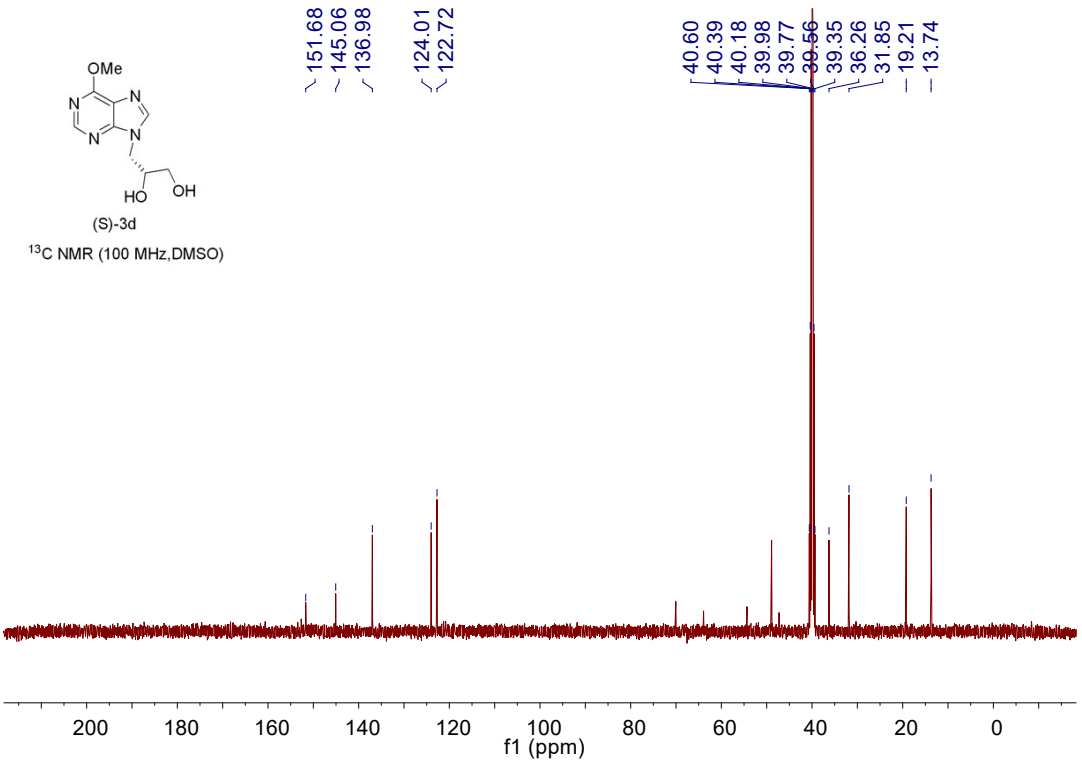

Cl
N
N
N
N
HO
OH
(S)-3a
13C NMR (100 MHz, CDCl3)
152.66
151.80
149.25
148.73
131.22
69.80
63.97
47.85
40.59
40.38
40.17
39.96
39.75
39.54
39.34
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

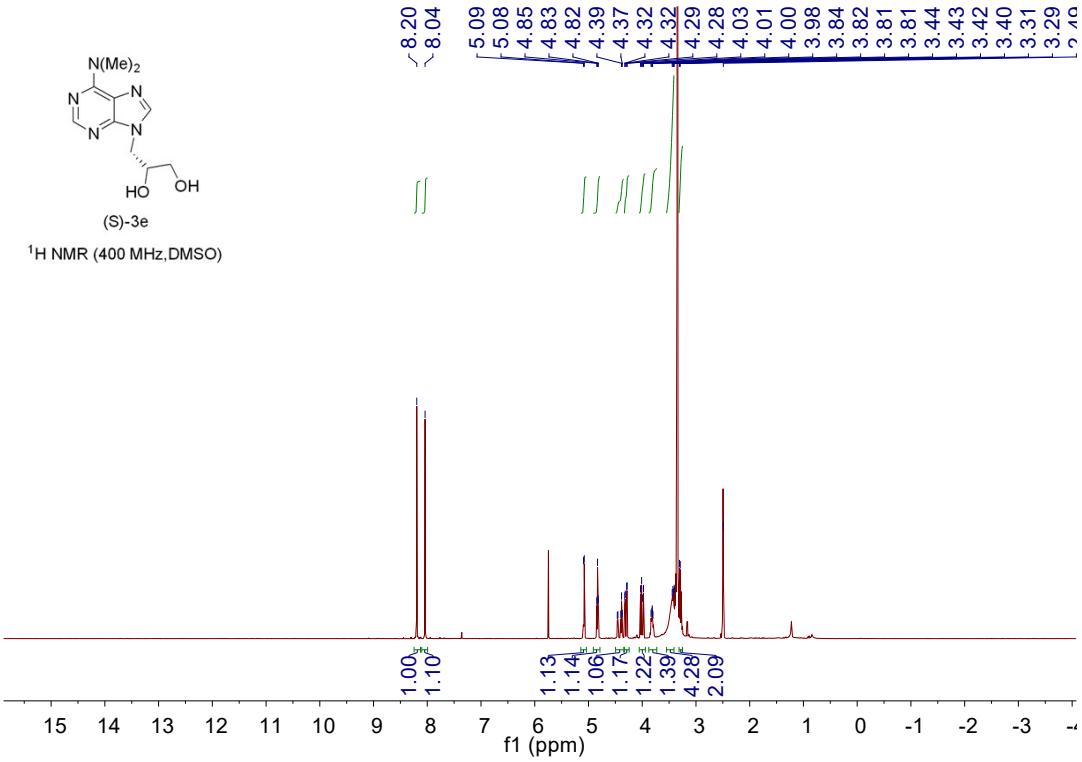

(S)-3b
1H NMR (400 MHz,DMSO)
8.19
8.02
5.11
4.87
4.85
4.33
4.32
4.30
4.29
4.05
4.03
4.01
3.99
3.83
3.64
3.33
3.31
3.30
2.52
2.51
2.51
2.50
2.50
1.95
1.00
1.09
1.05
1.05
1.19
3.07
1.14
1.99
1.99
4.25
f1 (ppm)

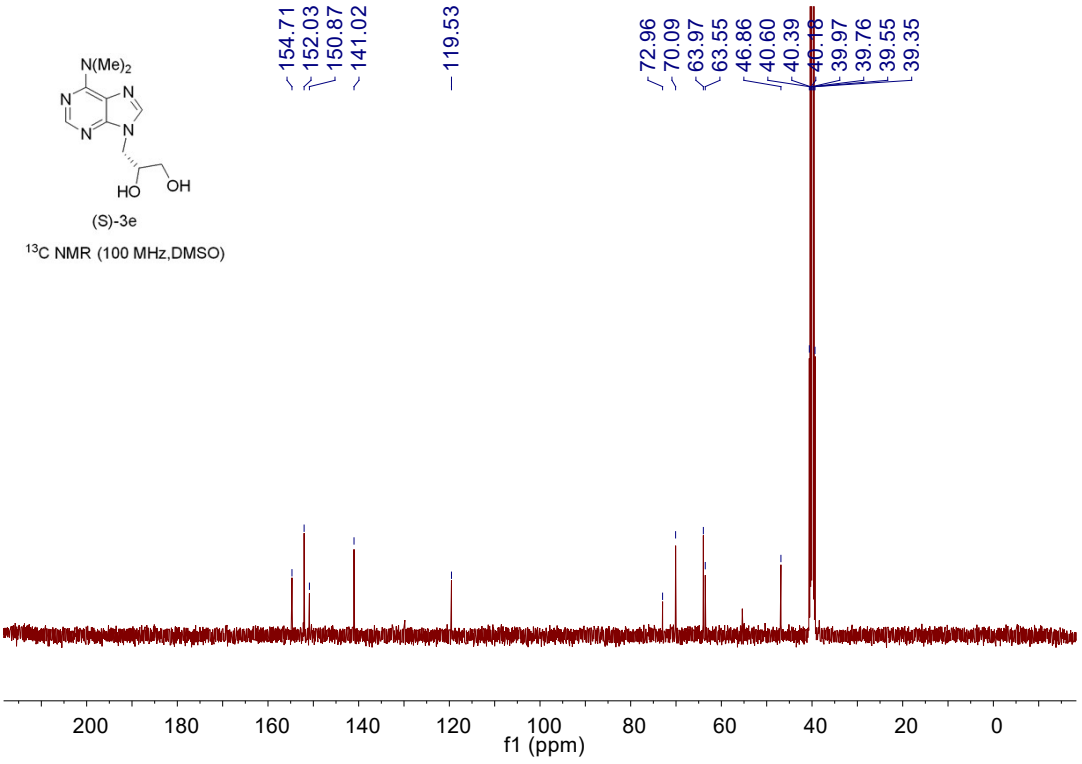

(S)-3b
13C NMR (100 MHz,DMSO)
152.96
152.42
150.51
141.45
119.66
70.14
63.94
46.78
40.57
40.36
40.15
39.94
39.74
39.53
39.32
f1 (ppm)

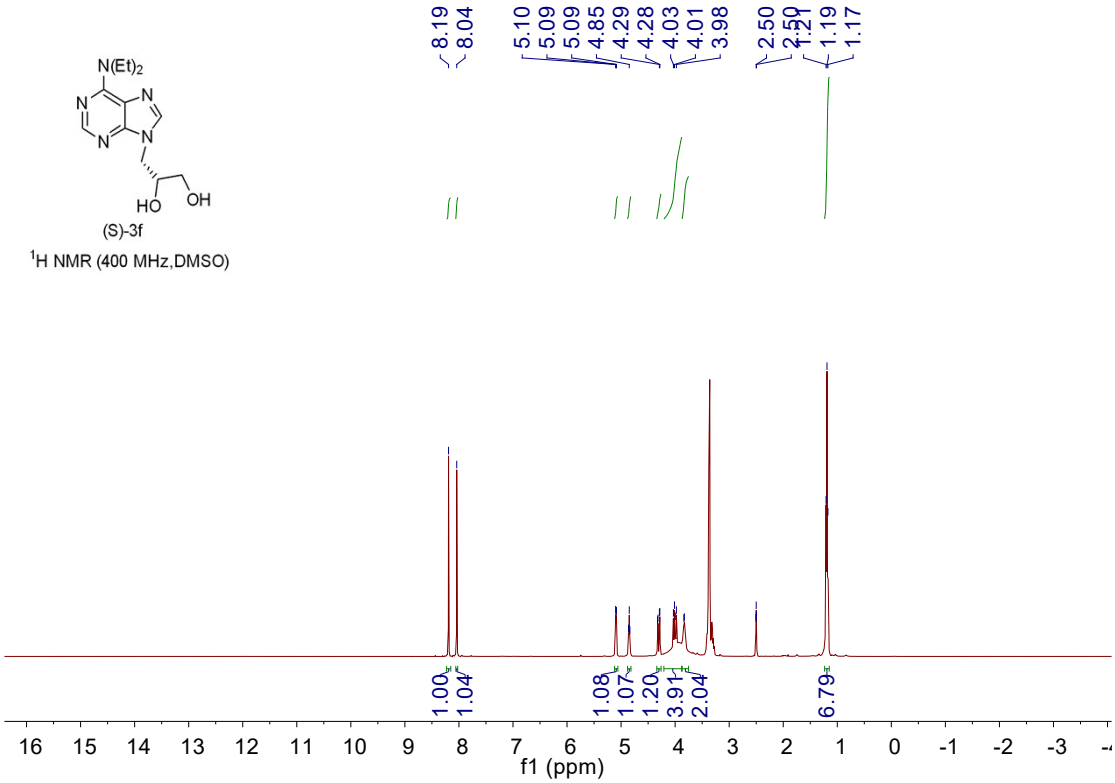

8.48
7.88
7.59
7.58
7.57
7.43
7.42
7.42
7.41
7.39
7.38
7.38
7.37
7.37
7.36
7.35
7.34
7.26
5.57
5.54
5.52
5.49
5.12
4.39
4.38
4.36
4.35
4.21
4.19
4.18
4.16
4.10
3.46
3.02
OBn
N
N
N
N
HO
OH
(S)-3c
1H NMR (400 MHz,CDCl3)
1.00
1.04
2.08
3.02
2.17
1.04
1.09
1.08
1.10
2.18
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)
159.84
151.72
151.67
143.62
135.68
128.87
128.56
128.49
120.50
77.36
77.04
76.72
69.45
68.88
63.38
47.35
OBn
N
N
N
N
HO
OH
(S)-3c
13C NMR (100 MHz,CDCl3)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

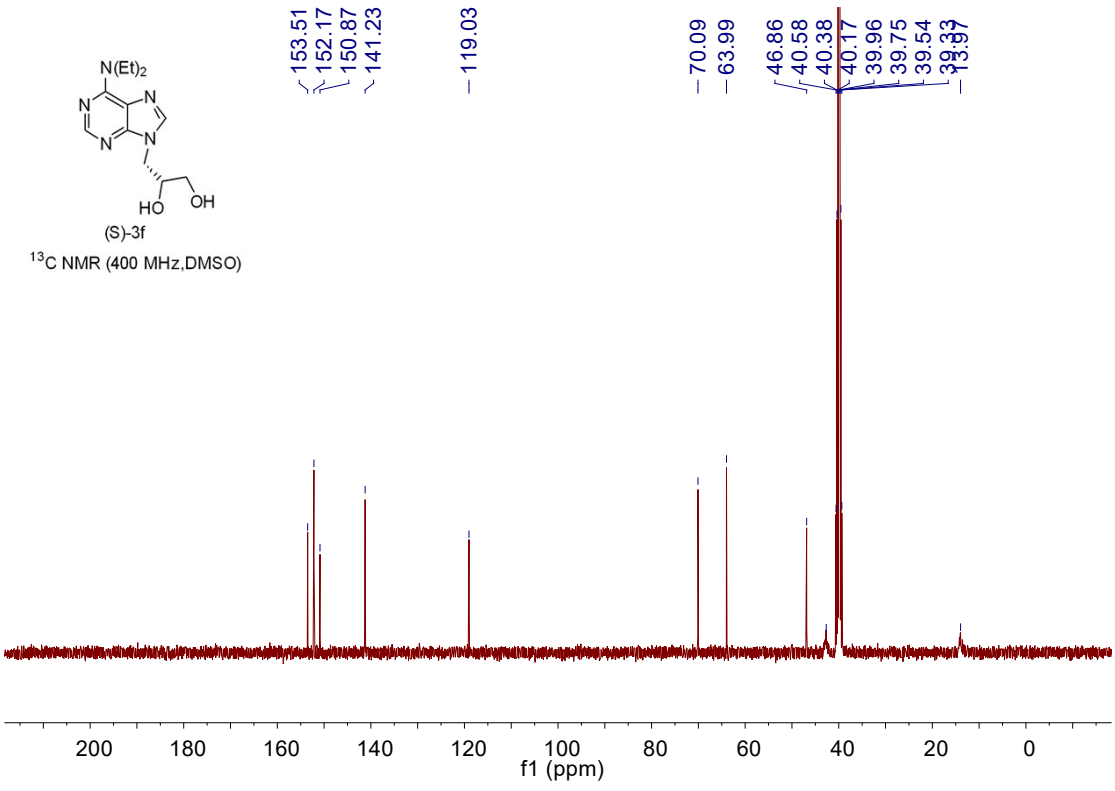

8.53
8.01
7.26
4.42
4.42
4.41
4.41
4.20
4.16
4.14
4.13
3.58
3.57
3.56
OMe
N
N
N
N
HO
OH
(S)-3d
1H NMR (400 MHz,CDCl3)
1.00
1.04
2.01
3.19
1.19
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

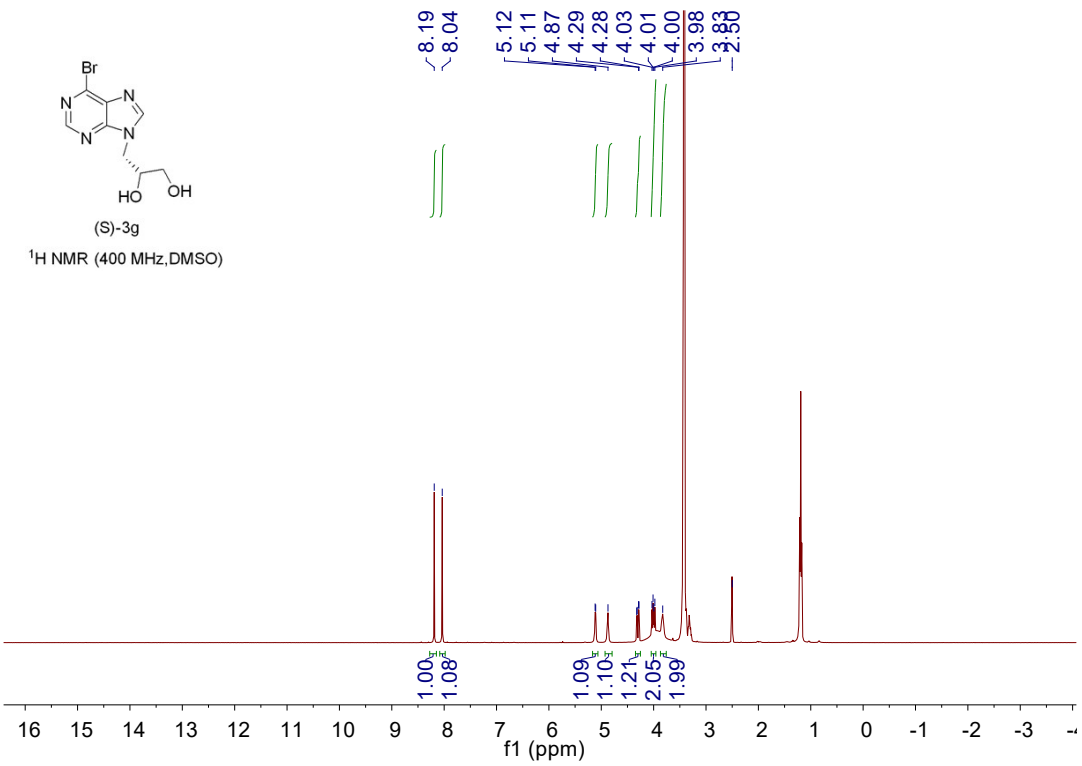

151.68
145.06
136.98
124.01
122.72
40.60
40.39
40.18
39.98
39.77
39.56
39.35
36.26
31.85
19.21
13.74
OMe
N
N
N
N
HO
OH
(S)-3d
13C NMR (100 MHz,DMSO)
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

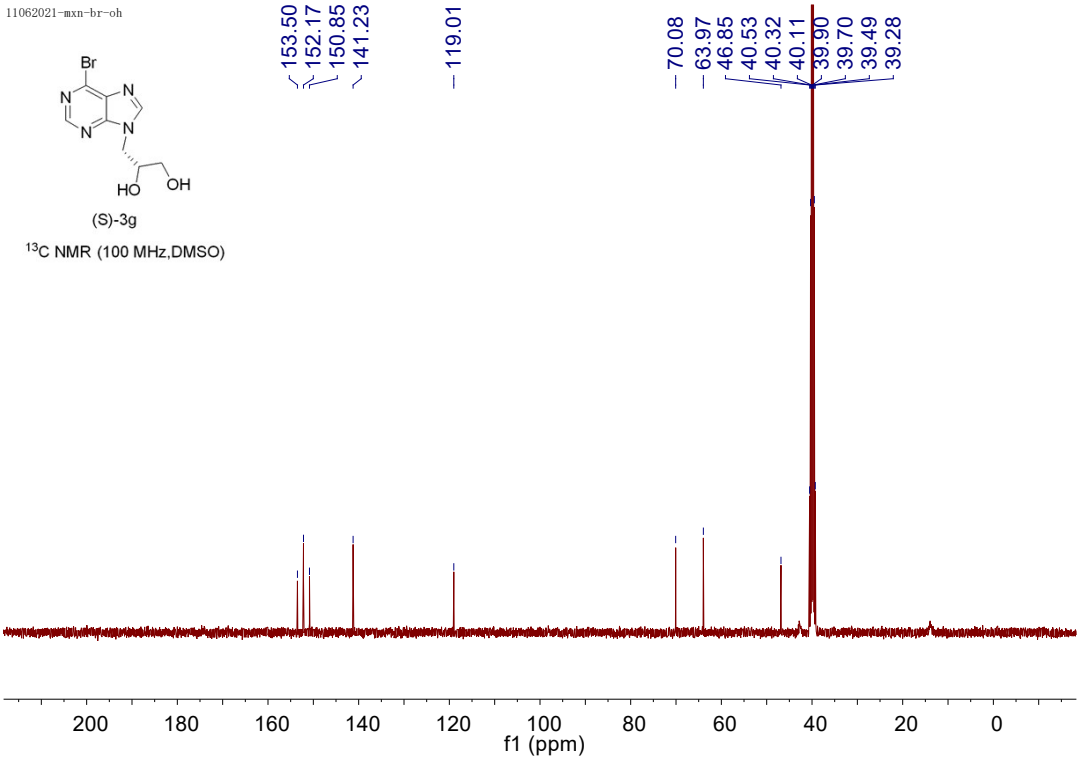

N(Me)2
HO
OH
(S)-3e
1H NMR (400 MHz,DMSO)
8.20
8.04
5.09
5.08
4.85
4.83
4.82
4.39
4.37
4.32
4.32
4.29
4.28
4.03
4.01
4.00
3.98
3.84
3.82
3.81
3.81
3.44
3.43
3.42
3.40
3.31
3.29
1.00
1.10
1.13
1.14
1.06
1.17
1.22
1.39
4.28
2.09
f1 (ppm)

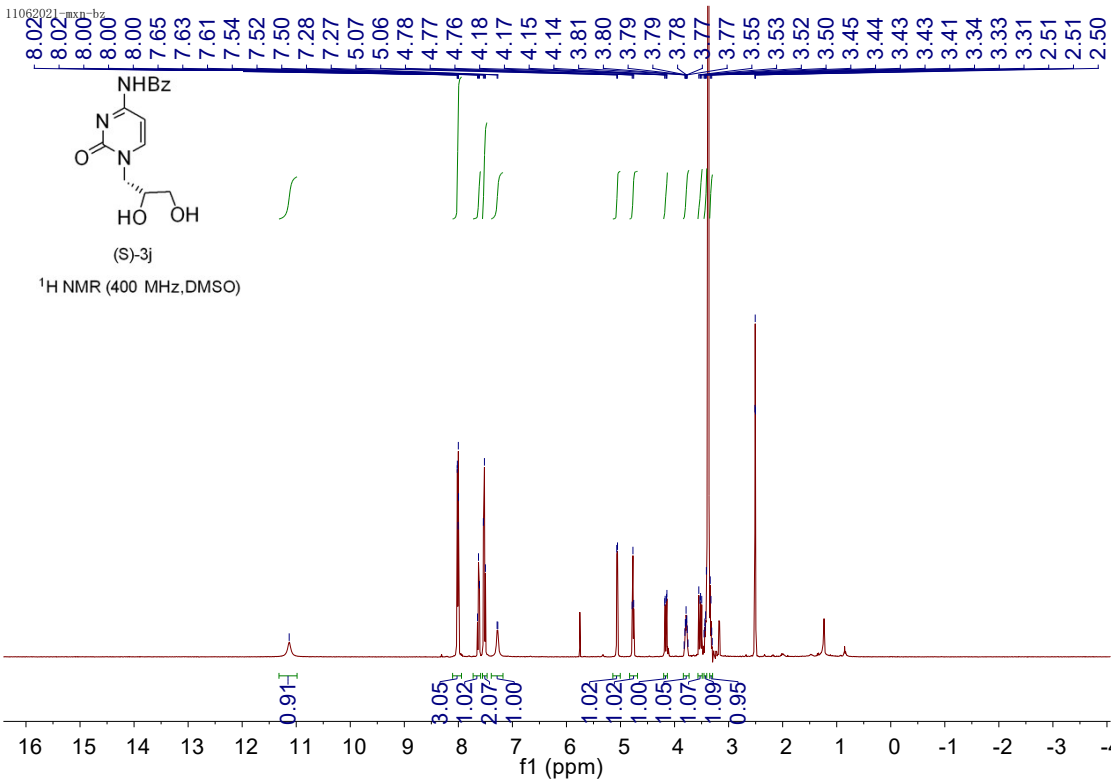

N(Me)2
HO
OH
(S)-3e
13C NMR (100 MHz,DMSO)
154.71
152.03
150.87
141.02
119.53
72.96
70.09
63.97
63.55
46.86
40.60
40.39
40.18
39.97
39.76
39.55
39.35
f1 (ppm)

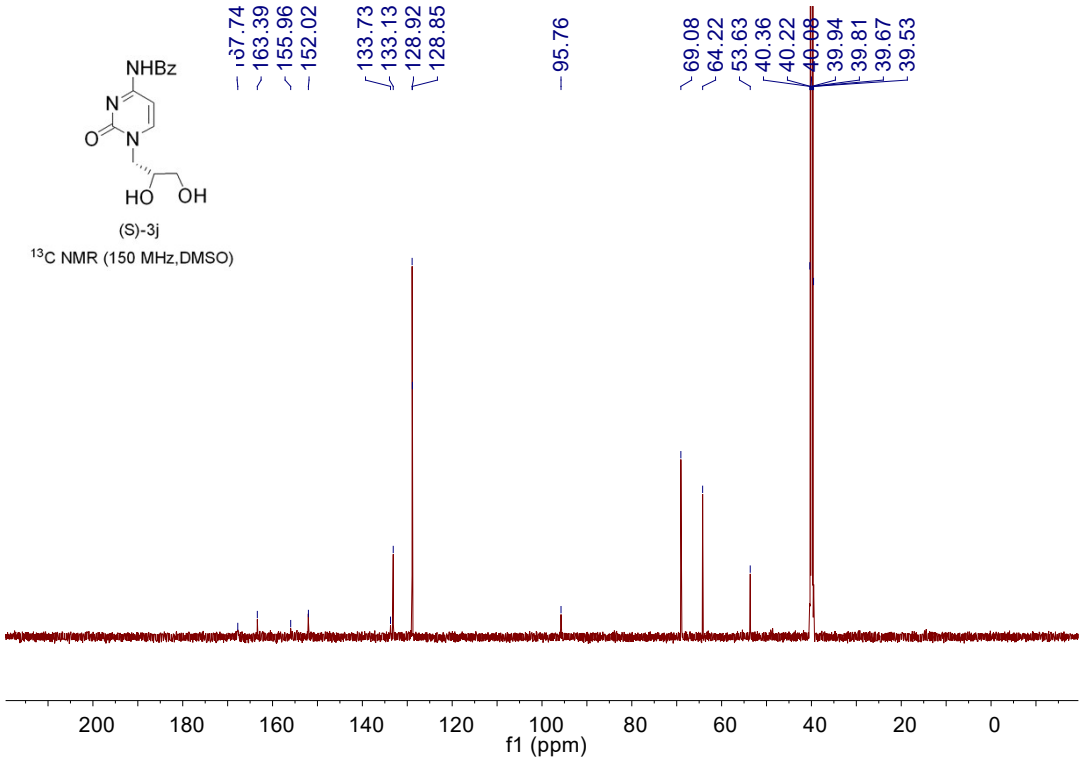

N(Et)2
HO
OH
(S)-3f
1H NMR (400 MHz,DMSO)
8.19
8.04
5.10
5.09
5.09
4.85
4.29
4.28
4.03
4.01
3.98
2.50
1.21
1.19
1.17
1.00
1.04
1.08
1.07
1.20
3.91
2.04
6.79
f1 (ppm)


N(Et)2
HO
OH
(S)-3f
13C NMR (400 MHz,DMSO)
153.51
152.17
150.87
141.23
119.03
70.09
63.99
46.86
40.58
40.38
40.17
39.96
39.75
39.54
39.33
13.97
f1 (ppm)

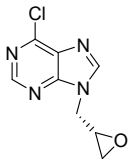

Br
N
N
N
N
HO
OH
(S)-3g
1H NMR (400 MHz,DMSO)
8.19
8.04
5.12
5.11
4.87
4.29
4.28
4.03
4.01
4.00
3.98
3.83
2.50
1.00
1.08
1.09
1.10
1.21
2.05
1.99
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


11062021-mxn-br-oh
Br
N
N
N
N
HO
OH
(S)-3g
13C NMR (100 MHz,DMSO)
153.50
152.17
150.85
141.23
119.01
70.08
63.97
46.85
40.53
40.32
40.11
39.90
39.70
39.49
39.28
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)


NHBz
N
O
N
HO
OH
(S)-3j
1H NMR (400 MHz,DMSO)
f1 (ppm)

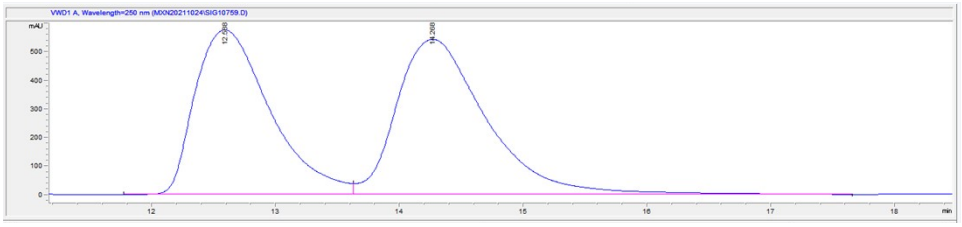

NHBz
N
O
N
HO
OH
(S)-3j
13C NMR (150 MHz,DMSO)
f1 (ppm)

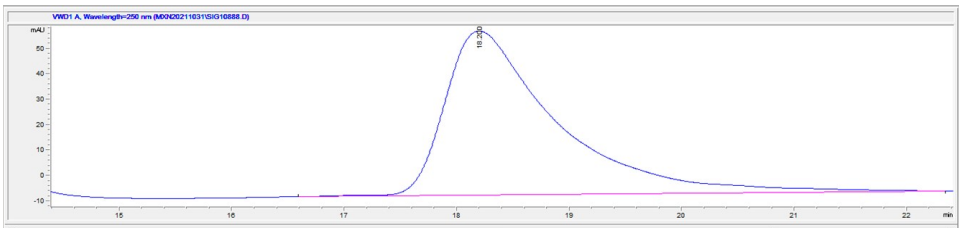
HPLC data

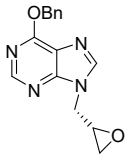


(S)-1a

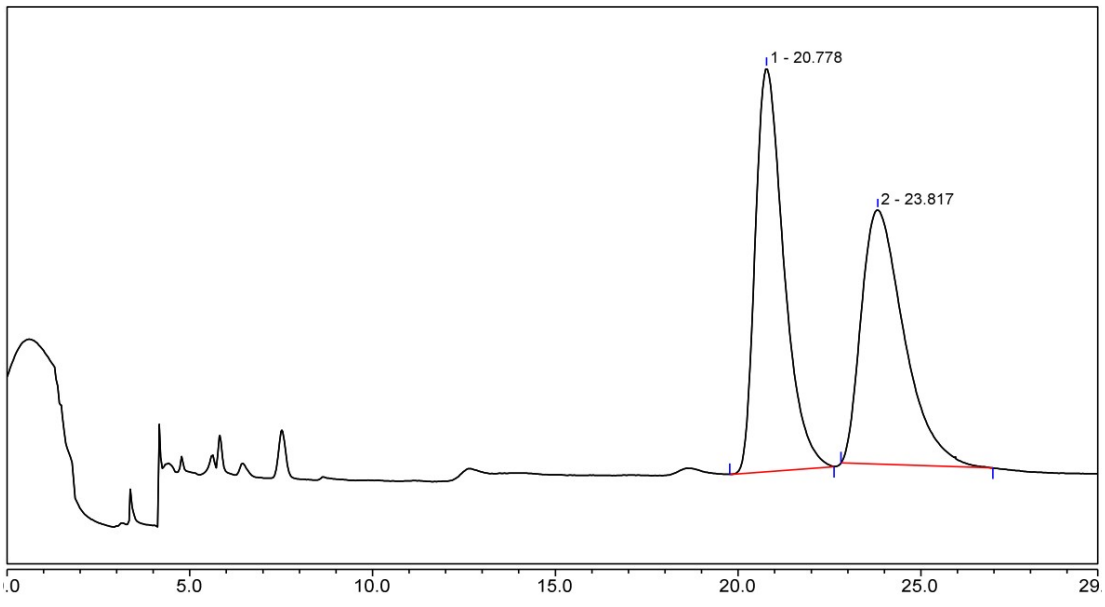
HPLC chromatograms (Daicel chiralpak OD, Hexanes/i-PrOH = 70:30, flow rate = 1 mL/min): 12.5 min (minor), 14.2 min (major), >99% ee



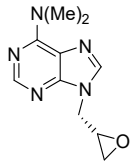




(S)-1c

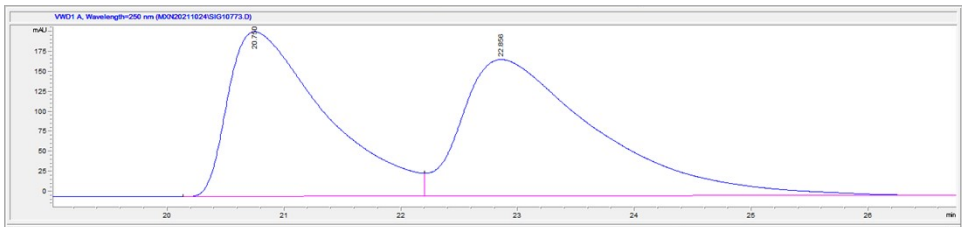


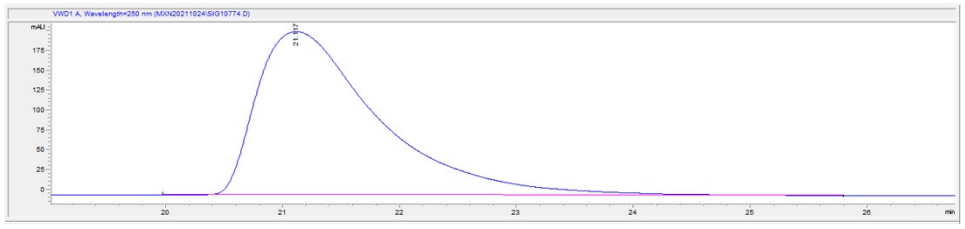
HPLC chromatograms (Daicel chiralpak OD, Hexanes/i-PrOH = 70:30, flow rate = 1 mL/min): 30.3 min (minor), 36.8 min (major), >99% ee

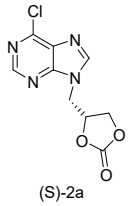


(S)-1e

HPLC chromatograms (Daicel chiralpak OJ, Hexanes/i-PrOH = 85:15, flow rate = 1 mL/min): 20.7 min (minor), 22.8 min (major), >99% ee

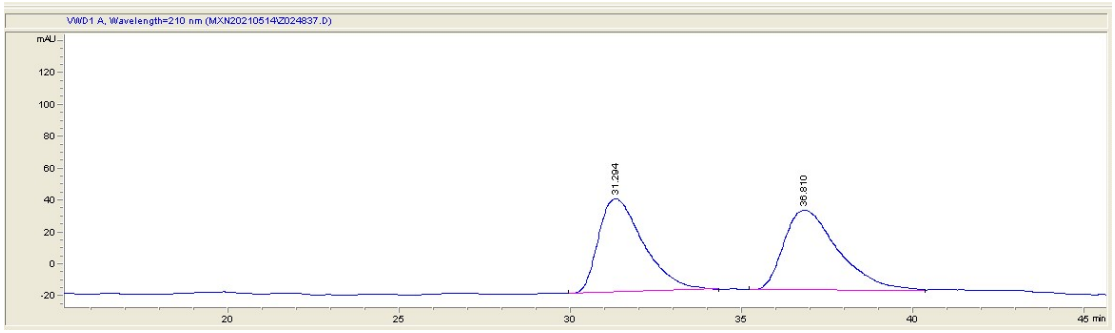


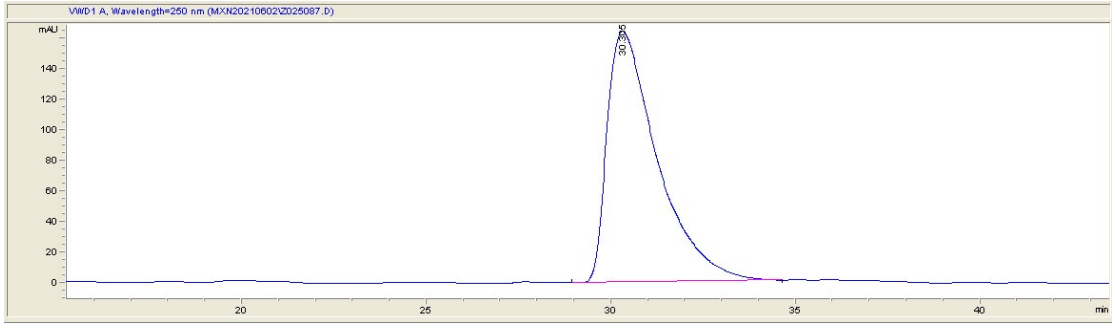


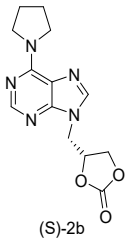


(S)-2a

HPLC chromatograms (Daicel chiralpak OD, Hexanes/i-PrOH = 70:30, flow rate = 1 mL/min): 30.3 min (minor), 36.8 min (major), >99% ee

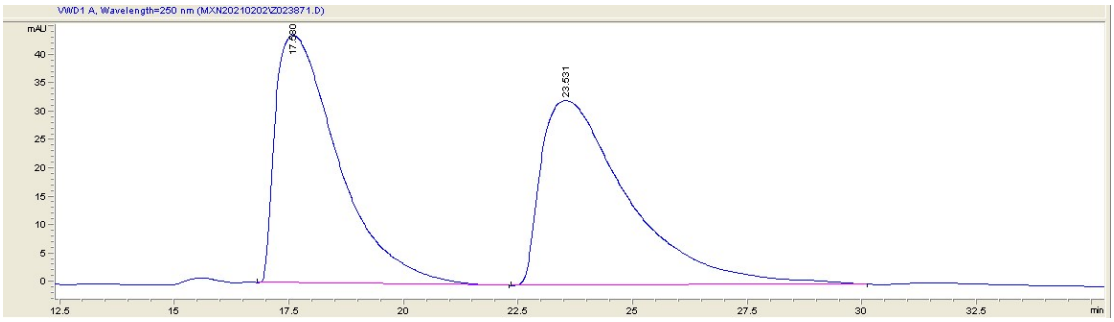


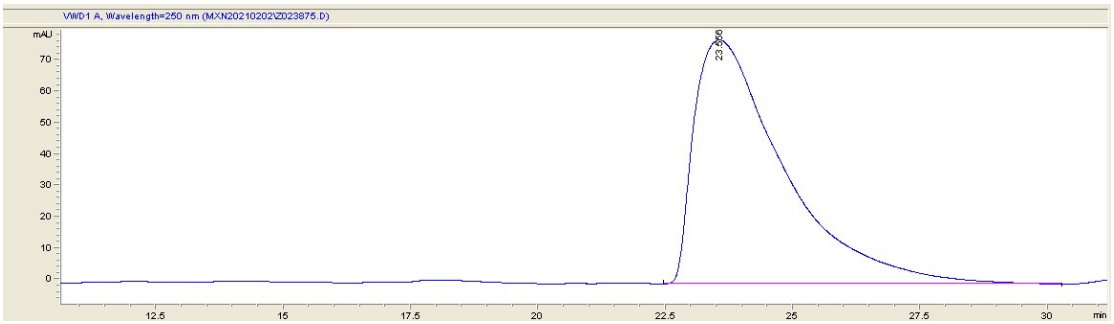


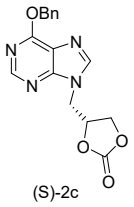


(S)-2b

HPLC chromatograms (Daicel chiralpak AD, Hexanes/i-PrOH = 80:20, flow rate = 0.8 mL/min): 17.5 min (minor), 23.5 min (major), >99% ee

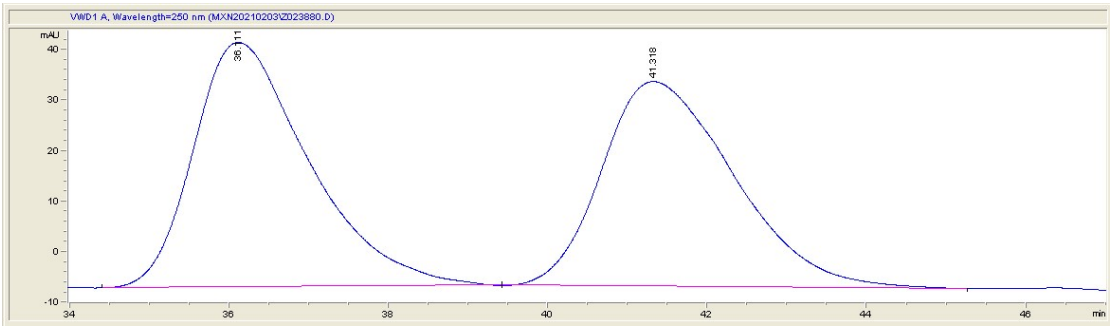


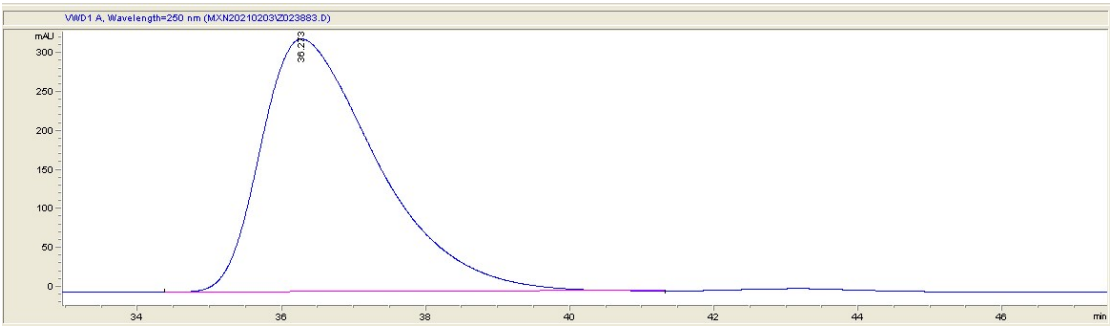


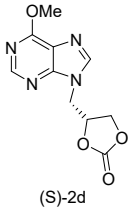


(S)-2c

HPLC chromatograms (Daicel chiralpak OD, Hexanes/i-PrOH = 70:30, flow rate = 1 mL/min): 36.2 min (minor), 41.3 min (major), >99% ee

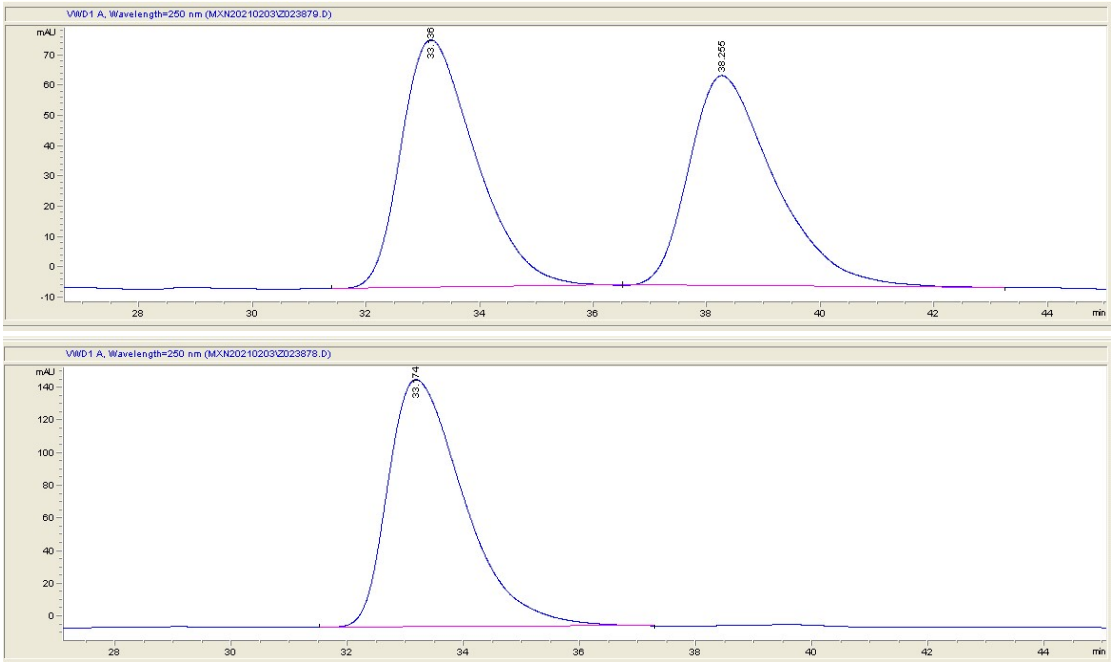


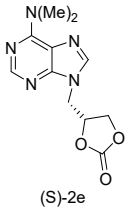




(S)-2d

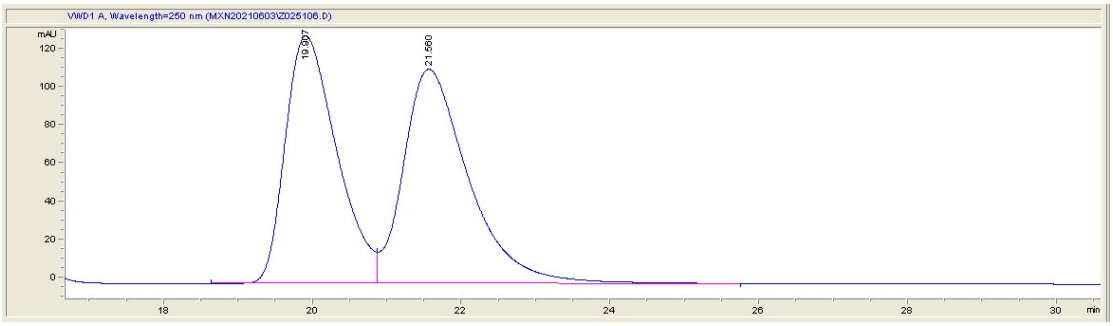
HPLC chromatograms (Daicel chiralpak OD, Hexanes/i-PrOH = 70:30, flow rate = 1 mL/min): 33.1 min (minor), 38.2 min (major), >99% ee

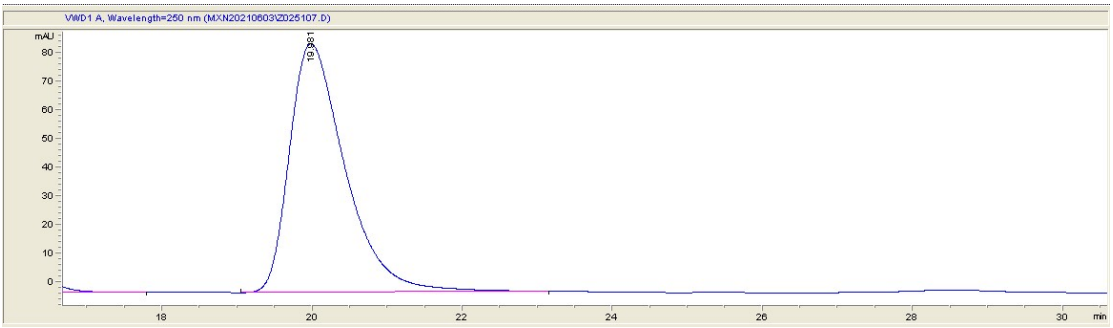


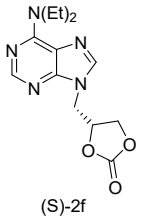


(S)-2e

HPLC chromatograms (Daicel chiralpak OD, Hexanes/i-PrOH = 70:30, flow rate = 1 mL/min): 19.9 min (minor), 21.5 min (major), >99% ee

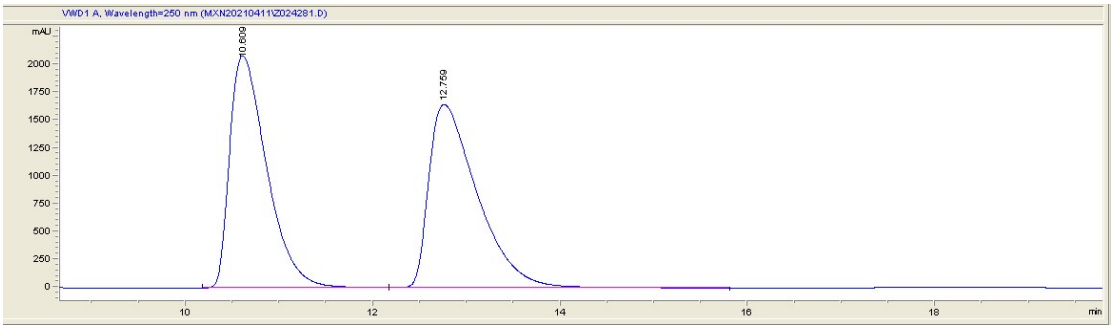


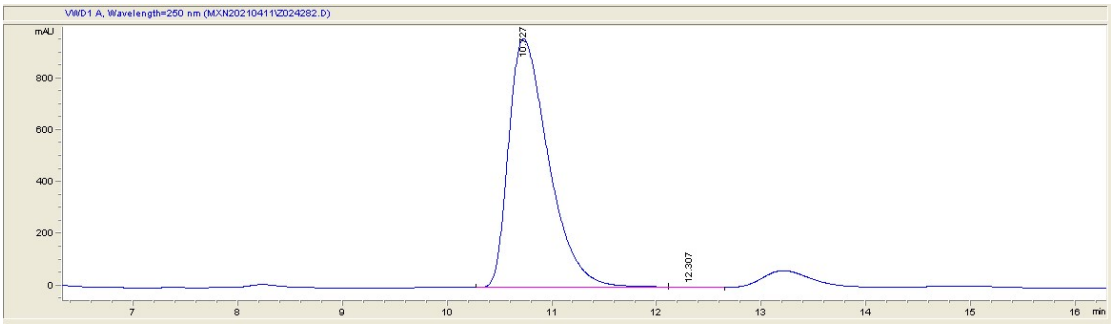


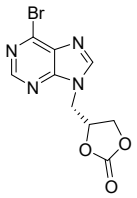


(S)-2f

HPLC chromatograms (Daicel chiralpak OD, Hexanes/i-PrOH = 70:30, flow rate = 1 mL/min): 10.7 min (minor), 12.7 min (major), >99% ee

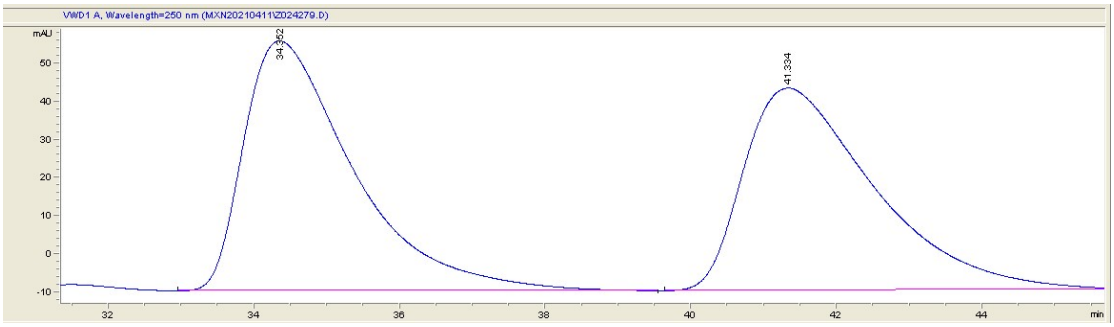


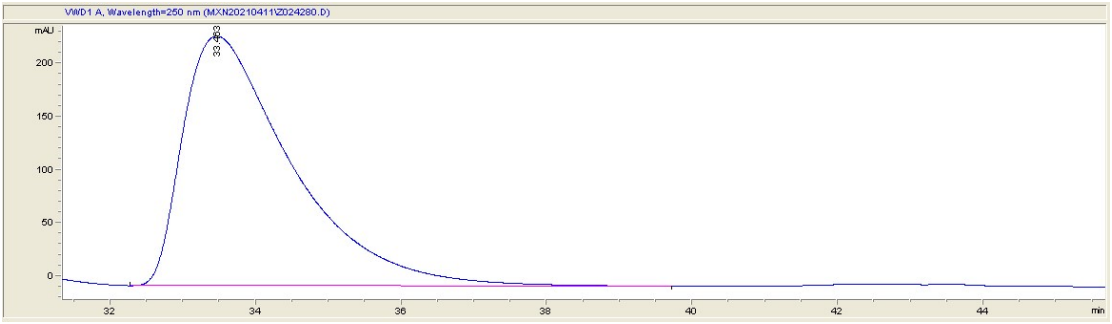


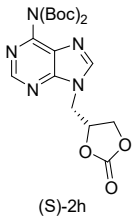


(S)-2g

HPLC chromatograms (Daicel chiralpak OD, Hexanes/i-PrOH = 70:30, flow rate = 1 mL/min): 33.4 min (minor), 41.3 min (major), >99% ee

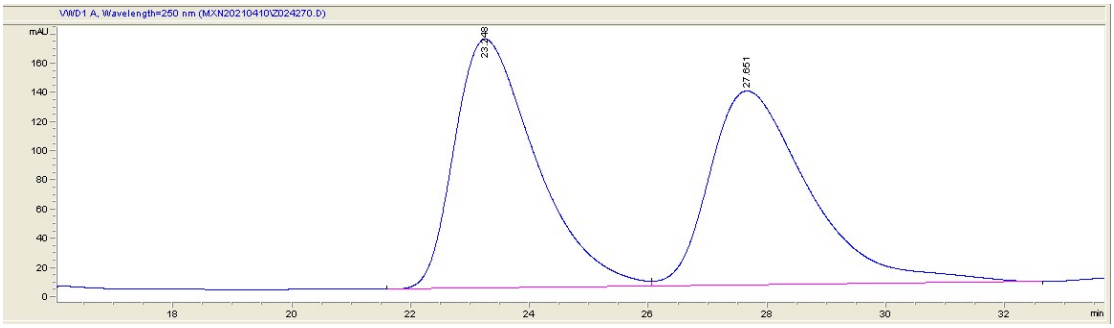


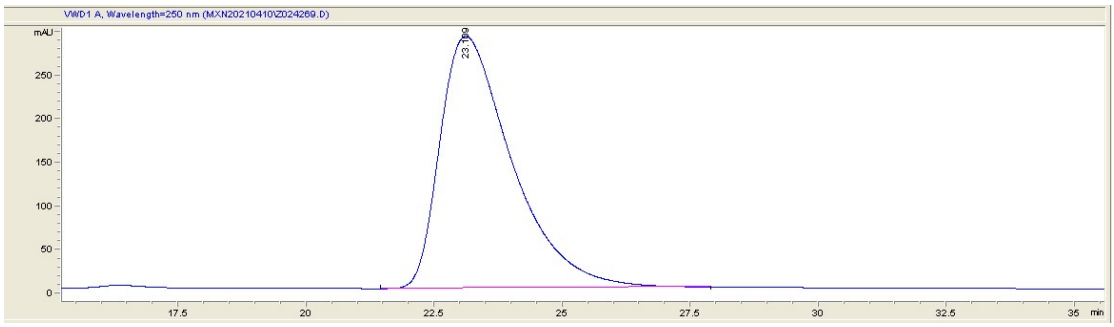


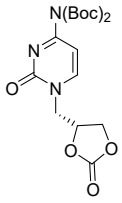


(S)-2h

HPLC chromatograms (Daicel chiralpak OD, Hexanes/i-PrOH = 70:30, flow rate = 0.8 mL/min): 23.1 min (minor), 27.6 min (major), >99% ee

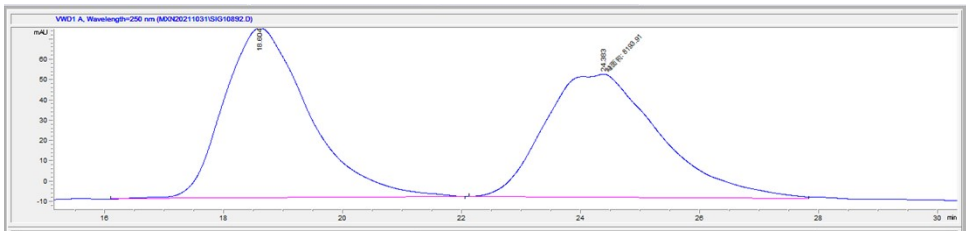


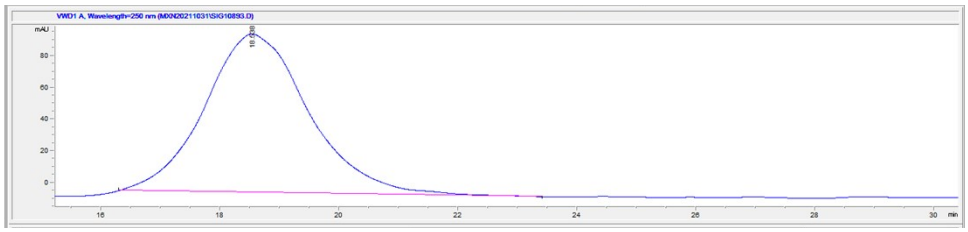


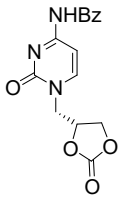


(S)-2i

HPLC chromatograms (Daicel chiralpak AD, Hexanes/i-PrOH = 70:30, flow rate = 1 mL/min): 18.6 min (minor), 24.3min (major), >99% ee

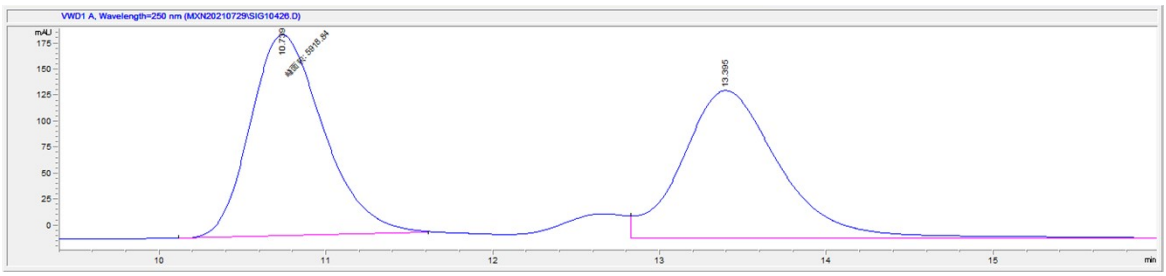


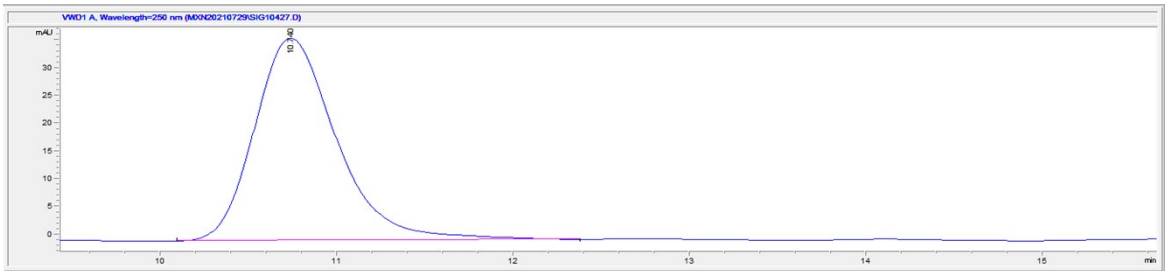


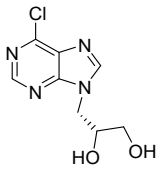


(S)-2j

HPLC chromatograms (Daicel chiralpak OD, Hexanes/i-PrOH = 70:30, flow rate = 1 mL/min): 10.7 min (minor), 13.3min (major), >99% ee

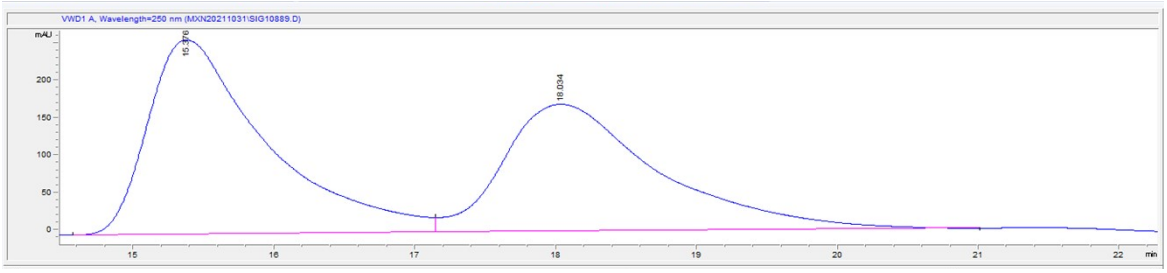


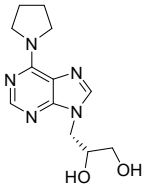




(S)-3a

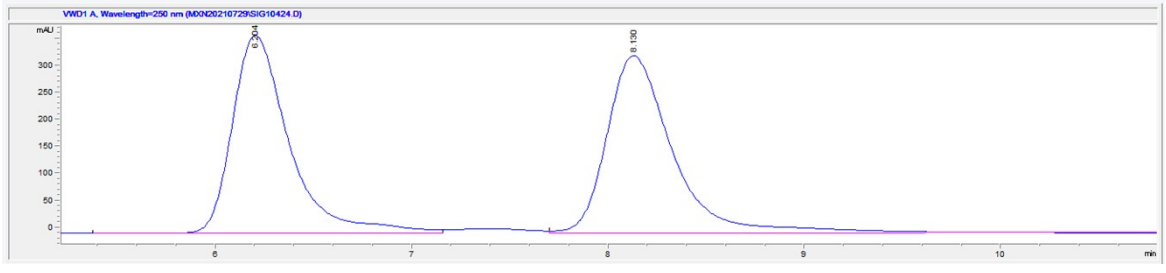
HPLC chromatograms (Daicel chiralpak OD, Hexanes/i-PrOH = 85:15, flow rate = 0.8 mL/min): 15.3min (minor), 18.2 min (major), >99% ee

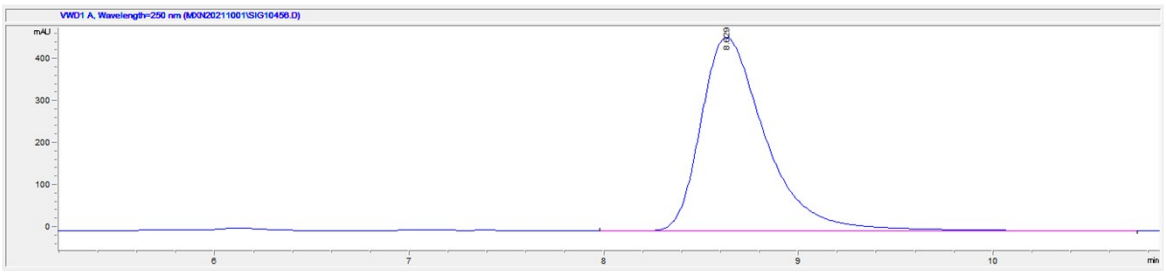


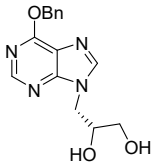


(S)-3b

HPLC chromatograms (Daicel chiralpak OD, Hexanes/i-PrOH = 70:30, flow rate = 1 mL/min): 6.2 min (minor), 8.1 min (major), >99% ee

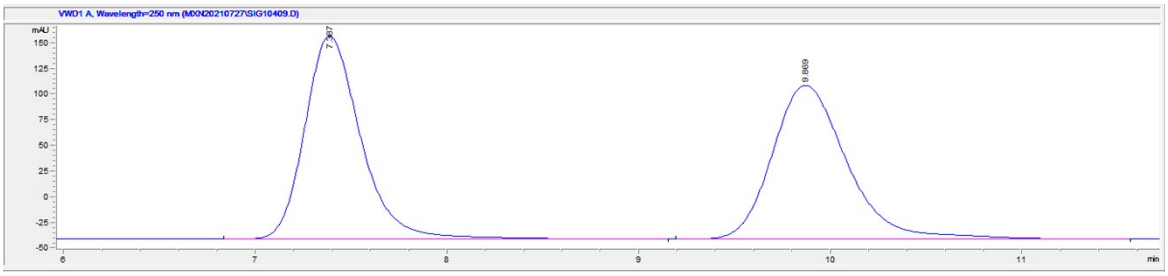


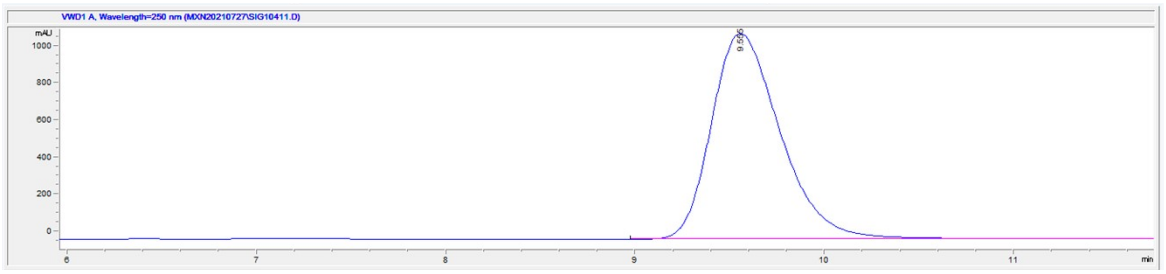


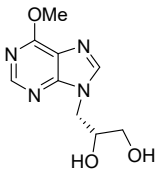


(S)-3c

HPLC chromatograms (Daicel chiralpak OD, Hexanes/i-PrOH = 70:30, flow rate = 1 mL/min):
6.2 min (minor), 8.1 min (major), >99% ee

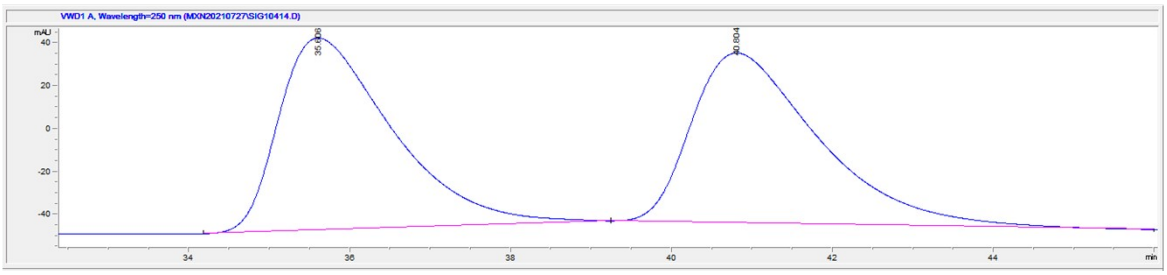


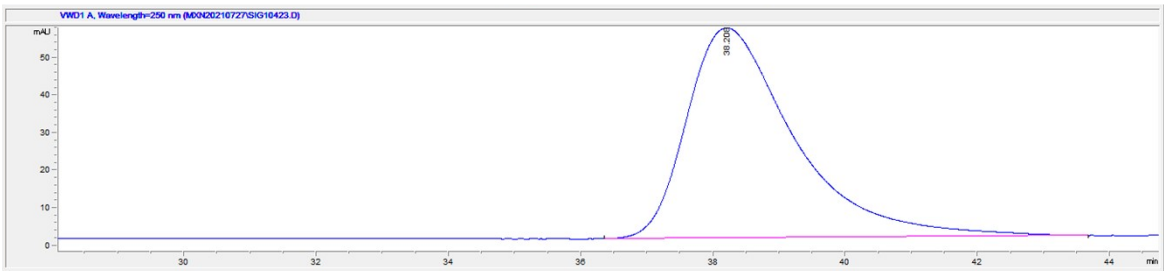


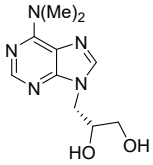


(S)-3d

HPLC chromatograms (Daicel chiralpak OD, Hexanes/i-PrOH = 90:10, flow rate =0.8 mL/min):
35.6 min (minor), 40.8 min (major), >99% ee

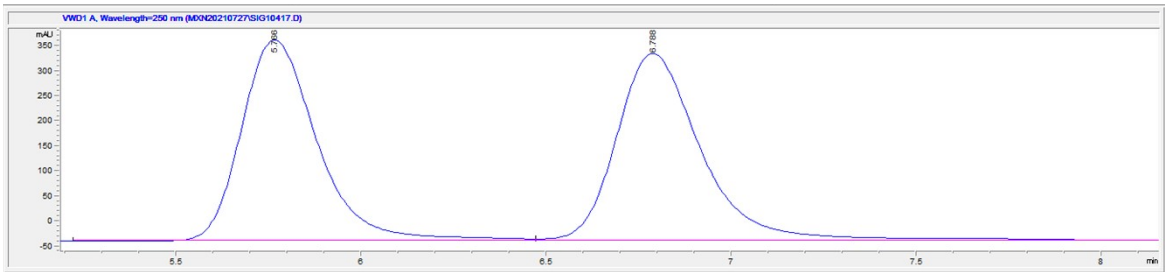


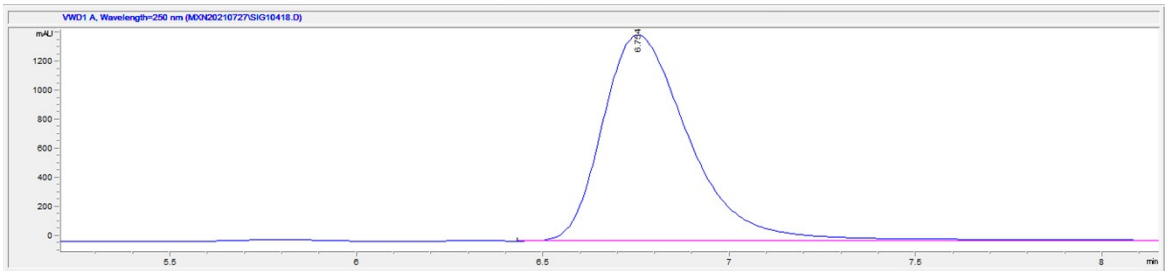


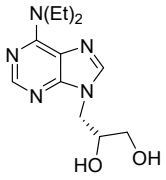


(S)-3e

HPLC chromatograms (Daicel chiralpak OD, Hexanes/i-PrOH = 70:30, flow rate =1 mL/min): 5.7 min (minor), 6.7 min (major), >99% ee

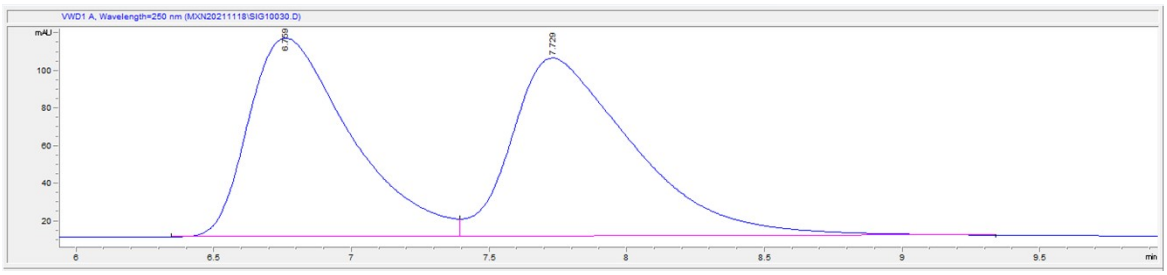


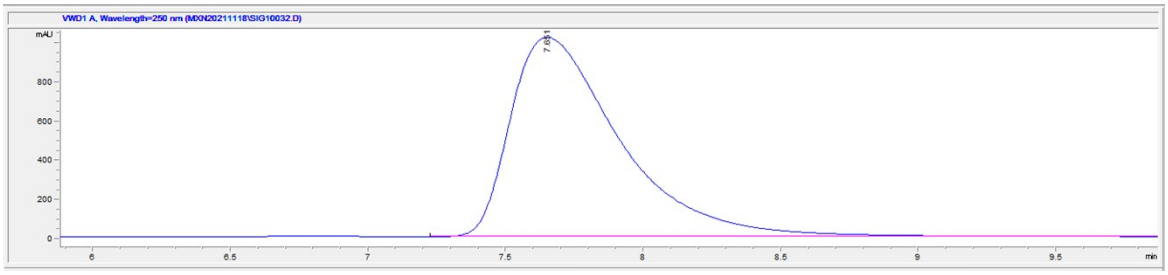


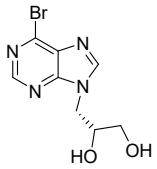


(S)-3f

HPLC chromatograms (Daicel chiralpak OD, Hexanes/i-PrOH = 85:15, flow rate =1 mL/min): 6.7 min (minor), 7.7 min (major), >99% ee

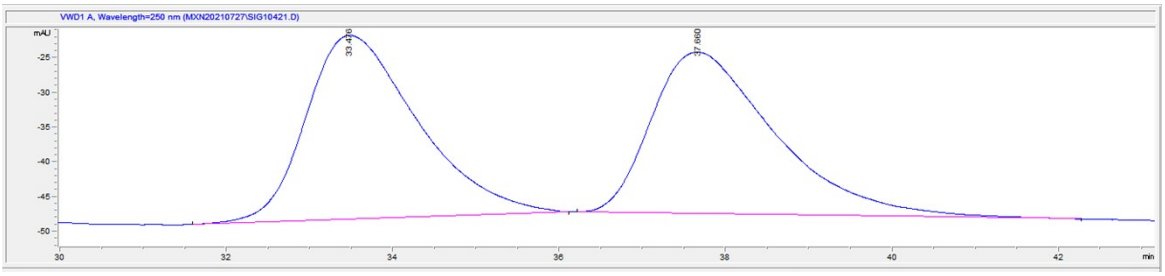


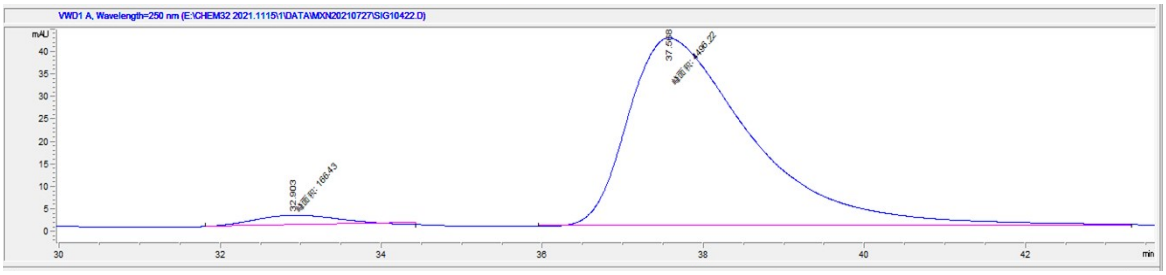


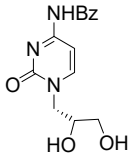


(S)-3g

HPLC chromatograms (Daicel chiralpak OD, Hexanes/i-PrOH = 90:10, flow rate =1 mL/min):
33.4 min (minor), 37.6 min (major), 93% ee

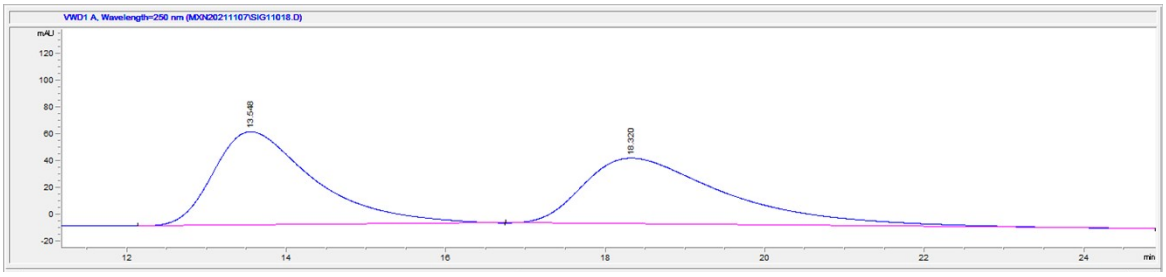


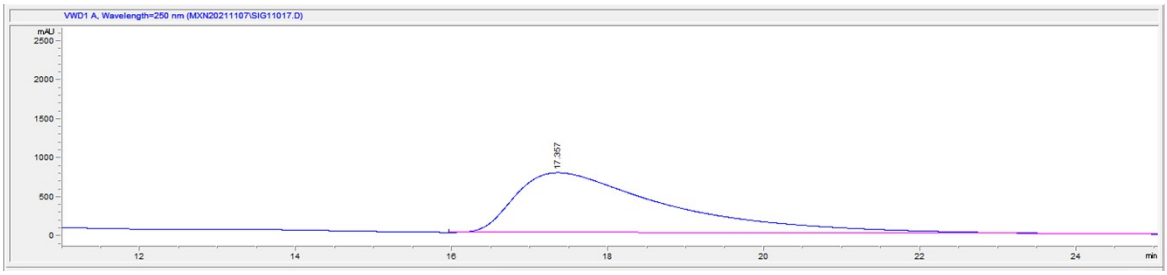




(S)-3j

HPLC chromatograms (Daicel chiralpak OD, Hexanes/i-PrOH = 70:30, flow rate =1 mL/min):
13.5 min (minor), 18.3 min (major), >99% ee





Notes and references

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