ORGANIC LETTERS

Toward Daisy Chain Polymers: 'Wittig Exchange' of Stoppers in [2]Rotaxane Monomers

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SUPPORTING INFORMATION

(20 PAGES)

EXPERIMENTAL PROCEDURES FOR **7**-H·2PF_6 AND **8**-H·2PF_6

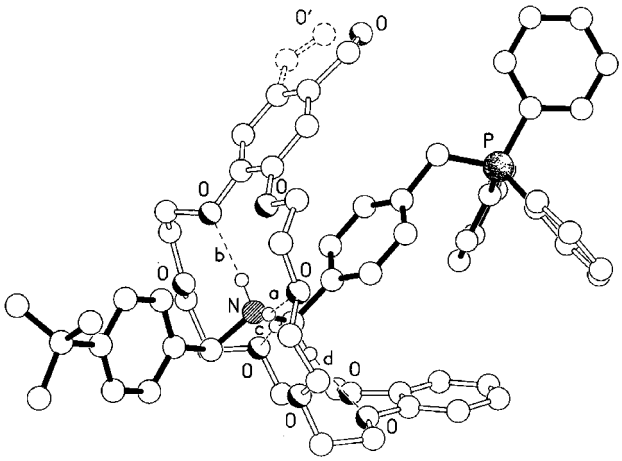
CYCLIZATION PROTOCOL FOR **8**-H·2PF_6

^{1}H NMR, ^{13}C NMR AND FAB-MS FOR **7**-H·2PF_6 AND **8**-H·2PF_6

FAB-MS OF THE MIXTURE OBTAINED UPON CYCLIZATION OF **7**-H·2PF_6

^{1}H NMR AND FAB-MS FOR **9**-H·2PF_6 AND **10**-H_2·2PF_6

CRYSTAL DATA FOR **7**-H·2PF_6



Experimental Section

7-H·2PF_6

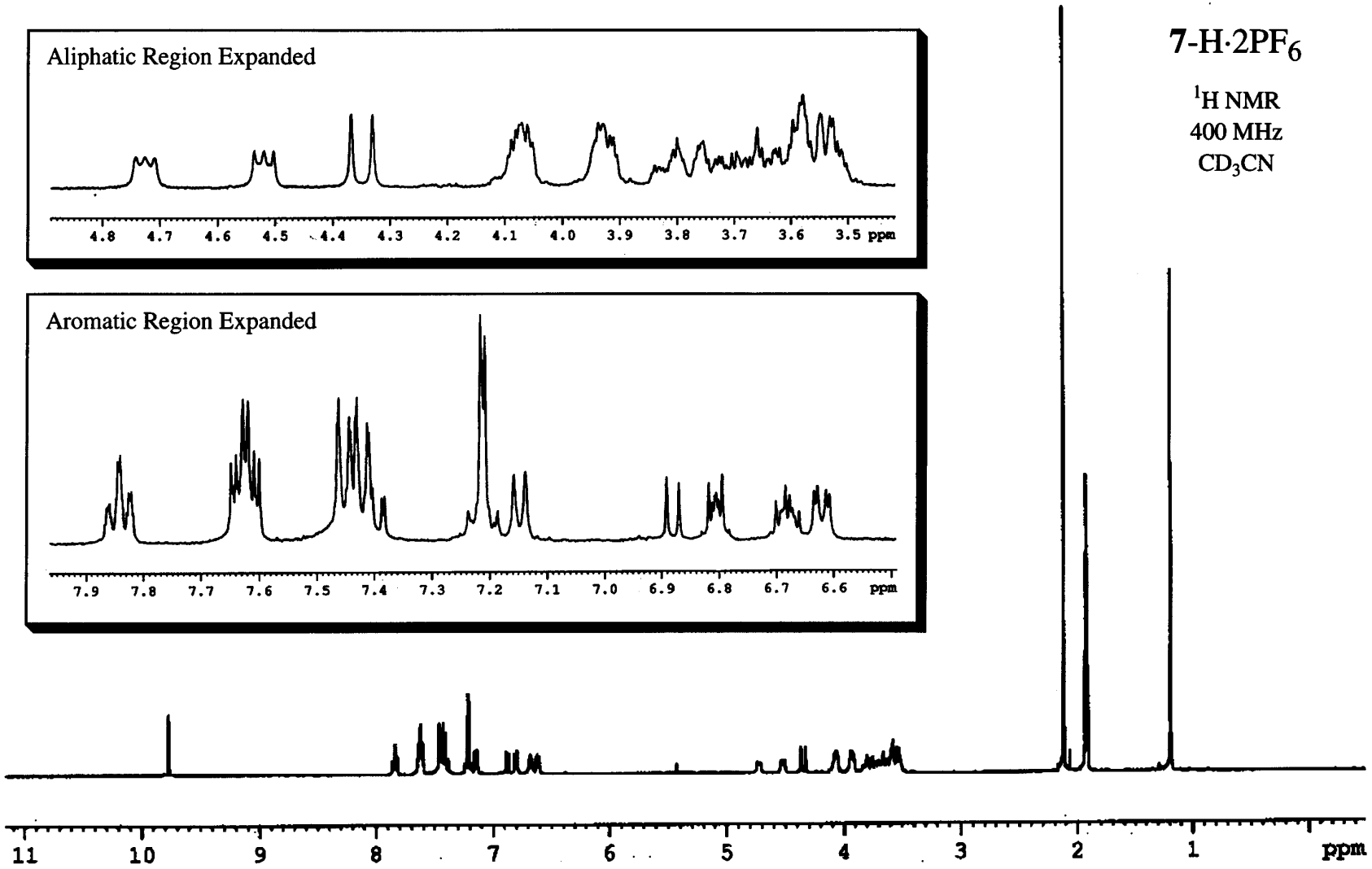
Triphenylphosphine (144 mg, 5.5 x 10^{-4} mol) was added to a solution of the (*p*-*t*-butylbenzyl bromomethylbenzyl)ammonium hexafluorophosphate salt **3**-H·PF_6 (135 mg, 2.7 x 10^{-4} mol) and formyl-DB24C8 **5** (261 mg, 5.5 x 10^{-4} mol) in CH_2Cl_2 (2.7 ml) and this solution was left to stir overnight. Et_2O was added to the reaction mixture and the resulting white precipitate filtered and washed with more Et_2O. This solid was dissolved in MeCN and aqueous NH_4PF_6 was added. The MeCN was then removed *in vacuo* and the resulting solid was collected and washed with water. Further purification was carried out by flash chromatography (SiO_2) with CH_2Cl_2/MeOH (100:0, 99:1,..., 95:5), yielding the [2]rotaxane **7**-H·2PF_6 as a white solid (234 mg, 52 %). ^{1}H NMR (400 MHz, CD_3CN) δ = 9.77 (s, 1H), 7.82-7.87 (m, 3H), 7.61-7.65 (m, 6H), 7.38-7.49 (m, 8H,), 7.18-7.25 (m, 4H), 7.10 (d, *J* = 8 Hz, 2H), 6.88 (d, *J* = 8 Hz, 2H), 6.81 (m, 2H), 6.67 (m, 2H), 6.61 (dd, *J* = 2.4, 8 Hz, 2H), 4.73 (m, 2H), 4.51 (m, 2H), 4.34 (d, *J* = 14.8 Hz, 2H), 4.07 (m, 4H), 3.91 (m, 4H), 3.50-3.85 (m, 16H), 1.19 (s, 9H); ^{13}C NMR (100 MHz, CD_3CN) δ = 191.0, 152.7, 152.3, 148.0, 147.0, 135.3 (J_{PC} = 3 Hz), 134.0 (J_{PC} = 9.7 Hz), 132.9 (J_{PC} = 3.8 Hz), 131.0 (J_{PC} = 5.4 Hz), 130.3, 130.2 (J_{PC} = 12.5 Hz), 129.7 (J_{PC} = 3.3 Hz), 129.1, 128.6, 127.7 (J_{PC} = 8.3 Hz), 126.3, 125.5, 121.2, 117.3 (J_{PC} = 85.7 Hz), 112.1, 111.9, 110.0, 70.7, 70.6, 70.5, 70.0, 69.9, 69.8, 68.4, 68.1, 67.7, 67.6 52.2, 51.6, 34.2, 30.4, 29.3 (J_{PC} = 48.2 Hz); MS (FAB) 1150.5 $[M\text{-}PF_6]^+$, 1004.5 $[M\text{-}2PF_6]^+$.

8-H·2PF_6

Triphenylphosphine (392 mg, 1.5 mmol) was added to a solution of the 3,5-di-*t*-butylbenzylbromomethylbenzyl)ammonium hexafluorophosphate salt **4**-H·PF_6 (410 mg, 7.5 x 10^{-4} mol) and formyl-BMP25C8 **6** (534 mg, 1.1 mmol) in CH_2Cl_2 (7.5 mL) and the reaction was then left to stir at room temperature overnight. Further CH_2Cl_2 was added and the solution washed with saturated aqueous NH_4PF_6. The organic layer was collected and the solvent removed. The resulting solid was purified by flash chromatography with CH_2Cl_2/MeOH (100:0, 99:1,...,90:0) and recrystallized from CH_2Cl_2/Et_2O to yield the [2]rotaxane **8**-H·2PF_6 as a white crystalline solid (98 mg, 10 %). ^{1}H NMR (400 MHz, CD_3CN) δ = 9.82 (s, 1H), 7.83-7.87 (m, 5H), 7.59-7.66 (m, 6H), 7.45-7.50 (m, 7H), 7.31 (d, *J* = 2 Hz, 2H), 7.12 (d, *J* = 8 Hz, 2H), 7.05 (d, *J* = 2 Hz), 6.84-6.91 (m, 2H), 6.74 (t, *J* = 2 Hz, 1H), 6.59-6.67 (m, 4H), 4.43 (m, 2H), 4.37 (m, 2H), 4.36 (d, *J* = 14.8 Hz, 2H), 4.10-4.24 (m, 4H), 3.35-3.95 (m, 20H), 1.20 (s, 18H); ^{13}C NMR (100 MHz, CD_3CN) δ = 192.0, 160.4, 151.7, 146.0, 139.0, 135.4 (J_{PC} = 3 Hz), 134.0 (J_{PC} = 9.7 Hz), 131.5 (J_{PC} = 3.8 Hz), 131.0 (J_{PC} = 5.4 Hz), 130.5, 130.3(J_{PC} = 3.3 Hz), 130.1 (J_{PC} = 12.5 Hz), 128.4 (J_{PC} = 8.4 Hz), 124.0, 123.7, 121.5, 117.2 (J_{PC} = 85.7 Hz), 112.0, 109.4, 108.3, 71.0, 70.2, 70.3, 69.0, 68.1, 67.8, 52.8, 51.7, 34.6, 30.5, 29.4 (J_{PC} = 48.1 Hz); MS (FAB) 1206.4 $[M\text{-}PF_6]^+$, 1060.5 $[M\text{-}2PF_6]^+$.

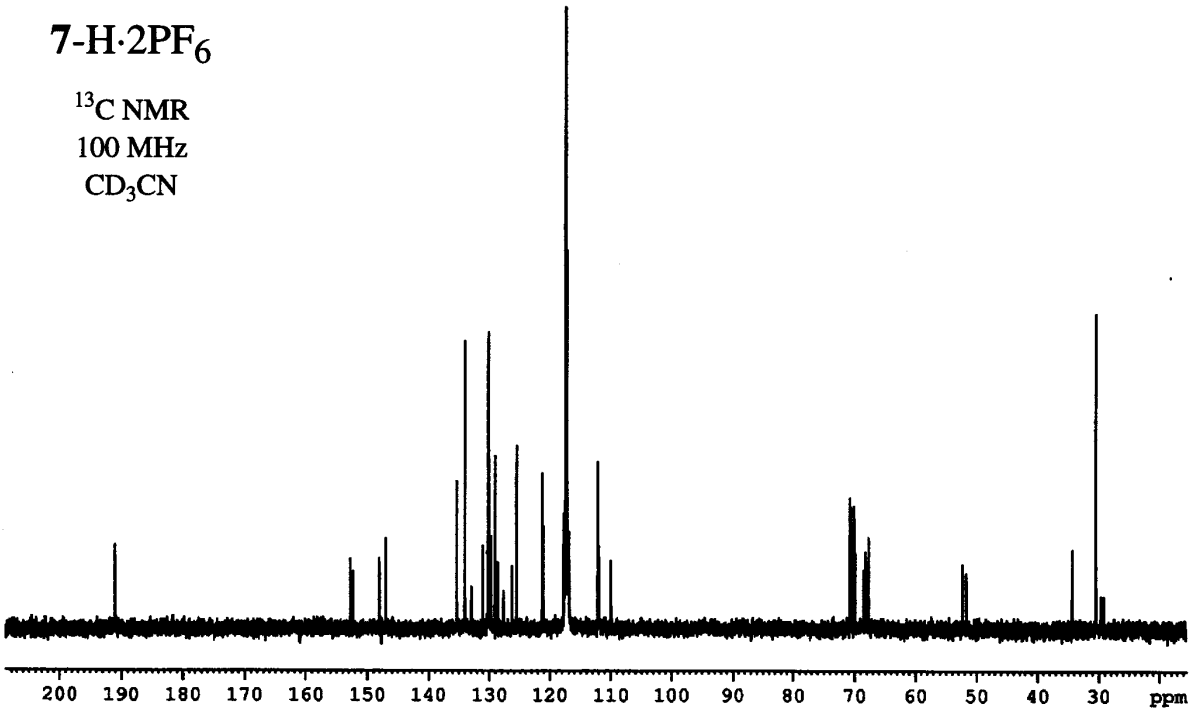
Cyclization of **8**-H·2PF_6

NaH (7 mg, 2.9 x 10^{-4} mol) was added to a solution of the **8**-H·2PF_6 (75 mg, 5.55 x 10^{-5} mol) and the reaction was left to stir for 2 days at room temperature. The reaction mixture was then neutralized with HCl (1N) and the product extracted into CH_2Cl_2. The solvent was removed *in vacuo* and the resulting material was dissolved in MeCN and added to aqueous NH_4PF_6. Upon removal of the MeCN and filtration of the resulting precipitate, ^{1}H NMR spectroscopic analysis revealed the presence of peaks corresponding to aldehydic protons and so the reaction mixture was resubmitted to the above reaction conditions and purified as before. After the second anion exchange the solid was dissolved in a small amount of CH_2Cl_2 and precipitated with Et_2O. This suspension was filtered and both the solid and liquid collected. The solid (50 %) was shown to contain cyclic dimers (FAB-MS: 1709 $[M\text{-}PF_6]^+$, 2346 $[M\text{-}2PF_6]^+$) and a small amount of cyclic trimers (FAB-MS: 2491 $[M\text{-}2PF_6]^+$, 2346 $[M\text{-}3PF_6]^+$). The Et_2O fraction was purified by precipitation with MeOH followed by flash chromatography on SiO_2 with CH_2Cl_2/MeOH (100:0, 99:1,..., 90:10), affording two products. The first product was shown to be the cyclic dimer **10**-H_2·2PF_6 (5 mg, 10 %). ^{1}H NMR (CD_3CN, 400 MHz) δ = 7.82 (br s, 2H), 7.51 (t, *J* = 2 Hz, 1H), 7.39 (d, *J* = 2 Hz, 2H), 6.98 (AA' of AA'BB', *J* = 8 Hz, 2H), 6.92 (BB' of AA'BB', *J* = 8 Hz, 2H), 6.86-6.91 (m, 4H), 6.42-6.50 (m, 3H), 6.30 (d, *J* = 2 Hz, 2H), 4.51 (m, 2H), 4.35 (m, 2H), 3.98-4.12 (m, 6H), 3.74-3.79 (m, 2H), 3.42-3.70 (m, 16H), 1.24 (s, 18H); ^{13}C NMR (CD_3CN, 100 MHz) δ = 159.5, 151.7, 147.8, 146.7, 139.6, 138.1, 136.2, 130.7, 130.6, 129.9, 129.8, 129.3, 128.9, 124.2, 124.1, 121.6, 112.5, 108.1, 102.2, 70.8, 70.3, 69.7, 69.5, 68.1, 67.7, 53.2, 52.1, 34.6, 30.6; MS (FAB) 1562.6 $[M\text{-}2PF_6]^+$, 782.2 $[M\text{-}2PF_6]^{2+}$. The second product that was eluted from the column was the linear monomer **9**-H·PF_6 (17 mg, 33 %). ^{1}H NMR (CD_3CN, 400 MHz) δ = 7.35 (t, *J* = 2 Hz, 1H), 7.21 (AA' of AA'BB', *J* = 8 Hz, 2H), 7.18 (BB' of AA'BB', *J* = 8 Hz, 2H), 7.17 (d, *J* = 2 Hz, 2H), 6.91 (m, 2H), 6.86 (m, 2H), 6.60 (A of AB, *J* = 12 Hz, 1H), 6.54 (B of AB, *J* = 12 Hz, 1H), 6.44 (t, *J* = 2 Hz, 1H), 6.34 (d, *J* = 2 Hz, 2H), 4.04 (m, 4H), 3.94 (m, 4H), 3.70-3.74 (m, 8H), 3.55-3.62 (m, 12H), 1.34 (s, 18H); ^{13}C NMR (CD_3CN, 100 MHz) δ = 159.8, 150.8, 148.6, 147.8, 139.2, 138.5, 136.2, 130.4, 130.0, 129.1, 128.8, 128.4, 122.6, 121.2, 121.1 114.1, 107.9, 101.8, 70.5, 70.4, 69.4, 69.2, 68.2, 67.7, 52.9, 52.2, 34.5, 30.7; MS (FAB) 782.5 $[M\text{-}PF_6]^+$.

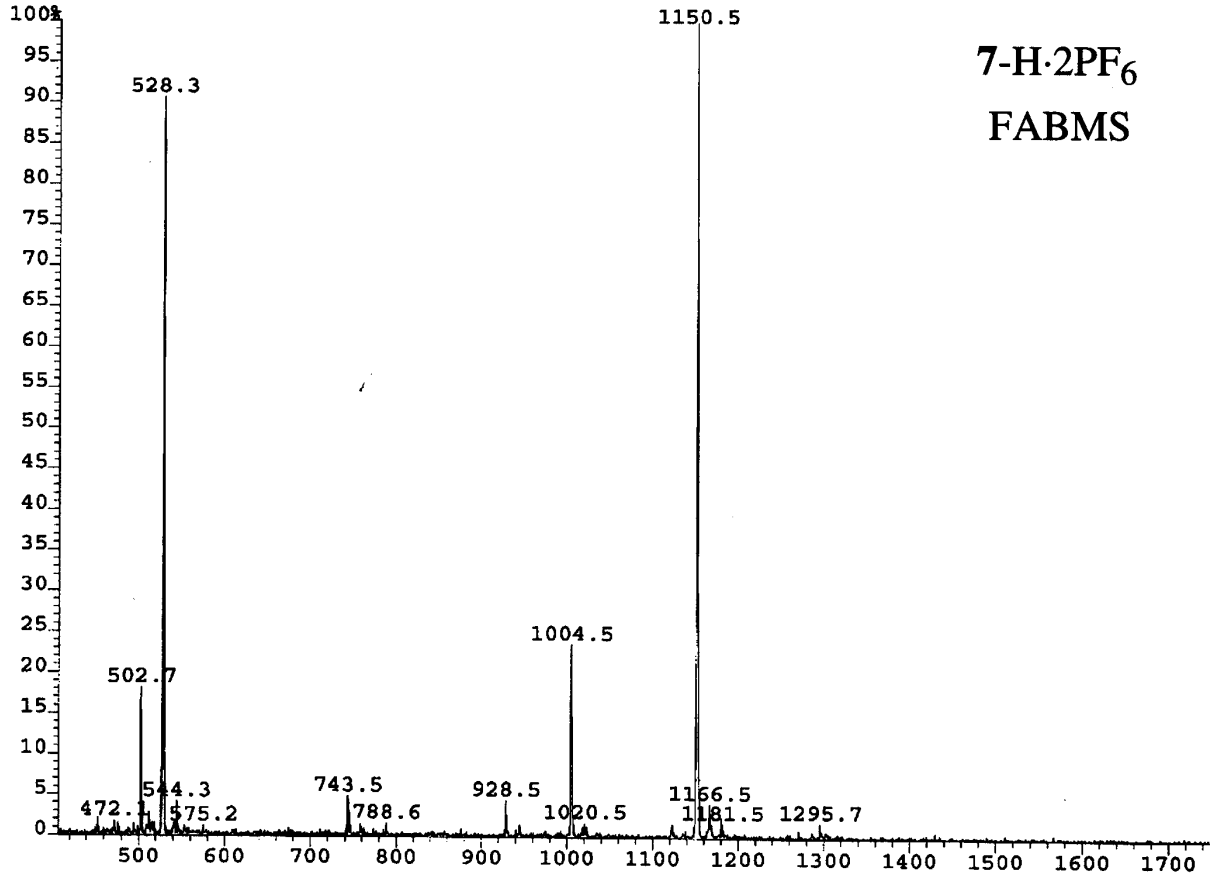

Aliphatic Region Expanded
4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 ppm
Aromatic Region Expanded
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 ppm
7-H·2PF6
1H NMR
400 MHz
CD3CN
11 10 9 8 7 6 5 4 3 2 1 ppm

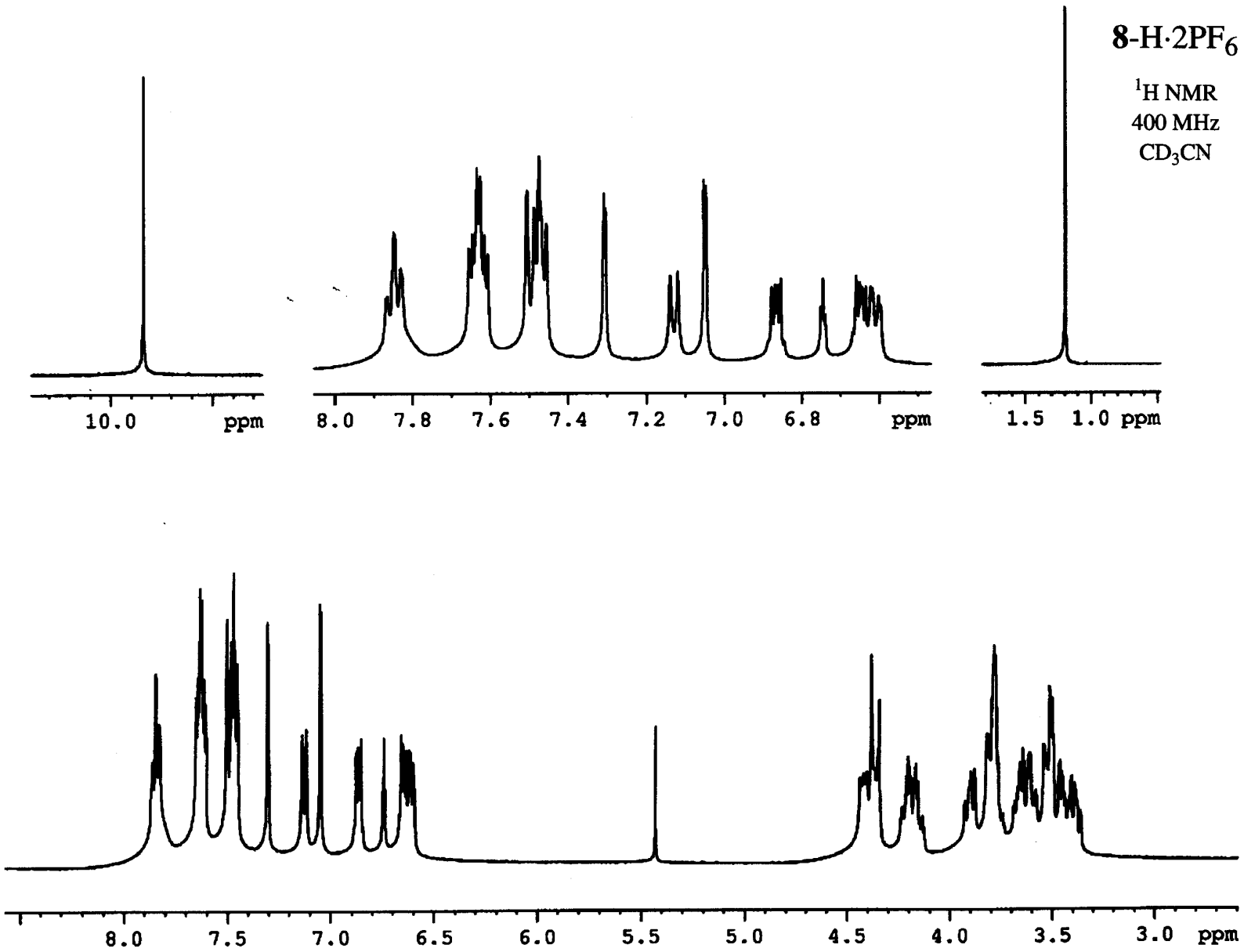
7-H·2PF$_6$

^{13}C NMR
100 MHz
CD_3CN



7-H·2PF$_6$
FABMS

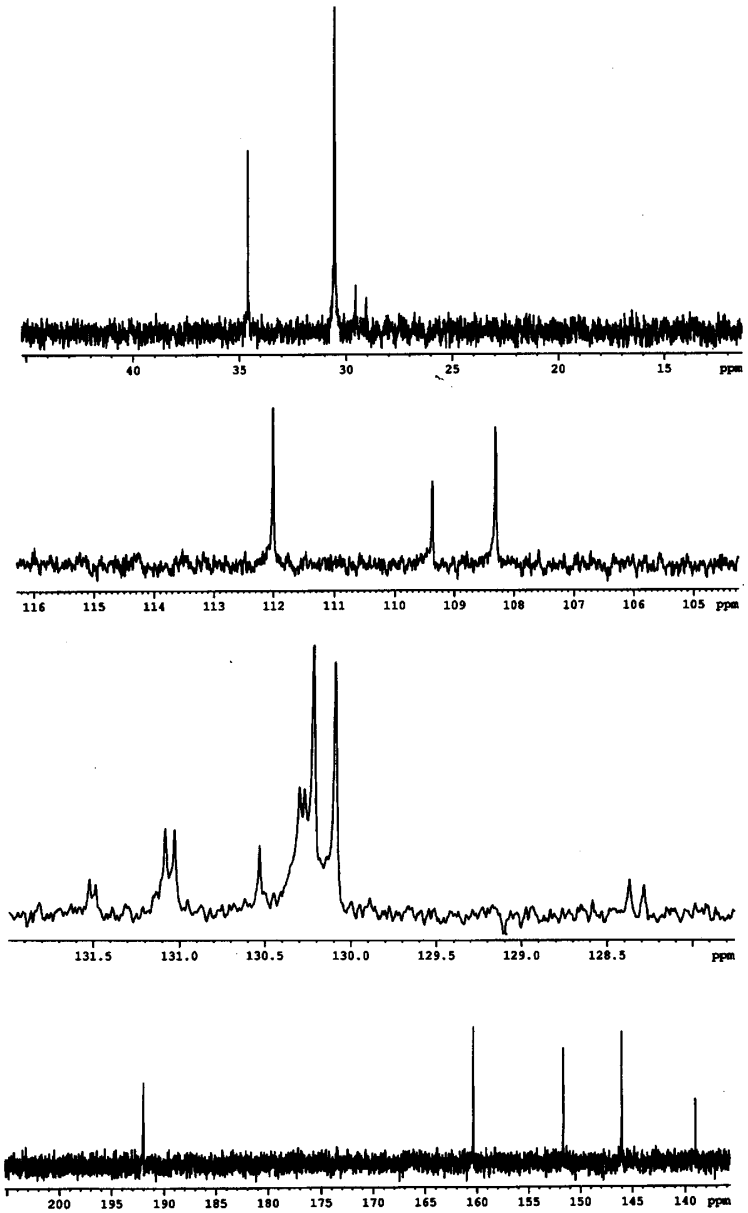


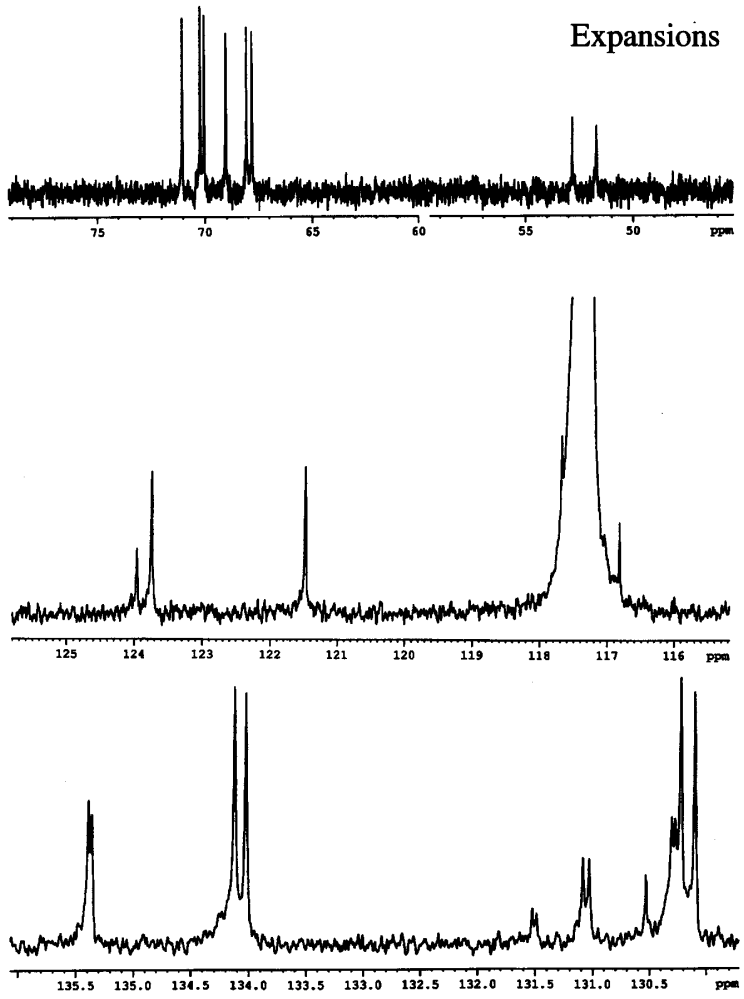

8-H·2PF6
1H NMR
400 MHz
CD3CN
10.0
ppm
8.0
7.8
7.6
7.4
7.2
7.0
6.8
ppm
1.5
1.0 ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm

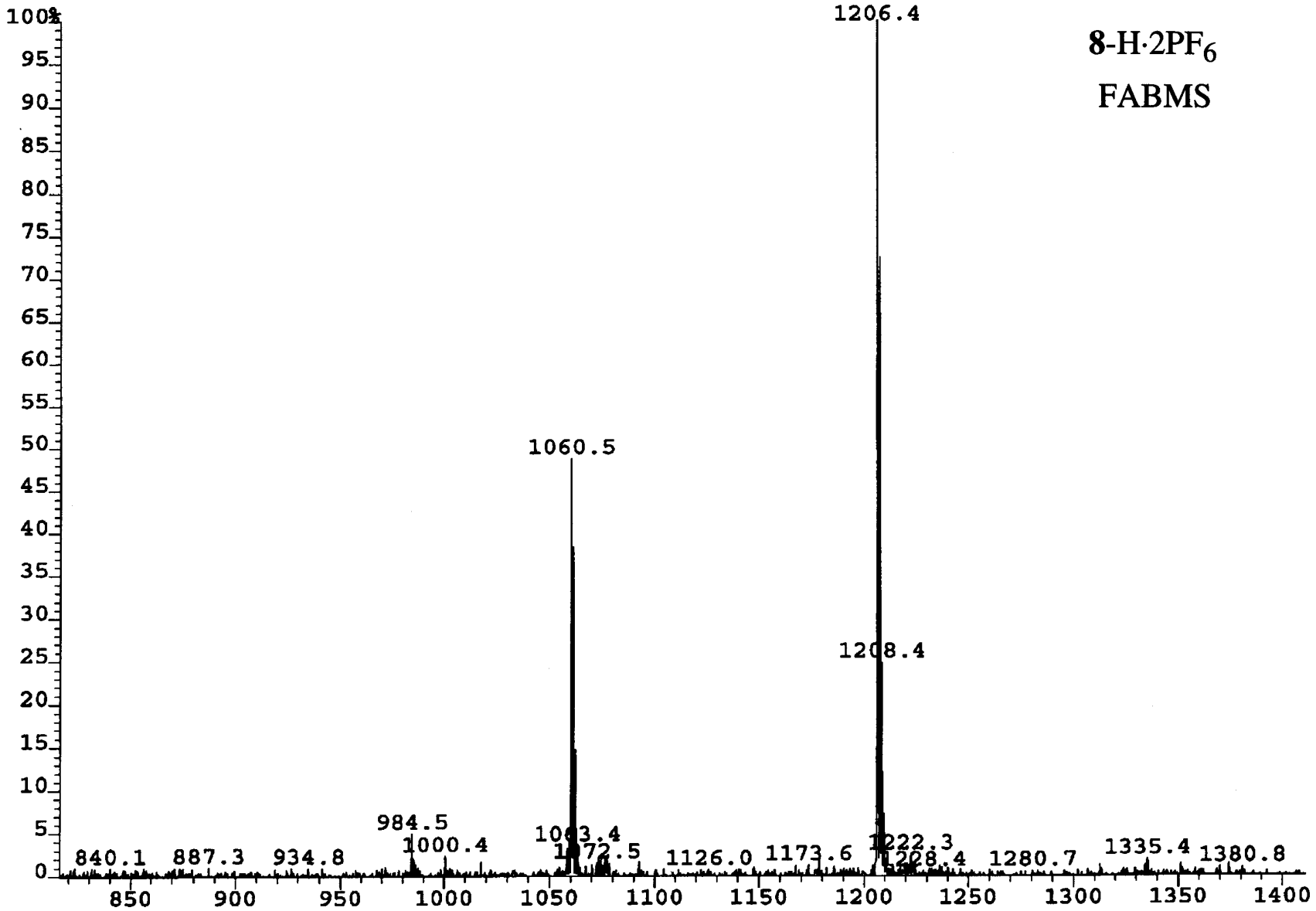
8-H·2PF_6

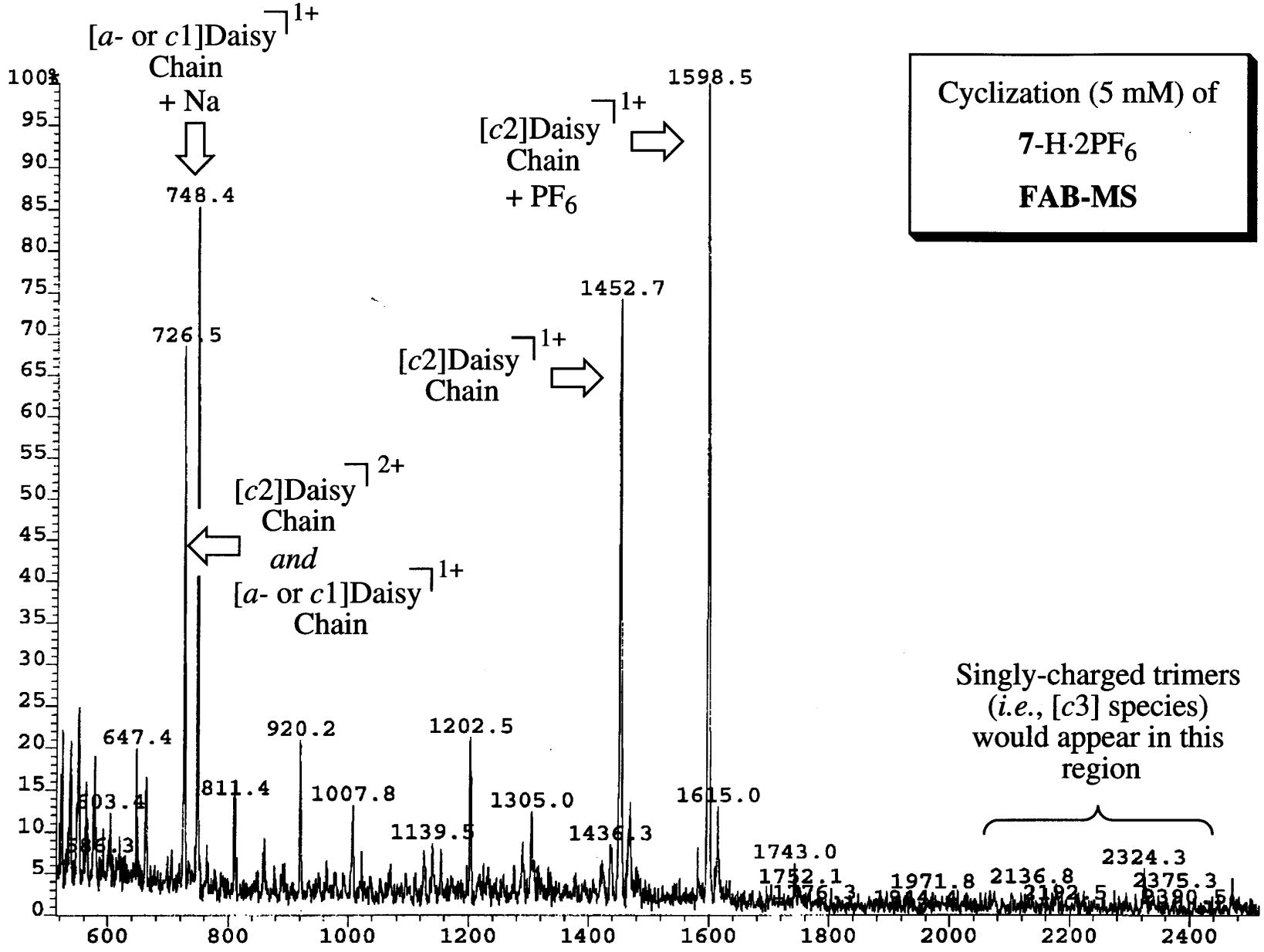
^{13}C NMR
100 MHz
CD_3CN

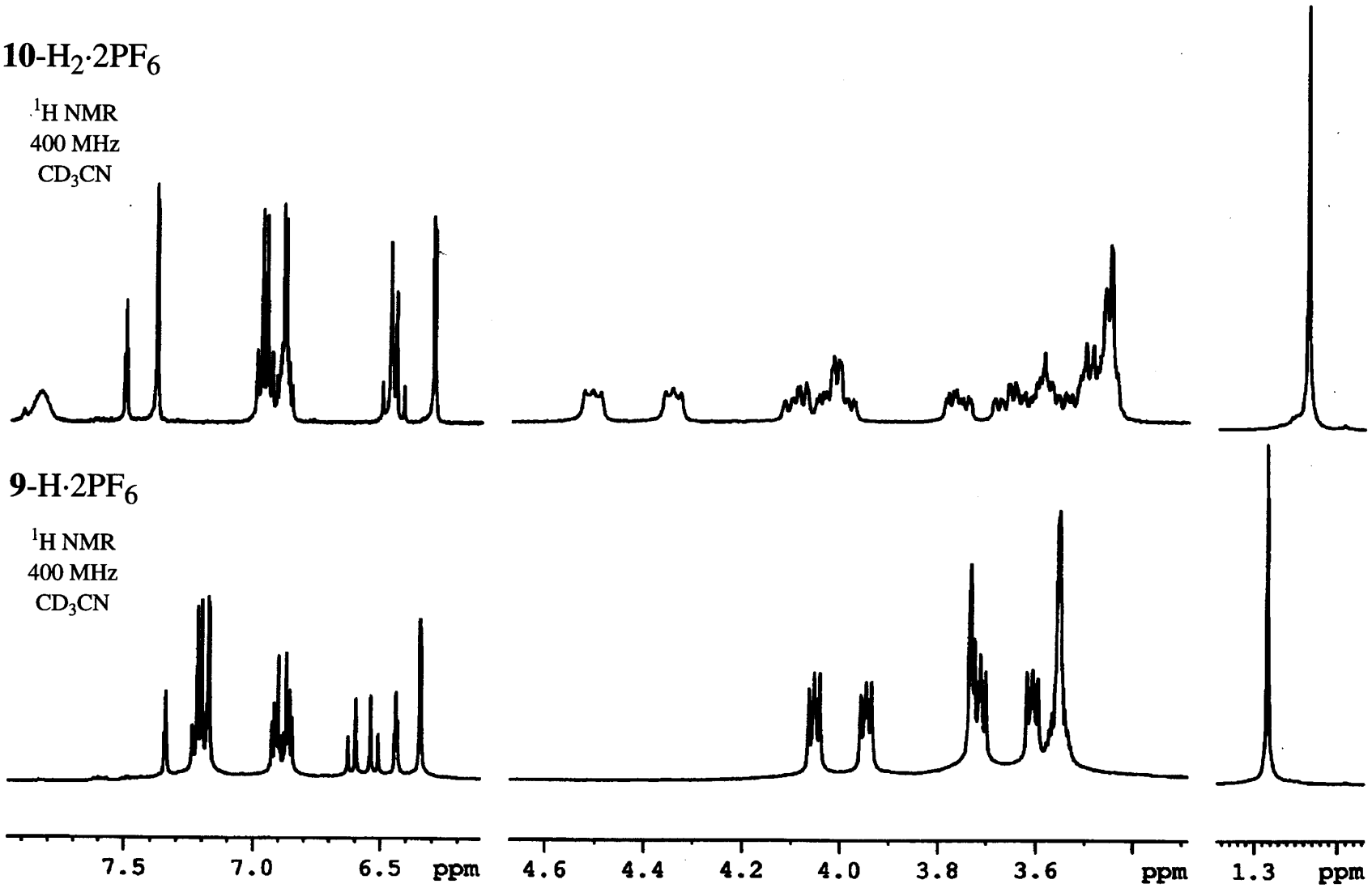
Expansions

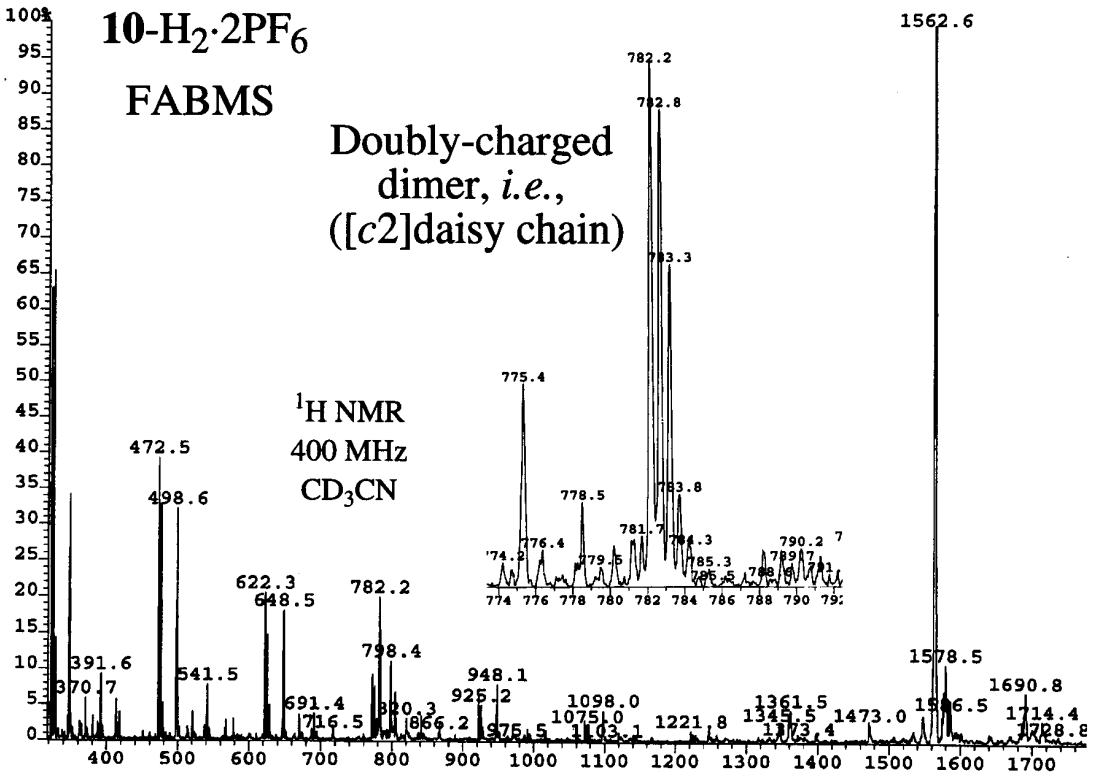





8-H·2PF6
FABMS
1206.4
1060.5
1208.4
984.5
1000.4
1063.4
1072.5
1222.3
1208.4
840.1
887.3
934.8
1126.0
1173.6
1280.7
1335.4
1380.8
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
850
900
950
1000
1050
1100
1150
1200
1250
1300
1350
1400


[a- or c1]Daisy Chain + Na 1+
748.4
726.5
[c2]Daisy Chain + PF6 1+
1598.5
[c2]Daisy Chain 1+
1452.7
[c2]Daisy Chain 2+
and
[a- or c1]Daisy Chain 1+
Cyclization (5 mM) of
7-H·2PF6
FAB-MS
Singly-charged trimers (i.e., [c3] species) would appear in this region
647.4
603.4
586.3
811.4
920.2
1007.8
1139.5
1202.5
1305.0
1436.3
1615.0
1743.0
1752.1
1971.8
2136.8
2324.3
2375.3
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
600
800
1000
1200
1400
1600
1800
2000
2200
2400


10-H2·2PF6
1H NMR
400 MHz
CD3CN
9-H·2PF6
1H NMR
400 MHz
CD3CN
7.5
7.0
6.5
ppm
4.6
4.4
4.2
4.0
3.8
3.6
ppm
1.3
ppm


10-H2·2PF6
FABMS
Doubly-charged
dimer, i.e.,
([c2]daisy chain)
1H NMR
400 MHz
CD3CN
1562.6
782.2
782.8
783.3
775.4
778.5
783.8
472.5
498.6
622.3
648.5
782.2
798.4
391.6
370.7
541.5
691.4
948.1
925.2
1098.0
1578.5
1690.8
1714.4
1473.0

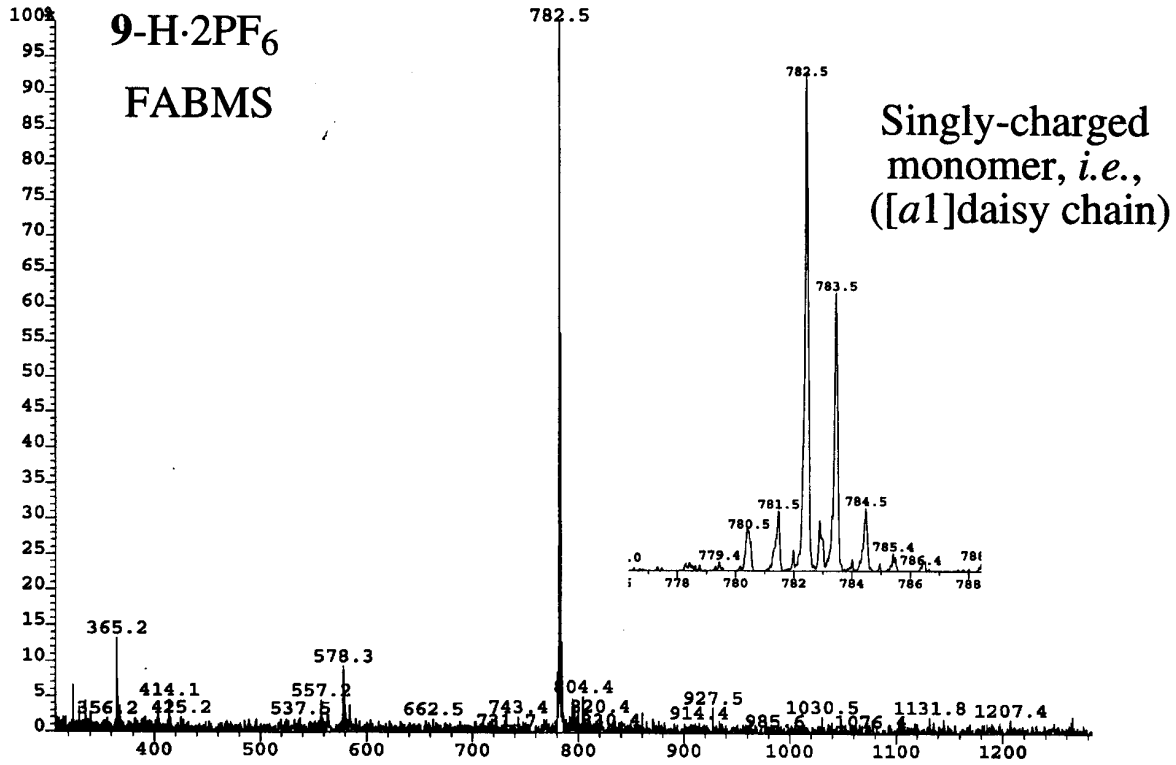

9-H·2PF6
FABMS
Singly-charged
monomer, i.e.,
([a1]daisy chain)
782.5
782.5
783.5
781.5
784.5
780.5
779.4
785.4
365.2
578.3
414.1
557.2
425.2
537.5
662.5
743.4
804.4
927.5
914.4
1030.5
1131.8
1207.4

Table 1. Crystal data and structure refinement for **7**-H·2PF_6

Identification code	FS9909
Empirical formula	$[C_{62}H_{72}NO_9P][PF_6]_2 \cdot 0.25H_2O$
Formula weight	1300.62
Temperature	293(2) K
Diffractometer Used	Siemens P4/RA
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 10.6321(10) Å alpha = 81.826(8)° b = 14.913(2) Å beta = 82.964(7)° c = 21.145(2) Å gamma = 80.729(9)°
Volume, Z	3258.1(6) $Å^3$, 2
Density (calculated)	1.326 Mg/m^3
Absorption coefficient	1.610 mm^{-1}
F(000)	1357
Crystal colour/morphology	Clear blocky prisms
Crystal size	0.50 x 0.40 x 0.40 mm
θ range for data collection	2.12 to 59.99°
Limiting indices	$0 \le h \le 11$, $-16 \le k \le 16$, $-23 \le l \le 23$
Scan type	ω-scans
Reflections collected	10122
Independent reflections	9529 (R_{int} = 0.0457)
Observed reflections [F>4σ(F)]	5309
Absorption correction	None
Structure solution method	Direct
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8229 / 219 / 815
Goodness-of-fit on F^2	1.066
Final R indices [F>4σ(F)]	R1 = 0.0836, wR2 = 0.2191
R indices (all data)	R1 = 0.1420, wR2 = 0.2854
Extinction coefficient	0.0010(2)
Largest diff. peak and hole	0.511 and -0.325 $eÅ^{-3}$
Mean and maximum shift/error	0.000 and -0.001

Table 2. Atomic coordinates [x 10^4], equivalent isotropic displacement parameters [$Å^2$ x 10^3] and site occupancy factors for **7**-H·2PF_6. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)	sof
O(1)	6601(4)	4772(3)	3750(2)	77(1)	1
C(2)	7904(7)	4573(7)	3880(3)	99(2)	1
C(3)	8794(8)	5035(9)	3465(4)	128(4)	1
O(4)	8815(4)	4866(4)	2811(2)	100(2)	1
C(5)	9727(7)	5347(7)	2440(4)	103(2)	1
C(6)	9654(7)	5339(7)	1742(4)	108(3)	1
O(7)	8556(5)	5898(4)	1551(2)	93(1)	1
C(8)	8553(9)	5992(8)	878(4)	122(3)	1
C(9)	7431(10)	6651(7)	686(4)	119(3)	1
O(10)	6321(5)	6209(4)	778(2)	97(1)	1
C(11)	5131(11)	6621(8)	611(4)	95(3)	0.75
C(12)	4856(12)	7540(9)	419(5)	115(4)	0.75
C(13)	3662(17)	7905(11)	219(8)	168(12)	0.75
C(14)	2751(15)	7359(13)	230(8)	173(9)	0.75
C(15)	3025(11)	6419(10)	415(6)	132(5)	0.75
C(16)	4205(10)	6059(10)	619(5)	87(3)	0.75
O(17)	4547(6)	5173(6)	813(3)	89(2)	0.75
C(18)	3675(10)	4511(9)	770(4)	92(3)	0.75
C(19)	4275(11)	3630(8)	1033(4)	104(3)	0.75
O(20)	4138(5)	3498(4)	1726(2)	79(2)	0.75
C(11')	5465(24)	6918(18)	524(19)	109(16)	0.25
C(12')	5589(25)	7819(18)	314(15)	103(10)	0.25
C(13')	4527(32)	8431(18)	132(21)	170(23)	0.25
C(14')	3362(28)	8133(20)	149(23)	107(15)	0.25
C(15')	3245(26)	7226(21)	351(25)	209(43)	0.25
C(16')	4296(26)	6609(16)	528(18)	104(14)	0.25
O(17')	4194(34)	5748(22)	752(21)	128(17)	0.25
C(18')	3276(38)	5194(24)	683(16)	131(15)	0.25
C(19')	3480(79)	4269(26)	995(15)	290(63)	0.25
O(20')	3218(38)	4149(18)	1666(12)	178(13)	0.25
C(21)	2945(8)	3282(6)	1987(4)	107(2)	1
C(22)	2918(8)	3055(6)	2664(4)	106(3)	1
O(23)	3116(4)	3796(3)	2962(2)	82(1)	1
C(24)	2810(7)	3654(5)	3644(3)	86(2)	1
C(25)	2892(6)	4503(5)	3912(3)	79(2)	1
O(26)	4213(4)	4628(3)	3836(2)	71(1)	1
C(27)	4496(6)	5338(4)	4107(2)	66(1)	1
C(28)	3609(6)	5978(5)	4409(3)	80(2)	1
C(29)	4026(8)	6665(5)	4661(3)	91(2)	1
C(30)	5281(9)	6725(5)	4630(3)	93(2)	1
C(31)	6193(7)	6095(5)	4340(3)	84(2)	1
C(32)	5791(6)	5410(4)	4076(2)	68(1)	1
C(33)	3178(25)	7438(15)	4886(14)	132(9)	0.35
O(34)	3497(26)	8188(15)	4903(13)	171(9)	0.35
C(33')	5576(36)	7513(20)	4857(22)	147(15)	0.25
O(34')	4679(33)	8091(19)	4977(15)	152(10)	0.25
C(33")	3054(31)	8862(16)	90(18)	117(11)	0.25
O(34")	3634(30)	9466(18)	72(15)	149(10)	0.25
C(33*)	2204(38)	8749(26)	-59(31)	126(20)	0.15
O(34*)	2283(40)	9555(24)	-197(21)	126(13)	0.15
N(40)	5786(5)	4319(3)	2563(2)	63(1)	1
C(41)	6795(6)	3578(4)	2348(3)	78(2)	1
C(42)	6661(5)	2659(4)	2721(3)	70(2)	1

C(43)	7026(6)	1886(4)	2421(3)	81(2)	1
C(44)	6936(7)	1024(5)	2753(4)	90(2)	1
C(45)	6495(6)	893(4)	3389(4)	81(2)	1
C(46)	6148(7)	1671(5)	3700(4)	99(2)	1
C(47)	6247(7)	2546(5)	3371(4)	92(2)	1
C(48)	6352(8)	-48(5)	3766(5)	106(2)	1
C(49)	7154(10)	-219(6)	4318(5)	131(3)	1
C(50)	6739(12)	-813(6)	3338(6)	147(4)	1
C(51)	4954(9)	-63(8)	3998(6)	166(5)	1
C(52)	5824(6)	5177(4)	2114(3)	70(2)	1
C(53)	4974(5)	5984(4)	2379(2)	62(1)	1
C(54)	5491(6)	6639(4)	2619(3)	76(2)	1
C(55)	4719(6)	7357(4)	2885(3)	76(2)	1
C(56)	3411(6)	7435(4)	2908(3)	65(1)	1
C(57)	2866(6)	6791(4)	2665(3)	71(2)	1
C(58)	3650(6)	6074(4)	2405(3)	68(1)	1
C(59)	2582(7)	8215(4)	3226(3)	76(2)	1
P(60)	1973(2)	9204(1)	2703(1)	67(1)	1
C(61)	1348(4)	10010(3)	3830(2)	89(2)	1
C(62)	782(5)	10721(3)	4177(2)	100(2)	1
C(63)	31(5)	11476(3)	3880(2)	97(2)	1
C(64)	-153(5)	11520(3)	3236(2)	100(2)	1
C(65)	413(4)	10809(3)	2889(2)	88(2)	1
C(66)	1164(4)	10053(2)	3186(2)	68(1)	1
C(67)	3532(4)	10517(3)	2267(2)	90(2)	1
C(68)	4566(5)	10857(3)	1898(3)	112(3)	1
C(69)	5334(4)	10332(4)	1464(3)	115(3)	1
C(70)	5069(5)	9469(4)	1401(2)	119(3)	1
C(71)	4035(5)	9129(3)	1771(2)	95(2)	1
C(72)	3266(4)	9653(3)	2204(2)	71(2)	1
C(73)	875(6)	9332(5)	1576(2)	159(5)	1
C(74)	-21(8)	9156(7)	1200(3)	201(7)	1
C(75)	-906(7)	8577(6)	1458(4)	188(7)	1
C(76)	-894(5)	8173(5)	2092(4)	158(5)	1
C(77)	1(5)	8348(4)	2468(3)	105(2)	1
C(78)	886(4)	8928(4)	2210(2)	84(2)	1
P(10)	9605(2)	7068(1)	4544(1)	74(1)	1
F(11)	9185(5)	6089(3)	4710(2)	118(2)	1
F(12)	8666(5)	7283(4)	3995(2)	123(2)	1
F(13)	8519(5)	7456(4)	5037(3)	134(2)	1
F(14)	10537(6)	6831(4)	5071(3)	149(2)	1
F(15)	10686(4)	6693(3)	4022(2)	120(2)	1
F(16)	9989(5)	8061(3)	4358(3)	134(2)	1
P(20)	10150(2)	2567(2)	1005(1)	109(1)	1
F(21)	9469(8)	1713(5)	1210(4)	198(3)	1
F(22)	8850(8)	3164(7)	949(4)	214(4)	1
F(23)	10030(8)	2781(5)	1716(3)	176(3)	1
F(24)	11468(8)	1983(7)	1096(5)	226(4)	1
F(25)	10250(7)	2402(5)	291(2)	167(3)	1
F(26)	10875(8)	3426(5)	813(3)	177(3)	1
O(80)	2634(23)	10954(17)	-84(12)	116(7)	0.25

Table 3. Bond Lengths [Å] and angles [°] for **7**-H·2PF_6.

O(1)-C(32)	1.379(7)	O(1)-C(2)	1.422(8)
C(2)-C(3)	1.404(12)	C(3)-O(4)	1.439(9)
O(4)-C(5)	1.396(9)	C(5)-C(6)	1.491(11)
C(6)-O(7)	1.388(9)	O(7)-C(8)	1.409(9)
C(8)-C(9)	1.478(13)	C(9)-O(10)	1.423(10)
O(10)-C(11')	1.37(2)	O(10)-C(11)	1.379(11)
C(11)-C(12)	1.366(13)	C(11)-C(16)	1.39(2)
C(12)-C(13)	1.39(2)	C(13)-C(14)	1.36(2)
C(13)-C(33")	1.47(2)	C(14)-C(15)	1.39(2)
C(15)-C(16)	1.379(13)	C(16)-O(17)	1.33(2)
O(17)-C(18)	1.478(11)	C(18)-C(19)	1.43(2)
C(19)-O(20)	1.443(10)	O(20)-C(21)	1.388(9)
C(11')-C(12')	1.38(2)	C(11')-C(16')	1.39(2)
C(12')-C(13')	1.39(2)	C(13')-C(14')	1.38(2)
C(14')-C(15')	1.38(2)	C(14')-C(33*)	1.49(2)
C(15')-C(16')	1.38(2)	C(16')-O(17')	1.32(2)
O(17')-C(18')	1.41(2)	C(18')-C(19')	1.44(4)
C(19')-O(20')	1.40(2)	O(20')-C(21)	1.43(2)
C(21)-C(22)	1.422(11)	C(22)-O(23)	1.403(8)
O(23)-C(24)	1.432(7)	C(24)-C(25)	1.477(9)
C(25)-O(26)	1.434(7)	O(26)-C(27)	1.362(7)
C(27)-C(32)	1.391(8)	C(27)-C(28)	1.395(8)
C(28)-C(29)	1.374(10)	C(29)-C(30)	1.345(11)
C(29)-C(33)	1.44(2)	C(30)-C(31)	1.387(10)
C(30)-C(33')	1.42(2)	C(31)-C(32)	1.377(9)
C(33)-O(34)	1.23(2)	C(33')-O(34')	1.21(2)
C(33")-O(34")	1.17(2)	C(33*)-O(34*)	1.21(2)
N(40)-C(52)	1.484(7)	N(40)-C(41)	1.490(7)
C(41)-C(42)	1.499(9)	C(42)-C(43)	1.374(9)
C(42)-C(47)	1.385(9)	C(43)-C(44)	1.386(10)
C(44)-C(45)	1.366(10)	C(45)-C(46)	1.392(10)
C(45)-C(48)	1.532(10)	C(46)-C(47)	1.402(10)
C(48)-C(49)	1.498(12)	C(48)-C(51)	1.510(12)
C(48)-C(50)	1.531(13)	C(52)-C(53)	1.515(8)
C(53)-C(54)	1.378(8)	C(53)-C(58)	1.388(8)
C(54)-C(55)	1.382(9)	C(55)-C(56)	1.372(9)
C(56)-C(57)	1.384(8)	C(56)-C(59)	1.526(8)
C(57)-C(58)	1.381(8)	C(59)-P(60)	1.795(6)
P(60)-C(78)	1.778(4)	P(60)-C(66)	1.787(3)
P(60)-C(72)	1.787(3)	C(61)-C(62)	1.39
C(61)-C(66)	1.39	C(62)-C(63)	1.39
C(63)-C(64)	1.39	C(64)-C(65)	1.39
C(65)-C(66)	1.39	C(67)-C(68)	1.39
C(67)-C(72)	1.39	C(68)-C(69)	1.39
C(69)-C(70)	1.39	C(70)-C(71)	1.39
C(71)-C(72)	1.39	C(73)-C(74)	1.39
C(73)-C(78)	1.39	C(74)-C(75)	1.39
C(75)-C(76)	1.39	C(76)-C(77)	1.39
C(77)-C(78)	1.39		

C(32)-O(1)-C(2)	118.5(5)	C(3)-C(2)-O(1)	117.6(7)
C(2)-C(3)-O(4)	112.0(8)	C(5)-O(4)-C(3)	107.6(6)
O(4)-C(5)-C(6)	111.0(7)	O(7)-C(6)-C(5)	110.1(6)
C(6)-O(7)-C(8)	110.8(6)	O(7)-C(8)-C(9)	109.5(8)
O(10)-C(9)-C(8)	109.9(7)	C(11')-O(10)-C(9)	98.9(12)
C(11)-O(10)-C(9)	124.4(8)	C(12)-C(11)-O(10)	122.7(10)
C(12)-C(11)-C(16)	119.9(9)	O(10)-C(11)-C(16)	117.3(9)
C(11)-C(12)-C(13)	119.9(10)	C(14)-C(13)-C(12)	120.4(10)
C(14)-C(13)-C(33")	108(2)	C(12)-C(13)-C(33")	131(2)

C(13)-C(14)-C(15)	120.3(11)	C(16)-C(15)-C(14)	119.3(10)
O(17)-C(16)-C(15)	123.6(9)	O(17)-C(16)-C(11)	116.2(9)
C(15)-C(16)-C(11)	120.1(10)	C(16)-O(17)-C(18)	119.8(8)
C(19)-C(18)-O(17)	107.0(8)	C(18)-C(19)-O(20)	113.0(8)
C(21)-O(20)-C(19)	113.0(7)	O(10)-C(11')-C(12')	131(2)
O(10)-C(11')-C(16')	109(2)	C(12')-C(11')-C(16')	120.4(12)
C(11')-C(12')-C(13')	119.7(12)	C(14')-C(13')-C(12')	120.1(12)
C(13')-C(14')-C(15')	120.0(12)	C(13')-C(14')-C(33*)	123(3)
C(15')-C(14')-C(33*)	117(3)	C(16')-C(15')-C(14')	120.4(12)
O(17')-C(16')-C(15')	122(2)	O(17')-C(16')-C(11')	119(2)
C(15')-C(16')-C(11')	119.3(11)	C(16')-O(17')-C(18')	131(3)
O(17')-C(18')-C(19')	116(3)	O(20')-C(19')-C(18')	116(3)
C(19')-O(20')-C(21)	120(2)	O(20)-C(21)-C(22)	110.5(7)
C(22)-C(21)-O(20')	122.5(13)	O(23)-C(22)-C(21)	111.6(7)
C(22)-O(23)-C(24)	112.2(5)	O(23)-C(24)-C(25)	109.0(5)
O(26)-C(25)-C(24)	107.5(5)	C(27)-O(26)-C(25)	116.1(4)
O(26)-C(27)-C(32)	115.8(5)	O(26)-C(27)-C(28)	125.7(6)
C(32)-C(27)-C(28)	118.5(6)	C(29)-C(28)-C(27)	119.7(7)
C(30)-C(29)-C(28)	121.2(7)	C(30)-C(29)-C(33)	114.9(13)
C(28)-C(29)-C(33)	123.3(14)	C(29)-C(30)-C(31)	120.7(7)
C(29)-C(30)-C(33')	115(2)	C(31)-C(30)-C(33')	124(2)
C(32)-C(31)-C(30)	118.9(7)	C(31)-C(32)-O(1)	124.1(6)
C(31)-C(32)-C(27)	121.0(6)	O(1)-C(32)-C(27)	114.8(5)
O(34)-C(33)-C(29)	124(2)	O(34')-C(33')-C(30)	116(3)
O(34")-C(33")-C(13)	121(3)	O(34*)-C(33*)-C(14')	117(3)
C(52)-N(40)-C(41)	110.8(4)	N(40)-C(41)-C(42)	112.9(5)
C(43)-C(42)-C(47)	117.8(6)	C(43)-C(42)-C(41)	119.3(6)
C(47)-C(42)-C(41)	122.9(6)	C(42)-C(43)-C(44)	120.9(7)
C(45)-C(44)-C(43)	122.6(7)	C(44)-C(45)-C(46)	116.9(6)
C(44)-C(45)-C(48)	123.9(7)	C(46)-C(45)-C(48)	119.2(7)
C(45)-C(46)-C(47)	121.0(7)	C(42)-C(47)-C(46)	120.7(7)
C(49)-C(48)-C(51)	111.1(9)	C(49)-C(48)-C(50)	109.9(8)
C(51)-C(48)-C(50)	106.2(9)	C(49)-C(48)-C(45)	109.6(7)
C(51)-C(48)-C(45)	108.4(7)	C(50)-C(48)-C(45)	111.5(8)
N(40)-C(52)-C(53)	111.9(4)	C(54)-C(53)-C(58)	117.8(5)
C(54)-C(53)-C(52)	120.9(6)	C(58)-C(53)-C(52)	121.3(5)
C(53)-C(54)-C(55)	121.2(6)	C(56)-C(55)-C(54)	120.2(5)
C(55)-C(56)-C(57)	119.8(6)	C(55)-C(56)-C(59)	119.1(5)
C(57)-C(56)-C(59)	121.1(6)	C(58)-C(57)-C(56)	119.3(6)
C(57)-C(58)-C(53)	121.6(5)	C(56)-C(59)-P(60)	116.8(4)
C(78)-P(60)-C(66)	109.4(2)	C(78)-P(60)-C(72)	109.2(2)
C(66)-P(60)-C(72)	108.9(2)	C(78)-P(60)-C(59)	111.1(3)
C(66)-P(60)-C(59)	108.3(2)	C(72)-P(60)-C(59)	109.9(3)
C(62)-C(61)-C(66)	120.0	C(61)-C(62)-C(63)	120.0
C(64)-C(63)-C(62)	120.0	C(63)-C(64)-C(65)	120.0
C(64)-C(65)-C(66)	120.0	C(65)-C(66)-C(61)	120.0
C(65)-C(66)-P(60)	118.1(2)	C(61)-C(66)-P(60)	121.7(2)
C(68)-C(67)-C(72)	120.0	C(67)-C(68)-C(69)	120.0
C(70)-C(69)-C(68)	120.0	C(69)-C(70)-C(71)	120.0
C(70)-C(71)-C(72)	120.0	C(71)-C(72)-C(67)	120.0
C(71)-C(72)-P(60)	120.2(2)	C(67)-C(72)-P(60)	119.7(2)
C(74)-C(73)-C(78)	120.0	C(73)-C(74)-C(75)	120.0
C(76)-C(75)-C(74)	120.0	C(75)-C(76)-C(77)	120.0
C(78)-C(77)-C(76)	120.0	C(77)-C(78)-C(73)	120.0
C(77)-C(78)-P(60)	120.0(3)	C(73)-C(78)-P(60)	119.9(3)

Table 4. Anisotropic displacement parameters [Å^2 x 10^3] for **7**-H·2PF$_6$. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [(ha*)^{2}U$_{11}$ + ... + 2hka*b*U$_{12}$].

	U11	U22	U33	U23	U13	U12
O(1)	55(2)	105(3)	69(2)	-20(2)	-1(2)	-4(2)
C(2)	71(4)	158(7)	61(3)	-9(4)	-7(3)	2(4)
C(3)	80(5)	230(11)	74(5)	-18(6)	-9(4)	-22(6)
O(4)	74(3)	152(5)	71(3)	-14(3)	5(2)	-13(3)
C(5)	68(4)	142(7)	101(5)	-20(5)	-5(4)	-17(4)
C(6)	75(5)	148(7)	95(5)	-15(5)	23(4)	-22(5)
O(7)	77(3)	130(4)	73(3)	-7(3)	4(2)	-31(3)
C(8)	111(7)	186(10)	71(4)	-1(5)	18(4)	-62(7)
C(9)	152(9)	130(7)	86(5)	14(5)	-16(5)	-71(7)
O(10)	100(4)	123(4)	72(3)	-9(3)	-10(3)	-29(3)
C(11)	114(10)	125(9)	41(4)	-6(5)	-5(5)	-9(9)
C(12)	146(11)	139(11)	66(6)	-18(6)	-20(7)	-31(9)
C(13)	201(22)	193(21)	82(9)	-23(11)	-46(12)	84(21)
C(14)	134(14)	273(28)	106(11)	-46(14)	-22(11)	17(16)
C(15)	114(11)	181(15)	97(8)	-7(9)	-25(7)	-10(10)
C(16)	81(8)	134(12)	48(5)	-5(7)	-6(4)	-31(7)
O(17)	82(4)	119(6)	68(3)	-8(4)	-14(3)	-22(4)
C(18)	84(7)	151(11)	56(5)	-35(6)	-6(4)	-46(7)
C(19)	106(8)	139(10)	78(6)	-49(6)	11(5)	-37(7)
O(20)	75(4)	105(4)	65(3)	-32(3)	6(3)	-30(3)
C(21)	113(6)	111(6)	115(6)	-38(5)	-22(5)	-40(5)
C(22)	106(6)	114(6)	113(6)	-46(5)	14(4)	-53(5)
O(23)	90(3)	86(3)	77(3)	-20(2)	-1(2)	-32(2)
C(24)	73(4)	103(5)	81(4)	-3(4)	11(3)	-32(4)
C(25)	58(4)	103(5)	75(4)	-16(3)	11(3)	-22(3)
O(26)	59(2)	93(3)	61(2)	-15(2)	5(2)	-15(2)
C(27)	65(4)	81(4)	50(3)	-4(3)	-3(2)	-7(3)
C(28)	67(4)	100(5)	65(3)	-8(3)	3(3)	2(3)
C(29)	111(6)	82(4)	76(4)	-14(3)	-6(4)	2(4)
C(30)	119(7)	82(4)	79(4)	-16(3)	-9(4)	-13(4)
C(31)	84(4)	102(5)	69(4)	-17(3)	-6(3)	-18(4)
C(32)	63(4)	86(4)	52(3)	-6(3)	-5(2)	-7(3)
N(40)	61(3)	63(3)	62(3)	-9(2)	0(2)	-11(2)
C(41)	68(4)	73(4)	87(4)	-13(3)	18(3)	-8(3)
C(42)	49(3)	71(3)	89(4)	-14(3)	3(3)	-11(3)
C(43)	72(4)	78(4)	93(4)	-18(3)	9(3)	-18(3)
C(44)	83(5)	73(4)	117(6)	-19(4)	-7(4)	-16(3)
C(45)	65(4)	63(3)	114(5)	-2(3)	-14(4)	-9(3)
C(46)	98(5)	88(5)	97(5)	2(4)	16(4)	-1(4)
C(47)	95(5)	70(4)	99(5)	-13(3)	15(4)	7(3)
C(48)	99(6)	79(5)	139(7)	9(4)	-24(5)	-16(4)
C(49)	139(8)	103(6)	154(8)	19(6)	-57(7)	-21(6)
C(50)	196(11)	73(5)	178(10)	-2(6)	-39(9)	-37(6)
C(51)	102(7)	159(10)	220(13)	73(9)	-15(7)	-56(7)
C(52)	74(4)	70(3)	63(3)	-4(3)	7(3)	-15(3)
C(53)	68(4)	64(3)	53(3)	-4(2)	0(2)	-11(3)
C(54)	71(4)	82(4)	80(4)	-7(3)	-13(3)	-22(3)
C(55)	86(5)	66(3)	83(4)	-11(3)	-21(3)	-23(3)
C(56)	81(4)	59(3)	56(3)	-6(2)	-1(3)	-18(3)
C(57)	65(4)	67(3)	83(4)	-16(3)	-4(3)	-12(3)
C(58)	68(4)	68(3)	73(3)	-12(3)	-4(3)	-24(3)
C(59)	97(5)	65(3)	65(3)	-11(3)	4(3)	-14(3)
P(60)	80(1)	63(1)	61(1)	-11(1)	-4(1)	-17(1)

C(61)	114(6)	80(4)	72(4)	-19(3)	-12(4)	-4(4)
C(62)	110(6)	109(6)	86(5)	-44(4)	-13(4)	4(5)
C(63)	86(5)	93(5)	117(6)	-47(4)	-9(4)	-2(4)
C(64)	86(5)	86(5)	127(6)	-27(4)	-21(4)	9(4)
C(65)	86(5)	85(4)	96(5)	-23(4)	-21(4)	-6(4)
C(66)	69(4)	65(3)	74(3)	-17(3)	-1(3)	-11(3)
C(67)	82(5)	75(4)	114(5)	-8(4)	-2(4)	-27(3)
C(68)	98(6)	95(5)	142(7)	3(5)	-5(5)	-36(5)
C(69)	97(6)	138(8)	108(6)	7(5)	4(5)	-47(5)
C(70)	127(7)	153(8)	78(5)	-13(5)	22(5)	-53(6)
C(71)	121(6)	98(5)	70(4)	-14(3)	12(4)	-36(4)
C(72)	82(4)	72(4)	60(3)	-3(3)	-7(3)	-19(3)
C(73)	148(9)	264(15)	92(6)	-17(7)	-32(6)	-101(10)
C(74)	184(13)	344(22)	113(8)	-46(11)	-54(8)	-106(14)
C(75)	135(10)	250(17)	223(15)	-109(14)	-59(11)	-57(11)
C(76)	100(7)	136(8)	262(16)	-62(10)	-36(9)	-44(6)
C(77)	79(5)	86(5)	153(7)	-16(5)	-16(5)	-20(4)
C(78)	88(5)	87(4)	83(4)	-23(3)	-3(3)	-27(4)
P(10)	65(1)	75(1)	79(1)	-7(1)	2(1)	-10(1)
F(11)	146(4)	83(3)	123(3)	12(2)	-9(3)	-36(3)
F(12)	118(4)	126(4)	126(4)	10(3)	-43(3)	-23(3)
F(13)	121(4)	131(4)	125(4)	-17(3)	49(3)	10(3)
F(14)	142(4)	161(5)	151(5)	-36(4)	-77(4)	16(4)
F(15)	95(3)	129(4)	128(4)	-37(3)	25(3)	0(3)
F(16)	138(4)	90(3)	177(5)	-16(3)	15(4)	-53(3)
P(20)	110(2)	139(2)	84(1)	-13(1)	8(1)	-47(2)
F(21)	245(8)	189(7)	177(6)	-34(5)	59(6)	-130(6)
F(22)	173(7)	264(10)	203(8)	-65(7)	-56(6)	31(6)
F(23)	221(7)	221(7)	93(3)	-41(4)	24(4)	-66(6)
F(24)	158(6)	264(10)	267(10)	-117(8)	-63(6)	40(6)
F(25)	183(6)	253(8)	89(3)	-41(4)	20(3)	-107(5)
F(26)	224(7)	198(7)	133(5)	-25(4)	22(5)	-123(6)

Table 5. Hydrogen coordinates (x 10^4), isotropic displacement parameters (Å^2 x 10^3) and site occupancy factors for **7**-H·2PF_6.

	x	y	z	U(eq)	sof
H(2A)	7948(7)	4706(7)	4312(3)	119	1
H(2B)	8175(7)	3921(7)	3876(3)	119	1
H(3A)	9641(8)	4837(9)	3606(4)	154	1
H(3B)	8580(8)	5687(9)	3489(4)	154	1
H(5A)	10576(7)	5071(7)	2549(4)	124	1
H(5B)	9586(7)	5975(7)	2536(4)	124	1
H(6A)	10404(7)	5554(7)	1497(4)	130	1
H(6B)	9640(7)	4718(7)	1657(4)	130	1
H(8A)	8516(9)	5402(8)	743(4)	146	1
H(8B)	9334(9)	6207(8)	672(4)	146	1
H(9A)	7298(10)	7157(7)	941(4)	143	1
H(9B)	7584(10)	6896(7)	237(4)	143	1
H(12A)	5467(12)	7920(9)	423(5)	137	0.75
H(13A)	3469(17)	8547(11)	75(8)	202	0.50
H(14A)	1941(15)	7613(13)	115(8)	208	0.75
H(15A)	2418(11)	6040(10)	400(6)	158	0.75
H(18A)	2854(10)	4677(9)	1011(4)	110	0.75
H(18B)	3536(10)	4504(9)	326(4)	110	0.75
H(19A)	5179(11)	3557(8)	880(4)	125	0.75
H(19B)	3902(11)	3160(8)	879(4)	125	0.75
H(12B)	6381(25)	8017(18)	293(15)	123	0.25
H(13B)	4604(32)	9044(18)	-1(21)	204	0.25
H(14B)	2636(28)	8565(20)	24(23)	128	0.10
H(15B)	2454(26)	7028(21)	368(25)	251	0.25
H(18C)	3247(38)	5176(24)	229(16)	158	0.25
H(18D)	2442(38)	5485(24)	850(16)	158	0.25
H(19C)	2952(79)	3915(26)	817(15)	348	0.25
H(19D)	4367(79)	4015(26)	888(15)	348	0.25
H(21A)	2760(8)	2768(6)	1798(4)	128	0.75
H(21B)	2292(8)	3801(6)	1887(4)	128	0.75
H(21C)	3417(8)	2760(6)	1803(4)	128	0.25
H(21D)	2074(8)	3317(6)	1897(4)	128	0.25
H(22A)	2095(8)	2872(6)	2835(4)	127	1
H(22B)	3577(8)	2540(6)	2762(4)	127	1
H(24A)	3405(7)	3153(5)	3831(3)	103	1
H(24B)	1952(7)	3496(5)	3744(3)	103	1
H(25A)	2384(6)	5021(5)	3687(3)	94	1
H(25B)	2569(6)	4451(5)	4363(3)	94	1
H(28A)	2739(6)	5940(5)	4440(3)	96	1
H(29A)	3430(8)	7096(5)	4855(3)	109	0.65
H(30A)	5541(9)	7194(5)	4806(3)	112	0.75
H(31A)	7060(7)	6134(5)	4323(3)	101	1
H(33A)	2334(25)	7362(15)	5027(14)	159	0.35
H(33B)	6411(36)	7579(20)	4909(22)	176	0.25
H(33C)	2192(31)	8987(16)	22(18)	141	0.25
H(33D)	1446(38)	8523(26)	-81(31)	151	0.15
H(40A)	5043(33)	4144(45)	2503(34)	94(23)	1
H(40B)	5756(55)	4401(38)	2978(8)	69(17)	1
H(41A)	7629(6)	3731(4)	2393(3)	94	1
H(41B)	6752(6)	3544(4)	1897(3)	94	1
H(43A)	7339(6)	1941(4)	1989(3)	98	1
H(44A)	7186(7)	515(5)	2535(4)	109	1
H(46A)	5845(7)	1610(5)	4133(4)	119	1
H(47A)	6032(7)	3055(5)	3591(4)	111	1
H(49A)	8037(10)	-206(6)	4158(5)	197	1

H(49B)	7061(10)	-807(6)	4554(5)	197	1
H(49C)	6879(10)	248(6)	4595(5)	197	1
H(50A)	6221(12)	-700(6)	2985(6)	220	1
H(50B)	6613(12)	-1390(6)	3584(6)	220	1
H(50C)	7625(12)	-831(6)	3175(6)	220	1
H(51A)	4461(9)	48(8)	3636(6)	249	1
H(51B)	4665(9)	404(8)	4274(6)	249	1
H(51C)	4846(9)	-651(8)	4232(6)	249	1
H(52A)	5547(6)	5095(4)	1708(3)	84	1
H(52B)	6699(6)	5307(4)	2033(3)	84	1
H(54A)	6377(6)	6597(4)	2603(3)	92	1
H(55A)	5087(6)	7788(4)	3048(3)	91	1
H(57A)	1980(6)	6841(4)	2676(3)	85	1
H(58A)	3280(6)	5641(4)	2244(3)	82	1
H(59A)	3081(7)	8412(4)	3521(3)	92	1
H(59B)	1859(7)	7973(4)	3479(3)	92	1
H(61A)	1851(4)	9504(3)	4029(2)	106	1
H(62A)	905(7)	10691(5)	4608(2)	120	1
H(63A)	-348(7)	11952(4)	4112(3)	116	1
H(64A)	-655(6)	12025(3)	3037(3)	120	1
H(65A)	290(7)	10838(4)	2458(2)	106	1
H(67A)	3018(4)	10868(3)	2557(2)	108	1
H(68A)	4743(7)	11434(3)	1940(4)	134	1
H(69A)	6026(6)	10559(5)	1217(4)	138	1
H(70A)	5583(7)	9118(5)	1111(3)	142	1
H(71A)	3857(7)	8551(3)	1728(3)	114	1
H(73A)	1467(6)	9720(5)	1403(2)	191	1
H(74A)	-28(12)	9427(9)	776(3)	241	1
H(75A)	-1505(9)	8459(9)	1207(5)	226	1
H(76A)	-1486(8)	7785(6)	2265(6)	189	1
H(77A)	9(8)	8078(6)	2892(3)	126	1