

Supporting Information

Novel 3',5'-Cyclic Nucleotide Analogue: Adenosine 3',5'-Cyclic Boranomonophosphate

Jinlai Lin, Kaizhang He and Barbara Ramsay Shaw*

General experimental procedures for the synthesis, separation and characterization of adenosine 3',5'-cyclic boranomonophosphate 7c (cAMPB) and its two diastereomers 7c-I and 7c-II

2. Separation of the two diastereomers 7c-I and 7c-II of adenosine 3',5'-cyclic boranomonophosphate 7c (cAMPB) The two diastereomers of 7c-I and 7c-II of adenosine 3',5'-cyclic boranomonophosphate 7c (cAMPB) were separated by ion-pairing chromatography on reverse phase column (Waters Delta Pak C18, 7.8 X 300 mm, 15 μ , 100 Å) using isocratic conditions [84% 50 mM triethylammonium acetate (TEAA), pH 7.0 and 16% methanol as eluants]. After HPLC separation, the solvents were removed under reduced pressure. The buffer components, TEAA and methanol, were removed by repeated lyophilization.

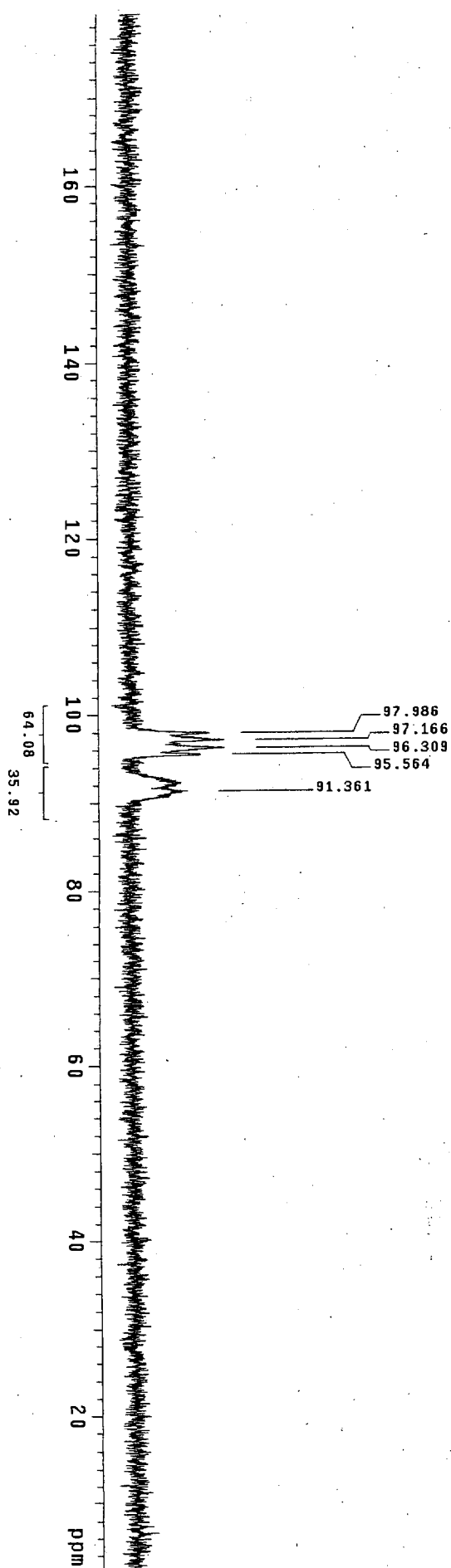
Cyclic AMPB isomer I, 7c-I. retention time 13.8 min. ^{31}P NMR (D_2O , 161.9 MHz): δ 94-90 (br); ^1H NMR (D_2O , 400 MHz): 8.03 (s, 1H, H-8), 8.02 (s, 1H, H-2), 5.92 (unresolved m, 1H, H-1'), 4.36-4.03 (2m, 4H, H-3', H-4', H-5'), 0.36, 0.09 (2br, 3H, BH_3). FAB-MS: 326.0 (M^-), HRMS: calcd. for $\text{C}_{10}\text{H}_{14}\text{N}_5\text{O}_5\text{PB}$ (M^-) 326.0825, found 326.0816.

Cyclic AMPB isomer II, 7c-II. retention time 15.1 min. ^{31}P NMR (D_2O , 161.9 MHz): δ 98.2, 97.3, 96.5, 95.7; ^1H NMR (D_2O , 400 MHz): 8.06 (s, 1H, H-8), 8.05 (s, 1H, H-2), 5.96 (unresolved m, 1H, H-1'), 4.61-4.13 (2m, 4H, H-3', H-4', H-5'), 0.41, 0.08 (2br, 3H, BH_3). FAB-MS: 326.1 (M^-), HRMS: calcd. for $\text{C}_{10}\text{H}_{14}\text{N}_5\text{O}_5\text{PB}$ (M^-) 326.0825, found 326.0831.

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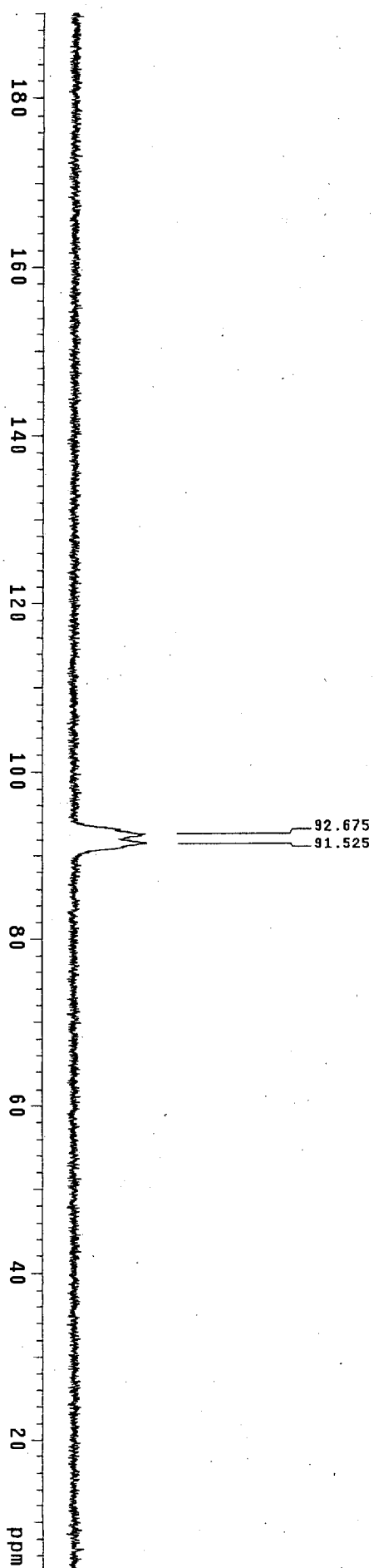
1. ^{31}P NMR (D_2O , 161.9 MHz, 85% aqueous phosphoric acid as external standard) spectrum for diastereomeric mixture of cyclic AMPB 7c, δ (ppm).



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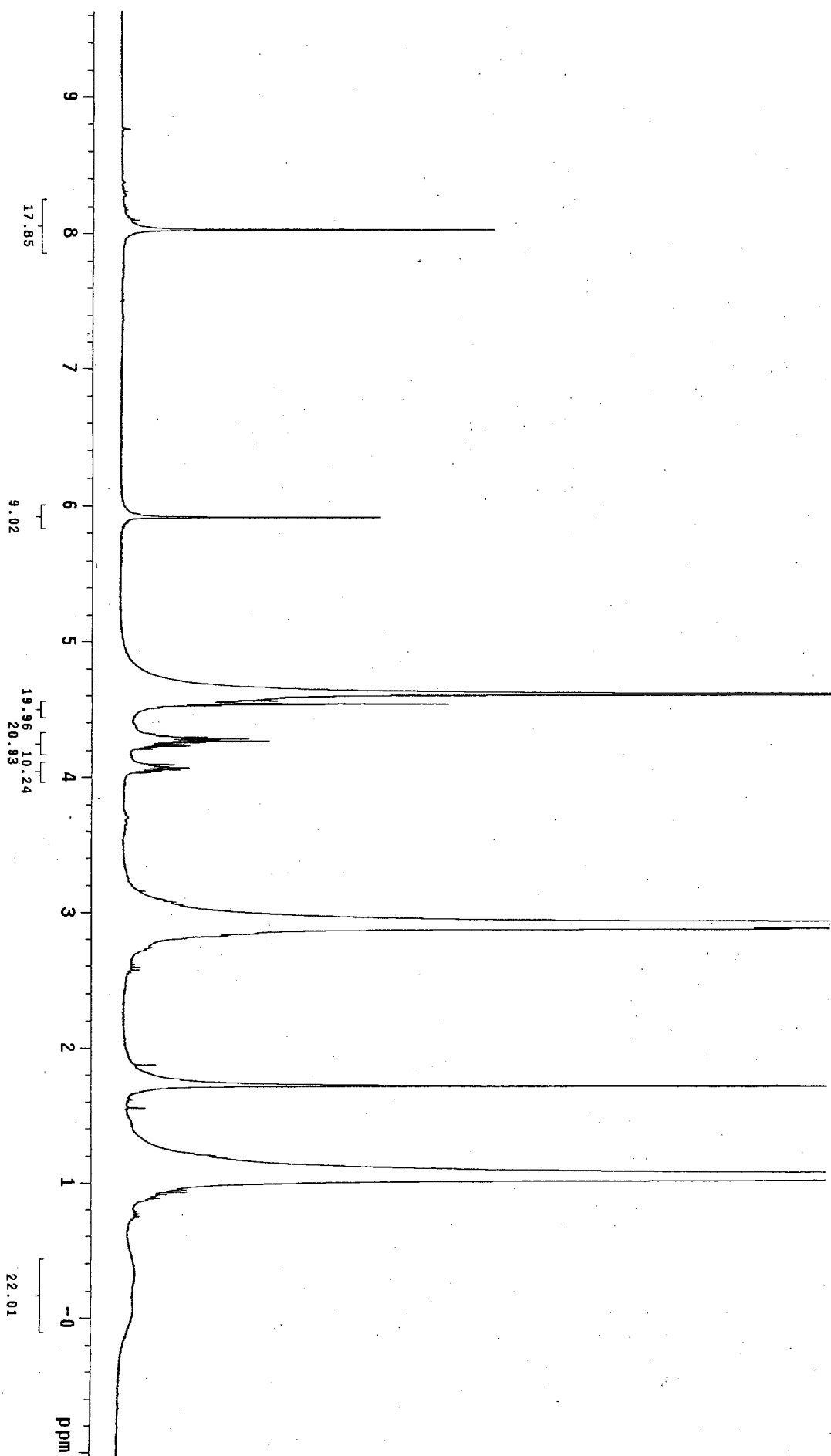
2. ^{31}P NMR (D_2O , 161.9 MHz, 85% aqueous phosphoric acid as external standard) spectrum for cyclic AMPB isomer I (first eluted isomer, 7c-I), δ (ppm).



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3. ^1H NMR (D_2O , 400 MHz) spectrum for cyclic AMPB isomer I (first eluted isomer, 7c-1), δ (ppm).



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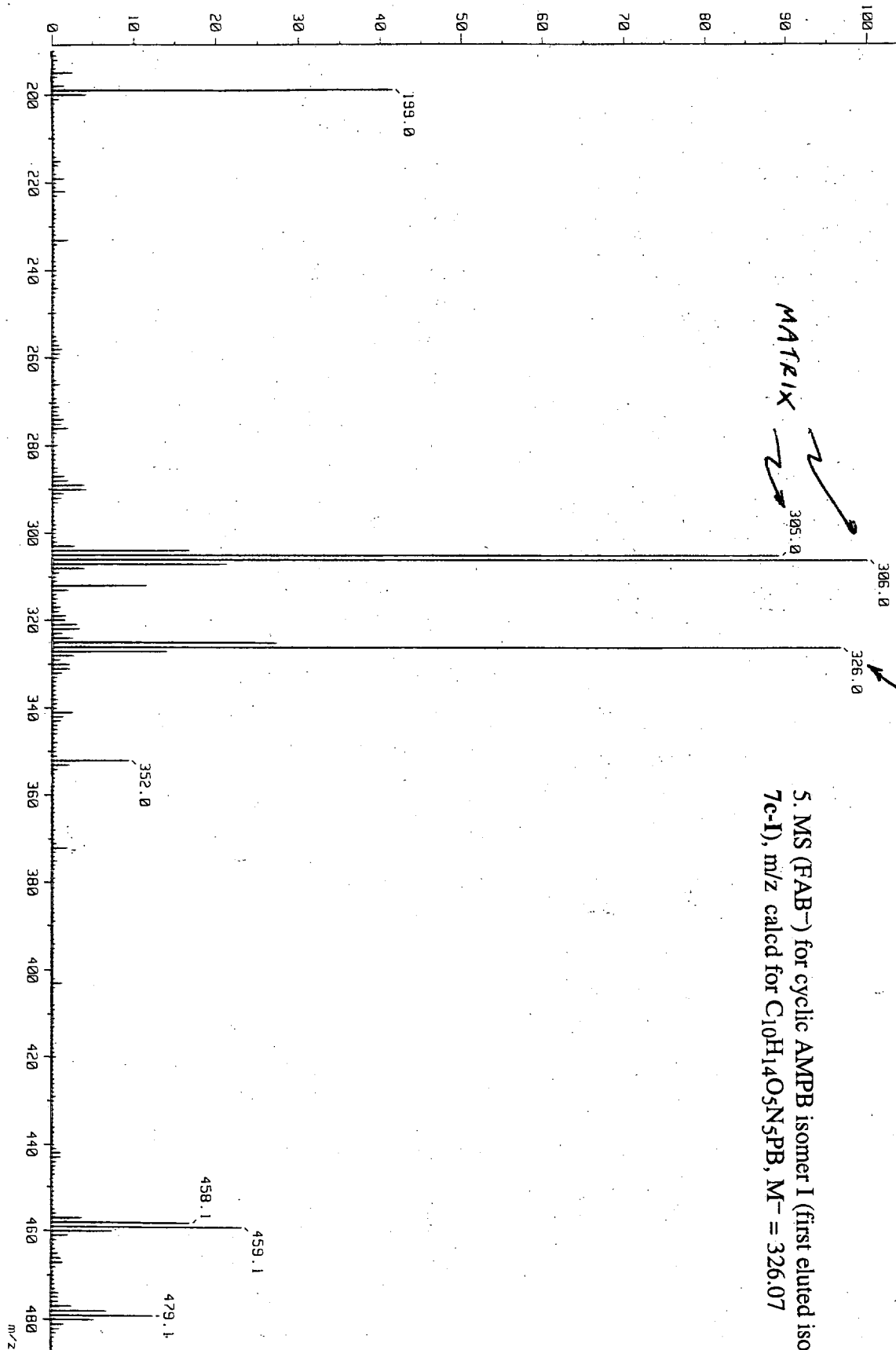
4. ^1H NMR (D_2O , 400 MHz) spectrum (enlarged part) for cyclic AMPB isomer I
(first eluted isomer, 7c-I), δ (ppm).



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RI : 0.93 min Scan# : (1,15)
BP : m/z 306.0481 Int. : 26.68
Output m/z range : 190.0330 to 487.0436 Cut Level : 0.00 %
4352422 Temp : 70.2 deg. C



5. MS (FAB-) for cyclic AMPB isomer I (first eluted isomer, 7c-I), m/z calcd for $C_{10}H_{14}O_5N_5PB$, $M^- = 326.07$

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6. HRMS (FAB-) for cyclic AMPB isomer I (first eluted isomer, 7c-I). Calcd for $C_{10}H_{14}O_5N_5PB$,
 $M^- = 326.0825$, found 326.0816

[Elemental Composition]

Data : Mrch00015

Date : 22-Mar-100 13:25

Page: 1

Sample: -J Lin mw=326 #35-18

Note : -matrix: 3-NBA & PEG-600

Inlet : Direct

RT : 1.30 min

Ion Mode : FAB-
Scan#: 13

Elements : C 25/0, H 45/0, O 12/0, N 7/3, P 1/1, B 1/1

Mass Tolerance : 10ppm, 10mmu if $m/z < 1000$, 20mmu if $m/z > 2000$

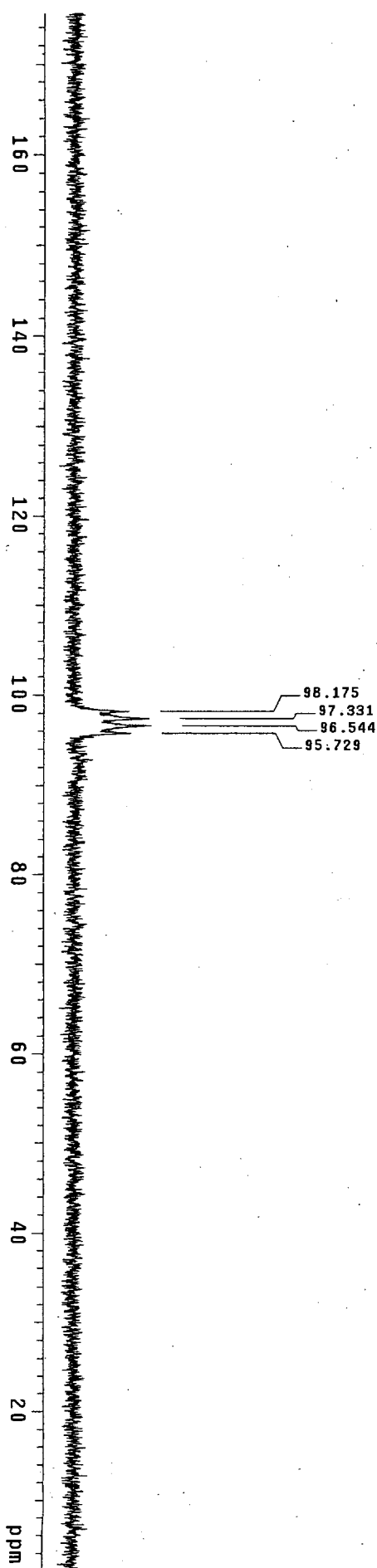
Unsaturation (U.S.) : 0.0 - 30.0

Observed m/z	Int%	Err(ppm)	U.S.	Composition
326.0816	100.0			
-15.4	/	-5.0	12.5	C 15 H 14 O 3 N 3 P B
-23.6	/	-7.7	17.0	C 18 H 12 N 4 P B
+23.2	/	+7.6	13.0	C 14 H 12 O 3 N 4 P B
+5.2	/	+1.7	4.0	C 7 H 16 O 8 N 4 P B
+15.0	/	+4.9	17.5	C 17 H 10 N 5 P B
-3.0	/	-1.0	8.5	C 10 H 14 O 5 N 5 P B
-11.3	/	-3.7	13.0	C 13 H 12 O 2 N 6 P B
-29.3	/	-9.5	4.0	C 6 H 16 O 7 N 6 P B
+17.5	/	+5.7	0.0	C 2 H 16 O 10 N 6 P B
+27.3	/	+8.9	13.5	C 12 H 10 O 2 N 7 P B
+9.3	/	+3.0	4.5	C 5 H 14 O 7 N 7 P B

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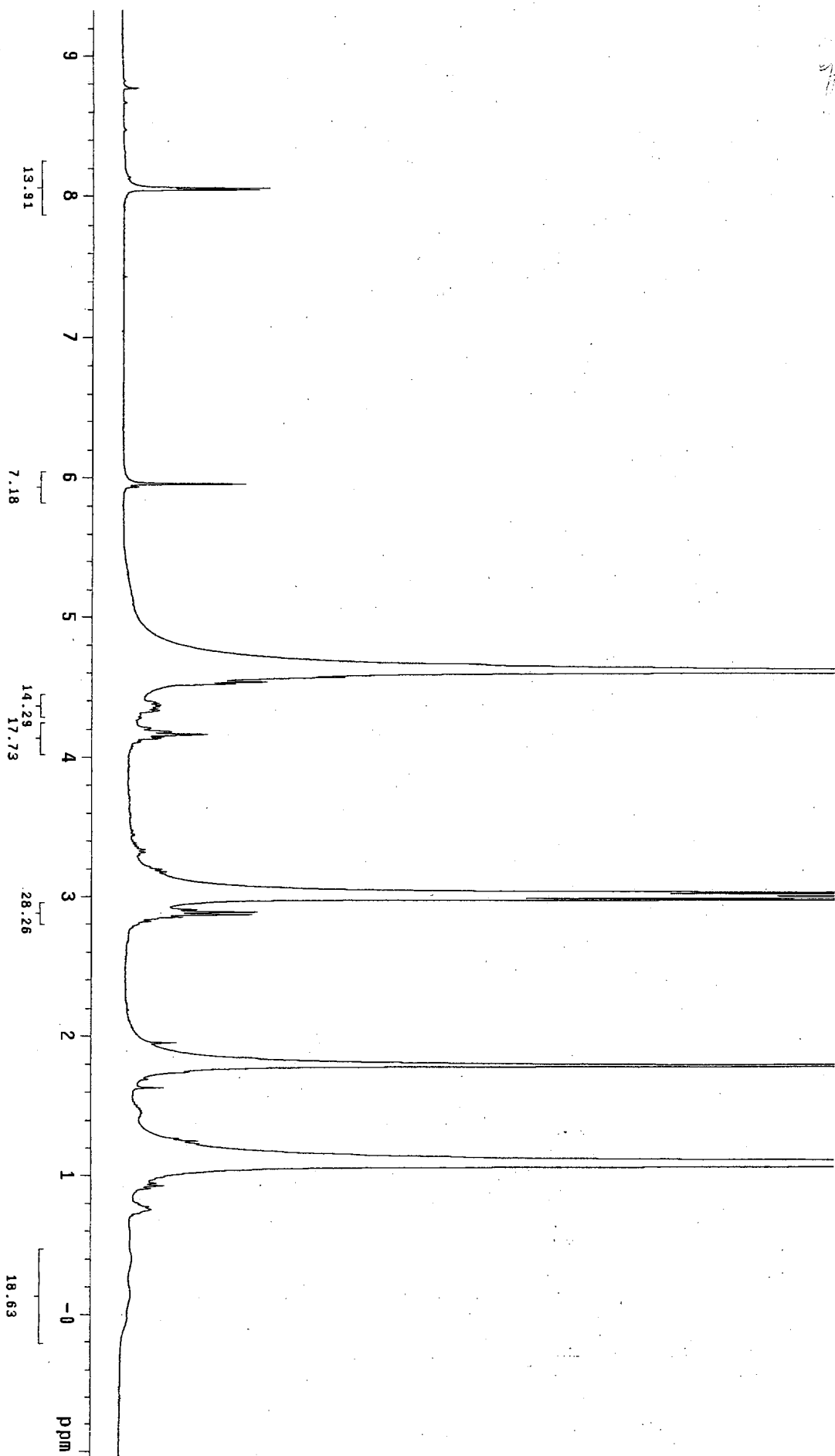
7. ^{31}P NMR (D_2O , 161.9 MHz, 85% aqueous phosphoric acid as external standard) spectrum for cyclic AMPB isomer II (second eluted isomer, 7c-II), δ (ppm).



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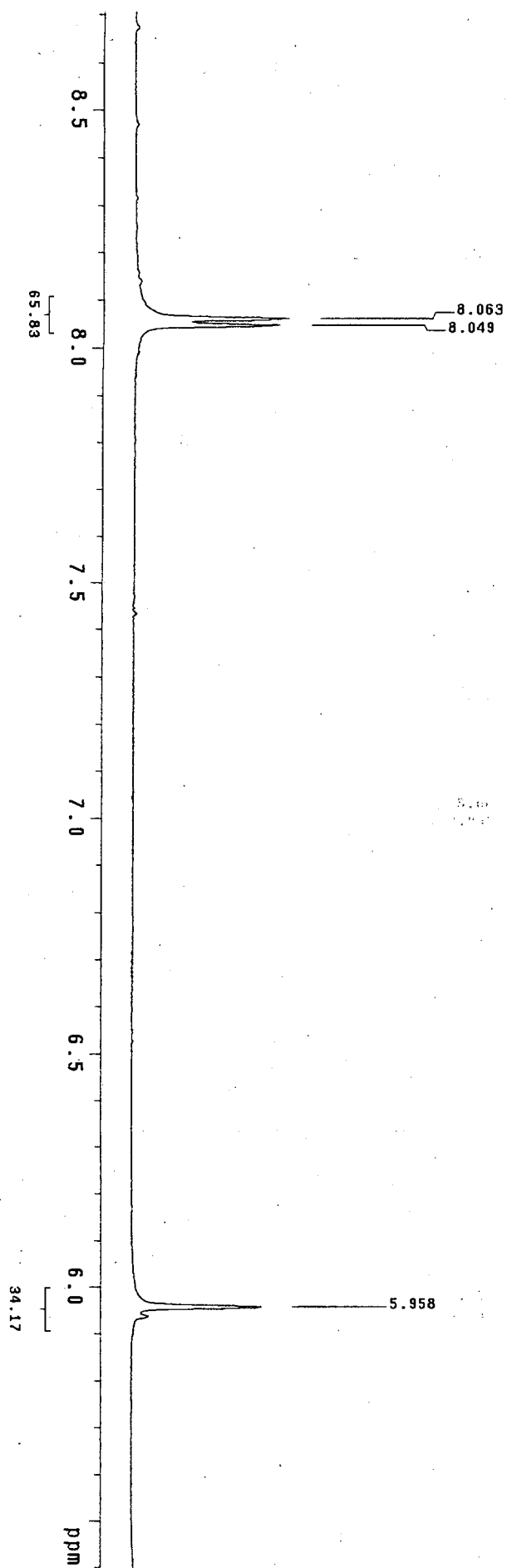
8. ^1H NMR (D_2O , 400 MHz) spectrum for cyclic AMPB isomer II (second eluted isomer, 7c-II), δ (ppm).



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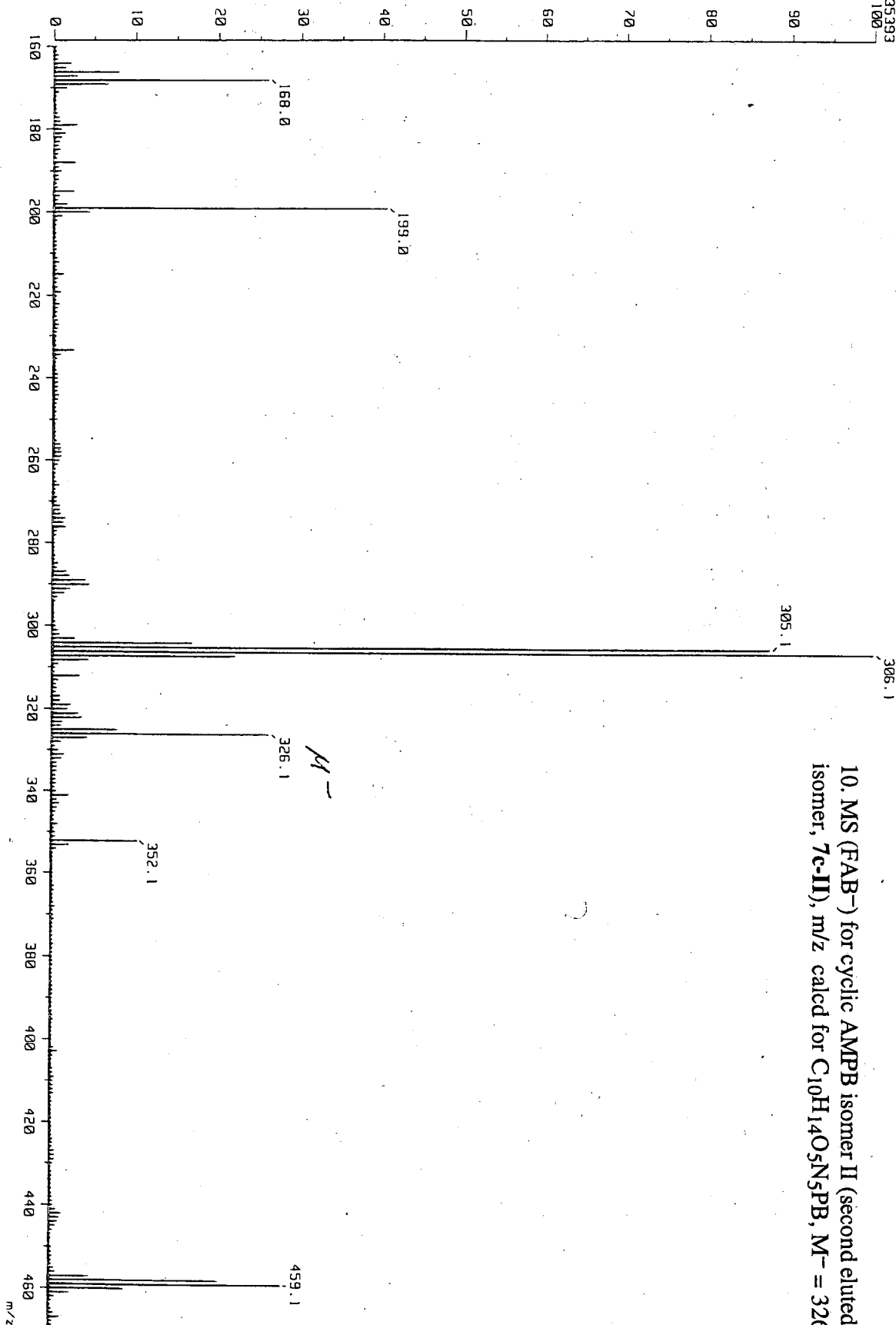
9. ^1H NMR (D_2O , 400 MHz) spectrum (enlarged part) for cyclic AMPB isomer II
(second eluted isomer, 7c-II), δ (ppm).



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Novel 3',5'-Cyclic Nucleotide Analogue: Adenosine 3',5'-Cyclic Boranomonophosphate Jinlai Lin, Kaizhang He and Barbara Ramsay Shaw*

RT : 0.47 min Scan# : (1,8)
BP : m/z 305.0724 Int. : 18.30
Output m/z range : 150.0000 to 469.7329 Cut Level : 0.00 %
1535393 Temp : 79.0 deg.C



10. MS (FAB-) for cyclic AMPB isomer II (second eluted isomer, 7c-II), m/z calcd for $C_{10}H_{14}O_5N_5PB$, $M^- = 326.07$